Evaluation of the "16MiKaMo" H_2O linelist using open-path atmospheric spectra: 5850-8340 cm^{-1}

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Introduction.

The 5850-8000 cm^{-1} region is important for atmospheric remote sensing. The TANSO instrument on board the GOSAT measures CH_4 at 6000 cm^{-1} and CO_2 around 6300 cm^{-1}. OCO-2 also uses the latter band. The ground-based TCCON network also uses these regions plus the O_2 band at 7900 cm^{-1}. In all cases H_2O is a major interferer, hence the importance of a good H_2O linelist.

Atmospheric Spectra.

To evaluate the new 16MiKaMo H_2O linelist, we performed a comparison of linelists by fitting ground-based (TCCON) solar absorption spectra measured under a wide range of conditions (temperature, SZA, and hence H_2O slant column).
The spectra were measured by Bruker IFS125 HR spectrometers at TCCON sites in Darwin Australia, (12S, 131E, 0.03 km asl) and Park Falls, Wisconsin (46N, 90W, 0.44 km asl), were fitted using the GFIT code (Voigt lineshape, no line-mixing) and various linelists. The T/P and H_2O profiles assumed in the spectral fitting were taken from NCEP re-analyses. Seven spectra were chosen representing a wide range of atmospheric conditions. All seven cover the 3900 to 15500 cm^{-1} wavenumber range, were measured at 45 cm MOPD, with a grid point spacing of 0.007533 cm^{-1}.

Spectrum_File_Name	Year	Day	Hour	Lat	Long	Alt	SZA
pa20050308saaaaa.120_125	2005	67	16.820	45.945	-90.27	0.44	53.4
pa20090312saaaaa.056_096	2009	71	19.059	45.945	-90.27	0.44	49.4
pa20041222saaaaa.019_020	2004	357	14.695	45.945	-90.27	0.44	82.6
pa20040721saaaaa.104_111	2004	203	22.623	45.945	-90.27	0.44	60.1
pa20040721saaaaa.176_179	2004	203	24.826	45.945	-90.27	0.44	82.5
db20070629seccaa.008_009	2007	180	-2.095	-12.425	130.89	0.03	87.1
db20070417seccaa.206_207	2007	107	8.913	-12.425	130.89	0.03	87.1

Five Park Falls spectra (pa) were fitted. The driest was measured in March 2009 under cold, dry surface conditions (-12C, 43%RH) at SZA=49°, with a measured H_2O slant column of 6E+21 molec./cm^{-2}. Two Darwin spectra were fitted (db), both measured at 87.1° SZA in 2007. In the wetter (30C; 66%RH) Darwin spectrum, we measured a H_2O slant column of 3E+24 molec./cm^{-2}. Thus the atmospheric H_2O slant columns in these seven spectra span a factor 500. This allows meaningful evaluation of the weak H_2O lines (using the high-airmass Darwin spectra) and the strong H_2O lines (using the cold, dry, low-airmass Park Falls spectra). Note that really dry spectra are only seen under cold conditions, and wet spectra under warm conditions. So the strong lines are only seen (i.e., unsaturated) under cold conditions. And the weak lines under warm conditions.

New Linelist.

The new H_2O linelist, denoted "16MiKaMo", is described by:

S.N.Mikhailenko, S.Kassi, D.Mondelain, R.R.Gamache, A.Campargue, A spectroscopic database for water vapor between 5850 and 8340 cm-1, Journal of Quantitative Spectroscopy & Radiative Transfer 179 (2016).

It contains 44,854 H_2O lines covering 5850-8340 cm^{-1}, as compared with 35,824 H_2O lines from HITRAN. The extra lines are generally very weak HDO.

Before fitting any atmospheric spectra, we identified matching lines between the two linelists, based on the quantum numbers, line frequencies, intensities, and E". Over 32,600 good matches were found to the 35824 HITRAN2012 lines. Figure 0 compares the attributes of these matching lines. The top-left panel shows the 16MiKAMo intensities plotted versus frequency. Over this interval, the strongest lines vary by 5 orders of magnitude in intensity.

The top right panel shows that frequency differences of up to 1 cm^{-1} exist between the HITRAN 2012 and 16MiKaMo linelists. Intensity changes of up to an order of magnitude are found. There seems to be several hundred lines for which the $\log_{10}$ of "Stren2" exceeds than of "Stren1" by 0.6, implying that in the new 16MiKaMo linelist these lines are a factor $10^{0.6}$ = 4 times stronger than in HITRAN2012. This population includes lines that are up to 10^{-21} in intensity.

Especially at high wavenumbers (red) the air-broadened widths (ABHW) in the new linelist are largely identical to those in HITRAN2012. At lower wavenumbers, however, there are some large differences, with the new widths being generally larger than this in HIYTAN2012.

HITRAN2012 had a large number of pressure shifts (PShift1) that were zero of close to zero (see lower right panel). This is not the case with the new linelist.

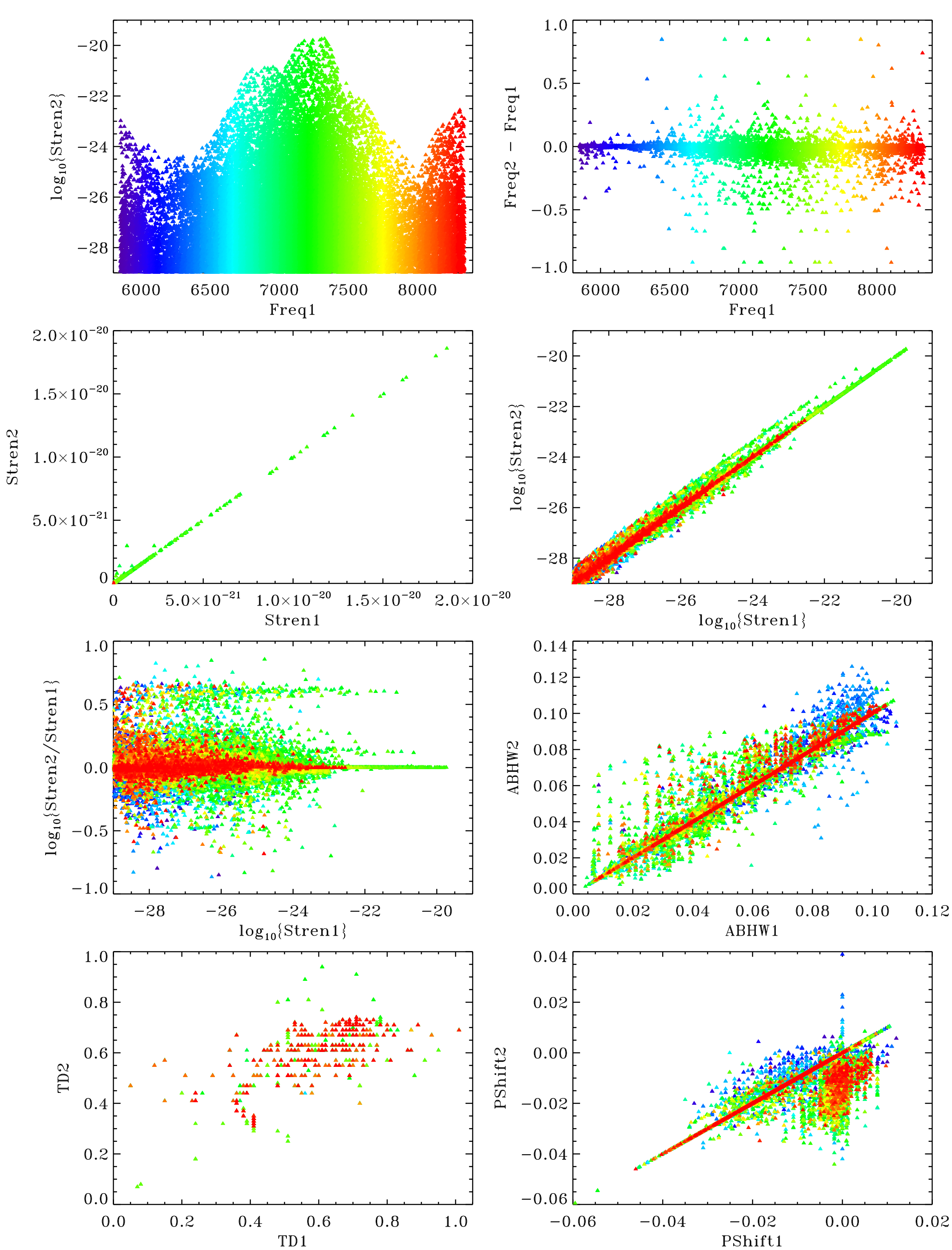

Figure 0. Direct comparison of various spectroscopic parameters of the 32,650 matching lines. The "1" suffix represents HITRAN2012, and the "2" suffix 16MiKaMo. Points are color-coded by wavenumber, as shown in top panels. Freq represent the line position, Stren the intensity, ABHW the Air-Broadened Half-Width, TD is its Temperature Dependence, and PShift the Pressure Shift.

Fits to Atmospheric Spectra

91 windows were defined contiguously covering the 5850 - 8340 cm^{-1} region. Their wavenumbers, width, and fitted parameters are listed in appendix A. In each spectral fit, the retrieved H_2O amount was saved, along with the rms fitting residual.

Four linelists were employed. In addition to HITRAN2012 and 16MiKaMO, we also used the HITRAN 2008 and ATM 16 linelists. The latter is a "greatest hits" compilation based mainly on HITRAN, but not necessarily HITRAN2012. In regions where earlier HITRAN versions gave better fits, these lines were retained. In the 5800 to 6200 cm^{-1} region, the CH_4 is based on Frankenberg et al., 2008. In regions where spectral fits revealed obvious errors in the ATM16 linelist, these were empirically corrected using fits to lab spectra. The ATM16 linelist is used by TCCON and others.

Note that an unambigous H_2O comparison can be made only between HITRAN2012 and 16MiKAMO. The other two linelists are included only for context since other gases are different (e.g., CO_2, and CH_4), besides H_2O.

With seven spectra, four linelists, and 91 windows, a total of 2500+ spectral fits were performed. It is not possible to show all these spectral fits in a brief report, so we first plotted the overall rms spectral fitting residual for each window. We also plotted the retrieved H_2O column amounts, relative to the mean of all windows, for each linelist. This allowed us to identify regions where the new linelist was under-performing relative to the others. We then plotted the spectral fits for these regions only.

The rms residual is not only influenced by spectroscopic errors, but also by instrumental noise and artifacts, and uncertainties in the assumed atmospheric conditions (temperature, pressure and vmr profiles). Since all linelists were analyzed using the same spectra and atmospheric conditions, the **changes** to the residuals are entirely attributable to spectroscopy.

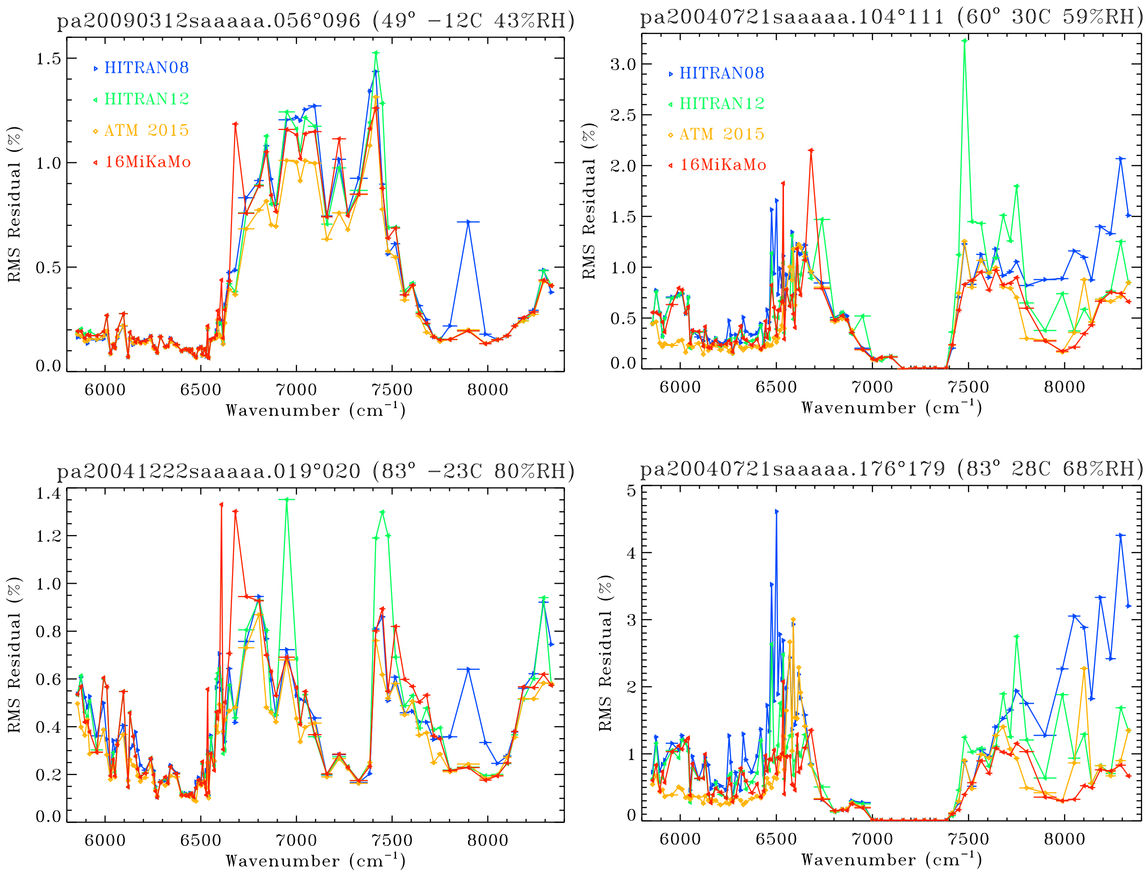

Figure 1. RMS residuals obtained by fitting four Park Falls spectra. Left panels show results from fitting dry winter spectra. Right panels show results from fitting humid summer spectra. Four different linelists are compared. In the humid spectra (right), the 6700 to 7400 cm^{-1} cm^{-1} region is mostly blacked out, hence the small residuals in the right-hand panels.

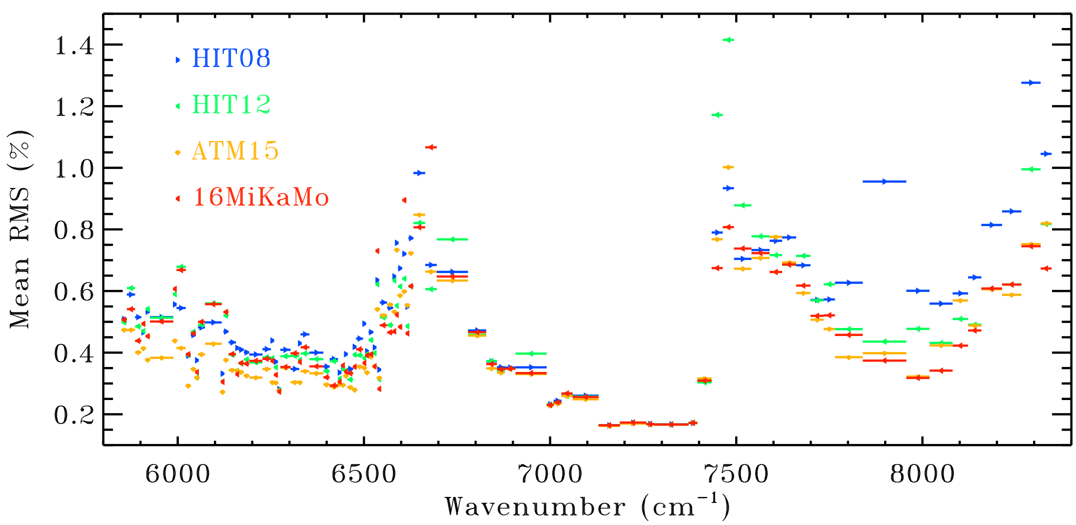

Figure 2. RMS residuals averaged over the 7 atmospheric spectra.

Figure 2 shows that the ATM16 linelist consistently produces the best residuals below 6500 cm^{-1}, although it is not clear whether this is due to improved H_2O, CO_2, or CH_4 spectroscopy. Between 6450 and 7750 cm^{-1} HIT2012 produces the worst residuals in most windows, even worse than HIT08. The 16MiKaDo linelist produces the worst residuals in several windows, including 6140, 6530, 6600, 6670 cm^{-1}. On the other hand, above 7850 cm^{-1}, 16MiKaMo is consistently the best.

Window-to-Window Consistency of Retrieved H_2O amounts

In addition to examining the rms fitting residuals, we also looked at the retrieved H_2O amounts. Even in windows that produce good fits, the retrieved H_2O amounts can be in error, especially if the H_2O lines are weak.

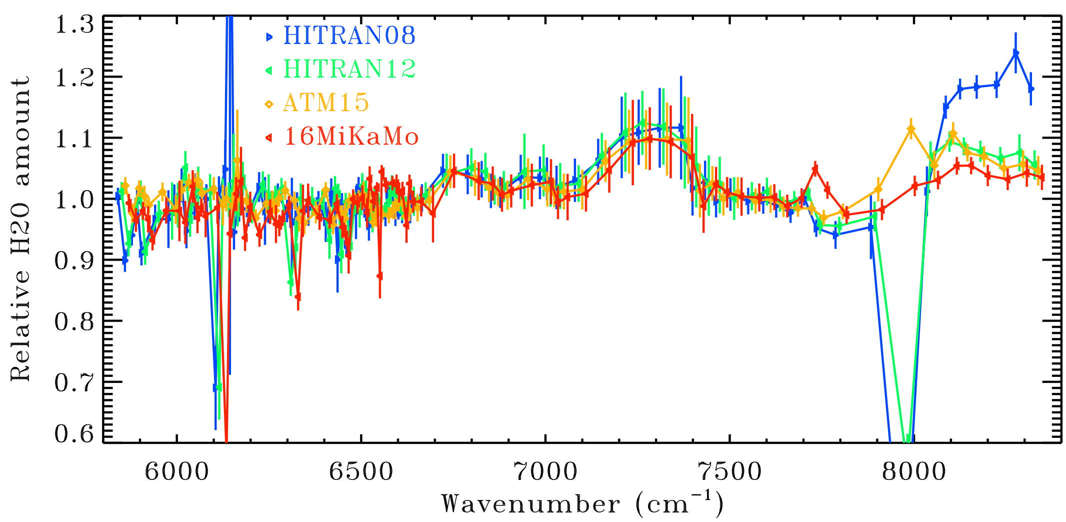

Figure 3. Retrieved H_2O column amounts from each window, divided by the mean of all windows, for four different linelists. If the linelist were perfect, these values should all be 1.0. Deviations from 1 imply window-to-window spectroscopic biases.

Figure 3c shows that around 6130 cm^{-1}, there is a large inconsistency in the H_2O retrieved by the 16MiKaMo linelist. This is also a window in which the 16MiKaMo linelist produces worse residuals than the other three linelists.

To investigate why, we plotted in Figure 4 spectral fits to this particular region. In each panel, the black diamonds show the measured spectrum and the black line the fitted calculation. The colored lines are the contributions of the various fitted gases to the calculated transmittance. At the top of each panel are the residuals (Measured - Calculated). These fits show that the main reason for the poor performance of the 16MiKaMo linelist in this region is that the water widths are under-estimated, especially the three lines between 6119 and 6126 cm^{-1}. This not only degrades the rms residuals but also low-biases the retrieved H_2O column amount.

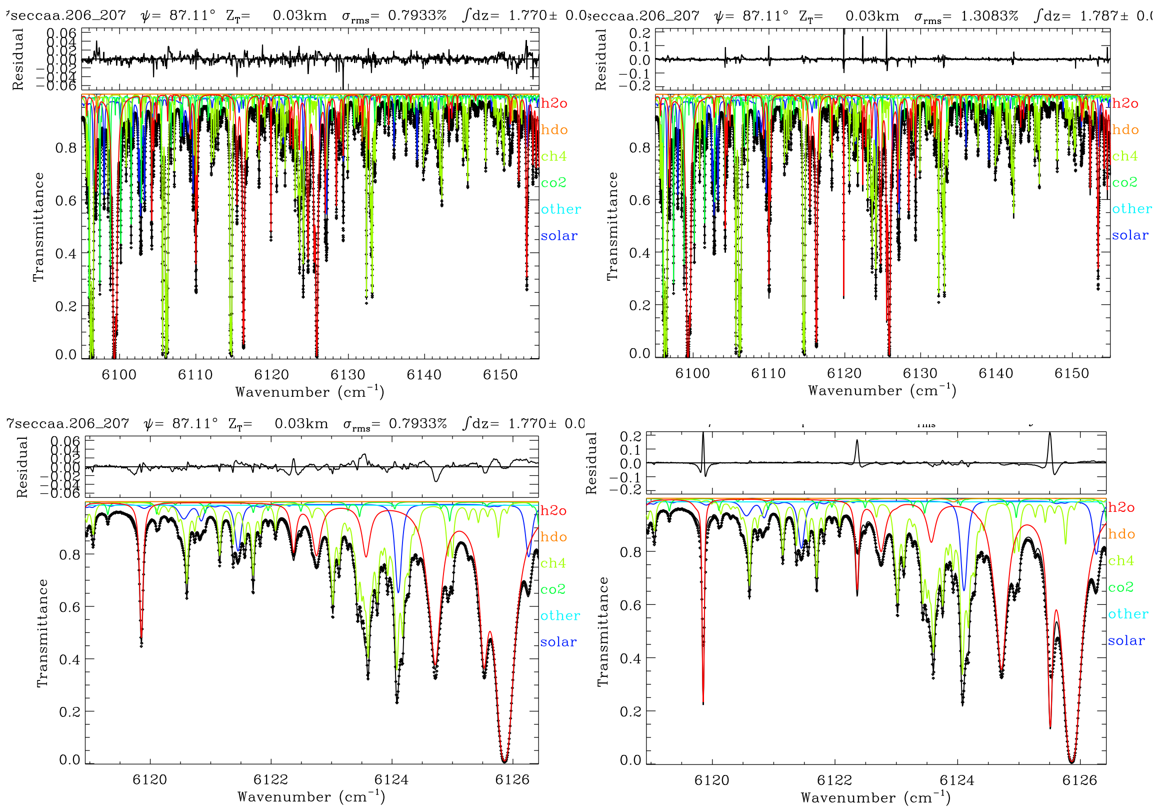

Figure 4. Spectral fits to the high-H_2O Darwin spectrum using the HITRAN2012 linelist (left panels) and the new 16MiKaMo H_2O linelist (right panels). Note the factor 3 scale change in the residual panels. The lower panels zoom into the 6119-6126 cm^{-1} region containing three H_2O lines, whose widths seem considerably under-estimated in the 16MiKaMo linelist (causing large residuals).

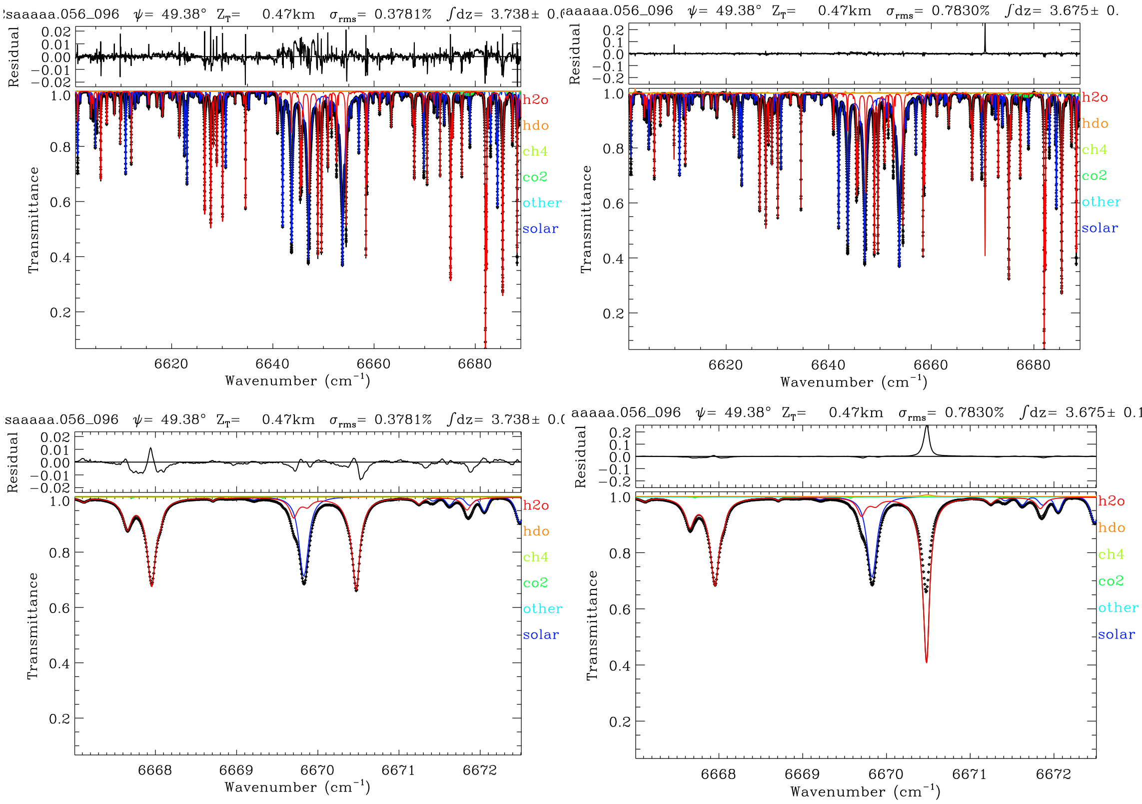

Figure 5. Spectral fits to the low-H_2O Park Falls spectrum using the HITRAN2012 linelist (left panels) and the new 16MiKaMo H_2O linelist (right panels). Note the factor 11 scale change of the residual panels. The lower panels zoom into the 6670.48 cm^{-1} H_2O line, whose intensity seems overestimated by a factor ~2 in the new 16MiKaMO linelist. This single bad line causes the rms residual at 6670 cm^{-1} in Fig. 2 to be much worse for the 16MiKaMO linelist than the others.

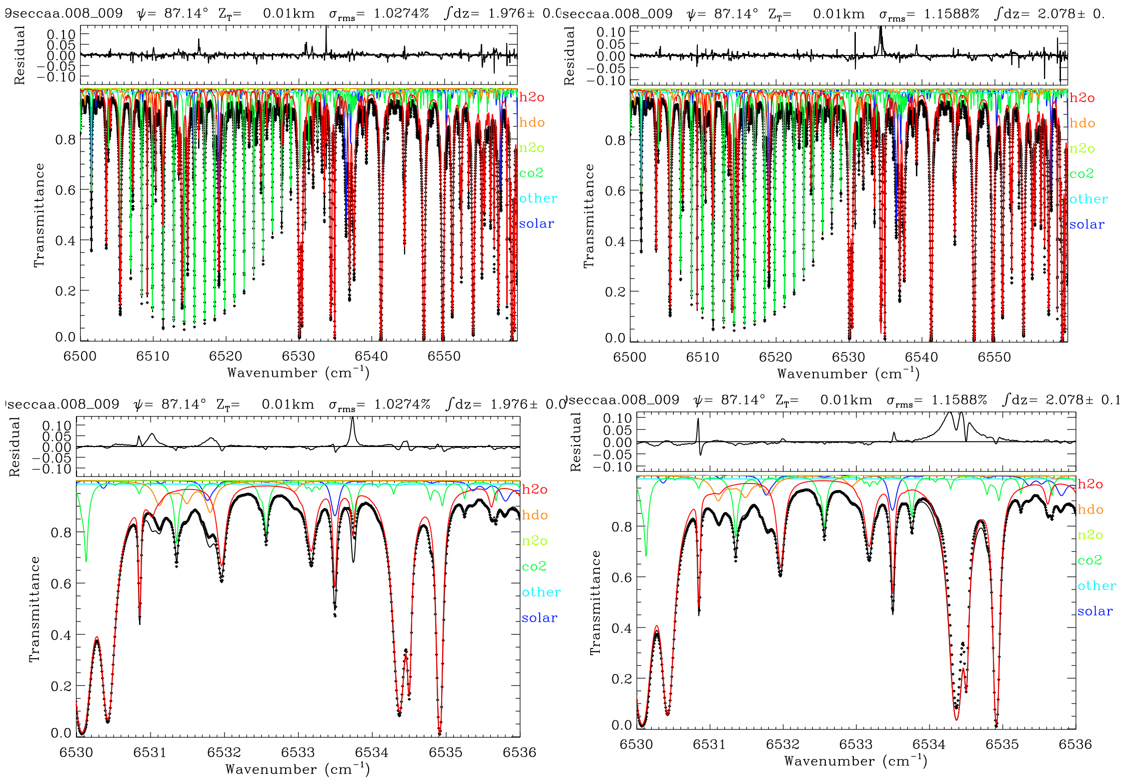

Figure 6. Spectral fits to the medium-H_2O Darwin spectrum using the HITRAN2012 linelist (left panels) and the new 16MiKaMo H_2O linelist (right panels). The lower panels zoom into the 6530-6536 cm^{-1} region that contains the largest residuals. HITRAN2012 contains a spurious H_2O line 6533.7 cm^{-1} which causes at 15% residual. This line is not present in the 16MiKaMo linelist. Unfortunately the 16MiKaMo linelist has two new problems: a possible pressure shift error at 6530.86 cm^{-1} and an overestimated H_2O line intensity around 6534.3 cm^{-1}. The net result is that the new 16MiKaMo linelist produces worse fits in terms of rms, although clearly a combination of the two linelists would do much better than either.

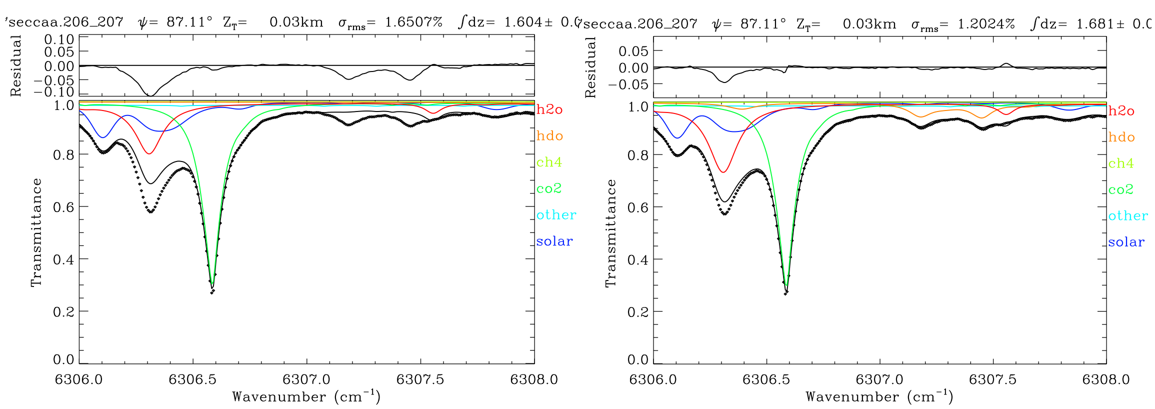

Figure 7. Spectral fits to the high-H_2O Darwin spectrum using the HITRAN2012 linelist (left panel) and the new 16MiKaMo H_2O linelist (right panel). The improvement in the 16MiKaMo linelist residuals is due to the addition of three HDO lines, as shown in Fig 10 of the 16MiKaMo paper.

Summary.

The atmospheric spectrum with the largest slant column, 3e+24 molec./cm^{-2}, has a SNR of ~600 (the lower SZA spectra are averages having much larger SNRs). So at 1 atm pressure the weakest observable H_2O line is ~5E-29. Most of the new lines in 16MiKaMo linelist, not present in HITRAN 2012, are weaker than this limit, and therefore cannot be evaluated using these spectra.

Above 7500 cm^{-1}, the new 16MiKaMo linelist is clearly superior to any others, but at lower wavenumbers it is a mixed bag. In some regions the new 16MiKaMo linelist fixes problems present in HITRAN (e.g. Fig.7), but in other regions new problems are introduced (e.g. figs 4, 5, 6). If these new problems were corrected, spectral fits would be significantly improved.

All linelists appear to have too-small line intensities in the 7100-7450 cm^{-1} region, leading to the retrieved H_2O to be over-estimated by ~10% (see fig. 3). Since this region contains the strongest H_2O lines, this hints at a possible weak/strong inconsistency in the H_2O line intensities.

Appendix A. Details of fitted windows.

5855.95	14.70	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	
5874.33	22.05	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	
5893.73	16.75	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	
5907.60	11.00	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	
5919.20	12.20	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	
5956.65	62.70	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	
5992.20	8.40	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	
6008.95	25.10	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6028.27	13.55	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6041.95	13.80	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6051.48	5.25	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6063.63	19.05	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6095.58	44.85	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6120.27	4.55	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6129.52	13.95	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6146.40	19.80	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6159.65	6.70	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6170.25	14.50	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6184.75	14.50	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	
6209.75	35.50	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6238.85	22.70	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6254.00	7.60	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6263.50	11.40	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo	ch4	co2
6272.35	6.30	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6289.20	27.40	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6314.50	23.20	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6327.925	3.66	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6341.73	23.95	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6372.35	37.30	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6399.55	17.10	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6419.25	22.30	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		
6434.75	8.70	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		
6443.73	9.25	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6451.75	6.80	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2
6463.22	16.15	15	1	1	1	ncbf=4	fs	sg	xf	xo	:	H2O	hdo		co2

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8332.15  29.50  15 1 1 1      ncbf=5  fs  sg  xf  xo  :  H2O hdo
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