

# Study of HD<sup>17</sup>O spectrum. Theory and experiment

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## ARTICLE INFO

### Keywords:

FTIR spectrum  
Variational calculations  
Potential energy surfaces  
Isotopologue

## ABSTRACT

A spectrum of HD<sup>17</sup>O in the region between 5 480 and 6 400 cm<sup>-1</sup> recorded in Tomsk is reported. In this region 4292 lines are observed belonging to 7 water isotopologues: 536 lines – H<sub>2</sub><sup>16</sup>O 1019 – HD<sup>16</sup>O, 122 – D<sub>2</sub><sup>16</sup>O, 447 – H<sub>2</sub><sup>17</sup>O 458 – HD<sup>17</sup>O, 151 – H<sub>2</sub><sup>18</sup>O, 181 – HD<sup>18</sup>O. A new potential energy surface (PES) of HD<sup>16</sup>O is obtained by fitting to empirical energy levels. This PES, with a diagonal Born–Oppenheimer correction (DBOC), is used to compute the HD<sup>17</sup>O spectrum. Pseudo-experimental isotopologue-extrapolation energy levels of HD<sup>17</sup>O are constructed using the method of Polyansky et al (MNRAS 466, 1363 (2017)). Assignment of the measured spectrum is conducted: 68 % of the lines can be assigned using assignments from previously published work. The remaining lines are assigned using the pseudo-experimental energy levels procedure. We compare the calculated pseudo-experimental values of energy levels with both existing 1285 experimental levels of HD<sup>17</sup>O and the 152 newly determined in this work energy levels. The standard deviation of levels with low J (up to J=10) is about 0.007 cm<sup>-1</sup> in both cases. Energy levels from both pseudo-experimental and variationally calculated are also compared with newly measured HD<sup>17</sup>O lines above 10 000 cm<sup>-1</sup>.

## 1. Introduction

Water molecule is arguably the most important molecule in the entire Universe. Its spectrum is very well studied. Much less well studied are its isotopologues spectra, though probably much better, than the major isotopologues of other molecules.

The energy levels of the water molecule, including its isotopologues, are important for a variety of applications. A decade ago some of us collaborated on a IUPAC (International Union of Pure and Applied Chemistry) project whose aim was to provide empirical energy levels for all isotopologues of water [1]. The project developed the MARVEL (measured active rotation–vibration energy levels) procedure [2] and used it to provides a set of recommended energy levels for all water isotopologues including HD<sup>16</sup>O, HD<sup>17</sup>O and HD<sup>18</sup>O [3], which we use here. While both the MARVEL procedure [4,5] and energy levels for H<sub>2</sub><sup>16</sup>O, and H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O have subsequently been regularly updated [5–8], there is as yet no systematic update of the IUPAC data for the deuterated isotopologues.

We report measurements and analysis of the vibrational–rotational absorption spectrum of the HD<sup>17</sup>O molecule in the IR range from 5480 to 6400 cm<sup>-1</sup>. The absorption spectrum of the H<sub>2</sub><sup>17</sup>O molecule in this region was recently investigated by us [9] as well as the higher

frequency spectrum of HD<sup>17</sup>O [10–12]; these studies are considered further below.

## 2. Measurements and data processing

The absorption spectrum of the HD<sup>17</sup>O molecule was recorded using an IFS-125M Fourier spectrometer in the range from 5480 cm<sup>-1</sup> to 6400 cm<sup>-1</sup>, at a pressure of 29 mbar and an optical path length of 24 m. The Doppler FWHM in this region is 0.0166 cm<sup>-1</sup>; measurements were performed with a spectral resolution of 0.02 cm<sup>-1</sup>. A multi-pass optical White cell with a base length of 60 cm was used for measurements. Measurements were carried out at a temperature of 25 ± 1 °C. A halogen lamp was used as the radiation source. We used a Mertz-phase correction with a 1 cm<sup>-1</sup> phase resolution, and no apodization were applied to the averaged interferograms. A background spectrum was first recorded at a resolution of 0.05 cm<sup>-1</sup> while the cell was being continuously evacuated. In order to prepare the HD<sup>17</sup>O vapor, liquid water enriched to 86% with H<sub>2</sub><sup>17</sup>O produced by the Sigma-Aldrich Chemical Company was mixed with an equal quantity of the D<sub>2</sub><sup>16</sup>O. It gives us approximate water isotopologues abundances: H<sub>2</sub><sup>16</sup>O – 12%, H<sub>2</sub><sup>17</sup>O – 12%, HD<sup>16</sup>O – 25%, HD<sup>17</sup>O – 25%, D<sub>2</sub><sup>16</sup>O – 12%.

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<https://doi.org/10.1016/j.jms.2024.111965>

Received 5 August 2024; Received in revised form 25 October 2024; Accepted 18 November 2024

Available online 26 November 2024

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**Table 1**

Experimental conditions.

Spectral resolution	0.02 cm <sup>-1</sup>
Optical path length	2400 cm
Pressure of H <sub>2</sub> O/HDO/D <sub>2</sub> O mixture	29 mbar
Temperature	25 ± 1 °C
Signal-to-noise ratio	About 10000
Diaphragm	0.9 mm
The total measurement time	7 days

Measurements were performed during several days; each spectrum was obtained by averaging over 37 584 scans during 168 h of recording. This procedure allowed us to obtain a signal-to-noise ratio of about 1000 and to detect weak absorption lines with intensities of the order of 10<sup>-26</sup> cm/molecule.

The volume of the cell is 2.765 L. The absorption spectra were recorded at a pressure of 29 mbar. The pressure measurements were performed using a pressure transducer AIR-20M. Considering the uncertainty arising from small variations of the pressure during the recording, the measurement uncertainty on the pressure was estimated as 0.5%. The signal-to-noise ratio on the strong lines is about 1000 despite the fact that the optical path was only 24 m; Fig. 1 gives an overview of the spectrum.

The FT-Spectrometer Bruker IFS-125M was not evacuated. Variations in the baseline due to changes in humidity and air pressure in the laboratory during measurements do not exceed 1.5%. Spectral noise is the most important source of error for the line strength measurements. For strong lines with an intensity  $6 \times 10^{-25} - 2 \times 10^{-25}$  cm/molecule, they are 0.5%, while for weak lines with an intensity of less than  $2 \times 10^{-25}$  cm/molecule they are 5%. The errors that occur when fitting a spectral line contour vary from 0.1% for strong lines to 1.5% for weak lines. This gives a total measurement uncertainty for the line broadening coefficients of 4% and 9% for strong and weak lines, respectively. The uncertainty in the determination of the line position does not exceed 0.003 cm<sup>-1</sup>. The measurement conditions are given in Table 1.

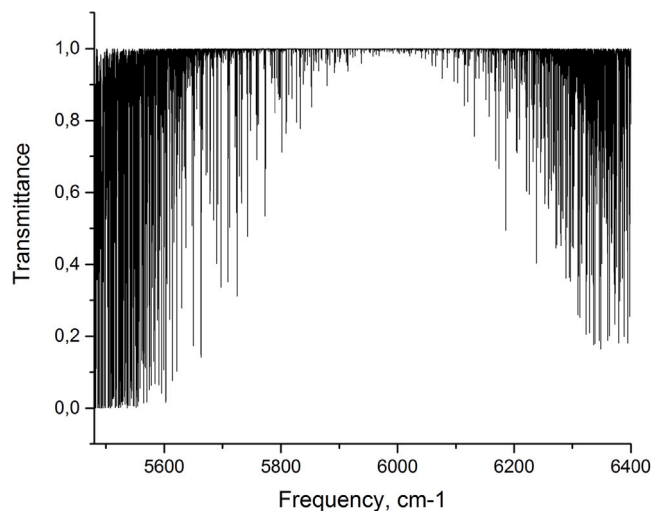
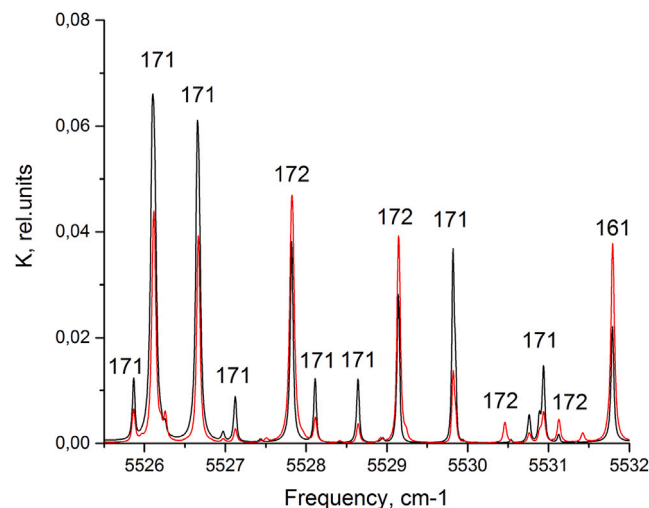
The measured spectrum was processed using the Wxspe software package [13] that uses pattern recognition algorithms. The software searches for lines in automatic mode. The centers, intensities, and half-widths were determined by least-squares fitting Voigt profile parameters to the experimental data taking into account an appropriate instrumental function.

32 H<sub>2</sub><sup>16</sup>O lines from the HITRAN data [14] were used to calibrate the measured line centers. In fact, the H<sub>2</sub><sup>16</sup>O spectroscopic data were used as secondary frequency standards. As a result of the calibration performed, the measurement error of the line centers can be estimated to be better than 0.003 cm<sup>-1</sup> for strong lines and not exceeding 0.02 cm<sup>-1</sup> for weak lines with intensities less than  $4 \times 10^{-26}$  cm/molecule.

The partial pressure of the component mixture was determined by comparing the HITRAN 2020 [14] line intensities, which for the deuterated isotopologues are actually derived from calculations [15], with the measured ones. We found the partial pressure of H<sub>2</sub><sup>16</sup>O to be 13 mbar; H<sub>2</sub><sup>17</sup>O – 7 mbar; HD<sup>16</sup>O – 5.5 mbar and that of HD<sup>17</sup>O isotopologue 3.5 mbar. The partial pressure of the <sup>18</sup>O isotopologues was very small and was neglected. The uncertainty in determining the line intensities can be estimated as 7%–10%. The recorded spectrum was compared with water isotopologues spectrum containing 86% H<sub>2</sub><sup>17</sup>O and 14% H<sub>2</sub><sup>16</sup>O. The comparison allowed to unambiguously tie the recorded lines with concrete water isotopologue. Fig. 2 shows a part of the recorded spectrum in the range 5524–5530 cm<sup>-1</sup> with water isotopologue lines identified.

### 3. Variational calculations for HDO

In order to perform a fit of the HDO PES, the rotation–vibration Schrödinger equation has to be solved. For that purpose we used the

**Fig. 1.** Overview of the recorded spectrum.**Fig. 2.** A short portion of the observed spectrum. Numbers denote the isotopologue associated with each line: 161 is H<sub>2</sub><sup>16</sup>O, 171 is H<sub>2</sub><sup>17</sup>O, and 172 is HD<sup>17</sup>O. The red and black lines represent different partial concentrations of water isotopologues in the sample.

DVR3D program suite [16]. DVR3D uses an exact representation of nuclear motion kinetic energy operator so that, within constraints of the Born–Oppenheimer approximation, any uncertainty in the wavefunctions is due to the PES and the failure of the Born–Oppenheimer approximation. Because of the lower symmetry of HDO and the higher density of states, achieving accuracy in HDO calculations comparable to that routinely achieved for H<sub>2</sub><sup>16</sup>O and its 17–18 oxygen isotopologues [17,18], requires the diagonalization of significantly larger matrices. The PES is represented as a polynomial in valence coordinates of the HDO molecule with 107 adjustable parameters. A file with fixed and adjusted parameters is presented in the SM.

Nuclear motion calculations were performed in Radau coordinates with the *z*-axis embedded close to the OH bond direction. The discrete variable representation (DVR) basis comprised 30 Gauss–Laguerre points in each radial coordinate and 48 (associated) Gauss–Legendre points in the angular coordinate. Basis set parameters for the radial coordinates were taken from Yurchenko et al. [19]. The final vibrational Hamiltonian matrix was of dimension 7000. For each rotational state *J*, two Hamiltonian matrices were diagonalized with dimensions  $1000 \times (J + 1)$  and  $1000 \times J$ , depending on their overall parity.

#### 4. Fitted PES

To get accurate values for the energy levels for the  $^{17}\text{O}$  isotopologues of HDO one has to construct the PES in a special form which separately identifies the mass-dependent part of the PES, namely the Diagonal Born–Oppenheimer Correction (DBOC). As a result the PES consists of a mass-independent term and a mass dependent-terms which varies for the different isotopologues.

$$V^{XX} = V^{all} + DBOC^{XX}, \text{ where } XX = 16, 17 \text{ or } 18. \quad (1)$$

The mass-independent term can be obtained by fitting  $\text{HD}^{16}\text{O}$  energy levels to the form which includes the  $^{16}\text{O}$  DBOC. We choose the most abundant isotopologue of HDO because it has the biggest set of experimental levels. In practice we took the HDO PES of Yurchenko et al. [19], added to it an  $\text{HD}^{16}\text{O}$  DBOC and then performed a refit to energy levels up to  $15\,000\text{ cm}^{-1}$  (637 energy levels with  $J$  values of 0, 2, 5); in this work we do not need levels with higher energies. Fitting to  $\text{HD}^{16}\text{O}$  levels with  $J$  values of 0, 2, 5 leads to HDO PESs which gives standard deviations,  $\sigma$ , equal to  $0.019\text{ cm}^{-1}$  for  $^{16}\text{O}$ ,  $0.020\text{ cm}^{-1}$  for  $^{17}\text{O}$  and  $0.027\text{ cm}^{-1}$  for  $^{18}\text{O}$  isotopologues; we call these PES16, PES17 and PES18, respectively. PES17 and PES18 are sub-products of the PES16 fitting procedure, using  $\text{HD}^{16}\text{O}$  energy levels. The form (1) is chosen due to its usefulness for assigning pseudo-experimental levels of 17 and 18 HDO isotopologues.

#### 5. Pseudo-experimental energy levels predictions for $\text{HD}^{17}\text{O}$

Polyansky et al. [20] developed a method for calculating  $\text{H}_2^{17}\text{O}$  and  $\text{H}_2^{18}\text{O}$  energy levels, based on experimental energy levels for  $\text{H}_2^{16}\text{O}$  and the calculated differences between the parent isotopologue levels and levels of the corresponding state for the  $^{17}\text{O}$  or  $^{18}\text{O}$  isotopologues. The energy levels calculated this way gave predictions with an accuracy of about  $0.005\text{ cm}^{-1}$ , which is close to the accuracy of the experimentally-determined energy levels of  $\text{H}_2^{16}\text{O}$ . The high accuracy achieved and the use of experimental values for the parent isotopologue led us to label the resulting energy levels “pseudo-experimental” originally, though this technique subsequently was also called isotopologue extrapolation (IE) by McKemmish et al. [21]. Subsequently [6] we were able to compare newly measured  $^{17}\text{O}$  and  $^{18}\text{O}$  water energy levels with the previously calculated pseudo-experimental energy levels. The excellent accuracy achieved with  $\sigma = 0.0039\text{ cm}^{-1}$  for 1031 experimental energy levels confirmed the usefulness of our methodology. In this paper we use the same procedure to determine  $\text{HD}^{17}\text{O}$  energy levels starting from the  $\text{HD}^{16}\text{O}$  experimentally known energy levels. These pseudo-experimental levels are compared with the energy levels obtained here from our newly measured experimental  $\text{HD}^{17}\text{O}$  line centers, see Table 2.

To obtain values for the pseudo experimental  $\text{HD}^{17}\text{O}$  levels one has to have experimental levels for  $\text{HD}^{16}\text{O}$ . The 2010 IUPAC compilation of HDO levels [3] provides 7200 experimental levels of  $\text{HD}^{16}\text{O}$ . Recent measurements [22–28] have increased this number almost to 8000. Exactly this set of ‘MARVEL extended’ levels are called MARVEL levels in this work. We managed to obtain 5800 pseudo experimental  $\text{HD}^{17}\text{O}$  energy levels. This number is lower than the number of available  $\text{HD}^{16}\text{O}$  energy levels due to the difficulties of correct transferring of  $\text{HD}^{16}\text{O}$  labeling to  $\text{HD}^{17}\text{O}$  isotopologue. The pseudo experimental  $\text{HD}^{17}\text{O}$  energy levels are in supplementary materials.

#### 6. Analysis of $\text{HD}^{17}\text{O}$ spectra

$\text{HD}^{17}\text{O}$  line positions have been measured in the IR range  $5500\text{--}6500\text{ cm}^{-1}$  previously in papers [10–12,22–39]. Comparing measured in this work lines with published spectra gives us the following assignment: 536 lines –  $\text{H}_2^{16}\text{O}$  1019 –  $\text{HD}^{16}\text{O}$ , 122 –  $\text{D}_2^{16}\text{O}$ , 447 –  $\text{H}_2^{17}\text{O}$  458 –  $\text{HD}^{17}\text{O}$ , 151 –  $\text{H}_2^{18}\text{O}$ , 181 –  $\text{HD}^{18}\text{O}$ . This meant that 68% of

**Table 2**

Standard deviations,  $\sigma$ , of calculated with PES17  $\text{HD}^{17}\text{O}$  energy levels for different  $J$  values (left) and  $\sigma$  for pseudo experimental levels (right).  $N$  is the number of experimental levels.

$J$	$N$	$\sigma\text{ (cm}^{-1}\text{)}$	$N$	$\sigma\text{ (cm}^{-1}\text{)}$
0	9	0.0169	11	0.0042
1	31	0.0166	41	0.0058
2	55	0.0159	67	0.0055
3	82	0.0144	98	0.0055
4	90	0.0113	113	0.0071
5	109	0.0095	128	0.0096
6	102	0.0113	131	0.0161
7	105	0.0162	134	0.0218
8	86	0.0206	104	0.0294
9	69	0.0258	71	0.0333
10	53	0.0295	43	0.0374
11	42	0.0339	43	0.0427
12	21	0.0399	15	0.0424
13	16	0.0386	13	0.0393
14	10	0.0436	4	0.0486
15	5	0.0305	4	0.0384

**Table 3**

Statistics for the assigned  $\text{HD}^{17}\text{O}$  lines.

Type	$N$ lines	$\sigma\text{ (cm}^{-1}\text{)}$
Pseudo and MARVEL	564	0.0110
MARVEL	290	0.0044
Pseudo	274	0.0173

the observed lines could be assigned from published papers, leaving us 1368 lines to assign.

29 newly determined upper energy levels are involved in two or more transitions which allow us to check the correctness of the assignment using ground state combination differences which showed a standard deviation of  $0.0071\text{ cm}^{-1}$ . 301 lines were assigned to  $\text{HD}^{17}\text{O}$  mostly using pseudo experimental levels. From these transitions we obtained values of 153 new energy  $\text{HD}^{17}\text{O}$  levels. 94 newly assigned lines do not directly lead to the determination of new levels as their lower levels remains unknown experimentally. These lines generally involve levels with higher values of  $J$  and  $K_a$ . The 2010 IUPAC compilation of HDO levels [3] contains just 162 experimental levels of  $\text{HD}^{17}\text{O}$ . Recent experimental studies [22–28] have increased this number to 1285. This set of experimental levels are called MARVEL levels below.

The standard deviation between experimental frequencies of  $\text{HD}^{17}\text{O}$  lines and our calculated ones is  $0.019\text{ cm}^{-1}$  (see Tables 3 and 4).

Subsequent to our main work on recording and analyzing the spectra around  $6000\text{ cm}^{-1}$ , three studies analyzing  $\text{HD}^{17}\text{O}$  spectra in  $10\,000\text{--}13\,000\text{ cm}^{-1}$  range [10–12] became available. Table 5 shows the quality of our prediction using PES17 and pseudo experimental levels in  $10\,000\text{--}13\,000\text{ cm}^{-1}$  range. For experimental levels around  $10\,000\text{ cm}^{-1}$   $\sigma = 0.11\text{ cm}^{-1}$ , while for levels around  $13\,000\text{ cm}^{-1}$  the  $\sigma = 0.02\text{ cm}^{-1}$ . In this region, the quality of the levels calculated with PES17 levels is about the same as for pseudo experimental levels. For the (400) band the deviation is two times bigger —  $0.202\text{ cm}^{-1}$  then for other bands in the region; this suggests that some levels of the (400) band may not be correctly assigned.

#### 7. Conclusions

This paper presents the results of the observation and analysis of the enriched spectrum of HDO molecule by the  $^{17}\text{O}$  isotopologue. In order to analyze the experimental spectrum we improved the fitted PES of  $\text{HD}^{17}\text{O}$  and calculated the 6000 pseudo-experimental values of energy levels. We compared the calculated pseudo-experimental values of energy levels with both existing 1300 levels of  $\text{HD}^{17}\text{O}$  and the 152 newly determined in this work energy levels. The standard deviation of low  $J$  (up to  $J = 10$ ) is about  $0.007\text{ cm}^{-1}$  in both cases. Note, that the newly determined number of 152 levels is higher than the entire 130

**Table 4**

Newly determined energy levels of HD<sup>17</sup>O. Calc.1 – energy levels calculated with the use of new HD<sup>17</sup>O PES (PES17), Calc.2 – pseudo experimental levels. 'cd' denotes levels determined with combinations differences, 's' and denotes levels of unresolved doublet split using the values from the theoretical calculations.

$v_1 v_2 v_3$ state	$J K_a K_c$	Obs. (cm <sup>-1</sup> )	Obs.-Calc.1 (cm <sup>-1</sup> )	Obs.-Calc.2 (cm <sup>-1</sup> )
011	6 5 2	5799.7529	-0.006 cd	0.000
011	6 5 1	5801.6658	-0.006 cd	0.000
011	9 5 4	6174.8925	0.019	0.024
011	11 3 9	6245.5243	-0.060	-0.054
021	4 1 4	6594.1379	-0.001	-0.004
021	4 1 3	6625.0098	0.011	0.007
021	4 2 3	6664.9406	-0.002	-0.006
021	4 3 1	6757.0341	-0.001	-0.005
021	5 2 3	6753.1835	-0.003	-0.007
021	5 3 3	6834.9870	-0.003 cd	-0.007
021	5 3 2	6835.8466	0.003	-0.001
021	6 2 5	6831.9743	-0.003	-0.007
021	6 4 3	7052.8349	-0.013	-0.012
021	6 4 2	7052.9119	-0.030	-0.028
021	7 0 7	6834.8102	0.003 cd	-0.001
021	7 1 7	6836.3386	-0.001	-0.005
021	7 2 6	6936.8442	-0.010	-0.014
021	7 2 5	6971.2352	-0.006	-0.010
021	7 4 3	7162.6270	-0.038	-0.042
021	7 5 3	7317.6459	-0.049 s	-0.053
021	7 5 2	7317.6357	-0.049 s	-0.004
021	8 0 8	6941.4673	0.000	-0.013
021	8 2 7	7055.4489	-0.009	-0.004
021	8 3 6	7162.8415	0.000	0.000
021	8 3 5	7174.4787	-0.002	0.001
021	9 1 9	7060.6397	0.000	-0.001
021	9 2 8	7187.4072	-0.004	-0.055
021	10 0 10	7191.2730	0.000	0.017
021	10 2 9	7332.3733	-0.004	-0.013
031	2 2 1	7864.1804	-0.017	-0.001
031	4 0 4	7887.1525	-0.005	0.005
040	3 3 1	5722.0495	0.036	0.005
040	4 4 1	6016.2464	0.011	
040	5 3 3	5861.1482	0.003	
040	5 4 2	6094.8725	0.000 s	-0.048
040	5 5 0	6308.6763	0.013 cd	-0.001
040	7 4 3	6299.7717	-0.011	0.070
040	8 4 4	6326.4738	0.001	-0.054
040	9 3 7	6324.3469	-0.007	
040	9 4 5	6568.8747	-0.033	
040	10 2 8	6417.9730	0.031 cd	-0.024
040	11 3 9	6600.0811	-0.029	
101	2 1 2	6458.9143	-0.001	0.001
101	3 1 2	6516.4022	0.002	0.004
101	3 2 2	6552.8612	0.002	0.004
101	4 1 3	6581.4430	0.009	0.011
101	4 2 2	6618.0910	0.006	0.008
101	5 1 4	6661.7172	0.013	0.015
101	5 1 5	6621.5808	0.003	0.005
101	5 2 3	6698.5359	0.007	0.009
101	5 3 2	6763.6248	0.014	0.016
101	5 3 3	6762.7628	0.012	0.014
101	6 0 6	6699.7704	0.006	0.008
101	6 1 5	6756.4345	0.017	0.019
101	6 1 6	6701.7289	0.002	0.004
101	7 0 7	6793.4389	0.004 cd	0.007
101	7 1 6	6864.6429	0.019	0.021
101	7 3 5	6960.7533	0.023 cd	0.025
101	7 4 4	7059.6053	-0.002	0.000
101	8 0 8	6899.2032	0.012	0.014
101	8 1 7	6985.4310	0.027	0.029
101	8 4 5	7181.6963	-0.004	-0.002
101	9 0 9	7017.1089	0.020	0.022
101	10 1 9	7262.5573	0.047	0.049
101	10 2 9	7265.9631	0.030	0.032
111	5 3 3	8137.3415	0.005	0.006

(continued on next page)

**Table 4 (continued).**

120	1 0 1	5504.9309	-0.016	
120	2 0 2	5535.3927	0.009	0.000
120	2 1 1	5561.5630	0.003	-0.006
120	2 1 2	5552.3240	0.005	-0.004
120	2 2 0	5622.3352	0.008	-0.001
120	2 2 1	5622.0044	0.002 cd	-0.007
120	3 0 3	5580.1993	0.008	-0.001
120	3 1 2	5612.1608	0.007	-0.002
120	3 2 1	5669.9801	0.006	-0.003
120	3 2 2	5668.3875	0.008 cd	-0.001
120	3 3 0	5784.1382	0.006 cd	-0.003
120	3 3 1	5784.1207	0.008	-0.001
120	4 0 4	5638.5416	0.009	0.000
120	4 1 4	5648.5367	0.006	-0.003
120	4 1 3	5679.1390	0.008	-0.002
120	4 2 3	5729.9461	0.005 cd	-0.004
120	4 2 2	5734.5567	0.004 cd	-0.005
120	4 3 1	5847.0491	0.005	-0.004
120	4 3 2	5846.9152	0.003 cd	-0.006
120	5 0 5	5709.7007	-0.012	-0.021
120	5 1 5	5716.5562	0.005	-0.004
120	5 1 4	5762.0258	0.003	-0.006
120	5 2 4	5806.4627	0.002	-0.007
120	5 2 3	5816.5965	0.002	-0.007
120	5 3 3	5925.5206	-0.001cd	-0.010
120	5 3 2	5926.0377	0.000 cd	-0.009
120	6 0 6	5793.0204	0.002	-0.007
120	6 1 6	5797.5343	0.003	-0.006
120	6 1 5	5860.1850	-0.003	-0.012
120	6 2 5	5897.6689	0.001	-0.008
120	6 2 4	5916.3080	-0.004	-0.013
120	6 3 4	6019.9244	-0.006	-0.015
120	6 4 3	6094.6072	0.003	-0.006
120	6 5 2	6263.3536	0.013	0.004
120	7 0 7	5888.4318	0.000	-0.009
120	7 1 7	5891.2613	-0.001 cd	-0.010
120	7 1 6	5972.8361	-0.003	-0.012
120	7 2 6	6003.2586	-0.001 cd	-0.010
120	7 2 5	6033.5260	-0.010	-0.019
120	7 3 5	6130.0461	-0.014	-0.023
120	7 3 4	6133.6285	-0.015	-0.024
120	7 5 3	6370.4172	-0.003 cd	-0.012
120	7 5 2	6370.4121	-0.003 s	-0.011
120	8 0 8	5995.8442	-0.002	-0.014
120	8 1 8	5997.5680	-0.005	-0.015
120	8 1 7	6099.1346	-0.006 cd	-0.021
120	8 2 7	6122.9061	-0.012	-0.033
120	8 2 6	6167.7802	-0.024	-0.010
120	8 4 5	6325.8110	-0.001	-0.024
120	8 5 4	6255.7432	-0.015	-0.003
120	8 6 3	6690.0765	0.006 s	-0.015
120	8 6 2	6690.0762	0.006 s	-0.015
120	9 0 9	6116.3269	-0.006 cd	-0.024
120	9 1 9	6115.2898	-0.006	-0.047
120	9 2 8	6256.3178	-0.015 cd	-0.019
120	9 3 6	6410.3893	-0.038	-0.049
120	10 0 10	6246.8155	-0.010	-0.054
120	10 2 8	6484.9096	-0.040	-0.059
120	10 3 8	6552.8619	-0.045	-0.021
120	10 3 7	6575.5978	-0.050	-0.018
120	11 0 11	6390.4535	-0.012 cd	-0.045
120	11 1 11	6390.8217	-0.009 cd	-0.067
120	11 2 10	6563.2591	-0.036	-0.027
120	11 3 9	6723.6744	-0.058	-0.023
120	12 0 12	6546.1874	-0.018 cd	-0.015
120	12 1 12	6546.4127	-0.014	-0.024
200	4 3 2	5634.6648	-0.022	-0.001
200	4 3 1	5634.8289	-0.026	-0.005
200	4 4 1	5738.8813	-0.032	-0.011
200	5 2 3	5641.4130	-0.009	0.012
200	5 3 3	5709.6410	0.004	0.025
200	5 4 2	5813.6144	-0.033 cd	0.002
200	5 5 1	5946.1305	-0.025 s	-0.004
200	5 5 0	5946.1306	-0.025 s	-0.007

(continued on next page)

Table 4 (continued).

200	6 4 3	5903.4151	−0.028	−0.001
200	6 4 2	5903.4895	−0.022	0.022
200	7 3 5	5904.7571	0.001	0.019
200	7 4 4	6008.3897	−0.002	0.027
200	7 4 3	6008.6431	0.006 cd	0.034
200	8 3 6	6024.5106	0.013	0.025
200	8 4 5	6128.5097	0.004	0.021
200	8 5 3	6259.2000	0.000	−0.012
200	10 2 8	6275.7877	−0.033	
200	11 3 8	6494.9810	−0.039	−0.010
200	11 4 7	6586.9720	−0.031	−0.016
200	12 1 11	6523.0623	−0.037	−0.030
200	12 3 9	6698.4137	−0.051	−0.012

Table 5

Comparison of recently measured HD<sup>17</sup>O levels with calculations made using PES17 and pseudo experimental (isotopologue extrapolation, IE) levels.  $E_{\min}$  denotes the energy of the lowest observed level for each band.

Band	$N$ levels PES17	$\sigma$ (cm <sup>−1</sup> )	$N$ levels IE	$\sigma$ (cm <sup>−1</sup> )	$E_{\min}$ cm <sup>−1</sup>
(003)	138	0.127	70	0.114	10 615.4
(022)	55	0.095	35	0.061	10 161.4
(400)	44	0.192	40	0.202	10 366.1
(102)	64	0.068	59	0.059	10 069.5
(112)	25	0.035	24	0.030	11 292.5
(004)	114	0.029	50	0.027	13 832.8
(023)	89	0.019	46	0.023	13 255.6
(103)	75	0.027	34	0.032	13 307.8

levels known up to 2010. The newly measured lines of HD<sup>17</sup>O and the newly determined energy levels as well as the 6000 predicted pseudo-experimental levels increase significantly our knowledge of this water isotopologue and will provide a sound basis for the future attempts to solve completely the water isotopologue problem via solution of the non-adiabatic problem (see for example [40–42]).

CRediT authorship contribution statement

**Leonid N. Sinita:** Project administration, Methodology, Data curation, Conceptualization. **Nikolai F. Zobov:** Writing – review & editing, Software, Investigation, Formal analysis, Conceptualization. **Mikhail A. Rogov:** Investigation, Formal analysis. **Jonathan Tennyson:** Writing – review & editing, Methodology, Funding acquisition. **Oleg L. Polyansky:** Writing – original draft, Project administration, Methodology, Investigation.

Declaration of competing interest

The authors declare no conflict of interest

Acknowledgments

This work was supported by the Ministry of Science and Higher Education of the Russian Federation. We acknowledge support by State Project IAP RAS No. FFUF-2024-0016 and ERC Advanced Investigator Project grant 883830 for supporting aspects of this project. O.L.P. acknowledges support from QuantumPascalproject 18SIB04, which has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme and NERC grant NE/F01967X/1.

Appendix A. Supporting material

The following are given as supporting material: 1. A full list of the assigned experimental spectrum; 2. The HD<sup>16</sup>O and HD<sup>17</sup>O potential energy surfaces; 3. The lists of HD<sup>16</sup>O and HD<sup>17</sup>O energy levels.

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.jms.2024.111965>.

Data availability

All data is included in the article or the supplementary material.

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