



HDO and D₂O long path spectroscopy: Ongoing work of the Brussels-Reims Team.

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UMR CNRS 6089

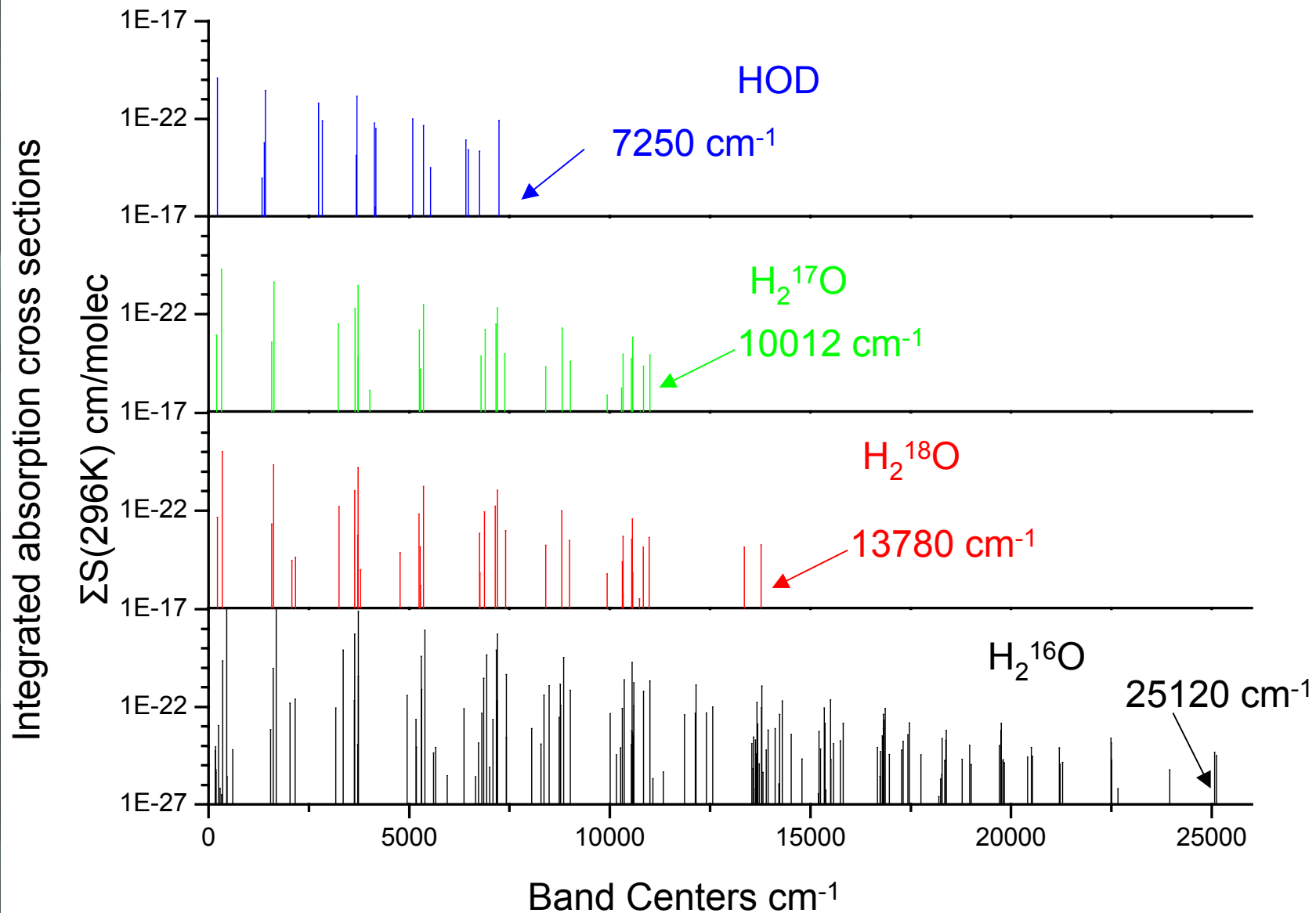
Université de Reims Champagne Ardenne

Reims, France

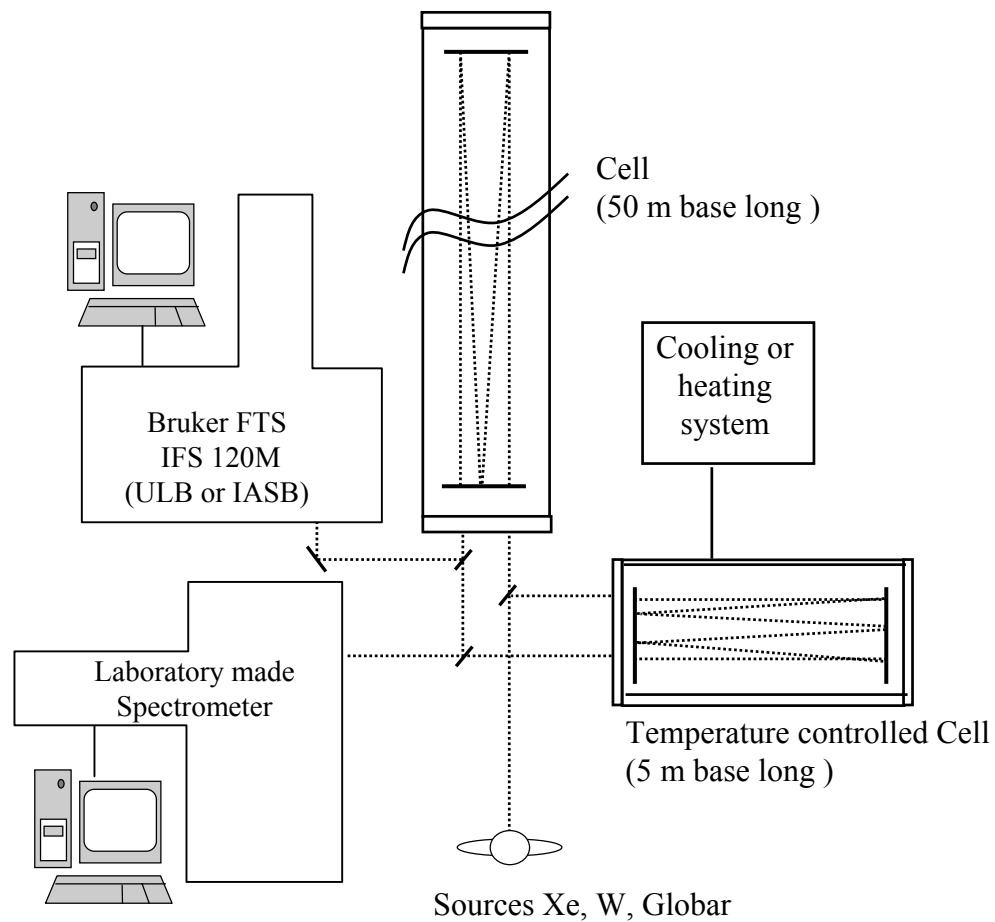
Workgroup involved in water vapor absorption measurements

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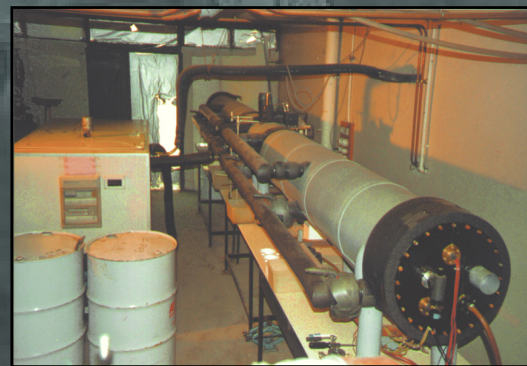
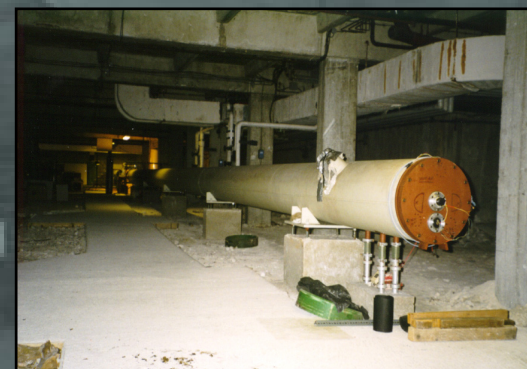
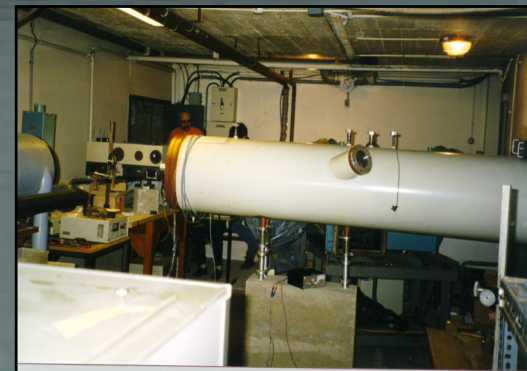
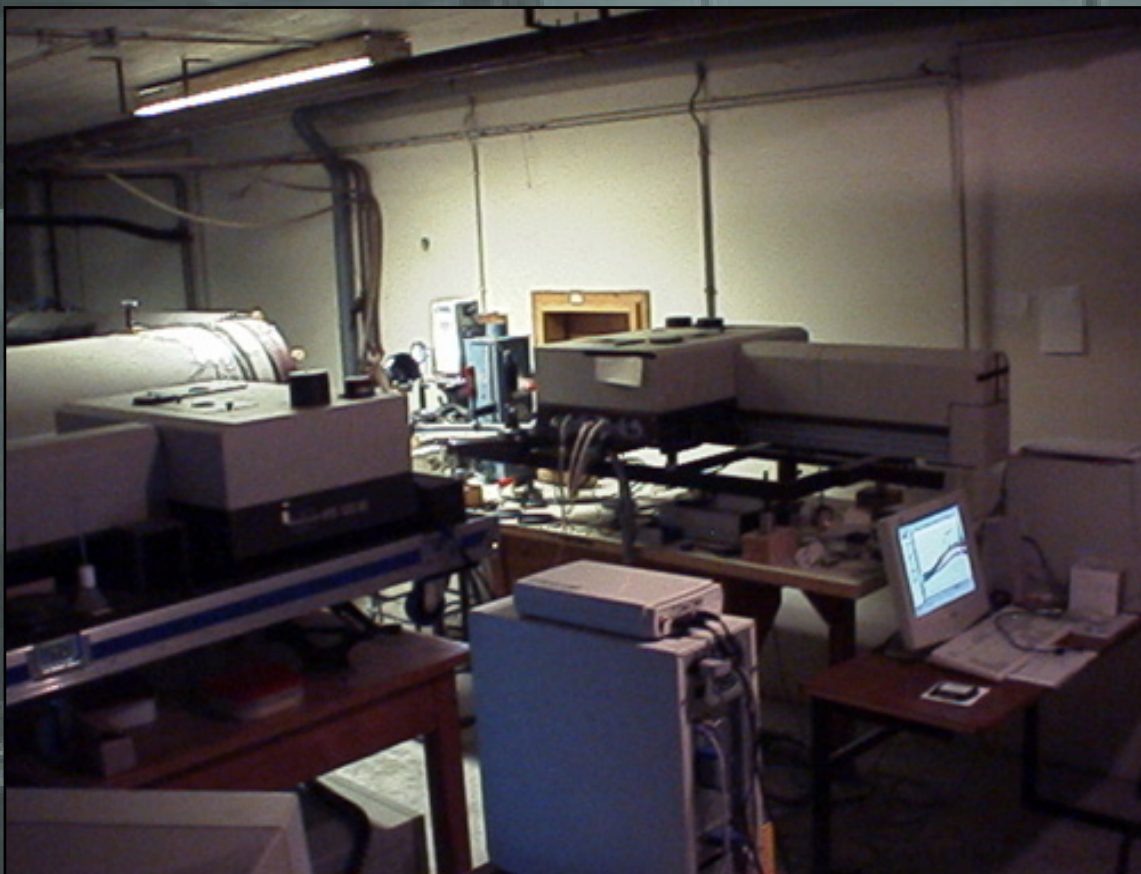
HITRAN 2004



Experimental setup



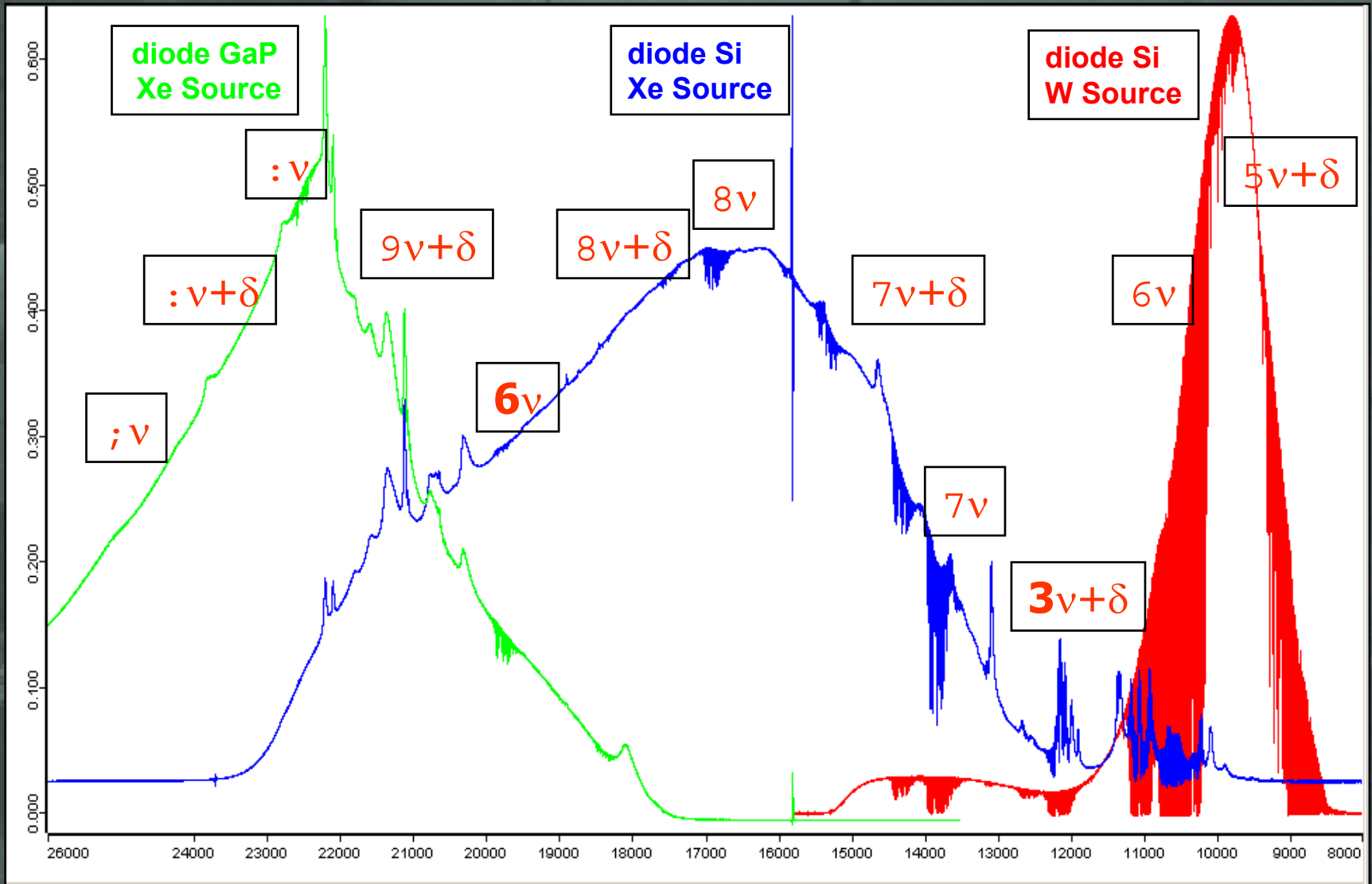
Experimental setup



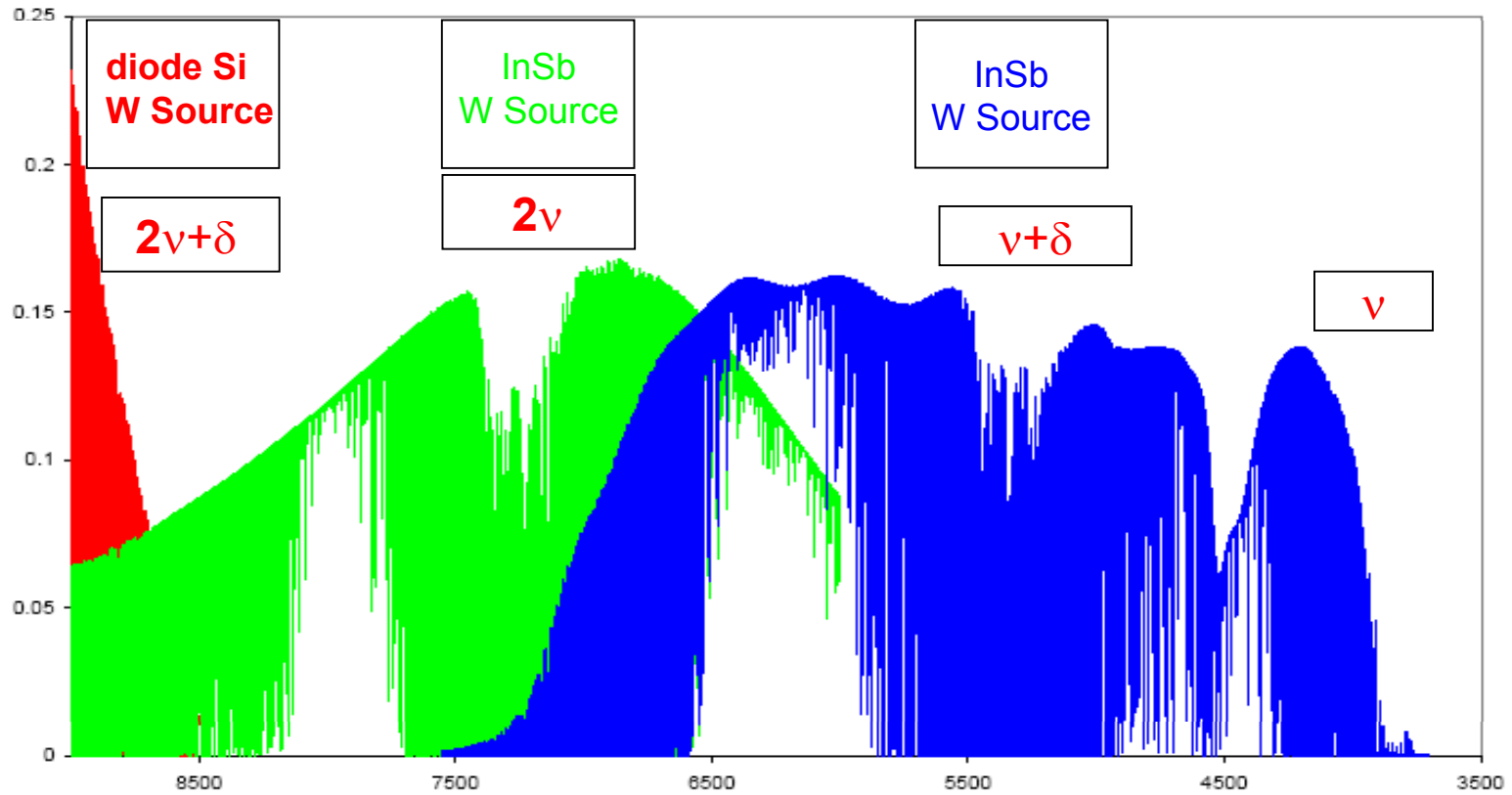
experimental conditions for HDO – D₂O spectra

- Absorption path: 600 m
- Resolution: down to 0.03 cm^{-1} (30 cm MOPD)
- Spectral range: 8800 - 10200 cm^{-1}
- H₂O + D₂O mixtures ($P_{\text{tot}} \sim 10 \text{ hPa}$)
- Room temperature: $T \sim 293 \text{ K}$
- Wavenumber calibration: I₂ (table of Gesternkorn)

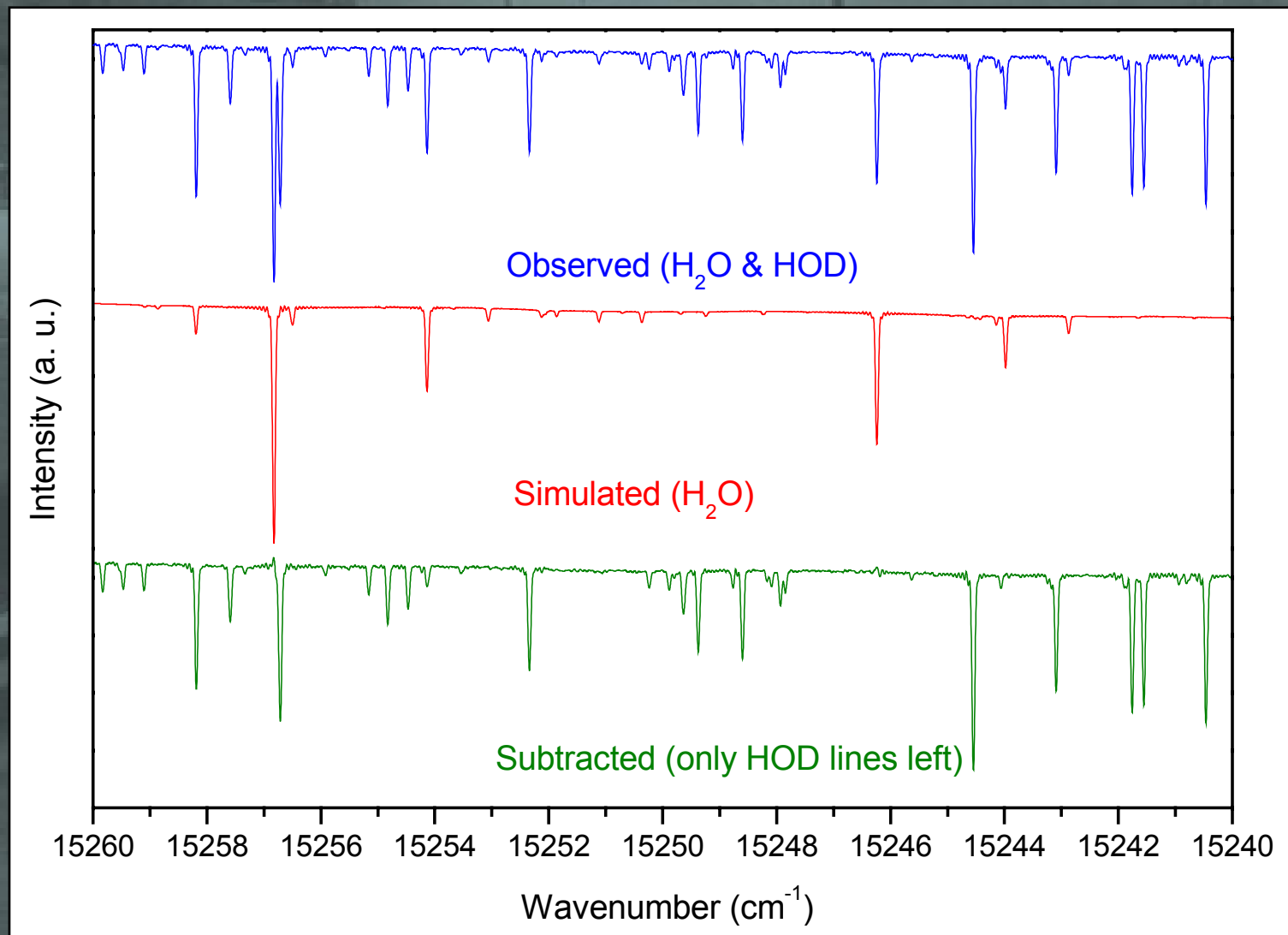
Vis-NIR water absorption spectra



IR Absorption spectra



Vis-NIR spectral range: Subtraction of the H₂O lines

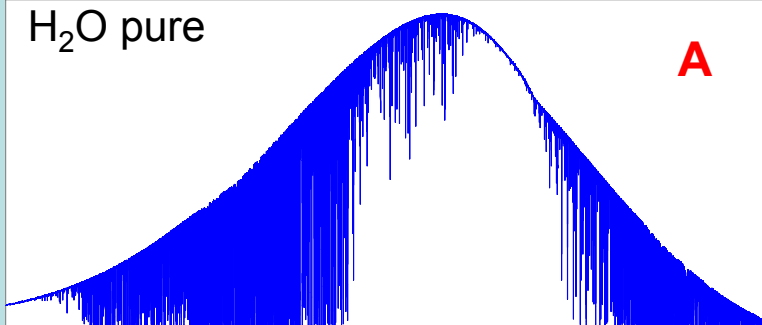


NIR spectral range:

H₂O, HDO and D₂O

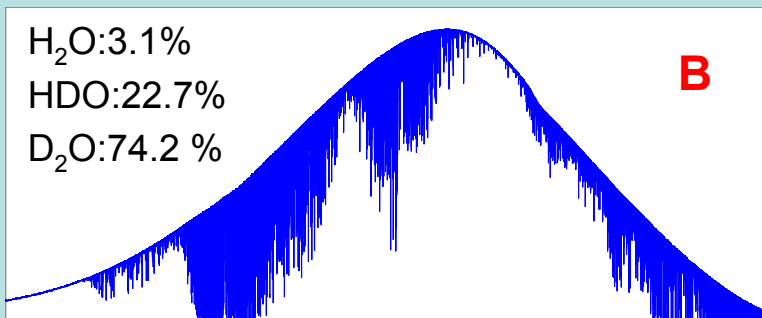
H₂O pure

A



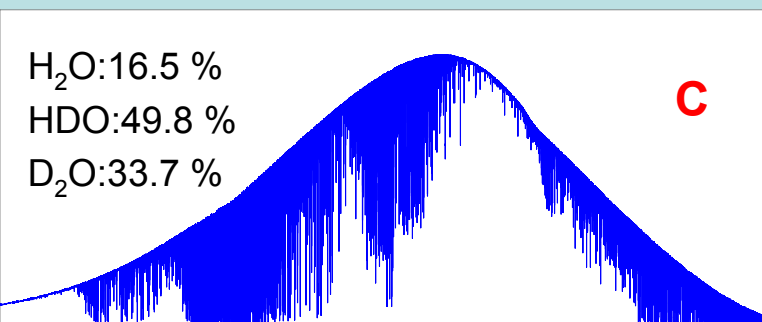
H₂O:3.1%
HDO:22.7%
D₂O:74.2 %

B



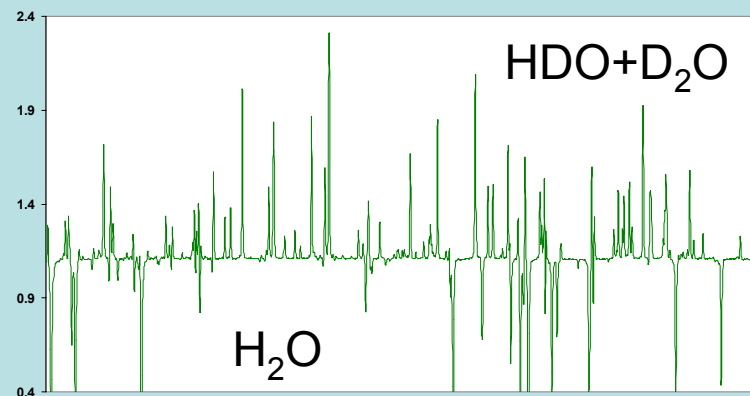
H₂O:16.5 %
HDO:49.8 %
D₂O:33.7 %

C

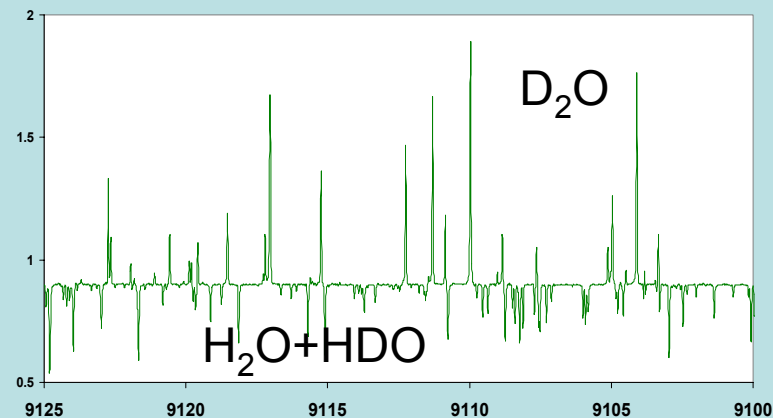


Path: 600 m, P: 13 hPa, Resol.: 0.03 cm⁻¹

A / C



C / B



11500 11000 10500 10000 9500 9000 8500

Partial pressures: IR region

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

• Use of BR list for $H_2^{16}O$ partial pressures (from natural H_2O spectra)

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

• Isotopologue assignment => Spectra Ratios

• Line surface measurements => with the good molar mass

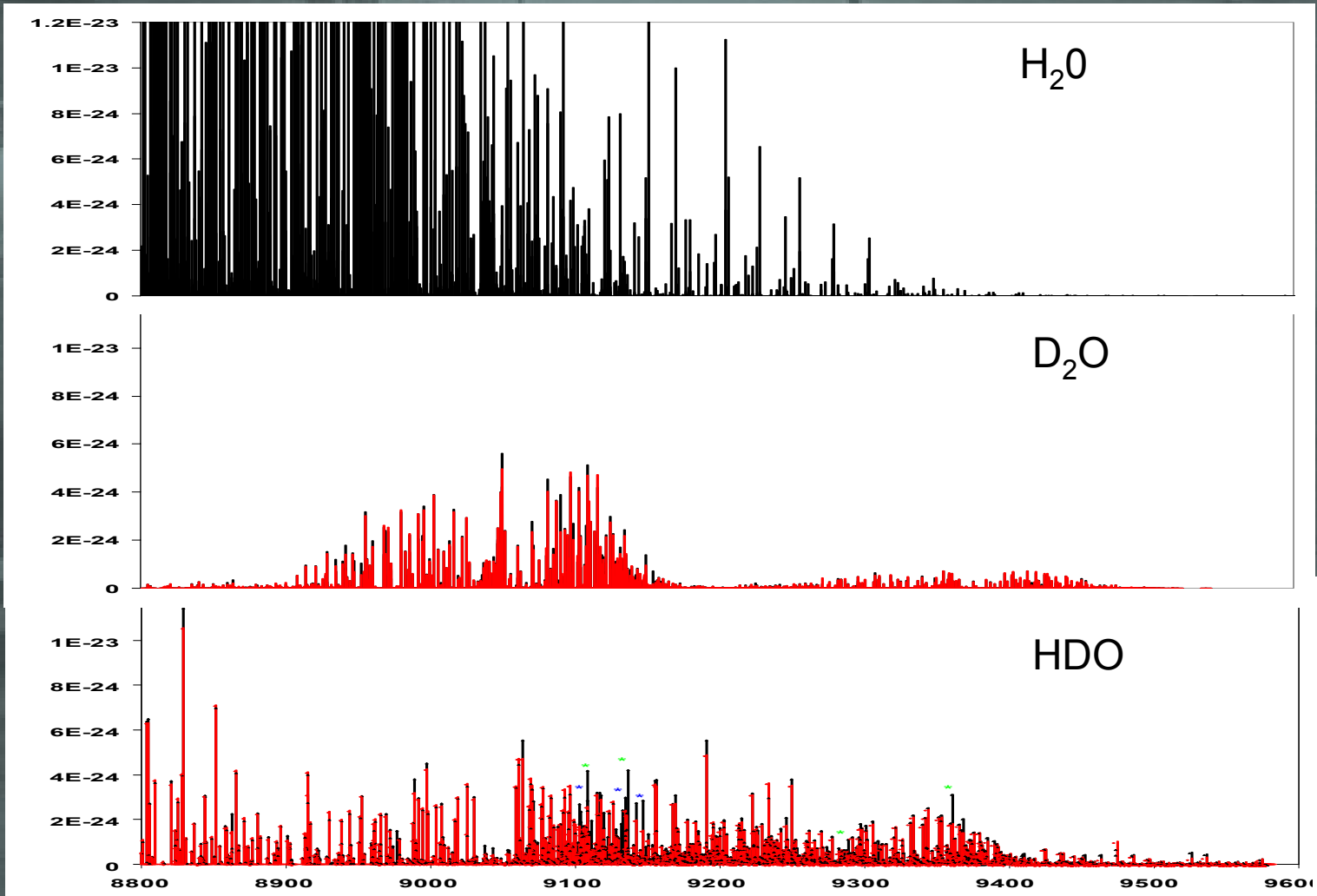
• Determination of the mean Surface ratios for HDO and D_2O

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

• Calculation of partial pressures and line intensities

IR region:

H₂O, D₂O 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 cm^{-1})

In the present work

HDO 8800-10200 cm^{-1} region:

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

5200 assignments

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

D₂O: 8800- 13200 cm^{-1} region:

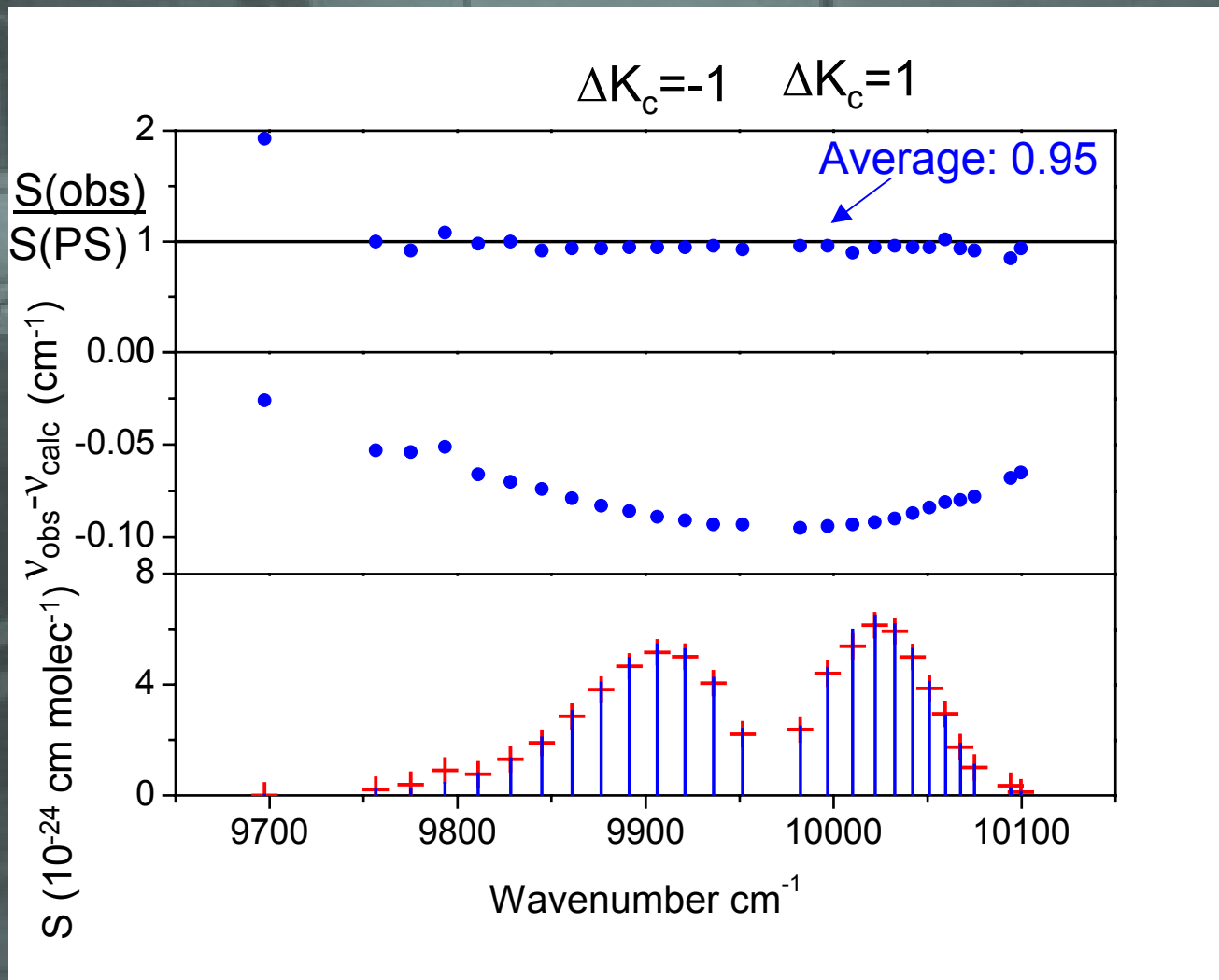
2160 observed lines mainly from $3\nu+\delta$, 4ν , $4\nu+\delta$ and 5ν polyads

2596 assignments

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

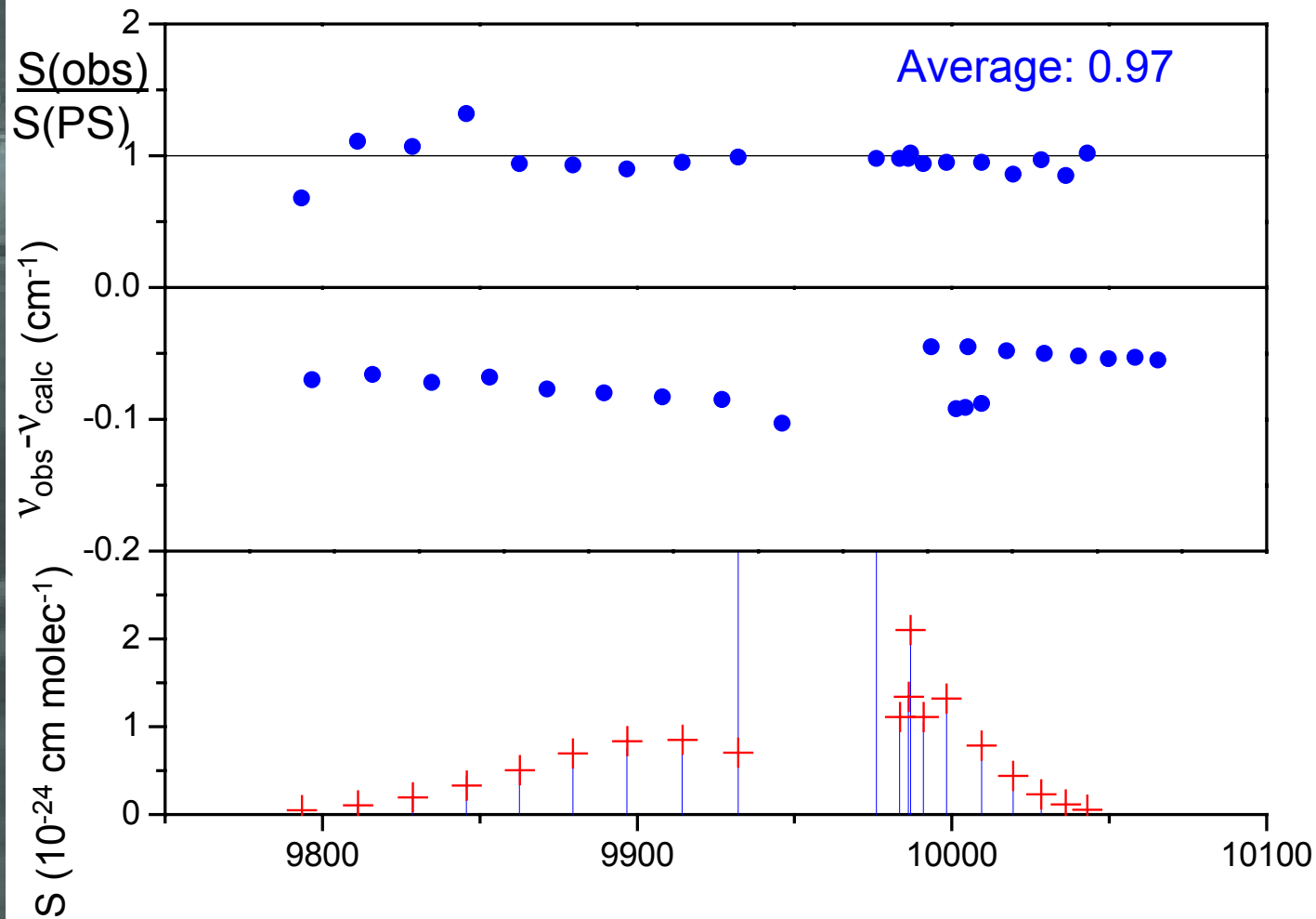
Example of a subband:

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



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 !

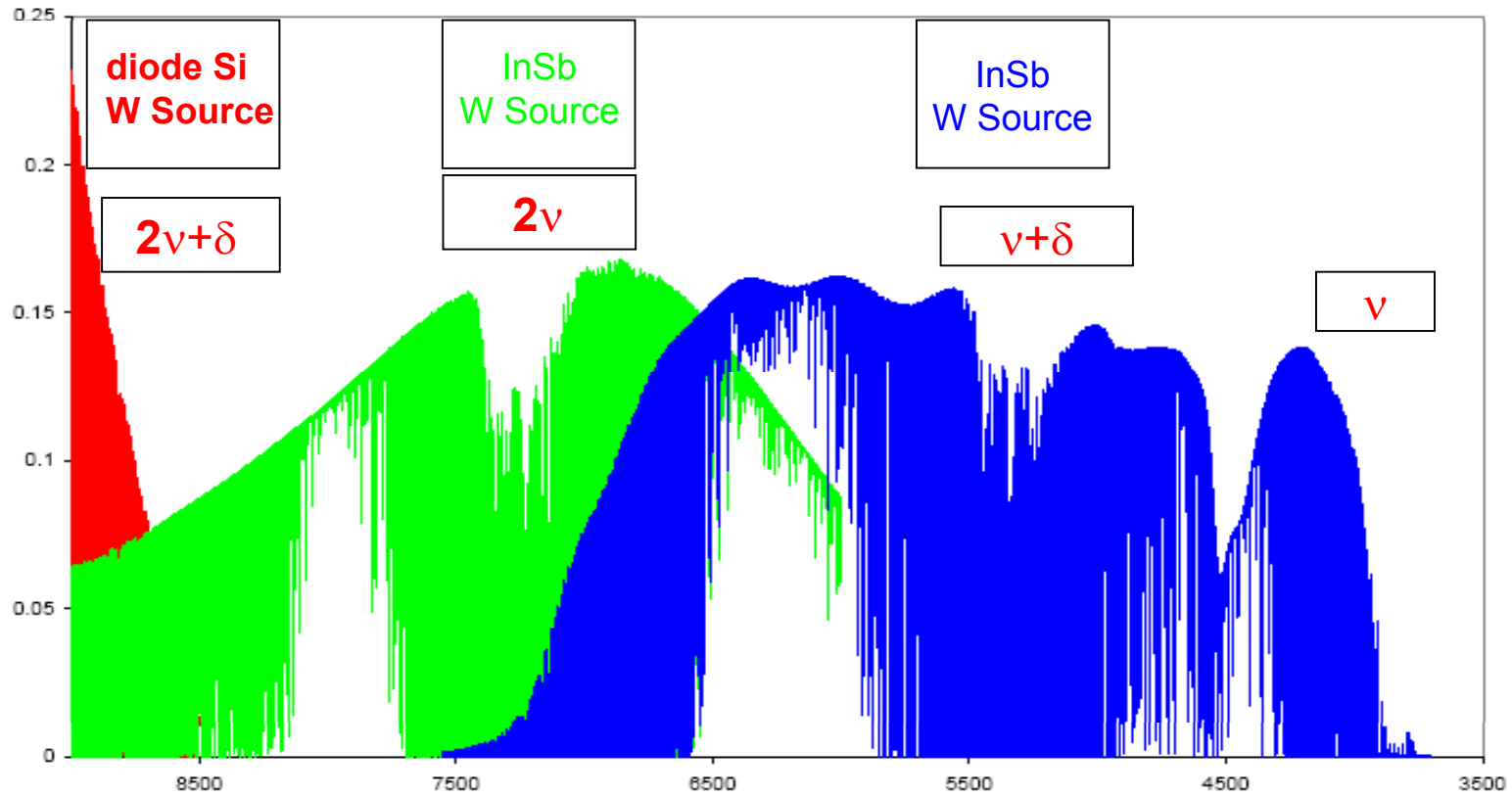
Available linelists and intensities

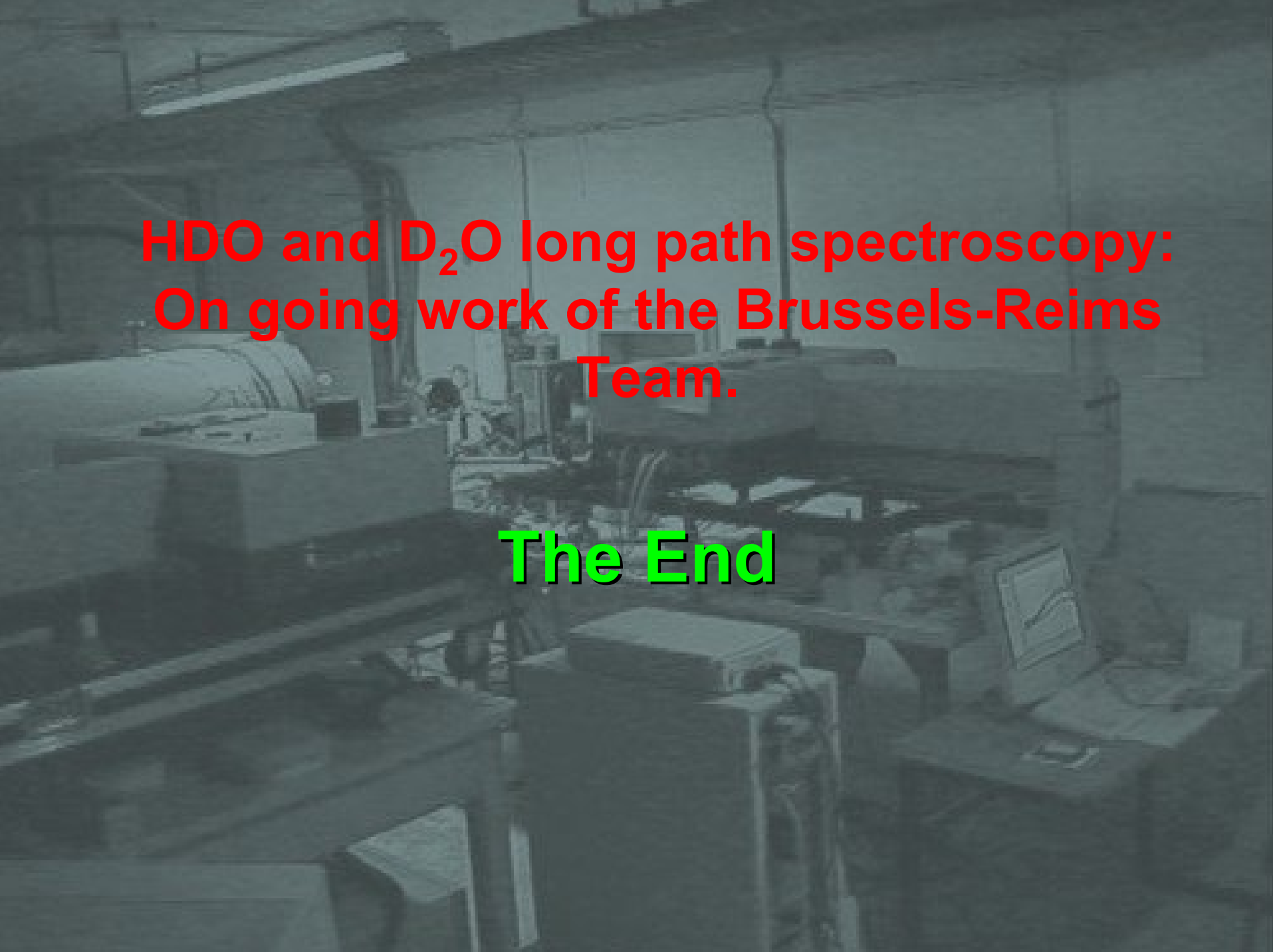
- **web site from ULB**
 - <http://www.ulb.ac.be/cpm/datafiles.html>
- **HITRAN 2004**
 - <http://cfa-www.harvard.edu/HITRAN>
- **GEISA 2003**
 - <http://ara.lmd.polytechnique.fr>

Continuing work

- **IUPAC**
 - Water vapor database constitution for all the isotopologues (experience and theory)
- **HOD- D₂O**
 - Measures down to 4200 cm⁻¹ (spectra being processed)
- **H₂O**
 - Analysis of the IR spectra (6600 – 8800 cm⁻¹)
- **H₂¹⁸O**
 -

IR Absorption spectra



A dimly lit laboratory with various scientific instruments and equipment. The room contains several large pieces of machinery, including what appears to be a spectrometer or similar analytical instrument. There are desks with computers and other smaller devices scattered throughout the space. The overall atmosphere is that of a busy research facility.

**HDO and D₂O long path spectroscopy:
On going work of the Brussels-Reims
Team.**

The End