Improved CH$_3$OH spectroscopy: Development of a Pseudo-Linelist

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Methanol (CH$_3$OH) 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$_3$OH 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.

$v_1$ O-H stretch 3681 cm$^{-1}$
$v_2$ C-H perpendicular asymmetric stretch ($A'$) 2999 cm$^{-1}$
$v_3$ C-H parallel symmetric stretch ($A'$) 2844 cm$^{-1}$
$v_4$ C-H in-plane asymmetric bend 1477 cm$^{-1}$
$v_5$ C-H in-plane symmetric bend 1454 cm$^{-1}$
$v_6$ O-H bend ($A'$) 1340 cm$^{-1}$
$v_7$ CH$_3$ rock ($A'$) 1074 cm$^{-1}$
$v_8$ C-O stretch ($A'$) 1033 cm$^{-1}$
$v_9$ C-H perpendicular asymmetric stretch ($A''$) 2970 cm$^{-1}$
$v_{10}$ C-H out of plane asymmetric bend 1465 cm$^{-1}$
$v_{11}$ CH$_3$ rock ($A''$) 1145 cm$^{-1}$
$v_{12}$ torsion 270 cm$^{-1}$
Current CH$_3$OH Spectroscopy

HITRAN CH$_3$OH 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$_3$OH lab spectra in both LWIR & SWIR regions.

Fitting Harrison’s data using the HITRAN 2012 CH$_3$OH 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$_3$OH lines in the 1185-1407 cm$^{-1}$ region have the same intensity (1.0E-26), which doesn’t seem right.
New assignments, line intensities, and HITRAN database for CH$_3$OH at 10 $\mu$m

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Abstract

The Fourier transform spectrum of CH$_3$OH in the 10 $\mu$m region has been re-examined at higher pressure and path length than heretofore, as part of a program to provide comprehensive CH$_3$OH 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-$K$, $v_{32} = 0$ subbands of the $v_9$ 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 $v_9$ substate origins. A variety of weaker subbands from other modes has also been identified in the 10 $\mu$m spectrum including $v_{12} = 0$, $v_{12} = 1$, and $v_{12} = 0$ $J = 1$ torsional subbands of the $v_7$ in-plane CH$_3$ rock, $v_{12} = 0$ $J = 1$ and $v_{12} = 0$ $J = 2$ torsional combination subbands of the $v_6$ OH bend, and $v_{12} = 0$ $J = 2$ subbands of the $v_5$ symmetric CH$_3$ bend. Line intensities have been retrieved line-by-line from the spectra. A large set of “unperturbed” $v_9$ 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 $v_9$ spectral lines in the fitting in order to obtain appropriate transition dipole terms. Together, a 10 $\mu$m methanol database in HITRAN format has been generated.

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Incorporated into HITRAN 2004 covering 911 to 1407 cm$^{-1}$. Minor tweaks in HITRAN 2008.
Infrared absorption cross sections for methanol

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ABSTRACT
Infrared absorption cross sections for methanol, CH₃OH, 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.

<table>
<thead>
<tr>
<th></th>
<th>Temperature (K)</th>
<th>Initial methanol pressure (Torr)</th>
<th>Total pressure (Torr)</th>
<th>Pathlength (m)</th>
<th>No. of scans</th>
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<td>0.0137</td>
<td>50.92 ± 0.10</td>
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<td>75.82 ± 0.10</td>
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<td>101.62 ± 0.10</td>
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<td>400</td>
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<td>760.8 ± 0.2</td>
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<td><strong>LWIR (10 (\mu)m)</strong></td>
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<td>604.4 ± 0.6</td>
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<td>369.7 ± 0.4</td>
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<td>0.2293</td>
<td>599.7 ± 0.8</td>
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<tr>
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<td>0.2872</td>
<td>761.3 ± 0.2</td>
<td>1.71</td>
<td>300</td>
</tr>
</tbody>
</table>

* MKS-690A Baratron readings are accurate to ± 0.05%.
* The error in the optical pathlength is estimated to be ± 0.2% at room temperature.
* 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

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>RMS %</th>
<th>VSF</th>
<th>VSF_error</th>
</tr>
</thead>
<tbody>
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<td>CH3OH_LWIR_203.9K_74.97Torr.bin</td>
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<tr>
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<td>1.2506</td>
<td>0.9753</td>
<td>3.8E-02</td>
</tr>
</tbody>
</table>

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$_3$OH amounts retrieved from warm (273K) and cold spectra (204K). Missing hot band? Partition function?
Figure 3 from Harrison et al. [2012]

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

Discrepancy reaches 25-30% at 205K.

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].
Interlude

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

Harrison’s solution to the problem with HITRAN 2012 CH$_3$OH 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$_3$OH 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$_3$OH 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

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>RMS</th>
<th>VSF</th>
<th>VSF_error</th>
</tr>
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</table>

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$_3$OH amounts retrieved from warm & cold spectra.
LWIR HITRAN/PLL Spectral Fits - Examples

HITRAN 2012
219K, 99Torr

PLL
219K, 99Torr

HITRAN 2012
295K, 761Torr

PLL
295K, 761Torr
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$_3$OH 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 $E^\prime$.

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$_3$OH and not other gases (e.g. H$_2$O) contaminating Harrison’s lab measurements?

Have tried fitting H$_2$O and several other gases, but detected none, i.e. no correlation between dips in residuals and H$_2$O line positions.

Fits below to 219K, 50 Torr Harrison spectrum: Left=HITRAN; Right=PLL
SWIR CH₃OH Fitting Result Summary

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>RMS</th>
<th>VSF</th>
<th>VSF_error</th>
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<tr>
<td>CH3OH_SWIR_296.0K_760.8Torr.bin</td>
<td>0.1143</td>
<td>1.0156</td>
<td>3.4E-03</td>
</tr>
</tbody>
</table>

Average % RMS fit = 0.132 %
Average VSF = 1.0037 +/- 0.0088

PLL fits SWIR CH₃OH 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.
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$_3$OH empirical pseudo-linelist has been developed based on the laboratory measurements of Harrison et al.[2012]


It covers the two main CH$_3$OH 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$_3$OH linelist does not even extend into the SWIR region.

CH$_3$OH 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$_3$OH linelist:
- Large residuals in the 1000-1100 cm$^{-1}$ region (factor 2 intensity errors)
- T-dependent inconsistency (25% enhancement at 220K)
- CH$_3$OH completely absent from the SWIR region
Acknowledgements

Jeremy Harrison for making such high quality lab measurements of CH$_3$OH.

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First ground-based infrared solar absorption measurements of free tropospheric methanol (CH$_3$OH): Multidecade infrared time series from Kitt Peak (31.9°N 111.6°W): Trend, seasonal cycle, and comparison with previous measurements

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Atmospheric CH$_3$OH (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 $\nu_8$ 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$_3$OH 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$_3$OH 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)$^{1.9}$
- 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$_3$OH 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$_2$O, 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.
Appendix: LWIR fits with HITRAN 2012
Appendix: LWIR fits with PLL
Appendix: SWIR fits with PLL