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Abstract

An accurate empirical list of about 58000 transitions is constructed for natural water in the 5690–8340 cm^{-1} near infrared region (1.71 – 1.20 μm). The new list represents an updated version of the list reported in S.N. Mikhailenko, S. Kassi, D. Mondelain, R. R. Gamache, A. Campargue *A spectroscopic database for water vapor between 5850 and 8340 cm^{-1}* J. Quant. Spectrosc. Radiat. Transfer 179 (2016) 198-216. doi:10.1016/j.jqsrt.2016.03.035. The spectral range is extended to lower energy and the transition frequencies benefited from a series of recent measurements mostly by Cavity Ring Down Spectroscopy (CRDS) referenced to a frequency comb. The intensity threshold is lowered from 1×10^{-29} to 5×10^{-30} cm/molecule at 296 K.

The line list construction uses as starting point the variational line lists computed on the basis of the results of Schwenke and Partridge for the six most abundant water isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{18}O$, and $HD^{17}O$) in natural isotopic abundance. Variational line positions are replaced by position values calculated from empirical rotation-vibration energy levels. On the basis of recent experimental data, the set of required empirical energy levels is improved in accuracy and enlarged, in particular for the minor isotopologues. A large number of energy levels and thus transition frequencies, relying on spectra recorded by CRDS referenced to a frequency comb, have accuracy on the order of 10^{-4} cm^{-1}. All the transitions are provided with unique vibrational labeling supported by effective Hamiltonian calculations in case of ambiguity.

A detailed comparison is presented with the list of natural water included in the HITRAN2016 database and with the very recent $H_2{}^{16}O$ and $H_2{}^{18}O$ lists reported in [Conway EK, Gordon IE, Kyuberis AA, Polyansky OL, Tennyson J, Zobov NF. Calculated line lists for $H_2{}^{16}O$ and $H_2{}^{18}O$ with extensive comparisons to theoretical and experimental sources including the HITRAN2016 database J. Quant. Spectrosc. Radiat. Transfer 241 (2020) 106711 doi:10.1016/j.jqsrt.2019.106711]. The advantage of our list in terms of line position accuracy is demonstrated and illustrated by direct comparison with CRDS recordings at disposal.

Intensity comparison shows a general agreement but a number of weaknesses of the most recent variational intensity calculations are evidenced (e.g. for the $4\nu_2$ transition intensities). All the considered theoretical line lists include a fraction of transitions with intensities deviating importantly from the observations (e.g. $4\nu_2$, $5\nu_2$ and $\nu_1+2\nu_2$ bands in our spectral region).

1. Introduction

In the two last decades, considerable progress has been achieved in the calculations of rovibrational spectra of small polyatomic molecules by *ab initio* and variational methods. Due to its importance for atmospheric applications, many works have been devoted to a better characterization of the water absorption spectrum (see for instance Refs. [1-5]). Completeness, reasonable line position accuracy and good line intensity accuracy give strong advantages to the variational line lists of small polyatomic molecules. The measurement of hundreds thousands line intensities with 1% accuracy is out of reach experimentally. In particular, the measurement of line intensities of water minor isotopologues is very challenging while theoretical intensity values have in general similar accuracy for the main and minor isotopologues. Nevertheless for line positions, theory cannot compete with experiment (except for H_2 and its isotopologues [6]). As a result, the general strategy for the best line list for water (and CO_2) is to use variational line lists as basis and adjust line positions according to experimental values or to position values calculated from empirically determined energy levels. This method is that adopted for a large fraction of the water and carbon dioxide list in the last edition of the HITRAN [7] and GEISA [8] databases.

Some years ago, under the project "A database of water transitions from experiment and theory", an IUPAC task group (IUPAC-TG) reported an exhaustive review and evaluation of rovibrational line positions, energy levels and assignments for all the main isotopologues of water. By using the procedure and code MARVEL (Measured Active Rotational-Vibrational Energy Levels) [9, 10], all the high quality absorption or emission line positions available in the literature at that time were used to determine and validate the energy levels [11-13]. This cooperative effort led to recommended set of energy level values with their self-consistent uncertainties. Since then, some deficiencies were evidenced in the quality of the determined levels and error bars. In particular, the inclusion in the MARVEL procedure of a considerable number of transition frequencies reported with underestimated error bars from poorly resolved emission spectra degraded the quality of a fraction of the IUPAC-TG empirical levels. In addition, a few erroneous assignments in the original sources used by the IUPAC-TG could not be detected by the MARVEL procedure and affected the recommended levels.

Water vapor spectrum was the first high sensitivity spectrum that we recorded in 2004 with a newly built high sensitivity Cavity Ring Down Spectrometer. The use of a series of Distributed Feedback (DFB) laser diodes, each of them with 30 cm^{-1} tuning range, allowed a full coverage of the 1.6 μm transparency window (6132-6748 cm^{-1}) [14]. Since then, the spectral coverage was extended over the wide 5690-8340 cm^{-1} range by using a collection of about one hundred DFB diodes [14-19] combined with an External Cavity Laser Diode (ECDL) in the 7920-8340 cm^{-1} region [20]. CRDS spectra of water vapor in natural isotopic abundance or enriched in D [21], ^{18}O [22] or ^{17}O [23-26] were recorded with increasing sensitivity and accuracy, over the last fifteen years. These spectra

revealed a considerable number of new observations. Those available at the date of the IUPAC-TG project were incorporated among the extensive sources of line positions used by the IUPAC-TG.

On the basis of these measurements [14-18, 20-23] and absorption data available in the literature mostly for the strongest lines [27-37], in 2016, we released an empirical line list for the 5850-8340 cm^{-1} range [38]. This list corrected a number of deficiencies of the HITRAN2012 line list [39], in particular the absence of many HDO lines of importance in the 1.6 μm window. Compared to the IUPAC-TG energy levels [11-13], new CRDS observations allowed extending the set of energy levels and correcting a number of inaccuracies. As a result, the GEISA database [8] reproduces our 2016 list in the considered region and the HITRAN2016 database used our list as main source of line positions of the main water isotopologue and reproduces part of the CRDS intensities. Let us underline the importance of the CRDS spectra at disposal for direct validation tests of the released water vapor lists. The available low pressure spectra of pure water vapor provide stringent tests to check the consistency of the empirical energy levels. This concerns in particular the large number of weak lines unobserved in atmospheric spectra or by Fourier Transform spectroscopy (FTS) associated with long absorption path (the weakest lines measured by CRDS have an intensity below 1×10^{-29}cm/ molecule).

In the present updated list, new experimental results obtained during the last five years are considered to further improve the accuracy of the line positions, extend the 2016 list down to 5690 cm^{-1} [19, 23] and lower the intensity cut-off from 1×10^{-29} to 5×10^{-30} cm/molecule at 296 K. Significant new information was retrieved from recordings performed with a sample highly enriched (~55 %) in ^{17}O:

(i) more than 1000 energy levels of $H_2{}^{17}O$ and $HD^{17}O$ were determined in the 1.6 μm transparency window (5850 and 6671 cm^{-1}) [24],

(ii) between 6667 and 7921 cm^{-1}, the spectra were recorded with a CRD spectrometer newly coupled to a self-referenced frequency comb (SRFC) providing accurate frequency value for each ring down event. The comb assisted CRDS method (CA-CRDS) allowed improving the accuracy of the line centers determination which greatly improved the transitions of all water isotopologues contributing to the spectrum [25, 26]. For instance, more than 5000 lines of the main isotopologue were used to decrease the uncertainties of the previously known $H_2{}^{16}O$ energy levels. Test comparisons of energy level values determined from different transitions sharing the same upper level agree within a few MHz (~10^{-4} cm^{-1}) [26], more than one order of magnitude better than the average accuracy claimed for the positions retrieved from standard CRDS recordings (~10^{-3} cm^{-1}). In addition, hundreds of new energy levels of $H_2{}^{17}O$ and $HD^{17}O$ were determined from these recordings [25, 26].

(iii) Finally, the new set of energy levels benefited from additional recent sources [40-43] including very accurate Lamb dip measurements [40] and some recent analysis of FTS spectra of ^{18}O enriched water [41, 42].

The rest of the paper is organized as follows. The line list construction is detailed in the next Section. In the sections 3 and 4, we present a systematic comparison of the positions and intensities to the corresponding values included in the HITRAN2016 database for natural water and to the very recent semi-empirical lists published by Conway *et al.* for $H_2{}^{16}O$ and $H_2{}^{18}O$ [44]. Several direct comparisons with the CRDS spectra at disposal will illustrate the advantages of our list. As concerned line intensities, a number of large deviations between measurements, HITRAN2016 and variational intensities will be discussed.

2. Line list construction

All transitions stronger than 5×10^{-30} cm/molecule at 296 K of the variational line lists computed by S. Tashkun (IAO SB RAS, Tomsk, Russia) [45] on the basis of the results of Schwenke and Partridge (SP) [1, 2] were gathered in a list for water in natural isotopic abundance. These 20 years old variational line lists are probably not the best-to-date variational lists (in particular for line positions) but they still have the unique advantage to be consistent for the six required isotopologues, to include reasonable rovibrational assignments and to be publicly available at http://spectra.iao.ru/.

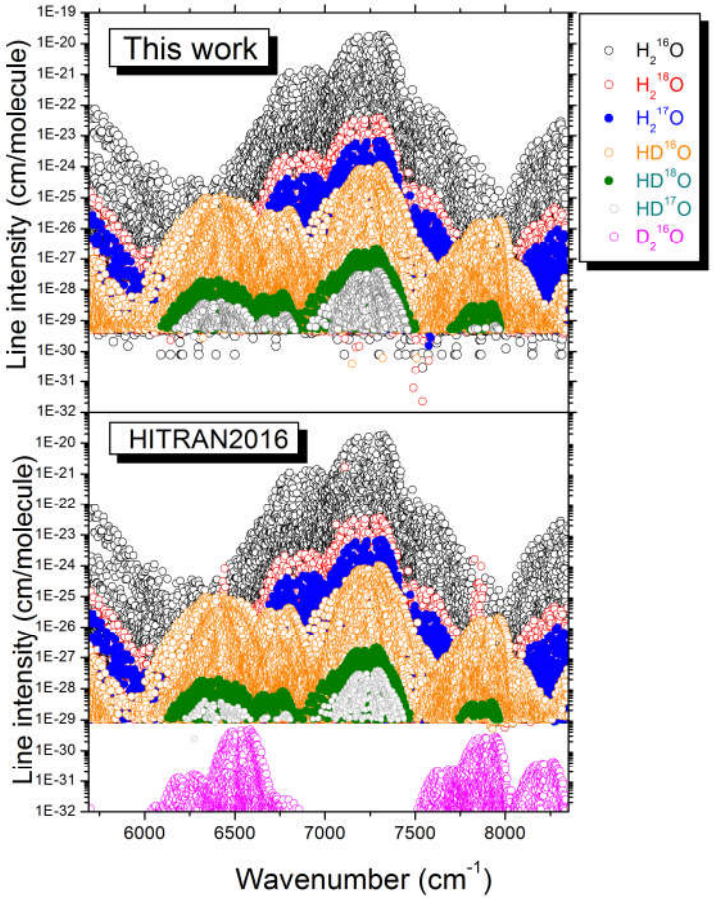

Fig. 1

Overview comparison between the list constructed in this work and the HITRAN2016 line list for water vapor between 5690 and 8340 cm^{-1}.

The resulting SP list for natural water at 296 K between 5690 and 8340 cm^{-1} includes 58,000 transitions with intensity larger than 5×10^{-30} cm/molecule for the six most abundant isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{18}O$, and $HD^{17}O$). Contrary to the available calculated line lists and the HITRAN list, all the transitions are provided with unique rovibrational assignment. Note that SP assignments were modified in some cases of strongly interacting rovibrational levels. These corrections were made according to calculations based on the effective Hamiltonian method. Some details about these re-labelings can be found, for example, in Refs. [20, 27, 43]. As mentioned above, the variational line positions are replaced by corresponding values calculated from empirical rotation-vibration energy levels. An overview of the resulting list is compared to the HITRAN list in **Fig.1**. Note that our intensity cut-off is twice lower than the HITRAN intensity cut-off (1×10^{-29} cm/molecule) but HITRAN list includes $D_2{}^{16}O$ lines with intensities down to 1×10^{-32} cm/molecule.

The experimental sources used to construct our set of upper empirical energies are absorption spectra summarized in **Table 1**. High sensitivity CRDS measurements [14-26, 36, 37, 40, 43] were complemented by the results of Fourier transform [27-35, 41, 42] and ICLAS [46] measurements, in particular for the deuterated species. Note that more than half of the $H_2{}^{16}O$ transitions rely on the high precision line positions obtained by CA-CRDS [25, 26, 36, 37, 40]. The considered experimental sources [14-37, 40-43, 46] did not provide upper energy empirical values for about 6000 weak transitions (~10 %). When available, we adopted the empirical energy levels recommended by the IUPAC-TG [11-13]. The energy levels adopted from IUPAC-TG concern mostly very weak hot band transitions with an upper energy level determined from experimental studies at higher energy, not included among our sources of line positions (the most excited upper level involved in the list is the (121) $15_{2\,14}$ level with an energy of about 12,902 cm^{-1}).

About 1750 transitions are left without empirical determination of their upper energy levels. For about 530 transitions reaching an upper level not yet observed experimentally, the frequencies could be estimated by *J, K* extrapolation of the deviations between empirical and SP variational positions of observed transitions of the considered band. This procedure which was not implemented in the 2016 list [38] is believed to improve significantly SP variational positions. About 1200 (very weak) transitions (0.2%) were left with their SP variational positions.

As concerned the lower energy levels, the IUPAC-TG values were adopted for $H_2{}^{16}O$ [13] and $HD^{16}O$ [12]. For $H_2{}^{17}O$ and $H_2{}^{18}O$ isotopologues, we use rotational energies of the (000) and (010) states derived from hot emission FTS spectra of water vapor enriched in ^{17}O and ^{18}O [47]. The lower energies for the $HD^{18}O$ and $HD^{17}O$ species were calculated in Refs. [48, 49] using an effective Hamiltonian approach [50].

Table 1
Number of transition frequencies between 5690 and 8340 cm^{-1} calculated from different upper energy sources.

	CA-CRDS [25,26,36,37]	Lamb dip [40]	CRDS [14-24,43]	FTS &ICLAS [27-35,41,42]	IUPAC [11-13]	Estimated	Variational [45]	Total
$H_2{}^{16}O$	12646	84	2441	6528	3403	225	288	25615
$H_2{}^{18}O$	4666		344	3013	553	114	287	8977
$H_2{}^{17}O$	5608		673	63	5	37	2	6388
$HD^{16}O$	1967		2610	8601	245	156	669	14248
$HD^{18}O$	132			1708				1840
$HD^{17}O$	545		60	316		6		927
Total	25564	84	6128	20229	4206	538	1246	57995

At the final step of the line list construction, it appears that 282 very weak transitions of $H_2{}^{16}O$, $H_2{}^{18}O$, $HD^{16}O$ and $HD^{17}O$ with SP intensities below our 5×10^{-30} cm/molecule intensity cut-off are present in HITRAN2016 [7] (1×10^{-29} cm/molecule intensity cut-off) or in the list of Conway *et al*. [44] with an intensity larger than 5×10^{-30} cm/molecule. For completeness, these transitions which are believed to have underestimated SP intensities were added to the list with empirical line positions.

Table 2
Comparison of the various determinations of upper energy levels determined from the line centers of transitions measured by CA-CRDS in refs. [25, 26]. In the last column, the average value is given with the standard deviation in the unit of the last quoted digit.

ISO	Line position (cm^{-1})	Upper level ($V_1V_2V_3$) J Ka Kc	Lower level J Ka Kc	Upper energy (cm^{-1})	Average value (cm^{-1})
$H_2{}^{16}O$	7843.31579	002 7 5 3	6 2 4	8446.08928	8446.08928(1)
	7688.30913	002 7 5 3	6 4 2	8446.08928	
	7401.03099	002 7 5 3	6 6 0	8446.08926	
	7518.34542	002 7 5 3	7 4 4	8446.08929	
	7421.24093	021 10 2 8	9 0 9	8341.40891	8341.40883(1)
	7047.77501	021 10 2 8	10 2 9	8341.40870	
	6760.07327	021 10 2 8	10 4 7	8341.40895	
	7014.29919	021 10 2 8	11 0 11	8341.40876	
	7356.64521	040 10 5 6	9 0 9	8276.81319	8276.81318(3)
	6983.17951	040 10 5 6	10 2 9	8276.81320	
	6695.47753	040 10 5 6	10 4 7	8276.81322	
	6949.70358	040 10 5 6	11 0 11	8276.81315	
	7708.32176	101 11 5 7	10 3 8	9154.44964	9154.44958(5)
	7435.73114	101 11 5 7	10 5 6	9154.44960	
	7629.60228	101 11 5 7	11 1 10	9154.44954	
	7155.45478	101 11 5 7	11 5 6	9154.44959	
	6832.54451	101 11 5 7	11 7 4	9154.44952	
$H_2{}^{18}O$	7508.72473	002 5 0 5	4 1 4	7732.55306	7732.55312(5)
	7226.82448	002 5 0 5	5 3 2	7732.55311	
	7287.20719	002 5 0 5	6 1 6	7732.55318	
	7087.17071	002 5 0 5	6 3 4	7732.55314	
	7462.95544	101 6 3 3	5 1 4	7861.31580	7861.31585(4)
	7215.93340	101 6 3 3	6 3 4	7861.31583	
	6981.23971	101 6 3 3	6 5 2	7861.31590	
	7021.76646	101 6 3 3	7 3 4	7861.31587	
	7190.39940	200 4 1 4	3 2 1	7401.19840	7401.19850(10)

	7102.57855	200	4	1	4	4	2	3	7401.19847	
	7077.15196	200	4	1	4	5	0	5	7401.19850	
	6956.04030	200	4	1	4	5	2	3	7401.19864	
$H_2{}^{17}O$	7905.61486	002	10	3	8	9	0	9	8823.71701	8823.71721(13)
	7623.75408	002	10	3	8	9	2	7	8823.71713	
	7466.16140	002	10	3	8	9	4	5	8823.71742	
	7532.91852	002	10	3	8	10	2	9	8823.71721	
	7246.02895	002	10	3	8	10	4	7	8823.71726	
	6955.38672	002	10	3	8	10	6	5	8823.71715	
	7136.33442	002	10	3	8	11	2	9	8823.71731	
	7360.16472	021	7	5	2	6	3	3	8020.15178	8020.15170(14)
	7136.03758	021	7	5	2	6	5	1	8020.15165	
	6965.09732	021	7	5	2	7	5	3	8020.15153	
	6971.49441	021	7	5	2	8	3	5	8020.15165	
	6768.86048	021	7	5	2	8	5	3	8020.15189	
	7569.80437	101	7	4	4	6	2	5	8121.41406	8121.41389(13)
	7536.47287	101	7	4	4	7	0	7	8121.41396	
	7340.03635	101	7	4	4	7	2	5	8121.41382	
	6911.59545	101	7	4	4	7	6	1	8121.41372	
	6716.26598	101	7	4	4	8	6	3	8121.41388	
	7378.14358	111	4	2	2	3	0	3	9106.40406	9106.40400(5)
	7291.32478	111	4	2	2	3	2	1	9106.40395	
	7202.83474	111	4	2	2	4	2	3	9106.40402	
	7056.69185	111	4	2	2	5	2	3	9106.40398	
	7568.63956	200	8	4	5	7	1	6	8271.52554	8271.52558(4)
	7430.66057	200	8	4	5	7	3	4	8271.52563	
	7267.74419	200	8	4	5	8	3	6	8271.52557	
	7021.02696	200	8	4	5	8	5	4	8271.52558	
$HD^{16}O$	7301.24803	002	3	1	3	2	0	2	7347.42114	7347.42117(15)
	7289.29444	002	3	1	3	2	1	2	7347.42132	
	7238.15185	002	3	1	3	2	2	0	7347.42094	
	7197.26499	002	3	1	3	4	0	4	7347.42130	
	7191.03890	002	3	1	3	4	1	4	7347.42116	
	7313.67622	002	4	1	3	3	1	2	7430.13757	7430.13743(12)
	7279.98112	002	4	1	3	4	0	4	7430.13743	
	7208.30111	002	4	1	3	4	2	2	7430.13728	
	7136.50091	002	4	1	3	5	2	4	7430.13744	
	7429.45104	002	7	4	4	6	3	3	7899.11465	7899.11462(6)
	7325.22399	002	7	4	4	6	4	3	7899.11467	
	7322.20986	002	7	4	4	7	3	5	7899.11454	
	7090.55168	002	7	4	4	8	4	5	7899.11460	
$HD^{17}O$	7277.85690	002	3	1	3	2	1	2	7335.70340	7335.70351(12)
	7186.05778	002	3	1	3	4	0	4	7335.70358	
	7179.94164	002	3	1	3	4	1	4	7335.70364	
	7114.85032	002	3	1	3	4	2	2	7335.70342	
	7377.68464	002	5	2	3	4	1	4	7533.44664	7533.44657(18)
	7312.59336	002	5	2	3	4	2	2	7533.44646	
	7160.94208	002	5	2	3	5	3	2	7533.44638	
	7131.34089	002	5	2	3	6	2	4	7533.44679	
	7430.42693	002	7	5	2	6	4	3	8001.19483	8001.19494(15)
	7296.30045	002	7	5	2	6	5	1	8001.19495	
	7321.02464	002	7	5	2	7	4	3	8001.19514	
	7187.79783	002	7	5	2	7	5	3	8001.19483	

In terms of accuracy only average estimates can be provided for the considered large amount of line positions. Experimentally, the line center accuracy depends on *(i)* the accuracy of the calibration of the frequency axis and *(ii)* the precision of the line center determination depending on the signal-to-noise ratio of the spectra, the blending with nearby lines provided etc. Note that we consider here

mainly absorption spectra of pure water vapor at room temperature, thus with a pressure value on the order of 20 Torr at most. Neither in the present study nor in the MARVEL treatment followed by the IUPAC-TG, the position values were corrected from the self-pressure shifts. Self-pressure shift coefficients vary typically in the $\pm 10^{-2}$ cm^{-1} atm^{-1} range which leads to shifts on the order of 10^{-4} cm^{-1} (~ 3 MHz) which is small in general but might be significant for the line centers determined by CA-CRDS line centers. Additional biases related to the choice of the line shape used to fit the measured line profile are also expected to affect the line center determination but these effects are smaller. Most of the line centers were obtained using the standard Voigt profile. Significant residuals are generally obtained showing the typical W signature due to the Dicke narrowing effect [51]. Nevertheless, the obtained residuals are generally symmetric indicating that the line center determination is mostly unaffected.

We present in **Table 2** some examples of determinations of the upper energy levels from line centers of different transitions measured by CA-CRDS. Similar accuracy tests included in Ref. [26] relative to the 6900-7400 cm^{-1} region, showed a consistency at the 10^{-4} cm^{-1} level between the various determinations. Here, together with line positions of Ref. [26], we consider the transition frequencies reported in the 7400-7800 cm^{-1} region [25] which enlarges importantly the possibilities of redundant determinations of a given upper level. A similar agreement on the order of 10^{-4} cm^{-1} is achieved, illustrating the consistency of the frequencies measured in Ref. [25] and Ref. [26]. As a result, the position accuracy for transitions frequencies derived from well isolated lines measured by CA-CRDS [25, 26] is estimated to be 2×10^{-4} cm^{-1}. For standard CRDS and FTS, an uncertainty of 10^{-3} cm^{-1} as given in Ref. [38] is a reasonable average value. For ICLAS line positions [46] and those estimated using an *J, K* empirical law correction of their SP positions, the uncertainty is on the order of 10^{-2} cm^{-1}. Finally, for the small fraction of purely SP variational positions [1] included in our list, various comparisons with experimental values have shown that in our region, SP positions may deviate by a few tenth of wavenumber (see below). The most accurate line positions are those related to the ten Lamb dip measurements reported in Ref. [40] which allowed computing 84 line positions with an accuracy better than 10^{-6} cm^{-1} (30 kHz). In the line list provided as Supplementary Material, the source of the upper energy level is provided for each transition. The number of decimal digits provided for each position has been adapted depending on the estimated uncertainties (for instance, five and six digits for the values relying on FC referenced CRDS and Lamb dips, respectively).

Fig. 2 shows a sample of the line list provided as Supplementary Material. Together with our recommended position and corresponding source, the list includes our rovibrational assignment, SP intensity, the lower state energy value and the corresponding HITRAN [7] and Conway *et al.* [44] values for the positions and intensities. When a different rovibrational assignment was proposed by Conway *et al* or in HITRAN2016 list, it is included for comparison. This global line list, gathering most of the information at disposal, was used for the systematic comparisons presented below.

In our region, the HITRAN list includes 48692 transitions for the six major water isotopologues. Although the HITRAN intensity cut-off is 1×10^{-29} cm/molecule, 40 transitions have an intensity below this value, down to 1.1×10^{-37} cm/molecule for the $5\nu_2$ $4_{4\,0}$ -$4_{1\,3}$ transition of $HD^{17}O$. In addition, many transitions of the $D_2{}^{16}O$ isotopologue with intensity below the cut-off are included in the HITRAN list (see **Fig. 1**). For the main isotopologue (about 21500 transitions), position and intensity values were taken from six and nine sources, respectively. Most of the line intensities (about 74%) have variational origin [52] while more than 80% of the positions are empirical values transferred from our 2016 list [38]. The remaining $H_2{}^{16}O$ positions are empirical from the IUPAC-TG (9.7%) or measured by FTS values from Toth's database (6.4%) [53], with a very small fraction of variational values and a few values with uncertain origin.

These $H_2{}^{16}O$ and $H_2{}^{18}O$ lists published by Conway *et al.* [44] have intensities calculated using a semi-empirical potential energy surface [4]. They were found to show a better agreement with experiment than the preceding 'POKAZATEL' line list [54]. In the 5690-8340 cm^{-1} interval, Conway list includes 32553 $H_2{}^{16}O$ transitions above an intensity cut-off fixed to 1×10^{-30} cm/molecule at 296 K. Note that the maximum J value of the lower and upper levels is 20 while our list includes transitions with J values up to 22 and 23, respectively (the $\nu_1+\nu_3$ $21_{1\,21} - 20_{1\,20}$ line at 7485.3914 cm^{-1} has for instance an intensity of about 5×10^{-28} cm/molecule significantly above the intensity cut-off).

In our region, the $H_2{}^{18}O$ list of Conway includes 9191 transitions with intensity (including the abundance factor) larger than 5×10^{-30} cm/molecule (to be compared to 8977 in our list). 263 of them are duplicate (same, position, same intensity, same assignment) and should be removed. In the whole Conway $H_2{}^{18}O$ line list (100% abundance for the line intensities) extending up to 20000 cm^{-1}, we could identify 5394 such duplicates.

Int_obs	Pos(SP)	Pos_empir	Int(SP)	E_low	ISO	Assignment	Source	Conway's Pos & Int	Conway's assignment	HITRAN2016 Pos & Int	HITRAN2016 assignment
	7448.5220	7448.522000	9.029E-30	2716.3293	HDO	002 19 2 17 000 18 3 16	variational				
	7448.5400	7448.540000	9.209E-30	2716.3293	HDO	002 19 3 17 000 18 3 16	variational			7448.5735 1.045E-29	
	7448.6642	7448.631000	2.829E-29	3629.0943	H2O	101 15 9 7 000 15 7 8	estimated	7449.2351 2.754E-29		7449.2351 2.806E-29	101 15 9 7 000 15 7 8
	7448.7192	7448.637400	4.283E-28	1875.4693	H2O	031 5 5 0 010 4 1 3	FTS	7448.6350 4.522E-28		7448.6374 4.300E-28	
	7448.7220	7448.722000	5.666E-30	2873.3223	H2O18	200 15 5 11 000 14 4 10	variational	7448.8730 5.372E-30	-222 15 -2 -2 000 14 4 10		
	7448.8214	7448.769600	9.423E-28	1774.6153	H2O	002 11 4 8 000 12 1 11	CRDS	7448.7701 9.475E-28		7448.7699 9.200E-28	
	7448.7278	7448.804720	7.779E-31	1360.2350	H2O	120 9 7 2 000 9 4 5	CA-CRDS	7448.8041 1.082E-29			
	7448.8790	7448.840200	1.977E-29	3935.3448	H2O	003 4 3 1 100 3 3 0	FTS	7448.8390 1.977E-29		7448.8402 1.971E-29	
	7449.1128	7448.885120	2.000E-29	1119.4883	H2O17	101 8 6 2 000 8 4 5	CA-CRDS			7448.8852 2.000E-29	
	7449.1776	7448.929140	1.256E-27	1055.2554	H2O17	002 8 4 5 000 7 5 2	CA-CRDS			7448.9299 1.740E-27	
	7448.9727	7448.934910	4.678E-28	604.5442	H2O18	002 6 3 3 000 5 4 2	CA-CRDS	7448.9359 5.124E-28		7448.9359 5.510E-28	
2.709E-26	7448.9625	7448.981600	3.272E-26	2927.9399	H2O	101 14 7 7 000 13 7 6	CA-CRDS	7448.9815 3.219E-26		7448.9821 2.830E-26	
	7448.9738	7449.020400	5.042E-28	2416.7832	H2O18	101 14 4 11 000 13 4 10	CRDS	7449.0200 5.000E-28		7449.0194 4.430E-28	
	7449.0428	7449.043000	1.038E-29	4184.8299	H2O	130 15 4 11 010 14 3 12	variational	7449.1490 1.036E-29	-222 15 -3 -3 010 14 3 12	7449.2451 1.010E-29	-222 15 -3 -3 010 14 3 12
	7449.1176	7449.087500	9.061E-28	752.1874	H2O18	002 7 3 5 000 6 4 2	CA-CRDS	7449.0885 1.041E-27		7449.0885 1.160E-27	
	7449.2336	7449.108650	5.422E-28	325.8804	H2O17	200 6 2 4 000 5 1 5	CA-CRDS			7449.1088 5.950E-28	
	7449.3113	7449.142920	2.497E-27	753.7052	H2O17	200 7 5 2 000 6 4 3	CA-CRDS			7449.1419 2.180E-27	
	7449.2013	7449.239860	7.118E-27	2813.5273	H2O	101 13 8 5 000 12 8 4	CA-CRDS	7449.2424 6.983E-27		7449.2407 6.984E-27	
	7449.2513	7449.251980	4.119E-26	885.6002	H2O	101 8 4 4 000 8 2 7	CA-CRDS	7449.2518 4.538E-26		7449.2518 4.279E-26	
	7449.2230	7449.255060	1.535E-25	1813.2226	H2O	021 12 5 7 000 11 3 8	CA-CRDS	7449.2535 1.578E-25		7449.2541 1.558E-25	
	7449.3471	7449.280500	5.204E-30	2388.0297	HDO	012 10 5 6 010 9 4 5	FTS				
	7449.3630	7449.318500	3.841E-28	1080.3853	H2O	050 8 1 7 000 9 2 8	CA-CRDS	7449.3194 5.321E-28		7449.3198 4.410E-28	
	7449.3189	7449.319000	8.942E-30	2715.5327	HDO	002 19 2 17 000 18 2 16	variational			7449.3582 1.016E-29	
	7449.3370	7449.337000	9.004E-30	2715.5327	HDO	002 19 3 17 000 18 2 16	variational				
	7449.4237	7449.356500	2.991E-29	3796.5397	H2O	003 4 1 4 100 3 1 3	FTS	7449.3549 2.988E-29		7449.3564 2.982E-29	
	7449.4225	7449.485700	7.247E-28	2595.8127	H2O	012 8 3 5 010 8 2 6	FTS	7449.4849 6.670E-28		7449.4849 6.510E-28	
3.247E-26	7449.4469	7449.487520	3.681E-26	1813.2226	H2O	200 11 6 5 000 11 3 8	CA-CRDS	7449.4871 3.520E-26		7449.4879 3.671E-26	
	7449.3754	7449.489200	1.042E-29	4728.2197	H2O	111 16 3 13 010 15 3 12	IUPAC	7449.4892 1.036E-29		7449.4892 1.037E-29	
	7449.8300	7449.497420	1.116E-29	1996.8541	H2O17	031 6 5 1 010 5 1 4	CA-CRDS			7449.4995 1.120E-29	
	7449.3149	7449.656000	7.854E-29	2471.2550	H2O	120 10 10 0 000 10 9 1	IUPAC	7449.6565 8.011E-29	040 10 10 0 000 10 9 1	7449.3315 7.722E-29	040 10 10 0 000 10 9 1
	7449.3138	7449.656400	2.370E-28	2471.2546	H2O	120 10 10 1 000 10 9 2	IUPAC	7449.6569 2.403E-28	040 10 10 1 000 10 9 2	7449.3315 2.317E-28	040 10 10 1 000 10 9 2
	7449.6956	7449.682190	3.810E-26	94.7886	H2O18	002 2 2 0 000 2 1 1	CA-CRDS	7449.6823 3.670E-26		7449.6826 3.630E-26	
	7449.7582	7449.774430	1.678E-24	1985.7842	H2O	101 12 5 8 000 11 5 7	CA-CRDS	7449.7747 1.658E-24		7449.7748 1.640E-24	
	7449.8542	7449.822760	6.662E-30	1437.9678	H2O	021 10 6 5 000 10 2 8	CA-CRDS	7449.8232 1.050E-29			
	7449.8259	7449.881700	1.658E-28	2939.9563	H2O18	101 17 2 16 000 16 2 15	CRDS	7449.8800 1.644E-28		7449.8808 2.200E-28	
	7449.8341	7449.888000	5.526E-29	2939.9470	H2O18	101 17 1 16 000 16 1 15	estimated	7449.9889 5.482E-29	-222 17 -2 -2-222 16 -2 -2		
	7449.8004	7449.895100	3.978E-29	1814.0870	H2O18	012 4 2 3 010 4 1 4	FTS	7449.8955 3.644E-29		7449.8951 3.980E-29	
1.781E-26	7449.9009	7449.933460	2.048E-26	2813.5114	H2O	101 13 8 6 000 12 8 5	CA-CRDS	7449.9336 2.010E-26		7449.9336 2.011E-26	

Fig. 2

Sample of the line list provided as Supplementary Material. The different columns are: Int_obs – the measured value of the intensity measured from the CRDS spectrum of natural water (the listed values are limited to well isolated $H_2{}^{16}O$ lines with intensity larger than10^{-27} cm/molecule); Pos(SP) – variational line center from Schwenke and Partridge results; Pos_empir – empirical value of the line center; Int(S) – SP variational line intensity [1,2,45]; ISO – isotopologue; Assignment – upper and lower level rovibrational assignment; Source – source of our empirical value of the upper energy level; Conway Pos & Int – line center and line intensity reported by Conway *et al.* [44] (for $H_2{}^{16}O$ and $H_2{}^{18}O$ transitions); Conway assignment – rovibrational assignment given only when it differs from ours; "HITRAN2016 Pos & Int" and "HITRAN2016 assignment" – same for the HITRAN database [7].

The systematic comparison to HITRAN and Conway lists is not straightforward because these two references do not provide complete rovibrational assignments for part of the transitions. For instance, 1442 $H_2{}^{16}O$ transitions of the Conway list are provided with incomplete rovibrational assignment of the upper level. In those circumstances, the transitions in common with our list were identified by using as criteria identical lower state energy, identical upper *J* value and reasonable position and intensity matching (typically 0.5 cm^{-1} and a factor of 2, respectively). We have included in the Supplementary Material the position and intensity columns for the HITRAN and Conway transitions in coincidence (see **Fig. 2**). When a different or incomplete rovibrational assignment was attached to the considered transition, it is reproduced in the comparison list. HITRAN erroneous assignments include more than 160 ortho-para transitions between 6048 and 8233 cm^{-1} which are strictly forbidden by symmetry (all of them were erroneously referenced to our 2016 list [38] in the HITRAN database).

As mentioned above less than 300 very weak lines (intensity smaller than 1.6×10^{-27} cm/molecule) present in the list of Conway *et al.* or HITRAN with intensity larger than our 5×10^{-30} cm/molecule intensity cut-off but with SP intensities below 5×10^{-30} cm/molecule, were added to our list (these transitions with SP intensity smaller than 5×10^{-30} cm/molecule are visible on the upper panel of **Fig. 1**).

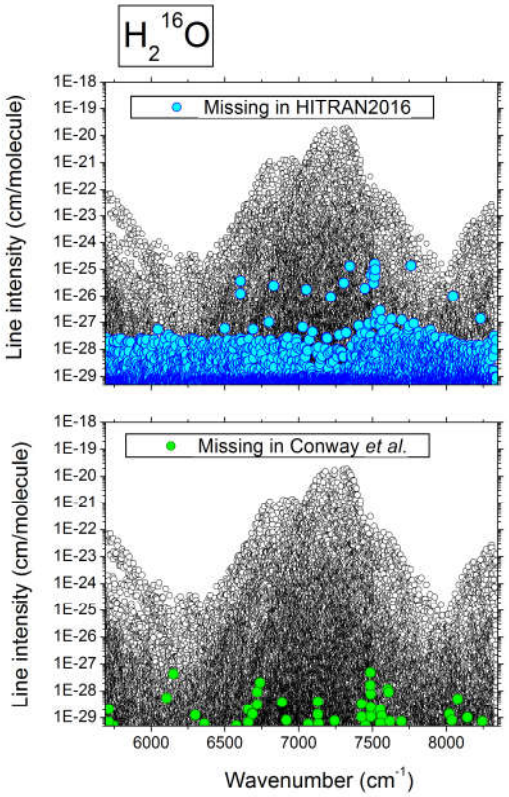

Fig. 3
Overview of the transitions missing in the $H_2{}^{16}O$ lists provided by the HITRAN2016 [7] database (upper panel) and Conway *et al.* [44] (lower panel). Missing transitions are highlighted in light blue and green, respectively.

More significant is the fact that our list based on SP results includes a number of $H_2{}^{16}O$ transitions missing in the HITRAN list and to a lesser extend in the list by Conway *et al*, some of them with relatively high intensity (see **Fig. 3)**. HITRAN list misses a few medium $H_2{}^{16}O$ transitions with intensity up to 1.6×10^{-25} cm/molecule (for the $2\nu_3$ $8_{7\,2} - 8_{6,3}$ line at 7514.916 cm^{-1}) and a large set of weak transitions with intensity below 5×10^{-28} cm/molecule. As concerned the list by Conway *et al.*, only about 50 weaker lines are missing, half of them corresponding to *J* values larger than 20. Both lists are practically complete for the $H_2{}^{18}O$ isotopologue. **Fig. 4** shows two examples of CRDS spectra of natural water in spectral intervals where strong $H_2{}^{16}O$ lines are missing in HITRAN.

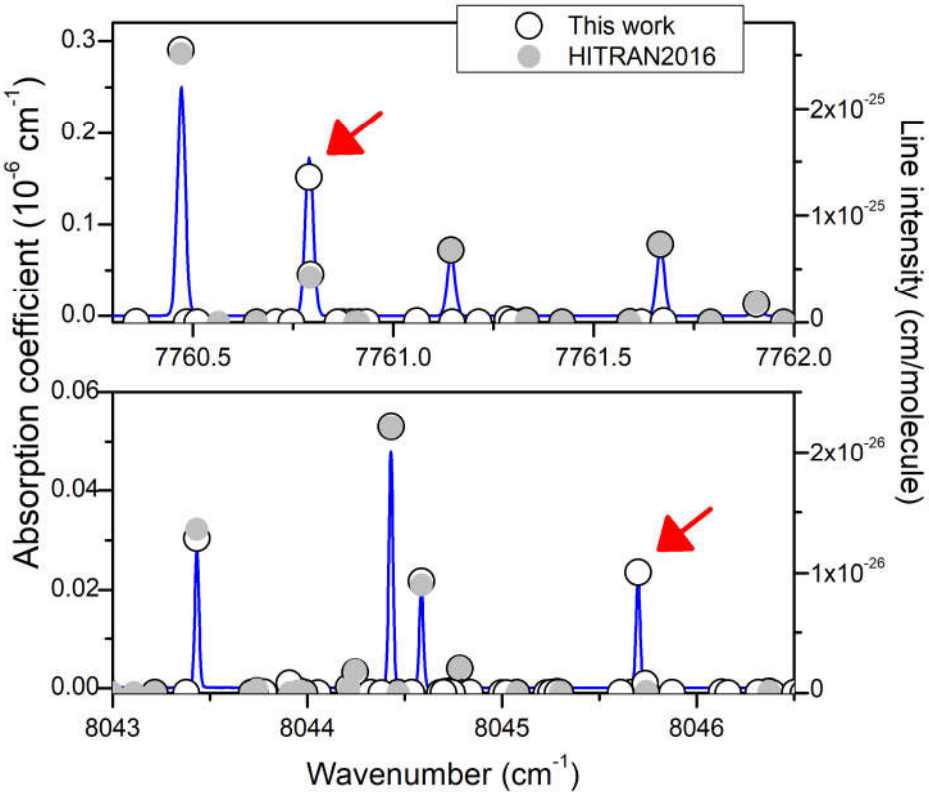

Fig. 4
Relatively strong $H_2{}^{16}O$ lines missing (red arrows) in the HITRAN2016 list. The present line list (open circles) is superimposed to the CRDS spectrum of natural water [16, 20] (blue solid line).

3. Line position comparison

Fig. 5 presents an overview of the differences between position values and those provided in our 2016 list [38], in HITRAN2016 [7], by Conway *et al.* [44], and the SP variational values [45]. The comparison is limited to the three first isotopologues and the position differences are plotted *versus* the line intensity in order to distinguish the weak lines for which experimental intensities are less accurate. Note that the comparison applies only to the lines for which an empirical value of the upper energy level was determined by CA-CRDS, CRDS or FTS (the line positions of our list with IUPAC-TG, estimated or variational position values are excluded from the comparison). As expected SP

variational positions show relatively large deviations. It is worth noting that SP average deviations are close to zero for $H_2{}^{16}O$ and $H_2{}^{18}O$ while $H_2{}^{17}O$ SP positions are systematically overestimated by about 0.25 cm^{-1} on average.

Compared to our 2016 list, a significant number of deviations are noted for the two minor isotopologues (in particular $H_2{}^{17}O$). This is due to the recent extension of the set of empirical energy levels of these two species [23-26, 41-43]. Most of the large deviations are related to newly determined energy levels for which SP variational values were used in the 2016 list (see for instance the set of large positive deviations around 0.25 cm^{-1} observed for $H_2{}^{17}O$).

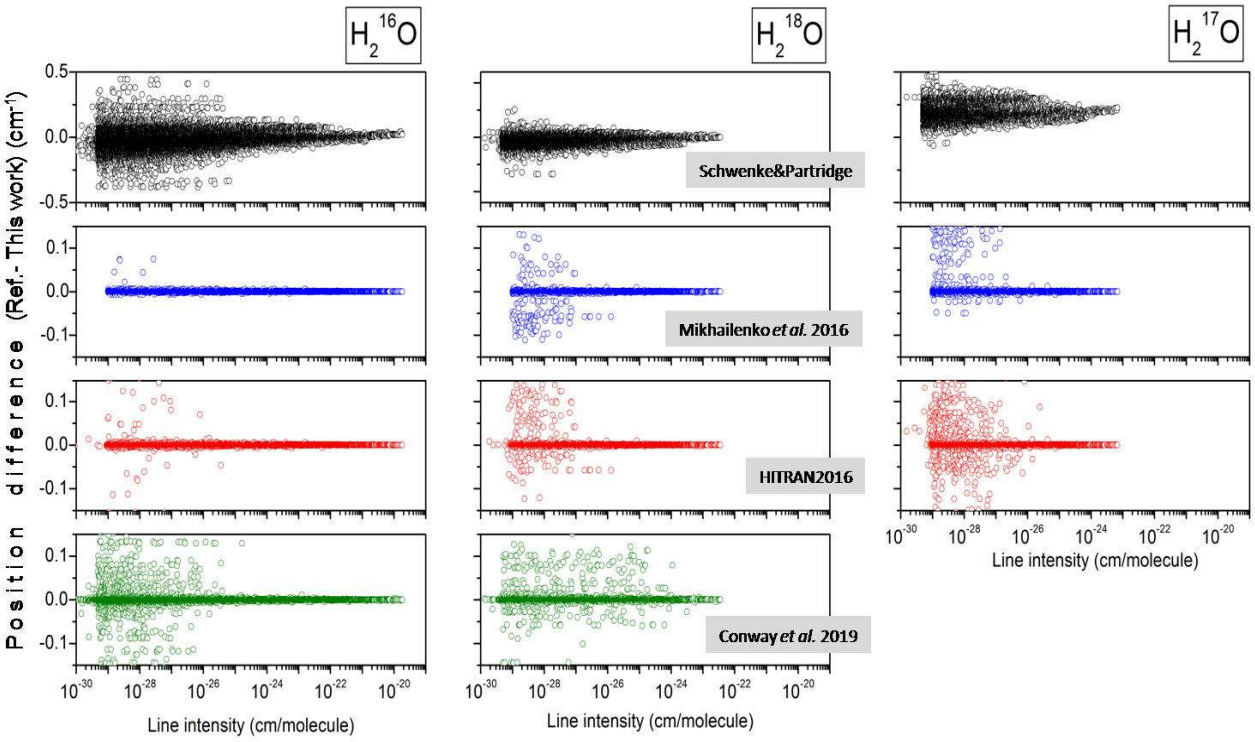

Fig. 5
Overview of the deviations between our position values and the values provided in different references (from to bottom): variational positions from Schwenke and Partridge (black) [1,2,45], our 2016 list (blue) [38], HITRAN2016 (red) [7] and Conway *et al.* (green) [44]. Note the different scale used for the SP deviations.

Fig. 5 illustrates the good agreement of the present and HITRAN positions of the main isotopologue. This simply reflects the fact that our 2016 list was adopted as HITRAN source for about 80% of the $H_2{}^{16}O$ positions in the region. For the $H_2{}^{18}O$ and $H_2{}^{17}O$ positions, a significant number of deviations are noted mostly due to variational position values used in HITRAN. Among the six sources used for HITRAN2016 positions in the region, most of the important deviations compared to the present position values are related to a variational value of the upper level, an erroneous determination of the IUPAC-TG energy level or some Toth's values. For instance; the maximum deviation ($\delta\nu$ = 4.898 cm^{-1}) concerns the $\nu_1+2\nu_2$ $12_{1\,12} - 12_{2\,11}$ transition observed at 6511.519 cm^{-1}

[14, 18] but reported by Toth [53] at 6516.418 cm^{-1}. Note that this last line corresponds to the hot transition $\nu_1+3\nu_2-\nu_2$ $7_{1\,7} - 8_{0\,8}$. Transition frequencies reaching the (040) $14_{8\,6}$ upper level shows inconsistencies: while the HITRAN line positions of the $4\nu_2$ $14_{8\,6} - 13_{5\,9}$ (7781.700 cm^{-1}) and $14_{8\,6} - 13_{7\,7}$ (7441.155 cm^{-1}) and $4\nu_2-\nu_2$ $14_{8\,6} - 13_{1\,13}$ (6977.101 cm^{-1}) transitions coincide with our values, the $4\nu_2$ $14_{8\,6} - 15_{1\,15}$ (8010.110 cm^{-1}) transitions deviates by 0.182 cm^{-1}. The line positions of the first three line centers were taken from our 2016 database [38] while the inaccurate position value is a variational value [48] provided without complete vibration-rotation assignment in HITRAN.

Unexpectedly, the $H_2{}^{16}O$ and $H_2{}^{18}O$ positions very recently reported by Conway *et al.* [44] show larger deviations than the HITRAN positions. No information is given about the experimental sources used by Conway *et al.* to determine their MARVEL energy levels. This lack of knowledge (and recognition) of the experimental results considered in the "MARVELization" of the measured transition frequencies hinders to trace the origin of these erroneous line positions. Our analysis in the 5690-8340 cm^{-1} region, does not support the proposition of Conway *et al.* to use their $H_2{}^{16}O$ and $H_2{}^{18}O$ lists to update the water vapor line list in the next edition of the HITRAN database [44].

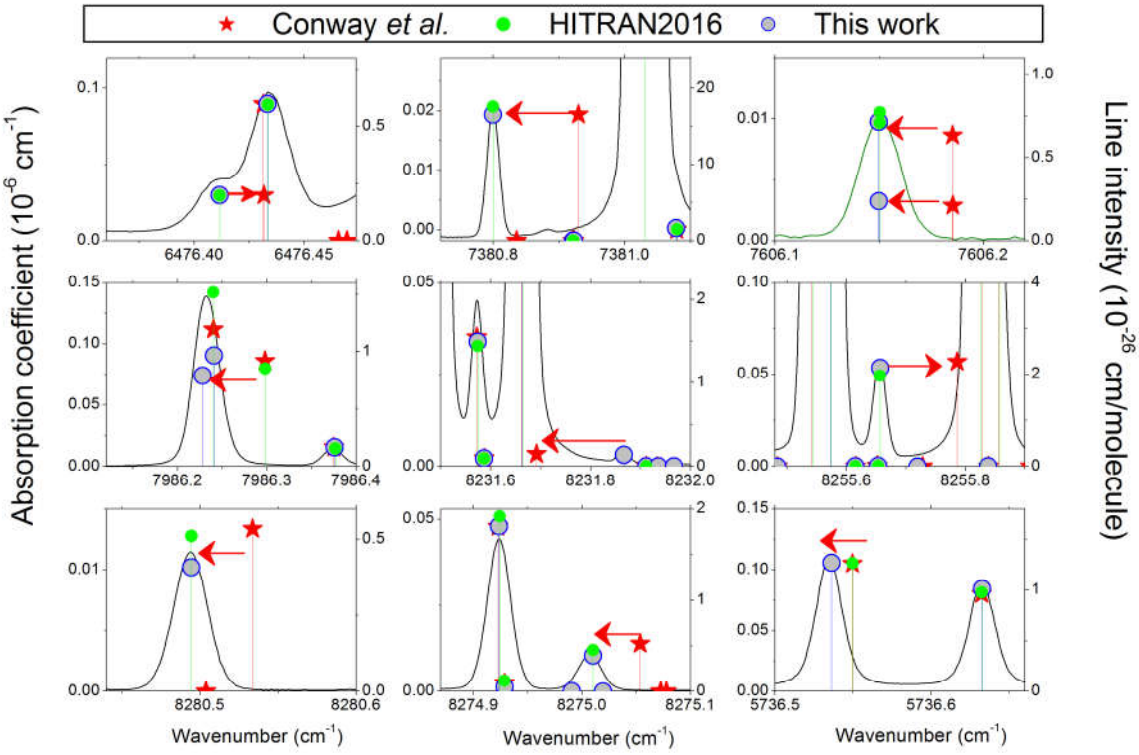

Fig. 6
Inaccurate positions of $H_2{}^{16}O$ lines in the HITRAN2016 list and in the list by Conway *et al.* [44] (full green circles and red stars, respectively). The present line list (full grey circles) is superimposed to the CRDS spectrum of natural water [16-20].

Nine examples of $H_2{}^{16}O$ transitions with inaccurate positions in the list of Conway *et al.* are illustrated on **Fig. 6** and compared to CRDS spectra of natural water [16-20]. The chosen examples

sample the entire 5690 – 8340 cm^{-1} range. The HITRAN stick spectrum superimposed on the plots (green circles) indicates that for only two of the nine plotted examples, HITRAN2016 positions disagree with the CRDS spectra. The two inaccurate HITRAN frequencies are those of the $\nu_1+\nu_2$ $15_{6\,10}$ – $14_{5\,9}$ and $5\nu_2$ $11_{3\,9}$ – $12_{0\,12}$ transitions at 5736.5361 and 7986.2015 cm^{-1}, respectively. Their positions were computed using inaccurate empirical IUPAC-TG energy of the (110) $15_{6\,10}$ and (050) $11_{3\,9}$ upper levels, respectively [13]. Correct values of the considered frequencies were included in our 2016 list [38].

4. Line intensity comparison

In Ref. [38], we provided a line list in the 5850 – 8340 cm^{-1} with empirical line positions and experimental values of the line intensities when available. FTS [27, 53] and CRDS [14-18, 20, 37] intensity values were used for the strong lines and weaker lines, respectively (see Fig. 5 of Ref. [38]). As in the present work, the list was made complete by including a number of weak transitions not yet measured, with empirical positions and SP variational intensities. Note that part of the same sets of FTS and CRDS intensity values are incorporated in the HITRAN2016 list. The discussion about the relative merit of experimental and variational line intensities was included in Ref. [38] and is not repeated here.

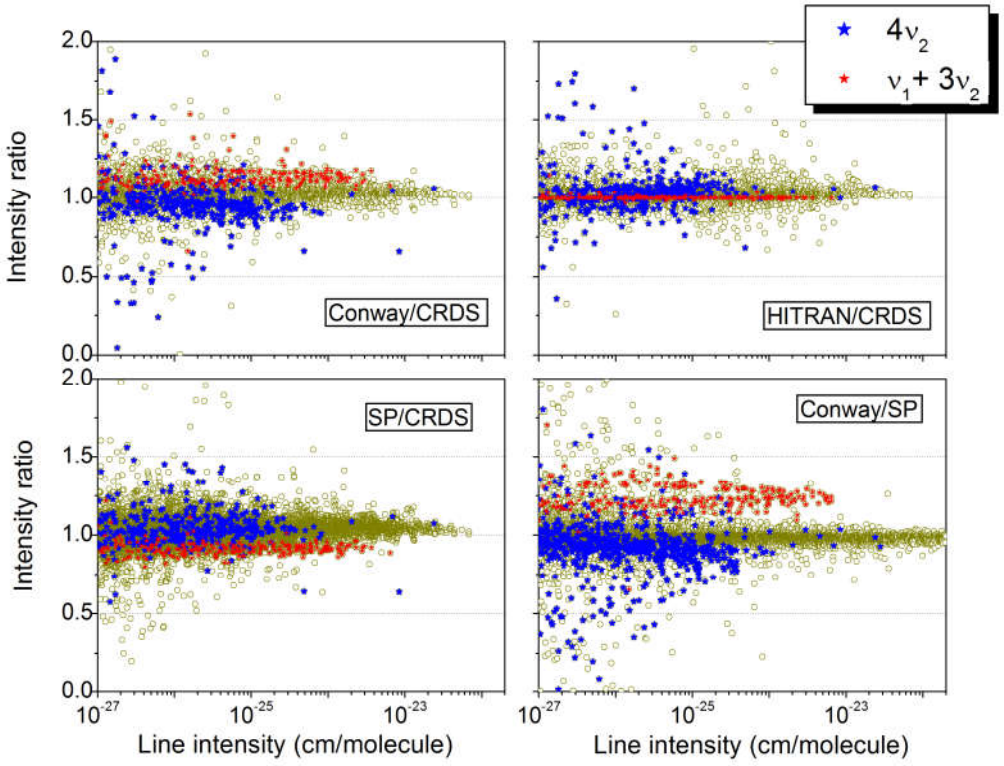

Fig. 7

Intensity ratios for the $H_2{}^{16}O$ main isotopologue. The values relative to the $4\nu_2$ and $\nu_1+3\nu_2$ transitions are highlighted (blue and red stars, respectively). The CRDS values are limited to lines of Refs. [] with intensity larger than 10^{-27} cm/molecule not affected by strong blendings with nearby lines are considered (see Text).

Overall a set of more than 20000 line intensities were measured by CRDS in Refs. [14-18, 20] but no individual error bars were attached to this large set of measurements. In the case of well-isolated $H_2{}^{16}O$ lines of intermediate intensity, a 2-5% relative accuracy was uniformly estimated [38] but the lines in questions were not identified. In the present work, we examined in details the spectra and selected the isolated $H_2{}^{16}O$ lines for which the intensity determination is believed to be most reliable. Only lines with intensity larger than 1×10^{-27} cm/molecule were considered. The following comparison is thus limited to these selected intensity values, about 5000 in total, which are listed in the Supplementary Material (see **Fig. 2**). Note that in the 7408 – 7920 cm^{-1} strong absorption region [16], low pressure values (≈0.1 Torr) were used for the CRDS recordings and a systematic error due to the pressure gauge calibration was evidenced [16, 37]. This systematic bias was corrected by applying a 1.044 multiplication factor to the intensities in the considered region (as done in the 2016 list [38]).

Fig. 7 presents an overview of the ratios of SP, HITRAN and Conway *et al.* intensities to the CRDS values of the 5000 selected $H_2{}^{16}O$ lines. Most of the HITRAN intensities have variational origin (from the BT2 [52] and Lodi *et al.* [55] line lists) but part of the CRDS intensity values [16, 17, 20, 36, 37] were adopted in the HITRAN list. An increasing dispersion of the ratios is observed for the lower intensities. A larger uncertainty on the experimental intensities of the weak lines is not believed to be the main reason of this observation. Indeed, the comparison between SP intensities and the semi empirical intensities by Conway *et al.* [44] (right panel of **Fig. 7**) shows similar or even larger dispersion.

Several studies have shown that the line intensities of pure bending bands are difficult to be predicted by theory [17, 18]. In **Fig. 7**, intensity ratios relative to the $4\nu_2$ and $\nu_1+3\nu_2$ bands are highlighted. Large differences are noted between SP and Conway intensities with a large dispersion for the $4\nu_2$ band and a systematic shift of about 25 % for the $\nu_1+3\nu_2$ band. It is interesting to note that the experimental values of the $\nu_1+3\nu_2$ transitions are on average intermediate between the two calculations: SP intensities are underestimated by 10 % while Conway intensities are overestimated by 15 %. We also note that the dispersion of the intensity ratios is smaller when compared to SP than to Conway *et al.* (HITRAN intensities of the $\nu_1+3\nu_2$ transitions were taken from our CRDS study [20]).

On average, SP variational values of the $4\nu_2$ band are closer to experiment than the recent semi-empirical values of Conway *et al.* which appear to be underestimated on average. We present in **Fig. 8** nine examples of comparisons between the various line lists and the CRDS spectra of Refs. [17, 18] showing discrepancies of the line intensities. Six of the displayed examples are relative to the $4\nu_2$ band and three concern transitions of the $\nu_1+2\nu_2$ band. Other clear examples were found for transitions of the $5\nu_2$, $\nu_1+\nu_3$ and $6\nu_2$ bands.

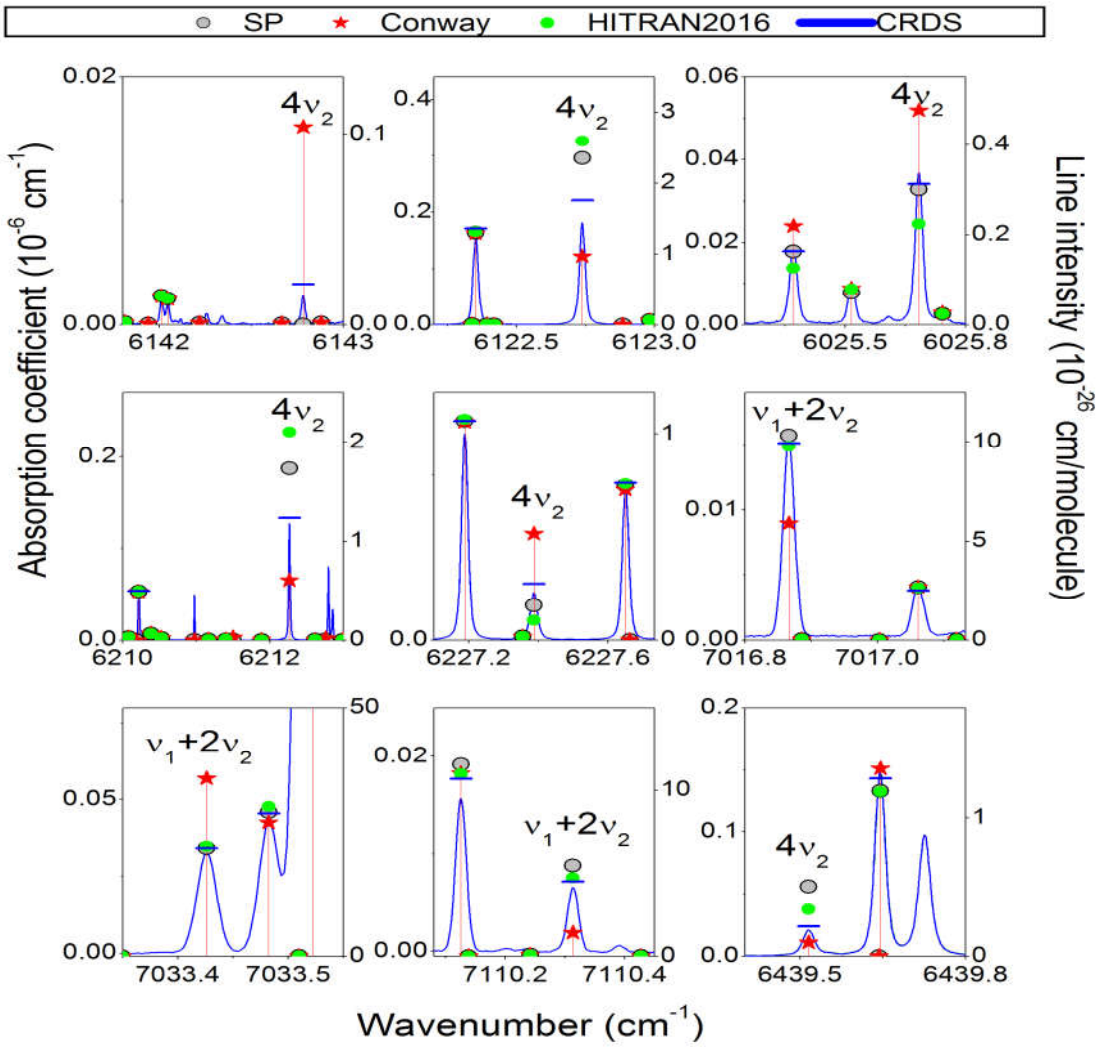

Fig. 8

Examples of disagreement between calculated intensities and the observed spectrum of natural water vapor. Line lists of the $H_2{}^{16}O$ main isotopologue as provided by Schwenke and Partridge (full grey circles), by the HITRAN2016 database (full green circles), by Conway *et al.* [44] (red stars) are compared to CRDS spectra. The blue hyphens correspond to the experimental CRDS intensities as reported in Refs. [17,18]. The problematic lines which belong to the $4\nu_2$ and $\nu_1+2\nu_2$ bands are indicated.

5. Concluding remarks

In the recent years, a relatively high number of theoretical line lists have been computed for water vapor. Although often called "calculated" line lists, their line positions have an experimental origin and credits should be given to considerable experimental efforts performed over several decades and used to compute their accurate line positions. The direct confrontation of the available line lists produced by different approaches to high quality spectra is a laborious and necessary validation task. Atmospheric validation provides tests in particular for the profile of air-broadened water lines but as concerned line centers, line intensities and completeness, high sensitivity recordings of pure water vapor at low pressure are necessary. In the present work, the CRDS spectra recorded in Grenoble over

nearly two decades were used to test the HITRAN2016 list [7] which is the standard list used for atmospheric applications. In the transparency windows, the sensitivity of our CRDS spectrometers allows detecting lines with intensity as small as the 10^{-29} cm/molecule HITRAN intensity cut-off [18]. This is significantly lower than the weakest lines which can be detected in atmospheric spectra. We have also considered in details the lists very recently released by Conway *et al.* [44] for $H_2{}^{16}O$ and $H_2{}^{18}O$ with intensities calculated from semi-empirical potential energy surfaces. According to the authors, their new dipole moment surface provides excellent calculated intensities and corrects some biases of their preceding POKAZATEL list [54] and their lists will be used to update many transition intensities and line positions in the HITRAN2016 database [44].

As concerned line positions, the IUPAC-TG approach consisting to collect and evaluate all the position measurements available in the literature in order to derive recommended values of the empirical energy levels by inversion of the transition frequencies using the MARVEL procedure, has proved to be efficient. Nevertheless, in absence of direct examination of the spectra, the weighting of frequency values according to their real accuracy is a major issue [11-13]. As said above the inclusion of a considerable number of transition frequencies reported with multiple assignments from highly congested emission spectra has degraded the quality of part of the IUPAC-TG empirical energy levels.

In the present updated version of the 2016 list of Ref. [38] covering the 5690 – 8340 cm^{-1} range, the set of empirical energy levels used to compute the line centers has benefited from a large set of new measurements by CRDS referenced to a frequency comb. This CA-CRDS data [25, 26] allowed achieving in routine an accuracy of the line center determination at the 10^{-4} cm^{-1} level for well isolated lines. We believe that the line list provided as supplementary material gathers most of the high quality experimental information at disposal for line positions in the considered region. In contrast with the HITRAN2016 and calculated lists, each transition is provided with unique rovibrational labeling (see **Fig. 2**) and the ambiguities in the vibrational labeling have been resolved using effective Hamiltonian calculations.

HITRAN line positions [7] used six sources for the $H_2{}^{16}O$ line positions in the region (eleven sources for the first six isotopologues). Although, important improvements were incorporated in the 2016 HITRAN list, a number of issues remain to be fixed concerning erroneous rovibrational assignments (including a number of ortho-para transitions), a small number of missing lines and inaccurate line positions and line intensities. As concerned the recent list of Conway *et al.* [44], it shows larger deficiencies in terms of line position accuracy. It seems that the set of empirical energy levels used for frequency calculations has to be significantly revised or updated using recent observations. In the considered region, our results clearly indicate that the line positions of the list of Conway *et al.* should not be used to update the HITRAN list (see **Figs. 5** and **6**). Other minor issues concerning the list of Conway *et al.* are that it is limited to *J* values smaller than 21 and thus some transitions are missing, it includes a high number duplicate transitions in the $H_2{}^{18}O$ list (263 in our

region) and it does not solve the intensity problem of the bending bands (*e.g.* $4\nu_2$, $5\nu_2$, $\nu_1+3\nu_2$) -see **Fig. 7**.

The laborious evaluation of different theoretical line intensities on the basis of the CRDS recordings of Refs. [14-20], suggests that at present, none of the line lists at disposal predicts all the observations in the considered region at experimental accuracy (a few % for isolated lines). Some of the most recent line lists show deviations comparable of even worse than the twenty-year old results obtained by Schwenke and Partridge [1, 2, 45]. To the best of our knowledge, no coherent set of line lists equivalent to the SP lists of the six required isotopologues is available in the literature. As demonstrated by Conway *et al.*, their list represents important improvements compared to SP for the intensities at high energy [44], in particular in the visible but in the very important near-infrared region presently considered we did not find improvement concerning line intensities compared to the SP list of $H_2{}^{16}O$ (see **Fig. 7**).

The best intensity column for water vapor remains thus an open issue for the spectroscopic databases. Compared to measurements, calculations have unique advantages in particular in case of strong line overlapping, very weak lines or for the minor isotopologues and the determination of tens of thousands line intensities with 1% accuracy is out of reach experimentally. Nevertheless, for a more or less important fraction of the transitions, all the considered calculated lists show deviations larger than the experimental uncertainty. The best compromise is thus to use calculated intensities as default values and replace them by experimental values when clear deficiencies are evidenced. Taking into account the difficulties to estimate quantitatively the uncertainties on the calculated and measured (when available) intensity values, the criterion of preference between theoretical or experimental intensities remain to be defined.

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