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2 **Water vapor absorption spectroscopy**
3 **and validation tests of databases in the far-infrared (50-720 cm⁻¹).**
4 **Part 1: Natural water**
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45

46 **Abstract**
47 The rotational spectrum of water vapor in natural isotopic abundance has been recorded by high
48 resolution ($\approx 0.001 \text{ cm}^{-1}$) Fourier transform spectroscopy at the AILES beam line of the SOLEIL
49 synchrotron. The room temperature absorption spectrum has been recorded between 50 and 720 cm^{-1}
50 using five pressure values up to 7 mbar and an absorption pathlength of 151.75 m. Line parameters were
51 retrieved for the five recorded spectra and then combined in a global list of 2867 water lines with line
52 intensity ranging between a few 10^{-26} and $10^{-19} \text{ cm/molecule}$. 454 of the measured lines are newly
53 observed by absorption spectroscopy. The spectral calibration based on a statistical matching with about
54 700 accurate reference line positions allows for line center determinations with an accuracy of $5 \times 10^{-5} \text{ cm}^{-1}$
55 for well isolated lines of intermediate intensity.

56 The large spectral coverage, the achieved position accuracy and sensitivity of the constructed line
57 list make it valuable for validation tests of the current spectroscopic databases. Six water isotopologues
58 (H_2^{18}O , H_2^{16}O , H_2^{17}O , HD^{18}O , HD^{16}O , and HD^{17}O) were found to contribute to the spectrum. The line
59 position comparison to the recent HITRAN2020 spectroscopic database and to the W2020 line lists of
60 H_2^{16}O , H_2^{17}O and H_2^{18}O , [Furtenbacher et al. J. Phys. Chem. Ref. Data 49 (2020) 043103;
61 <https://doi.org/10.1063/5.0030680>] shows an overall very good agreement. Nevertheless, a number of
62 significant deviations are observed. Part of them has an amplitude largely exceeding the W2020 claimed
63 error bars. On the basis of the experimental data at disposal for the main isotopologue (1310 transitions),
64 the best agreement is achieved with the positions calculated using the effective Bending–Rotation
65 Hamiltonian [Coudert et al. J Mol Spectrosc 2014;303:36-41. <https://doi.org/10.1016/j.jms.2014.07.003>].

66 **1. Introduction**

67 The present work is devoted to an experimental study of the high resolution absorption spectrum of
68 natural water vapor in the far infrared region (FIR) between 50 and 720 cm^{-1} . It follows a recent study of
69 the rotational spectrum of water vapor highly enriched in ^{18}O in the same region [1]. In fact, the ^{18}O
70 enriched spectrum analyzed in Ref. [1] was a “side-product” of a large measurement campaign performed
71 in 2018 at the AILES beam line of the SOLEIL synchrotron and dedicated to the characterization of the
72 water vapor FIR absorption continuum by Fourier transform spectroscopy (FTS) [2,3]. It turns out that,
73 while we believed that the rotational spectrum involving the lowest vibrational states of water vapor was
74 well characterized, some of the recorded SOLEIL high resolution spectra of ^{18}O water vapor allowed for a
75 substantial extension of the previous knowledge in the region, in addition to provide valuable tests of
76 existing databases. This is mainly the result of the unique characteristics of the AILES beamline of the
77 SOLEIL synchrotron light source in the “difficult” FIR spectral region where the performances of
78 laboratory spectrometers are usually not optimum (see the review of various experimental approaches for
79 FIR absorption spectroscopy in the introduction of Ref. [1]). The combination of the synchrotron radiation
80 with a long path absorption cell allows for broad-band high sensitivity FIR recordings with a spectral
81 resolution of about to 0.001 cm^{-1} . Note that in the case of the H_2^{18}O transitions assigned in [1], the weakest
82 measured lines have intensity on the order of $10^{-25} \text{ cm/molecule}$ which corresponds to a gain of 4 orders of
83 magnitude of the detectivity threshold compared to previous H_2^{18}O absorption measurements.

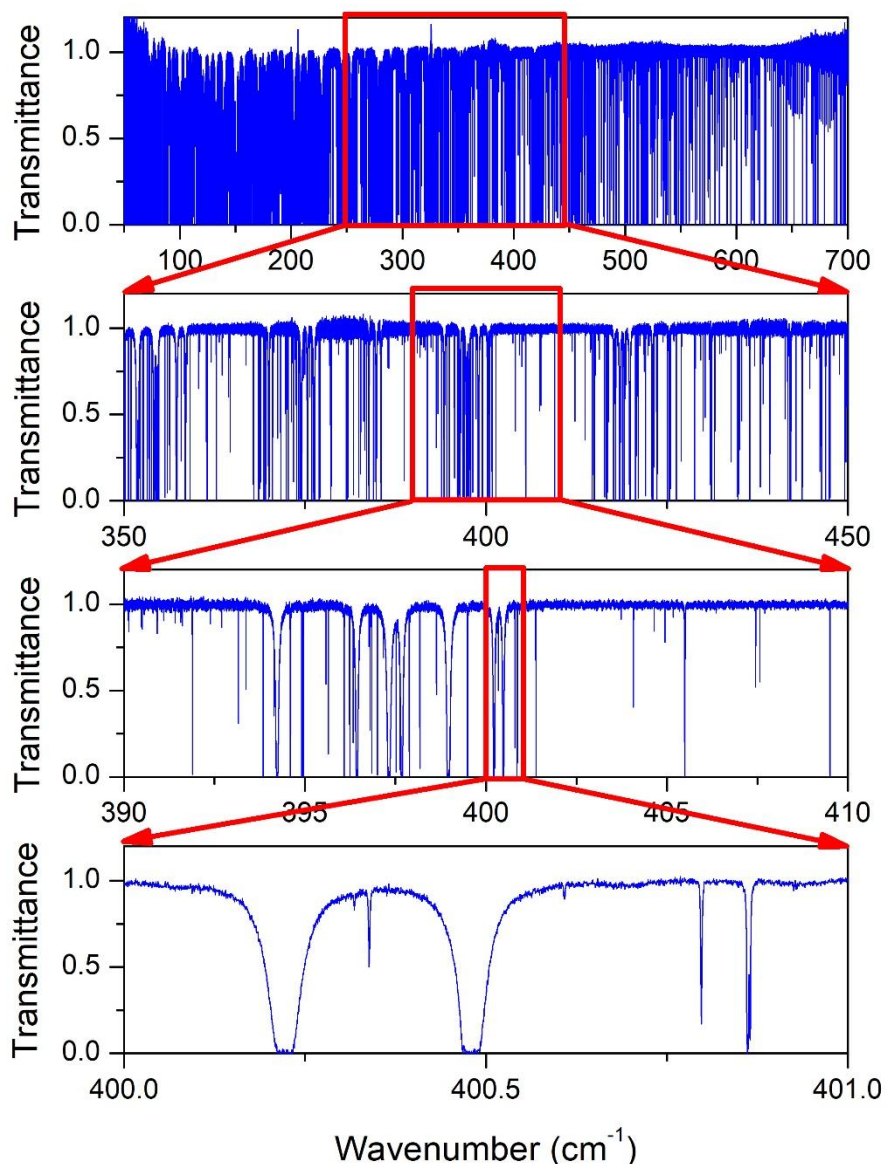
84 The importance of the FIR region in the Earth’s radiation budget is a major motivation of the Far-
85 infrared-Outgoing-Radiation Understanding and Monitoring (FORUM) mission of European Space
86 Agency (<https://www.forum-ee9.eu/>). One of the identified goals of this mission is to “fill the
87 observational gap across the far-infrared (from 100 to 667 cm^{-1}), never before sounded in its entirety from
88 space”. This requires an accurate knowledge of the water spectroscopy in the region and motivated us to
89 apply for beam time at SOLEIL synchrotron for a new measurement campaign dedicated to the high
90 resolution spectroscopy of various water isotopologues (natural, ^{17}O and D enriched) using the same
91 experimental setup as for the ^{18}O enriched water recordings. The present contribution dedicated to the
92 analysis and discussion of the natural water spectra recorded at five pressures up to 7 mbar, is the first one
93 of the series.

94 The paper is organized as follows. In Section 2, we recall the experimental details including the
95 spectrum acquisition, line list construction and spectra calibration. The main results are presented in
96 Section 3 which presents an overview of the transitions contributing to the spectra together with a line
97 position comparison with literature. In particular, we will consider (i) the HITRAN2020 spectroscopic
98 database [4], (ii) the W2020 line lists of H_2^{16}O , H_2^{18}O and H_2^{17}O with line positions computed from

99 empirically determined energy levels [5] and, (iii) the calculations by Coudert et al. for the H₂¹⁶O main
 100 isotopologue using an effective Bending–Rotation Hamiltonian [6].

101 **2. Experiment**

102 *2.1. Spectra acquisition*



103

104 **Fig. 1**

105 Successive zooms of the FTS spectrum #3 of natural water vapor recorded at SOLEIL synchrotron at
 106 room temperature ($P= 0.91$ mbar) between 50 and 720 cm⁻¹.

107 The FTS spectra were acquired on the AILES beam line of SOLEIL synchrotron facility operated in
 108 the 500 mA multibunch mode, in September 2021. A Bruker 125 interferometer with a 6 μm mylar-
 109 composite beam splitter and a 4 K cooled Si bolometer detector were used for the recordings. The

110 absorption cell is a multipass cell in White-type configuration. The total absorption path length was set to
 111 151.75±1.5 m corresponding to 60 passes between mirrors separated by 2.52 m and about 0.5 m of space
 112 between the 50 µm thick polypropylene films windows. Five spectra were recorded for different pressure
 113 values up to 7 mbar, measured by a capacitance gauge (Pfeiffer 10 mbar full range with corresponding
 114 accuracy of 0.01 mbar). The de-ionized water used for the recordings was frozen and liquefied several
 115 times before injection in the cell in order to minimize the presence of gas impurities. **Table 1** summarizes
 116 the experimental conditions and the sequence of the recordings.

117 **Table 1**

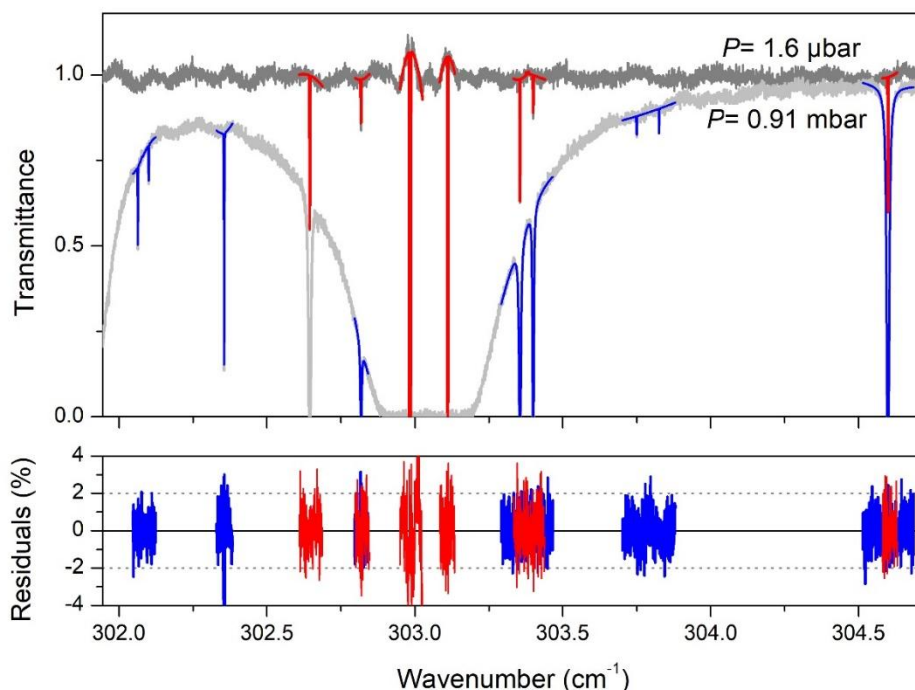
118 Experimental conditions of the five FTS spectra of natural water under analysis. The temperature
 119 was 295.5 K.

	Sample	Pressure	Resolution, cm ⁻¹	Nb of scans
#1	Empty cell	≈ 1.7 µbar	0.001	320
#2	Baseline	Pumping on the cell	0.05	200
	Sample	≈ 0.080 mbar	0.001	400
#3	Baseline	Pumping on the cell	0.05	200
	Sample	≈ 0.91 mbar	0.001	480
#4	Baseline	Pumping on the cell	0.05	200
	Sample	≈ 7 mbar	0.002	280
#5	Empty cell	≈ 0.15 µbar	0.001	220

120
 121 The first and last spectra were recorded at very low pressure, pumping on the cell in order to
 122 measure the strongest lines (intensity up to 10⁻¹⁸ cm/molecule) and to check the stability of the frequency
 123 scale (see below). The other pressure values were set to about 0.085, 0.91 and 7.0 mbar. Except for the 7
 124 mbar spectrum for which the pressure broadening allows for using a spectral resolution of 0.002 cm⁻¹, the
 125 other spectra were recorded at the maximum spectral resolution of 0.00102 cm⁻¹ (defined as 0.9/MOPD
 126 where MOPD= 882 cm is the maximum optical path difference). No apodization of the interferogram was
 127 used (boxcar option of the Bruker software). The number of co-added spectra ranges between 200 and 480
 128 (200 spectra corresponds to about 10 hours' acquisition at 0.001 cm⁻¹ spectral resolution or 5 hours at
 129 0.002 cm⁻¹ resolution). The baseline fluctuations were corrected by division by a lower resolution
 130 (0.05 cm⁻¹) spectrum acquired prior to each high resolution recording. The temperature of 295.5(3) K was
 131 monitored by a pair of platinum sensors mounted on the cell external surface. An overview of the
 132 spectrum recorded at 0.91 mbar is displayed on **Fig. 1**, which includes successive zooms. The absorption
 133 coefficient was determined as $\alpha_{total} = 1/L \ln(I_0(\nu)/I(\nu))$, where $L = 151.75$ m, and $I(\nu)$ and $I_0(\nu)$ correspond
 134 to the spectrum with the cell filled with water vapor and evacuated, respectively.

135 The observed line profiles result from different contributions. At 1 mbar, the pressure broadening
 136 (about 4×10⁻⁴ cm⁻¹ HWHM [4]) is equivalent to the width of the apparatus function (about 3.5×10⁻⁴ cm⁻¹
 137 HWHM) while the Doppler broadening (proportional to the transition frequency) is on the order of

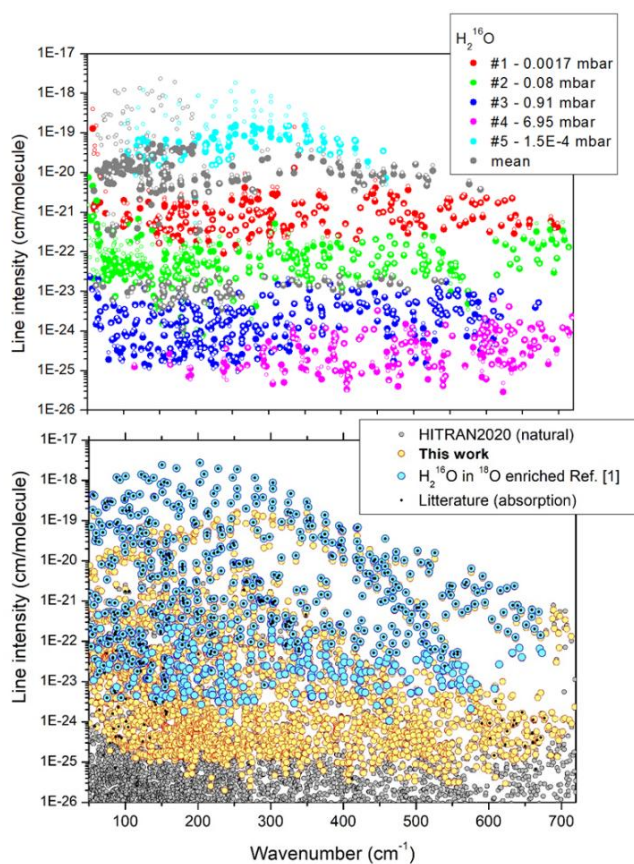
138 $1.5 \times 10^{-4} \text{ cm}^{-1}$ HWHM near 100 cm^{-1} . The present study being mainly focused on line positions, each of
 139 the five transmittance spectra was fitted independently assuming the standard Voigt line profile as line
 140 shape (with adjusted Gaussian and Lorentzian widths) and no particular care was taken for the treatment
 141 of the apparatus function. The line parameters retrieval was performed using a homemade multiline fitting
 142 program in LabVIEW and C++. The HITRAN2020 line list was taken as starting point of the fit. For each
 143 spectrum, we selected a ten of isolated lines of intermediate intensity and adjusted their position, area,
 144 Gaussian and Lorentzian widths. The obtained Gaussian widths are larger than the Doppler broadening as
 145 they include an important contribution of the apparatus function. The average value of the fitted Gaussian
 146 widths was adopted as default value for all the fitted lines of a given spectrum. **Fig. 2** illustrates the
 147 adopted procedure in a small spectral interval showing a very strong doublet (intensity larger than 10^{-19}
 148 $\text{cm}^2/\text{molecule}$) near 303 cm^{-1} for the spectra #1 (very low pressure) and #3 (0.91 mbar). During the fit of
 149 the 0.91 mbar spectrum, the doublet was omitted and line parameters of narrow lines were obtained from a
 150 local fit, even when these lines were located on the wing of the strong doublet. The line center of the two
 151 components of the doublet could be determined from a fit of the very low pressure spectrum (#1). The
 152 (obs. – calc.) residuals included in **Fig. 2** are at the noise level ($\sim 1\%$). This value corresponds to a noise
 153 equivalent absorption on the order of $7 \times 10^{-7} \text{ cm}^{-1}$ and a detectivity threshold of about $10^{-25} \text{ cm}^2/\text{molecule}$
 154 for the line intensities measured in the 0.91 mbar spectrum.



155
 156 **Fig. 2**
 157 Line parameter retrieval from the FTS spectra of water vapor near 303 cm^{-1} . The line profile fit was
 158 performed in narrow spectral intervals around the lines which are not too saturated.

159 *Upper panel:* Recorded spectra #1 and #3 at ~ 1.6 μbar and 0.91 mbar, respectively, (gray and light gray,
 160 respectively) with corresponding best fit spectra (red and blue, respectively).
 161 *Lower panel:* Corresponding (exp. – fit) residuals in %.

162 Overall, line parameters of 804, 1778, 1987, 1367 and 306 absorption features were retrieved for
 163 the spectra #1 to #5, respectively. In order to obtain a unique global line list, for each line, we selected the
 164 pressure condition of the best parameter determination of the considered line (intermediate transmittance
 165 value, limited overlapping with nearby lines) and kept the corresponding values for the global list. For a
 166 large fraction of lines, two spectra could be selected and the average line position and line intensity were
 167 adopted for the global list. In the list provided as Supplementary Material, the spectrum number (1 to 5,
 168 see **Table 1**) is attached to each line indicating the spectrum or spectra used for the retrieval. On the
 169 overview of the global list presented in the upper panel of **Fig. 3**, different colors are used according to the
 170 source of the line parameters.



171
 172 **Fig. 3.**
 173 Overview of different line lists for water vapor between 40 and 720 cm^{-1} .
 174 *Upper panel:* global line list constructed in this work from five spectra of natural water recorded at SOLEIL
 175 synchrotron at different pressures. Different colors are used for the spectrum chosen as source of the line parameters.
 176 Grey symbols mark the lines for which the position and intensity correspond to values averaged from two spectra.
 177 Small open circles correspond to the HITRAN list.
 178 *Lower panel:* comparison of our global list (yellow dots) to (i) previous measurements available in the literature by
 179 absorption spectroscopy [7-20] (black dots), (ii) H_2^{18}O transitions identified in the spectrum of ^{18}O enriched water

180 recorded at SOLEIL synchrotron in [1] (blue dots), (iii) present recordings for natural water (yellow dots) and (iv)
181 the HITRAN2020 line list [4] (grey dots).

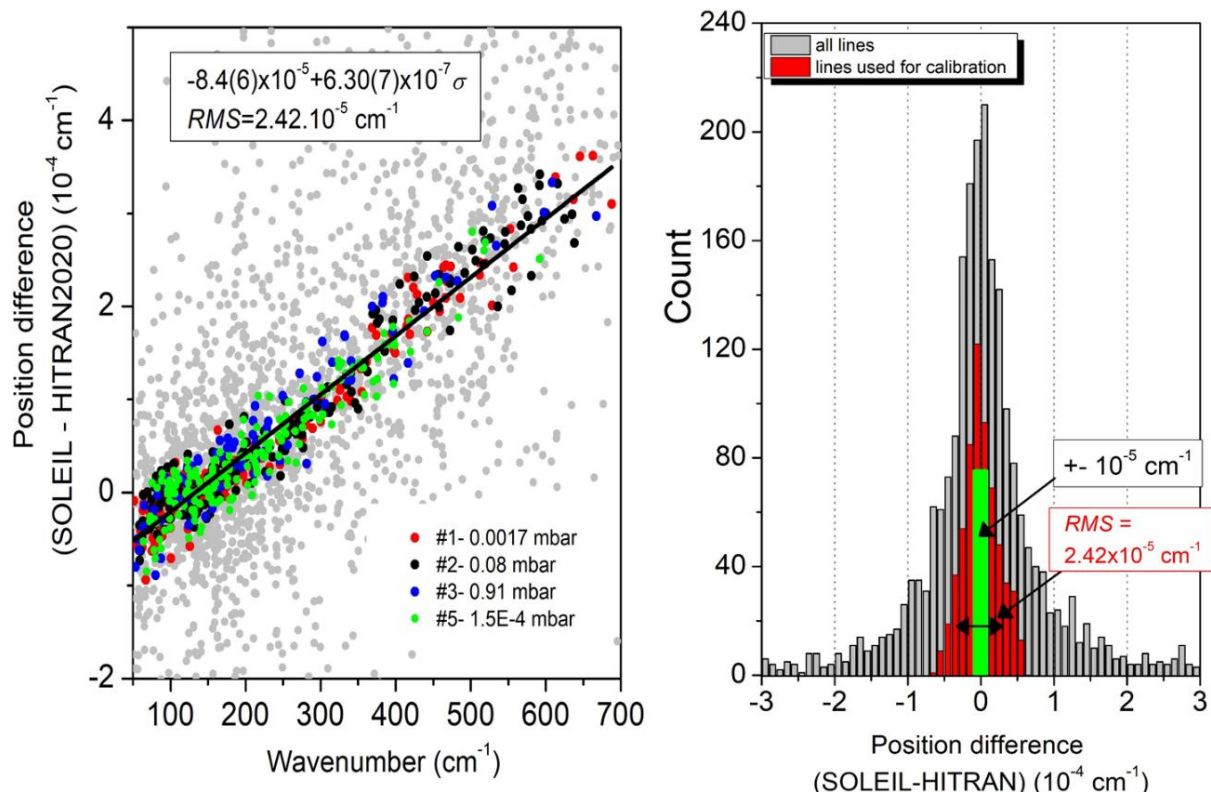
182 During the data treatment, a number of lines were found in addition to those included in the
183 HITRAN list of water vapor. They were identified as due to three impurity species: CO₂, NH₃ and HF.
184 The CO₂ lines are located in the high energy part of the recorded region above 640 cm⁻¹ and belong to the
185 ν₂ bending band. The relative abundance of CO₂ was found to decrease sharply (from 5000 to 5 ppm) with
186 the water vapor pressure indicating that it is due to a small leak or desorption. The HF and ammonia lines
187 are rotational lines. About six HF lines are observed between 100 and 350 cm⁻¹ while ammonia lines are
188 observed below 200 cm⁻¹. Ammonia with a relative concentration of a few ppm is believed to be present
189 as an impurity in the used water sample. HF is probably due to degassing from the O-ring seals of the cell.

190 After removal of the impurity lines and combination of the five datasets, the obtained global list
191 includes 2867 water lines with intensities above 2×10⁻²⁶ cm/molecule (see overview in **Fig. 3**). Note that
192 in the case of the spectra #1 and #5, the pressure was too small to be measured with the used pressure
193 gauge. Intensity comparison to the HITRAN values allowed to estimate the corresponding pressure values
194 to about 1.7 μbar and 0.15 μbar, respectively. These pressure values were used in the calculation of the
195 line intensities derived from these two spectra. As a result of the large pressure range of the recordings
196 (from 0.15 μbar to 7 mbar), the obtained experimental list includes line intensities spanning six orders of
197 magnitude.

198 2.2. Frequency calibration

199 Before combining the five line lists into a single global list, we checked that no significant variation
200 of the frequency calibration of the different spectra was observable: the position differences compared to
201 HITRAN were found independent on the spectrum (see left panel of **Fig. 4**). The absolute frequency
202 calibration was performed considering line positions provided in the HITRAN database with an
203 uncertainty better than 10⁻⁵ cm⁻¹. A total of about 700 isolated lines with good signal-to-noise ratio were
204 selected in the different recorded spectra and matched to the HITRAN reference lines. Note that the 7
205 mbar spectrum for which pressure shifts on the line positions might be significant was excluded.
206 According to Refs. [21-27], the self-pressure shifts for rotational lines are between -0.058 and +0.045 cm⁻¹
207 /atm. So, it means that at the maximum pressure of 7 mbar in our measurements, the line shifts can reach
208 ±4×10⁻⁴ cm⁻¹, a value larger than the precision of the line center determination in the 7 mbar spectrum.
209 The differences between the experimental line centers and the HITRAN values were globally linearly
210 fitted. Excluding a ten of outliers, an *rms* deviation of 2.42×10⁻⁵ cm⁻¹ was obtained for the linear fit, thus
211 larger than the accuracy of the position of the reference lines. The obtained empirical correction of the
212 frequencies (+8.4(6)×10⁻⁵-6.30(7)×10⁻⁷σ, where σ is the measured wavenumber in cm⁻¹) was applied to
213 all the values of the global list. A value of 5×10⁻⁵ cm⁻¹ seems to be a reasonable estimate for the resulting

214 uncertainty on the experimental position values of the “good” lines (isolated unsaturated lines measured in
 215 the low pressure spectra). In the global line list provided as Supplementary Material, the fit error on the
 216 line position determination is included. For a significant fraction of the lines, the fit uncertainty (thus
 217 excluding the frequency calibration error) was found smaller than $5 \times 10^{-5} \text{ cm}^{-1}$ and is thus believed to
 218 largely underestimate the real uncertainty on the line position. For all these lines, we replaced the fit
 219 uncertainty by a value of $5 \times 10^{-5} \text{ cm}^{-1}$. Note that the uncertainty of the weakest or highly blended lines can
 220 reach a value of $1 \times 10^{-3} \text{ cm}^{-1}$ in the worst cases.



221
 222 **Fig. 4**
 223 Frequency calibration of the FTS spectra of natural water recorded at SOLEIL synchrotron.
 224 *Left panel:* The colored symbols correspond to the differences between the line centers retrieved from the different
 225 recorded spectra and reference line positions provided with an uncertainty better than 10^{-5} cm^{-1} in the HITRAN
 226 database [4]. The 7 mbar spectrum for which pressure shifts on the line positions might be significant is excluded.
 227 The global dataset was fitted by a linear function providing the frequency correction to be applied to the
 228 measurements. Grey symbols correspond to the comparison to all the HITRAN line positions (*rms* deviation of
 229 $2.42 \times 10^{-5} \text{ cm}^{-1}$),
 230 *Right panel:* Histograms of the (meas. – HITRAN) position differences for the lines used for the frequency
 231 calibration (red) and for the whole set of measurements. The green bars correspond to the HITRAN uncertainty of
 232 the used reference lines ($\pm 10^{-5} \text{ cm}^{-1}$).

233 The histogram of the position differences is presented in **Fig. 4** for the lines used for the frequency
 234 calibration and for the whole set of measurements. A significant fraction of the measured lines shows
 235 position differences larger than our experimental error bar. In the following, we will examine these lines
 236 in order to determine the reasons for these discrepancies.

237 As concerns line intensities, we do not claim for a high accuracy of the reported values. The limited
 238 number of points describing the line profile and the impact of the apparatus function which was roughly
 239 taken into account in the line parameter retrieval limit the accuracy of the retrieved values. The fit
 240 uncertainty included in the global line list is only indicative. Comparisons to HITRAN intensity values
 241 indicate that, excluding the two lowest pressure spectra (#1 and #5), most of the line intensities agree with
 242 HITRAN values within $\pm 10\%$. The comparison of the fitted intensities to HITRAN values shows
 243 deviations largely exceeding the fit uncertainty. Relying on HITRAN values, we conclude that the fit error
 244 of our experimental intensities is probably underestimated for a small fraction of the measurements. Our
 245 accuracy was nevertheless sufficient to evidence a clear HDO enrichment in the spectra, probably due to a
 246 previous contamination by deuterated species adsorbed on the cell walls. Compared to the natural
 247 abundance, the enrichment was larger by about a factor of two for the first recorded spectra and then, as a
 248 consequence of the successive fillings and evacuations of the cell, gradually decreased to reach practically
 249 the natural value for the last recording. In the case of the most intense lines which were retrieved from
 250 spectra #1 and #5 (intensity up to 10^{-18} cm/molecule), saturation effects are considerable and the fitted
 251 values of the intensities are strongly underestimated by a factor up to 10 in the worst cases (see **Fig. 3**).

252 3. Analysis and comparison with literature

253 The HITRAN2020 rovibrational assignments of practically all observed water transitions have been
 254 validated and transferred to our list. The HITRAN rovibrational assignment of five high J transitions in
 255 the pure band of H_2^{17}O (from Lodi and Tennyson [28]) is incomplete in the HITRAN list [4]. The
 256 complete assignment is provided in our list. Overall, the 2867 measured water lines were assigned to 3001
 257 transitions of six isotopologues (H_2^{16}O , H_2^{18}O , H_2^{17}O , HD^{16}O , HD^{18}O , and HD^{17}O). **Table 2** presents
 258 some global characteristics of the assigned transitions, including the maximum values of the J and K_a
 259 rotation numbers and the numbers of transitions firstly observed compared to previous absorption studies
 260 available in the literature. Overall 454 transitions are newly observed by absorption. The list of these
 261 newly observed lines is provided as a second Supplementary Material. Part of these lines (306) was
 262 previously observed by emission spectroscopy (mostly in [19] and [29] – see below). The line position
 263 comparison to the most relevant emission study is included the Supplementary Material.

264 **Table 2**

265 Statistics of the rovibrational assignments of the five spectra of natural water recorded at SOLEIL at
 266 various pressures up to 7 mbar.

Molecule	NT^a	NT_{new}^b	J	K_a	Range, cm^{-1}
H_2^{16}O	1310	96 (385)	22	14	51.43 – 718.43
H_2^{18}O	564	3 (3)	18	12	53.57 – 702.59
H_2^{17}O	407	3 (3)	17	10	53.51 – 694.38
HD^{16}O	674	46 (63)	19	12	50.27 – 591.88
HD^{18}O	42		10	7	78.51 – 310.10
HD^{17}O	4		6	4	168.17 – 255.19

Total	3001	148 (454)	22	14	50.27 – 718.43
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267
 268 Notes
 269 ^a Number of assigned transitions
 270 ^b Number of newly observed transitions. The first number considers only previous studies by absorption. The number
 271 between parenthesis considers all previous studies (absorption and emission).

272 3.1. Overview of previous experimental studies in the region

273 The review of previous works on the rotation and vibration-rotation transitions of water in our
 274 region includes studies by absorption [7-20] and by emission spectroscopy in flames or discharges
 275 [6,19,29-34]. Overall, 686 H₂¹⁶O transitions were recorded in absorption [7-20] for the five lowest states –
 276 (000), (010), (020), (001), and (100) – up to maximum value of the rotation number $J_{\max} = 17$. About 240
 277 transitions were newly measured by absorption in Ref. [1], leaving 375 new observations for the present
 278 study. More than 6000 transitions involving 14 vibration states were assigned in emission spectra
 279 [6,19,29-33] in our region. The maximum value of the rotation number of the ground state (000) is
 280 $J_{\max} = 41$ [33]. The overall position accuracy of emission studies is generally worse than the present
 281 accuracy. The most precise set of line positions reported by emission spectroscopy [6,19,29] have an
 282 accuracy $4.0 \times 10^{-4} \text{ cm}^{-1}$ at best.

283 In the spectrum of water vapor highly enriched in ¹⁸O recorded at SOLEIL synchrotron with the
 284 same setup as the one used for the present recordings, 37 additional H₂¹⁶O transitions up to $J_{\max} = 19$ were
 285 reported [1]. Compared to this study, the average value of the position differences is $3.44 \times 10^{-5} \text{ cm}^{-1}$ with
 286 an *rms* deviation of $13.37 \times 10^{-5} \text{ cm}^{-1}$ for 604 transitions in common in the two studies. Taken into account
 287 that the H₂¹⁶O relative abundance was only 5% in the spectrum analyzed in Ref. [1], the achieved
 288 agreement is very satisfactory and illustrates the consistency of the independent frequency calibration of
 289 the two spectra.

290 The observations relative to the H₂¹⁸O minor isotopologue are more limited. Overall, 525 (mainly
 291 pure rotation) transitions were reported in seven absorption [7,9,13,34-37] and one emission [38] studies.
 292 Only six rotation transitions for the (010), (020) and (100) states were measured in these previous studies
 293 [9,34]. The most extended H₂¹⁸O line list (more than 730 transitions) was obtained from the SOLEIL
 294 spectrum analyzed in Ref. [1]. It includes more than 300 transitions of the (010) – (010) and (020) – (020)
 295 bands. The comparison of our H₂¹⁸O line positions with the observations shows very good agreement to
 296 highly precise data of Matsushima et al. [37]. The *rms* deviation is $6.19 \times 10^{-5} \text{ cm}^{-1}$ for 98 transitions
 297 observed in both measurements.

298 For H₂¹⁷O, 362 pure rotation transitions were reported by absorption in Refs. [7,13,35-37]. The list
 299 of H₂¹⁷O rotation transitions was extended up to 685 in Ref. [1], including 114 transitions of the (010) –
 300 (010) band. Now, we are reporting 407 transitions (see **Table 2**). A very good agreement is obtained with
 301 the highly precise positions of Matsushima et al. [37]. The *rms* deviation is $4.02 \times 10^{-5} \text{ cm}^{-1}$ for 103

302 transitions observed in both measurements. The comparison with our previous measurement [1] gives an
 303 *rms* deviation of $2.93 \times 10^{-4} \text{ cm}^{-1}$ for 345 transitions with position discrepancies greater than 0.001 cm^{-1} for
 304 weak component of unresolved pure rotational doublet $17_{117} - 16_{016}$ at 319.6949 cm^{-1} and strongly
 305 blended components of the doublet $6_{61} - 5_{50}$ and $6_{60} - 5_{51}$ at 301.142 cm^{-1} .

306 In the case of HD¹⁶O, 510 absorption and 1422 emission transitions were reported in Refs.
 307 [7,9,10,39,40]. In addition, 133 previously unobserved transitions were reported in Ref. [1]. 674 HD¹⁶O
 308 transitions were measured in the present work, 63 of which being firstly detected in absorption. The best
 309 agreement of the line position comparison is for Refs. [1,9,10] with corresponding *rms* values are 1.49×10^{-4} ,
 310 2.78×10^{-4} and $1.74 \times 10^{-4} \text{ cm}^{-1}$ for 488, 204 and 267 transitions respectively. The comparison to the less
 311 accurate data of Refs. [7,40] leads to *rms* values of 3.22×10^{-3} and $3.66 \times 10^{-3} \text{ cm}^{-1}$ for 60 and 55 transitions,
 312 respectively. The maximum deviation reaches a value of 0.0138 cm^{-1} for the absorption study of Ref. [7]
 313 and 0.0169 cm^{-1} for the emission study of Ref. [40].

314 For HD¹⁸O, the first measurements were due to Johns [9] who reported 148 pure rotation transitions
 315 between 78 and 220 cm^{-1} . In our recent study [1], we extended the observations to 1126 transitions in the
 316 range $44.86 - 645.74 \text{ cm}^{-1}$. All 42 transitions reported in the present work were observed in Ref. [1]. Note
 317 that some of the present line positions are nevertheless believed to be more precise because the
 318 corresponding lines were saturated in Ref. [1]. The line position comparison with data of Johns [9] gives
 319 the *rms* deviation of $3.66 \times 10^{-4} \text{ cm}^{-1}$ for 26 transitions.

320 3.2. Validation tests of the HITRAN2020, W2020 and 14CoMaPi line positions

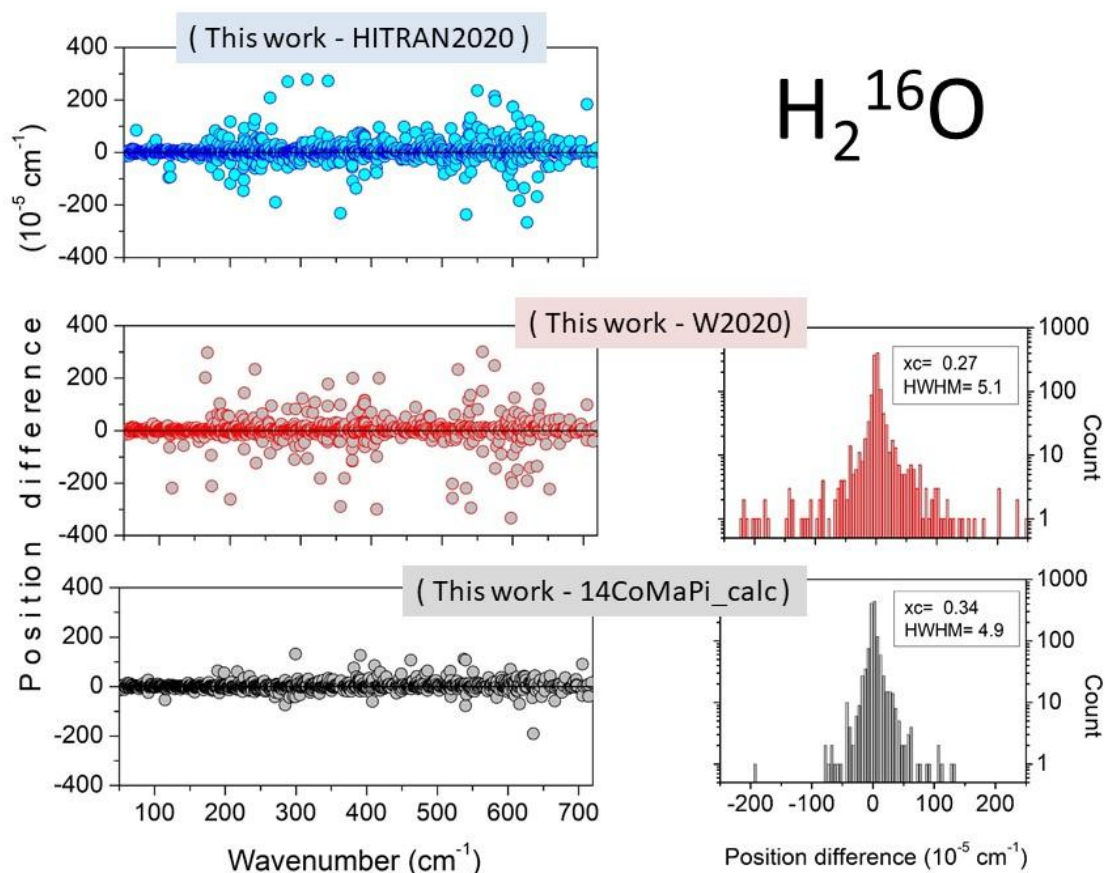
321 Let us now compare our results to the most relevant spectroscopic databases in our region.

322 Following the approach developed by a task group (TG) of the International Union of Pure and
 323 Applied Chemistry (IUPAC-TG) [41-44], improved sets of empirical energy levels have been recently
 324 released for H₂¹⁶O, H₂¹⁸O and H₂¹⁷O. The W2020 empirical energy levels of Ref. [5] were derived from an
 325 exhaustive collection and review of measured transitions in all spectral regions [5,45]. The procedure and
 326 code xMARVEL [46,47] were applied to the constructed catalog of measured absorption and emission
 327 line positions. In particular, all the above reviewed sources of measurements in the rotational region of
 328 interest were incorporated in the transition datasets. In the present work, no new energy levels could be
 329 determined from the recorded spectra *i.e.* all the energy levels involved in the transitions presently
 330 measured have been determined empirically (tag “M” in the W2020 lists [5]). An important advantage of
 331 the Ritz principle which is the basis of the MARVEL procedure is that it allows to obtain line positions
 332 with experimental accuracy even for transitions which were not previously measured. Direct validation
 333 tests when experimental spectra become available are nevertheless suitable (see *e.g.* Refs. [48-50]). The
 334 transitions newly observed in the present SOLEIL spectra are particularly valuable in that context. Let us
 335 underline that the rotational region under analysis is of importance as a large fraction of the involved

336 energy levels are lower state of transitions located in the whole frequency range of the water absorption
 337 spectrum. Errors or inaccuracies evidenced in the rotational region may impact line positions calculated
 338 from empirical energy values in the entire water spectrum.

339 As mentioned above, according to the HITRAN2020 source list, most of the HITRAN position
 340 values should coincide to the W2020 empirical positions of Ref. [5]. In fact, as already discussed in Ref.
 341 [50] and illustrated below, this is not the case. The origin of this situation remains unclear and might
 342 possibly lead to an update of the HITRAN2020 list. Thus separated comparison has to be performed to the
 343 HITRAN and W2020 line lists.

344 The bending-rotation Hamiltonian developed by Coudert et al. [6] (14CoMiPa, hereafter) provides
 345 an alternative source of calculated line positions in our region for the main isotopologue. Due to the
 346 failure of the approach based on a rotational Hamiltonian of a semi-rigid molecule in the case of water, a
 347 bending rotation Hamiltonian has been developed to account for the H_2^{16}O spectrum up to the second triad
 348 and to $J = 30$ [6]. The effective Hamiltonian parameters were determined from a weighted least-squares
 349 fitting of a large set of 24,461 literature data including rotational energy levels, microwave, far infrared,
 350 and infrared measured transition frequencies.



351
 352 **Fig. 5**
 353 Position comparison of the H_2^{16}O lines in the 50-720 cm^{-1} range.

354 *Left panels:* Differences between the experimental values presently determined from SOLEIL spectra to the
 355 HITRAN2020 data, to the W2020 empirical values and the values calculated using a rotation-bending Hamiltonian
 356 [6] (14CoMaPi),
 357 *Right panels:* Histograms of the deviations between the experiment and the W2020 and 14CoMaPi positions. The
 358 center (x_c) and HWHM obtained from a Gaussian fit of the histograms are given on the plot (in 10^{-5} cm^{-1} units).

359 We present in **Fig. 5** an overview comparison of our line positions of the main isotopologue to the
 360 values included in the HITRAN database, to the W2020 values and to the calculated values of Coudert et
 361 al. [6]. The corresponding comparison table is provided as a third Supplementary Material. **Fig. 5**
 362 illustrates that the overall agreement between the experiment and the three databases is excellent. For
 363 instance, the histograms of the W2020 and 14CoMaPi deviations from experiment show a similar
 364 Gaussian distribution centered at about of $3 \times 10^{-6} \text{ cm}^{-1}$ for 1310 transitions with a HWHM of $5 \times 10^{-5} \text{ cm}^{-1}$,
 365 corresponding to our claimed position uncertainty of the “good” lines. The most noticeable differences
 366 between the three comparisons is the presence of some relatively large deviations for the W2020 and
 367 HITRAN2020 data while these “outliers” are mostly absent for 14CoMiPa. At this point, it is worth
 368 mentioning that the comparison applies to the same set of 1310 transitions as all our H_2^{16}O observations
 369 have a counterpart in the three databases (except for a couple of doublets missing in the HITRAN database
 370 – see below).

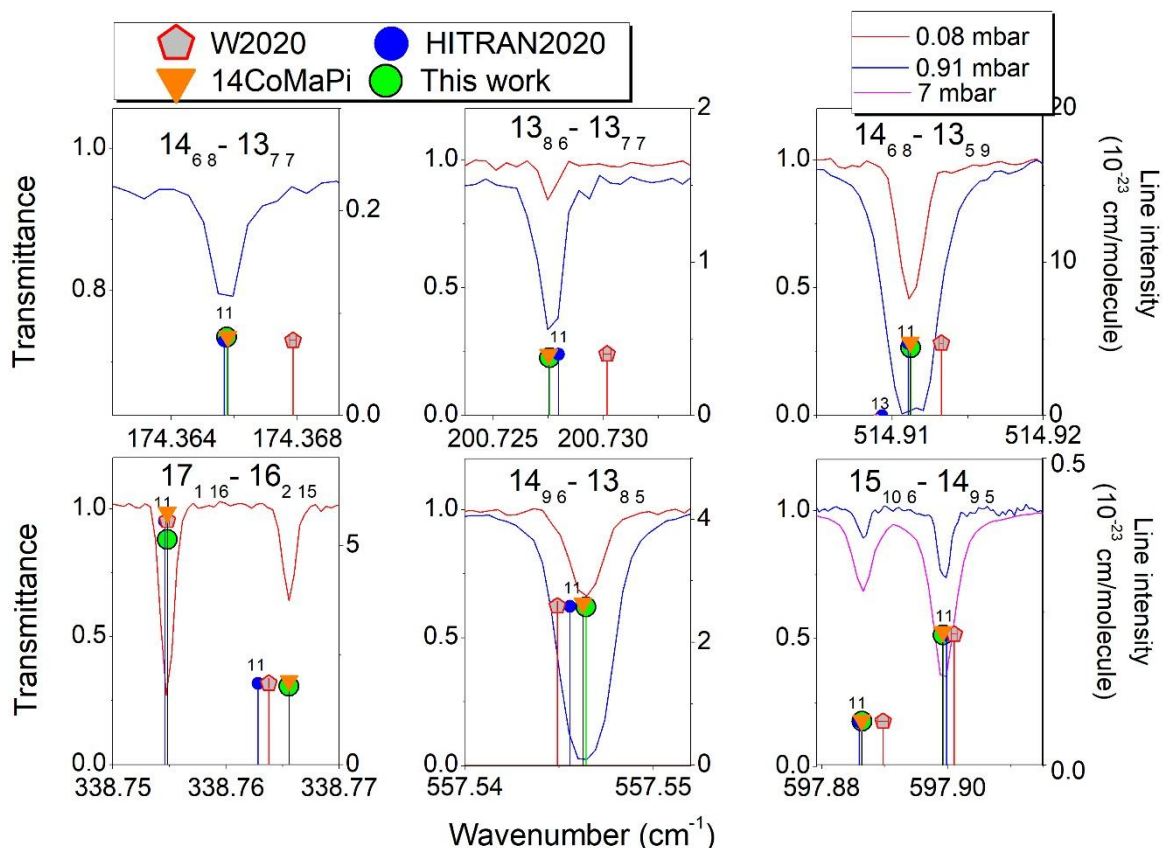
371 The direct comparison to the spectra presented in **Figs. 6** and **7** gives insights on the significance of
 372 these outliers. **Fig. 6** shows six examples for which clear deviations are observed for the W2020 line
 373 positions of Ref. [5] while HITRAN position (given with W2020 source!!) agree with the measurements.
 374 The W2020 position uncertainties (displayed on the figure) are significantly smaller than the observed
 375 deviations. For instance, for the lines displayed at 338.7656 and 557.5464 cm^{-1} , the (Meas. - W2020)
 376 position differences are 1.77×10^{-3} and $1.51 \times 10^{-3} \text{ cm}^{-1}$, respectively, 74 and 101 times larger than the
 377 claimed W2020 uncertainties (2.4×10^{-5} and $1.5 \times 10^{-5} \text{ cm}^{-1}$, respectively [5]).

378 In **Fig. 7**, we present six examples of H_2^{16}O transitions where neither the W2020 position nor the
 379 HITRAN position shows a satisfactory agreement with experiment. All these lines are supposed to have a
 380 W2020 source in the HITRAN2020 database.

381 The H_2^{16}O calculated stick spectrum of 14CoMaPi [6] is included in the different panels of **Figs. 6**
 382 and **7**. In all the displayed examples, the 14CoMaPi line positions agree with experiment. This observation
 383 nicely illustrates the fact that the physics included in the bending-rotation Hamiltonian of Ref. [33] brings
 384 constraints which improves the accuracy of the calculations beyond the experimental accuracy of the input
 385 data. Although the accuracy of the previous frequency measurements of the transitions observed in the
 386 SOLEIL spectra was not optimum, the fit of the effective Hamiltonian parameters benefitted from a large
 387 set of spectroscopic data extending beyond our spectral range. It is important to note that all the
 388 experimental sources used by Coudert et al. [6] in 2014 are publicly available and were used for the

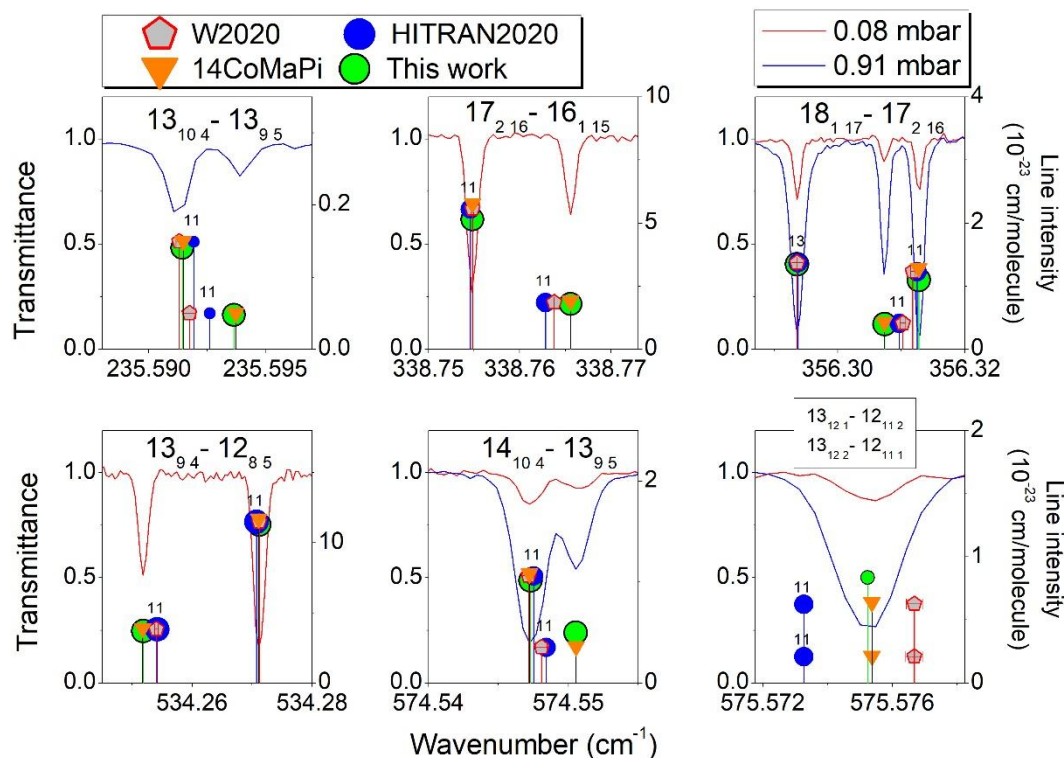
389 derivation of the W2020 energy levels. The absence of “outliers” in the 14CoMaPi list suggests that for
 390 our set of observations in the rotational range, the effective Hamiltonian approach is more efficient to
 391 avoid “outliers” than the xMARVEL approach [46,47] implemented to derive the W2020 energy levels
 392 [5,45].

393



394

395 **Fig. 6**
 396 Comparison of FTS spectra of natural water vapor recorded at SOLEIL and corresponding global line list
 397 constructed in this work (green circles) to the W2020 list of H₂¹⁶O [5] (red pentagons). The HITRAN2020 stick
 398 spectrum of natural water (blue circles) is superimposed together with the effective Hamiltonian calculated positions
 399 of Ref. [6] (orange triangles - 14CoMaPi). All the displayed examples correspond to inaccuracies of the
 400 HITRAN2020 positions of the H₂¹⁶O main isotopologue (isotopologue code “11”). All the problematic lines
 401 correspond pure rotational transitions. Their rotational assignments are given on each panel.



402

403 **Fig. 7**

404 Examples of inaccurate line positions in both the W2020 and HITRAN2020 lists.

405 Comparison of FTS spectra of natural water vapor recorded at SOLEIL and corresponding global line list
 406 constructed in this work (green circles) to the W2020 list of H_2^{16}O [5] (grey pentagons), to the HITRAN2020 stick
 407 spectrum of natural water (blue circles) and to the H_2^{16}O calculated positions of Ref. [33] (orange triangles -
 408 14CoMaPi). All the displayed examples correspond to inaccuracies of both the W2020 and HITRAN2020 positions
 409 of the H_2^{16}O main isotopologue (isotopologue code "11"). All the problematic lines correspond pure rotational
 410 transitions. Their rotational assignments are given on each panel.

411

412 In principle, the W2020 empirical energy levels and transition frequencies also benefitted from
 413 experimental sources in other spectral regions which should improve their accuracies but the constraints
 414 brought by the large networks connecting the energy levels are different compared to those brought by the
 415 effective Hamiltonian of Ref. [6]. As a result, some individual energy levels can be strongly impacted by
 416 an experimental source reported an inaccurate measurement and the resulting W2020 transitions
 417 frequency is inaccurate. In three previous contributions by cavity ring-down spectroscopy (CRDS), we
 418 presented validation tests of the W2020 positions. In the 8040-8630 cm^{-1} region and in the region of the
 419 A-band of O_2 near 760 nm [48-50], a significant number of substantial deviations of the W2020 positions
 420 from the measurements were evidenced. Part of the W2020 positions were found less accurate than some
 421 original sources included in the W2020 transition database and W2020 uncertainties were found
 422 unreliable. In particular, at high energy, a significant fraction of the W2020 position were found to deviate
 423 from observations by amounts exceeding their claimed uncertainty by factors >10-100 [49,50]. They are
 424 due to the fact that the authors of Ref. [5] used not only high-precision data to determine the energies and

425 some less accurate data are ‘spoiling’ higher quality data sources. For instance, a large number of
 426 transitions from emission spectra [30-33,51-58], including very old data [59-61] were incorporated in the
 427 xMARVEL procedure [5,45]. As a result, the few high-precision data did not have a decisive influence on
 428 the determination of the corresponding W2020 energies. For example, the very accurate line positions [1]
 429 of the pure rotation transitions $17_{216} - 16_{115}$ ($338.76545 \text{ cm}^{-1}$, [1]) and $18_{117} - 17_{216}$ ($356.30704 \text{ cm}^{-1}$
 430 [1]) were included in the input data file of Refs. [5,46] but the resulting W2020 values reported with error
 431 bars of 2.4×10^{-5} and $4.6 \times 10^{-4} \text{ cm}^{-1}$ deviate by $-1.67 \times 10^{-3} \text{ cm}^{-1}$ and $+3.21 \times 10^{-3} \text{ cm}^{-1}$, respectively. The
 432 position values of Ref. [1] are confirmed by the present measurements (differences of $1.0 \times 10^{-4} \text{ cm}^{-1}$ and
 433 $3.1 \times 10^{-4} \text{ cm}^{-1}$, respectively).

434 In a fourth Supplementary Material, we provide a table listing the lines of the global line list whose
 435 measured position differs from the W2020 value by more than $9 \times 10^{-4} \text{ cm}^{-1}$. A sample of the table is
 436 presented in **Fig. 8**. The ratio $R = \frac{|v_{exp} - v_{W2020}|}{Unc_{W2020}}$ which compares the absolute deviation of the W2020
 437 position from the measured value to the claimed W2020 position uncertainty has been added. Over the 60
 438 listed transitions, all but two have an R value larger than unity and 21 correspond to $R > 10$ (with
 439 maximum value $R = 459$ for pure rotational transition $15_{511} - 14_{410}$ at $388.70559 \text{ cm}^{-1}$), illustrating the
 440 limited reliability of the W2020 uncertainties for the considered set of lines. The (exp-14CoMaPi_calc)
 441 position differences are included in the table. For 45 of the 60 transitions listed, the deviation from the
 442 14CoMaPi calculated value is less than $2 \times 10^{-4} \text{ cm}^{-1}$. Only three (exp-14CoMaPi_calc) deviations
 443 exceeding $9 \times 10^{-4} \text{ cm}^{-1}$ are noted. They correspond to very weak lines (line intensity smaller than 1.6×10^{-25}
 444 cm/molecule) and have probably an experimental origin.

445 As concerns the HITRAN database, except for two $J' = 21$ doublets, the source given for the H_2^{16}O
 446 line positions is the W2020 line list [5]. Even if the position values are not exactly the original values
 447 published by Furtenbacher et al. [5] (see for instance the upper panels of **Fig. 6**), the presence of outliers
 448 in the HITRAN list has the W2020 origin discussed above. For the $(21_{021} - 20_{120}$ and $21_{121} - 20_{020})$ and
 449 $(21_{120} - 20_{219}$ and $21_{220} - 20_{119})$ doublets, the HITRAN database reproduces the values of Lanquetin et
 450 al. [62] (thus obtained following the same approach as adopted in 14CoMaPi). The comparison to
 451 experiment indicates that this choice was judicious as for instance, the measured position of the first
 452 doublet is closer to the value Lanquetin et al. [62] than to the W2020 value ($6.4 \times 10^{-4} \text{ cm}^{-1}$ and 1.1×10^{-3}
 453 cm^{-1} position differences, respectively).

454 The pure rotation H_2^{16}O doublet, $22_{122} - 21_{021}$ and $22_{022} - 21_{121}$, assigned to the line measured at
 455 $407.74639 \text{ cm}^{-1}$ (intensity of $1.313 \times 10^{-25} \text{ cm/molecule}$) is the only observed line absent in the
 456 HITRAN2020 list. The W2020 positions and intensities [5] agree satisfactorily with the measurements
 457 ($407.74939 \text{ cm}^{-1}$ and $1.04 \times 10^{-25} \text{ cm/molecule}$, respectively).

HITRAN2020													W2020											
spc	Nu_exp	dN	S_exp	dS	Nu	S	assignment					d1	Ratio_1	Nu	t	dN1	S	d2	Ratio_2	R	d3			
3	118.04454	5	1.869E-24	6	118.044535	1.997E-24	000	14	6	8	000	14	5	9	1	0.936	118.04673	M	4	2.002E-24	-219	0.934	54.8	-9
3	165.07328	5	1.435E-24	3	165.073002	1.598E-24	000	14	7	7	000	14	6	8	28	0.898	165.07126	M	35	1.601E-24	202	0.896	5.8	1
3	168.09872	11	2.589E-25	11	168.098288	2.399E-25	000	15	5	11	000	14	6	8	43	1.079	168.09575	M	16	2.405E-25	297	1.077	18.6	-8
3	173.65217	8	8.392E-25	8	173.652719	8.024E-25	000	15	6	10	000	15	5	11	-55	1.046	173.65311	M	20	8.044E-25	-94	1.043	4.7	1
3	174.36575	5	7.695E-25	4	174.365673	7.317E-25	000	14	6	8	000	13	7	7	8	1.052	174.36787	M	11	7.338E-25	-212	1.049	19.3	-3
3	185.67453	5	1.807E-24	3	185.673836	1.911E-24	000	15	5	11	000	15	4	12	69	0.946	185.67350	M	14	1.916E-24	103	0.943	7.4	-2
3	200.72759	5	3.778E-24	5	200.727999	4.003E-24	000	13	8	6	000	13	7	7	-41	0.944	200.73021	M	17	4.013E-24	-262	0.941	15.4	3
3	220.52085	5	1.150E-24	3	220.519932	1.041E-24	000	14	9	6	000	14	8	7	92	1.105	220.51942	M	6	1.043E-24	143	1.103	23.8	4
3	235.59390	5	4.761E-25	7	235.592641	4.969E-25	000	13	10	4	000	13	9	5	126	0.958	235.59157	M	33	4.983E-25	233	0.955	7.1	-9
3	236.92234	7	3.869E-25	6	236.922838	3.507E-25	000	14	10	5	000	14	9	6	-50	1.103	236.92358	M	35	3.516E-25	-124	1.100	3.5	0
3	258.66921	5	3.136E-24	3	258.668316	3.176E-24	000	16	2	14	000	16	1	15	89	0.987	258.66827	M	14	3.184E-24	94	0.985	6.7	5
2	291.44779	5	2.479E-23	3	291.448007	2.408E-23	000	16	2	15	000	16	1	16	-22	1.029	291.44889	M	8	2.415E-23	-110	1.027	13.8	10
1	302.64445	5	1.114E-21	3	302.644081	9.033E-22	000	16	1	16	000	15	0	15	37	0.925	302.64323	M	3	9.059E-22	122	0.922	40.7	-16
3	309.78911	5	5.228E-24	3	309.789058	5.544E-24	000	17	1	16	000	17	0	17	5	0.943	309.79017	M	8	5.560E-24	-106	0.940	13.3	14

458

459

Fig. 8

460

461

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463

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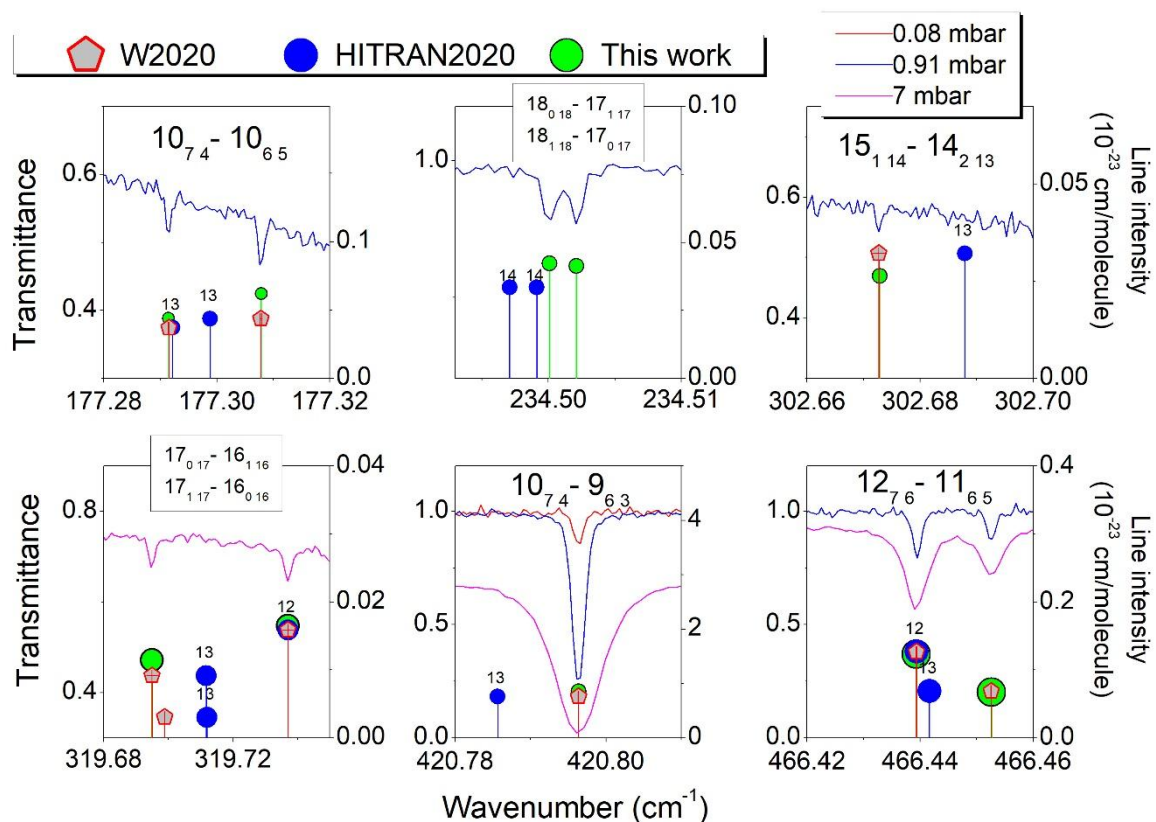
Beginning of a Table provided as a Supplementary Material listing the absorption lines extracted from the global line list of water vapor between 50-720 cm^{-1} whose measured position differs from the W2020 position by more than 0.0009 cm^{-1} . The (exp-HITRAN2020), (exp-W2020) and (exp-14CoMaPi_calc) position differences are given in 10^{-5} cm^{-1} units in columns, d1, d2 and d3, respectively. The ratio $R = |d2|/dN1$ compares the absolute deviation of the W2020 position to the W2020 position uncertainty (dN1).

465 Let us now consider the minor isotopologues

466 The W2020 transition frequencies have been published only for the non-deuterated species (H_2^{16}O ,
 467 H_2^{18}O , H_2^{17}O) [5]. In the case of the deuterated species – HD^{16}O , HD^{18}O , and HD^{17}O –, the HITRAN
 468 database reproduces the line positions calculated by Kyuberis et al. [63] from updated IUPAC-TG energy
 469 levels [42]. The general agreement is satisfactory for the line positions of deuterated species. The *rms*
 470 deviations of our line positions from those of HITRAN [4] are 3.74×10^{-4} , 6.62×10^{-4} and $4.54 \times 10^{-4} \text{ cm}^{-1}$ for
 471 674, 42 and 4 transitions of HD^{16}O , HD^{18}O and HD^{17}O respectively. Nevertheless, the line position
 472 differences exceed 0.001 cm^{-1} for twelve HD^{16}O and one HD^{18}O transitions. The maximum deviations are
 473 for high J, K_a transitions of HD^{16}O (up to 0.0043 cm^{-1}) and for the $2_{20} - 1_{11}$ HD^{18}O transition (0.0042 cm^{-1}).
 474 Note, the *rms* deviation for 41 transitions of HD^{18}O (excluding the $2_{20} - 1_{11}$ transition) is 1.26×10^{-4}
 475 cm^{-1} .

476 For the H_2^{18}O species, again we noted some differences between HITRAN2020 and W2020 line
 477 positions while the HITRAN source of all the considered H_2^{18}O positions is supposed to be the W2020
 478 line list [5]. For example, the HITRAN position of the $13_{113} - 12_{102}$ transition is $558.84113 \text{ cm}^{-1}$ differs
 479 by more than 10^{-3} from its W2020 value ($558.84022 \text{ cm}^{-1}$ [5]). Our measured value of $558.84025 \text{ cm}^{-1}$
 480 coincides to the W2020 value. The *rms* deviation of the present SOLEIL line positions from those of
 481 HITRAN2020 is $1.57 \times 10^{-4} \text{ cm}^{-1}$ for all 565 assigned H_2^{18}O transitions

482 In the case of the H_2^{17}O isotopologue, for an unknown reason, the W2020 source was rejected for
 483 83 transitions: five and 78 were taken from Lodi and Tennyson [28] and updated values determined by a
 484 task group (TG) of the International Union of Pure and Applied Chemistry (IUPAC-TG) [41],
 485 respectively. Five examples of deviations between the HITRAN H_2^{17}O positions and the SOLEIL spectra
 486 are presented in **Fig. 9** (one additional panel concerns HD^{16}O). Interestingly, the original W2020 line
 487 positions of Ref. [5] of all the problematic H_2^{17}O lines agree very well with the experimental spectrum.
 488 Note that the HITRAN positions of the lines near 319.71 and 320.12 cm^{-1} are due to Lodi and Tennyson
 489 [28] while the W2020 source is given for the three other H_2^{17}O lines. For the 78 positions with IUPAC-TG
 490 origin, the average position difference compared to our measurements is $1.09 \times 10^{-4} \text{ cm}^{-1}$ with a large *rms*
 491 deviation of $2.87 \times 10^{-3} \text{ cm}^{-1}$. These values are reduced to $5.06 \times 10^{-5} \text{ cm}^{-1}$ and $1.79 \times 10^{-4} \text{ cm}^{-1}$ for the
 492 corresponding W2020 values, respectively, indicating that overall, the corresponding W2020 position
 493 values of Ref. [5] should have been preferred.



494
 495 **Fig. 9**
 496 Examples of inaccurate line positions in the HITRAN database.
 497 Comparison of FTS spectra of natural water vapor recorded at SOLEIL and corresponding global line list
 498 constructed in this work (green circles) to the HITRAN2020 list of natural water [4] (blue circles). All but the HD¹⁶O
 499 doublet (isotopologue code “14”) near 234.50 cm⁻¹ are relative to the H₂¹⁷O minor isotopologue (isotopologue code
 500 “13”). The W2020 line list of H₂¹⁷O [5] is superimposed (grey pentagons) with corresponding error bars. In all the
 501 displayed examples, the W2020 line positions are in good agreement with experiment. All the problematic lines
 502 correspond pure rotational transitions. Their rotational assignments are given on each panel.
 503

504 **4. Concluding remarks**

505 A series of five high quality FTS spectra of natural water at room temperature has been recorded in
 506 the far infrared region using the SOLEIL synchrotron radiation source combined with a cell providing a
 507 151.75-m absorption pathlength. The spectral coverage (50-720 cm^{-1}), the high position accuracy (on the
 508 order of and $5 \times 10^{-5} \text{ cm}^{-1}$ for isolated lines of intermediate intensity), and the high sensitivity of the
 509 recorded spectra make them valuable for stringent validation tests of spectroscopic databases. An
 510 experimental list of more than 3000 transitions of six water isotopologues (H_2^{16}O , H_2^{17}O , H_2^{18}O , HD^{18}O ,
 511 HD^{16}O , HD^{17}O) were constructed from the five spectra recorded at different pressures up to 7 mbar. The
 512 measured line intensities span more than five orders of magnitude. More than 450 lines are newly detected
 513 by absorption spectroscopy. The HITRAN2020 [4] and W2020 [5] line lists and the effective Hamiltonian
 514 predictions of the H_2^{16}O spectrum by Coudert et al. [6] (14CoMaPi) were compared to the experimental
 515 results.

516 The comparison shows an overall very satisfactory agreement but, even scarce, inaccuracies are of
 517 importance as the observed transitions involve rotational levels of the lowest vibrational states – (000),
 518 (010) and (020) – which are the lower states of most of the water vapor transitions. Energy levels
 519 corrections will thus propagate to calculated line positions in all the energy ranges of the water spectrum.
 520 The main results of the comparison can be summarized as follows,

521 (i) The 14CoMaPi calculated positions of the main isotopologue agree with the observations within
 522 the experimental accuracy,

523 (ii) Although the agreement with the W2020 and HITRAN2020 positions is in general very good, a
 524 number of transition deviates from the observations significantly. These situations are less numerous in
 525 the presently studied rotational range but confirm the conclusion of the validation tests of the W2020
 526 positions in the near infrared region [49] and in the region of the oxygen A-band near 760 nm [48,50]. The
 527 evidence of such general problem underlines the necessity of a careful validation tests before
 528 implementing the W2020 empirical line positions in reference spectroscopic databases used for
 529 atmospheric applications,

530 (iv) the uncertainty values attached to the W2020 empirical positions and energy levels can be
 531 strongly underestimated. A few examples show deviations exceeding the W2020 uncertainty by factors
 532 larger than 10 (up to 459) (see **Fig. 8**),

533 (v) according to the HITRAN2020 database, the W2020 empirical positions of Ref. [5] were
 534 adopted as the main source of line positions in the region. In fact, the HITRAN2020 and the W2020
 535 original line positions do not coincide. As a result, we found series of examples where the position
 536 agreement of the recorded spectra was better for HITRAN2020 list than for W2020 list and *vice versa* (see
 537 **Figs. 6 and 7**),

538 (vi) overall, the W2020 line positions of H_2^{17}O show a better agreement with measurements than
539 some HITRAN values and should have been systematically preferred.

540 Although relatively limited (no new energy levels were determined), the present study has allowed
541 to illustrate the advantage of the state-of-the-art effective Hamiltonian approach for the first variational
542 levels of the main isotopologue. Note that only 1310 of the 3001 reported line positions belong to the main
543 isotopologue. Transitions of the minor isotopologues could be used for testing the rotation-bending
544 Hamiltonian developed some years ago for the H_2^{18}O and HD^{16}O species [64,65]. During the measurement
545 campaign of the natural water spectra at SOLEIL, FTS spectra of water samples enriched in ^{17}O or D (and
546 both) were recorded. The analysis of these spectra will make available a large amount of new information
547 for validation tests of transition frequencies and energy levels of the minor isotopologues (in particular for
548 doubly-substituted species). The obtained results will be reported in separated contributions.

549
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555

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