N_2 COLLISIONAL BROADENING OF METHANE IN THE THZ REGION MEASURED AT THE SOLEIL SYNCHROTRON

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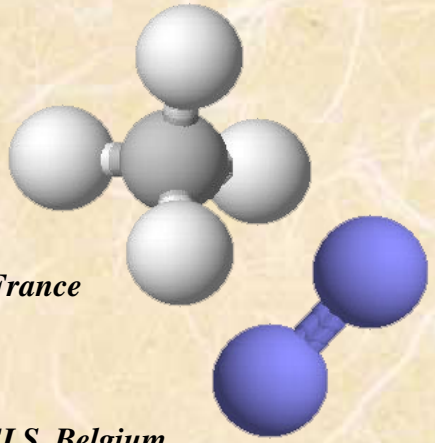

SOLEIL SYNCHROTRON

ICB Laboratoire Interdisciplinaire Carnot de Bourgogne UMR 5209 CNRS - Université de Bourgogne

Laboratoire de Dynamique, Interactions et Réactivité

ULB

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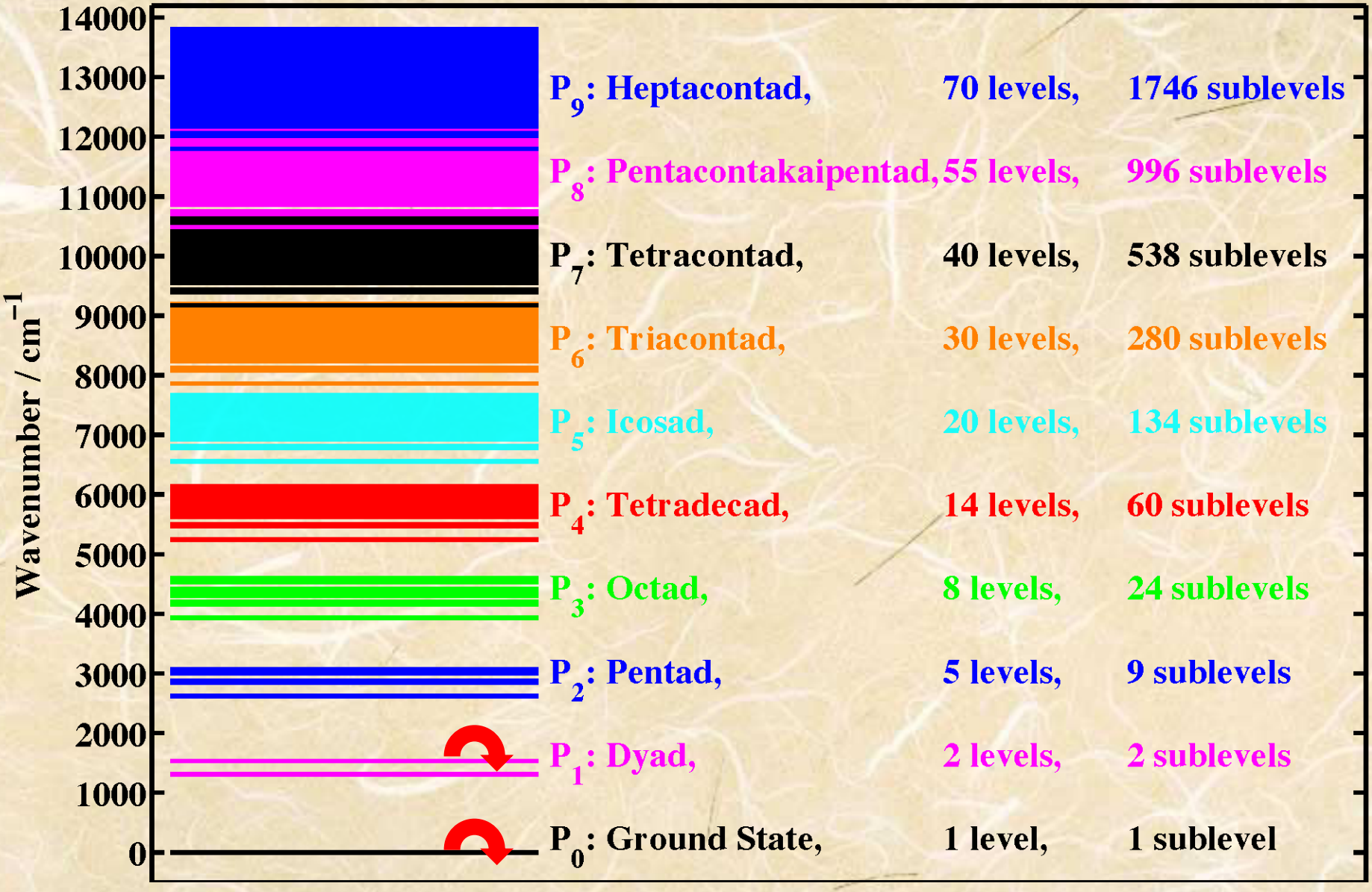
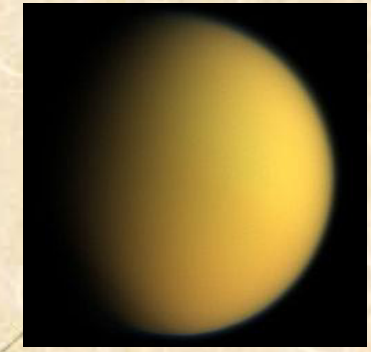
I. The THz spectrum of CH_4

The polyads of CH_4



Far-infrared CH_4 lines on Titan

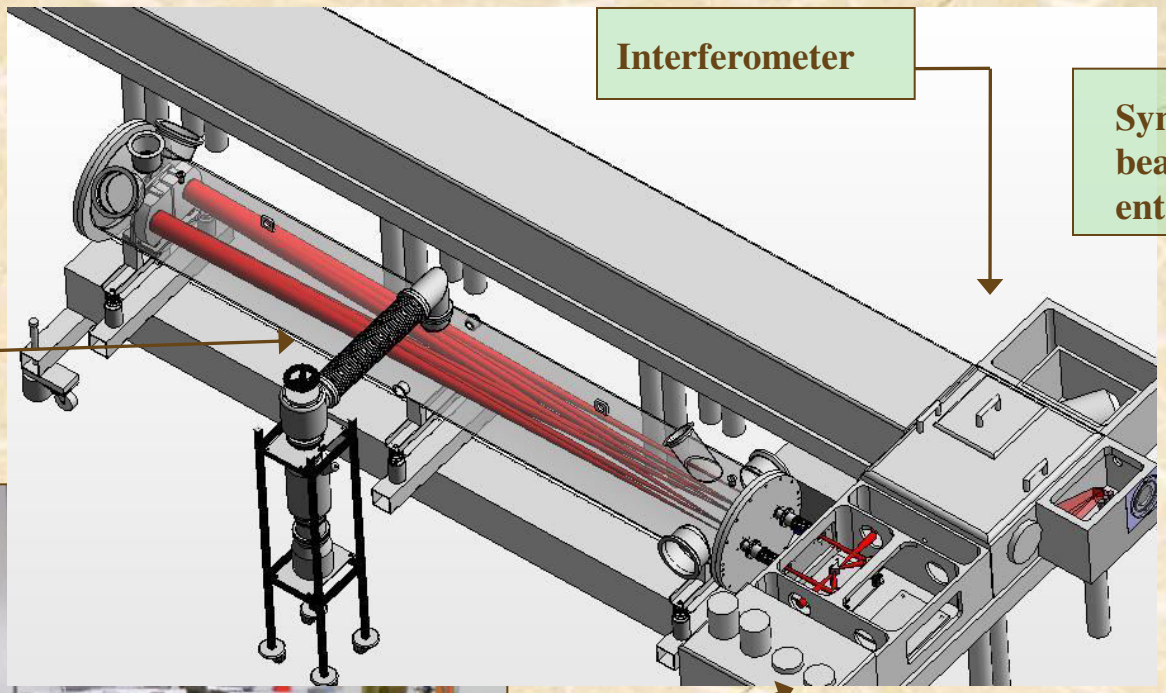


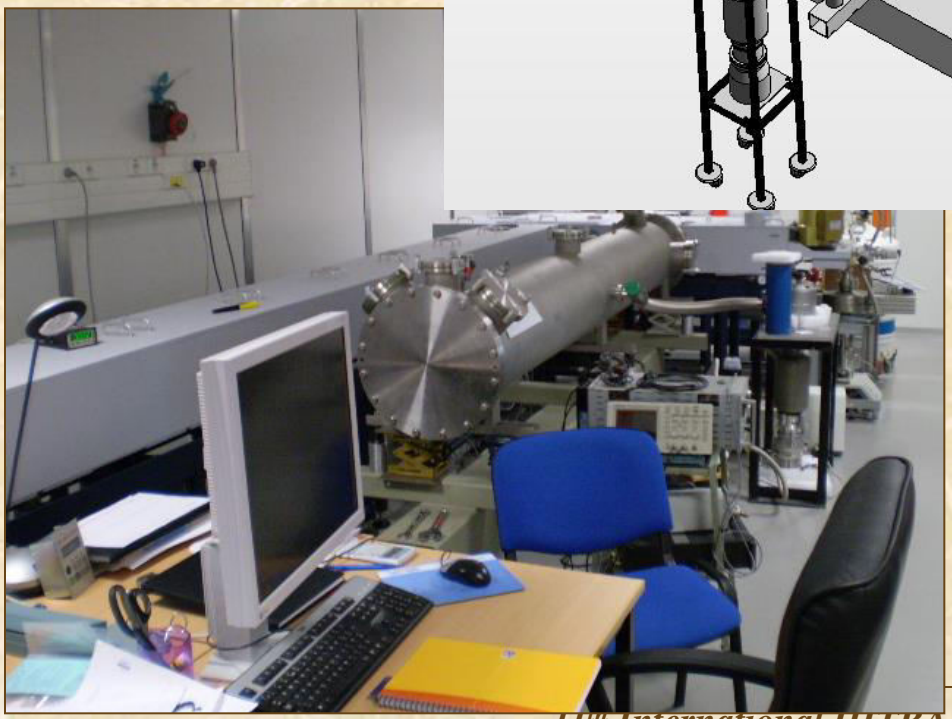
II. Experimental details

AILES beamline at SOLEIL

High Resolution Absorption Spectroscopy in the Far-IR

Laboratoire de Photophysique Moléculaire



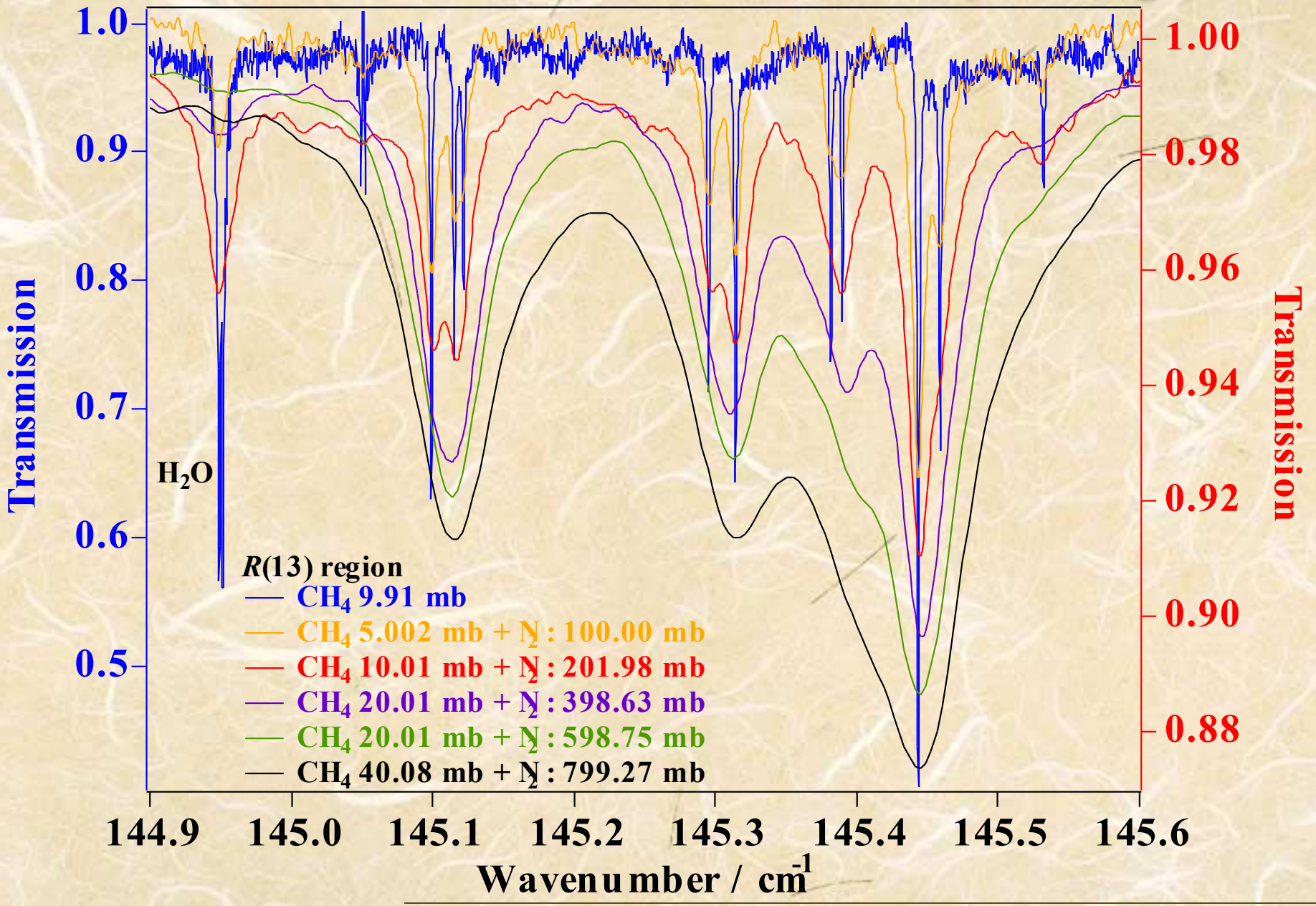


Maximum spectral resolution = 0.001 cm^{-1}
Spectral range= 7-1000 cm^{-1}

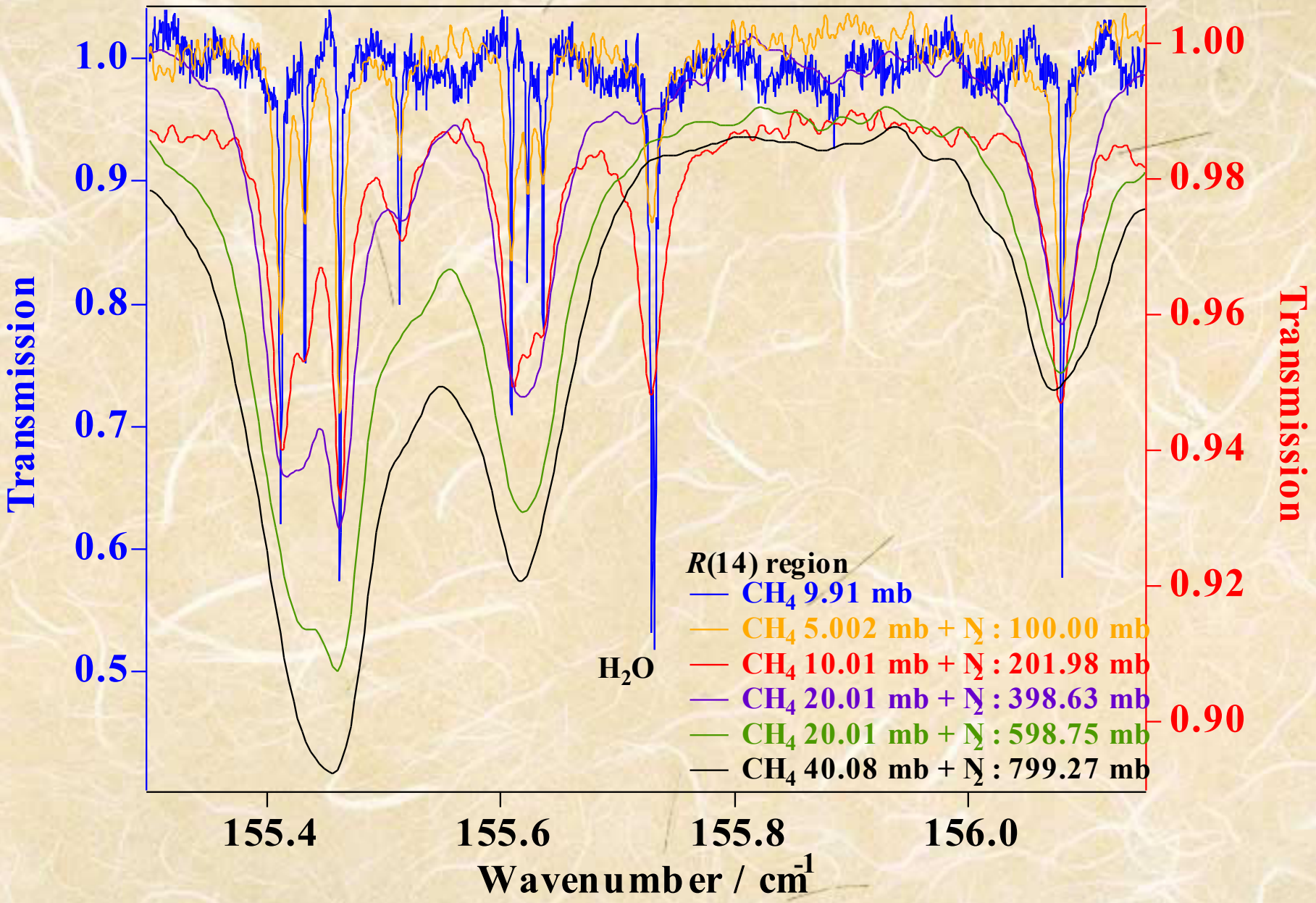
Multipass White cell: *L* = 151.748 m
Ambiant temperature (*T* = 296 K)

Example with pure CH_4

R(13) region with 5% of CH_4 in N_2



R(14) region with 5% of CH_4 in N_2



III. Analysis of pressure broadening

Retrievals

✓ Line parameters (initial or fixed values)

- **Positions and intensities of cold and hot bands : Boudon *et al*, JQSRT 111 (2010) 1117**
- **Self-broadening : Estimates from Brown *et al*, JQSRT 48 (1992) 617**
- **N_2-broadening : $b_L^0 = 0.0429\ cm^{-1}atm^{-1}$ (T. Gabard)**

Retrievals – *Continued*

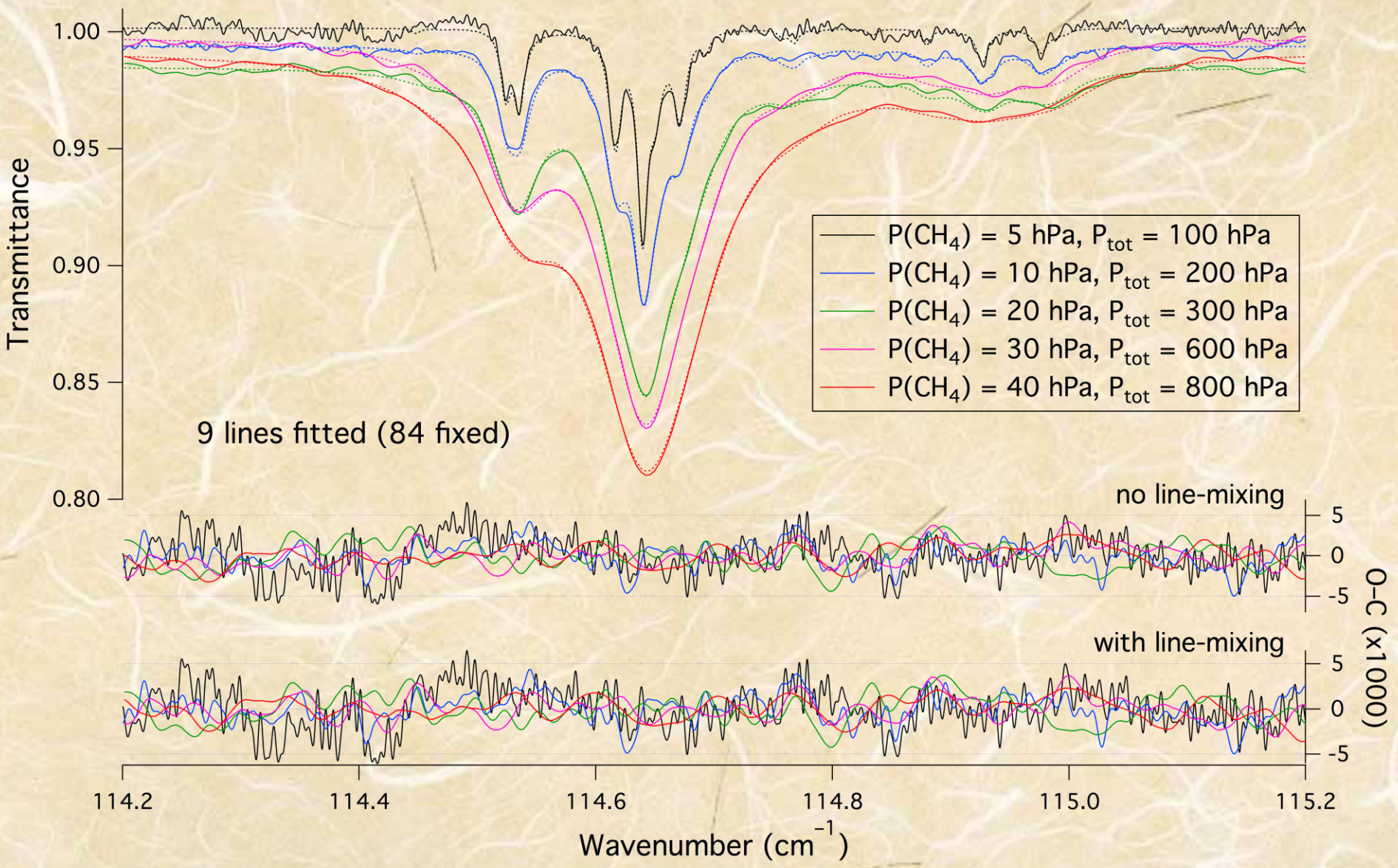
✓ Multispectrum fitting

- Whole Multiplets fitted at once
- Lines with intensity > 7×10^{-26} cm/molecule fitted, others fixed

✓ Fitted parameters [in addition to $b_L^0(N_2)$]

- Single wavenumber calibration for all spectra
- CH_4 mixing ratio
- Single pressure-induced shift for each multiplet
- Line-mixing (Rosenkranz)
- Baseline : polynomial, up to 2nd order

Example: multispectrum fit of *R*(10)



Theoretical model

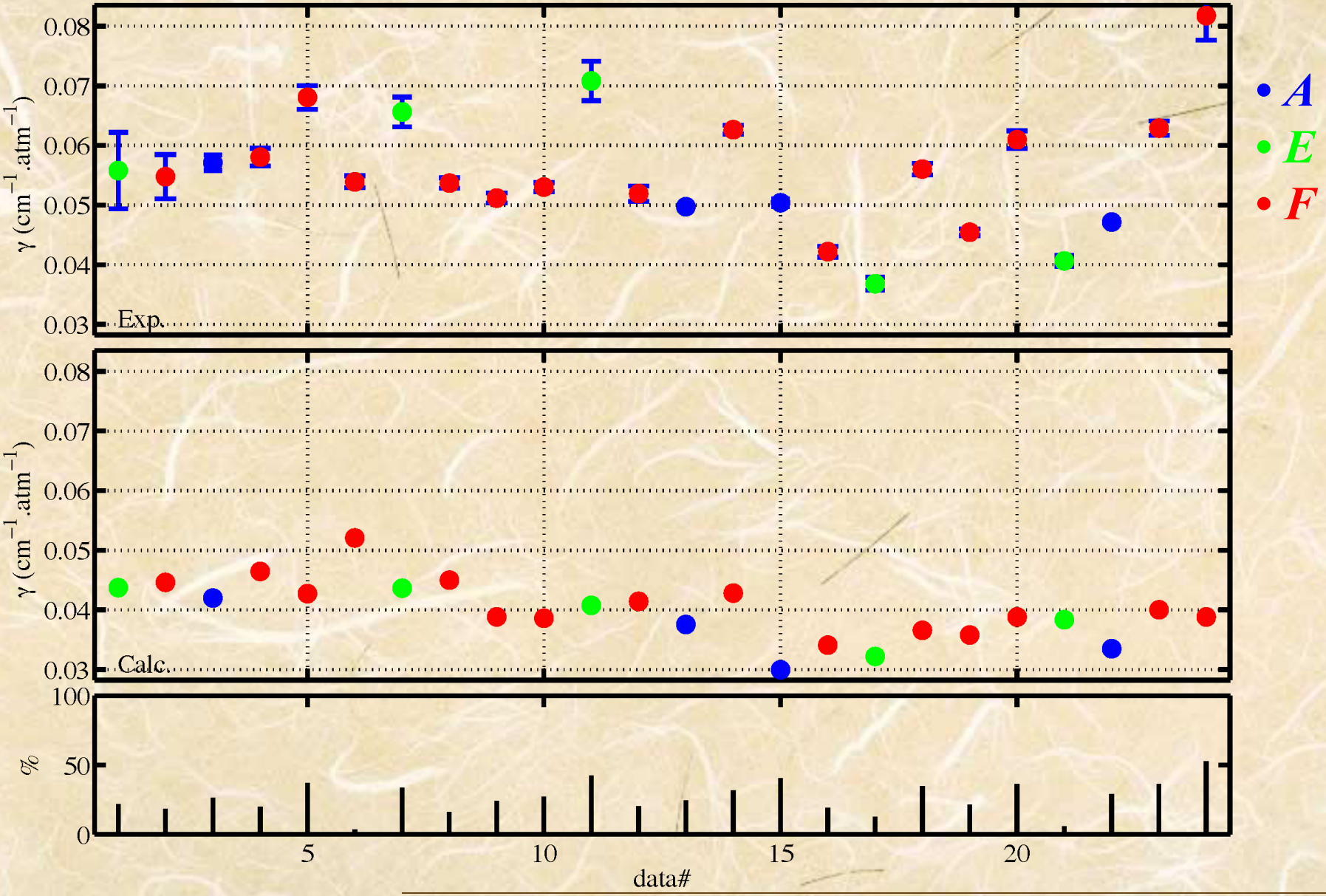
- Lines broadenings are calculated through a **semiclassical theory**.
- Spectrum:

(Average over both initial conditions and evolutions.)

- Binary collisions, **impact approximation**.
- Quantum internal dynamics, tetrahedral formalism for CH_4.
- Electrostatic interactions and at short range (major contribution).
- Relative trajectories: paraboloidal (classical), computed from the isotropic potential (molecules = spheres!).
- **Symmetrized formalism** (T_d).
- Very complicated, but **without any fitted parameter**.
- See *T. Gabard and V. Boudon, JQSRT 111, 1328–1343 (2010).*

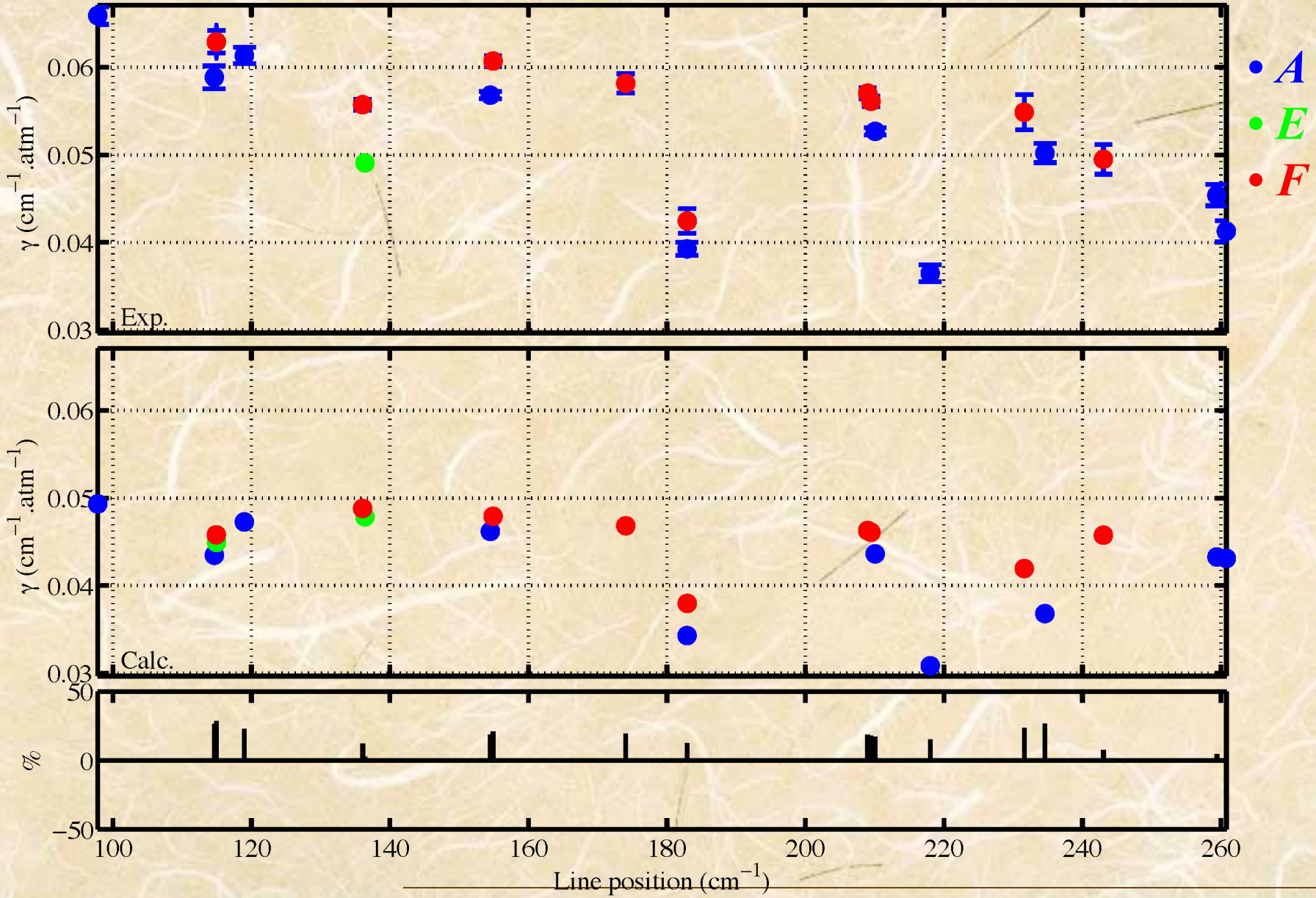
First trial modelling

Broadening coefficients for the cold band



First trial modelling

Broadening coefficients for the hot band



IV. Conclusion

Conclusion

- These results constitute the first measurements and analysis ever attempted for the collisional broadening coefficients of CH_4 by N_2 in the far infrared.

- The values we measure are close to those observed for excited vibrational states (*ca.* 0.06 $cm^{-1}.atm^{-1}$) The *J* dependence is also consistent.

- As expected, we see that the values obtained for the collisional broadening coefficients depend on the fine structure of the rotational states. Thus, taking constant values would lead to errors.

- Even with the long absorption path achieved, the spectrum is rather weak, preventing extraction of line-mixing information.

- The present collisional broadening coefficients could be included into the HITRAN database.