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Inconsistency in Some Spectroscopic Data Provided in HITRAN-2004 in the 10µm Region

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Abstract

We report some inconsistencies noticed in the spectroscopic data provided for some species in the new High resolution Transmission (HITRAN) model compilation (HITRAN-2004) based on a study conducted using the Institute fur Meteorologie und Klimaforschung- Forschungszentrum Karlsruhe (IMK-FZKA) micro window selection. The earlier compilation with updates (HITRAN-2001) gave much better fit qualities compared to HITRAN-2004, expecially for methane (CH_4) at the 10 micron region. The problem noticed for CH_4 might be related to the changes in the air-broadening coefficients in the later HITRAN version. These results have been communicated informally to the HITRAN compilers. This paper has been written to enable atmospheric spectroscopists expecially those working with the HITRAN data in Africa to be aware of this inherent problem with the 2004 HITRAN version.

Keywords: HITRAN, inconsistencies, methane, spectroscopy, IMK-FZKA.

1.0 Introduction

Radiative transfer in a purely gaseous atmosphere is complicated. Several approaches are adopted to help to improve our understanding of absorption by gases in the atmosphere through compilations of molecular line absorption spectra. Very important contributions of spectroscopic parameters of atmospheric gases are included in the High Resolution Transmission Model (HITRAN) database of Rothman et al (1992). These data base continually undergo constant revision. In the present investigation, spectroscopic data based on the new HITRAN 2004 compilation, (Rothman et al. (2005) was compared with that based on the old HITRAN 2001 (Rothman et al. (2003) in order to ascertain the level of improvement in using the new line data compared to the old one for radiative transfer calculations. The comparison has been based on the Institute fur Meteorologie und Klimaforschung (IMK), Forschungszentrum Karlsruhe (FZKA) micro window selection for ground-based FTIR measurements, using the Karlsruhe Optimized and Precise Radiative transition Algorithm (KOPRA) (Stiller, 2000). KOPRA is a FORTRAN based forward code used in the retrieval code PROFFIT (Hase, 2000) developed for the analysis of solar absorption spectra of trace gases from satellite, aircraft, balloon, and ground-based measurements. The procedures and results are summarized in this paper.

2.0 Methods

The new HITRAN 2004 line data was compared with the old HITRAN 2001, using spectra from Izana and Kiruna, two sites operated by the IMK, Forschungszentrum Karlsruhe. The spectroscopic quantities used for the comparison were the fit quality in terms of Root Mean Square (RMS), and the Total Columns of the species. The spectra of some of the species were also examined. RMS and Total Columns of a total of 30 species were considered, (C_2H_2-b, C_2H_6-a, CCl_2F_2-a, CCL_3F-a, CH_4-a, CH_4-b, $CHCLF_2$-a, $CLNO_3$-a, CLO-a, CO-a, CO_2-a, CO_2-b, H_2O-a, H_2O-b, HCL-a, HCL-b, HCN-a, HDO, HF-a, HNO_3-a, N_2-a, N_2O-a, N_2O-b, NO-a, NO_2-a, O_3-a, O_3-b, OCS-a.). The disparities between the two line data for the species were evaluated using the ratio of HITRAN 2001 (HIT01) to that of the original HITRAN 2004 (HIT04a). Hence the RMS ratios should be larger than 1 if there are improvements with the new line data; otherwise the ratios will be smaller than 1. The expectation is that the new line data should offer overall and clear improvement in fit qualities and consistency in columns.

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3.0 Results

3.1 Overall

Both the results for Izana using measurements made on 26th February 2003 and those for Kiruna using measurements made on the 28th of January, showed remarkably low RMS ratios (far less than 1) with respect to HIT04 (HIT01/HIT04) for C_2H_6-a and CH_4-a. Considering such large disparities with regard to C_2H_6- and CH_4-a, a modified HITRAN 2004 (HIT04b) spectral data was generated using C_2H_6 and CH_4 from the old HITRAN 2001 data after which the ratios were re-evaluated using this modified HITRAN 2004 now referred to here as HIT04b. Comparisons of the first ratio (HIT01:HIT04) with the second ratio (HIT01:HIT04b) were made. These comparisons of RMS and Total Column of all the species for the two sites (Izana & Kiruna) are presented in Figures 1 and 2. Less than 30% (CCL_2F_2-a, CLO-a, CO-a, H_2O-b, HCL-a, HCN-a, HDO-a, N_2O-a, N_2O-b, O_3-a, O_3-b, and COF_2-b) of the species showed improvements in RMS with the new HITRAN 2004 line data (HIT01/HIT04) 1. H_2O-b improvement was the most pronounced one. The remaining species did not show any visible change with HIT04. No discernible changes were seen in the Total Columns for most species except perhaps for CLO-a, H_2O-b and OCS-a, which were quite minimal.

3.2 H_2O-b

Using the modified HITRAN 2004 line data, there were improvements in RMS for H_2O-b for measurements made at Izana in February. For the January data at Kiruna, the H_2O-b was not improved. The examination of data for key species selected on the basis of either very bad fits or perceived inconsistent improvements was made using more days of data. These include C_2H_6-a, CH_4-a, CH_4-b, and H_2O-b. The data (Figure 3) show that the days of measurement were not correlated with the bad fits observed for most of the species except for H_2O-b where there were improvements for Kiruna using the March and July measurements. The Izana-H_2O-b was also better in July. On the average the improvements in H_2O-b seem to be correlated with large solar zenith angles (SZA) and large water columns.

H_2O-b improvements were not the same in all microwindows. The biggest improvements are in the microwindow (2941.6-2941.9cm^{-1}) and microwindow (2991-2996cm^{-1}) both of which showed about 60% improvement in the RMS at Izana but none at Kiruna in January (very large SZA; large air mass). The 2974.2-2975.6cm^{-1} and 2983-2985.2cm^{-1} windows showed 48% and 35% improvements of the H_2O-b lines respectively using HIT04b. It is however useful to note that microwin-

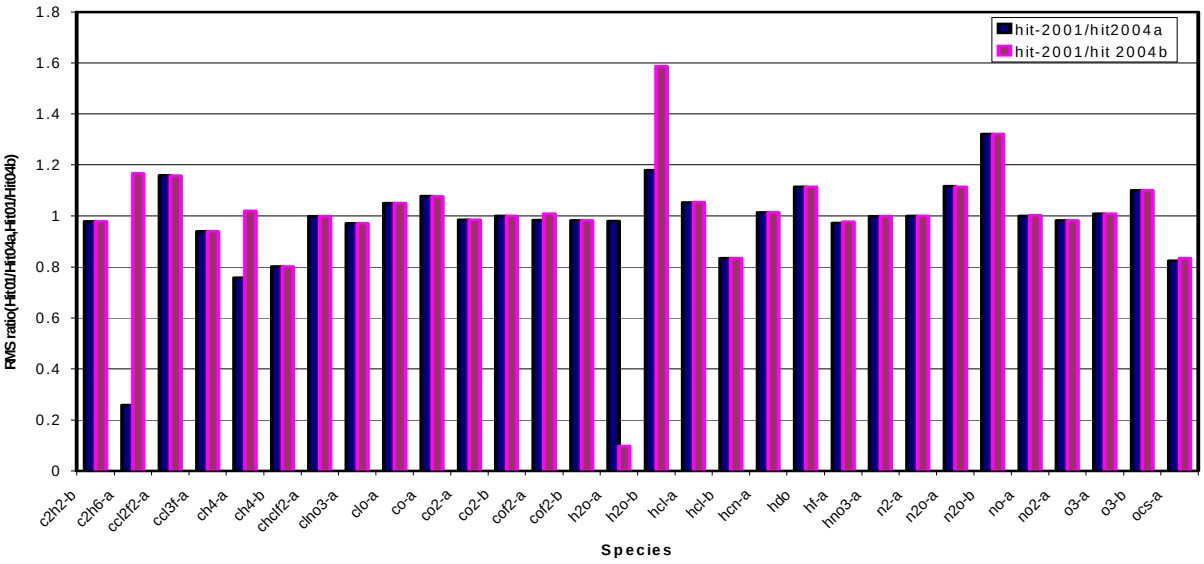


Figure 1: Ratio of RMS of species based on Hitran 2001 and Hitran 2004 (Hit-2001/Hit2004a) and Hitran 2001 and modified Hitran 2004 (Hit-2001/Hit-2004b) for Izana Tenerife, using measurements made on 26/02/03.

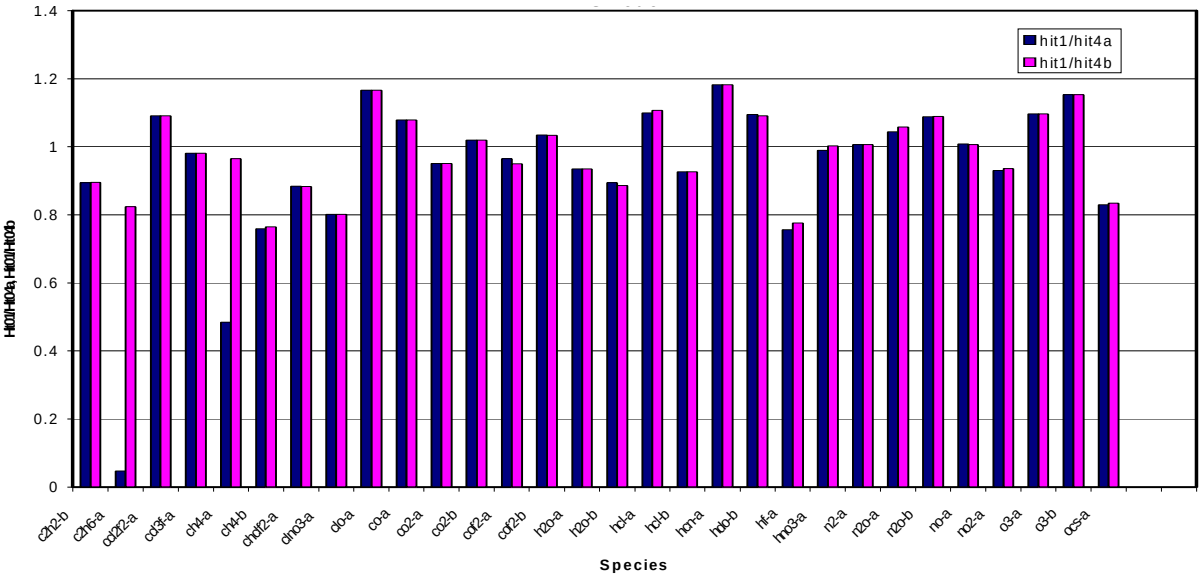


Figure 2: RMS ratio of species evaluated for Hitran 2001 and Hitran 2004 (Hit01/Hit04a) and Hitran 2001 and the modified Hitran 2004 (Hit01/Hit04b) using measurements made on 28/01/02 at Kiruna, Sweden.

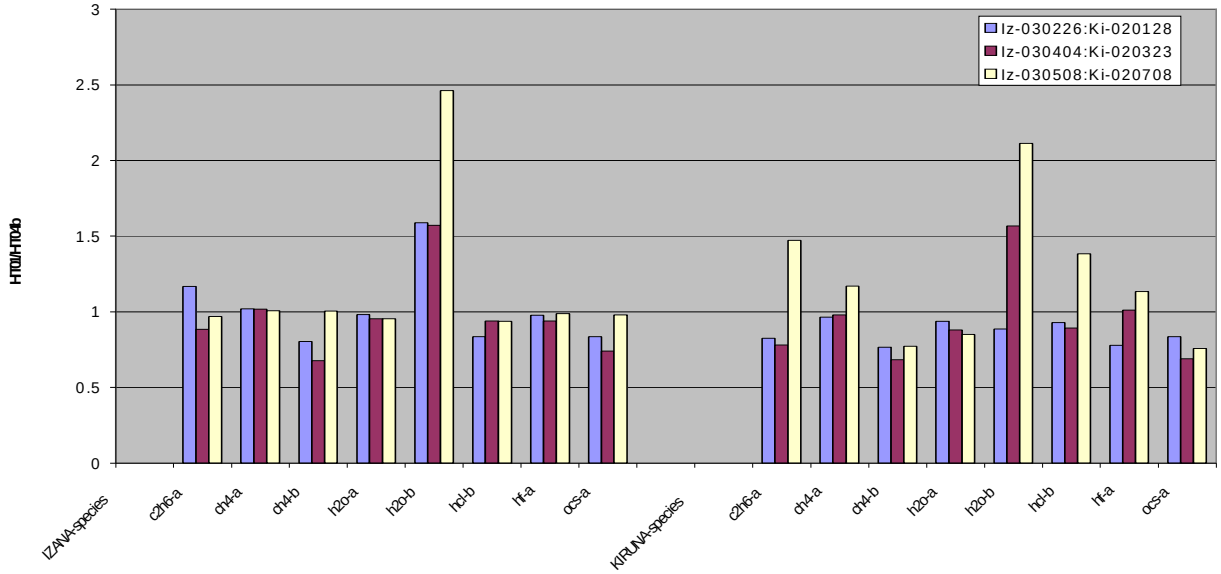


Figure 3: Comparison of RMS ratio (HITRAN 01:HITRAN 04b) of key problem species for Izana and Kiruna using 3-days of data – the days of the measurements for the two sites are shown in the legend.

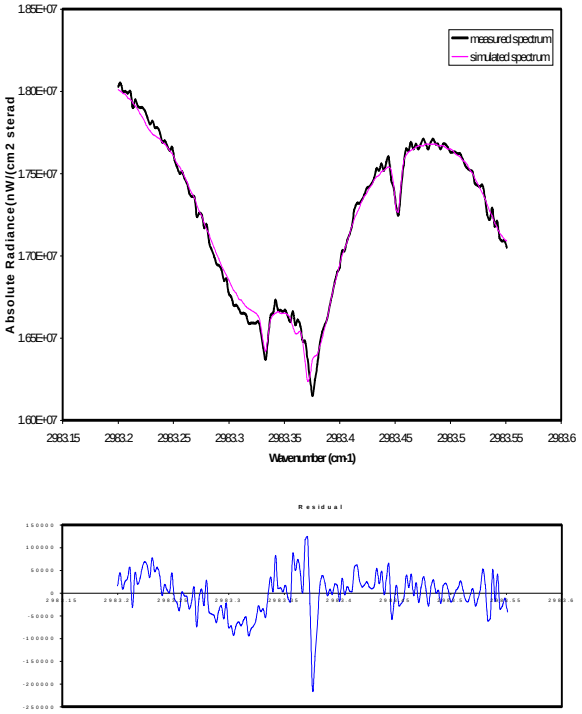
dows are not retrieved individually. The apparent improvement in H_2O-b lines needs further investigations.

3.3 C_2H_6-a and CH_4-a

The measured spectra for C_2H_6-a and CH_4-b, and simulations based on HIT01, HIT04 and HIT04b and the residuals are shown in Figure 4. The results show improved fits for C_2H_6-a with HIT04b which was more pronounced using the Izana data. Standard Deviations (SD) have been used to enhance comparison of the residuals (Table 1). The table shows that the HIT04-C_2H_6-a residuals which are more than 200% larger as compared to HIT01 are reduced to a value below that of HIT01 by 23% using the modified HIT04 (HIT04b). The band at 2983.4 cm^{-1} seems to be missing entirely. C_2H_6-a RMS is 15% reduced in the modified HIT04 (HIT04b) as compared to HIT01. HIT04-CH_4-a RMS increased by more than 30% for Izana data and by more than 100% for Kiruna as compared to HIT01.No reduction in RMS is achieved with the modified HIT04 using Kiruna data - and only insignificantly for Izana. CH_4-a fits have large residuals at different micro windows with HIT04. Note: The CH_4-b lines did not show any considerable change with HIT04. (Other CH_4-sample spectra are shown

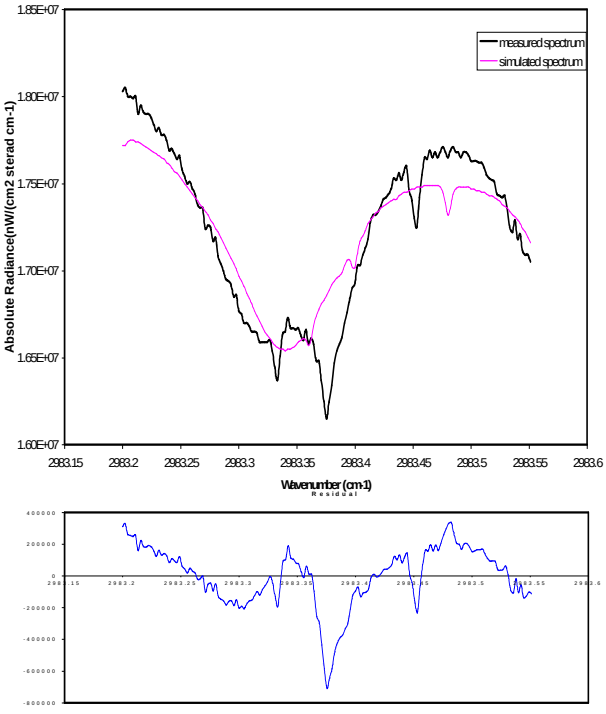
in Figure5).

Spectrum of C_2H_6-a for Izana based on HITRAN 2001



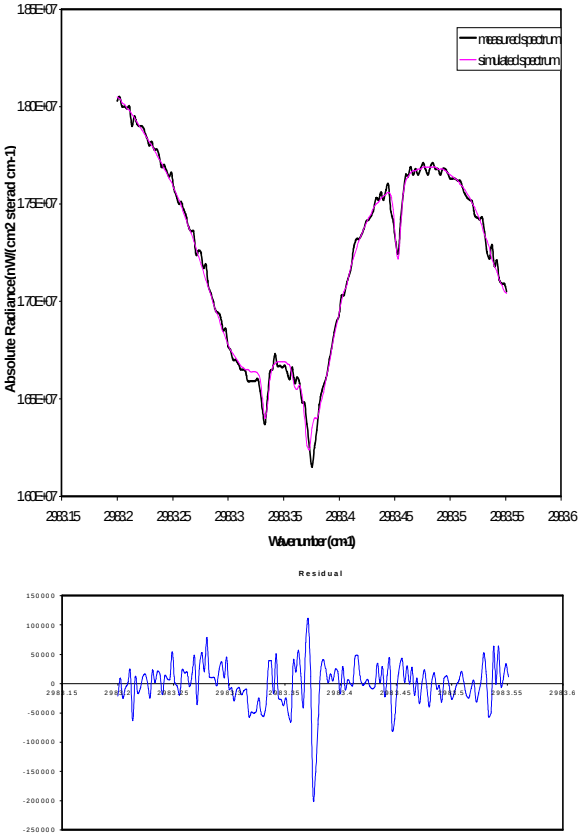
a. Iz-C_2H_6-a/Spectra/HIT01

Spectrum of C_2H_6-a for Izana based on HITRAN 2004



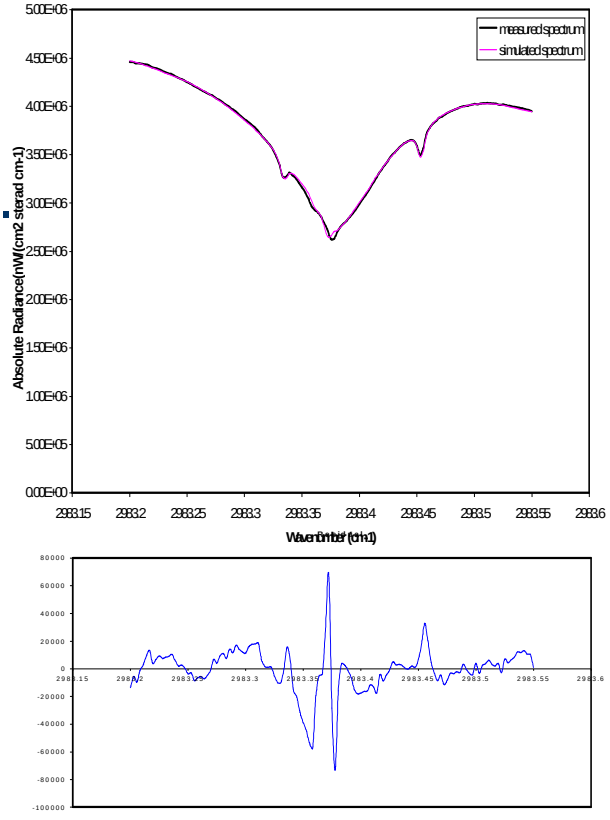
b. Iz-C_2H_6-a/Spectra/HIT04

Spectrum of C_2H_6-a for Izana based on modified HITRAN 2004

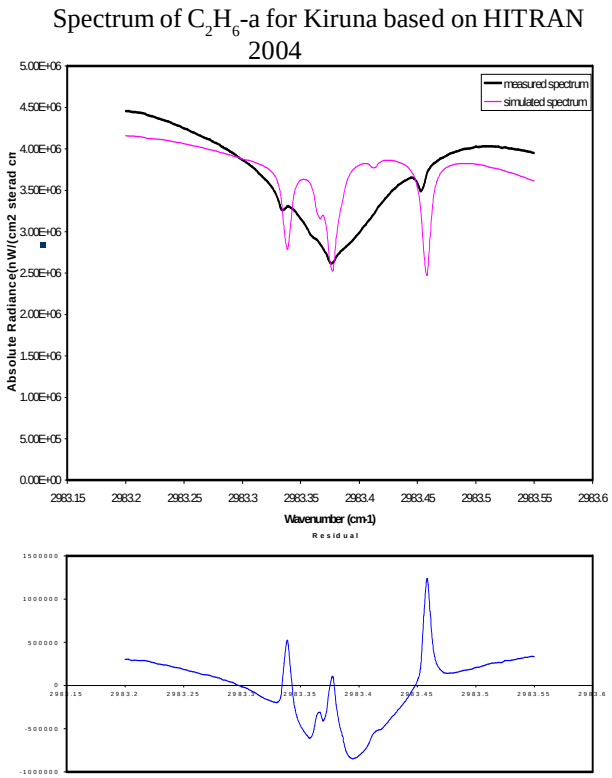


c. Iz-C_2H_6-a/Spectra/HIT04b

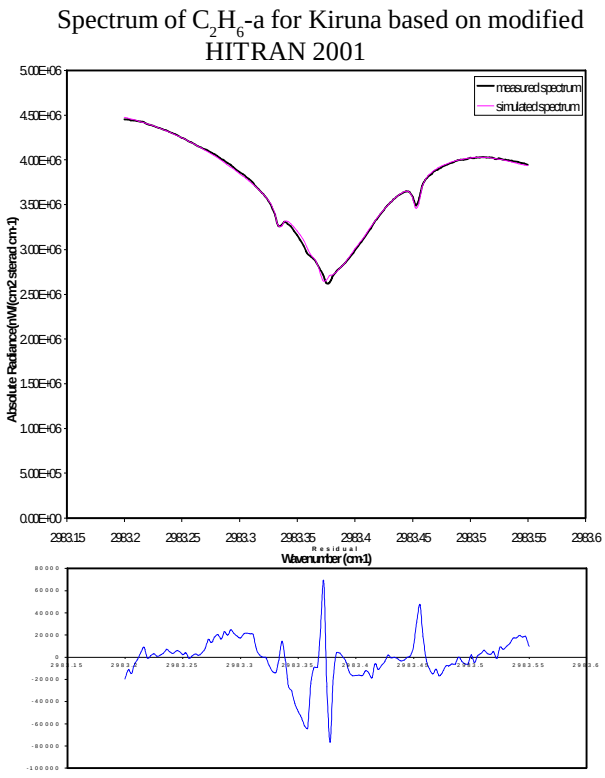
Spectrum of C_2H_6-a for Kiruna based on HITRAN 2001



d. Ki-C_2H_6-a/Spectra/HIT01

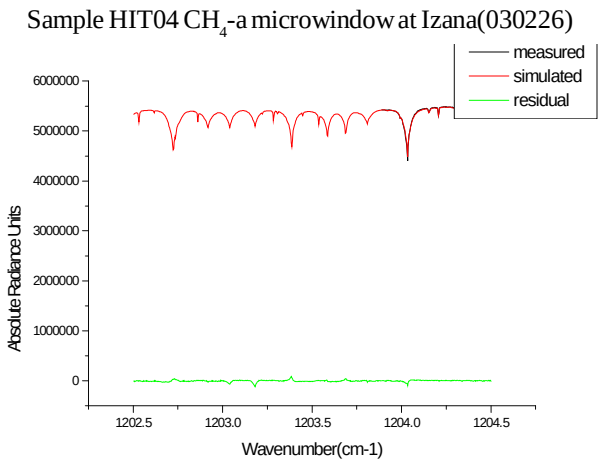


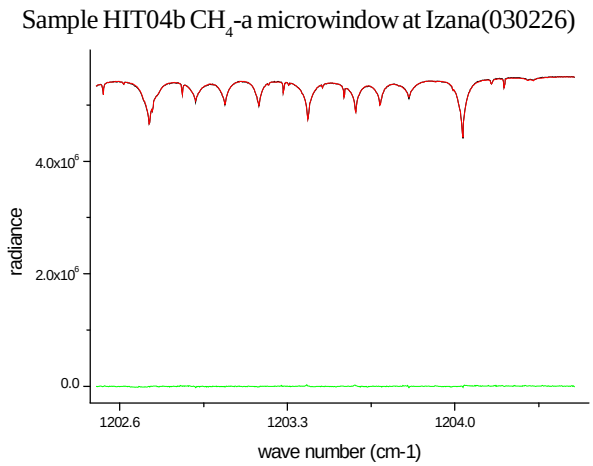
e. Ki - C_2H_6-a/Spectra/HIT04

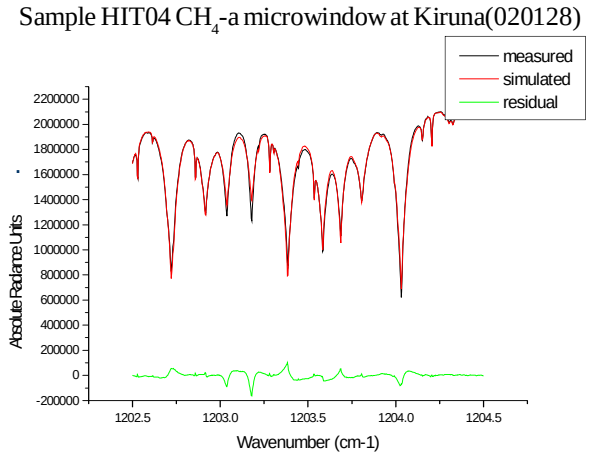


f. Ki - C_2H_6-a/Spectra/HIT04b

Figure 4 (a-f): Spectra for C_2H_6-a and CH_4-a; simulations based on HIT01, HIT04 and HIT04b and the residuals.







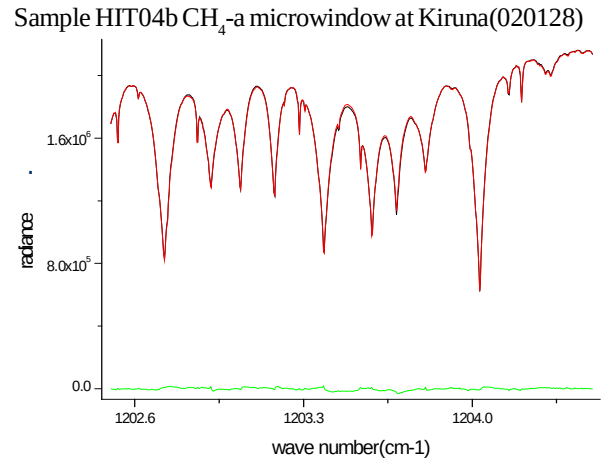


Figure 5: Other Sample Spectra

Table 1: H_2O-b improvements correlated with Solar Zenith Angle (SZA) and H_2O-b Columns.

Site	Day of measurement	Time of measurement	SZA(deg)	H_2O-b Total Column
Izana	30226	111659	42.6710	1.39E+26
	30404	174147	21.9110	1.45E+26
	30508	102006	51.1080	5.16E+25
Kiruna	20128	104049	4.1590	7.58E+25
	20323	105606	23.2250	1.24E+26
	20708	93705	43.4212	4.96E+26

Table 2: Comparison of H_2O-b residuals at different micro-windows in Standard Deviation(SD) units-Measurement day were 26/02/03 of Izana and 28/01/02 for Kiruna.

Spec-Interval (cm-1)		HIT01	HIT04	HIT04b
SpecA: 2941.6-2941.9	Izana	98293	61642	60385
	Kiruna	29825	47601	47356
SpecB: 2974.2-2975.6	Izana	144286	98041	97751
	Kiruna	15258	14159	13947
Spec C: 2983-2985.2	Izana	91048	179016	67269
	Kiruna	15878	765170	15100
Spec D: 2991-2996	Izana	224250	164720	138370
	Kiruna	21349	23923	24291

Table3: Comparison of residuals of C_2H_6-a and CH_4-a using different HITRAN data in Standard Deviation(SD) units-Measurement days were 26/02/03 for Izana and 20/02/02 for Kiruna.

	HIT01	HIT04	HIT04b
C_2H_6-a:Izana	45206	192098	36890
Kiruna	16321	364138	19222
CH_4-a:Izana	8658	10505	8745
Kiruna	4245	5449	4197

Table 4: Column ratios of O_3-a to O_3-b (O_3-a/ O_3-b) for Izana and kiruna based on the different compilations.

Site	Day	HIT01	HIT04	HIT04b
Izana	30226	1.03	0.98	0.98
	30404	1.02	0.98	0.98
	30508	1.08	1.04	1.04
Kiruna	20128	1.07	1.05	1.03
	20220	1.04	0.98	0.98
	20323	1.06	1.01	1.01
	20708	1.06	1.00	1.00

4.0 Conclusions

From the above investigations, we conclude as follows;

1. There are improvements in H_2O-b lines using the HIT2004b line data.
2. For other species there are no significant improvements in fit quality.
3. The new CH_4 line data are incorrect in the MCT region.
4. Using old C_2H_6-a and CH_4 data from the old compilation gave improvements in some species but mainly for H_2O where the core of lines seem to be improved.
5. O_3 seems to show greater consistency within different sets of micro windows with the new line data.

The new line data therefore does not seem to meet the expectation of offering overall clear improvements in fit quality and consistency of columns and more investigations need to be carried out to investigate the nature of these observed inconsistencies.

These conclusions (also see Nwofor, 2005) have been communicated to Dr Larry Rothman of the Atomic and Molecular Physics Division of the Harvard Smithsonian Center for Astrophysics, Cambridge, MA, USA. These results as reported above are however intended to enable a larger audience of atmospheric scientists especially those working with the HITRAN data in Africa to be aware of the problem inherent with the 2004 version.

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