What about the spectral parameters when performing synergistic atmospheric measurements?

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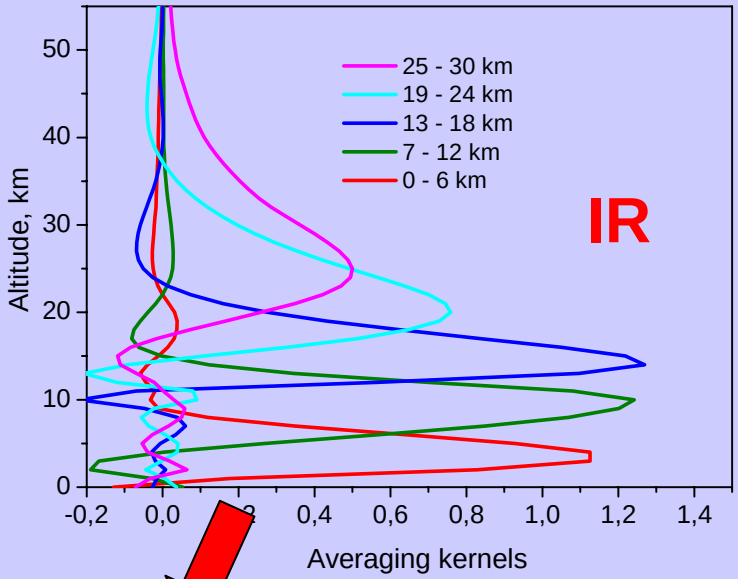
What is the problem?

Many species(O_3, HCHO, H_2O,...) are measured in various spectral regions with different instruments

- How to perform really meaningful comparisons of concentration profiles obtained by spectrometric measurements in various spectral regions
- How to perform simultaneous retrievals in different spectral regions

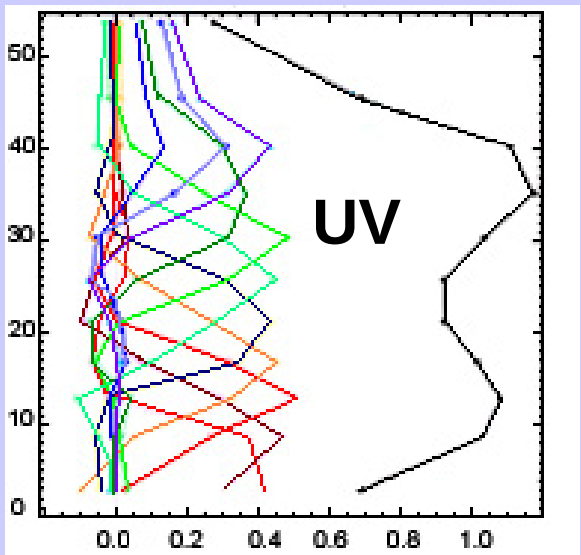
if the corresponding cross-sections are not consistent

Tropospheric Ozone

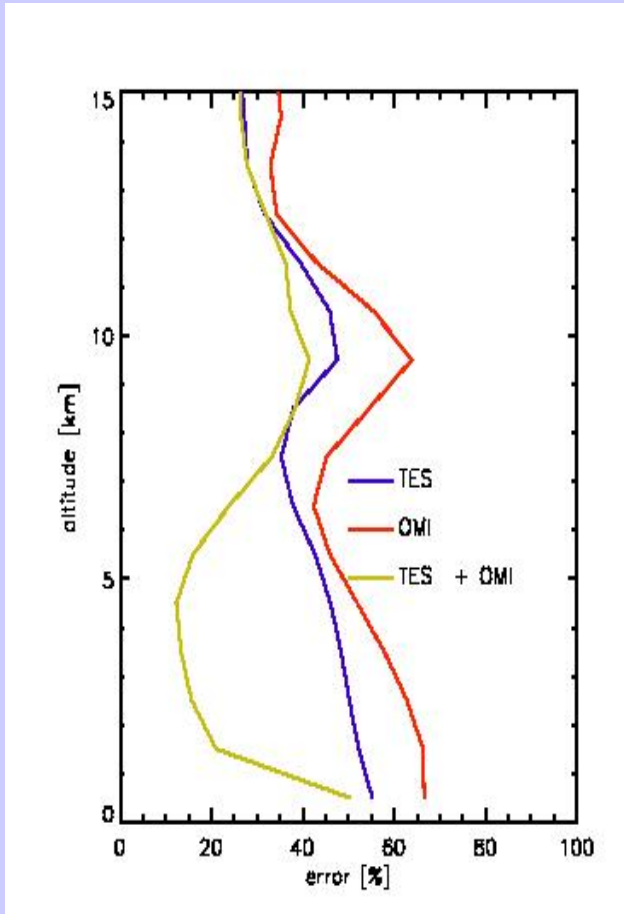


3/4 independent points

column



Reduced errors when IR + UV



O_3

Intercomparison of recent measurements at 10µm

Intercomparison of the ozone absorption coefficients in the mid-infrared (10 µm) and ultraviolet (300-350 nm) spectral regions

Concentration measurements of ozone in the 1200–300 ppbv range:an intercomparison between the BNM ultraviolet standard(253.7nm) and infrared methods

O_3:Previous Situation in the IR

The mean difference between the Pickett *et al.* [1992] intensity values and the HITRAN2K values is **+ 8.3%**.

The intensity of the ν_3 line $10_{56} \leftarrow 9_{55}$ located at 1048.674 cm^{-1} measured by De Backer *et al.* [1995] is **in excellent agreement** with HITRAN2K.

The weighted mean difference of the De Backer-----Barilly and Courtois [1997] values with respect to HITRAN2K values is **- 5%.**

It was really necessary to try to improve the ozone line intensities at 10 μm

O_3

Recent measurements at 10µm

G. Wagner, M. Birk, F. Schreir and J.-M. Flaud,
Spectroscopic database of the three ozone fundamentals,
J. Geophys. Res., 107,4626,doi:10.1029/2001JD000818,2002

WAG

C. Claveau, C. Camy-Peyret, A. Valentin and J.-M. Flaud,
Absolute intensities of the ν_1 and ν_3 bands of $^{16}O_3$,
J. Mol. Spectrosc., 206, 115-125,2001

CLA

M.A.H. Smith, V. Malathy Devi, D.C. Benner and C.P. Rinsland,
Absolute intensities $^{16}O_3$ of lines in the 9-11mm region,
J. Geophys. Res., 106, 9909-9921, 2001

SMI

M.R. De Backer-Barilly and A. Barbe,
Absolute intensities of the 10 mm bands of $^{16}O_3$,
J. Mol. spectrosc., 205, 43-53, 2001

DEB

Direct comparison of experimental intensities

	Number of lines	Ratio
CLA/WAG	262	0.986(51)[a]
DEB/WAG	257	0.987(35)
SMI/WAG	350	1.036(47)
SMI/DEB	101	1.056(39)
SMI/CLA	61	1.046(32)

[a] Uncertainties are one standard deviation

Comparison of experimental and calculated intensities

	Number of lines	Ratio
CLA/CALC	296	0.991(27)[a]
DEB/CALC	291	0.998(18)
WAG/CALC	2597	1.010(18)
SMI/CALC	376	1.044(18)

BAND	ν_1	ν_3
HIT2000/CALC	1.044(35)	1.035(14)

[a] Uncertainties are one standard deviation

First discussion

* Three independent experimental sets of ozone line intensities agree very well: **dispersion of ~0.8%, RMS of ~1.9%**
* The fourth independent experimental set is **highly consistent on a relative basis** but the intensities are systematically ~4% higher
* When comparing with ATMOS spectra smaller residuals are obtained with new calculation for more than 90% of the microwindows at altitude(34 and 26 km).

On a relative basis the new intensities are better than the HITRAN2K ones.

The situation is not so clear as far as the absolute intensities are concerned:

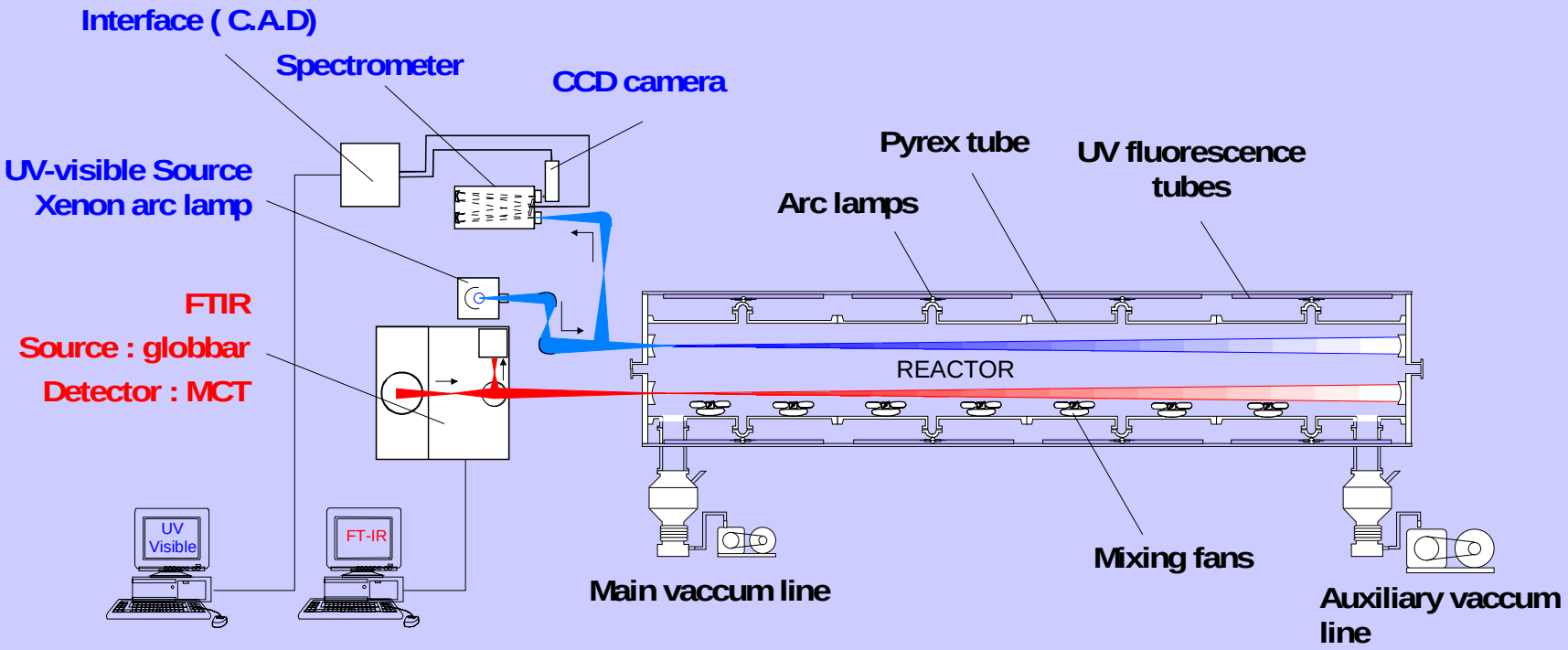
J. M. FLAUD, G. WAGNER, M. BIRK, C. CAMY-PEYRET, C. CLAVEAU, M. R. DE BACKER-BARILLY, A. BARBE, AND C. PICCOLO, Ozone absorption around 10 μm, J. GEOPHYS. RES. , VOL. 108, NO. D9, 4269, doi:10.1029/2002JD002755, 2003

Laboratory intercomparison of the ozone absorption coefficients in the mid-infrared (10 μm) and ultraviolet (300-350 nm) spectral regions

B. Picquet-Varrault, J. Orphal, J-F. Doussin, P. Carlier and J-M. Flaud,

J. Phys. Chem. A 2005, 109, 1008-1014

Experimental set-up



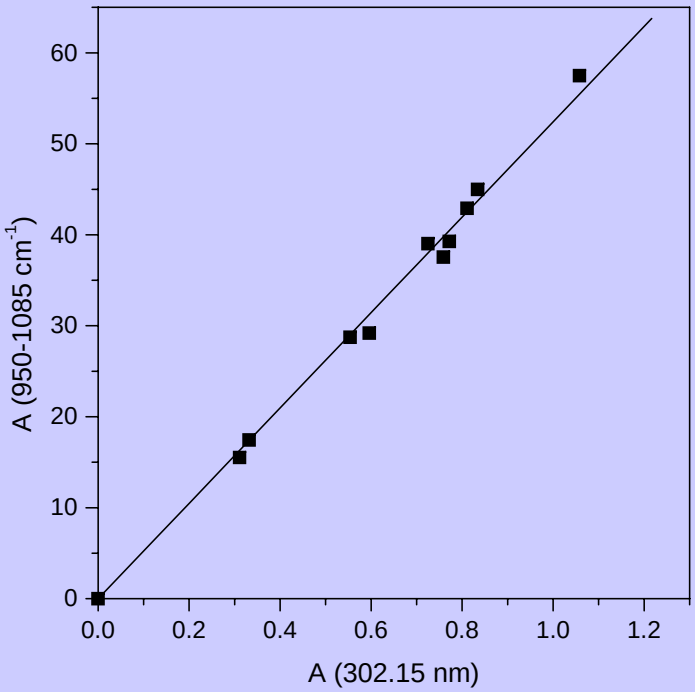
Reactor :
Pyrex tube
Volume : 0.977 m^3
Mixing : 8 teflon fans
Vaccum :2 turbomolecular pumps 2 rotary pumps Max vaccum : 10^{-3} mbar

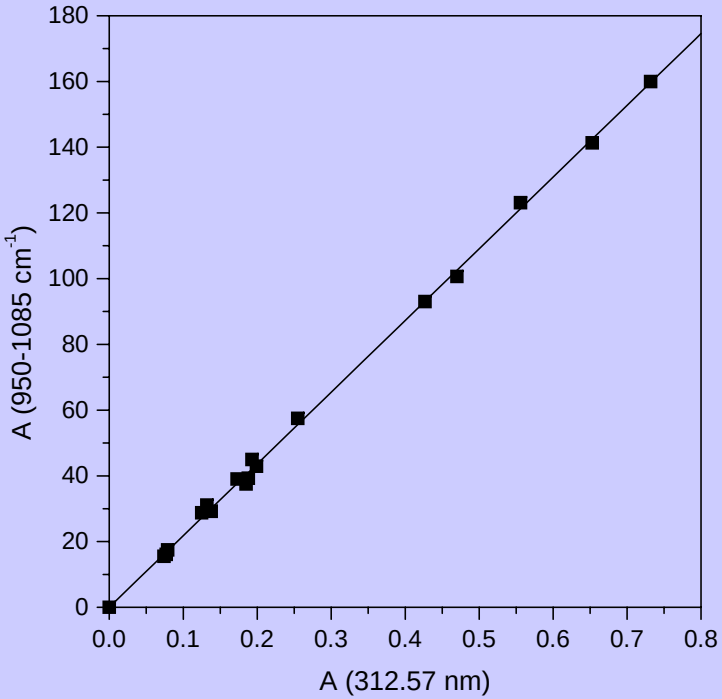
Irradiation :
48 UV fluorescence tubes centred on 360 nm
48 UV fluorescence tubes centred on 420 nm
16 arc lamps

UV-Visible spectrometry :
DOAS system
Multipass White cell
Optical path length : 12 - 72 m
Source : XBO lamp
Spectral range : 290-650 nm
resolution 0.15 nm

FTIR spectrometry :
Stabilised multipass cell
Optical path length : 12 - 672 m
Bomem DA 8 system
Spectral range : 500-5000 cm^{-1}
resolution 0.04 cm^{-1}

Example of IR/UV calibration plots





Results

UV wavelength (nm)	$\frac{\left(\int (A.d\sigma).I\right)_{IR}}{(A_\lambda.I)_{UV}}$		
	EXP	HIT2000	NEW
302.15	52.3 ± 1.2	51.3	49.3
307.59	111.9 ± 2.6	110.6	106.3
308.08	115.5 ± 2.7	113.6	109.1
312.57	217.6 ± 2.2	214.3	205.9
313.17	230.4 ± 2.5	226.3	217.5
		0.9834(0.023)	0.9455(0.023)

To get rid of possible UV wavelengths scale errors, the ratios are calculated for UV wavelengths corresponding to reference spectral lines of Hg, Zn or Cd namely 302.15, 307.59, 308.08, 312.57 and 313.17 nm

Second discussion

On the average the HITRAN2K cross sections and those derived from the review of Flaud et al., 2003 are about **1.7% and 5.3 %** lower respectively than the values derived from the UV/IR experiment.

→ The previous HITRAN2K data seem better .

Concentration measurements of ozone in the 1200-300 ppbv range:an intercomparison between the BNM ultraviolet Standard and infrared methods

G. Dufour , A. Valentin , A. Henry, D. Hurtmans, C.Camy-Peyret

Spectrochimica Acta Part A 60 (2004) 3345–3352

Experiment

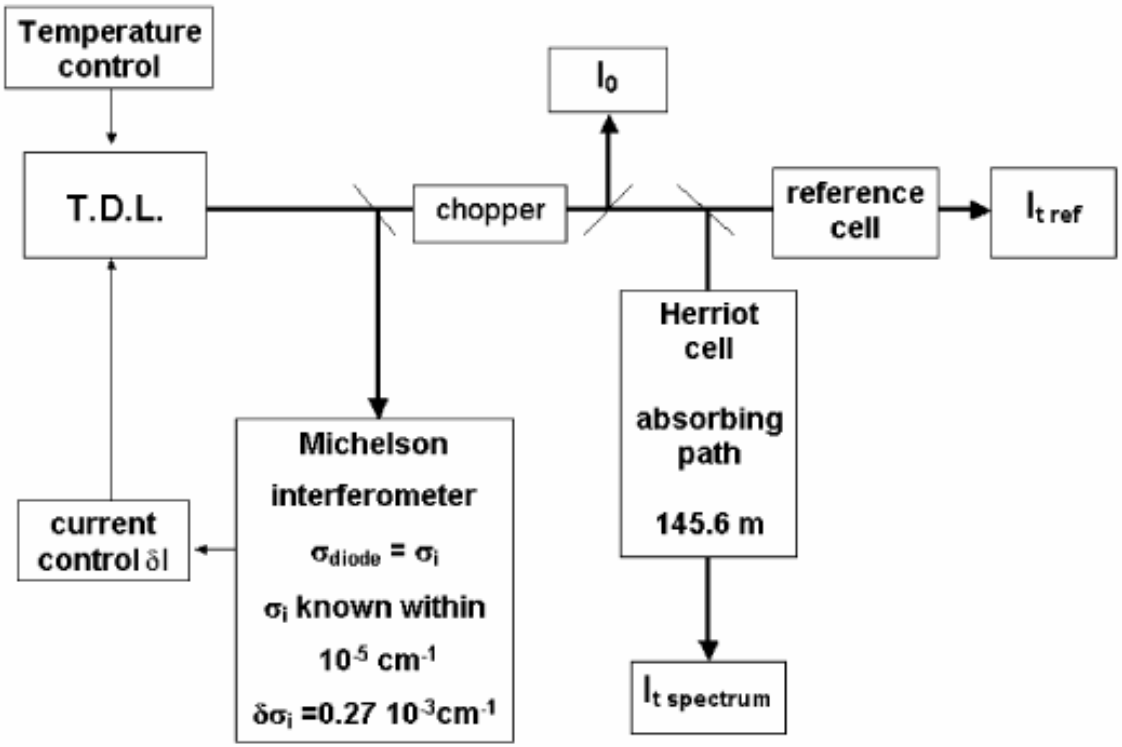


Fig. 1. TDL spectrometer design.

Example of Spectrum

Line intensity
Apparatus function

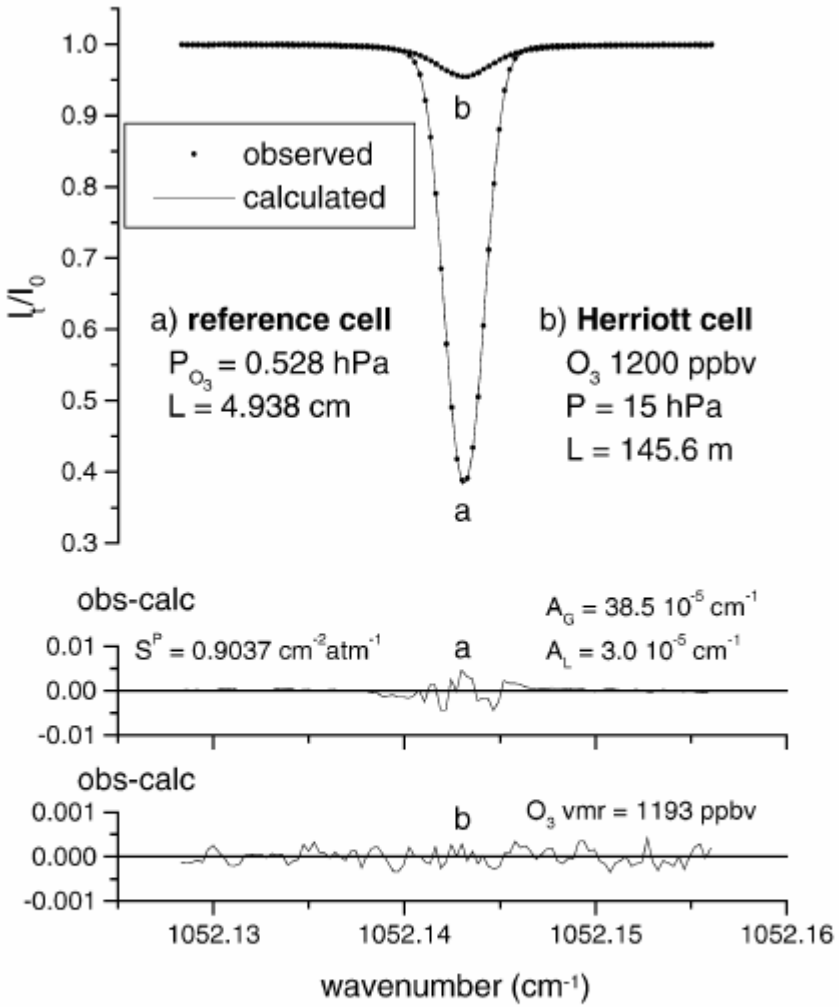


Fig. 3. Two spectra of the ozone line at 1052.143 cm^{-1} simultaneously recorded are compared in a least squares fit with calculated spectra. The line intensity and the apparatus function parameter are derived from spectrum (a) and the ozone concentration from spectrum (b).

Concentration

Line parameters

Line position (cm^{-1})	Meas. line intensity ($cm^{-2}\,atm^{-1}$)	Calc. intensity (Flaud et. al, 2003)	Diff
1026.47600	(0.9596 ± 0.0030)	0.9657	-0.7%
1026.47418	(0.0644±0.0021)	0.0619	4%
	1.0240	1.0276	**-0.35%**

Analoguous agreement(1.2%) for the line at 1052.143cm^{-1}

Results

Table 2
Comparison of ozone concentration measurement using UV absorption at 253.7 nm and IR absorption at 1052.143 cm^{-1}

Ozone volume mixing ratio (ppbv)				
UV absorption (display of 49PS)	UV absorption (with NIST scaling)	IR absorption ± 2σ	(UV − IR)/IR	$\alpha_{UV/IR}$ (cm^{-1} atm^{-1}) at 273.15 K
1200 ± 10[a]	1202.3 ± 18	1193 ± 6	+ 0.8	310.7 ± 0.4
900 ± 8	901.4 ± 13.5	900 ± 5	+ 0.1	308.7 ± 0.4
600 ± 5	600.8 ± 9	603 ± 5	− 0.4	307.2 ± 0.7
400 ± 3	400.5 ± 6	398 ± 4	+ 0.4	309.5 ± 1.1
300 ± 3	300.1 ± 4.5	296 ± 5	+ 0.7	311.0 ± 1.4

Ozone UV absorption coefficient at 253.7 nm (cm^{-1} atm^{-1} at 273.15 K) measured at the temperature T

References	Year	T (K)	α_{uv}
Inn and Tanaka [2] (interpolated)	1953	300	306.5
Hearn [3]	1961	295	308.3 ± 4
Griggs [5]	1968	303	305.5
Barnes and Mauersberger [7]	1987	297	305.2
Malicet et al. [8]	1995	295	303.7 ± 3
This work	–	297.5	309.1 ± 1.2

Third(and likely not final!!) discussion

1 The new calculation based on three independent experimental sets of ozone line intensities which agree very well (**dispersion of ~0.8%, RMS of ~1.9%) is ~4% lower than the HITRAN2K values**

2 On the average the HITRAN2K cross sections and those of the new calculation are about **1.7% and 5.3 %** lower respectively than the UV cross sections **in the 300-320 nm spectral region.**

3 The cross sections of the new calculation are in excellent agreement(~1.2%) with the UV cross sections **at 253.7 nm**

CONCLUSION: We have a problem!!!!!!!!!!!

- Experiment 2 is not correct??
-The UV cross sections at 253.7 and 300-350nm are not consistent??
- Or????

Accurate quantitative spectroscopy is a challenging field

FORMALDEHYDE: H_2CO

Intercomparison of the 5µm band and the 300-360 nm region

A. Gratien, B. Picquet-Varrault, J. Orphal, E. Perraudin,
B. J-F. Doussin and J-M. Flaud

JGR, Submitted

HCHO atmospheric measurements

Many ground-based, air-borne or satellite measurements of HCHO are performed routinely using spectrometers working in the UV(300-400 nm) and infrared spectral ranges(3.5 and 5-6 µm bands).

For these reasons, accurate but also consistent UV and IR cross-sections are needed.

If many UV and IR absorption coefficients have been published in the literature to our knowledge no study has ever verified the consistency between the cross-sections in both spectral ranges.

Previous spectroscopic studies

UV spectral range (240-360 nm)

• Numerous studies with good resolution and large spectral range : *Cantrell et al., 1990; Meller and Moortgat, 2000; Rogers, 1990; Bogumil et al., 2003.*

However large discrepancies
(70% for selected portions; 13% for integrated band 300-360 nm)

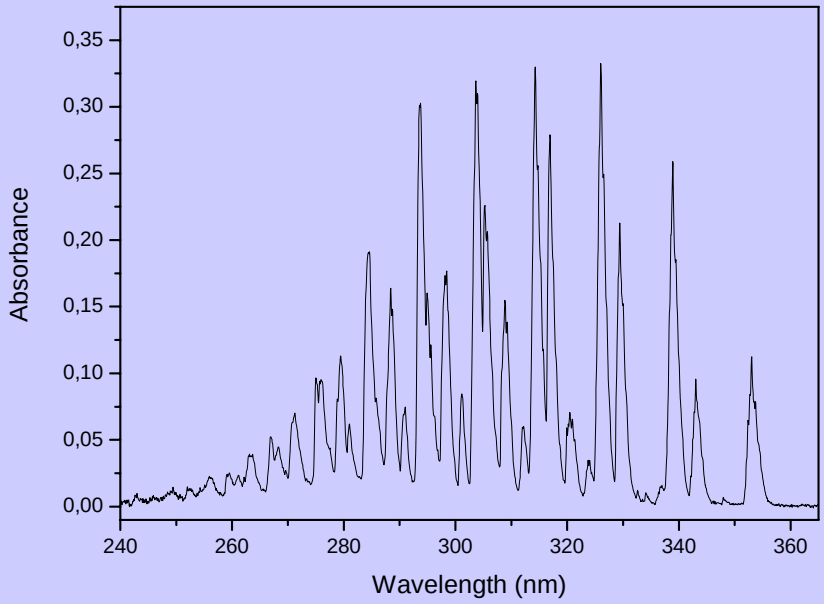
IR spectral range (1660-1820 cm^{-1})

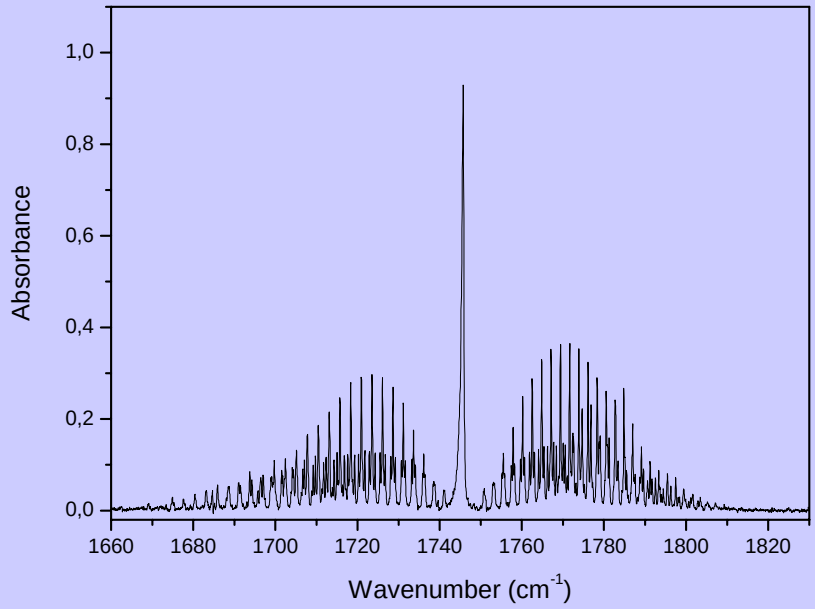
• 5 studies have been published

✓ *Nakanaga et al., 1982; Klotz et al., 2004; Sharpe et al., 2004; Herndon et al. 2005;* are **in good agreement (better than 5%)** ,

✓ *Hisatsune et al., 1955* is 20% lower.

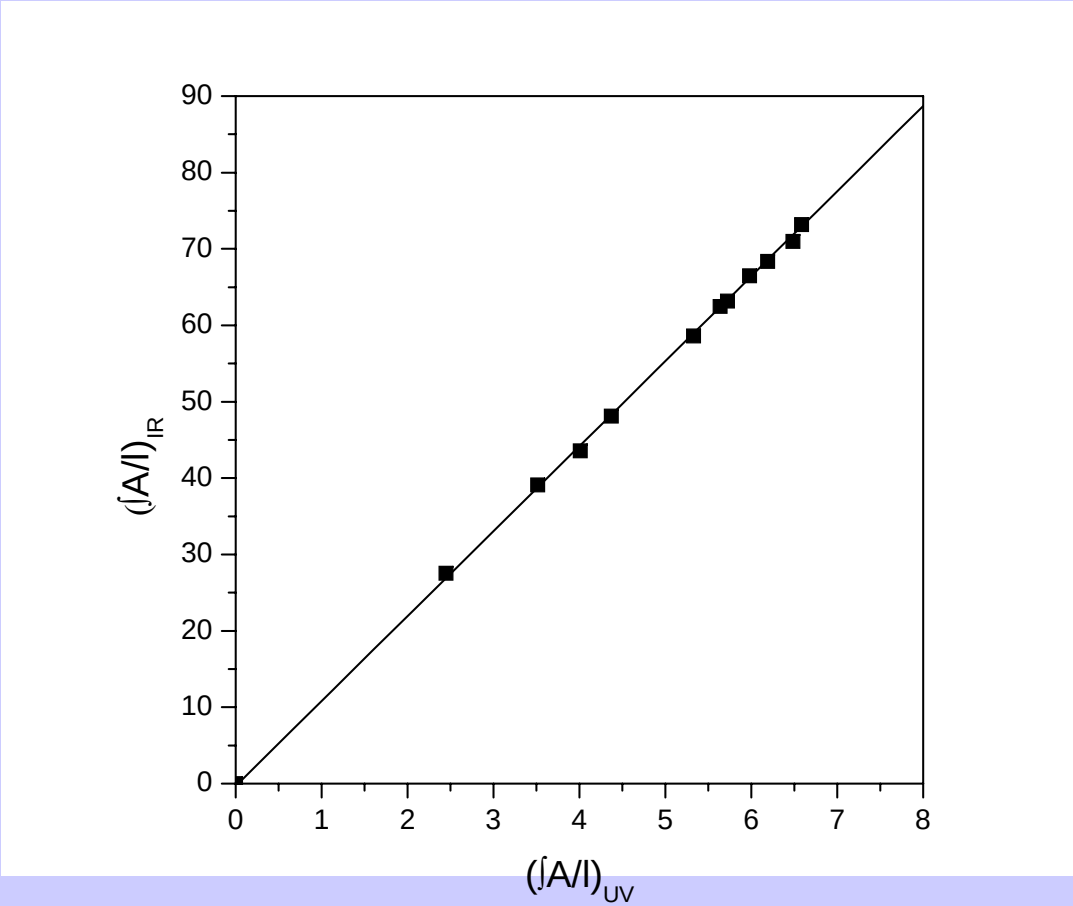
Example of spectra





- UV and IR spectra were acquired simultaneously
- 12 UV/IR data sets (*different concentrations*)

IR/UV calibration plots



$$p = IBI_{IR} / IBI_{UV} = 11.04 \pm 0.05$$

Comparison with literature

IBI_{IR} / IBI_{UV} ratios

< 6 %
> 5 %

FORMALDEHYDE

	Our ratio	Hisatsune et al.	Nakanaga et al.	Sharpe et al.	Herndon et al.	Klotz et al.
		Meller et al.	Meller et al.	Meller et al.	Meller et al.	Meller et al.
IBI_{IR} / IBI_{UV}	**11.04**	8.84	11.28	11.79	11.58	11.45
Deviation	**-**	**22%**	**-2%**	**-6%**	**-5%**	**-4%**

	Our ratio	Hisatsune et al.	Nakanaga et al.	Sharpe et al.	Herndon et al.	Klotz et al.
		Rogers	Rogers	Rogers	Rogers	Rogers
IBI_{IR} / IBI_{UV}	**11.04**	9.95	12.70	13.27	13.04	12.89
Deviation	**-**	**10%**	**-14%**	**-19%**	**-17%**	**-15%**

	Our ratio	Hisatsune et al.	Nakanaga et al.	Sharpe et al.	Herndon et al.	Klotz et al.
		Cantrell et al.	Cantrell et al.	Cantrell et al.	Cantrell et al.	Cantrell et al.
IBI_{IR} / IBI_{UV}	**11.04**	10.03	12.83	13.40	13.18	13.03
Deviation	**-**	**9%**	**-15%**	**-19%**	**-18%**	**-17%**

Discussion

Good agreement (better than 5%) between *Meller and Moortgat* and the 4 consistent IR data set

~15% discrepancy between *Cantrell et al*. and *Rogers* with the 4 IR data sets.

Data of *Cantrell et al.* are used in HITRAN 2003

Assuming that IR data are correct as well as our experiment:

- HITRAN cross-sections would be underestimated by 15%,
- HCHO concentrations would be overestimated by 15% !
- Would lead to systematic differences in concentration profiles derived from both spectral ranges