→ ATMOS 2015

Advances in Atmospheric Science and Applications

Spectroscopic database for TROPOMI/Sentinel-5 Precursor

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European Space Agency

ESA project „SEOM-Improved Atmospheric Spectroscopy Databases" (IAS)

Goals:

- **Improve spectroscopic database of CH_4, H_2O and CO in 2.3 µm region for TROPOMI**
  - **data products CH_4 column (<2%), CO column (<15%)**
- **Resolve discrepancy of O_3 spectroscopy in UV/MIR region**
- **Improve spectroscopic database of SO_2 in the UV**

- **First two years: 2.3 µm spectroscopy (Kick-off Feb 2014)**
- **Project sequence: Literature study, user requirements, measurement plan, measurements, analysis, validation**
- **Spectroscopy of H_2O, CH_4, CO needed**
  - **Goal: max. 30% error contribution from spectroscopy**
- **Measurements by two different techniques: FTS + CRDS**

- O_3 and SO_2 covered in third year

Retrieval simulations

- User requirements needed retrieval simulations
- Concept and implementation
  - Synthetic TROPOMI spectrum with distorted spectroscopic parameters
  - Atmosphere: AFGL tropical, 6 layers, NADIR, airmass factor 3, no scattering
  - Distortion amount is arbitrary since sensitivity=Δcolumn/Δspec_par is determined – linearity provided
  - Fit of H_2O, CH_4, CO column amounts using undistorted parameters
  - Spectroscopy: HITRAN 2012
  - Line model in fit: Voigt
  - Instrumental line shape: Gauss 0.25 nm FWHM
  - Uncorrelated errors: Monte Carlo runs with Gaussian error distribution for parameter of interest
  - Correlated errors: Change of parameter for specified intensity range by same amount/fraction

Retrieval simulations

Spectroscopic parameters investigated

Parameter	Symbol	CH_4	H_2O	CO
Line position	σ	X	X	X
Line intensity	S	X	X	X
Air broadening	γ_{air}	X	X	X
Air broadening temperature exponent	n	X	X	X
H_2O broadening	γ_{H2O}	X	X	
Air pressure-induced line shift	δ	X	X	
Speed dependent narrowing air	γ_2	X	X	
Line mixing	Y	X		

Retrieval simulations

Summary of error contributions

Typical uncorrelated spectroscopic errors:

- 10% absorption
- Bruker FTS
- 150 cm MOPD
- Ca. 1 h measurement time
- Total pressure 100 mbar
- Precisions:
  σ: 6e-5 cm^{-1}
  S: 0.7%
  γ_{air}: 2%

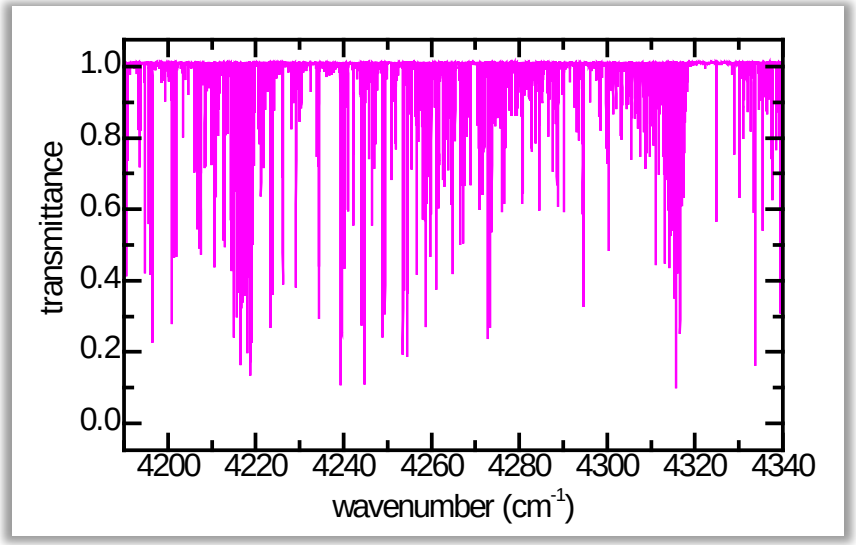
Spectroscopy error	CH4 colum error contribution/%	CO colum error contribution/%
CH4 intensity cutoff	0.07	0.4
CH4 S uncor	0.15	1.2
CH4 γ_{air} cor	0.23	2.0
CH4 γ_{air} uncor	0.06	0.4
CH4 γ_{H2O}	0.05	0.4
CH4 n cor	0.20	0.0
CH4 n uncor	0.04	0.2
CH4 δ cor	0.04	0.2
CH4 SDV	0.05	0.0
CH4 LM	0.10	1.8
H2O intensity cutoff	0.08	0.4
H2O σ cor	0.04	0.0
H2O S uncor	0.17	2.3
H2O γ_{air} cor	0.25	2.4
H2O γ_{air} uncor	0.17	2.0
H2O γ_{H2O} cor	0.13	1.2
H2O γ_{H2O} uncor	0.08	1.0
H2O δ cor	0.16	1.1
H2O SDV	0.03	0.0
CO S uncor	0.00	0.6
RSS:	**0.57**	**5.3**

Measurement plan DLR

Molecule	P_{sample}/ mbar	$p_{air/H2O}$/ mbar	T/K	Abs.path/m	Number of meas.	Target parameters	Comment
CH_4	0.3-50	-	296	8-168	9	σ S γ_{CH4}	ambient T
CH_4	0.1-8	30-1000	296	8-168	24	γ_{air} γ_{2air} δ Y	ambient T
CH_4	0.1-1.6	20	296	8-168	6	γ_{H2O}	ambient T
CH_4	0.1-2	0-1000	190-261	8-168	10	n δ(T) Y(T)	low T
H_2O	0.75-20	-	296	8-168	6	σ S γ_{H2O}	ambient T
H_2O	0.6-20	30-1000	296	59-168	19	γ_{air} γ_{2air} δ	ambient T
H_2O	0.7-20	0-100	253-361	59-168	8	n δ(T)	low/high T
D_2O	0.3-1	-	296	21-168	4	σ S	ambient T
HDO	0.7-2	-	296	21-168	4	σ S	ambient T
CO	0.3-1.5	0-1000	296	8	5	σ S γ_{air}	ambient T

FTS Measurements at DLR

- Bruker IFS 125HR Fourier transform spectrometer
- White-type multireflection cell directly attached to the interferometer
  - absorption path 14.4-206.4 m
  - temperature range 198-360 K
- Gas mixture preparation
- Flow experiments for H_2O



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CH_4	0.1-1.6	20	296	8-168	6	γ_{H2O}	ambient T	
CH_4	0.1-2	0-1000	190-261	8-168	10	n δ(T) Y(T)	low T	
H_2O	0.75-20	-	296	8-168	6	σ S γ_{H2O}	ambient T	✓
H_2O	0.6-20	30-1000	296	59-168	19	γ_{air} γ_{2air} δ	ambient T	✓
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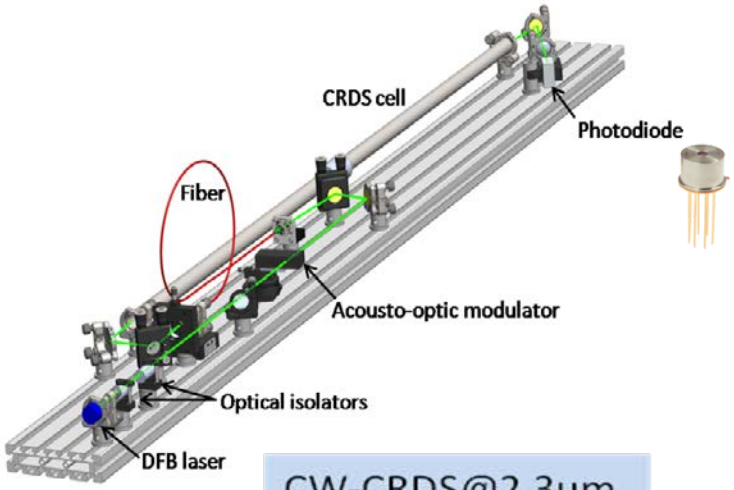
HDO	0.7-2	-	296	21-168	4	σ S	ambient T	
CO	0.3-1.5	0-1000	296	8	5	σ S γ_{air}	ambient T	✓

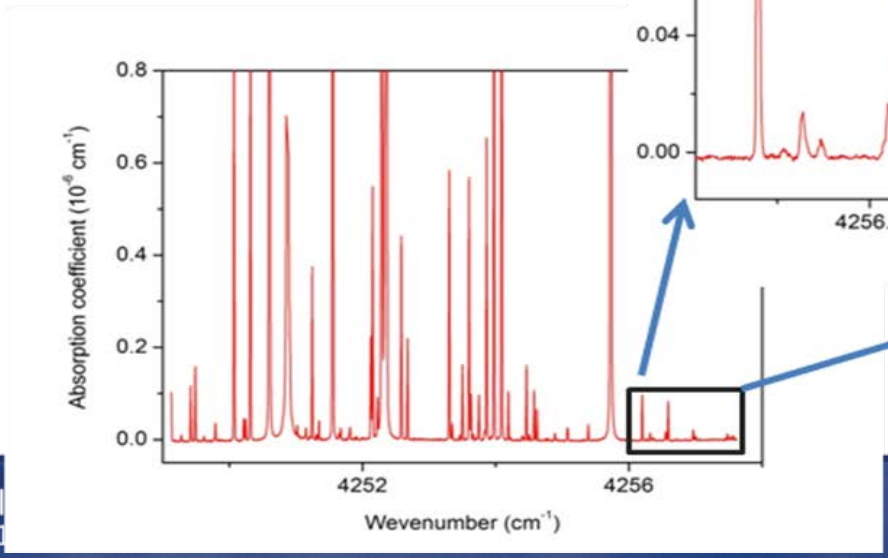
CRDS Measurements at LIPhy

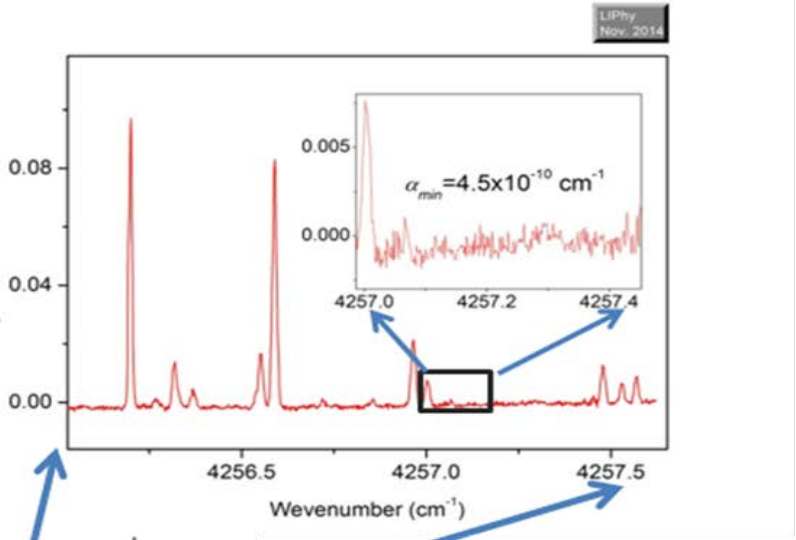


DFB laser based spectrometer

4248 – 4257cm^{-1} (~2.35 µm)

CW-CRDS@2.3µm
Water 1.00 Torr

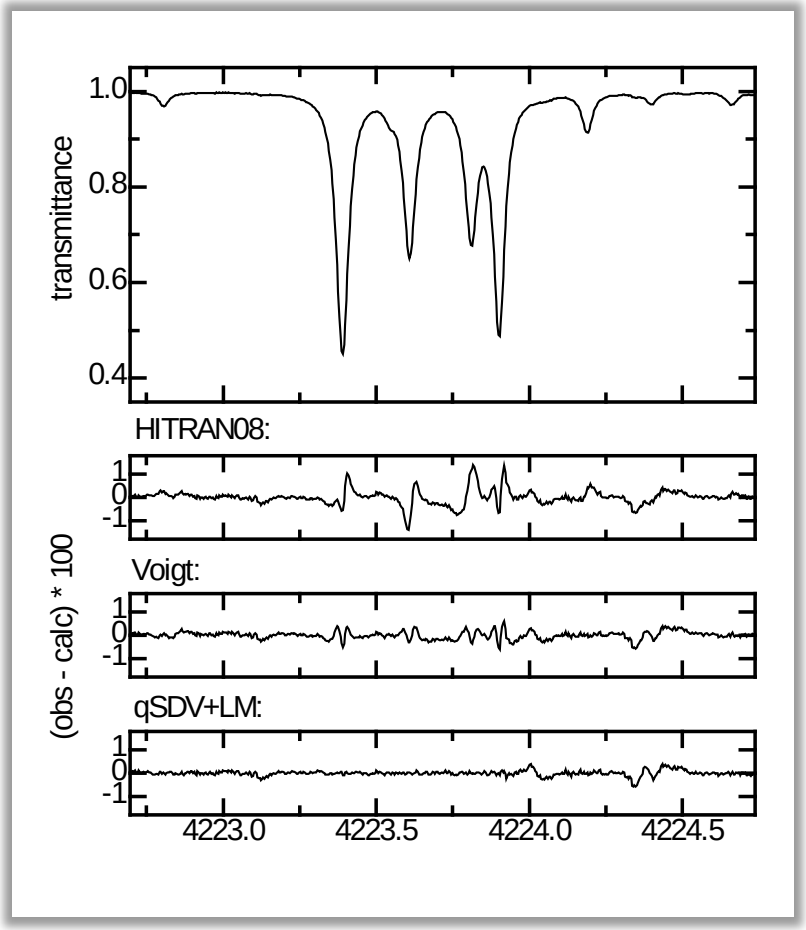




α_{min}~5×10^{-10} cm^{-1}

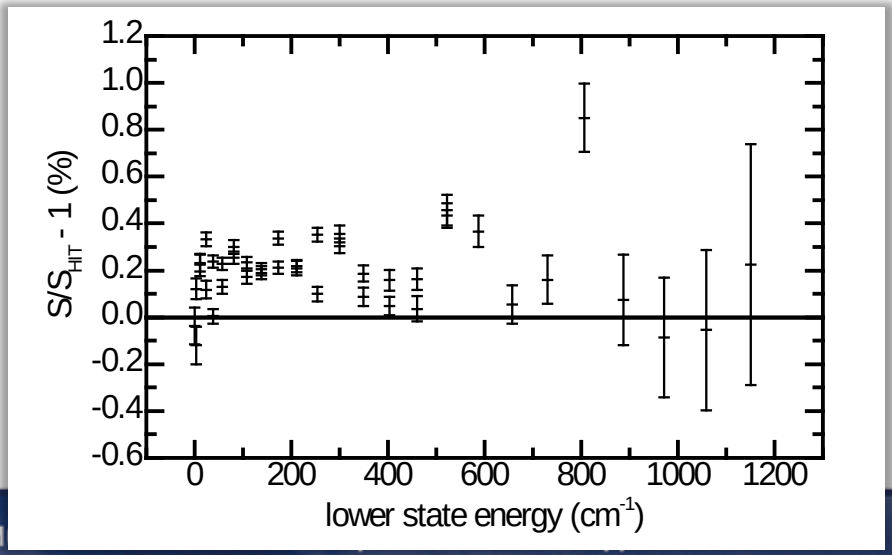
First results – CH_4

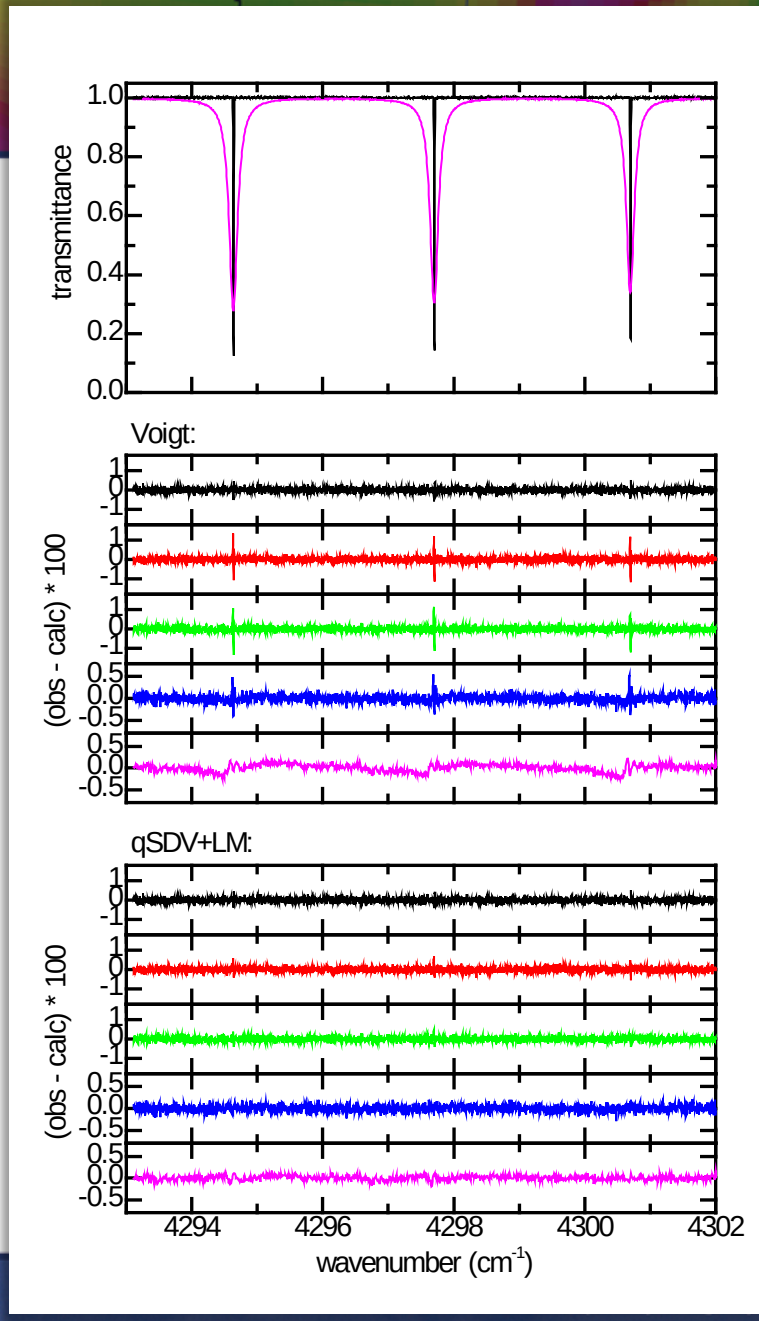
- Single spectrum fits of selection of microwindows of CH_4/air spectra
- Comparison with HITRAN2008 forward calculation gives large residuals
- HITRAN2012 turned out worse than 2008
- Voigt-profile fit
  - W-shaped residuals -> narrowing
  - Asymmetric residuals -> line mixing
- Speed-dependent Voigt + line mixing
  - Residuals significantly reduced
- Missing/misplaced lines in HITRAN
- Multispectrum fit of pure and mixture spectra will be done



First results – CO

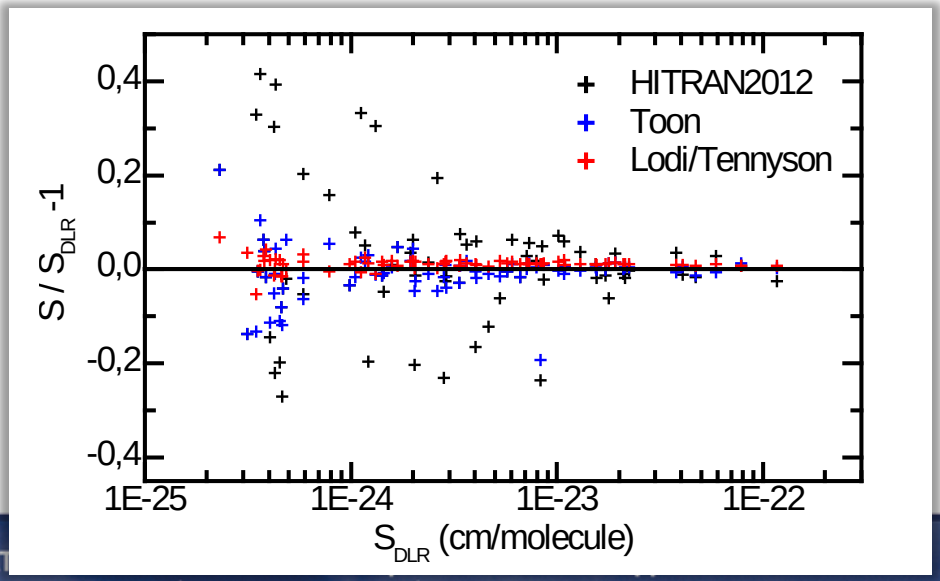
- Multispectrum fit of pure and CO/air spectra
- Voigt-profile
  - W-shaped residuals -> narrowing
  - Asymmetric residuals -> line mixing
- Speed-dependent Voigt + line mixing
  - Fitted almost (Dicke?) to the noise level
- Retrieved intensities in good agreement with HITRAN2012

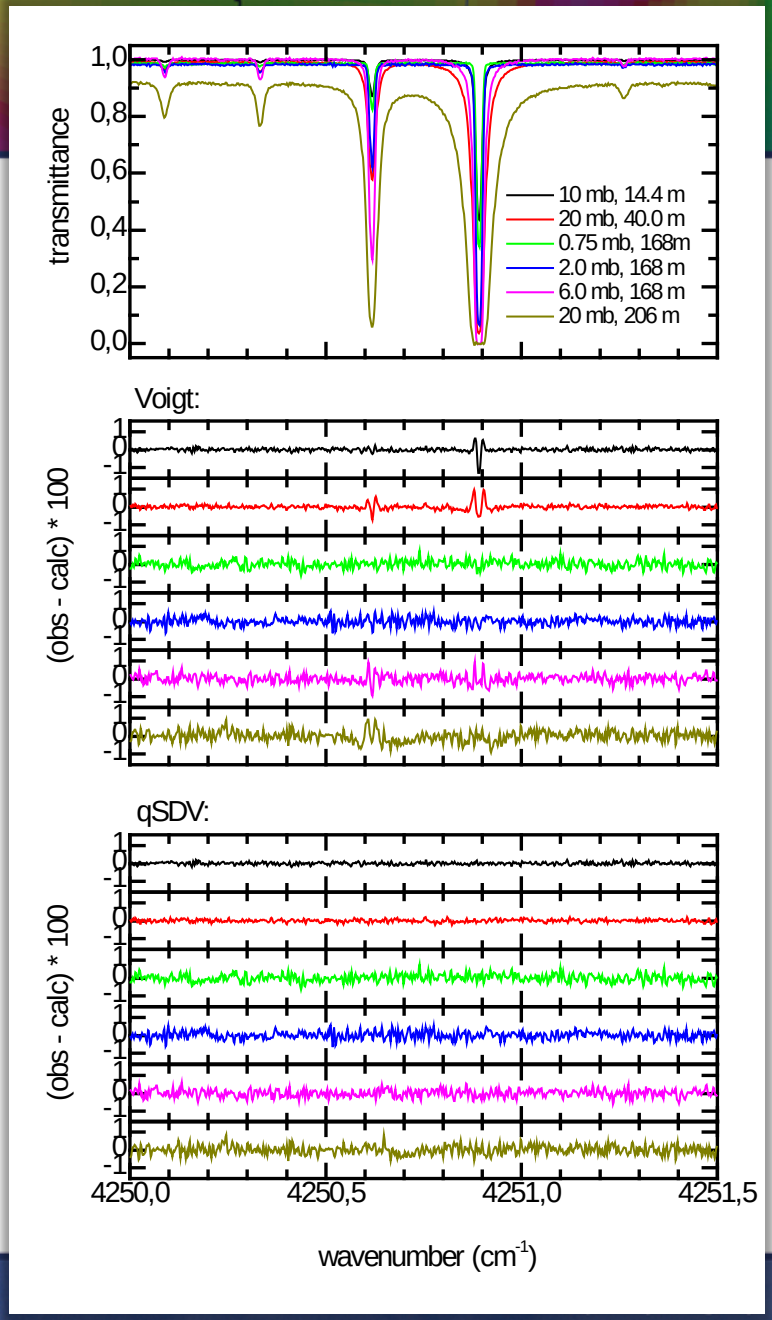




First results – H_2O

- Multispectrum fit of pure H_2O spectra
- Voigt-profile: W-shaped residuals -> narrowing
- Speed-dependent Voigt: Fitted to the noise level
- Intensities:
  - HITRAN show deviations up to 40%
  - Agreement with ab initio values <1.5%
  - Reasonable agreement between FTS and CRDS results





Summary

- Extended retrieval simulations have been carried out to specify the accuracy required for the spectroscopic database
  -> non-Voigt line shapes have to be used
  -> spectroscopy of CH_4, H_2O has to be improved

- Most of the ambient temperature measurements are completed
- CO: collisional narrowing and line mixing visible, intensities agree with HITRAN
- CH_4: line mixing and collisional narrowing has to be accounted for
- H_2O: satisfactory agreement of FTS and CRDS intensity results
- H_2O: major intensity differences to HITRAN, good agreement wiith ab initio

- Remaining measurements will be conducted in the coming months