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1 Frequency comb-referenced Cavity Ring Down Spectroscopy
2 of natural water between 8041 and 8633 cm⁻¹

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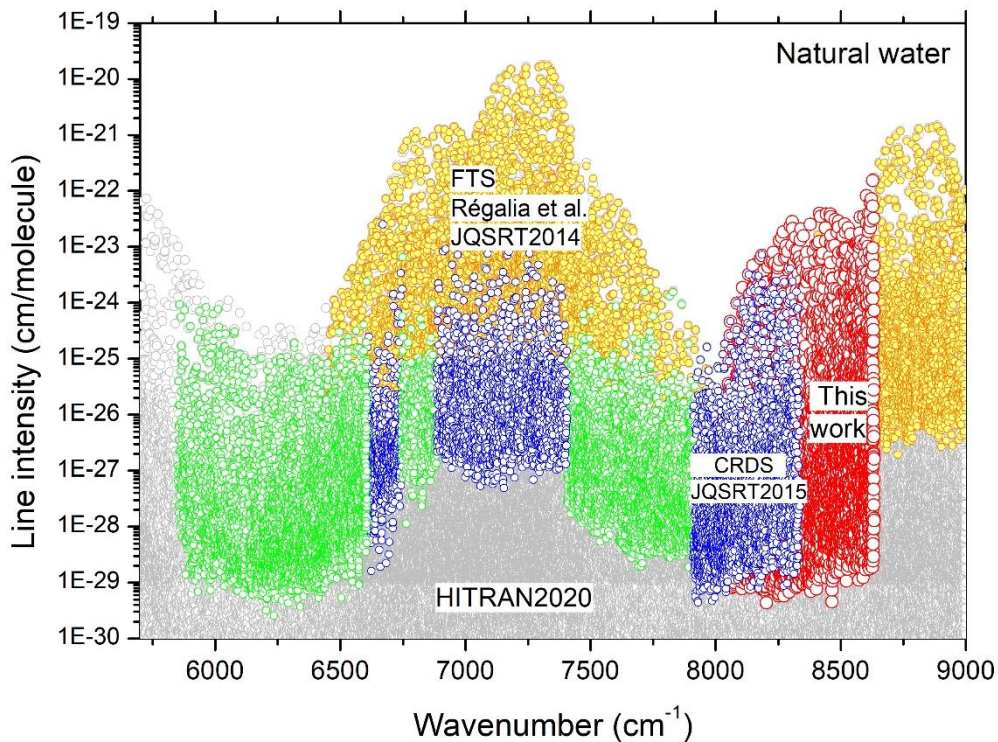
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40

Abstract

41
42 The 1.25 μm atmospheric transparency window is of importance for a number of atmospheric
43 applications. As a continuation of our previous works on the improvement of water vapour line parameters in
44 the near infrared, the room temperature absorption spectrum of water vapour in natural isotopic abundance is
45 recorded with unprecedented sensitivity between 8041 and 8633 cm^{-1} using comb referenced cavity ring-
46 down spectroscopy. The line positions and intensities of more than 5400 lines were retrieved. Their
47 intensities range between 3.6×10^{-30} and 1.5×10^{-22} $\text{cm}/\text{molecule}$. The high sensitivity and low noise level of
48 the recordings ($\alpha_{\text{min}} \approx 10^{-11}$ cm^{-1}) allow for measuring more than 1600 new lines and determine their positions
49 with an accuracy of about 10^{-4} cm^{-1} in the case of isolated features. The rovibrational assignments were
50 performed using known experimental energy levels and calculated spectra based on variational calculations
51 by Schwenke and Partridge. The final line list is assigned to more than 5400 transitions of the first six water
52 isotopologues (H_2^{16}O , H_2^{18}O , H_2^{17}O , HD^{16}O , HD^{18}O and HD^{17}O). The measured line positions allow to
53 determine the energy of 79 new levels of H_2^{16}O , H_2^{18}O , H_2^{17}O , and HD^{16}O , and to correct 141 previously
54 reported term values. Although a good agreement is generally observed, the comparison to the water vapor
55 line lists provided by the HITRAN2020 spectroscopic database and to the W2020 transition frequencies
56 reveals a number of discrepancies both for line positions and line intensities. The lack of traceability of some
57 HITRAN line parameters and some biases in the derivation procedure of the W2020 energy levels are
58 confirmed in the studied range. Validation tests of the theoretical values of the line intensities against
59 measured values show both band-by-band variations of the deviations on the order of a few % and line-by-
60 line fluctuations within a given band.

61 **1. Introduction**

62 The present work is devoted to a detailed analysis of the highly sensitive water vapor absorption
63 spectrum between 8041.46 and 8633.41 cm^{-1} by comb-referenced cavity ring down spectroscopy (CR-
64 CRDS). The investigated spectral interval is included in the overview displayed in **Fig. 1**. It corresponds to
65 the high energy edge of the 1.25 μm atmospheric window. The present study extends to higher energy the
66 spectral range of our series of CRDS studies which now cover continuously the 5690-8633 cm^{-1} range [1-7].
67 Note that the 7911 – 8337 cm^{-1} interval, largely overlapping with the presently studied region, was
68 previously investigated by CRDS in 2015 [6]. In the present work, a higher accuracy on the line parameters
69 is expected from the referencing of the CRDS ring downs to a self-referenced frequency-comb (line position
70 accuracy at a 1×10^{-4} cm^{-1} level or better are achieved for unblended lines). This improvement compared to
71 the 2015 measurements results from (i) the absolute frequency calibration of the spectra recorded in this
72 work while reference line positions had to be used to calibrate the spectra of Ref. [6] and (ii) a better line
73 profile determination as an absolute frequency value is associated to each ring-down event.



74
75 **Fig. 1.**
76 Overview of the water vapor spectrum between 5700 and 9000 cm^{-1} . Experimental observations are superimposed to the
77 HITRAN2020 line list [9] (grey circles). The present study (red open circles) extends to higher energy our series of
78 previous CRDS studies (alternate green and blue circles) [1-7]. Note in particular, the CRDS study in the 7911 – 8337
79 cm^{-1} interval [6], largely overlapping the present study. The line list elaborated by Régalia et al. from a series of FTS
80 spectra [8] is also plotted for comparison (yellow dots).
81

82 We have included in **Fig. 1**, the line list of the most sensitive study by Fourier transform spectroscopy
83 (FTS) available in the literature. It was performed by Régalia et al, in 2014, with absorption pathlengths up
84 to 1203 m [8]. The sensitivity of the CRDS technique allows lowering the detection limit by two to three
85 orders of magnitude (The weakest lines measured by CRDS have an intensity smaller than 10^{-29}
86 $\text{cm}/\text{molecule}$). As a result, in the present work, an important number of transitions are newly observed above

87 8337 cm^{-1} . These transitions are included in the usual spectroscopic databases (HITRAN [9], GEISA [10])
88 with calculated values of their line positions and line intensities. The present set of measurements will thus
89 allow for valuable validation tests of the existing databases (see Section 4). In the next Section 2, the
90 experimental set-up and the line list construction are presented. The rovibrational analysis leading to the
91 derivation of a number of new energy levels will be detailed in Section 3.

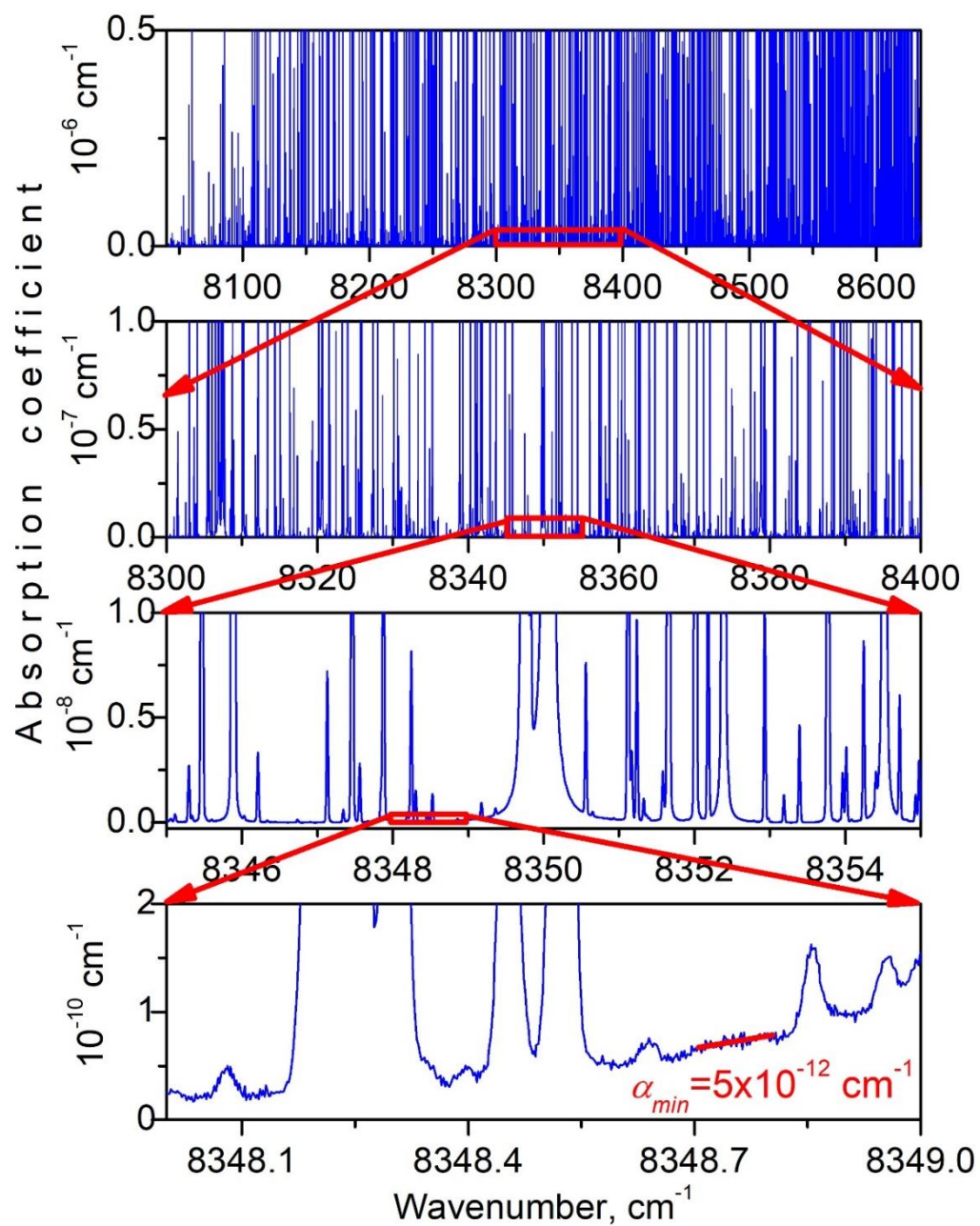
92 **2. Experimental set up**

93 The room temperature absorption spectrum of natural water vapor was recorded by high sensitivity
94 frequency comb referenced cavity ring-down spectroscopy [11], in flow regime at a pressure of 1.0 Torr. The
95 weak flow was set through a needle valve connecting the cell to a turbo pump group. The pressure was
96 continuously measured by a capacitance gauge (MKS Baratron, 10 Torr, 0.25% accuracy of the reading) and
97 actively regulated to 1.0 Torr using a computer based Proportional/Integral controller.

98 An external cavity diode laser (ECDL) was used as light source to cover the 8040 – 8630 cm^{-1} range.
99 The spectrum quality is illustrated by three successive zooms presented in **Fig. 2**. The noise equivalent
100 absorption is lower than 10^{-11} cm^{-1} .

101 Following Refs. [12,13], a self-referenced frequency comb (Model FC 1500-250 WG from Menlo
102 Systems) was used for the frequency calibration of the CRDS spectra. As detailed in Ref. [11], an accurate
103 frequency is determined “on the fly” and attached to each ring down event. The frequency determination
104 requires (*i*) the frequency measurement of the beat note between a fraction of the ECDL light and a tooth of
105 the frequency comb and (*ii*) the tooth number deduced from the frequency value provided by a commercial
106 Fizeau type wavemeter (HighFinesse WSU7-IR, 5 MHz resolution, 20 MHz accuracy over 10 hours). As
107 illustrated in Ref. [12], the CR-CRDS line centers have in routine an absolute accuracy at the $1 \times 10^{-4} \text{ cm}^{-1}$
108 level or better for unblended lines.

109 The line parameters were retrieved from the spectra by using a homemade interactive least squares
110 multi-lines fitting written in LabVIEW. A Voigt profile with the width of the Gaussian component fixed to
111 the calculated Doppler broadening was adopted for each line (see an example of spectrum reproduction in
112 **Fig. 3**). Note that, in order to improve the retrieved line parameters, in a number of spectral intervals
113 corresponding to strong overlapping of several transitions, we included in the fit lines with line parameters
114 constrained to their literature values (empirical line positions and variational line intensity). The parameters
115 of these 1213 “frozen” lines cannot be reliably retrieved but their inclusion in the fit is expected to help to
116 increase the accuracy of the fitted parameters of the nearby overlapping lines. The “frozen” lines are given
117 for information in the experimental list (tag “F” in the first column) but are excluded from the following
118 discussion and comparisons.



119

120

121 **Fig. 2.** Room temperature CRDS spectrum of natural water vapor around 8348 cm⁻¹. The sample pressure was about 1.0 Torr.

122 The successive enlargements illustrate the high dynamics of the recordings and the noise level on the order of $\alpha_{min} \sim$

123 $5 \times 10^{-12} \text{ cm}^{-1}$.

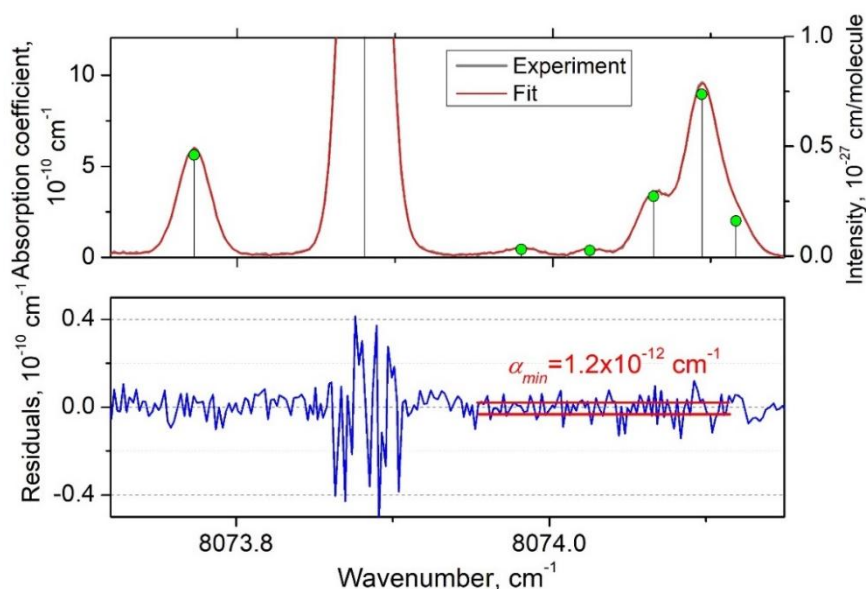


Fig. 3.

Example of spectrum reproduction of the CRDS spectrum of water vapor near 8074 cm^{-1} . The obtained line list is superimposed as a stick spectrum (green dots). The two weak lines around 8074 cm^{-1} have an intensity of about $2 \times 10^{-29}\text{ cm/molecule}$.

Overall, line parameters of 5447 absorption features were retrieved from the recorded spectrum between 8041.46 and 8633.41 cm^{-1} . 184 and 55 of them are due to NH_3 and CO_2 molecules, respectively. They were identified by position and intensity comparison with HITRAN values. As detailed in the next section, 5191 lines were assigned to 5430 transitions of six water isotopologues (red open circles in **Fig. 1**). Their intensities range between 3.6×10^{-30} and $1.5 \times 10^{-22}\text{ cm/molecule}$. Detailed information about the assignment procedure is given in the next section and summarized in **Table 1**. Twenty weak lines were left unassigned at the end of the assignment process.

Table 1.

Statistical overview of the water transitions previously reported and observed in the present study between 8041.4 and 8633.5 cm^{-1} .

Molecule	This study			Published data			N_{new}^c
	N_{TW}^a	Region, cm^{-1}	$J_{max} K_{a\max}$	N_{Lit}^b	Region, cm^{-1}	$J_{max} K_{a\max}$	
H_2^{16}O	3237	8041.4 – 8633.4	19 10	2508	8041.4 – 8633.4	20 10	980 ^d
H_2^{18}O	911	8043.9 – 8632.5	15 8	869	8043.9 – 8632.5	14 7	208
H_2^{17}O	540	8042.5 – 8632.5	15 7	282	8042.6 – 8632.3	13 6	291
HD^{16}O	707	8041.6 – 8631.1	15 9	785	8041.6 – 8633.5	16 8	170
HD^{18}O	32	8443.0 – 8633.2	8 5	382	8042.7 – 8633.2	13 8	
HD^{17}O	3	8538.3 – 8595.3	3 2	30	8469.3 – 8629.8	7 4	

Notes

^a N_{TW} – number of transitions assigned in the present work

^b N_{Lit} – number of transitions reported from previous absorption studies

^c N_{new} – number of new transitions reported in this work. Note that N_{new} is not equal to $N_{TW} - N_{Lit}$, because due to saturation effect of some strong lines or spectral gaps in our CRDS spectrum, some previously reported transitions (N_{Lit}) could not be measured in the current study.

^d This number does not consider the (less accurate) measurements by emission spectroscopy [14].

3. Rovibrational assignments

As in our previous studies (see, for example, Refs. [6,8,15]) the vibration-rotation assignments of the water lines were performed using variational vibration-rotation (VR) line lists computed by S.A. Tashkun

152 [16] based on the results of Schwenke and Partridge [17,18] (hereafter “SP line lists”) and empirical values
 153 of VR levels known from previous studies. Here, we are using a set of VR energies previously used for the
 154 construction of an accurate empirical water line list in the 5690 – 8340 cm⁻¹ region [19].

155 Most of the lines could be straightforwardly assigned by comparison to the literature and/or using line
 156 positions calculated using empirical VR energies (so called “trivial assignment”). This is in particular the
 157 case of the HD¹⁸O and HD¹⁷O isotopologues which are present at very low abundance in our natural water
 158 sample (6.23×10⁻⁷ and 1.16×10⁻⁷, respectively). All lines associated to these two molecules (35 transitions of
 159 the ν₂+2ν₃ band, in total) were previously observed by FTS of deuterated water highly enriched in ¹⁸O [15].

160 **Table 2.** Term values of newly determined energies of four water isotopologues
 161

V ₁ V ₂ V ₃	J	K _a	K _c	Energy	dE	NT
H₂¹⁶O						
012	15	1	15	11267.59539	76	
040	13	9	4	10491.32266	217	
050	11	6	6	10469.34626	80	
050	12	7	5	11095.00221	305	
051	3	3	0	11763.21886	426	
070	2	0	2	10155.14662	71	
070	4	0	4	10314.95101	58	
111	13	7	6	11709.19591	186	
111	14	7	7	12075.24608	308	
120	14	10	5	11005.62060	540	
130	10	6	4	10458.46562	54	3
130	12	7	6	11271.80777	120	
130	12	7	5	11271.87771	371	
130	13	5	9	11073.64853	369	
130	14	4	10	11271.89153	104	2
130	15	4	11	11633.90887	46	
210	9	9	1	11034.93160	423	
210	9	9	0	11034.93160	423	
210	11	7	5	11114.88878	198	
210	12	2	10	10683.92477	342	
210	12	4	8	10937.90318	212	
210	14	0	14	10743.67461	97	
210	14	2	12	11244.99079	218	
210	15	1	14	11309.67474	274	
H₂¹⁷O						
031	8	6	2	10032.79258	108	
031	9	2	7	9610.15869	280	
031	9	6	4	10250.76622	338	
031	9	6	3	10250.86402	771	
031	10	3	8	9887.88534	527	
111	11	3	8	10584.43224	255	
111	11	5	6	10768.69671	443	
111	15	1	15	11047.63569	241	
130	7	3	5	9167.12046	51	
130	9	3	6	9625.44662	365	
130	9	4	5	9758.80525	226	
130	10	2	9	9596.49369	221	
210	7	3	5	9557.02032	236	
210	9	4	6	10084.37692	124	2

V ₁ V ₂ V ₃	J	K _a	K _c	Energy	dE	NT
H₂¹⁸O						
002	14	2	12	9873.26122	330	
012	9	5	5	10429.63069	210	
012	10	5	6	10669.45636	138	
031	12	5	7	10808.76445	200	
050	4	4	0	8445.45262	169	
060	9	1	8	10106.07540	201	
111	11	4	7	10651.83616	82	
111	11	6	5	10900.36303	352	
111	14	2	12	11264.23450	163	
111	15	2	14	11321.67216	268	
130	8	4	4	9523.28133	216	
130	8	5	3	9724.54545	174	2
130	8	6	3	9958.65018	371	
130	9	3	7	9548.31109	303	
130	9	4	6	9734.02573	194	3
130	9	5	4	9940.45713	93	
130	13	3	10	10764.20530	155	
140	1	1	0	9760.92728	315	
140	2	1	2	9794.92167	498	
140	2	2	1	9911.44404	245	
140	4	2	3	10074.51093	391	
210	10	2	8	10147.62425	240	
HD¹⁶O						
012	10	9	2	10604.62588	1085	
012	10	9	1	10604.62619	1085	
012	14	3	12	10342.65890	149	
012	15	1	15	10191.11483	278	
012	15	1	14	10388.94771	538	
012	15	2	14	10389.07700	498	
012	15	2	13	10557.95975	423	
031	8	7	2	9303.89502	135	2
031	8	7	1	9303.89510	135	2
031	10	5	6	9156.80832	515	
031	11	4	7	9164.40425	419	
220	6	4	2	8724.78613	480	
220	6	6	1	9088.02358	78	
220	6	6	0	9088.02355	79	
220	7	4	4	8830.65087	390	
220	7	5	3	8996.39853	251	
220	7	5	2	8996.39920	249	
300	10	8	3	9650.68217	615	
300	10	8	2	9650.68200	619	

162 Notes

163 V₁V₂V₃ – vibration quantum numbers; J K_a K_c – rotation quantum numbers; Energy/cm⁻¹ – empirical term values;
 164 dE – estimated uncertainty of the term value in 10⁻⁵ cm⁻¹ units; NT – number of line positions used for the energy
 165 determination if it is larger than 1.

166

167 Overall, less than 300 lines corresponding to new or inaccurate upper state energy levels
168 required a non-trivial identification. The term values of the 79 newly determined levels are listed in
169 **Table 2**. In a number of cases, it was possible to use several lines to determine a given upper level.
170 The number (NT) of used line positions is given in the last column of the table. One hundred and forty
171 energy levels were found to deviate by more than $5 \times 10^{-3} \text{ cm}^{-1}$ compared to the literature. They will be
172 given and discussed in the following sections. The experimental line list is provided as Supplementary
173 Material. It includes for each line, the line position and line intensity with their uncertainty as provided
174 by the fit, the empirical value of the lower state energy, together with the comparison with the line
175 parameters provided by the HITRAN database [9] or included in the W2020 list [20] (see next
176 section), when available.

177 **4. Line positions - Comparison with literature**

178 **4.1. Overview comparison**

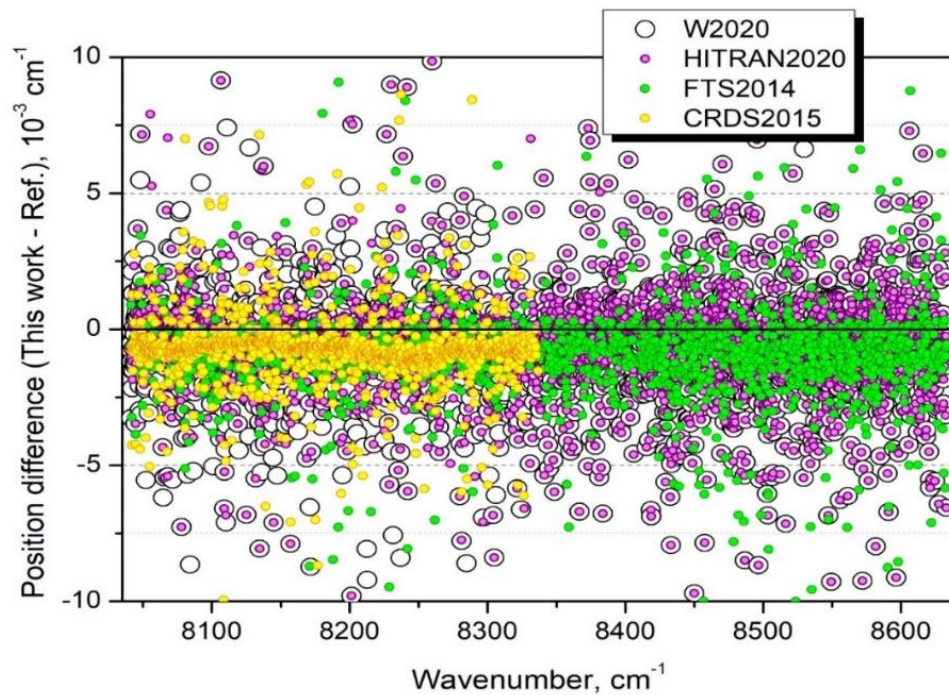
179 The literature review indicates that previous analyses of high resolution absorption spectra of
180 water vapor in the $8041 - 8633 \text{ cm}^{-1}$ range were reported in Refs. [6,8,21-25] for the main
181 isotopologue (H_2^{16}O) and in Refs. [6,8,15,24,26], Refs. [6,8,24,26], Refs. [6,8,15,24,27,28], and Refs.
182 [12,29,30] for the H_2^{18}O , H_2^{17}O , HD^{16}O , and HD^{18}O minor isotopologues, respectively. HD^{17}O
183 transitions were reported in Ref. [15]. Additional vibration-rotation transitions of the H_2^{16}O molecule
184 have been published by Zobov et al. [14] from an analysis of high temperature emission spectra. A
185 statistical comparison of our observations to previous data is included in **Table 1**. Overall, more than
186 1600 transitions of the four most abundant isotopologues were observed for the first time (they include
187 the about 300 transitions used to derive new or corrected energy levels, discussed just above).

188 In the following, we limit mainly the position and intensity comparisons to the following line
189 lists: the FTS study by Régalia et al. [8] (hereafter, FTS2014), our previous CRDS study in the $7911 -$
190 8337 cm^{-1} interval (hereafter, CRDS2015) [6], the HITRAN2020 list [9] and the W2020 lists [20] (the
191 latter being available only for non-deuterated species, H_2^{16}O , H_2^{18}O and H_2^{17}O). In the case of the
192 deuterated species, the energy levels and transition wavenumbers recommended by an IUPAC task
193 group (IUPAC-TG, hereafter) will be considered for HD^{16}O , HD^{17}O , and HD^{18}O [31].

194 The overview of the deviations of the positions provided by these four sources from the present
195 measurements is plotted in **Fig. 4**. This figure deserves several comments.

196 An overall reasonable agreement is observed but all the four considered references [6,8,9,20]
197 seem to have their positions systematically larger than our values (TW). The histograms of the ($\nu_{TW} -$
198 $\nu_{Ref.}$) position differences between our values and those of the FTS2014, CRDS2015 and W2020 lists
199 were plotted and fitted with a Gaussian. The fitted value of the center of the Gaussian was found to be
200 -8.2×10^{-4} , -7.4×10^{-4} , and $-3.4 \times 10^{-4} \text{ cm}^{-1}$, respectively. These values are largely above the claimed
201 uncertainty of our frequency calibration performed with the help of a self-referenced frequency comb.
202 In order to understand the origin of these apparent systematic shifts, we examine the frequency

203 calibration of the other sources. In our spectral region, the frequency calibration of the FTS2014
 204 spectrum [8] was made difficult by the lack of accurate reference lines which obliged Régalia et al. to
 205 calibrate their spectra on « a set of accurate line positions of the main isotopologue with positions
 206 calculated with well-known experimental energy levels ». The accuracy of the resulting calibration of
 207 the FTS2014 spectra is not reported in Ref. [8]. The frequency calibration of the CRDS2015 spectra
 208 required also accurate reference lines to refine frequency values provided by a wavemeter [6].
 209 Although it is not explicitly indicated in Ref. [6], we used the most accurate line positions available at
 210 that time, namely the FTS2014 position values to calibrate the CRDS spectra. This is confirmed by the
 211 very similar average deviation of the FTS2014 and CRDS2015 line positions compared to the present
 212 values (see Fig. 4).



213
 214 **Fig. 4.**
 215 Position differences of the water vapor lines measured by CRDS between 8040 and 8620 cm⁻¹ compared to
 216 various literature sources: FTS line list elaborated by Régalia et al. (FTS2014 – green dots) [8], pour previous
 217 CRDS line list in the 7911 – 8337 cm⁻¹ interval (CRDS2015 – yellow dots) [6], HITRAN2020 values [9] and
 218 W2020 line list [20].
 219

220 As concerns the systematic difference with HITRAN2020 position values, it is difficult to draw
 221 a conclusion as the HITRAN2020 list uses a variety of sources with experimental or theoretical origins
 222 of different quality (see below). In particular, many of the HITRAN2020 positions coincide with
 223 W2020 empirical line positions which explains the close average deviations of the two datasets
 224 compared to our values.

225 The W2020 line positions [20] have the advantage to be provided with individual error bars
 226 which should, in principle, help to disentangle the situation. Although our previous studies have
 227 demonstrated that the W2020 error bars should be used with caution [32,33] because they are
 228 frequently strongly underestimated, we selected for comparison the most accurate W2020 line

229 positions *i.e.* those which are given with an uncertainty smaller than $5 \times 10^{-4} \text{ cm}^{-1}$. About 1400 lines of
230 H_2^{16}O , H_2^{18}O and H_2^{17}O were found in common (see Supplementary Material where the W2020
231 position uncertainty is reproduced). The center of the corresponding histogram of the position
232 deviations was fitted at $-1.7 \times 10^{-4} \text{ cm}^{-1}$, instead of $-3.4 \times 10^{-4} \text{ cm}^{-1}$ if the whole W2020 dataset is used.
233 This improvement of the level of agreement by a factor of 2 may be interpreted as a confirmation of
234 the accuracy of the calibration of our spectra. Although the FTS2014 and CRDS2015 line positions are
235 part of the large number of sources used to derive the W2020 empirical energy levels, the impact of
236 the small calibration error of these two sources on the W2020 positions is probably reduced by the
237 involvement of other sources in the W2020 transition database used to derive the W2020 energy levels
238 [20].

239 As further checks of the accuracy of the frequency calibration of our spectra, we consider a few
240 individual lines with line positions accurately measured in the literature. We first compared the water
241 position values to those measured in low pressure CO spectra where water was present as an impurity
242 [34]. The CO spectra were recorded by comb-reference CRDS with the same setup used in this work.
243 Over a set of 34 lines, excluding two outliers, the average of the water line position differences was
244 found to be of $-2.9 \times 10^{-5} \text{ cm}^{-1}$ with a standard deviation of $1.4 \times 10^{-4} \text{ cm}^{-1}$. This excellent agreement
245 obtained for water lines which are very weak in the CO spectrum and strong ($S > 10^{-24} \text{ cm/molecule}$)
246 in the pure water spectrum gives confidence in the absence of bias in the calibration of the two
247 considered spectra. The same conclusion was drawn from validation tests performed using lower state
248 combination difference relations between the present measurements and H_2^{16}O line positions measured
249 at lower frequency by frequency-comb spectroscopy of water vapor enriched in ^{17}O [12,13].

250 Finally, for an independent check, we consider the set of 70 positions of isolated lines measured
251 by Sironneau and Hodges between 7710 and 7920 cm^{-1} , reported with an average combined
252 uncertainty of approximately 3 MHz (10^{-4} cm^{-1}) [35]. From these measured positions, it was possible
253 to determine accurate upper state energy levels shared by 26 transitions observed in our region. These
254 transitions are all weak ($10^{-29} < S < 5 \times 10^{-27} \text{ cm/molecule}$). If we limit the comparison to the four lines
255 with intensity larger than $S > 10^{-27} \text{ cm/molecule}$, we obtain an average position differences of 2.2×10^{-5}
256 cm^{-1} with a standard deviation of $7.5 \times 10^{-5} \text{ cm}^{-1}$ (if all but one transitions are compared, the average
257 and standard errors are $2.5 \times 10^{-5} \text{ cm}^{-1}$ and $7.5 \times 10^{-4} \text{ cm}^{-1}$, respectively). This comparison to an
258 independent dataset confirms the reliability of the frequency calibration of our spectra and that the
259 systematic shifts observed compared to FTS2014, CRDS2015, HITRAN2020 and W2020 are not due
260 to the present data.

261 The position deviations displayed on **Fig. 4** show a significantly smaller dispersion for
262 CRDS2015 compared to the three other sources (roughly by a factor of 4). The visual impression
263 given by **Fig. 4** is valid when CRDS data (below 8337 cm^{-1}) are compared to HITRAN2020 and
264 W2020 because these lists are mostly complete and thus the number of plotted position differences is
265 similar. In the case of the less sensitive FTS2014 data, the number of lines in common is reduced but

266 the average scattering of the position differences is similar to that of the HITRAN2020 and W2020
267 lists. A number of large discrepancies (or position outliers) are noted for all the sources but appear to
268 be more frequent for HITRAN2020 and W2020. In the following we will examine in details some of
269 these outliers.

270 **4.2. Comparison with FTS2014 [8] (Régalia et al. JQSRT 136 (2014) 119-136)**

271 The overview of the FTS2014 list is included in **Fig. 1**. In our region, the FTS2014 list includes
272 2008 lines attributed to 2225 transitions of four water isotopologues (H_2^{16}O , H_2^{18}O , H_2^{17}O , and
273 HD^{16}O) with minimum intensity values of a few 10^{-27} cm/molecule. Although a number of absorption
274 features could be fitted as multiplets while they are reported as single lines in FTS2014, all the
275 FTS2014 assignments are confirmed in the present analysis. The comparison shows a good agreement
276 for the line positions. Nevertheless, as discussed above (**Fig. 4**), there is a systematic difference
277 between two sets of the line positions. The average deviation for 1910 line positions is -9.67×10^{-4} cm⁻¹
278 with a largest difference of about 0.018 cm⁻¹ for the H_2^{18}O $\nu_1 + \nu_2 + \nu_3$ $3_{2,2} - 4_{4,1}$ line at 8502.54803
279 cm⁻¹. The root mean square ratio for 1907 line intensities is 0.975.

280 **4.3. Comparison with CRDS2015 [6] (Campargue et al. JQSRT 157 (2015) 135-152)**

281 In the 8041 - 8337 cm⁻¹ interval in common, the CRDS2015 spectrum and the present study
282 count 2163 and 2176 lines assigned to 2284 and 2262 water transitions, respectively. In spite of the
283 very good consistency of the two datasets, the position differences of 72 transitions were found to
284 exceed 0.005 cm⁻¹. This is mainly related to the presence of lines of ammonia present as an impurity in
285 both spectra. In the CRDS2015 spectrum, the overlapping with ammonia lines limited the accuracy of
286 the line parameters of some weak water lines [6]. A direct comparison of the two spectra shows that
287 the amount of ammonia in the new spectrum is about 20 times smaller than in CRDS2015 spectrum.
288 However, a small number of significant differences in the line positions are due to other reasons. In
289 order to give to interested readers an idea of the origin of the largest deviations, we detail below the
290 few transitions showing position differences larger than 0.015 cm⁻¹.

291 First, let us mention that the term value of the H_2^{16}O $002\ 17_{3\ 15}$ level (10892.9135 cm⁻¹ in Table
292 2 of Ref. [6]) appears to be incorrect. This value was derived in Ref. [6] from a single transition $2\nu_3\ 17_{3\ 15} - 16_{0\ 16}$
293 at 8231.9671 cm⁻¹. This line is absent in the (more sensitive) new spectrum under analysis.
294 It is thus probably due to an impurity and should be removed from the water list of Ref. [6].

295 The largest difference, $\nu_{TW} - \nu_{CRDS2015} = 0.0605$ cm⁻¹, corresponds to the $2\nu_3\ 17_{5\ 12} - 16_{4\ 13}$
296 transition of H_2^{16}O . In Ref. [6], this transition was attributed as second assignment of the line at
297 8065.4741 cm⁻¹ assigned to the $5\nu_2\ 7_{5\ 2} - 8_{4\ 5}$ transition of H_2^{18}O . As indicated in the Supplementary
298 Materials of Ref. [19], this assignment of the $2\nu_3\ 17_{5\ 12} - 16_{4\ 13}$ transition relied on the IUPAC energy
299 value of the $002\ 17_{5\ 12}$ upper level, 11504.759237(1905) cm⁻¹ [36]. In fact, the $2\nu_3\ 17_{5\ 12} - 16_{4\ 13}$
300 transition of H_2^{16}O should be attributed to the line at 8065.5346 cm⁻¹. Note that this line is present in
301 the CRDS2015 spectrum but was missed in the line list of Ref. [6]. Consequently, the upper energy of

302 the 002 17_{5 12} level should be corrected by +0.0605 cm⁻¹ compared to the value given in Table 3 of
303 Ref. [6].

304 The next large difference, ($\nu_{TW} - \nu_{CRDS2015}$) = -0.04745 cm⁻¹, concerns the H₂¹⁶O 050 11_{6 5} upper
305 level. In Ref. [6], the 5ν₂ 11_{6 5} – 12_{5 8} assignment was attributed to the line at 8194.1965 cm⁻¹, the first
306 assignment being to the H₂¹⁸O ν₁+3ν₂ 4_{2 3} – 5_{1 4} transition. This assignment of the 5ν₂ 11_{6 5} – 12_{5 8}
307 transition relied on the IUPAC energy value of the 050 11_{6 5} upper level, 10469.566775(3062) cm⁻¹
308 [36]. Now we attribute the 5ν₂ 11_{6 5} – 12_{5 8} transition to the line at 8194.14905 cm⁻¹ observed in the
309 present work. This assignment is confirmed by ground state combination difference relations (GSCD)
310 with the 5ν₂ 11_{6 5} – 11_{5 6} transition at 8470.52401 cm⁻¹.

311 The H₂¹⁷O ν₁+3ν₂ 4_{3 2} – 5_{2 3} transition, ($\nu_{TW} - \nu_{CRDS2015}$) = -0.03312 cm⁻¹, should be attributed to
312 the line at 8294.67838 cm⁻¹ (this study) and not to the line at 8294.7115 cm⁻¹ (Ref. [6]). This
313 assignment is confirmed by GSCD relation with the ν₁+3ν₂ 4_{3 2} – 4_{2 3} transition at 8441.03301 cm⁻¹.
314 Note the line at 8294.6811 cm⁻¹ was left unassigned in Ref. [6].

315 The lines of the H₂¹⁶O ν₁+2ν₂ 13_{10 4} – 12_{7 5} transition in both spectra (Ref. [6] and this study)
316 are very weak noisy lines but we prefer the new value of the line position (8058.48831 cm⁻¹ instead of
317 8058.4674 cm⁻¹ [6]).

318 In Ref. [6], the H₂¹⁶O ν₁+ν₃ 18_{3 16} – 17_{1 17} transition was attributed to the line of an unresolved
319 doublet at 8068.2458 cm⁻¹. In the present spectrum, this line was fitted as two components at
320 8068.24613 cm⁻¹ (18_{2 16} – 17_{0 17}) and 8068.22529 cm⁻¹ (18_{3 16} – 17_{1 17}). The upper energy of the 101
321 18_{3 16} level obtained from this latter position is 11049.58373 cm⁻¹. This term value is confirmed by its
322 agreement with the IUPAC-TG value of 11049.5814 cm⁻¹ [36] and by the line position of the ν₁+ν₃
323 18_{3 16} – 17_{3 15} transition predicted at 7482.32953 cm⁻¹, in excellent agreement with its experimental
324 value of Ref. [3] (7482.3297 cm⁻¹). We thus conclude that the 101 18_{3 16} level should have not be
325 corrected in Ref. [6] (11049.6061 cm⁻¹ in Table 3 of this reference).

326 From the present spectra, a more precise line center was derived for the very weak H₂¹⁶O ν₁+3ν₂
327 14_{5 10} – 15_{4 11} transition at 8157.37971 cm⁻¹ ($S = 5.3 \times 10^{-29}$ cm/molecule) instead of 8157.3604 cm⁻¹ (S
328 = 6.5 × 10⁻²⁹ cm/molecule) in Ref. [6]. The corresponding 130 14_{5 10} upper level is thus corrected by
329 0.01931 cm⁻¹.

330 A similar situation is found for the line corresponding to the H₂¹⁶O 4ν₂+ν₃-ν₂ 10_{5 5} – 11_{5 6}
331 transition at 8231.9271 cm⁻¹ which is blended by impurity lines in the CRDS2015 spectra. The present
332 line center determination at 8231.91083 cm⁻¹ is confirmed by GSCD relation with the line position
333 8450.77756 cm⁻¹ of the 4ν₂+ν₃-ν₂ 10_{5 5} – 11_{3 8} transition.

334 The line at 8249.5876 cm⁻¹ assigned to the H₂¹⁶O ν₂+2ν₃ 13_{2 12} – 14_{3 11} transition in Ref. [6] is
335 not observed in the present spectra and is believed to be due to an impurity. In the present work, the
336 H₂¹⁶O ν₂+2ν₃ 13_{2 12} – 14_{3 11} transition is assigned to an extremely weak line at 8249.56889 cm⁻¹. (S
337 = 7.4 × 10⁻³⁰ cm/molecule). This assignment is confirmed by GSCD with the ν₂+2ν₃ 13_{2 12} – 13_{1 13}

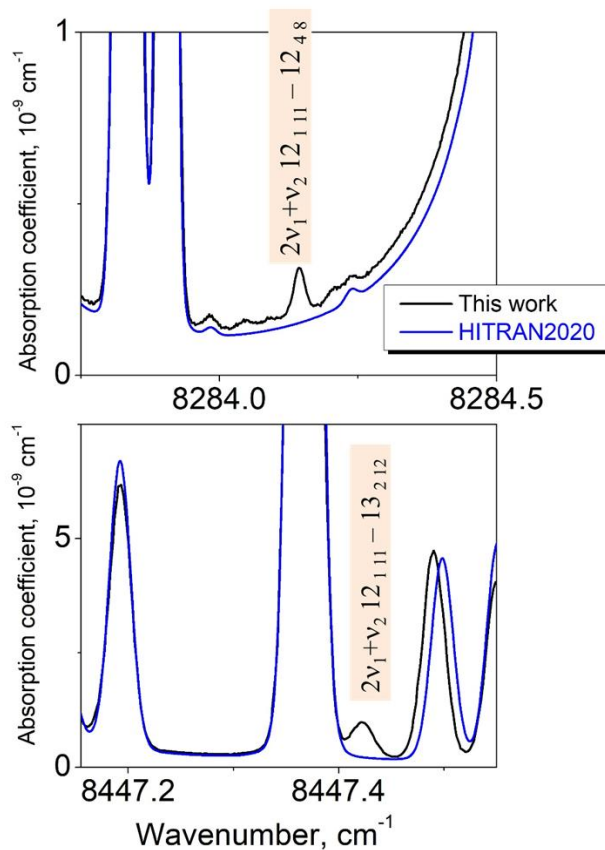
338 transition observed by Régalia et al. at 9182.3256 cm^{-1} [8]. The corresponding $012\ 13_{2\ 12}$ upper level is
 339 thus corrected by -0.018 cm^{-1} .

340 The present determination of the line position of the $\text{HD}^{16}\text{O}\ 3\nu_1\ 8_{3\ 6} - 7_{1\ 7}$ transition at
 341 $8179.97385\text{ cm}^{-1}$ instead of 8179.9901 cm^{-1} (Ref. [6]) is more correct. This position is much more
 342 consistent with line positions of other transitions reaching the $300\ 8_{3\ 6}$ upper state present in both
 343 spectra.

344 In Ref. [6], the $\text{H}_2^{18}\text{O}\ 3\nu_2+\nu_3\ 8_{5\ 4} - 9_{5\ 5}$ transition was attributed to the line of two unresolved
 345 transitions at 8325.5676 cm^{-1} . In the present spectrum, the corresponding line could be fitted as two
 346 components at $8325.56436\text{ cm}^{-1}$ ($\text{H}_2^{16}\text{O}\ \nu_2+2\nu_3\ 9_{3\ 7} - 10_{6\ 4}$) and $8325.58345\text{ cm}^{-1}$ ($\text{H}_2^{18}\text{O}\ 3\nu_2+\nu_3\ 8_{5\ 4} -$
 347 $9_{5\ 5}$), leading to a 0.016 cm^{-1} correction on the position of the latter transition.

348 **4.4. Comparison with HITRAN2020 database**

349 In our region, the water line list of the HITRAN2020 database [9] includes 11,650 transitions of
 350 seven isotopologues (H_2^{16}O , H_2^{18}O , H_2^{17}O , HD^{16}O , HD^{18}O , HD^{17}O , and D_2^{16}O) between 8041.45 and
 351 8633.41 cm^{-1} (see Fig. 1). The HITRAN intensity cut off is $10^{-30}\text{ cm/molecule}$, except for the D_2^{16}O
 352 species for which the intensity cut off was fixed to $10^{-32}\text{ cm/molecule}$, for an unknown reason. Note
 353 that 1124 transitions of H_2^{16}O , H_2^{18}O and H_2^{17}O species do not have complete vibration-rotation
 354 assignment.



355
 356 **Fig. 5.**
 357 Two of the four H_2^{16}O lines of the $2\nu_1+\nu_2$ band missing in the HITRAN2020 database.
 358

359 First of all, among our 5429 assigned transitions, 49 are missing in the HITRAN line list. 45 of
360 these 49 transitions belong to minor isotopologues and have their intensity near the HITRAN intensity
361 cut-off: H₂¹⁸O (6 transitions), H₂¹⁷O (10 transitions) and HD¹⁶O (29 transitions). Nevertheless, the four
362 H₂¹⁶O lines missing have larger intensities between 7.90×10^{-29} and 2.26×10^{-27} cm/molecule. They are
363 $2\nu_1 + \nu_2$ 12₁₁₁ – 12₄₈ (8284.14410, 1.04×10^{-28}), $2\nu_1 + \nu_2$ 12₁₁₁ – 13₂₁₂ (8447.42231, 5.58×10^{-28}), $2\nu_1 + \nu_2$
364 $10_{010} - 11_{111}$ (8503.04576, 7.90×10^{-29}), and $2\nu_1 + \nu_2$ 12₁₁₁ – 12₂₁₀ (8529.59296, 2.26×10^{-27}). Two of
365 them are shown in **Fig. 5**.

366 According to HITRAN reference code, 5608 of the 7141 of the line positions of the main
367 isotopologue, H₂¹⁶O, were taken from the W2020 line list [20]. This dataset is supplemented with
368 positions from Refs. [19,37,38] (more than 1500) and several lines from Refs. [8,36]. Note none of the
369 502 transitions of Ref. [37] has full vibration-rotation assignment. Their line positions are not
370 empirical but calculated using a semi-empirical potential energy surface. The main set of electric-
371 dipole transitions is supplemented by 47 very weak electric quadrupole transitions with line positions
372 calculated from W2020 empirical energy levels [20] and calculated line intensities [39].

373 As mentioned above, for 5608 transitions, the source of the line positions is the W2020 line list.
374 However, a careful analysis of these data shows that for 40 transitions, the HITRAN positions differ
375 from the original W2020 values [20]. The position difference reaches a value of 0.00569 cm^{-1} . The
376 vibration-rotation identification of the transitions does not match for 25 transitions. In addition, the
377 positions of seven transitions cannot be calculated from W2020 energies since the corresponding
378 upper levels (060 8₈₁, 070 6₀₆ and 080 2₀₂) are not in the list of energies of Ref. [20].

379 According to HITRAN's reference code, 1421 line positions of the H₂¹⁸O isotopologue are
380 empirical values from the W2020 line list [20] and 180 are calculated values from Bubukina et al. [37]
381 given with incomplete vibration-rotation assignment. The line positions of 210 transitions given with
382 W2020 source do not coincide with those from the W2020 line list [20].

383 Unlike the first two species, only twelve H₂¹⁷O transitions are marked as taken from the W2020
384 line list [20]. But the positions of all these twelve transitions do not coincide with the original W2020
385 values [20]. The position differences reach 0.03 cm^{-1} . All the 442 transitions from Lodi & Tennyson
386 [40] are provided with calculated positions and incomplete vibration-rotation assignment.

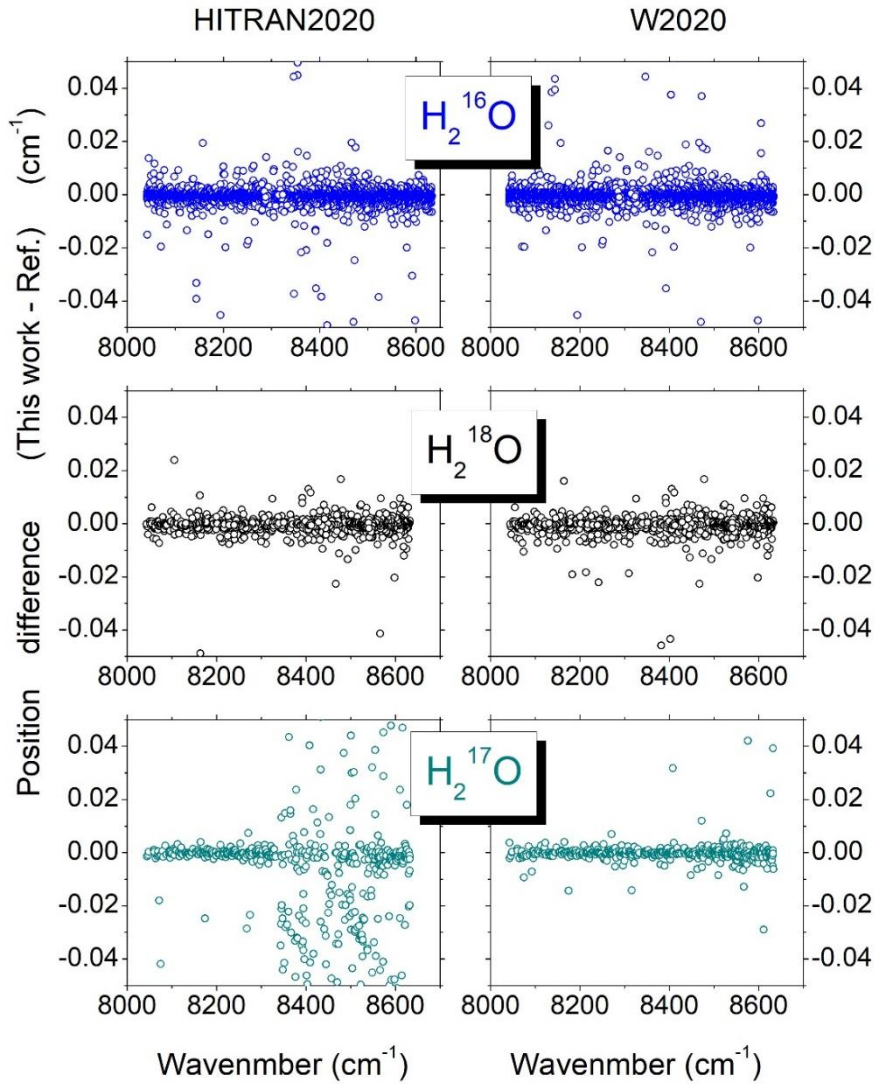
387 All HITRAN line positions of HD¹⁶O are due to Kyuberis et al. [41]. 1273 of them are empirical
388 values obtained from updated IUPAC energy levels [31] and 53 positions are *ab initio* values.

389 All positions and intensities of HD¹⁷O, HD¹⁸O and D₂¹⁶O are taking from Kyuberis et al. [41].
390 According to HITRAN reference code, the line positions of HD¹⁷O and HD¹⁸O are empirical values
391 obtained from updated IUPAC energy levels [31] and *ab initio* values for D₂¹⁶O.

392 As mentioned above, an overall satisfactory agreement is observed between our line positions
393 and HITRAN2020 values. The average ($\nu_{TW} - \nu_{HITRAN2020}$) deviation for 5238 line positions is -2.05×10^{-3}
394 cm^{-1} . Excluding lines marked as “noisy”, “blended”, “overlapped” in our experimental list and

395 excluding differences larger than 0.05 cm^{-1} , it leads to an average deviation of $-1.06 \times 10^{-3} \text{ cm}^{-1}$ for
 396 5141 line positions

397 The graphical overviews of the line position differences are presented on **Fig. 6** (left panels) for
 398 H_2^{16}O , H_2^{18}O and H_2^{17}O . The most noticeable global observation is the clear increase of outliers for
 399 H_2^{17}O above 8340 cm^{-1} corresponding to the change of the main source for HITRAN position from
 400 Ref. [38] to Ref. [40], below and above 8340 cm^{-1} , respectively. In the following, we discuss some of
 401 the most significant positions differences ($|v_{TW} - v_{\text{HITRAN2020}}| \geq 0.015 \text{ cm}^{-1}$) between the two line lists.



402
 403 **Fig.6.**
 404 Comparison of the H_2^{16}O , H_2^{18}O and H_2^{17}O line positions retrieved in this work (TW) between 8041.45 and
 405 8633.41 cm^{-1} and the HITRAN2020 [9] and W2020 values [20] (left and right panels, respectively).
 406

407 As mentioned above, the largest deviation (0.278 cm^{-1}) is observed for the $\text{H}_2^{16}\text{O } 2\nu_3 17_{512} - 16$
 408 4_{13} ($8065.53458 \text{ cm}^{-1}$, $S = 2.491 \times 10^{-29} \text{ cm/molecule}$ instead of $8065.25653 \text{ cm}^{-1}$, $S = 2.913 \times 10^{-29}$
 409 cm/molecule in HITRAN). It is due to an incorrect assignment of the upper level ($030 17_{134}$) and an
 410 incorrect value of the line position. The HITRAN reference to the position of this line is a “private
 411 communication (2008)”. The W2020 line list gives a very close line position ($8065.25729 \text{ cm}^{-1}$) and

412 the same incorrect assignment ($3\nu_2 17_{13\ 4} - 16_{4\ 13}$). The W2020 energy value corresponding to our
413 vibration-rotation assignment ($002 17_{5\ 12}$ instead of $030 17_{13\ 4}$) is $11504.775(10) \text{ cm}^{-1}$, about 0.066 cm^{-1}
414 1 below our value ($11504.841(3) \text{ cm}^{-1}$) but the $\text{H}_2^{16}\text{O } 2\nu_3 17_{5\ 12} - 16_{4\ 13}$ transition is absent in the
415 W2020 list.

416 The fifteen HITRAN2020 positions showing position deviations larger than 0.1 cm^{-1} compared
417 to our measurements correspond to H_2^{16}O lines of high bending bands ($3\nu_2+\nu_3$, $4\nu_2+\nu_3$, $5\nu_2$, $6\nu_2$, and
418 $7\nu_2$) and three transitions of the $2\nu_3$, $\nu_2+2\nu_3$, and $2\nu_1+\nu_2$ bands. Eleven of these deviations are due to
419 incorrect values of the upper energies in W2020 list.

420 The line position of the $\text{H}_2^{16}\text{O } 2\nu_3 14_{8\ 7} - 13_{5\ 8}$ transition is given at $8134.50567 \text{ cm}^{-1} - (v_{TW} -$
421 $v_{\text{HITRAN2020}}) = -0.1275 \text{ cm}^{-1}$ – with position reference to Mikhailenko et al. [38]. This is not correct: in
422 our line list covering the $5850 - 8340 \text{ cm}^{-1}$ region [38], this line position (calculated from empirical
423 energies) was given at $8134.3788 \text{ cm}^{-1}$. This value is close to the CRDS line position measured in Ref.
424 [6] ($8134.3807 \text{ cm}^{-1}$) which is itself in excellent agreement with the $8134.37816 \text{ cm}^{-1}$ position
425 determined in the present study.

426 The $\text{H}_2^{16}\text{O } 2\nu_3 17_{4\ 14} - 16_{1\ 15}$ transition with measured line position at $8173.7364 \text{ cm}^{-1} - (v_{TW} -$
427 $v_{\text{HITRAN2020}}) = -0.14 \text{ cm}^{-1}$ – is given without complete VR assignment and with variational position in
428 HITRAN2020 ($8173.87670 \text{ cm}^{-1}$, Ref. [37]) and in W2020 ($8173.44656 \text{ cm}^{-1}$, Ref. [42]). This
429 transition which was assigned by Campargue et al. [6] to the line at $8173.7328 \text{ cm}^{-1}$ but was excluded
430 from the W2020 transition database probably due to its superposition with an ammonia line.

431 The $\text{H}_2^{16}\text{O } 2\nu_3 16_{7\ 10} - 15_{4\ 11}$ transition $- (v_{TW} - v_{\text{HITRAN2020}}) = -0.068 \text{ cm}^{-1}$ – is measured in the
432 present work at $8077.75668 \text{ cm}^{-1}$ instead of $8077.82494 \text{ cm}^{-1}$ in the HITRAN/W2020 lists. This last
433 value relies on the W2020 upper term value [20] derived from four emission positions reported by
434 Zobov et al. [14,43] and Rutkowski et al. [44], three of them having multiple VR assignments.

435 The measured position of the $6\nu_2 8_{2\ 7} - 9_{5\ 4}$ transition at $8569.95452 \text{ cm}^{-1}$ deviates from the
436 HITRAN/W2020 value by $(v_{TW} - v_{\text{HITRAN2020}}) = -0.056 \text{ cm}^{-1}$. HITRAN/W2020 line position was
437 calculated from W2020 upper energy level derived in Ref. [23] from four emission line positions
438 given by Coheur et al. [45] and Zobov et al. [14,43], two of them having multiple VR assignments.

439 The $(v_{TW} - v_{\text{HITRAN2020}})$ differences are -0.052 cm^{-1} and -0.047 cm^{-1} for the $3\nu_2+\nu_3 12_{5\ 8} - 12_{5\ 7}$ and
440 $3\nu_2+\nu_3 12_{5\ 8} - 13_{3\ 11}$ transition, respectively. These two transitions at 8545.77779 and 8598.40303
441 cm^{-1} , respectively, reach the same $031 12_{5\ 8}$ upper level. Our experimental uncertainties on the line
442 positions of these weak lines are about 0.003 cm^{-1} . The W2020 energy of the level ($10846.51486 \text{ cm}^{-1}$)
443 was determined from nine transitions assigned in emission spectra [14,43,44,46] and one CRDS
444 transition [6]. Eight of the emission lines have multiple VR assignments. Interestingly, three
445 transitions observed by absorption by Régalia et al. [8] were weighted with a very large uncertainty
446 between 0.075 and 0.1 cm^{-1} by the xMARVEL procedure which is equivalent to discard these data.
447 The erroneous assignment of the $3\nu_2+\nu_3 12_{5\ 8} - 13_{5\ 9}$ transition to the line at $8259.9848 \text{ cm}^{-1}$ reported

448 in Ref. [6] relied on the inaccurate IUPAC upper energy of the $031\ 12\ 5\ 8$ ($10846.513718\ \text{cm}^{-1}$) [36].
449 This IUPAC energy value relied itself on emission line positions of Refs. [14,43]. Taking into account
450 the W2020 uncertainty of different positions, only two of them ($8259.9848\ \text{cm}^{-1}$ [6] and 6887.261822
451 cm^{-1} of the $3\nu_2+\nu_3-\nu_2\ 12\ 5\ 8 - 12\ 5\ 7$ [36]) were really used for the determination of the W2020 term
452 value. In summary, only emission data was used for the both IUPAC [36] and W2020 [20] energy
453 values. This is a typical example of biases of the xMARVEL procedure used to derive the W2020
454 energy levels [20]: the W2020 energy value of the considered $031\ 12\ 5\ 8$ upper level relies exclusively
455 on emission data while three reliable transitions observed by absorption by Régalia et al. [8] were not
456 taken into account for the energy determination. Our line positions of the $3\nu_2+\nu_3\ 12\ 5\ 8 - 12\ 5\ 7$ and
457 $3\nu_2+\nu_3\ 12\ 5\ 8 - 13\ 3\ 11$ transitions are very consistent with the $3\nu_2+\nu_3\ 12\ 5\ 8 - 11\ 5\ 7$ FTS position reported
458 at $8860.6800\ \text{cm}^{-1}$ [8] and in satisfactory agreement with two additional transitions reported by Régalia
459 et al. [8]: our term value is $10846.4652\ \text{cm}^{-1}$ to be compared to the FTS values of 10846.4649 and
460 $10846.4785\ \text{cm}^{-1}$, respectively.

461 For the H_2^{17}O isotopologue, the $(\nu_{TW} - \nu_{\text{HITRAN2020}})$ differences range from -0.0764 to $+0.0897\ \text{cm}^{-1}$
462 ¹. The absolute values of the differences exceed $0.005\ \text{cm}^{-1}$ for 181 transitions. The main part of these
463 large differences is due to variational positions from Lodi & Tennyson [40], according to HITRAN
464 reference code. Sixteen of the line positions with large $(\nu_{TW} - \nu_{\text{HITRAN2020}})$ differences rely on an
465 (unpublished) update of the IUPAC database [47]. In addition, four transitions ($3\nu_2+\nu_3\ 5\ 2\ 4 - 5\ 2\ 3$,
466 $\nu_1+3\nu_2\ 3\ 2\ 2 - 3\ 1\ 3$, $\nu_1+3\nu_2\ 4\ 3\ 1 - 4\ 2\ 2$, and $\nu_1+3\nu_2\ 4\ 2\ 3 - 3\ 1\ 2$) are referenced to W2020 line list while
467 their HITRAN's positions differ from their W2020 counterpart by a value up to $0.017\ \text{cm}^{-1}$.

468 The same situation of incorrect sourcing is found for eleven H_2^{18}O transitions. All of them
469 (according to HITRAN reference code) are coming from our $5850 - 8340\ \text{cm}^{-1}$ line list [38]. But in
470 fact, none of these line positions coincide with the values of Ref. [38]. The deviations reach a value of
471 $0.05443\ \text{cm}^{-1}$ and the position reported in Ref. [38] are confirmed in the present study.

472 **Table 3.**

473 Term values of the HD^{16}O isotopologue corrected compared to published values [31,48].
474

$V_1V_2V_3$	J	K_a	K_c	Energy	dE	NT	E [31]	unc	ΔE	Ratio	E [48]	$d2$
012	9	8	2	10224.16027	337		10224.06221	500	9806	19.61		
012	9	8	1	10224.16030	337		10224.06238	500	9792	19.58		
012	11	6	6	10162.17475	208		10162.16664	500	811	1.62		
012	11	6	5	10162.25323	201		10162.24747	500	576	1.15		
012	14	3	11	10453.35835	171		10453.33780	500	2055	4.11		
012	15	0	15	10191.15764	269		10191.11790	514	3974	7.73		
022	6	3	3	10438.87664	427		10438.88316	570	-652	1.14		
111	8	7	2	9096.20106	434		9096.21122	500	-1016	2.03		
111	8	7	1	9096.20117	434		9096.21111	500	-994	1.99		
220	7	1	6	8566.01312	208	2	8484.16639	500	-15327	30.65	8566.0068	632
220	7	3	4	8697.53845	240						8697.5323	615
220	9	0	9	8702.17405	239		8702.17946	500	-541	1.08	8702.1731	95
300	11	7	4	9599.24330	354		9599.23597	500	733	1.47		
300	13	3	10	9447.67038	116		9447.66474	500	564	1.13		

475 Notes

476 $V_1V_2V_3$ – vibration quantum numbers; $J K_a K_c$ – rotation quantum numbers; Energy/cm⁻¹ – empirical term values;
477 dE – estimated uncertainty on the term value in 10⁻⁵ cm⁻¹ units; NT – number of line positions used for the
478 energy determination if it is larger than 1; E [31] and E [48] – empirical term values published in corresponding
479 references in cm⁻¹; unc – IUPAC term value uncertainties in 10⁻⁵ cm⁻¹ units; ΔE – term value differences between
480 empirical values of this work and those of Ref. [31] in 10⁻⁵ cm⁻¹ units; $Ratio = \Delta E / unc$; $d2$ – term value
481 differences between empirical values of this work and those of Ref. [48] in 10⁻⁵ cm⁻¹ units.

482 In **Table 3**, we list 14 corrected term values of the HD¹⁶O molecule corresponding to $|v_{TW} -$
483 $v_{HITRAN2020}|$ deviations larger than 0.005 cm⁻¹. According to HITRAN reference code, HITRAN
484 positions rely on an update of the IUPAC-TG levels [31] reported by Kyuberis et al. [41]. The table
485 compares our energy values to the IUPAC-TG values [31] and to the values given by Liu et al. [48].

486 **4.5. Comparison to the W2020 line lists**

487 Following the approach developed a decade ago by a task group (TG) of the International Union
488 of Pure and Applied Chemistry (IUPAC) [31,36,47], the xMARVEL procedure and code were applied
489 to an exhaustive catalog of absorption and emission measured line positions collected in the literature,
490 in order to derive accurate sets of empirical energy levels of H₂¹⁶O, H₂¹⁸O and H₂¹⁷O. For the main
491 isotopologue, the collected W2020-H₂¹⁶O transition dataset gathers 286,987 non-redundant
492 rovibrational transitions, and 19,225 empirical energy levels were determined [20]. Most of the line
493 positions of the W2020 lists (tagged with “M”) were obtained by difference of empirical energy levels
494 and released with their self-consistent uncertainties [20]. In absence of empirically determined energy
495 levels, less accurate calculated values were used (tag “C”).

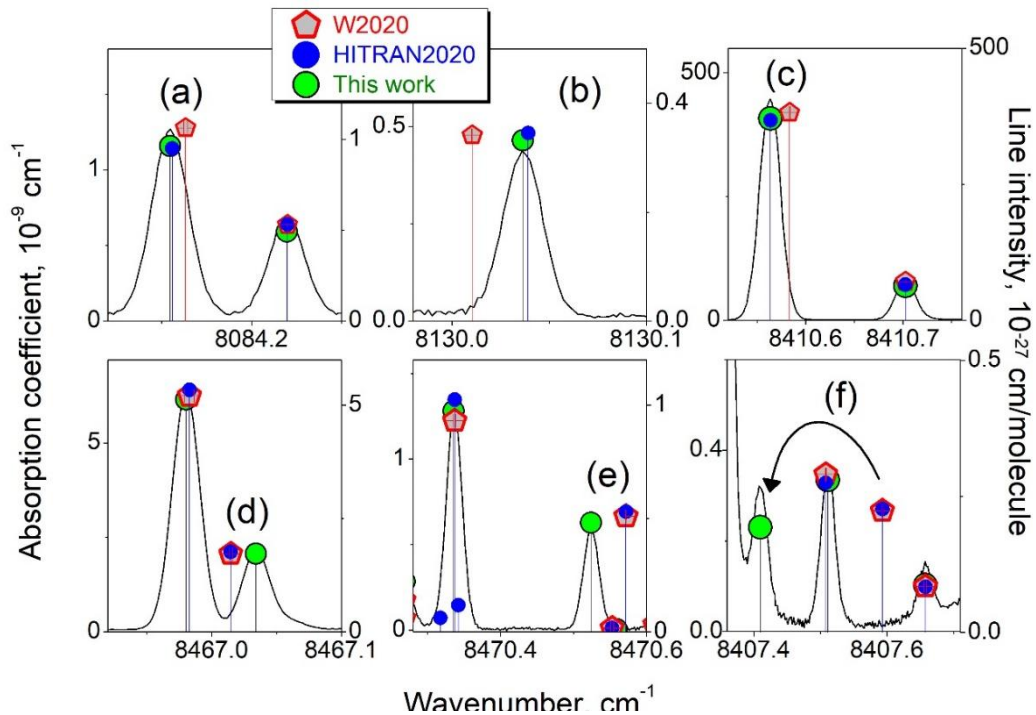
496 All 4687 transitions of the H₂^xO ($x=16,17,18$) isotopologues assigned in our spectrum are
497 present in the W2020 line list [20]. Note that the complete VR assignment of 71 transitions missing in
498 the W2020 list is included in the list provided as Supplementary Material. These transitions
499 correspond to the 60 H₂^xO newly determined upper energy levels listed in **Table 2**. The H₂¹⁶O 002
500 17_{4 14} and H₂¹⁸O 031 11_{1 10} levels included in the table are “new” compared to the W2020 energy lists
501 but they were previously reported in Ref. [6] from the H₂¹⁶O 002 17_{4 14} – 000 16_{1 15} and H₂¹⁸O 031
502 11_{1 10} – 000 12_{1 11} transitions at 8173.7328 and 8130.8295 cm⁻¹, respectively. These positions have not
503 been used for W2020 input file probably due to the overlapping with ammonia lines mentioned in Ref.
504 [6]. In the present work, the positions of these very weak lines ($S \sim 4 \times 10^{-29}$ cm/molecule) is found at
505 8173.73640 and 8130.82895 cm⁻¹, respectively, in agreement with the values of Ref. [6].

506 As mentioned above, the general agreement with the W2020 line position is very good (see **Fig.**
507 **4**) with average deviations between -1.7×10^{-4} cm⁻¹ and -3.4×10^{-4} cm⁻¹, depending on the set of outliers
508 excluded from the comparison.

509 The overviews of the $(v_{TW} - v_{W2020})$ position differences are included in **Fig. 6** for H₂¹⁶O, H₂¹⁸O
510 and H₂¹⁷O (right panels). Let us mention that 27 transitions have their W2020 positions showing a
511 large deviation compared to the present measurements (between 0.0052 and 0.0260 cm⁻¹) while
512 HITRAN value agree with experiment within 0.004 cm⁻¹. Three of such examples are illustrated on the
513 upper panels of **Fig. 7**. These lines are tagged as “bad position in W2020” in the experimental list

514 provided as supplementary material. All but two of these (good) HITRAN positions originate from our
 515 5850 – 8340 cm^{-1} list [38]. The most inaccurate W2020 position from this group of transitions, (ν_{TW} -
 516 ν_{W2020}) = 0.026 cm^{-1} , is that of the H_2^{16}O $5\nu_2 14_{4 11} - 15_{1 14}$ transition (see Fig. 7 (b)). The W2020
 517 position is at 8130.01045 cm^{-1} while the present measurement gives a value at 8130.03640 cm^{-1} , in
 518 very good agreement with our previous determination at 8130.0371 cm^{-1} [6] and with HITRAN value
 519 (8130.0391 cm^{-1}). Interestingly, the W2020 energy derivation of the $050 14_{4 11}$ upper level relies on
 520 the $5\nu_2 14_{4 11} - 15_{1 14}$ position of Ref. [6] and on the $5\nu_2-4\nu_2 14_{4 11} - 15_{5 10}$ emission transition
 521 reported with an inaccurate value at 928.52266 cm^{-1} [45]. For an unknown reason, the xMARVEL
 522 procedure attached the same uncertainty of 0.02665 cm^{-1} to the absorption and emission line positions
 523 [20]. This is a typical example of a good absorption data “spoiled” by inaccurate emission data leading
 524 to an inaccurate W2020 energy level.

525 Overall, 191 of our positions deviate from the W2020 positions by more than 0.005 cm^{-1} . Our
 526 recommended values of the corresponding upper energy levels are listed in **Table 4** together with
 527 W2020 values. This table includes the ratio $R = \frac{|E_{TW} - E_{W2020}|}{Unc_{W2020}}$ which compares the absolute deviation
 528 of the W2020 energy level from our value to the claimed W2020 uncertainty (Unc_{W2020}). Among the
 529 127 corrected levels, 48 have a term value which deviates from our observations by more than ten
 530 times their W2020 uncertainty (R larger than 10, up to 375). Six examples of inaccurate W2020 line
 531 positions with deviations largely exceeding the W2020 error bars are displayed in **Fig. 7** (the very
 532 small W2020 error bars plotted on the figure are hardly visible at the scale of the graphs). The
 533 assignment of the problematic lines is given in the caption of the figure.



534 **Fig. 7.**
 535 Examples of comparison of the CRDS spectrum of water vapor and corresponding line list (green circles) to the
 536 W2020 line list of H_2^{16}O [20] (grey pentagons) and the HITRAN2020 list of natural water [19] (blue circles).
 537

538 The W2020 line positions are based on empirically determined energy levels. The (very small) W2020 error bars
 539 displayed on the different panels are considerably smaller than the observed deviations.
 540 The right-hand intensity scale is adjusted to correspond approximately to the peak heights.
 541 In the three examples displayed on the upper panels [(a) $4\nu_2+\nu_3-\nu_2$ $2_{02}-3_{21}$, (b) $5\nu_2$ $14_{411}-15_{114}$, (c) $3\nu_2+\nu_3$
 542 $6_{52}-7_{53}$], the W2020 positions deviate from the observation while the HITRAN positions show a good
 543 agreement. On the three lower panels [(d) $\nu_1+\nu_2+\nu_3$ $14_{114}-14_{113}$, (e) $5\nu_2$ $11_{65}-11_{56}$, (f) $6\nu_2$ $7_{17}-8_{44}$], the
 544 W2020 and HITRAN2020 positions coincide and deviate both from the recorded spectrum.

545 The largest discrepancy (about 0.38 cm^{-1}) concerns the $15_{015}-16_{116}$ and $15_{115}-16_{016}$
 546 doublet of the $2\nu_1+\nu_2$ band of H_2^{16}O that we assign to the line at $8354.08116\text{ cm}^{-1}$ in accordance with
 547 the J -dependence of the ($\nu^{OBS} - \nu^{SP}$) deviations of the experimental (ν^{OBS}) and calculated (ν^{SP}) positions
 548 for the $2\nu_1+\nu_2$ $J_{0J}-J+1_{1J+1}$ series of transitions. The 210_{15015} and 15_{115} term values of W2020
 549 were derived from the $2\nu_1+\nu_2$ $15_{015}-14_{114}$ absorption line reported at 8941.888 cm^{-1} given by
 550 Tolchenov & Tennyson [24] which is believed to be erroneously assigned. In the HITRAN2020 line
 551 list, this doublet is assigned the $\nu_1+\nu_2$ $15_{151}-16_{016}$ transition and to a $15_{150}-16_{116}$ transition of an
 552 unidentified band with W2020 position ($8354.03627\text{ cm}^{-1}$) and variational position ($8354.03153\text{ cm}^{-1}$
 553 [37]), respectively. Note that this last assignment is incorrect as the $15_{150}-16_{116}$ rotational
 554 assignment is forbidden for both A and B type bands.

555 We have examined in details the origin of the inaccuracy of the W2020 energy value for a
 556 sample of H_2^{16}O levels of **Table 4**. Obviously, these situations result from the existence of an
 557 inaccurate line position in the W2020 transition dataset which impacts the resulting W2020 energy
 558 level value but the amplitude of the impact depends on the W2020 weighting of the experimental line
 559 positions. (Note that among the 127 corrected levels of H_2^{16}O , only 36 involve CRDS line positions, a
 560 small fraction of them being inaccurate or wrong as discussed in section 4.3). The point is that in a
 561 number of cases where conflicting experimental values exist, the xMARVEL procedure fails in
 562 discriminating the good data from the less accurate data. The difficulty of the process is due to the lack
 563 of reliable line-by-line error bars in most of the experimental sources. In some problematic situations,
 564 for an unknown reason, the MARVEL procedure attached unrealistically small uncertainty value to
 565 some inaccurate experimental values which have then a considerable weight on the resulting energy
 566 value (see the example of the 031_{1258} discussed in section 4.4). Another typical situation is when a
 567 uniform error bar is attached to all the position values of a given source, while obviously the position
 568 of weak blended lines is much less accurate than that of “an isolated line of intermediate intensity”.
 569 Again, this is due the fact that the error bars needed by the xMARVEL procedure are not available and
 570 can hardly be guessed. In the number of problematic cases examined in details, we found examples
 571 where our present measurements coincide with some previous results which were *de facto* excluded
 572 from the energy determination due to the W2020 decision to attach them excessive error bars.

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Table 4

Term values of H₂^xO (x= 16,17,18) water isotopologues corrected by more than 0.005 cm⁻¹ compared to the W2020 empirical energy levels [20].

$V_1V_2V_3$	J	K_a	K_c	Energy (cm ⁻¹)	dE (10 ⁻⁵ cm ⁻¹)	NT	E_{W2020} [20] (cm ⁻¹)	Unc_{W2020} (10 ⁻⁵ cm ⁻¹)	ΔE (10 ⁻⁵ cm ⁻¹)	Ratio
H₂¹⁶O										
002	16	7	10	11322.35736	297		11322.42562	1710	-6826	3.99
002	17	5	12	11504.84120	268		11504.77535	1080	6585	6.10
002	18	4	15	11503.51499	107		11503.38094	389	13405	34.50
012	8	8	1	10786.81160	12		10786.81774	13	-614	48.58
012	8	8	0	10786.81160	12		10786.81774	13	-614	48.46
012	10	1	10	10074.46086	81		10074.46764	51	-678	13.42
012	10	7	4	11043.78788	128		11043.78215	50	573	11.40
012	13	2	12	10988.99744	746		10989.01615	105	-1871	17.87
012	13	4	9	11518.89796	163		11518.90828	793	-1032	1.30
012	13	5	9	11566.01465	47		11565.78065	1333	23400	17.55
012	13	8	5	12094.78477	648		12094.73357	632	5120	8.11
012	14	4	11	11701.36744	228		11701.36188	609	556	0.91
012	15	1	14	11558.06940	501		11558.05387	1460	1553	1.06
012	15	2	14	11557.73092	103		11557.70404	1745	2688	1.54
022	7	3	4	11386.13814	338		11386.14398	228	-584	2.56
031	6	5	2	9470.20970	19	3	9470.22957	60	-1987	32.99
031	9	7	2	10519.22737	178	2	10519.22222	36	515	14.26
031	10	6	5	10517.31559	11		10517.30864	50	695	13.83
031	11	4	8	10356.52419	18	4	10356.53216	51	-797	15.67
031	12	4	9	10638.92985	66	4	10638.93901	51	-916	18.13
031	12	5	8	10846.46518	251	2	10846.51486	134	-4968	37.05
031	13	6	7	11383.69381	42		11383.80423	601	-11042	18.38
031	14	2	13	10738.00571	52		10737.99657	922	914	0.99
031	14	4	10	11373.27104	107		11373.27805	536	-701	1.31
031	14	6	8	11719.39308	364		11719.37540	601	1768	2.94
031	15	2	13	11335.35830	292		11335.37176	2461	-1346	0.55
031	15	6	10	12063.93046	570		12063.92157	88	889	10.07
031	16	1	15	11356.00250	126	2	11356.00882	414	-632	1.53
031	17	0	17	11261.86083	41		11261.86776	347	-693	2.00
041	6	3	3	10633.97536	11	5	10633.98201	51	-665	12.97
041	9	4	5	11413.20972	179		11413.19366	276	1606	5.81
041	10	6	5	12137.16876	494	2	12137.17758	879	-882	1.00
041	11	2	9	11640.91011	143		11640.92096	1388	-1085	0.78
041	11	3	8	11775.41233	219		11775.28222	1144	13011	11.37
041	12	4	8	12226.36835	464		12226.37946	995	-1111	1.12
041	14	0	14	11850.96054	368		11850.95208	341	846	2.48
050	5	5	1	8906.91550	32	5	8906.92237	100	-687	6.85
050	8	4	5	9117.28554	9	4	9117.27813	25	741	29.35
050	9	6	4	9961.82189	14	2	9961.83034	51	-845	16.50
050	10	5	5	9869.74092	45		9869.74602	407	-510	1.25
050	11	4	8	9822.62023	28	4	9822.61334	51	689	13.38
050	11	5	6	10135.02266	35	3	10135.01166	51	1100	21.61
050	11	6	5	10469.51933	18	2	10469.56722	226	-4789	21.20
050	13	3	10	10230.53718	152		10230.72899	323	-19181	59.38
050	14	4	11	10761.30524	25		10761.27930	5331	2594	0.49
060	7	1	7	9539.18577	69		9539.36866	179	-18289	102.12
060	7	1	6	9714.49067	86		9714.75867	183	-26800	146.77
060	7	5	2	10837.70631	563		10837.71662	696	-1031	1.48
060	8	2	7	10047.25190	164		10047.30825	1068	-5635	5.28
060	9	0	9	9837.80195	23	2	9837.81511	1800	-1316	0.73
060	9	5	4	11250.37347	547		11250.39088	2001	-1741	0.87
060	9	6	3	11613.17589	174		11613.08115	408	9474	23.22

060	10	0	10	10039.61145	140	2	10039.60106	1002	1039	1.04
060	10	4	7	11143.39648	630		11143.41604	572	-1956	3.42
060	13	0	13	10756.15497	56		10756.17475	3654	-1978	0.54
070	3	0	3	10223.87421	17		10223.86799	300	622	2.07
070	3	1	3	10435.52253	318	2	10435.52787	184	-534	2.90
070	5	0	5	10428.00278	27	2	10428.15128	506	-14850	29.34
070	7	0	7	10718.88596	148		10718.89141	530	-545	1.03
070	10	1	10	11425.02327	424		11425.03050	300	-723	2.41
070	11	0	11	11573.11404	553		11573.24735	1323	-13331	10.08
111	11	9	2	11526.52882	80		11526.54096	1783	-1214	0.68
111	12	8	5	11560.51311	29		11560.51929	276	-618	2.24
111	12	9	4	11813.62903	70		11813.63488	1172	-585	0.50
111	13	8	6	11868.38386	37		11868.37523	1369	863	0.63
111	13	9	5	12122.69489	166		12122.68722	1091	767	0.70
111	14	1	14	10794.91759	39	2	10794.89846	128	1913	14.98
111	14	6	9	11861.29848	72		11861.22782	1142	7066	6.19
111	14	8	7	12198.09808	223		12198.08346	1013	1462	1.44
111	15	3	12	11829.52983	37		11829.56510	1600	-3527	2.20
111	15	4	11	12006.20806	81		12006.21315	604	-509	0.84
111	16	3	13	12177.70070	74		12177.70741	1013	-671	0.66
111	16	4	13	12173.85277	165		12173.87453	1877	-2176	1.16
111	17	2	16	11995.91261	119		11995.91860	729	-599	0.82
111	17	2	15	12286.98353	291		12286.93924	603	4429	7.35
121	14	1	14	12305.58544	271		12305.59729	1436	-1185	0.82
130	8	4	4	9557.47160	10	5	9557.47698	60	-538	8.92
130	9	7	2	10481.20100	25	2	10481.19377	54	723	13.42
130	10	6	5	10458.18408	65	3	10458.18948	52	-540	10.31
130	11	6	5	10721.85103	129		10721.85762	467	-659	1.41
130	14	5	10	11401.98039	161		11401.96108	103	1931	18.71
140	1	1	0	9791.61828	7		9791.60323	50	1505	29.95
140	10	3	7	11389.66218	331		11389.65099	300	1118	3.73
140	12	3	10	11841.26194	320		11841.27165	555	-971	1.75
210	7	5	3	9840.83208	14	2	9840.83768	60	-560	9.30
210	10	9	2	11277.81268	291		11277.80304	1003	964	0.96
210	10	9	1	11277.81268	291		11277.80307	1006	961	0.96
210	11	1	11	10031.64566	5	2	10031.65114	51	-548	10.83
210	12	4	9	10848.17535	13	3	10848.18042	52	-507	9.66
210	13	3	10	11140.37874	66		11140.53272	1701	-15398	9.05
210	14	1	14	10743.70487	94		10743.69587	611	900	1.47
210	15	0	15	11015.02598	56		11015.40361	101	-37763	375.38
210	15	1	15	11015.02716	100		11015.41085	1006	-38369	38.14
210	15	4	11	11944.06956	381		11944.06072	1003	884	0.88
$H_2^{17}O$										
111	7	6	1	10016.18577	67		10016.21475	10	-2898	287.54
111	11	0	11	10064.14958	462		10064.15817	3351	-859	0.26
111	13	2	12	10771.07055	213		10771.07912	504	-857	1.70
210	5	1	5	9064.74820	48	2	9064.75439	387	-619	1.60
$H_2^{18}O$										
012	7	1	7	9532.06362	129		9532.06939	163	-577	3.55
031	7	4	4	9403.31670	57	2	9403.32273	50	-603	12.05
031	8	5	4	9791.60152	170		9791.59215	1296	937	0.72
031	8	6	3	10010.64952	48		10010.63985	502	967	1.93
031	9	4	5	9824.45326	141	2	9824.46046	51	-720	14.01
031	9	6	3	10228.58454	125		10228.59167	500	-713	1.43
031	10	4	7	10054.74314	185		10054.73716	501	598	1.19
031	10	7	3	10710.96180	229		10710.94880	502	1300	2.59
031	12	2	11	10147.65947	235		10147.65335	56	612	10.89
050	7	5	2	9182.10769	69	4	9182.11391	10	-622	60.06
111	6	5	2	9670.59957	80		9670.61163	11	-1206	110.04
111	7	6	1	9997.65723	23		9997.67753	638	-2030	3.18

111	7	7	0	10187.36809	25		10187.36267	176	542	3.09
111	8	8	0	10588.71087	70		10588.71610	595	-523	0.88
111	9	4	6	10103.21716	26	2	10103.22282	10	-566	54.65
111	9	4	5	10123.49012	166		10123.49996	101	-984	9.71
111	13	1	13	10505.27762	61		10505.26993	1426	769	0.54
111	13	3	11	10972.77924	183		10972.78524	501	-600	1.20
111	14	1	14	10759.33413	325		10759.32248	505	1165	2.31
130	0	0	0	8249.03287	84		8249.03837	50	-550	10.98
130	5	5	1	9219.57938	199		9219.60199	51	-2261	44.52
130	9	2	7	9499.30103	58	3	9499.30665	838	-562	0.67
130	9	3	6	9608.77167	101		9608.70833	100	6334	63.34
210	4	1	3	9010.25415	22		9010.24725	10	690	67.34
210	5	4	2	9358.20451	161		9358.18782	3749	1669	0.45
210	5	5	0	9498.99357	81		9498.98782	472	575	1.22
210	7	1	7	9301.25496	21	2	9301.26294	50	-798	15.81
210	8	1	7	9599.67536	88		9599.66811	144	725	5.03
210	8	2	6	9704.95432	478		9704.96775	500	-1343	2.69

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Notes

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$V_1V_2V_3$ – vibration quantum numbers; $J K_a K_c$ – rotation quantum numbers; Energy/cm⁻¹ – empirical term values; dE – term value uncertainties in 10⁻⁵ cm⁻¹ units; NT – number of line positions used for the energy determination if it is larger than 1; E_{W2020} – W2020 empirical term values [20] in cm⁻¹; Unc – W2020 term value uncertainties in 10⁻⁵ cm⁻¹ units; ΔE – term value differences between empirical values of this work and those of Ref. [20] in 10⁻⁵ cm⁻¹ units; Ratio = $\Delta E/\text{Unc}$.

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5. Line intensities - Comparison with literature

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5.1. Overview comparison

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The S_{Ref}/S_{TW} line intensity ratios comparing our measured values to the FTS values of Ref. [8], to the CRDS values of Ref. [6] and to the HITRAN2020 [9] and W2020 [20] intensities are displayed on **Fig. 8**. This plot is limited to the main isotopologue, H₂¹⁶O. Overall, the agreement appears to be reasonable, although significantly better between the experimental datasets. Let us recall that all the W2020 intensities are calculated values from the POKAZATEL list [42]. In our region of interest, most of the HITRAN line intensities are calculated values from Conway et al. [49] (6036 of 7141) and experimental values of Campargue et al. below 8340 cm⁻¹ [6] (927 entries). 121 line intensities are from Refs. [8,19,50]. The W2020 and Conway et al. intensities were computed from different variants of the semi-empirical potential energy and *ab initio* dipole moment surfaces of the water molecules. Differences between the calculated intensities of the HITRAN2020 and W2020 lists reflect the sensitivity of the calculations to small changes in the used surfaces in the considered region. According to **Fig. 8**, the W2020 and HITRAN2020 intensity values are validated by experiment within 10-15% for most of the lines although a number of outliers are observed (see below). We also note that, contrary to HITRAN values, the POKAZATEL intensities of the W2020 list present a systematic overestimation by about 10% in the considered region.

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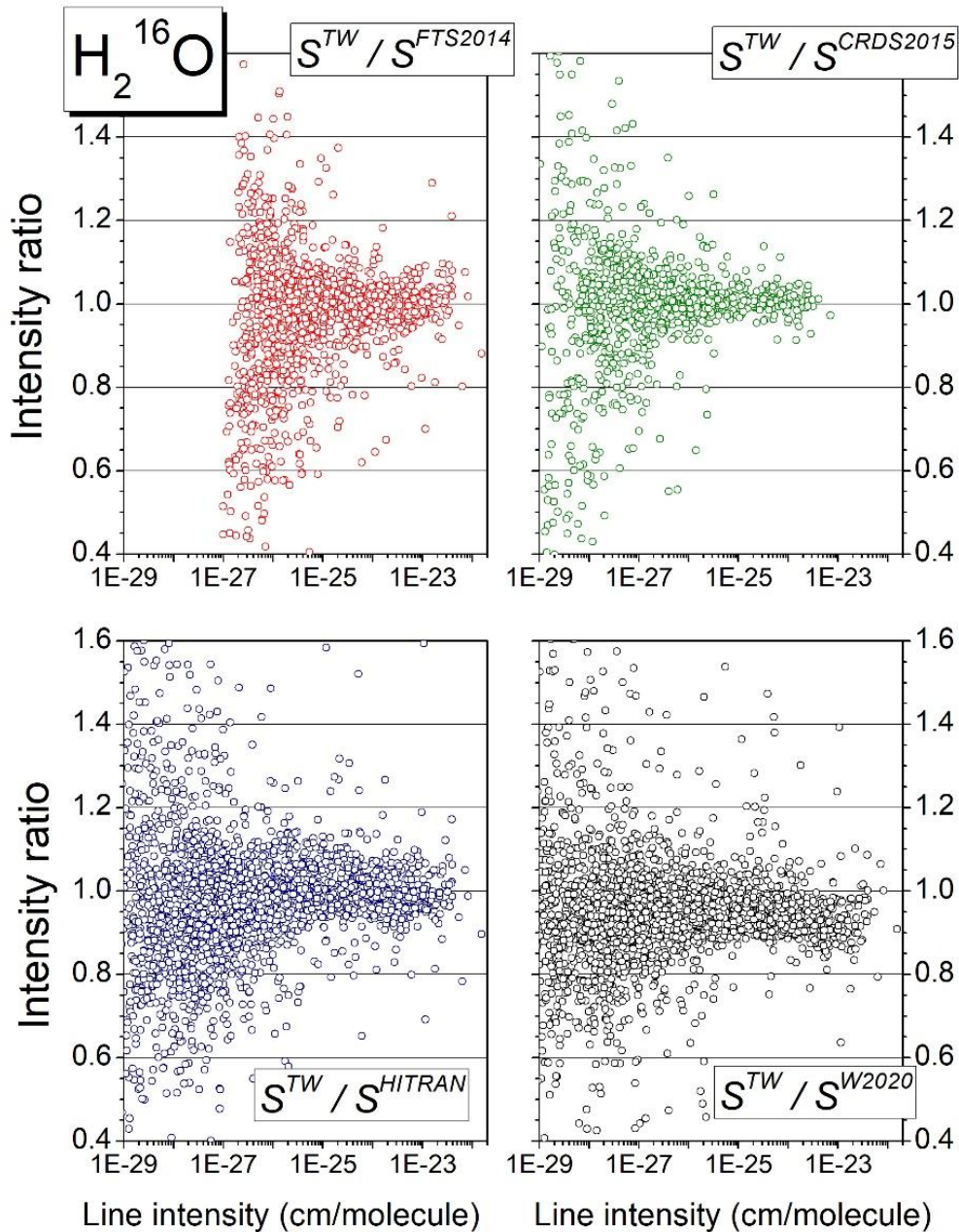
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In order to examine the situation in more details, the intensity ratios of the $\nu_1+3\nu_2$, $3\nu_2+\nu_3$ and $2\nu_1+\nu_2$ bands of the second hexade have been separated in different panels in **Fig. 9**. The differences between the general appearance of the upper and lower panels (corresponding to W2020 and HITRAN2020, respectively) reflect the differences between the POKAZATEL intensities and those of

605 Conway et al. [49]. The 10% systematic overestimation of the W2020 intensities is clearly apparent
 606 for the $\nu_1+3\nu_2$ and $3\nu_2+\nu_3$ bands while HITRAN average values mostly coincide with experiment,
 607 although with a larger dispersion than W2020 dataset in the case of the first band. Interestingly, a
 608 larger dispersion of the intensity ratios is observed for the $2\nu_1+\nu_2$ band both for HITRAN2020 and
 609 W2020. This situation is unusual as, in general, calculated intensities are known to be less accurate in
 610 the case of bands involving a high vibrational excitation of the bending mode ν_2 (see discussion and
 611 Figs. 7 and 8 in Ref. [19]).



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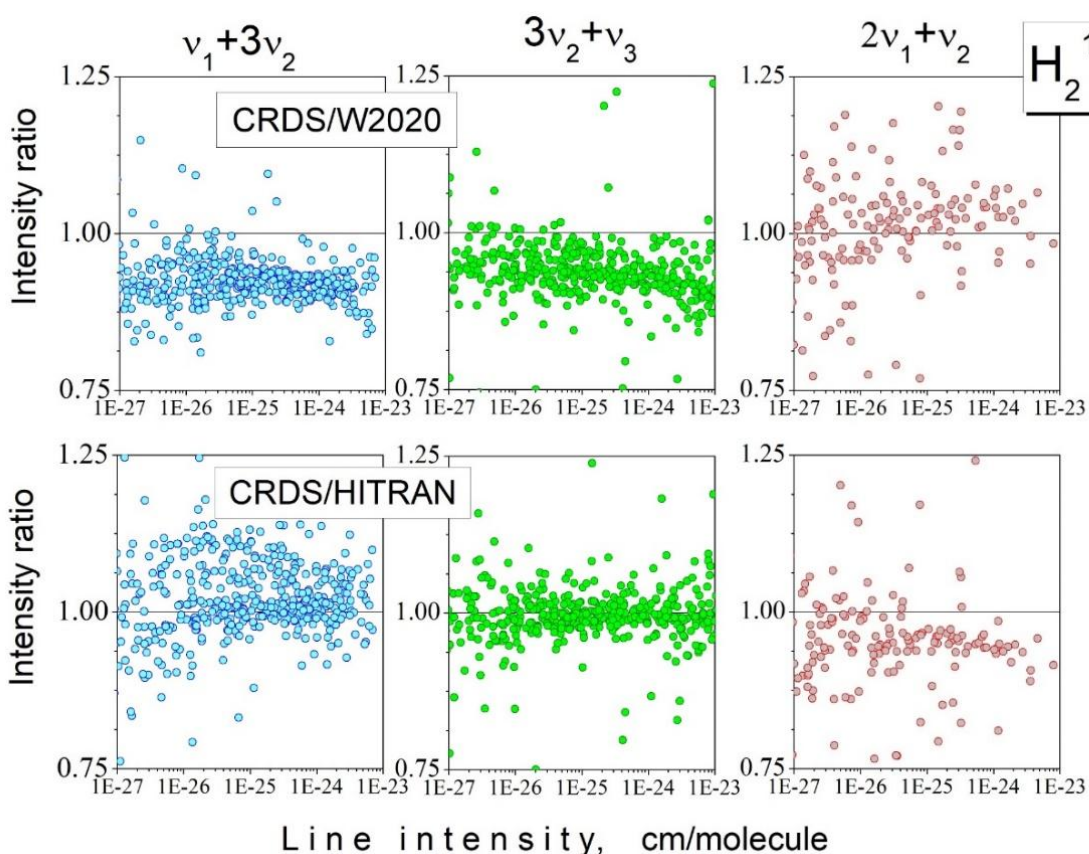
613 **Fig. 8.**

614 Ratios of the CRDS intensity values to the FTS values of Ref. [8] (FTS2014, red circles), to the CRDS values of
 615 Ref. [6] (CRDS2015, green circles), and to the HITRAN2020 and W2020 intensities (violet and black circles,
 616 respectively). The plots are limited to the transitions of the main isotopologue, H_2^{16}O , measured in the present
 617 work in the 8041 – 8633 cm^{-1} region.

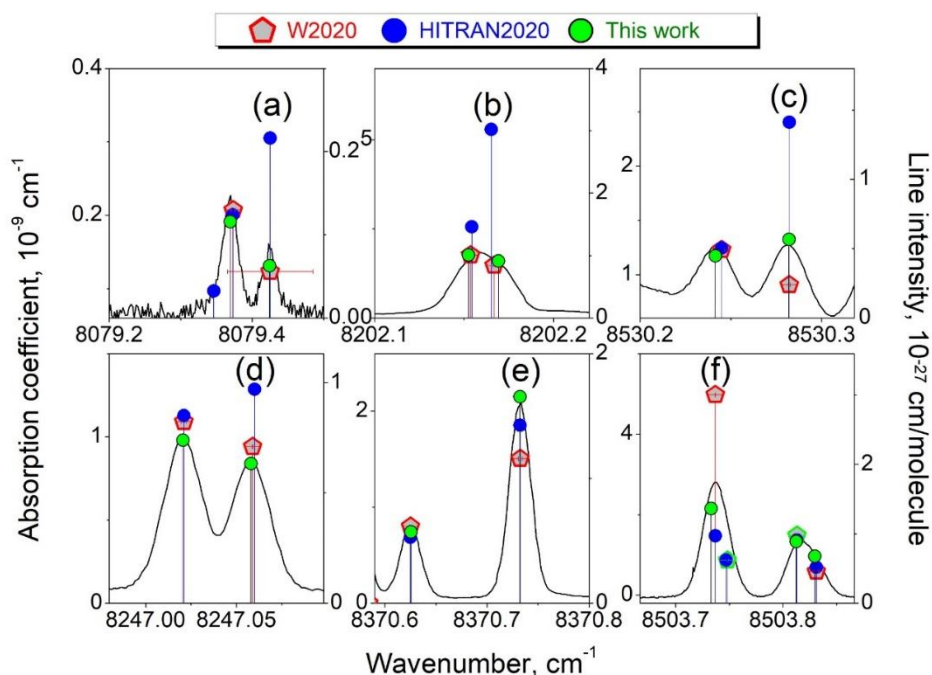
618 Six spectral intervals showing disagreement between the experimental spectrum and the
 619 HITRAN2020 and W2020 line intensities are displayed in **Fig. 10** (the rovibrational assignment of the
 620 problematic lines is given in the caption of the figure). In the first panels (a)-(d), HITRAN intensity
 621 values are clearly overestimated while W2020 intensities agree with experiment except in case (c)
 622 where the W2020 intensity of the $2\nu_1+\nu_2$ $9_{1,9} - 10_{0,10}$ transition is strongly underestimated. This
 623 situation contrasts with that shown on panel (e) where the $10_{1,10} - 11_{0,11}$ of the same $2\nu_1+\nu_2$ band
 624 shows a W2020 line intensity largely overestimated. (Note that in (c), the HITRAN and W2020
 625 intensities differ by a factor of 6).

626 The above examples illustrate the fact that it is difficult to propose empirical corrections of the
 627 calculated intensity values and that successive calculation might lead to large variation of the
 628 intensities in the case of “unstable” transitions very sensitive to small changes of the potential energy
 629 surface used for the calculations.

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631
 632 **Fig. 9.**
 633 Ratios of the CRDS intensity values to the W2020 [20] and HITRAN2020 [9] intensities for H_2^{16}O transitions of
 634 the $\nu_1+3\nu_2$, $3\nu_2+\nu_3$ and $2\nu_1+\nu_2$ bands measured in the $8041 - 8633 \text{ cm}^{-1}$ interval.
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636

637 **Fig. 10.**

638 Examples of comparison of the CRDS spectrum of water vapor and corresponding line list (green circles) to the
 639 W2020 line list [20] (grey pentagons) and to the HITRAN2020 list of natural water [9] (blue circles). The right-
 640 hand intensity scale is adjusted to correspond approximately to the peak heights.

641 The rovibrational of the problematic lines is the following: (a) $\nu_1+\nu_3$ $13_{68} - 13_{013}$, (b) $\nu_1+3\nu_2$ $12_{310} - 12_{49}$, (c)
 642 $2\nu_1+\nu_2$ $9_{19} - 10_{010}$, (d) $\nu_1+4\nu_2$ $5_{14} - 4_{23}$, (e) $3\nu_2+\nu_3$ $6_{06} - 5_{23}$, and (f) $2\nu_1+\nu_2$ $10_{110} - 11_{011}$.

643 6. Conclusion

644 The room temperature absorption spectrum of water vapor has been recorded with
 645 unprecedented sensitivity in the high energy range of the 1.25 μm atmospheric transparency window
 646 ($8040 - 8620 \text{ cm}^{-1}$). The use of a comb-referenced cavity ring-down spectrometer allowed for an
 647 absolute frequency calibration of the spectra. A list of about 5200 lines with intensity as weak as a few
 648 $10^{-30} \text{ cm/molecule}$ was constructed and rovibrationally assigned to more than 5400 transitions of the
 649 first six water isotopologues (H_2^{16}O , H_2^{18}O , H_2^{17}O , HD^{16}O , HD^{18}O and HD^{17}O). About one third of the
 650 assigned transitions are newly measured and the first experimental determination of 81 rovibrational
 651 levels of (H_2^{16}O , H_2^{18}O , H_2^{17}O , and HD^{16}O) is reported.

652 This large dataset with high position accuracy (on the order of 10^{-4} cm^{-1} for isolated lines of
 653 intermediate intensity), provides stringent validation tests for previous experimental investigations and
 654 spectroscopic databases in the region. The comparison shows an overall satisfactory agreement but a
 655 systematic shift on the order of $-8 \times 10^{-4} \text{ cm}^{-1}$ is evidenced compared to the most relevant FTS [8] and
 656 CRDS [6] studies in the region. As concerns the current version of the HITRAN database, the overall
 657 agreement is satisfactory but several issues are pointed, some of them having been already mentioned
 658 in other spectral regions from the far infrared [51] to the near infrared [32,33,52].

659 (i) Part of the HITRAN line positions lacks traceability. For instance, a large part of HITRAN
 660 positions is given with W2020 source but their positions may differ by a few 10^{-3} cm^{-1} from the

661 published W2020 position values [20]. Interestingly, we found examples where HITRAN positions
662 with W2020 source agree much better with experiment than the original W2020 position values (**Fig.**
663 **7**). In addition, for an unknown reason, old position sources [31,36,37,47] have been kept for several
664 transitions while they have been superseded by recent works, in particular the W2020 lists [20].
665 Finally, some examples discussed above concern inaccurate positions given in HITRAN with our Ref.
666 [38] as source while this reference provides a correct position value,

667 (ii) A few weak lines are missing in the HITRAN database. The strongest one belonging to the
668 main isotopologue is assigned to $2\nu_1+\nu_2$ $12_1\ 11 - 12_2\ 10$ and has an intensity larger than 2×10^{-27}
669 cm/molecule (see **Fig. 5**),

670 (iii) A series of important deviations is noted for the H_2^{17}O line positions above 8340 cm^{-1}
671 where Ref. [40] is used as main HITRAN source. The comparison to the measurements (**Fig. 6**)
672 indicates that the W2020 positions should have been preferred.

673 (iv) As concerns line intensities, most HITRAN values are calculated values by Conway et al.
674 [49]. Overall, the comparison to our measurements indicates that these more recent calculations
675 improve the POKAZATEL intensities of the W2020 list. We noticed that the observed deviations from
676 our intensity measurements do not show systematic tendency which prevents empirical band-by-band
677 corrections. As a large part of the observed deviations exceeds our experimental uncertainty, we
678 believe that experimental intensity values should be preferred for most of the lines in the region.

679 The comparison of the measurements to the W2020 line positions has confirmed that the
680 uncertainty values attached to the W2020 empirical positions and energy levels can be strongly
681 underestimated. A few examples show deviations exceeding the W2020 uncertainty by factors larger
682 than 10 (up to 350) (see **Fig. 7**). The complex procedure elaborated to determine the empirical W2020
683 energy levels uses as basis a transition database including all the experimental sources available in the
684 literature. As a result, the accuracy of the W2020 energy levels should ideally supersede the accuracy
685 of all the sources used as input data. This is not the case [32,33,51,52]. For instance, in Ref. [52], we
686 gave series of examples where the W2020 line positions differ from our previous CRDS measurements
687 [6] while these measurements, confirmed by the present spectra, were included in the W2020
688 transition database. A serious issue identified in the derivation of the W2020 energy levels is related to
689 the large datasets from emission spectra incorporated in the transition databases used to determine the
690 W2020 energy levels. These emission line positions are generally reported with a poor accuracy
691 compared to absorption data but they have a strong impact on the resulting energy values. In addition,
692 many of these emission lines were assigned to several transitions. In the present study, some errors of
693 the W2020 line positions were identified as due to the determination of the upper energy level from
694 emission lines while (more accurate) absorption data were excluded. We are convinced that the overall
695 quality of most W2020 energy levels and line positions would benefit from the exclusion of emission
696 data.

697 The W2020 energy levels may also benefit from a stricter selection of the experimental sources.
698 If we consider for instance a same spectral region studied successively by a same group, it would be
699 reasonable to exclude the first measurements from the transition database. This is for example the case
700 of the 8110 – 8340 cm^{-1} region in common between the present study and Ref. [6] (CRDS2015).
701 Besides the more accurate frequency calibration of the present spectra, we corrected a few position
702 values and assignments (see Section 3). For future derivation of the empirical energy levels, the best
703 choice would be to keep only the transition frequencies of the present work and exclude those of Ref.
704 [6]. The inclusion of the CRDS2015 line positions can only have a negative impact on the accuracy of
705 the resulting energy levels.

706 As a final conclusion, let us underline that water calculated line lists have unique advantages in
707 terms of spectral coverage and completeness. Our recent studies [32,33,51,52] and the present work
708 have demonstrated that validation tests of the resulting calculated line lists against high quality
709 experimental data are highly suitable to point deficiencies and bring hints for further improvements of
710 calculated line lists.

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