Radiance Calculations Comparing version 3.1 and version 3.2 of the MIPAS Spectral Databases

Jane Hurley

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Contents

1 Introduction

The version 3.1 MIPAS spectroscopic line database has been utilized since 2003 as a standardized library for reference radiance spectra. However recently in late 2005, a new version, the version 3.2 MIPAS spectroscopic line database was released to replace the existing database. As these databases are intended to provide a comprehensive and conclusive reference base, it is necessary to conduct a complete review of the new data as compared to the tried-and-trusted old data [2].

This note describes some tests used to verify the reported evolution of the databases by comparing spectra calculated for each molecule over the spectral range of 600-2500 cm^{-1} at a tangent height of 12 km.

2 Calculations

To this end, all 38 species were compared using the Reference Forward Model (RFM), a line-by-line radiative transfer model based upon GENLN2 which was developed at Atmospheric, Oceanic and Planetary Physics, University of Oxford [1]. The RFM calculates radiance spectra of many gaseous species commonly found in the Earth's atmosphere, using the HITRAN bianry line data as a database of standardized spectroscopic data [1].

For this comparative study, RFM was used to calculate the radiance spectra for each gas using the new and old databases. These calculations were performed at a tangent height of 12 km and over a wavenumber range of 600 cm^{-1} to 2500 cm^{-1} in a standard atmosphere. The radiance spectra were thus calculated, compared and the residuals between the two databases determined, where the residual is straightforwardly defined as

$$res(\nu) = r_{old}(\nu) - r_{new}(\nu) \tag{1}$$

where $r_{old}(\nu)$ is the radiance at wavenumber ν as reported from the old spectral database and accordingly $r_{new}(\nu)$ is that of the new.

Thus, if res(ν) is identically zero for the whole range of wavenumbers studied, the two databases are said to be unchanged for the particular species. If res(ν) is nonzero for certain values or ranges of ν, it is obvious that there have been changes made in the new database.

3 Results

Table 1 summarizes the findings of this comparison. There are three possible outcomes: either each new species spectrum are consistent("unchanged")

Species (HITRAN Index)	*Status*	*Species (HITRAN Index) cont'd*	*Status cont'd*
(1) H_2O	changed	(20) H_2CO	absent *
(2) CO_2		(21) HOCl	
(3) O_3		(22) N_2	
(4) N_2O		(23) HCN	
(5) CO		(24) CH_3 Cl	
(6) CH_4		(25) H_2O_2	changed
(7) O_2		(26) C_2H_2	
(8) NO	changed	(27) C_2H_6	
(9) SO_2		(28) PH_3	*
(10) NO_2		(29) COF_2	
(11) NH_3	changed	(30) SF_6	changed
(12) HNO_3	changed	(31) H_2S	
(13) OH	*	(32) HCOOH	*
(14) HF	*	(33) HO_2	*
(15) HCl	*	(34) O	absent *
(16) HBr	*	(35) $ClONO_2$	changed
(17) HI	*	(36) NO+	absent *
(18) ClO		(37) HOBr	absent *
(19) OCS	changed	(38) C_2H_4	absent *

Table 1: Chemical species compared in study. Here "changed" indicates that the new spectroscopic data is different from the old, '*' means that the comparison was carried out at a much higher-than-normal concentration, 'absent' means that both spectra are identically zero for all the wavenumbers, and a blank space indicates that the spectra are" unchanged".

or inconsistent ("changed")with that of the previous database or there are no available spectroscopic data ("absent"). If gases have spectra which are identically zero for all wavenumbers tested, they are sorted as "absent".

For nearly half of the trace gases tested, the species did not have atmospheric profiles in the chosen standard atmosphere and so these (indicated with an * in Table 1) were run in an atmospheric set-up at a larger concentration (1 ppmv) than they would normally be present.

The majority of the spectra indeed remained consistent with and unchanged from the previous version. These species displayed a residual equalling identically zero for all of the compared range of wavenumbers (600 cm^{-1} to 2500 cm^{-1}), indicating that the database remains unchanged for most of the species. H_2O, NO, HNO_3, H_2O_2, NH_3, OCS, SF_6 and $ClONO_2$ have newly calculated spectra which exhibit differences with the old MIPAS database.

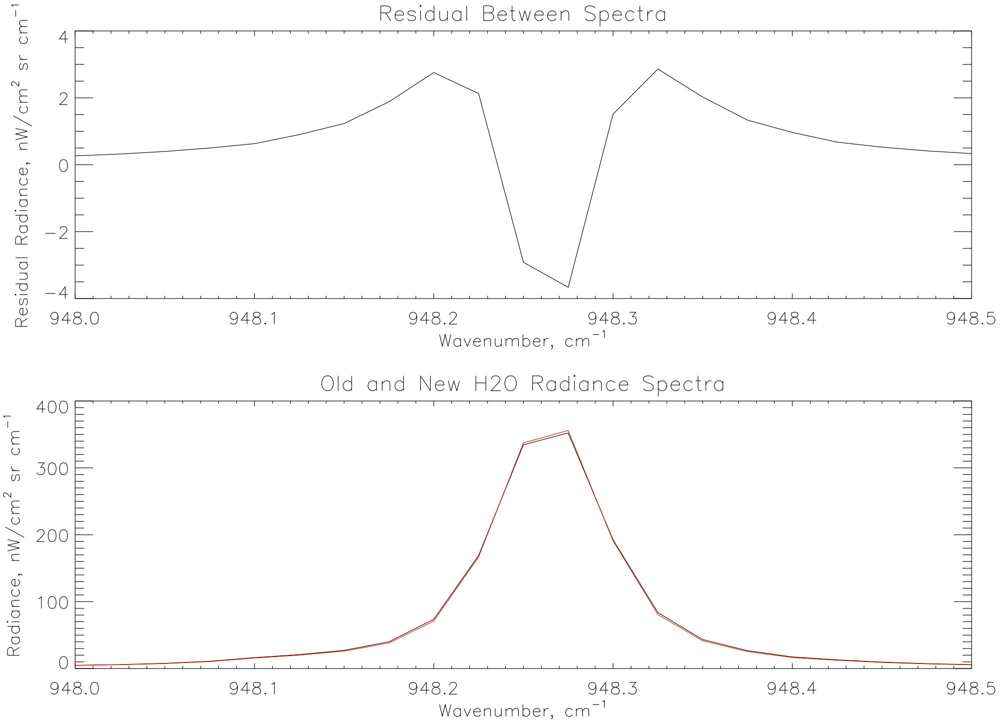


Figure 1: Top plot shows residual between the two water vapour spectra from the old and new databases. Bottom plot shows the region where there exist changes between the "new" and "old" water vapour spectra, where the old spectrum is plotted in black (solid) and the new in red (dotted).

For the most part, the changes and differences in the spectra are quite minor, having maximum differences that are much less than a percent of the maximum radiance value from the old spectral database.

3.1 Water Vapour H_2O

The spectrum calculated using the new database for water vapour matches that of the old database with the exception of a feature occuring in the range of $\nu \in [948, 948.5]$ cm^{-1}, as highlighted in Fig. 1. There exists a small difference in the line shape at this wavenumber, although the maximum absolute difference between the two spectra is 3 nW/(cm^2 sr cm^{-1}) in a feature of absolute strength of 350 nW/(cm^2 sr cm^{-1}). Clearly, this is a small discrepancy with a relative error of less than 1%.

The developers of the MIPAS spectroscopic line database acknowledge

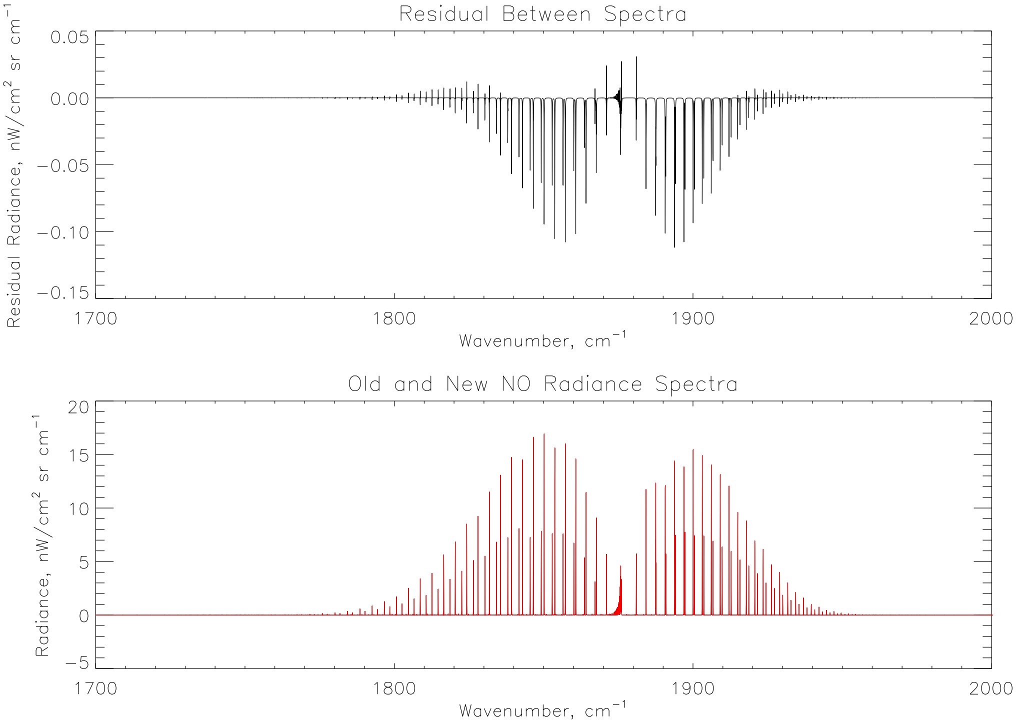


Figure 2: Top plot shows residual between the two nitric oxide spectra from the old and new databases. Bottom plot shows the region where there exist changes between the "new" and "old" nitric oxide spectra, where the old spectrum is plotted in black (solid) and the new in red (dotted).

changes in the evolution of spectroscopic data of the H_2O molecule in the database over the years. Notably, H_2O was altered in April 2003 by updating the pressure-broadening and temperature-dependence parameters for the line occuring at 948.262880 cm^{-1} [2], the feature observed here.

3.2 Nitric Oxide NO

Nitric oxide NO shows more variation in the spectral comparison, as there are differences in the line intensity and shape wherever the original radiance spectrum was non-zero. The inconsistencies occur in the wavenumber range from 1770 cm^{-1} to 1960 cm^{-1}, as exhibited in Fig. 2. Again, the absolute and relative differences between the two spectra are quite minimal at 0.1 nW/(cm^2 sr cm^{-1}) when compared with the spectral measurement of approximately 16 nW/(cm^2 sr cm^{-1}) - a relative difference of a 0.5%.

The database developers acknowledge that NO was altered in November 2003 when certain NO lines were removed and updated using HITRAN01 parameters [3]. Changes were made to the 5.9 μm spectral region where the $1 \leftarrow 0$ fundamental band absorbs, as observed in the corresponding wavenumber range (1700 cm^{-1}) in this study. As well, the developers report a relative change in line intensity of between $3-5\%$, which is well in keeping with the observations here [2].

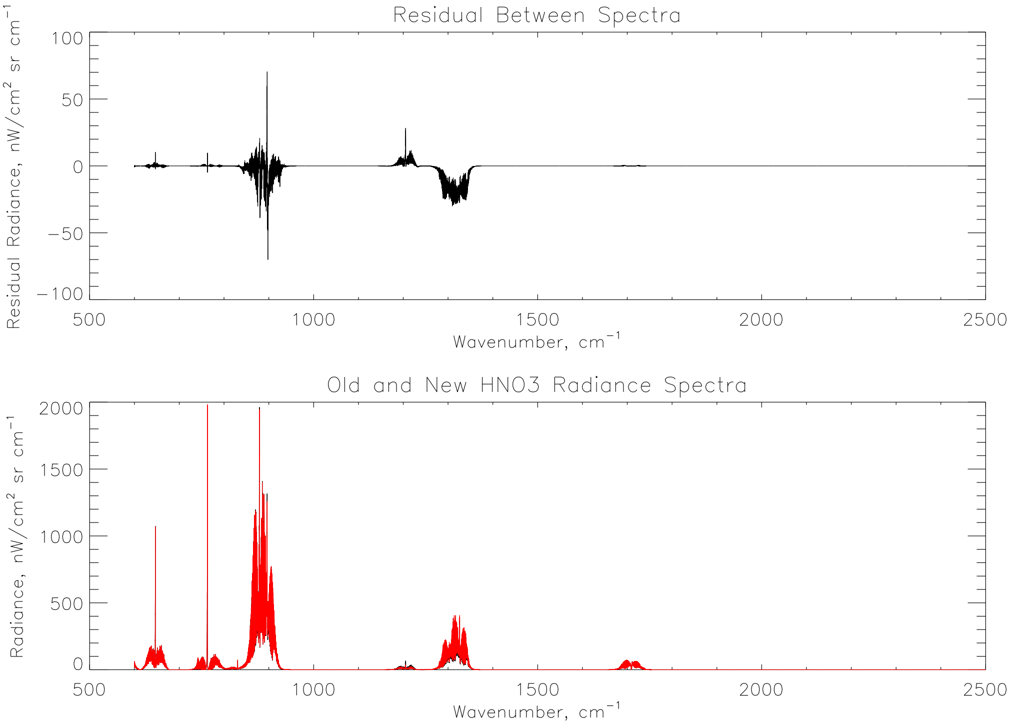
3.3 Nitric acid HNO_3

The differences between the new and old spectra for nitric acid are more marked than for the other species noted. In fact, there exist differences in the spectra wherever the original spectrum is non-zero and, unlike the previous two examples, the discrepancies in line shape and intensity are easily observable in the full spectrum. There are five changed areas:

- 650 cm^{-1}: absolute error of 10 nW/(cm^2 sr cm^{-1}) in a feature of 1000 nW/(cm^2 sr cm^{-1}), or of 1%;
- 775 cm^{-1}: absolute error of 10 nW/(cm^2 sr cm^{-1}) in a feature of 2000 nW/(cm^2 sr cm^{-1}), or of 0.5%;
- between 830 cm^{-1} and 950 cm^{-1}: absolute error of 70 nW/(cm^2 sr cm^{-1}) in a feature of 1900 nW/(cm^2 sr cm^{-1}), or of about 4%;
- between 1170 cm^{-1} and 1230 cm^{-1}: absolute error of 20 nW/(cm^2 sr cm^{-1}) in a feature of 50 nW/(cm^2 sr cm^{-1}), or of about 40%;
- between 1350 cm^{-1} and 1475 cm^{-1}: absolute error of 30 nW/(cm^2 sr cm^{-1}) in a feature of 100 nW/(cm^2 sr cm^{-1}), or of 30%.

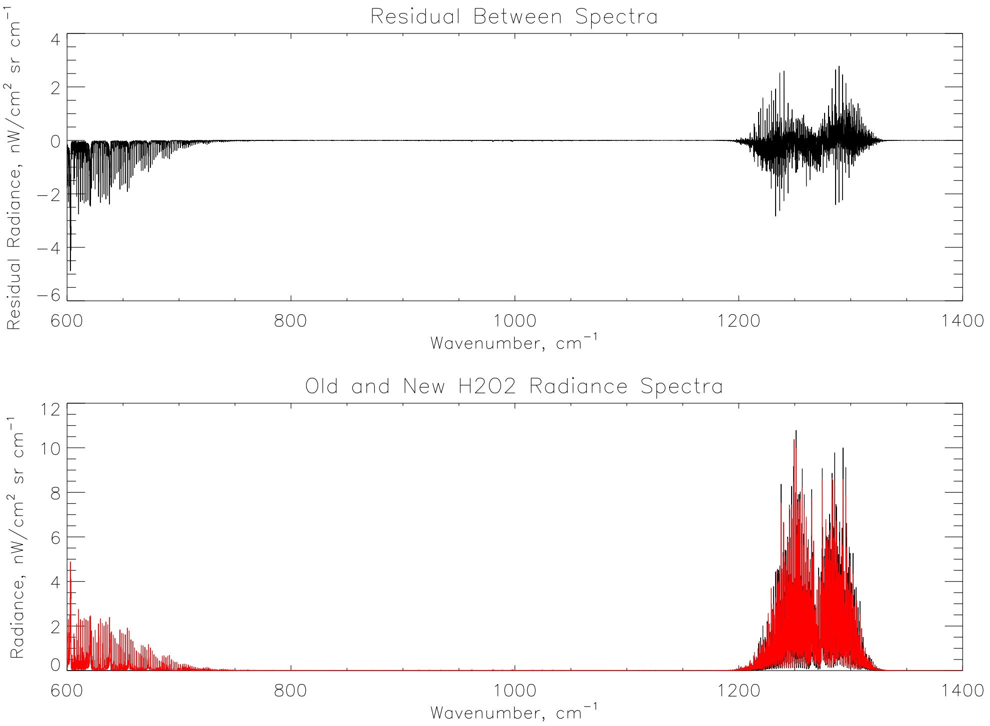
As can be easily seen in the spectra exhibited in Fig. 3, these differences are quite noticable and of non-negligible magnitude.

According to the database developers, HNO_3 was altered in November 2004 by updating the line parameters as defined in the ATBD of MIPAS-SM study. The developers report quite a number of changes in the spectral data of nitric acid. Nominally, it is reported that for all of the bands the broadening coefficients were changed and that there were improvements in the line positions in several spectral regions (11.2 μm and 8.3 μm) [2, 4].


Residual Between Spectra

Old and New HNO3 Radiance Spectra

Figure 3: Top plot shows residual between the two nitric acid spectra from the old and new databases. Bottom plot shows the region where there exist changes between the “new” and “old” nitric acid spectra, where the old spectrum is plotted in black (solid) and the new in red (dotted).


Residual Between Spectra

Old and New H2O2 Radiance Spectra

Figure 4: Top plot shows residual between the two hydrogen peroxide spectra from the old and new databases. Bottom plot shows the region where there exist changes between the "new" and "old" hydrogen peroxide spectra, where the old spectrum is plotted in black (solid) and the new in red (dotted).

3.4 Hydrogen peroxide H_2O_2

The changes introduced in the hydrogen peroxide spectrum are even more significant. The existing group of lines in the wavenumber range of 1200 cm^{-1} to 1350 cm^{-1} exhibit quite noticable differences in both line shape and intensity from the original database's output of about 3 nW/(cm^2 sr cm^{-1}) in a feature of about 10 nW/(cm^2 sr cm^{-1}). However the most prominent difference is that the new database actually introduces a new group of lines at the lowest range of wavenumbers considered, easily showing between 600 cm^{-1} and 750 cm^{-1}. These extra lines have a magnitude of about 6 nW/(cm^2 sr cm^{-1}). There are also some finer structure lines joining the two visibly large features such that changes are actually present up to about 1500 cm^{-1} - but these small changed features are quite negligible at an order of 0.005 nW/(cm^2 sr cm^{-1}) to 0.05 nW/(cm^2 sr cm^{-1}). Fig. 4 highlights these observations.

The developers indicate that H_2O_2 was altered in November 2003 when certain H_2O_2 lines [3] were removed and updated using parameters from [Perr et al., 1990] and [Klee et al., 1999]. These alterations have primarily affected the ν_6 band occuring at approximatly 7.9 μm or 1266 cm^{-1}, as observed in this study. Again, they report a line intensity difference of $8 - 30\%$, which is reflected in the observed residual intensity differences here [2].

3.5 Ammonia NH_3

There are several notable differences in the spectra generated from the new and old databases, however they seem to be mostly due to changes in line intensity. Around 625 cm^{-1}, there is an absolute intensity difference of about 0.5 nW/(cm^2 sr cm^{-1}) in a feature of about 1 nW/(cm^2 sr cm^{-1}). In the range of 700 cm^{-1} to 1200 cm^{-1}, the maximum difference between the two spectra is registered, having a value of 24 nW/(cm^2 sr cm^{-1}) in a feature of about 400 nW/(cm^2 sr cm^{-1}). Finally, in the range of 1450 cm^{-1} to 1800 cm^{-1} there exist differences of about a magnitude of 1 nW/(cm^2 sr cm^{-1}) occuring in a feature of approximately the same spectral magnitude. Fig. 5 exhibits these features and observations.

The developers have documented changes in the spectroscopic data of NH_3 which was altered and updated in April 2003 with HITRAN-2K data [2].

3.6 Carbonyl sulfide OCS

There are quite a few discrepancies between the two databases as exhibited in the radiance spectra shown in Fig. 6. Firstly, in the spectral range of 800 cm^{-1} to 900 cm^{-1} there are residuals of magnitude 7 nW/(cm^2 sr cm^{-1}) in a feature of approximate magnitude of 90 nW/(cm^2 sr cm^{-1}). Futhermore, in the range of 2000 cm^{-1} to 2150 cm^{-1}, the residuals have a magnitude comparable to that of the feature of 2 nW/(cm^2 sr cm^{-1}). More interestingly though, there appear to be new features arising in the ranges of 1000 cm^{-1} to 1100 cm^{-1} (magnitude 15 nW/(cm^2 sr cm^{-1})), 1650 cm^{-1} to 1750 cm^{-1} (magnitude 1 nW/(cm^2 sr cm^{-1})), and 1870 cm^{-1} to 1930 cm^{-1} (magnitude 0.5 nW/(cm^2 sr cm^{-1})). These features are not present in the original database spectrum.

Development documentation indicates that OCS was altered and updated in April 2003 with HITRAN-2K lines and had certain bandlines intensified by a factor of 1.13 [2].

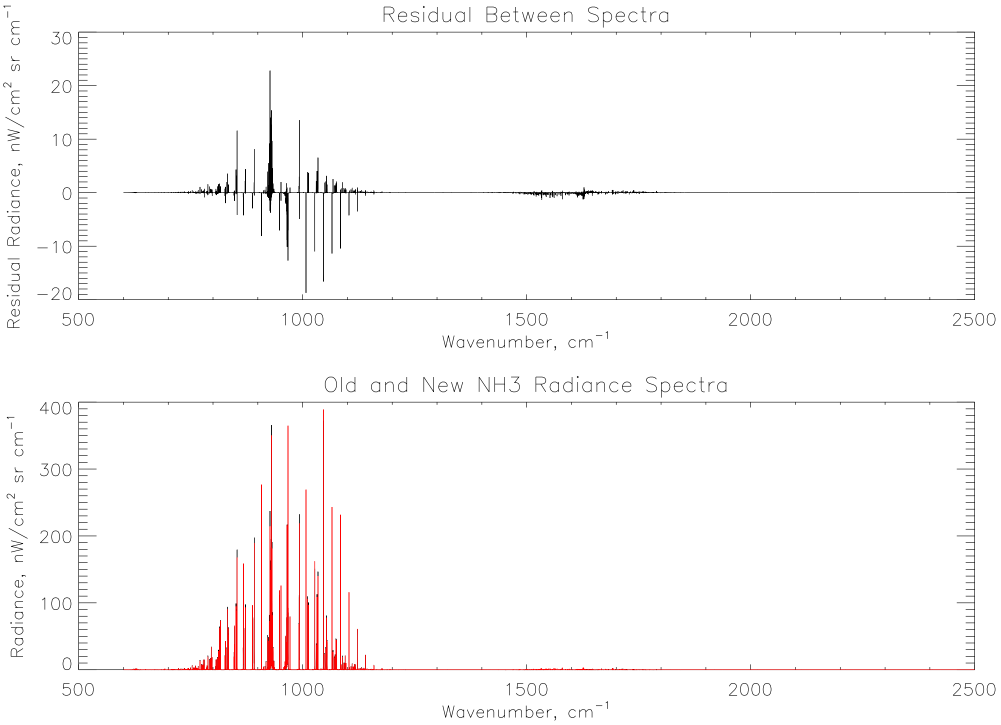


Figure 5: Top plot shows residual between the two ammonia spectra from the old and new databases. Bottom plot shows the region where there exist changes between the "new" and "old" ammonia spectra, where the old spectrum is plotted in black (solid) and the new in red (dotted).

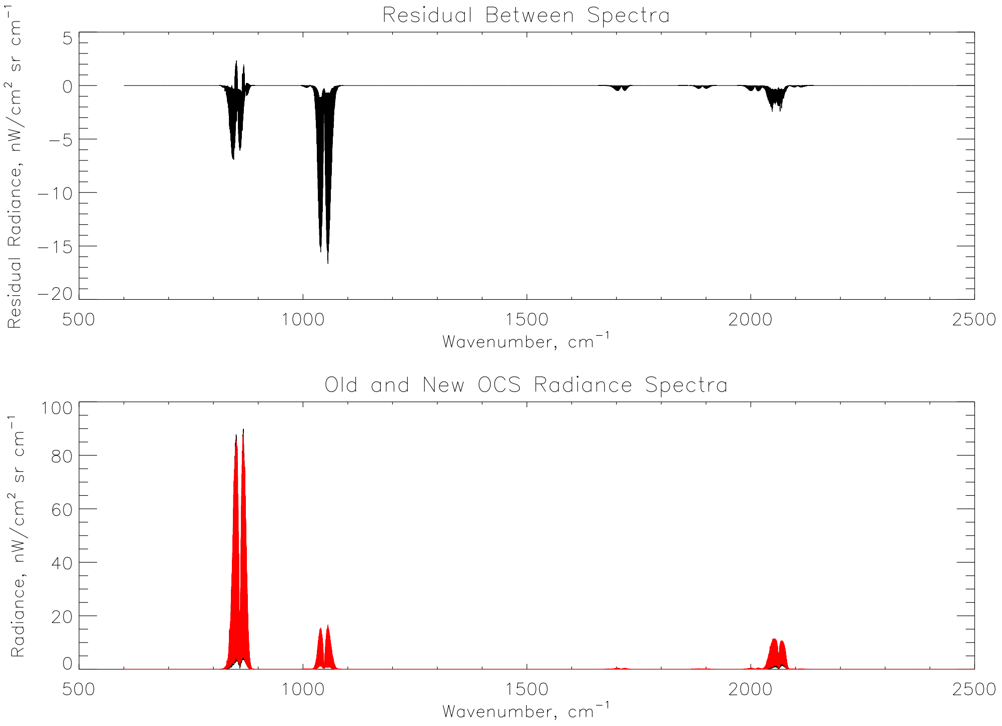


Figure 6: Top plot shows residual between the two carbonyl sulfate spectra from the old and new databases. Bottom plot shows the region where there exist changes between the "new" and "old" carbonyl sulfate spectra, where the old spectrum is plotted in black (solid) and the new in red (dotted).

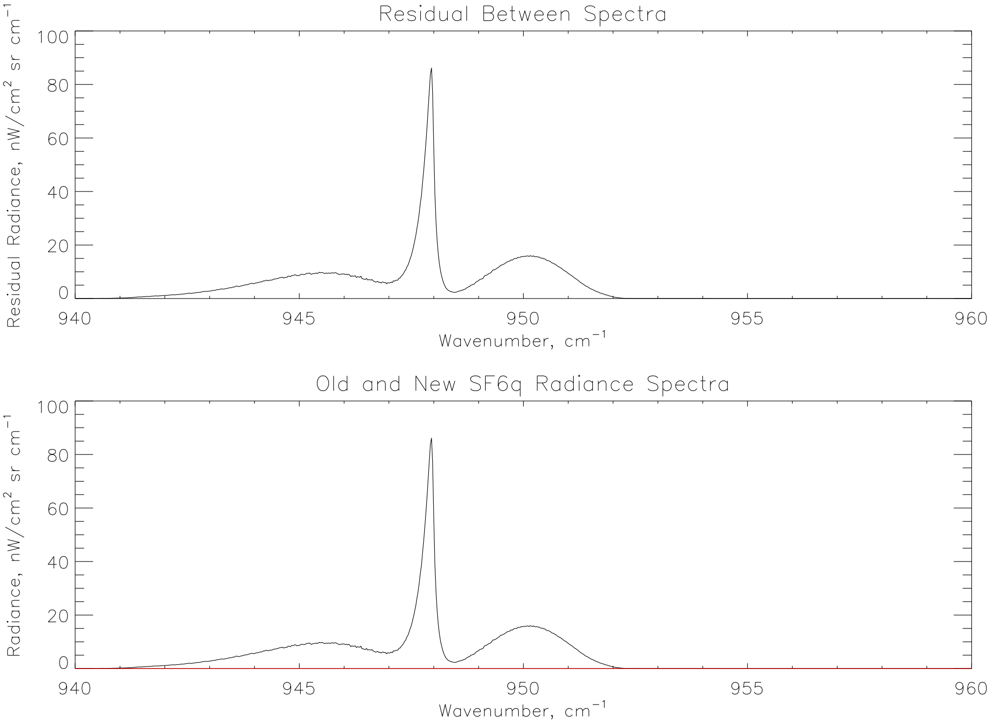


Figure 7: Top plot shows residual between the two sulfur hexafluoride spectra from the old and new databases. Bottom plot shows the region where there exist changes between the "new" and "old" sulfur hexafluoride spectra, where the old spectrum is plotted in black (solid) and the new in red (dotted).

3.7 Sulfur hexafluoride SF_6 and Chlorine nitrate $ClONO_2$

It appears as if the spectral data for both sulfur hexafluoride and chlorine nitrate have been removed from the new database as the lines present in the old database are no longer present. Indeed the radiance spectrum is identically zero for the whole wavenumber range studied. Figs. 7 and 8 indicate the now missing line information.

The developers indicate that SF_6 and $ClONO_2$ were altered in April 2003 when the lines were removed altogether. The line-by-line parameters were removed because they simply were not adequate and it is recommended that one use absorption cross sections for these species [2].

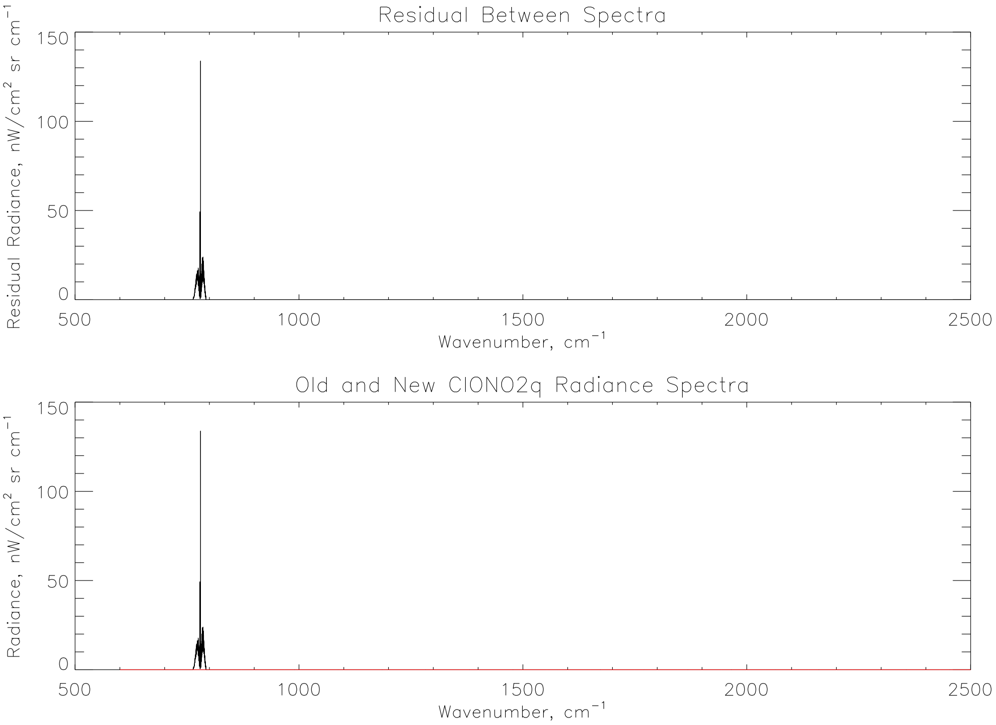


Figure 8: Top plot shows residual between the two chlorine nitrate spectra from the old and new databases. Bottom plot shows the region where there exist changes between the “new” and “old” chlorine nitrate spectra, where the old spectrum is plotted in black (solid) and the new in red (dotted).

Changed Species	*Wavenumber Region*	*Changes Attributed to:*
H_2O	948 – 948.5 cm^{-1}	pressure and temperature parameters
NO	1770 – 1960 cm^{-1}	updated HITRAN01 parameters
HNO_3	multiple - see Sec. 3.3	updated line parameters
H_2O_2	multiple - see Sec. 3.4	line intensity changes
NH_3	multiple - see Sec. 3.5	updated HITRAN-2K parameters
OCS	multiple - see Sec. 3.6	updated HITRAN-2K parameters
SF_6	all	removal of all lines
$ClONO_2$	all	removal of all lines
H_2CO	?	documented by developers but not observed here

Table 2: Summary of differences between old and new MIPAS databases.

3.8 Formaldehyde H_2CO

The developers mention in the documentation [3] that they have carried out changes in Formaldehyde H_2CO that were not observed in this study due to the unavailability of the spectra for analysis since the feature changed occurs outside the spectral range considered. Formaldehyde was updated in November 2003 with new parameters from Flaud and Perrin, and then again in August 2005 when unpublished line material was removed [3].

4 Conclusions

There exist several changes in the MIPAS spectral databases version 3.1 and version 3.2, notably in H_2O, NO, HNO_3, H_2O_2, NH_3, OCS, SF_6 and $ClONO_2$, as briefly noted in Table 2. For the most part, these changes are quite minor and of the order of a few percent in the difference between the intensities of the produced radiance spectra. However, there do exist completely new features in several of the spectra, indicating more serious changes and improvements. In any case, all discrepancies can be attributed to changes in line intensity or position, or in removal of lines from the database, as fully documented by the developers [2, 4].

References

[1] Dudhia, Anu, “Reference Forward Model Software User’s Manual”, www.atm.ox.ac.uk/RFM/sum

[2] Flaud, J.-M. et al., "From MIPAS PF 3.1 to MIPAS PF 3.2", *technical report,* **issue** (1), (October 2005): 1–14.

[3] Flaud, J.-M. et al., "HITRAN MIPAS spectroscopic line database summary of the evolution since version 3.1"

[4] Flaud, J.-M. et al., "Nitric acid (HNO_3 line parameters", *technical report,* **issue**(1), (October 2005): 1–17.