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
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

447-m WLEF tower

← 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 H₂O 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 CO₂ 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)
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 ($S_{\text{min}} = 4.\times10^{-28}$)
- HITRAN 2004 spectral parameters for other isotopes
- Air-broadened widths similar to HITRAN 2004
- Air-broadened shifts estimated from near-infrared N$_2$O
  (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$^{-1}$
The high-resolution \textbf{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.
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.
Fits to **MkIV** spectrum (31 km tangent altitude) with HITRAN 2004 (upper panel) and JPL 2006 (lower panel) CO$_2$ spectroscopy, respectively.

The $\sigma_{rms}$ has improved nearly 70%.

Note the low amount of H$_2$O 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$_2$. 
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 $\sigma_{rms}$ has improved nearly 50%.

Note the significant H$_2$O absorption in the ground-based spectrum.
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 $\sigma_{\text{rms}}$ has improved nearly 40%.

The 1.6 $\mu$m (30013←00001) band will also be used by OCO to measure atmospheric CO$_2$. 

**Spectroscopy of CO$_2$: The 1.6 $\mu$m 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 $\sigma_{\text{rms}}$ has improved nearly 30%.

The 1.58 $\mu$m (30012←00001) band is used by SCIAMACHY to measure atmospheric CO$_2$. 
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 \( \mu \text{m} \) (30014→00001) region is fitted poorly compared to the much stronger 1.6 \( \mu \text{m} \) 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\(_4\).
**Observed Differences Between In Situ and Remote CO$_2$ Column Measurements**

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<tr>
<td>1.58 $\mu$m</td>
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<td>-0.3%</td>
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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%.

**Spectroscopy of CO$_2$: Biases in Band Strengths**
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%.