Spectroscopy Evaluation 2740-2830 cm^{-1}

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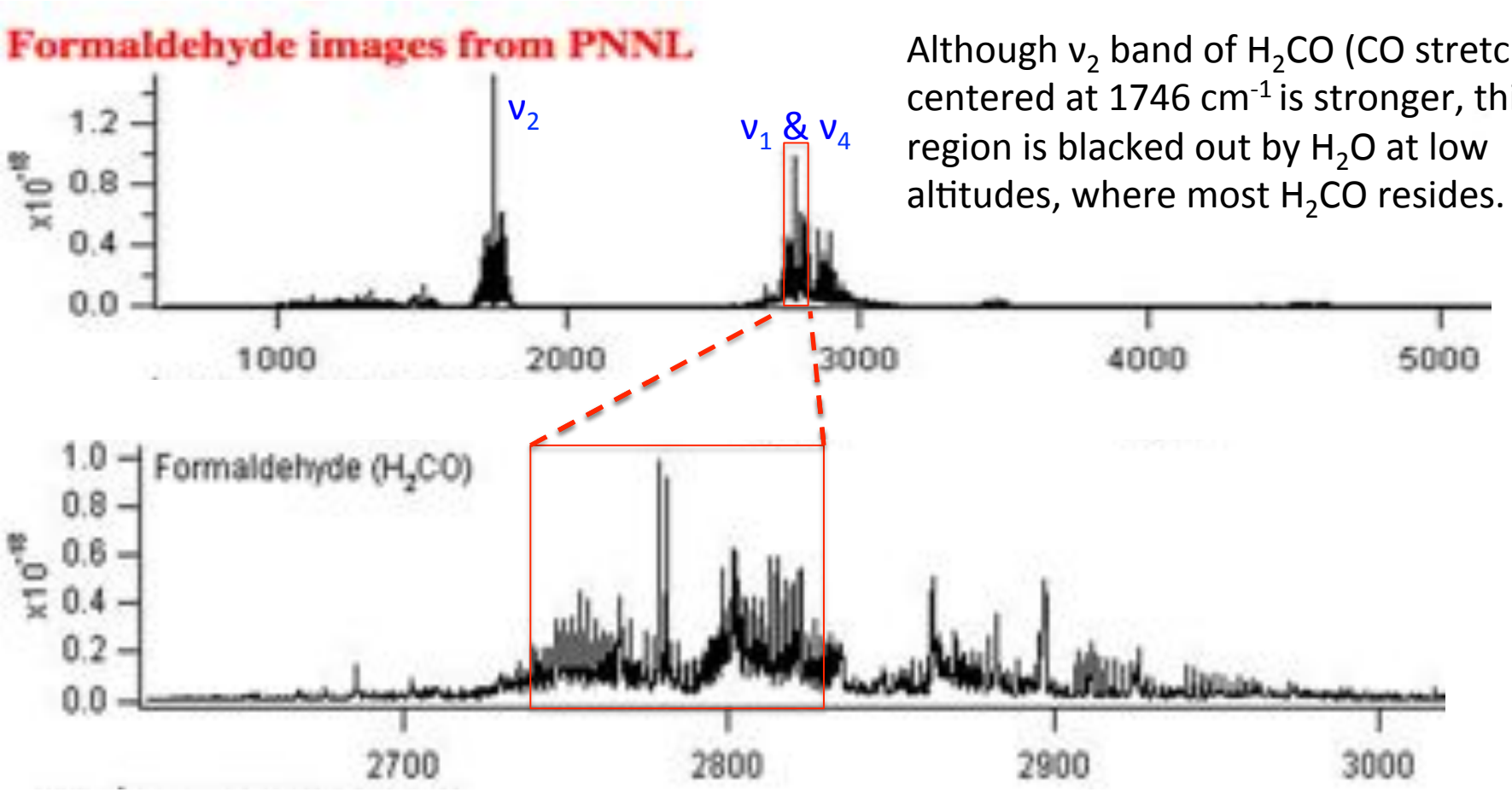
For H_2CO this region provides the best spectral windows in the IR due to the presence of the ν_1 band of H_2CO (CH_2 symmetric stretch) centered at 2783 cm^{-1}.

This spectral region contains strong absorptions of several gases including:
CH_4, HDO, N_2O, O_3, H_2O, CO_2, HCl, H_2CO

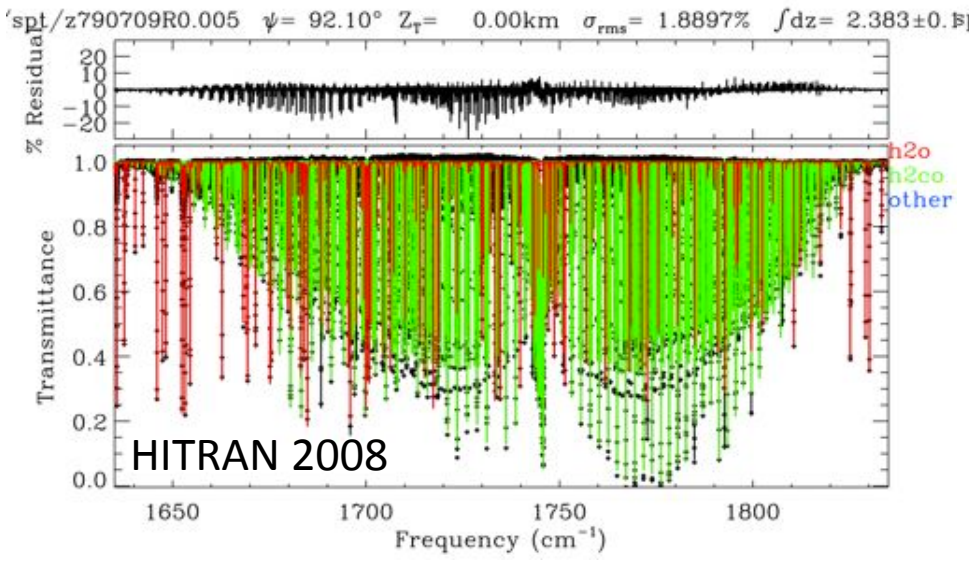
PNNL spectra of H_2CO

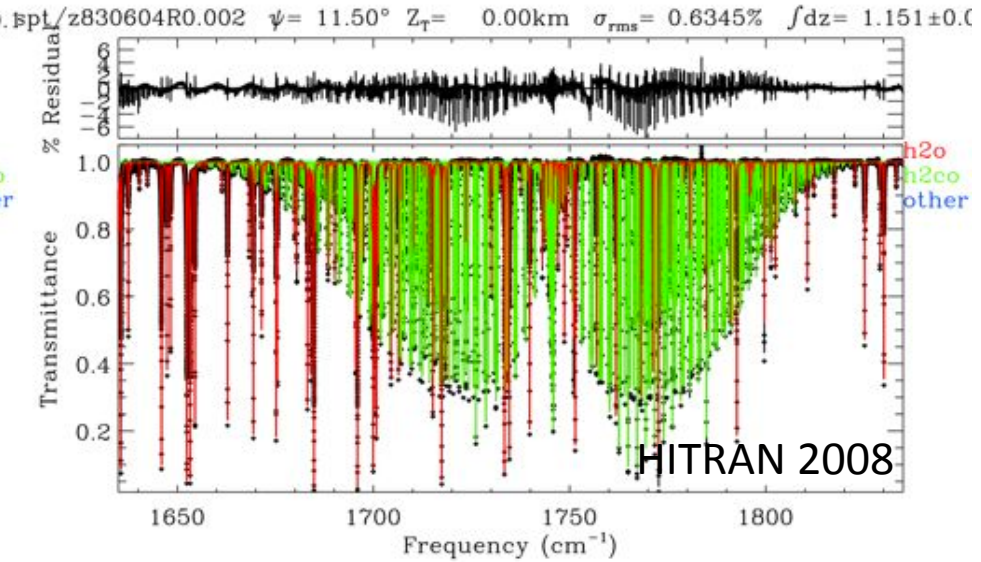


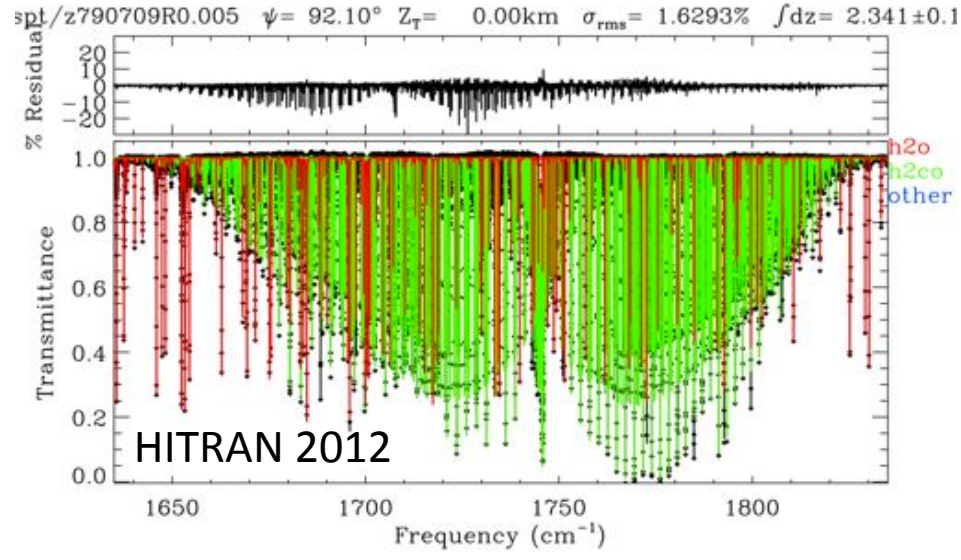
Although v_2 band of H_2CO (CO stretch) centered at 1746 cm^{-1} is stronger, this region is blacked out by H_2O at low altitudes, where most H_2CO resides.

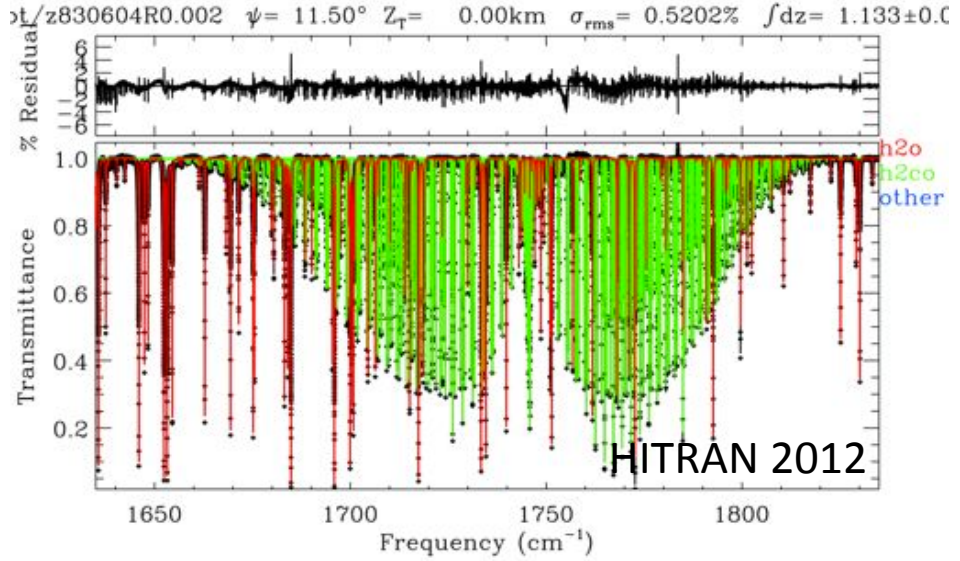
The 2740-2830 cm^{-1} region contains dozens of H_2CO absorption features, all blended with much stronger absorption from HDO, CH_4, N_2O etc. If these interferences are well fitted, however, it might be possible, to nevertheless accurately infer H_2CO column amounts.

Spectral Fits to Kitt Peak H_2CO v_2 band

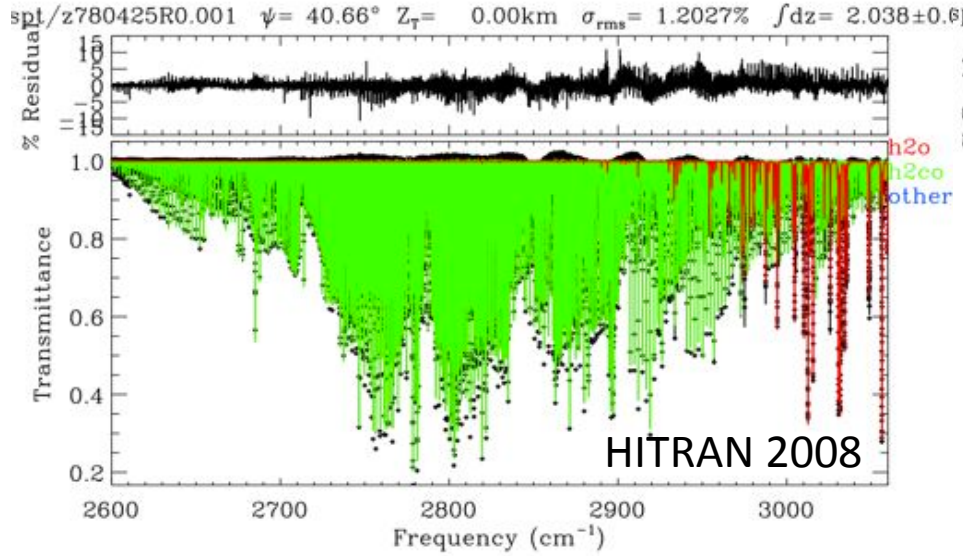


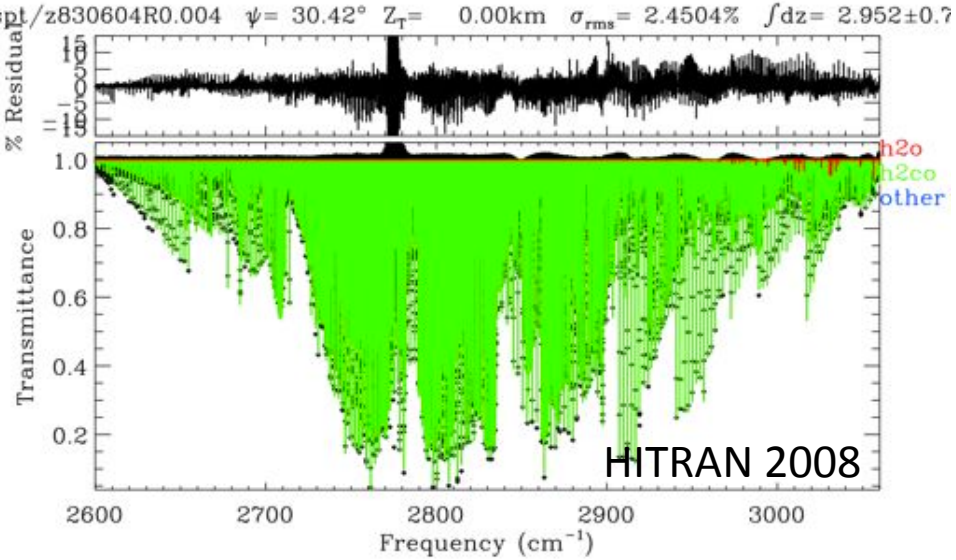


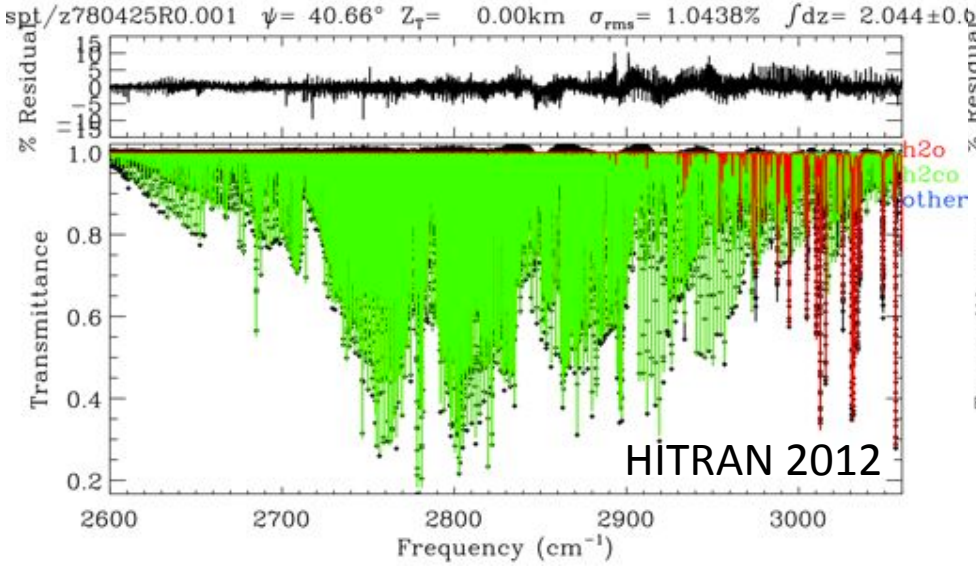


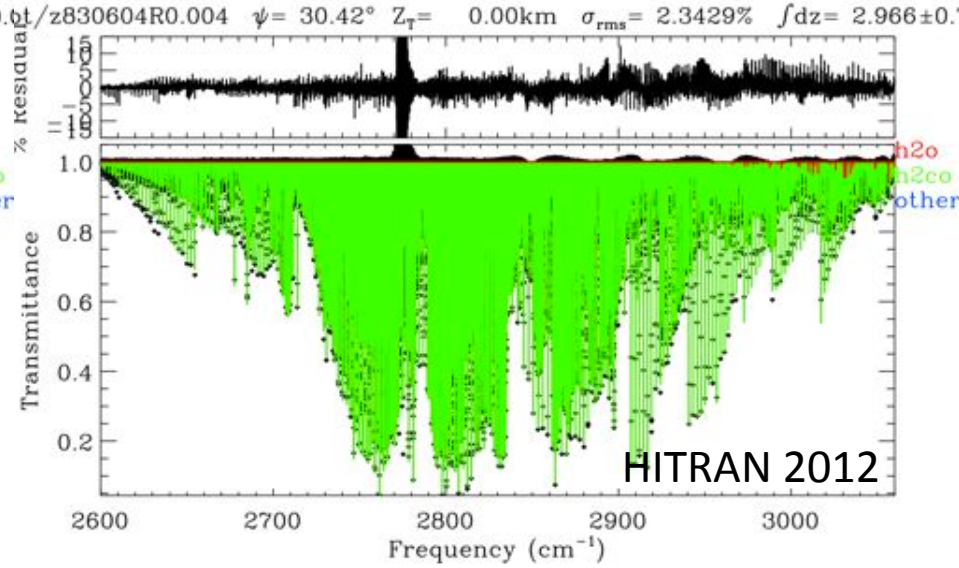


Spectral Fits to KP H_2CO v_1 & v_4 bands









H_2CO Spectroscopy Conclusions

Fits to Kitt Peak laboratory spectra of H_2CO reveal HITRAN 2012 an improvement over HITRAN 2008 due to the improved width parameters of Jacquemert et al. [2010]. This is true both in the ν_2 band around 1745 cm^{-1} and the ν_1 & ν_4 bands around 2800 cm^{-1}

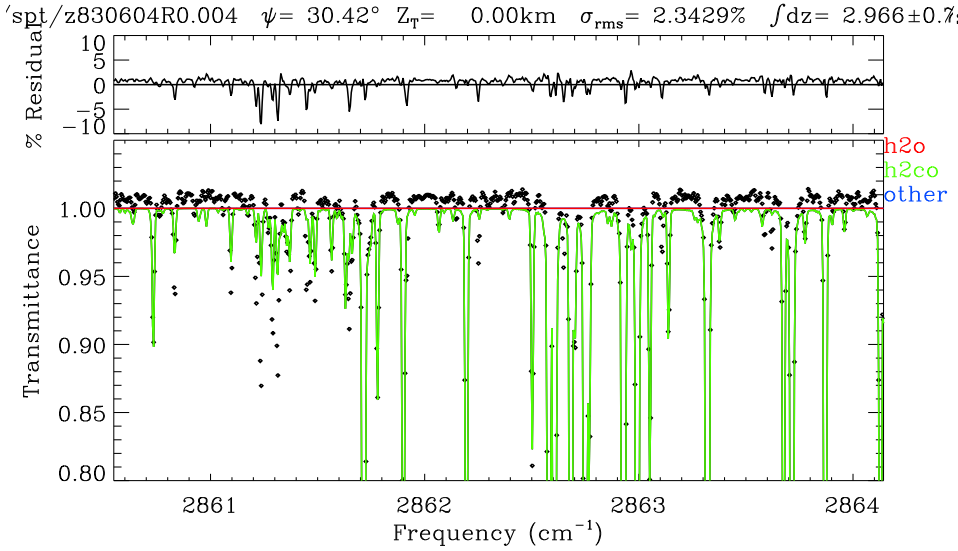
Formaldehyde around 3.5 and 5.7-μm: Measurement and calculation of broadening coefficients

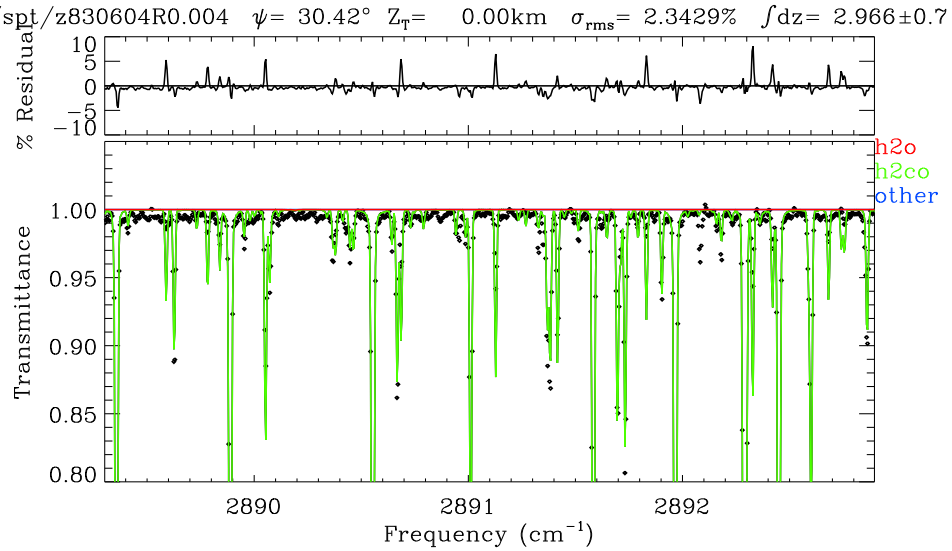
D. Jacquemart[a, b], A. Laraia[c], F. Kwabia Tchana[a, b, 1], R.R. Gamache[c], A. Perrin[d], N. Lacome[a, b]

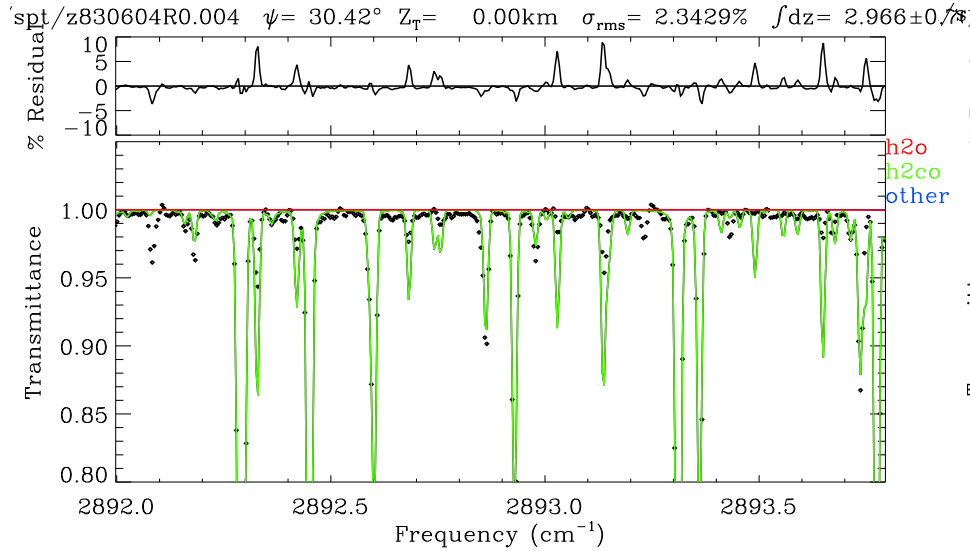
There are still some obvious deficiencies in the HITRAN 2012 H_2CO:

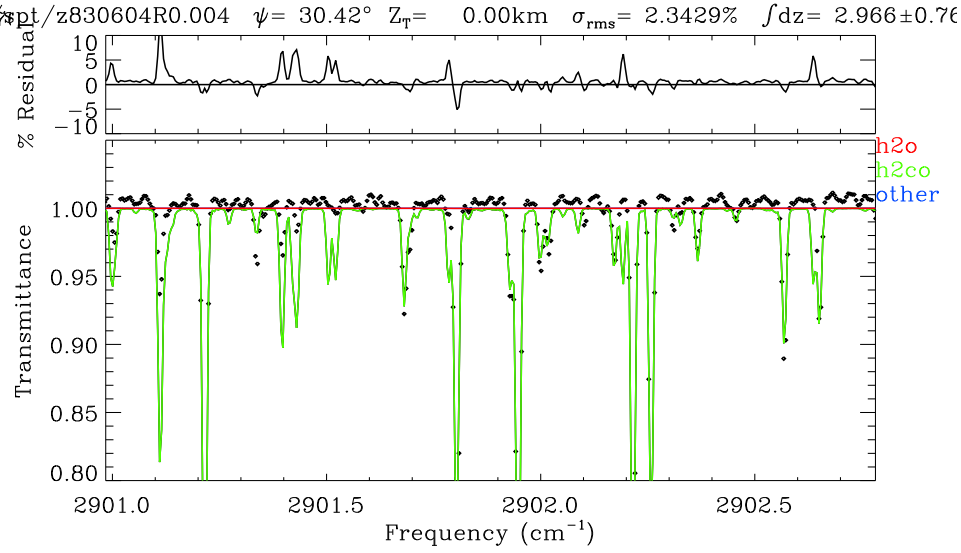
- The missing ν_2 $H_2{}^{13}CO$ band with its Q-branch at 1708 cm^{-1}
- Many lines throughout the bands have large intensity & position errors.

Examples of large residuals 2800-3000 cm^{-1}









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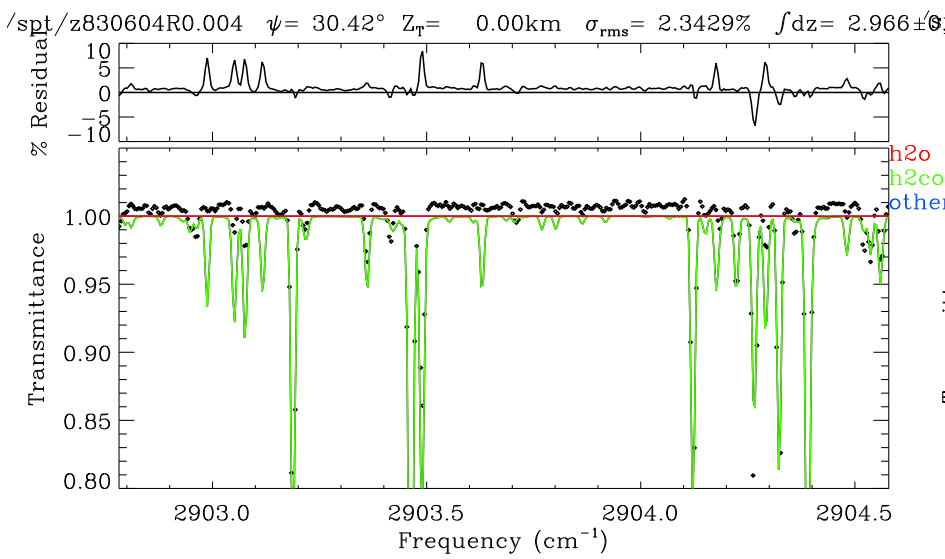

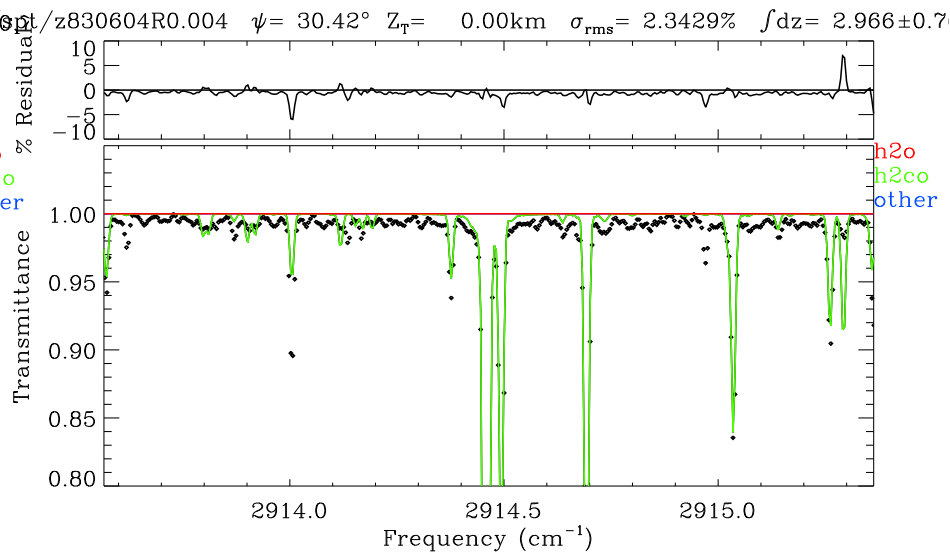

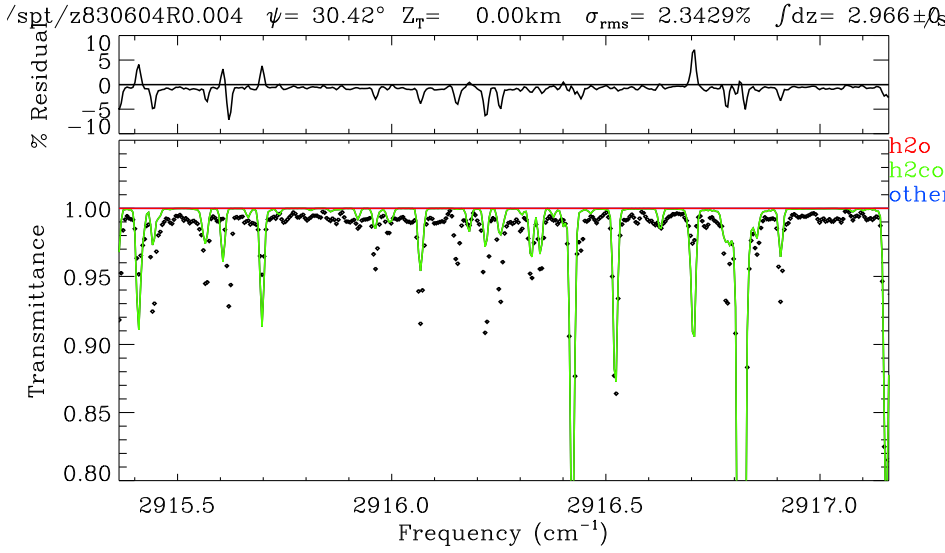

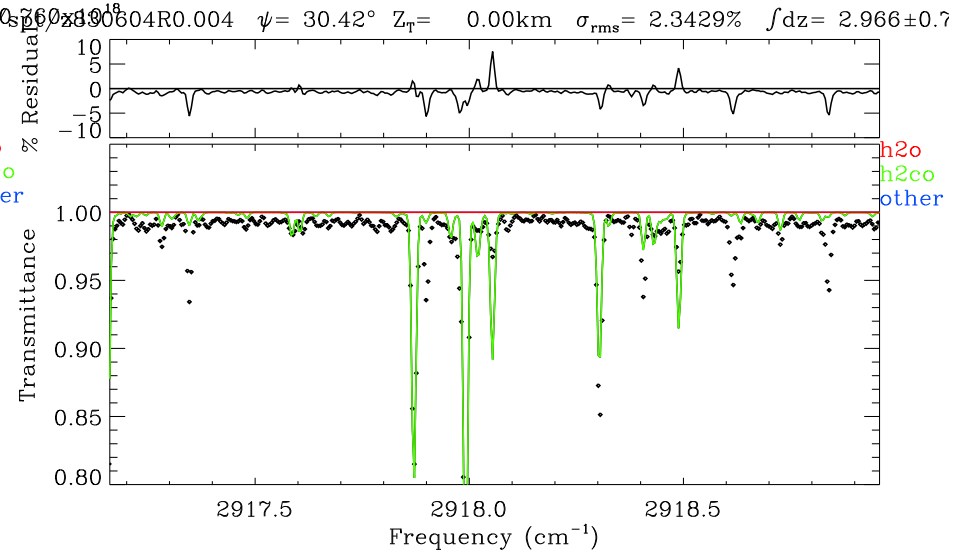

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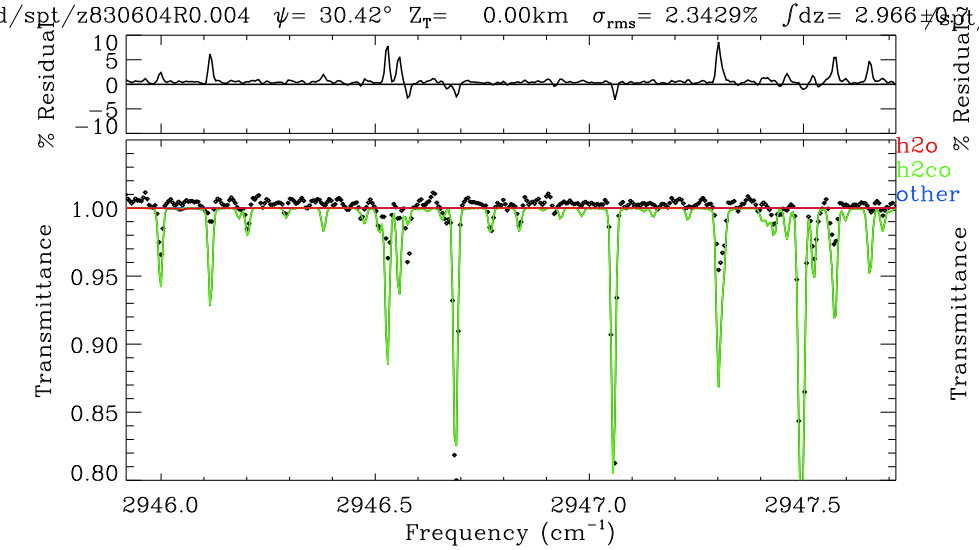

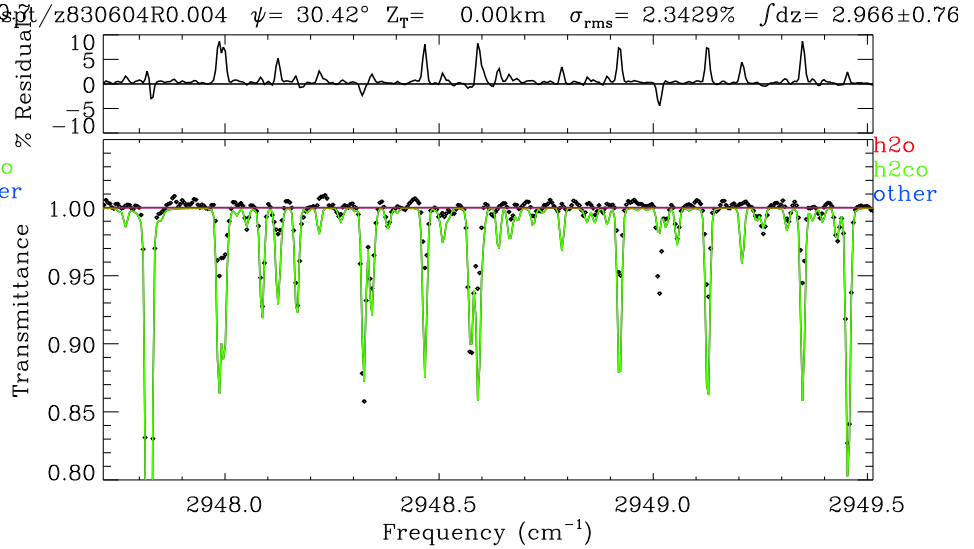

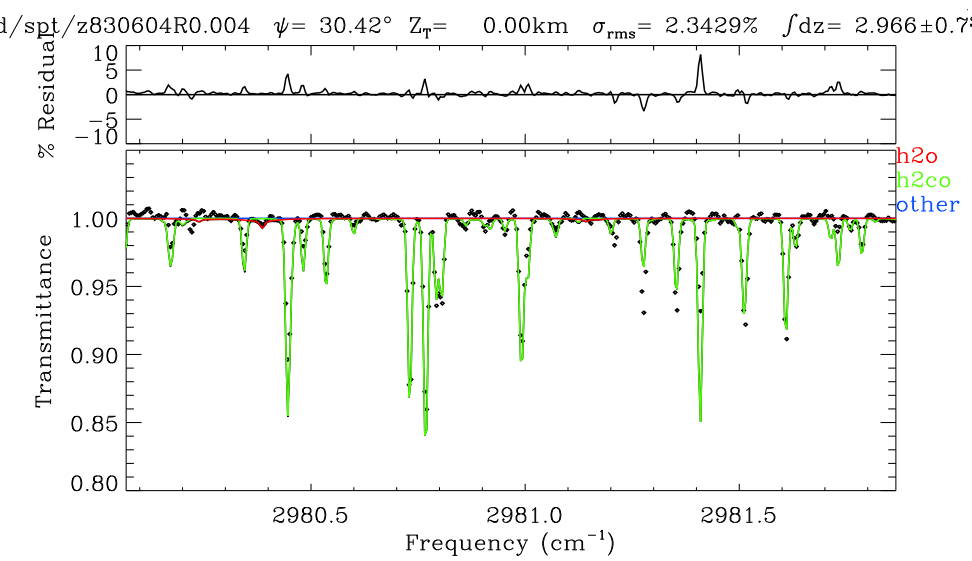

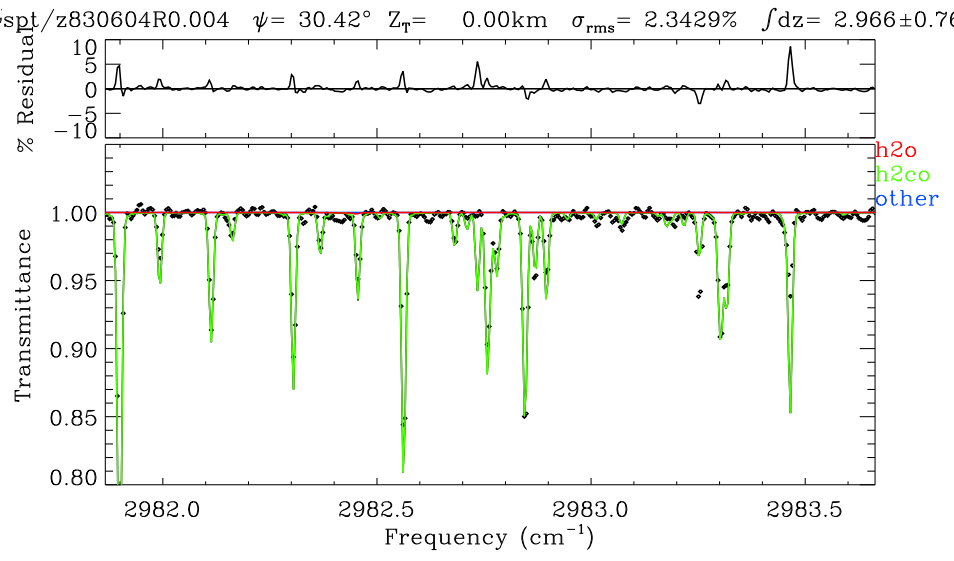

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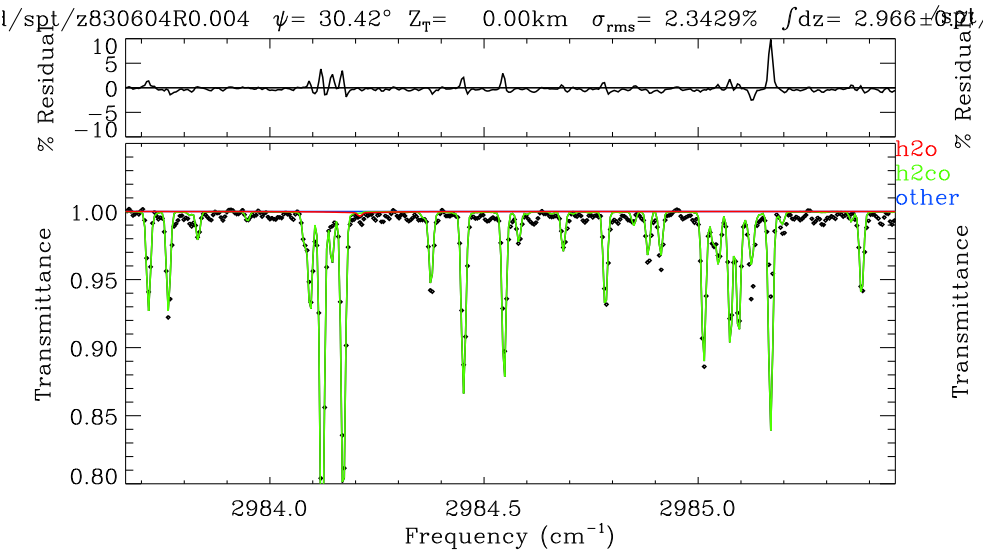
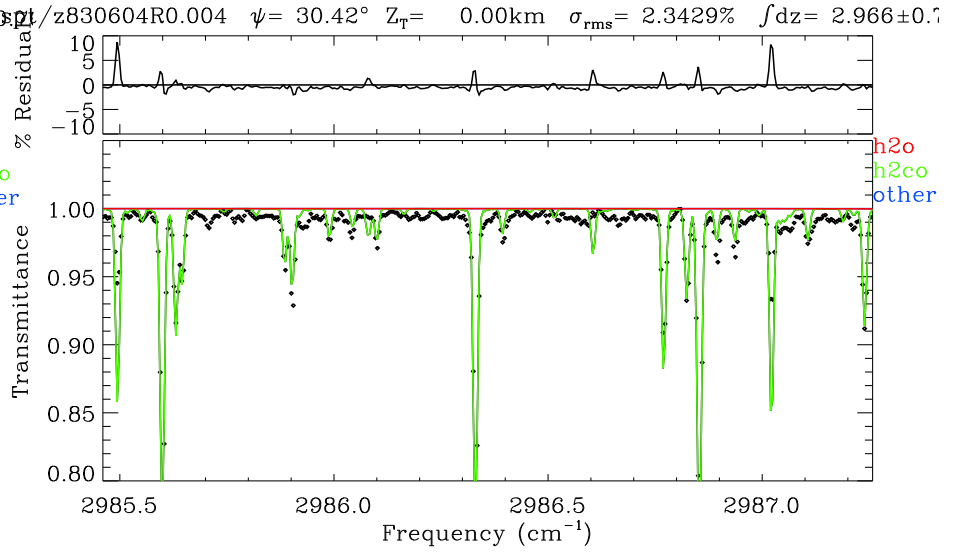
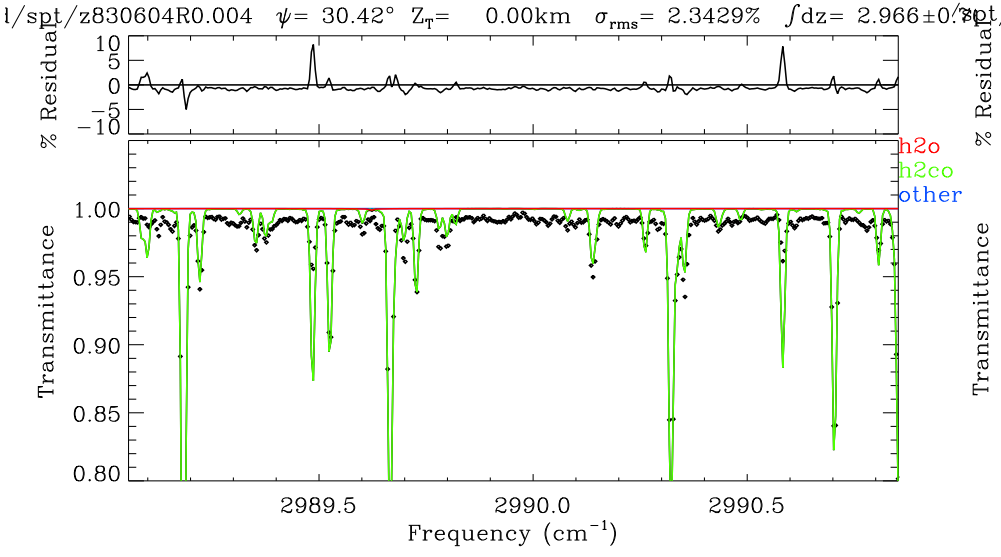
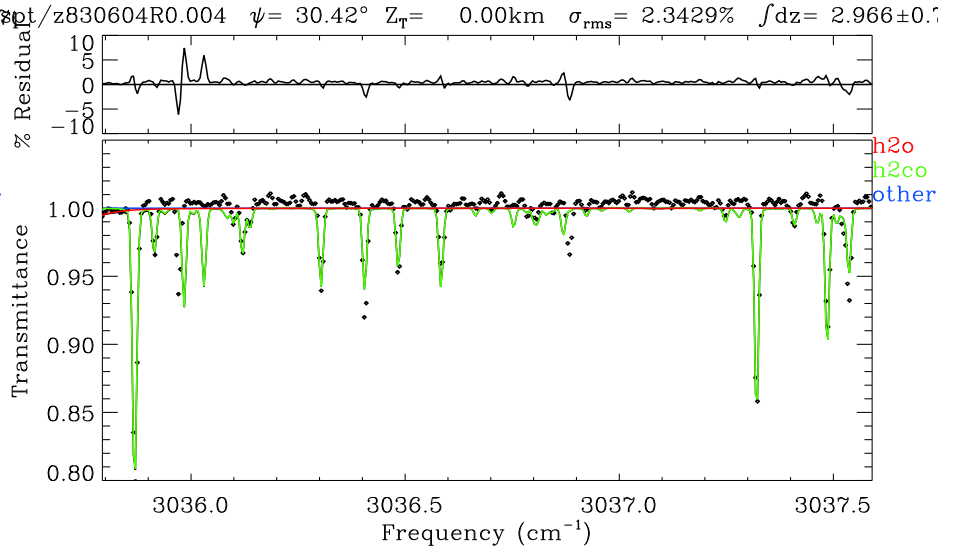
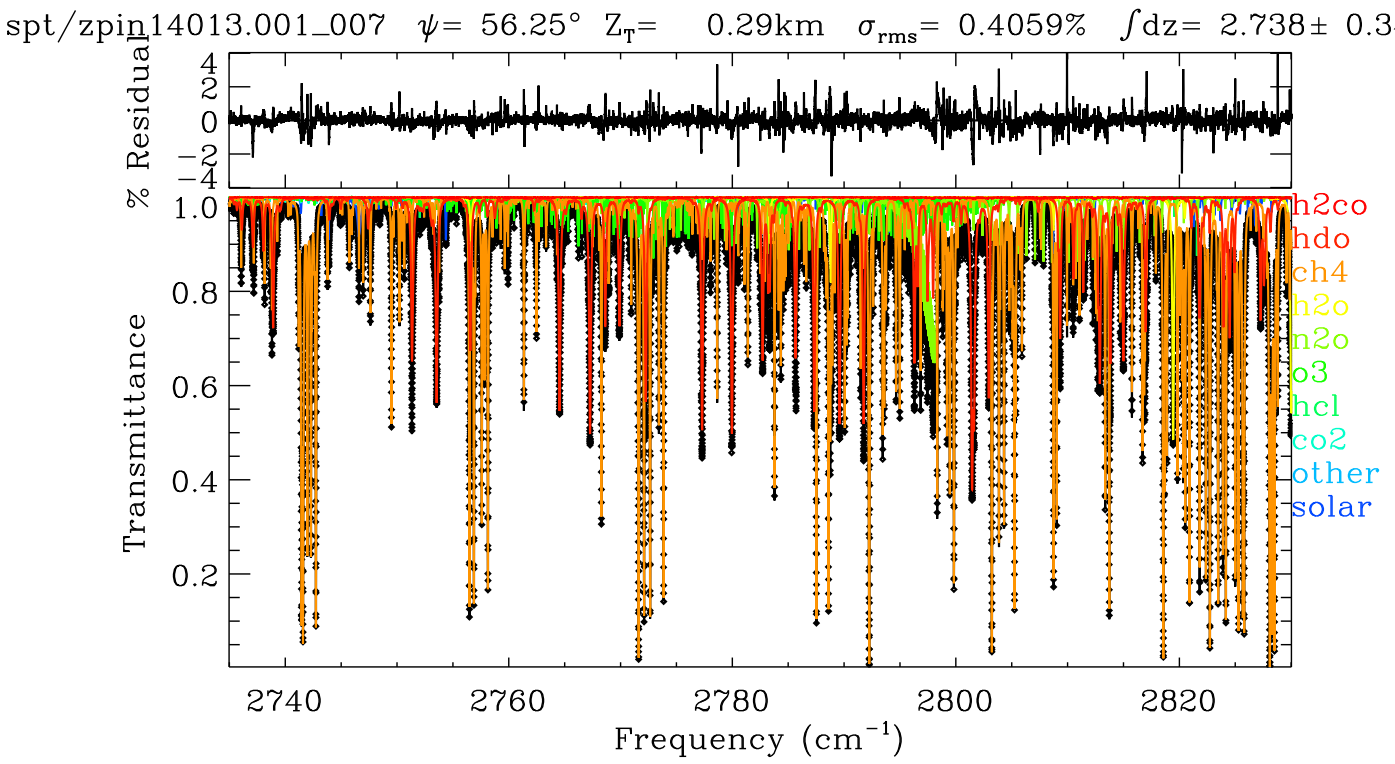


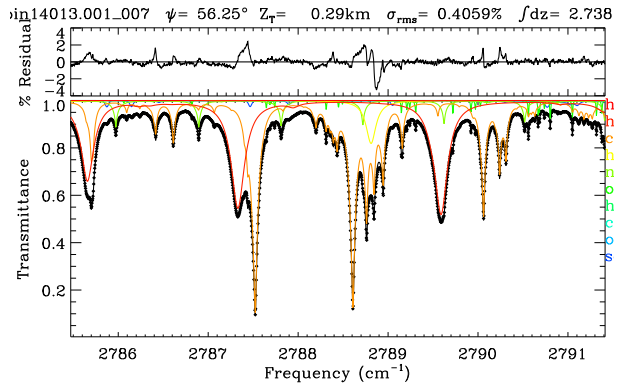


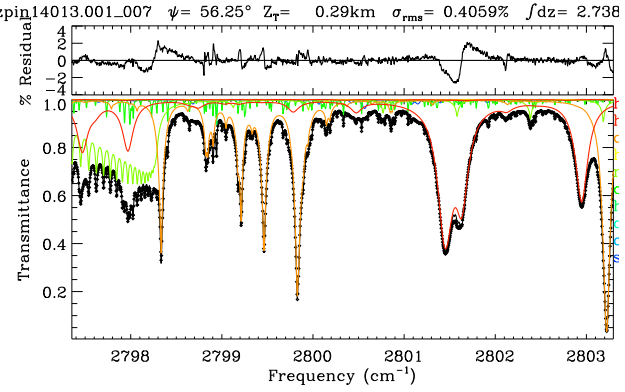


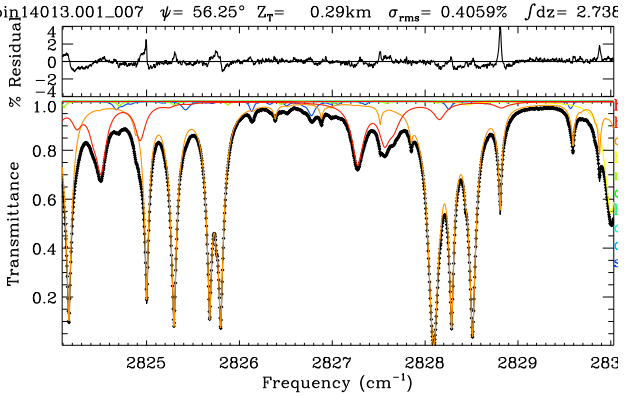


MkIV ground-based: HITRAN 2012

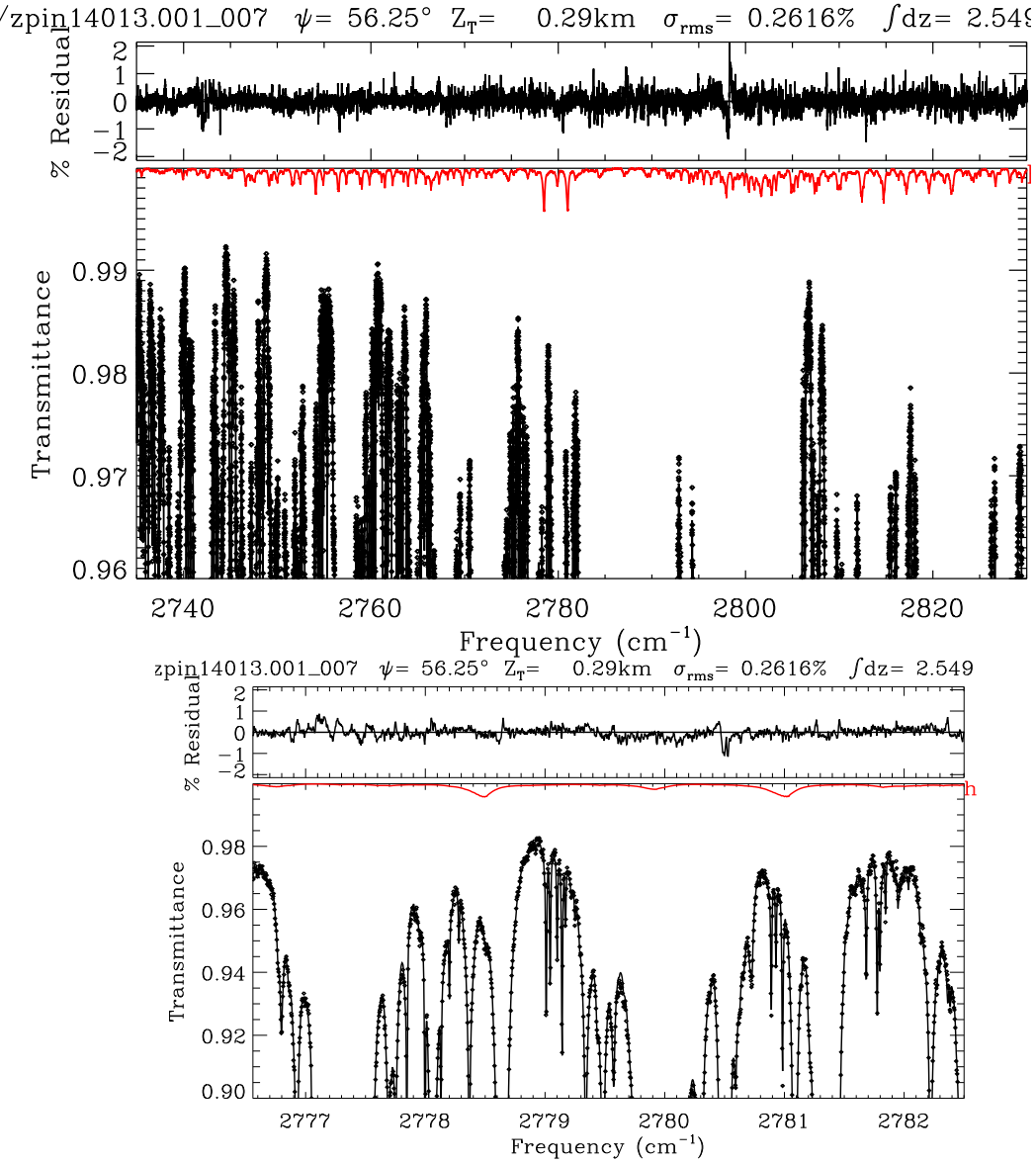








H_2CO absorption



H_2CO never contributes more than 20% of the total absorption anywhere in the spectrum, at least at a column of 2.5×10^{15} molec/cm^2

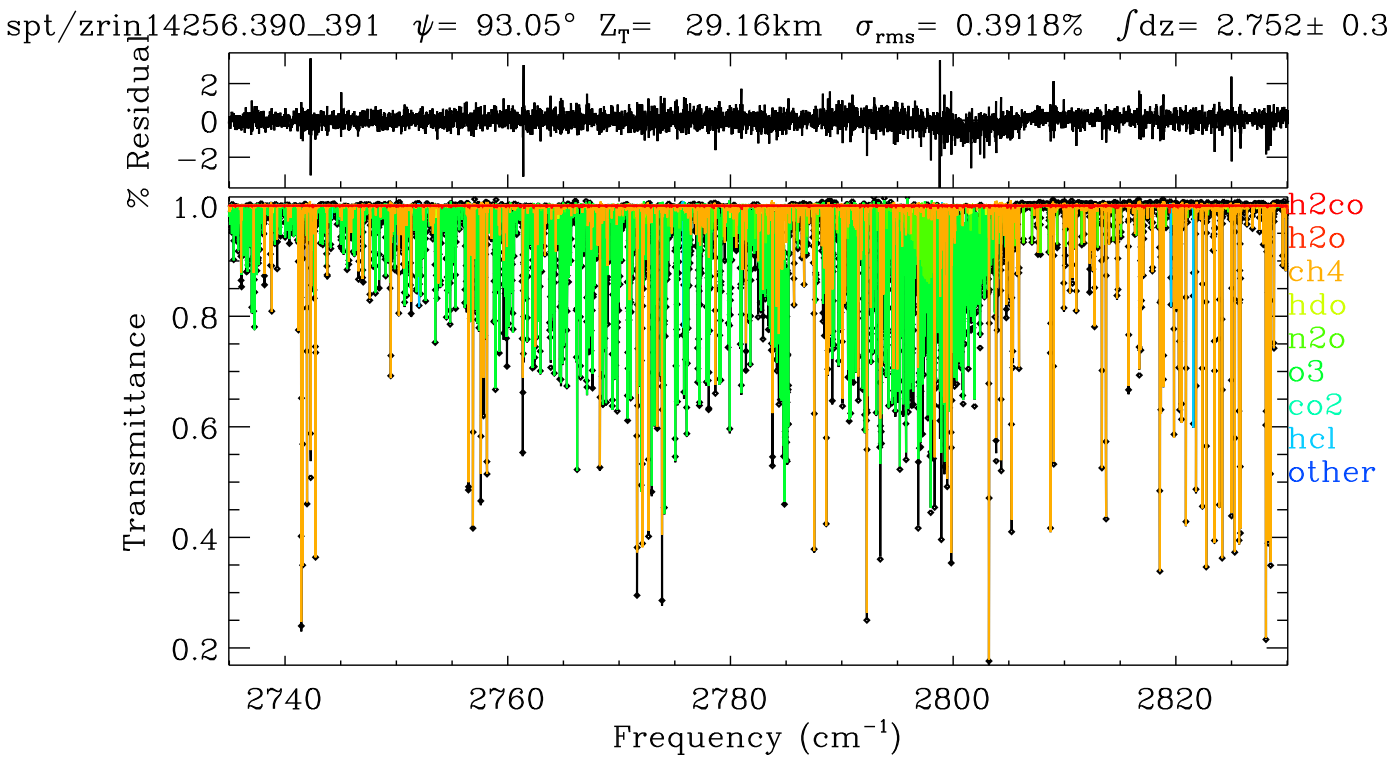
The retrieved column amounts will therefore be critically dependent on the modeling of the strong interfering absorptions.

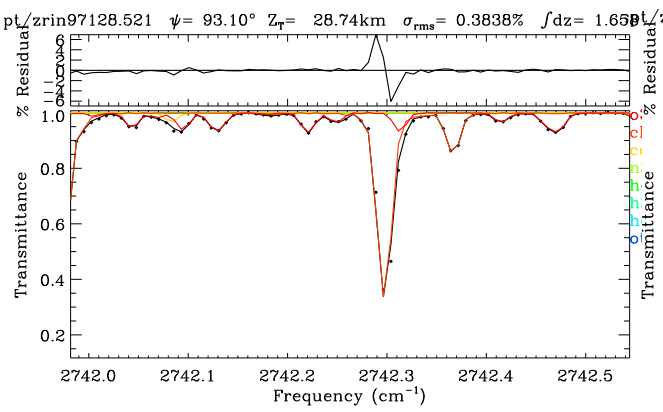
Traditionally narrow H_2CO windows have been defined centered on the strongest H_2CO absorption features.

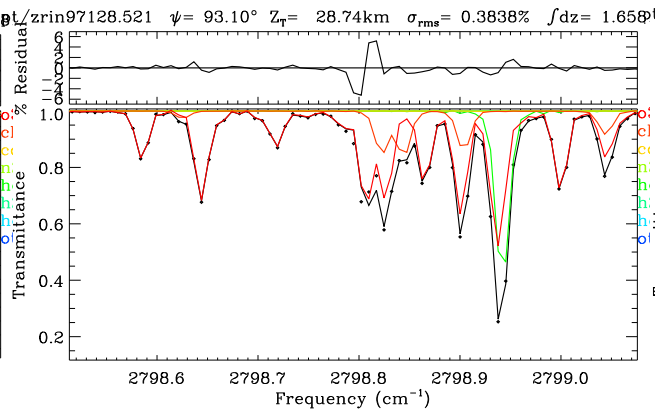
But potentially much more H_2CO information could be extracted if a very wide window were fitted.

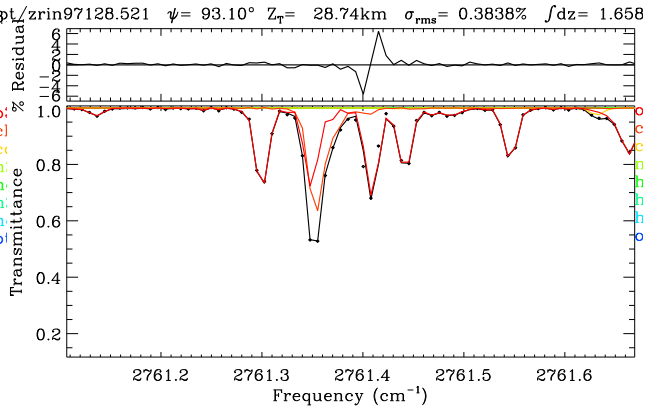
Would require all interfering gas absorptions to be well fitted

MkIV Balloon 30 km (HITRAN 2012)









Strategy for improving spectroscopy

1) Fit ground-based and balloon borne MkIV solar absorption spectra

2) Examine large systematic residuals and find out which gas is responsible

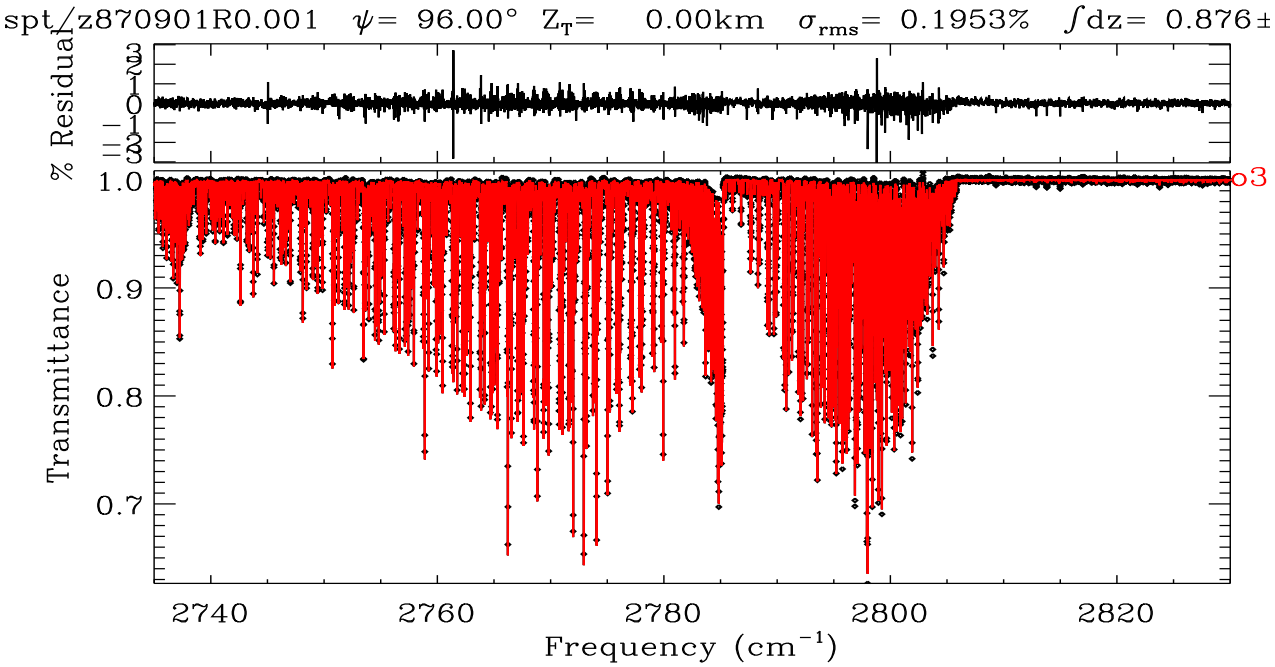
3) Fit laboratory spectra of responsible gas in same spectral region:

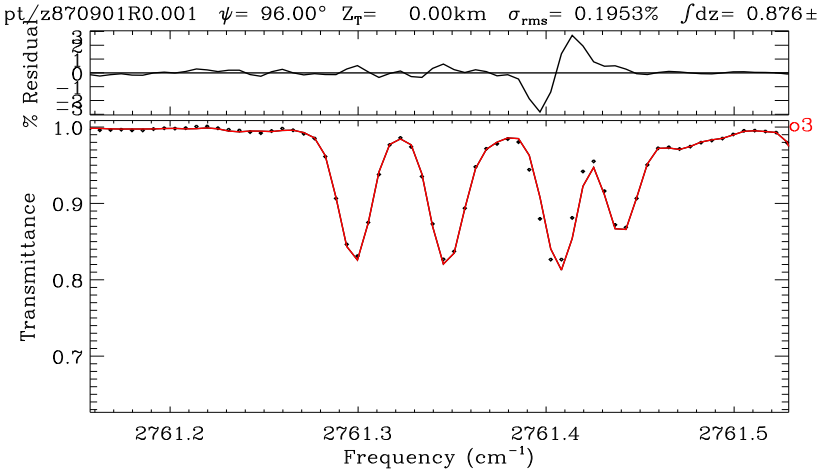
4) Adjust spectroscopic parameters to improve fits to laboratory spectra
- From low pressure spectra adjust positions and intensities
- From air-broadened spectra adjust widths and shifts

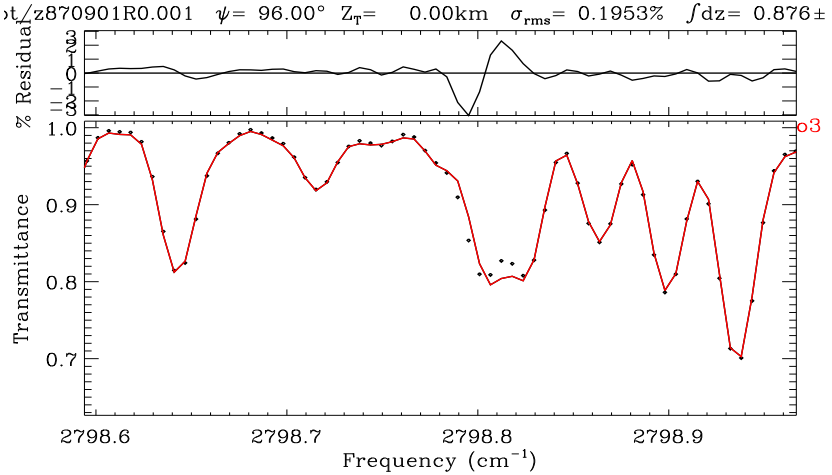
5) Go to 1 (until all large residuals have been removed)

Although spectroscopic problems are identified from atmospheric spectral fits, the adjustments are based solely on laboratory spectra (except for weak H_2O, O_2, and N_2).

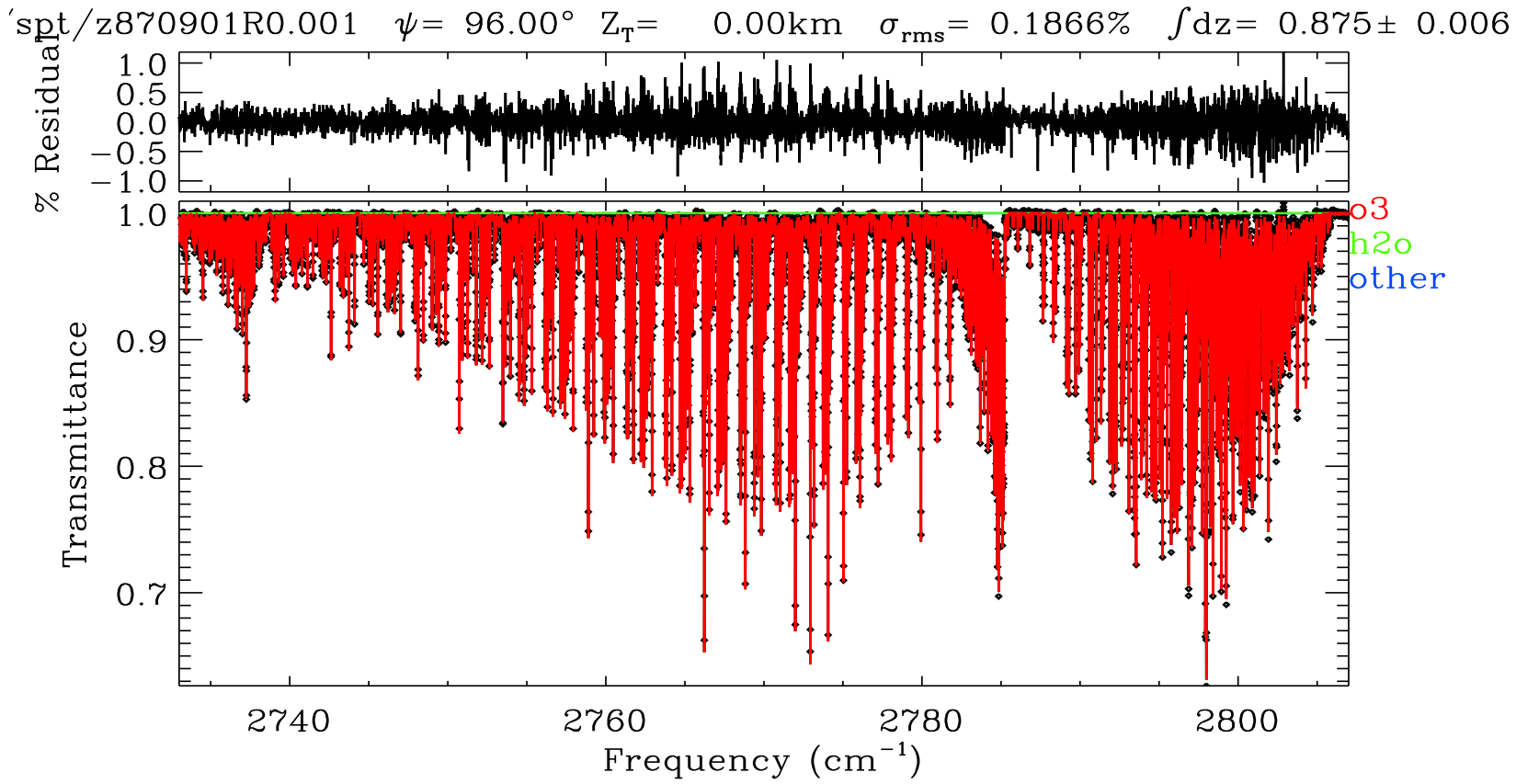
Kitt Peak Lab O_3 spectra (HIT 2012)





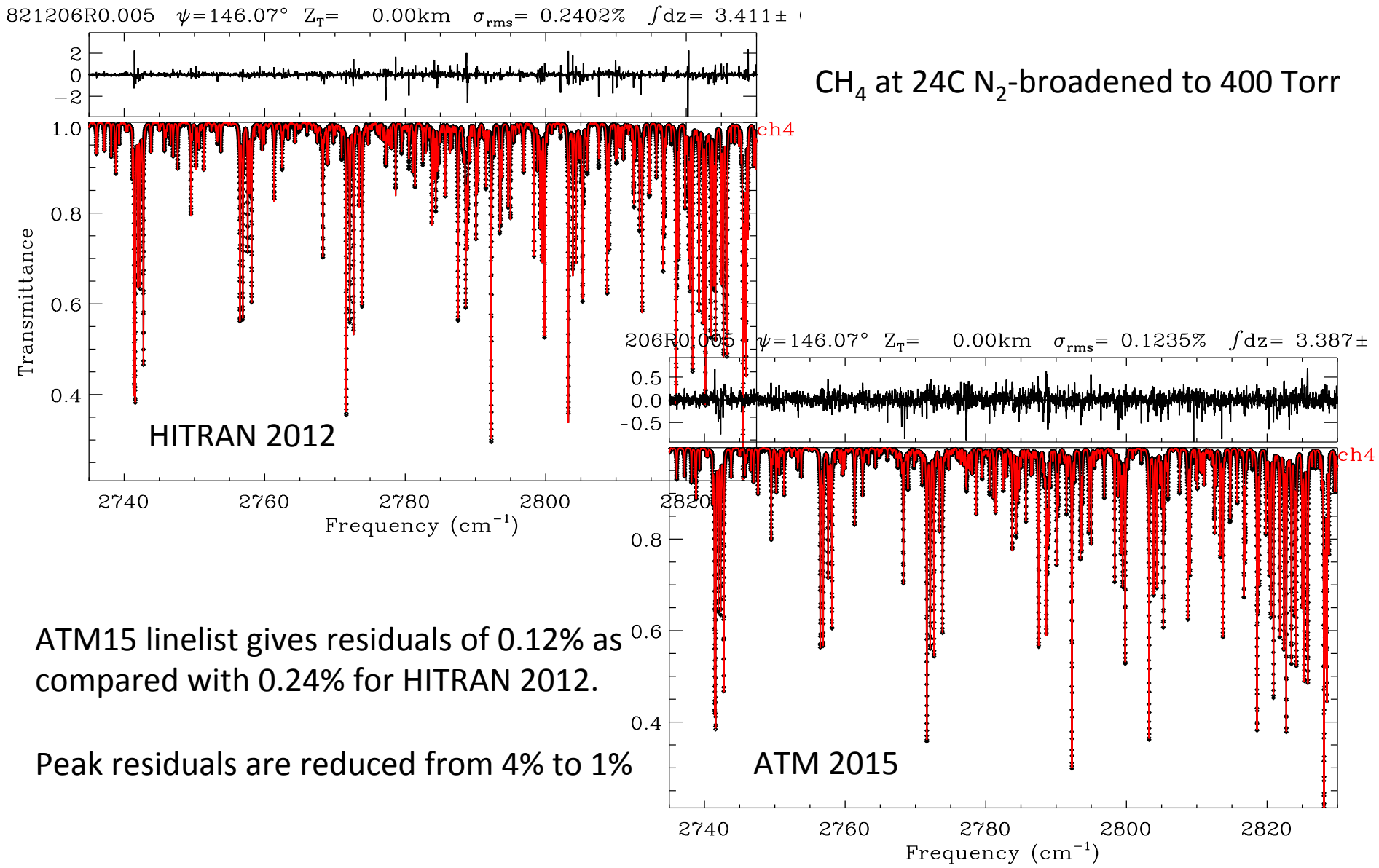


Kitt Peak lab O_3 spectra (ATM15)



Peak residuals reduced from 3% to 1% by adjusting line positions. Offending O_3 lines are “in resonance” and so their calculated positions are inaccurate

Kitt Peak Lab CH_4

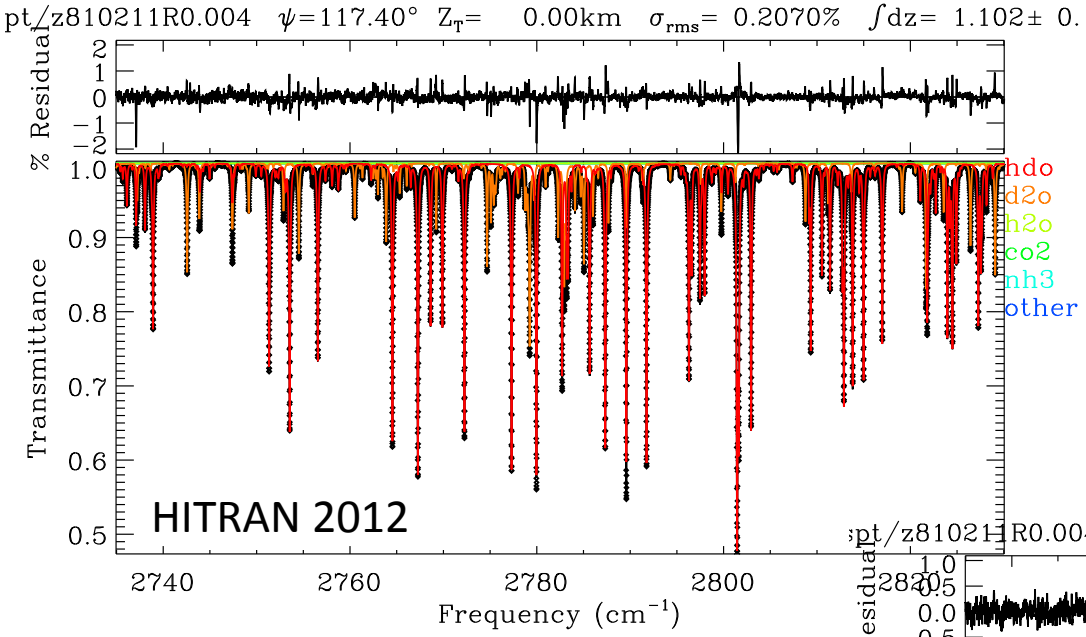


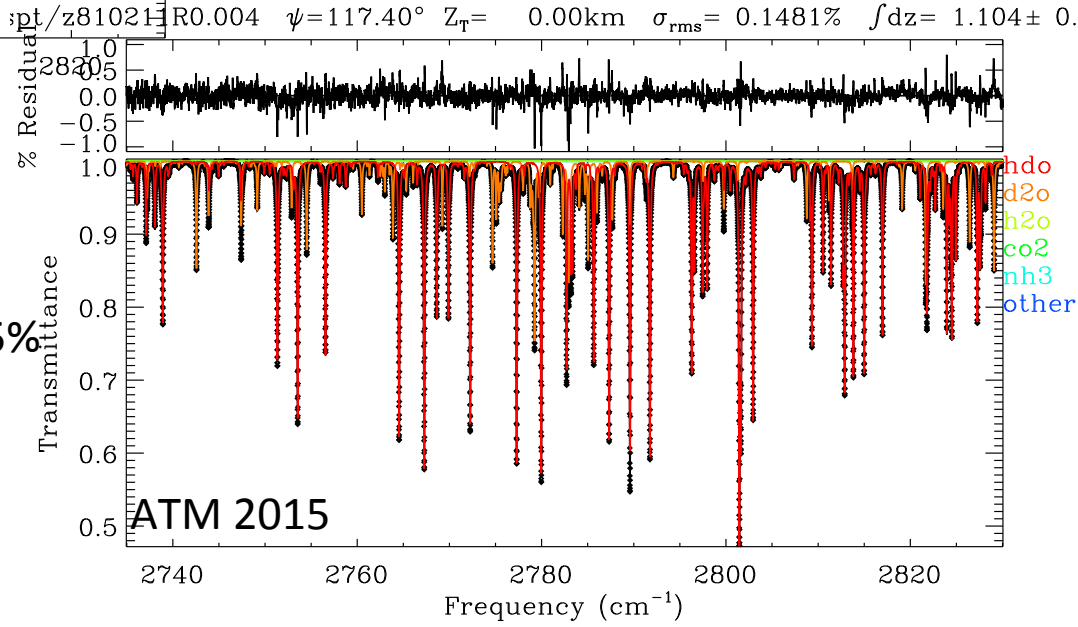
CH_4 at 24C N_2-broadened to 400 Torr

ATM15 linelist gives residuals of 0.12% as compared with 0.24% for HITRAN 2012.

Peak residuals are reduced from 4% to 1%

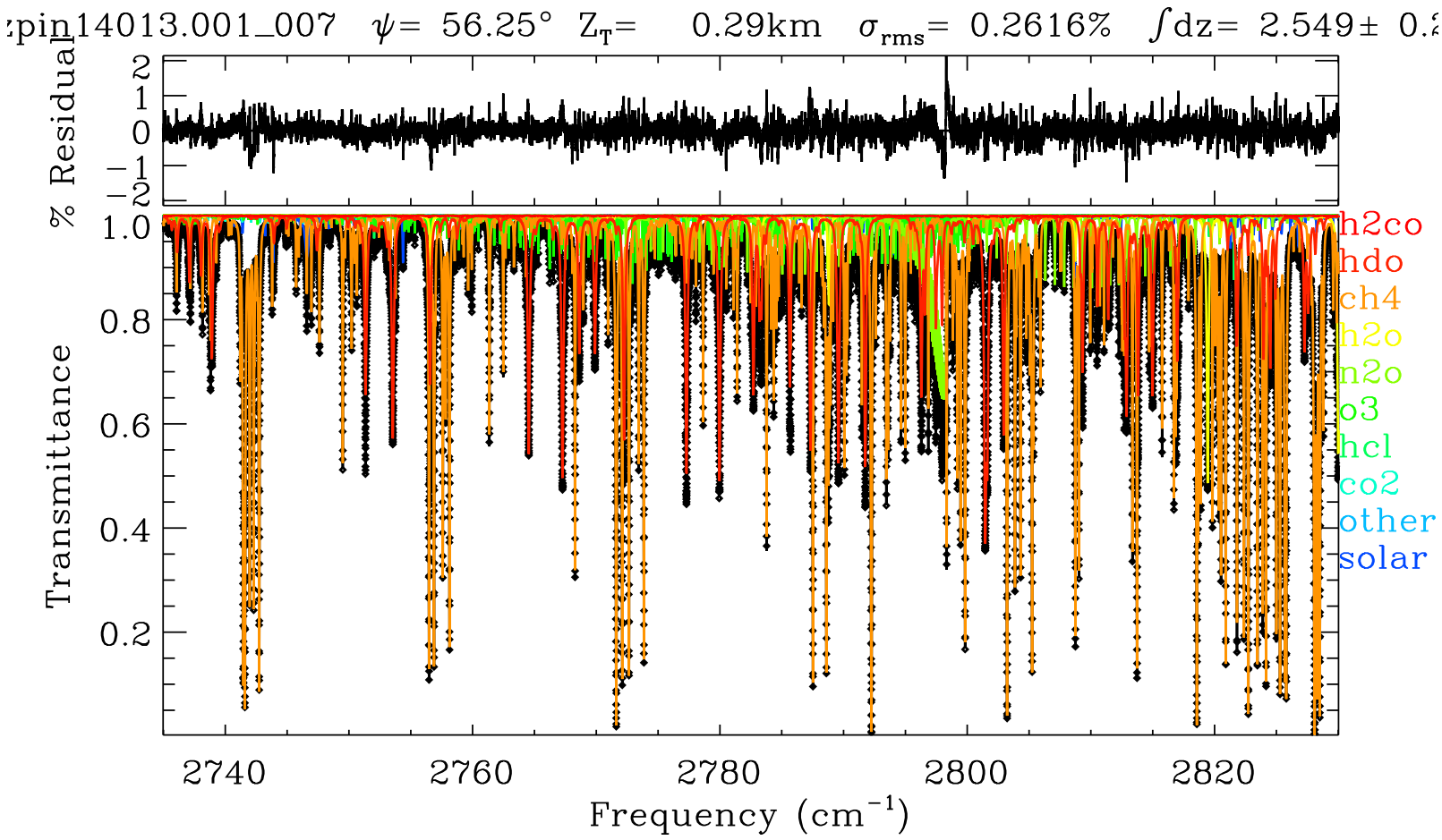
Kitt Peak lab HDO





After adjusting widths and pressure shifts
Rms residuals reduced from 0.21% to 0.15%
Peak residuals reduced from 2% to 1%

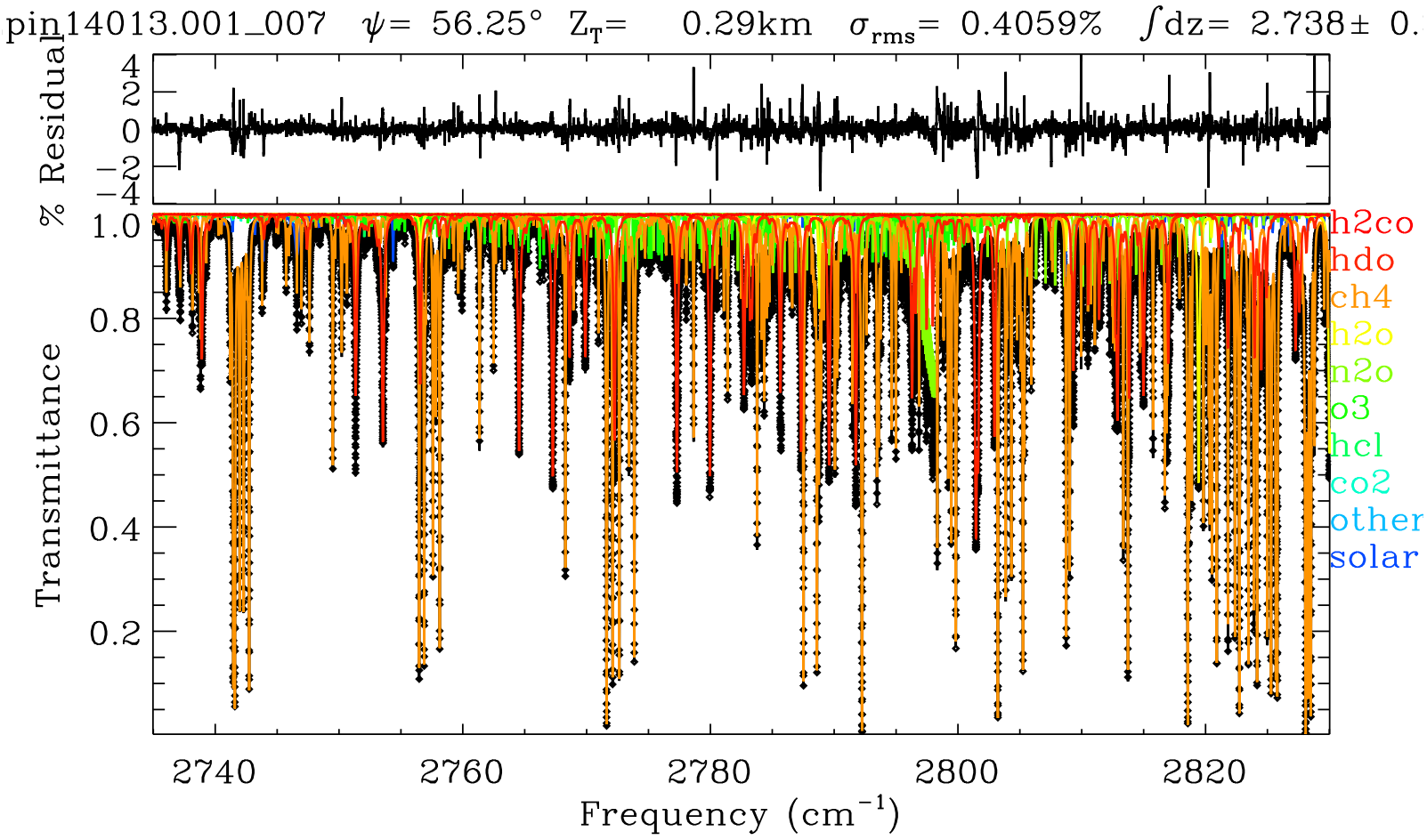
MkIV ground-based: ATM 2015



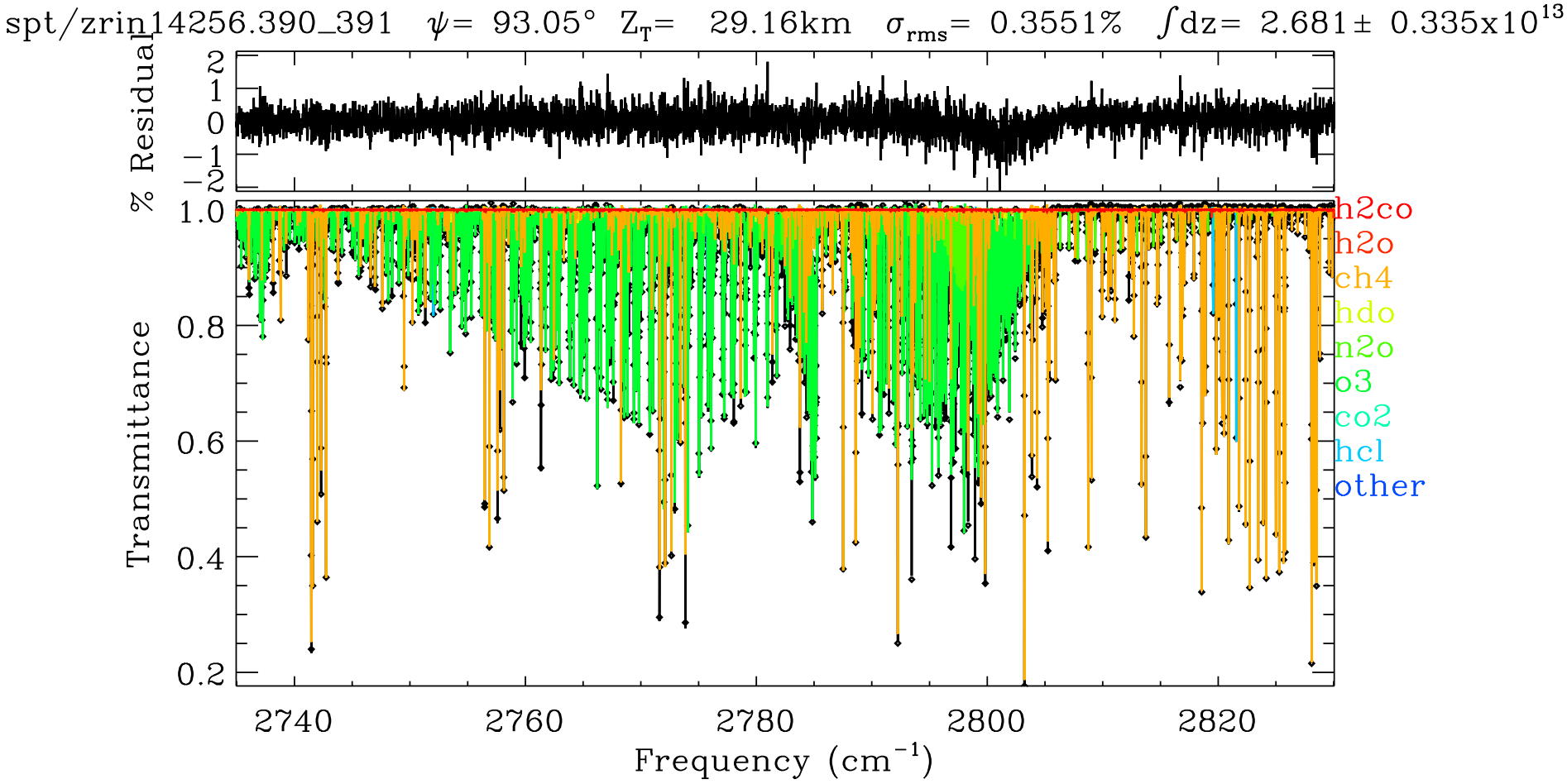
Fits to MkIV ground-based spectra using empirically-adjusted ATM15 linelist are much better than using HITRAN 2012: 0.26% rms versus 0.40%

Main remaining problem is line-mixing from N_2O Q-branch at 2798 cm^{-1}

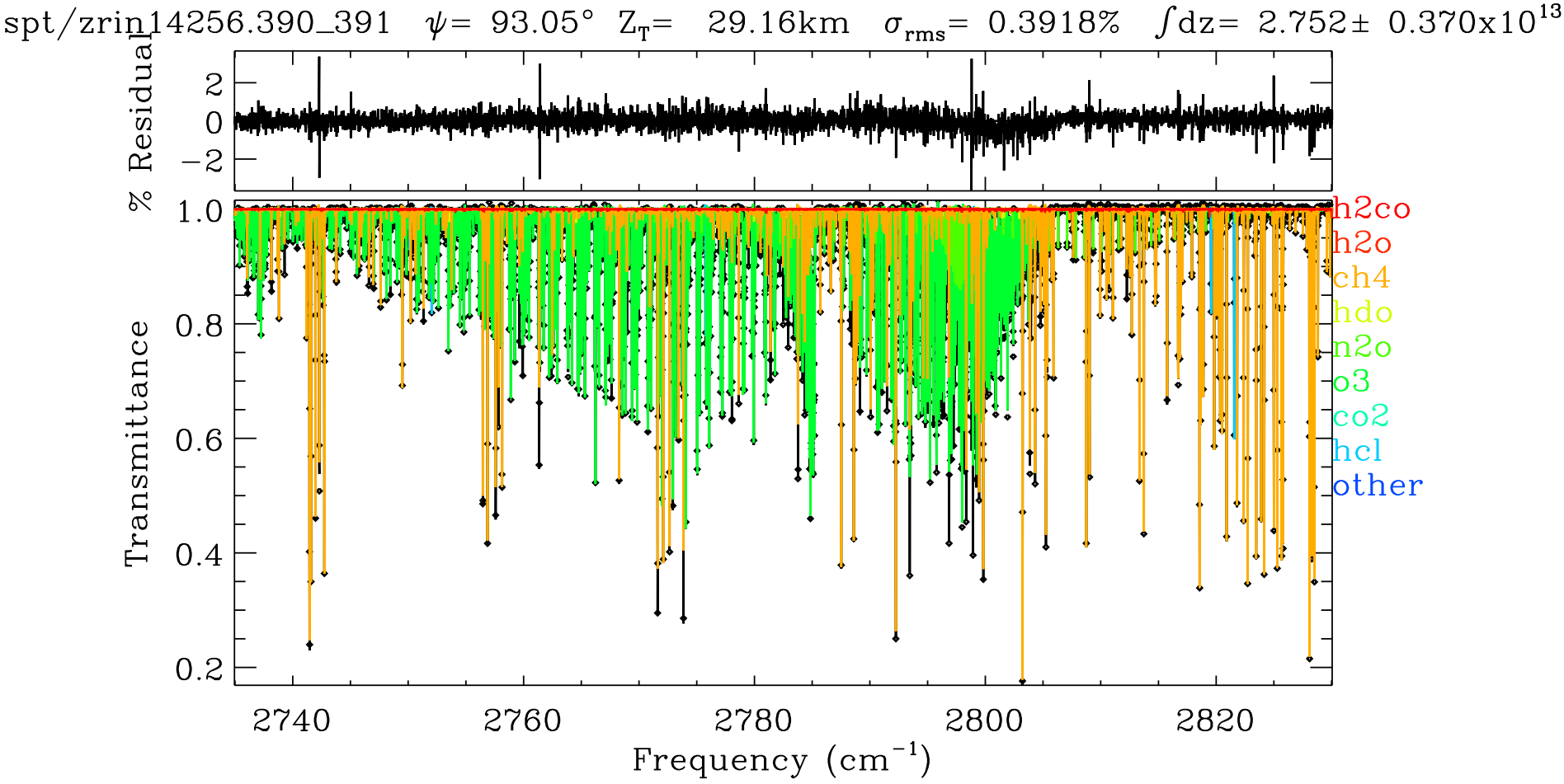
MkIV ground-based: HITRAN 2012



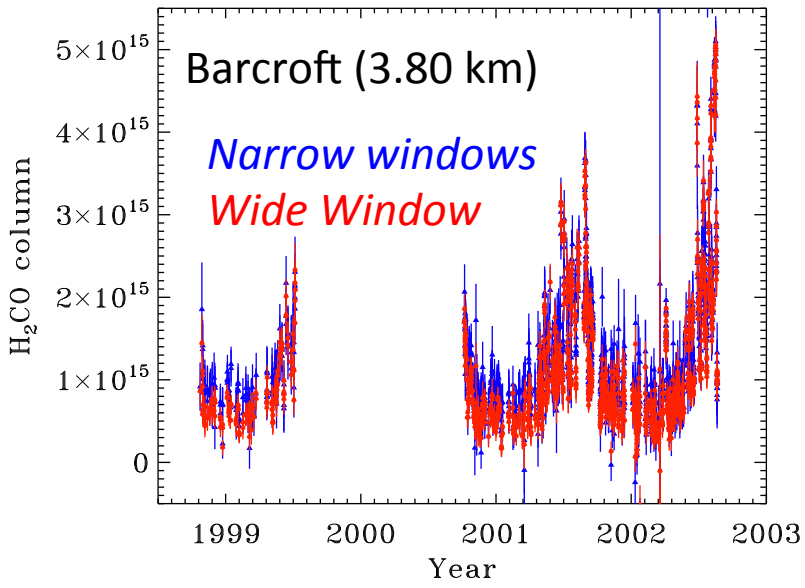
MkIV Balloon (ATM 2015)

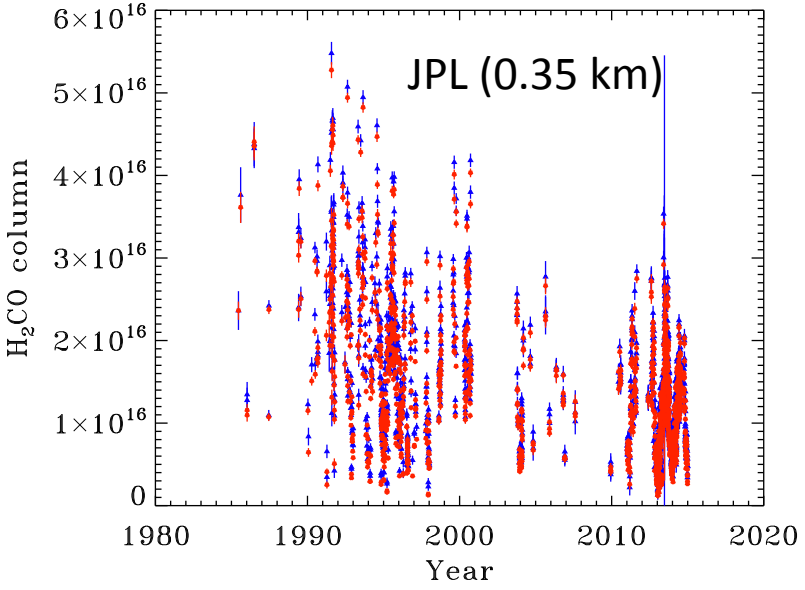


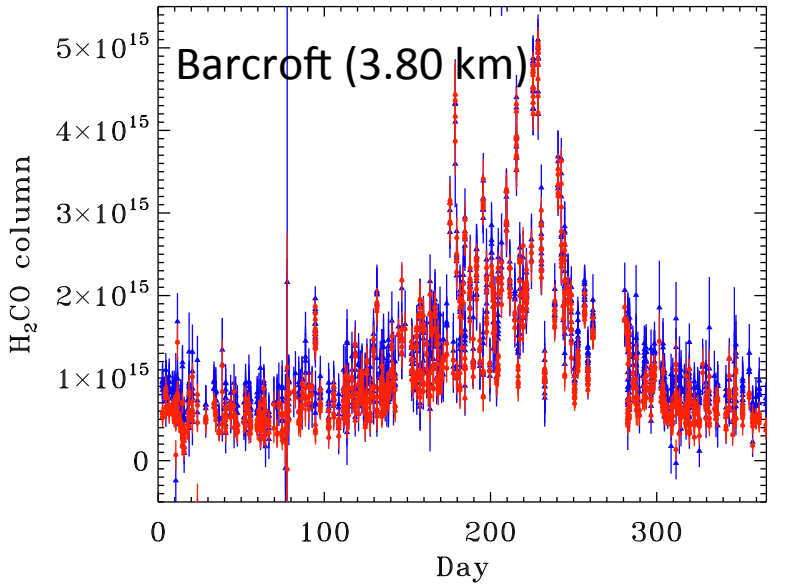
MkIV Balloon (HITRAN 2012)

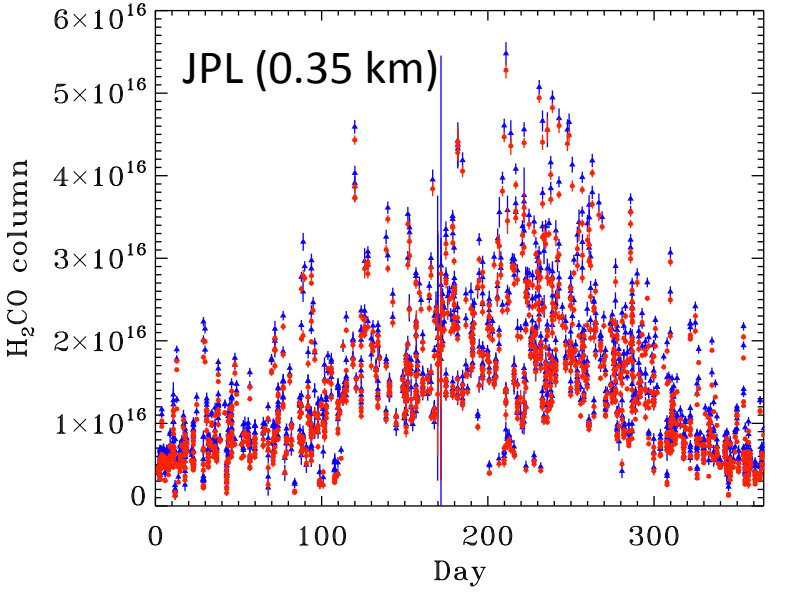


MkIV ground-based H_2CO column

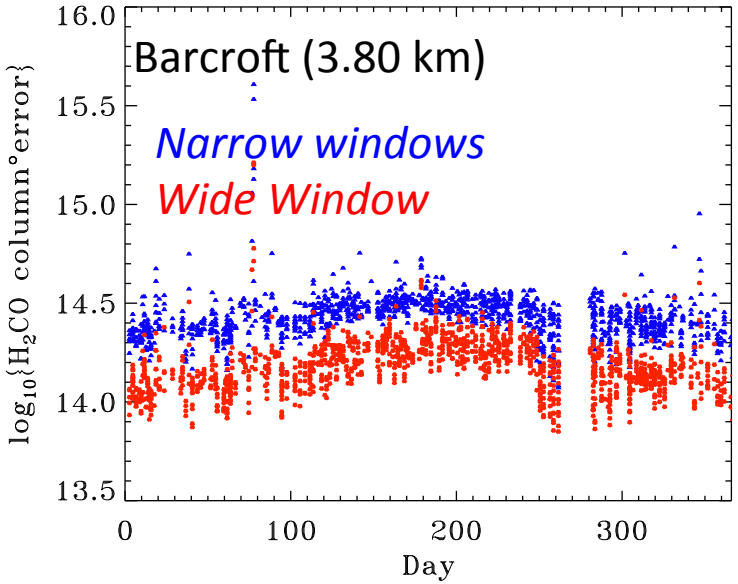


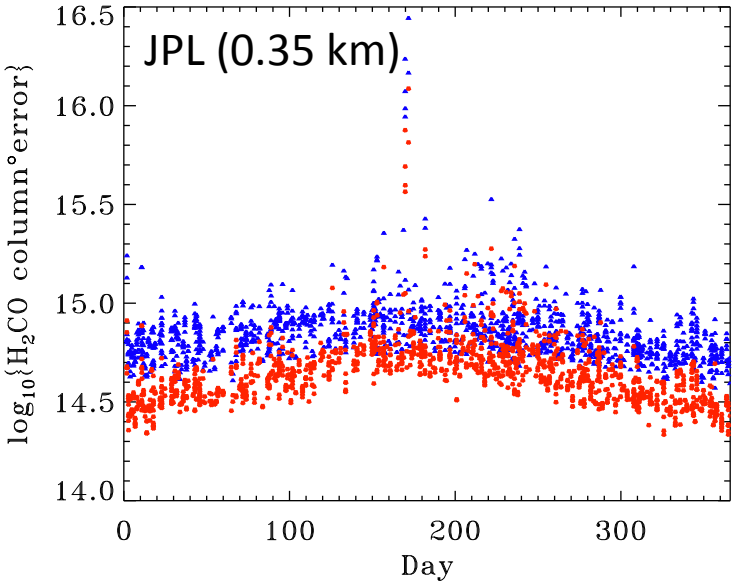


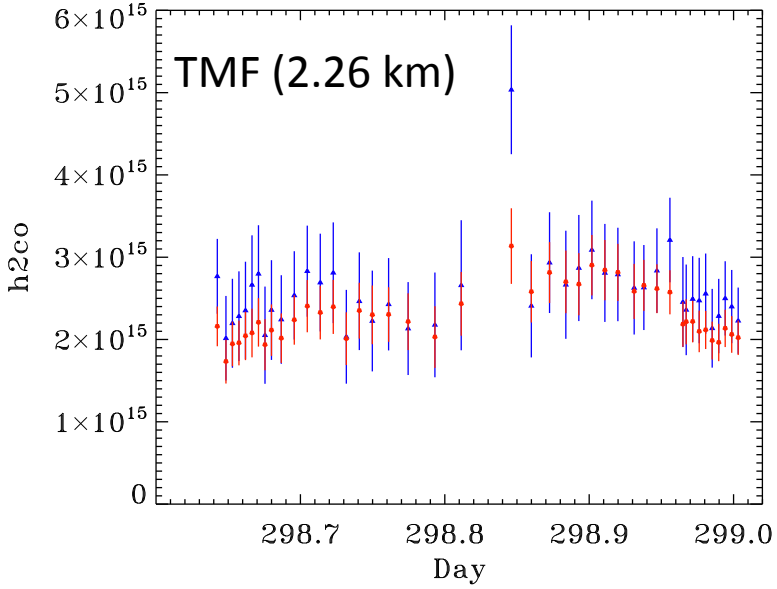


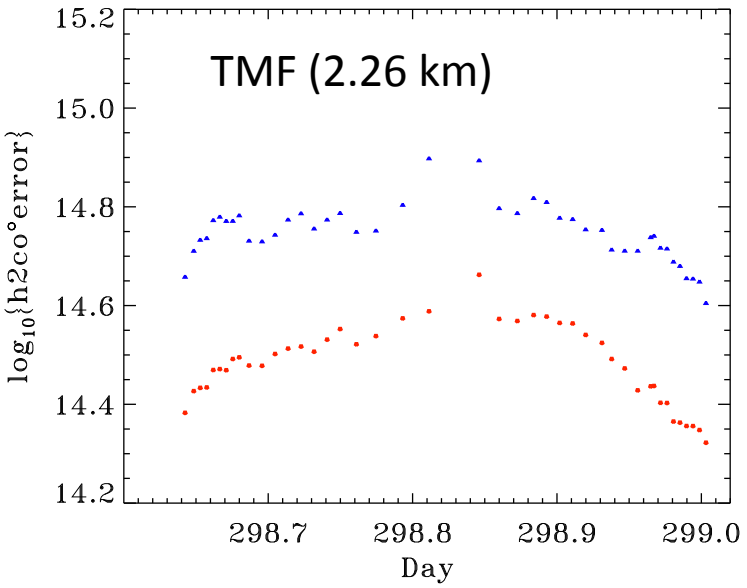


MkIV ground-based H_2CO column









Summary

H_2CO spectroscopy was evaluated using Kitt Peak lab spectra. HITRAN 2012 improved over 2008, but problem remain. No adjustments made.

Main inaccuracies in H_2CO retrievals result from interfering gases (HDO, CH_4, O_3, N_2O)

MkIV solar spectra acquired from the ground and balloon were fitted over 2740 to 2830 cm^{-1}

- Balloon spectra good for evaluating line positions and relative intensities
- Ground-based spectra good for evaluating widths and pressure shifts

Persistent fitting residuals were seen at several wavenumbers. Most of these same residuals also appeared in fits to Kitt Peak lab spectra of the absorbing gases.

Spectroscopic parameters were then adjusted to improve the fits to the KP lab spectra. In the vast majority of cases, also improved fits to the MkIV spectra. The main adjustments were:

- O_3 positions (resonance lines)
- CH_4 widths & shifts
- HDO widths & Shifts

[In HITRAN 2012, HDO shifts are currently all 0.000 in this region]

The largest remaining residuals are due to:

- Incorrect HDO vertical profile
- Neglect of Line Mixing in the N_2O Q-branch at 2798 cm^{-1}

Spectroscopy Discussion

Spectroscopy Bug Website

Jim Hannigan and Eric Nussbaumer set up a Bugzilla site for reporting spectroscopic problems. So if a user sees persistent systematic residuals at a particular frequency, they should file a bug report.

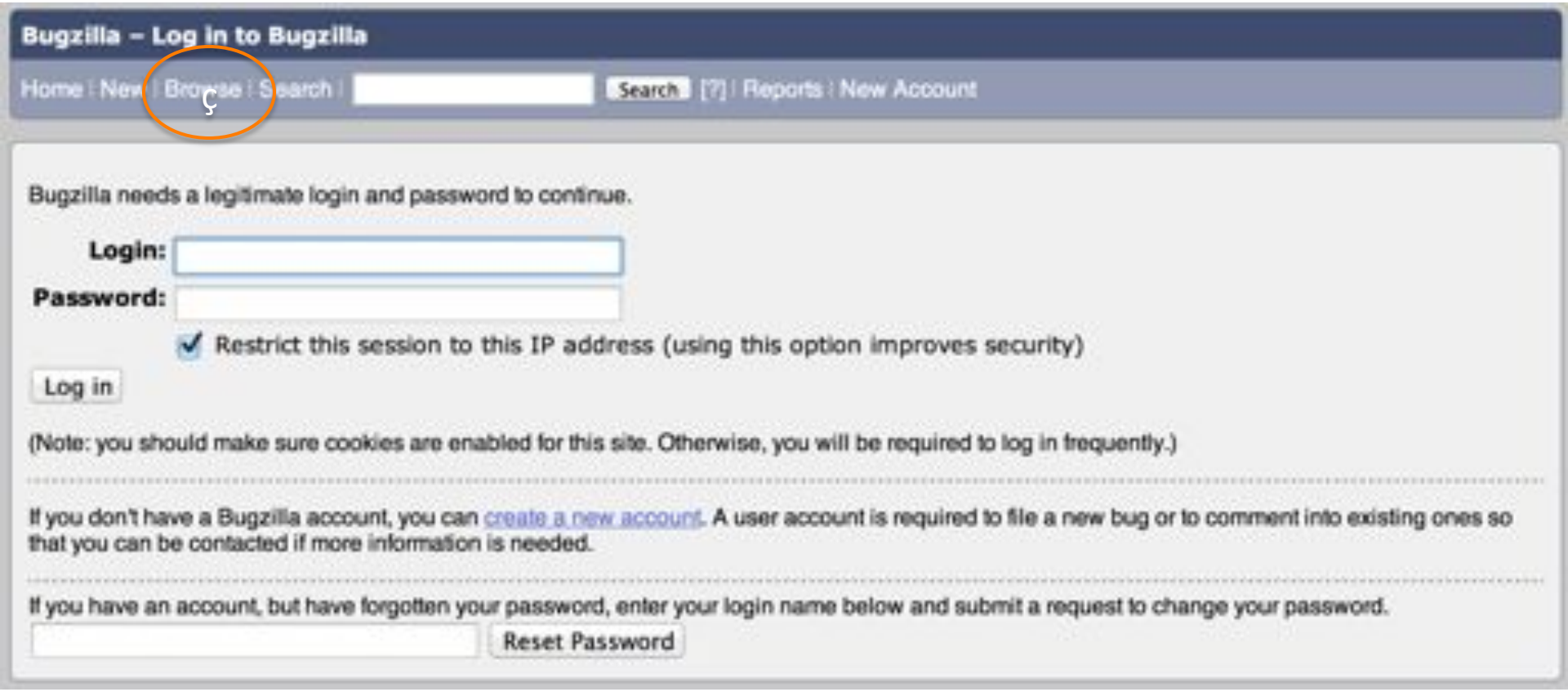
http://acd.ucar.edu/~ebaumer/bugzilla/index.cgi

This is to be used for both NDACC and TCCON.

Unfortunately this site has seen very little use.

Bugzilla

Bugzilla Main Page
acd.ucar.edu/~ebaumer/bugzilla/index.cgi
Bugzilla – Main Page
version 4.4
Home | New | Browse | Search | Search [?] | Reports | New Account | Log In | Forgot Password
Welcome to Bugzilla
File a Bug
Search
Open a New Account
Quick Search
Quick Search help
Bugzilla User's Guide | Release Notes
Home | New | Browse | Search | Search [?] | Reports | New Account | Log In | Forgot Password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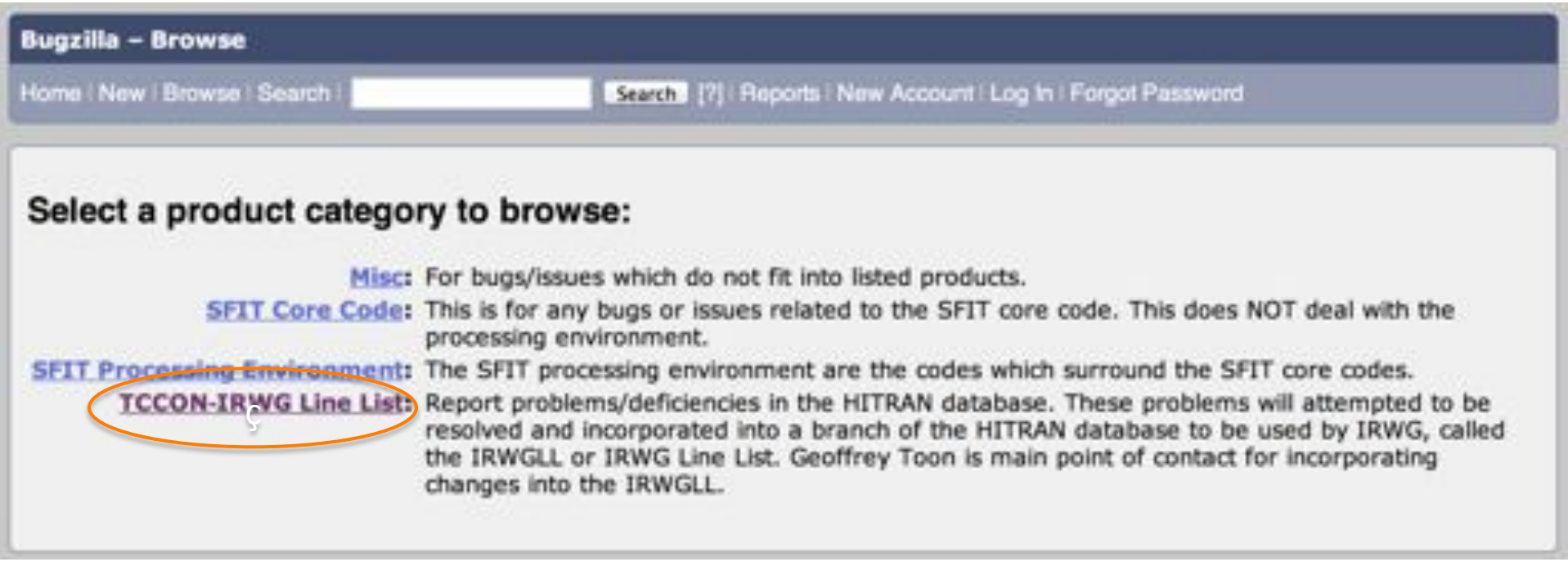
Reset Password


Bugzilla – Browse
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Select a product category to browse:
Misc: For bugs/issues which do not fit into listed products.
SFIT Core Code: This is for any bugs or issues related to the SFIT core code. This does NOT deal with the processing environment.
SFIT Processing Environment: The SFIT processing environment are the codes which surround the SFIT core codes.
TCCON-IRWG Line List: Report problems/deficiencies in the HITRAN database. These problems will attempted to be resolved and incorporated into a branch of the HITRAN database to be used by IRWG, called the IRWGLL or IRWG Line List. Geoffrey Toon is main point of contact for incorporating changes into the IRWGLL.

Bugzilla – Components for TCCON-IRWG Line List

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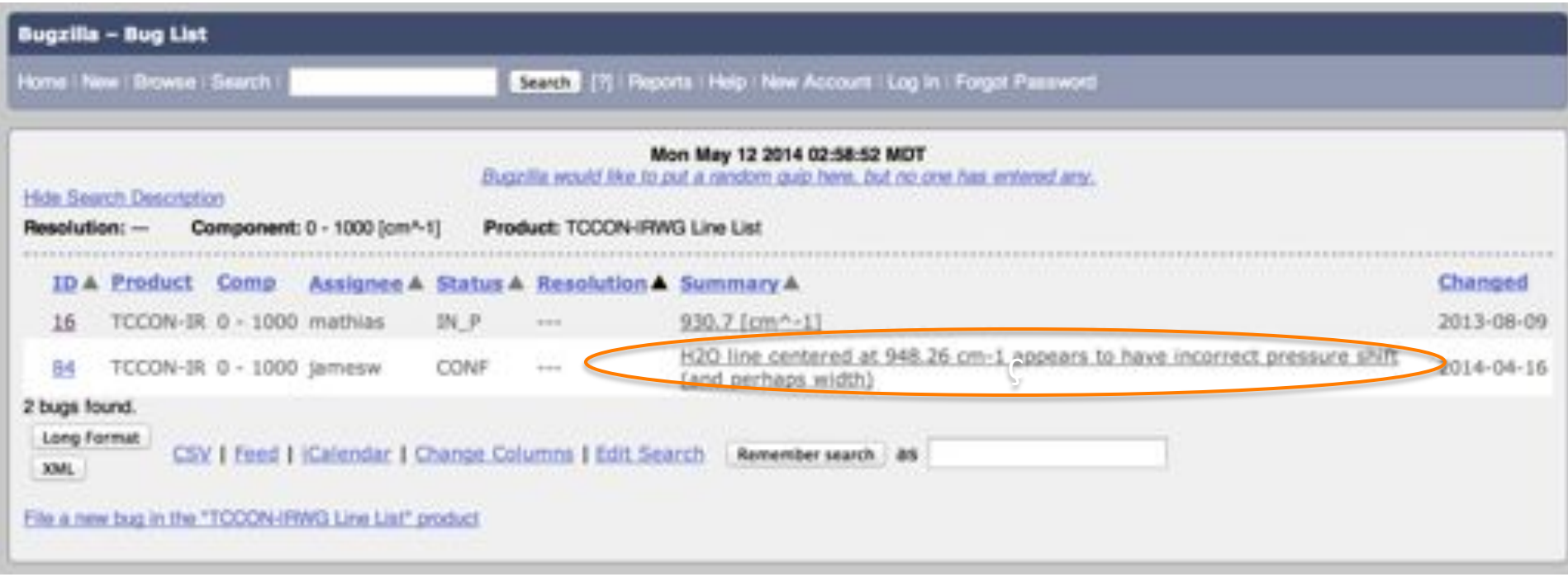
TCCON-IRWG Line List

Select a component to see open bugs in that component:

Report problems/deficiencies in the HITRAN database. These problems will attempted to be resolved and incorporated into a branch of the HITRAN database to be used by IRWG, called the IRWGLL or IRWG Line List. Geoffrey Toon is main point of contact for incorporating changes into the IRWGLL.

Components	Default Assignee
0 - 1000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 0 - 1000 [cm^-1].
1000 - 2000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 1000 - 2000 [cm^-1]
10000 - 12000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 10000 - 12000 [cm^-1]
12000 - 14000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 12000 - 14000 [cm^-1]
14000 - 16000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 14000 - 16000 [cm^-1]
16000 - 18000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 16000 - 18000 [cm^-1]
18000 - 20000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 18000 - 20000 [cm^-1]
2000 - 3000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 2000 - 3000 [cm^-1]
3000 - 4000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 3000 - 4000 [cm^-1]
4000 - 5000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 4000 - 5000 [cm^-1]
5000 - 6000 [cm^-1]	Jim Hannigan For issues in which the central wavenumber of the spectral fitting residual fall between 5000 - 6000 [cm^-1]


Bugzilla – Bug List
Home | New | Browse | Search | Search [?] | Reports | Help | New Account | Log In | Forgot Password
Mon May 12 2014 02:58:52 MDT
Bugzilla would like to put a random quip here, but no one has entered any.
Hide Search Description
Resolution: --- Component: 0 - 1000 [cm^-1] Product: TCCON-IRWG Line List
ID Product Comp Assignee Status Resolution Summary Changed
16 TCCON-IR 0 - 1000 mathias IN_P --- 930.7 [cm^-1] 2013-08-09
84 TCCON-IR 0 - 1000 jamesw CONF --- H2O line centered at 948.26 cm-1 appears to have incorrect pressure shift (and perhaps width) 2014-04-16
2 bugs found.
Long Format
XML
CSV | Feed | iCalendar | Change Columns | Edit Search Remember search as
File a new bug in the "TCCON-IRWG Line List" product

Bugzilla – Bug 84 H2O line centered at 948.26 cm-1 appears to have incorrect pressure shift (and perhaps width) Last modified: 2014-04-16 18:46:35 MDT

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Bug List: (2 of 2) First Last Prev Next Show last search results

Bug 84 - H2O line centered at 948.26 cm-1 appears to have incorrect pressure shift (and perhaps width)

Status: CONFIRMED

Product: TCCON-IRWG Line List
Component: 0 - 1000 [cm^-1]
Version: 1.0
Hardware: PC Mac OS

Importance: --- enhancement
Assigned To: Jim Hannigan

URL:

Depends on:
Blocks:

Show dependency tree / graph

Reported: 2014-04-16 18:46 MDT by Geoffrey Toon
Modified: 2014-04-16 18:46 MDT (History)
CC List: 2 users (show)

See Also:
Central wavenumber of the spectral fitting residual: 948.3

Attachments	
Report containing figures (text/pdf, 2.07 KB, application/pdf) 2014-04-16 18:46 MDT, Geoffrey Toon	Details
Add an attachment (proposed patch, testcase, etc.)	

Note
You need to log in before you can comment on or make changes to this bug.

Geoffrey Toon 2014-04-16 18:46:35 MDT Description

Created attachment 16 [details]
Report containing figures

H2O line at 938.26 cm-1 overlaps the SF6 Q-branch. So even a small error in the H2O pressure shift causes large H2O-dependent artificial variations on the retrieved SF6 column. See attached report.