

IR Molecular Spectroscopy - Laboratory measurements

Laurence Régalia

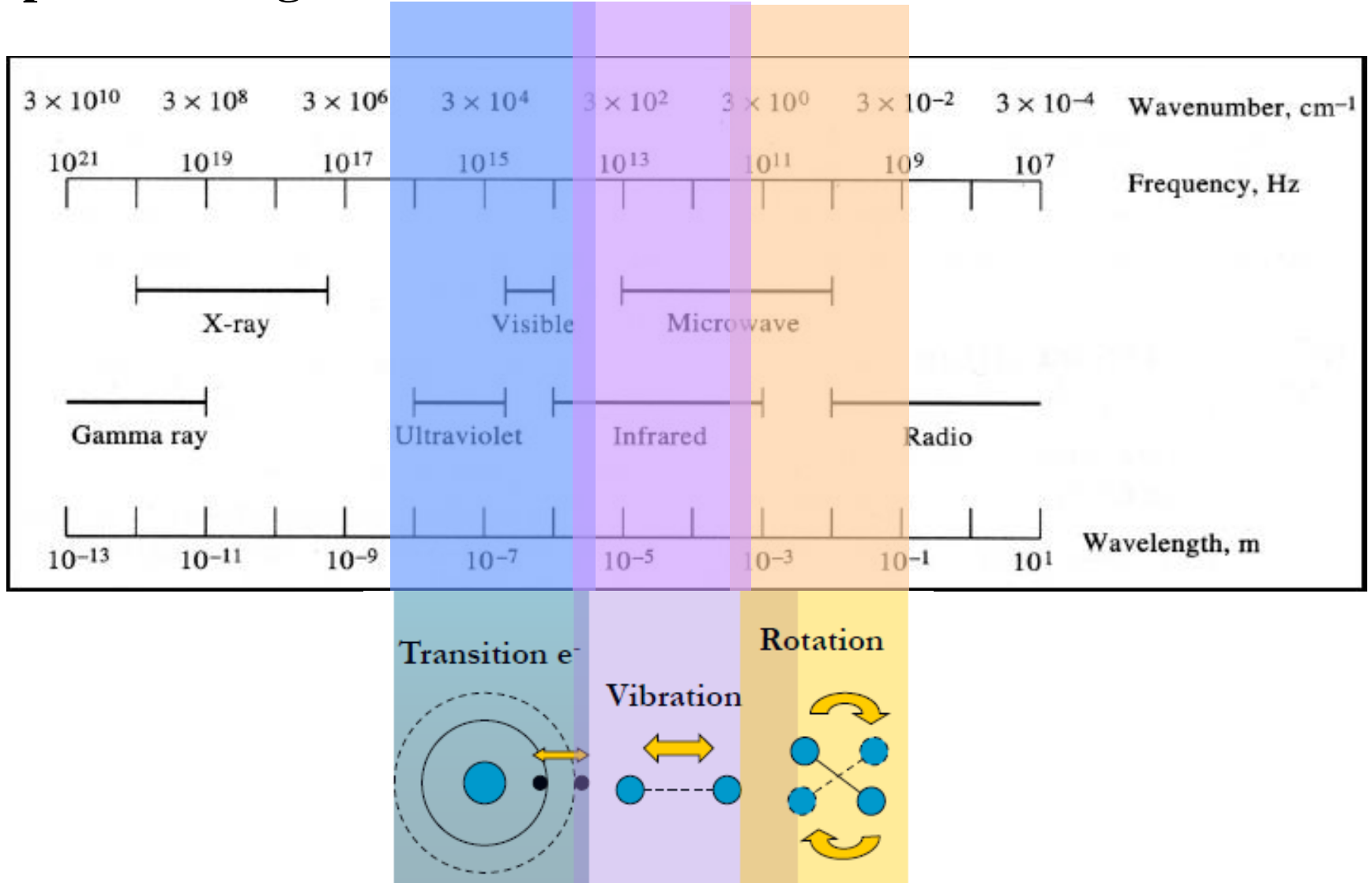


- ▶ Line parameters
- ▶ IR instrumental devices
- ▶ Line parameters retrieval
- ▶ Databases
- ▶ Databases evaluation and improvement

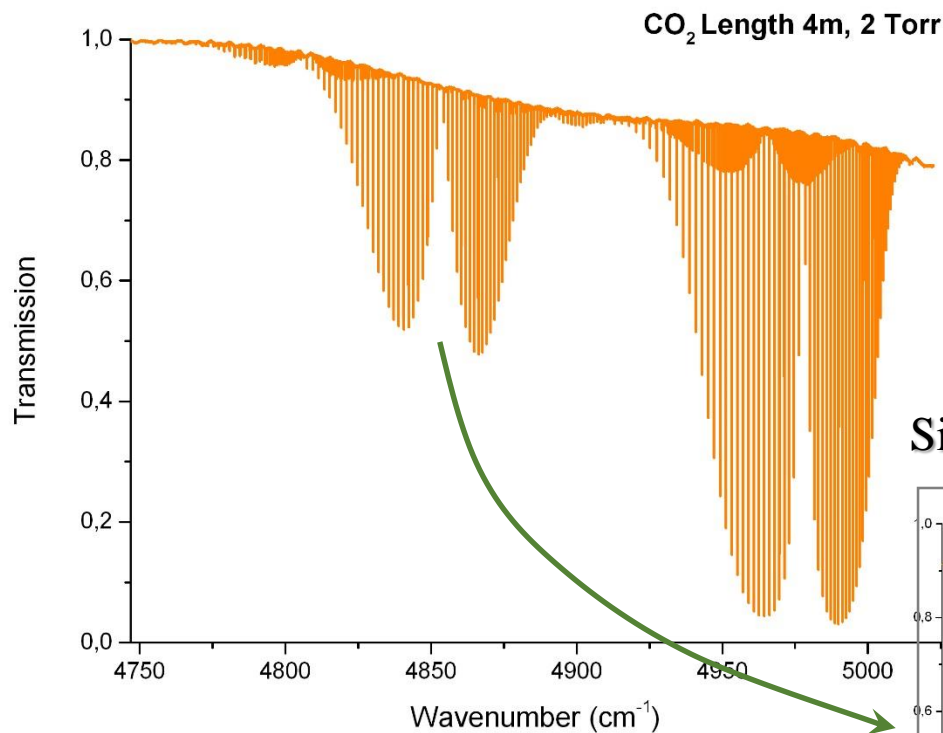
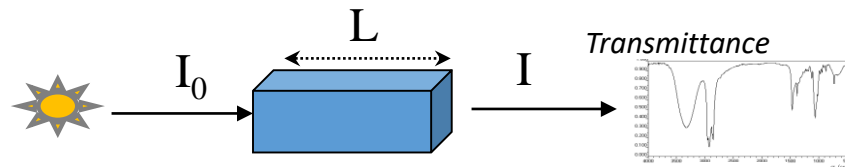


Line parameters

Spectral Range

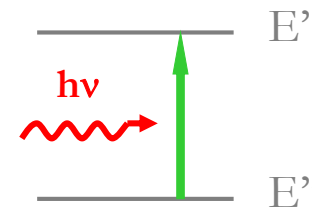
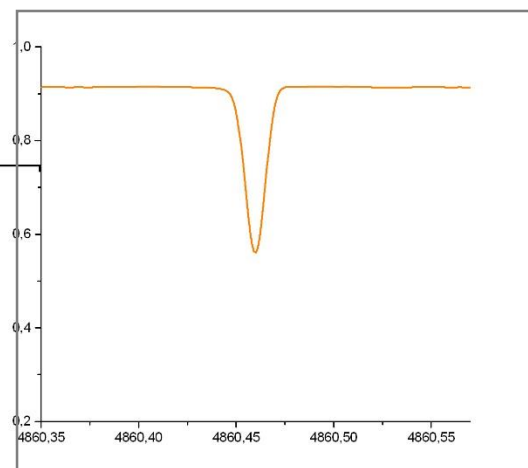


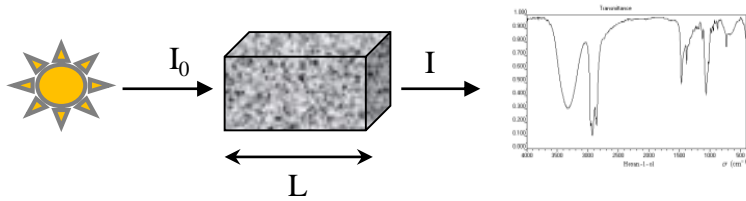
Beer-Lambert's absorption law



$$T(\sigma) = \frac{I(\sigma)}{I_0(\sigma)}$$

Signature of a transition between 2 energy levels





$$T_{th}(\sigma) = \frac{I(\sigma)}{I_0(\sigma)} = e^{-\alpha(\sigma)L}$$

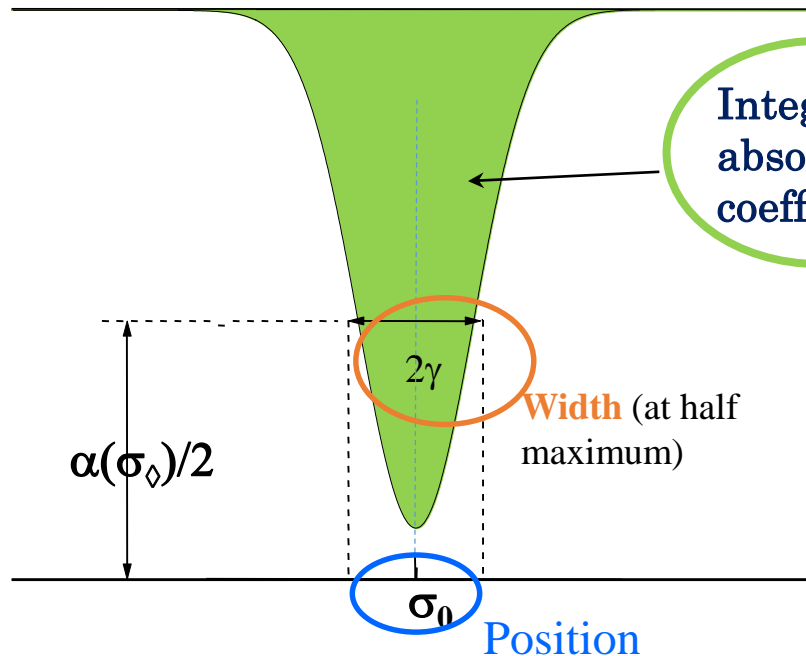
$\alpha(\sigma)$ is the absorption coefficient per unit length (en cm^{-1})

3 important parameters :

✓ Position

✓ Intensity

✓ Width



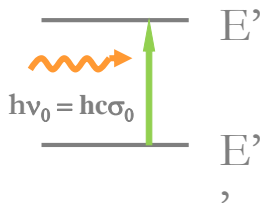
Integrated absorption coefficient

$$\alpha^{int} = \int_{-\infty}^{+\infty} \alpha(\sigma) d(\sigma)$$

Width (at half maximum)

$$\alpha(\sigma) = \alpha^{int} \cdot \Phi(\sigma - \sigma_0)$$

Line profile (normalized)



Integrated absorption coefficient $\alpha(\sigma - \sigma_0) = \alpha^{\text{int}} \cdot \Phi(\sigma - \sigma_0)$

$$\alpha^{\text{int}} = S_{\sigma}^{\text{P}} \times P = S_{\sigma}^{\text{N}} \times N$$

(parameter listed in databases in natural abundance)

with S_{σ}^{P} ($\text{cm}^{-2}/\text{atm}$) : integrated absorption coefficient (per unit of pressure)

or S_{σ}^{N} ($\text{cm}^{-2}/\text{molec.cm}^{-3}$) : integrated absorption cross section

$$S_{\sigma}^{\text{N}}(T) = \frac{8\pi^3}{3hc} \frac{1}{4\pi\epsilon_0} \frac{\sigma_0}{Q(T)} I_a \exp(-hcE_a/kT) [1 - \exp(-hc\sigma_{b \leftarrow a}/kT)] |\mu|^2$$

Temperature conversion :

$$T_0 = 296 \text{ K (Reference temperature)}$$

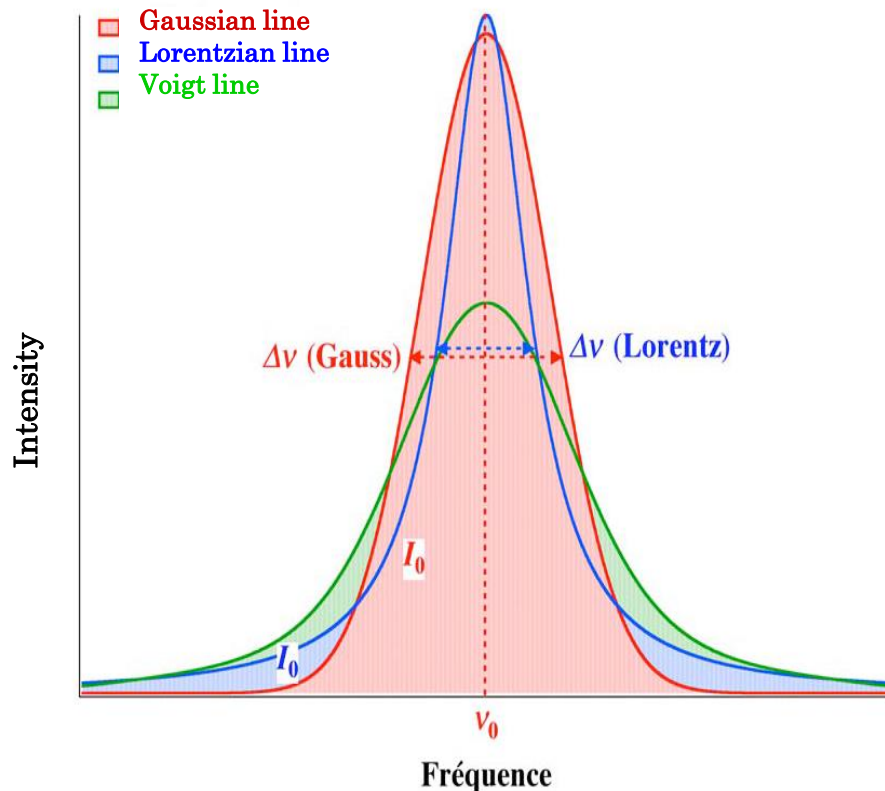
✓ Line intensity:

$$S_{\sigma}^{\text{N}}(T) = S_{\sigma}^{\text{N}}(T_0) \cdot \left[\frac{Q(T_{\text{stand}})}{Q(T)} \right] \exp \left[\frac{E''}{k} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]$$

The lower state energy E'' is required

Normalized line profile

$$\alpha(\sigma - \sigma_0) = \alpha^{\text{int}} \cdot \Phi(\sigma - \sigma_0)$$



Lorentzian Profile

Collisions effect

$$\gamma_L(T) = \gamma^0_S \times P_{\text{abs}} + \sum_j \gamma^0_{j,I} \times P_j$$

$\text{cm}^{-1}/\text{atm}$

Voigt Profile

$$\gamma_V = \sqrt{\gamma_D^2 + \gamma_L^2}$$

Gaussian Profile

Doppler effect

$$\gamma_D \propto \sqrt{\frac{T}{M}} \cdot \sigma_0$$

pression



New refined profiles are now available that take into account collisions with modification of the molecular speed

⇒ **Lecture of Ha Tran** « *Spectral shape modelling* »

Temperature conversion : ($T_0 = 296 \text{ K}$)

✓ Half-width broadened by pressure :

$$\gamma^0_{\text{L}}(T) = \gamma^0_{\text{L}}(T_0) \left[\frac{T_0}{T} \right]^n$$

($\text{cm}^{-1}/\text{atm}$)



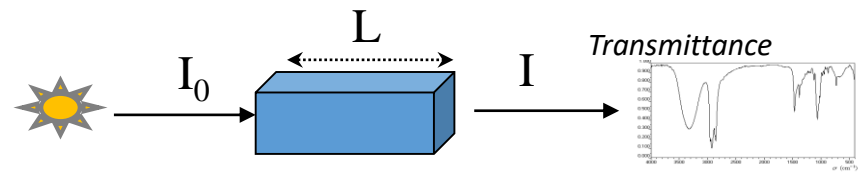
Journal of Quantitative Spectroscopy and Radiative Transfer

Volume 217, September 2018, Pages 440-452



On the temperature dependence of half-widths and line shifts for molecular transitions in the microwave and infrared regions

Robert R. Gamache  , Bastien Vispoel



ILS (Instrumental line shape)

The natural line profile is modified by the spectral response of the spectrometer: Instrumental Line Shape **ILS** (σ)

The measured spectral distribution : $T_{\text{measured}}(\sigma) = T(\sigma) \otimes \mathbf{ILS}(\sigma)$

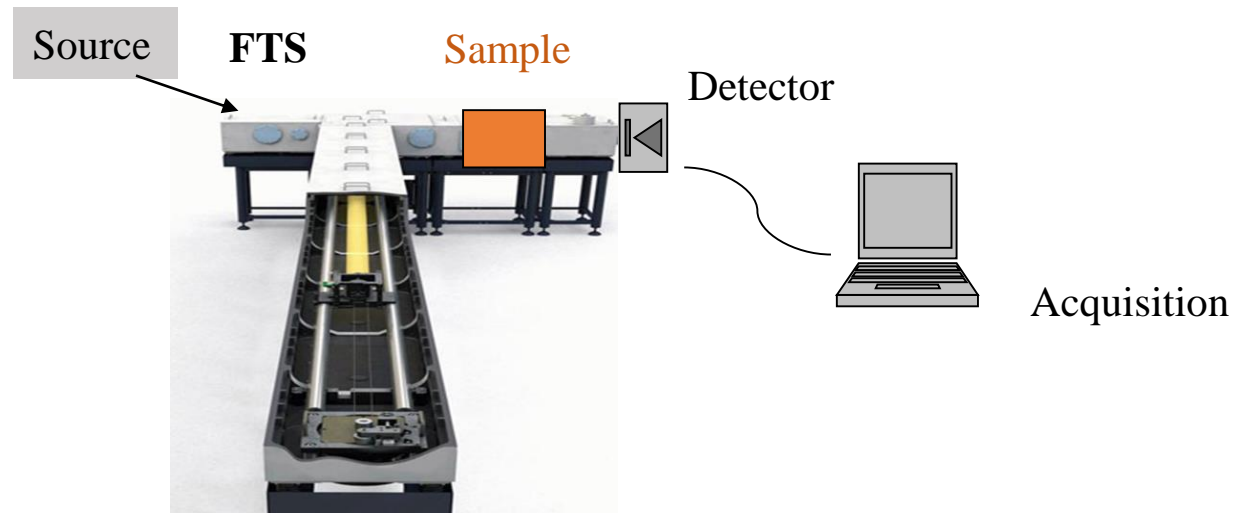
- **According to the spectrometers the impact of ILS is different.**
- **The knowledge of the ILS is very important for the retrieval of the line parameters.**



Instrumental devices

➡ FTIR Spectrometer

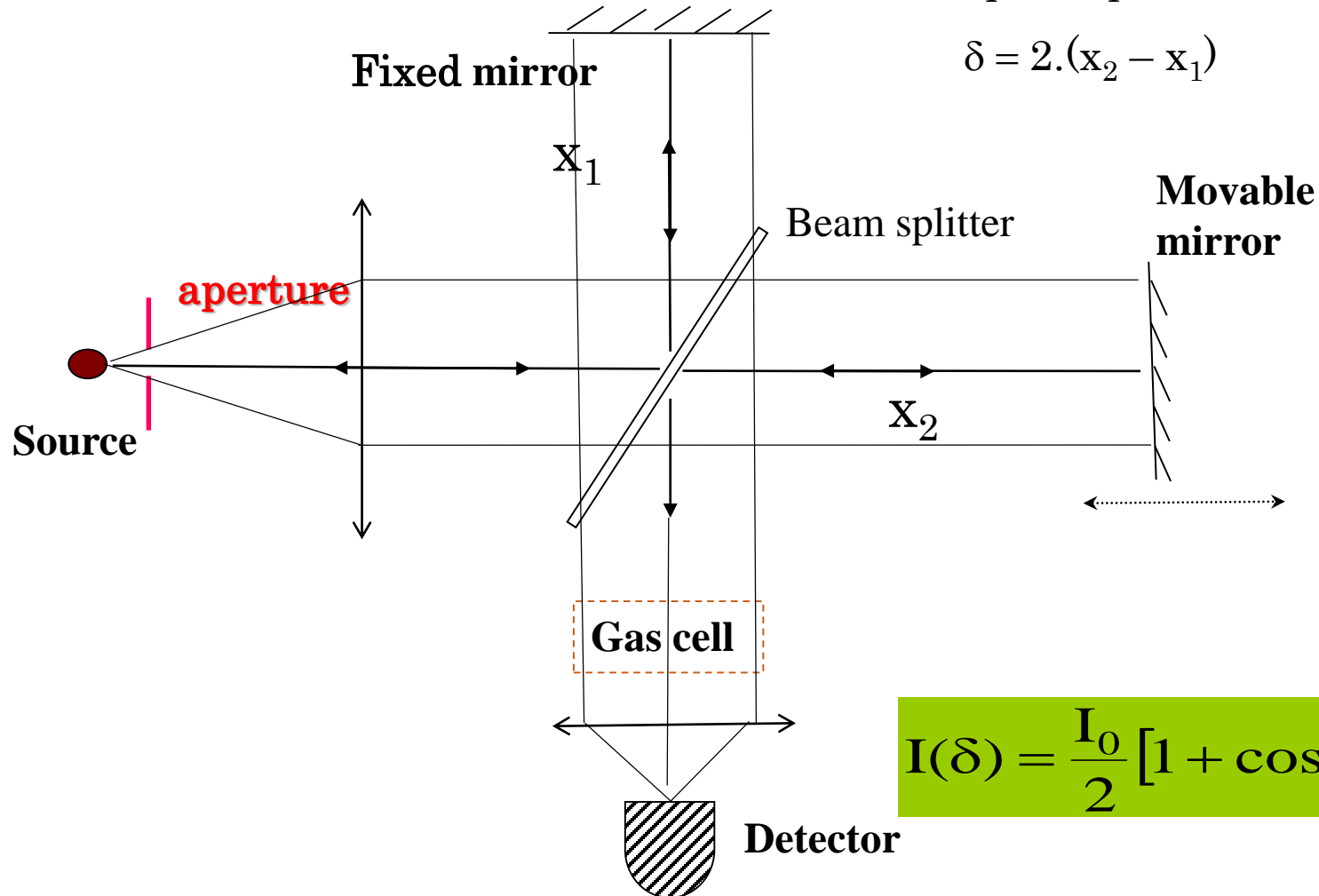
Principle of the FT Spectrometer



Michelson interferometer

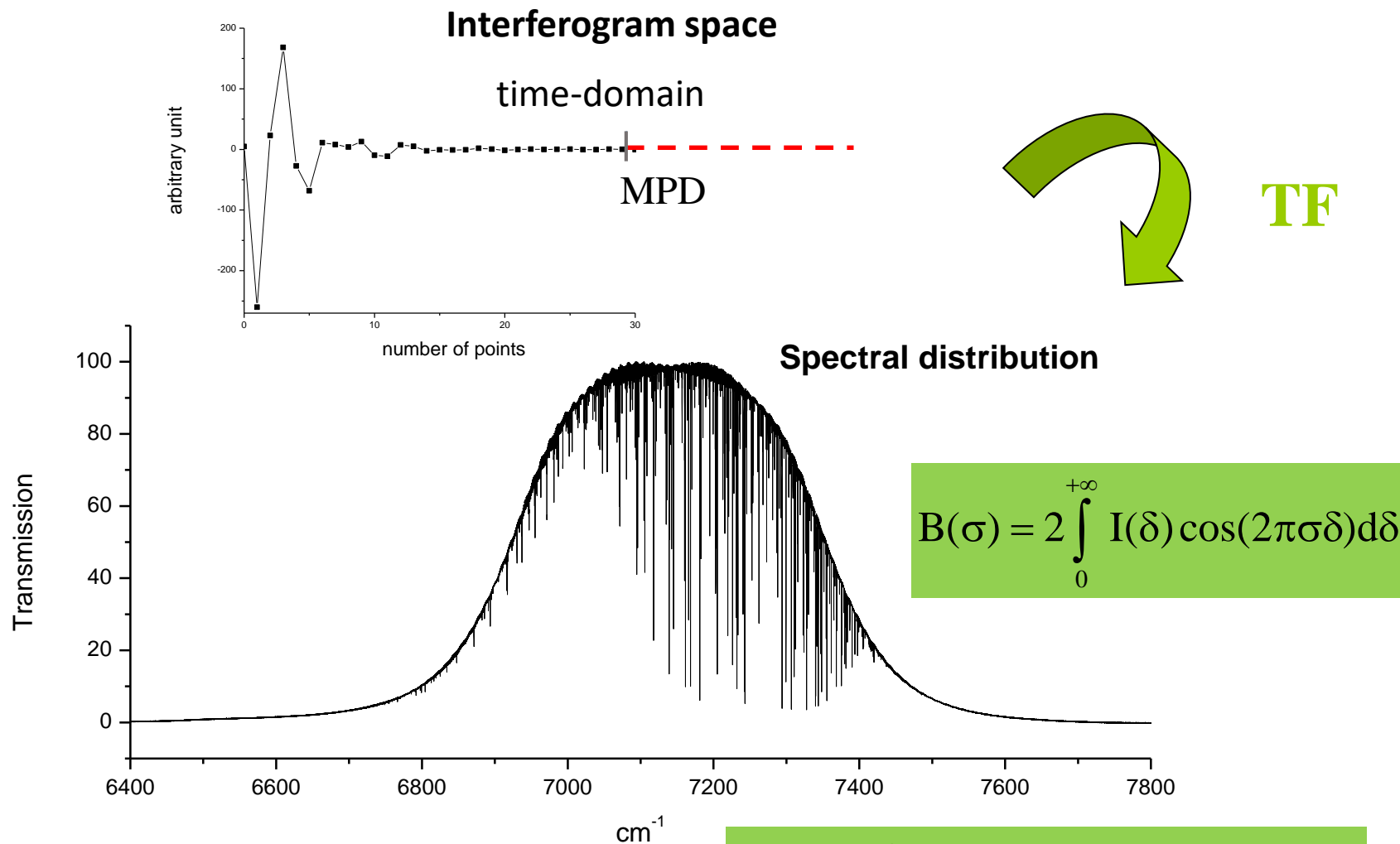
Optical path difference:

$$\delta = 2.(x_2 - x_1)$$



$$I(\delta) = \frac{I_0}{2} [1 + \cos(2\pi\sigma_0\delta)]$$

Polychromatic radiation:



Physical limitations of $I(\delta)$: MPD_{max}
and finite size of the aperture

$$B(\sigma) = 2 \int_0^{+\infty} I(\delta) f_{app}(\delta) \cos(2\pi\sigma\delta) d\delta$$

Instrumental Line Shape (ILS)

Physical limitations

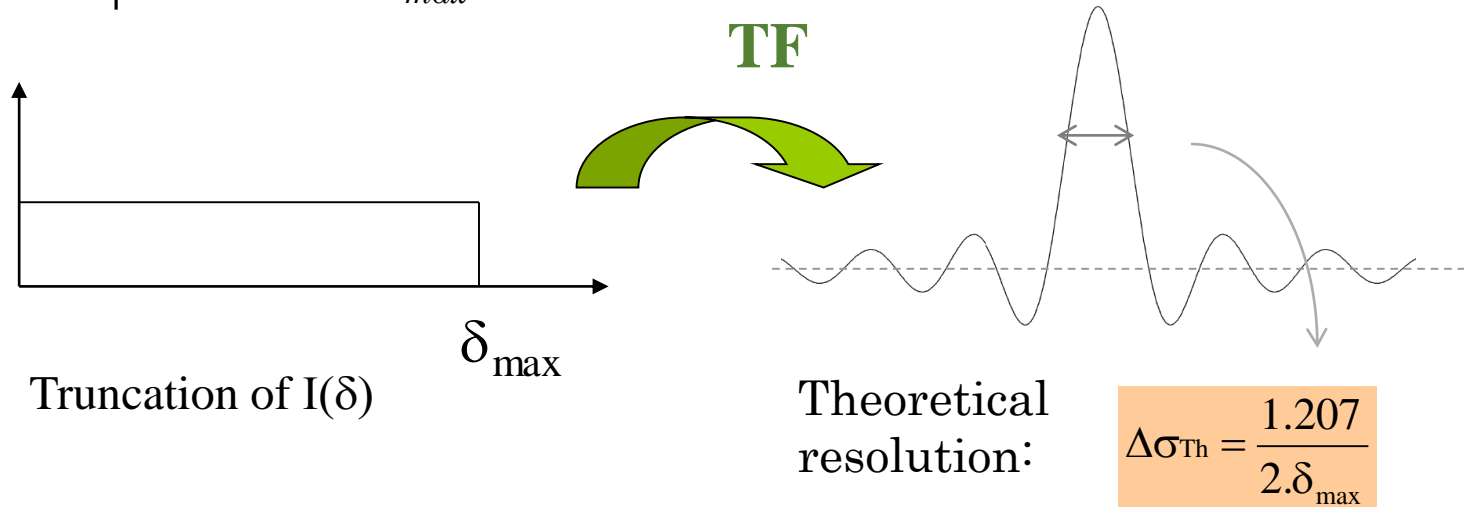
ILS of a FTS

$$f_{\text{app}}(\delta) = \Pi(\delta) \cdot P_{\text{opt}}(\delta)$$

* Limitation of the OPD (Optical Path Difference) :
(MPD or δ_{max})

$$\Pi(\delta) \left| \begin{array}{l} = 1 \quad \delta \leq \delta_{\text{max}} \\ = 0 \quad \delta > \delta_{\text{max}} \end{array} \right.$$

$$F(\sigma) = 2\delta_{\text{max}} \frac{\sin(2\pi\delta_{\text{max}}\sigma)}{2\pi\delta_{\text{max}}\sigma}$$

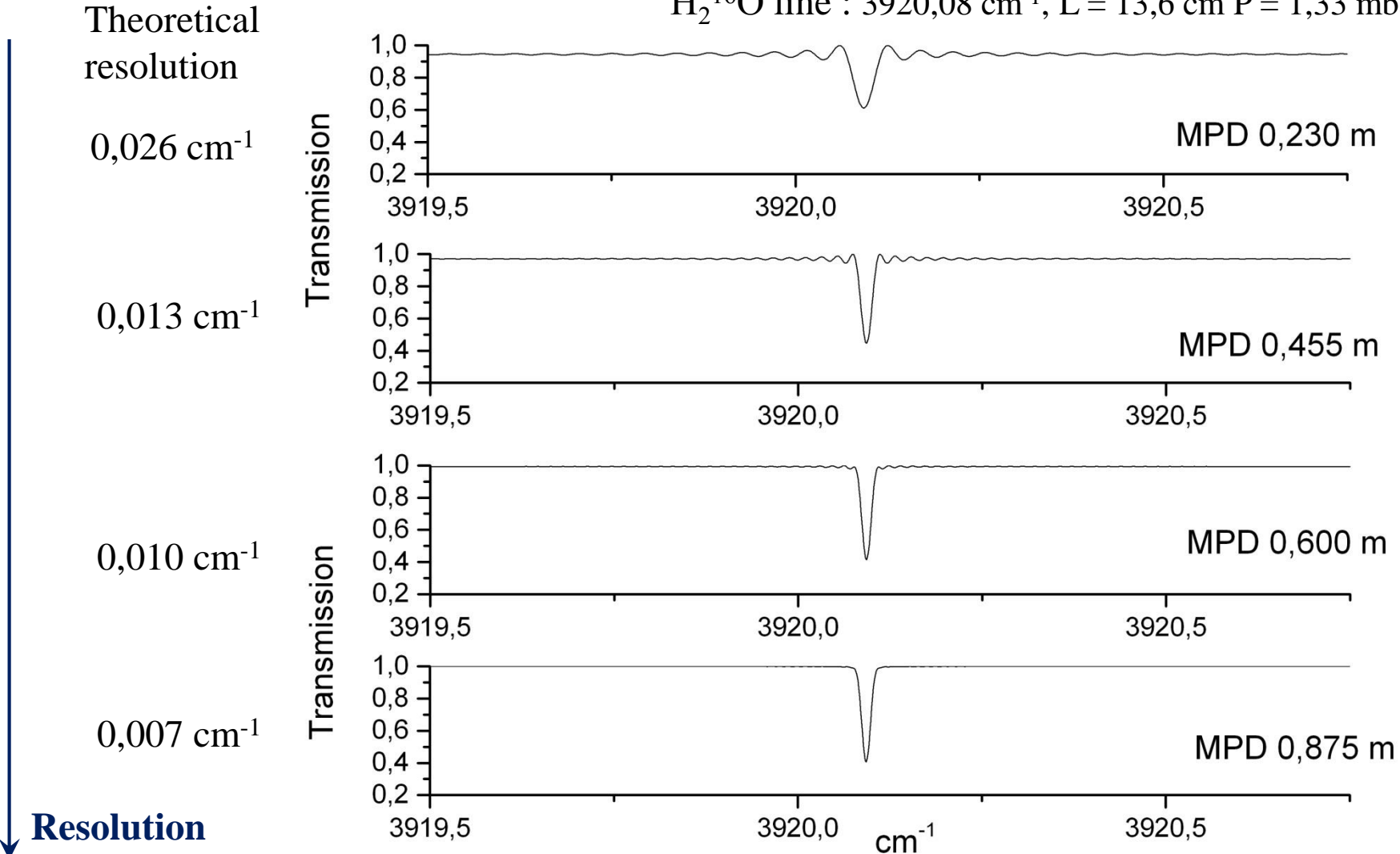


δ_{max} (or MPD) \nearrow \rightarrow narrower « sinc » function and better resolution

$$\gamma_D = 5,7 \cdot 10^{-3} \text{ cm}^{-1}$$

Line shape with different MPD values

H₂¹⁶O line : 3920,08 cm⁻¹, L = 13,6 cm P = 1,33 mbar

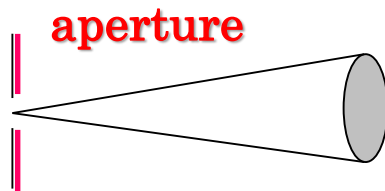


ILS of a FTS

$$f_{\text{app}}(\delta) = \Pi(\delta) \cdot \mathbf{P}_{\text{opt}}(\delta)$$

* Finite size of aperture

The input beam is limited by an aperture (iris) at the entrance of the interferometer



$$\mathbf{P}_{\text{opt}}(\delta) = \left| \sin c \frac{\sigma_0 \Omega \delta}{2} \right|, \quad \text{with } \Omega = \pi \frac{r^2}{f^2}$$

with r : aperture **radius** and

f : focal length of the collimating mirror

$$\Gamma(\delta) = B(\sigma_0) \cdot \Pi(\delta) \cdot \left| \sin c \frac{\sigma_0 \Omega \delta}{2} \right| \cdot \cos \left[2\pi \sigma_0 \delta \left(1 - \frac{\Omega}{4\pi} \right) \right] \delta'$$

Aperture broadening

shift of the wavenumber scale

Instrumental Line Shape (ILS)

Distorsions

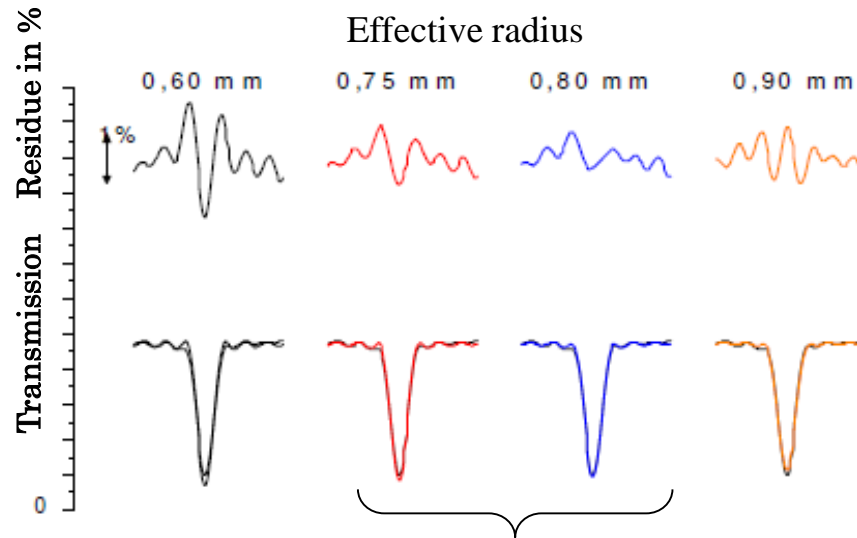
Due to the diffraction or bad alignments, the ILS can be broadened.

In first approximation, the broadening of the ILS can artificially be corrected by giving an effective value to the aperture radius

$$P_{\text{opt}}(\delta) = \left| \text{sinc} \frac{\sigma_0 \Omega \delta}{2} \right|, \quad \text{with } \Omega = \pi \frac{r^2}{f^2} \quad \text{Effective value}$$

CH₃Cl spectra recorded with a Bruker IFS 120HR (MONARIS laboratory, ex. LADIR)
(Cédric Bray, Thesis 2012, UPMC)

Residuals of the fit depending on the effective radius value (spectra at low pressure and on isolated lines)



Line intensity 1%

Self-broadening coefficient : 4 %

Impact on the line parameters retrieval

LINEFIT : To take into account the error sources in the ILS of a FTS, F. Hase developed a software.

He starts from the principle that the ILS can be affected by two main imperfections (mainly due to misalignment in the interferometer): a modulation loss that broadens the ILS and a phase error that makes the ILS asymmetric.

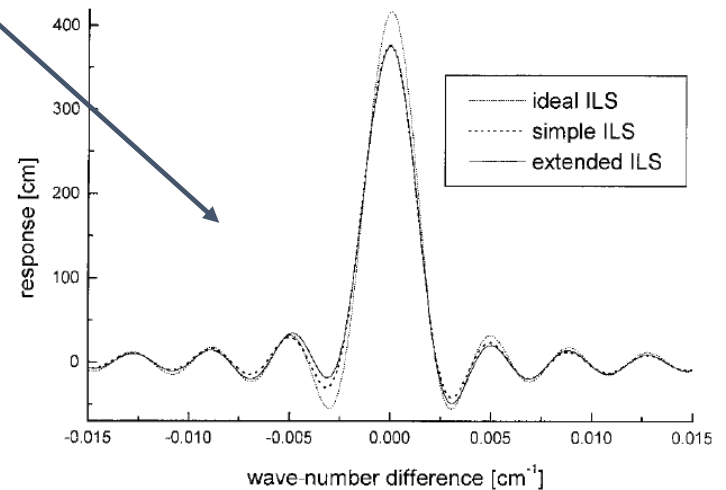
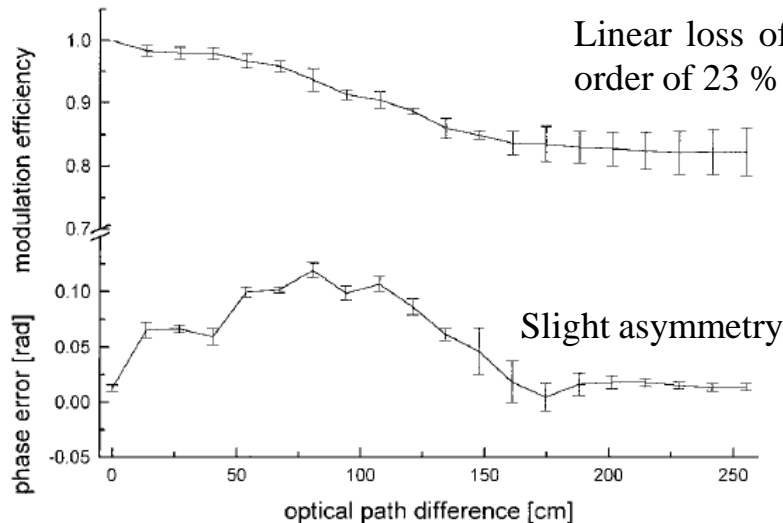
Analysis of the instrumental line shape of high-resolution Fourier transform IR spectrometers with gas cell measurements and new retrieval software

F. Hase et al. Applied Optics Vol. 38, No. 15 (1999)

Determination of the real shape of the ILS

Several microwindows, containing an isolated, non-saturated line

$$\left(\frac{\text{Mod}_{\text{eff}}(\text{present FTS})}{\text{Mod}_{\text{eff}}(\text{Nominal FTS})} \right)$$



In the case of an ideal ILS, modulation and phase parameters should be equal to 1 and 0, respectively for all optical path difference.

Example of fit result of N₂O line around 2200 cm⁻¹

T = 296 K; P = 0,15 mbar

Applied Optics Vol. 38, No. 15 (1999)

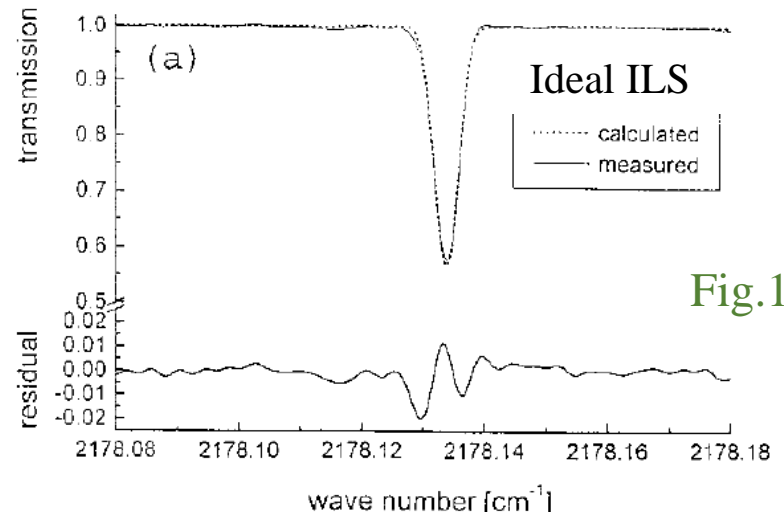
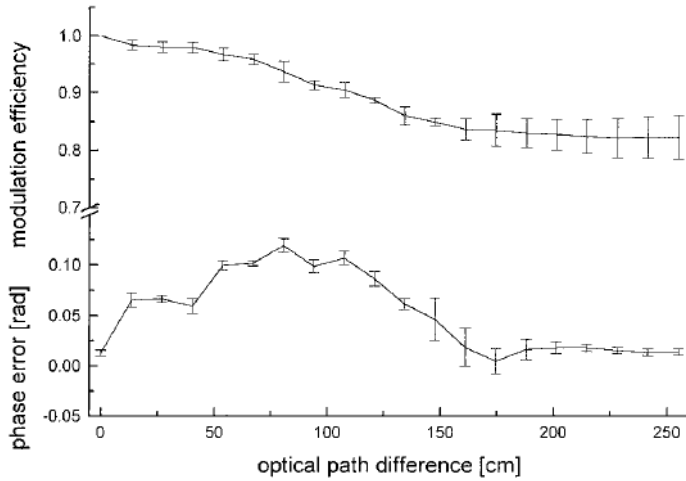


Fig.1

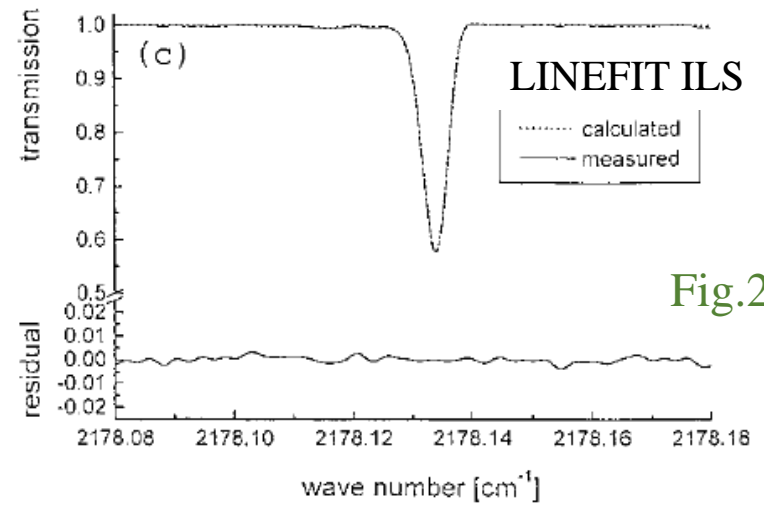
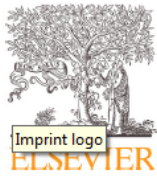


Fig.2

Between the 2 treatments (Fig 1 and 2) the difference from resulting column amount is about 4 %. Notice that the fit residual is similar on Fig. 1 as those obtained with poor line profile (difficult to separate the problems...).

Example: Using LINEFIT to retrieve more accurate line parameters

Journal of Quantitative Spectroscopy & Radiative Transfer 279 (2022) 108050



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journal homepage: www.elsevier.com/locate/jqstr



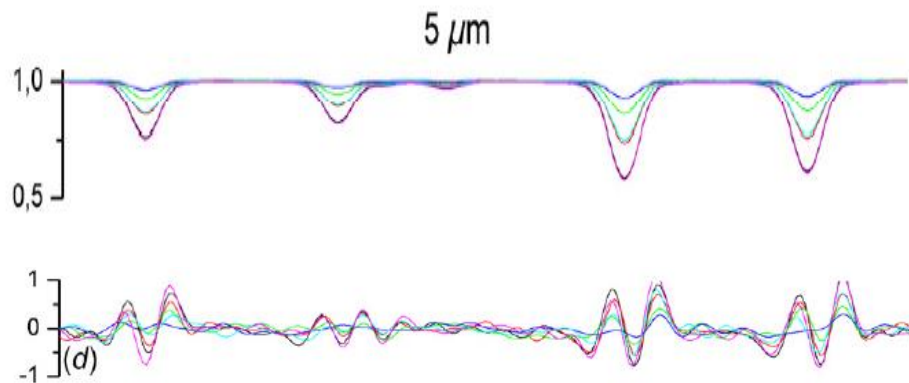
Multi-spectral investigation of ozone: Part II. Line intensity measurements at one percent accuracy around 5 μm and 10 μm



David Jacquemart^{a,*}, Corinne Boursier^b, Hadj Elandaloussi^b, Pascal Jeseck^b, Yao Té^b, Christof Janssen^b

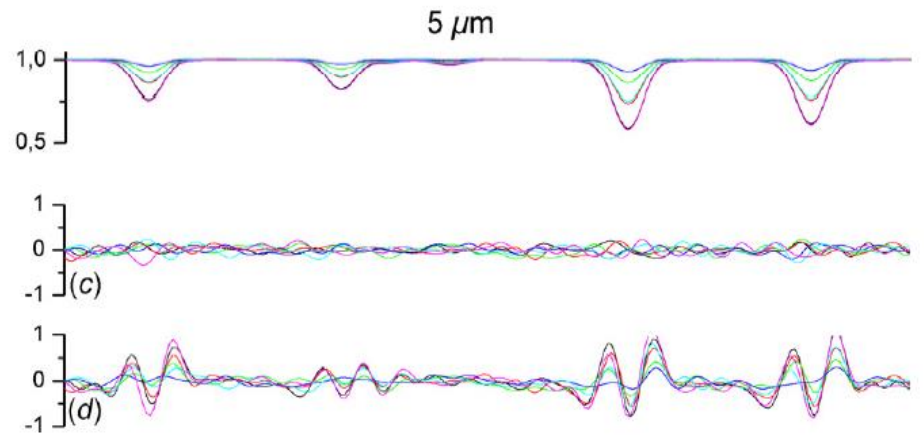
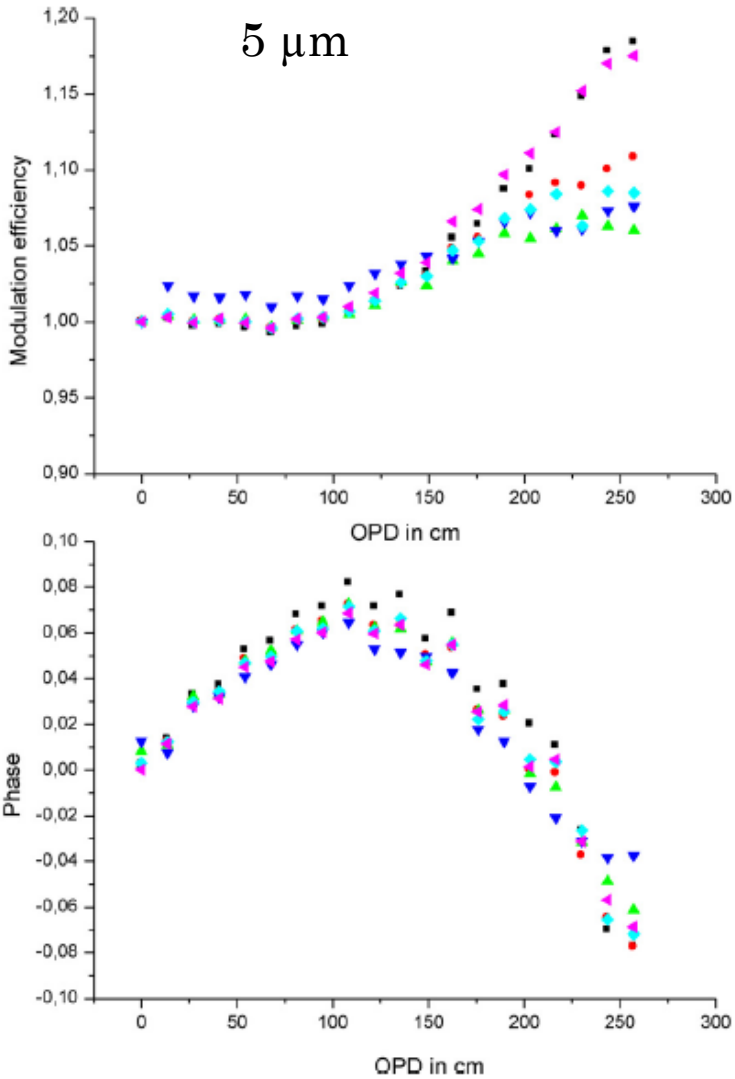
^a Sorbonne Université, CNRS, De la Molécule aux Nano-objets: Réactivité, Interactions et Spectroscopies, MONARIS, 75005 Paris, France

^b Sorbonne Université, Observatoire de Paris, Université PSL, CNRS, Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères, LERMA-IPSL, 75005 Paris, France

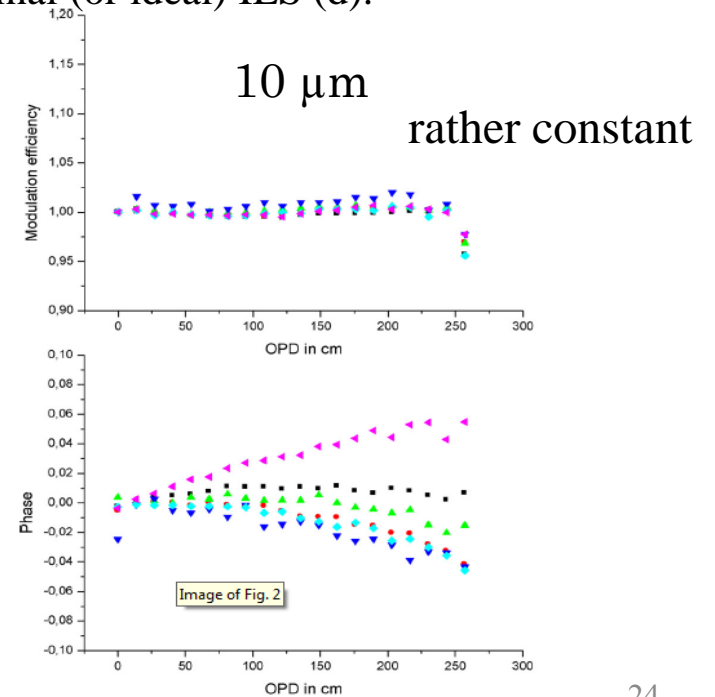


Spectra at 5 μm were fitted individually or using a multispectrum fitting procedure :
=>The fit residuals let always see a W-sharped signature.

Notice that such signature may be due to either an inaccurate line profile or an incorrect ILS or pressure inconsistencies...



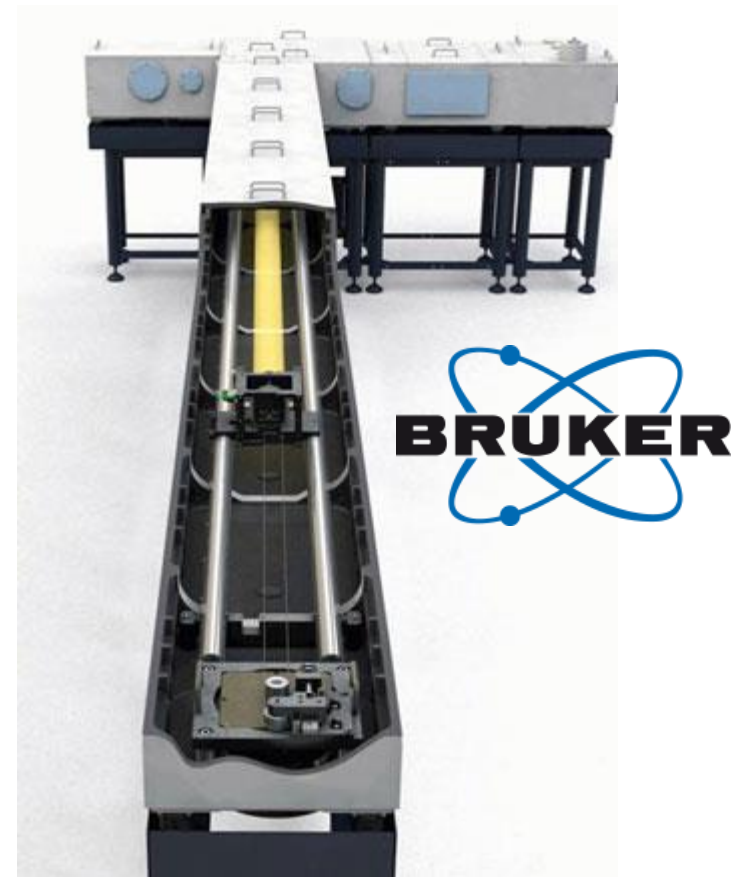
The resulting ILS was used to do new fits, using the ILS derived from LINEFIT (c) and the figure above shows a real improvement compared to fits obtained using the nominal (or ideal) ILS (d).



High resolution FTIR Spectrometer

Commercial FTS

- The movable mirror moves by scan.
- Only one scan gives a spectrum with a **high resolution** but a very **poor signal to noise ratio**.
- To increase the signal to noise ratio, **numerous scans have to be added**.

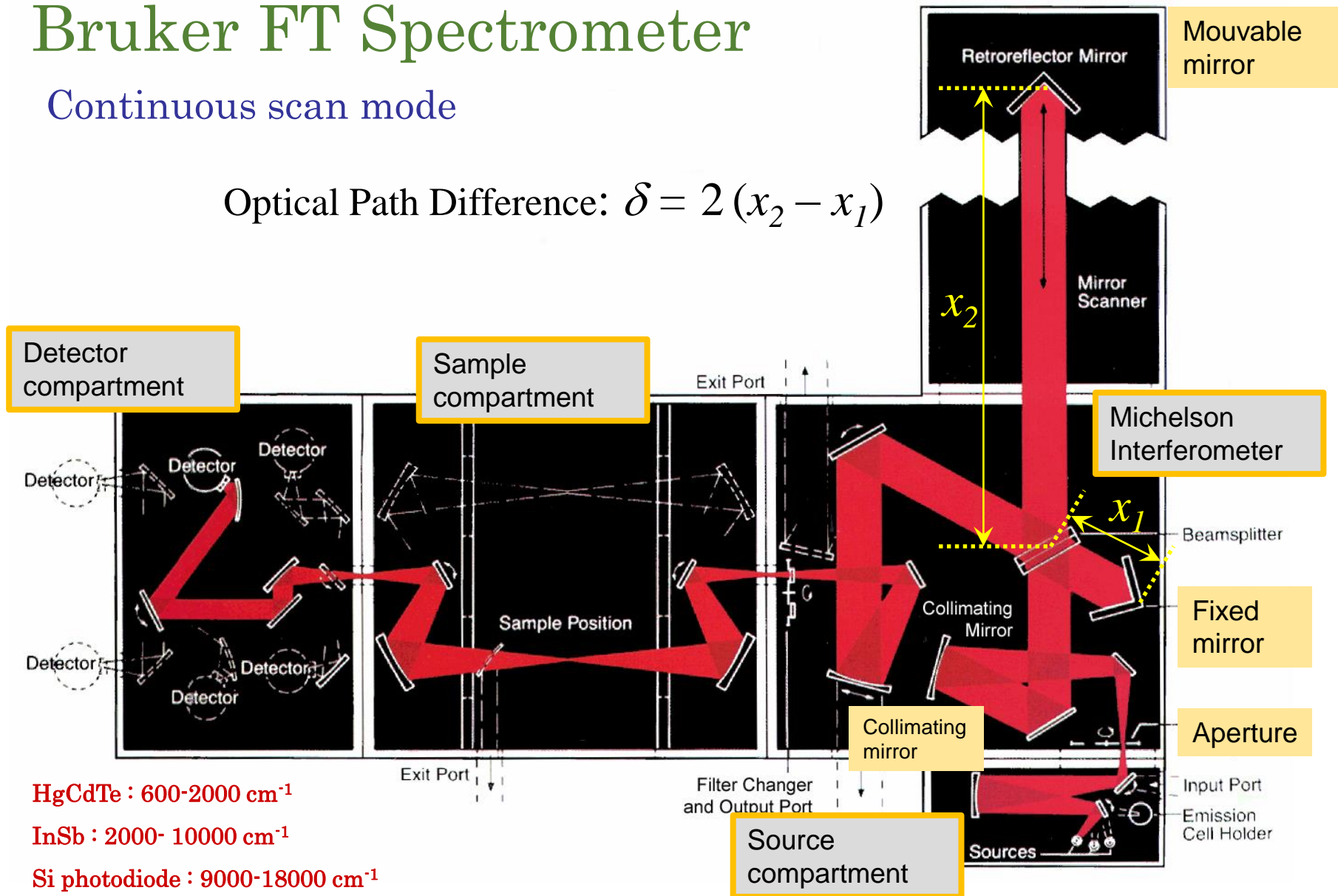


STF IR IFS 125HR (BRUKER)

Bruker FT Spectrometer

Continuous scan mode

$$\text{Optical Path Difference: } \delta = 2(x_2 - x_1)$$

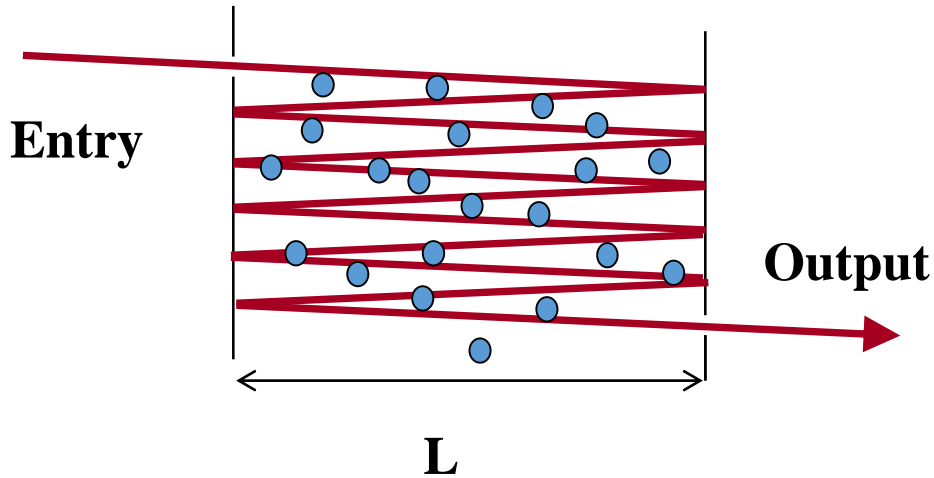


HgCdTe : 600-2000 cm^{-1}

InSb : 2000- 10000 cm^{-1}

Si photodiode : 9000-18000 cm^{-1}

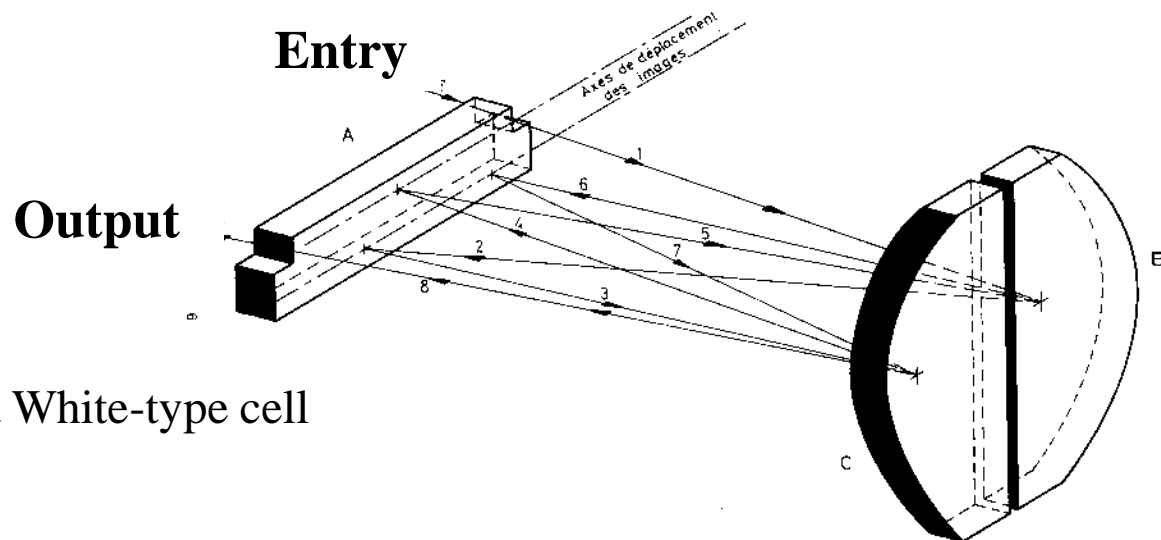
Traditionnal method to increase the sensitivity = increase the **absorption path length (L)**



Loi de Beer-Lambert:

$$T(\sigma) = e^{-\alpha(\sigma)L}$$

Long multi-path cell:

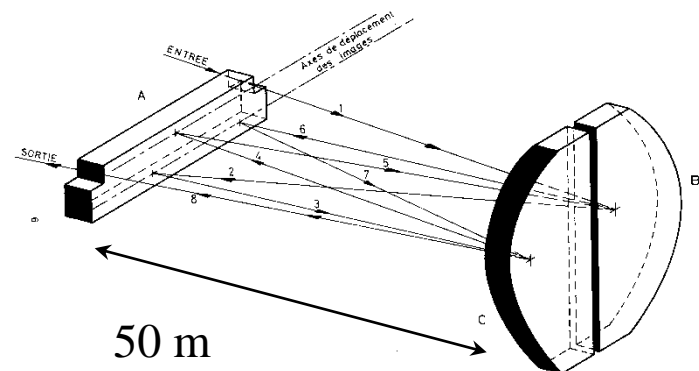


Optical configuration of a White-type cell

J. U. White, "Long optical path of large aperture," J. Opt. soc. Am. **32**, p. 285-288 (1942).

50-meter White cell

=> from 200 m up to 2 km

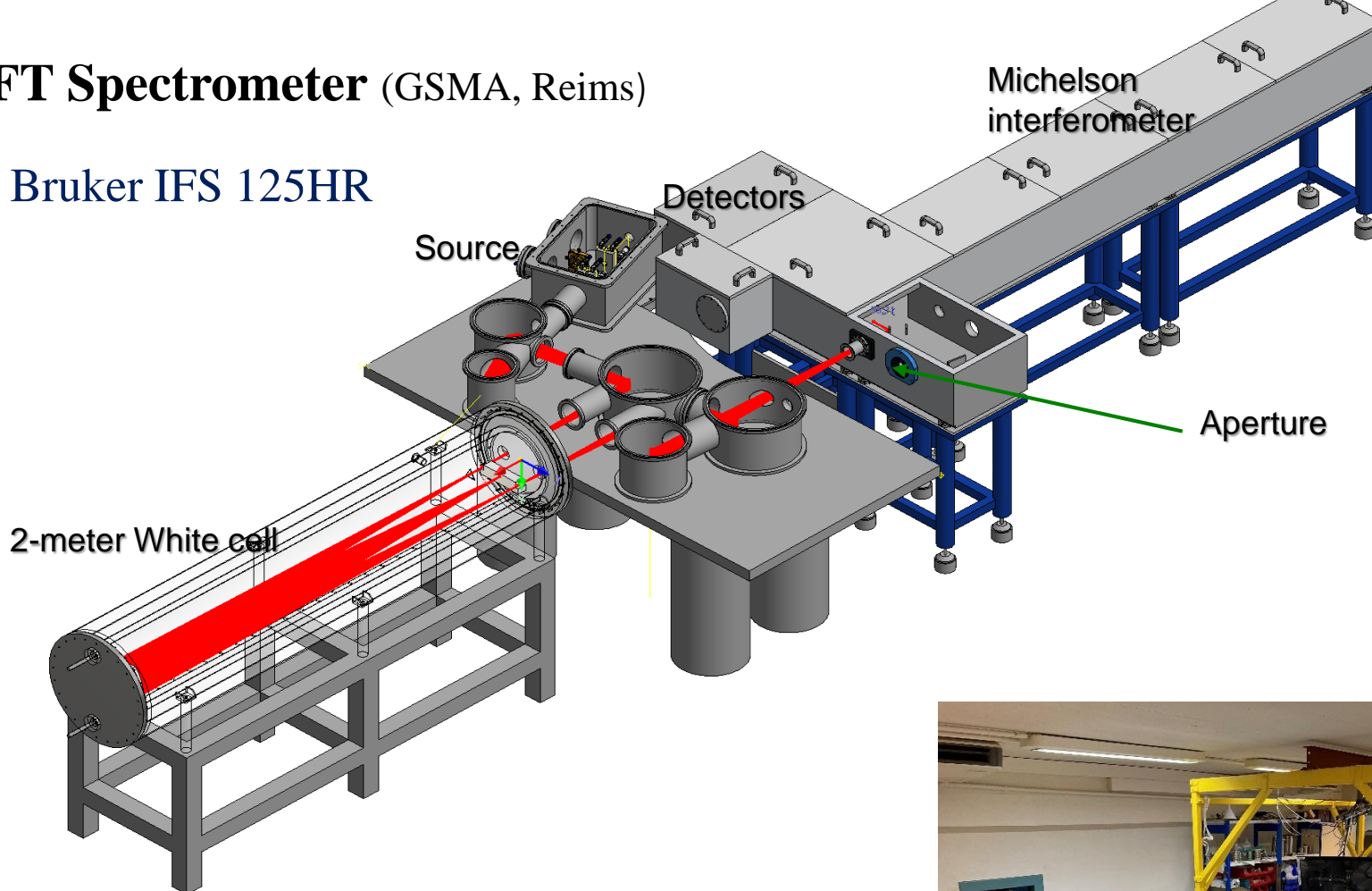


50-meter White cell connected
with the FTS GSMA (Reims)

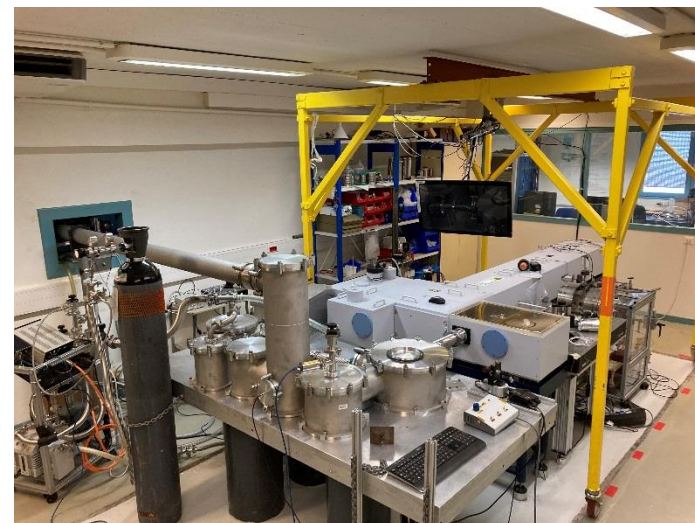


FT Spectrometer (GSMA, Reims)

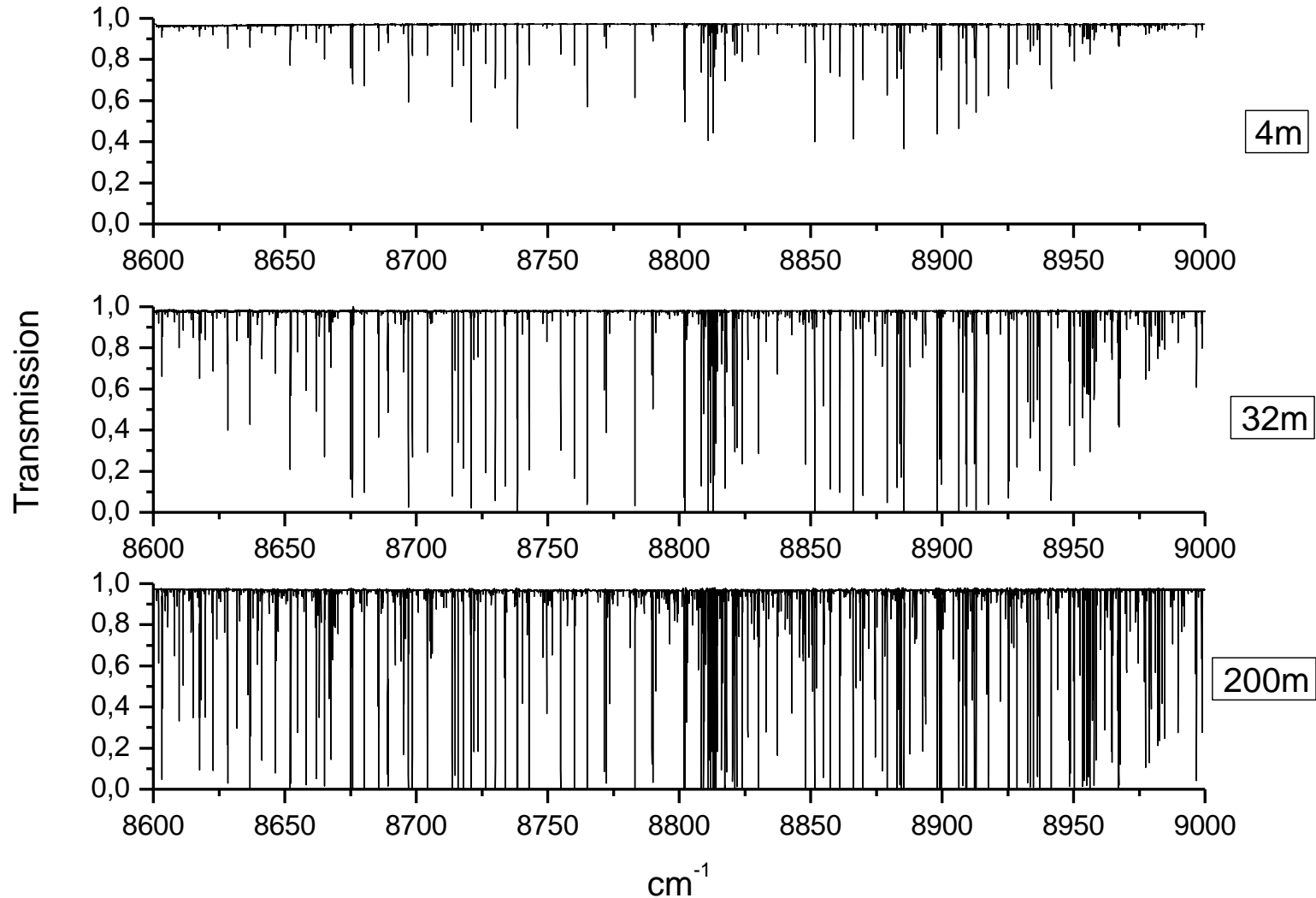
Bruker IFS 125HR



Scan mode, MPD : 3,72 m
Resolution : 0,0024 cm^{-1}
Spectral range: 700-33000 cm^{-1}
Beam splitters: KBr, CaF_2 ,
Quartz vis
Detectors : HgCdTe, InSb



Example of H₂O spectra at room temperature

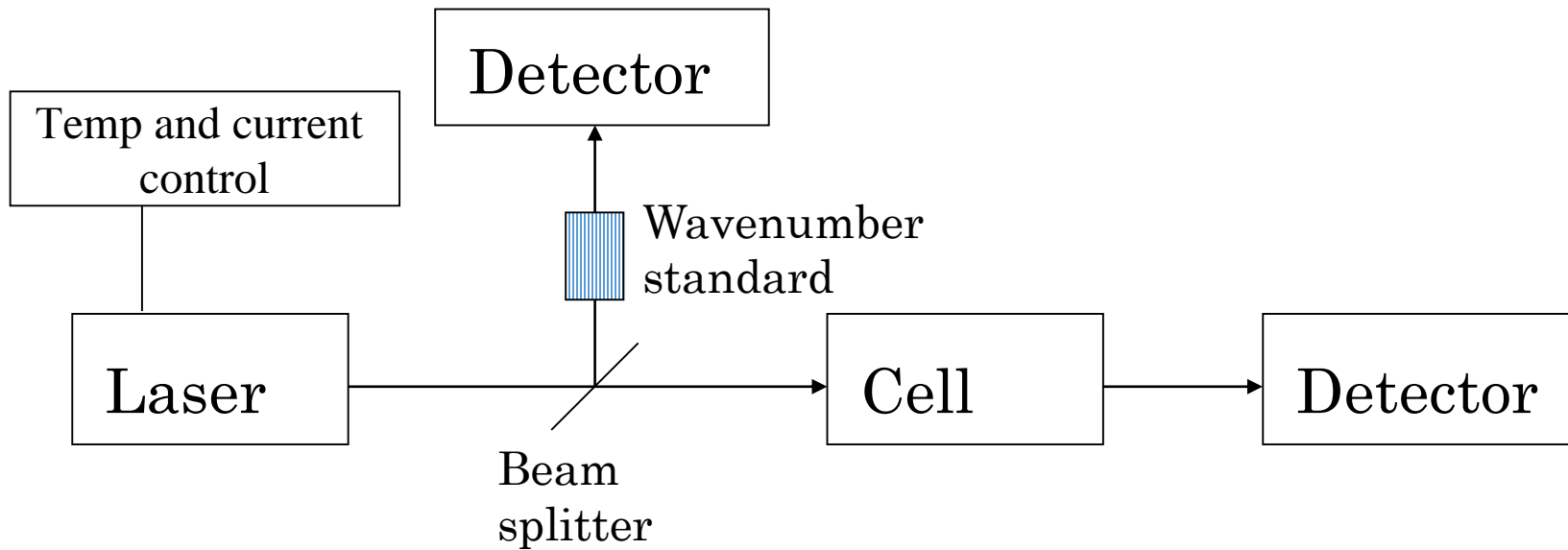




Instrumental devices

👉 Laser Spectrometer

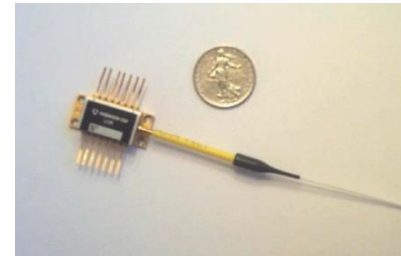
Schematic set-up



LASER Sources

Different technologies to cover the spectral ranges from the near IR to the mid IR

Telecom Laser Diode : 1.3 to 1.7 μm (near IR)

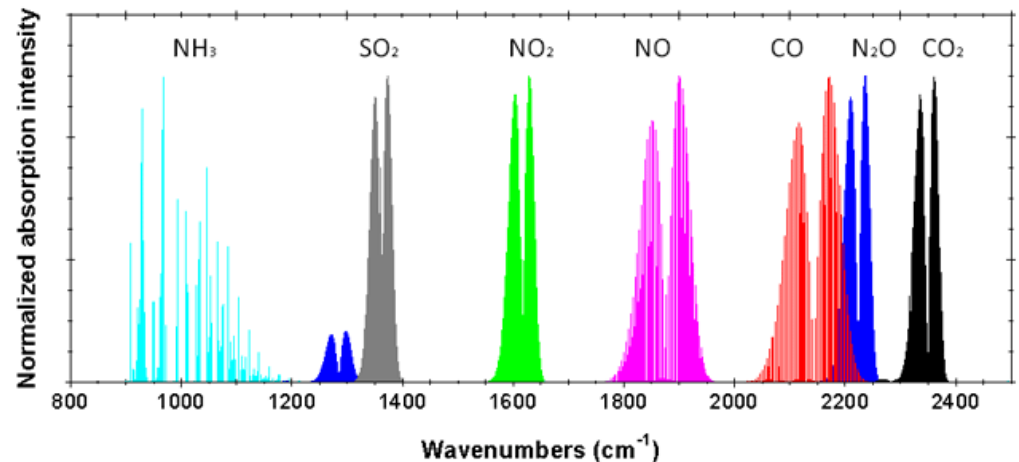


GaSb diode : 2-3 μm

Pb salts : 4.5 - 6 μm (low power μW - mid-IR)

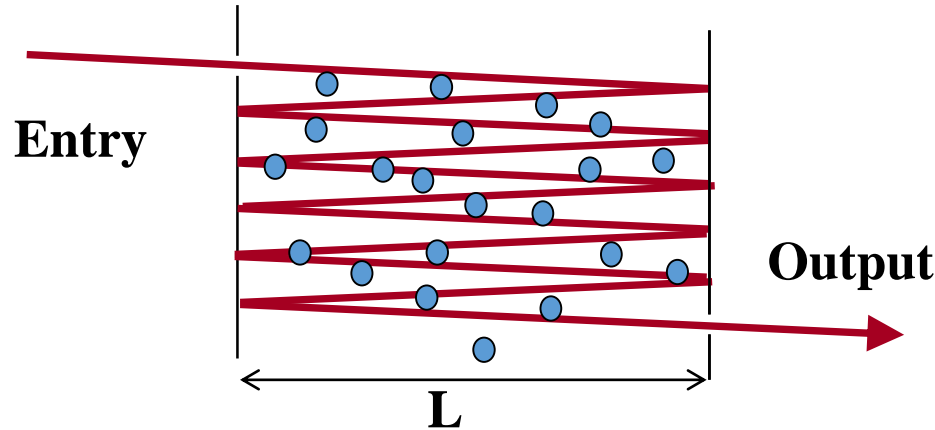
Improvement => **Quantum Cascade Laser (QCL)** Science, 264, n°5158 p.553 (1994)

Emission range : from 4 to 10 μm



Power better of a hundred compared to diode laser, with tunable area up to 200 cm^{-1}

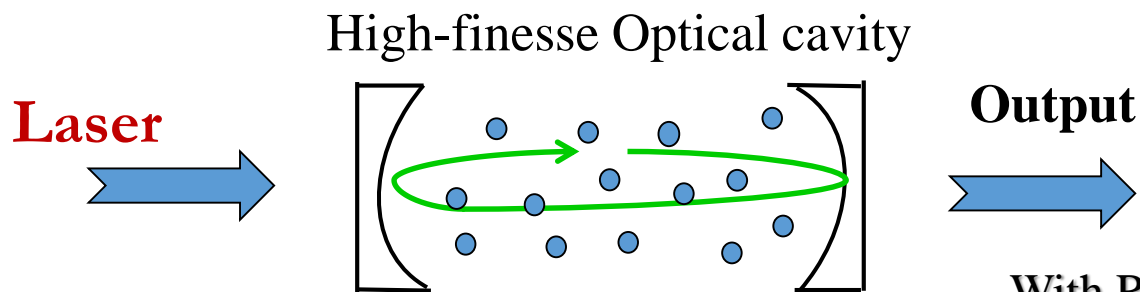
Traditional method: increase the **absorption path length (L)**



Loi de Beer-Lambert:

$$T(\sigma) = e^{-\alpha(\sigma)L}$$

To increase the sensitivity, laser spectroscopy uses high-finesse optical cavities
=> Cavity Ring Down Spectroscopy (CRDS) or Cavity enhanced spectroscopy (CEAS)

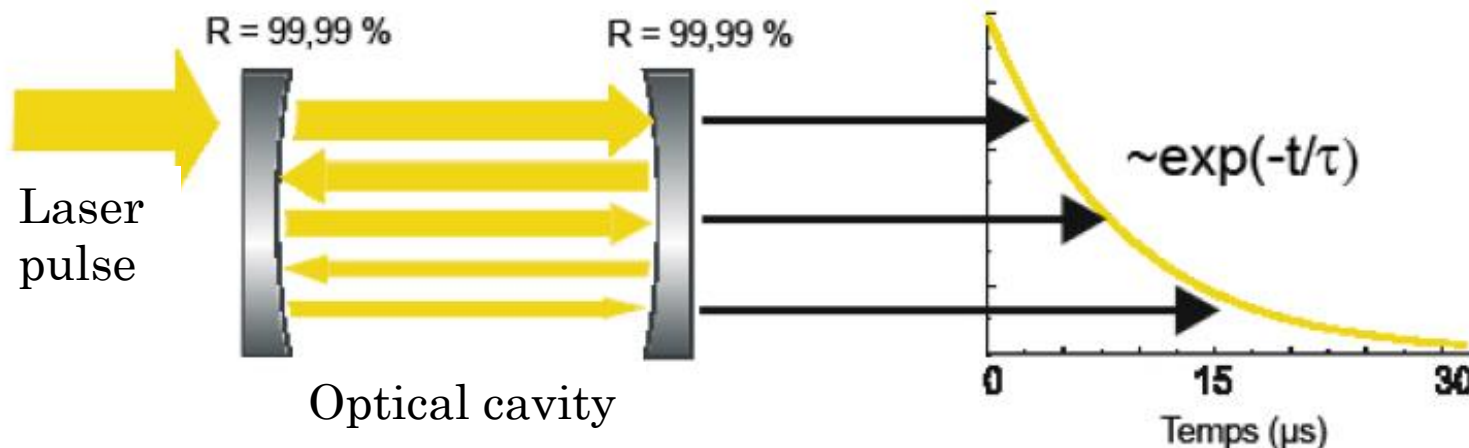


With $R = 1 - T$ – losses $\approx 99,99\%$
and mirrors separated by 50 cm
 \equiv an effective absorption length of
5000 m.

A. O'Keef et al, Rev. Sci. Instrum. **59**, p. 2544-2551 (1988).

CW-CRDS (Cavity Ring Down Spectroscopy)

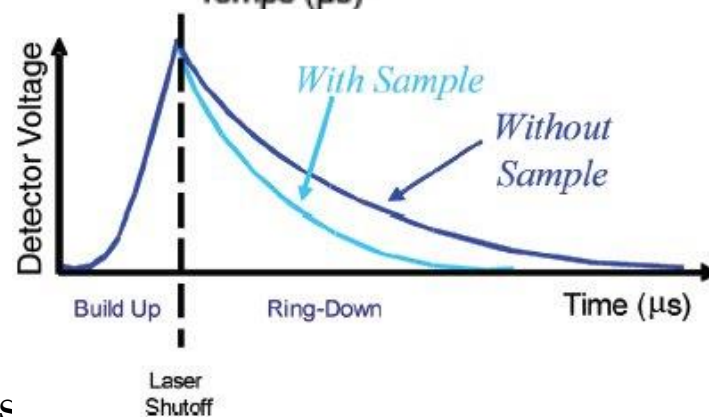
CW cavity ring down spectroscopy D. Romanini et al. Chemical Physics Letters 264 (1997) 316-322



The absorption coefficient is obtained as follow:

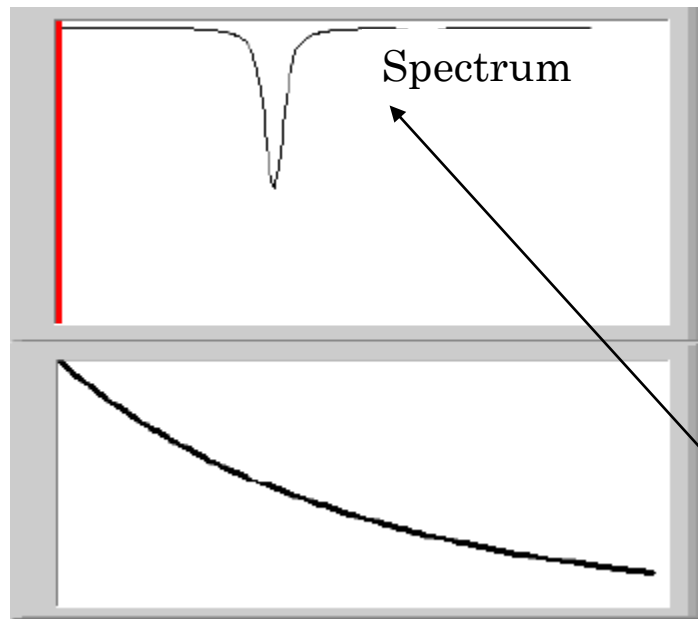
$$\alpha(\nu) = \frac{1}{c\tau_g(\nu)} - \frac{1}{c\tau_0}$$

The decrease of the signal depends of the losses in the cavity and is directly correlated to the absorption coefficient.



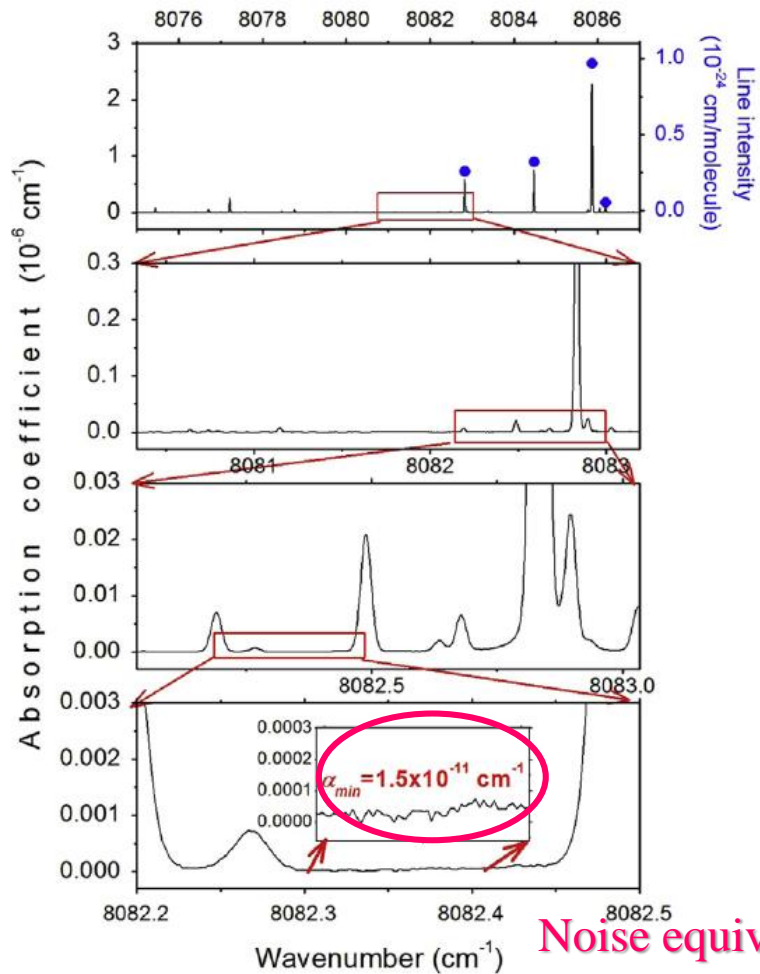
Decay time with gas (τ_g) or without gas (τ_0)

CRDS Cavity Ring Down Spectroscopy



Increase of sensitivity by a factor of 100 or 1000.

by scanning in wavenumber

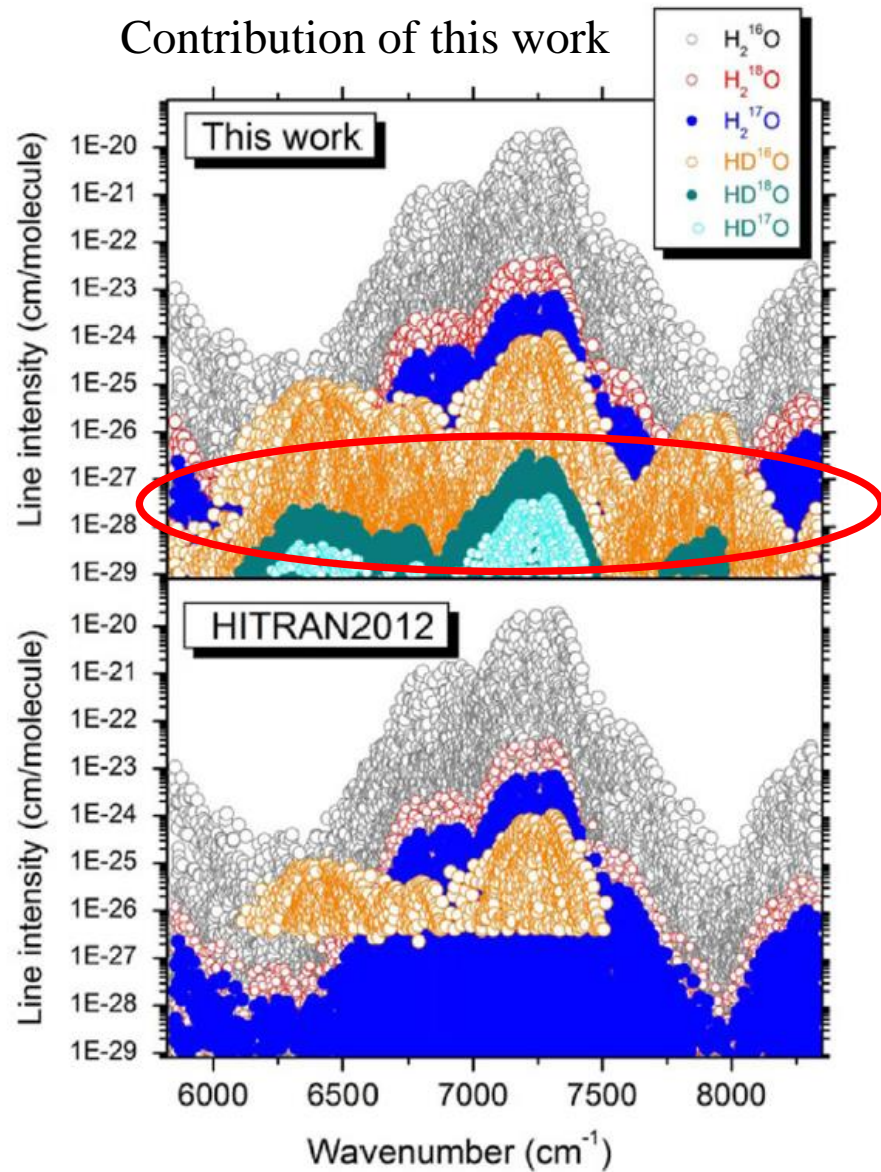


Noise equivalent
absorption: 500 times
less than with traditional
spectroscopy

CRDS Spectrum of water vapor around 8000 cm⁻¹

S.N. Mikhailenko et al., JQSRT 179 (2016) 198-216

Contribution of this work



Advantages and drawbacks

FT Spectrometry

- 😊 FTS allows measurements **on several hundreds cm^{-1}** (broad spectrum) with good signal to noise ratio thanks to *Fellgett's advantage*
- 😊 With suitable optical elements, FTS covers the whole IR spectral region.
- 😞 FTS is limited by the resolution given by the instrumental line shape function (MPD and size of the aperture). Compromise between the recording time and the signal to noise ratio.
- 😞 Improvement of sensitivity \Rightarrow increase of the absorption length (but not infinite!!)

Laser Spectrometry

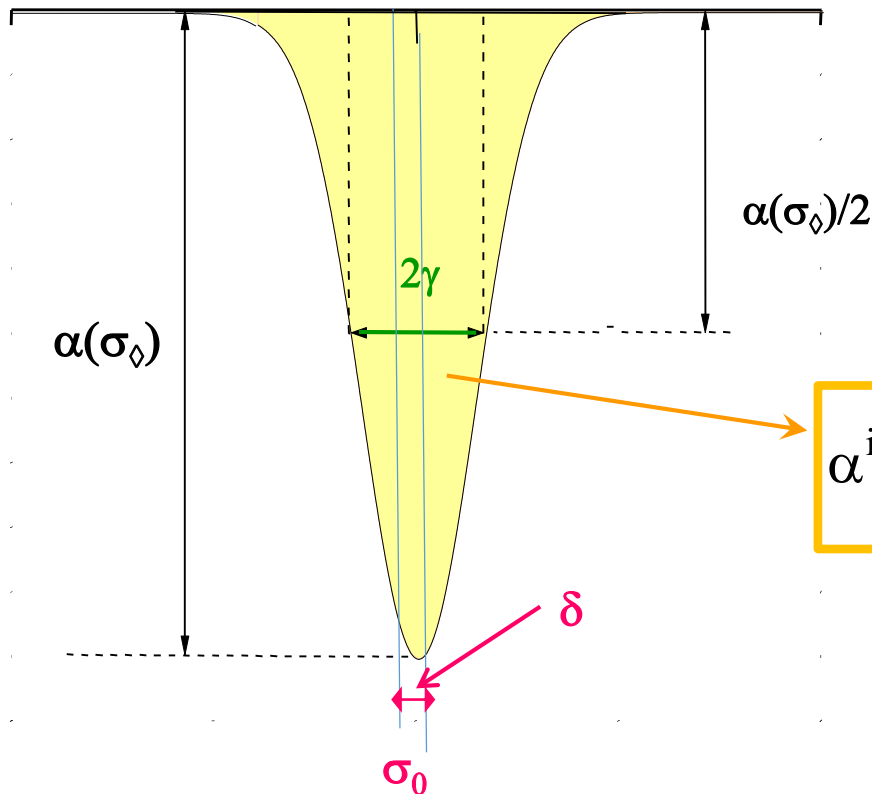
- 😞 Narrow emission spectral range (several tens cm^{-1}), need of numerous sources to cover a large spectral range.
- 😞 The emission spectral range of each laser source have to be calibrate in wavenumber and problems can appear in overlap areas.
- 😊 Very narrow apparatus function (10^{-4} - 10^{-5} cm^{-1}) \Rightarrow studies on the line profile without interaction with the instrumental line shape function.
- 😊 Improvement of sensitivity \Rightarrow High-finesse optical cavity



Line parameters retrieval

Retrieval of the line parameters

- ✓ σ_0 position
- ✓ δ pressure shift
- ✓ α^{int} intensity
- ✓ γ Half-width (at the half maximum)



$$\alpha^{\text{int}} = \int_{-\infty}^{+\infty} \alpha(\sigma) d(\sigma)$$

Choice of molecule

(molar mass, Doppler width)

Databases

Calculation of the ILS
Needs : spectrometer specifications

Convolution

Calculation of a synthetic line with algorithms simulating line profile
Needs : experimental conditions (Pressure, Temperature, absorption length,...)

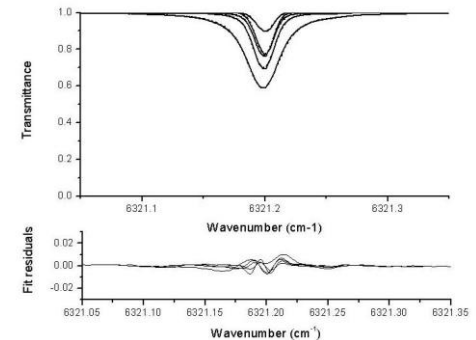
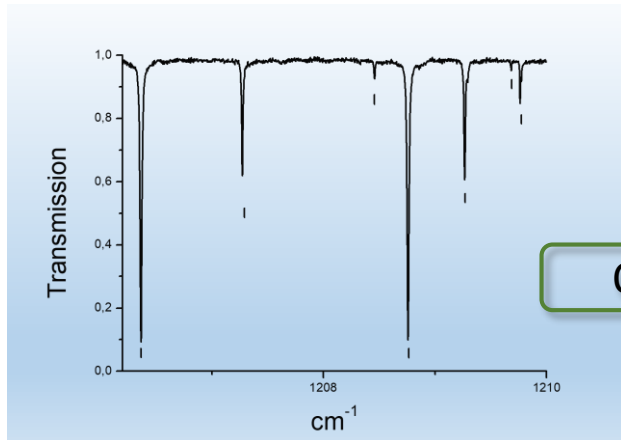
Calculated spectrum

Line by line least square fit

The fit of the parameters p_1, \dots, p_k allows to minimize the function F :

$$F(p_1, p_2, \dots, p_k) = \sum_{j=1}^M \sum_{i=1}^{N_j} \left[T_{j\sigma_i}^{\text{Obs}} - T_{j\sigma_i}^{\text{calc}}(p_1, p_2, \dots, p_k) \right]^2$$

Observed spectrum



Single spectrum

First step:

Fit of low pressure spectrum
(Doppler broadening)

Intensity measurement

(with fixed broadening
coefficients)

Start again

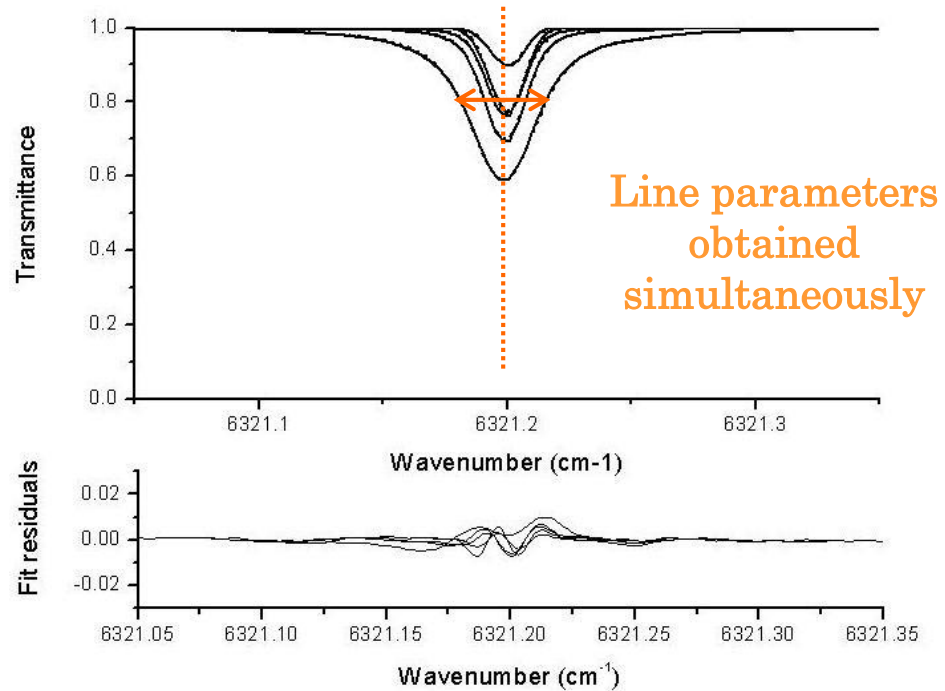
Second step:

Spectra at higher pressure
(Lorentz broadening)

**Fit of broadening
parameters**

(with fixed intensity)

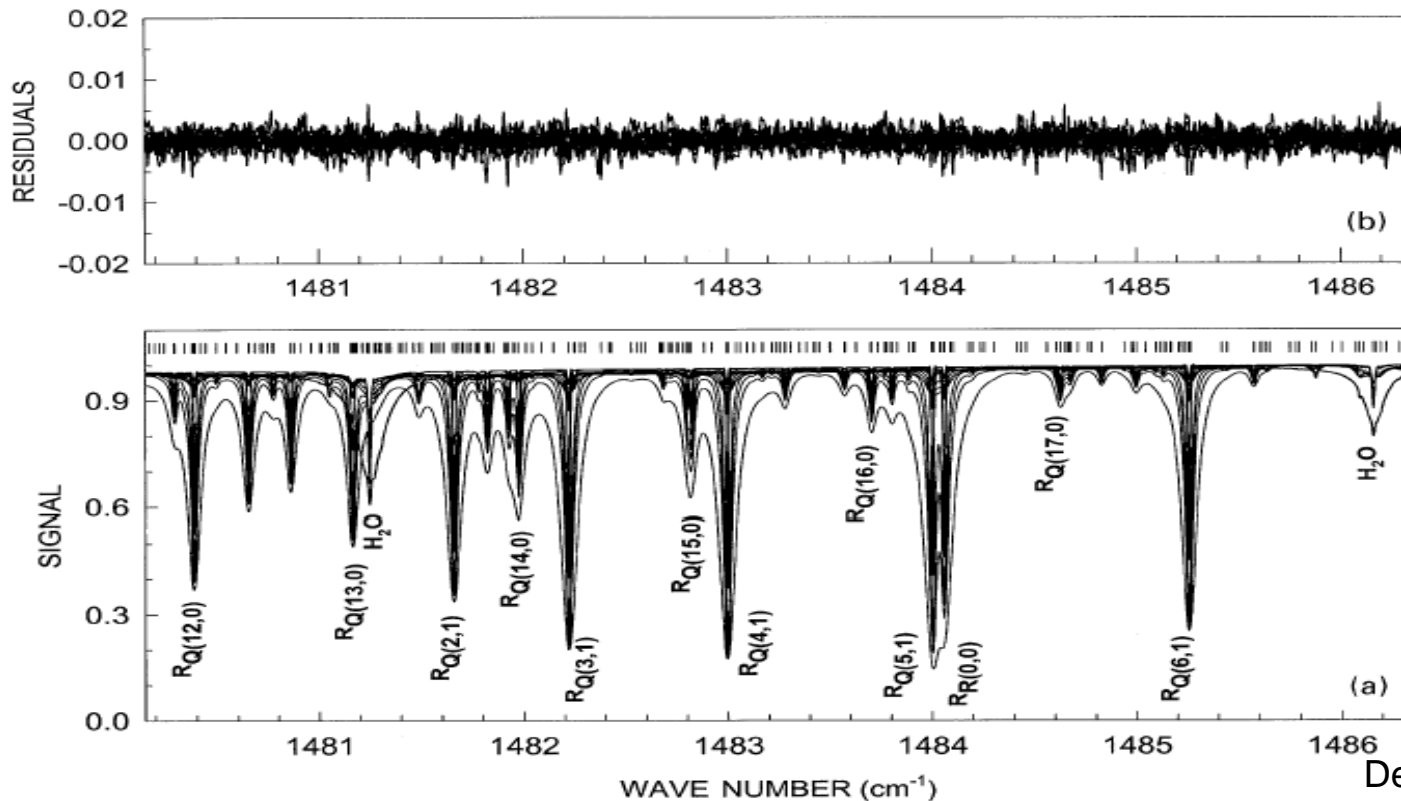
Multispectrum



- Fit of several spectra simultaneously
- Time saving
- Choice of experimental conditions of spectra is very important : to have information simultaneously on intensity and broadening coefficients.

Multispectrum fit

MULTISPECTRUM FIT AROUND 1483 cm⁻¹ IN THE ν_5 BAND OF ¹²CH₃D



¹²CH₃D

14 spectra

296 K

10 – 2458 cm

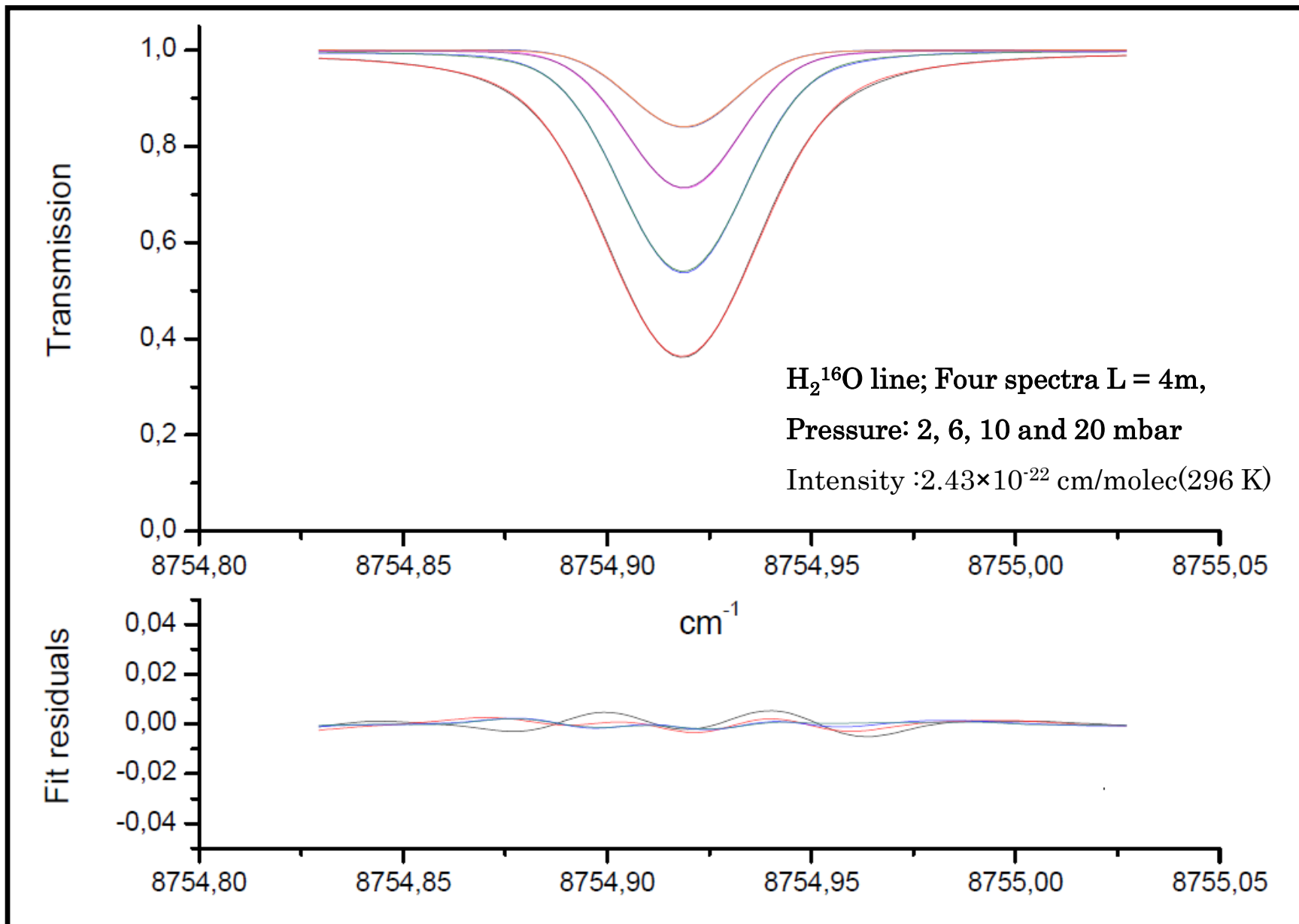
5 low pressures

4 higher

Broadened by N₂

Devi *et al.*, JQSRT 74, 1 (2002)

- MFT software GSMA (2001) J.-J. Plateaux *et al.*, JQSRT 68, 507-520 (2001)
- D. Jacquemart, Thesis, LPMAA 2002, O. Lyulin *Atmospheric and Oceanic Optics*, 2015, Vol. 28, No. 6, pp. 487-495
- Hurtmans *et al.*, JMS 215 (2002) 128-133
- and many other groups now....



Several sets of fitting parameters:

Parameters related to the spectrometer specifications : 100% Transmission (measured with a polynomial function), parameters of the instrumental line shape (effective value of the iris radius), shift in wavenumber by the optical setup, partial pressure...

Parameters related to the line shape model

can be different from one spectrum to another

Parameters related to the studied molecule: line parameters (wavenumber, intensity, broadening parameters...)

same from one spectrum to the other



Databases

Spectroscopic databases

By Molecule:

- CDSD (Carbon Dioxide Spectroscopic Databank) at room temperature (<ftp://ftp.iao.ru/pub/CDSD-296>)
Higher temperature 1000K et 3000K (<ftp://ftp.iao.ru/pub/CDSD-1000>)
- S&MPO (Spectroscopy and Molecular Properties of Ozone) (<https://smpo.univ-reims.fr/>)
- MeCaSDa – Methane Calculated Spectroscopic Database (<vamdc.icb.cnrs.fr/PHP/methane.php>)

Atmospheric or astrophysic applications


- **HITRAN**: <http://www.cfa.harvard.edu/hitran/>
- **GEISA** <https://geisa.aeris-data.fr/> *Spectroscopic databases, tutorial - Thibault Delahaye*
- **HITEMP** like HITRAN for teledetection applications, high temperature (1000 K) (**CO, H₂O, CO₂**)

High-resolution TRANsmission molecular absorption database

Information: line parameters, IR cross section, UV absorption data, refraction index of aerosols, algorithms for the line coupling...

The screenshot shows the HITRANonline website header. The logo "HITRANonline" is on the left, with a URL "https://hitran.org/" and "Login | Register" on the right. Below the logo is a navigation menu with items: Home, Data Access, Documentation, Conferences, Links, and About. Under "Data Access", it says "The HITRAN Database" and "55 molecules available in the line-by-line portion". There are also icons for settings, a clock, and a user profile.

HITRAN is an acronym for *high-resolution transmission* molecular absorption database. HITRAN is a compilation of spectroscopic parameters that a variety of computer codes use to predict and simulate the transmission and emission of light in the atmosphere.

 @hitran

 Tutorials

Updates, improvements, and corrections are posted in this panel.

The screenshot shows the "News" section of the HITRAN website. It lists several news items with dates and titles. The "Database Updates" section is highlighted with a red oval. The news items are:

- Mar 2022 | 23000 users milestone
- Oct 2021 | The data on this website corresponds to the HITRAN2020 edition
- Apr 2021 | History of HITRAN by Dr. Laurence S. Rothman
- Apr 2020 | HITEMP now includes methane
- Jul 2015 | All inquiries can be made to HITRAN's support team at info@hitran.org
- Nov 2021 | Lines of $^{16}\text{O}_3$ in 850-980 cm^{-1} region restored
- Oct 2021 | The updates to the HITRAN2020 edition will be announced in this section as they appear

HITRAN2020 molecular spectroscopic database.
J. Quant. Spectrosc. Radiat. Transf. 277, 107949 (2022).
[doi:10.1016/j.jqsrt.2021.107949.](https://doi.org/10.1016/j.jqsrt.2021.107949)

HITRAN Line-by-line Parameters

Parameter	Field size	Definition
Mol	I2	Molecule number
Iso	I1	Isotopologue no. (1 = most abundant, 2 = second most abundant, ...)
ν_{if}	F12.6	Transition wavenumber in vacuum [cm ⁻¹]
S_{if}	E10.3	Intensity [cm ⁻¹ /(molecule-cm ⁻²) @ 296K]
A_{if}	E10.3	Einstein A-coefficient [s ⁻¹]
γ_{air}	F5.4	Air-broadened half-width (HWHM) [cm ⁻¹ /atm @ 296K]
γ_{self}	F5.3	Self-broadened half-width (HWHM) [cm ⁻¹ /atm @ 296K]
E''	F10.4	Lower-state energy [cm ⁻¹]
n_{air}	F4.2	Temperature-dependence coefficient of γ_{air}
δ_{air}	F8.6	Air pressure-induced shift [cm ⁻¹ /atm @ 296K]
ν', ν''	2A15	Upper and Lower "global" quanta
q', q''	2A15	Upper and Lower "local" quanta
ierr	6I1	Uncertainty indices for ν_{if} , S_{if} , γ_{air} , γ_{self} , n_{air} , δ_{air}
iref	6I2	Reference pointers for ν_{if} , S_{if} , γ_{air} , γ_{self} , n_{air} , δ_{air}
*	A1	Flag for line-coupling algorithm
g', g''	2F7.1	Upper and Lower statistical weights

reference temperature

160-character total

The uncertainty codes used by the HITRAN database (as presented in HITRANonline) are based on Table 5 of the HITRAN2004 paper [13]. There are two types of uncertainty code corresponding to absolute uncertainty in cm⁻¹ (used for the line position and pressure-induced line shift parameters) and relative uncertainty in % (used for the line intensity and line-shape parameters).

Code	Absolute uncertainty range	Code	Relative uncertainty range
0	≥ 1 or Unreported	0	Unreported or unavailable
1	≥ 0.1 and < 1	1	Default or constant
2	≥ 0.01 and < 0.1	2	Average or estimate
3	≥ 0.001 and < 0.01	3	≥ 20%
4	≥ 0.0001 and < 0.001	4	≥ 10% and < 20%
5	≥ 0.00001 and < 0.0001	5	≥ 5% and < 10%
6	≥ 0.000001 and < 0.00001	6	≥ 2% and < 5%
7	≥ 0.0000001 and < 0.000001	7	≥ 1% and < 2%
8	≥ 0.00000001 and < 0.0000001	8	< 1%
9	≥ 0.000000001 and < 0.00000001		

H₂O [1] 161, 181, 171, 162, 182, 172

Positions

0. L.S. Rothman, R.R. Gamache, A. Goldman, L.R. Brown, R.A. Toth, H.M. Pickett, R.L. Poynter, J.-M. Flaud, C. Camy-Peyret, A. Barbe, N. Husson, C.P. Rinsland, and M.A.H. Smith, "The HITRAN database: 1986 Edition," *Appl. Opt.* **26**, 4058-4097 (1987).
1. C. Camy-Peyret, J.-M. Flaud, J.-Y. Mandin, J.P. Chevillard, J. Brault, D.A. Ramsay, M. Vervloet, and J. Chauville, "The High-Resolution Spectrum of Water Vapor between 16500 and 25250 cm⁻¹," *J.Mol.Spectrosc.* **113**, 208-228 (1985); J.-Y. Mandin, J.-P. Chevillard, C. Camy-Peyret, J.-M. Flaud, and J.W. Brault, "The High-Resolution Spectrum of Water Vapor between 13 200 and 16 500 cm⁻¹," *J.Mol.Spectrosc.* **116**, 167-190 (1986).

Part of line list of Hitran2020 edition

First six digits = uncertainty codes

14	5008.290751	6.231E-29	8.085E-04	08550.394	573.97060	.63-	.018780	2 0 0	0 0 0	5 1 5	6 4 2	44240504133832754	66.0	78.0
11	5008.365554	1.317E-29	2.773E-05	03460.250	2246.88480	.35-	.012580	1 1 0	0 0 0	14 1 14	13 2 11	43423307294713152	87.0	81.0
17	5008.367599	7.440E-32	1.188E-02	07900.404	702.70210	.620-	0.000000	1 2 0	0 0 0	8 5 3	9 4 6	4624205141 98635 0	153.0	171.0
13	5008.379900	1.790E-26	2.130E-01	05400.391	737.62400	.69-	0.006500	1 1 0	0 0 0	4 4 1	5 5 0	564240543633712754	162.0	198.0
13	5008.379902	5.990E-27	2.139E-01	05400.391	737.62040	.69-	0.010000	1 1 0	0 0 0	4 4 0	5 5 1	664240543633712754	54.0	66.0
14	5008.385041	5.758E-27	2.617E-01	07800.340	964.85050	.51-	0.007800	0 1 1	0 0 0	10 1 9	10 2 8	564240504133832754	126.0	126.0
11	5008.433992	1.092E-29	2.439E-01	06960.265	4123.28530	.63-	0.014100	0 2 1	0 1 0	12 4 8	12 6 7	43423307294713152	75.0	75.0
11	5008.461406	2.230E-27	6.002E-02	05920.250	2756.41530	.59-	0.040000	0 1 1	0 0 0	13 4 10	13 6 7	434223807294713152	81.0	81.0
17	5008.468735	1.230E-32	1.121E-04	09700.516	73.67640	.620-	0.000000	1 2 0	0 0 0	3 1 2	2 2 1	4624205141 98635 0	126.0	90.0
11	5008.498047	2.167E-30	1.414E+01	03570.281	5255.34670	.28-	0.014140	0 1 2	0 0 1	10 2 9	11 2 10	332230807294713152	63.0	69.0
13	5008.633610	1.220E-28	8.182E+00	02720.235	2740.42120	.36-	0.007000	0 1 1	0 0 0	13 4 10	14 4 11	364240543633712754	486.0	522.0
11	5008.642515	2.077E-29	4.918E+00	02630.208	4427.22620	.22-	0.014570	0 1 1	0 0 0	15 9 6	16 9 7	334233807294713152	31.0	33.0
11	5008.659733	1.540E-26	2.257E-04	05800.352	1059.83550	.59-	0.009000	0 3 0	0 0 0	6 6 1	7 5 2	454323803333712754	39.0	45.0
11	5008.705387	1.447E-26	1.738E-01	05360.333	2495.16590	.53-	0.010500	1 2 0	0 1 0	8 1 8	8 2 7	464323807233712754	51.0	51.0
11	5008.715772	6.234E-29	4.918E+00	02620.208	4427.12060	.21-	0.014500	0 1 1	0 0 0	15 9 7	16 9 8	334233807294713152	93.0	99.0
11	5008.729114	1.105E-30	3.041E-06	07060.298	2254.28380	.700-	0.008230	1 1 0	0 0 0	11 5 6	10 8 3	432230807294713152	69.0	63.0
16	5008.742871	1.138E-28	1.829E+00	08390.410	372.50390	.67-	0.005150	0 1 1	0 0 0	4 3 1	5 3 2	46424054133832754	324.0	396.0
14	5008.746117	3.094E-29	2.495E-03	05630.351	1082.78490	.55-	0.010840	0 1 1	0 0 0	10 3 8	9 5 5	564240504133832754	126.0	114.0
13	5008.781871	8.910E-29	4.594E-04	07700.391	415.14500	.670-	0.000000	-2-2-2	0 0 0	6 -1 -1	5 2 4	1422304636917122 0	78.0	66.0
11	5008.848788	4.937E-27	2.169E-04	05800.352	1059.64670	.59-	0.004000	0 3 0	0 0 0	6 6 0	7 5 3	454523803333712754	13.0	15.0
11	5008.863697	3.016E-30	2.810E-05	05350.281	2522.26520	.55-	0.005140	1 1 0	0 0 0	12 5 8	11 8 3	432230807294713152	75.0	69.0
11	5008.890182	6.018E-29	5.350E-02	02290.195	3291.14970	.21-	0.005290	0 3 0	0 0 0	16 3 13	17 2 16	38423303360713049	33.0	35.0
12	5008.903338	1.108E-28	1.952E-01	08080.371	2152.18210	.64-	0.006000	1 2 0	0 1 0	5 1 4	6 2 5	434233807233712754	33.0	39.0
12	5008.934659	2.249E-26	1.317E-01	08720.420	752.18740	.64-	0.008100	0 1 1	0 0 0	5 2 3	6 4 2	555340507233622754	11.0	13.0
11	5008.942484	1.812E-27	2.918E-01	04870.298	3072.72640	.44-	0.020540	1 2 0	0 1 0	10 2 9	10 3 8	334223807294713152	63.0	63.0
14	5008.949120	1.288E-29	1.161E-02	07500.320	1598.06810	.44-	0.012880	2 0 0	0 0 0	11 4 7	12 5 8	564240504133832754	138.0	150.0
11	5008.968254	6.481E-30	1.156E+00	05190.315	4268.24080	.45-	0.014420	0 3 1	0 2 0	9 0 9	9 2 8	432230807294713152	19.0	19.0

Position

Intensity

Broadening parameters

Lower state energy

The uncertainty codes used by the HITRAN database (as presented in HITRANonline) are based on Table 5 of the HITRAN2004 paper [13]. There are two types of uncertainty code corresponding to absolute uncertainty in cm^{-1} (used for the line position and pressure-induced line shift parameters) and relative uncertainty in % (used for the line intensity and line-shape parameters).

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7	≥ 0.0000001 and < 0.000001	7	$\geq 1\%$ and $< 2\%$
8	≥ 0.00000001 and < 0.0000001	8	$< 1\%$
9	≥ 0.000000001 and < 0.00000001		

SPECTRA (Spectroscopy of Atmospheric Gases)

<http://spectra.iao.ru>

Implemented by

S. MIKHAILENKO, Y. BABIKOV, VI. GOLOVKO, and S. TASHKUN

Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Tomsk, Russia

- Use several databases (Hitran, Geisa, theoretical data, ...)
- Spectroscopic parameters (line by line) of 45 molecules, 0 – 25 000 cm^{-1} (spectrum calculation: stick-diagram, absorption coefficient, transmission, emission, absorption) versus the wavenumber by selecting **Molecule / isotopologue / Band(s)**
- spectrum calculation by selecting a gas mixing and the spectral region with the convolution of the apparatus function of a spectrometer

Spectroscopy of Atmospheric Gases - Microsoft Internet Explorer
 Адрес: http://spectra.lao.ru/en/mixt/spectr/

[Home](#)
[Molecules](#)
[Gas mixture spectra](#)
[Cross-Sections](#)
[Direct problem](#)
[Auxiliary data](#)
[Saved spectra](#)
[Help](#)

[Parameters](#)
[Simulation](#)
[Help](#)

SPECTRA. Mixt: Water Vapor, PS-296, 6 species. Transmission spectrum. Contour=Voigt; T=296K; P=0.3atm; L=1000m.

Input selection		Options	
Gas mixture	Water Vapor, PS-296, 6 species	<input type="checkbox"/> Separate molecules	
Function type	Transmittance	Stick scale	
General parameters:		<input checked="" type="radio"/> Natural <input type="radio"/> Logarithmic	
WN _{min} , cm ⁻¹	9390	WN _{max} , cm ⁻¹	9430
T, K	296	P, atm	0.3
I _{out} , cm/mol		1E-30	
Contour parameters:			
Shape	Voigt	WN _{step} , cm ⁻¹	0.001
Wing, HW		50	
Function parameters:			
App.func. (AF)	Sinc square (Diffraction)	Opt.path, m	1000
App.Resolution (AR), cm ⁻¹	0.01	AF wing, AR	50
<input type="button" value="Simulate spectrum"/>			

Готово



Databases

Evaluation and improvement

Study of Geoffrey C. Toon

Identify deficiencies in linelist of databases

Journal of Quantitative Spectroscopy & Radiative Transfer 182 (2016) 324–336



Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt



HITRAN spectroscopy evaluation using solar occultation FTIR spectra

Geoffrey C. Toon^{a,*}, Jean-Francois Blavier^a, Keeyoon Sung^a, Laurence S. Rothman^b, Iouli E. Gordon^b

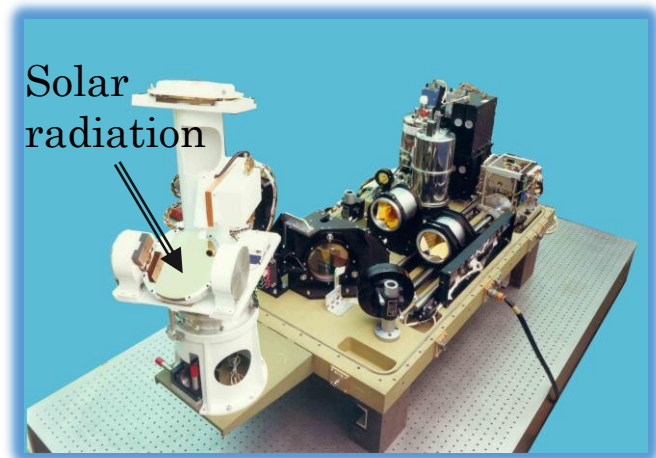
^a Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, United States

^b Harvard-Smithsonian Center for Astrophysics, Cambridge, MA, United States

Atmospheric spectra and spectra simulated using the four latest versions of HITRAN (from 2000 to 2012)

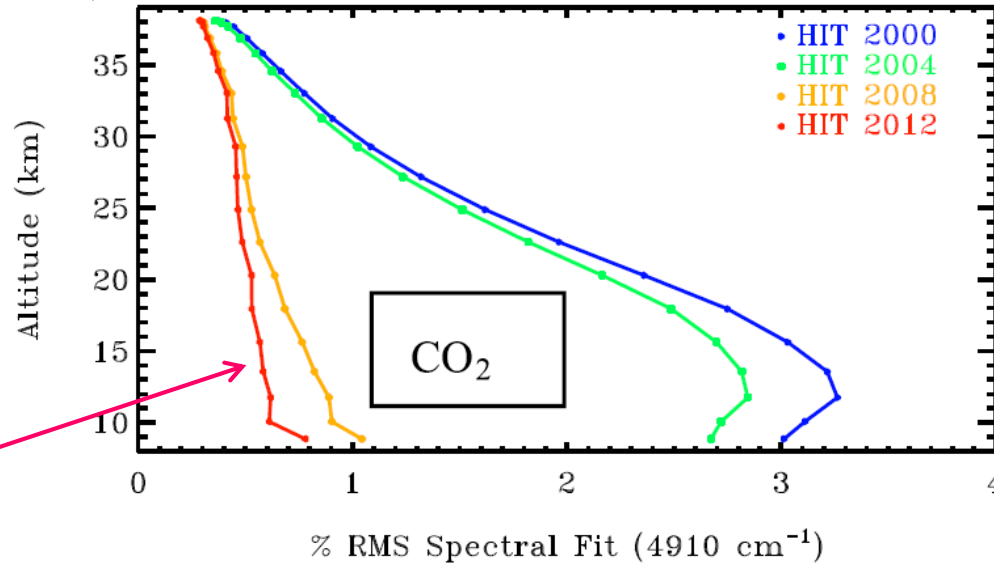


JPL MkIV Interferometer



RMS spectral fitting residuals plotted as a function of tangent altitude for eight selected windows (between 670 to 5600 cm^{-1})

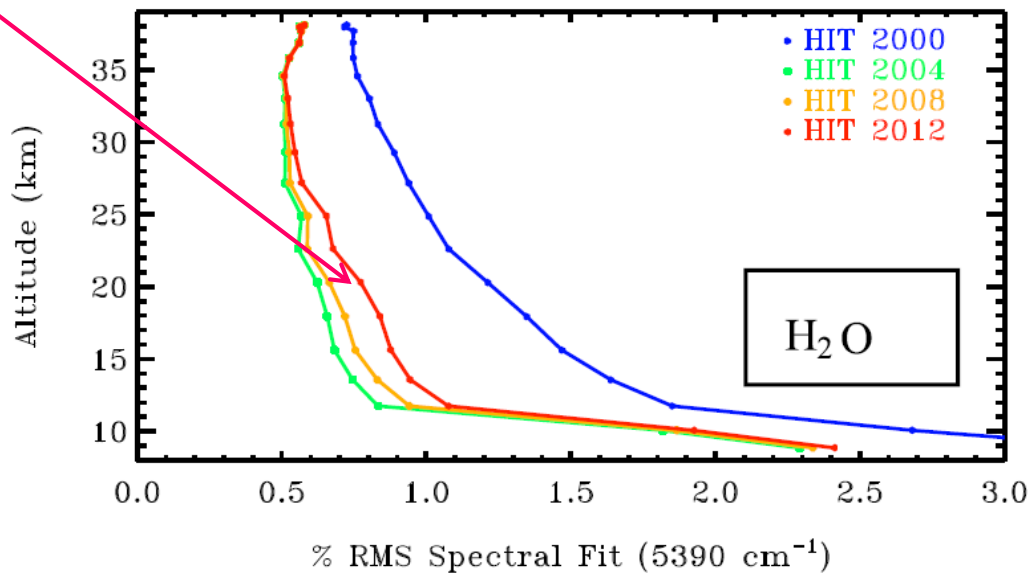
Fig. 1



RMS spectral fit
4910 cm^{-1}

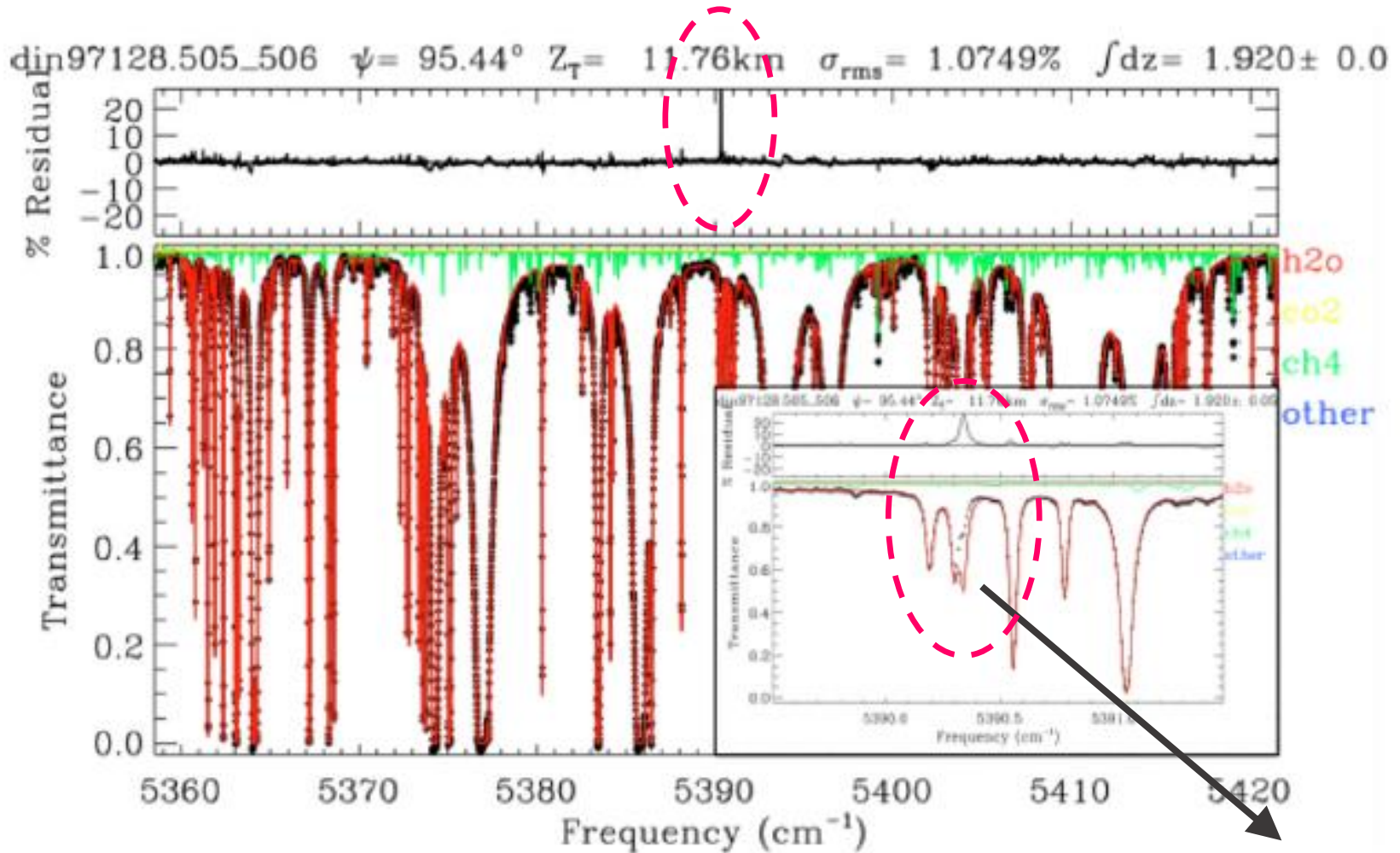
HITRAN 2012

Fig. 2



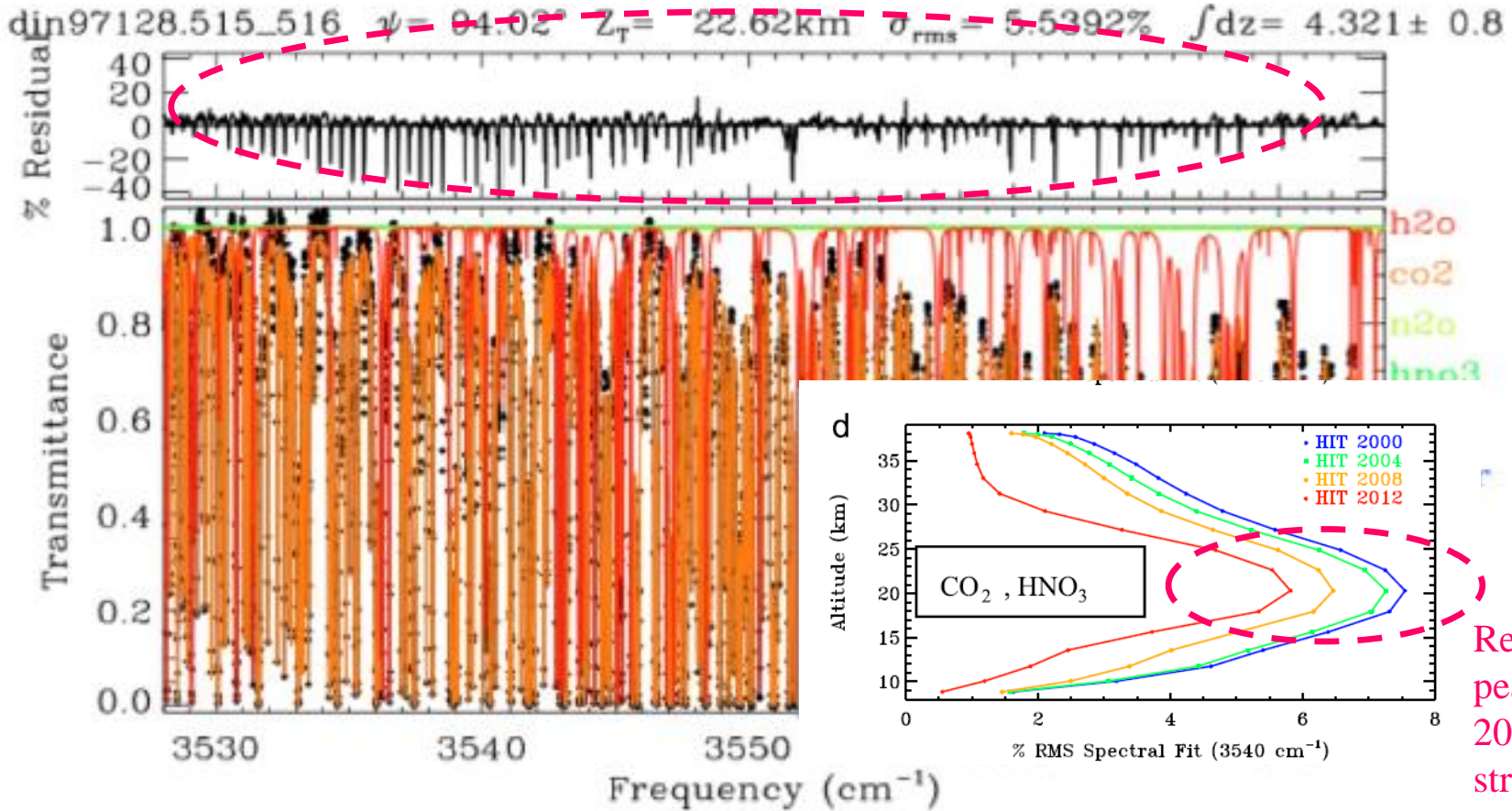
RMS spectral fit
5390 cm^{-1}

Spectral fit to a 12km altitude in the 5360-5420 cm⁻¹ window



Large positive residual due to a factor 4 intensity over-estimate: H₂O line 5390.339 cm⁻¹
The large residual not present in fits using HITRAN 2004 or 2008.

Spectral fit at 23 km in the 3528-3574 cm⁻¹ window



Residuals peaking at 20km due to stratospheric gas HNO₃

main absorbers : CO₂ and H₂O

BUT the entire HNO₃ v₁ fundamental band is missing from HITRAN2012 edition.



Validation of the HITRAN 2016 and GEISA 2015 line lists using ACE-FTS solar occultation observations

K.S. Olsen ^a, C.D. Boone ^b, G.C. Toon ^c, F. Montmessin ^a, A.A. Fedorova ^d, O. Korablev ^d, A. Trokhimovskiy ^d

Notice that the presence of 96% of CO₂ in the Martian atmosphere needs the determination of broadening parameters by CO₂

spectral region between 2325 - 4350 cm⁻¹ : application of Mars Atmosphere



The 2020 edition of the GEISA spectroscopic database

T. Delahaye ^a, R. Armante ^a, N.A. Scott ^a, N. Jacquinet-Husson ^a, A. Chédin ^a, L. Crépeau ^a, C. Crevoisier ^a, V. Douet ^b, A. Perrin ^a, A. Barbe ^c, V. Boudon ^d, A. Campargue ^e, L.H. Coudert ^f, V. Ebert ^{g, h}, J.-M. Flaud ^g, R.R. Gamache ^h, D. Jacquemart ⁱ, A. Jolly ^g ... S. Yurchenko ^h

comparisons with TCCON observations

Thank you for your attention