

# Light-emitting-diode Fourier-Transform spectroscopy of HD<sup>16</sup>O between 11200–and 12400 cm<sup>-1</sup>

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## ABSTRACT

The absorption spectrum of monodeuterated water, HDO has been investigated between 11200 and 12400 cm<sup>-1</sup>. The spectrum has been recorded using IFS-125M interferometer with spectral resolution of 0.05 cm<sup>-1</sup>. For measurements White's-type cell were used. The bright light emitting diode (LED) EDEI-1LS3-R was applied as a source of radiation. Signal to noise ratio was about 10<sup>4</sup>. The spectral line parameters - line positions, intensities and half-widths were obtained by least square fitting. As a result of the spectrum analysis the line list containing more than 1500 lines was created. The spectral line parameters have been compared with the previous measured and calculated data.

**Keyword:** Fourier-Transform spectrum of HD<sup>16</sup>O, spectral line parameters.

## 1. INTRODUCTION

The study of high-resolution spectra of mono-deuterated water molecule HD<sup>16</sup>O is of interest from a theoretical point of view, and for a various practical applications. The content of these species in the earth's atmosphere is 0.000310693 (in relative units) <sup>1</sup>; HD<sup>16</sup>O absorption lines are easily observable in the spectra of solar radiation transmitted through the atmosphere. Data on the concentration of HD<sup>16</sup>O in the atmosphere of the Earth are needed to describe the qualitative and quantitative characteristics of the evaporation and condensation processes, air mass origin, etc., see <sup>2</sup>. The investigations of HD<sup>16</sup>O spectra are also need to solve problems of astrophysics. In particular, in the atmosphere of Venus relative concentration of HD<sup>16</sup>O is by 2 orders of magnitude larger than on earth <sup>3,4</sup>. So-called "deuterium test" <sup>5</sup> and the content of deuterium in stars are important for astrophysicists. Of theoretical interest is the fact that HD<sup>16</sup>O molecule is asymmetrically substituted isotopologue of H<sub>2</sub><sup>16</sup>O and has the same electronic structure but, owing to the difference of the nuclei masses has different from H<sub>2</sub><sup>16</sup>O vibration-rotation energy spectrum, consequently, HD<sup>16</sup>O absorption spectra are qualitatively different from the spectra of the main isotopic modification.

A number of works have been devoted to theoretical and experimental studies of the spectra of HD<sup>16</sup>O <sup>6-20</sup>. Among these theoretical work on the HD<sup>16</sup>O spectra calculation one has to allocate *ab initio* calculations <sup>14,15</sup> and several later works on the determination of the potential function of this molecule, for example <sup>16,18</sup>. In work <sup>17</sup> the most complete calculations of centers and intensities of HD<sup>16</sup>O spectral lines (VTT calculation) were made and the spectral parameters for almost 700.000.000 transitions were determined. All available experimental data for HD<sup>16</sup>O were analyzed in the framework of the international IUPAC project, and as a result the most accurate at the moment energy levels of this molecule, were obtained <sup>19</sup>. Our spectral assignments were carried out with using the results of previous studies <sup>4,17,19</sup>. Spectroscopic parameters of HD<sup>16</sup>O absorption lines are included in known databases HITRAN and GEISA. However, there is an urgent need for further, more detailed study of these spectra. In this work, measurements and analysis of the absorption spectrum of HD<sup>16</sup>O molecule near 0.84 μm were carried out by Light-emitting-diode Fourier-Transform spectroscopy technique.

## RESULTS AND DISCUSSIONS

The high resolution absorption spectrum of monodeuterated water, HD<sup>16</sup>O has been recorded in 11200 - 12400 cm<sup>-1</sup> spectral region by IFS-125M Fourier transform spectrometer with spectral resolution of 0.05 cm<sup>-1</sup>. As a source of

radiation the bright light emitting diode <sup>21-24</sup> EDEI-1LS3-R was applied. White type optical system and the cell of 60 cm of length were used. The spectrum was recorded at room temperature (297°K ± 1°K), which was stabilized by Midea MSE-24HR conditioner along the cell. Signal to noise ratio was about 10000. Three spectra were measured: the spectrum of pure water H<sub>2</sub><sup>16</sup>O with natural abundance of water isotopic species; spectrum of deuterated water with maximal concentration of deuterium and spectrum of mixture H<sub>2</sub><sup>16</sup>O+HD<sup>16</sup>O+D<sub>2</sub><sup>16</sup>O with maximum concentration of HD<sup>16</sup>O. Comparison of all three spectra allows one to easily refer each absorption line to given isotopic variant. The overview of HD<sup>16</sup>O transmittance spectrum is shown in Fig. 1. The additional panel shows the small spectral interval near 0.84 μm. It can be seen from Fig.1 that HD<sup>16</sup>O absorption is rather weak in this region - the transmission for the strongest lines is about 0.915 for the strongest lines. The possibility of very weak line observation with small-size cell is provided by use of LED as source of radiation. Main experimental conditions are listed in Table 1.

The spectral line parameters (line positions, intensities and half-widths) were calculated with using Wxspe software <sup>25</sup> which allows to find line peaks and to fit contour parameters to measured data by least square method. The lines were fitted one by one to a Voigt profile convolved by the instrumental function. Wavenumber calibration procedure is based on the calculation <sup>4</sup>. To obtain the calibration factor the ratio (1) was used

$$\tilde{\nu}_n = a \cdot \nu_n + b \cdot \nu_n^2 \quad (1)$$

where  $\tilde{\nu}_n$  is the wavenumber of calibration lines,  $\nu_n$  - is the wavenumber of reference lines,  $n$  is the number of lines,  $a$  and  $b$  are fitting parameters. The definition of these parameters were performed by the least squares method, as a result  $a=1.00000764277 \pm 0.000001062$  and  $b=5.68086 \cdot 10^{-10} \pm 8.9983 \cdot 10^{-11}$ . Estimated corrections are, on average,  $10^{-2} \text{ cm}^{-1}$ .

Spectral line of HD<sup>16</sup>O molecule in the region of 11200 – 12400 cm<sup>-1</sup> are formed by the transitions to highly excited vibrational - rotational states belonging to the strongest bands (013)-(000); (301)-(000) ; (410)-(000) and also to states (023), (032), (061), (103), (112), (141), (160), (170), (221), (250), (330), associated with ones by resonances of Fermi and Coriolis type. A set of more than 1500 transitions of the HD<sup>16</sup>O molecule has been assigned in the 11200–12400cm<sup>-1</sup> region. The number of assigned transitions and the maximal values of the rotational numbers  $J$  and  $K_a$  are presented in Table 2 for the 14 bands. Also, the maximum and minimum line intensity values for each band are presented in Table 2. Comparison of intensities of our strongest experimental lines (intensity from  $1.0 \cdot 10^{-24} \text{ cm}^2/\text{mol}$  to  $1.4 \cdot 10^{-23} \text{ cm}^2/\text{mol}$ ) with the calculating intensities<sup>4</sup> is shown in Fig2. Line intensities ratio  $I^{\text{our}}/I^4$  is 1.09 for the 130 strongest lines.

During our study new experimental information on absorption HD<sup>16</sup>O was obtained in the 11600- 11640 cm<sup>-1</sup> spectral region. 103 transitions belonging  $3\nu_1 + \nu_3$ ,  $4\nu_1 + \nu_2$ ,  $2\nu_1 + 2\nu_2 + \nu_3$ ,  $6\nu_2 + \nu_3$  and  $\nu_2 + 3\nu_3$  bands were assigned. In Fig.3 the accuracy of the determination of HD<sup>16</sup>O line centers in the measured spectrum with using Rydberg-Ritz combination principle is presented. Deviation for our experimental line centers relative to the calculated data can be achieved to  $0.02 \text{ cm}^{-1}$  for weak lines and for strong lines it is equal to about  $0.0015 \text{ cm}^{-1}$ .

Results, obtained in our study shows, that the use of Led- based Fourier-Transform spectroscopy technique allows to measure very weak spectral lines of monodeuterated water vapor with high sensitivity. The obtained spectral information can be used to refine the existing data on the HD<sup>16</sup>O absorption in the range 11200-12400 cm<sup>-1</sup>.

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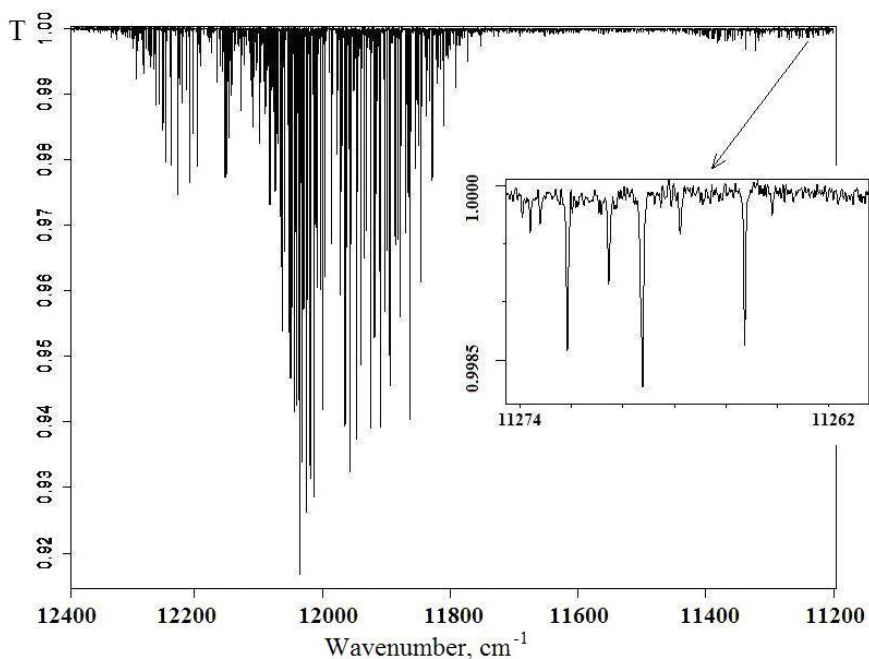


Fig.1 HD<sup>16</sup>O transmittance spectrum near 0.844 μm region.

Table 1. Experimental conditions.

Spectral resolution	0.05 cm <sup>-1</sup>
Optical path length	2400 cm
Pressure of H <sub>2</sub> O/HDO/D <sub>2</sub> O mixture	27 mBar
Temperature	24 ± 1° C
Signal-to-noise ratio	about 10000
Light-emitting diode	EDEI-1LS3-R
The total measurement time	12 days

Table 2.  
Statistics of the observed transitions of the HD<sup>16</sup>O molecule.

Band	Spectral region, cm <sup>-1</sup>	Number of assignments	J <sub>max.</sub>	K <sub>a,max.</sub>	Intensity max., cm/molecule	Intensity min., cm/molecule
v <sub>2</sub> +3v <sub>3</sub>	11615-12325	579	15	8	1.4*10 <sup>-23</sup>	4.5*10 <sup>-27</sup>
2v <sub>2</sub> +3v <sub>3</sub>	11730-11866	9	7	2	2.1*10 <sup>-26</sup>	2.6*10 <sup>-27</sup>
3v <sub>2</sub> +2v <sub>3</sub>	11203-11515	113	10	7	1.3*10 <sup>-25</sup>	4.8*10 <sup>-27</sup>
6v <sub>2</sub> +v <sub>3</sub>	11452-12234	26	10	4	1.6*10 <sup>-25</sup>	3.1*10 <sup>-27</sup>
v <sub>1</sub> +3v <sub>3</sub>	11865	1	4	4	1.35*10 <sup>-26</sup>	1.35*10 <sup>-26</sup>
v <sub>1</sub> +v <sub>2</sub> +2v <sub>3</sub>	11200-12090	149	10	7	3.1*10 <sup>-25</sup>	5.4*10 <sup>-27</sup>
v <sub>1</sub> +4v <sub>2</sub> +v <sub>3</sub>	11749-12241	22	7	4	5.1*10 <sup>-25</sup>	6.8*10 <sup>-27</sup>
v <sub>1</sub> +6v <sub>2</sub>	11653	1	7	5	1.1*10 <sup>-26</sup>	1.1*10 <sup>-26</sup>
v <sub>1</sub> +7v <sub>2</sub>	11540-11815	11	5	4	8.5*10 <sup>-26</sup>	9.6*10 <sup>-27</sup>
2v <sub>1</sub> +2v <sub>2</sub> +v <sub>3</sub>	11500-11943	96	11	4	9.6*10 <sup>-26</sup>	4.7*10 <sup>-27</sup>
2v <sub>1</sub> +5v <sub>2</sub>	11800	1	8	2	2.4*10 <sup>-26</sup>	2.4*10 <sup>-26</sup>

$3\nu_1 + \nu_3$	11319-11808	325	13	6	$2.0 \cdot 10^{-25}$	$3.7 \cdot 10^{-27}$
$3\nu_1 + 3\nu_2$	11794-12089	44	9	2	$4.1 \cdot 10^{-24}$	$7.0 \cdot 10^{-27}$
$4\nu_1 + \nu_2$	11517-11980	214	11	6	$3.7 \cdot 10^{-25}$	$4.4 \cdot 10^{-27}$

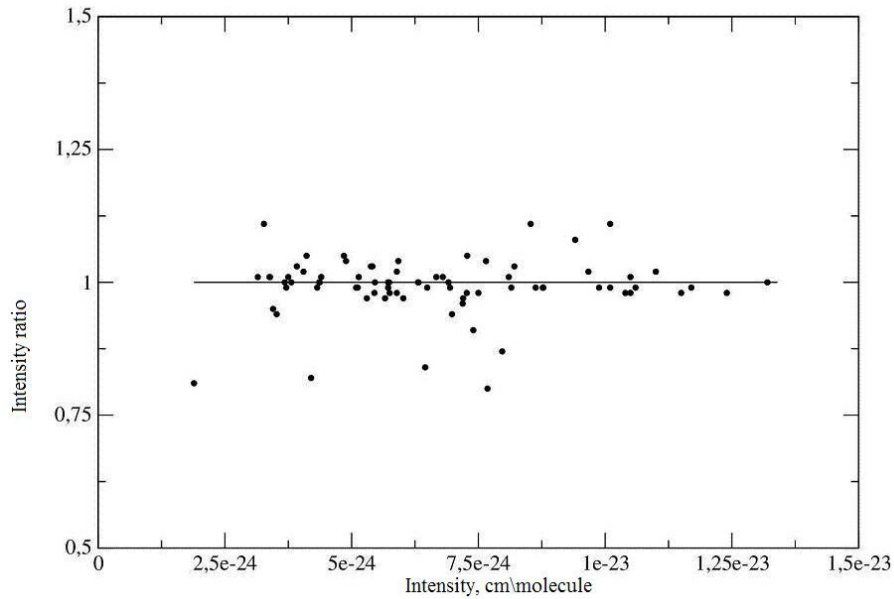


Fig.2. Comparison of our experimental line intensities with the calculating intensities from Ref.<sup>4</sup>

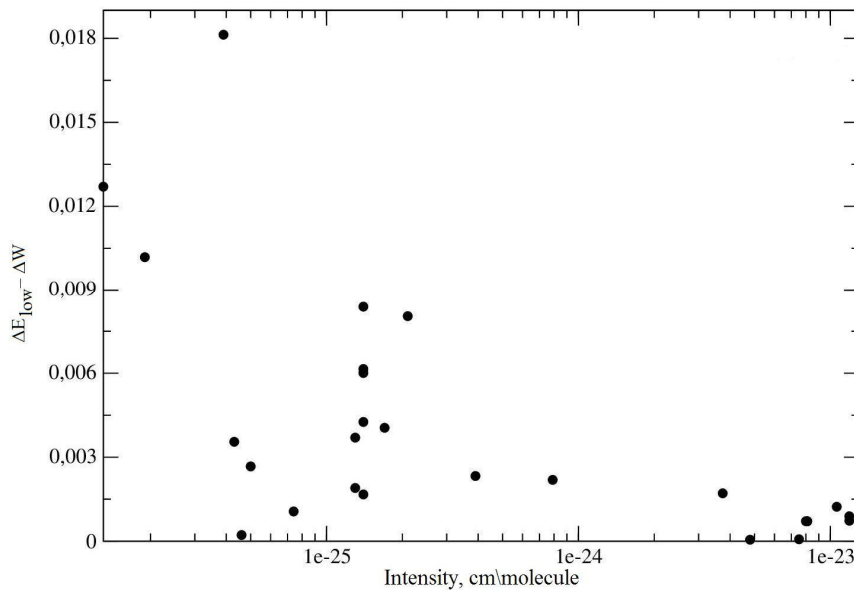


Fig.3 The accuracy of the determination of HD<sup>16</sup>O line centers in the measured spectrum estimated with using Rydberg-Ritz combination principle;  $\Delta E_{\text{low}}$  - difference between lower energy levels;  $\Delta W$  - difference between wavenumber values of corresponding transitions.