C2

TDLS SPECTROSCOPY OF WATER ISOTOPOMERS NEAR 1.39 μ

***A.Kuzmichev*[1]*, Ya.Ponurovskiy*[2]*, A.Nadezhdinskii*[2]**
***V.Khattatov*[3]**

[1] *Moscow Institute of Physics and Technology, Dolgoprudniy, Moscow Region, Russia;*
[2] *A.M.Prokhorov General Physics Institute of RAS, Vavilov str. 38, 119991 Moscow, Russia*
[3] *Central Aerological Observatory, Dolgoprudniy, Moscow region, Russia*

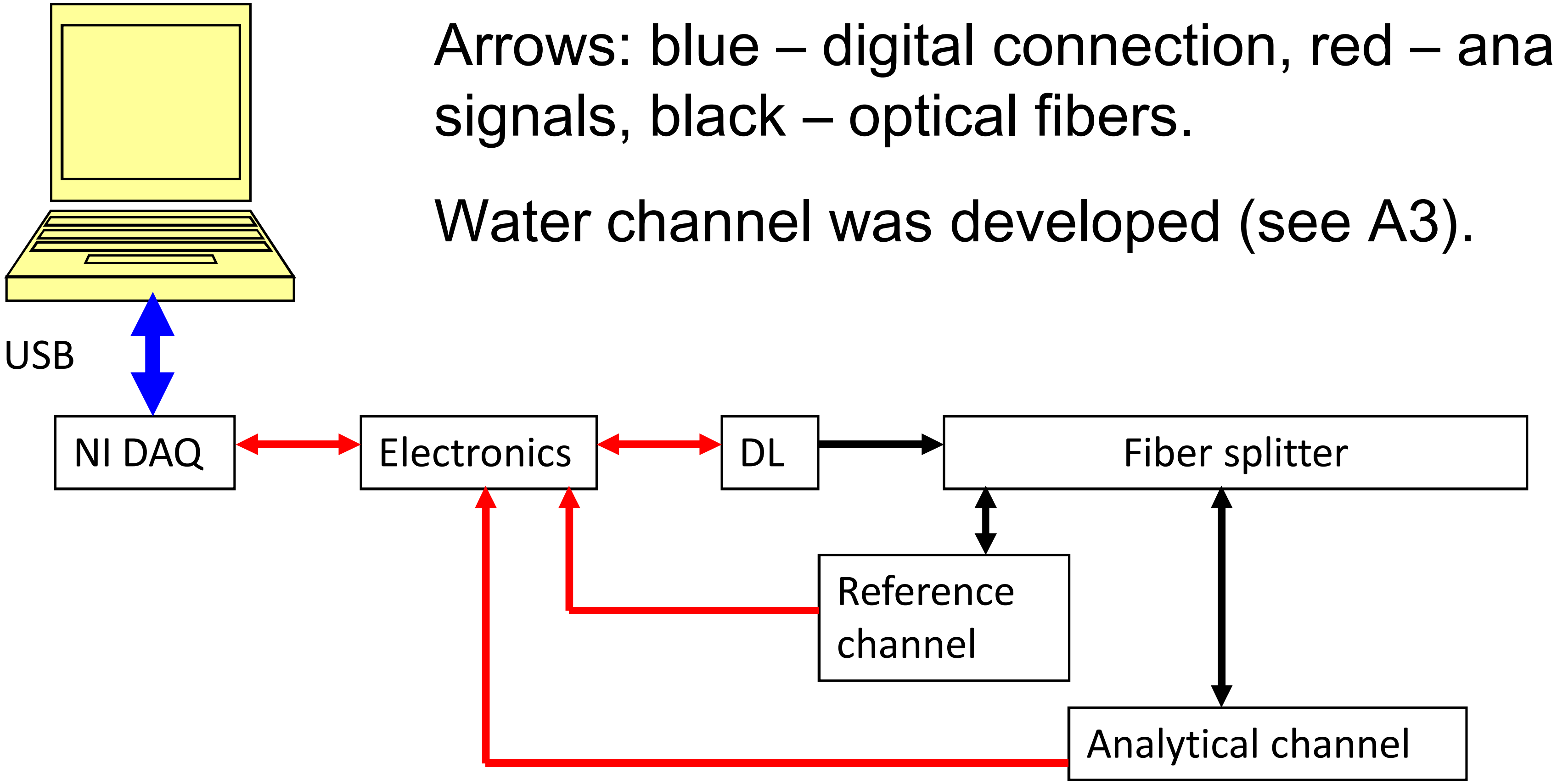
Introduction

Accurate measurement of greenhouse gases is significant goal with respect to global warming. Water is one of the most important greenhouse gases. Measurement of water molecules isotopes abundance ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and HDO) gives additional information for atmosphere monitoring. Accurate data of analytical spectral lines are needed for such monitoring. Currently available information (HITRAN 2008 [1]) is not enough accurate for goal under consideration. Accurate measurement of $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and HDO lines parameters is subject of present paper.

Block scheme of experiment

Arrows: blue – digital connection, red – analog signals, black – optical fibers.

Water channel was developed (see A3).



USB

NI DAQ

Electronics

DL

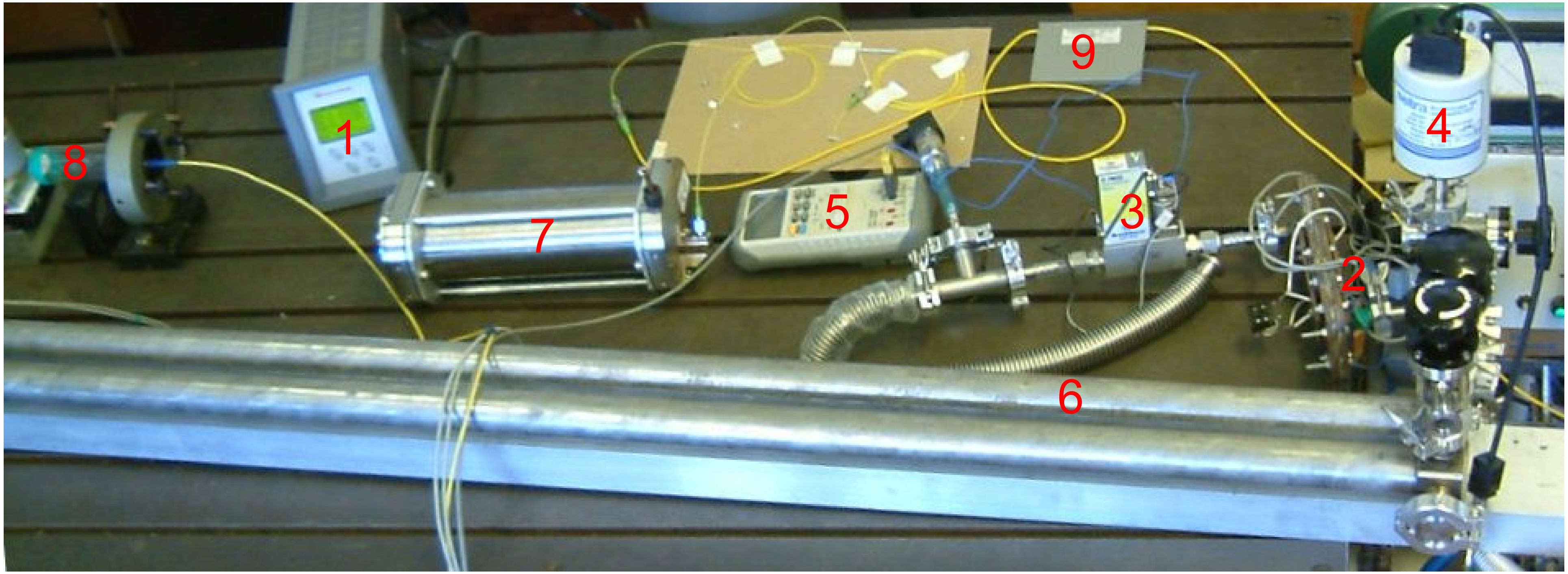
Fiber splitter

Reference channel

Analytical channel

Reference channel is using to stabilize DL frequency tuning cycles with respect to position of water vapor line in reference cell.

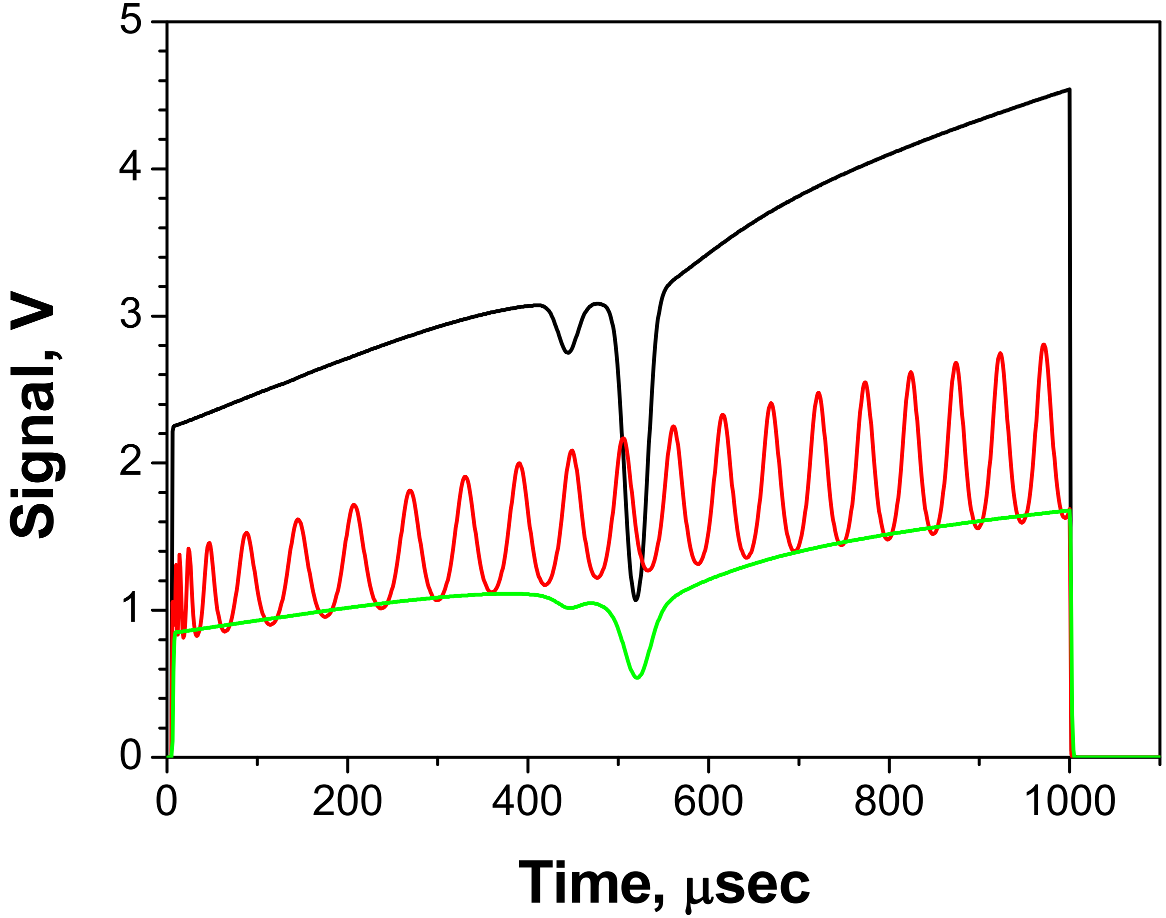
Set up view



1 – indicator of pump vacuum, 2 – connection to vacuum system, 3 – pressure stabilization, 4 – pressure sensor, 5 - gas cell temperature indicator, 6 – gas cell L = 198.8(2) cm, 7 - Chernin cell L = 3900 cm, 8 – reference channel, 9 – fiber interferometer.

System operation

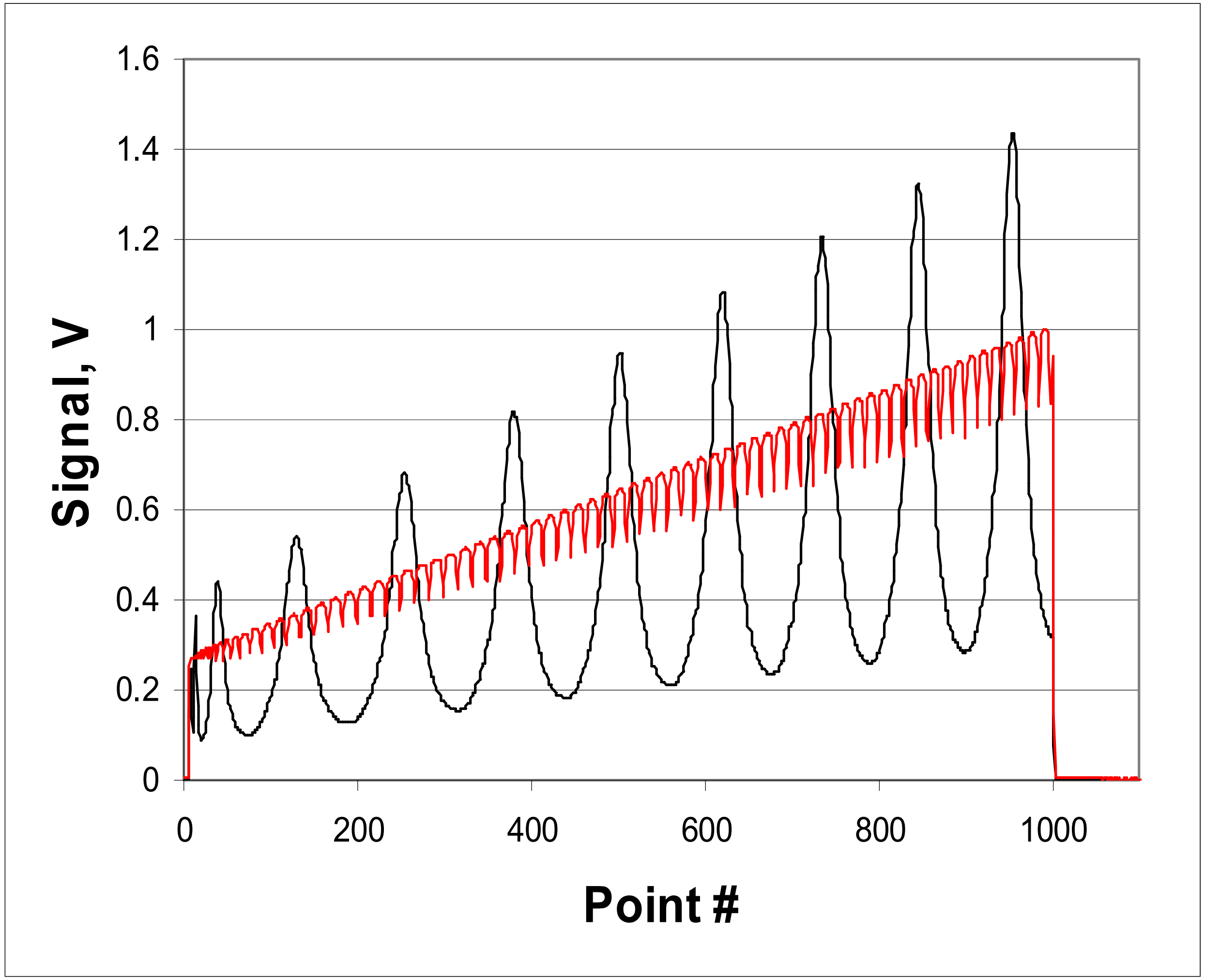
Tree signal are recorded simultaneously to record water vapor absorbance in analytical and reference channels (black and green respectively), calibrated FP transmittance (red).



Analytical – P_{H2O} = 1.3 mBar, L= 199.8 cm;
Reference – P_{H2O} = 9 mBar L=20см
Calibrated FP etalon D* = 0.049286(2) см$^{-1}$.
Presence of open atmosphere absorbance can be observed.
In present version fiber interferometer is using (see next slide).

S/N ratio is above 10^5, DL frequency calibration accuracy – 2 10^{-5} cm^{-1}.

DL frequency tuning accuracy



Recorded signals when calibrated FP (black) and fiber (red) etalons were installed in DL beam.

Using data presented, fiber etalon free dispersion range refer to calibrated FP one was determined.

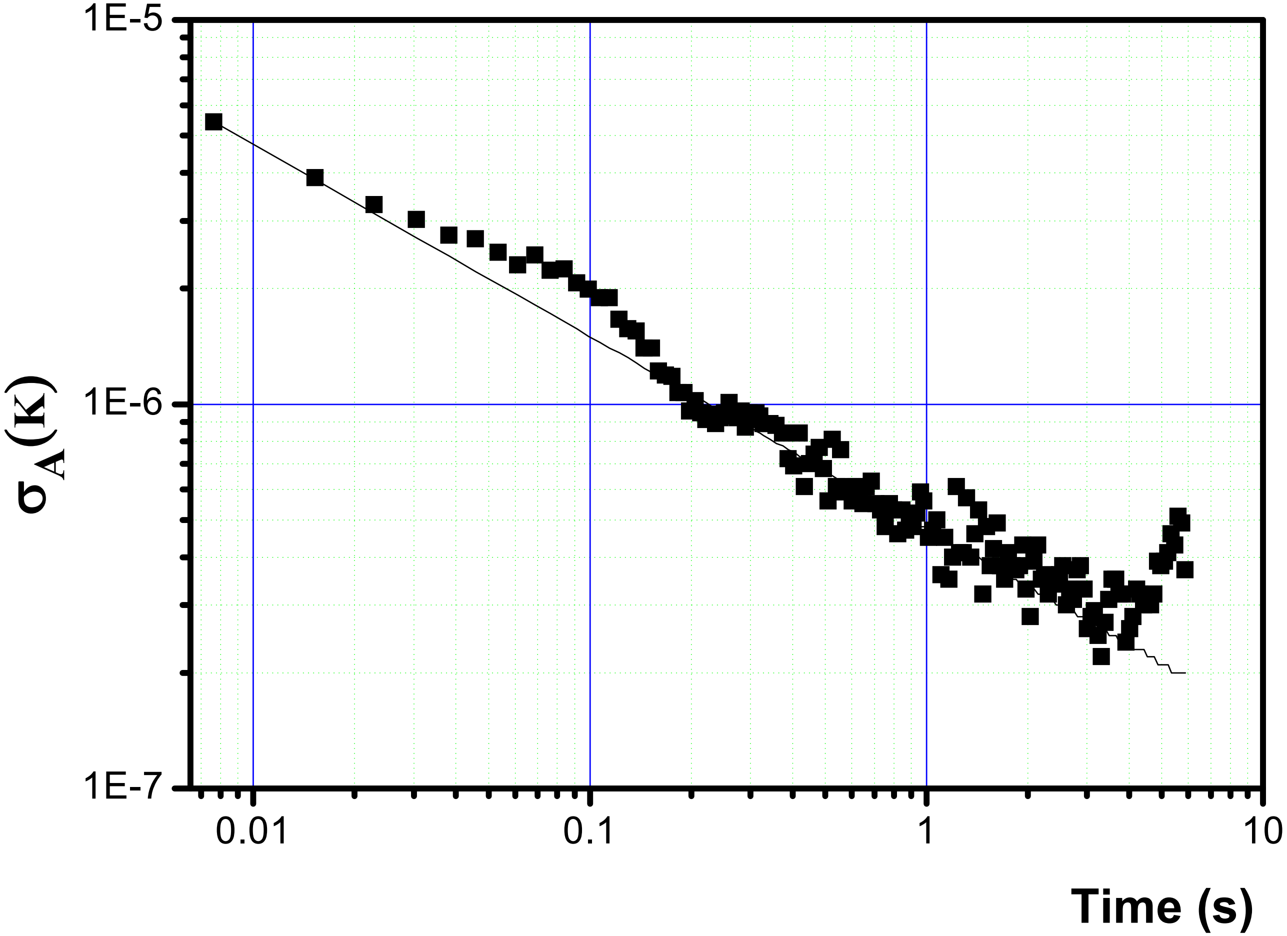
$FD_{fiber} = 0.131747(8)\ FD_{FP} =$

$= 0.131747(1 \pm 6\ 10^{-5})\ FD_{FP}$

DL frequency calibration accuracy is about 2 10^{-5} $см^{-1}$.

NEA

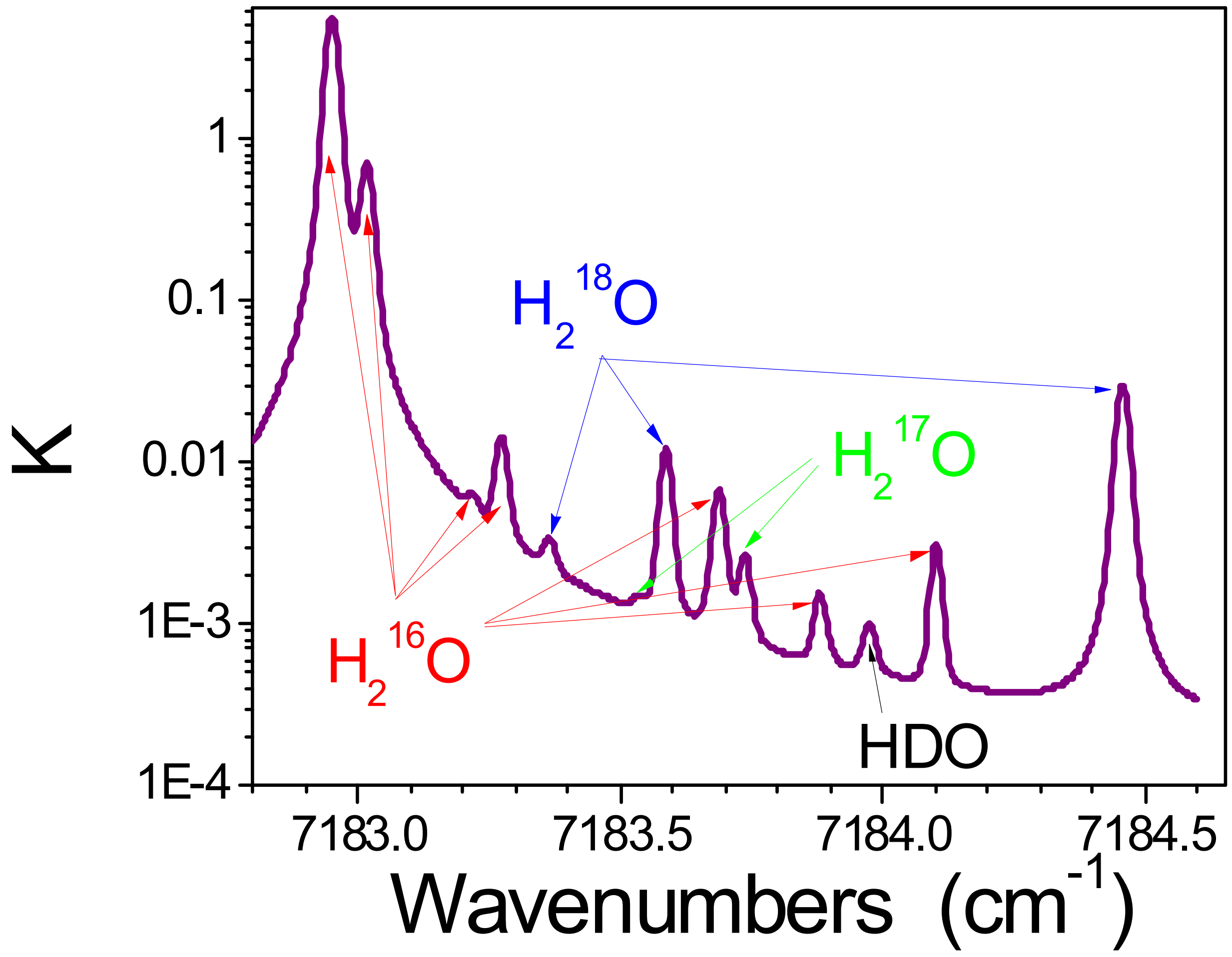
For trace molecules detection NEA - Noise Equivalent Absorbance (relative photocurrent noise) is using.



NEA ($\sigma_A(K)$) as function of averaging time.

For 1 sec averaging NEA is equal to 5 10^{-7}.

Water vapor absorbance in analytical spectral range

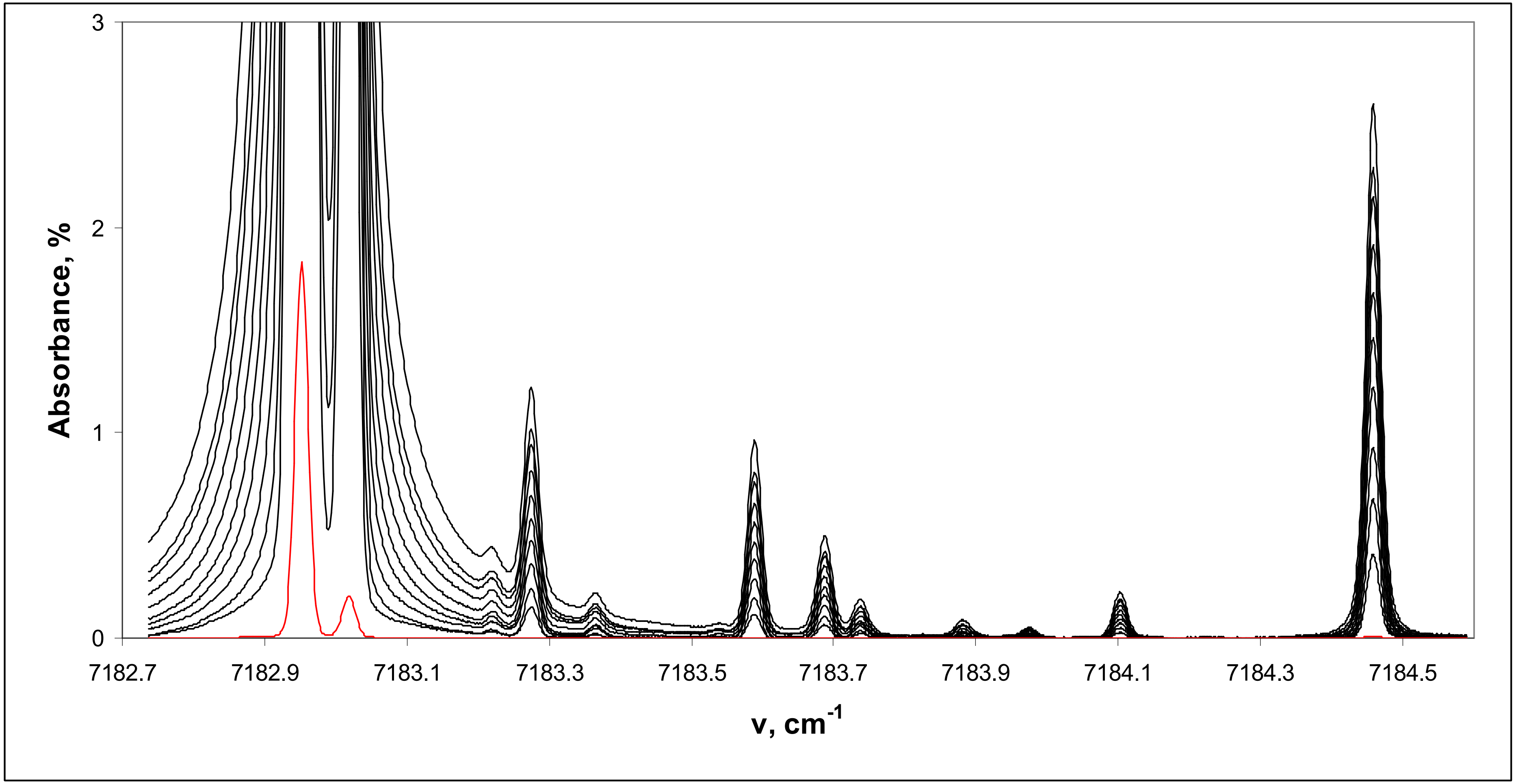


Spectral range near 1.39 μ was selected as analytical one for water channel of TDLS complex for airplane laboratory.

Model spectrum (HITRAN 2008) for following parameters: pure water, L = 2 m, P = 6 mBar, natural isotopes abundance.

Identification of water vapor lines in analytical spectral range. Absorbance due to strong lines wings is significant in spectral range to detect isotopes.

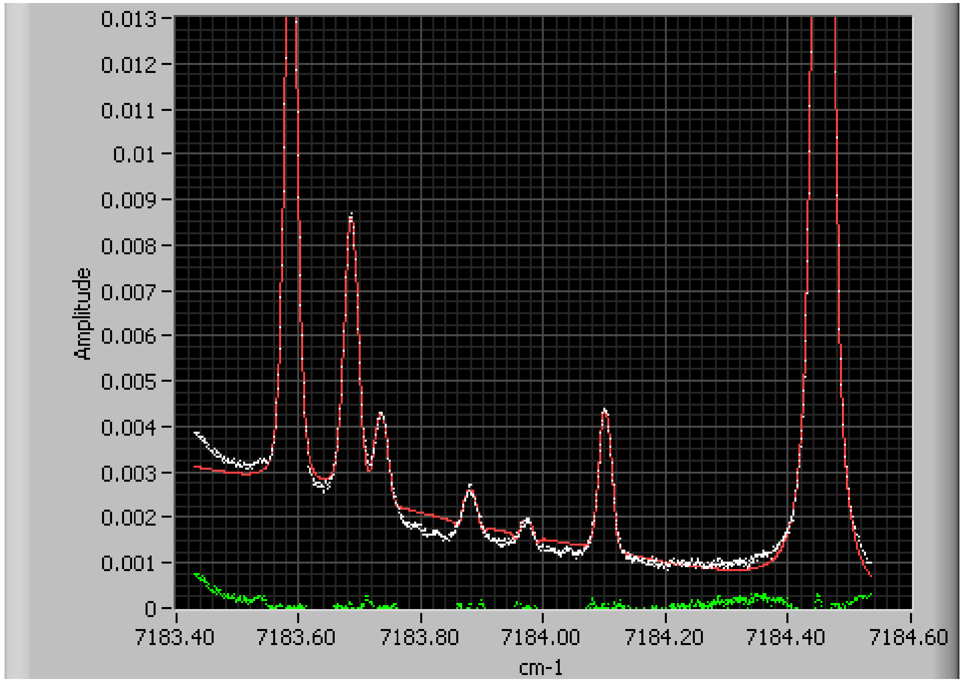
Experimental spectra



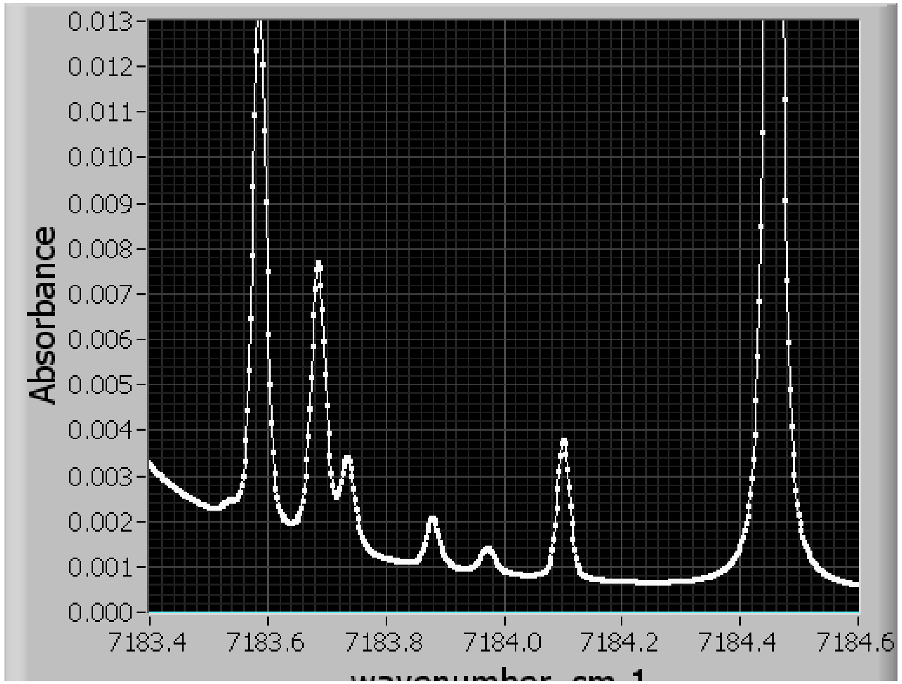
Absorbance spectra for different pressures P = 0.5-6.1 mBar, L=2м. Influence of strong lines wings can be observed.

For strongest line frequency 7182.94962 cm^{-1} was used [HITRAN 2008].

Strong lines influence



Experimental spectrum for P = 10.13 mBar and L = 200 cm (white), its fitting (red), and residual (green).

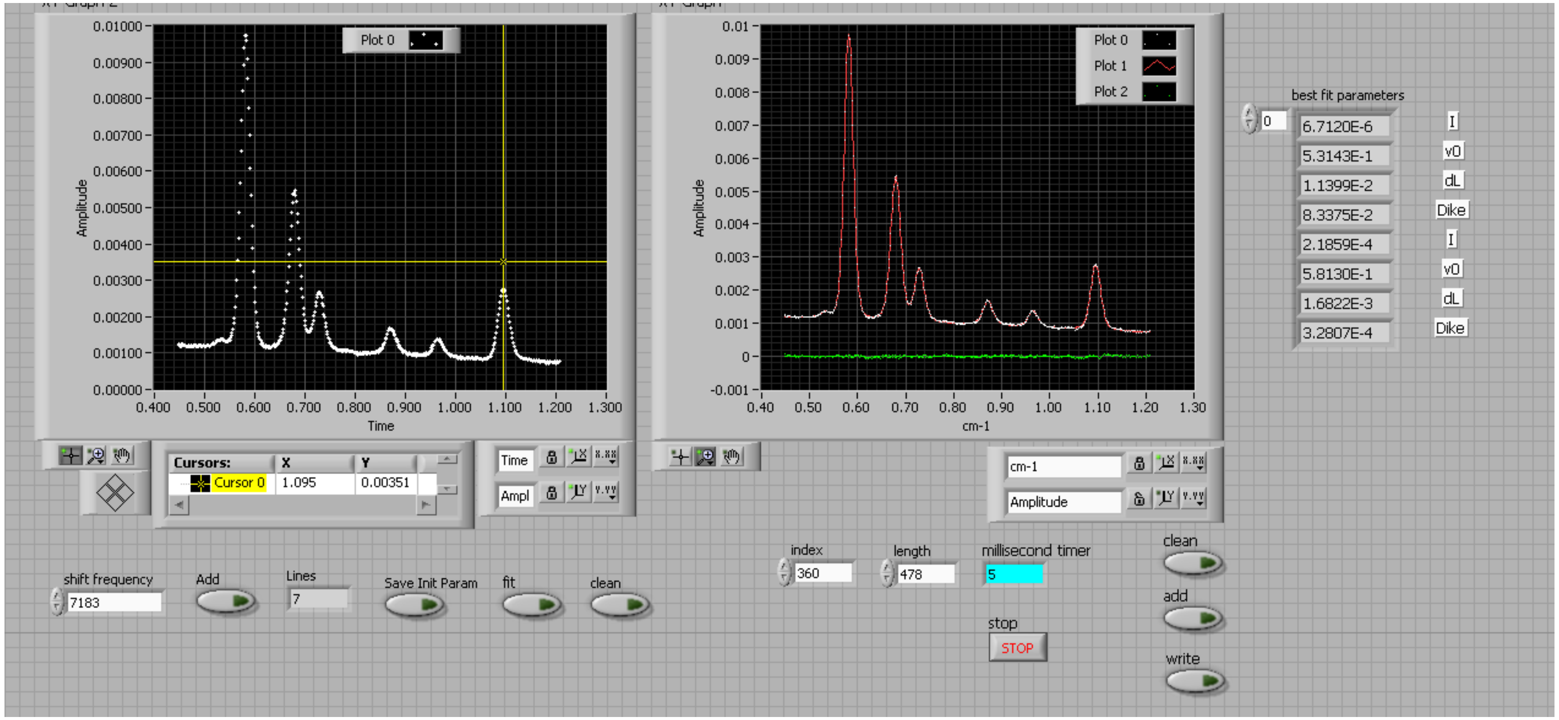


Model spectrum using HITRAN 2008

Presence of wings of neighboring strong lines changes significantly absorbance in spectral range under consideration leading to wrong fitting.

Experimental spectra fitting

Special software was developed to determine lines parameters using Rautian-Sobel’man spectral line shape (hard collisions model) to fit experimental spectra.



Cursors:	X	Y
Cursor 0	1.095	0.00351

shift frequency: 7183

Lines: 7

index: 360

length: 478

millisecond timer: 5

best fit parameters: 0

6.7120E-6	I
5.3143E-1	v0
1.1399E-2	dL
8.3375E-2	Dike
2.1859E-4	I
5.8130E-1	v0
1.6822E-3	dL
3.2807E-4	Dike

Example of software interface. Left graph – experimental spectrum, spectral range with weak water lines (absorbance < 1 %) was investigated. Operator determines location of lines to be analyzed. In present case 7 lines. Right graph result of fitting (red) and residual (green). Results of fitting for 2 lines are presented on right part of picture.

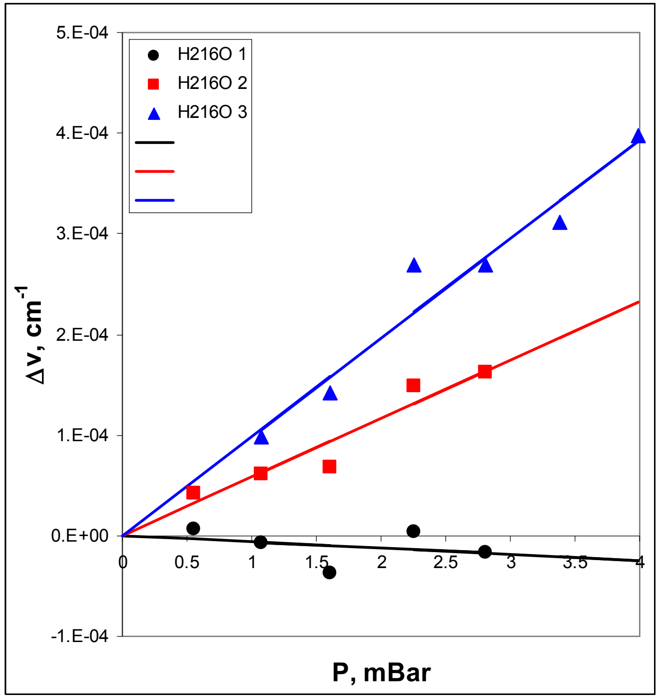
Frequency

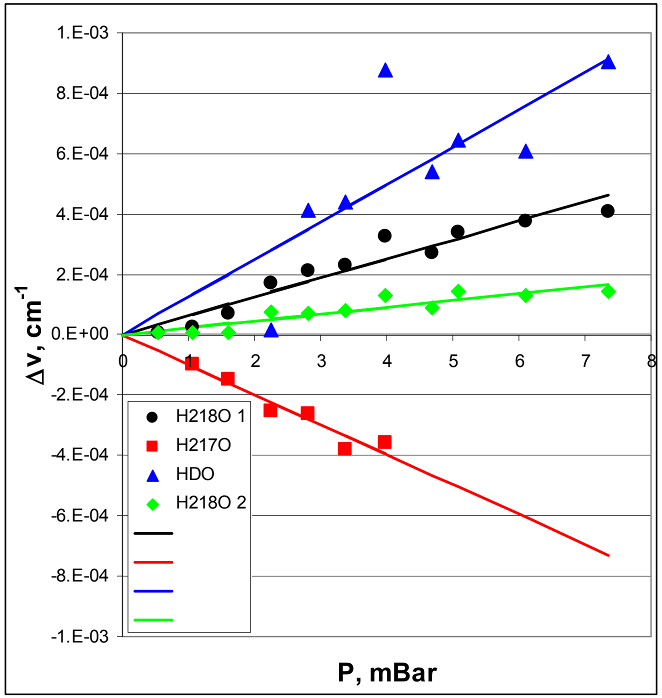
9 lines were selected as analytical ones: 5, 2, 1, and 1 for $H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and $HD^{16}O$, respectively.

	Present work	**std, 10^{-3} cm^{-1}**	**HITRAN 2008**	**dif, 10^{-3} cm^{-1}**
$H_2{}^{16}O$ 1	**7182.94962**	**0.020**	**7182.94962**	**0.00**
$H_2{}^{16}O$ 2	**7183.01580**	**0.019**	**7183.01579**	**0.01**
$H_2{}^{18}O$ 1	**7183.58580**	**0.025**	**7183.58578**	**0.02**
$H_2{}^{16}O$ 3	**7183.68440**	**0.031**	**7183.6858**	**-1.40**
$H_2{}^{17}O$	**7183.73555**	**0.037**	**7183.73545**	**0.10**
$H_2{}^{16}O$ 4	**7183.87939**	**0.174**	**7183.87854**	**0.85**
$HD^{16}O$	**7183.97108**	**0.208**	**7183.97279**	**-1.71**
$H_2{}^{16}O$ 5	**7184.10048**	**0.072**	**7184.10093**	**-0.45**
$H_2{}^{18}O$ 2	**7184.45568**	**0.015**	**7184.45637**	**-0.69**
			std	**0.80**

Analytical lines frequencies were measured and compared with HITRAN 2008. Difference std was found 0.80 10^{-3} cm^{-1} in agreement with HITRAN accuracy 0.001-0.01 cm^{-1}.

Self shift



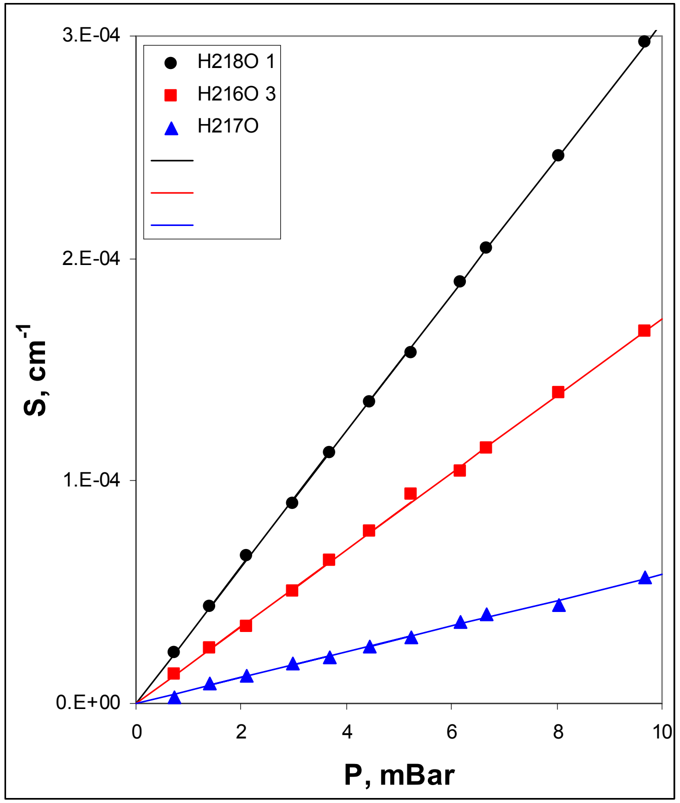


Frequency pressure dependences of different $H_2{}^{16}O$ lines (upper graph) and water isotopomers (lower graph) were measured and pressure self shift coefficients were determined.

	ν	**Shift, 10^{-2} cm^{-1}/Bar**	**std, 10^{-2} cm^{-1}/Bar**
$H_2{}^{16}O$ 1	**7182.94962**	**-1.05**	**0.84**
$H_2{}^{16}O$ 2	**7183.01579**	**4.42**	**0.70**
$H_2{}^{18}O$ 1	**7183.58580**	**4.77**	**0.47**
$H_2{}^{16}O$ 3	**7183.68440**	**7.47**	**0.86**
$H_2{}^{17}O$	**7183.73555**	**-7.54**	**1.05**
$H_2{}^{16}O$ 4	**7183.87939**	**-1.99**	**2.80**
$HD^{16}O$	**7183.97108**	**9.26**	**3.34**
$H_2{}^{16}O$ 5	**7184.10048**	**-4.02**	**1.33**
$H_2{}^{18}O$ 2	**7184.45567**	**1.72**	**0.27**

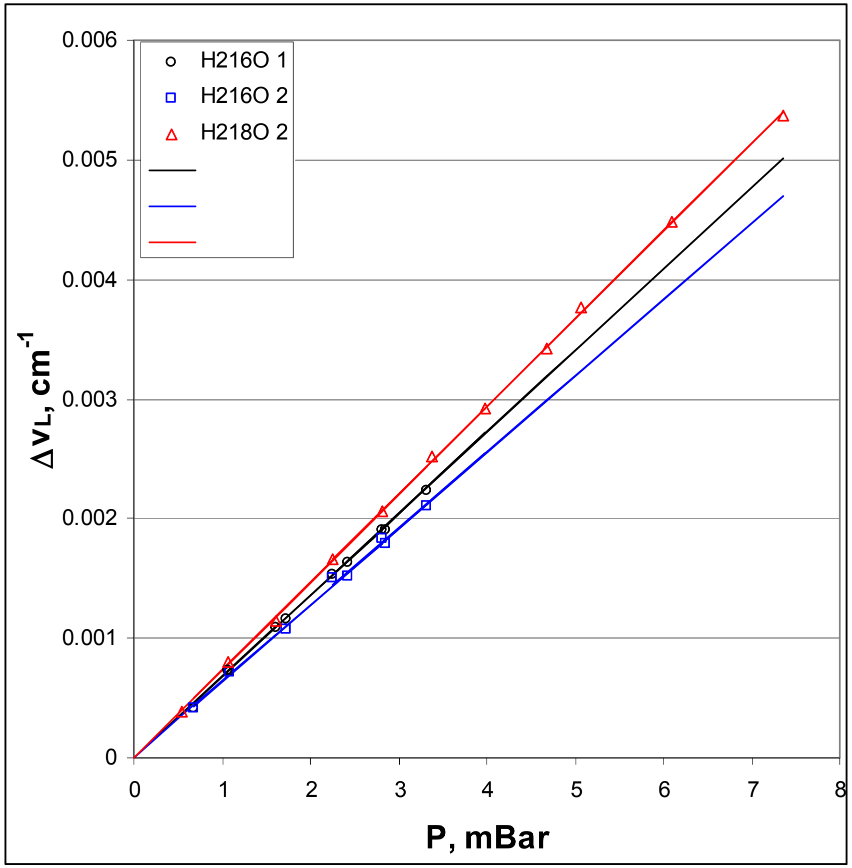
Integral intensity

Analytical lines intensities were measured and compared with HITRAN 2008. Difference was in agreement with HITRAN accuracy 5 - 10 %.



	Present work	std, %	HITRAN 2008	dif, %
$H_2{}^{16}O$ 1	3.675E-21	0.16	3.752E-21	-2.10
$H_2{}^{16}O$ 2	3.926E-22	0.20	4.115E-22	-4.81
$H_2{}^{18}O$ 1	6.175E-24	0.45	6.334E-24	-2.57
$H_2{}^{16}O$ 3	3.577E-24	2.03	3.671E-24	-2.62
$H_2{}^{17}O$	1.139E-24	4.07	1.194E-24	-4.83
$H_2{}^{16}O$ 4	5.508E-25	5.99	4.922E-25	10.64
$H_2{}^{16}O$ 5	1.382E-24	1.97	1.493E-24	-8.02
$H_2{}^{18}O$ 2	1.903E-23	0.15	1.993E-23	-4.74

Self-broadening



Strongest lines self-broadening was measured and compared with HITRAN 2008. Difference was in agreement with HITRAN accuracy 5 - 10 %.

	γ_{self}, cm^{-1}/Bar	std, %	HITRAN 2008	dif, %
$H_2{}^{16}O$ 1	0.517	0.8	0.51	1.40
$H_2{}^{16}O$ 2	0.485	2.6	0.492	-1.50
$H_2{}^{18}O$ 2	0.558	0.5	0.537	3.69

Accuracy estimate

	Value	Error	Error %
L, cm	199.8	0.2	0.1
T, ^{o}C	20 - 25	0.2	0.07
P, mBar	0 - 20	0.1	0.5
H_2O sample purity, %	99.9	0.1	0.1
PD non-linearity			0.02
Total			0.52
NEA for averaging time 1 sec	$5\ 10^{-7}$		
DL frequency tuning, cm^{-1}	$2\ 10^{-5}$		

Estimated experimental accuracy is 0.52 %. Accuracy of spectral line parameters depends also on accuracy of fitting procedure – subject for future investigations.