Spectroscopy of PAHs at IR/Submm wavelenghts

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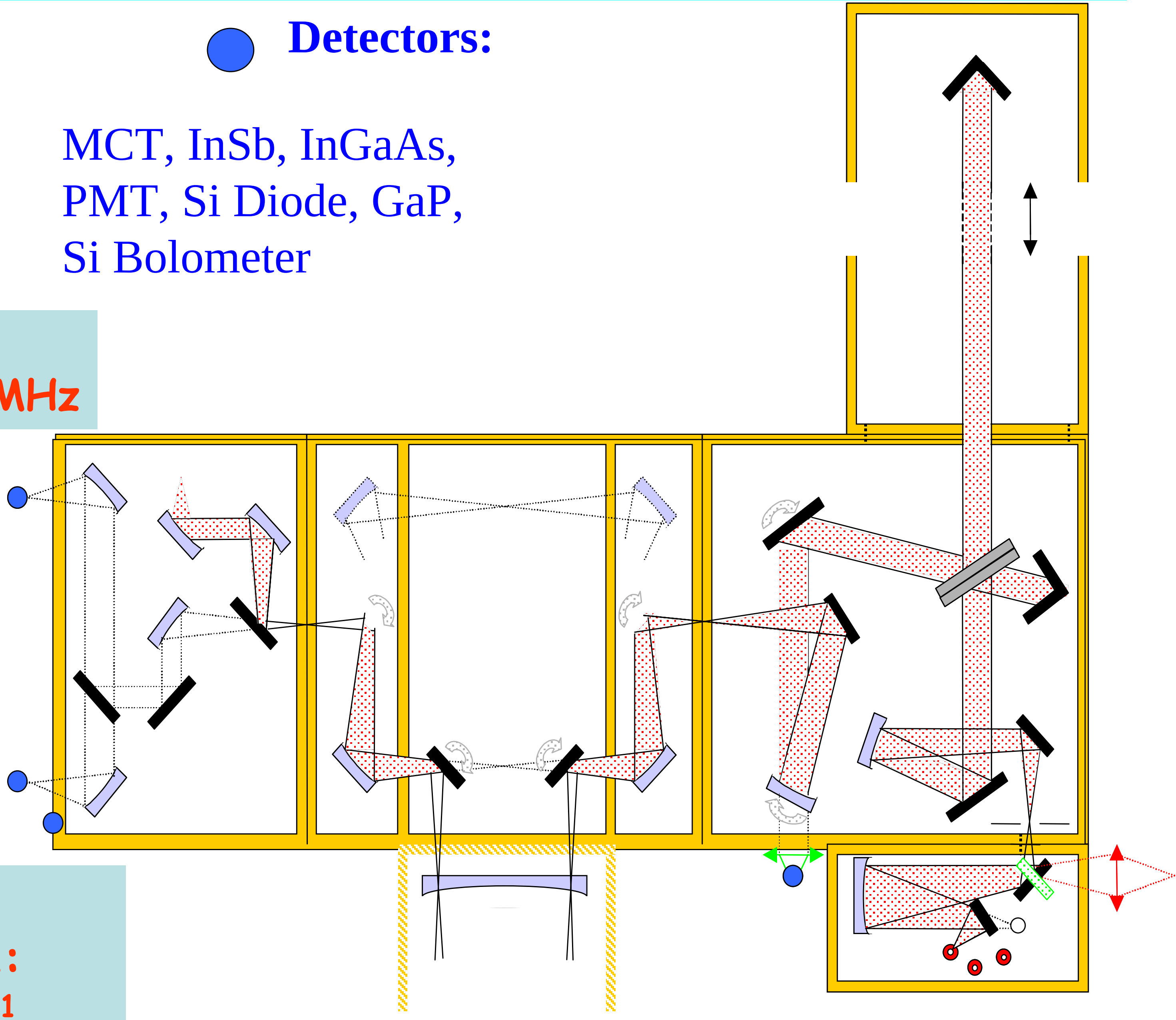
The Fourier transform spectrometer Brucker IFS 120

Detectors:

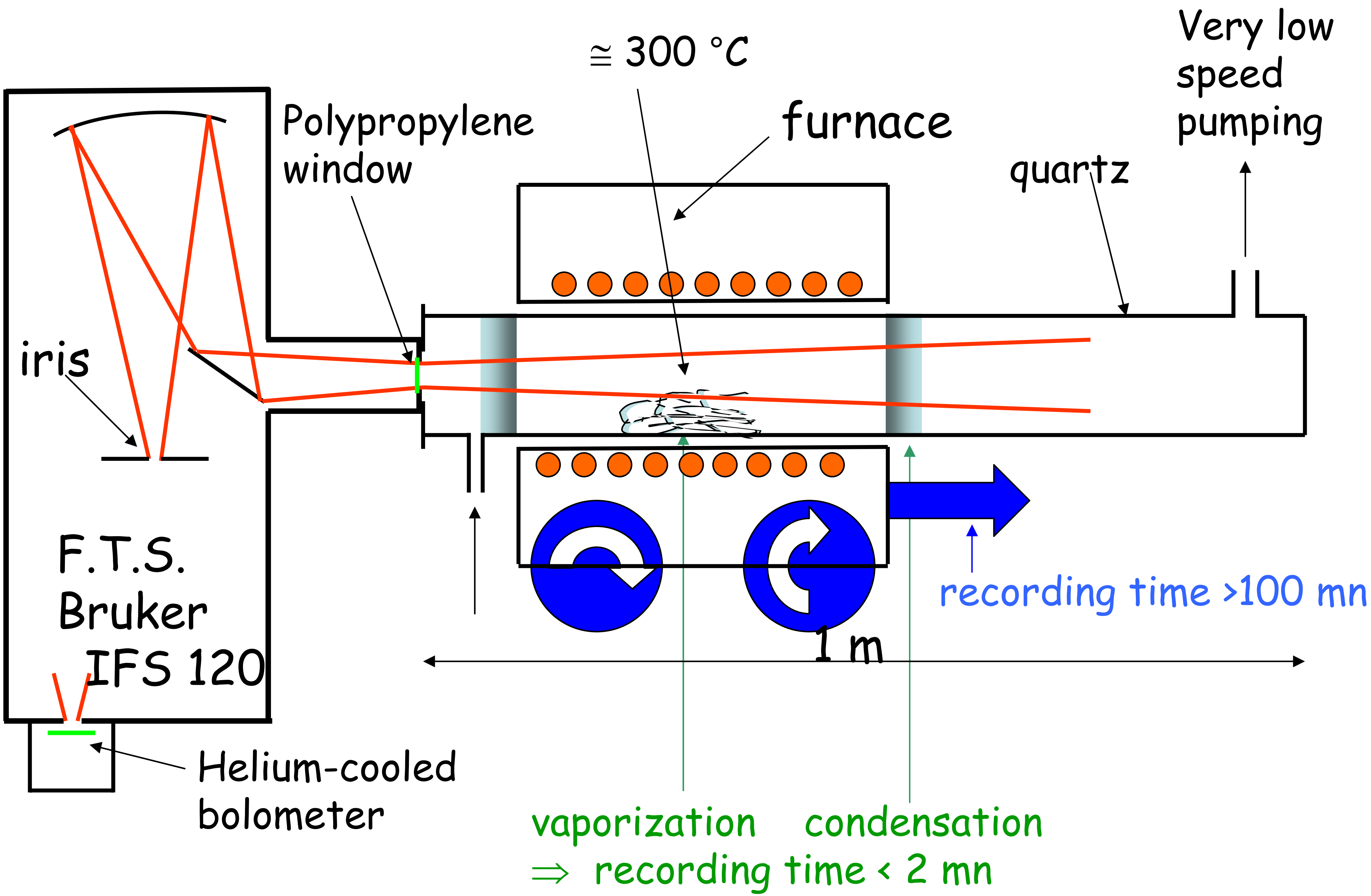
MCT, InSb, InGaAs,
PMT, Si Diode, GaP,
Si Bolometer

R = 0.002 cm^{-1}
0.001 cm^{-1} = 30 MHz

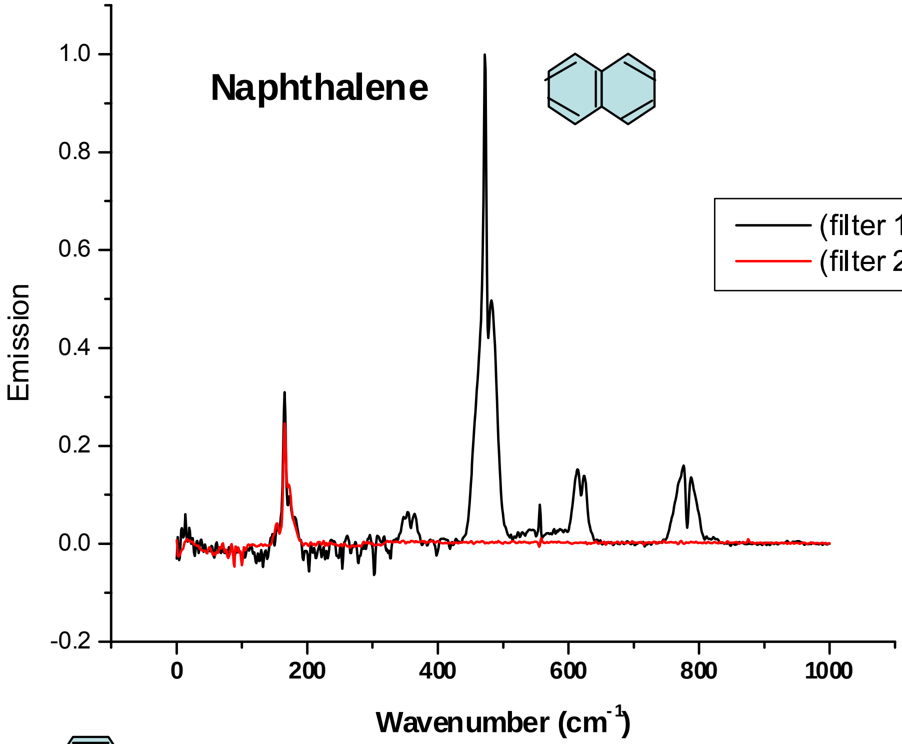


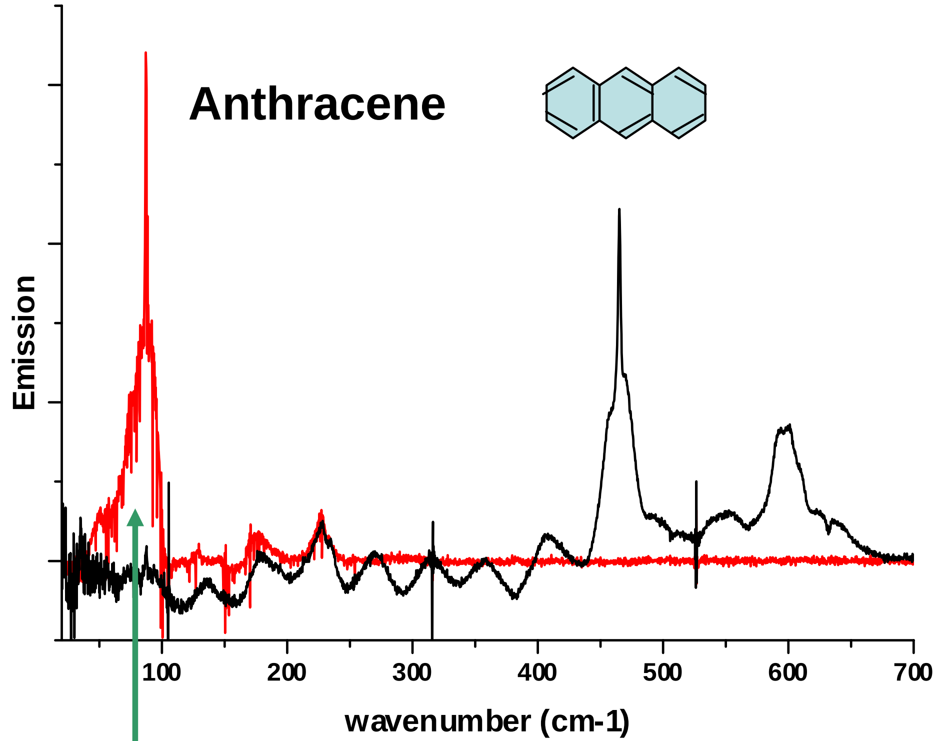
The operating Spectral range:
8 – 33000 cm^{-1}
(1.25 mm – 300nm)

Thermal emission experimental set-up

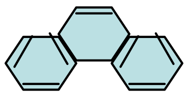


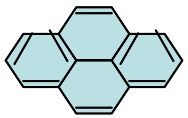
PAH 's ro-vibrational emission

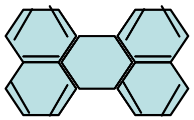


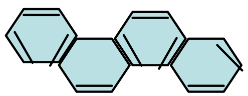


ν_{66} (b_{3u}) obs: 87.3 cm^{-1}
predicted[1] DFT: 87 cm^{-1}


Phenantrene


Pyrene


Perylene


Chrysene

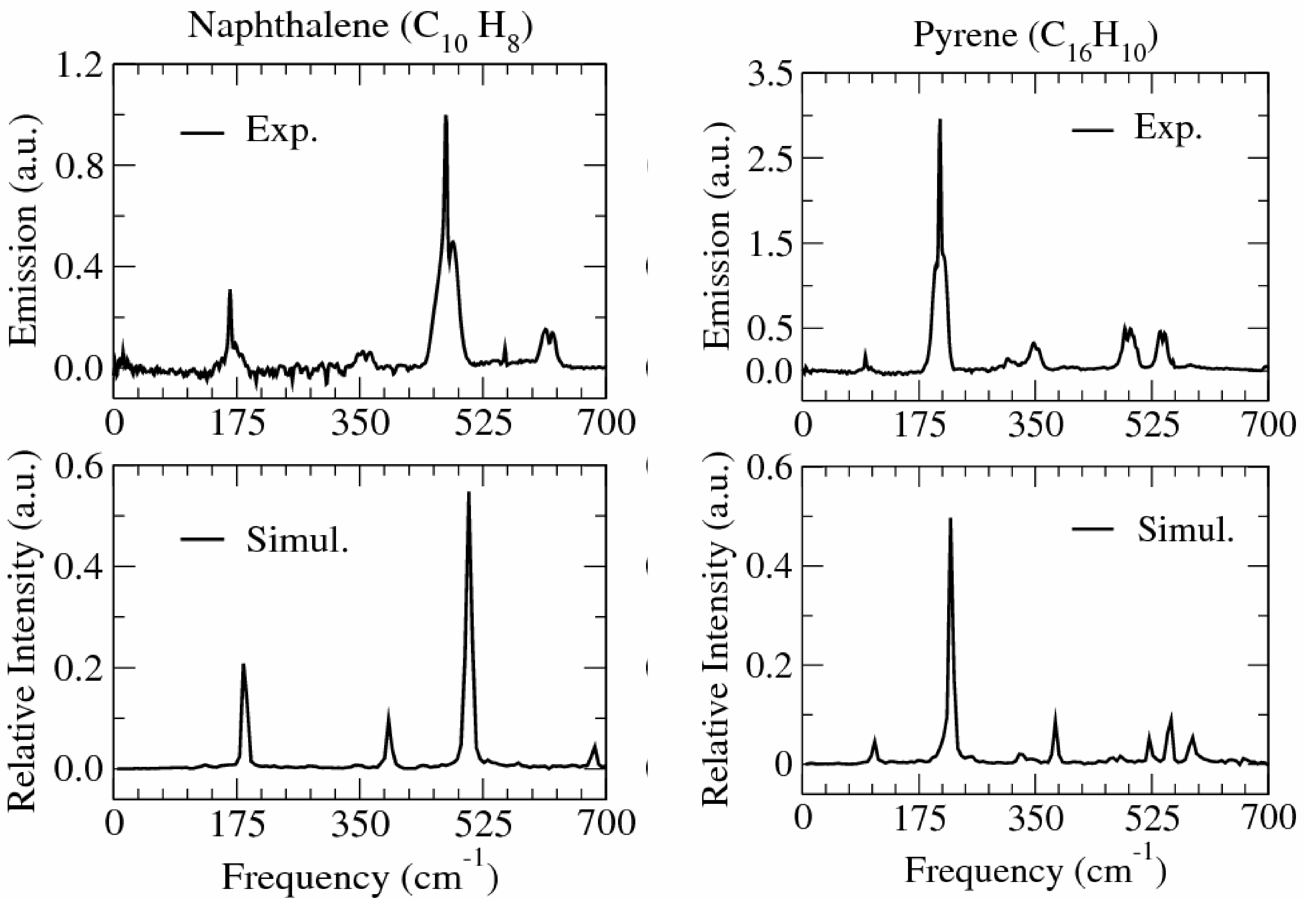
The far infrared bands of the PAHs are due to the motion of their carbon skeleton ⟷ they are the signature of each PAH.

Previous works below 400 cm^{-1} on PAHs (naphtalene, pyrene, chrysene):

K. Zhang et al., Science, 274, 582 (1996)

[1] E. Cane et al., J. Chem. Phys., 106, 9004 (1997)

Obs. and Calc. (tight-binding approach) spectra of Naphtalene and Pyrene

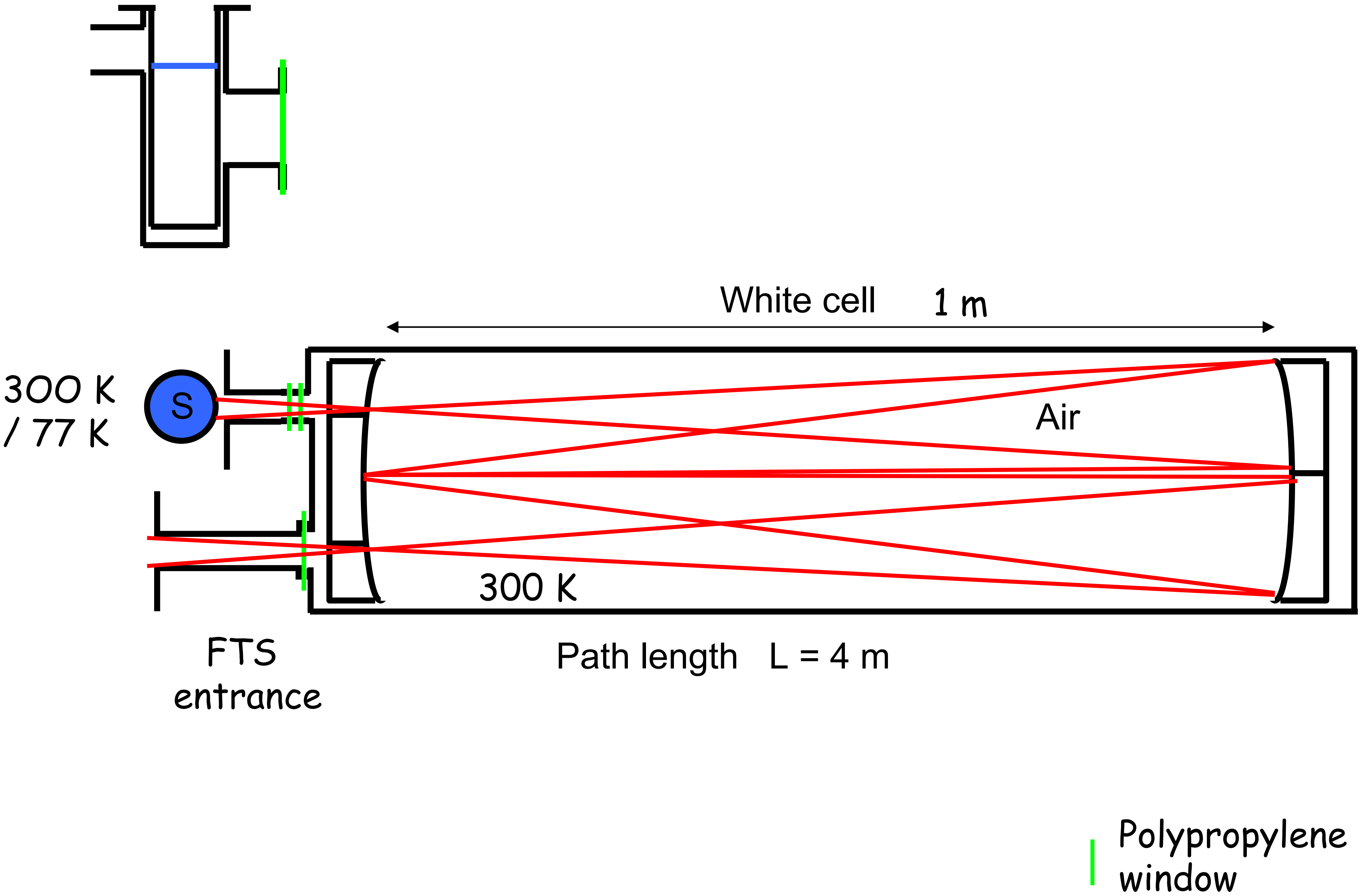


O. Pirali, N. Van-Oanh, P. Parneix, M. Vervloet, and P. Bréchignac, submitted PCCP

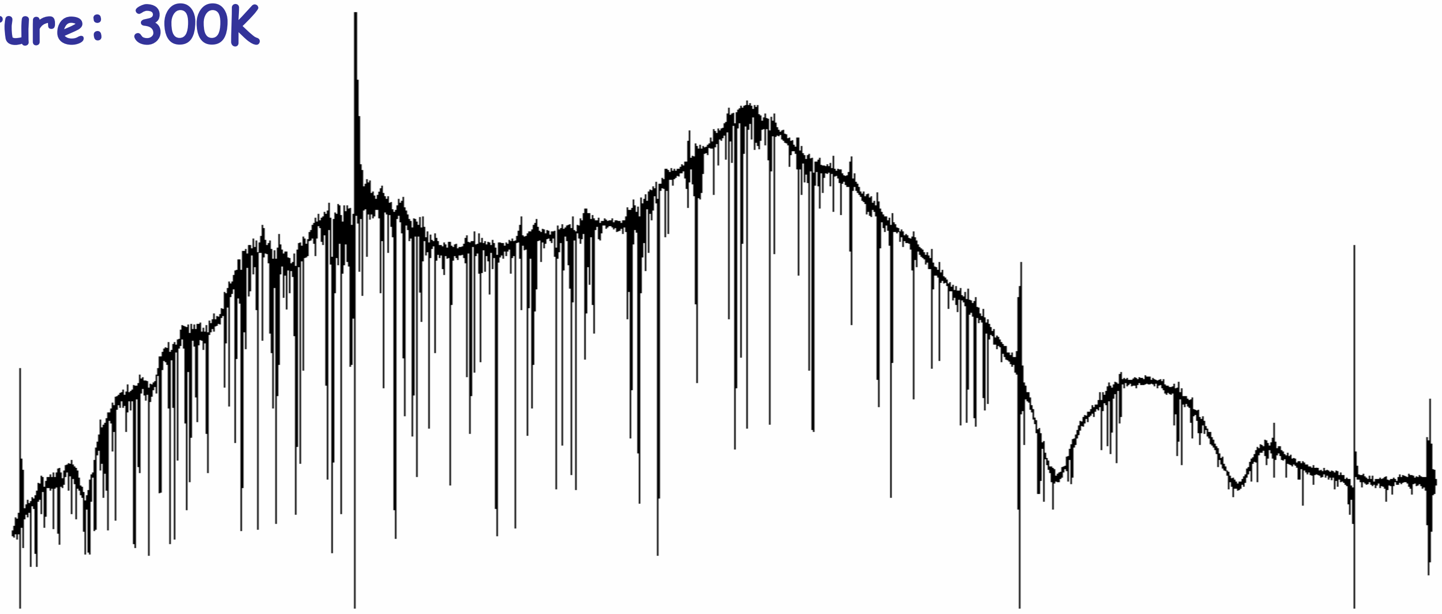
In this experiment, the temperature of the PAHs vapours was about 550 °K
→ the width of their emission bands is relatively broad.

Is it possible to record thermal emission spectra of gas phase PAHs at room temperature (300 °K) in order to get narrower band widths ?

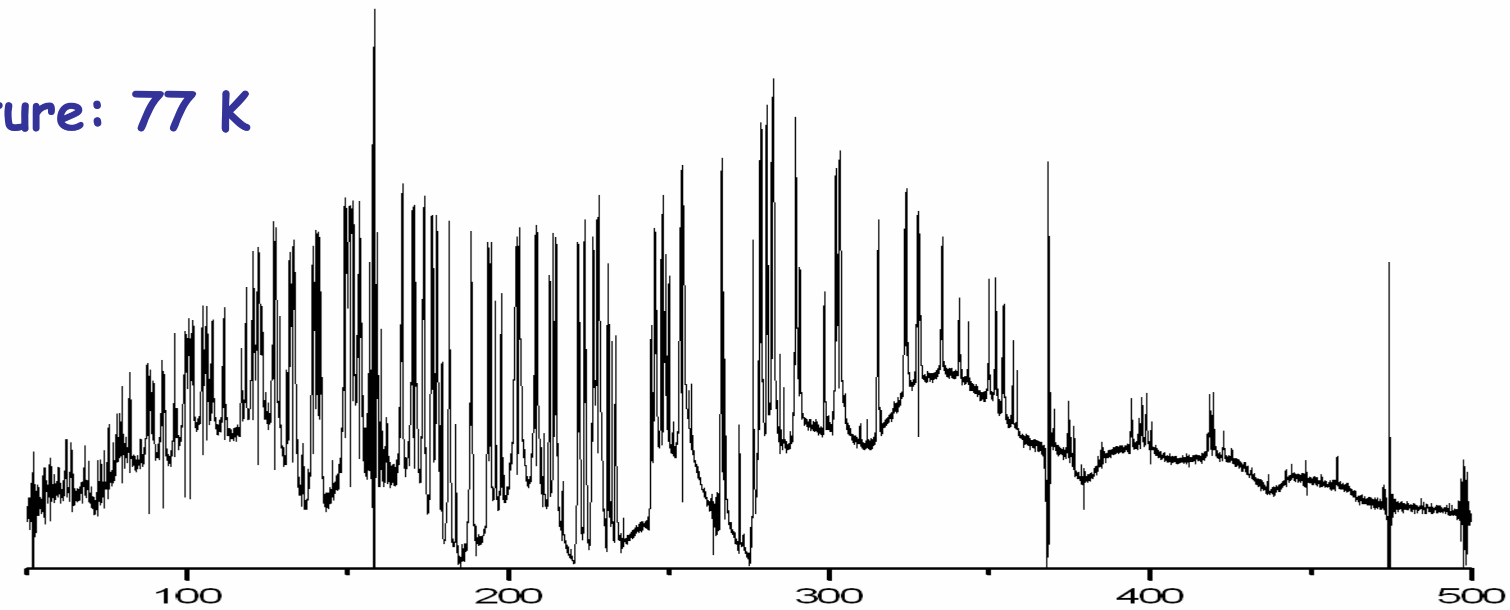
Thermal Emission of air at 300 °K



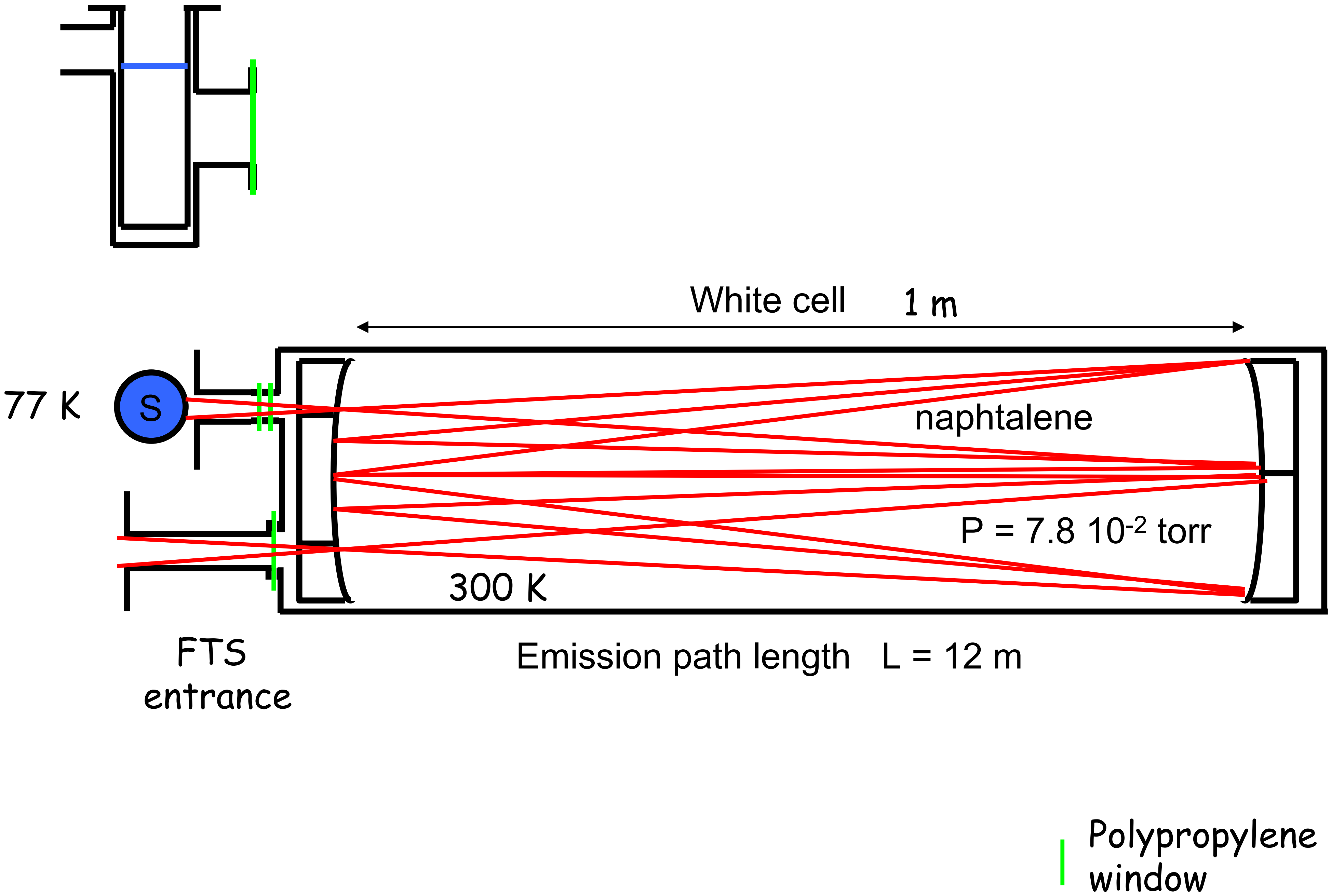
S temperature: 300K

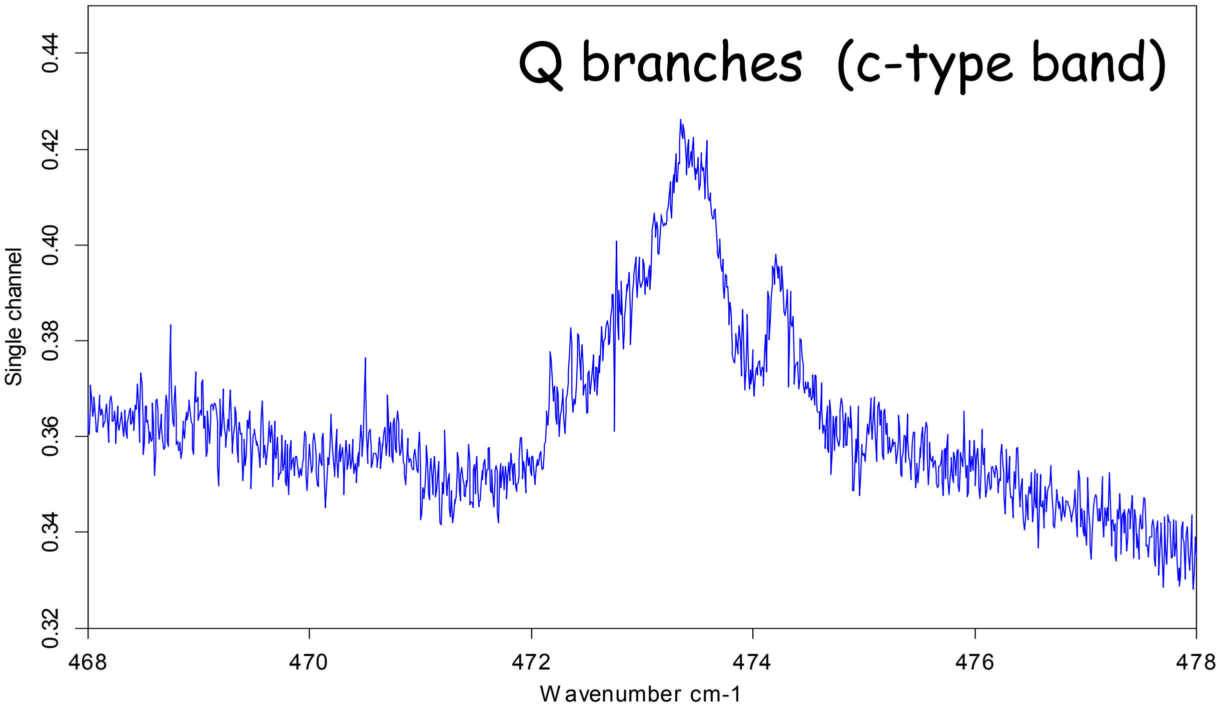


S temperature: 77 K



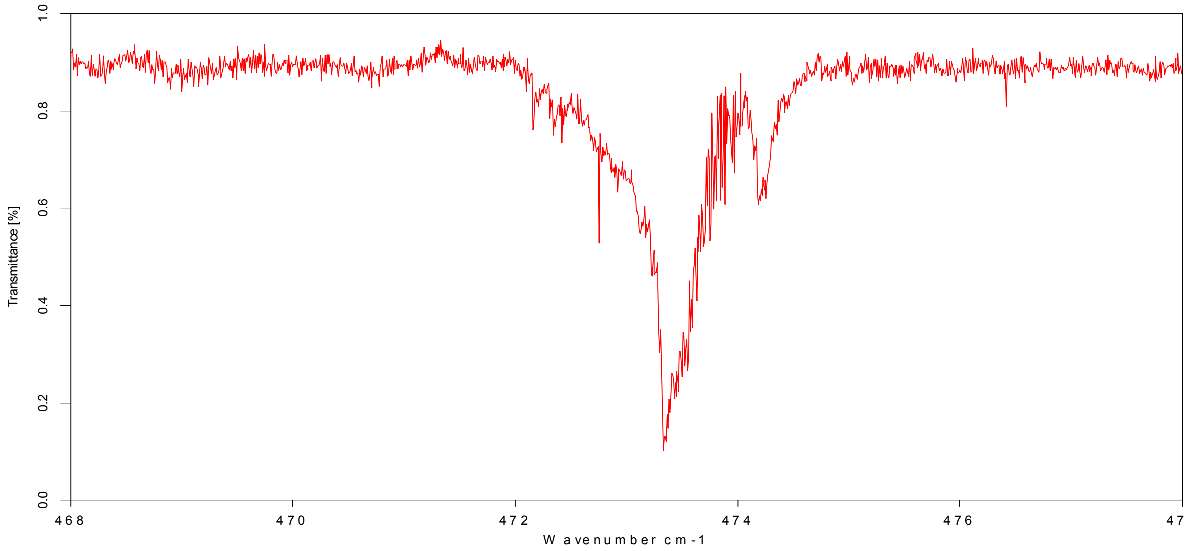
Thermal Emission at 300 K: increasing the emission path length





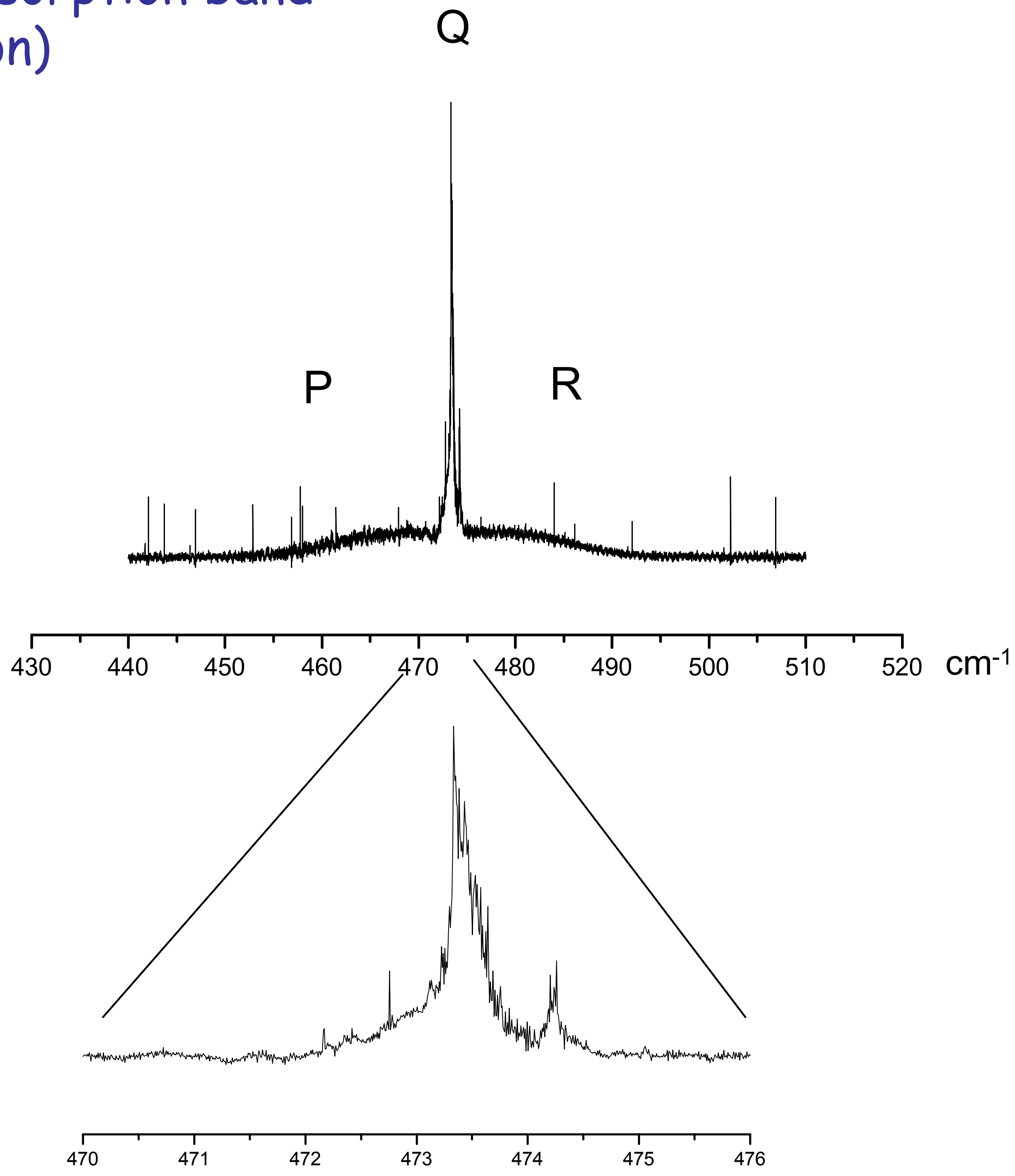
Naphtalene $C_{10}H_8$

Emission at 300 K
L = 12 m



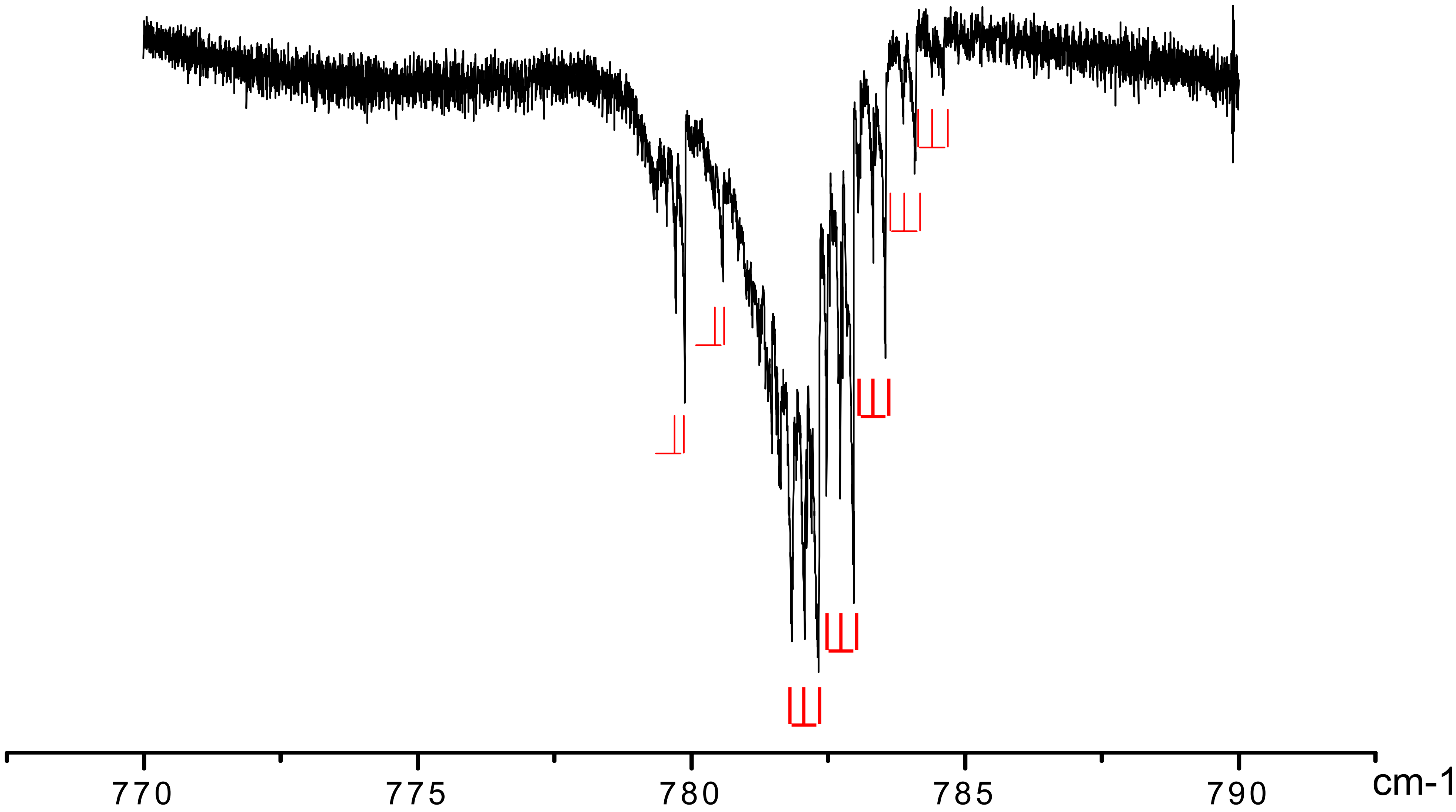
Absorption at 300 K
L = 12 m

The 473 cm^{-1} absorption band
(c-type transition)

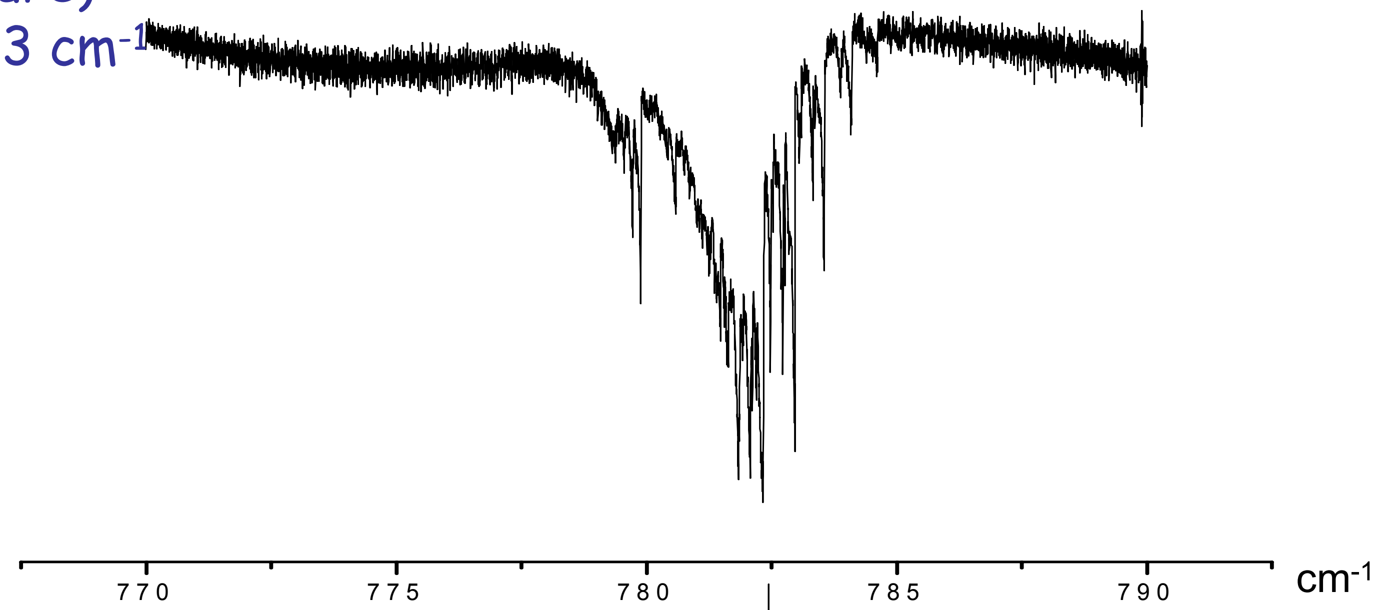


The Q branches of the 782 cm^{-1} (ν_{35}) band of naphtalene (48 vibration normal modes)

many peaks are observed; can we assign them?



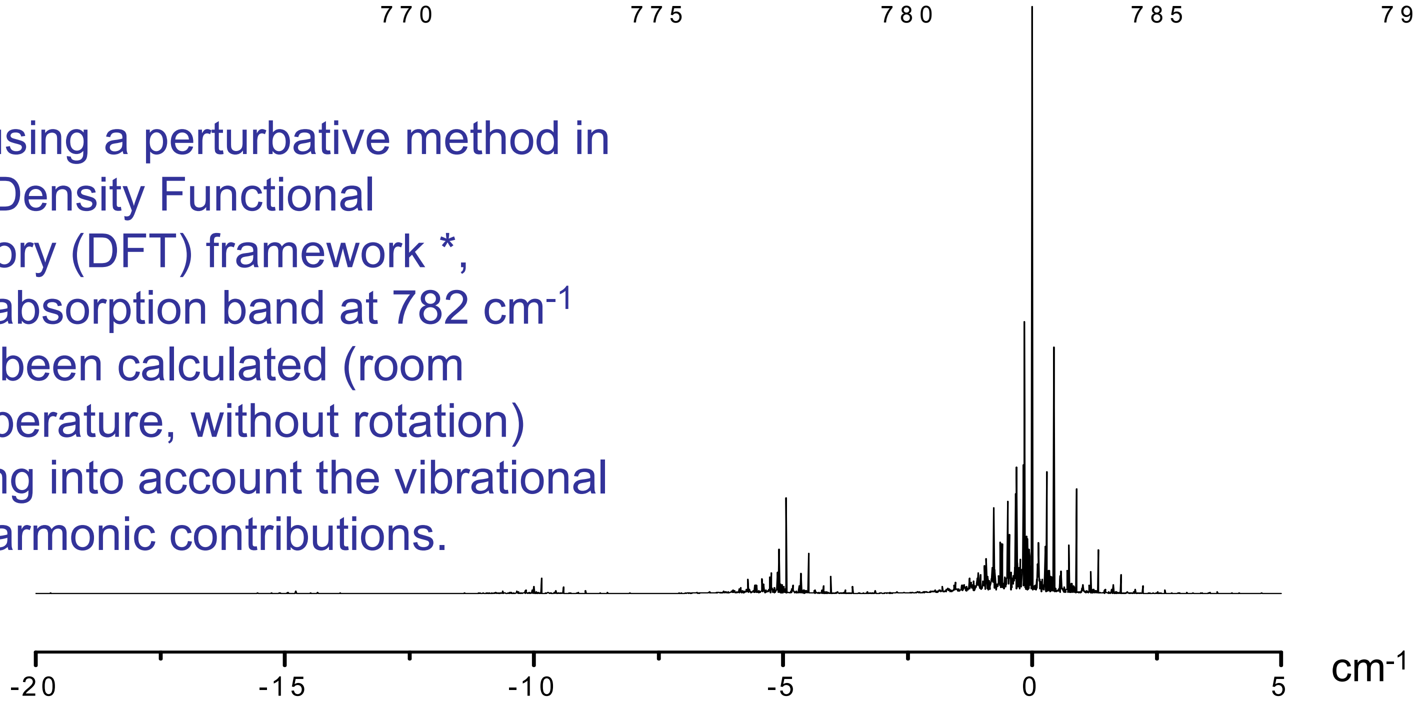
The observed absorption band at 782 cm^{-1}
(room temperature)
Resolution: 0.003 cm^{-1}



Calculated harmonic frequencies (in cm^{-1}) of the lowest vibrational levels:

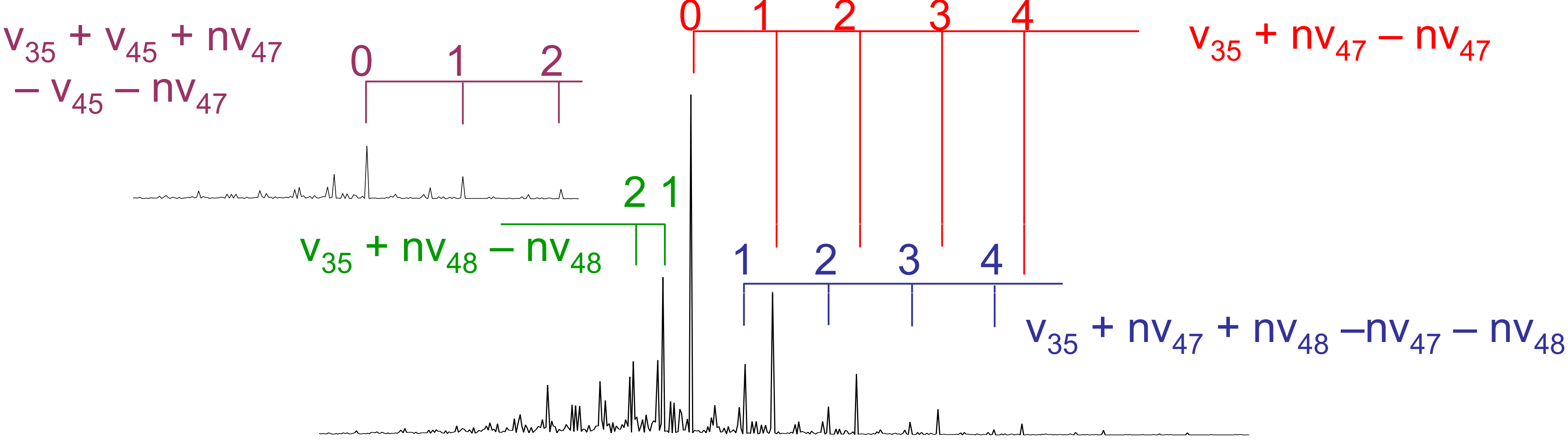
v_{48}	166
v_{47}	195
v_{46}	359
v_{45}	385
v_{44}	465
v_{43}	473
v_{42}	511
v_{41}	512
	- - -
	- - -

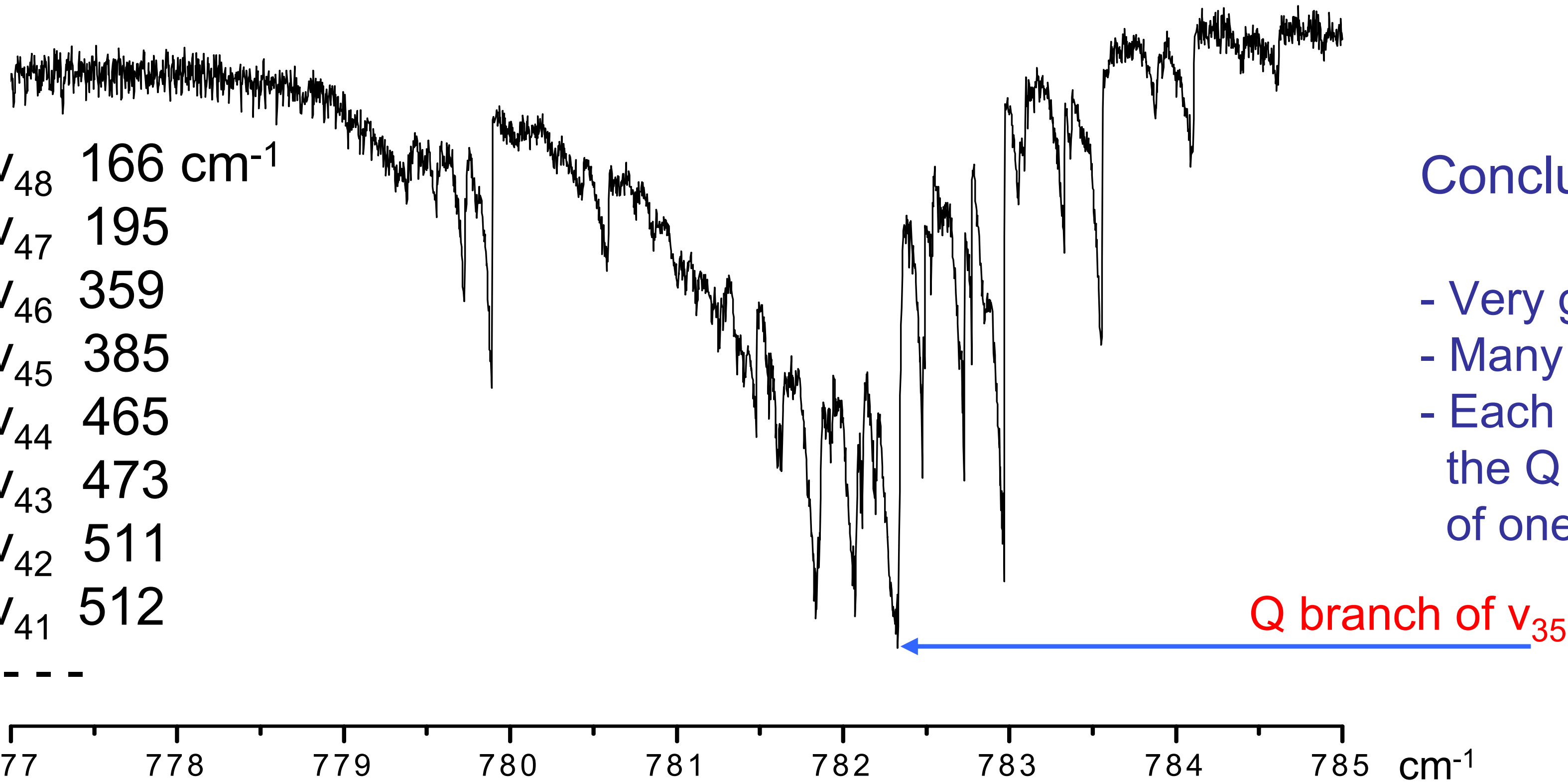
By using a perturbative method in the Density Functional Theory (DFT) framework *, the absorption band at 782 cm^{-1} has been calculated (room temperature, without rotation) taking into account the vibrational anharmonic contributions.



Fermi resonance predicted between $v_{35} + v_{45}$ and v_{23} at around 1185 cm^{-1}

* Mulas et al., 2006, A&A, in press



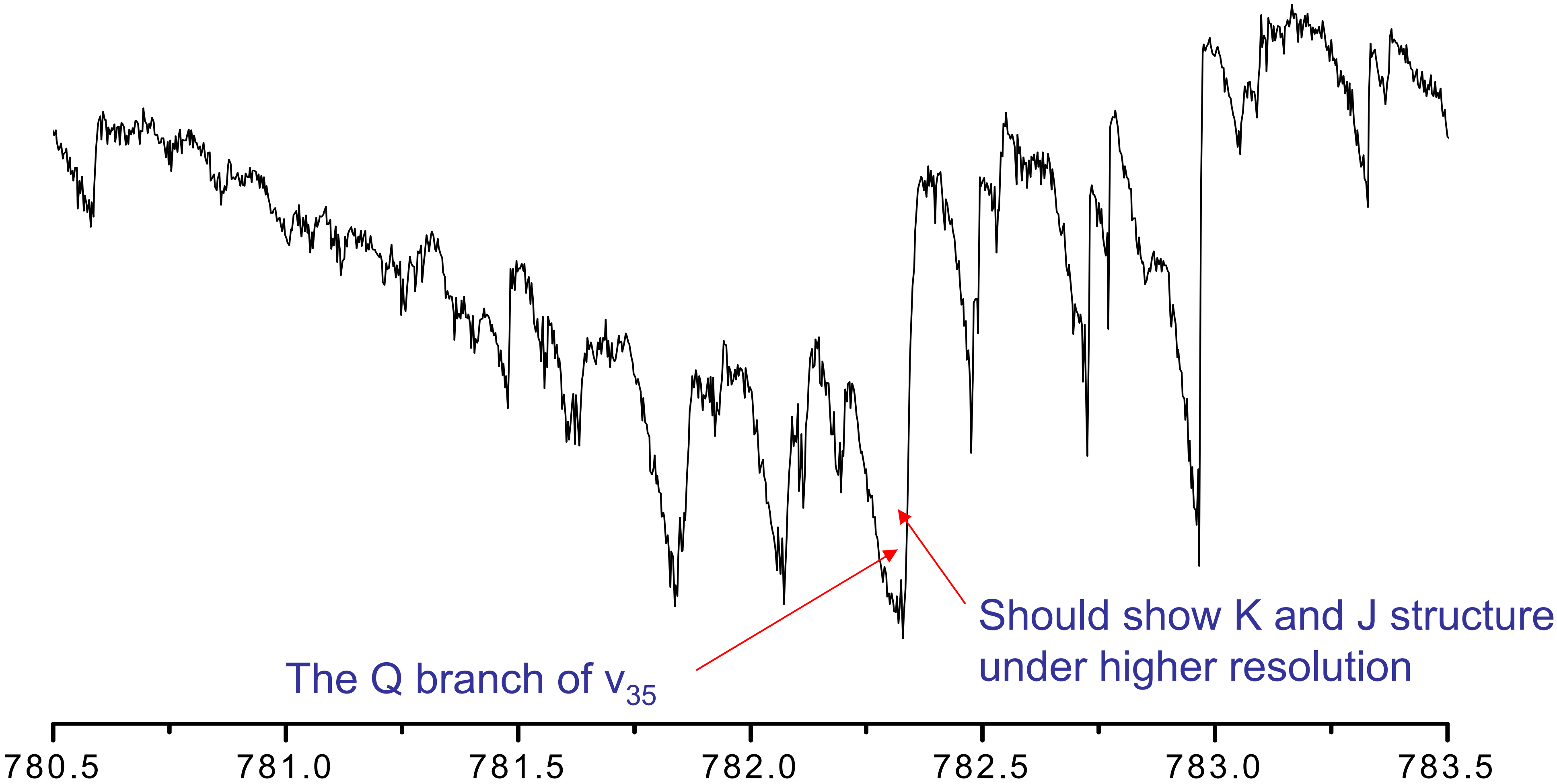


v_{48} 166 cm^{-1}
v_{47} 195
v_{46} 359
v_{45} 385
v_{44} 465
v_{43} 473
v_{42} 511
v_{41} 512
- - -

Conclusion:

- Very good predictions
- Many hot bands
- Each peak represents the Q (J,K) branch of one vibrational band.

O. Pirali, M. Vervloet, G. Mulas, G. Malloci, C. Joblin, in preparation



The Q branch of ν_{35}
Should show K and J structure under higher resolution
780.5
781.0
781.5
782.0
782.5
783.0
783.5

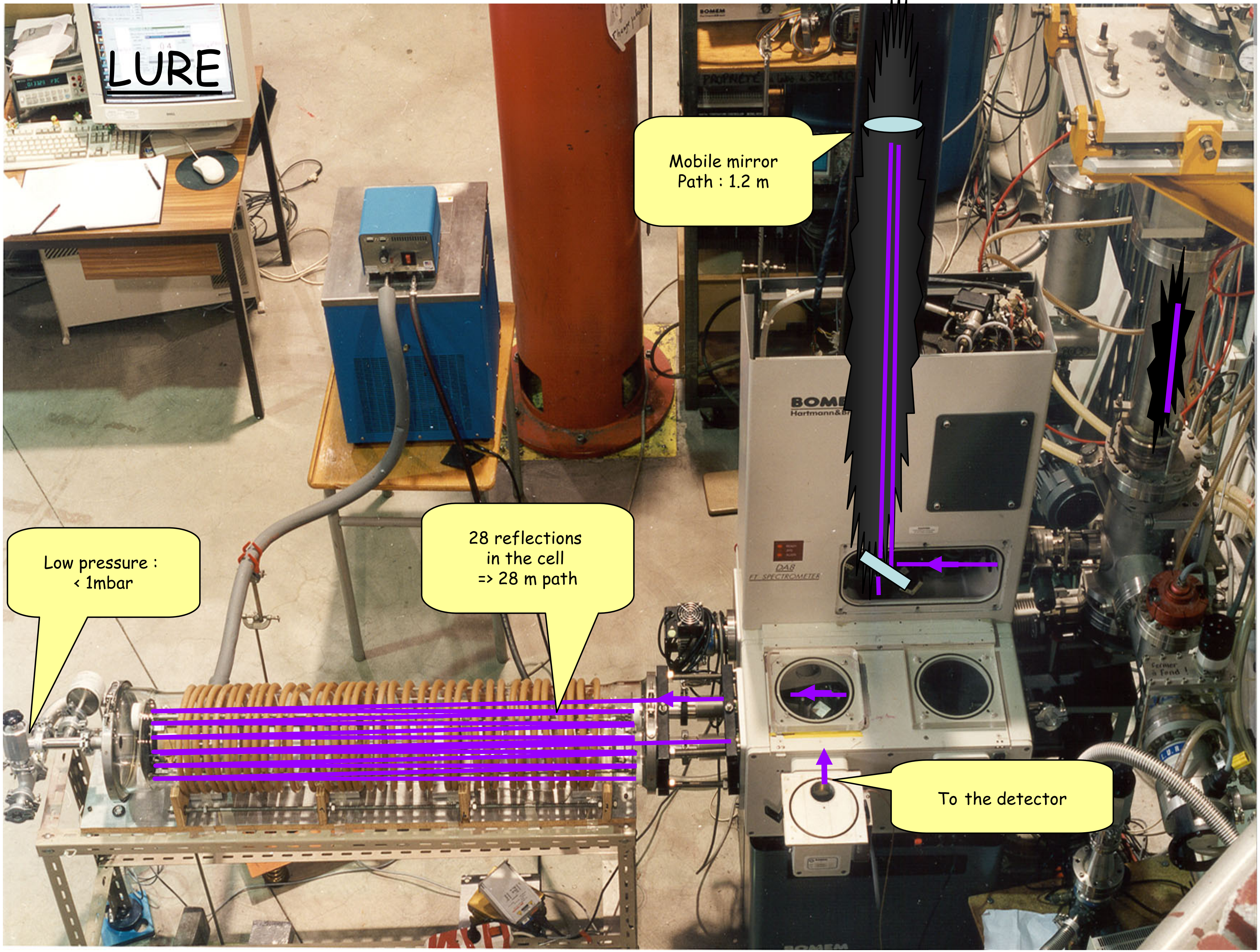
To record high resolution absorption spectra by Fourier transform spectroscopy in the far-infrared region, it is highly suitable to use a much brighter continuum source than the conventional ones (glowbar, Hg arc lamp).

Far-infrared Fourier Transform Absorption Spectroscopy

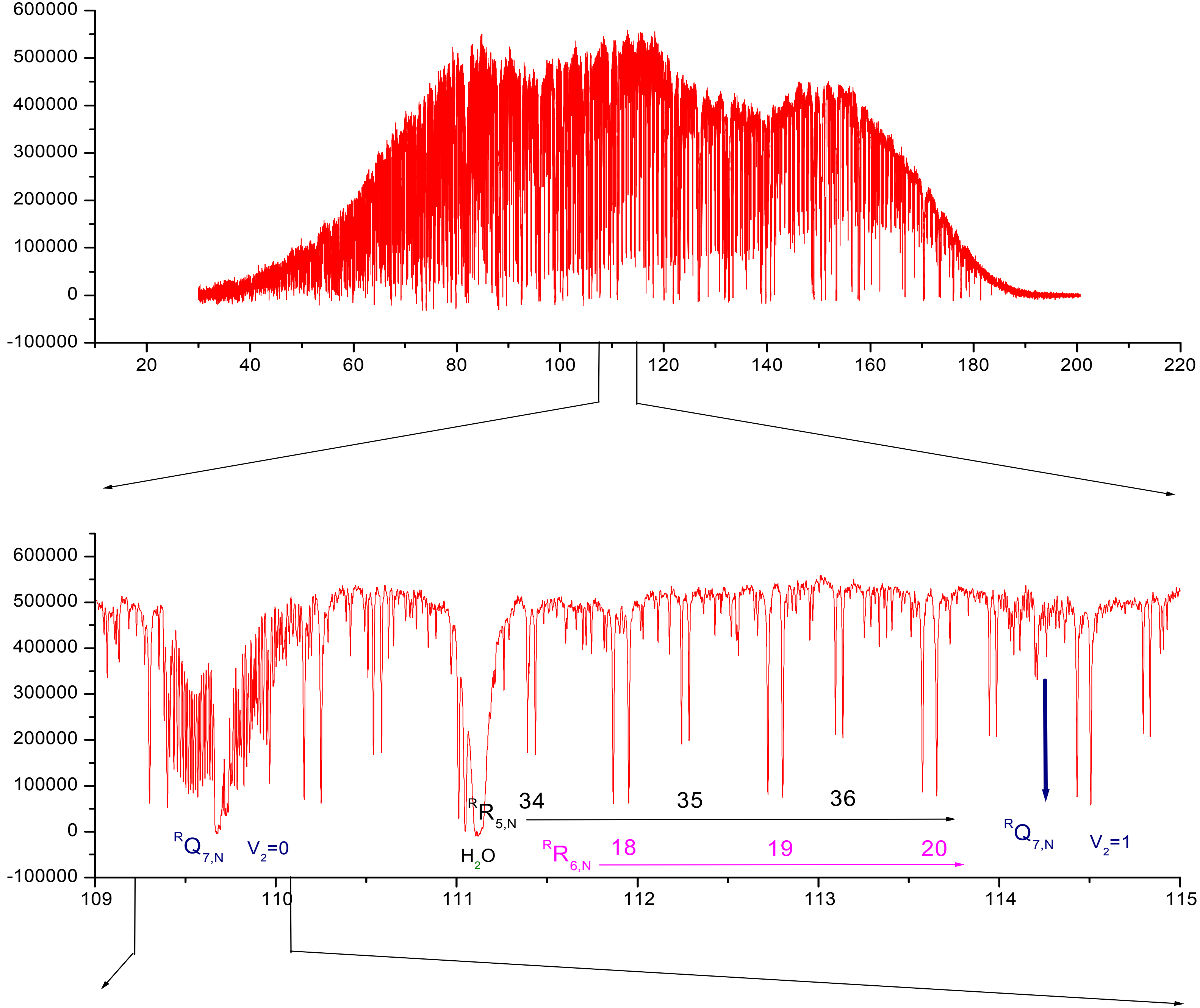
with Synchrotron Radiation

LURE: the previous french synchrotron facility

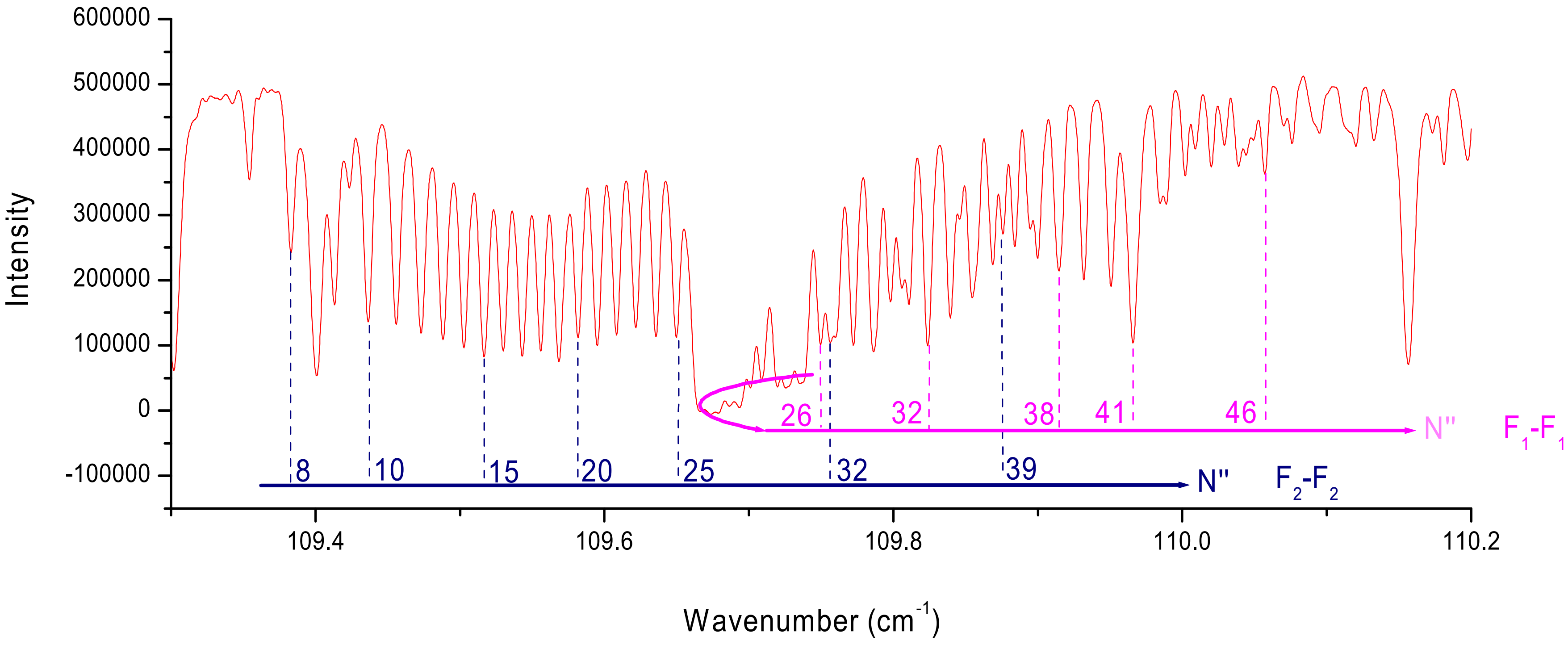
SOLEIL: the new french synchrotron facility


LURE
Mobile mirror
Path : 1.2 m
Low pressure :
< 1mbar
28 reflections
in the cell
=> 28 m path
To the detector

NO_2 Absorption with S. R.

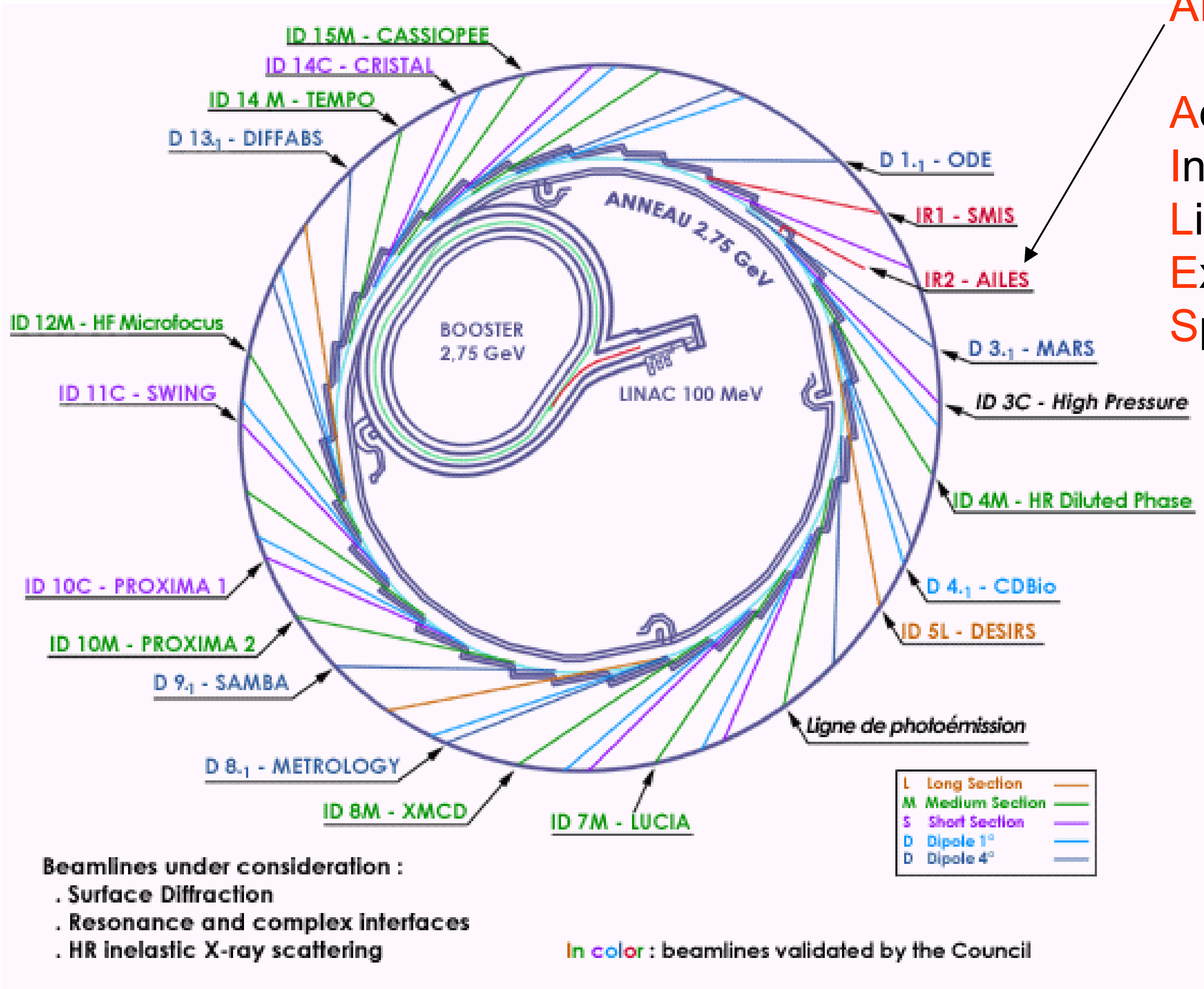


$^{R}Q_{7,N}$ (0,0,0)



Line width = 0.004 cm^{-1} (limited by the maximum resolution of the FTS)

The beam lines of the synchrotron SOLEIL

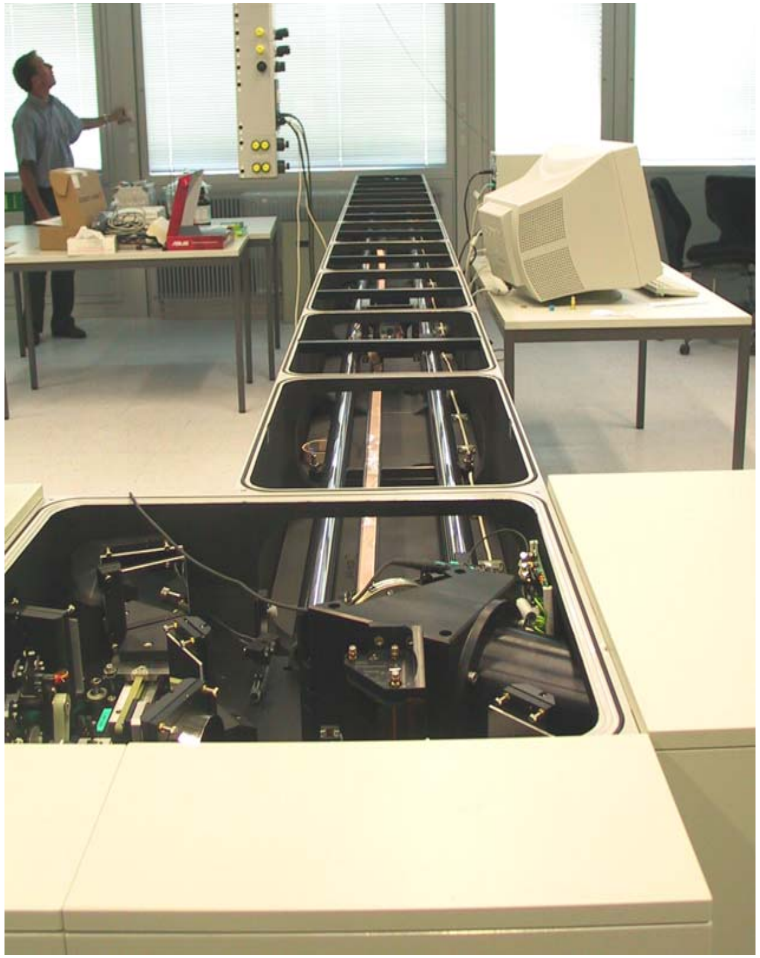


AILES

Advanced
Infrared
Line
Exploited for
Spectroscopy

SOLEIL: the new french synchrotron facility

The Bruker interferometer IFS 125 HR



IFS 125HR

- Maximum optical path difference = 900 cm
- Line width < 0.001 cm-1
- Resolving power 2,000,000

Acknowledgments:

- PN PCMI: Programme National « Physique et Chimie du Milieu Interstellaire »

-The Molecular Universe (Marie Curie Research training European Network)

- SOLEIL (the new french synchrotron facility)