CO_2 Spectroscopy Evaluation Using Atmospheric Solar Absorption Spectra

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Why Use Solar Absorption Spectra?

The broad spectral coverage of FTS solar absorption spectra, together with their high SNR and resolving power, make them very useful for assessing the adequacy of the CO_2 spectroscopic databases.

- **Unambiguous photon path history**
  - All measured photons come from the Sun.
- **Achieve large optical densities**
  - Path lengths of up to 100 km
- **Evaluate significant omissions in the current linelist**
  - Missing gases, isotopologues, hot bands.
- **Evaluate pressure-dependent parameters**
  - Widths, shifts, collision-induced absorption
- **Evaluate adequacy of physics**
  - Far-wing line shapes, line-mixing.
- **Assess consistency of spectral parameters between different regions**
  - Broad spectral coverage

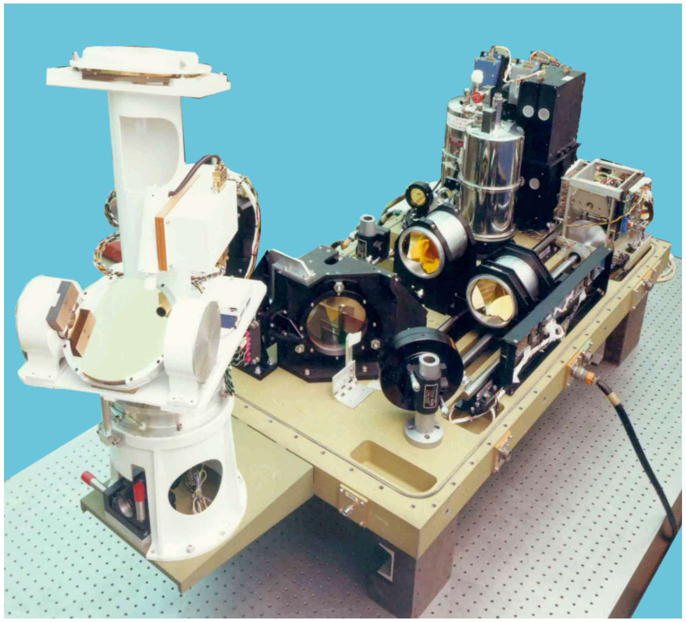
The JPL MkIV Balloon-Borne Interferometer

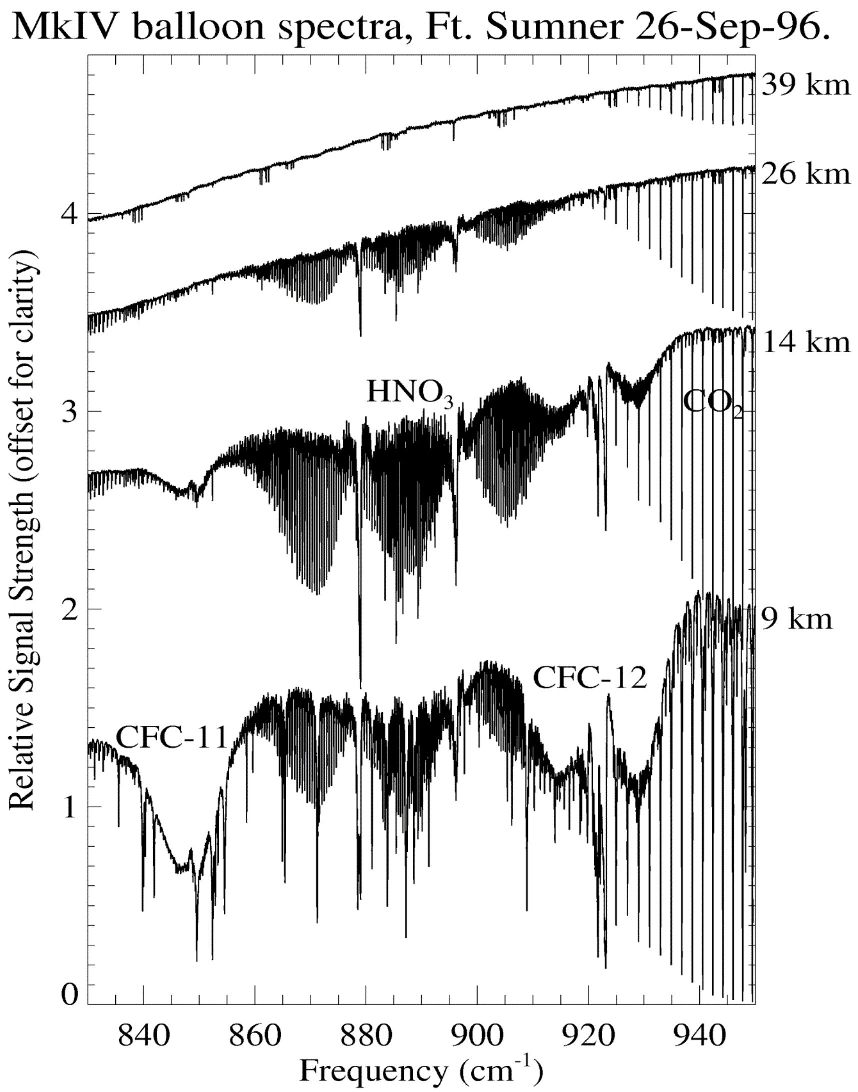
Mass: 250 kg, Size: 1.4 x 0.7 x 0.8 m.

Parallel HgCdTe & InSb detectors simultaneously cover 650-5650 cm^{-1}.

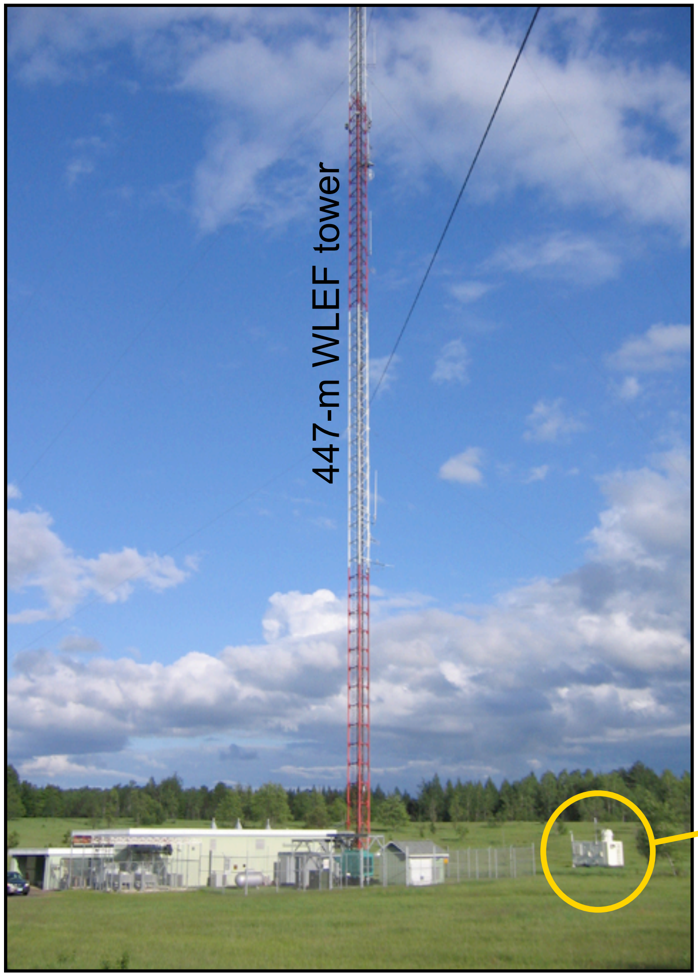
KBr beamsplitter & compensator.

Double-passed configuration up to 120 cm OPD (0.008 cm^{-1} resolution).





Park Falls Automated Solar Observatory



← In situ and Ground-based FTIR ↓

The IFS 125HR Interferometer

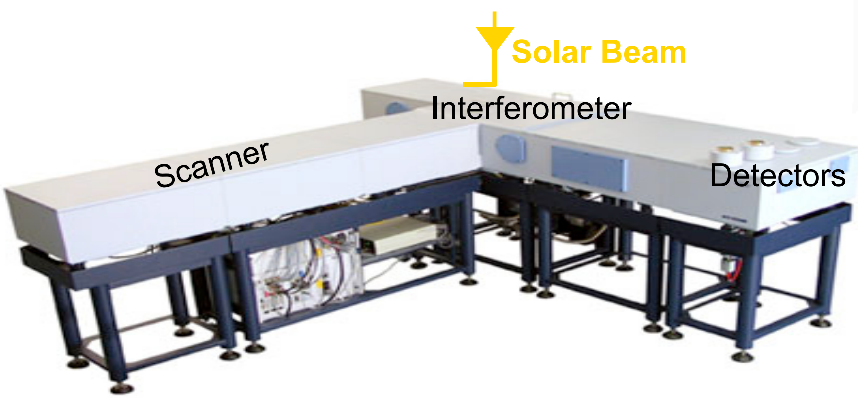
Size: 3 x 2 x 1 m.

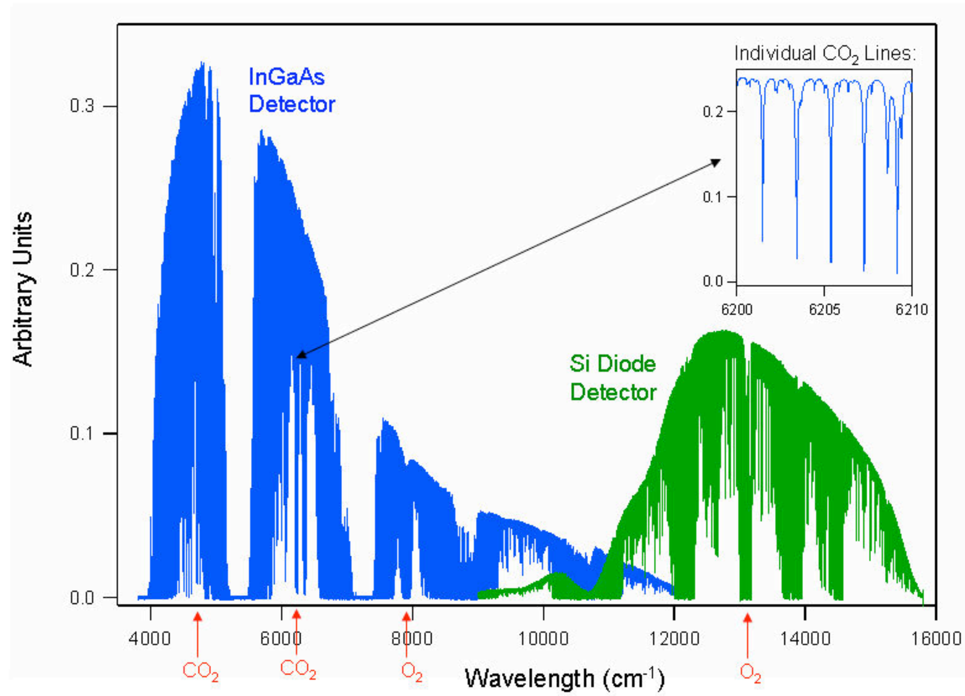
Parallel Si Diode & InGaAs detectors simultaneously cover 3900-15600 cm^{-1}.

CaF_2 beamsplitter & compensator.

Double-passed configuration up to 159 cm OPD (0.0062 cm^{-1} resolution.)

HCl cell for wavelength and ILS calibration





Relative Advantages of Solar Absorption Spectra: Balloon-Borne versus Ground-Based

MkIV balloon-borne solar occultation spectra

- Evaluate line positions
- Evaluate relative band strengths
- Small line-of-sight H_2O column
- Solar and instrumental features are removed by ratioing with low-airmass spectrum

IFS 125HR ground-based solar absorption spectra

- Evaluate air-broadened widths and pressure-induces shifts
- Absolute band strengths
  - Continuous P_{surf} measurements by CIT (0.1 hPa precision)
  - In situ CO_2 profile (0.1 ppmv precision)
    - Continuous profiles by NOAA (0 - 400 m)
    - Weekly air-borne profile by NOAA (<4 km)
    - Periodic air-borne profile by Harvard University (<12 km)
  - Radiosonde temperature profile (1 K <30 km)

*The JPL 2006 CO_2 Interim Linelist**

- **Based on new analysis of 42 CO_2 laboratory spectra recorded with the Kitt Peak FTS at 0.01 cm^{-1} resolution.**
  - Cell lengths of 3.47 cm, 2.46 m and 25 - 410 m
  - $^{12}C^{16}O_2$ with normal (0.9842) and enhanced (0.9952) abundance
  - Assumes Voigt line shapes
  - Band strength uncertainties < 0.5% ($J' \leq 40$)
  - 58 new band strengths measured for the main isotope
  - Self-broadened widths and pressure-induced shifts for 15 bands
- **Improved $^{12}C^{16}O_2$ molecular line parameters: 4500 - 6989 cm^{-1}**
  - 4188 transitions for 8 isotopologues ($S_{min} = 4.x10^{-28}$)
  - HITRAN 2004 spectral parameters for other isotopes
  - Air-broadened widths similar to HITRAN 2004
  - Air-broadened shifts estimated from near-infrared N_2O
    (HITRAN 2004 has shifts equal zero in this spectral range)

*C.E. Miller: Line mixing in pure CO_2 at 6348 cm^{-1}

*R.A. Toth: Line strengths and self-broadening coefficients of CO_2 from 4600 - 7000 cm^{-1}

Spectroscopy of CO_2: Line Position Error

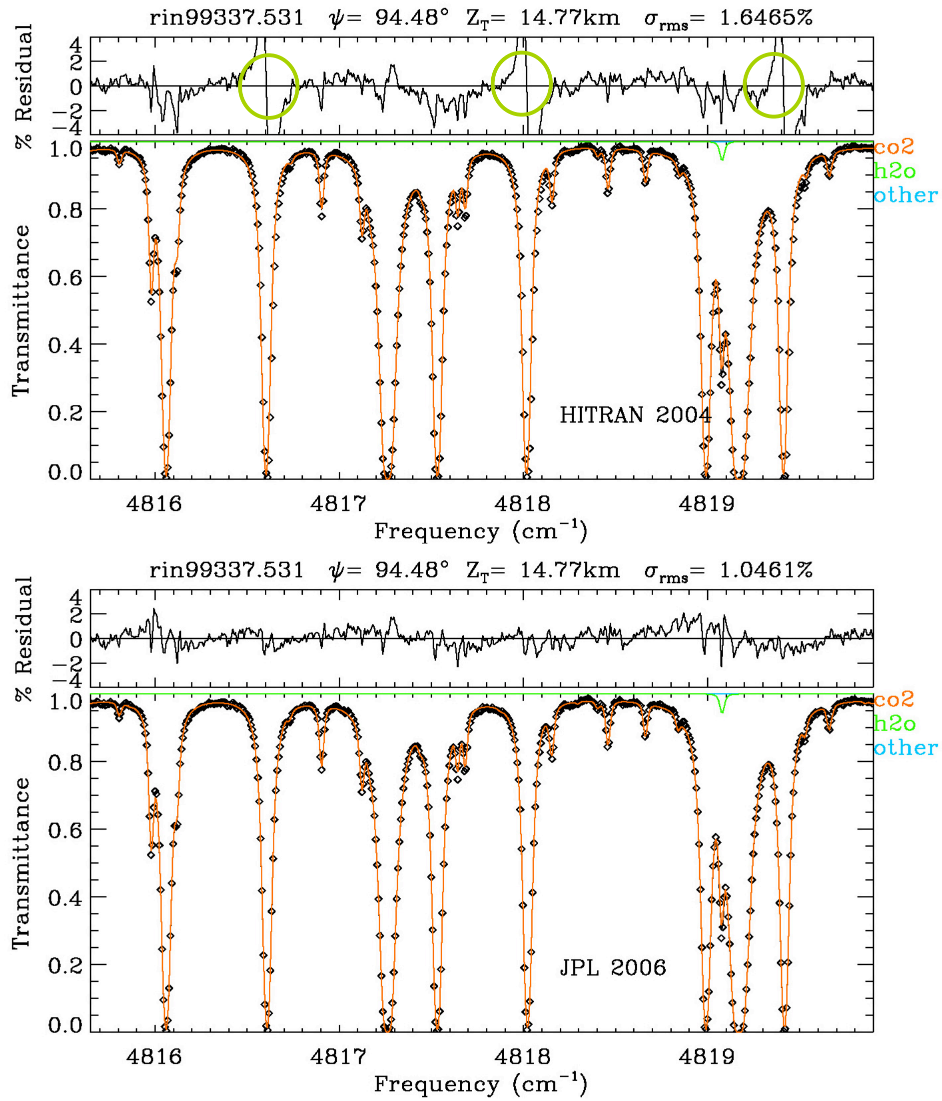
The high-resolution **MkIV** balloon spectrum allows us to investigate errors in the line positions.

In this and all following figures, diamond symbols represent measured spectrum. Line represents fitted calculation.

The upper panel illustrates 3 wrong CO_2 line positions in HITRAN 2004.

The lower panel illustrates fits to the same spectrum using the improved JPL 2006 CO_2 spectroscopy.

The error in the CO_2 line positions is resolved.

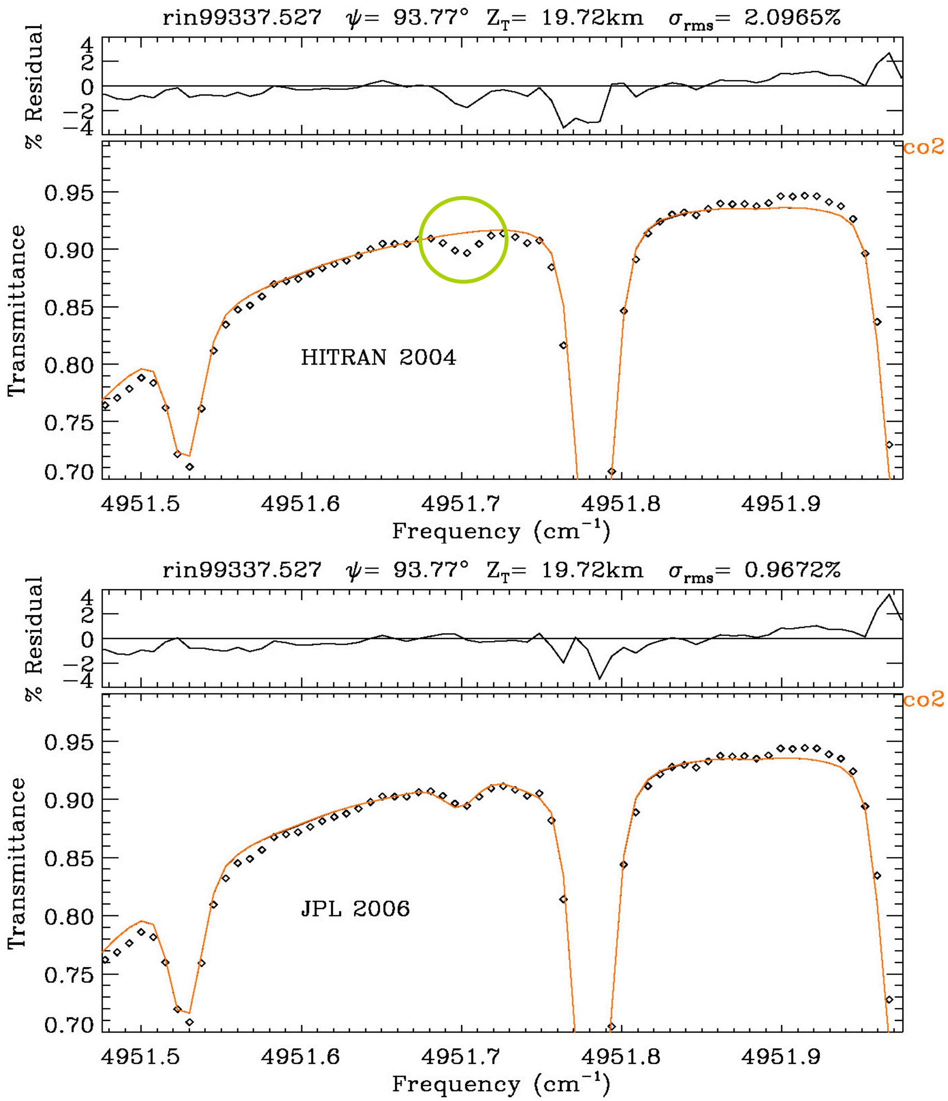


Spectroscopy of CO_2: Missing Lines

The high-resolution **MkIV** balloon spectrum allows us to investigate missing lines.

The upper panel illustrates a weak missing CO_2 transition in HITRAN 2004.

The lower panel illustrates fits to the same spectrum using the JPL 2006 CO_2 spectroscopy.



Spectroscopy of CO_2: The 2 μm Fermi Triad

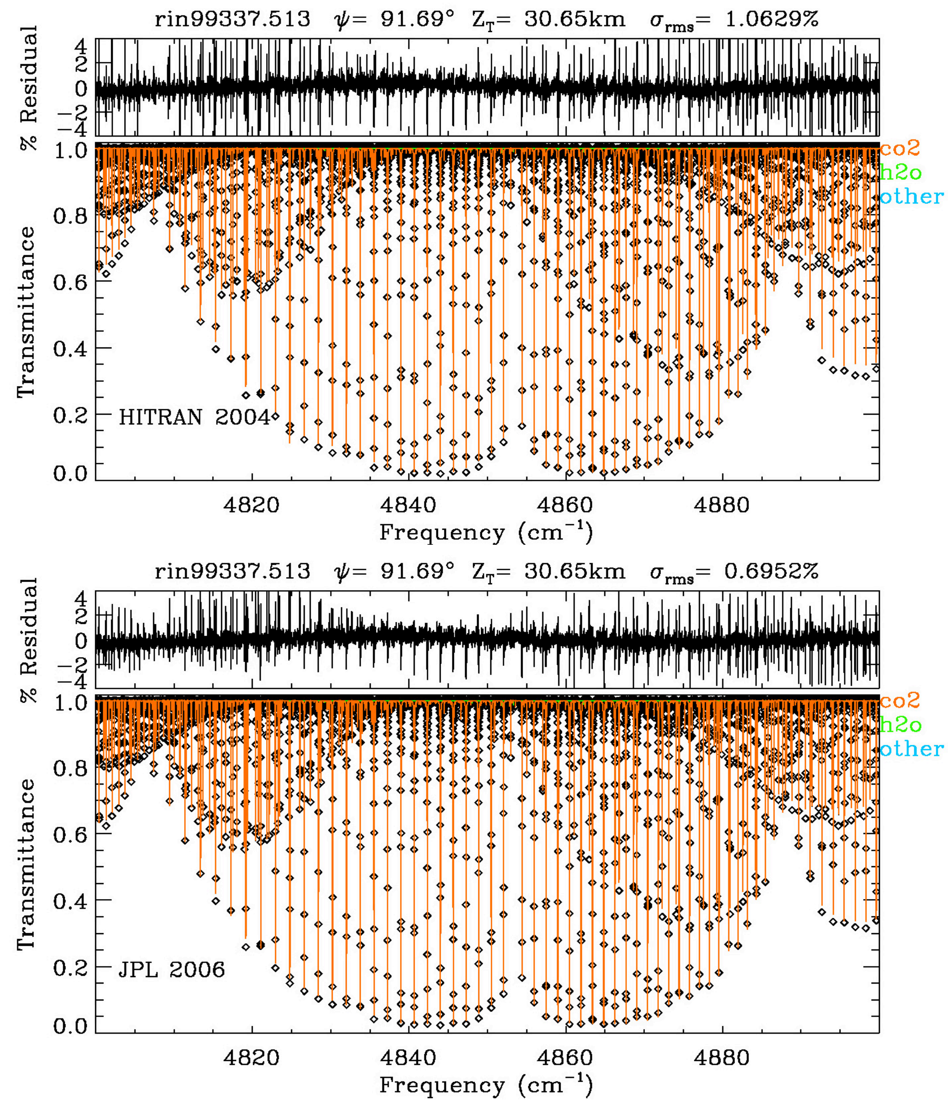
Fits to **MkIV** spectrum (31 km tangent altitude) with HITRAN 2004 (upper panel) and JPL 2006 (lower panel) CO_2spectroscopy, respectively.

The σ_{rms} has improved nearly 70%.

Note the low amount of H_2O absorption in the limb spectrum.

The 20013←00001 band is used by MkIV to determine observation geometry.

It will also be used by OCO to measure atmospheric CO_2.

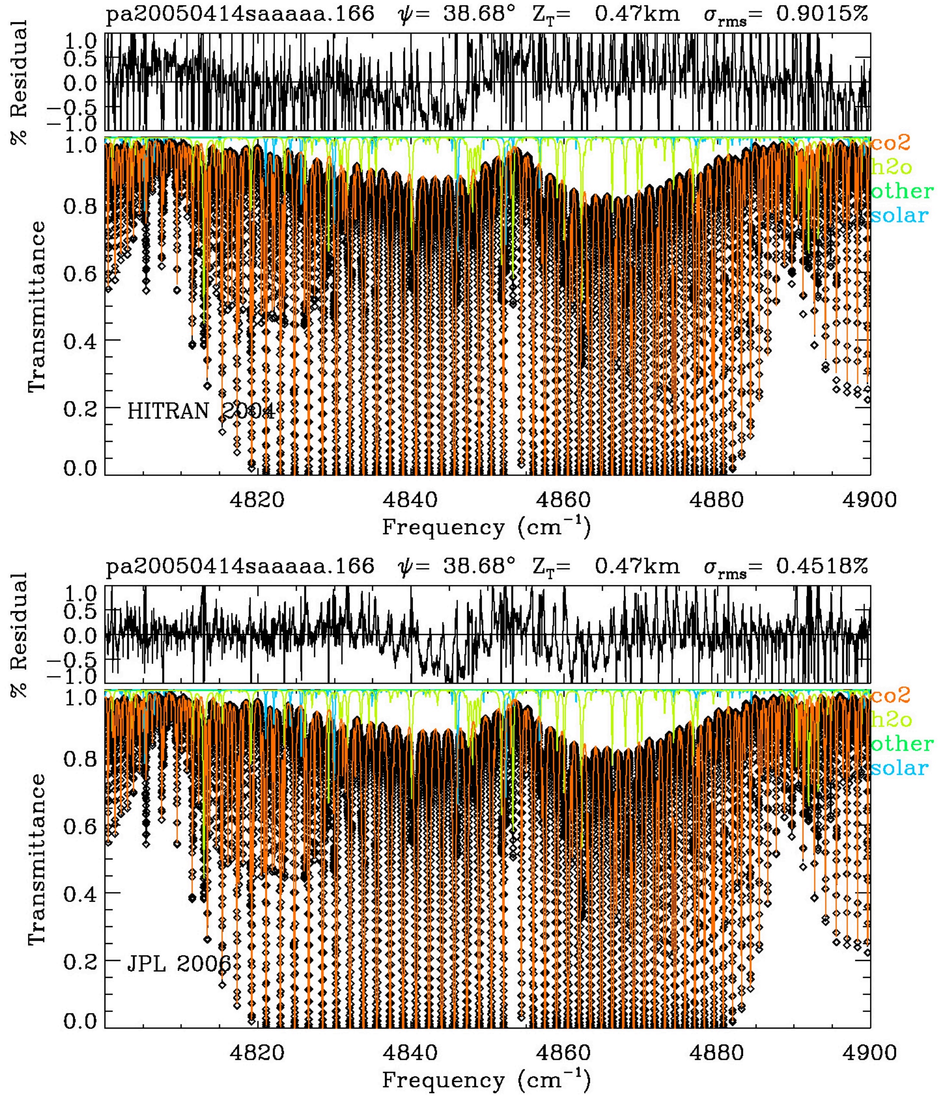


Spectroscopy of CO_2: The 2 μm Fermi Triad

Fits to the **IFS 125HR** ground-based solar absorption spectrum with HITRAN 2004 (upper panel) and JPL 2006 (lower panel) CO_2 spectroscopy, respectively.

The σ_{rms} has improved nearly 50%.

Note the significant H_2O absorption in the ground-based spectrum.

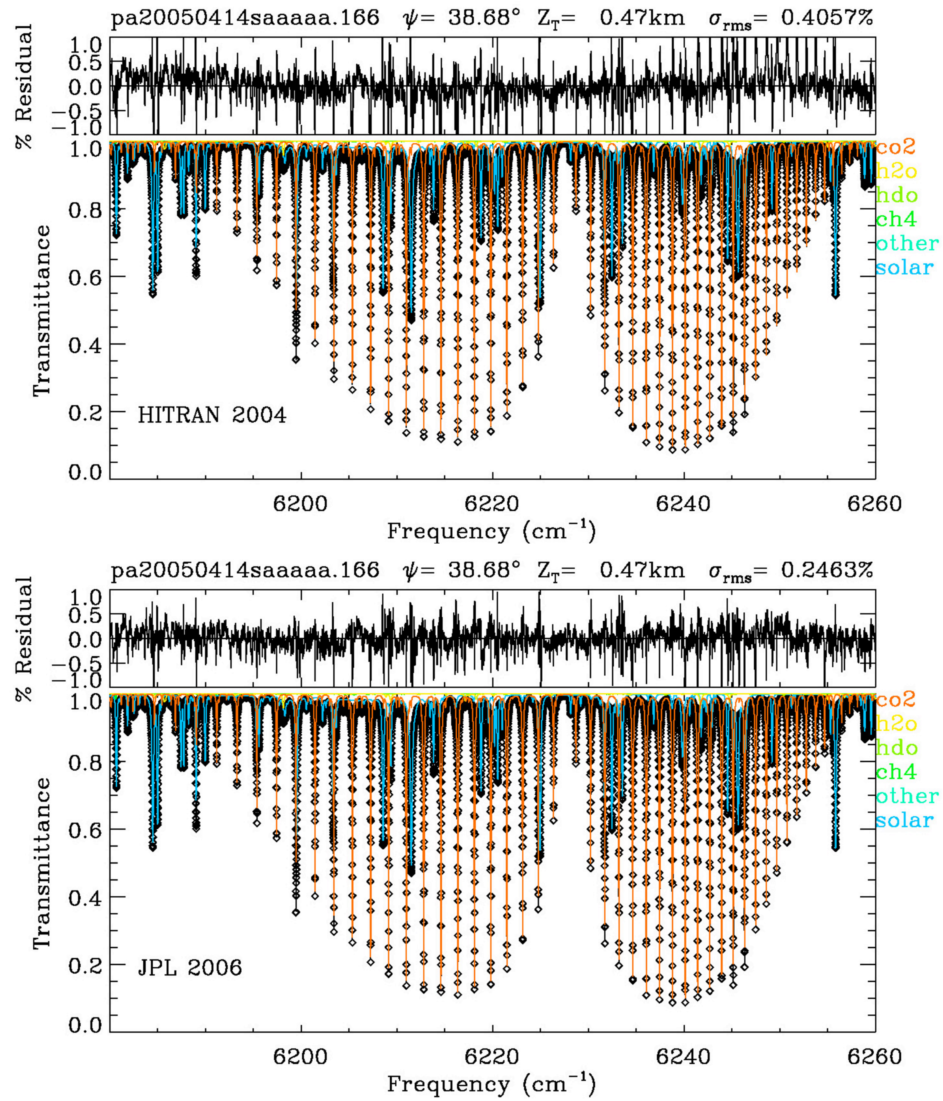


Spectroscopy of CO_2: The 1.6 μm Fermi Tetrad

Fits to the **IFS 125HR** ground-based solar absorption spectrum with HITRAN 2004 (upper panel) and JPL 2006 (lower panel) CO_2 spectroscopy, respectively.

The σ_{rms} has improved nearly 40%.

The 1.6 μm (30013←00001) band will also be used by OCO to measure atmospheric CO_2.

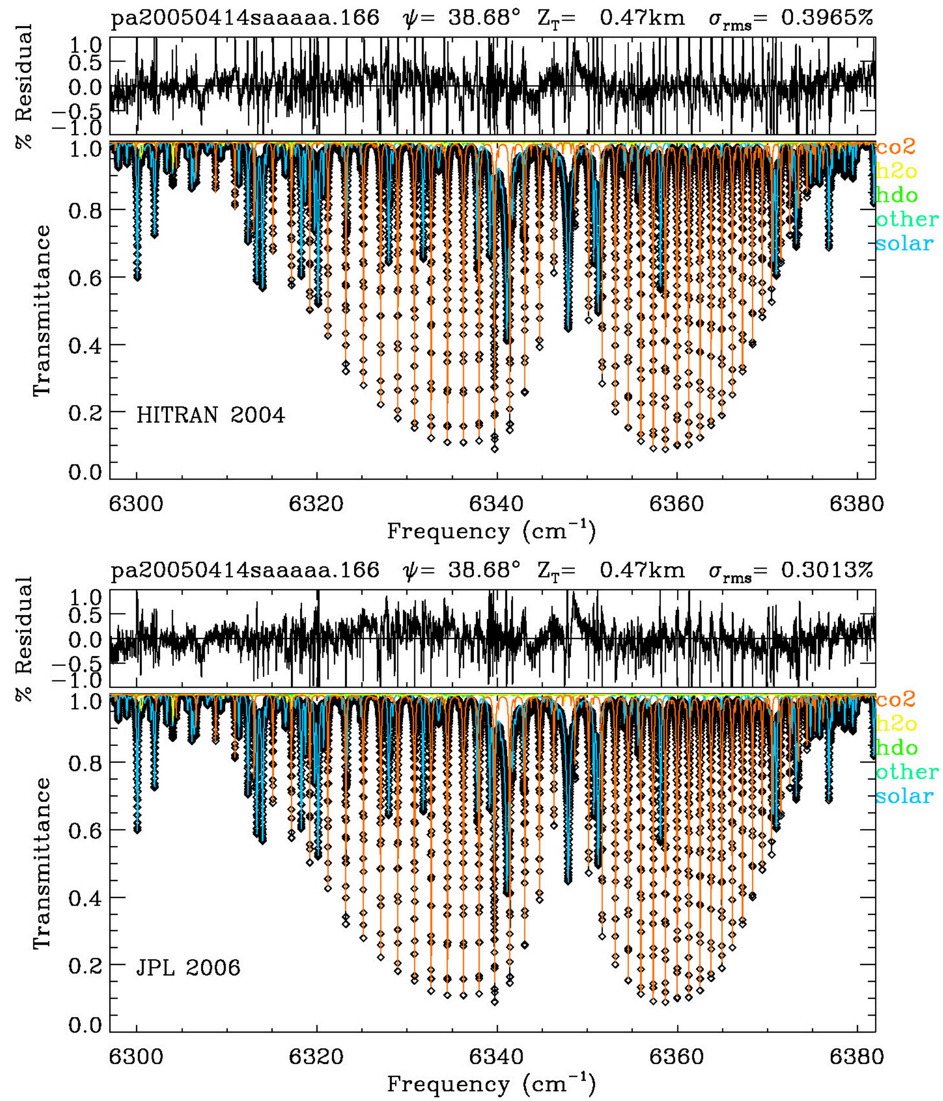


Spectroscopy of CO_2: The 1.58 μm Fermi Tetrad

Fits to the **IFS 125HR** ground-based solar absorption spectrum with HITRAN 2004 (upper panel) and JPL 2006 (lower panel) CO_2 spectroscopy, respectively.

The σ_{rms} has improved nearly 30%.

The 1.58 μm (30012←00001) band is used by SCIAMACHY to measure atmospheric CO_2.



Spectroscopy of CO_2: Biases in Band Strengths

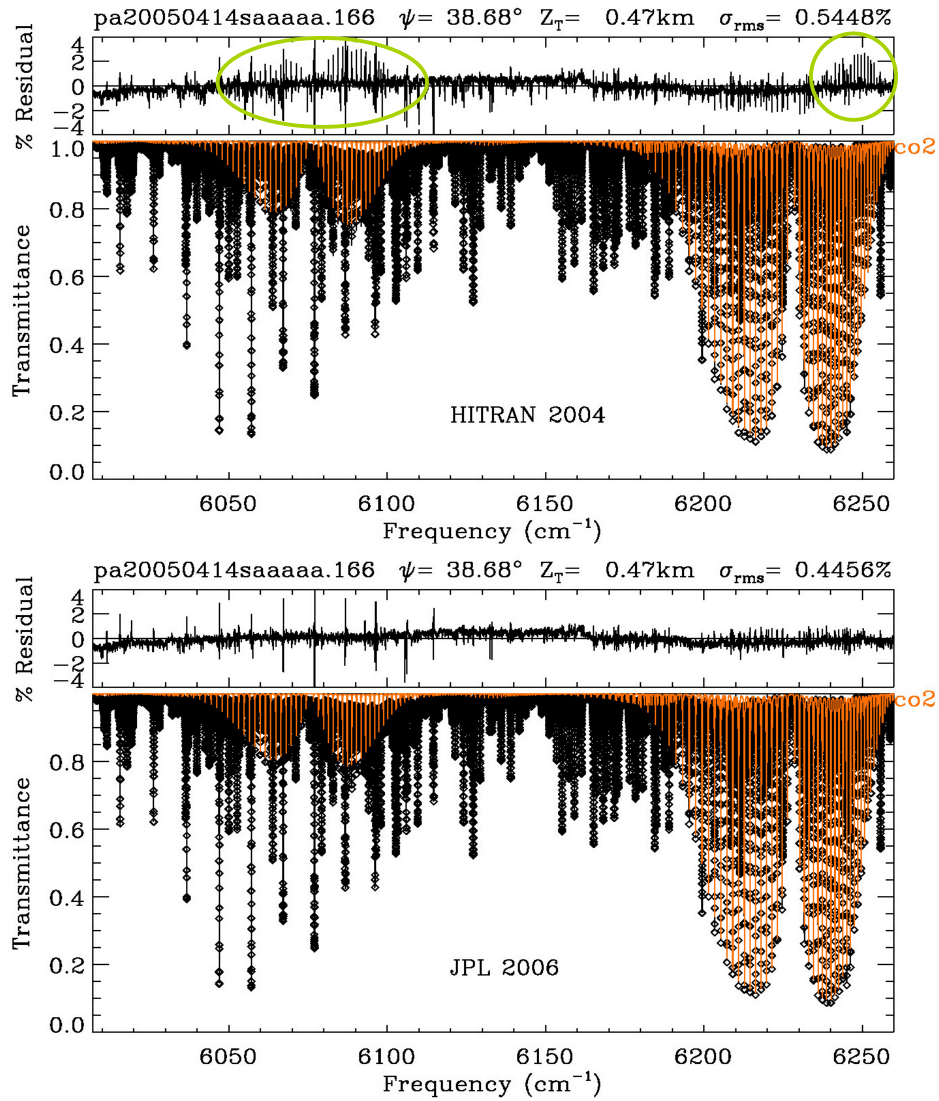
Fits to the **IFS 125HR** ground-based solar absorption spectrum with HITRAN 2004 (upper panel) and JPL 2006 (lower panel).

Using HITRAN 2004, the 1.65 μm (30014←00001) region is fitted poorly compared to the much stronger 1.6 μm band. The 6077 cm^{-1} band strength is 15% too large.

Also, the high-J lines of the R-branch of the 6228 cm^{-1} band are inconsistent.

In JPL 2006, the two CO_2 bands are in much better agreement.

The remaining large residuals are due to pressure shift errors in CH_4.



Spectroscopy of CO_2: Biases in Band Strengths

Observed Differences Between In Situ and Remote CO_2 Column Measurements				
	IFS 125 HR Z_{min}: 0.47 km; SZA: 38.7°		**MkIV** Z_{min}: 31.65 km; SZA: 91.7°	
Region	**HITRAN 2004**	**JPL 2006**	**HITRAN 2004**	**JPL 2006**
2 μm	**9%**	**0.3%**	**7%**	**0.2%**
1.65 μm	**16%**	**0.4%**		
1.6 μm	**4%**	**-0.1%**		
1.58 μm	**-1%**	**-0.3%**		

HITRAN 2004 CO_2 band strengths exceeds the 0.3% accuracy needed to measure atmospheric CO_2.

JPL 2006 CO_2 band strengths are accurate to ±0.4%.

Conclusions

Solar absorption spectrometry has the high SNR and spectral resolving power necessary to demonstrate that:

- **The JPL 2006 CO_2 interim linelist is a significant improvement**
  - Spectral fits using non-Voigt line shapes give 30% - 50% better results
  - Need to improve band strengths of other CO_2 isotopologues
- **Iterative analysis of laboratory spectra and atmospheric retrievals drives refinement of CO_2 spectral parameters**
  - Atmospheric retrievals used to identify discrepancies
- **Evaluated inadequacies in the spectroscopic database**
  - Line position error around 4817 cm^{-1}
  - Missing lines around 4946 cm^{-1}
- **Assessed discrepancies in relative strengths in different near-IR regions.**
  - CO_2 band strengths agree to within ±0.4%.