CH_3Cl Linelist Evaluation

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A CH_3Cl linelist has been developed by Bray, Perrin, Jacquemart, et al. See:

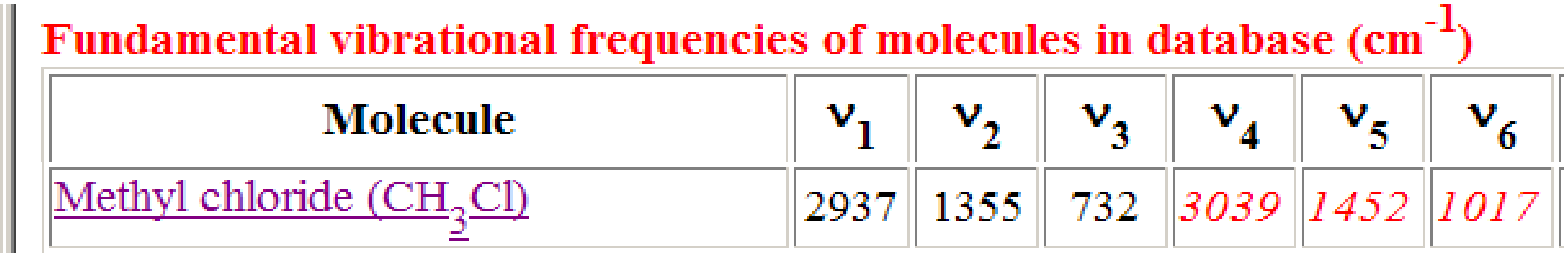
C. Bray, A. Perrin, D. Jacquemart, N. Lacome, The ν_1, ν_4 *and* $3\nu_6$ *bands of methyl chloride in the 3.4-um region: Line positions and intensities, Journal of Quantitative Spectroscopy & Radiative Transfer 112 (2011) 2446–2462*

C. Bray, D. Jacquemart, J. Buldyreva, N. Lacome, A. Perrin, N_2*-broadening coefficients of methyl chloride at room temperature, Journal of Quantitative Spectroscopy & Radiative Transfer, 113, (2012) 1102-1112*

This is a proper quantum-mechanically-based linelist generated by highly reputable spectroscopists (not a pseudo-linelist).

In this presentation, Kitt Peak laboratory spectra and MkIV balloon spectra are used to evaluate this new linelist.

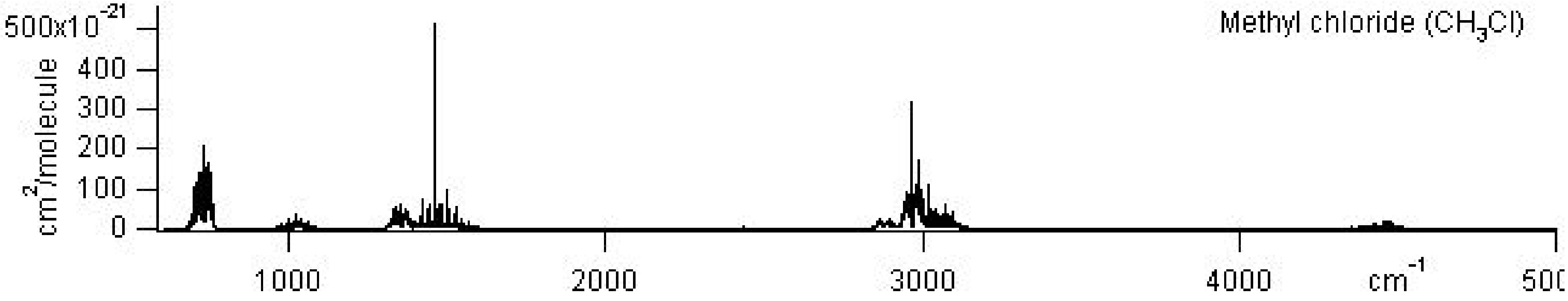
http://vpl.astro.washington.edu



Fundamental vibrational frequencies of molecules in database (cm^{-1})

Molecule	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Methyl chloride (CH_3Cl)	2937	1355	732	*3039*	*1452*	*1017*

Methyl chloride images from PNNL



2960 cm^{-1} region does not contain the strongest IR CH_3Cl feature, but it is the best for remote sensing of the troposphere since the 1500 cm^{-1} region blacks out below 12 km.

2960 cm^{-1} region is messy due to overlap (and interaction) of ν_1, ν_4, $2\nu_5$, $2\nu_3+\nu_5$ & $3\nu_6$

FIRST RETRIEVALS of METHYL CHLORIDE (CH_3Cl) from GROUND-BASED HIGH-RESOLUTION FTIR SOLAR OBSERVATIONS

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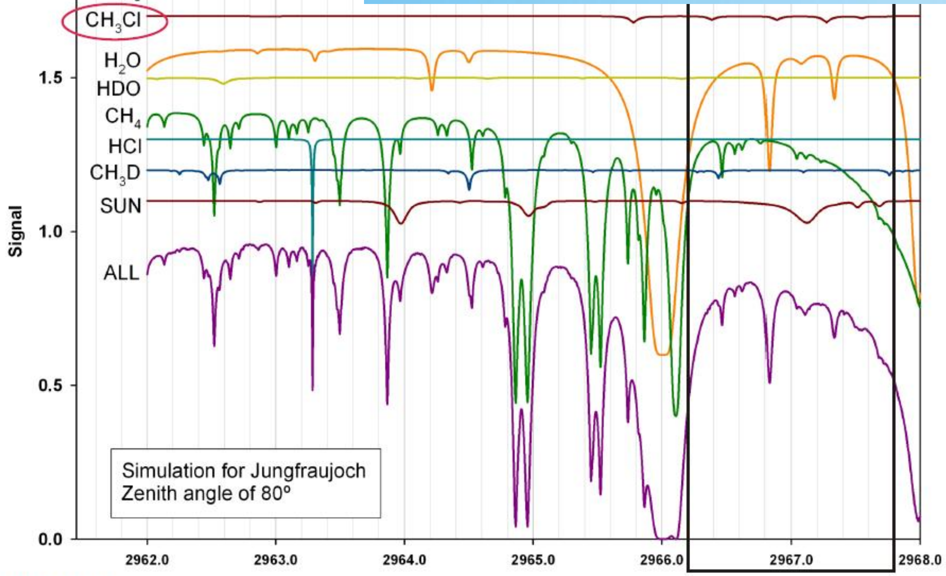
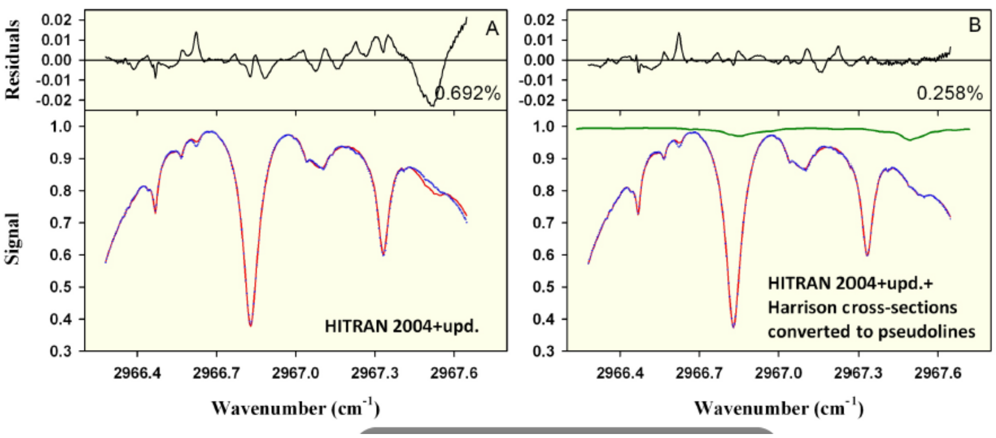


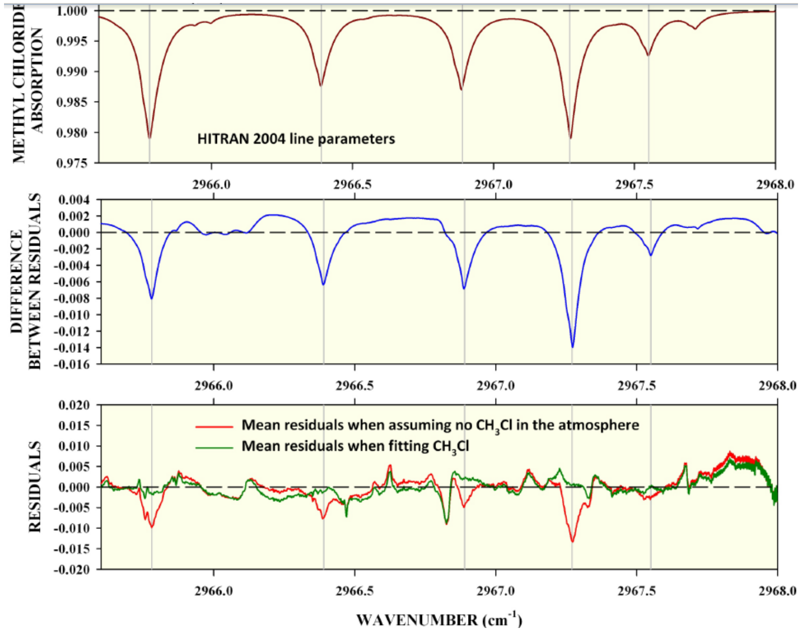
People are now retrieving CH_3Cl from ground-based spectra.

There are serious spectroscopic problems in this region (C_2H_6, CH_4)

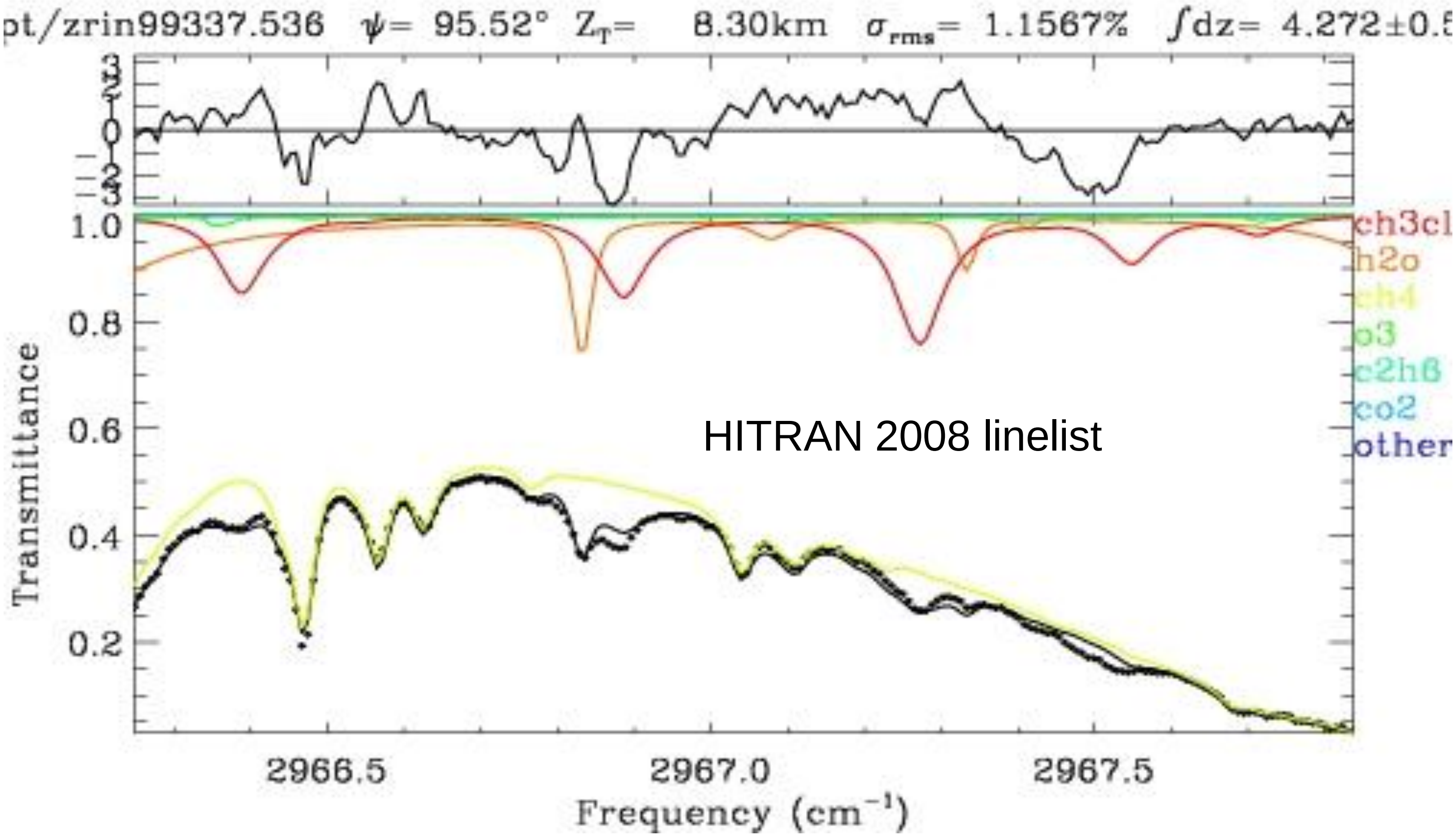
This talk focuses on CH_3Cl itself

Retrieval of CH_3Cl from Jungfraujoch:
Mean observed/simulated spectra and residuals for 220 spectral fits (4.96 mk), using two different sets of linelist





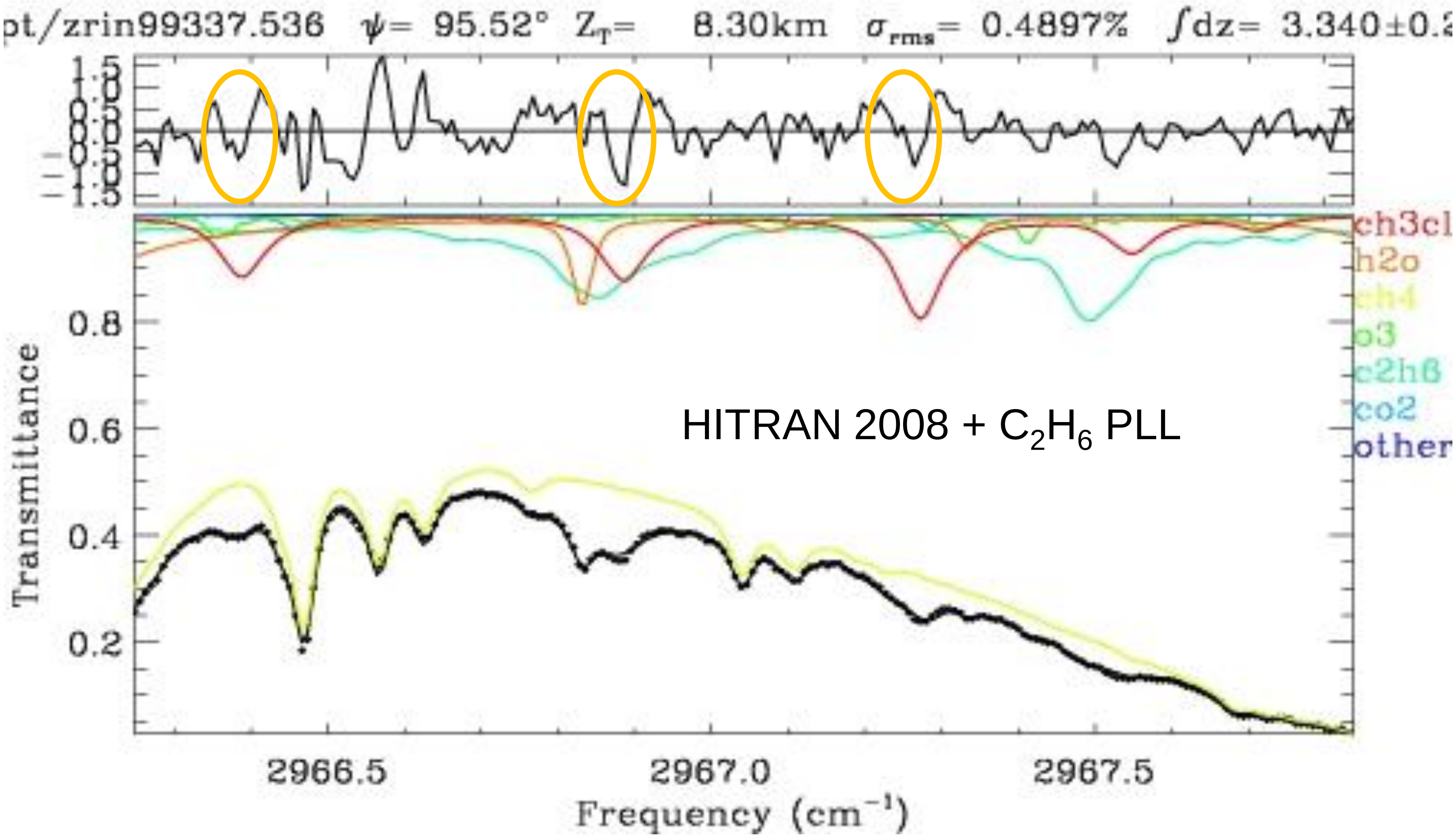
Fit to MkIV balloon spectrum at 8.3 km



HITRAN 2008 linelist

Largest residuals result from omission of C_2H_6 in this region of HITRAN_2008. Henceforth, in this presentation, a C_2H_6 pseudo-linelist (PLL) will be used, based on the work of Harrison and Bernath [2011].

Fit to some MkIV balloon spectrum



HITRAN 2008 + C_2H_6 PLL

Including C_2H_6 PLL results in a factor 2-3 improvement in the residuals.
But two serious problems remain with the HITRAN CH_3Cl:
(1) Systematic “dips” in the residuals, (2) Limited spectral coverage

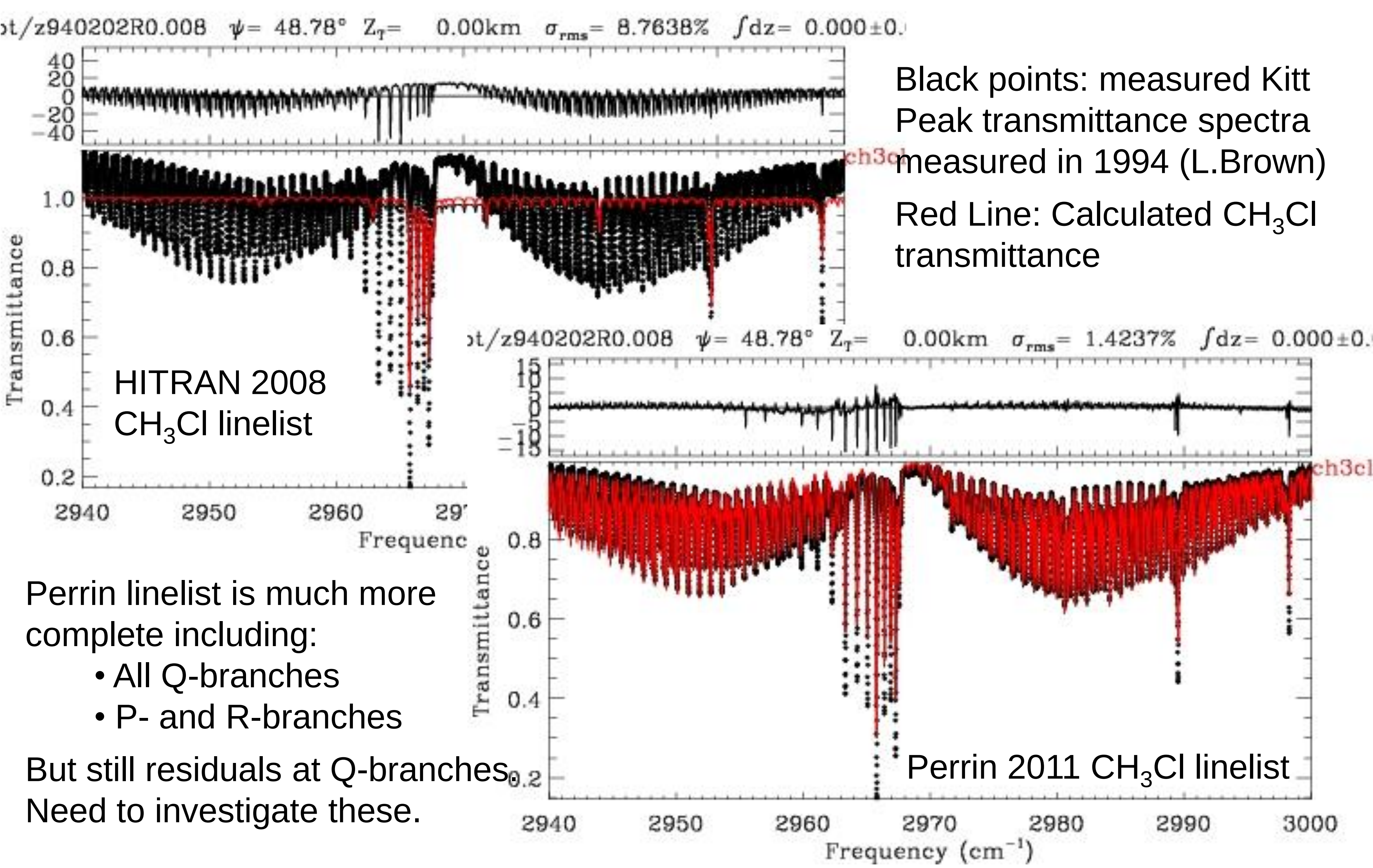
Kitt Peak Laboratory Spectra

Look at some laboratory spectra of CH_3Cl measured by Linda Brown in 1994 at Kitt Peak. Used a 4.4m cell at 0.02 cm^{-1} spectral resolution.

Pure gas sample at 290K and 0.3 Torr
Air-broadened sample at 290K and 289 Torr

See if same systematic residuals appear in fits to the lab spectra.

Fit to Kitt Peak Lab spectrum (289 Torr)



Black points: measured Kitt Peak transmittance spectra measured in 1994 (L.Brown)

Red Line: Calculated CH_3Cl transmittance

HITRAN 2008 CH_3Cl linelist

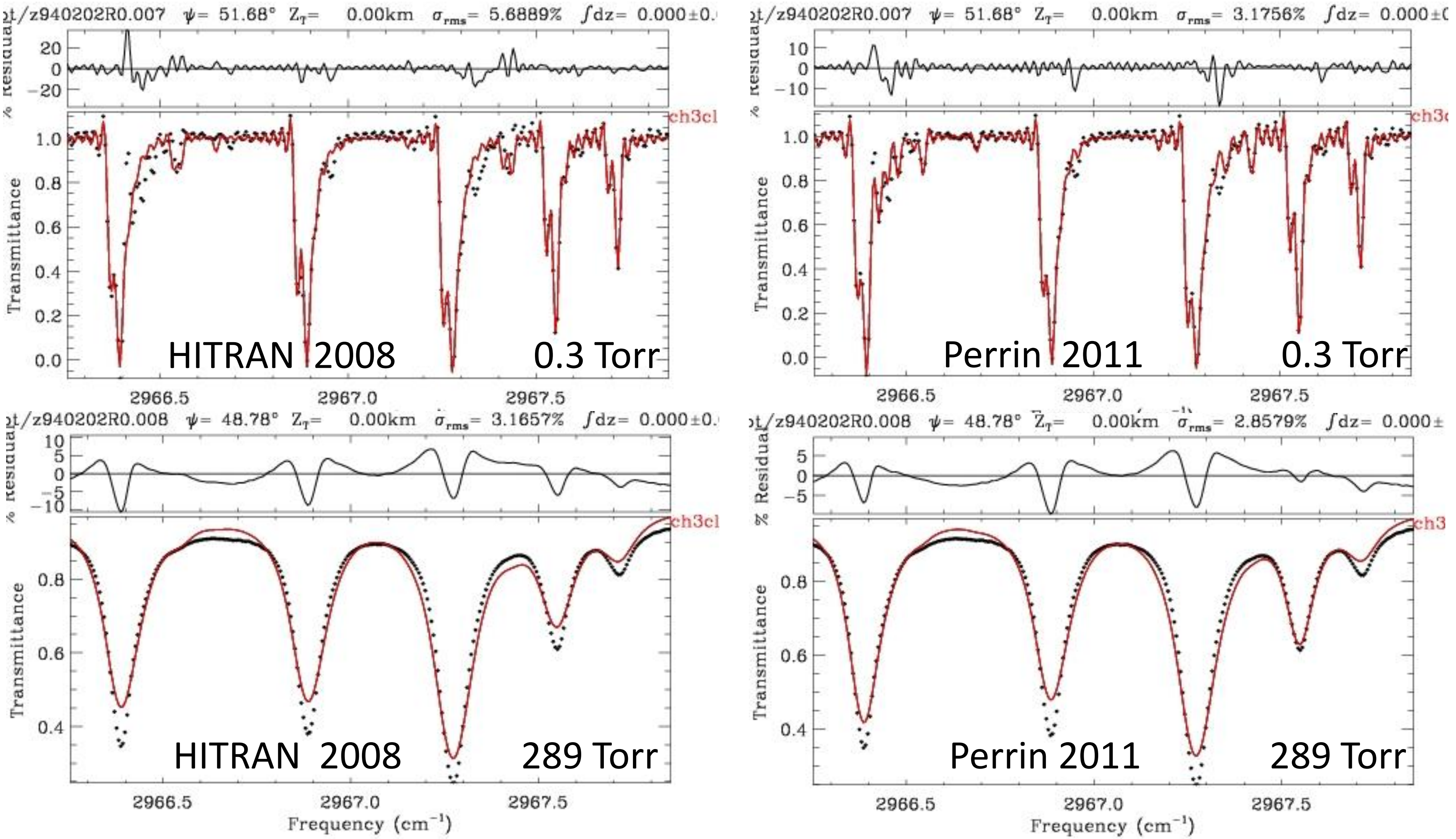
Perrin 2011 CH_3Cl linelist

Perrin linelist is much more complete including:

- All Q-branches
- P- and R-branches

But still residuals at Q-branches. Need to investigate these.

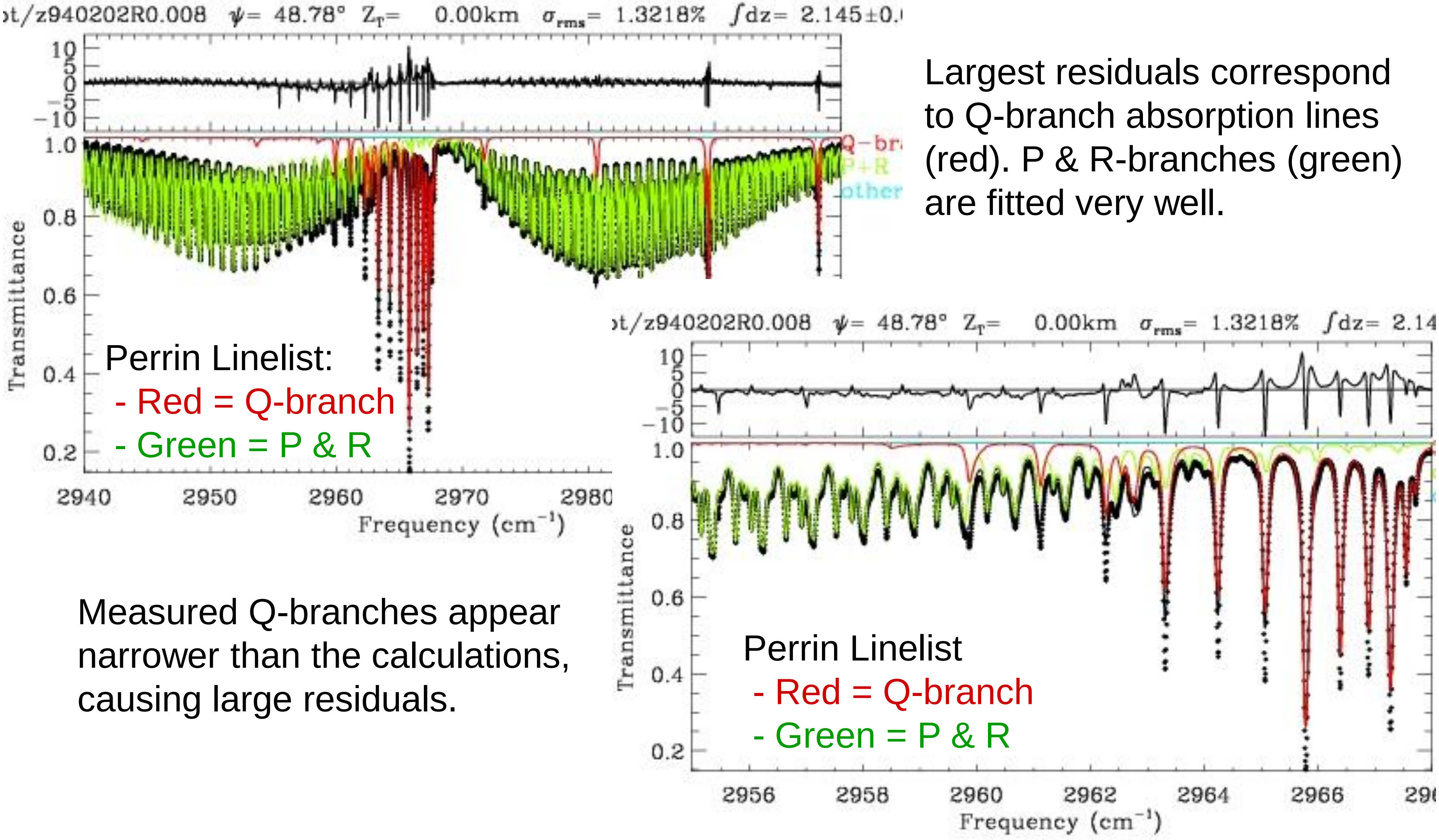
Fits to Kitt Peak Laboratory Spectra



Even for the Q-branches covered by HITRAN 2008, the Perrin linelist is better, both at 0.3 Torr and at 289 Torr. But the systematic over-estimation of the widths remains.

Fits to Kitt Peak Lab spectra (289 Torr)

To understand residuals, plot the fits using different colors for P/R- & Q-branches



Largest residuals correspond to Q-branch absorption lines (red). P & R-branches (green) are fitted very well.

Perrin Linelist:

- Red = Q-branch
- Green = P & R

Measured Q-branches appear narrower than the calculations, causing large residuals.

Perrin Linelist

- Red = Q-branch
- Green = P & R

Line Mixing in CH_3Cl ?

What could cause the Q-branches to be over-broadened in the Voigt calculation, but the P & R-branches fit so nicely?

The Q-branches consist of many overlapping individual lines. These would mix with each other causing the width of the feature to appear narrower than expected.

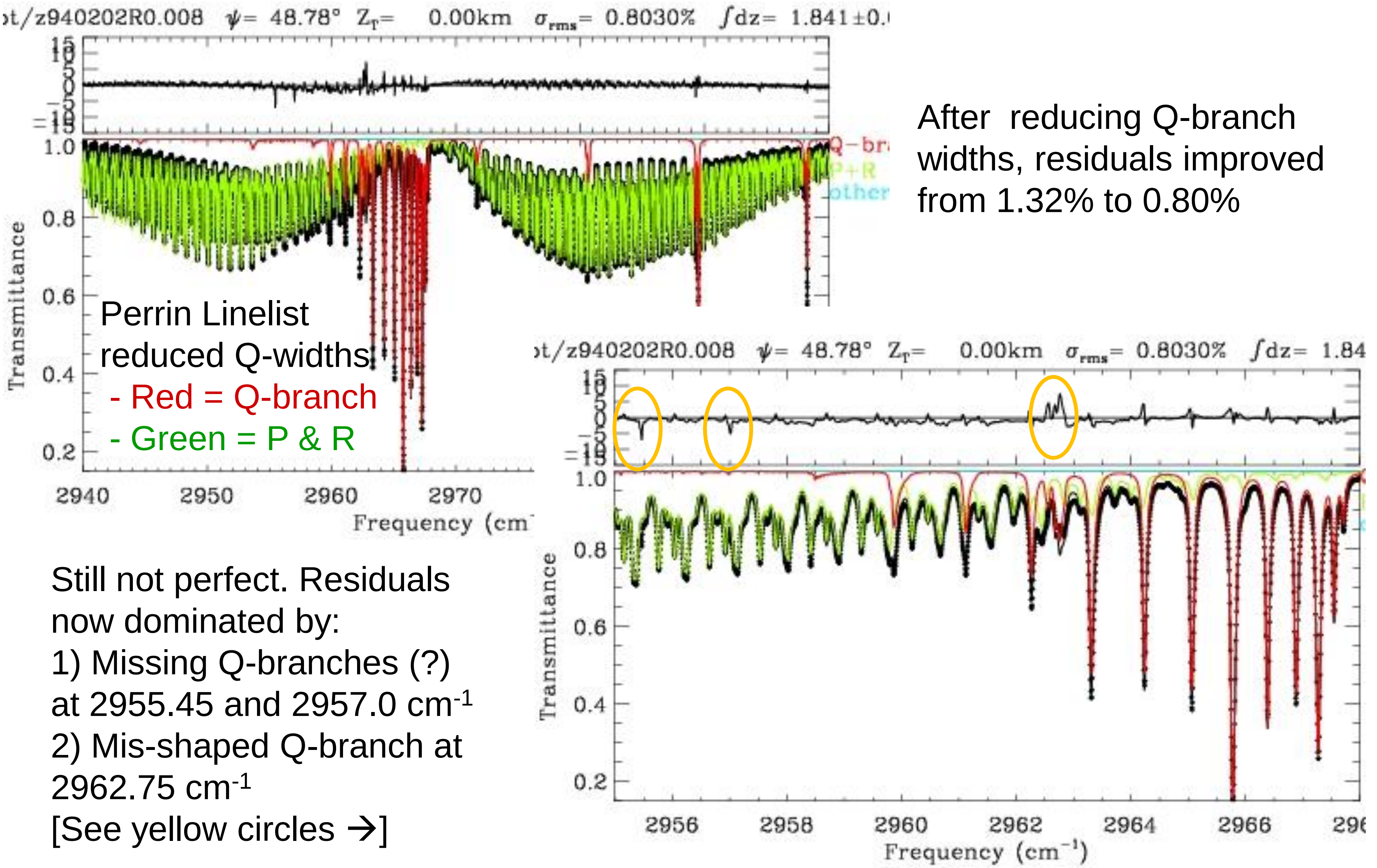
Unfortunately, I have no code to compute line-mixing in CH_3Cl. Neglecting LM not only causes poor fitting residuals, it also causes the retrieved VMR profiles to be biased high in the lower atmosphere.

So, how to take advantage of the major spectroscopic advances embodied in Perrin’s CH_3Cl linelist, and not get skewed CH_3Cl profiles with worse fits than previously?

Implemented a “kludge” in the line-by-line code that reads the linelist and computes the absorption coefficients: Reduces widths by 37% for CH_3Cl Q-branch lines, leaving the P & R-branch line widths unchanged.

This is a temporary solution, until a proper line-mixing code is available. David Jacquemart is working on this.

New Fits to Kitt Peak Lab spectra



After reducing Q-branch widths, residuals improved from 1.32% to 0.80%

Perrin Linelist reduced Q-widths

- Red = Q-branch
- Green = P & R

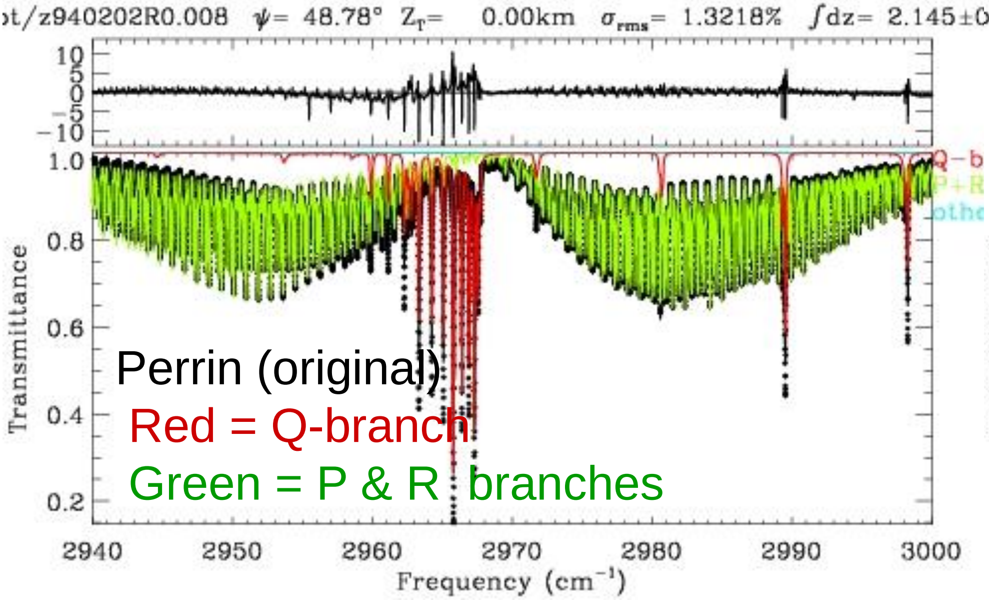
Still not perfect. Residuals now dominated by:

1) Missing Q-branches (?) at 2955.45 and 2957.0 cm^{-1}

2) Mis-shaped Q-branch at 2962.75 cm^{-1}

[See yellow circles →]

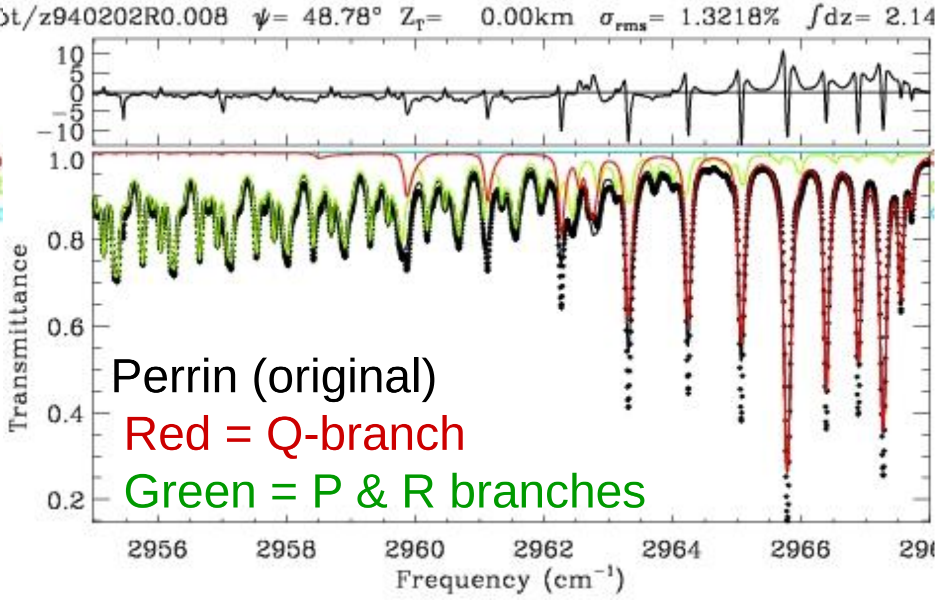
Fits to Kitt Peak Lab spectrum (289 Torr)



Perrin (original)

Red = Q-branch

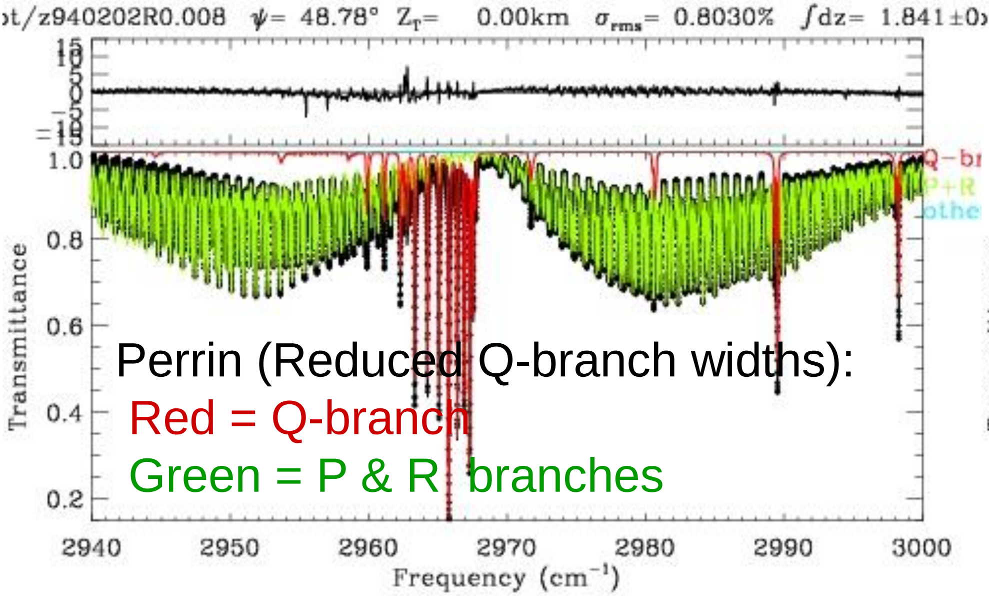
Green = P & R branches



Perrin (original)

Red = Q-branch

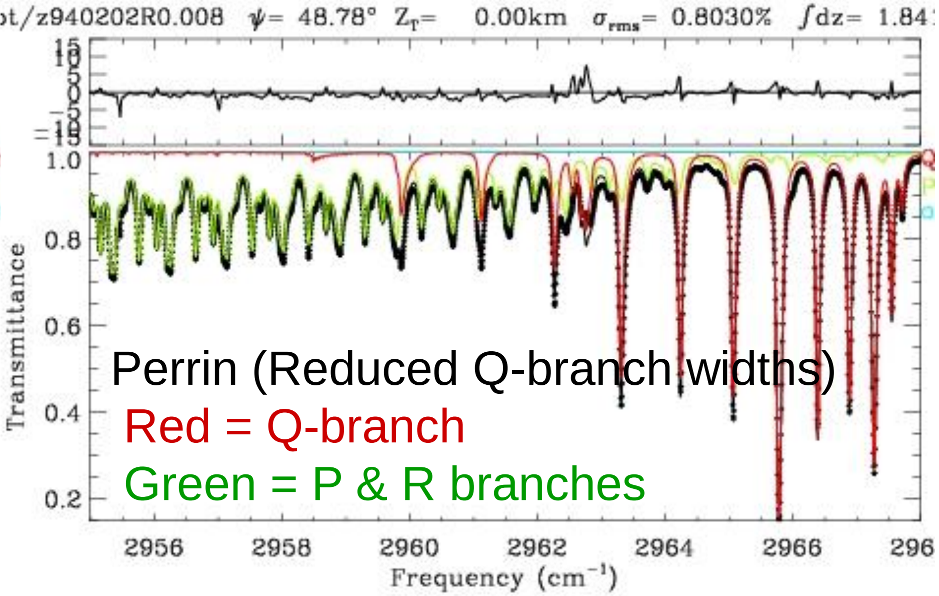
Green = P & R branches



Perrin (Reduced Q-branch widths):

Red = Q-branch

Green = P & R branches



Perrin (Reduced Q-branch widths)

Red = Q-branch

Green = P & R branches

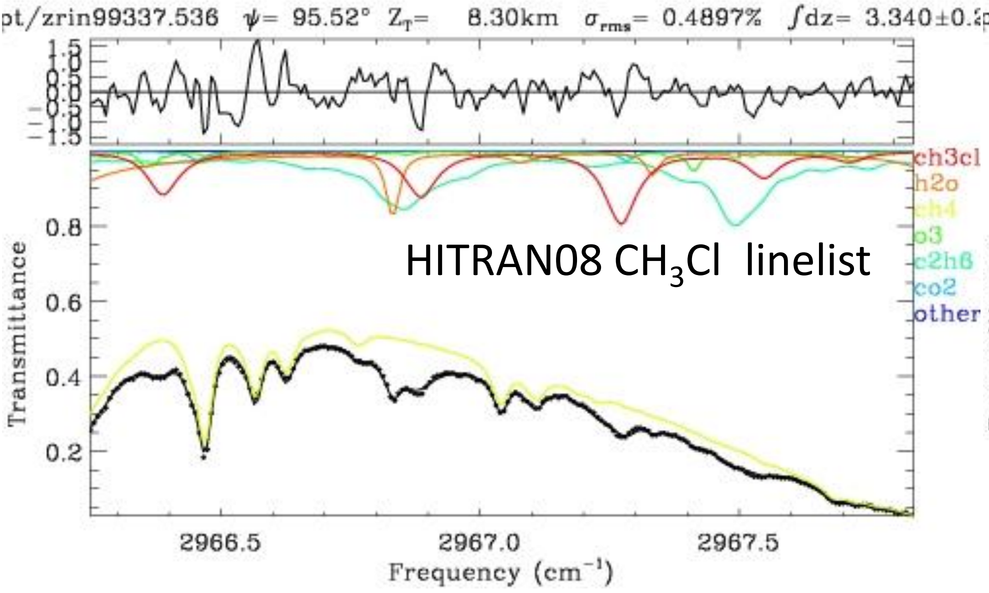
Effect on MkIV balloon retrievals

Three main benefits:

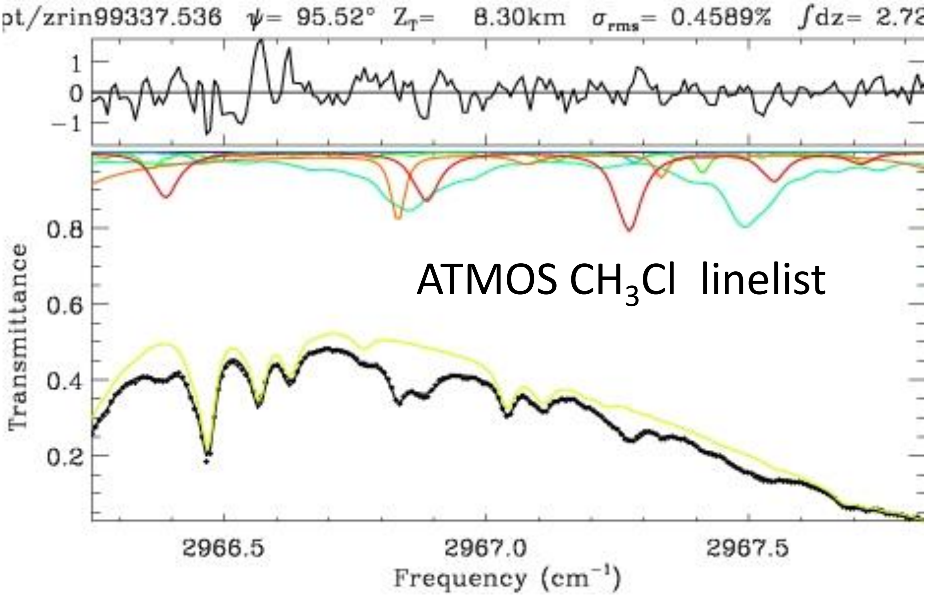
1) Better fits in the 2967.05 +/- 0.8 cm^{-1} window leading to a more accurate retrieved vmr profile
2) Enables the use of a wider CH_3Cl fitting window, which was precluded by the HITRAN CH_3Cl linelist [Some of the CH_3Cl Q-branches missing from HITRAN 2008 are 10% deep in solar occultation spectra at 8 km tangent altitude].
3) Improved retrievals of other gases whose absorption lines are overlapped by missing CH_3Cl lines.

These same benefits also apply to ground-based measurements.

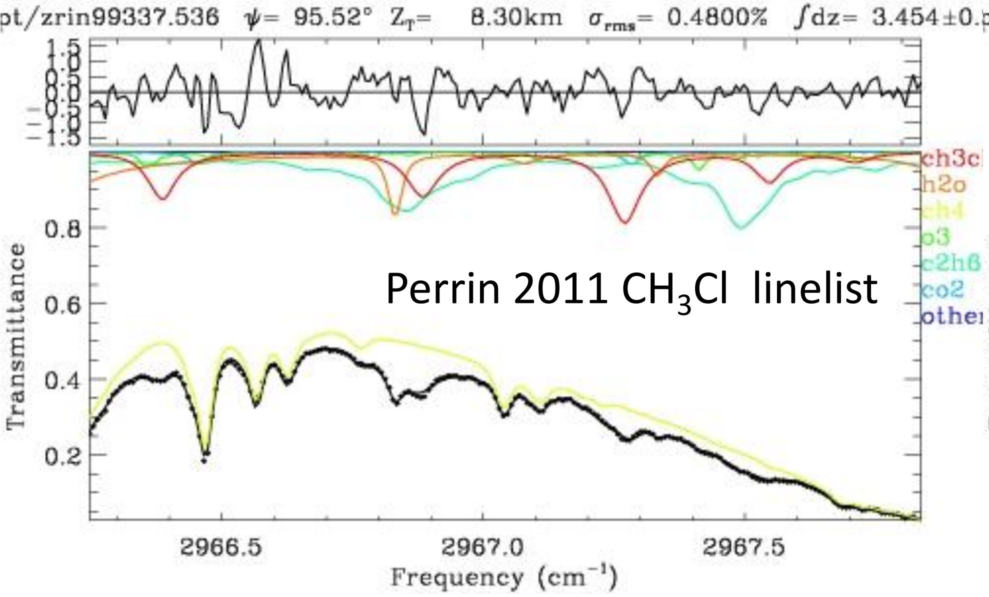
Fits to MkIV balloon spectra (Z_T=8.3 km)



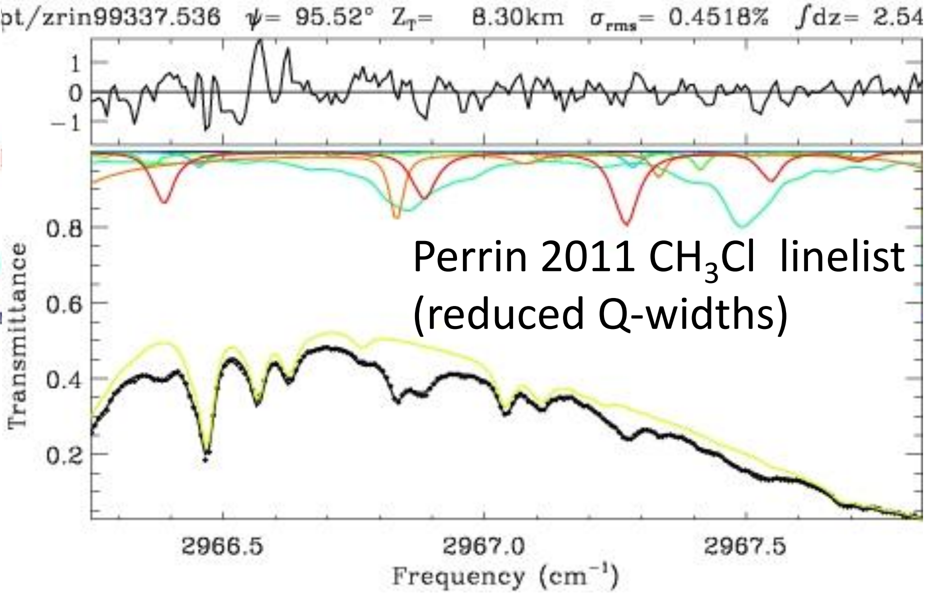
HITRAN08 CH_3Cl linelist



ATMOS CH_3Cl linelist

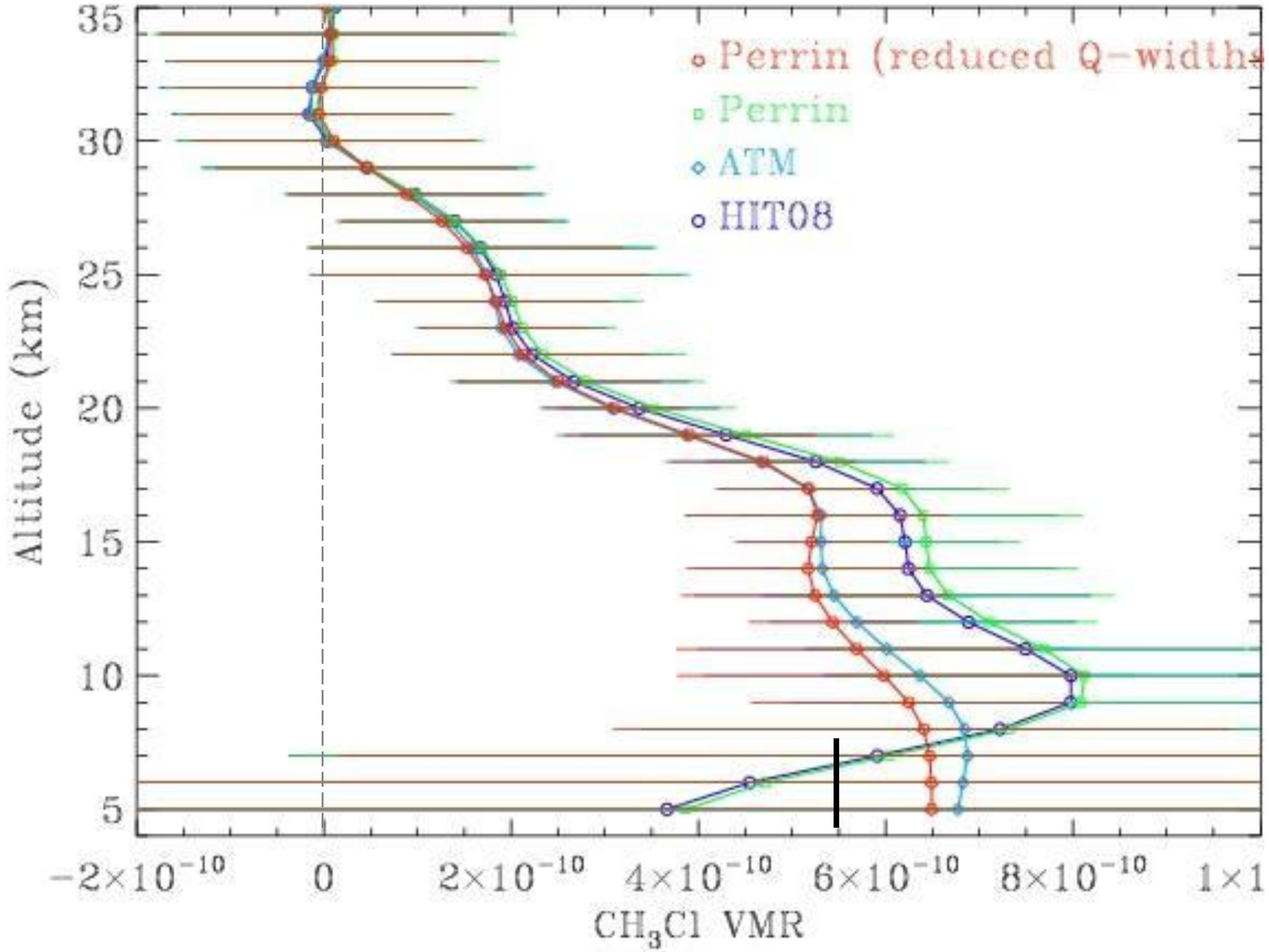


Perrin 2011 CH_3Cl linelist

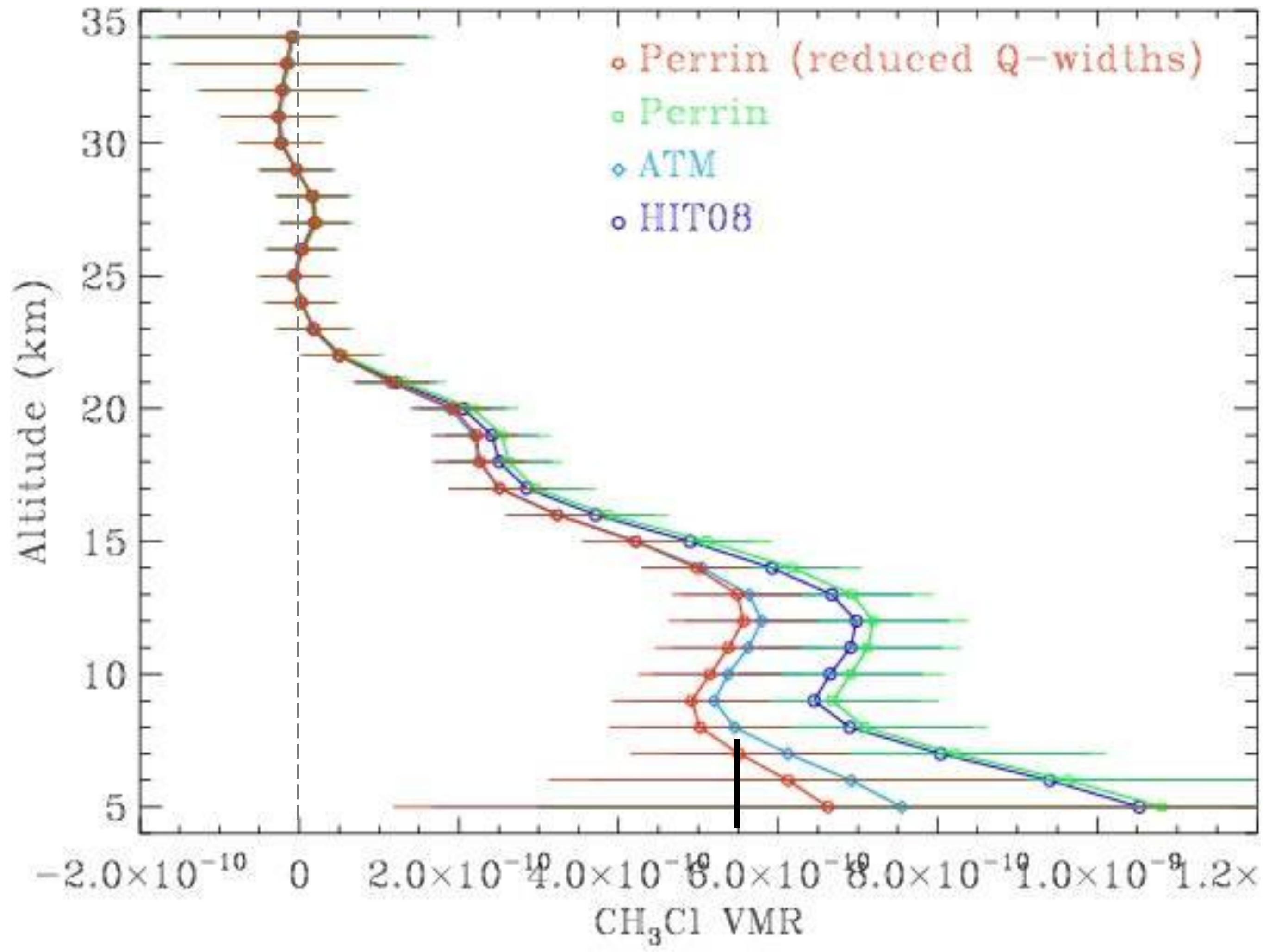


Perrin 2011 CH_3Cl linelist
(reduced Q-widths)

MkIV Balloon CH_3Cl profiles (1999)



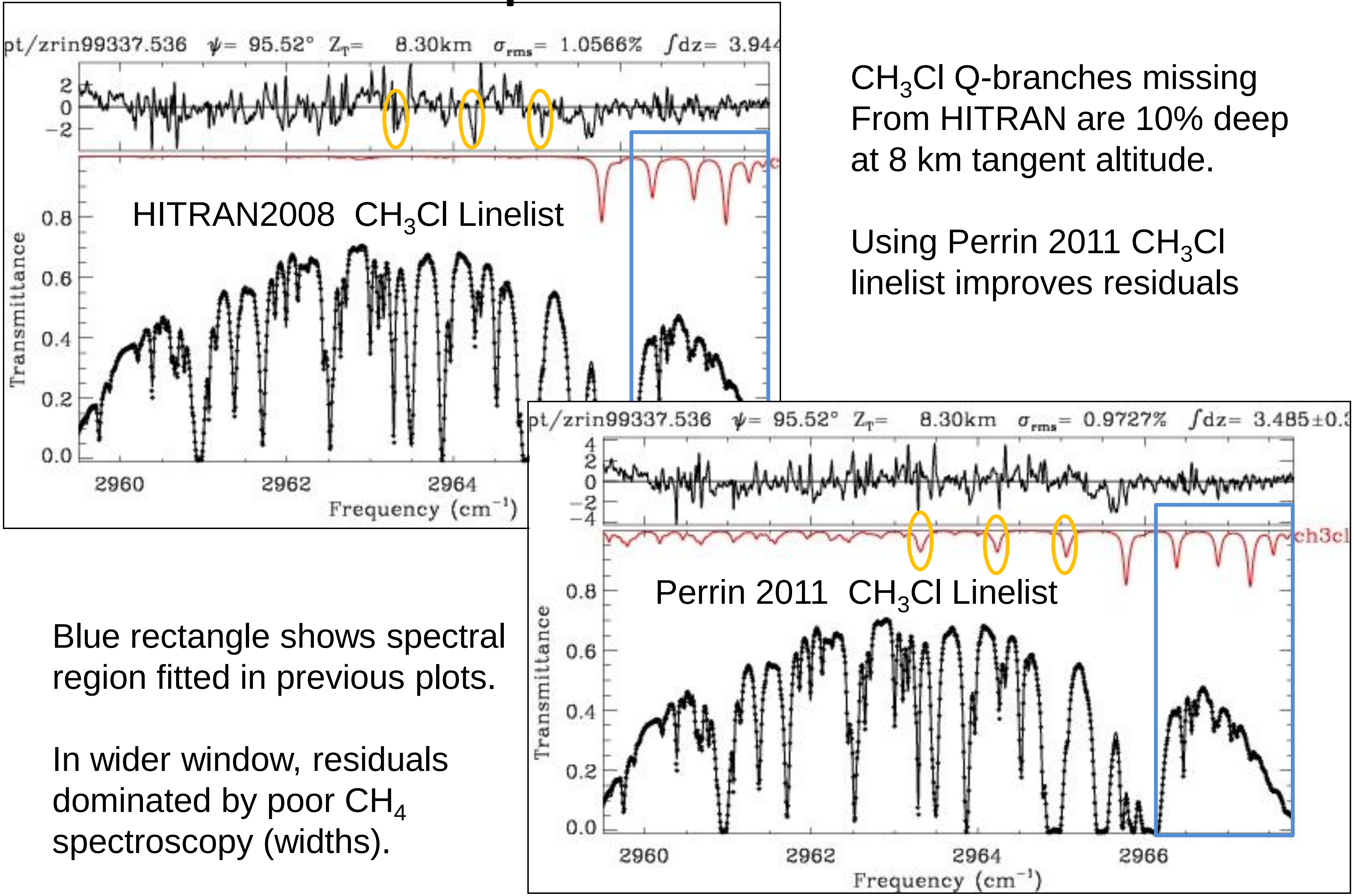
MkIV Balloon CH_3Cl Profiles (2003)



Fits to same spectrum: wider window

CH_3Cl Q-branches missing From HITRAN are 10% deep at 8 km tangent altitude.

Using Perrin 2011 CH_3Cl linelist improves residuals



HITRAN2008 CH_3Cl Linelist

Perrin 2011 CH_3Cl Linelist

Blue rectangle shows spectral region fitted in previous plots.

In wider window, residuals dominated by poor CH_4 spectroscopy (widths).

Summary/Conclusions (1)

HITRAN 2008 CH_3Cl linelist is severely deficient:
- contains only 5/10 strongest Q-branches in the 2960-2968 cm^{-1} region.
- most of the P- and R-branch structure is missing or under-represented.

Fits to Kitt Peak Lab spectra with Perrin 2011 linelist are better than with HITRAN:
- factor of 6 times better RMS residual over entire band
- 10% better RMS residual over Q-branches represented in HITRAN 2008

Widths of the Q-branch features over-estimated in a Voigt line-by-line calculation, both in lab and atmospheric spectra. Widths of P- & R-branch features are good.

Likely that neglect of line mixing is the cause of this over-broadening. Awaiting line-mixing parameterization from David Jacquemart.

In the absence of CH_3Cl line-mixing code, reducing the Q-branch line widths by 37% improves fits to lab and atmospheric spectra.

[To be clear, there is no problem with Perrin's widths. Reducing them is just a convenient way of representing the main effects of line-mixing]

Summary/Conclusions (2)

In fits to laboratory spectra, performed with the 37% Q-branch width reduction:

- Perrin's ^{35}Cl and ^{37}Cl intensities are consistent to better than 3%
- Perrin's P-, Q- and R-branch intensities are consistent to better than 2%

In fits to MkIV atmospheric spectra:

- Retrieved CH_3Cl profiles are more realistic (closer to 500 ppt in the lower trop)
- Retrieval uncertainties are smaller

Future Work

- Implement Line Mixing into CH_3Cl LBL calculations (instead of reducing Q-widths)
- Explore the use of wider windows for the retrieval of CH_3Cl (incl. P- & R-branch)
- Quantify effect of new CH_3Cl linelist on other gases in 2900-3100 cm^{-1} region

This linelist should be incorporated into HITRAN at the earliest opportunity

Even without line-mixing code, new linelist is much better than current HITRAN CH_3Cl

Reducing Q-branch widths by 37% is highly recommended to avoid over-broadening

CH_4 *is then main spectroscopic problem in this region (provided you use* C_2H_6 *PLL)*

Supplemental Material

Journal of Quantitative Spectroscopy & Radiative Transfer 113 (2012) 1102–1112

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N_2-broadening coefficients of methyl chloride at room temperature

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ABSTRACT

Methyl chloride is of interest for atmospheric applications, since this molecule is directly involved in the catalytic destruction of ozone in the lower stratosphere. In a previous work [Bray et al. JQSRT 2011;112:2446], lines positions and intensities of self-perturbed $^{12}CH_3^{35}Cl$ and $^{12}CH_3^{37}Cl$ have been studied into details for the 3.4 µm spectral region. The present work is focused on measurement and calculation of N_2-broadening coefficients of the $^{12}CH_3^{35}Cl$ and $^{12}CH_3^{37}Cl$ isotopologues. High-resolution Fourier Transform spectra of CH_3Cl–N_2 mixtures at room-temperature have been recorded between 2800 and 3200 cm^{-1} at LADIR (using a classical source) and between 47 and 59 cm^{-1} at SOLEIL (using the synchrotron source on the AILES beamline). 612 mid-infrared transitions of the ν_1 band and 86 far-infrared transitions of the pure rotational band have been analyzed using a multispectrum fitting procedure. Average accuracy on the deduced N_2-broadening coefficients has been estimated to 5% and 10% in the mid- and far-infrared spectral regions, respectively. The *J*- and *K*-rotational dependences of these coefficients have been observed in the mid-infrared region and then a simulation has

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The ν_1, ν_4 and $3\nu_6$ bands of methyl chloride in the 3.4-μm region: Line positions and intensities

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ABSTRACT

Methyl chloride (CH_3Cl) is one of the most abundant chlorine-containing molecules in the atmosphere. For this reason a recent update was performed in HITRAN in the 640–2600 cm^{-1} region based on the line parameters generated in Nikitin et al. [Nikitin A, Champion JP, Bürger H. J Mol Spectrosc 2005;230:174–84] with the intensities scaled to existing experimental data. CH_3Cl has a rather strong signature around 3000 cm^{-1} which was used recently by the Atmospheric Chemistry Experiment (ACE) satellite mission to produce the first study of the global distribution of methyl chloride in the upper troposphere and stratosphere. However, it was mentioned that the CH_3Cl line positions and intensities spectroscopic parameters are of very low quality in this spectral region in the public access HITRAN or GEISA databases. We present a complete update of the line positions and line intensities for the ν_1, ν_4, $3\nu_6$ bands of $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ in the 3.4 μm region. For this task, Fourier transform spectra have been recorded at high resolution at the Laboratoire de Dynamique, Interactions et Réactivité in France. Measurements of line positions and line intensities have been retrieved for both isotopologues $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$ in the ν_1, ν_4, $3\nu_6$ bands. The theoretical model accounts for the interactions coupling the ($\nu_1=1$; $\ell=0$), ($\nu_4=1$; $\ell=\pm1$) and ($\nu_6=3$; $\ell=\pm1$) energy levels, together with additional resonances involving several