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New transitions and energy levels of water vapor by high sensitivity CRDS near 1.73 and 1.54 μm

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Abstract

This contribution is part of a long term project aiming at improving the water absorption spectroscopy by high sensitivity cavity ring down spectroscopy (CRDS) in the near infrared.

Two new sources of CRDS spectra are considered:

(i) The room temperature absorption spectrum of water vapor in natural isotopic abundance is recorded near 1.73 μm . A series of recordings was performed from 5693 to 5991 cm^{-1} with a pressure value of about 6 Torr. The noise equivalent absorption (α_{min}) of the spectra is better than 10^{-10} cm^{-1} . A total of 1453 lines were assigned to 1573 transitions of four water isotopologues (H_2^{16}O , H_2^{17}O , H_2^{18}O and HD^{16}O). Their intensities span more than five orders of magnitude from 3.0×10^{-30} to 4.7×10^{-25} $\text{cm}/\text{molecule}$ at 296 K. The assignments were performed using known experimental energy levels as well as calculated line lists based on the results of Schwenke and Partridge.

Two hundred fifty-one lines (assigned to 280 transitions) are observed for the first time and twelve energy levels are newly determined. The comparison of the obtained line parameters with those of the HITRAN database is discussed. Forty-six line positions are observed to significantly differ from their HITRAN values ($\delta\nu = |\nu^{\text{HITRAN}} - \nu^{\text{CRDS}}| > 0.02$ cm^{-1}). The derived set of energy levels is compared to those recommended by an IUPAC task group.

(ii) The room temperature CRDS spectrum of water vapor highly enriched in ^{17}O was recorded near 1.54 μm (6223 – 6672 cm^{-1}) at a pressure of 12 Torr. Compared to a previous study, the higher pressure of the recordings allowed for extending the observations. Overall, twenty-six new levels were determined for both H_2^{17}O and HD^{17}O .

All these observations together with other recent measurements will allow for an extension and an update of our empirical database in the 5693 – 8340 cm^{-1} region.

1. Introduction

The present work is a continuation of previous studies devoted to an extensive investigation of the near infrared water vapor absorption spectrum by highly sensitive cavity ring down spectroscopy (CRDS) [1-6]. From these investigations, we have constructed an empirical spectroscopic database for water vapor in the 5850-8340 cm^{-1} region [7] which is reproduced in the GEISA database [8] and constitutes the main source of water line positions used in the current version of the HITRAN database [9] in the region.

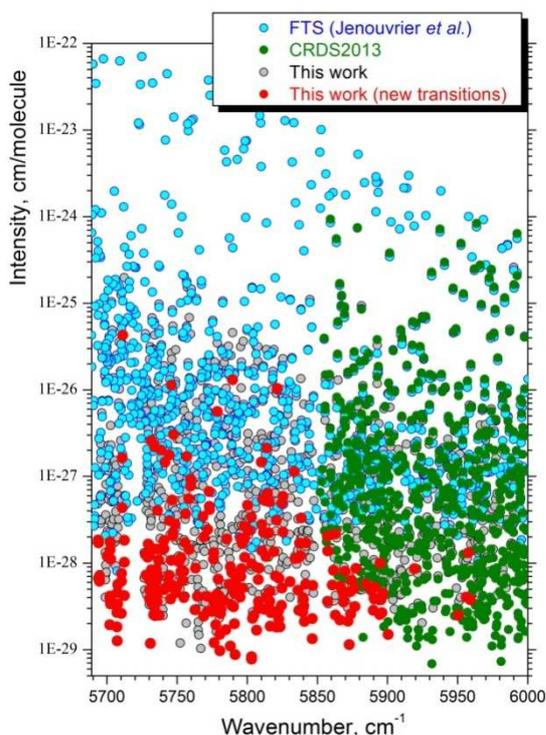


Fig. 1.

Overview of different line lists of water vapor in the investigated region (5693-5991 cm^{-1}) obtained by FTS with long absorption path length (blue dots) [10], by CRDS above 5851 cm^{-1} (green dots) [5] and in this work (red dots for the newly detected lines, grey dots otherwise).

In the present contribution we extend the CRDS recordings to lower wavenumbers, down to 5693 cm^{-1} . As illustrated in **Fig. 1**, the investigated region corresponds to the low energy edge of the 1.6 μm atmospheric window mainly formed by transitions of the second triad (cold bands) and first hexad (hot bands). Some lines near 5700 cm^{-1} are very strong (line intensity up to 10^{-22} cm/molecule) and not suitable for measurements by CRDS. Consequently, new observations are mostly limited to spectral intervals between the strong lines. The most sensitive previous study in the region is due to Jenouvrier *et al.* which could measure lines with intensity as small as 5×10^{-27} cm/molecule by Fourier transform spectroscopy (FTS) using an absorption path length up to 1.8 km [10]. Above 5851 cm^{-1} , our previous CRDS study lowered the detection threshold down to 10^{-29} cm/molecule [5]. The newly recorded spectra cover the 5693 – 5991 cm^{-1} interval. As expected, most of the new observations (highlighted on **Fig. 1**) concern the 5693 – 5851 cm^{-1} region, newly investigated by CRDS.

In the last years we have devoted specific efforts to the H_2^{17}O minor isotopologue [11-14] (3.72×10^{-4} relative natural abundance [9]) for which the knowledge of the near infrared spectrum was particularly scarce. For instance, very recently, we determined about one hundred new energy levels, mostly of H_2^{17}O and HD^{17}O , from a CRDS study performed with water vapor highly enriched in ^{17}O in the same spectral region considered in the present study for natural water [14]. We take the opportunity of the present contribution to report on new observations relative to the ^{17}O isotopologues in the $6223 - 6672 \text{ cm}^{-1}$ region, already investigated in Ref. [11] from CRDS spectra of water vapor highly enriched in ^{17}O recorded at about 1 Torr. Here, the analysed CRDS spectra were recorded at a pressure of 12 Torr. The higher pressure of the recordings allowed a total of 52 levels of H_2^{17}O and HD^{17}O to be newly determined.

In the next paragraph, the CRDS recordings performed with natural water are described together with the retrieval of the spectroscopic parameters and the construction of the line list. The rovibrational analysis is presented in Section 3 which includes the comparison to literature in particular to the present version of the water vapor list in the HITRAN database [7] and to the energy levels recommended by an IUPAC task group (IUPAC-TG hereafter) [15-17]. The results relative to the analysis of the ^{17}O isotopologues near 6500 cm^{-1} are presented in Section 4 before the concluding remarks (Section 5).

2. Experimental set up

The description of the CRD spectrometer has been presented in Refs. [1,18]. In the present work, thirteen fibered Distributed Feedback (DFB) laser diodes were used as light sources. The typical tuning range of each laser diode was about 25 cm^{-1} by temperature variation from -5°C to 55°C allowing the coverage of the $5693 - 5991 \text{ cm}^{-1}$ range except for a few spectral gaps: $5712.9 - 5722.1$, $5742.1 - 5744.1$, $5774.1 - 5774.9$, $5847.6 - 5854.3 \text{ cm}^{-1}$. The finesse of the cavity varied from 130,000 at 5850 cm^{-1} to 200,000 at 5700 cm^{-1} resulting in measured ring down (RD) times from 200 μs to 300 μs , respectively. About 30 to 100 RD events were averaged per spectral point leading to a minimum detectable absorption coefficient (evaluated as the *rms* of the baseline fluctuation), α_{min} , between $1 \times 10^{-10} \text{ cm}^{-1}$ and $2 \times 10^{-11} \text{ cm}^{-1}$ depending on the RD time. The sensitivity and high dynamics of the recordings are illustrated on **Fig. 2**.

The cell temperature was measured with a temperature sensor (TSic 501, IST-AG, 0.1 K accuracy) fixed on the cell surface, covered by an external blanket of foam for thermal isolation. During the measurement campaign, the cell temperature varied between 295.20 and 297.14 K. The frequency calibration of the spectra relies on the frequency values provided by a commercial wavelength meter (Bristol 621A, $\pm 10 \text{ MHz}$ repeatability over 5 min, $\pm 34 \text{ MHz}$ accuracy at 5700 cm^{-1}). This calibration was then refined using accurate water line positions provided by the HITRAN2016 database [9]. The uncertainty on the line center is estimated to be $1 \times 10^{-3} \text{ cm}^{-1}$ for unblended. A larger error bar on the order of 0.002 cm^{-1} is probably a reasonable estimate in the case of the weak lines considered in this work.

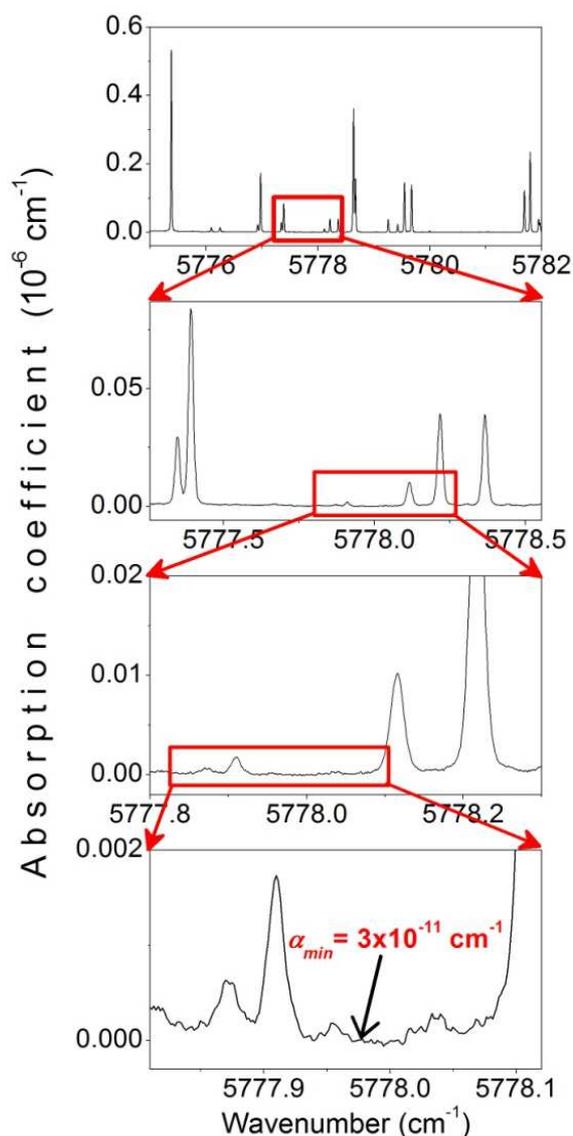


Fig. 2.

CRDS spectrum of natural water vapor near 5778 cm^{-1} . The sample pressure was 5.65 Torr. The successive enlargements illustrate the high dynamics of the recordings and the noise level on the order of $\alpha_{min} \sim 3 \times 10^{-11} \text{ cm}^{-1}$.

At the beginning of each recording, the water sample was purified by cooling with liquid nitrogen and pumping on the residual vapor phase. During the recordings, performed in static regime, the gas pressure was continuously measured by a capacitance gauge (MKS Baratron, 10 Torr, 0.15% accuracy of the reading). The average pressure value was about 6 Torr but the pressure was observed to vary during the spectra recordings (typically 2 hours for each DFB laser diode). This is due to the adsorption of water molecules on the walls of the CRDS cell after a long pumping period (and to the high surface/volume ratio of the cell). A pressure decrease up to 1 Torr was observed during some recordings. Consequently, in the derivation of the line intensities the exact pressure value at the time of the recording of the considered line was used.

The line parameters were obtained by using a homemade interactive least squares multi-lines fitting program written in LabVIEW. A Voigt profile with the width of the Gaussian component fixed

to the calculated Doppler broadening was adopted for each line. The global line list provided as Supplementary Material gathers line parameters retrieved from the different recordings. It counts a total of about 2100 lines whose assignment is discussed in the next paragraph.

3. Spectrum analysis and comparison to literature

3.1 Rovibrational assignments

Among the 2064 absorption lines of the global list, 1453 lines were assigned to 1573 transitions of the four most abundant water isotopologues (H_2^{16}O , H_2^{18}O , H_2^{17}O and HD^{16}O). The assignments were performed using known experimental energy levels [11,13-17,31] as well as calculated line lists based on the results of Schwenke and Partridge [20,21]. Previous studies in the region were reported in Refs. [2,5,10,22-25] for natural water vapor and in Refs. [26-29], Refs. [11,14] and Refs. [30,31] for samples highly enriched in ^{18}O , ^{17}O and D, respectively. Most of the overall set of measurements (about 2500 lines in total) were obtained from CRDS studies [2,5,11,14,29,31].

Among the water lines, 251 lines (assigned to 280 transitions) are observed for the first time (191, 3, 7 and 50 for H_2^{16}O , H_2^{18}O , H_2^{17}O and HD^{16}O , respectively). Most of the new lines have intensity smaller than 5×10^{-28} cm/molecule and are located below 5850 cm^{-1} (see **Fig. 1**). New lines of H_2^{16}O , H_2^{17}O and HD^{16}O allowed the determination of twelve new upper energy levels with corresponding term values listed in **Table 1**. Their error bar is estimated to be around 0.002 cm^{-1} .

Table 1.

Term values of H_2^{16}O , H_2^{17}O and HD^{16}O levels newly determined from the CRDS water vapor spectrum between 5693 and 5991 cm^{-1} .

$\mathbf{v_1 v_2 v_3 J K_a K_c}$	Term value (cm^{-1})
H_2^{16}O	
050 1 1 1	7622.6470
H_2^{17}O	
110 11 3 9	6922.5500
HD^{16}O	
040 4 4 1	5943.4355
040 4 4 0	5943.4338
040 6 3 3	5972.4165
040 12 2 10	6882.3271
040 14 1 13	7139.9806
040 14 2 13	7143.1366
040 14 2 12	7313.5033
120 9 5 5	6652.0999
120 11 6 6	7171.1371
120 12 3 9	6901.5553

A large part of the 610 remaining lines was identified as due to impurities in the water sample: methane (52 lines), formaldehyde (150 lines) and ammonia (214 lines). Lines due to CH_4 , H_2CO and

NH₃ were identified by comparison to the HITRAN database [9], Ref. [32] and a FTS spectrum (with reference 910606R016) in open access at the Kitt Peak data center, respectively. Lines of formaldehyde which is probably desorbing from the set up were identified in the low energy part of the spectrum below 5850 cm⁻¹. As no data are provided by the HITRAN database in the studied region, the CH₂O lines were identified by comparison with the FTS spectrum of Ref. [32].

All the impurity lines found in our list have intensity (including the abundance factor) less than 10⁻²⁷ cm/molecule. Estimated values of the relative abundances of CH₄, H₂CO and NH₃, are 0.1 ppm, 10 and 5 ppm, respectively. One hundred ninety-four weak lines, probably due to unidentified impurities, were left unassigned (intensity smaller than 3×10⁻²⁸ cm/molecule).

3.2 Comparison to the HITRAN database and to the IUPAC-TG energy levels

The HITRAN line list [9] contains 2625 transitions of the four most abundant water isotopologues between 5693 and 5991 cm⁻¹. Among the 1051 H₂¹⁶O transitions assigned in our spectrum, 67 transitions (maximum intensity of 4.4×10⁻²⁸ cm/molecule) are missing in the HITRAN list. Twenty of them have intensity below the HITRAN cut-off (10⁻²⁹ cm/molecule). Among the other missing transitions, 29 belong to the 3ν₂, 4ν₂ and 5ν₂-ν₂ pure bending bands and 15 are transitions with high Δ*K_a* value of the ν₁+ν₂ and ν₂+ν₃ bands. The absence of these weak transitions in the HITRAN database is related to the variational origin of the HITRAN line intensities. Most of the HITRAN intensities in the region have been computed by variational calculations based on an empirically adjusted potential energy surface (PES) and an *ab initio* dipole moment surface (DMS) [33-36]. In general, variational intensities are known to be accurate but this is not the case for purely bending bands or in case of local resonance interactions (the high Δ*K_a* lines are observed through an intensity transfer induced by a local resonance interaction). In some cases, variational intensities are calculated significantly smaller than measured. Part of the missing lines may have their variational intensities underestimated and thus below the HITRAN intensity cut-off.

Conversely, we show on **Fig. 3** an example where a 4ν₂ transition is given in the HITRAN database with a strongly overestimated intensity. The 4ν₂ 12_{4 9} – 13_{5 8} line at 5940.796 cm⁻¹ is not observed by CRDS while it has a 5.487×10⁻²⁷ cm/molecule HITRAN intensity due to Toth [37] (the line position was calculated from the IUPAC-TG energy levels [17]). Note that the variational intensity calculated by Schwenke and Partridge (5.5×10⁻³⁰ cm/molecule) [20,21] is 3 orders of magnitude smaller than HITRAN value.

As concerned line positions, the overall agreement between CRDS and HITRAN values is satisfactory. Nevertheless, as illustrated in **Fig. 4**, differences $\delta\nu = |\nu^{\text{HITRAN}} - \nu^{\text{CRDS}}|$ larger than 0.015 cm⁻¹ are noted for four lines, with a maximum value of 0.257 cm⁻¹ for the ν₂+ν₃ 18_{7 12} – 17_{7 11} line position at 5776.0016 cm⁻¹. Their HITRAN positions were derived from inaccurate empirical energy levels.

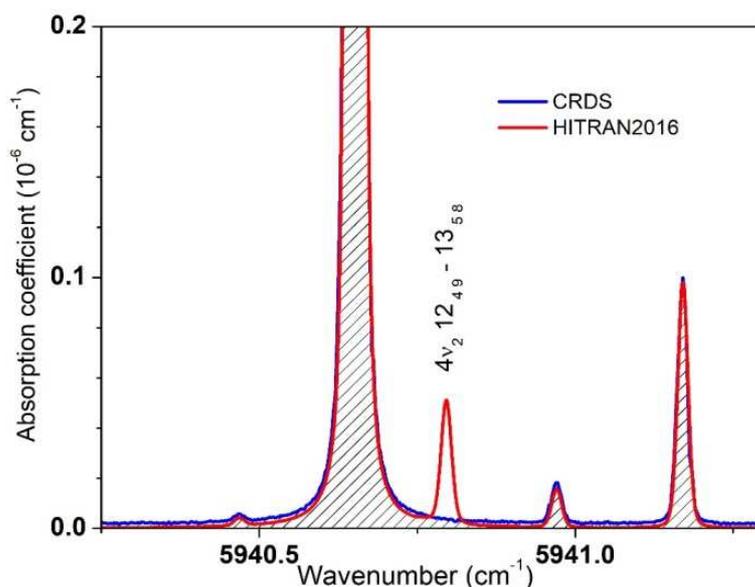


Fig. 3.

Comparison of the CRDS spectrum (blue line) to a simulation performed using the HITRAN line list [9] (red line). The pressure of water vapor in natural isotopic abundance is 6.26 Torr. The HITRAN intensity of the $4v_2 12_{49} - 13_{58}$ line of $H_2^{16}O$ from Toth [37] is strongly overestimated.

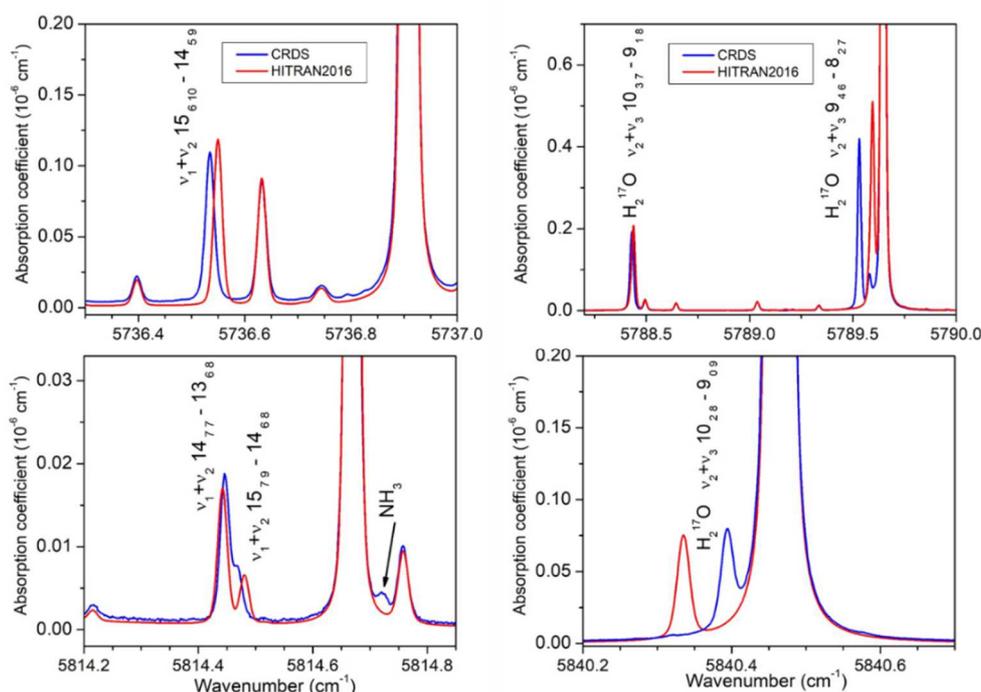


Fig. 4.

Comparison of the CRDS spectrum (blue line) to a simulation performed using the HITRAN line list [9] (red line) for water in natural isotopic abundance.

The pressure of water vapor was about 6 Torr.

Left panels: Inaccurate HITRAN positions of lines of the v_1+v_2 band of $H_2^{16}O$,

Right panels: Inaccurate HITRAN positions of lines of the v_2+v_3 band of $H_2^{17}O$ (in natural isotopic abundance).

Among the 523 transitions assigned to $H_2^{18}O$, $H_2^{17}O$ and $HD^{16}O$, 57 are not included in the HITRAN line list because their intensity is below the HITRAN intensity cut-off. The largest position

discrepancies concern the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands of H_2^{17}O ($\delta\nu_{max} = 0.086 \text{ cm}^{-1}$ for $\nu_1+\nu_2 \ 8_{54} - 7_{25}$) at $5739.09622 \text{ cm}^{-1}$) and H_2^{18}O ($\delta\nu_{max} = 0.064 \text{ cm}^{-1}$ for $\nu_1+\nu_2 \ 13_{49} - 12_{310}$ at $5801.30686 \text{ cm}^{-1}$) and the $4\nu_2$ band of HD^{16}O ($\delta\nu_{max} = 0.1012 \text{ cm}^{-1}$ for the $4\nu_2 \ 14_{212} - 13_{211}$ at $5780.77138 \text{ cm}^{-1}$).

In summary, our recordings will help to correct a number of inaccuracies in the present version of the HITRAN list and to complete it with at least 47 H_2^{16}O transitions and one H_2^{17}O transition with intensity above the HITRAN cut-off.

We have performed a systematic comparison of the upper energy levels derived from the present CRDS recordings to those recommended by the IUPAC-TG [15-17]. Among the 1051 H_2^{16}O transitions assigned in our spectra, all but one ($5\nu_2-\nu_2 \ 1_{11} - 2_{02}$ at $5957.68242 \text{ cm}^{-1}$) can be calculated from IUPAC-TG empirical energy levels [17]. The differences are all within 0.018 cm^{-1} .

Among the 189 H_2^{17}O transitions, 64 reach an upper energy level missing in the IUPAC-TG dataset [15] (mainly for the (030), (011) and (110) states of the second triad). The largest differences concern the $\nu_1+\nu_2$ and $\nu_2+\nu_3$ bands (maximum deviation of 0.048 cm^{-1} for the $\nu_1+\nu_2 \ 8_{53} - 7_{26}$ line position).

Only eight transitions of the $\nu_1+\nu_2 \ \text{H}_2^{18}\text{O}$ band cannot be calculated using the IUPAC-TG energy levels [15]. Other 196 calculated positions are in good agreement with our CRDS values. All but one differences are within 0.01 cm^{-1} . The $\nu_2+\nu_3 \ 7_{61} - 6_{25}$ line position shows the largest deviation (0.025 cm^{-1}).

Forty-one HD^{16}O transitions of the $4\nu_2$, $\nu_1+2\nu_3$ and $\nu_1+\nu_3$ bands reach upper energy levels absent in the corresponding IUPAC-TG dataset [16]. All but two position differences are within 0.014 cm^{-1} . The two largest deviations concern transitions of $4\nu_2$ band: $10_{47} - 9_{46}$ line at $5798.15917 \text{ cm}^{-1}$ ($\delta\nu = 0.061 \text{ cm}^{-1}$) and $10_{46} - 9_{45}$ line at $5798.26085 \text{ cm}^{-1}$ ($\delta\nu = 0.067 \text{ cm}^{-1}$).

4. CRDS spectrum of ^{17}O highly enriched water vapor between 6223 and 6672 cm^{-1}

In Ref. [11], we reported on the study of the absorption spectrum of water vapor highly enriched in ^{17}O between 5850 and 6671 cm^{-1} . This spectral region corresponds to a transparency window of the water molecule (see **Fig. 6**) which was poorly characterized for ^{17}O isotopologues. More than 1000 energy levels of H_2^{17}O and HD^{17}O were newly determined in Ref. [11]. The analysis relied on recordings at 12.0 and 1.0 Torr for the spectral region below and above 6223 cm^{-1} , respectively. We take the opportunity of the present contribution to report some additional results obtained by considering the spectra recorded at 12 Torr above 6223 cm^{-1} not considered in Ref. [11]. The higher pressure allowed detecting a number of weak lines and thus the determination of a set of new energy levels of H_2^{17}O and HD^{17}O . The reader is referred to Ref. [11] for the details about the spectra recordings. Let us recall that estimated values of the relative abundances of the H_2^{17}O and HD^{17}O isotopologues in our sample are 62.7 % and 0.0126 %, respectively [11].

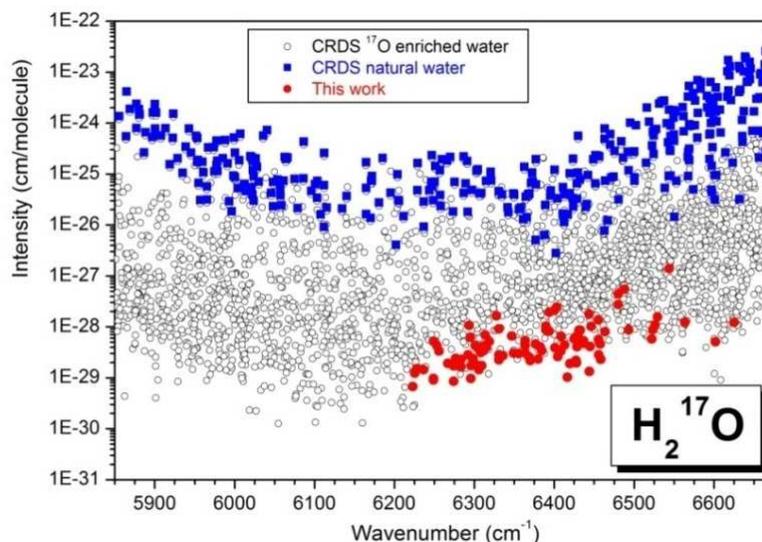


Fig. 5.

Available experimental line lists for the H_2^{17}O isotopologue in the 5850 – 6630 cm^{-1} range. Previous observations of H_2^{17}O lines in the region were reported from CRDS spectra of natural water [1,2,5] (blue squares) and from Ref. [11] by CRDS of a ^{17}O highly enriched water sample (open circles). The very weak H_2^{17}O lines assigned in this work in the 12 Torr spectrum are highlighted (red circles).

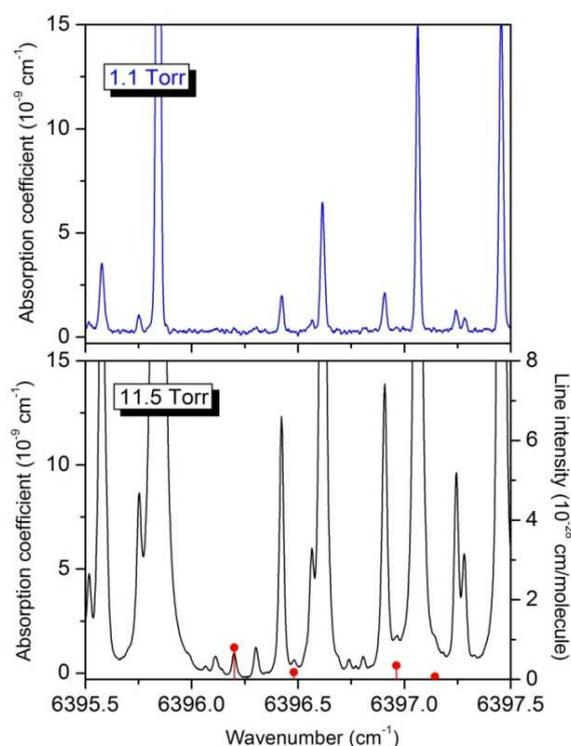


Fig. 6.

Comparison of the CRDS spectra recorded at 1.1 Torr (upper panel) and 11.5 Torr (lower panel). The 1.1 Torr spectrum was analyzed in Ref. [11]. In the present work, the 11.5 Torr spectrum was used to measure weak H_2^{17}O and HD^{17}O as those marked with red sticks on the lower panel.

We did not construct a global line list of the 12 Torr spectra but focused on new lines of H_2^{17}O and HD^{17}O too weak to be measured at 1 Torr. As illustrated in **Fig. 7**, these lines are located between

the strong absorption lines in the region, some of latter having intensity larger by more than four orders of magnitude.

Overall, line parameters of 257 lines were obtained by using the same interactive least squares multi-lines fitting program as described above for the analysis of the natural water spectrum. These lines were assigned to 106 and 165 transitions of H₂¹⁷O and HD¹⁷O, respectively (see Supplementary Material). Thirty-one of them were observed but not identified in Ref. [11]. Fifty-seven lines were assigned to 60 transitions of H₂¹⁷O and HD¹⁷O associated with new energy levels. These assignments allow obtaining 52 previously unknown energy levels listed in **Table 2**.

Table 2.

Term values of H₂¹⁷O and HD¹⁷O levels newly determined from the spectrum of water vapor enriched in ¹⁷O recorded between 6223 and 6672 cm⁻¹ at a pressure of about 12 Torr. The estimated error bar is estimated to 0.002 cm⁻¹.

$\nu_1\nu_2\nu_3$ J K_a K_c	Term value (cm ⁻¹)	$\nu_1\nu_2\nu_3$ J K_a K_c	Term value (cm ⁻¹)
H ₂ ¹⁷ O		HD ¹⁷ O	
000 15 8 8	3812.8539	021 10 3 8	7456.7680
021 17 2 16	10127.3159	021 10 4 6	7590.5913
031 12 2 10	10391.1302	021 10 5 5	7738.9162
031 14 0 14	10365.7816	021 10 6 5	7921.6412
040 12 4 8	8570.8779	021 11 3 8	7673.2096
040 15 4 11	9608.6735	021 11 5 6	7911.6773
040 16 1 16	8753.4649	021 11 6 6	8092.3587
040 17 0 17	9068.1282	021 11 6 5	8092.4713
040 18 0 18	9401.8436	021 12 2 10	7787.7044
040 18 1 18	9401.8431	021 13 2 11	7989.2423
050 5 4 2	8586.5033	031 0 0 0	7738.8543
050 10 3 8	9273.3687	031 1 1 1	7773.2642
050 10 4 7	9548.7163	031 2 1 2	7800.7381
110 12 7 5	7901.7601	031 6 0 6	8039.5927
110 14 7 8	8543.2416	031 10 1 10	8486.3341
120 14 2 12	9346.5673	050 12 1 12	7735.7358
120 15 3 13	9661.8632	101 13 5 9	8142.5300
120 17 0 17	9642.7214	101 13 5 8	8148.1653
120 17 1 17	9642.7368	101 14 2 12	8097.7469
130 8 4 5	9535.7165	101 15 4 11	8513.0022
130 9 4 5	9758.8155	111 5 2 3	8057.7927
130 10 1 9	9587.7020	111 5 3 2	8138.2131
200 12 12 1	10741.8477	210 11 3 8	7908.0994
200 12 12 0	10741.8483	210 11 4 7	7997.6054
200 13 10 4	10574.5287	210 12 1 12	7764.9213
200 13 10 3	10574.5296		
200 14 6 8	10178.4870		

It is worth mentioning that the $\nu_2+\nu_3$ $16_{107} - 15_{88}$ transition at $6223.0418 \text{ cm}^{-1}$ allows the first determination of the 15_{88} rotational energy level in the vibrational ground state. The energy of the (011) 16_{107} upper level ($10035.8957 \text{ cm}^{-1}$) was determined in Ref. [11] from the line position of the $\nu_2+\nu_3$ $16_{107} - 15_{106}$ transition at $5769.46908 \text{ cm}^{-1}$. A value of $3812.8539 \text{ cm}^{-1}$ is derived for the (000) 15_{88} rotational level in very good agreement with a value ($3812.8555 \text{ cm}^{-1}$) calculated using ground state constants [38]. As the empirical value of the 15_{79} ground state level is unknown, the term value of the (200) 14_{68} upper level ($10178.4870 \text{ cm}^{-1}$) was obtained from the line position of the $2\nu_1$ $14_{68} - 15_{79}$ transition at $6563.6130 \text{ cm}^{-1}$ using the 15_{79} calculated rotational energy level (3614.874 cm^{-1} [38]).

5. Conclusion

A total of 64 new empirical energy levels have been determined from two CRDS investigations of the near infrared absorption spectrum of water vapour with a natural sample near $1.73 \mu\text{m}$ and a ^{17}O enriched sample near $1.54 \mu\text{m}$. Some inaccuracies in the water list provided by the HITRAN database have been evidenced and discussed both for line positions and line intensities.

The present results together with other measurements obtained by CRDS in the recent years [11-14, 39] will allow for an extension and an update of our empirical database in the $5693 - 8340 \text{ cm}^{-1}$ region [7]. In particular the set of empirical energy levels have been significantly extended and the accuracy of the level determinations has been improved in several studies using CRDS referenced to a frequency comb [12,13,39].

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