LASER SPECTROSCOPY

Measurement of the absorption line profiles of water vapour isotopomers at 1.39 μm using the methods of diode laser spectroscopy

A.S. Kuzmichev, A.I. Nadezhdinskii, Ya.Ya Ponurovskii

Abstract. **The issues related to high-precision measurement of the absorption line profiles of water vapour and its isotopomers using the methods of diode laser spectroscopy in the near IR range aimed at the analysis and detection of greenhouse gases are considered. The absorption line shape of $H_2^{16}O$ is investigated as a function of pressure of different buffer gases. The influence of the instrument function of the diode laser (DL) on the precision of measuring the line profile is studied. From fitting the profile of Doppler-broadened $H_2^{16}O$ absorption line to a model profile the lasing line width of the DL with a fibre pigtail is determined. The frequencies and intensities of absorption lines of water isotopomers $H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$, and HDO are measured in the range of DL oscillation. Analytical spectral regions are chosen for distant probing of water vapour using an airborne lab.**

Keywords: diode laser, optical fibre, line profile, spectroscopy.

1. Introduction

Monitoring the content of greenhouse gases H_2O, CO_2, CO, and CH_4 in the troposphere is one of the most urgent topics in the studies of climate changes. Its urgency follows from the necessity for continuous control of greenhouse gases in the atmosphere. This is related to the extensively discussed problems of global warming and the climate changes, caused by the human activity. From the point of view of mobility, the use of airborne labs is of primary importance. The airplane-based laboratory is an ideal platform for the study of spatio-temporal distributions of small concentrations of various gases in the troposphere over large areas, including hard-to-reach ones. For monitoring the climate changes it is also important to know the origin of the greenhouse gases and their flow in the atmosphere, based on the analysis of the isotopic composition of these gases. Such analysis is possible owing to the detailed study of absorption lines using modern diode lasers (DL) that provide narrow lasing lines. The importance of studying the isotopic composition of greenhouse gases is determined by the fact that the ratio of natural isotopic constituents indentifies the origin of the gas. To measure the

content of the main gaseous constituents, an airborne DL spectrometer is being developed. The main unit of the airborne spectrometer is a near-IR DL with a fibre pigtail. To obtain the objective data on the concentration of impurity gases, the precise knowledge of such absorption spectral line parameters as the line centre position, intensity and width is necessary.

Here we present the results of high-precision measurements of absorption line profiles for vapours of water and its isotopomers in the near-IR region. A 1.39-μm DL with distributed feedback and fibre pigtail was used. The work was carried out within the framework of the 'Atmosfera' project (No. 09-09/GF), jointly conducted by the Central Administrative District and General Physics Institute of RAS, and devoted to the creation of a DL spectrometer for measuring small concentrations of greenhouse gases. It was also motivated by the necessity to specify the parameters of the spectral lines of water vapour isotopomers in the vicinity of 1.39 μm for correcting the HITRAN-2008 [1], GEIZA [2], VPL [3] spectral databases.

2. Experimental setup

The schematic diagram of a two-channel DL-spectrometer is presented in Fig.1. The optoelectronic DL module with distributed feedback consisted of the DL (NTT Electronics, USA [4]) with a single-mode fibre pigtail, optical isolator, providing the isolation of 30 dB, and thermal control system, including a Peltier element and a thermoresistor. The DL operated in a repetitively pulsed regime with a pulse duration of 4 – 10 ms and a repetition rate of 40 Hz. The temperature stabilising system provided the temperature stability within $\sim 10^{-4}$ K in the range of temperature values 4 – 50 °C. The DL radiation through the fibre pigtail was coupled to the collimator and beamsplitter, and then was directed into the analytical and reference channels. The beamsplitter was a 2-mm-thick glass plate with a diameter 30 mm.

The analytical channel consisted of a set of vacuum optical cells 5 – 200 cm long. The cells were made of stainless steel and their windows – of CaF_2. Depending on the cell length, the wedge windows were used with the angles 10′ and 1.5°. It was also possible to use the matrix multi-pass Chernin cell [5] with the 25-cm base and the 39-m total optical path length as an analytical cell. The reference channel consisted of the 20-cm-long cell, photodetector and preamplifier. The vapour pressure in the cell was 10 Torr at a temperature of $T = 25$ °C.

The pressure in the cells was controlled using the digital pressure meters Elemer [6] (measurement range 0 – 100 kPa, error 0.2 %) and Sensor [7] (measurement range 0 – 100 mbar,

A.S. Kuzmichev Moscow Institute of Physics and Technology (State University), Institutskii per. 9, 141700 Dolgoprudnyi, Moscow region, Russia; e-mail: askuzmichev@gmail.com;
A.I. Nadezhdinskii, Ya.Ya Ponurovskii A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, ul. Vavilova 38, 119991 Moscow, Russia; e-mail: nad@nsc.gpi.ru, jak@nsc.gpi.ru
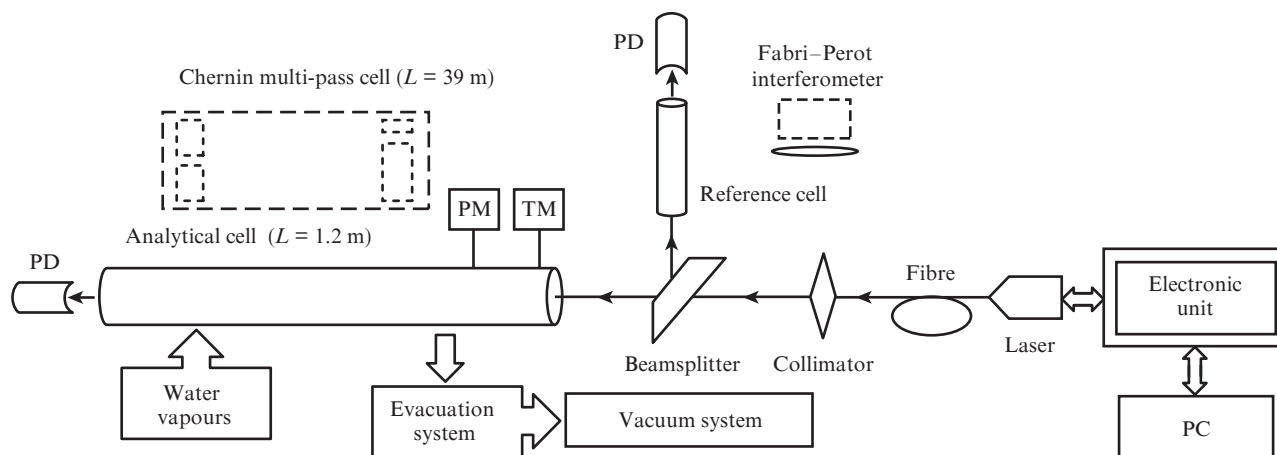
Figure 1. Schematic diagram of the DL spectrometer: (PD) photodetector; (PM) and (TM) pressure and temperature meters, respectively.

error 0.1 %). The temperature was controlled using the NTS-termistor temperature meter (resistance 3 kΩ, error 0.5 %) [8].

The InGaAs photodetectors were used with the diameter of the sensitive area 2 mm and the detection ability $D^* = 3 \times 10^{12}$ W^{-1} cm Hz$^{1/2}$, as well as the Hamamatsu photodetectors (Japan) [9]. The transformation coefficients of preamplifiers in the reference and analytical channels were 12 V mA^{-1} with the bandwidths of 120 kHz. The electronic control and recording unit consisted of the NI DAQ 6052-E input/output board (National Instruments, USA [10]), the power supply, the board of interface between the electronic unit and the i/o board, the current sources for the DL, the Peltier thermoelement, the preamplifiers of the reference and the analytical channel, the board of power supply distribution. The programme for the DL control and signal recording is written in the LabView 9.0 graphical software environment using the drivers from National Instruments, USA.

The performance of the two-channel DL spectrometer is illustrated in Fig. 2. The signal from the analytical channel is actually the absorption spectrum of the substance studied; the signal from the reference channel including a Fabri–Perot interferometer is used to linearise the frequency scale of spectra.
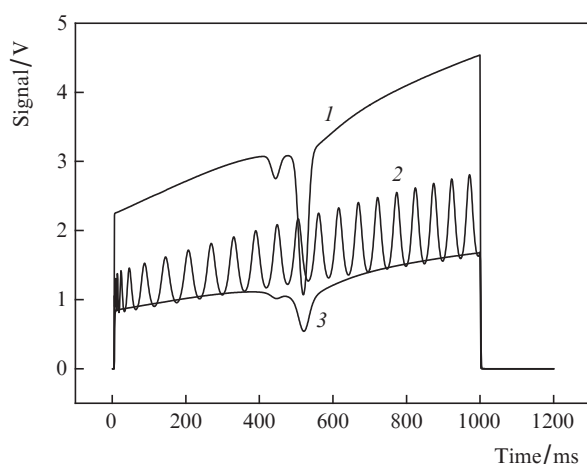
The signal from the reference channel with the reference cell serves for absolute frequency referencing of the spectra and additional temperature stabilisation of DL radiation using the absorption line of a reference gas. The basic spectrometer characteristics are the following: the relative error of frequency measurement is less than 2×10^{-5} cm^{-1}, the signal-to-noise ratio at acquisition and processing the sample, consisting of 64 spectra, is greater than 10^5.

3. Absorption spectra of water vapours in the near-IR region

The spectral region at 1.39 μm contains sufficiently intense IR absorption bands of water isotopomers $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$ and HDO that belong to overtones and combined frequencies of molecular vibrations. To find the optimal spectral range for detecting water vapour by means of diode laser spectroscopy (DLS) we performed preliminary modelling of the absorption spectra using the HITRAN-2008 database and the altitude profiles of water isotopomer concentrations (the standard atmosphere model). The spectral range 7170–7190 cm^{-1} is optimal for H_2O gas analysing by means of DLS, and the region 7183.0–7184.6 cm^{-1} allows simultaneous detection of four isotopic modifications of water. Figure 3 presents the experimental absorption spectrum of water vapour having a natural
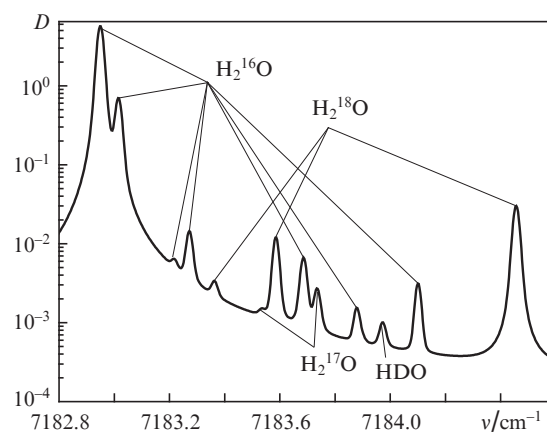

Figure 2. Typical signals from the two-channel DL spectrometer: the signal from the analytical channel (200-cm-long cell with water vapour at a pressure of 10 Torr) (*1*), signals from the reference channel, including the Fabri–Perot interferometer (*2*) or the cell with a reference gas (*3*).

Figure 3. Optical density *D* of water vapours in the DL oscillation spectral range at the wavelength 1.39 μm.

Table 1. Spectroscopic parameters of absorption lines of water vapour isotopomers.

Isotopomer	ν_0/cm^{-1}	S_H/ cm^{-1} molec. cm^2	S_{exp}/ cm^{-1} molec. cm^2	$(S_H - S_{exp})/S_H$ (%)	γ^0_{airH}/ cm^{-1} atm^{-1}	γ^0_{selfH}/ cm^{-1} atm^{-1}	δ^0_{airH}/ cm^{-1} atm^{-1}
$H_2^{16}O$	7183.6858	3.671×10^{-24}	$3.27(3) \times 10^{-24}$	10.8	0.0888	0.455	0.0108
$H_2^{18}O$	7183.5857	6.334×10^{-24}	$5.73(6) \times 10^{-24}$	9.47	0.054	0.32	0.01176
$H_2^{17}O$	7183.7354	1.194×10^{-24}	$1.04(1) \times 10^{-25}$	12.9	0.1	0.47	0.0045
HDO	7183.9727	3.385×10^{-25}	$2.73(2) \times 10^{-25}$	19.3	0.0961	0.52	–
$H_2^{16}O$	7184.1009	1.49×10^{-24}	$1.38(1) \times 10^{-24}$	7.69	0.0389	0.25	0.01496
$H_2^{18}O$	7184.4563	1.99×10^{-23}	$1.945(2) \times 10^{-23}$	2.36	0.098	0.537	0.00691

N o t e s : S_H is the line intensity in the HITRAN-2008 database; S_{exp} is the line intensity measured in the present work; γ^0_{airH} and γ^0_{selfH} are the broadening coefficients in air and in water vapours according to HITRAN-2008 data; δ^0_{airH} is the frequency shift coefficient according to HITRAN-2008 data; ν_0 is the frequency of the line centre; the errors of intensity measurement are given in parentheses.

isotopic composition, recorded with the two-channel DL spectrometer. The cell used had the optical path length 2 m, the pressure of the vapour being 7 Torr at the temperature T = 23 °C.

Table 1 lists the basic parameters of the lines under study. The most intense doublet at 7183 cm^{-1} belongs to the dominant isotopomer $H_2^{16}O$. It may be used for open-trace gas analysis of water vapour at small optical path lengths (up to 50 cm) for variations in water concentration in the atmosphere up to the altitude of ~7 km. The multiplet in the spectral region 7182 – 7185 cm^{-1} consists of six lines of the isotopomers $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$ and HDO. It is optimal for simultaneous detection of the isotopomers in atmosphere. In this case, a multi-pass cell with the total optical path length not less than 40 m should be used.

Figure 4 presents the results of modelling the optical densities at the maxima of absorption lines $H_2^{16}O$ (7182.94 cm^{-1}), $H_2^{18}O$ (7184.45 cm^{-1}), $H_2^{17}O$ (7183.73 cm^{-1}) and HDO (7183.97 cm^{-1}) versus the detection altitude. The precision of the reconstruction of the vertical profile of water vapour concentrations is directly determined by the error of the spectral parameters of the lines used, which vary from 5% to 20% in the databases and grow with decreasing wavelength [1]. At 1.39 µm these errors are maximal. In this connection our goal was to determine the spectroscopic parameters of the absorption lines of water vapours with higher precision in the vicinity of 1.39 µm for further use in detecting the greenhouse gases by means of DLS methods.

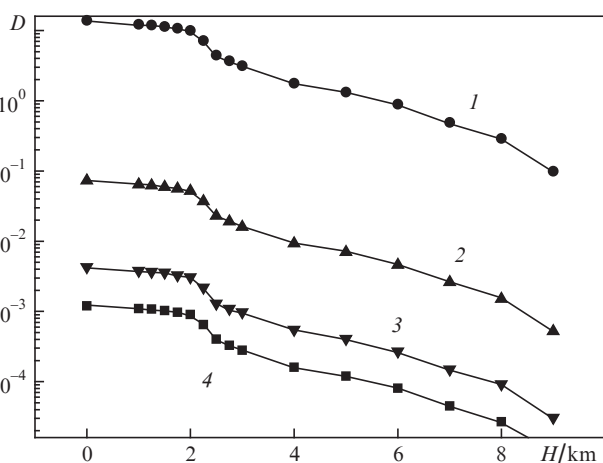**Figure 4.** Optical density D in the maxima of the absorption lines $H_2^{16}O$ (7182.94 cm^{-1}) (*1*), $H_2^{18}O$ (7184.45 cm^{-1}) (*2*), $H_2^{17}O$ (7183.73 cm^{-1}) (*3*) and HDO (7183.97 cm^{-1}) (*4*) versus the detection altitude H.

4. The DL instrument function

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. To obtain the true spectra one has to know the IF of the spectrometer. Then, according to the Bouguer – Lambert – Beer law, the real absorption coefficient K is determined from the convolution of the absorption spectrum and the IF:

$$K(\nu_i) = -\ln\left\{\int f_a(\nu - \nu_i)\exp[-k(\nu)L]\right\}L^{-1}, \qquad (1)$$

where f_a is the IF of the spectrometer; ν_i is the frequency; L is the cell length; $k(\nu)$ is the absorption index. We used a Gaussian IF profile with the width γ_a:

$$f_a(\nu - \nu_i) = \sqrt{\frac{\ln 2}{\pi}}\frac{1}{\gamma_a}\exp\left[-\ln 2\left(\frac{\nu - \nu_i}{\gamma_a}\right)^2\right]. \qquad (2)$$

The procedure of determining γ_a included fitting the Doppler-broadened H_2O absorption line profile (7182.94 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 [11]

$$W(x,y) = \frac{i}{\pi}\int_{-\infty}^{+\infty}\frac{\exp(-t^2)dt}{x - t + iy}, \qquad (3)$$

where

$$y = \sqrt{\ln 2}\,\frac{\gamma_a}{\gamma_D}; \quad x = \sqrt{\ln 2}\,\frac{\nu - \nu_0}{\gamma_D};$$

$$\gamma_D = 3.5812 \times 10^{-7}\sqrt{\frac{T}{M}}\,\nu_0; \qquad (4)$$

ν_0 is the frequency of the line centre; M is the mass of the molecule. The Doppler line width γ_D (in cm^{-1}) in this case must coincide with its value at the given gas temperature T.

Figure 5 shows the experimental and the model spectra of the absorption doublet (7182.9496 cm^{-1}, 7183.0157 cm^{-1}). As a result of fitting the experimental spectrum to the model one we obtained γ_a = 0.00016(4) cm^{-1} (5.3 MHz) и γ_D = 0.01037(4) cm^{-1}, which differs from the calculated value γ_D = 0.01041 cm^{-1} at T = 25 °C by 0.38%.

To linearise the frequency scale of the absorption spectra, we used a Fabri – Perot interferometer with the region of free dispersion 0.04925 cm^{-1}.
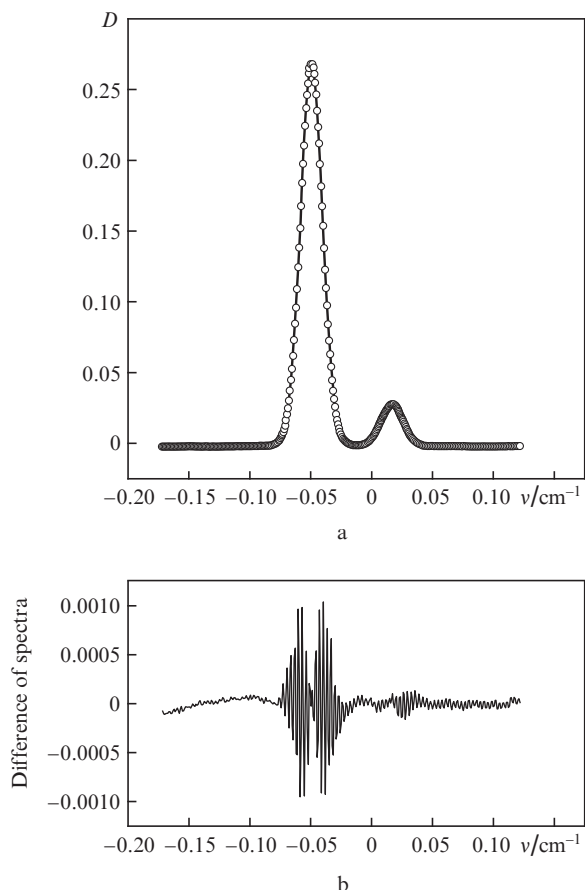
Figure 5. The experimental absorption spectrum of water vapour (points) and the result of its fitting to the model spectrum using Voigt profiles (solid curve) (a) and the difference between the experimental and the model spectrum (b). The length of the cell is 1 m, the pressure of water vapour is 0.5 Torr, $T = 25\,°C$.

To determine the minimal detectable absorption of water vapour, the Allan procedure was used [12]. In Fig. 6 the Allan variance is plotted versus the averaging time. It is seen that the minimal detectable optical density at the path length 2 m approaches 3×10^{-7} for the averaging time 3 s.
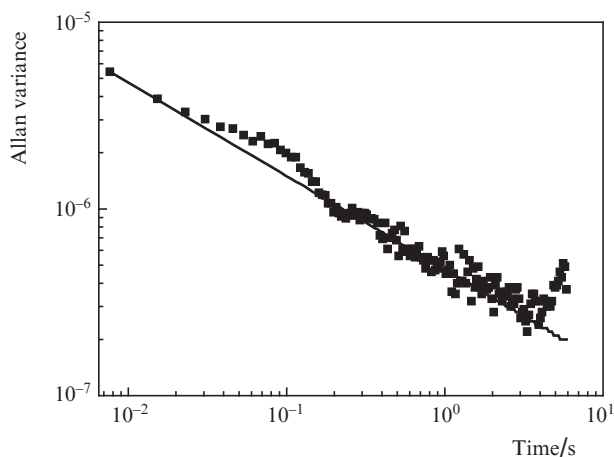

Figure 6. Allan variance for the optical density D versus the time of averaging.

5. Measuring the line intensities for $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$, and HDO in the range 7182–7185 cm^{-1}

Using the DL spectrometer described above (Fig. 1), the absorption spectra were obtained for the water vapour isotopomers in the range 7182–7185 cm^{-1}. The water vapour at the temperature 24 °C was let into a 2-m-long evacuated cell. The pressure of the vapours varied from 0.4 to 9.5 Torr. Before recording each spectrum, the cell was blown off with dry nitrogen, and the baseline (the line of zero absorption) was recorded. Figure 7 presents the result of processing of more than 15 spectra of water vapours at different pressures. It is seen that practically all isotopes, presented in Fig. 3, are experimentally detectable.
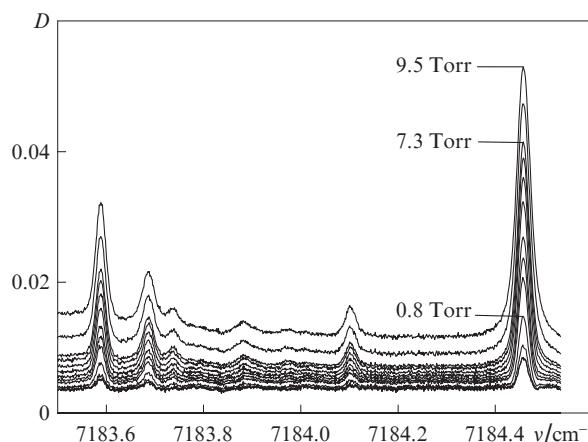

Figure 7. Experimental absorption spectra of water vapours at the pressures from 0.4 to 9.5 Torr and the length of the cell $L = 2$ m.

To determine the intensities of the absorption lines of water vapours we used the Rautian–Sobel'man model of molecular collisions [13]. In this model the profile of the absorption line has the following form:

$$K(\nu - \nu_0) = A\,\mathrm{Re}\left[\frac{W(x, y + z)}{1 - \sqrt{\pi z}\,W(x, y + z)}\right], \qquad (5)$$

where the parameter $z = \sqrt{\ln 2}\,\zeta/\gamma_D$ describes the effect of narrowing of the absorption line (Dicke effect) under variation of the pressure p; $\zeta = \zeta^0 p$ is the narrowing parameter; ζ^0 is the narrowing coefficient (in cm^{-1} atm^{-1}).

To fit the experimental line profiles to the model ones using the Rautian–Sobel'man and Voigt profiles, a computer programme was developed that allows simultaneous processing of up to 10 absorption lines in real time. The fitting procedure was run in the line-by-line regime, when each experimental value of D was a sum of contributions from each absorption line in the considered spectral range. In the process of fitting four parameters were varied for each line, namely, the intensity, the line shift δ, the collision-induced width γ, and the narrowing parameter ζ. The Doppler line width was fixed and calculated using Eqn (4). Hence, for fitting the profile of the multiplet lines (Fig. 8) to the model profiles 24 variational parameters were used. Figure 8a presents the result of fitting the multiplet spectrum to the model spectrum using the Rautian–Sobel'man profiles. The fitting programme was embedded into the main programme controlling the perform-
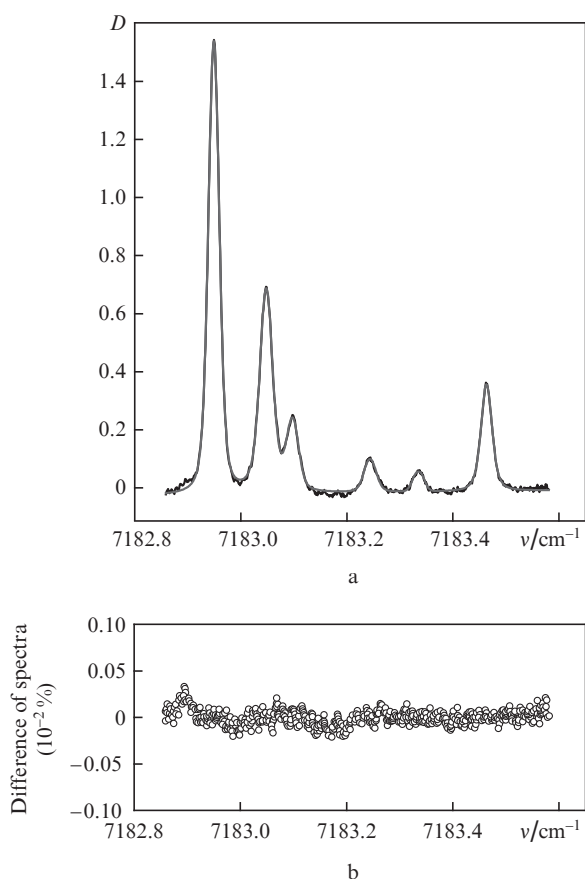
Figure 8. The result of fitting the experimental spectrum of the multiplet to the model one using the Rautian–Sobel'man profiles (a) and difference of the experimental and the model spectrum in per cent of the maximal optical density (b).

ance of the DL spectrometer. The fitting of the profiles of multiplet lines was carried out in real time. The time of processing of one spectrum was less than 300 ms. For more precise determination of the parameters of lines a change in the DL pump current pulse front slope was provided that led to the change in the range of the DL frequency tuning. This procedure allowed variation of the line number in the multiplet, thus significantly increasing the precision of the fitting parameters determined.

The results of processing the absorption line profiles for water vapour isotopomers, presented in Table 1, revealed substantial discrepancies between our parameters and the data from the HITRAN-2008 spectral database. These disagreements may be due to different conditions of experimental measurement. Based on the data on the intensity of the absorption lines, one can estimate the minimal detectable concentrations of the isotopomers for different path lengths. For example, for the HDO isotope at the wavelength 1.39 μm and the path length 2 m the detectable concentration is 50 ppm at the buffer gas pressure 40 Torr.

6. Broadening and shift of the line at 7182.94 cm^{-1} of the H$_2$^{16}O molecule

To investigate the processes of broadening and shift of the absorption lines of water vapours in the presence of buffer gas, particularly, air or xenon, the line 7182.9496 cm^{-1} was used. This line forms a doublet with the line 7183.0157 cm^{-1};

therefore, the procedure of fitting their profiles was performed for both lines together.

To obtain a mixture of water vapours with air or xenon 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 litres. Diffusion mixing lasted during a day at room temperature. The concentration of water vapour was 1.15% in the mixture with air and 2.24% in the mixture with xenon. The 100-cm-long cell was used. Before filling with the mixture it was degased and evaquated; the recording of the baseline was also performed. While recording a series of spectra, the temperature and the pressure in the cell were controlled.

Figure 9 presents the absorption spectra of water vapours in a mixture with xenon. The total pressure of the mixture varied from 2 to 450 Torr. The fitting of the line profiles was accomplished using the Rautian–Sobel'man model. As a result, the parameters $\gamma = \gamma^0 p$, $\delta = \delta^0 p$ and $\zeta = \zeta^0 p$ for the line 7182.9496 cm^{-1} were obtained. Figure 10 illustrates these parameters versus the pressure of buffer gases, i.e., air and xenon. Table 2 summarises the broadening, shift and narrowing coefficients, found from processing of the line profiles.

Table 2. The coefficients of shift, collision broadening and narrowing of the line 7182.9496 cm^{-1} of H$_2$^{16}O molecule in air and in xenon, obtained in the present work, and the values of δ^0 and γ^0 from the database HITRAN-2008 for air (italics).

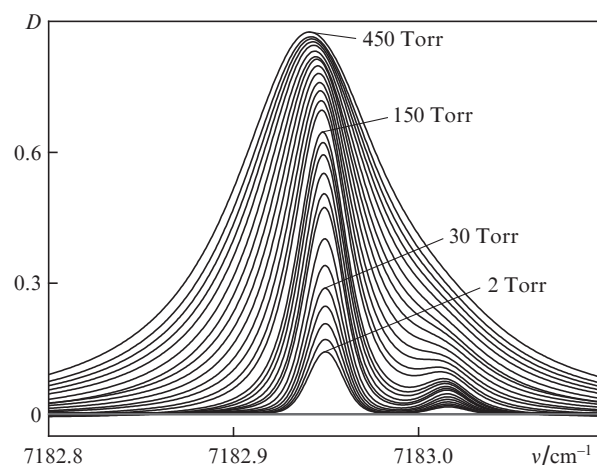| Buffer gas	δ^0/cm^{-1} atm^{-1}	γ^0/cm^{-1} atm^{-1}	ζ^0/cm^{-1} atm^{-1}
Air	0.00889(4)	0.103(2)	0.0331(2)
	0.00867	*0.097*	–
Xenon	0.01869(5)	0.095(2)	0.0192(2)

Figure 9. Absorption spectra of water vapours in the mixture with xenon at the mixture pressure 2–450 Torr, cell length L = 1 m and the water vapour concentration 2.54%.

Note that the broadening of H$_2$^{16}O line in xenon was accompanied with asymmetry of the line profile (see Fig. 8).

7. Conclusions

Now we briefly summarise the main results of the work.

The experimental setup for investigating the absorption spectra of water using a 1.39-μm DL with a fibre pigtail is developed. The noises of the optoelectronic tract are analysed by means of the Allan procedure. The influence of the instru-
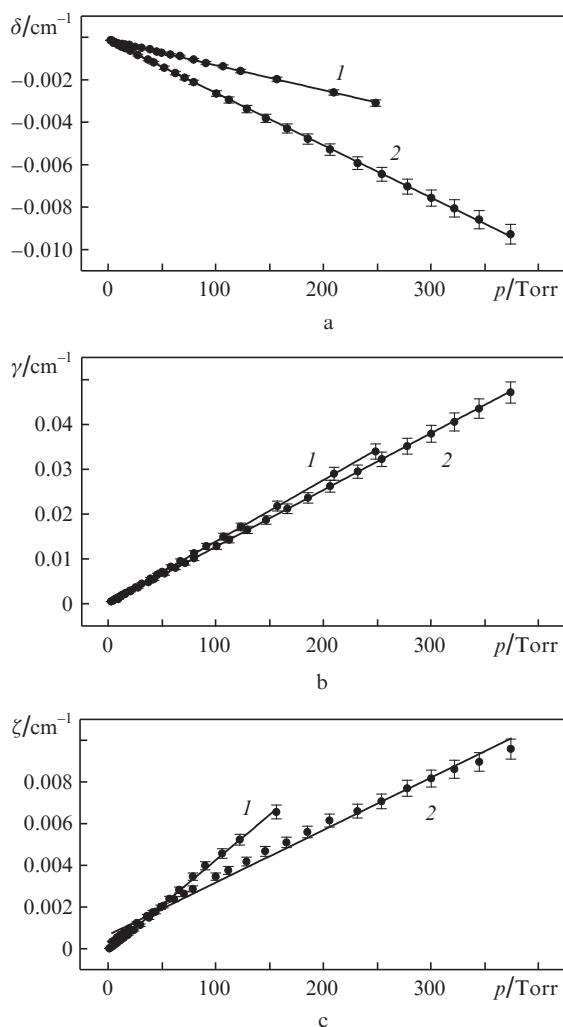
Figure 10. Experimental dependences of the parameters δ (a), γ (b), and ζ (c) on the pressure of buffer gases: air (*1*) and xenon (*2*).

ment function of the DL, leading to the distortion of the absorption spectral line profile, is taken into account. By fitting the profile of the Doppler-broadened line of the $H_2^{16}O$ molecule (7182.9496 cm^{-1}) to the model profile, the linewidth of the DL oscillation is determined. The computer programmes that allow simultaneous fitting of up to 10 profiles of absorption lines to the model ones using the Voigt and Rautian–Sobel'man functions are developed. The spectral regions for the gas analysis of water vapour isotopomers are determined and the sensitivity limit of their detectivity is estimated. The intensities of the absorption lines of the molecules $H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$ and HDO in the spectral range 7182–7185 cm^{-1} are measured and compared with the data of the HITRAN-2008 database. The coefficients of broadening, shift and narrowing of the line 7182.9496 cm^{-1} of water molecule in the presence of air and xenon are obtained. The asymmetry of the absorption line profile broadened by xenon is observed.

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