Evaluation of Lattanzi C_2H_6 spectral linelist

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Fitted to RAL spectra (Harrison et al. 2010) over the 2950-3020 cm^{-1} region

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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

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 :

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

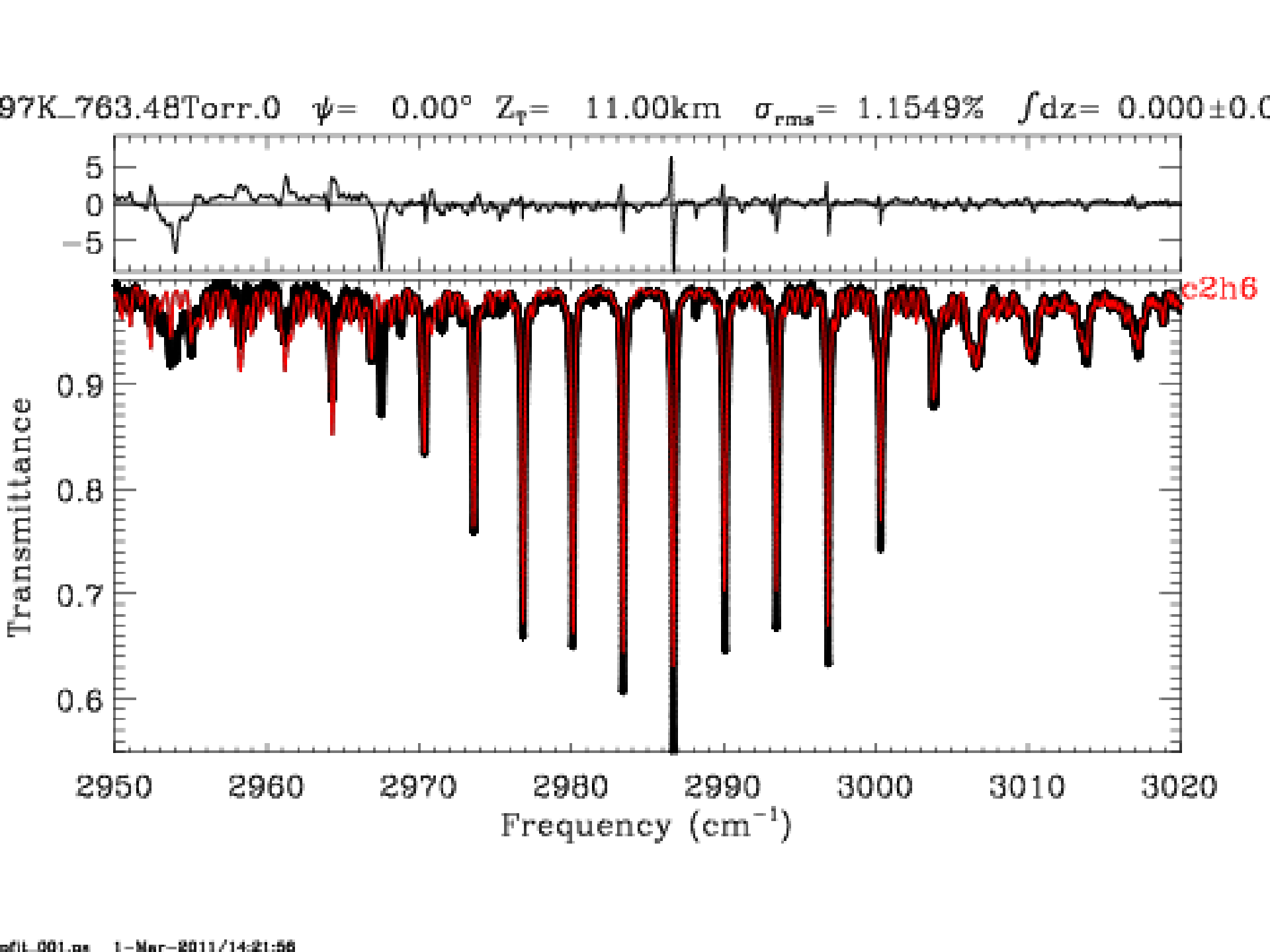
Overall, the new linelist is a factor 2 better than HITRAN in terms of the rms spectral fits over the 2950-3020 cm-1 region. And the C_2H_6 amounts are less biased and more consistent from spectrum to spectrum. But most of this improvement comes from an improved representation of the P- and R-branch "grass", which is completely missing from HITRAN. The strong Q-branches themselves are more poorly represented in Lattanzi than in HITRAN 2008 which, apart from the PQ_3 branch, comes from work that Linda Brown did for ATMOS in 1985. The attached figures show examples of spectral fits to various lab spectra using the Lattanzi linelist. There are evidently problems. The Q-branch at 2967.5 cm^{-1} is missing, and that at 2986.7 cm^{-1} is mis-shapen.

The table below summarizes the spectral fitting diagnostics of the 29 spectra, using 3 different linelists: (1) HITRAN 2008, (2) Lattanzi, and (3) the pseudo-line-list that I generated last year (GCT PLL). For each linelist I've tabulated the rms spectral fit over the 29 spectra, the vmr scale factor (VSF) and its standard deviation (SD). For a perfect fit to all spectra the VSF should be 1.0 with a SD of 0.0. When the VSF departs from 1.0, this implies a bias. Large SDs imply an inconsistency between spectra.

1. HITRAN: RMS= 4.0%; VSF=0.89 +/- 0.140
2. Lattanzi : RMS= 2.1%; VSF=1.03 +/- 0.100
3. GCT PLL: RMS= 0.2%; VSF=1.00 +/- 0.017

Of course, this isn't a fair comparison because the GCT PLL was generated by fitting 24/29 spectra used here. But it at least gives an idea of the magnitude of the improvement still to be won.

Following plots show calculations using Lattanzi's linelist (red) fitted to Harrison & Bernath's lab spectra (black).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c2h6
Transmittance
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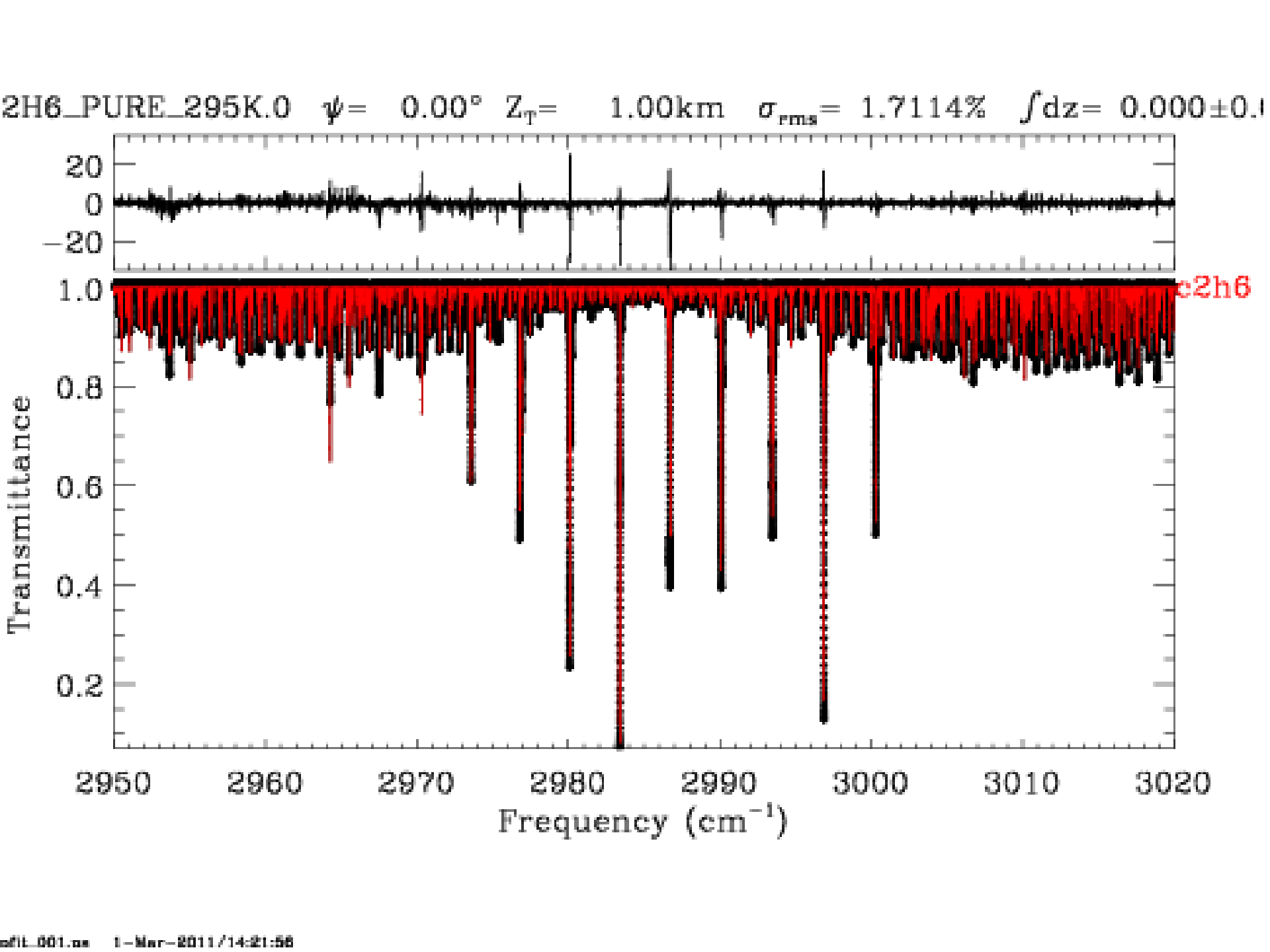
0.7
0.6
2950
2960
2970
2980
2990
3000
3010
3020
Frequency (cm^-1)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0.8
0.6
0.4
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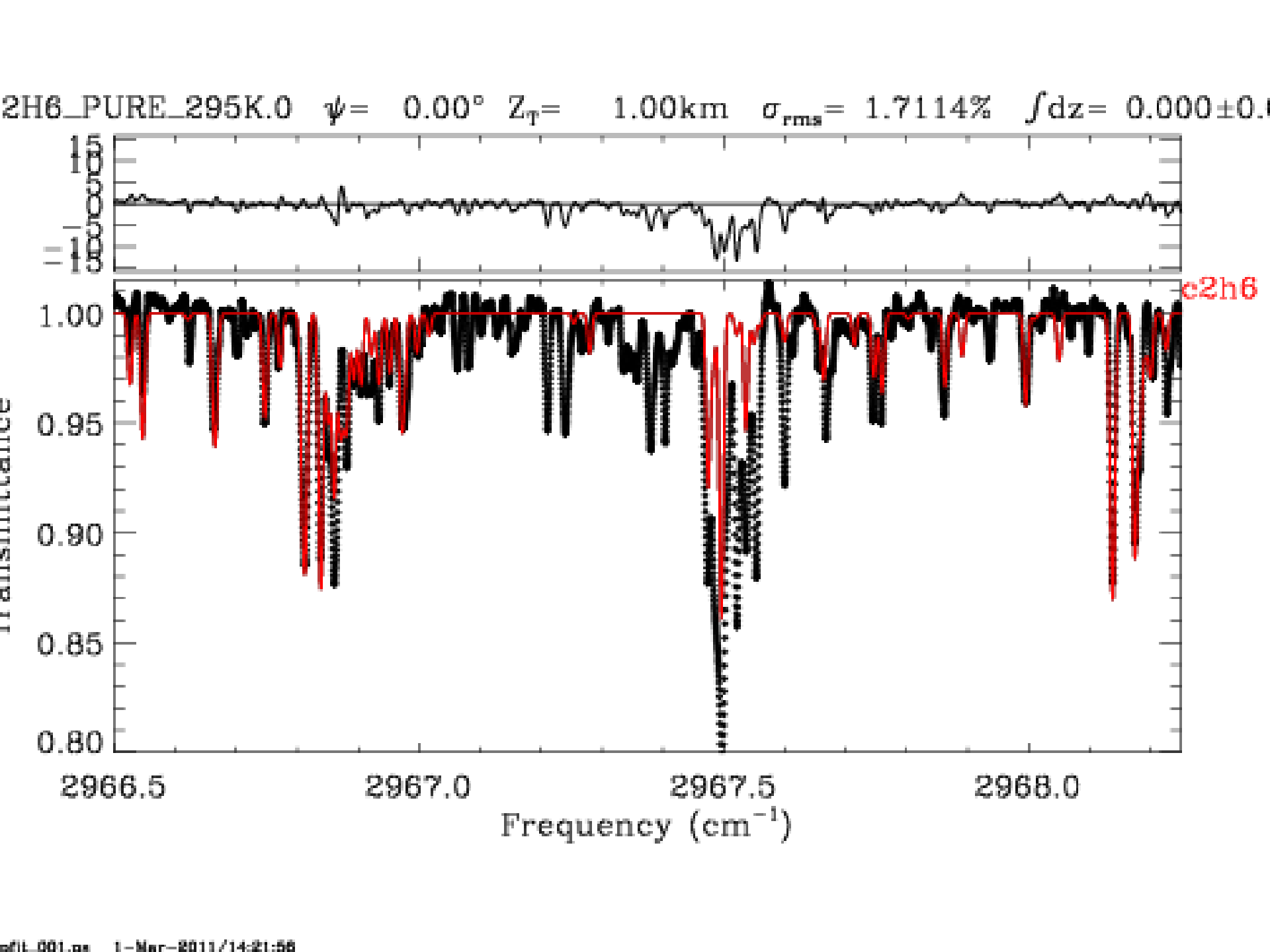
c2h6
Transmittance
2950
2960
2970
2980
2990
3000
3010
3020
Frequency (cm^-1)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10
5
0
-5
-10
-15
1.00
0.95
0.90
0.85
0.80
Transmittance
c2h6
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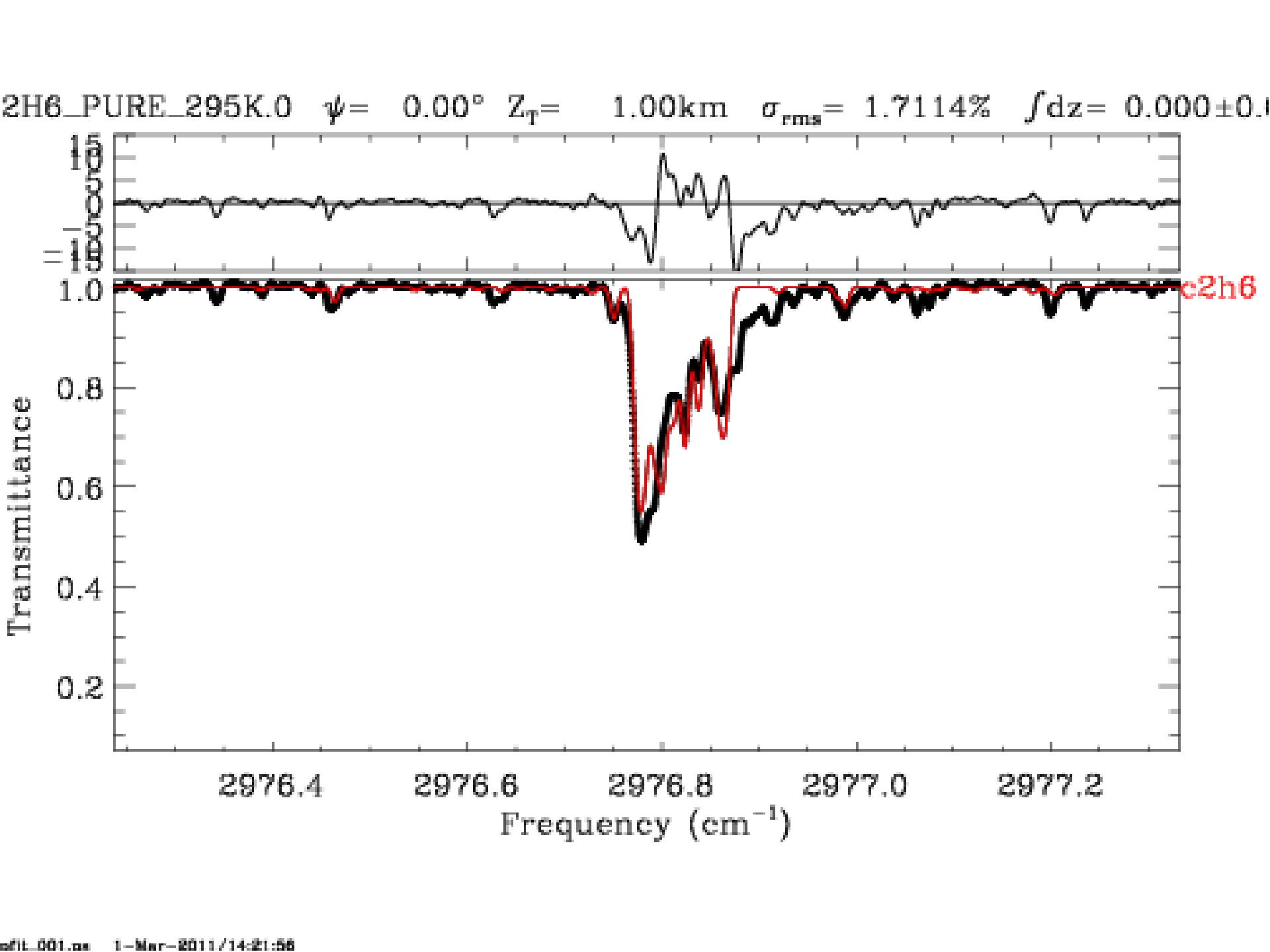
2967.5
2968.0
Frequency (cm^-1)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0.6
0.4
0.2
Transmittance
c2h6
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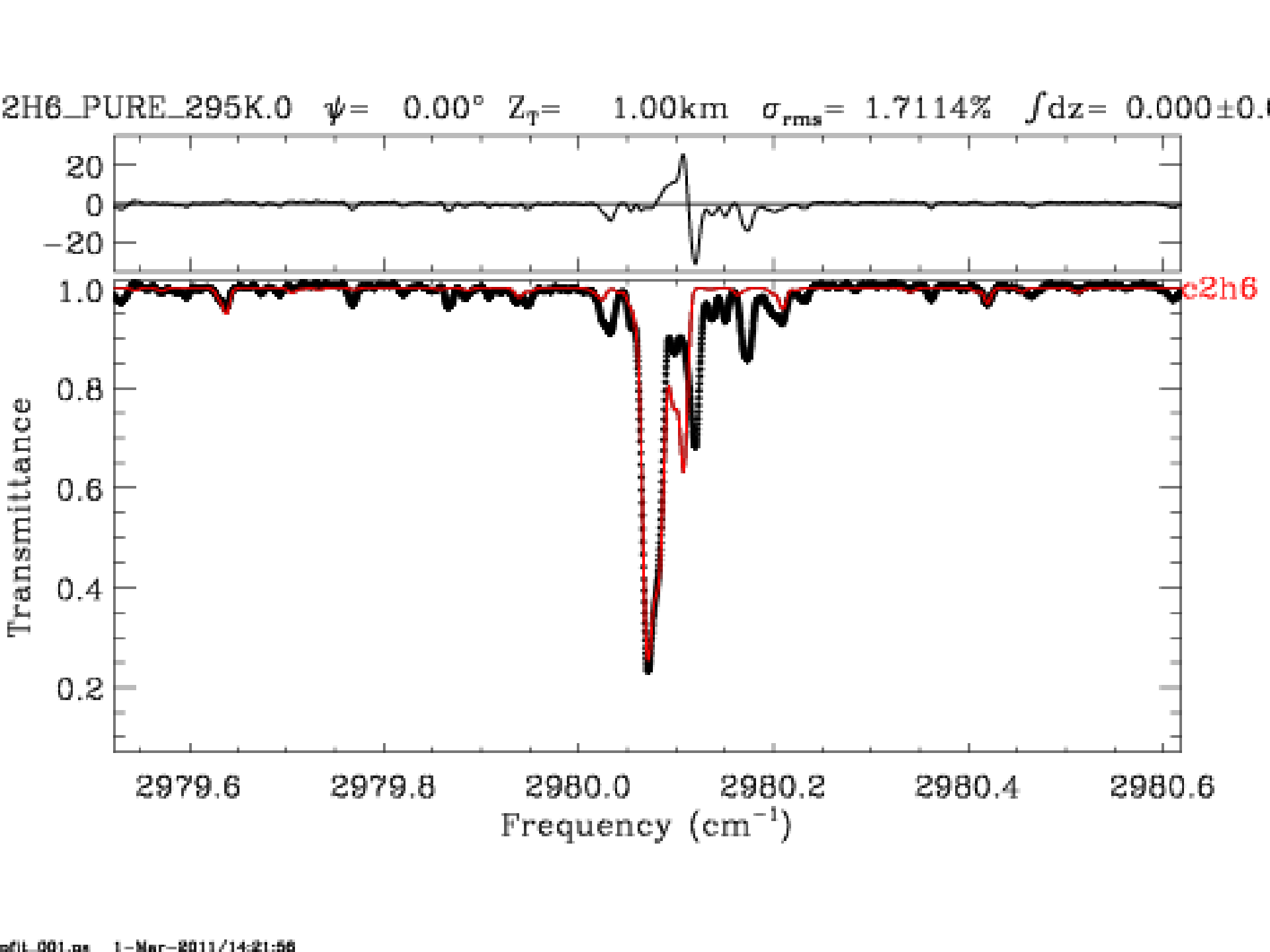
2976.6
2976.8
2977.0
2977.2
Frequency (cm⁻¹)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0
−20
1.0
0.8
0.6
0.4
0.2
Transmittance
c2h6
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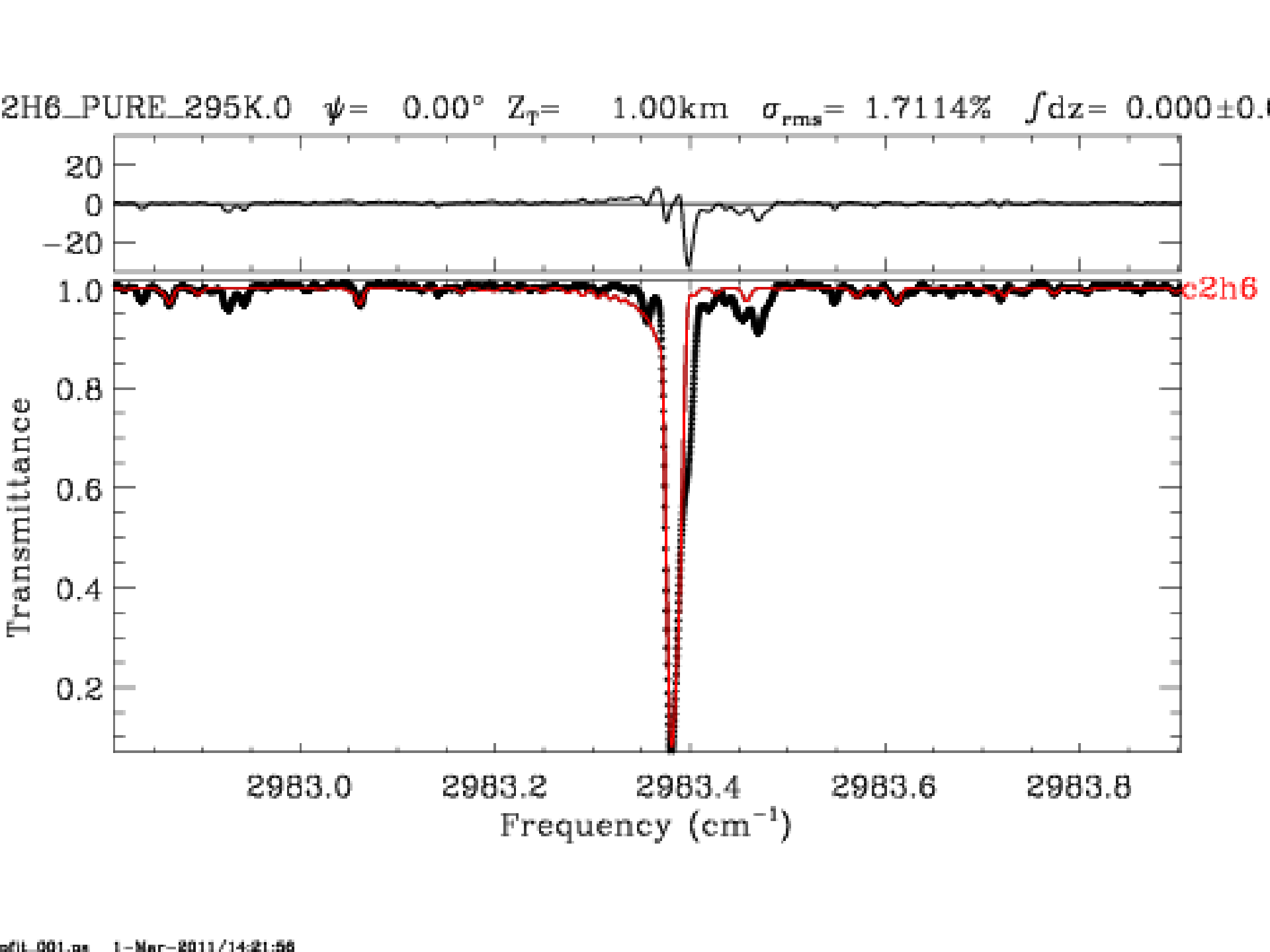
2980.6
Frequency (cm^-1)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0
−20
1.0
0.8
0.6
0.4
0.2
Transmittance
c2h6
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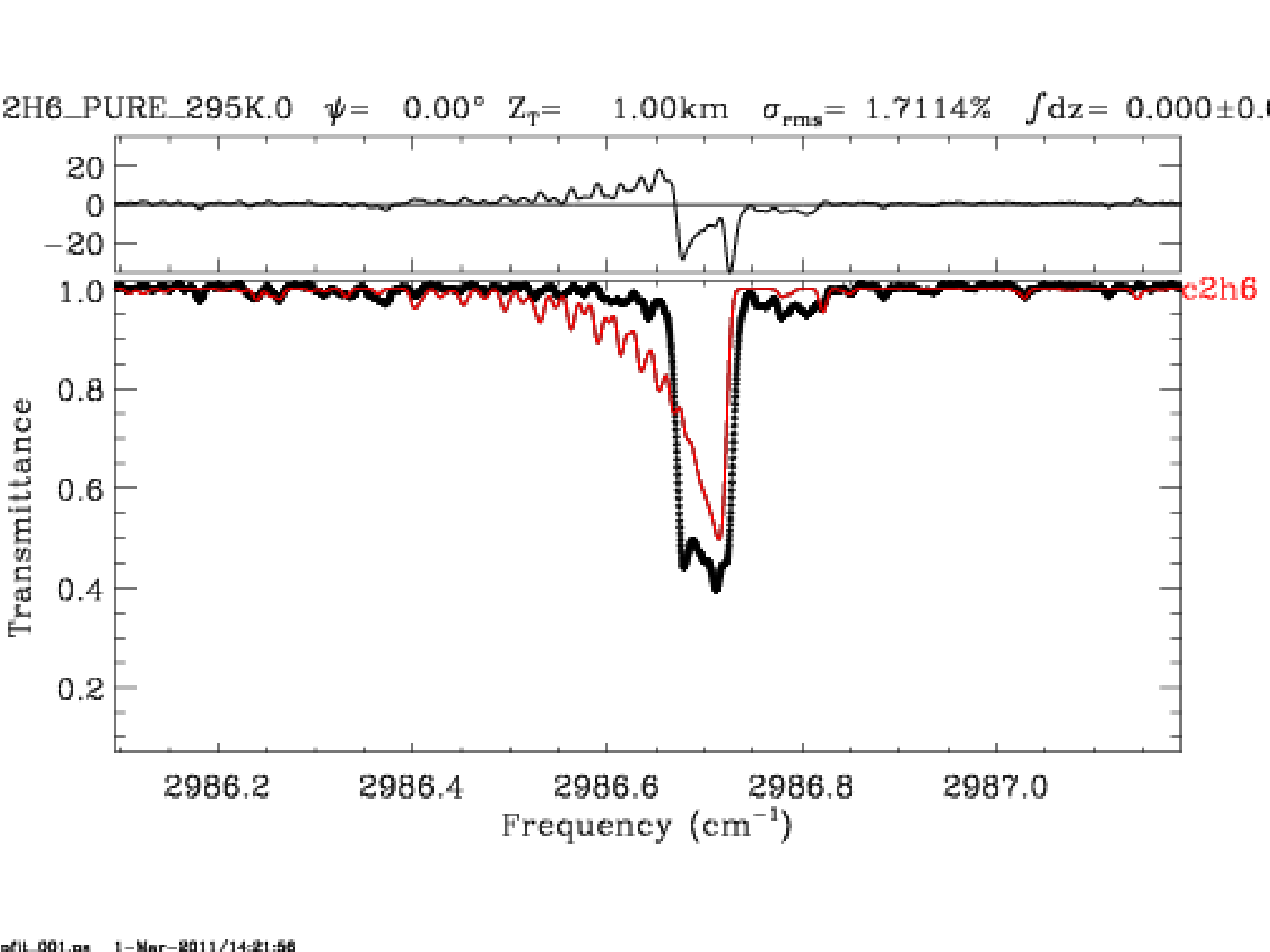
2983.4
2983.6
2983.8
Frequency (cm⁻¹)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0
−20
1.0
0.8
0.6
0.4
0.2
Transmittance
c2h6
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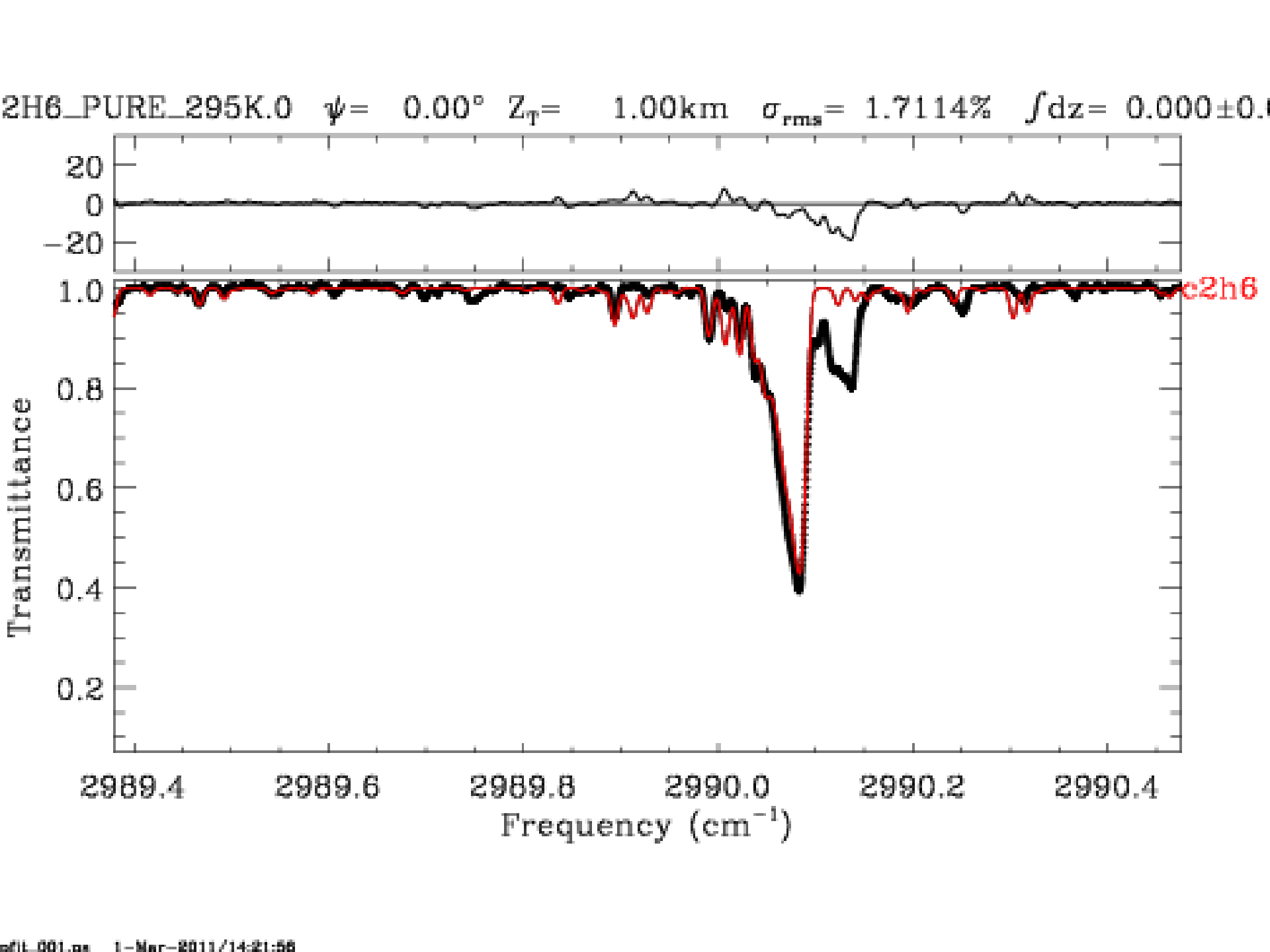
2986.6
2986.8
2987.0
Frequency (cm^-1)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0
−20
1.0
0.8
0.6
0.4
0.2
Transmittance
c2h6
2989.4
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2989.8
2990.0
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Frequency (cm^-1)
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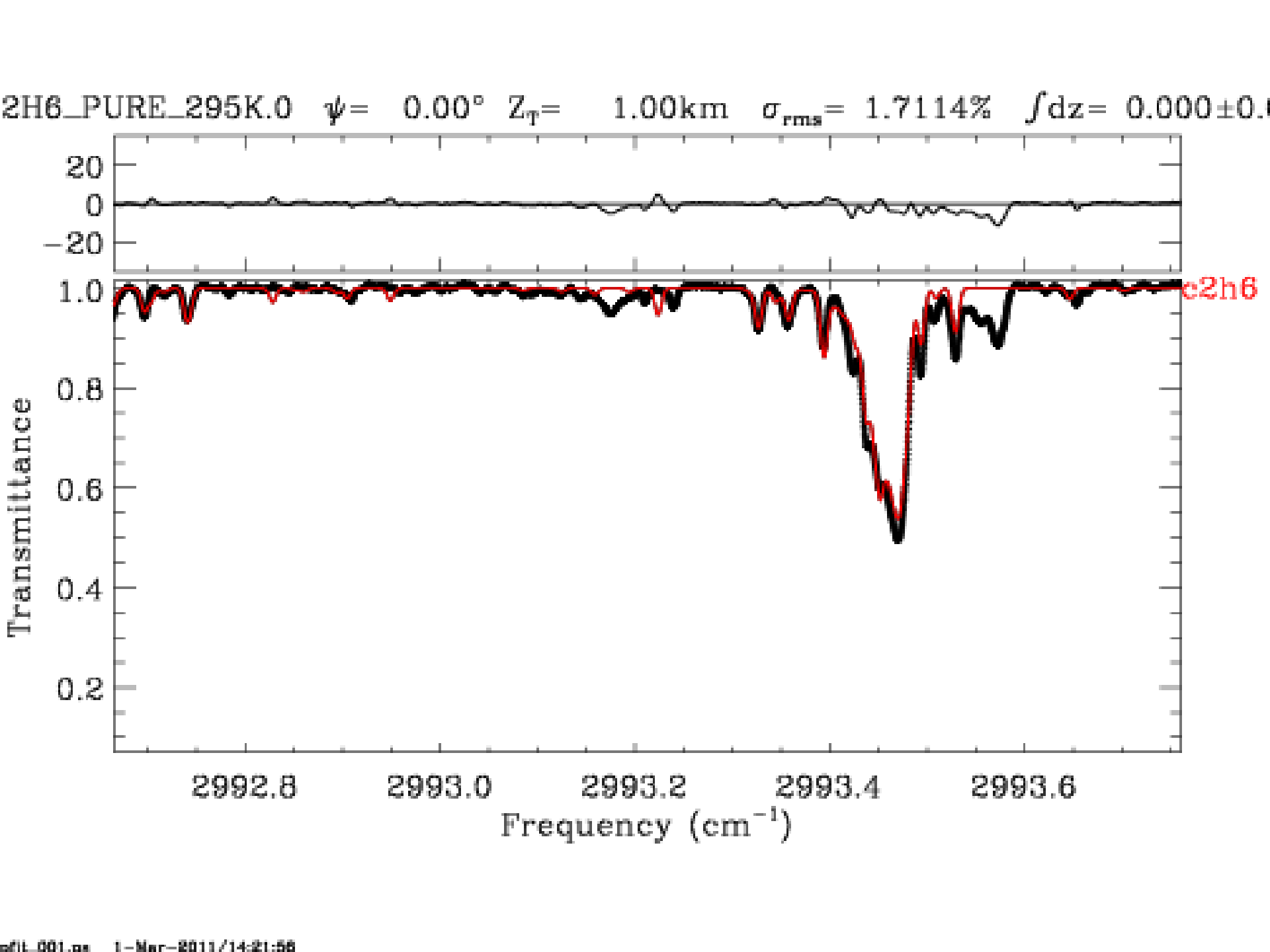
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0
−20
1.0
0.8
0.6
0.4
0.2
Transmittance
c2h6
2992.8
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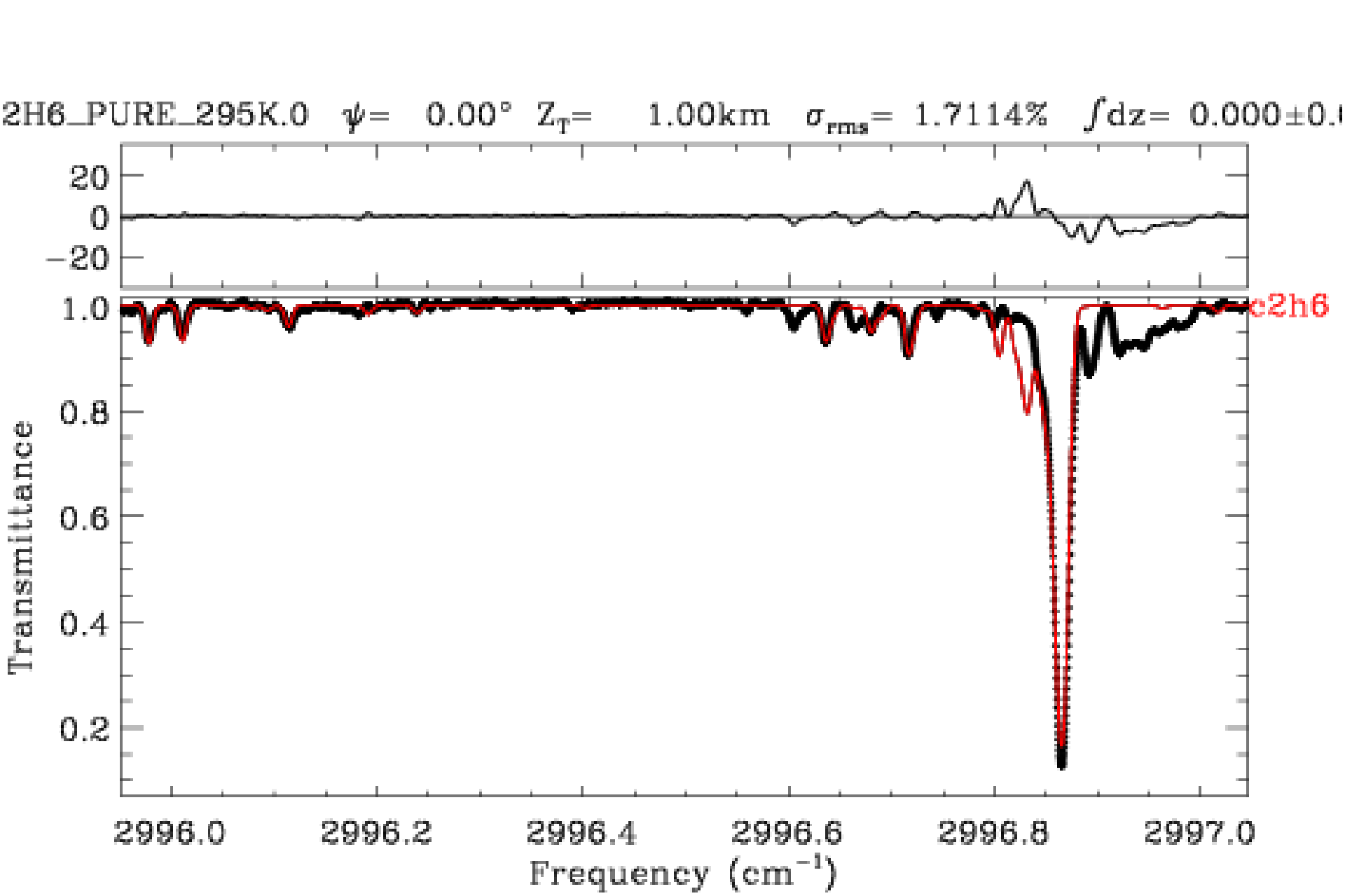
2993.2
2993.4
2993.6
Frequency (cm^-1)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0
−20
1.0
0.8
0.6
0.4
0.2
Transmittance
c2h6
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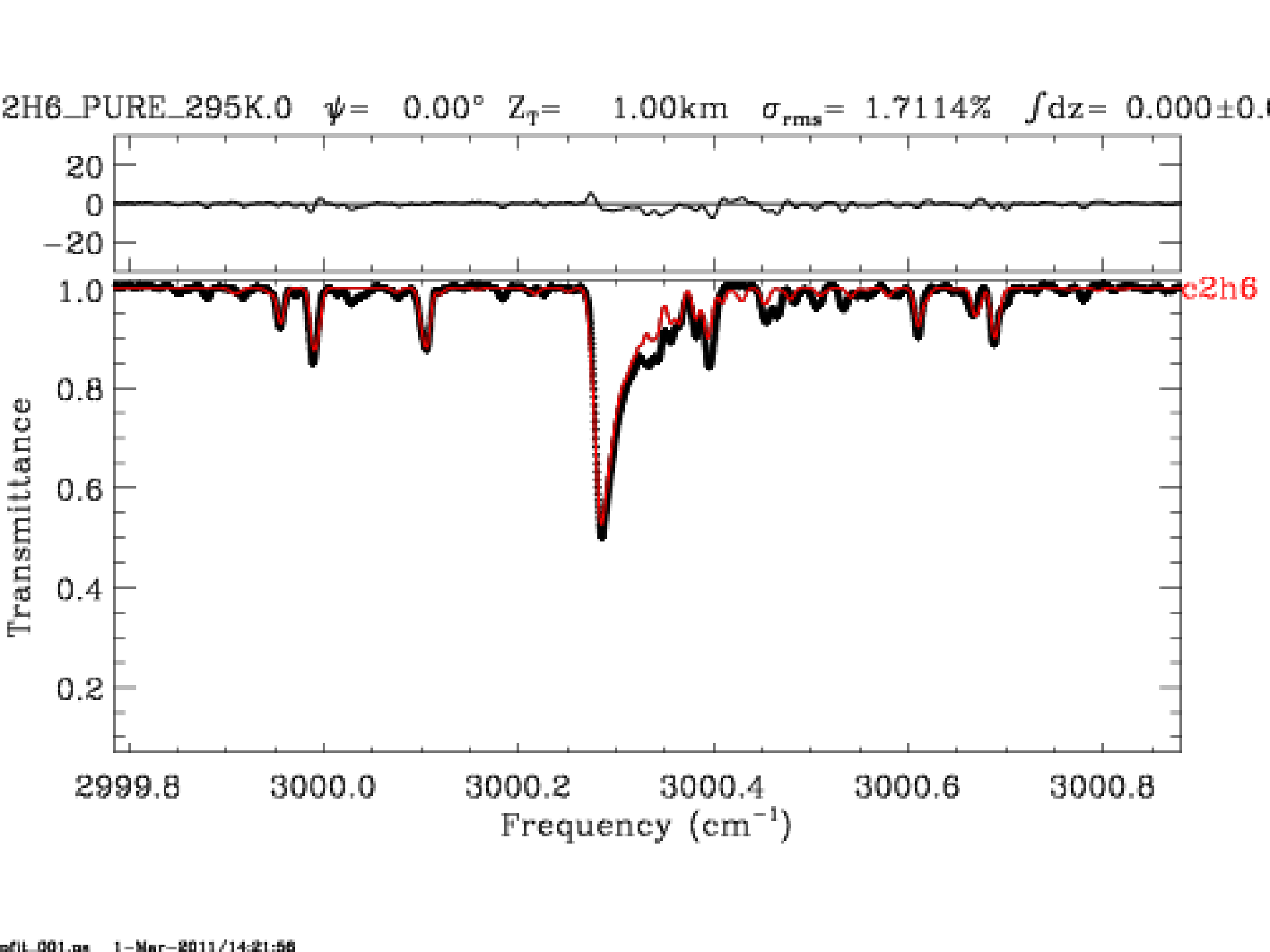
2996.2
2996.4
2996.6
2996.8
2997.0
Frequency (cm^-1)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1.0
0.8
0.6
0.4
0.2
Transmittance
c2h6
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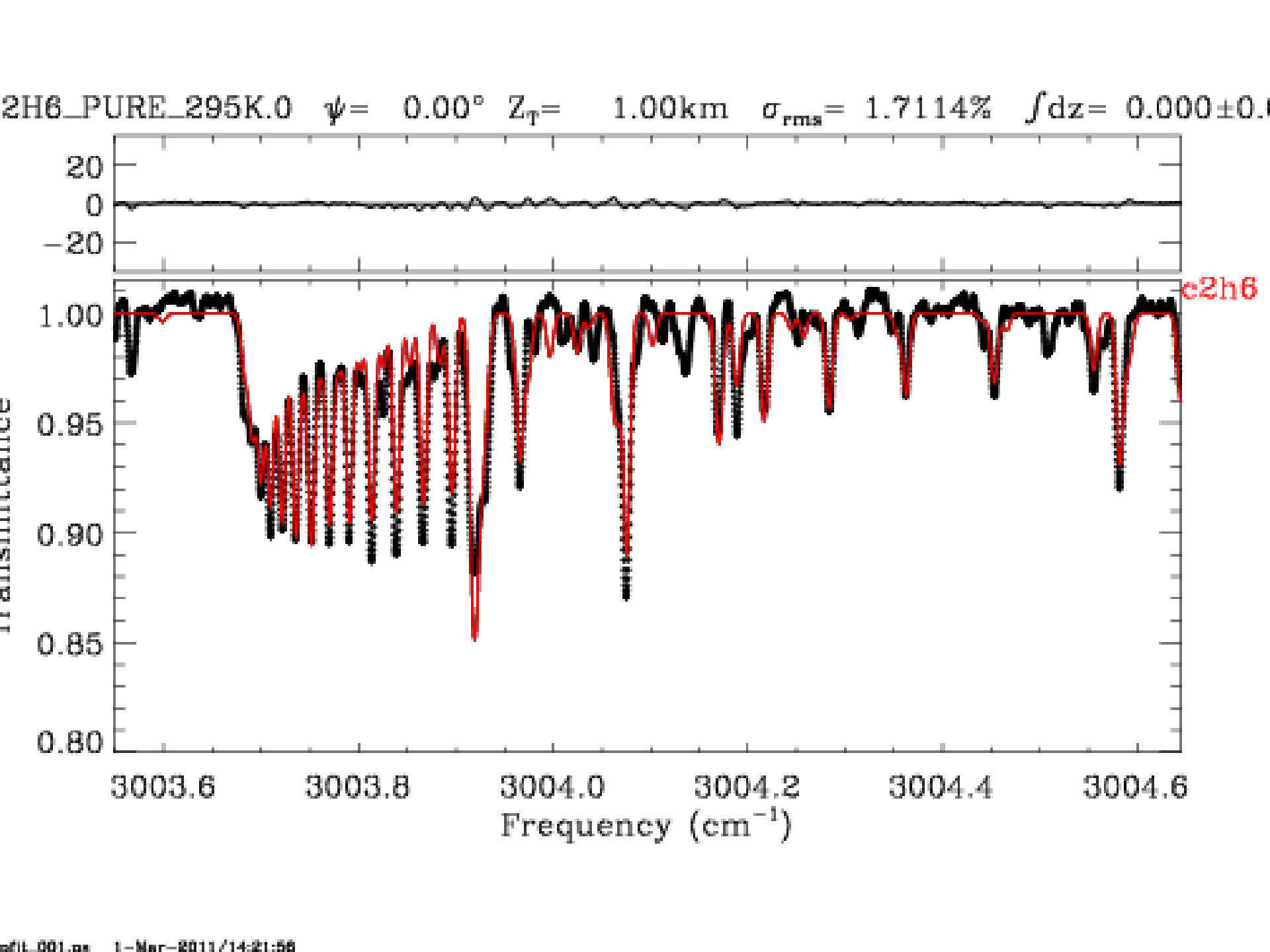
3000.4
3000.6
3000.8
Frequency (cm^-1)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0
−20
c2h6
1.00
0.95
0.90
0.85
0.80
Transmittance
3003.6
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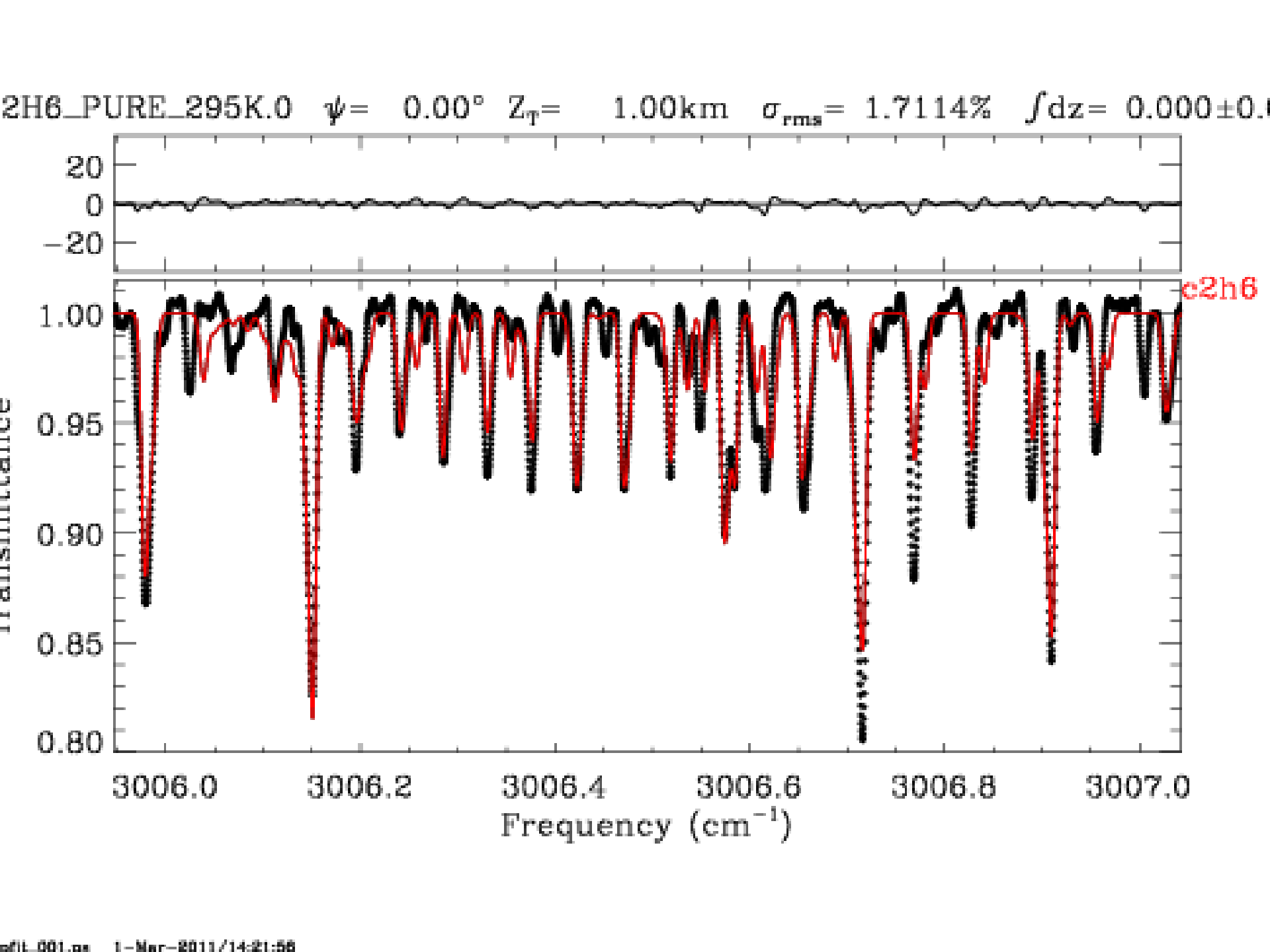
Frequency (cm^-1)
nofit_001.ps 1-Mar-2011/14:21:56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0
−20
c2h6
1.00
0.95
0.90
0.85
0.80
Transmittance
3006.0
3006.2
3006.4
3006.6
3006.8
3007.0
Frequency (cm^-1)