FORUM :Spectroscopy of minor constituents

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Overview

Introduction: Who are we ? What are we able to do ?

What can we do for this *FORUM* project ?

Molecules of first priority for *FORUM*

Reactive trace species to be considered in case of bush fires

Are we able to produce spectroscopic parameters for *FORUM* ?

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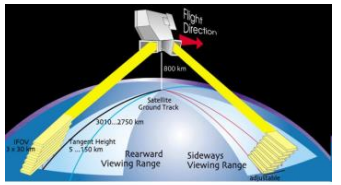
Who are we ?

- We (JM Flaud & Agnès Perrin) are specialists in theoretical molecular spectroscopy (positions & intensities) for infrared spectra of molecules of atmospheric interest

- Jean-Marie Flaud is from the LISA laboratory at Creteil.

- I (AP) belongs to the ABC(t) group at LMD laboratory (Ecole Polytechnique).
- Raymond Armante and myself are now responsible of the GEISA database. Some of my colleagues are well known specialists in line shape parameters (non Voigt, line mixing, continua)

What are we able to do ?



- For the MIPAS project, Jean-Marie Flaud and Marco Ridolfi are responsible of the definition of the MIPAS spectroscopic database.

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- I (AP) was (very) partially collaboring on the MIPAS project with Marco Ridolfi & Jean-Marie.

- I was also involved in several ESA project with S.Bühler.

IASI « Nouvelle Génération in ≈2022)

As far as IASI-NG is concerned, we are using **MIPAS** spectra to

« validate » the line by line lists for the future IASI>NG

(on going collaboration with the **Bologna group (Marco Ridolfi)**

Atmos. Meas. Tech., 9, 2067–2076, 2016
www.atmos-meas-tech.net/9/2067/2016/
doi:10.5194/amt-9-2067-2016

Agnès Perrin[1], Jean-Marie Flaud[1], Marco Ridolfi[2,3], Jean Vander Auwera[4], and Massimo Carlotti[5]

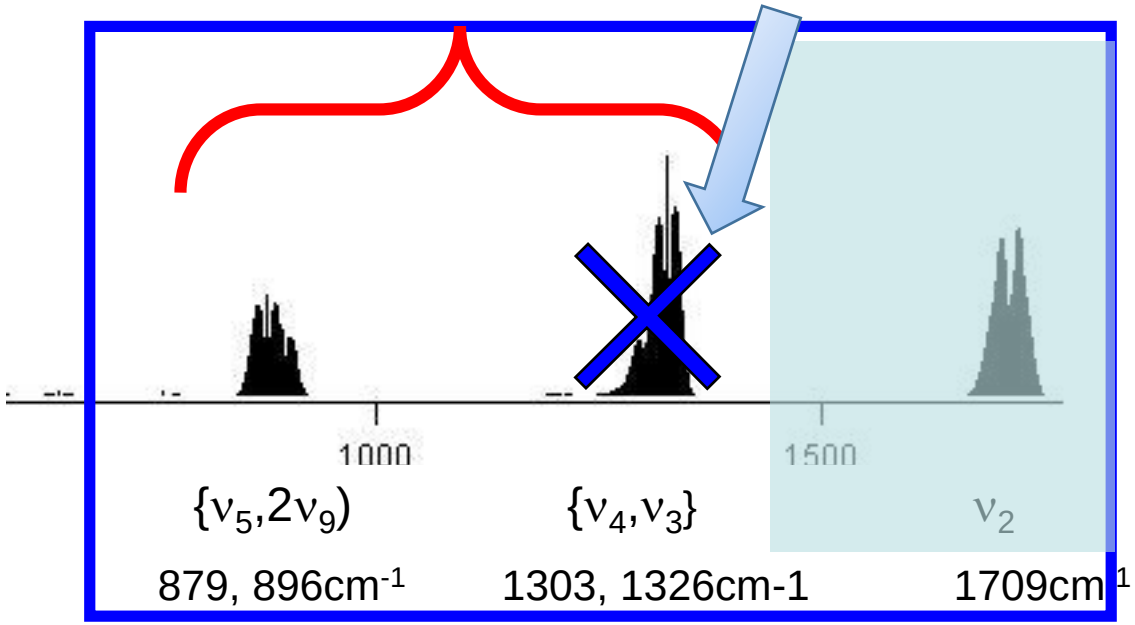
MIPAS database: new HNO_3 line parameters at 7.6 µm validated with MIPAS satellite measurements

IASI on METOP

Preparation of **IASI-New Generation** (2021)

HNO_3

Bad quality of the HNO3 spectroscopic paramaters at 7.6 µm



11µm 7.6µm

5.85 µm (in water)

Goal for **IASI -NG**: to enable simultaneous detection of HNO_3 both at 11 µm & 7.6 µm using MIPAS spectra

Strategy for HNO_3 **11 µm** & 7.6 µm bands :

¤ We kept the **11 µm** band line parameters as they are in GEISA or HITRAN

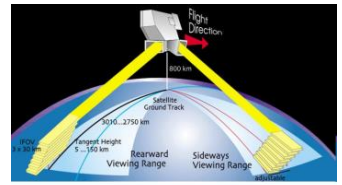
¤ For the 7.6 µm region: new linelist (better line positions & intensities)

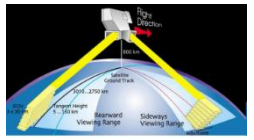
¤ 7.6 µm region improved line parameters during a laboratory spectroscopic analysis (A.P. & JMF). :

(i) Laboratory spectra recorded in well defined conditions

(ii) theoretical computations of line positions & relative line intensities.

¤ **Satellite validation (**by **M.Ridolfi @ Bologna)** using MIPAS spectra: Intercalibration of line intensities for the new 7.6 µm linelist relatively to **11 µm band**





Marco Ridolfi

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Obs (MIPAS orbit 04712 24 january 2003)
Obs-Calc **New line list**
Obs-Calc **GEISA or HITRAN**

11 µm
Not updated

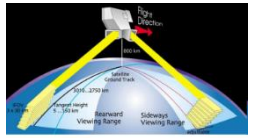
7.6 µm
updated

Limb radiance (nW/(cm^2 sr cm^{-1}))

1500
1200
900
600
300
0

870 880 890 1310 1320 1330

Wavenumber in cm^{-1}



M.Ridolfi & M.Carlotti

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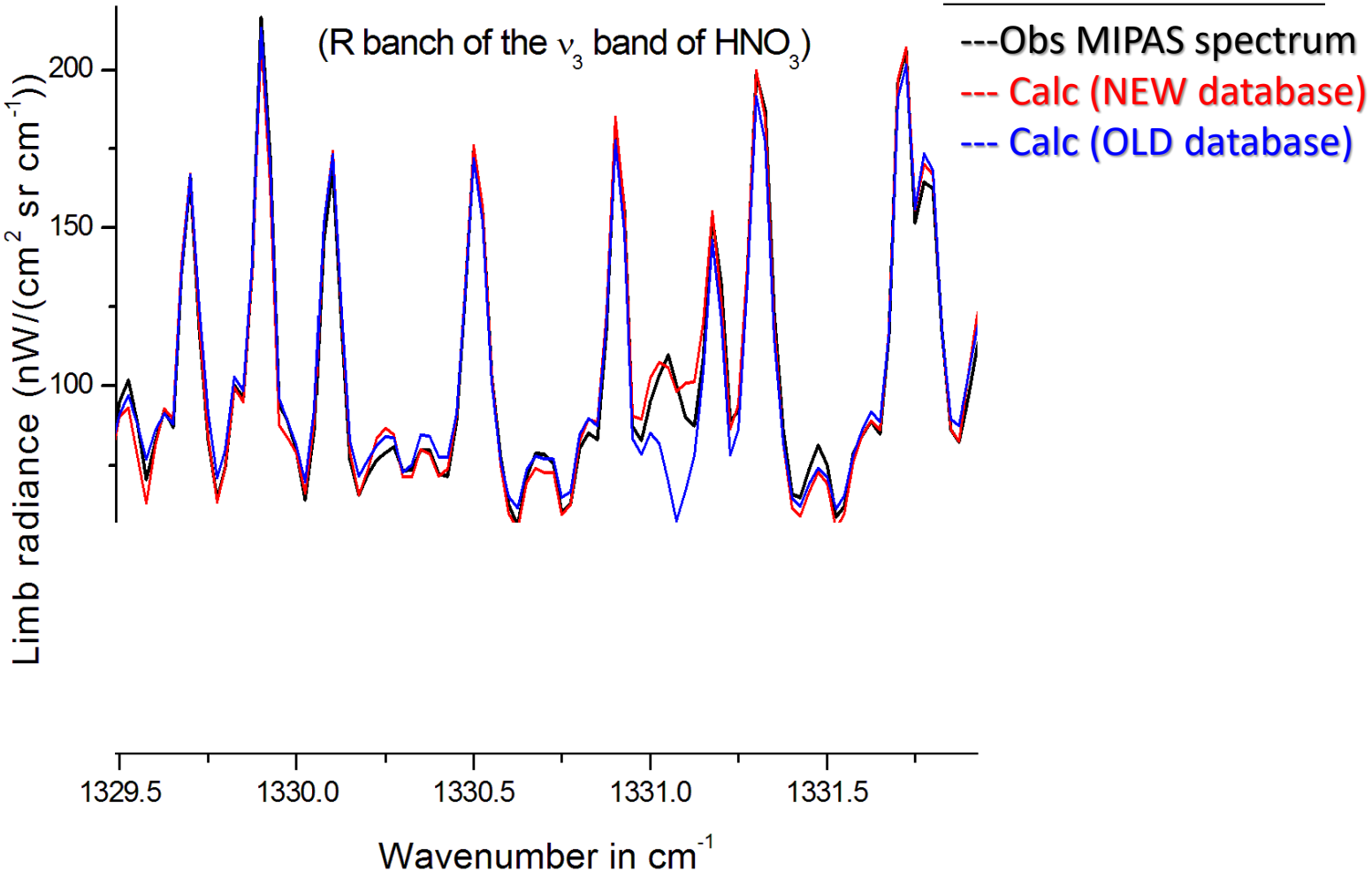
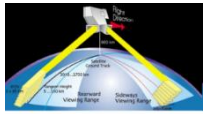
Obs (MIPAS orbit 04712 24 january 2003)





HNO_3 concentration profile (v.s. altitude) using the « old » database…

7.6 µm
⇔ 11 µm

M.Ridolfi & M.Carlotti

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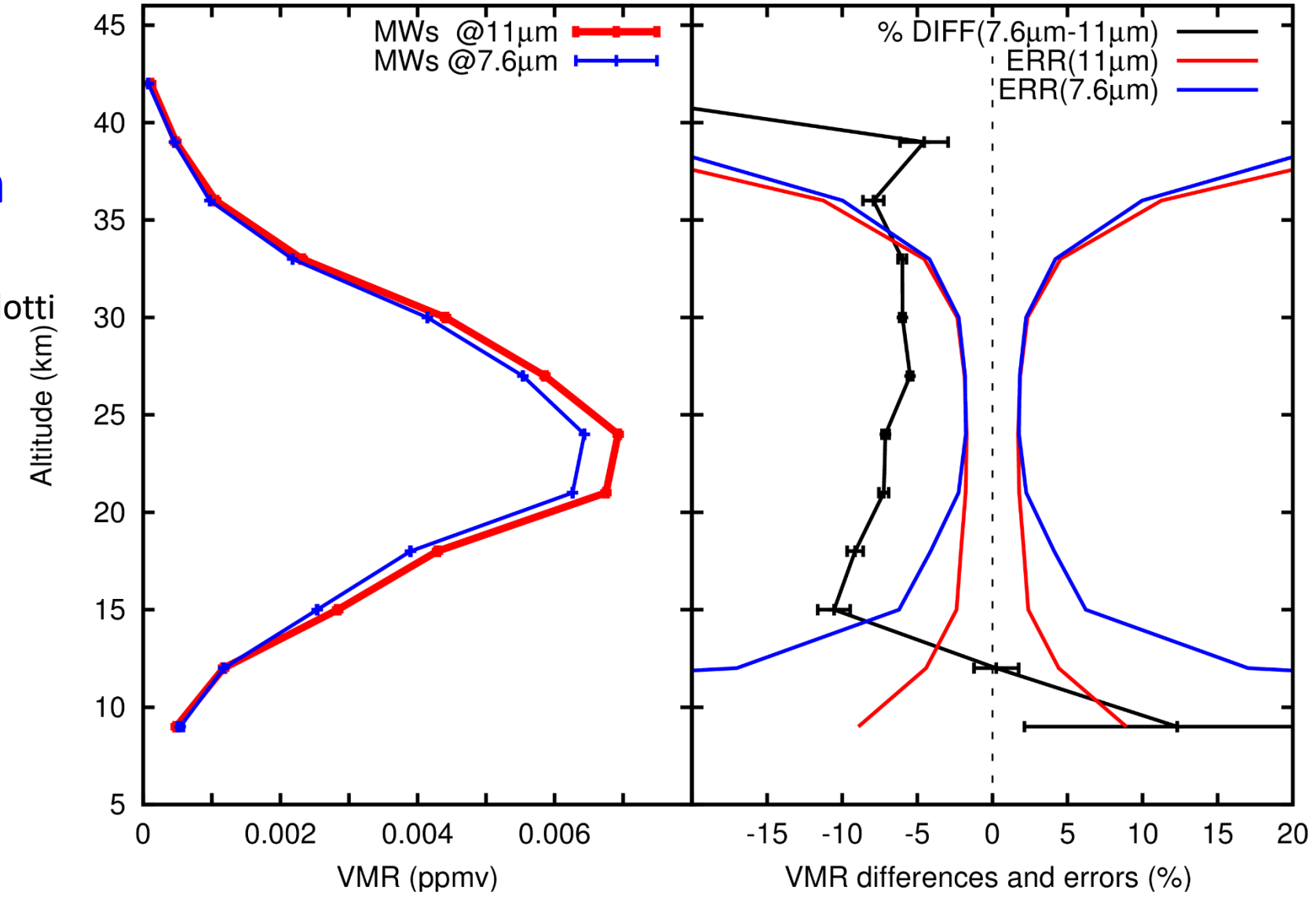
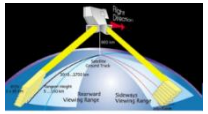
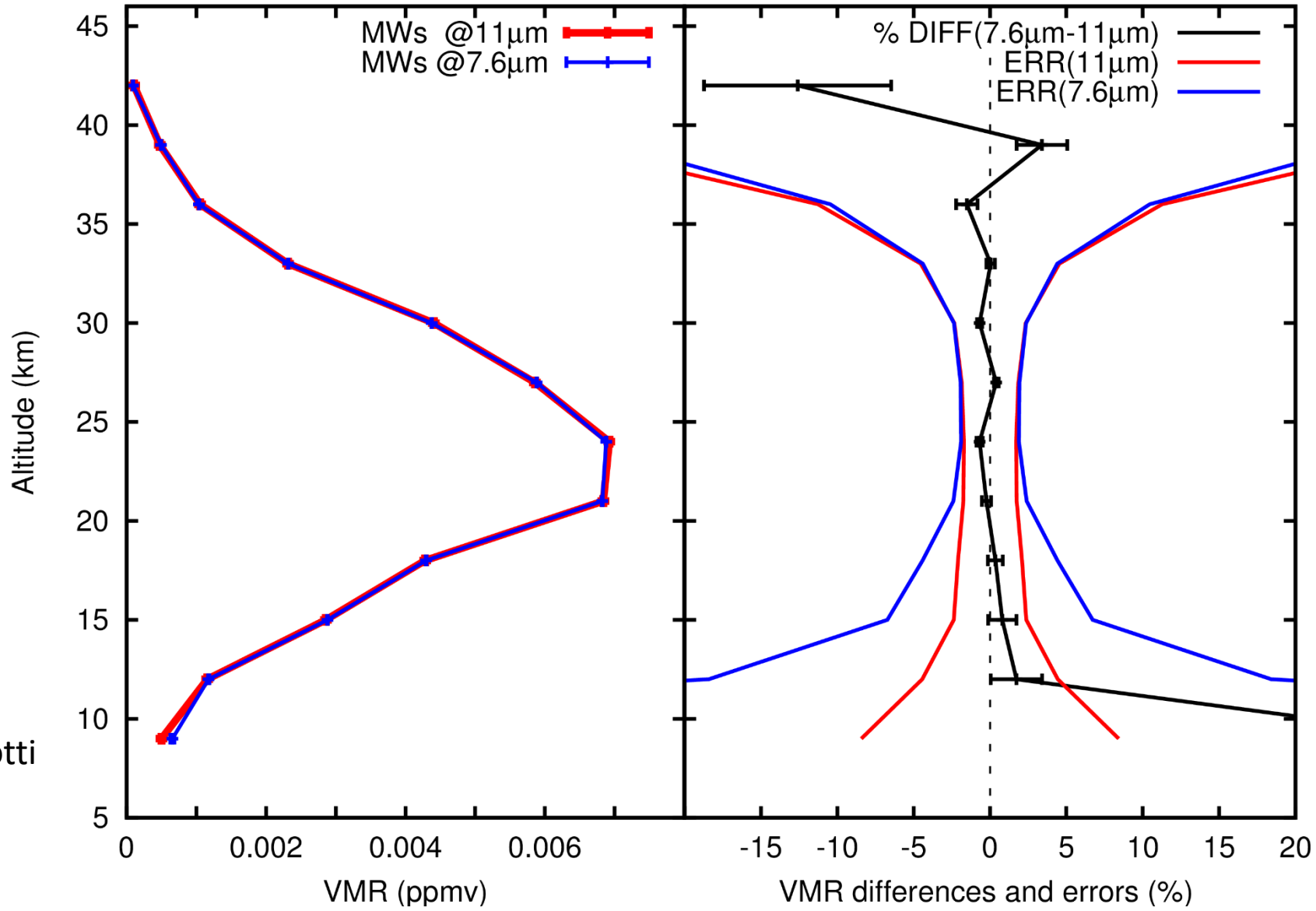


Before…



HNO_3 concentration profile (v.s. altitude) using the « new » database…

7.6 µm
⇔ 11 µm



After …

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M.Ridolfi & M.Carlotti

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Introduction: Who are we ? What are we able to do ?

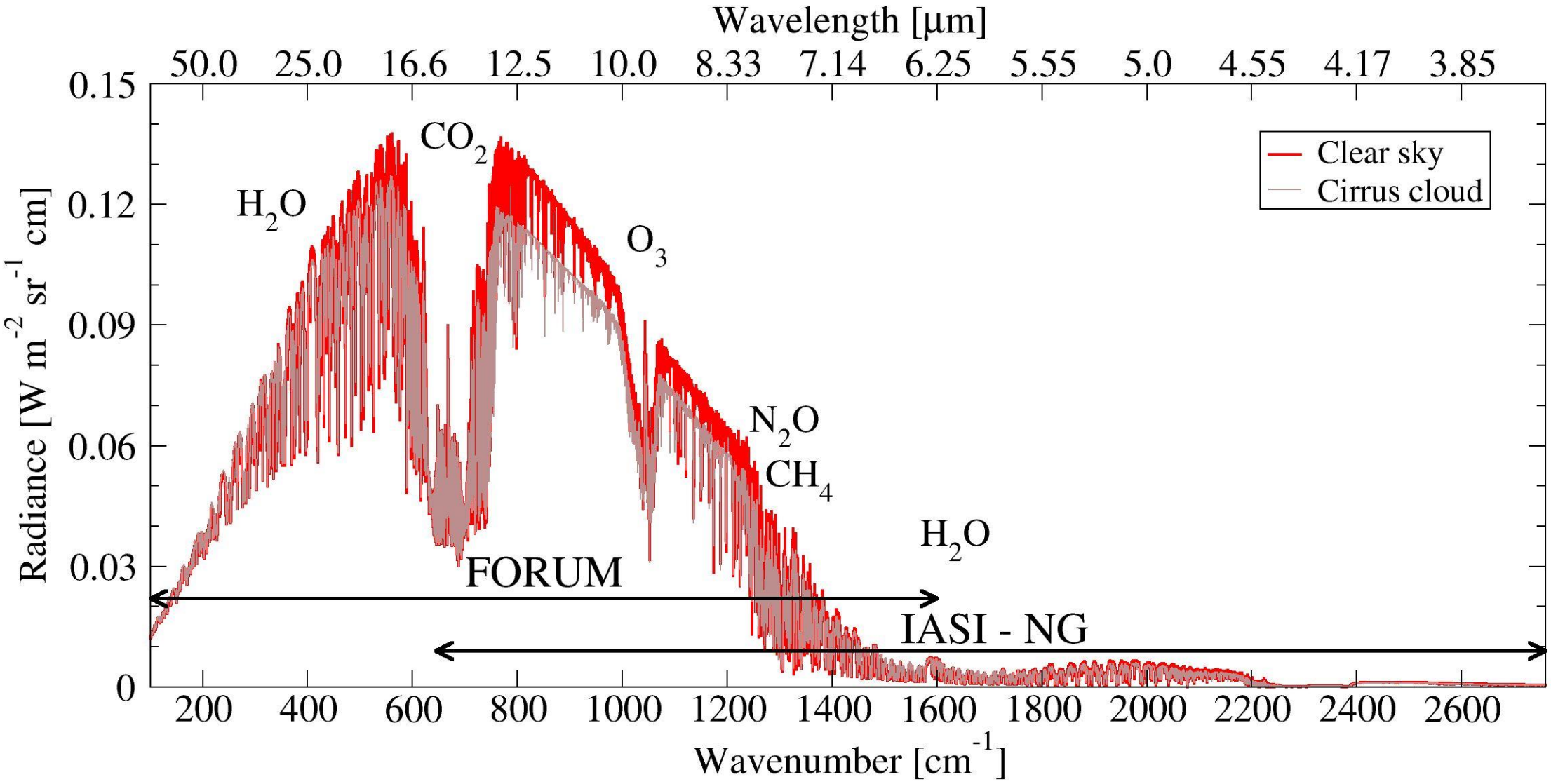
What can we do for this *FORUM* project ?

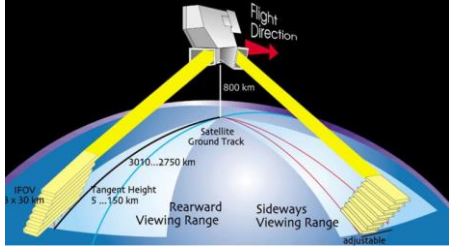
Molecules of first priority for *FORUM*

Reactive trace species to be considered in case of bush fires

Are we able to produce spectroscopic parameters for *FORUM* ?

FORUM versus IASI-NG





Several spectroscopic studies were performed recently for IASI-NG. The **MIPAS** (700 – 2300 cm^{-1}) spectra **Refs: see the co-authors in this room)** can be « used » for the validation of the database for **IASI-NG**

IASI-NG and *FORUM* ≠ MIPAS

For ***FORUM*** informations are requested for

(i) the molecules of **tropospheric interest** (which were not always considered by MIPAS)

(ii) « line by line » parameters are preferred (if possible) to cross sections parameters

→ (they lead to better atmospheric retrievals)

(iii) the line shape (and continua) for molecules present in the troposphere need precise description

FORUM is covering the **150- 1400 cm^{-1}** spectral region and **none of the recent satellite instruments** (**MIPAS, IASI or ACE-FTS)** are covering the low frequency region **120 cm^{-1} < σ < 700 cm^{-1}**.

We have to provide **accurate spectroscopic parameters** for preparing this mission

Unplanned observations ????

IASI (instrument with a rather weak resolution $\mathscr{R}$=0.5 cm^{-1})

dedicated for (mainly) meteorological applications

(température, humidity & eventually ozone columns)

During the preparation of the IASI mission (before the launching of METOP-A in 2006) a spectroscopic linelist was prepared for a restricted list of molecules (Water, CO_2, O_3, N_2O, CO, methane, NO)

IASI: « unplanned » observations: acid rains (formic acid, **HCOOH**), « **NH3** global map , detection of **SO_2** in **volcanic plumes**, (cf *LATMOS* et *ULB-Bruxelles*), etc…

Strategy: short review of the status of the spectroscopic parameters for molecules of interest for FORUM

- We search for molecules of atmospheric interest which have a rather strong infrared signature in the spectral range of FORUM (200-1300 cm^{-1}).
- At this level, we do NOT try to identify the possible interferences of the infrared signature of these species with absorption due to species with strong IR signature (water, CO_2, etc…)

In this talk, I did not consider the problem of continua (water, N_2-N_2, O_2-N_2 etc) or of indices (water ice…).

The first investigation concerns molecules observed in IASI spectra in so-called «regular conditions »

Journal of Quantitative Spectroscopy & Radiative Transfer 182 (2016) 128–157

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Physical inversion of the full IASI spectra: Assessment of atmospheric parameters retrievals, consistency of spectroscopy and forward modelling

G. Liuzzi [a], G. Masiello [a], C. Serio [a,*], S. Venafra [a], C. Camy-Peyret [b]

(H_2O, HDO, CO_2, CO, CH_4, O_3, N_2O, CO, N_2O, OCS, HNO_3, CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), and CF_4)

Can we detect these species with FORUM ??

….second, we look for molecules identified in « special » conditions in IASI spectra:

GEOPHYSICAL RESEARCH LETTERS, VOL. 38, L10802, doi:10.1029/2011GL047271, 2011

Thermal infrared nadir observations of 24 atmospheric gases

Lieven Clarisse,[1] Yasmina R'Honi,[1] Pierre-François Coheur,[1] Daniel Hurtmans,[1] and Cathy Clerbaux[1,2]

Received 25 February 2011; revised 8 April 2011; accepted 10 April 2011; published 21 May 2011.

….(mostly) short-lived trace gases: sulfur dioxide (SO_2), ammonia (NH_3), OCS, methanol (CH_3OH), formic acid (HCOOH), ethene (C_2H_4) and PAN ($C_2H_3O_5N$) … observable above the Po valley or during Volcano eruptions

… and rare reactive trace gas species … (like nitrous acid, furan, acetylene, propylene, acetic acid, formaldehyde and hydrogen cyanide, acetylene) , observable during Australian bush fires of February 2009.

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Except for Water & associated continua (S.Buëhler , E.Hegglin, M. Mlawer)

Water & CO_2 spectroscopy (C.Serio et al.)

Reactive trace species to be considered in case of bush fires

Are we able to produce spectroscopic parameters for *FORUM* ?

Molecules which do not have a strong infrared signature in the FORUM spectral range

. CO, O_2, N_2, NO, OH, HF, HCl, HI: => not relevant

OCS (carbonyl sulfide)

⇒ Strongest signature is at 2062 cm^{-1} (not usable by ***FORUM***) compared to IASI-NG !

⇒ For details: see Camy-Peyret, Liuzzi, Masiello, Serio, Venafra, Montzka, JQSRT 201 (2017) 197-208

- Nitrous oxide (N_2O) ⇒ Probably not observable by FORUM

For N_2O: Band ν_2 (589cm^{-1}) , ν_3 (1285 cm^{-1}) , ν_1 (2224 cm^{-1})
Intensities ratio: 0.10 / 1. / 5.7
in 10^{-17}cm^{-1} cm^{-1}/(molecule.cm^{-2})

Evidence of line mixing effets (see C. Camy-Peyret for details)

- Nitrogen dioxide: NO_2 ⇒same infrared signature as IASI-NG

For NO_2: Band ν_2 (750) , ν_1 (1320 cm^{-1}) , ν_3 (1617 cm^{-1})
Intensities ~ 0.57 / 0.005 / 5.8
in 10^{-17}cm^{-1}/(molecule.cm^{-2})

Ozone (O_3)

$\Rightarrow$same infrared signature as for IASI-NG

For $^{16}O_3$: Band ν_2 **(700.93)** , ν_3 **(1042.08 cm^{-1})** $\Leftrightarrow$ ν_1 **(1103.14 cm^{-1})**

Intensities: **0.59** **14.1** **0.54**

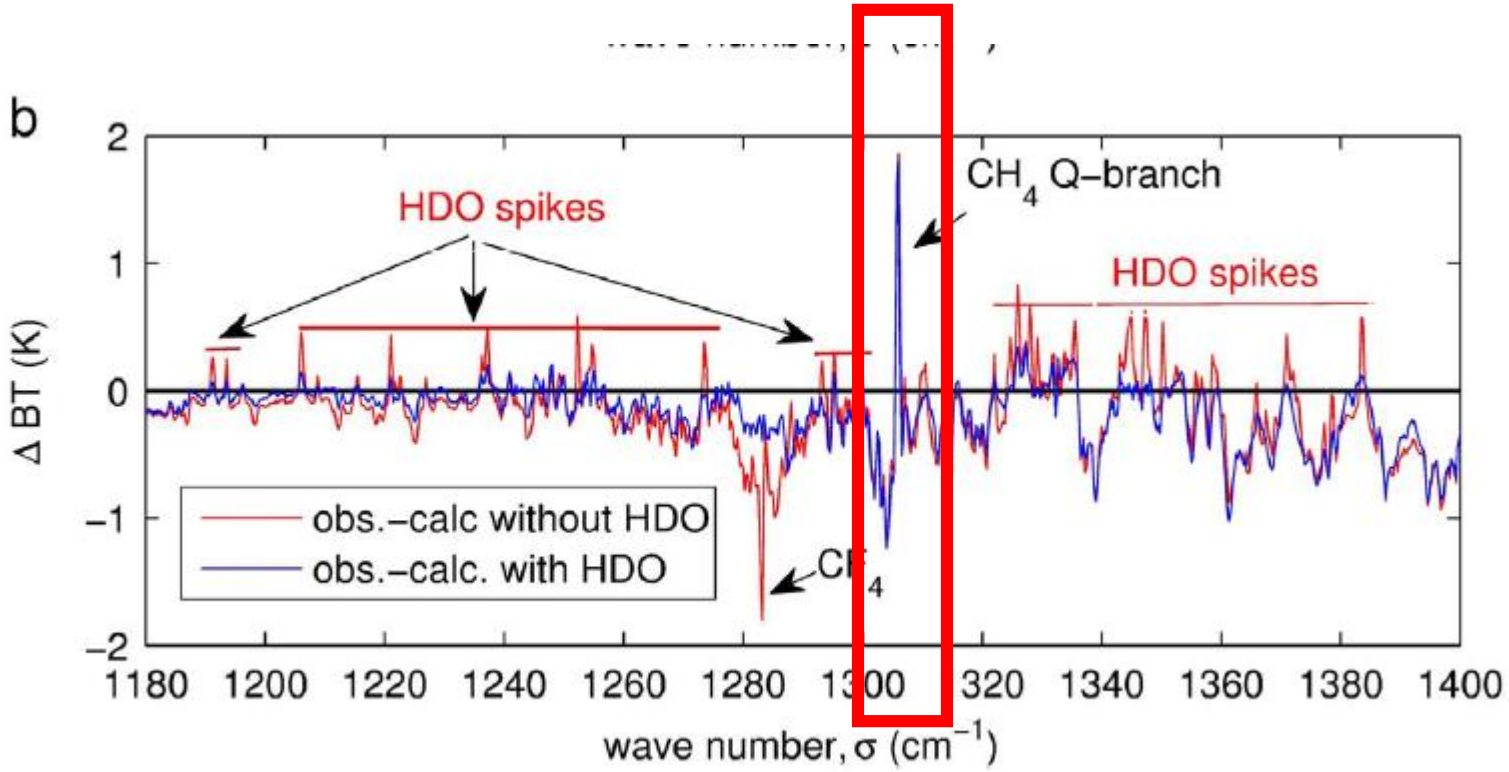
in 10^{-18}.cm^{-1}/(molecule.cm^{-2})

Q: Check the relative intensity of the ν_2 band versus the {$\nu_3 \Leftrightarrow \nu_1$} interacting bands

Methane: (see Liuzzi *et al* 2016)

⇒Same infrared signature as IASI-NG (see Liuzzi *et al.* 2016)

- For the ν_4 Q branch: intense spike at 1306 cm^{-1} in IASI spectra

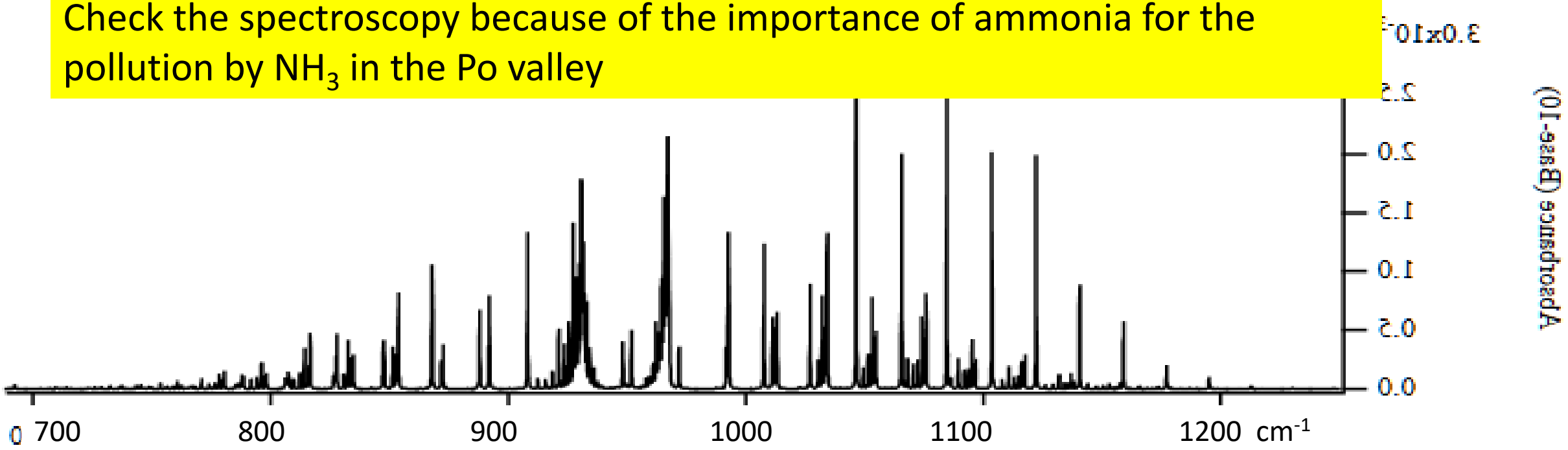


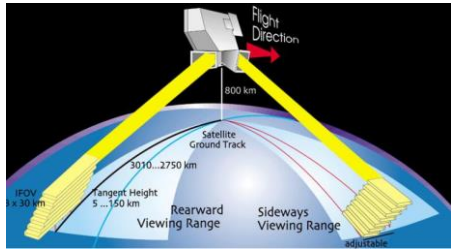
From: **Liuzzi, Masiello, Serio, Venafra, Camy-Peyret JQSRT 182 (2016) 128**

. **Ammonia (NH_3)** => ν_2 region (at 10 µm) like for IASI

⇒Same infrared signature as IASI-NG

Check the spectroscopy because of the importance of ammonia for the pollution by NH_3 in the Po valley

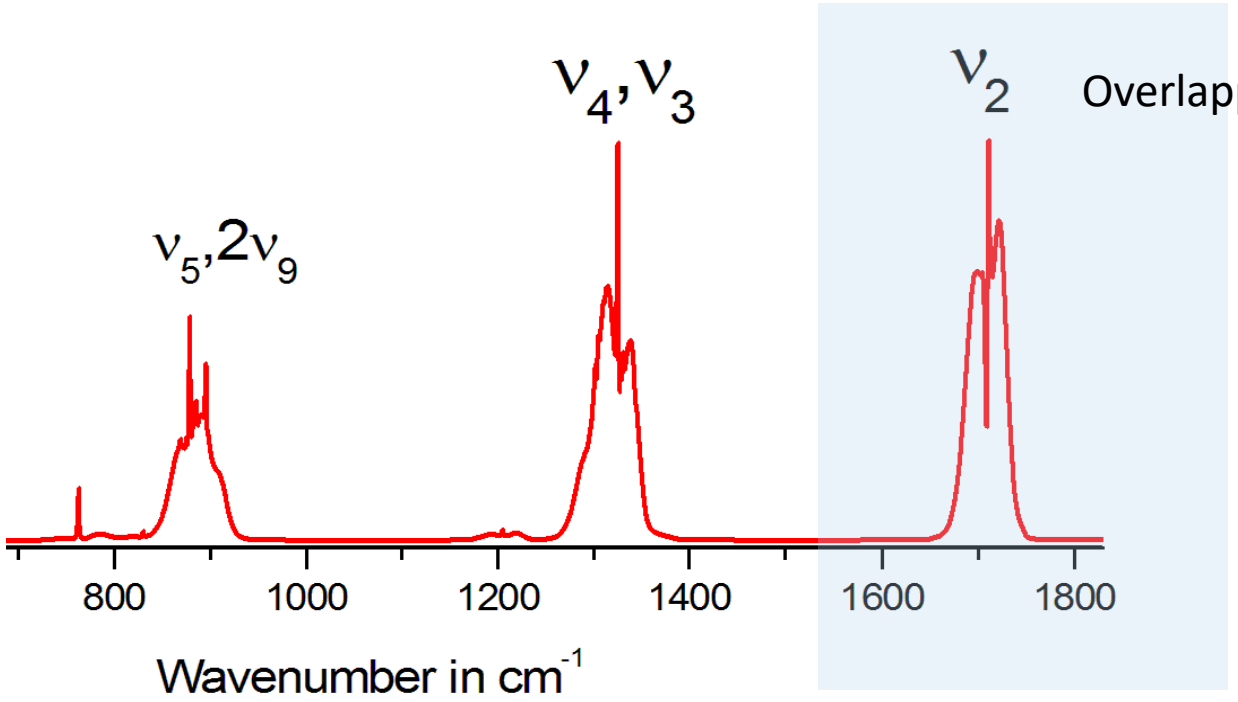




Nitric acid (HNO3)

For MIPAS, IASI or ACE-FTS

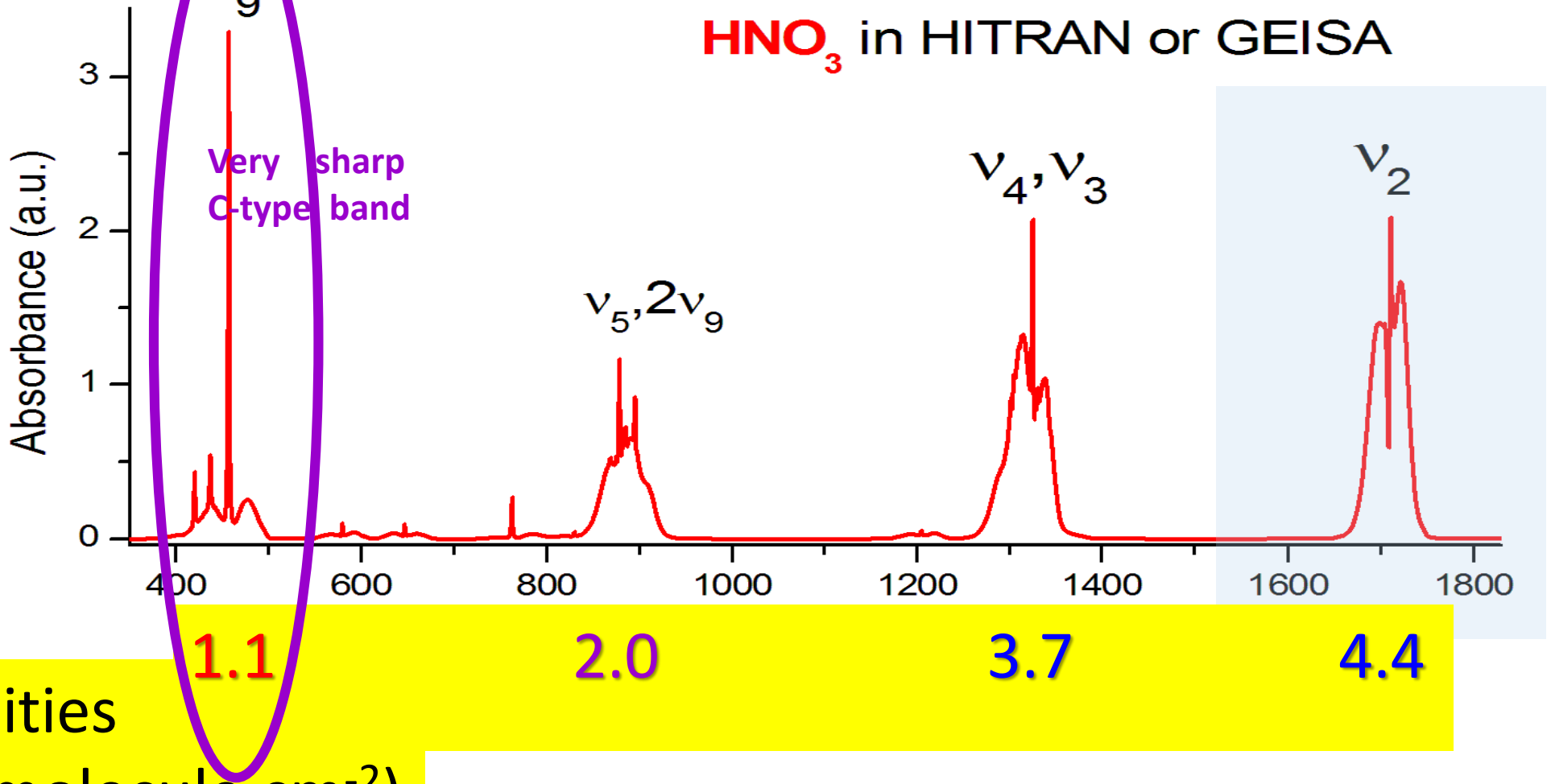
HNO_3 in HITRAN or GEISA



Overlapped by water

Nitric acid (HNO_3)

C-type band

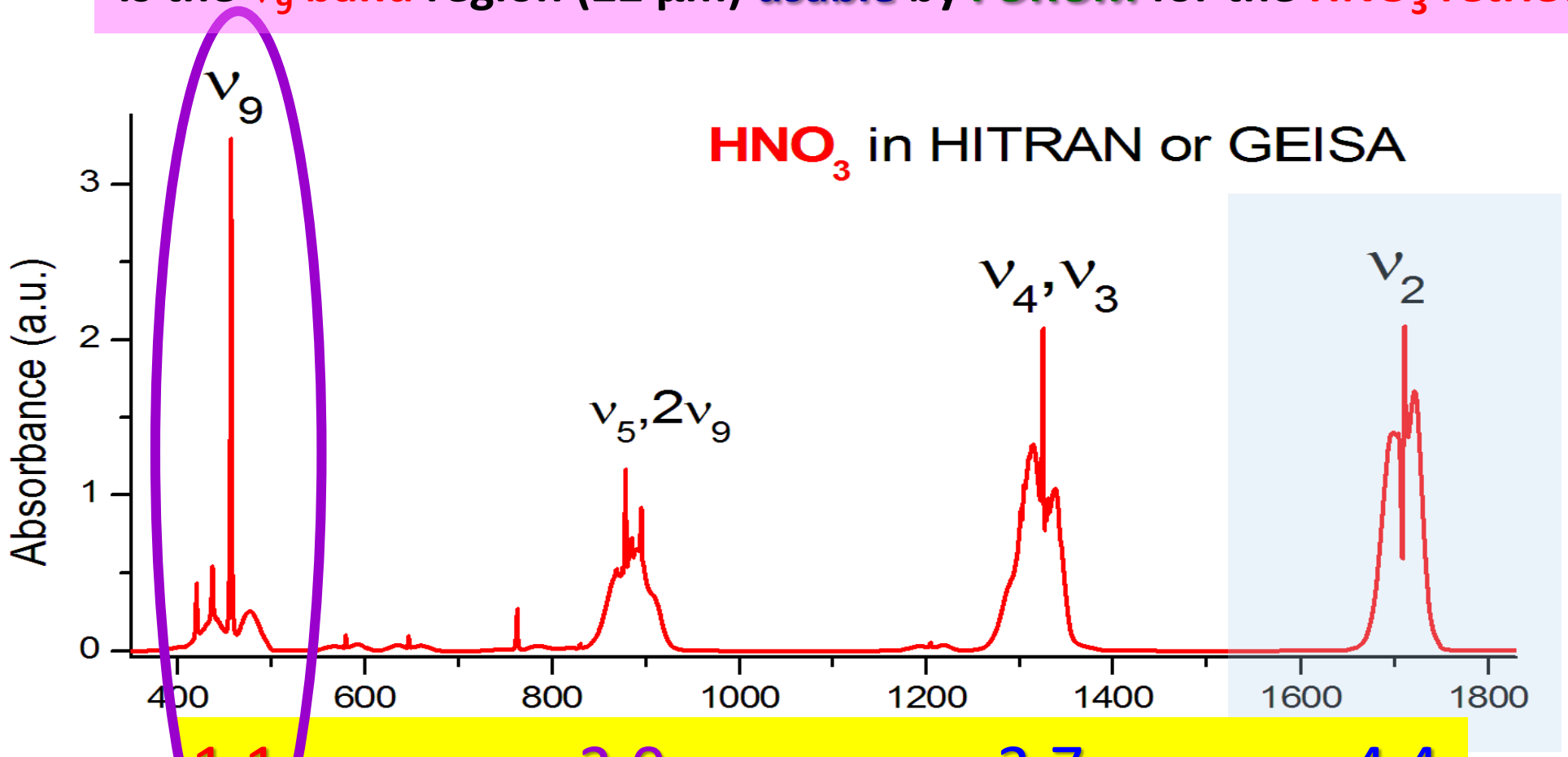


1.1 2.0 3.7 4.4

Band Intensities

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

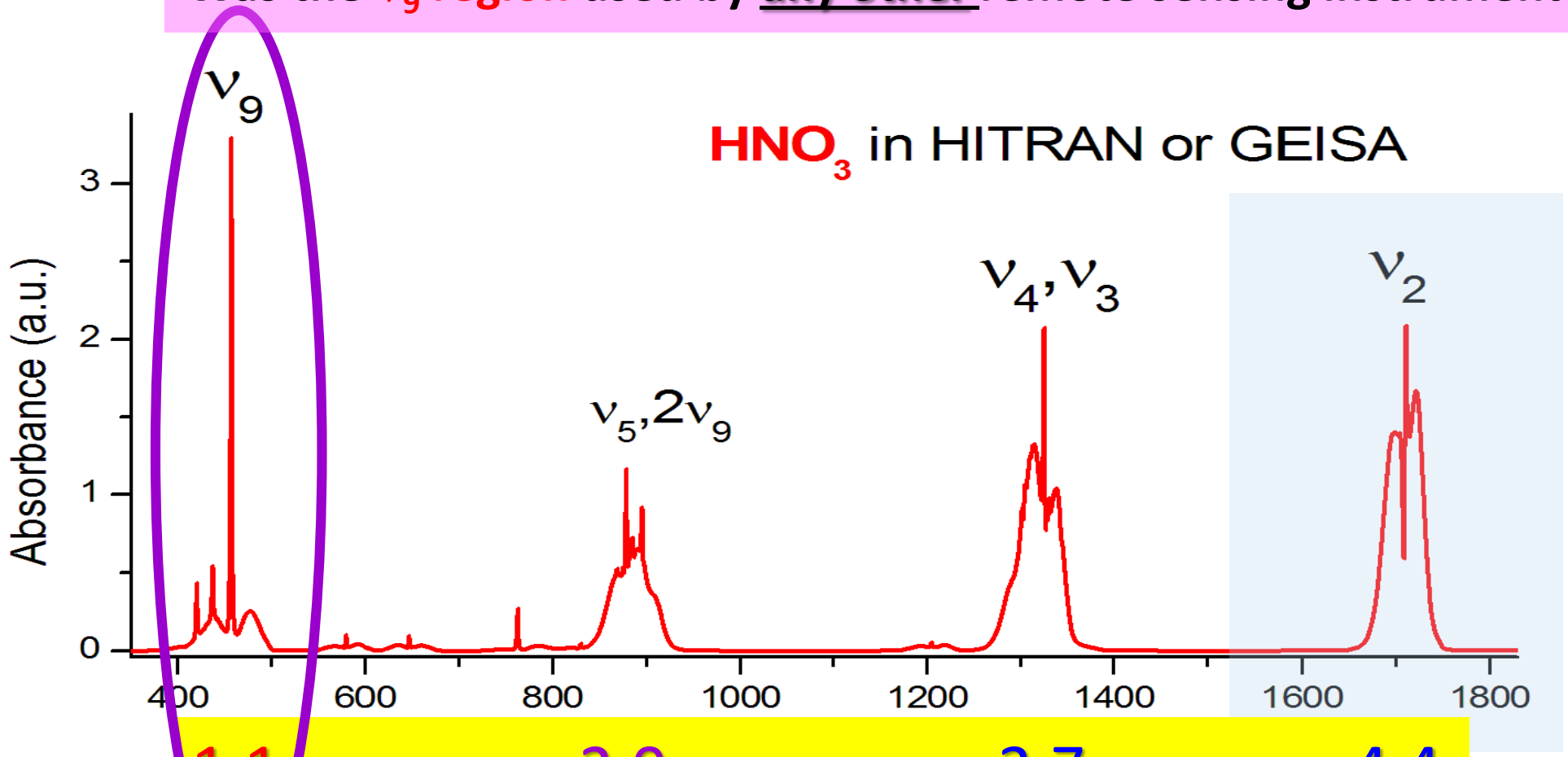
Is the ν_9 band region (22 µm) usable by *FORUM* for the HNO_3 retrievals ?



1.1 2.0 3.7 4.4

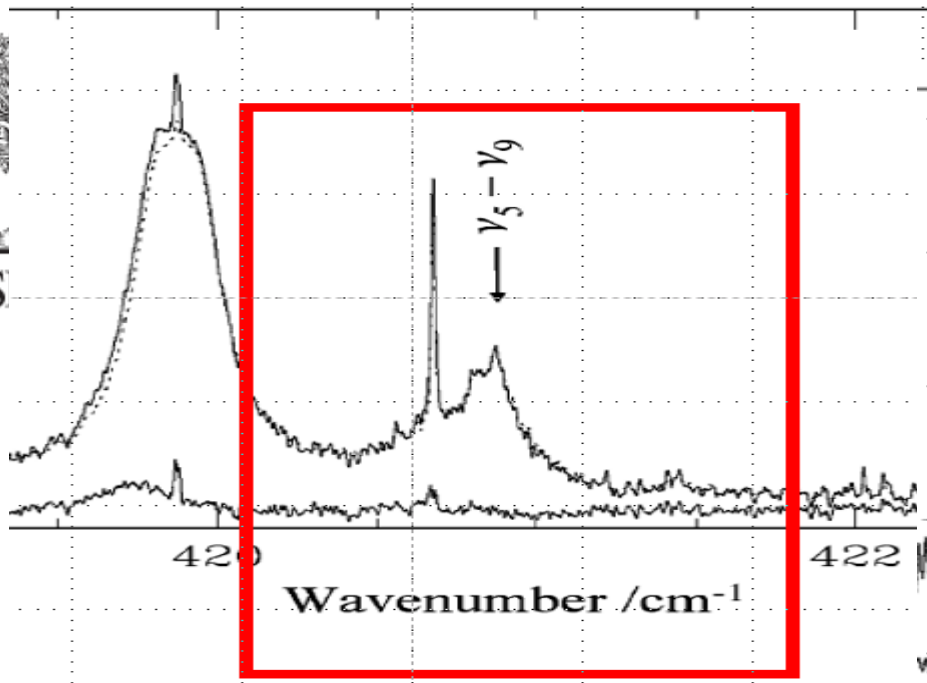
Band Intensities
10^{-17} $cm^{-1}/(molecule.cm^{-2})$

Was the ν_9 region used by <u>any other</u> remote sensing instrument ?



Band Intensities

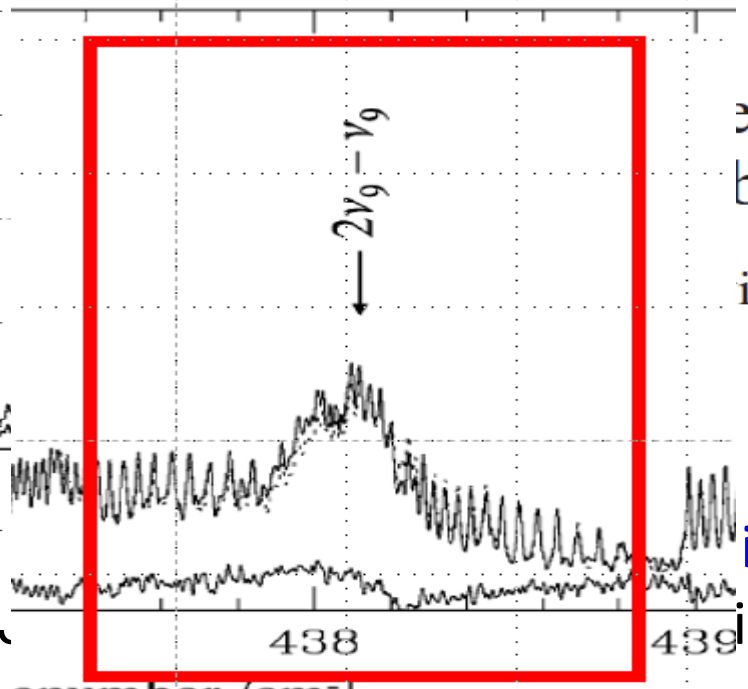
10^{-17} $cm^{-1}/(molecule.cm^{-2})$



Quantitative Spectroscopy &

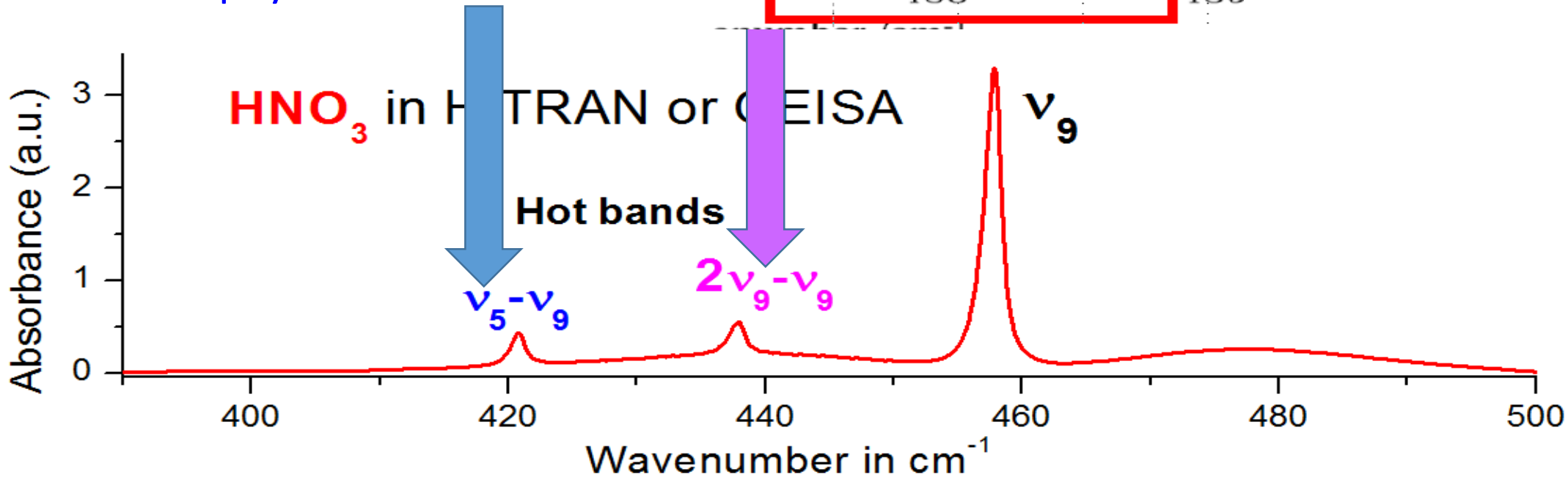
e analyses of
bands of HNO_3

isser[c], R.A.H. Butler[d],



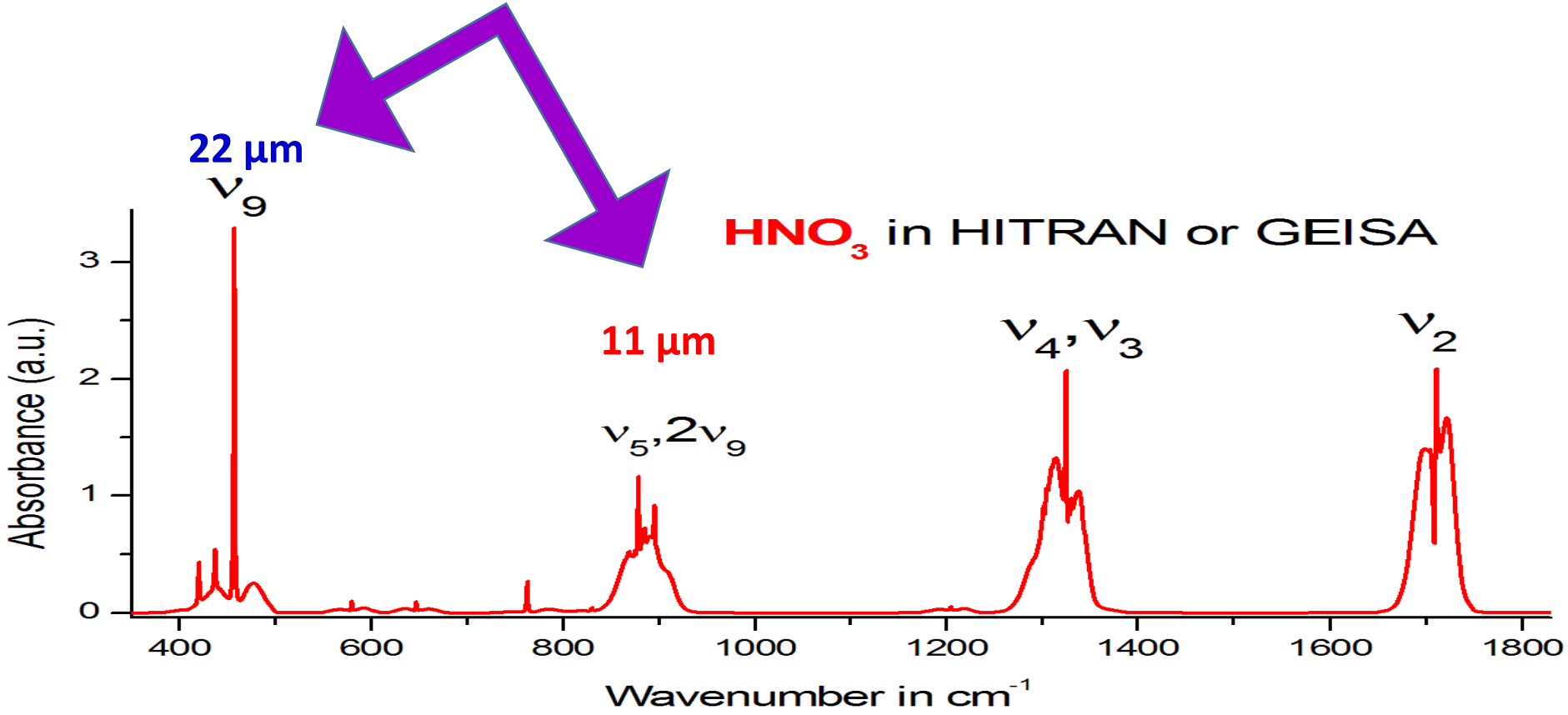
ithsonian Center

for Astrophysics .... thermal emissi ion of 0.004 cm^{-1}.



HNO_3: spectroscopic problems for

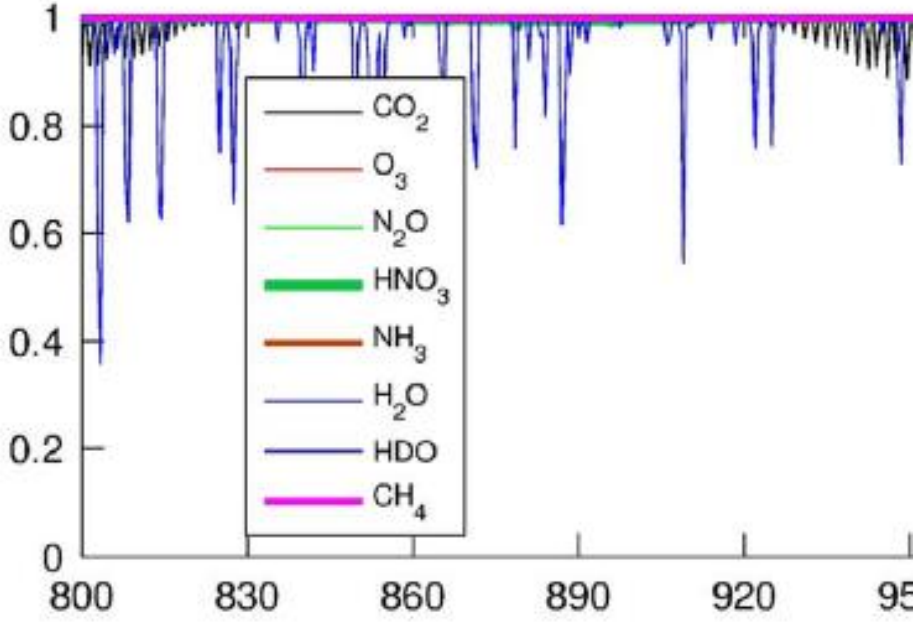
(1) Internal consistency of the line intensities for the 22 µm region (ν_9 band) relative to the 11 µm region {ν_5 , $2\nu_9$ } bands

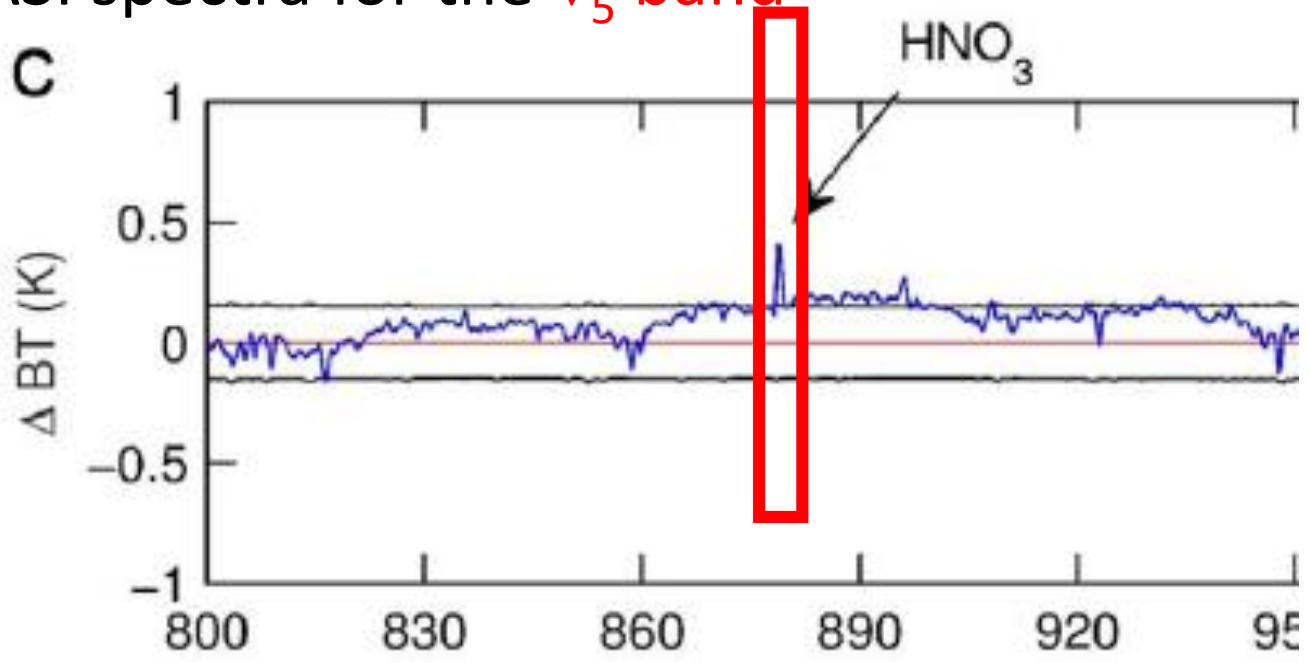


HNO_3: spectroscopic problems for

(2) Line mixing problems

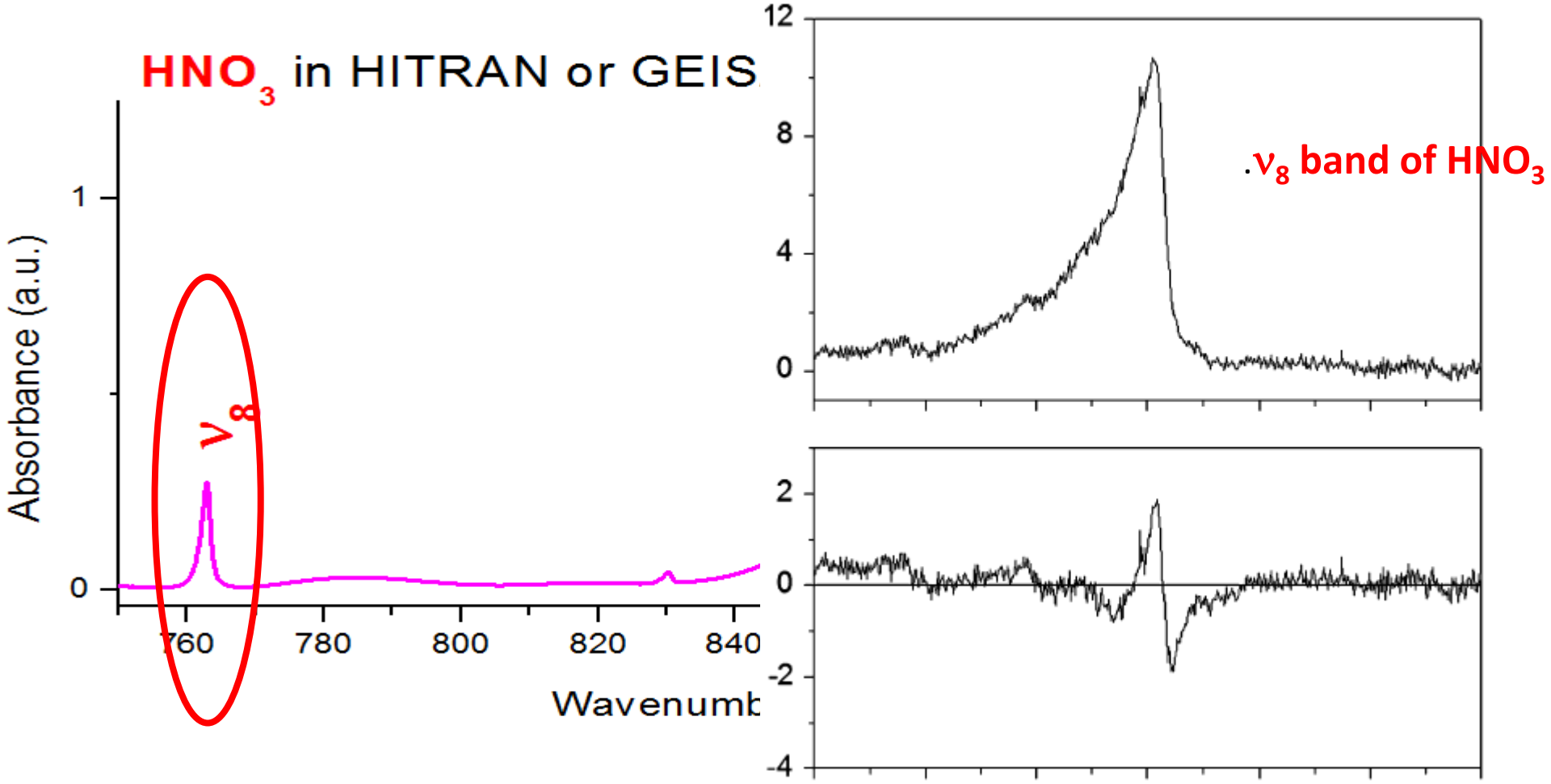
- Were already identified in IASI spectra for the ν_5 band



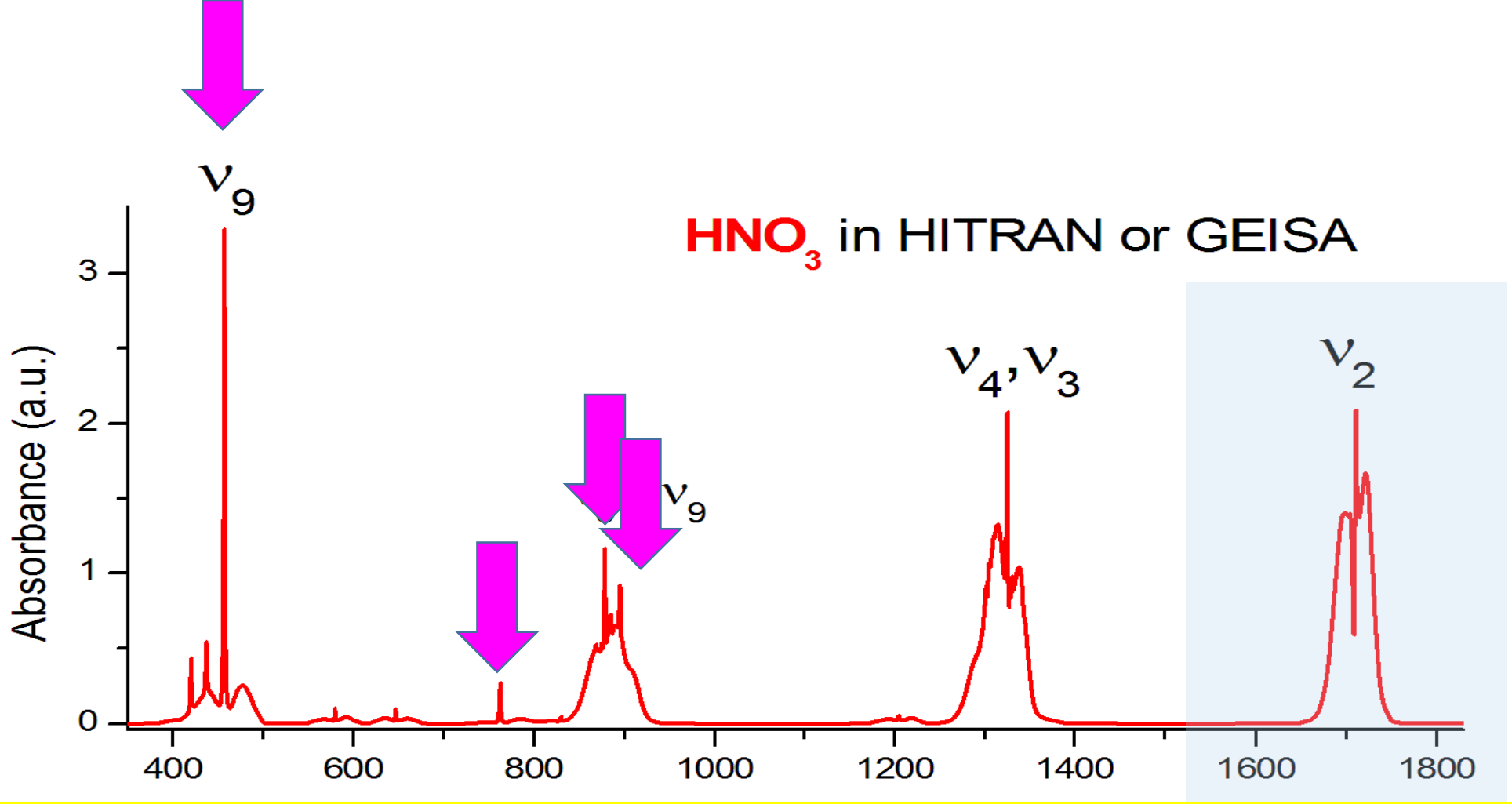


Liuzzi, Masiello, Serio, Venafra , Camy-Peyret, JQSRT 182 (2016) 128-157

In laboratory conditions, line mixing effects already observed for several HNO3 bands for narrow Q branches of HNO3



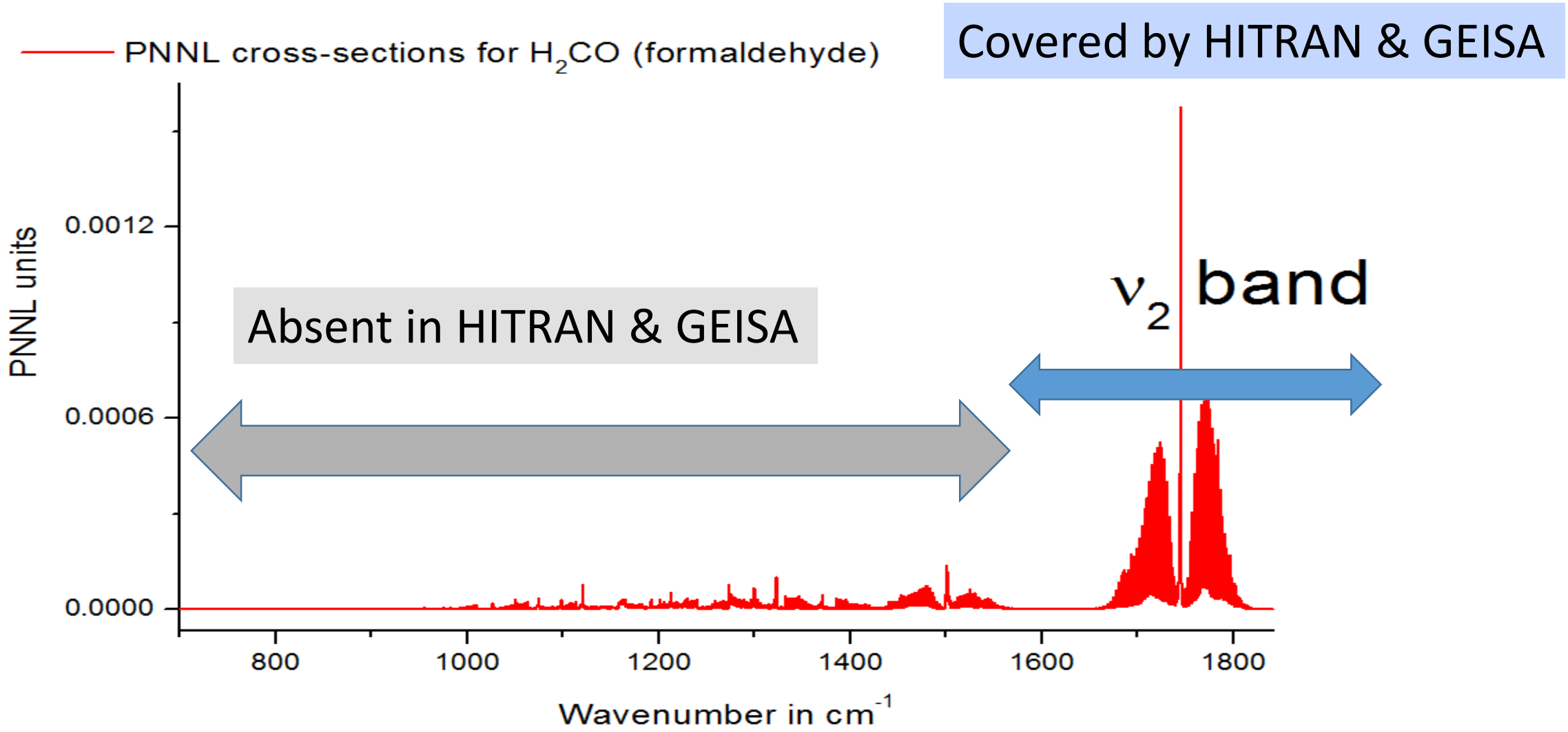
Gomez, Tran, Perrin, Gamache, Laraia, Orphal, Chelin, Fellows, Hartmann, JQSRT, 110 (2009) 675



Line mixing effects are (also) highly probable in atmospheric spectra in the Q- branch of the ν_9 region (22 µm)

Formaldehyde (H_2CO)

⇒Same infrared signature as for IASI-NG



Hypochlorous acid (HOCl) (^{35}Cl and ^{37}Cl)

- For $HO^{35}Cl$: ν_2 at 1238.62 cm^{-1} ; ν_3 at 724.36 cm^{-1}
- For $HO^{37}Cl$: ν_2 at 1238.12 cm^{-1} ; ν_3 at 718.17 cm^{-1}
- Intensity ratio (ν_2/ν_3) ≈ 6 . The ν_3 band at ~720 cm^{-1} is likely too weak to be usable

⇒Same infrared signature than for IASI-NG

Lafferty & Olson, J. Mol. Spectrosc 120 (1986) 359

Overview

Introduction: Who are we ? What are we able to do ?

What can we do for this ***FORUM*** project ?

Molecules of first priority for ***FORUM***

Reactive trace species to be considered in case of bush fires

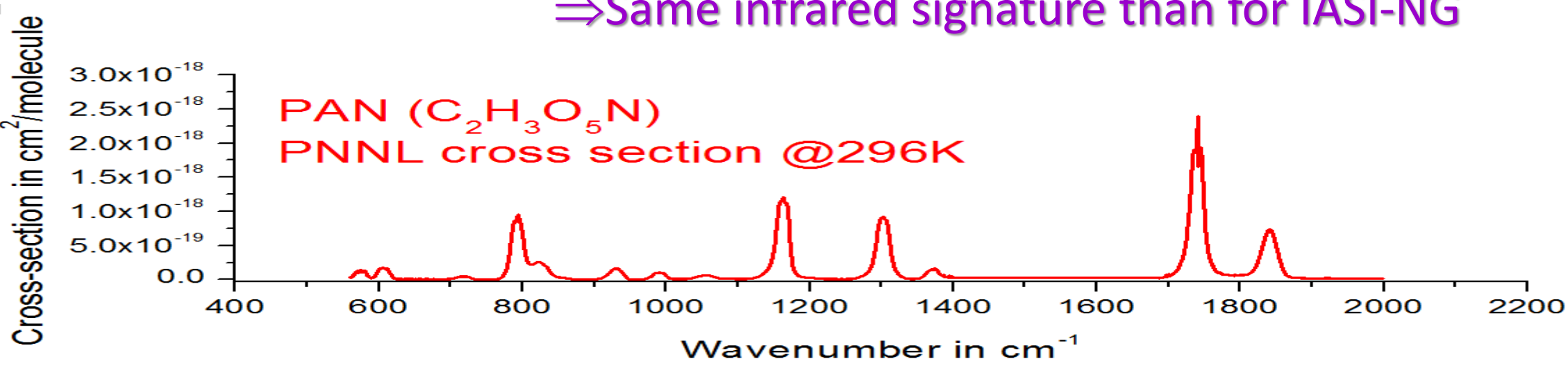
Furan, HONO, Acetylene, HCN, …

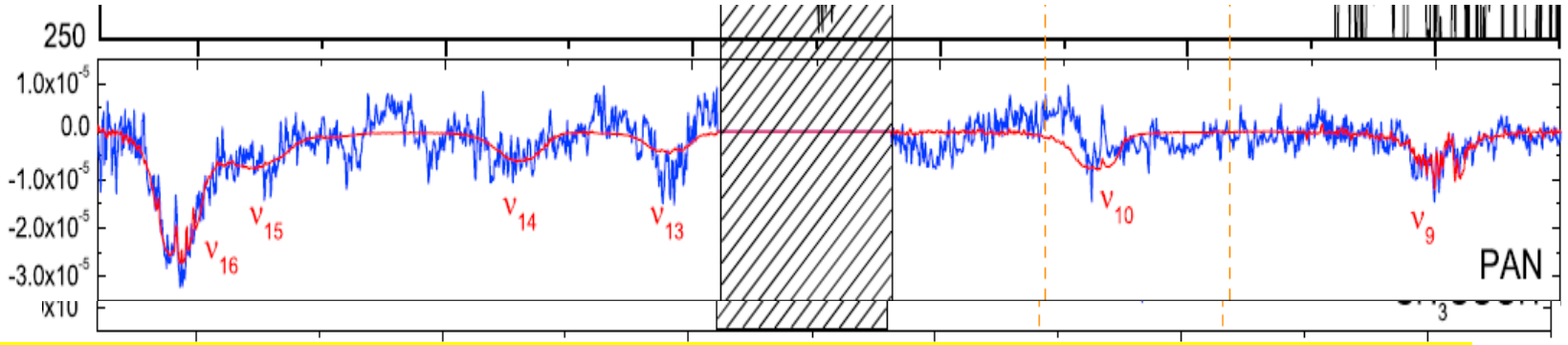
Observed in IASI spectra (Australia fires)
Clarisse et al. GRL 38, L10802,
doi:10.1029/2011GL047271, 2011

Are we able to produce spectroscopic parameters for *FORUM* ?

PAN ($C_2H_3O_5N$)

⇒Same infrared signature than for IASI-NG





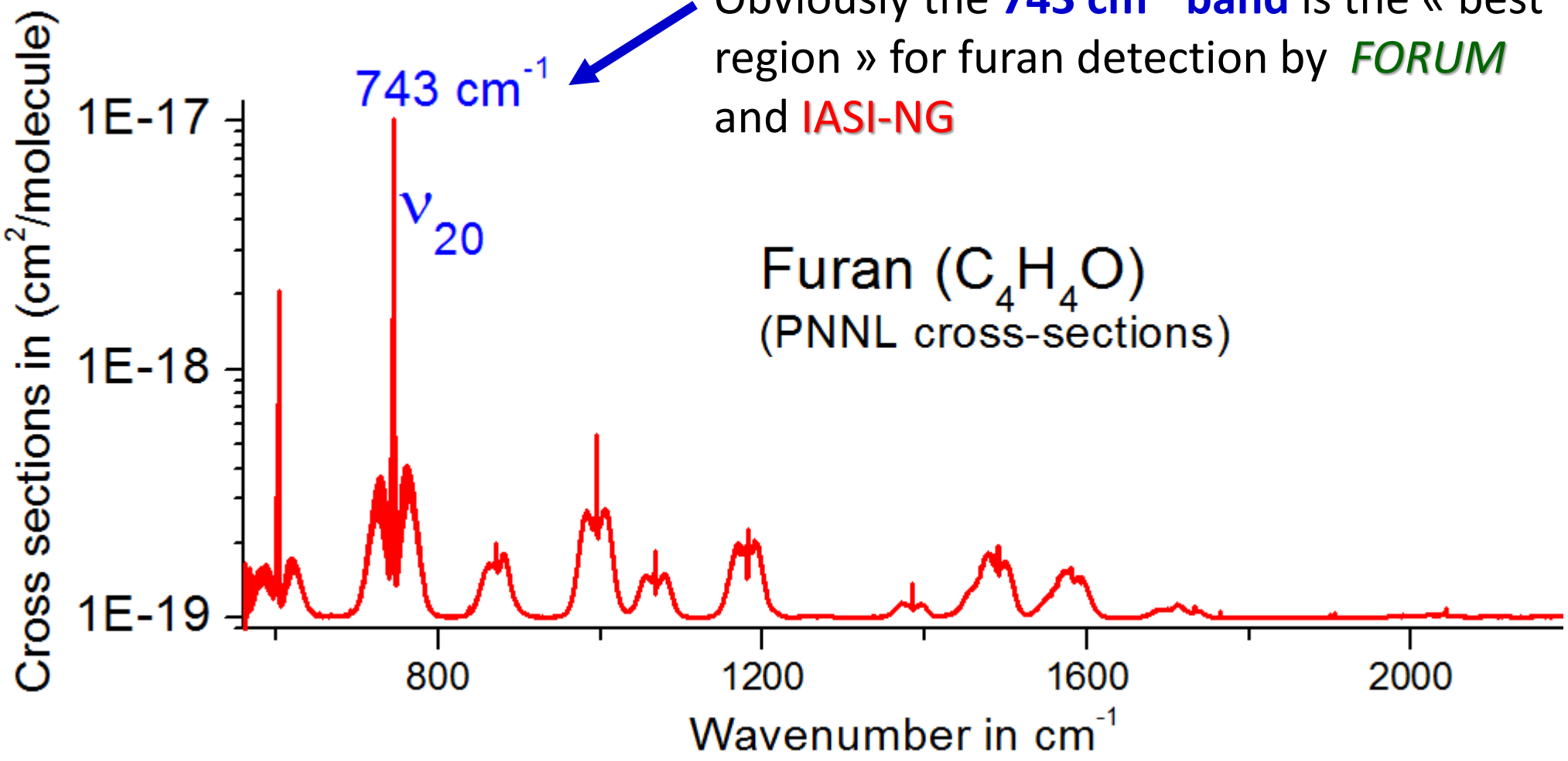
Observed in IASI spectra (Australia bush fires in 2009)
Clarisse et al. GRL 38, L10802, doi:10.1029/2011GL047271, 2011

PNNL cross sections. Sharpe et al. Applied Spectroscopy 58 (2004) 1452-1461

PNNL cross sections.
Sharpe et al. Applied Spectroscopy 58 (2004) 1452-1461

FURAN (C_4H_4O)

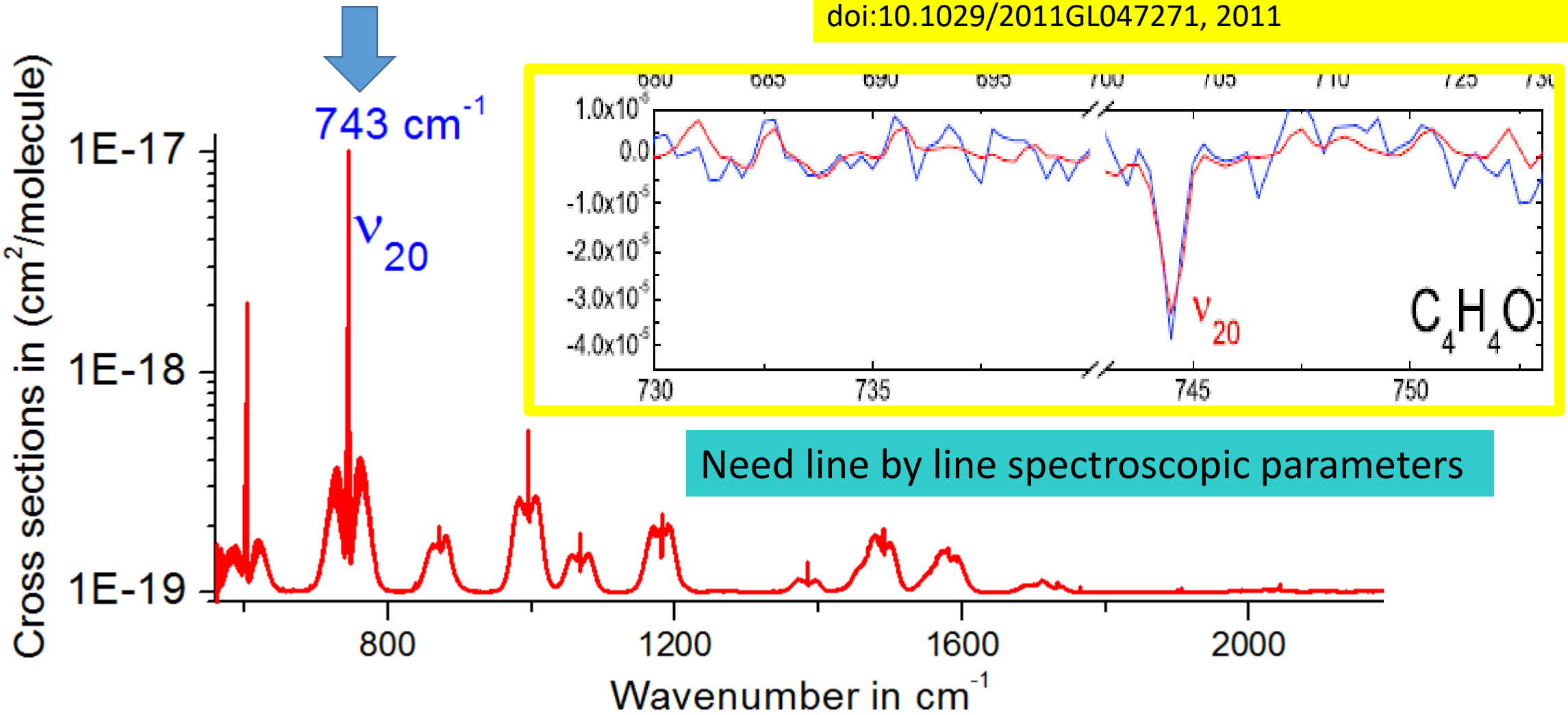
Obviously the **743 cm^{-1} band** is the « best region » for furan detection by *FORUM* and IASI-NG



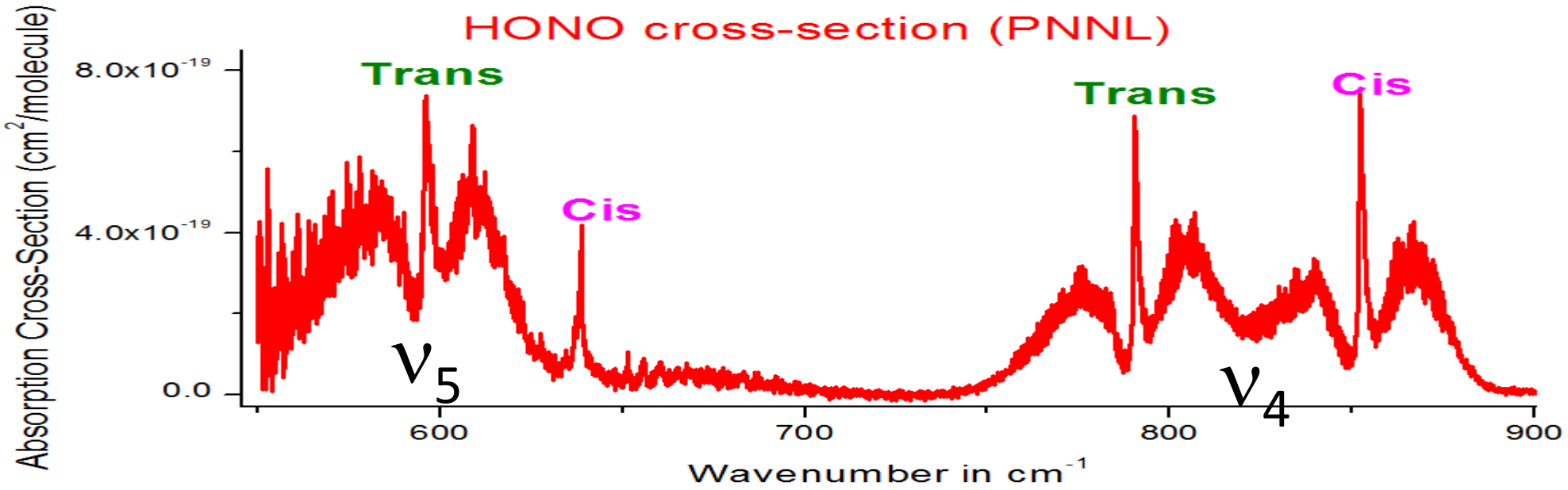
PNNL cross sections. Sharpe et al. Applied Spectroscopy 58 (2004) 1452-1461

FURAN (C_4H_4O) must be detected by forum

Observed in IASI spectra (Australia fires)
Clarisse et al. GRL 38, L10802, doi:10.1029/2011GL047271, 2011

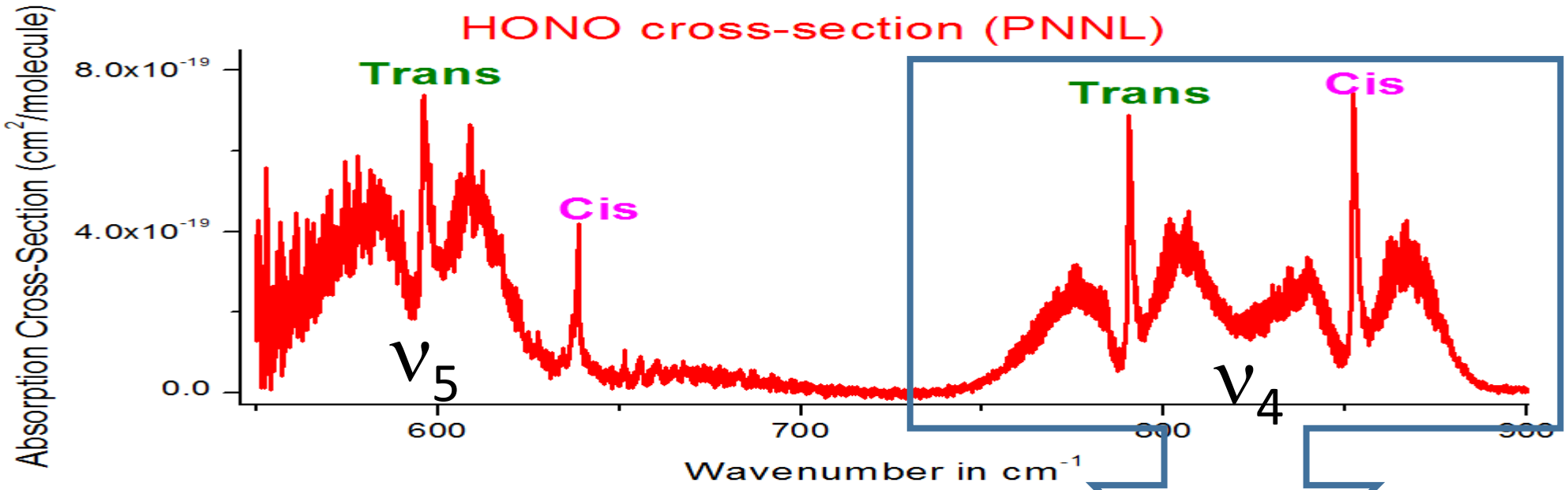


Need line by line spectroscopic parameters



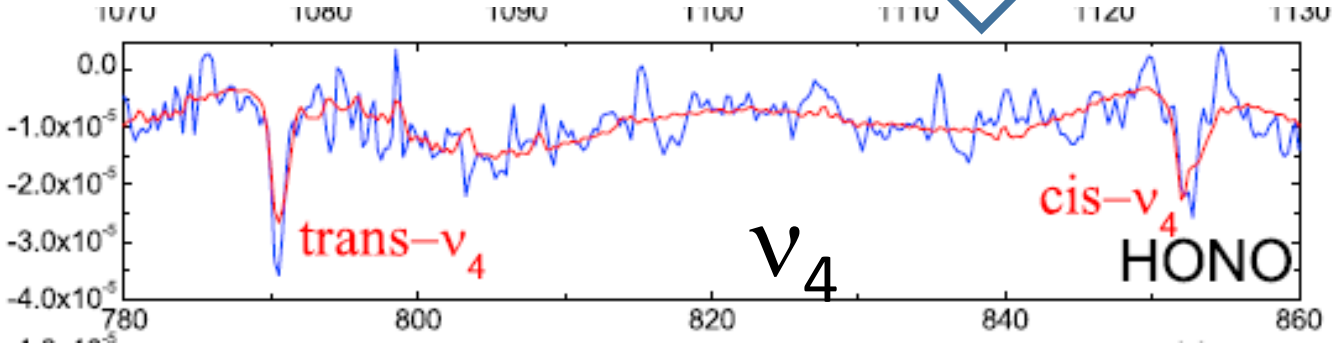
PNNL cross sections of **HONO (nitrous acid)**.

Sharpe et al. Applied Spectroscopy 58 (2004) 1452-1461

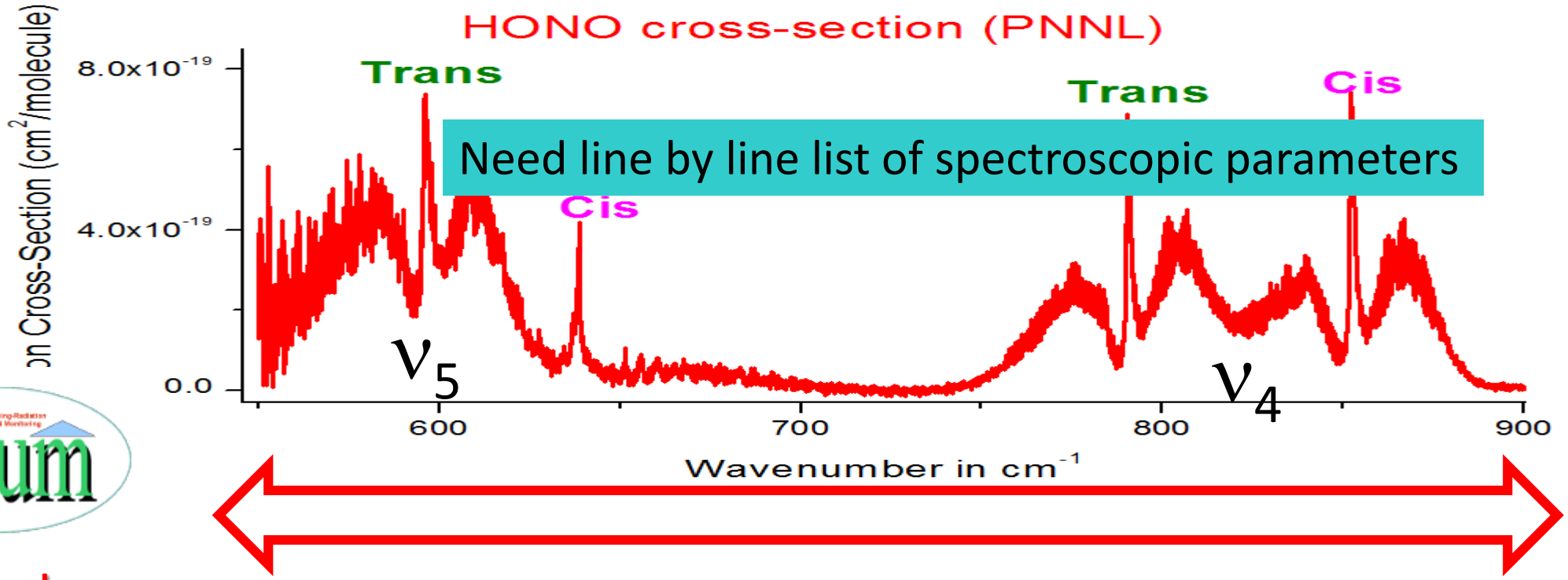


For IASI

only the ν_4 band region is usable !

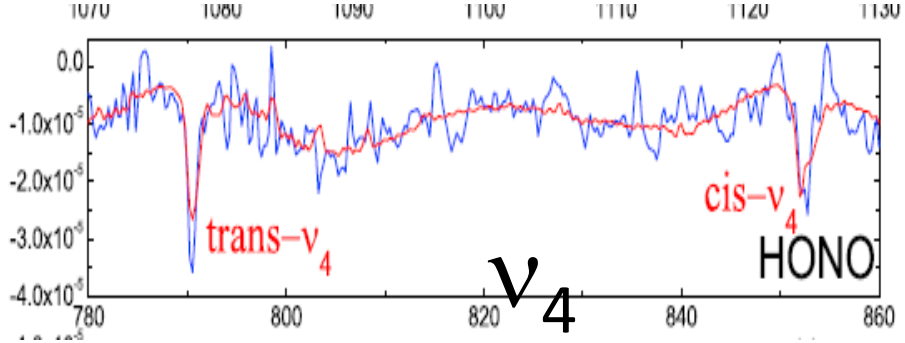


HONO observed in IASI spectra (Australia bush fires in 2009)
Clarisse et al. GRL 38, L10802, doi:10.1029/2011GL047271, 2011



Good news:

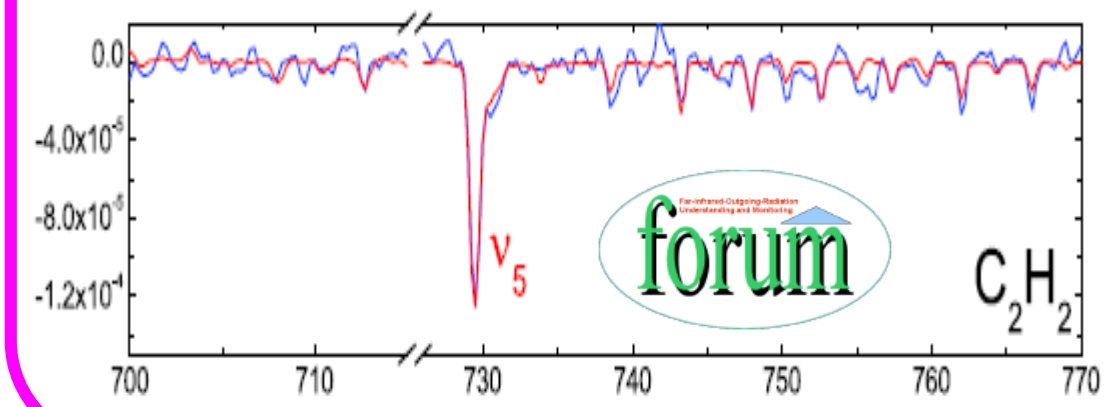
FORUM will possibly detect ????? Trans-HONO and Cis-HONO in both the ν_4 band & ν_5 band regions.



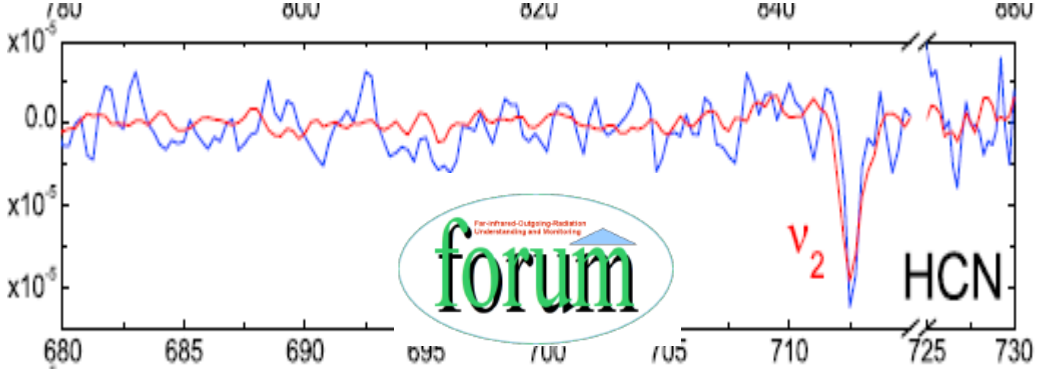
Perrin et al. JMS (2007)

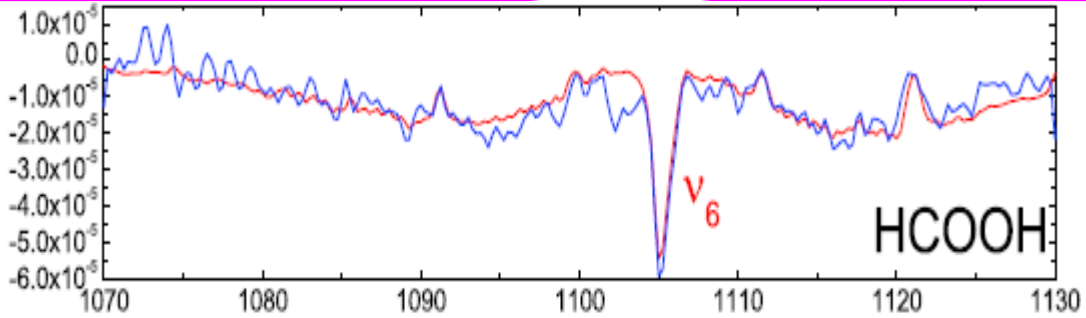
HONO observed in IASI spectra (Australia bush fires in 2009)
Clarisse et al. GRL 38, L10802, doi:10.1029/2011GL047271, 2011

Acetylene (C_2H_2) ~729 cm^{-1}



Hydrogen cyanide (HCN) ~713cm^{-1}





Linelist (line by line) available in HITRAN & GEISA

Formic acid (HCOOH): ~1033 cm^{-1}

Observed in IASI spectra (Australia bush fires in 2009)
Clarisse et al. GRL 38, L10802, doi:10.1029/2011GL047271, 2011

Overview

Introduction: Who are we ? What are we able to do ?

What can we do for this ***FORUM*** project ?

Molecules of first priority for ***FORUM***

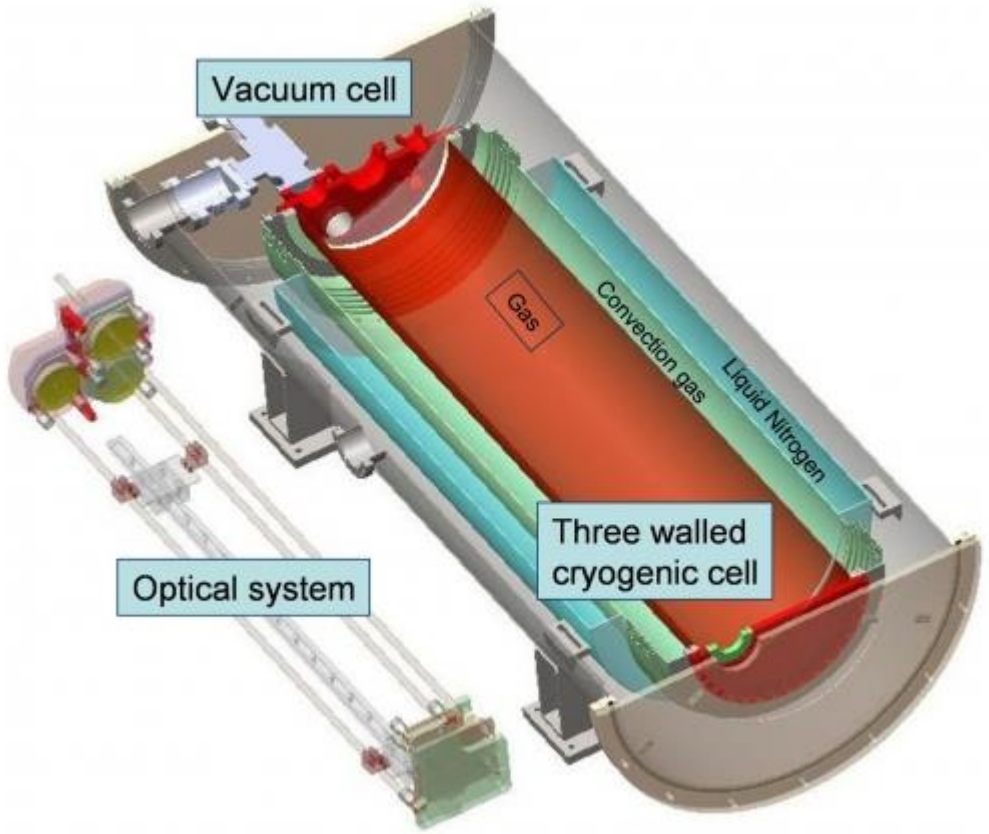
Reactive trace species to be considered in case of bush fires

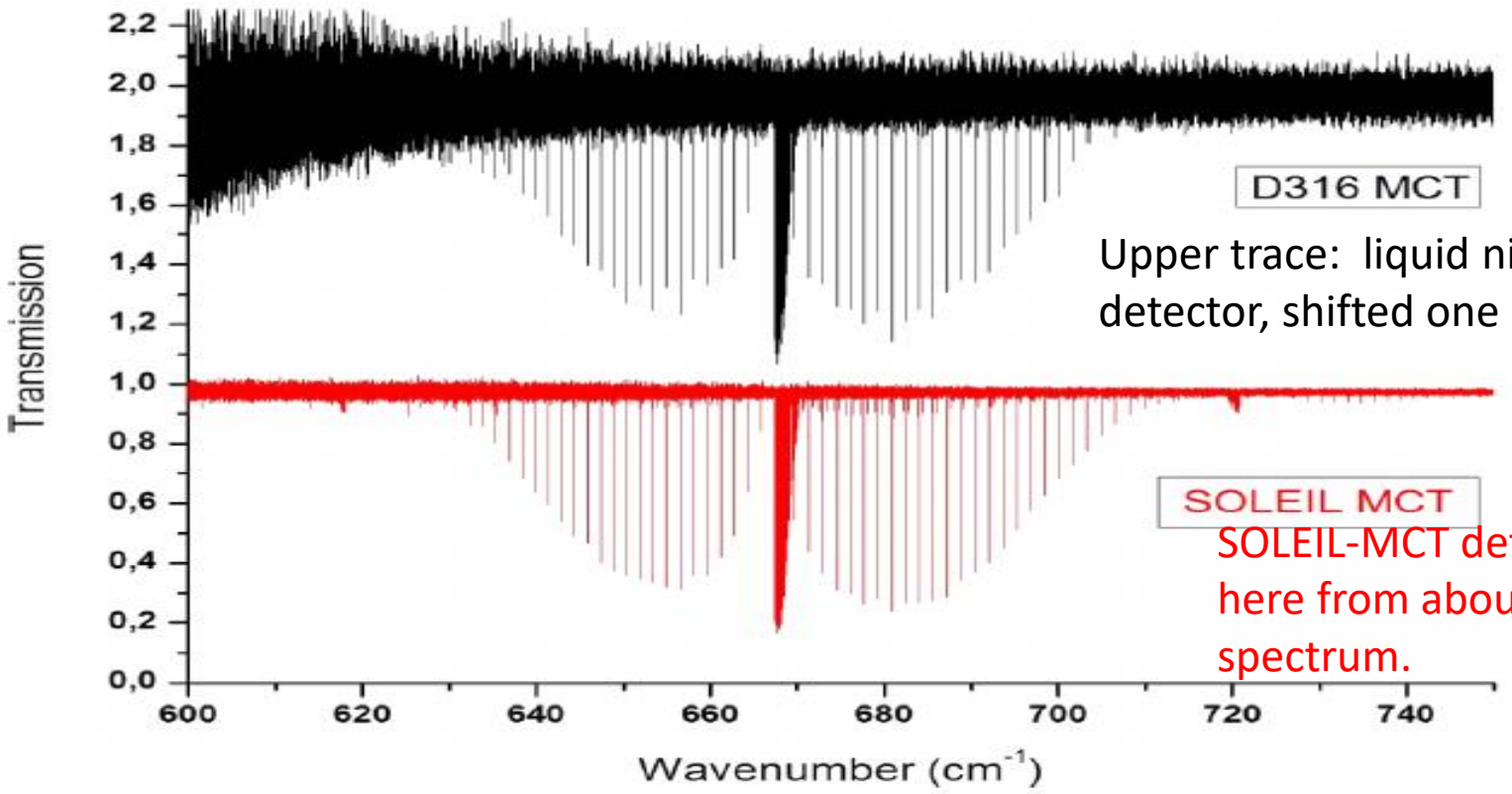
Are we able to produce spectroscopic parameters for *FORUM* ?

We need good quality laboratory spectra in the 150 – 1400 cm^{-1} spectral range

We have a **large experience** in **theoretical models** for line positions and intensities for numerous molecular species

We are working in close contact with high qualified experimental spectroscopists (L.Manceron, F.Kwabia)





Upper trace: liquid nitrogen cooled D316 commercial detector, shifted one unit of transmission.

SOLEIL-MCT detector at 4 K. The gain in RMS S/N ratio varies here from about 12 to 6 from one end to the other of the spectrum.

Comparison of two spectra taken at identical experimental conditions for the v2 region of CO2 in 5 mb of air with a resolution of 0.002 cm−1, 42 min recording time, APT = 2 mm, and KBr/Ge beam splitter.

Mbaye Faye, Bordessoule, Kanouté,Brubach, Roy, Manceron, Rev of Scient. Inst. 87, 063119 (2016)

Conclusion

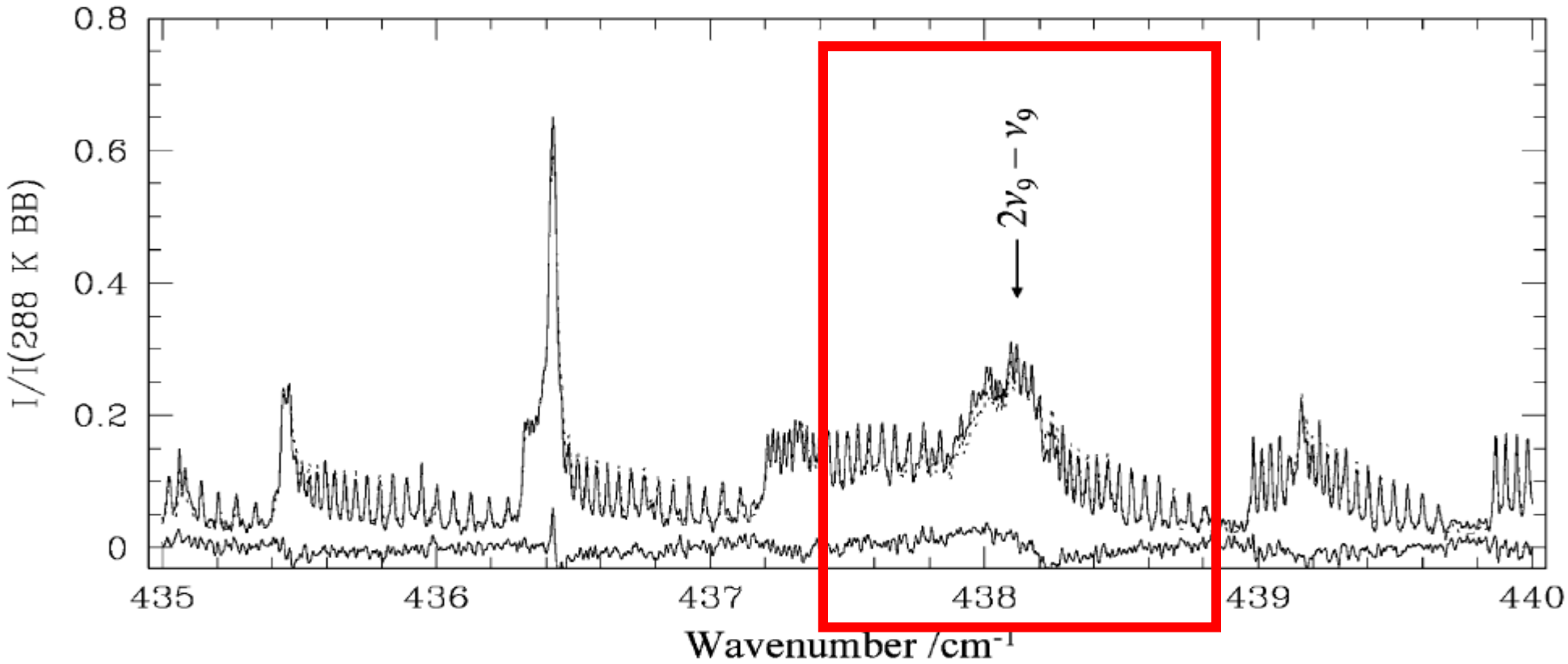
- We presented a short overview of the status of the spectroscopic parameters for the molecules of interest for ***FORUM***
- This review concerns molecules of "first priority" and also molecules which may possibly be detected in case of "unusual conditions" in for ***FORUM*** atmospheric spectra
- We are ready to produce the spectroscopic parameters to help these detections by ***FORUM***

Continua ????

(new CIA section of the HITRAN database)

CIA system	Spectral range (cm^{-1})	Temperature range (K)	Number of sets	Band(s)
N_2–N_2	0.02 – 554	40 – 400	10	Roto-translational
	2000 – 2698	228 – 272	5	Fundamental
	1850 – 3000	300 – 362	5	Fundamental
O2-O2	1150 – 1950	193 – 353	15	Fundamental
CO_2–CO_2	1 – 250	200 – 800	7	Roto-translational

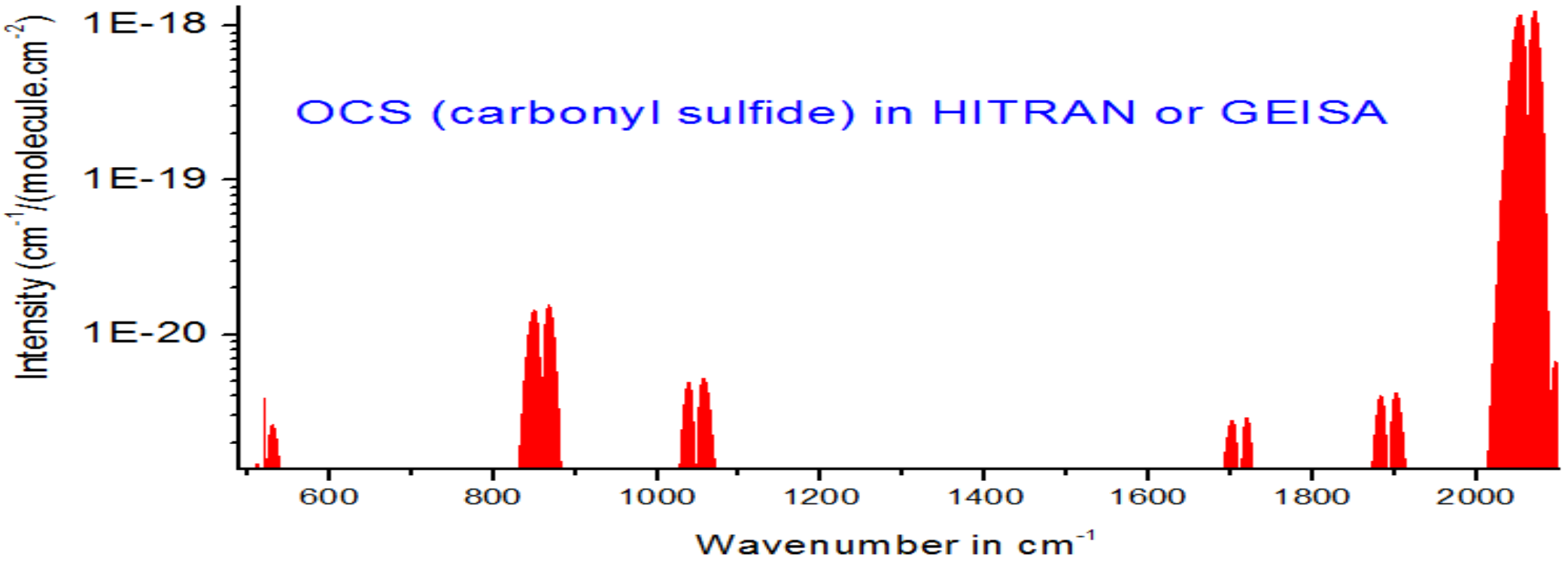
Balloon flight of the FIRS-2 spectrometer from the Harvard–Smithsonian Center



The FIRS-2 balloon spectrum of the v5–v9 and 2v9–v9 regions along with radiative transfer simulations of the bands.
Upper solid trace: observed balloon spectrum
Dashed trace is the simulated spectrum
Lower solid line is the residual (observed–simulated).
Limb viewing geometry with balloon altitude of 37 km and a tangent altitude of 20 km.

OCS (carbonyl sulfide)

⇒ Strongest signature is at 2062 cm^{-1} (not usable by ***FORUM***) compared to IASI-NG !



For details: see Camy-Peyret, Liuzzi, Masiello, Serio, Venafra, Montzka, JQSRT 201 (2017) 197-208