On the potential of space- and ground-based FTS measurements for remote sensing of atmospheric CO_2 isotopologues

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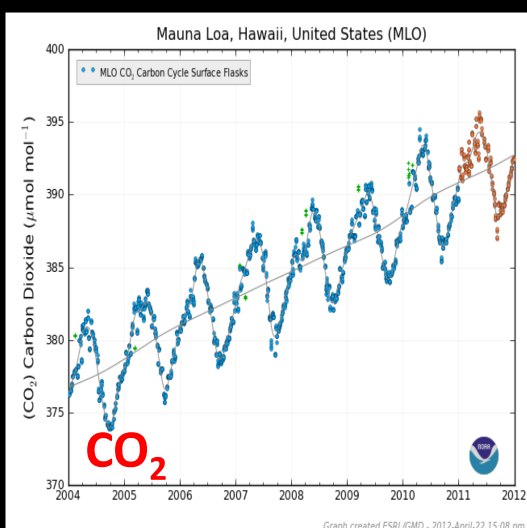
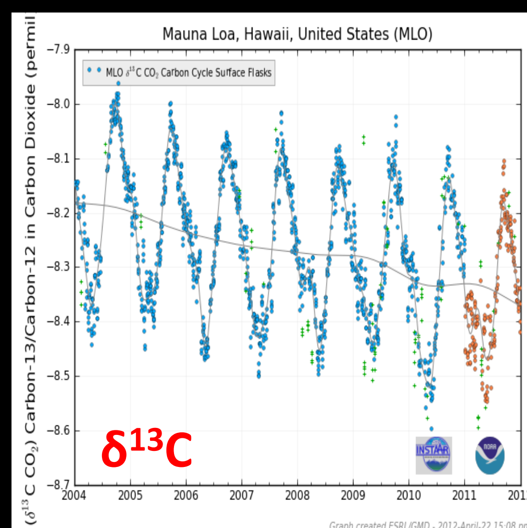
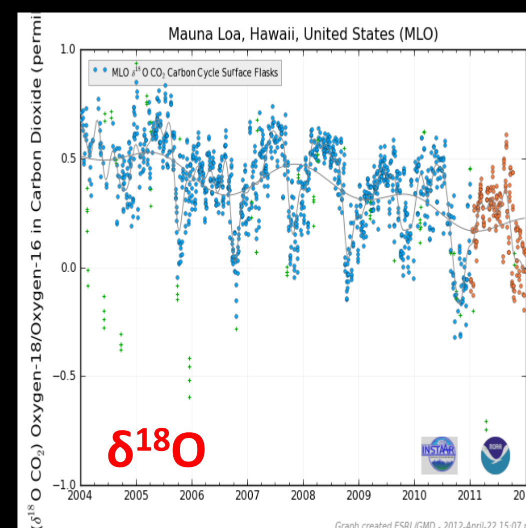
CO_2 Isotopologues in the Atmosphere

- Natural abundances:
  $^{16}O\ ^{12}C\ ^{16}O$ (~98.4%), $^{16}O\ ^{13}C\ ^{16}O$ (~1.1%), $^{18}O\ ^{12}C\ ^{16}O$ (~0.4%)
- Some processes of the terrestrial carbon cycle modify the abundances and leave their fingerprints in the atmosphere
- Analyzing the atmospheres composition of CO_2 Isotopologues can be used to trace back to individual processes and CO_2 sources and sinks
- The background variations are very small (~1‰), larger variations near local sources and sinks







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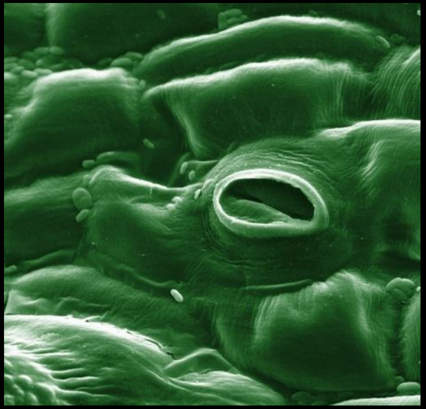
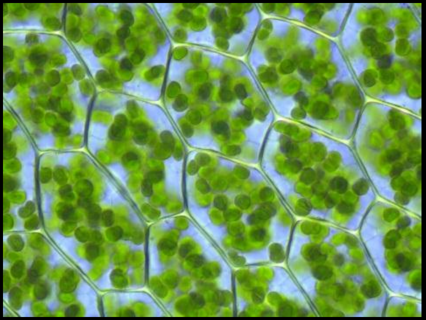
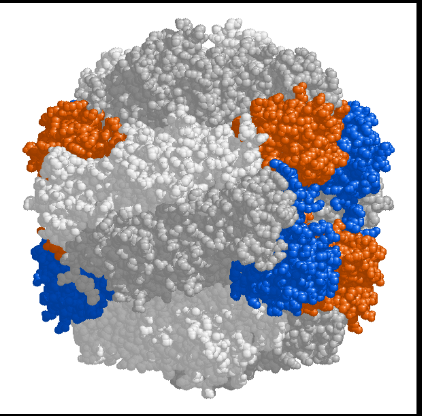
Photosynthesis and ^{16}O ^{13}C ^{16}O

- Plants use atmospheric CO_2 to build up biomass
- Atmospheric CO_2 diffuses through the leaves stomata which is more likely for lighter CO_2 molecules, i.e., ^{16}O ^{12}C ^{16}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}C
- Relative enrichment of ^{16}O ^{13}C ^{16}O in the ambient air
- 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

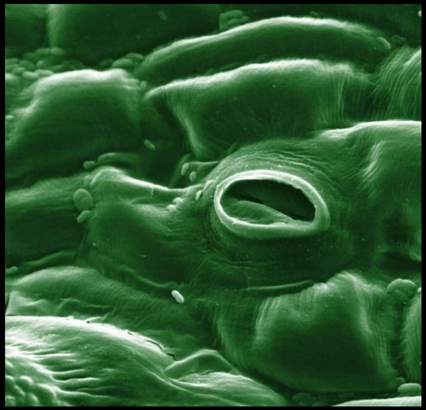


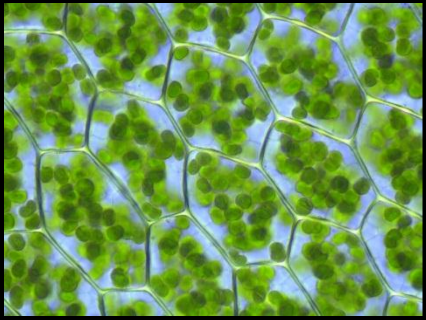


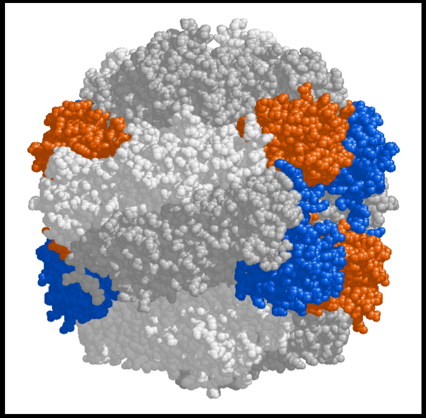


Photosynthesis and ^{18}O ^{12}C ^{16}O

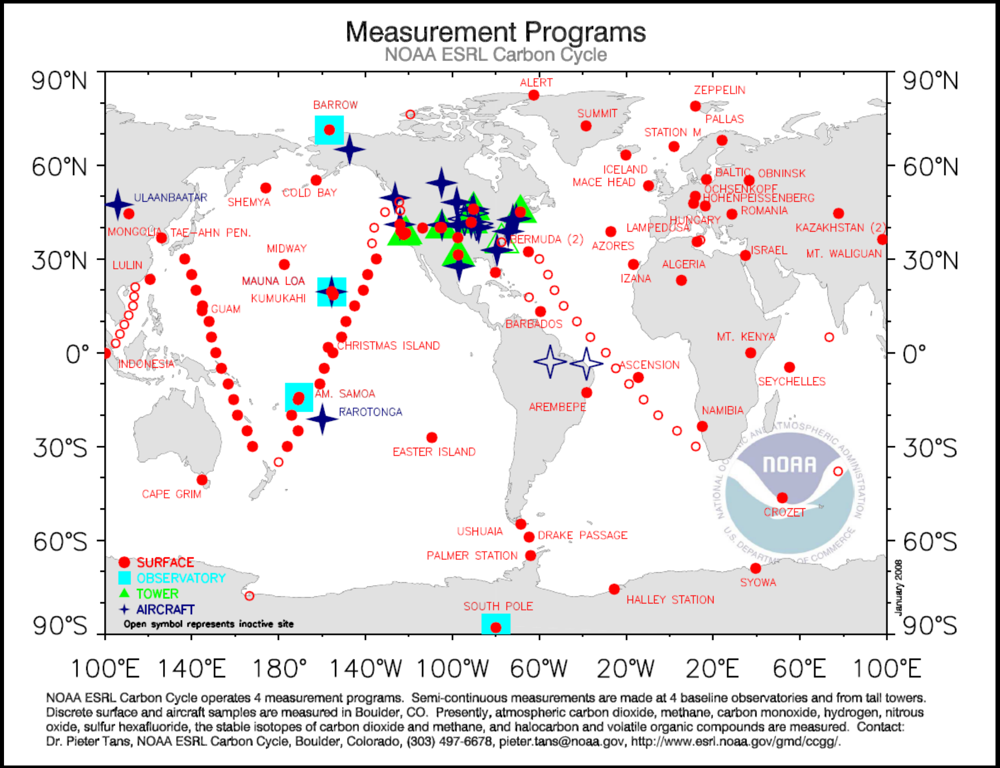
- During daytime (when photosynthesis takes place), the stomata of most plants are open so that atmospheric CO_2 can diffuses into the plant cells' chloroplasts
- Here an isotope exchange reaction takes place between oxygen in CO_2 and H_2O
- Diffusion of ^{18}O ^{12}C ^{16}O back out of the leaf enriches 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 CO_2 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 CO_2 isotopologues composition is based on these measurements

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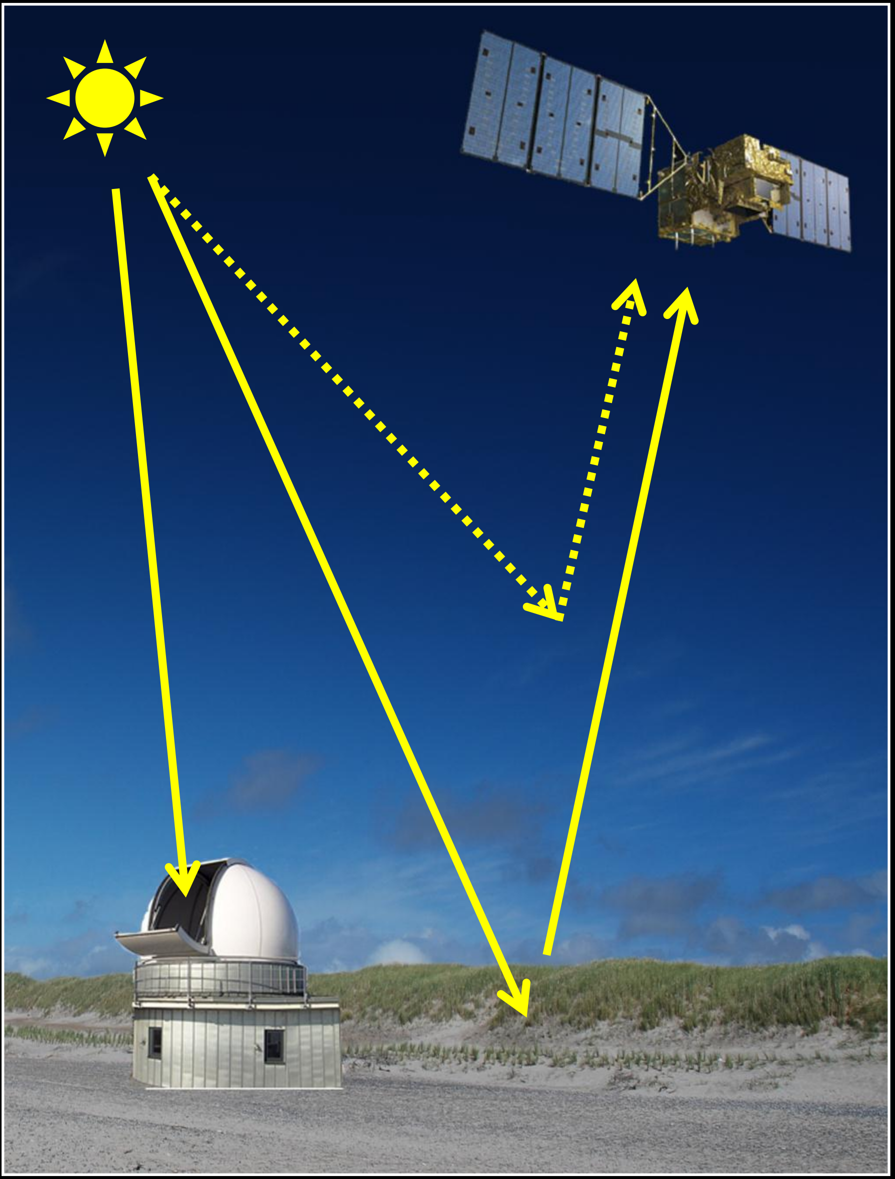
GOSAT and ground-based FTS light-paths

- 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

$$\delta^{13}C = \left(\frac{\left(\frac{^{16}O\ ^{13}C\ ^{16}O}{^{16}O\ ^{12}C\ ^{16}O} \right)_{sample}}{\left(\frac{^{16}O\ ^{13}C\ ^{16}O}{^{16}O\ ^{12}C\ ^{16}O} \right)_{standard}} - 1 \right) 1000‰$$

measurement

- 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

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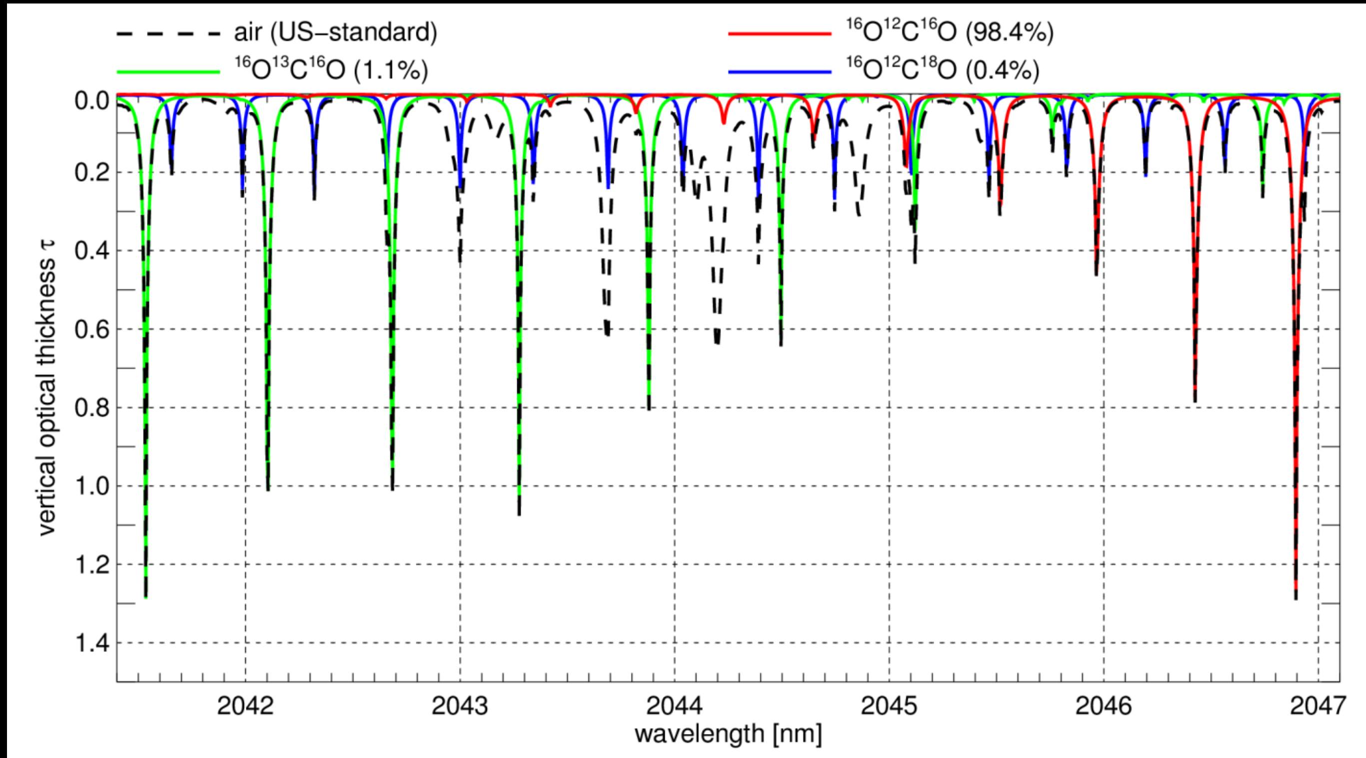
M. Reuter et al.

DOAS = Differential Optical Absorption Spectroscopy



- Due to their different masses, CO_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

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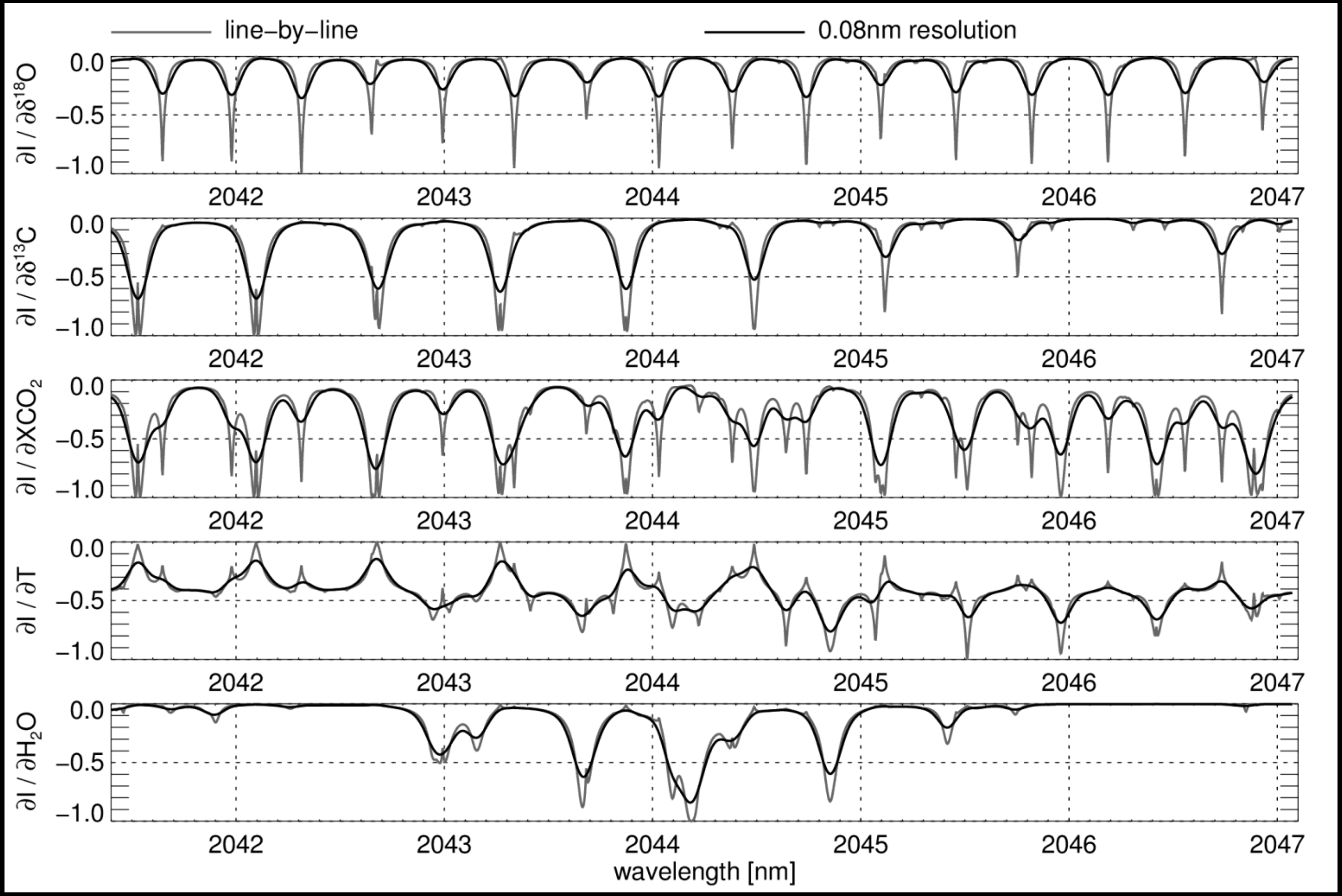
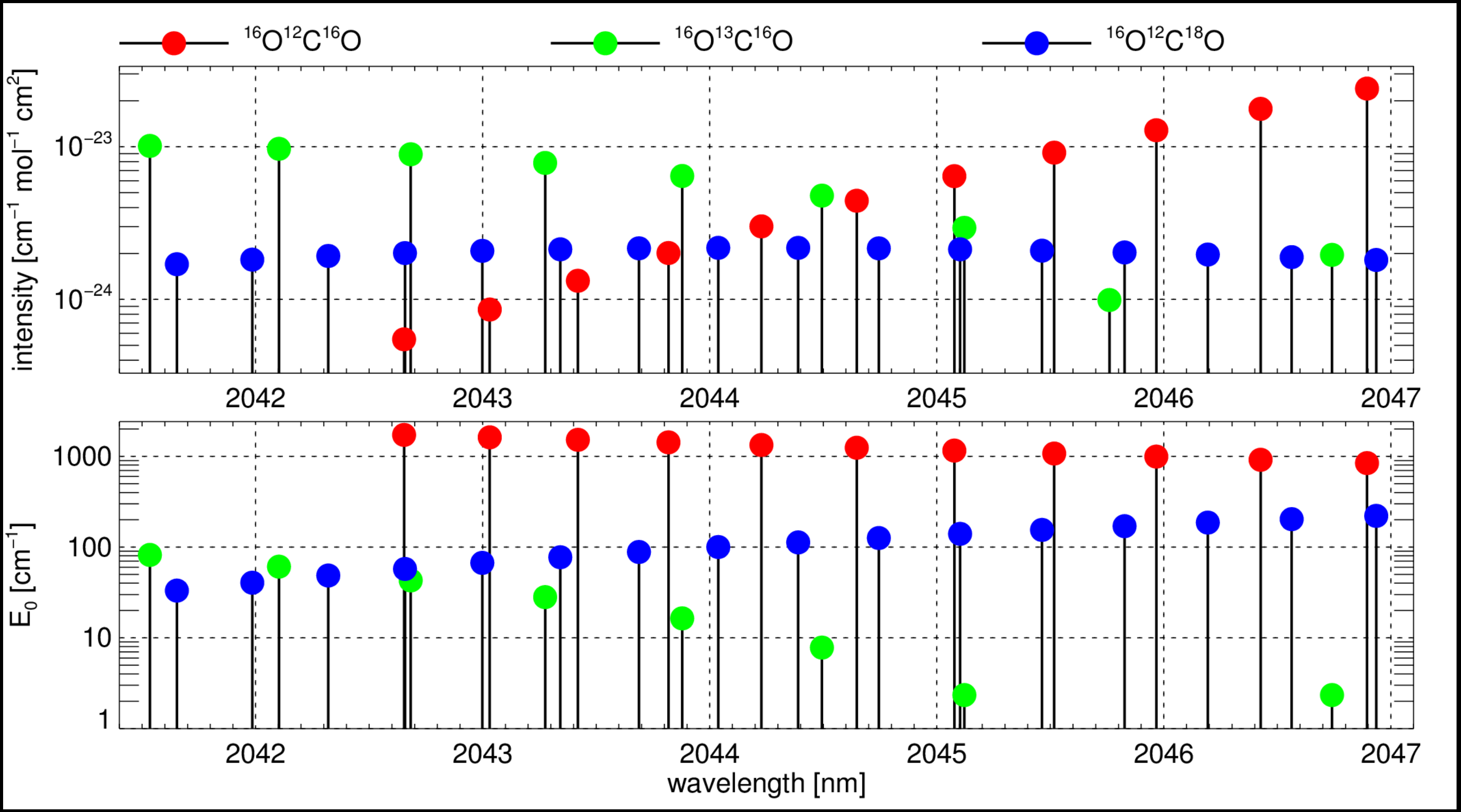
Fit window 2042nm – 2047nm



- An optimal estimation framework "adjusts" the input of an radiative transfer simulation to fit measured with simulated absorption spectra
- Uncorrelated Jacobean (how does a fit parameter change the radiance)

Temperature Sensitivity



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

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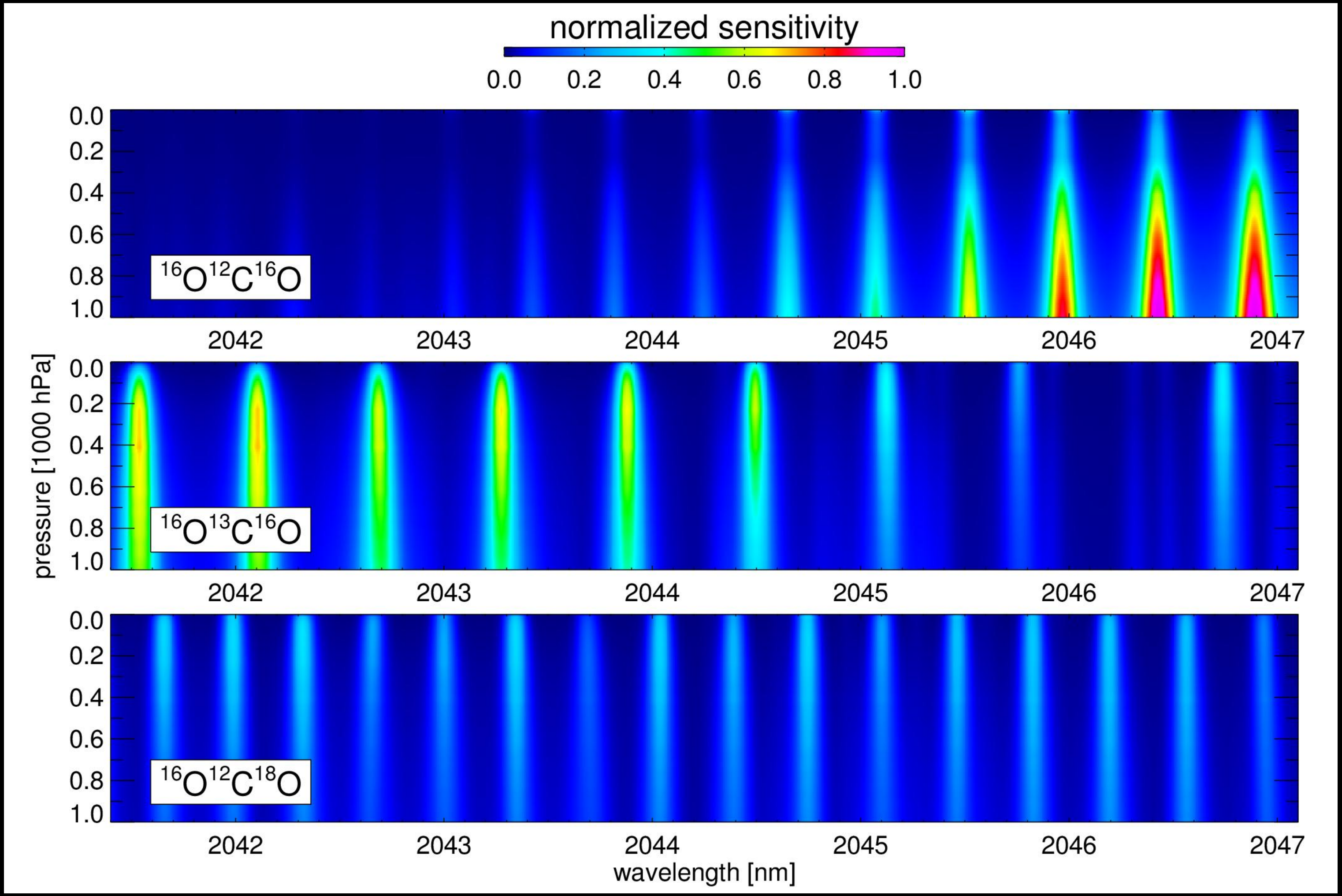
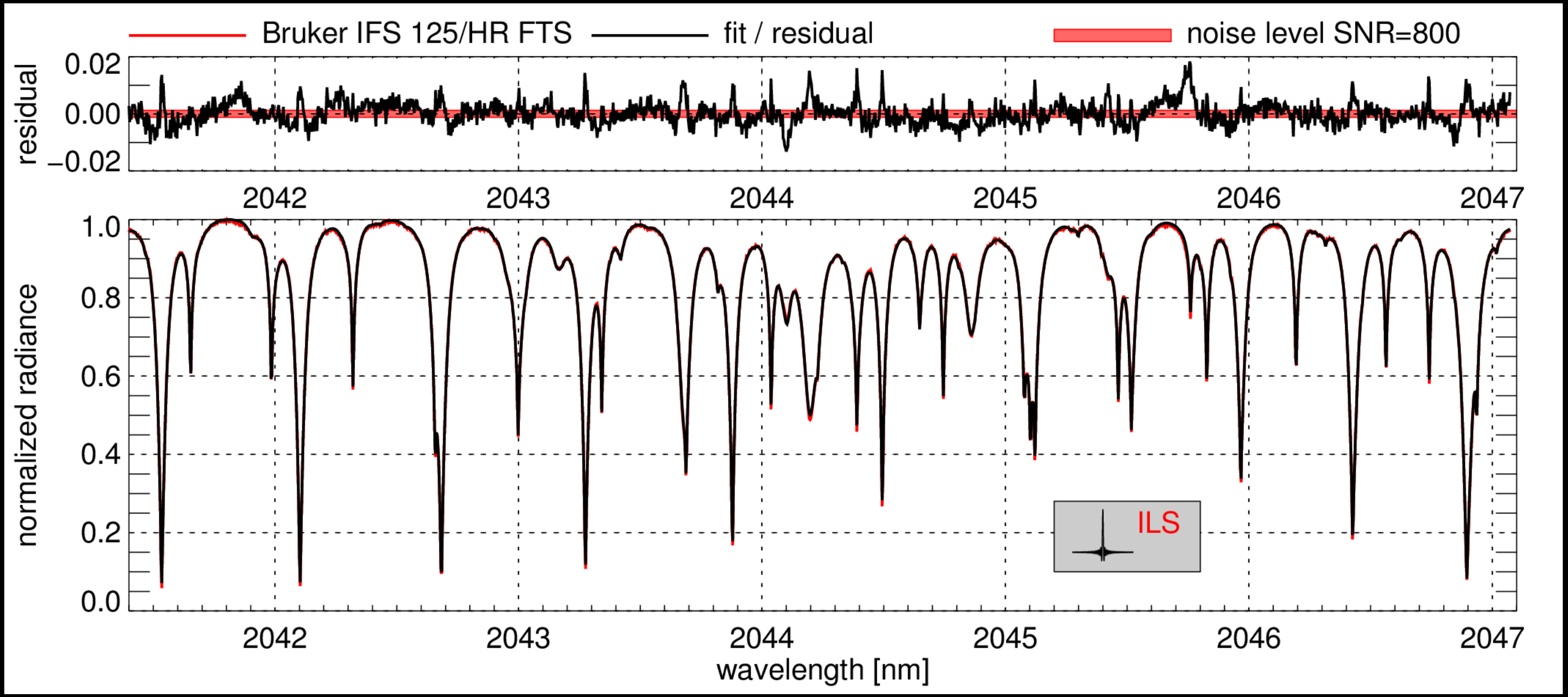
Temperature Sensitivity



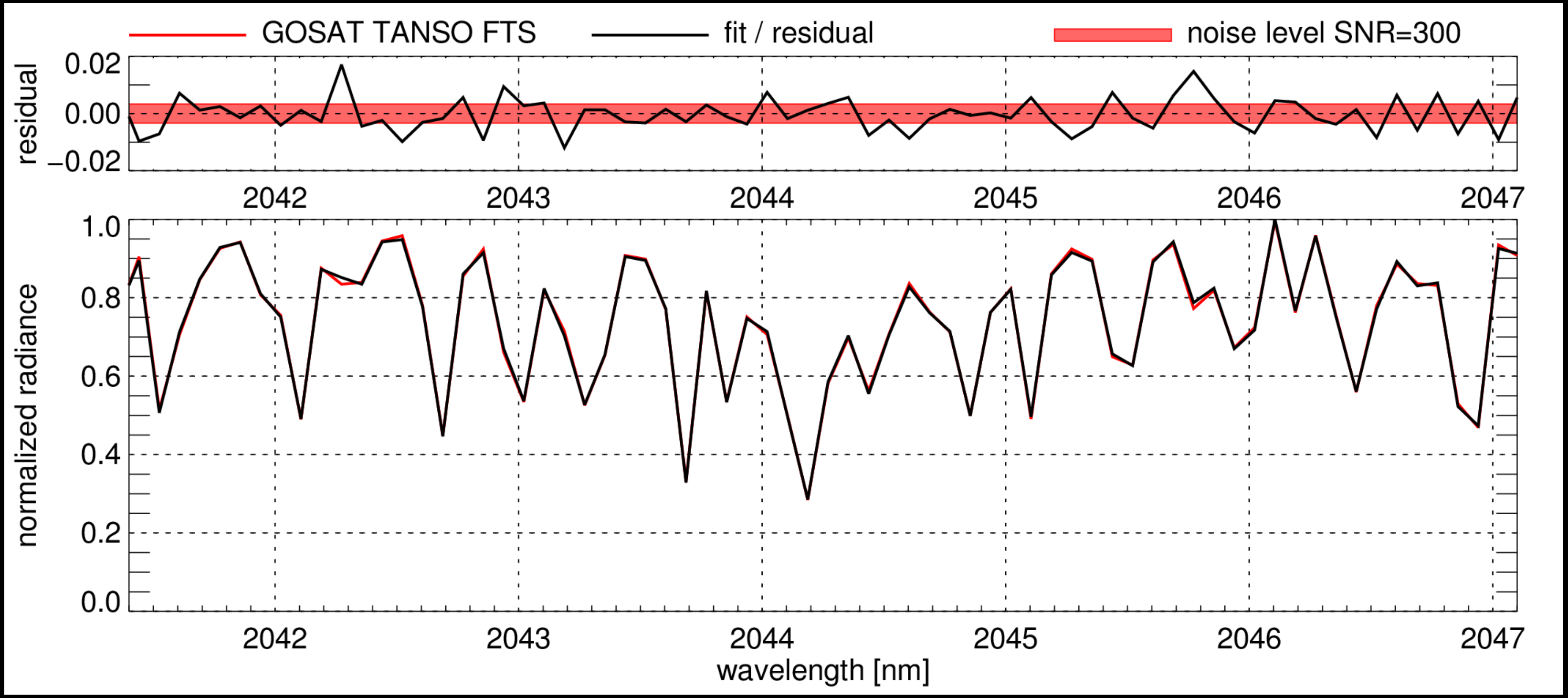
Simulations show that this can result in potential inaccuracies esp. in satellite viewing geometry where light paths are more uncertain

Ground-based FTS, Orleans, France, 18.10.2009



- High resolution ~0.006nm (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!