OH reactivity and kinetic measurements by FAGE

Damien AMEDRO, Alex PARKER,
Coralie SCHOEMAECKER and Christa FITTSCHEN

PhysicoChimie des Processus de Combustion et de l'Atmosphère
PC2A
UMR CNRS 8522 – Université Lille 1

OTEM 2010

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Outline

- $OH/\ HO_2$ interest

- FAGE instrument for quantitative OH et HO_2 measurements

- FAGE instrument for time resolved OH et HO_2 measurements

- Conclusions and perspectives

Outline

- OH/ HO_2 interest

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- Conclusions and perspectives

Why OH and HO_2 ?

OH

- Main oxidant in the atmosphere
- Initiates most of the oxidation processes

But :

- Difficult to quantify (very low concentration, 10^6 molecule.cm^{-3})
- Discrepancy between measurements and modelisation
- Unknown source and consumption of OH

Needs :

- Data on elementary reactions
- Absolute concentrations during field campaigns
- Global measurement of OH reactivity (all consumption pathways)

HO_2

High correlation with OH

$OH + CO + O_2 \rightarrow HO_2 + CO_2$

$HO_2 + NO \rightarrow OH + NO_2$

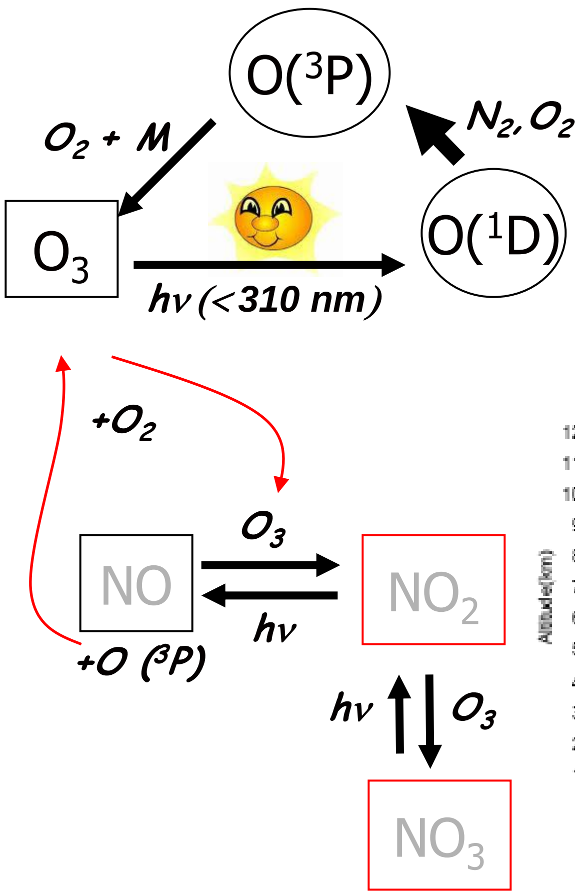
OH in the atmosphere: complex system!!

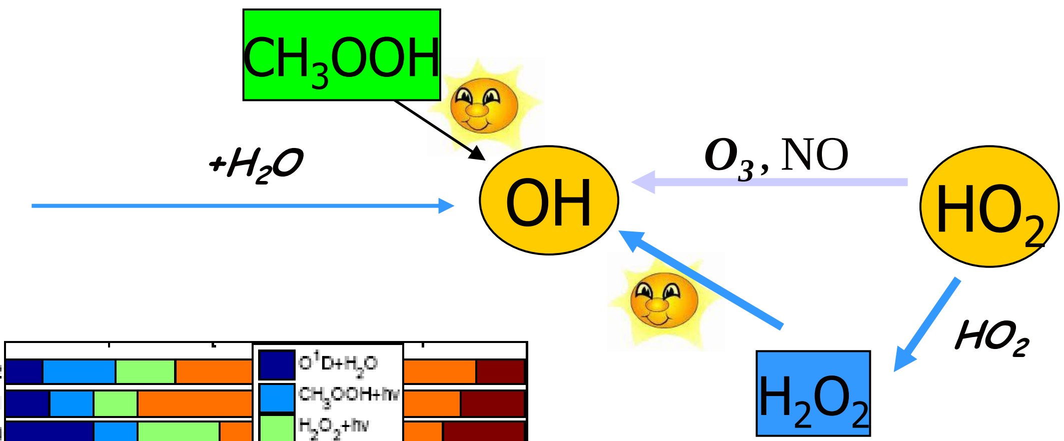
OH has a short life time $\rightarrow$ around 1 sec

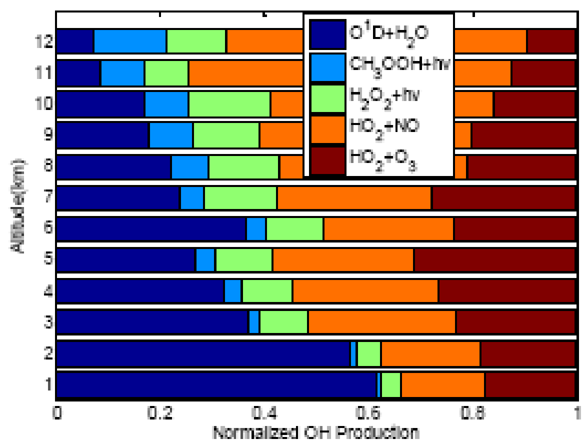
Equilibrium between production and consumption is rapidly adjusted:

$$[OH]_{ss} = \frac{\mathrm{Pr}\,oduction}{Consumption}$$

OH in the atmosphere : production

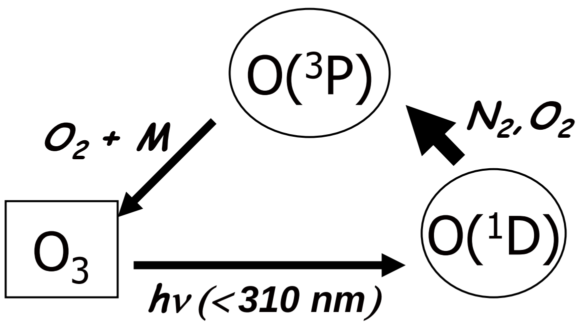


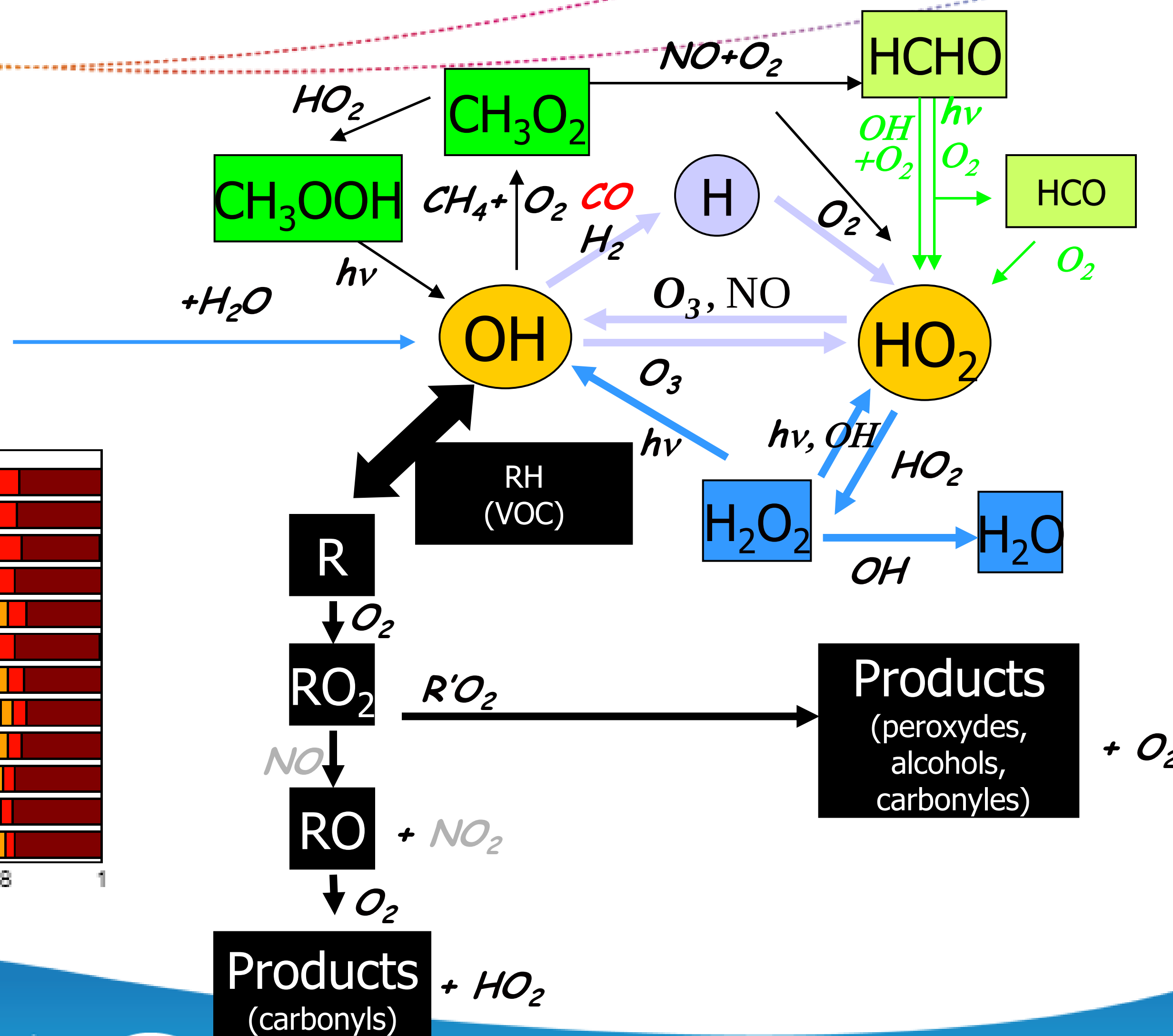


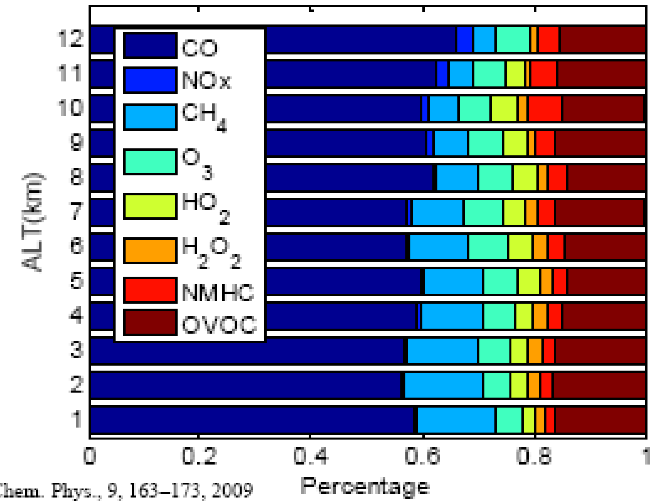


Atmos. Chem. Phys., 9, 163–173, 2009

OH in the atmosphere : consumption







Atmos. Chem. Phys., 9, 163–173, 2009

OH in the atmosphere: complex system!!

OH has a short life time → around 1 sec

Equilibrium between production and consumption is rapidly adjusted:

$$[OH]_{ss} = \frac{Production}{Consumption}$$

FAGE can be used to measure both parameters

Outline

- OH/ HO_2 interest

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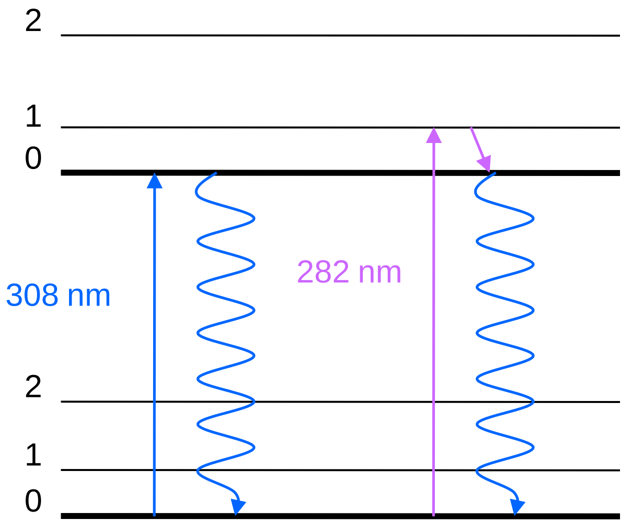
- FAGE instrument for time resolved OH et HO_2 measurements

- Conclusions and perspectives

What is FAGE???

Fluorescence Assay by Gas Expansion

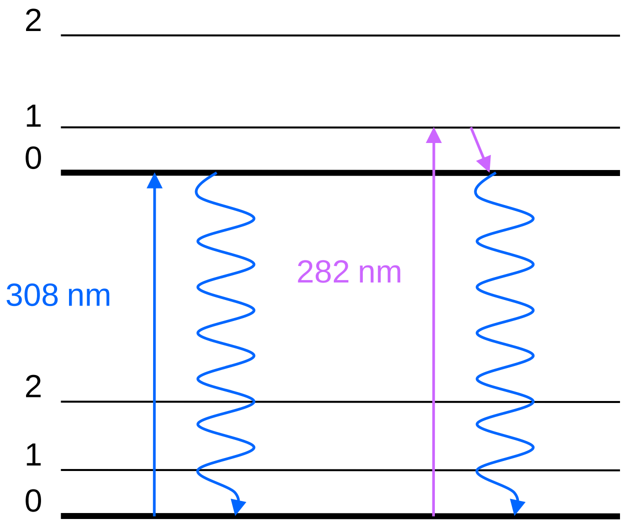


Problem at 282 nm: OH is formed by the laser from ozone photolysis:

$O_3 + h\nu \rightarrow O(^1D) + O_2$
$O(^1D) + H_2O \rightarrow 2OH$

What is FAGE???

Fluorescence Assay by Gas Expansion



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Problem at 308 nm: excitation and collection at the same wavelength

Solution: work at low pressure to extend the OH fluorescence lifetime

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What is FAGE???

Fluorescence **A**ssay by **G**as **E**xpansion

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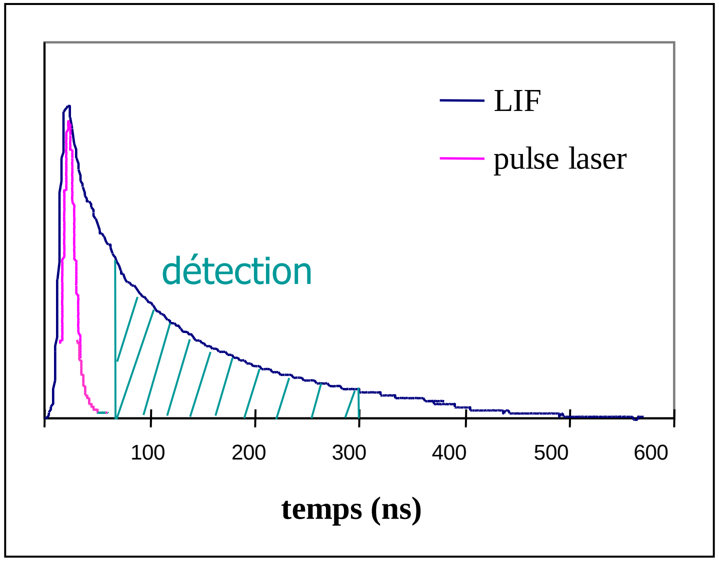

Problem at 308 nm: excitation and collection at the same wavelength

Solution: work at low pressure to extend the OH fluorescence lifetime

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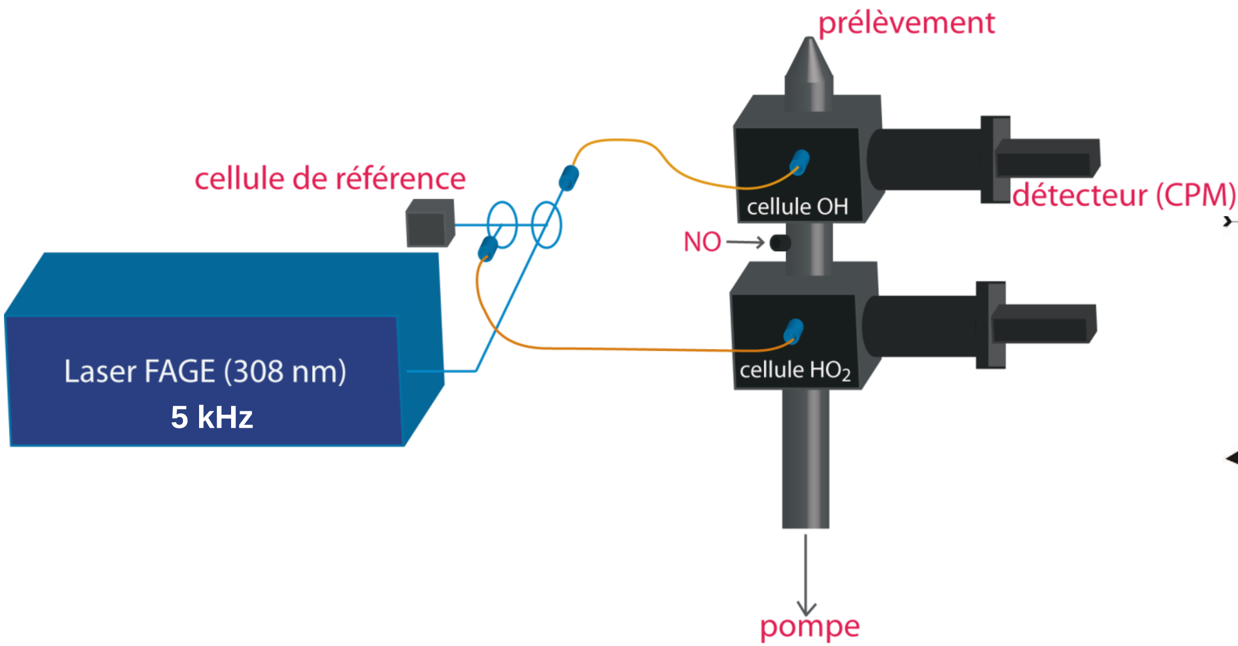
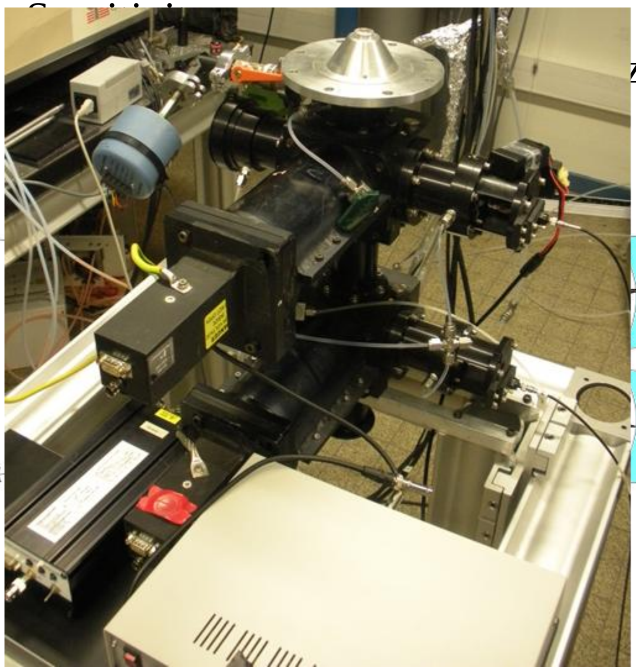
Experimental set-up

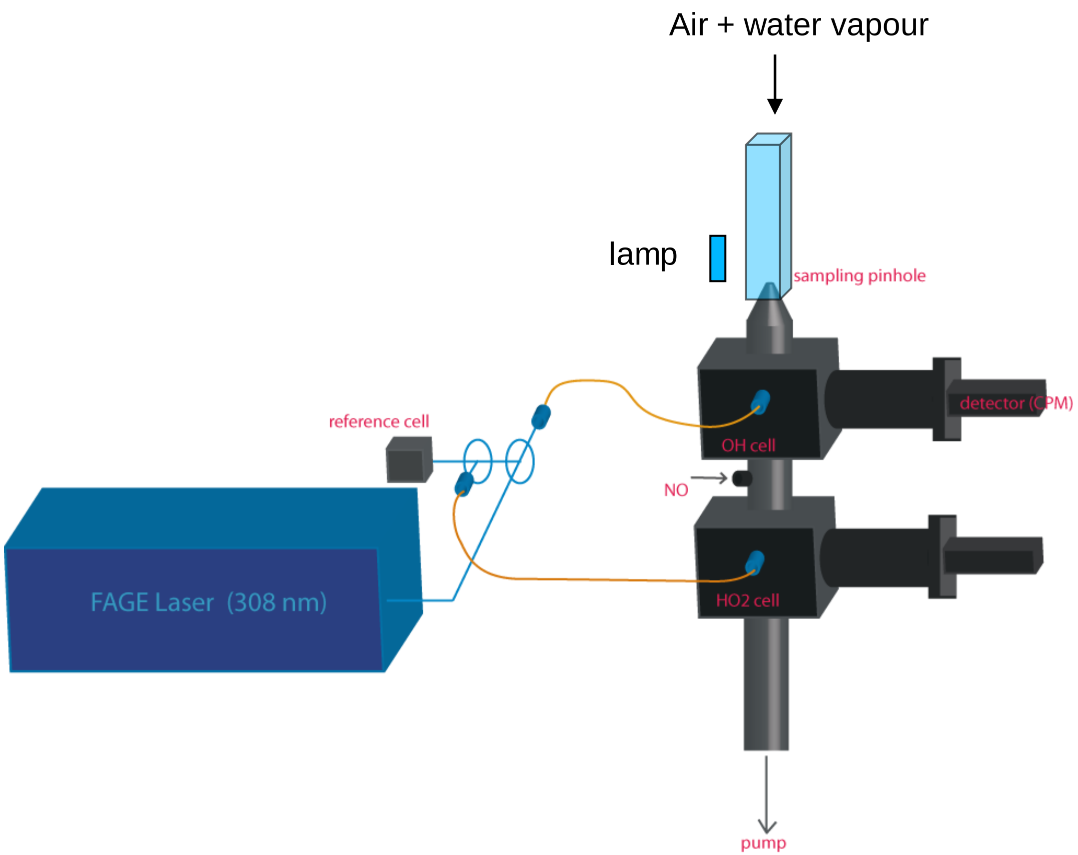
- $HO_2 + NO \rightarrow OH + NO_2$





Detection limit: 3 x10^5 molecules.cm^{-3}.min^{-1}

Calibration



Laser Induced Fluorescence :

Sensitive BUT not absolute

↓

Calibration necessary

Generation of a known [OH]

Water vapour photolysis

$H_2O + h\nu\ (184{,}9\ nm) \rightarrow OH + H$

$H + O_2 \rightarrow HO_2$

Calibration

Generation of OH : photolysis of water vapour

$H_2O + h\nu_{(184,9\ nm\ ;\ mercury\ lamp)} \rightarrow OH + H$

$H + O_2 \rightarrow HO_2$

$[OH] = [HO_2] = F_{184,9} \cdot \sigma_{H2O} \cdot [H_2O] \cdot \phi \cdot \Delta t$

High accuracy hygrometer

Lamp flux mesured by Actinometry

sur O_3 : $O_2 + h\nu_{(184,9\ nm)} \rightarrow 2\ O$

$2\ (O + O_2 + M) \rightarrow 2\ O_3$

$$F_{184,9} = \frac{[O_3]}{2.[O_2].\sigma_{O_2}.\Delta t}$$

$[O_3]$ by analyser

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FAGE instruments in the world

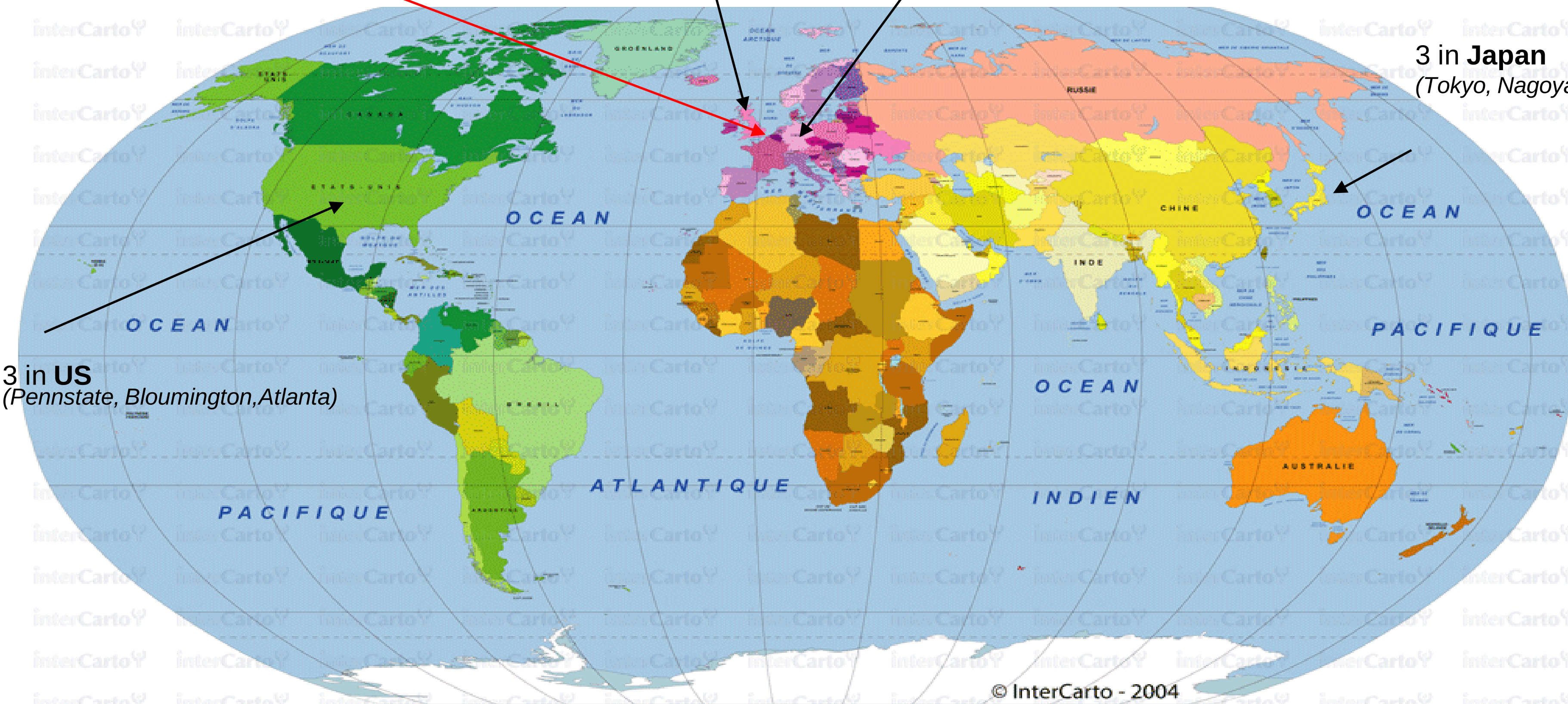
1 in **France** *(Lille, PC2A)*

2 **Great Britain** *(Leeds)*

2 in **Germany**
(Julïch, Mainz)

3 in **Japan**
(Tokyo, Nagoya)

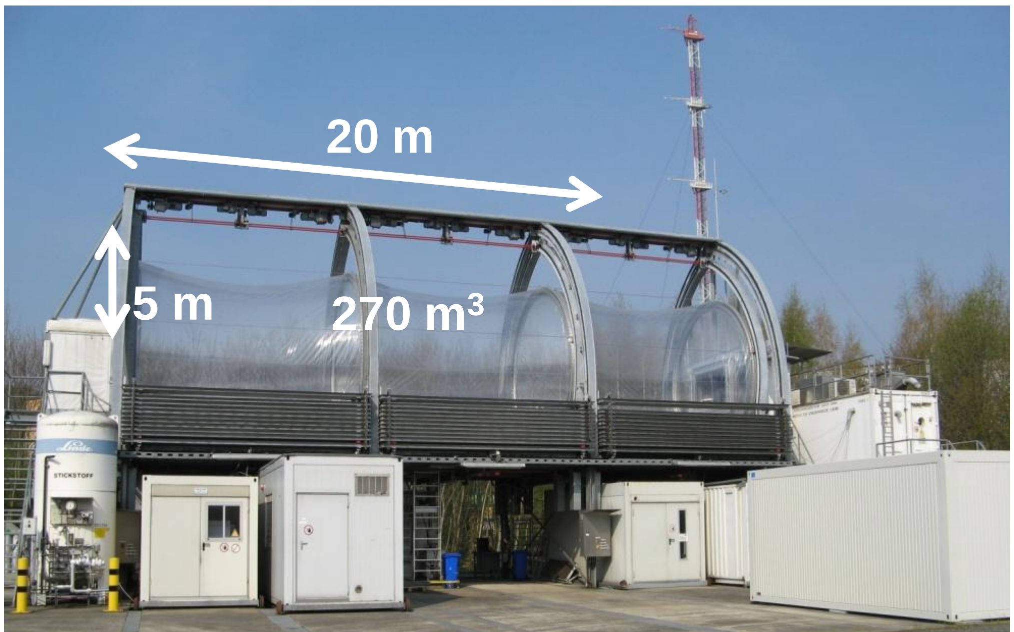
3 in **US**
(Pennstate, Bloumington,Atlanta)



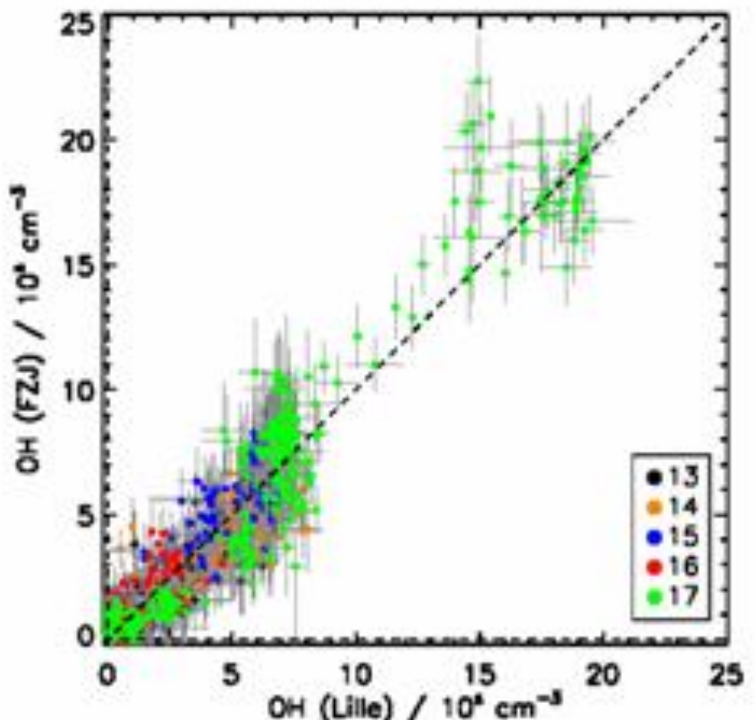
Our 1st field campaign April 2010

SAPHIR (Jülich, Germany)

(**S**imulation of **A**tmosperic **PH**otochemistry in a large **R**eaction chamber)



Intercomparison with Jülich instrument

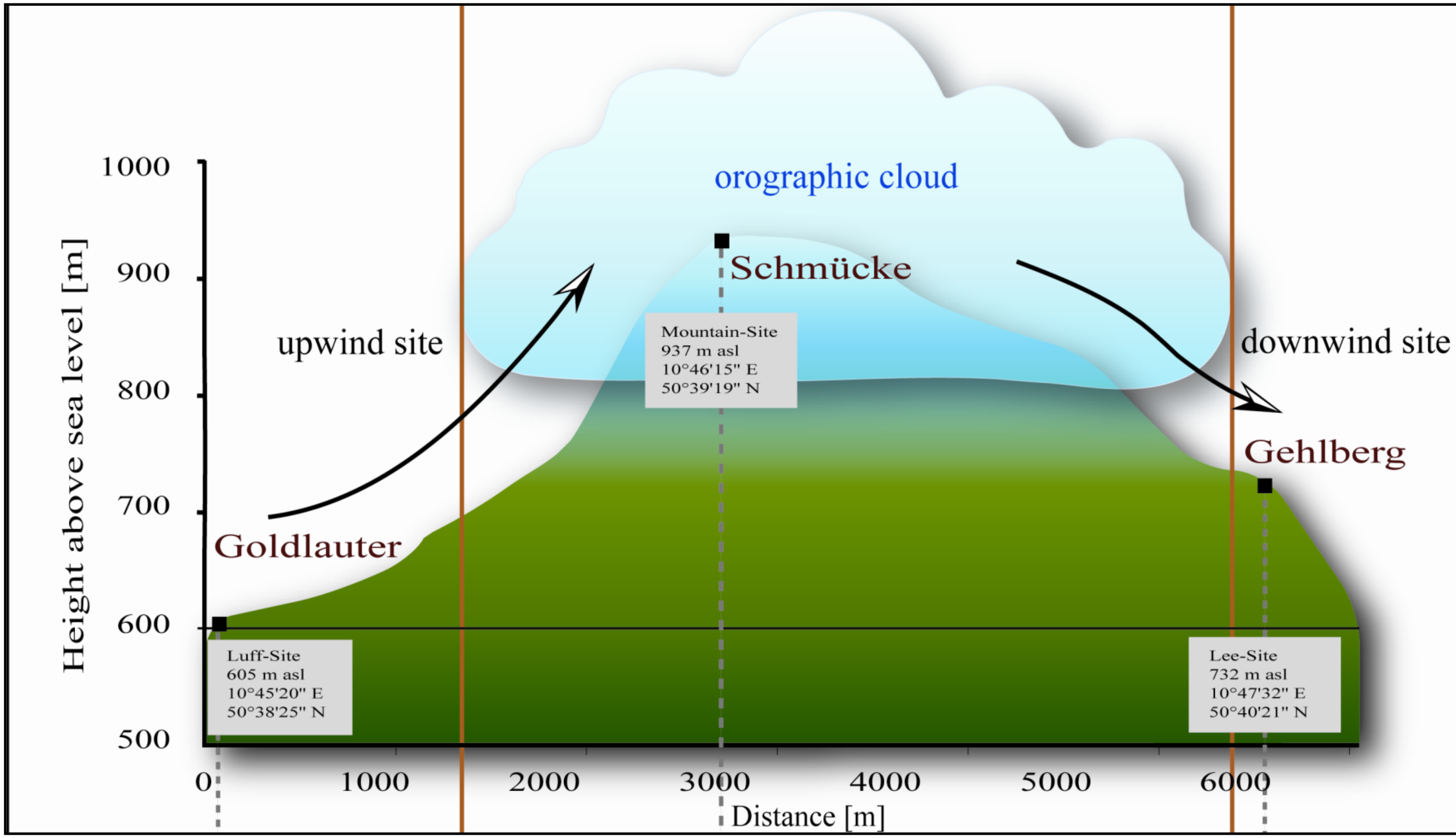


Our 2nd field campaign still ongoing

Hill Cap Cloud Thuringia
HCCT 2010

IfT Leipzig
MPI Mainz
University of Leeds, GB
CNRS/University of Lyon, F
CNRS/University of Lille, F
CSU, Fort Collins, CO, USA

Understanding cloud chemistry



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IFTU 038105-9

OH in the atmosphere: complex system!!

OH has a short life time → around 1 sec

Equilibrium between production and consumption is rapidly adjusted:

$$[OH]_{ss} = \frac{\mathrm{Pr}\,oduction}{Consumption}$$

Measurement of OH consumption: time resolution is needed

Outline

- OH/ HO_2 interest

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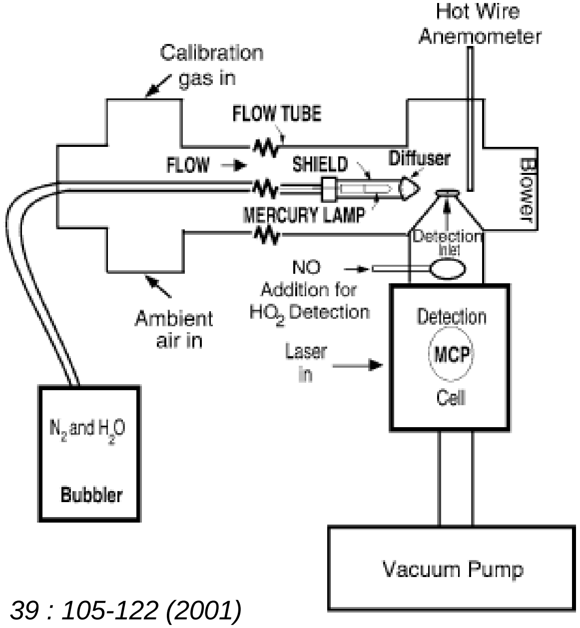
FAGE instrument + time resolution

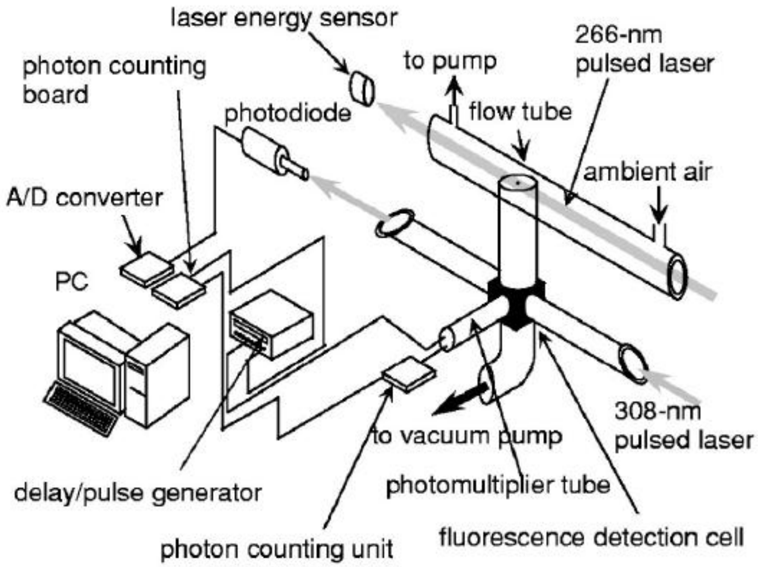
2 types of configurations

Continuous OH generation



J. Atm. Chem. 39 : 105-122 (2001)
Pennsylvania university

Pulsed generation



Review of Scientific Instrument : 75, 8 (2004)
Tokyo Metropolitan university

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Lille configuration

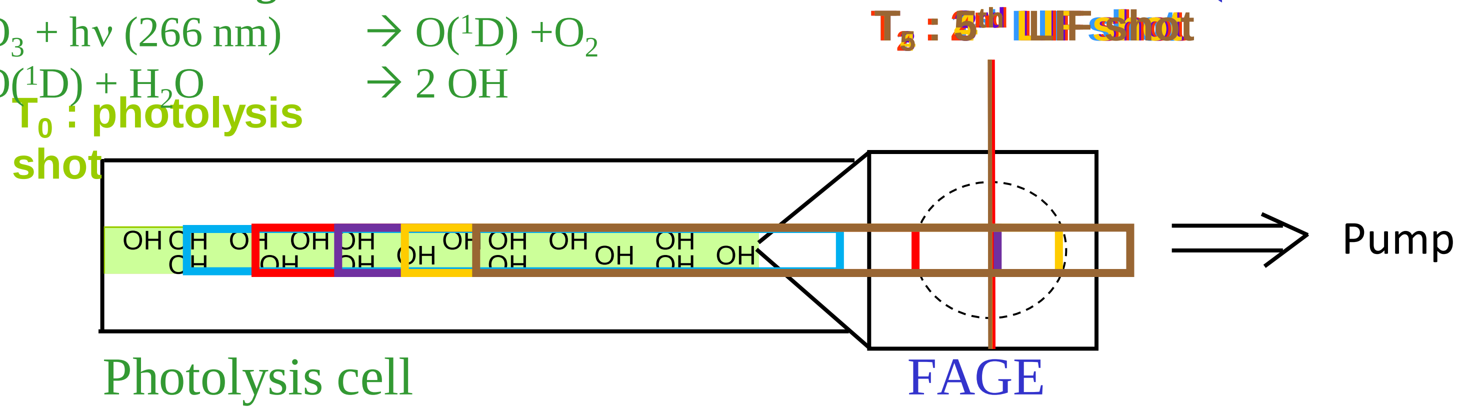
- photolysis cell (on axis) + FAGE

OH generation

$O_3 + h\nu$ (266 nm) → $O(^1D) + O_2$

$O(^1D) + H_2O$ → 2 OH

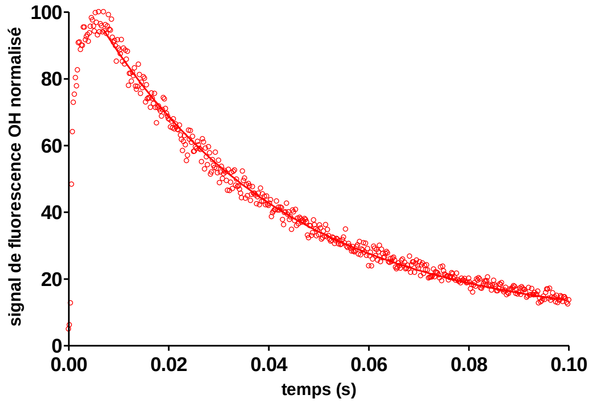
OH (resolution : 100 µs)



Advantages :

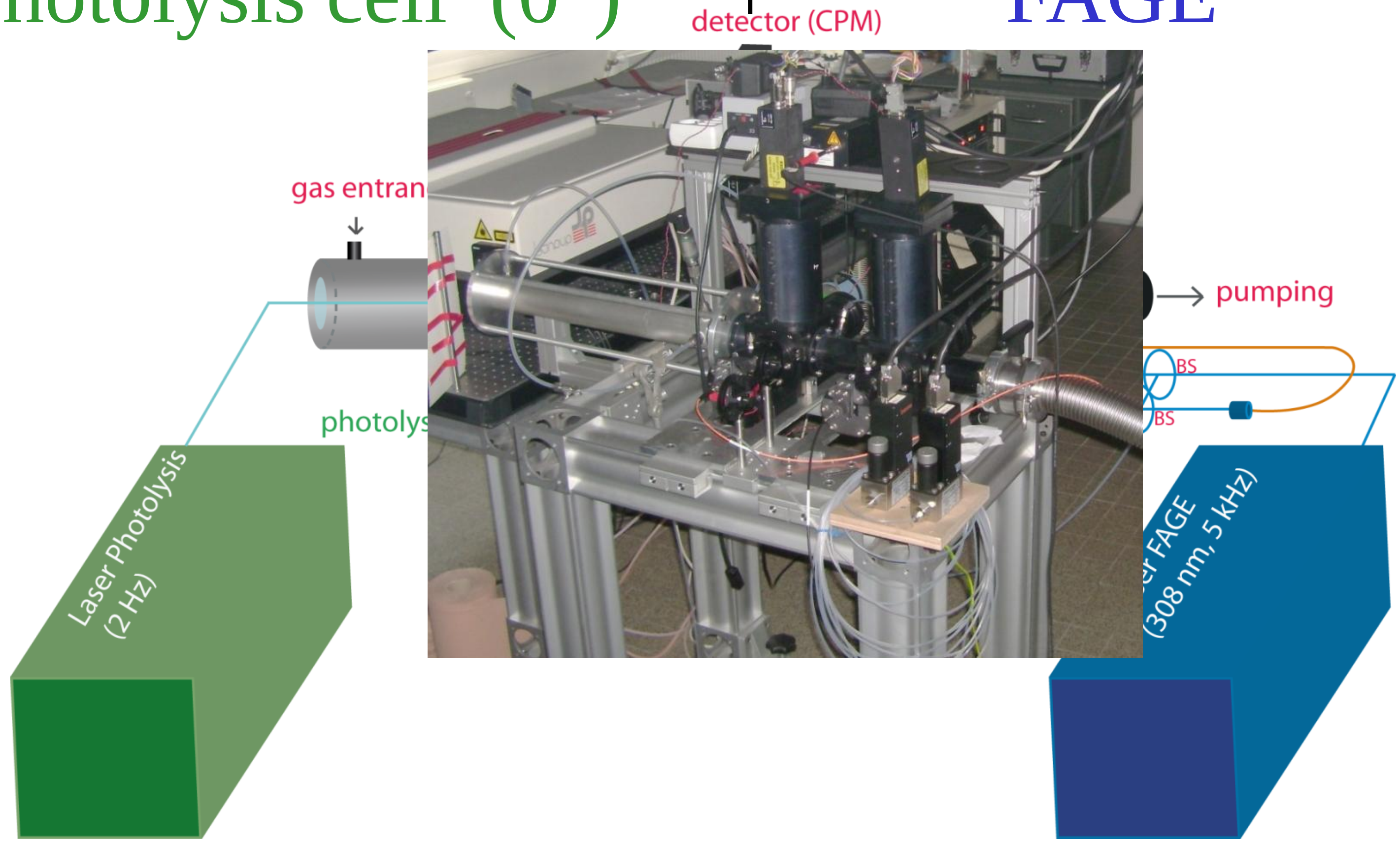
- more homogeneous probing

- less flux perturbation



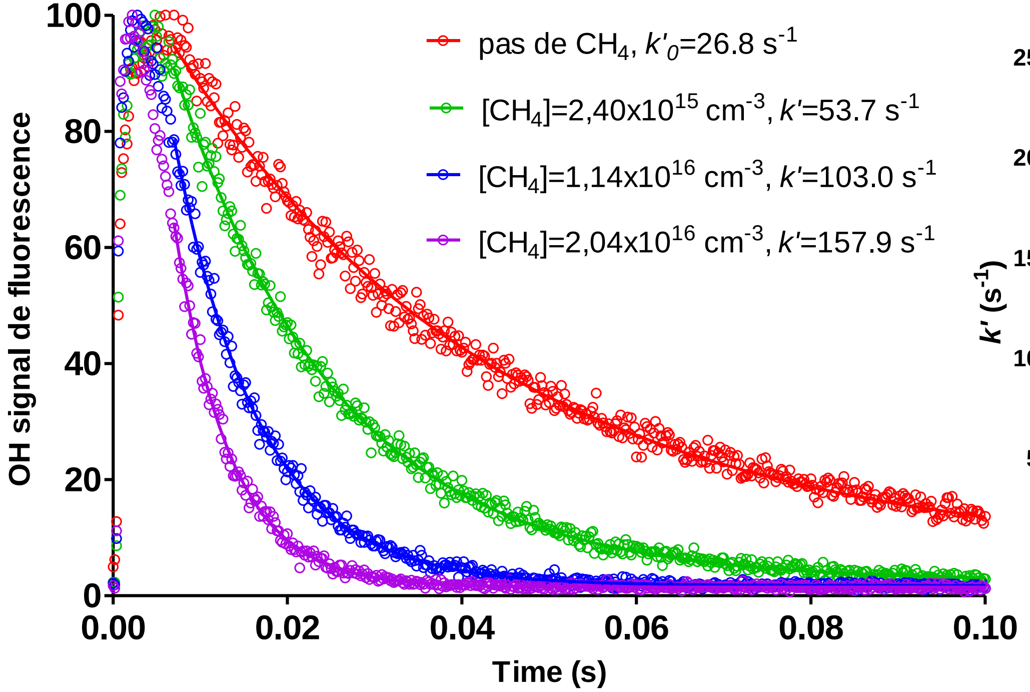
Lille configuration

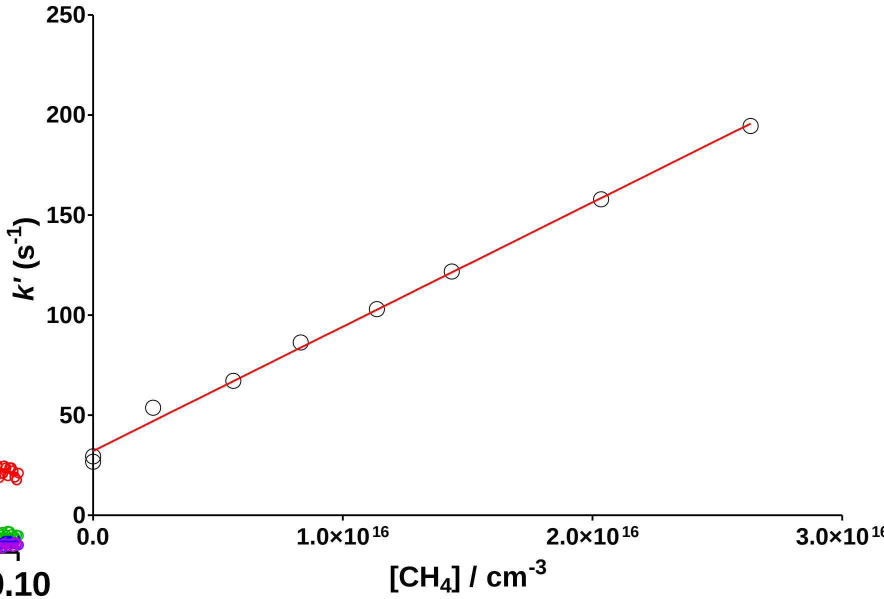
- photolysis cell (0°) + FAGE



Validation

- $CH_4 + OH$





$k_{measured}$ = (6.21±0.6) x10^{-15} cm^{3}s^{-1} à 295 K

$k_{recommanded}$ = 6.01 x10^{-15} cm^{3}s^{-1} à 295 K

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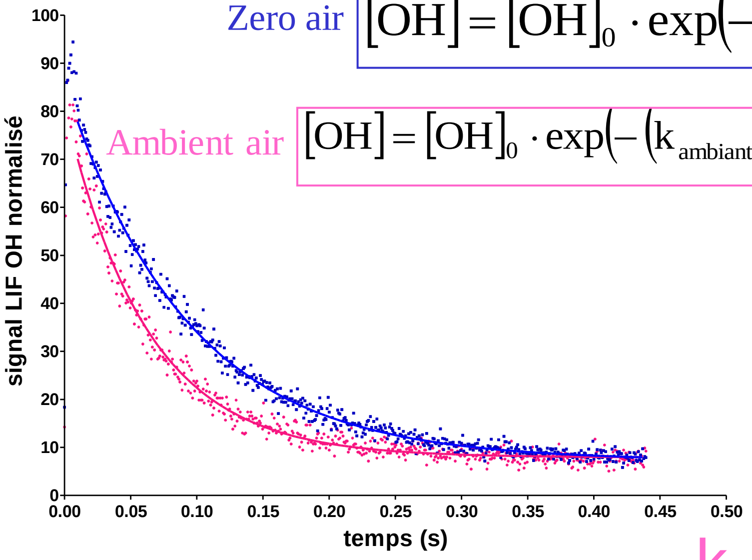
Application to OH reactivity

- Direct atmospheric measurement

Mesure by FAGE

Zero air $$[OH] = [OH]_0 \cdot \exp(-(k_{air\ zéro}) \cdot t)$$

Ambient air $$[OH] = [OH]_0 \cdot \exp(-(k_{ambiant} + k_{air\ zéro}) \cdot t)$$



Calculation

$$k_{calcOH} = k_{CO} \cdot [CO] + k_{CH_4}[CH_4] + \ldots + \sum_i^n k_{COV_i}[COV_i]$$

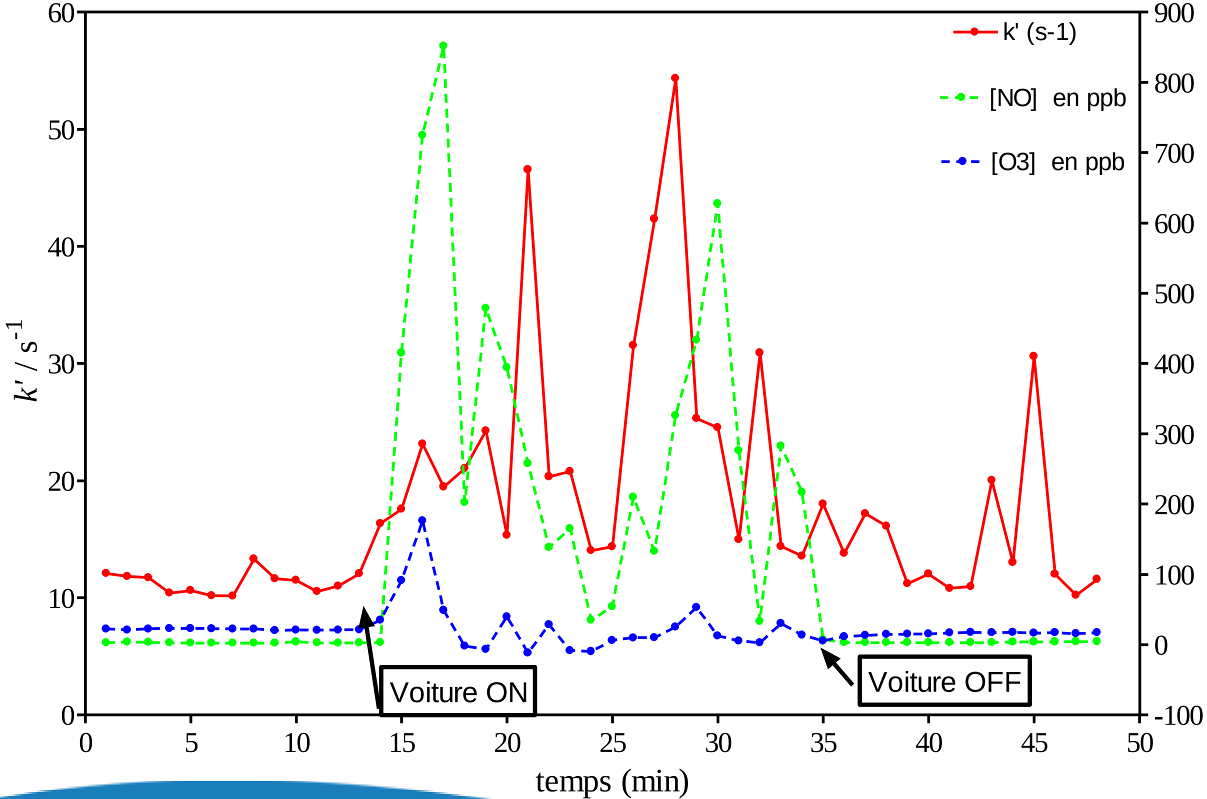
[CO], [CH_4], … to measure

[VOC]$_i$ measured by PTR-TOF-MS

$k_{ambient}$ = ou ≠ $k_{calc\ OH}$

OH Reactivity

Mesurements in ambient air – e.g. car exhaust



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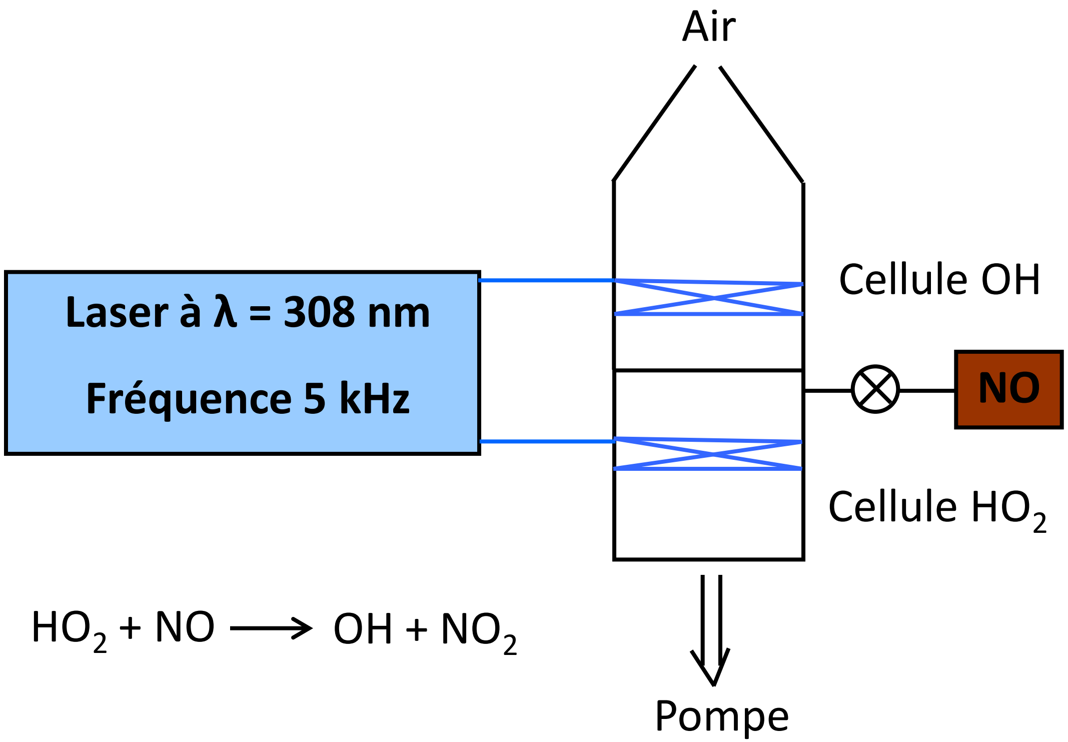
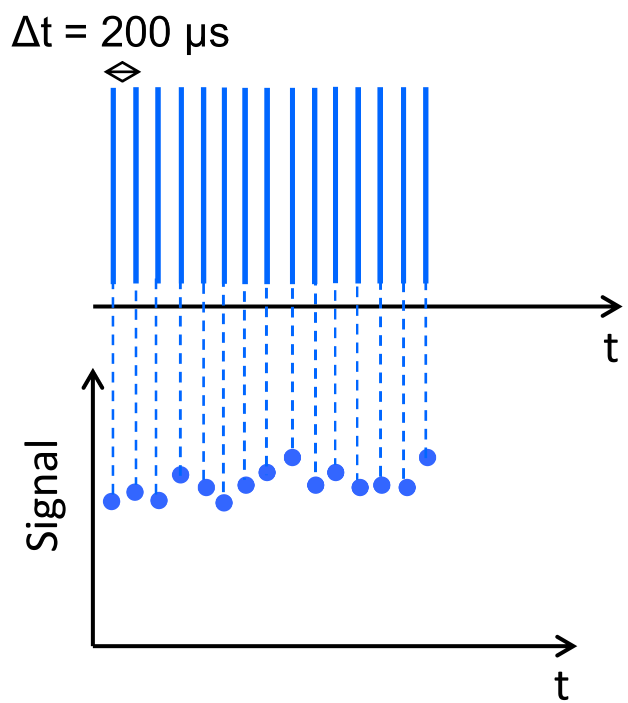
FAGE for quantitative measurments

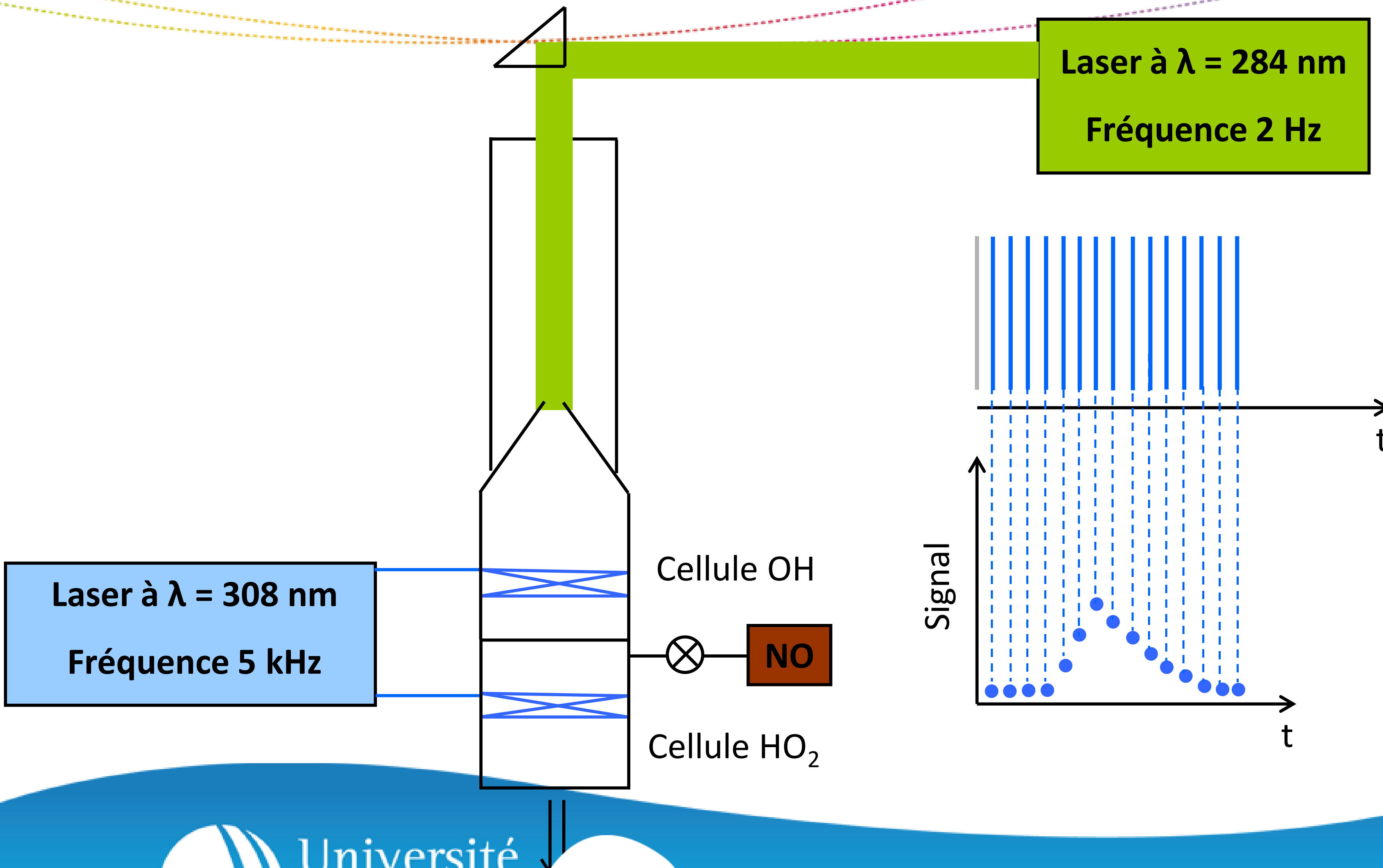


$HO_2 + NO \longrightarrow OH + NO_2$



5 kHz => Intégration du signal => sensibilité

FAGE for time resolved measurements



Conclusions and perspectives

- Conclusions

  - Lille FAGE instrument is working very well
  - Quantitative measurements have been performed during two field campaigns
  - Time resolved measurement mode has been validated through measurement of well known rate constants

- Perspectives

  Intercomparaison (CRM)
  Field measurements (indoor, Charmex)
  Kinetic measurements (up to 800 K ,10 bar)

Acknowledgements :

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Marie Curie Actions Human resources and mobility

IRENI

RÉGION Nord-Pas de Calais

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Bât C11- Lille 1- 59655 Villeneuve d'Ascq
Tél. +33 (0)[20337266] | Fax. +33 (0)[20436977]
Christa.fittschen@univ-lille1.fr
www.univ-lille1.fr