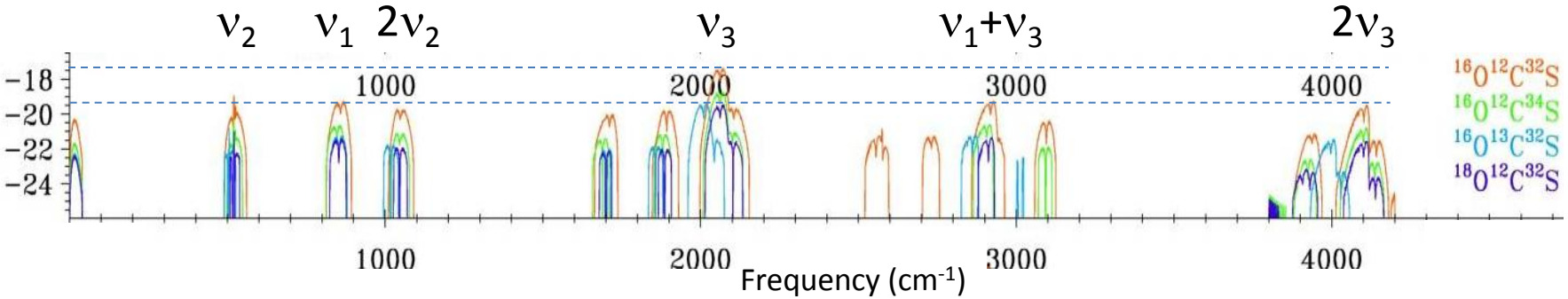
Missing ν_3 Bands of OCS

Geoff Toon, JPL
2012-06-12

Low-pressure OCS cells are used to check the ILS of FTIR spectrometers.

OCS has a molecular mass of 60, hence a fairly small doppler width.

OCS also has the virtue of having several usable absorption bands that span a wide spectral range from 500 to 4100 cm^{-1}.



Thus a single OCS cell can be used to check the ILS in different spectral regions, which may be covered by different detectors (e.g. HgCdTe & InSb).

OCS also has the virtue of a very strong ν_3 band, which results in saturated lines. This provides additional ILS information and an independent check on the cell pressure, preventing cell pressure errors from biasing the derived ILS.

MkIV and MATMOS spectra

While attempting to measure the ILS of MkIV and MATMOS test-bed instruments, the ν_3 band of OCS was fitted.

Equally-spaced absorption dips were observed in the residuals that could not be fitted using the July 2009 OCS update of the HITRAN linelist [Auwera & Fayt, 2006].

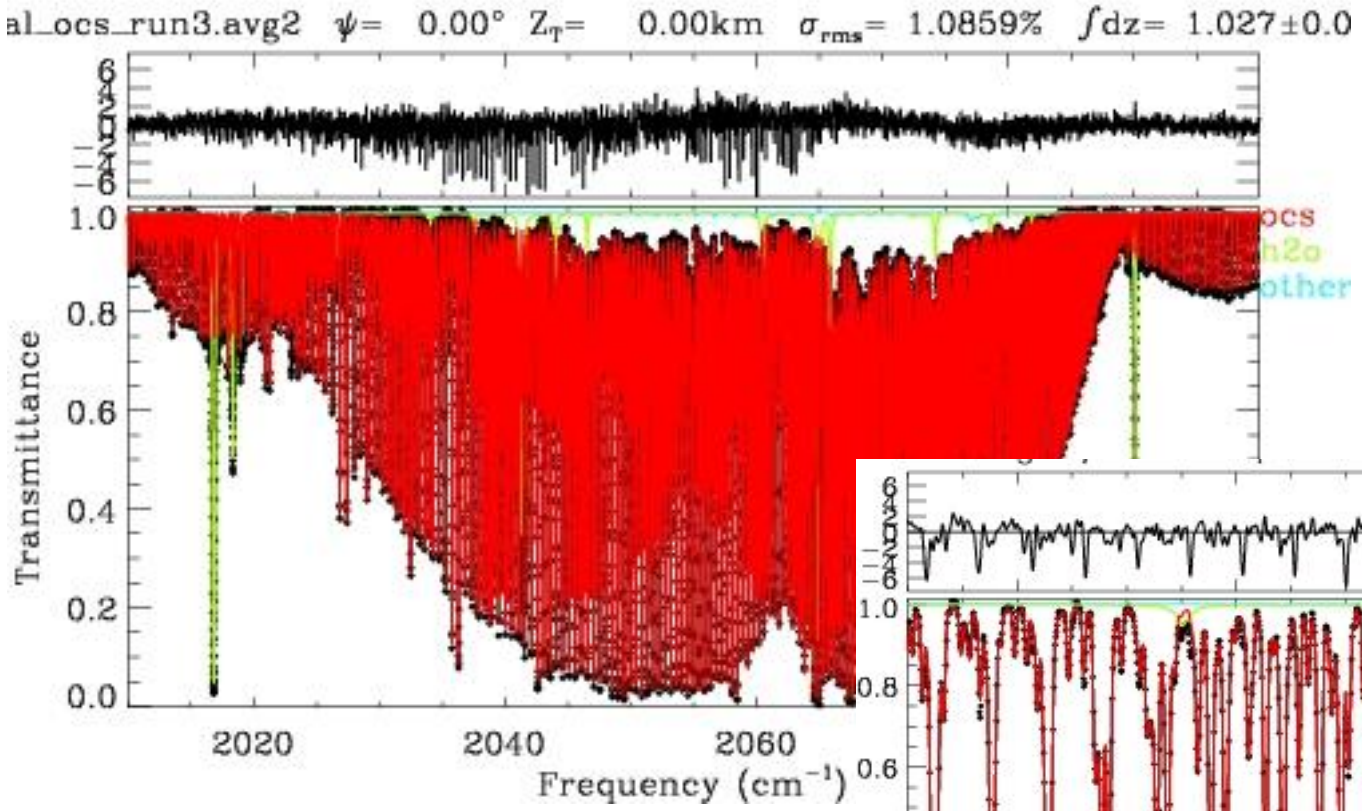
These missing absorption dips were narrow, implying that the absorber was at low pressure (i.e. inside the cell).

These dips were regularly spaced, with a separation of 0.3 to 0.5 cm^{-1}, which is exactly the same as the OCS lines.

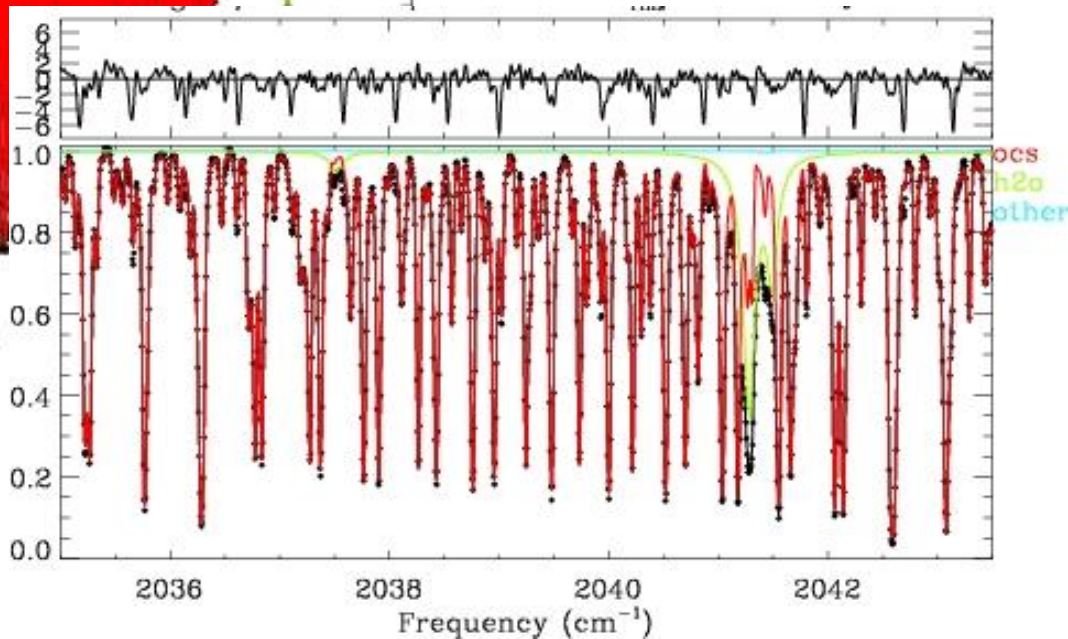
In two different OCS cells, observed by two different instruments, the same missing absorption lines were observed.

This carries a strong suggestion that the missing lines are from OCS, perhaps a hot band or an isotopolog.

MATMOS-Testbed Globar spectra Fitted Using HITRAN 2009 OCS Update

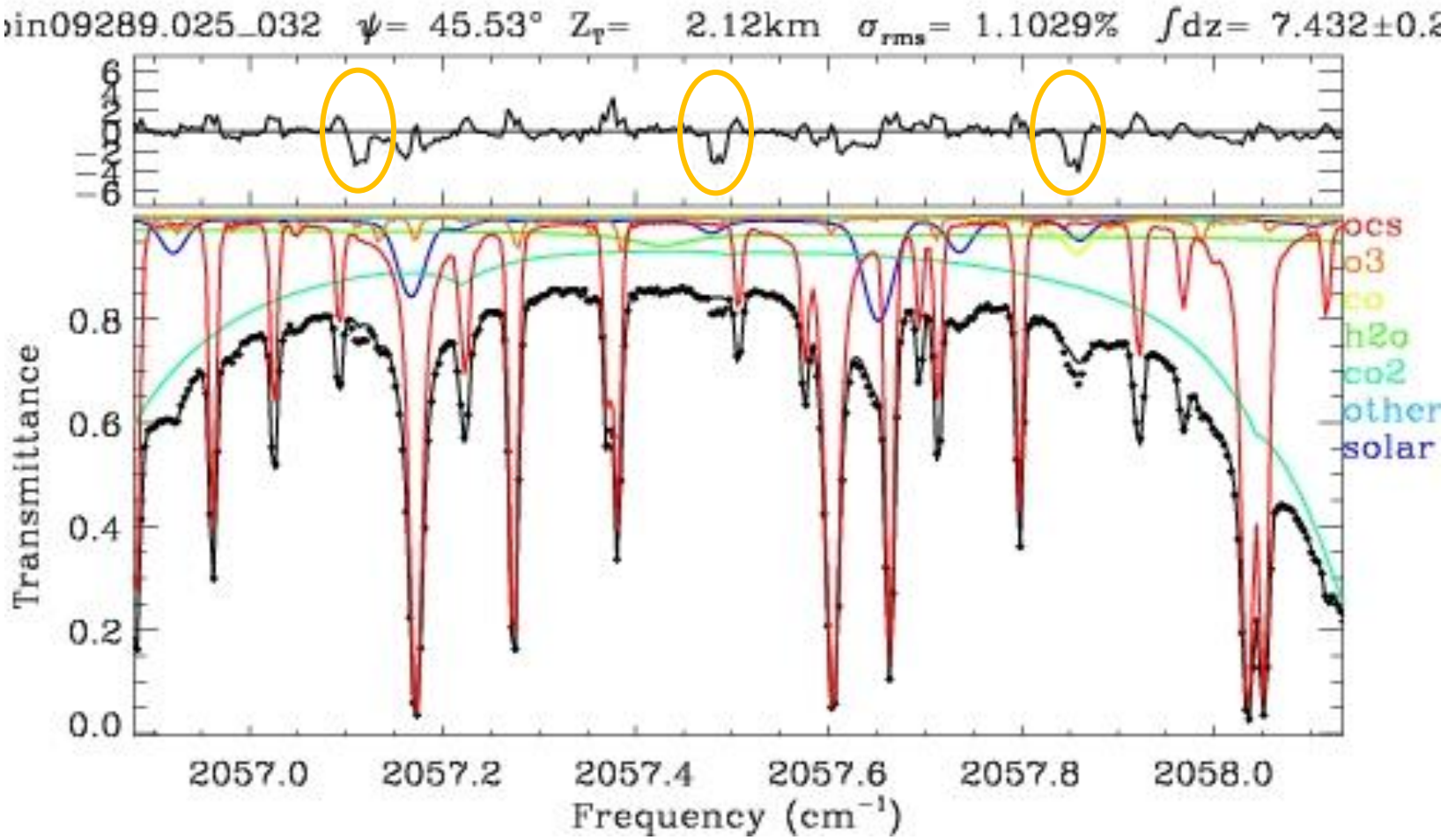


25 cm OPD



Regularly-spaced missing absorptions are clearly apparent.

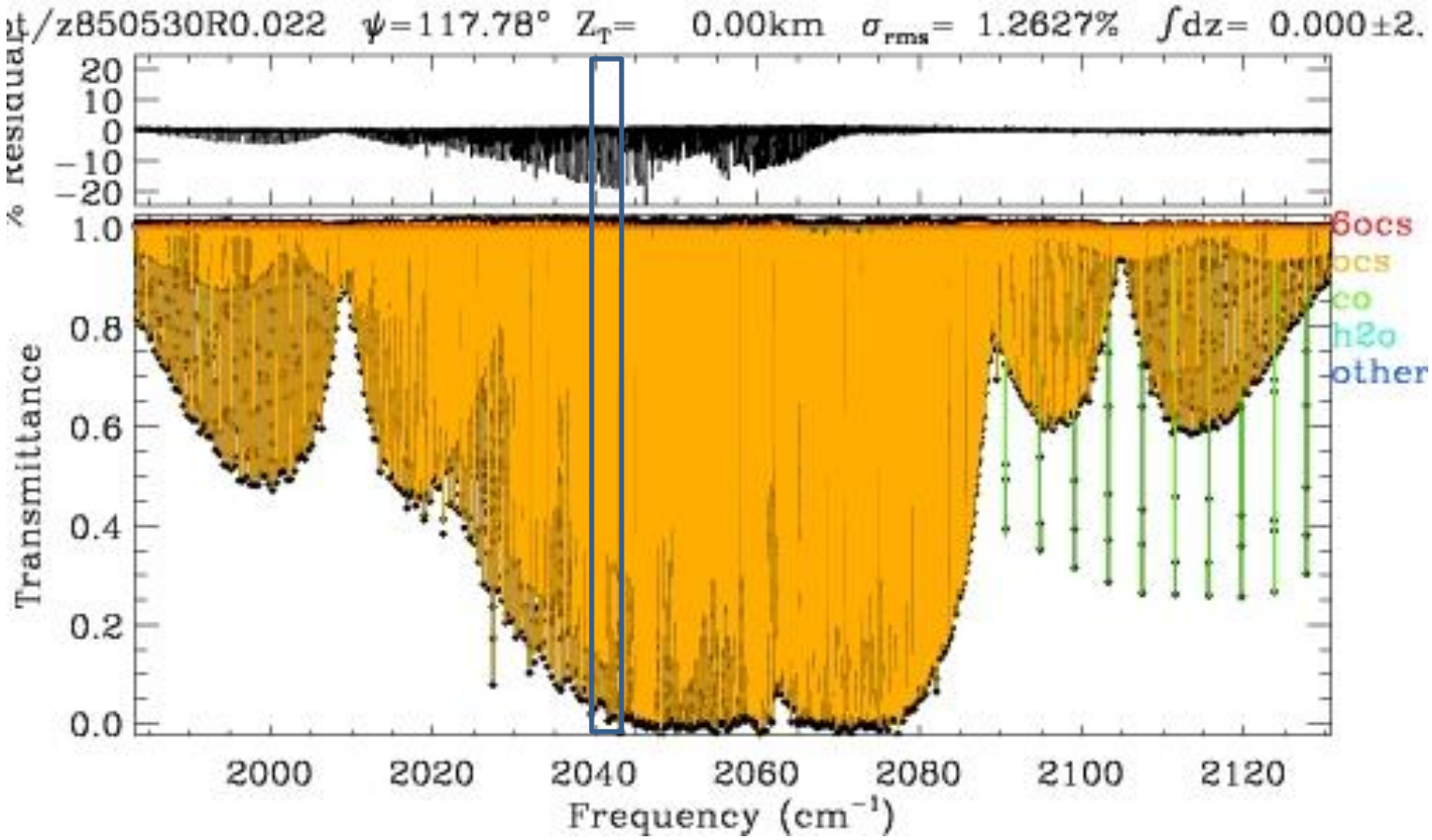
MkIV solar spectrum (120 cm OPD) thru 10 cm OCS cell (HITRAN 2009)



Regularly-spaced missing absorptions (clearly doublets in this region)

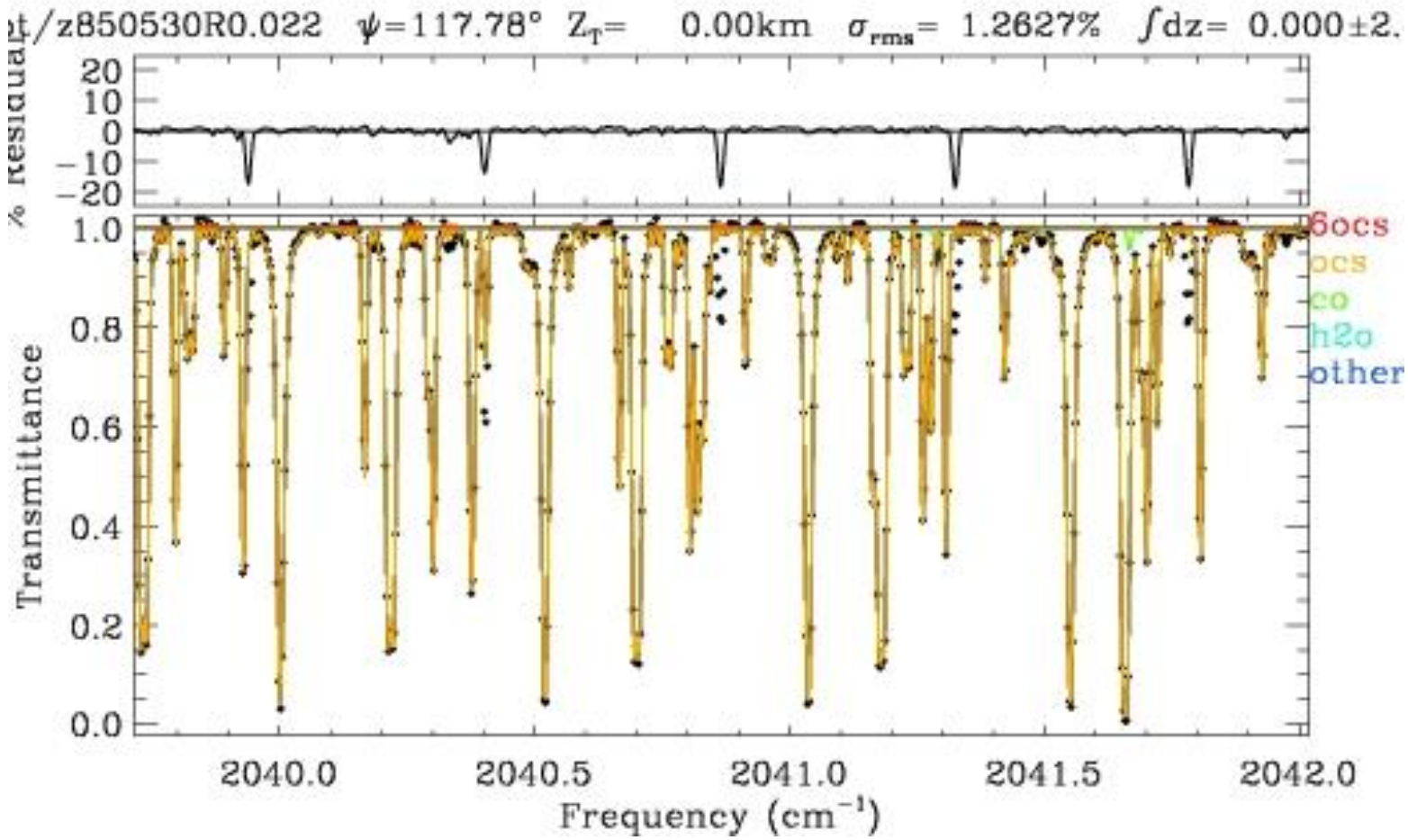
Fit to Kitt Peak Lab OCS spectrum

Spectrum measured in 1985: 85 cm OPD; 1.244 Torr; 25 cm cell 25.6C.
Path also contains H_2O and CO (frequency calibration); HITRAN 2009 Update



Several missing bands are apparent in the residuals, which reach 25%.

Zoom into Kitt Peak Missing Lines



Missing lines are narrow (low pressure) and have a very similar spacing (0.3 to 0.5 cm^{-1}) to those of OCS. Missing lines are likely an OCS isotopolog or hot-band.

Empirical Supplemental OCS linelist

Used 1985 Kitt Peak lab spectra to develop an empirical OCS linelist containing 709 lines to represent the missing bands.

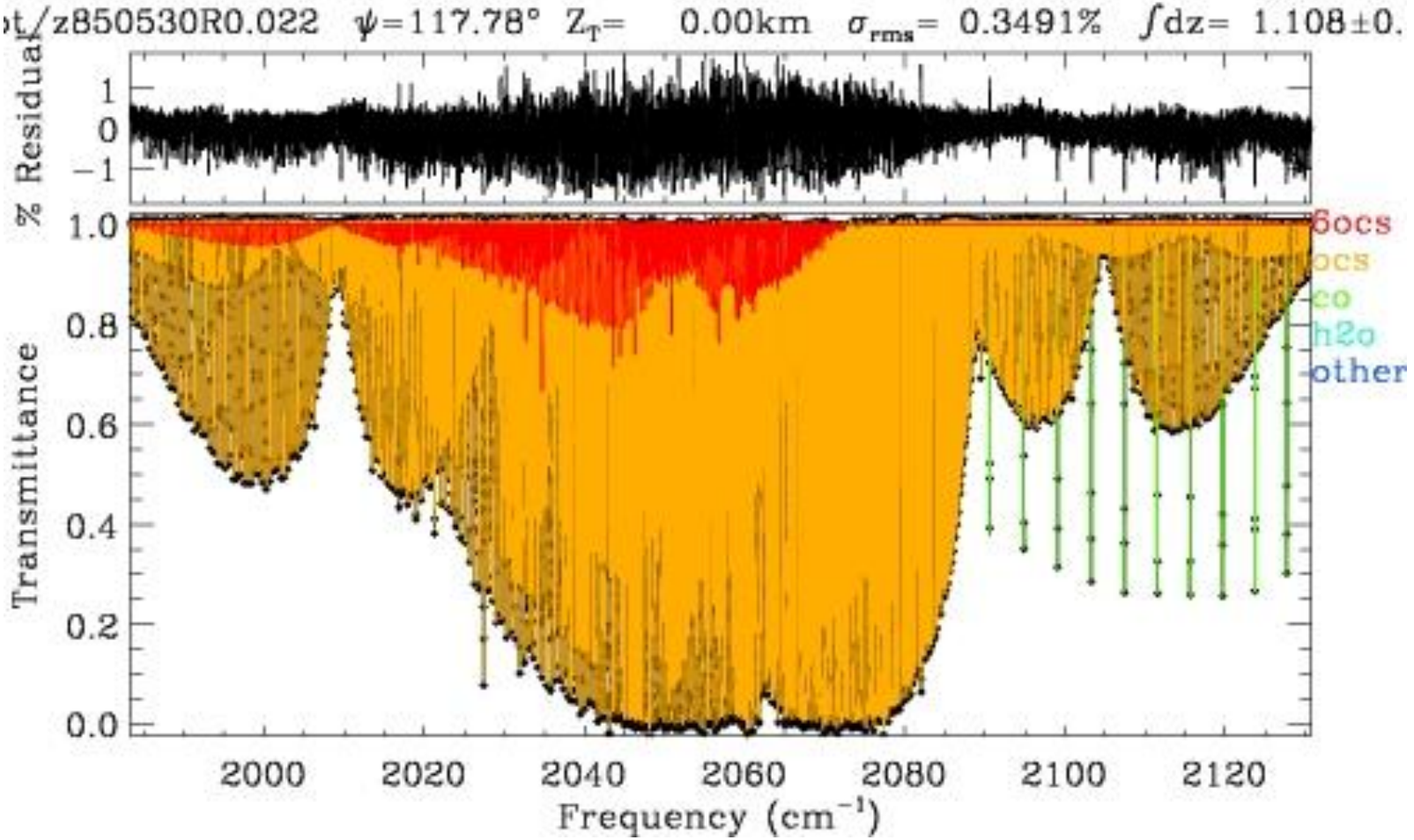
Strengths of missing lines are from 5E-23 to 3E-21, which is 400 times weaker than the strongest v_3 lines of isotopolog #1.

These missing lines are similar in strength to the bands at 850 cm^{-1}, 2900 cm^{-1} and 4100 cm^{-1} that we plan to use for ILS validation.

E" of empirical lines are all 300 cm^{-1}, which is fine for ILS calibration using a room-T cell.

Used isotopolog #6 to represent the missing lines. Missing lines are too strong to really be isotoplog #6, but this designation avoids confusion.

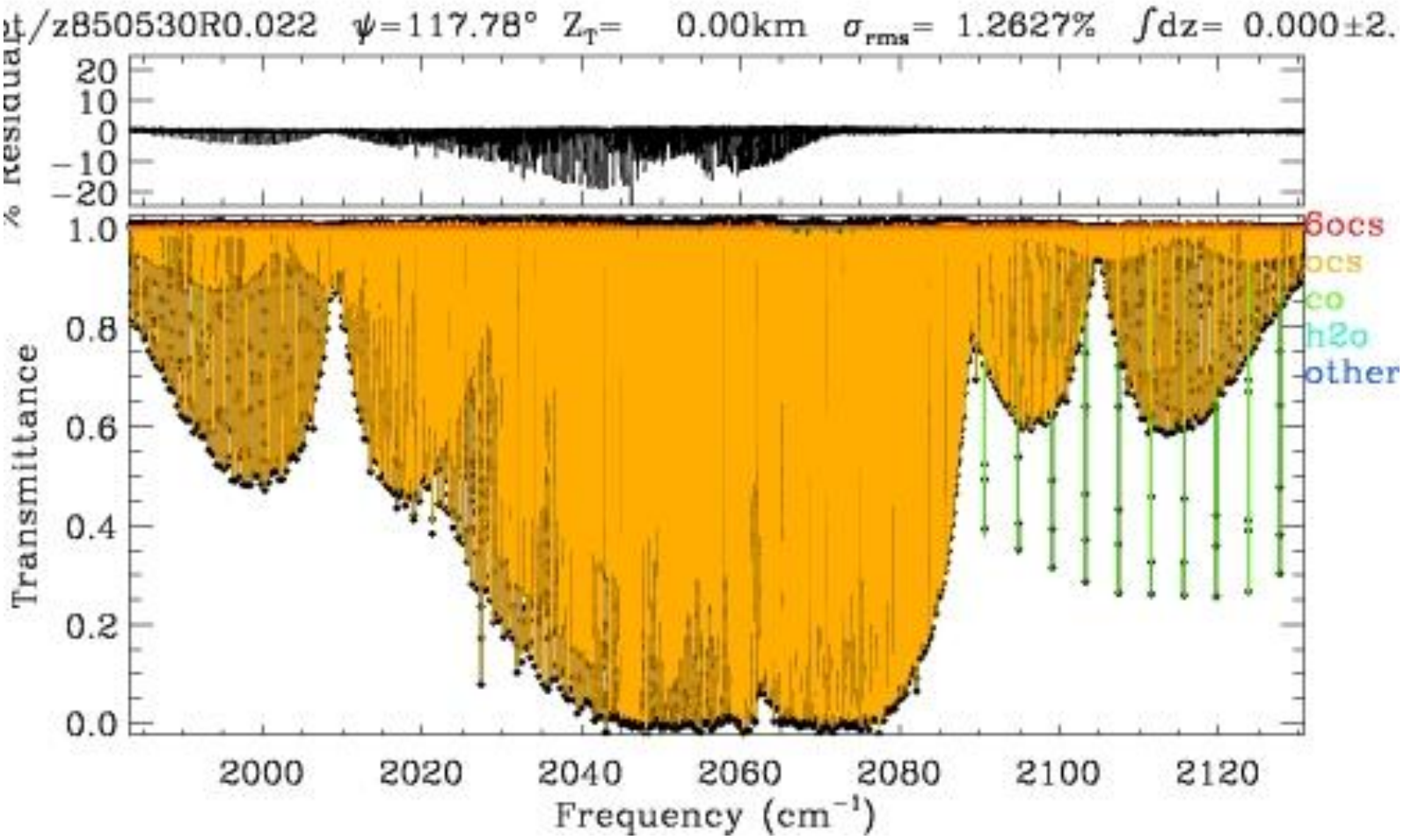
Fits to Kitt Peak lab spectra with HITRAN + Supplemental OCS Linelist



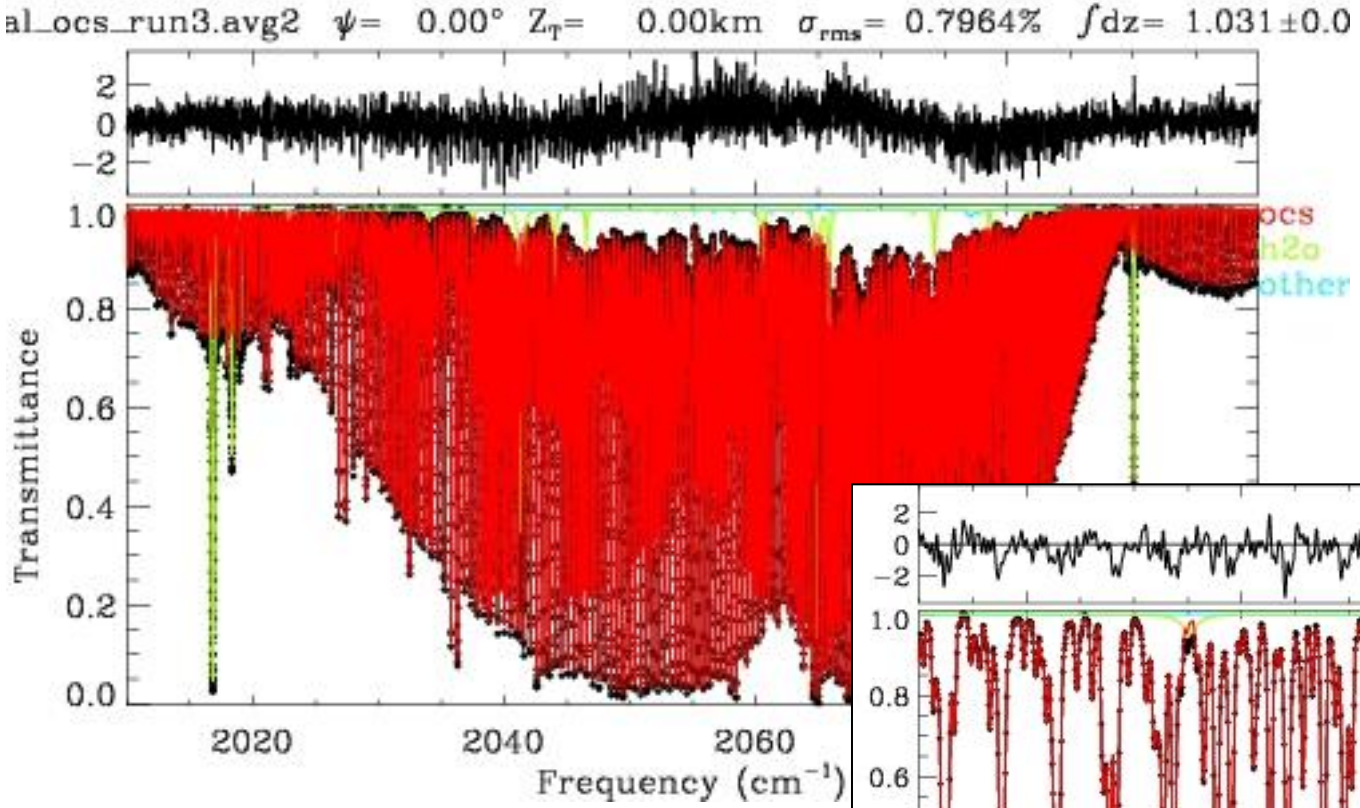
RMS residuals reduced from 1.26% to 0.35%. Maximum residuals are reduced from 25% to < 2%. Red trace shows supplemental lines "6ocs".

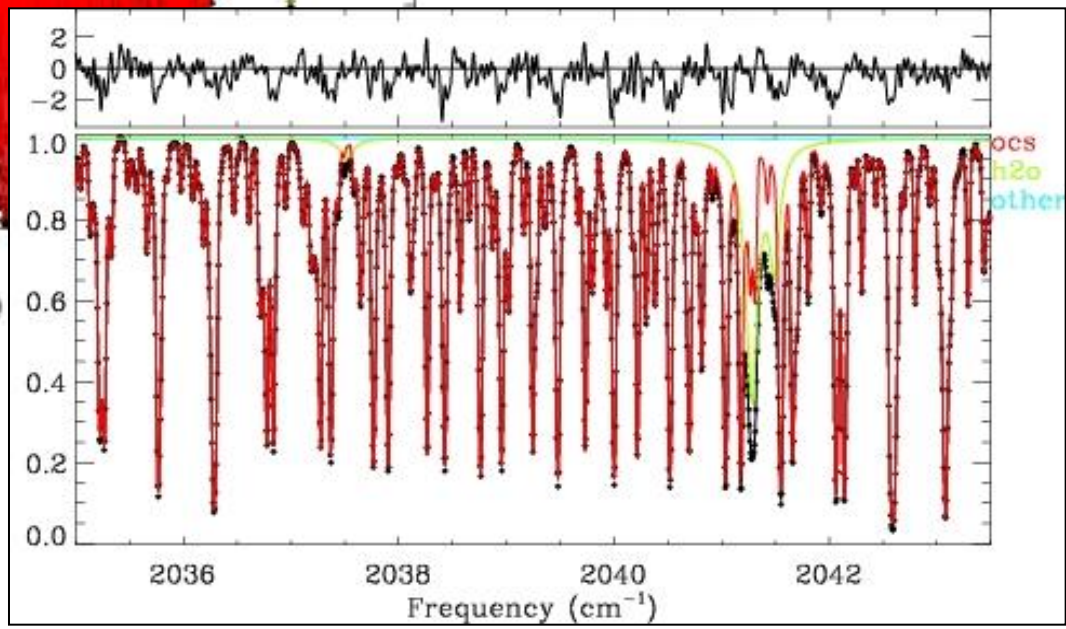
Reminder: without supplemental OCS

1.244 Torr; 25 cm cell 25.6C



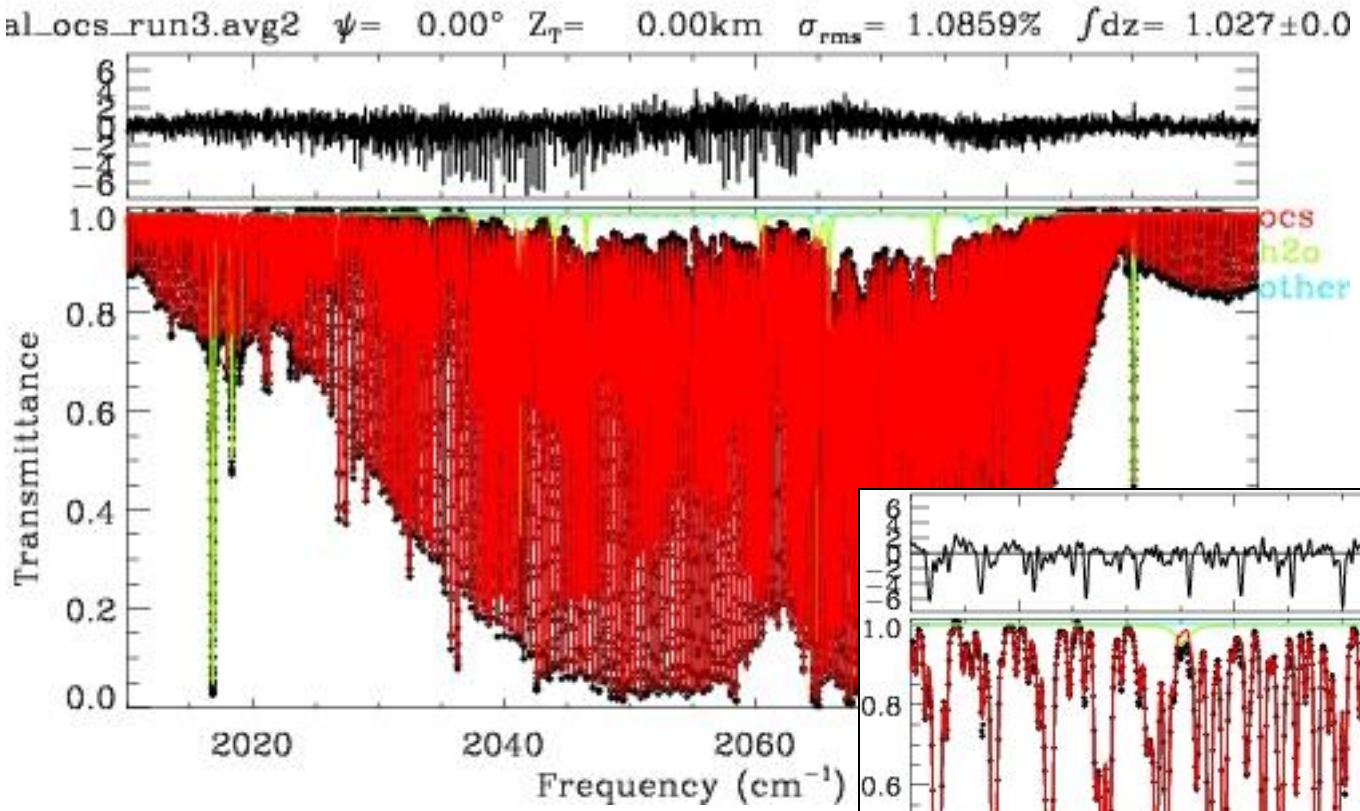
Fits to MATMOS spectra using HITRAN + Supplemental OCS



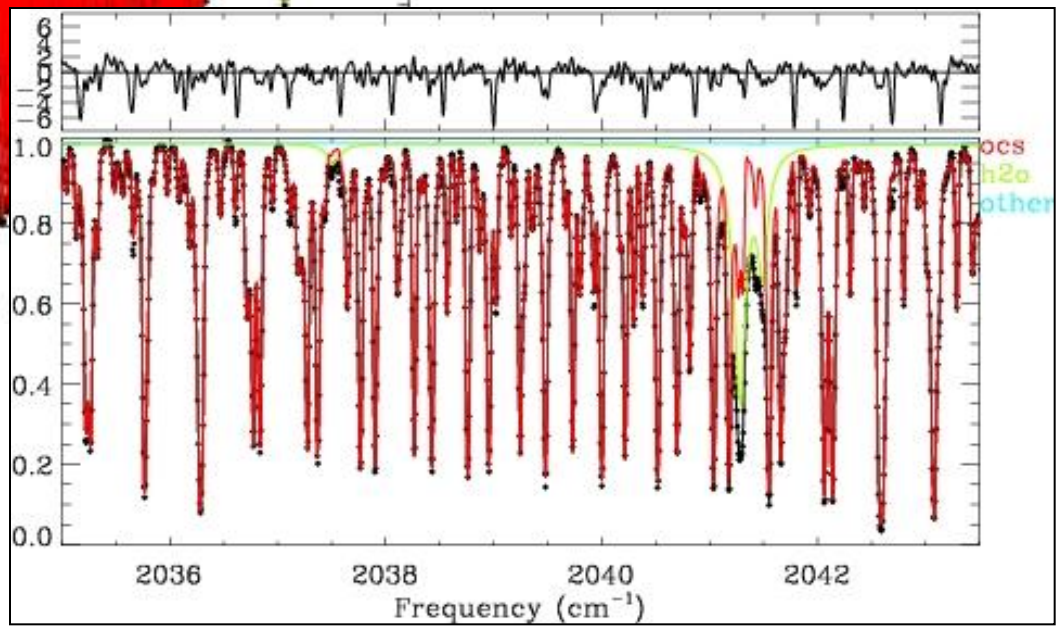


RMS Residuals are reduced from 1.08% to 0.79%.
Peak residuals reduced from 7% to 3 %

Reminder: without supplemental OCS

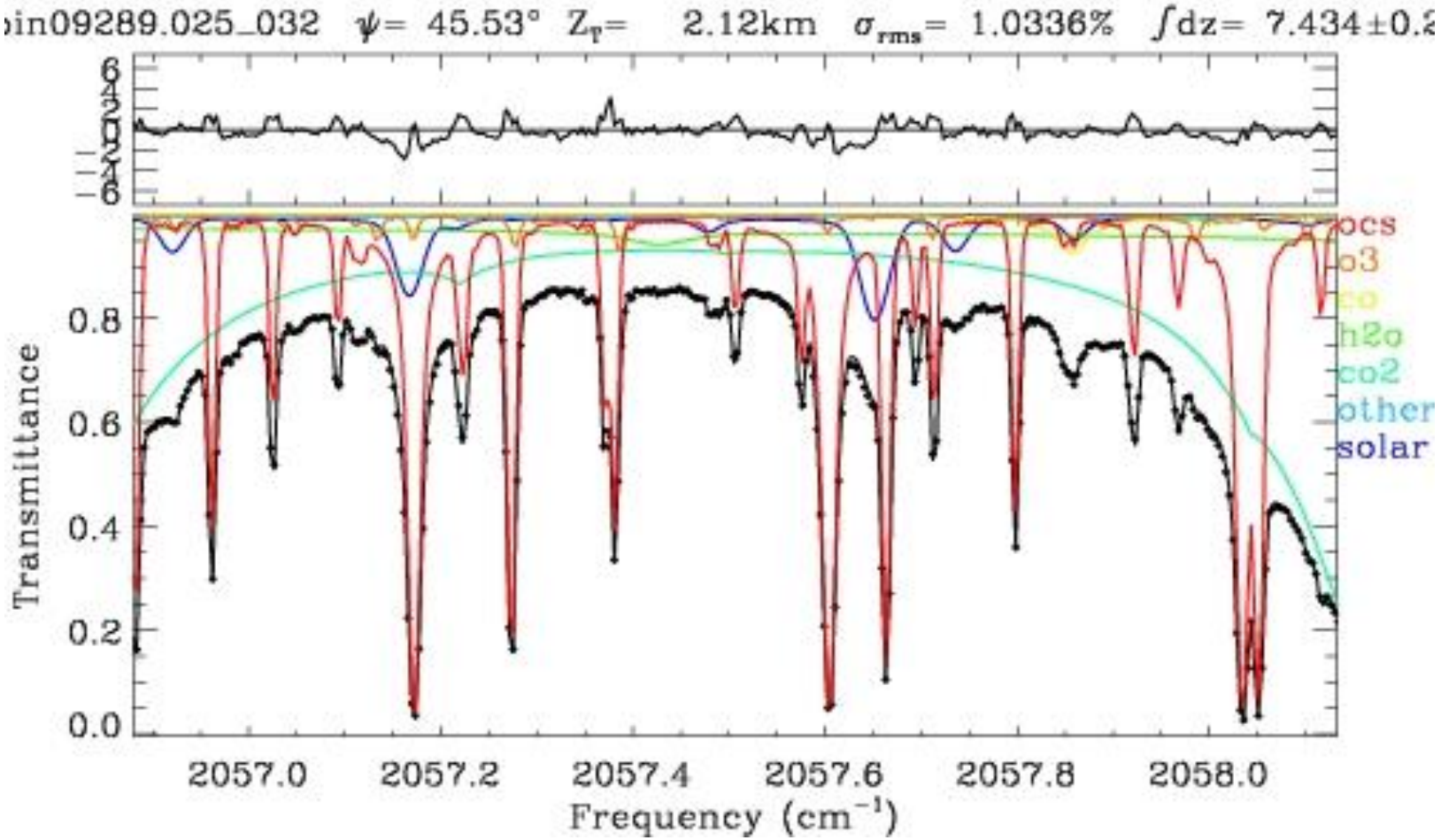


25 cm OPD



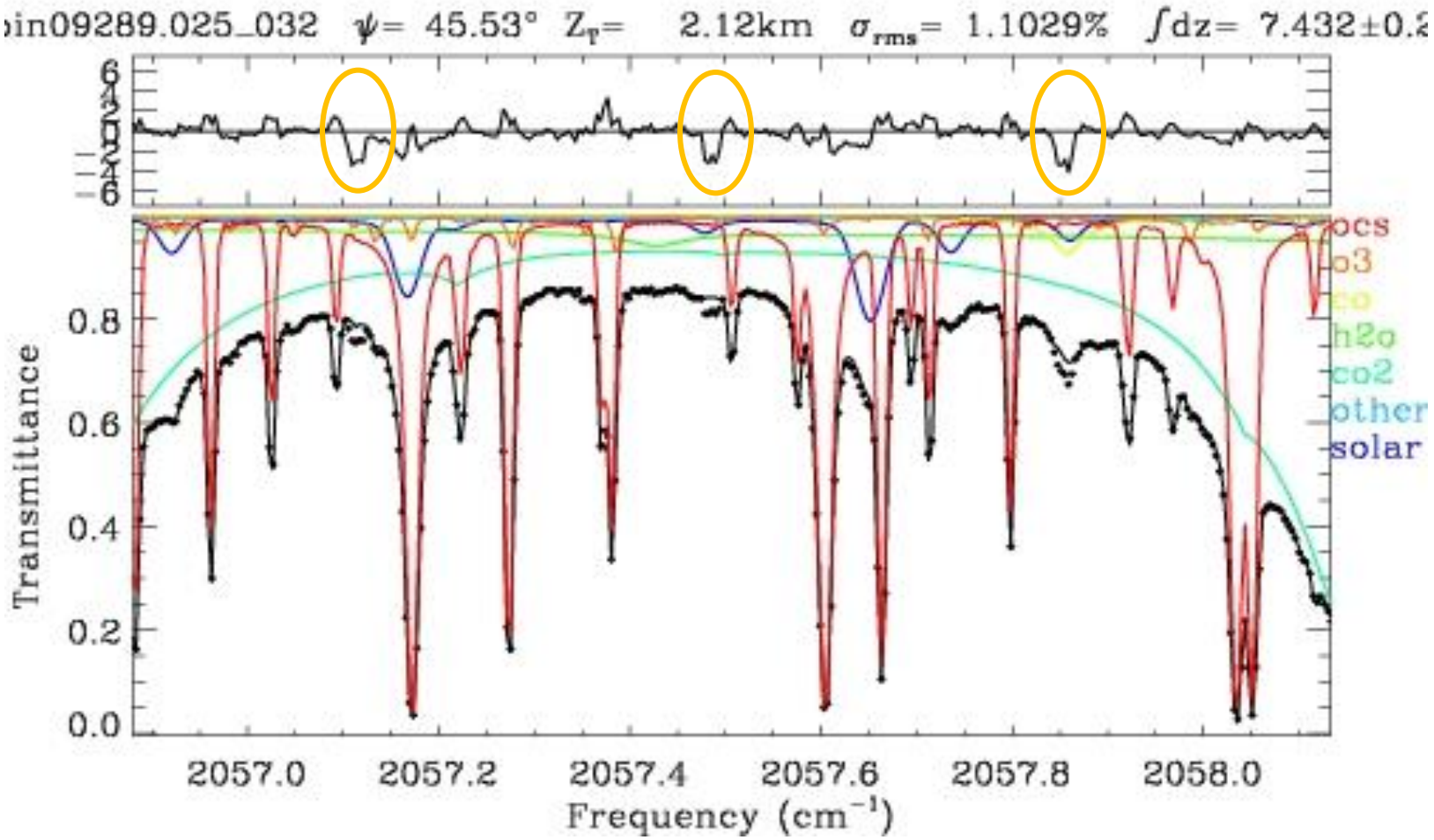
Regularly-spaced missing absorptions are clearly apparent.

Fits to MkIV cell spectrum using HITRAN + supplemental OCS



Dips in residuals are gone. Overall RMS spectral fit reduced from 1.10% to 1.03%

Reminder: without supplemental OCS



Regularly-spaced missing absorptions (clearly doublets in this region)

Initial Conclusions

July 2009 update to HITRAN OCS linelist is missing some weaker bands in the ν_3 region (1975-2100 cm^{-1}). These missing bands produce prominent residuals in fits to low-pressure gas cell spectra, in MkIV, MATMOS and in Kitt Peak spectra.

Although the missing lines are too weak to be observable in atmospheric spectra, they dominate fits to low-pressure OCS cell spectra used for ILS determination.

Kitt Peak spectra were used to derive an empirical OCS linelist consisting of 709 lines. This can be used to supplement the OCS in the HITRAN 2009 OCS update.

Using the supplemental OCS significantly improves the spectral fits in all cases.

I have contacted Jean Vander Auwera and Andre Fayt who have confirmed that the strongest missing bands are the 110 and 030 hot-bands of the main isotopolog.

Fitting the strong v_3 band lines in OCS gas cell spectra provides an important check on the cell pressure. Without which, pressure error will bias the derived ILS width.

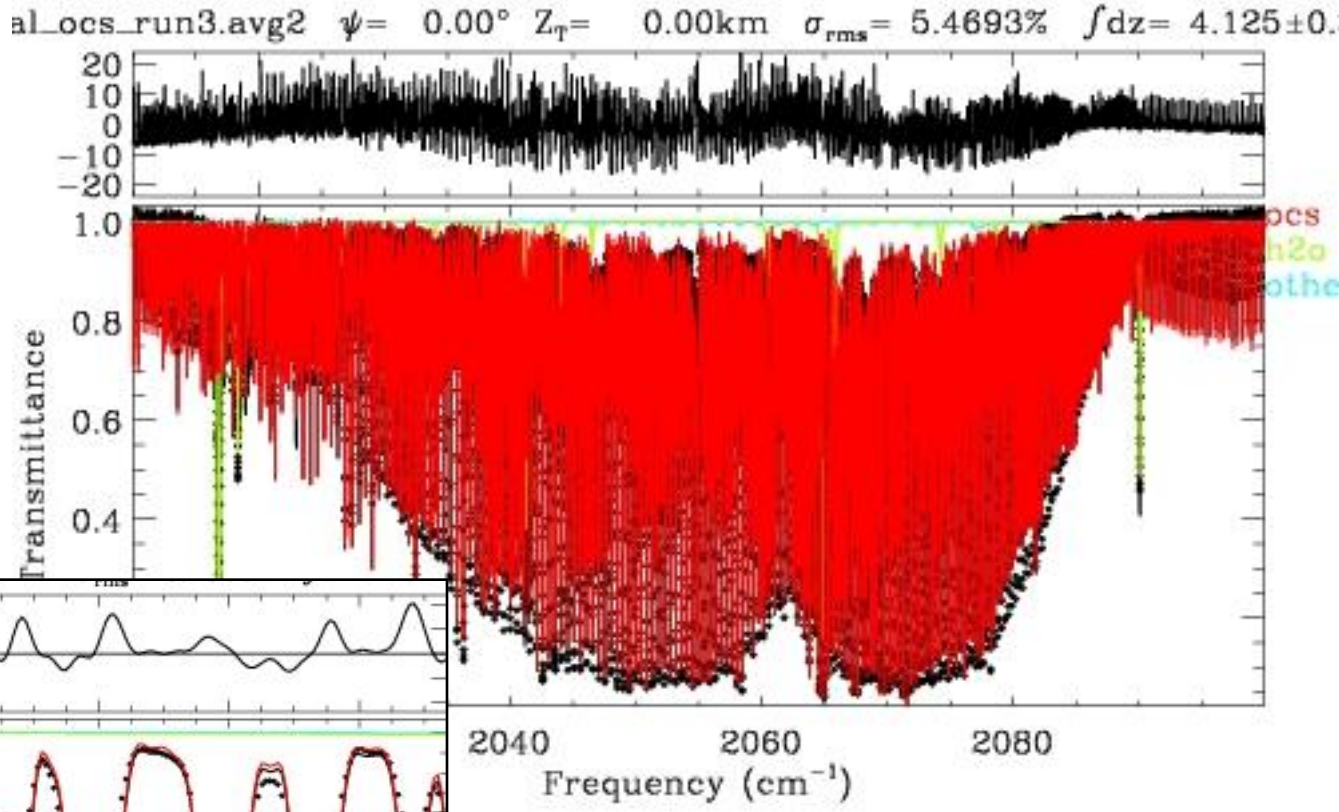
Combination of strong and weak OCS lines in nu_3 region provides more comprehensive evaluation of ILS than is possible by weak lines only.

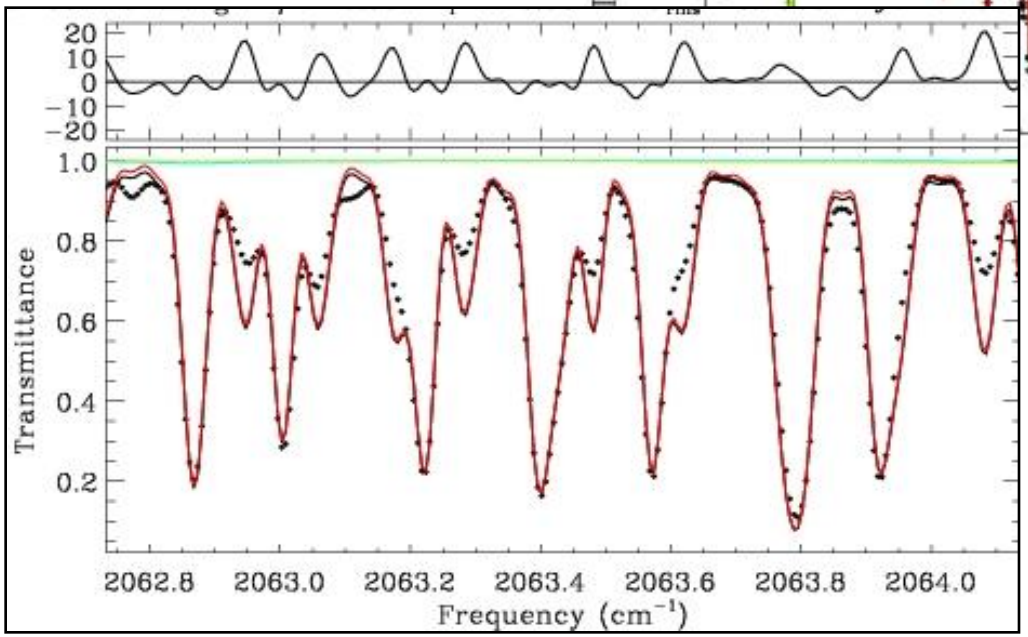
OCS fitted using nominal cell pressure

Back to MATMOS spectra, which started this issue.

Assume nominal 2 Torr fill pressure.

Fits using HITRAN + empirical OCS





Large residuals caused by weakly absorbing lines being inconsistent with the stronger lines.

Absorption of weak lines is over-estimated in calculation.

Determining True Cell Pressure

Assumed Cell Pressure (mbar/Torr)	RMS Fitting Residual
2.66 / 2.0	**5.469 %**
10.0 / 7.6	2.224 %
16.0 / 12.0	1.078 %
19.2 / 14.6	0.807 %
20.1 / 15.0	**0.791 %**
21.0 / 16.0	0.802 %
25.0 / 19.0	1.072 %

The assumed cell pressure was adjusted and the OCS ν_3 band was re-fitted.

The OCS vmr inside the cell was also adjusted to be consistent with an air leak. i.e.

$$VMR = 2 \text{ Torr} / P_{CELL\ (Torr)}$$

Fitting the entire ν_3 OCS region, the RMS fitting residuals are quite sensitive to the cell pressure, even though the MATMOS ILS is much broader than the lines.

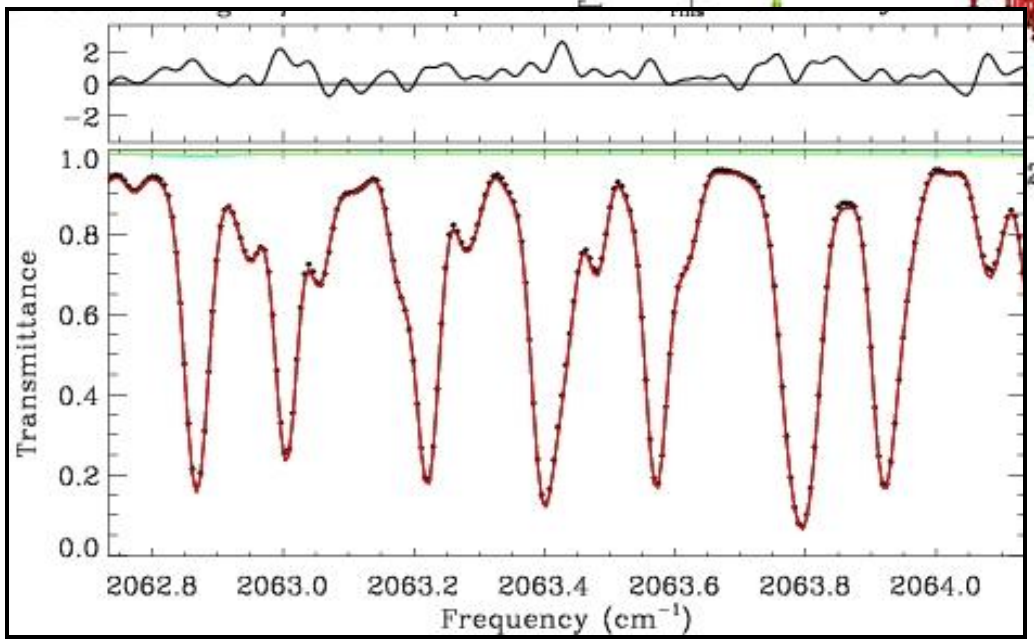
25% error in the cell pressure causes a 35% increase in the rms residual.

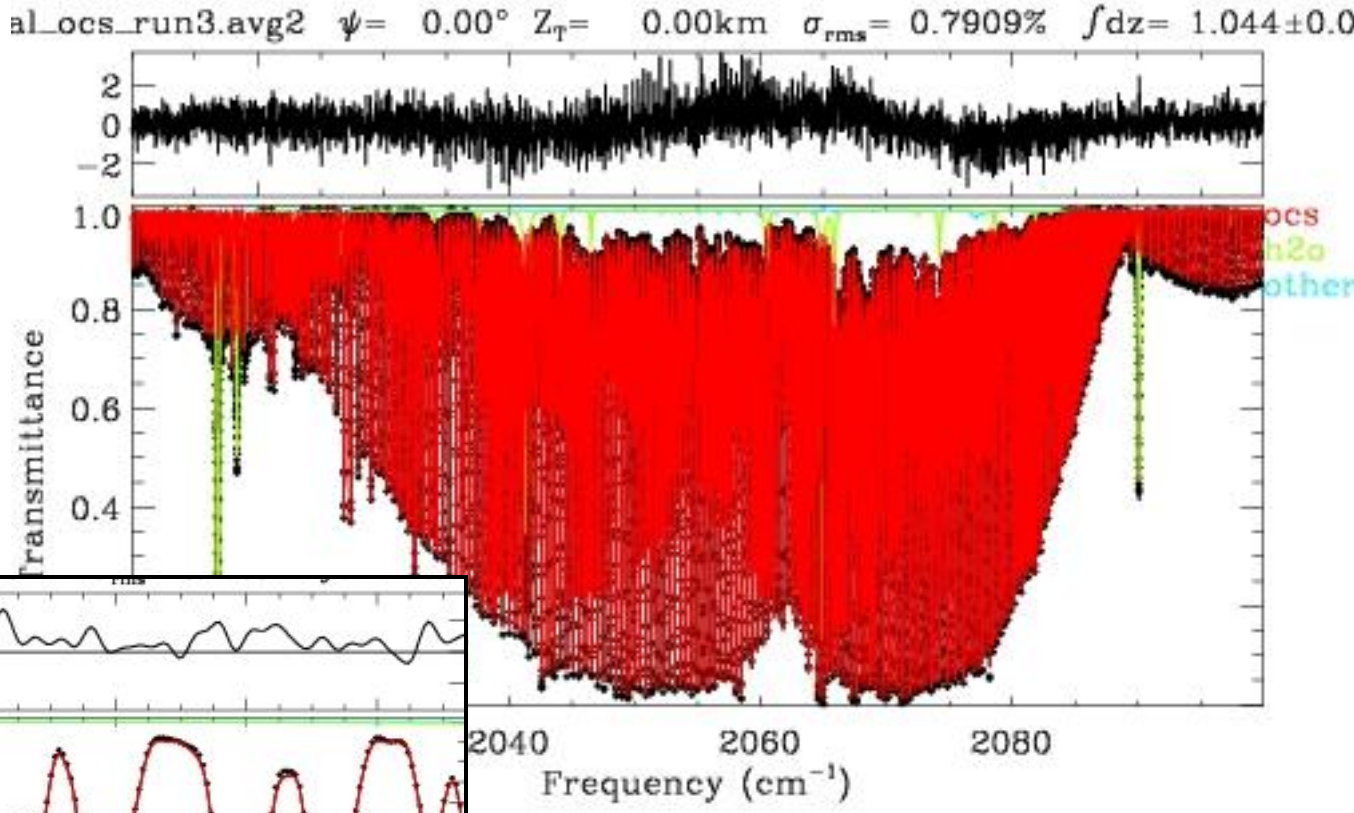
Sensitivity due to range of line strengths in different parts of their curve of growth.

After correcting cell pressure to 15 Torr

RMS residuals reduced by factor 7. Weak lines are now consistent with strong lines.

RMS is surprisingly sensitive to assumed cell pressure





The OCS data can now be used to determine the ILS, without fear of bias.

Final Summary

During the course of measuring the ILS of MATMOS and MkIV, two obstacles were encountered:

1) Missing OCS bands in nu3 region
2) Gas cell leak (2 Torr → 15 Torr)

OCS has several advantages for ILS determination:

1) At least 6 usable bands covering 500-4100 cm^{-1}
2) High'ish molecular weight (60)
3) Wide range of line strengths provide more ILS info
4) Strong nu_3 band provides cell pressure information

Also Disadvantages:

1) Need long cell (10+ cm) to use weaker bands
2) Significant atmospheric vmr (0.5ppb)
3) Flammable and mildly toxic

Improved OCS linelist coming soon!

----- Back-Up Material -----

July 2009 HITRAN OCS Update

July, 2009

Update for OCS (Carbonyl sulfide) It was found that due to a programming error some of the air- and self-broadening halfwidths for all isotopologues of OCS were in error by as much as 50%. It was also found in the process that there is a typo in the b_3 coefficient for the O_2-broadening Padé approximant given in M.A. Koshelev and M.Y. Tretyakov, "Collisional broadening and shifting of OCS rotational spectrum lines," *JQSRT* **110,** 118-128 (2009). This b_3 coefficient needs to be divided by 10. These mistakes have now been fixed, yielding much improved broadening parameters. We thank Maxim Koshelev from the Institute of Applied Physics (Nizhny Novgorod, Russia) for pointing out these errors. While performing this correction, the line positions and intensities in the pure rotational band for all of the HITRAN OCS isotopologues were updated using parameters from the Cologne Database for Molecular Spectroscopy (CDMS). The intensities were converted using the procedure described in the appendix of the HITRAN2008 paper, which includes scaling of the partition functions.
The data can be downloaded here either in ASCII: 19_hit09.par
or compressed format: 19_hit09.zip
These files should be used as a complete replacement of the 2008 carbonyl sulfide linelist.

From Rothman et al. [2009]

2.19. OCS (molecule 19)

In the HITRAN2004 edition, the intensities of the ν_3 band of the principal isotopologue (the region around 5 μm) were increased by 15.79% to match the average of the measurements reported by Régalia-Jarlot et al. [207] and Vander Auwera and Fayt [208]. However, for the sake of consistency, such a scaling should also have been applied to the other $\Delta v_3 = 1$ transitions. They are the hot bands of ν_3 involving ν_1, ν_2 and $2\nu_2$ of the $^{16}O^{12}C^{32}S$, $^{16}O^{12}C^{34}S$, $^{16}O^{12}C^{33}S$, and $^{18}O^{12}C^{32}S$ isotopologues (622, 624, 623, and 822 in the old AFGL abbreviation), and the ν_3 band of $^{16}O^{12}C^{34}S$, $^{16}O^{12}C^{33}S$, and $^{18}O^{12}C^{32}S$. This situation has been corrected in the current edition. The line intensities of the ν_3 fundamental of $^{16}O^{13}C^{32}S$ in HITRAN2004 were found to agree within 5% with the measurements of Vander Auwera and Fayt [208]. They were therefore not changed.

Compared to the HITRAN2004 database, which gave about 1100 OCS transitions in the 3800–4200 cm^{-1} region for seven bands ($2\nu_3$ of the five isotopologues and the $\nu_2+2\nu_3-\nu_2$ of $^{16}O^{12}C^{32}S$ and $^{16}O^{12}C^{34}S$), substantial updates were made for 2008. The new database now includes 10,425 transitions of 51 bands involving the five isotopologues $^{16}O^{12}C^{32}S$, $^{16}O^{12}C^{34}S$, $^{16}O^{13}C^{32}S$, $^{16}O^{12}C^{33}S$, and $^{18}O^{12}C^{32}S$. Of these, two are forbidden bands, 15 are allowed cold bands arising from the ground state, and the remaining 34 are hot bands arising from various vibrational states.

The line positions in this region were calculated using the effective rovibrational energy constants based on the global analysis [209–213]. Although the accuracy in line position was reported to be 5×10^{-5} cm^{-1} [209], conservative values for the *HITRAN* uncertainty criteria were assigned, depending on J value and line intensity.

Intensities were taken from new FTIR measurements [214,215] performed at JPL to support Venus studies. Sung et al. [214] measured line intensities of the $2\nu_3$ band at 4101.387 cm^{-1}, $\nu_1+2\nu_2+\nu_3$ at 3937.421 cm^{-1}, and $4\nu_2+\nu_3$ at 4141.212 cm^{-1} of $^{16}O^{12}C^{32}S$. The new $2\nu_3$ band intensity of $6.315(13)\times10^{-19}$ $cm^{-1}/(molecule\,cm^{-2})$ for 100% abundance of $^{16}O^{12}C^{32}S$ was within 1.3% of the average of two earlier measurements, $6.528(96)\times10^{-19}$ and 6.27×10^{-19} $cm^{-1}/molecule\,cm^{-2}$, respectively, by Bermejo et al. [216] and Naïm et al. [209]. The band intensities corresponding to 100% abundance of isotopologue $^{16}O^{12}C^{32}S$ for the $\nu_1+2\nu_2+\nu_3$ and $4\nu_2+\nu_3$ bands were also in similar agreement (1%) with those from Naïm et al. [209]. Intensities of all the other 43 bands of the five isotopologues in this region were taken from the exhaustive work by Toth et al. [215], in which many bands were measured for the first time. Uncertainties of the line intensities in this region were adopted from measurement precisions, which range from 1% to 6% depending on the bands. However, conservative values coupled with evaluation depending on the line intensities were assigned for the *HITRAN* uncertainty criteria. The line intensities vary through five orders of magnitude, but very weak unassigned features were omitted from the database pending further analysis.

The γ_{self} in the pure-rotation band have been updated using a recent improvement [217] to the work of Matton et al. [218], while γ_{air} and γ_{self} in the rest of the database have been updated using a Padé approximation from Ref. [219]. Air-pressure induced frequency shifts, δ, for OCS were given for the first time based on the $2\nu_3$ work of Domenech et al. [220].

Auwera and Fayt [2006]

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Absolute line intensities for carbonyl sulfide from 827 to 2939 cm^{-1}

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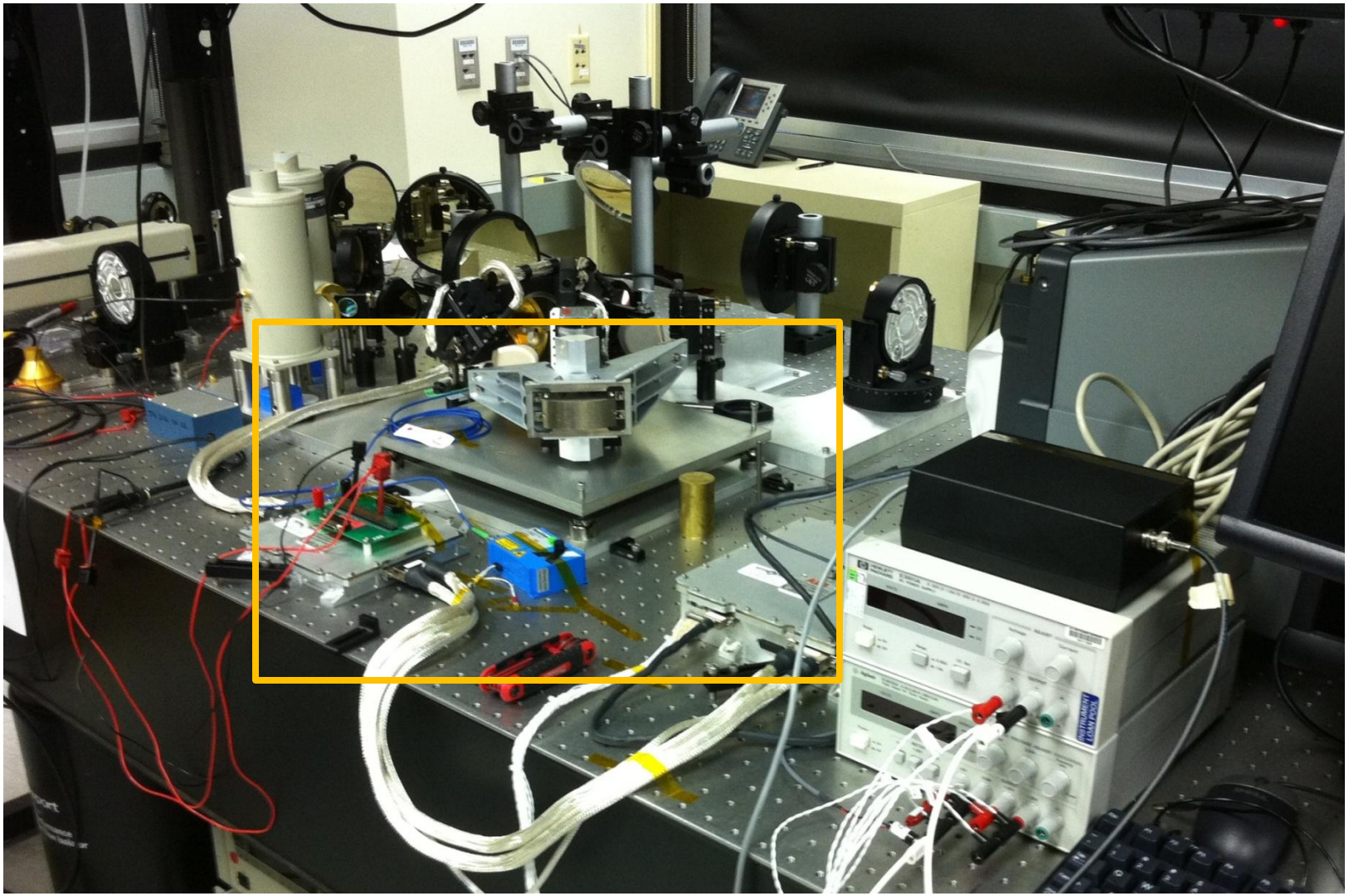
This article is dedicated to Dr Jean Demaison and Dr Walter J. Lafferty for their many contributions to science.

Abstract

Using a total of 18 unapodized high-resolution (MOPD = 300 and 450 cm) Fourier transform absorption spectra of carbonyl sulfide ($P \times \ell$ = 14.3–60,600 Pa × cm, T = 296.0 K), we measured 1340 absolute line intensities in 8 bands ($\nu_1 + \nu_2^1 - \nu_2^1, 2\nu_2^0, 2\nu_1, \nu_1 + 2\nu_2^0, 4\nu_2^0, \nu_3, \nu_2^1 + \nu_3 - \nu_2^1, \nu_1 + \nu_3$) of the main isotopologue, located between 827 and 2939 cm^{-1}. In addition, we measured 307 absolute line intensities in the ν_3 fundamental band of $^{16}O^{12}C^{34}S$ and $^{16}O^{13}C^{32}S$, observed near 2061.45 and 2009.23 cm^{-1}, respectively. The observed Herman–Wallis dependences are in most cases reproduced by the global model of OCS [E. Rbaihi, A. Belafhal, J. Vander Auwera, S. Naïm, and A. Fayt, J. Mol. Spectrosc., 191:32–44, 1998]. The pressure self-broadening parameter was also measured up to J = 83.

EDU in MATMOS Test-Bed at JPL



EDU built by ABB Bomem, is a non-flight version of the MATMOS interferometer

Fits to MATMOS Test-bed spectra