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222 very weak transitions were newly detected.

50 new or corrected H_2^{16}O energy levels were determined

The most complete line list for water between 13500 and 14100 cm^{-1} was constructed.

**The absorption spectrum of water between 13540 and 14070 cm^{-1} :
ICLAS detection of weak lines and a complete line list**

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The H_2O absorption spectrum between 13540 and 14070 cm^{-1}

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ABSTRACT

The absorption spectrum of water vapor has been investigated by Intracavity Laser Spectroscopy (ICLAS) between 13540 and 14070 cm^{-1} . This spectrum is dominated by relatively strong transitions of the 4δ polyad of vibrational states. The achieved sensitivity – on the order of $\alpha_{min} \sim 10^{-9} \text{ cm}^{-1}$ – has allowed one to newly measure 222 very weak transitions with intensities down to $5 \times 10^{-28} \text{ cm/molecule}$ at 296 K. 50 new or corrected H_2^{16}O energy levels belonging to a total of 13 vibrational states could be determined from the rovibrational analysis based on variational calculations by Schwenke and Partridge. The previous investigations in the region by Fourier Transform Spectroscopy were critically evaluated and used to construct the best to date set of energy levels accessed by transitions in the considered region. All the rovibrational transitions reaching these upper energy levels and having intensities larger than $4.0 \times 10^{-28} \text{ cm/mol}$ were calculated. In the resulting line list, the positions at the level of experimental accuracy were augmented with variational intensities leading to the most complete line list for water in normal isotopic abundance in the 13500-14100 cm^{-1} region.

1. INTRODUCTION

This contribution continues our investigation of the weak absorption spectrum of water by Intracavity Laser Absorption Spectroscopy (ICLAS) in the spectral region accessible with a Ti:Sapphire laser (11300-14100 cm^{-1}). Our ICLAS–Ti:Sa spectrometer allows for the detection of weak transitions with intensity as small as $1\text{-}5\times 10^{-28}$ $\text{cm}/\text{molecule}$. In a first contribution, we reported on the analysis of the 11335-11947 and 12336-12843 cm^{-1} spectral regions dominated by the $\nu_1+3\nu_2+\nu_3$ and $\nu_2+3\nu_3$ bands of H_2^{16}O [1]. A second work was devoted to the 12746 - 13558 cm^{-1} region corresponding to an important transparency window of the atmosphere [2]. In the present work, we analyse the 13540-14070 cm^{-1} range dominated by the relatively strong $3\nu_1+\nu_3$ band centered at 13831 cm^{-1} .

In its 2008 version, the HITRAN database [3] has adopted the line list constructed by Tolchenov and Tennyson for the 9500-14500 cm^{-1} region [4]. These authors performed a fit of six experimental spectra recorded at Rutherford Appleton Laboratory (RAL) [5,6] by Fourier Transform Spectroscopy (FTS) associated with long multi pass cells. Optical path lengths up to 800.8 m were used and the spectral resolution was 0.03 cm^{-1} . In order to improve quality of the spectroscopic parameters of blended or weak lines, Tolchenov and Tennyson (TT) constrained the empirical upper energy levels to the values determined from other transitions sharing the same upper levels [4]. Prior to TT work, the same RAL spectra were analyzed by Schermaul et al who constructed a line list (called RAL hereafter) for the 13200-15000 cm^{-1} region [7]. Note that this RAL line list includes weak features which are absent from the TT line list (see Fig. 6 of Ref. 2).

Another extensive line list is due to the Reims-Brussels collaboration [8-11]. It was adopted for the HITRAN database in its 2004 version. The Reims-Brussels line list [12] was constructed from FTS spectra recorded at a spectral resolution of 0.06 cm^{-1} with a total absorption path length up to 602.32 m.

A gain in sensitivity by at least a factor of 10 can be achieved by using ICLAS. The additional information provided by ICLAS is particularly significant in the region of weak absorption [2]. Nevertheless, even in the region of (relatively) strong absorption as the one presently analyzed, weak transitions can be newly detected between the strong absorption lines. In the present work, we focused on the detection of the weak absorption features in the 13540-14070 cm^{-1} region which is the highest frequency spectral interval accessible with our Ti:Sapphire laser.

2. EXPERIMENTAL DETAILS

The reader is referred to Refs. [1,13,14] for a detailed description of our ICLAS spectrometer and the data acquisition procedure. The length of the intracavity absorption cell was 65 cm which resulted in a 42% filling ratio of the Ti:Sa laser cavity. The generation time was fixed to 190 μs corresponding to an equivalent absorption pathlength of 23.9 km. The cell was filled with water at pressures ranging between 2 and 20 hPa but most of the recordings were performed at a pressure of 15.8 hPa (12.0 Torr). The spectral resolution fixed by the grating spectrograph was close to the Doppler line broadening.

The main experimental difficulty was the necessity to reduce drastically the intracavity absorption of water in the atmosphere occupying the 52% remaining part of the Ti:Sa cavity. The laser cavity was placed in a box where a continuous flow of dry nitrogen was injected. After a few minutes, the atmospheric water absorption was decreased by a factor of 30. The residual absorption was further suppressed by filling the cell with water, recording the spectrum, vacuuming the cell and recording the background spectrum. By division of the spectrum by the background, the atmospheric contribution was eliminated. Each 12 cm^{-1} wide portion of the spectrum was recorded with a 3754 silicon diode array placed in the focal plane of the grating spectrograph and then accurately calibrated using H_2^{16}O reference lines taken from RAL line list [7]. The average accuracy of the ICLAS line positions is estimated to be around 0.008 cm^{-1} .

As the considered spectral region has been subject of several extensive FTS investigations, we did not undertake a systematic analysis of the spectra and focused on newly detected transitions. The retrieval of the line positions and line intensities was then limited to these very weak lines. Line position, integrated line absorbance, Gaussian and Lorentzian widths of each line and the corresponding baseline were derived using an interactive least square multi-line fitting program assuming a Voigt profile. Absolute line intensities were then derived by scaling the integrated line absorbances using the FTS intensity value [7] of a well isolated nearby line. The uncertainty on the obtained intensities was large (up to 100%) as a consequence of the weakness of the considered lines and of the frequent overlapping with much stronger lines. Nevertheless, the obtained intensities values constituted a highly valuable criterion for the rovibrational assignment of the spectrum (see below). As an example, Fig. 1 illustrates the detection of new weak lines lying between much stronger lines near 13715 cm^{-1} .

Overall 222 transitions absent in the TT, RAL, HITRAN2008 and Reims-Brussels line lists could be detected. They are presented in Fig. 2, superimposed to the TT [4] and RAL [7] line lists. Most of these new lines have intensity in the 5×10^{-28} - 3×10^{-27} cm/molecule range i.e. up to four orders of magnitude smaller than the strongest intensities in the region.

3. LINE ASSIGNMENT AND CONSTRUCTION OF A COMPLETE LINE LIST

The first step of the assignment consisted in determining whether the new transitions reached upper energy levels previously determined from other transitions.

For this purpose, we constructed a database of the H_2^{16}O energy levels by completing the upper levels compiled in Ref. [16] with those of the following works: TT [4], Reims-Brussels [12], CRDS study near 750 nm [15] and ICLAS [1,2]. For the minor isotopologues (H_2^{18}O , H_2^{17}O , HDO), we benefited of the recent works of an international IUPAC-sponsored Task Group which has performed an exhaustive critical evaluation of all rovibrational line positions and energy levels available in the literature for these three species [17,18].

These experimentally determined energy levels of the four major isotopologues of water were combined with the variational intensities calculated by S.A. Tashkun (IAO, Tomsk) [19] using the potential energy [20] and dipole moment [21] surfaces obtained by Schwenke and Partridge (SP) in order to predict the transitions of water in normal isotopic abundance in our spectral region. The accurate matching of the line positions and reasonable agreement between the ICLAS and variational intensities allowed assigning 172 of the 222 newly observed transitions. The 50 remaining transitions reach newly determined energy levels. Their assignment relied entirely on the comparison to SP variational calculation [19]. The newly derived energy levels are listed in Table 1 together with their SP rovibrational labeling. These levels which are all levels of the main isotopologue belong to 13 vibrational states. Six of them are marked in bold in Table 1 because they correspond to energy values which were significantly corrected compared to previous literature values. Table 1 includes the deviation of SP values compared to our experimental values. The maximum difference is on the order of 0.6 cm^{-1} .

The positions, SP intensities and assignment of the 222 transitions newly detected by ICLAS are provided as Supplementary Material.

The above described database of the H_2^{16}O energy levels augmented with the 50 ICLAS levels listed in Table 1, and the IUPAC database of H_2^{18}O , H_2^{17}O and HDO [18] were used to assign transitions left unassigned in the TT and RAL line lists. The 113 newly assigned transitions are provided as Supplementary Material. Interestingly, some of these

assignments were included in the HITRAN 2004 line list [22] but have been lost in the most recent version of the HITRAN database [3].

Finally, all the rovibrational transitions reaching the experimentally determined energy levels were calculated for water in “natural” isotopic abundance in the 13500-14100 cm^{-1} range. The line positions calculated at the level of experimental accuracy were augmented with variational intensities [19, 21]. The line intensity cut off was fixed at 4.0×10^{-28} $\text{cm}/\text{molecule}$. On the basis of SP calculations, we have evaluated that 434 transitions with intensities larger than 4.0×10^{-28} cm/mol are predicted in the region but are absent from our list because their upper levels were not yet determined experimentally. The strongest intensity value of these “missing” lines is 1.88×10^{-26} cm/mol . They represent only 4.8×10^{-4} of the total absorbance in the considered region. At the final stage, these 432 purely calculated transitions (marked with “SP”) were gathered with our list yielding a global line list of 4672 transitions provided as Supplementary Material. For comparison, TT [4], RAL [7] and Reims-Brussels [12] line lists include 1988, 1958 and 1695 transitions, respectively in the same region. The HITRAN2008 list includes a total of 2688 lines with intensity above 4.0×10^{-28} $\text{cm}/\text{molecule}$. 437 additional transitions are provided in HITRAN2008 with intensities in the 1.0 - 4.0×10^{-28} $\text{cm}/\text{molecule}$ range. These transitions are all due to H_2^{18}O , H_2^{17}O and HDO minor isotopologues as a result of the abundance factor included in the intensity values provided in HITRAN.

4. CONCLUSION

This work completes our high sensitivity study of the water absorption spectrum by ICLAS using a Ti:Sapphire laser. In this last contribution, we analyzed the 13540- 4070 cm^{-1} region corresponding to a strong absorption range which has been extensively studied by FTS with very long absorption path length [4-11]. Although more limited than in the weak absorption regions [2], the new spectroscopic observation obtained by ICLAS is still significant: 222 very weak transitions were newly detected yielding 50 new or corrected H_2^{16}O energy levels.

From an exhaustive review of the literature, a database of the experimental energy levels of H_2^{16}O was constructed for the spectral region of interest. This H_2^{16}O database and the IUPAC databases of the H_2^{18}O , H_2^{17}O and HDO energy levels [17,18] were used to generate a list of all the transitions of water in “natural” abundance in the 13500-14100 cm^{-1} region (intensity cut off fixed at 4.0×10^{-28} $\text{cm}/\text{molecule}$). This line list is the most complete in

the considered region. It was constructed by combining the positions of the transitions reaching the experimental energy levels with variational intensities [19].

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FIGURE CAPTIONS

Figure 1

Comparison of the ICLAS spectrum of water with the line lists provided by HITRAN2008 and Ref. [4] near 13715 cm^{-1} . The pressure and equivalent absorption path length were $P \approx 12$ Torr and $l_{eq} = 23.9$ km, respectively. Note the logarithmic scale of the line intensities on the two upper panels.

Figure 2

Overview of the water spectrum in the $13500\text{-}14100\text{ cm}^{-1}$ region as obtained by Tolchenov and Tennyson [4] (upper panel) and Schermaul et al. (lower panel) [7]. The very weak transitions newly detected by ICLAS are highlighted on both panels.

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Table 1

New energy levels of H₂¹⁶O derived from the analysis of the ICLAS spectrum of water in the 13540-14070 cm⁻¹ region.

V ₁ V ₂ V ₃	J	K _a	K _c	E ^{obs}	ΔE	V ₁ V ₂ V ₃	J	K _a	K _c	E ^{obs}	ΔE
023	8	1	8	14772.7209	1	240	11	5	7	15689.7484	14
023	8	4	5	15193.7121^a	21						
023	9	1	8	15119.6746	5	301	8	8	1	15492.7767	17
						301	8	8	0	15492.7765	17
042	4	2	3	13810.9739^b	-15	301	9	8	2	16075.8439	-5
042	5	1	5	13782.6863	-14	301	9	8	1	16075.8443	-5
042	8	4	5	14757.7642	-8	301	10	6	5	15539.3915	10
042	10	4	6	15262.5956	18	301	10	8	3	15840.7995^c	4
042	10	5	6	15431.4937	-4	301	11	3	9	15408.1069^d	18
122	7	4	4	14868.3246	13	311	3	3	0	15626.7209^e	13
122	8	5	3	15225.5791	-1	311	7	2	6	16020.1106	10
122	9	3	7	15118.8410	4						
122	9	4	6	15267.5314	15	320	9	4	5	15009.6156	15
122	12	1	12	15370.5629	13	320	10	6	4	15487.6801	26
						320	11	5	6	15708.1030	22
141	11	5	6	15519.4735	8	320	11	6	5	15745.0166	26
						320	13	1	12	15603.8018	27
160	7	7	1	14915.5554	-60						
160	7	7	0	14915.5598	-60	400	7	6	2	14988.0466	32
						400	8	3	5	14809.2387^f	22
170	10	1	10	14951.1780	-26	400	9	9	1	15800.0313	-13
						400	9	9	0	15800.0311	-13
202	10	3	7	15663.2842	-18	400	10	5	5	15380.4364	15
202	11	2	9	15789.2191	41	400	10	6	4	15539.2094	-14
202	11	3	8	15913.5364	3	400	11	1	11	15062.3819	14
						400	11	3	9	15403.7597	23
221	12	4	8	15824.9675	25	400	11	8	4	16088.8169	-8
						400	11	8	3	16088.7933	-9
240	6	5	1	14426.5889	-3	400	12	2	10	15652.8233	21
240	9	6	4	15252.7014	26	400	12	4	9	15794.7459	20

V₁V₂V₃ J K_a K_c – vibration-rotation quantum numbers; E^{obs} – experimental energy, cm⁻¹; ΔE – difference (E^{obs} - E^{SP}) between the experimental and variational [19,20] values of the energy level, 10⁻² cm⁻¹

Notes

The six levels marked in bold correspond to energy values which were significantly corrected compared to previous literature values.

^a The value of 15193.5046 cm⁻¹ in Ref. [8] was obtained from one single transition (023) 8₄₅ – (000) 7₂₆ at 14483.8948 cm⁻¹. This level was also obtained at 15193.503 cm⁻¹ in Ref. [16] from one single line which could not be identified. Our value was derived from the (023) 8₄₅ – (000) 8₄₄ transition at 14061.9362 cm⁻¹ (6.28E-28 cm/mol). If the value of Refs. [8, 16] was correct, we should have measured this line at 14061.7287 cm⁻¹.

^b This level has been obtained in Ref. [4] at 13811.0046 cm⁻¹ from one single line at 13637.6388 cm⁻¹, 1.09E-26 cm/mol. This line is close to a very strong line at 13637.2937 cm⁻¹ (2.47 E-24 cm/mol). In this study we determined the (042) 4₂₃ level from the (042) 4₂₃ – (000) 4₁₄ transition at 13586.1357 cm⁻¹ (1.64E-27 cm/mol). If the value of Ref. [4] was correct, we should have measured this line at 13586.1664 cm⁻¹.

^c This level was obtained in Ref. [15] at 15840.7236 cm⁻¹ from a single line at 13318.4622 cm⁻¹. This line was assigned to two transitions: (301) 10₈₃ – (000) 11₈₄ and the stronger (301) 10₈₂ – (000) 11₈₃ transition. We believe that the line at 13318.5066 cm⁻¹ which was left unassigned in Ref. [15] should be assigned to (301) 10₈₃ – (000) 11₈₄.

^d Values of 15408.1369 and 15408.1353 cm⁻¹ were reported Ref. [4] and in Ref. [2] from two and one line, respectively. If these values were correct, the (301) 11_{3 9} – (000) 11_{1 10} transition should be observed at 13883.289 cm⁻¹ while we measured it at 13883.259 cm⁻¹.

^e This level has been determined at 15626.7467 cm⁻¹ in Ref. [16] from four lines but we have no information about these lines. A value of 15626.7465 cm⁻¹ was also reported in Ref. [8] from four lines. Our value was derived from the (311) 3_{3 0} – (010) 3_{3 1} transition at 13719.2691 cm⁻¹, (2.49E-27 cm/mol) which is significantly shifted compared to the values calculated from the previous level values (13719.2947 cm⁻¹)

^f This level was obtained at 14809.1617 cm⁻¹ in Ref. [2] from a single transition: (400) 8_{3 5} – (000) 9_{4 6} at 13468.2764 cm⁻¹ (1.28E-26 cm/mol). We believe that this assignment is not correct: the (400) 8_{3 5} – (000) 9_{4 6} transition must be at 13468.3534 cm⁻¹ and is overlapped by the stronger (221) 7_{3 5} – (000) 8_{3 6} transition. In this study we determined the (400) 8_{3 5} level from the (400) 8_{3 5} – (000) 9_{4 6} transition at 13728.8531 cm⁻¹ (2.05E-27 cm/mol). If the previous value (14809.1617 cm⁻¹) of this level was correct, we should have observed this line at 13728.7761 cm⁻¹.

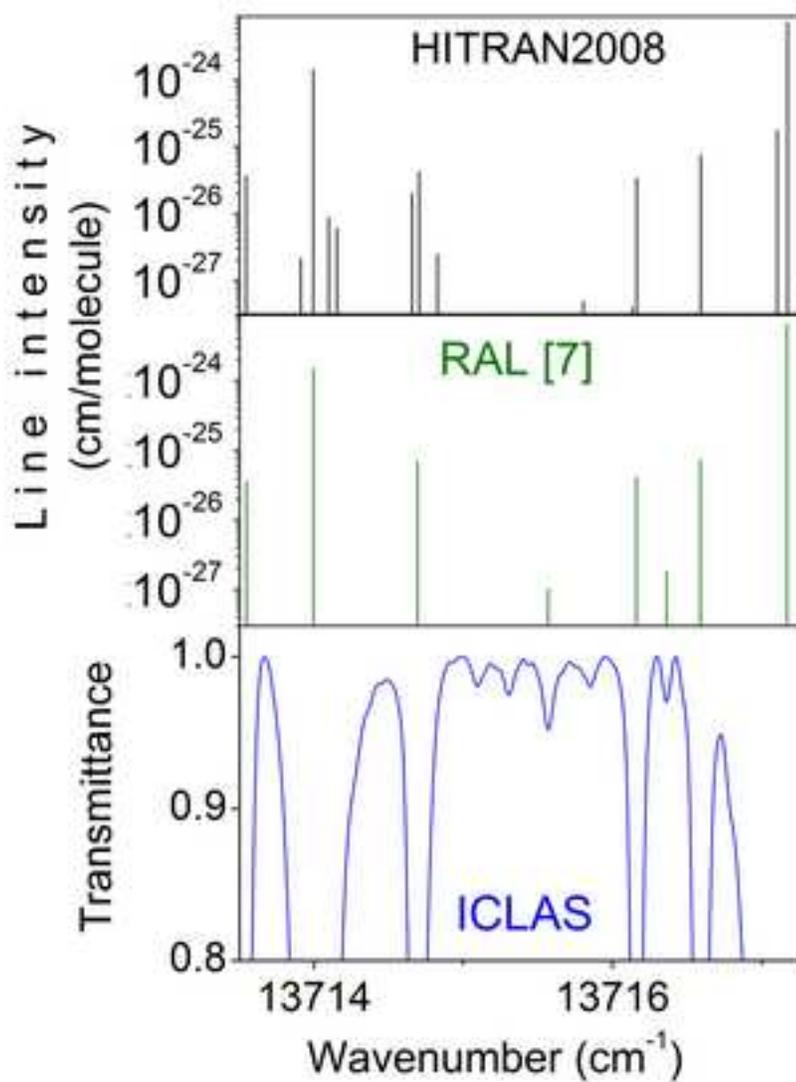
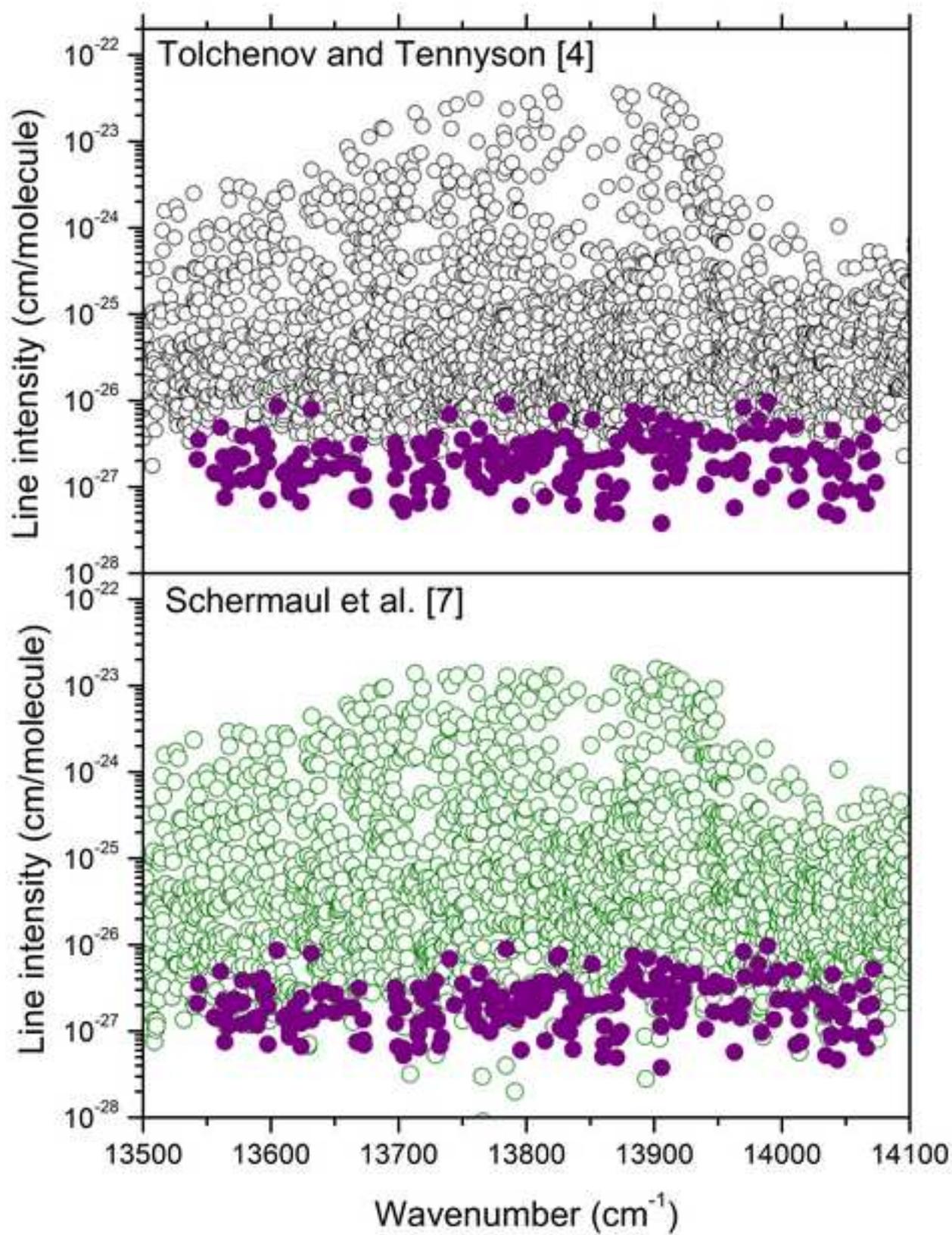


Fig.1

Fig. 2



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Supplementary material to the paper

"The absorption spectrum of water between 13540 and 14070 cm^{-1} :

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Sup Mat I: List of newly observed transitions between 13500 and 14100 cm^{-1}

Sup Mat II: Complete line list of water transitions between 13500 and 14100 cm^{-1}

Sup Mat III: Rovibrational assignments of some of the transitions
unassigned in Schermaul et al. (2002) and Tolchenov & Tennyson (2008)