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► **To cite this version:**

L. Regalia, X. Thomas, T. Rennesson, S. Mikhailenko. Line parameters of water vapor enriched by  $^{18}\text{O}$  from 6525 to 8011  $\text{cm}^{-1}$ . *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2019, 235, pp.257-271. 10.1016/j.jqsrt.2019.06.031 . hal-02189145

**HAL Id: hal-02189145**

**<https://hal.univ-reims.fr/hal-02189145>**

Submitted on 25 Oct 2021

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## Line parameters of water vapor enriched by $^{18}\text{O}$ from 6525 to 8011 $\text{cm}^{-1}$

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**Keywords:** infrared spectroscopy; line intensity measurements; FTS spectra; water vapor;  $^{18}\text{O}$

Number of Pages: 24

Number of Figures: 14

Number of Tables: 7

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## Abstract

This study is a continuation of experimental efforts on the analysis of the near-infrared absorption spectrum of water vapor. Our previous studies were focused on water vapor in natural isotopic abundance. Now we are interested in the  $\text{H}_2^{18}\text{O}$  water isotopologue. New spectra of water samples enriched by  $^{18}\text{O}$  were recorded between 6400 and 9400  $\text{cm}^{-1}$  in Reims with the Connes-type Fourier Transform Spectrometer, built in our laboratory. The spectra were recorded at room temperature with a  $\text{H}_2^{18}\text{O}$  abundance enrichment of about 95% and a non apodized resolution of 0.010  $\text{cm}^{-1}$ . Pressure varied from 2 to 13 torr and the absorption path length was from 67 cm to 1001 m.

This article presents the results of the analysis of the first part of the whole recorded spectral range below 8000  $\text{cm}^{-1}$ . About 8100 absorption lines were found in the recorded spectra with an absorption path length from 8 to 88 m between 6525 and 8011  $\text{cm}^{-1}$ . Overall, 7993 lines were assigned to 8647 transitions of six water isotopologues ( $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $\text{HD}^{16}\text{O}$ ,  $\text{HD}^{17}\text{O}$ , and  $\text{HD}^{18}\text{O}$ ). Ninety-eight lines with intensity values between  $6 \times 10^{-27}$  and  $1.45 \times 10^{-25}$  cm/molecule were left unassigned. More than 870  $\text{H}_2^{18}\text{O}$ ,  $\text{H}_2^{17}\text{O}$  and  $\text{HD}^{18}\text{O}$  lines were observed for the first time. The observed line positions allow to obtain about 90 new or corrected rotation-vibration energy levels of  $\text{H}_2^{18}\text{O}$  and  $\text{H}_2^{17}\text{O}$ .

Comparison of line positions and intensities with literature data are presented and discussed. Some examples of disagreements between the measurements and data from the literature are presented in the last part of this article.

## 1. Introduction

The knowledge of spectroscopic parameters of atmospheric species is very important for the studies on the Earth atmosphere. Among these species, the water vapor plays a special role as it participates in the global radiative balance of the Earth atmosphere. Monitoring of water isotopologues in the atmosphere provides information about the water cycle. For planetary studies like Venus or Mars, the knowledge of the quantification of water vapor isotopologues is also essential, indeed this information is a tracer which can inform on the solar system evolution.

The aim of this work is to propose a new set of line intensities of water vapor enriched by  $^{18}\text{O}$  in the spectral range between 6400 and 8000  $\text{cm}^{-1}$ . However, to ensure the consistency of the whole dataset, line positions and self-broadening coefficients were analyzed simultaneously using a multispectrum fitting software. This present study is the continuation of a previous work performed in the same range from 6400 to 9400  $\text{cm}^{-1}$  in natural abundance [1] and this completes also the systemic review of the near infrared absorption of water vapor started since 1999 [1-6].

The paper is organized as follows, a short review of previous spectroscopic studies of  $\text{H}_2^{18}\text{O}$  absorption in the near infrared is presented in Section 1. The water line list contents of the spectroscopic databases are given in Section 2. Experimental conditions and the line parameters retrieval procedure are described in Section 3. Section 4 contains some details of vibration-rotation transition assignments and also intensity measurements results. Finally, Section 5 is devoted to a comparison with results obtained from previous studies and the conclusions are presented in Section 6.

## 2. Previous studies and spectroscopic databases

The study of H<sub>2</sub><sup>18</sup>O absorption spectra in the region of interest have been done in several papers. The spectra of <sup>18</sup>O enriched water vapor were studied by Fourier transform spectroscopy (FTS) in Refs. [7-10]. Later Liu et al [11] studied a spectrum of highly enriched by oxygen <sup>18</sup>O water vapor near 1.6 μm (between 5905 and 6726 cm<sup>-1</sup>) using high sensitivity continuous wave cavity ring down spectroscopy (cw-CRDS) technique. Additional H<sub>2</sub><sup>18</sup>O absorption lines were obtained from the absorption spectrum studies of natural water vapor [1, 4, 12-18] and of deuterium [19] and <sup>17</sup>O [20] enriched water vapor. Line positions of Refs. [4, 7-14] were used by an IUPAC task group (IUPAC-TG) [21, 22] for the energy level determination of H<sub>2</sub><sup>18</sup>O molecule. According to Refs. [21, 22], about 3470 H<sub>2</sub><sup>18</sup>O transitions have been reported in Refs. [4, 7-14] between 6526 and 8011 cm<sup>-1</sup>. On **Figure 1** are shown the transition set used in Refs. [21, 22] (red stars) and more than 220 transitions observed later in Refs. [15-20] (blue circles). Note, all transitions with an intensity below 1×10<sup>-26</sup> cm/molecule which are plotted on **Figure 1**, have been observed using CRDS measurements [11, 12, 14-20].

### Figure 1

The HITRAN2016 database [23] contains 6368 H<sub>2</sub><sup>18</sup>O transitions between 6525 and 8011 cm<sup>-1</sup>. The minimum intensity corresponds to a cut-off of 5.5×10<sup>-30</sup> cm<sup>-1</sup> / (molecule cm<sup>-2</sup>) at T=296 K taking into account natural abundance of 0.199983%. Line intensities are partly from FTS [24] and cw-CRDS [15, 16, 18, 25] and partly from variational calculations [26, 27] for this region. 5802 of 6368 line positions correspond to cw-CRDS results [25]. The line positions of thirteen transitions are observed values given by Toth [24]. 262 line positions are calculated using empirical energy levels of IUPAC-TG [21, 22]. In addition 291 weak transitions (S<sub>RV</sub> < 7.5×10<sup>-28</sup> cm/molecule) have variational line positions calculated by Bubukina et al. [28].

Current version of the GEISA database [29] includes 6044 transitions in the 6525 – 8011 cm<sup>-1</sup> range. The intensity cut-off is 1×10<sup>-29</sup> cm/molecule. Six origins for line positions and line intensities are given in **Table 1**. The first reference of the second column shows the origin of the line position and the second one shows the origin of the line intensity. The experimental line parameters corresponding to M11, L12 and L13 origins are from CRDS

studies of natural water vapor [15-17]. Line positions [26] were generated from empirical energy levels [21]. Empirical values of the line intensities are coming from CRDS studies [15-17] or from FTS measurements of Toth [24]. Calculated line intensities were taken either from web accessible information system SPECTRA [27] or were computed from *ab initio* dipole moment surface of Lodi et al [30].

### Table 1

Recently two empirical line lists of natural water were constructed by Mikhailenko et al in the 5850 – 7920  $\text{cm}^{-1}$  [31] and later in the 5850 – 8340  $\text{cm}^{-1}$  [25] spectral range. These lists are based on the results of CRDS studies of water vapor spectra [11, 12, 14-19]. Both lists have an intensity cut-off of  $1 \times 10^{-29}$   $\text{cm}/\text{molecule}$ . The list [31] was adopted for current version of the GEISA database [29]. The list [25] contains about 6400  $\text{H}_2^{18}\text{O}$  transitions between 6525 and 8011  $\text{cm}^{-1}$ . Line positions were obtained by difference of empirical energy levels. These empirical energy values are mostly based on cw-CRDS studies of water vapor [11, 12, 14-19] completed by literature data. Obtained energy levels are quite different compare to those of IUPAC-TG [21]. The energy level differences are discussed in Ref. [25].

### 3. Experimental conditions and line parameter retrievals

#### 3.1. Spectra recording

For this study of water vapor enriched by  $^{18}\text{O}$ , a set of 36 spectra were recorded using the Connes' type FTS [32] built in GSMA (Group of Molecular and Atmospheric Spectrometry) laboratory [33, 34]. These are among the last recorded spectra of this apparatus; indeed, it has since been demounted. This instrument had a 3-meter maximum path difference that corresponds to a non-apodized resolution of  $0.0017\text{ cm}^{-1}$ . All the spectra were recorded with the following optical setup: a  $\text{CaF}_2$  beamsplitter, two InSb detectors and some lenses and windows in  $\text{BaF}_2$ . During the recording time the whole absorption path was maintained under vacuum. For this study several absorption cells were used: a single-path cell with an optical path of 67 cm and two other White cells [35], a 2-meter and 50-meter cell to obtain the absorption lengths up to 88 and 1000 meters respectively. The samples used for these experiments were water vapor with an  $\text{H}_2^{18}\text{O}$  abundance enrichment of about 95%. The pressure and the temperature were continuously monitored during the whole recording time. The pressure was measured with an uncertainty smaller than 0.3% using MKS Baratron manometers and the temperature was measured with platinum-resistance thermometers placed on the absorption cell, with an uncertainty smaller than 0.5 K.

The FTS's room was air-conditioned and any variation of temperature during the records was observed. To ensure stabilization of gas pressures and temperatures, the record was started several hours after the filling of the gas sample into the absorption cell.

To avoid possible problems due to the chromaticity of the beamsplitter that we have already observed with our step-by-step FTS, we chose to separate in two parts the whole recorded spectral range: the first spectral range named Region 1 from  $6450$  to  $8150\text{ cm}^{-1}$  and the second named Region 2 from  $8000$  to  $9400\text{ cm}^{-1}$ . For the moment we focus on the first region (Region 1), an example of spectra is given in **Figure 2**.

#### Figure 2

Experimental conditions of the nine spectra used for the line intensity determination in the Region 1 are summarized in **Table 2**. To avoid variations of isotopologues partial pressures, we introduced the water vapor sample only one time (about 12.8 Torr) for all recordings listed in the **Table 2**. So we had the same sample for different lengths of the cell

and we only pumped on the gas sample to modify the total pressure. Before to pump on the gas cell, for each value of the cell length, we recorded also a spectrum in the second spectral window from 8000 to 9400  $\text{cm}^{-1}$ , these spectra will be used in a further study. We also used a simple path cell with an optical path of 67 cm and our 50-meter White cell with an absorption path length of 1001 meter, to perform the determination of line positions but the [knowledge of partial pressure values](#) was not sufficient to obtain accurate intensity values for the strong and the weakest lines (see **Figure 12** below).

**Table 2**

For the line profile, a Voigt profile was adopted in this study and [no particular signature corresponding to a problem of profile was observed](#) on the fit residuals. Spectra were analyzed using a software developed at GSMA (Reims) named “MultiFiT” (MFT) [36] in order to obtain simultaneously line parameters. Several pressures were selected for each absorption path length to obtain simultaneously the line position, the line intensity and the self-broadening coefficient with a multi-spectrum fitting procedure. The [chosen](#) absorption path lengths allowed us to measure line intensities distributed in an absorption range from  $10^{-27}$  to  $10^{-21} \text{ cm}^{-1} / (\text{molecule cm}^{-2})$  at 296 K.

### **3.2. Determination of the partial pressure of water vapor isotopologues**

The sample of water vapor used for the records came from the company Euriso-top and was enriched by  $^{18}\text{O}$  of about 95%. To ensure the measurement of intensities with accuracy, before the [measurement](#) of line parameters, we took time to determine the partial pressure of each isotopologue, their abundances, except for  $\text{H}_2^{18}\text{O}$ , are estimated with the intensities of line referenced in the literature (see **Table 3**). [The pressure parameter was fitted on isolated lines to determine the partial pressures using low pressure spectra \(lower than 2 Torr\), indeed, in these experimental conditions, the influence of the broadening parameters can be neglected.](#) Of course, to obtain the pressure parameter, the intensity parameter has to be fixed at the value found in several “reference” articles (**Table 3**).

**Table 3**

Then we determine the partial pressure of  $\text{H}_2^{18}\text{O}$  by using the following formula where  $P_{\text{tot}}$  is the total pressure of each used spectrum:

$$P(\text{H}_2^{18}\text{O}) = P_{\text{tot}} - [P(\text{H}_2^{16}\text{O}) + P(\text{H}_2^{17}\text{O}) + P(\text{HD}^{16}\text{O}) + P(\text{HD}^{18}\text{O}) + P(\text{HD}^{17}\text{O})].$$

For the determination of line intensities, [only the spectra listed in Table 2 are used](#). These spectra were recorded with the same cell [where the water vapor sample was introduced only one time for the three series \(as explained above\)](#). Indeed, we remark that the isotopic abundance is slightly different in other spectra after a new introduction of water vapor [sample](#) in the cell. We recorded at first the spectra with higher pressure with three different absorption path lengths, and then water vapor sample was pumped and new spectra were recorded with different absorption lengths, etc. The single introduction of water vapor ensures us to keep the same partial pressures. In **Table 2**, are listed the spectra in the order of their recording.

The abundance of the studied sample and the reference of the articles used to estimate the abundance of each isotopologue, except  $\text{H}_2^{18}\text{O}$ , are given in **Table 3**. The determined abundances are in good agreement with those reported in our previous study in the 1000 – 2300  $\text{cm}^{-1}$  region [38] using the same sample enriched by  $^{18}\text{O}$ .

### 3.3. Line parameters retrieval

First of all, [we checked the real value of the iris radius of the aperture at the entry of the Michelson interferometer to minimize the effect of the apparatus function on the retrieval parameters](#). The nominal iris radius value was 2.5 mm and the iris radius parameter was fitted to obtain the effective value on the spectrum with the lowest pressure for each cell length. The fitted effective value was equal to 2.35 mm. This value was applied to each spectrum even for those with higher pressure, [as the experimental conditions staying the same for all records](#). The effective iris radius value is more realistic considering the optical effects at the input of the interferometer or variations of the signal during the displacement of the movable mirror.

**Figure 3** shows the difference on the residual of a single spectrum fit at low pressure between the case using the nominal iris radius value and the case using the effective one. In addition, **Figure 4** shows the same effect in multispectrum fitting procedure. [The impact of this type of error on the line parameters retrieval](#) is around 1% for the intensity determination and more for the collisional coefficients, around 5%.

**Figure 3**

**Figure 4**

### 3.4. Wavenumber calibration

As it was explained in section 3.2, we took care of the conditions for spectra recording especially to keep the same isotopic abundance. Unfortunately, these conditions are not suitable to the wavenumber calibration. In our optical configuration, the cell is placed before the interferometer so when we change the absorption path length we change also the way of the light beam arriving at the entry of the interferometer. So each time we change the absorption path length, the optical set-up is modified and it can induce a slight wavenumber shift.

Nevertheless we managed to calibrate spectra in wavenumber by using previous CRDS data of the region. The most accurate recent data [20, 39, 40] were used for this purpose. The

root mean square deviation ( $rmsd = \sqrt{\sum_{i=1}^{NT} (v_i^{OBS} - v_i^{CRDS})^2 / NT}$ ) and mean deviation

( $\sum_{i=1}^{NT} (v_i^{OBS} - v_i^{CRDS}) / NT$ ) between our calibrated and CRDS data [20, 39, 40] are  $0.0013 \text{ cm}^{-1}$

and  $5 \times 10^{-5} \text{ cm}^{-1}$  respectively for more than 5000 lines between  $6526$  and  $7920 \text{ cm}^{-1}$ .

## 4. Line list assignments and energy level determination

The nine spectra listed in **Table 2** were used for determination of the line parameters. As note in Section 3.1, all these spectra were recorded using 2-meter White cell. As mentioned above, two spectra with an optical path of 67 cm and 1001 m were used to precise line positions of some strongest (67 cm) and weakest (1001 m) lines. Overall 8092 lines were found in mentioned above spectra. 7993 lines were assigned to 8647 transitions of the six water isotopologues ( $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{HD}^{16}\text{O}$ ,  $\text{HD}^{18}\text{O}$ , and  $\text{HD}^{17}\text{O}$ ). Finally 98 lines (1.2%) were left unassigned.

Like in our previous studies on the analysis of water spectra [1, 14-18, 20], spectra line assignments were performed on the basis of available sets of (i) empirical line lists [24, 25, 31], (ii) empirical energy levels [21, 22, 25, 37] and (iii) calculated variational water spectra [27] based on the results of Partridge and Schwenke [41, 42] (SP line lists). The summary of assigned transitions is shown in **Table 4** for all six water isotopologues.

**Table 4**

The first step of water [lines analysis](#) is so-called “trivial assignment”, i.e. [a direct](#) comparison of the experimental line list needs to be assigned against one of the empirical lists [24, 25, 31]. We made assignment by comparison of our list against data of Ref. [25]. By this way we were able to assign all lines of H<sub>2</sub><sup>16</sup>O, HD<sup>16</sup>O and HD<sup>17</sup>O species. All but two transitions of H<sub>2</sub><sup>17</sup>O, 4106 of the 4236 transitions of H<sub>2</sub><sup>18</sup>O and 745 of the 1267 transitions of HD<sup>18</sup>O isotopologues were also assigned using the list [25]. The second step of the assignment procedure is a comparison of the lines which left unassigned against one of variational lists. We used SP line lists [27] on this step. Our experience of the analysis of water absorption spectra [1, 4, 12, 14-18, 20] shows that the differences between observed ( $\nu^{OBS}$ ) and calculated ( $\nu^{SP}$ ) line positions are smooth series ( $\nu^{OBS} - \nu^{SP}$ ) for the same rotational number  $J$  or  $K_a$  with increasing of the number  $K_a$  or  $J$  respectively for a given band. The second criteria of the line assignment is a coincidence of observed ( $S_{RV}^{OBS}$ ) and calculated ( $S_{RV}^{SP}$ ) line intensities. Of course, the coincidence is limited by experimental accuracy of the line intensity determination (less than 2% when [line parameter measurements](#) are done on lines with an absorption depth from 20 to 60%) and by calculation inaccuracy.

#### 4.1. H<sub>2</sub><sup>16</sup>O, HD<sup>16</sup>O, H<sub>2</sub><sup>17</sup>O, and HD<sup>17</sup>O

[There are no new](#) or corrected data for H<sub>2</sub><sup>16</sup>O, HD<sup>16</sup>O and HD<sup>17</sup>O isotopologues compared to previous studies, observed line positions are in very good agreement with the positions of Ref. [25]. Corresponding root mean square deviations ( $rmsd =$

$$\sqrt{\sum_{i=1}^{NT} (\nu_i^{OBS} - \nu_i^{Ref.[25]})^2 / NT}$$

,  $NT$  is the number of observed transitions) are 0.0021, 0.0024 and 0.0025 cm<sup>-1</sup> respectively. The maximum deviation of observed line positions from those of Ref. [25] does not exceed 0.02 cm<sup>-1</sup>. The biggest discrepancies correspond to very weak and blended lines.

Two of 1136 H<sub>2</sub><sup>17</sup>O assigned transitions in recorded spectra were not observed in the CRDS studies summarized in Ref. [25]. Corresponding lines are due to the  $2\nu_1$  transitions  $8_{53} - 9_{46}$  at 7055.9516 cm<sup>-1</sup>,  $S_{RV} = 2.77 \times 10^{-26}$  cm/molecule and  $11_{29} - 10_{38}$  at 7376.7301 cm<sup>-1</sup>,  $S_{RV} = 2.7 \times 10^{-26}$  cm/molecule. These line positions give two previously unknown upper energy values 8393.4412 and 8819.7711 cm<sup>-1</sup> of the (200)  $8_{53}$  and (200)  $11_{29}$  levels. Our assignments of these lines were later confirmed by the observation of others transitions associated with these upper levels from analysis of CRDS <sup>17</sup>O enriched water vapor spectrum

[39]. The comparison of observed line positions against the line list [25] gives  $rmsd = 0.0024$   $\text{cm}^{-1}$  for 1134 transitions with maximum deviation of  $0.013$   $\text{cm}^{-1}$ .

#### 4.2. $\text{H}_2^{18}\text{O}$

Overall we assigned 4236  $\text{H}_2^{18}\text{O}$  transitions in studied spectra (see **Table 4**). **Table 5** shows band-by-band statistics of assigned transitions. **Table 5** includes the number of transitions ( $NT$ ), maximum values of the rotational numbers ( $J K_a$ ) and the location for each of nine cold and five hot bands. **Figure 5** demonstrates all assigned transitions (left panel) and 785 transitions reported for the first time (right panel). The minimum intensity of assigned transitions is about  $1 \times 10^{-27}$   $\text{cm}/\text{molecule}$ . Main part of the transitions (4106) was assigned by direct comparison of experimental line list against the list [25]. Thirty-nine assigned **transitions are not included** in the list [25] due to their weakness. Corresponding line positions were calculated using empirical energy levels. The transitions assigned for the first time allow us to determine 65 new vibration-rotation energies of seven vibrational states. Sixty-five new empirical energies as well as 12 corrected ones are listed in **Table 6**. Corrected term values differ from the literature data on the value bigger than  $0.015$   $\text{cm}^{-1}$ . At least a part of firstly obtained and corrected energies are confirmed by the transition observation in recently reported CRDS studies [39, 40]. The comparison of 4124 observed line positions against the line list [25] gives  $rmsd = 0.0022$   $\text{cm}^{-1}$  with maximum deviation of  $0.02$   $\text{cm}^{-1}$ .

**Table 5**

**Figure 5**

**Table 6**

#### 4.3. $\text{HD}^{18}\text{O}$

The most extended set of  $\text{HD}^{18}\text{O}$  transitions in near infrared region was reported by Mikhailenko et al [37] from analysis of deuterated water vapor enriched by  $^{18}\text{O}$ . **Now we are able** to assign 1267 transitions of ten vibrational bands. **The** general comparison of two transition sets is shown on **Figure 6**. Line intensities on **Figure 6** are given for 100% abundance. First of all, it should be noted that the concentration of  $\text{HD}^{18}\text{O}$  in the studied sample of Ref. [37] was estimated at more than 15.5% while in our samples it does not exceed the value of 0.5% (see **Table 3**). Despite this we observed the lines of twenty transitions

which were not observed in Ref. [37]. The line at  $7922.4333 \text{ cm}^{-1}$ ,  $S_{RV} = 6.3 \times 10^{-27}$  cm/molecule is due to the  $3\nu_2 + \nu_3 \ 8_{26} - 7_{25}$  transition. This line position gives new empirical energy  $E^{Obs} = 8439.2324 \text{ cm}^{-1}$  of the upper level  $(031) \ 8_{26}$ .

Comparisons of observed line positions with two literature data sets give  $rmsd = 0.0019 \text{ cm}^{-1}$  for 739 transitions with maximum deviation of  $0.01 \text{ cm}^{-1}$  for Ref. [23] and  $rmsd = 0.0031 \text{ cm}^{-1}$  for 1247 transitions with maximum deviation of  $0.017 \text{ cm}^{-1}$  for Ref. [37].

**Figure 6**

## 5. Comparisons and discussions

### 5.1. Comparison with IUPAC-TG data for the line positions

We made comparisons of our line positions with those calculated from empirical energy levels recommended by an IUPAC task group [21, 22, 43]. It was possible for five isotopologues except HD<sup>17</sup>O because the corresponding energy set [22] contains only energies for the ground and first excited states. General statistics of comparisons are shown in **Table 7** for each isotopologue. Note, a part of observed frequencies cannot be calculated due to the lack of corresponding energy levels in the energy sets [21, 22, 43].

**Table 7**

As can be seen from **Table 7**, there are no significant differences between observed and calculated line positions for H<sub>2</sub><sup>16</sup>O and HD<sup>16</sup>O species. The maximum deviation  $d_{max} = \max |v^{OBS} - v^{IUPAC}|$  does not exceed  $0.02$  and  $0.009 \text{ cm}^{-1}$  for H<sub>2</sub><sup>16</sup>O and HD<sup>16</sup>O respectively. All fifteen H<sub>2</sub><sup>16</sup>O transitions with the deviations bigger than  $0.01 \text{ cm}^{-1}$  associated with very weak or blended lines.

In general, a good agreement was found for H<sub>2</sub><sup>17</sup>O. The deviations  $d_1 = |v^{OBS} - v^{IUPAC}|$  which are bigger than  $0.015 \text{ cm}^{-1}$  correspond to upper energy levels  $(120) \ 4_{32}$ ,  $(120) \ 7_{16}$ ,  $(200) \ 8_{81}$ ,  $(200) \ 8_{17}$  and  $(101) \ 11_{011}$ . The  $\nu_1 + 2\nu_2 \ 4_{32} - 4_{41}$  and  $7_{16} - 7_{07}$  transitions correspond to very weak blended lines in our spectrum. So, reported here observed line positions of these two transitions are not accurate enough. The observed line positions of the last three energies are in very good agreement with CRDS observations [15, 16, 39, 40] for the  $(200) \ 8_{81}$ ,  $(200) \ 8_{17}$  and  $(101) \ 11_{011}$  levels. The differences of the IUPAC values from CRDS observations for these energy levels were discussed in Refs. [15, 16]. 148 assigned

transitions cannot be calculated using IUPAC energy levels due to the absence of corresponding upper levels in Ref. [21]. All these line positions are in good agreement with calculated values using energy levels obtained from CRDS measurements [20].

The situation for  $\text{H}_2^{18}\text{O}$  is similar to those for  $\text{H}_2^{17}\text{O}$ . The  $rmsd = 0.0031 \text{ cm}^{-1}$  for 4107 transitions with maximum deviation  $d_{max} \approx 0.043 \text{ cm}^{-1}$  for the line positions of the (002)  $10_7 4$  upper level. The deviations  $d_1$  are within the limit of  $0.005 \text{ cm}^{-1}$  for more than 95% transitions (see **Table 7**). All line positions but five, for which the deviations  $d_1$  are bigger than  $0.015 \text{ cm}^{-1}$ , are due to the difference in used upper energy levels. Seven corrected energies are given in **Table 6**. The differences between observed and calculated line positions using IUPAC energies [21] of the (002)  $11_7 4$ , (101)  $11_9 2$  and (120)  $7_6 1$  levels were recently discussed in Refs. [15-17]. 128 assigned transitions cannot be calculated using IUPAC energy levels [21].

Maximum deviation  $d_{max}$  for 1058  $\text{HD}^{18}\text{O}$  transitions is about  $0.09 \text{ cm}^{-1}$  (see **Table 7**). The deviations  $d_1$  for thirty-five transitions are bigger than  $0.01 \text{ cm}^{-1}$ . The term values of all corresponding IUPAC energies [22] were corrected by Mikhailenko et al [37]. Note maximum value of the deviations  $d_{max} = |v^{\text{OBS}} - v^{\text{Ref. [37]}}|$  is about  $0.017 \text{ cm}^{-1}$  with  $rmsd = 0.0031 \text{ cm}^{-1}$  for 1247 transitions.

## 5.2. Line position comparison with the HITRAN2016 database

The HITRAN2016 database [23] includes 38372 transitions of seven water isotopologues  $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{HD}^{16}\text{O}$ ,  $\text{HD}^{18}\text{O}$ ,  $\text{HD}^{17}\text{O}$ , and  $\text{D}_2^{16}\text{O}$  between  $6525$  and  $8011 \text{ cm}^{-1}$ .

The line positions of  $\text{H}_2^{16}\text{O}$  are mainly from cw-CRDS empirical line list [25] or from Toth's water database [24]. Only a small portion of transitions (1206 of 15792) are from empirical energy levels of Refs. [43, 44] or from variational calculations [28, 45]. The differences between 1875 observed line positions and those of the HITRAN2016 line list are within  $0.019 \text{ cm}^{-1}$ .

As well as for  $\text{H}_2^{16}\text{O}$ , 4332 positions of  $\text{H}_2^{17}\text{O}$  are from cw-CRDS empirical line list [25]. 318 line positions are from Lodi and Tennyson [26]. At least 277 of them are variationally calculated line positions. About 40 positions are from Toth's water database [24] or calculated from IUPAC-TG energies [21]. The differences between our observed  $\text{H}_2^{17}\text{O}$  line positions and those of the HITRAN2016 are up to  $0.16 \text{ cm}^{-1}$ . [The greatest deviations come from the variational line positions given in Ref. \[26\].](#)

161 positions of  $\text{HD}^{16}\text{O}$  transitions are observed values from Toth's water database [24]. 7607 of 8267 positions are empirical values obtained from energy levels of Refs. [22,

46] and about 500 positions are variationally calculated values by Kyuberis et al. [46]. The differences between 116 observed HD<sup>16</sup>O line positions from our spectra and the values found in the HITRAN2016 line list are within 0.009 cm<sup>-1</sup>.

More than 1500 transitions of HD<sup>17</sup>O and HD<sup>18</sup>O [23] are coming from the line lists constructed by Kyuberis et al. [46]. The differences between 768 our observed HD<sup>17</sup>O and HD<sup>18</sup>O line positions and those coming from the HITRAN2016 line list are within 0.011 cm<sup>-1</sup>. More than 500 observed HD<sup>18</sup>O transitions are not included in the HITRAN2016 list due to a cut-off of 1.0×10<sup>-29</sup> cm/molecule [23].

Empirical H<sub>2</sub><sup>18</sup>O line positions [23] are from IUPAC-TG energy levels [22] (262 positions), Toth's water database [24] (13 positions) and cw-CRDS empirical line list [25] (5802 positions). Twenty-nine assigned in our spectra transitions are not included in the HITRAN2016 line list due to a cut-off of 1.0×10<sup>-29</sup> cm/molecule [23]. Maximum deviations between our observed H<sub>2</sub><sup>18</sup>O line positions and those coming from the HITRAN2016 line list are up to 18.0 cm<sup>-1</sup>. The biggest differences are for the line positions wrongly assigned in the line list [24]. They are 2ν<sub>1</sub> 8<sub>54</sub> – 8<sub>45</sub> at 7262.1077 cm<sup>-1</sup> instead of 7270.3154 cm<sup>-1</sup> [24]; 2ν<sub>1</sub> 9<sub>46</sub> – 8<sub>35</sub> at 7413.5221 cm<sup>-1</sup> instead of 7431.5260 cm<sup>-1</sup> [24]; ν<sub>1</sub>+ν<sub>3</sub> 11<sub>48</sub> – 10<sub>47</sub> at 7420.4995 cm<sup>-1</sup> instead of 7418.5935 cm<sup>-1</sup> [24]; ν<sub>1</sub>+ν<sub>3</sub> 11<sub>38</sub> – 10<sub>37</sub> at 7446.9879 cm<sup>-1</sup> instead of 7448.0820 cm<sup>-1</sup> [24].

In general, the HITRAN2016 line list gives a satisfactory quality of the spectrum modelization for our experimental conditions (see **Table 2**) below 8000 cm<sup>-1</sup>. Nevertheless, we observed several significant disagreements between observed and calculated spectra due to incorrect H<sub>2</sub><sup>18</sup>O line positions in the line list [23]. Some examples of such disagreements are given between 7265 to 7415 cm<sup>-1</sup> and 7418 to 7527 cm<sup>-1</sup> respectively on **Figures 7** and **8**.

Four transitions involving the (002) 6<sub>16</sub> upper level coming from the list [24] have wrong positions in the HITRAN2016. Upper and lower panels of **Figure 7** demonstrate an offset of 0.31 cm<sup>-1</sup> for the 2ν<sub>3</sub> 6<sub>16</sub> – 7<sub>07</sub> near 7266 cm<sup>-1</sup> and 2ν<sub>3</sub> 6<sub>16</sub> – 5<sub>05</sub> near 7525.7 cm<sup>-1</sup> transitions respectively. In the same time, two correct line positions (6924.0189 and 7299.2679 cm<sup>-1</sup>) of the weak transitions 2ν<sub>3</sub> 6<sub>16</sub> – 7<sub>43</sub> and 2ν<sub>3</sub> 6<sub>16</sub> – 6<sub>25</sub> were calculated using empirical energy levels [21].

Correct positions of seven weak transitions involving the (200) 9<sub>46</sub> upper level were calculated using empirical energy level [21]. But the line position of the strongest transition 2ν<sub>1</sub> 9<sub>46</sub> – 8<sub>35</sub> (7431.5260 cm<sup>-1</sup>) was taken from the list [24]. The real position of corresponding line is at 7413.5221 cm<sup>-1</sup> (see upper panel of **Figure 8**).

## Figure 7

## Figure 8

Similar situations are for the transitions involving the  $(101) 11_{38}$  and  $(101) 11_{48}$  upper levels (see **Figure 8**). Overall fifteen positions of weak [transitions with these two levels](#) were calculated using empirical energy [levels](#) [21]. They are in very good agreement with our observations ( $d_{max} < 0.003 \text{ cm}^{-1}$ ). But line positions for strongest transitions of the mentioned above energies are taken from the list [24]. Both corresponding lines are shown on the middle and lower panels of **Figure 8** for the  $\nu_1+\nu_3 11_{48} - 10_{47}$  (near  $7419.5 \text{ cm}^{-1}$ ) and  $\nu_1+\nu_3 11_{38} - 10_{37}$  (near  $7447.5 \text{ cm}^{-1}$ ) transitions respectively. Two significant disagreements are shown also in the middle panel of the **Figure 8**. The first one is the line  $\nu_1+\nu_3 11_{48} - 10_{47}$  which is [missing](#) in the HITRAN2016 line list, but clearly visible on the observed spectrum at  $7420.5017 \text{ cm}^{-1}$ . Indeed, this line is indicated at the position  $7418.593 \text{ cm}^{-1}$  in the HITRAN2016 line list, with a rather good intensity. In the same figure, we can observe the line  $\nu_1+\nu_3 13_{112} - 12_{111}$  with a difference of  $3 \times 10^{-5} \text{ cm}^{-1}$  for the line position and an error of a factor about 2.5 on the line intensity parameter. The intensity value listed in the HITRAN2016 line list [is significantly](#) underestimated.

## Figure 9

Finally, **Figure 9** shows another missing line which is belonging to the  $2\nu_1$  band with the assignment  $8_{54} - 8_{45}$ . Its position in the HITRAN2016 line list is  $7270.315 \text{ cm}^{-1}$  [contrary to the](#) observed position at  $7262.1077 \text{ cm}^{-1}$ .

### 5.3. Line intensity comparison with the HITRAN2016 database

We calculated a spectrum using the line parameters listed in the HITRAN2016 line list for a pressure of 13 Torr and a cell length of 88 meters, and we directly compared this spectrum [with the observed one](#). The line intensity and broadening line parameters of the HITRAN2016 line list allow us to calculate a spectrum with a satisfactory quality compared to the observed one for the spectral region below  $8000 \text{ cm}^{-1}$ . Nevertheless, the following Figures highlight several spectral windows with problems of overestimated or, in the contrary, underestimated line intensities.

The following figures gives examples of line intensity problems in the HITRAN2016 line list for different lines belonging to the  $2\nu_3$  band. **Figure 10** shows examples of overestimated line intensities on the upper and middle panel and on the contrary, the line intensity is underestimated in the HITRAN2016 line list for the  $2\nu_3 4_{04} - 3_{13}$  transition in the lower panel. The  $2\nu_3$  band is not the only one affected by the intensity problems. **Figure 11** gives similar examples for the  $2\nu_1$ ,  $2\nu_2+\nu_3$  and  $\nu_1+\nu_3$  bands.

**Figure 10**

**Figure 11**

#### 5.4. Line intensity comparison with variational calculations

The observed line intensities of  $\text{H}_2^{18}\text{O}$  lines were compared to two variational calculations. The first one is SP line list [27] based on the results of Partridge and Schwenke [41, 42]. As it was mentioned above, this line list was used for line assignments. The second one is new calculated Exomol line list provided by Polyansky et al [47]. An overview of the intensity ratios  $R = S^{\text{OBS}} / S^{\text{Ref}}$  is shown on **Figure 12**. The  $S^{\text{Ref}}$  corresponds to SP line list and to ExoMol list on the left and right panel respectively. These two calculated line lists seem to be rather similar in the studied region (**Figure 13**) but [if we look more in detail](#), we can observe some small differences. First we have to remind that the partial pressure of the spectrum (67 cm) was not sufficiently precise to determine accurate intensity values for the strong lines. This could explain why the ratio  $S^{\text{OBS}} / S^{\text{Ref}}$  in **Figure 12** is smaller than 1 for the intensity range from  $5 \times 10^{-22}$  to  $2 \times 10^{-20}$  with the two calculated line lists. If we compare the intensity range from  $10^{-24}$  to  $5 \times 10^{-22}$ , the ratio with the Ref. [47] seems to be slightly greater than 1, while the ratio with the Ref. [27] shows a rather good agreement. For the intensity range from  $10^{-24}$  to  $10^{-26}$ , it seems to be different and the measures are in better agreement with the calculated Exomol line list [47].

**Figure 12**

**Figure 13**

#### 5.5. Line intensity comparison with Ref. [1]

It is interesting to compare the line intensities of Ref. [1] against those obtained in this study. This comparison can give an estimation of intensity precision of reported data set. Next pictures (**Figure 14**) show the comparisons of line intensities reported in our previous studies using water vapor spectra in natural abundance [1] against the data obtained in this study for the two principal observed isotopologues ( $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$ ). Note the line intensities are for the natural abundance of the isotopologues on the X-axis. In Ref. [1] with water vapor spectra in natural abundance, we observed  $\text{H}_2^{18}\text{O}$  lines in the intensity range from  $3 \times 10^{-27}$  to  $3 \times 10^{-23}$ . Left panel of **Figure 14** shows that the two data sets are consistent, except for the intensity range from  $5 \times 10^{-24}$  to  $3 \times 10^{-23}$ , where there is the same disagreement as observed in **Figure 12**. On the right panel of **Figure 14**, the situation is slightly different, it concerns the  $\text{H}_2^{16}\text{O}$  isotopologue, and we can observe that the values of the ratio between intensities determined on the spectra in natural abundance and those obtained on the spectra enriched in  $^{18}\text{O}$  are different depending the intensity range. Indeed, within the range between  $1 \times 10^{-21}$  to  $5 \times 10^{-20}$  cm/molec, the ratio is slightly higher than 1 while between  $1 \times 10^{-22}$  to  $1 \times 10^{-21}$  it is smaller than 1. This type of problem is not observed on the left panel for the  $\text{H}_2^{18}\text{O}$  isotopologue. It is certainly due to the experimental conditions of the spectra in this work mainly dedicated to the study of  $\text{H}_2^{18}\text{O}$ . The line intensities for  $\text{H}_2^{16}\text{O}$  were not determined for all lines in the best conditions, meaning in an absorption range between from 20 to 60 %, as we did it with the spectra recorded in natural abundance [1]. With this isotopic abundance (**Table 3**), it is also more difficult to find  $\text{H}_2^{16}\text{O}$  isolated lines and the determination of line intensity parameters is consequently more delicate.

**Figure 14**

## Conclusion

New absorption spectra of enriched by  $^{18}\text{O}$  water vapor were recorded between 6400 and  $9500\text{ cm}^{-1}$  at room temperature with a resolution of  $0.01\text{ cm}^{-1}$  using the Connes' type FTS built in the GSMA laboratory. The absorption path length was from 67 cm up to 1001 m with a pressure varying from 2 to 13 torr. The  $\text{H}_2^{18}\text{O}$  enrichment reached 95%.

In the spectral region between  $6525$  and  $8010\text{ cm}^{-1}$ , the spectra were analyzed and assigned. About 8100 absorption lines were [detected in this region](#). 7993 of them were assigned to about 8647 transitions of six water isotopologues ( $\text{H}_2^{16}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ ,  $\text{H}_2^{18}\text{O}$ ,  $\text{HD}^{16}\text{O}$ ,  $\text{HD}^{17}\text{O}$ , and  $\text{HD}^{18}\text{O}$ ). Only 98 weak lines ( $S_{RV} < 1.4 \times 10^{-25}\text{ cm/molecule}$ ) left unassigned. The lines of more than 800 transitions of  $\text{H}_2^{18}\text{O}$ ,  $\text{HD}^{18}\text{O}$ ,  $\text{H}_2^{17}\text{O}$ , and  $\text{HD}^{17}\text{O}$  were observed for the first time. Assigned transitions allow us to determine 76 new and 12 corrected vibration-rotation energies of  $\text{H}_2^{18}\text{O}$  and  $\text{HD}^{18}\text{O}$  molecules.

Obtained data can be used to improve and complete existed sets of empirical energy levels [21, 22, 25, 43] and created [line lists such as](#) HITRAN [23] and GEISA [29].

## Acknowledgements

The authors would like to thank Prof. O. Polyansky and Dr. A. Kyuberis for providing their data for the comparisons. This work was partly done in the frame of the International Associated Laboratory SAMIA, supported by CNRS (France) and RFBR (Russia). SM activity was supported in the frame of the Russian Science Foundation, grant no. 18-11-00024.

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## Table captions

Table 1. List of the origins of the H<sub>2</sub><sup>18</sup>O transitions between 6525 and 8011 cm<sup>-1</sup> in the GEISA2015 line list [29]

Table 2. Experimental conditions of recorded spectra (Region 1)

Table 3. Isotopic abundance in the <sup>18</sup>O enriched sample and origins of the reference lines

Table 4. Number of assigned transitions for each water isotopologues

Table 5. Band-by-band statistics of H<sub>2</sub><sup>18</sup>O assigned transitions

Table 6. New and corrected empirical energies of H<sub>2</sub><sup>18</sup>O

Table 7. General statistics of the comparison of observed line positions against calculated values using empirical energy values [21, 22]

## Figure captions

Figure 1. Overview of previously reported  $\text{H}_2^{18}\text{O}$  transitions from FTS (red stars) and CRDS (blue circles). Transitions with red stars were used in Refs. [21, 22] for the energy level determination.

Figure 2. Overview of recorded spectra for Region 1 and a zoom of three spectra between 6750 and 7100  $\text{cm}^{-1}$  in lower panel

Figure 3. Influence of the normal and effective iris radius value on the (Obs-Calc) difference in single spectrum fitting;  $\text{H}_2^{16}\text{O}$  line, 6917.3648  $\text{cm}^{-1}$ ,  $4.504 \times 10^{-23}$  cm/molec (296 K),  $L = 48$  m

Figure 4. Influence of the normal and effective iris radius value on the (Obs-Calc) difference in multi spectrum fitting;  $\text{H}_2^{18}\text{O}$  line, 7239.59215  $\text{cm}^{-1}$ ,  $1.172 \times 10^{-22}$  cm/molec (296 K),  $L = 8$  m

Figure 5.  $\text{H}_2^{18}\text{O}$  transitions observed in this study (left panel). The firstly observed transitions are given in open triangles (right panel)

Figure 6. Overview comparison of the literature  $\text{HD}^{18}\text{O}$  transitions [37] (blue circles) against those obtained in this study (green stars)

Figure 7. Comparison of observed spectrum ( $P=13$  torr,  $L=88$  m, blue line) against simulation (orange line) using the HITRAN2016 line list [23] around 7266  $\text{cm}^{-1}$  (upper panel) and 7526  $\text{cm}^{-1}$  (lower panel), see text

Figure 8. Comparison of observed spectrum ( $P=13$  torr,  $L=88$  m, blue line) against simulation (orange line) using the HITRAN2016 line list [23] around 7414  $\text{cm}^{-1}$  (upper panel), 7420  $\text{cm}^{-1}$  (middle panel) and 7447  $\text{cm}^{-1}$  (lower panel), see text

Figure 9. Comparison of observed spectrum ( $P=13$  torr,  $L=88$  m, blue line) against simulation (orange line) using the HITRAN2016 line list [23] around 7262  $\text{cm}^{-1}$ , see text.

Figure 10. Comparison of observed spectrum ( $P=13$  torr,  $L=88$  m, blue line) against simulation (red line) using the HITRAN2016 line list [23] around 7683  $\text{cm}^{-1}$  (upper panel), 7495  $\text{cm}^{-1}$  (middle panel) and 7492  $\text{cm}^{-1}$  (lower panel), see text

Figure 11. Comparison of observed spectrum ( $P=13$  torr,  $L=88$  m, blue line) against simulation (orange line) using the HITRAN2016 line list [23] around 7106  $\text{cm}^{-1}$  (upper panel), 7134  $\text{cm}^{-1}$  (middle panel) and 7252  $\text{cm}^{-1}$  (lower panel), see text.

Figure 12. Comparison of  $\text{H}_2^{18}\text{O}$  observed line intensities against variational SP (Ref. [27], left panel) and Exomol (Ref. [47], right panel) line lists

Figure 13. Ratio between variational SP [27] and Exomol [47] intensity values for  $\text{H}_2^{18}\text{O}$

Figure 14. Comparison of the line intensities reported in our previous studies using water vapor spectra in natural abundance [1] against the data obtained in this study. In X-axis, are reported the line intensities in the natural abundance for both  $\text{H}_2^{16}\text{O}$  and  $\text{H}_2^{18}\text{O}$  species.

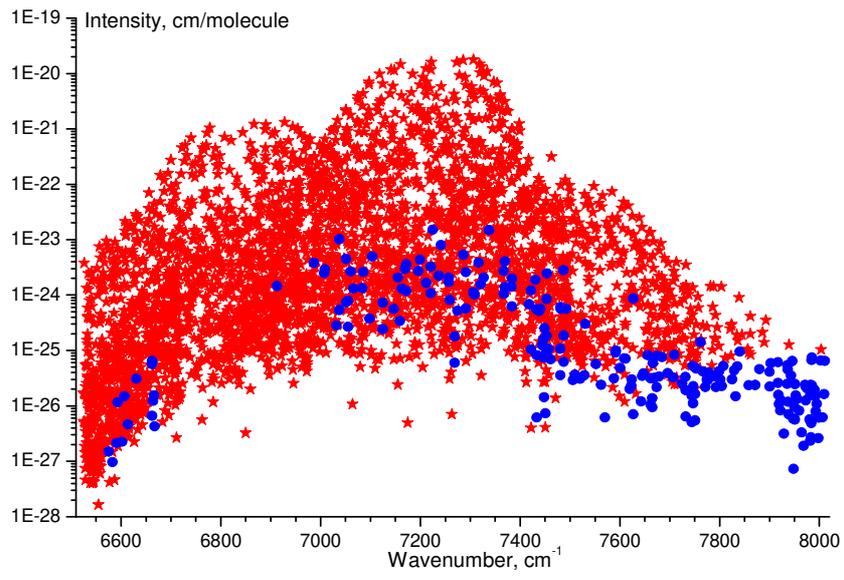


Figure 1

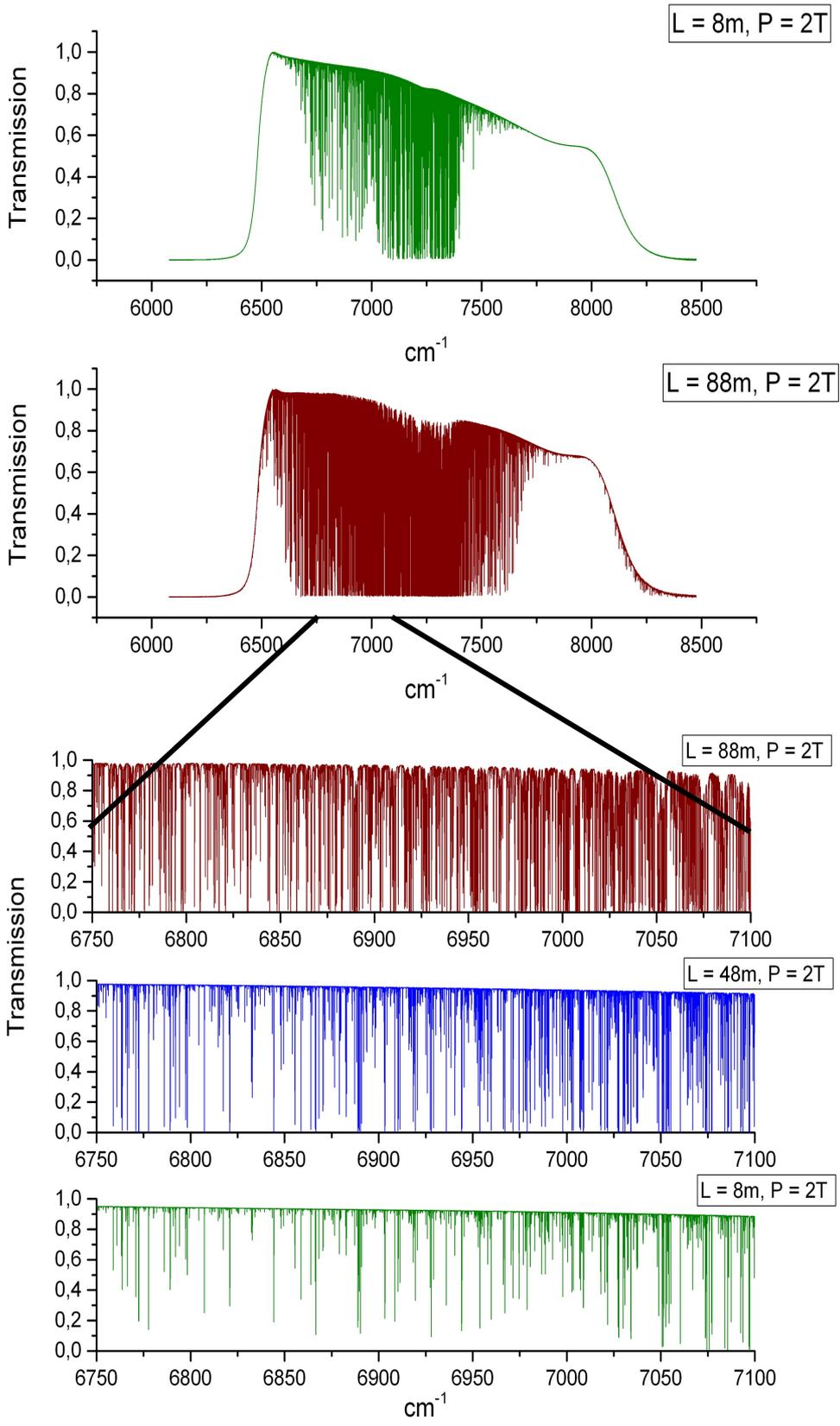


Figure 2

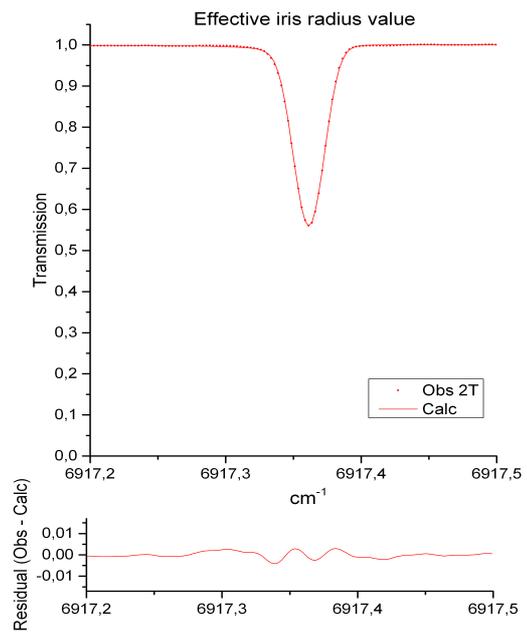
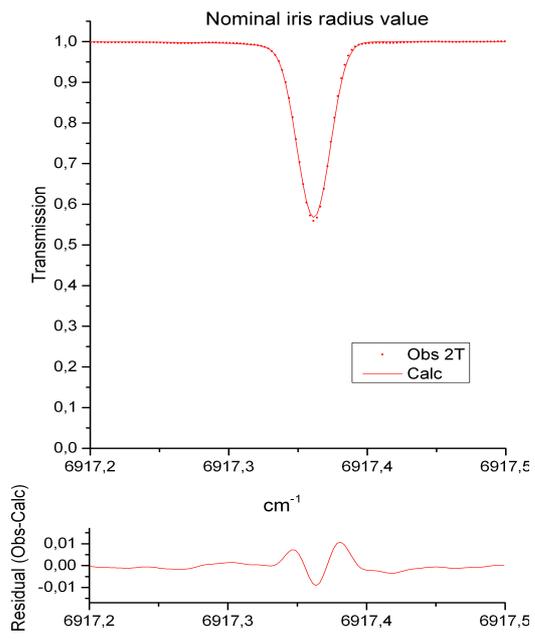


Figure 3

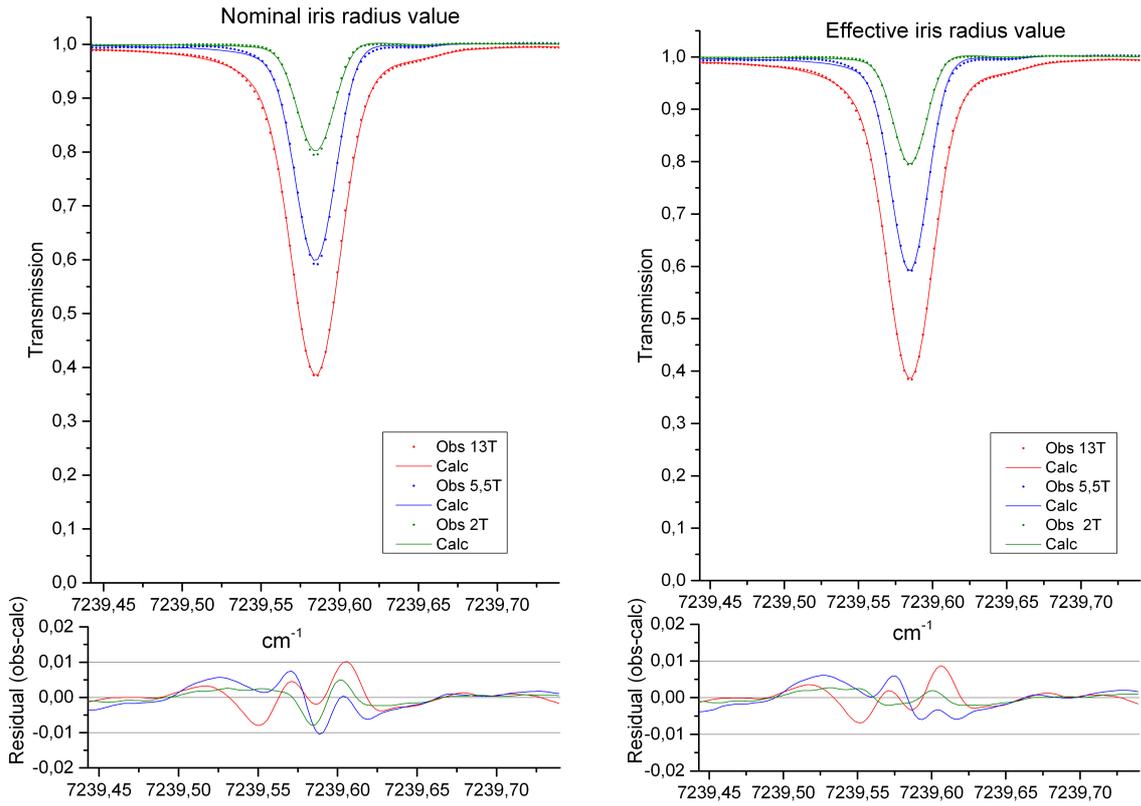


Figure 4

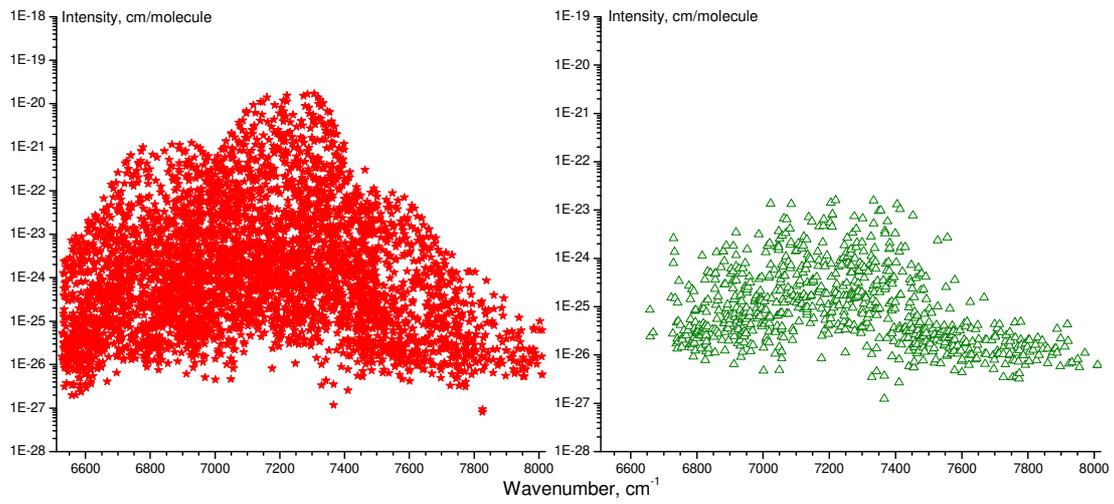


Figure 5

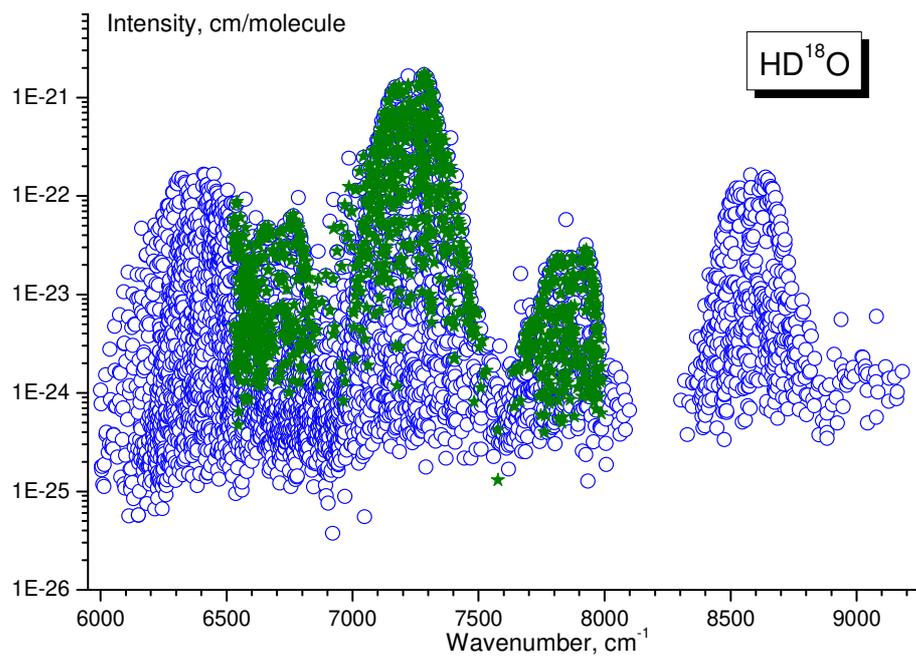


Figure 6

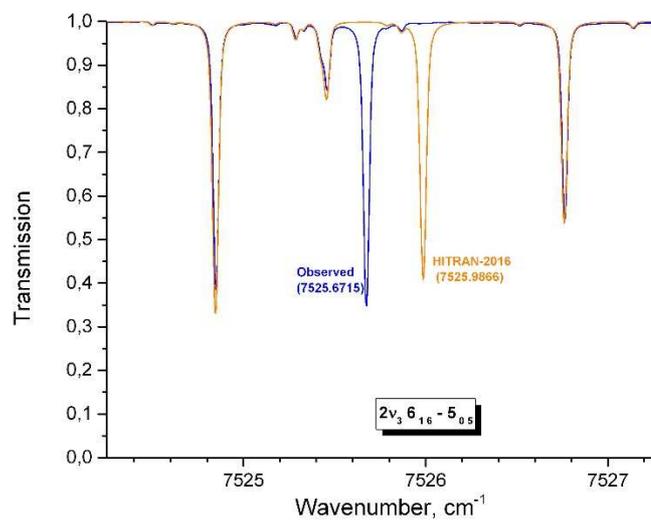
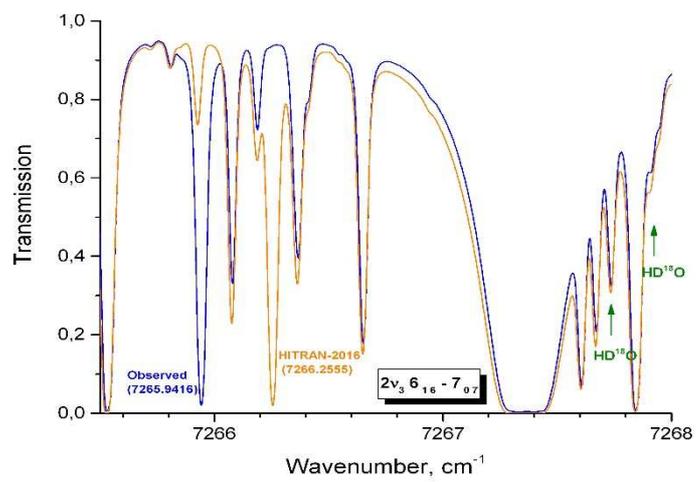


Figure 7

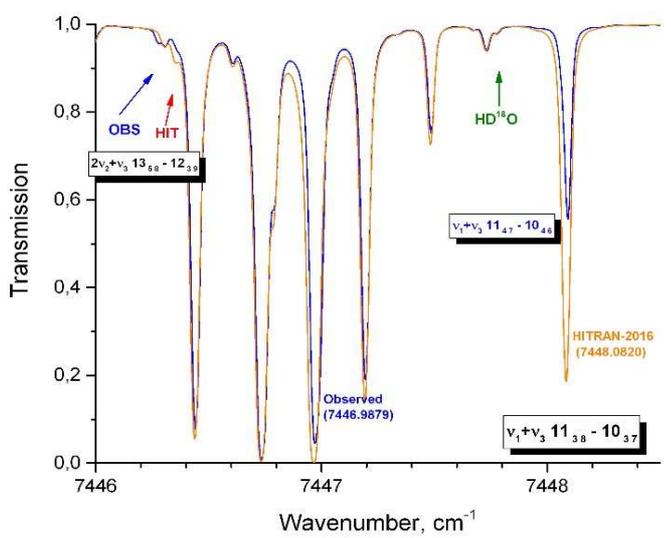
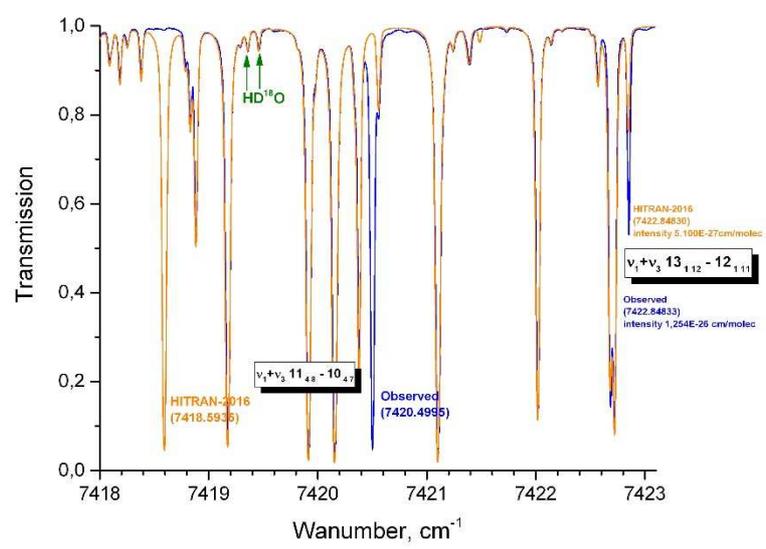
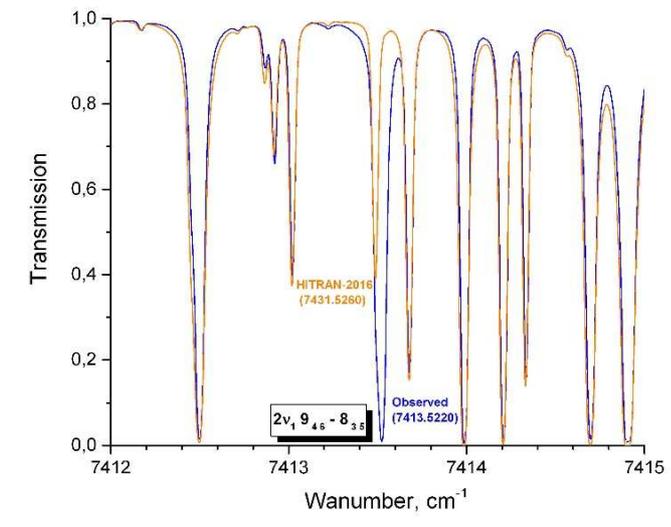


Figure 8

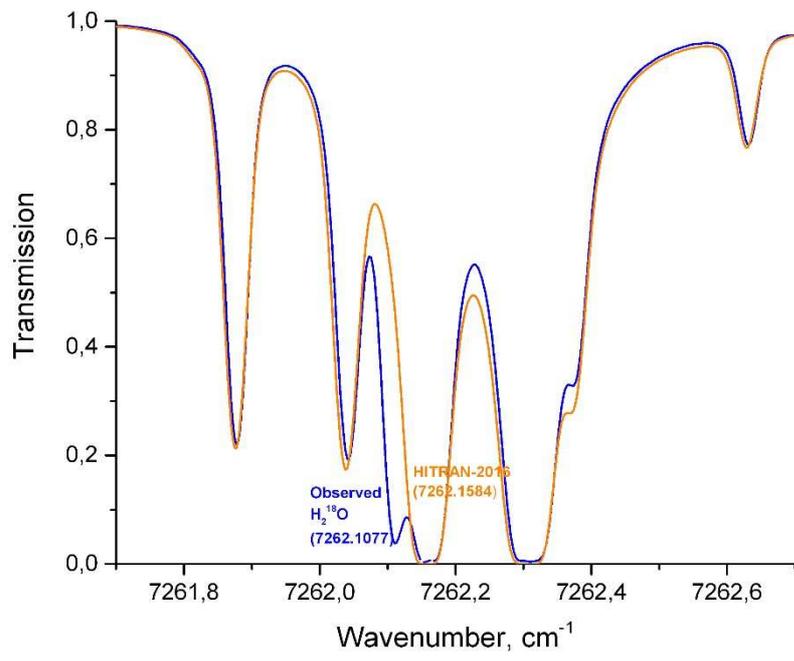


Figure 9

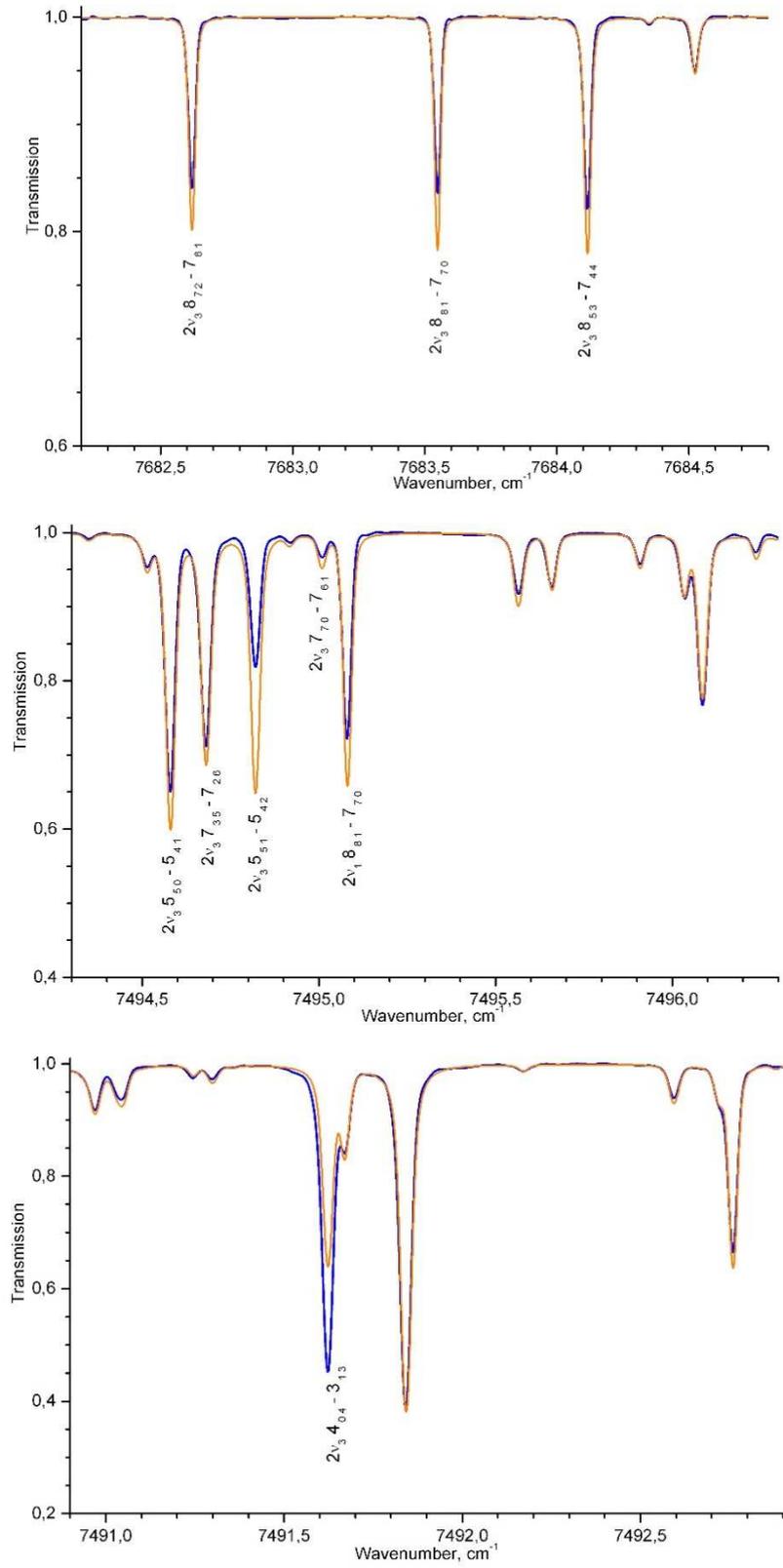


Figure 10

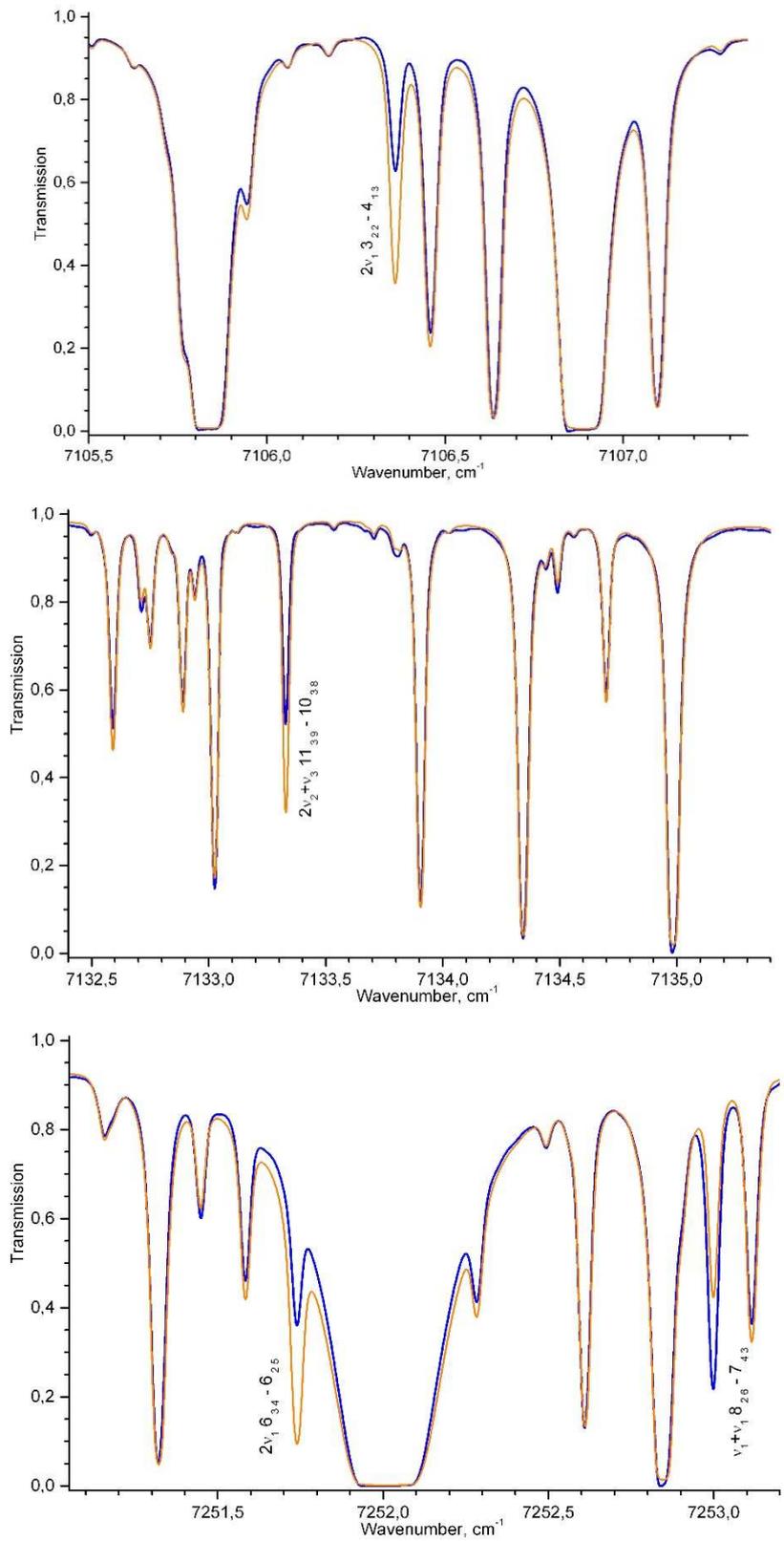


Figure 11

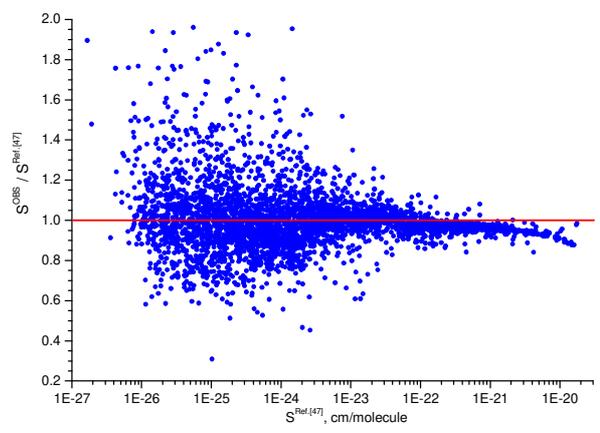
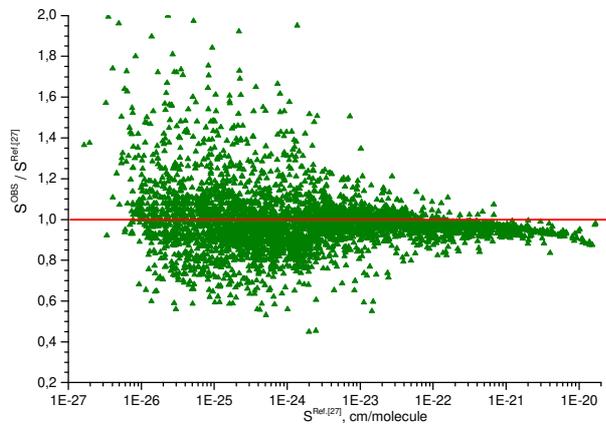


Figure 12

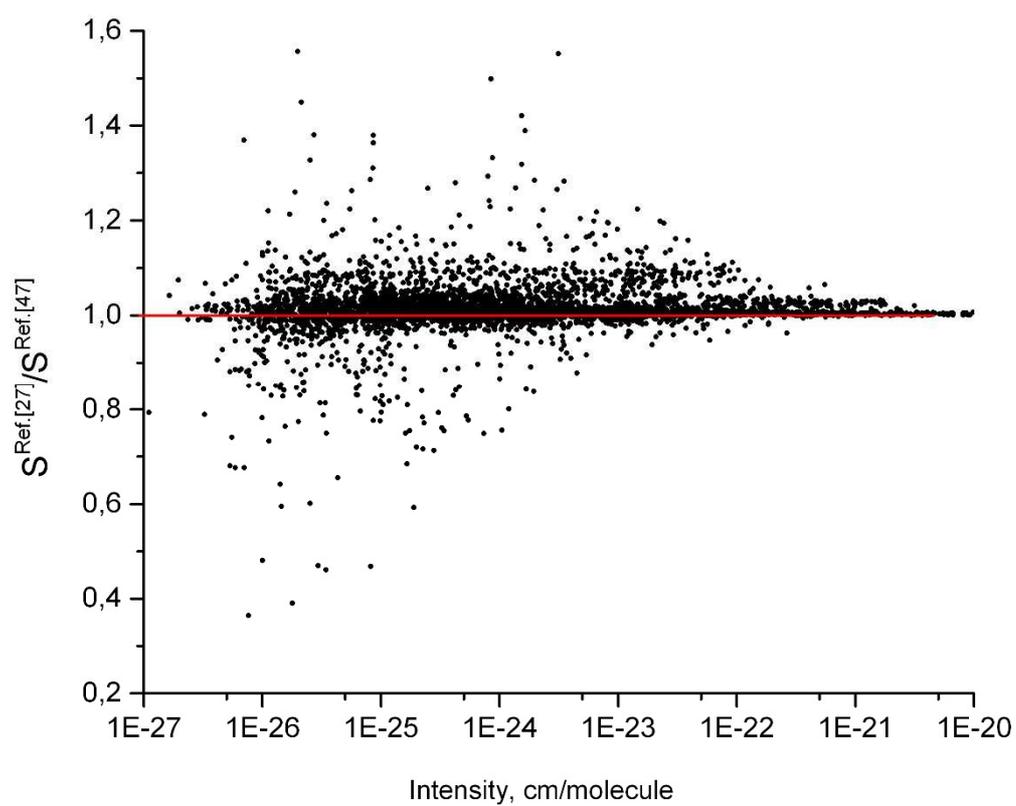


Figure 13

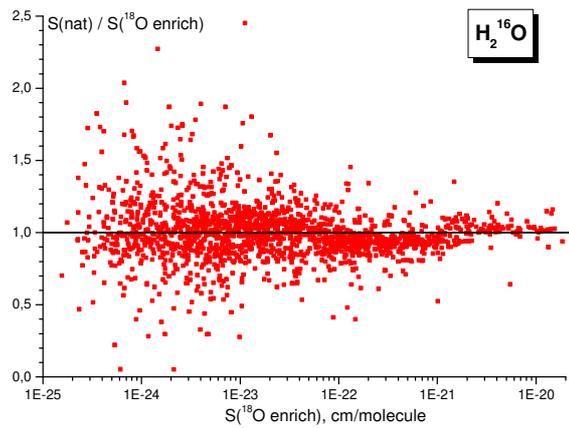
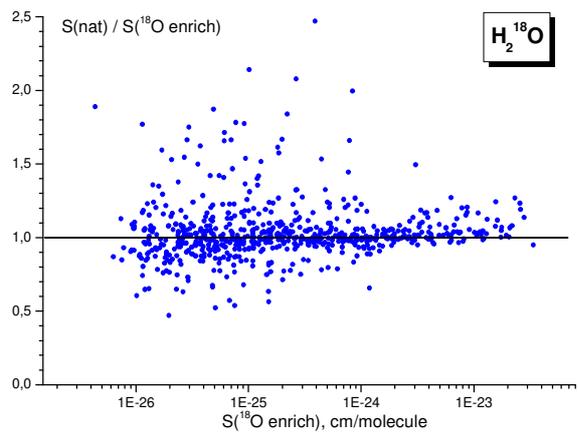


Figure 14

Table 1

Notation	Refs.	Number of transitions	Range / $\text{cm}^{-1}$	Intensity cut-off / $\text{cm}/\text{molecule}$
L12	[16], [16]	758	6886.7 – 7405.8	$6.8 \times 10^{-28}$
L13	[17], [17]	77	6525.3 – 6606.3	$2.7 \times 10^{-29}$
M11	[15], [15]	398	7410.5 – 7900.0	$2.7 \times 10^{-29}$
T04	[31], [24]	498	6588.0 – 7681.8	$8.2 \times 10^{-27}$
T13	[31], [27]	4260	6525.9 – 7919.0	$1.0 \times 10^{-29}$
TE3	[26], [30]	53	7921.6 – 8011.0	$1.0 \times 10^{-29}$

Table 2

<b>Spectrum</b>	<b>Recording range</b>	<b>Cell length (cm)</b>	<b>Pressure (Torr)</b>
1	6450 – 8100	8826.2	12.86
2	6450 – 8100	4826.2	12.85
3	6450 – 8100	826.2	12.85
4	6450 – 8100	826.2	5.41
5	6450 – 8100	4826.2	5.42
6	6450 – 8100	8826.2	5.42
7	6450 – 8100	8826.2	2.03
8	6450 – 8100	4826.2	2.03
9	6450 – 8100	826.2	2.03

Table 3

Molecule	Reference lines	Abundance (%)	
		Sample enriched by $^{18}\text{O}$	Natural
$\text{H}_2^{16}\text{O}$	Régalia et al. [1]	4.05	99.73171
$\text{H}_2^{18}\text{O}$		95.0106	0.199983
$\text{H}_2^{17}\text{O}$	Régalia et al. [1]	0.587	0.0371884
$\text{HD}^{16}\text{O}$	Hitran2016 [23]	0.0167	0.0310693
$\text{HD}^{18}\text{O}$	Mikhailenko et al. [37]	0.32	$6.23003 \times 10^{-5}$
$\text{HD}^{17}\text{O}$	Mikhailenko et al. [37]	0.0157	$1.15853 \times 10^{-5}$

Table 4

Molecule	Number of transitions ( <i>NT</i> )	Range, cm <sup>-1</sup>
H <sub>2</sub> <sup>16</sup> O	1875	6530 – 7920
H <sub>2</sub> <sup>18</sup> O	4236	6527 – 8011
H <sub>2</sub> <sup>17</sup> O	1136	6531 – 7801
HD <sup>16</sup> O	116	6528 – 7966
HD <sup>18</sup> O	1267	6526 – 7990
HD <sup>17</sup> O	17	7105 – 7390

Table 5

Band	$NT$	$J K_a$	Region, $\text{cm}^{-1}$
$\nu_1+3\nu_2-\nu_2$	42	7 6	6527 – 7206
$\nu_1+2\nu_2$	485	14 9	6529 – 7936
$2\nu_1$	861	16 10	6530 – 7917
$4\nu_2$	59	14 7	6533 – 7425
$2\nu_2+\nu_3$	710	15 9	6533 – 7804
$\nu_1+\nu_3$	993	19 11	6533 – 7950
$3\nu_2+\nu_3-\nu_2$	150	10 7	6547 – 7311
$2\nu_3$	657	14 10	6558 – 7985
$2\nu_1+\nu_2-\nu_2$	72	10 4	6792 – 7396
$\nu_1+\nu_2+\nu_3-\nu_2$	154	12 5	6803 – 7577
$\nu_2+2\nu_3-\nu_2$	16	7 5	7288 – 7598
$5\nu_2$	18	11 3	7338 – 7972
$\nu_1+3\nu_2$	11	12 3	7912 – 8011
$3\nu_2+\nu_3$	8	8 3	7918 – 8010

Table 6

Vib	J	Ka	Kc	$E^{Obs}$	$dE^a)$	Vib	J	Ka	Kc	$E^{Obs}$	$dE^a)$
002	10	7	4	<b>9336.7666</b>	-0.0435	101	11	11	1	10216.7644	
002	10	7	3	9336.8043		101	11	11	0	10216.7620	
002	10	10	1	9908.2845		101	12	8	5	9910.4452	
002	10	10	0	9908.2845		101	12	8	4	9910.1372	
002	11	7	5	9623.9504		101	12	10	3	10285.4483	
002	11	8	4	<b>9789.6546</b>	-0.0165	101	12	10	2	10285.4486	
002	11	9	3	<b>9965.8097</b>	0.2827 <sup>b)</sup>	101	13	7	7	10012.1510	
002	11	9	2	<b>9965.8098</b>	0.2828 <sup>b)</sup>	101	14	6	9	10180.7682	
002	11	10	2	10172.4655		101	14	7	7	10341.3118	
002	11	10	1	10172.4655		101	15	3	13	<b>9987.1588</b>	-0.0182
002	12	2	10	9303.0149		101	15	3	12	10189.3256	
002	12	3	9	9453.9148		101	15	4	12	10191.5444	
002	12	7	6	9881.5411		101	15	4	11	10357.8369	
002	12	8	4	10076.6411		101	15	5	11	<b>10367.5710</b>	0.0462 <sup>b)</sup>
002	13	2	11	9580.6569		101	16	3	14	10312.4792	
002	13	3	10	9749.5873		101	16	4	12	10718.8624	
002	13	4	9	9876.2274		101	17	0	17	10094.2594	
002	13	5	8	9962.4332		101	17	1	17	10094.2604	
002	13	6	8	10053.5403		101	17	2	15	10654.4900	
002	13	6	7	10067.2792		101	17	3	15	10654.4843	
002	13	7	6	10219.7315		101	18	1	17	10732.1589	
002	14	3	12	9873.4667		101	18	2	17	10732.1589	
021	10	9	2	9568.9441		101	19	0	19	10760.9583	
021	10	9	1	9568.9487		101	19	1	19	10760.9583	
021	11	9	3	9835.8044		120	11	9	3	9830.4534	
021	11	9	2	9835.8044		120	11	9	2	9830.4550	
021	12	6	7	9401.1124		130	11	1	11	9540.9280	
021	12	8	4	9840.3833		130	12	1	12	9749.8285	
021	12	9	4	10125.4233		130	12	2	11	10044.6767	
021	12	9	3	10125.4233		200	10	10	1	9694.3576	
021	13	5	8	9545.8332		200	10	10	0	9694.3576	
021	13	6	7	9717.8008		200	11	7	5	<b>9399.3182</b>	0.0273
021	14	5	9	<b>9899.6750</b>	0.0266	200	12	4	8	9313.8326	
021	15	3	13	9742.7625		200	13	6	8	9823.4681	
050	2	2	1	7795.9877		200	13	7	6	<b>9990.9220</b>	-0.0326
050	5	0	5	7849.3183		200	14	3	12	<b>9632.5068</b>	0.0152
050	10	3	8	9255.2613		200	14	4	11	9820.1901	
050	11	3	9	9506.8093		200	15	0	15	9446.0041	
101	10	8	3	9360.4914		200	15	1	15	9446.0062	
101	10	10	1	<b>9733.6659</b>	0.0572 <sup>b)</sup>	200	16	0	16	9736.0065	
101	10	10	0	<b>9733.6661</b>	0.0573 <sup>b)</sup>	200	16	1	16	9736.0069	
101	11	8	4	9597.6423		200	16	2	15	10015.6281	
101	11	10	2	9998.4711		210	3	3	1	9031.9220	
101	11	10	1	9998.4711							

a)  $dE = E^{Obs} (TW) - E^{Obs} (Ref.[21])$

b)  $dE = E^{Obs} (TW) - E^{Obs} (Ref.[15])$

Table 7

Molecule	$NCT^a)$	$NAT^b)$	Maximum deviation, $10^{-3} \text{ cm}^{-1}$				$d_{max}, 10^{-3} \text{ cm}^{-1}$	$rmsd, 10^{-3} \text{ cm}^{-1}$
			$d_1 \leq 1$	$1 < d_1 \leq 5$	$5 < d_1 \leq 10$	$d_1 > 10$		
$H_2^{16}O$	1875	0	1128	668	64	15	20.0	2.26
$H_2^{18}O$	4107	128	2186	1717	158	46	43.5	3.12
$H_2^{17}O$	988	148	496	419	55	18	147.4	2.95 <sup>c)</sup>
$HD^{16}O$	116	0	55	56	5		9.0	2.43
$HD^{18}O$	1058	209	466	474	83	35	88.7	5.23 <sup>d)</sup>
$HD^{17}O$	0	17						

<sup>a)</sup> Number of transitions calculated using energy sets [21, 22, 43]

<sup>b)</sup> Number of transitions which cannot be calculated using energy sets [21, 22, 43]

<sup>c)</sup> Excluding the  $2\nu_1 8_{17} - 9_{28}$  transition with a deviation of  $0.1474 \text{ cm}^{-1}$

<sup>d)</sup> Excluding the  $2\nu_1 + \nu_2 9_{27} - 8_{26}$  transition with a deviation of  $0.0887 \text{ cm}^{-1}$