

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

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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 ($700\text{-}2400\text{cm}^{-1}$)
- Validation of the HNO_3 atmospheric (**MIPAS measurements (@ $11\mu\text{m}$)** \Leftrightarrow **IBEX (Infrared Balloon EXperiment)** in the far infrared).
- First observation of H^{15}NO_3 in MIPAS spectra

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

2.8 μm ($\sim 3551\text{cm}^{-1}$) ν_1 band NOT INCLUDED Int ≈ 1.2

5.9 μm (1710cm^{-1}) ν_2 band Int ≈ 5.6

7.5 μm ($1303, 1326\text{cm}^{-1}$) ν_4, ν_3 bands Int ≈ 5.0

8.3 μm (1205cm^{-1}) $\nu_8 + \nu_9$ band Int ≈ 0.1

11 μm ($879, 896\text{cm}^{-1}$) $\nu_5, 2\nu_9$ bands + H.B. Int ≈ 2.4

13.1 μm (763cm^{-1}) ν_8 Int ≈ 0.1

15.5 μm (647cm^{-1}) ν_6 (not updated) Int ≈ 0.1

17.2 μm : (580cm^{-1}) ν_7 Int ≈ 0.1

22 μm (458cm^{-1}) ν_9 band + H.B. Int $\approx 1??$

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 $v=0 \Leftrightarrow v=0$ (ground \Leftrightarrow ground) only

In HITRAN-04 all the « hot bands » are missing (as compared to JPL)

(Total contribution of the hot bands $\approx 13\%$ @ 296K)

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

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

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

$$\text{Int}(300\text{K})_{\text{JPL}} = \frac{8\pi^3\sigma}{3hc4\pi\epsilon_0} (e^{-E''/kT} - e^{-E'/kT}) 1/\mathbf{Z}_{\text{JPL}}(\mathbf{T}) |\langle \phi' | \mu_0 | \phi'' \rangle|^2$$

$\mathbf{Z}_{\text{JPL}} \Leftrightarrow$ **rotation** partition function

$$\mathbf{Z}_{\text{vib}}(\mathbf{T}=300\text{K}) \approx 1.30$$

$\neq \mathbf{Z}_{\text{Tot}}(\mathbf{T})$ This problem is now fixed in the JPL catalog (Brian Drouin) integrated for


$$\text{Int}(\mathbf{T})_{\text{JPL}} = \text{Int}_{\text{TRUE}}(\mathbf{T}) * \mathbf{Z}_{\text{vib}}(\mathbf{T}=300\text{K})$$

Intensities overestimated of 30%

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 \approx 5.6
7.5 μm ($1303, 1326\text{cm}^{-1}$) ν_4, ν_3 bands	Int \approx 5.0
8.3 μm (1205 cm^{-1}) $\nu_8+\nu_9$ band	Int \approx 0.1
11 μm ($879, 896\text{cm}^{-1}$) $\nu_5, 2\nu_9$ bands + H.B.	Int \approx 2.4
Intensities in $10^{-17}\text{cm}^{-1}/(\text{molecule.cm}^{-2})$	
 22 μm (458cm^{-1}) ν_9 band + H.B.	Int \approx 1??
MW to far infrared: (rotation in $\nu=0$ + H.B.)	Int \approx 0.06

H.B.: Hot bands

The 22 μm region

- ν_9 cold band: not updated
- $\nu_5-\nu_9$ & $2\nu_9-\nu_9$ 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 22 μm (balloon-borne FIRS-2 instrument, **Ken Jucks** of the Harvard-Smithsonian Center for Astrophysics and 11 μm regions ⁽²⁾

-Update of the $\nu_5-\nu_9$ & $2\nu_9-\nu_9$ hot bands ⁽¹⁾
(need clarifications)

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

Situation of the MIPAS-PF3.2 database

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



5.9 μm (1710cm^{-1}) ν_2 band	Int \approx 5.6
7.5 μm ($1303, 1326\text{cm}^{-1}$) ν_4, ν_3 bands	Int \approx 5.0
8.3 μm (1205 cm^{-1}) $\nu_8+\nu_9$ band	Int \approx 0.1
11 μm ($879, 896\text{cm}^{-1}$) $\nu_5, 2\nu_9$ bands + H.B.	Int \approx 2.4
22 μm (458cm^{-1}) ν_9 band + H.B.	Int \approx 1??
MW to far infrared: (rotation in $\nu=0$ + H.B.)	Int \approx 0.06

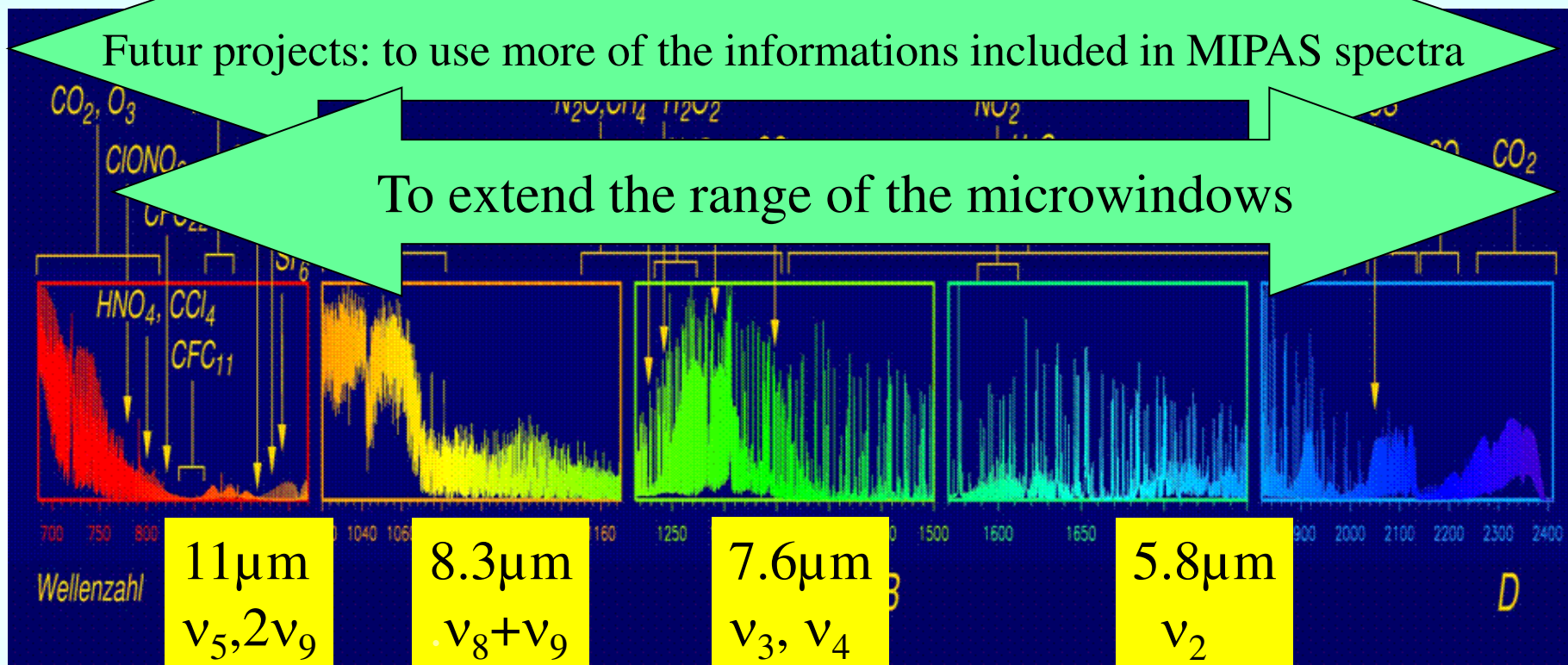
H.B.: Hot bands

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

MIPAS is an high resolution IR FTS spectrometer onboard (6km) the *ENVISAT* satellite since march 2002

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\approx4
7.5μm ($1303, 1326\text{cm}^{-1}$) ν_4, ν_3 bands	Int\approx4
8.3 μm (1205 cm^{-1}) $\nu_8+\nu_9$ band	Int \approx 0.1
11 μm ($879, 896\text{cm}^{-1}$) $\nu_5, 2\nu_9$ bands + H.B.	Int\approx2

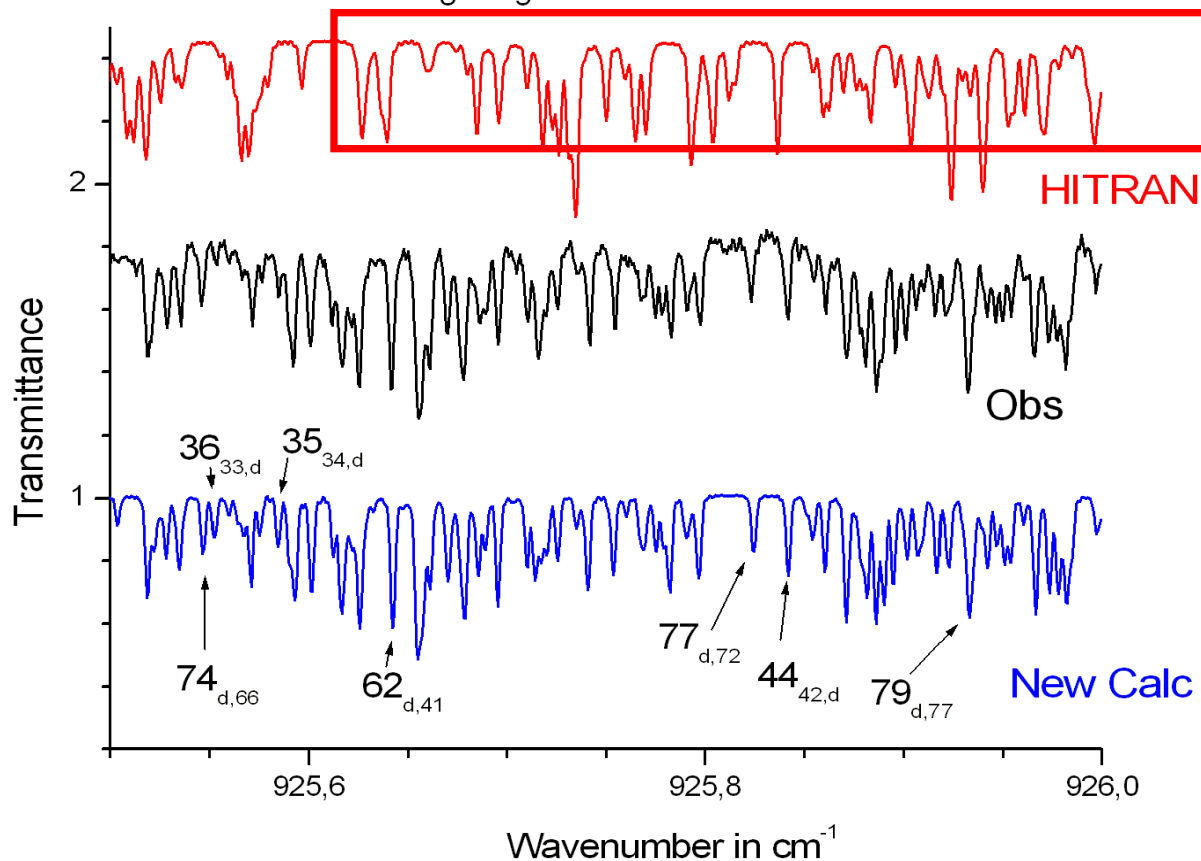
- Improved line positions (11 μm & 8.3 μm)
- Improved line intensities (all)
- Improved line air-broadening parameters (all)

Improved line positions

11 μ m (improved)

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

HNO₃ 2 ν_9 band R-branch



ν_8

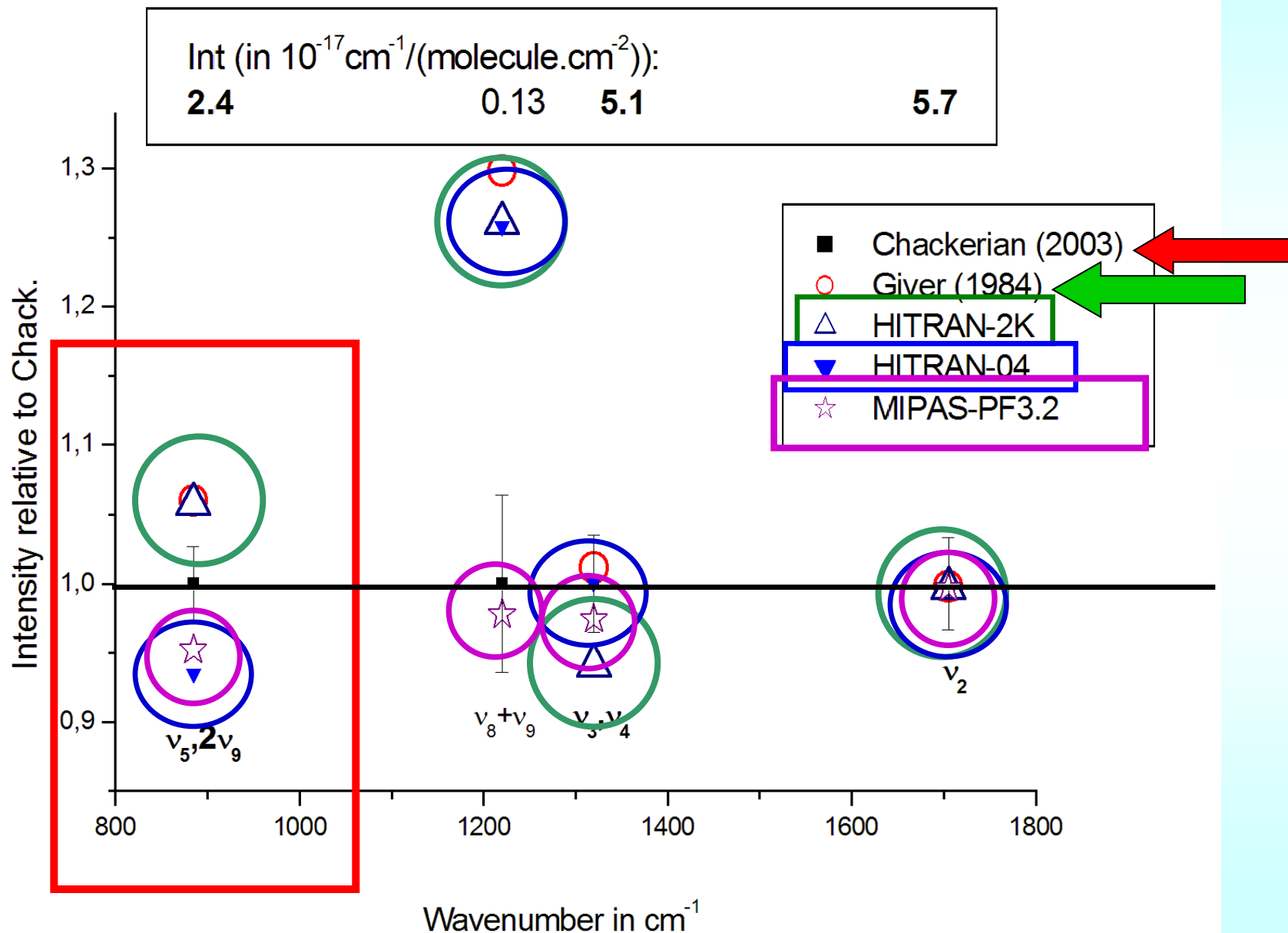
d for #)

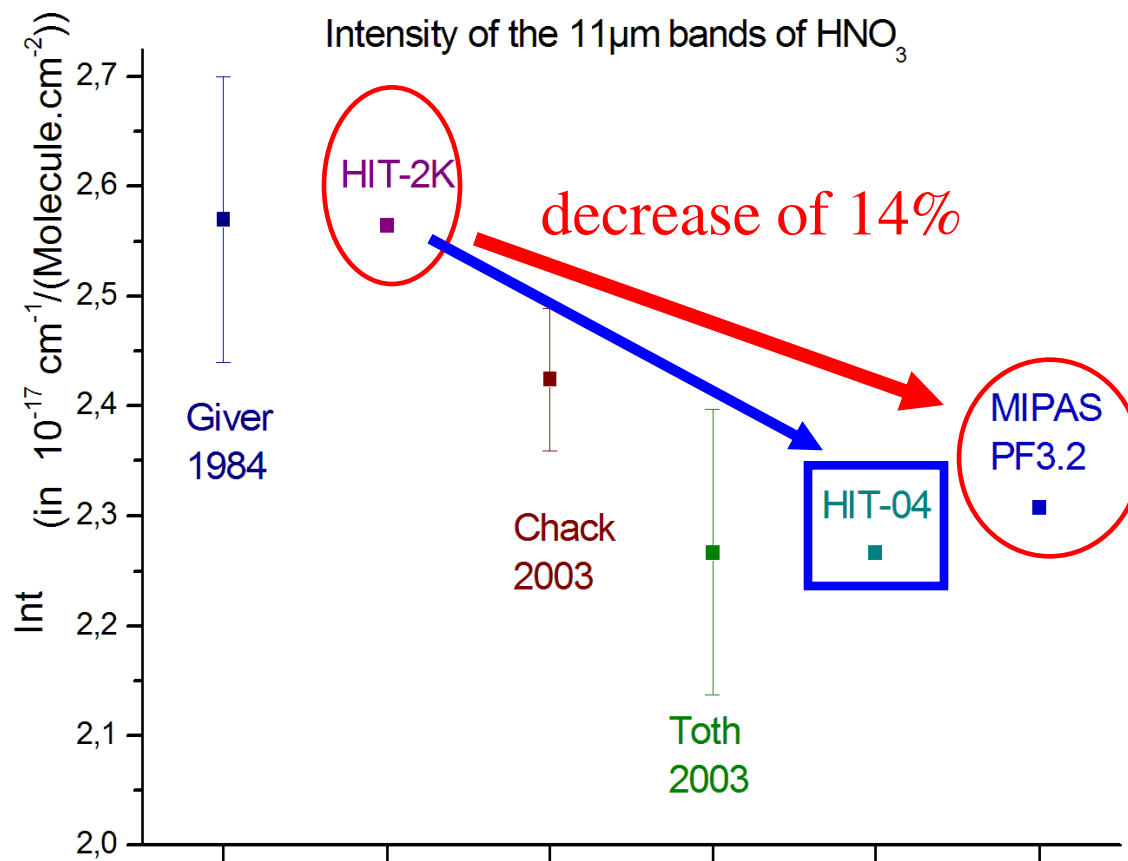
#Perri
Perri
Flaud
Flaud
Flaud

Jun

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

Improved HNO_3 line intensities





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)

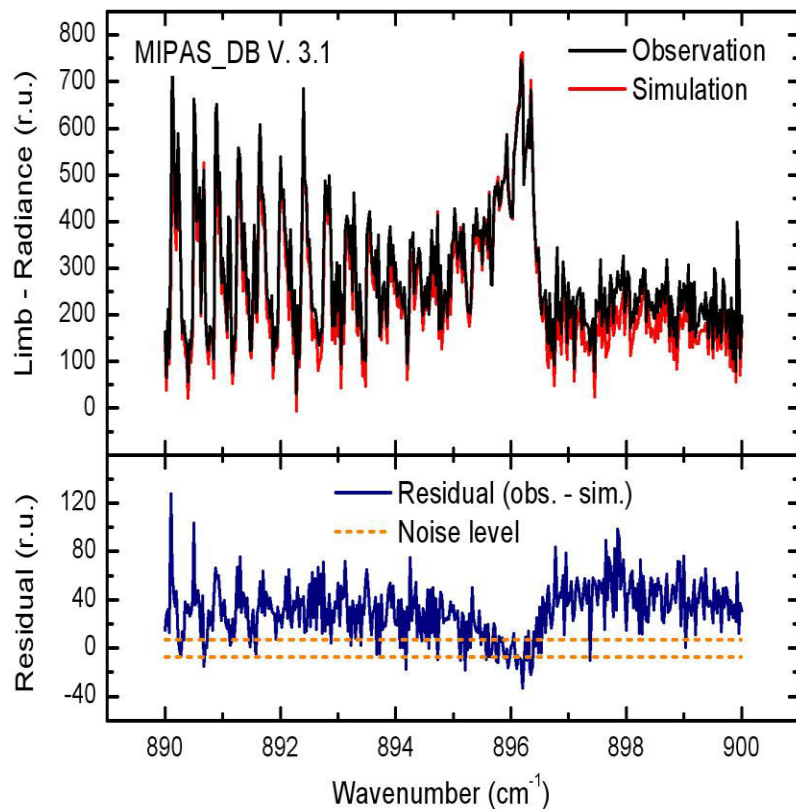
HIT-2K & HIT-04: Rothman et al. JQSRT **82**, 5 (2003), **96**, 139 (2005)

MIPAS: Flaud et al. Atmos Oceanic Opt. **16**, 172 (2003)

First validations...

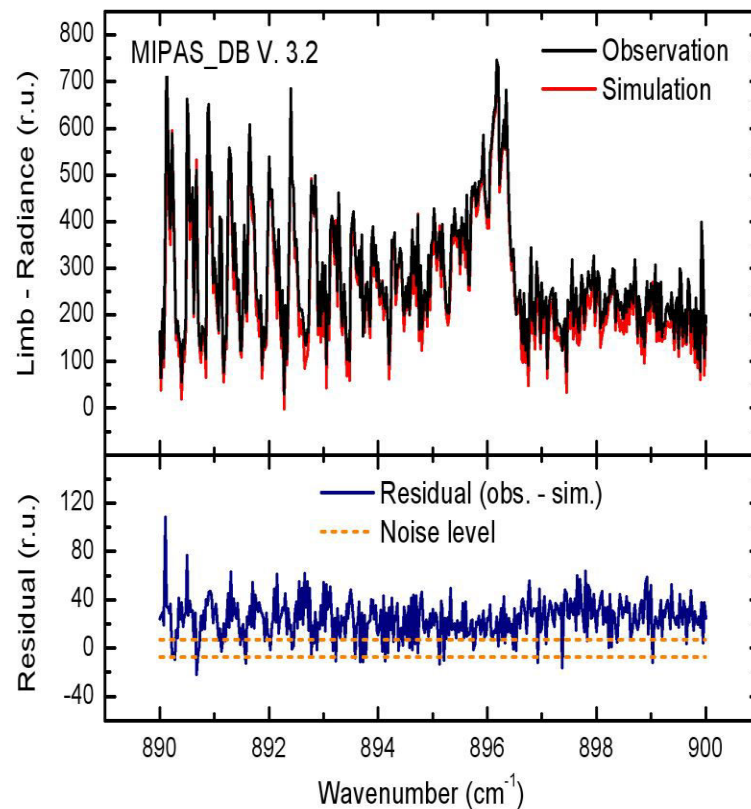
Comparison of observed and simulated MIPAS spectra in band A for an altitude of 24km

$2\nu_9$ Q branch



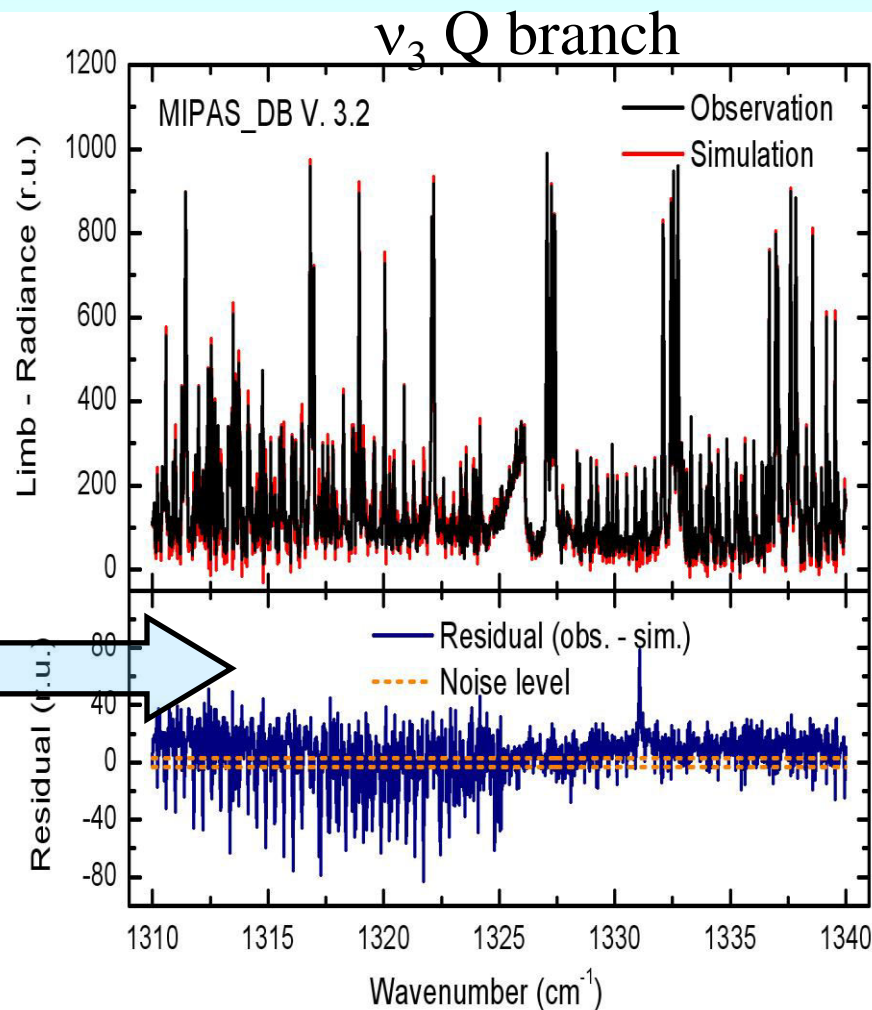
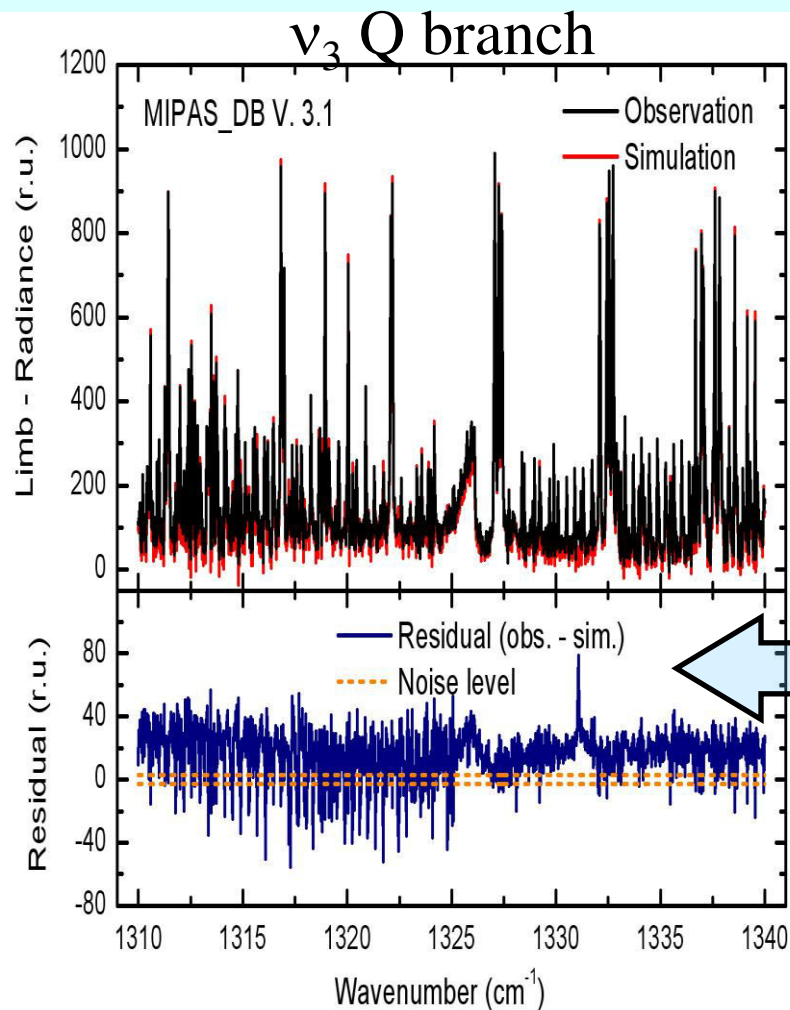
Old database

$2\nu_9$ Q branch



New database

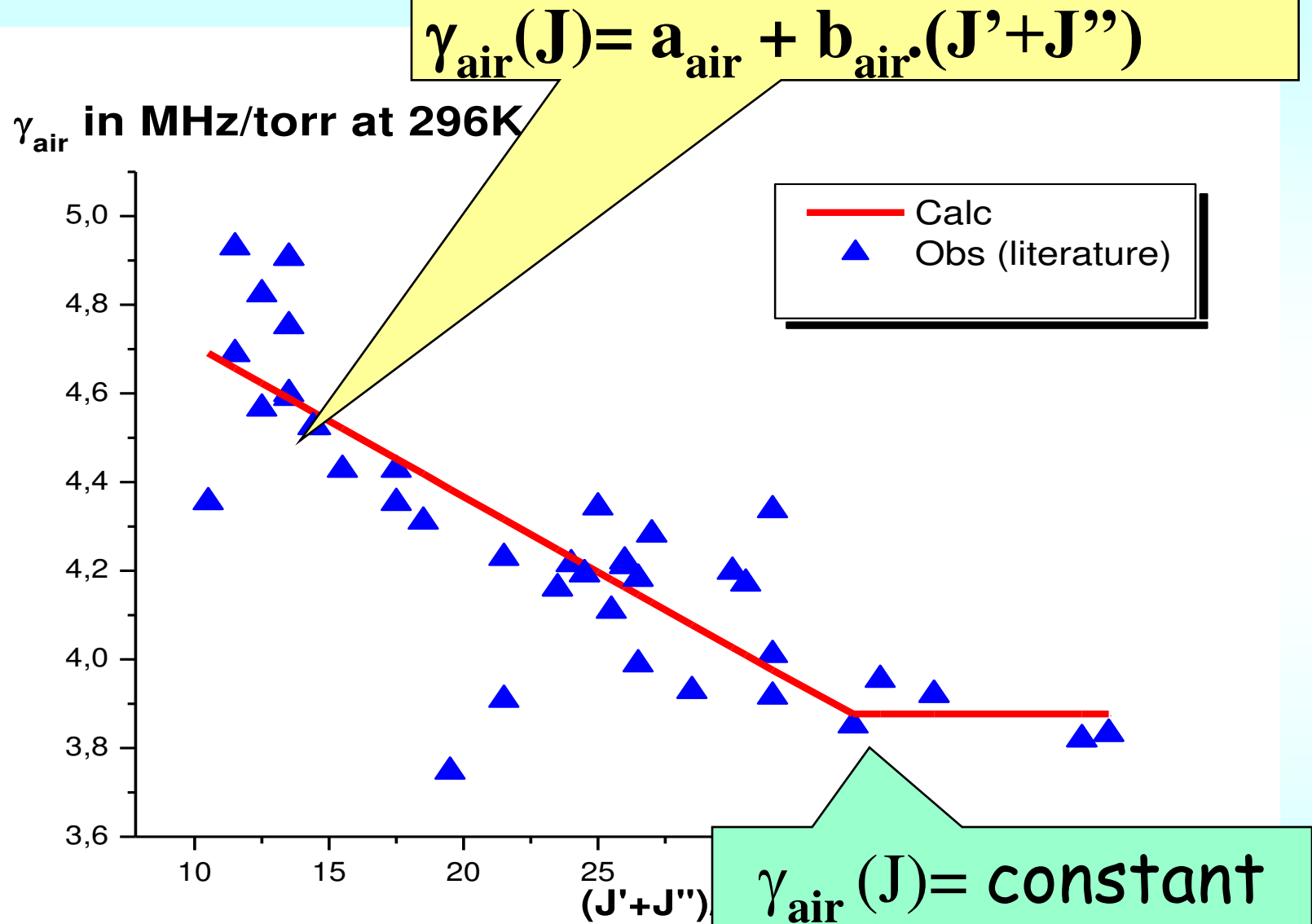
Status of the ν_3 & ν_4 bands ($7.5\mu\text{m}$) ...*still unsatisfactory* !!!!!!!!!



Improved line broadening parameters for HNO_3

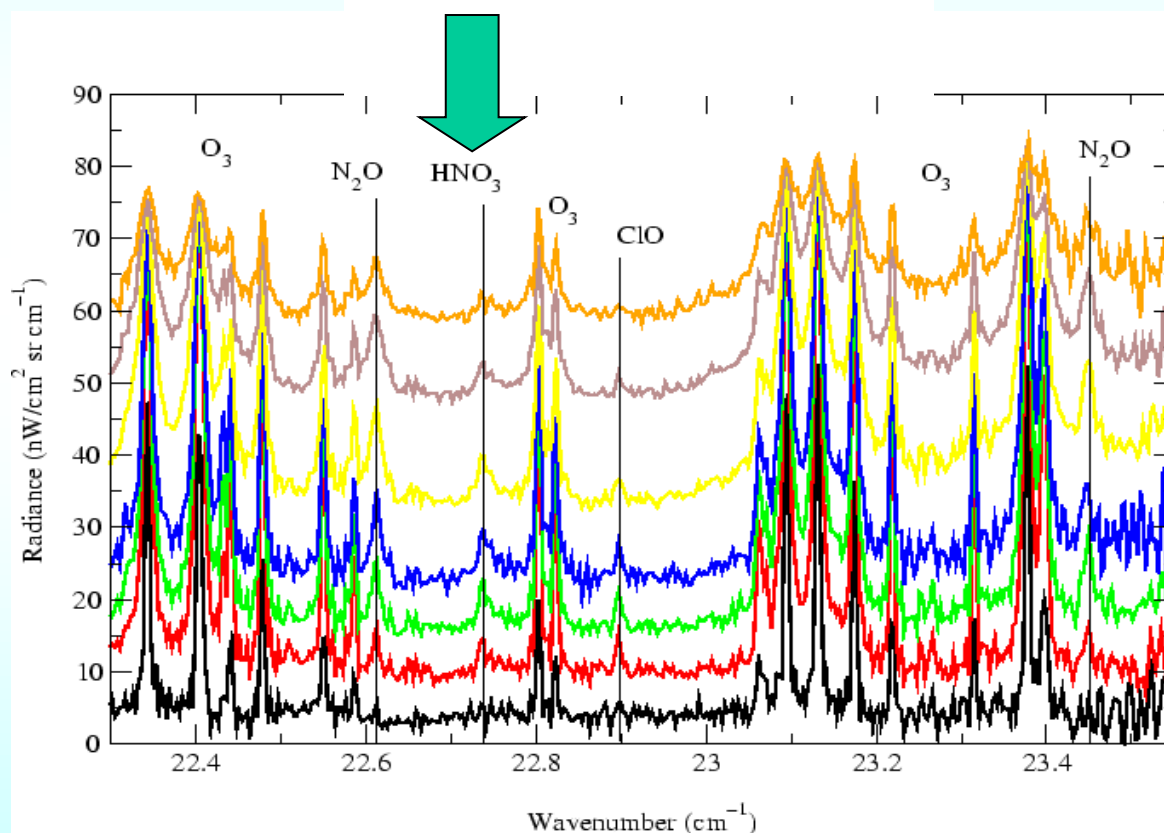
- Numerous excellent line broadening measurements were performed mainly in the millimeter wave spectral range
- Strong rotational dependence of the broadenings
- Sometime, the n - temperature dependance of the γ was also measured.

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.

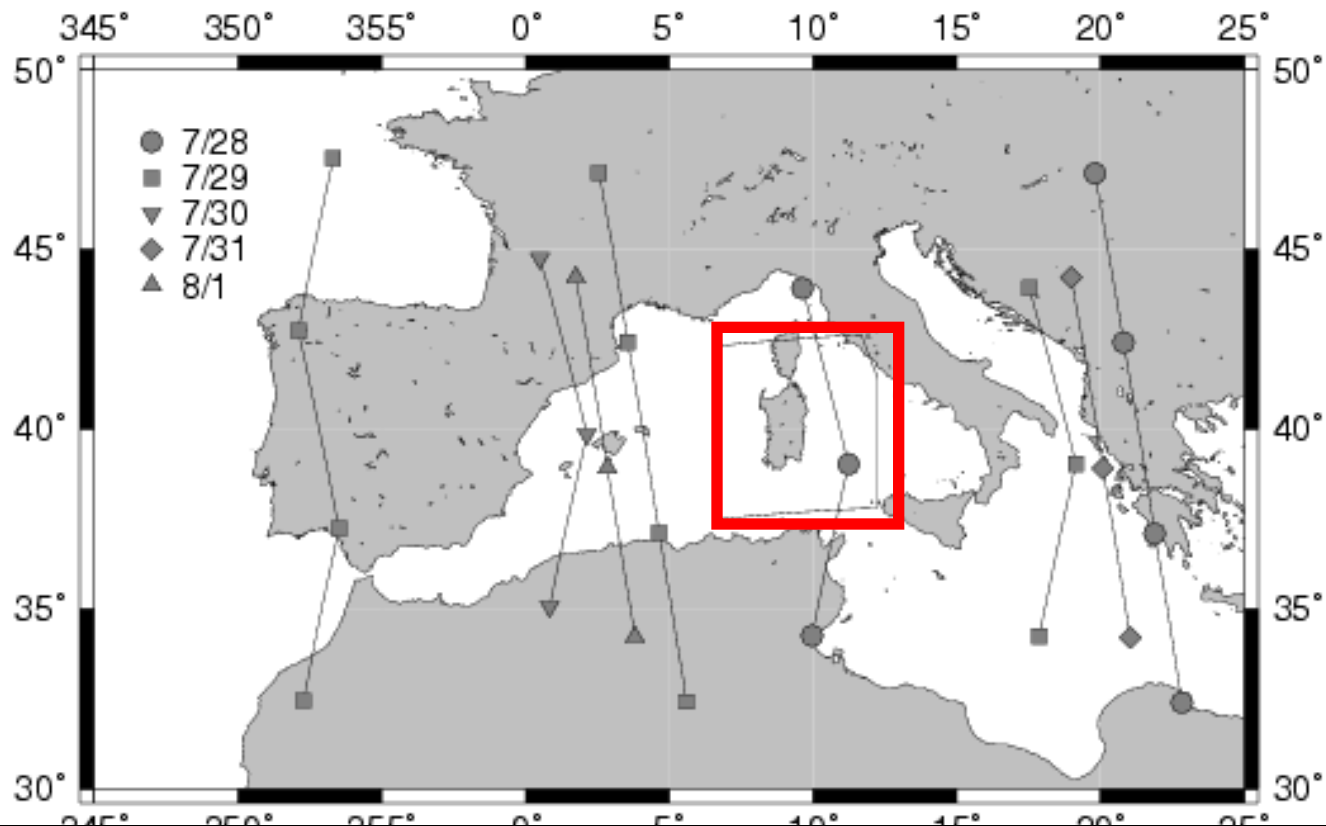
Model for HNO_3 line broadening

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

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



Comparison MIPAS ⇔ IBEX



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

Exact "rendez-vous" satellite ⇔ balloon.

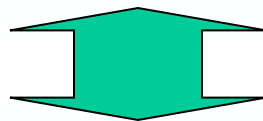
Preliminary intercomparison of HNO₃ profiles

MIPAS

FTS on ENVISAT

11 μm $\Leftrightarrow \approx 900\text{cm}^{-1}$

Line parameters
From HITRAN-2K



IBEX

FTS on a balloon

Far infrared $\Leftrightarrow \approx 20\text{cm}^{-1}$

Parameters from
JPL catalog

Concentration profile of HNO_3

MIPAS \Leftrightarrow **IBEX**

These two profiles disagree....

....., 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 **11 μm** ... (or/and) in the **far infrared**

Final results

11 μm

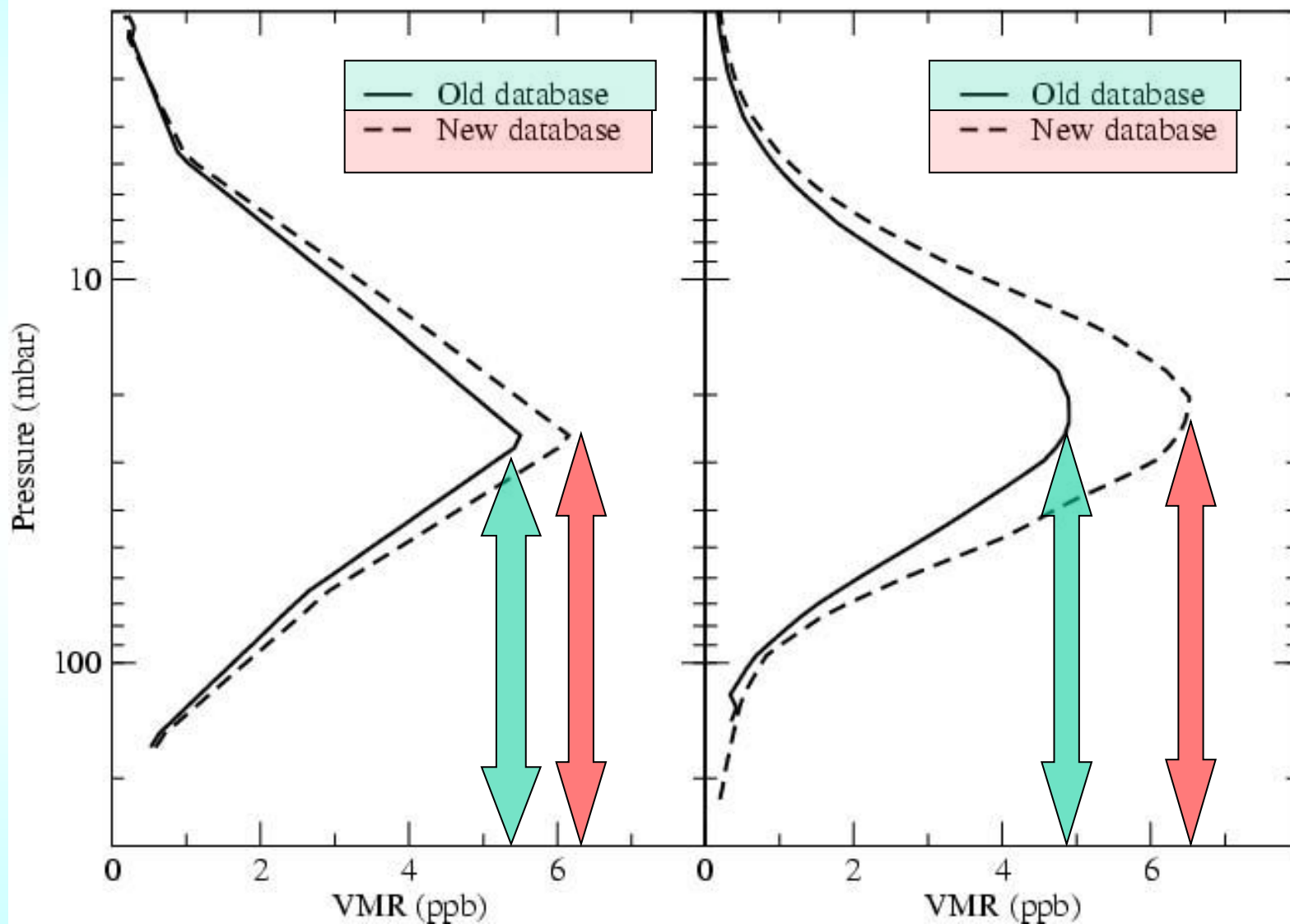
- New line positions
- Overall intensities were divided by ≈ 1.14

Far infrared ($\sim 22\text{cm}^{-1}$)

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

MIPAS: $11\mu\text{m}$

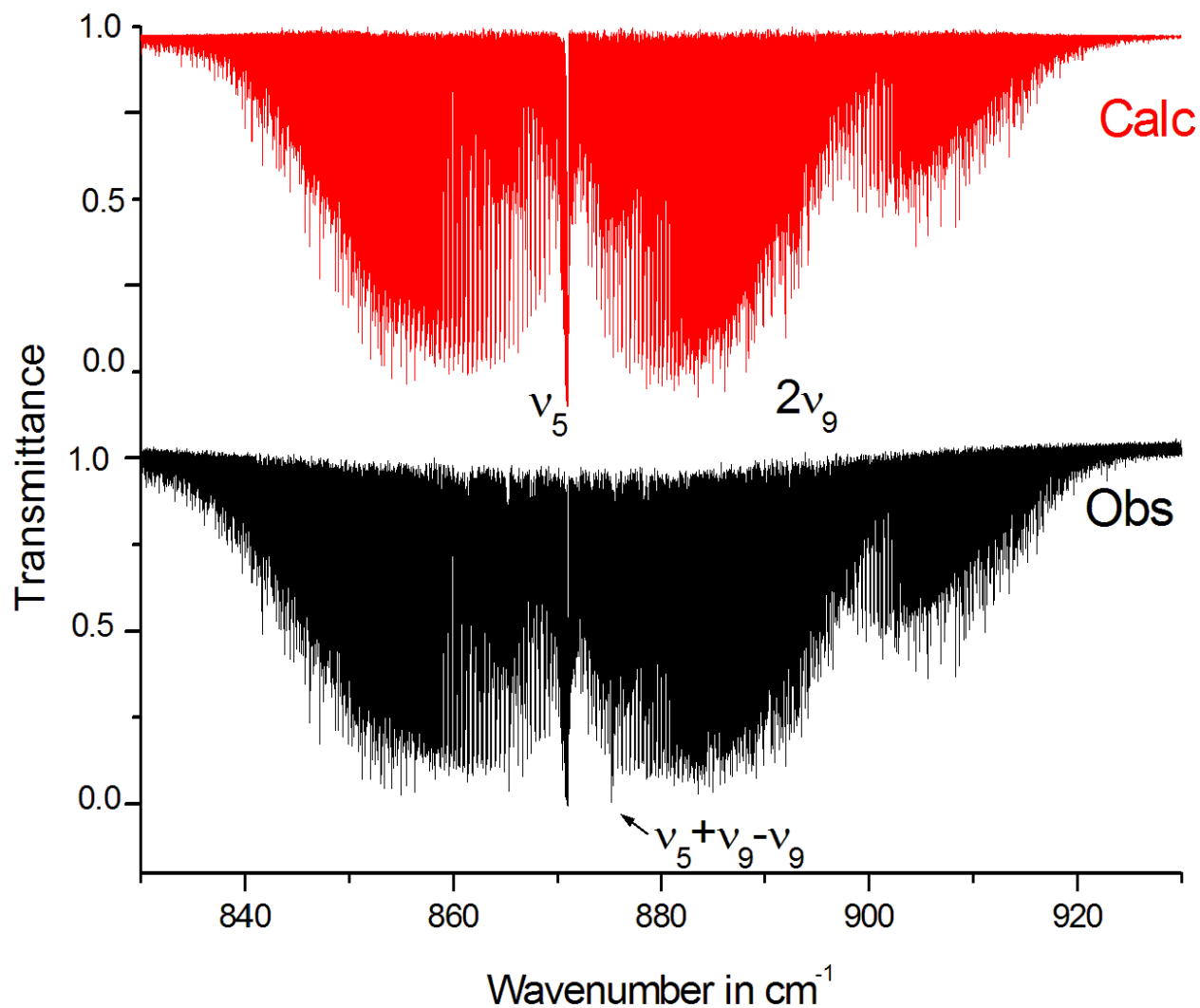
IBEX: Far IR



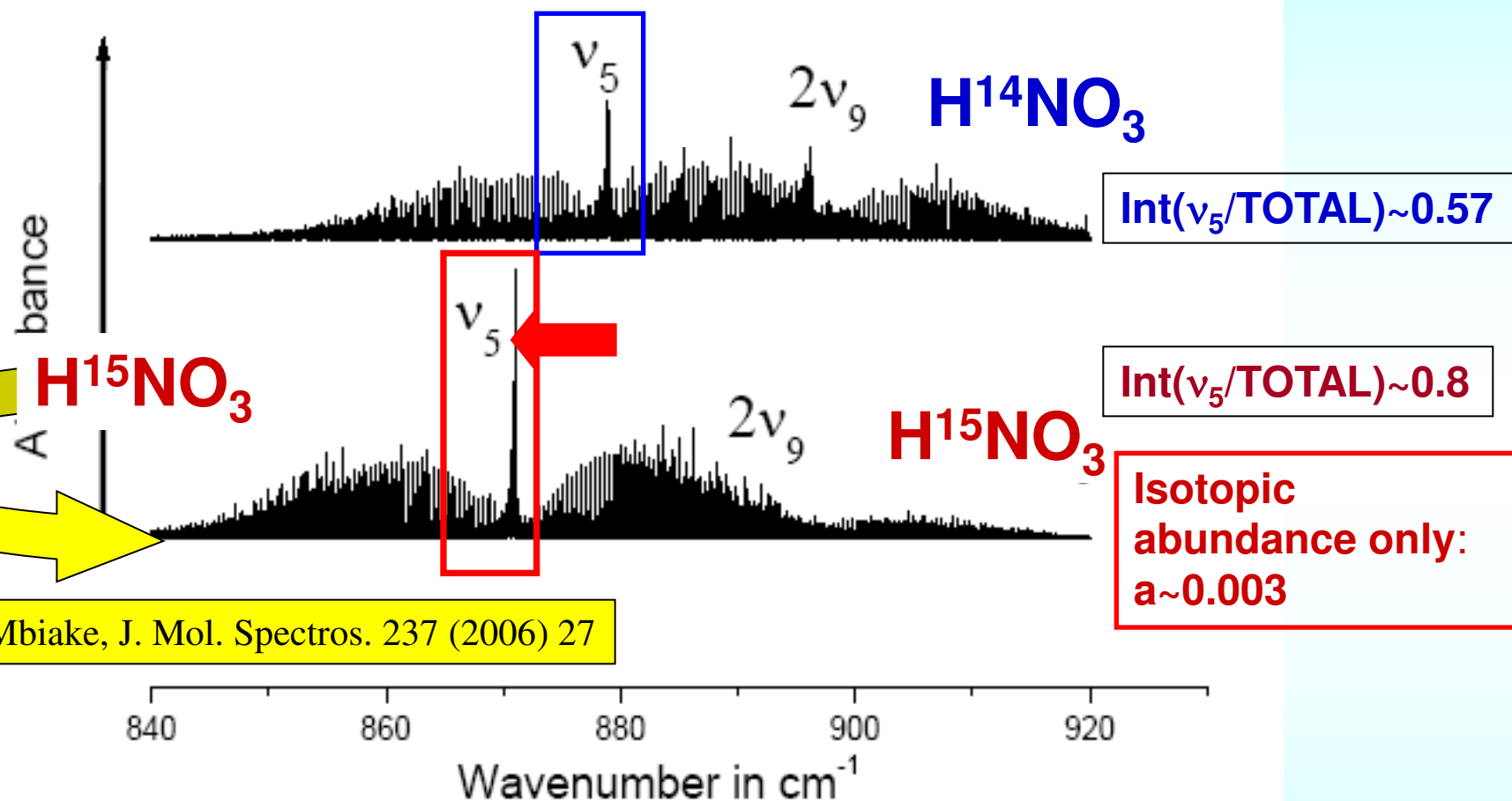
June 2006

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



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



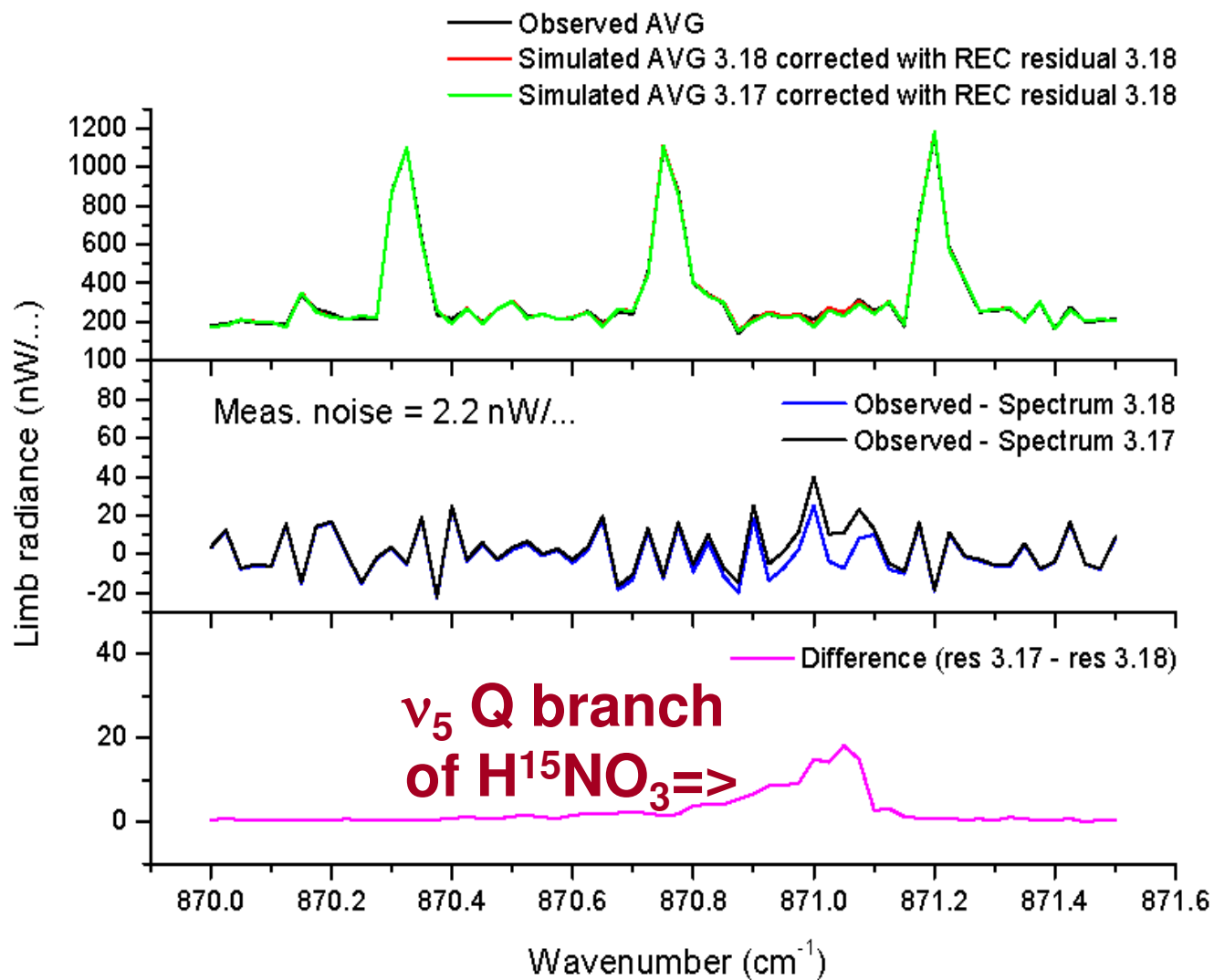
Perrin, Mbiake, J. Mol. Spectros. 237 (2006) 27

For H^{15}NO_3 :  isotopic shift to the low frequency range
only weak part of the ν_5 band intensity is transferred to the $2\nu_9$ band

June 2006

Agnes Perrin HITRAN

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 ($700\text{-}2400\text{cm}^{-1}$) in term of line positions, line intensities & line broadening parameters.
- Validation of the HNO_3 atmospheric (**MIPAS measurements (@11 μm)** \Leftrightarrow **IBEX (Infrared Balloon EXperiment) in the far infrared**).
- First observation of H^{15}NO_3 in MIPAS spectra

Looking for a sabbatical stay

- Subject: ν_3 & ν_4 bands of HNO_3
- One or two months

The 11 μ m region: $\nu_5(879\text{cm}^{-1})$ & $2\nu_9(896\text{cm}^{-1})$

			HIT_2K				
		Nb	Int_tot	Int_Min	Int_Max	Sig_Min	Sig_Max
V5	Gr	19302	0.1144D-16	0.715D-23	0.129D-19	816.1885	946.4932
2V9	Gr	18666	0.8292D-17	0.715D-23	0.869D-20	826.2680	959.1856
V5+V9	V9	14829	0.1608D-17	0.105D-24	0.188D-20	829.1235	949.3461
Total		52797	0.2134D-16				
			HIT_04				
V5	Gr	21195	0.1006D-16	0.493D-23	0.104D-19	816.1885	946.4932
2V9	Gr	20319	0.7375D-17	0.496D-23	0.764D-20	826.2680	959.1856
V5+V9	V9	14521	0.1067D-17	0.987D-24	0.700D-21	832.1165	942.9013
3V9	V9	17720	0.5290D-18	0.384D-24	0.672D-21	769.6870	884.4384
Tot		73755	0.1903D-16				
			HIT_04/HIT_2K				
V5	Gr		0.8792				
2V9	Gr		0.8894				
V5+V9	V9		0.6635				

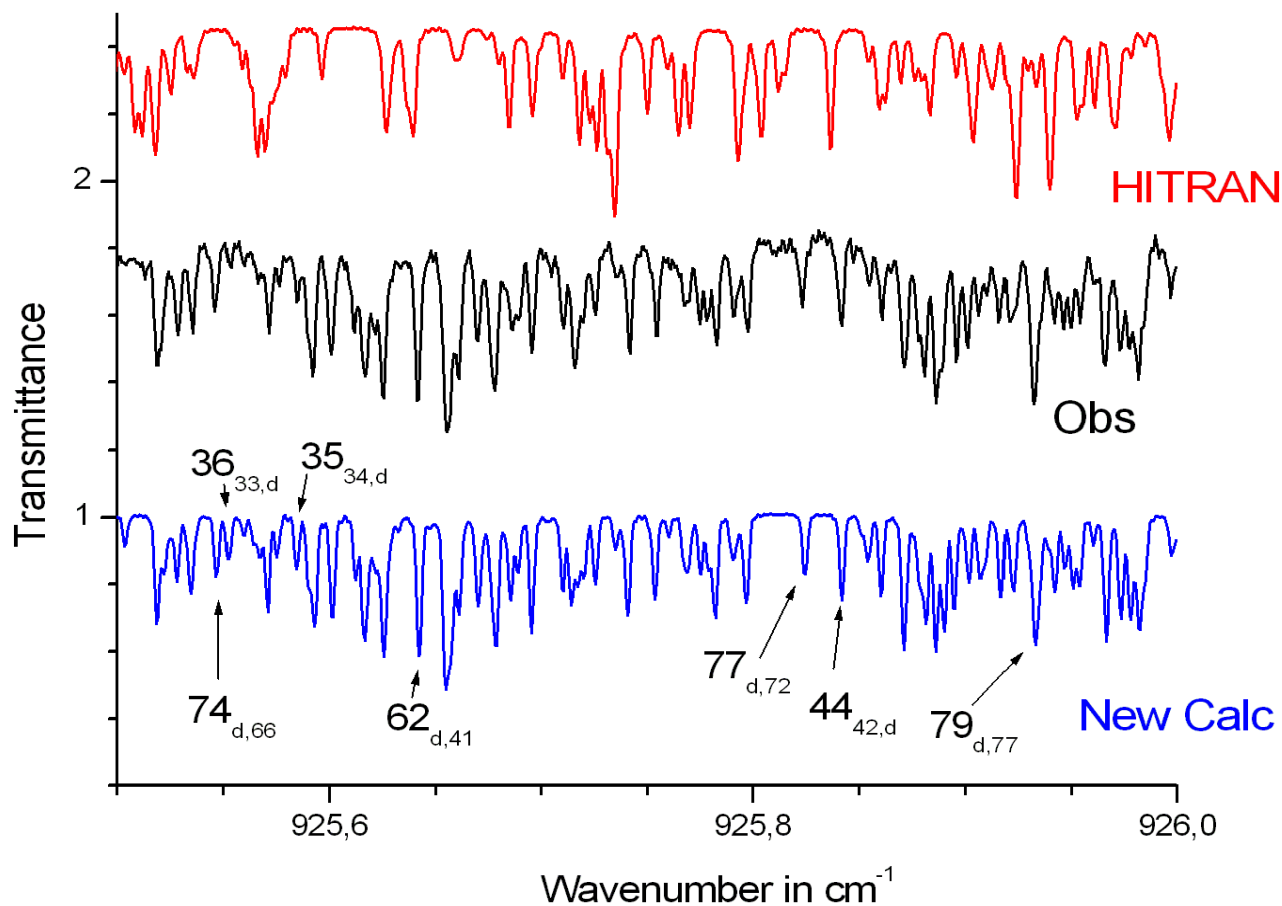
The 7.6 μm region: $\nu_3(1326\text{cm}^{-1})$ & $\nu_4(1303\text{cm}^{-1})$

			HIT_2K				
		Nb	Int-Tot	Int_Min	Int_Max	Sig_Min	Sig_Max
V3	Gr	21308	0.2446D-16	0.100D-22	0.302D-19	1098.3760	1387.8490
V4	Gr	19584	0.1232D-16	0.100D-22	0.180D-19	1229.8670	1387.5610
Tot		40892	0.3677D-16				
			HIT_04				
V3	Gr	21308	0.2610D-16	0.107D-22	0.322D-19	1098.3760	1387.8490
V4	Gr	19584	0.1314D-16	0.107D-22	0.192D-19	1229.8670	1387.5610
Tot		40892	0.3924D-16				
			HIT_04/HIT_2K				
V3	Gr		1.067				
V4	Gr		1.067				

ν_5 & $2\nu_9$ cold bands

=> recent line improvement (now in MIPAS-PF3.2)

HNO_3 $2\nu_9$ band R-branch

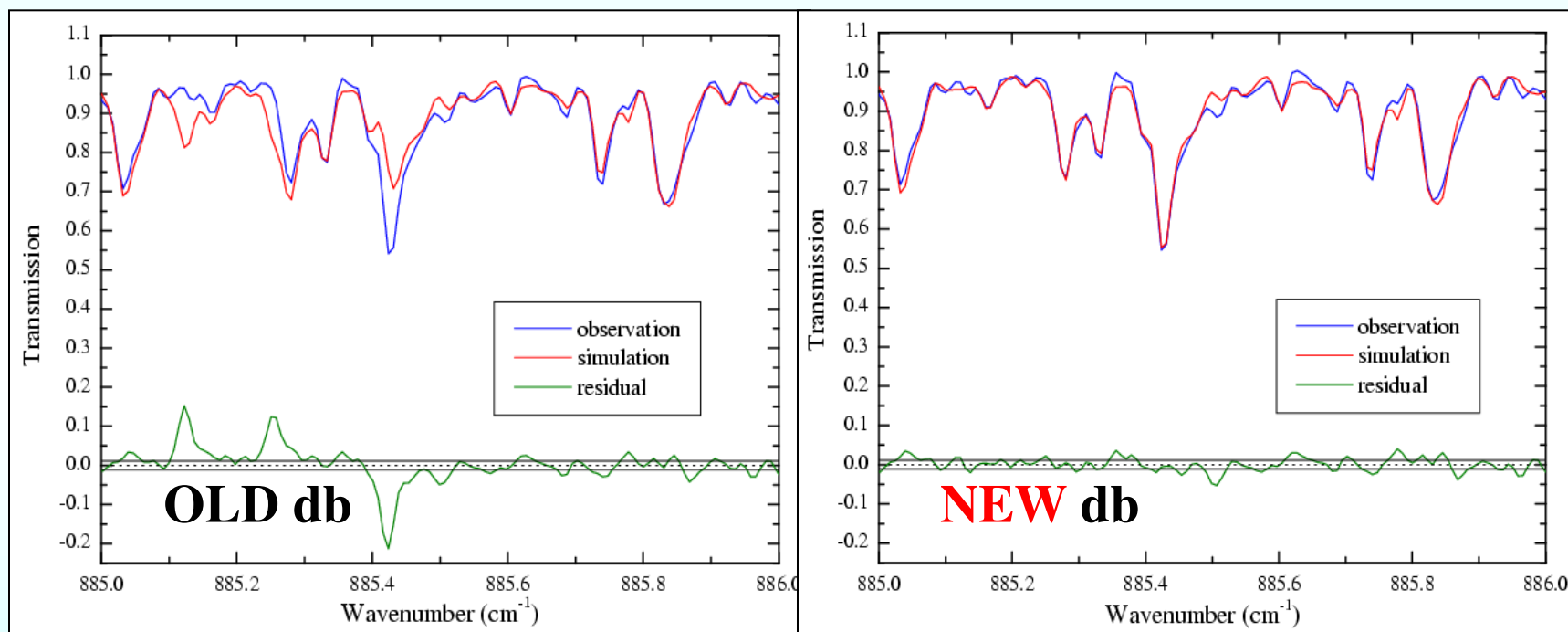


Perrin, Orphal, Flaud, Klee, Mellau, Mäder, Walbrodt, Winnewisser,
J. Mol. Spect. 228 (2004) 375.

Spectroscopic Database for MIPAS

Comparison between **ATMOS** measurements and atmospheric simulations obtained using the **NEW** and the **OLD** database

Example of the $\nu_5 + \nu_9 - \nu_9$ hot band of **HNO₃**



J.-M. FLAUD , C. PICCOLO, B. CARLI, A. PERRIN , L. H. COUDERT , J.-L. TEFFO AND L. R. BROWN, Molecular line parameters for the MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) experiment, J. Atmospheric and Oceanic Technology, 16, 172-182 (2003)

June 2006

Agnes Perrin HITRAN

HNO₃ : transitions to consider

HITRAN

within the ground vibrational state

JPL

within the first vibrational states

(ν_9 , ν_7 , ν_6 , ν_8 , ν_5 and $2\nu_9$)

@ 458, 580, 647, 763, 879 and 896 cm⁻¹)

("hot transitions")[#]

⇒ Total contribution of the hot bands ≈ 13% @ 296K

New parameters are available from the new studies performed in the millimeter region for various excited at ~1000cm⁻¹ (and/or) for other isotopic species (Ohio State & JPL[#])

[#]Petkie Helming, Markus Behnke, Ivan R. Medvedev and De Lucia JMS 233 (2005) 189.

[#] Drouin, Miller, Fry, Petkie, Helming and Medvedev, JMS 236 (2006) 29.