Improved CH_3OH spectroscopy: Development of a Pseudo-Linelist

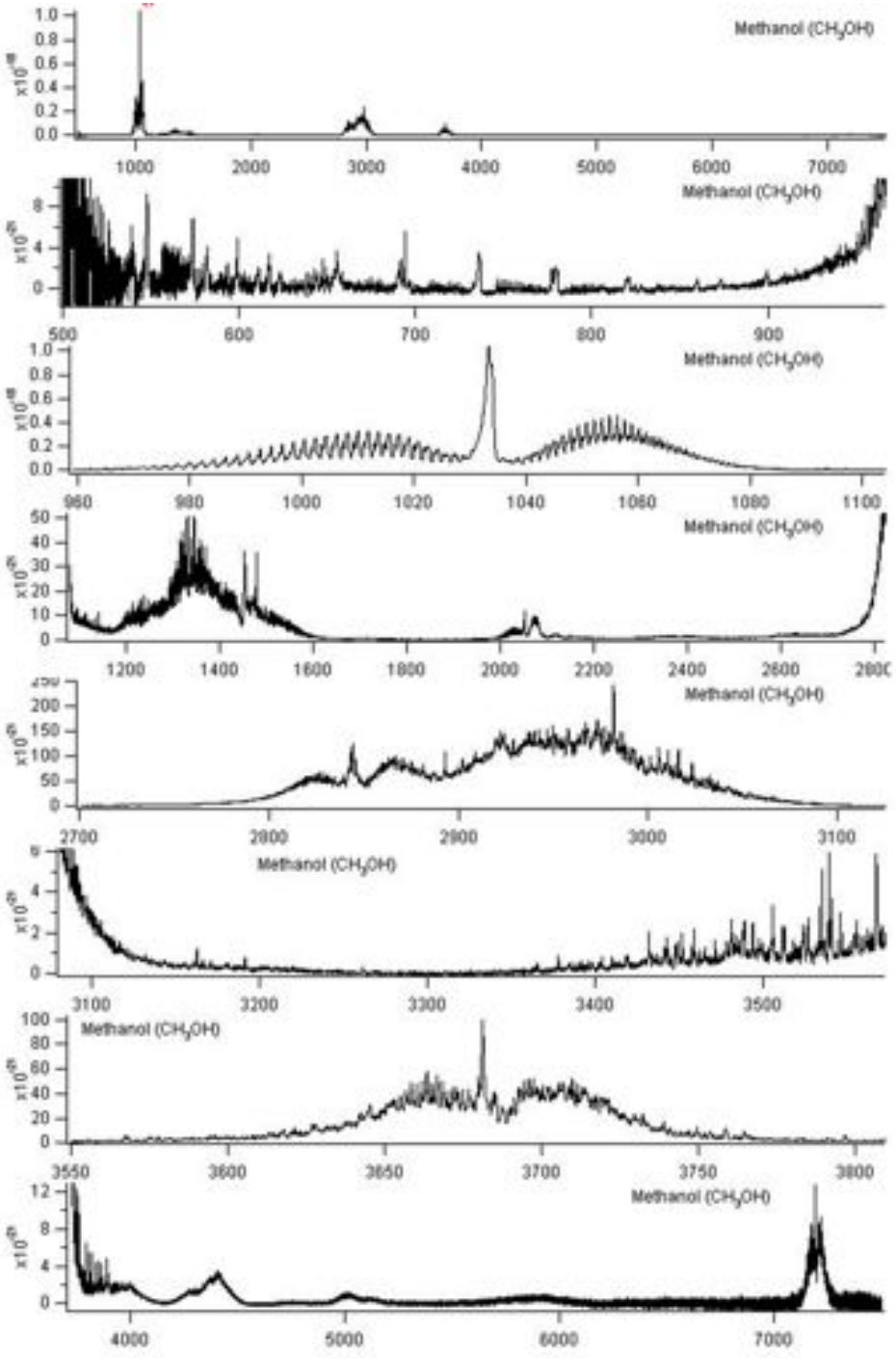
Geoffrey Toon
Jet Propulsion Laboratory
California Institute of Technology

Methanol (CH_3OH) is the second most abundant organic gas (after CH_4) and one of the most abundant atmospheric Volatile Organic Compounds (VOCs). Emitted from the surface, VOCs are precursors of tropospheric ozone and therefore have an important role in controlling the oxidizing capacity of the atmosphere.

Satellite measurements of atmospheric CH_3OH have been made by ACE, TES, and IASI in biomass burning plumes. Also by ground-based FTS measurements.

Under background conditions, remote sensing of methanol is difficult.

A major impediment to remote sensing of methanol is the spectroscopy.



PNNL CH_3OH

ν_1 O-H stretch 3681 cm^{-1}

ν_2 C-H perpendicular asymmetric stretch (A') 2999 cm^{-1}

ν_3 C-H parallel symmetric stretch (A') 2844 cm^{-1}

ν_4 C-H in-plane asymmetric bend 1477 cm^{-1}

ν_5 C-H in-plane symmetric bend 1454 cm^{-1}

ν_6 O-H bend (A') 1340 cm^{-1}

ν_7 CH_3 rock (A') 1074 cm^{-1}

ν_8 C-O stretch (A') 1033 cm^{-1}

ν_9 C-H perpendicular asymmetric stretch (A") 2970 cm^{-1}

ν_{10} C-H out of plane asymmetric bend 1465 cm^{-1}

ν_{11} CH_3 rock (A") 1145 cm^{-1}

ν_{12} torsion 270 cm^{-1}

Current CH_3OH Spectroscopy

HITRAN CH_3OH linelist, based on Xu et al. 2004, covers 911-1407 cm^{-1}, containing the strong C-O stretch absorption band at 1033 cm^{-1}.

Although this is the strongest absorption band, it is mostly obscured by O_3 absorption when remote sensing the Earth's atmosphere, especially limb viewing.

The C-H stretch absorption bands around 3000 cm^{-1} only 5x weaker, and better suited for solar absorption spectrometry, but completely missing from HITRAN.

Harrison et al. [2012] measured CH_3OH lab spectra in both LWIR & SWIR regions.

Fitting Harrison's data using the HITRAN 2012 CH_3OH linelist reveals serious discrepancies in the 1000-1100 cm^{-1} region:

- Some missing lines (or under-estimated intensities)
- A warm/cold inconsistency

Additionally, all HITRAN CH_3OH lines in the 1185-1407 cm^{-1} region have the same intensity (1.0E-26), which doesn't seem right.

Xu et al., 2004 - Abstract

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Spectroscopy 228 (2004) 453–470
ELSEVIER
Journal of MOLECULAR SPECTROSCOPY
www.elsevier.com/locate/jms

New assignments, line intensities, and HITRAN database for CH_3OH at 10 μm☆

Li-Hong Xu,[a,*] R.M. Lees,[a] Peng Wang,[a] L.R. Brown,[b] I. Kleiner,[c] and J.W.C. Johns[d]

[a] *Department of Physical Sciences, University of New Brunswick, Saint John, NB, Canada E2L 4L5*
[b] *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109, USA*
[c] *Laboratoire de Physique Moléculaire et Applications, Université Paris Sud, Batiment 350, 91405, Orsay Cedex, France*
[d] *Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ont., Canada K1A 0R6*

Received 24 February 2004; in revised form 24 May 2004
Available online 3 July 2004

Abstract

The Fourier transform spectrum of CH_3OH in the 10 μm region has been re-examined at higher pressure and path length than heretofore, as part of a program to provide comprehensive CH_3OH spectral data for astrophysical and atmospheric applications. With the increase in spectral sensitivity, it has been possible to assign new torsionally excited $v_{12} = 1$ and $v_{12} = 2$ subbands plus further high-K, $v_{12} = 0$ subbands of the ν_8 CO-stretching band. Upper-state term values have been determined, and have been fitted to $J(J+1)$ power-series expansions in order to obtain the excited ν_8 substate origins. A variety of weaker subbands from other modes has also been identified in the 10 μm spectrum including $v_{12} = 0$, $v_{12} = 1$, and $v_{12} = 0 \leftarrow 1$ torsional subbands of the ν_7 in-plane CH_3 rock, $v_{12} = 0 \leftarrow 1$ and $v_{12} = 0 \leftarrow 2$ torsional combination subbands of the ν_6 OH bend, and $v_{12} = 0 \leftarrow 2$ subbands of the ν_5 symmetric CH_3 bend. Line intensities have been retrieved line-by-line from the spectra. A large set of "unperturbed" ν_8 transitions has been modeled using the same type of multi-parameter effective Hamiltonian employed successfully for the ground state, with inclusion of the intensities of a subset of the stronger ν_8 spectral lines in the fitting in order to obtain appropriate transition dipole terms. Together, a 10 μm methanol database in HITRAN format has been generated.

Incorporated into HITRAN 2004 covering 911 to 1407 cm^{-1}. Minor tweaks in HITRAN 2008.

Journal of Quantitative Spectroscopy & Radiative Transfer 113 (2012) 2189–2196

Contents lists available at SciVerse ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Infrared absorption cross sections for methanol

Jeremy J. Harrison *, Nicholas D.C. Allen, Peter F. Bernath [1]

Department of Chemistry, University of York, Heslington, York YO10 5DD, United Kingdom

ARTICLE INFO

Article history:
Received 21 February 2012
Received in revised form
18 July 2012
Accepted 19 July 2012
Available online 27 July 2012

Keywords:
Methanol
High-resolution Fourier transform spectroscopy
Infrared absorption cross sections
Remote-sensing
Atmospheric chemistry

ABSTRACT

Infrared absorption cross sections for methanol, CH_3OH, have been determined near 3.4 and 10 μm from spectra recorded using a high-resolution FTIR spectrometer (Bruker IFS 125HR) and a multipass cell with a maximum optical path length of 19.3 m. Methanol/dry synthetic air mixtures were prepared and spectra were recorded at 0.015 cm^{-1} resolution (calculated as 0.9/MOPD) at a number of temperatures and pressures (50–760 Torr and 204–296 K) appropriate for atmospheric conditions. Intensities were calibrated using composite methanol spectra taken from the Pacific Northwest National Laboratory (PNNL) IR database. The new measurements in the 10 μm region indicate problems with the existing methanol spectroscopic line parameters in the HITRAN database, which will impact the accuracy of satellite retrievals.

Harrison et al. 2012 – Figure 1

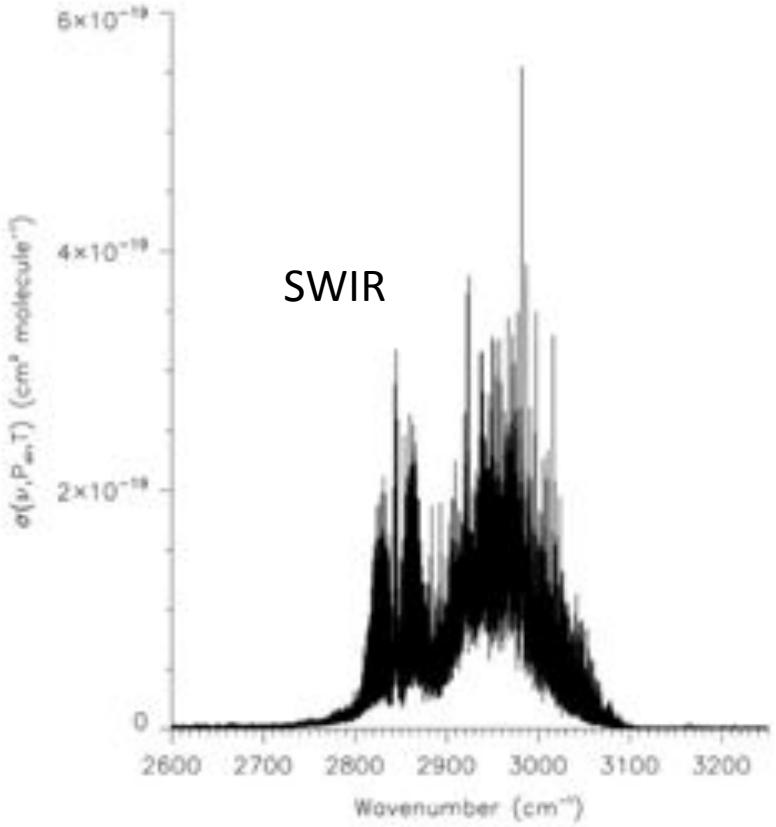


Fig. 1. Methanol absorption cross section near 3.4 μm at 204.5 K and 50.92 Torr.

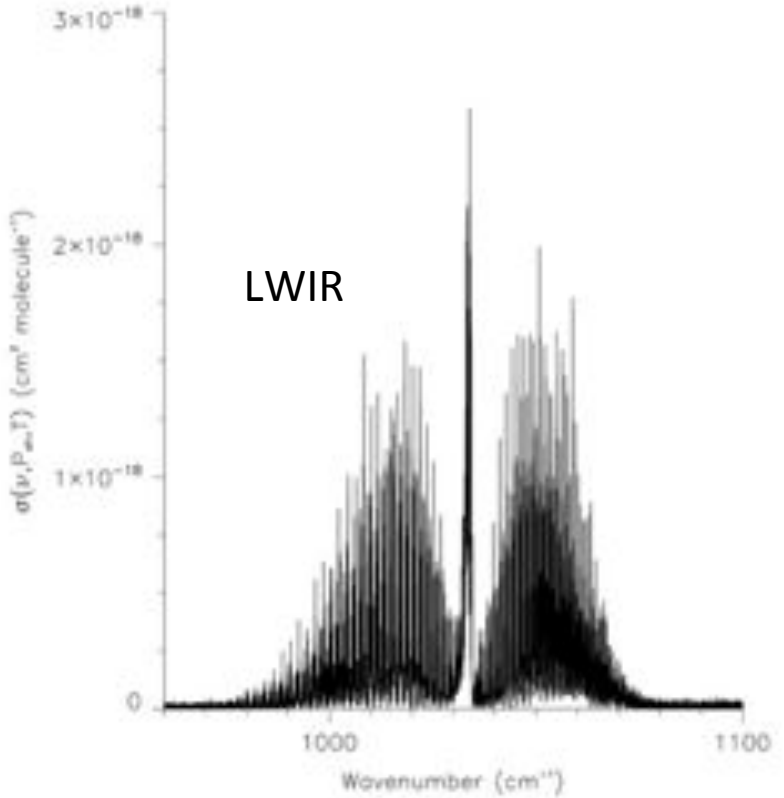


Fig. 2. Methanol absorption cross section near 10 μm at 204.0 K at 50.17 Torr.

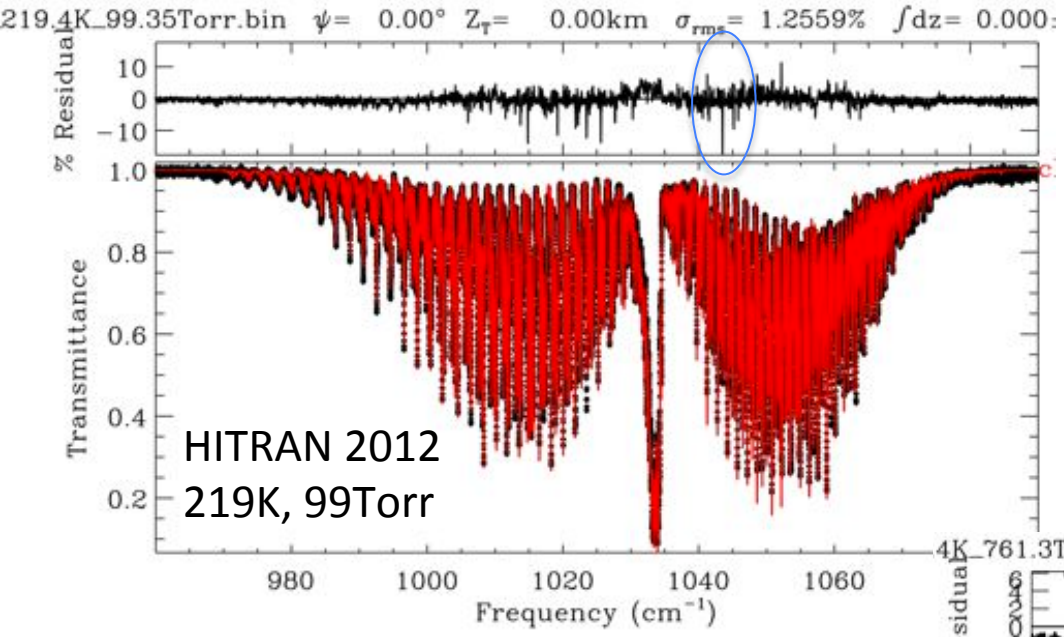
Peak cross-sections: SWIR = 0.55E-18; LWIR = 2.6E-18

Table 2
Summary of the sample conditions for all scans.

	Temperature (K)	Initial methanol pressure (Torr)[a]	Total pressure (Torr)	Pathlength[b] (m)	No. of scans[c]
SWIR (3.4 μm)	204.5 ± 0.7	0.0137	50.92 ± 0.10	19.31	320
	204.3 ± 0.4	0.0137	75.82 ± 0.10	19.31	322
	204.4 ± 0.4	0.0137	101.62 ± 0.10	19.31	380
	214.2 ± 0.9	0.0531	50.52 ± 0.10	19.31	300
	214.2 ± 0.8	0.0562	102.67 ± 0.15	19.31	286
	214.3 ± 0.9	0.0560	260.0 ± 0.4	19.31	244
	248.1 ± 1.0	0.4924	205.3 ± 0.3	3.31	300
	247.8 ± 1.0	0.5080	402.5 ± 0.5	3.31	300
	247.8 ± 1.0	0.5051	600.3 ± 0.6	3.31	300
	272.1 ± 0.6	0.5001	369.6 ± 0.4	3.31	400
	272.3 ± 0.7	0.5169	600.1 ± 0.6	3.31	400
	296.0 ± 0.2	0.8210	760.8 ± 0.2	1.71	350
LWIR (10 μm)	204.0 ± 0.8	0.0107	50.17 ± 0.10	19.31	200
	203.9 ± 0.8	0.0107	74.97 ± 0.10	19.31	300
	203.9 ± 0.9	0.0107	98.54 ± 0.15	19.31	300
	219.2 ± 1.1	0.0166	49.95 ± 0.10	19.31	300
	219.4 ± 1.2	0.0166	99.35 ± 0.15	19.31	300
	219.5 ± 1.0	0.0130	249.2 ± 0.8	19.31	280
	249.0 ± 0.6	0.1881	201.7 ± 0.2	1.71	400
	249.4 ± 0.7	0.1864	400.7 ± 0.5	1.71	300
	249.2 ± 0.7	0.1924	604.4 ± 0.6	1.71	300
	273.1 ± 1.0	0.2392	369.7 ± 0.4	1.71	300
	272.9 ± 0.9	0.2293	599.7 ± 0.8	1.71	300
	295.4 ± 0.2	0.2872	761.3 ± 0.2	1.71	300

[a] MKS-690A Baratron readings are accurate to ± 0.05%.
[b] The error in the optical pathlength is estimated to be ± 0.2% at room temperature.
[c] Note that each sample requires the measurement of a similar number of background scans taken with the same spectrometer settings. One scan takes about 33 s.

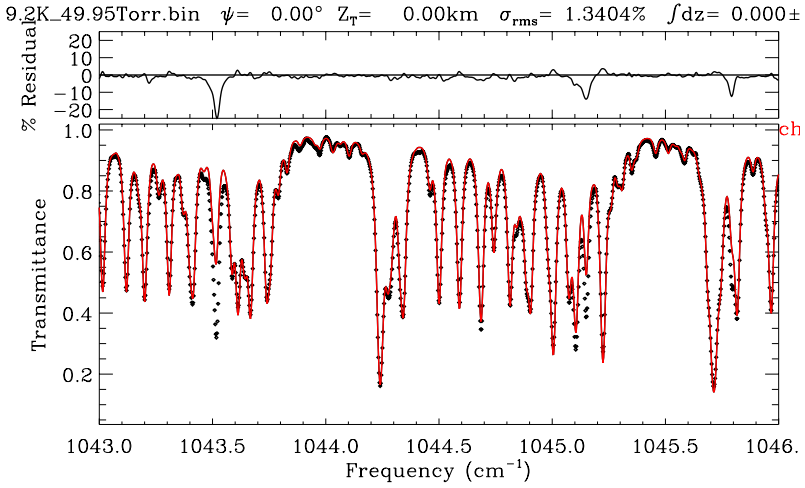
LWIR HITRAN_2012 Spectral Fits



Fitted Harrison's spectra using HITRAN 2012 linelist.

Spectral fits are poor with several strong missing lines.

Even worse, T-dependence is wrong.



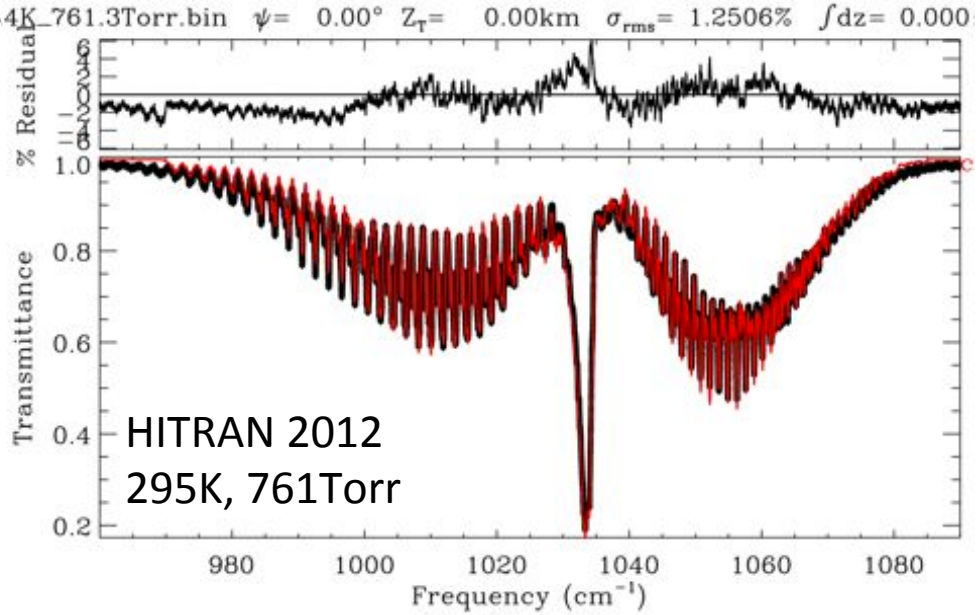


Figure from Harrison et al. 2012

Strong similarity to figure on previous page, after taking account different wavenumber ranges

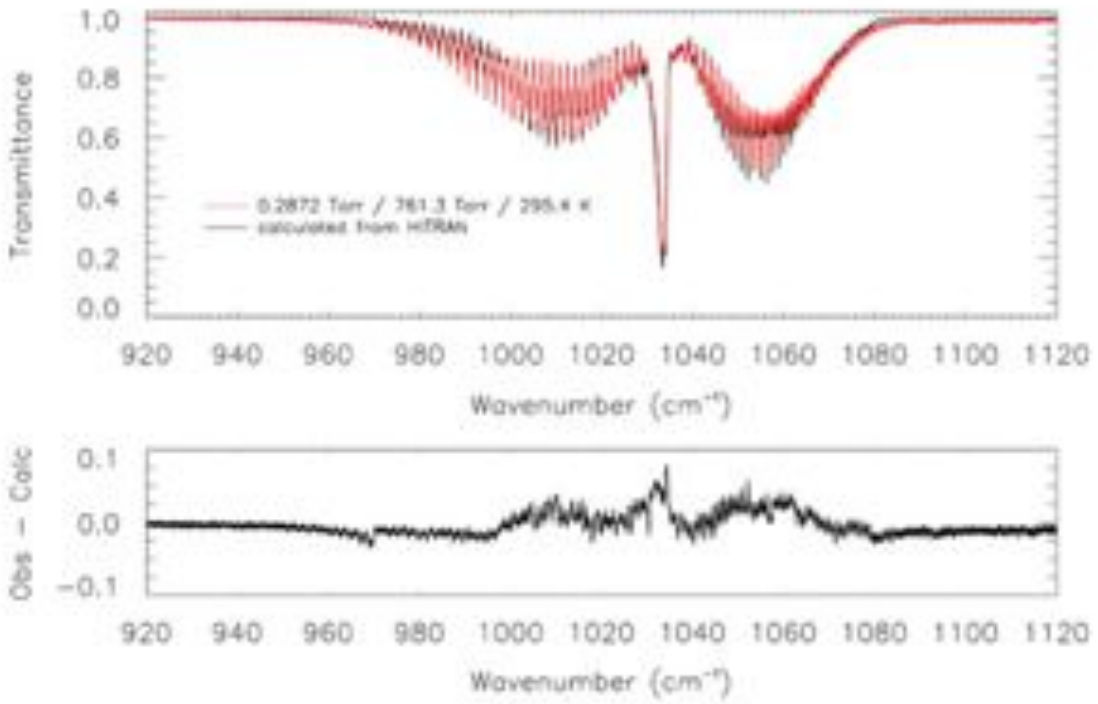


Fig. 4. Comparison between the air-broadened laboratory transmittance spectrum (10 μm) of methanol at 295.4 K (0.2872 Torr methanol, 761.3 Torr total pressure) with the corresponding synthetic spectrum calculated using the HITRAN linelist.

LWIR Result Summary: HITRAN 2012

Spectrum	RMS %	VSF	VSF_error
CH3OH_LWIR_203.9K_74.97Torr.bin	1.6432	1.2657	4.9E-02
CH3OH_LWIR_203.9K_98.54Torr.bin	1.6583	1.2623	5.0E-02
CH3OH_LWIR_204.0K_50.17Torr.bin	1.6325	1.2899	4.9E-02
CH3OH_LWIR_219.2K_49.95Torr.bin	1.3404	1.2346	4.0E-02
CH3OH_LWIR_219.4K_99.35Torr.bin	1.2559	1.2192	3.8E-02
CH3OH_LWIR_219.5K_249.2Torr.bin	1.0445	1.2082	3.1E-02
CH3OH_LWIR_249.0K_201.7Torr.bin	0.9499	1.0916	2.9E-02
CH3OH_LWIR_249.2K_604.4Torr.bin	0.8523	1.0981	2.6E-02
CH3OH_LWIR_249.4K_400.7Torr.bin	0.8635	1.0955	2.6E-02
CH3OH_LWIR_272.9K_599.7Torr.bin	0.9870	1.0277	3.0E-02
CH3OH_LWIR_273.1K_369.7Torr.bin	1.0650	1.0275	3.2E-02
CH3OH_LWIR_295.4K_761.3Torr.bin	1.2506	0.9753	3.8E-02

Average % RMS fit = 1.147

Average VSF = 1.12 +- 0.09

Used HITRAN linelist to fit Harrison's LWIR spectra. Average RMS spectral fit is 1.15% with peak residuals up to 30%. 25% discrepancy between CH_3OH amounts retrieved from warm (273K) and cold spectra (204K). Missing hot band? Partition function?

Figure 3 from Harrison et al. [2012]

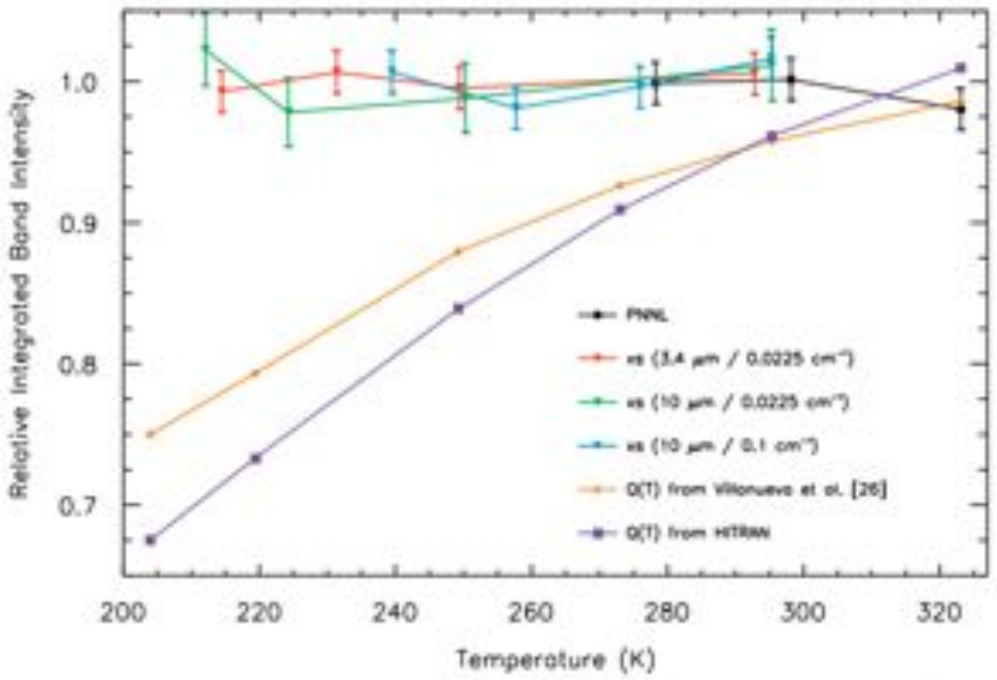


Fig. 3. Integrated band intensities for the three composite PNNL spectra (the average of those at 278 K and 298 K is given a value of one), compared with the relative band intensities for the low-resolution, pure measurements described in Section 4. Also plotted are relative band intensities from simulations using HITRAN line parameters in the 10 μm region; partition sums come from two sources: the HITRAN database file "parsum.dat" and the new data from Villanueva et al. [26].

Showing the discrepancy between the almost T-independent lab measurements and the HITRAN prediction.

Discrepancy reaches 25-30% at 205K

Interlude

Everything so far has been already discussed by Harrison et al. [2012]

Harrison's solution to the problem with HITRAN 2012 CH_3OH is to use his lab cross-sections in the forward model.

Nothing wrong with this provided atmospheric conditions fall within range of lab measurement (and lab measurements are free of artifacts/contamination).

But NDACC instruments have made measurements from sea-level at 235K. This is 60 K colder than the 760 Torr Harrison measurement, or 3 times the pressure of the 220K measurement. What to do?

Need a way of extrapolating Harrison's measurements in T/P that is better behaved than standard mathematical bi-variate interpolation/extrapolation.

This is a major motivation for developing a pseudo-linelist, since this will have physics-based P- and T-dependences, which are more likely to extrapolate well.

CH_3OH Pseudo-Line-List

Decided to develop an empirical Pseudo-Line-List (PLL) based on Harrison's lab measurements, to remedy the deficiencies in HITRAN:

- Large residuals in 1000-1100 cm^{-1} region
- T-dependent bias in retrieved CH_3OH amounts
- Missing C-H stretch absorption bands around 3000 cm^{-1}

Non-uniform line spacing adopted, with positions based on fits to low-total pressure (50 Torr) high resolution spectra.

- 6935 lines covering 900-1150 cm^{-1}
- 31690 lines covering 2725 to 3115 cm^{-1}

Intensities and E"s calculated from fits to ALL lab spectra.

Widths assumed to be 0.1 cm^{-1}/atm (ABHW) and 0.4 cm^{-1}/atm (SBHW).
Pressure shifts assumed to be -0.003 cm^{-1}/atm in LWIR, -0.005 cm^{-1}/atm in SWIR

LWIR Result Summary: PLL

Spectrum	RMS	VSF	VSF_error
CH3OH_LWIR_203.9K_74.97Torr.bin	1.0581	0.9751	3.2E-02
CH3OH_LWIR_203.9K_98.54Torr.bin	1.1265	0.9717	3.4E-02
CH3OH_LWIR_204.0K_50.17Torr.bin	0.9811	0.9971	2.9E-02
CH3OH_LWIR_219.2K_49.95Torr.bin	0.9639	1.0165	2.9E-02
CH3OH_LWIR_219.4K_99.35Torr.bin	0.7006	1.0023	2.1E-02
CH3OH_LWIR_219.5K_249.2Torr.bin	0.6424	0.9975	1.9E-02
CH3OH_LWIR_249.0K_201.7Torr.bin	0.3260	1.0045	9.8E-03
CH3OH_LWIR_249.2K_604.4Torr.bin	0.3051	1.0081	9.2E-03
CH3OH_LWIR_249.4K_400.7Torr.bin	0.3044	1.0075	9.1E-03
CH3OH_LWIR_272.9K_599.7Torr.bin	0.2528	1.0027	7.6E-03
CH3OH_LWIR_273.1K_369.7Torr.bin	0.2752	1.0031	8.3E-03
CH3OH_LWIR_295.4K_761.3Torr.bin	0.3442	0.9911	1.0E-02

Average % RMS fit = 0.444

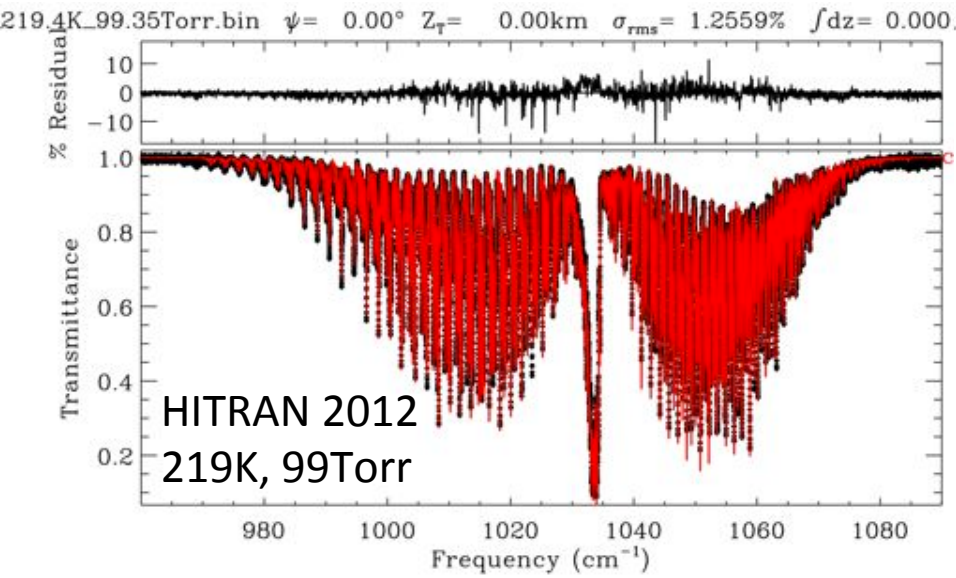
Average VSF = 1.002 +- 0.007

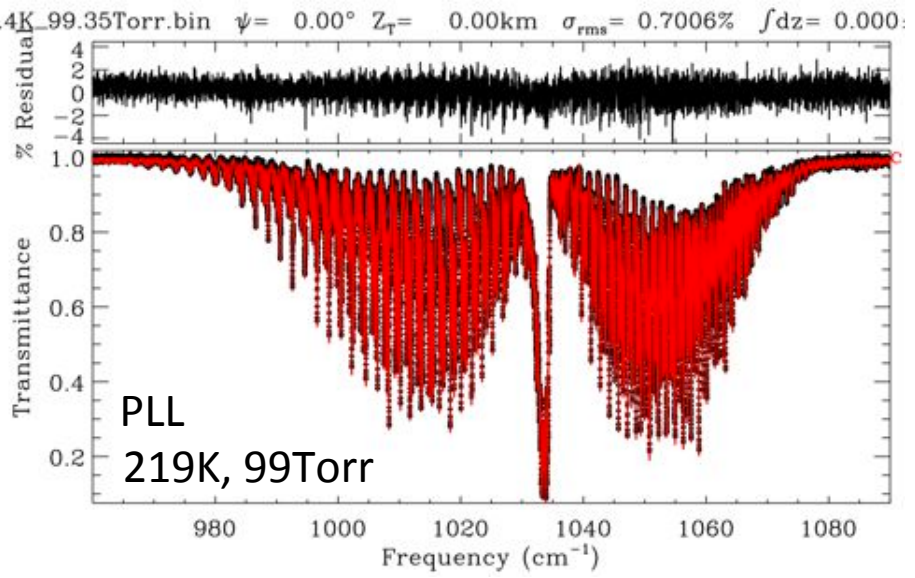
Used PLL to fit Harrison's LWIR spectra.

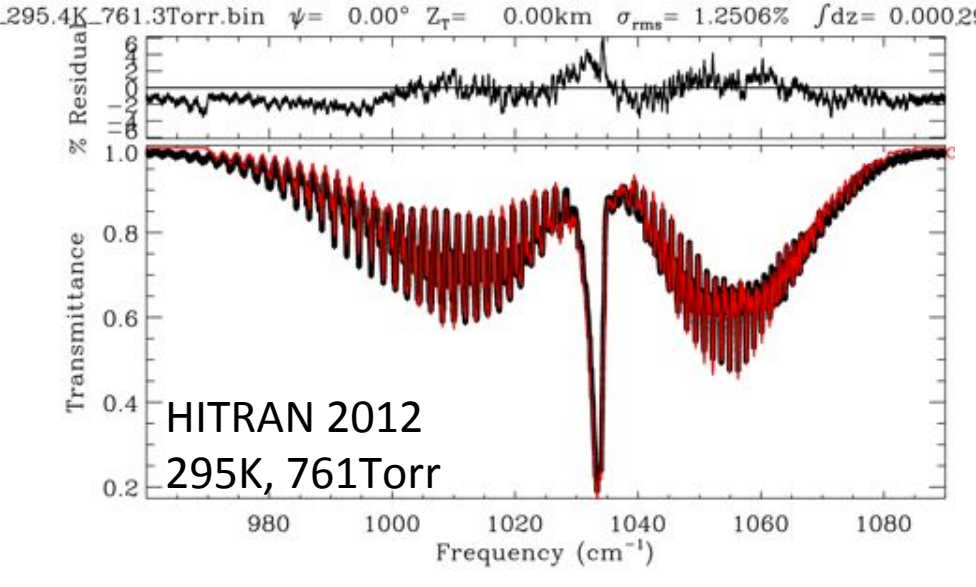
Average RMS spectral fit is 0.44% with peak residuals up to 6%.

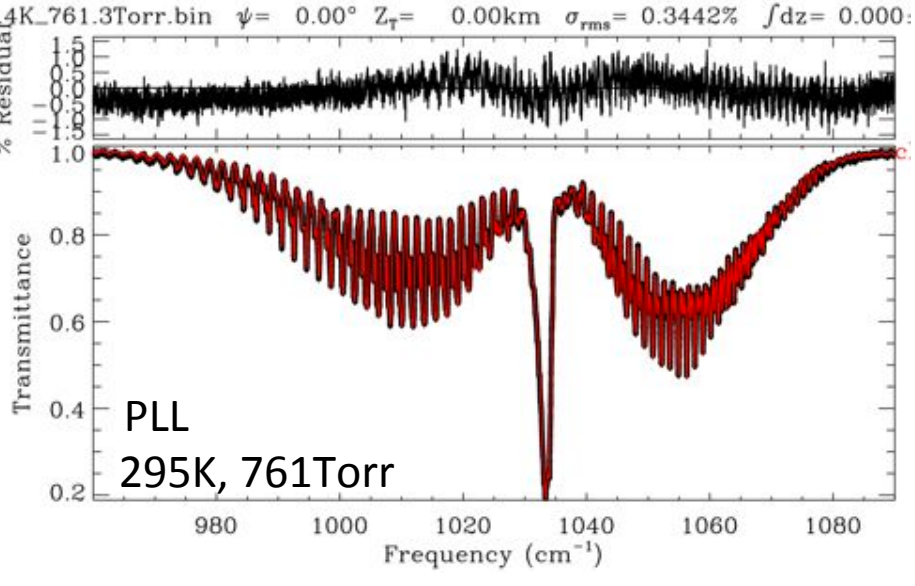
No discrepancy between CH_3OH amounts retrieved from warm & cold spectra.

LWIR HITRAN/PLL Spectral Fits - Examples









LWIR HITRAN/PLL Comparison

Spectral fits to Harrisons spectra are 4-5 times better using the PLL than those using HITRAN 2012, in terms of RMS spectral fit and peak residuals. Using HITRAN, absorption is under-estimated by a factor 2 at some wavenumbers.

Additionally, CH_3OH amounts retrieved using HITRAN 2012 have 12 times more spectrum-to-spectrum variation than those retrieved using the PLL, due to the poor match to the T-dependence.

This does not necessarily mean that the PLL is better than HITRAN. Since the PLL was derived from Harrison's spectra, it **should** fit them better. And any error in the assumed PF will be compensated by a bias to the E".

But if you consider Harrison's spectra to be correct, then using the PLL will reproduce their absorption cross-sections far better than HITRAN 2012.

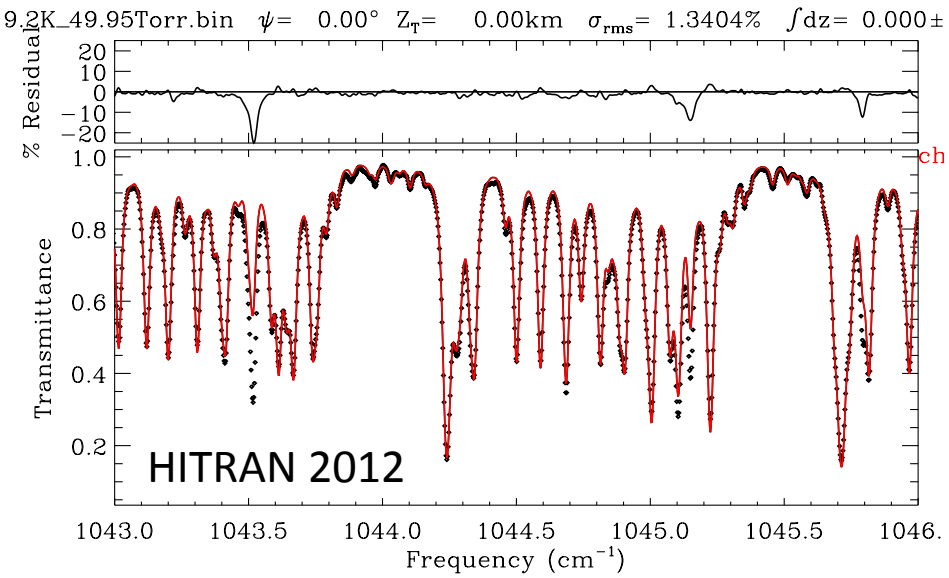
LWIR HITRAN/PLL Comparison

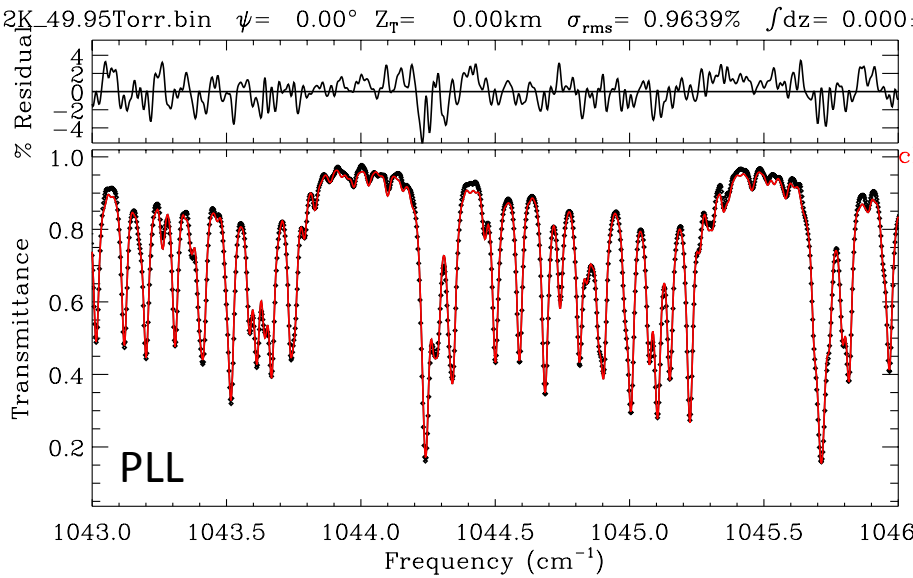
Examples of HITRAN under-estimating absorption (lower left).

How do we know that these dips in the residuals are due to CH_3OH and not other gases (e.g. H_2O) contaminating Harrison's lab measurements?

Have tried fitting H_2O and several other gases, but detected none, i.e. no correlation between dips in residuals and H_2O line positions.

Fits below to 219K, 50 Torr Harrison spectrum: Left=HITRAN; Right=PLL





SWIR CH_3OH Fitting Result Summary

Spectrum	RMS	VSF	VSF_error
CH3OH_SWIR_204.5K_50.92Torr.bin	0.1926	1.0112	5.8E-03
CH3OH_SWIR_204.3K_75.82Torr.bin	0.1474	1.0180	4.4E-03
CH3OH_SWIR_204.4K_101.62Torr.bin	0.1237	1.0204	3.7E-03
CH3OH_SWIR_214.2K_50.52Torr.bin	0.2509	1.0060	7.5E-03
CH3OH_SWIR_214.2K_102.67Torr.bin	0.1335	1.0048	4.0E-03
CH3OH_SWIR_214.3K_260.0Torr.bin	0.2272	0.9991	6.8E-03
CH3OH_SWIR_248.1K_205.3Torr.bin	0.2106	0.9923	6.3E-03
CH3OH_SWIR_247.8K_402.5Torr.bin	0.1002	0.9949	3.0E-03
CH3OH_SWIR_247.8K_600.3Torr.bin	0.1380	0.9930	4.1E-03
CH3OH_SWIR_272.1K_369.6Torr.bin	0.1152	1.0002	3.5E-03
CH3OH_SWIR_272.3K_600.1Torr.bin	0.0640	0.9998	1.9E-03
CH3OH_SWIR_296.0K_760.8Torr.bin	0.1143	1.0156	3.4E-03

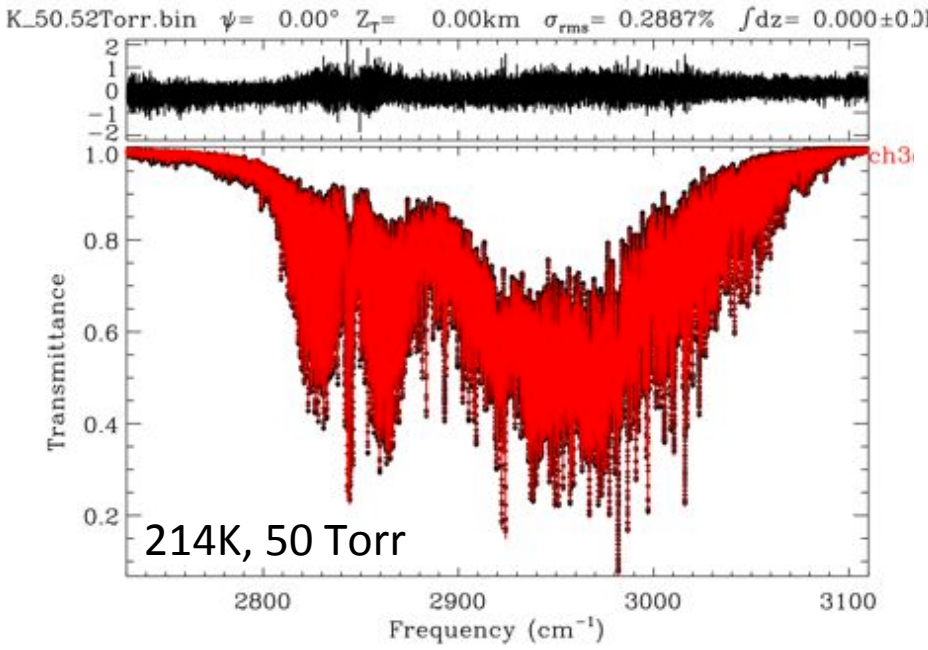
Average % RMS fit = 0.132 %

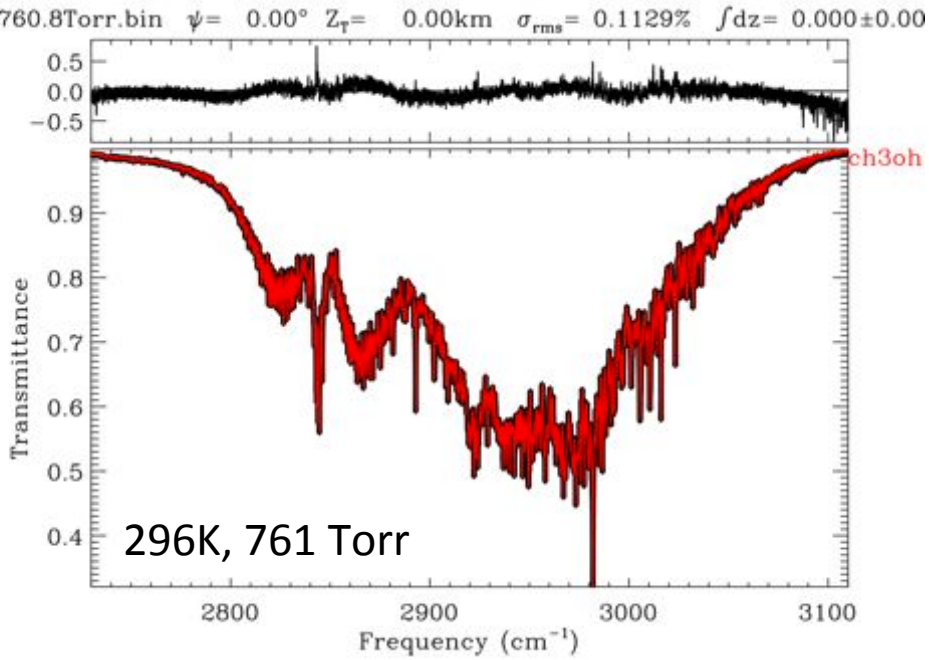
Average VSF = 1.0037 +- 0.0088

PLL fits SWIR CH_3OH spectra with an average RMS fit of 0.13%
And a VMR scale factor of 1.0037 +/- 0.0088

No SWIR comparisons with HITRAN 2012 -- no lines in this region.

SWIR Spectral fits using PLL - Examples





At low pressure (left) the PLL fits the spectra almost down to the noise level.
At 1 atm pressure the noise level is smaller and systematic features become evident.

Summary/Conclusions

A CH_3OH empirical pseudo-linelist has been developed based on the laboratory measurements of Harrison et al.[2012]

Available soon from http://mark4sun.jpl.nasa.gov/pseudo.html

It covers the two main CH_3OH absorption regions:

- LWIR: 6935 lines covering 900-1150 cm^{-1}
- SWIR: 31690 lines covering 2725 to 3115 cm^{-1}

In the LWIR region, the new PLL give much better fits to the lab spectra than HITRAN. The HITRAN CH_3OH linelist does not even extend into the SWIR region.

CH_3OH amounts retrieved from Harrison's measurements are self-consistent to better than 1% in both regions (excellent lab spectra)

The PLL fixes the main deficiencies of the HITRAN CH_3OH linelist:

- Large residuals in the 1000-1100 cm^{-1} region (factor 2 intensity errors)
- T-dependent inconsistency (25% enhancement at 220K)
- CH_3OH completely absent from the SWIR region

Acknowledgements

Jeremy Harrison for making such high quality lab measurements of CH_3OH.

NASA UARP funding.

Rinsland Kitt Peak paper

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 114, D04309, doi:10.1029/2008JD011003, 2009

First ground-based infrared solar absorption measurements of free tropospheric methanol (CH_3OH): Multidecade infrared time series from Kitt Peak (31.9°N 111.6°W): Trend, seasonal cycle, and comparison with previous measurements

Curtis P. Rinsland,[1] Emmanuel Mahieu,[2] Linda Chiou,[3] and Hervé Herbin[4]

Received 19 August 2008; revised 11 December 2008; accepted 24 December 2008; published 27 February 2009.

[1] Atmospheric CH_3OH (methanol) free tropospheric (2.09–14-km altitude) time series spanning 22 years has been analyzed on the basis of high-spectral resolution infrared solar absorption spectra of the strong ν_8 band recorded from the U.S. National Solar Observatory on Kitt Peak (latitude 31.9°N, 111.6°W, 2.09-km altitude) with a 1-m Fourier transform spectrometer (FTS). The measurements span October 1981 to December 2003 and are the first long time series of CH_3OH measurements obtained from the ground. The results were analyzed with SFIT2 version 3.93 and show a factor of three variations with season, a maximum at the beginning of July, a winter minimum, and no statistically significant long-term trend over the measurement time span.

CH_3OH Partition Function

Vibrational PF:

- Uses 11/12 fundamental modes (dropping torsional mode at 270 cm^{-1})
- 3681, 2999, 2844, 1477, 1454, 1340, 1074, 1033, 2970, 1465, 1145 cm^{-1}

Rotational PF:

- Uses $(296/T)^{\mathbf{1.9}}$
- Use of the 1.9 exponent instead of 1.5 compensates for dropping torsional mode.

This is supposed to be more accurate than the nominal approach of using all vib modes, and assuming a Rotational PF of $(296/T)^{1.5}$ (i.e., harmonic oscillator approximation).

Brauer et al. [2012] discuss CH_3OH PF

Why use a PLL

More accurate interpolation/extrapolation to P/T conditions not covered by lab measurements (physics-based, not mathematical).

Fitting the lab spectra provides an opportunity to identify and correct artifacts and inconsistencies

Common artifacts include:

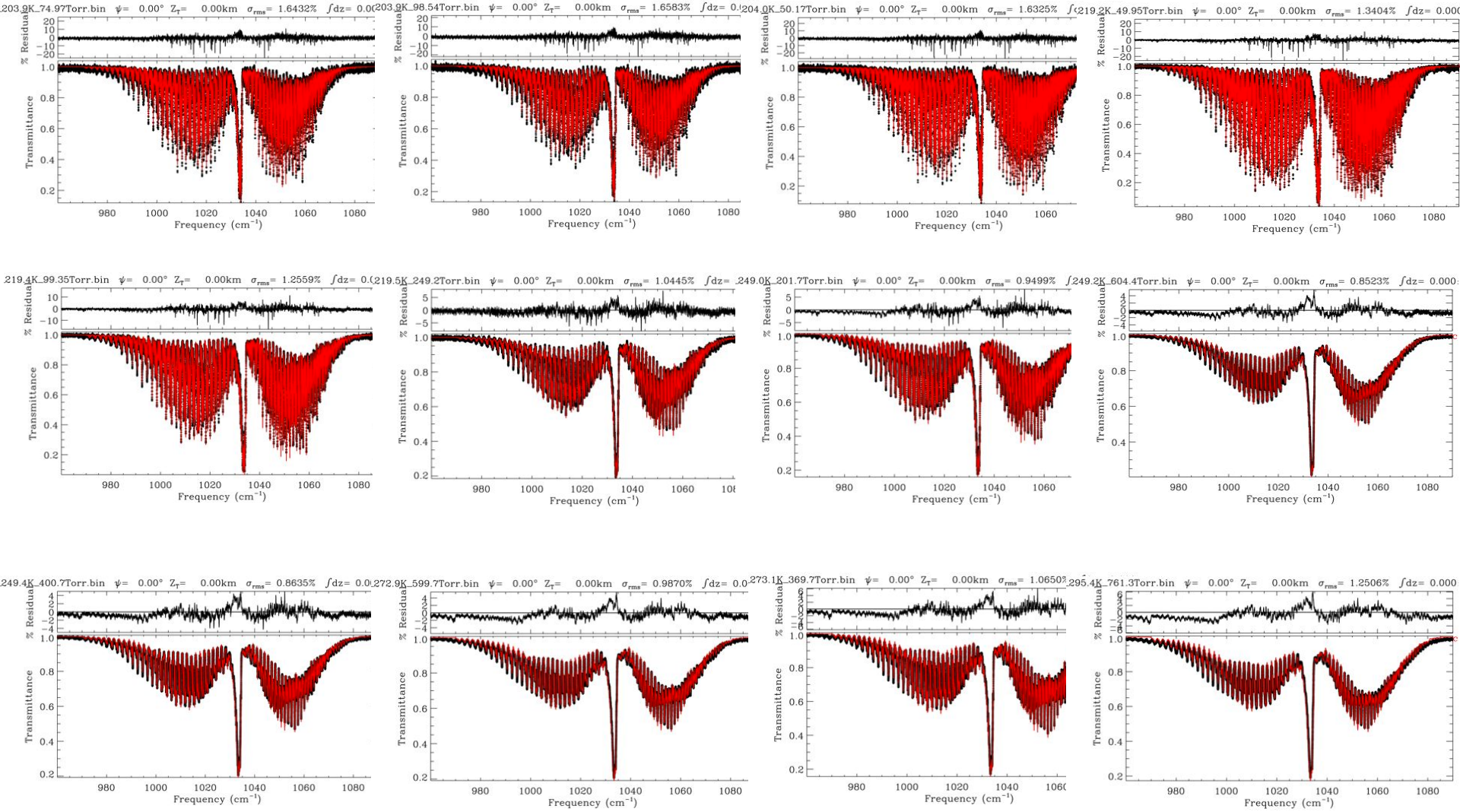
- Contamination (e.g. H_2O, NH_3)
- Channel fringes
- The ILS of the lab spectrometer
- Zero level offsets

Inconsistencies can be cause by incorrect knowledge of the cell conditions (gas amount, P, T). Outlier spectra can be corrected or omitted.

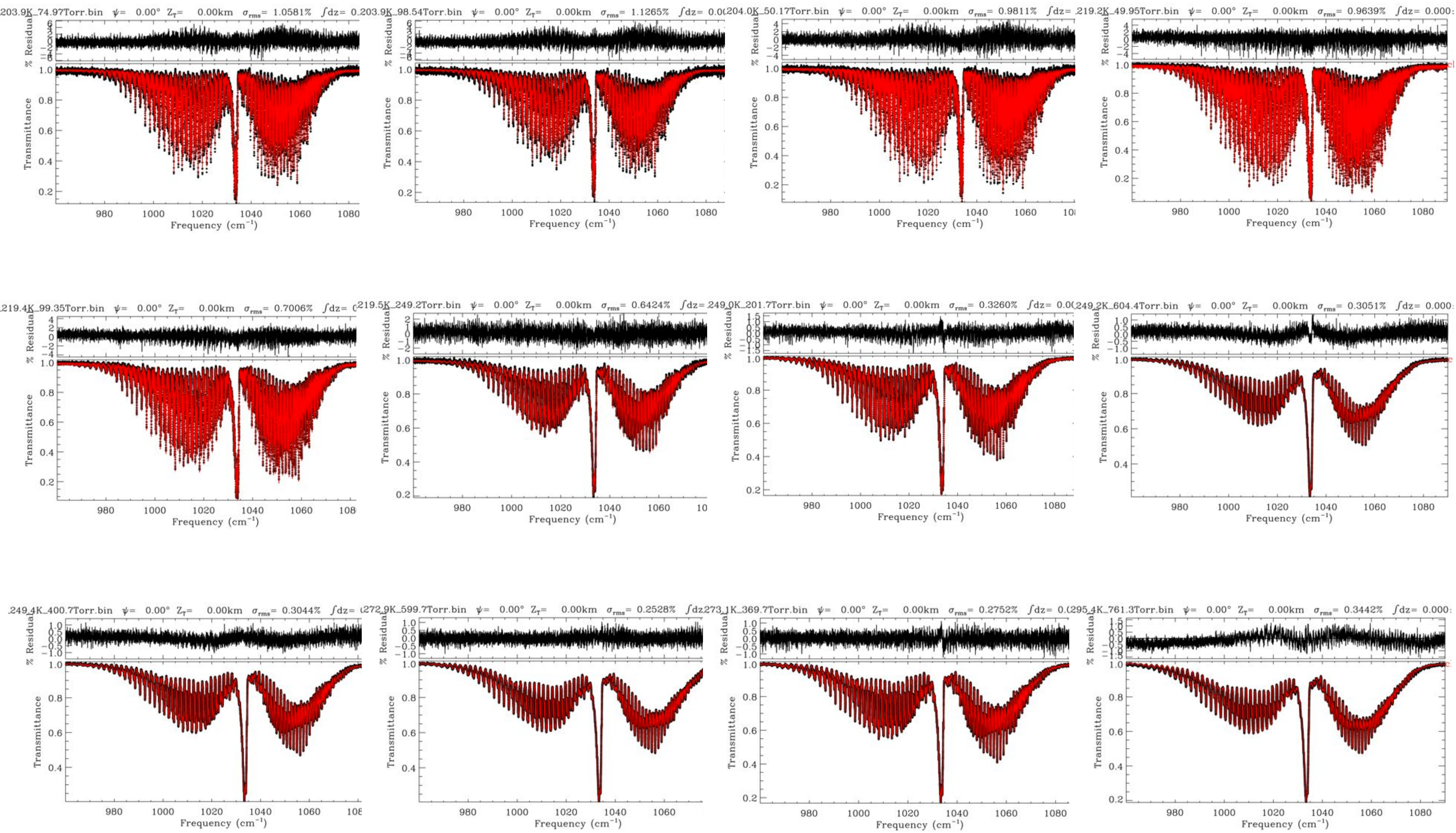
PLL facilitates assimilation of multiple laboratory data sets.

Appendices

Appendix: LWIR fits with HITRAN 2012



Appendix: LWIR fits with PLL



Appendix: SWIR fits with PLL