



# HDO and D<sub>2</sub>O long path spectroscopy: Ongoing work of the Brussels-Reims Team.

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**UMR CNRS 6089**

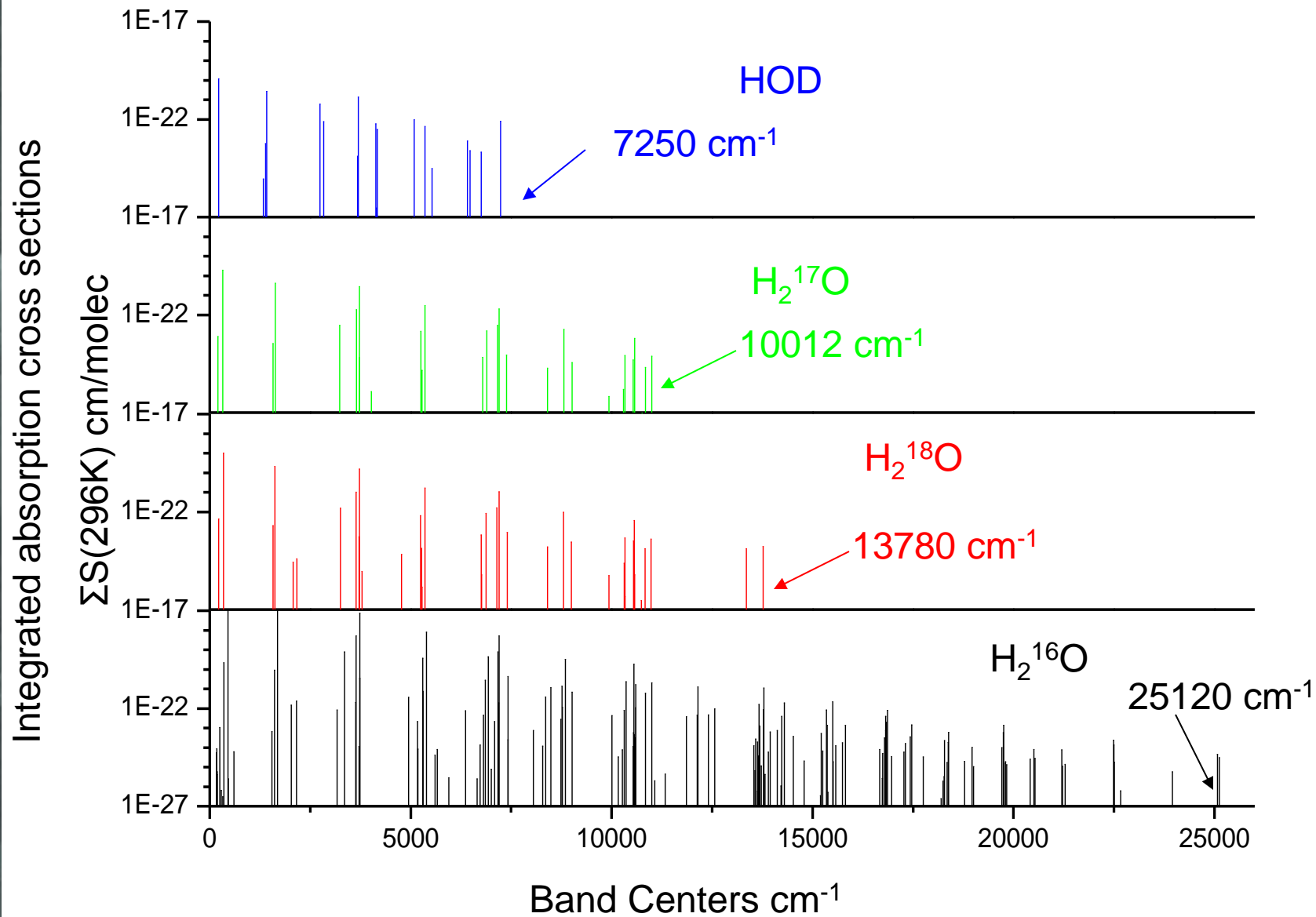
**Université de Reims Champagne Ardenne**

**Reims, France**

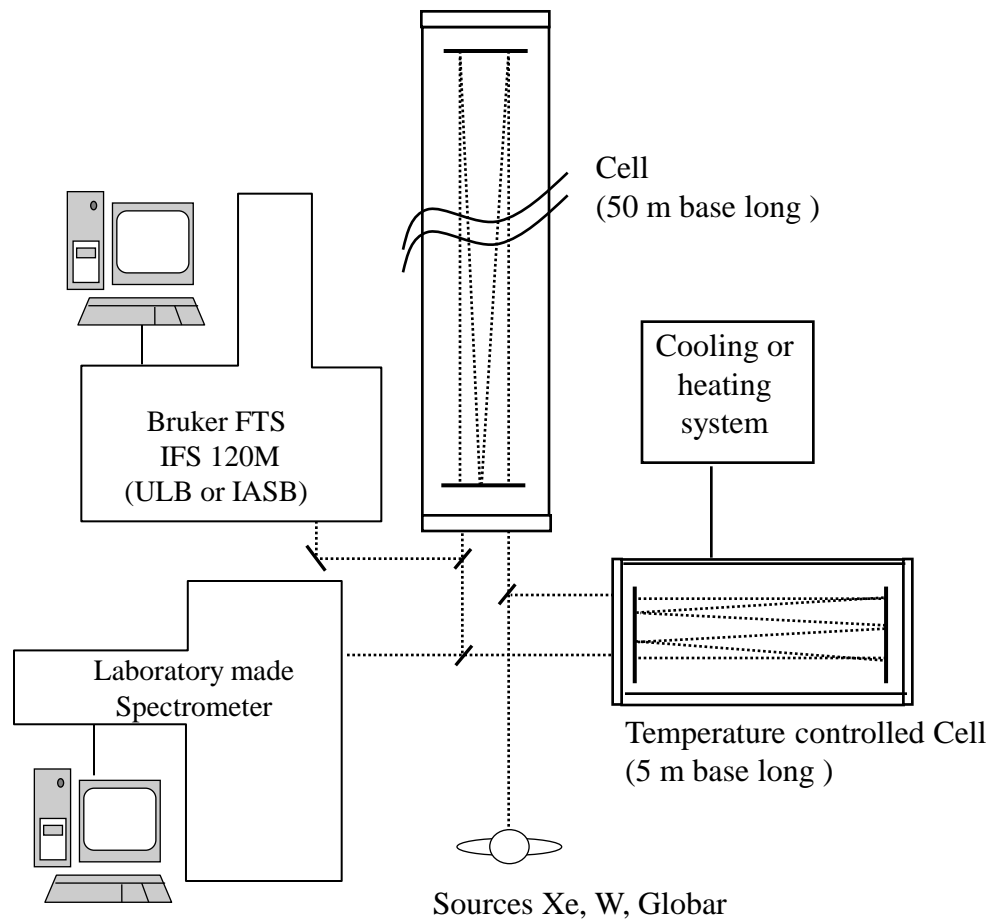
# Workgroup involved in water vapor absorption measurements

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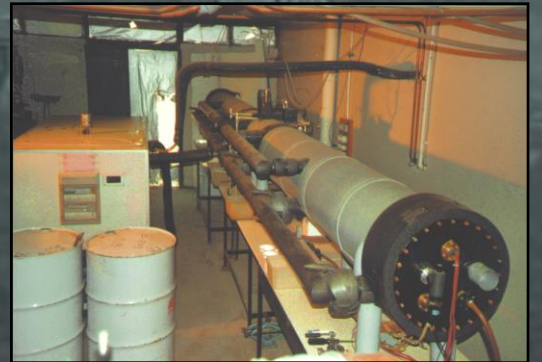
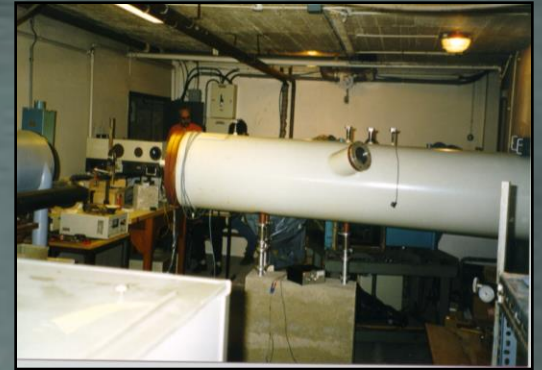
# HITRAN 2004



# Experimental setup



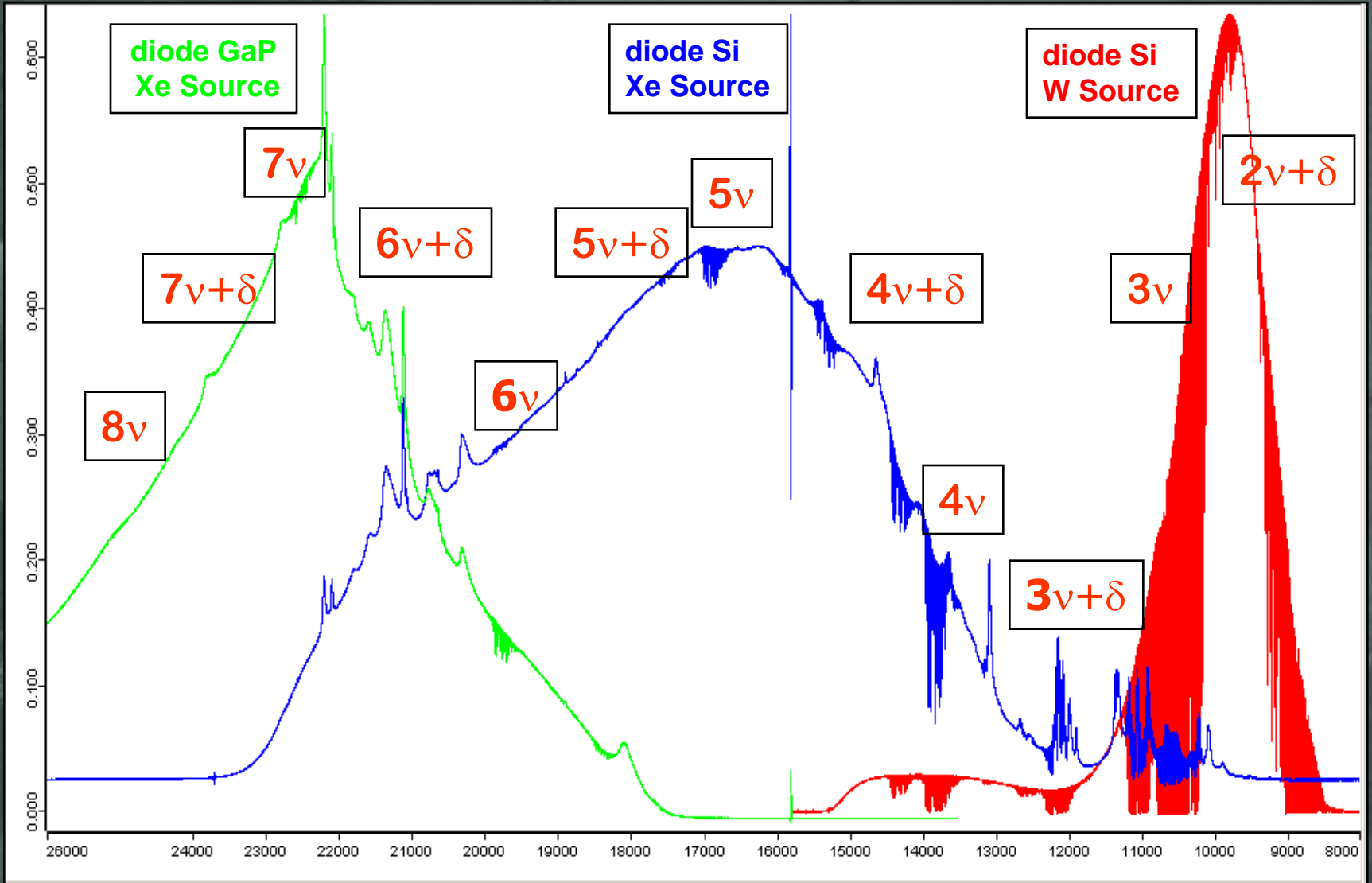
# Experimental setup



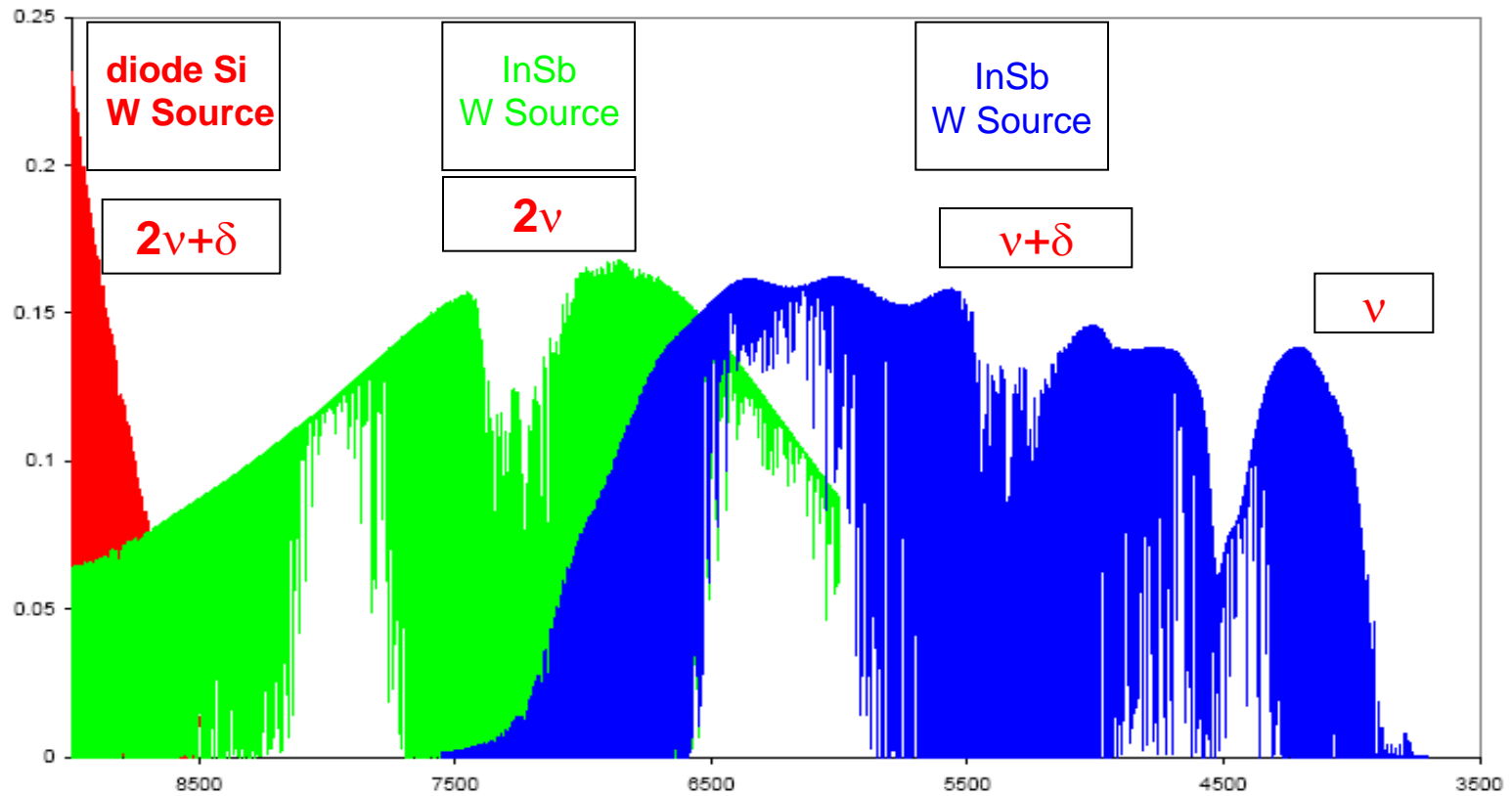
# experimental conditions for HDO – D<sub>2</sub>O spectra

- Absorption path: 600 m
- Resolution: down to  $0.03 \text{ cm}^{-1}$  (30 cm MOPD)
- Spectral range: 8800 - 10200  $\text{cm}^{-1}$
- H<sub>2</sub>O + D<sub>2</sub>O mixtures (  $P_{\text{tot}} \sim 10 \text{ hPa}$  )
- Room temperature:  $T \sim 293 \text{ K}$
- Wavenumber calibration: I<sub>2</sub> ( table of Gesternkorn )

# Vis-NIR water absorption spectra

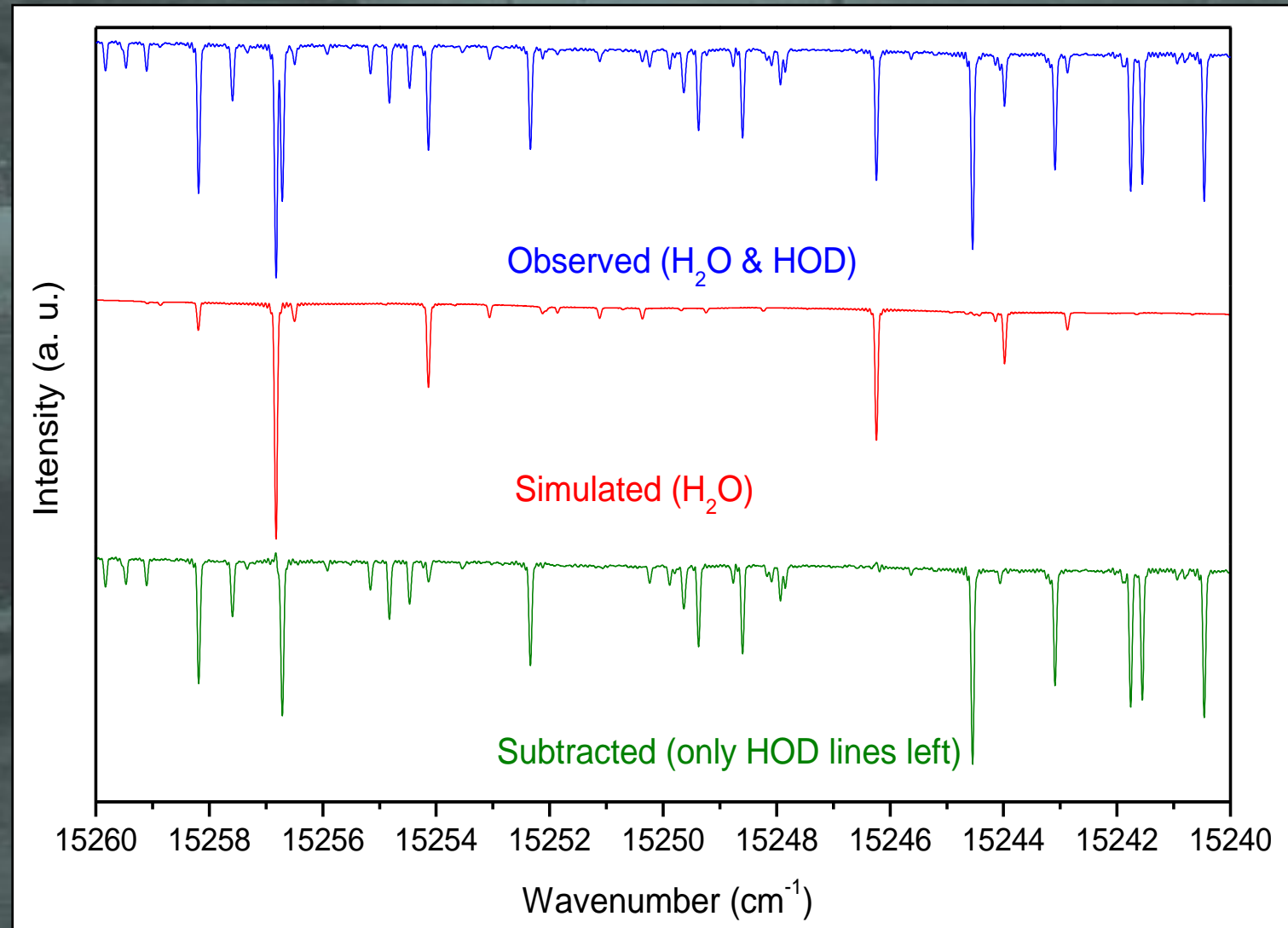


# IR Absorption spectra



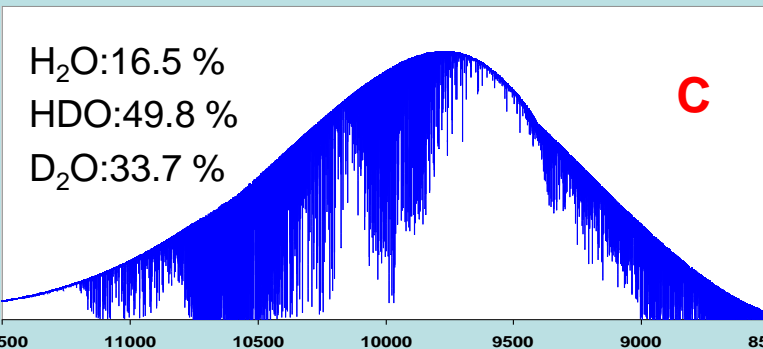
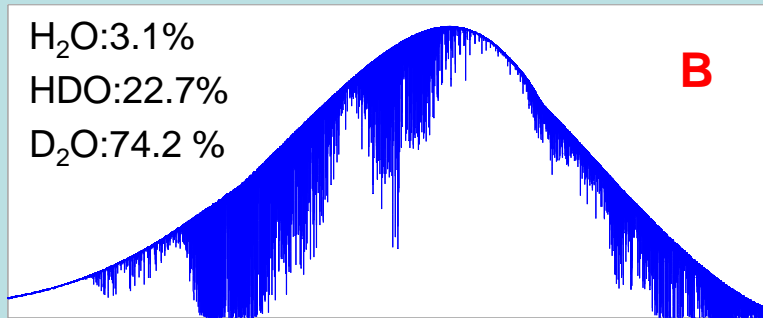
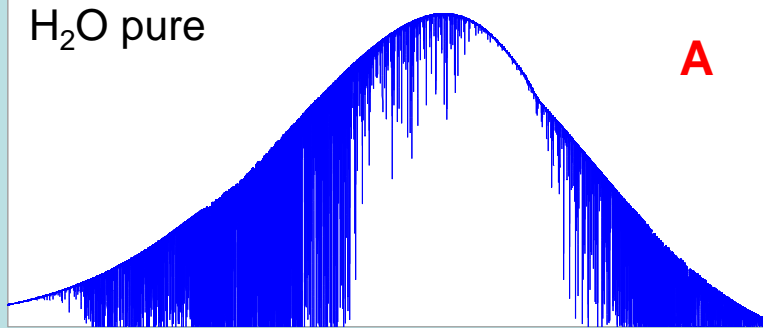


# Vis-NIR spectral range: Subtraction of the H<sub>2</sub>O lines



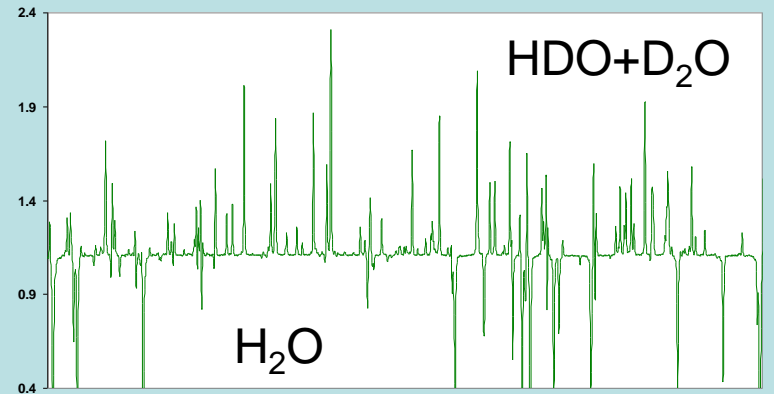
# NIR spectral range:

## H<sub>2</sub>O, HDO and D<sub>2</sub>O

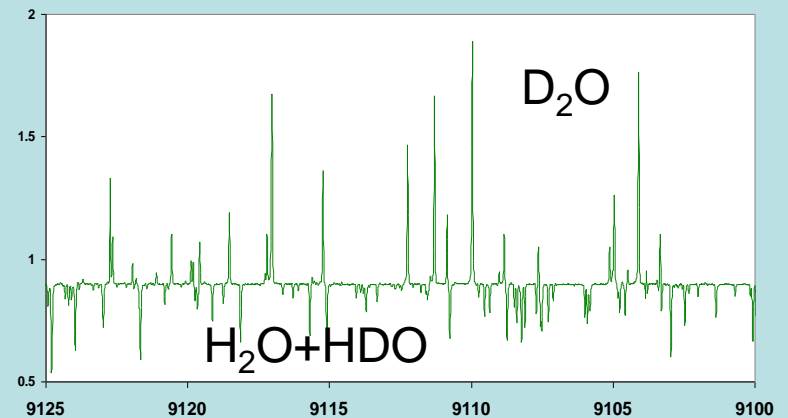


Path: 600 m, P: 13 hPa, Resol.: 0.03 cm<sup>-1</sup>

A / C  
⇒



C / B  
⇒



# Partial pressures: IR region

• Total Pressures: Baratron  $P_{1}^{\text{tot}} = P_{1}^{116} + P_{1}^{126} + P_{1}^{226}$        $P_{2}^{\text{tot}} = P_{2}^{116} + P_{2}^{126} + P_{2}^{226}$

• Use of BR list for  $\text{H}_2^{16}\text{O}$  partial pressures (from natural  $\text{H}_2\text{O}$  spectra)

$$P_{1}^{\text{tot}} = P_{1}^{116} + P_{1}^{126} + P_{1}^{226} \qquad P_{2}^{\text{tot}} = P_{2}^{116} + P_{2}^{126} + P_{2}^{226}$$

• Isotopologue assignment => Spectra Ratios

• Line surface measurements => with the good molar mass

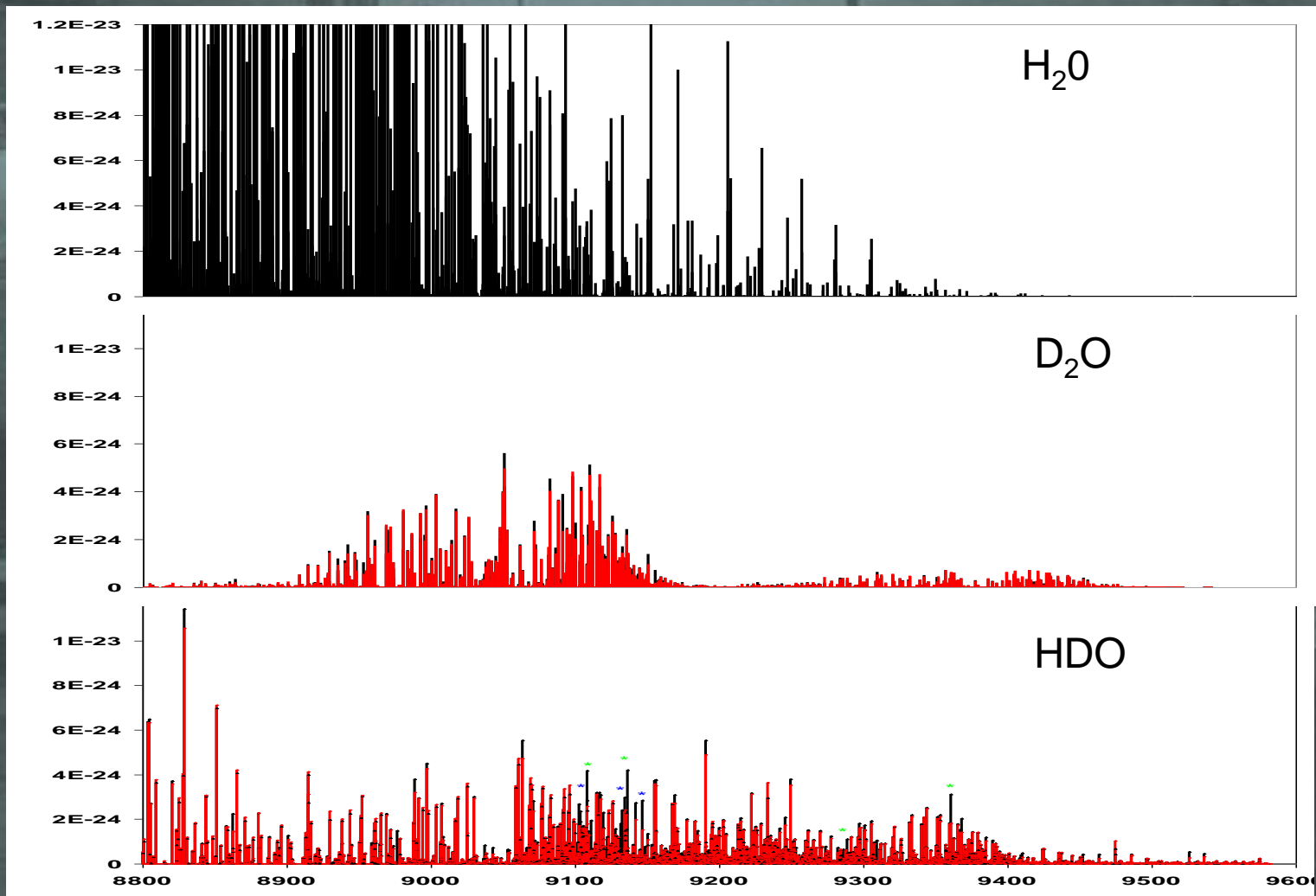
• Determination of the mean Surface ratios for HDO and  $\text{D}_2\text{O}$

$$r_1 = P_{1}^{126} / P_{2}^{126} \qquad r_2 = P_{1}^{226} / P_{2}^{226}$$

• Calculation of partial pressures and line intensities

# IR region:

## H<sub>2</sub>O, D<sub>2</sub>O and HDO line intensities



# IR region: HDO line assignement

Based on the new calculation of Partridge and Schwenke for both positions and intensities

Still under progress in this region (8800-10200  $\text{cm}^{-1}$ )

In the present work

HDO 8800-10200  $\text{cm}^{-1}$  region:

4380 observed lines mainly from  $2\nu+\delta$ ,  $3\nu$  and  $3\nu+\delta$  polyads

5200 assignments

An integrated intensity of  $2 \cdot 10^{-21}$   $\text{cm molec}^{-1}$  for this region

D<sub>2</sub>O: 8800- 13200  $\text{cm}^{-1}$  region:

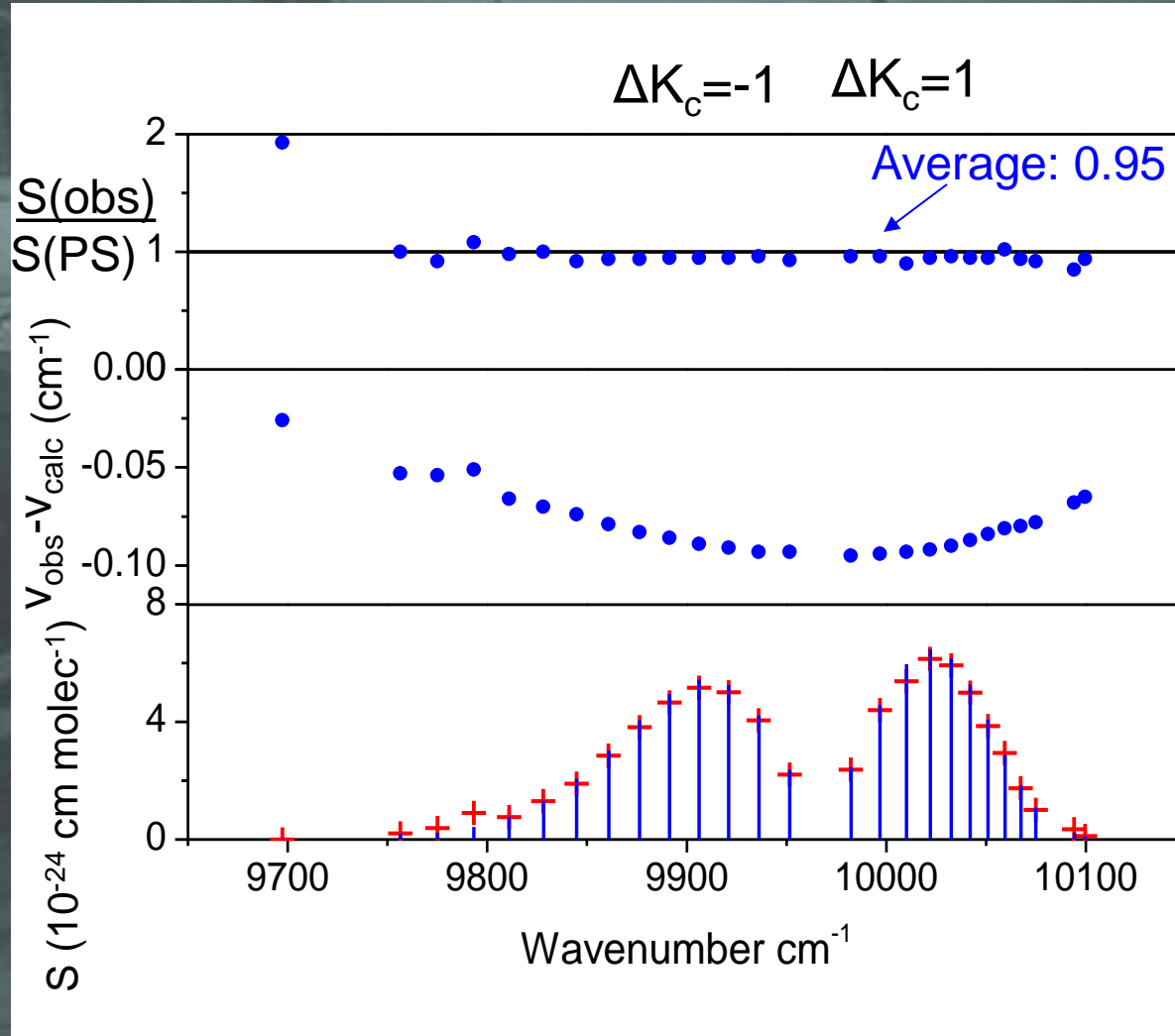
2160 observed lines mainly from  $3\nu+\delta$ ,  $4\nu$ ,  $4\nu+\delta$  and  $5\nu$  polyads

2596 assignements

An integrated intensity of  $8 \cdot 10^{-22}$   $\text{cm molec}^{-1}$  for this region

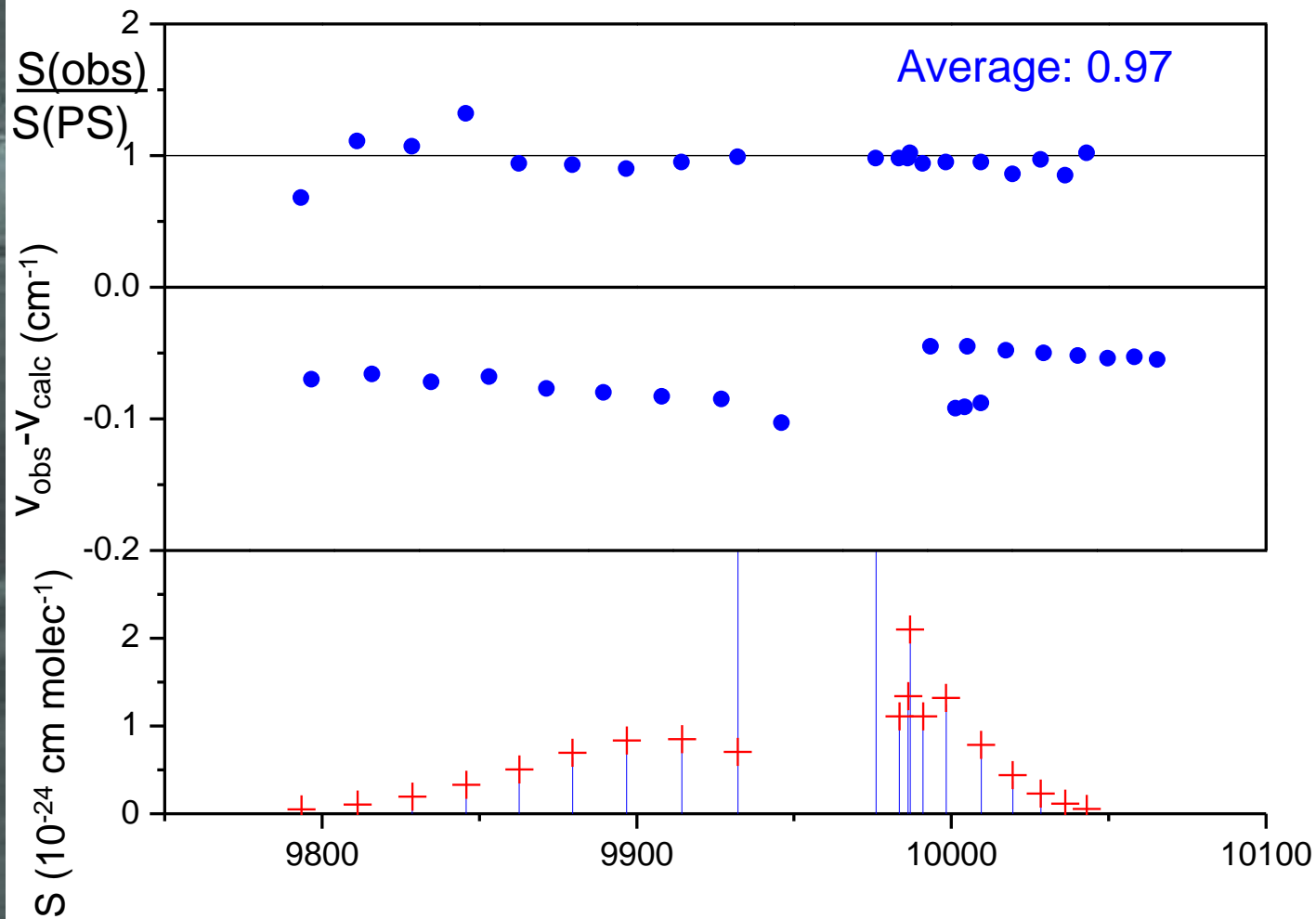
# Example of a subband:

$$\nu_1 + 2 \nu_3$$
$$\Delta K_a = 0 \quad K''_a = 0$$



# Example II of a subband:

$$\nu_1 + 2 \nu_3$$
$$\Delta K_a = 1 \quad K''_a = 0, \quad \Delta K_c = 1$$



# Global comments

- Entire spectral range → Better agreement between different spectral ranges.
- A lot of weak lines → Better atmospheric spectra simulation.
- Convergence of the theory towards the experimental needs.
- The discrete bands can now be taken off to study the underlying continuum.
- A lot of unresolved blended lines
- Water vapor pressure measurement still difficult.
- Longer absorption paths needed to compare to atmospheric horizontal (10 - 20 km) measurement at sea level !



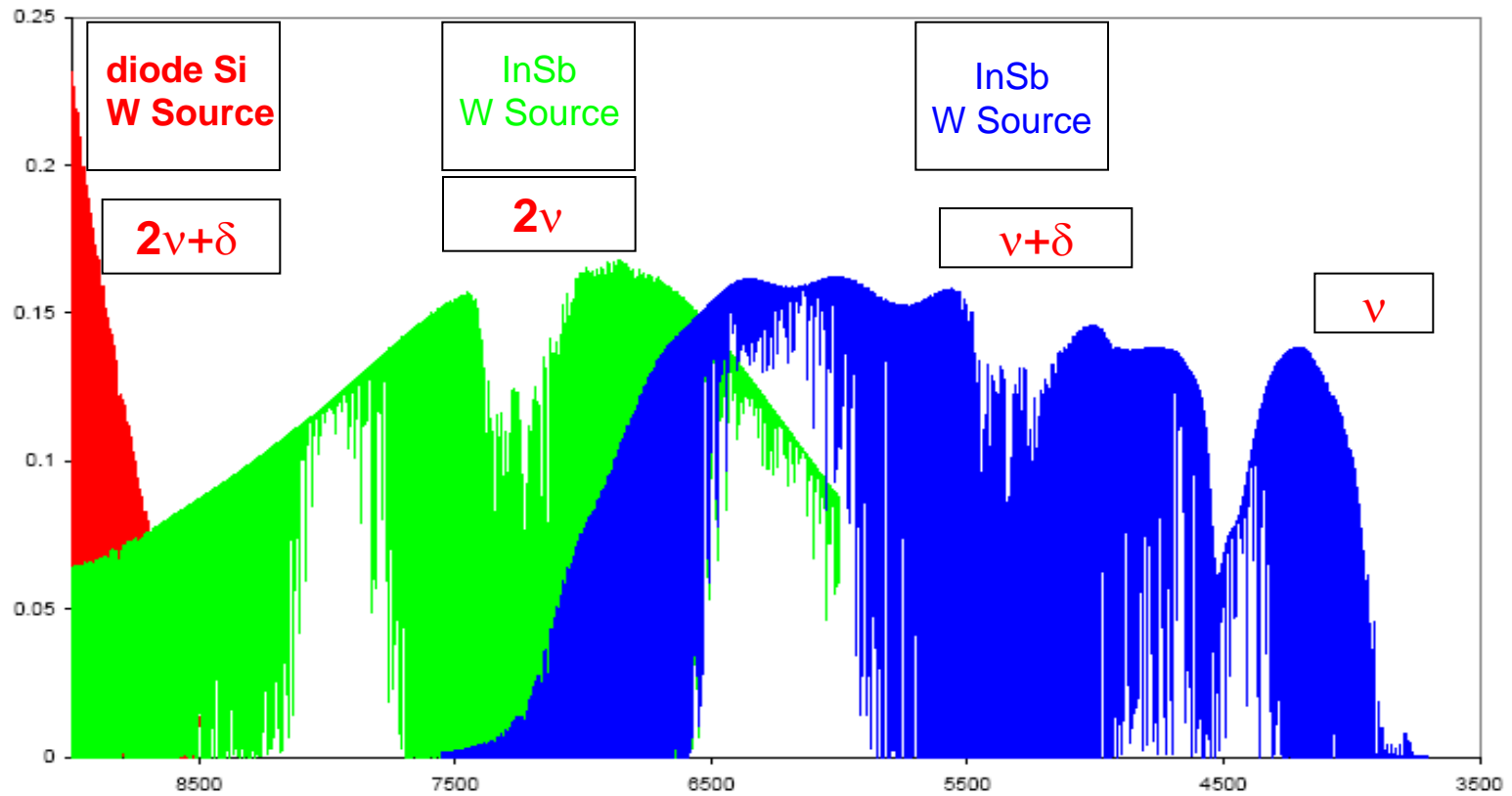
# Available linelists and intensities

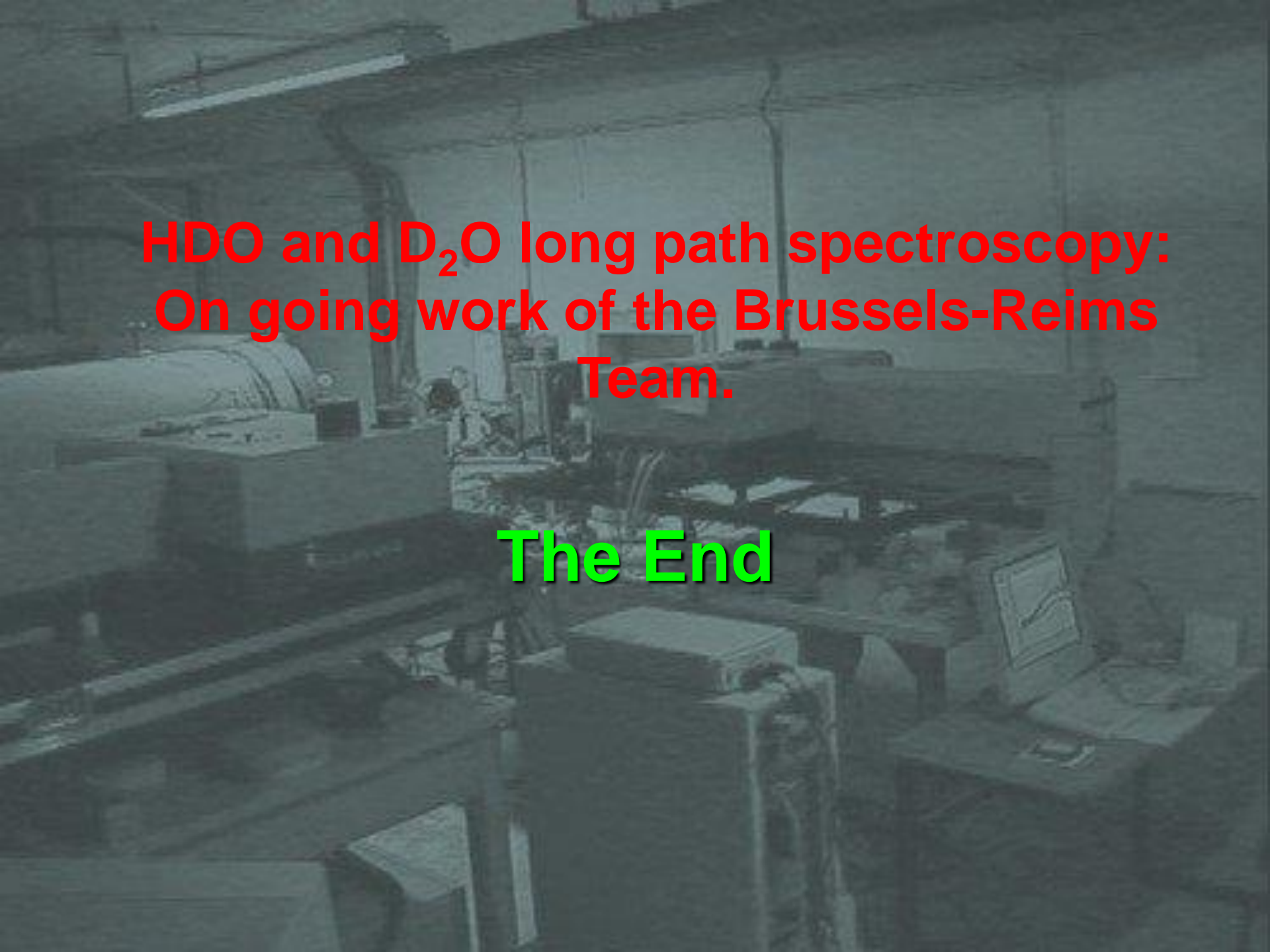
- **web site from ULB**
  - <http://www.ulb.ac.be/cpm/datafiles.html>
- **HITRAN 2004**
  - <http://cfa-www.harvard.edu/HITRAN>
- **GEISA 2003**
  - <http://ara.lmd.polytechnique.fr>

## Continuing work

- **IUPAC**
  - Water vapor database constitution for all the isotopologues (experience and theory)
- **HOD- D<sub>2</sub>O**
  - Measures down to 4200 cm<sup>-1</sup> (spectra being processed)
- **H<sub>2</sub>O**
  - Analysis of the IR spectra (6600 – 8800 cm<sup>-1</sup>)
- **H<sub>2</sub><sup>18</sup>O**
  - .....

# IR Absorption spectra



A dimly lit laboratory with various scientific instruments and equipment. The room contains several workbenches, a large cylindrical tank on the left, and a computer workstation on the right. The overall atmosphere is that of a busy research facility.

**HDO and D<sub>2</sub>O long path spectroscopy:  
On going work of the Brussels-Reims  
Team.**

**The End**