New analysis of the ν_3 & ν_4 bands of HNO_3 by high resolution Fourier transform spectroscopy in the 7.6 µm region

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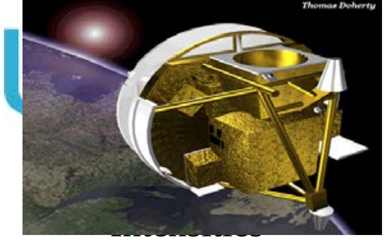
« status & evolution of the operational IASI L2 products at *EUMETSAT* (**Thomas August** talk on yesterday)

….plans for **version V6**…

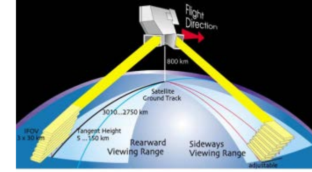
SO_2 columns

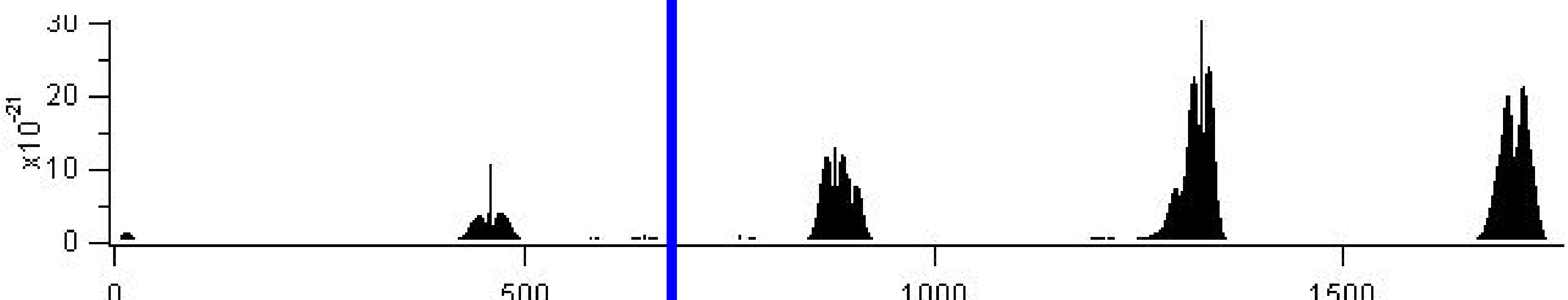
HNO_3 profiles

The present « pure spectroscopic study » will try to help (somehow…) this strategy…



HNO_3 in HITRAN-GEISA

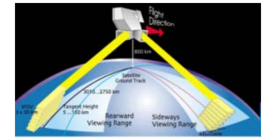


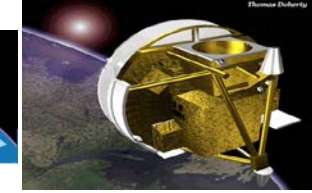


MW &	ν_9	$\{\nu_5, 2\nu_9)$	$\{\nu_4, \nu_3\}$	ν_2
0-10cm^{-1}	458cm^{-1}	879, 896cm^{-1}	1303, 1326cm-1	1709cm^{-1}
Far-IR	22µm	11µm	7.6µm	5.8µm

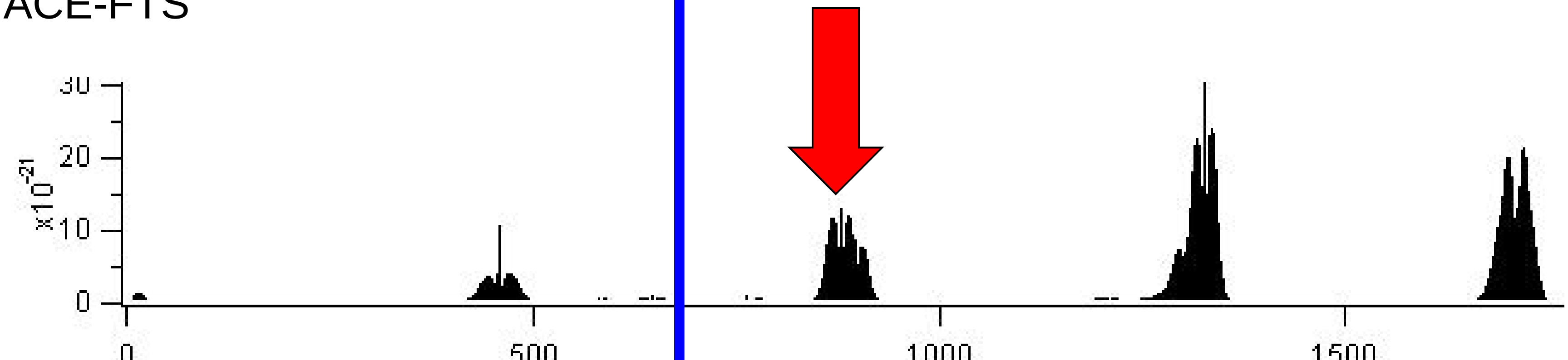
Spectral range covered by ACE-FTS & IASI, MIPAS(dead in 2012) & the (future) IASI-NG

Up to now HNO_3 is measured **(almost only)** in the **11 µm region which was updated recently in HITRAN & GEISA**





ACE-FTS



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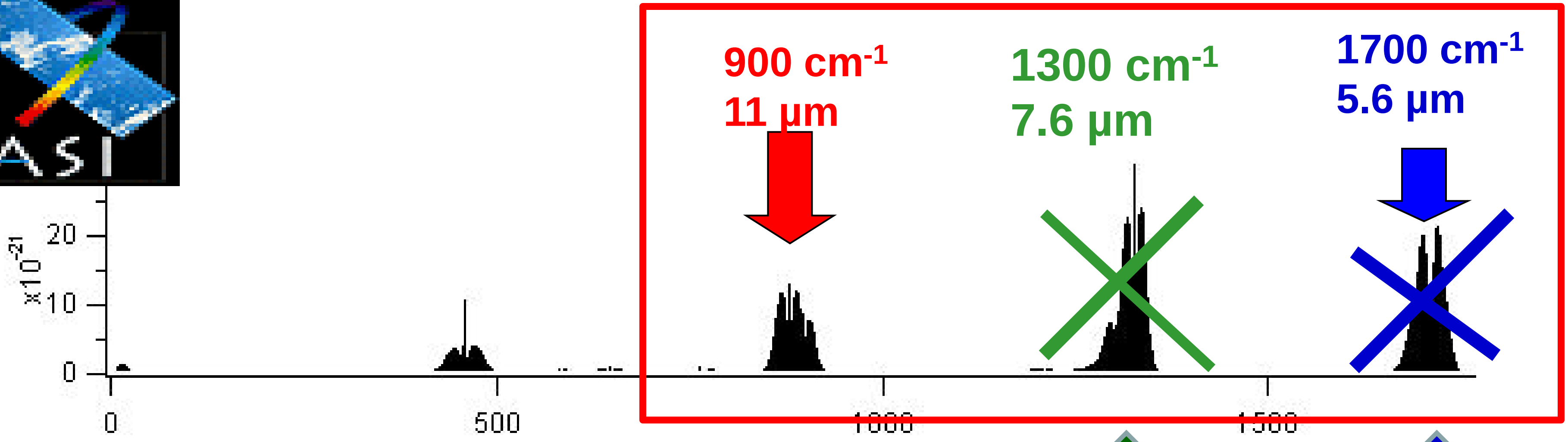
0-10cm^{-1}	458cm^{-1}	879, 896cm^{-1}	1303, 1326cm-1	1709cm^{-1}
Far-IR	22µm	11µm	7.6µm	5.8µm

Improved line positions & intensities at 11 µm (ν_5 and $2\nu_9$ bands):

Perrin, Orphal, Flaud, Klee, Mellau, Mäder, Walbrodt & Winnewisser, J. Mol. Spect 228 (2004)
Flaud, Brizzi, Carlotti, Perrin & Ridolfi *Atmos. Chem. Phys.*, *6*, 1–12, 2006.
Tran, Brizzi Gomez , Perrin, Hase, Ridolfi, Hartmann, JQSRT 110, 109-117 (2009).
Gomez, Tran, Perrin, Gamache, Laraia, Orphal, Chelin, Fellows, Hartmann JQSRT 110, 675-686 (2009).



High quality of the 11 µm spectroscopic parameters

Low quality of the spectroscopic parameters

Not favorable (overlapped by water absorption)

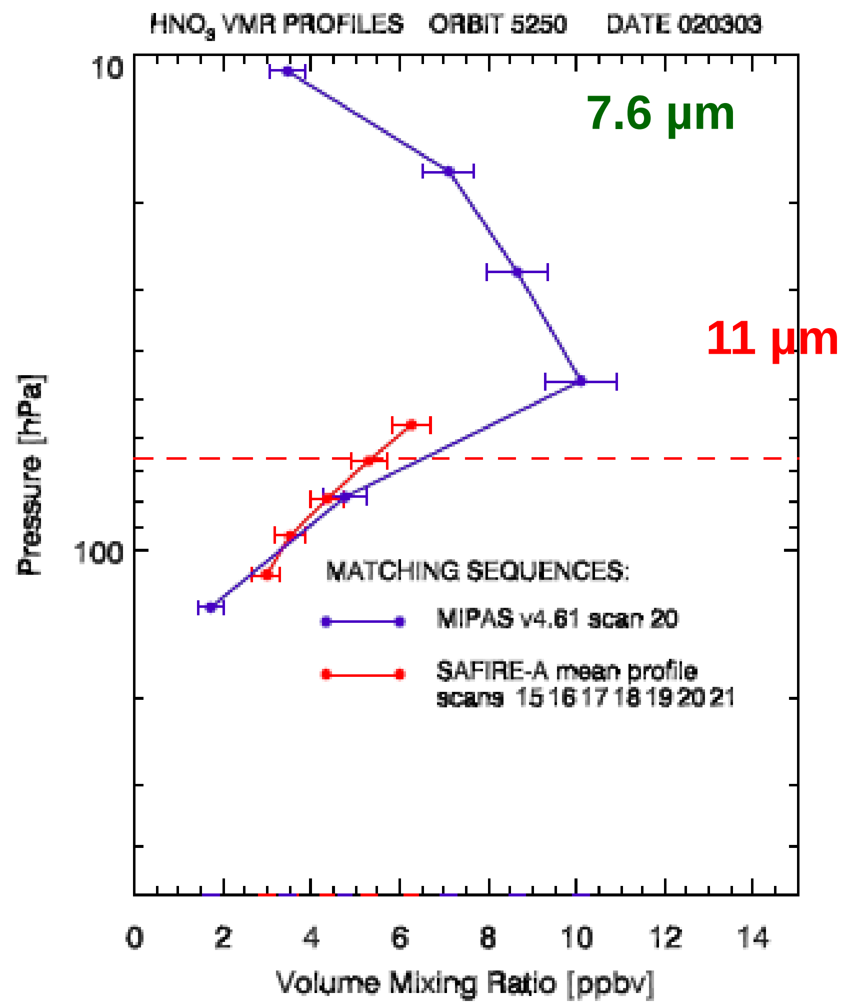
The 11 µm band is two times weaker than the 7.6 µm and 5.6 µm bands

We have to think to IASI-NG (new generation)

Low quality of the 7.6 µm spectroscopic parameters

The bad quality of the **HNO_3** parameters at **7.6 µm** is the problem for the **SO_2** retrievals (at **7.35 µm)**

Because the **7.6 µm** band is **two times stronger** than the **11 µm one** it could be possible to retrieve **HNO_3** in **both** the **11 µm** and **7.6 µm** regions (**IASI-NG** ??) (in order to get some informations on the **altitude profile** for **HNO_3**)



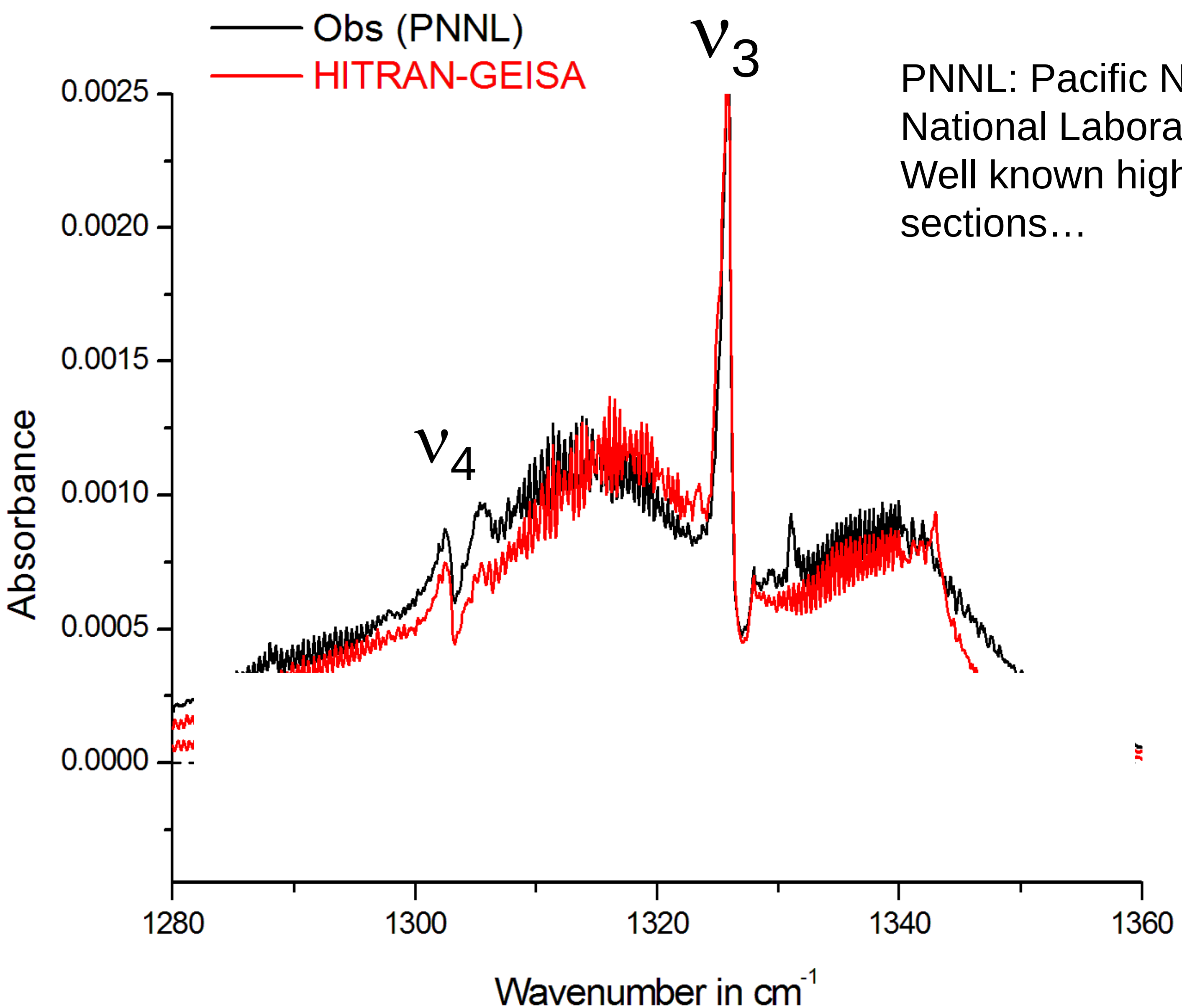
Wang et al. Validation of MIPAS HNO_3 operational data, Atmos. Chem. Phys., 7, 4905–4934, 2007

Only ONE source for the line positions & relative intensities parameters for HNO_3 @7.6 µm in the HITRAN or GEISA databases

¤ Perrin, Lado-Bordowski and Valentin, « The ν_3 and ν_4 bands of HNO_3 », Mol. Phys 67 p. 249 (**1989**)

The HITRAN or GEISA updates of HNO_3@7.6 µm concern *only* the total band intensity.

HNO_3 cross sections



PNNL: Pacific Northwest National Laboratory
Well known high quality cross sections…

7.6 μm(ν_3 & ν_4 bands) in 1989...

Only a partial analysis of the ν_3 & ν_4 bands was performed

Only the resonances coupling $\nu_3 \Leftrightarrow \nu_4$ were considered

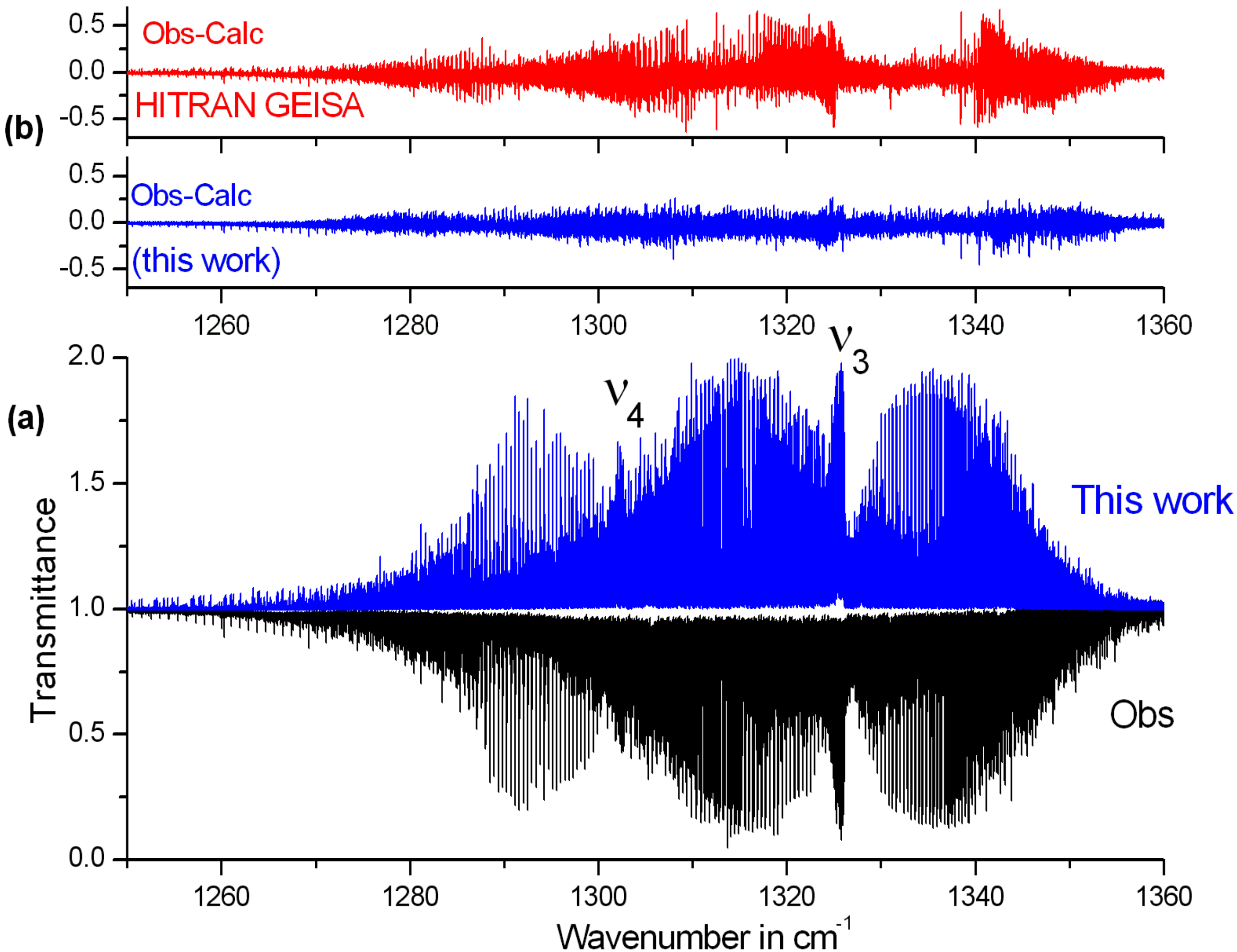
The model did not account from the resonances involving 4 dark bands

This work

- FTS spectra laboratory spectra recorded at high resolution in the 7.6 µm region.
- New analysis of the ν_3 and ν_4 bands at 7.6 µm bands

- PROBLEM:
- These bands are interacting with several « **dark bands** » like $3\nu_9$ and $\boldsymbol{\nu_5+\nu_9}$ …,
- The informations on these **dark bands** were achieved by the investigations of the hot bands
- $\boldsymbol{3\nu_9-\nu_9}$ hot band (at 12 µm) or $\boldsymbol{\nu_5+\nu_9-\nu_9}$ hot band 11 µm
- Analyses of these spectra:
- New theoretical model

Validation of the new linelist using MIPAS spectra.



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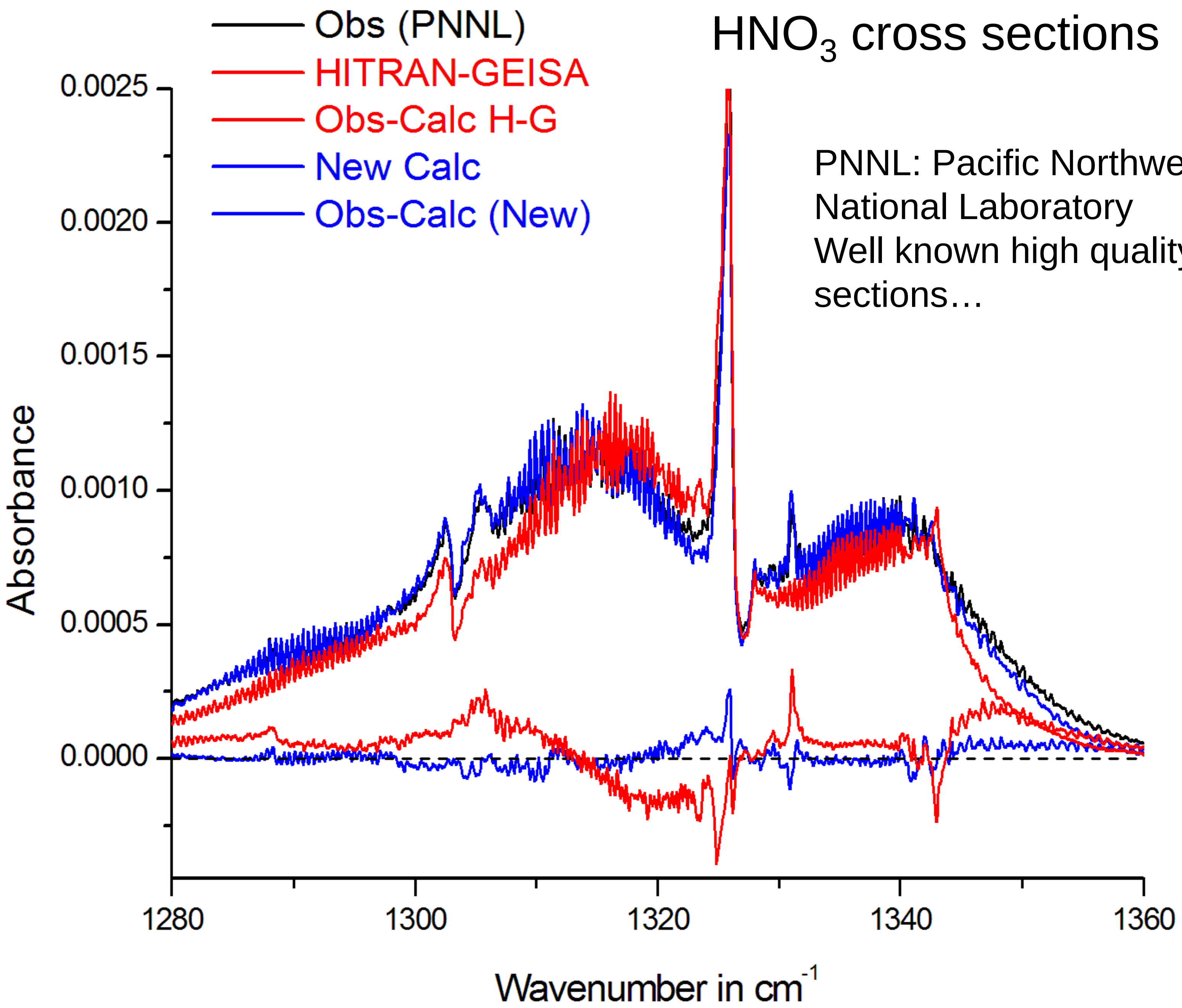
HNO_3 cross sections



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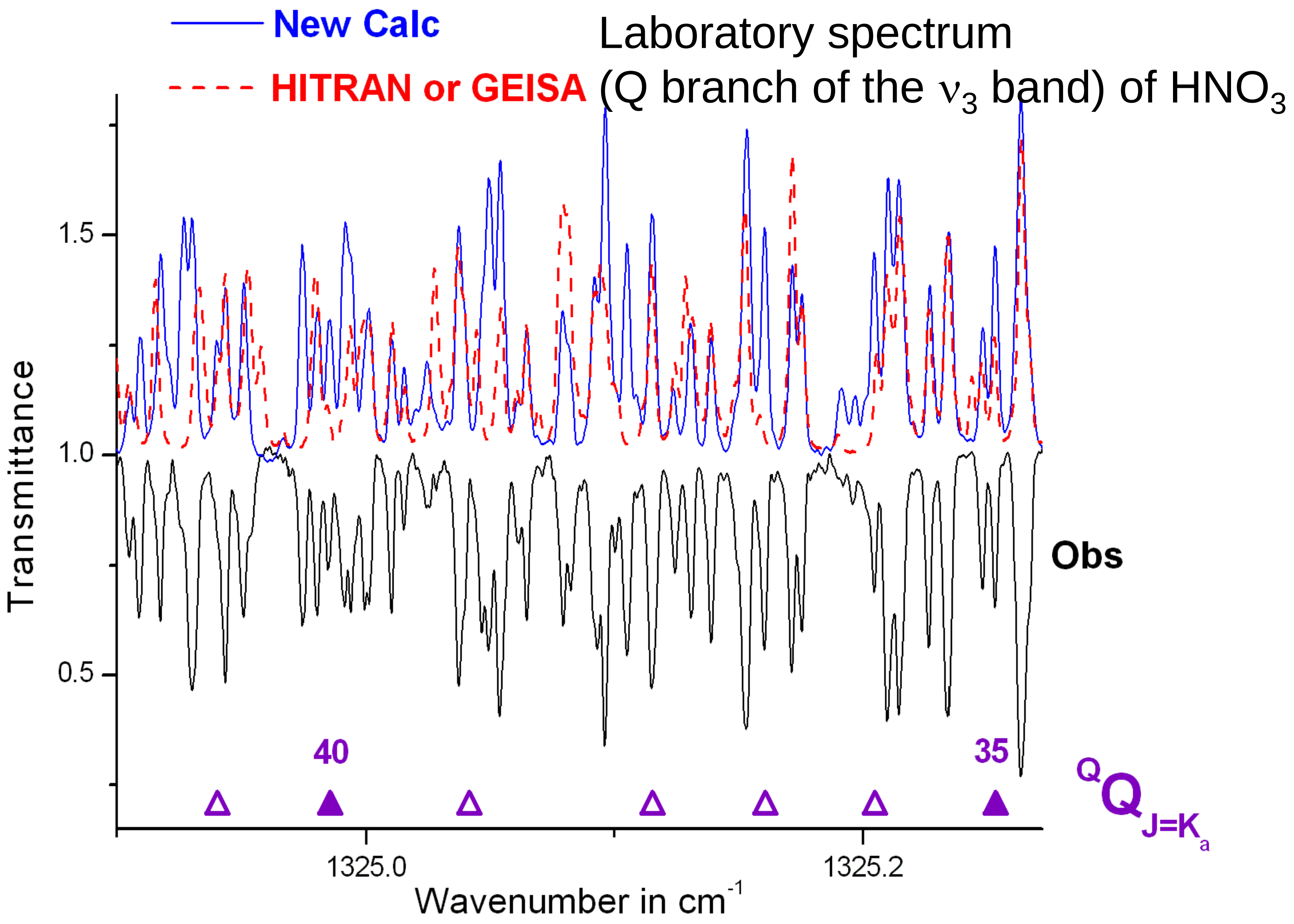


New Calc
HITRAN or GEISA
Laboratory spectrum
(Q branch of the ν3 band) of HNO3
Transmittance
1.5
1.0
0.5
Obs
40
35
QQJ=Ka
1325.0
1325.2
Wavenumber in cm-1

Hamiltonian matrix: the 7.6 µm bands of HNO_3

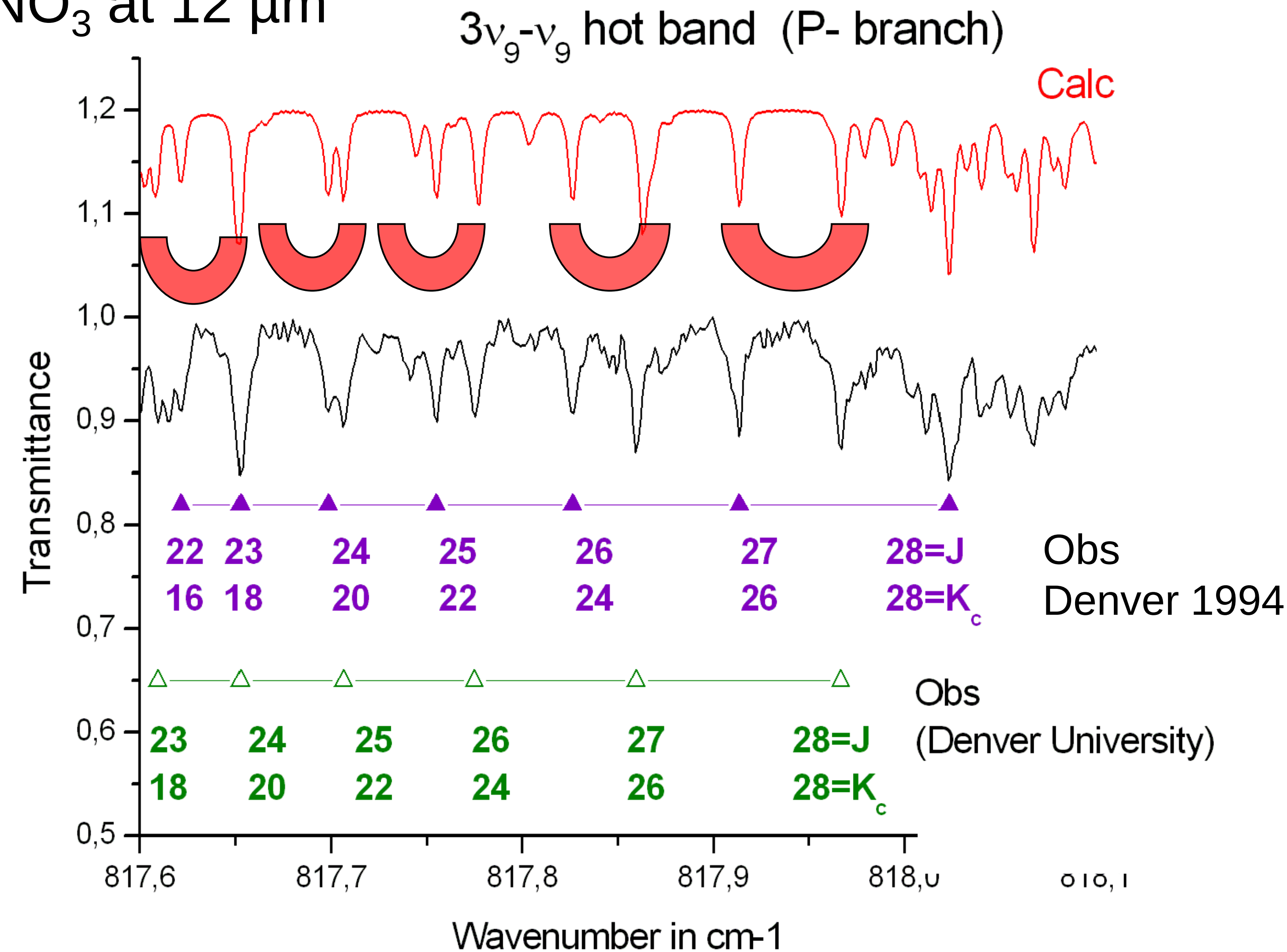
.$3\nu_9$

E_v= (cm^{-1})	1289.2	1293.2	1303.1	1326.2	1339.2	1342.9
	6^2	9^3	4^1	3^1	$5^1 9^1$	$7^1 8^1$
6^2	W		**Fermi+C**	**Fermi+C**		
9^3		W+Torsion	**B**	**B**	**strong Fermi**	
4^1	**Fermi+C**	**B**	W	**Anh**		
3^1	**Fermi+C**	**B**	**Anh**	W	**A+B**	**A+B**
$5^1 9^1$		**strong Fermi**	**A+B**	**A+B**	W	**A+B**
$7^1 8^1$			**A+B**	**A+B**		W

Informations on the 9^3 dark state
from the $3\nu_9$-ν_9 hot band

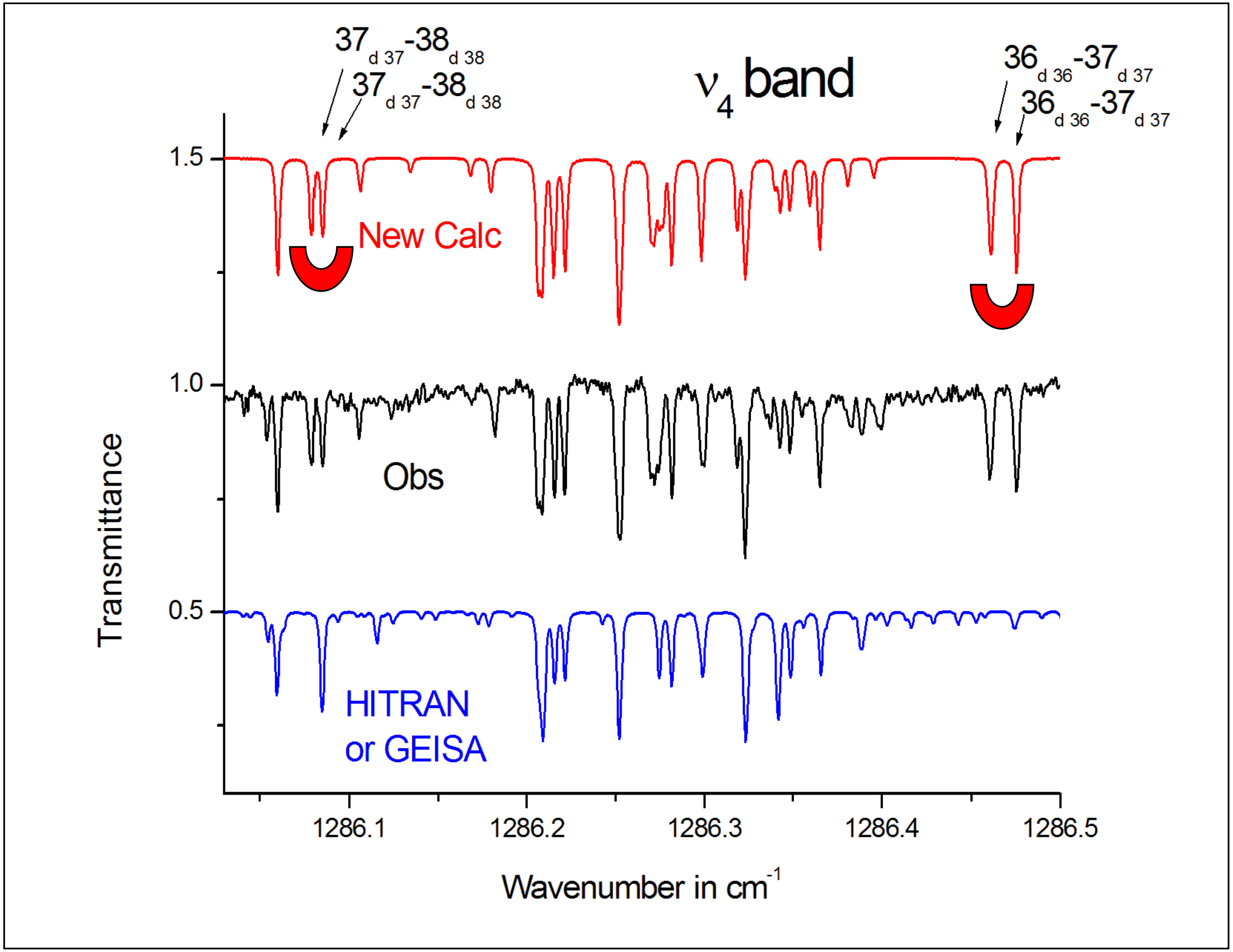
Large amplitude OH torsion

HNO_3 at 12 µm

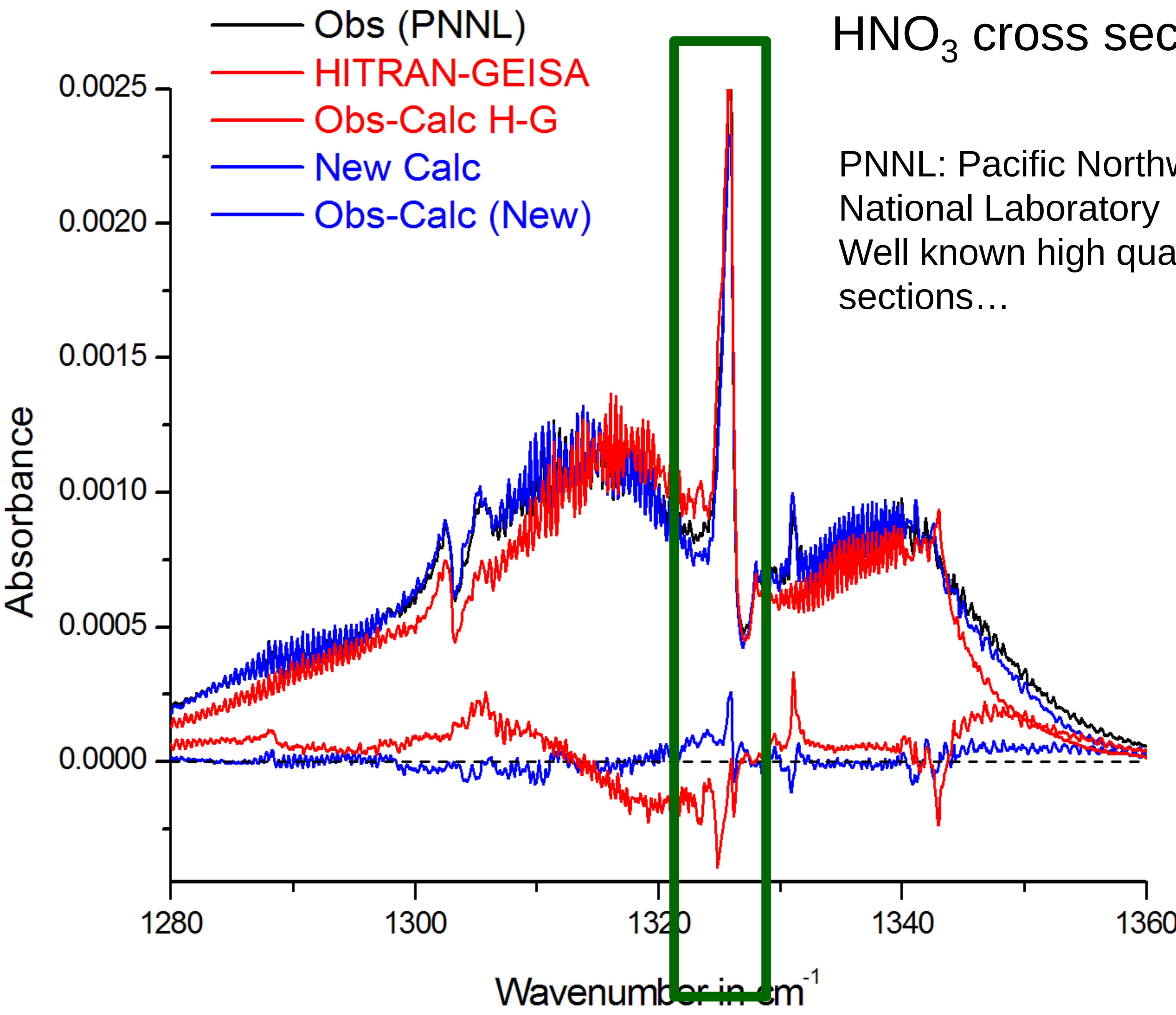


(2) **Perrin, Flaud, Camy-Peyret, Winnewisser, Klee, Goldman, Murcray, Blatherwick, Bonomo, Murcray, J. Mol. Spectrosc. 166 (1994) 224–243**

Transfert of the **torsional splitting** via the $\nu_4 \Leftrightarrow 3\nu_9$ interaction at 7.6 µm



HNO_3 cross sections



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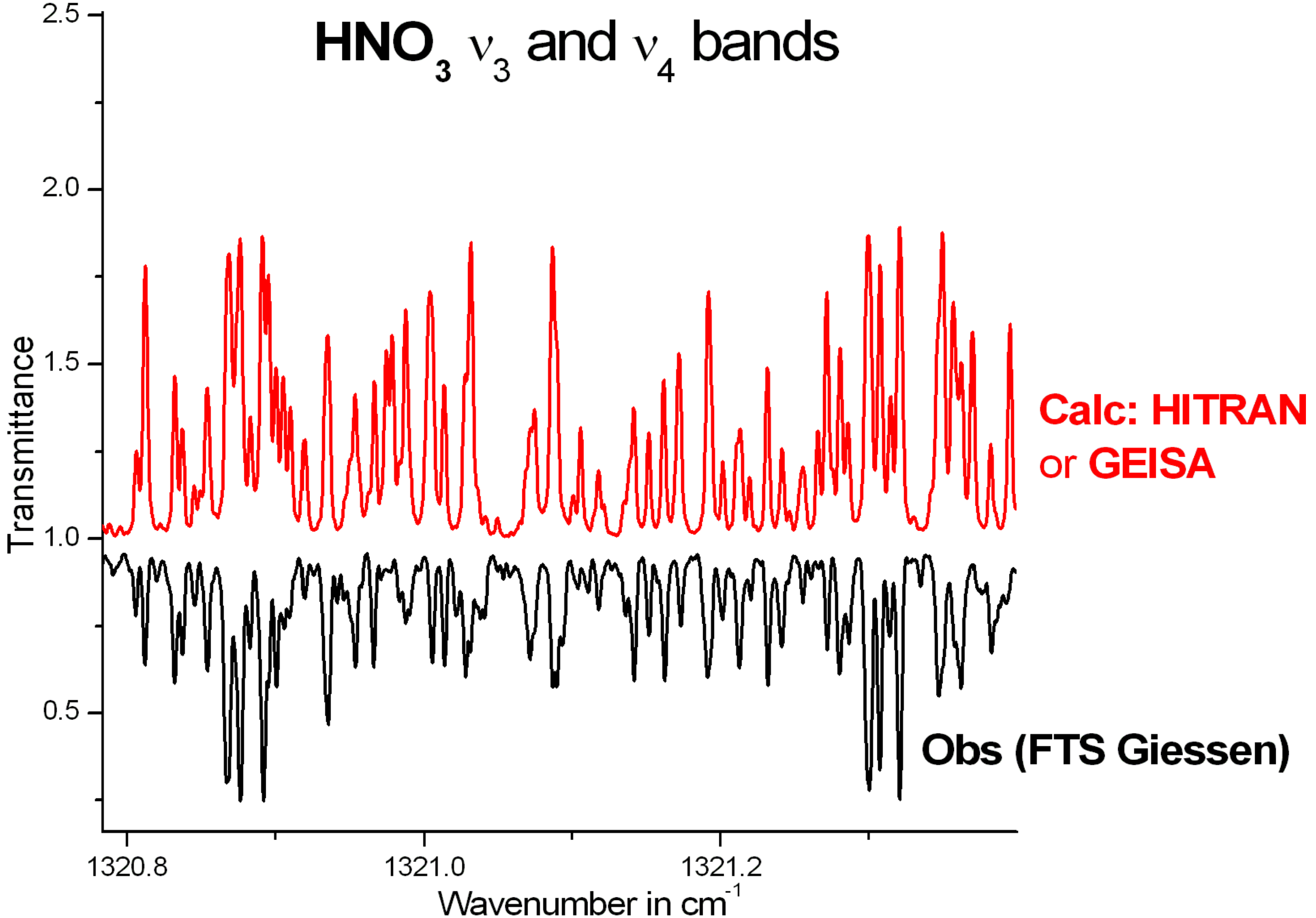
Well known high quality cross sections…

Laboratory FTS spectrum (Univ. Giessen)

Near 1320 cm^{-1}



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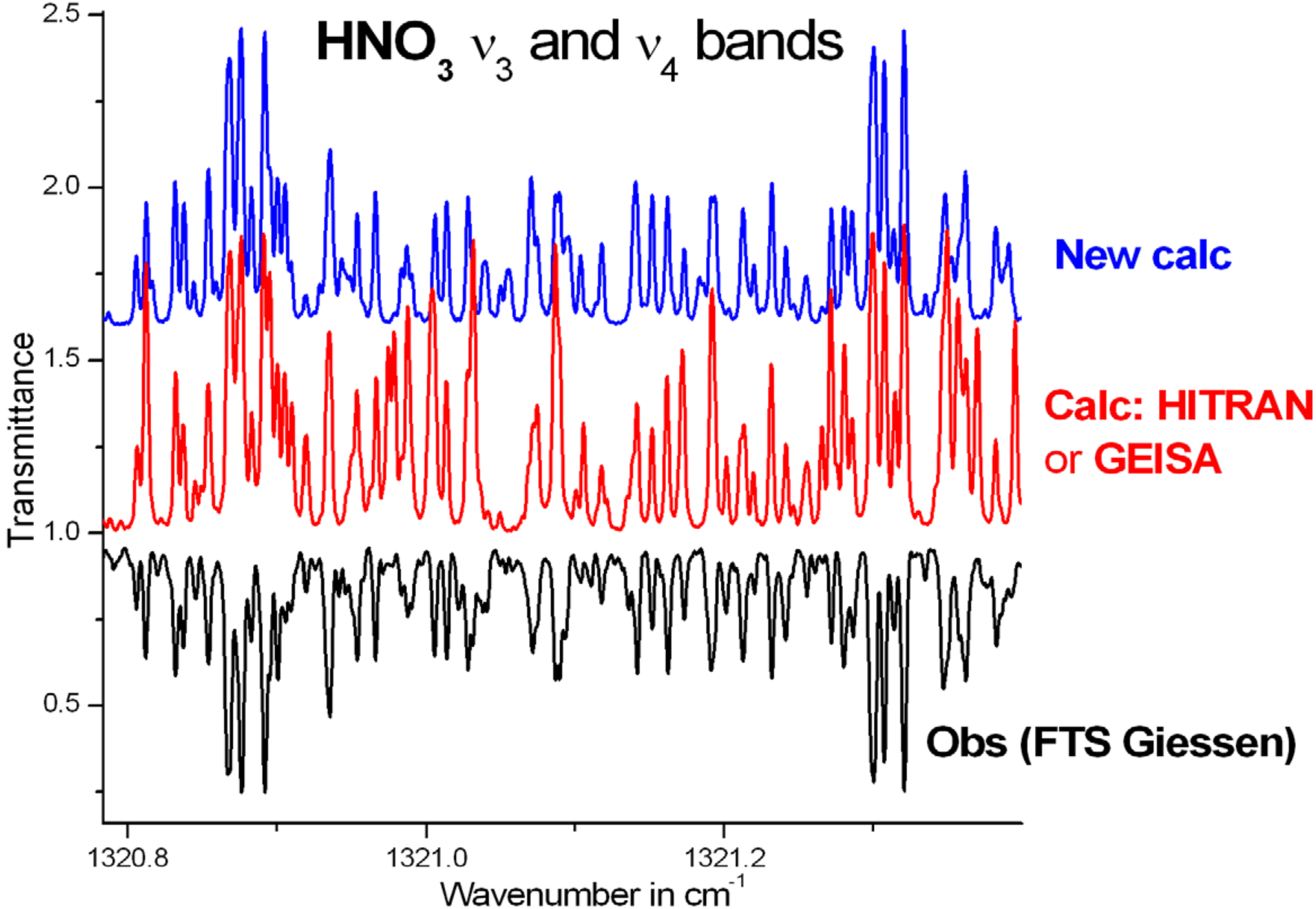
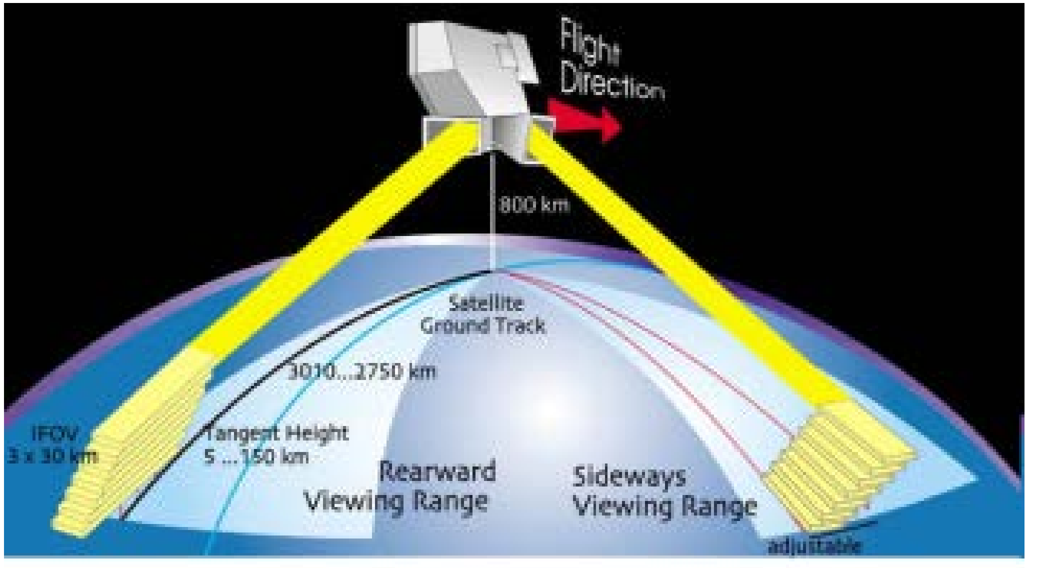
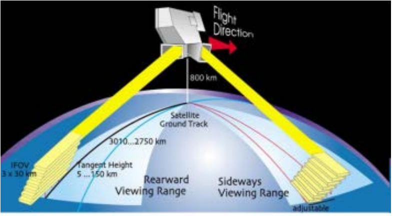


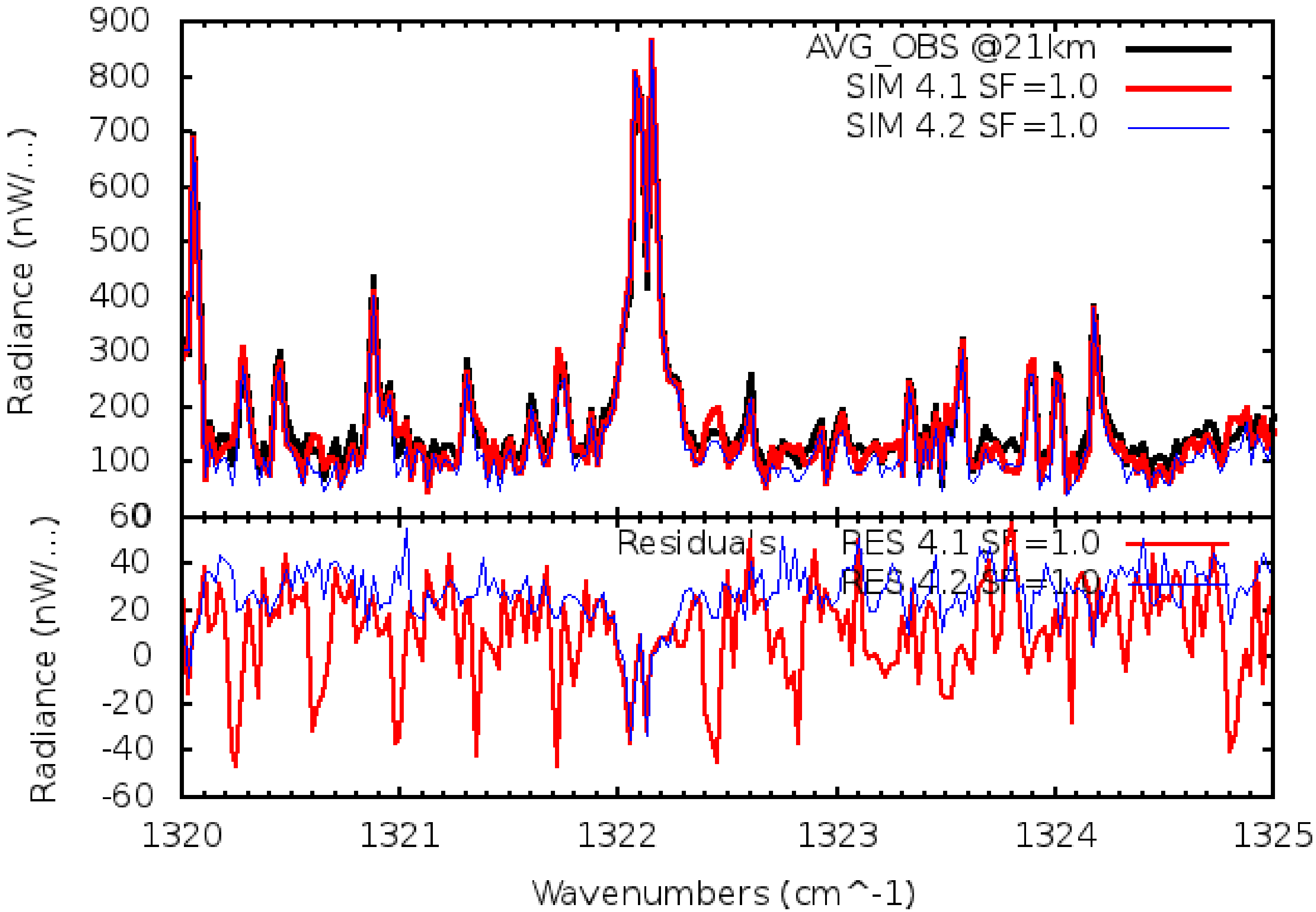
Validation using MIPAS spectra





HNO_3 detection by MIPAS at 1321 cm^{-1}

MIPAS orbit 2081, July 2002, 0.025 cm^{-1} resolution



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Obs

HITRAN-GEISA

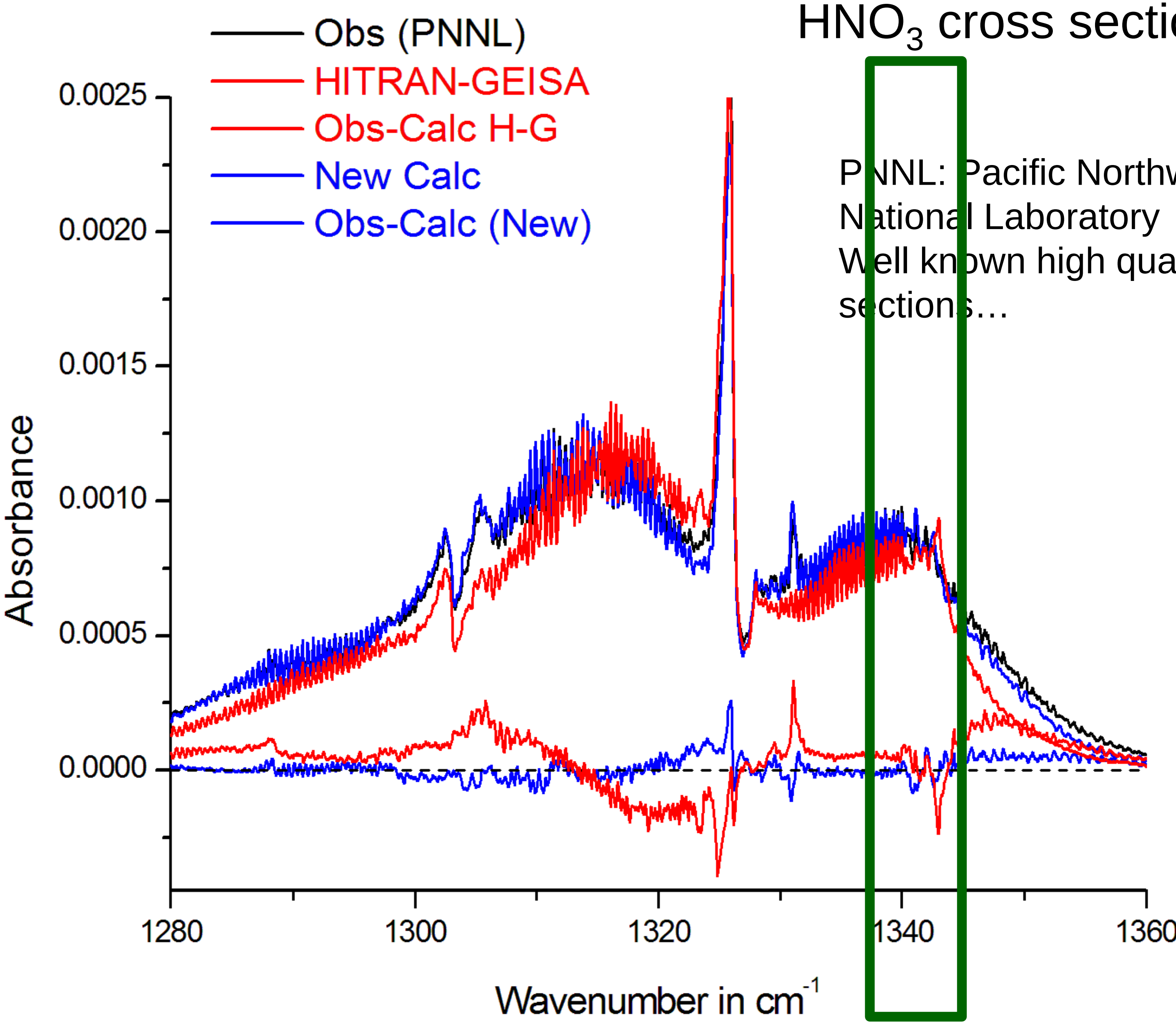
NEW

Obs-Calc

HITRAN-GEISA

NEW

HNO_3 cross sections



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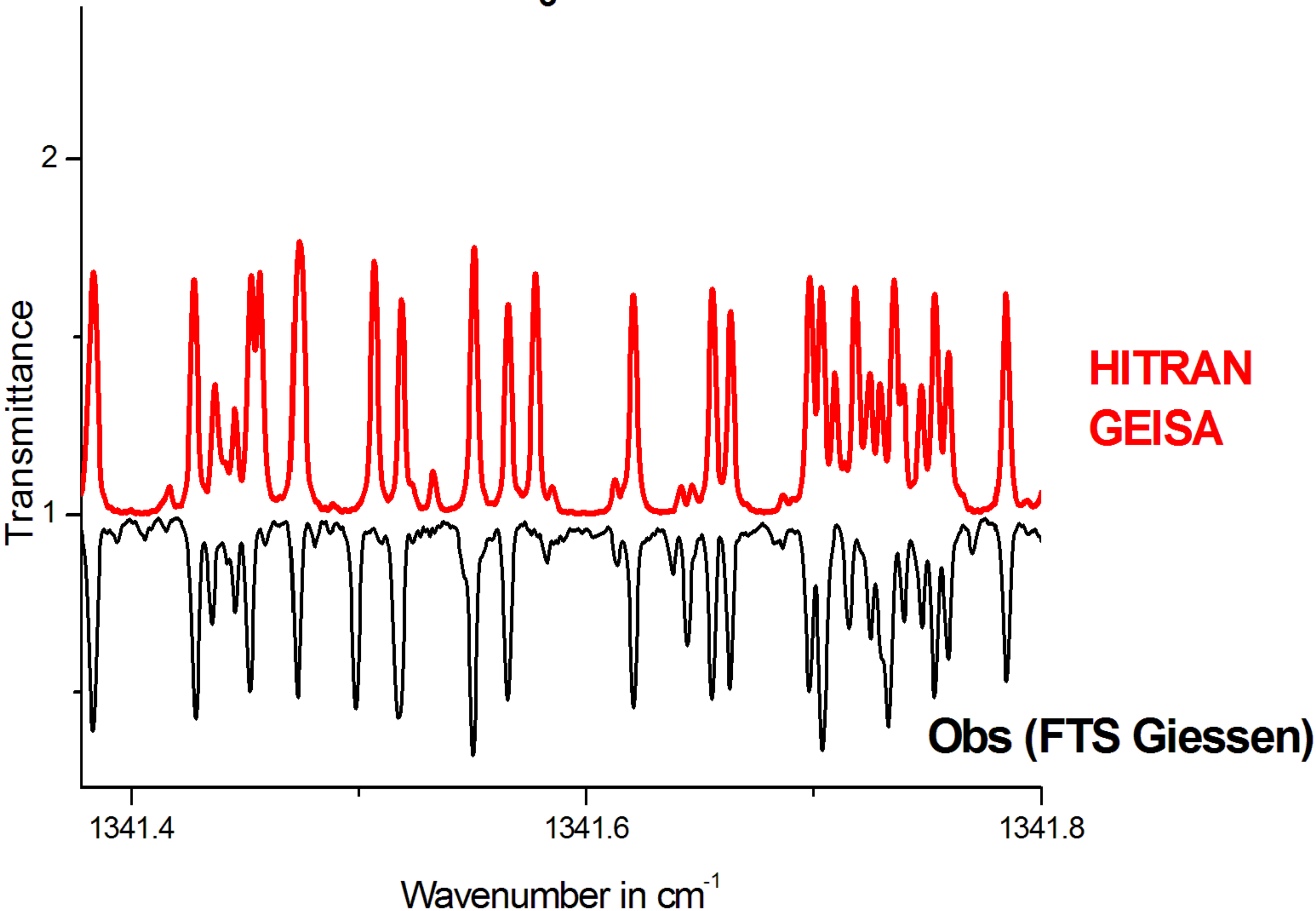
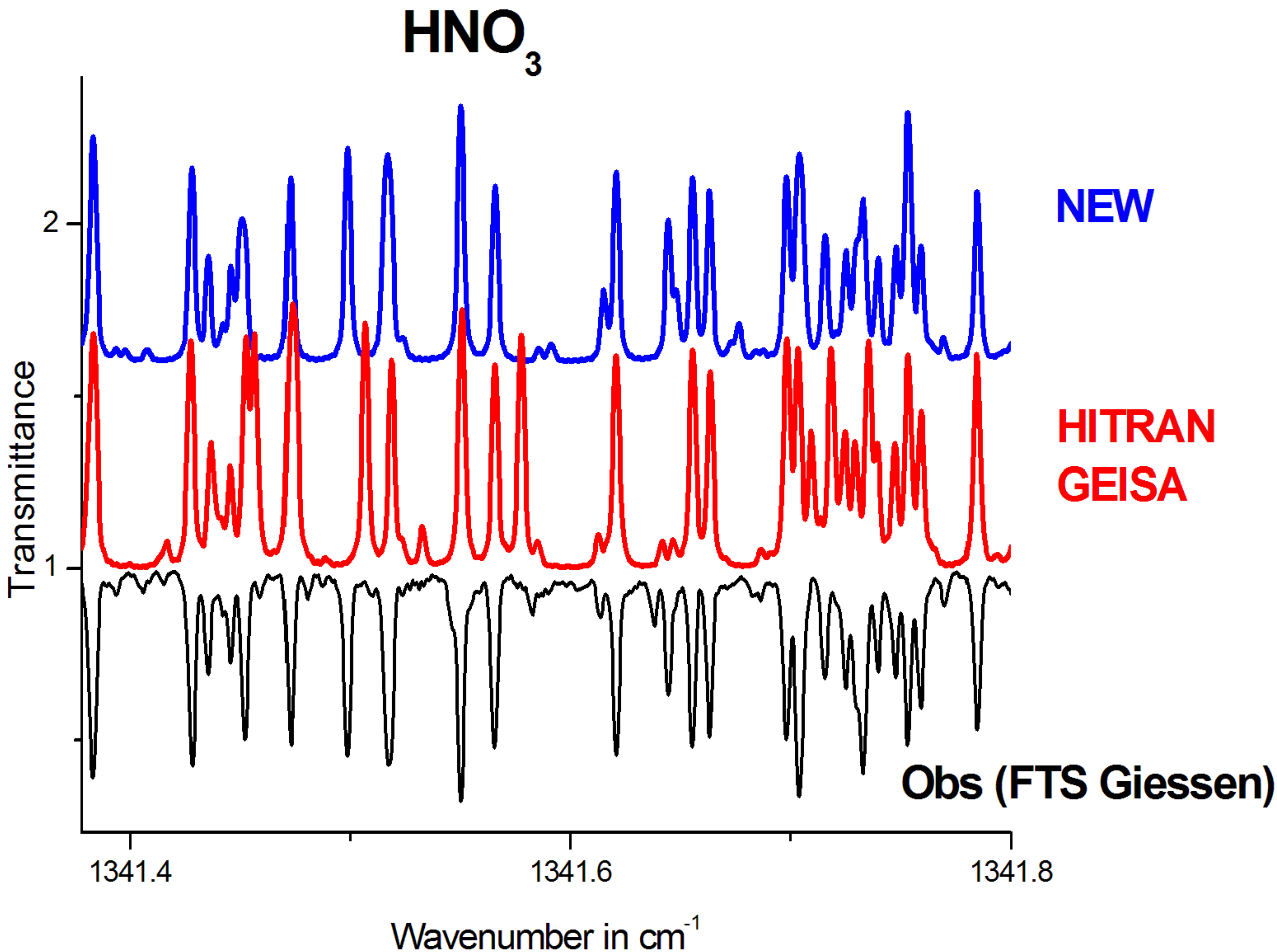
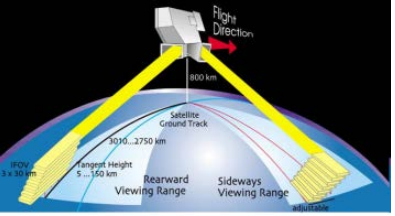
HNO_3



Transmittance
2
1
HITRAN
GEISA
Obs (FTS Giessen)
1341.4
1341.6
1341.8
Wavenumber in cm-1



HNO3
NEW
HITRAN
GEISA
Obs (FTS Giessen)
Transmittance
2
1
1341.4
1341.6
1341.8
Wavenumber in cm-1



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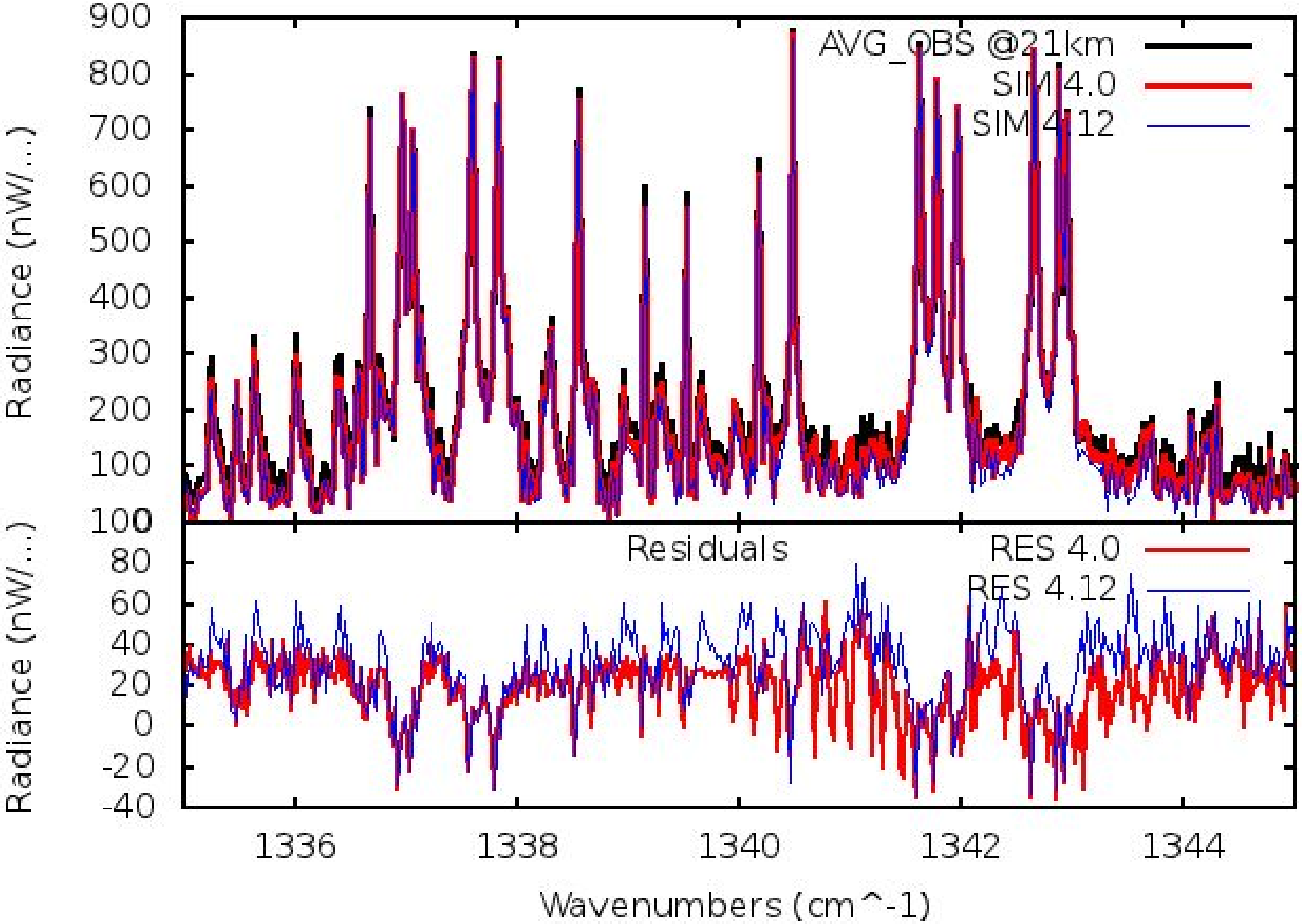
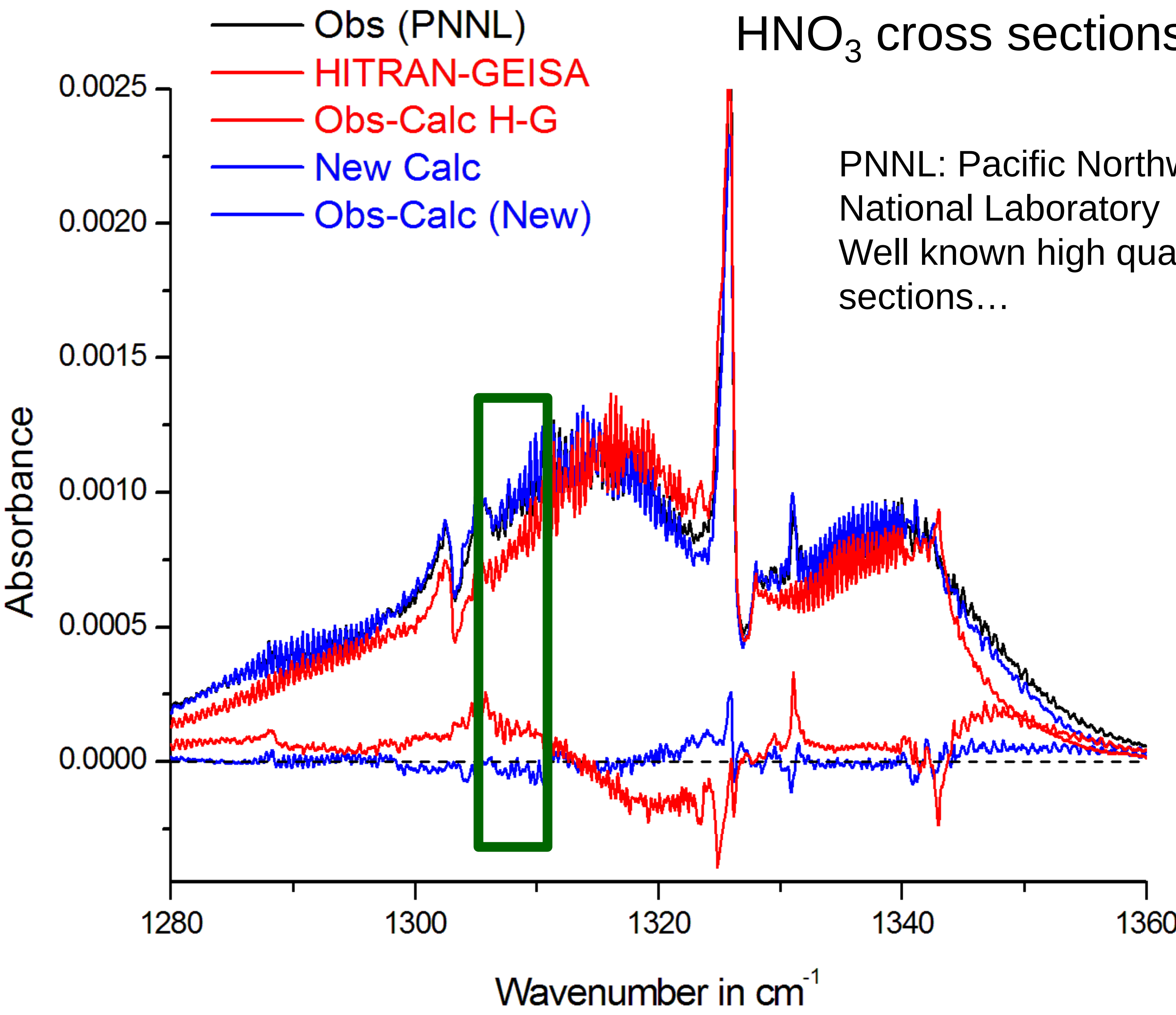


Obs
HITRAN
NEW

Obs-Calc
HITRAN
NEW

HNO_3 cross sections



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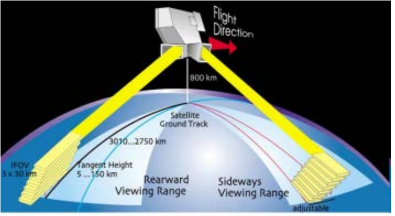
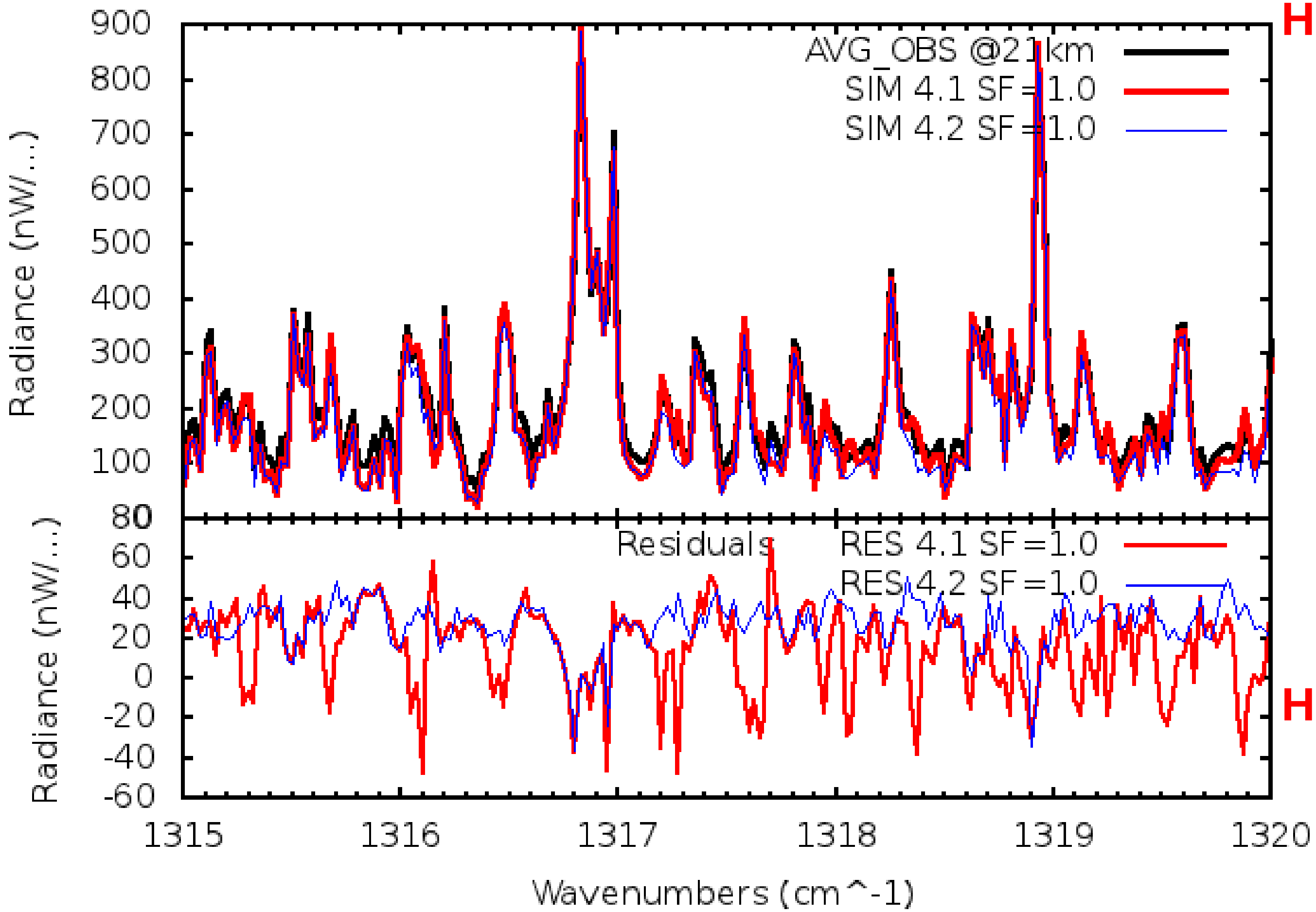


Obs
HITRAN-GEISA
NEW



Obs-Calc
HITRAN-GEISA
NEW

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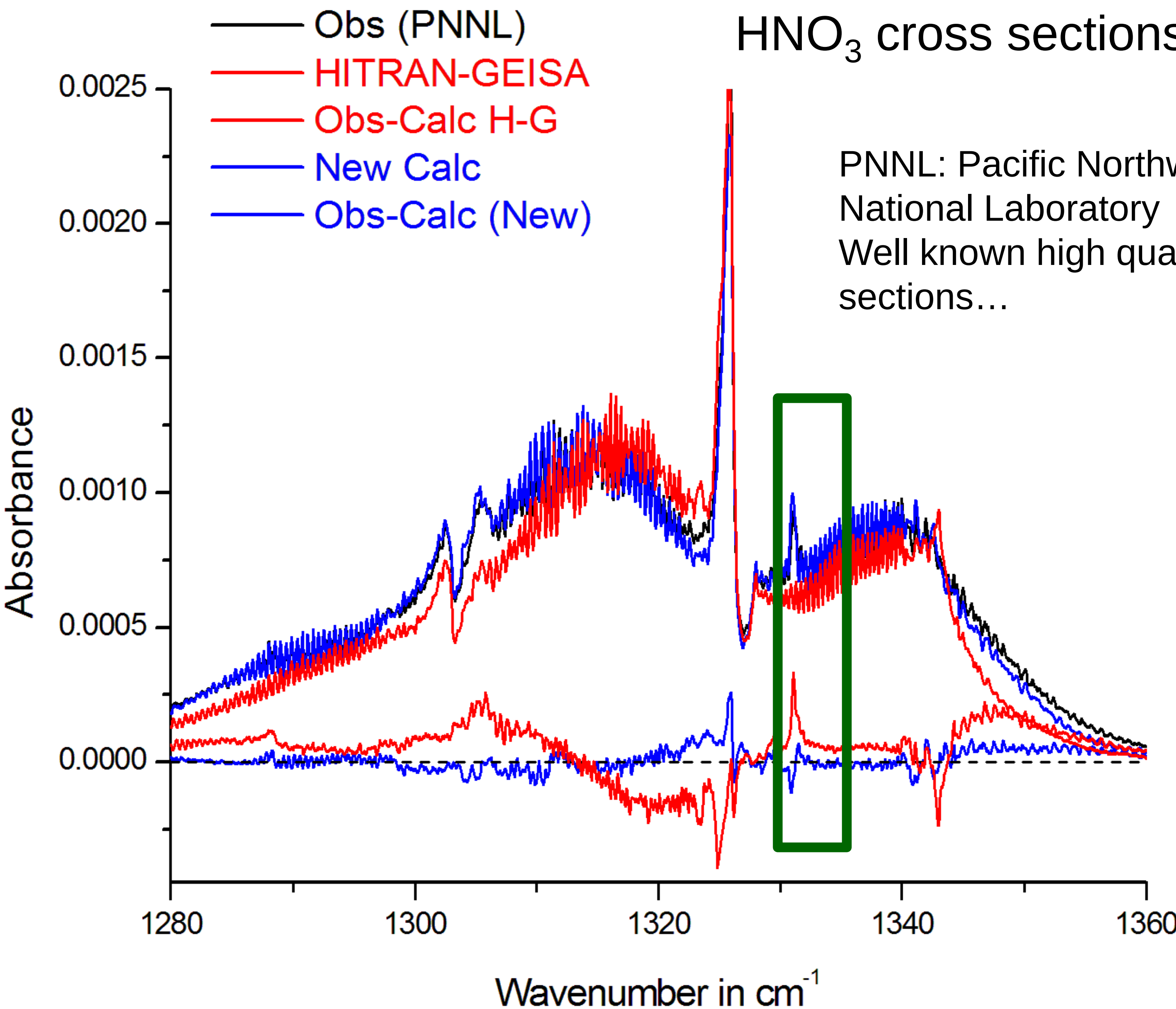
HNO_3 cross sections



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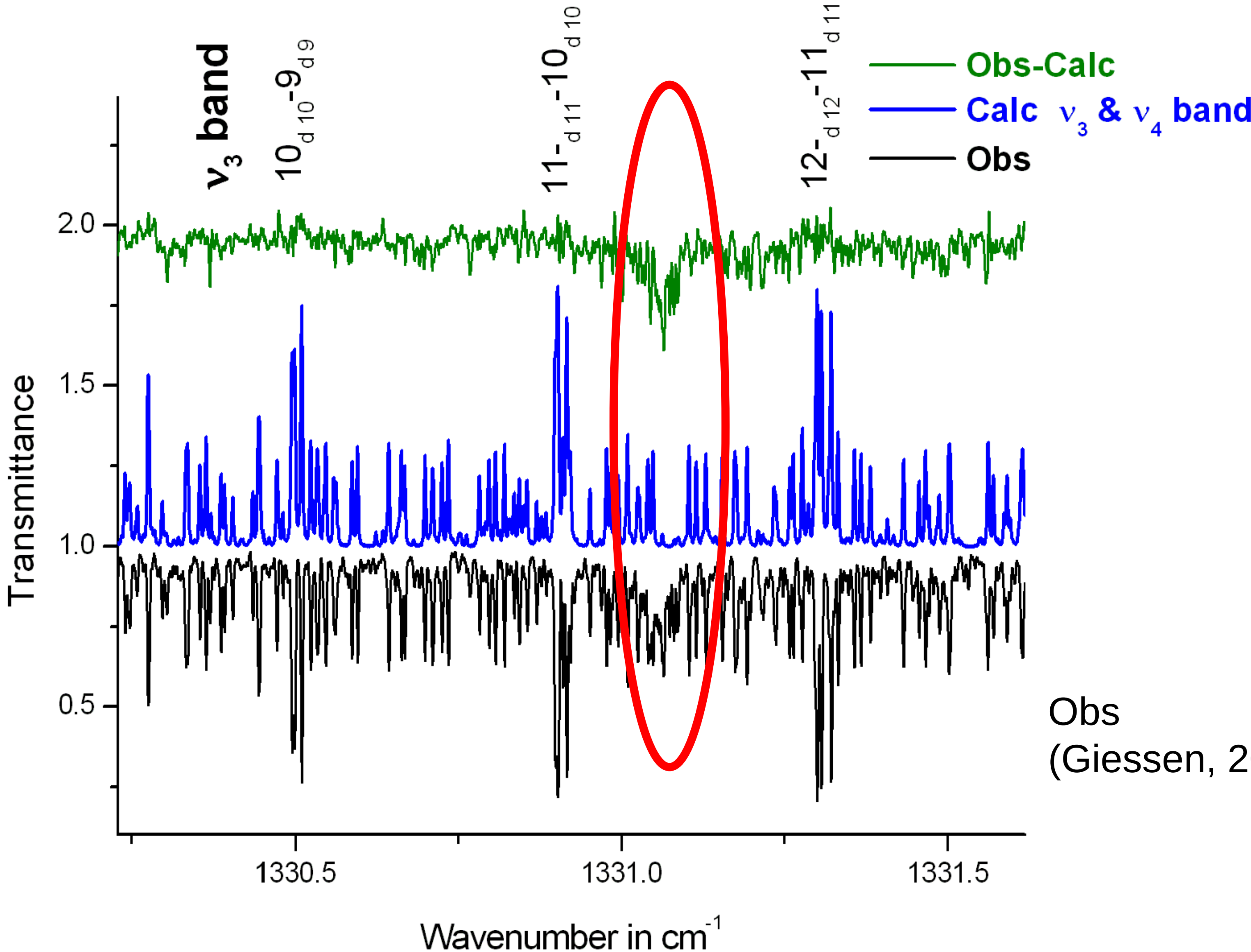
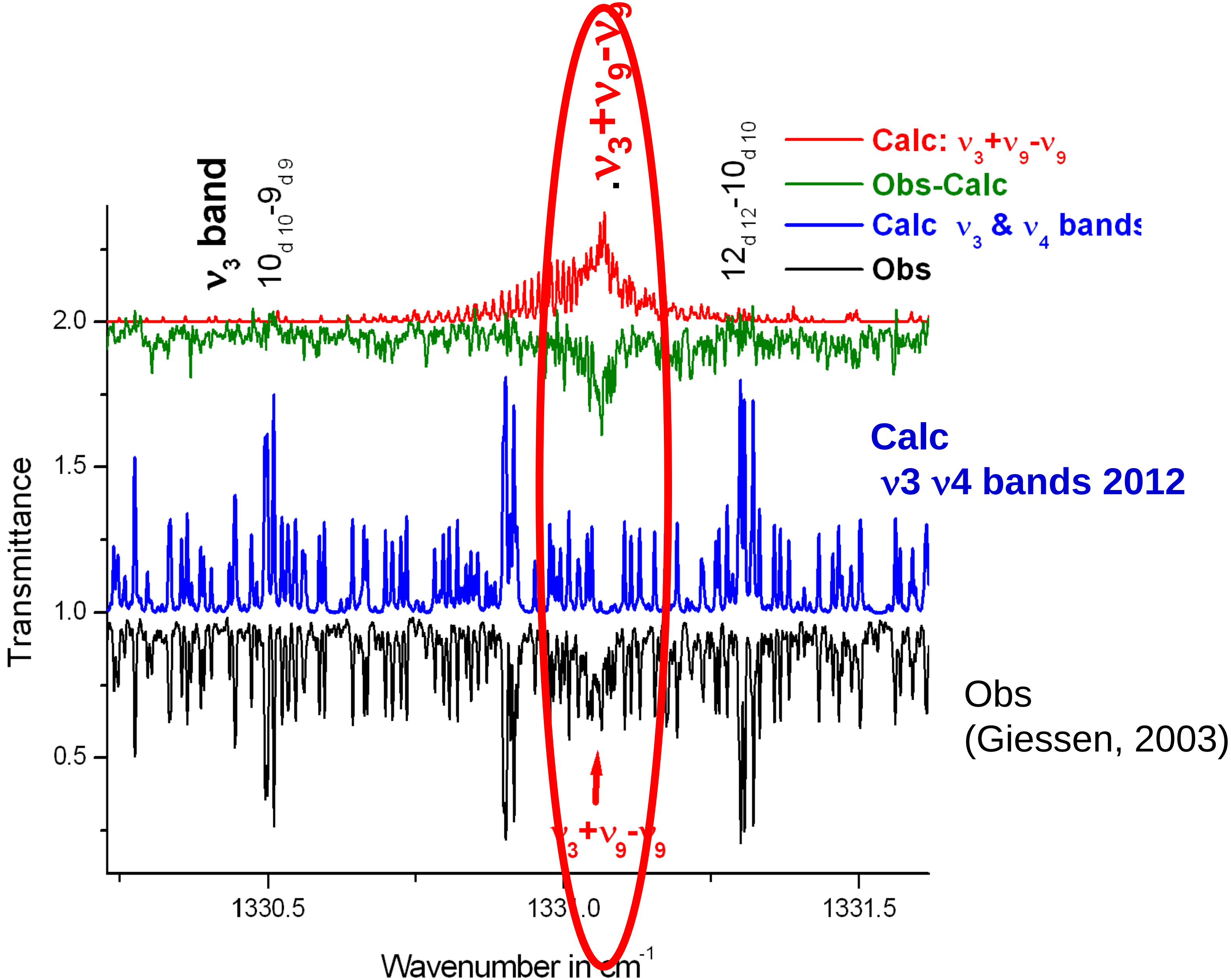
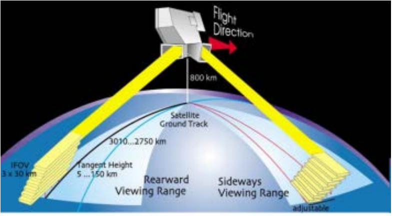


Obs
(Giessen, 2003)



ν3 band
10d 10-9d 9
ν3+ν9-ν9
12d 12-10d 10
Calc: ν3+ν9-ν9
Obs-Calc
Calc ν3 & ν4 bands
Obs
Calc
ν3 ν4 bands 2012
Obs
(Giessen, 2003)
Transmittance
2.0
1.5
1.0
0.5
1330.5
1331.0
1331.5
Wavenumber in cm-1
ν3+ν9-ν9



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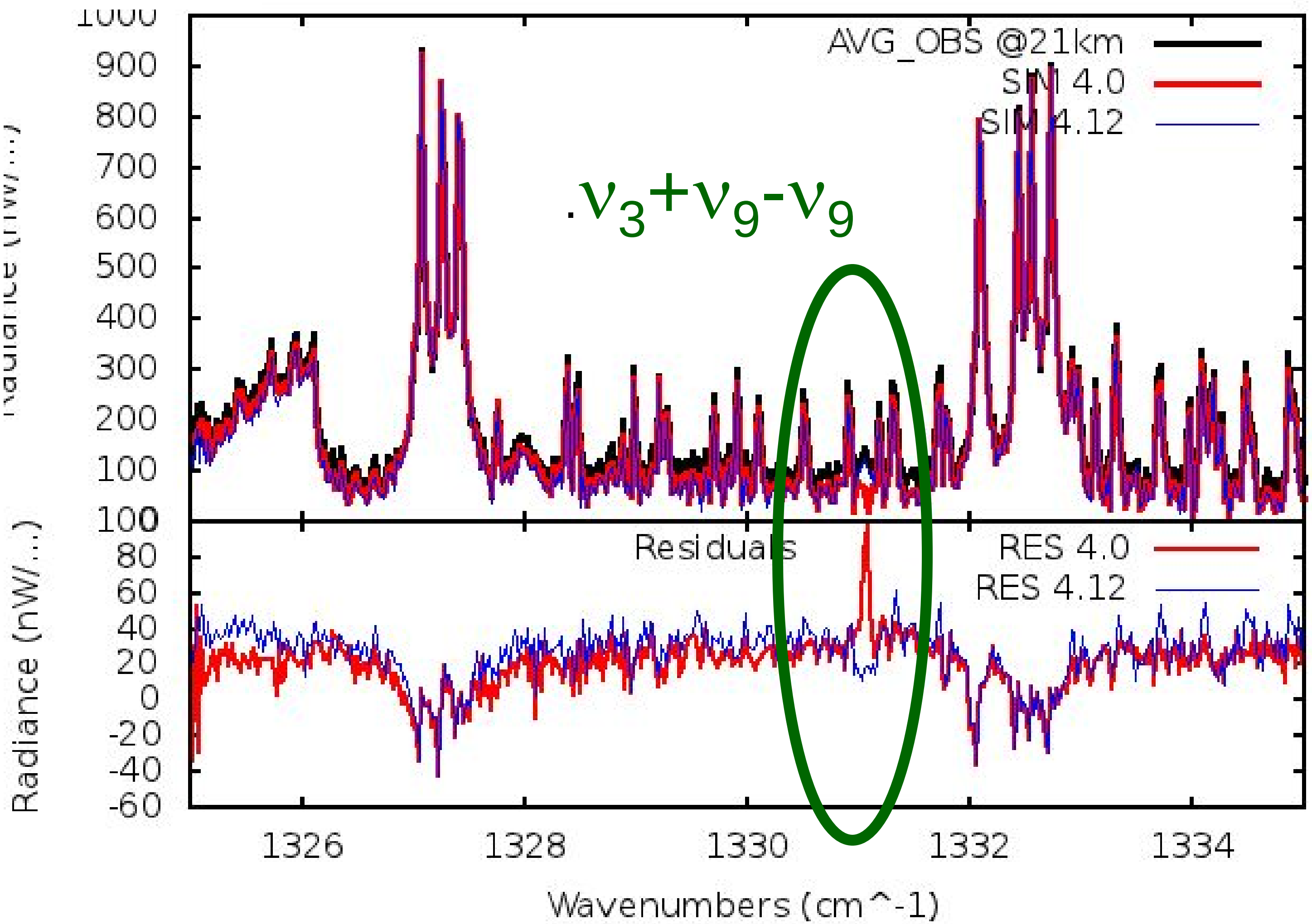


Obs
HITRAN
GEISA

NEW

Obs-Calc
HITRAN
GEISA

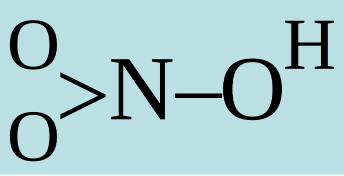
NEW

A.Perrin: IASI conference 2013

CONCLUSION

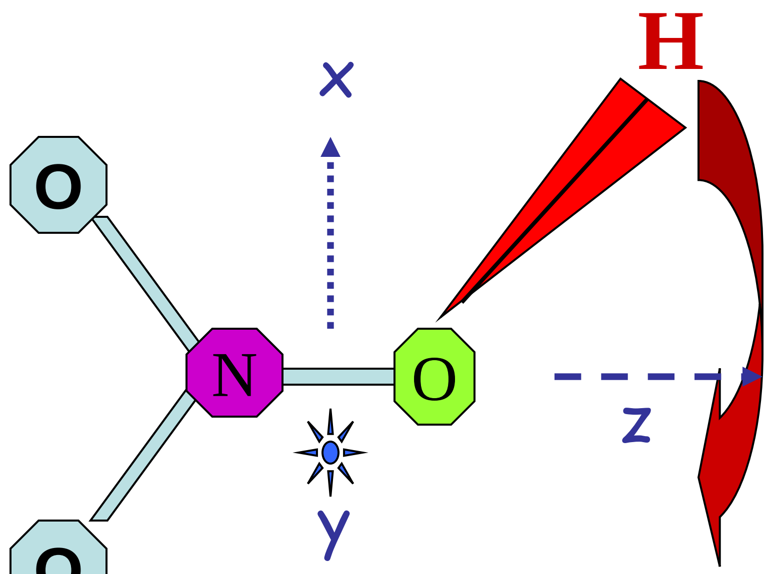
- A new study of the ν_3 et ν_4 bands of HNO_3 was performed
- It is necessary to account for resonances involving the $3\nu_9$, $2\nu_6$ et $\nu_5+\nu_9$. & $\nu_7+\nu_8$ dark bands.
- **Financial support from the CNES (Centre National de la Recherche Spatiale) through the programme "IASI-chimie: coordination des activités IASI pour l'étude de la chimie atmosphérique et du climat" is gratefully acknowledged.**

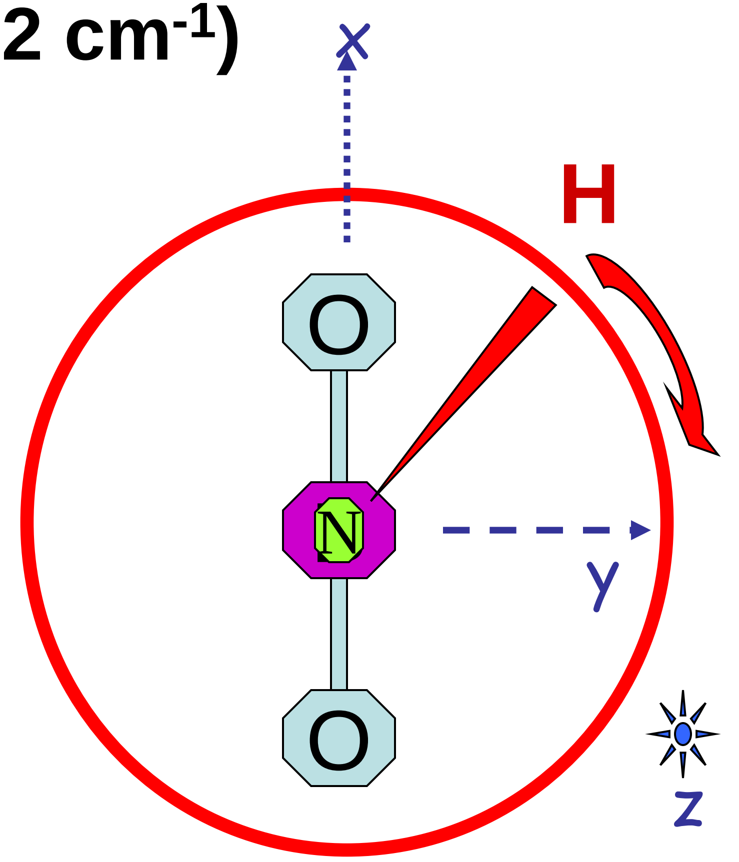
De l'espace pour la Terre



ν_9 torsion OH/NO_2

($3\nu_9$ at 1293.2 cm^{-1})





ν_9 torsion of OH/NO_2 ⇔ large amplitude

Splitting of ~ 0.06 cm^{-1} in 9^3