New analysis of the $\nu_3$ & $\nu_4$ bands of HNO$_3$ by high resolution Fourier transform spectroscopy in the 7.6 $\mu$m 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\textsubscript{2} columns
HNO\textsubscript{3} profiles

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

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HNO$_3$ in HITRAN-GEISA

MW & $\nu_9$

0-10cm$^{-1}$ 458cm$^{-1}$

Far-IR 22µm

$\{\nu_5, 2\nu_9\}$ $\{\nu_4, \nu_3\}$ $\nu_2$

879, 896cm$^{-1}$ 1303, 1326cm$^{-1}$ 1709cm$^{-1}$

11µm 7.6µm 5.8µm

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

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Up to now HNO$_3$ is measured **(almost only)** in the 11 µm region which was updated recently in HITRAN & GEISA.

ACE-FTS

<table>
<thead>
<tr>
<th>MW &amp; 0-10cm$^{-1}$</th>
<th>458cm$^{-1}$</th>
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</tr>
</thead>
<tbody>
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<td>Far-IR</td>
<td>22µm</td>
<td>11µm</td>
<td>7.6µm</td>
<td>5.8µm</td>
</tr>
</tbody>
</table>

Improved line positions & intensities at 11 µm ($v_5$ and $2v_9$ bands):


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

High quality of the 11 µm spectroscopic parameters

Low quality of the spectroscopic parameters

Not favorable (overlapped by water absorption)
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$_3$)

Only ONE source for the line positions & relative intensities parameters for HNO$_3$ @7.6 µm in the HITRAN or GEISA databases


The HITRAN or GEISA updates of HNO$_3$@7.6 µm concern only the total band intensity.
HNO₃ cross sections

Obs (PNNL)
HITRAN-GEISA

PNNL: Pacific Northwest National Laboratory
Well known high quality cross sections...
7.6 μm(ν₃ & ν₄ bands) in 1989...

Only a partial analysis of the ν₃ & ν₄ bands was performed

Only the resonances coupling ν₃ ↔ ν₄ 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 $\nu_3$ and $\nu_4$ bands at 7.6 µm bands

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

Validation of the new linelist using MIPAS spectra.

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Obs-Calc
HITRAN GEISA

Obs-Calc
(this work)

(a)

Transmittance

Wavenumber in cm$^{-1}$

V4
V3

This work

Obs
HNO₃ cross sections

PNNL: Pacific Northwest National Laboratory
Well known high quality cross sections…
Laboratory spectrum (Q branch of the $\nu_3$ band) of HNO$_3$

- **New Calc**
- **HITRAN or GEISA**
Hamiltonian matrix: the 7.6 µm bands of HNO$_3$

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

**Large amplitude OH torsion**
HNO$_3$ at 12 µm

$3v_g$-$v_g$ hot band (P- branch)

Calc

Obs

Denver 1994

Transfer of the torsional splitting via the $\nu_4 \leftrightarrow 3\nu_9$ interaction at 7.6 $\mu$m
HNO₃ cross sections

PNNL: Pacific Northwest National Laboratory
Well known high quality cross sections...
Laboratory FTS spectrum (Univ. Giessen)
Near 1320 cm\(^{-1}\)

\(\text{HNO}_3\) \(\nu_3\) and \(\nu_4\) bands

Calc: HITRAN or GEISA
Obs (FTS Giessen)
Laboratory FTS spectrum (Univ. Giessen)
Near 1320 cm\(^{-1}\)

HNO\(_3\) \(\nu_3\) and \(\nu_4\) bands

New calc
Calc: HITRAN or GEISA

Obs (FTS Giessen)

July 2012
Validation using MIPAS spectra

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HNO$_3$ detection by MIPAS at 1321 cm$^{-1}$
MIPAS orbit 2081, July 2002, 0.025 cm$^{-1}$ resolution

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PNNL: Pacific Northwest National Laboratory

Well known high quality cross sections…

HNO$_3$ cross sections

PNNL: Pacific Northwest National Laboratory
Well known high quality cross sections…
MIPAS orbit 2081, July 2002, 0.025 cm\(^{-1}\) resolution
HNO$_3$ cross sections

Absorbance

Wavenumber in cm$^{-1}$
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HNO₃ cross sections

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Well known high quality cross sections…
Obs (Giessen, 2003)
Calc: $\nu_3 + \nu_9 - \nu_9$

Calc $\nu_3$ & $\nu_4$ bands 2012

Obs (Giessen, 2003)
MIPAS orbit 2081, July 2002, 0.025 cm$^{-1}$ resolution

$\nu_3 + \nu_9 - \nu_9$

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CONCLUSION

• A new study of the ν3 et ν4 bands of HNO₃ was performed.

• It is necessary to account for resonances involving the 3ν₉, 2ν₆ et ν₅+ν₉. & ν₇+ν₈ dark bands.

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\[ \nu_9 \text{ torsion } \text{OH/NO}_2 \]

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

\[\nu_9 \text{ torsion of } \text{OH /NO}_2 \leftrightarrow \text{large amplitude}\]

Splitting of \(\sim 0.06 \text{ cm}^{-1}\) in \(9^3\)