Broadening and shift of the lines $H_2{}^{16}O$ near 1.392 μm

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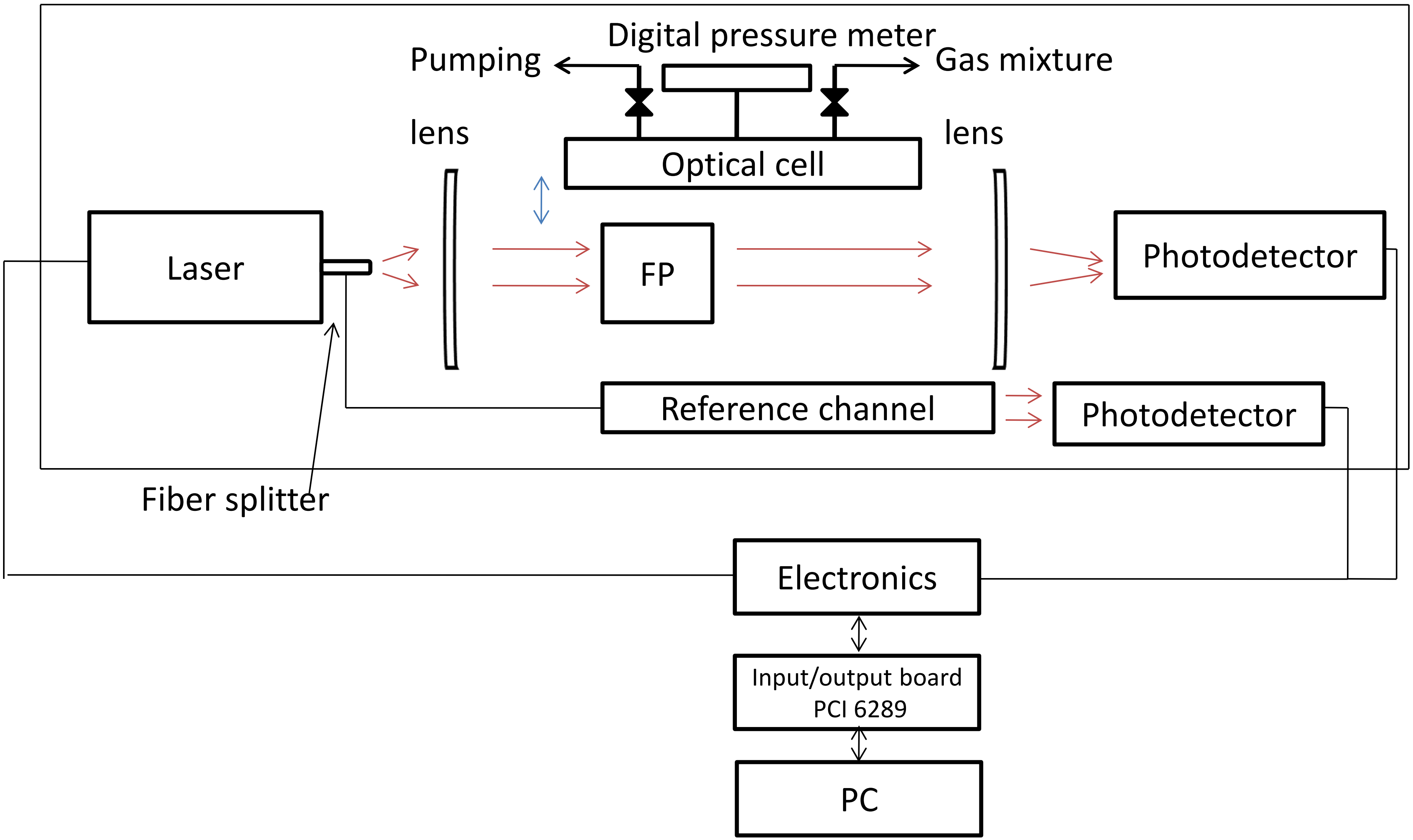
Introduction

- Broadening and shift of the $H_2^{16}O$ lines in the range 7184-7186 cm^{-1} have been measured at high resolution. There was used 1.39-µm diode laser with fiber output (NEL DL). Recording and processing of spectra were carried out with the help of three-channel diode laser spectrometer (DLS) [1]. The analytical channel consisted of a set of vacuum optical cells 20-200 cm long and was oriented on measurements of absorption spectra. The reference channel was used for temperature stabilization of cycles of scanning DL's current and for absolute frequency scale tuning. The channel had a vacuum cell 20 cm^{-1} long with water vapour at temperature 23 ^0C. The third channel with an interferometer was used for linearization of frequency scale. There were used usual Fabry-Perot interferometer ($D^*=0.4936$ $см^{-1}$) and the fiber ring resonator ($D^*=0.0064$ $см^{-1}$). DLS operating was made through multichannel 16-bit input/output board. The sampling rate was 111 kHz. The relative error of detecting line centers was less than $2.5*10^{-5}$ cm^{-1}. The signal-to-noise ratio at acquisition and processing the sample, consisting of 20 spectra, is greater than $2.0*10^4$.
- There have been recorded self and N_2, Ar, He, Xe, air- broadened lines of absorption of water vapour. The Rautian-Sobel'man and Galatry models of molecular collisions have been used for spectral fitting experimental data. For asymmetrical Xe-broadened line profiles to be fitted the universal asymptotic contour of the Rautian have been used [2]. There have been obtained some parameters of lines: absorption cross-section, broadening and shift coefficients and Dicke narrowing coefficient.

References

1. A.S. Kuzmichev, A.I. Nadezhdinskii, Ya.Ya. Ponurovskii *Quantum Electronics* ***41****(7) 650-655 (2011)*
2. S.G. Rautian *Quantum Electronics* ***90****(1) 36-47 (2001)*

Block diagram of DLS



Example of DLS operation

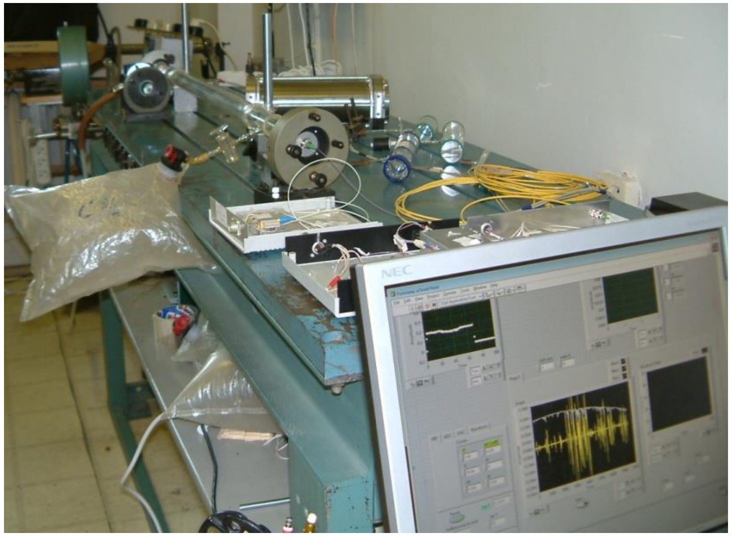
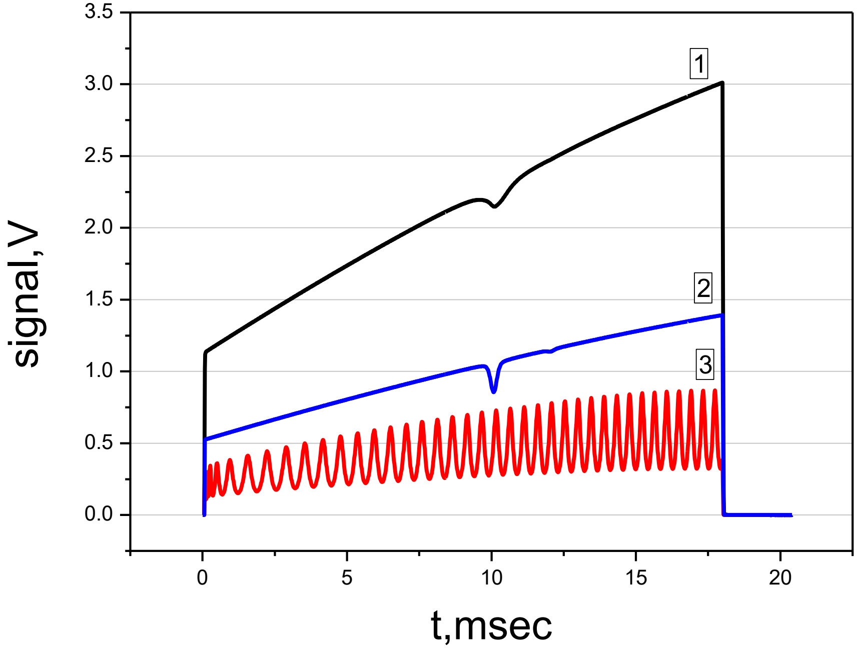
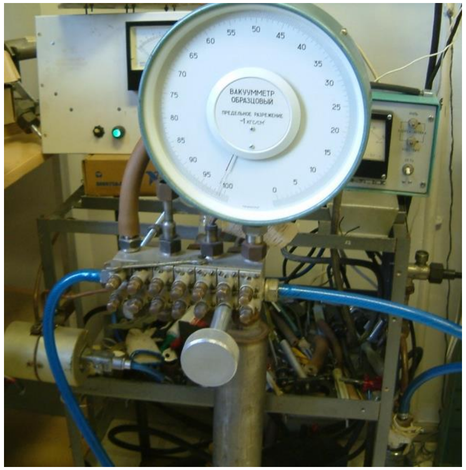


Photo of the 2-channel DLS



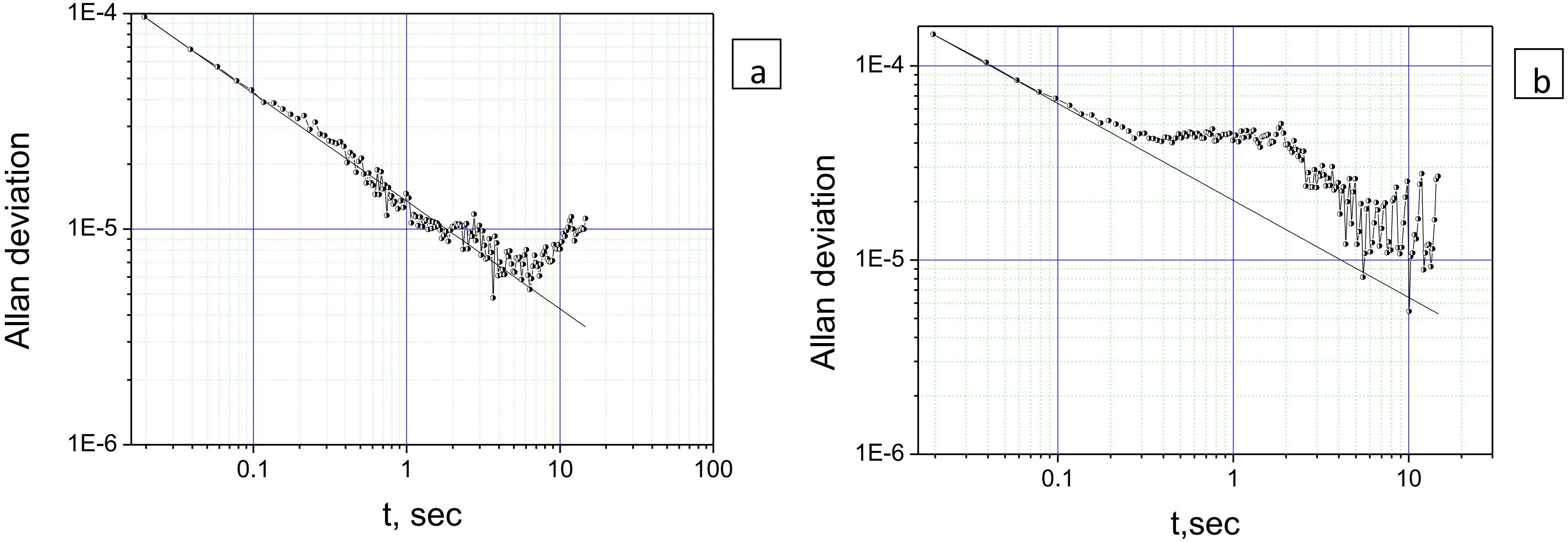
1 – Signal in the analytical channel, 2 – Signal in the reference channel, 3 – Signal in FP



Forvacuum Post

Allan Plots

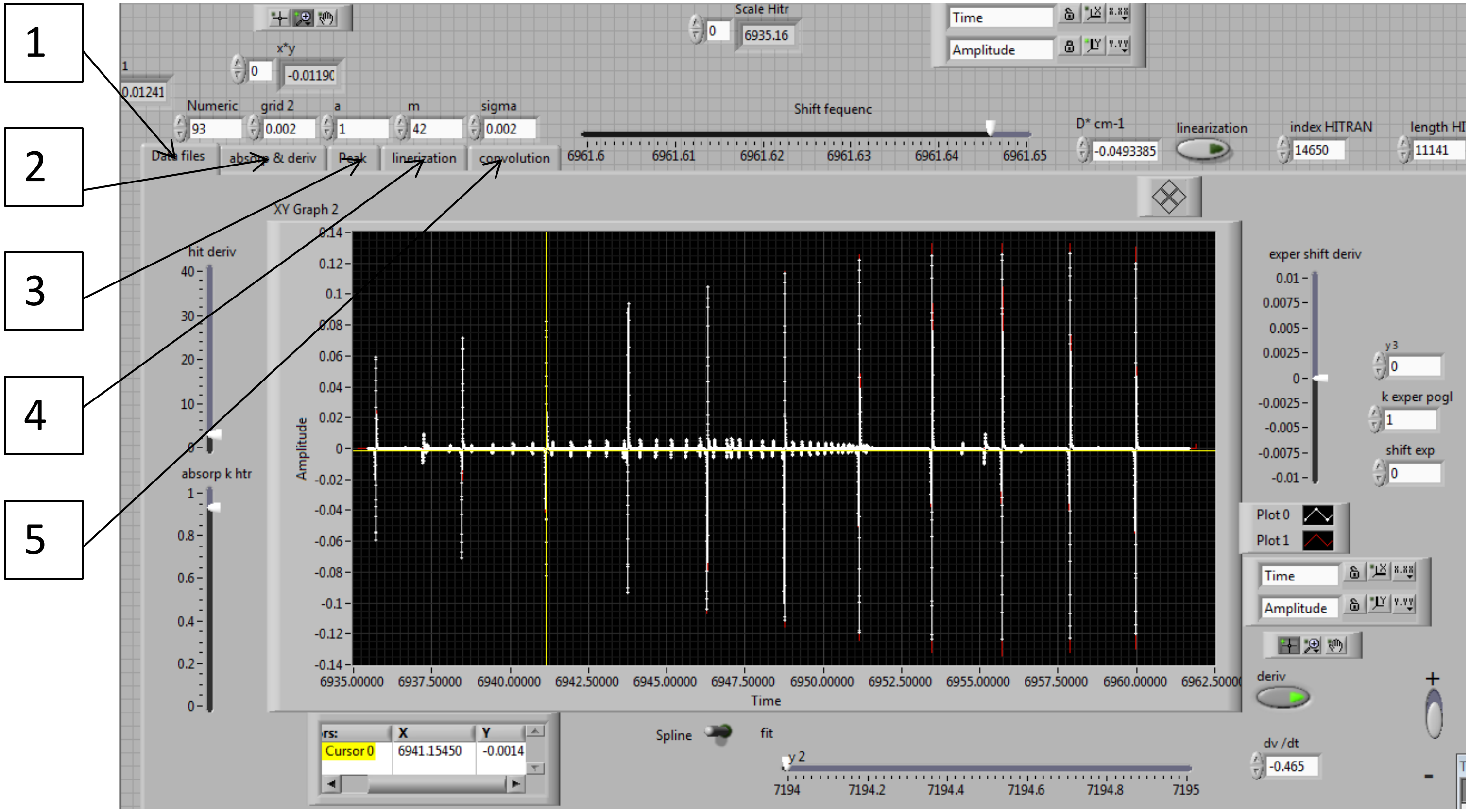
The relative error of detecting line centers was less than $2.5*10^{-5}$ cm^{-1}. The signal-to-noise ratio at acquisition and processing the sample, consisting of 20 spectra, is greater than $2.0*10^4$.



Allan deviation for minimal detectable absorption (a) and for temperature stabilizing system of DLS (b)

The minimal detectable absorption at the path length 2 m approaches $4*10^{-6}$ and temperature instability is about $2*10^{-5}$ ^0C for the averaging time 5 s.

Processing experimental spectrum using Spectral Database “HITRAN”, “GEISA”



Scale Hitr 0 6935.16

x*y 0 -0.01190

1 0.01241

Numeric 93

grid 2 0.002

a 1

m 42

sigma 0.002

D* cm-1 -0.0493385

index HITRAN 14650

length HI 11141

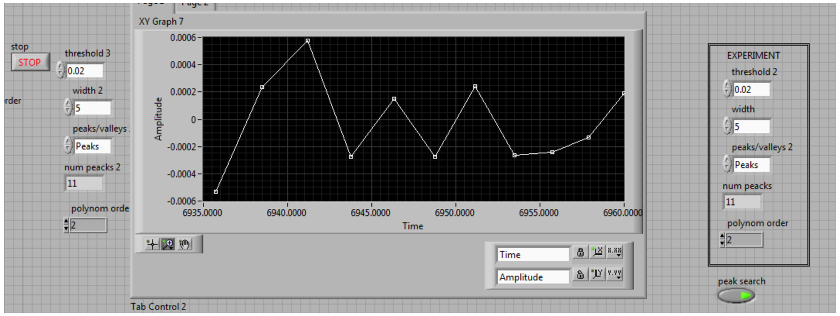
y3 0

k exper pogl 1

shift exp 0

dv /dt -0.465

rs:	X	Y
Cursor 0	6941.15450	-0.0014



threshold 3 0.02

width 2 5

peaks/valleys Peaks

num peacks 2 11

polynom orde 2

threshold 2 0.02

width 5

peaks/valleys 2 Peaks

num peacks 11

polynom order 2

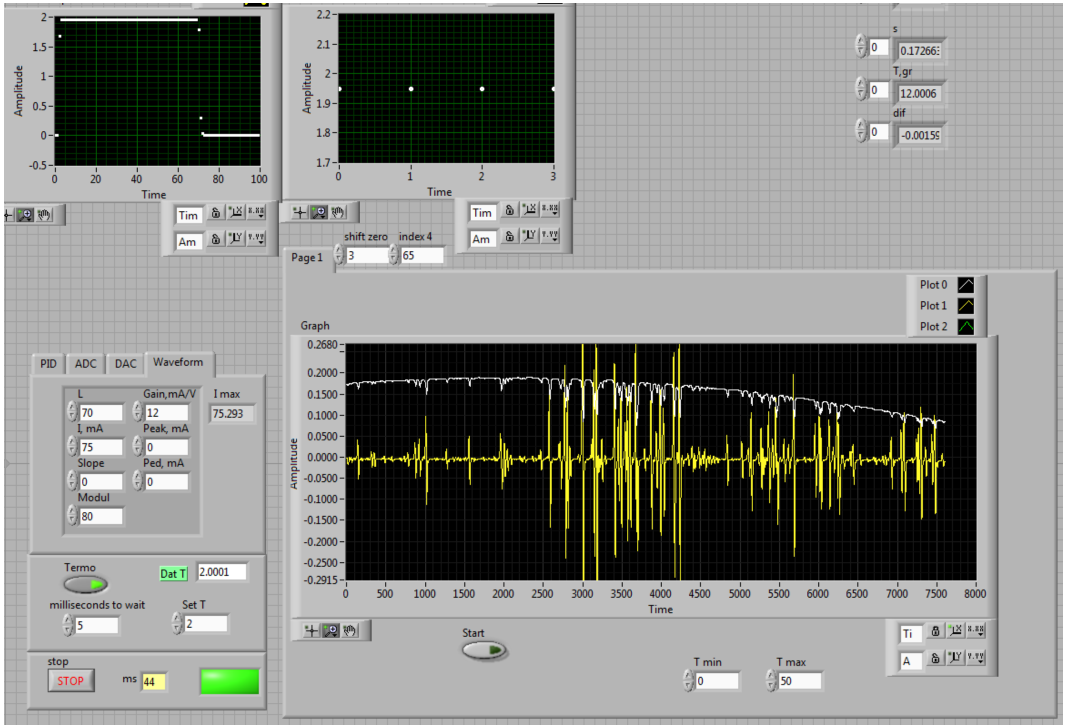
1. Entry of experimental data
2. Calculation of absorption factor
3. Soft Peak detection in FP spectrum
4. Linearization procedure
5. Convolution with Gauss mono impuls

Research of the free spectral range (FSR) of Fabry–Perot interferometer and fiber ring resonator.

The wavelength separation between adjacent transmission peaks is called the free spectral range (FSR) of the etalon, Δλ, and in case of the small angle the light travels through the etalon, FSR is given by:

$$\Delta\lambda = \frac{\lambda^2}{2Ln} \qquad D^* = \frac{\Delta\lambda}{\lambda^2} = \frac{1}{2Ln}$$

For the FSR of Fabry-Perot interferometer to be analyzed there were recorded absorption spectra of different molecules with the help of program “Panorama.vi”. The program helps to control DL operation and to change the temperature of the laser module from 2 to 55°C.



s: 0 / 0.17266

T,gr: 0 / 12.0006

dif: 0 / -0.00159

shift zero: 3

index 4: 65

L: 70

Gain,mA/V: 12

I max: 75.293

I, mA: 75

Peak, mA: 0

Slope: 0

Ped, mA: 0

Modul: 80

Dat T: 2.0001

milliseconds to wait: 5

Set T: 2

stop

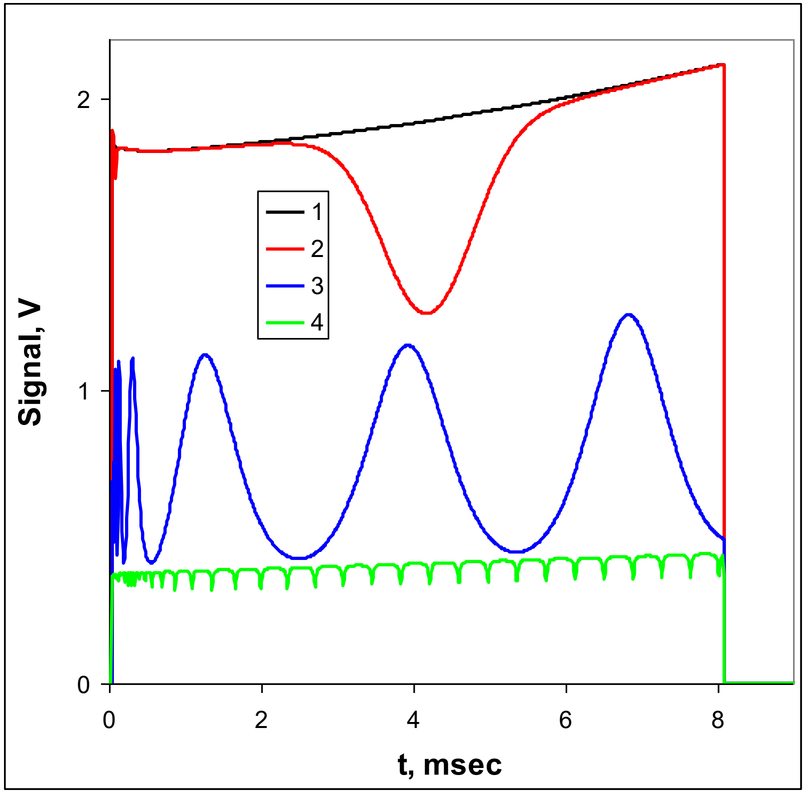
ms: 44

T min: 0

T max: 50

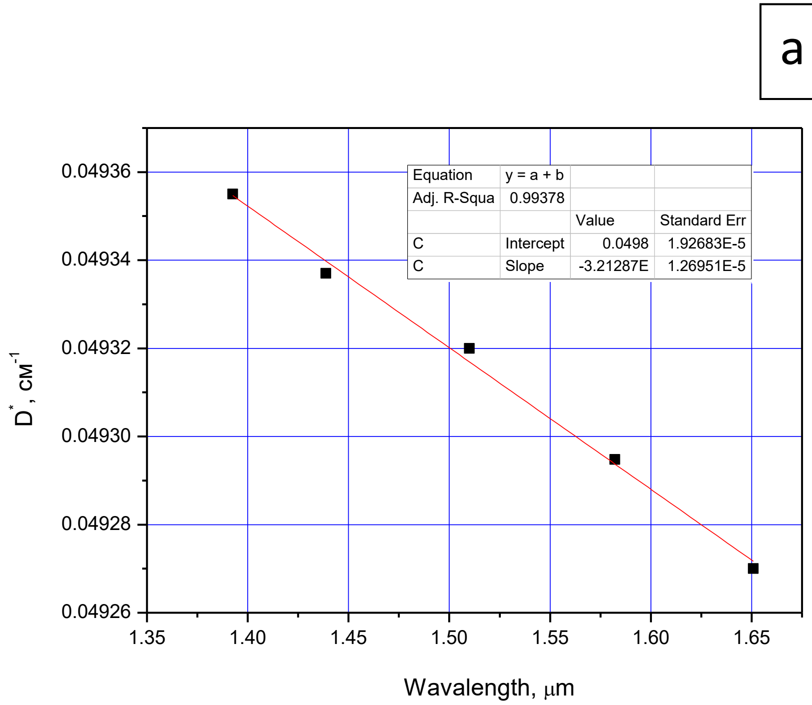
Research of the free spectral range (FSR) of Fabry–Perot interferometer and fiber ring resonator.

Fabry-Perot interferometer (left),
Fiber ring resonator (right).

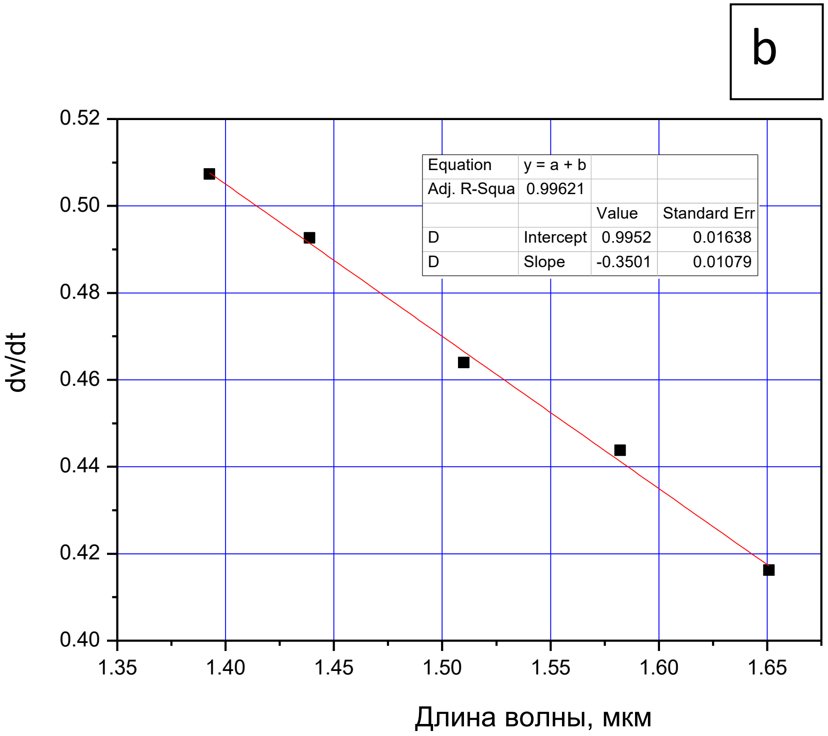


Signals recorded for analysis of DL spectrum
1 – DL intensity
2 – signal with absorption of the molecule
3 – transmission spectrum of Fabry-Perot interferometer
4 – transmission spectrum of fiber ring resonator

Results of the research



Experimental dependence of D* of FP on the wavelength of DL emission



Experimental dependence of dv/dT on the wavelength of DL emission

For FSR of fiber ring resonator to be determined there was used 1.51-µm DL. The DL operated in a repetitively pulsed regime with pulse duration of 10 ms and a repetition rate of 150 KHz, current I=60мА, T=23°C. D*=0,00643(2) см$^{-1}$ for fiber ring resonator.

Instrument function of a DL

The absorption spectrum of any molecule is distorted by the instrument function (IF) of the recording spectrometer. In the case of a DL spectrometer the influence of IF is directly related to the finite line width of radiation produced by the DL.

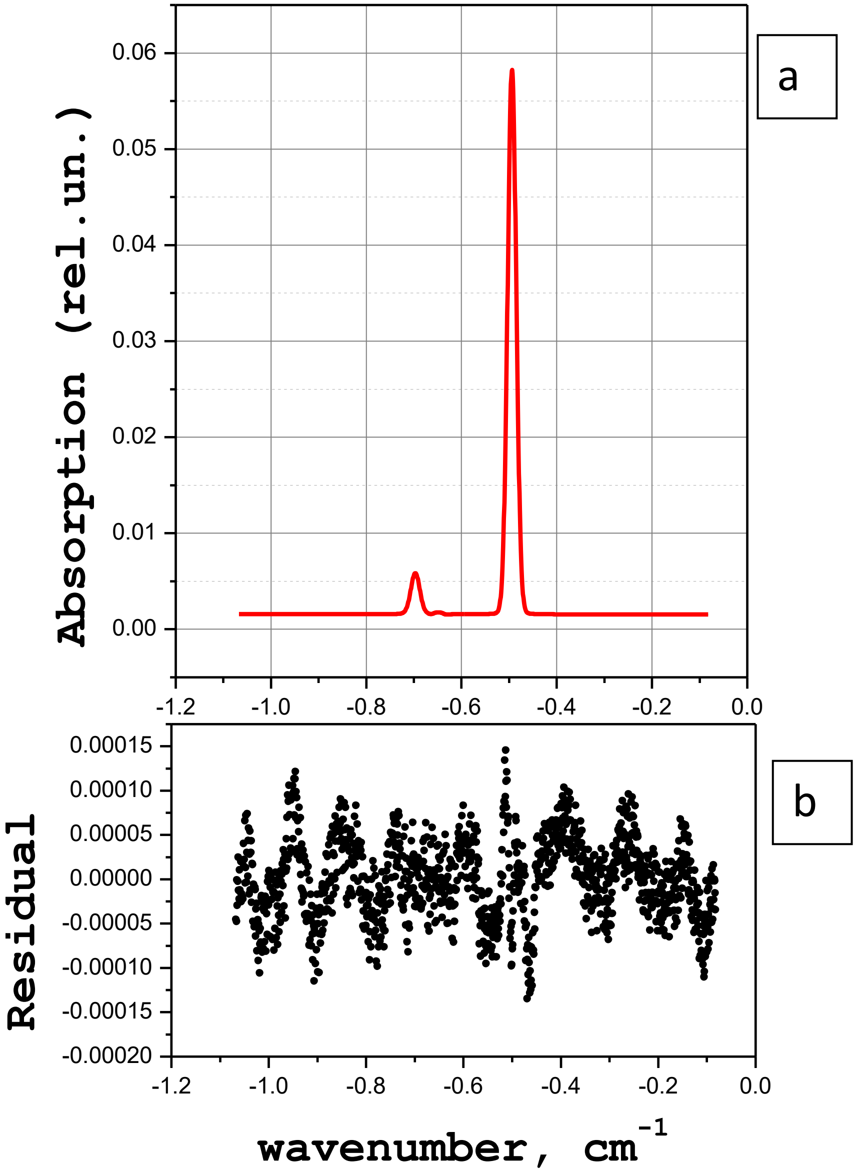
The procedure of determining γ_a included fitting the Doppler-broadened H_2O absorption line profile (7184-7186 cm^{-1}) to the Voigt profile *W(x,y)* and finding the Lorentz component of the line width, determined by the DL instrument function. The Voigt profile of the line was taken as

$$W(x,y) = \frac{i}{\pi} \int_{-\infty}^{+\infty} \frac{\exp(-t^2)dt}{x - t + iy},$$

где $y = \sqrt{\ln 2} \bullet \frac{\gamma_a}{\gamma_d}$, $x = \sqrt{\ln 2} \bullet \frac{\sigma - \sigma_0}{\gamma_d}$ $\gamma_d = 3.5812 \bullet 10^{-7} \bullet \sqrt{\frac{T}{M}} \cdot \sigma_0$

The Doppler line width γ_d (см$^{-1}$) in this case must coincide with its theoretical value at the given gas temperature T.

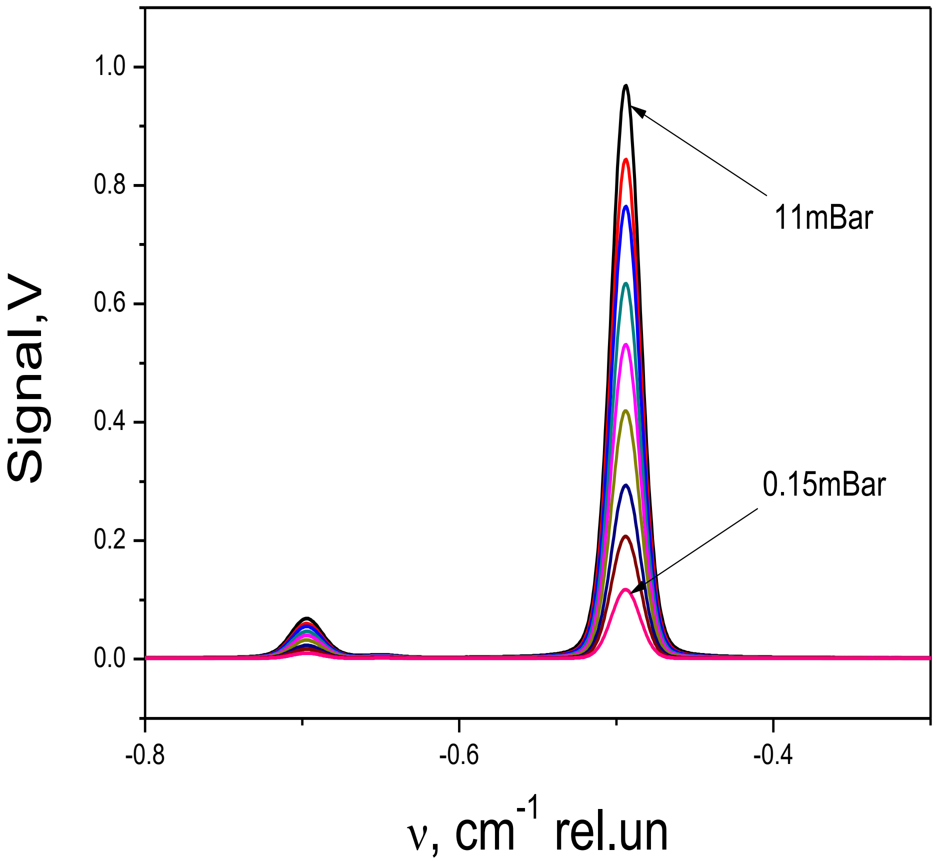
Instrument function of a DL



γ_a =0.00016 (1) см$^{-1}$ (5.3 MHz);

(a) – The experimental absorption spectrum of water vapour used to determine IF of DL, (b) – difference between the experimental and the model spectrum.

Measuring the line intensities for $H_2{}^{16}O$ in the range 7184-7186 см$^{-1}$



Experimental absorption spectra of water vapours at pressures from 0.15 to 11 mBar and the length of the cell L=2 m.

Absolute Line Intensities in the 1.39-μm Region for H_2O in Natural Isotopic Abundances at 296 K: Comparison with Previous Determinations

	S_0 (10^{-3} cm^{-2}atm^{-1})			
	This work	Lepere Et Al.	Hitran	Toth
660←661$^{(a,b)}$ (7185.597cm^{-1})	19.2(6)	19.5(3)	20(1)	18.8(4)
523←616$^{(c)}$ (7185.394cm^{-1})	15.1(2)*10^{-1}	13.1(6)*10^{-1}	13(1)*10^{-1}	11(1)*10^{-1}

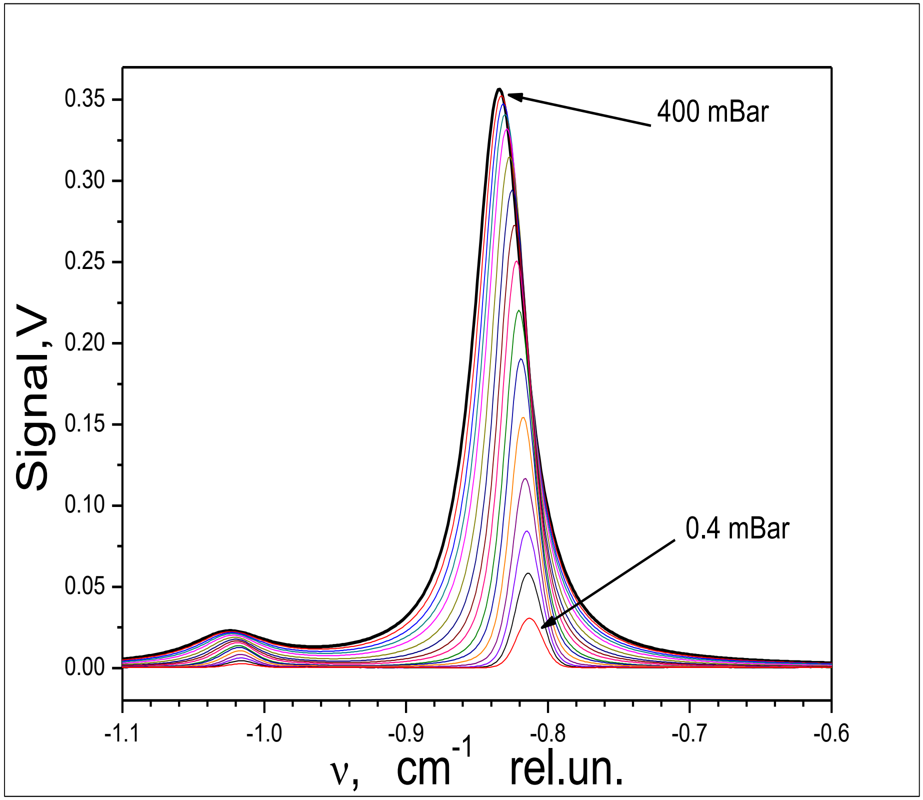
$$k(\sigma-\sigma_0)=A\cdot\mathrm{Re}\left[\frac{W(x,y+z)}{1-\sqrt{\pi z}\cdot W(x,y+z)}\right],$$

где, $W(x,y)$-контур Фойгта, $z=\sqrt{\ln 2}\cdot\dfrac{\zeta}{\gamma_d}$

Broadening and shift lines of $H_2{}^{16}O$ in the range 7184-7186 cm^{-1}

To investigate the processes of broadening and shift of the absorption lines $H_2{}^{16}O$ in the presence of buffer gas there were used N_2, Ar, He, Xe and air.

To obtain a mixture of water vapour with different buffer gases the water vapours with natural isotope composition were mixed in a certain proportion with the buffer gas and let into a preliminarily evacuated vessel having the volume 5 liters. Diffusion mixing lasted during a day at room temperature. The 2-m – long cell was used. Before filling with the mixture it was degased and evaquated; the recording of the baseline was also performed. While a series of spectra was recorded the temperature and the pressure in the cell were controlled. Mixture pressure was controlled by digital pressure meter "ELEMER". Partial pressure of water vapour in gas mixture was 13-17 mBar. Total pressure was 1 atm.



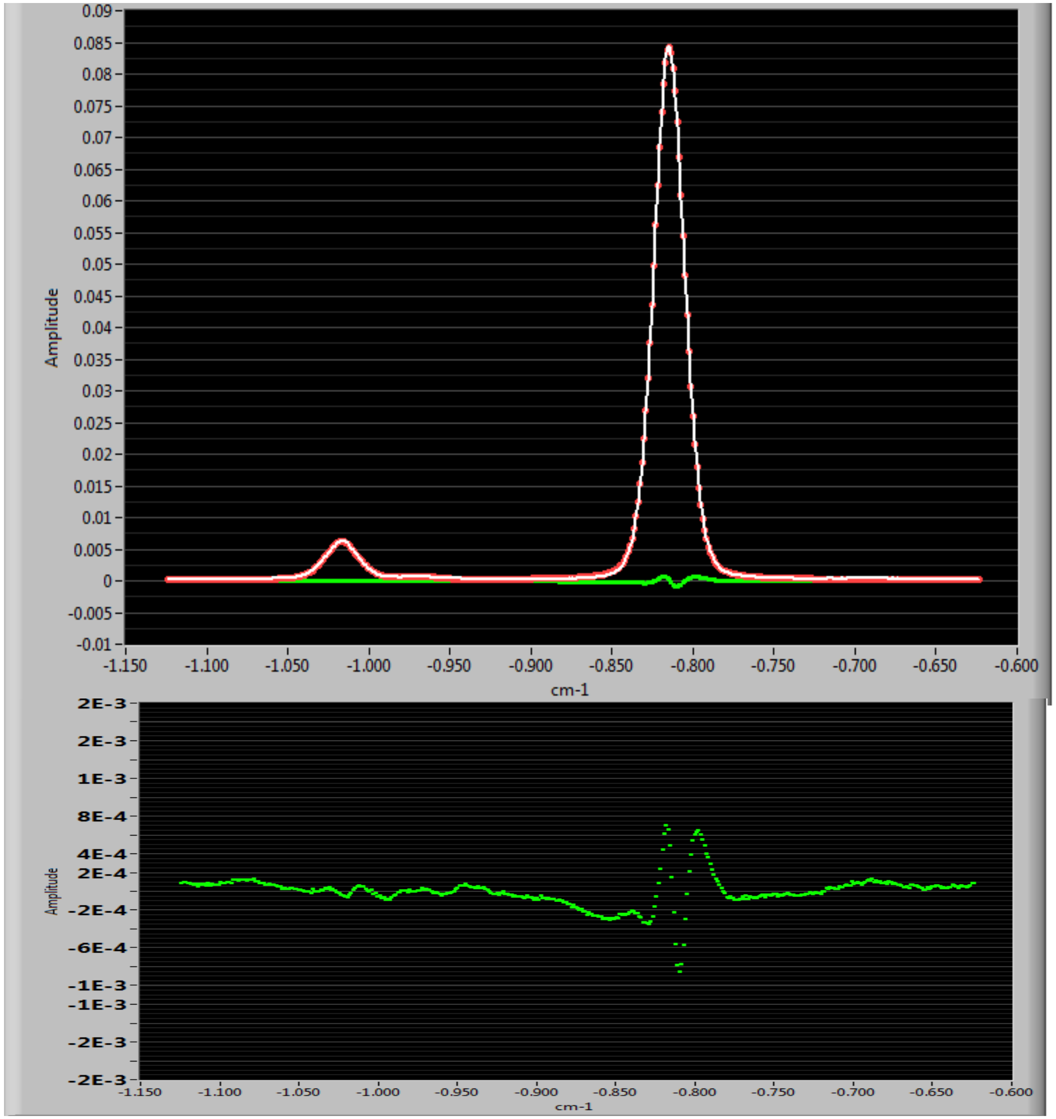
Absorption spectra of water vapour in the mixture with xenon at the mixture pressure 0.4-400 mBar, cell length L=2 m, water vapour concentration 1,47 %.

Fitting the experimental spectra to the model ones

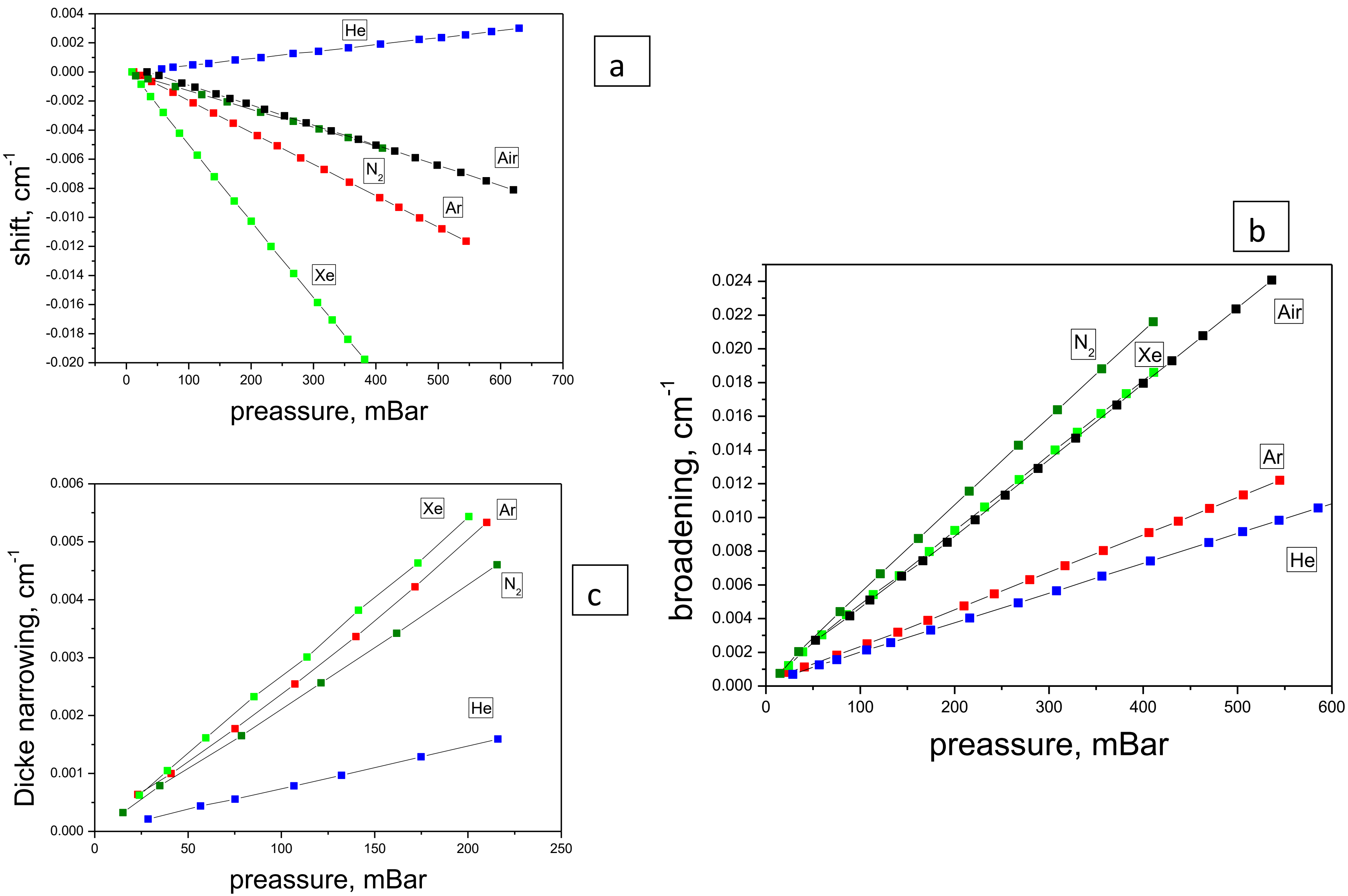
$$k(\sigma-\sigma_0)=A\cdot\mathrm{Re}\left[\frac{W(x,y+z)}{1-\sqrt{\pi z}\cdot W(x,y+z)}\right],$$

где, $W(x,y)$-контур Фойгта, $z=\sqrt{\ln 2}\bullet\frac{\zeta}{\gamma_d}$

The result of fitting the experimental spectrum of water vapour in the mixture with xenon to the model one using the Rautian-Sobel’man profiles and difference of the experimental and the model spectrum.
Cell length L=2 m,
P=39 mBar, T=23^{0}C



Experimental dependences of (a) line shift, (b) broadening and (c) Dicke narrowing on the pressure of gas mixture for different buffer gases.



Broadening and shift of the $H_2^{16}O$ line at 7185.597 cm^{-1} (660←661, v_1+v_3)

Coefficients of line shift (δ), broadening (γ) and Dicke narrowing (ζ) of $H_2^{16}O$ in N_2, Ar, He, Xe, air.

(Diode-Laser Spectroscopy: Line Profiles of H2O in the Region of 1.39 µm
Journal of Molecular Spectroscopy, Volume 208, Issue 1, July 2001, Pages 25-31
Muriel Lepère, Annie Henry, Alain Valentin, Claude Camy-Peyret)

Buffer gas	δ, cm-1*atm-1	γ, cm-1*atm-1	γ (Lepere Et Al.), cm-1*atm-1	ζ , cm-1*atm-1	ζ (Lepere Et Al.), cm-1*atm-1	n, %
self	0.012(4)	2.02(2)*10^{-1}	2.30(2)*10^{-1}	4.2(2)*10^{-2}	-	100
He	4.81(9)*10^{-3}	1.76(2)*10^{-2}	1.42(9)*10^{-2}	8.7(4)*10^{-3}	6(2)*10^{-3}	1.26
N_2	-1.24(1)*10^{-2}	5.0(2)*10^{-2}	4.69(5)*10^{-2}	2.5(2)*10^{-2}	2.4(2)*10^{-2}	1.49
air	-1.362(8)*10^{-2}	4.37(4)*10^{-2}	-	2.14(4)*10^{-2}	-	0.5
Ar	-2.18(1)*10^{-2}	2.20(2)*10^{-2}	1.92(4)*10^{-2}	3.4(4)*10^{-2}	3.0(2)*10^{-2}	1.24
Xe	-5.28(4)*10^{-2}	4.5(1)*10^{-2}	-	3.2(3)*10^{-2}	-	1.47