On the potential of space- and ground-based FTS measurements for remote sensing of atmospheric CO$_2$ isotopologues


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CO₂ Isotopologues in the Atmosphere

• Natural abundances:
  $^{16}\text{O}^{12}\text{C}^{16}\text{O} (\sim 98.4\%), ~^{16}\text{O}^{13}\text{C}^{16}\text{O} (\sim 1.1\%), ~^{18}\text{O}^{12}\text{C}^{16}\text{O} (\sim 0.4\%)$

• Some processes of the terrestrial carbon cycle modify the abundances and leave their fingerprints in the atmosphere

• Analyzing the atmospheres composition of CO₂ Isotopologues can be used to trace back to individual processes and CO₂ sources and sinks

• The background variations are very small ($\sim 1‰$), larger variations near local sources and sinks
Photosynthesis and $^{16}\text{O}^{13}\text{C}^{16}\text{O}$

- Plants use atmospheric $\text{CO}_2$ to build up biomass
- Atmospheric $\text{CO}_2$ diffuses through the leaves stomata which is more likely for lighter $\text{CO}_2$ molecules, i.e., $^{16}\text{O}^{12}\text{C}^{16}\text{O}$
- The majority of plants are using the C3 carbon fixation pathway based on the enzyme RuBisCO (Ribulose-1,5-bisphosphate carboxylase) discriminates against $^{13}\text{C}$
- Relative enrichment of $^{16}\text{O}^{13}\text{C}^{16}\text{O}$ in the ambient air
- $\text{CO}_2$ exchange with the ocean has no significant fractionating effect
- This effect can be used to, e.g., distinguish between oceanic and biospheric net fluxes
Photosynthesis and $^{18}$O $^{12}$C $^{16}$O

• During daytime (when photosynthesis takes place), the stomata of most plants are open so that atmospheric CO$_2$ can diffuse into the plant cells’ chloroplasts

• Here an isotope exchange reaction takes place between oxygen in CO$_2$ and H$_2$O

• Diffusion of $^{18}$O $^{12}$C $^{16}$O back out of the leaf enriches the ambient air with $^{18}$O $^{12}$C $^{16}$O

• Respiration has no significant fractionating effect

• This effect can be used to, e.g., differentiate between the gross biospheric fluxes photosynthesis and respiration
Air Sampling Networks

- Air sampling networks such as NOAA’s perform highly accurate ground-based measurements of CO₂ isotopologues.
- The networks are very sparse and measurements are taken near the surface in the boundary layer.
- Large parts of our current knowledge about the atmosphere’s CO₂ isotopologues composition is based on these measurements.
GOSAT and ground-based FTS light-paths

- FTS and satellite **measure** direct or back scattered radiation
- Their viewing geometry allow **column measurements**
- Satellite measurements allow **global coverage**
- Light-path sometimes **unknown**, e.g., due to scattering (esp. satellite)
- Fraction of scattered light depends, e.g., on albedo
Delta nomenclature and light-path proxy

- Isotopologues measurements of a sample are typically given in per mil as ratios of heavier to lighter isotopologues relative to a standard:

\[ \delta^{13}C = \left( \frac{\left( \frac{^{16}O \ 13C \ 16O}{^{16}O \ 12C \ 16O} \right)}{\left( \frac{^{16}O \ 13C \ 16O}{^{16}O \ 12C \ 16O} \right)} \right)_{standard} - 1 \times 1000\% \]

- The number of molecules along a light-path can accurately be retrieved.
- However, the exact light-path is sometimes unknown.
- The light-path errors cancel out when building the ratio of two species retrieved along the same light-path.
Due to their different masses, CO\textsubscript{2} isotopologues have different vibrational and rotational absorption spectra.

The depth of an absorption line is related to the number of molecules along the light-path.

Absorption lines: separated, similar strength, optical thickness about one.

Spectrally narrow fit window, little interference with other absorbers.
An optimal estimation framework “adjusts” the input of a radiative transfer simulation to fit measured with simulated absorption spectra.

Uncorrelated Jacobean (how does a fit parameter change the radiances)
Temperature Sensitivity

Large ground state energies $E_0$ of $^{16}\text{O} \ ^{12}\text{C} \ ^{16}\text{O}$ result in large temperature sensitivity of corresponding line intensities.
Temperature Sensitivity

Simulations show that this can result in potential inaccuracies esp. in satellite viewing geometry where light paths are more uncertain.
Ground-based FTS, Orleans, France, 18.10.2009

- High resolution \( \sim 0.006 \text{nm} \) (much finer than line width)
- Reasonable fit residuals (RMS=0.004) but larger than expected from SNR
- Line-mixing is expected to only slightly improve the RMS
- Precision of retrieved \( \delta^{13}C \) and \( \delta^{18}O \) about 1.5‰
- Best case simulations indicate that 0.6‰ could be possible
GOSAT, Saharan desert, 24.11.2010

- GOSAT resolution ~0.15nm (in the order of line width)
- Reasonable fit residuals (RMS=0.006) but larger than expected from SNR
- Precision of retrieved $\delta^{13}C$ and $\delta^{18}O$ about 30‰
Conclusions

Can we expect to gain new knowledge about $\delta^{13}C$ and $\delta^{18}O$ from...

...**GOSAT** satellite measurements?
- Probably not (within the analyzed spectral region)
- The precision is too low (30‰)
- The satellite viewing geometry is conceptually more sensitive to scattering along the light-path especially with large $E_0$ values resulting in different height sensitivities

...**ground-based FTS** measurements?
- Potentially yes (esp. when averaging measurements)
- The estimated precision is 0.6-1.5‰
- Further analyzes of the residuals recommended
Thanks!