Advanced MIPAS Level 2 Data Analysis (AMIL2DA)

Complementary Spectroscopic Data, Deliverable D20

July 2001

Project EVG1-CT-1999-00015

J.-M. Flaud (LPM)

1 Complementary Spectroscopic Data

In this Section we present the spectroscopic data which are made available. The spectral interval spanned by the data is adapted to the spectral domain covered by the MIPAS experiment, namely 600-2500 cm^{-1}.

1.1 Ozone $^{16}O_3$

The ozone molecule $^{16}O_3$ has been recently the subject of extensive laboratory studies [1] [2] [3] [4] in the 10μm region in order to improve the line positions and intensities in this spectral domain which is extensively used for atmospheric retrievals and in particular by MIPAS. We have compared the four sets of experimental data and the following conclusions have been reached:

- The four sets of data are highly consistent on a relative basis (agreement better than 2%)
- The three sets of data from ref. [1] [2] [3] agree very well as far as absolute intensities are concerned (dispersion of $\approx$ 0.8 %, 1σ standard deviation of $\approx$ 1.7 %) whereas the intensities from ref. [4] are consistently $\approx$ 4 % higher.

As a consequence it was decided to rely on the sets of data from ref. [1] [2] [3] and these intensities were fitted to derive the relevant transition moment constants. Using these constants a new line list was generated for the two bands absorbing at 10μm, namely ν_1 (HIT4-1)[1] and ν_3 (HIT5-1).

When comparing to HITRAN96 one gets :

BAND	ν_1	ν_3
HIT96/NEWCAL	1.044(35)	1.035(14)

Precisely the newly calculated data concern the cold bands ν_1 (HIT4-1) and ν_3 (HIT5-1) as well as the ν_2 (HIT2-1) band which was also measured in ref. [3]. It is worth noticing that, if one wants to use these new data, the intensities of all the other bands (hot bands, isotopic species) have to be divided by 1.04 in order to account for the change in the absolute intensities of the cold bands and hence be consistent.

1.2 Hypochlorous acid HOCl

Recent studies [5] [6] of the spectroscopic properties of this molecule have shown that the HITRAN96 spectral parameters concerning the ^{35}Cl and ^{37}Cl isotopic variants of this species were not of sufficient quality both for the line positions and intensities. As far as the atmospheric databases are concerned, the main problem was related to the line intensities in the 8.1μm spectral region. Indeed, this molecule is unstable and always exists in the equilibrium.

$$H_2O + Cl_2O \leftrightarrows HOCl$$

The main difficulty is then to estimate its partial pressure in the cell. Different methods can be used (see ref. [6] 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. [6]). To avoid this difficulty, the method used in ref. [6] was to measure simultaneously the far infrared and the 8.1μm 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

[1]HITn-m gives the HITRAN notation of a band

accurately the partial pressure of HOCl and hence to get reliable intensities at 8.1μm. These new intensities are on the average 66

1.3 Nitrogen dioxide NO_2

The 6μm region is widely used to retrieve atmospheric NO_2 profiles from balloon borne or satellite instruments since it corresponds by far to the strongest absorption of this molecule: ν_3 band (HIT 5 -1).
On the other band, 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 through a perturbation method or directly, the latter method giving much more accurate results.
In HITRAN96 only two bands appear in the 6.2νm region :

- The fundamental ν_3 (HIT5-1) band for which the spin-rotation interaction was taken fully into account [7].
- The first hot band $\nu_2 + \nu_3 - \nu_2$ (HIT8-2) for which this interaction was treated through a perturbation method [8], hence providing one with results of a quality not sufficient for experiments like MIPAS.

It is worth noticing that no other hot bands are available in this spectral region in the HITRAN database preventing one to deal with possible NLTE phenomena.
Based on recent spectroscopic studies, new spectral parameters have been generated
.
They are :

- The band system[2][9] $\{011, 030\} \longleftarrow (010)$ which replaces the first hot band $\nu_2 + \nu_3 - \nu_2$
- The band system [10] $\{120, 101\} \longleftarrow \{100, 020, 001\}$, the strongest band of which is $\nu_1 + \nu_3 - \nu_1$ (HIT13-4)
- The band system [11] $\{040, 021, 002\} \longleftarrow \{100, 020, 001\}$ the strongest bands of which are $2\nu_3 - \nu_3$ (HIT14-5) and $2\nu_2 + \nu_3 - 2\nu_2$ (HIT11-3)
- The band system [12] $\{022, 003\} \longleftarrow \{040, 021, 002\}$ the strongest bands of which are $3\nu_3 - 2\nu_3$ (HIT27-14) and $2\nu_2 + 2\nu_3 - (2\nu_2 + \nu_3)$(HIT23-11)

Table 1 presents the characteristics of the new 23 bands which have been newly calculated.

The meaning of the different columns in Table 1 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

[2]The spectroscopic notation ν_1 ν_2 ν_3 is used here

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	1142.0215	1612.7745	0.180D-27	0.113D-24	0.381D-22	5268
2	120020	1144.4766	1517.8400	0.180D-27	0.337D-25	0.157D-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
20	002020	1507.8867	1768.1095	0.388D-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	1532.0191	1984.5359	0.388D-28	0.105D-25	0.193D-23	1458
23	040100	1808.9781	1855.6778	0.388D-28	0.392D-28	0.780D-28	2

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

Table 1: Summary of the NO_2 hot bands included in the MIPAS database

References

[1] M.-R. De Backer-Barilly and A. Barbe, "Absolute intensities of the 10–μm bands of $^{16}O_3$," *J. Mol. Spectrosc.* **205**(1), pp. 43–53, 2001.

[2] C. Claveau, C. Camy-Peyret, A. Valentin, and J.-M. Flaud, "Absolute intensities of the ν_1 and ν_3 bands of $^{16}O_3$," *J. Mol. Spectrosc.* **206**(2), pp. 115–125, 2001.

[3] T. Wagner, C. Leue, K. Pfeilsticker, and U. Platt, "Monitoring of the stratospheric chlorine activation by Global Ozone Monitoring Experiment (GOME) OClO measurements in the austral and boreal winters 1995 through 1999," *J. Geophys. Res.* **106**(D5), pp. 4971–4986, 2001.

[4] M. A. H. Smith, V. Malathy Devi, D. C. Benner, and C. P. Rinsland, "Absolute intensities of $^{16}O_3$ lines in the 9-11 μm region," *J. Geophys. Res.* **106**(D9), pp. 9909–9921, 2001.

[5] J.-M. Flaud, M. Birk, G. Wagner, J. Orphal, S. Klee, and W. J. Lafferty, "The far infrared spectrum of HOCl: Line positions and intensities," *J. Mol. Spectrosc.* **191**(2), pp. 362–367, 1998.

[6] J. Vander Auwera, J. Kleffmann, J.-M. Flaud, G. Pawelke, H. Bürger, D. Hurtmans, and R. Pétrisse, "Absolute ν_2 line intensities of HOCl by simultaneous measurements in the infrared with a tunable diode laser and far–infrared region using a Fourier transform spectrometer," *J. Mol. Spectrosc.* **204**(1), pp. 36–47, 2000.

[7] A. Perrin, J.-M. Flaud, C. Camy-Peyret, A. M. Vasserot, G. Guelachvili, A. Goldman, F. J. Murcray, and R. D. Blatherwick, "The ν_1, $2\nu_2$ and ν_3 interacting bands of NO_2: line positions and intensities," *J. Mol. Spectrosc.* **154**, pp. 391–406, 1992.

[8] C. Camy-Peyret, J. Flaud, and A. Perrin, "Improved line parameters for the ν_3 and the $\nu_2 + \nu_3 - \nu_2$ bands of NO_2," *J. Mol. Spectrosc.* **95**, pp. 72–79, 1982.

[9] A. Perrin, J.-M. Flaud, C. Camy-Peyret, D. Hurtmans, and G. Guelachvili, "The $\nu_2 + \nu_3$ and $\nu_2 + \nu_3 - \nu_2$ bands of NO_2: line positions and intensities," *J. Mol. Spectrosc.* **168**, pp. 54–66, 1994.

[10] J. Y. Mandin, V. Dana, A. Perrin, J. Flaud, C. Camy-Peyret, L. Régalia, and A. Barbe, "The $\nu_1 + 2\nu_2, \nu_1 + 2\nu_3$ bands of NO_2: line positions and intensities, line intensities in the $\nu_1 + \nu_2 + \nu_3 - \nu_2$ hot band," *J. Mol. Spectrosc.* **181**, pp. 379–388, 1997.

[11] A. Perrin, J.-M. Flaud, C. Camy-Peyret, D. Hurtmans, and M. Herman, "The $2\nu_3$, $4\nu_3$, $2\nu_2 + \nu_3$ and $2\nu_3$ - ν_3 bands of NO_2: line positions and intensities," *J. Mol. Spectrosc.* **177**, pp. 58–65, 1996.

[12] T. M. Stephen, A. Goldman, A. Perrin, J.-M. Flaud, F. Keller, and C. P. Rinsland, "New high–resolution analysis of the $3\nu_3$ and $2\nu_1 + \nu_3$ bands of nitrogen dioxide (NO_2) by Fourier transform spectroscopy," *J. Mol. Spectrosc.* **201**(1), pp. 134–142, 2000.