Spectroscopy database

Jean-Marie Flaud (LISA-CNRS, Paris)
Marco Ridolfi (University of Bologna)

• **MIPAS spectroscopic line database summary of the evolution since version 3.1**

  • 15 April 2003: from HITRAN_MIPAS_PF_3.1 to 3.13
    • PF_3.1 to PF_3.11: removed SF₆ and ClONO₂ lines from PF_3.1, generated PF_3.11.
    • PF_3.11 to PF_3.12: NH₃ lines (code = 11) in PF_3.11 were replaced with HITRAN_2K NH₃ lines. Updated parameters (pressure broadening and T-dep.) of H₂O line @ 948.262880 cm⁻¹.
    • PF_3.12 to PF_3.13: replaced OCS lines in PF_3.12 with OCS HITRAN_2K lines. OCS line intensities of the 14 - 1 bands were multiplied by 1.13
  • 3 November 2003: from HITRAN_MIPAS_PF_3.13 to 3.16
    • PF_3.13 to PF_3.14: removed NO (code 8) lines from PF_3.13, generated PF_3.14 including NO parameters from HITRAN01
    • PF_3.14 to PF_3.15: removed H₂O₂ (code 25) lines from PF_3.14, generated PF_3.15 including H₂O₂ parameters from [PERR et al., 1990] and [KLEE et al., 1999]
    • PF_3.15 to PF_3.16: generated PF_3.16 including H₂CO (code 20) parameters from J.-M. FLAUD and A. PERRIN, Private Communication.
• November 2004: from HITRAN_MIPAS_PF_3.16 to 3.17
  • PF_3.16 to PF_3.17: Updated HNO3 line parameters as described in the tech. Note from Jean-Marie Flaud included in Appendix of the ATBD of MIPAS_SM study.

• 1 August 2005: from HITRAN_MIPAS_PF_3.17 to 3.2
  • PF_3.17 --> PF_3.2: Removed from PF_3.17 H2CO lines that are unpublished material and are not relevant for ESA Level 2 retrievals. PF_3.2 is an official release of the database to ESA.

• 11 July 2007: from HITRAN_MIPAS_PF3.2 to 3.3:
  • new MIPAS database version 3.3 issued, compared to V3.2 includes new C2H6 and NO+ line lists. TN from Jean-Marie available at:
    • http://www2.fci.unibo.it/~ridolfi/mipas_special_modes/db/TN-C2H6-NO+_JMF_noax.pdf

• 3 May 2008: from HITRAN_MIPAS_PF3.3 to 3.31:
  • PF3.31 includes new SO2 line data from Jean-Marie. The NU2 region (non usable I think in MIPAS spectra), the NU1 and NU3 regions. The NU3 region is by far the strongest.
9 August 2008: from HITRAN_MIPAS_PF3.31 to 3.32:
- Compared to v3.31, v3.32 includes also the 34SO2 contribution.

3 November 2010: from HITRAN_MIPAS_PF3.32 to 3.33:
- In v3.33 we include the C3H8 (propane) line data provided by Jean-Marie on 27 November 2009. Note that in the data provided by Jean-Marie the molecule code of C3H8 is 47, whereas in the RFM convention it should be 41 (Marco's error in communication to JM). Therefore while including the data in v3.33 we changed the C3H8 code from 47 to 41.

November 2010: new line data for H2O were supplied by Jean-Marie and tested by Marco. The presentation prepared for the QWG25 meeting (Firenze, 21-23 March 2011) showing the results of the tests is available here:
- [http://www2.fci.unibo.it/~ridolfi/mipas_special_modes/db/ridolfi_h2o_residuals_qwg25.pdf](http://www2.fci.unibo.it/~ridolfi/mipas_special_modes/db/ridolfi_h2o_residuals_qwg25.pdf)

**ATTENTION:** at this point the database contains some lines (e.g. SO2 and CH4) with HWHM (pressure broadening coefficient) equal to zero. Therefore now a check has been put on the line selection tool: if HWHM = 0 the line is discarded.

October – November 2012: Towards the release of hitran_mipas_pf4.n. We started with Jean-Marie and Agnes the validation / refinement of the new line list for HNO3 in the 7.6um band (v3 and v4 bands of HNO3, located in the B band of MIPAS

Database HITRAN_MIPAS_PF4.45: can be downloaded from this (unreferenced) web page: [http://atmos.difa.unibo.it/spectdb/](http://atmos.difa.unibo.it/spectdb/)
Procedure used to build the database hitran_mipas_pf4.45 released on 16 February 2015:

As a starting basis we use HITRAN08.par. We cut the database to the interval from 597 to 2600 cm**-1 and remove lines of the following molecules: 1,7,9,12,19,24,26,27, 37,42.

Then we merge the database obtained at 1. with the following line lists:

- 01_hit09.par <= H2O lines improved at LISA see presentation at QWG 26
- 07_hit09.par expected change in H2O_VMR: + 0.2 ppmv
- 09_hit09.par
- 12_A.P.4.43.par <= HNO3 improved data provided by Agnes on 16/01/2015
- 19_hit09.par
- 24_hit10.par
- 26_hit11.par
- 27_hit09.par
- 48_jmf13.par <= propane (C3H8) data provided by Jean-Marie on 17/12/2013
- 49_jmf14.par <= phosgene (COCl2) data from Jean-Marie 21/10/2014

Notes:

- We introduced two new codes (48 and 49) for propane (C3H8) and phosgene (COCl2)
- Molecule 37 (HOBr) data is still excluded from the DB as the available data relate only to pure rotational transitions and are outside MIPAS bands
- Molecule 42 (CF4q) data are still excluded from the DB as the quality is very poor (included in HITRAN only as supplemental data)
Example of spectroscopic database validation with MIPAS measurements

Retrieval of HNO₃ is performed using MWs in the well characterized 11.3 μm region and the 7.6 μm region is not used because affected by spectroscopic errors.

HNO₃ spectroscopy in the 7.6 μm region has been improved with new laboratory measurements.
Example of spectroscopic database validation with MIPAS measurements

Some inconsistencies were detected between intensities of the two bands.
Method

• We calculate the average of 72 simulated limb emission spectra around 21 km tangent height, corresponding to MIPAS measurements from orbit 2081 (FR).
• For the simulation we use the HNO3 VMR retrieved from the 11 μm region.
• We analyze the average residuals in the 1295 – 1345 cm⁻¹ interval (7.6 μm region).
Overview of the residuals

• HITRAN (V. 4.0) versus new (V. 4.3) line data
Overview of the residuals

- Old (V. 4.0) versus new (V. 4.3) line data
Example of spectroscopic database validation with MIPAS measurements

Improved HNO3 spectroscopy at 7.6 μm leads to smaller residuals
Check with medium resolution PNNL spectra
Using MIPAS radiances, an absolute intensity calibration was performed to “convert” the relative line intensities at 7.6 μm to absolute intensities.

Improved HNO3 spectroscopy at 7.6 μm leads to better consistency between the 11 and 7.6 μm regions

A.Perrin et al., AMT, 2016
CONCLUSION

• Version 4.3 is not perfect (Some hot bands are still missing) but gives much better residuals and is consistent with the line parameters in the 11 micron region.
Phosgene (COCl$_2$) cross sections at 11.65µm
Incomplete spectroscopic database

Bias in retrieved CFC-11 profile

Engel et al., AMT, 2016
Incomplete spectroscopic database

CFC-11 retrieval residuals (= observations – simulations)

Residuals have a spectroscopic structure.

They resemble the absorption of the COCl₂ whose interference was not taken into account.
Example of spectroscopic database improvements made for MIPAS

Phosgene (COCl₂) in the 20th century was mainly used by chemical industry in the preparation of insecticides, pharmaceuticals and herbicides.

Cross-sections from PNNL were available, measured at low resolution, but did not cover the full atmospheric temperature range.

New measurements and new calculations filled this gap.

High resolution analysis of the $\nu_1$ and $\nu_5$ bands of phosgene $^{35}$Cl$_2$CO and $^{35}$Cl$^{37}$ClCO

Fourier transform spectra of phosgene have been recorded in the 11.75 $\mu$m and 5.47 $\mu$m spectral regions using a Bruker IFS125HR spectrometer at a resolution of $\sim 0.00125$ cm$^{-1}$ leading to the observation of the $\nu_5$ and $\nu_1$ vibrational bands of the two isotopologues $^{35}$Cl$_2$CO and $^{35}$Cl$^{37}$ClCO.

The upper state ro-vibrational levels were fit using a Hamiltonian matrix accounting for resonance effects when necessary. The upper state ro-vibrational levels were fit to within the experimental accuracy i.e. $\sim 0.17 \times 10^{-3}$ cm$^{-1}$.

Very accurate rotational and centrifugal distortion constants were derived from the fit allowing to simulate the observed spectra to within experimental accuracy.
A Portion of the P-branch of the $\nu_5$ Bands of Cl$_2$CO

Absorbance vs. Wavenumber (cm$^{-1}$)

- Observed
- Calculated
Estimation of the abundances of the various isotopic species of phosgene

<table>
<thead>
<tr>
<th></th>
<th>Abundance</th>
<th>Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl 35</td>
<td>0.7578</td>
<td>CO $^{35}\text{Cl}$$^{35}\text{Cl}$</td>
</tr>
<tr>
<td>Cl 37</td>
<td>0.2422</td>
<td>CO $^{35}\text{Cl}$$^{37}\text{Cl}$</td>
</tr>
<tr>
<td>Cl 37</td>
<td>0.0587</td>
<td>CO $^{37}\text{Cl}$$^{37}\text{Cl}$</td>
</tr>
</tbody>
</table>
Phosgene low resolution spectrum [PNNL] around 11.65µm
Bands calculated to model the absorption cross sections of Phosgene at 11.65µm

<table>
<thead>
<tr>
<th>ISOTOPIC SPECIES</th>
<th>VIBRATIONAL BAND</th>
<th>INTENSITY (cm⁻¹ / molecule.cm⁻²)</th>
<th>Number of lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>3535Cl₂</td>
<td>GROUND--&gt;V5</td>
<td>0.216D-16</td>
<td>46052</td>
</tr>
<tr>
<td>3535Cl₂</td>
<td>V3--&gt;V3+V5</td>
<td>0.105D-16</td>
<td>42104</td>
</tr>
<tr>
<td>3535Cl₂</td>
<td>V6--&gt;V5+V6</td>
<td>0.602D-17</td>
<td>38440</td>
</tr>
<tr>
<td>3535Cl₂</td>
<td>V2--&gt;V2+V5</td>
<td>0.162D-17</td>
<td>29500</td>
</tr>
<tr>
<td>3537Cl₂</td>
<td>GROUND--&gt;V5</td>
<td>0.139D-16</td>
<td>43784</td>
</tr>
<tr>
<td>3537Cl₂</td>
<td>V3--&gt;V3+V5</td>
<td>0.625D-17</td>
<td>38699</td>
</tr>
<tr>
<td>3537Cl₂</td>
<td>V6--&gt;V5+V6</td>
<td>0.313D-17</td>
<td>33872</td>
</tr>
<tr>
<td>3737Cl₂</td>
<td>GROUND--&gt;V5</td>
<td>0.387D-17</td>
<td>35361</td>
</tr>
</tbody>
</table>

(The intensities account for the isotopic abundances)
Observed (red line) and calculated (green line) cross sections at 5 C
Completeness of the spectroscopic database leads to reduction of the bias

MIPAS/ENVISAT – MIPAS/balloon CFC-11 difference

with COCl$_2$ NOT taken into account

with COCl$_2$ taken into account
COCl$_2$ retrieved with the new spectroscopic database: some results

Valeri et al., AMT, 2016

The average profiles do not exceed 30 pptv with maxima at around 100 hPa. Only in the polar region we observe a weak seasonality.
As a conclusion one can say that, given the existing results, a reasonable modeling of the phosgene absorption cross sections has been obtained. However:

Better results could be obtained if high resolution spectra of the $\nu_5$ bands of CO $^{35}$Cl $^{37}$Cl and (CO $^{37}$Cl $^{37}$Cl) were available, Better information on the vibrational bands of the isotopic species of phosgene was available in order to better model the hot bands.
Interim report on ozone line width parameters
From Glatthor et al: Differences in ozone retrieval in MIPAS channels A and AB: a spectroscopic issue

Since the relative differences between band intensities in the spectral ranges used in MIPAS channels A and AB are assumed to be considerably lower than the observed bias of 6–8%, we suggest that a major part of the channel AB-A differences might be caused by inconsistencies in air-broadened halfwidths in the individual line databases as well. To substantiate this assumption we identified several ozone lines in the HITRAN-2008 database, which exhibit too large air-broadened halfwidths. The bias between channel A and AB can partly be reduced by increasing the air broadened halfwidths of the lines in channel AB.

According to our investigations, for the time being the best choice of an ozone line data compilation for evaluation of MIPAS measurements is the MIPAS spectroscopy (Flaud et al., 2003b), because on the one hand the channel AB-A differences are somewhat smaller than those resulting from the HITRAN databases and on the other hand it does not contain the inconsistency in some air-broadened halfwidths identified in HITRAN-2008, which was also transferred to later HITRAN versions.
$\text{O}_3$ Line lists

- $\text{mipas\_pf3.2}$ ozone line list is the HITRAN91 line list
- $\text{mipas\_pf4.45}$ ozone line list is the HITRAN08 line list
- $\text{O}_3$ lines from weak bands have been added in HITRAN16 but no consequences for the retrieval given their weakness
For air-broadened halfwidths of ozone, the theoretical nitrogen-broadened calculations of Gamache and Rothman scaled to air by multiplying by 0.95, and increased systematically as recommended by Smith et al. (1988), were used. The calculations included values of the rotational quantum number J up to 35. Above this value, the air-broadened halfwidth was estimated via a polynomial in J given by Flaud et al.

For the self-broadened halfwidths on the database, a polynomial in J and K, from Smith et al. (1991) has been utilized. Although some measurements of pressure-induced line shifts of ozone exist, no values of this parameter have been included on the current compilation.

HITRAN08: The majority of HITRAN2004/2008 air-broadened half-width parameters of ozone lines and their temperature dependences were calculated using polynomials derived by Wagner et al. separately for the ν1/ν2 and ν3 bands. The ν1/ν2 polynomials from Wagner et al. were used for all B-type bands and the ones from the ν3 band were used for all A-type bands. Contrary to the previous HITRAN calculation, the new data as well as other air-broadened width measurements show neither a strong $K_a$ dependence nor a large difference between the subbands. In HITRAN04/08 a polynomial derived by Flaud et al. was used to calculate $\gamma_{air}$ for the transitions outside the range of applicability of the Wagner et al. polynomials. These coefficients have been scaled by a factor of 1.05, as it was found that they are underestimated at higher J.

AIR BROADENING COEFFICIENTS $\nu_1$ AND $\nu_3$ BANDS, $K_a' = 0$

- P BRANCH $\nu_1$
- R BRANCH $\nu_1$
- P BRANCH $\nu_3$
- R BRANCH $\nu_3$
Interim conclusion

Perform tests

• using air broadening coefficients divided by ~ 1.05/1.07 for J above 44

• If it does not work allow the uncertainties in band intensity of the ν2 versus ν1/ν3 fundamentals observed in channels A and AB, respectively to be 4% instead than the assumed 2% value.