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## **1. Reference documents**

[RD1] TN-IROE-RSA9601, Issue: 2A

Title: High level algorithm definition and physical and mathematical optimisations

## **2. Introduction**

A scientific code for near real time Level 2 analysis, called the Optimised Retrieval Model (ORM), has been developed in the framework of ESA contract 117171 95/NL/CN/. This code is suitable for the retrieval of profiles of pressure, temperature, and volume mixing ratio of six key species (H<sub>2</sub>O, O<sub>3</sub>, HNO<sub>3</sub>, CH<sub>4</sub>, N<sub>2</sub>O and NO<sub>2</sub>) from infrared limb spectra recorded by MIPAS experiment on board ENVISAT-1.

In absence of MIPAS measurements, measurements obtained by instruments similar to the ENVISAT version of MIPAS are used to validate the ORM [RD1]: the balloon instrument MIPAS-B2 (same instrument but different geometry) and the Space Shuttle instrument ATMOS (satellite geometry but higher signal to noise ratio and higher resolution than MIPAS).

In particular, in this technical note the analysis is reported that was made using ATMOS data for the characterisation of possible spectroscopic errors. The objective of the present technical note is to generate a database for MIPAS experiment and to report and characterise its updates.

In Sect. 3 a brief description of ATMOS experiment and of characterisation of ATMOS data sets is reported. In Sect. 4 the approach adopted for the update of the spectroscopic database is described. In Sect. 5 sections the improvements and changes are presented molecule by molecule.

The issue 1 of this technical note was limited to the HOCl,  $HNO_3$ ,  $O_3$ ,  $NO_2$ ,  $CH_4$  and  $H_2O$  molecules. The present version includes in respect to the previous version considerations on spectroscopic errors and the correlations between them (Sect. 6).

# **3. ATMOS experiment**

For a comprehensive characterisation of spectroscopic data, the ATMOS (Atmospheric Trace MOlecule Spectroscopy) experiment [1] has been chosen because it provides measurements with a limb geometry, spectral region and spectral resolution comparable to those of MIPAS. The ATMOS experiment is a solar occultation limb-sounding experiment, that performs measurements when the atmosphere is between the Sun and the instrument (i.e., at sunrise and sunset as seen from the spacecraft). The ATMOS experiment provided a broadband ( $625-4800 \text{ cm}^{-1}$ ,  $2.1-16 \mu\text{m}$ ) infrared solar spectra at an unapodized spectral resolution of  $0.01 \text{ cm}^{-1}$ . The full spectral response of the spectrometer observed by the detector in a single band is defined by the filter. A total of six filters that define smaller overlapping spectral intervals are available: filter 1 600-1200 cm<sup>-1</sup>, filter 2 1100-2000 cm<sup>-1</sup>, filter 3 1580-3400 cm<sup>-1</sup>, filter 4 3100-4700 cm<sup>-1</sup>, filter 9 625-2450 cm<sup>-1</sup> and filter 12 625-1400 cm<sup>-1</sup>.

Spectral interval covered	625-4800 cm <sup>-1</sup> (2.1 to 18 μm)
Spectral resolution	0.01 cm <sup>-1</sup> unapodized (50 cm OPD)
Spectral precision	<b>0.001 cm<sup>-1</sup> (He-Ne reference laser)</b>
Spatial resolution	1 to 2.5 km
Field of View	1, 2, or 4 mrad, selectable
Signal to noise ratios	300:1 to 50:1
Time per spectrum	2.2 seconds
Pointing accuracy	0.1 mrad (2-axis suntracker)
Detector	HgCdTe (77K)

The key performance parameters can be summarised in the following table:

ATMOS measurements from **filter 9** match the requirements of the spectral region of MIPAS and the high spectral resolution of ATMOS resolves the spectroscopic features of most atmospheric constituents. Among the measurements made with filter 9, a limb-scanning sequence (labelled at3ss03 ratio spectrum) of ATMOS of the ATLAS-3 mission (launched in 1994) has been made available by JPL. This limb sequence is a sun-set sequence that cover an altitude range from 7.34 km to 98.2 km with a vertical resolution ranging from 1 km at low altitudes to 3 km at high altitudes. For this sequence the signal to noise ratio is approximately 100 and the unapodized spectral resolution is  $0.0102 \text{ cm}^{-1}$  (the Norton-Beer medium function is used as an apodization function).

## 4. Spectroscopic databases

The database of MIPAS is built starting from the HITRAN96 database. This report presents changes and improvements on the basis of tests performed with ATMOS measurements and in the light of new results obtained with laboratory spectroscopy. The molecules for which the spectroscopic database will be reviewed are the main gases and some special cases. This technical note is written molecule by molecule since the recommendations and changes are different for each one.

The updated databases for the MIPAS experiment are named in the following ways:

hitran\_mipas\_pf1.0: Old database provided by IMK

- hitran96 database for each gas except for  $O_3$
- O<sub>3</sub>-lines from hitran96 and additional updated lines provided by J.-M. Flaud (O<sub>3</sub> hot-bands at 11 μm and at 4.8 μm)

#### hitran\_mipas\_pf1.1: hitran\_mipas\_pf1.0 / new HOCl lines

- hitran\_mipas\_pf1.0 database for each gas except for HOCl
- HOCl lines from hitran96 (2703) replaced by updated HOCl lines (3972)

## hitran\_mipas\_pf1.2: *hitran\_mipas\_pf1.1 / new HNO<sub>3</sub> lines*

- hitran\_mipas\_pf1.1 database for each gas except for HNO<sub>3</sub>
- HNO<sub>3</sub> lines from hitran96 (146342) replaced by updated HNO<sub>3</sub> lines (169833)

## hitran\_mipas\_pf1.3: hitran\_mipas\_pf1.2 / new O<sub>3</sub> lines

- hitran\_mipas\_pf1.2 database for each gas except for O<sub>3</sub>
- O<sub>3</sub> lines from hitran96 (20297) replaced by updated O<sub>3</sub> lines (20742)

#### hitran\_mipas\_pf1.4: *hitra\_mipas\_pf1.3 / new NO*<sub>2</sub> *lines*

- hitran\_mipas\_pf1.3 database for each gas except for NO<sub>2</sub>
- NO<sub>2</sub> lines from hitran96 (3220) replaced by updated NO<sub>2</sub> lines (103848)

#### hitran\_mipas\_pf1.5: hitra\_mipas\_pf1.4 / new CH<sub>4</sub> lines

- hitran\_mipas\_pf1.4 database for each gas except for CH<sub>4</sub>
- $CH_4$  lines from hitran96 (23260) replaced by updated  $CH_4$  lines (75251)

#### hitran\_mipas\_pf2.0: hitra\_mipas\_pf1.5 / new H<sub>2</sub>O lines

- hitran\_mipas\_pf1.5 database for each gas except for H<sub>2</sub>O
- $H_2O$  lines from hitran96 (8184) replaced by updated  $H_2O$  lines (10828)

The first number in the name provides the issue of the database while the second number provides the version of the database.

In the ORM code the cross sections of the atmospheric constituents can either be calculated line by line (LBL) using a pre-selected spectroscopic database, or be read from look-up tables (LUT). The progressive changes and improvements of MIPAS database will be checked with LBL calculations made with different versions of the database, whereas new look-up tables will be generated only when a new issue of the database is produced.

# 5. Updates of MIPAS database

## 5.1. Hypochlorous acid HOCI

Recent studies [2, 3] of the spectroscopic properties of HOCl have shown that the HITRAN96 spectral parameters concerning the <sup>35</sup>Cl and <sup>37</sup>Cl isotopic variants of this species were not of sufficient quality both for the line positions and intensities. As far as the MIPAS database is concerned, the main problem was related to the line intensities in the 8.1  $\mu$ m spectral region. Indeed, this molecule is unstable and always exists in the equilibrium.

$$H_2O + Cl_2O \xrightarrow{\leftarrow} 2 HOCl$$

The main difficulty is then to estimate its partial pressure in the cell. Different methods can be used (see ref. [3] for their description), but when one looks at the literature it appears that there is a huge scatter among the various results concerning the total band intensities (Table 8 of ref. [3]). To avoid this difficulty, the method used in ref. [3] was to measure simultaneously the far infrared and the 8.1  $\mu$ m line intensities. Since the intensities can be precisely calculated in the far infrared using the dipole moment derived from Stark experiments, one can use them to estimate accurately the partial pressure of HOCl and hence to get reliable intensities at 8.1  $\mu$ m. These new intensities are on the average 66% lower than the HITRAN96 ones. These new data have been included in the MIPAS database.

Since HOCl is an interfering species and since the change is mainly a scaling factor of the intensities, ATMOS data do not provide a validation for this update.



#### 5.2. Nitric acid HNO<sub>3</sub>

A simulation of the ATMOS spectra using HITRAN96 demonstrated that in particular around 885cm<sup>-1</sup> the agreement with the observation was rather poor (Fig. 1). A careful analysis showed that this was due to very poor spectral parameters for the hot band  $v_5$  $+ v_9 - v_9$  of HNO<sub>3</sub> (HIT24-19). A new version for the spectral parameters was available in HITRAN2K. Fig. 2 presents a simulation with these new data. It is clear that, even if the situation has improved, the agreement is far from being satisfactory (shift of the absorption peak in particular). Another simulation was made shifting the lines by 0.008cm<sup>-1</sup> (Fig. 3) improving the situation but not in a fully satisfactory manner (shape of the absorption peak not correct). This can be understood when looking at Fig. 4 where a comparison is made with a high resolution laboratory spectrum: clearly the shape of the simulation peak at 885.4cm<sup>-1</sup> is not correct. It was then decided to perform a spectroscopic theoretical modelling of the hot band [4] and the results are presented in Fig. 5. The excellent agreement between observation and calculation is obvious and is confirmed in Fig. 6 by the comparison with the ATMOS data. An improvement is also detected in another spectral region around 878 cm<sup>-1</sup> which corresponds to an important MIPAS microwindow, HNO30001 (Figures 7 and 8). Accordingly the new data are included in the MIPAS database.

The  $3v_3 - v_3$  band (HIT23-19) was also calculated and included in the MIPAS database: it is worth noticing that the spectral parameters for this band present in HITRAN96 are completely wrong (it is no longer included in HITRAN2K). However the effect of these new data on atmospheric simulations could not yet be checked due to the fact that the ATMOS data are not of sufficient quality in the corresponding spectral domain.



Fig. 1: Simulation of an ATMOS spectrum using HITRAN96









# 5.3. Ozone <sup>16</sup>O<sub>3</sub>

The ozone molecule  ${}^{16}O_3$  has been recently the subject of extensive laboratory studies performed by four different groups [5-8] in the 10µm region in order to improve line positions and intensities in this spectral domain which is extensively used for atmospheric retrievals by several instruments and in particular by MIPAS. We have compared the four sets of experimental data and the following conclusions have been reached (see Appendix 1 for more details):

- The four sets of data are highly consistent on a relative basis (agreement better than 2%)
- Three sets of data from ref. [5-7] agree very well as far as absolute intensities are concerned (dispersion of ≈ 0.8 %, 1σ standard deviation of ≈ 1.7 %) whereas intensities from ref. [8] are consistently ≈ 4 % higher.

As a consequence it was decided to rely on the sets of data from ref. [5-7] and these intensities were fitted to derive the relevant transition moment constants (Appendix 1). Using these constants a new line list was generated for the two bands absorbing at 10 $\mu$ m, namely v<sub>1</sub> (HIT4-1)<sup>1</sup> and v<sub>3</sub> (HIT5-1).

 $\nu_3$ 

When comparing to HITRAN96 one gets the following intensity ratios:

BAND  $v_1$ 

HIT96/NEWCAL 1.044(35) 1.035(14)

<sup>&</sup>lt;sup>1</sup> HITn-m gives the HITRAN notation of the band

The new line list was checked against the ATMOS data and the results are gathered in Table 1. It appears that:

- The overall RMS is, for the two altitudes, better with the new data than with the HITRAN96 data.
- The statistical analysis of the residuals obtained for the 3 cm<sup>-1</sup> wide intervals covering the spectral domains usable from the ATMOS spectra shows that for more than 90% of the intervals the new data give better results.

This proves that, on a relative basis, the new data allow one to perform better simulations.

As a consequence of all these findings, it was decided to include the new data in the MIPAS database. More precisely:

- The cold bands  $v_1$  (HIT4-1),  $v_3$  (HIT5-1) and  $v_2$  (HIT2-1) (the latter being an additional measurement provided by ref. [7]) have been included in the MIPAS database.
- The intensities of all the other bands (hot bands, isotopic species) were divided by 1.04 to account for the change in the absolute intensities of the cold bands.

#### Table 1

Comparisons of simulated and observed ATMOS spectra using HITRAN96 and the new calculations<sup>2</sup>

	-
023 - 1170	1065 - 1170
669/0.725	0.460/0.482
44 of 49	33 of 35
)	23 – 1170 669/0.725 44 of 49

## 5.4. Nitrogen dioxide NO<sub>2</sub>

The 6.2  $\mu$ m region is widely used to retrieve atmospheric NO<sub>2</sub> profiles from balloon borne or satellite instruments since it corresponds by far to the strongest absorption of this molecule: v<sub>3</sub> band (HIT 5 -1).

As far as spectroscopy is concerned, due to the spin – rotation interaction the infrared vibration – rotation lines appear as doublets. This spin rotation interaction can be treated either through a perturbation method or directly, the latter method giving much more accurate results.

In HITRAN96 only two bands appear in the 6.2  $\mu m$  region:

- The fundamental  $v_3$  (HIT5-1) band for which the spin-rotation interaction is taken fully into account [9].
- The first hot band  $v_2 + v_3 v_2$  (HIT8-2) for which this interaction is treated through a perturbation method [10], hence providing one with results of a quality not sufficient for an experiment like MIPAS.

<sup>2</sup> CAL stands for new calculations HIT96 stands for HITRAN96 It is worth noticing that no other hot band is available in this spectral region in the HITRAN database preventing one from dealing with possible NLTE phenomena.

Based on recent spectroscopic studies, new spectral parameters are generated and included in the MIPAS database.

They are:

- The band system [11] {011,030}  $\leftarrow$  (010) which replaces the first hot band  $\nu_2$  +  $\nu_3-\nu_2$
- The band system [12] {120,101}  $\leftarrow$  {100, 020, 001}, the strongest band of which is  $v_1 + v_3 v_1$  (HIT13-4)
- The band system [13] {040, 021, 002}  $\leftarrow$  {100, 020, 001} the strongest bands of which are  $2v_3 v_3$  (HIT14-5) and  $2v_2 + v_3 2v_2$  (HIT11-3)
- The band system [14]  $\{022,003\} \leftarrow \{040, 021, 002\}$  the strongest bands of which are  $3v_3 2v_3$  (HIT27-14) and  $2v_2 + 2v_3 (2v_2 + v_3)$ (HIT23-11)

Table 2 presents the characteristics of the new 23 bands, which have been included in the MIPAS database.

## Table 2

# SUMMARY OF THE NO2 HOT BANDS INCLUDED IN THE MIPAS DATABASE

NUMBER OF LINES = 103848 NUMBER OF BANDS = 23

NUM	BAND	XMIN	XMAX	SMIN	SMAX	STOT	NB
1	101001	1140 0015	1610 7745	0 1005 27	0 1120 04	0 2015 22	FDCO
1	101001	1142.0215	1612.7745	0.180D-27	0.113D-24	0.381D-22	5208
2	120020	1144.4/66	1517.8400	0.180D-27	0.337D-25	0.15/D-22	4425
3	101020	1175.6815	1612.1739	0.183D-27	0.270D-26	0.199D-24	253
4	022021	1226.0473	1881.4318	0.176D-31	0.757D-25	0.307D-22	11892
5	120001	1327.0051	1365.8081	0.181D-27	0.469D-27	0.176D-26	7
6	003002	1348.1076	1788.3529	0.176D-31	0.664D-25	0.297D-22	9679
7	022002	1353.0833	1803.4869	0.176D-31	0.252D-26	0.756D-25	3554
8	040020	1367.6299	1727.4077	0.388D-28	0.198D-22	0.142D-20	4772
9	030010	1372.8892	1797.4293	0.261D-26	0.659D-22	0.121D-20	5783
10	022040	1380.6887	1752.2183	0.176D-31	0.175D-25	0.123D-23	6561
11	021020	1390.7158	1833.4969	0.389D-28	0.882D-22	0.352D-19	7571
12	021001	1395.0056	1726.4321	0.388D-28	0.460D-23	0.427D-21	2554
13	120100	1397.1888	1695.0039	0.180D-27	0.208D-24	0.311D-22	2591
14	002001	1401.6565	1843.2518	0.388D-28	0.988D-22	0.433D-19	7687
15	011010	1410.5613	1836.3982	0.261D-26	0.338D-20	0.145D-17	9215
16	040001	1430.0087	1678.6526	0.391D-28	0.319D-26	0.161D-24	504
17	003021	1432.8641	1739.7821	0.176D-31	0.263D-26	0.138D-24	2267
18	101100	1457.7296	1828.6348	0.180D-27	0.209D-21	0.912D-19	7454
19	003040	1459.2100	1731.3784	0.176D-31	0.199D-29	0.105D-27	616
2.0	002020	1507 8867	1768 1095	0 3880-28	0 326D-23	0 299D-21	1008
21	002100	1526 4612	2035 5122	0 388D-28	0 719D-24	0 289D-21	8727
22	021100	1532 01012	1084 5350	0 3880-28	0.105D - 25	0 1030-23	1458
പപറാ	040100	1000 0701	1055 6770	0.2000 20	0 2020 20	0.100 20	0.FT
43	040100	1010.9/01	T000.0110	0.3000-20	0.3920-20	0./000-20	2

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				-	-						
NUM	BAND	JUMI	KUMI	JUMA	KUMA	JLMI	KLMI	JLMA	KLMA	EMIN	EMAX
1	101001	1	0	58	13	1	0	57	12	1617.6872	2998.6074
2	120020	0	0	59	12	0	0	58	11	1498.3469	2918.0489
3	101020	22	4	53	8	21	6	52	6	1988.8478	2954.1185
4	022021	0	0	66	12	1	0	66	12	3093.3116	5490.5662
5	120001	38	3	57	5	37	1	56	3	2272.8978	2937.7730
6	003002	1	0	66	12	0	0	66	12	3201.4489	5493.6184
7	022002	4	0	66	10	3	0	66	9	3209.7803	5157.0789
8	040020	3	0	60	12	2	0	59	11	1500.8718	2989.6164
9	030010	1	0	70	13	1	0	70	14	758.0805	2980.3964
10	022040	1	0	66	11	1	0	66	12	2995.2977	5232.0619
11	021020	1	0	60	12	0	0	59	12	1498.3469	2996.1030
12	021001	5	0	58	9	4	0	57	8	1629.4253	2998.6074
13	120100	5	0	63	9	4	0	62	8	1337.3801	2994.2046
14	002001	0	0	58	12	1	0	57	12	1617.6872	2998.6074
15	011010	1	0	70	13	0	0	70	13	749.6526	3998.5833
16	040001	7	3	56	7	6	1	54	5	1700.5598	2998.6074
17	003021	3	0	66	6	4	0	66	7	3105.0202	5228.3710
18	101100	1	0	64	12	0	0	63	12	1319.7659	2997.9454
19	003040	6	3	62	5	6	5	61	7	3238.4857	4906.8751
20	002020	5	1	56	7	6	4	55	7	1719.3809	2955.2192
21	002100	0	0	64	12	1	0	63	12	1322.2819	2997.9454
22	021100	6	0	64	7	5	0	63	8	1454.1506	2985.3550
23	040100	45	3	49	5	43	0	48	4	2235.6980	2295.4124

The meaning of the different columns is :

BAND: Vibrational assignment

XMIN,XMAX: Minimum and maximum line positions

SMIN,SMAX: Minimum and maximum line intensities

STOT: Total band intensity

NB: Number of lines

JUMI,KUMI,JUMA,KUMA: Minimum and maximum values of the rotational quantum numbers J and K for the upper state

JLMI,KLMI,JLMA,KLMA: Minimum and maximum values of the rotational quantum numbers J and K for the lower state

EMIN, EMAX: Minimum and maximum lower state energies

# 5.5. Methane <sup>12</sup>CH<sub>4</sub>, <sup>13</sup>CH<sub>4</sub>, CH<sub>3</sub>D

The file 06.HIT01.par, which is not included in HITRAN2K, and which has been recently updated by L. Brown (JPL, USA) is a total replacement of the 1996 spectroscopic parameters for the three isotopic species of methane. In this new database the most recent studies for all three isotopes have been merged and include line shape assessments. Also many lines weaker than  $1 \cdot 10^{-24}$  cm<sup>-1</sup>/(molecule·cm<sup>-2</sup>) were included for the benefit of planetary and stellar applications.

It is important to notice that the main changes of this new database with respect to HITRAN96 are in the region between 850 and 4810 cm<sup>-1</sup>, while no change has been made in the regions below 600 and above 5500 cm<sup>-1</sup>.

The format of the rotational field has been changed so that the upper and lower state "n" can be written as a three digit number and the format for  $CH_3D$  is no longer compatible with the  $CH_4$  one. A summary kindly provided by L. Brown is given in Appendix 2 and contains details about the changes and improvements.

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These new data were compared with the previous one (HITRAN 96) using ATMOS spectra. The statistical analysis of the residuals in the the main absorption ranges of CH<sub>4</sub> (1050-1899 cm<sup>-1</sup> and 2149-2500 cm<sup>-1</sup>) performed using ATMOS spectra recorded at altitude of 23.334 km (See Table 3) confirms that the new data are more reliable. Accordingly in the MIPAS database the methane HITRAN96 data have been replaced by the new data.

# Table 3

Comparisons of simulated and observed ATMOS spectra using HITRAN96 and the new methane data (at 23.3 km)

Band	Spectral domain (cm <sup>-1</sup> )	Number of intervals where CAL gives better results
AB	1065 - 1170	34 of 35
В	1215 - 1278 & 1350 - 1500	45 of 71
С	1570 - 1690	27 of 36
D	2123 - 2258	30 of 46

# 5.6. Water vapour H<sub>2</sub>O

In our study, four sets of spectral parameters were taken into account for the  $\rm H_2O$  molecule  $^3$  . They are :

- the HITRAN96 parameters denoted in the following as 01\_HIT96
- the HITRAN2K parameters denoted in the following as 01\_HIT2K
- the updated parameters which can be found on the HITRAN website and which are denoted in the following as 01\_HIT01
- the parameters derived for the main isotope from recent calculations using a new theoretical model [15-16 and references therein] and denoted in the following as 01\_CAL01.

**The first step** was to compare the spectroscopic parameters of the files 01\_HIT2K and 01\_HIT01. Table 4 presents the results and it is clear that the two files are identical except for the HD<sup>16</sup>O species for which the 01\_HIT2K file does not include the  $v_3 - v_2$  (HIT 5-2) band.

As a consequence, since 01\_HIT01 is more complete, in the following we will concentrate on the file 01\_HIT01 and will no longer consider the file 01\_HIT2K.

In a second step we compared for all the isotopic species <u>except H<sub>2</sub></u><sup>16</sup>O the spectral parameters included in the files 01\_HIT01 and 01\_HIT96. The results are gathered in Table 5 and one can make the following comments:

- On the average, there is a rather good agreement between the two sets of data for the strongest band  $v_2$  (HIT 2-1). This is also true to a lesser extent for the weaker bands  $2v_2 v_2$  (HIT 3-2) and  $v_3 v_2$  (HIT 5-2).
- The main differences ( $\cong \pm 20\%$ ) exist for the pure rotation band (HIT 1-1) but it should be noticed that in the spectral region that we are considering this band is

<sup>&</sup>lt;sup>3</sup> Unless the isotopic species is clearly specified, the "H<sub>2</sub>O molecule" means in the following the various isotopic variants of this molecule, namely  $H_2^{16}O$ ,  $H_2^{18}O$ ,  $H_2^{17}O$ ,  $HD^{16}O$ ,  $HD^{18}O$  and  $HD^{17}O$ .

rather weak and, also considering the abundance of the various isotopic species, it is unlikely that the corresponding lines will be clearly seen in the MIPAS spectra in the stratosphere.

Given the fact that the new data are the end product of precise laboratory studies performed in the recent years [17] for all the isotopic species except  $H_2^{16}O$  we decided to use these new data in the MIPAS database. Indeed it should be noticed that it may be difficult to discriminate between the two sets of data using the ATMOS spectra since the main differences exist for weak lines which cause small signatures in the ATMOS spectra.

The third step was devoted to the comparison of the line intensities of the  $H_2^{16}O$  isotopic species. Three sets of data 01\_HIT96, 01\_HIT01 and 01\_CAL01 were compared and the results are given in Table 6.

Such comparisons were performed:

- for all pairs of common lines and
- for a pair of common lines with intensities larger than  $10^{-25}$  cm<sup>-1</sup>/(mol. cm<sup>-2</sup>), this value, while somewhat arbitrary, being considered as a lower limit for significantly absorbing lines in atmospheric spectra.

Concentrating on the strong and medium intensities (Intensities larger than  $10^{-25}$  cm<sup>-1</sup> /(mol. cm<sup>-2</sup>)), one can draw the following conclusions:

- For all the bands there is an excellent agreement between the 01\_CAL01 and 01\_HIT01 data sets,
- Whereas there is a good agreement between 01\_CAL01, 01\_HIT01 and 01\_HIT96 for the strong band  $v_2$  (HIT 2-1) and for the medium hot band  $2v_2 v_2$  (HIT 3-2), 01\_HIT96 shows larger discrepancies from the other two data sets for the other bands (between ~ 5% and + 20% depending on the band). As far as MIPAS is concerned such effects should be sensitive in the 14 9 µm spectral region where the pure rotation band (HIT 1-1) appears to be about 8 9 % too weak in 01\_HIT96.

Considering now the comparisons made when including all the lines it appears that:

- The agreement is still very good on the average for all bands when comparing 01\_CAL01 and 01\_HIT01 but it is worth noticing the increase of the standard deviations: this means that for the weak lines there are stronger differences.
- On the contrary both the comparisons between 01\_HIT01 and 01\_HIT96 and the comparison between 01\_CAL01 and 01\_HIT96 show i) a strong change of the average ratios as compared to the ones obtained with the strong and medium intensities and ii) a strong increase in the standard deviation. All this means that very strong differences exist between the weak lines.

Given the fact that:

- as already said, the 01\_HIT01 data set is based on a number of precise laboratory studies [17],
- the 01\_CAL01 file was generated using a theoretical model [15,16] which treats simultaneously all the bands (this insures that on a relative basis the intensities are much more consistent than when a band per band treatment is used),
- the comparisons made in Table 6 show a much better agreement of 01\_CAL01 with 01\_HIT01 than with 01\_HIT96,

one can certainly conclude that the two files 01\_CAL01 and 01\_HIT01 provide better spectral parameters than 01\_HIT96.

This is confirmed by the simulation of ATMOS spectra as shown in Table 7 where a statistical analysis of the residuals was performed comparing 01\_HIT96 and 01\_HIT01 data at 14 km. As in the case of the analysis of the other species, the statistics was made for 3 cm<sup>-1</sup> wide intervals covering the spectral MIPAS bands, excluding those regions in which the observed ATMOS spectra were opaque and in which the effect of atmospheric continuum was significant. For each spectral band three columns are given. The first column shows the spectral intervals of the band in which the statistics was performed, the second column shows the RMS of residuals using the two different sets of data, and the third column shows the number of intervals, where the new data (in this case 01\_HIT01 data) give better results, compared with the total number of intervals. From this comparison it appears that, even if the percentage of intervals in which the new data are better is not decisive, the overall RMS both in each band (except band AB in which the difference between the RMS of the two sets is on the fourth decimal digit) and in all bands together is better with the new data (01\_HIT01) than with the old data (01\_HIT96).

Established that 01\_HIT01 provided better spectral parameters than 01\_HIT96, the statistical analysis of the residuals was performed comparing 01\_HIT01 and 01\_CAL01 data (only  $H_2^{16}O$  band) at 23 km. Table 8 shows the results of this comparison and provides the same statistical results in Table 7.

Except the results in band AB and B in which the overall RMS of the residuals are comparable, considering the total effect it is possible to conclude that there is some indication that the 01\_CAL01 data set is likely to give better results than 01\_HIT01.

As a conclusion the  $H_2O$  line parameters included in the MIPAS database are:

- For all isotopic variants of  $H_2O$  except  $H_2^{16}O$  the line parameters of 01\_HIT01,
- For  $H_2^{16}O$  the line parameters of 01\_CAL01. It is worth noticing that these new data, which are summarised in Table 9, include also the pure rotation bands in the excited states  $2v_2$ ,  $v_3$  and  $v_3$  (Bands 3-3, 4-4 and 5-5 in Hitran notation) which do not exist in the other databases,
- For the band HIT 6-3 of the main isotope the data from 01\_HIT01 were kept.

#### Table 4

Comparison of the line intensities included in the files 01\_HIT2K and 01\_HIT01 (spectral domain  $600 - 2500 \text{ cm}^{-1}$ )

Band	Isotopic species						
HITRAN notation	$H_2^{16}O$	$H_2^{18}O$	H2 <sup>17</sup> O	HD <sup>16</sup> O	HD <sup>18</sup> O	$HD^{17}O$	
1-1	1.	1.	1.	1.			
	(482)	(137)	(87)	(78)			
2-2	1.	1.					
	(120)	(6)					
2-1	1.	1.	1.	1.	1.	1.	
	(1826)	(1031)	(841)	(1710)	(438)	(175)	
3-2	1.	1.	1.	1.			
	(870)	(303)	(190)	(435)			
4-2	1.	1.		1.			
	(524)	(63)		(33)			
5-2	1.	1.		$(99)^{a}$			
	(449)	(59)					
6-3	1.						
	(380)						
N (01_HIT01)	4651	1599	1118	2355	438	175	
N (01_HIT2K)	4651	1599	1118	2256	438	175	

We give for each isotope and for each band the average ratio of the intensities and the number of lines in common (below in parenthesis). N (01\_HITxx) gives for each isotope the number of lines included in the file 01\_HITxx.

<sup>a</sup> Number of lines included in 01\_HIT01 and absent in 01\_HIT2K.

## Table 5

Comparison of the line intensities included in the files 01\_HIT01 and 01\_HIT96 for the less abundant water isotopic variants (spectral domain  $600 - 2500 \text{ cm}^{-1}$ )

Band	Isotopic species							
HITRAN notation	$H_2^{18}O$	$H_2^{17}O$	HD <sup>16</sup> O	HD <sup>18</sup> O	$HD^{17}O$			
1-1	1.176 (86)	1.163(47)	0.748(64)					
	(104)	(65)	(17)					
2-2								
2-1	0.997(54)	0.969(46)	0.984(240)					
	(968)	(840)	(1542)					
3-2	1.044(200)	1.017(54)						
	(262)	(190)						
4-2								
5-2	1.084(48)							
	(16)							
6-3								
N (01_HIT01)	1599	1118	2355	438	175			
N (01_HIT96)	1350	1148	1773	0	0			

We give for each isotope and for each band the average ratio of the intensities (01\_HIT01/01\_HIT96), the corresponding standard deviation and the number of lines in common (below in parenthesis). N (01\_HITxx) gives for each isotope the number of lines included in the file 01\_HITxx.

## Table 6

Comparison of the line intensities included in the three files 01\_CAL01, 01\_HIT01 and 01\_HIT96 for the  $H_2^{16}O$  molecule (spectral domain 600 – 2500 cm<sup>-1</sup>)

Band	01_HIT01/	01_HIT96	01_CAL02	1/01_HIT96	01_CAL01/01_HIT01		
	$I \ge 10^{-25}$	All lines	$I \ge 10^{-25}$	All lines	$I \ge 10^{-25}$	All lines	
1-1	1.093(274)	1.541(1571)	1.084(276)	1.709(1960)	0.987(58)	1.063(823)	
	(253)	(463)	(252)	(491)	(252)	(461)	
2-2	0.937(40)	0.958(97)	0.956(40)	0.906(110)	1.026(51)	0.955(125)	
	(35)	(84)	(34)	(92)	(36)	(118)	
2-1	1.023(97)	1.351(2466)	1.021(121)	1.387(3059)	0.998(64)	1.021(352)	
	(1286)	(1671)	(1288)	(1671)	(1288)	(1796)	
3-2	1.020(125)	1.100(364)	1.012(109)	1.084(450)	0.993(73)	1.014(788)	
	(483)	(724)	(491)	(728)	(491)	(861)	
4-2	1.170(289)	1.437(942)	1.201(289)	1.322(743)	1.013(120)	1.088(878)	
	(188)	(395)	(186)	(399)	(186)	(510)	
5-2	1.081(133)	1.099(265)	1.117(137)	1.236(445)	1.034(66)	1.178(432)	
	(173)	(350)	(169)	(350)	(169)	(434)	
6-3	0.640(255)	0.871(433)					
	(22)	(121)					

We give for each band the average ratio of the intensities, the corresponding standard deviation and the number of line in common (below in parenthesis).  $I \ge 10^{-25}$  means that only lines with intensity larger than  $10^{-25}$  cm<sup>-1</sup>/(mol. cm<sup>-2</sup>) were compared.

## Table 7

Comparison of simulated and observed ATMOS spectra using 01\_HIT01 and 01\_HIT96 data for the all  $H_2O$  isotopic variants at 14 km

Band	Spectral domain (cm <sup>-1</sup> )	RMS ·10 <sup>-2</sup> 01_HIT01/01_HIT96	Number of intervals where HIT01 give better results
А	769-844 & 859-910	2.9865/2.9920	32 of 53
	& 934-970		
AB	1065-1092 & 1122-1170	3.1956/3.1955	7 of 21
В	1215-1278 & 1310-1500	2.5609/2.6527	57 of 81
С	1573-1612 & 1627-1642 &	2.2557/2.2595	20 of 45
	1669-1750		
D	1820-2102 & 2111-2201	2.0777/2.1221	73 of 121
Total	-	2.4478/2.4891	189 of 321

# Table 8

Comparison of simulated and observed ATMOS spectra using 01\_CAL01 and 01\_HIT01 data for the  $H_2^{16}O$  molecule at 23 km

Band	Spectral domain (cm <sup>-1</sup> )	RMS 10 <sup>-2</sup> 01_CAL01/01_HIT01	Number of intervals where CAL01 give better results					
А	745-970	2.3581/2.4941	45 of 75					
AB	1041-1170	1.9230/1.9229	16 of 38					
В	1215-1500	2.2379/2.2357	29 of 91					
С	1573-1750	2.6402/2.6583	32 of 59					
D	1820-2240	1.8160/1.8444	85 of 160					
Total	-	2.1275/2.1644	207 of 423					



### Table 9

Summary of the  $H_2^{16}O$  bands coming from 01\_CAL01 included in the MIPAS database (spectral domain 600 – 2500 cm<sup>-1</sup>)

NUM			BA	ND			XM	IIN		XMAX		SMIN		SM	AX		STOI	Г	Ν	В
1	0	0	0	0	0	0	600.	0273	145	7.6674	0.1	.01D-2	6 0.	248D-	-20	0.22	24D-	19	506	5
2	0	0	1	0	2	0	600.	8882	91	3.0041	0.1	01D-2	6 0.8	838D-	-25	0.11	L2D-	23	78	3
3	0	2	0	0	2	0	601.	0321	64	5.1868	0.1	.37D-2	6 0.4	466D-	-26	0.80	)3D-	26	3	3
4	0	1	0	0	1	0	601.	5922	188	3.9023	0.1	.00D-2	6 0.3	326D-	-23	0.21	L5D-	22	152	2
5	1	0	0	0	2	0	634.	2877	82	9.0096	0.1	24D-2	6 0.	514D-	-26	0.27	70D-	25	11	_
6	0	1	0	0	0	0	640.	5014	249	7.2495	0.1	.00D-2	6 0.	314D-	-18	0.11	L1D-	16	1928	3
7	0	2	0	0	1	0	819.	7767	240	6.1835	0.1	.03D-2	6 0.3	277D-	-21	0.95	53D-	20	971	L
8	1	0	0	0	1	0	1221.	4098	249	6.8647	0.1	01D-2	6 0.3	377D-	-23	0.15	50D-	21	624	ł
9	0	0	1	0	1	0	1298.	1170	249	7.6887	0.1	03D-2	6 0.9	915D-	-23	0.23	34D-	21	477	7
10	0	2	0	0	0	0	2387.	9933	244	9.9804	0.2	256D-2	6 0.	718D-	-26	0.97	75D-	26	2	2
NUM			BA	ND			J1MIN	K1M	IN J	1MAX K	1AX	J2IN	K2IN	J2A	х к2	2AX	EN	4IN	E	MAX
-	~	~	•	~	~	~	~	~	~ ~		-		1.0			~ ~	0 F F			
Ţ	0	0	0	0	0	0	6	2	20	15	5	0	19	14	32	16.6	255	533	39.6	665
2	0	0	Ţ	0	2	0	1	0	11	4	0	0	10	4	315	1.6	314	426	53.L	503
3	0	2	0	0	2	0		2		5	6	0	10	2	3/3	56.1	106	426	0.4	670
4	0	T	0	0	T	0	6	2	17		5	0	16	9	192	20.7	666	520	18.8	958
5	T	0	0	0	2	0	4	2	.7	4	3	Ţ	6	3	338	31.7	043	386	54.9	661
6	0	T	0	0	0	0	0	0	20	13	0	0	20	13	1 - 0	0.0	000	453	34.9	634
.7	0	2	0	0	1	0	0	0	18	10	0	0	17	10	159	94.7	463	458	35.3	496
8	T	U	0	0	1	U	0	U	15	9	0	0	14	T0	159	94.7	463	449	∮/.⊥	905
9	0	0	Ţ	0	T	0	0	0	16	8	0	0	15	8	159	94.7	463	393	37.5	717
10	0	2	0	0	0	0	12	1	13	3	12	2	13	10	224	6.8	850	326	56.7	648

The legend is the same as Table 2.

#### 6. Spectroscopic Errors and Correlations between Errors

To assess the accuracy of spectral parameters in the set of microwindows selected by selection program MWMAKE a subroutine PTBHIT.for is used. This subroutine is a part of the MIPAS Reference Model supplied the European Space Agency under contract No. 11886/96/NL/GS (Version of PTBHIT.for: 01-JUN-97 Derived from program TVC2 by H. Kemnitzer at IMK). This subroutine perturbs HITRAN data by suitable uncertainties for each spectral parameter and effectively creates an "alternative" HITRAN database. Spectroscopic errors are represented in measurement space by the difference in calculations between these two databases [18].

The most relevant spectroscopic parameters that show characteristic effects on residuals are the line strength, the pressure broadening coefficients and the line position. A new estimation of the line strength errors for the updated data is reported in Appendix 3, whereas the estimation of the pressure broadening coefficients is not changed and new values are not given. The line positions are known with a very good accuracy and the corresponding errors are not considered in PTBHIT.

As far as correlations between spectroscopic errors are concerned, it is extremely difficult to quantify them since one has to face different problems depending on how the spectroscopic parameters were obtained :

• if the line intensities were derived from measurements it is almost impossible to say something reasonable. Indeed usually each line is fitted independently, but the fits are performed either on the same spectrum or on a set of spectra obtained with the same apparatus so that there may exist some correlation.

- if the line intensities were generated from a 'band per band' calculation (i.e. each band is calculated separately) there is no correlation between line intensities of different bands and, within a given band, the intensity errors are correlated. However, to our knowledge, nobody gives any hint on that : in fact people do not usually even propagate the errors!
- Very often the problem is even more complicated since, because of the vibrationrotation resonances, calculations are performed using polyads of interacting states. This means that all the line intensities belonging to the bands involved in the polyad are generated simultaneously. Again nobody gives any hint on the correlations.

Given the above points it is reasonable to expect that, in general, within a given band the intensities are highly correlated. However, is possible to state the existance of this correlation only for those molecules for which we know the process used to generated the lines. One can therefore consider that for the bands listed below the intensities are correlated :

 $\begin{array}{l} \mathbf{H_2O^{16}} \implies \text{Bands 1-1, 5-3, 3-3, 2-2, 2-1, 3-2, 4-2, 5-2} \\ \mathbf{Other H_2O isotopes} \implies \text{Bands 3-2, 4-2, 5-2} \\ \mathbf{HNO_3} \implies \text{Bands 18-14, 21-14} \\ \mathbf{NO_2} \implies \text{Bands 2-1, 3-2} \\ & \text{Bands 3-1, 4-1, 5-1} \\ & \text{Bands 8-2, 6-2} \\ & \text{Bands 11-3, 9-3} \\ \mathbf{O_3} \implies \text{Bands 2-1, 3-2} \\ & \text{Bands 4-1, 5-1, 7-2, 8-2} \\ & \text{Bands 7-1, 8-1} \\ & \text{Bands 12-1, 13-1, 14-1} \end{array}$ 

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