Study of molecular line parameters at very low temperature (down to 12 K)

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- Motivations for spectroscopic measurements at low temperature.
- Technical aspects (cooling systems, cold Herriott cell)
- Collisional cooling technique
- Examples of temperature dependence of spectroscopic parameters and their applications
- Conclusion

Motivations

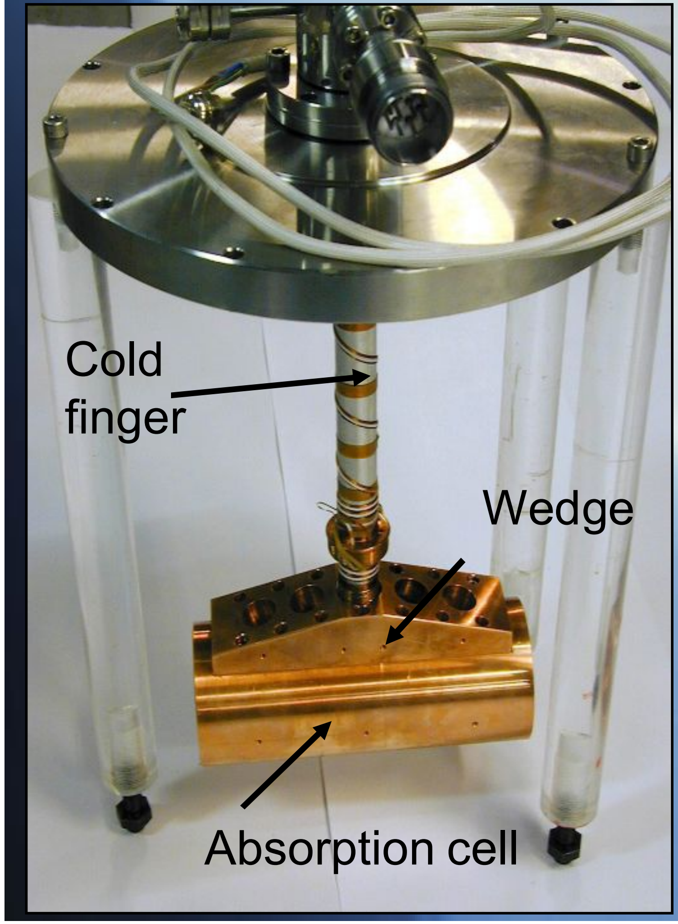
- Temperature dependence of spectroscopic line parameters (γ, β, ζ, δ) are required for precise atmospheric sounding of the Earth and outer planets.
- CH_4: important minor constituent for planetary atmospheres (Earth, Jupiter, Saturn, Titan,…).
- CO – He used as a model system for theoretical studies (validation of Potential Energy Surfaces).
- CO - X (with X = H_2 , N_2 , Ar) is of great importance for astrophysics (composition of interstellar molecular clouds and atmospheres of the outer planets).

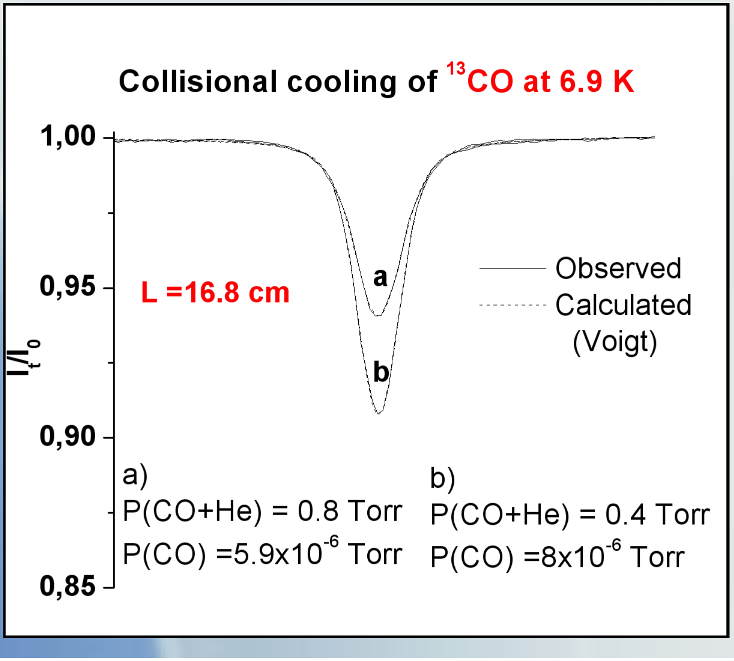
⇒ data at very low temperature are needed.

Different cooling systems

Cryogenic fluids:
- alcohol (T = 200 K)
- nitrogen (T = 77 K)
- helium (T = 7 K or lower).

Closed-cycle helium refrigeration system ⇒ T = 12 K



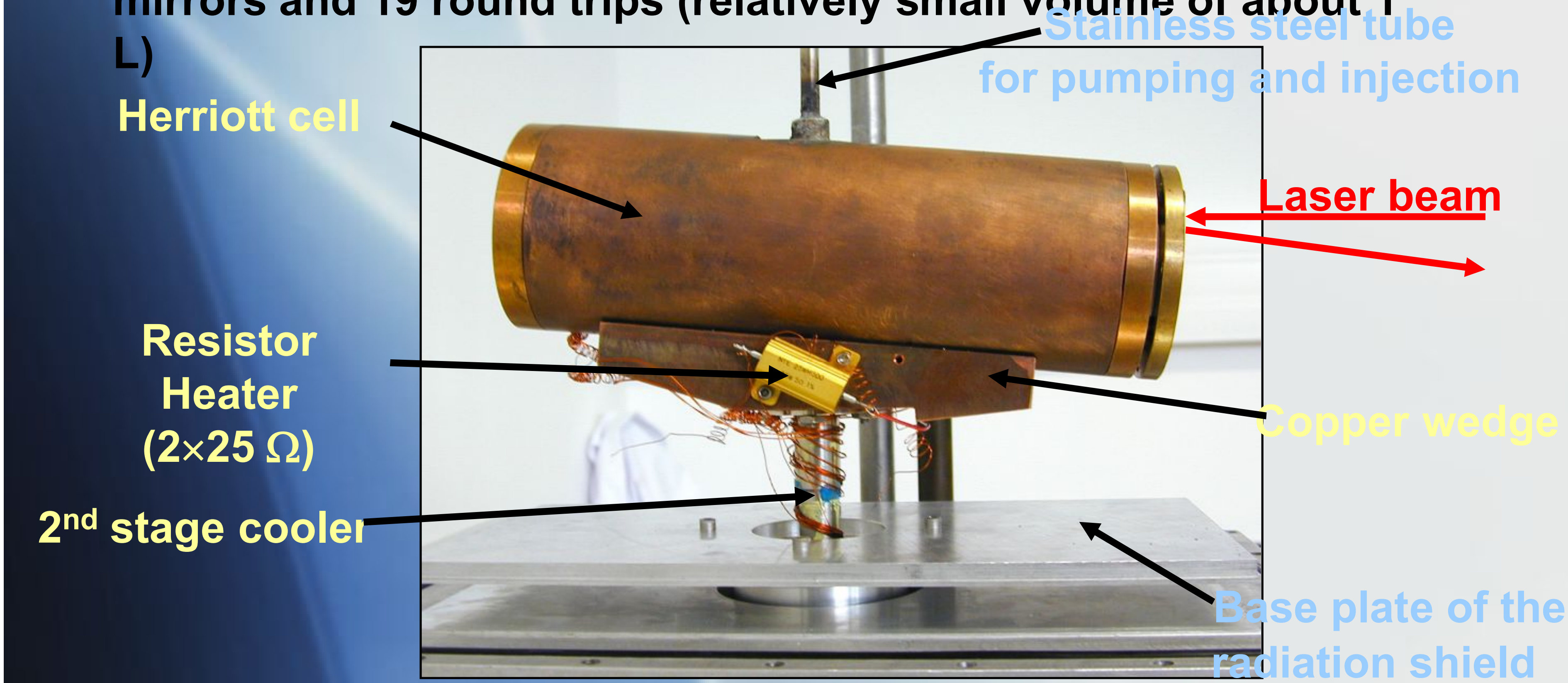


Cold Herriott cell*

4th generation cold cell (important progress in the temperature stabilization technique).

Material: ultra-pure copper (OFHC) for good thermal conductivity

Absorption pathlength: 537 cm with 14 cm between the mirrors and 19 round trips (relatively small volume of about 1 L)



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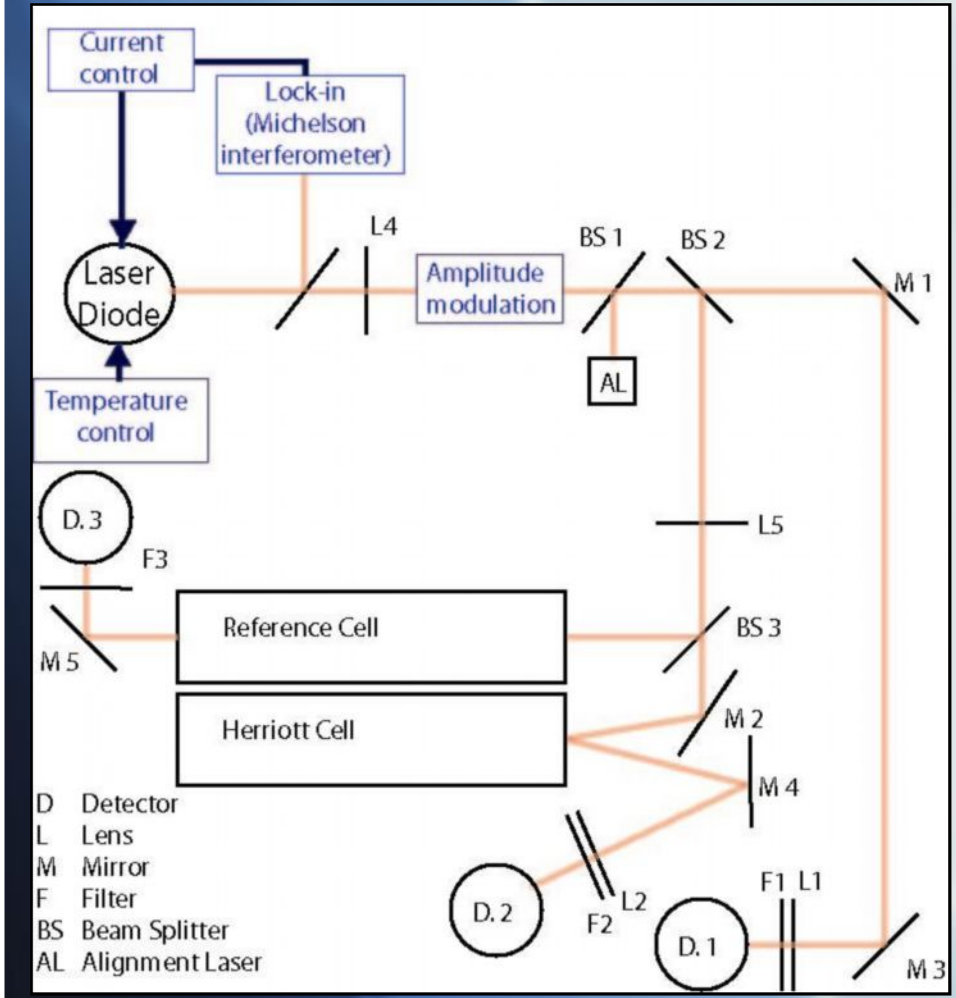
[*] D. Mondelain *et al.*, J. Mol.Spectrosc. 241 (2007) 18-25.

Instrumental setup



Cold Herriott cell coupled with an interferometrically stabilized diode laser spectrometer

-actively stabilized wavelength (residual wavenumber fluctuation: 4×10^{-5} cm^{-1})

-step-by-step acquisition mode (typical step size: 5×10^{-4} cm^{-1})

⇒ high spectral resolution spectra

IR laser source: lead-salt laser diode

Three channels:

-I_0 : no cell

-I_{ref} : absorption cell at room temperature

-I_t : cold Herriott cell

⇒ I_{ref}/I_0 and I_{spl}/I_0 (precision ~5 $\times10^{-4}$)

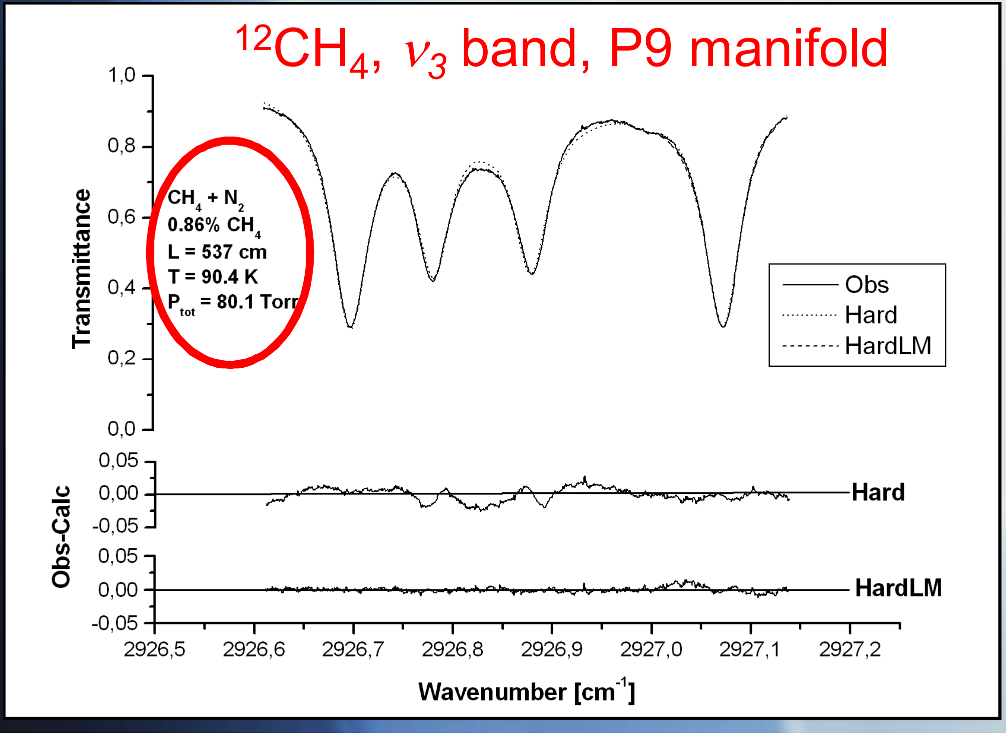
Spectral fitting

Acquired spectra = Absorption lines ⊗ Laser emission profile

Laser emission described with a Voigt profile and determined with the reference spectra at low pressure.

Absorption lines represented with complex profiles taking into account different physical effects (confinement narrowing (β), line mixing (ζ)...)

Synthetic spectra are fitted on the acquired spectra with a global least-squares fit procedure.

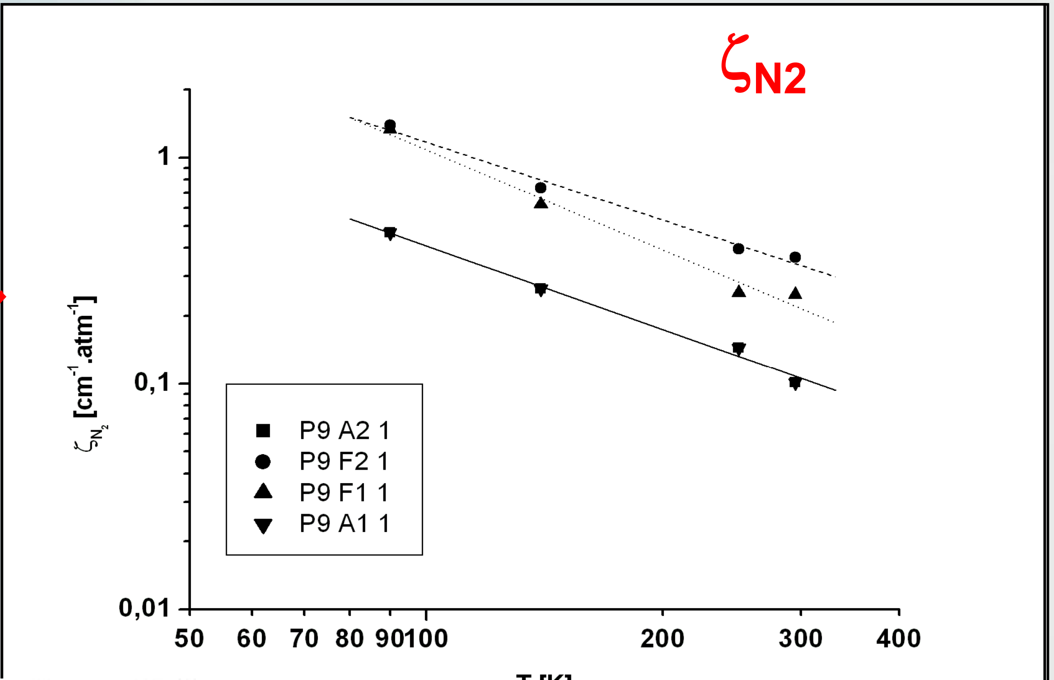


$^{12}CH_4$, ν_3 band, P9 manifold

Better residuals (Obs-Calc) ⇒ better determination of the fitted parameters

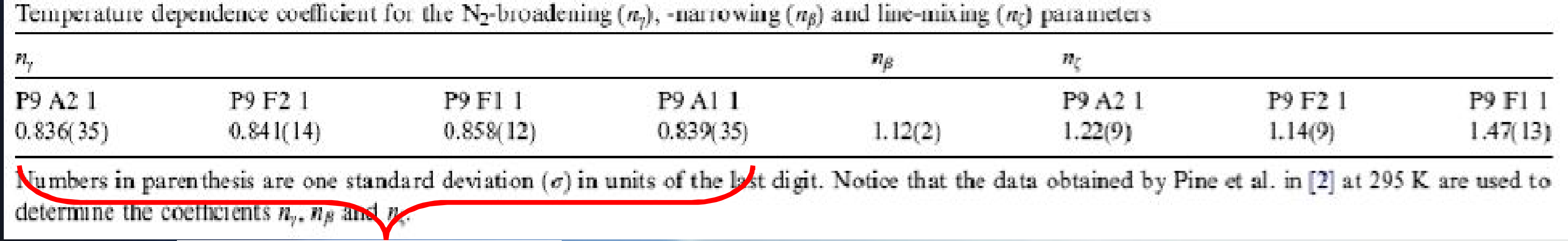
Temperature dependence of parameters for the P9 manifold in the ν_3 band of $^{12}CH_4$*

*** Mondelain et al. J. Mol. Spectrosc. (2007) doi:10.1016/j.jms.2007.05.005**



$$X(T) = \boxed{X(T_{\mathrm{Ref}})}\left(\frac{T_{\mathrm{ref}}}{T}\right)^{\boxed{n_X}}$$

where X refers to γ, β, ζ and n_X to n_γ, n_β and n_ζ and $T_{\mathrm{ref}} = 296$ K.



Temperature dependence coefficient for the N_2-broadening (n_γ), -narrowing (n_β) and line-mixing (n_ζ) parameters

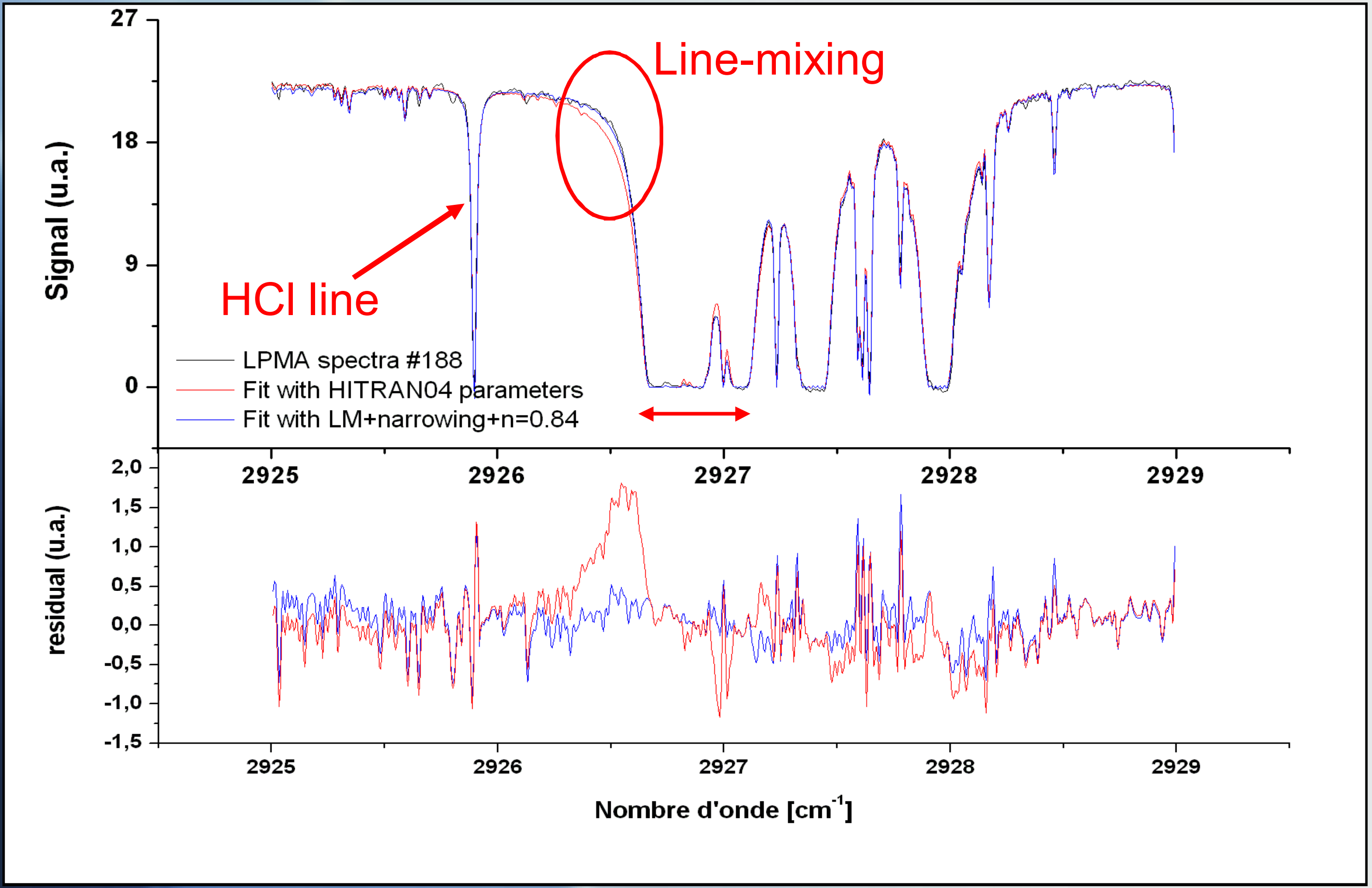
n_γ				n_β	n_ζ		
P9 A2 1	P9 F2 1	P9 F1 1	P9 A1 1		P9 A2 1	P9 F2 1	P9 F1 1
0.836(35)	0.841(14)	0.858(12)	0.839(35)	1.12(2)	1.22(9)	1.14(9)	1.47(13)

Numbers in parenthesis are one standard deviation (σ) in units of the last digit. Notice that the data obtained by Pine et al. in [2] at 295 K are used to determine the coefficients n_γ, n_β and n_ζ.

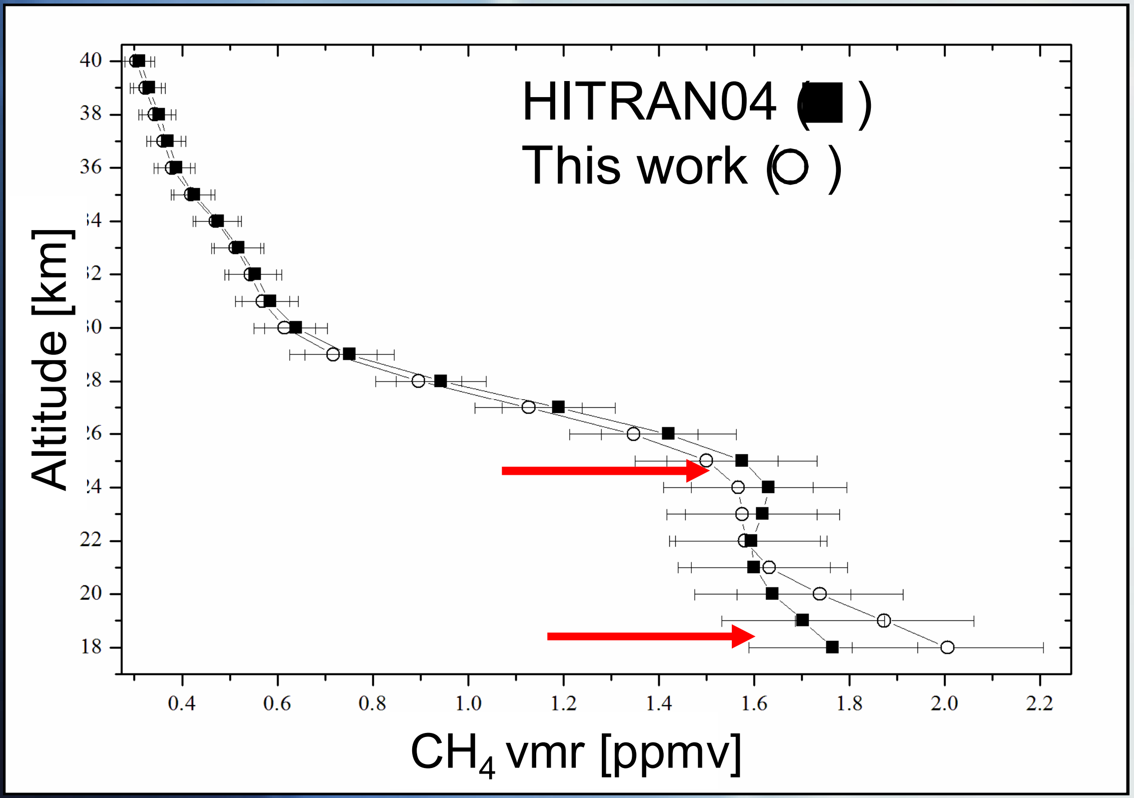
HITRAN04: $n = 0.67$

Application to atmospheric spectra

Atmospheric spectra obtained with LPMA (*Limb Profile Monitor of the Atmosphere*) a balloon-borne remote sensing FTIR instrument operating in absorption against the sun.



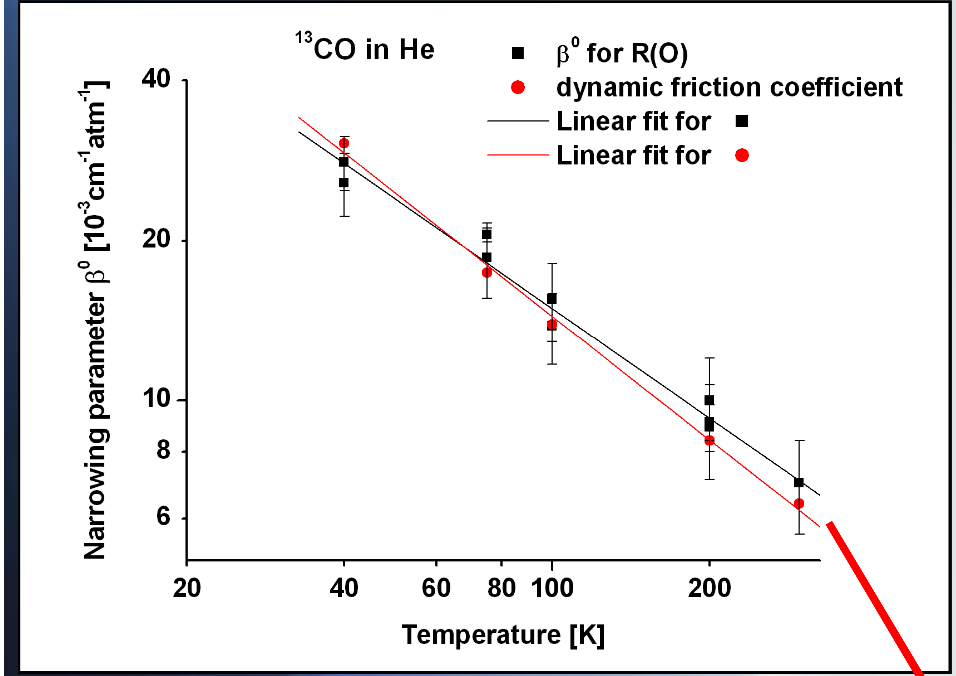
VMR retrievals from atmospheric spectra



Differences up to 7% on the retrieved **V**olume **M**ixing **R**atio were found comparing to an inversion model using only HITRAN04 spectroscopic parameters.

Confinement narrowing of a ^{13}CO line broadened by helium

A. Henry *et al.*, J. Mol. Spectrosc. 214, 28-34 (2002)



R(0) line of ^{13}CO fundamental band

The dynamic friction coefficient β_{Diff} calculated from:

$$\beta^0_{Diff} = \frac{k_B T}{2\pi c m_1 \boxed{D_{12}}}$$

with D_{12} the diffusion coefficient [cm^2/s]

$$D_{12} = \frac{0.002628}{P\sigma_{12}^2}\sqrt{T^3\frac{m_1+m_2}{2m_1m_2}}\frac{1}{\Omega_{12}^{(1,1)}(T_{12})}$$

Temperature dependence in T^{-n}
with n = 0.772 ± 0.026 (meas.)
and n = 0.687 ± 0.024 (kinetic theory)
⇒ Relatively good agreement for CO-He

We normally write the temperature dependence of the pressure broadening parameter as

$$\gamma(\mathrm{T}) = \gamma(\mathrm{T}_{\mathrm{ref}}) \times \left(\frac{T_{ref}}{T}\right)^{n_\gamma} \text{ or } \ln\gamma(T) = \ln\gamma(\mathrm{T}_{\mathrm{ref}}) + n_\gamma \ln\left(\frac{T_{ref}}{T}\right)$$

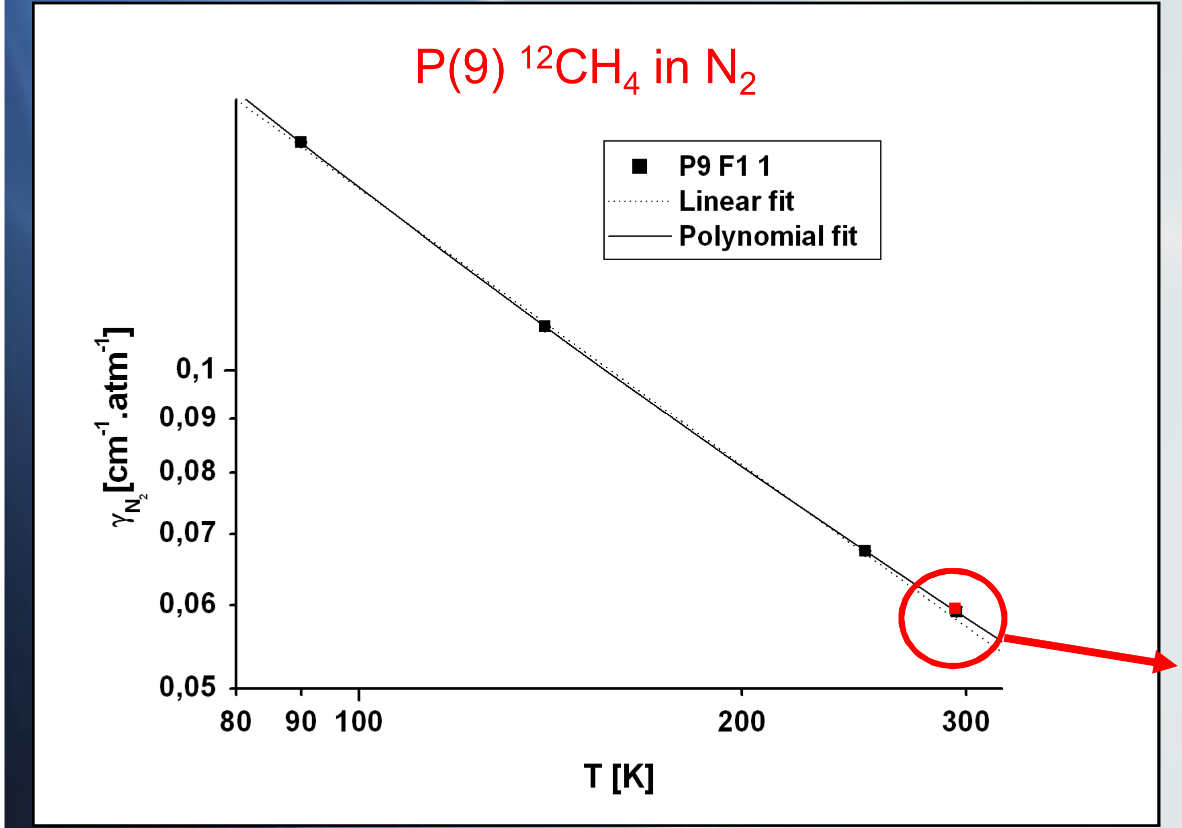
or $y = a + b_1 x$

If we include data between room temperature and temperatures down to 10 to 60 Kelvin, we find that we need to change the linear log - log function from a linear function to a 2nd order polyniomial as shown below in order to fit the data and to make precise extrapolations to other temperatures

$$\gamma(\mathrm{T}) = \gamma(\mathrm{T}_{\mathrm{ref}}) \times \left(\frac{T_{ref}}{T}\right)^{n_\gamma} \times \left[\exp\left(\ln\left(\frac{T_{ref}}{T}\right)^2\right)\right]^{b_2} \text{ or } \ln\gamma(T) = \ln\gamma(\mathrm{T}_{\mathrm{ref}}) + n_\gamma \ln\left(\frac{T_{ref}}{T}\right) + b_2 \ln\left(\frac{T_{ref}}{T}\right)^2$$

or $y = a + b_1 x + b_2 x^2$

Broadening temperature dependence



^{13}CO in Ar: A.W. Mantz *et al.*, J. Mol. Spectrosc. 222 (2003) 131.

$^{12}CH_4$ in N_2: D. Mondelain *et al.*, J. Mol. Spectrsoc. (2007) doi:10.1016/j.jms.2007.05.005

Pine *et al.* JQSRT 57 (1997) 157.

Temperature dependence:

$$\gamma(T)=\gamma(T_{ref})\left(\frac{T_{ref}}{T}\right)^{n}$$

with $n = (q+1)/(2q-2)$

Intermolecular potential $V(R) \propto R^{-q}$

n ➚ when T ➘ ⇒ q ➘ when T ➘

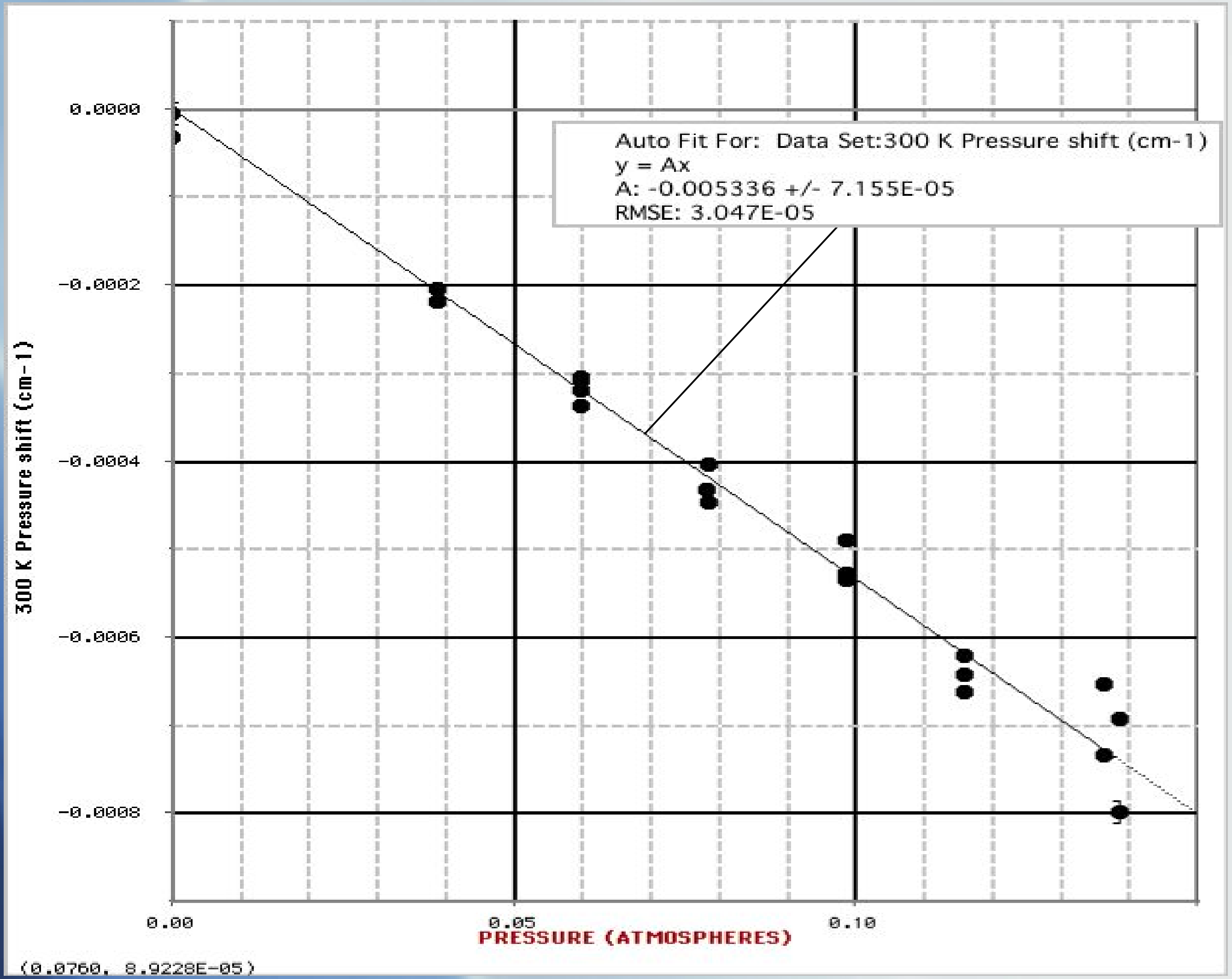
Collision broadening is more sensitive to the long-range attractive forces when the temperature

Molec.	Band	Branch	*J*	*C N*	Perturber	*a*	b_1	b_2
^{13}CO	1-0	R	0	_	He	-3.01□0.01	0.489□0.014	0.035□0.004
^{13}CO	1-0	P	2	_	He	-3.06□0.01	0.510□0.013	0.019□0.004
^{13}CO	1-0	R	0	_	Ar	-2.677□0.007	0.796□0.022	-0.018□0.016
^{13}CO	1-0	R	7	_	Ar	-3.073□0.002	0.721□0.007	0.057□0.005
$^{12}CH_4$	□$_3$	P	9	A2 1	N_2	-2.860□0.003	0.783□0.016	0.039□0.013
$^{12}CH_4$	□$_3$	P	9	F2 1	N_2	-2.842□0.002	0.760□0.011	0.069□0.009
$^{12}CH_4$	□$_3$	P	9	F1 1	N_2	-2.831□0.001	0.787□0.001	0.060□0.001
$^{12}CH_4$	□$_3$	P	9	A1 1	N_2	-2.880□0.019	0.657□0.096	0.154□0.079

Recently we developed a method to precisely measure pressure shifts at all temperatures where we could record spectra at sufficiently high pressures

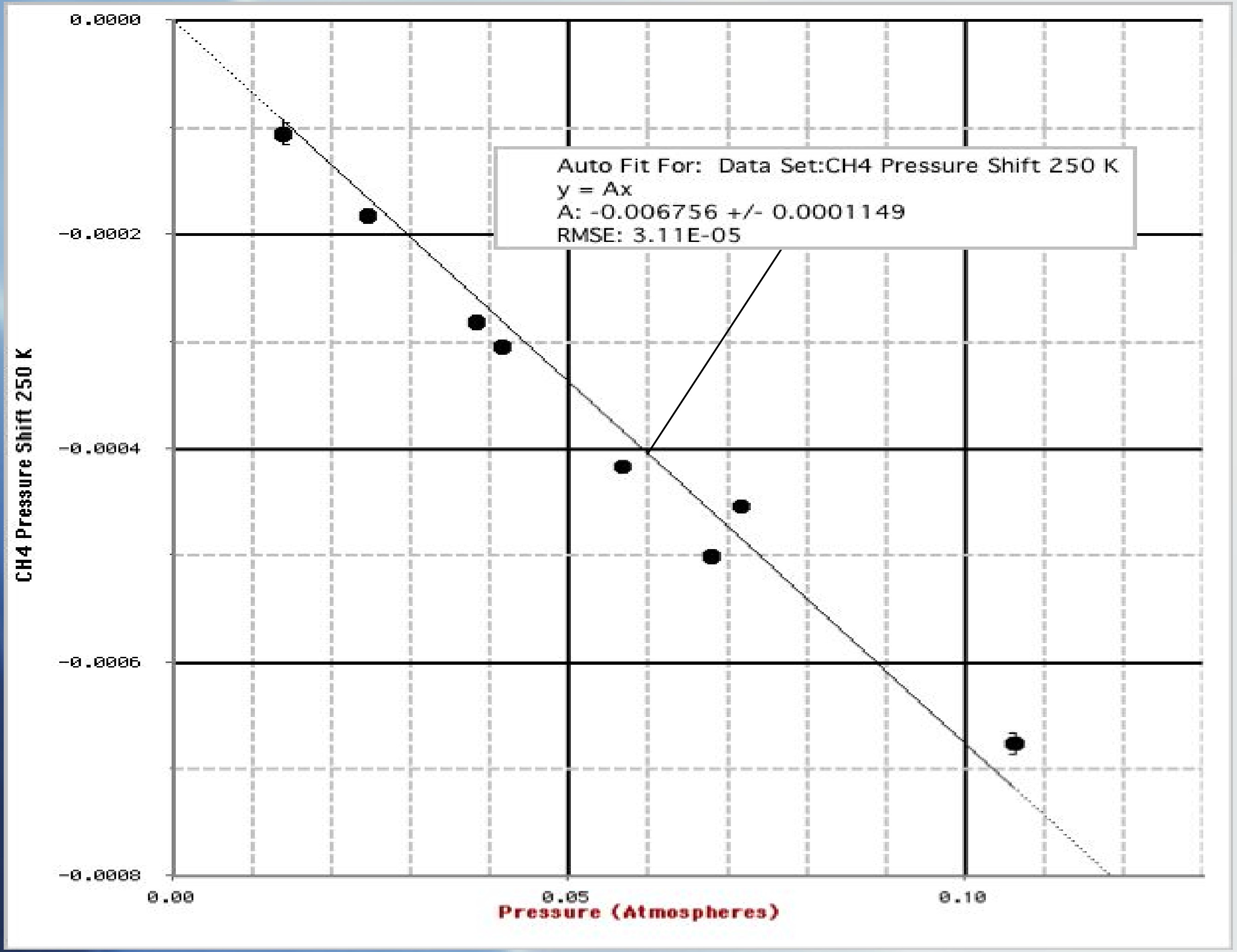
Results for methane broadened by nitrogen are shown next

Pressure shift Data at 300 K for Methane by nitrogen

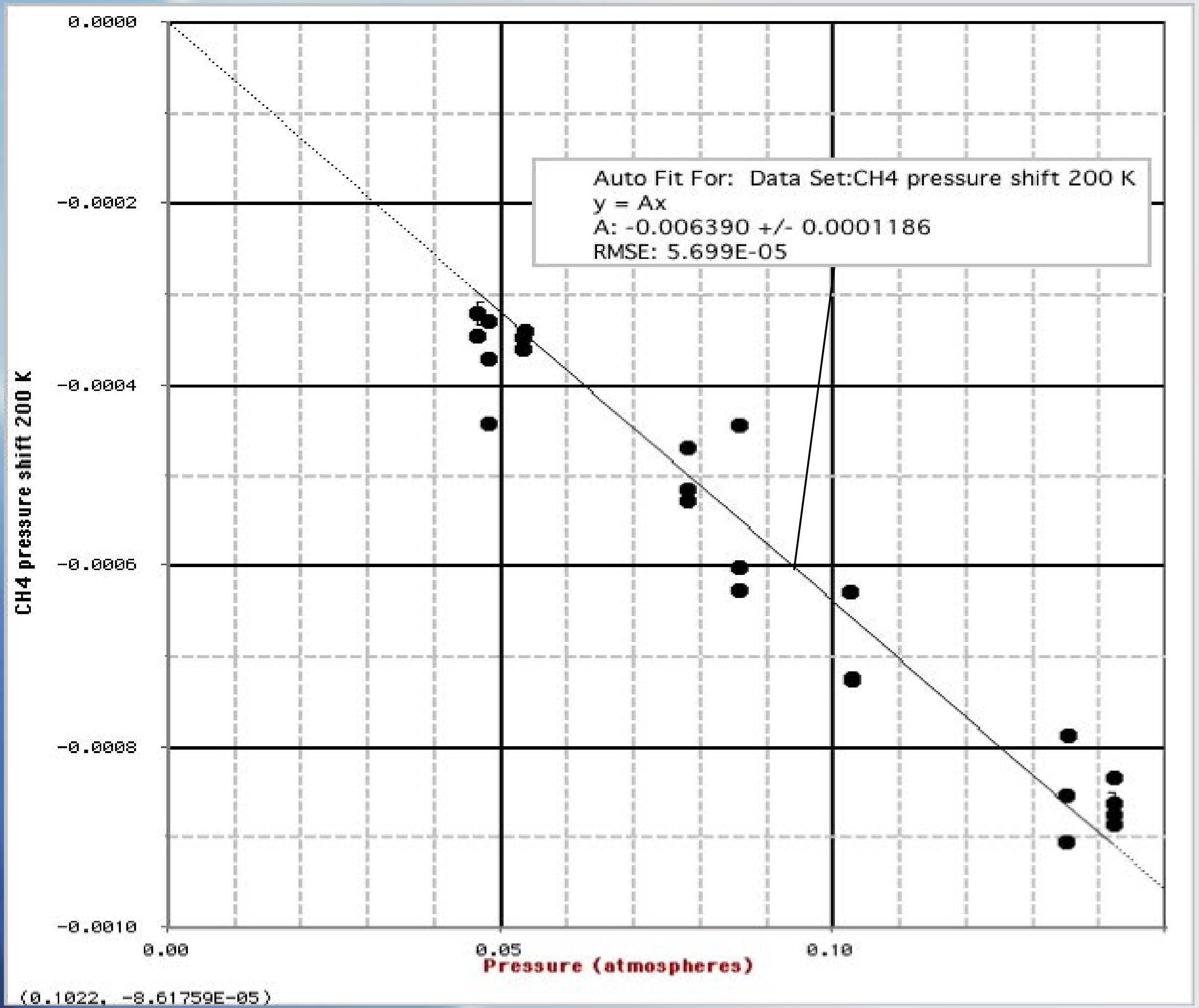


Auto Fit For: Data Set:300 K Pressure shift (cm-1)
y = Ax
A: -0.005336 +/- 7.155E-05
RMSE: 3.047E-05

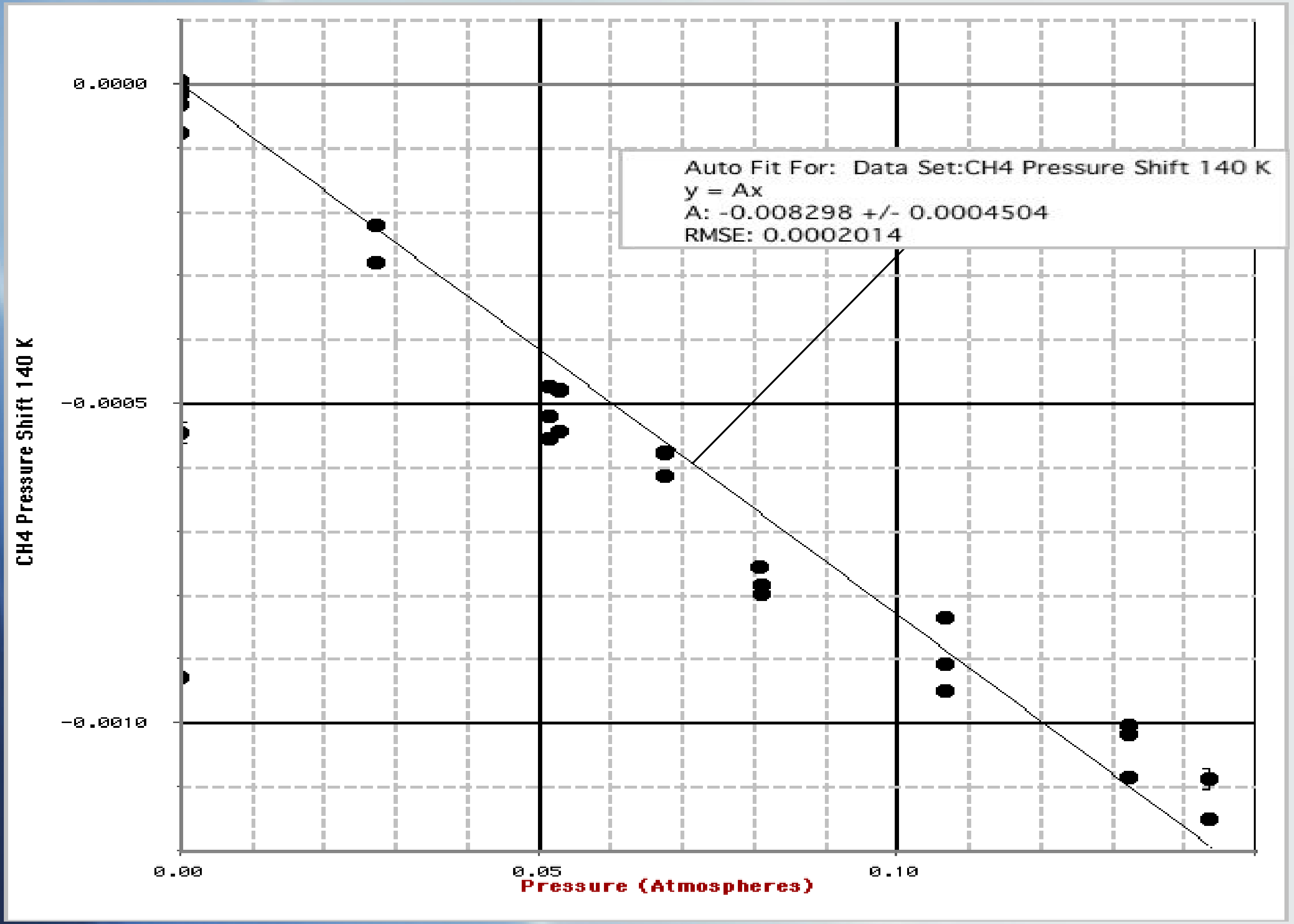
Pressure shift of Methane by Nitrogen at 250 K



Pressure Shift of Methane by Nitrogen at 200 K

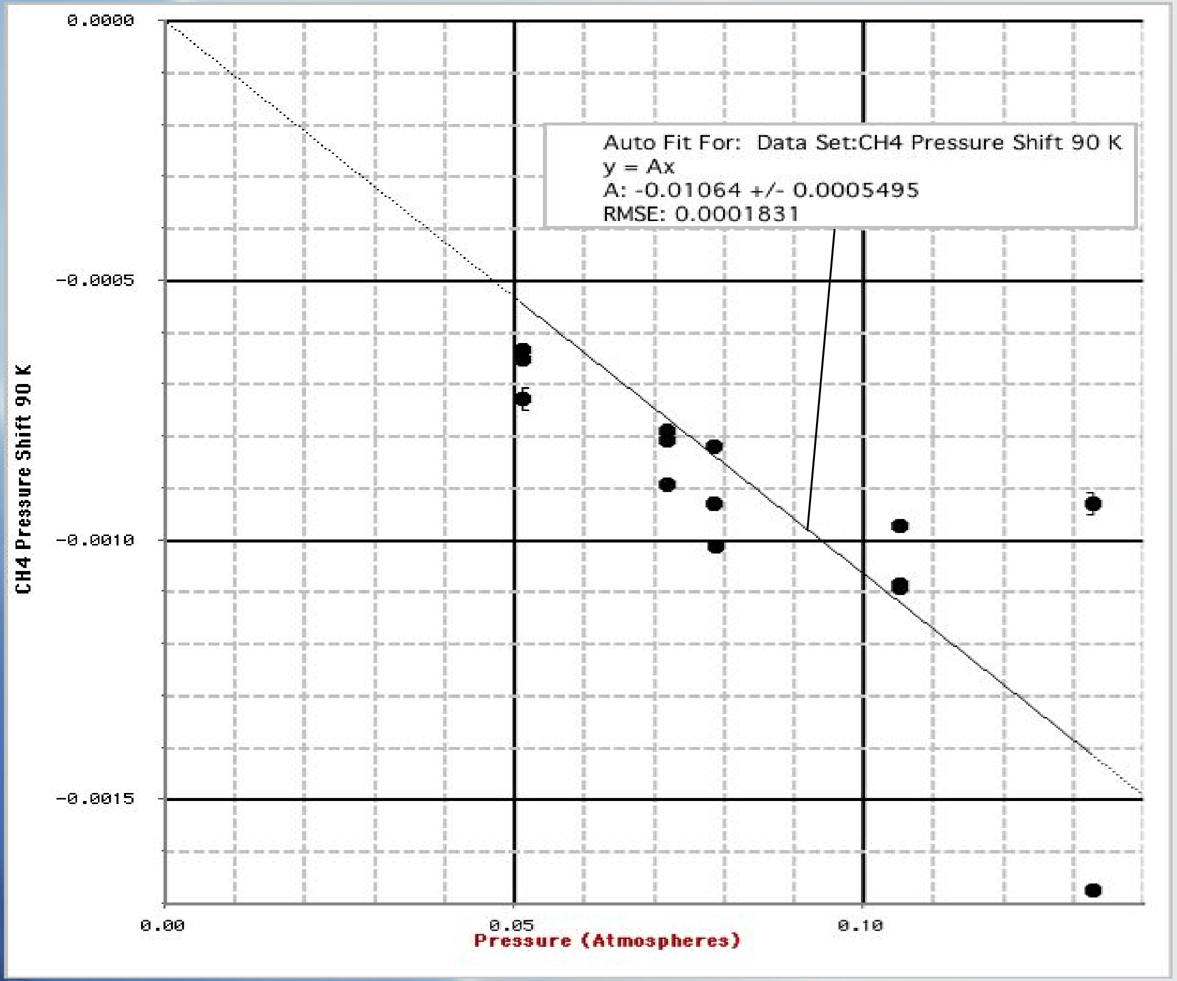


Pressure Shift of Methane by Nitrogen at 140 K



Auto Fit For: Data Set:CH4 Pressure Shift 140 K
y = Ax
A: -0.008298 +/- 0.0004504
RMSE: 0.0002014

pressure shift in Methane by nitrogen at 90 K



Low temperature measurements as a test for Potential Energy Surface

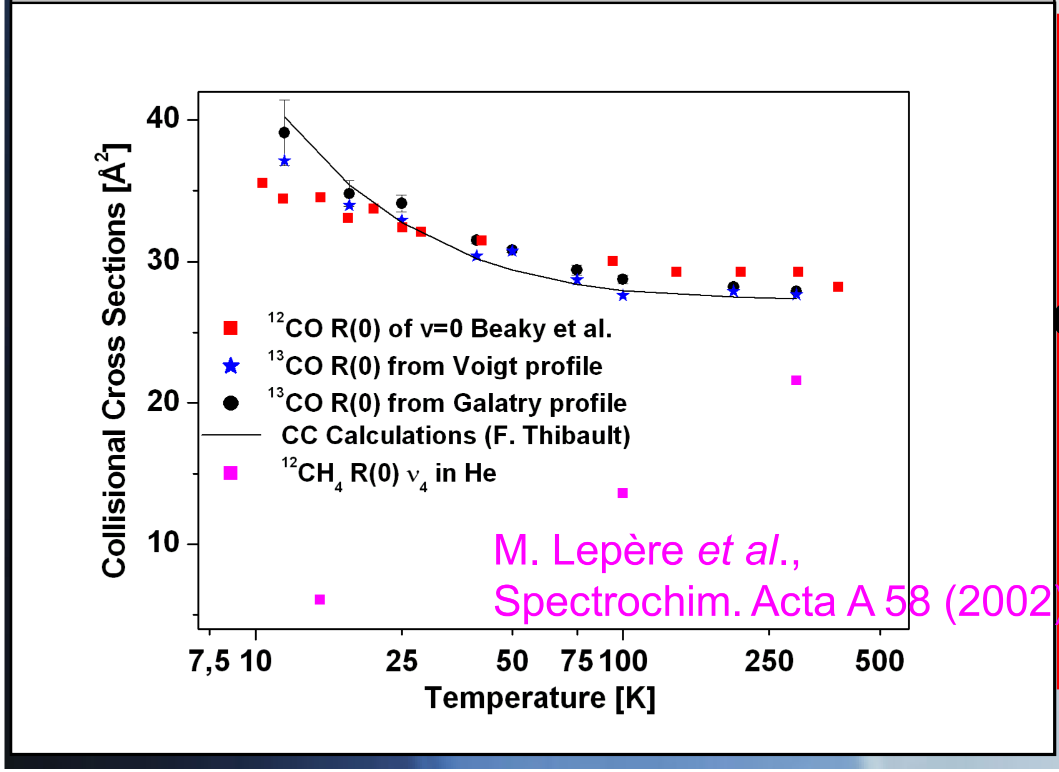
- Collisional cross sections σ can be deduced from the pressure broadening meas. with:

$$\sigma = 17.64(\mu T)^{1/2}\gamma^{0}$$

where μ is the reduced mass of the collision pair and γ^{0} the broadening coefficient.

- σ are derived from quantal close-coupling (C-C) calculations.

⇒ evaluation of the PES from the broadening coefficient.



M. Lepère *et al.*, Spectrochim. Acta A 58 (2002).

⇒ Discrepancy between microwave data and C-C calculations at low temperature.

⇒ Choice of the profile is critical Galatry (better residuals) instead of Voigt profile

⇒ IR data appear to support the theoretical results at low temperature providing a new test for the PES and collision dynamic calculations.

Conclusions

- A very uniform temperature is achieved from room temperature down to 20 K and is accuratly measured.
- Temperature dependence measured over a large range of temperature was demonstrated for different spectroscopic parameters (γ, β, ζ) and gases (CO, CH_4, CO_2).
- These results are applied to the inversion of real atmospheric spectra leading to a large decrease of the residuals and significant changes in vmr retrievals.
- The CO – He data and CO_2 – He data obtained down to very low temperature will certainly be usefull for testing PES.
- Pressure shift data to low temperatures should be very useful
- Pressure shifts in carbon dioxide by helium are at least an order of magnitude smaller than the ones I showed here.

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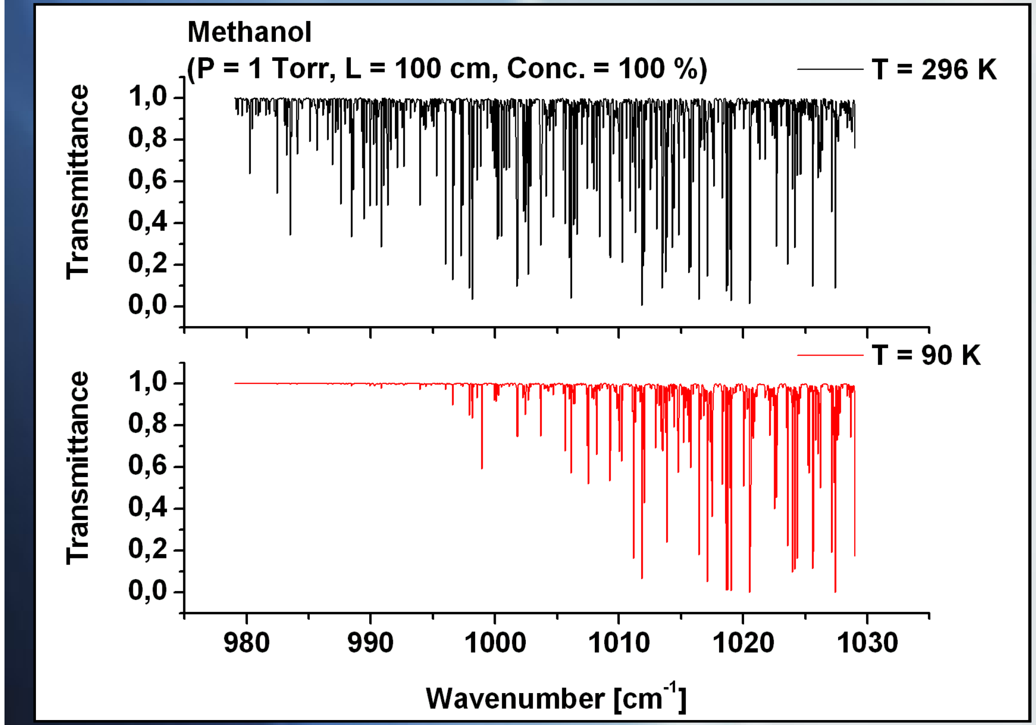
Motivations (2)



Rotational structure simplifications occur at low temperature ⇒ easier assignment for complex spectra (i.e. methanol, acetone ...)

Line profile and laser emission models can be tested against the very narrow absorption lines at low temperature and pressure.

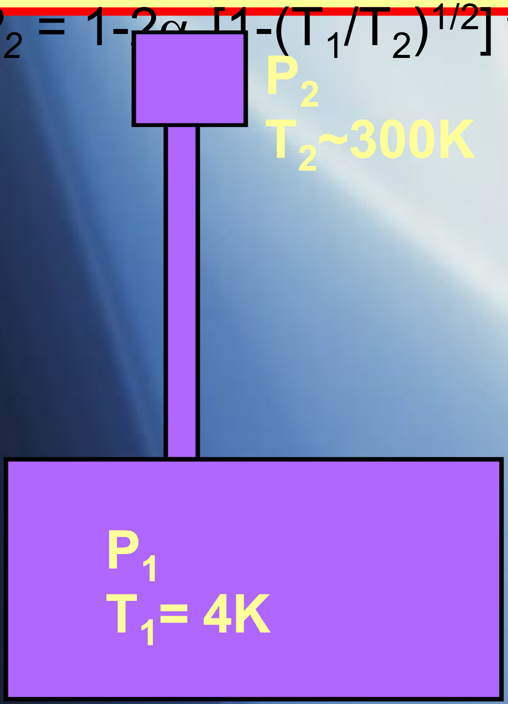
Thermal transpiration phenomenon

The pressure measurement has to be corrected from the thermal transpiration phenomenon: a pressure gradient is always associated with a temperature gradient.

The relation between P_{mes} and P_{True} depends on the gas and on the diameter ***D*** of the tube compared to the molecular mean free path λ.

$P_1/P_2 = 1$ for $D >> \lambda$

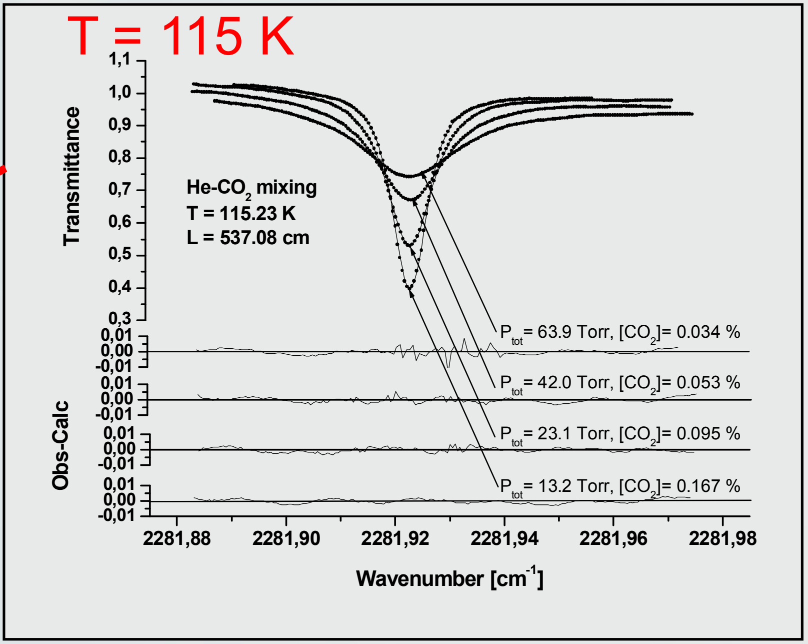
$P_1/P_2 = 1-2\alpha\,[1-(T_1/T_2)^{1/2}]$ for $D << \lambda$

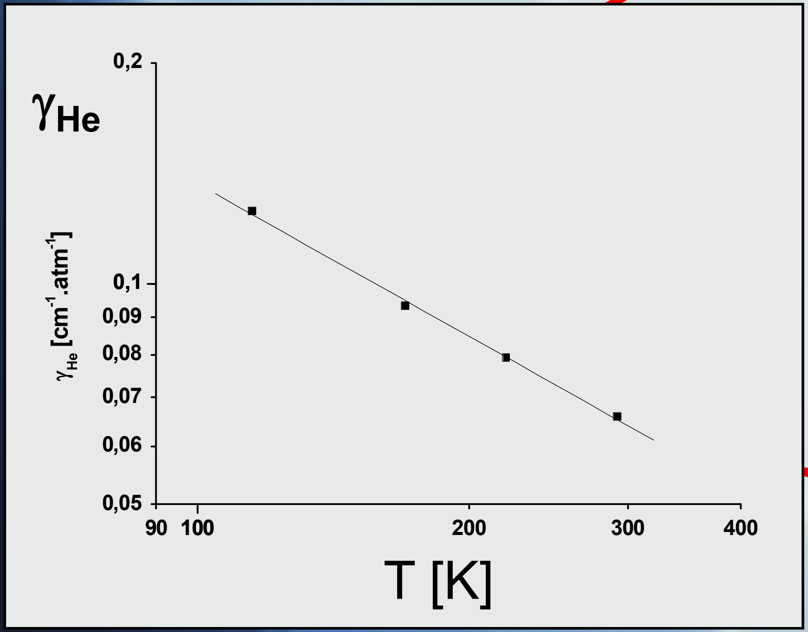


Example of correction for He at 40 K:
7 mTorr for P_{tot}=1.134 Torr
Example of correction for He at 11.5 K:
16 mTorr for P_{tot}=0.250 Torr

Temperature dependence of the He broadening for the studied CO_2 line

$^{13}CO_2$ ν_3 band $P(2)^e$





$$\gamma_{He}(T) = \gamma_{He}^{0}(T_{Ref})\left(\frac{T_{Ref}}{T}\right)^{n_\gamma}$$

Determination of the translational temperature from spectra ($^{13}CO_2$ example)

-P_{tot} is fixed to the measured value corrected from the thermal transpiration effect.

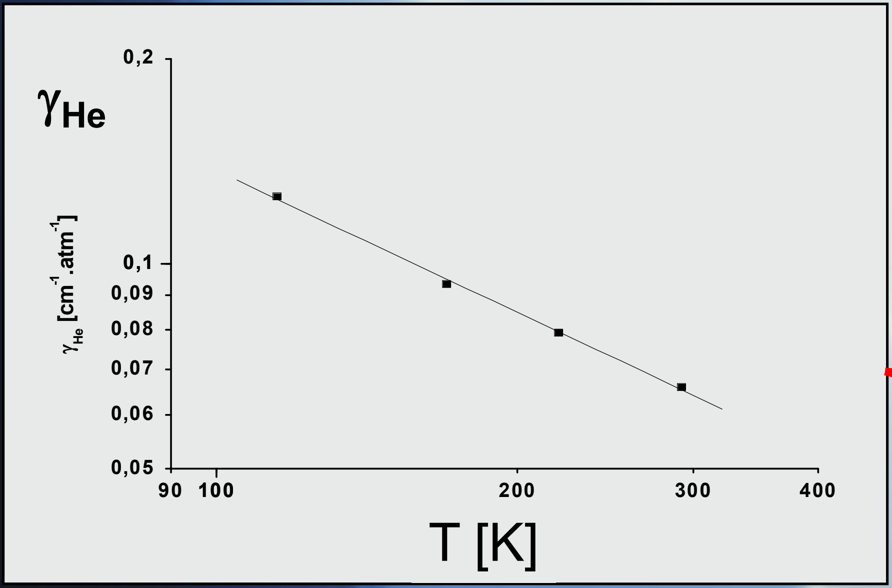
-Absorption pathlength fixed to L= 537 cm (checked with pure CO_2 down to 90 K)

-Laser emission linewidth determined with a reference cell (pure CO_2 at room temperature).

-S(T) is calculated for the temperature of the fit (T_{Fit}).

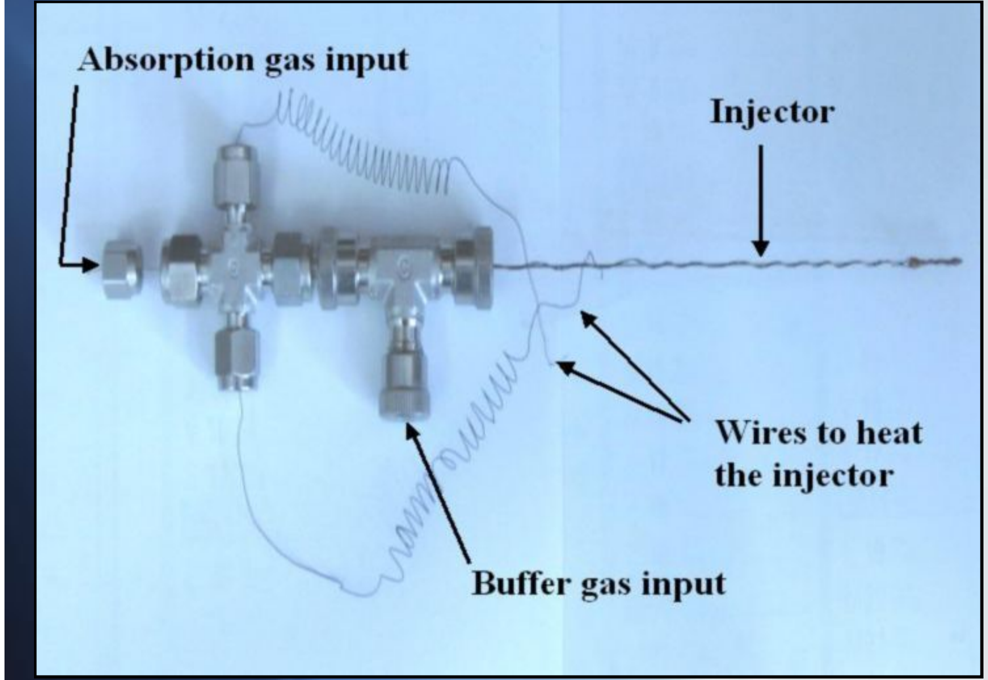
-γ_{He}(T) is extrapolated from temperature dependence measurements.

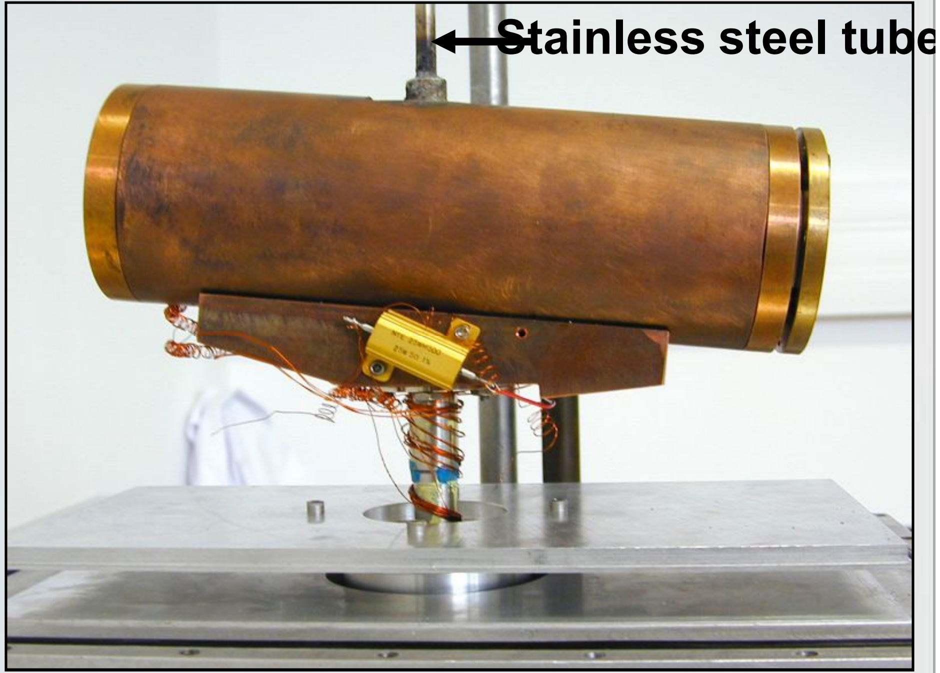
The fitted parameters (at a given temperature T_{Fit}) are: the $^{13}CO_2$ concentration and the base line (2^{nd} order polynomial).



$$\gamma_{He}(T)=\gamma_{He}^{0}(T_{\mathrm{Ref}})\left(\frac{T_{\mathrm{Ref}}}{T}\right)^{n_\gamma}$$

Collisional cooling with the cold Herriott cell





The vertical level of the injector can be adjusted.

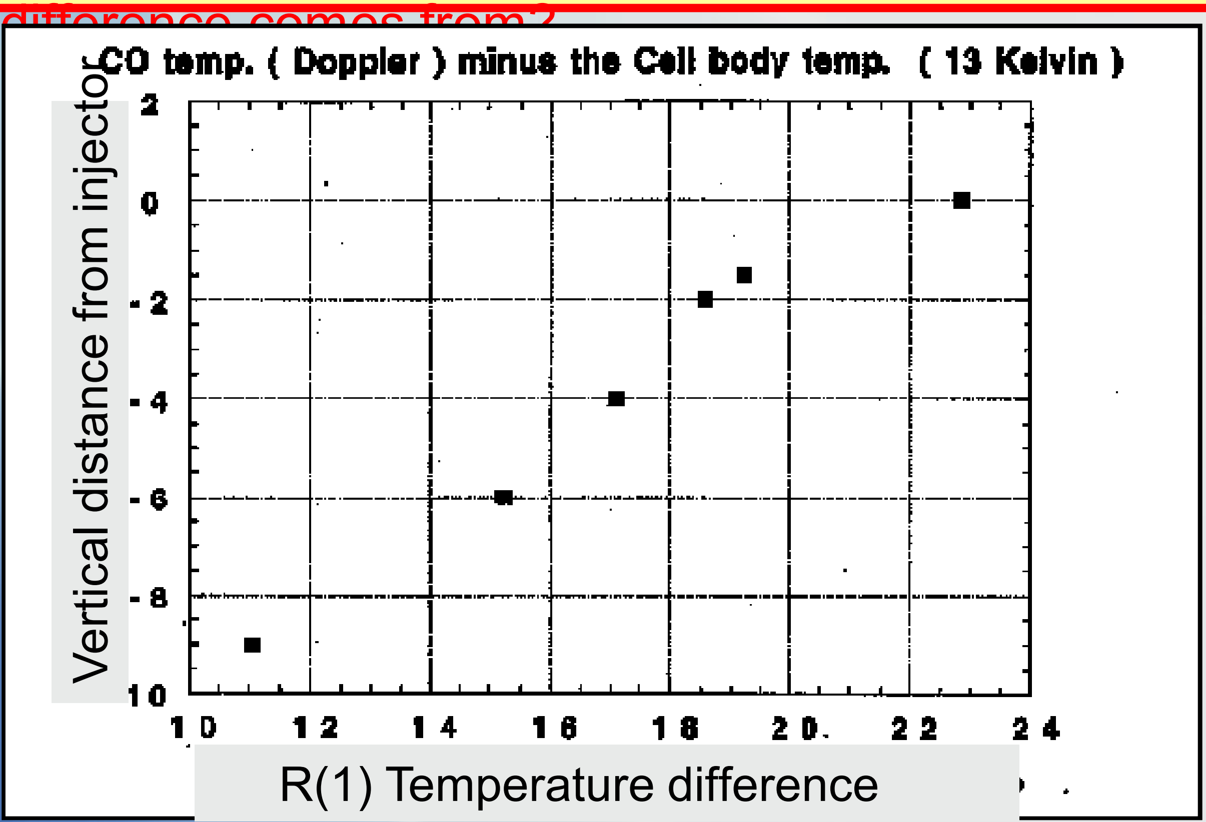
The injector tip is heated to avoid freezing during injection of the gas

537 cm pathlength ⇒ access to weak absorption lines and not only to strong absorbers.

Injector position

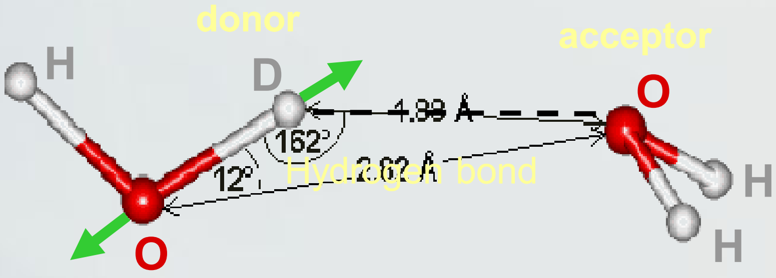
Willey et al. (J. Mol. Spectrosc. **168** (1994)) determined a temperature of 16 K for their absorption gas (CH_3F) instead of 7.5 K (the temperature of the cell).

⇒ Where this difference comes from?



Y. Abebe *et al.*, Spectrochimica Acta A 55 (1999)

⇒ The injector position is very important as the molecules needs a hundred of collisions with helium to be thermalized.



Very low temperatures significantely enhance the production and lifetime of weakly bound complexes (van der Waals molecules)

$$N_{HOD-HOH} \propto N_{H_2O} \times N_{HDO} \times K_P$$

$$K_P \propto \exp(\text{Д}H^\circ/RT)$$

Performance of the cold Herriott cell

- Temperature control and measurement with:

Resistor heater

Silicon diodes

PID

- nge: 300 - 15 K
- No temperature gradient: limited by the c
  to a few mK over the whole cell length.
- Accuracy: ± 0.5 K (10 – 30 K), ± 0.25 K (30 – 60 K),

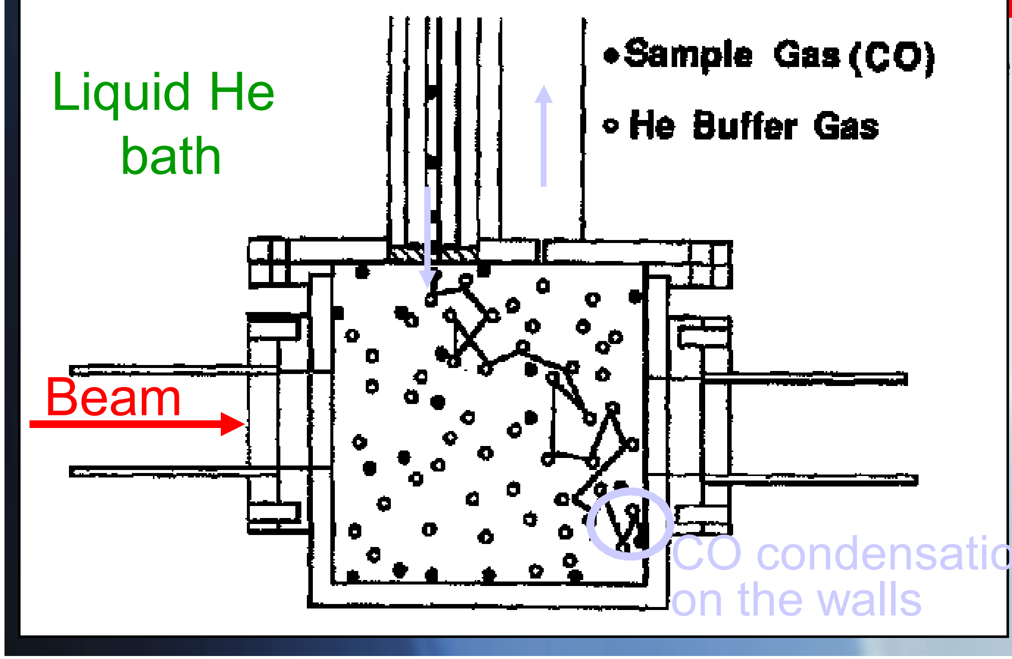
± 0.15 K (60 – 300 K)

- Temperature stability: < 10 mK over one hour
- The cell can be used in a usual (static) way or with the collisional cooling technique.

Collisional cooling principle

Proposed by Messer and De Lucia (PRL **53** (1984) 2555) in the microwave range.
Cooling: absorption cell in a liquid He bath ($1.78 < T_{He} < 4.24$ K)
Buffer gas: He thermalized at the cell temperature (P_{He} ~ 30 mTorr)
Absorbing gas: CO cooled by collisions with He molecules with small dilution ratio (CO/He < 1/10 000)
This allows the spectroscopically active gas to be cooled to very low temperatures.
⇒Very general experimental technique (can be used in the IR)

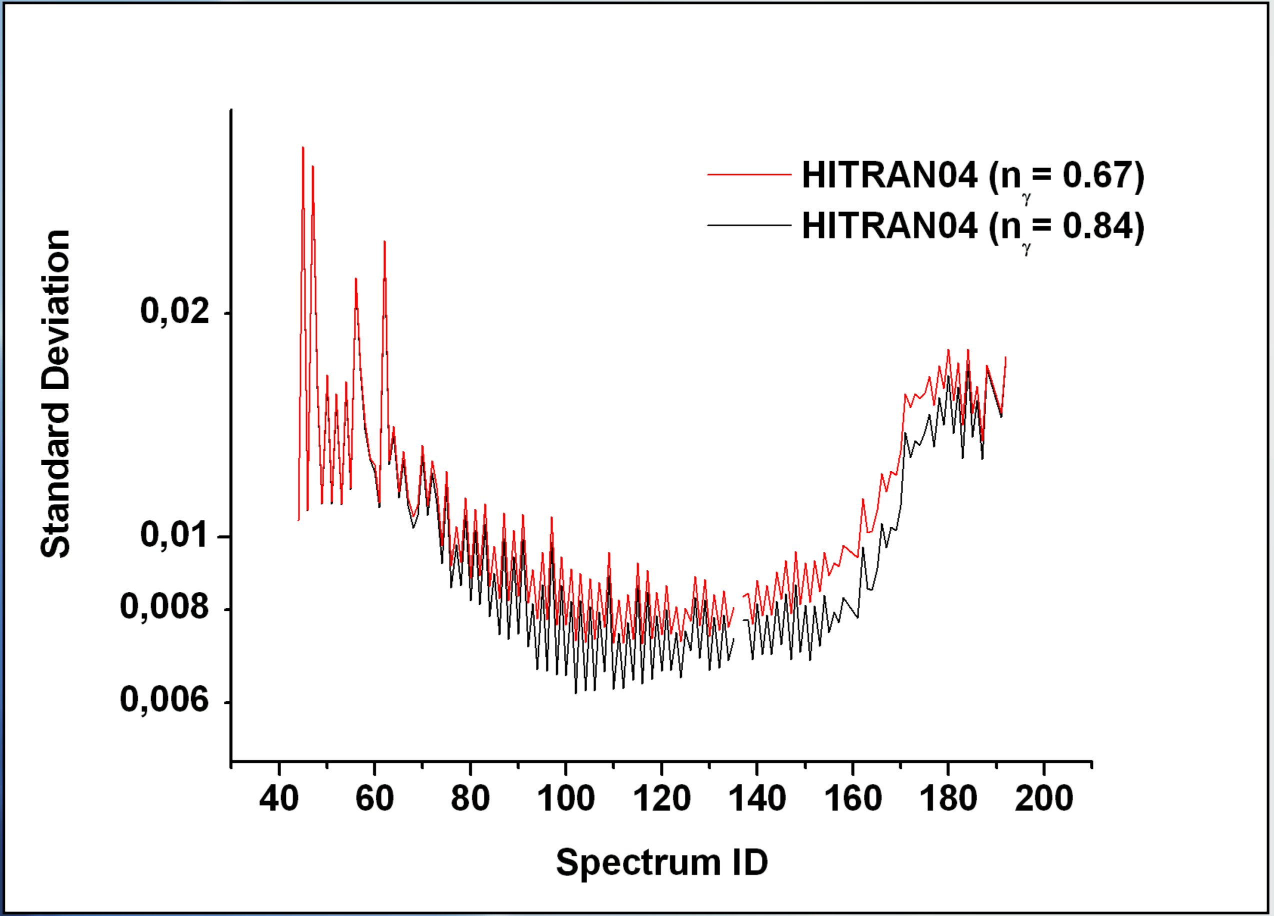
The pathlength (few cm) is **OK** for the **microwave** spectral region (strong line



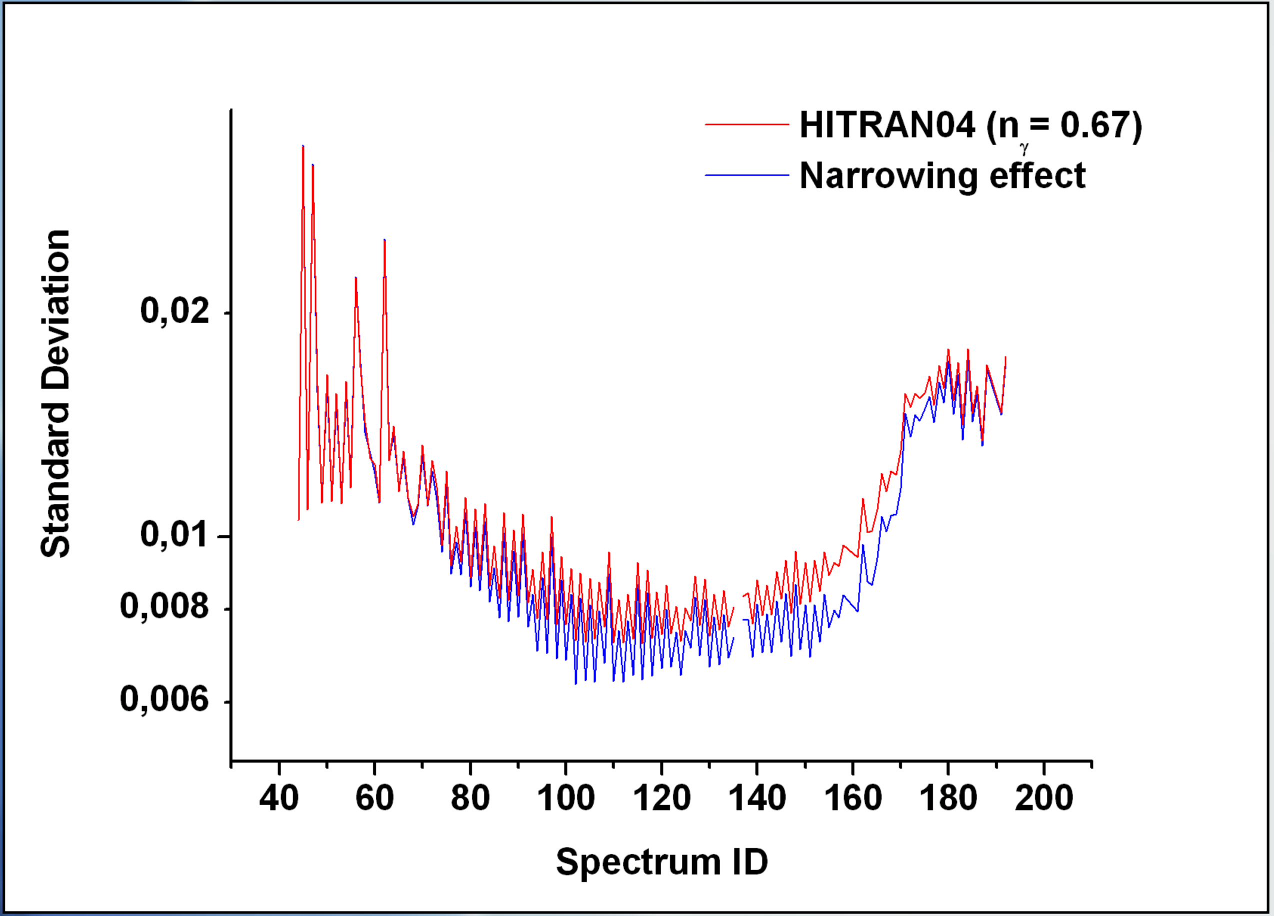
Complementary to free expansion jets (which can access to lower temperature) with some advantages:

- Thermal equilibrium
- Well-defined lineshape
- Easily measured/variable T and P
- Possibility of long absorption path with uniform temperature
- Lower pumping capacity

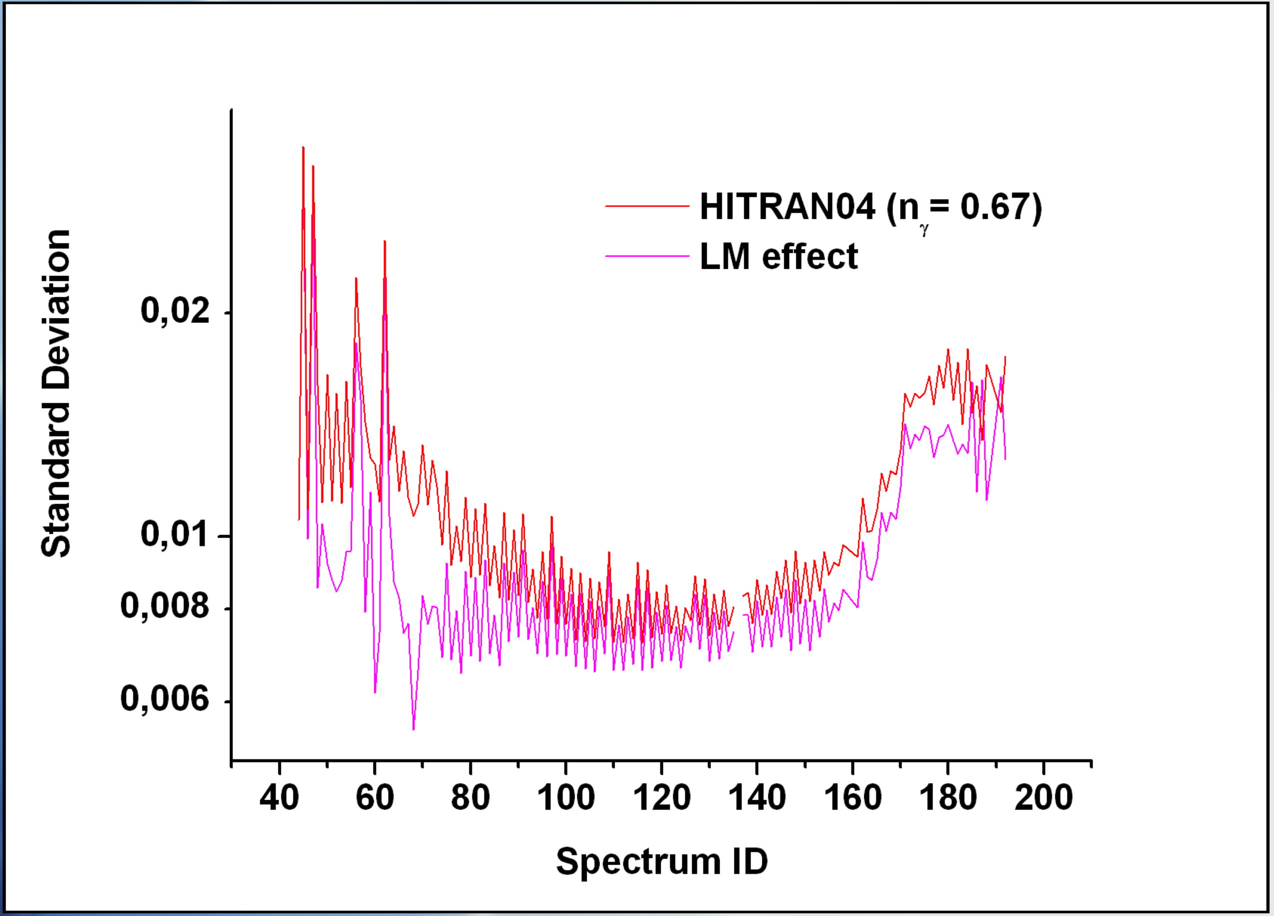
Effect of the broadening temperature dependence



Effect of the narrowing



Effect of the line-mixing



Comparison with all the effects included