A2

# Diode laser spectroscopy of water isotopomers in near IR


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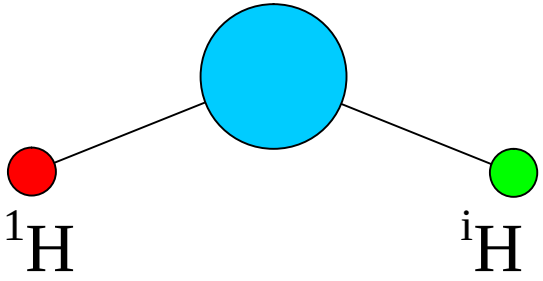
# Introduction

$H_2O$ spectra were investigated recently with very high sensitivity [1], while HDO spectra were obtained only for natural abundance. For HTO there are only 4 papers [2-5]. Experimental spectra of $v_2$ [2] and $v_1$ [4] bands and their theoretical analysis [4, 5]. Up to authors knowledge there is no information about $v_3$ band. Paper [3] is related to trace HTO detection.


References:
[1] R.Toth, Linelists of water vapor parameters from 500 to 8000 cm-1, ttp://mark4sun.jpl.nasa.gov
[2] P. P. Cherrier, P. H. Beckwith and J. Reid, Linewidths and linestrengths in the v2 band of HTO as measured with a tunable diode laser, *JMS, 121, 69-74 (1987)*
[3] Pierre P. Cherrier and John Reid, High-sensitivity detection of tritiated water vapour using tunable diode lasers, Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, Volume 257, 412-416 (1987)
[4] S. D. Cope, D. K. Russell, H. A. Fry, L. H. Jones and J. E. Barefield, Analysis of the $v_1$ fundamental mode of HTO, JMS, 127, 464-471 (1988)
[5] O. N. Ulenikov, V. N. Cherepanov and A. B. Malikova, On analysis of the $v_2$ band of the HTO molecule, JMS, 146, 97-103 (1991)

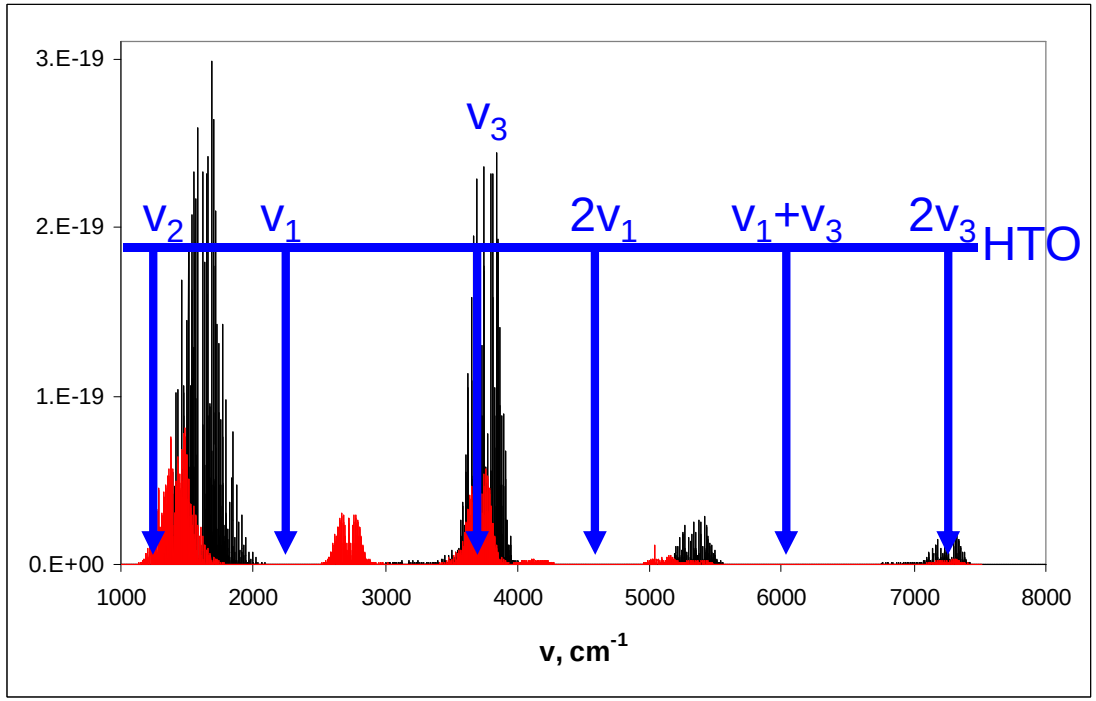
# Water molecule vibration modes



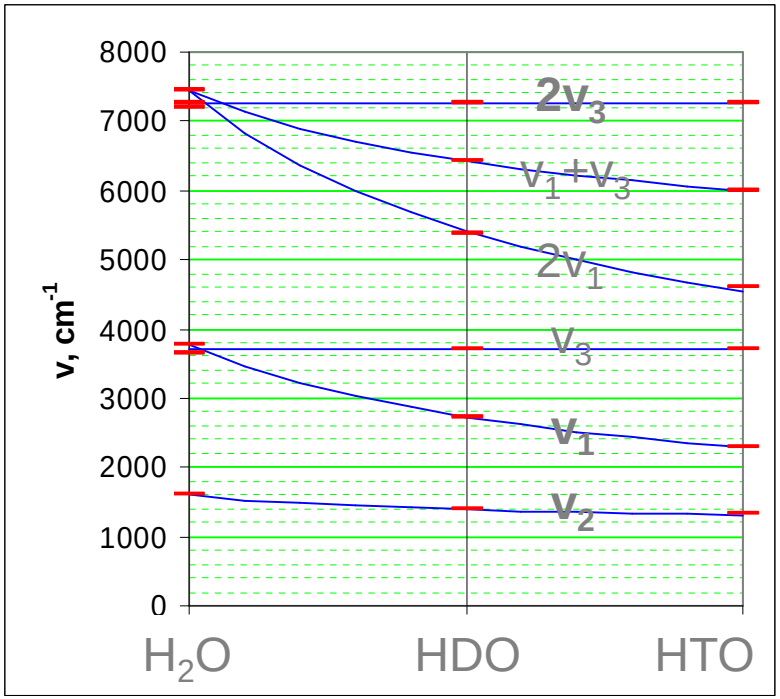

$^{1}$H = H

$^{2}$H = D

$^{3}$H = T




Spectra of $H_2O$ (black) and HDO (red).



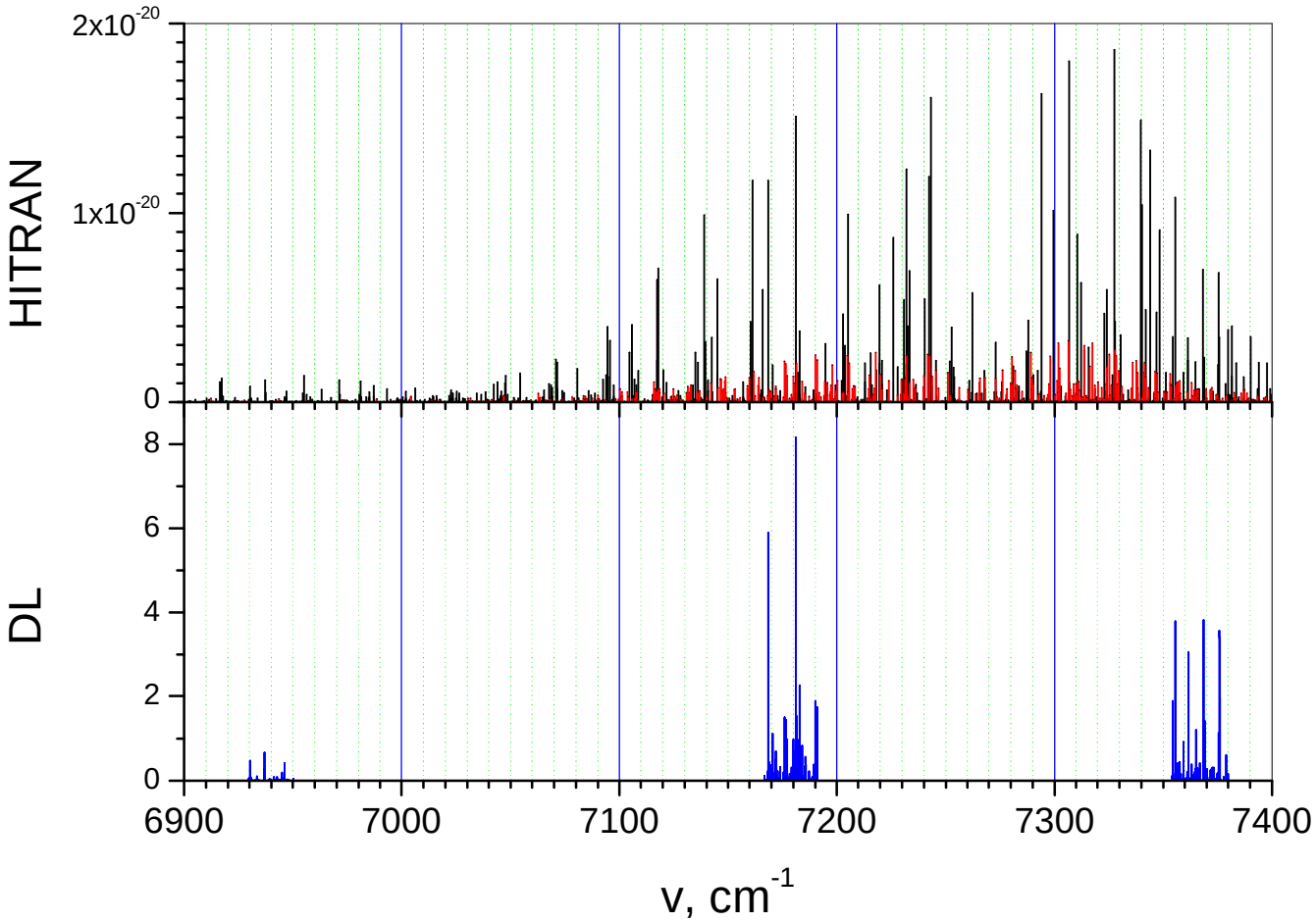

Isotope shifts of water vapour bands ($H_2O$, HDO, HTO).

$v_1$ – (O)-($^{i}$H) stretching vibration

$v_2$ – bending vibration

$v_3$ – (O)-(H) stretching vibration

# $2v_3$ water spectra




HITRAN spectra of $H_2O$ (black) and HDO (red)

Water samples spectra were recorded using 3 Diode Lasers (blue) operated near 1.44, 1.39, and 1.36 μ

***Water vapor spectra near 1.39 m were analyzed and are presented in present paper.***

4 water samples were investigated

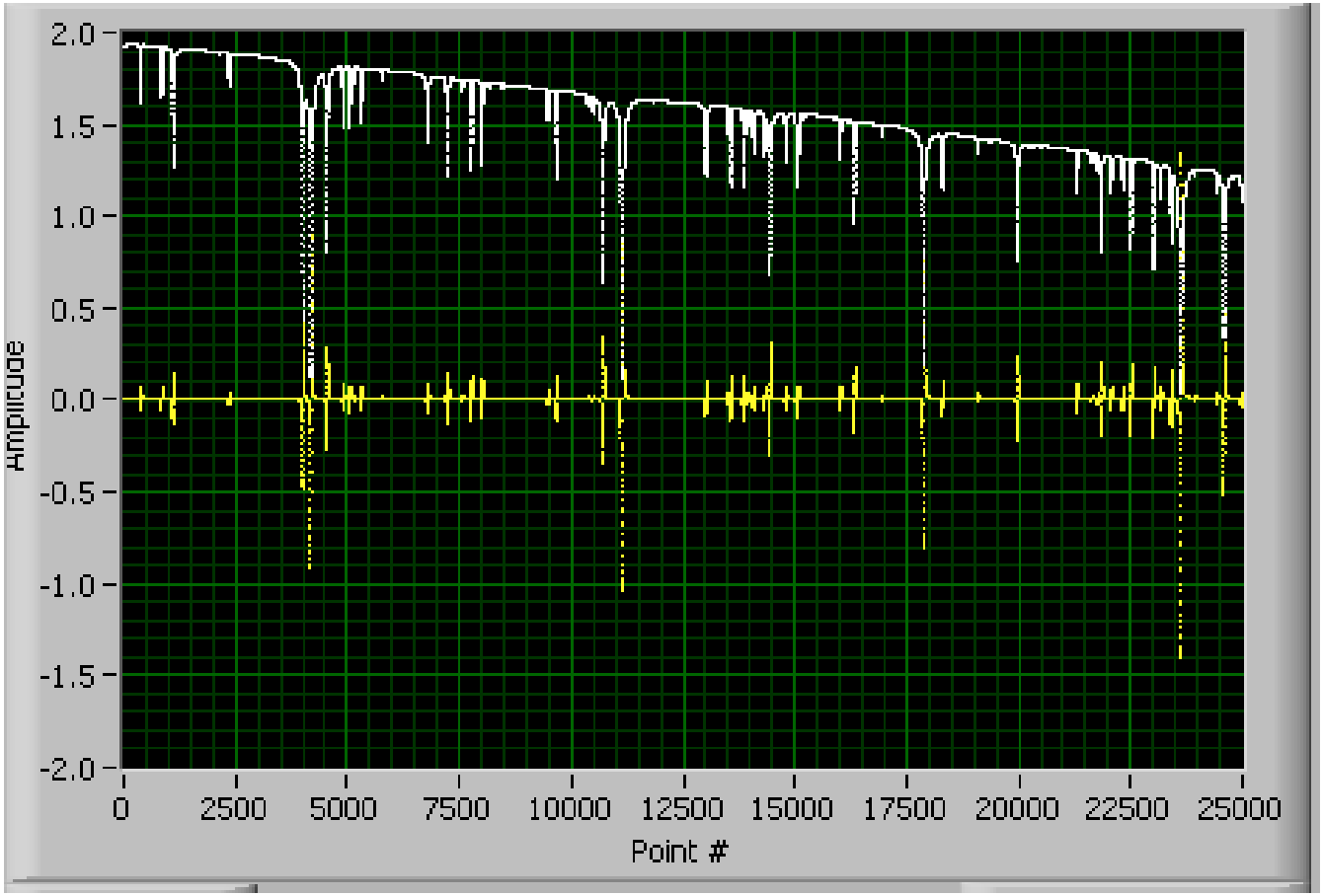
Table 1 Water samples

| Sample # | Origin | D:H |
|---|---|---|
| 1 | Natural water | 0.00016 |
| 2 | Heavy water | 10.5 |
| 3 | Heavy and natural water mixture | 0.87 |
| 4 | Mixture of heavy water from reactor and natural water | 0.51 |

Mixtures (3, 4) were prepared by adding natural water to heavy water under consideration. Liquid water samples before experiment kept in container for several weeks to have equilibrium isotopes distribution between water isotopomers.

Cell (2 m) was filled by vapor from sample container at pressure 5-10 mBar. During experiment attention was focused to reduce influence of memory effects.

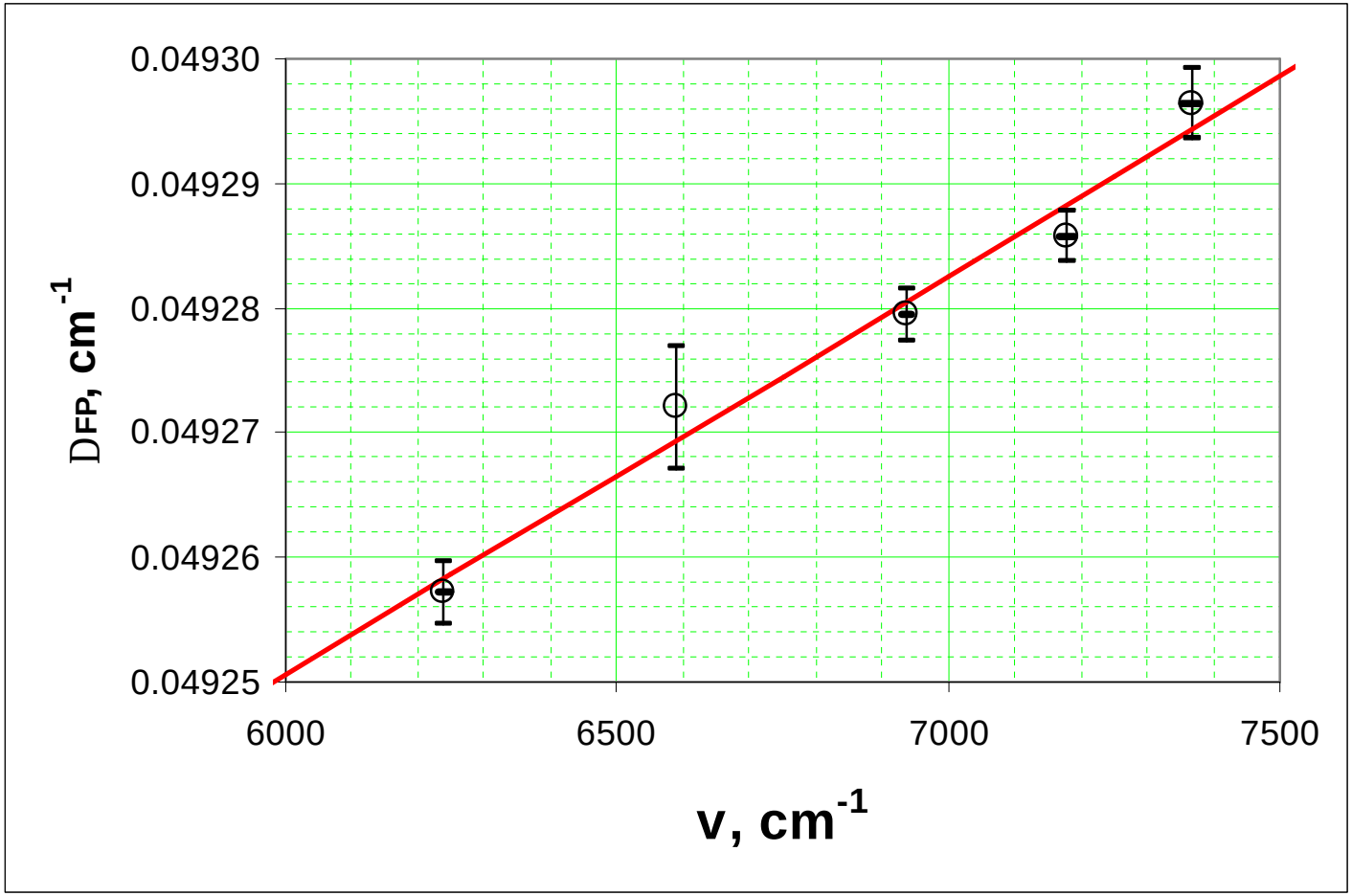
# Spectra recording




Spectra in broad spectral range were obtained by DL temperature slow changing.
DL temperature, DL intensity passed though cell (white), and its logarithmic derivative (yellow) were recorded. Time of recording was 15 min.

Frequency scale was determined using transmission of calibrated FP etalon with $\Delta\nu_{FP}$ = 0.049286(2) in this spectral range (see C11).

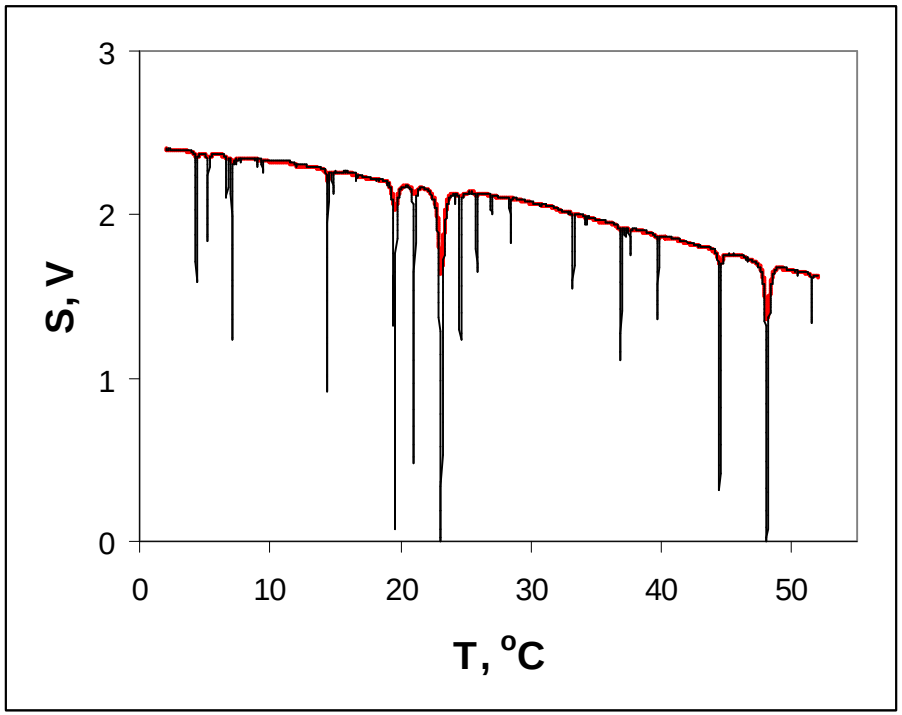
# FP etalon calibration

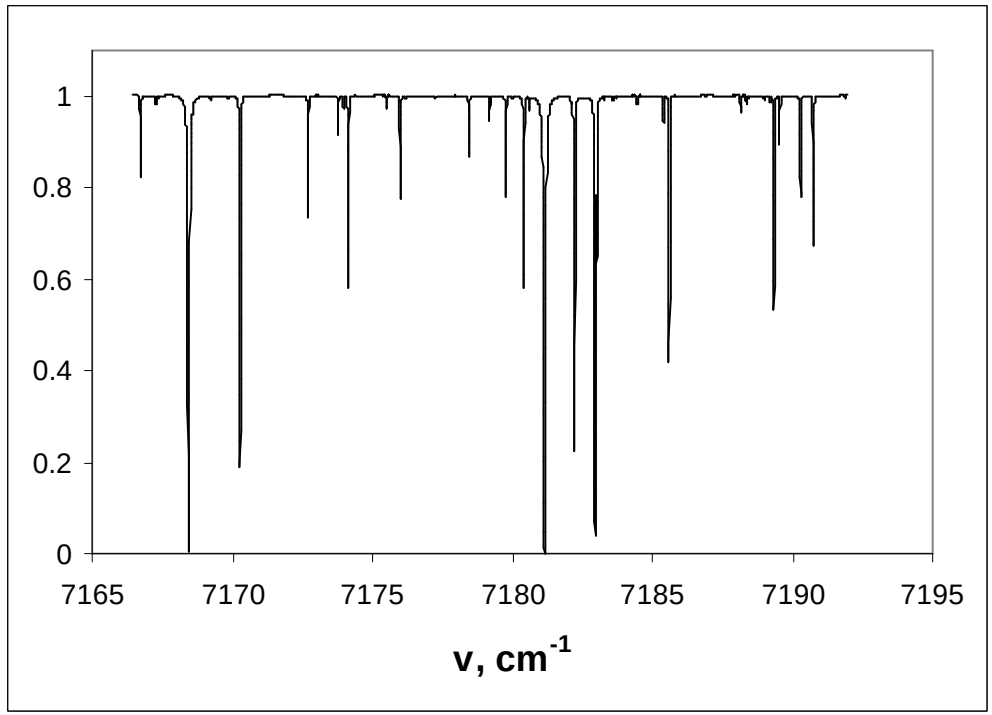



FP etalon in use was calibrated using different DLs and different molecules.

# Transmission

Recorded spectra as function of DL temperature for sample #1



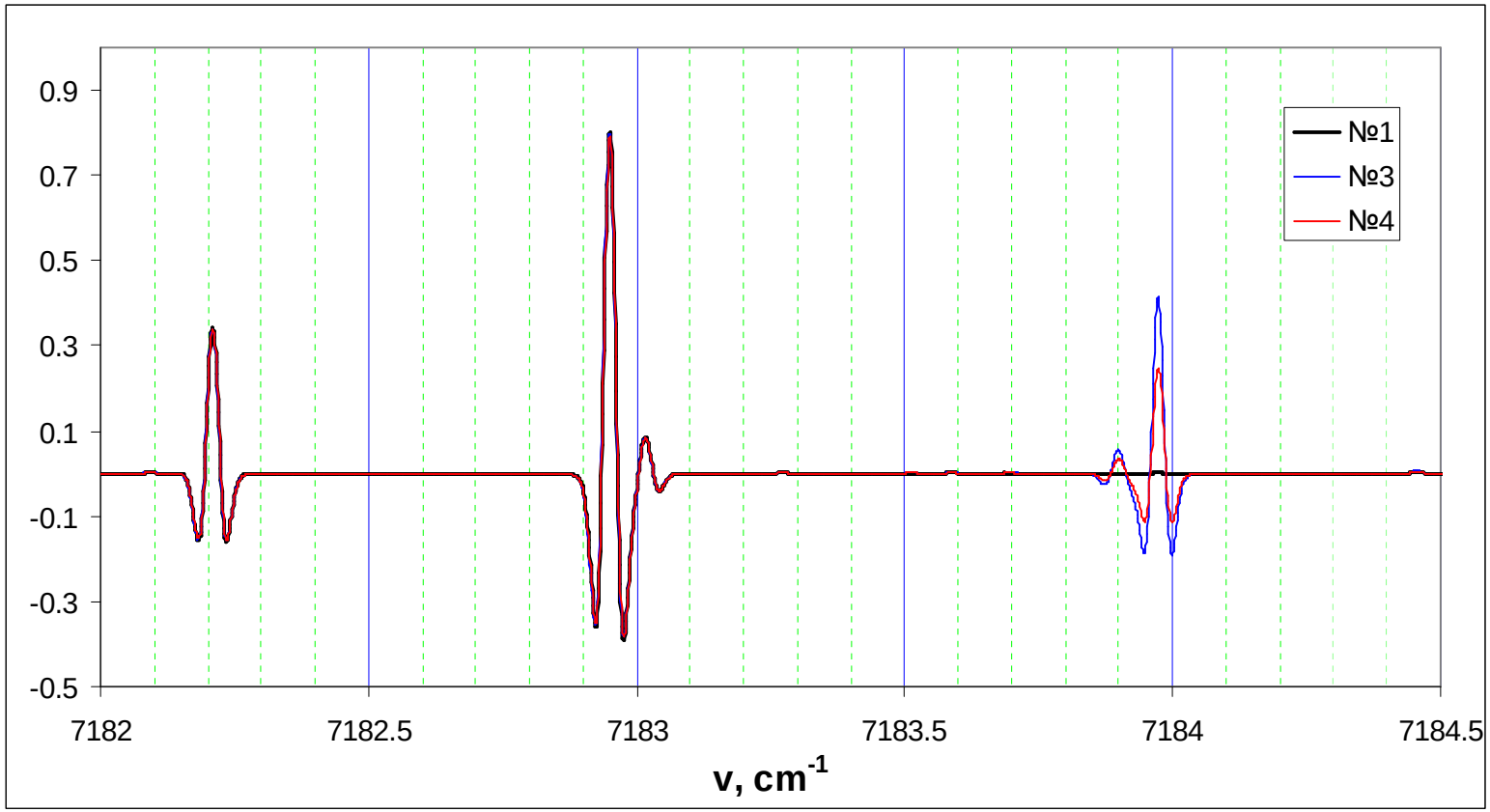




Recorded signal for empty cell (red) and cell filled with sample #1 (black) with broad atmosphere water absorption.

Transmission spectrum for sample #1. Similar empty cell subtraction procedure was used for signal logarithmic derivative.

# D:H ratio determination

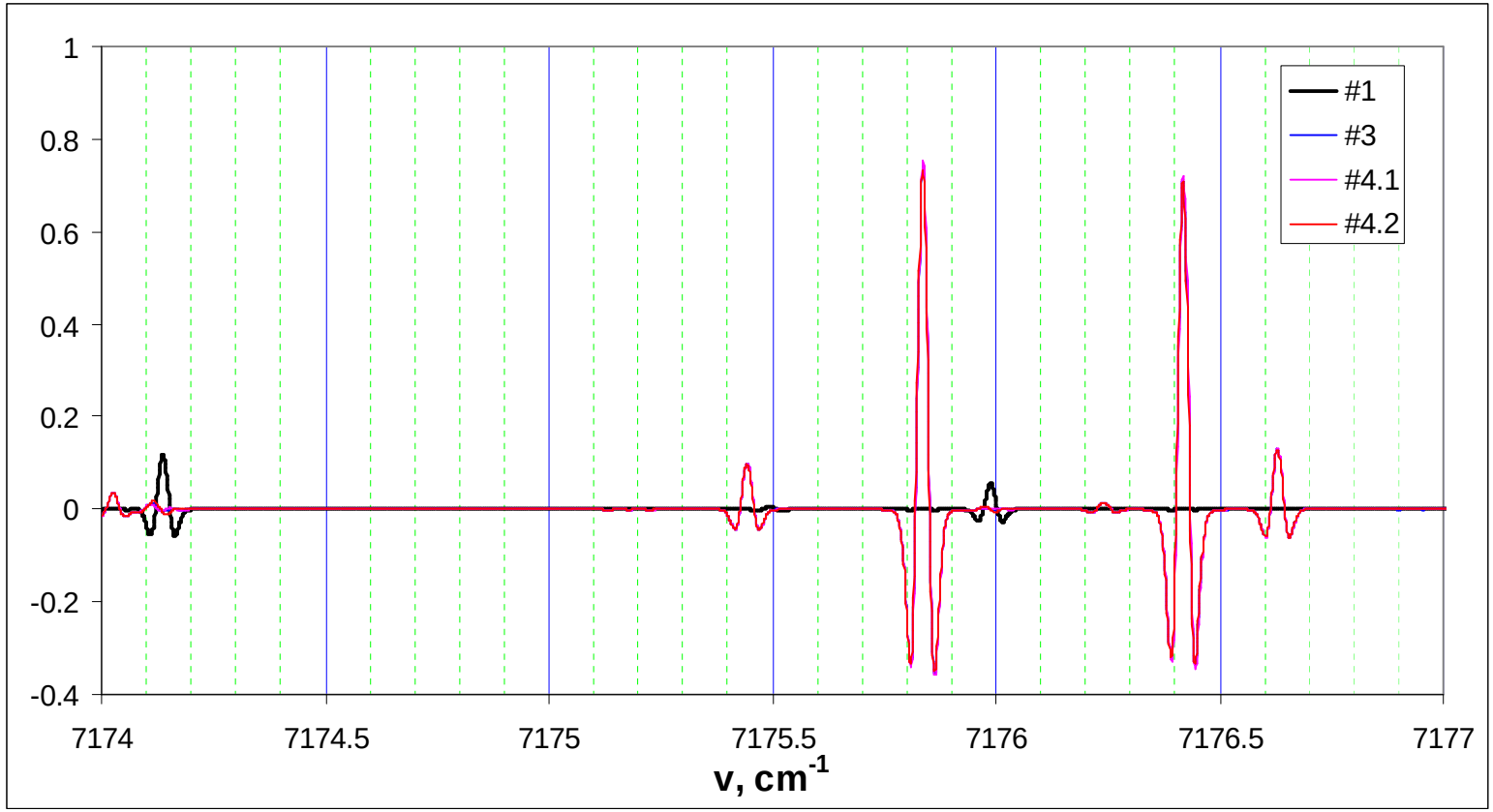
After filtering logarithmic derivative spectra looks like second derivative.




These spectra were normalized by one of water lines to have for them the same intensity. HDO line near 7184 $cm^{-1}$ was used to measure D:H ratio (HITRAN) presented in Tabl.1.

# Strong lines identification

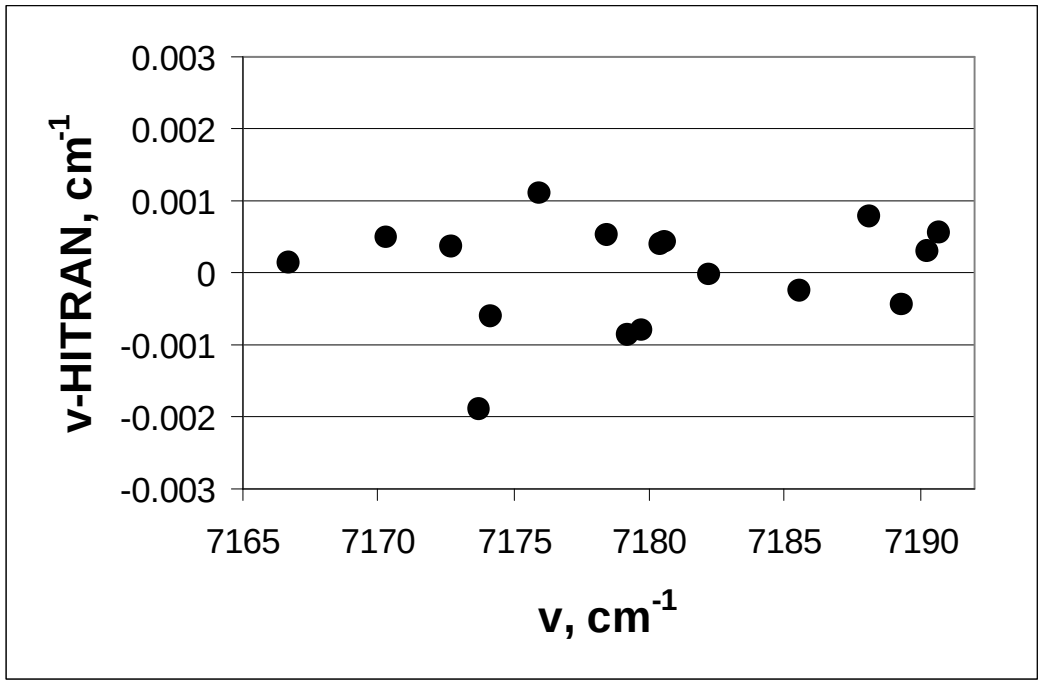
Finally sample #1 spectrum (black) was subtracted from others and they were normalized to HDO line considered above. H2O and HDO lines can be easily distinguished and identified.




Refer to HITRAN in spectral range under consideration there are 192 lines of $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and $HD^{16}O$. 103 of them having highest intensity (above sensitivity limit) were identified and measured.

# Comparison with HITRAN

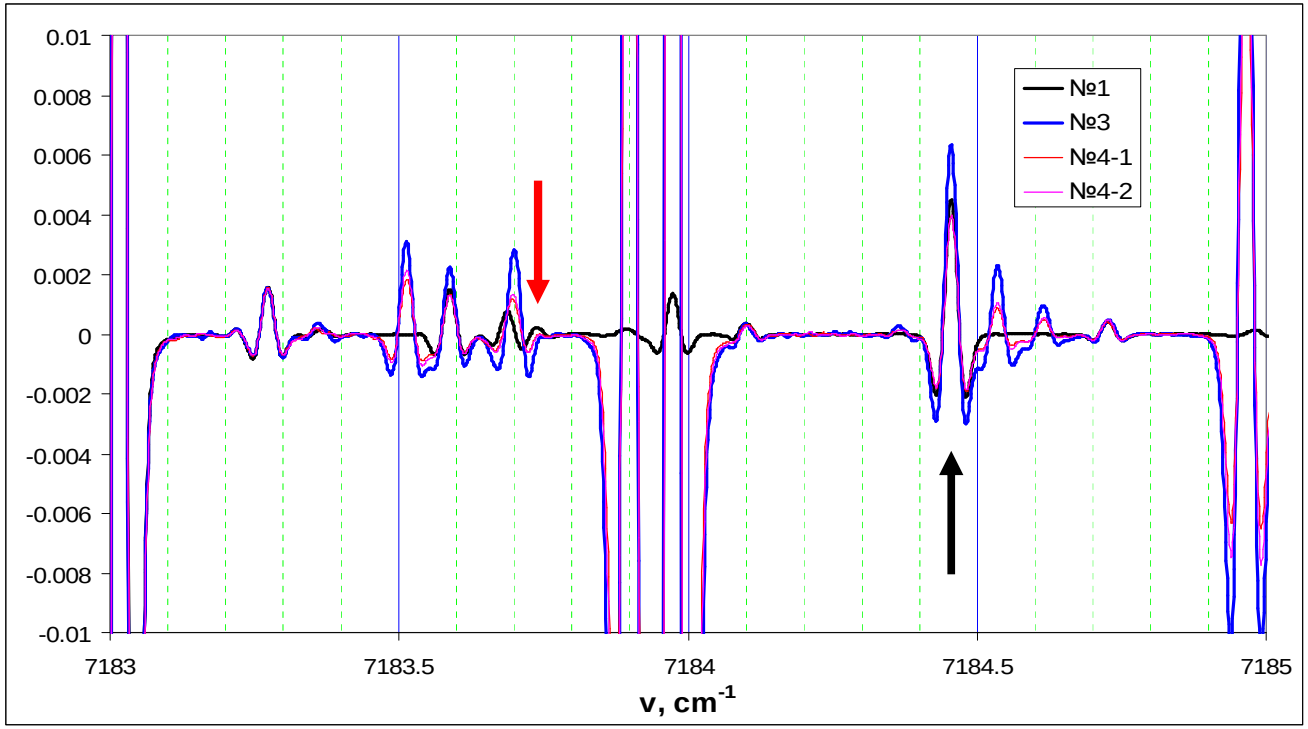
Several strong $H_2O$ lines were selected to compare results obtained with HITRAN spectral data base.




Difference between measured frequencies and HITRAN data. The difference std was found equal 0.00075 $cm^{-1}$ close to accuracy of DL frequency calibration in present case of broad spectral range recording. For weaker lines difference is several times higher and is related to HITRAN accuracy.

For spectral line intensity measurements broad spectral range recording approach is not the best solution. However, agreement between data obtained and with HITRAN was found within 20 %.

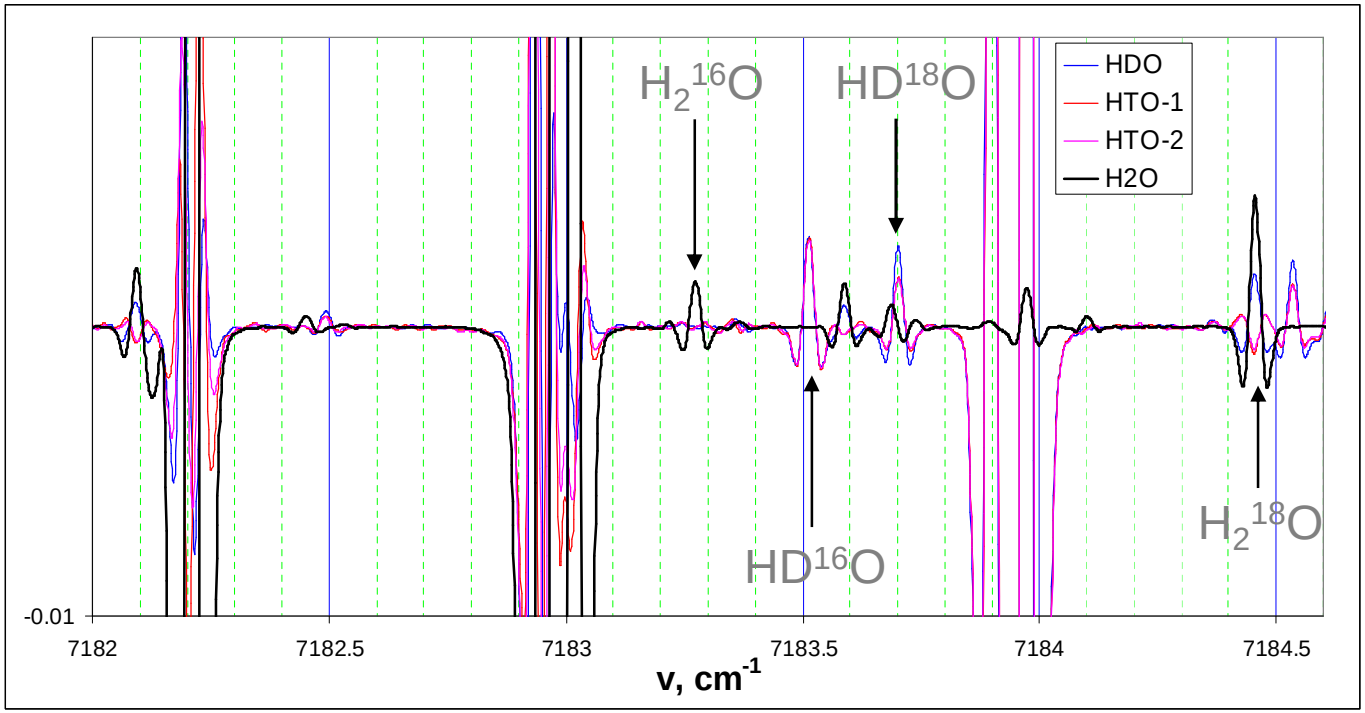
# Oxygen isotopes ratio measurement




Line labeled by black arrow belongs to $H_2{}^{18}O$. Using this line it was found that water samples under investigation have different $^{18}O$:$^{16}O$ ratios. Heavy water was enriched by $^{18}O$ with respect to normal water due to heavy isotope enrichment process. While heavy water from reactor was depleted eaven with respect to normal water because to nuclear reactions inside reactor.
We were not be able to do similar measurement for $H_2{}^{17}O$ (red arrow). Below we'll assume $^{17}O$ is between $^{16}O$ and $^{18}O$.

# Weak lines identification

Due to HITRAN, 38 lines here belongs to $HD^{16}O$, no information about other HDO isotopomers. With present sensitivity in spectral range under consideration 70 new HDO lines were observed and measured.




Example of HDO lines identification

Part of new lines was identified as $HD^{16}O$ (same intensity for all samples) and $HD^{18}O$ lines (ratio for sample #3 and #4 around 1.7). There were lines having ratio between 1 and 1.7. It can be related to present accuracy of our measurements or detection $HD^{17}O$ lines.

# Measured lines statistics

Number of water isotopomers spectral lines known at the moment and measured in present work.

| | $H_2{}^{16}O$ | $H_2{}^{18}O$ | $H_2{}^{17}O$ | $HD^{16}O$ | $HD^{18}O$ | No ID | Total |
|---|---|---|---|---|---|---|---|
| HITRAN | 100 | 32 | 25 | 35 | 0 | | 192 |
| Present work | 60 | 7 | 2 | 58 | 10 | 34 | 171 |
| New lines | 0 | 0 | 0 | 24 | 10 | 34 | 68 |

For $H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$ all lines presented in HITRAN and being above present sensitivity threshold were observed and measured with accuracy corresponding to HITRAN.
New 24 lines of $HD^{16}O$ were observed and measured.
New 10 lines of $HD^{18}O$ were observed and measured.
New 24 non identified HDO and 10 HTO(?) lines were observed and measured.