

PRESSURE BROADENING AND SHIFT OF H₂O LINE NEAR 1.39 μ

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DLS

LAB

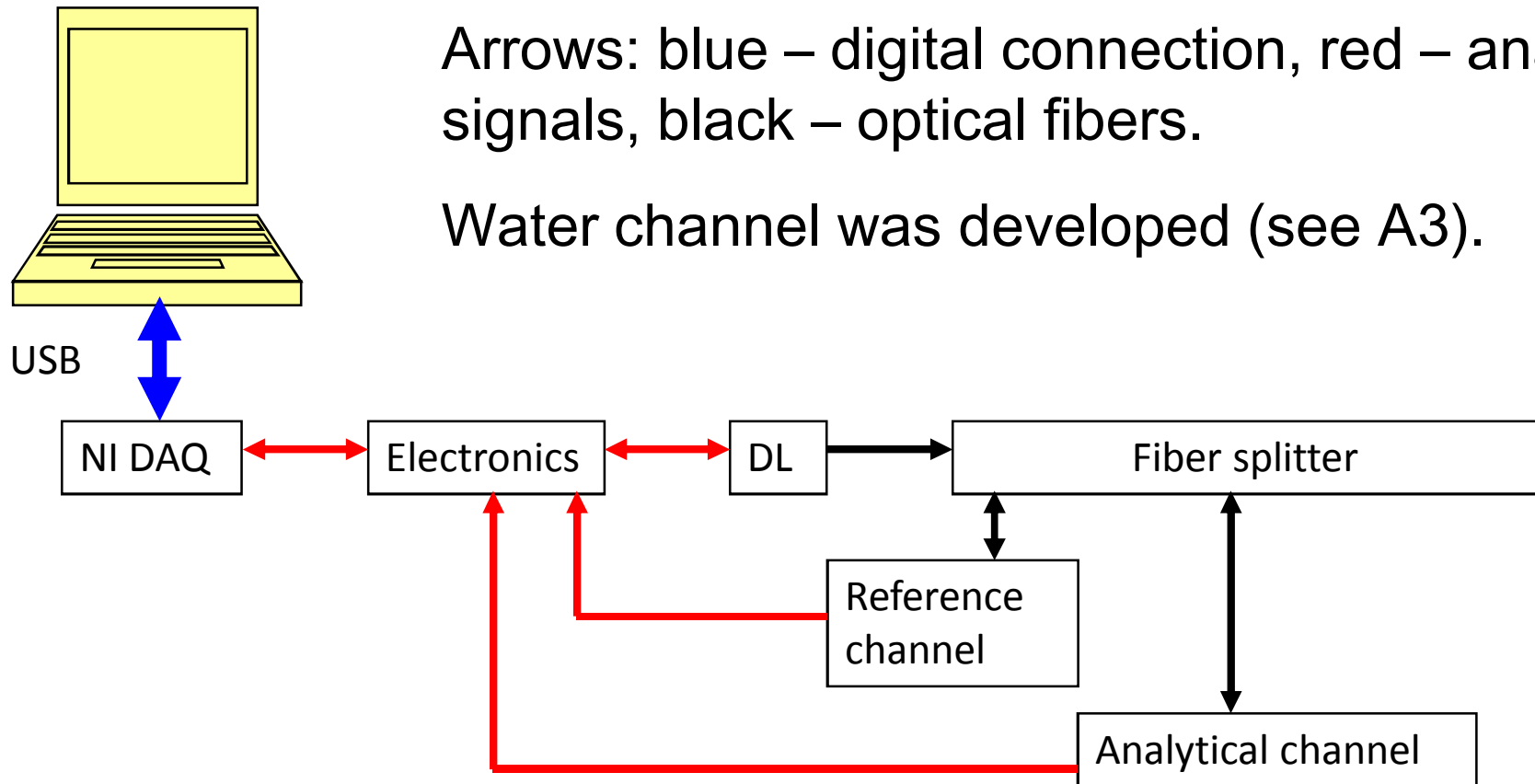
Introduction

Accurate measurement of greenhouse gases is significant goal with respect to global warming. Water is one of the most important greenhouse gases.

Currently available information (HITRAN 2008 [1]) is not enough accurate for goal under consideration. Purpose of present paper was investigation of 000-101 $2_{12} - 3_{13}$ H_2^{16}O line. This line was selected as analytical one for water channel of airplane-laboratory TDLs complex.

[1] <http://www.cfa.harvard.edu/hitran/>

Block scheme of experiment

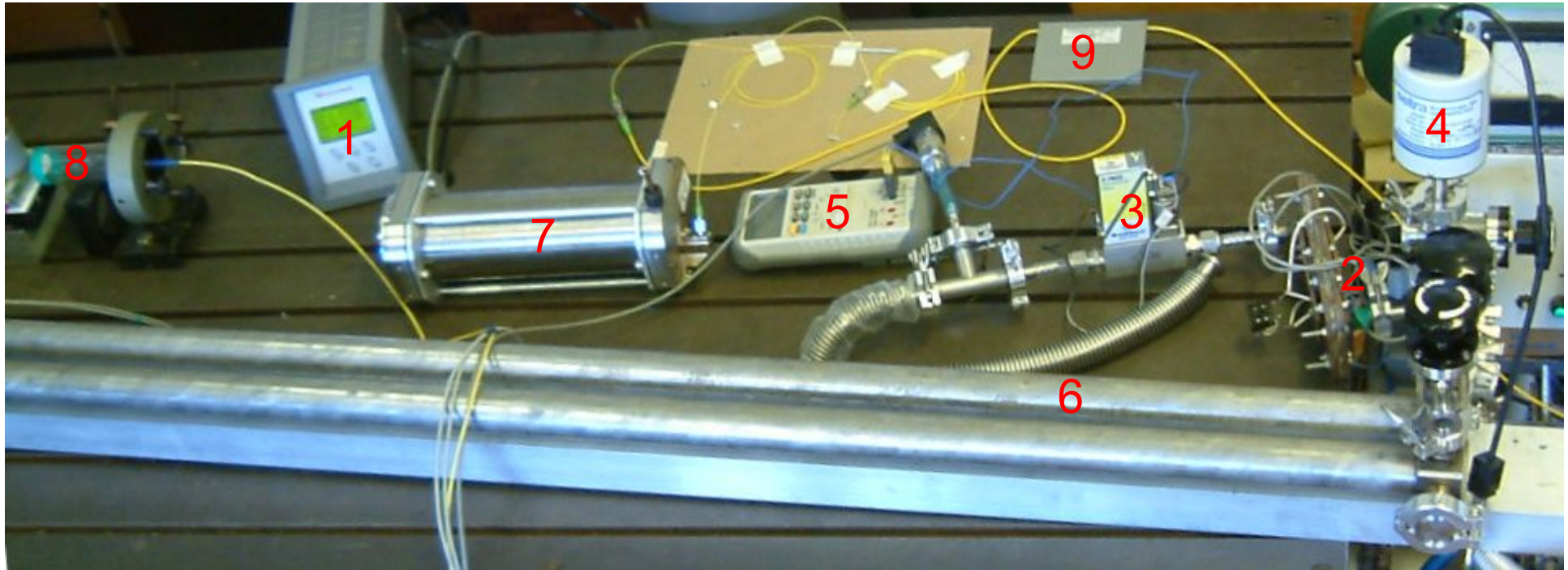


Arrows: blue – digital connection, red – analog signals, black – optical fibers.

Water channel was developed (see A3).

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

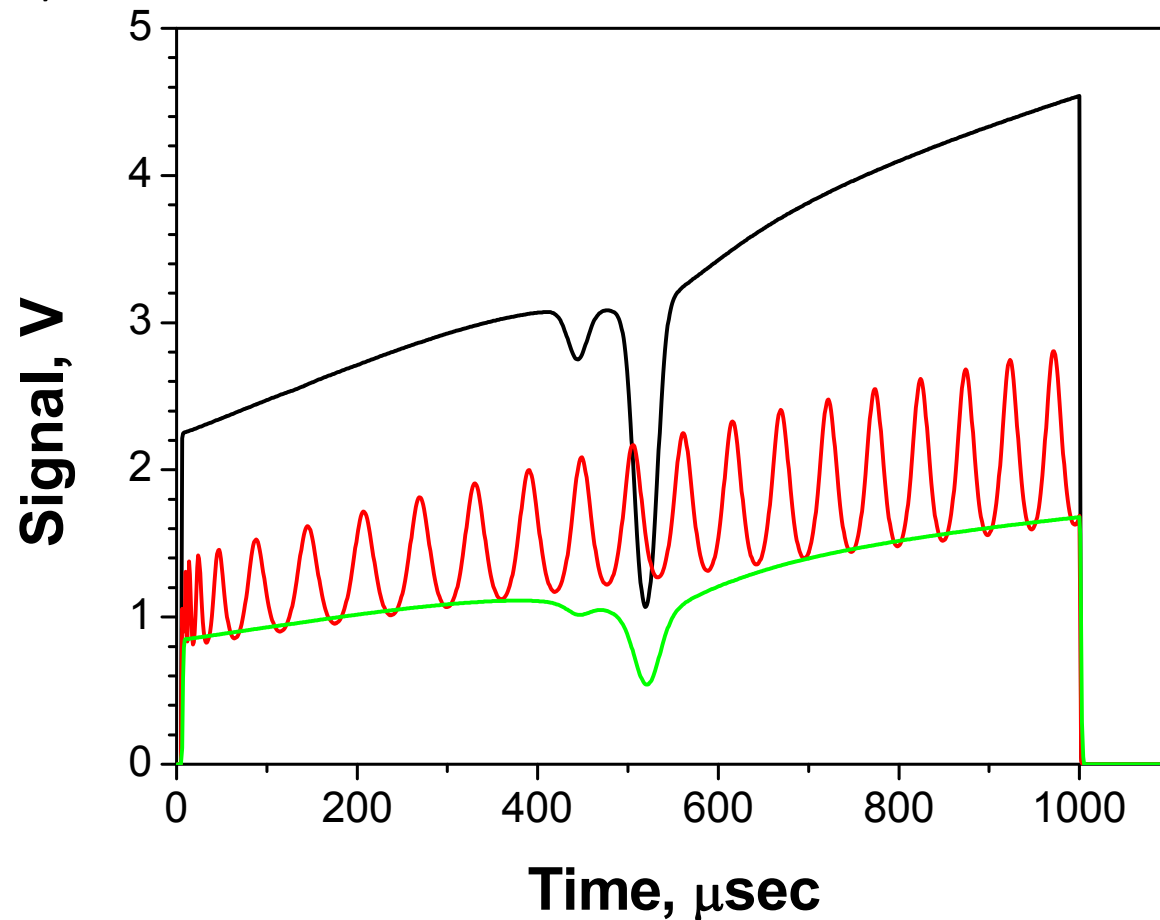
Set up view



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 – $P_{\text{H}_2\text{O}} = 1.3 \text{ mBar}$,
 $L = 199.8 \text{ cm}$;
Reference – $P_{\text{H}_2\text{O}} = 9 \text{ mBar}$
 $L = 20 \text{ cm}$

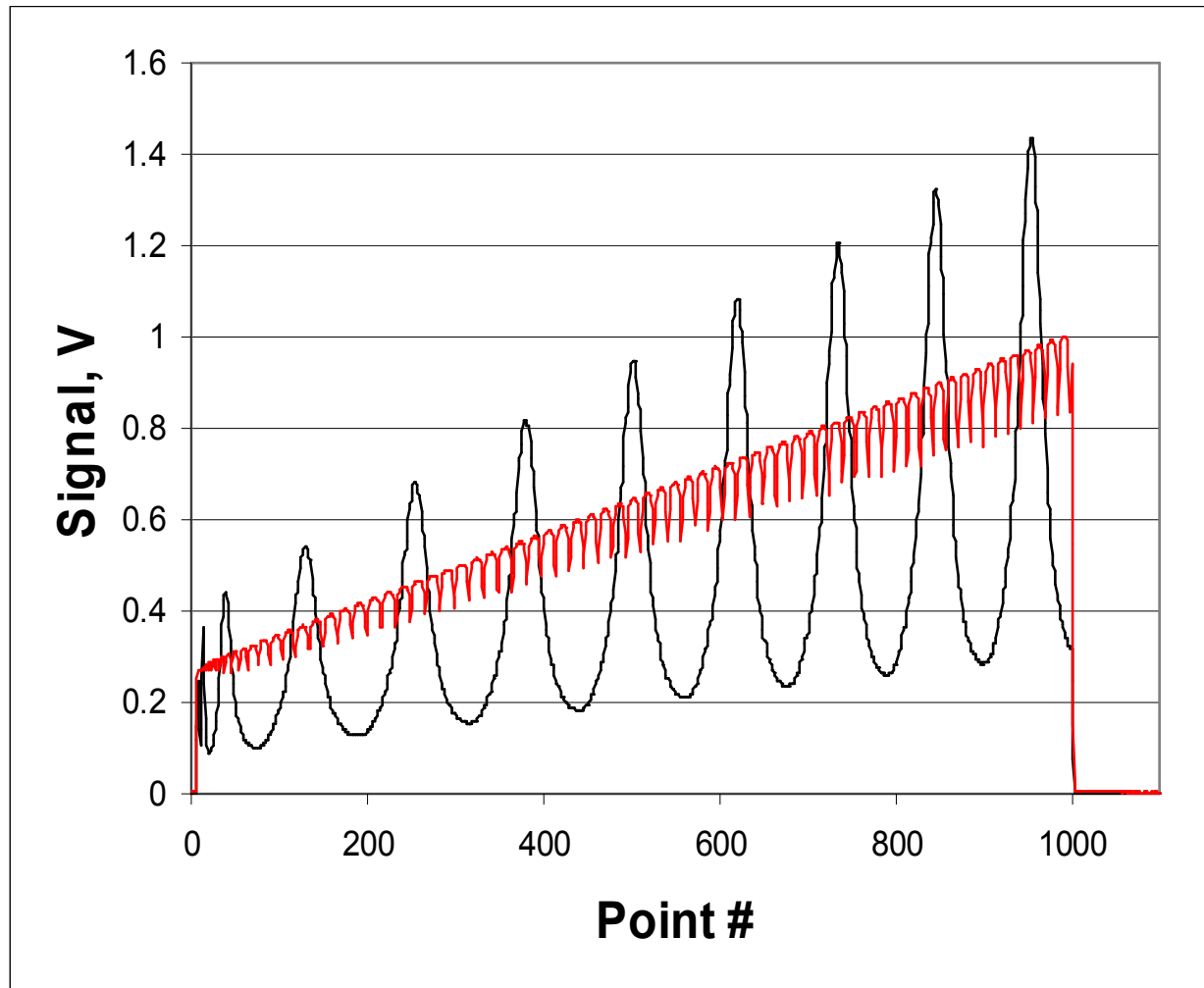
Calibrated FP etalon $D^* = 0.049286(2) \text{ cm}^{-1}$.

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 – $2 \cdot 10^{-5} \text{ cm}^{-1}$.

DL frequency tuning accuracy



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

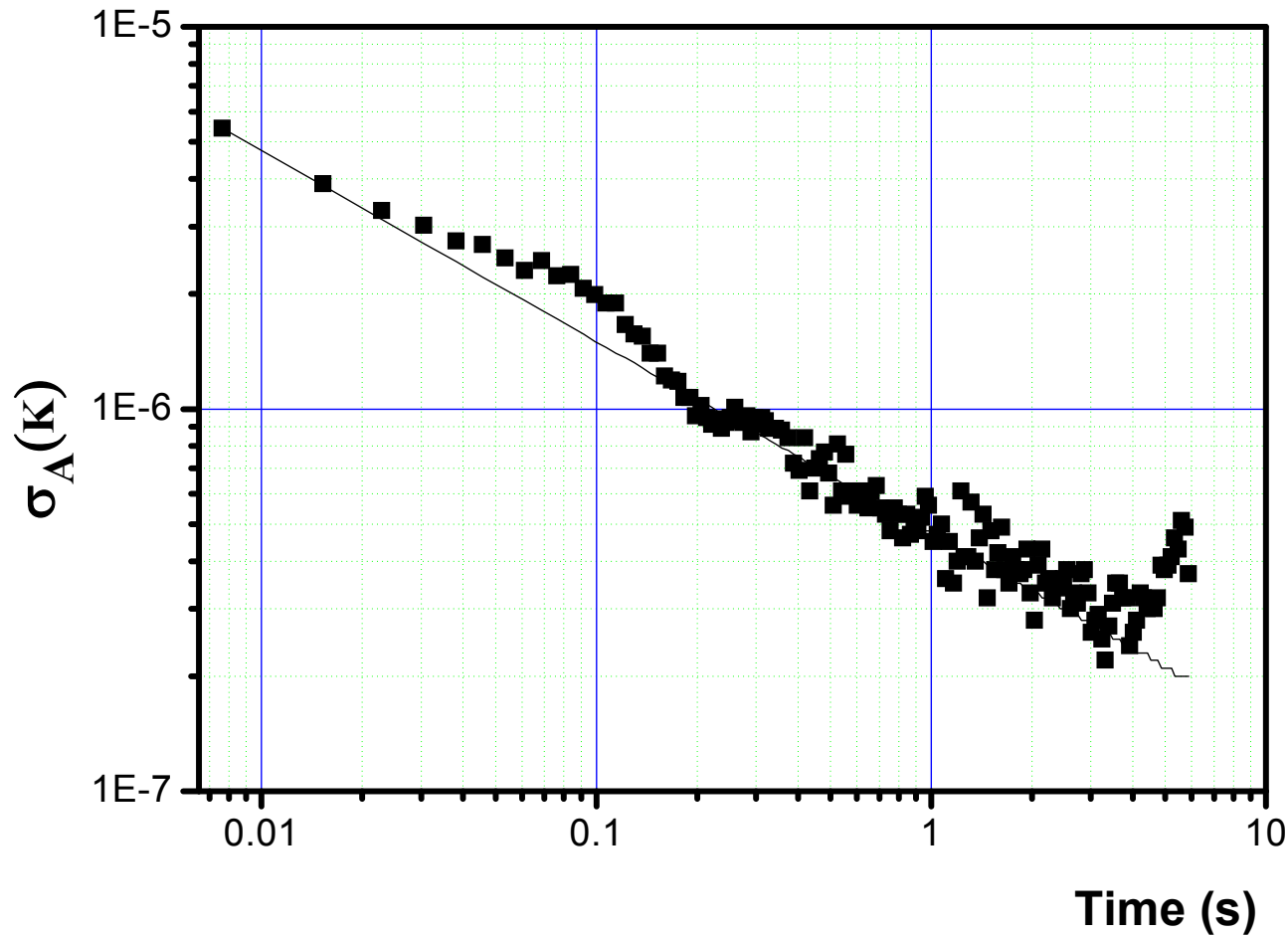
Using data presented, fiber etalon free dispersion range refer to calibrated FP one was determined.

$$\begin{aligned} FD_{\text{fiber}} &= 0.131747(8) FD_{\text{FP}} \\ &= 0.131747(1 \pm 6 \cdot 10^{-5}) FD_{\text{FP}} \end{aligned}$$

DL frequency calibration accuracy is about $2 \cdot 10^{-5} \text{ cm}^{-1}$.

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} .

Vacuum system and samples preparation

Following gases were used to prepare gas mixtures under investigation.

Pure H₂O > 99.9 %,

Pure N₂ > 99.99 %

Pure Xe > 99.99 %

Three gas mixtures were prepared:

Pure H₂O

H₂O:N₂ = 2.299(7) %

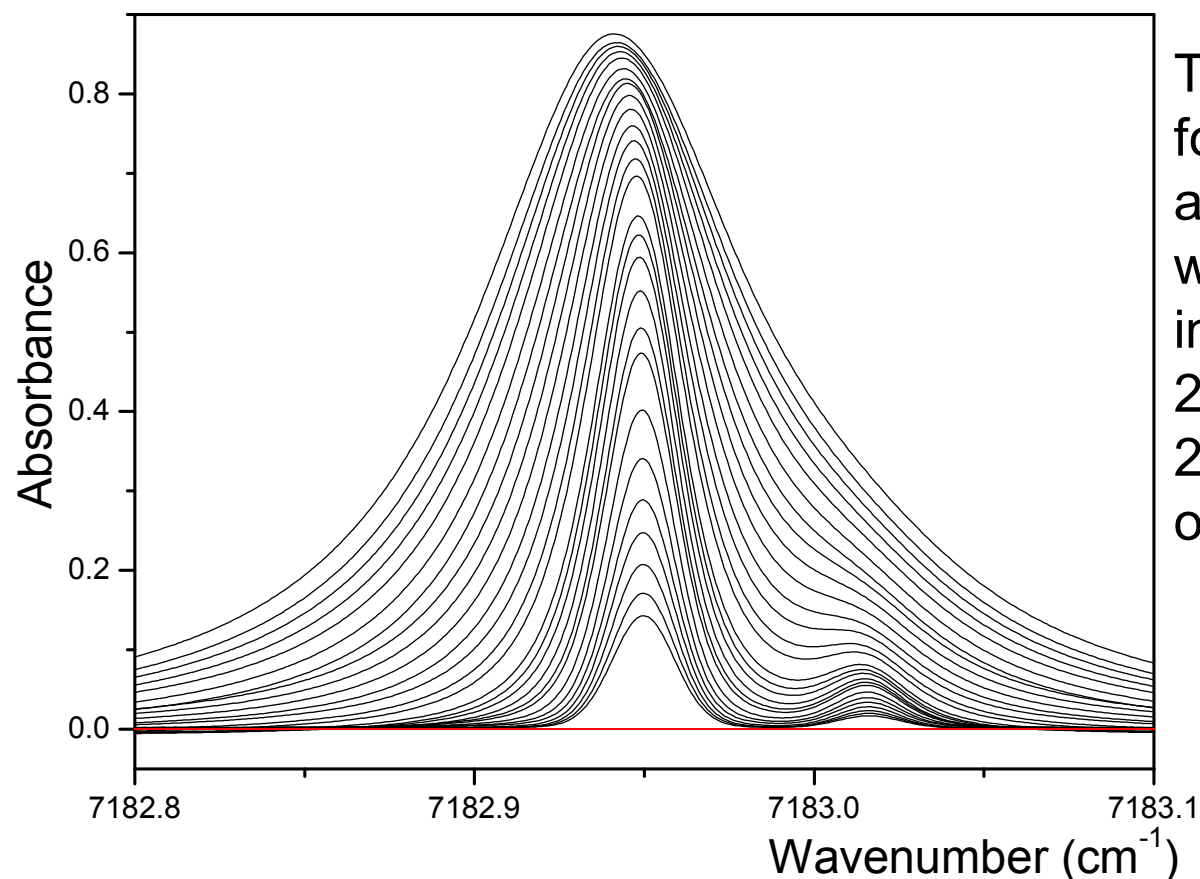
H₂O:Xe = 1.925(8) %

Gas mixtures prepared remained in container for several days to have homogeneous spatial concentration distribution.

View of vacuum system.



Experimental spectra

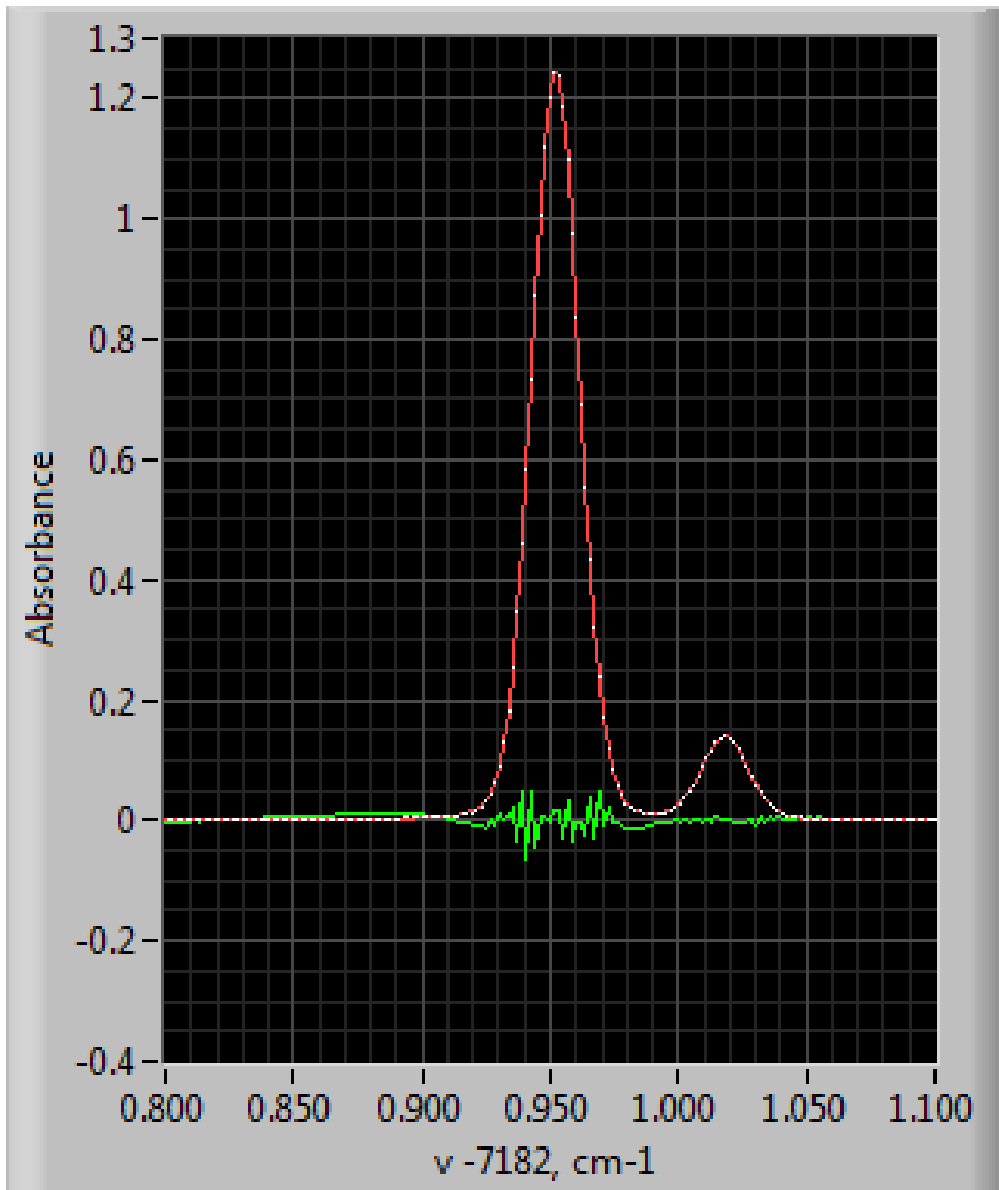


Two water vapor lines using for humidity monitoring by airplane based TDLS complex were selected for investigation:

$2_{12} - 3_{13}$ (7182.949 cm⁻¹) and
 $2_{02} - 2_{21}$ (7183.016 cm⁻¹)
of 101 - 000 band

Absorbance spectra for different pressures $P = 1 - 400$ mBar of H₂O:Xe gas mixture, $L=1$ m.

Fitting of pure H₂O spectra



Experimental spectra were fitted using both Rautian - Sobel'man (hard collisions model) and Voigt (all parameters free) line profiles.

Example of fitting for $P = 1.41$ mBar, $L = 2$ m, $\Gamma = 0.733 \cdot 10^{-3}$ cm⁻¹.

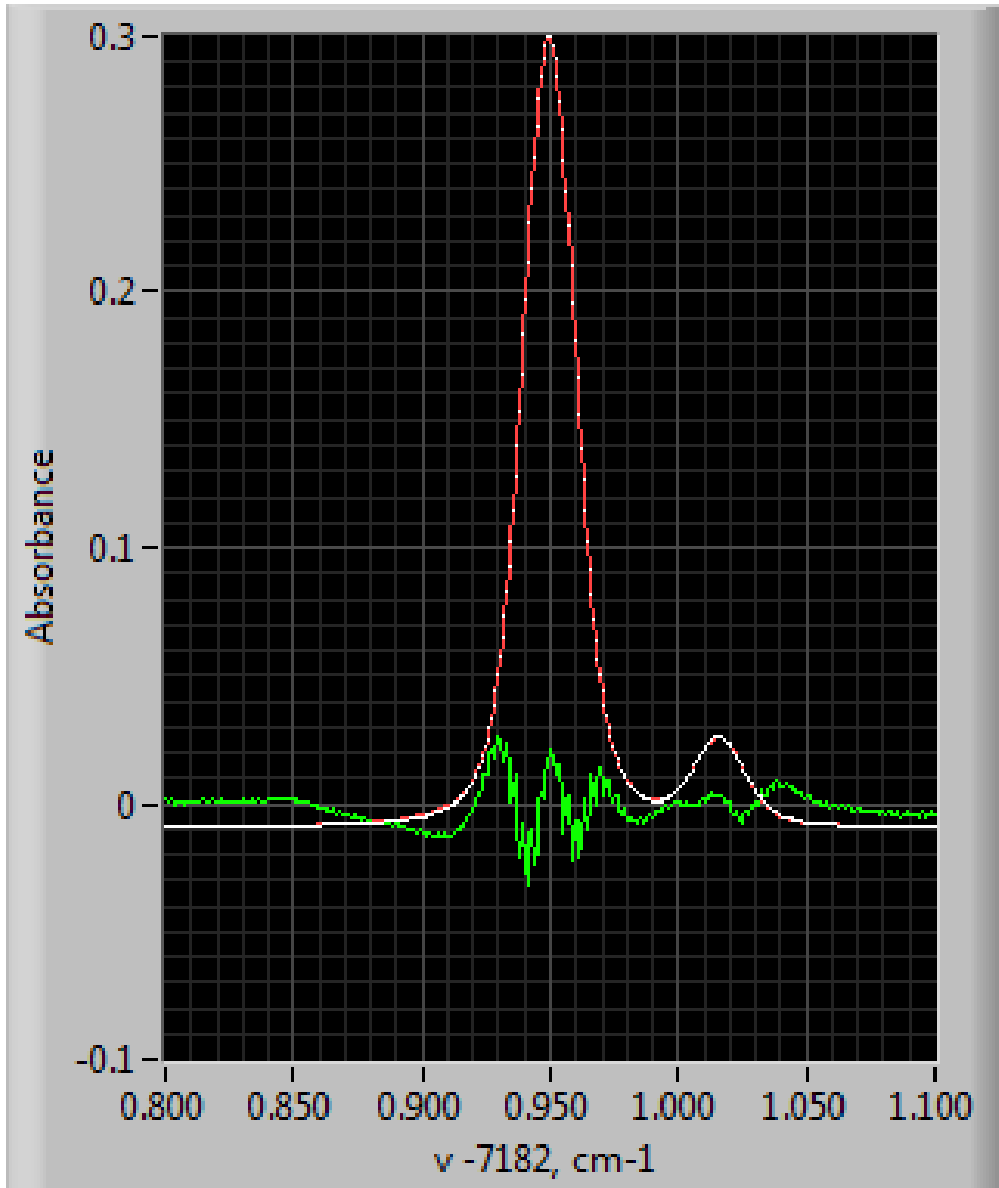
For low pressures Voigt profile is preferable (see B2).

White – experiment, red – fitting, green – residual*20.

Experimental line shape in this case is close to Doppler profile. Residual is due to DL frequency noise.

Details of results obtained for pure water vapor can be found in C2.

Spectra fitting for H₂O:N₂



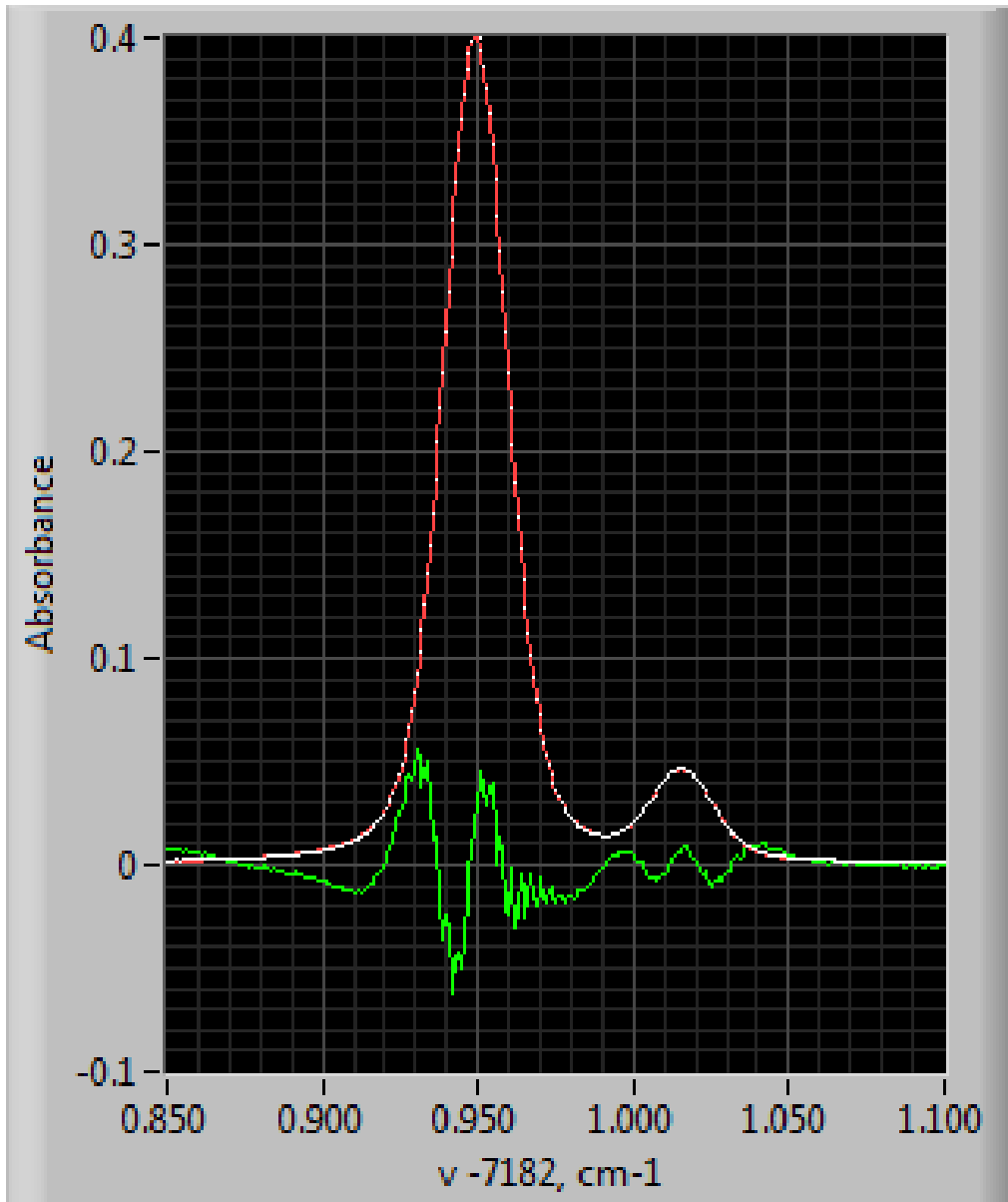
Experimental spectra were fitted using both Rautian - Sobel'man (hard collisions model) and Voigt (all parameters free) line profiles.

Example of fitting for $P = 25.1$ mBar, $L = 1$ m, $\Gamma = 4.24 \cdot 10^{-3}$ cm⁻¹.

For intermediate pressures Rautian - Sobel'man profile is preferable (see B2). White – experiment, red – fitting, green – residual*20.

Significant ($\sim 10^{-3}$) difference between experiment and fitting as well as line asymmetry can be observed.

Spectra fitting for H₂O:Xe



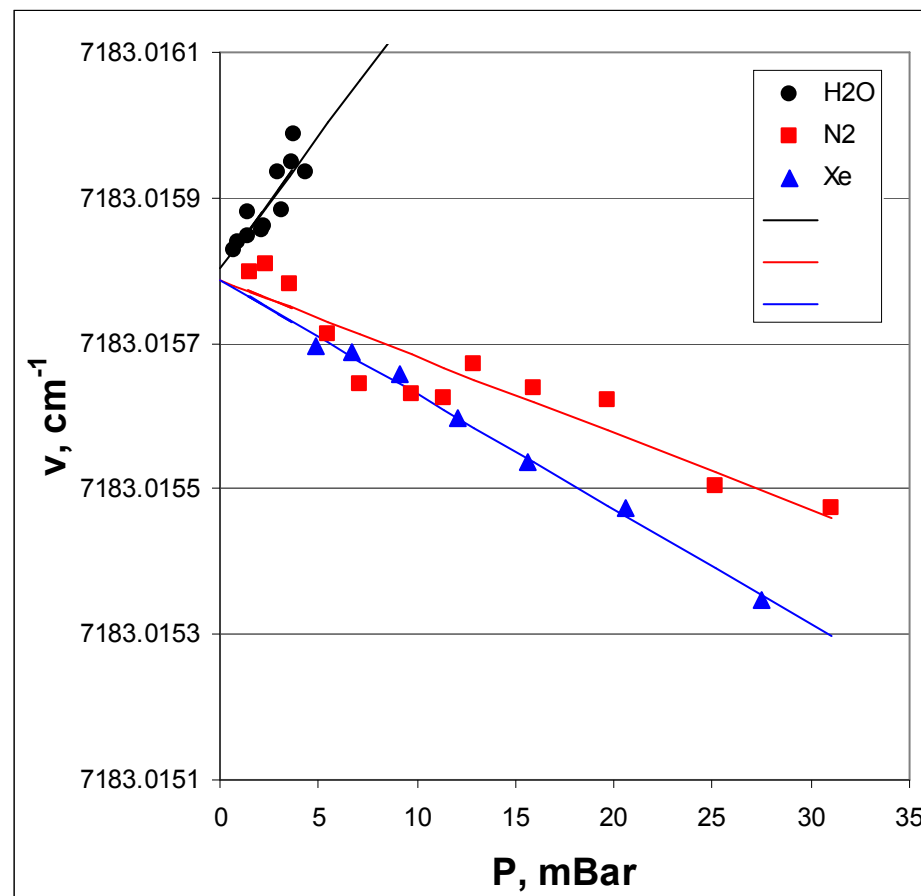
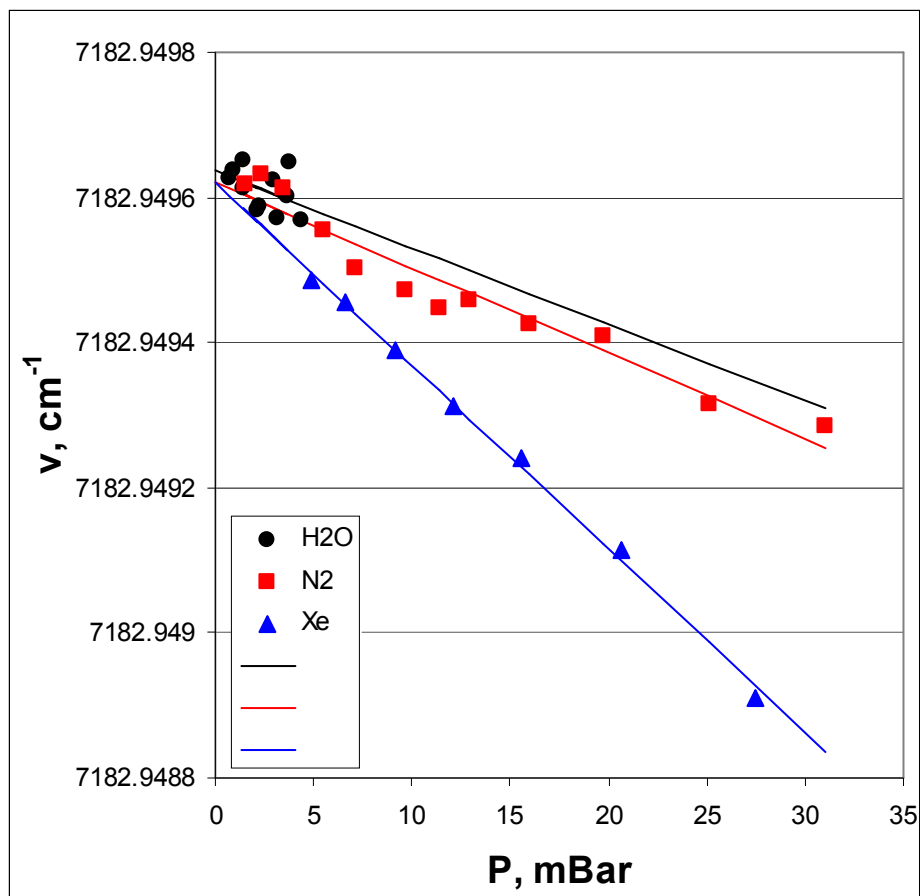
Experimental spectra were fitted using Rautian - Sobel'man line shape (hard collisions model).

Example of fitting for $P = 27.5$ mBar, $L = 1$ m, $\Gamma = 9.80 \cdot 10^{-3}$ cm⁻¹.

For intermediate pressures Rautian - Sobel'man profile is preferable (see B2). White – experiment, red – fitting, green – residual*20.

Significant ($\sim 10^{-3}$) difference between experiment and fitting as well as strong line asymmetry can be observed.

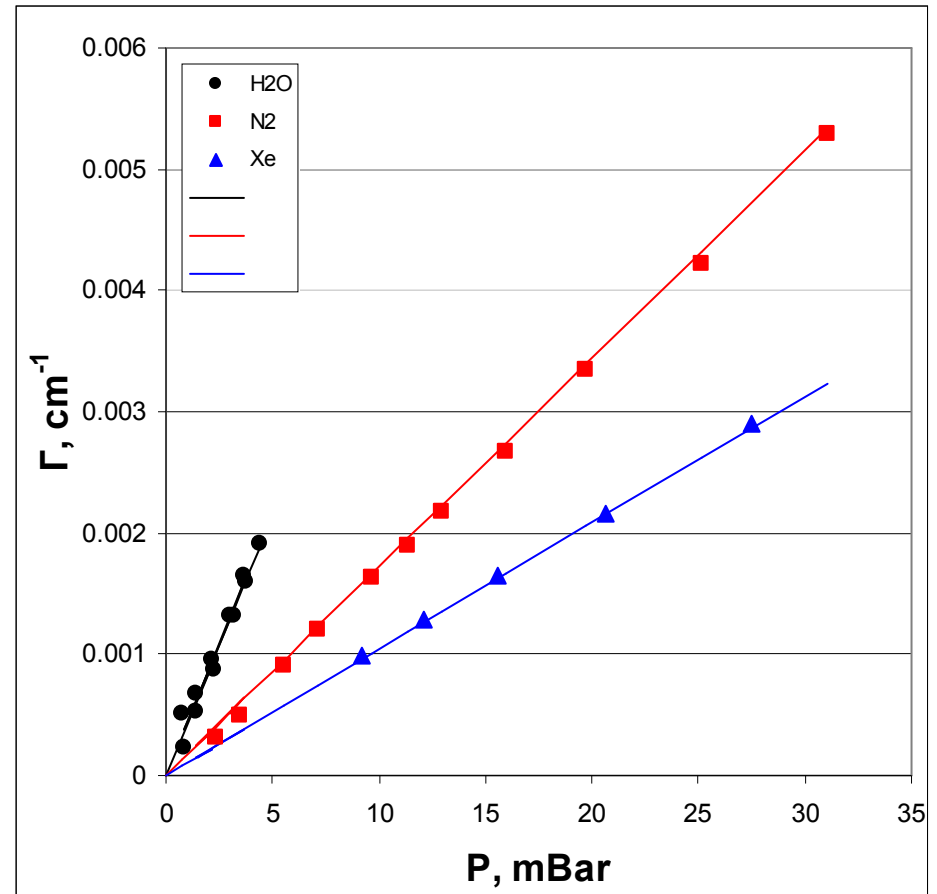
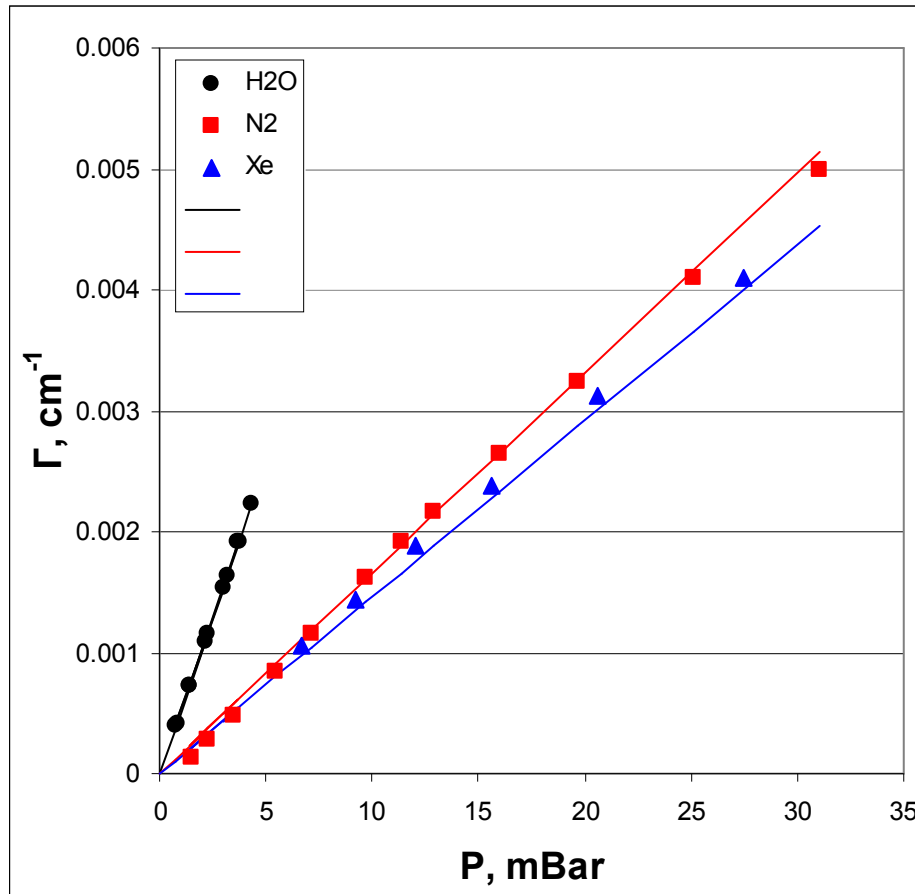
Pressure shift



Pressure shift for two analytical lines for gas mixtures under investigation.

	$\text{H}_2\text{O},$ $10^{-2} \text{ cm}^{-1}/\text{Bar}$	$\text{N}_2,$ $10^{-2} \text{ cm}^{-1}/\text{Bar}$	$\text{Xe},$ $10^{-2} \text{ cm}^{-1}/\text{Bar}$
$\text{H}_2^{16}\text{O} 1$	-1.05(84)	-1.18(9)	-2.53(4)
$\text{H}_2^{16}\text{O} 2$	4.42(70)	-1.05(13)	-1.57(4)

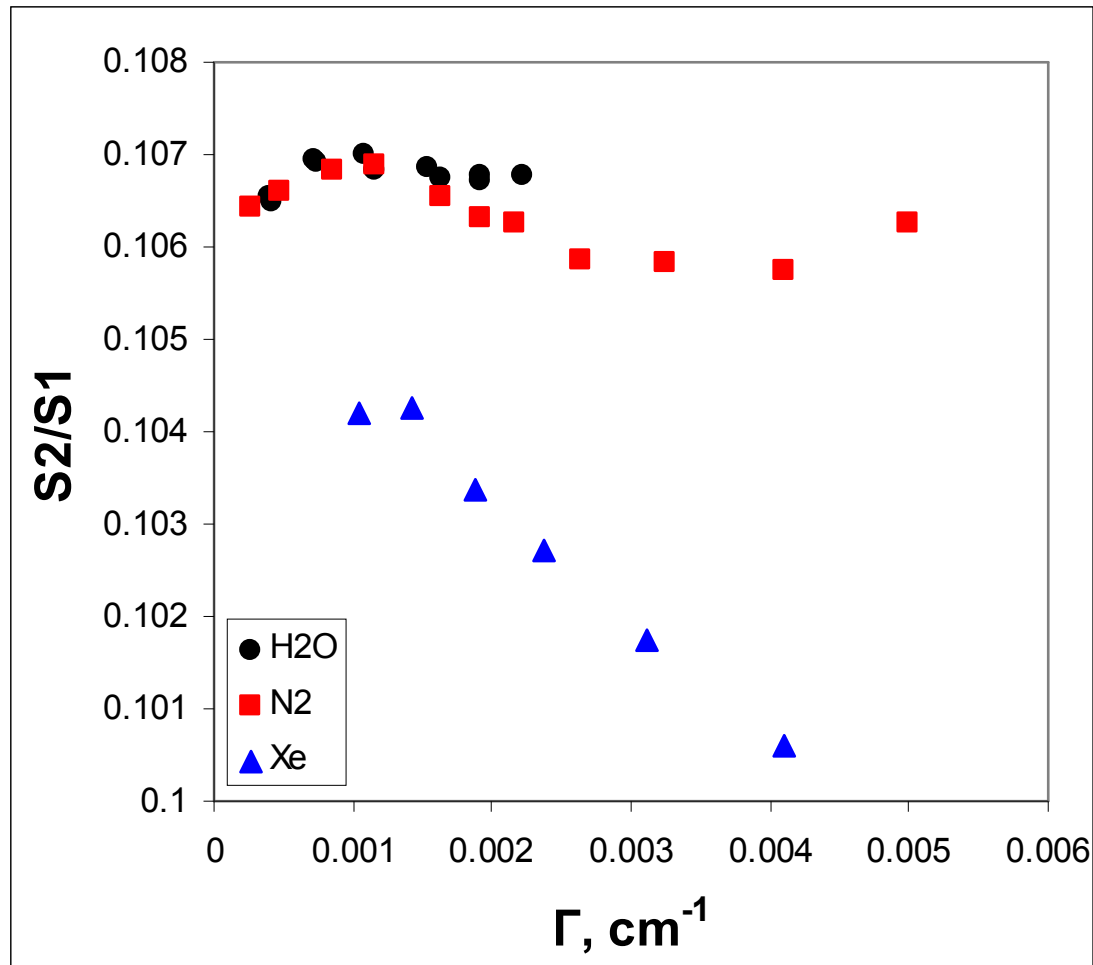
Pressure broadening



Pressure broadening for gas mixtures under investigation two analytical lines.

	H ₂ O, cm ⁻¹ /Bar	N ₂ , cm ⁻¹ /Bar	Xe, cm ⁻¹ /Bar
H ₂ ¹⁶ O 1	0.517(8)	0.166(2)	0.145(6)
H ₂ ¹⁶ O 2	0.484(26)	0.172(2)	0.104(4)

Integral intensity



Pressure dependence of two analytical lines integral intensities ratio.

Lines mixing effect can be observed for H₂O:N₂ and very strong for H₂O:Xe. For pure H₂O no lines mixing.

Ground levels of these two lines are close enough 142 and 135 cm^{-1} , respectively. So lines mixing can take place.

Transition between these two levels is forbidden for dipole-dipole interaction (pure water – black circles).

Accuracy estimate

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

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