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## Absorption of deuterated water vapor in the 1.98 $\mu\text{m}$ spectral region

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### Highlights:

Analysis of deuterated water vapor absorption between 4850 and 5600  $\text{cm}^{-1}$

HITRAN2016 water line list versus laboratory observations

New line parameters of  $\text{D}_2^{16}\text{O}$ ,  $\text{D}_2^{17}\text{O}$ ,  $\text{HD}^{16}\text{O}$ , and  $\text{HD}^{17}\text{O}$

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## Abstract

New spectra of water samples enriched by deuterium were recorded between 4500 and 5800  $\text{cm}^{-1}$  using a Fourier transform spectrometer Bruker IFS 125HR combined to multi-pass cells. The spectra were recorded at room temperature with a non apodized resolution of 0.01  $\text{cm}^{-1}$ , using water evaporated from a  $\text{D}_2\text{O}+\text{H}_2\text{O}$  mixture in the liquid phase. The water vapor pressure was about 1.5 Torr and the absorption path was more than 100 m. A special attention was paid to the experimental procedure allowing to obtain HDO in the gas phase, and also to determine the partial pressure of all isotopologues. Synthetic spectra were compared to the observed ones. Numerous examples of disagreements between measurements and simulations using existing water line lists were observed for deuterated water species. Some lacks were found in the HITRAN2016 line list. A list of 580 transitions is reported that corrects erroneous and missing lines.

## 1. Introduction

The concentration of deuterated water in the Earth's atmosphere is small but not negligible. In some spectral ranges, the absorption of the atmosphere is determined by the absorption of this small component. The GSMA laboratory is involved in a research project named WaVIL (Water Vapor Isotope Lidar), whose aim is the remote determination of  $\text{H}_2^{16}\text{O}$  and  $\text{HD}^{16}\text{O}$  concentrations at high spatio-temporal resolution in the lower troposphere using differential absorption lidar instrument. For these purposes, it is assumed to use selected lines of  $\text{H}_2^{16}\text{O}$  and  $\text{HD}^{16}\text{O}$  near  $1.98\ \mu\text{m}$ . In particular, two lines were chosen at  $5043.0475\ \text{cm}^{-1}$  ( $1982.9280\ \text{nm}$ ) and  $5044.2277\ \text{cm}^{-1}$  ( $1982.4640\ \text{nm}$ ), respectively for  $\text{H}_2\text{O}$  and  $\text{HDO}$ , allowing for a sufficiently high absorption over several kilometers with negligible interferences with other gas species (see **Figure 1**). The spectral window was chosen by a study done before the submission of the project in the LATMOS laboratory (Laboratoire Atmosphères, Observations Spatiales), using calculated transmission in atmospheric conditions at an altitude of 5 km. One of the most constraint was that the gap between the two lines does not exceed 50 GHz. In order to assess the spectroscopy of our targeted species in the  $1.98\ \mu\text{m}$  spectral region, the GSMA laboratory has recorded new experimental spectra to perform measurements of deuterated water vapor isotopologues. These new spectra gave us the opportunity to observe significant disagreements between recorded and calculated spectra using the HITRAN2016 database [1]. Examples of observed disagreements are shown, the work on a list of improved water vapor line parameters is still in progress. A complete line list is not presented here, it will be the subject of another article. Now we present only a line list of rare isotopic species, which significantly improves the list of the HITRAN2016 between  $4850$  and  $5600\ \text{cm}^{-1}$ .

The spectra of deuterated water vapor in the  $4850 - 5600\ \text{cm}^{-1}$  range are much less studied than the spectra of the three most abundant isotopologues ( $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{17}\text{O}$ ). The  $\text{HD}^{16}\text{O}$  line parameters were reported only in two studies. First, Toth [2] reported more than 1600 transitions from analysis of water vapor enriched by deuterium ( $\sim 50\%$   $\text{HDO}$ ). Later Jenouvrier et al. [3] completed this data set by 212 transitions of  $\text{HD}^{16}\text{O}$  isotopologue obtained from an analysis of long path absorption spectra of natural abundance water vapor. About 750 transitions of  $\text{HD}^{18}\text{O}$  between  $4850$  and  $5530\ \text{cm}^{-1}$  were obtained by Liu et al. [4] using absorption spectra of  $^{18}\text{O}$  enriched water vapor. About 1700  $\text{D}_2^{16}\text{O}$  transitions were reported by Wang et al. [5] from spectra of water vapor highly enriched by deuterium (started abundance of deuterium was  $\sim 99.8\%$ ). There are no experimental data in the range of interest for  $\text{HD}^{17}\text{O}$ ,  $\text{D}_2^{18}\text{O}$  and  $\text{D}_2^{17}\text{O}$  species.

## 2. Water vapor and isotopologue line parameters through high resolution spectroscopy measurements

Our group has been working for several years on the absorption water vapor spectrum analysis in the near infrared [4, 6-10]. New high-resolution spectra were recorded with a Fourier Transform Spectrometer Bruker IFS 125HR combined to multipass cells, from 2-meter to 50-meter

base [7]. The retrieval of the line parameters was performed using a multi-spectrum fitting procedure developed in the GSMA laboratory [11].

## 2.1. Experimental conditions

New high-resolution measurements were recorded at room temperature with a Bruker IFS 125HR in the 4500 – 5800  $\text{cm}^{-1}$  spectral region. The instrument was fitted to several cells. The optical source is a tungsten lamp, cooled with a water flow. All spectra were recorded with the following optical setup: a  $\text{CaF}_2$  beam splitter, a liquid-nitrogen cooled InSb detector with an infrared filtering between 4500 and 6000  $\text{cm}^{-1}$  and  $\text{BaF}_2$  lenses and windows. The whole absorption path was maintained under vacuum during the recording time.

To evaporate the liquid solution into a gas phase, we pumped on a vacuum glass flask filled with distilled water. Then, the saturation vapor pressure was introduced in the cell. To access the widest range of line intensities, we used two White cells: a 2-meter and a 50-meter base optical length, with an accessible optical path length up to 104.262-meter and 2-kilometers, respectively. The cells are made of steel, with  $\text{BaF}_2$  windows and gold-plated mirrors. Pressures in the cell were continuously monitored with three ceramic capacitance-diaphragm gauges (CTR100N – 10-Temperature compensated, 100 and 1000 Torr), covering the entire pressure range while ensuring a linear response and the best signal-to-noise ratio (SNR) for each sensor. The FTS room was air-conditioned, and any variation of the temperature was observed with platinum resistance thermometers (four PT100 4 wires connected to Redlab-TEMP temperature data logger from Meilhaus Electronic GmbH). During the recording time, the whole absorption path was maintained under vacuum. After each introduction of water sample, pressure and temperature were monitored to wait for the stabilization of the cell pressure before the beginning of the spectra recording (several hours were needed). **Figure 1** shows the spectral area where both transitions are located in five pure  $\text{H}_2\text{O}$  spectra with pressure ranging from 0.5 to 10 Torr and a pathlength of 32.3 m. The zoom panel shows small portion of the spectrum between 5042  $\text{cm}^{-1}$  and 5044.5  $\text{cm}^{-1}$ , containing the two lines of  $\text{H}_2^{16}\text{O}$  and  $\text{HD}^{16}\text{O}$  ("two WaVIL transitions ") chosen for the WaVIL project.

### Figure 1

To obtain a good SNR up to 2500 the total recording time was around 20 hours by cumulating recorded interferograms. For each spectrum, optical parameters were chosen to prevent any sinc function artifact. In our case, the heaviest measurable molecule is the  $\text{D}_2^{18}\text{O}$  isotopologue. It brings to a Doppler width of 0.0138  $\text{cm}^{-1}$  (around 5044  $\text{cm}^{-1}$  at 294 K), so we recorded spectra with a resolution of 0.01  $\text{cm}^{-1}$  (following Bruker resolution definition<sup>1</sup>). The iris diameter aperture is fixed to 1.7 mm. By this way, recorded spectra will not show any apparatus function oscillation, even with the simplest boxcar apodization function. All interferograms were averaged and converted to transmission spectra using a Fourier transform algorithm with the OPUS software.

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<sup>1</sup>  $\text{RES} = 0.9/\text{OPD}_{\text{max}}$ , where RES is the Bruker resolution value parameter into OPUS, and  $\text{OPD}_{\text{max}}$  is the maximum optical path difference.

The spectra were analyzed with a multispectrum fitting software [11], named MultiFit, developed in the GSMA laboratory. The advantage of this technique is the retrieval of more realistic line parameters using several spectra recorded in different experimental conditions, indeed the lines parameters are determined simultaneously. The retrieval of the line parameters requires a set of spectra with increasing pressure, in the pure water case from 1 Torr up to a maximum of 13 Torr at the recorded temperature (possible maximum of pressure for water vapor at room temperature). For the line profile, a Voigt profile was adopted in this study. **Figure 2** showing an example of the multispectrum fit on the main isotopologue of water vapor. This figure shows the fit of five spectra of  $\text{H}_2^{16}\text{O}$  in natural abundance with the same absorption path length (32.3 m) and different pressures in the upper panel and the residuals of the fit in the lower panel. As can be seen from the picture on the lower panel of **Figure 2**, at pressures above 2 torr, the difference between recorded and calculated spectra, let appear a little W-shaped structure typical for the Voigt contour. However, even for a pressure of 10 torr, the amplitude of this systematic structure does not exceed 0.5%. Note **Figure 2** also demonstrates the quality of the recorded spectra. The noise level is so low that it allows us to see subtle differences between the observations and the simulation.

**Figure 2**

## 2.2. Sample of water vapor isotopologues and partial pressure determination

The HDO gas sample was made with a combination of a liquid solution of  $\text{D}_2\text{O}$  (EurisoTop, ref. D215H, stated purity of 99.96%) with distilled water. An experimental setup (see **Figure 3**) was developed to obtain a repeatable process and to achieve a fine injection of the water vapor sample. Two graduated burettes allow us to get an accurate visual reading of the volume of each water sample isotopologue. Then the liquids are blended in the round bottom flask thanks to a magnetic stirrer and heated to prevent ice formation during the vacuum process.

**Figure 3**

Even if the main glass container and the rest of the system is firstly under vacuum (at least  $10^{-4}$  mbar), some ambient air remains. To prevent any perturbing gas in the final introduced sample, a cold trap was added, with a mixture of liquid nitrogen and alcohol. After pumping on this system, the Dewar is removed and the  $\text{D}_2\text{O} + \text{H}_2\text{O}$  mixture in gas phase is introduced in the cell. Three different volume ratios were used: 25%  $\text{H}_2\text{O} / 75\% \text{D}_2\text{O}$ , 50%  $\text{H}_2\text{O} / 50\% \text{D}_2\text{O}$ , and 75%  $\text{H}_2\text{O} / 25\% \text{D}_2\text{O}$ . **Table 1** contains the parameters of the  $\text{D}_2\text{O} + \text{H}_2\text{O}$  experimental spectra. These ratios are sufficient to obtain significant partial pressure of each species in the final gas sample. One can see in **Figure 4** an example of three spectra with the same total pressure (1.5 Torr), the same absorption path length of 104.26 m, and different mixture ratios.

**Table 1**

**Figure 4**

The identification of H<sub>2</sub>O isotopologues and the determination of partial pressure ratio of each molecule is the next step. A primary synthetic spectrum is performed using the data from the HITRAN2016 database [1] and compared to experimental spectra to identify the major species. HD<sup>18</sup>O and D<sub>2</sub><sup>18</sup>O have been identified with line positions from Kyuberis et al. [12].

Once each isotopologue was assigned in the spectrum, the next step to perform line parameter measurements on the HD<sup>16</sup>O isotopologue, is to precisely determine the partial pressure of each isotopologue. This step is crucial for the line parameters determination.

We developed a method to determine the partial pressure of each isotopologue. If we want to fit the pressure parameter, we have to fix the line intensity parameter. Equation (1) shows the different partial isotopologue pressures to take into account in the total pressure. For some isotopologues as HD<sup>18</sup>O and D<sub>2</sub><sup>18</sup>O, we fixed the intensity parameters to the calculated values of Kyuberis et al. [12], even if their contributions are very weak. The intensity parameters for the H<sub>2</sub><sup>16</sup>O molecule were fixed to the values published by Lodi et al. [13]. For D<sub>2</sub><sup>16</sup>O and HD<sup>16</sup>O, as we were not convinced that the intensity parameters listed in the HITRAN2016 database were accurate enough, we determined their pressure using another method. For these two species, we determined ratios of partial pressure (Eqs. (2)) by fitting simultaneously the pressure of one of these two isotopologues on two spectra A and B recorded with different mixing proportions and the line intensity being fixed to the value listed in the HITRAN2016 database. That way, the determined pressures were not precise enough but the ratio of pressures between the two spectra was correct.

$$P_{total} = P_{H_2^{16}O} + P_{H_2^{18}O} + P_{HD^{16}O} + P_{HD^{18}O} + P_{D_2^{16}O} + P_{D_2^{18}O} \quad (1)$$

$$\eta_{D_2^{16}O} = \frac{P_B^{D_2^{16}O}}{P_A^{D_2^{16}O}} \text{ and } \eta_{HD^{16}O} = \frac{P_B^{HD^{16}O}}{P_A^{HD^{16}O}} \quad (2)$$

These fits were performed on spectra at low pressure (lower than 2 Torr), to neglect as much as possible the influence of the self-broadening coefficient in the determination of the pressure. The ratio was computed only on lines with similar intensity between two different mixture proportions; and the line intensity must be within reasonable absorption range, not saturated or too weak.

From Eq. (1), we obtained the sum of D<sub>2</sub><sup>16</sup>O and HD<sup>16</sup>O pressures:

$$\begin{cases} P'_A = P_{A,total} - [P_A^{HD^{18}O} - P_A^{H_2^{16}O} - P_A^{D_2^{18}O}] = P_A^{D_2^{16}O} + P_A^{HD^{16}O} \\ P'_B = P_{B,total} - [P_B^{HD^{18}O} - P_B^{H_2^{16}O} - P_B^{D_2^{18}O}] = P_B^{D_2^{16}O} + P_B^{HD^{16}O} \end{cases} \quad (3)$$

By combining Eqs. (2) and (3), we were able to retrieve two following Eqs. (4) and (5) and the partial pressures of the D<sub>2</sub><sup>16</sup>O and HD<sup>16</sup>O isotopologues with Eq. (6):

$$P_A^{D_2^{16}O} = P'_A - P_A^{HD^{16}O} \quad (4)$$

$$\eta_{D_2^{16}O} (P'_A - P_A^{HD^{16}O}) + \eta_{HD^{16}O} P_A^{HD^{16}O} = P'_B \quad (5)$$

$$P_A^{HD^{16}O} = \frac{P'_B - \eta_{D_2^{16}O} P'_A}{\eta_{HD^{16}O} - \eta_{D_2^{16}O}} \quad (6)$$

The results of our partial pressure determination are compiled in **Table 2** showing each isotopologue proportion.

**Table 2**

### **3. HITRAN2016 water line list and comparison with observations**

#### **3.1. Inventory of the HITRAN2016 line list**

The HITRAN2016 database edition [1] contains more than 23,300 transitions of seven water isotopologues between 4850 and 5600  $\text{cm}^{-1}$ . An overview of this data is shown in **Table 3**, notice that the isotopologues  $\text{D}_2^{18}\text{O}$  and  $\text{D}_2^{17}\text{O}$  are missing in the line list [1].

**Table 3**

Spectrum simulations showed very good agreement with recorded spectra for the first three isotopologues of **Table 3**. We found no significant difference between the observed and simulated absorption for these species. But it is not the case for deuterated species. Line positions of 57 transitions of  $\text{HD}^{16}\text{O}$  must be at least significantly corrected. Using the spectrum with the highest deuterium enrichment (see **Table 1**), we found fifteen lines of  $\text{HD}^{18}\text{O}$  and  $\text{HD}^{17}\text{O}$  that are not included in the line list [1]. The situation is much worse for double deuterated species. First of all, the  $\text{D}_2^{16}\text{O}$  list of Ref. [1] contains 255 strictly forbidden transitions according to the selection rules for the electric dipole transitions. Note  $\text{D}_2^{16}\text{O}$  line positions for the HITRAN2016 list were calculated using empirical values of the upper and lower energies. Thus a wrong assignment of one of these levels induces an incorrect value of the line position. The second problem is duplicate assignments of more than 200 transitions. Third, some of  $\text{D}_2^{16}\text{O}$  transitions above the cut-off of  $1.0 \times 10^{-29}$  cm / molecule are missing in the HITRAN2016 line list [1]. In addition, 222  $\text{D}_2^{16}\text{O}$  transitions are given without complete VR labeling. These transitions have variationally calculated line positions. Using recorded spectra we were able to observe 233  $\text{HD}^{18}\text{O}$  and 35  $\text{HD}^{17}\text{O}$  lines. Note that there are no published observations of  $\text{HD}^{18}\text{O}$  and  $\text{HD}^{17}\text{O}$  lines in the range of interest in the literature.

Finally, we found the lines of more than 1000 transitions of six isotopologues ( $\text{HD}^{16}\text{O}$ ,  $\text{HD}^{17}\text{O}$ ,  $\text{HD}^{18}\text{O}$ ,  $\text{D}_2^{16}\text{O}$ ,  $\text{D}_2^{17}\text{O}$ , and  $\text{D}_2^{18}\text{O}$ ) observed in recorded spectra, that cannot be correctly described using HITRAN2016 line list. This is due to either incorrect line positions (or intensity) or the absence of corresponding transitions in the line list [1]. Note a part of these problematic lines can be better reproduced using the lists published by Kyuberis et al. [12]. Nevertheless, both line lists [1, 12] do not allow us to model correctly the observed spectra.

#### **3.2. Observed disagreements with the HITRAN2016 database and discussion**

We present some examples of disagreements between observed and simulated spectra in this section. As it was explained above, simulations were calculated using the line parameters of the



HITRAN2016 line list [1]. The observed spectrum is the spectrum (a) of **Table 1** (75% D<sub>2</sub>O & 25% H<sub>2</sub>O mixture with a total water vapor pressure of 1.55 Torr). Vibration-rotation assignments of the lines missing from the lists [1, 12] were performed using so called SP (Schwenke & Partridge) line lists of HD<sup>16</sup>O and D<sub>2</sub><sup>16</sup>O from SPECTRA system [14]. These lists have been computed by S.A. Tashkun (IAO SB RAS, Russia) using results of variational calculations by Schwenke and Partridge (SP) [15, 16]. Variational line positions were corrected by empirical values calculated from the experimental energy levels known from previous studies.

### Figure 5

**Figure 5** shows a part of spectrum around 5189.8 cm<sup>-1</sup> where two major problems of the HITRAN2016 line list [1] are shown. First of all, the position 5189.869 cm<sup>-1</sup> is a wrong line position due to a D<sub>2</sub><sup>16</sup>O forbidden transition 2ν<sub>2</sub>+ν<sub>3</sub> 9<sub>19</sub> – 8<sub>08</sub> [1]. The correct position (5189.8103 cm<sup>-1</sup>) of this D<sub>2</sub><sup>16</sup>O line with the correct assignment (2ν<sub>2</sub>+ν<sub>3</sub> 9<sub>09</sub> – 8<sub>08</sub>) is given in the list [12]. The second problem is the D<sub>2</sub><sup>16</sup>O line at variationally calculated position 5189.581 cm<sup>-1</sup> with incomplete VR assignment. The complete assignment for this line (ν<sub>1</sub>+ν<sub>3</sub> 12<sub>39</sub> – 13<sub>310</sub>) is given by Kyuberis et al. [12], on the other hand the line position of this transition is the same in the two line lists [1,12].

### Figure 6

**Figure 6** shows another example of a typical issue of the HITRAN2016 line list for D<sub>2</sub><sup>16</sup>O isotopologue. Forbidden transition 2ν<sub>2</sub>+ν<sub>3</sub> 10<sub>010</sub> – 9<sub>19</sub> at 5196.991 cm<sup>-1</sup> (line (a) in **Figure 6**) listed twice in HITRAN2016 instead of two transitions 10<sub>110</sub> – 9<sub>19</sub> at 5197.022 cm<sup>-1</sup> and 10<sub>010</sub> – 9<sub>09</sub> at 5197.046 cm<sup>-1</sup> (lines (b) and (c) in **Figure 6**). Correct positions and assignments of these lines are given by Kyuberis et al. [12] and confirmed by our observation.

Some additional disagreements between observed spectra and the simulations using the HITRAN [1] and Kyuberis et al. [12] line lists are given on the figures in Supplementary materials to the paper. Three of these figures show the observed D<sub>2</sub><sup>16</sup>O lines of the ν<sub>1</sub>+ν<sub>3</sub> and 2ν<sub>1</sub> bands whose transitions have disappeared from the lists [1, 12].

Overall we observe more than 200 lines of six cold (2ν<sub>1</sub>, 2ν<sub>3</sub>, ν<sub>1</sub>+ν<sub>3</sub>, 4ν<sub>2</sub>, 2ν<sub>2</sub>+ν<sub>3</sub>, and ν<sub>1</sub>+2ν<sub>2</sub>) and three hot (3ν<sub>2</sub>+ν<sub>3</sub>-ν<sub>2</sub>, ν<sub>1</sub>+ν<sub>2</sub>+ν<sub>3</sub>-ν<sub>2</sub> and 2ν<sub>1</sub>+ν<sub>2</sub>-ν<sub>2</sub>) D<sub>2</sub><sup>16</sup>O bands, some of these transitions are not included in the lists [1, 12]. Line intensities of these missing transitions are above the cut-off of the HITRAN2016 list at 1×10<sup>-32</sup> cm/molecule (see **Table 3**).

The figure below demonstrates inaccuracies of HD<sup>16</sup>O line positions in both HITRAN2016 [1] and Kyuberis et al. [12] line lists. **Figure 7** shows the difference of about 0.01 cm<sup>-1</sup> between observed (5486.2812 cm<sup>-1</sup>) and calculated (5486.2905 cm<sup>-1</sup>, [1, 12]) HD<sup>16</sup>O line position of the 2ν<sub>1</sub> 10<sub>46</sub> – 9<sub>45</sub> transition. Incorrect position of the ν<sub>1</sub>+ν<sub>3</sub> 11<sub>29</sub> – 10<sub>28</sub> line of D<sub>2</sub><sup>16</sup>O (5486.2281 cm<sup>-1</sup> [1] instead of 5486.2115 cm<sup>-1</sup> (observed value)) is due to wrong rotation assignment (11<sub>39</sub> – 10<sub>28</sub>) of this transition in the HITRAN2016 list. Inaccuracies reaching 0.2 cm<sup>-1</sup> of some HD<sup>16</sup>O lines of the ν<sub>1</sub>+2ν<sub>2</sub>, ν<sub>1</sub>+ν<sub>3</sub> and 4ν<sub>2</sub> bands are shown on the figures in Supplementary materials.

## Figure 7

Despite the fact that the list of the spectral line parameters given by Kyuberis et al. [12] is significantly better than those of the HITRAN2016 database [1] for deuterated isotopologues, some of the observed lines cannot be identified using both lists. At least for  $D_2^{16}O$  molecule, most of missing transitions have intensities higher than the cut-off accepted in the HITRAN2016 database. For example, the line of the  $2\nu_1 10_6 4 - 10_5 5$  transition at  $5365.9 \text{ cm}^{-1}$  (**Figure 2SM of Supplementary materials**) has an intensity ( $1.4 \times 10^{-30} \text{ cm/molecule}$ ) two orders higher. Now we are reporting a list of the transitions that have erroneous positions or intensities or are not included in any of the lists of the HITRAN2016 [1] and Kyuberis et al. [12]. The line list available in Supplementary Materials includes the lines of  $HD^{16}O$ ,  $HD^{17}O$ ,  $D_2^{16}O$ ,  $D_2^{17}O$ , and  $D_2^{18}O$  isotopologues. Thus, **the results of the analysis of the recorded spectra allow us to refine and supplement the existing databases for at least five isotopologues mentioned above. Figure 8 shows differences for the  $D_2^{16}O$  isotopologue** between observed line positions and those included in the line lists [1, 12]. The maximum deviation reaches  $0.3 \text{ cm}^{-1}$  for the  $2\nu_2 + \nu_3 11_{110} - 11_{111}$  and  $11_{111} - 11_{110}$  transitions at  $5249.725 \text{ cm}^{-1}$ .

## Figure 8

### 4. Conclusions

The main conclusion from the spectroscopic point of view is that available line lists ([1] and [12] in particular) are sufficient for precise simulations of spectra of water vapor highly enriched by deuterium in the region of interest. Recorded spectra demonstrate numerous examples of incompleteness ( $D_2^{16}O$ ,  $D_2^{17}O$  and  $D_2^{18}O$ ) and inaccuracies of available line lists [1, 12] for both line positions ( $D_2^{16}O$ ,  $D_2^{17}O$ ,  $HD^{16}O$ , and  $HD^{17}O$ ) and intensities ( $4\nu_2$  of  $HD^{16}O$ ). At the same time we can conclude that the list of Kyuberis et al. [12] gives a significant improvement for the  $HD^{16}O$  and  $D_2^{16}O$  line parameters in comparison with the HITRAN2016 database. Work on an improved and complete water vapor line list obtained by the analysis of recorded spectra is in progress. The list of 580 transitions that corrects erroneous lines and makes up for lost lines in the database is given in Supplementary Materials. The list of  $D_2^{16}O$  forbidden *para-ortho* transitions included in the HITRAN2016 database is also given in Supplementary Materials.

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## Figure captions

**Figure 1.** Five experimental spectra in natural abundance, in the 5000 – 5100  $\text{cm}^{-1}$  spectral range and in the zoom panel of the “two WaVIL transitions” ( $\text{H}_2^{16}\text{O}$  and  $\text{HD}^{16}\text{O}$ )

**Figure 2.** Example of multispectrum fitting on five spectra of  $\text{H}_2^{16}\text{O}$  in natural abundance with pressures varying from 0.5 to 10 Torr and pathlength of 32.3 m

**Figure 3.** Experimental setup for the  $\text{D}_2\text{O}/\text{H}_2\text{O}$  mixing solution with cold trap controlling

**Figure 4.** Recorded spectra in the 5172 – 5176  $\text{cm}^{-1}$  spectral range with different proportions in the  $\text{D}_2\text{O} / \text{H}_2\text{O}$  mixture: (a) 25%  $\text{H}_2\text{O} / 75\%$   $\text{D}_2\text{O}$ ; (b) 50%  $\text{H}_2\text{O} / 50\%$   $\text{D}_2\text{O}$ ; (c) 75%  $\text{H}_2\text{O} / 25\%$   $\text{D}_2\text{O}$ . Some transitions are identified on the upper spectrum.

**Figure 5.** Comparison between the observed spectrum in black line and a simulation (red line) with the line parameters from the HITRAN2016 database [1] around 5189.8  $\text{cm}^{-1}$ .

**Figure 6.** Comparison between the observed spectrum in black line and a simulation with the line parameters from the HITRAN2016 database [1] around 5197  $\text{cm}^{-1}$ . The contributions of different isotopologues are given in different colors.

**Figure 7.** Comparison between the observed spectrum in black line and a simulation (red line) with the line parameters from the HITRAN2016 database [1] around 5486.3  $\text{cm}^{-1}$ .

**Figure 8.** Differences between observed  $\text{D}_2^{16}\text{O}$  line positions and those of the Refs. [1, 12].

## Table captions

**Table 1.** Experimental conditions of D<sub>2</sub>O/H<sub>2</sub>O mixture recorded spectra

**Table 2.** Proportions of water vapor isotopologues

**Table 3.** Contents of HITRAN's water line list in the 4850 – 5600 cm<sup>-1</sup> region

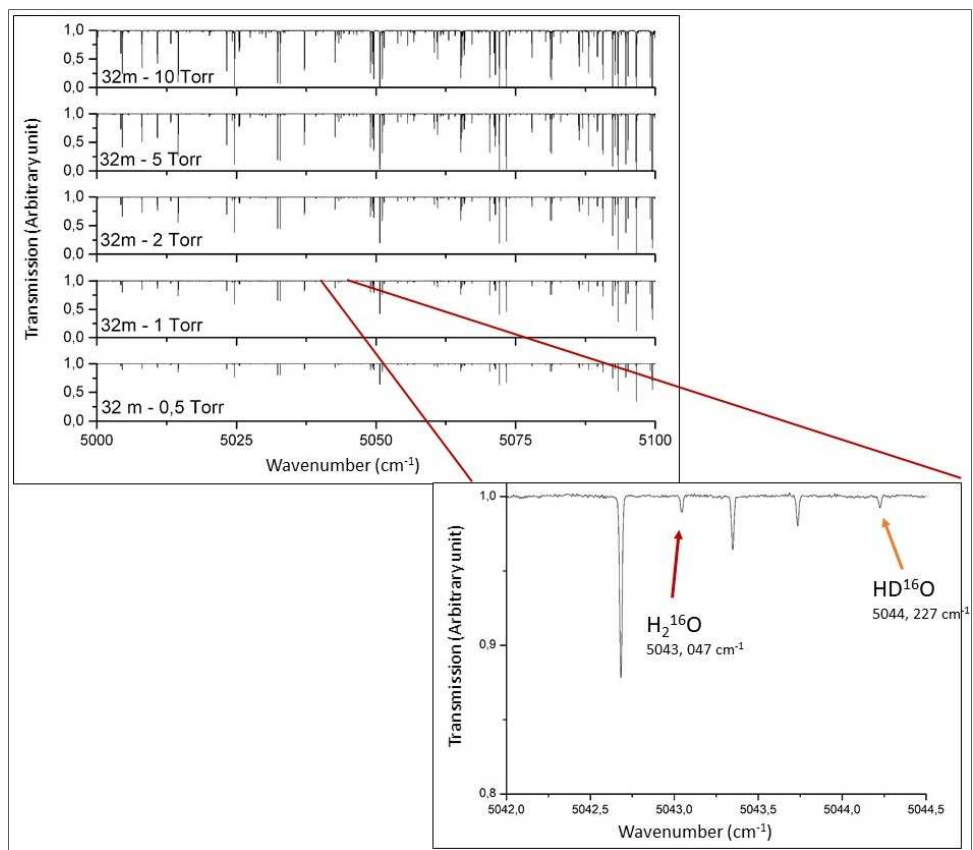


Figure 1

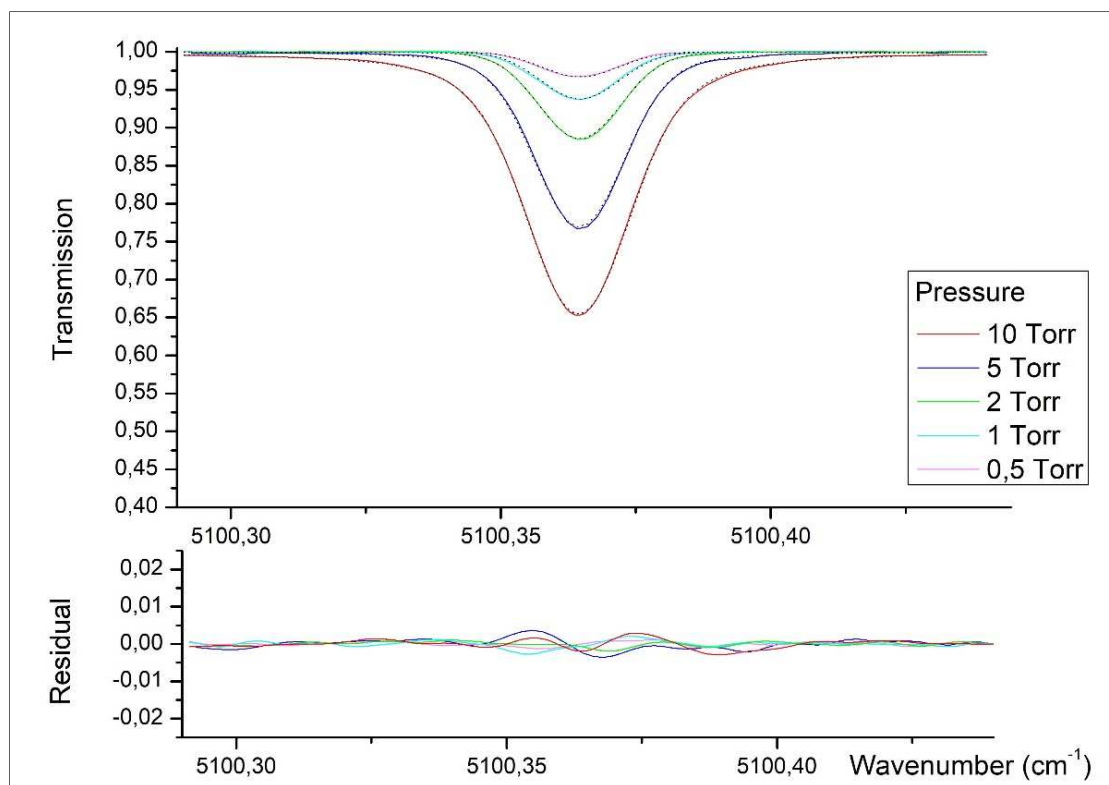


Figure 2



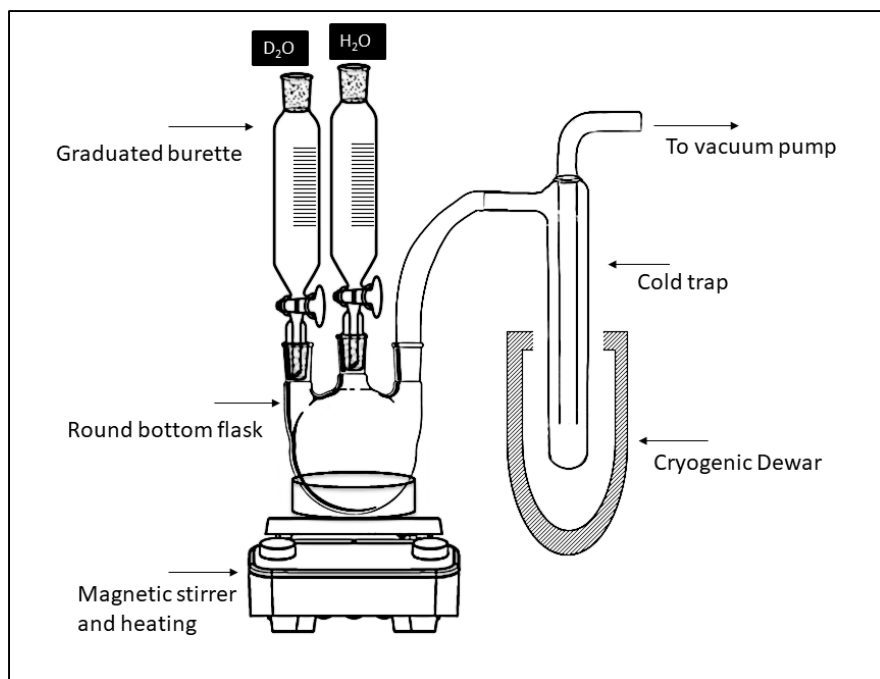


Figure 3

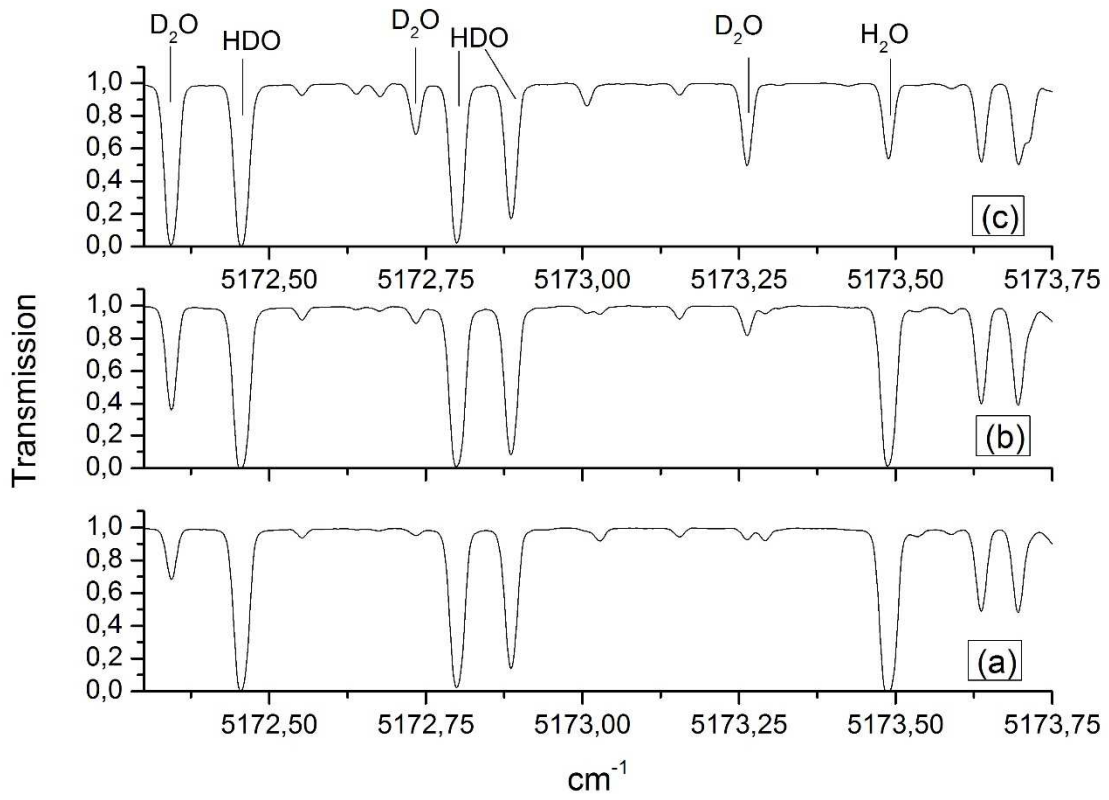


Figure 4

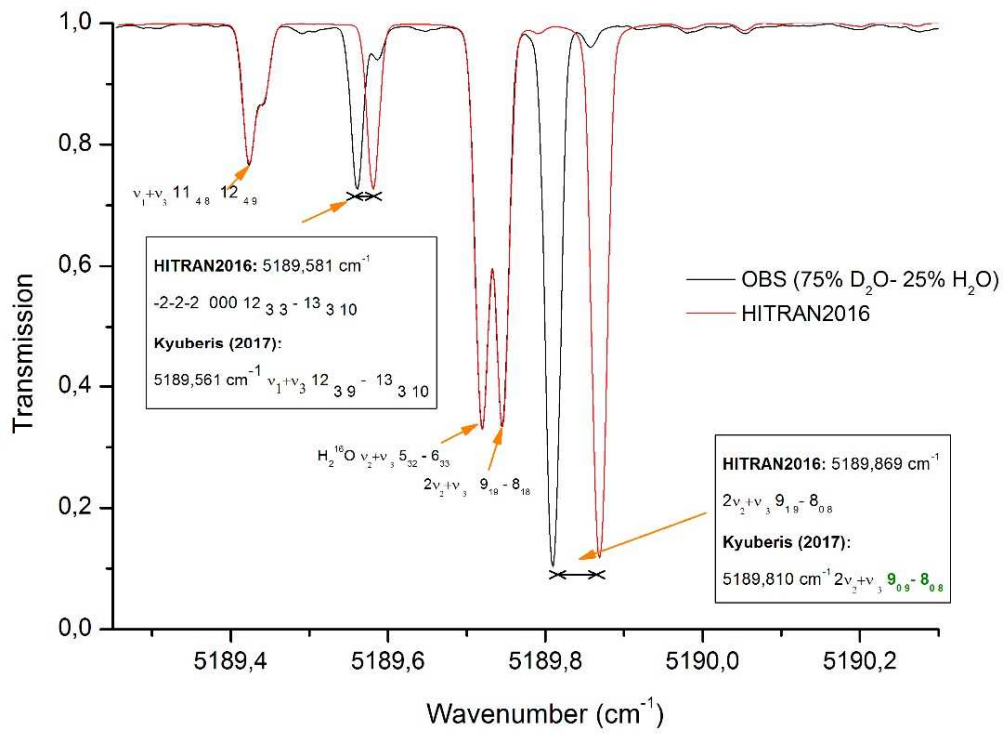


Figure 5

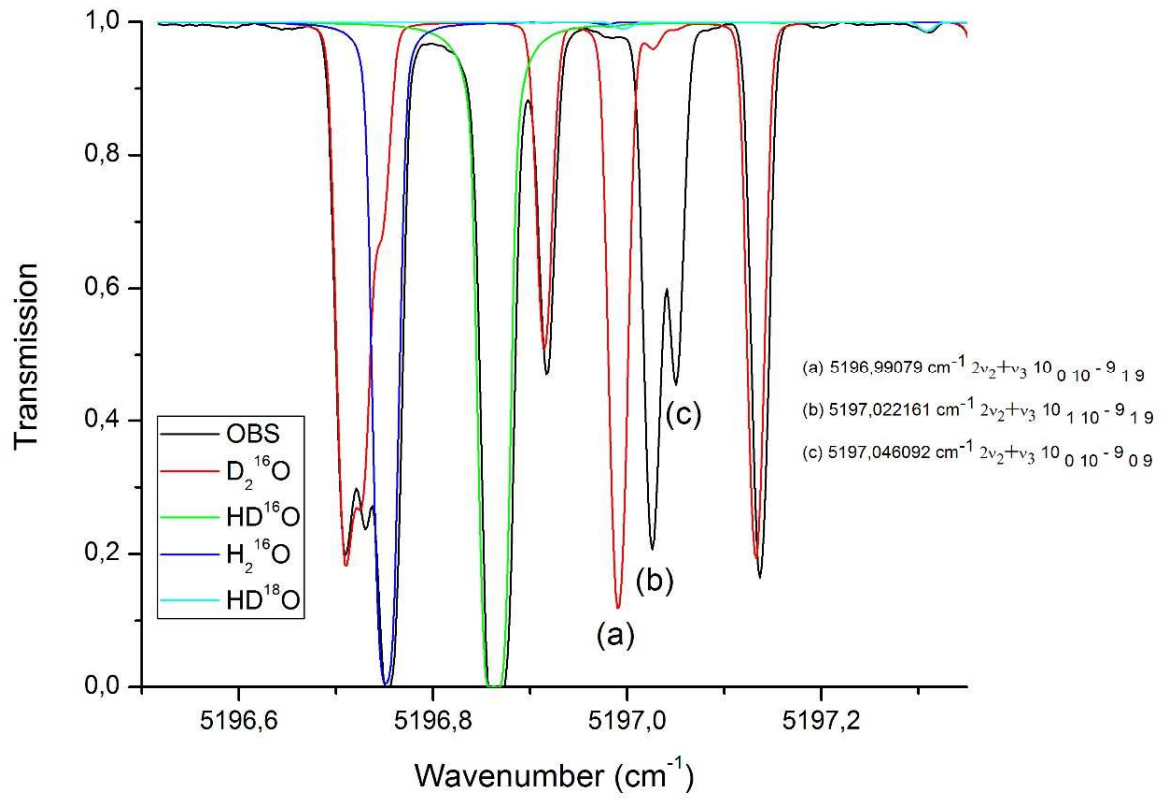


Figure 6

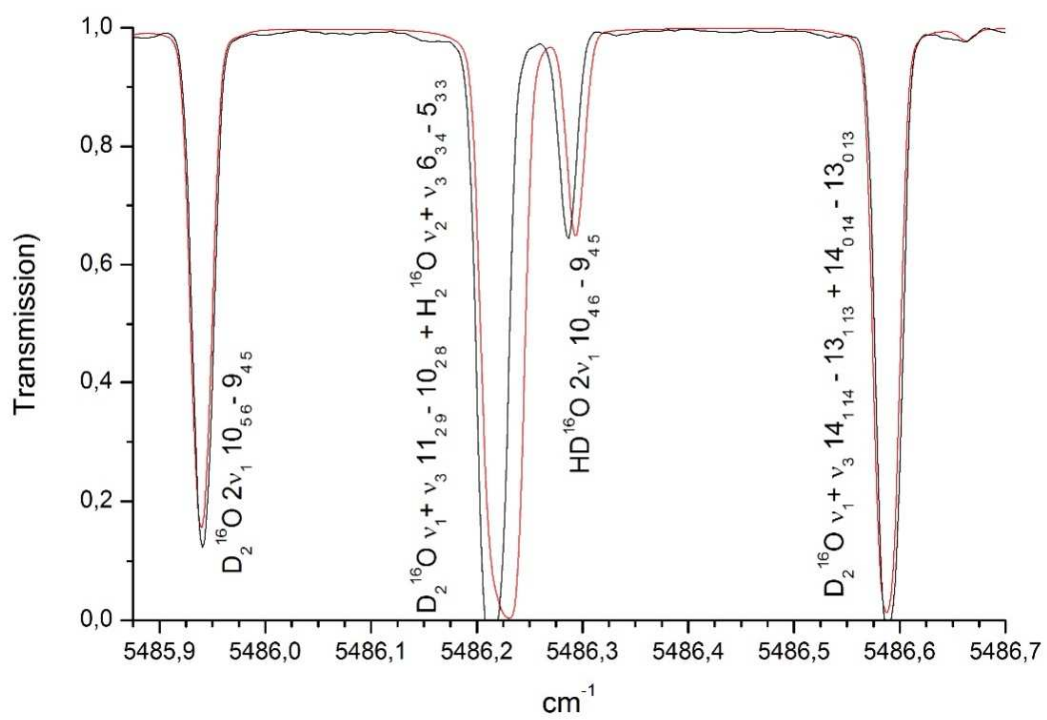


Figure 7

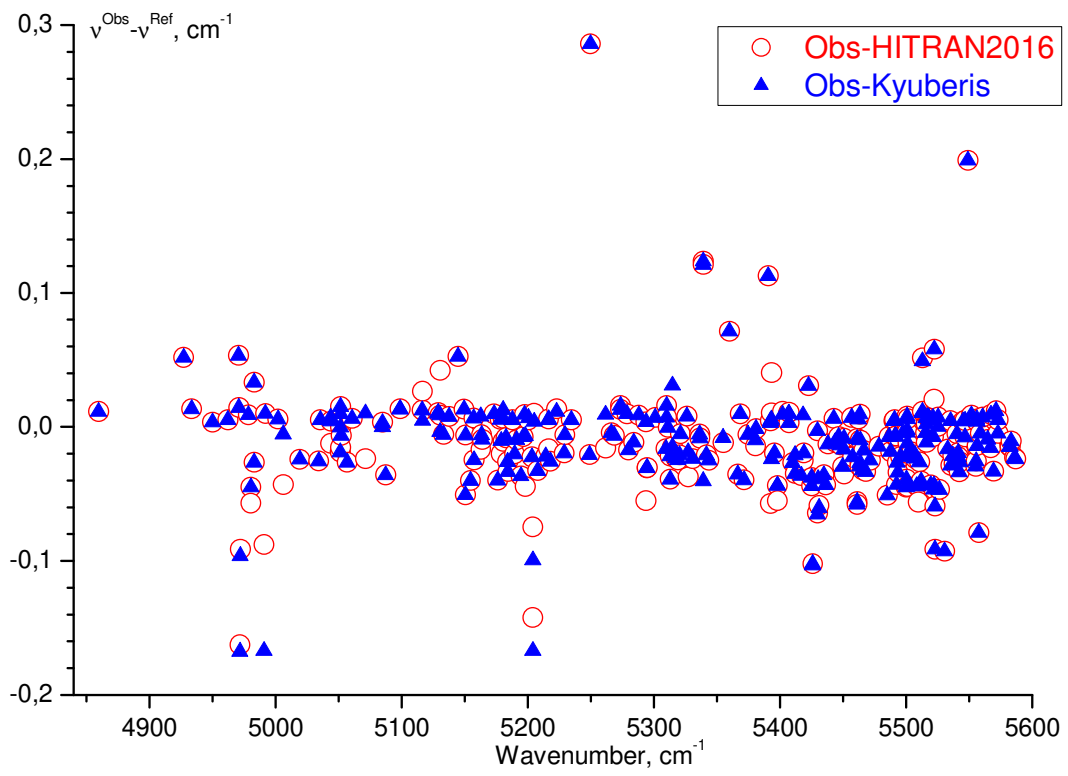


Figure 8

Table 1

Spectrum	Recording range ( $\text{cm}^{-1}$ )	Absorption path length (cm)	Pressure (Torr)	Mixing ratio (% $\text{D}_2\text{O}$ / % $\text{H}_2\text{O}$ )
(a)	4500 – 6500	10426.2	1.55	75 / 25
(b)	4500 – 6500	10426.2	1.47	50 / 50
(c)	4500 – 6500	10426.2	1.46	25 / 75

Table 2

ID	Molecule	Mixing ratio (%)			Natural abundance
		75% D <sub>2</sub> O / 25% H <sub>2</sub> O	50% D <sub>2</sub> O / 50% H <sub>2</sub> O	25% D <sub>2</sub> O / 75% H <sub>2</sub> O	
11	H <sub>2</sub> <sup>16</sup> O	4.68	29.9	54.0	99.73
14	HD <sup>16</sup> O	33.0	50.0	39.0	0.031069
15	HD <sup>18</sup> O	0.37	0.3	0.2	6.23×10 <sup>-5</sup>
17	D <sub>2</sub> <sup>16</sup> O	62.0	19.8	6.98	2.42×10 <sup>-6</sup>
18	D <sub>2</sub> <sup>18</sup> O	0.2	0.2	0.01	3.6×10 <sup>-9</sup>

Note: H<sub>2</sub><sup>18</sup>O and H<sub>2</sub><sup>17</sup>O isotopologues were not listed in the table due to the absence of their significant absorption in the recorded spectra. Because the H<sub>2</sub><sup>16</sup>O percentage in used mixtures does not exceed 55%, the H<sub>2</sub><sup>18</sup>O and H<sub>2</sub><sup>17</sup>O expected percentage is below 0.1% and 0.02% respectively.



Table 3

Isotopologue	Number of transitions	Spectral range, cm <sup>-1</sup>	Intensity cut-off, cm <sup>-1</sup> /molecule cm <sup>-2</sup> at 296 K
H <sub>2</sub> <sup>16</sup> O	6635	4851 – 5600	1.0×10 <sup>-29</sup>
H <sub>2</sub> <sup>18</sup> O	2792	4850 – 5600	1.0×10 <sup>-29</sup>
H <sub>2</sub> <sup>17</sup> O	2078	4850 – 5600	1.0×10 <sup>-29</sup>
HD <sup>16</sup> O	6025	4850 – 5600	1.0×10 <sup>-29</sup>
HD <sup>18</sup> O	1029	4853 – 5598	1.0×10 <sup>-29</sup>
HD <sup>17</sup> O	618	4880 – 5477	7.3×10 <sup>-33</sup> a)
D <sub>2</sub> <sup>16</sup> O	4089	4850 – 5600	1.0×10 <sup>-32</sup> b)
Total	23 336	4850 – 5600	7.3×10 <sup>-33</sup>

a) 14 transitions below 1.0×10<sup>-29</sup>

b) 171 transitions below 1.0×10<sup>-29</sup>