The absorption spectrum of water vapor in the 2.2 μm transparency window: high sensitivity measurements and spectroscopic database

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Abstract

The weak absorption spectrum of water vapor in the important 2.2 μm transparency window is investigated with very high sensitivity. Overall, about 400 absorption lines were measured by Cavity Ring Down Spectroscopy (CRDS) and Optical-Feedback-Cavity Enhanced Laser Spectroscopy (OF-CEAS) in five spectral intervals: 4248.2-4257.3, 4298.4-4302.6, 4336.8.5-4367.5, 4422.4-4441.2 and 4514.6-4533.7 cm^{-1} . The achieved sensitivity of the recordings (noise equivalent absorption, α_{min} , on the order of $2 \times 10^{-10} \text{ cm}^{-1}$) allowed detecting transitions with intensity values down to $1 \times 10^{-28} \text{ cm/molecule}$, more than one order of magnitude better than previous studies by Fourier Transform spectroscopy. The rovibrational assignment was performed on the basis of variational calculations and of previously determined empirical energy values. Most of the newly assigned lines correspond to transitions of the ν_1 , ν_3 and $3\nu_2$ bands of H_2^{17}O in natural isotopic abundance. Fourteen energy levels of H_2^{17}O , H_2^{18}O and HD^{18}O are newly determined.

An accurate and complete spectroscopic database is constructed for natural water in the 4190–4550 cm^{-1} region (2.39 – 2.20 μm). The list includes about 4500 transitions with intensity greater than $1 \times 10^{-29} \text{ cm/molecule}$, for the six most abundant isotopologues in natural isotopic abundance. Line positions were obtained by difference of empirical energy values determined from literature data and complemented with the present CRDS results. The list is made mostly complete by including weak transitions not yet detected, with positions calculated from empirical levels and variational intensities. The variational intensities computed at University College London are found to improve significantly previous results by Schwenke and Partridge. Examples of comparison of the constructed line list to CRDS spectra and to simulations based on the HITRAN2012 list illustrate the advantages of the list combining our empirical line positions and UCL variational calculations. The absence of many HDO lines is identified as most important deficiency of the HITRAN2012 list in the region.

1. Introduction

The 2.2 μm atmospheric window corresponds to a spectral region of weak absorption of the Earth atmosphere of particular importance for trace gas detection and astronomical observations. For instance, the Total Carbon Column Observing Network (TCCON) [1], the SCIAMACHY satellite [2], the future TROPOMI/Sentinel 5 and its precursor [3] and the Geostationary Emission Explorer [4] are using (or will use) this particular window to retrieve methane, carbon monoxide or nitrous oxide. Because of possible interference with absorption lines used to retrieve the target trace gases, an accurate characterization of the weak water absorption is a prerequisite for trace detection in the region. For instance, the insufficient knowledge of the water spectroscopy in the 2.3 μm region has been identified as an important error source for the TROPOMI/Sentinel 5 precursor ESA mission [5].

In the present work, we measure weak water lines in the 2.2 μm window by high sensitivity laser spectroscopy, mainly Cavity Ring Down Spectroscopy (CRDS). As laser sources at disposal do not allow for a continuous coverage of the window, five spectral intervals of the 4190-4550 cm^{-1} region, accessible with four Distributed Feed Back (DFB) diode lasers and a VECSEL (Vertical external Cavity Surface Emitting Laser), are used to record the spectra with unprecedented sensitivity, providing valuable data to test the most currently used spectroscopic databases, in particular the HITRAN database [6].

After the description of the CRDS recordings and of the line list construction (Section 2), we will present in Section 3 the rovibrational assignment of the newly detected transitions on the basis of previously determined empirical energy values and of variational calculations by Schwenke and Partridge (SP) [7, 8]. In Section 4, an accurate spectroscopic database is constructed for natural water in the 4190–4550 cm^{-1} region and the most recent variational calculations performed at University College London (UCL). Finally, the obtained global list including about 4500 transitions of the six most abundant isotopologues (H_2^{16}O , H_2^{18}O , H_2^{17}O , HD^{16}O , HD^{17}O , HD^{18}O) is tested and validated using previous measurements by Fourier Transform Spectroscopy (FTS) and the present CRDS/OF-CEAS results.

2. Experiment

Table 1 lists the five spectral intervals of the spectra recordings together with the corresponding experimental technique and used laser source. Except for a 3 cm^{-1} spectral interval around 4300 cm^{-1} studied by Optical-Feedback-Cavity Enhanced Laser Spectroscopy (OF-CEAS), the spectra were recorded with a recently developed CRDS spectrometer.

Both techniques use the measurement of the cavity response time (ring-down, τ) to retrieve the absorption coefficient of the studied gas sample, $\alpha(\nu)=n/c\tau$ (ν is the wavenumber, c is the speed of light and n is the refractive index considered as equal to 1). In CRDS [9-11], this is done by measuring sequences of ring downs for each spectral point, whereas in OF-CEAS a single ring down measurement is used to calibrate a feedback enhanced low noise transmission spectrum of the optical cavity for given laser frequency scan [12-14].

Table 1

Summary of the CRDS and OF-CEAS measurements of the absorption spectrum of water vapor in the $2.2\text{ }\mu\text{m}$ window

Spectral interval (cm^{-1})	Method	Laser source ^a	T (K)	Regime/Pressure	Main impurities	Number of lines
4248.2-4257.3	CRDS	DFB	298	Static/1, 4, 8.5 Torr	NH_3 , CH_4	55
4298.4-4302.6	OF-CEAS	DFB	323	Flow/ 7.6 Torr	NH_3	23
4336.8-4367.5	CRDS	VECSEL	297	Flow/ 7-8 Torr	NH_3	150
4422.4-4441.2	CRDS	DFB	297	Static/ 7-8 Torr	NH_3 , CH_2O , CH_4	82
4514.8-4533.7	CRDS	DFB	296.3 ± 0.5	Flow/ 8 Torr	NH_3 , CH_2O	81

Note.

^a DFB: Distributed Feed Back diode laser; VECSEL: Vertical External Cavity Surface Emitting Laser.

The reader is referred to Refs. [15-17] and Refs. [12-14, 18] for detailed descriptions of our CRDS and OF-CEAS spectrometer, respectively. Briefly, the same CRDS cavity (1.42 meter long stainless steel cylinder with 10 mm diameter fitted by two super mirrors) was used for all of the CRDS recordings. The finesse of the cavity varied from 78000 around 4250 cm^{-1} to 50000 around 4520 cm^{-1} (corresponding to ring down times of 120 and 76 μs , respectively). The laser high-finesse cavity (HFC) coupling was very similar in all of the CRDS spectrometers: after passing through an acousto-optic modulator (AOM) the beam was injected into a single mode fluoride fiber for spatial mode filtering. On the output, a series of mode matching mirrors and lenses (adapted for each wavelength region) was used to superpose the beam on the HFC transverse electromagnetic mode 00. The resonance between the laser light and a longitudinal mode of the cavity was achieved by changing the cavity length over one Free Spectral Range (FSR) thanks to the rear mirror of the cavity mounted on a piezoelectric transducer. At resonance, the injection of the laser beam into the cavity was interrupted with the AOM and a ring down time was measured with a long wavelength type InGaAs PIN photodiode.

The DFB diode lasers were frequency tuned over about 20 cm^{-1} by changing the temperature step by step, the laser current being fixed. The spectral coverage allowed by the VECSEL was achieved by stabilizing the VCSEL sample at different temperatures from $-4 \text{ }^{\circ}\text{C}$ to $+10 \text{ }^{\circ}\text{C}$ and applying a current of typically 340 to 380 mA to the pump laser diode. Six individual spectra corresponding to different temperature-pump current conditions were needed to cover the $4337\text{-}4367 \text{ cm}^{-1}$ spectral range. A detailed description of the characteristics of the CRDS-VECSEL set up and a discussion of its performances compared to those of CRDS-DFB can be found in Ref. [16]. As first applications of our CRDS-VECSEL set up, we have recently reported the new detection of a very weak $S(3) 1\text{-}0$ quadrupole electric transition of HD [19] and the characterization of the very weak CO_2 spectrum near 4350 cm^{-1} with unprecedented sensitivity [20, 21].

The typical Limit Of detection (LOD) of the spectra, ranges between 1 and $6 \times 10^{-10} \text{ cm}^{-1}$ for both DFB and VECSEL light sources (The LOD is evaluated as the 1σ standard deviation on a section of the spectrum baseline free of absorption lines). It is worth mentioning, that in the $4422.4\text{-}4441.2 \text{ cm}^{-1}$ region, an optical feedback narrowing scheme similar to that proposed by Lin et al. [22] was applied to increase the HFC injection efficiency and improve the absorption sensitivity. The feedback was produced by an external mirror mounted on a piezoelectric transducer in order to insure a fine frequency tuning (within the FSR of the laser external cavity). As a result, the limit of detection can be improved. For instance, a LOD of $\alpha_{\min} \sim 1.2 \times 10^{-11} \text{ cm}^{-1}$ was achieved after one day of spectra averaging, allowing for the first detection of a line of the first overtone band of N_2 (line intensity of about $1.5 \times 10^{-30} \text{ cm/molecule}$) [17].

The frequency calibration of the CRDS-DFB spectra relied on the frequency measurements provided by a lambda meter (model 621-A IR from Bristol) with a refresh rate of 2.5 Hz. To refine the calibration, some accurate reference lines (water, methane or carbon dioxide) from the HITRAN database [6] were used to correct the lambda-meter offset (around 0.006 cm^{-1}), leading to an absolute precision of $\pm 0.001 \text{ cm}^{-1}$.

The frequency calibration of the CRDS-VECSEL spectra was achieved by deflecting about 10% of the light emitted by the VECSEL to a double reference channel composed of a Fabry-Pérot étalon and of a 6 cm reference cell filled with CH_4 at atmospheric pressure. The fringes of the Fabry-Pérot signal (0.05 cm^{-1} FSR) were used as a ruler to correct the non-linearity of the PZT and temperature scanning. After linearization of the frequency axis, a rough absolute spectral calibration was performed using the spectrum of the methane reference cell. The calibration was then refined by using accurate water reference lines from the HITRAN database [6]. We estimate the error on the reported line positions to be about $\pm 2 \times 10^{-3} \text{ cm}^{-1}$, mostly limited by the error related to the linearization of the frequency axis using the étalon fringes.

The measurements were performed with purified water vapor either in a static cell or in flow. The flow of water vapor was regulated with a downstream proportional electro-valve controlled by a

proportional-integral loop to maintain a constant pressure inside the CRDS cell. In both static and flow regimes, the water vapor pressure in the cell was continuously monitored with a capacitive transducer (in the line intensity calculation, we used for each line the pressure value at the recording time). The flow was necessary to minimize the impact of impurity lines due to desorption from the cell (see below).

The CRDS spectrum recorded with the VECSEL presented in **Fig. 1** illustrates the performances in terms of sensitivity and dynamics on the intensity scale.

Fig. 1

CW-CRDS spectrum of water vapor near 4353 cm^{-1} recorded with a VECSEL. The sample pressure was about 7.6 Torr. Three successive enlargements illustrate the sensitivity and high dynamics of the recordings allowing for the measurement of absorption coefficient spanning more than four orders of magnitude.

The line centers and intensities were determined using an interactive least squares multi-line fitting program assuming a Voigt profile, the HWHM of the Gaussian component being generally fixed to the theoretical value of the Doppler width. It is difficult to give an average uncertainty value for line intensities. Comparisons with literature values and between various determinations from different CRDS spectra indicate that a value of 2-5% is a reasonable estimate for well-isolated H_2^{16}O lines of intermediate intensity. Larger error bars should be attached to blended lines and the relative abundance of the minor isotopologues adds uncertainty to the line intensities of these species.

The number of water lines derived in the five studied spectral intervals is included in **Table 1**. Overall a total of 391 absorption lines was measured. The smallest line intensities are on the order of 1×10^{-28} cm/molecule, more than one order of magnitude better than previous studies by Fourier Transform spectroscopy (see below). Let us mention that due to impurity lines and a few narrow gaps in the recordings, a number of water lines are missing in our experimental list.

3. Rovibrational assignments

The first step of the analysis consisted in “cleaning” the recorded spectra from impurity lines. Indeed, lines of NH_3 , CH_4 and CH_2O (formaldehyde) were found superimposed to the weak water vapor lines of interest. The lines due to ammonia and methane were identified by comparison with the HITRAN2012 database [6]. In spite of our attempts to minimize their concentration, ammonia (which is believed to come from the water sample itself), and methane contribute significantly to the spectra because their strongest lines have an intensity on the order of 10^{-20} cm/molecule, *i.e.* eight orders of magnitude larger than our detectivity threshold for water lines. The relative concentration of ammonia and methane was estimated to be a few ppm. The presence of formaldehyde which is probably desorbing from the set up was significantly minimized in flow regime but many lines were identified in the high energy part of the spectrum where formaldehyde absorption is very strong. As no data are provided by the HITRAN database in the studied region, the CH_2O lines were identified by comparison with an FTS spectrum available in open access at the Kitt Peak data center (Ref. 840109R003). Note that the formaldehyde spectrum in the $2.3 \mu\text{m}$ range was investigated in Refs. [23,24] (some lines are rovibrationally assigned). A rough estimation using the FTS spectrum displayed in Ref. [24] indicates that the CH_2O relative concentration in our sample was at most 5 ppm.

The rovibrational assignment of the remaining lines uses as starting point the variational calculation results of Schwenke and Partridge [7, 8] and the values of empirical energy levels of 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) recommended by an IUPAC-task group (IUPAC-TG) [25-28].

Finally, 391 lines have been assigned to 443 transitions of six water isotopologues (H_2^{16}O – 183 transitions, H_2^{18}O – 39 transitions, H_2^{17}O – 20 transitions, HD^{16}O – 201 transitions, HD^{18}O – 5 transitions, and HD^{17}O – 2 transitions). Among the 391 measured lines, 189 are detected for the first time.

Table 2.

Term values of newly determined and corrected energy levels.

Isotopologue	vib	J	K_a	K_c	Value (cm ⁻¹)
H ₂ ¹⁷ O	001	12	3	10	5673.0696
	001	14	4	10	6584.4038
	030	4	2	2	5022.7917
	030	5	3	2	5274.1795
	030	6	0	6	5107.3902
	030	6	1	5	5229.4875
	030	8	2	7	5602.2807
	100	12	3	10	5577.3413
	100	13	2	11	5853.7726
	100	13	3	11	5853.7288
	100	13	3	10	6020.7478
H ₂ ¹⁸ O	001	14	7	8	6916.5464
HD ¹⁸ O	110	7	6	2	5115.1082
	110	7	6	1	5115.1082

Note that the detection of lines of HD¹⁸O and HD¹⁷O with natural abundance of 6.23×10^{-7} and 1.16×10^{-7} , respectively, illustrates the sensitivity of the recordings [5]. The important contribution of the deuterated species is similar to that found in the 1.58 and 1.25 μm windows [29-32] and results from the strong isotopic shifts of the vibrational frequencies by H→D substitution.

The rovibrational assignments allowed determining 14 new energy levels of three isotopologues (H₂¹⁷O, H₂¹⁸O and HD¹⁸O) listed in **Table 2**. Eleven of them correspond to transitions of the ν_1 , ν_3 and $3\nu_2$ bands of H₂¹⁷O. Note that the (001) 12_{3 10} level was obtained from the ν_1 12_{3 10} – 11_{1 11} transition at 4348.9409 cm⁻¹. This line was measured and assigned by Jenouvrier et al. [33] but not included in the IUPAC database [25].

The (110) 7_{6 2} and (110) 7_{6 1} levels of HD¹⁸O were previously determined by Liu et al. with an isotopically enriched sample [34] but their energy value relied on an erroneous assignment of the $\nu_1 + \nu_2$ 7_{6 1} – 7_{6 2} and $\nu_1 + \nu_2$ 7_{6 2} – 7_{6 1} transitions at 4144.596 cm⁻¹. These data were included in the IUPAC database [26]. The difference between our values (5115.108 cm⁻¹) and those of Refs. [26, 34] (5114.496 cm⁻¹) is larger than 0.6 cm⁻¹.

Fig. 2

Comparison of the main experimental studies of water absorption in the 2.2 μm window to the line list provided by the HITRAN2012 database. The four spectral intervals presently studied by CRDS and OF-CEAS are highlighted. Previous studies were performed by FTS by Toth [35] (blue circles), Jenouvrier et al. [33] (light blue cross), Loos et al. [36] (“DLR”, orange circles) and Mikhailenko et al. [37] (“Giessen”, green stars).

Our experimental list including CRDS and OF-CEAS line positions and intensities, corresponding SP values [7, 8] and full rovibrational assignment is provided as Supplementary Material. An overview comparison to the HITRAN2012 water line list between 4190 and 4550 cm^{-1} is presented on **Fig. 2**. The HITRAN2012 list includes lines of the H_2^{16}O , H_2^{18}O , H_2^{17}O and HD^{16}O isotopologues with intensity larger than 1×10^{-29} $\text{cm}/\text{molecule}$. HITRAN line parameters have experimental or theoretical origins. For instance, among the 2303 transitions included in HITRAN, less than 700 are provided with experimental intensities. These experimental intensity values, all belonging to H_2^{16}O and HD^{16}O , were retrieved by Toth from FTS spectra recorded at Kitt Peak with absorption path length up to 433 m [35]. The minimum intensity values reported by Toth are on the order of 1×10^{-26} $\text{cm}/\text{molecule}$, about two orders of magnitude above our detectivity threshold. A more detailed discussion of the HITRAN line list is presented Section 5.

For comparison purpose, we have also included in **Fig. 2** three additional FTS line lists reported in the region: (i) the most complete previous line list is due to Jenouvrier et al. who measured lines with intensities down to about 1×10^{-27} $\text{cm}/\text{molecule}$ from FTS spectra recorded in Reims with pathlengths up to 1203 m [33], (ii) very recently, in the frame of the ESA project SEOM-Improved Atmospheric Spectroscopy Databases (IAS), accurate spectroscopic parameters of water lines were measured at DLR [36]. The DLR study was focused on the strongest water lines in the 4190-4350 cm^{-1} region which interfere with the CO and CH_4 atmospheric lines used by the TROPOMI instrument

aboard the Sentinel-5 precursor, (iii) finally, Mikhailenko et al. reported a line list from FTS spectra recorded at Giessen with pathlength of 288.5 m and pressure up to 24 Torr [37].

4. An accurate spectroscopic database for water vapor in the 2.2 μm window

In this section, our aim is to construct a complete and accurate database for water vapor between 4190 and 4550 cm^{-1} , following the same procedure as adopted for the 5850-8340 cm^{-1} region [32]. We use as starting point the variational line lists computed by S.A. Tashkun [38] based on the variational calculation results of Schwenke and Partridge [7,8] for each of 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). As it will be shown below, these variational line lists are not the best to date variational lists but they have the advantage of being complete, providing reasonable rovibrational assignment and being publicly available at <http://spectra.iao.ru/> for all the six required isotopologues.

4.1 Line positions

In a first step, the variational line positions were replaced by their corresponding values calculated using empirical values of the lower and upper energy levels. As shown below, in the considered region, this is possible for the quasi totality of the transitions of the six most abundant isotopologues which have lines with intensity larger than 1×10^{-29} cm/molecule. We adopted as empirical values of the energy levels the IUPAC-IUPAC-TG values for the lower states of H_2^{16}O [27] and HD^{16}O [26]. The upper state energies of these two isotopologues have been obtained using the RITZ program [39, 40] and all available absorption data at room temperature. As discussed below, the main differences compared to the IUPAC-TG levels is due to the fact that emission data were involved in the IUPAC-TG determinations but excluded from our experimental datasets. For the lower and upper energies of the H_2^{17}O and H_2^{18}O isotopologues, we adopted those derived in Ref. [41] from hot emission spectra of ^{18}O and ^{17}O enriched water. For HD^{18}O and HD^{17}O , energies of Ref. [42] and Ref. [43] calculated within the effective Hamiltonian approach were used for the lower states while empirical values from Ref. [44] and Ref. [45] were selected for the upper states, respectively. The newly derived or corrected energy levels (**Table 2**) were added to the empirical datasets.

Table 3 gives, for each isotopologue, the number of upper energy levels used to construct the line list. This Table includes in the third column, the number of additional energy levels compared to those of the IUPAC-TG datasets [25-27]. Our energy values were systematically compared to the corresponding IUPAC-TG value, when available. As illustrated by the histograms of the differences displayed in **Fig. 3**, the agreement is not fully satisfactory, in particular for the main isotopologue: excluding outliers with deviations greater than 0.1 cm^{-1} , the average and standard deviations are $+6.3 \times 10^{-4} \text{ cm}^{-1}$ and $4.0 \times 10^{-3} \text{ cm}^{-1}$, respectively, and more than half of the energy levels in common with the IUPAC-TG differ by more $2 \times 10^{-3} \text{ cm}^{-1}$. The IUPAC-TG energy levels considered all the transition frequencies reported in the literature from the microwave to the visible range. In particular,

according to Table 2 of Ref. [27], previous FTS studies in our region by Jenouvrier et al. [33] and Toth et al. [35] were used by the MARVEL procedure [46, 47] to derive the IUPAC-TG energy levels (for an unknown reason the FTS results reported by the Giessen group [37] were missed in the IUPAC-TG review [27]). However, contrary to our set of transitions, the IUPAC-TG dataset includes many hot band transitions from emission spectra in the medium infrared which have a limited accuracy on the order of 0.02 cm^{-1} [48-51]. In those references, as a result of the high spectra congestion at high temperature, the measured emission lines were frequently assigned to several rovibrational assignments leading to an increase uncertainty on the transition frequencies. In Refs. [29, 32, 52], we have discussed in details a number of weighting of the experimental input data used by the MARVEL procedure leading to inaccurate energy values. We believe that most of the deviations between our energy levels and the IUPAC-TG energy levels are due to the impact of such emission transition frequencies on IUPAC-TG values. This is consistent with the fact that the deviations are larger for the main isotopologue than for the minor ones.

Table 3

Upper energy levels used for the construction of the line list of water between 4190 and 4550 cm^{-1} and comparison to the IUPAC-TG energy levels [25-27].

Isotopologue	Number of upper levels used for line list	Upper levels absent in the IUPAC-TG sets [25-27]	Number of levels according to the difference $\delta = E_{\text{This work}} - E_{\text{IUPAC}} $ in 10^{-3} cm^{-1} unit				
			$\delta = 0^a$	$0 < \delta < 2$	$2 < \delta < 10$	$10 < \delta < 100$	$100 < \delta$
H_2^{16}O	942	0	106	629	198	7	2
H_2^{18}O	273	15	186	61	10	1	0
H_2^{17}O	181	90	20	61	7	3	0
HD^{16}O	656	23	548	71	11	3	0
HD^{18}O	192	50	34	96	7	3	2
HD^{17}O	122	122					
Total	2366	300	894	918	233	17	4

Note

^a $\delta = 0$ indicates that the upper energy level value provided by the IUPAC-TG was adopted for the line list construction.

Fig. 3.

Histograms of the differences between the energy levels used to construct our line list between 4190 and 4550 cm^{-1} and their corresponding IUPAC-TG values [25-27] (when available).

Using the derived sets of empirical energy levels, the frequencies of a total of 4338 transitions with SP variational intensity larger than 1×10^{-29} cm/molecule were calculated for the six most abundant water isotopologues. According to SP variational calculations, all the frequencies of the H_2^{16}O transitions can be calculated from empirical energy levels. A total of 133 upper energy levels are missing for H_2^{18}O , H_2^{17}O , HD^{16}O and HD^{17}O leading to a total of 146 very weak transitions without empirical determination of their frequencies, as presented in **Fig. 4**.

Fig. 4

Variational line list by Schwenke and Partridge [7,8] for natural water between 4190 and 4550 cm^{-1} (grey dots). Lines predicted by variational calculations and corresponding to transitions reaching an upper level which is not yet experimentally determined are highlighted with colored symbols. No H_2^{16}O and HD^{18}O lines are missing above the 1×10^{-29} cm/molecule intensity cut off.

4.2 Line intensities

The choice of the line intensities to be associated to the empirical values of the transition frequencies is a difficult issue. In the 5850-8340 cm^{-1} region [32], we used experimental intensity values obtained by FTS or CRDS when available and SP variational intensity values for the large number of weak transitions not yet measured.

In the present case, the CRDS spectral coverage is only partial (**Fig. 2**) and the set of experimental intensities is more limited. On the theory side, a variational line list for natural water vapor has been recently compiled in a consistent way [53] using the most recent line lists calculated for the various water isotopologues by a collaboration between the University College London and the Institute of Applied Physics in Nizhniy Novgorod [54-60]. This list (UCL2016 hereafter) will be used as source of variational intensities for the 2016 version of the HITRAN database [53]. It is believed to improve significantly the overall accuracy of the more than fifteen years old SP variational intensities. Even if it is not complete down to the 1×10^{-29} cm/molecule intensity cut off and if some issues concerning rovibrational assignments and intensities were identified for a very small number of lines, we adopted this UCL2016 list as reference list to compare the available set of line intensities. The

association of the transitions of the UCL2016 list to the other datasets is not straightforward as the UCL2016 list does not provide full rovibrational assignments for a number of lines. In general, UCL2016 variational positions have an accuracy better than 0.05 cm^{-1} but for the majority of the transition frequencies the accuracy is much better, near 0.002 cm^{-1} . Transitions of the UCL2016 list and of the other datasets were considered identical when they fulfill the three following criteria: identical rovibrational quantum numbers of the lower state, identical value of the J rotational quantum number of the upper state and position agreement within a conservative value of 0.3 cm^{-1} .

Fig. 5

Comparison of the various sets of intensity data available for natural water between 4190 and 4550 cm^{-1} . Ratios of the FTS [33, 35, 36] (upper panel) and SP variational (lower panel) values to the recent UCL2016 intensity values. Transitions corresponding to the $3v_2$ and $4v_2$ bands are highlighted on the lower panel.

In **Fig. 5**, we have plotted the ratios of the FTS and SP intensities to the UCL2016 values in the 4190 - 4550 cm^{-1} region *versus* the UCL2016 line intensities. The FTS values recently measured at DLR [36] in the 4190 - 4365 cm^{-1} region show an excellent agreement with UCL2016 values. For

intensity values higher than 1×10^{-24} cm/molecule, the agreement is at the 1 % level, the UCL2016 values being systematically larger than DLR values by about 1 %. This level of agreement can be considered as a mutual validation of the variational and FTS intensity values for the considered transitions. The larger dispersion of the intensity ratios of the weaker lines should be investigated. The two other FTS sets from Toth [35] and Jenouvrier et al. [33] show larger dispersion and some systematic trends for the strongest lines of about +4% and -9 %, respectively.

Compared to UCL2016, SP intensities are overall overestimated by 5 % and show larger deviations for the transitions of the $3\nu_2$ and $4\nu_2$ bands (see **Fig. 5**). The overestimation of the variational intensities of the purely bending bands has already been evidenced in Ref. [29] for SP and previous UCL calculations (see Figs 6 and 7 of Ref. [29]). As illustrated in **Fig. 6** which shows our CRDS-DFB spectrum in an interval showing two $3\nu_2$ transitions, the new UCL calculations agree satisfactorily with the measurements.

Fig. 6

CRDS-DFB spectrum of water vapor at 8 Torr near 4530 cm^{-1} compared to variational calculations by Schwenke and Partridge (SO, red circles) [8] SP and by the UCL group (black stars) [53]. Two $3\nu_2$ transitions of H_2^{16}O fall in the displayed interval. The positions of the lines were fixed to their experimental values.

The most satisfactory line list in the region is then obtained using transition frequencies calculated from our empirical energy levels and the UCL2016 variational intensities (when available). The association of UCL2016 intensities to the empirical position values relies on the position and assignments criteria mentioned above. The UCL2016 line list was re-assigned according to SP quantum numbers, more precisely, according to the assignments of our set of empirical energy levels, as the assignment of part of SP transitions had to be modified. In order to allow for atmospheric applications, the air-broadened half-width, γ_{air} , its temperature dependence, n_{air} , the air-induced line shift, δ_{air} , and the self-broadened half-width, γ_{self} were added to each transition. These line profile

parameters were transferred from the GEISA database [60]. The GEISA line profile values were obtained by R. A. Gamache using the algorithm described in Ref. [61]. In fact, the GEISA line list includes a high number of transitions (in particular for H_2^{18}O and H_2^{17}O) without full rovibrational assignment for which the GEISA line profile parameters depend only on the lower J value. For these lines, the vibrational dependence of the line profile parameters could not be taken into account in the GEISA list. All these transitions are now reliably assigned in our list and we could adjust the line profile parameters according to their rovibrational assignments. In particular, the absence of isotopic dependence of the line parameters allowed transferring the H_2^{16}O values to H_2^{18}O and H_2^{17}O transitions with identical assignment. Other differences between GEISA and the present line profile parameters are due to some corrections of the rovibrational assignments.

We provide as Supplementary Material the resulting water vapor list. As mentioned above the UCL2016 intensity column is not complete down to the 1×10^{-29} cm/molecule intensity cut off. On a total of about 4500 transitions, about 750 have no UCL2016 intensity value. All but 15 of these missing transitions belong to H_2^{16}O ; they all have intensity smaller than 1×10^{-27} cm/molecule. For completeness of the list, we also provide all the SP positions and intensities datasets which have the advantage to be complete. In order to allow for comparison to the most relevant experimental studies, the supplementary file also includes the line parameters obtained by CRDS/OF-CEAS in the present work and by FTS from DLR [36], Giessen [37] and from previous studies by Jenouvrier et al. [33] and Toth [35].

5. Discussion

5.1 Comparison to HITRAN2012

Table 4

Sources of line positions for water vapor between 4190 and 4550 cm^{-1} in the HITRAN2012 database and in this work.

Molecule	HITRAN2012			This work	
	Toth [35]	IUPAC-TG [25-28]	Variational [62]	Empirical	Variational [7]
H_2^{16}O	303	973	8	1520	
H_2^{18}O	21	290	55	333	41
H_2^{17}O	3	250		199	55
HD^{16}O	400			1845	46
HD^{18}O				285	
HD^{17}O				127	4
Total	727	1513	63	4309	146
Total	2303			4455	

The overview comparison of our water line list to HITRAN2012 between 4190 and 4550 cm^{-1} is presented in **Fig. 7**. Overall, the HITRAN2012 line list contains 2303 transitions of four

isotopologues. Transition frequencies are experimental values by Toth for part of the H_2^{16}O lines and all the HD^{16}O lines, empirical values calculated from the IUPAC-TG energy levels [25-28] or variational values [62] for some tens of transitions of H_2^{16}O and H_2^{18}O transitions (see **Table 4**). Our list contains a total of 4309 entries with empirical line positions for six isotopologues. In addition, above the chosen 1×10^{-29} cm/molecule intensity cut off, 146 transitions with small intensity reach an upper level which is not yet determined experimentally (see **Fig. 4**) and only variational position values are available.

Fig. 7
Overview comparison between our list and the HITRAN2012 line list for water vapor between 4190 and 4550 cm^{-1} .

It is obvious from **Fig. 7**, that an important deficiency of the HITRAN2012 list is the absence of many HD^{16}O lines which contribute importantly to the absorption in the considered transparency window, similarly to the situation found in the 1.58 and 1.25 μm windows [29-32]. Including the abundance factor, the intensity cut off of the HD^{16}O lines in the HITRAN list is about 2×10^{-27} cm/molecule intensity. Consequently, the number of HD^{16}O lines in our list is more than four times larger (1845 compared to 400). **Fig. 8** presents a sample of the CRDS spectrum in a spectral interval where HDO lines are missing in the HITRAN list. These lines are well accounted for using the line list constructed with UCL2016 intensities.

Other possible improvement of the HITRAN2012 list concerns a number of line positions which have a variational origin and can now be replaced by empirical values. This concerns mainly weak lines with deviations up to 0.2 cm^{-1} . As mentioned above, the HITRAN2012 list includes both variational intensities from UCL [54, 55] for the weak lines and FTS intensity from Toth [33] for the strongest lines (see **Fig. 2**). In a number of cases, mostly for lines with intensity on the order of $10^{-26}\text{ cm/molecule}$ corresponding to the FTS detectivity, strong discrepancies were evidenced. Examples of strong overestimation and underestimation are presented in **Fig. 9** (see details in the caption).

Fig. 8

Comparison of the CRDS–VECSEL spectrum of water vapor ($P= 7.5\text{ Torr}$) (middle panel) to simulations based on the HITRAN2012 list (upper panel) and to the database constructed in this work. In the chosen spectral interval, HDO lines are missing in the HITRAN database. Note that the highest energy HDO line at 4341.75 cm^{-1} has very close intensities but the HITRAN simulation shows a line profile more narrow than observed.

Fig. 9

Comparison of the CRDS-VECSEL spectrum of water vapor ($P \approx 7.5$ Torr) (middle panel) to simulations based on the HITRAN2012 list (upper panel) and on the database constructed in this work. *Left hand panels:* The HITRAN intensity of the H_2^{16}O line at $4353.1425 \text{ cm}^{-1}$ ($11_{74} - 10_{47}$ transition of the ν_1 band) is strongly overestimated. The HITRAN intensity ($3.37 \times 10^{-26} \text{ cm/molecule}$) is the experimental value by Toth [33]. The CRDS value ($7.11 \times 10^{-27} \text{ cm/molecule}$) agrees very well with the UCL2016 value ($7.26 \times 10^{-27} \text{ cm/molecule}$).

Right hand panels: The $15_{312} - 14_{213}$ transition of the ν_1 band of H_2^{16}O at $4354.0908 \text{ cm}^{-1}$ has a strongly underestimated value in HITRAN2012 (1.21×10^{-26} versus $1.19 \times 10^{-25} \text{ cm/molecule}$ by CRDS). The HITRAN intensity is the experimental value by Toth [33]; interestingly Toth reported a correct measured value of $1.19 \times 10^{-25} \text{ cm/molecule}$ but suggested a 10 times larger value for HITRAN.

5. Conclusion

Using newly developed spectrometers, the spectrum of water vapor has been recorded with unprecedented sensitivity in five selected spectral intervals of the $2.2 \mu\text{m}$ window (noise equivalent absorption, α_{min} , on the order of $2 \times 10^{-10} \text{ cm}^{-1}$). An experimental difficulty was the interference with lines due to impurities (CH_4 , CH_2O , NH_3) which strongly interfere with the water vapor in spite of relative concentration at the ppm level. About 400 absorption lines of water vapor were measured and rovibrationally assigned, about half of them are detected for the first time. Fourteen energy levels could be newly determined for H_2^{17}O , H_2^{18}O and HD^{18}O minor isotopologues in natural isotopic abundance. Let us mention that a motivation of the development of the CRDS and OF-CEAS set ups used in this work was not only the characterization of the rovibrational lines of water vapor but also of

its continuum absorption [15, 18]. Indeed, in the considered transparency window, the water vapor absorption continuum is weak but has a comparable or even stronger contribution than the integrated absorption of the local rovibrational lines.

Using the CRDS and OF-CEAS measurements as validation tests, a spectroscopic database in the 4190-4550 cm^{-1} has been constructed by associating line positions derived from empirical energy levels, the most recent UCL variational intensities, line profile parameters and air pressure shifts from Gamache transferred from the GEISA database, rovibrational assignments relying on Schwenke and Partridge variational calculations. A similar procedure will be used to construct a part of the water line list in the next edition of the HITRAN database. In the considered region, our empirical line positions may slightly differ from the future HITRAN2016 values as (i) our set of empirical energy levels is extended compared to the IUPAC-TG sets (over 2366 energy levels required to construct the list in the region, 300 are missing the IUPAC-TG datasets [25-27] - see **Table 3**) and (ii) we chose to exclude emission line positions with insufficient accuracy from the input dataset of experimental line positions used to derive our empirical energy levels. Note above the chosen 1×10^{-29} cm/molecule intensity cut off, in absence of UCL intensities we provide SP line intensities in order to be complete.

The new UCL calculations improve significantly previous variational intensity values in the region. This improvement is illustrated by (i) the comparison with the presently measured CRDS intensities of some $3\nu_2$ transitions which show a good agreement while previous variational calculations strongly overestimated the intensity of the purely bending bands, (ii) the agreement at the 1 % level with very recent FTS measurements at DLR [36] for a set of about one hundred lines with intensity larger than 1×10^{-24} cm/molecule.

The comparison of our spectra to the HITRAN2012 list indicates that the list obtained in this work and the future HITRAN2016 list will lead to a significant improvement in terms of completeness (the absence of a large fraction of HDO lines being the major deficiency of the present HITRAN2012 list) and in terms of accuracy of line intensities (part of the intensities with experimental origin in HITRAN2012 are not accurate).

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CRDS and OF-CEAS