



Challenges and opportunities for photonic sensing of key atmospheric short-lived species

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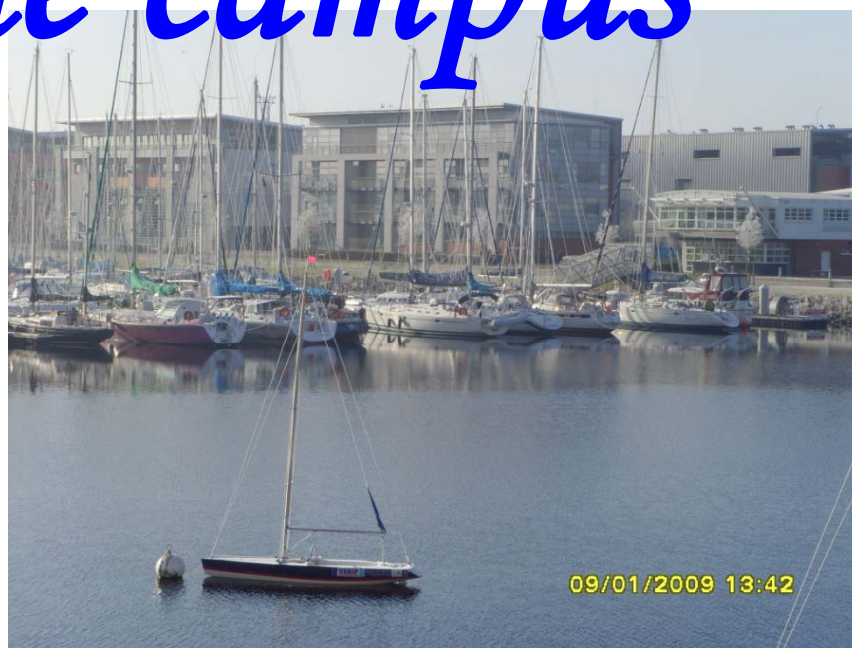
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Dunkerque campus



Outline of Talk

➤ Introduction

- Motivation & Challenge
- State of the art spectroscopic technologies
- Spectral manipulation

➤ Photonic sensing by IR lasers

ICOS – FSR – Multipass direct absorption

➤ Photonic sensing by UV-VIS LEDs

IBBCEAS

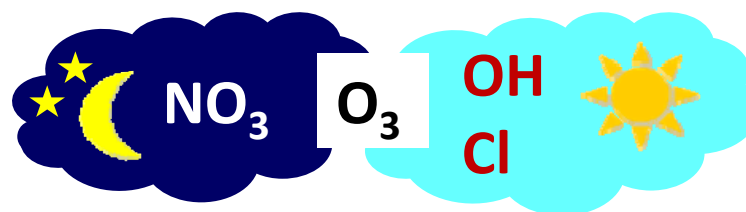
➤ Applications

- Field observation
- Chemical reaction study in smog chamber

➤ Summary

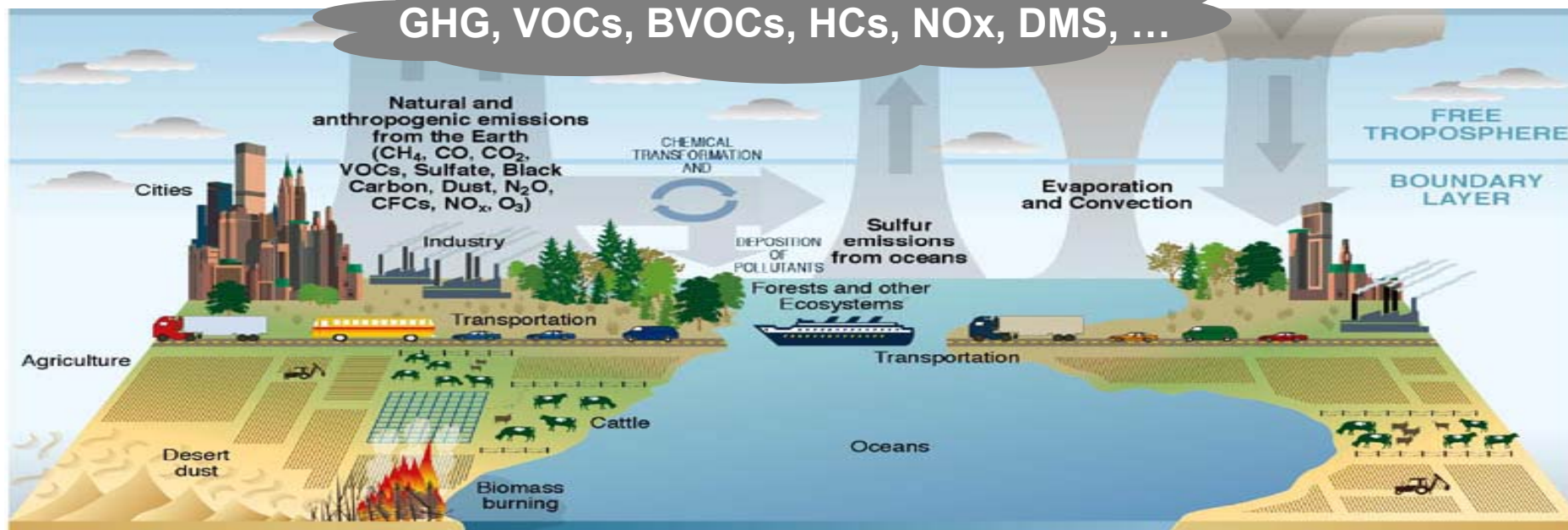


Motivation



OXIDATION

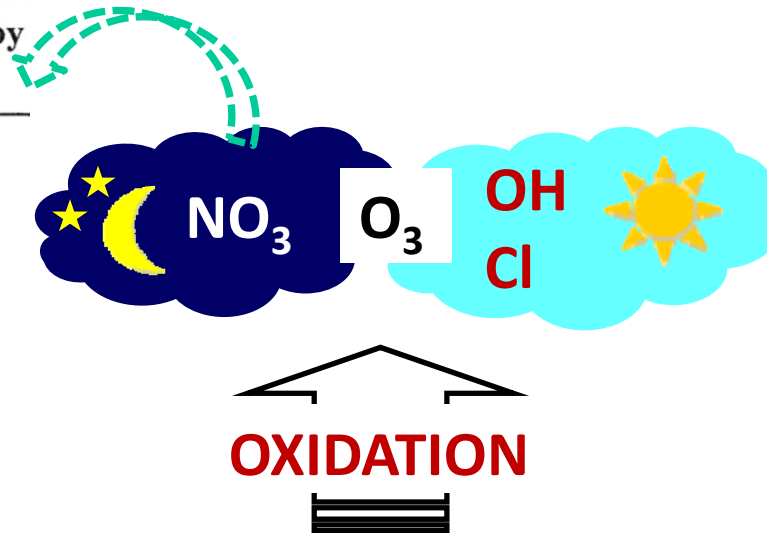
GHG, VOCs, BVOCs, HCs, NO_x , DMS, ...



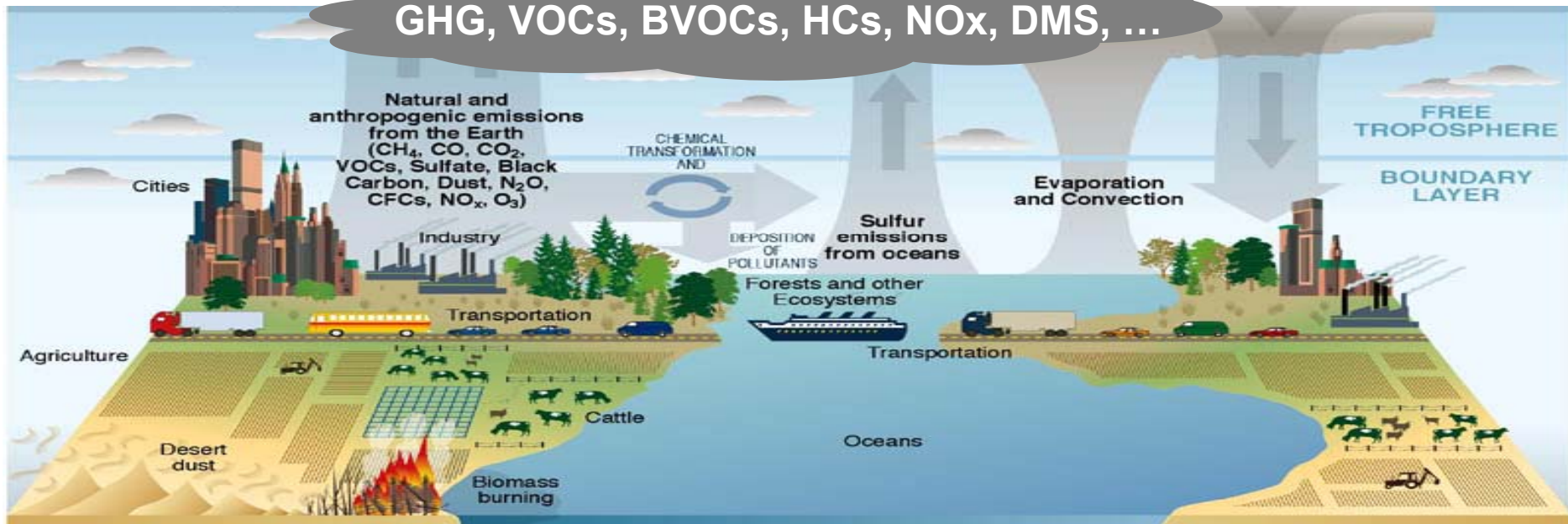
Motivation

(Prinn 2003)

Trace gas	Global emission rate (Tg/yr)	Removal by OH (%)
CO	2800	85
CH ₄	530	90
C ₂ H ₆	20	90
Isoprene	570	90
Terpenes	140	50
NO ₂	150	50
SO ₂	300	30
(CH ₃) ₂ S	30	90



GHG, VOCs, BVOCs, HCs, NO_x, DMS, ...



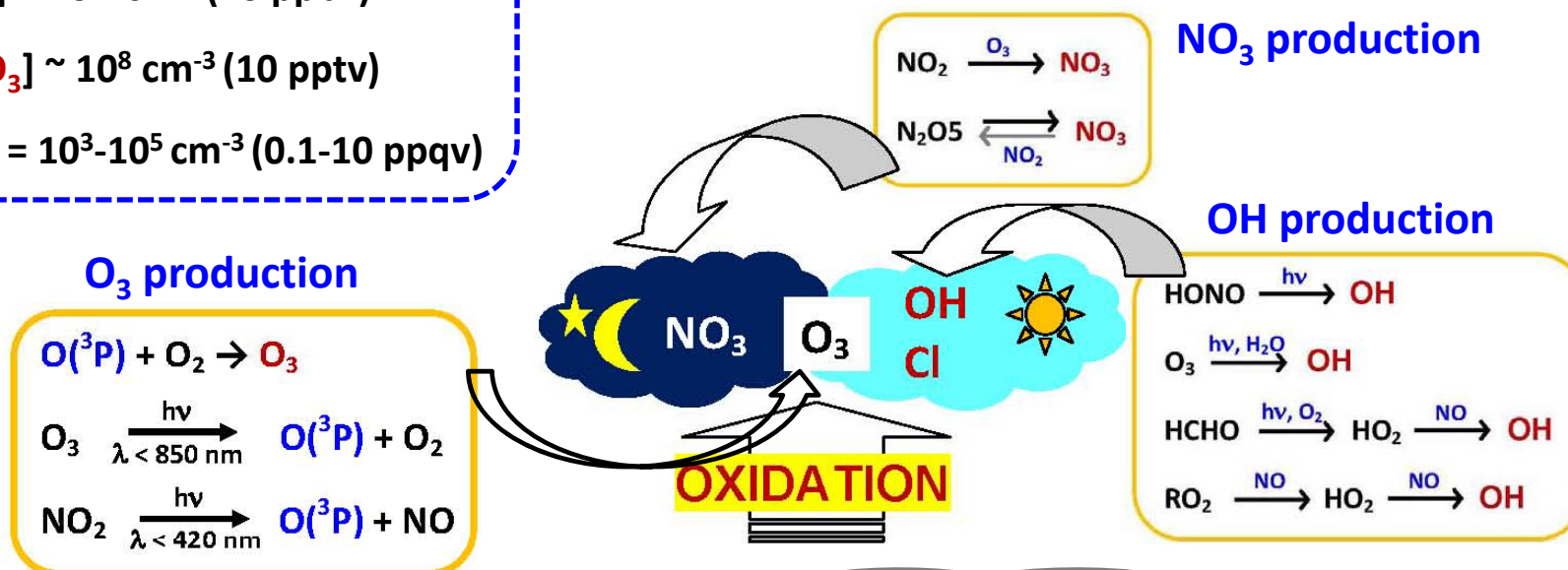
$[\text{OH}] \sim 10^6 \text{ cm}^{-3}$ (0.1 pptv)

$[\text{O}_3] \sim 10^{11} \text{ cm}^{-3}$ (10 ppbv)

$[\text{NO}_3] \sim 10^8 \text{ cm}^{-3}$ (10 pptv)

$[\text{Cl}] = 10^3\text{-}10^5 \text{ cm}^{-3}$ (0.1-10 ppqv)

Motivation



GHG, VOCs, BVOCs, HCs, NO_x, DMS, ...

Study of the major atmospheric oxidant budget is thus very important to understand the ability of the atmosphere to oxidize trace pollutants (so called “atmospheric oxidant capacity”).

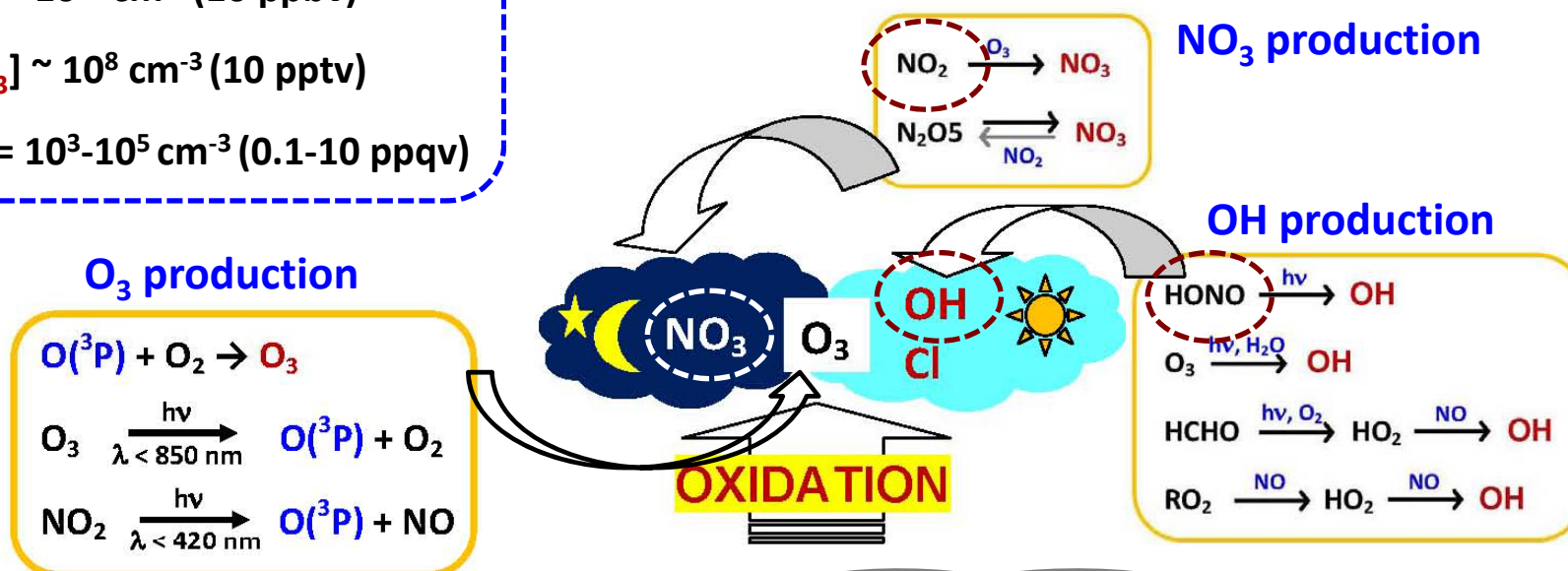
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Motivation



GHG, VOCs, BVOCs, HCs, NO_x, DMS, ...

Precise concentration assessment of the key atmospheric oxidants and their precursors is very important for understanding & prediction of regional air quality and global climate change.

Challenges

No commercially available instruments for direct concentration measurements. All routine measurements are based on *chemical conversion + measurements with IC, FL, CL, LOPAP, HPLC*.

Main problem : *chemical interference* due to *sample preparation* (such as *species separation, trapping, chemical conversion, ionization, pre-concentration, etc.*) and *analytical artifacts*

Photonic sensing => non-intrusive measurements with *fast time response, high specificity without additional sample preparation*

- Challenges**
- Ultralow concentration : ppb (10^{-9}) - ppq (10^{-15});
 - Very short lifetime : down to seconds;
 - Free of chemical interference;
 - No standard gas reference available for validation and calibration;
 - No spectral data available in the common databases (HITRAN, ..)

High performance probing source-detector & sensitive sensing scheme

+

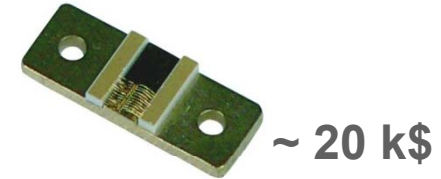
Lab. production of sample & Intercomparison campaigns

CW mid-Infrared Lasers (fdr vibration)

DFB Quantum Cascade Lasers (QCL) : 4 - 16 μm

CW output power : 10 mW to > 1 W (@ TEC)

Limited spectral coverage : < 10 cm^{-1}

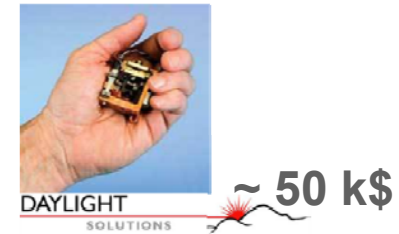


Interband Cascade Lasers (ICL) : 3 - 6 μm

External cavity QCL : 4.4 - 10.5 μm

CW output power : > 70 mW

Wide spectral coverage : > 30 cm^{-1} up to ~ 400 cm^{-1}



Quantum well DFB lasers : 2.9 – 3.5 μm

CW output power : > 1 mW

Limited spectral coverage : < 10 cm^{-1}

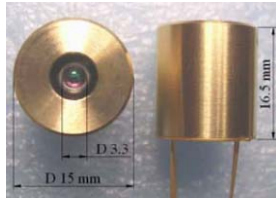
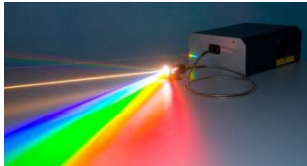


Multi-chip laser sources : 6-13 μm / 3 chips
in pulsed operation



Optical parametrical sources: DFG, OPO (powerful tool for lab. study)

Broadband light sources

Sources	Xenon arc lamp	Light Emitting Diode (LED)		Superconituum (white light)
				
Spectral Range	185 – 2000 nm	350 – 1550 nm	3 – 7 μm	400 – 2200 nm
Linewidth (FWHM)	180 – 2000 nm	$\sim 20 \text{ nm}$ (UV) $> 100 \text{ nm}$ (VIS)	0.4 – 2 μm (0.1 - 0.2 λ_{max})	400 – 2200 nm
Beam Quality	Black body emission in all direction*	Viewing half angle $\theta_{1/2} = \pm (7-70)^\circ$	$\leq 40^\circ$	laser-like beam quality ($\phi 2 \text{ mm}$ @ 633 nm)
Optical Power Output	35 – 300 W	50 - 1000 mW	10 – 500 μW	6 W
Cooling	Convection cooling	TE cooling	TE cooling	air-cooling
Cost	$\sim 5000 \text{ €}$ (system) **	10 – 60 \$	$\sim 100 \text{ \$}$	Some tens of k\$

* $\theta_{1/2} = 0.8^\circ$ & $\phi 33 \text{ mm}$ after collimation; ** $\sim 150 \text{ €}$ per lamp (75 W)

High sensitivity spectroscopy techniques

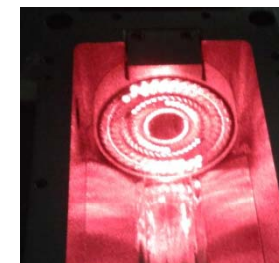
(high sensitivity => high Signal to Noise Ratio, SNR)

✓ Long optical path length absorption spectroscopy (“S” ↗)

➤ Multipass cell => 100-200 m (ppm-ppb)

➤ Optical cavity (Cavity enhanced spectroscopy :

OA-ICOS, IBBCEAS, CRDS) => 1-10 km (ppb-ppt)



✓ Low noise spectroscopic detection approaches (“N” ↘)

1) Light modulation-phase sensitive detection methods:

➤ Frequency / Wavelength Modulation Spectroscopy (FMS / WMS) => BG free

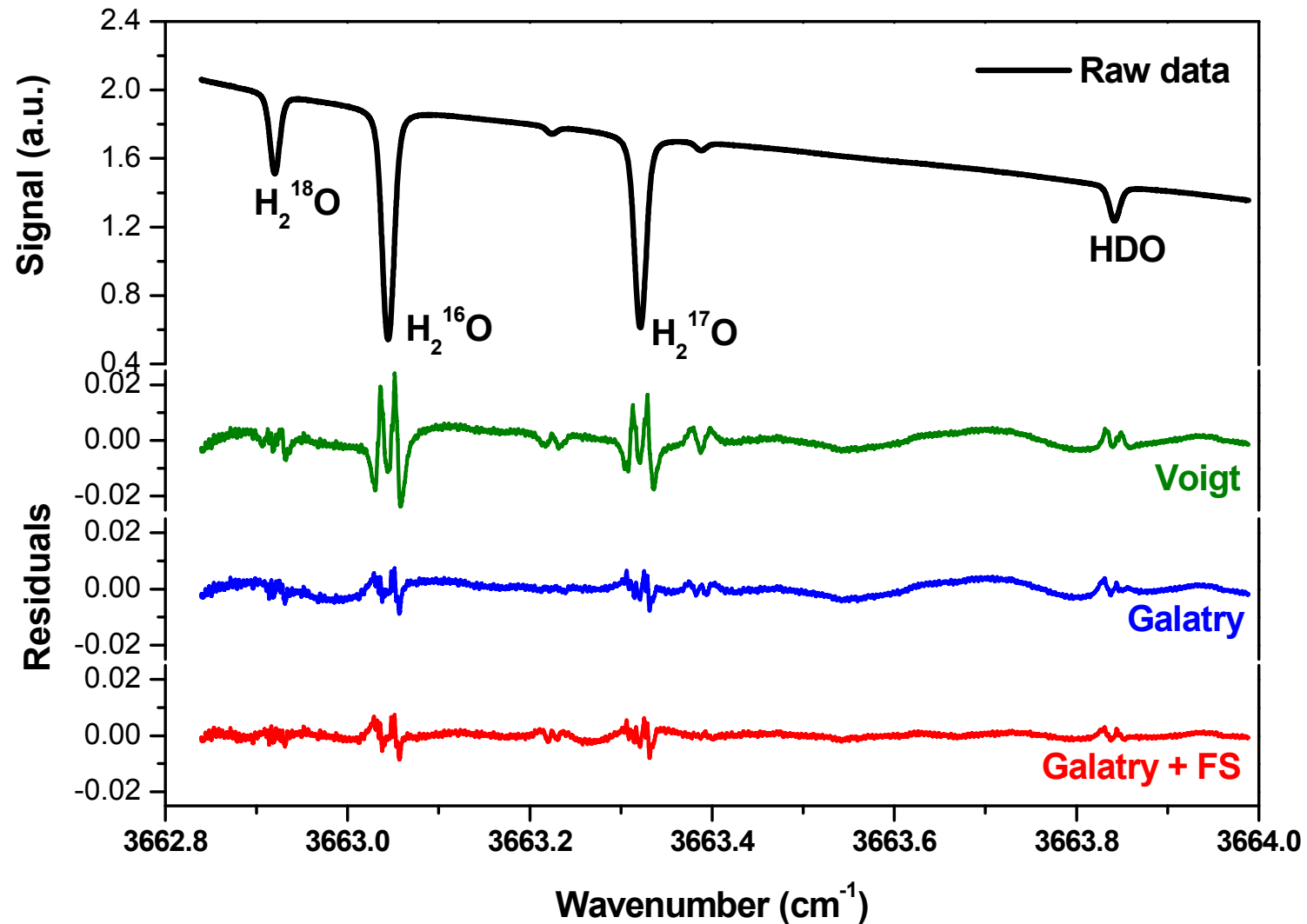
2) Indirect measurements (of absorption induced physical parameter from which the absorber concentration can be inferred)

➤ CRDS => BG free

➤ Photoacoustic spectroscopy (PAS / QEPAS) => BG free

➤ Faraday rotation spectroscopy (FRS) => BG free

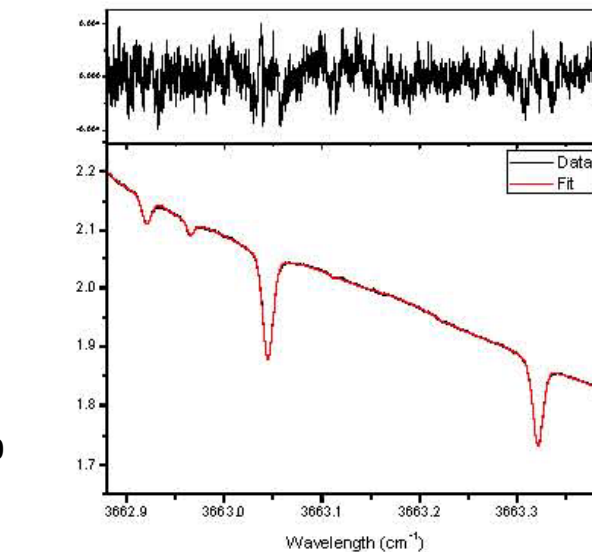
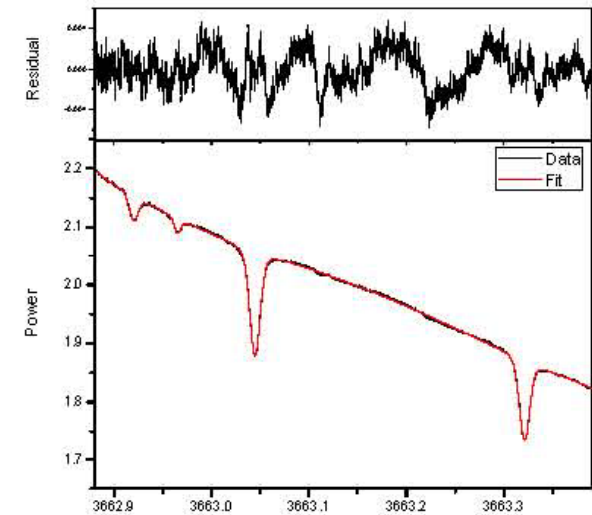
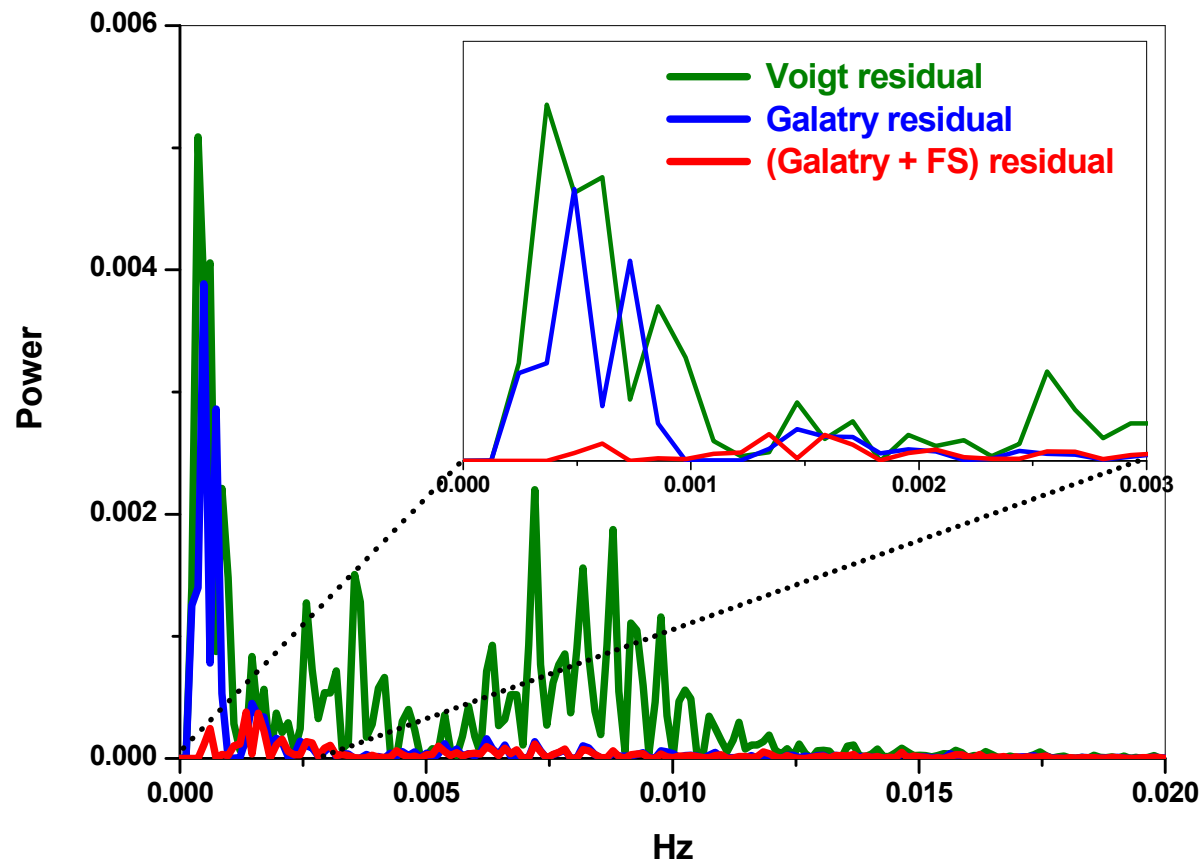
Spectral manipulation : Lineshape fits using Voigt and Galatry profiles for integrated area determination



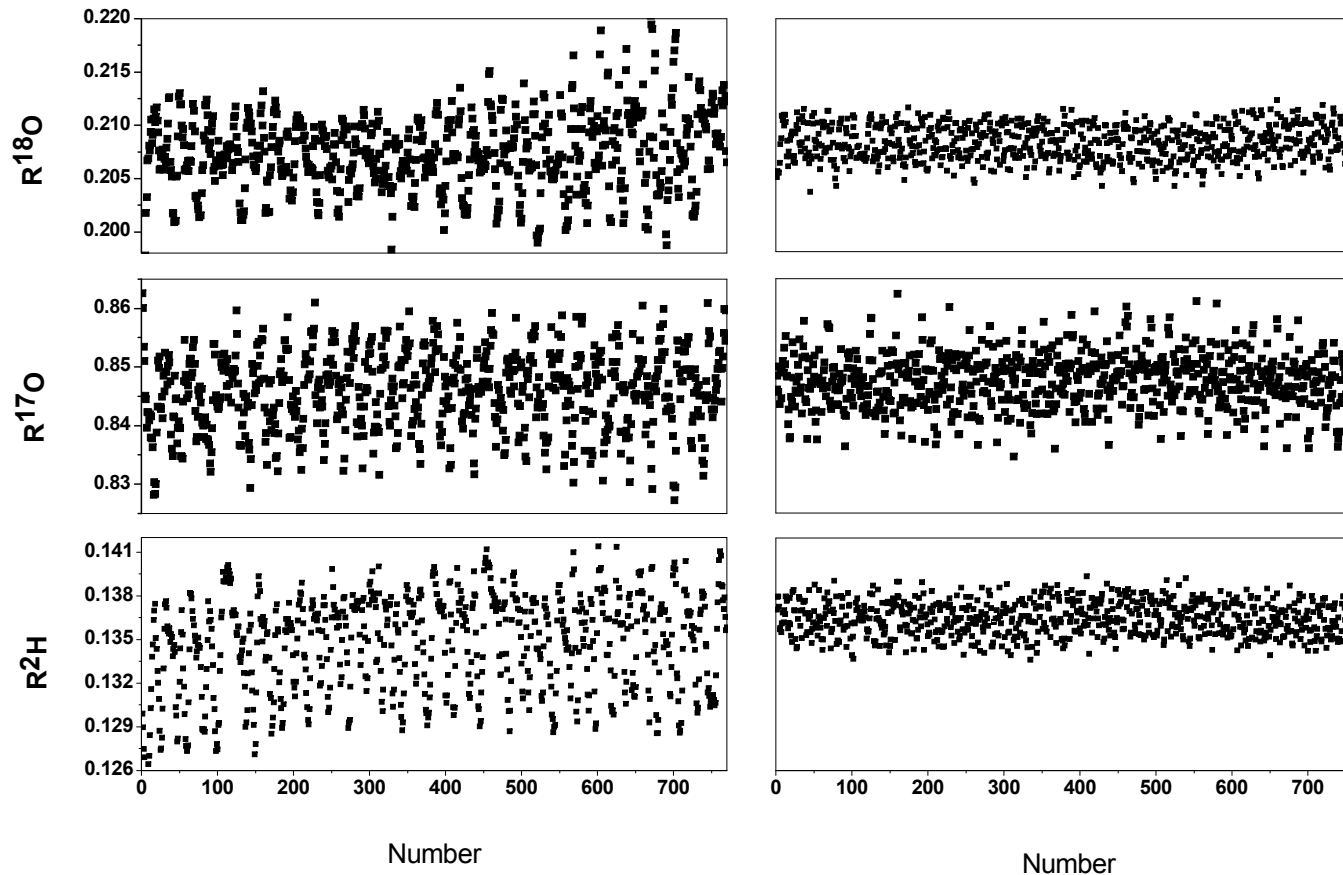
Spectral manipulation : « Fourier filtering »

for cancellation of the oscillation structure in baseline

Fourier transform of residual spectrum



Spectral manipulation : Improvement in measurement precision

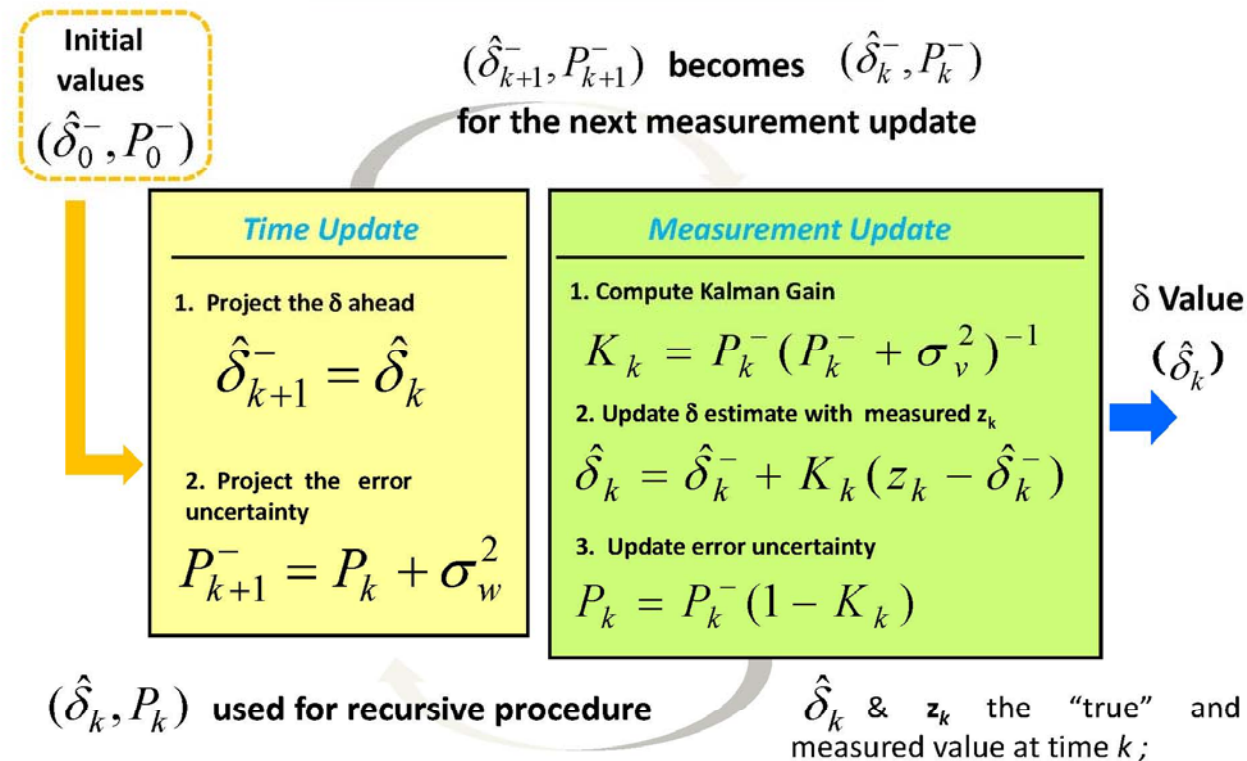


Left panel : Before (left panel) and after (right panel) spectral manipulation

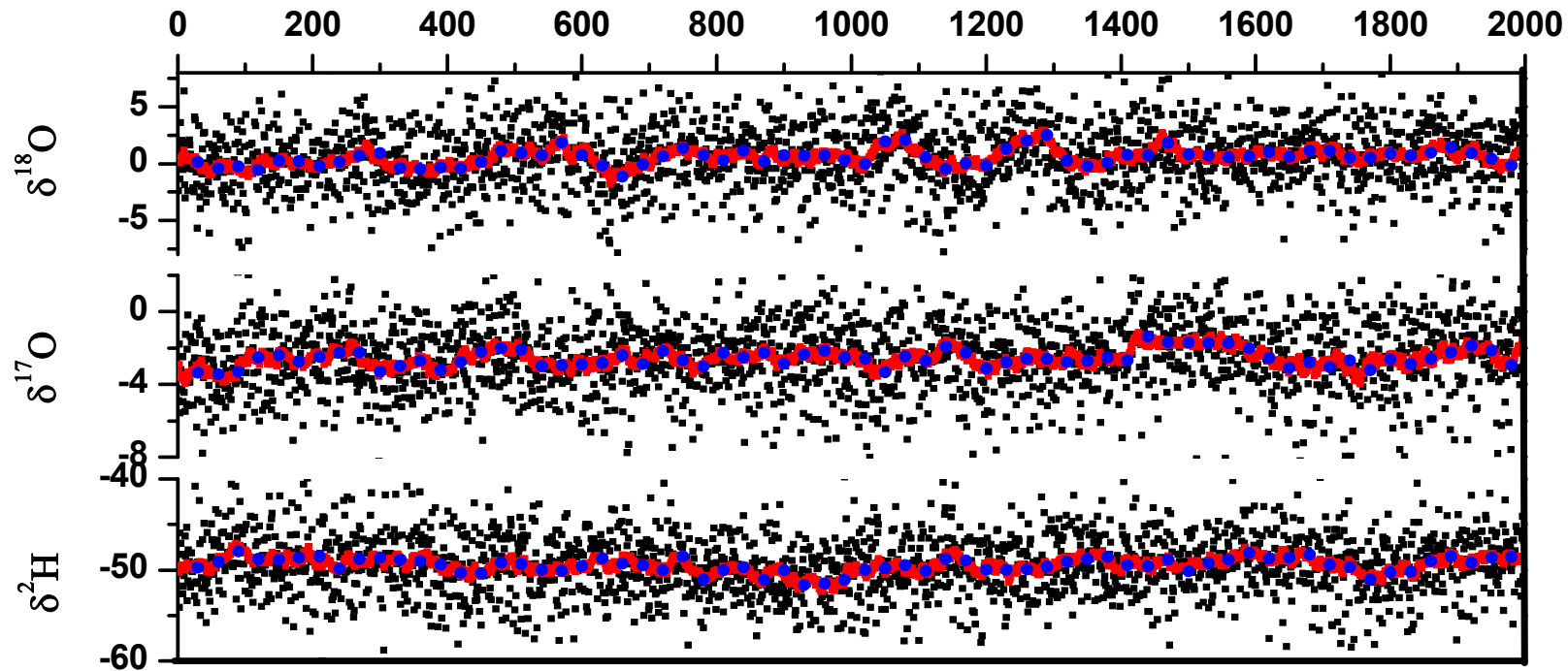
➤ up to 3-fold reduction in standard deviation

Spectral manipulation : « Kalman filtering »

Kalman filtering, originally developed by R.E. Kalman for aerospace navigation applications (*J. Basic Eng.* **82** (1960) 35), uses a recursive procedure for “true value” prediction based on the previously determined value : **filtering out the shot-to-shot real-time noise while following the true variation in measured physical quantity.**



Time series of the δ -value for ^{18}O , ^{17}O and ^2H in water



Raw measurement of the δ -value for ^{18}O , ^{17}O , ^2H (black dots, in 1-s), the corresponding Kalman filter output (red lines, $q=150$ in 1-s), and the averaged value of 30 δ values (blue dots, in 30-s).

Kalman filtering : high measurement precision while keeping a fast system response, not affecting the mean value of the data.

Ref. T. Wu, W. Chen et al, Opt. Lett. **35** (2010) 634-636

Photonic sensing by IR lasers

ICOS – FSR – Multipass cell

OH radical concentration measurements

Lifetimes : ~ 1 s in clean air

< 1 s in polluted environment

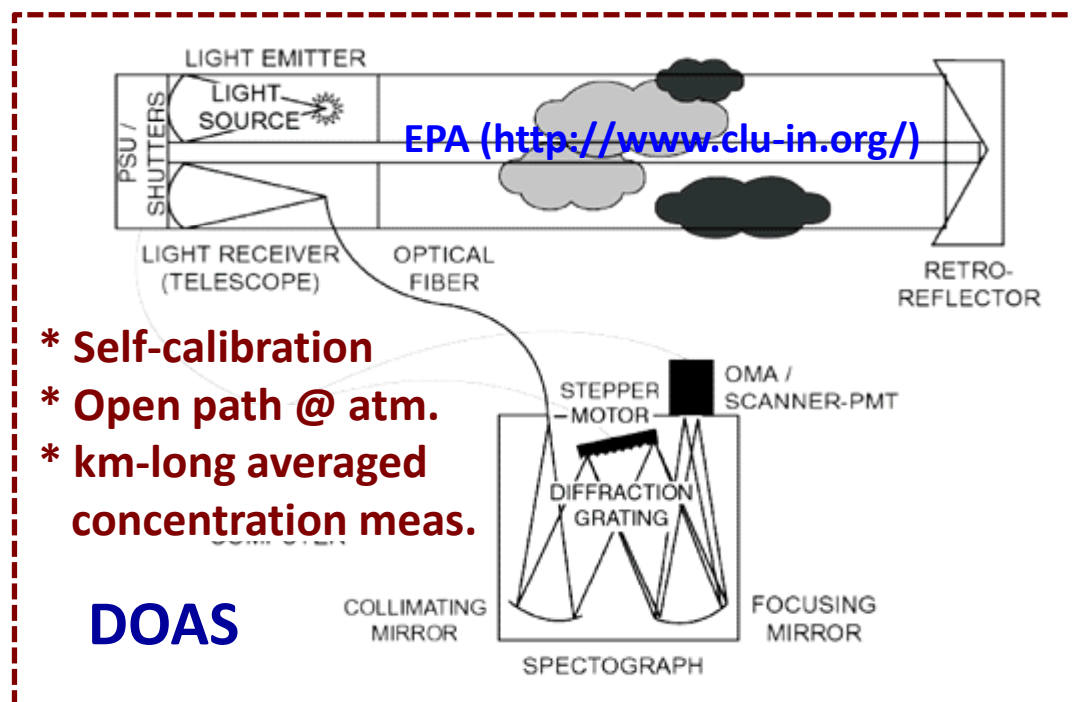
Typical concentration : $10^5 - 10^7$ OH/cm³ or 0.01-1 ppt @ STP

- ✓ primary “cleansing agent” removing pollutants in the atmosphere
- ✓ initiating reactions leading to the production of O₃
- ✓ effecting on the formation of aerosol

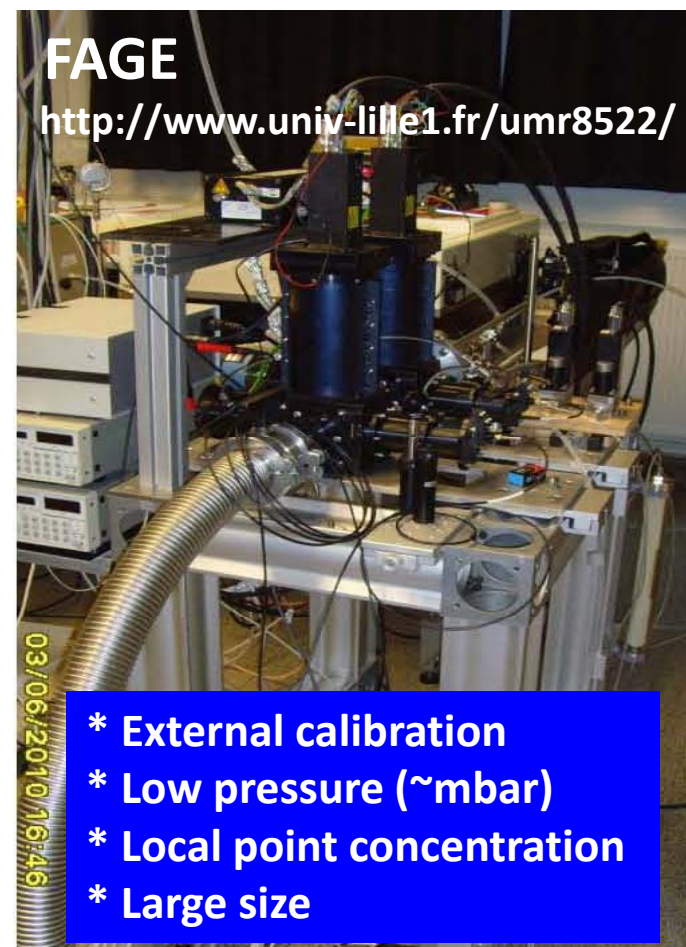
Current OH sensing technologies

Spectroscopic methods currently used for measurements of OH :

- Long-path Differential Optical Absorption Spectroscopy (DOAS)
- Laser induced Fluorescence Assay by Gas Expansion (FAGE)



*sensitive to visibility conditions
*low spectral & spatial resolution



OH radical monitoring

*Needs of compact instrument for self-calibration,
direct concentration assessment with high
spatial resolution & fast temporal response*

WMS enhanced OA-ICOS @ 1434 nm
(WMS lowering noise / cavity enhancing signal)

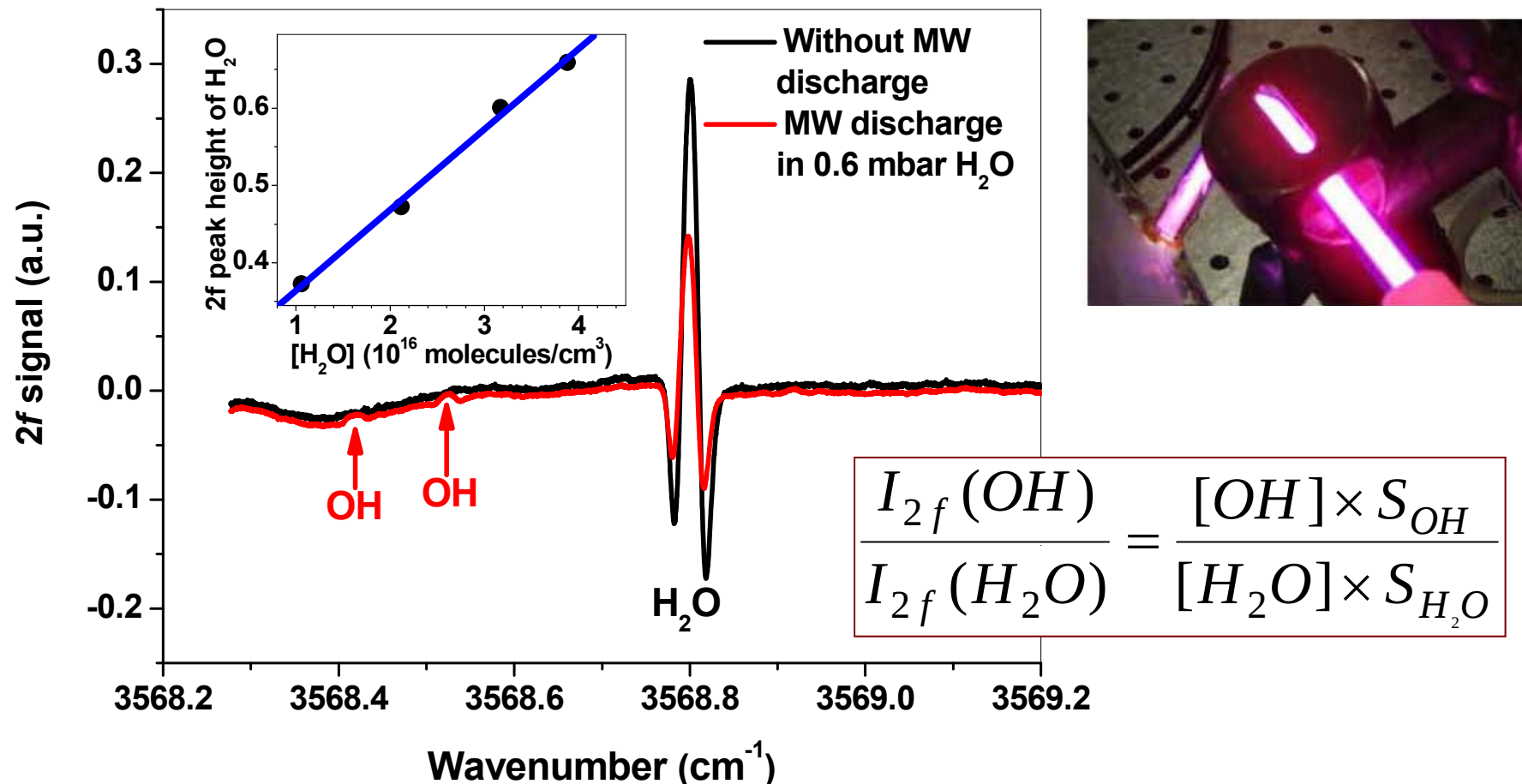


FRS @ 2.8 μm
(shot noise dominated detection)



Production & calibration of OH radicals

The OH free radical was produced by **microwave (MW) discharge** in water vapor. The generated OH concentration was determined with the help of **wavelength modulation spectrum using a close-by H₂O absorption line**.



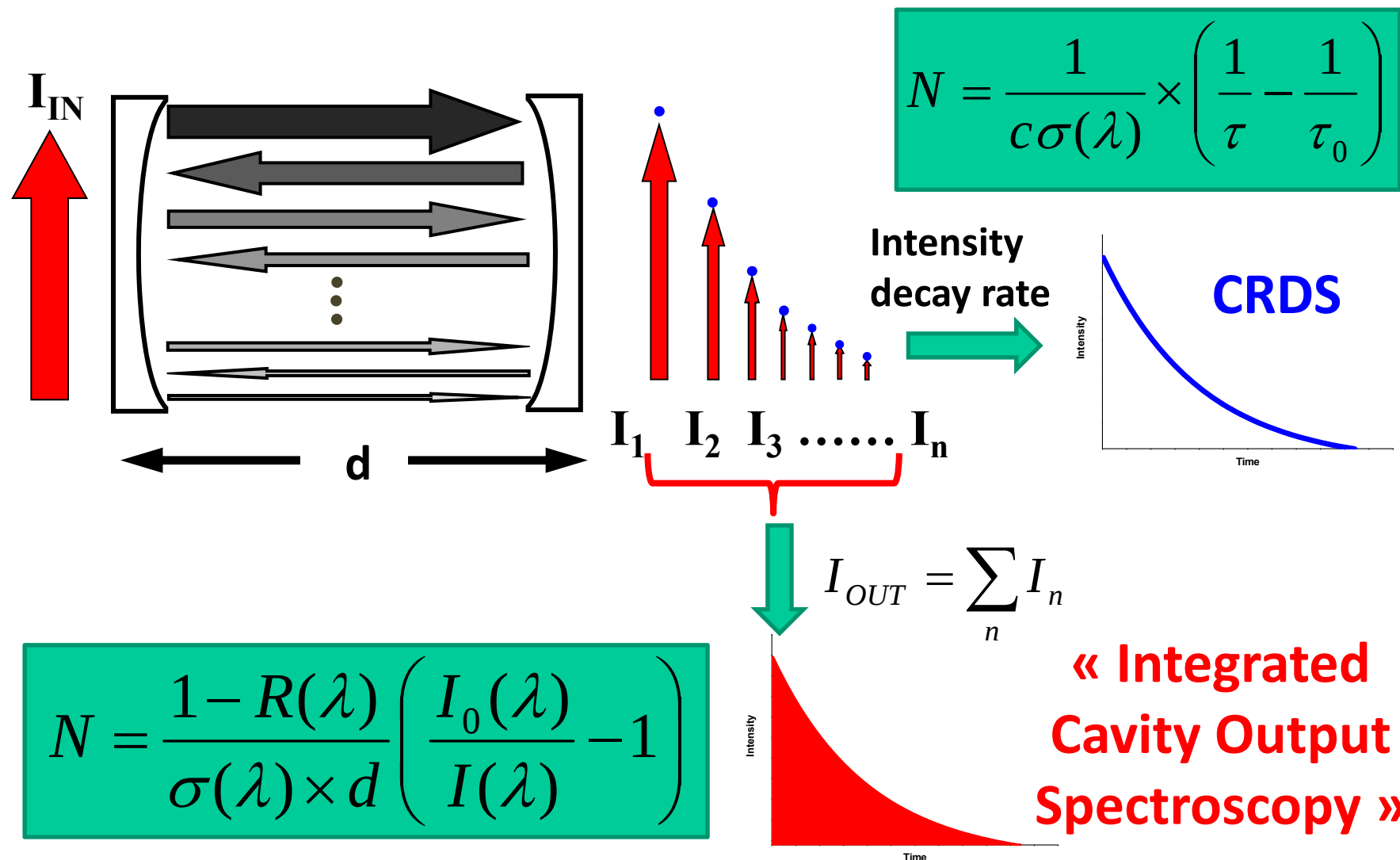
OH radical monitoring by

WMS enhanced OA-ICOS @ 1434 nm

(WMS lowering noise / cavity enhancing signal)



Cavity Enhanced Absorption Spectroscopy (CEAS)



Calibration: determination of the mirror reflectivity R

$$N = \frac{1 - R(\lambda)}{\sigma(\lambda) \times d} \left(\frac{I_0(\lambda)}{I(\lambda)} - 1 \right)$$

ICOS is not an absolute technique : R (λ) to be known

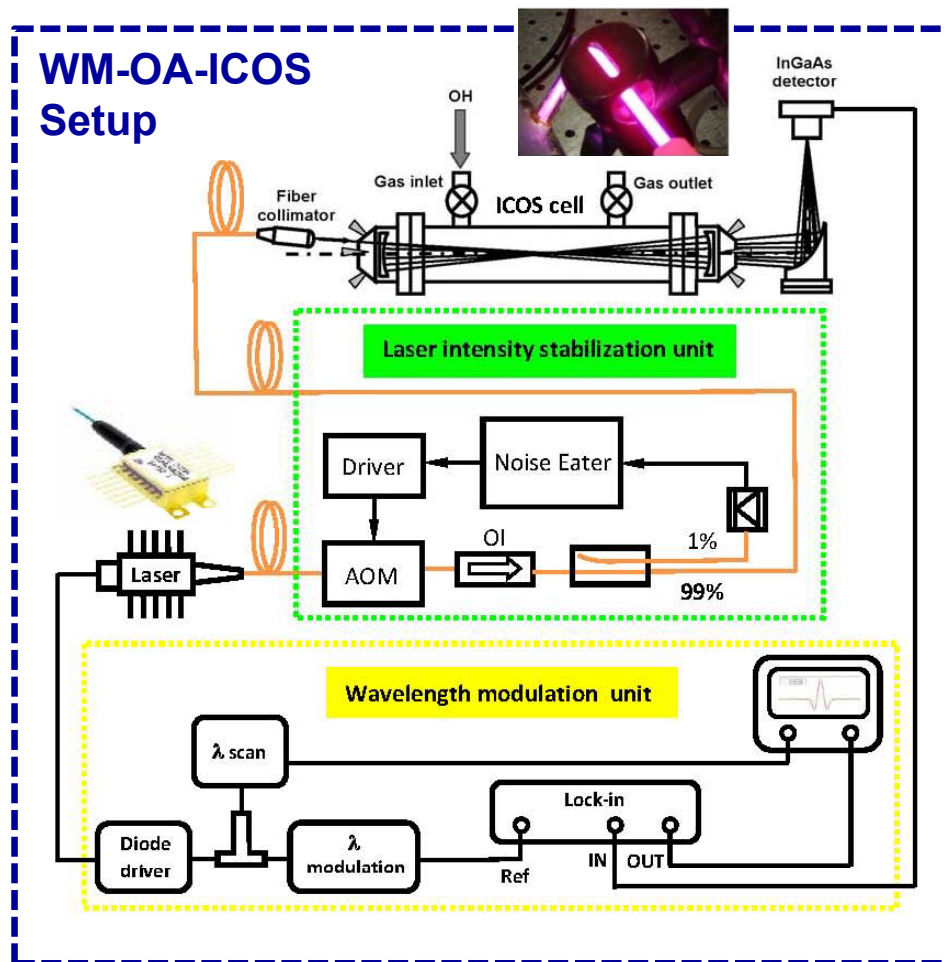
Cavity physical length

Experimentally measured spectrum

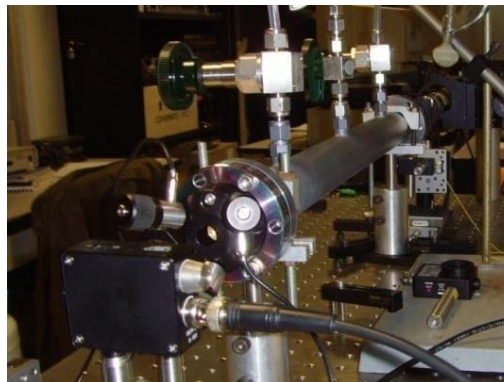
R(λ) can be determined by measuring :

- absorber with known concentration [Environ. Sci. Technol. **40** (2006) 6758] ;
- Rayleigh scattering difference of two species (e.g. He and Zero air) [Atmos. Chem. Phys. **8** (2008)7779] ;
- calibrated low-loss of an optical substrate [Appl. Opt. **48** (2009) B159] ;
- phase shift CRDS [Rev. Sci. Instrum. **79** (2008) 123110] ;

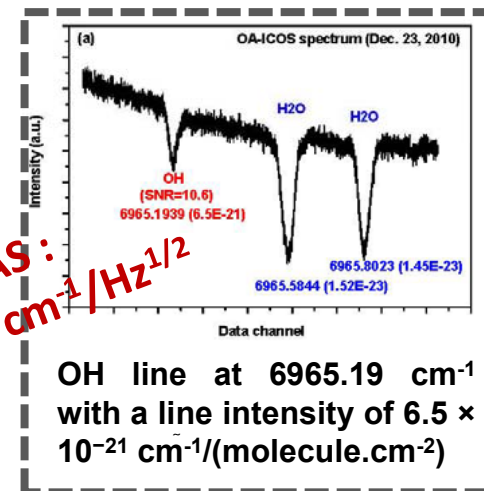
WM-OA-ICOS Setup



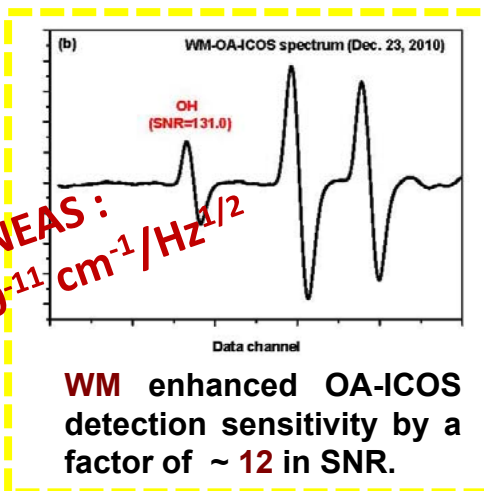
Using OA-ICOS with an effective absorption path length of L_{eff} of $\sim 1.2 \text{ km} \Rightarrow \text{DL of } \sim 5 \times 10^9 \text{ OH/cm}^3$



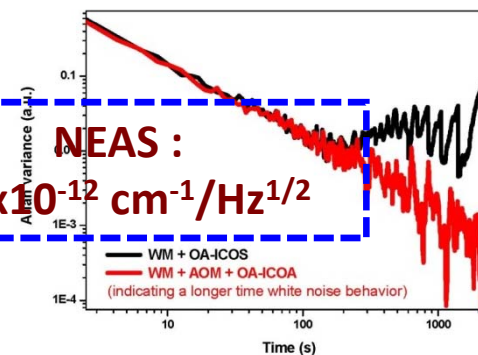
NEAS : $1.0 \times 10^{-10} \text{ cm}^{-1}/\text{Hz}^{1/2}$



NEAS : $2.7 \times 10^{-11} \text{ cm}^{-1}/\text{Hz}^{1/2}$



NEAS : $4.5 \times 10^{-12} \text{ cm}^{-1}/\text{Hz}^{1/2}$



OH radical monitoring by

FRS @ 2.8 μm

(shot noise dominated detection)



Faraday Rotation Spectroscopy (FRS)

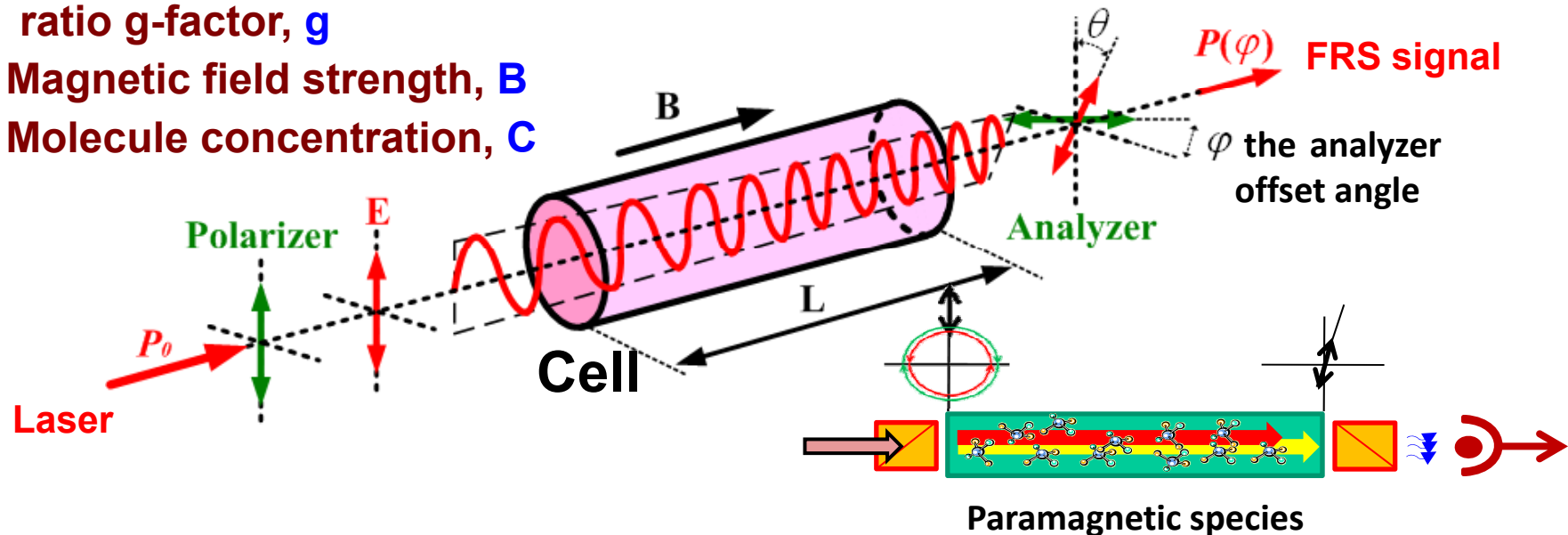
The FRS relies on the particular magneto-optic effect observed for paramagnetic species (OH, HO₂, CH₂O, NO, O₂, NO₂, etc.) : Interaction of incident laser beam with the paramagnetic species under a magnetic field results in a rotation of the polarization plane of a linearly polarized laser beam => FRS signal $P(\varphi)$

The FRS signal depends on :

- ✓ Molecular line strength, S
- ✓ Optical path length, L
- ✓ The rotational gyromagnetic ratio g-factor, g
- ✓ Magnetic field strength, B
- ✓ Molecule concentration, C

$$P(\varphi) = \frac{P_0}{2} (1 - \cos 2\varphi + R_{\Delta} L \sin 2\varphi)$$

and $R_{\Delta} = k_0(n_+ - n_-)$, responsible for creation of the FRS signal*



Merits of FRS

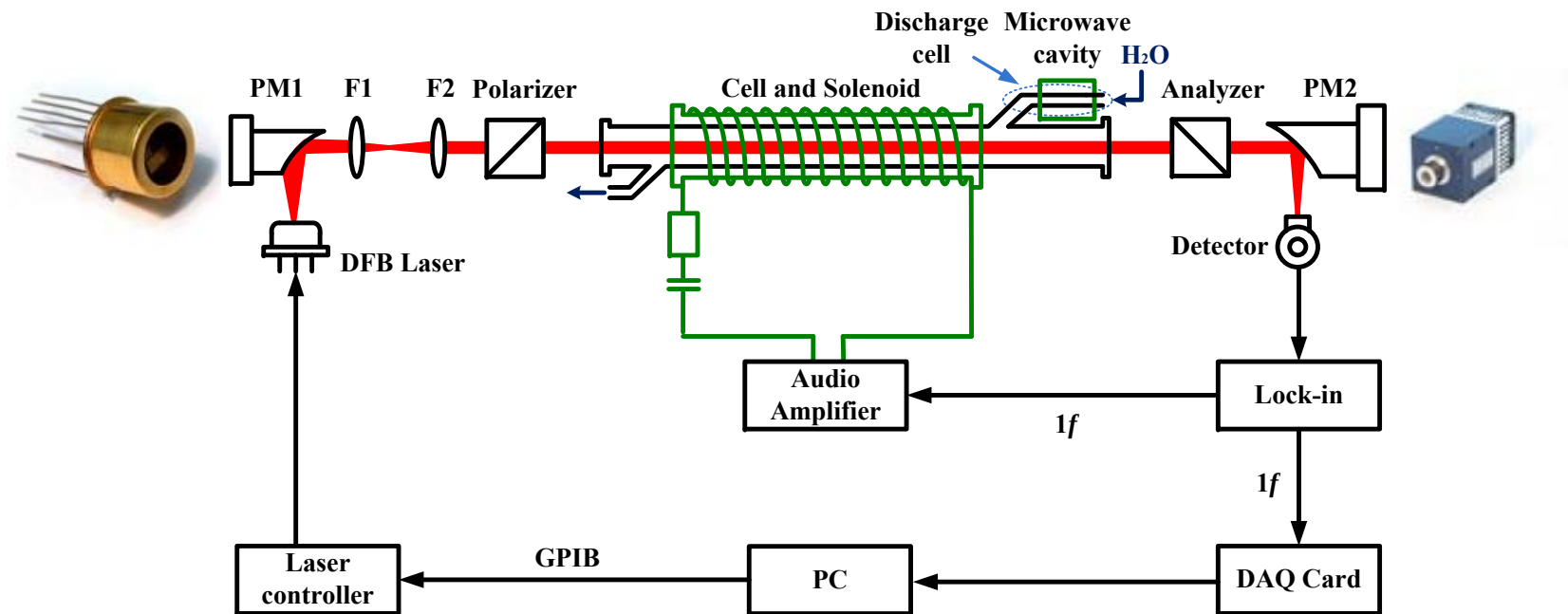
FRS strongly enhances the detection **sensitivity** and **selectivity**:

⇒ **Detection of Faraday rotation** effect provides selectivity to paramagnetic species. No interference from diamagnetic species (CO_2 , H_2O) in the atmosphere ;

⇒ Two nearly **crossed polarizers** with high extinction ratio provide significant reduction of the laser source noise ;

⇒ **Internal sample modulation through** molecular Zeeman energy split provides excellent suppression of all external noise (like stray modulation and most importantly interference fringes).

OH monitoring by FRS @ 2.8 μm



Zhao et al., Opt. Express 19 (2011) 2493-2501 & Appl. Phys. B 109 (2012) 511-519

RT DFB diode laser at 2.8 μm (nanoplus GmbH)

- Single-mode tuning range : $\sim 5 \text{ cm}^{-1}$
- CW laser emission power : $\sim 2 \text{ mW}$
- λ -tuning coefficients: 0.05 nm/mA & 0.25 nm/K

Polarizers : high extinction ratio of $\xi < 5 \times 10^{-6}$

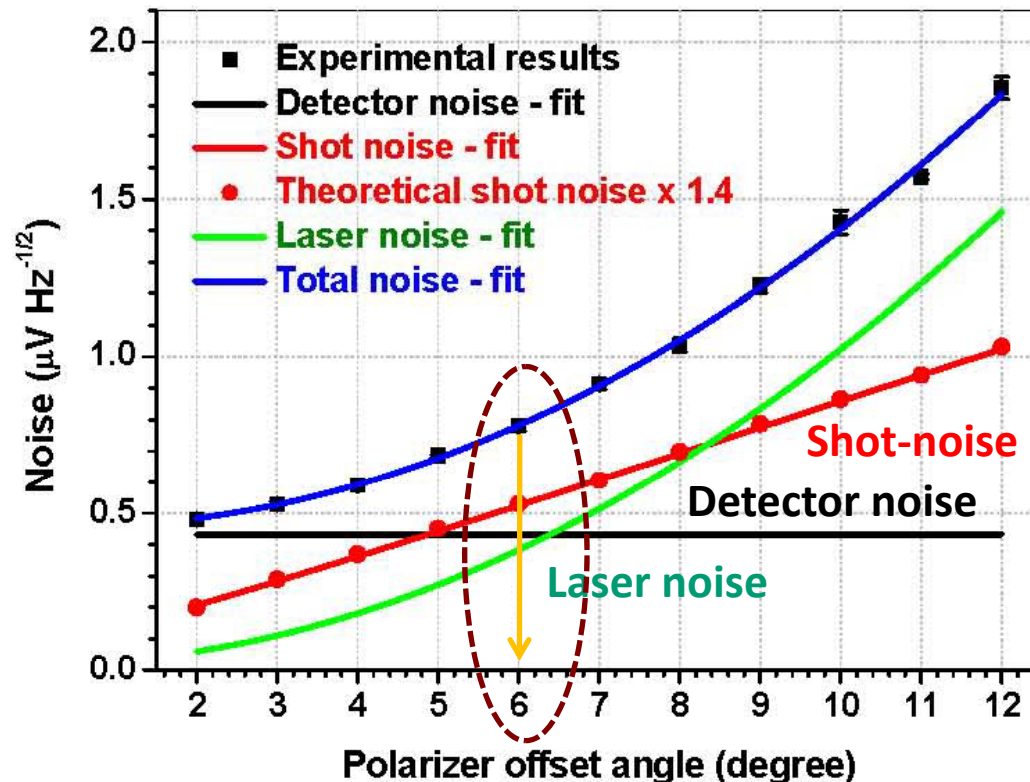
Solenoid : 25 cm long, operating in AC mode at a resonant frequency of 1.302 kHz, with a magnetic field of $B \sim 95 \text{ Gauss}_{\text{rms}}$



Shot-noise dominated detection of OH radical

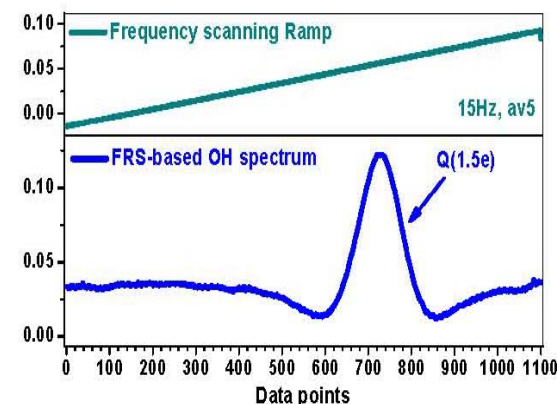
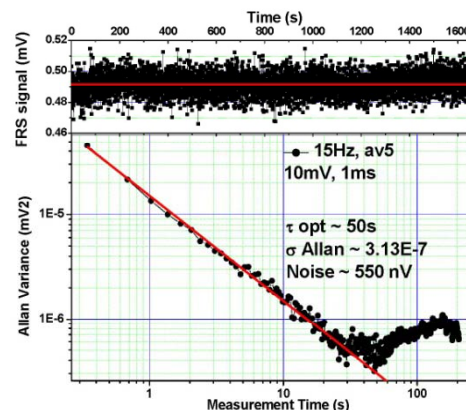
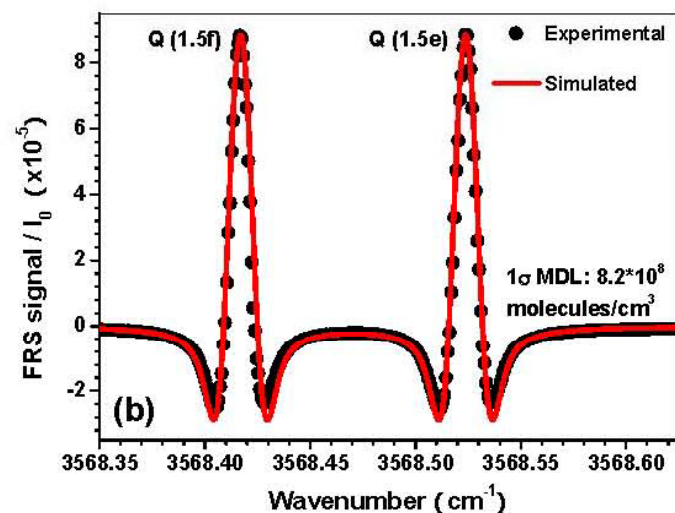
System noise $N_{tot}(\varphi) = \sqrt{N_0^2 + N_1^2(\sin^2(\varphi) + \xi) + N_2^2(\sin^2(\varphi) + \xi)^2}$

- The **shot noise** $N_1 = 4.897 \pm 0.292 \mu\text{V Hz}^{-1/2}$
- The **laser noise** $N_2 = 3.298 \pm 1.152 \mu\text{V Hz}^{-1/2}$
- The **detection system noise** $N_0 = 0.433 \pm 0.019 \mu\text{V Hz}^{-1/2}$



- The total noise at $\varphi_{opt} = 6^\circ$:
 $0.78 \mu\text{V Hz}^{-1/2}$
- Operation at **$\sim 2\times$ theoretical shot-noise** of **$0.38 \mu\text{V/Hz}^{1/2}$**
- A minimum detectable Faraday rotation angle:
 $1.39 \times 10^{-7} \text{ rad Hz}^{-1/2}$
- **System noise is shot-noise predominated**

OH monitoring by FRS



Point-by-point frequency tuning mode

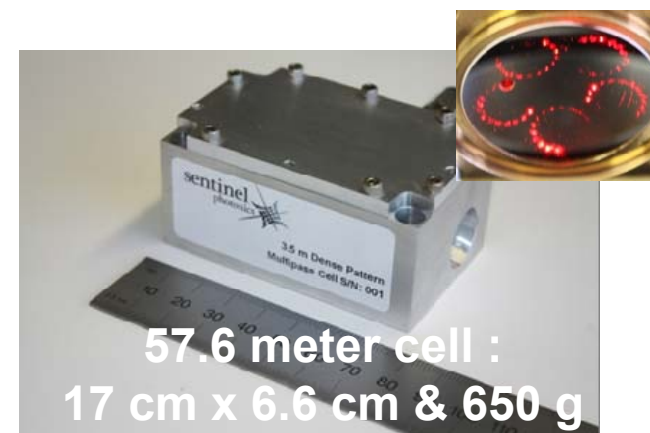
1σ MDL : 8.2×10^8 OH/ cm^3 in a 25-cm long single pass cell (lock-in time = 100 ms)

Fast scanning mode

1σ MDL : $\sim 5.5 \times 10^8$ OH/ cm^3 in a 25-cm long single pass cell.

(Scan rate : 15 Hz & average time : 50 s)

The prototype instrument shows high potential for field applications: compact, self-calibration, direct concentration assessment. Longer absorption pathlength approach to be implemented to lower the minimum detection limit ($\sim 10^6$ OH/ cm^3).



57.6 meter cell :
17 cm x 6.6 cm & 650 g

HONO detection

Lifetimes: ~ a few minutes

Environment: ~ ppbv / indoor: ~10 ppbv / in car: tens of ppbv

HONO is a very important source of the OH radical. Recent researches show that the photolysis of HONO accounts for up to 60% of the integrated OH radical source strengths ([Nature 440 \(2006\) 195-198](#)). Modeled HONO concentrations are often significantly below field observed values, which suggest a large missing source of HONO ([Science 333 \(2011\) 1616-1618](#))

Campaigns: PRIDE-PRD 2004 (China), BEARPEX 2007 (California), DOMINO 2008 (Spain), CINDI 2009 (The Netherlands), SHARP 2009 (Houston), CalNex 2010 (California), FIONA 2010 (Spain),

Needs to better understand the contribution of HONO to the atmospheric photochemical processes and the OH budget

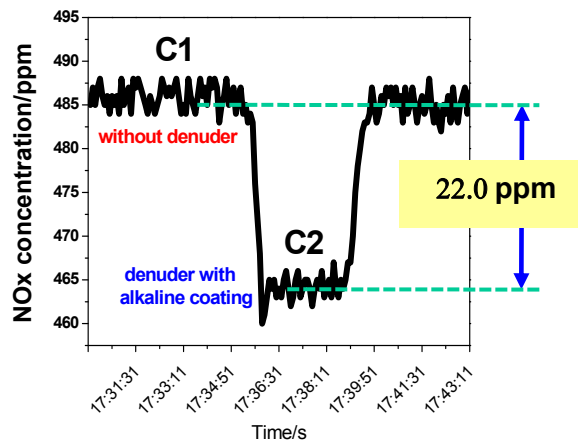
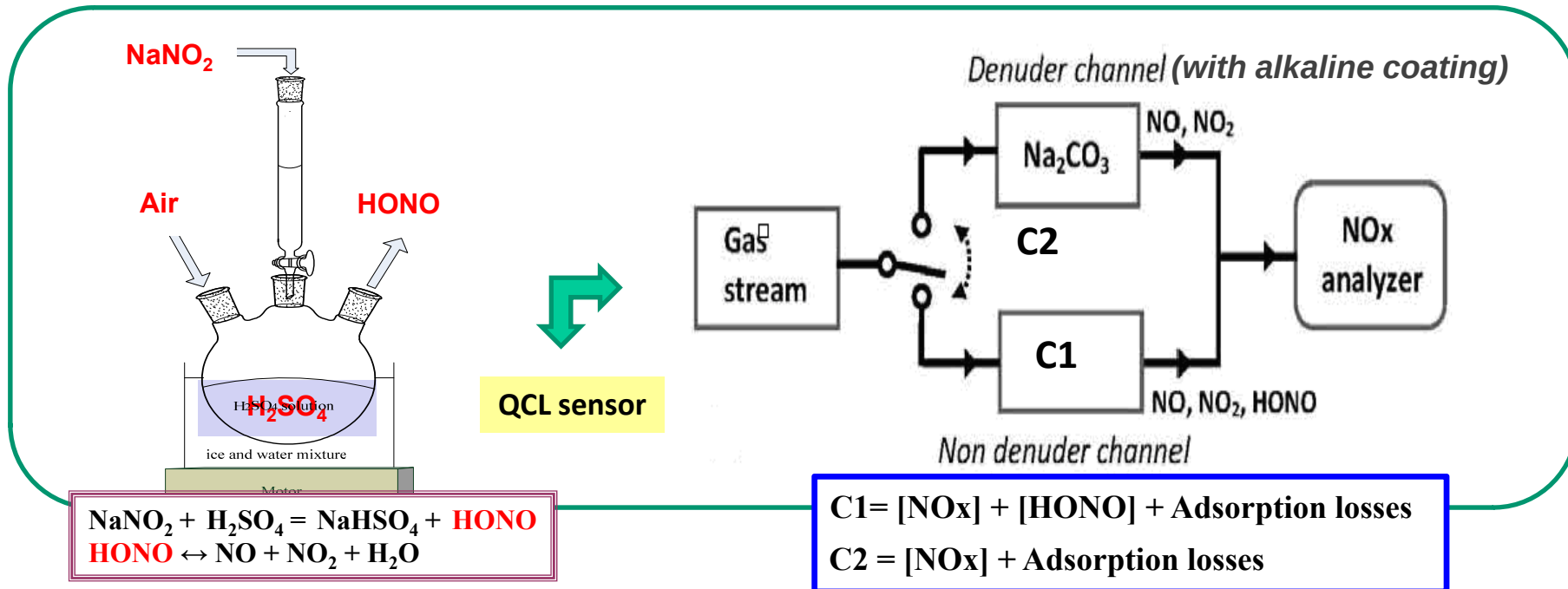
Quantitative analyses of HONO

Accurate and precise *in situ* assessment of HONO concentration is hence highly desirable. Quantitative analysis of HONO is usually made **in the aqueous phase** after wet chemical conversion or **in the gas phase** using spectroscopic techniques.

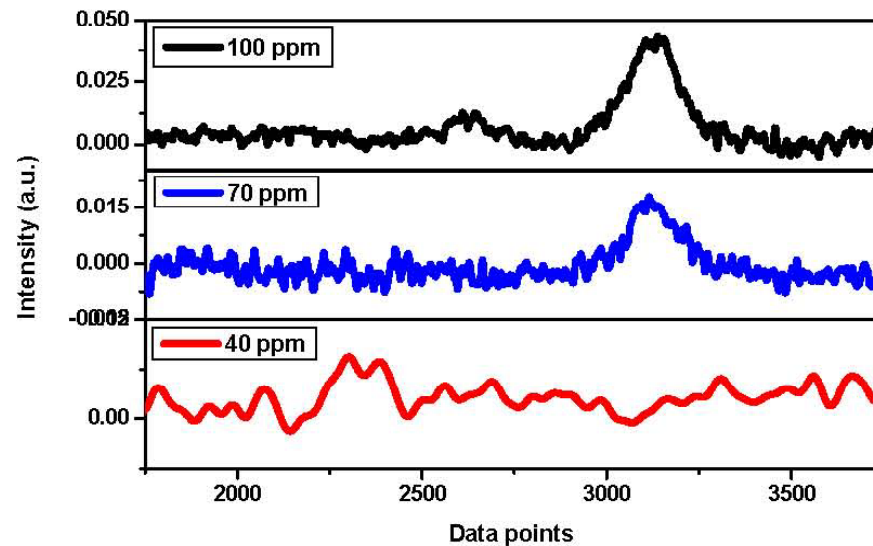
Chemical instruments (denuder, mist chamber or stripping coil + IC, FL, CL, LOPAP, HPLC) : typically **cheap, easy to use** and very **sensitive** (down to ~ pptv) with a time resolution of minutes to hours. Unquantified **chemical interferences** and **sampling induced artifacts**. Validation and calibration of chemical instruments against spectroscopic instruments are of paramount importance.

Spectroscopic instruments (TDLS, IBBCEA, DOAS) : **free of sampling artifacts & chemical interference, self-calibration.**

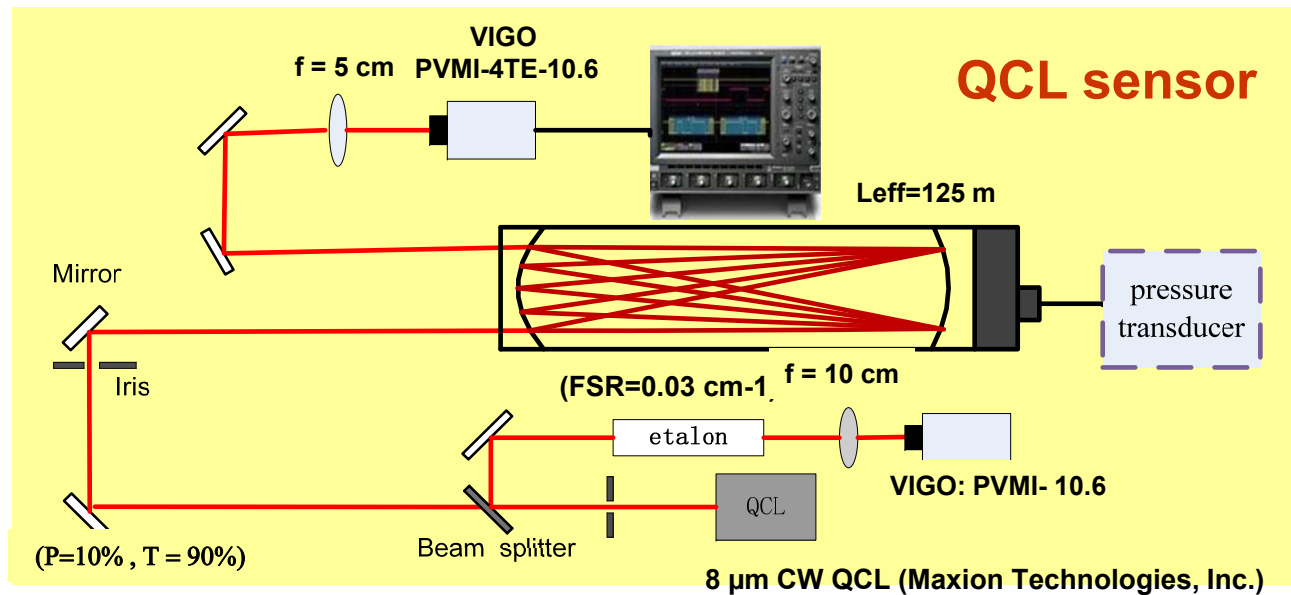
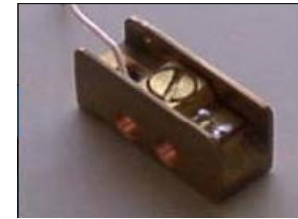
HONO generation & quantification



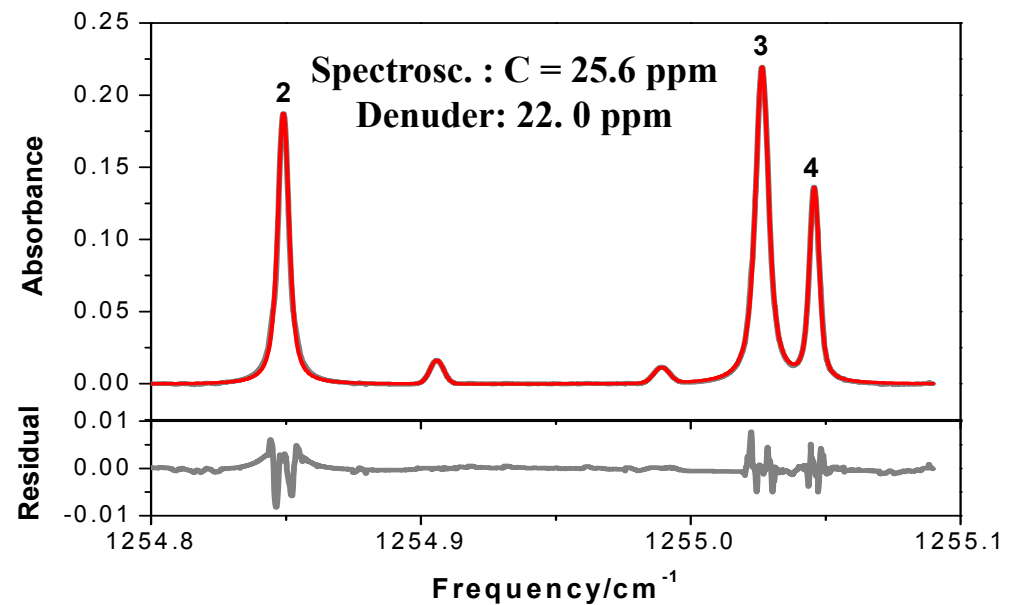
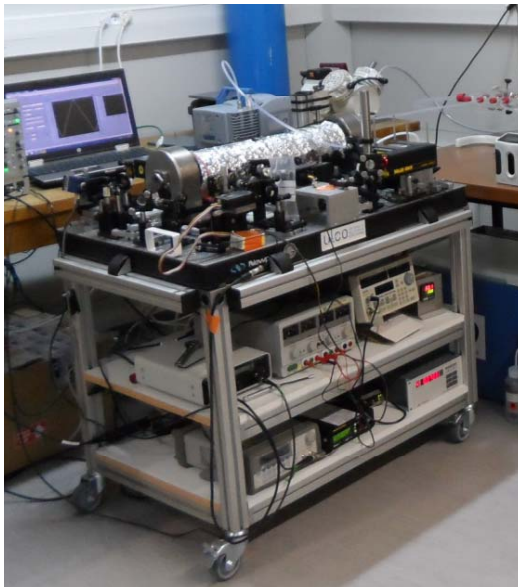
$$[\text{HONO}] = \text{C1} - \text{C2}$$



QCL-based HONO Sensor



1 σ det. Sen. (1 s) :
HONO : < 400 ppt
CH₄ : 4 ppb

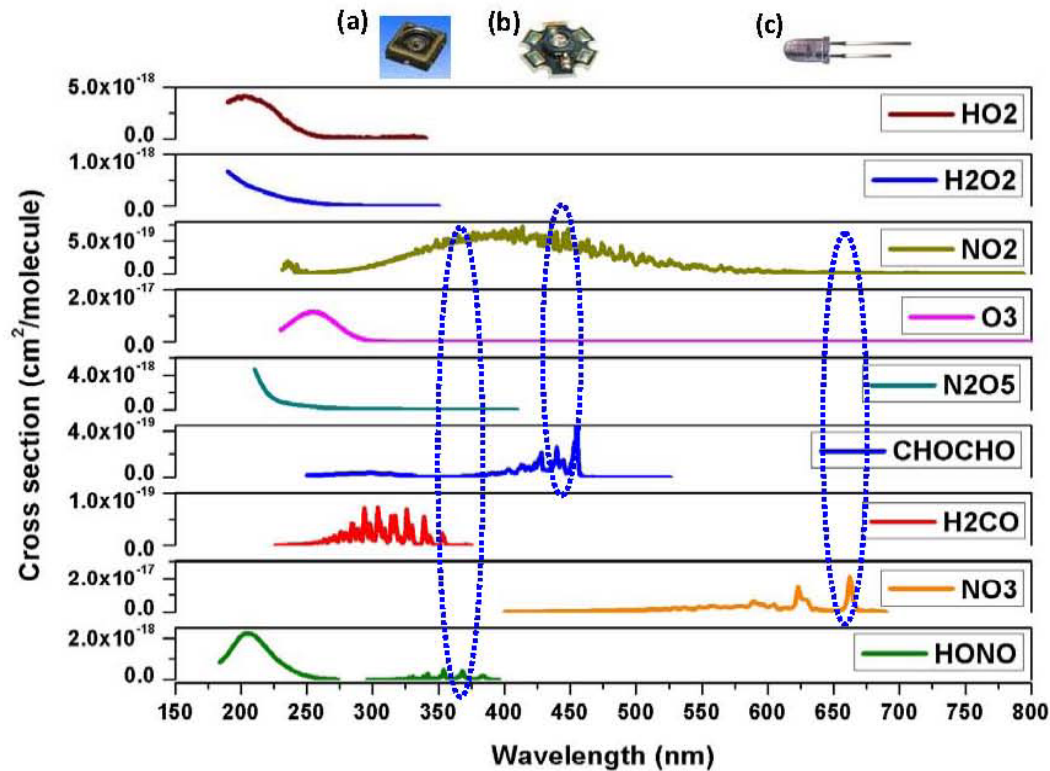


Sensing by Light Emitting Diodes (LED)



HONO, NO₂ & NO₃ radical monitoring

Structured absorptions in the visible and UV spectral region (fdl electronic transition)



	(a) NCSU033AT (NICHIA)	(b) LXHL-LR3C (LUMILEDS)	(c) SMB660N (USHIO)
Optical power	250 mW (@ 500 mA)	340 mW (@ 700 mA)	300 mW (@ 500 mA)
Peak wavelength	365 nm	455 nm	660 nm
Bandwidth (FWHM)	18 nm	20 nm	25 nm
Viewing ½ angle	± 20°	± 70°	± 7°
lifetime	~ 100 000 hr		
Cost per LED	\$60	\$8	\$8
Target molecules	HONO / NO ₂ [1] CH ₂ O	NO ₂ / CHOCHO [2]	NO ₃ / NO ₂ [3]

[1] T. Wu, W. Chen, E. Fertein et al., Appl. Phys. B **106** (2012) 501–509

[2] T. Wu, W. Zhao, W. Chen et al., Appl. Phys. B **94** (2009) 85–94

[3] T. Wu, C. Coeur, G. Dhont et al., EST (2013)

Strong and structured broadband molecular absorptions in the VIS and UV regions, arising from the fdl electronic transition, allow for high sensitivity detection of multiple key atmospheric species at the ppbv-pptv levels.

Sensitive spectroscopic approaches in the VIS and UV

Differential Optical Absorption Spectroscopy (DOAS)

- ✓ Long pathlength absorption ($\sim$ km)
- ✓ Using broadband light for multiple species detection
- ✓ Low spatial resolution - Cumbersome ($L_{\text{Base}} \sim$ km)

Cavity Ringdown Spectroscopy (CRDS)

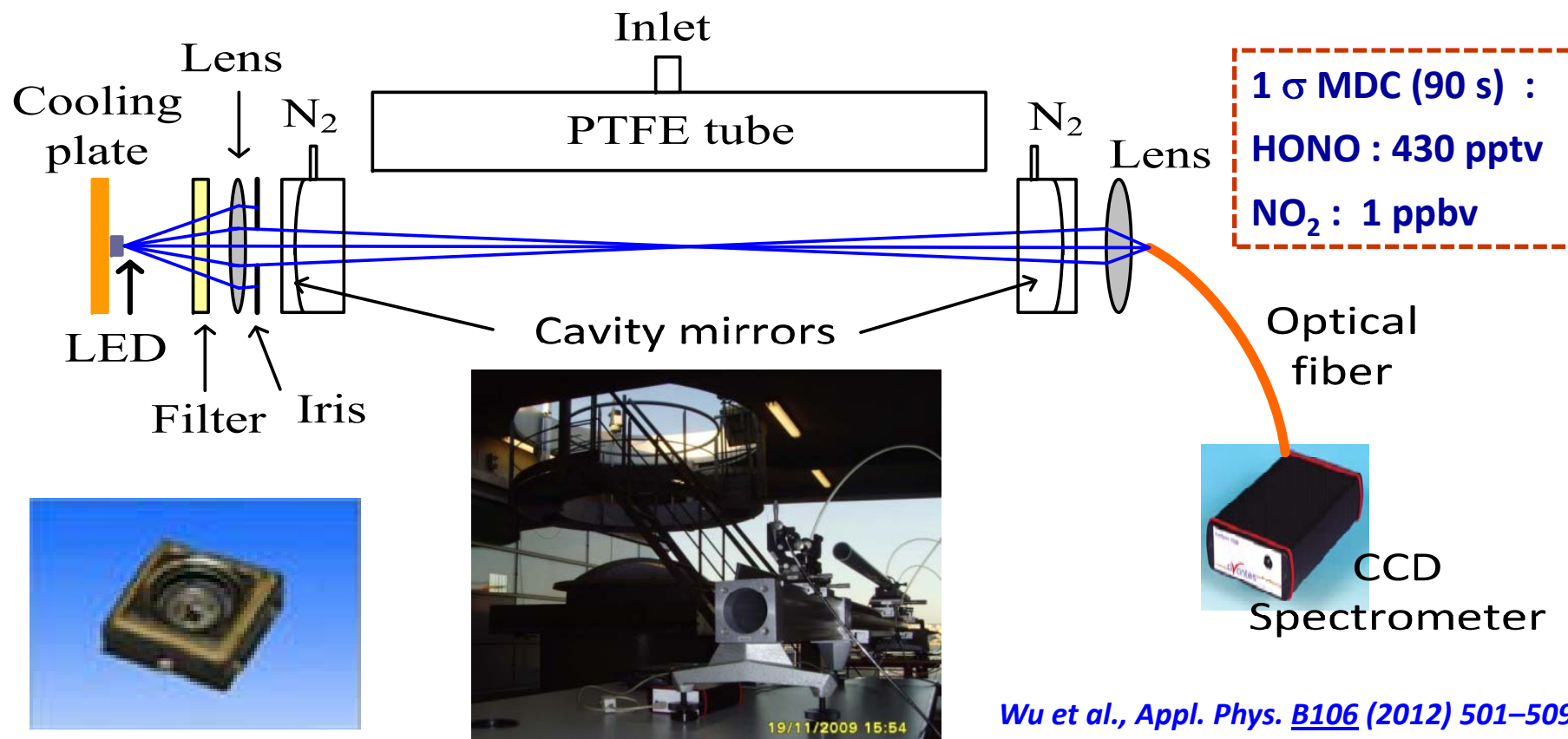
- ✓ Cavity enhanced long effective pathlength ($\sim$ km)
- ✓ High spatial resolution - Compact ($L_{\text{Base}} \sim$ m)
- ✓ Narrow laser spectral coverage, limited for multi-species detection

Broadband Cavity Enhanced Spectroscopy (BBCEAS)

- ✓ Cavity enhance (high spatial resolution for reactive species) :
=> Long effective pathlength ($\sim$ km) & Compact ($L_{\text{Base}} \sim$ m)
- ✓ Broadband light => Simultaneous multi-species measurement

Open path IBBCEAS of HONO & NO₂ detection @ 365 nm

No wall losses or heterogeneous production of HONO

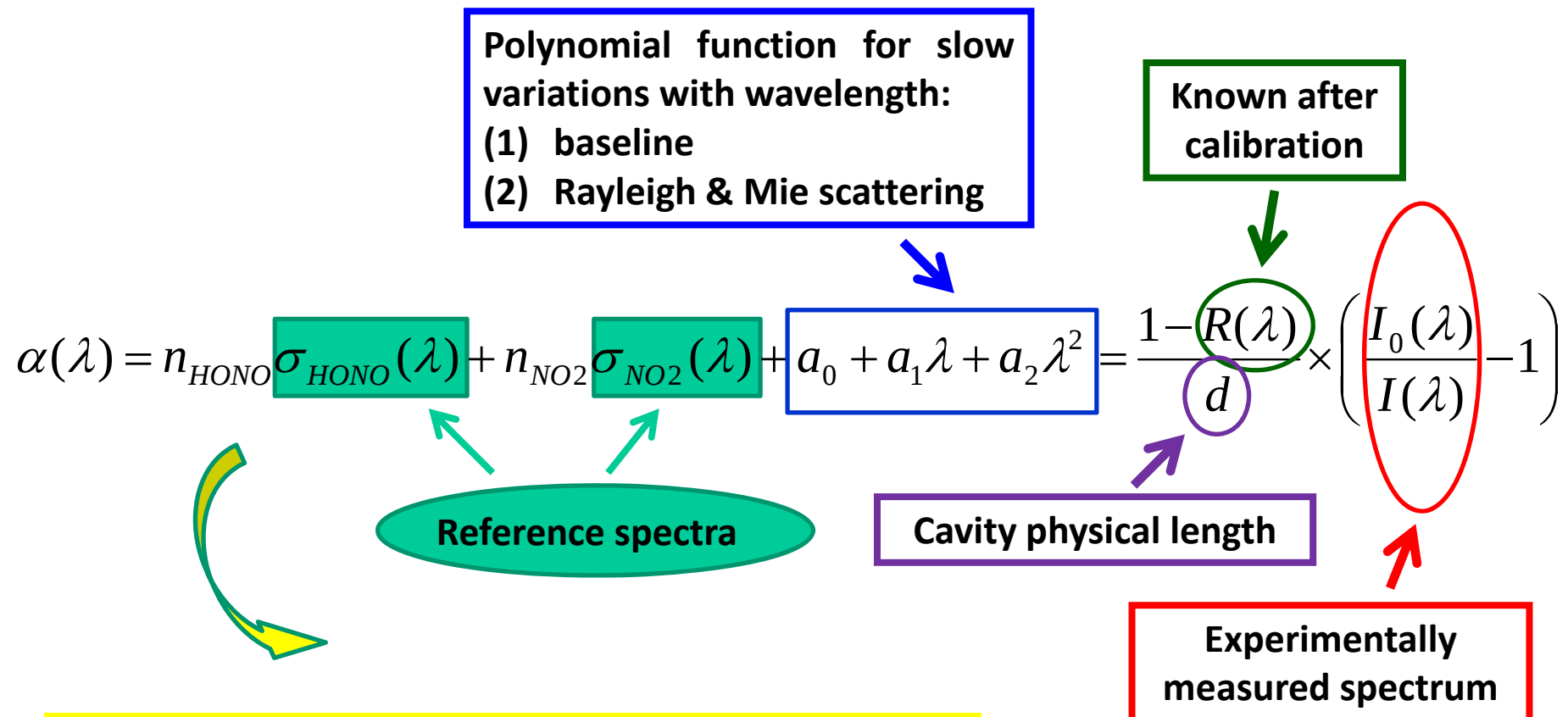


Wu et al., *Appl. Phys. B*106 (2012) 501–509



Simultaneous concentration retrieval of multiple species

Nonlinear least-square fitting based on the Levenberg-Marquardt algorithm

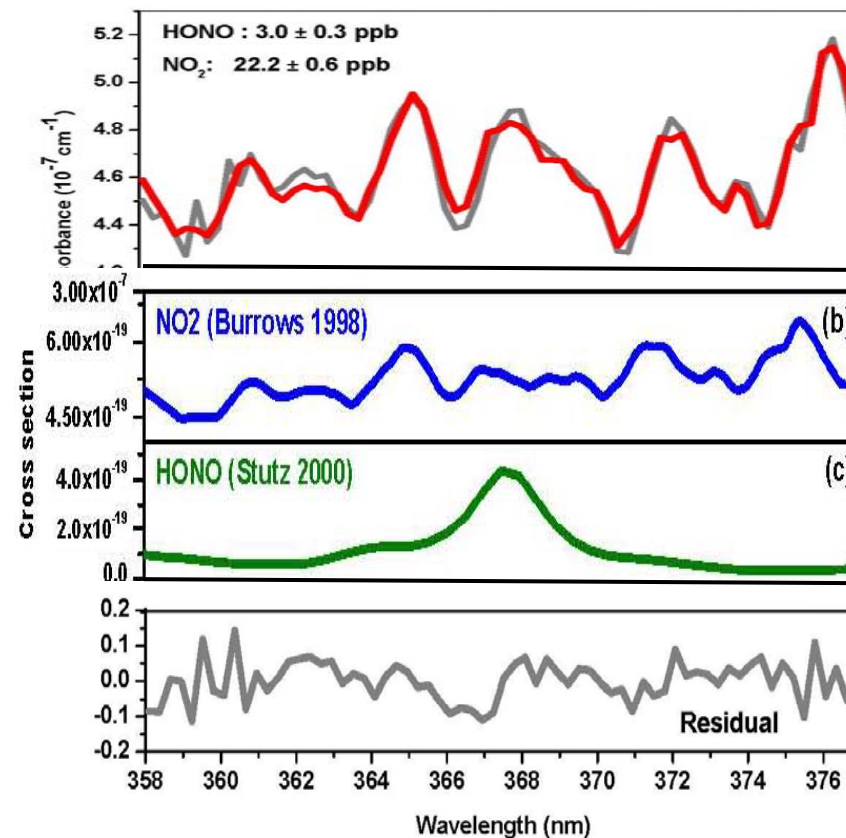


Target species concentrations can be simultaneously retrieved by a multivariate fit

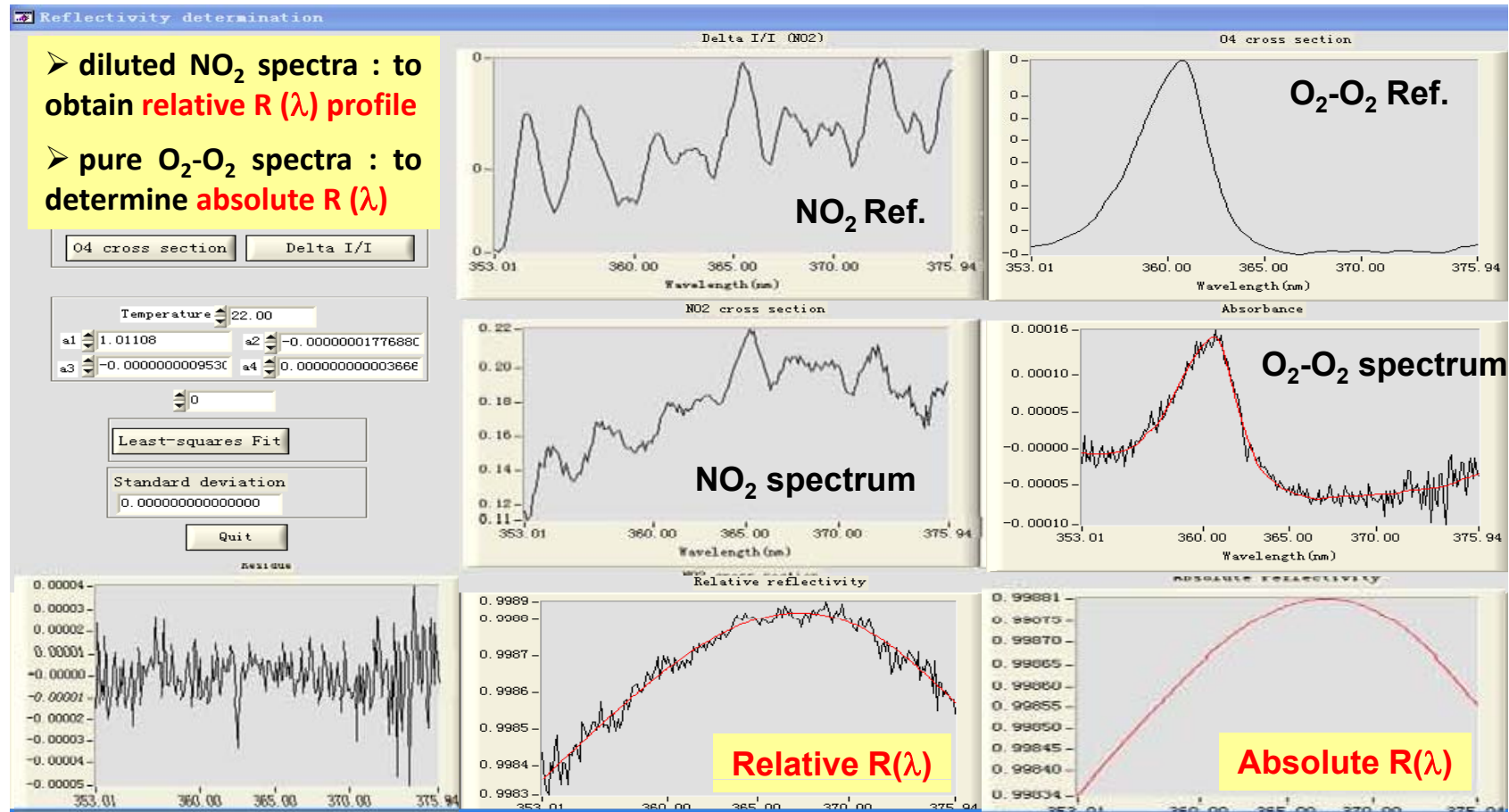
Simultaneous measurement of HONO and NO₂

(using multivariate fit of ref. σ to exp. spectrum)

$$\frac{1 - R(\lambda)}{d} \left(\underbrace{\frac{I_0(\lambda)}{I(\lambda)}}_{\text{Exp. spectrum}} - 1 \right) = n_{\text{HONO}} \underbrace{\sigma(\lambda)_{\text{HONO}}}_{\text{Ref. } \sigma(\lambda)} + n_{\text{NO}_2} \underbrace{\sigma(\lambda)_{\text{NO}_2}}_{\text{Ref. } \sigma(\lambda)} + \underbrace{a_0 + a_1\lambda + a_2\lambda^2}_{\text{Baseline}}$$



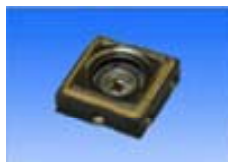
Determination of the cavity mirrors' reflectivity: $R(\lambda)$



By using measured absorption spectra of 100 ppbv NO_2 (generated with a gas dilution calibrator, Sabio instruments) and pure O_2 , the max. cavity mirror's reflectivity was determined to be **~ 0.99916** , which corresponded to an **effective pathlength of ~ 2.1 km** (based on a **cavity length of $L=1.76$ m**).

Applications

- Field observation of HONO & NO₂ in sub-urban @ 356 nm



- NO₂ & NO₃ radical monitoring for kinetic study in smog chamber @ 660 nm

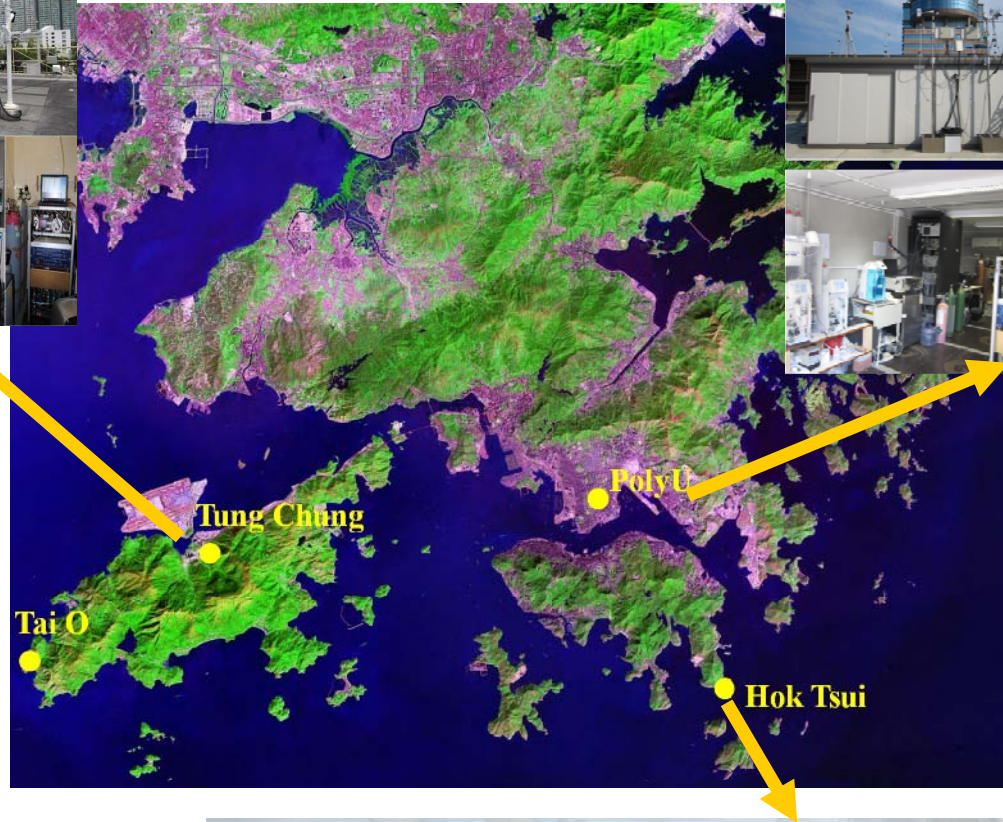


1) Field application in a Hong Kong Campaign

Hong Kong Polytechnic University & Environmental Protection Department of Hong Kong



Tung Chung
(sub-urban site)



Poly U

Long-term **background site** on south-eastern Hong Kong Island (since 1993)

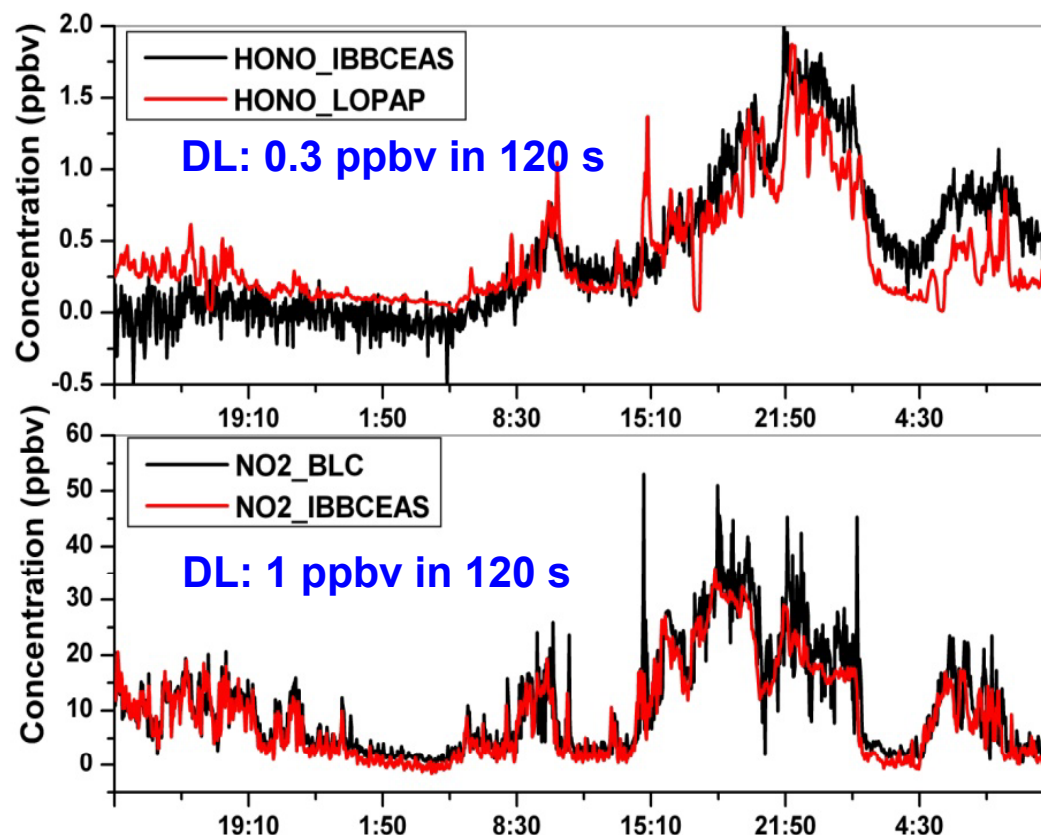


Hok Tsui

HONO : IBBCEAS vs. LOPAP

(HONO converted into color azo dye & det. in long path abs.)

NO₂ : IBBCEAS vs. BL-NOx analyzer



Time (12-14 May) *Chen et al., SPIE Newsroom (2013) DOI: 10.1117/2.1201301.004689*



Detection sensitivity

1 σ detection limits (120 s) :

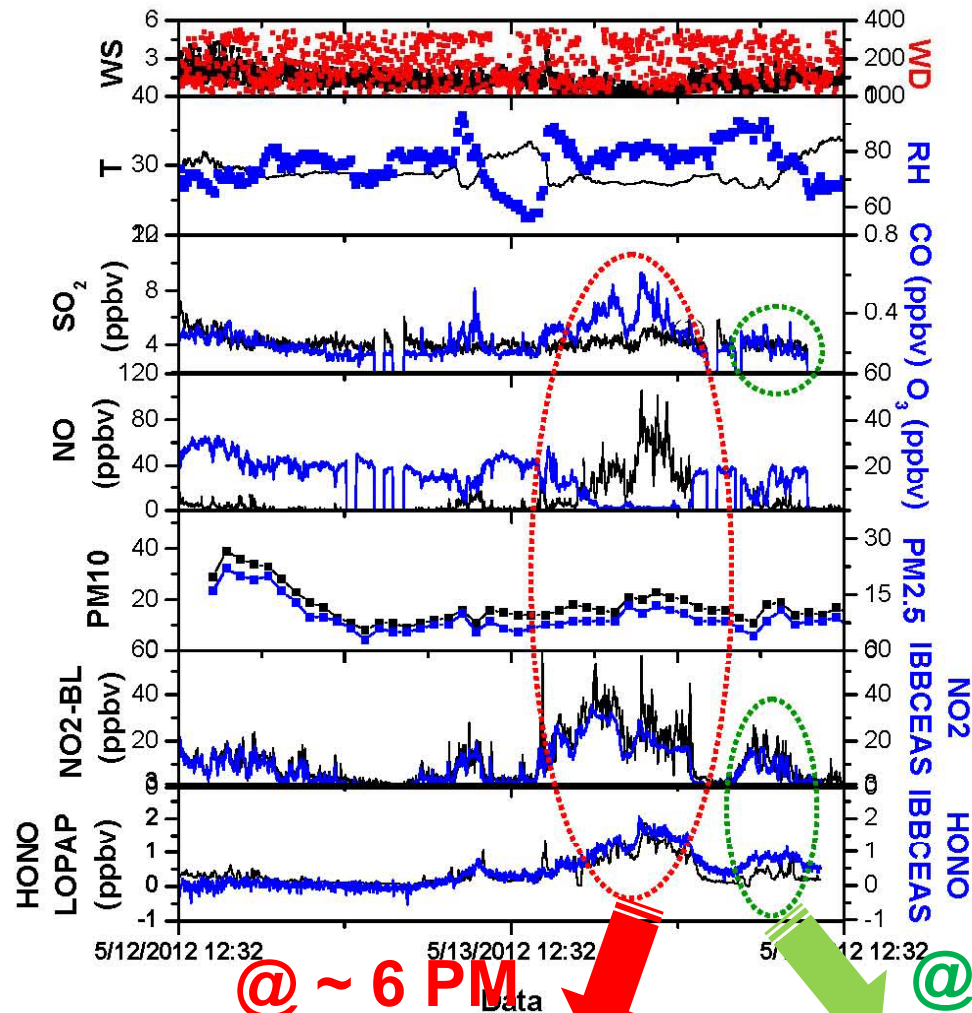
HONO: 300 pptv

NO₂ : 1 ppbv

Precision: < 10%

Time series of HONO and NO₂ concentrations measured by IBBCEAS, LOPAP and blue light (BL) based NOx analyzer at the TC site on 12-14th May 2012.

Field observation of HONO concentration variation

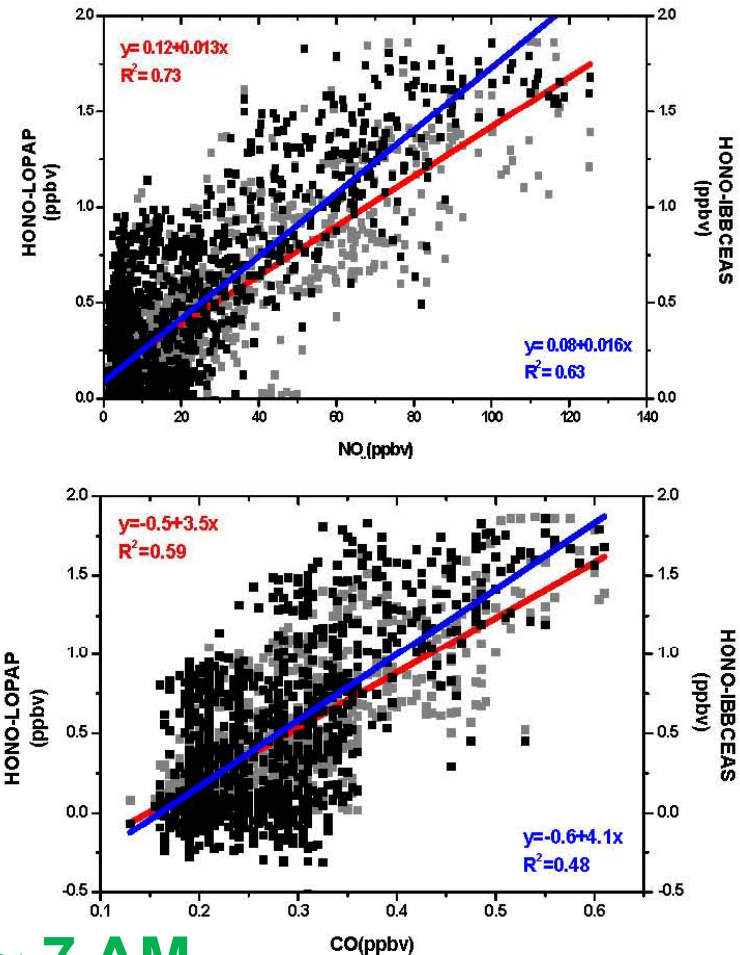


@ ~ 6 PM

CO combustion tracer
=> HONO from traffic emission

@ ~ 7 AM

Heterogeneous nighttime formation
from NO₂ hydrolysis on surfaces

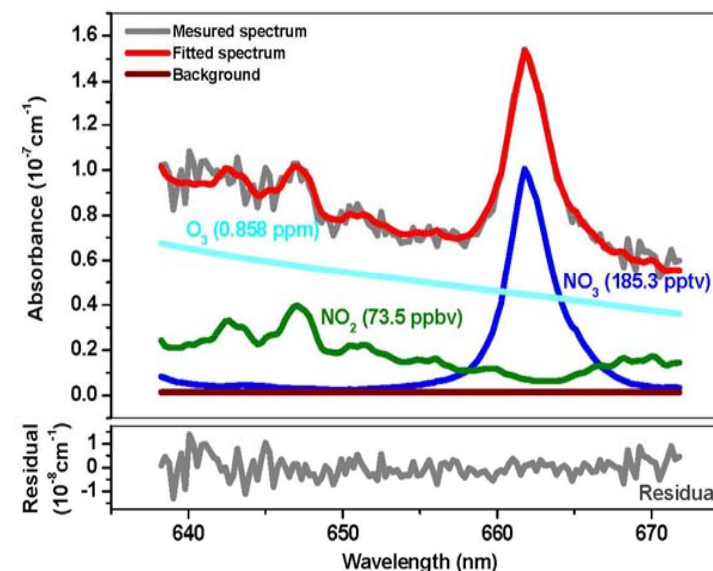


2) Monitoring NO_3 & NO_2 in a smog chamber

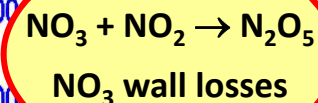
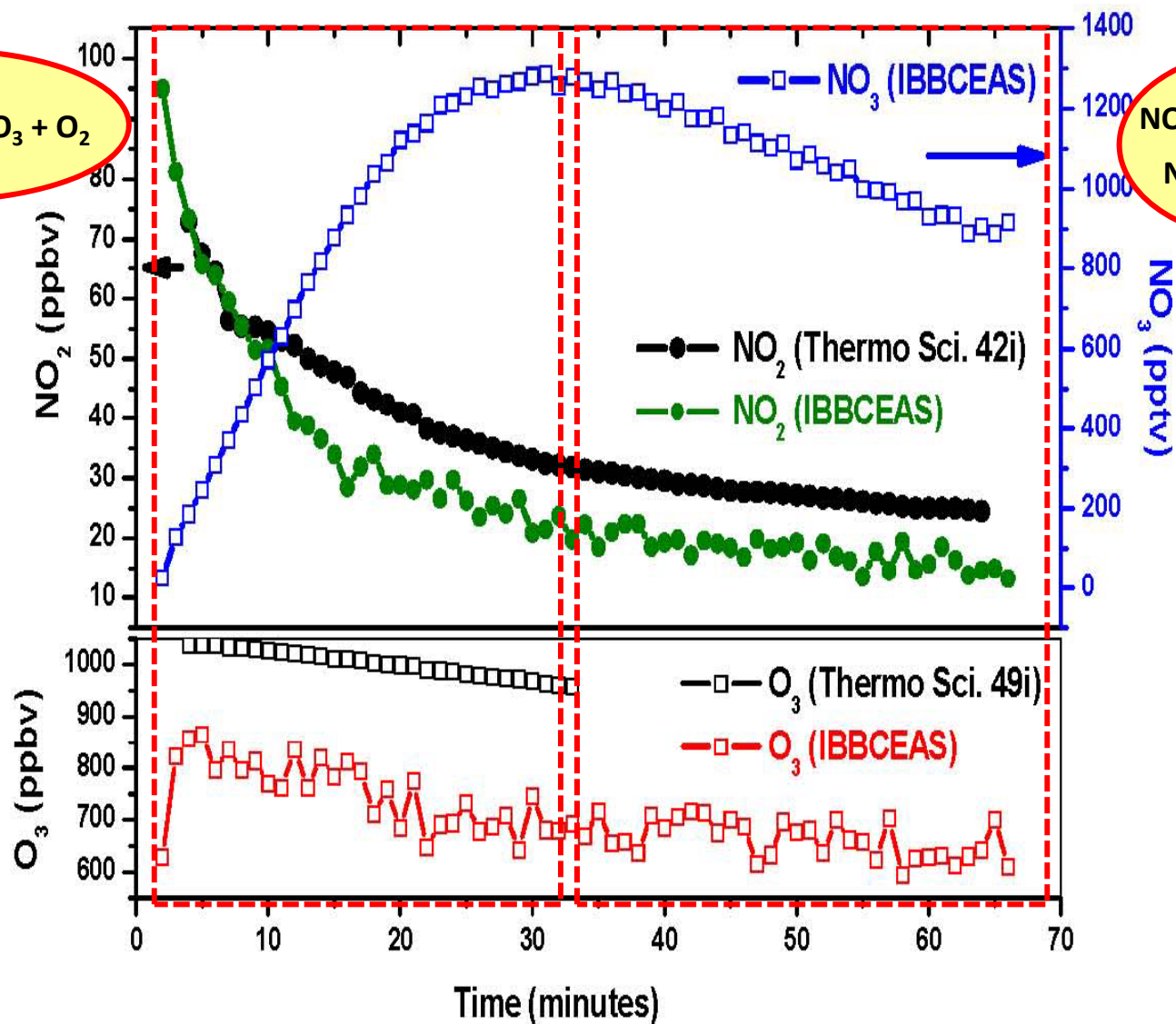
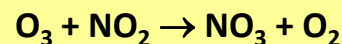
The most important nighttime oxidant with lifetimes: in seconds in daytime & in minutes in nighttime / Typical concentration : 5-400 ppt



2 m X 2 m X 2 m in plexiglas, illuminated with 10 fluorescence tubes (400–800 nm, 40 W).



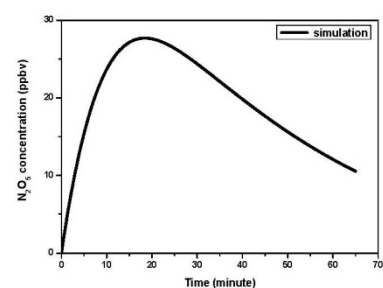
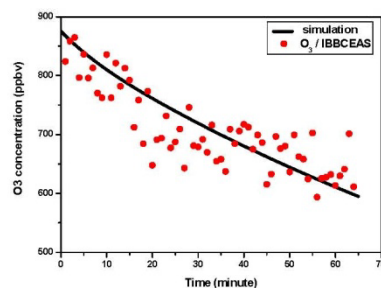
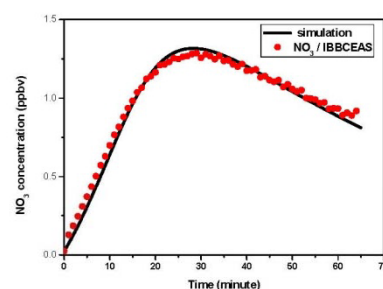
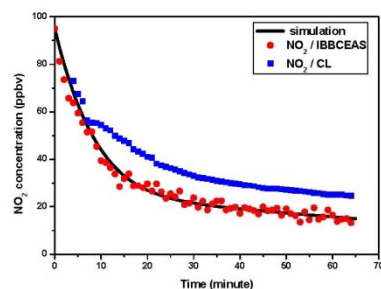
Real time monitoring photochemical processes in smog chamber



Temporal profiles of NO₃, NO₂ and O₃ concentrations measured by IBBCEAS (red) for kinetic study of the NO₃ + NO₂ ↔ N₂O₅ system to determine reaction rate constants

$$\begin{aligned}\frac{d[\text{NO}_2]}{dt} &= -k_1 [\text{NO}_2] [\text{O}_3] - k_2 [\text{NO}_2] [\text{NO}_3] + k_3 [\text{N}_2\text{O}_5], \\ \frac{d[\text{NO}_3]}{dt} &= k_1 [\text{NO}_2] [\text{O}_3] - k_2 [\text{NO}_2] [\text{NO}_3] + k_3 [\text{N}_2\text{O}_5] - k_4 [\text{NO}_3], \\ \frac{d[\text{N}_2\text{O}_5]}{dt} &= k_2 [\text{NO}_2] [\text{NO}_3] - k_3 [\text{N}_2\text{O}_5].\end{aligned}$$

Wu et al., EST (2013)



chemical reaction	constant	k (this work) at 296 K with k ₂ fixed ^(a)	k (this work) at 296 K with k ₋₂ fixed ^(a)	k (literature data) at 296 K
NO ₂ + O ₃ → NO ₃ + O ₂	k ₁ (cm ³ molecule ⁻¹ s ⁻¹)	3.32 × 10 ⁻¹⁷	3.31 × 10 ⁻¹⁷	3.33 × 10 ⁻¹⁷ ^(a)
NO ₂ + NO ₃ + M ↔ N ₂ O ₅ + M	k ₂ (cm ³ molecule ⁻¹ s ⁻¹)		1.19 × 10 ⁻¹²	1.25 × 10 ⁻¹² ^(a)
	k ₋₂ (s ⁻¹)	3.62 × 10 ⁻² s ⁻¹		3.48 × 10 ⁻² s ⁻¹ ^(a)
	K _{eq}			2.9 × 10 ⁻¹¹ ^(b) 3.59 × 10 ⁻¹¹ ^(c)
NO ₃ → wall losses	k ₃ (s ⁻¹)	1.53 × 10 ⁻² s ⁻¹ ^(d)	1.53 × 10 ⁻² s ⁻¹ ^(d)	
O ₃ → wall losses	k ₄ (s ⁻¹)	7.54 × 10 ⁻⁵ s ⁻¹ ^(d)	7.53 × 10 ⁻⁵ s ⁻¹ ^(d)	

^(a) Recommended value at 296 K, Atkinson et al., 2004 (IUPAC-web version, 2004).

^(b) Recommended value at 298 K (Cantrell et al., 1993).

^(c) Calculated from the ratio (k₂/k₋₂) of the Atkinson's recommended values at 296 K.

^(d) These rate constants are chamber dependent (on the size and the material of the chamber).

chemical reaction	constant	k (this work) at 296 K with k_2 fixed ^(a)	k (this work) at 296 K with k_{-2} fixed ^(a)	k (literature data) at 296 K
$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$	k_1 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	3.32×10^{-17}	3.31×10^{-17}	$3.33 \times 10^{-17} \text{ (a)}$
$\text{NO}_2 + \text{NO}_3 + \text{M} \leftrightarrow$ $\text{N}_2\text{O}_5 + \text{M}$	k_2 ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)		1.19×10^{-12}	$1.25 \times 10^{-12} \text{ (a)}$
	$k_{-2} \text{ (s}^{-1}\text{)}$	$3.62 \times 10^{-2} \text{ s}^{-1}$		$3.48 \times 10^{-2} \text{ s}^{-1} \text{ (a)}$
	K_{eq}			$2.9 \times 10^{-11} \text{ (b)}$ $3.59 \times 10^{-11} \text{ (c)}$
$\text{NO}_3 \rightarrow \text{wall losses}$	$k_3 \text{ (s}^{-1}\text{)}$	$1.53 \times 10^{-2} \text{ s}^{-1} \text{ (d)}$	$1.53 \times 10^{-2} \text{ s}^{-1} \text{ (d)}$	
$\text{O}_3 \rightarrow \text{wall losses}$	$k_4 \text{ (s}^{-1}\text{)}$	$7.54 \times 10^{-5} \text{ s}^{-1} \text{ (d)}$	$7.53 \times 10^{-5} \text{ s}^{-1} \text{ (d)}$	

^(a) Recommended value at 296 K, Atkinson et al., 2004 (IUPAC-web version, 2004).

^(b) Recommended value at 298 K (Cantrell et al., 1993).

^(c) Calculated from the ratio (k_2/k_{-2}) of the Atkinson's recommended values at 296 K.

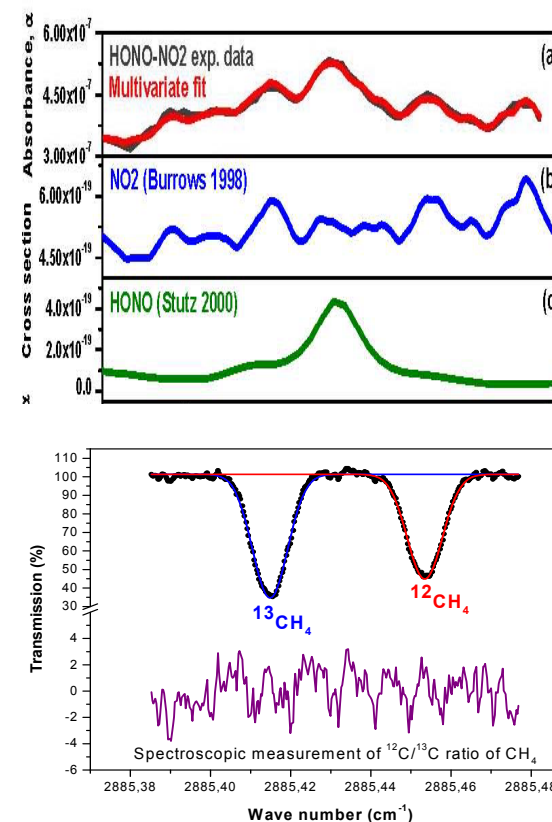
^(d) These rate constants are chamber dependent (on the size and the material of the chamber).

Summary

Contrary to long-lived species such as GHG, monitoring of strongly reactive short-lived species (**concentration, flux, vertical profile**) represent a real challenge in terms of **sensitivity, accuracy, precision, time response, interference from sampling / analytical artifacts, calibration,**

Very low-cost **UV-VIS LED** sources permits *multiple species quantification with high sensitivity*

Mid-IR LASER offers the unique advantage of *real time spectroscopic analysis of the isotopic composition* of the key atmospheric species, which is crucial for study of the **origin, evolution** and **dispersion** of these chemical species in the atmosphere for well understanding tropospheric process.



Collaborators



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The IRENI program of the Région Nord-Pas de Calais.



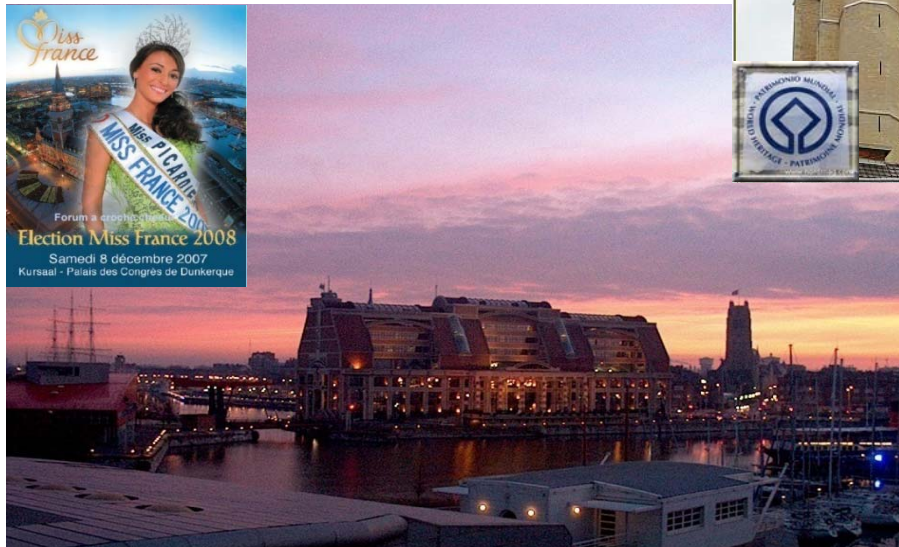
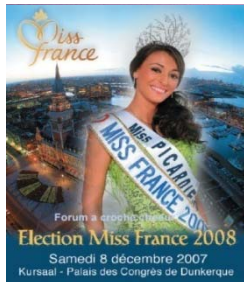
The Program of the Groupement de Recherche International SAMIA between CNRS (France), RFBR (Russia) and CAS (China)



The FR-ANR & US-NSF International Program

Thank You

Questions & Comments





MIOMD 2014

Infrared Optoelectronics : Materials and Devices
October 5-8, 2014, Montpellier, FRANCE

Infrared Emission and Detection:

Interband and inter-subband physics/modeling, material growth and characterization, and device processing. Novel architectures. Non-linear technologies. Radiation effects. Systems components.



Infrared Integrated Systems:

Monolithic and heterogeneous integration of lasers, detectors, and passive components.

Scene illumination, standoff chemical-specific imaging, environmental monitoring, LIDAR, free-space communication.



Infrared Applications of Infrared Emission / Detection:

Applications of infrared detectors and lasers.



New in MIOMD 2014: larger “Sensing session”

