Spectroscopic Evaluations and Recommendations

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Three Topics:

1. C_2H_6 spectroscopy in 3000 cm^{-1} region
2. H_2O spectroscopy evaluation (650 to 15,000 cm^{-1})
3. Fitting NDACC-IRWG windows (HITRAN 22 vs ATM24)

New Ground-based C_3H_8 Measurements

Atmospheric propane (C_3H_8) column retrievals from ground-based FTIR observations at Xianghe, China

Minqiang Zhou, Pucai Wang, Bart Dils, Bavo Langerock, Geoff Toon, Christian Hermans, Weidong Nan, Qun Cheng, and Martine DeMaziere

Abstract. Propane (C_3H_8) is an important trace gas in the atmosphere, as it is a proxy for oil and gas production and has a significant impact on atmospheric chemical reactions related to the hydroxyl radical and tropospheric ozone formation. In this study, solar direct absorption spectra near 2967 cm^{-1} recorded by a ground-based Fourier Transform InfraRed spectrometer (FTIR) are applied to retrieve C_3H_8 total columns between June 2018 and July 2022 at Xianghe in North China. The systematic and random uncertainties of the C_3H_8 column retrieval are estimated to be 18.2 % and 18.1 %, respectively. The mean and standard deviation of the C_3H_8 columns derived from the FTIR spectra at Xianghe are $1.80\pm0.81(1\sigma) \times 10^{15}$ *molecules / cm*^{2}. Good correlations are found between C_3H_8 and other non-methane hydrocarbons, such as C_2H_6 (R=0.84) and C_2H_2 (R=0.79), as well as between C_3H_8 and CO (R=0.72). However, the correlation between C_3H_8 and CH_4 is relatively weak (R=0.45). The FTIR C_3H_8 measurements are also compared against two atmospheric chemical transport model simulations (the Whole Atmosphere Community Climate Model (WACCM) and the Copernicus Atmosphere Monitoring Service (CAMS)). We find that the C_3H_8 columns from both models have different seasonal variations as compared to the FTIR measurements. Moreover, the mean C_3H_8 columns derived from the WACCM and CAMS models are about 68 % larger than the FTIR retrievals. The new FTIR measurements at Xianghe provide us an insight into the C_3H_8 column variations and underlying processes in North China.

et al. (2010). For C_2H_6, we use HITRAN2020. We tested more than 1000 spectra recorded in 2019 at Xianghe, and we observed that the lowest root-mean-square error (RMSE) of the fitting residual is obtained when the ATM2020 spectral database is used for CH_4 and H_2O. Table 1 lists the spectral datasets finally used for each species in the C_3H_8 retrieval strategy.

Table 1. The retrieval window, interfering specie, spectroscopy, fitting parameters for C_3H_8 at Xianghe.

Parameters	settings
Retrieval window (cm^{-1})	2964.5-2970.0
Profile retrieval species	C_3H_8, H_2O
Column retrieval species	C_2H_6, CH_4, HDO
Retrieved parameters	slope, phase, instrument line shape, wavenumber shift solar intensity, solar wavenumber shift
A priori profile	NCEP for H_2O, HDO; WACCM for C_2H_6, C_3H_8, CH_4
Spectroscopy	PLL for C_3H_8; ATM20 for H_2O, HDO, CH_4; HITRAN2020 for C_2H_6
Regularization	Tikhonov $\mathbf{L}_1$ method
DOFS	1.1

Zhou et al.[2023] recently published propane amounts from Xianghe. I was co-author, by virtue of having produced the C_3H_8 EPLL used. They use HITRAN 2020 spectroscopy for the interfering C_2H_6 because it gave better fits than the EPLL that I developed in 2009.

I was surprised to hear this, because C_2H_6 is a complicated molecule. So I fitted some MKIV ground-based spectra. Indeed, the HIT2020 C_2H_6 linelist produced a slightly better rms fit in the C_3H_8 window than the EPLL. Unfortunately, I did not look at the spectral fits very carefully at this time.

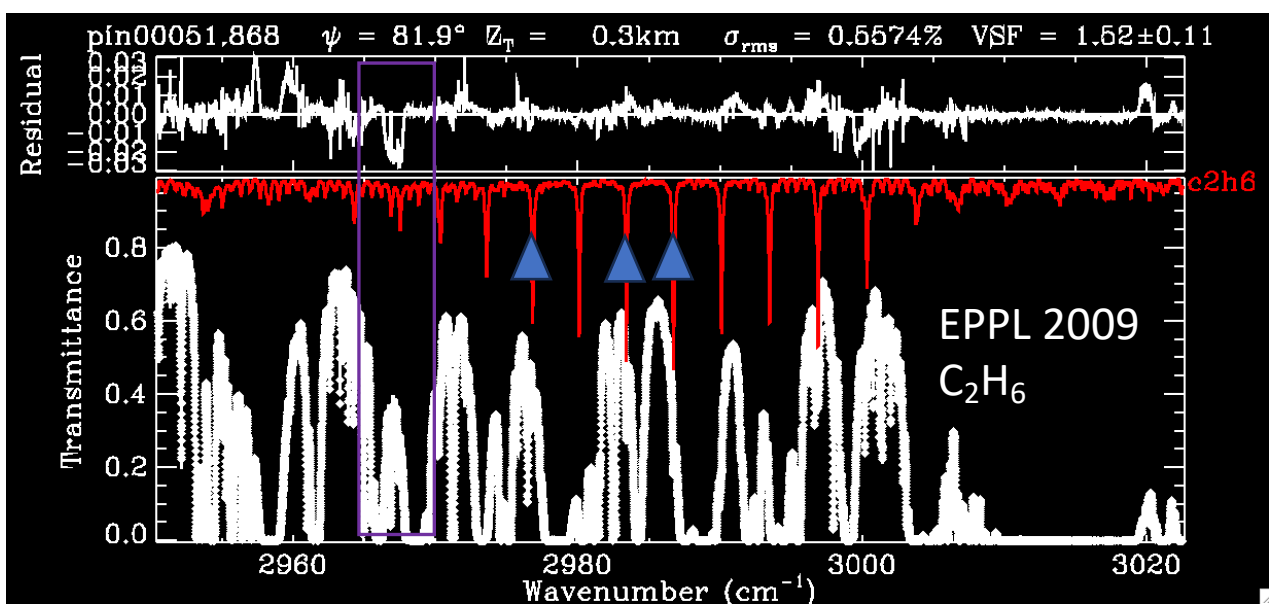
Fits to MkIV ground-based Atmospheric Spectra over wide window

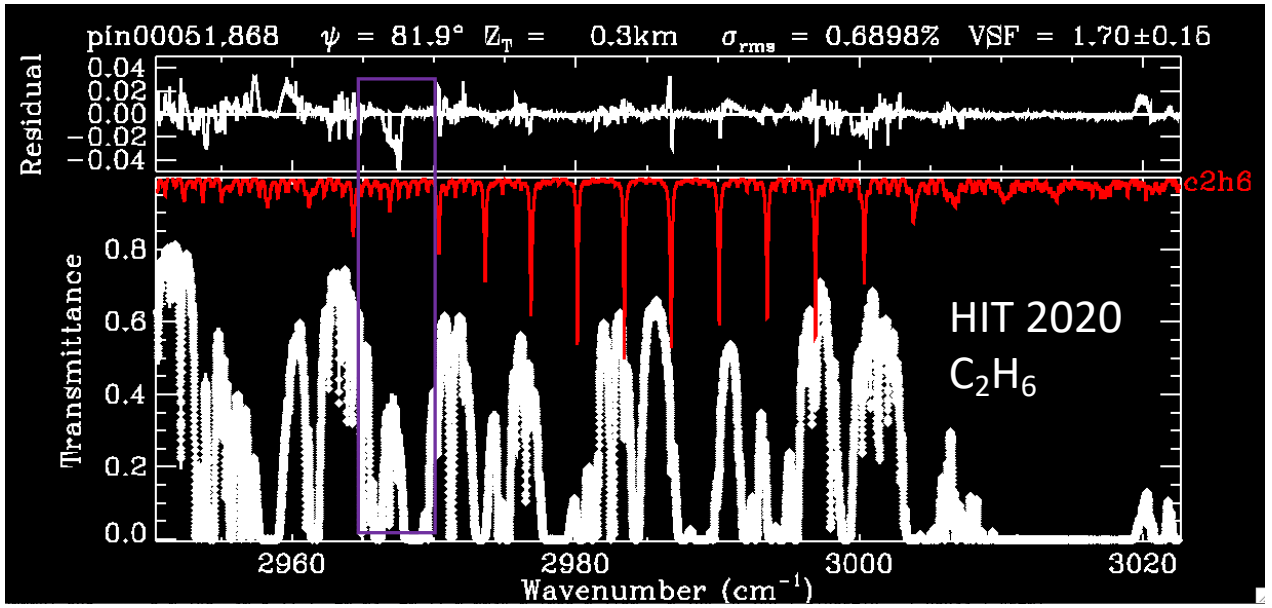
Months later, I decided to check whether the new HITRAN 2020 C_2H_6 linelist also produces better results for C_2H_6 itself.

Despite residuals being dominated by CH_4, mainly due to neglect of line-mixing, the HITRAN 2020 C_2H_6 produces noticeably worse fits then EPLL 2009 (0.557% vs 0.690%) over the 2950-3024 cm-1 window.

Note the change of residual scale from ±3% on left to ± 5% on right. Blue triangles denote features used by NDACC-IRWG.

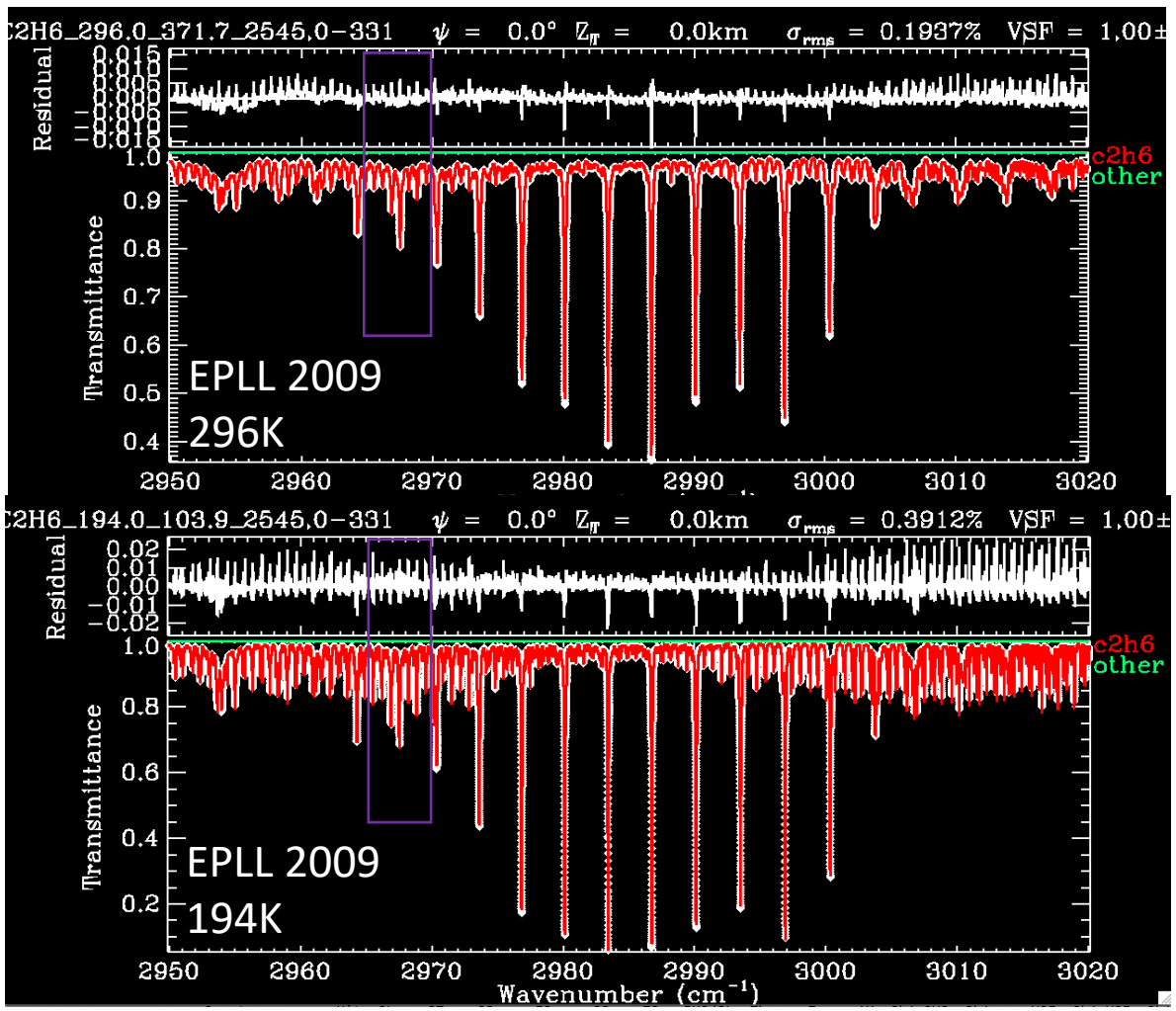
The non-C_2H_6 spectroscopy is identical between the two panels, as are the other parameters.

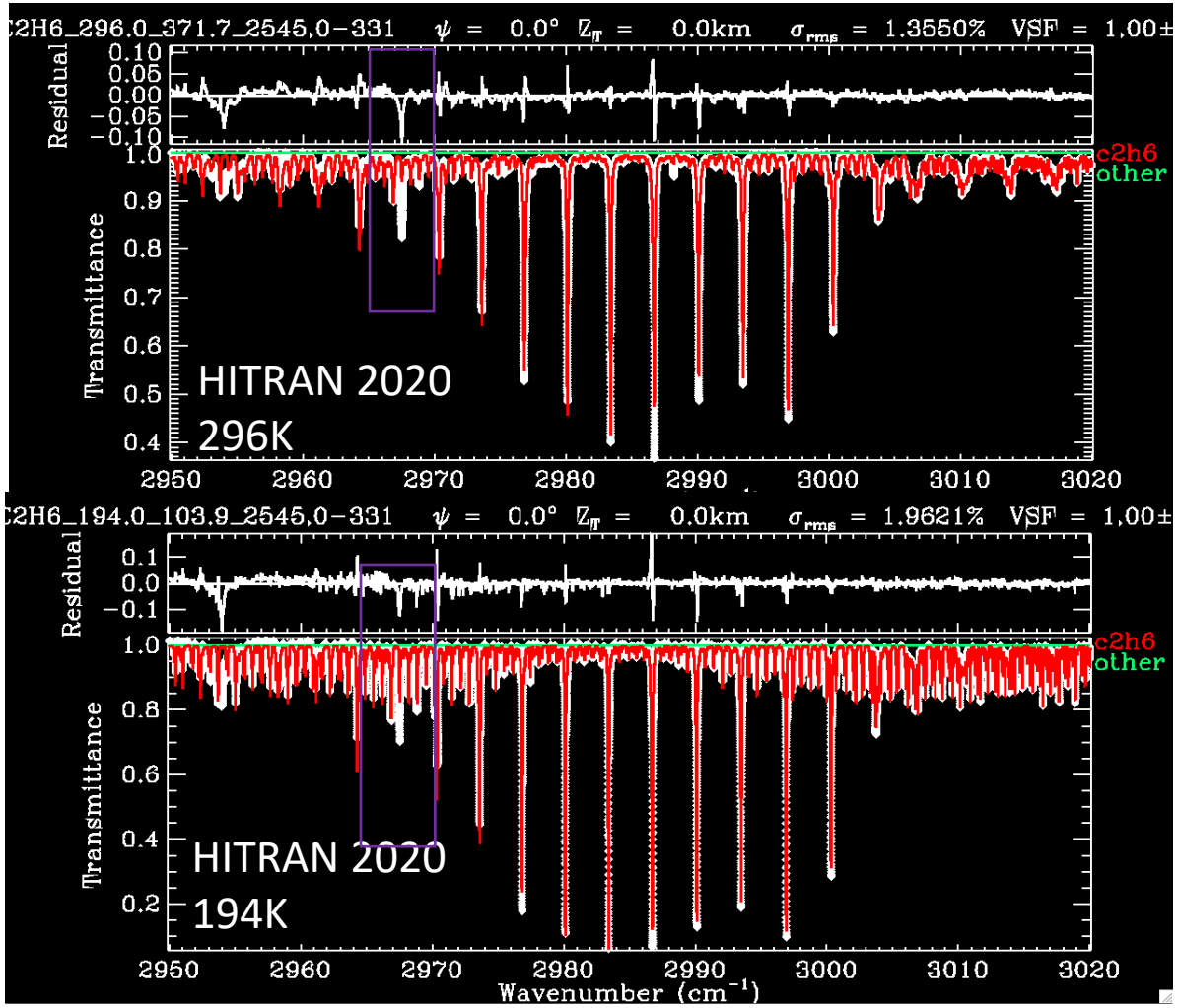




So the EPLL 2009 produces much better fits to this wide window, which includes the propane window (purple rectangles), than HITRAN 2020 C_2H_6. So which C_2H_6 linelist is better?

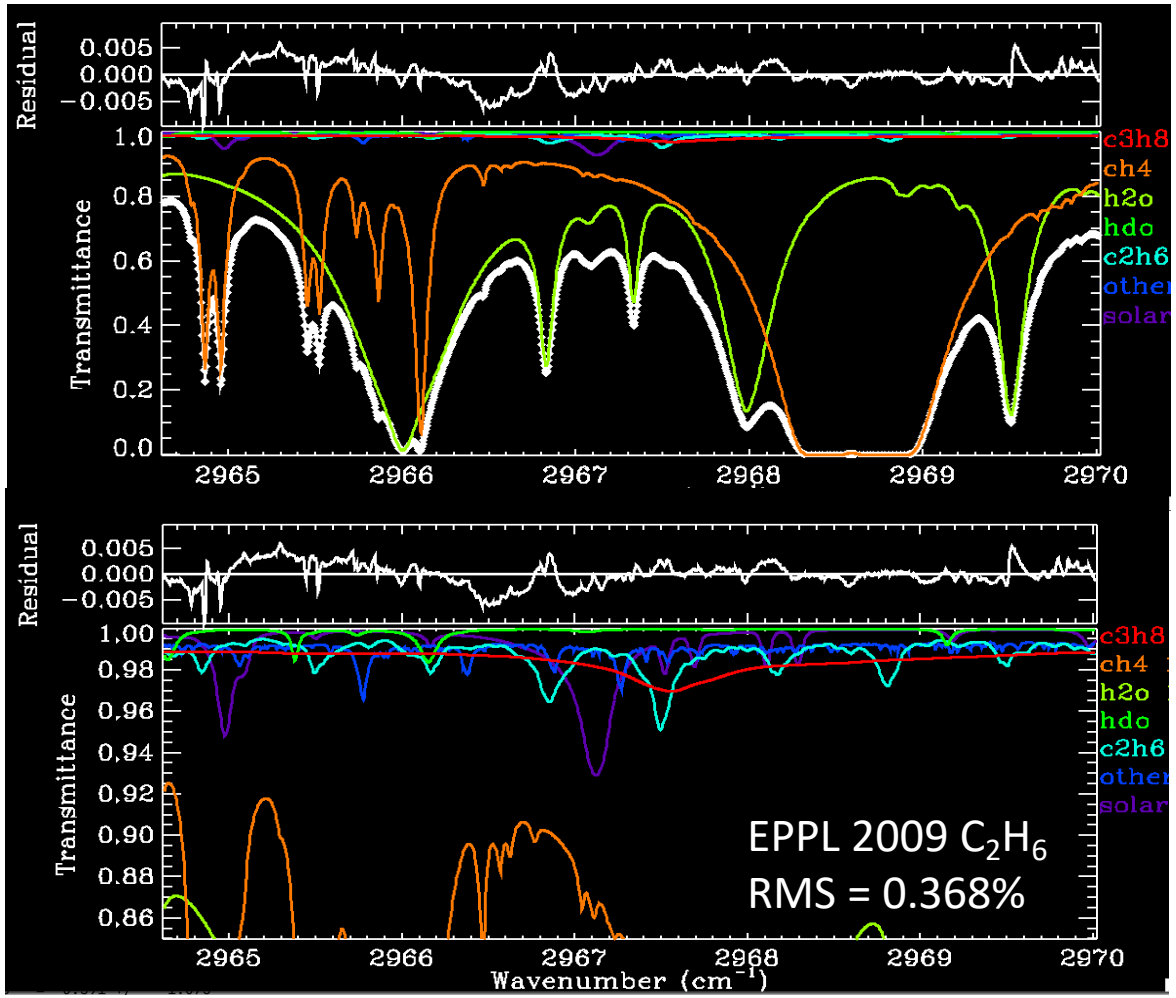
Re-Fitted Harrison (2010) laboratory C_2H_6 spectra using EPLL2009 and HIT 2020

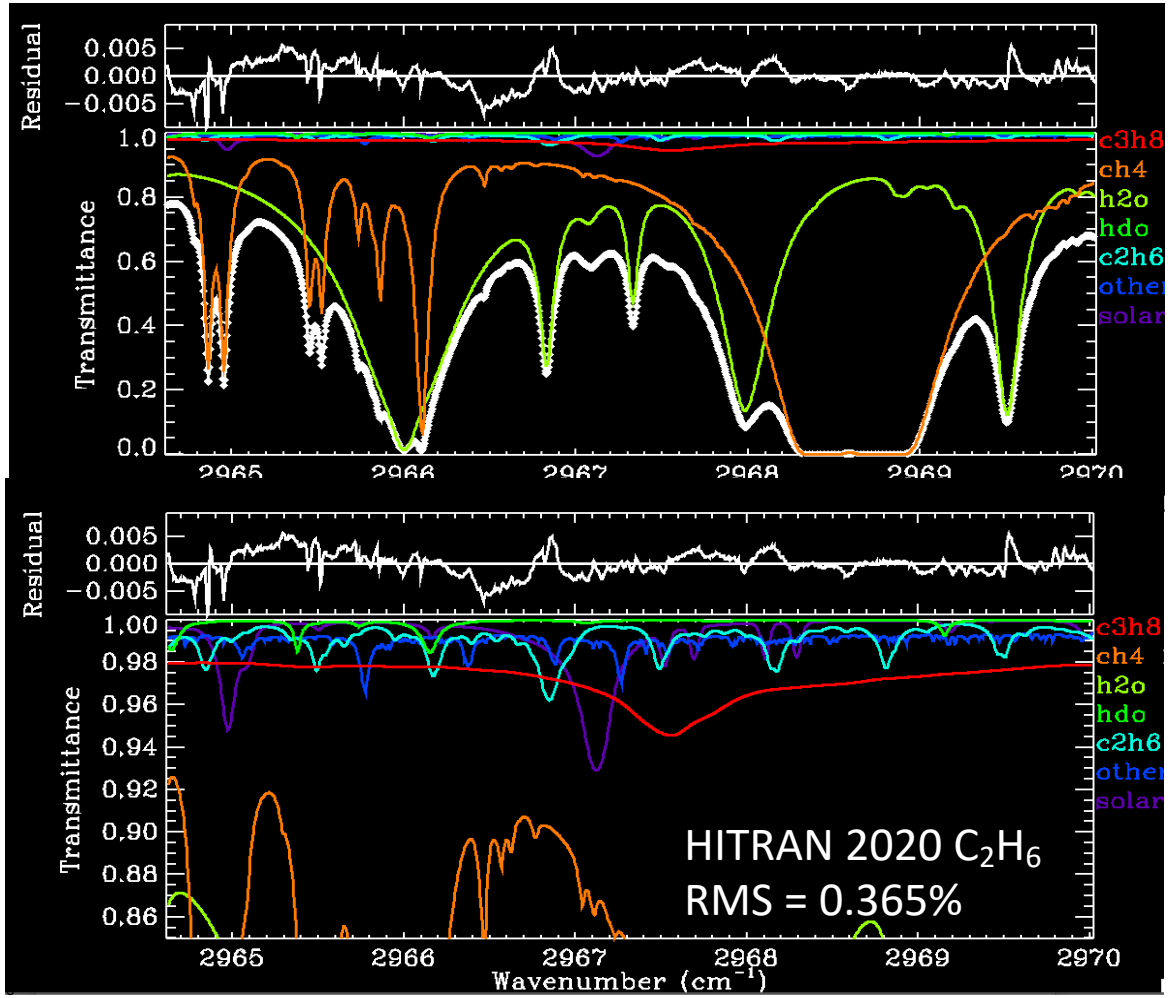




In the absence of interfering CH_4 and H_2O, the effects on the RMS are much greater. Note the factor **8** scale change for the "Residual" panel between the EPPL fits and the HITRAN 2020 fits, and a factor **7** difference in the 296K RMS fitting residuals. So from Harrison's laboratory data, EPPL 2009 C_2H_6 looks **MUCH** better than HITRAN 2020.

Fits to MkIV ground-based Atmospheric Spectra – in C_3H_8 window





Top panel shows fits. Lower panels zoom into the transmittance in order to more clearly see the weak absorbers (e.g. C_3H_8 and C_2H_6). Although the differences here in RMS fitting residuals; 0.365% versus 0.368%, confirm Zhou's statement, the retrieved C_3H_8 changes by a factor 3 as a result of changing the C_2H_6 spectroscopy. This is because the C_2H_6 feature at 2967.5 cm^{-1}, that overlaps the C_3H_8 Q-branch, is 2 times stronger in EPPL 2009 than in HITRAN 2020 so the C_3H_8 reduces to compensate.

Summary: Effect of C_2H_6 Spectroscopy on C_3H_8 retrievals

C_3H_8 retrievals are extremely sensitive to the chosen C_2H_6 spectroscopy. Propane measurements that use different C_2H_6 spectroscopies are not comparable.

For useful C_3H_8 retrievals, almost perfect C_2H_6 spectroscopy is needed.

Based on fits to laboratory spectra, I strongly recommend using the C_2H_6 EPPL when fitting any gas in this region, even though it might provide slightly worse fits in some windows (e.g., C_3H_8).

If you achieve good fits for the wrong reason (e.g., compensating errors), fixing just one of the errors makes the fits worse.

When evaluating spectroscopies, use the widest possible range of spectra, including lab spectra.

H_2O Spectroscopy Evaluation 650-15,000 cm^{-1}

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H_2O is a major impediment to measurements of telluric trace gases and of stellar doppler shifts (indicative of exo-planets). So every 4 years I perform a H_2O evaluation to see which parts of the new HITRAN are improved over my current H_2O linelist.

In 2000 I performed a water vapor spectroscopy evaluation study available from:
https://mark4sun.jpl.nasa.gov/report/H2O_spectroscopy_evaluation_700_12000-compressed.pdf

The goal of this new work is to update that evaluation while extending the wavenumber coverage. To do so, I fitted measured Kitt Peak laboratory spectra, and also atmospheric spectra, using six different H_2O linelists: HIT2020, its May 2022 update, and the historical lists: HIT2008, HIT2012 and HIT2016.

I also compare the ATM23 linelist, which is a compilation that I maintain that "cherry picks" the best aspects of the predecessor linelists going back to Toth (2003) in the case of H_2O. Additionally, many ad hoc "repairs" have been made, especially to the widths and shifts, to fix fitting issues. This linelist is used by TCCON and for analysis of MkIV spectra.

To quantify the quality of a linelist we look at rms spectral fitting residuals and the retrieved H_2O VMR scale factors. It is desirable that linelists produce small RMS fitting residuals, VMR scale factors close to the nominal 1.0, with small window-to-window variations.

Description of May 2022 H_2O Update (from HITRAN website)

☔ **H_2O line list update above 4340 cm^{-1}**

The line list for water vapor above 4340 cm^{-1} has been revised based on the evaluations carried out by Eli Mlawer and Mike Iacono (AER) using TCCON spectra from the Lamont site. The changes could be summarized into these categories:

1. Line shift parameters in HITRAN2020 that originated from Ref. (https://doi.org/10.1016/j.jqsrt.2020.107030) were found to have errors for certain bands, resulting for instance in a large amount of positive values. While these models are being improved, the issue was fixed in the following way: The shifts that affected the quality of the residuals have been reverted back to the HITRAN2016 values or replaced with those from the AER list, which contains manual modifications of the HITRAN2016 parameters to better match the TCCON spectra.
2. The air-broadened half-widths that affected the quality of the residuals have been reverted back to the HITRAN2016 values or replaced with those from the AER list "aer3.8.1" (https://doi.org/10.5281/zenodo.5120012), which contains manual modifications of the HITRAN2016 parameters to better match the TCCON spectra.
3. The intensities in the $4\nu_2+\nu_3$ band were scaled down by 22%, while individual intensities (of *ab initio* origin) in different bands had to be scaled to match the TCCON spectra.
4. As pointed out by Alain Campargue (Grenoble), a large percentage of the lines in HITRAN2020 that were referencing W2020 MARVEL line list for the line positions were deviating slightly from the line positions in the original W2020 work. This has now been fixed.

It should be noted that the aforementioned changes affect primarily the principal isotopologue. Also, the line position changes proposed in (https://doi.org/10.1080/00268976.2022.2051762) have not been implemented yet, but they are unlikely to impact the strong lines.

Spectra Fitted

Performed an evaluation of six different H_2O linelists using four different spectral datasets:

- 148 Kitt Peak Laboratory (670 to 15000 cm^{-1}; 296K)
- 34 MkIV balloon (670 to 5600 cm^{-1} at 0.010 cm^{-1} resolution; -50C to -25C)
- 92 MkIV ground-based (670 to 5600 cm^{-1} at 0.006 cm^{-1} resolution; -30 to +40C)
- 65 TCCON ground-based (4000 to 15000 cm^{-1} at 0.02 cm^{-1} resolution -30C to +40C) (Park Falls, Darwin, Lamont, ETL)

Available Kitt Peak laboratory spectra are all around 25C and therefore do not test the T-dependencies. Therefore, necessary to use atmospheric spectra: measured from balloon (MkIV) and ground (MkIV & TCCON) to evaluate the 6 linelists (described on next page).

Defined 128 windows covering 670 to 15000 cm^{-1}, everywhere that there were measurable H_2O lines.

This resulted in (148+34+92+65)*6*128 = ~250,000 spectral fits went into this evaluation.

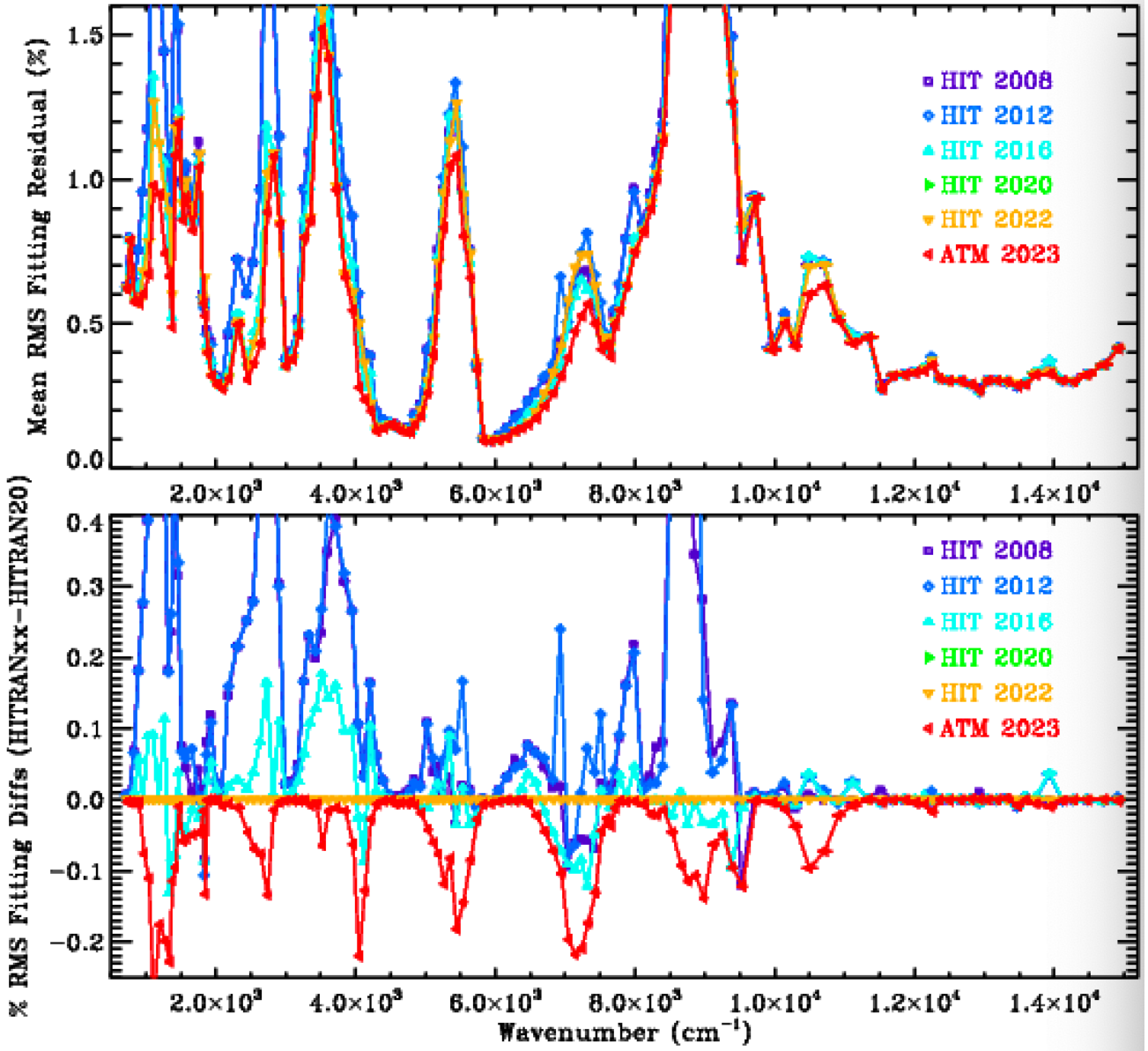
The GFIT code was used to fit the spectra, using atmospheric models (T, P, VMR profiles) based of GEOS FP-IT. Assumed Voigt lineshape without H_2O line mixing.

RMS spectral fitting residuals for 130 windows averaged over 148 KP Lab spectra

iwin	fcen	width/2	Nrow	Npp	HIT08	HIT12	HIT16	HIT20	HIT22	ATM23
1	724.05	11.50	63	166	0.6300	0.6288	0.6220	0.6222	0.6222	0.6191
2	768.00	32.05	63	166	0.7990	0.7974	0.7906	0.7916	0.7916	0.7877
3	834.07	32.53	67	166	0.6485	0.6450	0.5891	0.5792	0.5792	0.5751
4	897.40	27.85	81	166	0.7566	0.7565	0.6316	0.5749	0.5749	0.5710
5	961.20	34.90	83	166	0.9554	0.9578	0.6795	0.6797	0.6797	0.6040
6	1033.10	37.05	83	166	1.1757	1.1757	0.8728	0.7828	0.7828	0.6720
7	1103.00	33.00	83	166	1.8648	1.8638	1.3578	1.2665	1.2665	0.9791
8	1181.85	44.75	87	166	1.7643	1.7622	1.1251	1.1236	1.1236	0.9478
9	1264.55	38.00	90	166	1.4428	1.4443	1.0559	0.9420	0.9420	0.7434
10	1328.70	24.85	93	166	1.0731	1.0712	0.7602	0.8915	0.8915	0.6638
.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.
122	13323.05	68.75	9	166	0.3003	0.2994	0.3010	0.3002	0.2991	0.3014
123	13473.00	81.50	9	166	0.2846	0.2844	0.2848	0.2936	0.2935	0.2848
124	13588.50	34.20	9	166	0.2895	0.2952	0.2951	0.2902	0.2899	0.2895
125	13732.70	110.00	9	166	0.3278	0.3289	0.3326	0.3306	0.3284	0.3225
126	13935.50	93.00	9	166	0.3346	0.3717	0.3731	0.3359	0.3358	0.3261
127	14121.50	93.30	9	166	0.3038	0.3034	0.3037	0.3037	0.3042	0.3034
128	14281.90	67.10	9	166	0.2994	0.2995	0.2996	0.2995	0.2997	0.2993
129	14471.90	122.90	9	166	0.3254	0.3252	0.3254	0.3254	0.3254	0.3250
130	14712.40	117.60	9	166	0.3566	0.3576	0.3557	0.3586	0.3585	0.3589
Mean % RMS fits over windows:					**0.7962**	**0.8056**	**0.6939**	**0.6841**	**0.6867**	**0.6410**

Table is too large to fit on slide so I only show the top and bottom nine entries, omitting 113 rows in the middle.
HIT12 produces the worst/largest overall RMS fitting residuals (0.8056%), ATM23 the best.
HIT22 update produces worse fits to KP lab spectra than HIT20 above 4340 cm^{-1}, and identical fits below.

Kitt Peak Lab: RMS Spectral Fitting Residuals



Top-Left panel shows absolute RMS. The different H_2O linelists are depicted by different colors. The RMS varies considerably from window to window: small where absorptions are weak and large where lines are inaccurate and strong.

The absolute RMS is not important, what is important is the variation of the RMS from linelist to linelist.

The lower–left panel shows RMS differences wrt HIT20. So the green HIT 2020 points are a straight line at zero. Negative values imply improvement. The older HITRAN linelists are generally worse than HIT 2020 (except for the 7000-7500 cm^{-1} region).

ATM23 (red points) is the best/smallest in almost every individual window and overall (0.64%). This should not be a surprise: if it had been worse anywhere, I would have already cut and pasted the offending lines.

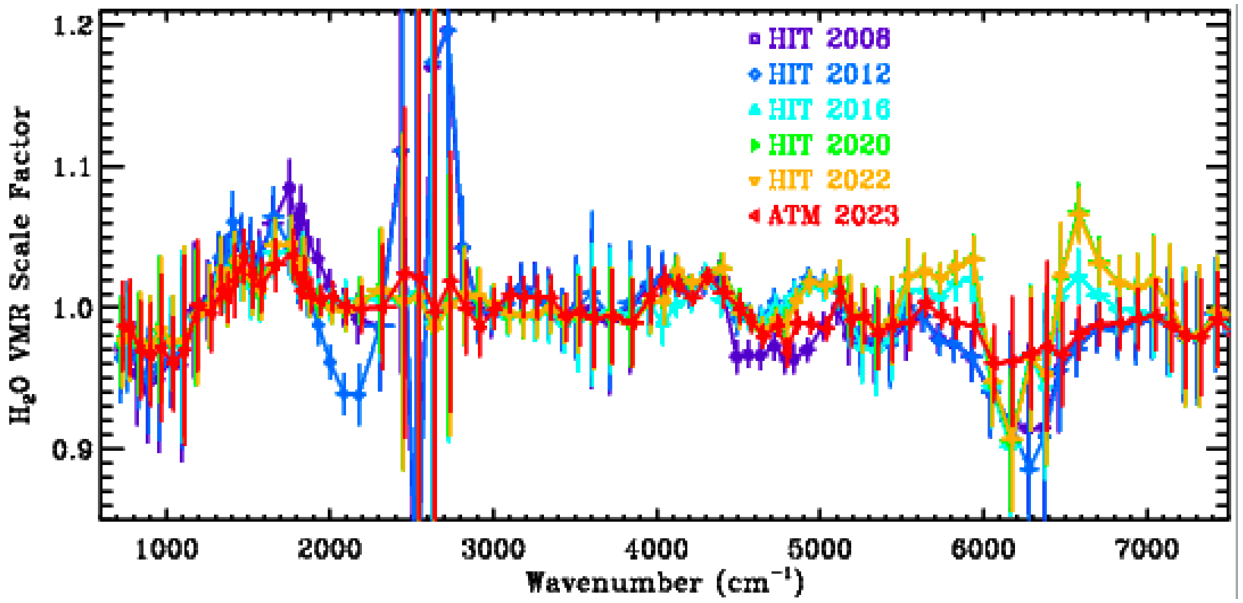
VMR Scale Factors averaged over Kitt Peak Lab spectra for each window & linelist

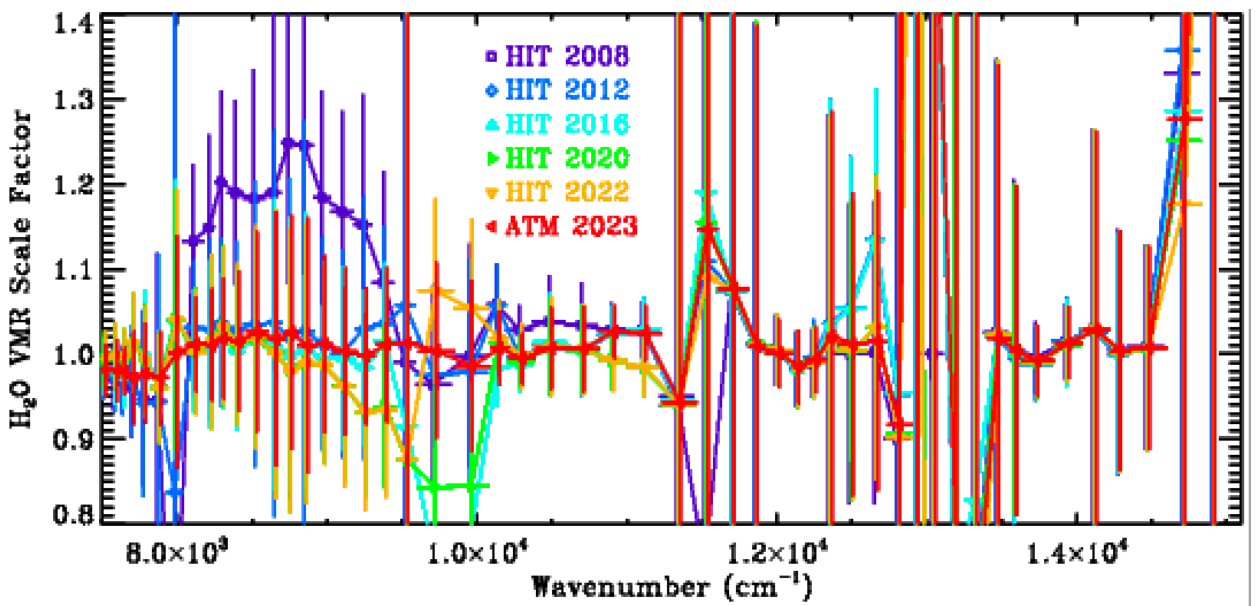
iwin	fcen	Width/2	Nrow	Npp	HIT08	HIT12	HIT16	HIT20	HIT22	ATM23
1	724.05	11.50	63	166	0.9715	0.9646	0.9761	0.9760	0.9760	0.9869
2	768.00	32.05	63	166	0.9836	0.9753	0.9834	0.9821	0.9821	0.9862
3	834.07	32.53	67	166	0.9536	0.9642	0.9747	0.9749	0.9749	0.9698
4	897.40	27.85	81	166	0.9418	0.9486	0.9708	0.9718	0.9718	0.9664
5	961.20	34.90	83	166	0.9498	0.9587	0.9842	0.9848	0.9848	0.9717
6	1033.10	37.05	83	166	0.9625	0.9623	0.9751	0.9751	0.9751	0.9604
7	1103.00	33.00	83	166	0.9598	0.9678	0.9725	0.9760	0.9760	0.9699
8	1181.85	44.75	87	166	0.9980	0.9937	0.9926	0.9935	0.9935	1.0018
9	1264.55	38.00	90	166	1.0055	1.0042	0.9998	1.0010	1.0010	0.9960
10	1328.70	24.85	93	166	1.0335	1.0351	1.0222	1.0252	1.0252	1.0125
.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.
122	13323.05	68.75	9	166	0.6212	0.7059	0.8277	0.6864	0.5588	0.6902
123	13473.00	81.50	9	166	1.0259	1.0213	1.0235	1.0230	1.0232	1.0183
124	13588.50	34.20	9	166	1.0102	0.9963	1.0009	1.0060	1.0043	1.0038
125	13732.70	110.00	9	166	0.9953	0.9883	0.9902	0.9905	0.9912	0.9922
126	13935.50	93.00	9	166	1.0143	1.0158	1.0130	1.0103	1.0112	1.0133
127	14121.50	93.30	9	166	1.0304	1.0260	1.0292	1.0288	1.0297	1.0283
128	14281.90	67.10	9	166	1.0054	0.9986	1.0027	1.0024	1.0022	1.0039
129	14471.90	122.90	9	166	1.0082	1.0065	1.0063	1.0062	1.0063	1.0081
130	14712.40	117.60	9	166	1.3311	1.3574	1.2854	1.2510	1.1765	1.2765
Average VSF (over windows)					**0.9969**	**1.0013**	**1.0057**	**1.0088**	**1.0087**	**1.0001**
					±0.0312	**±0.0239**	**±0.0149**	**±0.0169**	**±0.0166**	**±0.0150**

ATM 2023 has average VSF that is closest to the nominal 1. HIT16 & ATM23, has smallest window-to window variation (1.5%)

Kitt Peak Lab: VMR Scale Factors averaged over spectra

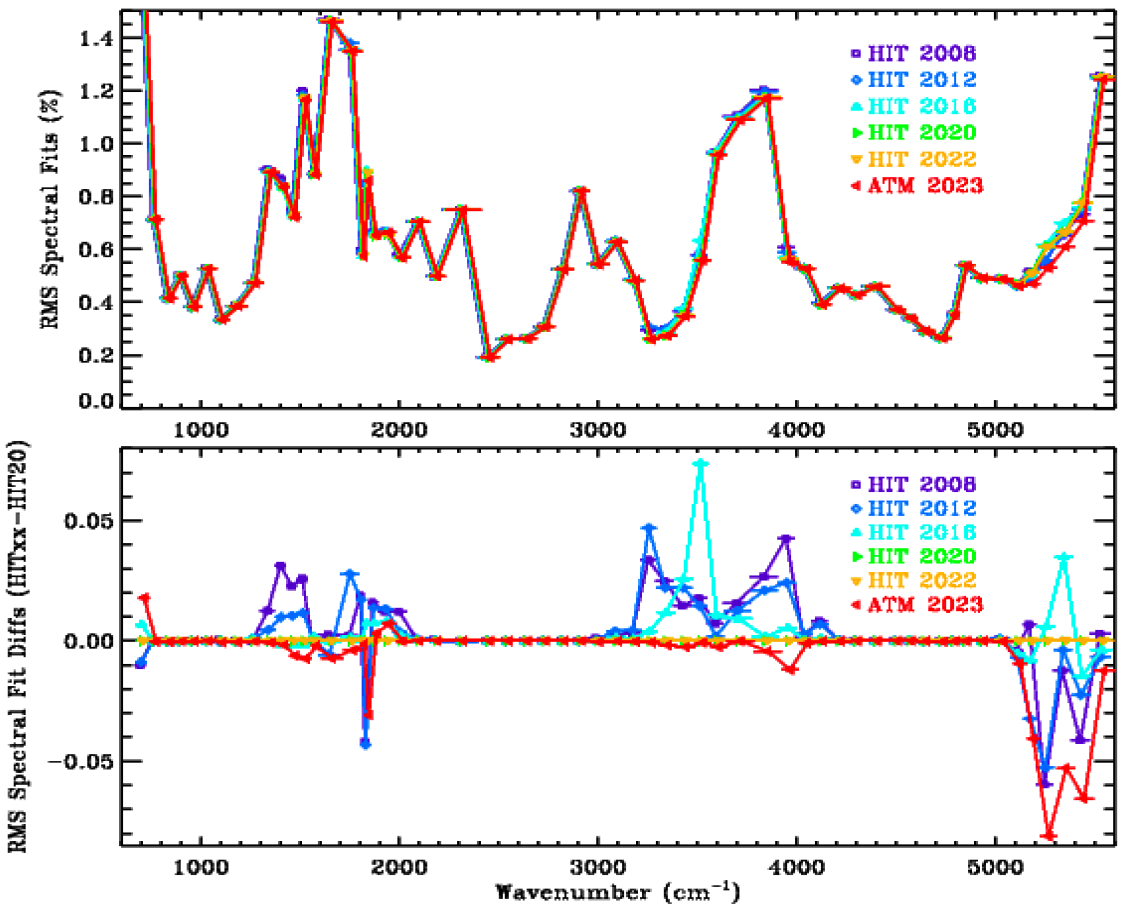
The VSF is the average ratio of the retrieved H_2O amount to the nominal amount (computed from the cell conditions) averaged over the spectra that could be analyzed. So in a perfect world, these values should all be 1.0. The error bars are its standard deviation from spectrum to spectrum. Error bars become large around 11500 cm^{-1} and 13,000 cm^{-1} where as the H_2O line intensities become very weak. In this region the TCCON ground-based spectra become more useful.
In the 9600 to 10000 cm^{-1} region the VSFs increased by ~25% between HIT2020 and the 2022 update.
Average VMR scale Factors (VSF) are all within 1% of the nominal value (1.00).
Window-to-window rms variation of VSF is worst/largest (3.1%) for HIT08 and best/smallest for HIT16 & ATM23 (1.5%)



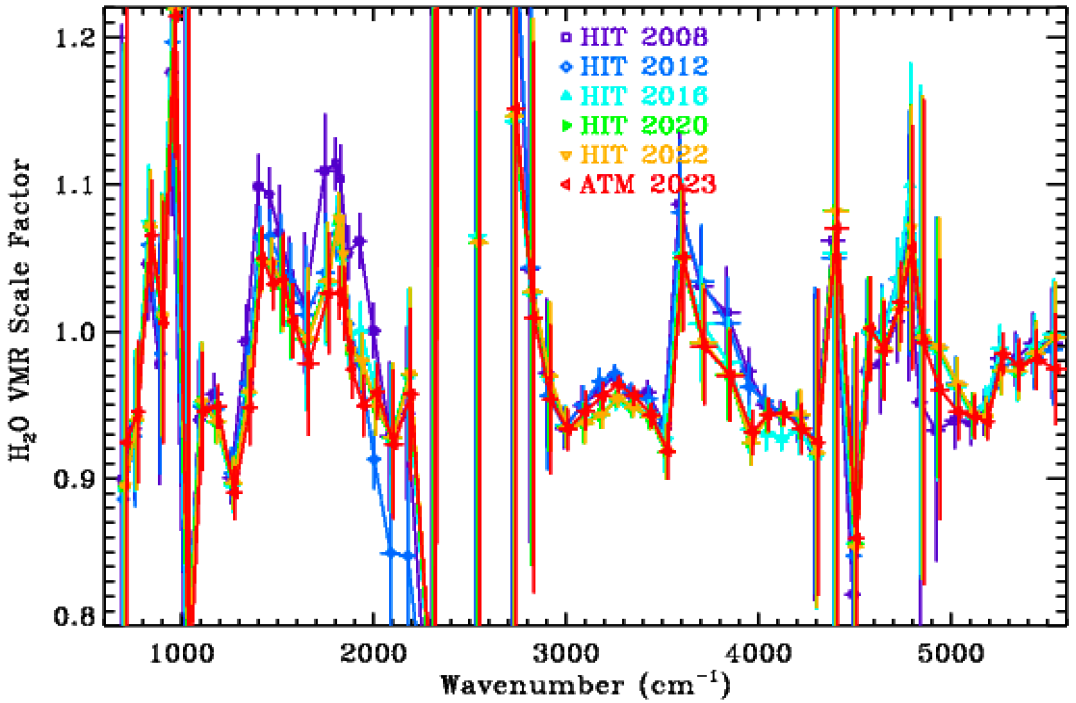


	HIT08	HIT12	HIT16	HIT20	HIT22	ATM23
Average VSF (over windows)	0.9969	1.0013	1.0057	1.0088	1.0087	1.0001
RMS deviation from mean	±0.0312	±0.0239	±0.0149	±0.0169	±0.0166	±0.0150

MkIV Balloon: RMS Spectral Fitting Residuals and VMR Scale Factors



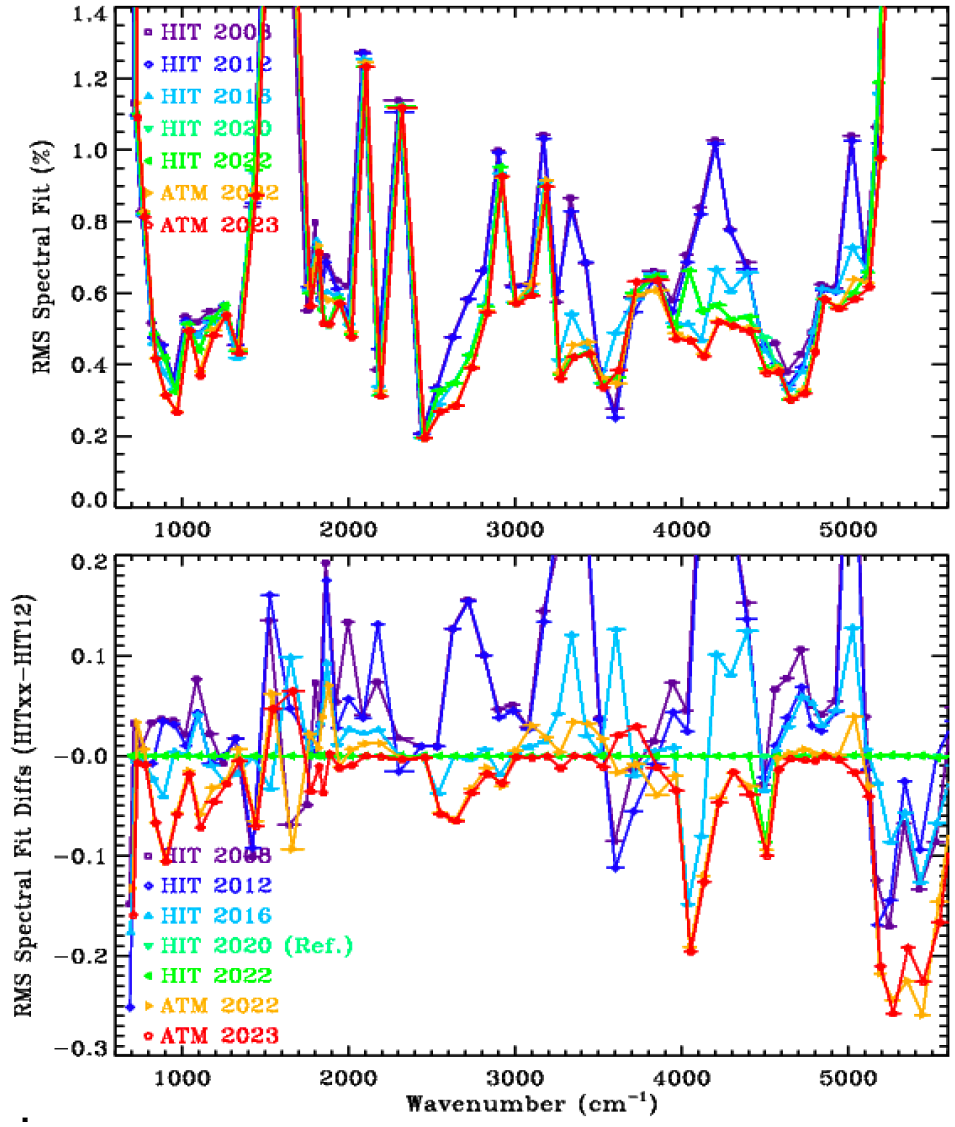
Residuals are mostly due to non-H_2O gases and so don't vary much from linelist to linelist. Mean % RMS fits, averaged over windows is best for ATM23. HIT20 and HIT22 give same RMS. Window_to_window variation in VSF is smallest for ATM23.

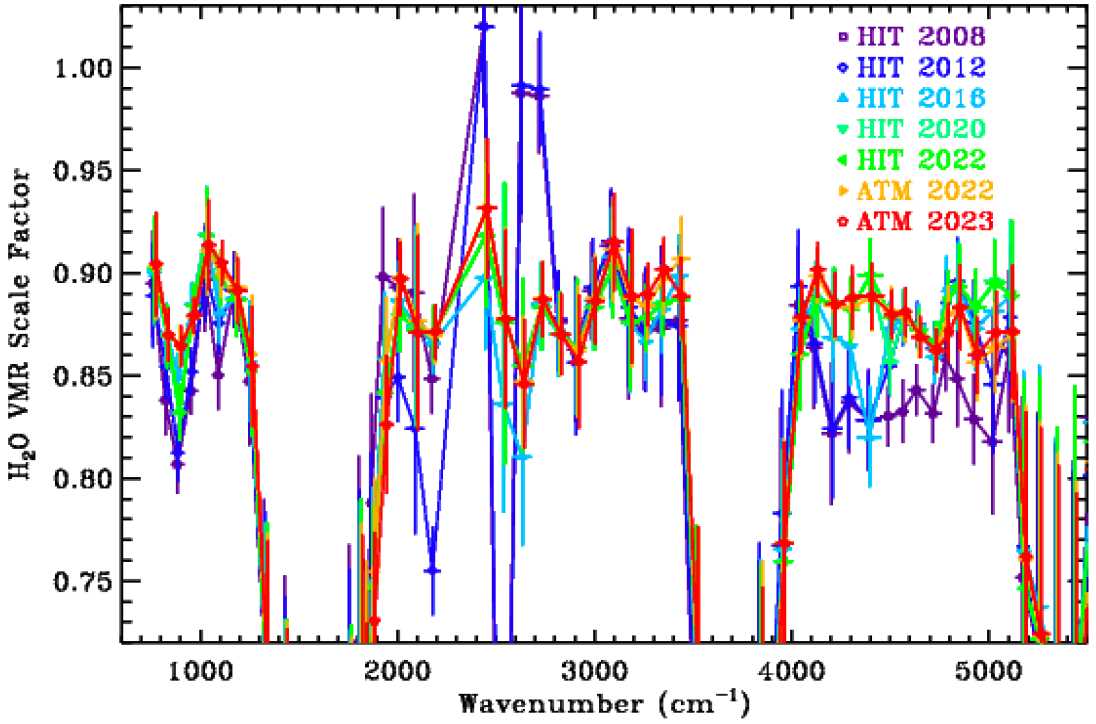


	HIT08	HIT12	HIT16	HIT20	HIT22	ATM23
Mean %RMS fits over windows:	0.6203	0.6189	0.6201	0.6170	0.6170	0.6115
Average VSF (over windows)	0.9726	0.9665	0.9573	0.9572	0.9572	0.9587
RMS deviation from mean	±0.0456	±0.0364	±0.0383	±0.0364	±0.0364	±0.0313

MkIV ground-based: RMS Residuals and VSFs

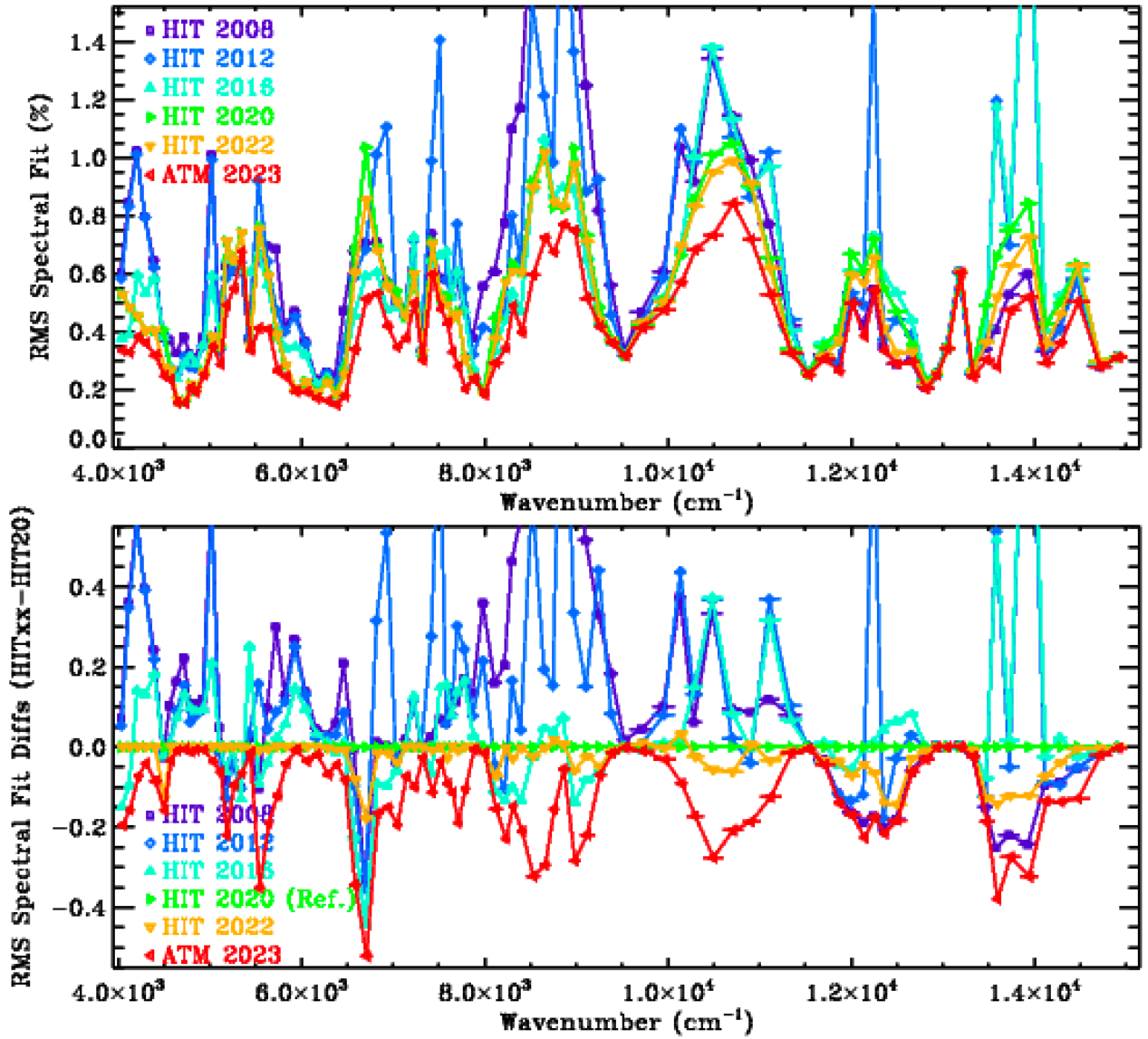
HIT22 produces slightly better RMS fitting residuals than HIT20, but ATM23 is better (0.88%).





	HIT08	HIT12	HIT16	HIT20	HIT22	ATM23
Mean % RMS fits over windows:	0.9863	0.9771	0.9292	0.9233	0.9219	0.8804
Average VSF (over windows):	0.8513	0.8632	0.8729	0.8756	0.8763	0.8780
RMS deviation from Mean	±0.0419	±0.0428	±0.0273	±0.0272	±0.0267	±0.0267

TCCON RMS Fitting Residuals averaged over spectra



Upper Left: The average RMS fitting residual (averaged over 65 spectra) is plotted vs wavenumber for each window and each linelist.

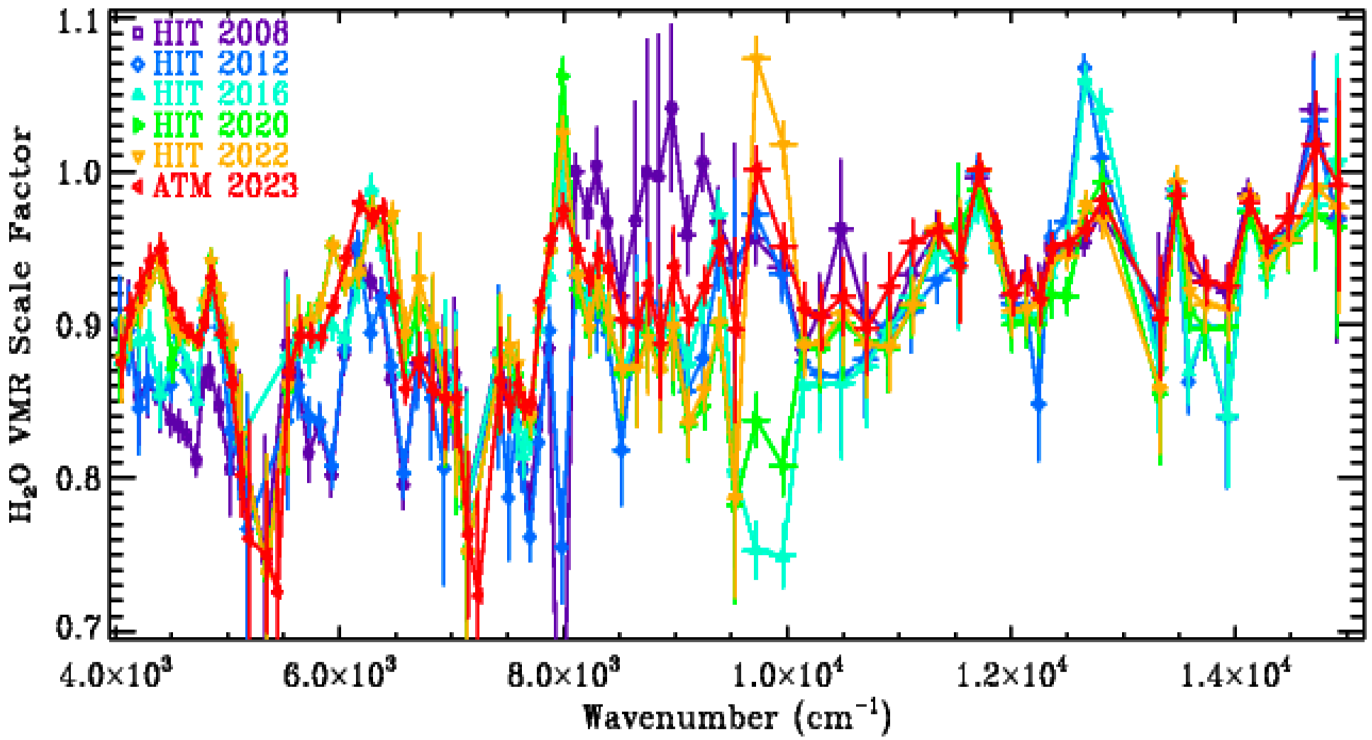
Lower Left: The difference in the RMS residuals from the HITRAN 2020 values. Positive values mean that linelist is worse then HIT 2020 and vice versa.

Residuals are small where the lines are weak or very strong (the window blacks out).
HIT22 linelist provides smaller/improved residuals than HIT20, but ATM23 provides the best fits, which it should because is is based on the best of predecessor linelists. [If a HITRAN linelist was doing better in a particular region, these lines would already been cut and pasted into ATM23]. Plus, ad hoc corrections have been made, esp. to the widths and shifts.

In some windows, e.g. 6703 cm^{-1}, 13500-14000 cm^{-1}, HIT2008/12 are better than HIT2020 or 2022.

	HIT08	HIT12	HIT16	HIT22	HIT22	ATM23
Mean % RMS fits over windows:	0.6682	0.6446	0.5417	0.5051	0.4811	0.3860

TCCON (ground-based) VMR Scale Factors



Since atmospheric H_2O amounts not accurately known, absolute values of VSF values not significant. But relative variation of VSF from window to window should be precise, provided that the data are analyzed correctly.

Plot shows the average VSF values for each window, for each linelist. This appears to shows an increasing trends with wavenumber.

As seen in KP lab data, the FSF values at 9600-10,000 cm-1 increased by ~25% due to the HIT22 update. A correction was needed, but 25% was perhaps too much.

ATM23 linelist had he smallest window-to-window variation

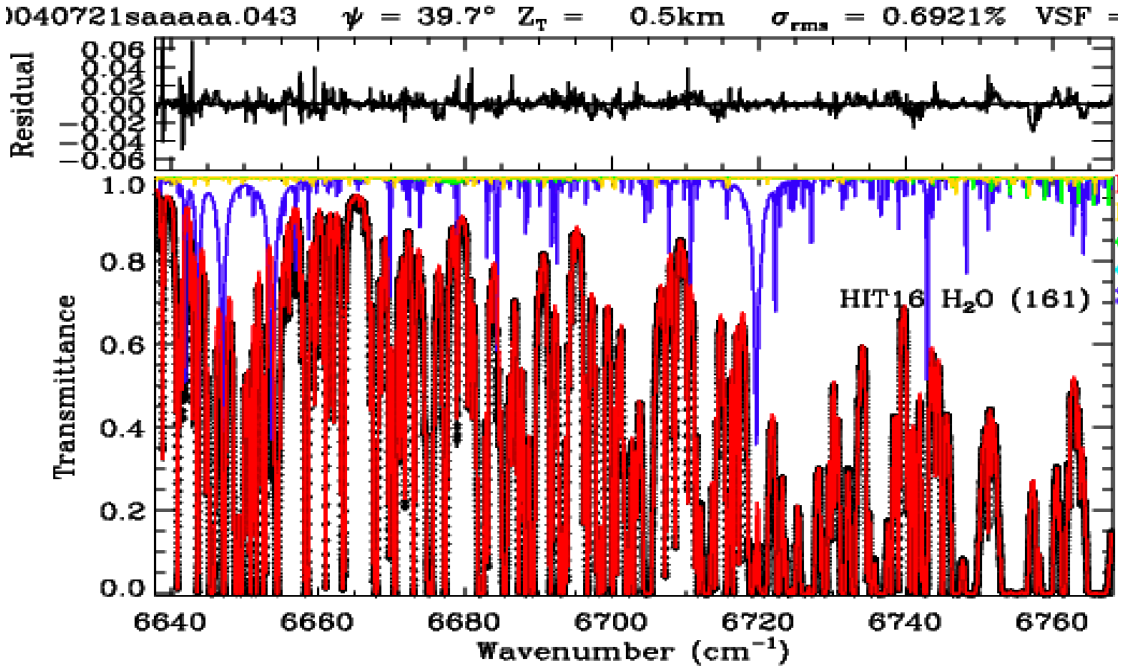
	HIT08	HIT12	HIT16	HIT20	HIT22	ATM23
Average VSF (over windows)	0.9076	0.9079	0.9132	0.9192	0.9261	0.9247
RMS deviation from mean	±0.0638	±0.0619	±0.0534	±0.0413	±0.0417	±0.0386

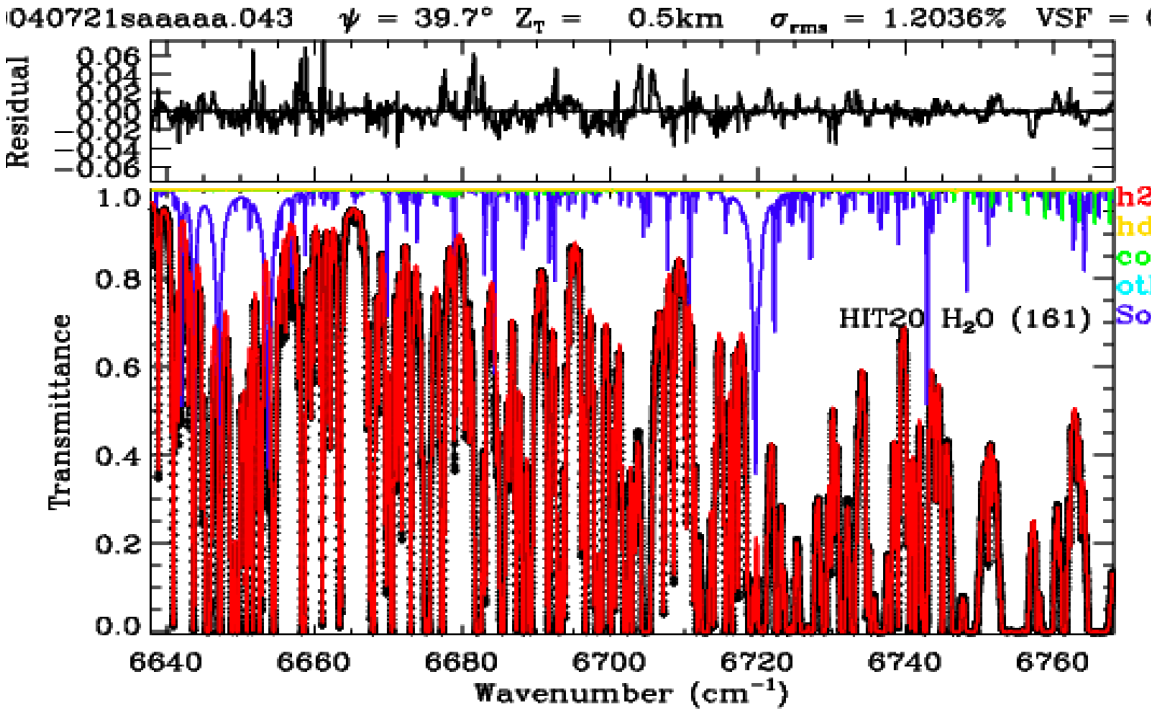
Example of TCCON spectral fits in the window centered at 6703 cm^{-1}

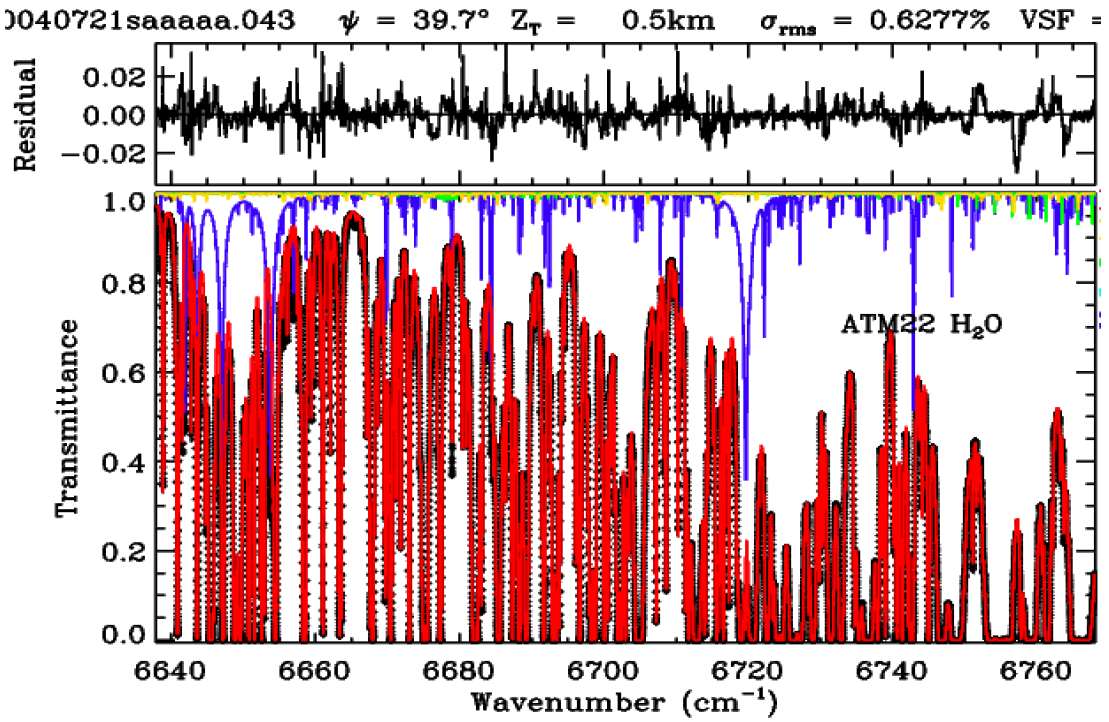
This window produces the worst residuals of all 33 windows, Showing fits to a July spectrum (30C) measured from Park Falls.

In this region HIT20 produces worse residuals than HIT16.

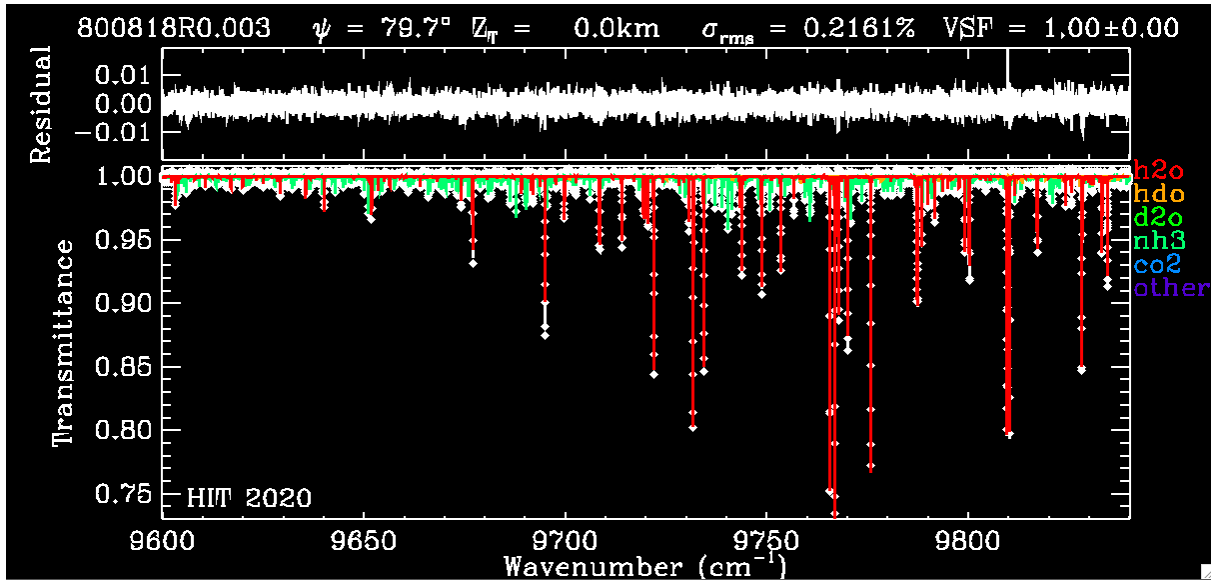
ATM23 (lower-right) has the best residuals

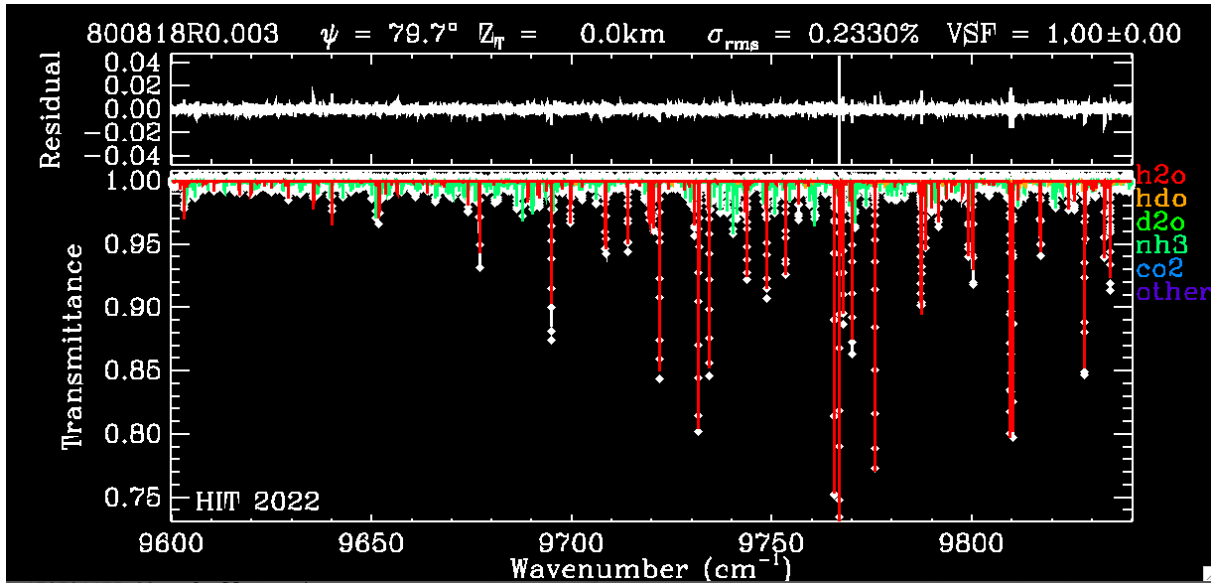


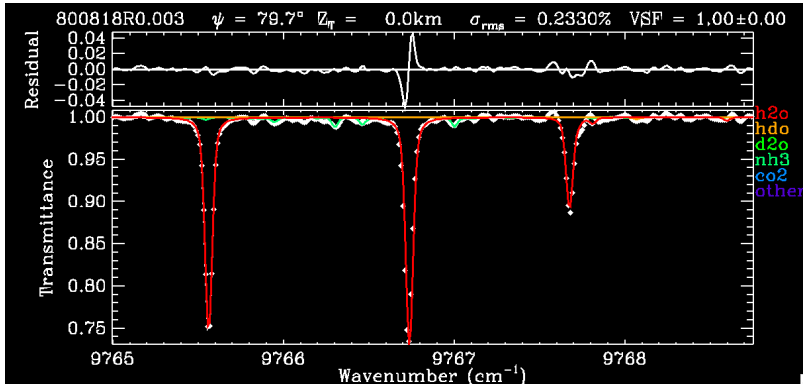




Example of the HIT22 being worse than HIT20 in fitted Kitt Peak lab spectra







KP spectrum measured 433 m path at 19 Torr of pure H_2O.

Left: Fitted with HIT 2020 linelist

Right: Fitted with HIT 2022 update

Mis-positioned line at 9766 .7 cm^{-1} drives up the RMS fitting residuals vary from 0.2161% for HIT20 to 0.2330% for the HIT22 update. This residual is not obvious in TCCON spectra broadened by 1 atm of air.

```
HIT20: 11 9766.729392 8.860E-25 1.445E-03.09690.428  136.76170.75-.010310          0 4 1
HIT22: 11 9766.736617 6.911E-25 1.127E-03.09690.428  136.76170.75-.010310          0 4 1
```

Summary and Conclusions

Four spectral datasets (lab, balloon, ground-based) have been fitted for in 134 windows covering 670 to 15,000 cm^{-1}.

Six different linelists were used for the H_2O spectroscopy. For non-H_2O spectroscopy, the same linelist was used (ATM23).

The assumed cell/atmospheric conditions were identical for all linelists. So the differences in RMS or VSF values are entirely attributable to H_2O spectroscopy

ATM 2023 linelist produces the best fitting residuals and the smallest window-to-window variation in retrieved H_2O amount for almost every dataset.

HITRAN 2022 update produces better RMS fitting residuals and window-to-window consistency for ground-based spectra above 4340 cm^{-1}, but not for lab spectra. For balloon spectra it made little difference.

If the ATM H_2O linelist is so good, why doesn't HITRAN adopt it for HIT24?

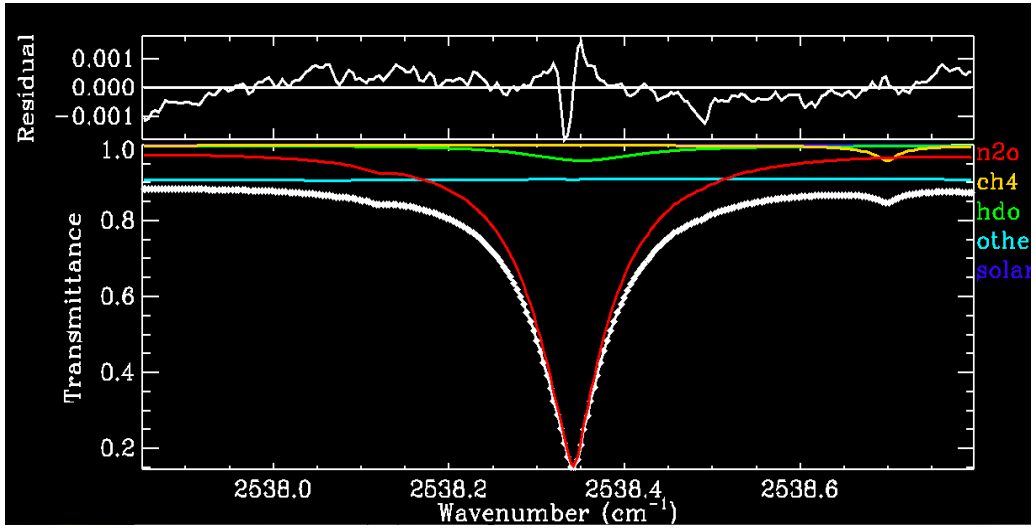
- Many of the transitions have obsolete quantum assignments, dating back to Toth (2003), or none at all.
- No accuracy/reference codes
- No publication.
- Lines that cannot be seen in atmospheric or lab spectra (S < 2e-28) are missing from ATM linelist (HITRAN has them)
- To evaluate the linelist, I used the same spectra as were used to decide which lines to correct/adopt.
- No evaluation of H_2O above 15000 cm^{-1} (lines are too weak to be seen in lab spectra; no TCCON spectra)

NDACC Windows

Fitted an assortment of MkIV ground-based spectra using all 42 of the NDACC-IRWG windows (required and optional) in table on right. I used using two linelists: HIT 2022 update and ATM24.

Comment: most of these windows are very narrow: usually a single target line plus some interferers. In my experience, narrow windows are less robust than wide ones, resulting in more variation in retrieved gas amounts, even though fits are better.

Some NDACC windows have potentially serious issues, for example, the N_2O window covering 2537.85 – 2538.80 cm^{-1} has a HDO line perfectly centered under the target N_2O line. Of course, the HDO line is less pointy and so stratospheric contributions can be clearly distinguished, but not the tropospheric contributions.



Gas	Required μ-w(s) [cm^{-1}]	Optional μw	OPD [cm]	Interfering species to be fit (pre- or simul-)	a Priori Linelist	Column or Profile	Note
O3	1000.0-1005.0	782.56-782.86 788.85-789.37 993.30-993.80	250	H2O, CO2, C2H4, O668, O686	WACCMV5 HIT08	P	a,e
HCl	2727.73-2727.83 2775.70-2775.80 2925.80-2926.00		>180	O3, HDO N2O, O3 O3, CH4, NO2	WACCMV5 HIT08	P	
HF	4038.81 4039.07	4000.86-4001.10 4109.77-4110.07	>180	H2O, HDO, CH4 H2O, O3 H2O, HDO, CH4	WACCMV6 HIT08	P	c
ClONO2	780.10-780.35	780.0-781.3 779.0-780.0	>50	H2O CO2, O3 H2O	WACCMV5 HIT-XC/PL	C	d,g
HNO3	867.05-870.00	872.25-874.00			WACCMV5 HIT08	P	
N2O	2481.30-2482.60 2526.40-2528.20 2537.85-2538.80 2540.10-2540.70		250		WACCMV5 HIT08	P	
CH4	2613.70-2615.40 2835.50-2835.80 2921.00-2921.60	2650.60-2651.30 2903.60-2904.03 2611.60-2613.35 2613.70-2615.40 2914.70-2915.15 2941.23-2942.23	250	HDO, CO2 HDO HDO, NO2, H2O HDO, CO2 NO2 HDO, CO2 CH4, CO2, HDO CH4, NO2,H2O,HDO CH4,H2O,O3	WACCMV5 HIT00	P	b
CO	2057.70-2058.00 2069.56-2069.76 2157.50-2159.15		250	O3, CO2, OCS O3, CO2,OCS O3, CO2, N2O, H2O	WACCMV5 HIT08	P	
C2H6	2976.66-2976.95 2983.20-2983.55	2986.50-2986.95	250	H2O, O3, CH4 H2O, O3, CH4 H2O, O3, CH4	WACCMV5.1 HIT-XC/PL	by site	d,f
HCN	3268.05 - 3268.40 3287.10 - 3287.35 3299.40 - 3299.60	3277.775 – 3277.950 3286.168 – 3288.482 3331.400 – 3331.800 3301.030 – 3301.300 3304.825 – 3305.600	250	H2O, C2H2 H2O, CO2, C2H2 H2O, H218O H2O H2O H2O, H217O, CO2, N2O H217O H2O, H218O, H217O, C2H2	WACCMV5.1 HIT08	by site	d

% RMS fitting residuals for the NDACC windows: HIT22 vs ATM24

In 11/42 windows HIT 22 provides the lowest RMS fitting residuals.

In 31/41 windows ATM 2024 provides the lowest RMS fitting residuals

Overall, ATM24 has an average RMS fitting residual of 0.2536%, versus 0.2676% for HIT22.

This was a pleasant surprise because the NDACC-IRWG windows are selected to avoid large residuals, whereas the main motivation for improving the ATM linelist was reducing overall fitting residuals, which are are dominated by strong H_2O lines with poor spectroscopy. So the ATM linelist was optimized mainly on the badly fitted lines that NDACC avoids. Yet it still provides better fits.

iwin	fcen	fcen_error	Nrow	Npp	hit22	atm24		
1	782.71	0.15	86	86	0.3055	0.3059	1	2
2	789.11	0.26	86	86	0.3204	0.3213	1	2
3	993.55	0.25	86	86	0.2702	0.2803	1	2
4	1002.50	2.50	86	86	0.5228	0.4887	2	1
5	2727.78	0.05	86	86	0.1594	0.1594	2	2
6	2775.75	0.05	86	86	0.2627	0.2606	2	1
7	2925.90	0.10	86	86	0.3523	0.3368	2	1
8	4000.98	0.12	86	86	0.2518	0.2697	1	2
9	4038.94	0.13	86	86	0.3225	0.3211	2	1
10	4109.92	0.15	86	86	0.2746	0.2722	2	1
11	780.22	0.12	86	86	0.2533	0.2532	2	1
12	780.65	0.65	86	86	0.3443	0.3459	1	2
13	779.50	0.50	86	86	0.4489	0.4165	2	1
14	868.53	1.48	86	86	0.2799	0.2808	1	2
15	873.12	0.88	86	86	0.2923	0.2684	2	1
16	2481.95	0.65	86	86	0.2107	0.2100	2	1
17	2527.30	0.90	86	86	0.2025	0.1943	2	1
18	2538.32	0.47	86	86	0.2055	0.2051	2	1
19	2540.40	0.30	86	86	0.2294	0.2264	2	1
20	2614.55	0.85	86	86	0.2389	0.2264	2	1
21	2635.65	0.15	86	86	0.1989	0.1918	2	1
22	2921.30	0.30	86	86	0.4211	0.3094	2	1
23	2650.95	0.35	86	86	0.2204	0.1961	2	1
24	2903.81	0.22	86	86	0.3031	0.3010	2	1
25	2612.48	0.88	86	86	0.8045	0.8004	2	1
26	2614.55	0.85	86	86	0.2389	0.2264	2	1
27	2914.93	0.22	86	86	0.4588	0.3328	2	1
28	2941.73	0.50	86	86	0.4311	0.3370	2	1
29	2057.85	0.15	86	86	0.1974	0.1994	1	2
30	2069.66	0.10	86	86	0.2331	0.2305	2	1
31	2158.32	0.82	86	86	0.2636	0.2577	2	1
32	2976.80	0.14	86	86	0.1616	0.1559	2	1
33	2983.38	0.17	86	86	0.2081	0.1997	2	1
34	2986.73	0.22	86	86	0.2110	0.1559	2	1
35	3268.23	0.17	86	86	0.1404	0.1422	1	2
36	3287.23	0.12	86	86	0.1298	0.1298	2	2
37	3299.50	0.10	86	86	0.1295	0.1298	1	2
38	3277.86	0.09	86	86	0.1121	0.1131	1	2
39	3287.32	1.16	86	86	0.1953	0.1932	2	1
40	3331.60	0.20	86	86	0.1687	0.1422	2	1
41	3331.17	0.14	86	86	0.1335	0.1316	2	1
42	3305.21	0.39	86	86	0.1323	0.1325	1	2
Mean % RMS fits over windows:					**0.2676**	**0.2536**		

VSFs for the NDACC windows: HIT22 vs ATM24

ATM 24 provides a smaller overall window-to-window variation in retrieved VSF than HIT 22.

Look at the consistency of the retrieved O_3 VSFs (red rectangle)

Conclusions and Recommendations regarding NDACC-IRWG windows

You should be using the ATM linelist, especially the H_2O.

I'm not guaranteeing that it will produces better results in every window in every spectrum. But in general, it will perform better than HIT2020, based on my experience with fitting MKIV ground spectra. It will allow NDACC-IRWG to use wider windows in the future.

iwin	Gas	fcen	Widrg/2	Nrow	Npp	HIT22	ATM24
1	o3	782.71	0.15	86	86	1.0152	1.0288
2	o3	789.11	0.26	86	86	1.0141	1.0296
3	o3	993.55	0.25	86	86	1.0088	1.0282
4	o3	1002.50	2.50	86	86	1.0051	1.0291
5	hcl	2727.78	0.05	86	86	0.9200	0.9198
6	hcl	2775.75	0.05	86	86	0.9523	0.9543
7	hcl	2925.90	0.10	86	86	0.9701	0.9783
8	hf	4000.98	0.12	86	86	0.8487	0.8460
9	hf	4038.94	0.13	86	86	0.8526	0.8564
10	hf	4109.92	0.15	86	86	0.8339	0.8388
11	clno3	780.22	0.12	86	86	0.6008	0.5769
12	clno3	780.65	0.65	86	86	0.7028	0.6786
13	clno3	779.50	0.50	86	86	0.3364	0.1160
14	hno3	868.53	1.48	86	86	0.9137	0.9142
15	hno3	873.12	0.88	86	86	1.0104	1.0099
16	n2o	2481.95	0.65	86	86	0.9799	0.9766
17	n2o	2527.30	0.90	86	86	0.9707	0.9701
18	n2o	2538.32	0.47	86	86	0.9681	0.9664
19	n2o	2540.40	0.30	86	86	0.9765	0.9767
20	CH4	2614.55	0.85	86	86	0.9879	0.9894
21	CH4	2635.65	0.15	86	86	0.9741	0.9810
22	CH4	2921.30	0.30	86	86	1.0152	0.9914
23	CH4	2650.95	0.35	86	86	0.9423	0.9900
24	CH4	2903.81	0.22	86	86	0.9616	0.9736
25	CH4	2612.48	0.88	86	86	1.1857	1.1852
26	CH4	2614.55	0.85	86	86	0.9879	0.9894
27	CH4	2914.93	0.22	86	86	0.9751	0.9928
28	CH4	2941.73	0.50	86	86	0.9201	0.9306
29	CO	2057.85	0.15	86	86	0.9957	0.9907
30	CO	2069.66	0.10	86	86	1.0421	1.0370
31	CO	2158.32	0.82	86	86	0.9135	0.9089
32	C2H6	2976.80	0.14	86	86	0.4113	0.7653
33	C2H6	2983.38	0.17	86	86	0.3977	0.7474
34	C2H6	2986.73	0.22	86	86	0.4730	0.7811
35	HCN	3268.23	0.17	86	86	1.0813	1.0611
36	HCN	3287.23	0.12	86	86	1.1657	1.1543
37	HCN	3299.50	0.10	86	86	1.1637	1.1513
38	HCN	3277.86	0.09	86	86	1.1529	1.1417
39	HCN	3287.32	1.16	86	86	1.1349	1.1282
40	HCN	3331.60	0.20	86	86	1.0379	1.0366
41	HCN	3331.17	0.14	86	86	1.2046	1.2497
42	HCN	3305.21	0.39	86	86	0.9881	1.0035
Average VSF (over windows)						**0.9702**	**0.9764**
RMS deviation from mean						**0.0554**	**0.0390**