JPL Update

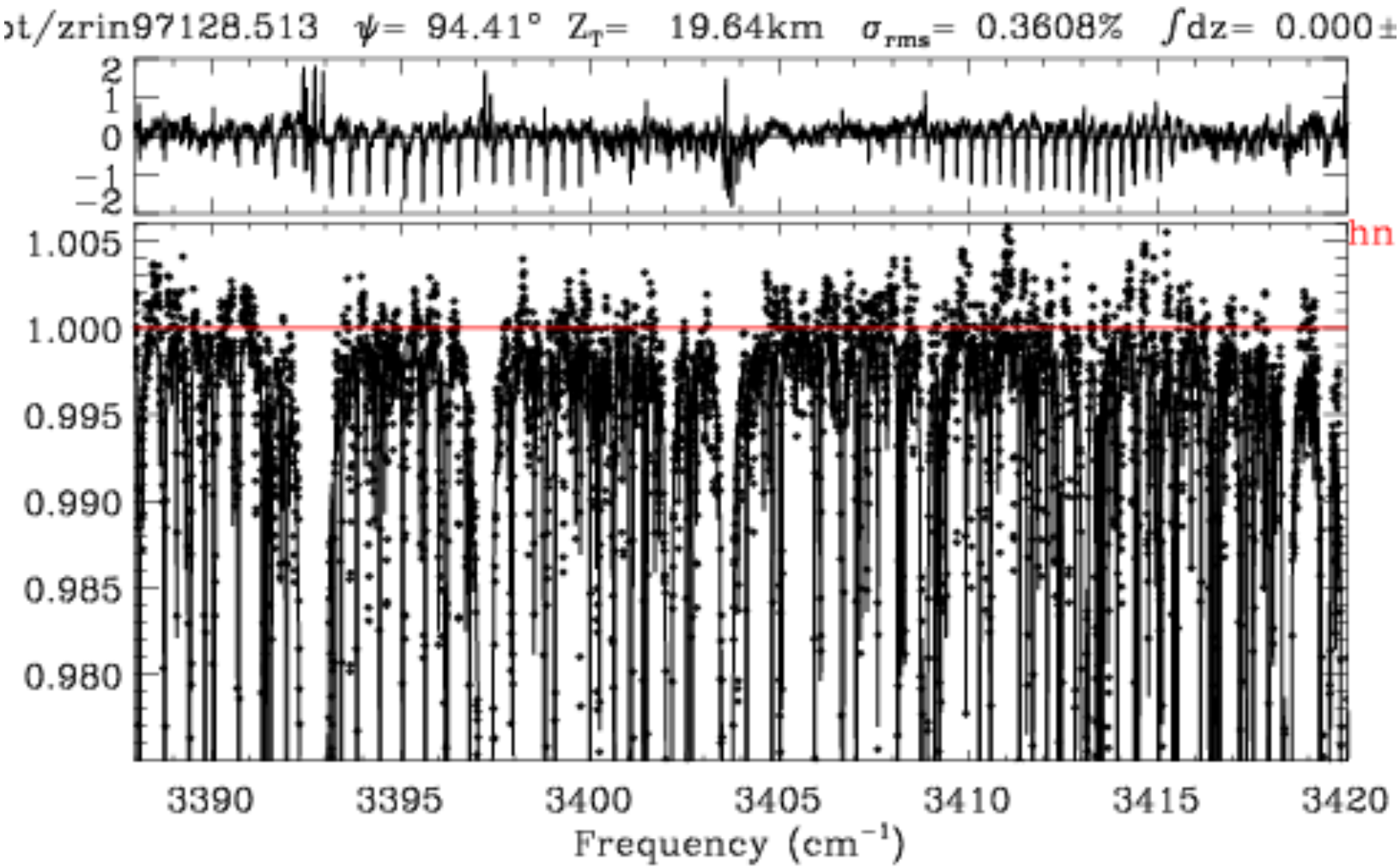
Four topics:

- HNO_3 Update
- New COFCl linelist
- C_2H_6 linelist evaluation
- MATMOS

ACE Science Team meeting

Waterloo, May 11-12, 2011

Yet another HNO_3 band missing from HITRAN – $2\nu_2$ at 3404 cm^{-1}



HNO_3 -- Background

At the 2008 ACE STM, I complained about the large number of HNO_3 bands missing from HITRAN, and described empirical HNO_3 linelists developed to crudely represent their absorption.

This is not to facilitate HNO_3 retrievals, but to improve retrievals of gases whose absorption lines overlap missing HNO3 bands.

Here I recap on the current state of HNO_3 spectroscopy and identify another missing HNO_3 band – the $2\nu_2$ at 3404 cm^{-1}.

HITRAN 2008 covers only 11/54 possible ground-state bands:

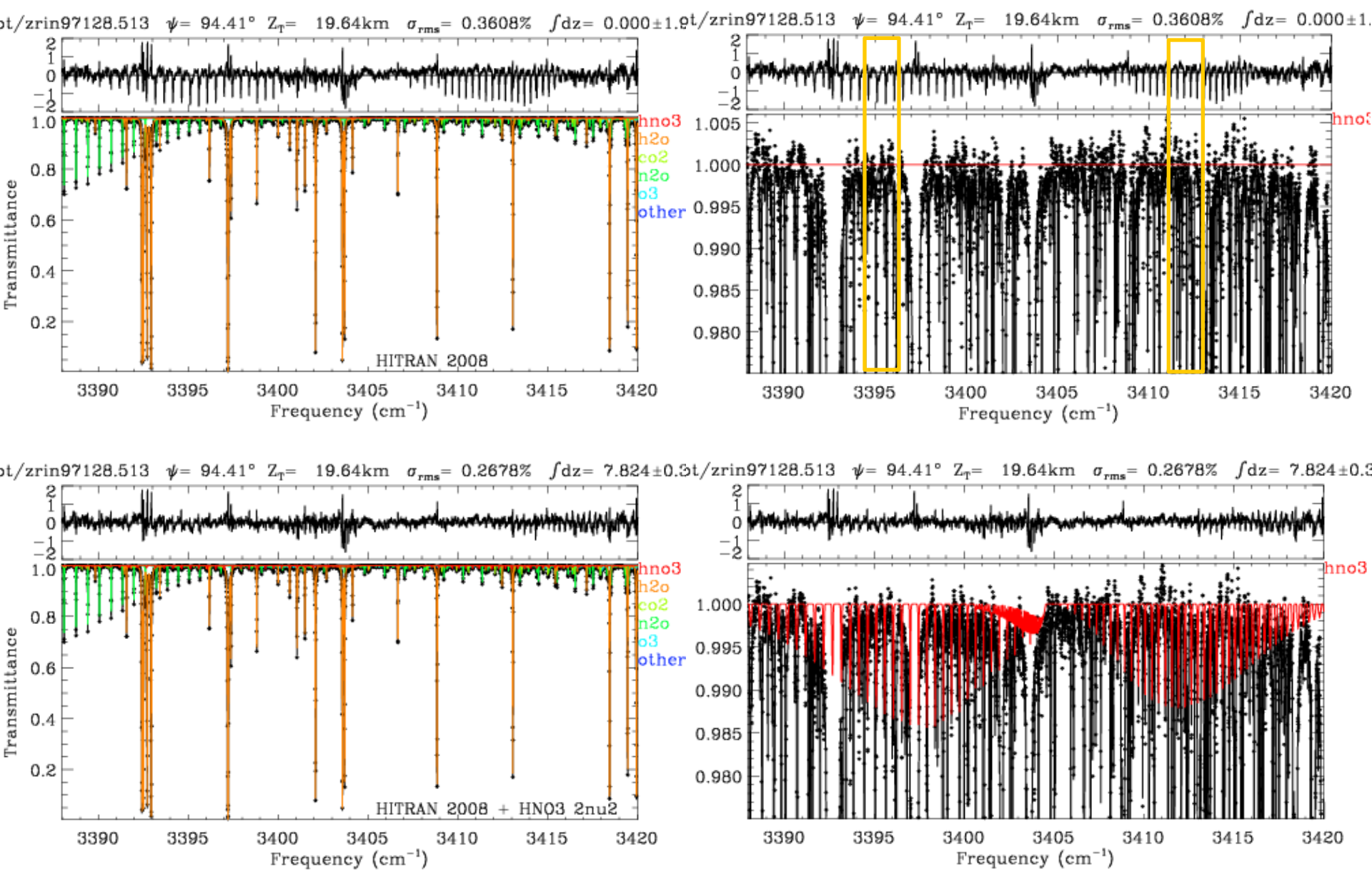
- 8/9 fundamentals (missing ν_1)
- 1/9 overtones ($2\nu_9$ only)
- 2/36 combination bands
- 4/100+ hot-bands
- 1/5 single-substituted isotopologs

Possible HNO_3 Bands

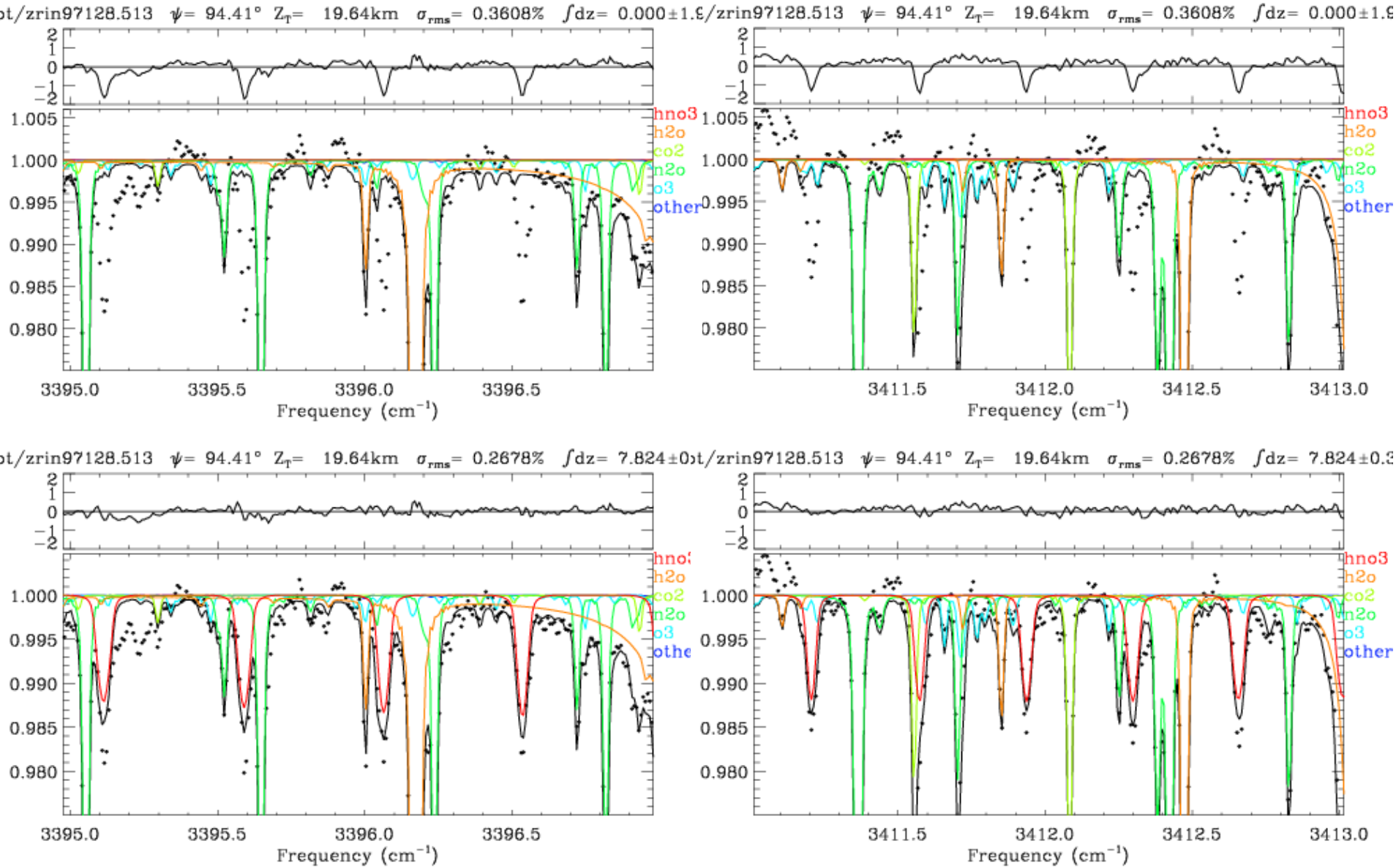
458.2	ν_9
580.3	ν_7
646.8	ν_6
763.2	ν_8
879.1	ν_5
914.6	$2\nu_9$
1036.4	$\nu_7 + \nu_9$
1102.8	$\nu_6 + \nu_9$
1158.3	$2\nu_7$
1205.0	$\nu_8 + \nu_9$
1224.6	$\nu_6 + \nu_7$
1291.0	$2\nu_6$
1303.2	ν_4
1326.2	ν_3
1334.6	$\nu_5 + \nu_9$
1340.8	$\nu_7 + \nu_8$
1407.2	$\nu_6 + \nu_8$
1456.5	$\nu_5 + \nu_7$
1522.8	$\nu_5 + \nu_6$
1523.3	$2\nu_8$
1639.0	$\nu_5 + \nu_8$
1709.6	ν_2
1754.7	$2\nu_5$
1757.9	$\nu_4 + \nu_9$
1780.8	$\nu_3 + \nu_9$
1879.7	$\nu_4 + \nu_7$
1902.7	$\nu_3 + \nu_7$
1946.1	$\nu_4 + \nu_6$
1969.1	$\nu_3 + \nu_6$
2062.3	$\nu_4 + \nu_8$
2085.2	$\nu_3 + \nu_8$
2163.5	$\nu_2 + \nu_9$
2177.9	$\nu_4 + \nu_5$
2200.9	$\nu_3 + \nu_5$
2285.3	$\nu_2 + \nu_7$
2351.7	$\nu_2 + \nu_6$
2467.9	$\nu_2 + \nu_8$
2583.5	$\nu_2 + \nu_5$
2601.2	$2\nu_4$
2624.1	$\nu_3 + \nu_4$
2645.1	$2\nu_3$
3006.8	$\nu_2 + \nu_4$
3029.7	$\nu_2 + \nu_3$
3404.4	$2\nu_2$
3551.7	ν_1
4006.9	$\nu_1 + \nu_9$
4123.7	$\nu_1 + \nu_7$
4190.1	$\nu_1 + \nu_6$
4306.3	$\nu_1 + \nu_8$
4421.9	$\nu_1 + \nu_5$
4845.2	$\nu_1 + \nu_4$
4868.1	$\nu_1 + \nu_3$
5250.8	$\nu_1 + \nu_2$
7089.2	$2\nu_1$

Green: HITRAN 2008 *Red: Empirical linelists developed*

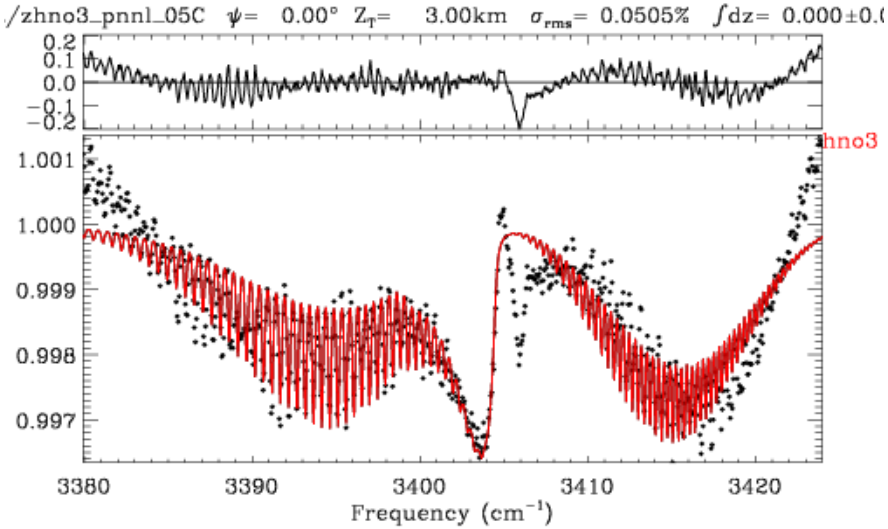
Fits to MkIV balloon spectra



Zoom into fits to MkIV balloon

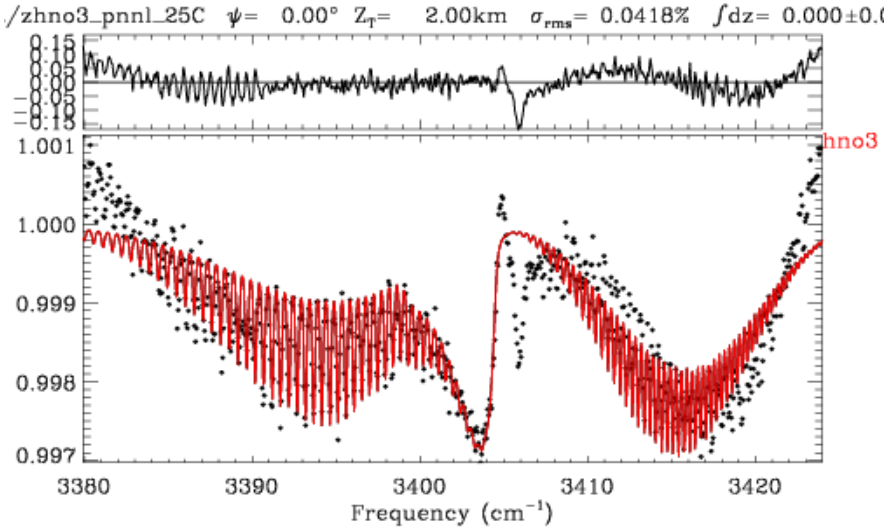


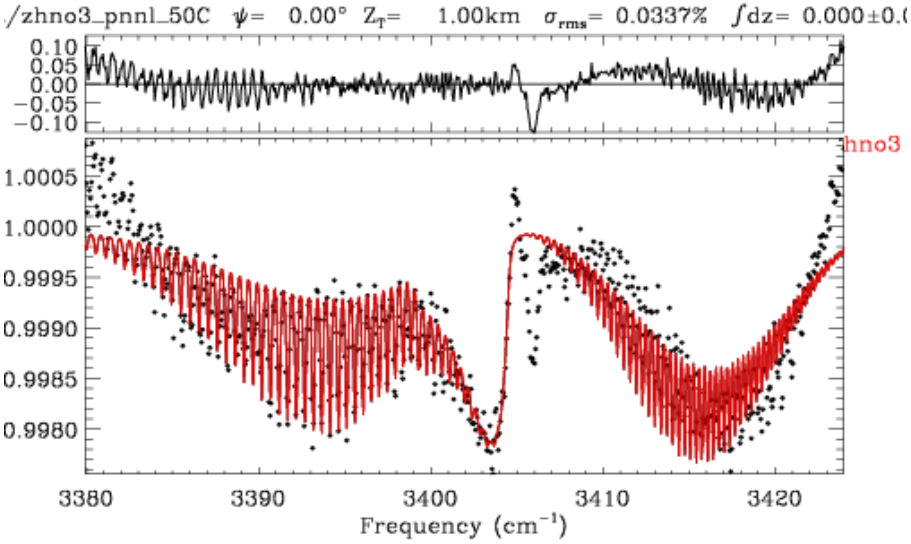
Fitting PNNL Laboratory spectra



Used new HNO_3 linelist to fit low resolution PNNL spectra measured at 1 atm and 5, 25, and 50C.

Does a reasonable job, except for the missing absorption feature at 3406 cm^{-1}





HNO_3 Summary/Conclusions

Another missing HNO_3 band ($2\nu_2$ centered at 3404 cm^{-1}) has been identified in MkIV balloon spectra.

At 20 km tangent altitude, the missing HNO_3 absorptions can reach 1.5% deep, and dominate the spectral fitting residuals in the 3390-3420 cm^{-1} region.

A crude, empirical HNO_3 linelist has been developed to represent the $2\nu_2$ band of HNO_3. This contains 9407 lines covering 3377 to 3424 cm^{-1}.

The new linelist gives improved spectral fitting residuals to MkIV balloon spectra and reasonable fits to PNNL laboratory HNO_3 spectra.

So far, empirical HNO_3 linelists have been created for:

- $2\nu_3$ at 2645 cm^{-1} 2 % deep
- $2\nu_2$ at 3404 cm^{-1} 1½ % deep
- ν_1 at 3551 cm^{-1} 60 % deep
- $\nu_1+\nu_9$ at 4007 cm^{-1} 10 % deep

Linelists should **not** be used for retrieving HNO_3 itself. They should only be used for fitting other gases of interest in these regions, where HNO_3 is an interferent.

COFCl spectroscopy

Contents lists available at ScienceDirect

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The ν_1, ν_2, and ν_3 bands of carbonyl chlorofluoride (COFCl) at 5.3, 9.1, and 13.1 μm: position and intensity parameters and their use for atmospheric studies

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ABSTRACT

Q2 A list of line positions and, for the first time, of line intensities was generated for the ν_1, ν_2, and ν_3 fundamental bands of the $^{12}C^{16}OF^{35}Cl$ and $^{12}C^{16}OF^{37}Cl$ isotopologs of carbonyl chlorofluoride, located at 5.3, 9.1, and 13.1 μm, respectively. In addition, for the most abundant isotopolog ($^{12}C^{16}OF^{35}Cl$) this linelist includes also the contributions from the first two associated hot bands. The parameters included in this database were

PROOF

COFCl Spectroscopy --History

ATMOS Linelist (Brown et al., 1987)
Included ν_3 Q-branch of the ^{35}Cl isotopolog (764.1-764.7 cm^{-1}, 413 lines)

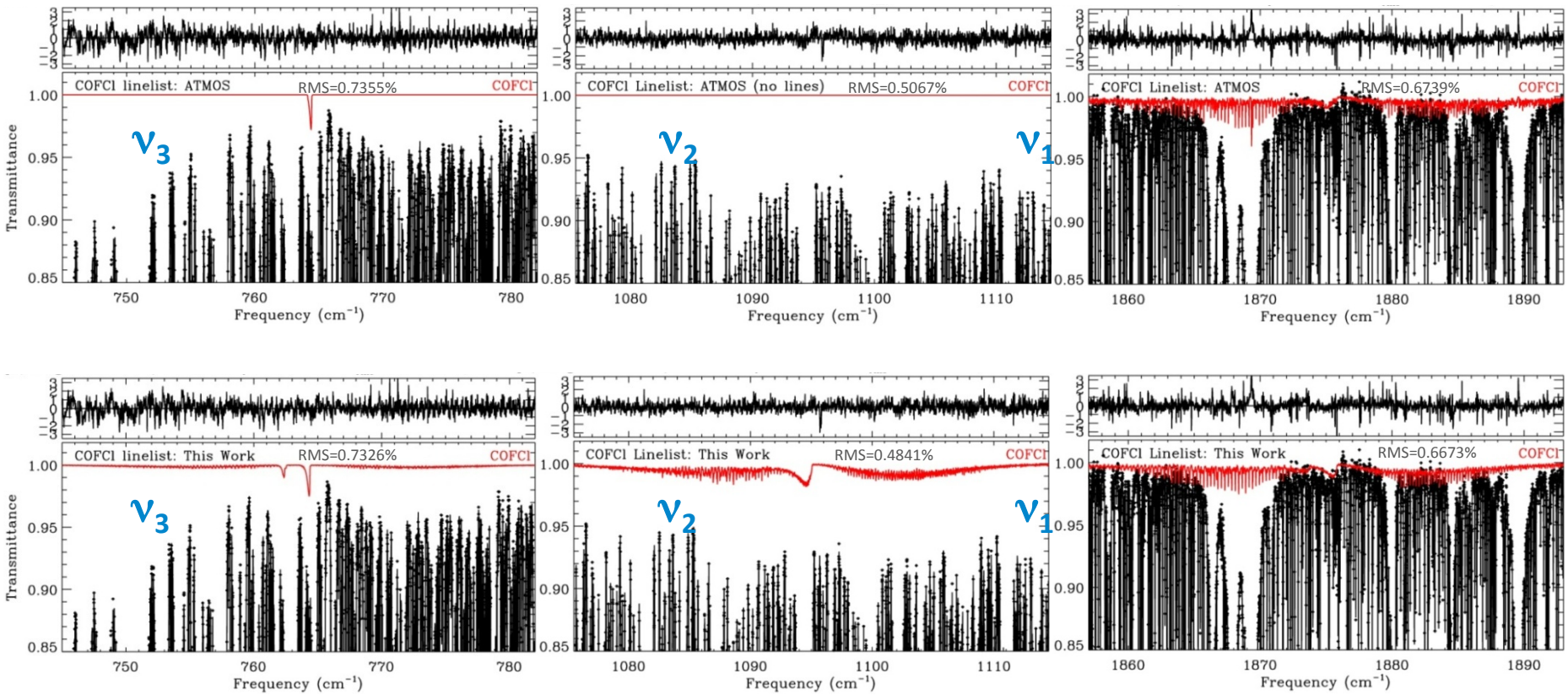
ATMOS Linelist (Brown et al., 1996)
Added ν_1 band of the ^{35}Cl isotopolog (1850.0-1907.9 cm^{-1}, 2036 lines) based on a sample of COFCl measured at Kitt Peak by Brown/Toth. Strength accurate to within a factor 3. All ν_1 lines had E"=345 cm^{-1}
Parts of the ν_1 linelist were used by Rinsland et al., (2007) and Fu et al., (2009) for the measurement of COFCl profiles from ACE, obtaining surprisingly good agreement with model predictions.

Perrin/Demaison Linelist (July 2010, unpublished)
Based on earlier work (Perrin et al. 2001; Demaison et al., 2003)
Covers ν_1, ν_2, ν_3 bands, P, Q, R-branches, ^{35}Cl and ^{37}Cl isotopologs

- ν_1 covers 1805 -1913 cm^{-1} 67797 lines
- ν_2 covers 1049 -1136 cm^{-1} 70125 lines
- ν_3 covers 735 - 796 cm^{-1} 55856 lines

MkIV balloon spectral fits at 20 km

Upper Panels: Old linelist (Brown et al., 1996)
Lower Panels: New linelist (Perrin et al., 2011)



Consistency of Retrieved COFCl

Band	Brown et al., (1996)	Perrin et al. (2011)
ν_3 763 (cm^{-1})	0.81 ± 0.02	0.96 ± 0.02
ν_2 1095 (cm^{-1})	N/A	1.00 ± 0.01
ν_1 1875 (cm^{-1})	1.25 ± 0.01	1.04 ± 0.01

Table shows the bias of the COFCl retrieved from MkIV balloon spectra for a particular band/linelist relative to the ν_2 band

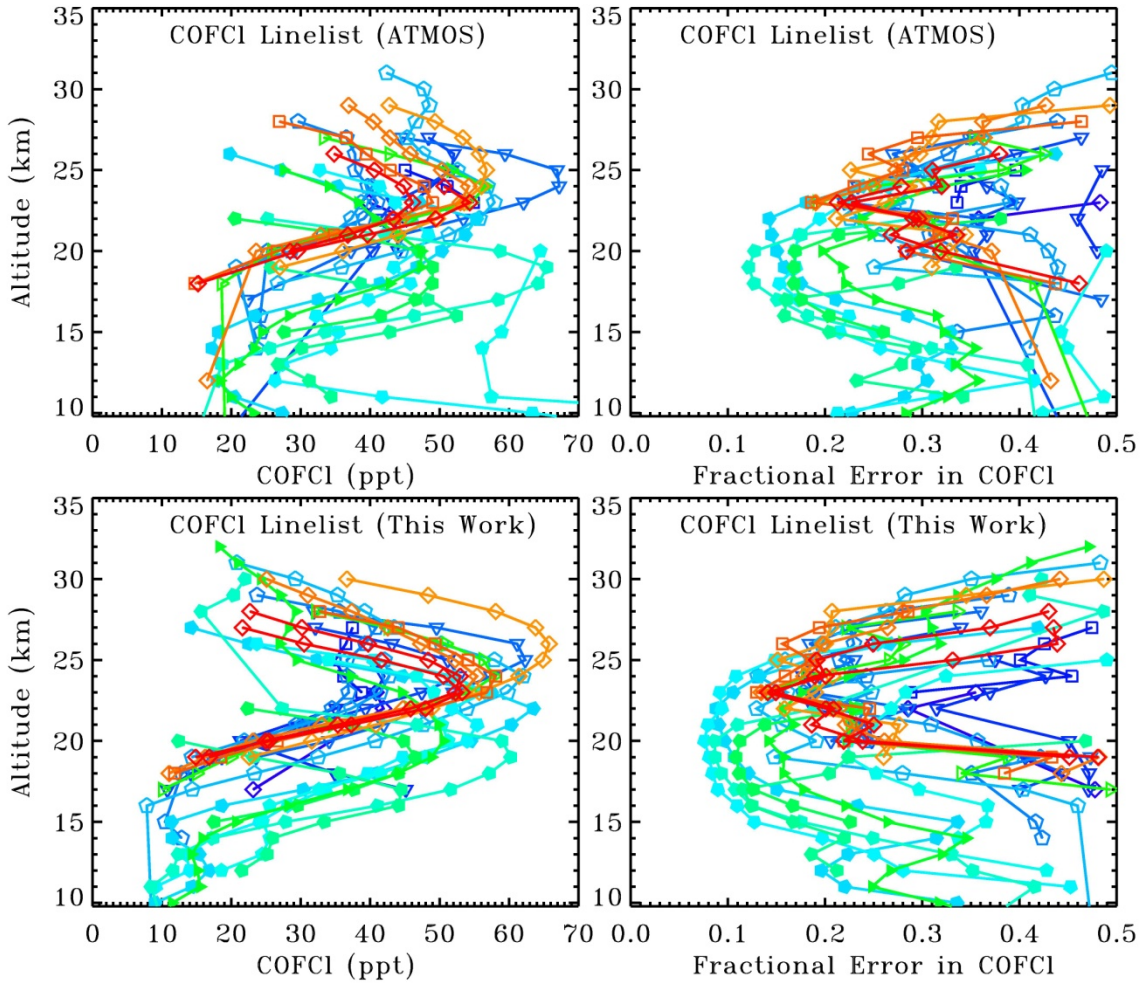
COFCl retrieved from the ν_1 band at 1875 cm^{-1} is 21% smaller using the new Perrin/Demaison linelist than the Brown et al., (1996) linelist.

COFCl retrieved from the ν_3 band at 763 cm^{-1} is 15% larger using the new Perrin/Demaison linelist than the Brown et al., (1996) linelist.

Band-to-band biases are ±4% with new linelist. This is much better than the Brown et al., (1996) linelist (± 25%)

Retrieved MkIV COFCl profiles – Old versus New linelists

Left: Retrieved vmr profiles Right: Uncertainties



Old Linelist (ATMOS)
(Brown et al., 1996)

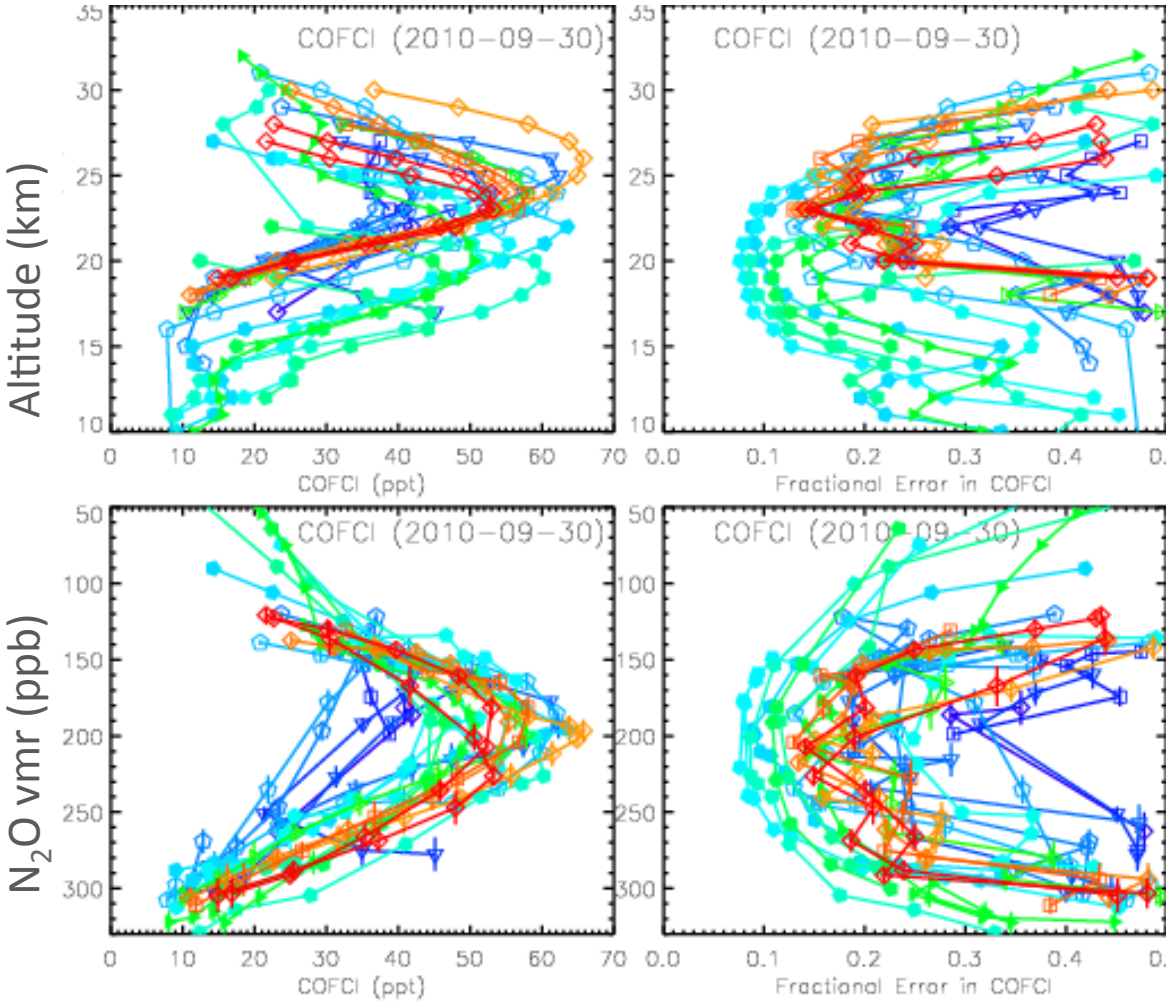
Profiles are inconsistent
Uncertainties are > 12%

New Linelist
(Perrin et al., 2011)

Profiles are more consistent
Uncertainties are 7+ %

Retrieved MkIV COFCl profiles – New linelist - Z versus N_2O

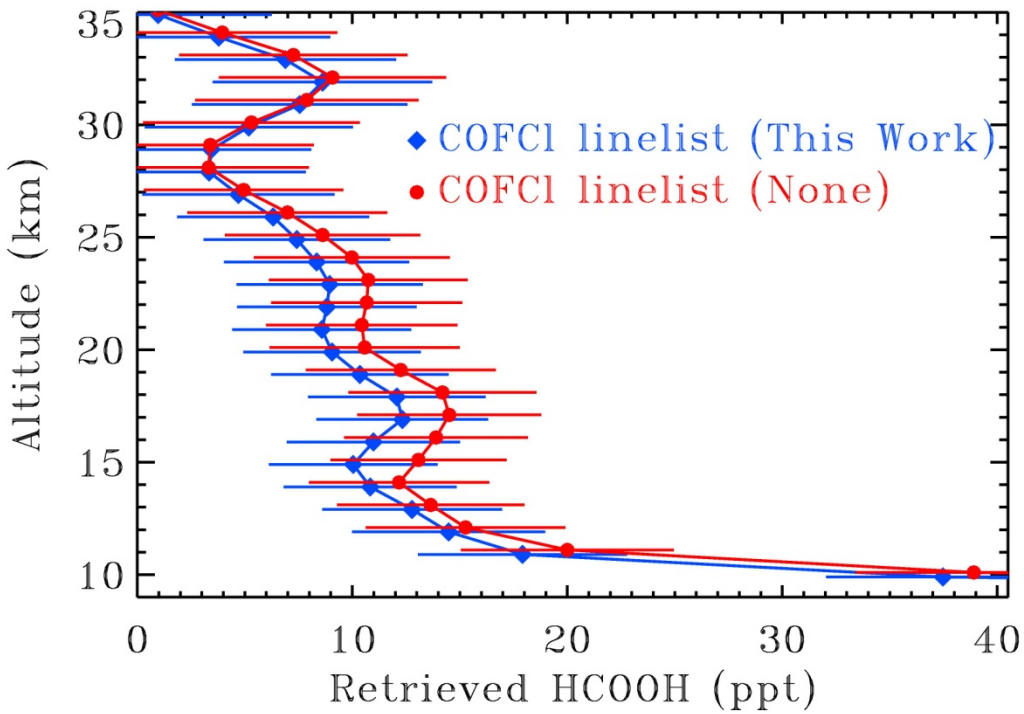
Left: Retrieved vmr profiles Right: Uncertainties



Plotted versus altitude, the mid-latitude COFCl profiles peak at ~25 km, whereas the high latitude COFCl profiles peak at 20 km.

Plotted versus N_2O, all COFCl profiles peak at ~200 ppb of N_2O.

Impact on ν_2 COFCl band on HCOOH



Atmospheric HCOOH profiles retrieved from MkIV balloon spectra. The fitted window extends from 1075 to 1135 cm^{-1}, encompassing the entire ν_6 band of HCOOH centered at 1105 cm^{-1}, which overlaps the ν_2 band of COFCl. Retrievals were performed with (blue) and without (red) the new COFCl linelist. In the absence of the ν_2 COFCl lines, the retrieval incorrectly attributes the COFCl absorption to HCOOH. This results in retrieved HCOOH vmr profile being over-estimated by 20% in the 15–25 km altitude range, where COFCl absorption is a maximum relative to HCOOH.

COFCl Summary

A new COFCl linelist, described by Perrin et al., (2011), has been evaluated

It covers 600-2000 cm^{-1} region containing the ν_1, ν_2, ν_3 bands

In all cases, use of the new linelist improves the MkIV spectral fits

Consistency of the retrievals between the different bands is better than ±4%

The absolute accuracy of the retrievals is probably better than 20%, judging by comparisons of MkIV profiles with 2-D model predictions

The ν_2 band, which was missing from the ATMOS 1995 linelist, is the strongest of the three that can be measured in MkIV and ACE spectra

Retrieved profiles of COFCl are much improved: the strongest band (ν_2) is no longer missing, and the existing bands have better spectroscopy

New ν_2 band linelist not only provides for better COFCl retrievals, it also improves retrievals of other gases (e.g. HCOOH) that absorb near 1095 cm^{-1}

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Toward the understanding of the high resolution infrared spectrum of C_2H_6 near 3.3 μm☆

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Abstract

The Fourier transform infrared spectrum of ethane between 2860 and 3060 cm^{-1} has been re-investigated under high resolution at 229 K. The infrared absorption in this region is due mainly to the CH stretching fundamentals ν_5 (parallel band) and ν_7 (degenerate perpendicular band), and to the parallel combination system $\nu_8 + \nu_{11}$ (A_{4s}, A_{3s}). All the relevant perturbation mechanisms affecting the

Evaluation of Lattanzi C_2H_6 linelist

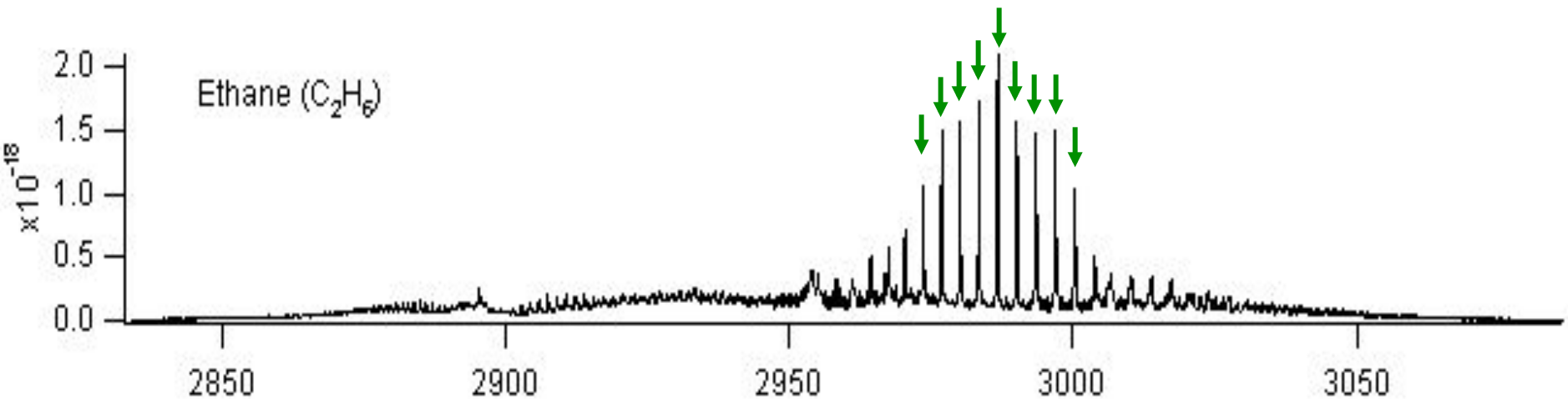
The poor state of C_2H_6 spectroscopy at 3 um has long been a pet peeve of mine

C_2H_6 absorptions that are missing from HITRAN can reach 15% deep limb spectra, perturbing retrievals of weakly absorbing trace gases in this region (e.g. CH_3Cl)

HITRAN 2008 contains lines for just the 9 strongest PQ branches. There were derived empirically by Linda Brown in 1985 (except for PQ_3)

Harrison et al. [2010] made a comprehensive set of lab C_2H_6 measurements

I used these data to develop an empirical pseudo-linelist (PLL) to represent the C_2H_6 absorptions in the 3 um region, as described at the previous ACE meeting

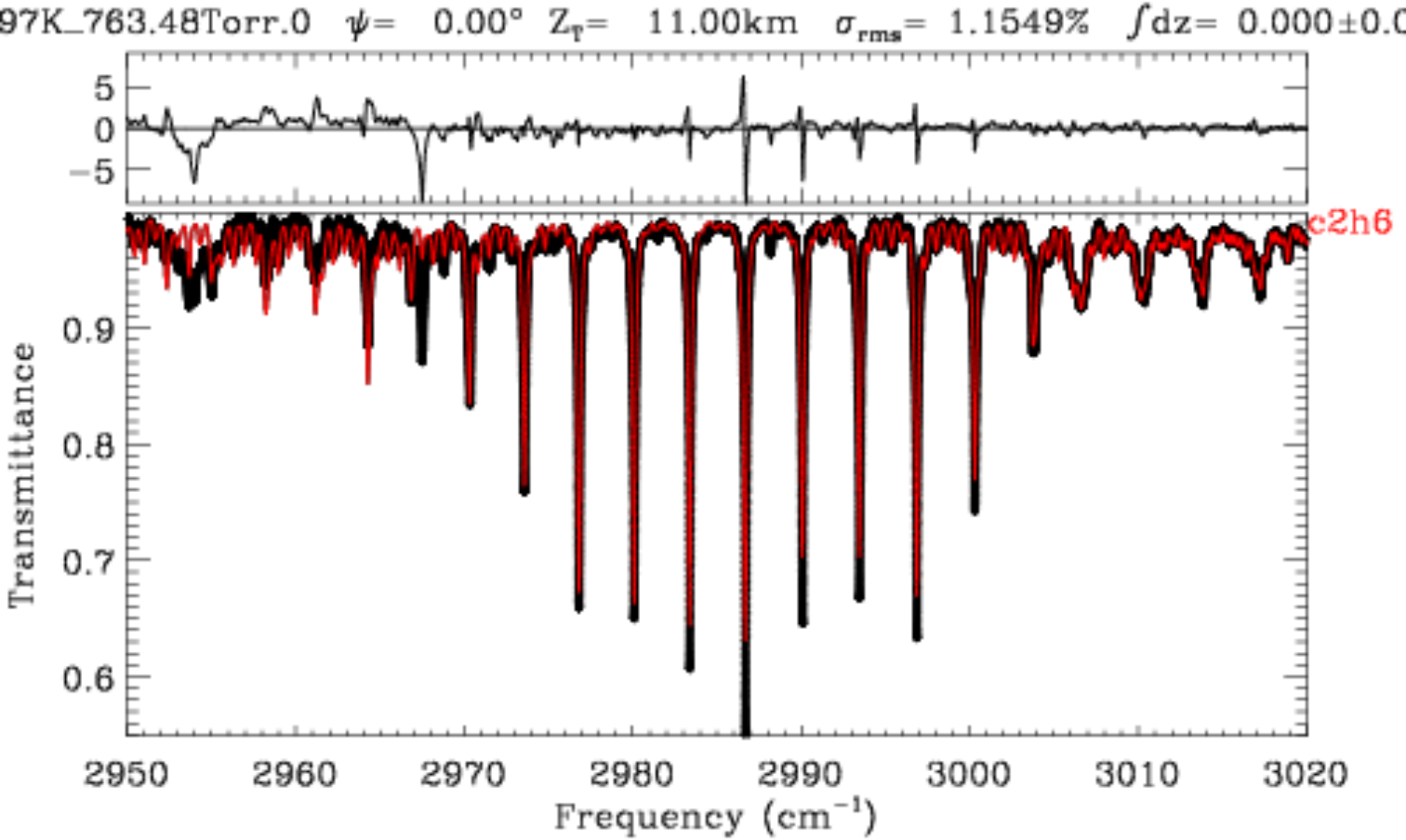


Use Lattanzi C_2H_6 linelist to fit Laboratory Spectra

The Lattanzi paper contains no figures showing fits to lab spectra. So I decided to do some of my own by using this new linelist to fit 29 different laboratory spectra:

- 24 spectra measured by Harrison et al.[2010] at RAL (195-300K)
- 3 spectra measured at PNNL at P=1 atm (5C, 25C, 50C)
- 2 spectra from Kitt Peak (May 30, 1985)

The following plots show spectral fits to some of these lab spectra.
The black points represent the measured lab spectra
The red line is the calculated spectrum based on the Lattanzi linelist



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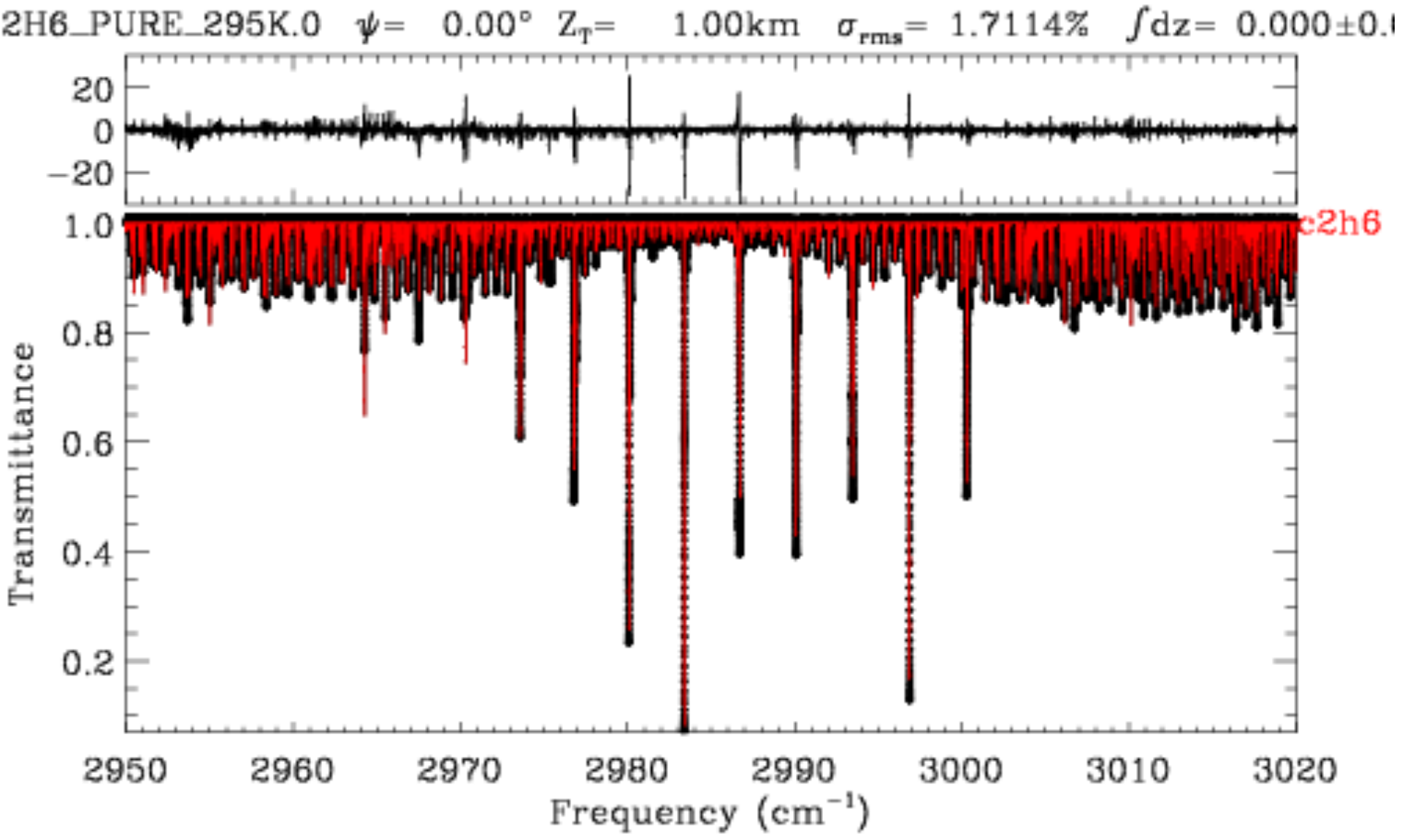

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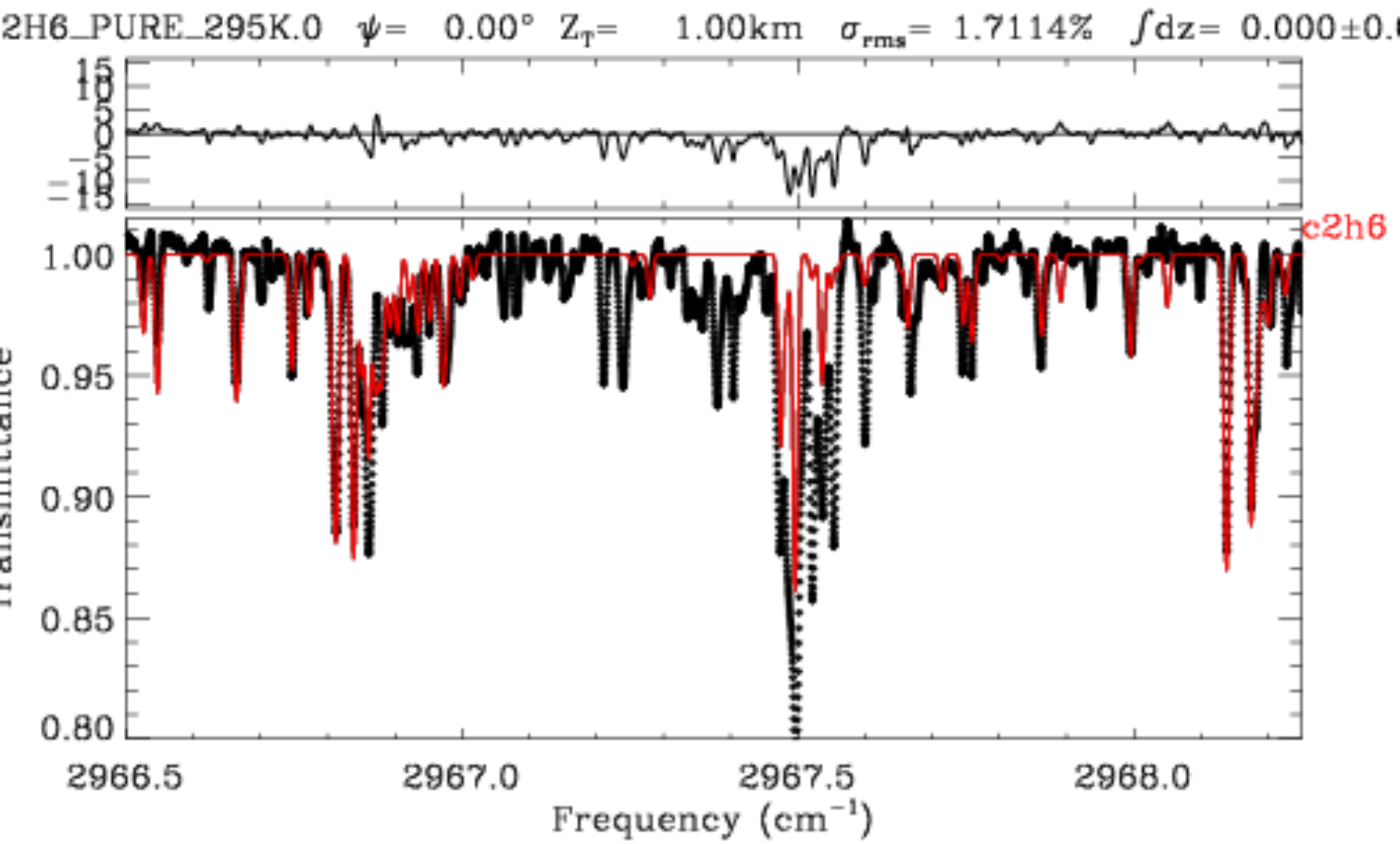

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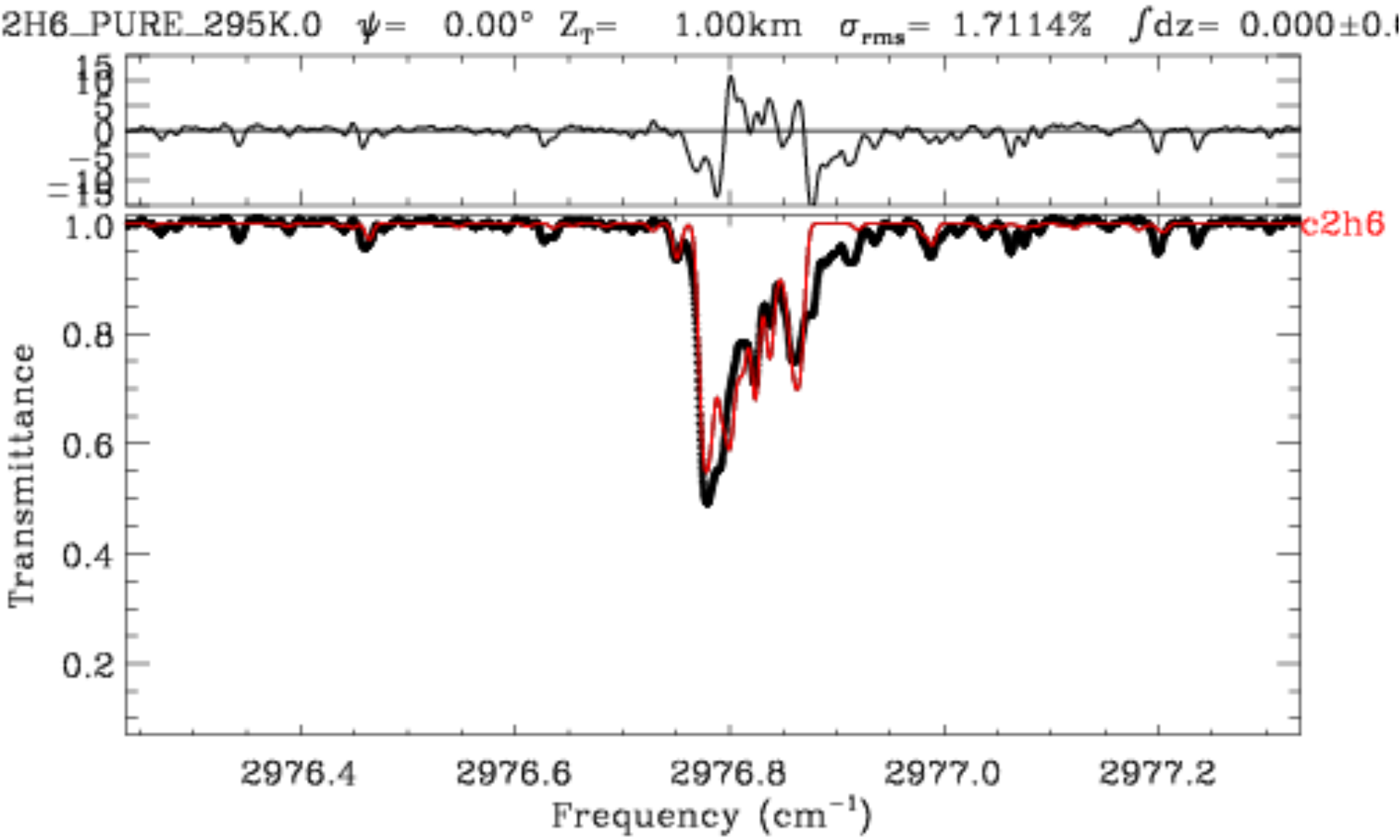

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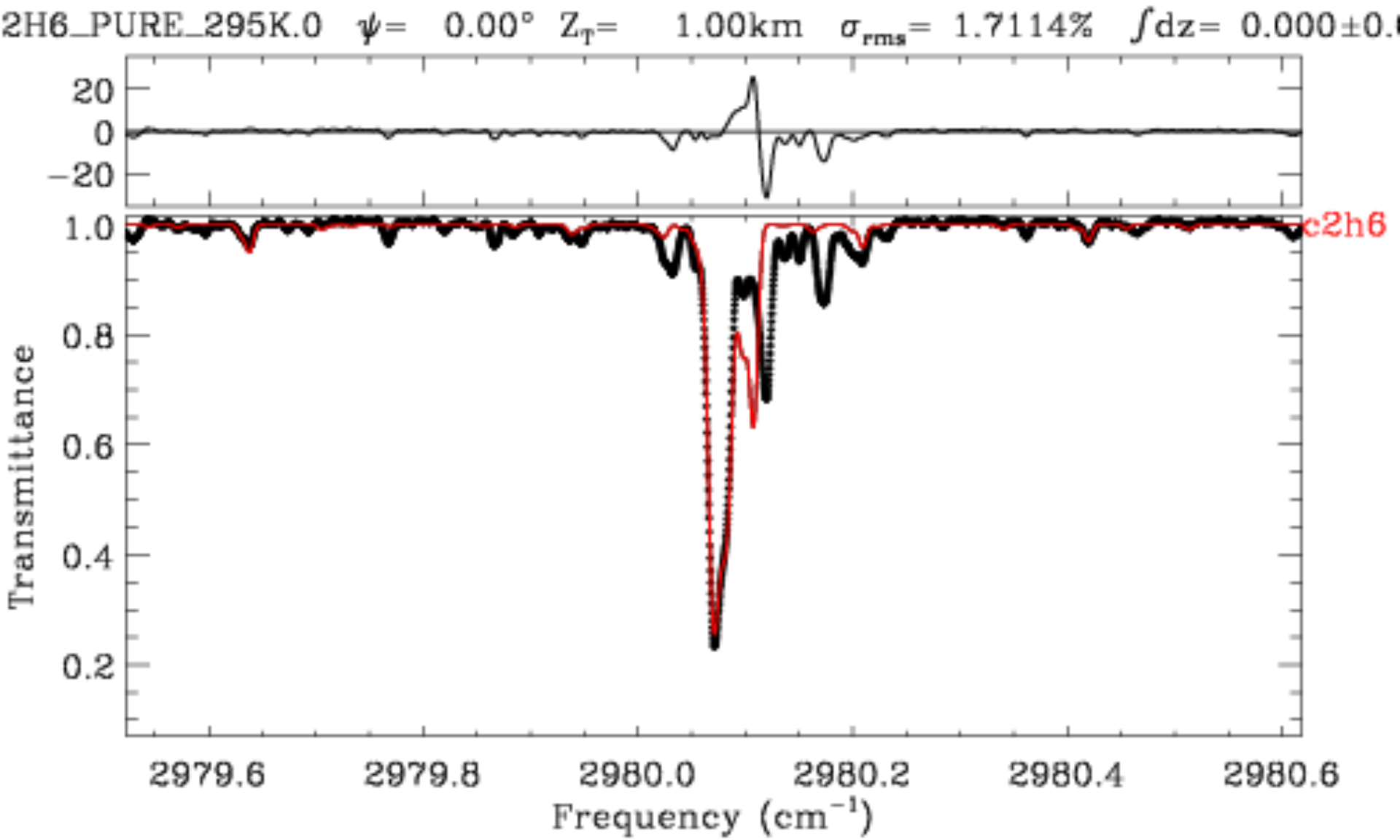

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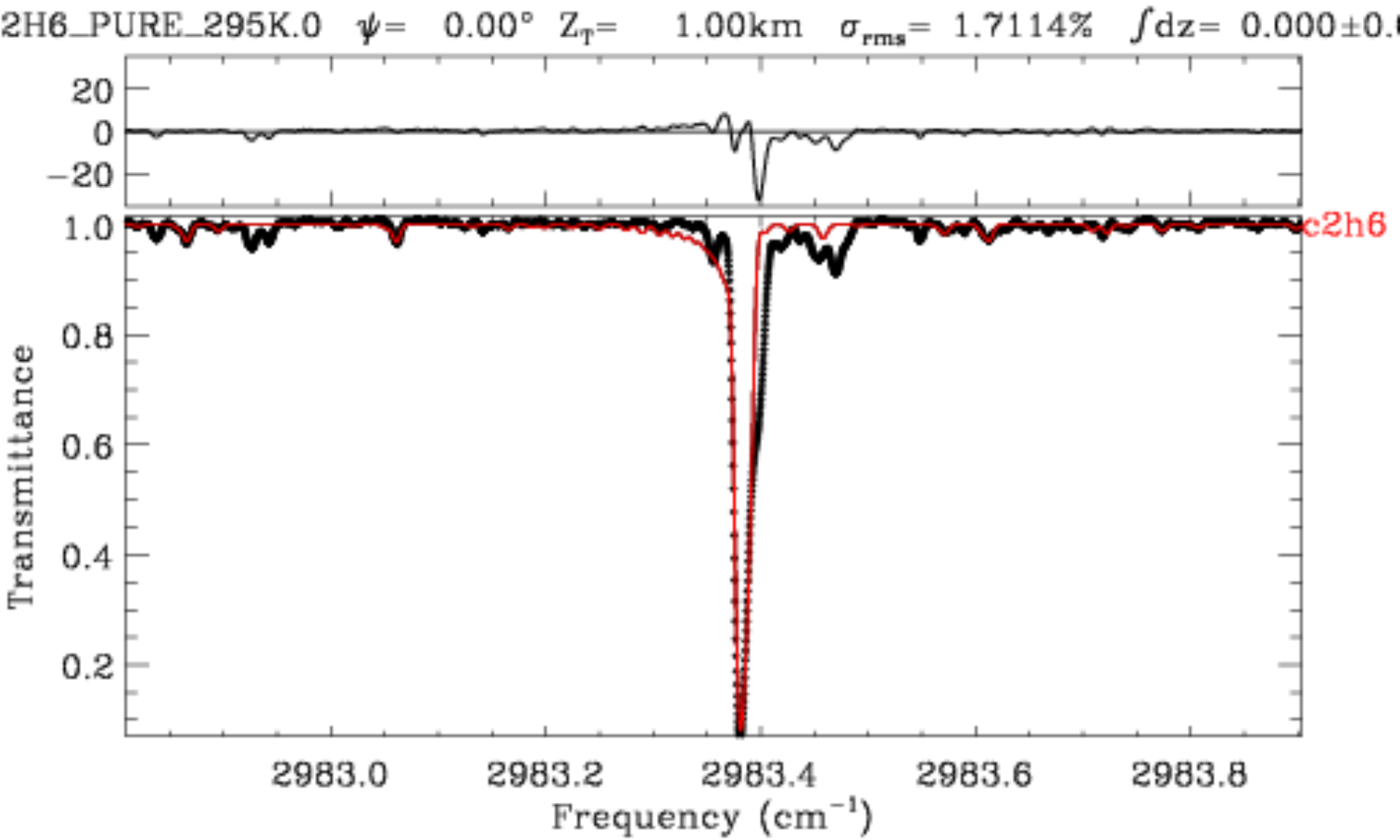
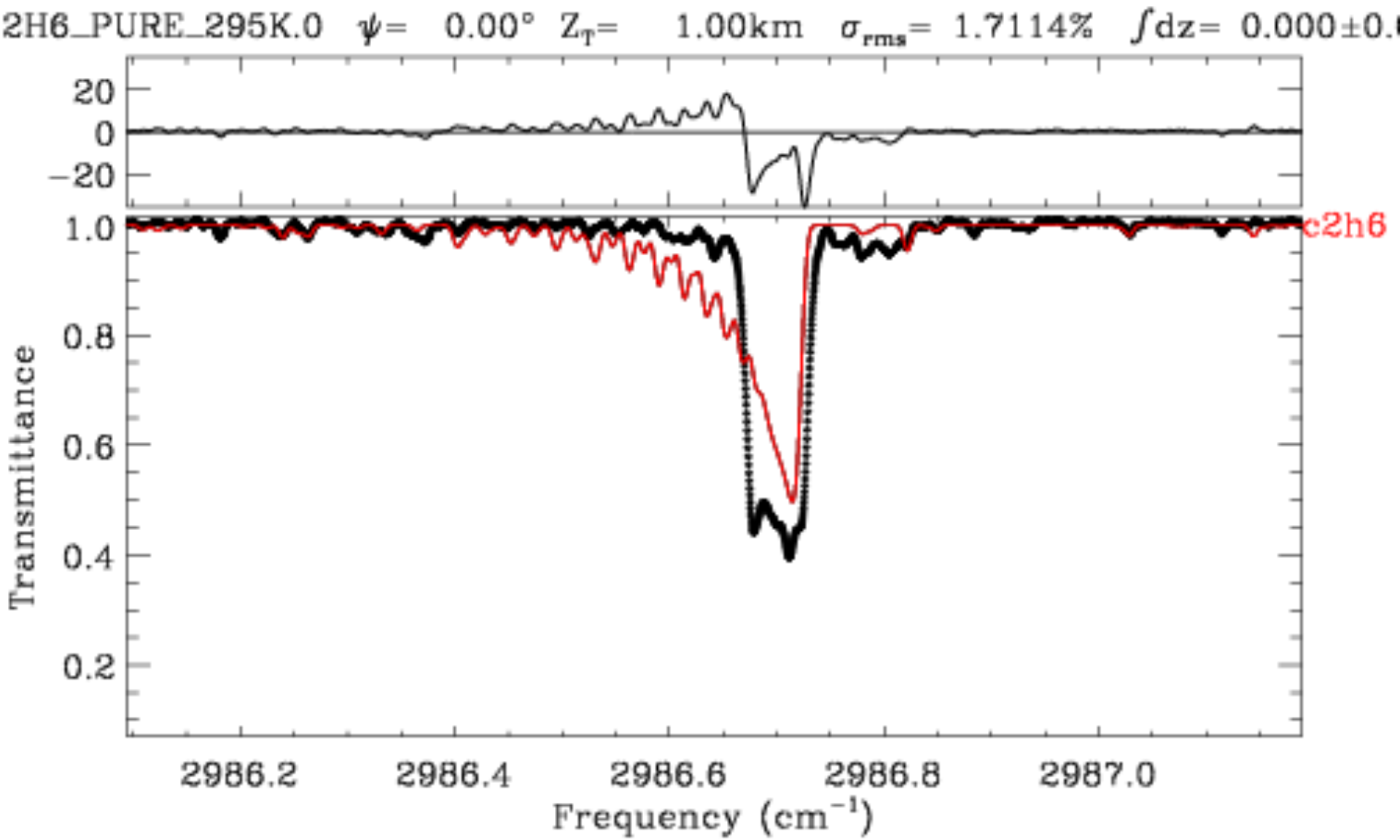

2H6_PURE_295K.0 ψ= 0.00° Z_T= 1.00km σ_rms= 1.7114% ∫dz= 0.000±0.
20
0
−20
1.0
0.8
0.6
0.4
0.2
Transmittance
c2h6
2983.0
2983.2
2983.4
2983.6
2983.8
Frequency (cm⁻¹)



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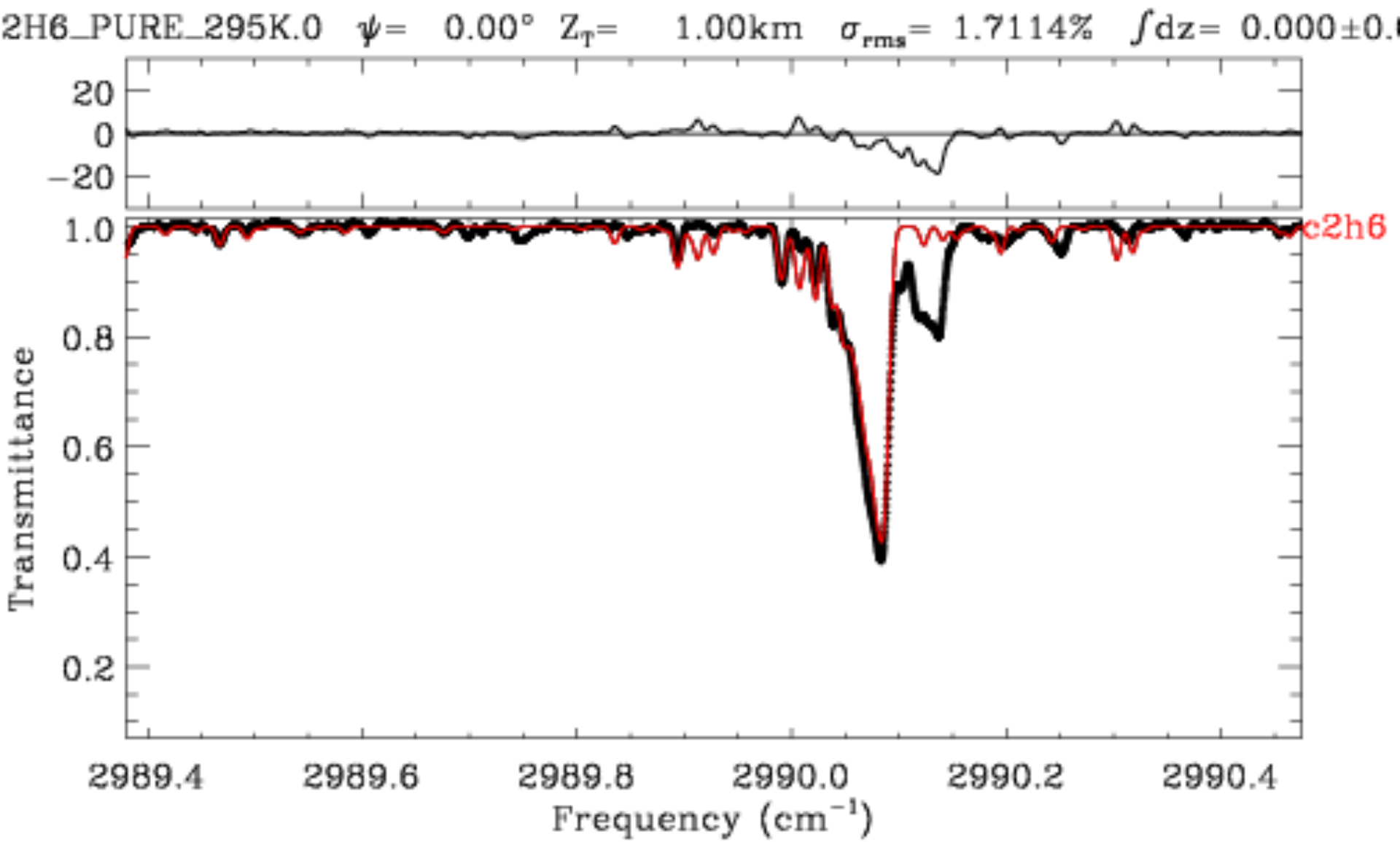

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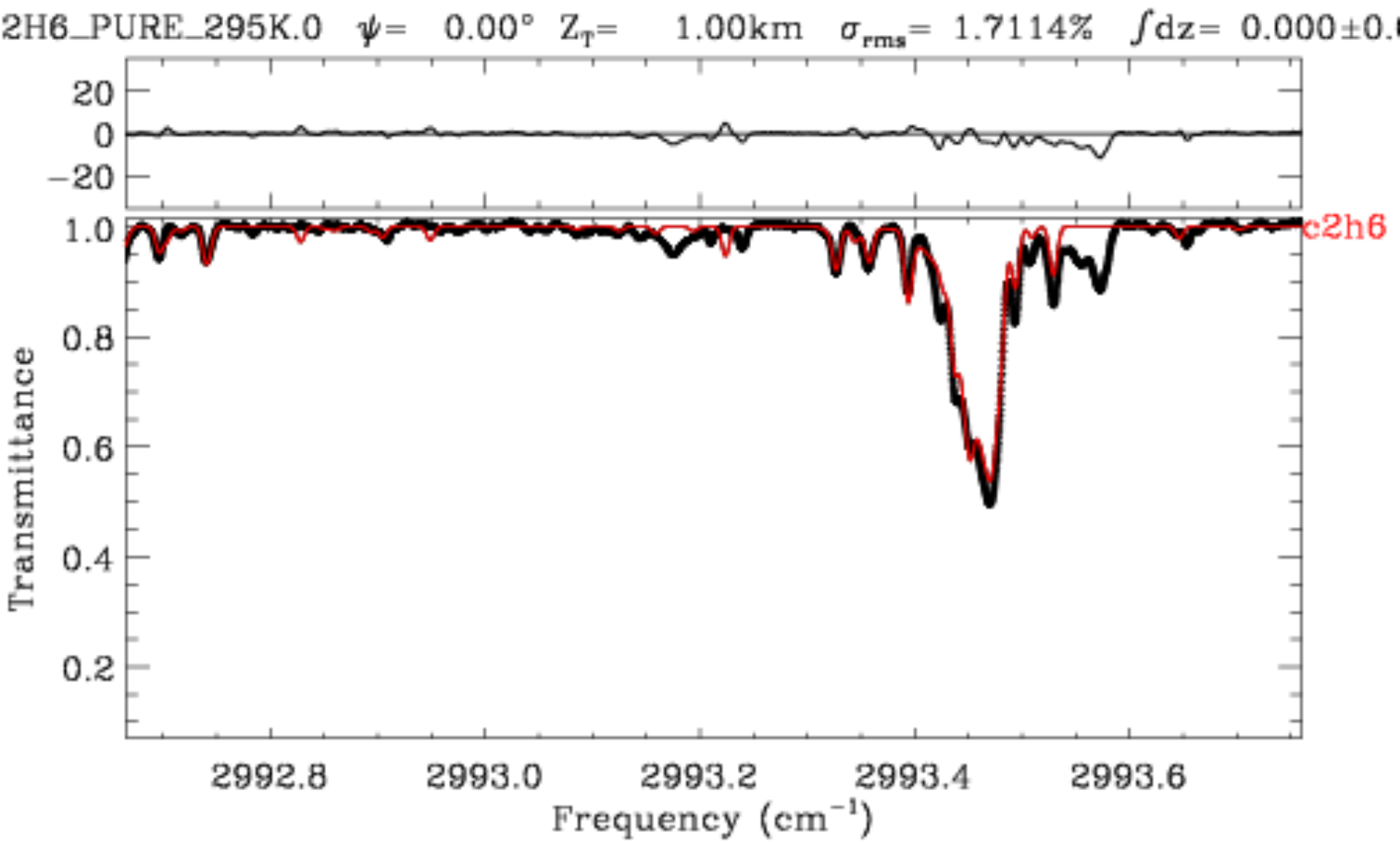

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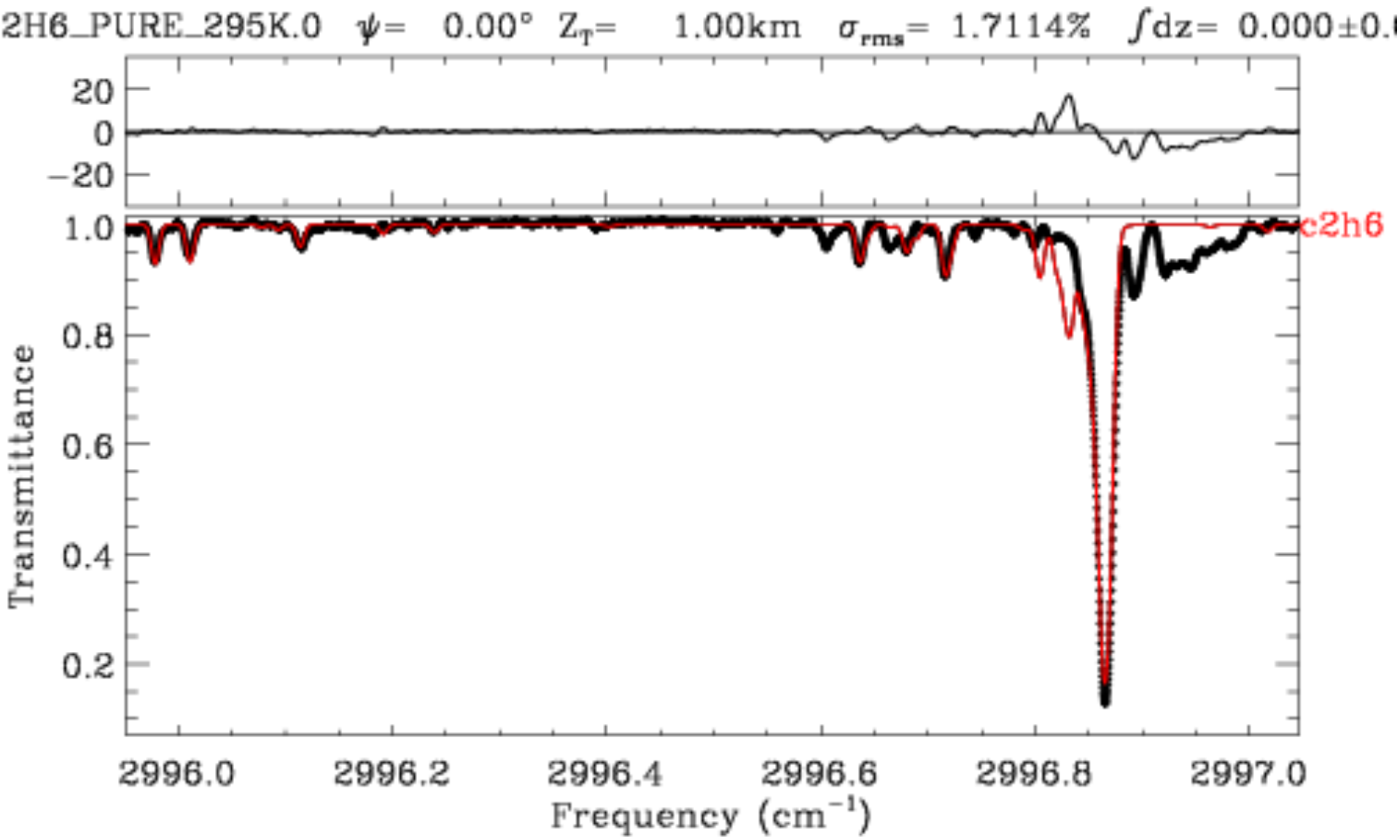

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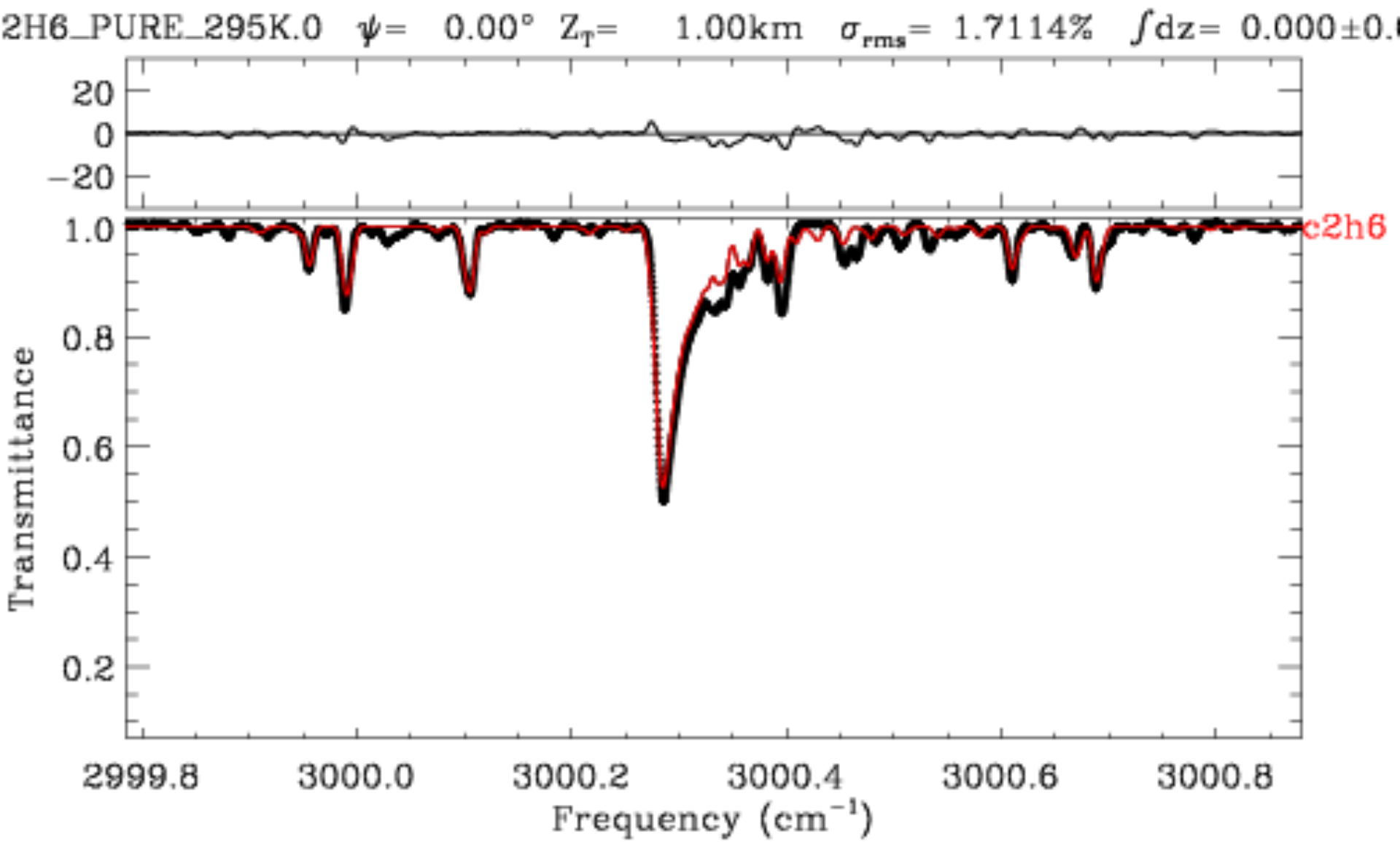

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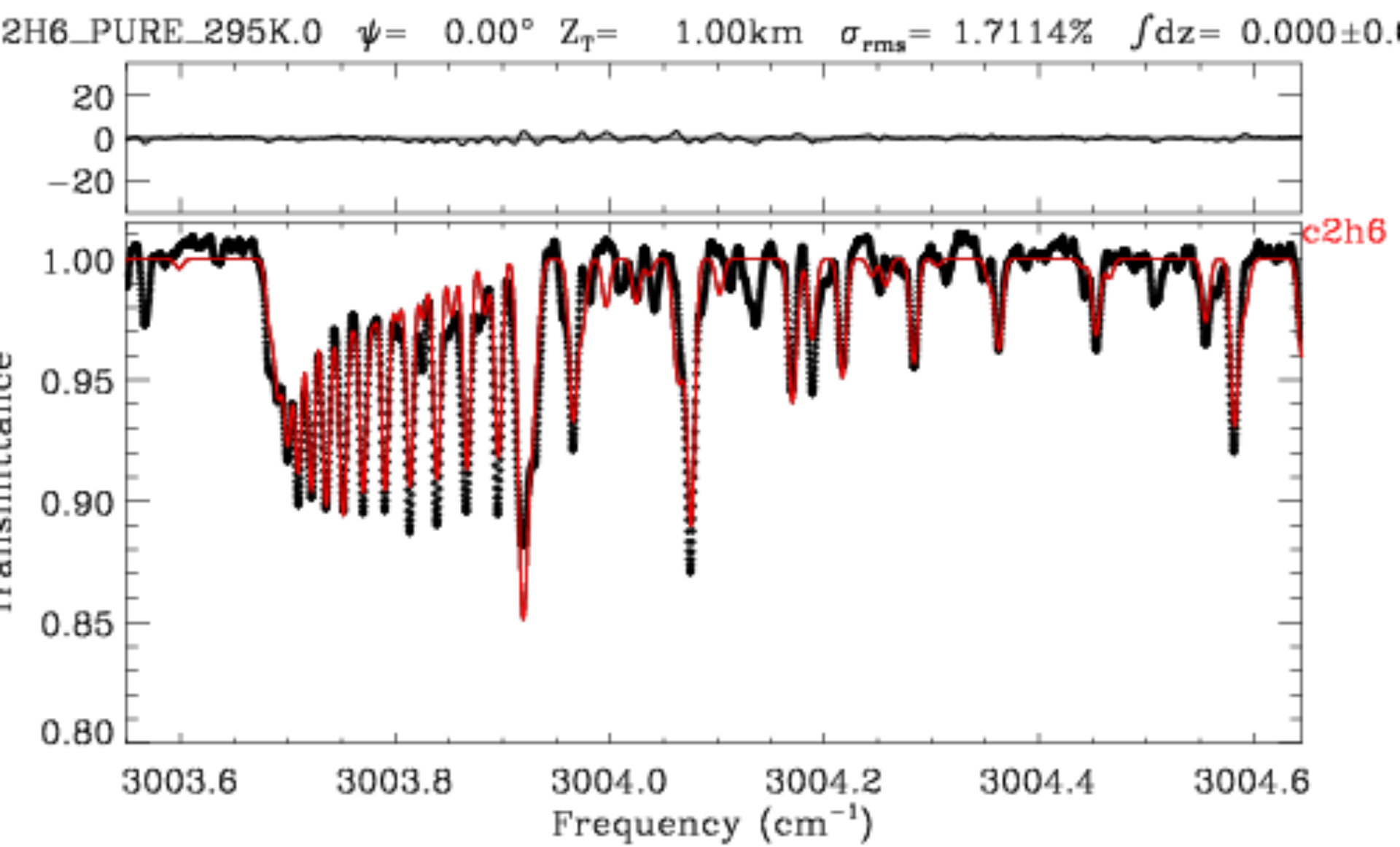

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Summary & Conclusions

Good News:

- New Lattanzi linelist is a factor 2 better than HITRAN in terms of the rms spectral fits over the entire 2950-3020 cm^{-1} region
- Fitted C_2H_6 amounts less biased and more consistent from spectrum to spectrum
- Main improvement comes from representation of the P- and R-branch "grass".

Bad News:

- Several Q-branches are less well represented in Lattanzi than in HITRAN 2008

The table below summarizes the spectral fitting diagnostics of the 29 spectra

Linelist	RMS fit (%)	Scale Factor
HITRAN 2008	4.0	0.89±0.14
Lattanzi (2011)	2.1	1.03±0.10
GCT PLL	0.2	1.00±0.02

Not a fair comparison because the GCT PLL was generated from 24/29 spectra fitted here. But it gives an idea of the size of the improvement still to be won.

Lattanzi linelist represents major spectroscopic advance, but there's still a long way to go. Empirical approaches (cross-sections or PLL) still best for 3 um C_2H_6

Mars Atmosphere Trace Molecule Occultation Spectrometer (MATMOS)

ESA/NASA ExoMars 2016 mission consists of:

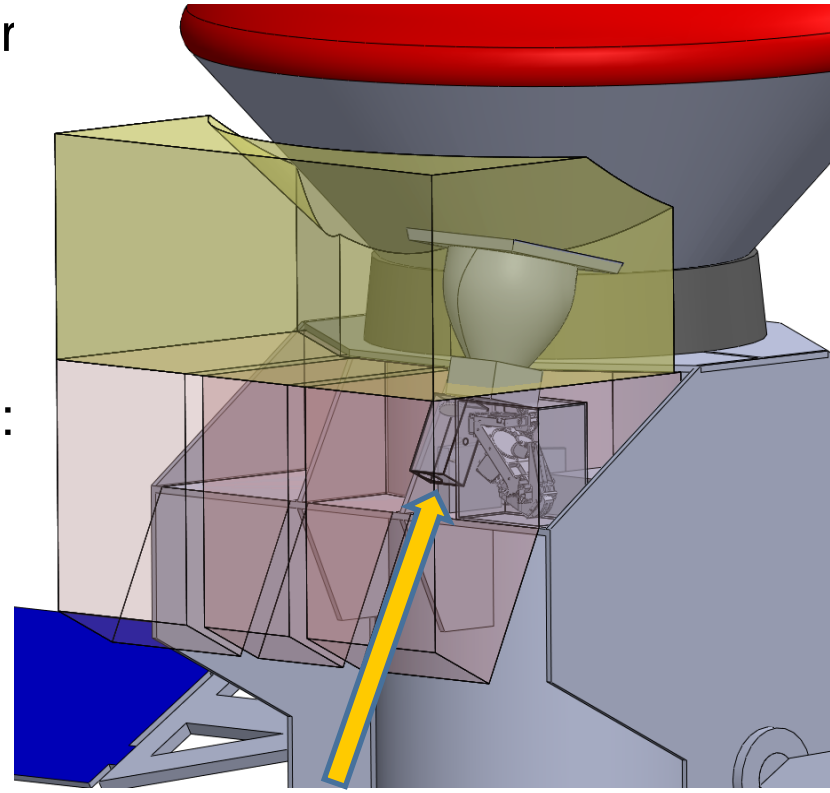
- Trace Gas Orbiter (EMTGO)
- Entry Demonstration Lander (EDL)

Launch in 2016, arrive at Mars 9 months later
Aerobraked into 385 x 440 km, 74 deg orbit.

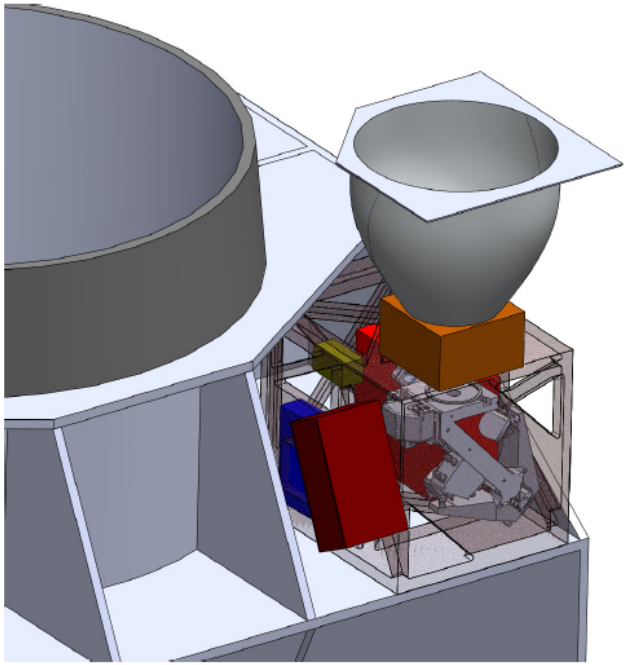
Two Earth-Year Science mission 2017-2019
(one Mars Year)

Five remote sensing instruments on EMTGO:

- MATMOS (Solar Occ FTS)
- SOIR NOMAD (IR Solar Occ & Nadir)
- EMCS (Thermal IR)
- HISCI (Camera)
- MAGIE (Camera)



MATMOS FTS



The MATMOS instrument is heavily based on ACE.

ABB-Bomem is the prime contractor for the FTS interferometer sub-system, the telescope, and the imager, which are CSA contributions to the instrument.

Ball Aerospace will build the radiative cryo-cooler.

Everything else provided by JPL.

The MATMOS project is managed by NASA's Jet Propulsion Laboratory where:
- signal chains and on-board processing hardware/software will be developed
- the final flight instrument will undergo assembly, testing, and calibration.

MATMOS Science Team is led by Paul Wennberg (PI, CalTech) and Victoria Hipkin (Co-PI, Canadian Space Agency (CSA)). It combines key member of the FTS community with planetary and terrestrial atmospheric scientists.

Mars Atmosphere

Currently only 6 IR-active gases have been definitively detected in Martian atmosphere: CO_2, CO, O_3, H_2O, H_2O_2, CH_4?

MATMOS promises to reduce detection limits by a couple of orders of magnitude, adding several more gases to the list.

The table (right) shows the MATMOS sensitivity to currently undetected gases

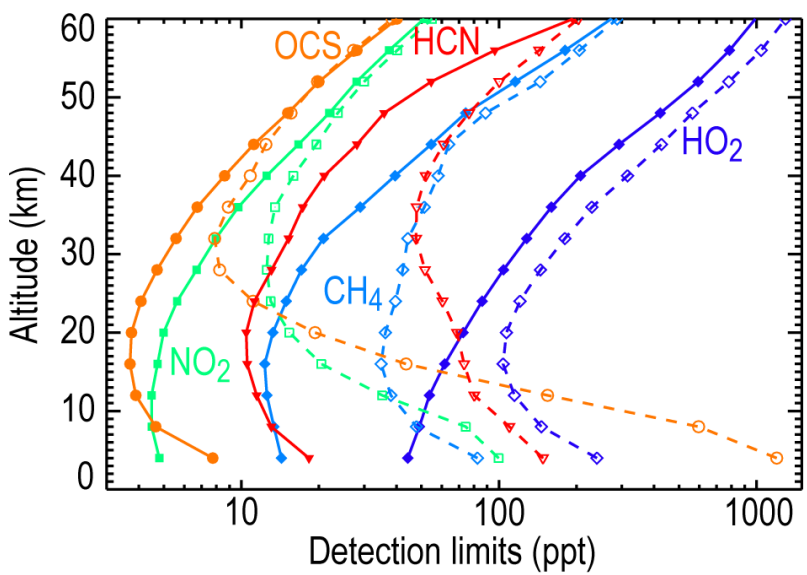
Gases Already Detected	Measured Abundance[5]	Expected Precision (%)	
		τ=0.1	τ=0.6
H_2O	10–1000 ppm	1	1.5
CO	700 ppm	1.5	2
O_3	40–200 ppb	5	8
H_2O_2	18 ppb[6]	3	4
CH_4	10 ppb[1-3]	4	10

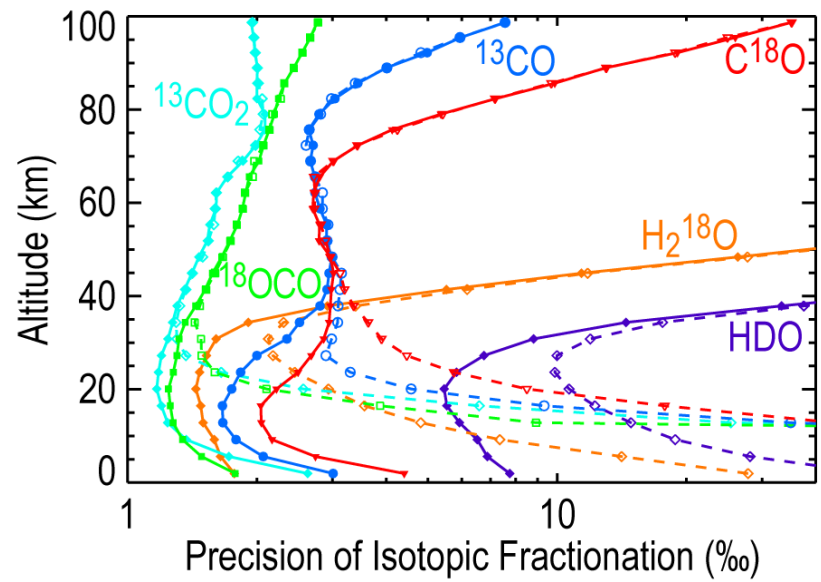
Gases Not Yet Detected	Measured Upper Limit[7] (ppt)	Predicted Abundance (ppt)	Expected Detection Limit (ppt)	
			τ=0.1	τ=0.6
HO_2		PC: 800	12	46
NO_2	<10,000	PC: 84	1	4
NO		PC: 300	8	45
N_2O	<100,000	PC: 1	1	2
C_2H_2	<2,000		3	10
C_2H_4	<500,000		8	42
C_2H_6	<400,000	G:1000	5	23
H_2CO	<3,000		6	42
NH_3	<5,000		2	10
HNO_3			2	5
CH_3OH			6	60
CH_3CN			26	107
HCN		G: 5-2000	3	21
H_2S	<20,000	G: <<1	500	2500
OCS	<10,000	G: <<1	1	3
SO_2	<1,000[8]	G: <<1	2	5
HCl	<2,000		4	26
HF			1	7
PH_3	<100,000		3	74

MATMOS Science Goals

The proposed MATMOS investigation will:

- Determine the origin of trace gases diagnostic of active geological and biogenic activity
- Quantify the lifetimes of these diagnostic gases in the context of the atmospheric state
- Provide definitive detections and support for the TGO localization effort
- Determine the sources, lifetime and sinks of Mars methane





MATMOS – Main Differences from ACE

Different Planet:
- Dust can cause large limb extinctions near surface at short λ
- Larger dynamic range of signals

Restricted Telemetry Rate back to Earth (as low as 1.9 Gb/day)
- Interferograms must be processed into spectra on board spacecraft
- Scan speed must vary from 2.0 to 5.7 s per scan

Use 24-bit ADC to avoid gain switching during interferograms
- Higher quality spectra (lower sensitivity to vibration)
- Requires Uniform Time Sampling (UTS) of raw interferograms
- Additional on-board processing

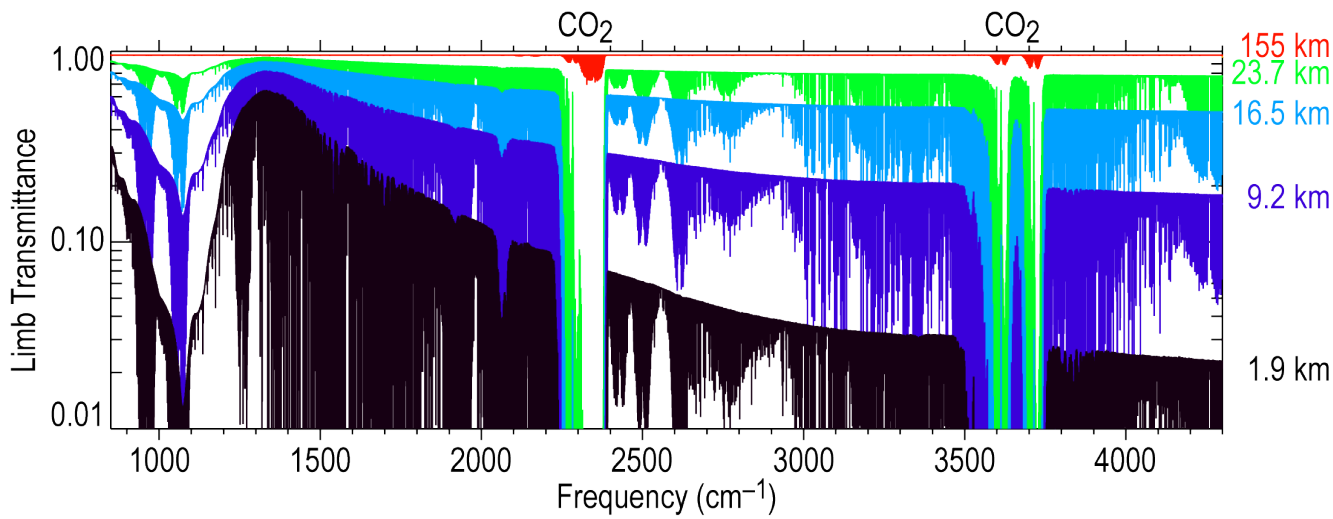
Uses spacecraft to point at sun (feasible because little refraction at Mars)
- no solar tracking mirror

Interferometer improvements
- higher modulation efficiency at short λ (better mirror mounts)
- GOSAT scan electronics

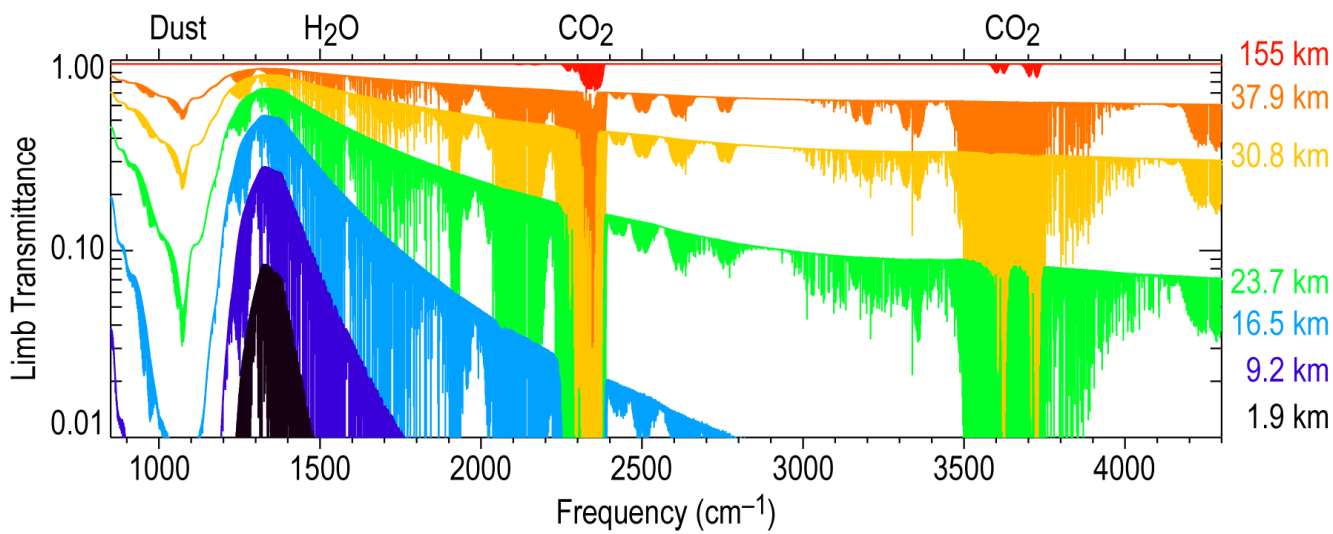
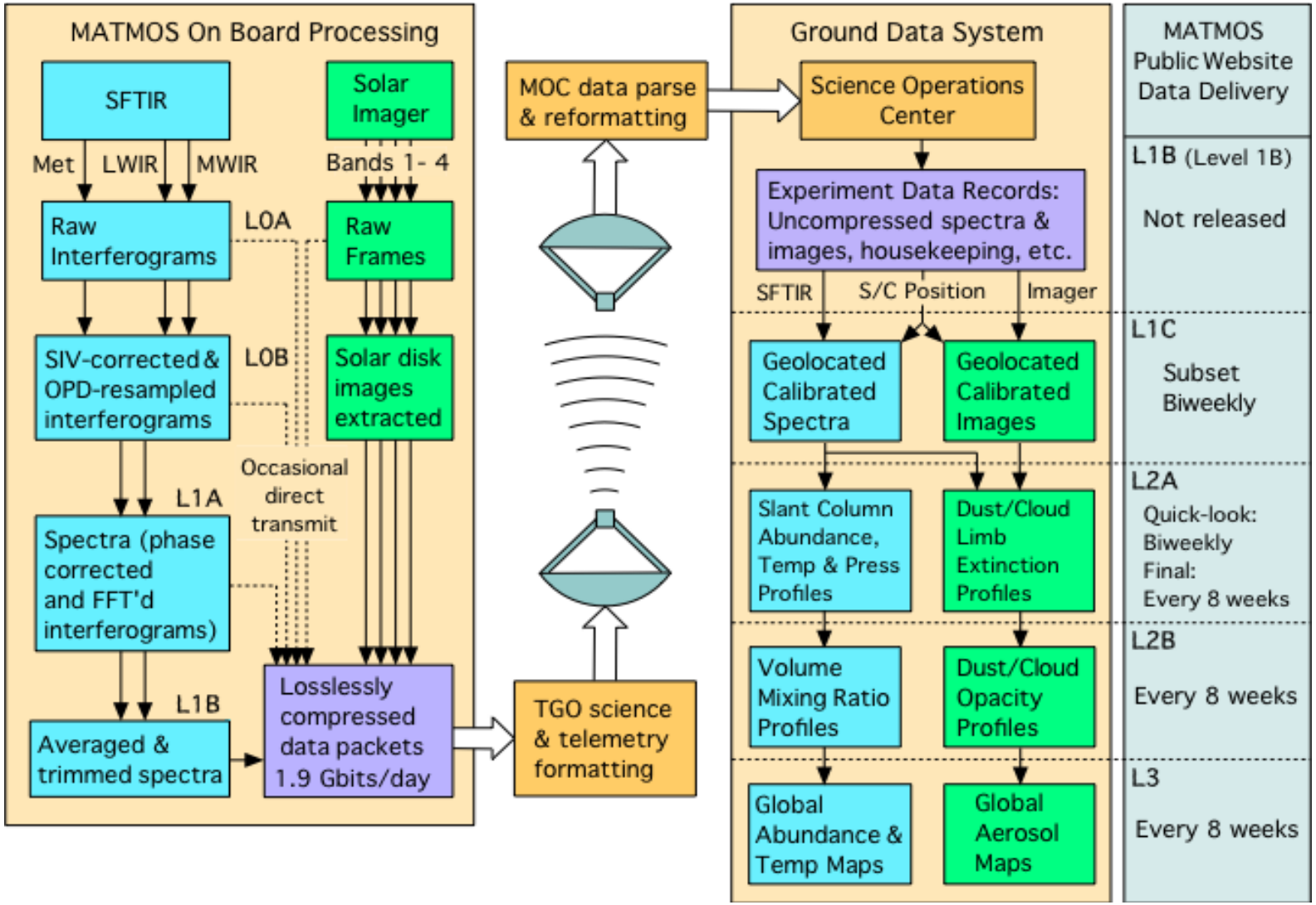
Simulated Mars Occultation Spectra

Atmospheric dust: scattering at short λ, absorption by silicate around 9 um

Low Dust



High Dust



MATMOS Data Processing