Line shape modeling and application to remote sensing

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Research interests

Molecular Spectroscopy; Diode laser and FTS spectroscopy; Spectra modelling; Intermolecular Collisions and impact on the line shape; Molecular Dynamic Simulations
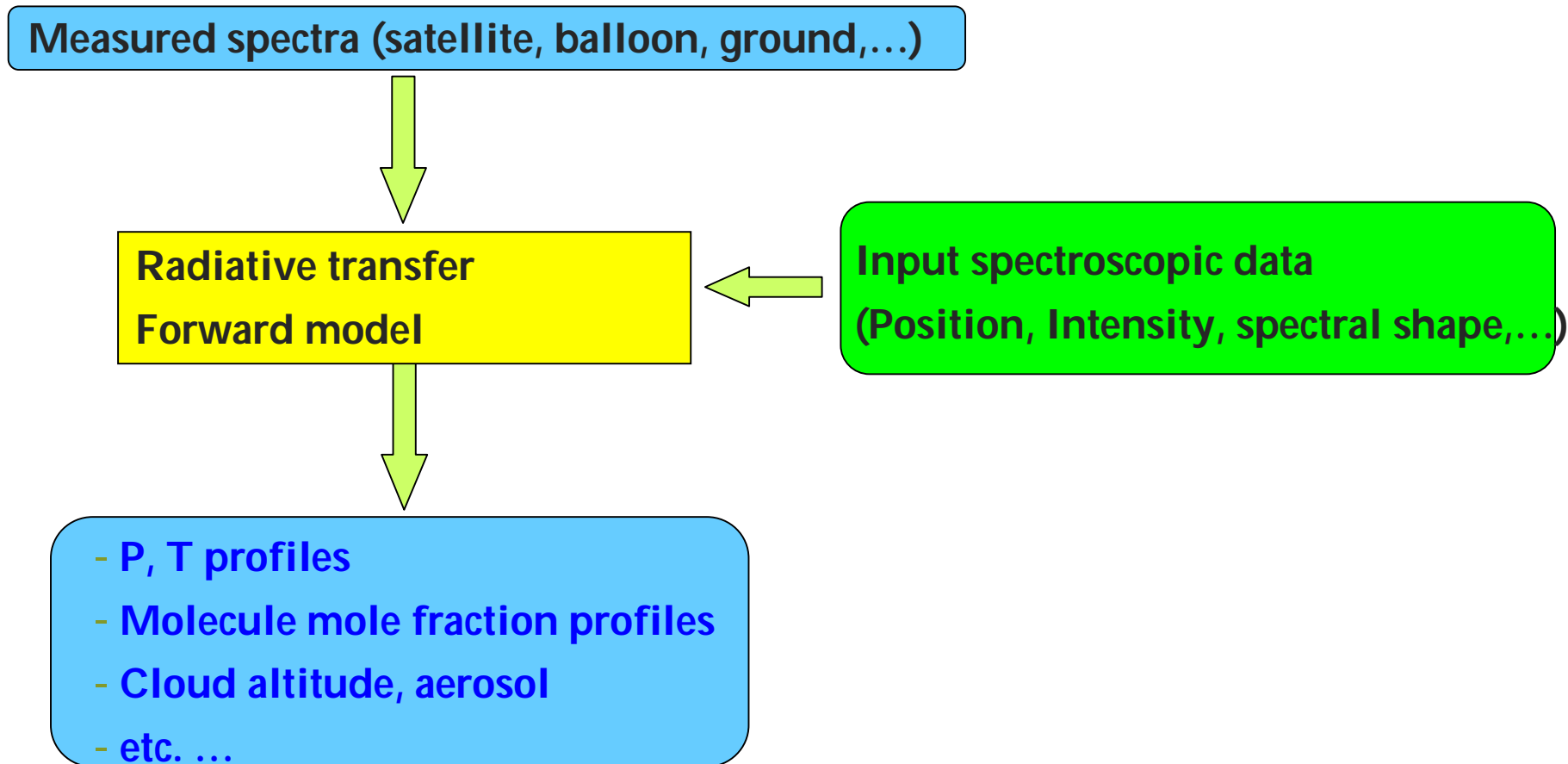Atmospheric spectra analysis; Green House Gases Remote Sensing

Education and Professional Experience

2013	Habilitation thesis, senior researcher at National Center for Scientific Research (CNRS)
Since 2007	Researcher at CNRS
2006-2007	Postdoctoral research associate, Laboratoire de Physique Moléculaire et Application, Pierre and Marie Curie University
2004-2006	Postdoctoral research associate, Laboratoire Interuniversitaire des Systèmes Atmosphériques, Université Paris 12
2004	Ph. D. Thesis, Université de Franche-Comté
2001	Master of Science in Physics, Université de Franche-Comté
2000	Bachelor of Science in Physics, Hanoi National University of Education

Outline

- **Introduction: Atmospheric observation and spectral shape**

- **The Doppler, Lorentz and Voigt profiles**

- **The limits of the Voigt profile**

- **Widely-used non-Voigt approaches**

- **A new line-shape model for spectroscopic databases and applications**

- **Line-mixing for closely spaced lines**

- **Conclusions**

Introduction: atmospheric retrieval

Measured spectra (satellite, balloon, ground,…)

↓

Radiative transfer Forward model ← **Input spectroscopic data (Position, Intensity, spectral shape,…)**

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

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

Introduction: Atmospheric observations

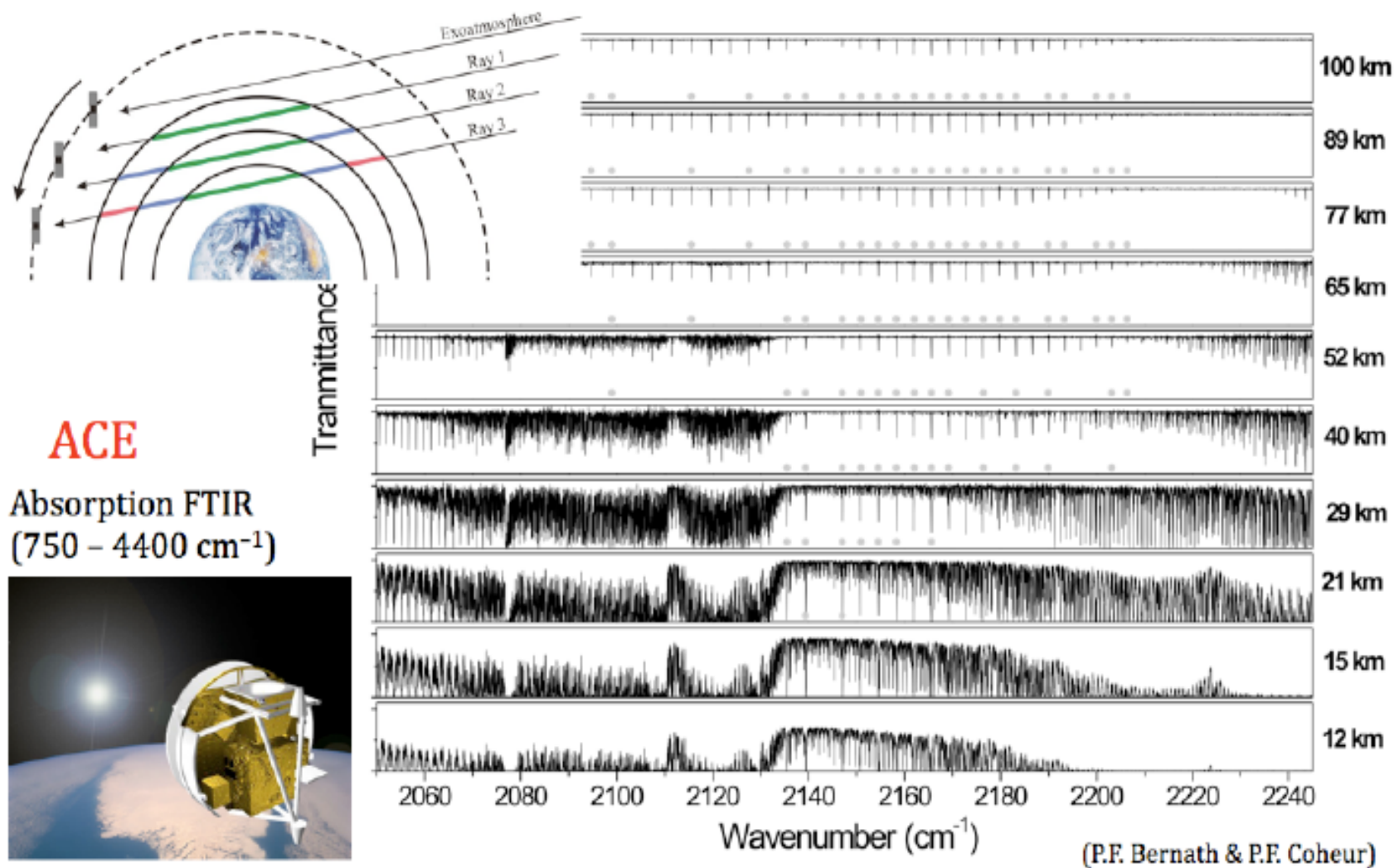- *In situ* measurements, generally using lasers.
    On ground, balloons, air planes Sounding a short (<u>single</u> T,P,vmr) path

- Remote measurements, generally using Fourier Transform (FT) spectrometers ;
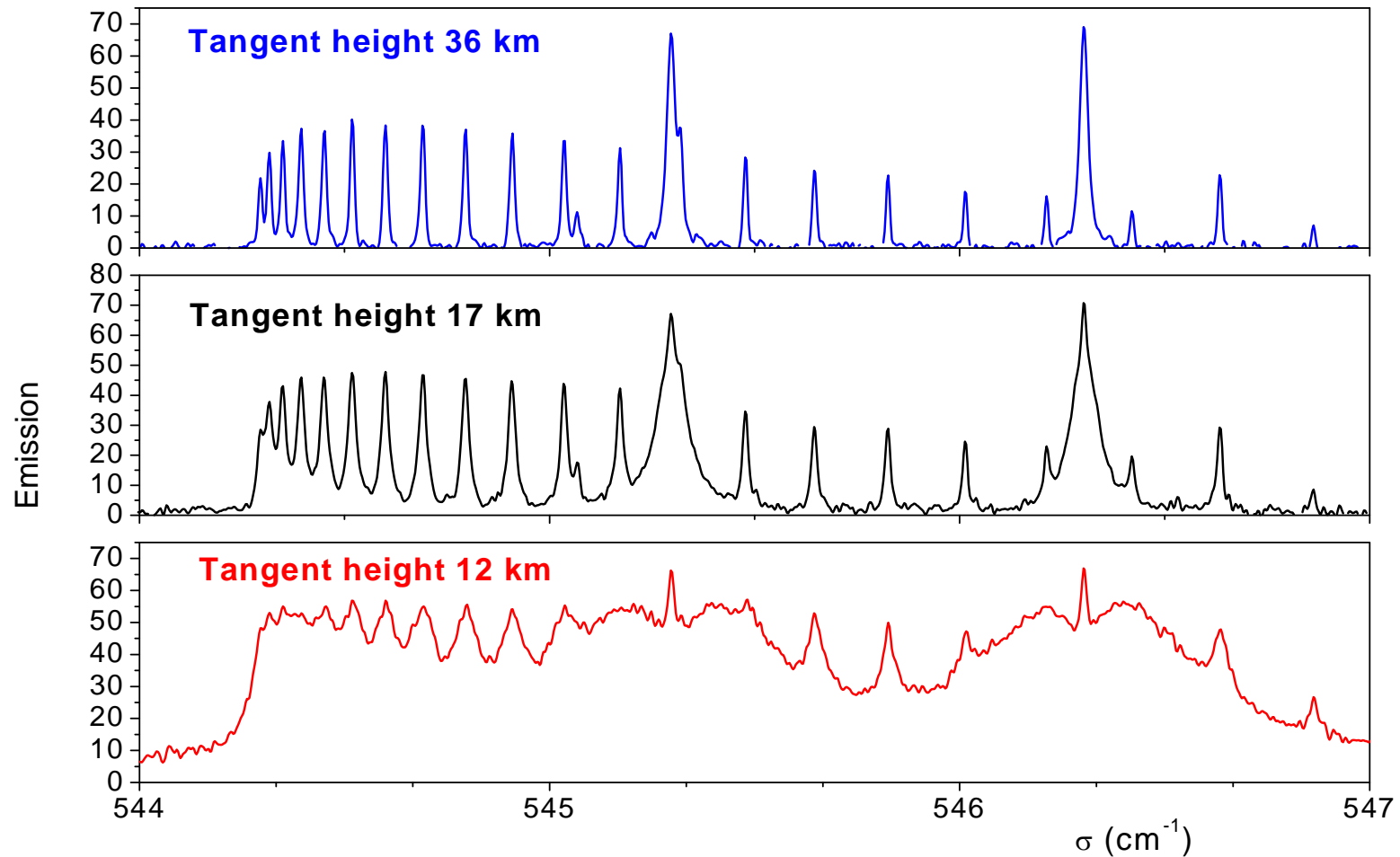   ground, balloons, air planes, satellites
Collecting the atmospheric emission or transmitted solar radiation (<u>many</u> T, P, vmr)

| Nadir | Ground based | Limb |
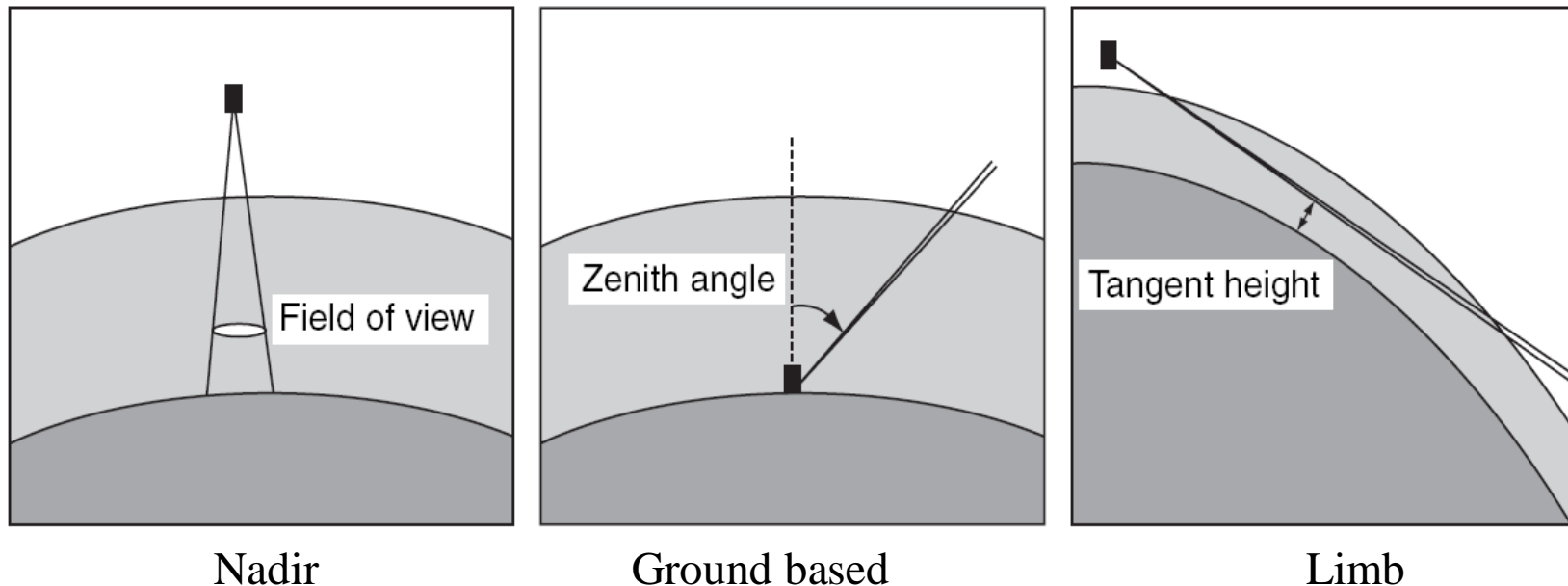
Remote sensing from space (occultation)

ACE

Absorption FTIR
$(750 - 4400 \text{ cm}^{-1})$

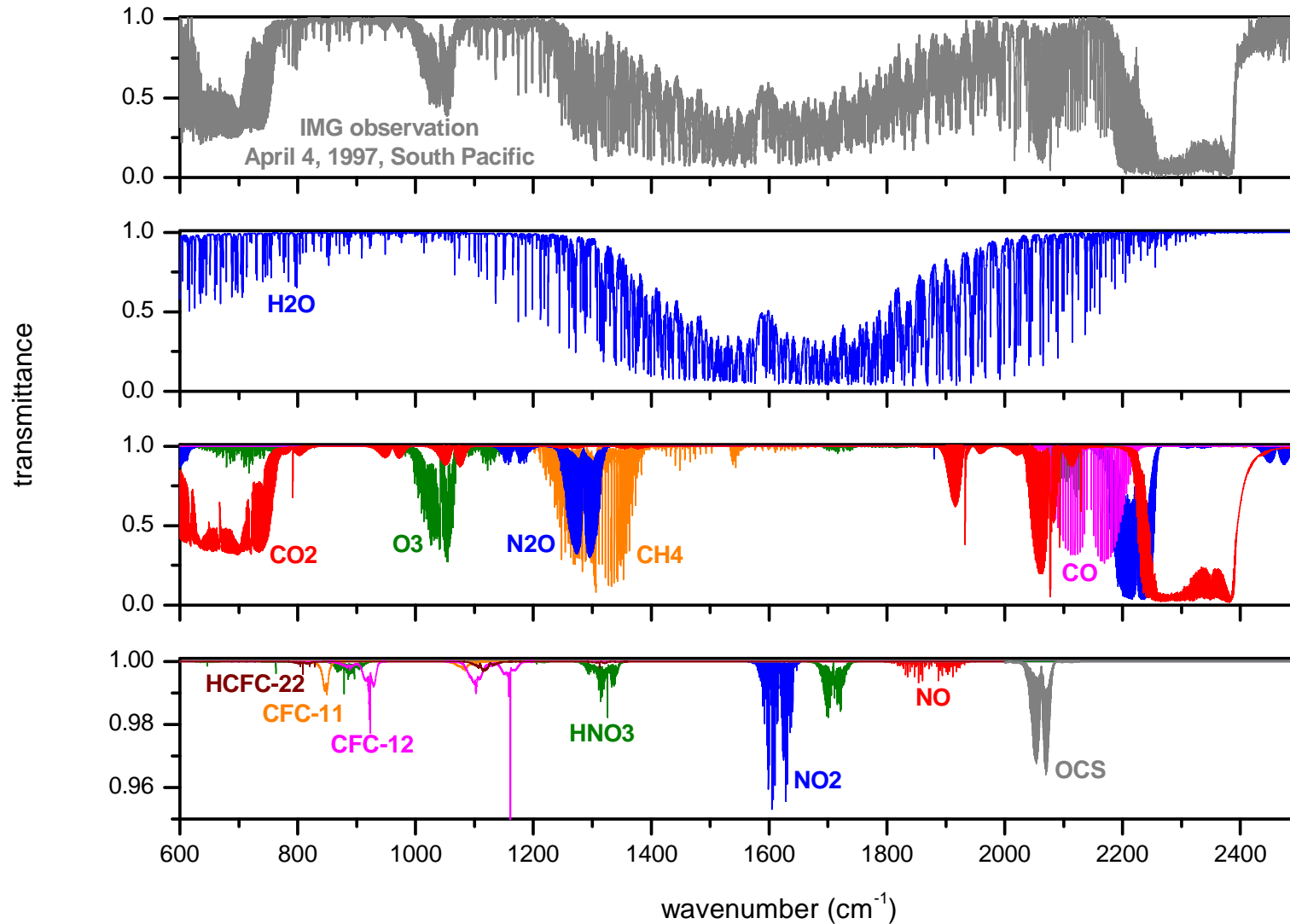(P.F. Bernath & P.F. Coheur)

# Atmospheric observations – example

Atmospheric emissions by a CO_2 Q-branch as observed by the balloon-borne Smithsonian Astrophysical Observatory FT Experiment for various tangent altitudes

Atmospheric observations – example

IMG: Interferometric Monitor for Greenhouse gases

Absorption coefficient

Gas sample
Cell of base length L,
$I_0(\sigma)$: input intensity
$I(\sigma)$: transmitted intensity
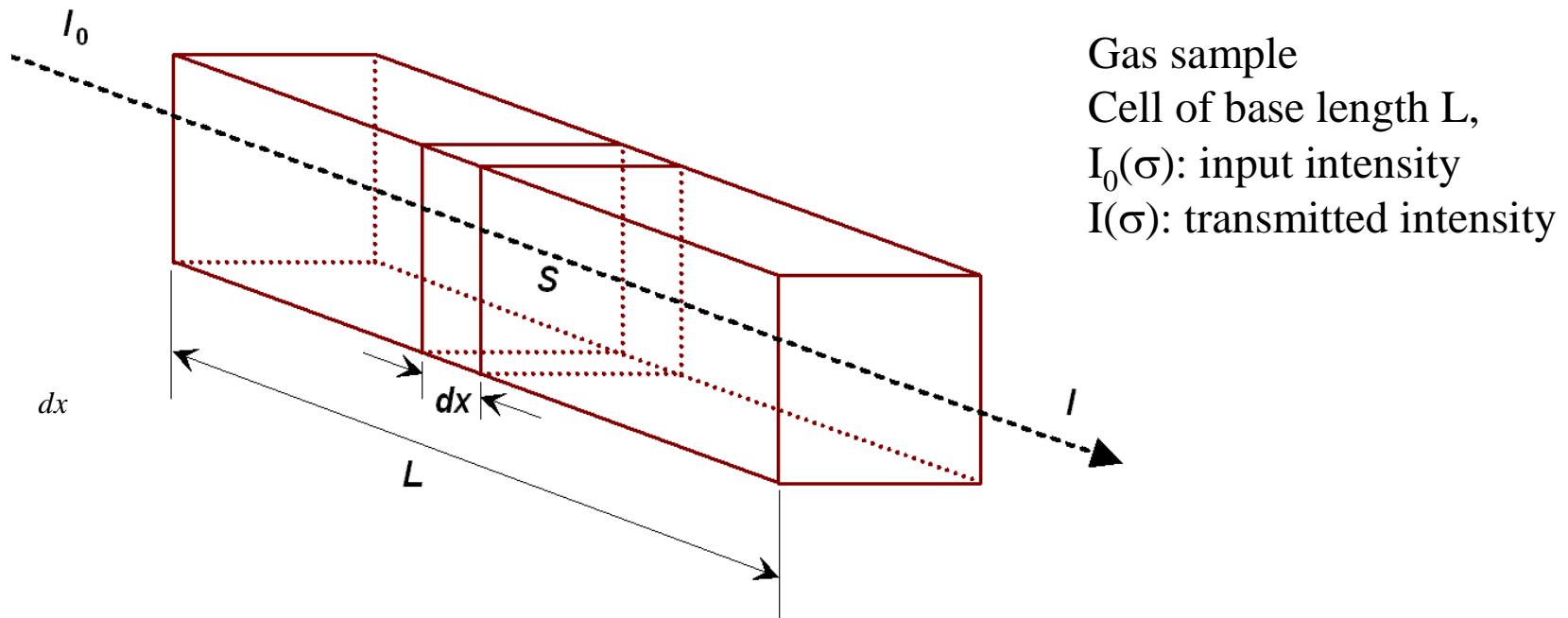
Let's consider a small volume of thickness dx.

$I(\sigma,x)$: Light intensity at the entrance of this volume

$dI(\sigma,x)$: its change due to absorption by the sample in this this volume. This change is:

- negative

- proportional to dx

- proportional to the incident intensity $I(\sigma,x)$
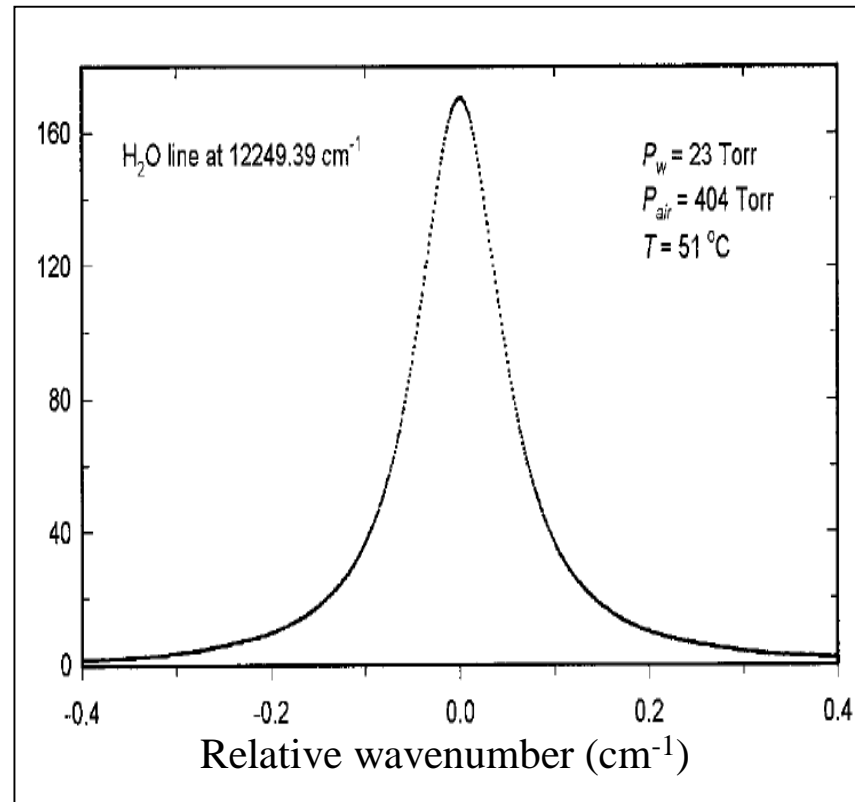
$$dI(\sigma,x) = -\alpha(\sigma,x)I(\sigma,x)dx$$

α (cm^{-1}) is the absorption coefficient

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Absorption coefficient
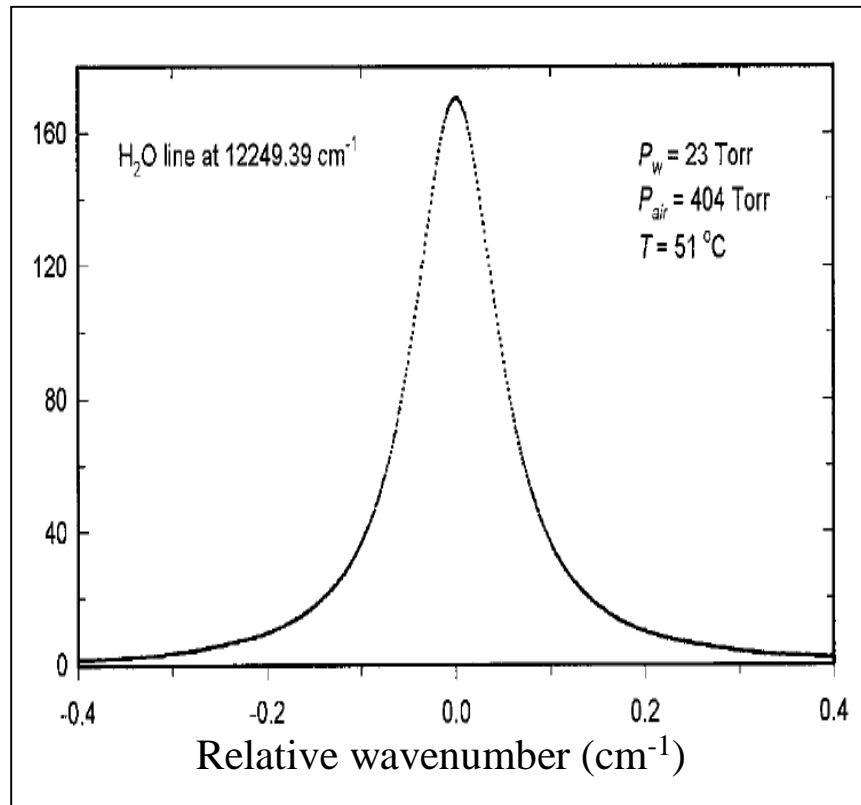
Homogeneous medium: absorption coefficient is independent of x

$$I_t(\sigma) = I_0(\sigma)e^{-\alpha(\sigma)L}$$ Beer-Lambert's law

$\alpha(\sigma)$ depends on the wavenumber since an absorption line (transition) is never strictly monochromatic

H_2O line at 12249.39 cm^{-1}

P_w = 23 Torr
P_{air} = 404 Torr
T = 51 $^\circ$C

Relative wavenumber (cm^{-1})

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Absorption coefficient

When line is isolated, its intensity is re-distributed over a spectral range around the resonance wavenumber σ_{fi}

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

S_{fi} is the integrated line intensity

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

I_{fi} is the normalized line shape

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

Doppler broadening

A molecule having a speed v#0, absorbs or emits at a wavenumber σ, which is different of σ_0 of this molecule at v=0.

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

The velocity distribution (1 dimension) is given by

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \exp\left(-\frac{mv^2}{2k_B T}\right)$$

with m the mass of the molecule, k_B the Boltzmann constant and T the temperature

Then the Doppler thermal width is given by :

$$\Delta v = \sqrt{2k_B T/m}$$

and in the wavenumber (frequency) domain :

$$\Delta\sigma_{thermal} = \sigma_{fi}\frac{\Delta v}{c} = \frac{\sigma_{fi}}{c}\sqrt{2k_B T/m}$$

Doppler broadening

Using these equations, wee can therefore deduce the Doppler broadened profile:

$$I_D\left(\sigma - \sigma_{fi}\right) = \frac{1}{\sqrt{\pi}\,\Delta\sigma_{thermal}} \exp\left\{-\left(\frac{\sigma - \sigma_{fi}}{\Delta\sigma_{thermal}}\right)^2\right\}.$$

The peak value at $\sigma = \sigma_{fi}$ is $I_0 = \dfrac{1}{\sqrt{\pi}\,\Delta\sigma_{thermal}}$

The value at the half-maximum is :

$$0.5 I_0 = 0.5 \frac{1}{\sqrt{\pi}\,\Delta\sigma_{thermal}} = \frac{1}{\sqrt{\pi}\,\Delta\sigma_{thermal}} \exp\left\{-\left(\frac{\sigma_{1/2} - \sigma_{fi}}{\Delta\sigma_{thermal}}\right)^2\right\}.$$
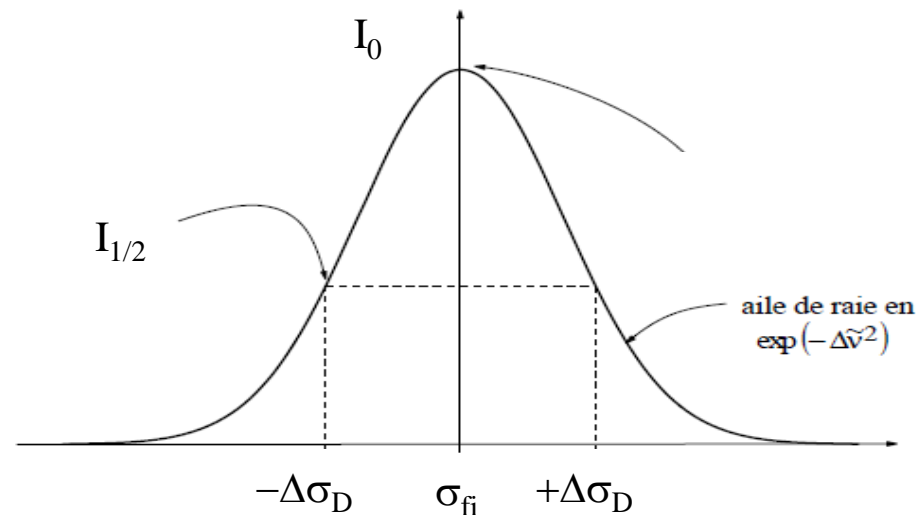
Doppler broadening

Therefore, the line-width (HWHM) of the Doppler profile is $\Delta\sigma_D = \Delta\sigma_{thermal}/\sqrt{ln2}$

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

where $\Delta\sigma_D = \left[\dfrac{2k_BT}{mc^2}ln2\right]^{1/2}\sigma_{fi}$ is the HWHM of the line.

$\Delta\sigma_D \approx 3.58\ 10^{-7}\sigma_{fi}\sqrt{\dfrac{T}{M}}$ (cm^{-1}) with M the molar mass (g/mol), σ_{fi} the wavenumber (cm^{-1})

Application:

- Given that $\int_{-\infty}^{\infty} e^{-ax^2}\, dx = \sqrt{\dfrac{\pi}{a}}$, showing that the Doppler profile is normalized to 1

Determine the Doppler HWHM of a transition of water vapor at 12249.3895 cm^{-1} at 23°C

The Lorentz broadening and shifting

For an isolated transition, the **main** effects of intermolecular collisions (pressure) are the broadening and shifting of the line
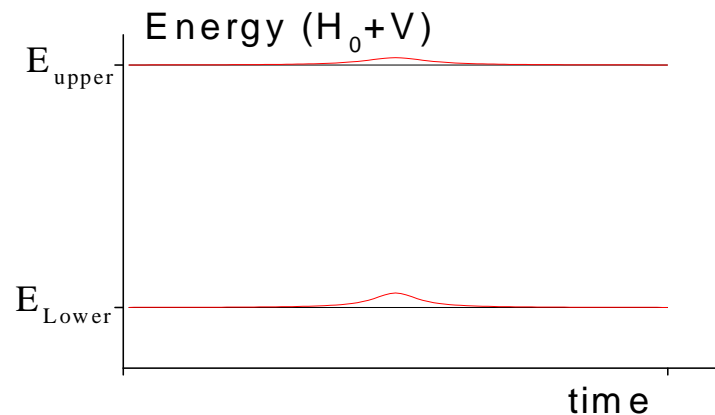
When a molecule A is in collision with another molecule, its lower and upper energy levels (E_{lower}, E_{upper}) will be modified due to collision. This modification depends on the distance and the relative orientation between the two molecules. The life time of the molecule on its energy levels is thus modified. Therefore, this leads to a broadening of the line.

In general, the modification of E_{lower} is different of that of E_{upper}, this difference thus leads to a line shifting. The profile is a Lorentz function
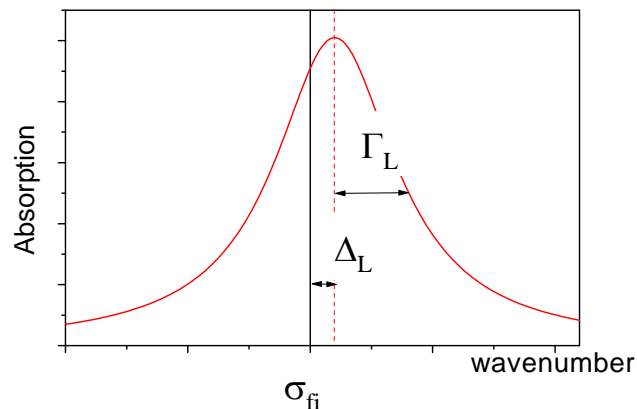
$$I_L(\sigma - \sigma_{fi}) = \frac{1}{\pi} \frac{\Gamma_L}{\left(\sigma - \sigma_{fi} - \Delta_L\right)^2 + \Gamma_L^2}$$

+ Γ_L is the HWHM

+ Δ_L is the line shift

The Lorentz broadening and shifting

ν_3, R(1) line of CH_4-N_2

— 0.50 atm
— 0.24 atm

Absorption

wavenumber

3038.4   3038.5   3038.6
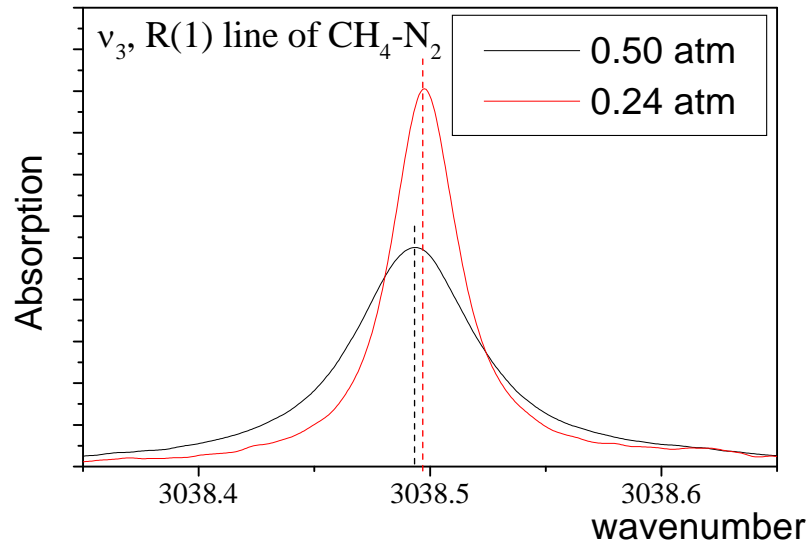
+ Γ_L (HWHM) and Δ_L (shift) proportional to the # of coll (dens or P)

+ In spectroscopy, we also use the pressure-normalized width and shift:

  $\gamma_L = \Gamma_L/P$ and $\delta_L = \Delta_L/P$

→ line broadening and line shifting coefficients

Application:

Given that $\int \frac{dx}{x^2+1} = \arctan(x)$, show that the Lorentz profile is normalized to 1

What is the main broadening mechanism for a transition of CO_2, located at 6000 cm^{-1} at room temperature (25°C) and 1000 mbar giving that its Lorentz broadening coefficient is 0.05 cm^{-1}/atm

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The Lorentz broadening and shifting: The case of a mixture

The active molecule   A
The collision-partner   B

$$\Gamma_L = \gamma_{A\text{-}A}\, P_A + \gamma_{A\text{-}B}\, P_B$$

$\gamma_{A\text{-}A}$: self-broadening coefficient
$\gamma_{A\text{-}B}$: broadening coefficient due to collision with molecules B

In the atmosphere, the two main perturbators are N_2 and O_2. However, sometimes we need to consider also self-broadening: for H_2O for instance, its partial pressure is relatively small with respect to that of N_2 and O_2 but its collision efficiency is about 5 times larger than that of N_2 and O_2.

For a species A in the atmosphere, one can write:

$$\Gamma_L = \gamma_{A\text{-}N2}\, P_{N2} + \gamma_{A\text{-}O2}\, P_{O2} + \ldots$$

$$P_{N2} = 0.78084\ P$$

$$P_{O2} = 0.209476\ P \qquad\qquad \Gamma_L = \gamma_{A\text{-}air}\, P$$

$$P_{Ar} = 0.00934\ P$$

The Lorentz broadening and shifting: Temperature dependence

For the Earth atmosphere, we need to know also the temperature dependence of the broadening coeficients. This temperature dependence is usually given by

$$\gamma_{A-air}(T) = \gamma_{A-air}(T_{ref})(\frac{T_{ref}}{T})^n$$

with T_{ref} = 296 K and n the temperature exponent of the broadening coefficient, n depends on the active molecule and on the collision-partner as well as on the considered line.

γ_{A-air} and n are given in (atmospheric) spectroscopic databases such as HITRAN, GEISA

<u>Application</u>: Calculate the Lorentz HWHM, Γ_L of a water vapor transition which has $\gamma_{L,H2O-N2}$ (296 K) = 0.0923 cm^{-1}/atm, $\gamma_{L,H2O-O2}$ (296 K) = 0.1153 cm^{-1}/atm, n=0.64 for the following atmospheric conditions:

1. At an altitude of 24 km of Polar Arctic Winter: T=300K, P=0.02 atm

2. At the surface: T = 300K, P=1 atm

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The Voigt profile

When the pressure increases from the pure Doppler regime (zero pressure) to the pure collisional regime (Doppler effect negligible) :

-There is an intermediate regime in which collisions will change the molecule velocities which will thus change the Doppler effect. In the same time, these collisions will also modify the internal state of the line and then broaden the line

-In this intermediate regime, the Doppler effect is not completely vanished and collisional broadenings occur. These two effects thus have to be taken into account → The Voigt profile

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:

$$I_D(\sigma'- \sigma_{fi}) \, d\sigma' \, I_L(\sigma- \sigma')$$
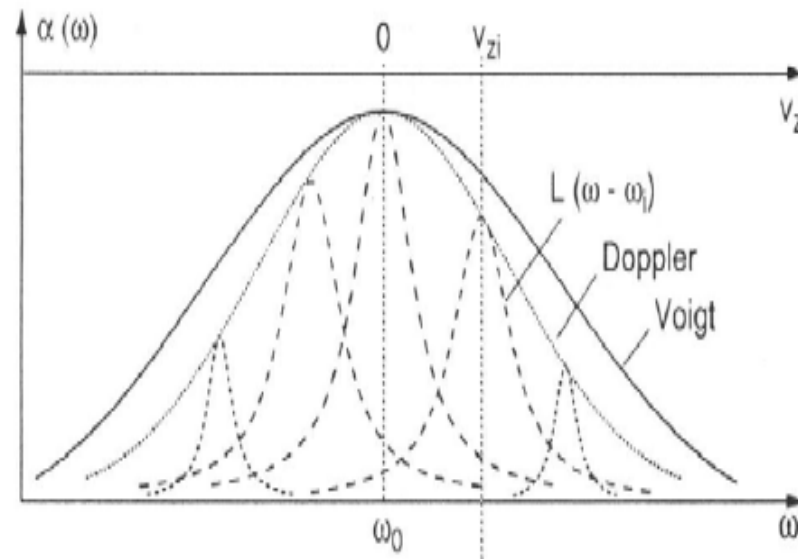
The resulting profile is then obtained by summing over all speed classes (or all σ') :

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

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

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The Voigt profile

The Voigt profile $\quad I_V(\sigma - \sigma_{fi}) = \displaystyle\int_{-\infty}^{+\infty} d\sigma' I_D(\sigma' - \sigma_{fi}) I_L(\sigma - \sigma')$

with :

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

and

$$I_L(\sigma - \sigma_{fi}) = \frac{1}{\pi} \frac{\Gamma_L}{(\sigma - \sigma_{fi})^2 + \Gamma_L^2}$$

Using $\quad x = \sqrt{\ln 2}\left(\dfrac{\sigma - \sigma_{fi}}{\Delta\sigma_D}\right) \qquad y = \sqrt{\ln 2}\,\dfrac{\Gamma_L}{\Delta\sigma_D}$

We have :

$$I_V(\sigma - \sigma_{fi}) = \frac{1}{\Delta\sigma_D}\sqrt{\frac{\ln 2}{\pi}} K(x, y) \qquad K(x, y) = \frac{y}{\pi} \int_{-\infty}^{+\infty} dt \frac{e^{-t^2}}{y^2 + (x - t)^2}$$

with K the error function

The Voigt profile

Application:

- Determine the Doppler and Lorentz broadenings for the H_2O transition considered above (position $\sigma=3064.4041$ cm^{-1}). Compare the two broadenings and conclude about the type of line profile which should be used for the two situations (polar stratosphere and tropical troposphere)

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The Doppler, Lorentzian and Voigt profiles

Pressure

Lorentzian

Doppler+Collision

Doppler

Usual behavior of an absorption line width
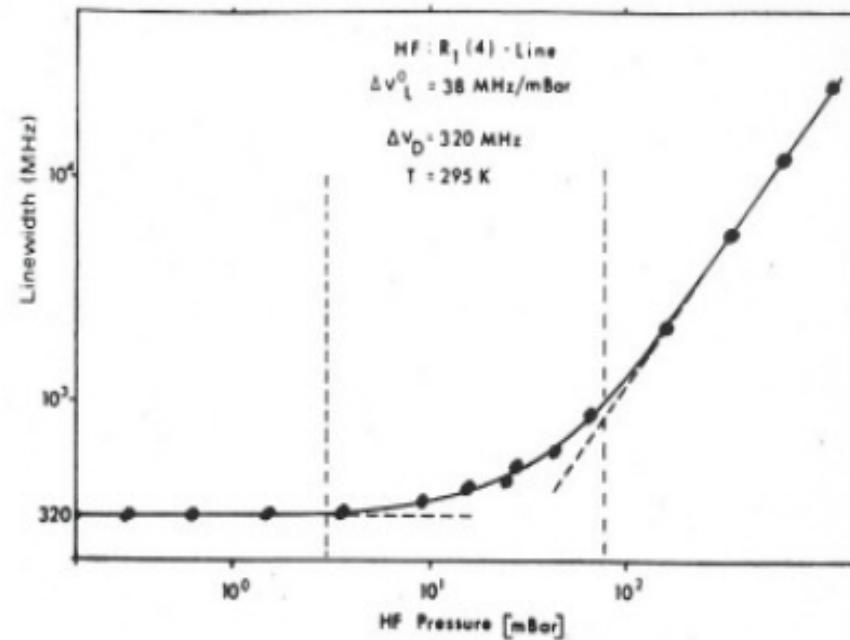
Linewidth dependence of HF absorption line on pressure.

The Gaussian, Lorentzian and Voigt profiles
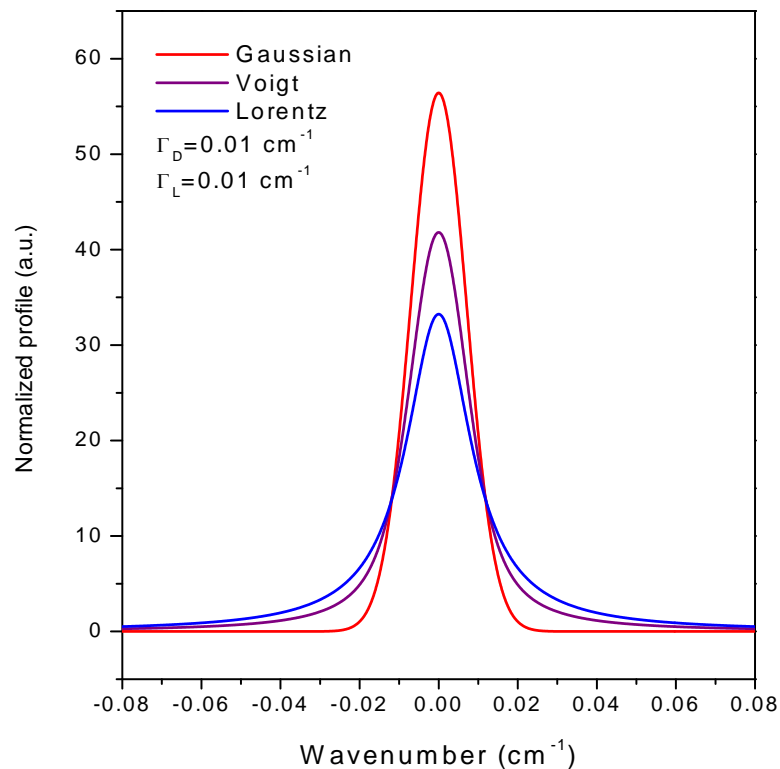
FTS ground-based absorption spectrum (CO_2)
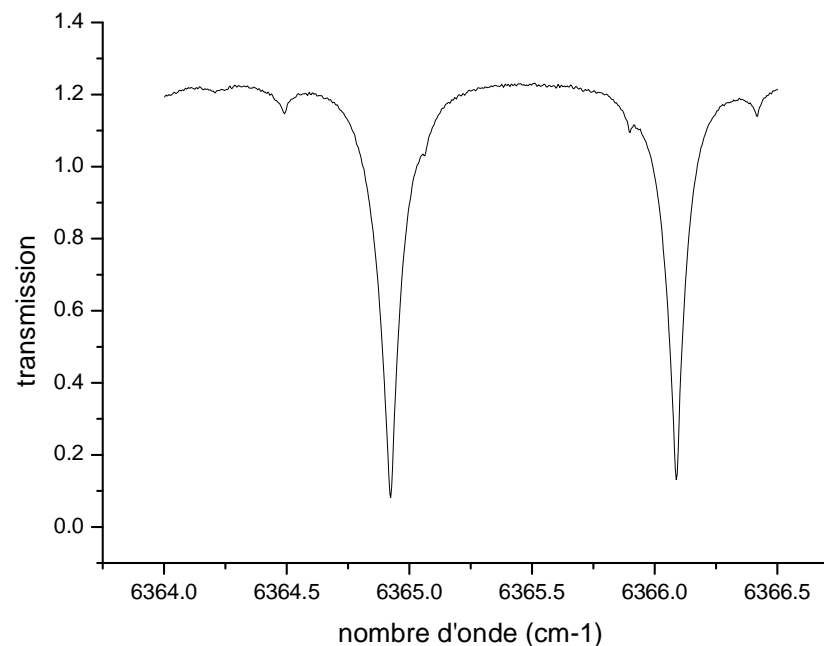
Comparaison between the Doppler, Lorentz and Voigt profiles.

The Gaussian, Lorentzian and Voigt profiles

Application: Absorption spectra of a CO line at room temperature and three pressures
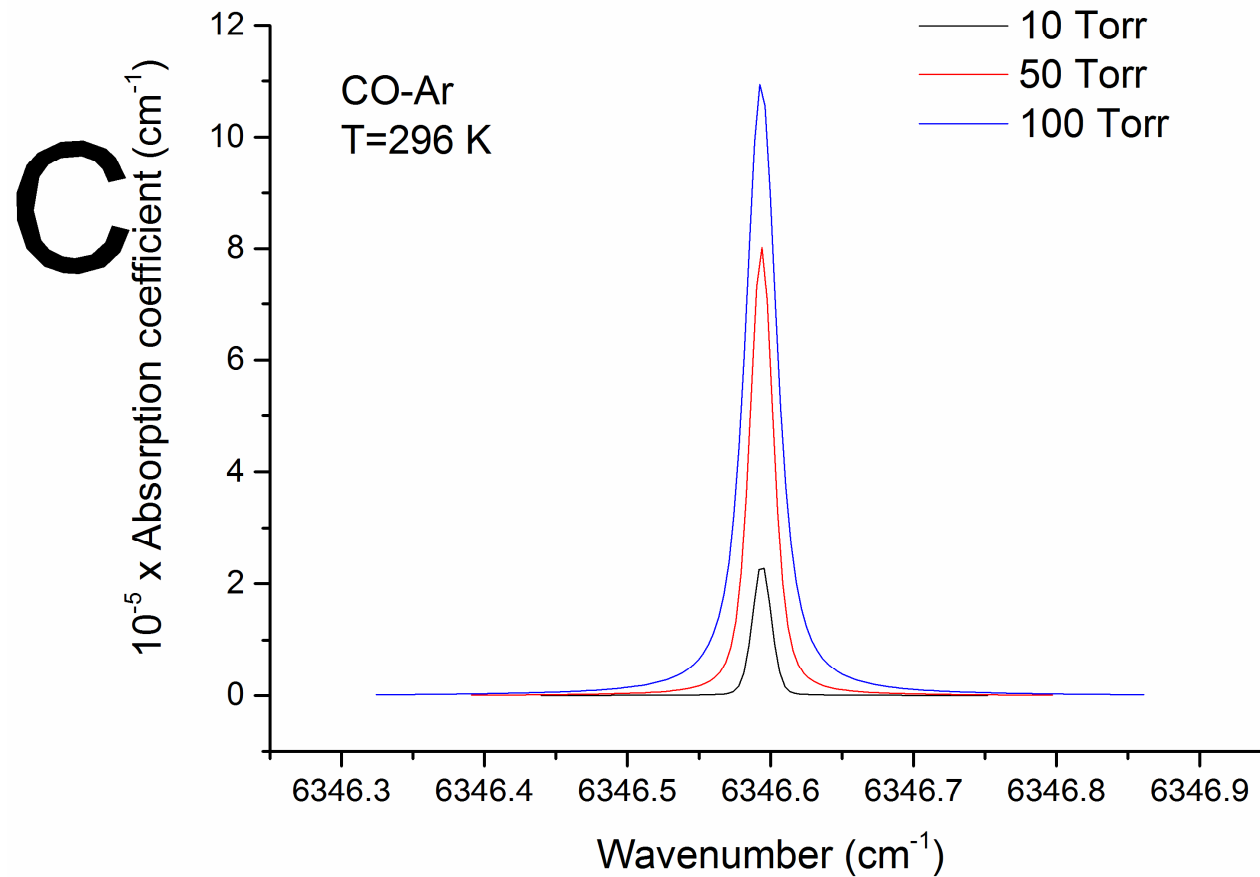
The Gaussian, Lorentzian and Voigt profiles

Application: Absorption spectra of a CO line at room temperature and three pressures

- Determine the Doppler broadening

- Use the executable to fit these spectra using the Voigt profile

In this fitting code the following parameters are adjusted:

1. The position of the maximum absorption

2. The half-width at half-maximum of the line

3. The area of the line

4. Two parameters describing a linear base line

- Compare the Lorentz and Doppler half width for each spectrum

- From the adjusted parameters, calculate the line position, line broadening coefficient and line shifting coefficient

Non-Voigt effects on the line-shape

Limits of the Voigt profile
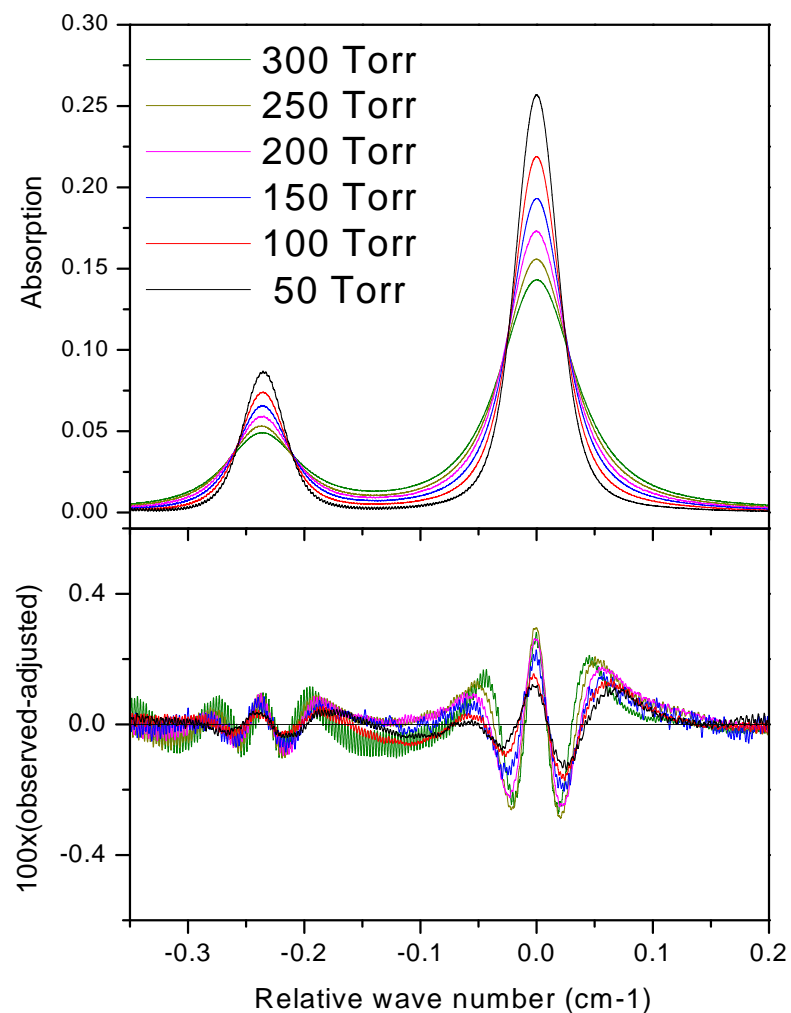
Measured and adjusted spectra using the Voigt profile.

H_2O/N_2, ν_3 band, $11_{1,11} \leftarrow 10_{1,10}$ $11_{0,11} \leftarrow 10_{0,10}$
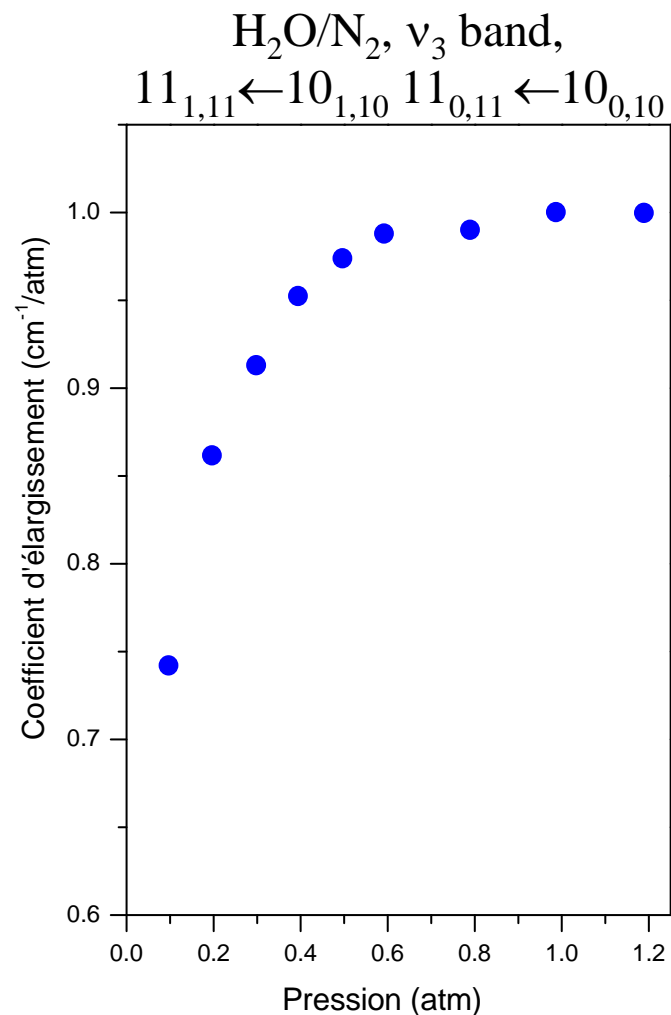
Ngo et al, JQSRT, 2012

Limits of the Voigt profile

The Voigt profile neglects:

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

   The detailed balance:

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

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

   $\to$ reduction of the Doppler broadening $\to$ collisional narrowing effect or Dicke narrowing effect

2. **The speed-dependences** of the collisional width $\Gamma(v)$ and shift $\Delta(v)$ of the line.

   This also (in general) leads to a narrowing of the line
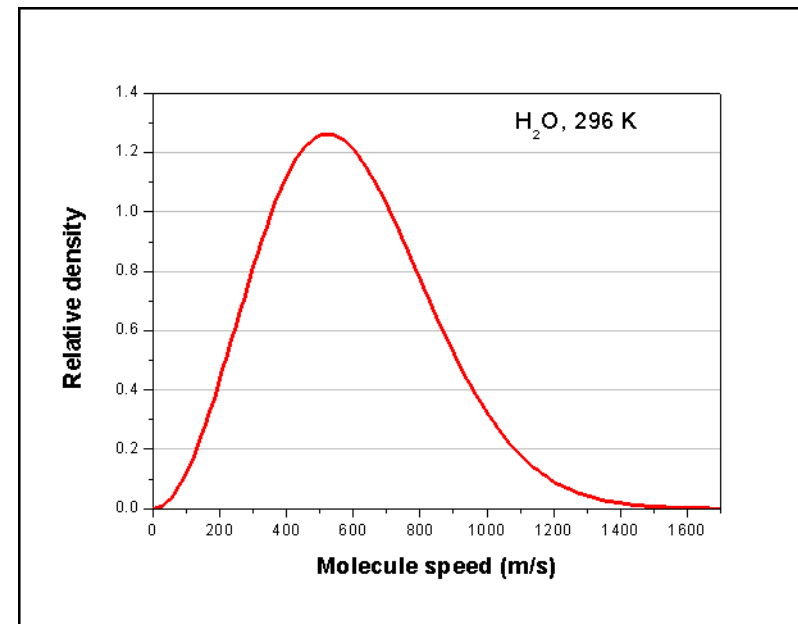
Limits of the Voigt profile: atmospheric retrieval

In situ absorption spectrum of tropospheric H_2O recorded by balloonborne diode laser and its fit using the Voigt profile
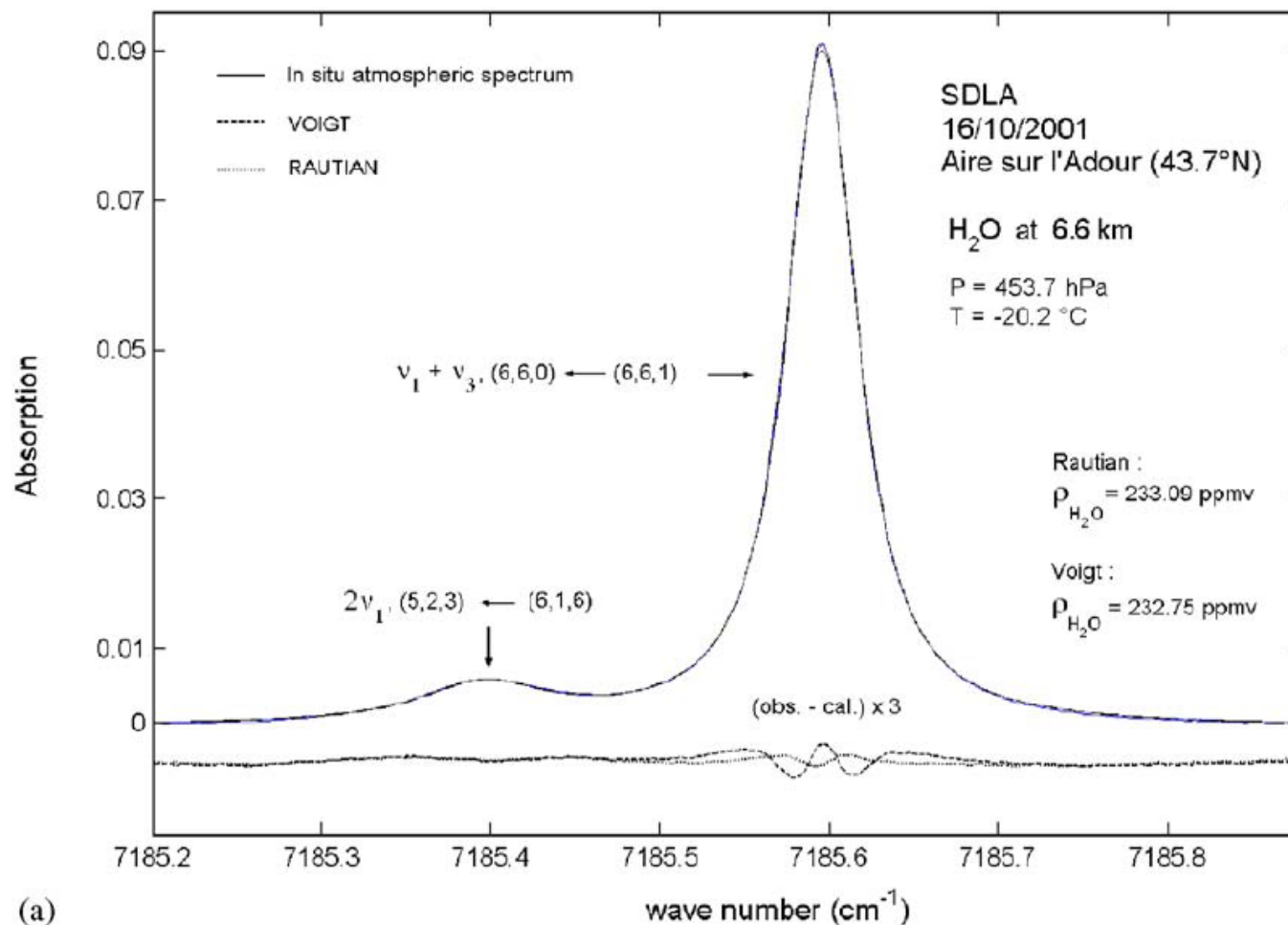
*Durry et al, JQSRT **94**, 387,2005*

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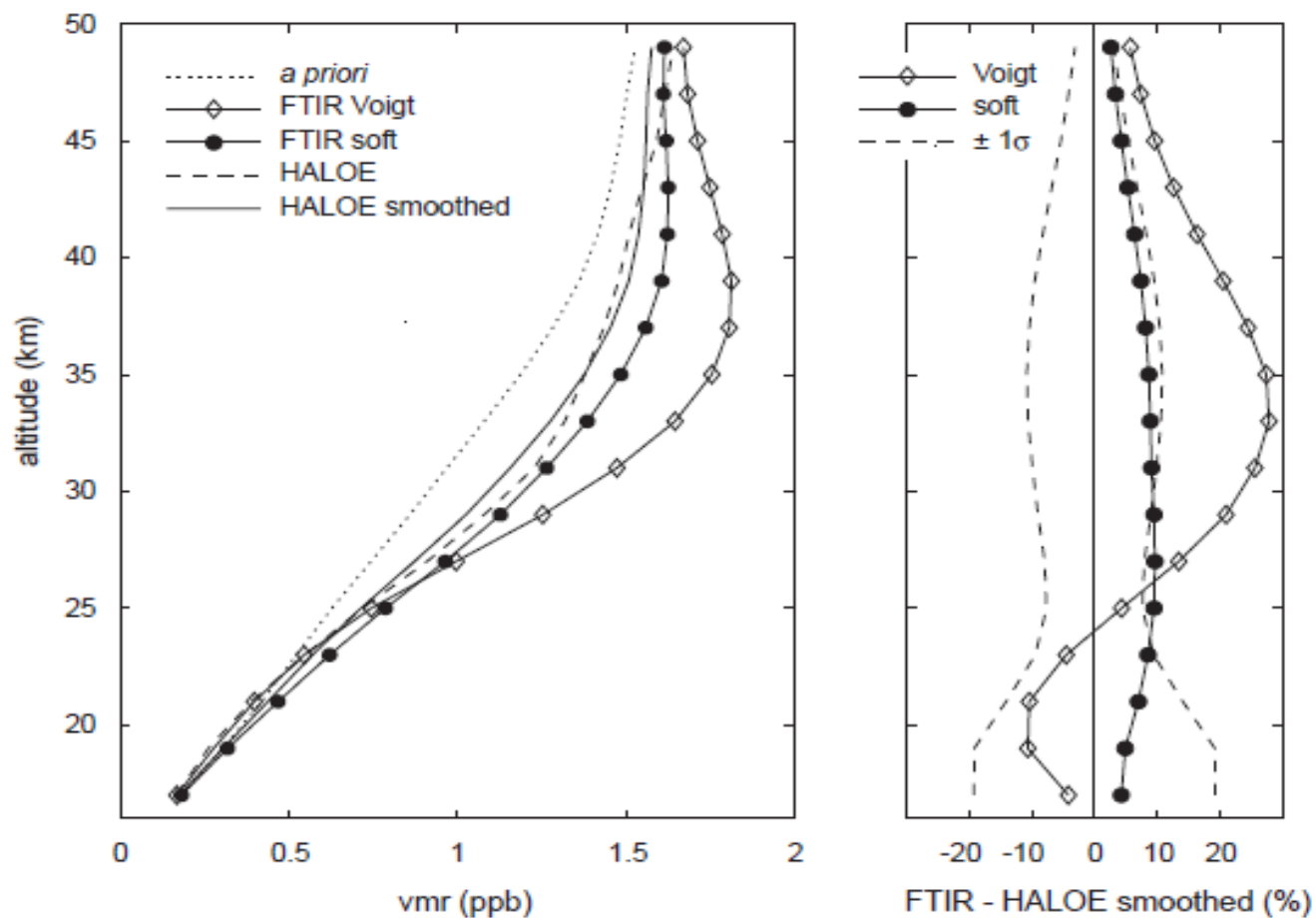
*Barret et al, JQSRT **95**, 499, 2005*

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 β

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

- Assumes that velocity memory is lost after each collision

- Introduces a velocity changing rate ν_{VC} also related to the diffusion coefficient

Experiences show that the Galatry profile and the Nelkin-Ghatak profile lead to similar quality in term of residual fit of measured spectra

Simple non-Voigt approaches: the velocity changes effect

Application: Absorption spectra of a CO line at room temperature and three pressures
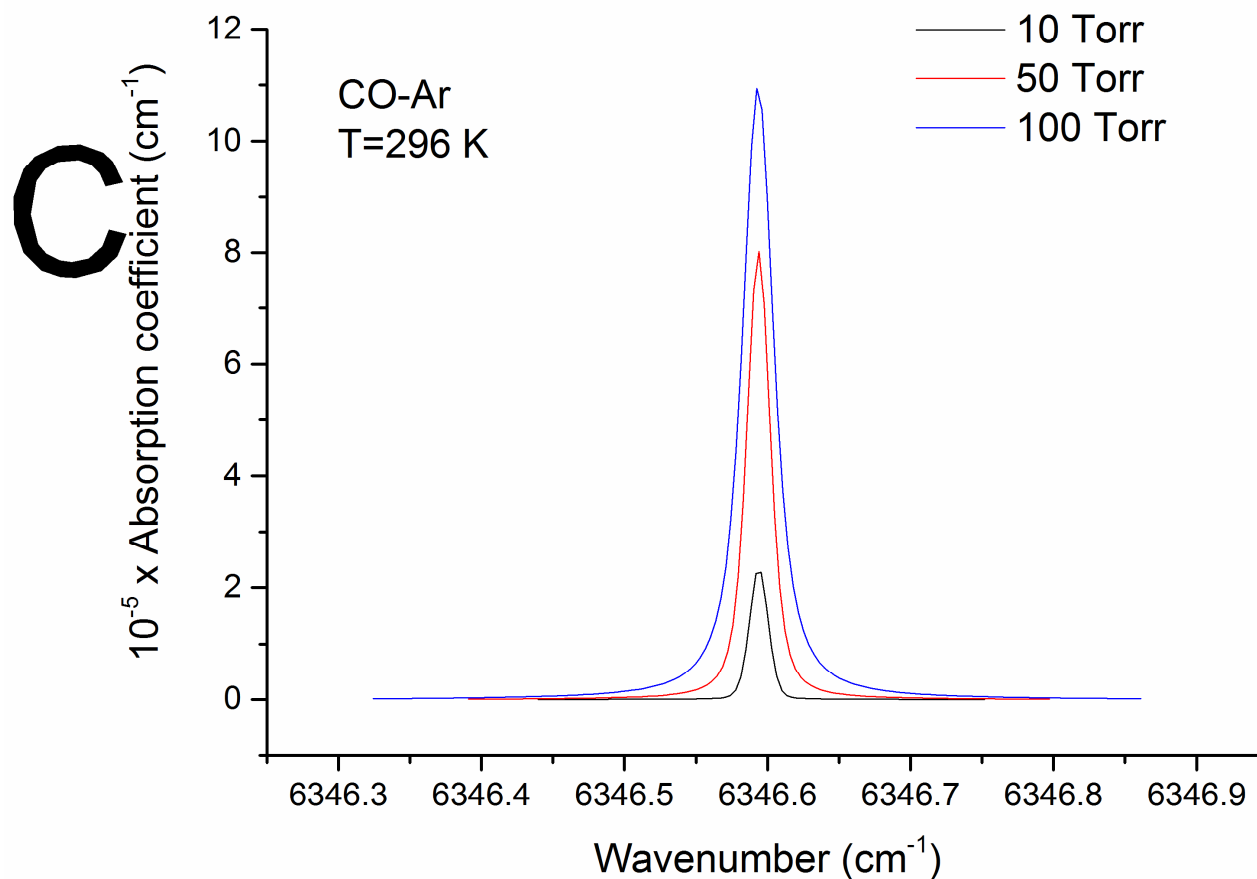
Simple non-Voigt approaches: the velocity changes effect

Application: Absorption spectra of a CO line at room temperature and three pressures

-Use the executable to fit the two first spectra using the Hard Collision profile

In this fitting code the following parameters are adjusted:

1. The position of the maximum absorption

2. The half-width at half-maximum of the line

3. The velocity changing rate β (the Dicke narrowing parameter $\nu_{VC}=\beta/P$)

4. The area of the line

5. Two parameters describing a linear base line

-From the adjusted parameters, determine the line position, line broadening, line shifting coefficients and the Dicke narrowing parameters

-Compare the fit residuals obtained with the HC and the Voigt profiles, compare the obtained parameters in the two cases

Simple non-Voigt approaches: the velocity changes effect
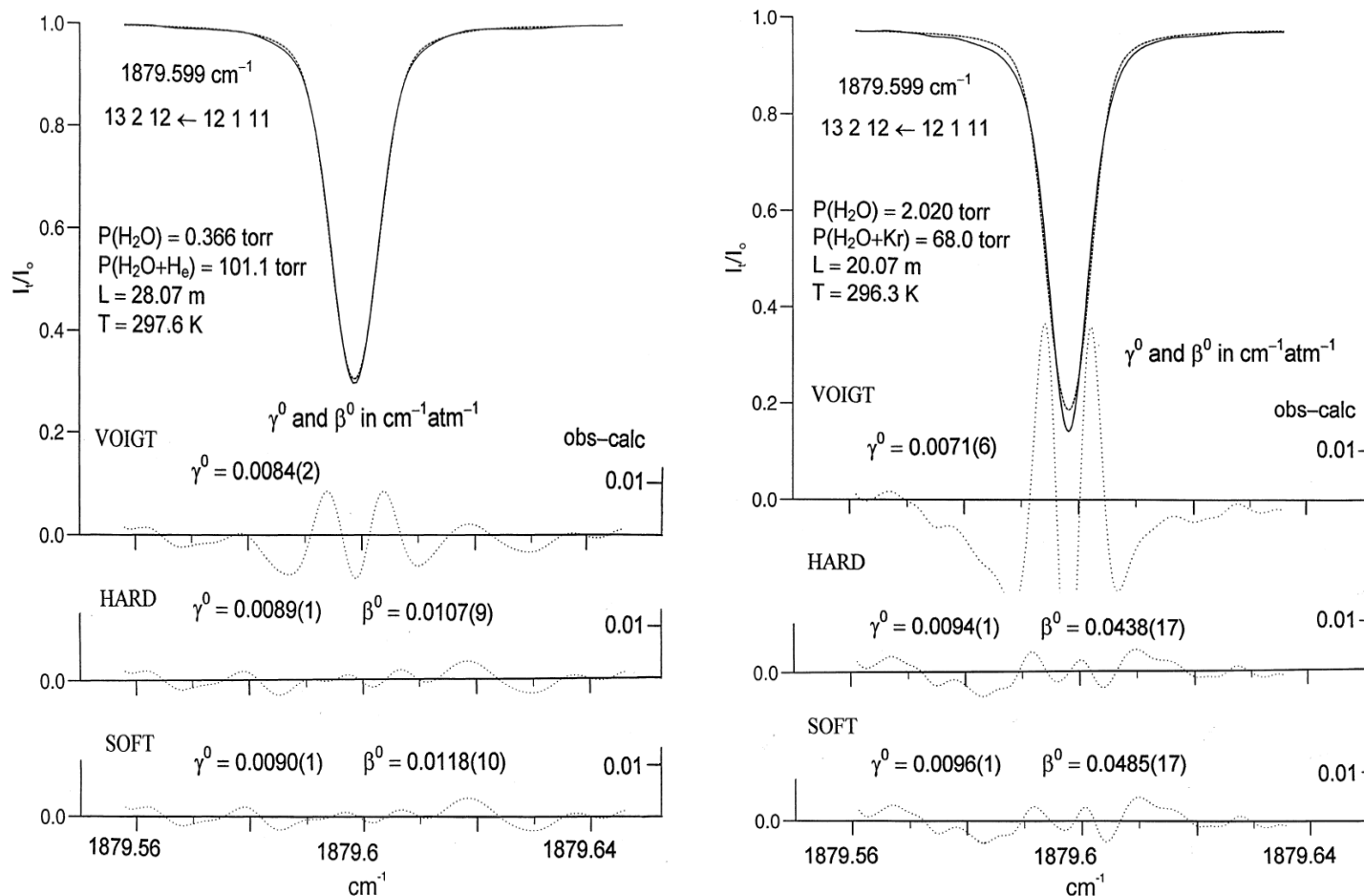
Claveau et al, JQSRT 68, 273, 2001

Velocity changes effects: Remaining problems
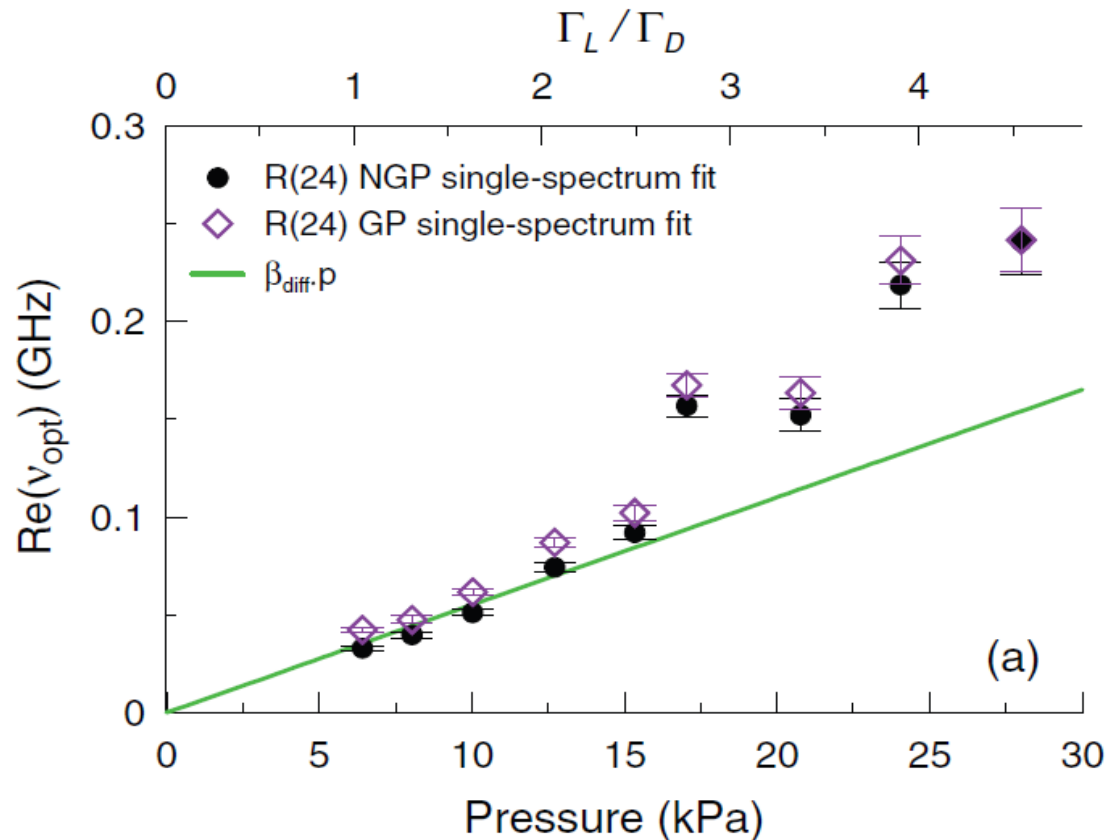
Bui et al, J. Chem. Phys., 141, 174301, 2014

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

Velocity changes effects: Remaining problems

4_{04}-3_{03} ν_3 band of H_2O in N_2: multi-spectrum fitting technique
99, 197, 294, 398, 499, 600, 797, 1000, 1200 hPa
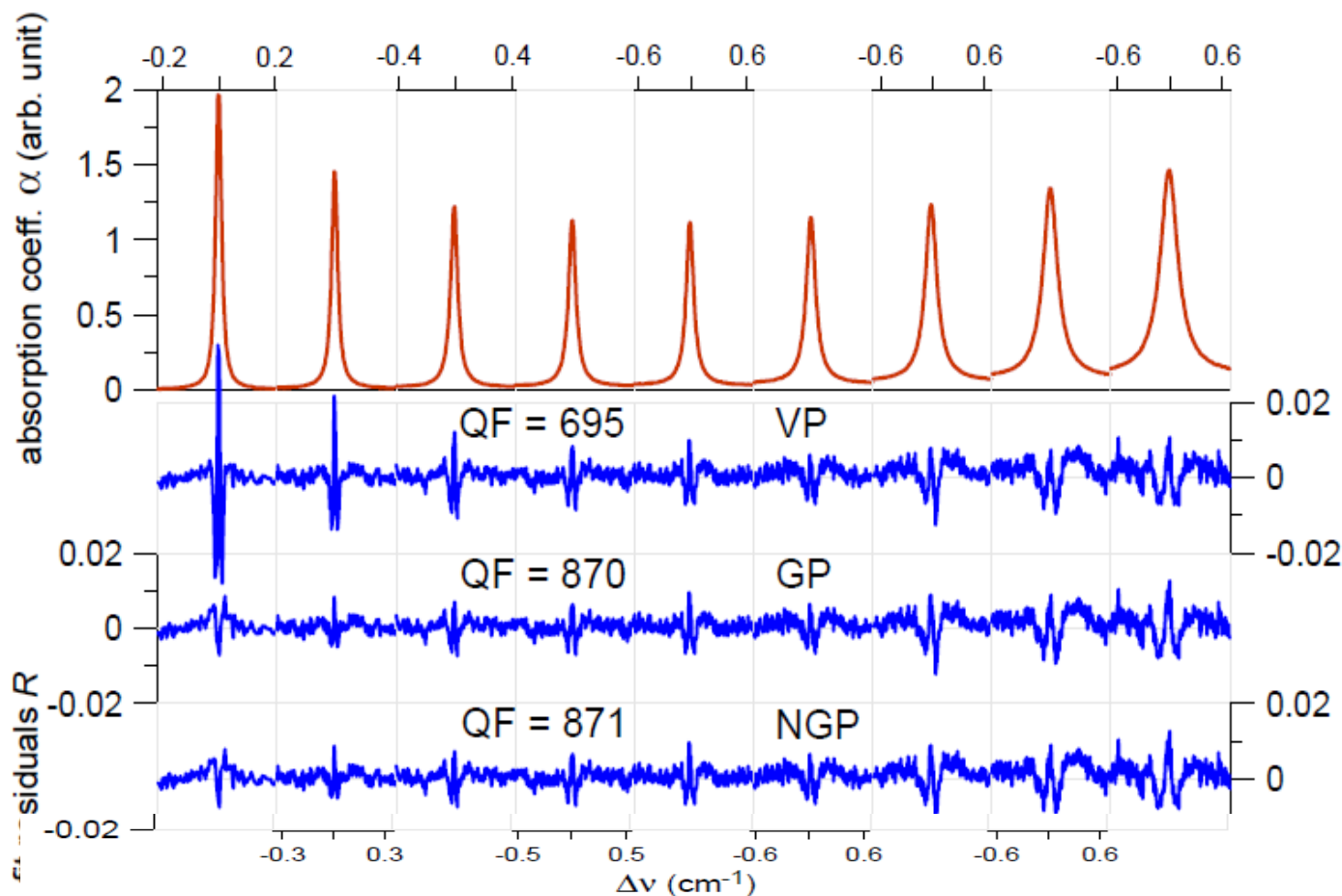
Lisak et al, JQSRT, 2015, accepted

→ *Only Dicke narrowing is insufficient*

Simple non-Voigt approaches: the speed dependences

- The polynomial dependence of Berman-Pickett

$$\Gamma(v_r) \propto v_r^{\,p} \qquad\qquad \Gamma(v_a) = \int \Gamma(v_r) . f(v_r | v_a) dv_r$$

- The quadratic dependence of Rohart

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

$m_{active} >> m_{buffer}$ $\qquad\qquad$ $m_{active} << m_{buffer}$

Weak speed dependence $\qquad\qquad$ Strong speed dependence

$v_a << v_r \# v_b$ $\qquad\qquad$ $v_a \# v_r >> v_b$

$\Gamma(v_a) \# \text{ Cte}$ $\qquad\qquad$ $\Gamma(v_a) \# \Gamma(v_r)$
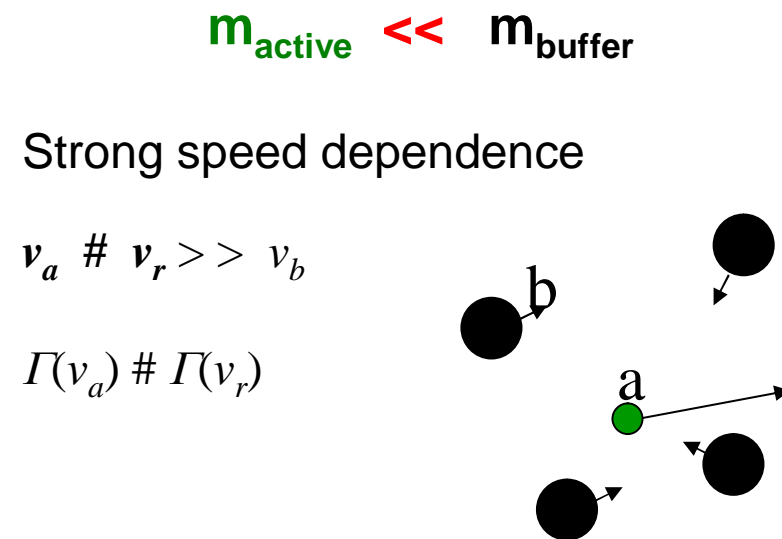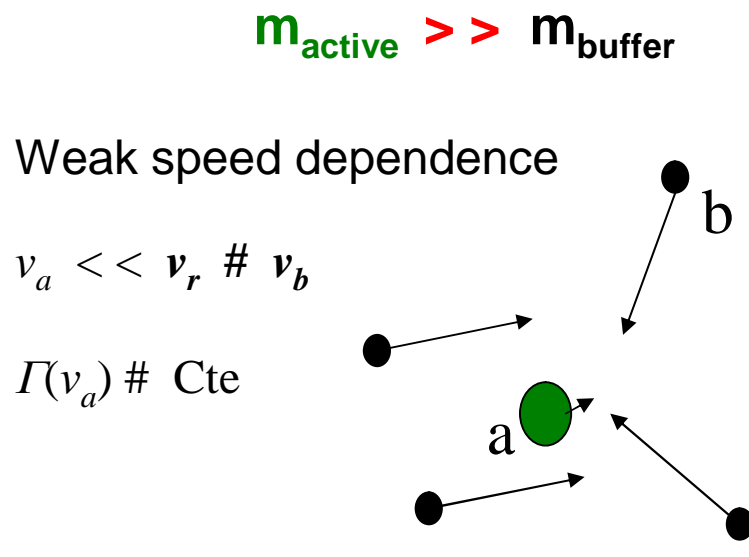
Courtesy of F. Rohart

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)
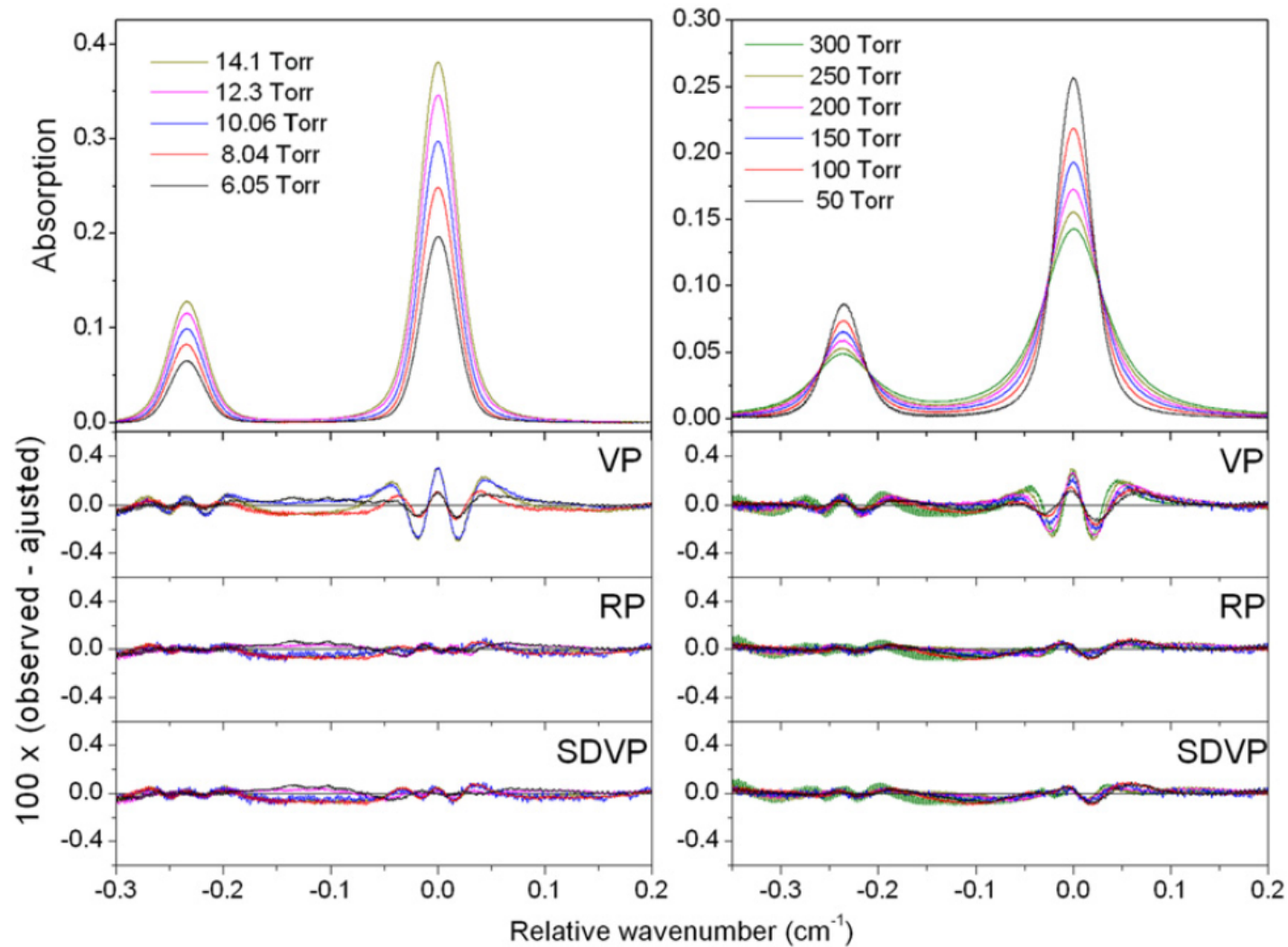
Ngo et al, JQSRT, 113, 870, 2012

Speed dependent Voigt profile: Remaining problems
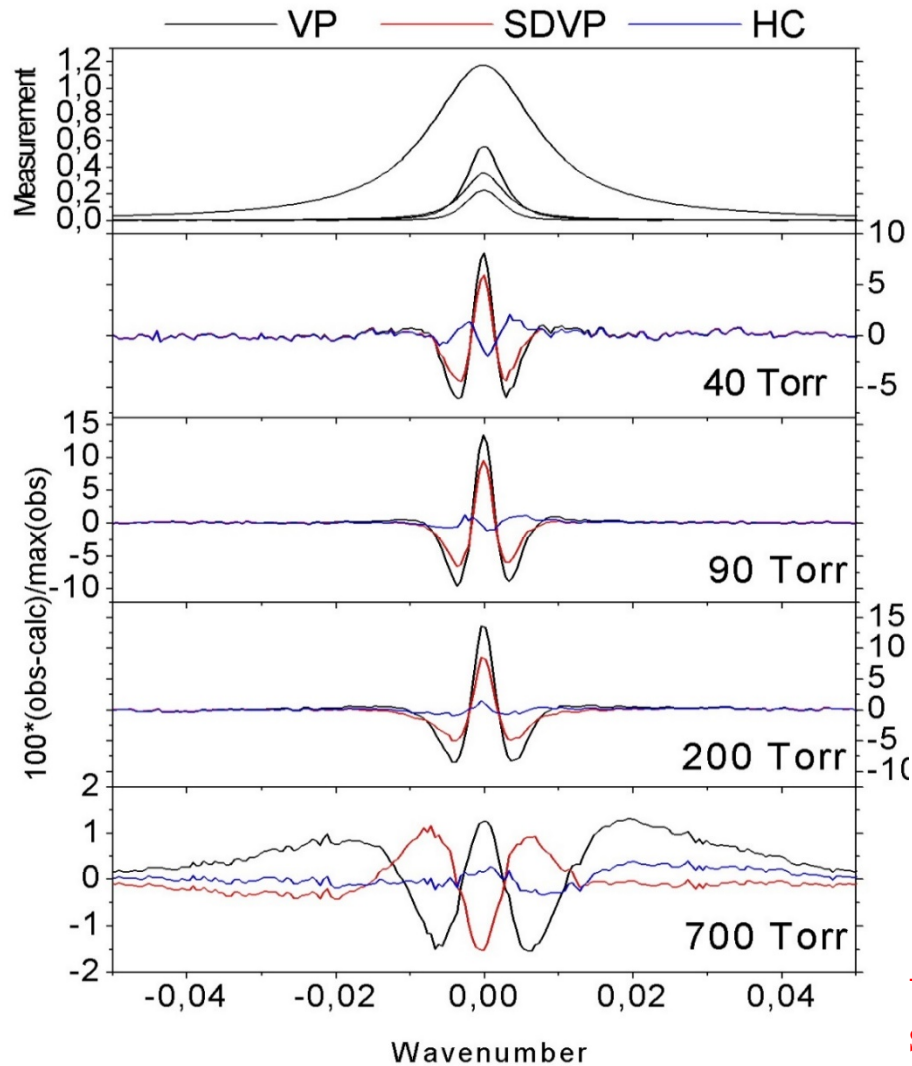
R(9) line of the fundamental band of HCl perturbed by Ar

→ Speed dependence only is not sufficient

Toward a new model: both speed dependences and Dicke narrowing
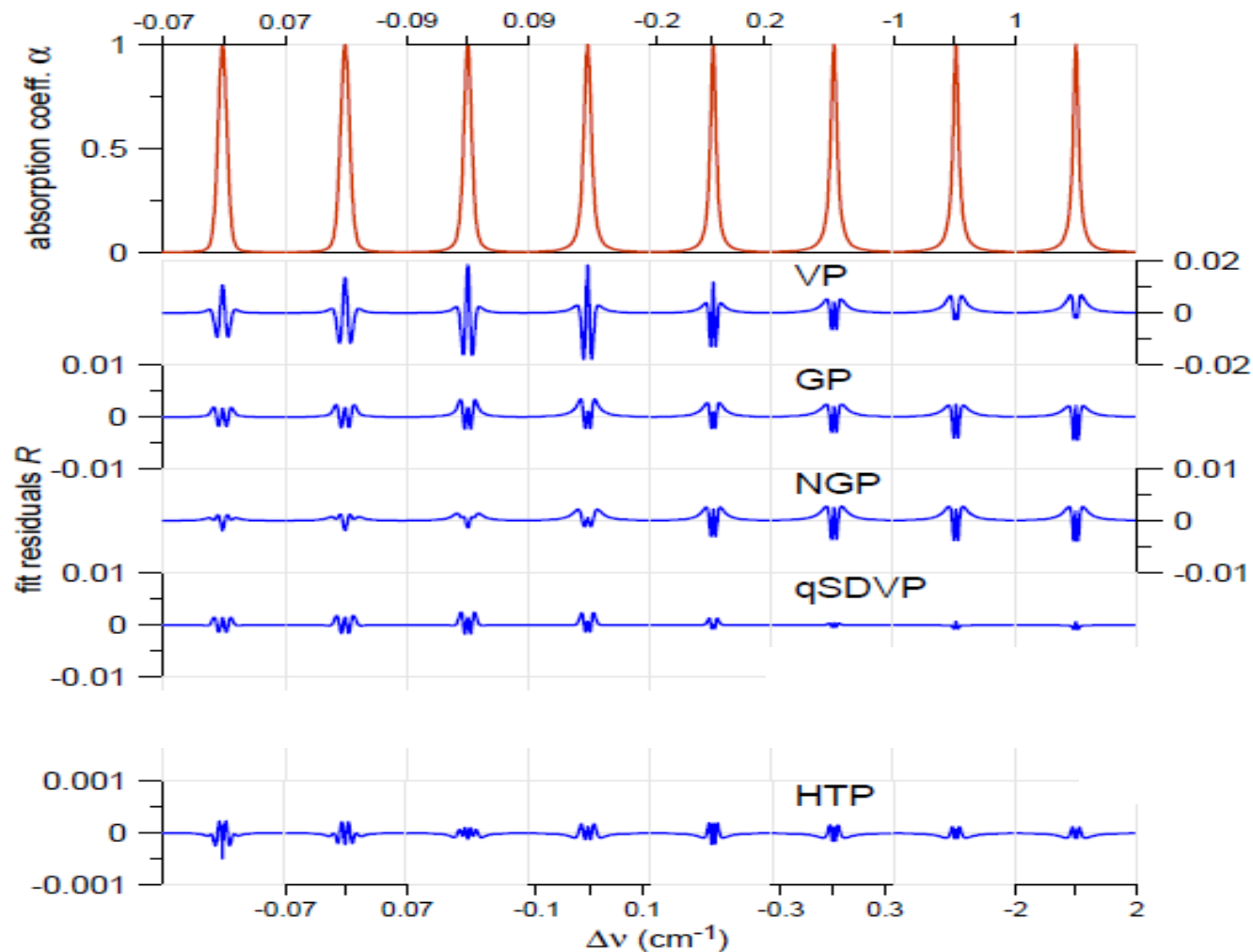
Lisak et al, JQSRT, 2015

Non-isolated transitions: Line-mixing effects

Line-mixing effects

CH$_4$/N$_2$,R(6) manifold, P=900.5 hPa, T=296 K
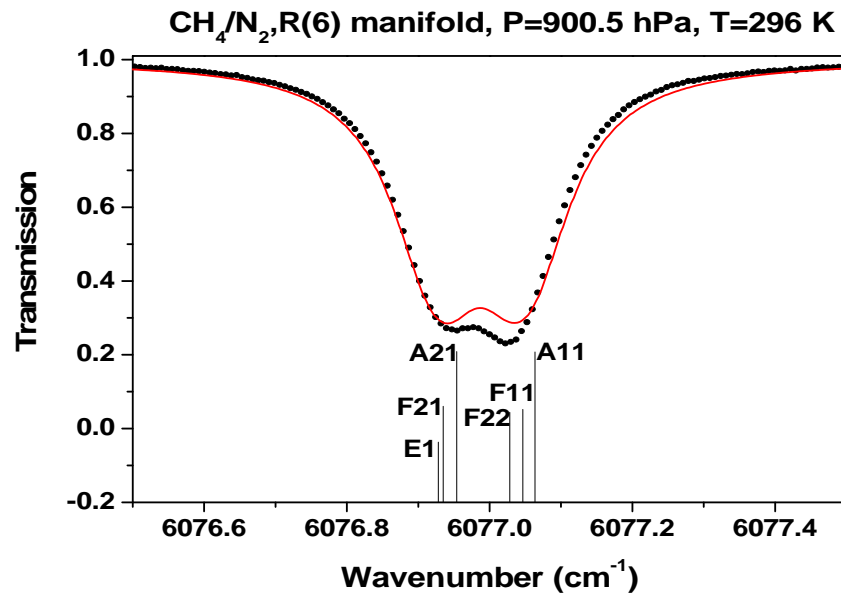
In some cases, for closely spaced lines, the Voigt profile fails when P increases. It predicts shapes that are too broad.

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

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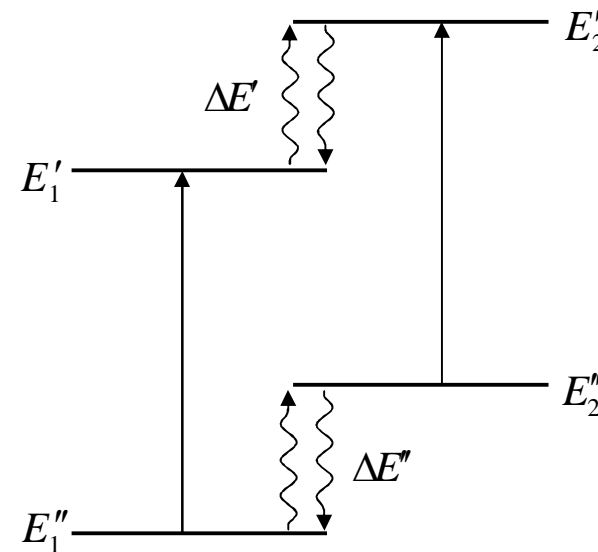
Line-mixing and remote sensing: Monitoring GreenHouse Gases from space

Nadir looking instruments onboard satellites

Greenhouse gases Observation SATellite (GOSAT, JAXA-NIES, in orbit)
Orbiting Carbon Observatory (OCO 2, NASA, in orbit)
MicroCarb (CNES, under study),
CarbonSat (ESA, under study)
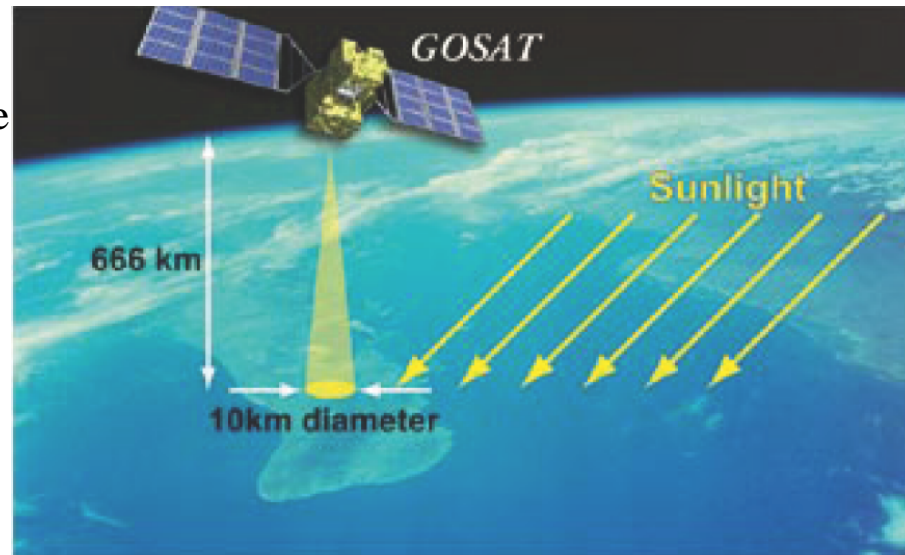
Spectral regions and aims
- CO_2 from 1.6 μm (weak) and 2.1 μm (strong) bands
- Air mass from O_2 A band (0.76 μm)
- CH_4 from $2\nu_3$ band (near 1.7 μm)
- aerosols from CO_2 and O_2 bands

Detection/quantifying sinks and sources (1 ppm for x_{CO2}, 0.3 %)
→ Extreme <u>accuracy</u> 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
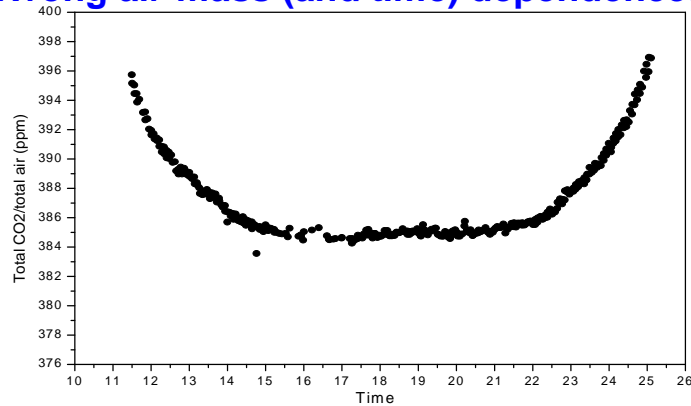
Sza 79.9°, Park Falls, region 2.1
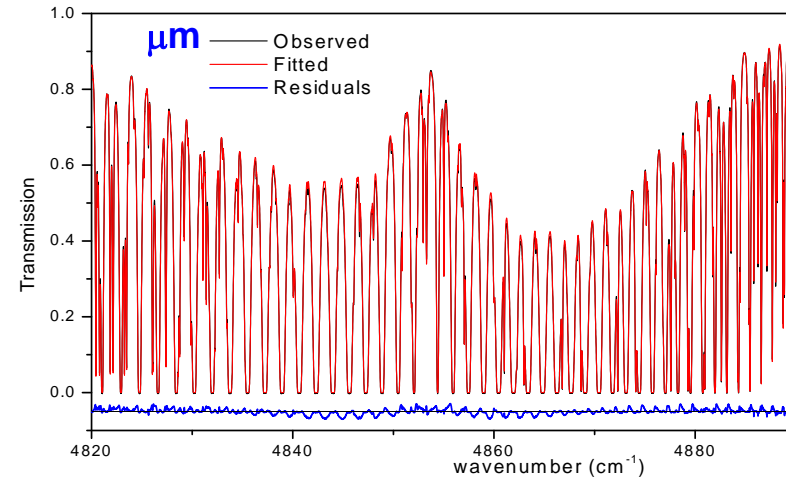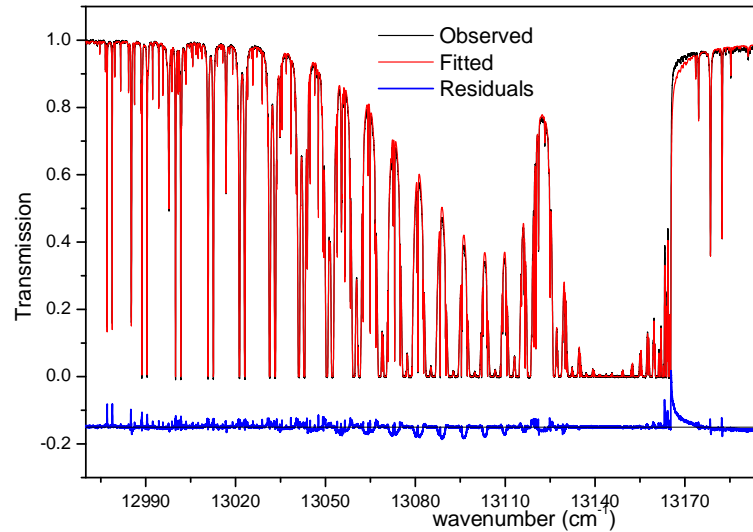

Sza 79.9°, Park Falls, region 1.6 μm

CO$_2$ retrieved

Atmospheric Remote Sensing and Molecular Spectroscopy
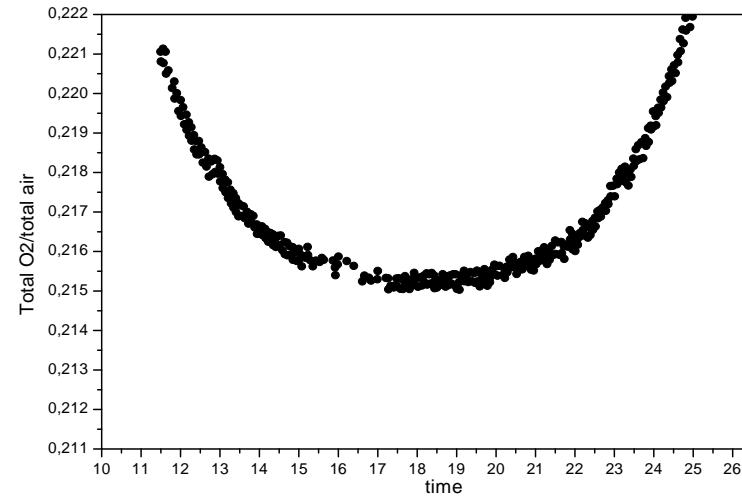Rencontres du Vietnam, ICISE Quy Nhon 27th to 31st August 2018
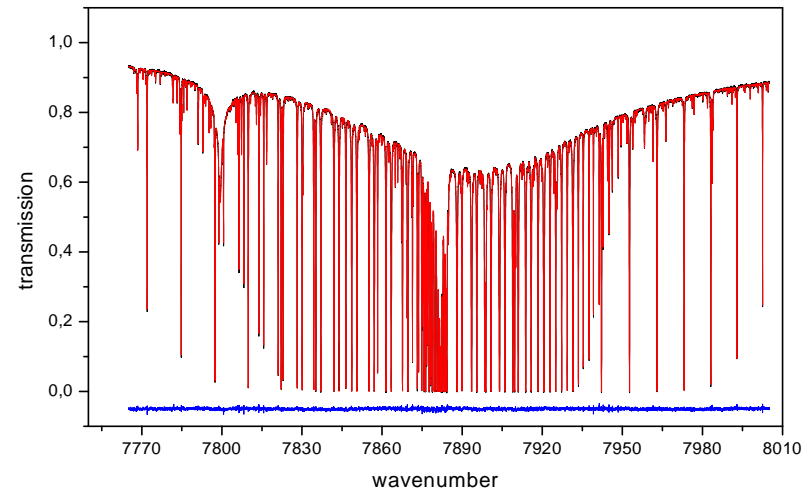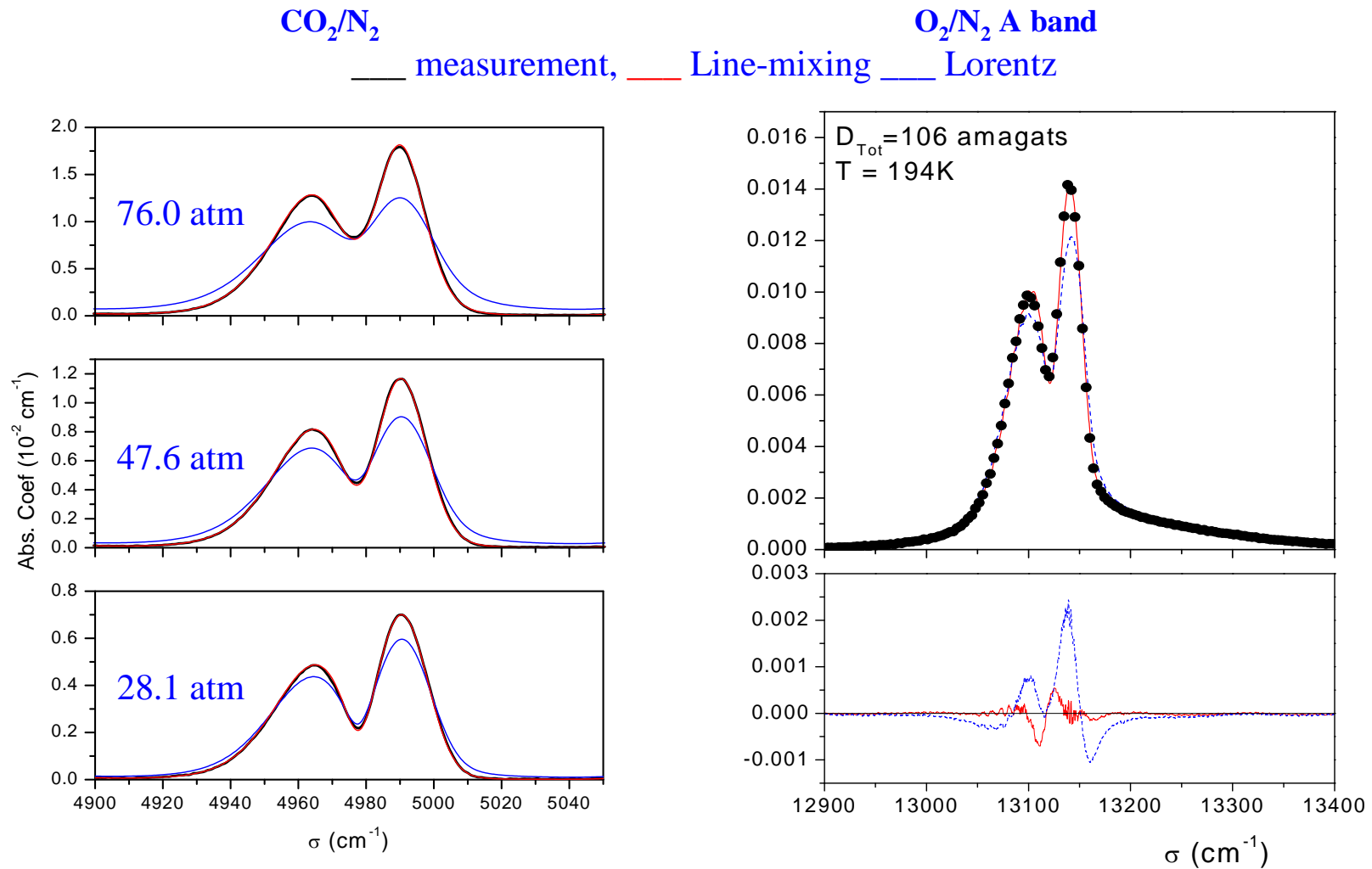
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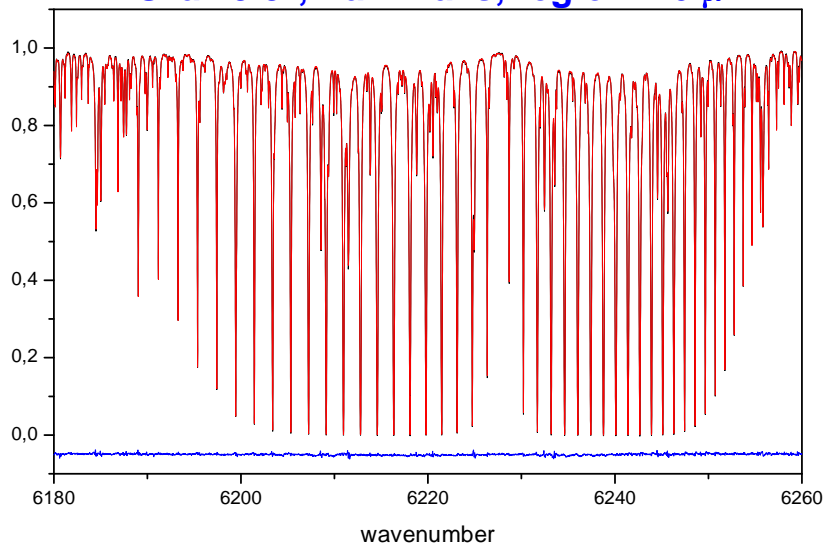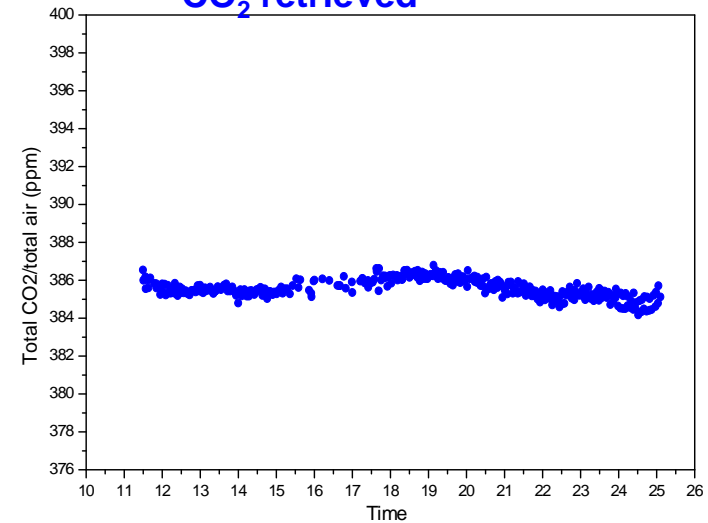
O₂: Ground-based measurements

Sza 79.9°, Park Falls, A band

Wrong time (and air-mass) dependences

Sza 79.9°, Park Falls, 1.27 μm band
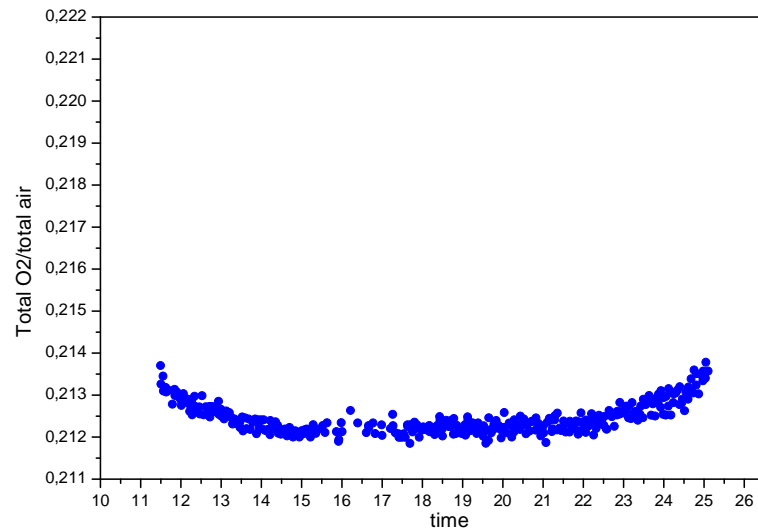
Line-mixing effects: Laboratory studies

CO$_2$/N$_2$ O$_2$/N$_2$ A band

___ measurement, ___ Line-mixing ___ Lorentz

76.0 atm

47.6 atm

28.1 atm

Abs. Coef (10^{-2} cm^{-1})

σ (cm^{-1})

D$_{Tot}$=106 amagats
T = 194K

σ (cm^{-1})

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Influence on retrievals: O_2 ground-based measurements

Spectra: Sza 79.9°, Park Falls
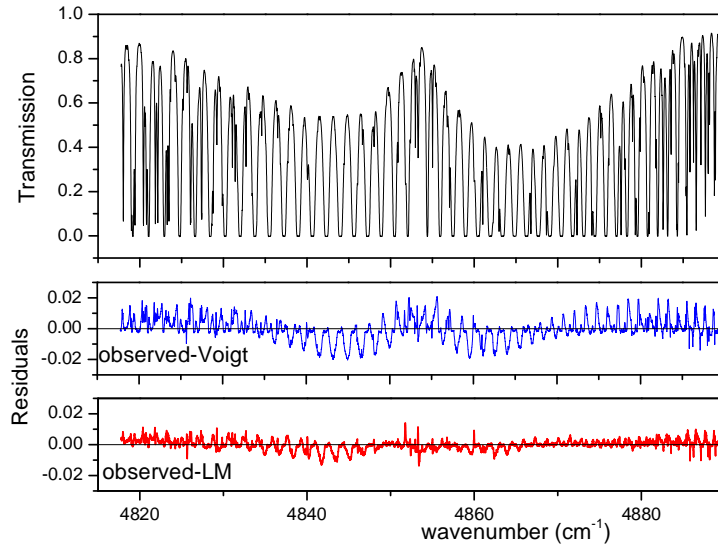
O_2 A band region
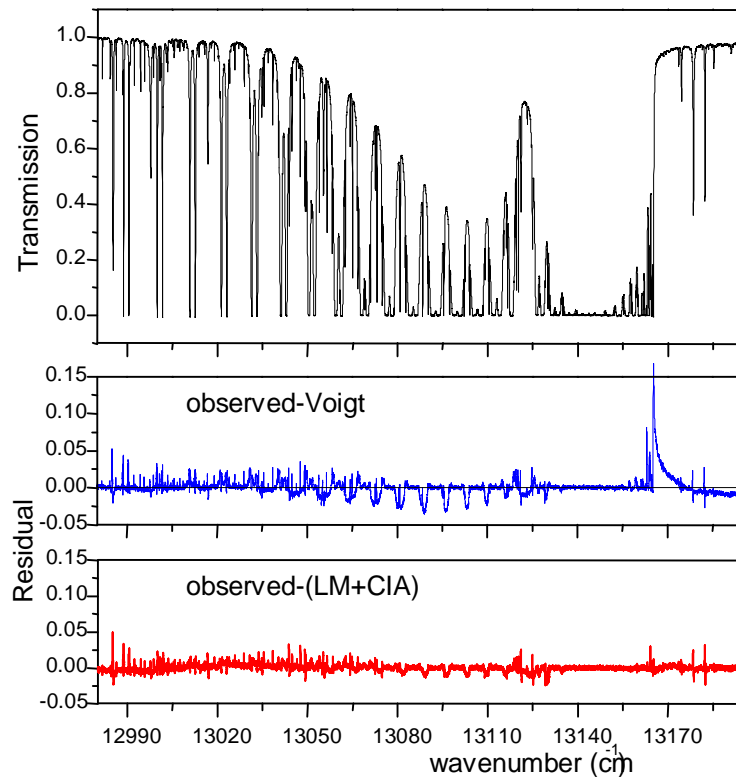
O_2 A band:
Relative errors on surface pressures retrieved from atmospheric spectra
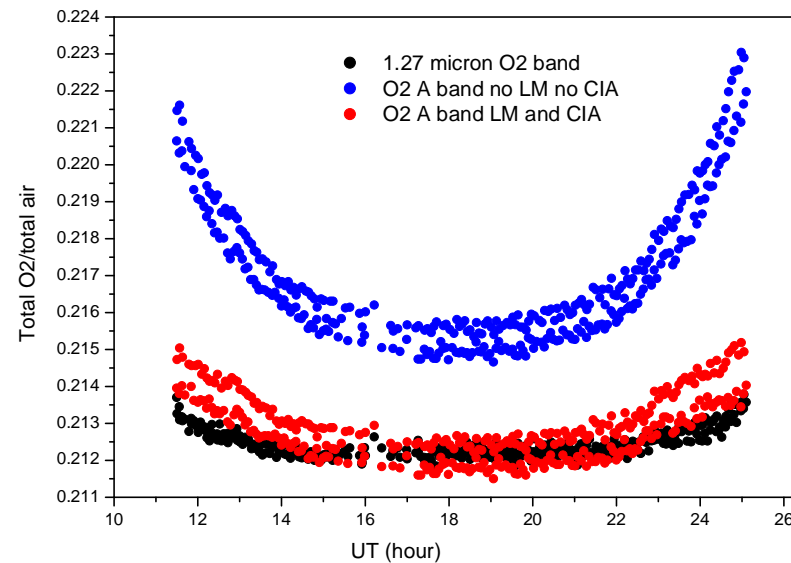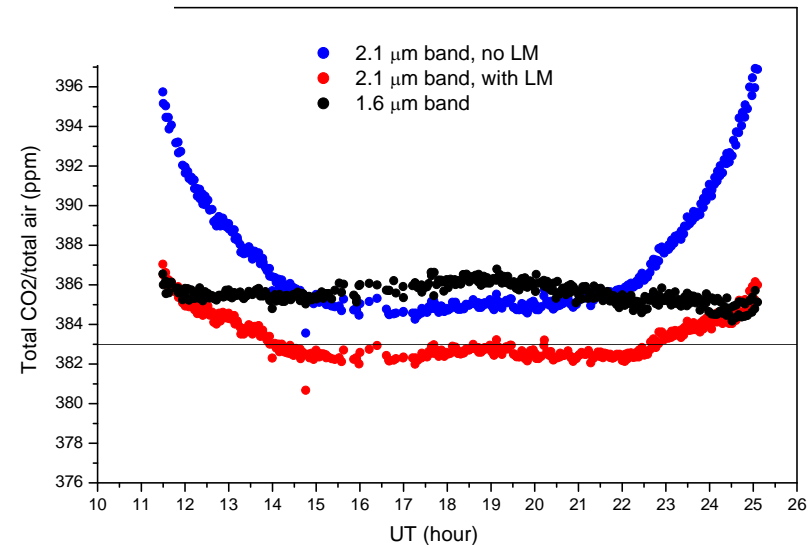
Influence on retrievals: CO_2 ground-based measurements
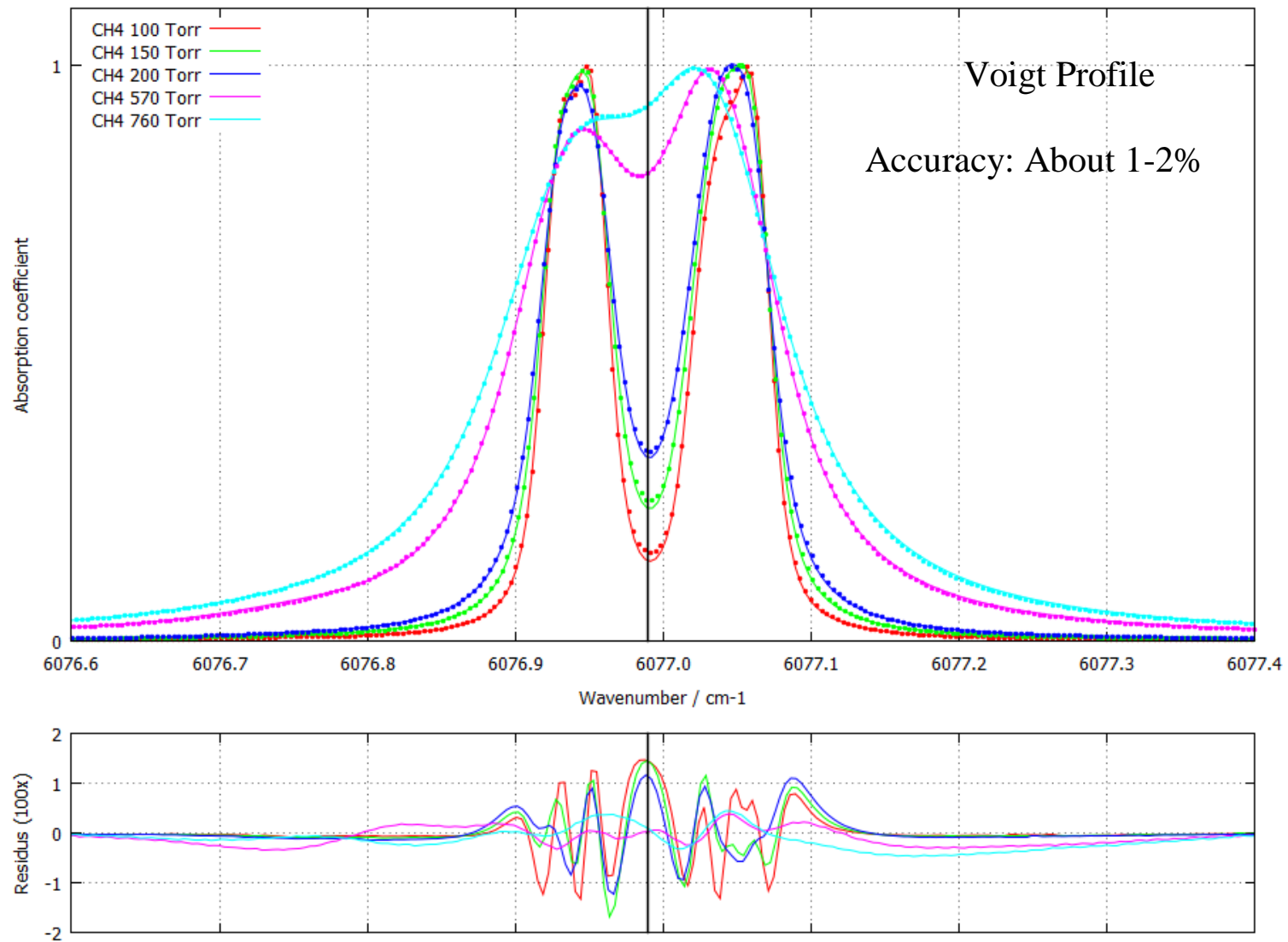

← Fits of a ground based transmission spectra in the region of the $2\nu_1 + \nu_3$ band of CO_2

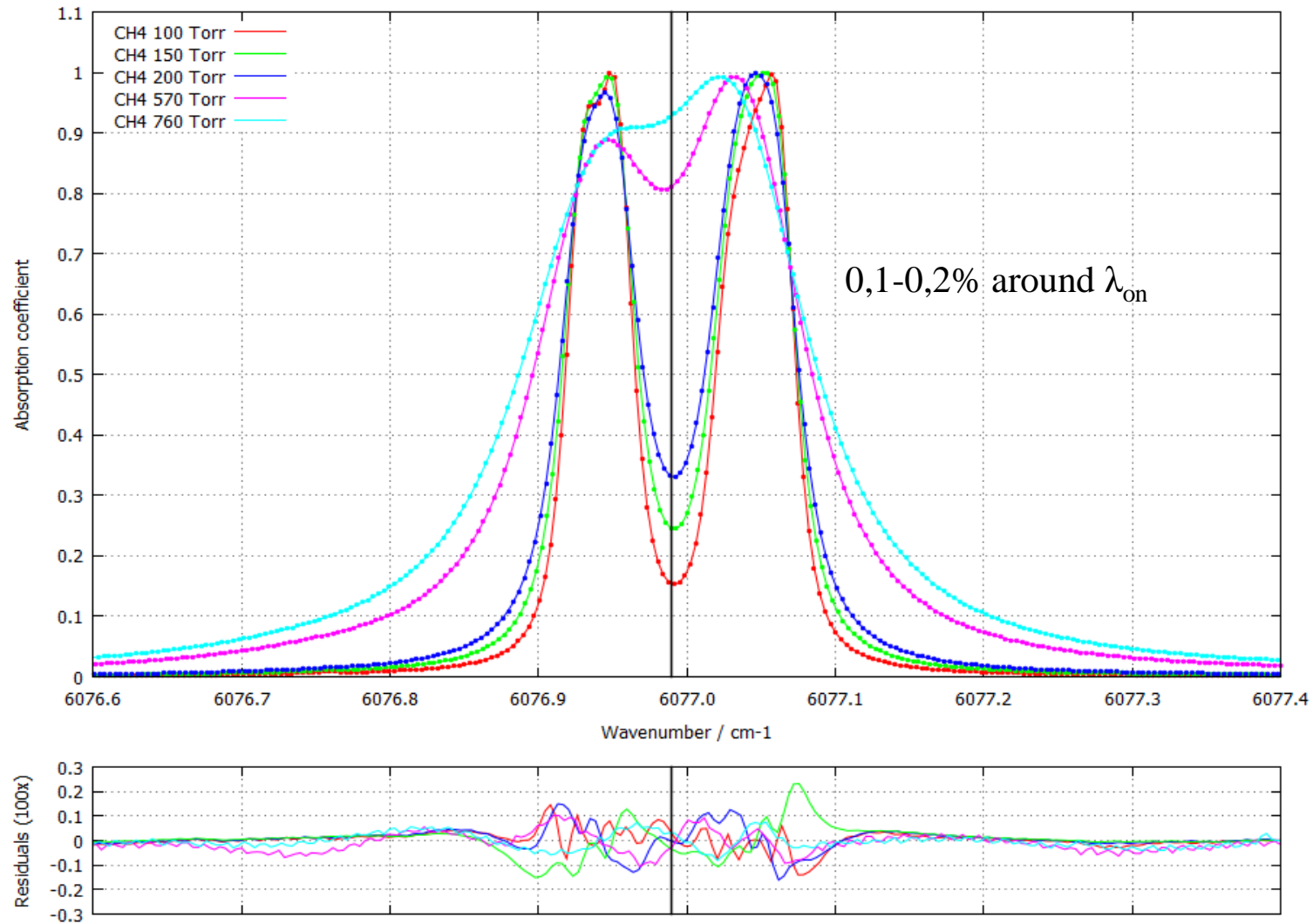Significant errors (10%) on the CO_2 atmospheric amount. Sinks and sources !!! →

Spectroscopy for MERLIN: 0.2% accuracy required!

Spectroscopy for MERLIN: 0,2% accuracy required!

Speed dependence + Dicke narrowing + Line-Mixing

0,1-0,2% around λ_{on}

Delahaye et al, 2015