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Weak water absorption lines around 1.455 and 1.66 µm by CW-CRDS

Semen N. Mikhailenko ^{a,*}, Wang Le ^{b,c}, Samir Kassi ^b, Alain Campargue ^b

^a Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, SB, Russian Academy of Science, 1, Akademicheskii av., 634055 Tomsk, Russia

^b Laboratoire de Spectrométrie Physique (associated with CNRS, UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87,

38402 Saint-Martin-d'Hères Cedex, France

^c Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, China

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Abstract

The absorption spectra of water vapor near 1.455 and 1.66 μ m have been recorded with a typical absorption sensitivity of 5×10^{-10} cm⁻¹ by using CW-cavity ring down spectroscopy. A series of 18 distributed feed-back (DFB) lasers was used as sources and allowed for the coverage of the 5911.0–5922.5, 5926–5941.8, 5957.0–6121.6, and 6745–7015.6 cm⁻¹ spectral regions. These regions extend to lower and higher energies our previous study of the water spectrum in the important 1.5 μ m transparency window [P. Macko, D. Romanini, S.N. Mikhailenko, O.V. Naumenko, S. Kassi, A. Jenouvrier, Vl.G. Tyuterev, J. Mol. Spectrosc. 227 (2004) 90–108]. The line parameters were determined with the help of an interactive least squares multi-lines fitting program which uses a Voigt function as line profile. More than 1900 water lines with intensities ranging between 10^{-28} and 5×10^{-24} cm/molecule at 296 K were measured, about 690 of them being reported for the first time. The rovibrational assignment was performed on the basis of previously determined energy levels and of the results of the variational global calculations [H. Partridge, D.W. Schwenke, J. Chem. Phys. 106 (1997) 4618–4639]. The assignment results were validated by using the Ritz combination principle together with previously reported water transitions. Several new energy levels were determined for the H₂¹⁶O, H₂¹⁷O, and HD¹⁶O isotopologues. The retrieved line lists of the H₂¹⁶O, H₂¹⁷O, H₂¹⁷O, and HD¹⁶O isotopologues. The retrieved line lists of the H₂¹⁶O, H₂¹⁷O, H₂¹⁸O, and HD¹⁶O isotopologues are compared with the available calculated and experimental (FTS) databases for water.

Keywords: Cavity ring down spectroscopy; Water molecule; H2¹⁶O; H2¹⁷O; HD¹⁶O; H2¹⁸O; Rovibrational assignments

1. Introduction

The detailed knowledge of the water spectrum in the spectra regions corresponding to very weak absorption (the transparency windows) is important for numerous atmospheric and astronomical applications. The water vapor absorption in the H transparency band of the atmosphere near 1.5 μ m was subject of several papers, see Refs. [1–14] and references therein. All these studies were performed using Fourier transform spectroscopy (FTS). The results in the full 500–8000 cm⁻¹ spectral region was summarized by R.A. Toth and included in the last version (updates of 2006) of the HITRAN database [15]. These

* Corresponding author. Fax: +7 382 2 49 20 86.

E-mail address: semen@lts.iao.ru (S.N. Mikhailenko).

data as well as energy levels, width, and shifts coefficients can also be obtained from a web site [16].

The comparison of the HITRAN database with the results of variational calculations of Partridge and Schwenke [17,18] is presented in Fig. 1, in the region of the 1.5 µm atmospheric window. It shows a lot of unaccounted for weak lines with intensities in the range 10^{-28} – 10^{-27} cm/molecule at 296 K which are detectable with high sensitivity experimental techniques. Our recent paper devoted to the 6131.4–6748.6 cm⁻¹ (1.63–1.48 µm) region [19] has demonstrated the advantages of CW-cavity ring down spectroscopy (CRDS) in terms of sensitivity of detection, linearity of response, dynamic range (absorption coefficients differing by four orders of magnitude can be measured from a single spectrum) and spectral resolution. As illustrated in Fig. 1, the detection limit was lowered by about two orders of magnitude (from 10^{-26} to



Fig. 1. Comparison of different line lists for the $H_2^{16}O$ absorption spectrum between 5800 and 7050 cm⁻¹. The two spectral regions investigated in this work are dashed. Note the logarithmic scale adopted for the line intensities. (a) CW-CRDS, the central 6131.4–6748.6 cm⁻¹ region was previously reported in Ref. [19] (Note that many strong lines with an intensity larger than 10^{-25} cm/molecule were not measured by CRDS above 6750 cm⁻¹ since our interest was the measurement of weak transitions.), (b) HITRAN database [15], (c) variational calculations [28].

 10^{-28} cm/molecule) and the number of observed transitions were multiplied by more than 4 compared to HITRAN. The present study is devoted to an extension to both high and low energies of the previously investigated region. The availability of distributed feed-back (DFB) laser diodes used as sources in our CW-CRDS set-up [19] has allowed the exploration of the 5911–6122 and 6745– 7016 cm⁻¹ spectral regions which are marked in dash in Fig. 1. It is worth underlining that the region around 1.455 µm corresponds to strong water absorption (line intensities up to 10^{-21} cm/molecule) while the 1.66 µm region corresponds to a high transparency window with maximum line intensities on the order of 10^{-24} cm/ molecule.

Very recently, the Reims–Brussels collaboration has reported the spectroscopic parameters of water in the $4400-6600 \text{ cm}^{-1}$ from FTS spectra recorded at a resolution of 0.015 cm^{-1} with total absorption path lengths up to 1803 m using a 50 m long white multiple-reflection cell [20]. Even if no new H₂¹⁶O energy level was determined from these FTS spectra, a significant improvement was achieved in terms of sensitivity compared to previous FTS studies. A high signal-to-noise (S/N) ratios (from 850 up to 5000) combined to very long absorption path lengths allowed the authors of Ref. [20] to achieve an absorption sensitivity not far from that routinely achieved with our CW-CRDS spectrometer (see below). The presently investigated 1.66 µm region, included in Ref. [20], will give the opportunity for a further comparison.

About 570 and 1850 transitions were detected in the 5911–6122 and 6745–7016 cm⁻¹ regions, respectively. The positions and intensities of about 690 of them were determined for the first time. We were able to assign these lines to rovibration transitions of 46 bands of four water species $(H_2^{16}O, H_2^{18}O, H_2^{17}O, and HD^{16}O)$. The procedure of line assignment and energy levels determination is described in Section 3.1 while the comparisons of experimental intensities with the theoretical predictions and HITRAN database are included in Section 3.2.

2. Experiment and data reduction

2.1. The CW-CRDS spectrometer

The fibered CW-CRDS spectrometer using DFB diode lasers developed in Grenoble (see Refs. [19,21]) is dedicated to the characterization of the important 1.5 µm atmospheric window of transparency by high sensitivity absorption spectroscopy. The typical noise equivalent absorption $(\alpha_{min} \sim 2-5 \times 10^{-10} \text{ cm}^{-1})$ and the 4 to 5 decades dynamics on the intensity scale, have allowed to significantly improve the knowledge of the absorption spectroscopy of a series of molecules of atmospheric interest: H₂O [19], ¹²CO₂ [22], ¹³CO₂ [23,24], O₂ [25], and ozone [26,27]. The DFB typical tuning range is about 7 nm ($\sim 30 \text{ cm}^{-1}$) by temperature tuning from -10 to 65 °C. Nine fibered DFB lasers were used to cover each of the 5911.0-6121.6 and 6745-7015.6 cm^{-1} region. While the higher wavenumber region could be covered continuously, our DFB sets did not allow for the coverage of the 5922.5-5926 and 5941.8-5957.0 cm⁻¹ spectral sections. The number of ringdown events averaged for each spectral data point was typically 80 while the duration of a temperature scan was about 70 min for each DFB laser. The pressure, measured by a capacitance gauge, as well as the ringdown cell temperature, was monitored during the spectrum recording. Pressure values on the order of 10-20 hPa were chosen in the 1.66 µm region. In the 1.455 µm region, lower pressures of about 1.5-5.0 hPa were used as lines as strong as 10^{-21} cm/molecule—seven orders of magnitude stronger than our detection limit—are observed in this region.

The two investigated spectral regions correspond to the limits of the high reflectivity region of the used mirror set. In consequence, the typical ringdown time (and consequently the sensitivity) decreases from 50 μ s at 6750 cm⁻¹ to 20 μ s at 5910 cm⁻¹ and 17 μ s at 7000 cm⁻¹. This is clearly illustrated in the upper panel of Fig. 1, which shows

that the intensities of the weakest lines detected in a spectral region, follows the wavelength dependence of the mirrors reflectivity. Fig. 2 shows that the baseline noise level has a typical value of $\alpha_{min} \sim 2 \times 10^{-10} \text{ cm}^{-1}$ around 6110 cm⁻¹ while values as large as $\alpha_{min} \sim 5 \times 10^{-9} \text{ cm}^{-1}$ are obtained at 7000 cm⁻¹. The same variation is followed by the minimum intensity values which increases from 10^{-28} to 10^{-27} cm/molecule between 6750 and 7000 cm⁻¹.

2.2. Line parameter retrieval

The wavenumber calibration of the spectrum is based on the wavelength values measured by a wavemeter (Burleigh WA1640) during the DFB frequency scan. The wavelength provided by the wavemeter is a value averaged during typically 1 s. Since during the temperature scan of the DFB laser, the speed of the wavelength scan is not constant, a non constant shift has to be applied to the wavelength value provided by the wavemeter. The treatment of this speed variation has been described in details in Ref. [24]. After this correction, the obtained absolute wavenumber calibration was typically accurate within 2×10^{-3} cm⁻¹. It was further refined by simply stretching the frequency scale (with an origin at 0) in agreement with highly accurate positions of reference line. H₂O lines from HITRAN [15] and from the line list attached to Ref. [20] were used as references in the 1.455 and 1.66 µm region, respectively. As a result, an agreement better than $2 \times 10^{-4} \text{ cm}^{-1}$ could be achieved in the overlapping part of two successive spectral regions. Maximum deviations of 1×10^{-3} cm⁻¹ were observed for a few H₂O reference lines which are then believed to be the maximum position error.



Fig. 2. Zoom of the CW-CRDS spectrum of water between 6109 and 6110.5 cm⁻¹ recorded at a pressure of 15.1 hPa (11.5 Torr). In the upper panel, the ordinate scale corresponding to the absorption coefficient (in 10^{-6} cm⁻¹ unit), has been multiplied by a factor 10. The insert, corresponding to a further enlargement, shows that the noise equivalent absorption defined as the rms value of the noise level is about 2×10^{-10} cm⁻¹.

The line parameters were determined by using an interactive least squares multi-lines fitting program written in C++ by S. Hu (USTC, Hefei). The Levenberg–Marquardt algorithm is used to minimize the deviation between the observed and calculated spectrum. Inside each complete laser scan, spectral sub-sections corresponding to isolated clusters of absorption lines were selected and fitted independently. For intensity retrieval, CW-CRDS has the advantage that the DFB linewidth is much smaller than the Doppler broadening (1–5 MHz compared to 1 GHz), so that the apparatus function is negligible. For each molecular line, the profile was assumed to be of Voigt type with a Gaussian contribution fixed to the Doppler broadening calculated from the measured cell temperature and the absorber mass. Line position, integrated line absorbance, Gaussian and Lorentzian contributions of each line and a baseline (assumed to be a linear or quadratic function of the wavenumber) are provided by the fitting procedure. Particular attention was paid to the baseline determination in the 1.455 µm region where it was necessary to take into account the far wings of very strong lines lying outside the fitted spectral window. Figs. 3 and 4 illustrate the agreement between the observed and simulated spectra in a section of the 1.66 and 1.455 µm regions, respectively. The observed minus calculated residuals are



Fig. 3. Comparison of the CW-CRDS spectrum of water between 6004.5 and 6005.5 cm⁻¹ with a simulated spectrum obtained as a sum of individual Voigt profiles. The residual is displayed on the lower panel with a magnification factor of about 40. Experimental conditions: p = 20.8 hPa (15.8 Torr) and T = 296 K.



Fig. 4. Same as Fig. 3 for the 6989.0–6990.1 cm⁻¹ spectral section. Experimental conditions: p = 3.95 hPa (3.0 Torr) and T = 296.3 K.

higher than the noise level, indicating that a more sophisticated profile including narrowing effects is required to better improve the simulation.

As the spectra were recorded during several measurement campaigns with different pressure gauges, we preferred, contrary to our preceding study [19], to normalize our relative intensities to previous accurate absolute intensity values in order to avoid systematic errors on the pressure values. Similarly to the wavenumber calibration, we adopted as reference the absolute intensity values from HITRAN and Ref. [20] for the 1.455 and 1.66 μ m regions, respectively. The comparison between the CW-CRDS observations, HITRAN and Ref. [20] presented in Fig. 5 for H₂¹⁶O, shows the increased sensitivity of the CW-CRDS spectra and the good agreement of the absolute line intensity values (see also Section 3.2 below).

Line intensities differing by five orders of magnitude (typically from 10^{-29} to 10^{-24} cm/molecule) can be retrieved from a single CW-CRDS spectrum. However, this high dynamics is not sufficient in the 1.455 µm region where lines as strong as 10^{-21} cm/molecule are present (see Fig. 1). Clipping effects due to the decrease of the light intensity because of too strong intra-cavity absorption were clearly observed for the lines stronger than 10^{-24} cm/molecule. Considering that the parameter values of these strong lines of the 1.455 µm region, had been accurately measured



Fig. 5. Comparison of the CW-CRDS spectrum of $H_2^{16}O$ in the 6000–6100 cm⁻¹ region. Note the logarithmic scale adopted for the line intensities. Upper panel: CW-CRDS (open circle) and HITRAN (full circle). Lower panel: CW-CRDS (open circle) and FTS [20] (full circle).

in previous FTS investigations, they were not considered in the present study.

3. Results and comparison with databases

3.1. Line assignments

After identification and removal of the transitions due to NH₃, CH₄, N₂O, CO₂, and CO present as impurities in the CRDS cell, a line list of 2126 transitions was obtained for the 5911.0-5922.5, 5926-5941.8, 5957.0-6121.6, and 6745-7015.6 cm⁻¹ regions. Among them, 2048 were assigned to 2338 transitions of the four major water isotopologues ($H_2^{16}O$, $H_2^{18}O$, $H_2^{17}O$, and $HD^{16}O$) leaving only 78 lines unassigned. These unassigned lines are probably lines due to impurities not listed in the current databases. Table 1 gives, for each isotopologue, the number of transitions obtained by CW-CRDS, provided by HITRAN or recently reported by FTS [20]. The new observations by CW-CRDS are particularly significant in the 1.66 µm high transparency region, where HITRAN line list includes only 147 transitions while 370 and 569 transitions were observed by FTS [20] and CW-CRDS, respectively.

The maximal value of the rotational quantum number J and the number of assigned transitions are given for each

1	7	4

HD¹⁶O

 $H_2^{17}O$

Total

88

7

569

Table 1						
Comparison between the number of lines measured by CW-CRDS and that provided by HITRAN [1] and FTS [20]						
	1.66 µm			1.455 μm		
	This work	HITRAN	BR-FTS [20]	HITRAN	This work (new lines only)	
H2 ¹⁶ O	411	146	306	1024	314	
$H_{2}^{18}O$	63		27	363	78	

45

2

370

1

147

band in Tables 2 and 3. Fig. 6 shows an example of line assignments around 6096 cm⁻¹. The rovibrational assignments of water lines were performed on the basis of both the available sets of experimental energy levels and the calculated water spectra of Ref. [28]. These spectra were generated by S.A. Tashkun (IAO, Tomsk) using the potential energy [17] and dipole moment [18] surfaces obtained by

Table 2 Summary of the obtained rovibrational assignments for H216O and HD¹⁶O transitions

Band	$H_2^{16}O$		HD ¹⁶ O		
	J _{max}	Number of transitions	J_{\max}	Number of transitions	
1.66 µm region ^a					
$2v_3 - v_2$	13	62			
$v_2 + v_3$	16	99			
$2v_2 + v_3$	13	4	9	12	
$2v_2 + v_3 - v_2$	14	18			
$3v_2$	15	23			
$4v_2$	14	118	10	7	
$5v_2$	7	18			
$v_1 + v_3$			17	67	
$v_1 + v_3 - v_2$	7	2			
$v_1 + v_2 + v_3 - v_2$			5	2	
$v_1 + v_2$	17	63			
$2v_1 + v_2$	12	2			
$2v_1$	7	2			
1.45 μm region ^b					
$2v_3$	13	81	10	30	
$v_2 + 2v_3 - v_2$	7	1			
$2v_2 + v_3$	13	118	8	2	
$3v_2 + v_3 - v_2$	12	102			
$4v_2$	13	49			
$4v_2 + v_3 - 2v_2$	5	6			
$5v_2$	13	2	11	24	
$5v_2 - v_2$	10	2			
$6v_2 - v_2$	6	3			
$v_1 + v_3$	18	175			
$v_1 + v_2 + v_3 - v_2$	15	67			
$v_1 + 2v_2$	14	133			
$v_1 + 3v_2 - v_2$	10	43			
$2v_1$	17	131			
$v_1 + 3v_2$			5	8	
$2v_1 + v_2$			13	122	
$2v_1 + v_2 - v_2$	12	50			

 a The 1.66 μm region corresponds to the 5911.0–5922.5, 5926–5941.8, and 5957.0-6121.6 cm⁻¹ spectral sections.

^b The 1.455 μ m region corresponds to the 6745–7016 cm⁻¹ spectral interval.

Table 3

Summary of the obtained rovibrational assignments for $H_2^{18}O$ and $H_2^{17}O$ transitions

46

68

506

115

263

1765

Band	$H_2^{18}O$		H ₂ ¹⁷ O		
	$J_{ m max}$	Number of transitions	$J_{\rm max}$	Number of transitions	
1.66 µm region ^a					
$v_2 + v_3$	14	38	10	2	
$4v_2$	9	25	7	5	
1.455 µm region ^b					
2v ₃	11	6	7	1	
$2v_2 + v_3$	10	125	9	106	
$3v_2 + v_3 - v_2$	8	20	3	2	
$4v_2$	9	2			
$v_1 + v_3$	14	95	12	45	
$v_1 + 2v_2$	11	68	8	38	
2v ₁	13	75	10	37	

^a The 1.66 µm region corresponds to the 5911.0–5922.5, 5926–5941.8, and 5957.0–6121.6 cm^{-1} spectral sections.

^b The 1.455 μ m region corresponds to the 6745–7016 cm⁻¹ spectral interval.



Fig. 6. Example of line assignments of the CW-CRDS spectrum of water vapor in the 6094.5–6098.5 cm⁻¹ region. Lines which are marked with x and o correspond to CO₂ and CH₄ lines, respectively, present as impurities. The rovibrational assignment of the lines due to the H216O and HDO isotopologues is indicated.

Partridge and Schwenke. The verification of the assignments and the determination of the experimental energy levels and their uncertainties were performed by using the RITZ program [29] for the four species. This program was successfully applied in previous studies of water spectra [5,19,30–32]. Three levels of HD¹⁶O and nine energy levels both for $H_2^{16}O$ and $H_2^{17}O$ could be newly determined (see below).

The full list of the observed lines assigned to water is given in electronic form as Supplementary Material. It includes the measured line positions and intensities, the molecule code, the line positions calculated from experimental energy levels when available, the calculated [28] intensities, the experimental lower energies and the rotation-vibration assignments for upper and lower levels. Note that line intensity value could not be determined for a few very weak lines marked by "+" in the line list.

3.1.1. $H_2^{16}O$ molecule

By using the experimental values of the known energy levels of $H_2^{16}O$ [4,5,16,19,20,33], we corrected the line positions of the calculated line list [28]. From the agreement (typically within 2×10^{-3} cm⁻¹) of the observed and corrected line positions, it was possible to assign more than 1370 transitions of 22 vibrational bands listed in Table 2. Finally, 871 observed line positions were combined with the literature data [1–6,16,19,20] in order to determine the upper states rotational energies.

The considered spectrum is mostly dominated by cold bands of the first hexade of interacting vibrational states $\{(040), (021), (120), (002), (101), (200)\}$. Seven new rotational levels of the (002), (031), (101), (110), and

(210) states were determined (see Table 4). In addition, the values of the (050) J = 7, $K_a = 1$, $K_c = 7$ and (200) J = 16, $K_a = 0$, $K_c = 16$ levels have been corrected from 8162.723 cm⁻¹ [33] to 8162.649 cm⁻¹ and from 9762.936 cm⁻¹ [33] to 9762.697 cm⁻¹, respectively.

3.1.2. The $H_2^{18}O$ molecule

The same procedure of correction of the theoretical line list [28] using the experimental energies from [7-12,16,19,20,30] was used for identification of the $H_2^{18}O$ transitions. 454 absorption lines belonging to eight bands were assigned to $H_2^{18}O$. A summary of the obtained rovibrational assignments is presented in Table 3. The spectroscopic parameters of more than 100 lines were determined for the first time. All the line positions and energies of the upper levels were found in very good agreement with previous studies and no new levels were determined compared to those reported in Refs. [16,19,20,34]. However, 84 line positions were found valuable to lower the uncertainty on the previous determination of the upper energy levels. Note that 28 of the $H_2^{18}O$ lines in the 5918–5998 cm⁻¹ region which are absent in the HITRAN database have been recently reported by Liu et al. [34] from FTS spectra recorded with an ¹⁸O enriched sample.

3.1.3. The $H_2^{17}O$ molecule

The experimental energy levels from Refs. [7,12,13,16,19,20] were used for correction of the $H_2^{17}O$ calculated line list [28]. Using this compilation, we were

Table 4

New (or corrected) experimental energy levels of H216O, H217O, and HD16O

$(v_1 v_2 v_3)$	J	K_a	K_c	$E_{ m obs}$	$E_{ m obs}$	Ref.	E_{calc} [28]
$H_2^{16}O$							
(002)	12	6	6	9789.5688			9789.625
(002)	12	7	5	9923.4960			9923.569
(031)	12	5	7	10861.0262			10861.198
(050)	7	1	7	8162.6489	8162.7226	[33]	8162.687
(101)	12	8	5	9885.1136			9885.260
(101)	16	3	14	10346.6858			10346.796
(110)	17	3	15	8776.0628			8776.070
(200)	16	0	16	9762.6974	9762.9361	[33]	9762.758
(210)	12	1	12	10252.1380			10252.175
$H_2^{17}O$							
(002)	7	1	7	7994.8017	7997.4337	[16]	7994.857
(021)	6	5	2	7850.0789	7849.7840	[16]	7850.118
(021)	8	6	2	8406.6560			8406.721
(031)	2	1	1	8463.2169			8463.281
(040)	2	1	2	6223.0727			6223.086
(040)	3	0	3	6259.9823			6260.004
(040)	4	1	4	6365.3530			6365.360
(101)	11	1	10	8704.9253	8704.7898	[16]	8704.951
(200)	8	0	8	7907.9957	7907.8781	[16]	7908.019
HD ¹⁶ O							
(040)	6	6	0	6676.2672			6676.198
(040)	6	6	1	6676.2664			6676.198
(101)	13	3	10	7997.0111			7997.053

 $(v_1 v_2 v_3)$, J, K_a , K_c , vibration and rotation quantum numbers; E_{obs} , experimentally determined rovibrational energy (cm⁻¹); E_{calc} , variational calculated rovibrational energy (cm⁻¹). Every of all the above energy levels was determined from one single line.

able to assign 236 transitions of eight vibrational bands (see Table 3). Among them, 52 lines were assigned for the first time. More than 200 observed transitions were gathered with data from Refs. [7,12,13,16,19] in order to refine the values of the experimental energy levels. Five new energy levels of the (021), (031), and (040) states could be determined. The values of these levels with their uncertainties are given in Table 4 together with the corrected values of four levels previously reported in Ref. [16]. A discrepancy of 2.5 cm^{-1} (7994.802 cm⁻¹ instead of 7997.734 cm⁻¹ [16]) was found for the (002) J = 7, $K_a = 1, K_c = 7$ level. Our experimental value is fully confirmed by our calculations in the frame of the effective Hamiltonian model for the first hexade of the $H_2^{17}O$ molecule (7994.788 cm^{-1}). This level is in very strong resonance coupling with the (101) J = 7, $K_a = 2$, $K_c = 5$ level that we predict at 7999.937 cm⁻¹. Our calculated values for these two levels are very close to the results of variational calculations [28]: 7994.857 and 7999.974 cm^{-1} , respectively.

3.1.4. The $HD^{16}O$ molecule

For the assignment of the HD¹⁶O lines, we corrected the calculated spectrum of Ref. [28] with the experimental energy levels from Refs. [14,16,19,20]. By this way, 274 transitions of six bands could be assigned (see Table 2), 110 transitions being newly reported. Most of them belong to the $v_1 + v_3$ and $2v_1 + v_2$ bands. More than one hundred line positions observed in this study were included in the input data of the RITZ program in order to refine the value of the corresponding energy levels. According to our assignment, three new levels of the (040) and (101) states were determined (see Table 4). Note that the HDO absorption lines measured from the CW-CRDS spectra are stronger by a factor 12 compared to the expected absorption for HDO in natural abundance. This deuterium enrichment is probably due to the use of pressure gauges or valves which have been previously in contact with deuterated water.

3.2. Line intensities

A total of 1929 line intensities ranging between 9.6×10^{-29} and 4.7×10^{-24} cm/molecule at 296 K were measured for the four water isotopologues. More than one hundred lines which correspond to a superposition of two and more transitions, due to different water isotopologues, were not considered for the following comparison with the predicted and experimental intensities of previous studies.

A root mean square (rms) ratio $R = \sqrt{\sum_{i=1}^{N} [I_i^{\text{obs}}/I_i^{\text{calc}}]^2/N}$ of 1.07 was obtained for the comparison with the predictions of Ref. [28] for the N = 1757 line intensities such as $0.6 < I^{\text{obs}}/I^{\text{calc}} < 2$. In Fig. 7, the ratios $R_i = I_i^{\text{obs}}/I_i^{\text{calc}}$ for the H₂¹⁶O and H₂¹⁸O isotopologues are plotted. As usual, the dispersion of the ratios values increases for the weakest lines as a result of the larger experimental uncertainty.



Fig. 7. Plots of the ratios of experimental intensity values by the calculated values obtained by variational calculations [28] versus the observed line intensity: (a) ${\rm H_2}^{16}O$, (b) ${\rm H_2}^{18}O$.

As illustrated in Fig. 1, the impact of the newly observed transitions is expected to be larger in the 1.66 μ m region where the absorption is very weak. For instance, the HITRAN database [15] provides only 147 lines in the 5912–6122 cm⁻¹ region (all but one due to H₂¹⁶O) while 380 additional lines were detected by CW-CRDS. They represent a total intensity of 7.82×10^{-25} cm/molecule which corresponds to a 2.3% additional absorbance in the region and may have a significant impact in a spectral interval of very high transparency.

Furthermore, it is worth mentioning that, in the 1.66 μ m region, the line list included in the current version of the HITRAN database includes at least two erroneous weak lines lying near much stronger transitions. The first one is the $4v_2$, 12_{49} – 13_{58} transition at 5940.774 cm⁻¹ with an intensity of 5.487×10^{-27} cm/molecule [15,16]. According to the energy level value obtained in this study and in Ref. [19], the line position of this transition should be 5940.797 cm⁻¹. But, more importantly, the calculated intensity of this transition is about 5.6×10^{-30} cm/molecule [28], i.e., about 1000 times weaker. This order of magnitude of the intensity is confirmed by the fact that this line is below the CW-CRDS detection limit (about 10^{-28} cm/molecule in the considered region). The situation is illustrated in Fig. 8, where the



Fig. 8. Two examples of erroneous lines in the HITRAN database. The CW-CRDS spectrum and the $H_2^{16}O$ simulation from HITRAN [15] are plotted with solid and dashed lines, respectively. Upper panel: the $4\nu_2$, $12_{49}-13_{58}$ line of $H_2^{16}O$ at 5940.774 cm⁻¹ lying between the two lines of the $\nu_2 + \nu_3$ band of $H_2^{16}O$, has an intensity value of 5.487×10^{-27} cm/molecule largely above the detection limit (see the line at 5940.973 cm⁻¹ with a 1.66×10^{-27} cm/molecule intensity for comparison). Lower panel: the $2\nu_2 + \nu_3$, $9_{19}-9_{72}$ line of $H_2^{16}O$ at 5962.343 cm⁻¹ is not observed while the intensity value provided by the HITRAN database is largely above the CW-CRDS detection limit.

spectrum as provided by HITRAN has been simulated and compared to the CW-CRDS spectrum around 5941 cm⁻¹.

The second erroneous line is the $2v_2 + v_3$, $9_{19}-9_{72}$ transition at 5962.343 cm⁻¹ with an intensity value of 2.223×10^{-26} cm/molecule [15,16]. The parameters of this transition are 5962.343 cm⁻¹ and 1.0×10^{-30} cm/molecule according to our experimental energy level value and the intensity calculations [28], respectively. As shown in the lower panel of Fig. 8, this line is absent from the CW-CRDS spectrum confirming that HITRAN intensity value is erroneous.

4. Conclusion

The absorption spectra of water vapor have been recorded by high sensitivity CW-CRDS around 1.45 and 1.66 μ m. The main goal of this study was the detection of

new very weak transitions and the measurement of their intensities. More than 1900 water lines with intensities ranging between 10^{-28} and 5×10^{-24} cm/molecule at 296 K were measured, about 690 of them being reported for the first time. An important improvement in sensitivity has allowed for the determination of the spectroscopic parameters of 886 weak lines not included in the HITRAN database. In particular, the sum of intensities of 380 new lines observed in the 5911.0–5922.5, 5926–5941.8, and 5957.0–6121.6 cm⁻¹ regions adds 2.3% to the total intensity (3.42×10^{-23} cm/molecule) of the 147 lines included in HITRAN. The sum of intensities of the 506 lines newly observed in the 6745–7022 cm⁻¹ region is about 5.6×10^{-24} cm/molecule.

The comparison of our results with data obtained by Fourier transform spectroscopy for the $H_2^{16}O$, $H_2^{18}O$, and $H_2^{17}O$ isotopologues has shown an overall very good agreement both for line positions and intensities. The present results like other recent papers [19,20,34] demonstrate the very good agreement of the experimental intensities with the theoretical predictions based on the variational calculations of Partridge and Schwenke [17,18].

This study has allowed to improve or newly determine some rovibrational energy levels of the $H_2^{16}O$, $H_2^{17}O$, and HDO species and to evidence a few erroneous lines present in the HITRAN database. We hope that the reported results devoted to an atmospheric transparency window of particular importance, will be useful for a further improvement of spectroscopic databases of water.

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Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm). Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa. lib.ohio-state.edu/jmsa_hp.htm).

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