Relief is on the Way: Status of the Line Positions and Intensities for Nitric Acid

<u>Agnés Perrin</u>, J.M.Flaud, J.Orphal

<u>L</u>aboratoire <u>I</u>nteruniversitaire des <u>S</u>ystémes <u>A</u>tmosphériques (LISA), CNRS, Université Paris XII, Créteil

Perrin@lisa.univ-paris12.fr

F. Mencaraglia, G. Bianchini, A. Boscaleri, B. Carli, Ceccherini, P. Raspollini,

Istituto di Fisica Applicata Carrara, Via Panciatichi 64 - 50127 Firenze - Italy

G. Brizzi, M. Carlotti, and M. Ridolfi

Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, Viale del Risorgimento, 4 – 40136 Bologna, Italia

Thank you very much for the committee (and to Larry Rothman) for giving me the opportunity to present this talk which I want to dedicate….

…. to the memory of Chuck Chackerian….

Outlines

- Status of HNO_3 in HITRAN
- Improved parameters for HNO_3 in the MIPAS spectral range (700-2400cm^{-1})
- Validation of the HNO_3 atmospheric (MIPAS measurements (@11µm) ⇔ IBEX (Infrared Balloon EXperiment) in the far infrared).
- First observation of $H^{15}NO_3$ in MIPAS spectra

Intensities in $10^{-17}cm^{-1}$/(molecule.cm-2)

2.8 µm (~3551cm^{-1})	ν_1 band	NOT INCLUDED	Int≈1.2
5.9 µm (1710cm^{-1})	ν_2 band		Int≈5.6
7.5µm (1303, 1326cm^{-1})	ν_4 , ν_3 bands		Int≈5.0
8.3 µm (1205 cm^{-1})	ν_8+ν_9 band		Int≈0.1
11 µm (879, 896cm^{-1})	ν_5 , 2ν_9 bands + H.B.		Int≈2.4
13.1µm (763cm^{-1})	ν_8	**(not updated)**	Int ≈ 0.1
15.5µm (647cm^{-1})	ν_6		Int ≈ 0.1
17.2µm: (580cm^{-1})	ν_7		Int ≈ 0.1
22 µm (458cm^{-1})	ν_9 band + H.B.		Int≈1??
MW to far infrared: (rotation in v=0 + H.B.)			Int ≈ 0.06

H.B.: Hot bands

The pure rotation band

HITRAN-04: was updated using the 2004- version of the JPL catalog

For the v=0 ⇔ v=0 (ground ⇔ ground) only

In HITRAN-04 all the « hot bands » are missing (as compared to JPL)
(Total contribution of the hot bands ≈13% @ 296K)

Intensities were incorrect for atmospheric uses in JPL-04 & therefore in HITRAN-04

This problem in now fixed in the JPL catalog (Brian Drouin)

JPL catalog in 2004 : status of the intensities (@300K)

$$\mathrm{Int}(300K)_{JPL} = \frac{8\pi^3\sigma}{3hc4\pi\varepsilon_0}\left(e^{-E''/kT} - e^{-E'/kT}\right) 1/Z_{JPL}(T) |\langle\phi'|\mu_0|\phi''\rangle|^2$$

Z_{JPL} ⇔ **rotation** partition function

$Z_{Vib}(T=300K) \approx 1.30$ ... unted for

$\neq Z_{Tot}(T)$ ...

This problem in now fixed in the JPL catalog (Brian Drouin)

$$\mathrm{Int}(T)_{JPL} = \mathrm{Int}_{TRUE}(T) * Z_{Vib}(T=300K)$$

Intensities overestimated of 30%

Picket, Poynter, Cohen, Delisky, Pearson & Müller, JQSRT:60, 1998

HITRAN

Sigma	Int	v'	v''	J'	Ka'	Kc'	J"	Ka"	Kc"
3.00218400	**0.108E-23**	Gr	Gr	21	20	2	21	19	3
3.00258200	**0.325E-25**	Gr	Gr	6	4	3	5	5	0
3.00344000	**0.137E-23**	Gr	Gr	23	21	2	23	20	3
3.00564100	**0.165E-23**	Gr	Gr	29	23	7	29	22	8
3.00566600	**0.590E-24**	Gr	Gr	40	30	10	40	29	11
3.00206715	0.711E-24	V9	V9	19	13	7	19	11	8
3.00207102	0.159E-25	V5	V5	27	23	4	27	22	5
3.00214123	0.438E-25	V6	V6	30	25	5	30	24	6
3.00218310	**0.832E-24**	Gr	Gr	21	20	2	21	19	3
3.00223280	0.956E-25	V5	V5	19	12	7	19	12	8
3.00258254	**0.250E-25**	Gr	Gr	6	4	3	5	5	0
3.00300660	0.540E-25	V6	V6	28	23	6	28	22	7
3.00343830	**0.105E-23**	Gr	Gr	23	21	2	23	20	3
3.00423271	0.238E-25	V5	V5	19	12	7	19	11	8
3.00426177	0.328E-24	V9	V9	24	19	6	24	17	7
3.00466625	0.166E-24	V8	V8	18	11	7	18	11	8
3.00471698	0.261E-25	V6	V6	14	13	2	14	11	3
3.00507343	0.105E-24	V9	V9	33	24	9	33	23	10
3.00529572	0.477E-25	V8	V8	18	11	7	18	10	8
3.00564046	**0.127E-23**	Gr	Gr	29	23	7	29	22	8

#Molecular line parameters for the MASTER database" , Perrin, Puzzarini, Colmont, Verdes, Wlodarczak, Cazzoli, Buehler, Flaud, and Demaison (*J. of Atmospheric Chemistry, 2004)*

Status in HITRAN

5.9 µm (1710cm^{-1}) ν_2 band	Int≈5.6
7.5µm (1303, 1326cm^{-1}) ν_4 , ν_3 bands	Int≈5.0
8.3 µm (1205 cm^{-1}) $\nu_8+\nu_9$ band	Int≈0.1
11 µm (879, 896cm^{-1}) ν_5 , $2\nu_9$ bands + H.B.	Int≈2.4

Intensities in
10^{-17}cm^{-1}/ (molecule.cm^{-2})

22 µm (458cm^{-1}) ν_9 band + H.B.	Int≈1??
MW to far infrared: (rotation in v=0 + H.B.)	Int ≈ 0.06

H.B.: Hot bands

The 22 μm region

- ν_9 cold band: not updated
- ν_5-ν_9 & $2\nu_9$-ν_9 hot bands (updated recently using Petkie et al. (2003))

Two problems for the 22 µm region:

-**Absolute intensities:** it is necessary to compare HNO_3 measurements in the **22μm** (balloon-borne FIRS-2 instrument, **Ken Jucks** of the Harvard-Smithsonian Center for Astrophysics and and **11μm** regions [(2)]

-**Update of the ν_5-ν_9 & $2\nu_9$-ν_9 hot bands** [(1)]
(need clarifications)

[(1)] **Petkie, Helminger,Winnewisser, Winnewisser, Butler Jucks & De Lucia . JQSRT (2003)**

Situation of the MIPAS-PF3.2 database

Michelson **I**nterferometer for **P**assive **A**tmospheric **S**ounding (on *ENVISAT* satellite)

MIPAS

5.9 µm (1710cm^{-1}) ν_2 band	Int≈5.6
7.5µm (1303, 1326cm^{-1}) ν_4 , ν_3 bands	Int≈5.0
8.3 µm (1205 cm^{-1}) $\nu_8+\nu_9$ band	Int≈0.1
11 µm (879, 896cm^{-1}) ν_5 , $2\nu_9$ bands + H.B.	Int≈2.4

22 µm (458cm^{-1}) ν_9 band + H.B.	Int≈1??
MW to far infrared: (rotation in v=0 + H.B.)	Int ≈ 0.06

H.B.: Hot bands

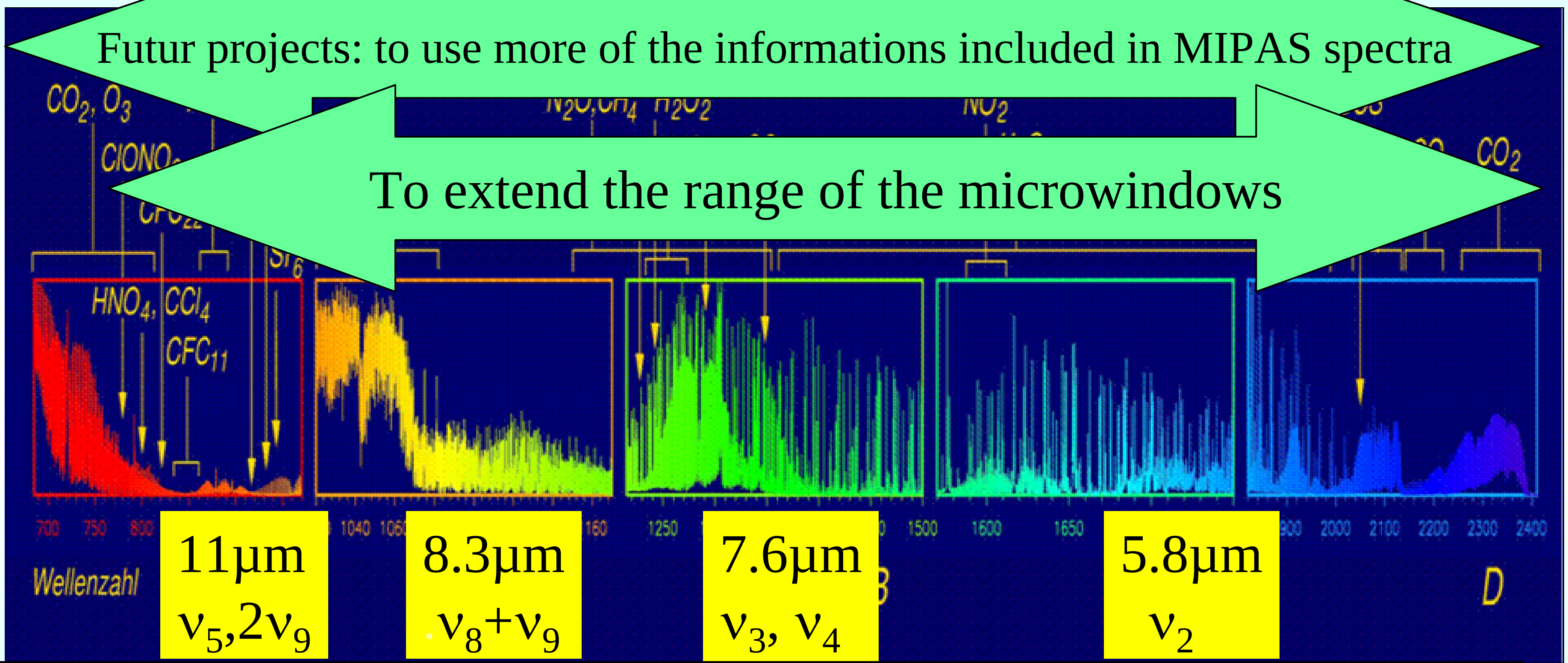
Intensities in 10^{-17}cm^{-1}/(molecule.cm-2)

MIPAS is an high resolution IR FTS spectrometer onboard the *ENVISAT* satellite since march 2002

6km)

Futur projects: to use more of the informations included in MIPAS spectra

To extend the range of the microwindows



—>MIPAS dedicated Database

***J-M.Flaud, C.Piccolo, B.Carli, A.Perrin, L.Coudert, J.L.Teffo, L.Brown, J. of Atmos. Ocean and Optics*, 16, 172-182 (2003).**

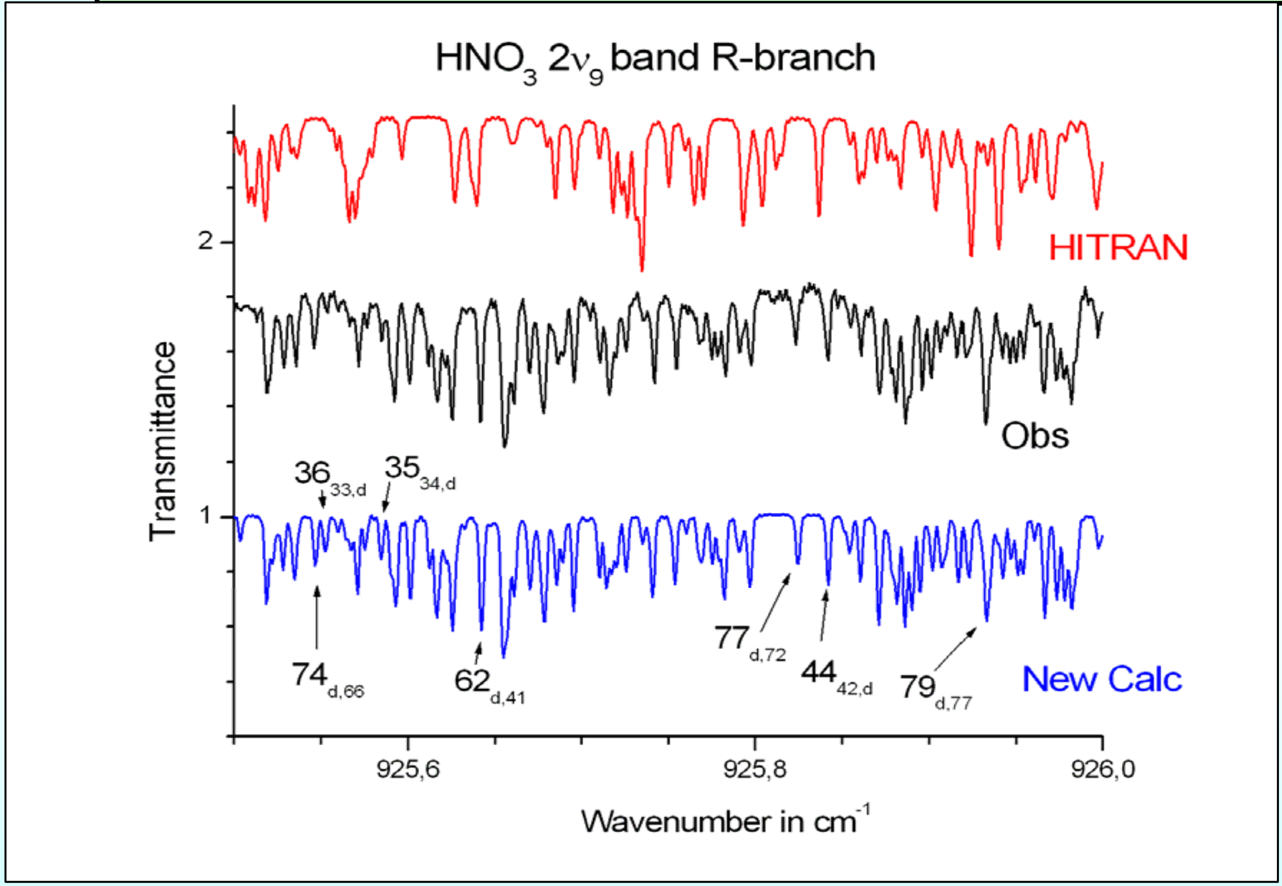
For the **MIPAS-PF3.2** database

5.9 µm (1710cm^{-1}) ν_2 band	**Int≈4**
7.5µm (1303, 1326cm^{-1}) ν_4 , ν_3 bands	**Int≈4**
8.3 µm (1205 cm^{-1}) $\nu_8+\nu_9$ band	Int≈0.1
11 µm (879, 896cm^{-1}) ν5 , 2ν_9 bands + H.B.	**Int≈2**

- Improved line positions (11µm & 8.3µm)
- Improved line intensities (all), (but no change for ν_2)
- Improved line air-broadening parameters (all)

Improved line positions

11µm (improved) Cold ν_5, $2\nu_9$;   Hot $\nu_5+\nu_9-\nu_5$



#Perrin, Flaud, Keller, Goldman, Blatherwick, Murcray, & Rinsland, J. Mol. Spectr 194 (1999) 113.
Perrin, Orphal, Flaud, Klee, Mellau, Mäder, Walbrodt, Winnewisser, J. Mol. Spect. 228 (2004) 375
Flaud, Piccolo, Carli, Perrin, Coudert, Teffo & Brown ,J. Atmospheric and Ocean Optics, 16 (2003), 172.
Flaud, Perrin, Orphal, Kou, Durkiewick & Piccolo, J.Q.S.R.T. 77 (2003) 355.
Flaud, Brizzi, Carlotti, Perrin, Ridolfi, Atmos. Chem. Phys. Discuss, 6 (2006) 4251

Improved line positions

11µm (improved)

Cold ν_5, $2\nu_9$;   Hot $\nu_5+\nu_9-\nu_5$

8.3µm (weak)

$\nu_8+\nu_9$ ⇒(improved) {$\nu_8+\nu_9$, $\nu_6+\nu_7$} (interactions accounted for [#])

No change (line positions)

7.6µm {ν_3,ν_4}   (strong) need to be improved !!!!!

5.8 µm ν_2 (strong) ?? need to be improved ????

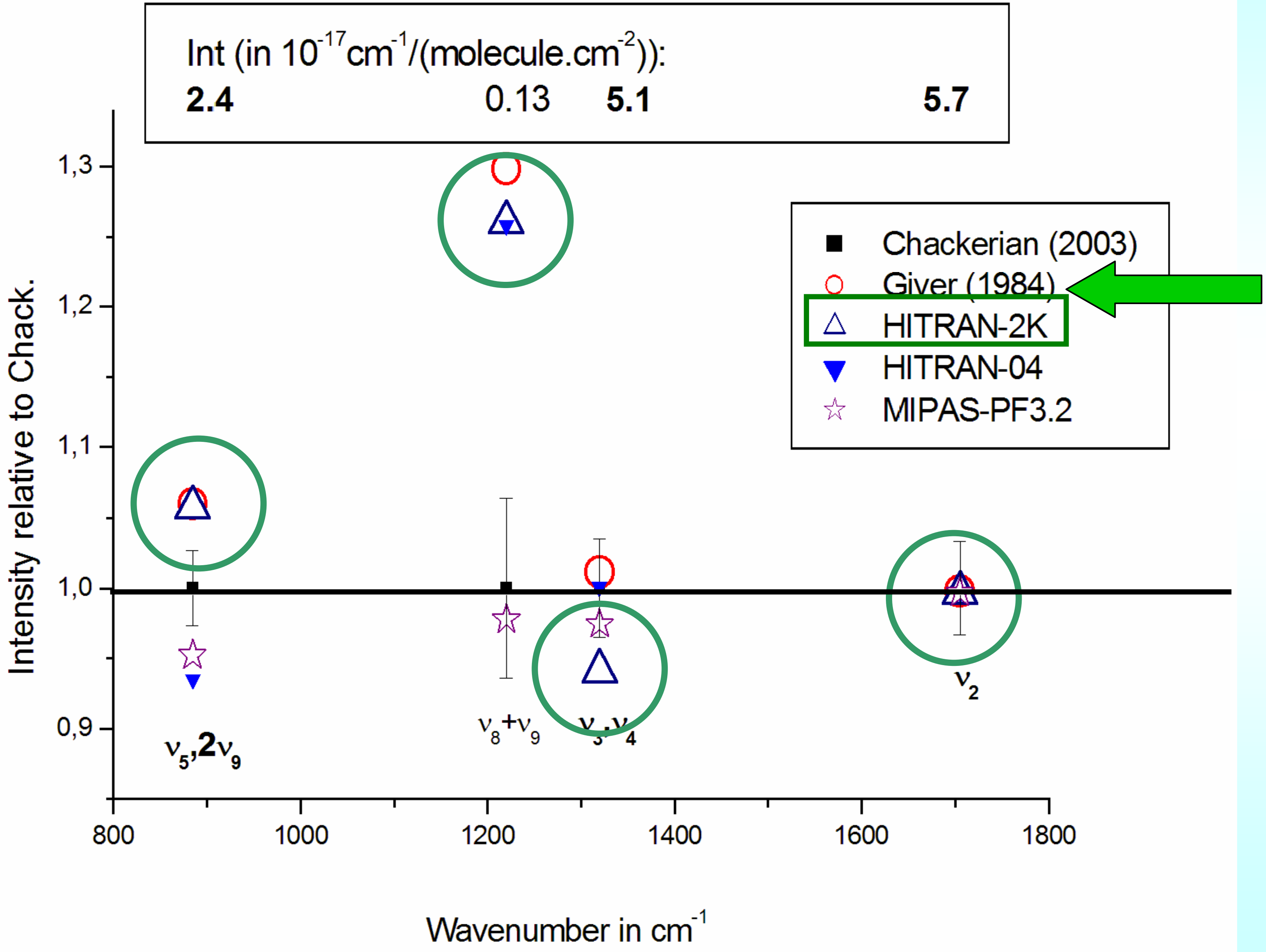
#Perrin, Flaud, Keller, Goldman, Blatherwick, Murcray, & Rinsland, J. Mol. Spectr 194 (1999) 113.
Perrin, Orphal, Flaud, Klee, Mellau, Mäder, Walbrodt, Winnewisser, J. Mol. Spect. 228 (2004) 375
Flaud, Piccolo, Carli, Perrin, Coudert, Teffo & Brown ,J. Atmospheric and Ocean Optics, 16 (2003), 172.
Flaud, Perrin, Orphal, Kou, Durkiewick & Piccolo, J.Q.S.R.T. 77 (2003) 355.
Flaud, Brizzi, Carlotti, Perrin, Ridolfi, Atmos. Chem. Phys. Discuss, 6 (2006) 4251

Improved line intensities for the 700-2400cm^{-1}

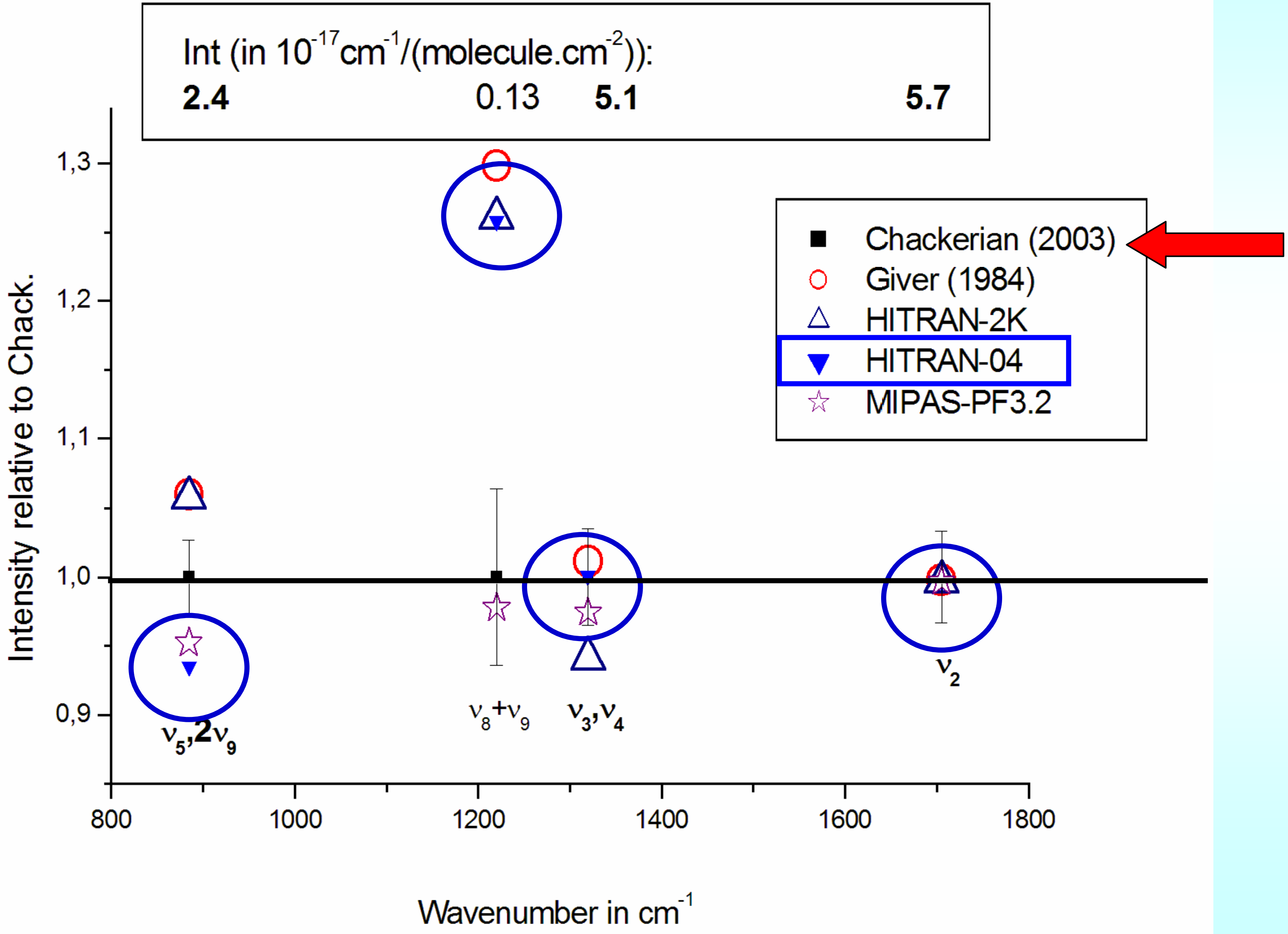
June 2006

Agnes Perrin HITRAN

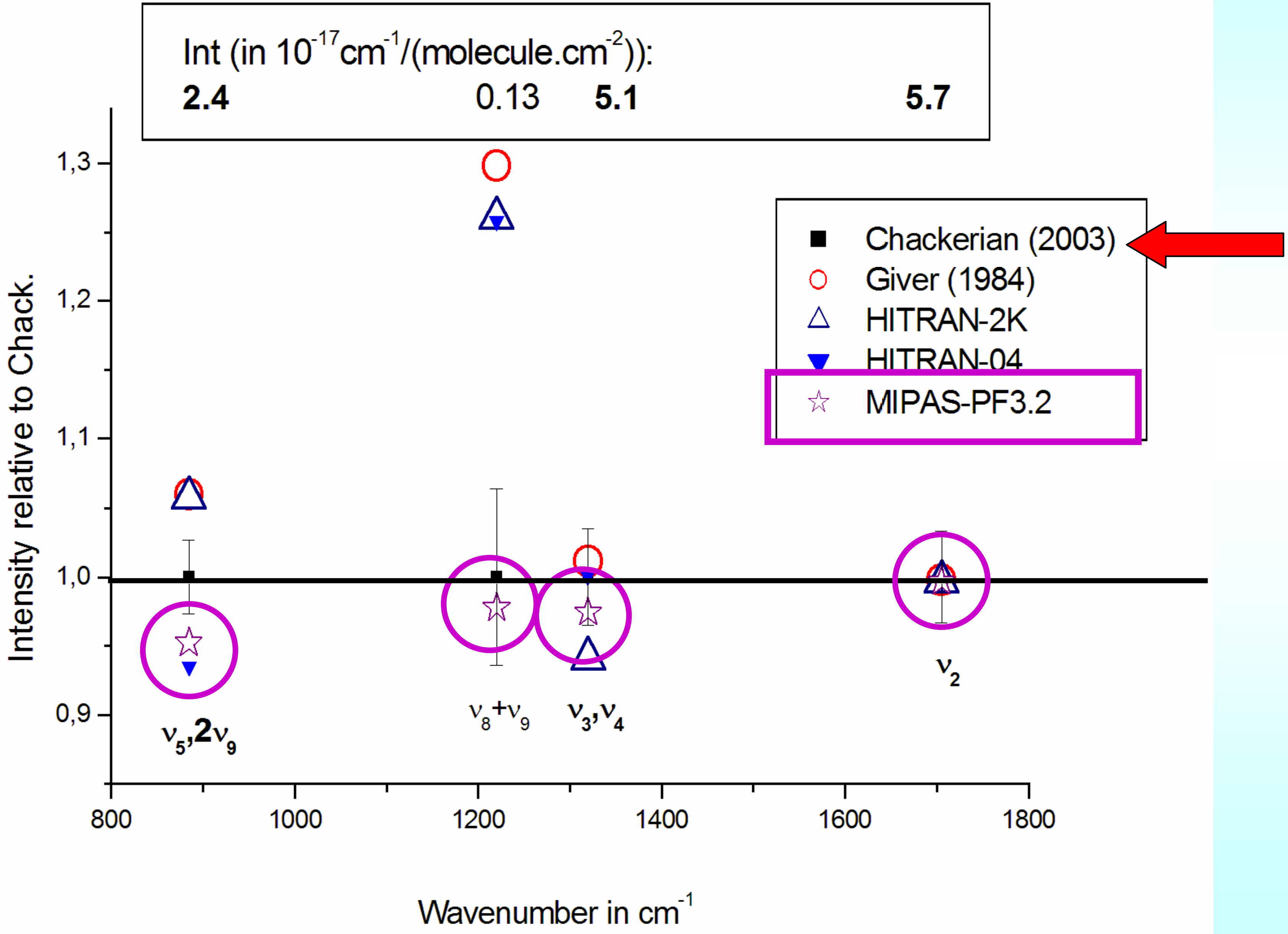
Improved HNO_3 line intensities



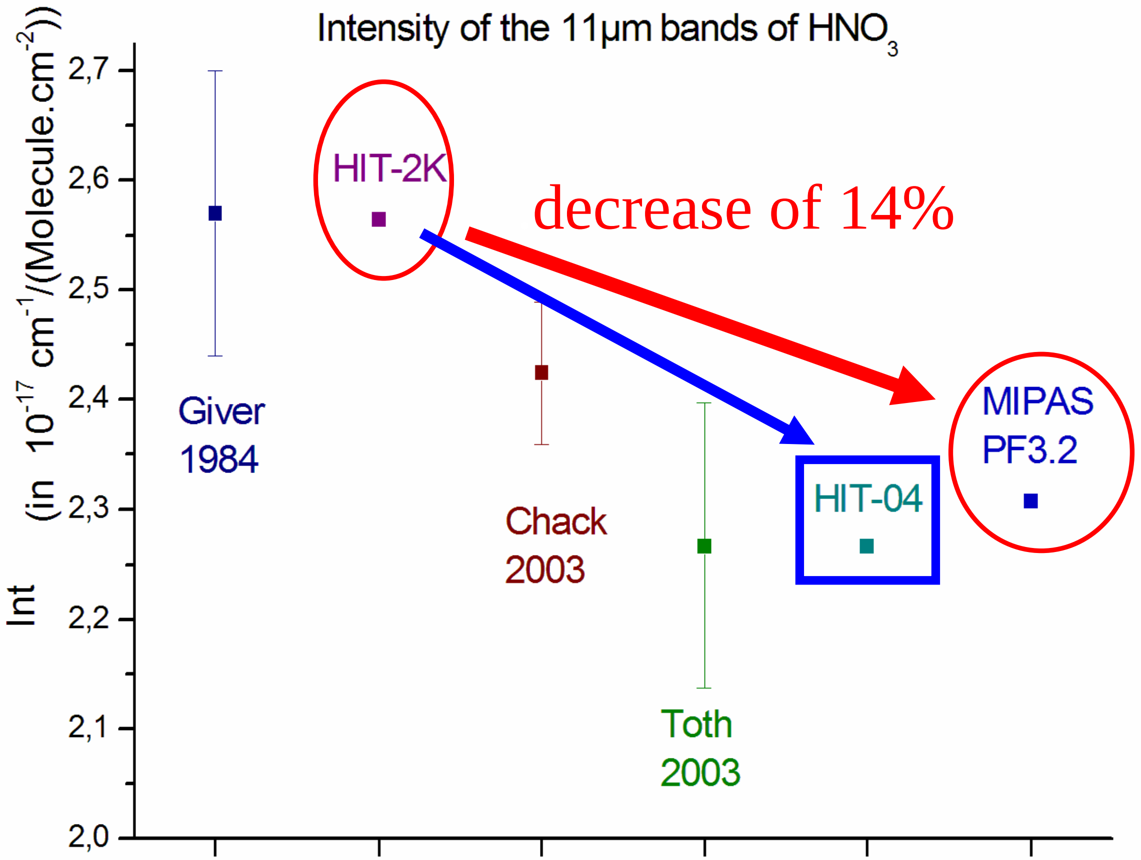
Improved HNO_3 line intensities



Improved HNO_3 line intensities



Intensities for the 11 µm bands



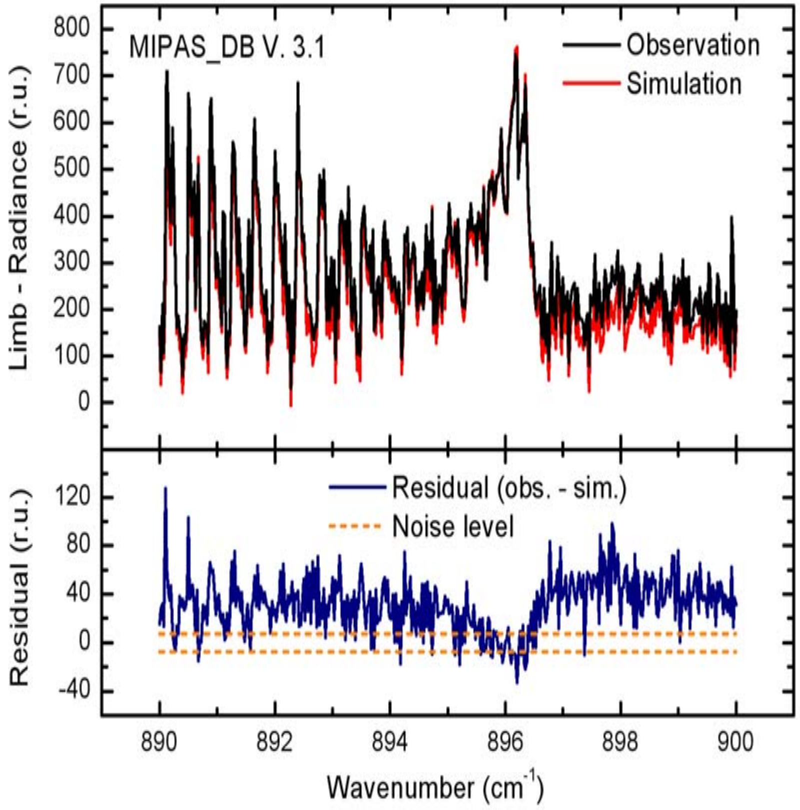
Giver et al. J. Opt. Soc. Am. **B1**, 715 (1984)
Chackerian, Sharpe & Blake, JQSRT **82**, 429 (2003)
Toth, Brown & Cohen J.Mol. Spectr **218**, 151 (2003)
HIT-2K & HIT-04: Rothman et al. JQSRT **82**, 5 (2003), **96**, 139 (2005)
MIPAS: Flaud et al. Atmos Oceanic Opt. **16**, 172 (2003)

First validations…

Comparison of observed and simulated MIPAS spectra in band A

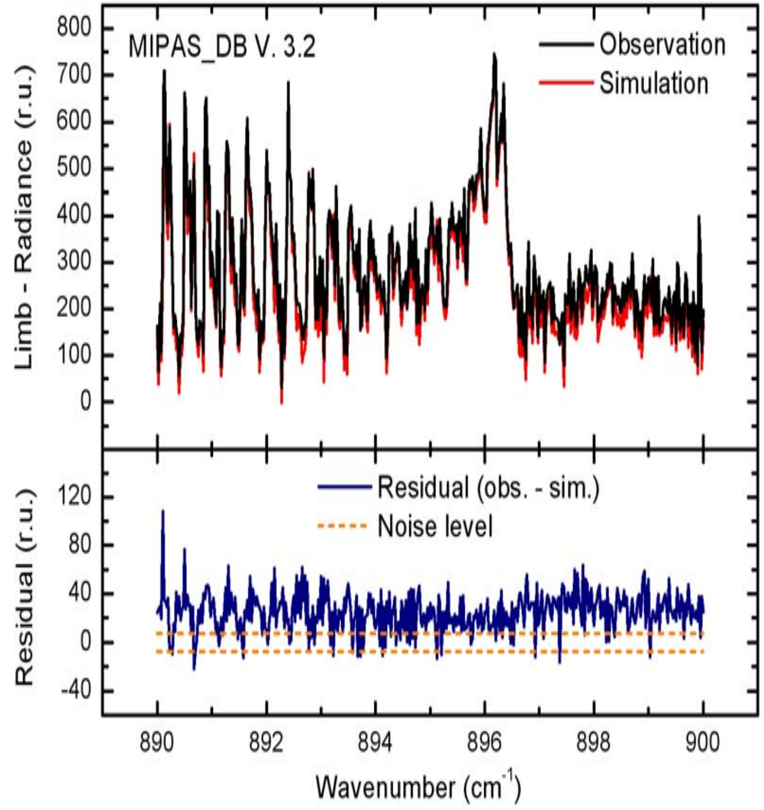
for an altitude of 24km

$2\nu_9$ Q branch



Old database

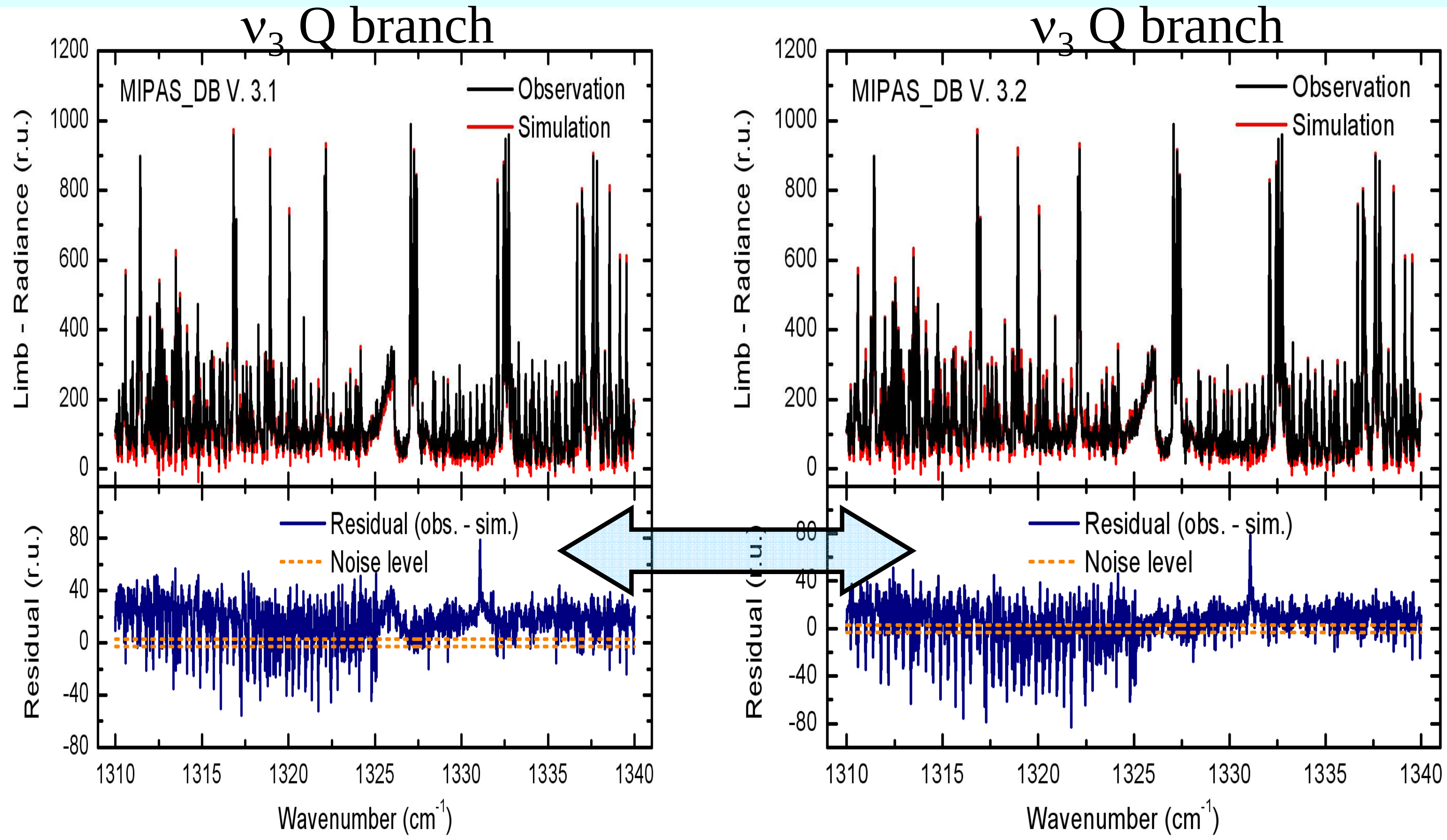
$2\nu_9$ Q branch



New database

Status of the ν_3 & ν_4 bands (7.5µm)

…still unsatisfactory !!!!!!!!!



Improved line broadening parameters for HNO_3

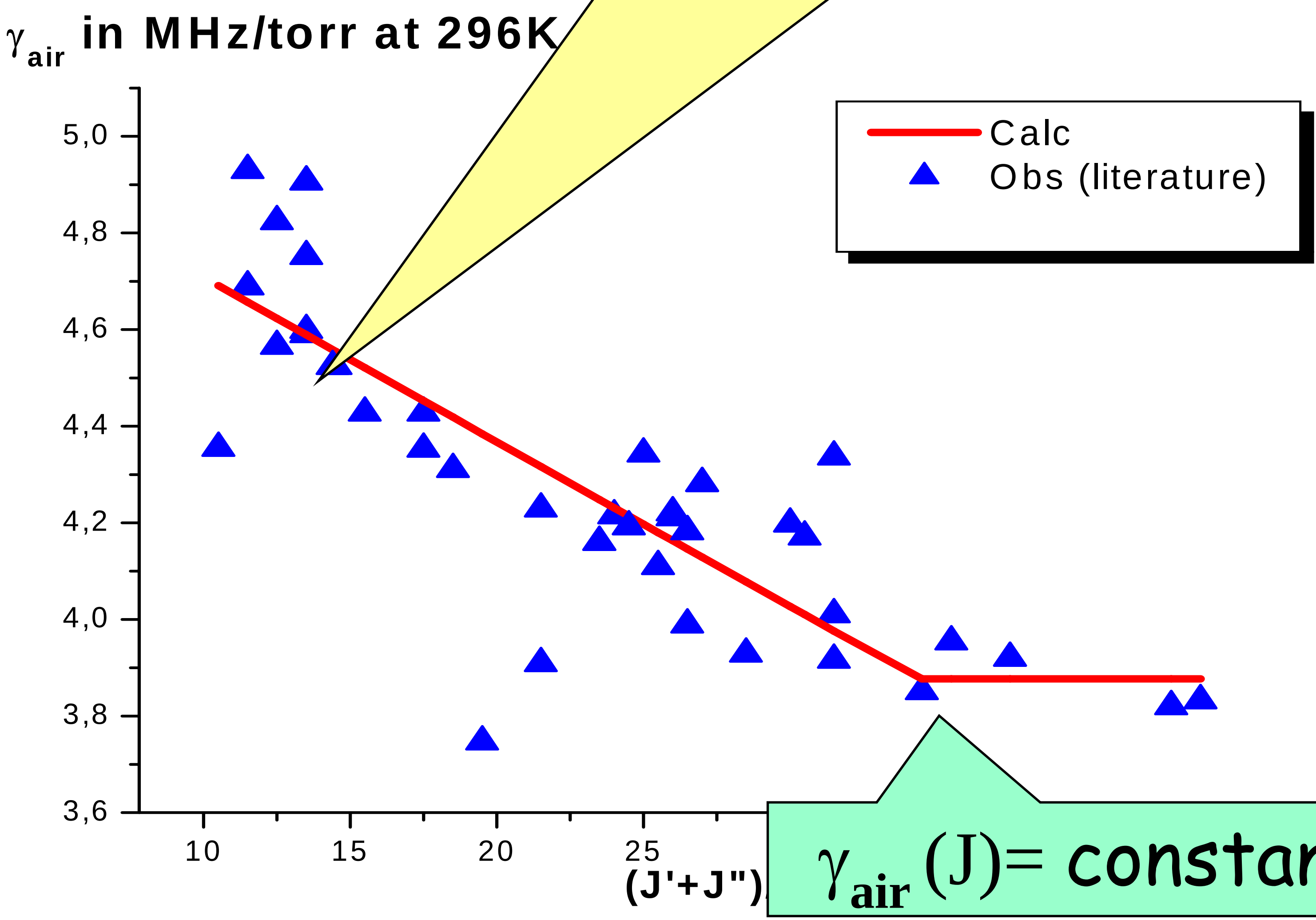
- Numerous excellent line broadening measurements were performed mainly in the millimeter wave spectral range
- Strong rotational dependence of the broadenings
- Sometime, the n- temperature dependance of the γ was also measured.

Goyette T.M., W.L.Ebenstein, F.C. De Lucia and P.Helminger, J. Mol. Spectrosc. 128, (1988) 108.
Goyette T.M., W.Guo, F.C. De Lucia and P.Helminger, J.Q.S.R.T. 46, (1991) 293.
Goyette T.M., E.A.Cohen, and F.De Lucia, J.Q.S.R.T. 60, (1998) 377.
Zu L., P.A.Hamilton and P.B.Davies, J.Q.S.R.T. 73, (2002) 545.
Colmont, Bakri, Rohart, Wlodarczak, J. Mol. Spectr. 220 (2003) 52.

Cazzoli, Dore, Puzzarini, Bakri, Colmont, Rohart and Wlodarczak J. Mol. Spect 229 (2005) 158.

Model for HNO_3 line broadening

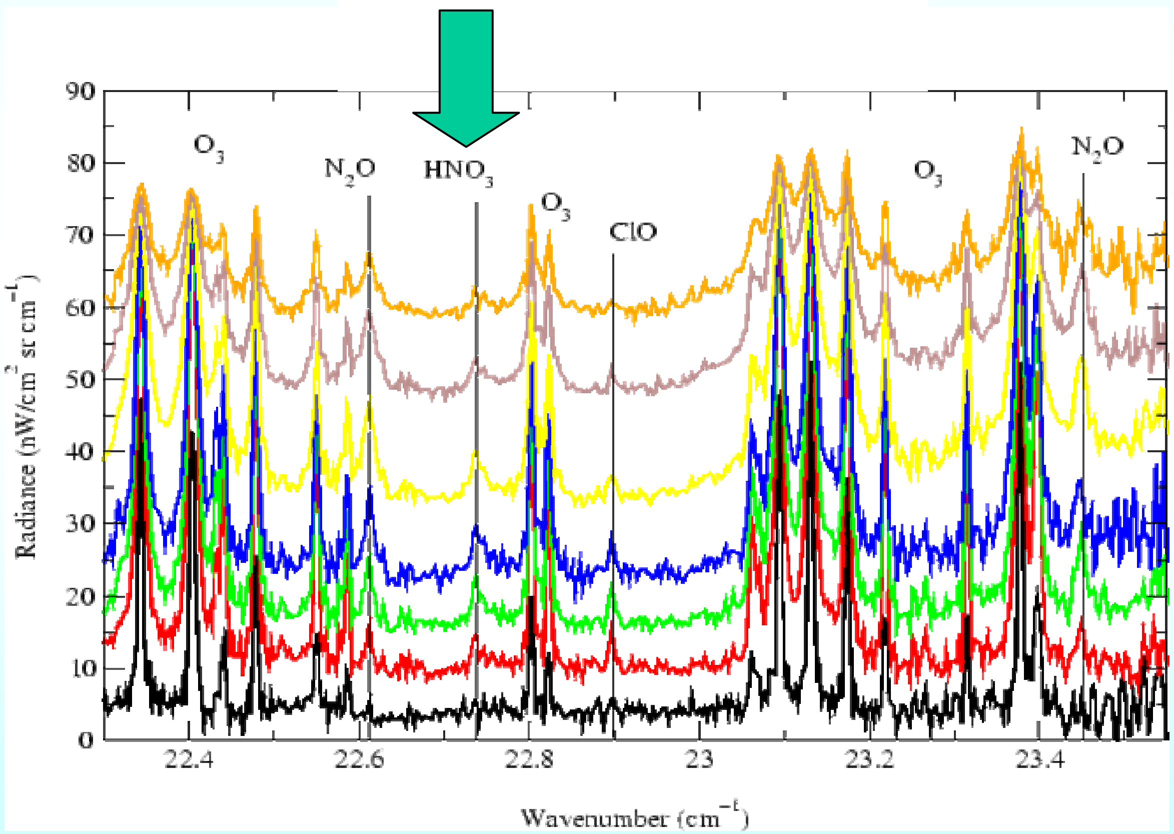
$$\gamma_{air}(J) = a_{air} + b_{air}.(J' + J'')$$



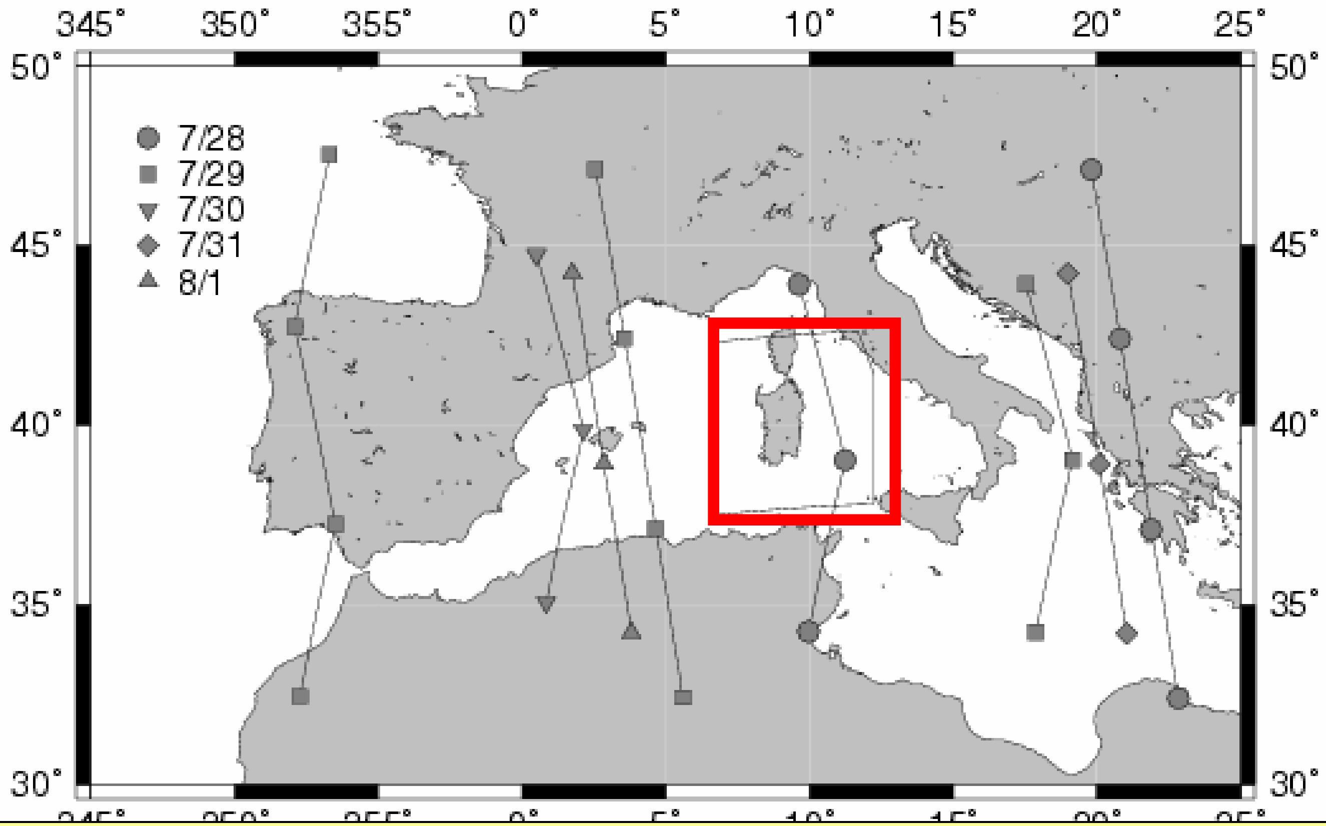
$$\gamma_{air}(J) = \text{constant}$$

There is need for a « correct » model for the broadening….

Validation of the HNO_3 atmospheric measurements: (MIPAS measurements (@11µm) ⇔ IBEX (Infrared Balloon EXperiment) in the far infrared



Comparison MIPAS ⇔ IBEX



Because of geographical and time dependence of the atmospheric composition ⇔ correlative measurements should done over the same air mass;

Exact "rendez-vous" satellite ⇔ balloon.

Preliminary intercomparison of HNO_3 profiles

MIPAS

FTS on ENVISAT
11μm ⇔ ≈900cm^{-1}

Line parameters
From HITRAN-2K

IBEX

FTS on a balloon
Far infrared ⇔ ≈ 20cm^{-1}

Parameters from
JPL catalog

Concentration profile of HNO_3

MIPAS ⇔ IBEX

These two profiles desagree….

…………., this may be due to a different geographical or time dependence of HNO_3……..

In our case this required an exact "rendez-vous" between two moving platforms: satellite and balloon.

….or to spectroscopic problems
in the 11μm… (or/and) in the far infrared

Final results

11 µm

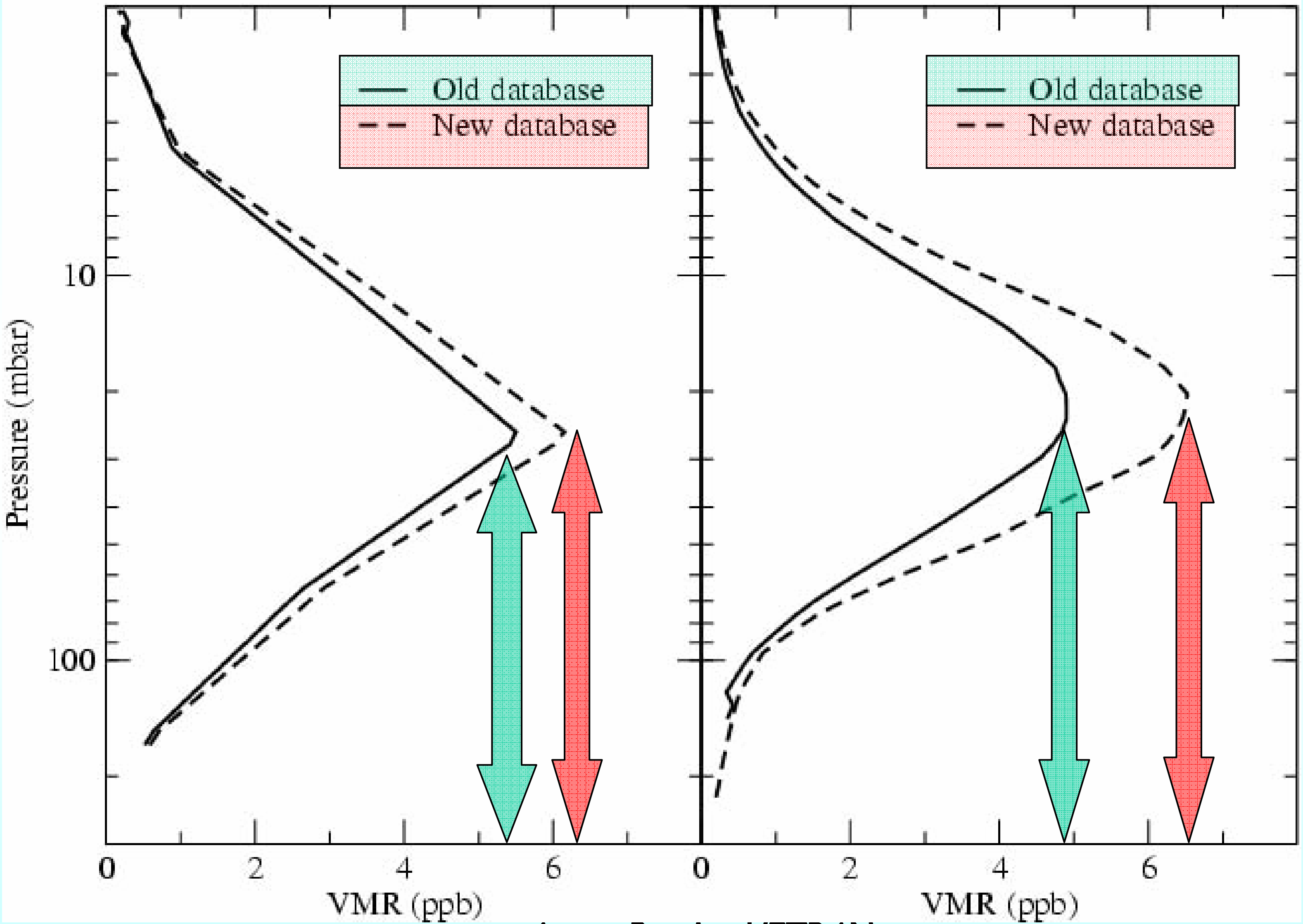
- ➢New line positions
- ➢Overall intensities were divided by ≈1.14

Far infrared (~22cm^{-1})

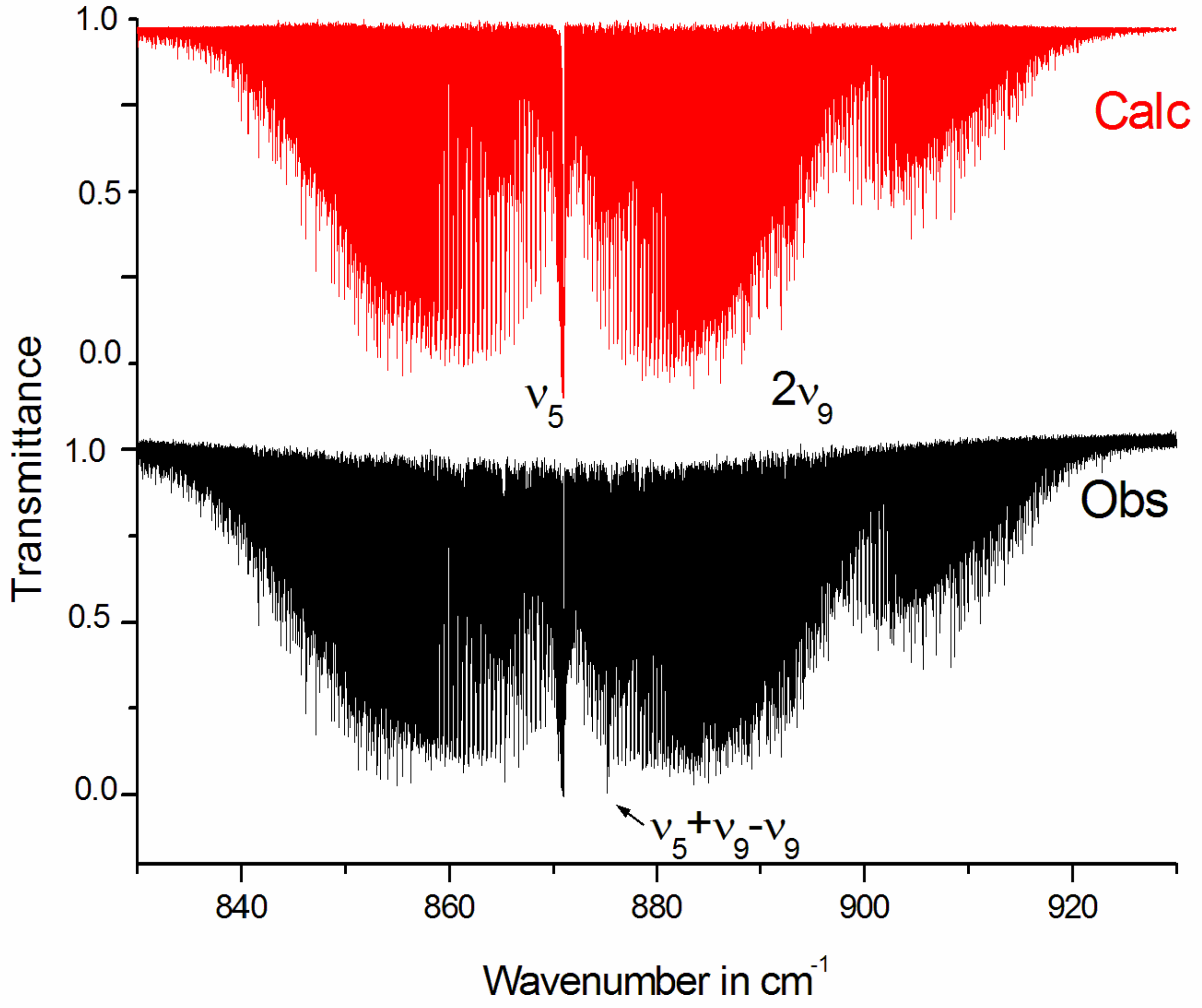
- ➢New line positions
- ➢Overall intensities were divided by≈1.30

MIPAS: 11µm

IBEX: Far IR

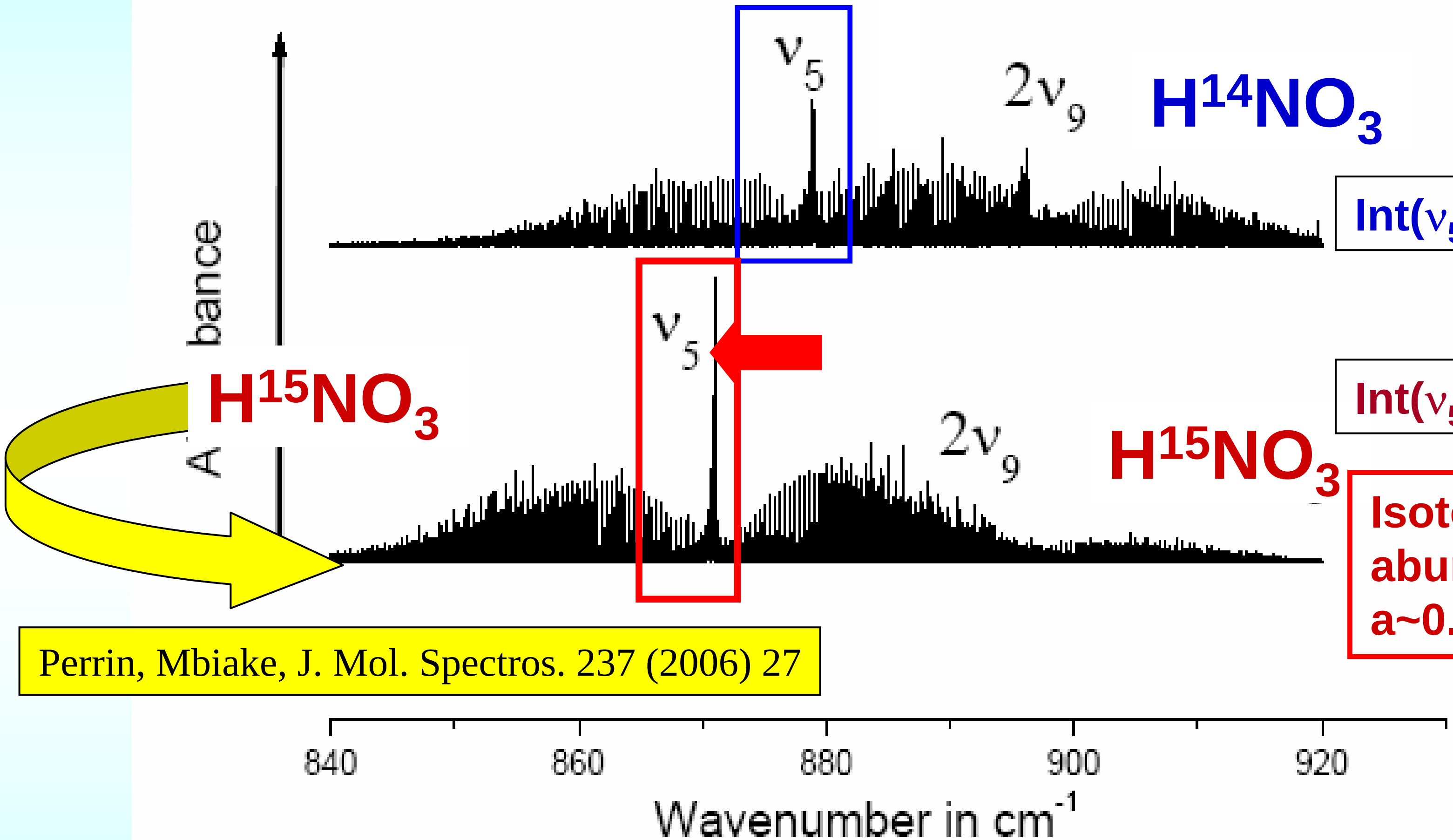


First observation of $H^{15}NO_3$ in MIPAS spectra



« The ν5 & 2ν9 interacting bands of $H^{15}NO_3$, » Perrin, Mbiake, J. Mol. Spectros. 237 (2006) 27

$H^{14}NO_3$ and $H^{15}NO_3$ simulated spectra .



Int(ν_5/TOTAL)~0.57

Int(ν_5/TOTAL)~0.8

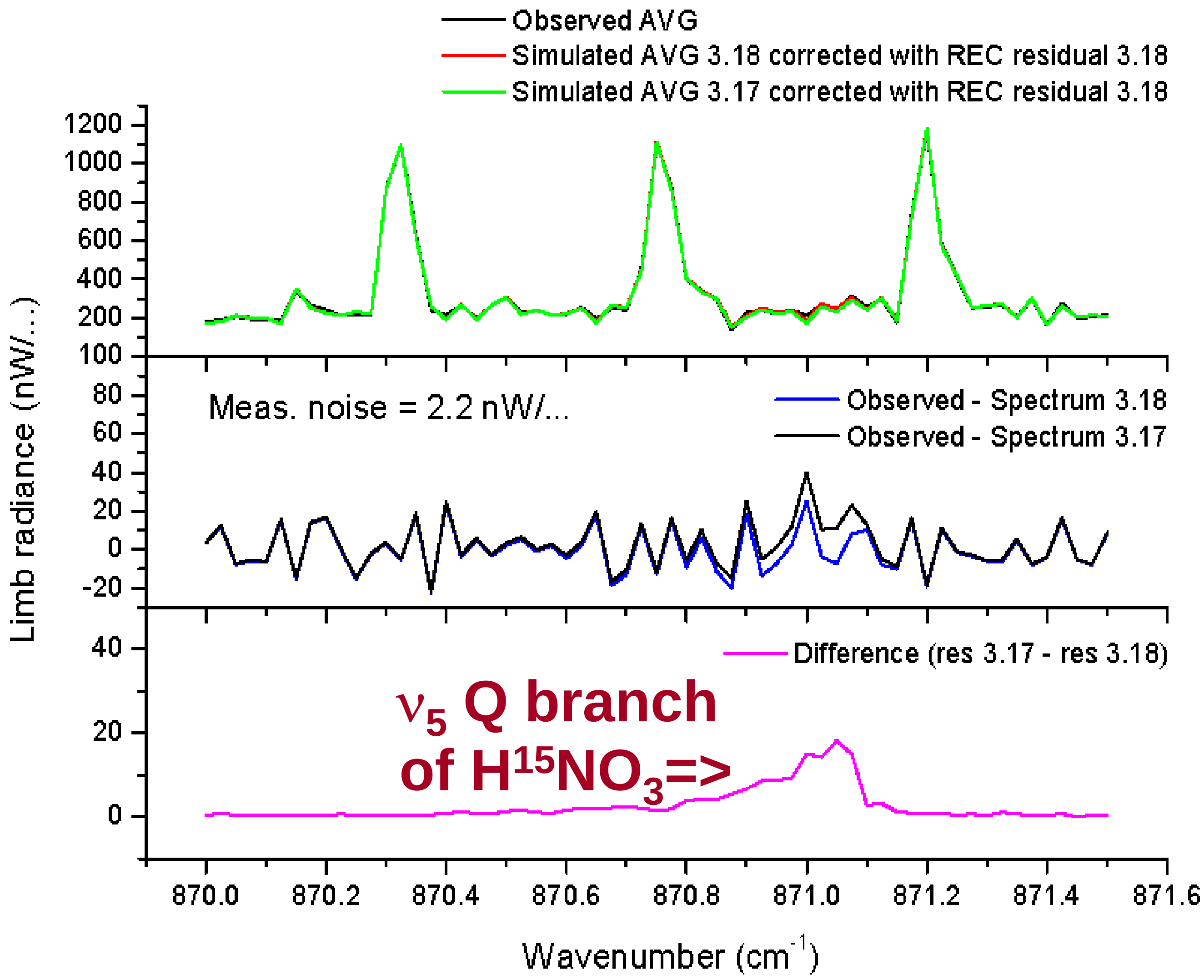
Isotopic abundance only: a~0.003

Perrin, Mbiake, J. Mol. Spectros. 237 (2006) 27

For $H^{15}NO_3$: ⬅ **isotopic shift to the low frequency** range

only weak part of the ν_5 band intensity is transfered to the $2\nu_9$ band

First observation of $H^{15}NO_3$ in an atmospheric spectrum (MIPAS on the ENVISAT satellite)



Conclusion

- Status of HNO_3 in HITRAN
- Improved parameters for HNO_3 in the MIPAS spectral range (700-2400cm^{-1}) in term of line positions, line intensities & line broadening parameters.
- Status of HNO_3 for the 7.6µm ($\{\nu_3,\nu_4\}$) not satisfactory
- No update for the 5.8µm region (ν_2 band).
- Validation of the HNO_3 atmospheric (MIPAS measurements (@11µm) ⇔ IBEX (Infrared Balloon EXperiment) in the far infrared).
- First observation of $H^{15}NO_3$ in MIPAS spectra