Spectral shape modeling and spectra analysis for laboratory and atmospheric measurements

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SPECATMOS: Spectroscopy and Atmosphere. Measurements and modeling
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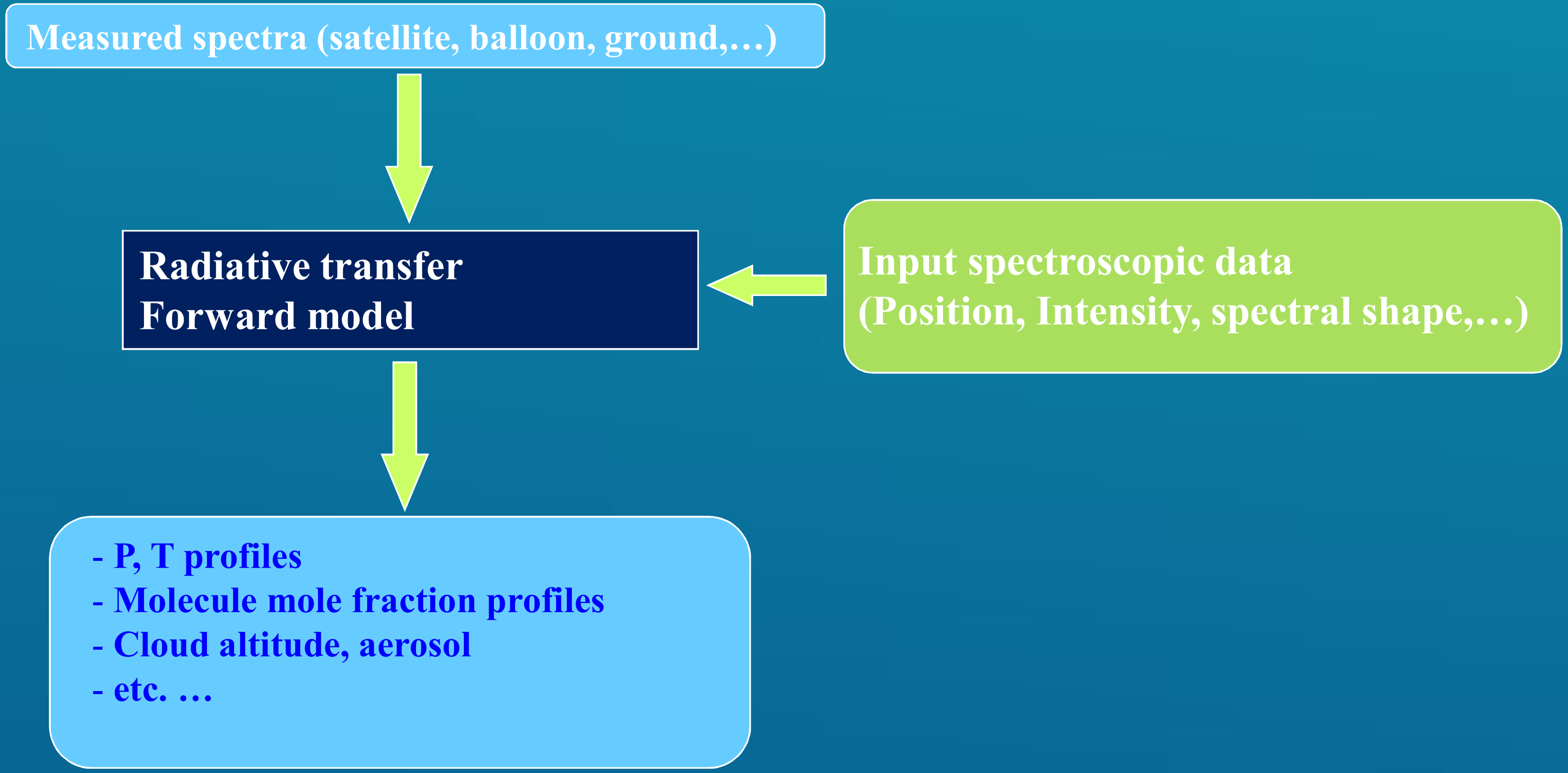
Introduction: Atmospheric retrievals



Measured spectra (satellite, balloon, ground,…)

Radiative transfer
Forward model

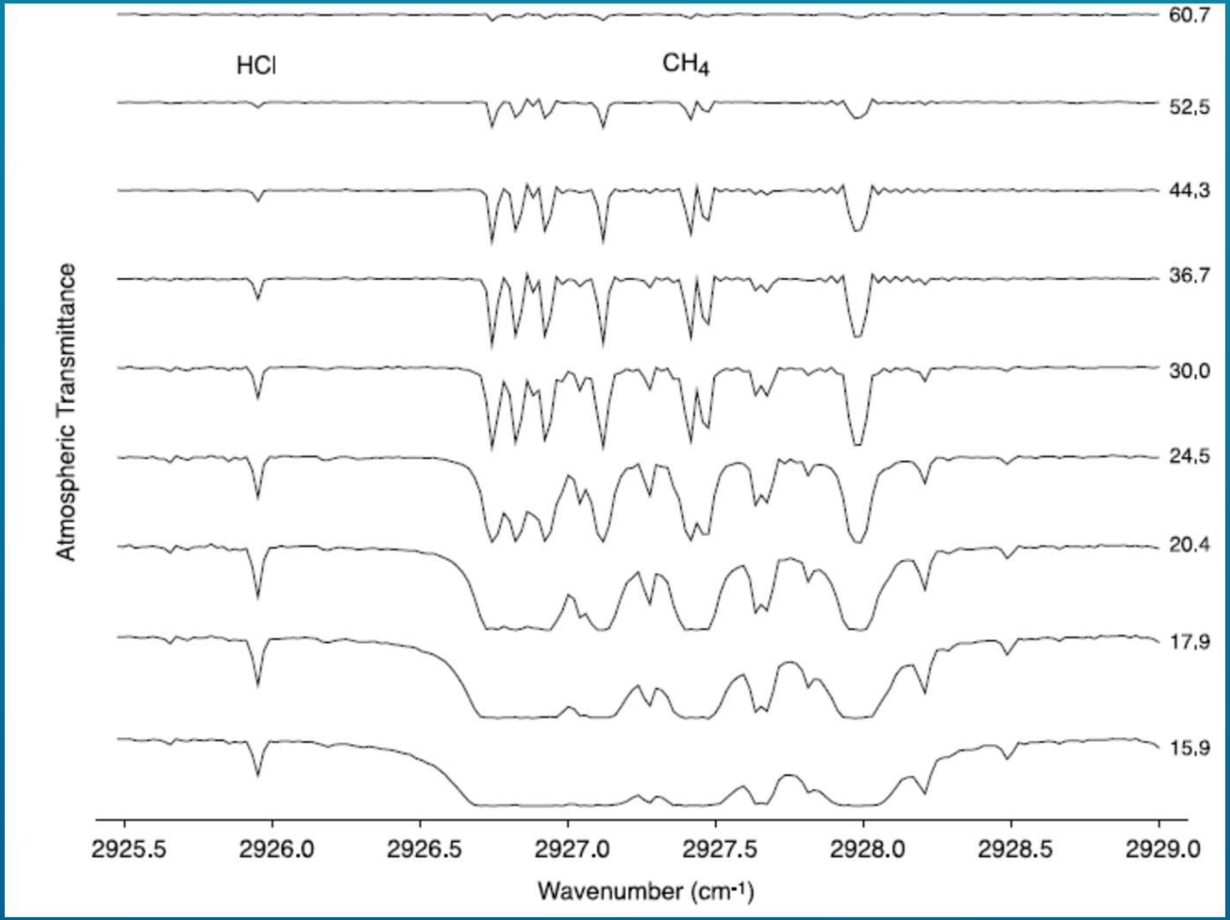
Input spectroscopic data
(Position, Intensity, spectral shape,…)

- P, T profiles
- Molecule mole fraction profiles
- Cloud altitude, aerosol
- etc. …

Spectral shapes → Collisional (pressure) effects on the spectral shape

Introduction: isolated lines and closely spaced lines

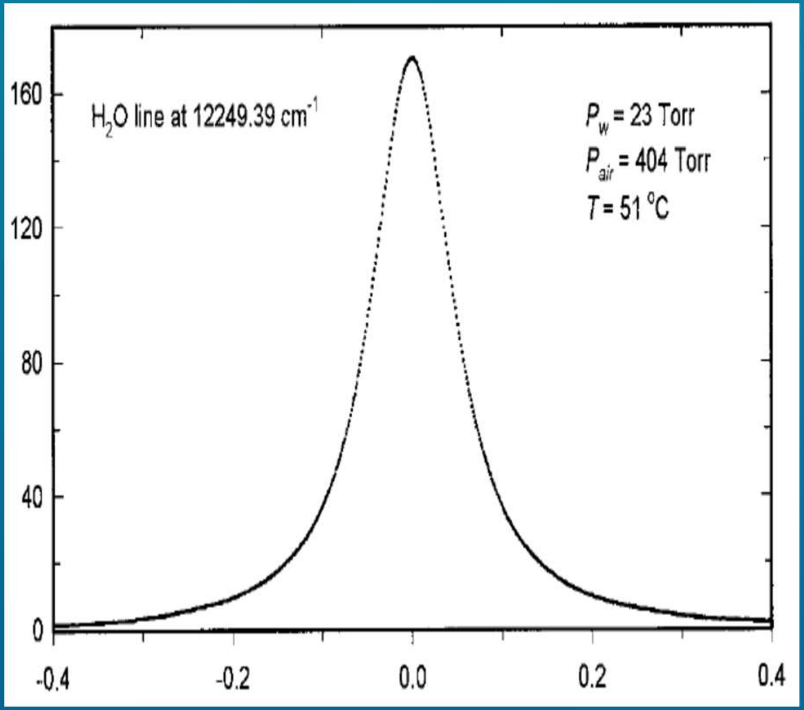
ACE spectra at different tangent altitudes



*Bernath et al., GRL, **32**, L15S01 (2005)*

The Voigt profile

Spectral shape of an isolated line



The absorption coefficient is given by

$$\alpha_{fi}(\sigma) = S_{fi} I_{fi}(\sigma - \sigma_{fi})$$

→ Line intensity is distributed around the line position

$$S_{fi} = \int_{\sigma_{fi}-\Delta}^{\sigma_{fi}+\Delta\sigma} d\sigma \alpha_{fi}(\sigma) \cong \int_{-\infty}^{+\infty} d\sigma \alpha_{fi}(\sigma)$$

→ Normalized line profile $I_{fi}(\sigma)$

$$\int_{-\Delta\sigma}^{+\Delta\sigma} d\sigma\ I_{fi}(\sigma) \cong \int_{-\infty}^{+\infty} d\sigma\ I_{fi}(\sigma) = 1$$

The Doppler broadening

A molecule having a speed v#0, absorbs or emits at a wavenumber σ, which is different of σ_{fi} of this molecule at v=0.

The corresponding Doppler shift is: $\sigma = \sigma_{fi}\,(1+v_z/c)$ where v_z the radiator velocity component along the wave propagation vector.

The line profile is a Gaussian profile

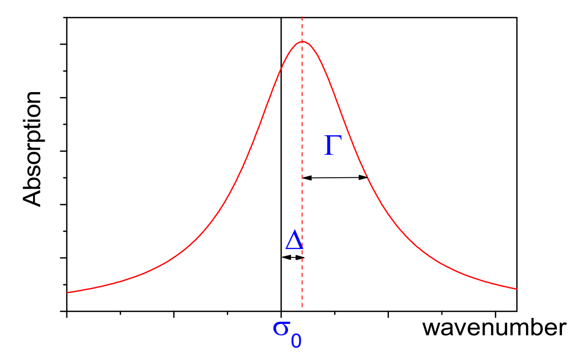
$$I_D(\sigma-\sigma_{fi}) = \sqrt{\frac{ln2}{\pi}}\frac{1}{\Delta\sigma_D}\exp\left(-\ln 2\left[\frac{\sigma-\sigma_{fi}}{\Delta\sigma_D}\right]^2\right)$$

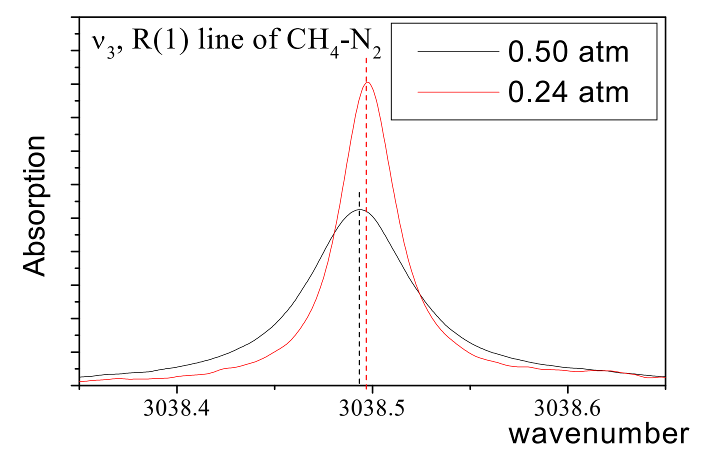
$$where\Delta\sigma_D = \left[\frac{2k_BT}{mc^2}\ln 2\right]^{\frac{1}{2}}\sigma_{fi}$$

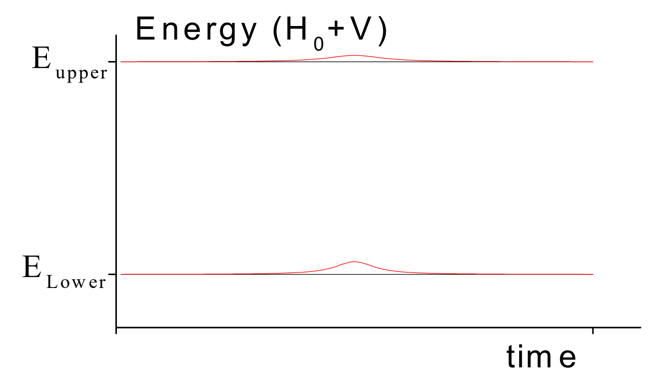
is the HWHM of the line.

The Lorentz broadening and shifting

For an isolated transition, the **main** effects of intermolecular collisions (pressure) are the (Lorentz) **broadening and shifting** of the line



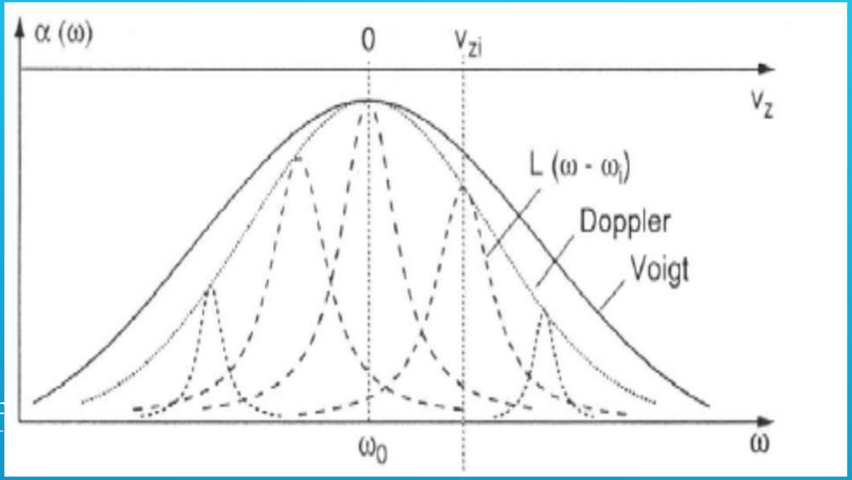




$$I_L(\sigma - \sigma_{fi}) = \frac{1}{\pi}\frac{\Gamma_{fi}}{\left(\sigma - \sigma_{fi} - \Delta_{fi}\right)^2 + \Gamma_{fi}^2}$$

Γ and Δ proportional to the # of coll (dens or P)

The Voigt profile



Let's consider a speed class: $[(v_z) - (v_z+dv_z)]$ the corresponding spectral domain is $[(\sigma') - (\sigma'+d\sigma')]$, with $\sigma' = \sigma_0(1+v_z/c)$

Due to collisions, the spectral intensity $I_D(\sigma' - \sigma_{fi})d\sigma'$ is redistributed as a Lorentz profile centered at σ'. The final contribution of this speed class at σ is thus:

$$I_D(\sigma' - \sigma_{fi})\, d\sigma'\, I_L(\sigma - \sigma')$$

The resulting profile is then obtained by summing over all speed classes (or all σ') :

$$I_V(\sigma - \sigma_{fi}) = \int_{-\infty}^{+\infty} d\sigma' I_D\left(\sigma' - \sigma_{fi}\right) I_L(\sigma - \sigma')$$

The Voigt profile is thus a convolution of a Gaussian profile (Doppler effect) and a Lorentzian profile (collisional effect).

The Gaussian, Lorentzian and Voigt profiles

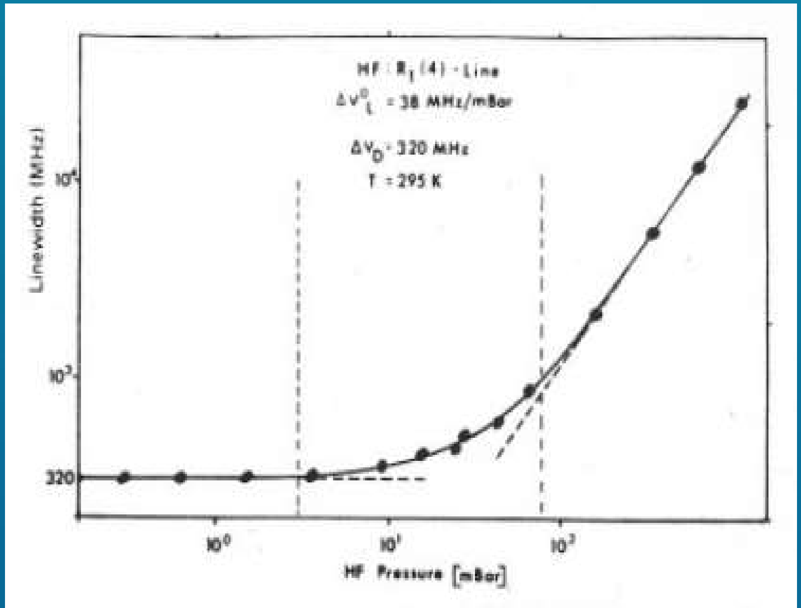
Pressure

Collisions
Lorentzian

Doppler+Collision
Voigt

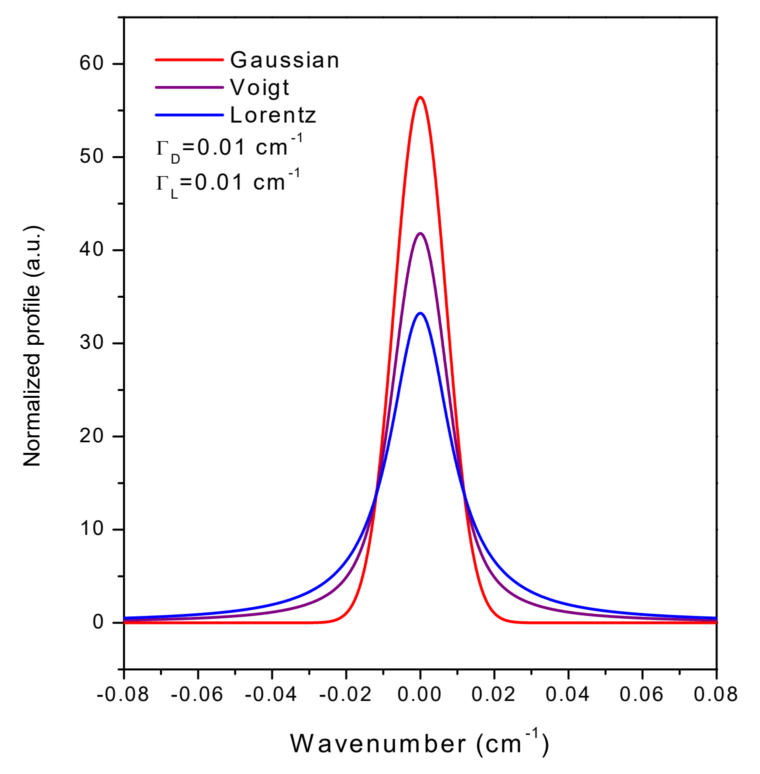
Doppler
Gaussien

Usual behavior of the line width



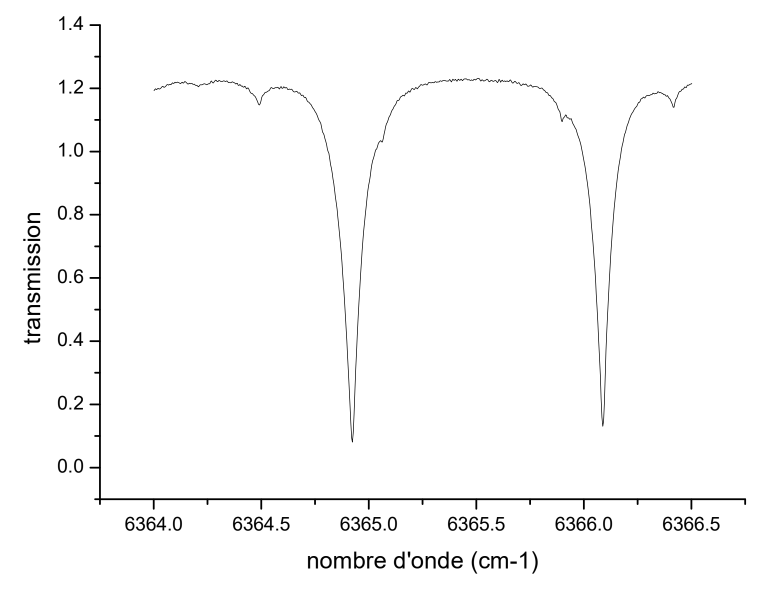
Linewidth dependence of HF absorption line on pressure.

The Gaussian, Lorentzian and Voigt profiles



Comparaison between the Gaussian, the Lorentz and the Voigt profiles.

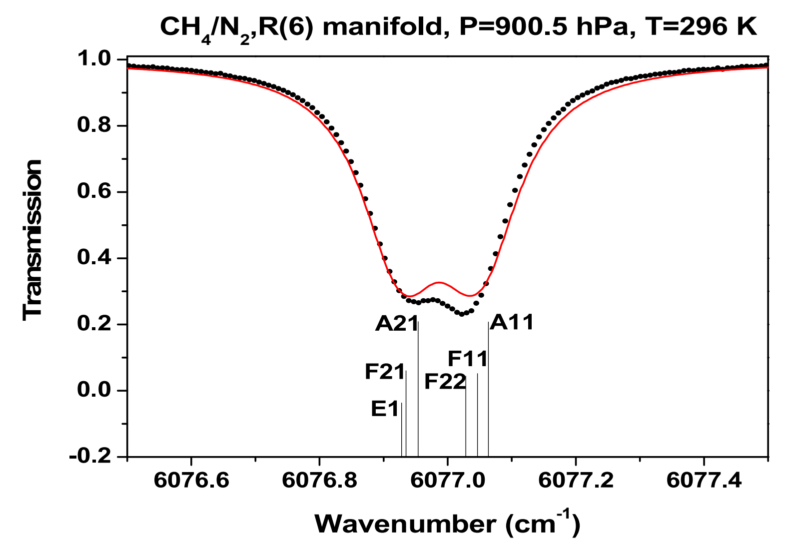
FTS ground-based absorption spectrum (CO_2)



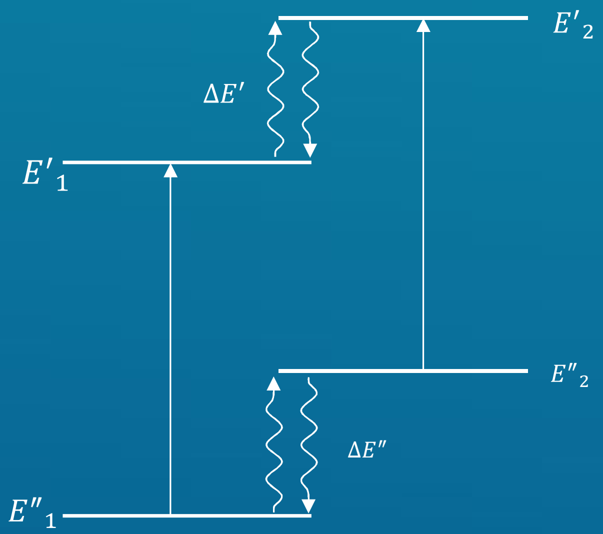
Courtesy of S. Payan

Non-isolated transitions: Line-mixing effects

Line-mixing effects



In some cases, for closely spaced lines, the Voigt profile fails when P increases. It predicts shapes that are too broad.



Collisions induce transfers of populations between the levels of the two lines that lead to transfers of intensity between the lines.

Line-mixing effects: Absorption coefficient

$$\alpha^{\mathrm{LM}}(\sigma) \propto \sum_{\text{line } \ell} \sum_{\text{line k}} \rho_\ell \, d_\ell \, d_k \, \langle k \, | \, [\Sigma - L_0 - iPW]^{-1} \, | \ell \rangle$$

ρ_k populations

d_k matrix element of radiation-matter coupling tensor

Σ, L_0 matrix of positions

W relaxation operator. All effects of collisions. Independent of σ within the impact approximation (not too far in the wings)

$W_{lk} \neq 0$ → Line coupling between |k> and |l>

$W_{lk} = 0$ → No line coupling (Lorentz)

$$\alpha^{Lo}(\sigma) \propto \sum_k \rho_k d_k^2 \times \left[\frac{\gamma_k}{(\sigma - \sigma_k - \delta_k)^2 + \gamma_k^2} \times \frac{1}{\pi} \right]$$

Line-mixing effects: Relaxation matrix

Relations for W

$$\langle k|\mathrm{W}|k\rangle = \Gamma_{\mathrm{k}} - \mathrm{i}\Delta_{\mathrm{k}}$$

$$\text{Det. } \mathit{Balance}: \ \rho_{l}\langle k|W|l\rangle = \rho_{k}\langle l|W|k\rangle$$

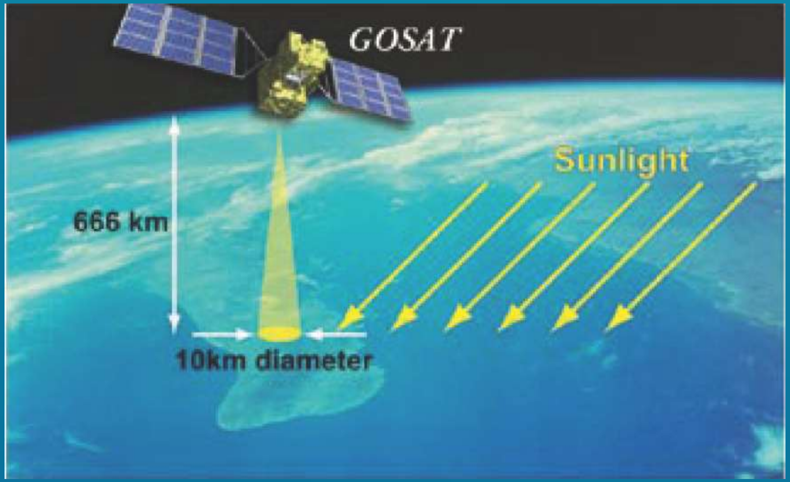
$$\text{Sum rule: } \sum_{\text{lines } \mathrm{l}} \mathrm{d}_{\mathrm{l}} \langle \mathrm{l}|\ \mathrm{W}\ |\mathrm{k}\rangle = 0$$

For moderate line overlapping, a first order perturbation approach is possible. Then we only need to know one coupling parameter (Y, related to the W matrix elements) per line

$$\mathrm{Y}_{\mathrm{k}} = 2\sum_{\ell \neq \mathrm{k}} \frac{\mathrm{d}_{\ell}}{\mathrm{d}_{\mathrm{k}}} \frac{\mathbf{W}_{\mathrm{k}\ell}}{\sigma_{\mathrm{k}} - \sigma_{\ell}}$$

Line-mixing and remote sensing: Monitoring Greenhouse Gases from space

Nadir looking instruments onboard satellites
Greenhouse gases Observation SATellite (GOSAT-2, in orbit)
Orbiting Carbon Observatory (OCO-2, NASA, in orbit)
MicroCarb (CNES, under study)
…..

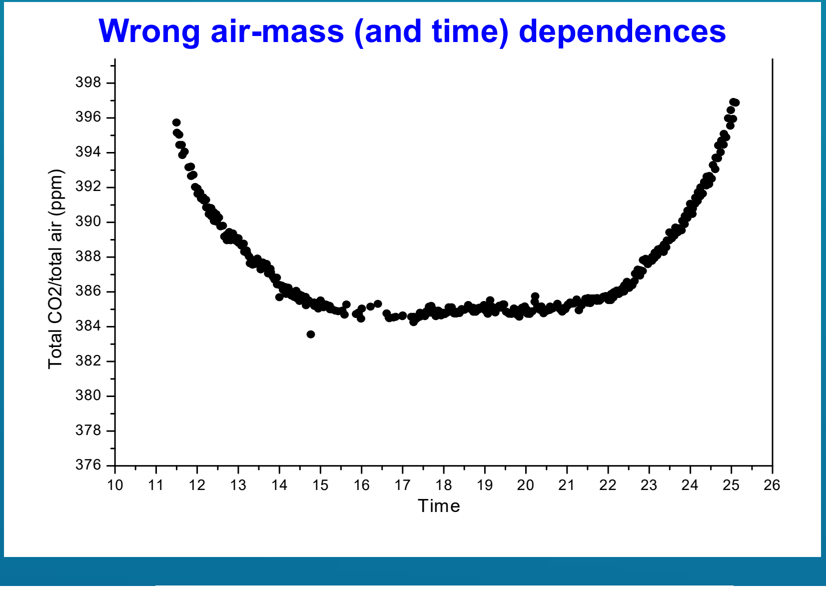


Spectral regions and aims

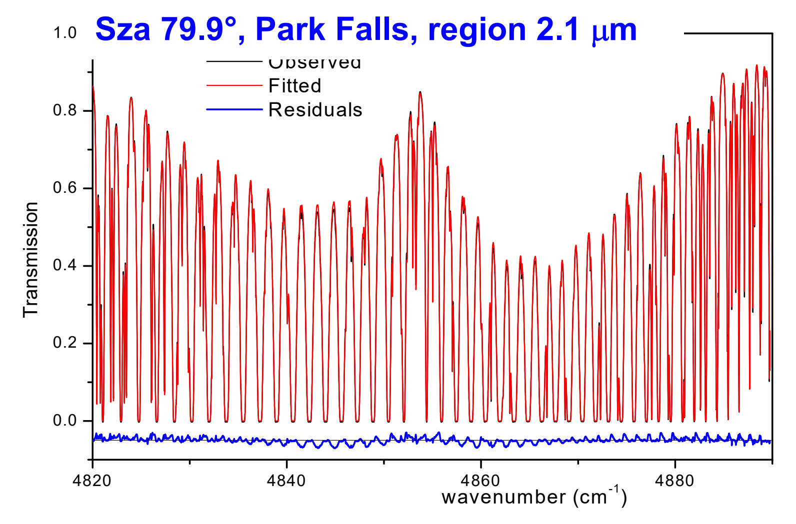
- CO_2 from 1.6 µm (weak) and 2.1 µm (strong) bands
- Air mass from O_2 A band (0.76 µm)
- CH_4 from $2\nu_3$ band (near 1.7 µm)
- aerosols from CO_2 and O_2 bands

Detection/quantifying sinks and sources (1 ppm for x_{CO2}, 0.3 %)
→ Extreme accuracy of spectra modelling**.** Huge constraints on the spectroscopic data and the prediction of pressure effects (collisions and spectral-shape)

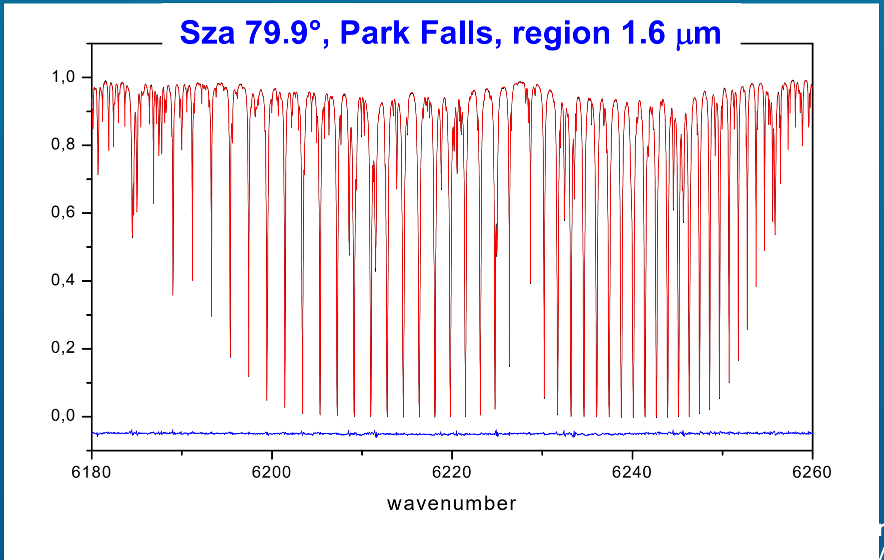
CO_2: ground-based measurements



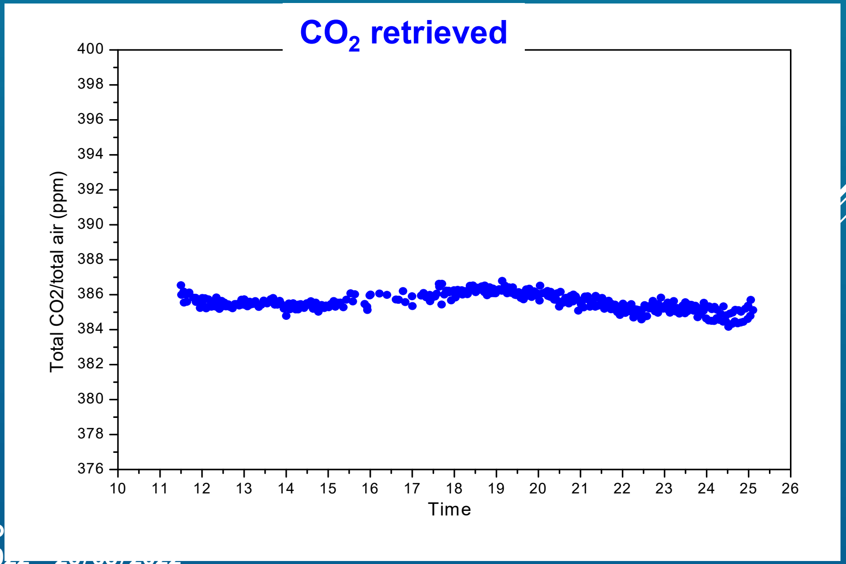
Wrong air-mass (and time) dependences



Sza 79.9°, Park Falls, region 2.1 μm

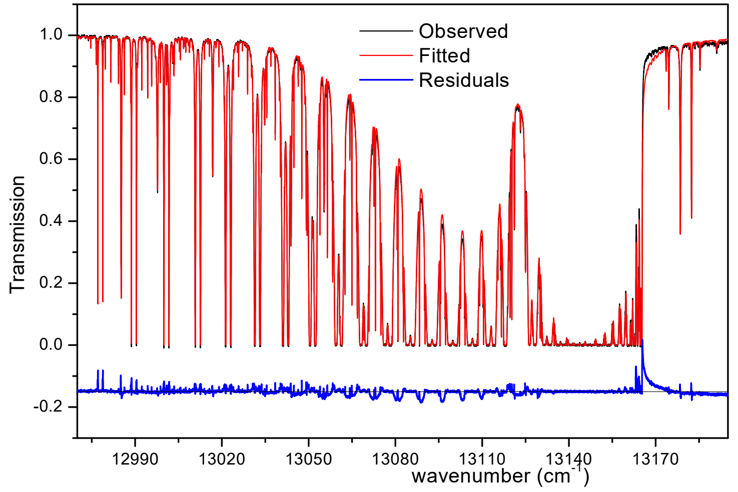


Sza 79.9°, Park Falls, region 1.6 μm

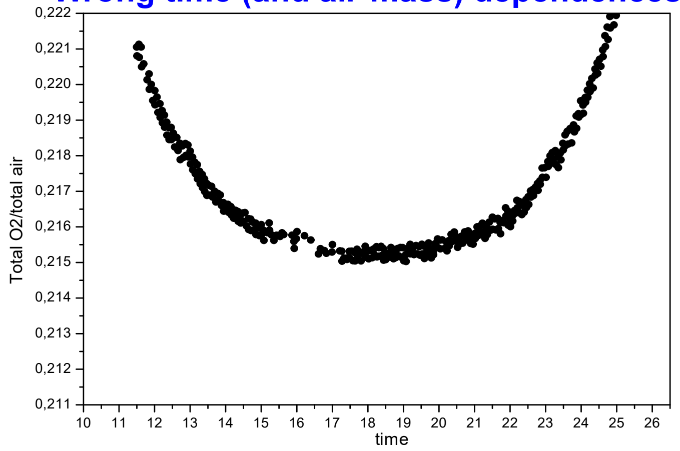


CO_2 retrieved

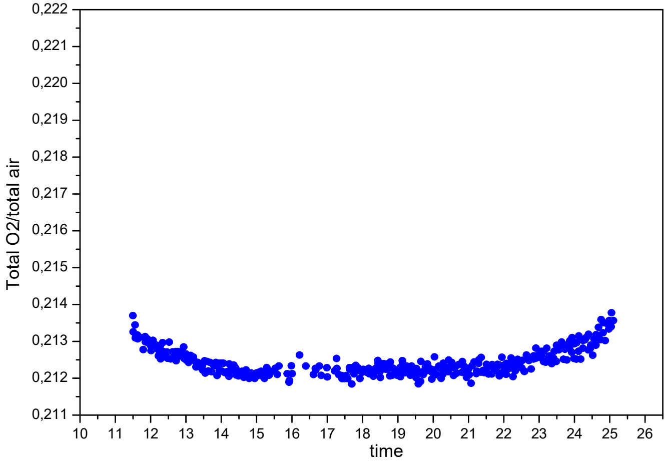
O_2: Ground-based measurements

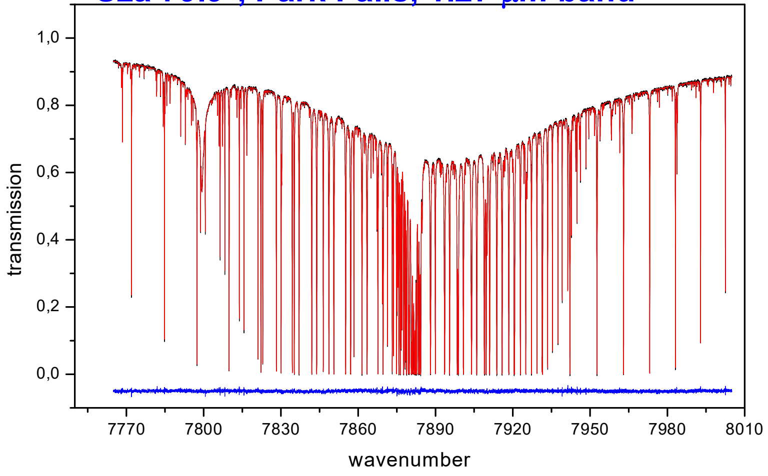


Sza 79.9°, Park Falls, A band



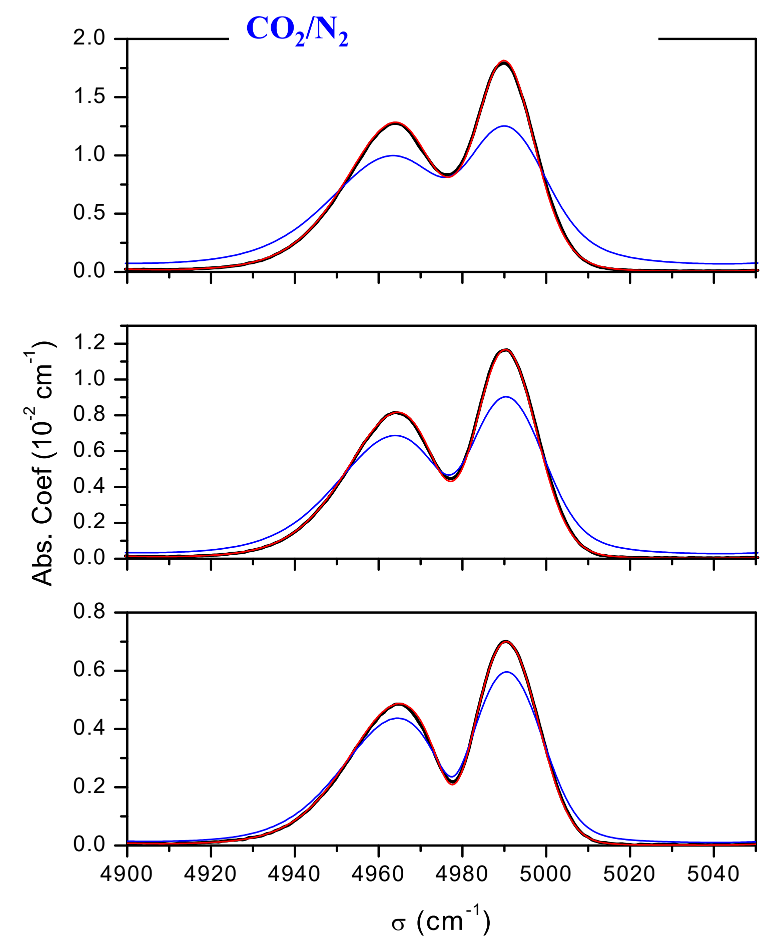
Wrong time (and air-mass) dependences

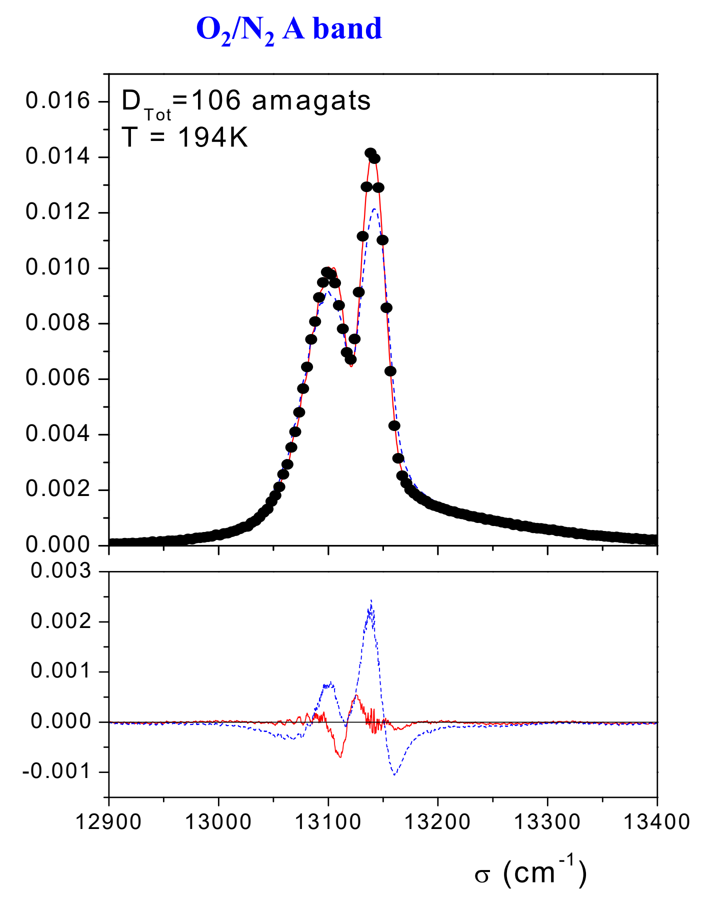




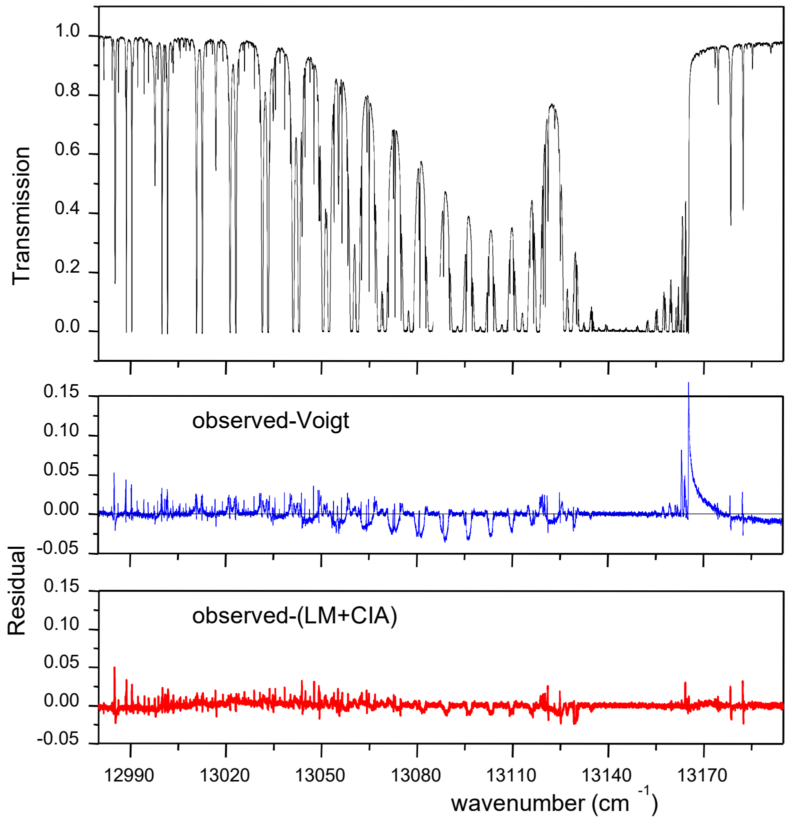
Sza 79.9°, Park Falls, 1.27 μm band

Line-mixing effects: Laboratory studies

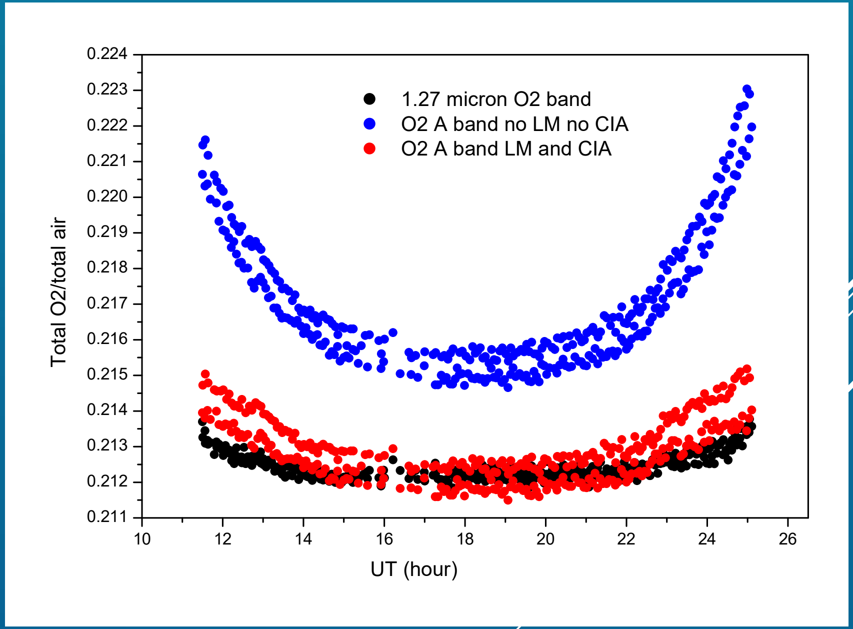




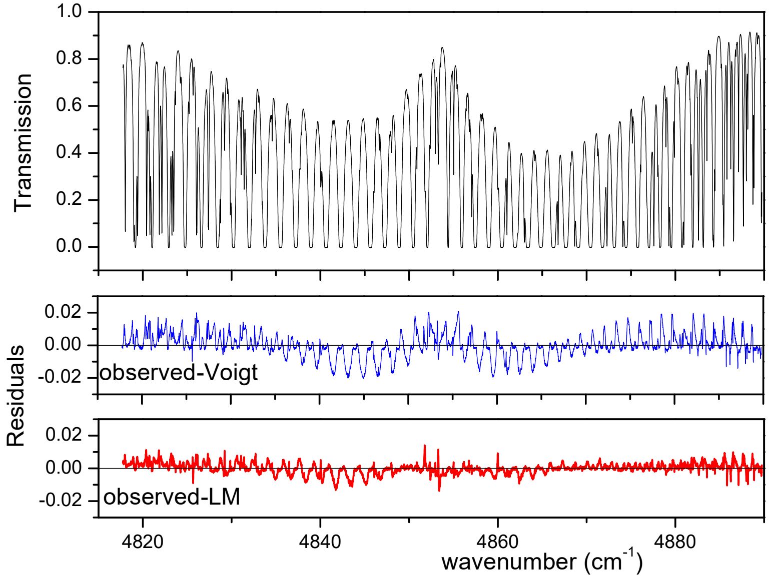
Influence on retrievals: O_2 ground-based measurements



O_2 A band:
Relative errors on surface pressures retrieved from atmospheric spectra

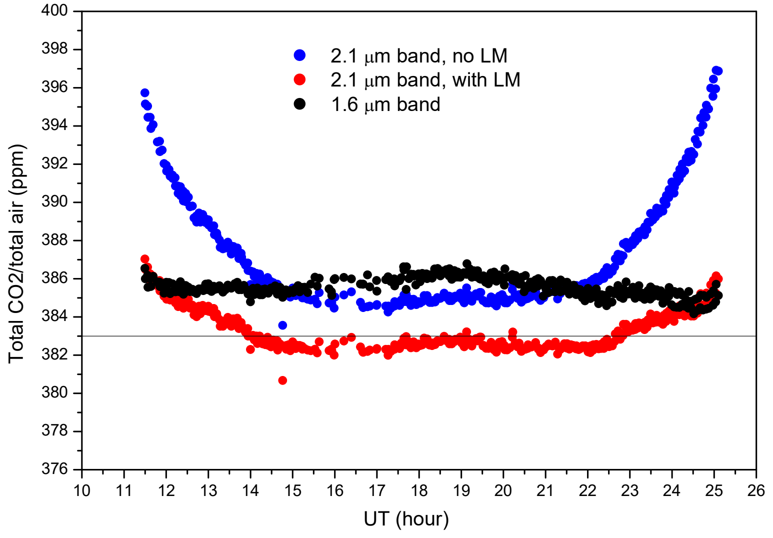


Influence on retrievals: CO_2 ground-based measurements

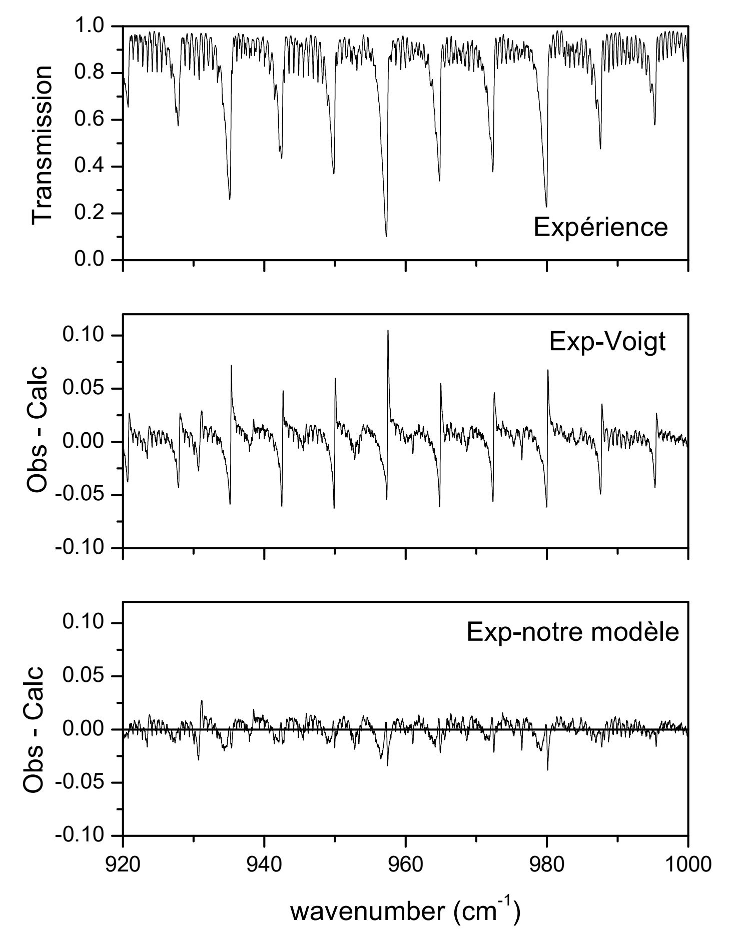


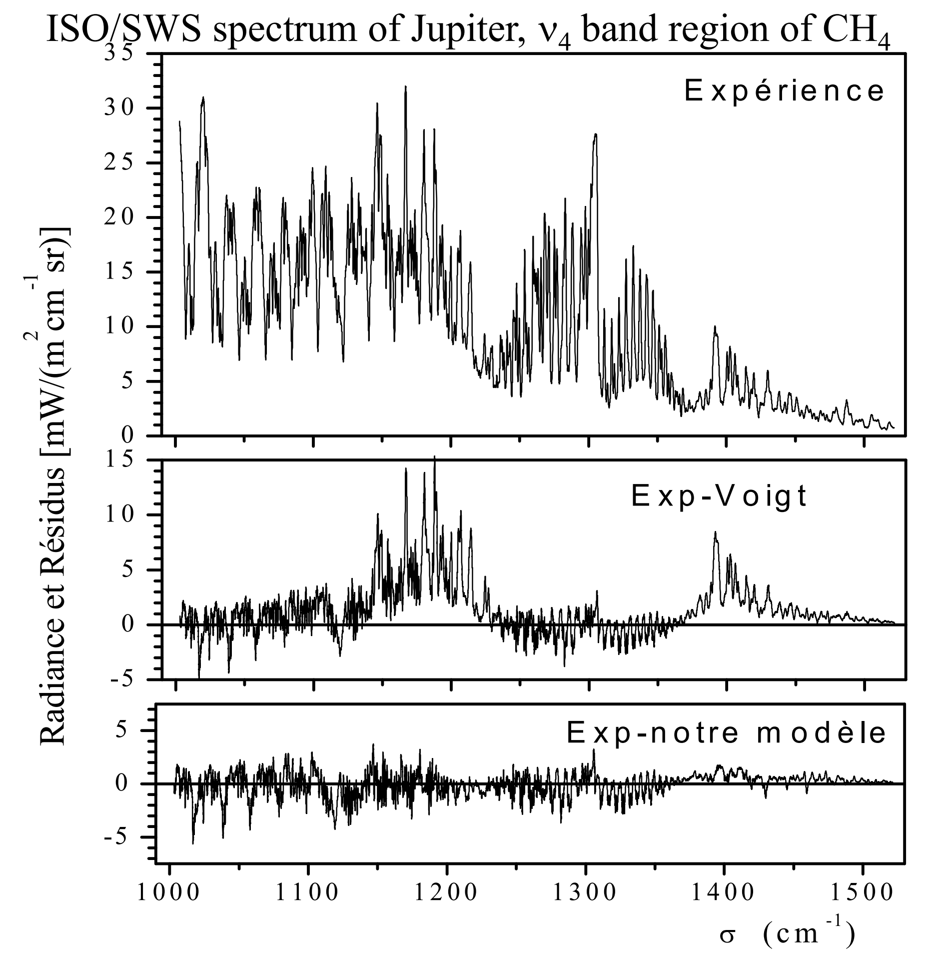
← Fits of a ground based transmission spectra in the region of the 2 $\nu_1 + \nu_3$ band of CO_2

Significant errors on the CO_2 atmospheric amount.
Sinks and sources !!!



Other systems

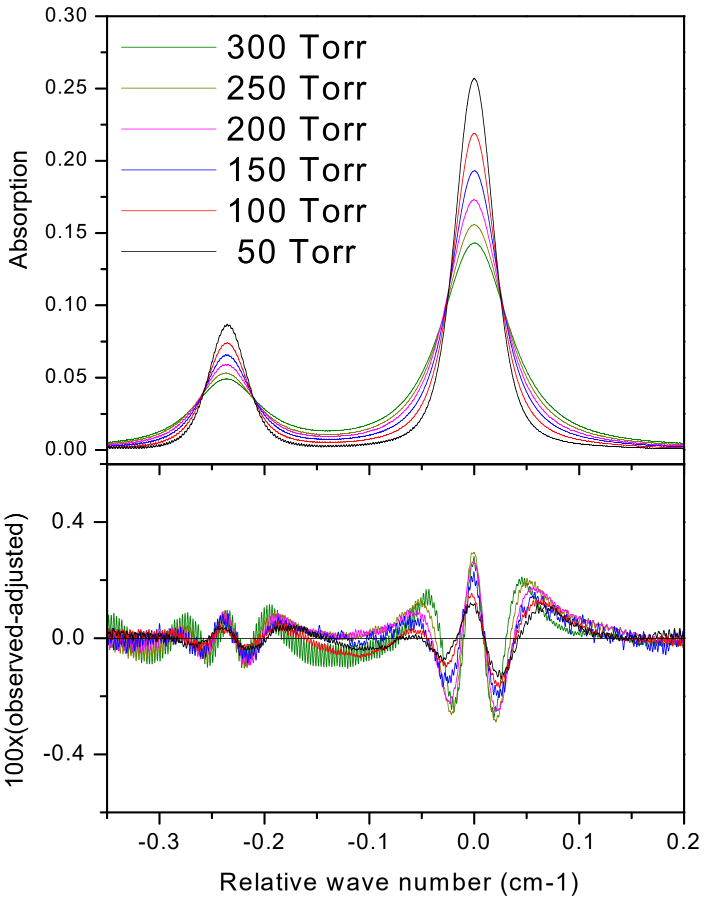


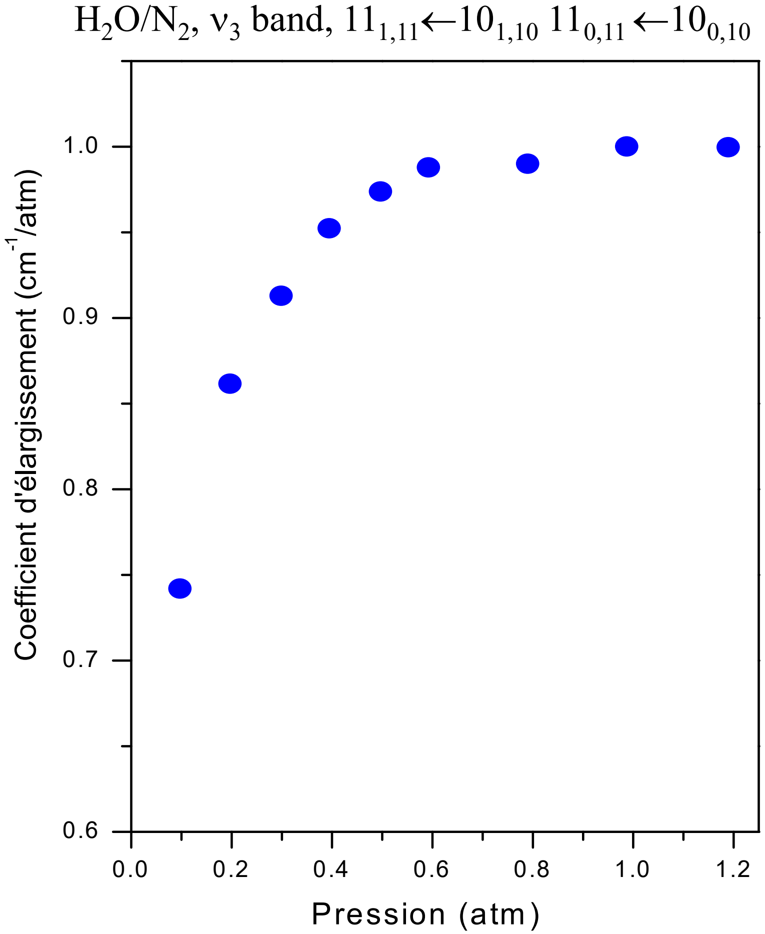


CH_3Br, 500 hPa, 234 K, ν_6 band

Isolated line

Limits of the Voigt profile





Measured and adjusted spectra using the Voigt profile.

Limits of the Voigt profile

The Voigt profile neglects:

1. **The velocity changes induced by collisions.**

The detailed balance:

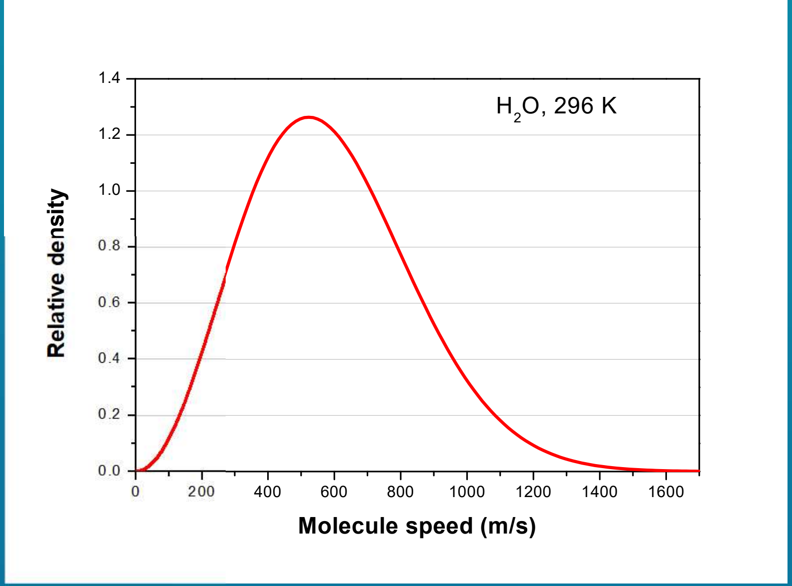
$$P(\vec{v} \rightarrow \vec{v}') \times f_{MB}(\vec{v}) = P(\vec{v}' \rightarrow \vec{v}) \times f_{MB}(\vec{v}')$$

→ change from v to v' < v is more probable than that from v to v' > v.

→ reduction of the Doppler broadening → collisional narrowing effect or Dicke narrowing effect

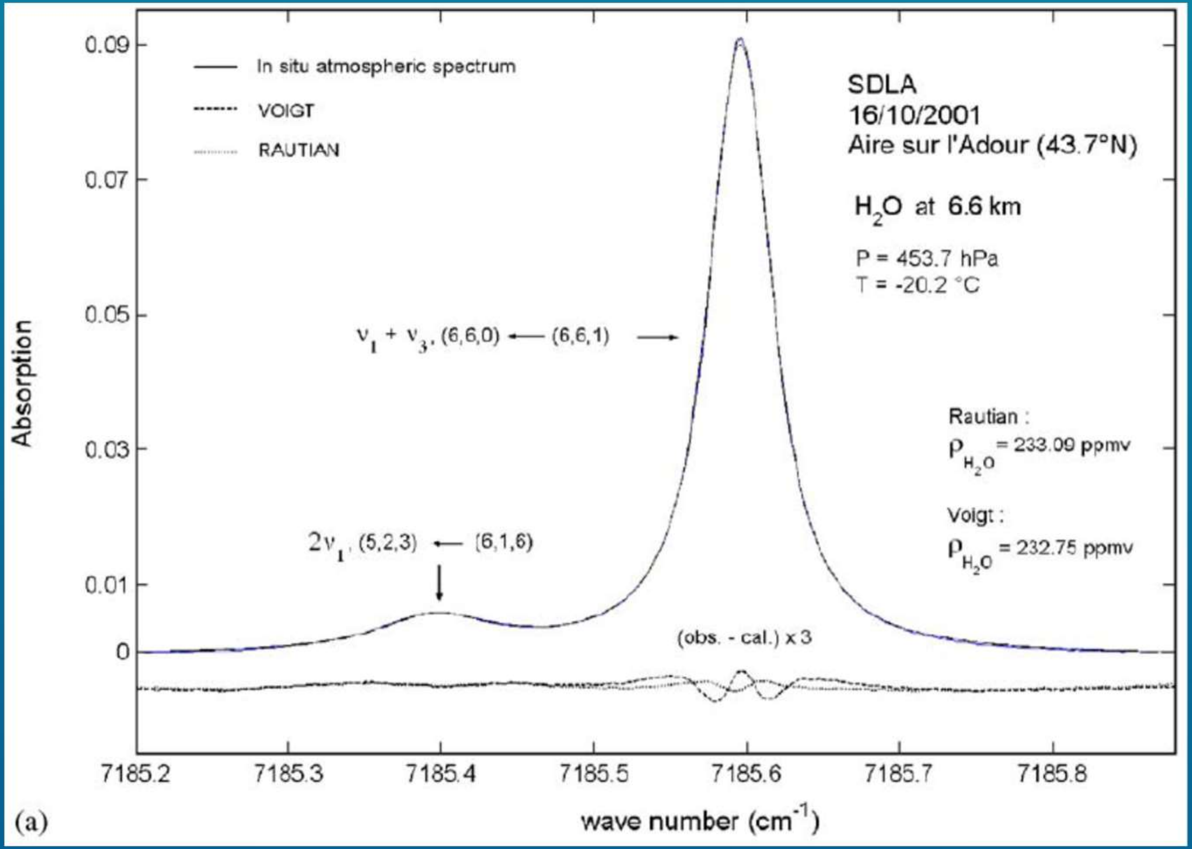
2. **The speed-dependences** of the collisional width Γ(v) and shift Δ(v) of the line.

This also (in general) leads to a narrowing of the line



Limits of the Voigt profile: atmospheric retrieval

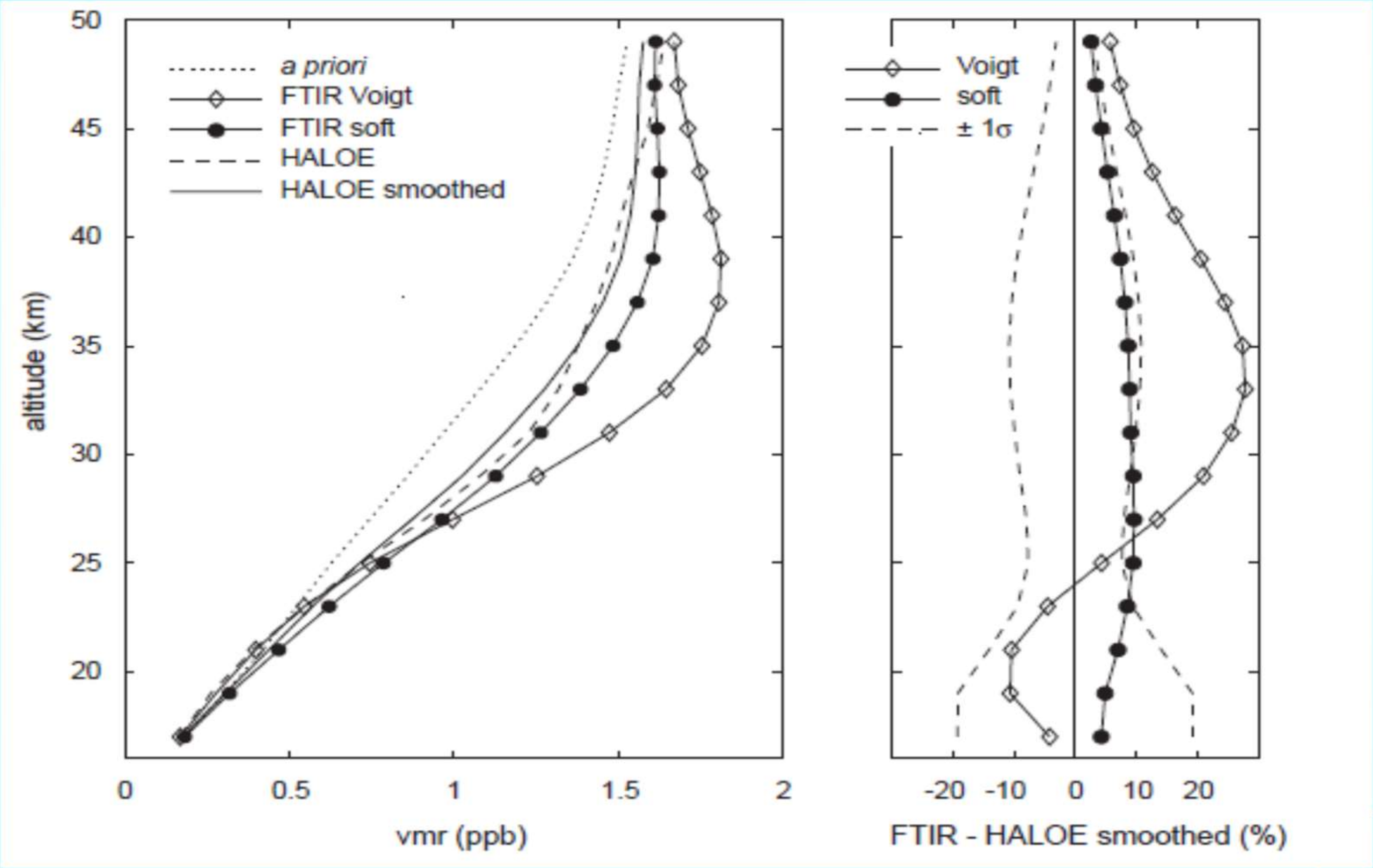
In situ absorption spectrum of tropospheric H_2O recorded by balloonborne diode laser and its fit using the Voigt profile



Durry et al, JQSRT ***94****, 387,2005*

Limits of the Voigt profile: Influence on atmospheric retrievals

HF profile retrieved from ground-based absorption FTIR measurements (Jungfraujoch station) in the (1-0) R(1) micro-window by using the Voigt profile and the Soft Collision model, compared with the HALOE (Halogen Occultation Experiment) profiles smoothed.



Barret et al, JQSRT ***95****, 499, 2005*

Widely used non-Voigt approaches

Simple non-Voigt approaches: the velocity changes effect

The Galatry (soft collisions, SC) profile:

- Assumes that radiators undergo only a very small changes per collision
- Introduces a velocity changing rate ν_{VC} related to the diffusion coefficient

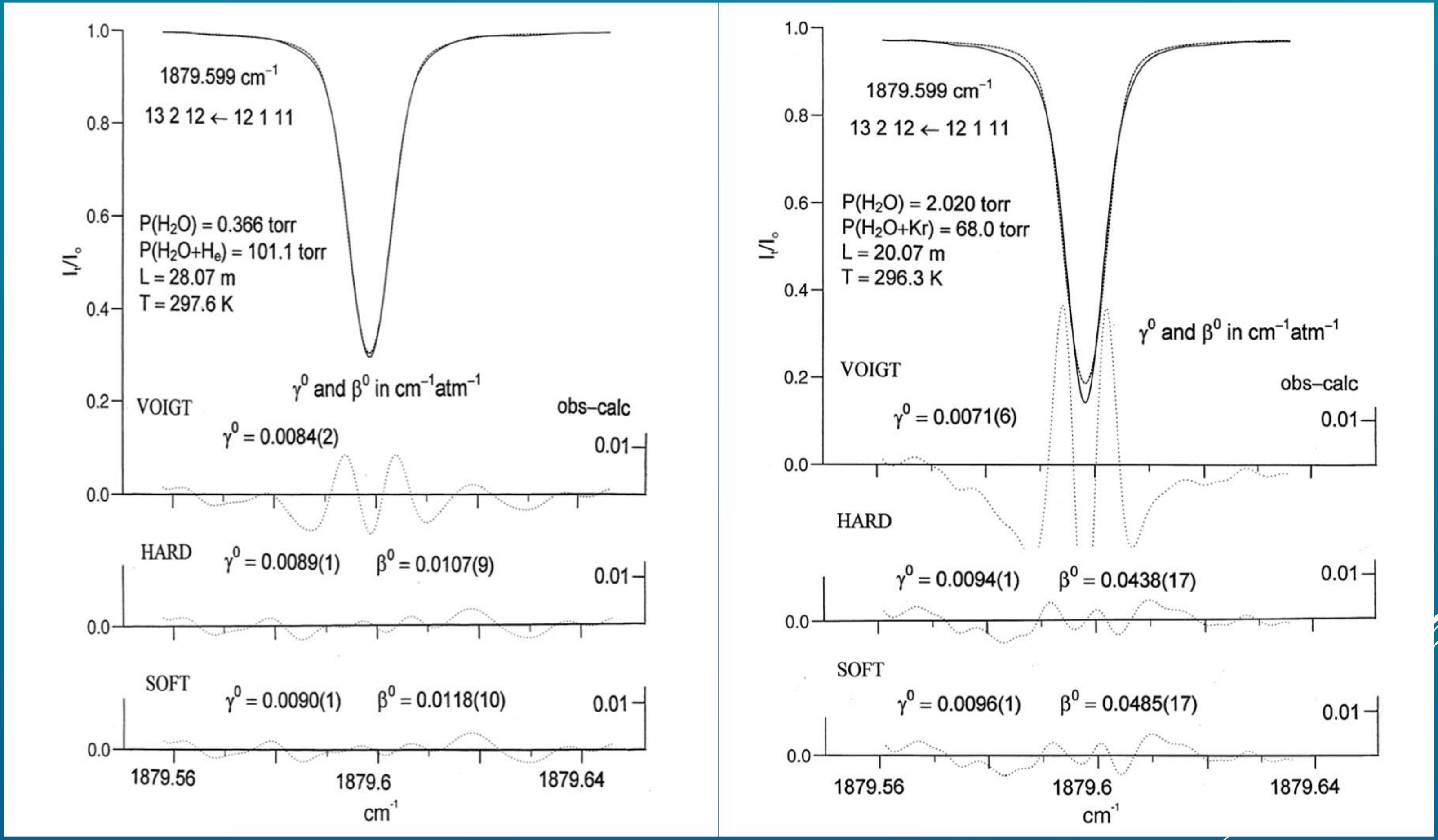
The Nelkin-Ghatak (hard collisions, HC) profile:

- Assumes that velocity memory is lost after each collision
- Introduces a velocity changing rate ν_{VC}

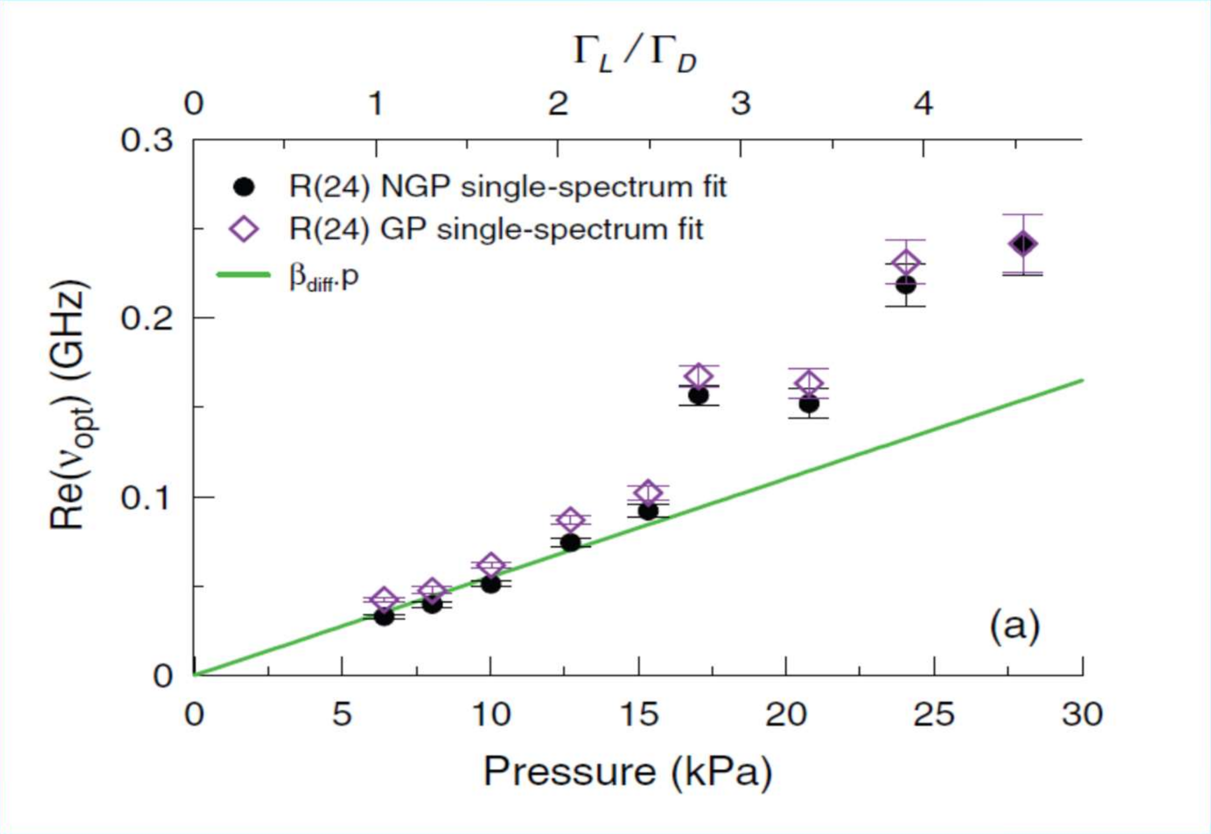
We can show that the SC model is more appropriate for systems for which the active molecule is much heavier than the perturber.

However, experiences show that the SC and HC models lead to similar quality in term of residual fit of measured spectra

Simple non-Voigt approaches: the velocity changes effect



Velocity changes effects: Remaining problems



Pressure dependence of the frequency optical collisions obtained for the R(24) line of CO_2 in air from the NGP, GP and single-spectrum fits. The green line is the frequency of optical collisions calculated from the mass diffusion coefficient

The collisional narrowing parameter is non linear with pressure

Simple non-Voigt approaches: the speed dependences

- The polynomial dependence of Berman-Pickett

$$\Gamma(v_r) \propto {v_r}^p$$

$$\Gamma(v_a) = \int \Gamma(v_r).\, f(v_r | v_a) \mathrm{d}v_r$$

- The quadratic dependence of Rohart

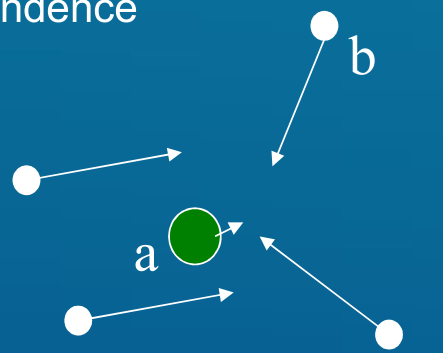
$$\Gamma(v_a) = \Gamma_0 + \Gamma_2[(v_a/\bar{v})^2 - 3/2] with \Gamma_0 = \langle \Gamma(v_a) \rangle_{v_a}$$

$m_{active} >> m_{buffer}$

Weak speed dependence

$v_a << \boldsymbol{v_r} \ \# \ \boldsymbol{v_b}$

$\Gamma(v_a) \ \# \ \mathrm{Cte}$

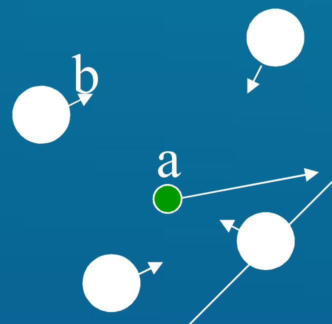


$m_{active} << m_{buffer}$

Strong speed dependence

$\boldsymbol{v_a} \ \# \ \boldsymbol{v_r} >> v_b$

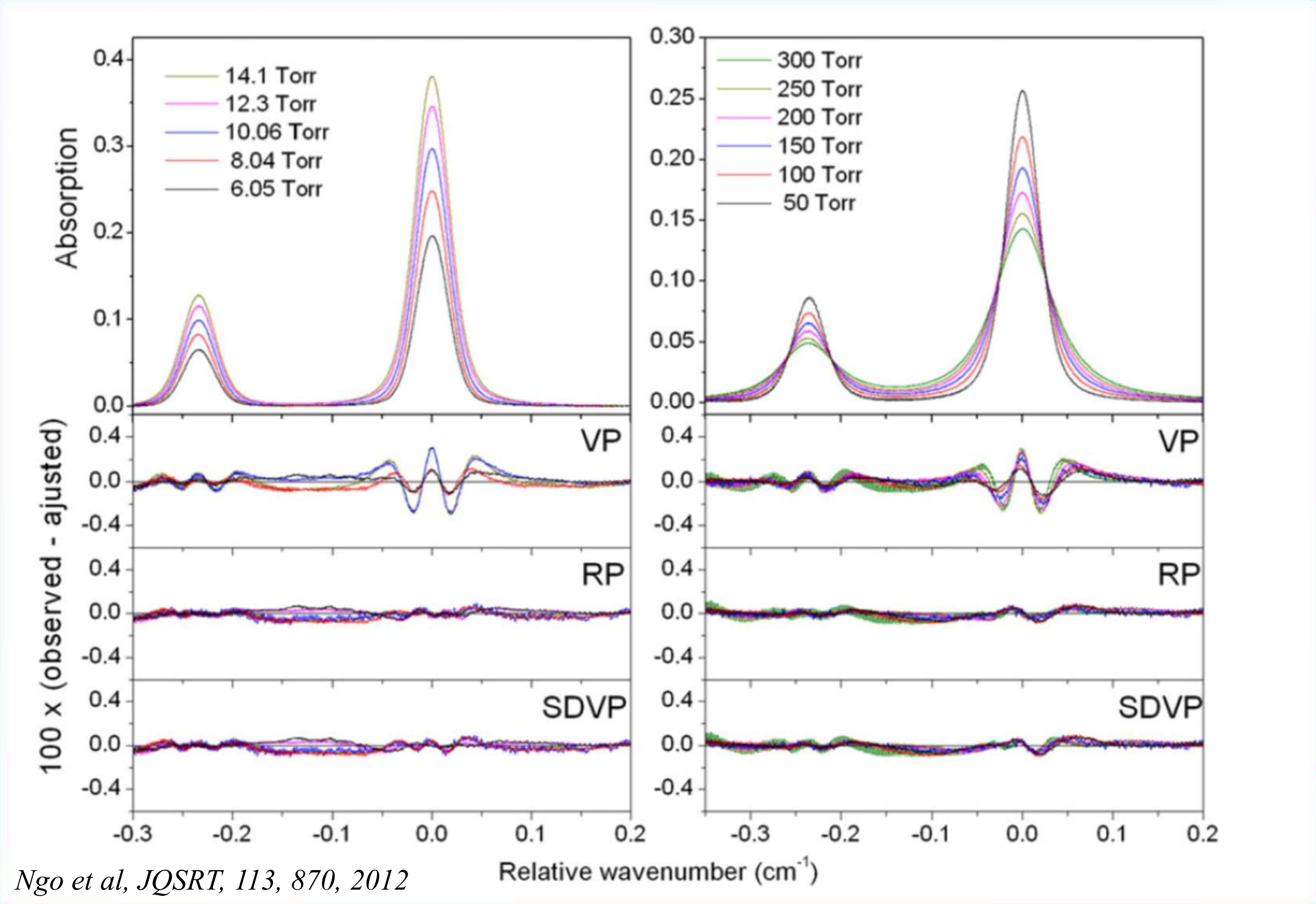
$\Gamma(v_a) \ \# \ \Gamma(v_r)$



Courtesy of F. Rohart

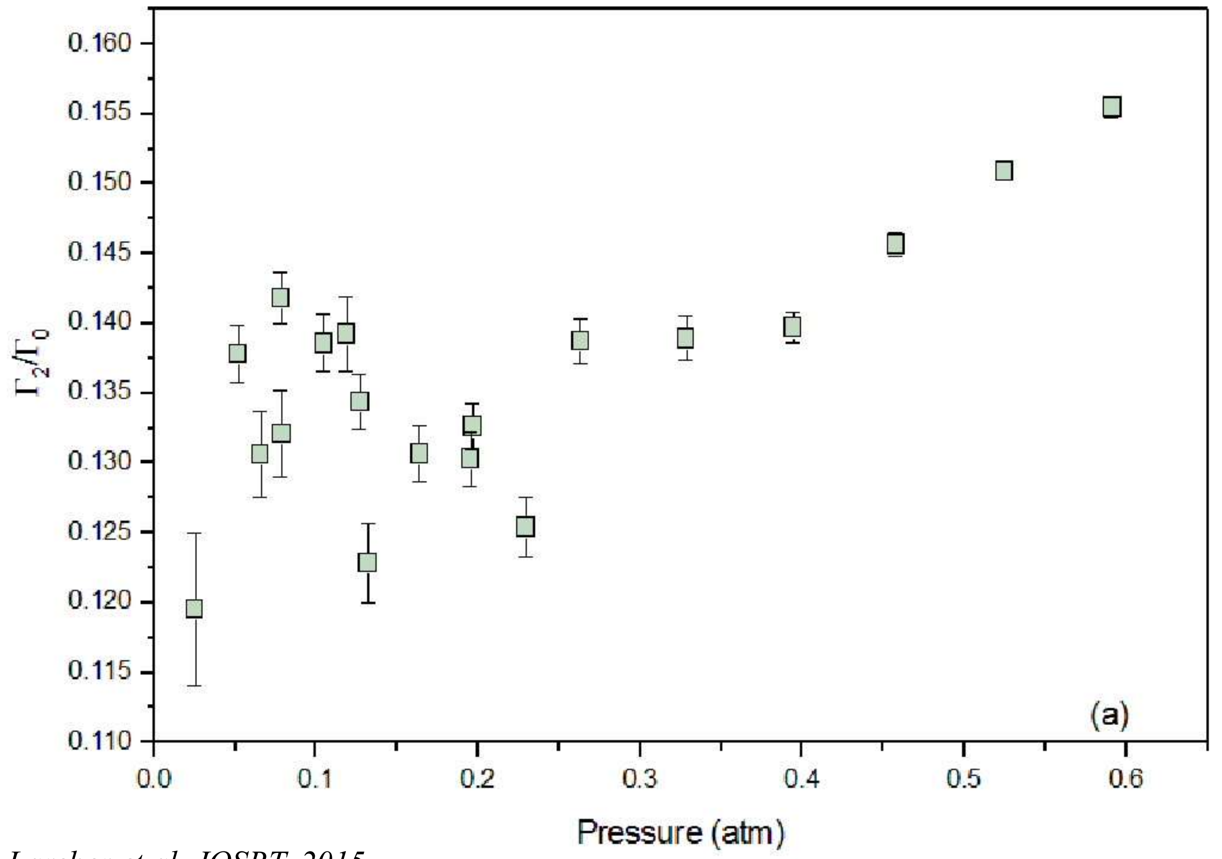
Simple non-Voigt approaches: the speed dependences

707<-606 and 717<-616 lines (at 0.83nm) of pure H_2O (left) and H_2O/air (right)



Ngo et al, JQSRT, 113, 870, 2012

Speed dependent Voigt profile: Remaining problems



Larcher et al, JQSRT, 2015

Γ_2/Γ_0 non constant vs pressure!

“Today” situation for line-shape study

- Thanks to the development of high resolution and S/N laboratory techniques (eg CEAS, CRDS) and spectra analysis techniques (multispectrum fits) the **vast majority of experimental** studies now **clearly evidence** the **limits of the Voigt**. **Various fitting line shapes** are used, chosen according to ad hoc criteria, so that the available data are inconsistent with no consensus.

- Very ambitious and precision-demanding **remote sensing experiments** are operational, under study or being developed (GOSAT, OCO, CarbonSat, MERLIN, Micro Carb) which **require an accuracy** of spectra simulations (<0.3%) that **prohibits the use of the Voigt** profile

A functional form for non-Voigt line shapes for spectroscopic databases and applications

Requirements for the proposed line-shape

Urgent need for a **better isolated line shape** model and associated data to fit experimental/calculated spectra and feed databases used for remote sensing. This line shape should fulfill various constraints:

1- **Take into account** the various processes that affect the line profile (Doppler, molecule velocity changes, speed dependences of broadening and shifting) and be sufficiently physically-based to describe the (experimental) line profiles of **various transitions** of **various gases** with an **accuracy (<0.1%) fulfilling** the remote sensing accuracy needs

2- Be **based** on **well identified line-by-line parameters** with **known** and physically based **pressure dependences** for storage in databases

3- **Contain simpler models** as limiting cases in order to maximize the possibility to use previously published results obtained using simpler profiles

4- Require **CPU time compatible** with a **use in atmospheric spectra calculations** (many lines and layers).

5- Be **compatible** with a treatment of **line-mixing**

The Hartmann-Tran (HT) profile

→ **The HT profile takes into account**

- The collision-induced velocity changes (Dicke narrowing, hard collision model): $\boldsymbol{\nu_{VC}}$
- The speed dependences of the collisional line width and shift (quadratic model): $\boldsymbol{\Delta_2,\Gamma_2}$
- The correlation between velocity- and internal-state-changes: $\boldsymbol{\eta}$

HTp

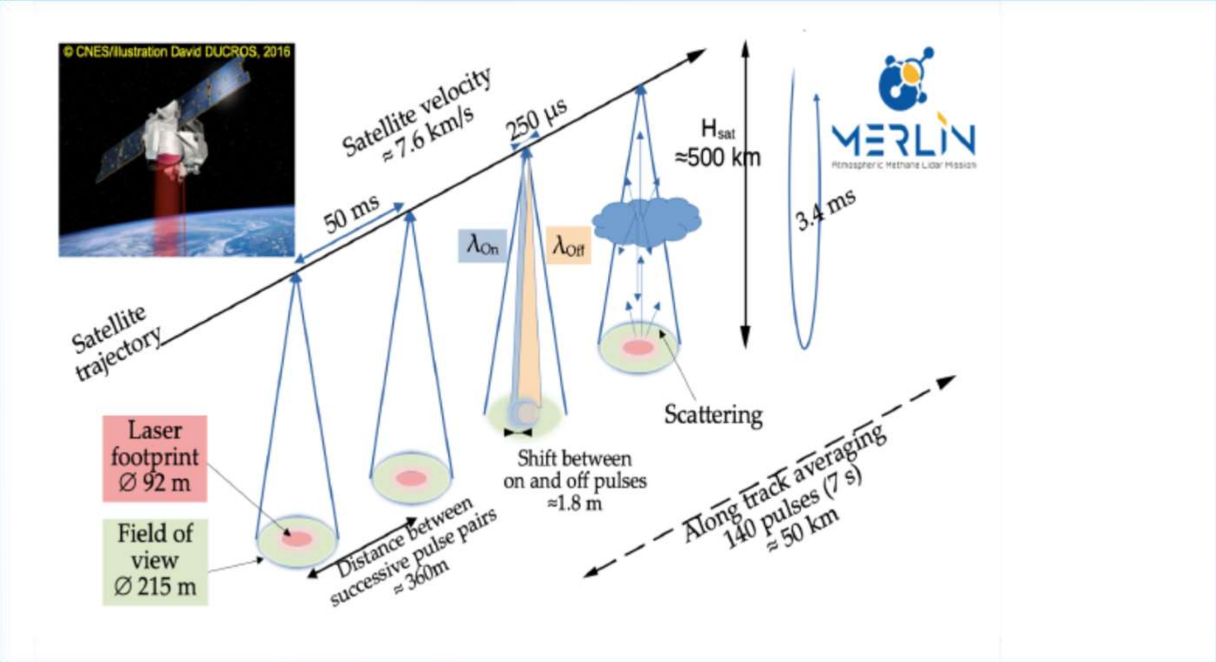
$(\Gamma_0,\Gamma_2,\Delta_0,\Delta_2,\nu_{VC},\eta)$

→ **The functional form of the model can be expressed as a combination of the Voigt functions → the HT profile can be calculated as quickly as the Voigt profile**

→ **The limits of the HT profile correspond to simplified line-shape models** → parameters obtained with these models can be used with the HT profile with the appropriated parameters set to zero.

Profile	Parameters	Limit of the HT profile
HT	$\Gamma_0, \Gamma_2, \Delta_0, \Delta_2, \nu_{VC}, \eta$	
qsdHC	$\Gamma_0, \Gamma_2, \Delta_0, \Delta_2, \nu_{VC}$	$\eta = 0$
qsdV	$\Gamma_0, \Gamma_2, \Delta_0, \Delta_2$	$\nu_{VC} = \eta = 0$
HC	$\Gamma_0, \Delta_0, \nu_{VC}$	$\eta = \Delta_2 = \Gamma_2 = 0$
V	Γ_0, Δ_0	$\nu_{VC} = \eta = \Delta_2 = \Gamma_2 = 0$

Example of the use of the HT profile: the MERLIN satellite project

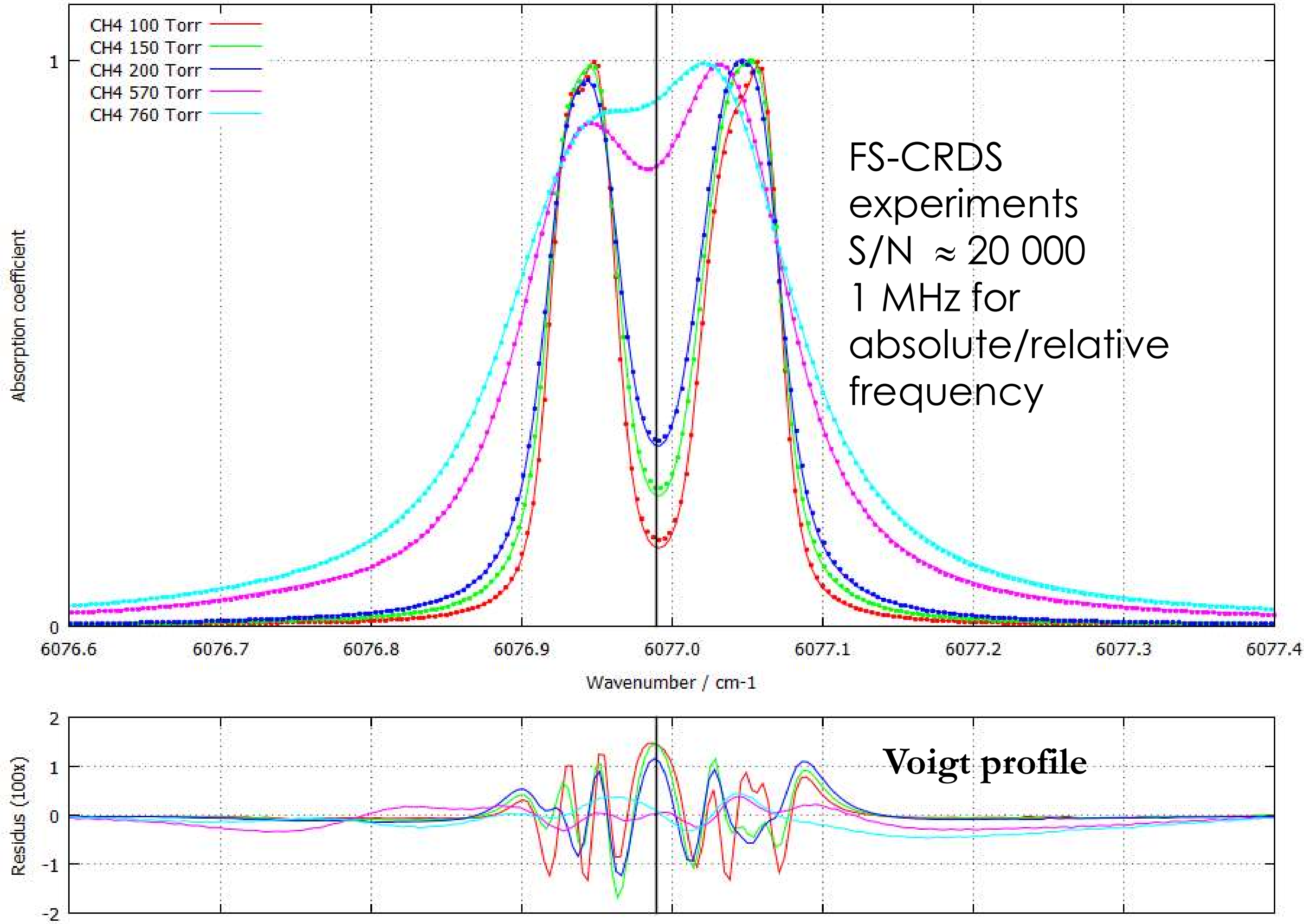


Objective: Measure methane amounts in the atmosphere

Observation method: differential absorption of gaseous methane at two laser wavelengths reelected from Earth surface

→ Measuring absorption cross-sections of methane at 1.645 μm ($2\nu_3$ band)

Spectroscopy for MERLIN: 0,2% accuracy required!



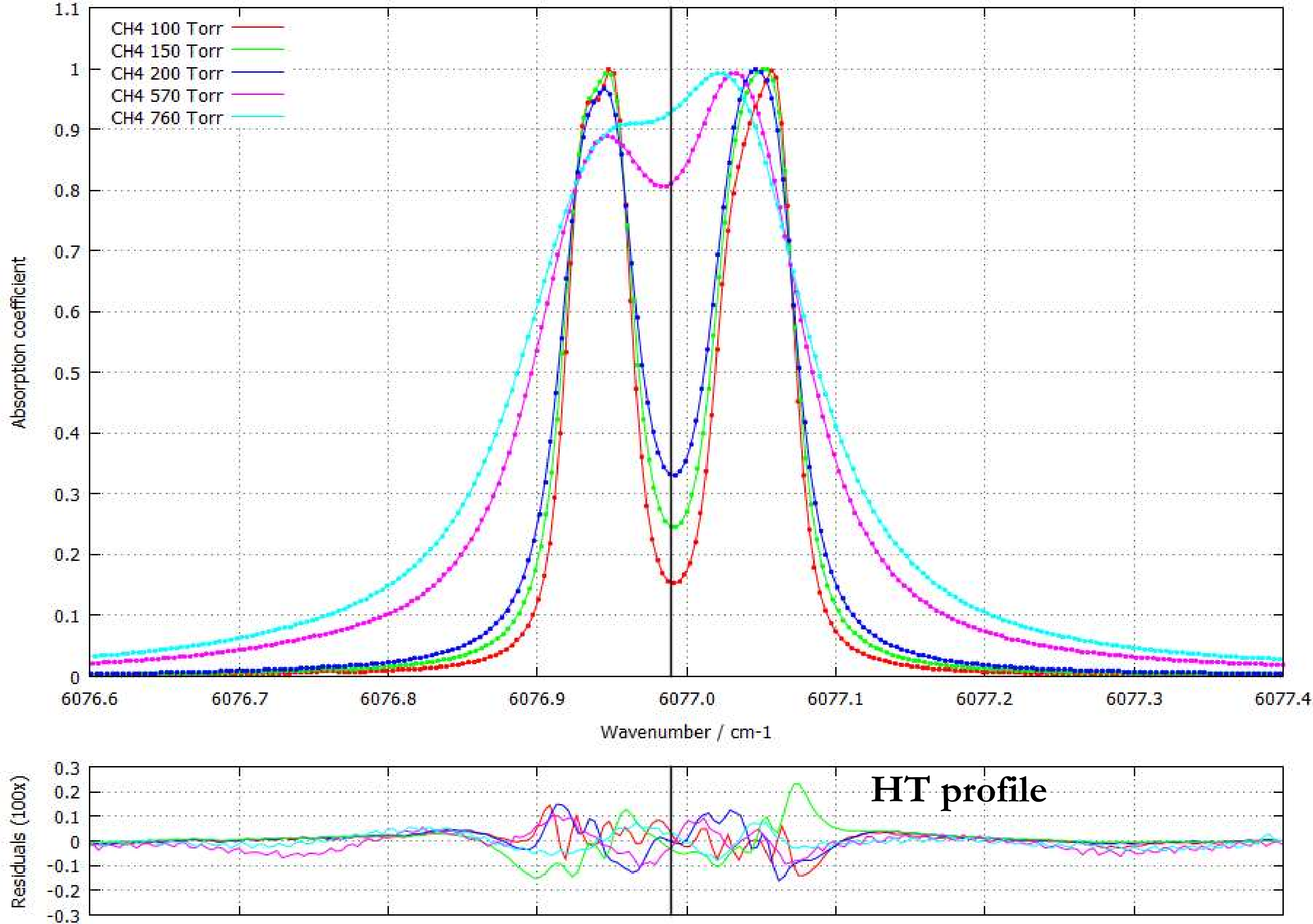
FS-CRDS experiments

S/N $\approx$ 20 000

1 MHz for absolute/relative frequency

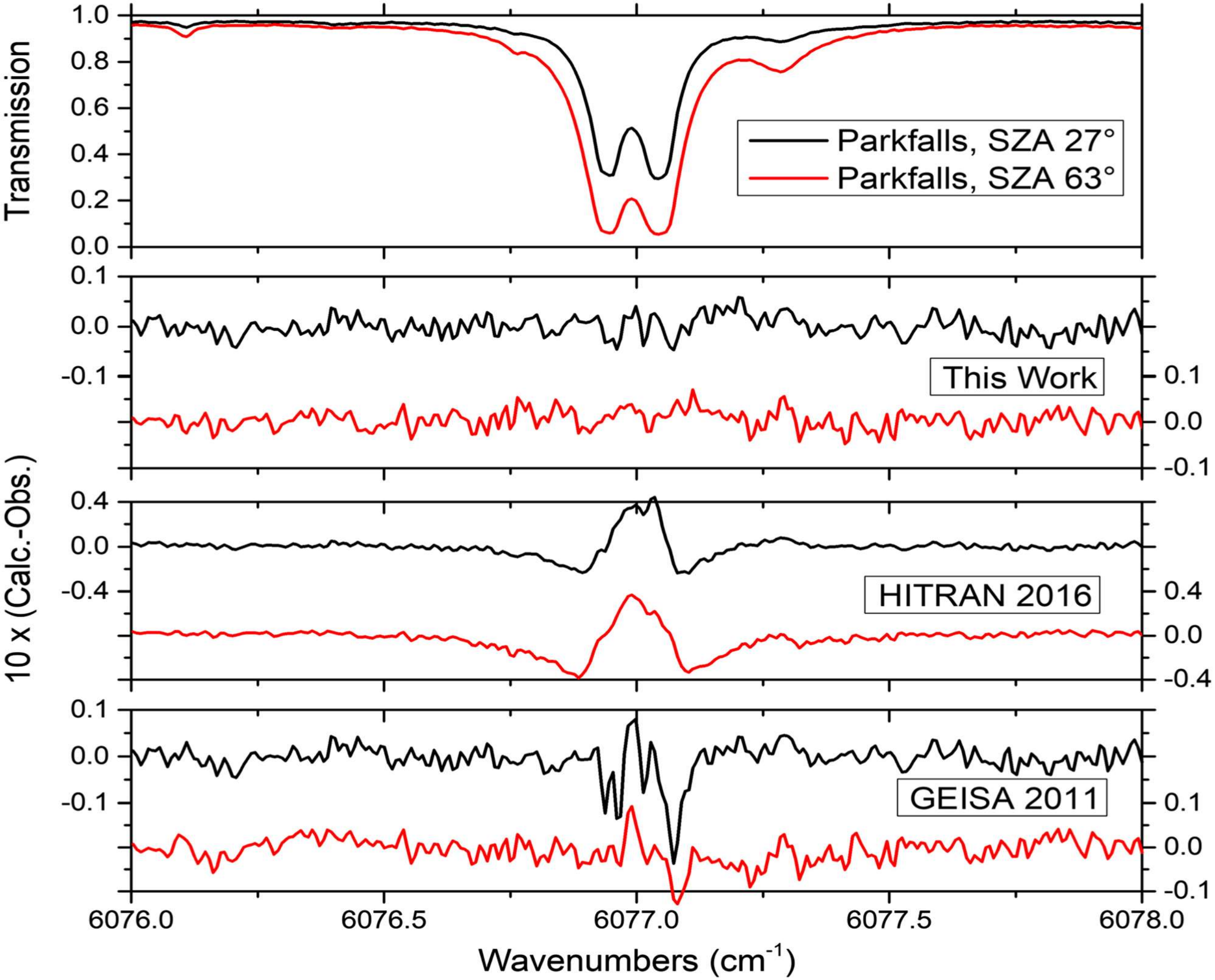
Delahaye et al, 2016

Spectroscopy for MERLIN: 0,2% accuracy required!



Delahaye et al, 2016

Validation with ground-based atmospheric spectra (TCCON)



Delahaye et al, 2019

Summary

- Spectral shape has become a key issue for high precision soundings (e.g. greenhouse gases)

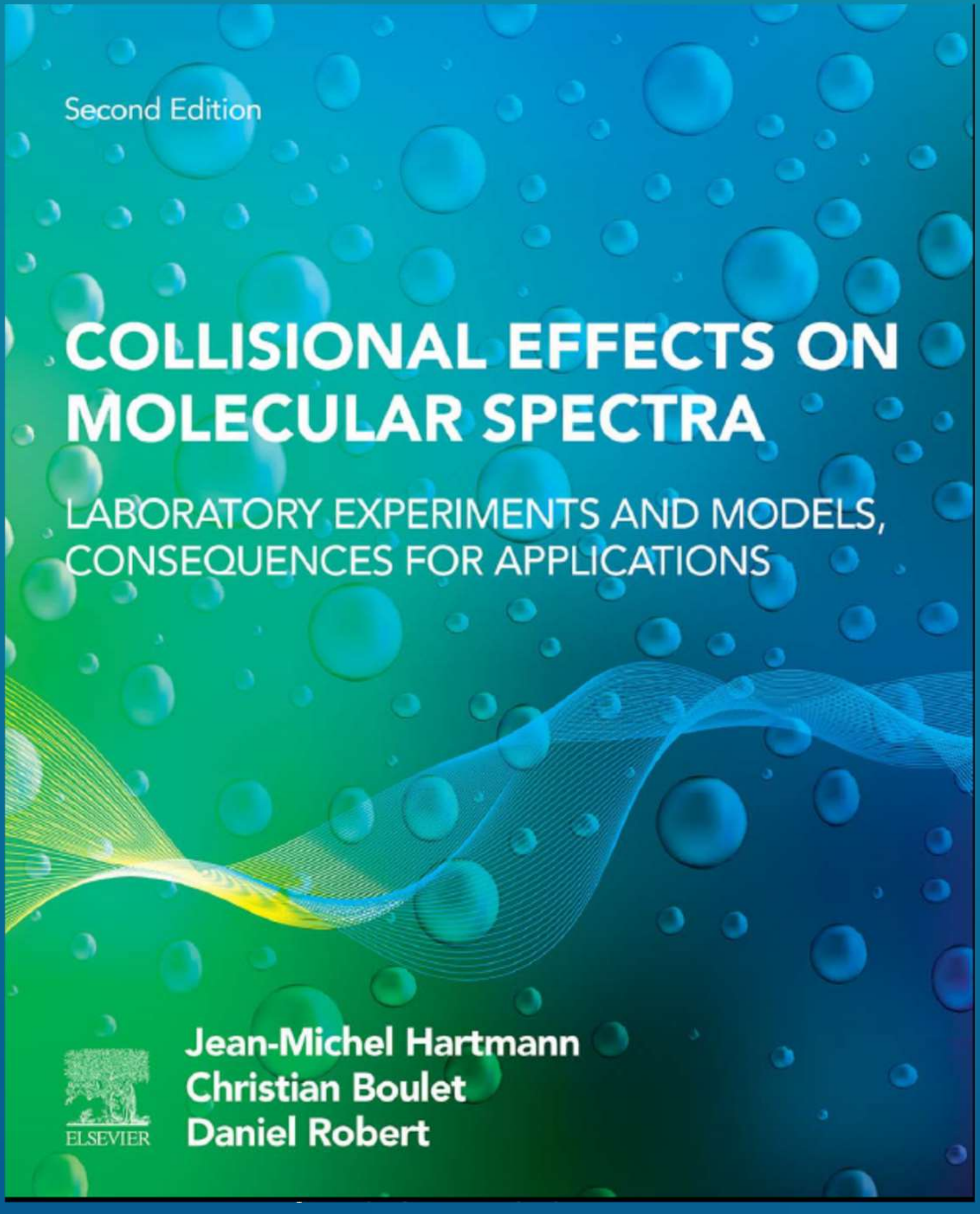
- When line is isolated, the Voigt profile fails to model isolated line-shape, velocity effects should be taken into account

- When lines are closely spaced, line-mixing should be taken into account

- Increasing evidences of influence of refined spectral shape effects for remote sensing

- Need to take into account both line-mixing and velocity effects; through the HT profile
  -> profile recommended by IUPAC and adopted by the HITRAN spectroscopic database

For more details



Second Edition

COLLISIONAL EFFECTS ON MOLECULAR SPECTRA

LABORATORY EXPERIMENTS AND MODELS,
CONSEQUENCES FOR APPLICATIONS

Jean-Michel Hartmann
Christian Boulet
Daniel Robert

ELSEVIER