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CO_2 spectroscopy in 4A/OP: new developments and applications to satellite missions

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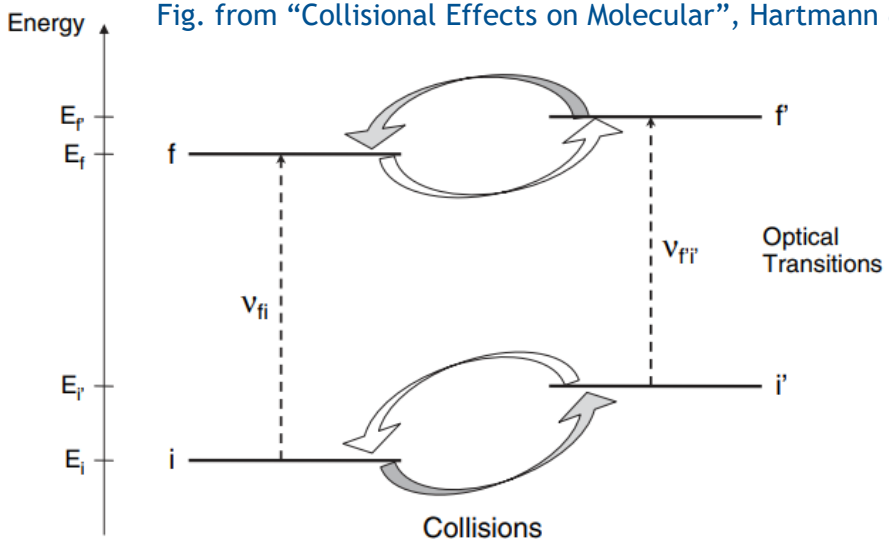
CO_2 spectroscopy and line-mixing

- During the past decades, substantial efforts have been made to monitor CO_2 sources and sinks.
- Several satellite missions have been designed (OCO-2/3, Microcarb) or used (IASI) in order to retrieve its atmospheric concentration, mainly by inversing infrared spectra products using radiative transfer-based algorithms to interpret measured atmospheric absorptions in terms of column-averaged dry-air mole fraction of CO2 (XCO_2).
- This method fundamentally relies on the precision of CO_2 molecular spectroscopy knowledge. In this work, we present a status of the CO_2 spectroscopy, and its implementation and validation in the radiative transfer software 4A/OP.
- A particular attention is devoted to the implementation of line-mixing effects.

- Collisional line mixing (or interference, or coupling) may significantly change the signals in the spectral and time domains when lines cannot be considered as collisionally "isolated", that is when the contributions of the various transitions overlap significantly.
- These collisional processes induce mixing terms and the optical transitions thus cannot be considered as isolated one from the other since population (*i.e.* absorption intensity) is exchanged between them.

Fig. from "Collisional Effects on Molecular", Hartmann *et al.*



Schematic view of the line-mixing process in the case of two optical transitions.

Line-mixing models

- Full relaxation matrix « W » approach

Within several approximations, the complex normalized profile for a binary mixture of radiators "a" and perturbers "p" with densities n_a and n_p ($n_a << n_p$) can be written as:

$$I(\sigma, n_p, T) = \frac{1}{\pi} \frac{\sum_{\ell} \sum_{\ell'} \rho_{\ell}(T) d_{\ell} d_{\ell'} \left\langle \left\langle \ell' \left| \left[\sum - L_a - i n_p W(T) \right]^{-1} \right| \ell \right\rangle \right\rangle}{\sum_{\ell} \rho_{\ell}(T) \times d_{\ell}^2}.$$

Relaxation Matrix

- Sums over all lines l and l' of the radiator (CO_2)
- Off-diagonal elements describe collisional interferences between lines, and the
- Diagonal terms are the pressure-broadening (γ_l, HWHM) and -shifting (δ_l) coefficients

$$\langle\langle \ell | W(T) | \ell \rangle\rangle = \gamma_{\ell}(T) - i\delta_{\ell}(T).$$

- First-order Rozenkranz's « Y » approximation

At sufficiently low densities within the weak overlapping approximation (perturbation theory):

$$I^{1st}(\sigma, n_p, T) = \frac{1}{\pi \sum_{\ell} \rho_{\ell}(T) d_{\ell}^2} \left\{ \sum_{\ell} \frac{\rho_{\ell}(T) d_{\ell}^2}{\sigma - \sigma_{\ell} - n_p \delta_{\ell}(T) - i n_p \gamma_{\ell}(T)} \left[1 + i n_p Y_{\ell}(T) \right] \right\}, \quad \text{with} \quad Y_{\ell}(T) = 2 \sum_{\ell' \neq \ell} \frac{d_{\ell'}}{d_{\ell}} \frac{\langle\langle \ell' | W(T) | \ell \rangle\rangle}{\sigma_{\ell} - \sigma_{\ell'}}.$$

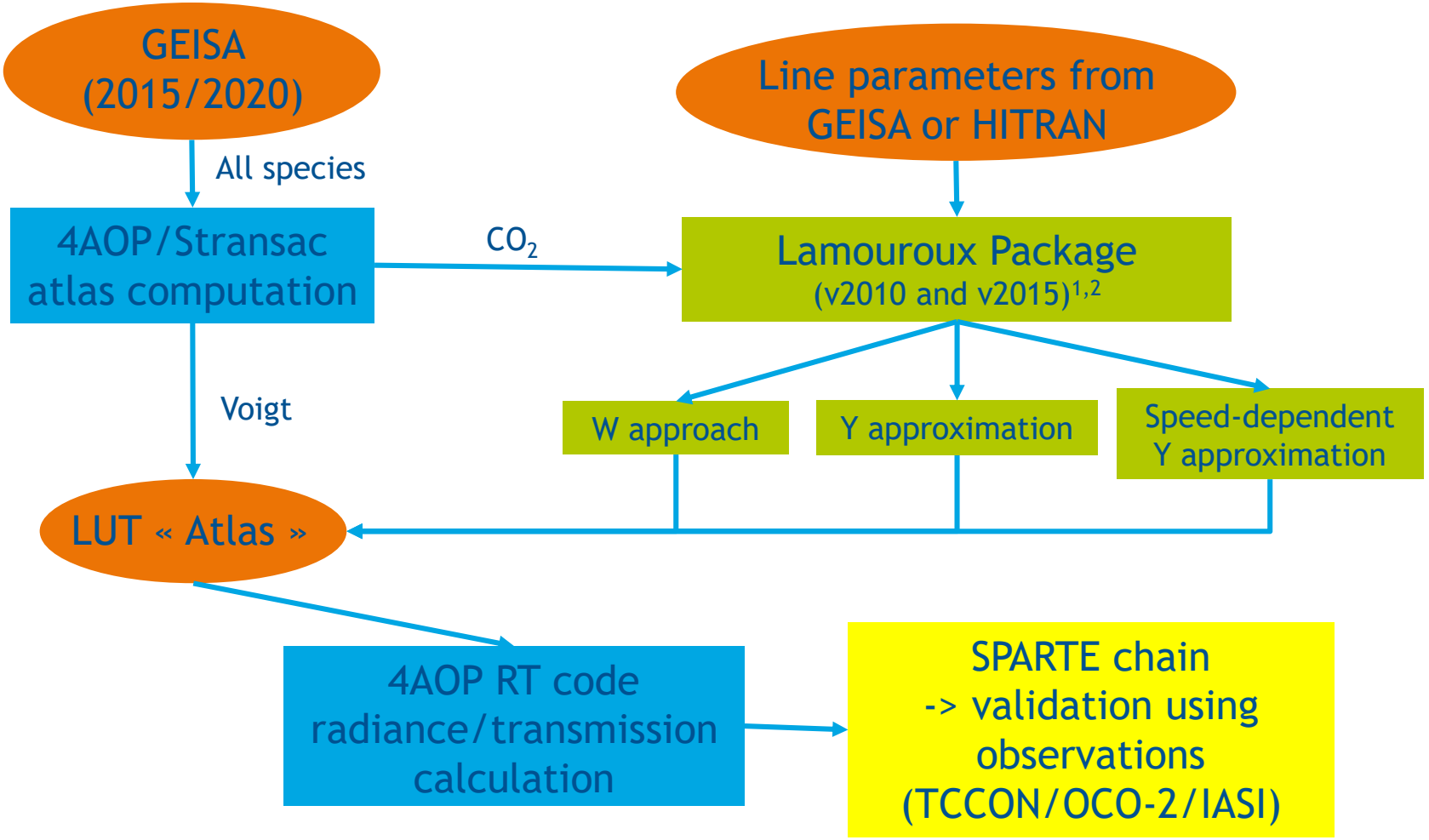
- Line-by-line form: computationally efficient and easy interfacing with molecular databases.
- Can lead to large errors (line overlapping, wings error accumulation,…).

For this reason, a careful study comparing absorption calculated using W and Y approach over a wide spectral range is necessary to precise the cases where Rosenkranz profile can be safely used.

CO_2 models in 4A/OP

- CO_2 line-mixing implementation based on Lamouroux packages (2010/2015), with in-house computational optimization of line profile calculation for radiative transfer applications.

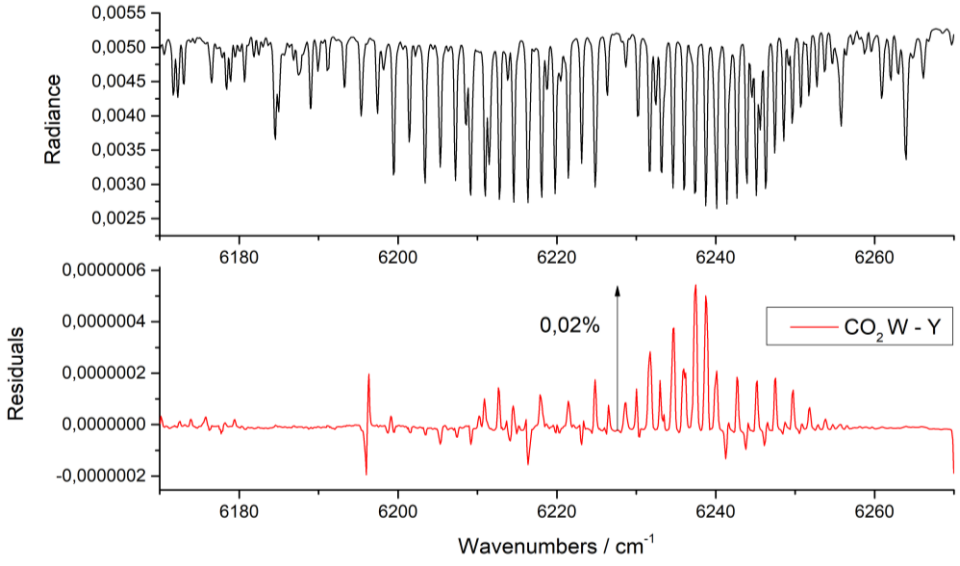
[1] Lamouroux *et al.*, JQSRT 111, DOI:10.1016/j.jqsrt.2010.03.006 ; [2] Lamouroux *et al.*, JQSRT 151, DOI:10.1016/j.jqsrt.2014.09.017



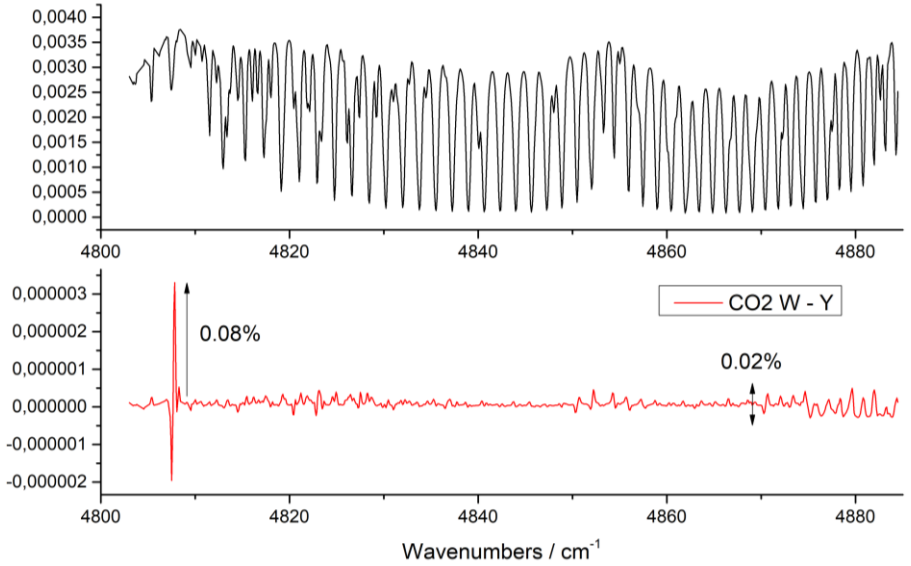
SWIR validations

- Validations of the « Y » approximation in the SWIR region: CO_2 B2/B3 Microcarb bands and "strong"/ "weak" OCO-2 bands
- Comparisons of direct calculations made with 4AOP at high resolution (5^{E-4} cm^{-1}) considering the "W" and "Y" approaches (using W(T) matrix from Lamouroux 2015).

CO_2 « weak » (1.6 µm)



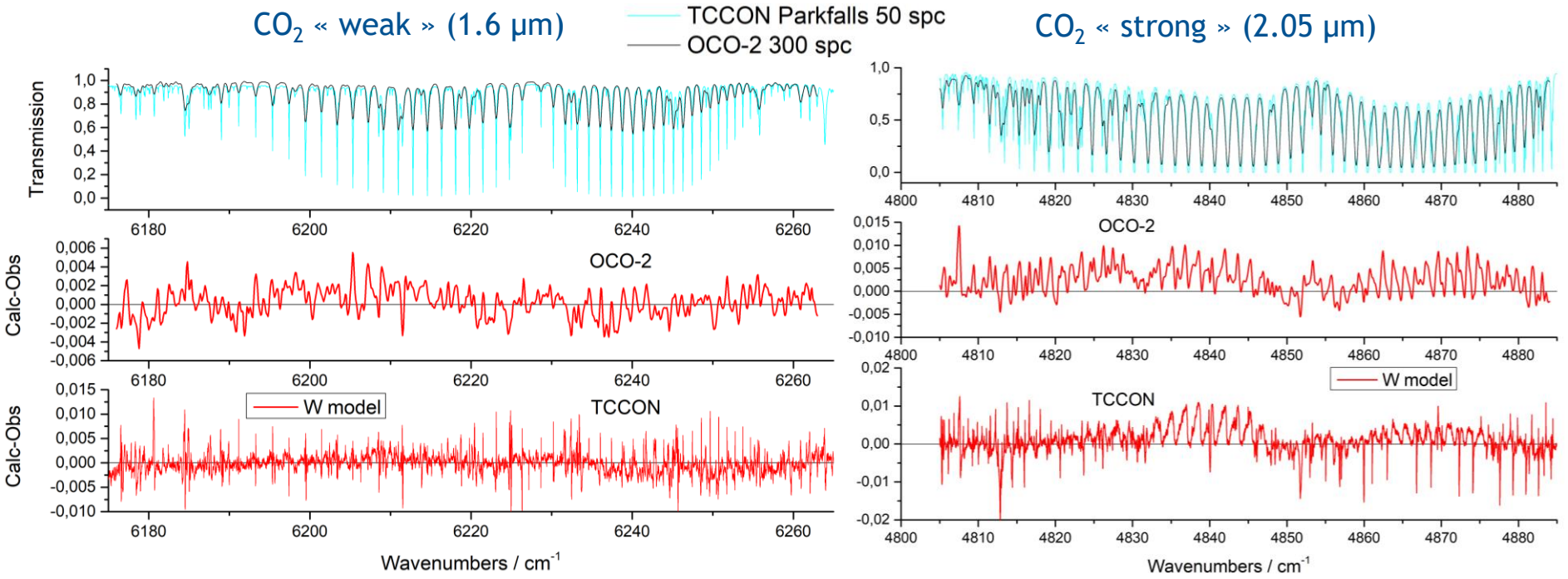
CO_2 « strong » (2.05 µm)



Very low to no impact on the precision using "Y" approach in these bands, but much faster.

TCCON and OCO-2 validations

- SPARTE validation chain is used to compute TCCON and OCO-2 spectra and systematically compare it to observations.
- In addition to “W” and “Y” models derived from Lamouroux W(T) relaxation matrix, the Speed-dependent Voigt profile combined with Y approach is also considered here. Speed-dependent parameters are computed from Lamouroux 2015.



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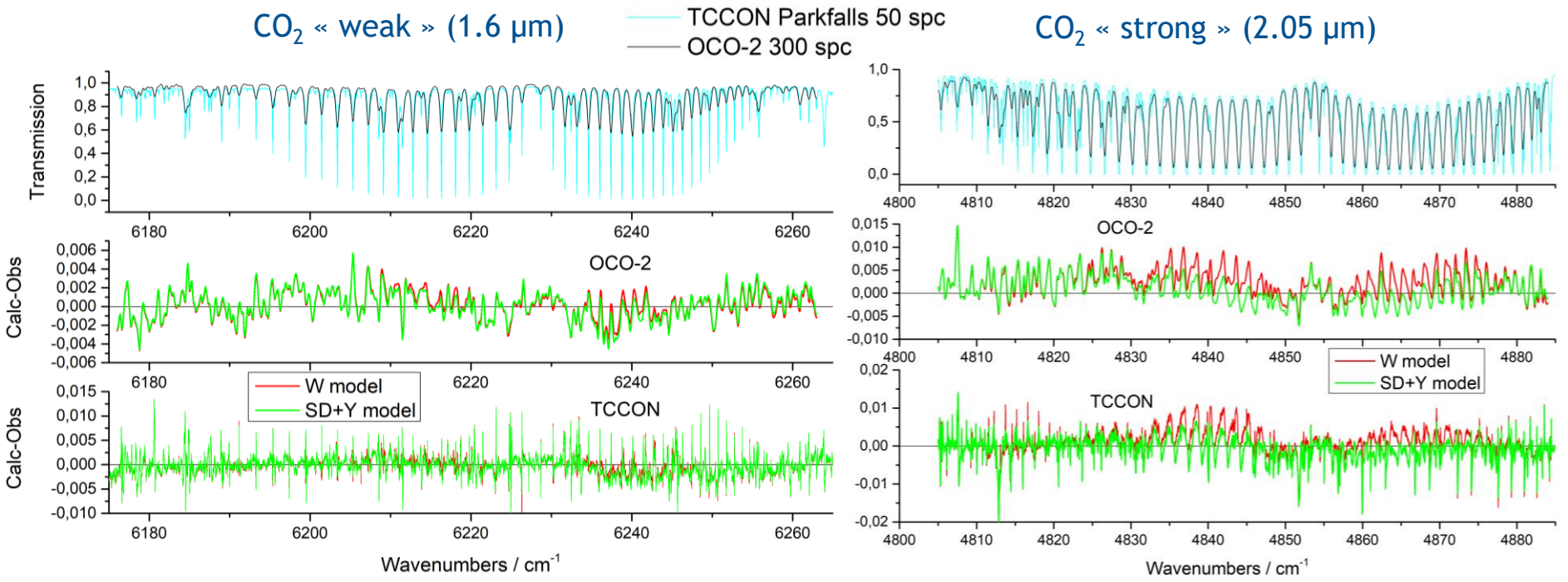
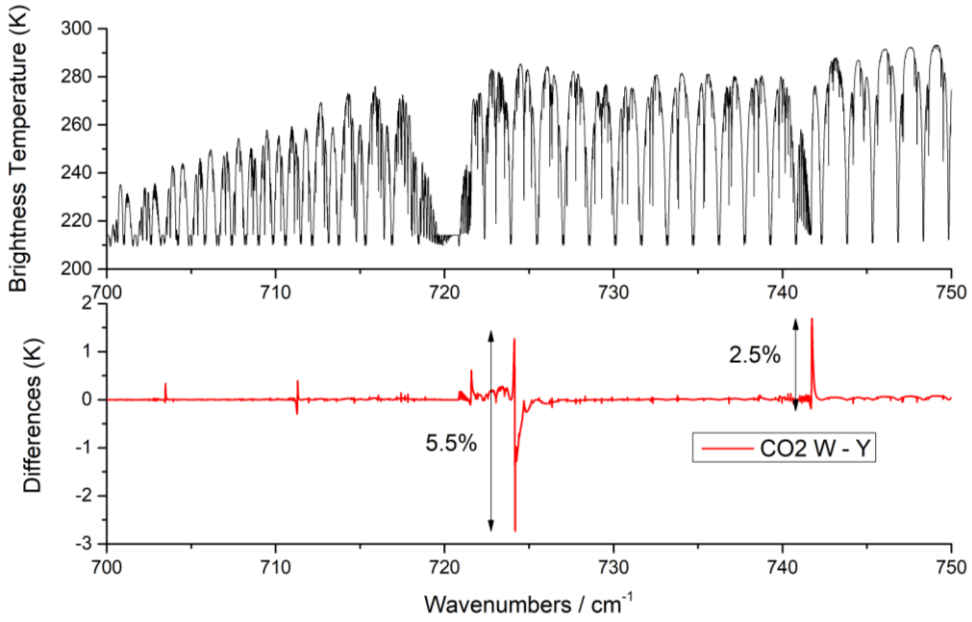
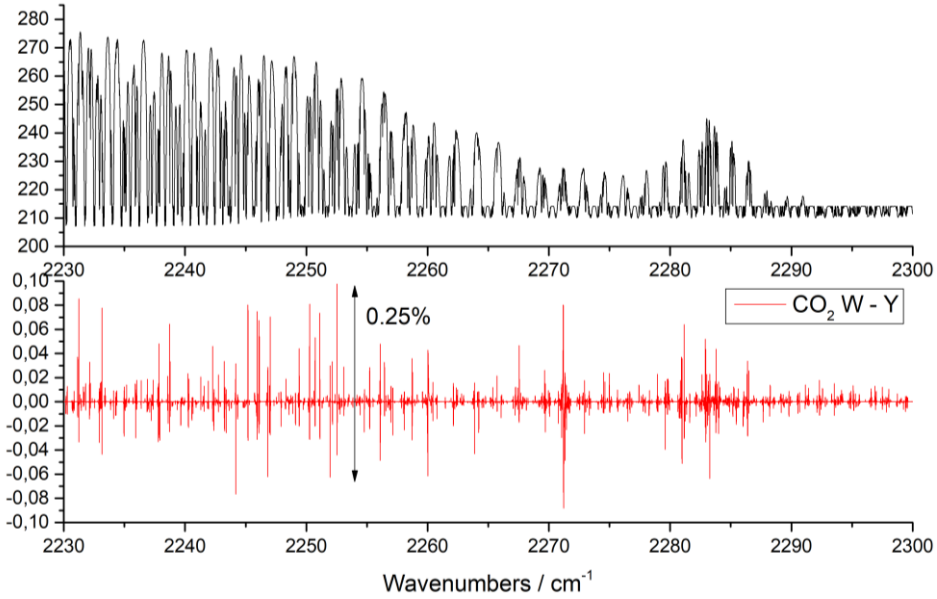
- In addition to “W” and “Y” models derived from Lamouroux W(T) relaxation matrix, the Speed-dependent Voigt profile combined with Y approach is also considered here. Speed-dependent parameters are computed from Lamouroux 2015.
- A fast algorithm, compatible with extensive radiative transfer calculations, was developped to compute speed-dependent profiles -> improved residuals.



TIR validations

- Validations of the “Y” approximation in the TIR region: 14 µm and 4.3 µm bands
- Comparisons of direct calculations made with 4AOP at high resolution (5^{E-4} cm^{-1}) considering the “W” and “Y” approaches (using W(T) matrix from Lamouroux 2015).





High local impact on the precision using “Y” approach in these bands, not recommended in TIR regions

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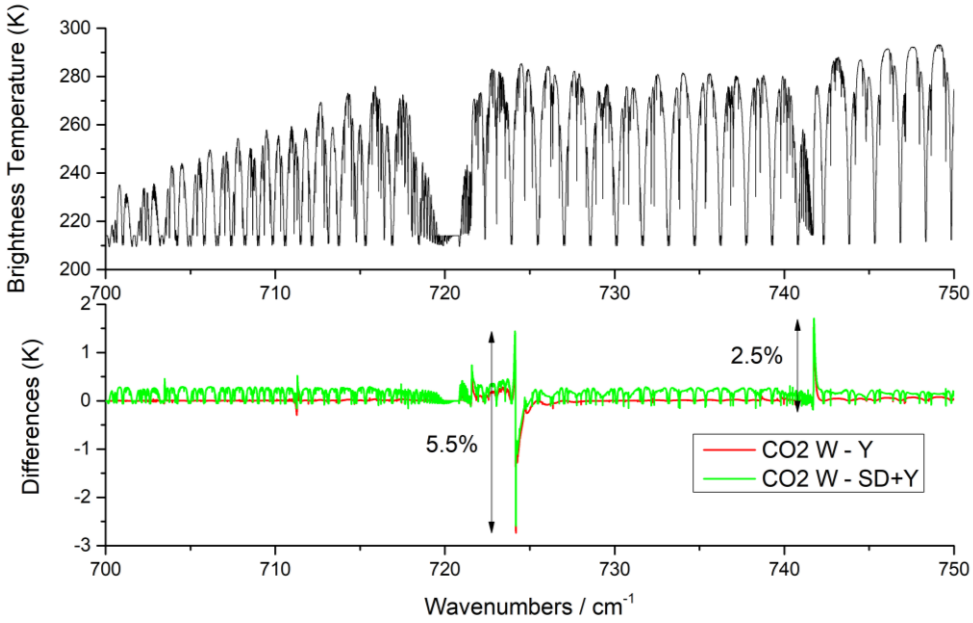

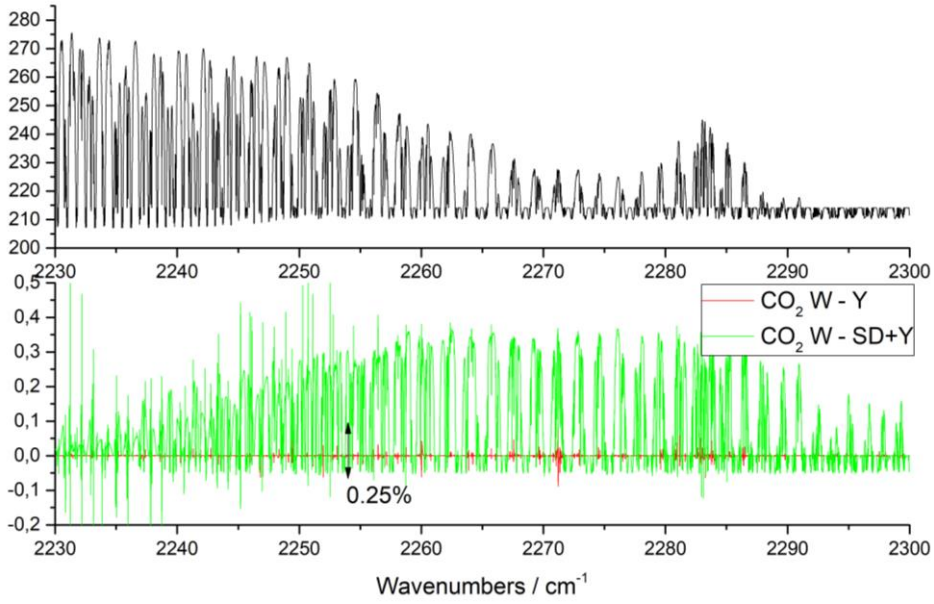

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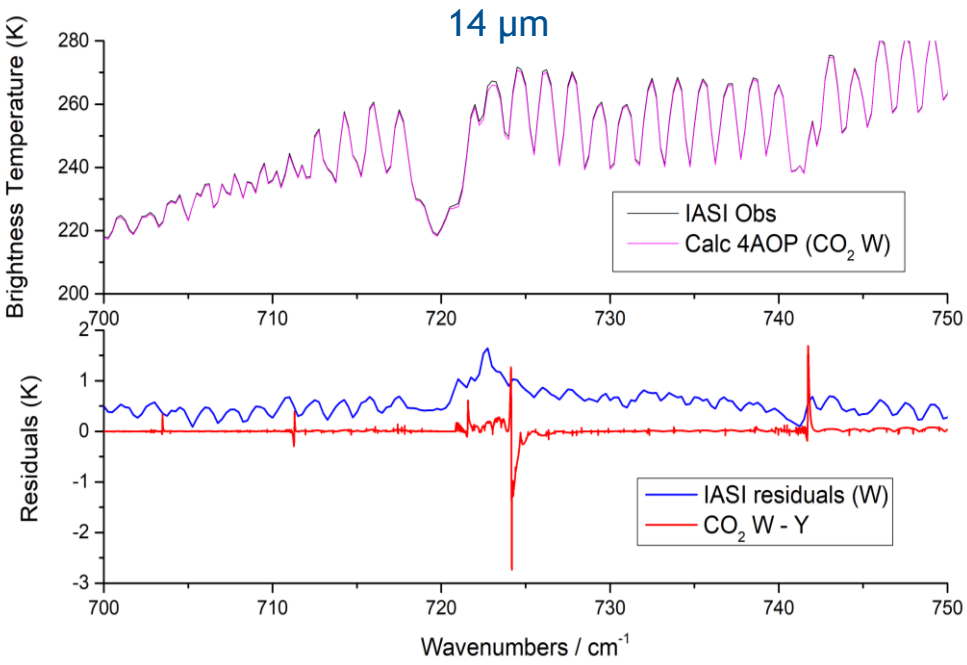
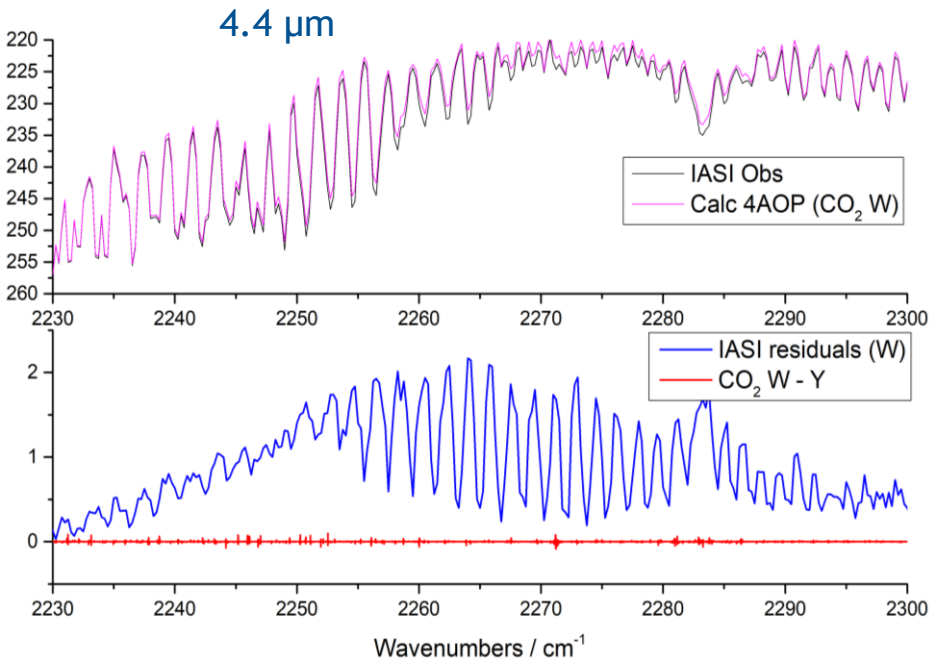
IASI comparisons

- Comparisons of IASI residuals (Calc-Obs with 4AOP) and differences obtained between “W” and “Y” models calculations

tropical, night, sea (IASI 2017, 15300 collocations)





The error made using the “Y” model is not negligible compared to typical IASI residuals at 14 µm but more acceptable at 4.4 µm. Impact of SD+Y at 4.4µm to be investigated.

Line-mixing second-order approximation

- Following the larges errors obtained using the “Y” approximation in the TIR region, the second-order approximation has been implemented in 4AOP to study its impact.
- An approach similar to that leading to the first-order expression can bee used to extend the expansion to second order, leading to the following expression:

$$I^{2nd}(\sigma, n_p, T) = \frac{1}{\pi \sum_\ell \rho_\ell(T) d_\ell^2} \sum_\ell \frac{\rho_\ell(T) d_\ell^2 [1 + i n_p Y_\ell(T) + n_p^2 g_\ell(T)]}{\sigma - \sigma_\ell - n_p \delta_\ell(T) - i n_p \gamma_\ell(T) + n_p^2 \delta\nu_\ell(T)},$$

- where the second-order line-mixing parameters are given by:

« divergent » square terms

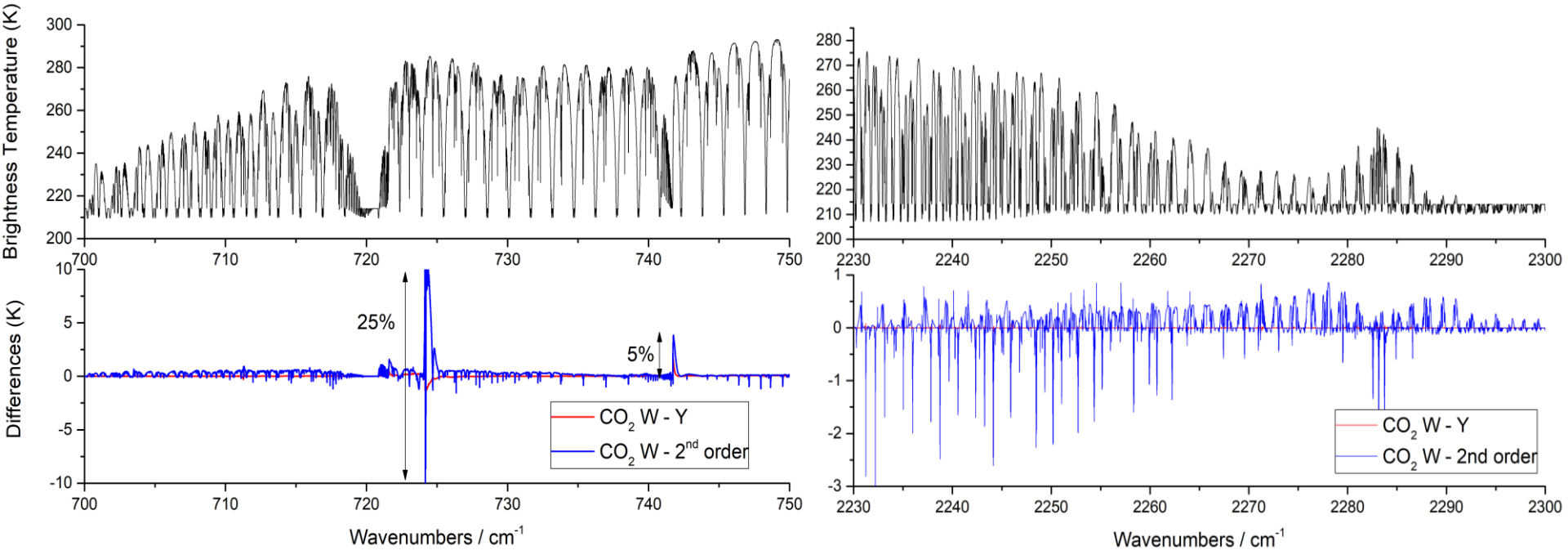
$$\delta\nu_\ell(T) = \sum_{\ell' \neq \ell} \frac{\langle\langle \ell' | W | \ell \rangle\rangle \langle\langle \ell | W | \ell' \rangle\rangle}{\sigma_{\ell'} - \sigma_\ell},$$

$$g_\ell(T) = \sum_{\ell' \neq \ell} \frac{\langle\langle \ell' | W | \ell \rangle\rangle \langle\langle \ell | W | \ell' \rangle\rangle}{(\sigma_\ell - \sigma_{\ell'})^2} - \left[\sum_{\ell' \neq \ell} \frac{d_{\ell'}}{d_\ell} \frac{\langle\langle \ell' | W | \ell \rangle\rangle}{\sigma_{\ell'} - \sigma_\ell} \right]^2 + 2 \sum_{\ell' \neq \ell} \frac{d_{\ell'}}{d_\ell} \frac{\langle\langle \ell' | W | \ell \rangle\rangle \langle\langle \ell | W | \ell \rangle\rangle}{(\sigma_\ell - \sigma_{\ell'})^2} - 2 \sum_{\substack{\ell' \neq \ell \\ \ell'' \neq \ell}} \frac{d_{\ell'}}{d_\ell} \frac{\langle\langle \ell' | W | \ell'' \rangle\rangle \langle\langle \ell'' | W | \ell \rangle\rangle}{(\sigma_\ell - \sigma_{\ell'})(\sigma_\ell - \sigma_{\ell''})}.$$

- It is generally assumed that significantly more accurate results can be obtained than when a first-order approximation is used, but generally in a very limited pressure range only (low but non negligible densities).
- At higher densities, very large errors can result from the second-order terms which rapidly increase with pressure.
- The interest of the second-order approach is not clear and is much less hazardous than the use of W/Y approaches. (*cf.* Rodrigues *et al.*, JQSRT 61, 1999)

Second-order impact on TIR regions

- Comparisons of direct calculations made with 4AOP at high resolution (5^{E-4} cm^{-1}) considering the "W", "Y" and second order approaches (using W(T) matrix from Lamouroux 2015).

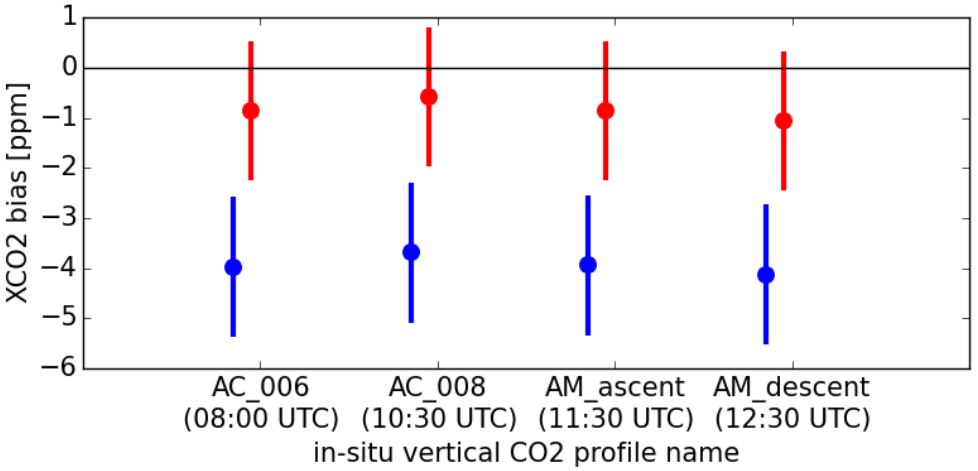


Very large deviations using the second-order approach compared to "W", not recommended in TIR regions.

Perspectives

- Impact of spectroscopy on OCO-2 inversions done by M. Dogniaux (LMD)
  - **5AI inverse scheme**[1] based on **Optimal Estimation**, relies on 4A/OP and GEISA.
  - The impact of XCO_2 retrieved with Lamouroux 2015 Speed-Dependent Y line mixing model (“**new spectro**”) against data from Lamouroux 2010 (W approach, “**old spectro**”) is studied.
- Next steps:
  - Updating the line-mixing models with GEISA-2020 data.
  - Impact of speed-dependent profiles on other molecules (e.g. H_2O, Birk).

XCO_2 retrieved from **OCO-2 against four MAGIC 2019 in-situ vertical CO_2 profiles**, acquired on the 13th of June, 2019.



- Unification of the CO_2 line-mixing package to other molecules packages (O_2, CH_4…).
- Tabulation of « Y » parameters to speedup the calculations by line-by-line RT codes. Implémentation dans GEISA.

Conclusion

- A **full line-mixing package** has been implemented in 4AOP and soon distributable.
- Several models can be considered: **"W", 1st order "Y", 2nd order** (not recommended), but also **speed-dependent profiles along with 1st order approach**.
- Validations were made in the TIR and SWIR regions on several instruments (IASI, TCCON, OCO-2).

➢ From these validations **we recommend the use of the "W" approach in TIR regions**, 1st and 2nd order resulting in several large residuals.

➢ In the **SWIR regions**, the use of **"Y" approach** results in **very limited loss of precision** but much **faster calculation**. It also enable the consideration of speed-dependent line-shapes.

➢ Residuals using speed-dependent "Y" model were improved with respect to "W"/ "Y" one in 1.6 and 2.05µm bands of OCO-2 (impact at 4.4µm to be investigated).

➢ "W" approach still is the reference for line-mixing applications, special attention is needed for the consideration of "Y" approximation, but it enables an easy implementation of speed-dependence.

- A **newly developped fast and efficient algorithm** enable the **computation of speed-dependent** profiles in radiative transfer codes. It will be soon distributed and extended for the efficient computation of **HTP profiles**.