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Fourier transform absorption spectra of $H_2{}^{18}O$ and $H_2{}^{17}O$ in the $3\nu + \delta$ and 4ν polyad region

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Abstract

Fourier transform absorption spectra of $H_2{}^{18}O$-enriched and $H_2{}^{17}O$-enriched water vapor in the $3\nu + \delta$ and 4ν polyad region have been analyzed. With the aid of theoretically calculated linelists, we have assigned 1014 lines attributed to $H_2{}^{18}O$ and 836 lines of 855 attributed to $H_2{}^{17}O$. Seven new band origins are found for $H_2{}^{17}O$ and one for $H_2{}^{18}O$.

Keywords: Water vapor; Visible; Isotopically substituted

1. Introduction

A precise knowledge of line positions and strengths of water vapor is crucial for accurate atmospheric modelling. Current models of the Earth's atmosphere may significantly underestimate the absorption of solar energy [1–4]. Water vapor is considered to be the major candidate for the missing absorption, although it already accounts for about 70 % of the known absorption of incoming solar radiation in the Earth's atmosphere [5]. Trace isotopologues of water, such as $H_2{}^{17}O$ and $H_2{}^{18}O$, have been less extensively studied than the most abundant $H_2{}^{16}O$, despite their significant possible contribution to the absorption of solar radiation in the atmosphere.

In 1981, Chevillard and co-workers recorded spectra with isotopically enriched $H_2{}^{18}O$ and $H_2{}^{17}O$ samples over a wide frequency range using the Fourier transform spectrometer at the National Solar Observatory (Kitt Peak, AZ). Many studies of the spectra have been made and the detailed information of the experiment can be found elsewhere [6–11]. Tanaka et al. [10] previously analyzed the $H_2{}^{18}O$ spectrum in the $3\nu + \delta$ and 4ν polyad region using a variational linelist generated by Partridge and Schwenke [12]. In this work, we re-analyzed this spectrum using newly calculated linelists. These allow us to extend the number of assignments made from 747 to 1014. The spectra of $H_2{}^{17}O$ have been extensively analyzed by Toth [13–17] in the past. The highest frequency region studied is by Camy-Payret et al. [11], in which they analyzed up to 11335 cm^{-1}. In this work, again using newly calculated linelists, we extend the analysis of $H_2{}^{17}O$ up to 14520 cm^{-1}, covering the entire $3\nu + \delta$ and 4ν polyad.

2. Experimental conditions

The spectra of two isotopically enriched samples of water vapor were recorded using the McMath-Pierce Fourier transform spectrometer. The first sample contained $H_2{}^{18}O$ at 73 ± 1% [7], referred as "^{18}O" below, and the second sample, "^{17}O" below, contained enriched

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$H_2{}^{17}O$ and $H_2{}^{18}O$ [8]. In both experiments, the sample was contained in a 6-m White type cell to create the absorption pathlength of 434 m. The experimental conditions of each spectrum can be found in Table 1. Lines in both spectra were fitted using the GREMLIN program of Brault (unpublished).

The ^{17}O and ^{18}O spectra contain transitions by $H_2{}^{16}O$, $H_2{}^{17}O$, and $H_2{}^{18}O$ and in some cases even by HDO. To filter the transitions due to the isotopologue of interest—$H_2{}^{17}O$ for ^{17}O spectrum and $H_2{}^{18}O$ for ^{18}O—we compared the spectra of natural abundance water, ^{17}O and ^{18}O simultaneously. In this work, the Fourier transform spectrum of natural abundance pure water measured by Schermaul et al. [18] at Rutherford Appleton Laboratory (UK) was used instead of the one by Mandin et al. [19] recorded at the same time as the isotopically enriched spectra at Kitt Peak. The spectrum by Schermaul et al. was selected as it is known to contain many lines that were not observed previously. The three spectra were read into a spreadsheet and lines of the same frequency were aligned. The ratio of intensities of these were calculated to allow us to look for the characteristic patterns that have been derived from the isotopic composition of each sample, which is tabulated in Table 2. For the ^{18}O spectrum, 1014 lines were attributed to $H_2{}^{18}O$ and for the ^{17}O spectrum, 855 lines were attributed to $H_2{}^{17}O$ in this fashion. A complete list of these lines including absolute intensities and rotational and vibrational quantum numbers are given in the electric archive. The ratio of $H_2{}^{18}O$ linestrengths in the ^{18}O to the natural abundance spectrum was found to be 30.7 in the previous analysis [10]. The abundance of $H_2{}^{17}O$ in the ^{17}O spectrum is fairly small, at only about the 5% of the total sample content. The ratio of $H_2{}^{17}O$ linestrengths to the natural abundance can be deduced to 19.6 from the Table 2. Absolute intensities (in cm molecule^{-1}) given in the electric archive are scaled to the natural abundance of each isotopologue and normalized to 296 K to match the HITRAN temperature.

3. Line assignments

Two linelists were used for line assignments. One was generated at University College London using the DVR3D program suite [20] with the fit B potential energy surface (PES) by Shirin et al. [21] and an ab initio dipole moment surface (DMS) fitted by Lynas-Gray et al. to the calculations of Polyansky et al. [22]. The parameters used in this calculation can be found in [23]. Another linelist, used at the Institute of Atmospheric Optics, was generated by Tashkun following the method in reference [12] with the PES by Partridge and Schwenke [12] and the ab initio DMS by Schwenke and Partridge [24].

The following procedure was used for making assignments. First we made "trivial" assignments, which are ones linking upper energy levels already determined experimentally. The remaining unassigned lines were compared to the spectra synthesized from the two linelists, which contain:

(1) Line positions in cm^{-1}
(2) Line intensity in cm molecule^{-1}
(3) Upper rotational quantum numbers, $J'K'_aK'_c$
(4) Lower rotational quantum numbers, $J''K''_aK''_c$
(5) Upper vibrational quantum numbers, $(v'_1v'_2v'_3)$
(6) Lower vibrational quantum numbers, $(v''_1v''_2v''_3)$

Initial assignments were made for each experimental line by selecting the theoretical lines whose line positions fall within the experimental position ±0.03 cm^{-1}. The value of error can be varied to narrow or broaden the selection window. Intensities were also taken into consideration to make initial assignments. The intensities of the 100 strongest experimental lines were compared with those of the corresponding theoretical lines to give the intensity ratios. These ratios were used as a rough guide for making the initial assignments.

Upper energy levels were then determined by adding the energies of lower levels, which were taken from the earlier study by Toth [14] and Mikhailenko et al. [25],

Table 2
Isotopic composition of the samples

Isotopologue	Natural	$H_2{}^{17}O$ enriched	$H_2{}^{18}O$ enriched
$H_2{}^{16}O$	4496.90	469.02	100.73
$H_2{}^{17}O$	1.676	32.81	1.05
$H_2{}^{18}O$	9.017	156.62	276.62

The number of molecules in each sample is given in 10^{19} molecules cm^{-3}.

Table 1
Experimental conditions of the spectra analyzed in this work

Type of spectrum (file name)	l (m)	P (hPa)	T (K)	R (cm^{-1})	Range (cm^{-1})
$H_2{}^{18}O$ enriched (810825R0.002)	434.0	3.62	300.5	0.0168	12400–14520
$H_2{}^{17}O$ enriched (810827R0.001)	434.0	6.32	301.2	0.0143	11500–12800
$H_2{}^{17}O$ enriched (810827R0.002)	434.0	6.32	301.4	0.0168	12900–14500

l is the absorption pathlength, P is the total pressure with error of ±1%, T is the temperature, and R is the resolution. These spectra can be found in the digital archive at the National Solar Observatory website (http://diglib.nso.edu/) under the file names given above.

to the experimental frequencies. All possible combinations of transitions with those upper energy levels were generated to search for further assignments by combination differences. Upper energy levels that were not confirmed by combination differences are re-considered and any necessary changes were made. The ratios of new upper energy levels to $H_2{}^{16}O$ energy levels were taken to check the reliability of assignments, as these ratios are approximately constant within a vibrational band [10]. Another way to check the assignments was to look at the differences between the observed and calculated energy levels. The obs − calc values tend to be systematic, like the ratios, and can be used to check the validity of energy levels. Further assignments were made using a small computer program that calculates all possible combinations of upper and lower energy levels with the observed transition frequencies. finally we could assign all the transitions attributed to the $H_2{}^{18}O$ species. The full identification list of the $H_2{}^{18}O$ transitions is in the electronic archive. It contains some of $H_2{}^{18}O$ lines blended with $H_2{}^{16}O$ or $H_2{}^{17}O$ transitions. Even so, a number of the relatively strong $H_2{}^{18}O$ lines were irrecoverably blended; these are not included in the final list.

The previous analysis of the ^{18}O spectrum assigned 746 out of 926 lines in the range of 12 400–14 520 cm^{-1} [10]. In this work, we extended the number of assigned lines to 1014. The same assignments were found in both works for 616 lines and different assignments for 125 lines. 169 previously unassigned lines were newly assigned in this work.

Table 3 gives a summary of $H_2{}^{18}O$ energy levels determined in the previously and this work. In this work, the lines are assigned to 15 different upper vibrational bands, giving 399 new energy levels; a great improvement on the previous analysis, in which 287 new energy levels were determined. In particular, the (3 0 1) vibrational state is significantly improved as almost twice as many levels are obtained in this work. The (2 0 2)–(0 0 0) and (4 0 0)–(0 0 0) band origins (at 14187.2824 and 13793.26 cm^{-1}, respectively) were newly derived. Although the (2 0 2)–(0 0 0) band origin was derived from blended line at 14151.2338 cm^{-1}, it can be considered reliable with an experimental accuracy of 0.03 cm^{-1}. The (4 0 0)–(0 0 0) band origin was obtained by fitting the low K_a energy levels of the (4 0 0) state up to $J = 7$ with the confidential interval 0.016 cm^{-1}.

Table 4 gives the derived energy levels for (2 2 1), (4 0 0), (3 0 1), (2 0 2), and (1 0 3) vibrational states. The complete list of the energy levels obtained for $H_2{}^{18}O$ is given in the electronic archive. Of the 502 energy levels derived, only 259 were confirmed through combination differences (CD) of two and more lines. The average experimental uncertainty for these levels was estimated to be of 0.00046 cm^{-1}, while levels derived from one (weak) line may have considerably larger uncertainty. An rms experimental uncertainty is given for all levels derived from the CD relations in the electronic archive.

Interestingly, the 3_{03} level of the highly excited (0 7 1) bending state at 13921.2505 cm^{-1} was determined in this study through two strong lines which borrow their intensities via high-order resonance links with the 3_{03} level at 13922.4724 cm^{-1} of the (3 0 1) state.

The ^{17}O spectrum was analyzed in the range of 11 335–14 520 cm^{-1}, which covers the entire $3\nu + \delta$ and 4ν polyad. We assigned 836 lines out of 855 lines attributed to $H_2{}^{17}O$, leaving only 19 lines unassigned. Table 5

Table 3
Summary of $H_2{}^{18}O$ energy levels determined in the previous analysis (*a*) and this work (*b*)

State	Origin (cm^{-1})	No. of levels		No. of transitions	
	b	*a*	*b*	*a*	*b*
(3 1 0) or $30^{+}1$		0	1(1)	1	1
(1 1 2) or $21^{+}1$		42	45(8)	57	69
(2 1 1) or $30^{-}1$		7	6(0)	12	6
(0 1 3) or $21^{-}1$	12520.123	62	72(12)	95	112
(1 4 1) or $20^{+}4$		1	3	2	4
(3 2 0) or $30^{+}2$		0	18	0	28
(0 4 2) or $11^{-}4$		1	1	2	3
(1 2 2) or $21^{+}2$		9	9	10	15
(2 2 1) or $30^{-}2$	13612.710	63	72	140	175
(0 2 3) or $21^{-}2$		11	12	15	17
(4 0 0) or $40^{+}0$	13793.263[a]	45	57	101	136
(3 0 1) or $40^{-}0$	13795.398	47	92	122	262
(2 0 2) or $31^{+}0$	14187.982	38	45	82	103
(1 0 3) or $31^{-}0$	14276.336	43	68	95	154
(0 7 1) or $10^{-}7$		0	1	0	2
	Total	287	399	746	1087

Vibrational states are labelled using normal mode (left) and local mode (right) notations. Number of levels shows the number of all determined energy levels. Number of transitions shows the number of transitions to the vibrational bands. Given in parentheses are new with respect to [9] levels.

[a] Vibrational energy was not determined from the observed line (see text).

Table 4
$H_2{}^{18}O$ energy levels determined in this work (in cm^{-1})

J	K_a	K_c	(221) or 30^-2		(400) or 40^+0		(301) or 40^-0		(202) or 31^+0		(103) or 31^-0	
0	0	0	13612.71019	1			13795.39819	1	14187.98240	1	14276.33579	1
1	0	1	13635.47509	1	13815.60054	1	13817.70366	2	14210.32373	2	14298.91161	2
1	1	1	13651.98318	2	13826.27203	1	13828.30983	2	14221.01990	2	14308.78638	2
1	1	0	13657.84489	2			13833.44884	2	14226.20854	2	14314.08164	2
2	0	2	13679.55817	2	13858.82439	2	13860.81818	3	14253.48229	2	14342.39991	3
2	1	2	13691.79188	3	13865.89802	2	13867.80601	3	14260.48426	2	14348.71201	3
2	1	1	13709.27945	3			13883.19075	3	14276.01061	1	14364.54446	2
2	2	1	13757.79230	2	13912.95803	2	13914.90380	2	14307.88585	2	14393.96765	2
2	2	0	13759.10078	2			13916.36203	2	14309.32524	1	14395.59238	2
3	0	3	13743.82871	2	13920.64219	2	13922.47241	2	14315.15652	2	14404.30896	2
3	1	3	13750.40614	2	13924.60966	2	13926.26713	3	14318.82996	2	14407.71184	2
3	1	2	13785.36542	2	13954.59998	3	13956.63093	3	14349.54451	2	14438.85819	2
3	2	2	13826.22807	4	13980.00652	2	13981.85195	4	14374.78865	1	14462.30225	4
3	2	1	13832.33302	2	13986.48677	2	13988.46619	3	14381.29893	3	14469.35990	2
3	3	1	13919.95361	3	14046.11380	1	14047.92904	2	14440.77575	2	14524.25994	2
3	3	0	13920.18039	2	14046.38138	2	14048.20109	2	14440.79932	2	14524.59329	2
4	0	4	13824.20332	3	13999.43164	2	14001.79836	3	14393.73397	2	14483.13230	2
4	1	4	13827.77209	2	14000.37965	2	14002.84001	2	14395.37871	2	14486.11039	2
4	1	3	13884.62002	2	14050.14869	2	14052.07045	3	14445.05700	1	14535.04030	2
4	2	3	13916.53051	2	14068.12679	4	14069.83169	2	14462.74860	2	14552.07371	2
4	2	2	13932.60767	2	14084.79276	1	14086.74979	4	14478.34976	2	14569.38970	3
4	3	2	14013.56880	4	14137.80563	4	14139.53911	3	14532.19127	1	14612.98408	2
4	3	1	14014.70927	2	14139.47929	2	14141.32240	3	14532.93125	1	14614.41487	2
4	4	1	14137.05421	1	14226.98004	2	14228.72811	2	14625.85404	2	14700.01971	2
4	4	0	14137.08539	2	14227.02544	2	14228.77409	2	14625.15834	2	14700.11589	2
5	0	5	13921.24262	1	14094.85734	1	14097.01521	2	14488.92503	2	14578.70296	2
5	1	5	13922.96658	2			14097.34313	2	14489.59341	2	14578.84293	2
5	1	4	14004.81808	2	14165.41130	2	14167.13543	3	14560.10068	3	14650.39566	1
5	2	4	14029.80110	2	14176.38088	2	14177.89075	4	14570.80723	1	14663.40660	2
5	2	3	14059.51203	3	14208.15452	3	14210.13413	3	14604.02443	2	14694.45375	1
5	3	3	14130.17722	2	14252.12665	2	14253.79799	3			14742.84806	2
5	3	2	14134.65713	2	14258.18007	3	14260.07992	3	14649.28400	2	14746.06671	1
5	4	2	14254.29840	1	14342.22061	1	14343.90917	3	14729.97926	1	14814.53426	2
5	4	1	14254.58101	1	14342.56142	3	14344.25508	3	14725.98432	2	14815.00881	1
5	5	1	14403.02332	2	14459.55381	1	14461.44409	1			14920.61979	1
5	5	0	14403.02258	1	14459.52476	1	14461.44038	1			14920.61608	1
6	0	6	14034.75836	2			14208.49543	4			14691.20846	2
6	1	6	14035.66052	2			14209.41417	3	14601.15051	2	14691.31112	1
6	1	5	14143.37766	2	14298.24532	1	14299.75104	4			14782.66716	2
6	2	5	14155.70090	2	14303.85695	3	14305.09232	3	14697.98986	2	14785.26742	1
6	2	4	14212.57820	2	14354.73652	2	14356.66512	4	14750.62619	1	14842.37136	2
6	3	4	14269.31715	2	14388.38322	3	14389.96037	3	14782.00924	1	14883.17200	1
6	3	3	14281.02267	2			14405.51475	3	14802.09748	1	14892.38722	3
6	4	3	14395.09206	2	14480.74467	3	14482.38697	3	14869.82267	2	14952.44181	2
6	4	2	14396.32696	4	14482.34086	1	14483.95803	3	14862.31449	1	14954.52456	2
6	5	2	14543.03882	1	14598.93036	2	14600.77600	2				
6	5	1	14543.06195	2			14600.90707	2			15058.79975	1
6	6	1			14699.06589	1					15185.26935	1
6	6	0			14699.06218	1					15185.26893	1
7	0	7	14164.98438	2	14336.00462	1	14338.16033	2	14729.68913	1	14820.77878	2
7	1	7	14166.15443	1			14338.19686	3			14821.32297	2
7	1	6	14299.34441	2	14450.08114	2	14449.58171	2			14931.11176	1
7	2	6	14305.53979	2	14445.64346	1	14451.94539	2			14931.67494	2
7	2	5			14521.98165	1	14523.75816	2			15010.21345	1
7	3	5	14430.31268	2			14546.88638	2			15047.61250	1
7	3	4	14457.58496	1	14575.32970	1	14577.28213	3			15065.09799	1
7	4	4	14559.95006	2	14642.23599	1	14643.89299	3			15113.44541	2
7	4	3	14563.03781	1			14648.90298	2	15021.00089	2		
7	5	3	14706.28809	4			14763.80655	2				
7	5	2			14762.19190	1			15153.18280	1		
7	6	2					14862.66014	2				
7	6	1			14861.21080	2	14862.66195	1				
7	7	1					15006.27242	1				

Table 4 (*continued*)

J	K_a	K_c	(221) or 30^-2		(400) or 40^+0		(301) or 40^-0		(202) or 31^+0		(103) or 31^-0	
7	7	0					15006.27242	1				
8	0	8	14312.77953	2			14484.28604	3			14967.26833	2
8	1	8	14310.23379	1			14484.31392	1	14875.95529	1	14967.30842	1
8	1	7	14470.92582	1	14610.56522	1	14613.41119	2			15095.98564	2
8	2	7			14611.18362	1	14613.83686	2				
8	2	6			14706.39065	1	14708.93869	2			15196.79065	1
8	3	6			14722.50535	1	14723.86385	1				
8	3	5	14656.46317	2			14773.49727	3			15261.97713	1
8	4	5	14746.52419	1	14826.16733	1	14827.79379	1				
8	4	4	14755.67733	2			14840.17362	2				
8	5	4			14948.36272	1			15340.64022	1		
8	5	3	14893.74964	2			14951.22385					
8	6	3			15046.44425	1						
8	6	2				1	15047.89495	1				
8	7	2					15191.25254	1				
8	7	1					15191.25235	1				
9	0	9	14470.24524	1			14647.38327	1			15130.93774	1
9	1	9	14474.76441	2			14647.43961	2			15130.94440	1
9	1	8	14658.72066	1			14794.39714	1				
9	2	8	14658.60964	1			14794.52404	2			15277.26854	1
9	2	7			14909.12475	1	14910.64307	1				
9	3	7	14812.29460	1	14918.54507	1	14919.63945	1				
9	4	6	14955.62792	1			15033.55502	1				
10	0	10	14654.06748	1			14827.40388	1			15311.61615	2
10	1	10					14827.39569	1				
10	1	9	14865.63957	1			14992.29012	2			15475.29607	1
10	2	9					14992.31431	1				
10	2	8	15028.64345	1			15132.67595	1				
10	3	7					15229.07436	1				
10	4	6					15301.95376	1				
11	0	11					15024.31039	2			15509.10967	1
11	1	11					15024.31932	2			15509.12470	1
12	0	12					15238.49753	1				
12	1	11					15438.05137	1				

Also given are the number of transitions used in level determination.

Table 5
Summary of $H_2{}^{17}O$ energy levels determined

Band	Origin (cm^{-1})	Levels	Trans
(003) or 21^-0		1	1
(131) or 10^-3	11792.827	34	51
(310) or 30^+1	12122.20[a]	29	37
(112) or 21^+1	12389.11[a]	27	46
(211) or 30^-1	12132.993	91	206
(013) or 21^-1	12541.226	39	66
(141) or 20^+4		1	1
(320) or 30^+2		3	7
(042) or 11^-4		1	1
(221) or 30^-2	13631.500	56	108
(400) or 40^+0	13809.72[a]	30	57
(301) or 40^-0	13812.158	77	195
(202) or 31^+0	14203.56[a]	14	24
(103) or 31^-0	14296.280	40	69
(071) or 10^-7	13808.273	2	4
	Total	445	873

Vibrational states are labelled using normal mode (left) and local mode (right) notations. "Levels" shows the number of newly determined energy levels. "Trans" shows the number of transitions to the vibrational bands.

[a] Vibrational energy was not determined from the observed line (see text).

gives the summary of energy levels derived in this work. All the lines originate in the (000) ground vibrational level and are assigned to 15 different upper vibrational levels. Vibrational energies of the (131), (211), (013), (221), (301), (103), and (071) states are newly determined at 11792.827, 12132.993, 12541.226, 13631.500, 13812.158, 14296.280, and 13808.273 cm^{-1}, respectively. As was recognised in the earlier analysis of the ^{18}O spectrum [10], the ratios of $H_2{}^{17}O$ to $H_2{}^{16}O$ energy levels were constant within the vibrational bands. Furthermore systematic differences between observed and calculated energy levels were seen, which helped to check the validity of the energy levels derived. Using this regular behaviour of the obs – calc values, it was then possible to determine vibrational energies for four further states: (310), (112), (400), and (202). These energies were also shown in Table 5. We estimate that they are accurate within 0.05 cm^{-1}.

Of 445 derived levels 236 were confirmed by combination differences, especially those in (211) and (301) vibrational states, which makes these derived energy levels much more reliable. An average experimental uncer-

Table 6
$H_2{}^{17}O$ energy levels determined using the newly calculated linelist $H_2{}^{17}O$ energy levels determined using the newly calculated linelist (cm^{-1})

J	K_a	K_c	(131) or $30^{-}2$		(310) or $40^{+}0$		(112) or $40^{-}0$		(211) or $31^{+}0$		(013) or $31^{-}0$	
0	0	0	11792.82700	1					12132.99260	1	12541.22550	1
1	0	1	11816.05370	1	12144.98240	1	12411.93410	2	12155.59840	1	12564.35220	1
1	1	1	11838.44175	2	12158.97125	2			12169.33615	2	12576.62510	2
1	1	0					12430.92190	2	12174.88130	2	12582.32490	1
2	0	2	11861.33315	2			12456.16020	1	12200.76660	3	12608.99765	2
2	1	2	11878.72090	1	12198.04125	2	12465.46120	1	12209.35240	2	12617.18940	1
2	1	1	11897.17285	2					12225.92685	2	12634.26450	3
2	2	1	11962.49950	1	12256.37200	1	12522.38610	2	12266.28460	2	12670.69500	1
2	2	0	11963.61530	2					12267.66660	2	12672.26090	1
3	0	3			12252.45340	2	12519.56720	2	12263.67650	2	12672.90415	2
3	1	3	11938.38175	2	12257.69180	1	12524.79360	1	12268.62720	3	12677.12280	2
3	1	2	11975.04370	1	12290.72490	1	12557.83495	2	12301.35840	3	12710.87990	1
3	2	2	12032.23413	3	12324.84220	1	12590.89930	2	12334.60160	4	12740.17430	2
3	2	1			12330.88050	1	12597.30240	1	12340.98620	3	12747.30710	2
3	3	1	12151.83090	1			12671.05740	2	12415.26155	2	12814.68590	2
3	3	0	12151.95690	1	12406.52930	1	12671.51660	2	12415.48680	2	12814.97060	1
4	0	4	12009.84515	2			12600.42520	1	12344.16630	2	12753.40920	2
4	1	4	12016.91640	1	12335.57130	1	12602.66560	2	12346.51193	3	12755.67965	2
4	1	3	12076.78420	2					12399.52863	3	12810.30530	1
4	2	3			12415.03810	2	12681.04295	2	12424.54793	4		
4	2	2	12138.65505	2			12697.78500	1	12441.17980	3	12849.68450	2
4	3	2	12246.90120	1	12499.80920	1	12765.08800	1	12508.65537	3		
4	3	1	12247.73900	1					12510.14947	4	12912.00185	2
4	4	1			12609.06200	1			12616.38520	1		
4	4	0	12402.72870	1	12609.09910	1			12616.41805	2	13008.49120	2
5	0	5			12430.27620	1	12696.99530	2	12441.42487	3	12851.19880	1
5	1	5			12431.39840	1			12442.42240	2	12852.33650	2
5	1	4					12775.58670	2	12517.88630	3	12929.91330	2
5	2	4	12237.70090	2	12526.37180	1			12535.36060	4	12943.35110	2
5	2	3					12824.43210	1	12567.59210	2		
5	3	3	12365.53960	1			12881.88360	1	12625.17810	2	13029.04750	2
5	3	2			12621.43380	1			12630.59070	2		
5	4	2	12521.62513	2					12733.62580	2	13131.38360	1
5	4	1			12726.84780	1			12733.89530	2		
5	5	1	12711.07360	1	12860.91340	1			12868.94150	1	13250.33360	1
5	5	0	12711.07010	1	12860.95650	1			12868.93800	1	13250.33000	1
6	0	6	12226.13790	2			12811.32850	1	12555.52350	2	12965.87370	2
6	1	6			12544.74850	1			12555.96850	2		
6	1	5	12346.86740	1					12658.94060	3	13067.16480	2
6	2	5	12372.01410	1	12653.09140	2	12922.38830	1	12662.09420	2		
6	2	4							12718.46860	3	13131.22100	1
6	3	4			12755.60590	1			12764.16620	3		
6	3	3	12516.28170	1					12778.04082	4	13186.71170	1
6	4	3	12668.36585	2			13130.32240	1	12874.51820	2		
6	4	2							12875.73650	2		
6	5	2			13001.73670	1			13009.97960	1		
6	5	1	12855.13170	1					13010.01190	2	13392.34550	1
6	6	1							13174.36900	1		
6	6	0							13174.36840	1		
7	0	7					12942.50990	1	12686.65870	1		
7	1	7							12687.18600	2	13097.77800	2
7	1	6					13066.53390	1	12811.88110	2		
7	2	6			12805.93200	1			12813.56620	2	13226.43090	1
7	2	5							12891.47220	1		
7	3	5	12670.65420	2	12916.31280	1			12924.66043	3		
7	3	4							12952.61200	1		
7	4	4	12833.07180	1					13038.78920	2		
7	5	3							13174.67000	2		
7	5	2	13022.69480	1								
7	6	2							13339.97860	1		
7	6	1							13339.97360	1		
7	7	1							13463.09680	1		
7	7	0							13463.09660	1		

Table 6 (*continued*)

J	K_a	K_c	(1 3 1) or $30^{-}2$		(3 1 0) or $40^{+}0$		(1 1 2) or $40^{-}0$		(2 1 1) or $31^{+}0$		(0 1 3) or $31^{-}0$	
8	0	8							12835.28430	2	13246.77950	1
8	1	8							12834.25040	2		
8	1	7							12979.83840	1	13390.76430	1
8	2	7							12981.25605	2		
8	2	6							13083.84330	2		
8	3	6			13099.62010	1						
8	3	5							13152.86400	2		
8	4	4							13236.13030	1		
8	5	3							13363.63090	1		
9	0	9							12999.13090	1		
9	1	9							12999.86090	2		
9	1	8							13166.39090	1		
9	2	8							13166.45910	2		
9	3	7					13293.19300	1	13306.68510	1		
9	3	6							13376.28000	1		
9	4	6							13435.89660	1		
9	4	5							13456.56100	1		
9	5	5							13574.60460	1		
10	0	10							13181.62100	2		
10	1	10							13181.57620	1		
10	1	9							13365.21210	1		
10	2	9							13368.73930	1		
10	2	8							13524.27980	1		
10	3	7							13618.93750	1		
10	4	6							13703.59770	1		
11	0	11							13380.81980	1		
11	1	11							13380.83600	1		
11	2	10							13586.32560	1		
12	0	12							13596.93430	1		
12	1	12							13596.94110	1		

Also given are the number of transitions used for level determination.

tainty for such levels is about 0.001 cm^{-1}, that is about twice that of the ^{18}O spectrum . Table 6 gives the newly determined energy levels of the $3v+\delta$ polyad, (1 3 1), (3 1 0), (1 1 2), (2 1 1), and (0 1 3) and Table 7 gives the energy levels of the $4v$ polyad, (2 2 1), (4 0 0), (3 0 1), (2 0 2), and (1 0 3). The number of transitions used for level determination is also given in those tables. Many lines are assigned to the (2 1 1) and (3 0 1) vibrational bands, which are the strongest bands in the $3v+\delta$ and $4v$ polyad, respectively.

The resonance interactions between the $H_2{}^{17}O$ states considered resemble those discussed above for the $H_2{}^{18}O$ molecule. Thus, there is considerable intensity borrowing between (3 0 1)–(0 0 0) transitions to the 0_{00} and 2_{02} upper levels and the corresponding (0 7 1)–(0 0 0) transitions. Two energy levels of the (0 7 1) state could be derived: 0_{00} at 13808.2733 cm^{-1} and 2_{02} at 13877.0172 cm^{-1}.

4. Discussion and conclusion

A new version of HITRAN (HITRAN2004) has just been released [26]; all the transitions of $H_2{}^{18}O$ analyzed previously[10] are included in this edition. The previous version of HITRAN (HITRAN2000) [27] contained 51 transitions assigned to $H_2{}^{18}O$ by Mandin et al. [19] in the region studied here, which are confined to the frequency range 13 608–13 893 cm^{-1}. These 51 common lines have been all replaced by the new lines obtained in this work.

The highest frequency listed for $H_2{}^{17}O$ in the HITRAN2000 is 11143 cm^{-1}, which is considerably lower than those for $H_2{}^{16}O$ and $H_2{}^{18}O$. Unlike the $H_2{}^{18}O$ transitions, the $H_2{}^{17}O$ lines analyzed are yet to be included in HITRAN. However the significance of this data to atmospheric modelling and other applications is beyond doubt.

Cavity ring-down spectra of $H_2{}^{18}O$ and $H_2{}^{17}O$ in the $5v$ polyad region have been analyzed recently [23,28]. To provide more complete data for water isotopologues, the missing $4v+\delta$ polyad region (14 500–16 700 cm^{-1}) need to be studied. The success of analyzing the $H_2{}^{18}O$ and $H_2{}^{17}O$ spectra in this work should encourage the measurements of isotopically enhanced spectra in the $4v+\delta$ and higher polyad regions.

In this work, the Fourier transform spectra of $H_2{}^{18}O$-enriched and $H_2{}^{17}O$-enriched water vapor have been analyzed using theoretically calculated linelists. We have assigned all of 1014 lines attributed to $H_2{}^{18}O$ and 836 out of 855 lines attributed to $H_2{}^{17}O$.

Table 7
$H_2{}^{17}O$ energy levels determined in this work (in cm^{-1})

J	K_a	K_c	(221) or 30^-2		(400) or 40^+0		(301) or 40^-0		(202) or 31^+0		(103) or 31^-0	
0	0	0	13631.49980	1			13812.15810	1			14296.27950	1
1	0	1	13654.26415	2	13832.08220	1	13834.48690	2	14225.90410	1	14318.87850	2
1	1	1	13670.98950	2			13845.21055	2			14328.88035	2
1	1	0	13676.85120	2			13850.33605	2	14241.93080	1	14334.16110	2
2	0	2	13698.30330	2	13875.37450	2	13877.91150	2			14362.42545	2
2	1	2	13710.87750	2	13882.60450	1	13884.75020	3	14276.28470	2	14368.86030	2
2	1	1	13728.28333	3			13900.08675	4	14291.73835	2	14384.64507	3
2	2	1	13777.38650	2	13930.08735	2	13932.28330	2			14414.46010	2
2	2	0	13778.67770	2			13933.71890	2			14416.06120	2
3	0	3	13762.75490	1	13937.30000	1	13939.16153	3	14330.92570	3	14424.45170	1
3	1	3	13769.54740	2	13941.46610	3	13943.34770	4			14427.92720	3
3	1	2	13804.39640	2	13971.27700	1	13973.56427	3	14365.31400	2	14459.02050	1
3	2	2	13845.86290	2	13997.19130	2	13999.27440	3			14482.79340	2
3	2	1	13851.88810	2			14005.79260	3	14397.46990	1	14489.79830	2
3	3	1	13940.42530	2			14066.13480	2			14545.42870	1
3	3	0	13940.69460	2			14066.39910	2				
4	0	4	13843.36830	2	14016.30700	1	14018.94760	3			14503.44420	1
4	1	4	13847.02420	2	14017.31170	2	14020.01550	3	14411.40560	2	14505.95540	2
4	1	3	13903.71290	3	14066.93010	1	14069.10650	3			14555.32065	2
4	2	3			14085.41360	2	14087.33160	3	14479.09300	1	14572.54210	1
4	2	2	13952.14920	2			14104.01350	3			14589.83377	3
4	3	2	14034.09110	2	14155.80910	2	14157.78740	3			14644.62260	1
4	3	1	14035.20990	2			14159.50800	2			14645.60570	1
4	4	1	14158.73180	1	14246.24060	1	14248.24330	2	14633.90990	1	14722.07530	1
4	4	0	14158.76175	2			14248.28025	2			14722.22560	1
5	0	5	13940.63320	1	14111.91690	2	14114.34650	2			14599.21430	1
5	1	5	13942.39620	3			14114.68570	2			14599.24510	2
5	1	4	14024.04630	2	14182.43810	2	14184.38260	3			14670.89620	2
5	2	4	14044.43740	1	14193.80840	1	14195.51950	2			14683.46170	2
5	2	3	14079.06155	2	14225.16720	1	14227.45070	2	14620.37150	1	14714.97440	1
5	3	3	14150.75130	2			14272.08798	4			14762.59420	1
5	3	2	14155.08010	1	14276.16390	2	14278.20600	2				
5	4	2	14275.88610	1			14363.48460	3				
5	4	1	14276.23720	1	14361.87920	1	14363.81610	2	14745.61500	1		
5	5	1	14425.48980	1			14483.46140	2				
5	5	0					14483.45510	1				
6	0	6	14054.38970	2	14225.02390	1	14226.21500	2			14711.95080	2
6	1	6	14055.33490	2			14227.04275	2			14712.05340	1
6	1	5	14163.58460	1	14315.65300	1	14317.38650	3			14803.46030	2
6	2	5	14176.12350	1	14321.54810	3	14322.91700	2				
6	2	4	14231.94270	3			14374.09750	3			14863.05215	2
6	3	4			14406.59490	3	14408.23570	2				
6	3	3	14301.24320	2			14423.54880	4	14820.10680	1		
6	4	3			14500.16210	1	14502.05900	2				
6	4	2	14417.95220	2			14503.53980	2				
6	5	2	14565.42750	1					15009.23130	1		
6	5	1	14565.43100	1			14623.13710	1				
6	6	1	14656.62060	1			14723.60150	1				
6	6	0	14656.62010	1			14723.60100	1				
7	0	7					14356.00595	2			14841.69650	1
7	1	7	14186.28530	2			14356.01660	3			14841.55310	1
7	1	6			14460.90970	1	14467.58300	2				
7	2	6	14325.93480	1	14463.70520	1	14468.27960	2			14952.64220	1
7	2	5			14538.86750	1	14541.45880	2			15031.17270	1
7	3	5	14451.09210	1	14563.62040	1	14565.48940	2				
7	3	4					14595.29060	2				
7	4	4	14581.57820	1			14663.64290	1				
7	4	3					14668.42560	1				
7	5	3	14786.21350	1			14728.54115	2				
7	6	2					14885.76170	1				
8	0	8	14333.14800	1			14502.39810	2			14988.56840	1
8	1	8					14502.43050	1				
8	1	7	14491.38290	1			14631.79173	3			15117.49090	1

Table 7 (*continued*)

J	K_a	K_c	(221) or $30^{-}2$		(400) or $40^{+}0$		(301) or $40^{-}0$		(202) or $31^{+}0$	(103) or $31^{-}0$
8	2	7					14632.24545	2		
8	2	6					14727.04580	2		
8	3	6	14632.47640	1	14741.23050	1	14742.54490	1		
8	3	5					14791.56180	2		
8	4	4	14777.09090	2			14859.78790	1		
9	0	9					14665.81940	1		
9	1	9					14665.92620	2		
9	1	8					14813.18690	2		
9	2	8	14679.52800	1			14813.32650	1		
9	3	7					14938.82250	1		
9	4	6					15053.79630	1		
10	0	10					14846.20660	2		
10	1	10					14846.19650	1		
10	1	9	14887.31860	1			15011.52960	2		
10	2	9					15011.59060	1		

Also given are the number of transitions used for level determination.

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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).

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