

SpecMo Workshop 2014  
Dijon, Bourgogne  
22 - 23.05.2014



# **Etudes multi-spectrales de l'O<sub>3</sub> pour l'amélioration des paramètres spectroscopiques (SMO<sub>3</sub>) : mesures de laboratoire et atmosphériques**

— LERMA<sup>2</sup> —

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*Institut  
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Laplace*



# Challenge of Atmospheric Composition Measurements by Remote Sensing

FTS-Paris

Té et al. JAOT, 2012

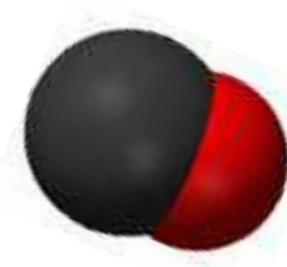
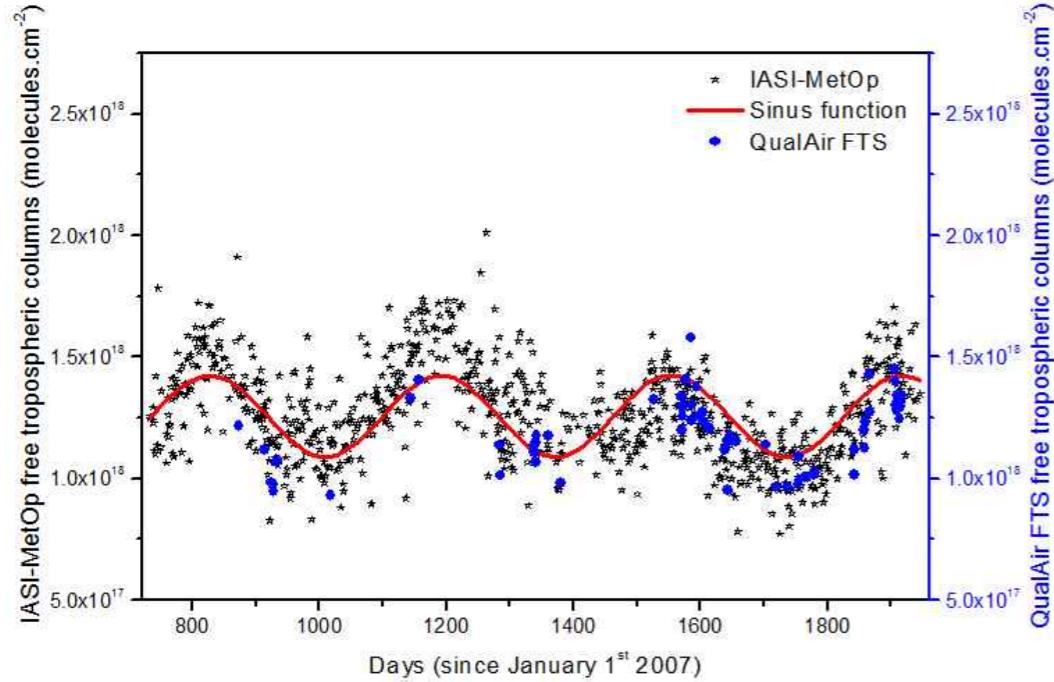
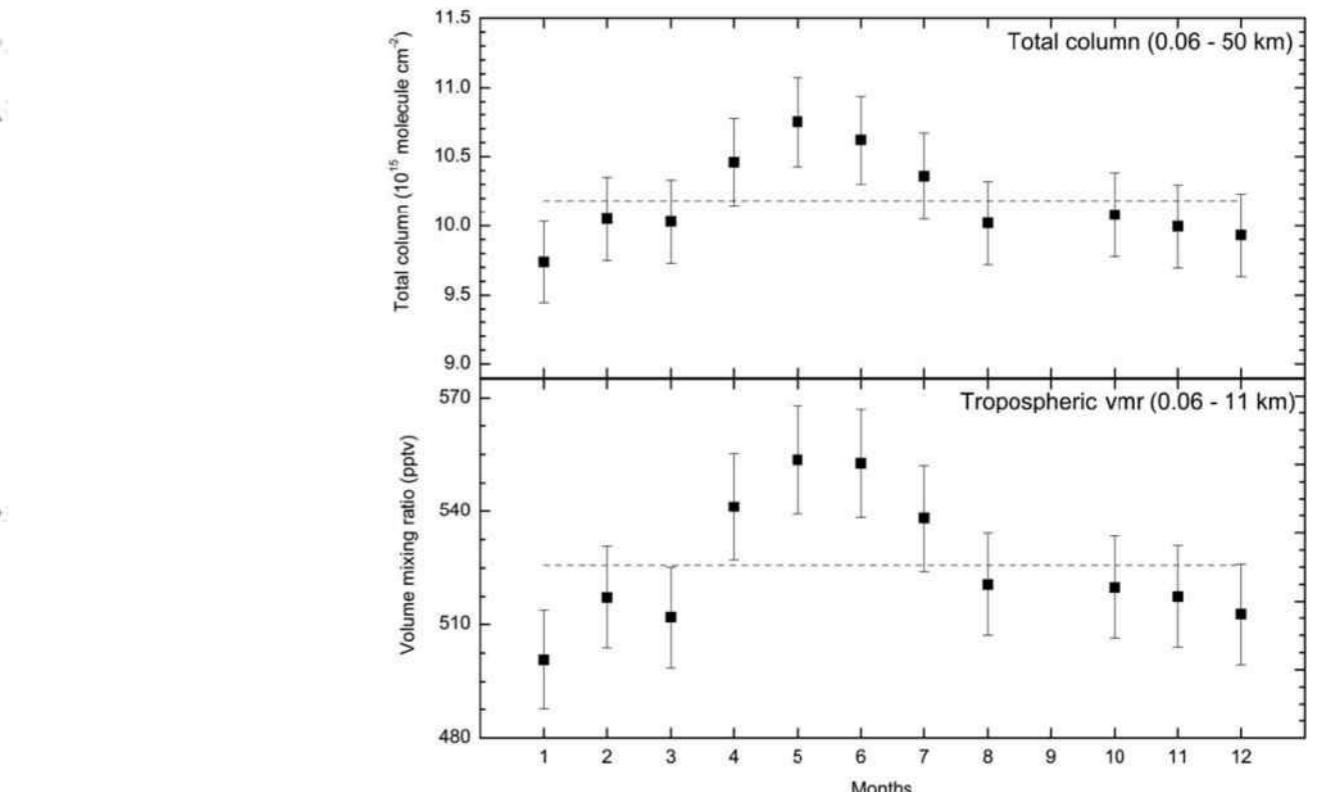


TABLE 1. CO retrieved total column uncertainties.

Error source	Random errors	
		CO error (%)
Temperature		1.8
Instrument noise		<1
Solar zenith angle		1.1
Interfering solar lines		<1
Total random error		2.4
Systematic errors		
Spectroscopic parameters		3–6.8
A priori profile		<1
Instrument line shape		<1
Total systematic error		3.1–6.9

Error source	OCS error (%)
Temperature	<0.5
Instrument noise	<0.5
Solar zenith angle	0.9
Interfering solar lines	<0.5
A priori profile	<0.5
Instrument line shape	1
Spectroscopic parameters	4.5 to 9.5
Total error	4.7 to 9.7



# Challenge of Atmospheric Composition Measurements by Remote Sensing

FTS-Paris

Té et al. JAOT, 2012

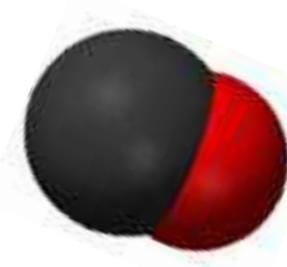
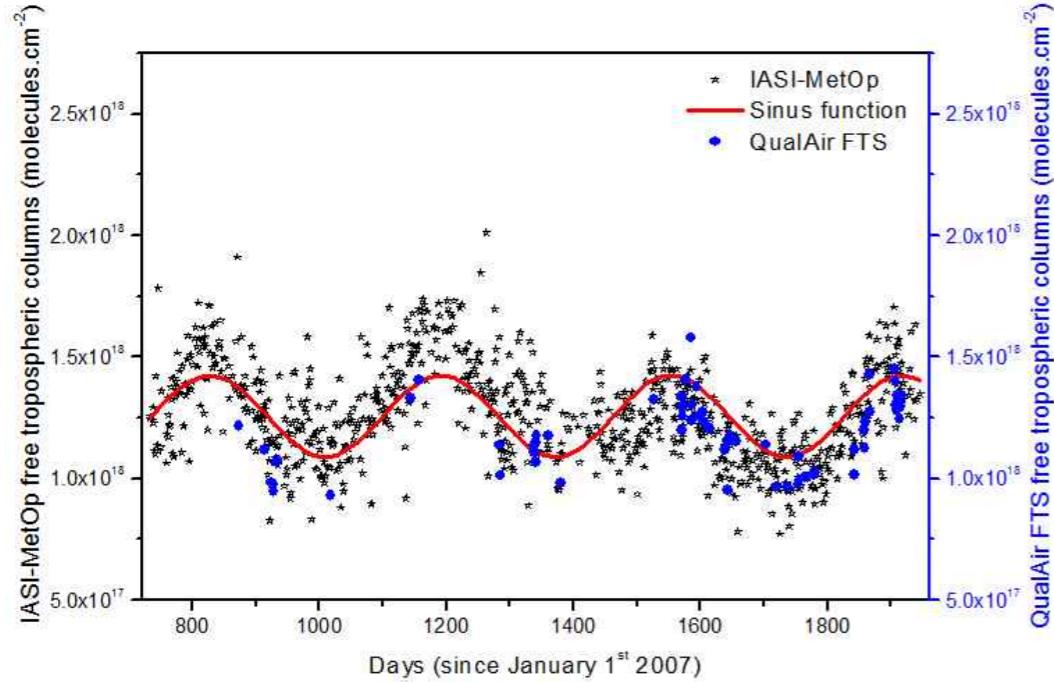
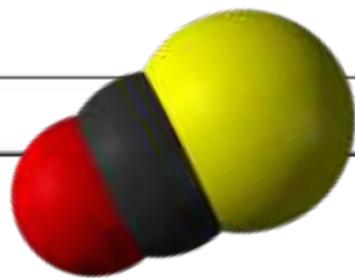


TABLE 1. CO retrieved total column uncertainties.

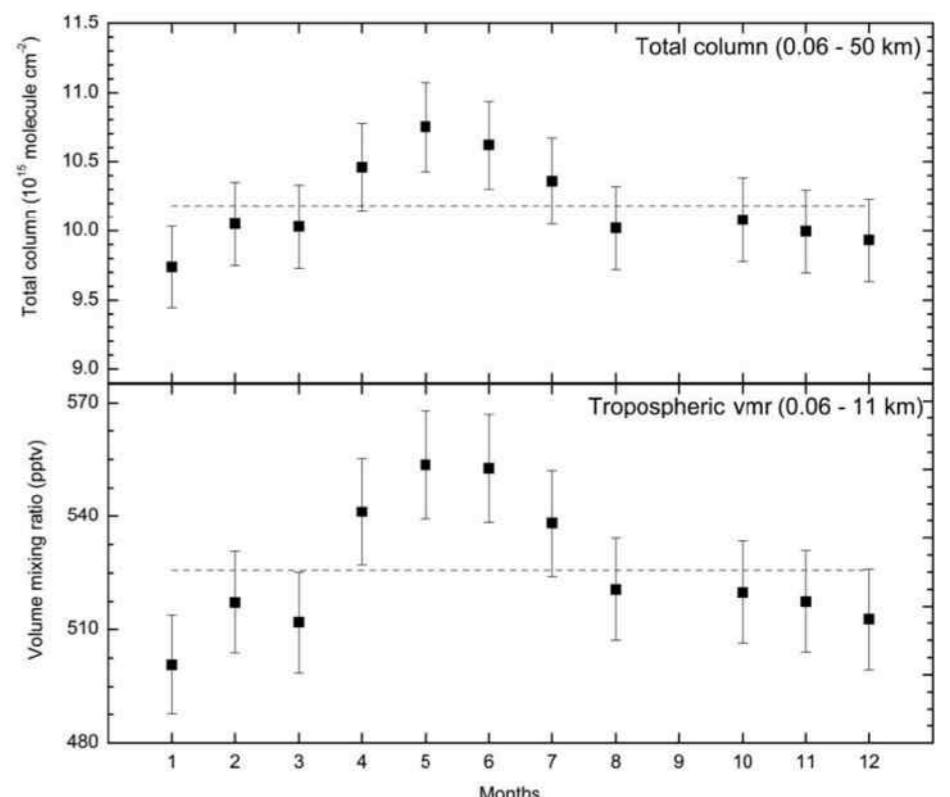
Error source	Random errors	
		CO error (%)
Temperature		1.8
Instrument noise	<1	
Solar zenith angle		1.1
Interfering solar lines	<1	
Total random error		2.4
Systematic errors		
Spectroscopic parameters		3–6.8
A priori profile	<1	
Instrument line shape	<1	
Other systematic error		3.1–6.9

Spectroscopic parameters  
Total systematic error

Error source	OCS error (%)
Temperature	<0.5
Instrument noise	<0.5
Solar zenith angle	0.9
Interfering solar lines	<0.5
A priori profile	<0.5
Instrument line shape	1
Spectroscopic parameters	4.5–9.5
Total error	4.7–9.7



Spectroscopic parameters 4.5 to 9.5  
Total error 4.7 to 9.7



# Challenge of Atmospheric Composition Measurements: LEFE-TCCON Paris

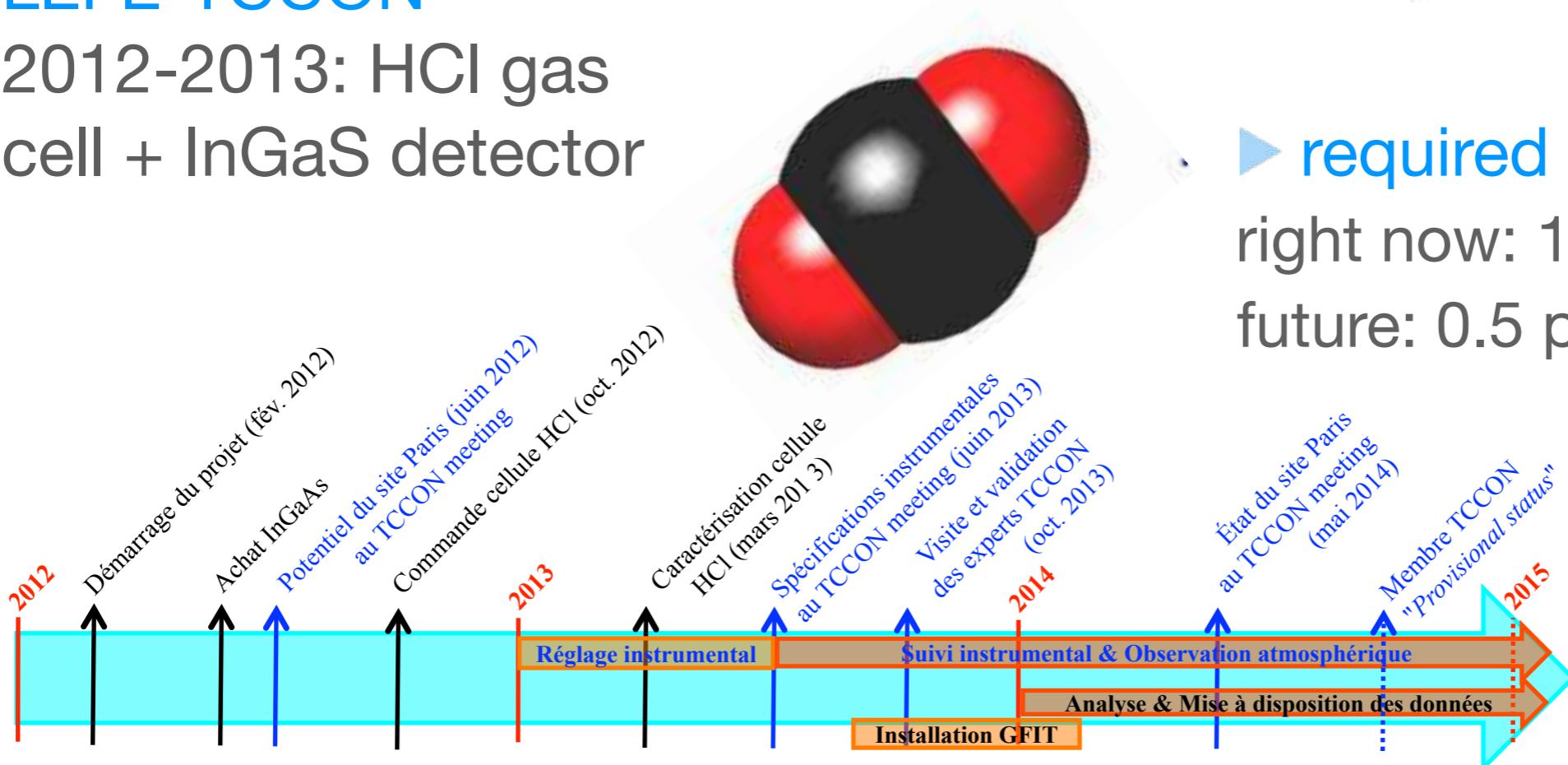
FTS-Paris

- ▶ 29 sites
- ▶ high-resolution
- ▶ GHG: CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, HF, CO, H<sub>2</sub>O, HDO
- ▶ LEFE-TCCON

2012-2013: HCl gas cell + InGaS detector

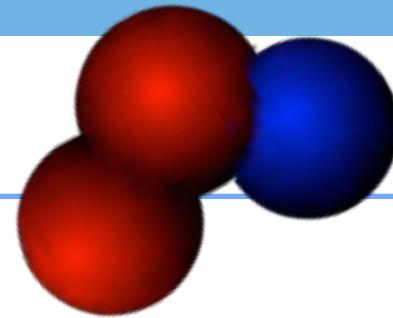


Paris, France  
TCCON Status: Preparatory  
48.846° N, 2.356° E, 111 meters above sea level  
FTS : Bruker IFS 125HR  
Operated by LERMA2 (Laboratoire d'Etudes du Rayonnement Atmosphérique, UMR8112), Université Pierre et Marie Curie / Collaborators : Yves Té (PI), Pascal Jeaick, Christof Jänecke

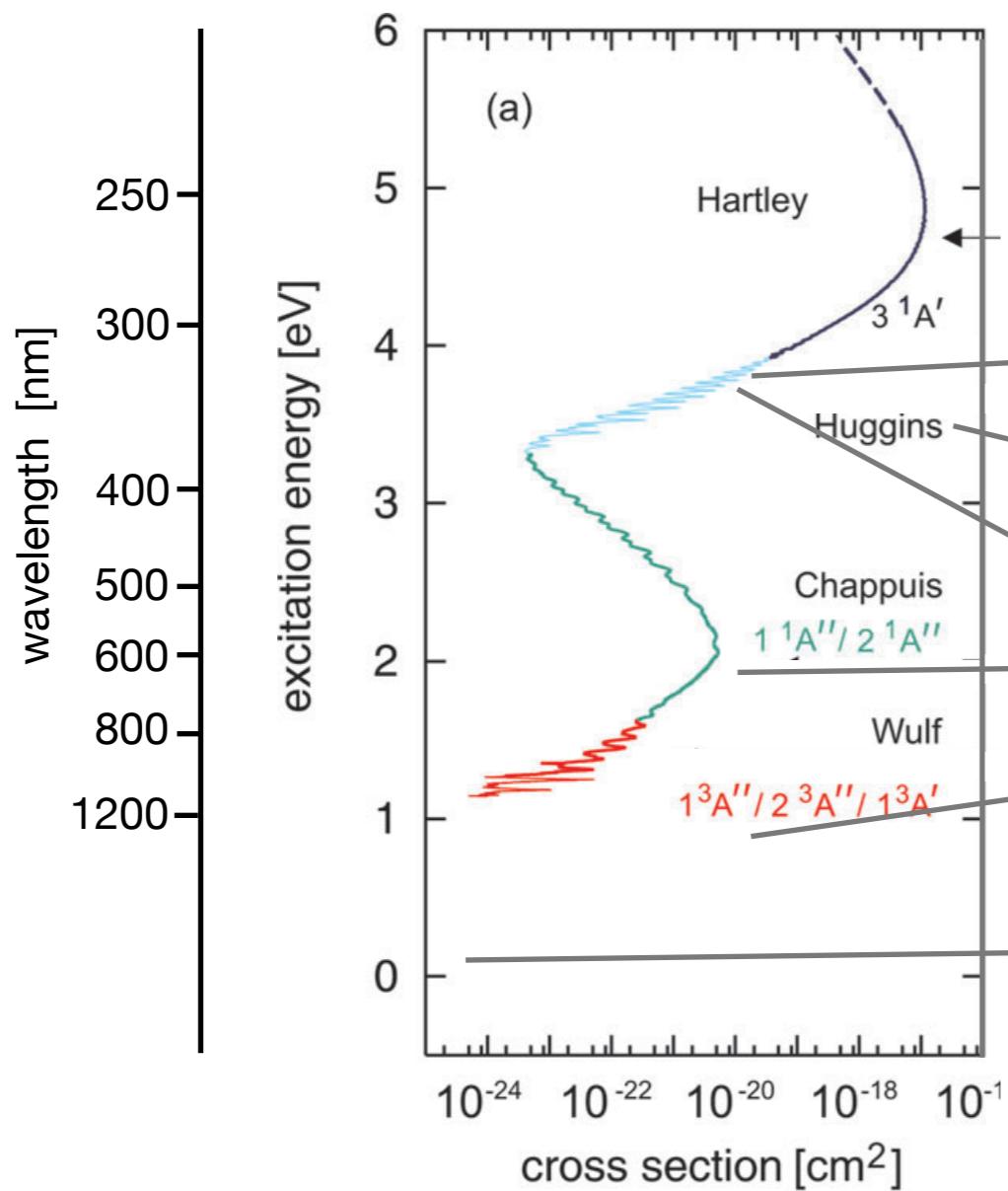


- ▶ required precision
  - right now: 1 ppm → 0.25 %
  - future: 0.5 ppm → 0.125 %

# Spectrometry of Atmospheric O<sub>3</sub>



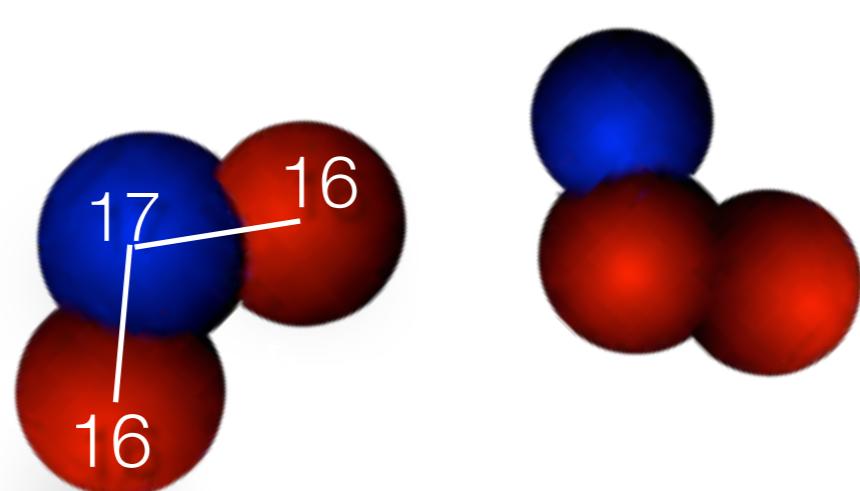
$$\ln \left( \frac{I}{I_0} \right) = -\sigma \cdot l \cdot n$$



cross section from: S. Y. Grebenschchikov, Z. W. Qu, H. Zhu, and R. Schinke,  
Phys. Chem. Chem. Phys. 9(17), 2044–2064 (2007)

# O<sub>3</sub> as Metrological Challenge

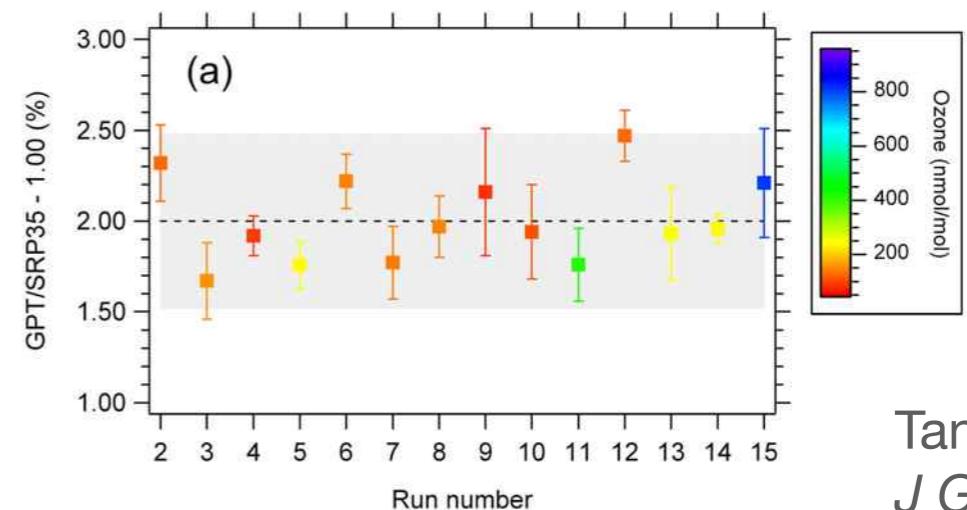
- ▶ Reactive molecule ( $E_0 = 1$  eV)
- ▶ Fragile, decomposes on surfaces
- ▶ Ozone is a key atmospheric compound
  - ▶ climate & composition change
  - ▶ air quality
- ▶ Large isotope anomaly, *i.e.* interesting tracer
- ▶ Use in industry & technology
  - ▶ *i.e.* water purification & plasma etching
- ▶ Health effects



## 2 recommended reference standards (BIPM)

- ▶ 1. *Gas Phase Titration (GPT)*  
 $O_3 + NO \rightarrow NO_2 + O_2$
- ▶ 2. *Absorption photometry (AP) at 253.65 nm (Hg)*  
spectroscopic, ozone, based on  $\sigma_{UV}$

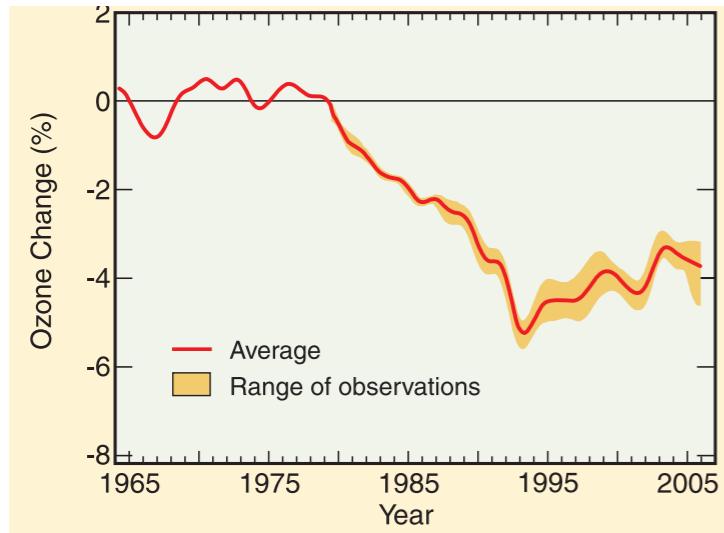
**Problem : current methods don't fit  
GPT ~ AP + 2%**



Tanimoto *et al.*,  
*J Geophys Res*,  
D16313, 2006

# Ozone Spectroscopic Data Quality

► target uncertainty : < 1%



Scientific  
Assessment of  
Ozone Depletion  
2010, WMO

Atmos. Meas. Tech. Discuss., 7, 2014, 2106, 2014  
www.atmos-meas-tech-discuss.net/7/2106/2014/  
doi:10.5194/amtd-7-2071-2014  
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This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

**Quality assessment of ozone total column amounts as monitored by ground-based solar absorption spectrometry in the near infrared ( $> 3000 \text{ cm}^{-1}$ )**

O. E. García<sup>1</sup>, M. Schneider<sup>1,2</sup>, F. Hase<sup>2</sup>, T. Blumenstock<sup>2</sup>, E. Sepúlveda<sup>1,3</sup>, and Y. González<sup>1</sup>

Rel. retrieval bias using recommended data

- Inconsistencies in atmospheric & laboratory data (+ data bases)
- Lab: IR (10  $\mu\text{m}$  / 1000  $\text{cm}^{-1}$ ) - UV (300 nm):
  - 5.5 % (Picquet-Varrault et al., 2005) &
  - 4.0 ( $\pm 0.1$ )% (Gratien et al., 2010)
- Column-O<sub>3</sub>: FTIR (962 -1044  $\text{cm}^{-1}$ ) - Brewer (303.2 - 320.1 nm) @ Izaña:
  - 4.2  $\pm$  0.7 % (e.g. Viatte et al., *Atmos. Meas. Tech.* 4, 2011)

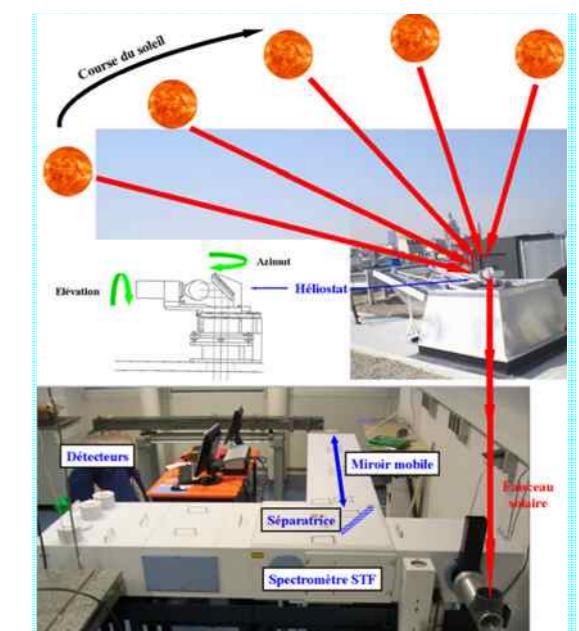
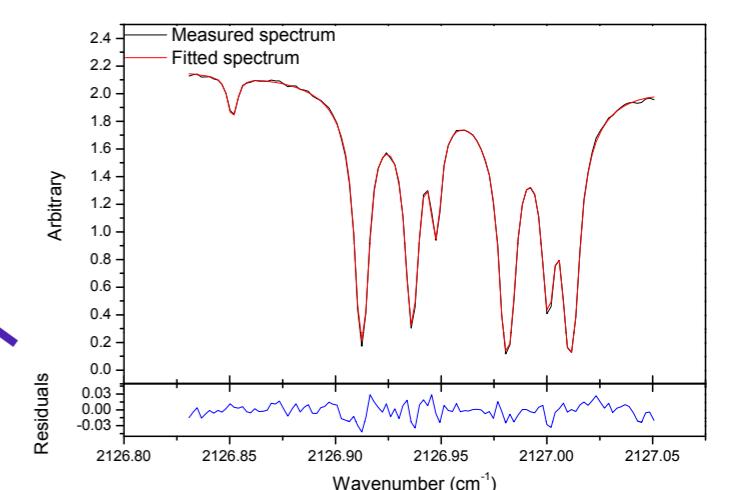
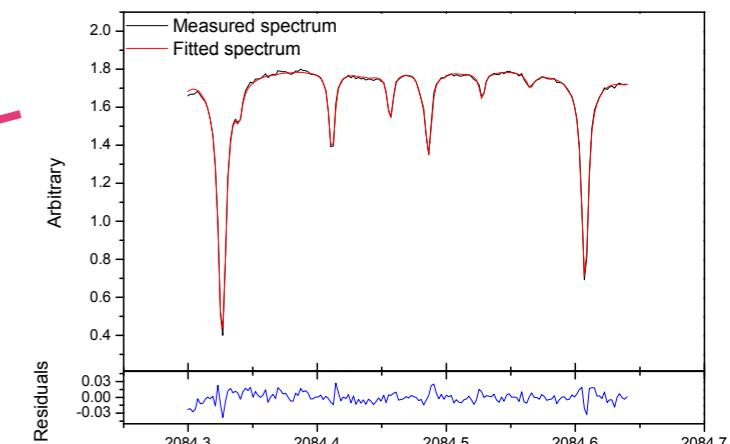
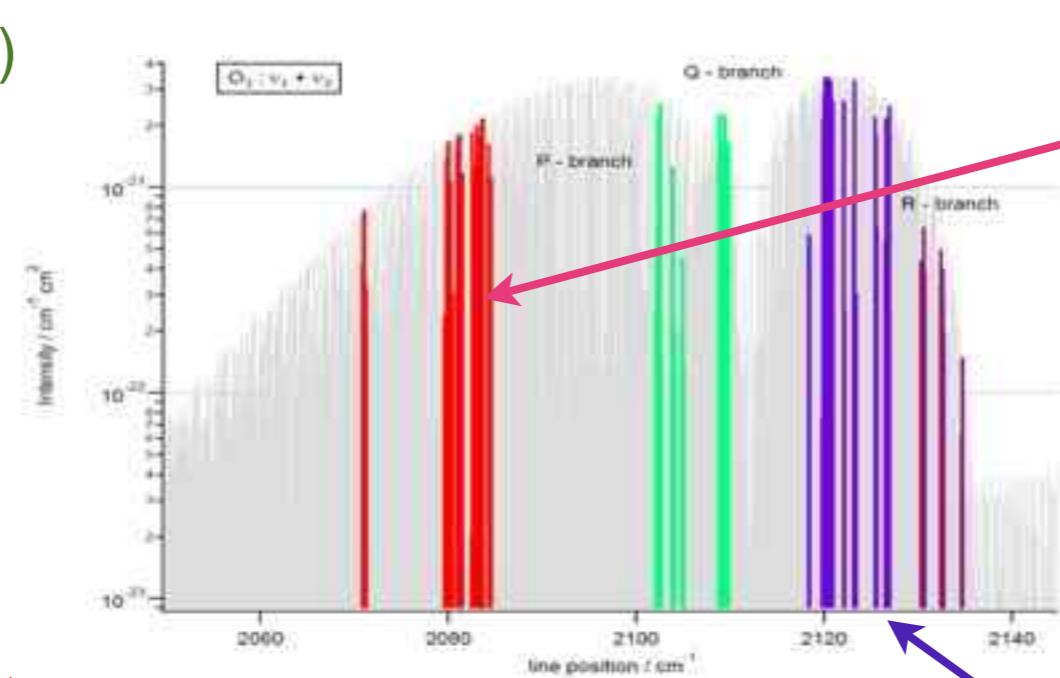
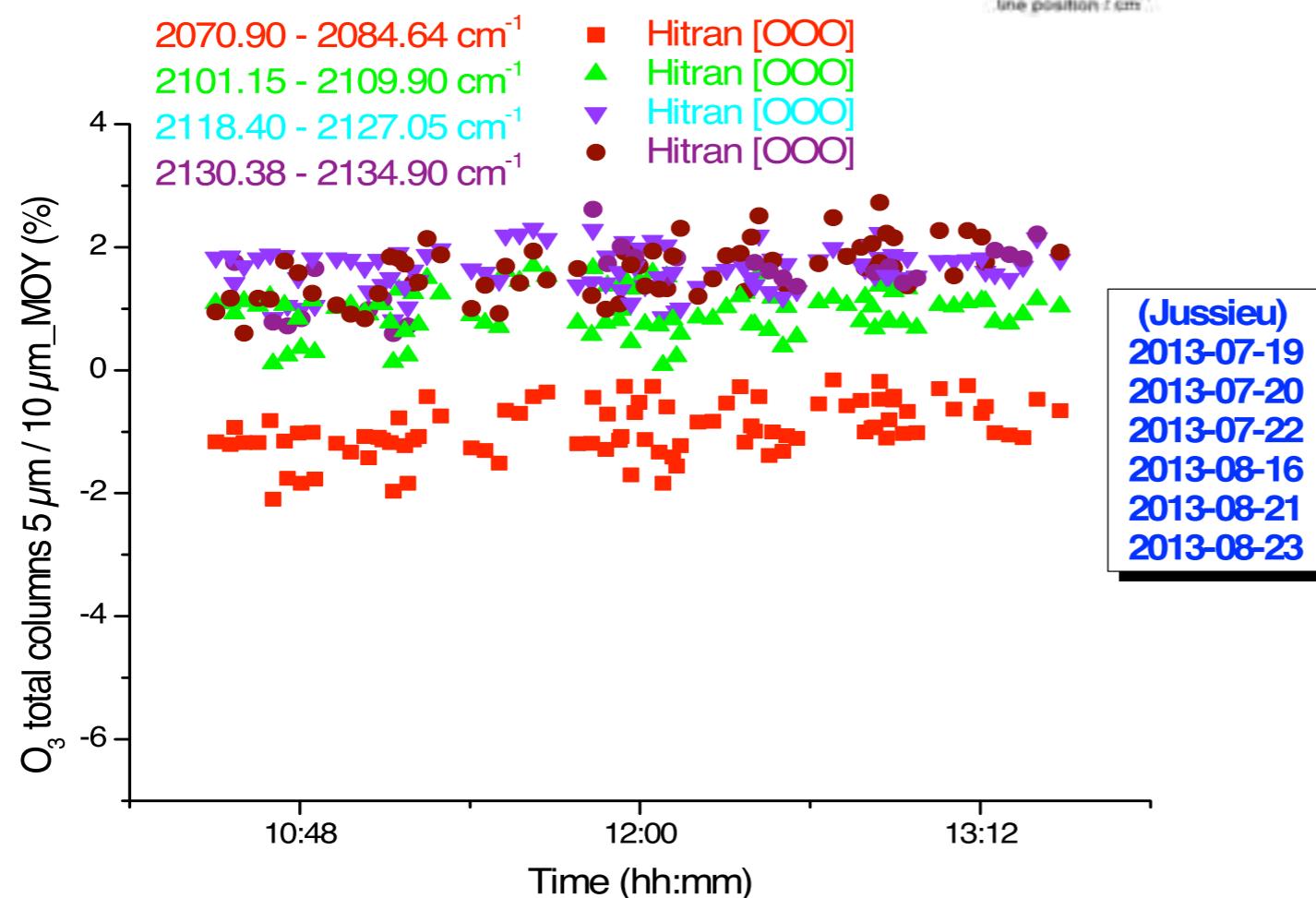
	UV	VIS	3 $\mu\text{m}$	5 $\mu\text{m}$	10 $\mu\text{m}$	14 $\mu\text{m}$
UV					-4 %	
VIS				0 ?		
3 $\mu\text{m}$						
5 $\mu\text{m}$		0 ?			?	
10 $\mu\text{m}$	4 %		-7 %	?		?
14 $\mu\text{m}$					?	

# O<sub>3</sub> Multispectral Study

FTS-Paris

Good agreement (< 2%)  
between 5 and 10  $\mu\text{m}$   
(Thomas et al. *JQSRT*  
**111**, 2010)

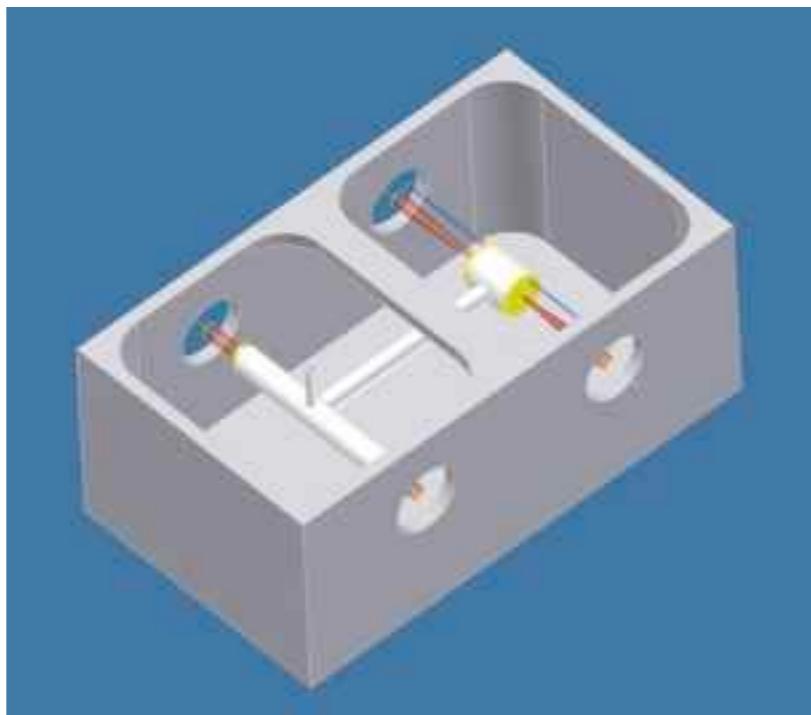
Problem with  
evaluation of (ACE)  
satellite data (Walker et  
al. 2007)



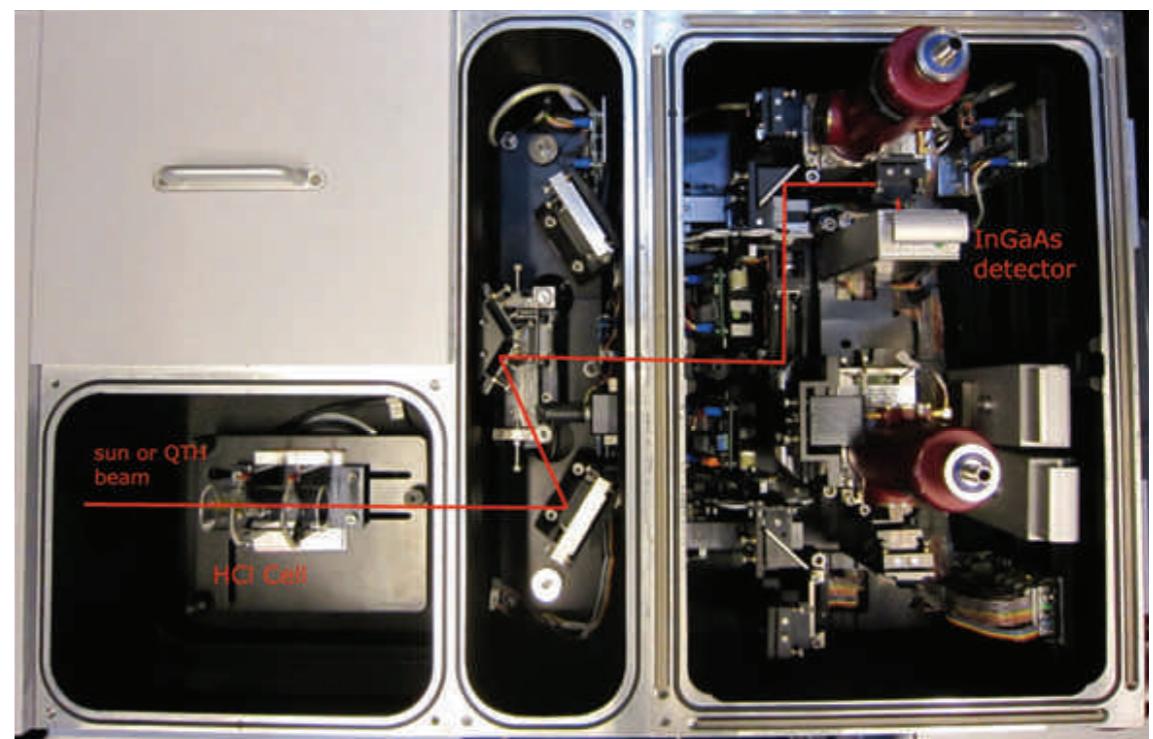
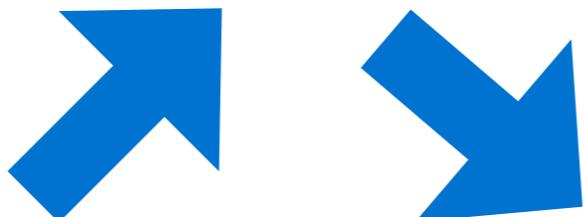
# O<sub>3</sub> Multispectral Study : Cell

FTS-Paris

- ▶ All pyrex, BaF<sub>2</sub>, KBr, teflon
- ▶ ozone decomposition :  
~ 2 or -4‰ / h (UV off/on)
- ▶ Pt100 sensors



- ▶ 2 parallel beams
- ▶ short (50 mm):  
UV + 10 µm
- ▶ long (~200 mm):  
5 or 14 µm
- ▶ Pt100 sensors
- ▶ connect to high purity O<sub>3</sub> production system



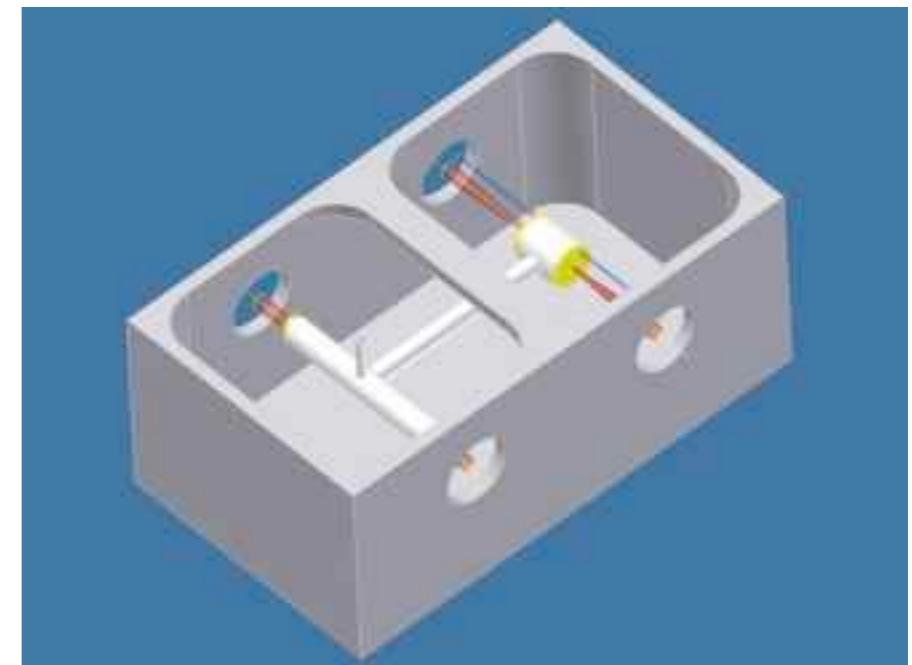
crossed beam cell

Bruker 125 HR of FTS Paris

**2014**

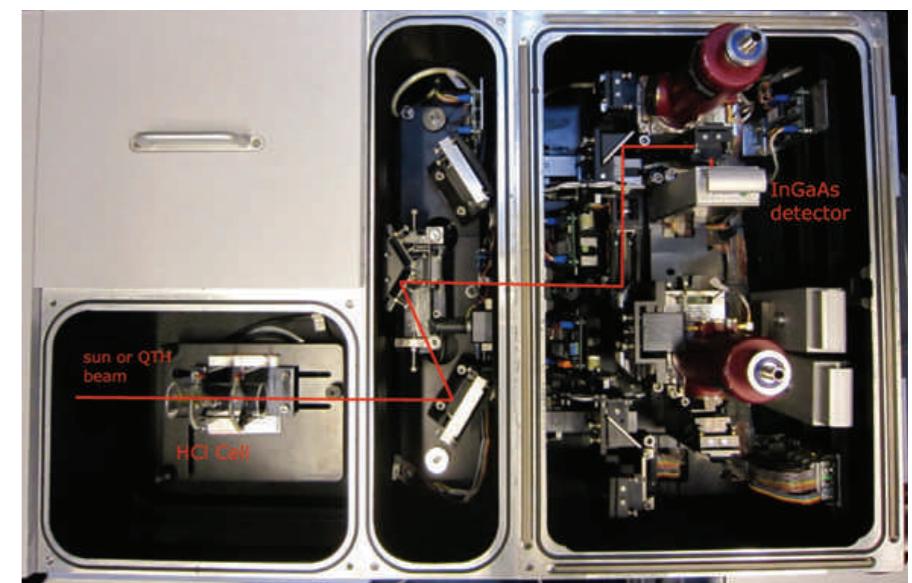
cell is being built in house with support  
from

F. Thibout (LKB) &  
M. Escudier (INSP)



**2014 - 2015**

first cell measurements  
in winter period



# O<sub>3</sub> Multispectral Study

- ▶ Quasi-simultaneous measurements in different bands
  - ▶ in cell @ UV, 5 μm, 10 μm, and 14 μm
  - ▶ Comparison with theory (GSMA / Reims)
  - ▶ Atmospheric validation (compare with other TCCON partners, eg Karlsruhe, Izana and Orléans/Trainou)



AO LEFE-CHAT 2014