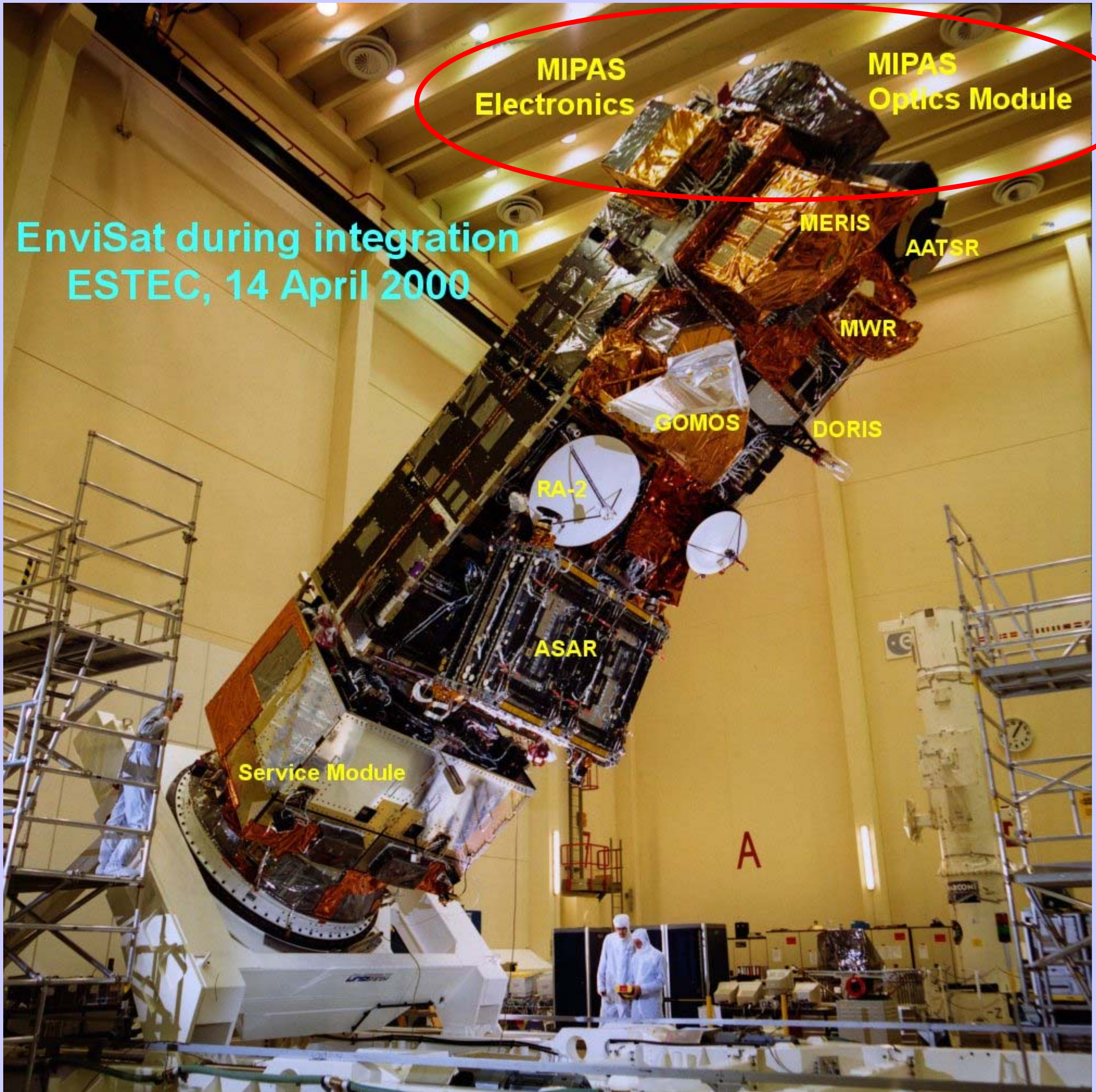
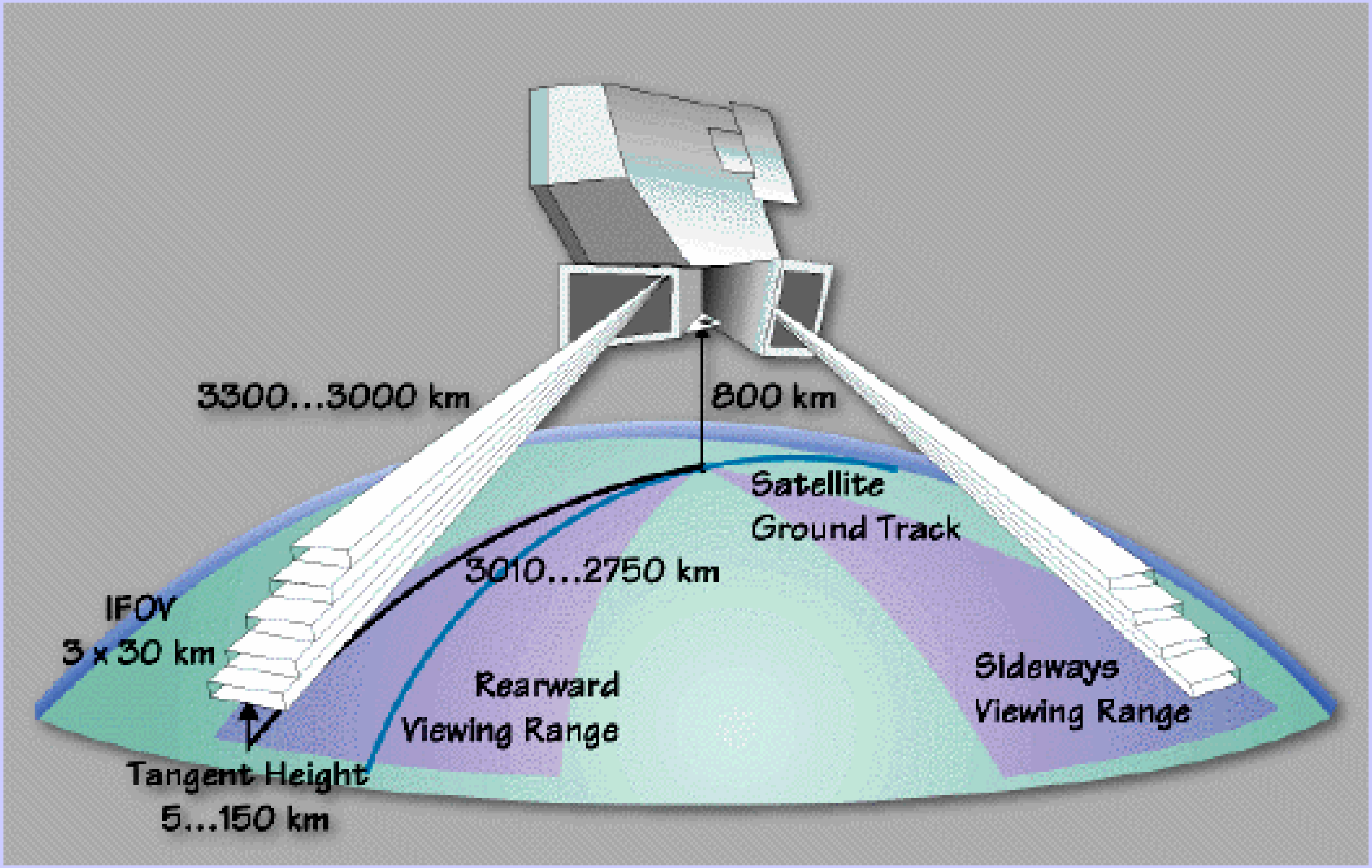
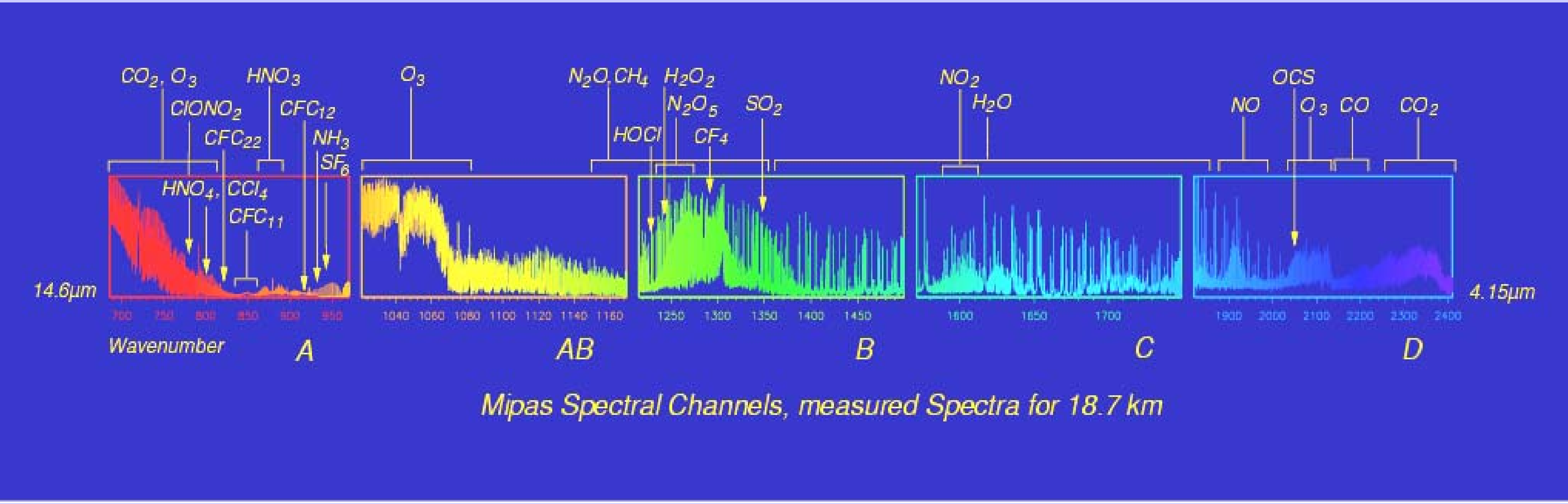
Spectroscopie des espèces traces : Application aux mesures atmosphériques

J.-M. Flaud


MIPAS
Electronics
MIPAS
Optics Module
EnviSat during integration
ESTEC, 14 April 2000
MERIS
AATSR
MWR
GOMOS
DORIS
RA-2
ASAR
Service Module


3300...3000 km
800 km
Satellite
Ground Track
3010...2750 km
IFOV
3 x 30 km
Rearward
Viewing Range
Sideways
Viewing Range
Tangent Height
5...150 km



(J.-M. Flaud and H. Oelhaf, Infrared spectroscopy and the terrestrial atmosphere, C. R. Physique 5 (2004) 259–271)

« OPERATIONAL SPECIES »

- P
- T
- H_2O
- O_3
- NO_2
- HNO_3
- CH_4
- N_2O

~5-140 km

What are the problems?

1 The possibility of the retrievals is directly linked to the availablity of the spectroscopic parameters

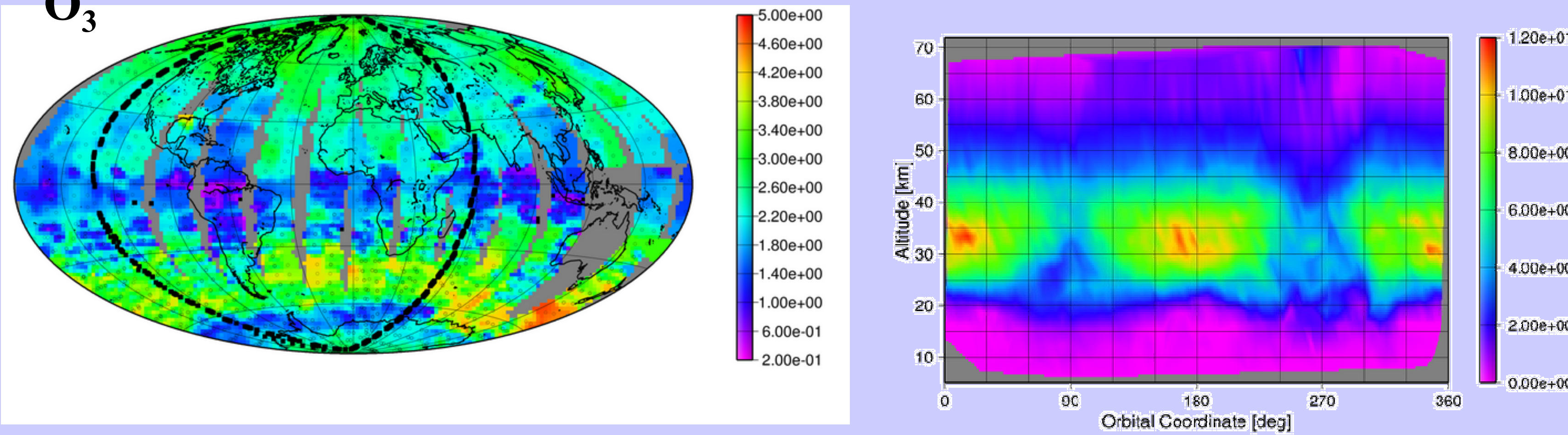
2 The quality of the retrievals is directly linked to the quality of the spectroscopic parameters

3 Many species(O_3, HCHO, H_2O,HNO_3, …) are measured in various spectral regions with different instruments

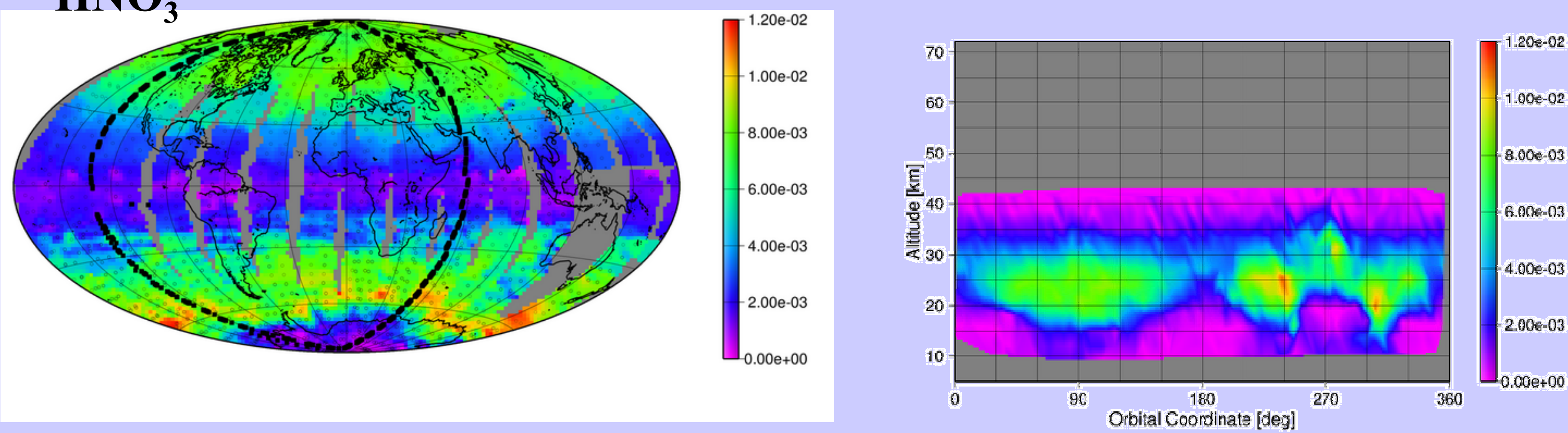
How to perform accurate retrievals and/or really meaningful comparisons of concentration profiles obtained by spectrometric measurements in various spectral regions

if the corresponding cross-sections are not accurate and / or consistent

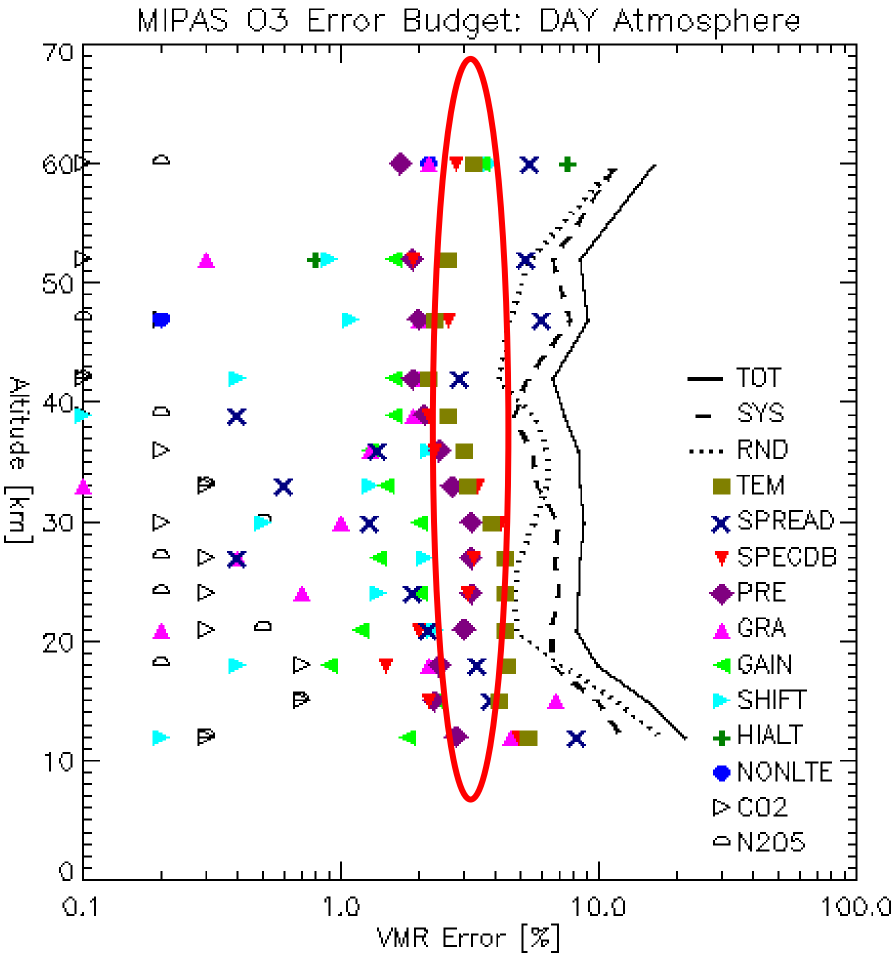
O_3

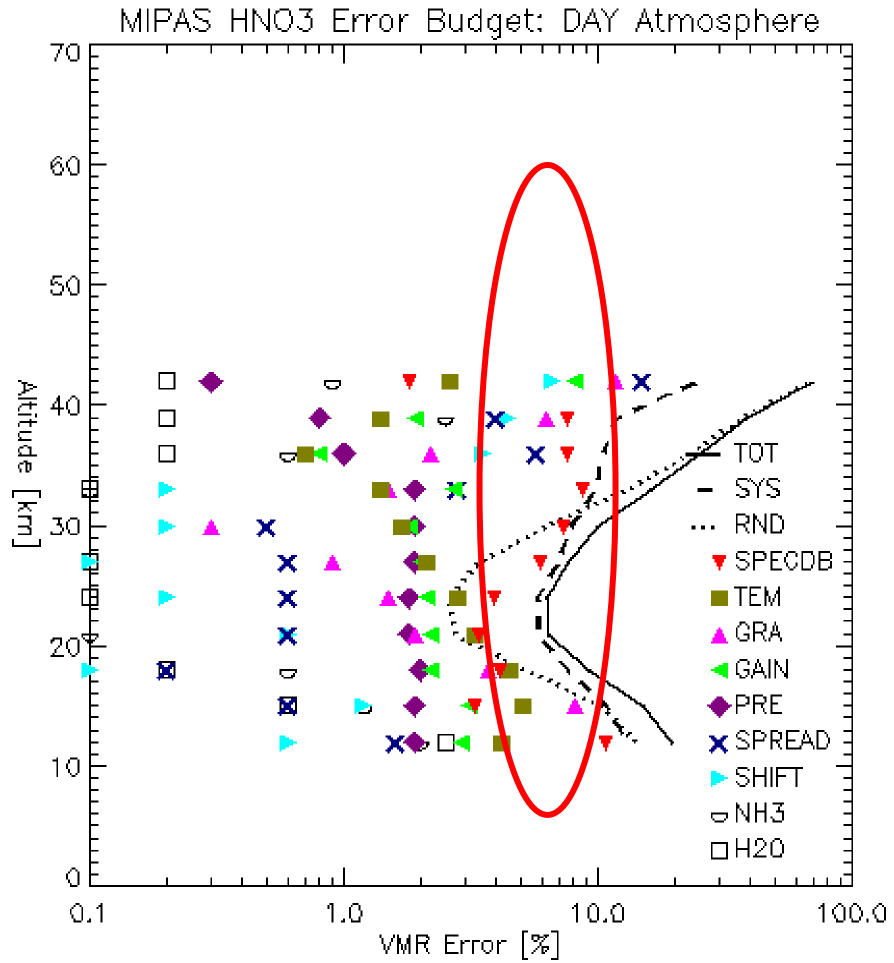


HNO_3



Global map at one altitude and vertical section of the VMR (measured in ppm) of the MIPAS target species. A black track shows the orbit of the vertical section in the global map and the altitude of the global map in the vertical section.





Error profile

Continuous line: total error; dotted line: contribution to the total error due to random error; dashed line: contribution to the total error due to the a-priori estimate of systematic errors.

LES INTENSITES POUR LA MOLECULE D'OZONE: UN CASSE TETE!!

O_3:Previous Situation

The mean difference between the Pickett *et al*. [1992] intensity values and the HITRAN 2000 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 HIT2000.

The weighted mean difference of the De Backer-----Barilly and Courtois [1997] values with respect to HIT2000 values is **- 5%** but there is a rather large scatter among the differences the arithmetic average of which is **- 8%.**

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

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

Meausurements 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

Experimental results

	Number of lines	Technique
CLA	296	P measurement
DEB	291	P measurement + UV calibration
WAG	2597	P measurement
SMI	376	UV calibration

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 MIPAS 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 HIT2000 ones.

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

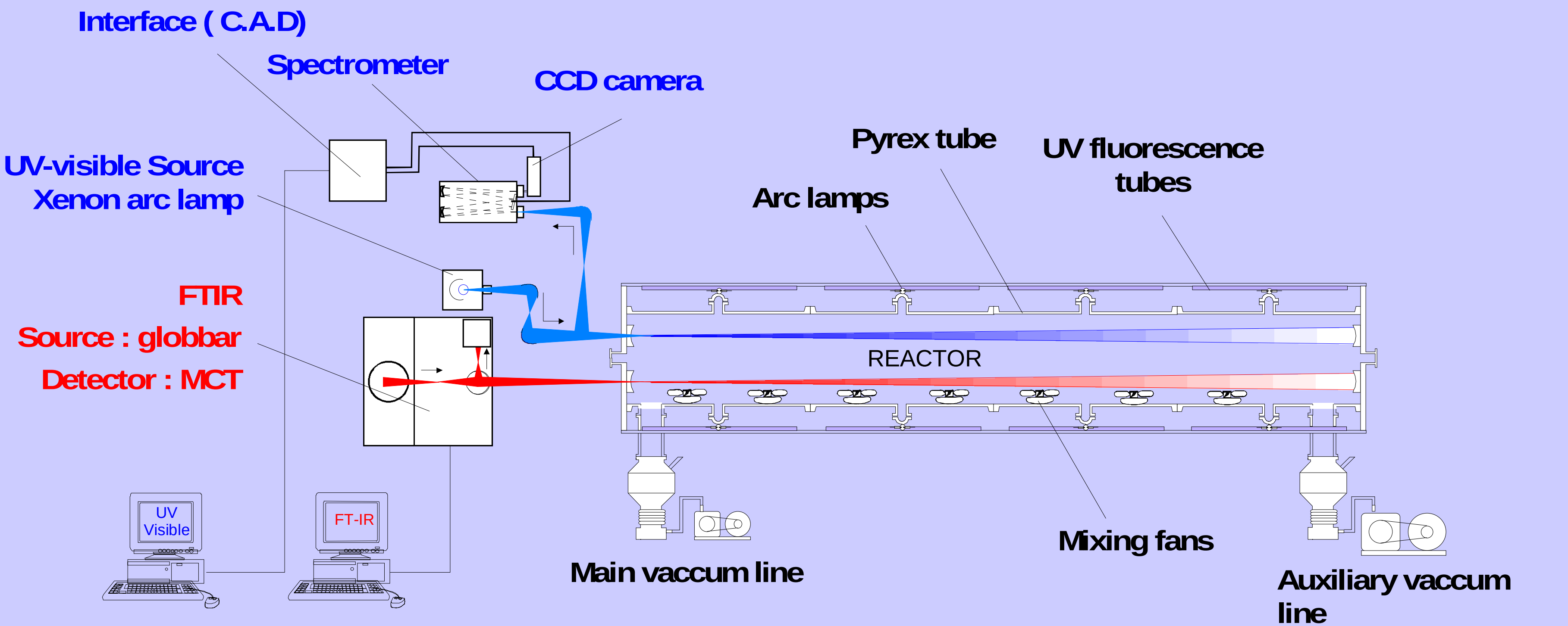
It seems indeed that the differences are not due to the method (P measurement or UV calibration) used to derive the amount of ozone in the cell.

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, The Journal of Physical Chemistry A, 2005, 109, 1008-1014

Experimental set-up



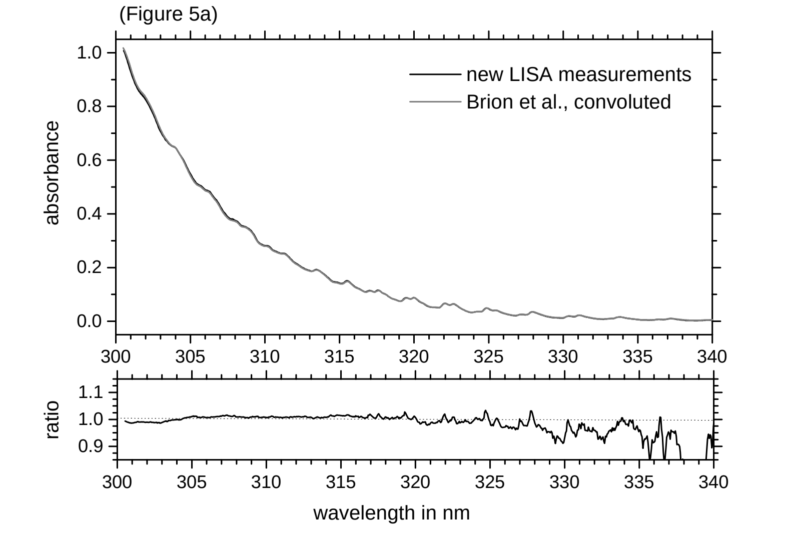
Reactor :
Pyrex tube
Volume : 0.977 m^3
Mixing : 8 teflon fans
Vaccum :2 turbomolecular pumps 2 rotary pumps Max vaccum : 10^{-3} mbar

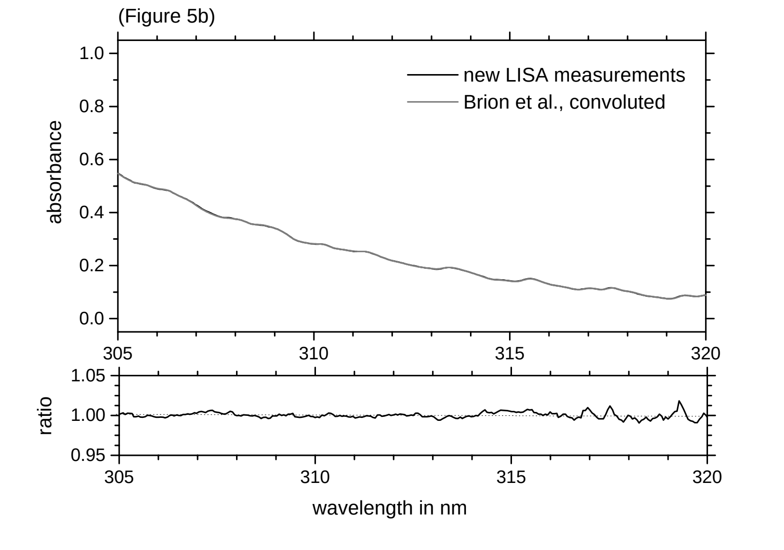
Irradiation :
48 UV fluorescence tubes centred on 360 nm
48 UV fluorescence tubes centred on 420 nm
16 arc lamps

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

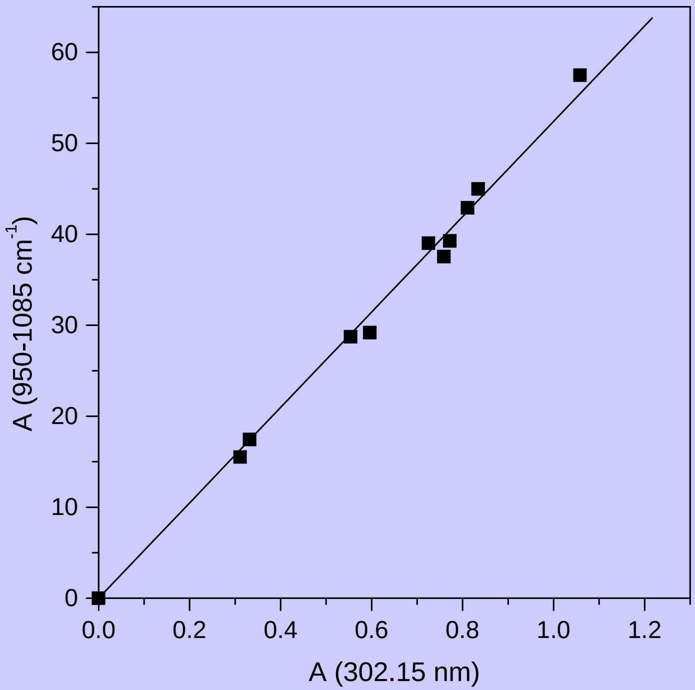
FTIR spectrometry :
Stabilised multipass cell
Optical path length : 12 - 672 m
Bomem DA 8 system
Spectral range : 500-5000 cm^{-1}
resolution 0.04 cm^{-1}

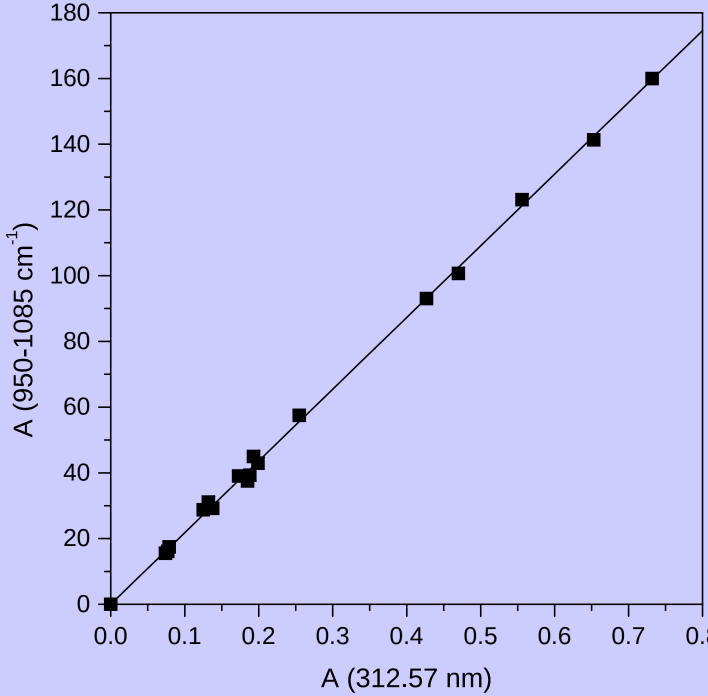
Comparison of UV spectra with Brion et al.





Example of IR/UV calibration plots





Results

UV wavelength (nm)	$\frac{\left(\int (A.d\sigma).I\right)_{IR}}{(A_{\lambda}.I)_{UV}}$		
	EXP	HITRAN	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 HIT2000 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 HITRAN data seem better .

Ô rage, Ô désespoir, Ô …

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**

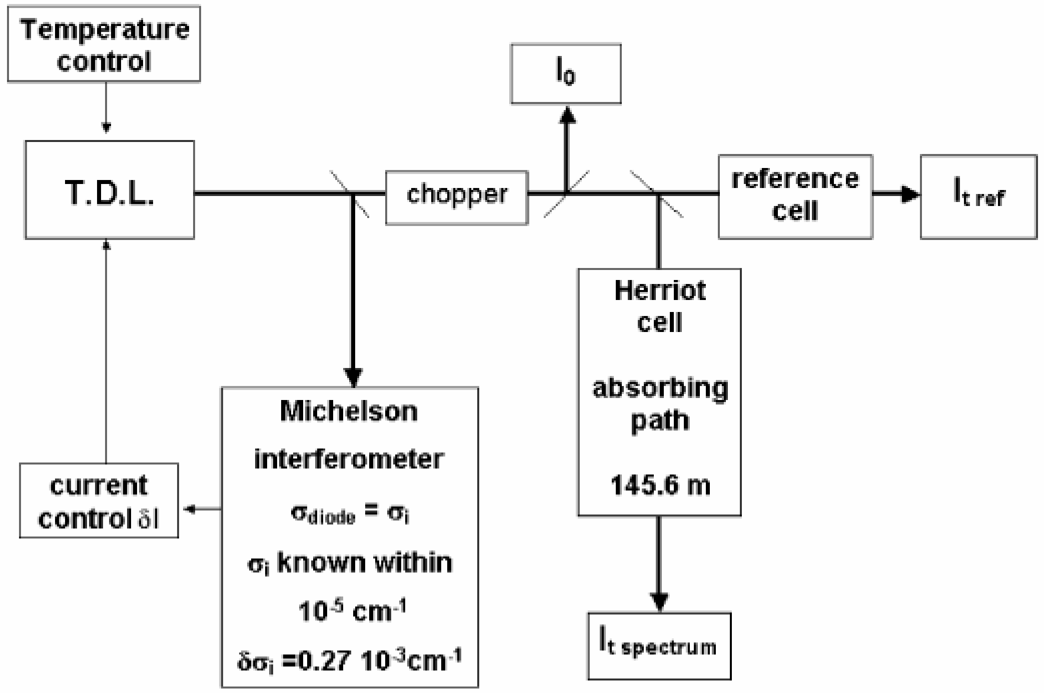


Fig. 1. TDL spectrometer design.

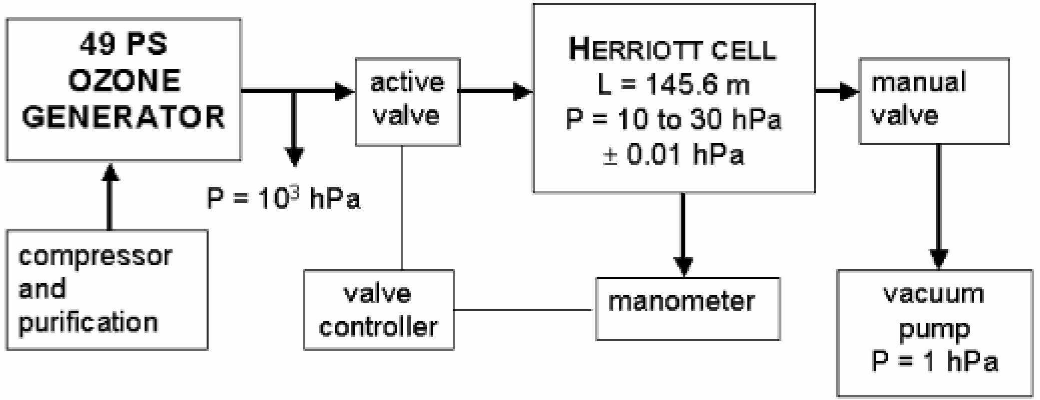


Fig. 2. Herriott cell connexion with the 49PS ozone generator.

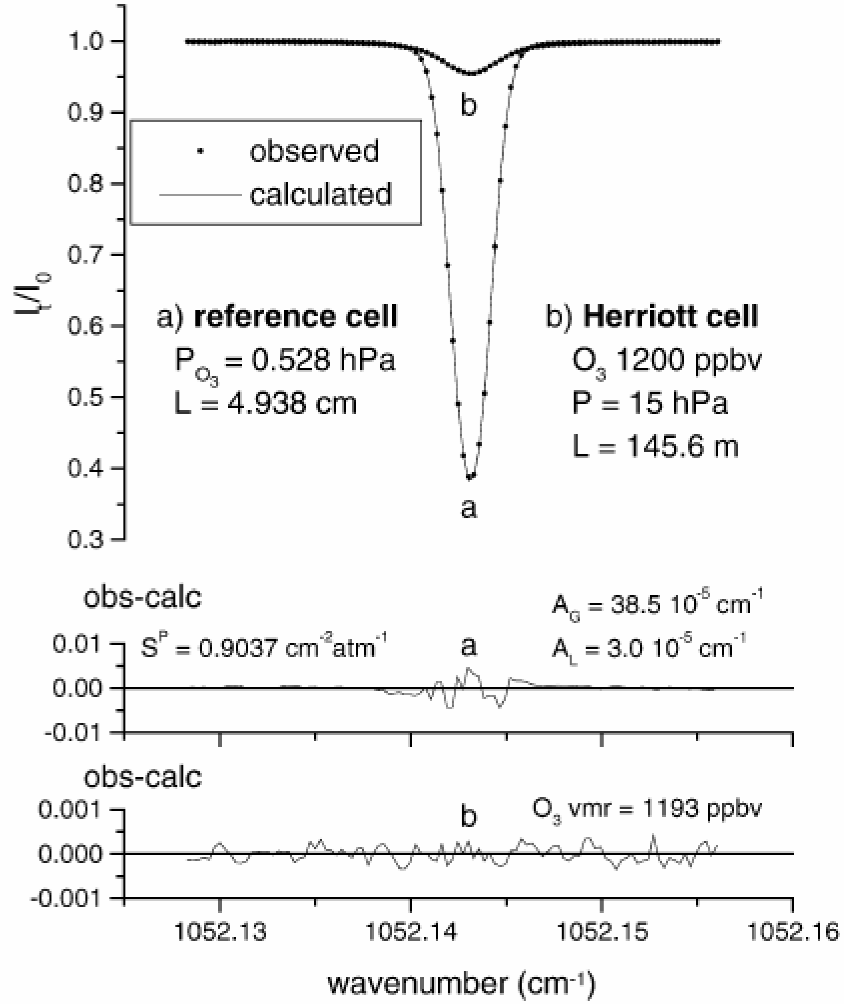


Fig. 3. Two spectra of the ozone line at 1052.143 cm^{-1} simultaneously recorded are compared in a least squares fit with calculated spectra. The line intensity and the apparatus function parameter are derived from spectrum (a) and the ozone concentration from spectrum (b).

Line parameters

Line position (cm^{-1})	Meas. line intensity ($cm^{-2}\ atm^{-1}$)	Calc. line intensity ($cm^{-2}\ atm^{-1}$) (Flaud et. al, 2003)	Diff (%)
1026.47600	(0.9596 ± 0.0030)	0.9657	-0.7%
1026.47418	(0.0644 ± 0.0021)	0.0619	4%
SUM:	**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 $\pm 2\sigma$	(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	303.5
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

Three independent experimental sets of ozone line intensities agree very well (**dispersion of ~0.8%, RMS of ~1.9%). They are ~4% lower than t**he fourth independent experimental set which is **highly consistent with the HITRAN2K database**

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 UV cross sections **in the 300-320 nm spectral region.**

On the average the cross sections derived from the review of **Flaud et al., 2003** are in excellent agreement(~1.2%) with the UV cross sections **at 253.7 nm**

CONCLUSIONS

We have a problem!!!!!!!!!!!!

Accurate quantitative spectroscopy is a challenging field

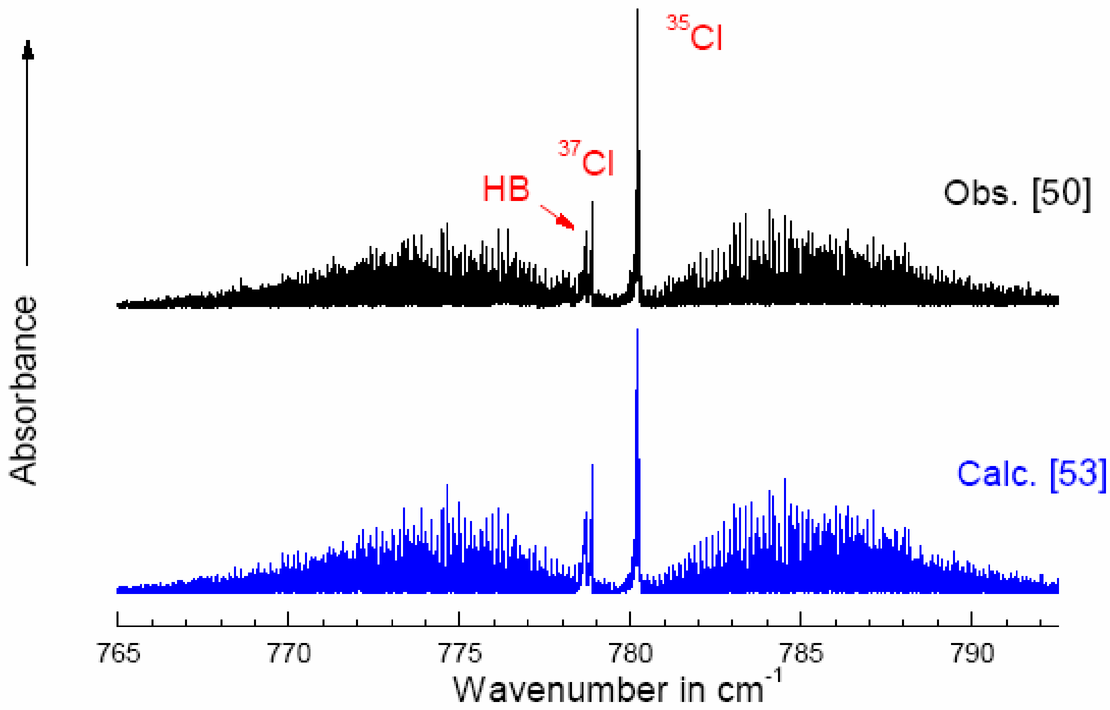
As usual more experiments are needed

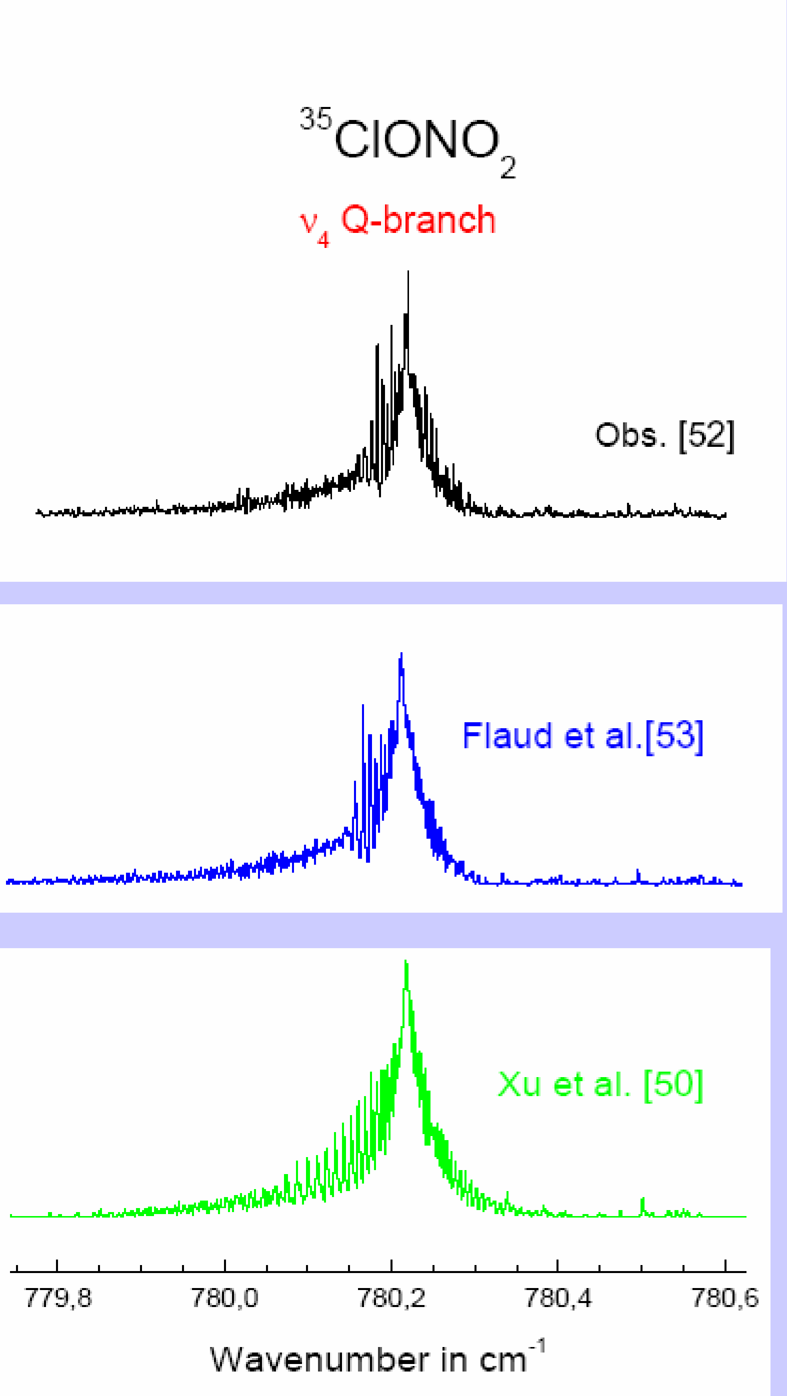
$ClONO_2$: A TRICKY MOLECULE

Assignment of the chlorine nitrate spectrum has been limited by the high density of lines resulting from :

- two chlorine isotopes,
- hot bands arising from low lying vibrational levels,
- rather small rotational constants.
- And lots of resonances.

→ **Extremely dense spectra**
Extremely difficult assignment


35Cl
37Cl
HB
Obs. [50]
Calc. [53]
Absorbance
765
770
775
780
785
790
Wavenumber in cm-1



$^{35}ClONO_2$
ν_4 Q-branch
Obs. [52]
Flaud et al.[53]
Xu et al. [50]
779,8
780,0
780,2
780,4
780,6
Wavenumber in cm^{-1}

$ClONO_2$: Line by line

➡ a synthetic spectrum of the ν_3, ν_4 and $\nu_4 + \nu_9 - \nu_9$ bands of $^{35}ClONO_2$ and of the ν_4 band of $^{37}ClONO_2$ has been generated.

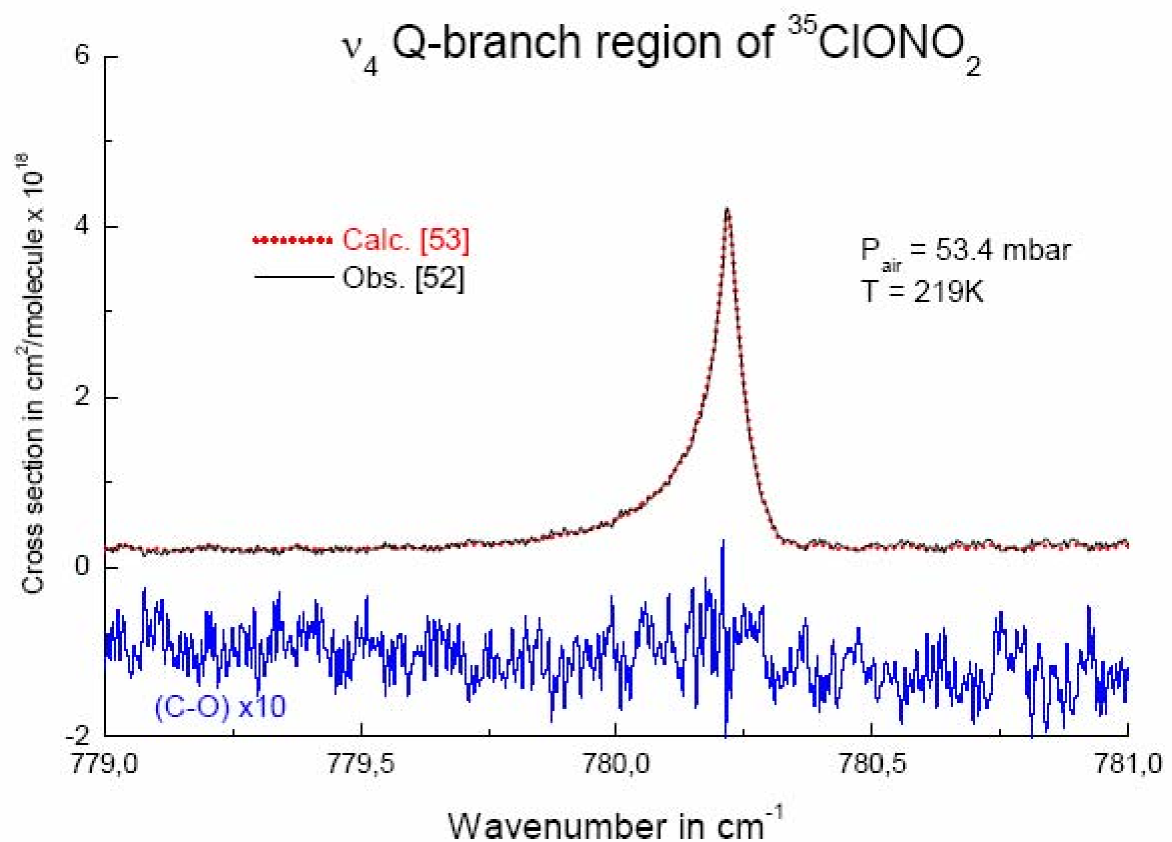
➡ The line intensities as well as an effective value of γ_{air} and an underlying pseudo continuum (unaccounted weak bands) have been determined.

➡ in the temperature range 190-300K, it was possible to reproduce accurately the **779-781 cm^{-1} spectral domain** of all the experiments.

Table 5. Total Partition Functions for $ClONO_2$[a]

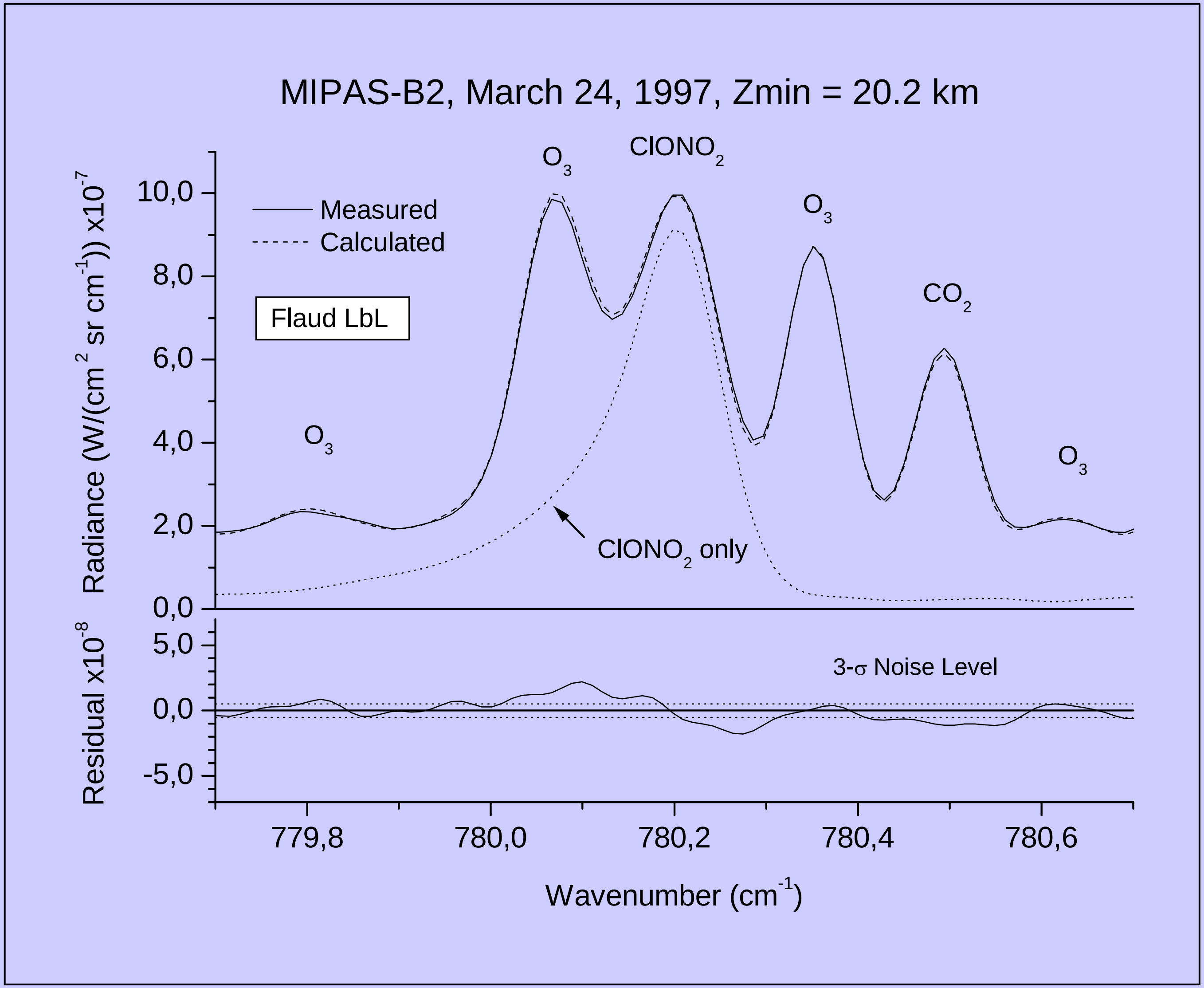
	^{35}Cl	^{37}Cl
A	116416.33241	119610.77305
B_1	−2262.52384	−2324.09554
B_2	19.38849	19.90779
B_3	−0.06369	−0.06539
B_4	1.18601×10^{-4}	1.21701×10^{-4}

[a]Where $Z(T) = A + B_1 T + B_2 T^2 + B_3 T^3 + B_4 T^4$.



ν4 Q-branch region of 35ClONO2
Calc. [53]
Obs. [52]
Pair = 53.4 mbar
T = 219K
(C-O) x10
Cross section in cm2/molecule x 1018
Wavenumber in cm-1
6
4
2
0
-2
779,0
779,5
780,0
780,5
781,0

Modeling of a MIPAS spectrum

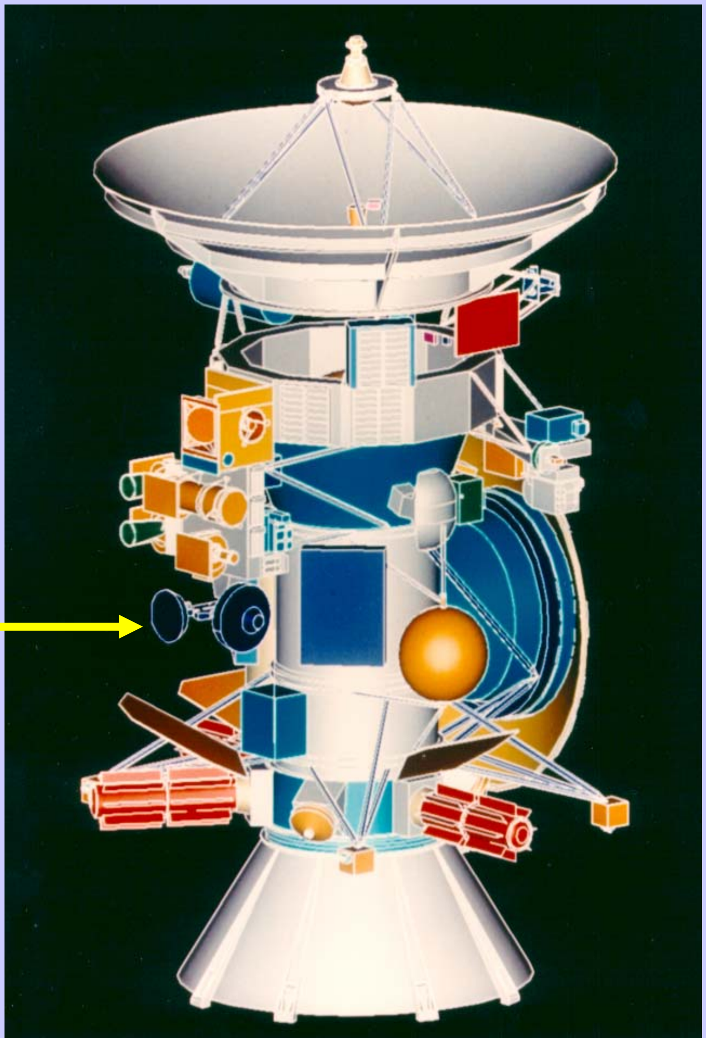


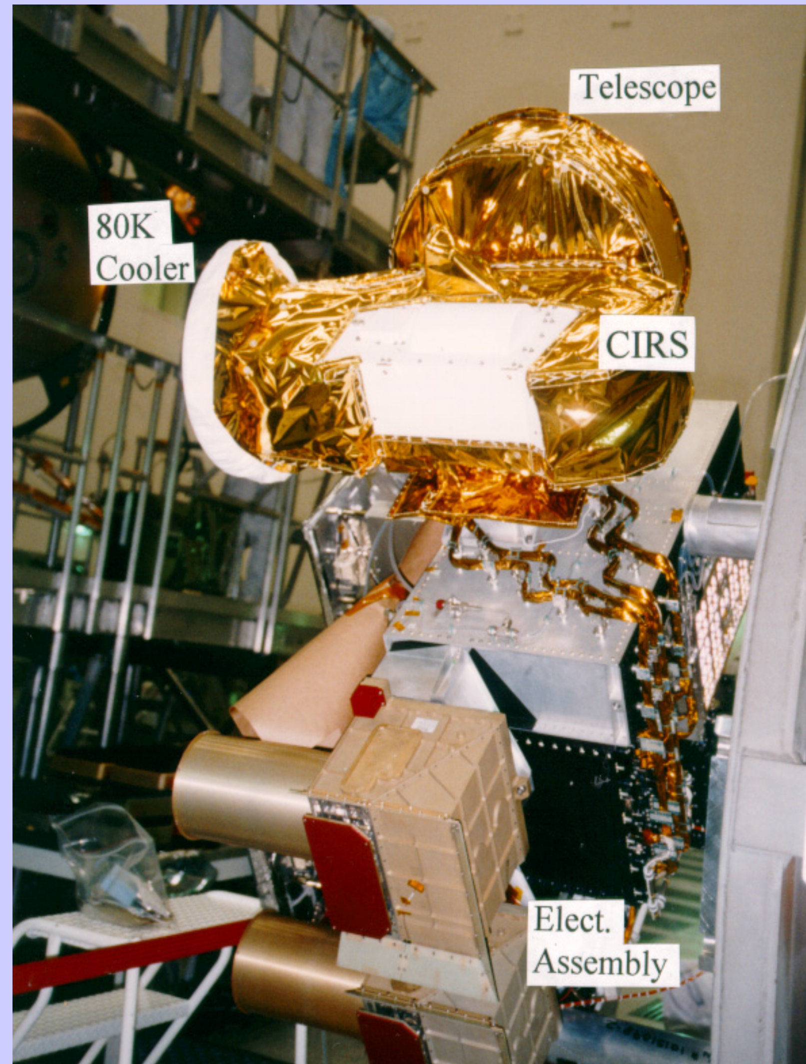
Titan’s Propane from Cassini CIRS Infrared Spectrosopy

C. A. Nixon, D. E. Jennings, J.-M. Flaud, B. Bézard,
N. A. Teanby, P. G. J. Irwin, T. M. Ansty, A. Coustenis,
F. M. Flasar, Cassini CIRS Science Team

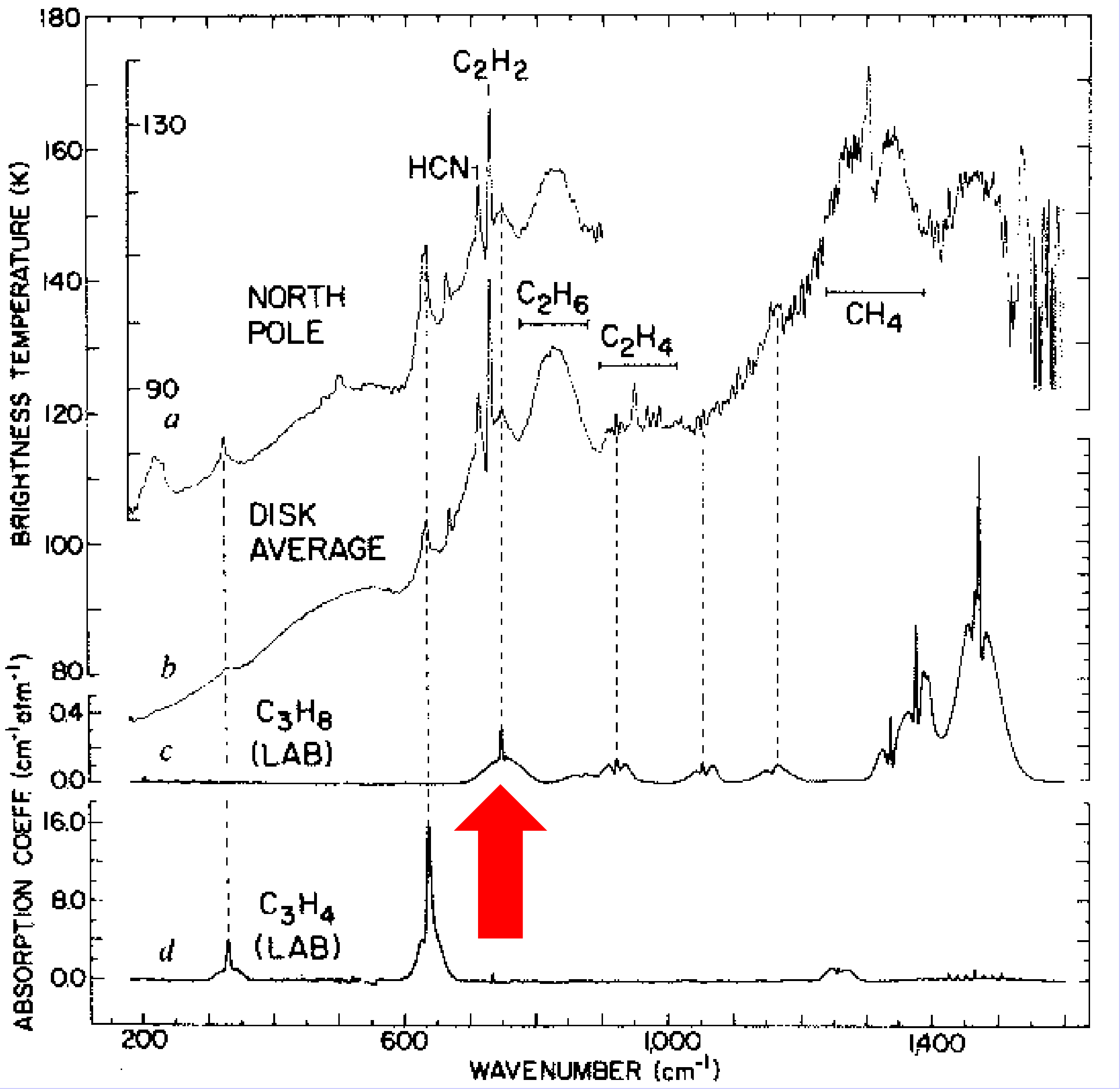
Cassini Composite Infrared Spectrometer (CIRS)

CIRS →



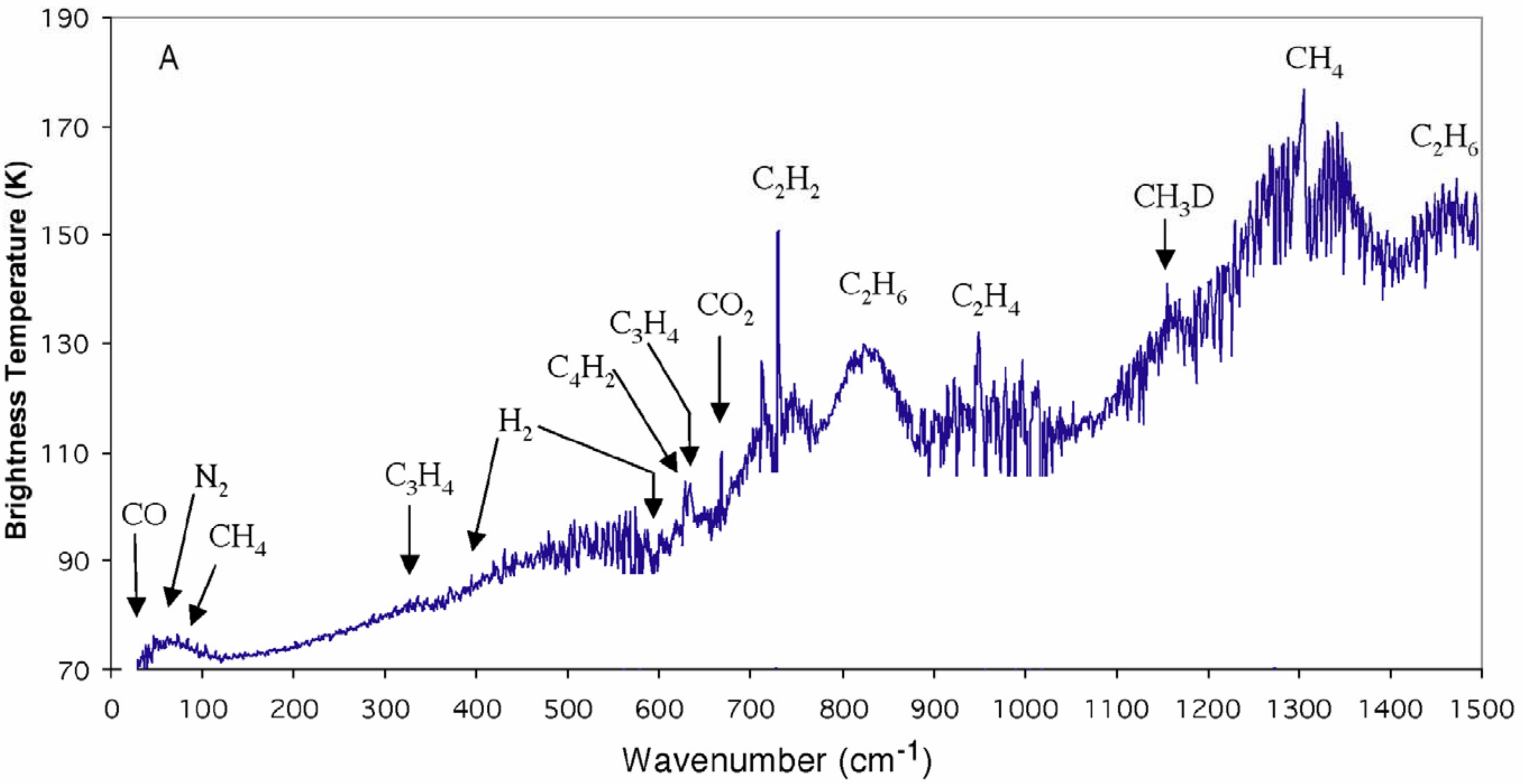


Propane - Historical Perspective



- First identification of C_3H_8 on Titan came from Voyager IRIS (Maguire *et al. Nature,1981)*
- Although multiple bands identified, the S/N was poor,
- Only the ν_{21} band at 721 cm^{-1} was ever used for VMR determination (papers by Coustenis et al.)

CIRS Titan Spectrum



Propane: spectroscopic data

- Propane has **27 IR** modes with low energy modes: v_{14} (216 cm^{-1}), v_{27} (268 cm^{-1}), v_9 (369cm^{-1})

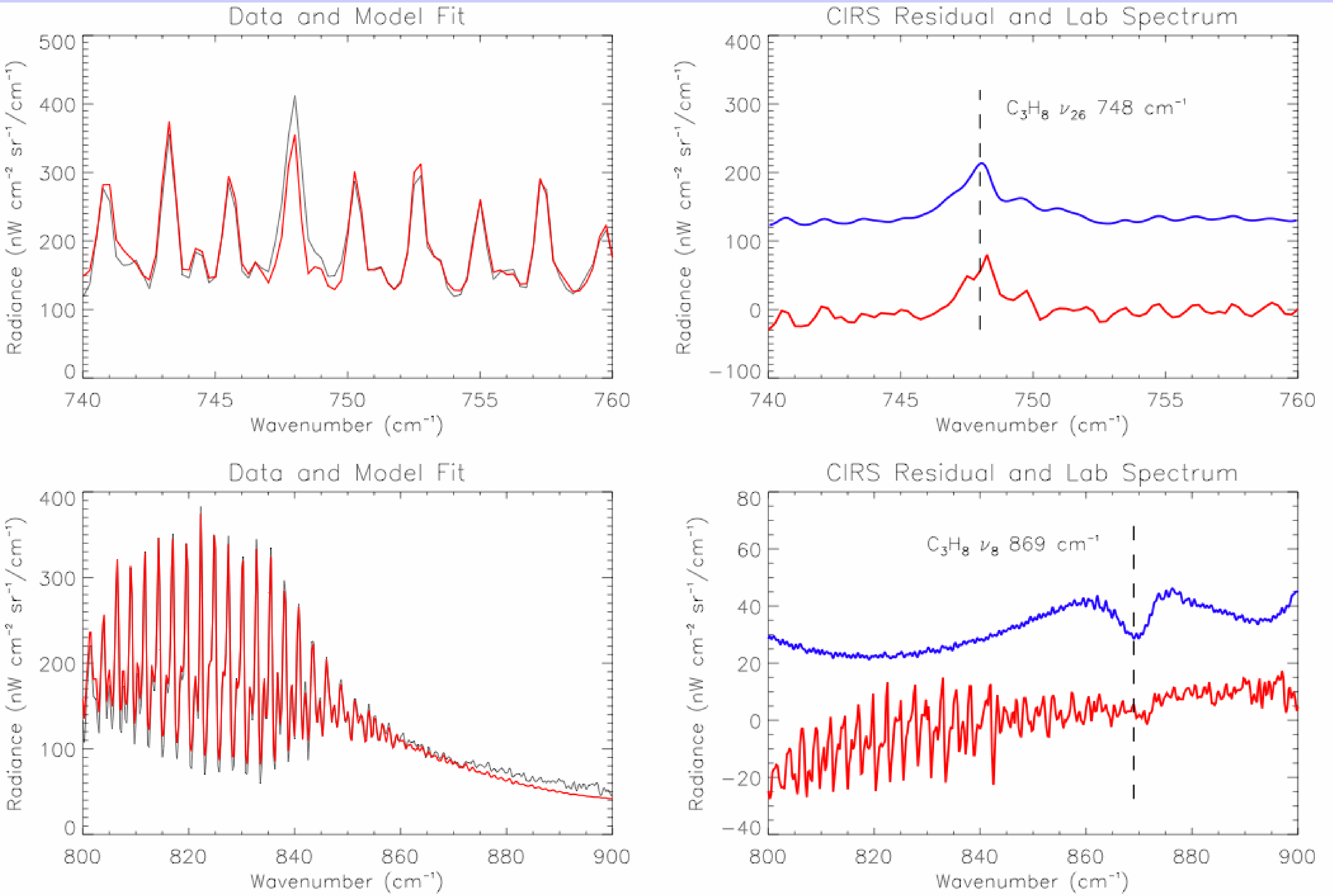
→ **lots of strong hot bands**

- **When starting the study**:

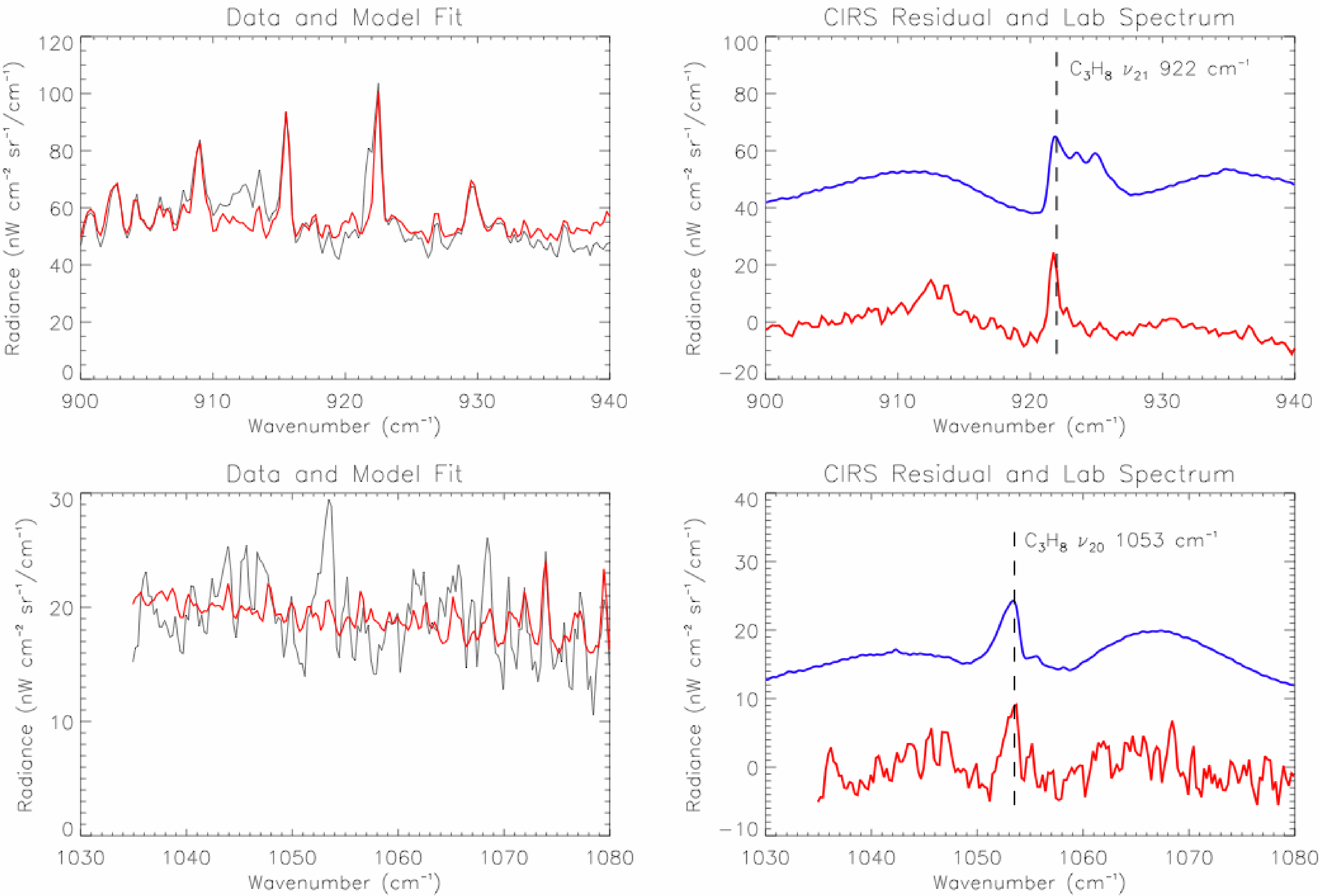
-line data only publicly available (GEISA 1992 and later) for the v_{26} mode at 748 cm^{-1}, based on unpublished measurements by S. Daunt.

- Medium resolution lab absorption spectra courtesy of S. Sharpe, PNNL recorded at room temperature

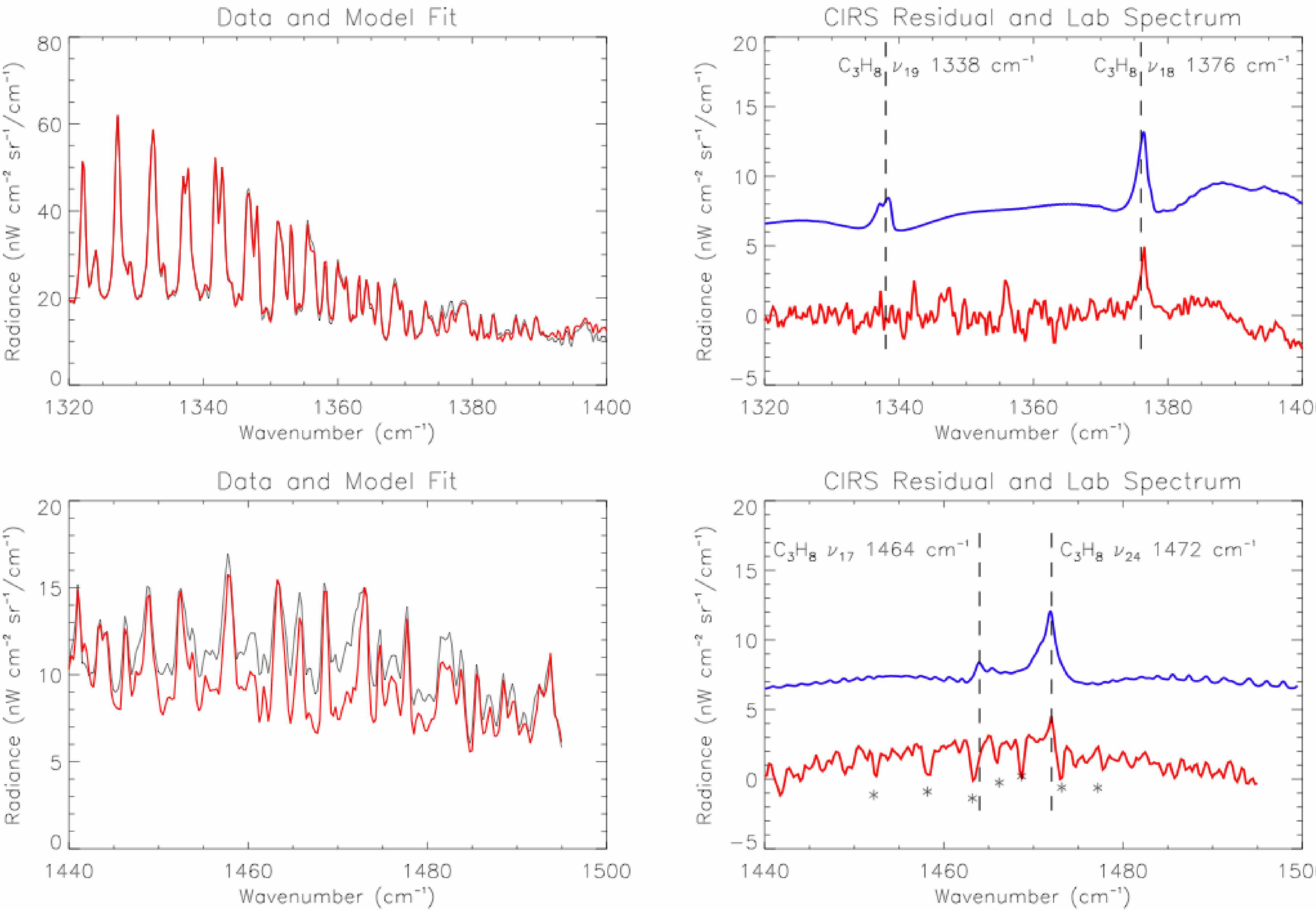
CIRS Propane Band Detections: 13-11 μm



CIRS Propane Band Detections: 11-9 μm



CIRS Propane Band Detections: 8-6 μm



Propane: spectroscopic data

We included in our study a new set of propane lines for several bands v_{19}(1338), v_{18} (1376),),{v_{24} ,v_4}(1472)in the region 1300-1500 cm^{-1}, as measured and modeled by Flaud et al. (2001).

We checked the fundamental mode v_{26} intensities in GEISA and found that they are about x 2.38 too high; probably because the band sum was scaled to lab spectra that includes hot bands

These enable an independent measurement of the Propane abundance from a different CIRS focal plane (FP4) to the v_{26} (FP3).

Central region of the C-type band ν_{24}

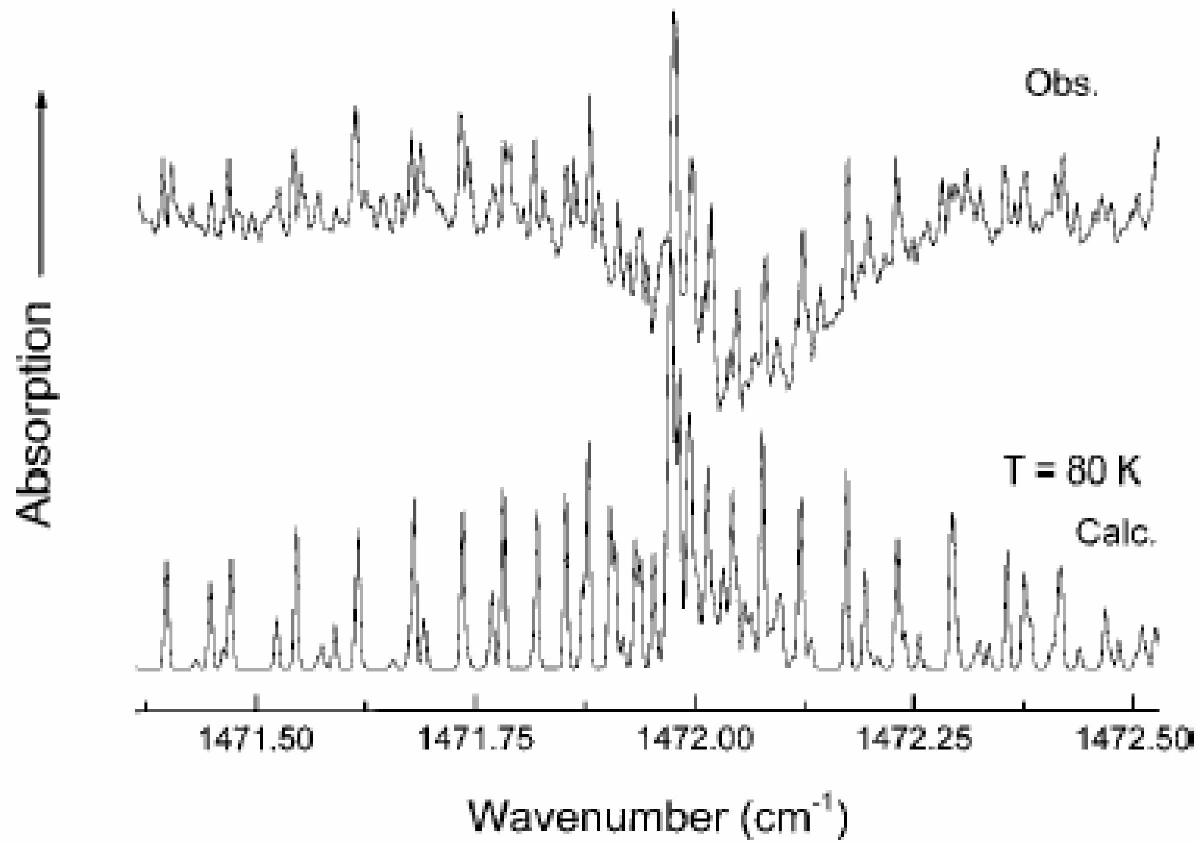


FIG. 6. Central region of the C-type jet-cooled ν_{24} band of propane. Because of the strong A-type Coriolis interaction with the levels of 4^1, the $^rQ_0$ and $^pQ_1$ lines of ν_{24} are highly perturbed.

Propane abundances on Titan

Region	Coustenis et al.(2007)	Vinatier et al.(2007)	This work
ν_{26}(748 cm^{-1})	5.0(1.0)	4.5(1.5)	4.4(0.2)
ν_{18}(1376 cm^{-1})			4.9(0.5)
ν_{24}(1472 cm^{-1})			**16.4(0.8)**

Propane – Summary

All four bands of propane tentatively identified by IRIS are now clearly seen by CIRS at much higher S/N.

In addition 3-4 further bands have now been detected.

Abundances retrieved here agree well with previous results for ν_{26}, and with new ν_{18} measurement.

ν_{24} measurement in very poor agreement: probably due to continuum fitting and/or aliasing.

Propane – Next Steps

Need further theoretical work and lab spectroscopy to understand, measure line positions and intensities for remaining bands:

- v_8 – 860 cm^{-1}
- v_{21} – 922 cm^{-1}
- v_{20} – 1054 cm^{-1}
- v_7 – 1157 cm^{-1}

- v_{26} also needs to be re-measured due to missing hotbands, and remodeled.

GENERAL CONCLUSIONS

HARD LABORATORY WORK IS REQUIRED TO MEET THE NEEDS OF ATMOSPHERIC RETRIEVALS.!!!

A NUMBER OF SPECTROSCOPIC STUDIES ARE STILL NEEDED IN ORDER TO MEET THE NEEDS OF MEASUREMENTS IN THE ATMOSPHERES:
Earth, planets, stars

→ **BE A FAN AND SUPPORT LAB SPECTROSCOPY**