Measurements of water isotopic composition by diode laser spectroscopy method

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A prototype of a device intended for express-measurements of water isotopic composition ($H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$, $HD^{16}O$, $D_2^{16}O$) by diode laser spectroscopy (DLS) methods is proposed for the first time. A diode laser (DL) with a distributed feedback (product of "Laser Components") with $\lambda = 1.39$ μm was used in the measurements. The DL was pumped by trapezoidal pulses with a pulse length of 0.5–1 ms, a pulse repetition frequency of 1–2 kHz, and tuning range in a mode of 1.5 cm^{-1} (7183.2–7185 cm^{-1}). These parameters allowed a simultaneous determination of concentration of five water isotopomers. Real-time detection and processing of absorption spectra for water isotopes were conducted with the use of a National Instruments data acquisition board and LabVIEW software. A single measurement of isotopic ratio factor took less than 3–5 min. The range of H_2O isotope measured concentrations made 0.01–100%.

Obtaining of oxygen isotopes by water vacuum rectification is an important area in the industrial production of stable isotopes. The ^{18}O (oxygen-18) isotope has found a wide application in medicine, first of all, in diagnosis by the positron-emission tomography method (PET-scanners) and in studying metabolic processes in living organisms: reactions of glucose oxidation; kinetics of different interaction cycles; lactic acid kinetics; metabolism of water, vitamins, and medicines. In the former case, a 95% ^{18}O-enriched water is used, in the latter case – a 10–15% ^{18}O-enriched one.

Production of the ^{18}O-enriched water by the vacuum rectification method occurs in many-step cascades with a fixed number of packed columns in each. Total number of columns can reach several tens depending on the required total productivity. In the cascade set at the Institute of Molecular Physics of the Russian Research Center "Kurchatov Institute," more than 20 packed columns operate with a calculated productivity of 8 kg/year of water with 95% ^{18}O-enrichment. For the cascade to operate properly, a regular isotope analysis of water in each column is required, both in the product and in the waste. Such measurements determine the degrees of enrichment and exhausting, which are the principal parameters of the packed column operation.

Thus, the number of test samples is very high, and this problem becomes sufficiently serious without reliable and rapid way of measuring the water isotope composition. The mass-spectrometer measurements are rather expensive and time-consuming; densitometry is a simple and rapid method, but insufficiently accurate. Therefore, a search for some accurate and rapid method for measuring the water isotope composition ($H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$, $HD^{16}O$, and $D_2^{16}O$) made us to turn to diode laser spectroscopy and to take advantage of the near-infrared DL.

Since it is necessary to control the ^{18}O-exhausting in the waste of columns of the first step, i.e., to measure isotope concentrations between 0.1 and 0.2%, a 1% and higher ^{18}O concentration must be under control in the enriched water. In addition, the degree of deuterium-enrichment must be also under control, therefore a choice of a proper spectral range is a very important problem.

To find the spectral range acceptable for simultaneous DL measurement of concentrations of different water isotopomers, we have preliminary analyzed the available literature data on IR absorption spectra of water and its isotope modifications.[1–5] To obtain some additional information, spectral analysis of samples with a known concentration of isotopes was conducted with the use of IFS-66 (Bruker Fourier spectrometer).

Figure 1 shows absorption spectra of water vapor with different isotope concentrations, which were recorded with a Fourier spectrometer of a 0.025 cm^{-1} spectral resolution.

A multi-path optical cell with an effective length of 4 m was used. The cell temperature was 40°C. The analysis of spectra has shown the frequency range from 7182.5 to 7185 cm^{-1} to be the most preferable for simultaneous detection of the $H_2^{16}O$, $H_2^{17}O$, $H_2^{18}O$, $HD^{16}O$, and $D_2^{16}O$ water isotopomers.

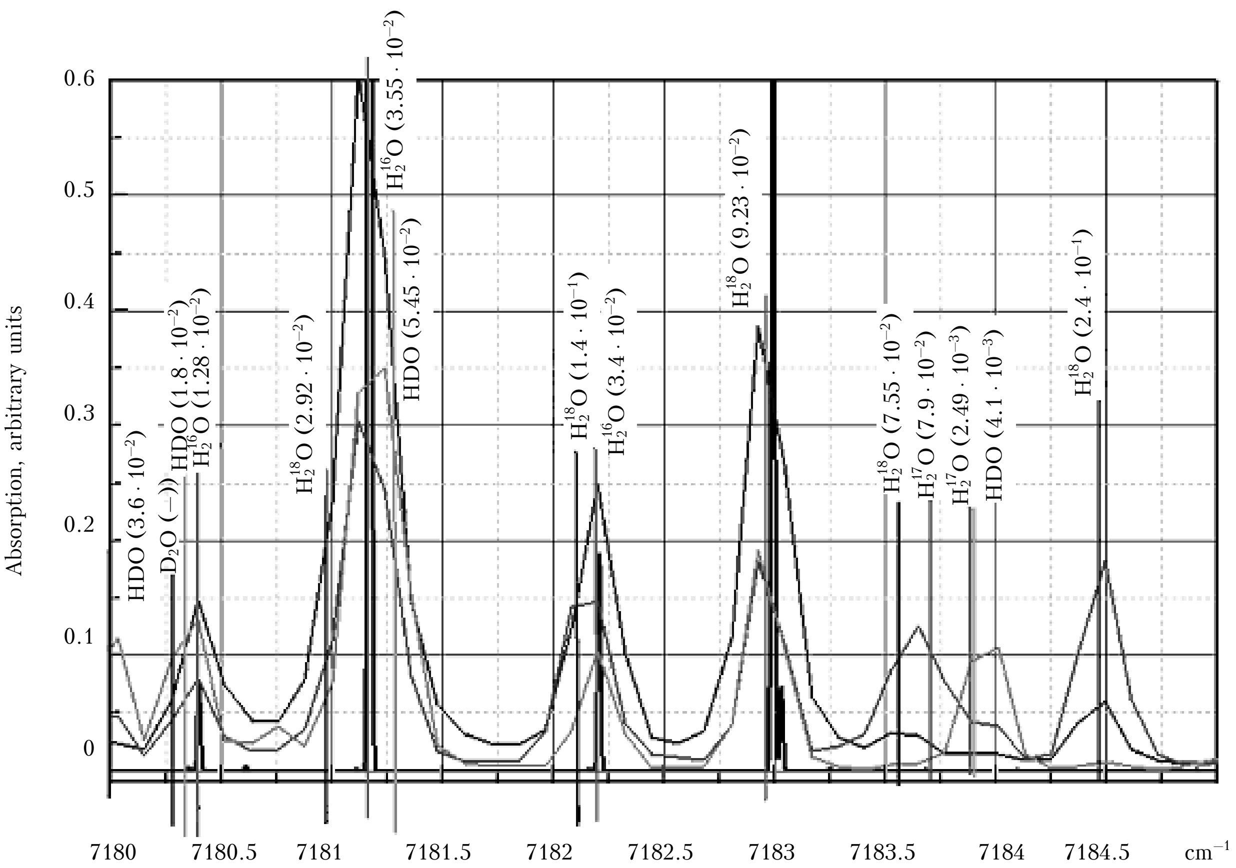

Fig. 1. H_2O absorption spectra obtained with a Fourier spectrometer with a 0.02 cm^{-1} spectral resolution.

The layout of the measurement setup is shown in Fig. 2.

A diode laser with distributed feedback produced by “Laser Components” was used (λ = 1.39 μm). It is equipped with the build-in thermal resistor and Peltier thermal element. To widen the range of the measured water isotopomer concentrations, two optical cells of 80 and 10 cm length were incorporated into the setup. The cells' bodies were made of stainless steel and windows from fused silica.

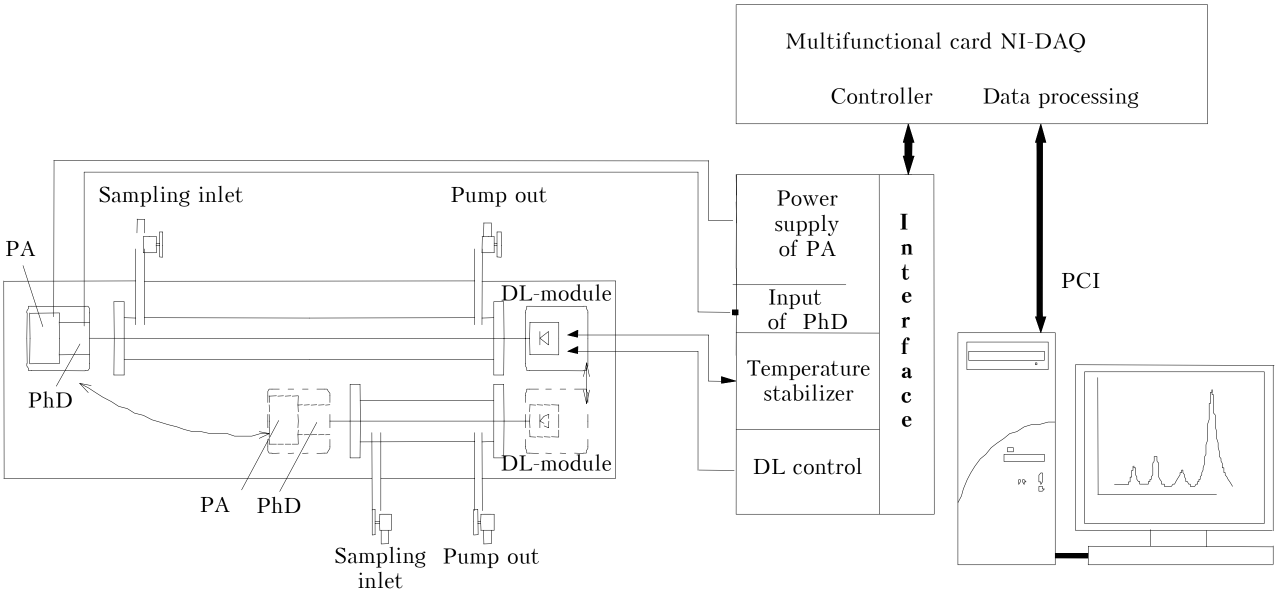

Fig. 2. Block-diagram of the DL detector for H_2O isotope composition measurements.

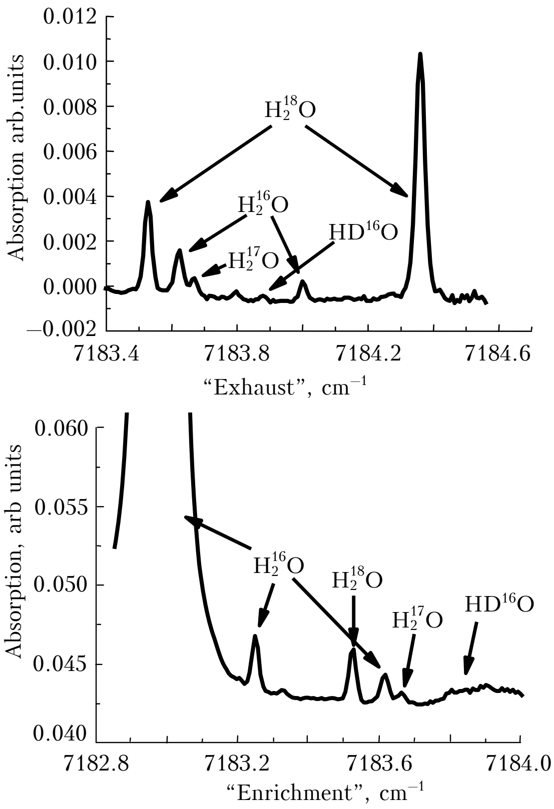

Fig. 3. DL-absorption spectra of water isotopes for different measurement regimes: exhaust (top) and enrichment (bottom).

The samples of water with different isotope compositions were filled under pressure of 3–10 Torr into the short or long cells depending on the task (enrichment or exhausting). The long cell was used for measurement of the water isotope composition at a relatively low (0.05–0.5%) concentration of the ^{18}O isotope; the short one for a higher concentration (0.5–99.9%). Figure 3 exemplifies the absorption water vapor spectra recorded with the use of DL under different measurement regimes.

Procedure of ^{18}O concentration measurement in the exhaust regime

In this regime, the following DL parameters were used: a $\tau \sim 200$ μs length of the pumping current trapezoidal pulse; a ~ 5 kHz pulse repetition frequency; 50 mA pumping current I. In the DL radiation mode, one ^{18}O line was recorded at the frequency of 7184.456 cm^{-1}. The DL crystal temperature was maintained at the level of (20.2 ± 0.0005)°C.

The computerized thermostabilizing system, equipped with a proportionally-integral controller, allowed quickly reaching the required temperature and its long-time maintenance with an accuracy of $5 \cdot 10^{-4}$ grad.

The controlling program allowed a change of pumping current parameters.

To reach the maximum sensitivity, the modulation regime of DL generation was used. It was realized by digitizing the frequency of the NI DAQ card of 200 kHz through division of a set of points of the pumping pulse into two components: even and odd. The depth of pulse modulation was chosen in the way that provides the frequency shift in the DL mode equal to the $H_2^{18}O$ absorption line half-width ($W \sim 0.007$ cm^{-1}). Further, the logarithm of the ratio of the even and odd components was calculated, and the following difference of the absorption coefficients

$$K(\nu,\ W)P_{^{18}O}L = \\ = [K(\nu - \nu_0 + W) - K(\nu - \nu_0)]P_{^{18}O}L, \qquad (1)$$

was obtained, where L is the optical path length for the absorbing layer (in analytical cell of 80 cm length); $P_{^{18}O}$ is the $H_2^{18}O$ vapor pressure in the water sample studied; $K(\nu - \nu_0)$ is the extinction coefficient (cm^{-1}/atm) described by

$$K(\nu - \nu_0) = S_{\nu_0}\varphi(\nu - \nu_0), \qquad (2)$$

where ν_0 is the frequency at the absorption line center, S_{ν_0} is the absorption line intensity, cm$^{-2} \cdot$ atm^{-1}; $\varphi(\nu - \nu_0)$ is the function describing the line shape, cm.

To reach the maximum repeatability of the ^{18}O concentration measurement, the water vapor pressure in the cell was maintained at the level of 9.2 ± ± 0.05 Torr. At such a pressure, the Gaussian function was used

$$y = \frac{2S_{\nu_0}}{W}\sqrt{\pi}\exp\left(-\frac{(\nu - \nu_0)^2}{W^2}\right), \qquad (3)$$

where W is the Doppler line half-width and ν is the current frequency.

To decrease the effect of flicker noise components, additional numerical differentiation and filtration were conducted at the next step of the pulse processing. The computerized filtering was performed using the Butterword band filter with the filter order of 2; the frequency of 200 kHz; and a bandwidth of 35 kHz. With these parameters of filtration, no distortions of the absorption line shape occur.

To transform the pulse from the time scale to the frequency one, a linear transformation function was used, the slope angle tangent of which was optimized through the procedure of the spectral line shape fitting to the Gaussian function.

The second derivative of the ^{18}O absorption coefficient resulted from the pulse processing and was fitted by a sum of the second derivative of the Gaussian function and a linear function:

$$y = \frac{2S_{\nu_0}}{W}\sqrt{\pi}\left(-1 + \frac{(\nu - \nu_0)^2}{W^2}\right)\times \\ \times\exp\left(-\frac{(\nu - \nu_0)^2}{W^2}\right) + K + R\nu, \qquad (4)$$

with the following fitting parameters: S as the integral absorption cross section; R as the slope coefficient; and K as the background.

To normalize the S magnitude on the ^{18}O natural concentration (0.199983%), the distilled water with a standard isotope composition was used (as a reference sample).

The proposed measurement procedure allows obtaining of the $H_2{}^{18}O$ concentration magnitude in a wide range (between 0.12 and 3.0%) at a random error no more than 5%.

To test the measurement validity, several water samples with different $H_2^{18}O$ concentrations were prepared. The relative ^{18}O concentration was preliminary measured with the mass-spectrometer. The comparison of results obtained with the DL-spectrometer and the mass-spectrometer has shown a difference no more than 0.5%.

Procedure of water isotope composition measurement in the enrichment regime

In the enrichment regime, a portion of the spectrum was recorded representing the following isotopomers: $H_2^{17}O$, $H_2^{18}O$, $HD^{16}O$, and $H_2^{16}O$. First the relative concentrations were calculated of the isotopomers $H_2^{17}O$, $H_2^{18}O$, $HD^{16}O$ (below designated as α, β, and γ). Let us denote the absolute concentrations of $H_2^{17}O$, $H_2^{18}O$, $HD^{16}O$, and $H_2^{16}O$ isotopomers by A, B, C, and D; then

$$\alpha = \frac{A}{D}; \ \beta = \frac{B}{D}; \ \gamma = \frac{C}{D}.$$

If to designate relative concentrations of D, ^{17}O, and ^{18}O by X, Y, Z, then the relative concentrations of all possible water isotopomers can be written in the form of the matrix:

$$\begin{array}{llll} & H_2 & HD & D_2 \\ ^{16}O & (1-X)^2(1-Y-Z) & \begin{array}{c}2X(1-X)\times \\ \times(1-Y-Z)\end{array} & X^2(1-Y-Z) \\ ^{17}O & Y(1-X)^2 & 2XY(1-X) & YX^2 \\ ^{18}O & Z(1-X)^2 & 2XZ(1-X) & ZX^2 \end{array}$$

It is seen that α, β, γ and X, Y, Z are related as:

$$\alpha = \frac{A}{D} = \frac{(1-X)^2 Y}{(1-X)^2(1-Y-Z)} = \frac{Y}{1-Y-Z};$$

$$\beta = \frac{B}{D} = \frac{Z}{1-Y-Z};$$

$$\gamma = \frac{C}{D} = \frac{2X}{1-X}.$$

Solving this system of equations with regard to X, Y, Z gives

$$X = \frac{2+\gamma}{\gamma}; \quad Y = \frac{\alpha}{1+\alpha+\beta}; \quad Z = \frac{\beta}{1+\alpha+\beta}.$$

After finding X, Y, Z, it is possible to calculate relative concentrations of all water isotopomers. The obtained relations were used in calculating the isotopomer concentrations in the enrichment regime.

Recording of absorption spectra of water isotopes and their processing were performed with the use of NI DAQ card and LabVIEW drivers. The time of a unit interval for measurement of isotopomers' relative concentrations made ~ 0.2 s. At a 100-fold accumulation and averaging, the relative random error in $H_2{}^{18}O$ concentration measurements was no more than 0.3%.[6–9]

At present, the device operates in the regime of regular measurements of samples from packing columns. The advent of the device has significantly simplified the problem of control for the technological maintenance of the "Water" complex.

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