Contents

List of Figures

Spectroscopy evaluation using MkIV balloon spectra

G.C. Toon and B. Sen

March 31, 2004

1 Proposal Abstract.

We will evaluate the adequacy of the HITRAN [1] database to correctly simulate infrared limb transmittance spectra. This will be done by fitting solar absorption spectra measured by the JPL MkIV interferometer [2] over the spectral regions used by instruments (i.e. HIRDLS [3] and TES) on board the EOS AURA platform. These high quality MkIV spectra cover the entire 650 to 5650 cm^{-1} spectral region simultaneously and were measured during recent balloon flights under closely monitored (by *in situ* sensors) conditions. This work will benefit HIRDLS and TES by documenting and highlighting inadequacies in the database, diagnosing their cause, and quantifying their likely effect on retrieved vmr profiles. Future additions or amendments to the database will be tested in terms of their ability to improve the fits to the measured spectra. Checks will be performed of their consistency with previous linelist versions and with lines/bands of the same gas. This work will provide an objective basis for assessing the adequacy of the existing database (i.e. HITRAN) in various spectral regions and for quantifying the improvements (or otherwise) produced by new linelists. It will also help to prioritize needs for additional laboratory studies.

2 Introduction

We have evaluated the adequacy of the HITRAN 2000 spectroscopic database using the MkIV balloon spectra. The HIRDLS and TES science teams have already used ATMOS spectra to test aspects of their forward model, but the MkIV balloon spectra have some important advantages:

- Substantially higher SNR, due mainly to the longer time taken for an occultation measured from balloon (60 min) versus the shuttle (2 min).
- Wider spectral bandwidth (650–5650 cm^{-1} simultaneously) at high-resolution (0.007 cm^{-1}), which allows the consistency of various absorption bands of the same gas to be examined.
- Smaller zero level offset due to the use of more linear detectors (i.e. InSb photodiode) for the short wavelengths.
- Recently acquired spectra, which are therefore more representative of the atmosphere during the EOS era. This is particularly important in spectral regions containing absorptions from rapidly increasing gases (e.g. HCFCs) absent in the ATMOS spectra.
- Accurate tangent pressure and temperature due to the availability of both T-dependent (from the 940 and 2390 cm^{-1} region) and T-independent (from the 4000–5000 cm^{-1} region) CO_2 lines in every MkIV balloon spectra.
- Co-located observations with highly accurate *in situ* measurements of atmospheric trace gas profiles made from NASA ER-2 aircraft and OMS balloon gondola during recent (e.g. POLARIS, SOLVE) field campaigns. The atmospheric conditions (T, P, vmr) are therefore well characterized [4].

We have fitted the MkIV balloon spectra from May 8, 1997, and December 3, 1999, to evaluate the adequacy of HITRAN 2000 to correctly simulate infrared (ir) limb transmittance spectra. The Sun rise and set spectra were acquired over Fairbanks (65°N), Alaska, and Esrange (68°N), Sweden, respectively. The airmass sampled was representative of the high-latitude spring 1997 and an incipient Arctic vortex during winter 1999/2000. These recently acquired spectra are not only more representative of the atmosphere during the EOS era but also sample a wide range of tropospheric and stratospheric altitudes (5–38 km). The retrieved gas abundances from these spectrometric measurements were validated using *in situ* measurements from the NASA ER-2 aircraft flying from Fairbanks during POLARIS [4] and from Esrange during SOLVE [5, 6, 7, 8].

3 Work Performed

3.1 CO_2

A new calculation of CO_2 line positions has been performed by R.A. Toth (JPL, private comm.) and Miller and Brown [9] covering the entire mid- and near-ir. We have fitted balloon and ground-based spectra using this new linelist and have compared the fits with those obtained using HITRAN 2000 database in various spectral regions.

Yang *et al.* [10] retrieved column-averaged CO_2 dry air mole fraction, X_{CO_2}, over Kitt Peak, Arizona, from high-resolution solar absorption spectra obtained with a Fourier transform spectrometer. Simultaneous column measurements of CO_2 at $\sim$6300 cm^{-1} and O_2 at $\sim$7900 cm^{-1} were ratioed to minimize systematic errors. These column ratios were then scaled by the mean O_2 mixing ratio (0.2095) to yield X_{CO_2}. During the period 1977–1995, X_{CO_2} increased at an average rate of 1.49$\pm$0.04 ppmv/yr with seasonal variations of $\sim$7 ppmv peak-to-peak. The analysis demonstrated that this remote technique is capable of X_{CO_2} precisions better than 0.5%.

However, retrieval errors are dominated by deficiencies in the spectroscopic parameters, as seen in the spectral fitting residuals in Figure 1 (top panel). The figure illustrates spectral fit to solar spectra measured by Wallace and Livingston [11] using the McMath-Pierce FTS at Kitt Peak National Solar Observatory. The CO_2 spectroscopic parameters are from HITRAN 2000 database. Analysis indicate for CO_2 line positions, uncertainties less that 5×10^{-4} cm^{-1} are required to reduce the residuals (C.E. Miller, JPL private comm.)

Recently improved characterization of mid- and near-ir CO_2 has been accomplished through the use of high signal-to-noise, high resolution spectra and accurate wavenumber calibration. In particular, transitions from the ground state to the 20013, 20012, 20011, 30013, and 00031 vibrational states have been measured with absolute wavenumber uncertainties $< 6\times10^{-5}$ cm^{-1}. Figures 1 (middle panel), 2 (bottom panel), and 3 illustrate improvements to the spectral fit using the updated spectroscopic parameters. For example in Figure 2, there is much improvement for most of the band centered at 4808 cm^{-1}.

Figure 4 is a plot of a 1 cm^{-1} wide window centered at 2299.5 cm^{-1} in the CO_2 ν_3 band. It illustrates an example of a systematic inaccuracy in the HITRAN 2000 CO_2 spectroscopic parameters (i.e., errors in line positions of the $^{17}O^{12}C^{16}O$ ($4CO_2$) isotopologue at 2299.4 and 2299.6 cm^{-1}). The error is significant as the mid-ir band is ideal for the retrieval of CO_2 isotopologues in the atmosphere and for *in situ* spectral analysis.

3.2 HNO_3

The region 1300–1355 cm^{-1} in the most poorly fitted in the mid-ir. For example, Figure 5 (top panel) illustrates a spectral fit to a limb transmittance spectrum measured by the JPL MkIV on Dec. 3, 1999, over Esrange, Sweden. However, spectral fits indicate that this region contains absorption lines (up to 10% deep in atmospheric limb spectra) that are missing from the HITRAN 2000 database.

By fitting a laboratory spectra of HNO_3 measured by Linda Brown at Kitt Peak, we have determined that the poor residuals arise primarily from HNO_3 (Figure 5, bottom panel). The pattern of noise in the residuals is very similar for the atmospheric occultation spectra and the laboratory HNO_3, indicating that the source of the problem is HNO_3. Figure 6 illustrates spectral fits to a microwindows in the MkIV and Kitt Peak spectra, respectively. The systematically missing HNO_3 ν_3 lines are clearly visible in both residuals.

The spectroscopic parameters which is available in HITRAN 2000 database for HNO_3 in the 7μm (ν_3, ν_4 bands) is based on a work by Perrin *et al.* [12] and Goldman and Rinsland [13]. However, this work is not perfect because:

- The spectrum was recorded in open air. This means that part of the HNO_3 spectrum are missing because of the existence of strong water absorption.
- The resonance scheme is more complex than for the bands located at 11μm. There is at least 4 vibrational states involved in the resonance: $3\nu_9$, ν_4, ν_3, and $\nu_5 + \nu_9$. In 1989, only resonances between ν_4 and ν_3 were considered.

We suspect that the poor quality of the HNO_3 linelist in this region is due to

- neglect of weak combination bands (e.g., ν_5+ν_9)
- interactions between the different bands.

4 Recommendations

1. ν_3 CO_2 is the strongest ir band, and is therefore commonly used for the measurement of CO_2 isotopologues both in the atmosphere and laboratory. Systematic errors in spectroscopic parameters (see Figure 4) will result in seasonal and latitudinal biases in the retrieved CO_2 and will contribute significantly to the errors in the calculated flux of CO_2.

   For precise ($<$ 0.3%) retrieval of atmospheric CO_2, significantly better spectroscopic parameters (line positions and widths) are needed for the ν_3 band.

2. New and improved HNO_3 spectroscopic parameters are needed for all mid-ir bands (i.e., 879, 1326, 1710, and 3550 cm^{-1}). It is particularly true for the representation of the Q-branches in these bands. However, the 7 μm ν_3 and ν_4 bands are particularly poorly fitted.

   Space-borne radiometers (e.g., HIRDLS) will attempt to retrieve stratospheric CH_4 and nitrogen oxides in this spectral region assuming a sufficiently accurate atmospheric forward model calculation. However, systematic errors in 7 μm HNO_3 spectroscopic parameters will propagate errors in the retrieval of other atmospheric species.

   Atmospheric SO_2 also absorbs strongly in the mid-ir around 1350 cm^{-1}. Although SO_2 is measured in the UV when enhanced, mid-ir is the most promising monitoring technique at all levels of atmospheric loading. However, the poor quality of 7μm HNO_3 spectroscopy prevents SO_2 measurement, as its lines are only $\sim$1% deep.

   There is little correlation between HITRAN 2000 and atmospheric HNO_3 lines in the wings of the ν_3 and ν_4 bands (see Figure 5). Furthermore, pressure-broadened half-widths are same for all 7μm HNO_3 lines in the HITRAN 2000 database. Both topics require immediate attention.

References

[1] L.S. Rothman, C.P. Rinsland, A. Goldman, S.T. Massie, D.P. Edwards, J.M. Flaud, A. Perrin, C. Camy-Peyret, V. Dana, J.Y. Mandin, J. Schroeder, A. McCann, R.R. Gamache, R.B. Wattson, K. Yoshino, K.V. Chance, K.W. Jucks, L.R. Brown, V. Nemtchinov, and P. Varanasi. The HITRAN molecular spectroscopic database and HAWKS (HITRAN Atmospheric Workstation): 1996 edition. *J. Quant. Spectros. Rad. Transfer*, 60(5):665, 1998.

[2] G.C. Toon. The JPL MkV Interferometer. *Optics and Photonics News*, 2:19, 1991.

[3] J. Gille and J. Barnett. The High-resolution Dynamic Limb Sounder (HIRDLS). An instrument for the study of global change. In J. Gille and G. Visconti, editors, *The Use of EOS for Studies of Atmospheric Physics*, page 433. North- Holland, 1992.

[4] G.C. Toon, J.F. Blavier, B. Sen, J.J. Margitan, C.R. Webster, R.D. May, D. Fahey, R. Gao, L. Del Negro, M. Proffitt, J. Elkins, P.A. Romashkin, D.F. Hurst, S. Oltmans, E. Atlas, S. Schauffler, F. Flocke, T.P. Bui, R.M. Stimpfle, G.P. Bonne, P.B. Voss, and R.C. Cohen. Comparison of MkIV balloon and ER-2 aircraft measurements of atmospheric trace gases. *J. Geophys. Res.*, 104(D21):26779, 1999.

[5] J.B. Greenblatt. Tracer-based determination of vortex descent in the 1999/2000 Arctic winter. *J. Geophys. Res.*, 107(D20):8279, 2002.

[6] J.D. Lumpe, M. Fromm, K. Hoppel, R.M. Bevilacqua, C.E. Randall, E.V. Browell, W.B. Grant, T. McGee, J. Burris, L. Twigg, E.C. Richard, G.C. Toon, J.J. Margitan, B. Sen, K. Pfeilsticker, H. Boesch, R. Fitzenberger, F. Goutail, and J.P. Pommereau. Comparison of POAM III ozone measurements with correlative aircraft and balloon data during SOLVE. *J. Geophys. Res.*, 108(D5):8316, 2002.

[7] M. Rex, R.J. Salawitch, N.R.P. Harris, P. von der Gathen, G.O. Braathen, A. Schulz, H. Deckelmann, M. Chipperfield, B.M. Sinnhuber, E. Reimer, R. Alfier, R. Bevilacqua, K. Hoppel, M. Fromm, J. Lumpe, H. Kullmann, A. Kleinbohl, H. Bremer, M. von Konig, K. Kunzi, D. Toohey, H. Vomel, E. Richard, K. Aikin, H. Jost, J.B. Greenblatt, M. Loewenstein, J.R. Podolske, C.R. Webster, G.J. Flesch, D.C. Scott, R.L. Herman, J.W. Elkins, E.A. Ray, F.L. Moore, D.F. Hurst, P. Romashkin, G.C. Toon, B. Sen, J.J. Margitan, P. Wennberg, R. Neuber, M. Allart, B.R. Bojkov, H. Claude, J. Davies, W. Davies, H. De Backer, H. Dier, V. Dorokhov, H. Fast, Y. Kondo, E. Kyro, Z. Litynska, I.S. Mikkelsen, M.J. Molyneux, E. Moran, T. Nagai, H. Nakane, C. Parrondo, F. Ravegnani, P. Skrivankova, P. Viatte, and V. Yushkov. Chemical depletion of Arctic ozone in winter 1999/2000. *J. Geophys. Res.*, 107(D20):8276, 2002.

[8] R.J. Salawitch, J.J. Margitan, B. Sen, G.C. Toon, G.B. Osterman, M. Rex, J.W. Elkins, E.A. Ray, F.L. Moore, D.F. Hurst, P.A. Romashkin, R.M. Bevilacqua, K.W. Hoppel, E.C. Richard, and T.P. Bui. Chemical loss of ozone during the Arctic winter of 1999/2000: An analysis based on balloon-borne observations. *J. Geophys. Res.*, 107(D20):8269, 2002.

[9] C.H. Miller and L.R. Brown. Near infrared spectroscopy of carbon dioxide I. $^{16}O^{12}C^{16}O$ line positions. *J. Molec. Spec.*, in press, 2002.

[10] Z.H. Yang, G.C. Toon, J.S. Margolis, and P.O. Wennberg. Atmospheric CO_2 retrieved from ground-based near IR solar spectra. *Geophys. Res. Lett.*, 29(9):1339, 2002.

[11] L. Wallace and W. Livingston. Spectroscopic observations of atmospheric trace gases over Kitt Peak. 1. Carbon-Dioxide and Methane from 1979 to 1985. *J. Geophys. Res.*, 95(D7):9823, 1990.

[12] A. Perrin, O. Ladobordowsky, and A. Valentin. The ν_3 and ν_4 Interacting Bands of HNO_3 Line Positions and Line-Intensities. *Mol. Phys.*, 67(2):249, 1989.

[13] A. Goldman and C.P. Rinsland. HNO_3 line parameters - new results and comparisons of simulations with high-resolution laboratory and atmospheric spectra. *J. Quant. Spectros. Rad. Trans.*, 48(5-6):653, 1992.

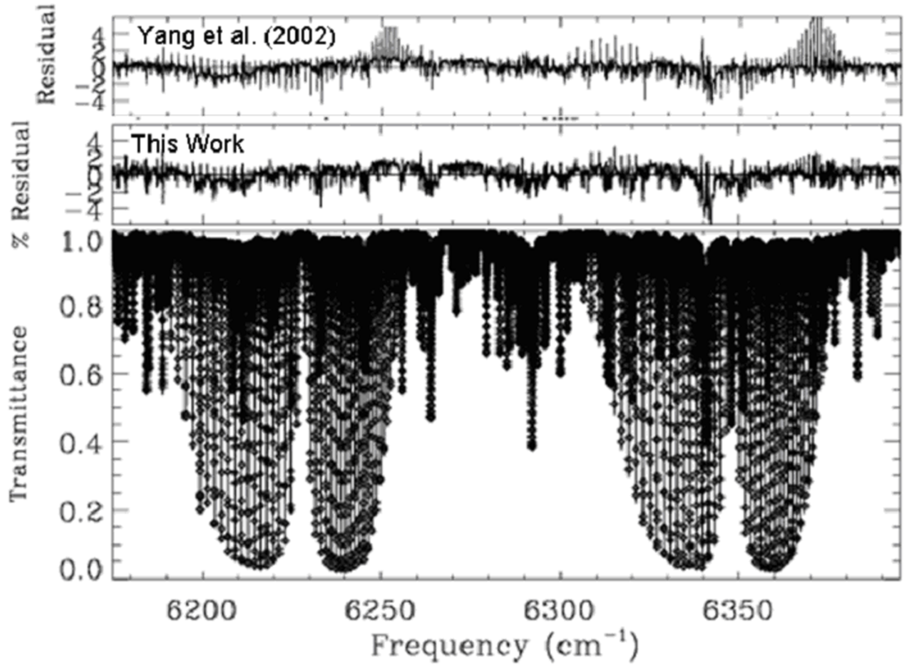

Figure 1: Bottom Panel: Experimental (symbols) and simulated (solid line) solar spectra in the region of the CO_2 30013←00001 and 30012←00001 band. Spectrum recorded by the McMath-Pierce FTS at Kitt Peak National Solar Observatory. Top Panel: Residuals from simulating the measured spectrum with the HITRAN 2000 database. Middle Panel: Fit to the same Kitt Peak spectrum with an improved CO_2 spectroscopic parameters based on the work at JPL (L.R. Brown, private comm.).

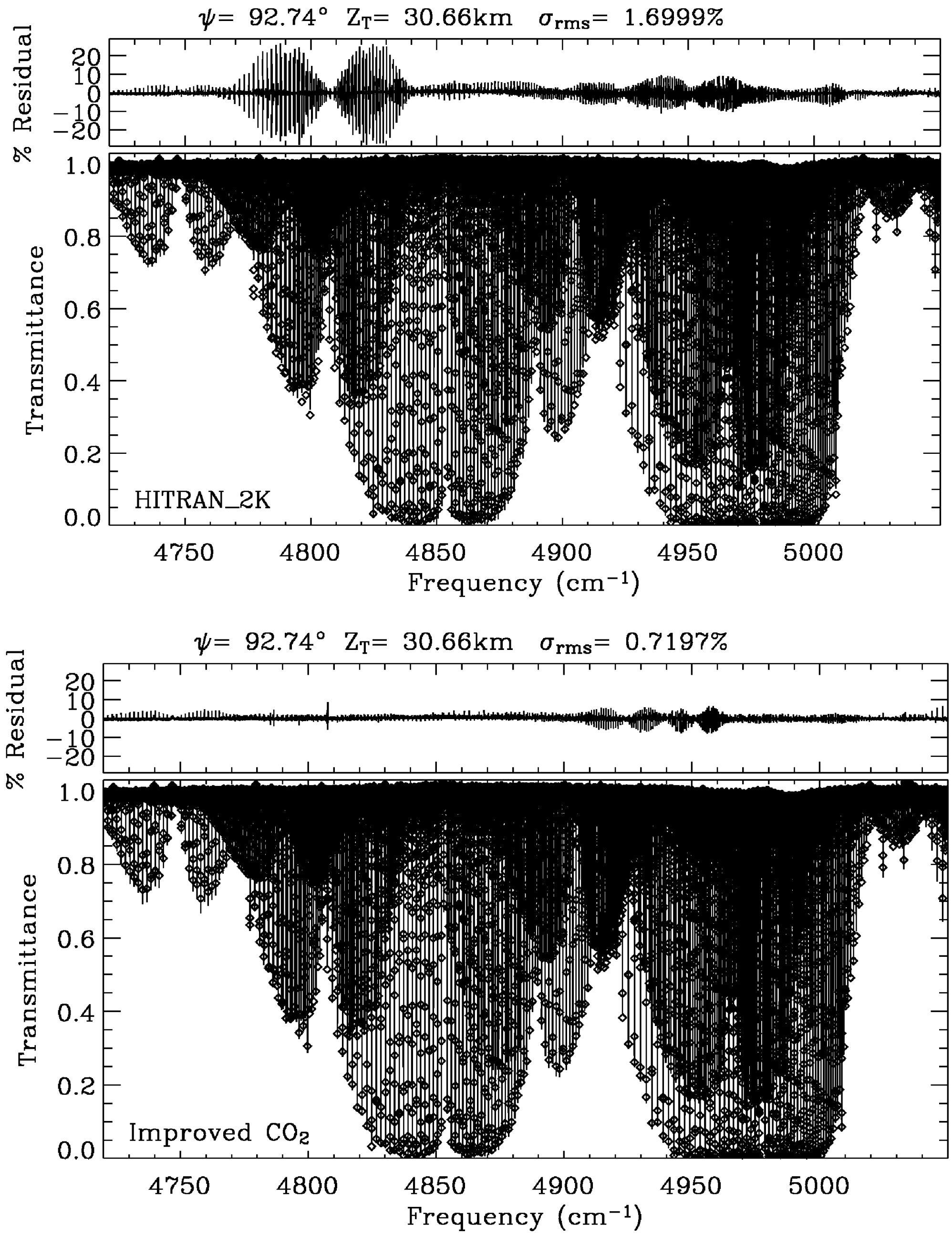

Figure 2: Top Panel: Experimental (symbols) and simulated (solid line) solar occultation spectra in the region of the CO_2 20013←00001 and 20012←00001 band. This band is used by MkIV to determine observation geometry. It will also be used by OCO to measure CO_2. Atmospheric limb transmittance spectrum recorded at an altitude of 38 km by the JPL MkIV on May 3, 1997, over Fairbanks, Alaska. The spectrum was acquired at 92.74° solar zenith angle (tangent altitude of 30.7 km). The CO_2 spectroscopic parameters are from HITRAN 2000 database. Bottom Panel: Fit to the same MkIV spectrum with an improved CO_2 spectroscopic parameters based on the work at JPL (L.R. Brown, private comm.). The σ_{rms} (= 0.7197%) has improved by ≈58%.

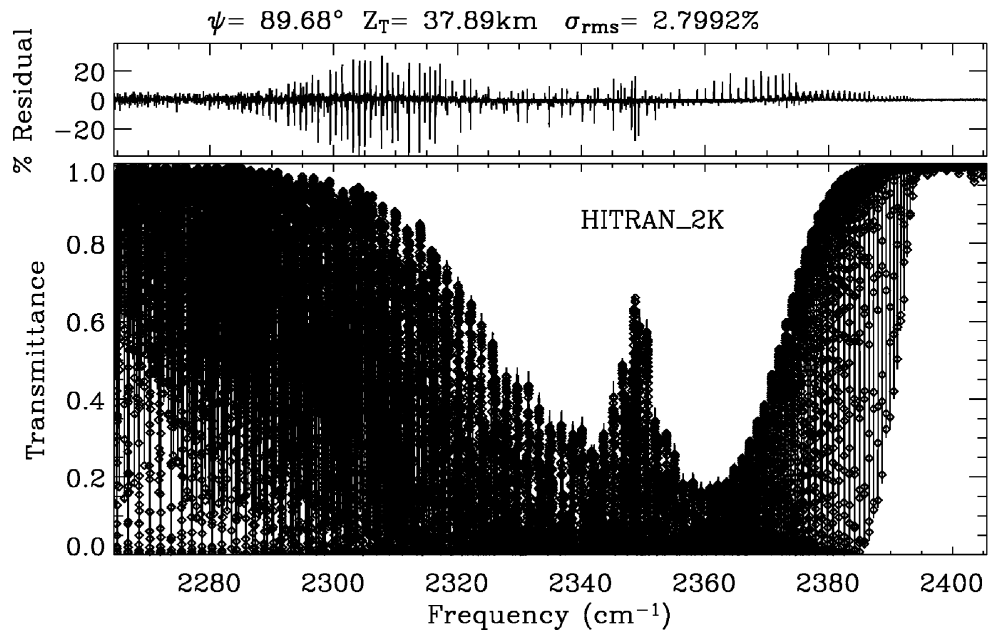

Figure 3: Experimental (symbols) and simulated (solid line) solar occultation spectra in the region of the CO_2 band. Atmospheric limb transmittance spectrum recorded at an altitude of 38 km by the JPL MkIV on May 8, 1997, over Fairbanks, Alaska. The spectrum was acquired at 89.68° solar zenith angle (tangent altitude of 37.9 km). Fit to the MkIV spectrum using the HITRAN 2000 database illustrates residual errors in the CO_2 spectroscopy.

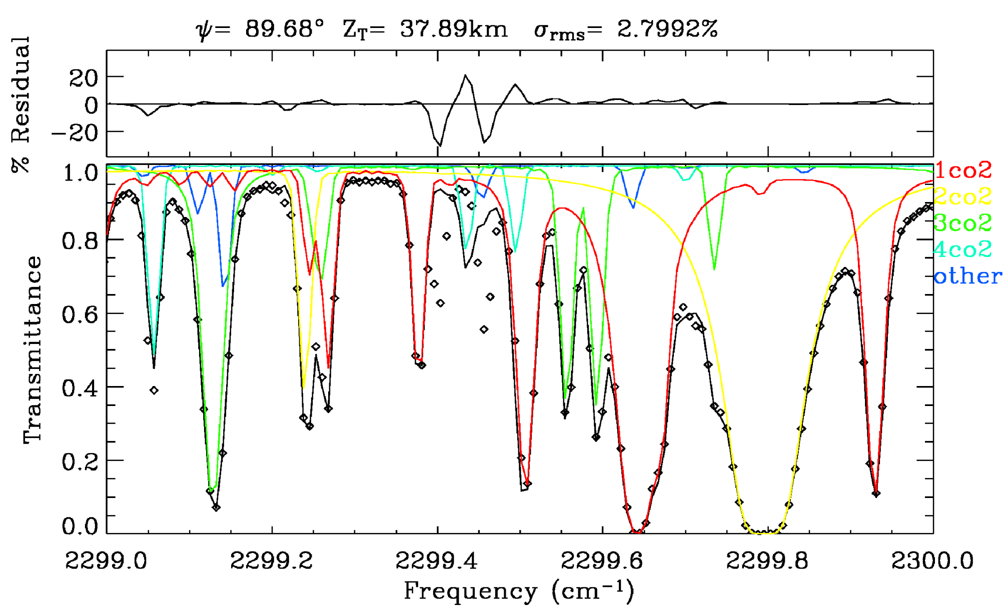

Figure 4: A 1 cm^{-1} microwindow in the CO_2 ν_3 band. The mid-ir band would be ideal for the retrieval of CO_2 isotopologues in the atmosphere except for the significant inaccuracies in line positions of $^{17}O^{12}C^{16}O$ ($4CO_2$) in the HITRAN 2000 database.

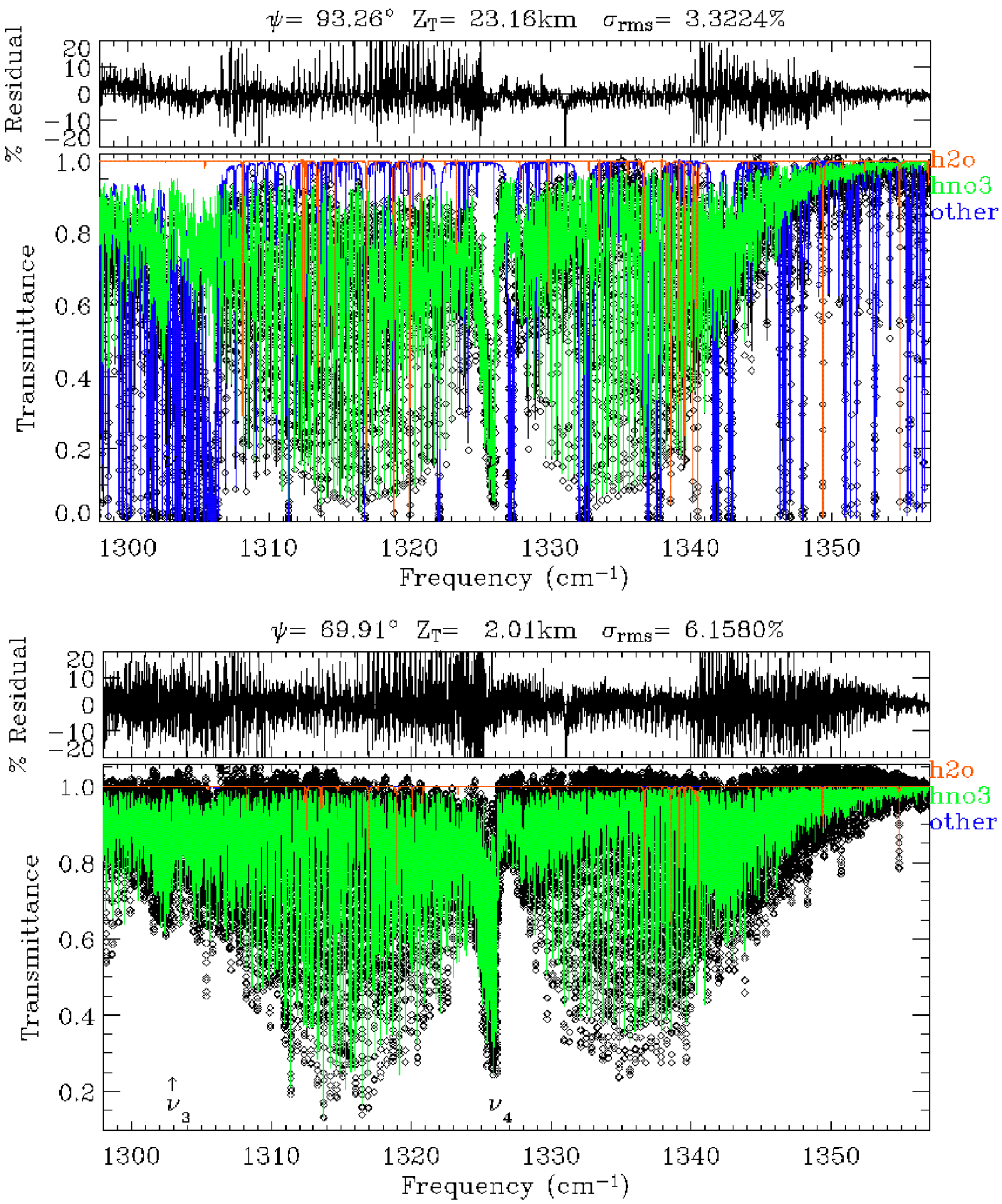

Figure 5: Top Panel: Experimental (symbols) and simulated (solid line) solar occultation spectra in the region of the HNO_3 ν_3 and ν_4 bands. Atmospheric limb transmittance spectrum recorded at an altitude of 33 km by the JPL MkIV on Dec. 3, 1999, over Esrange, Sweden. The spectrum was acquired at 93.26° solar zenith angle (tangent altitude of 23.2 km). Bottom Panel: Experimental (symbols) and simulated (solid line) laboratory spectra in the region of the HNO_3 ν_3 band. Laboratory spectrum recorded using the McMath-Pierce FTS at Kitt Peak National Solar Observatory.

Fit to the two spectra using the HITRAN 2000 database illustrates significant and similar residual error, confirming that the missing lines in the MkIV spectral fit arise primarily from HNO_3.

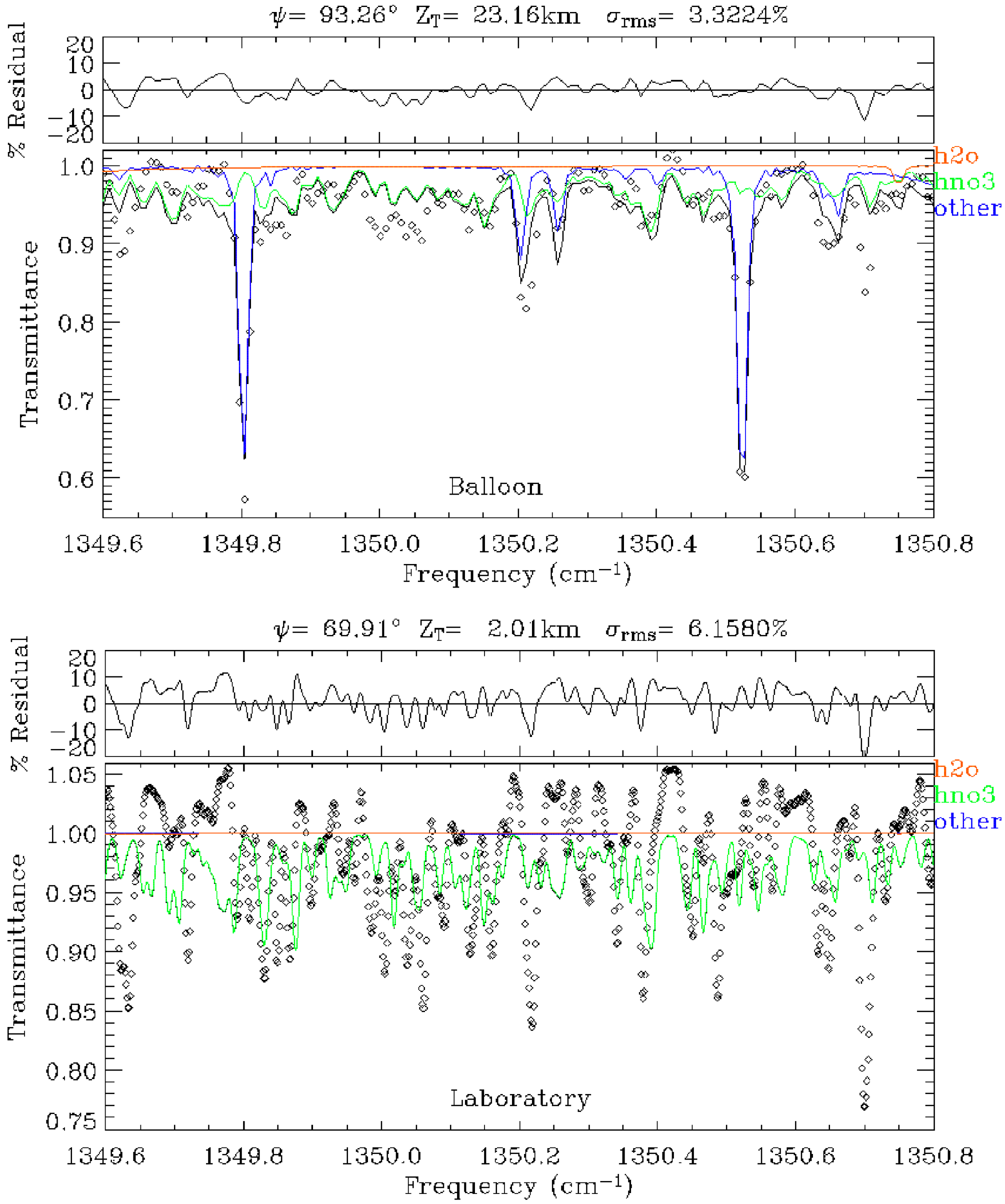

Figure 6: Same as Figure 5, but with an expanded frequency scale. A 1.2 cm^{-1} microwindow in the HNO_3 in the MkIV and Kitt Peak spectra. The residuals illustrate the many missing HNO_3 lines in this spectral region in the HITRAN 2000 database.