Spectroscopy evaluation using MkIV balloon spectra

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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.

Work Accomplished

We have evaluated the adequacy of the HITRAN 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[4-8].

HIRDLS and TES passband requirements on optical filters were dictated by two primary requirements: (i) the bands must be wide enough to permit the required molecular bands to be observed with as few breaks as possible and (ii) the passbands must be narrow enough to control the instrument background. Consequently, HIRDLS spectral regions are classified as:

- Spectral Region 1 (550–690 cm^{-1}; channels: 1–5) target species: N_2O, aerosols, CO_2,
- Spectral Region 2 (810–940 cm^{-1}; channels: 6–9) target species: aerosol, CCl_3F, HNO_3, CCl_2F_2,
- Spectral Region 3 (980–1150 cm^{-1}; channels: 10–12) target species: O_3,
- Spectral Region 4 (1190–1390 cm^{-1}; channels: 13–17) target species: N_2O_5, N_2O, $ClONO_2$, CH_4,
- Spectral Region 5 (1360–1660 cm^{-1}; channels: 18–21) target species: H_2O, NO_2.

While TES filters are classified as:

- Filter 1A1 (1900–2250 cm^{-1}) target species: O_3, CO, N_2O, NO, OCS, CH_3D,
- Filter 1A2 (2200–2450 cm^{-1}) target species: CO_2, N_2,
- Filter 1A3 (2425–2650 cm^{-1}) target species: N_2O,
- Filter 1A4 (2600–2850 cm^{-1}) target species: HDO,
- Filter 1A5 (2800–3050 cm^{-1}) target species: CH_4, HCl, O_3,
- Filter 1B1 (820–1050 cm^{-1}) target species: HNO_3, NH_3, CCl_3F, CCl_2F_2, SF_6, O_3, C_2H_4,
- Filter 1B2 (950–1150 cm^{-1}) target species: O_3, NH_3, CCl_3F, CCl_2F_2, N_2O,
- Filter 2A1 (1100–1325 cm^{-1}) target species: O_3, N_2O, HNO_3, CCl_2F_2, SO_2, CH_4, $CH_3C(O)CH_3$, H_2O_2,
- Filter 2A2 (1300–1550 cm^{-1}) target species: O_3, HNO_3, CH_4,
- Filter 2A3 (1500–1750 cm^{-1}) target species: H_2O, NO_2,
- Filter 2A4 (1700–1950 cm^{-1}) target species: H_2O, NO,
- Filter 2B1 (650–900 cm^{-1}) target species: CO_2, HNO_3, CCl_3F, NO_2, C_2H_2, HCN.

We have fitted the MkIV balloon spectra from December 3, 1999, to evaluate the adequacy of HITRAN to correctly simulate infrared limb transmittance spectra. The Sun set spectra were acquired over Esrange (68° N), Sweden, and the airmass sampled was representative of the 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 (5–33 km). The retrieved gas abundances from these spectrometric measurements were validated using in situ measurements from the NASA ER-2 aircraft flying from Esrange during SOLVE campaign[5-8].

The MkIV spectra were fitted over 6 wide spectral intervals covering the spectral range defined by HIRDLS and TES instrument teams. The wide intervals allow entire molecular bands to be fitted and inadequacies/discrepancies between bands easily identified. The spectral region classification, central frequency, window width, and simultaneously fitted gases are tabulated below.

Spectral Region	Center Frequency (cm^{-1})	Window Width (cm^{-1})	Fitted Gases
2	875.	130.	H_2O, CO_2, O_3, HNO_3, CCl_2F_2, CCl_3F, $CHClF_2$
3	1065.	170.	H_2O, CO_2, O_3, N_2O, CCl_2F_2, CCl_3F, $CHClF_2$
4	1290	200.	H_2O, CO_2, O_3, N_2O, CH_4, HNO_3, $ClONO_2$
5	1510.	300.	H_2O, CO_2, CH_4, N_2O, O_2 continuum
1A4	2725.	250.	H_2O, CO_2, O_3, N_2O, CH_4, HCl, HDO
1A5	2925.	250.	H_2O, O_3, N_2O, CH_4, NO_2, HCl, OCS, C_2H_6, HDO

Summary/Recommendations

We make the following recommendations:

- Inaccurate H_2O pressure-broadened half-widths are a problem in all spectral regions but especially in Spectral Region 5. Improved widths and temperature dependences are needed. Accurate H_2O parameters are important not just for the retrieval of H_2O, but also for other trace constituents whose absorptions are blended with those of H_2O.
- Improved pressure-broadened half-widths for O_3 are needed in the HIRDLS Spectral Region 3.
- New and improved HNO_3 spectroscopic parameters are needed in each of the main bands (i.e. 868, 1205, and 1290 cm^{-1}). It is particularly true for the representation of the many Q-branches in these bands. New HNO_3 spectroscopic data will shortly be available for the 868 cm^{-1} band (private communication, R.A. Toth, JPL).
- $COCl_2$ is a significant pseudo-continuum absorber between 840–870 cm^{-1} contributing 20–25 pptv of organic chlorine in the mid-latitude upper troposphere and lower stratosphere[9].
- Low temperature cross-sections are needed for some of the pseudo-continuum absorbers (e.g. CFC-113, N_2O_5) especially in HIRDLS Spectral Regions 1 and 4 where HNO_3, N_2O_5, and $ClNO_3$ are target gases for retrieval.
- New cross-sections are needed for replacement HCFCs and HFCs which will contribute absorption in the HIRDLS Spectral Regions 2 and 3.
- Investigations of line-mixing are needed for many atmospheric molecules (e.g. CO_2, CH_4). Theoretical representation of line-mixing also needs further work.
- The molecular spectroscopic database needs to be updated for tropospheric species currently not available. For example, in retrieving aerosol extinction from remotely measured emission spectra, it is important to fully account for all the gaseous contributions to the spectral continuum. The 821–836 cm^{-1} in Spectral Region 2 will be used by HIRDLS for retrieval of aerosol. Although this region is one of the best mid-infrared “windows”, there is nevertheless

significant gaseous absorptions from the minor species CFC-113, CFC-11, $ClNO_3$, and HCFC-22. However, features exceeding the noise level are persistent at 15 and 8 km from unknown species for which linelists are unavailable.

References

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Figure captions

Figure 1. This and all subsequent figures illustrate the fits to the MkIV balloon-borne solar absorption spectra acquired from an altitude of 33 km during Sun set on December 3, 1999, from Esrange (68° N), Sweden. The panels show fits to 25.11 km, 14.77 km, and 8.06 km tangent height spectrum.

In this and all subsequent figures, the HITRAN 2000 and the JPL pseudo-spectroscopic parameters were used. Tangent altitudes for MkIV spectra were retrieved using temperature insensitive CO_2 lines, and tangent temperatures were retrieved using temperature sensitive CO_2 lines, assuming CO_2 profile measured in situ by the Harvard CO_2 instrument launched on November 19, 1999, from Esrange as part of the NASA OMS balloon payload.

The 810–940 cm^{-1} region covers the HIRDLS Spectral Region 2 (Channels 6–9) where the principal target gases for retrieval are CCl_3F (CFC-11), HNO_3, and CCl_2F_2 (CFC-12). Here the target gases are simultaneously fitted along with the interfering gases H_2O, CO_2, O_3, and $CHClF_2$ (HCFC-22). Contributions to "Other" include a broad pseudo-continuum absorption by CCl_2FCClF_2 (CFC-113) between 810–825 and 900–920 cm^{-1}, $COCl_2$ between 840–870 cm^{-1} (underneath the CFC-11 absorption), and numerous line absorptions by OCS.

It is clear from the fits that the HNO_3 spectroscopic line parameters are the largest source of "Residual" (i.e., 100×(measured-calculated)). Particularly, the Q-branches at 885.4 and 896.2 cm^{-1} are poorly fitted. Updated line parameters for HNO_3 will shortly be available (private communication R.A. Toth, JPL) to test our ability to improve the fits to the measured spectra. However, hot bands of HNO_3 need further work.

Figure 2. The 980–1150 cm^{-1} region covers the HIRDLS Spectral Region 3 (Channels 10–12) where the principal target gas for retrieval is O_3. Here the target gas is simultaneously fitted with the interfering gases H_2O, CO_2, N_2O, CFC-11, CFC-12, and HCFC-22. "Other" contributions to this spectral region include CH_4 and HCOOH ($\approx$5% absorption at 8 km between 1104.5–1106.5 cm^{-1} from the ~150 pptv abundance in the troposphere at mid- and extra-vortex high-latitudes).

Although the spectral region is well fitted at 15 and 8 km altitudes, with rms fits of 0.86and 0.67%, respectively, significant "Residuals" remain above the spectral noise level. The primary absorber in the region is O_3 (i.e. 3rd panel in all three sheets) and better O_3 pressure-broadened half-widths and their temperature dependence will resolve some of the prominent residuals.

Figure 3. The 1190–1390 cm^{-1} region covers the HIRDLS Spectral Region 4 (Channels 13–17) where the target gases for retrieval are N_2O_5, N_2O, $ClONO_2$, and CH_4. Here the target gases were simultaneously fitted along with the interfering gases H_2O, CO_2, O_3, and HNO_3. The broad-band pseudo-continuum absorption between 1220–1260 cm^{-1} is due to N_2O_5 and is apparent at 25 km altitude. The strong absorption feature between 1275–1288 cm^{-1} is due to the organic source gas CF_4. The numerous line absorptions arise from HDO.

The largest "Residual" in this region is due to inadequate spectroscopic parameters for HNO_3. The poorly fitted HNO_3 Q-branch between 1205–1206 cm^{-1} is visible even at 25 km. HNO_3 band between 1280–1350 cm^{-1} needs significant improvement to allow fitting these high-resolution spectra down to their noise levels. Additionally, new measurements for N_2O_5 are needed at low-temperature since the current JPL pseudo-spectroscopic parameters are based on four spectra acquired between 293–233~K.

Figure 4. The 1360–1660 cm^{-1} region covers the HIRDLS Spectral Region 5 (Channels 18–21) where the target gases for retrieval are H_2O and NO_2. Here the target gases are simultaneously fitted with the interfering gases CO_2, CH_4, and O_2 continuum. Significant contribution to "Other" arises from HDO.

The largest "Residual" in this region is due to inadequate spectroscopic parameters for H_2O. Additional laboratory data are needed in H_2O pressure-broadened half-widths and their temperature dependence.

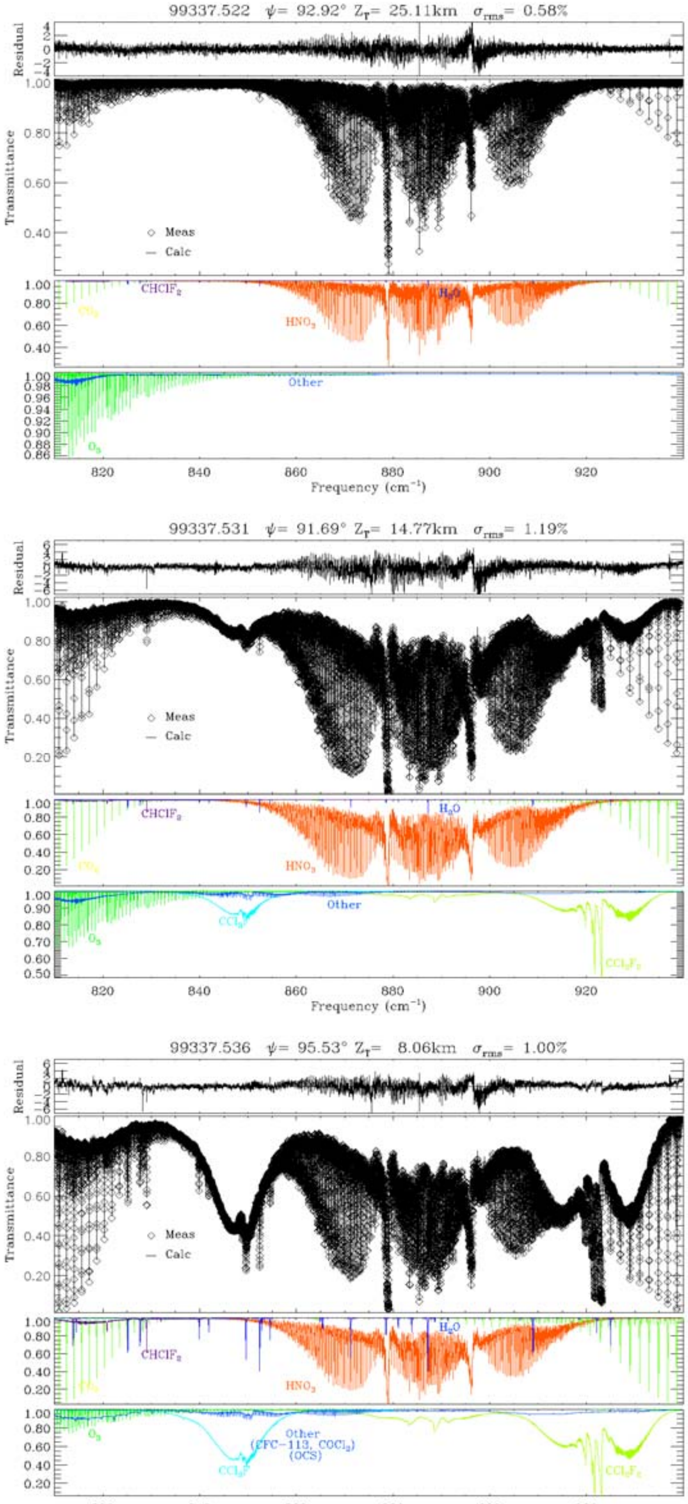
99337.522 ψ= 92.92° Z_T= 25.11km σ_{rms}= 0.58%
Residual
Transmittance
Meas
Calc
CHClF$_2$
H$_2$O
HNO$_3$
Other
O$_3$
99337.531 ψ= 91.69° Z_T= 14.77km σ_{rms}= 1.19%
Residual
Transmittance
Meas
Calc
CHClF$_2$
H$_2$O
HNO$_3$
CCl$_3$F
Other
O$_3$
CCl$_2$F$_2$
99337.536 ψ= 95.53° Z_T= 8.06km σ_{rms}= 1.00%
Residual
Transmittance
Meas
Calc
CHClF$_2$
H$_2$O
HNO$_3$
O$_3$
Other
(CFC-113, COCl$_2$)
(OCS)
CCl$_3$F
CCl$_2$F$_2$
820
840
860
880
900
920
Frequency (cm^{-1})

Figure 1

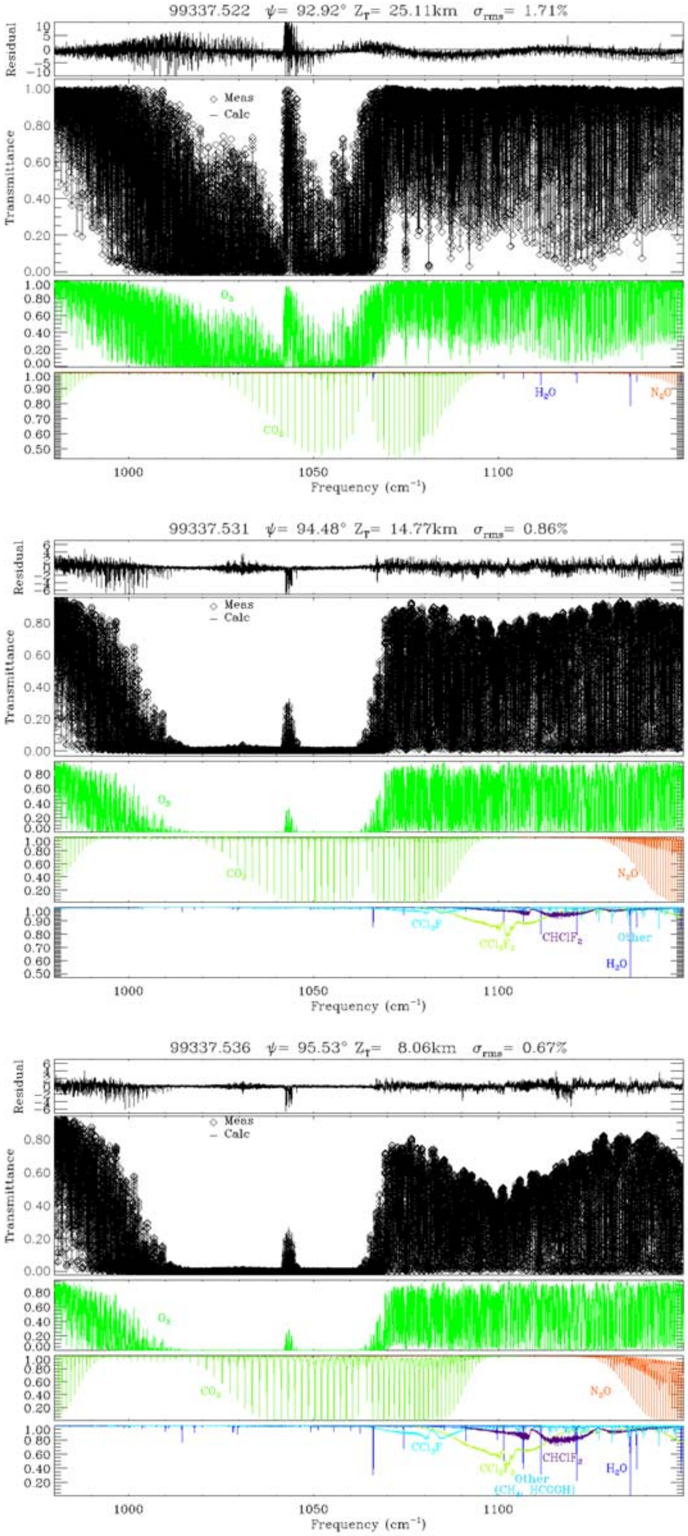
99337.522 ψ= 92.92° Z_T= 25.11km σ_rms= 1.71%
Residual
Transmittance
◇ Meas
— Calc
O3
CO2
H2O
N2O
99337.531 ψ= 94.48° Z_T= 14.77km σ_rms= 0.86%
CCl3F
CCl2F2
CHClF2
Other
99337.536 ψ= 95.53° Z_T= 8.06km σ_rms= 0.67%
Other (CH4, HCOOH)
1000
1050
1100
Frequency (cm⁻¹)

Figure 2

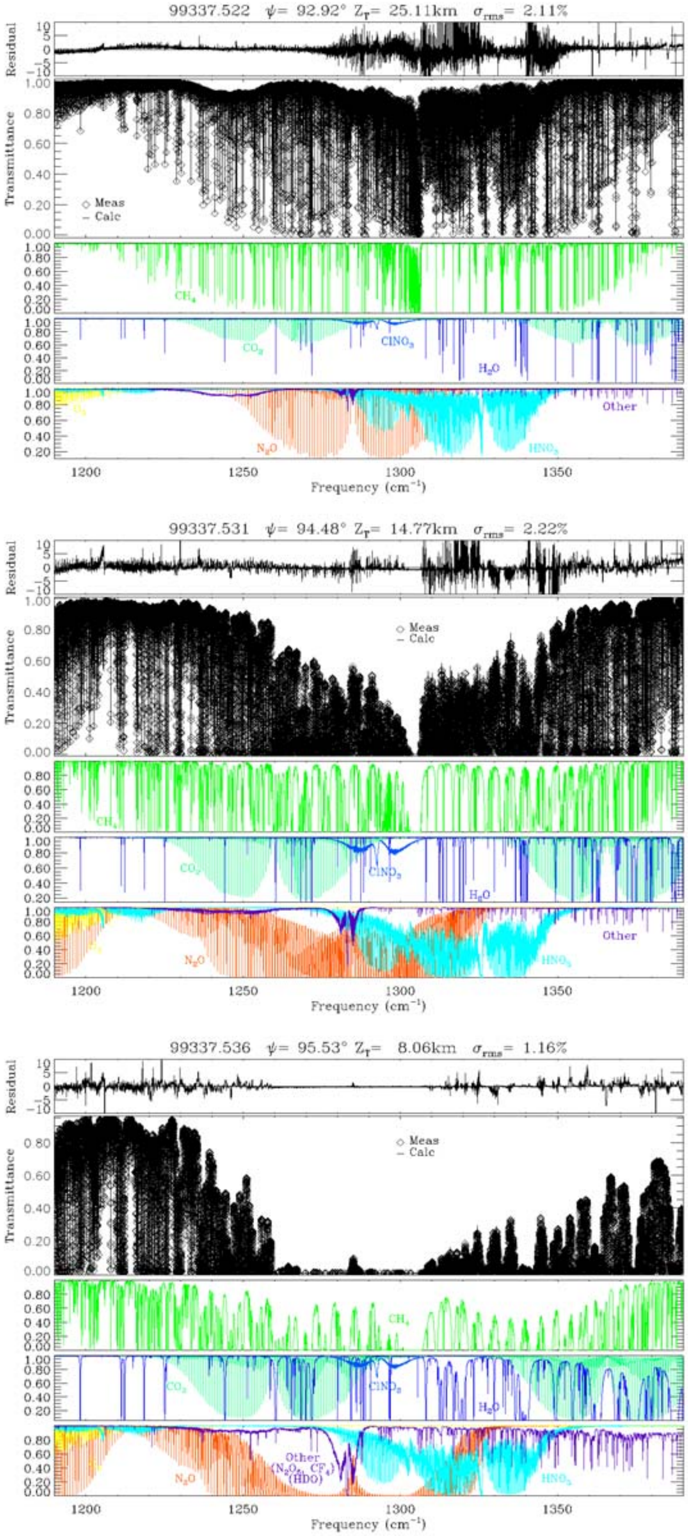
99337.522 ψ= 92.92° Z_T= 25.11km σ_rms= 2.11%
Residual
Transmittance
◇ Meas
– Calc
CH₄
CO₂
ClNO₃
H₂O
O₃
N₂O
HNO₃
Other
Frequency (cm⁻¹)
99337.531 ψ= 94.48° Z_T= 14.77km σ_rms= 2.22%
99337.536 ψ= 95.53° Z_T= 8.06km σ_rms= 1.16%
Other (N₂O₅, CF₄) (HDO)
1200
1250
1300
1350

Figure 3

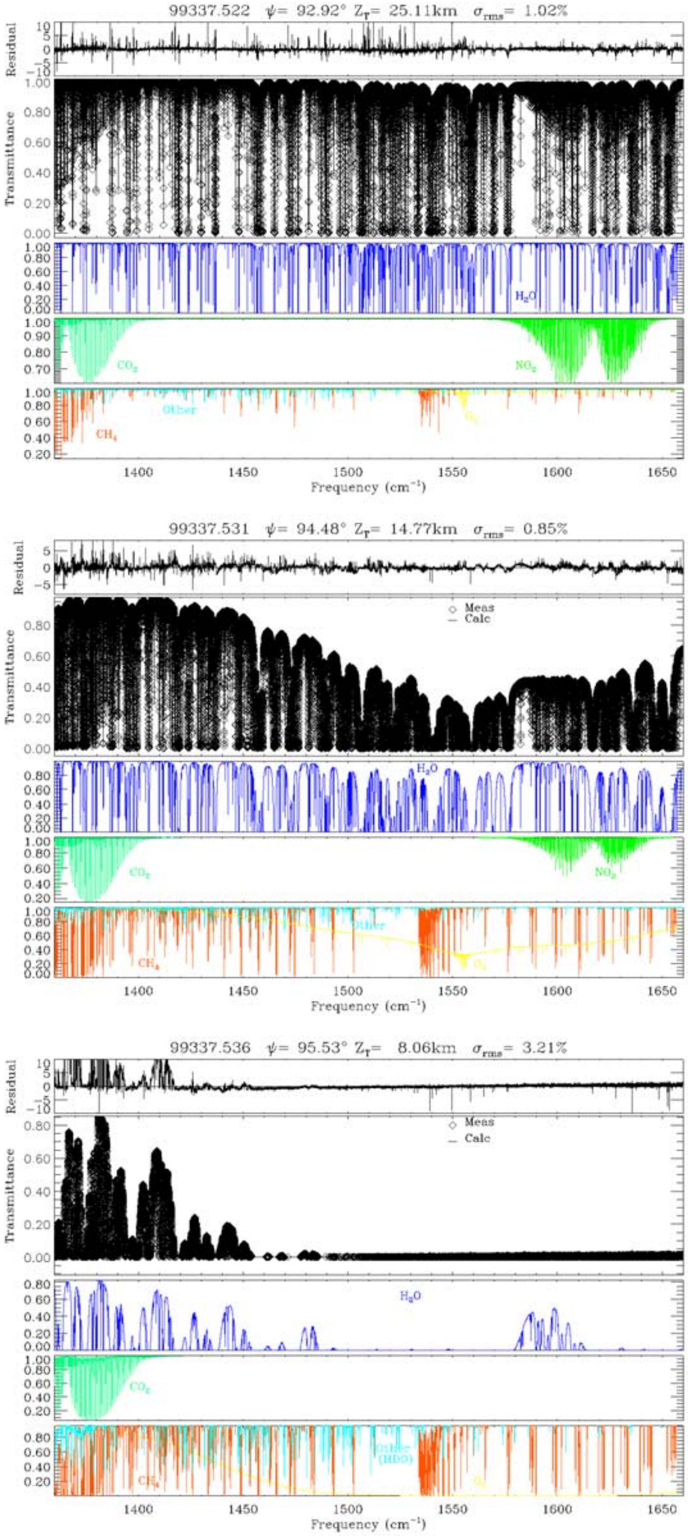
99337.522 ψ= 92.92° Z_T= 25.11km σ_rms= 1.02%
Residual
Transmittance
H2O
CO2
NO2
Other
CH4
O3
99337.531 ψ= 94.48° Z_T= 14.77km σ_rms= 0.85%
Meas
Calc
99337.536 ψ= 95.53° Z_T= 8.06km σ_rms= 3.21%
Other (HDO)
1400
1450
1500
1550
1600
1650
Frequency (cm⁻¹)

Figure 4