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The Rotational Spectrum of Water between 650 and 50 cm^{-1}

$H_2{}^{18}O$ and $H_2{}^{17}O$ in Natural Abundance[1]

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In the far infrared spectrum of water, 121 $H_2{}^{18}O$ and 48 $H_2{}^{17}O$ pure rotational lines have been identified. From the line frequencies and a minimum number of literature values of near infrared rotation–vibration transitions and lines from microwave spectra, the ground-state energy levels have been calculated up to $J = 12$ and 11, respectively. For low J levels, the agreement with earlier calculations from other microwave lines and near infrared results is within the experimental error, but deviations up to 0.6 cm^{-1} are found for high J, high K_a levels.

INTRODUCTION

The far infrared spectrum of natural water is of considerable interest, because rotational lines of the various isotopic species of water are responsible for most of the atmospheric absorption in the region below 650 cm^{-1}. The transitions of the $H_2{}^{16}O$ molecule are quite well known, partly from direct measurement (*1–4*), and partly as calculated from the ground-state levels of Flaud *et al.* (*5*) with an accuracy of a few thousandths of a cm^{-1}.

Contrary to this situation, no systematic investigation of the $H_2{}^{18}O$ and $H_2{}^{17}O$ rotational spectra has been made above 40 cm^{-1}. A few rotational lines of both isotopic species have been reported in the literature, generally in infrared test spectra (e.g., (*6–8*)) without frequency values or assignments. Two (unidentified) $H_2{}^{18}O$ line frequencies have been given: $3_{21} \leftarrow 3_{12}$ at 37.913 cm^{-1} (*9*) and $7_{07} \leftarrow 6_{16}$ at 138.431 cm^{-1} (*2*). (Here and in the following the quantum numbers are given in the order J, K_a, K_c, for the water molecule equivalent to J, K_{-1}, K_{+1}.) In the region below 30 cm^{-1}, 12 and 7 lines, respectively, of $H_2{}^{18}O$ and $H_2{}^{17}O$ have been measured using microwave techniques (see, e.g., (*11, 12*)). After completion of the present work, Fleming and Gibson (*10*) published frequencies and assignments of 12 $H_2{}^{18}O$ lines and 1 $H_2{}^{17}O$ line between 13 and 40 cm^{-1}. Their spectra were obtained with a Michelson-type interferometer.

For low quantum numbers, the ground-state levels of $H_2{}^{18}O$ have been calculated several times from rotation–vibration bands, most recently by Toth and Margolis (*13*). In their paper earlier determinations are listed for comparison. De Lucia and Helminger (*12*) have calculated a set of energy levels for $H_2{}^{17}O$ based upon the microwave lines

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Table I

Assignment and Positions (cm^{-1}) of $H_2^{18}O$ Rotational Lines

$H_2^{18}O$ Lines										Overlapping Lines								
J'	K_a'	K_c'	J"	K_a''	K_c''	Observed	Calc.- Obs.	Wt.	Inten.	J'	K_a'	K_c'	J"	K_a''	K_c''	Pos./Sep.	Isot.	Int.Rat.
2	2	1	2	1	2	54.498	-0.010	2	37	8	2	6	8	1	7	54.526	HDO	37/1
5	3	2	5	2	3	60.562	0.011	1	32									
3	2	2	3	1	3	63.192	-0.004	1	19	3	3	1	4	0	4	63.167	$H_2^{16}O$	1/1
5	2	3	4	3	2	65.878	-0.012	2	5.9	9	2	7	9	1	8	65.909	HDO	1/8
4	1	3	3	2	2	70.050	-0.003	2	10									
3	3	0	3	2	1	71.523	-0.014	2	43									
3	1	3	2	0	2	71.658	-0.017	2	55									
5	1	4	5	0	5	74.322	-0.008	1	44									
4	2	3	4	1	4	74.793	-0.001	1	61									
7	2	5	7	1	6	78.757	0.003	1	16									
4	0	4	3	1	3	79.665	0.001	2	61									
4	3	2	4	2	3	80.671	0.002	4	58									
4	1	4	3	0	3	87.491	0.002	8	239									
2	2	1	1	1	0	91.449	0.003	9	206									
2	2	0	1	1	1	98.064	-0.029	2	66	7	1	7	6	0	6	98.131	HDO	5/1
5	1	4	4	2	3	99.750		4	72	12	4	8	12	3	9	99.7763	$H_2^{16}O$	8/1
						(99.747)	-0.007											
5	0	5	4	1	4	100.198		13	255	10	3	7	10	2	8	100.1809	$H_2^{16}O$	1.4/1
						(100.211)	0.008											
8	2	6	8	1	7	100.751	-0.020	2	3.3									
4	4	0	4	3	1	101.965	0.007	2	12									
4	4	1	4	3	2	103.345	0.009	5	36	5	4	2	5	3	3	103.952	$H_2^{18}O$	7/1
5	1	5	4	0	4	104.005		10	94	10	4	7	9	5	4	104.0389	$H_2^{16}O$	1.6/1
						(103.984)	-0.001											
6	2	5	6	1	6	105.078		11	43	9	4	5	8	5	4	105.0690	$H_2^{16}O$	1/4
						(105.115)	-0.009											
7	4	4	7	3	5	109.176	-0.035	2	5.3									
3	2	2	2	1	1	109.973	-0.005	9	81	8	1	8	7	0	7	110.046	HDO	7/1
6	0	6	5	1	5	119.631	0.001	9	90	6	2	5	5	1	4	119.639	HDO	9/1
6	1	6	5	0	5	121.305	-0.004	17	279									
4	2	3	3	1	2	125.738	0.001	20	249									
6	5	1	6	4	2	127.907	0.025	1	5.5	7	2	6	6	1	5	127.920	HDO	1/1.6
5	5	0	5	4	1	128.901	-0.007	3	18	7	5	3	7	4	4	129.105	$H_2^{18}O$	4.8/1
6	5	2	6	4	3	129.044	0.004	3	17	7	1	6	7	0	7	129.0829	$H_2^{16}O$(010)	2.3/1
7	2	5	6	3	4	135.056	0.013	4	21									
7	0	7	6	1	6	138.434	-0.000	25	233	4	3	2	3	2	1	138.422	HDO	11/1
8	1	7	8	0	8	138.572	0.011	4	5.6									
7	1	7	6	0	6	139.162	-0.020	1	79									
5	2	4	4	1	3	139.405	-0.038	1	75	7	1	7	6	0	6	139.445	$H_2^{17}O$	5/1
8	2	7	8	1	8	140.959	-0.044	1	17									
3	3	1	2	2	0	147.309	0.003	15	159									
3	3	0	2	2	1	148.833	-0.001	8	483									
6	2	5	5	1	4	152.090	0.003	15	182	10	3	8	10	2	9	152.029	$H_2^{18}O$	6.8/1
										6	6	0	6	5	1	(-0.038)	$H_2^{18}O$	3/1
6	6	1	6	5	2	153.120	-0.015	3	6.4	8	6	3	8	5	4	153.066	$H_2^{18}O$	2/1

and upon higher-order centrifugal distortion constants taken from the other water isotopes. $H_2{}^{17}O$ lines have been observed in rotation–vibration bands *(14–16)*, but some assignments were uncertain, and energy levels from combination differences of these infrared lines have not been published.

A selection of $H_2{}^{16}O$ lines in the spectra which are the basis of this work have been used for calibration of the spectrometer. To avoid errors in the calibration due to overlapping lines a complete assignment had to be made, also including rotational transitions of HDO and of the (010) vibrational state of $H_2{}^{16}O$. These and the ground-state lines of $H_2{}^{16}O$ will be the subject of another paper.

TABLE I—*Continued*

$H_2^{18}O$ Lines										Overlapping Lines								
J'	K'_a	K'_c	J"	$K"_a$	$K"_c$	Observed	Calc.- Obs.	Wt.	Inten.	J'	K'_a	K'_c	J"	$K"_a$	$K"_c$	Pos./Sep.	Isot.	Int.Rat.
8	0	8	7	1	7	156.933	-0.005	3	57	11	1	10	10	2	9	156.901	HDO	29/1
8	1	8	7	0	7	157.222	0.001	12	172	8	0	8	7	1	7	157.239	$H_2^{17}O$	17/1
7	2	6	6	1	5	165.426	-0.006	8	44									
4	3	2	3	2	1	168.490	0.005	25	400									
4	2	2	3	1	3	172.900	-0.007	11	51	8	1	7	7	2	6	172.878	$H_2^{18}O$	2/1
9	0	9	8	1	8	175.263	-0.002	9	109									
9	1	9	8	0	8	175.384	-0.001	6	36									
8	2	7	7	1	6	180.218	0.004	6	87	11	4	7	10	5	6	180.2893	$H_2^{16}O$	1/1
5	3	2	5	0	5	181.680	0.007	2	6.9									
5	3	3	4	2	2	186.135	0.006	14	95									
9	1	8	8	2	7	192.852	-0.001	11	48									
9	2	8	8	1	7	196.423	-0.007	5	17									
9	2	7	8	3	6	196.505	-0.008	1	16									
6	3	4	5	2	3	200.210	0.019	15	179									
4	4	1	3	3	0	200.337	0.003	30	545	6 11	4 8	2 3	5 11	3 7	3 4	200.305 200.3617	HDO $H_2^{16}O$	30/1 32/1
4	4	0	3	3	1	200.578	0.004	20	182									
5	3	2	4	2	3	207.113	0.000	29	286									
7	3	5	6	2	4	211.519	0.010	10	34									
11	0	11	10	1	10	211.668		10	31	11	1	11	10	0	10	(0.021)	$H_2^{18}O$	3/1
						(211.662)	-0.010											
10	1	9	9	2	8	211.813	0.014	2	8.4									
10	2	9	9	1	8	213.499	0.007	5	26									
8	3	6	7	2	5	221.255	0.003	3	54									
5	2	3	4	1	4	221.347	-0.015	4	96	8	3	5	7	2	6	221.369	HDO	17/1
5	4	2	4	3	1	223.850	-0.002	6	129									
5	4	1	4	3	2	225.501	0.007	27	390									
12	1	12	11	0	11	229.748		6	4.5	12	0	12	11	1	11	(0.009)	$H_2^{18}O$	3/1
						(229.750)	-0.002											
11	1	10	10	2	9	230.288	-0.010	2	12	12	1	12	11	0	11	230.216	$H_2^{17}O$	3.6/1
10	3	8	9	2	7	242.089	0.005	6	12									
4	3	2	3	0	3	242.957	0.002	6	23									
6	3	3	5	2	4	244.393	0.055	1	54									
5	5	0	4	4	1	251.028		50	375	5	5	1	4	4	0	(-0.033)	$H_2^{18}O$	3/1
						(251.036)	0.011											
6	4	2	5	3	3	251.583	0.016	20	80									
7	4	4	6	3	3	263.275		28	40	4	4	1	4	1	4	263.2695	$H_2^{16}O$	1/4.8
						(263.300)	-0.006											
6	5	2	5	4	1	275.288	0.004	25	231									
6	5	1	5	4	2	275.579	0.000	14	77									
8	4	5	7	3	4	277.087	0.008	12	53									
5	3	3	4	0	4	279.351	0.017	2	11									
9	4	6	8	3	5	287.152		6	7.1	10	5	6	9	4	5	287.167	HDO	3/1
						(287.147)	0.013											
7	3	4	6	2	5	289.100	0.005	9	76									

EXPERIMENTAL DATA

A modified Beckman/RIIC FS-720 Michelson interferometer was used for obtaining the water spectra. The instrument and the computational procedures have been described in (*17*, *18*). Seven separate spectra were considered, each of these being the average of 4 to 11 Fourier transformations of single-sided interferograms run under identical conditions. The resolution of the spectra was in the range 0.08–0.15 cm^{-1}, and different pressures between 0.5 and 17.8 Torr were employed in a 3 m cell at 23 ± 2°C. All regions of the spectrum were recorded at least once at maximum resolution. The spectra were calibrated independently with $H_2{}^{16}O$ frequencies known to better than ±0.005 cm^{-1} (99% confidence interval), calculated from the levels of Ref. (*5*). Further details of the calibration procedure and a reproduction of the whole spectrum will be

Table I, continued

$H_2^{18}O$ Lines										Overlapping Lines								
J'	K_a'	K_c'	J"	$K_a"$	$K_c"$	Observed	Calc.- Obs.	Wt.	Inten.	J'	K_a'	K_c'	J"	$K_a"$	$K_c"$	Pos./Sep.	Isot.	Int.Rat.
10	4	7	9	3	6	294.654	0.007	3	7.8									
7	5	3	6	4	2	298.775		12	41	7 7	7 7	1 0	6 6	6 6	0 1	298.738	HDO	4/1(Σ)
						(298.784)	0.028											
6	6	1	5	5	0	299.514		29	176	6	6	0	5	5	1	(0.004)	$H_2^{18}O$	3/1
						(299.513)	-0.009											
7	5	2	6	4	3	300.173	0.007	26	124									
12	4	9	11	3	8	308.190	0.035	1	0.88									
4	4	1	3	1	2	309.766	0.000	1	2.4	17 17	1 2	16 16	17 17	0 1	17 17	309.7855 309.7891	$H_2^{16}O$	3/1(Σ)
8	4	4	7	3	5	313.693		15	19	8 8	7 7	2 1	7 7	6 6	1 2	313.714	HDO	2.7/1(Σ)
						(313.685)	0.000											
8	5	4	7	4	3	320.674	0.006	15	57									
6	3	4	5	0	5	321.341	0.002	10	33									
7	6	1	6	5	2	324.112		5	94	7	6	2	6	5	1	(-0.044)	$H_2^{18}O$	3/1
						(324.122)	-0.032											
8	5	3	7	4	4	325.302	0.019	3	19									
9	5	5	8	4	4	339.574	0.016	2	7.4									
8	3	5	7	2	6	340.732	0.005	1	10									
7	7	0	6	6	1	345.840		24	59	7 4	7 4	1 0	6 3	6 1	0 3	(-0.0006) 345.8556	$H_2^{18}O$ $H_2^{16}O$	3/1 (Σ)1/2.5
						(345.803)	-0.135											
8	6	3	7	5	2	348.229	-0.011	13	44									
8	6	2	7	5	3	348.472		13	15	9	6	3	9	3	6	348.4647	$H_2^{16}O$	1/3.2
						(348.495)	-0.028											
6	4	3	5	1	4	352.675	0.009	5	15									
9	4	5	8	3	6	353.483	0.017	2	21									
7	3	5	6	0	6	367.923	0.000	2	7.8									
8	7	2	7	6	1	370.508		6	27	8	7	1	7	6	2	(0.006)	$H_2^{18}O$	3.3/1
						(370.506)	-0.130											
9	6	4	8	5	3	371.700	-0.014	2	6.0	17	3	14	16	4	13	371.6322	$H_2^{16}O$	14/1
9	6	3	8	5	4	372.678	0.005	6	18									
10	5	5	9	4	6	381.783	-0.052	1	2.7									
8	8	1	7	7	0	389.818	-0.575	7	15	8	8	0	7	7	1	(0.0001)	$H_2^{18}O$	3/1
10	6	5	9	5	4	393.841	0.003	1	6.5									
9	7	2	8	6	3	394.945		3	11	9 16	7 5	3 12	8 15	6 4	2 11	(-0.041) 394.9360	$H_2^{18}O$ $H_2^{16}O$	3/1 (Σ)20/1
						(394.955)	-0.123											
9	3	6	8	2	7	397.887	0.005	1	12									
9	8	1	8	7	2	414.680		2	6.1	9 8	8 2	2 6	8 7	7 1	1 7	(0.001) 414.727	$H_2^{18}O$ $H_2^{16}O$(010)	3/1 (Σ)7/1
						(414.674)	-0.568											
8	4	5	7	1	6	414.937	0.019	2	13									
11	5	6	10	4	7	416.351	0.070	1	2.4									
10	7	4	9	6	3	418.730	0.041	1	4.1									
9	9	0	8	8	1	429.792	-0.025	1	2.9	9	9	1	8	8	0	(-0.0000)	$H_2^{18}O$	3/1
11	7	4	10	6	5	442.816	-0.046	1	1.3									
11	4	7	10	3	8	453.937	-0.012	1	1.9									
9	4	6	8	1	7	454.979	0.019	1	2.6	8	4	5	7	1	6	454.9714	$H_2^{16}O$(010)	1/1
9	2	7	8	1	8	457.195	0.014	2	7.2									
8	5	4	7	2	5	465.882	0.054	1	3.4									
9	3	7	8	0	8	470.281	0.000	1	2.3									
10	4	7	9	1	8	499.707	-0.005	1	3.6									
7	5	2	6	2	5	500.733	0.038	1	1.9									
11	3	8	10	2	9	520.198	-0.068	1	1.6									
10	3	8	9	0	9	524.059	-0.017	2	3.2									

presented in a succeeding report. Three short sections of the 17.8 Torr spectrum containing some $H_2{}^{18}O$ and $H_2{}^{17}O$ lines are given here as Fig. 1.

Most of the line frequencies were determined by the polynomial fit program described in (*17*), but all were checked manually for obvious distortions. Some partly resolved lines were separated graphically on a large scale plot. The digitizing interval of spectra extending to >400 cm^{-1} was 0.038 cm^{-1} and of those of the low-frequency region, 0.019 cm^{-1}. Each line in each spectrum was weighted according to its appearance as follows: 1, in noise, uncertain, ±0.04 cm^{-1}; 2, about two times the mean noise level,

±0.03 cm^{-1}; 3, weak but clear, ±0.025 cm^{-1}; 5, medium, slight distortions, ±0.01 cm^{-1}; 10, strong, undistorted, ±0.005 cm^{-1} (if a single line). The mean frequencies of Tables I and II were calculated accordingly from the spectra. The total weight (Wt.) of each line is given in Tables I and II, also as a rough indication of the line intensity, which was considered to be too uncertain to justify a more precise evaluation. Because the region below 150 cm^{-1} was not recorded at maximum pressure, it should be noticed that

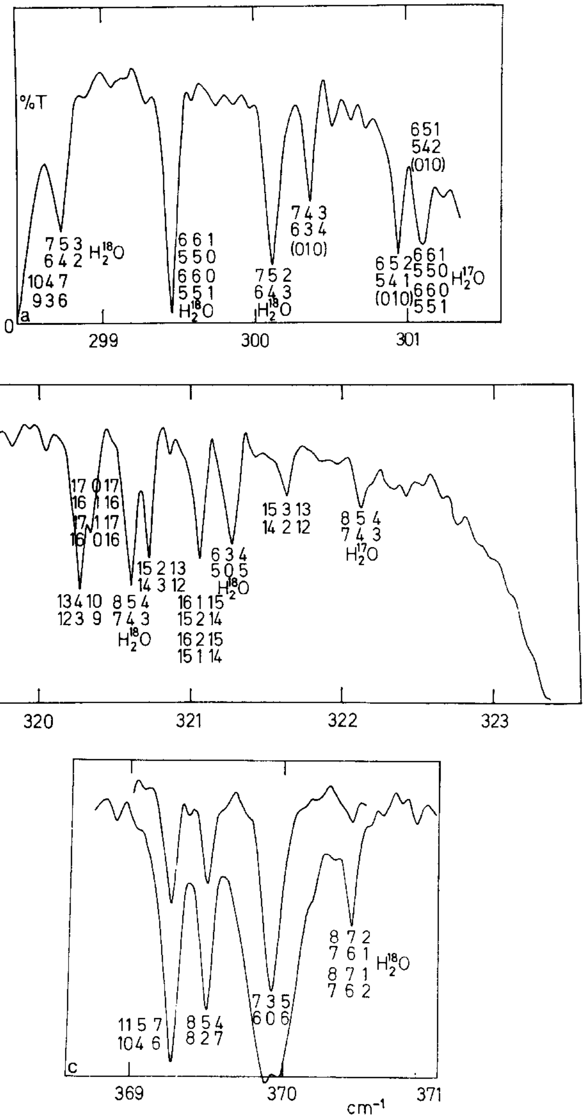

FIG. 1. Three sections of the room temperature water spectrum showing some $H_2{}^{18}O$ and $H_2{}^{17}O$ lines in natural abundance. The quantum numbers J, K_a, K_c are given in this order, with the upper state above the lower one. Lines without isotopic specification are due to $H_2{}^{16}O$ in the ground or (010) state. Path length = 3 m, pressures 17.8 and 5 Torr, and resolution 0.08 cm^{-1}.

Table II

Assignment and Positions (cm^{-1}) of $H_2^{17}O$ Rotational Lines

						$H_2^{17}O$ Lines				Overlapping Lines								
J'	K'_a	K'_c	J''	K''_a	K''_c	Observed	Calc.- Obs.	Wt.	Inten.	J'	K'_a	K'_c	J''	K''_a	K''_c	Pos./Sep.	Isot.	Int.Rat.
5	3	2	5	2	3	61.437	-0.051	1	5.8									
3	1	3	2	0	2	71.893	0.014	1	9.9									
4	2	3	4	1	4	75.184	-0.047	1	11									
2	2	1	1	1	0	91.958	0.001	2	37									
4	4	1	4	3	2	104.414	-0.011	1	6.6									
6	2	5	6	1	6	105.383	-0.017	2	7.8									
6	0	6	5	1	5	119.861	-0.022	2	16									
6	1	6	5	0	5	121.576	0.011	7	51	9	1	9	8	1	8	121.584	HDO	34/1
4	2	3	3	1	2	126.335	-0.003	5	45									
3	2	1	2	1	2	132.204	0.019	3	36									
7	0	7	6	1	6	138.684	0.012	4	42									
3	3	1	2	2	0	148.109	0.023	3	29									
3	3	0	2	2	1	149.623	0.003	10	88									
6	2	5	5	1	4	152.725	0.007	4	33									
7	2	6	6	1	5	165.988	0.040	2	8.0									
4	3	2	3	2	1	169.383	-0.012	4	72									
9	0	9	8	1	8	175.609	0.004	5	20									
4	3	1	3	2	2	176.705	-0.009	5	25									
8	2	7	7	1	6	180.761	0.007	3	16									
5	3	3	4	2	2	187.096		7	17	7	4	3	8	1	8	187.0743	$H_2^{16}O$	2/1
						(187.107)	-0.005											
9	1	8	8	2	7	193.157	-0.010	1	8.7									
10	1	10	9	0	9	193.943		2	11	10	0	10	9	1	9	(-0.054)	$H_2^{17}O$	3/1
						(193.956)	-0.018											
6	3	4	5	2	3	201.276	0.001	7	32									
4	4	1	3	3	0	201.443	0.002	14	99									
4	4	0	3	3	1	201.683	-0.005	6	33									
5	3	2	4	2	3	207.743	-0.001	10	52									
11	0	11	10	1	10	212.108		1	5.5	11 3	1 3	11 1	10 2	0 0	10 2	(0.023) 212.169	$H_2^{17}O$ $H_2^{18}O$	3/1 3/1
						(212.103)	-0.018											
5	2	3	4	1	4	221.481	0.012	1	17									
5	4	2	4	3	1	224.995	-0.004	3	23									
5	4	1	4	3	2	226.597	-0.002	7	71	8	4	5	7	3	4	226.603	HDO	10/1
10	3	8	9	2	7	243.069	0.028	1	2.2									
6	3	3	5	2	4	244.881	-0.042	1	9.8									
6	4	3	5	3	2	246.526	0.008	11	42									
5	5	0	4	4	1	252.402		20	68	5	5	1	4	4	0	(-0.031)	$H_2^{17}O$	3/1
						(252.409)	0.008											
6	4	2	5	3	3	252.627	0.006	2	15									
7	4	4	6	3	3	264.663	0.001	4	7.2									
6	5	2	5	4	1	276.682	0.006	6	42									
6	5	1	5	4	2	276.966	-0.002	3	14									
7	4	3	6	3	4	281.235	0.000	3	23									
6	6	1	5	5	0	301.157		11	32	6 6	5 6	1 0	5 5	4 5	2 1	301.1834 (0.004)	$H_2^{16}O(010)$ $H_2^{17}O$	2.5/1 3/1
						(301.141)	0.006											
7	5	2	6	4	3	301.581		3	22	7	3	4	6	2	5	301.5940	$H_2^{16}O(010)$	1.6/1
						(301.573)	-0.016											
8	4	4	7	3	5	314.334	0.009	1	3.4									
8	5	4	7	4	3	322.202	0.005	3	10									
7	6	1	6	5	2	325.744	0.014	10	17	7 7	5 6	2 2	6 6	4 5	3 1	325.7850 (-0.041)	$H_2^{16}O(010)$ $H_2^{17}O$	1/1.4 3/1
8	5	3	7	4	4	326.637	0.015	2	3.5									
7	7	0	6	6	1	347.657	0.008	3	11	7	7	1	6	6	0	(-0.001)	$H_2^{17}O$	3/1
8	7	2	7	6	1	372.370	0.015	3	5.0	8	7	1	7	6	2	(0.006)	$H_2^{17}O$	3.3/1
8	8	1	7	7	0	391.874	0.021	1	2.7	8	8	0	7	7	1	(0.000)	$H_2^{17}O$	3/1

the total weight of the lines here is lower than if it were corresponding to their actual intensity.

Tables I and II list all observed lines of $H_2{}^{13}O$ and $H_2{}^{17}O$, respectively. Some lines are unresolved doublets or are overlapped by lines due to other isotopic species. To obtain more accurate transition frequencies from such blended lines, it was assumed that

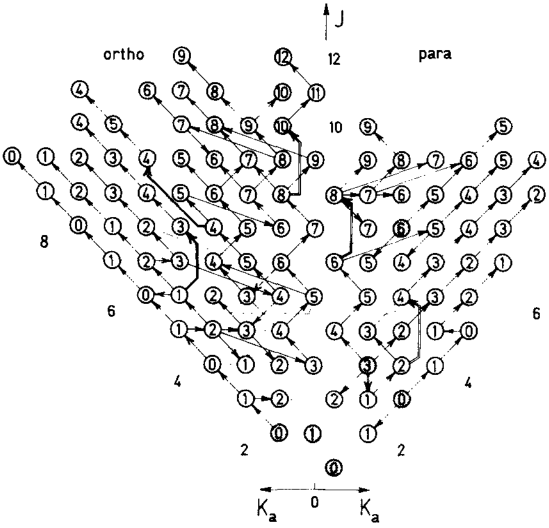

FIG. 2. Schematic representation of the ground-state rotational levels and far infrared transitions of $H_2{}^{18}O$. Each level is given as a circle with the K_c quantum number inside. J and K_a are ordinate and abscissa, respectively. Dotted lines indicate microwave measurements and double lines represent combination differences, both from Table V. All other lines in the scheme show far infrared transitions observed in this work and listed in Table I. Lines without arrowheads have not been used in the calculation of Table III. It should be noted that the arrows show the direction of calculation, not that of the transition of the molecule.

the observed line position was the mean of the frequencies of the components, weighted by their respective intensities. This has been verified for doublets recorded at spectral slit widths larger than five times the separation (*21*). The method is just approximate

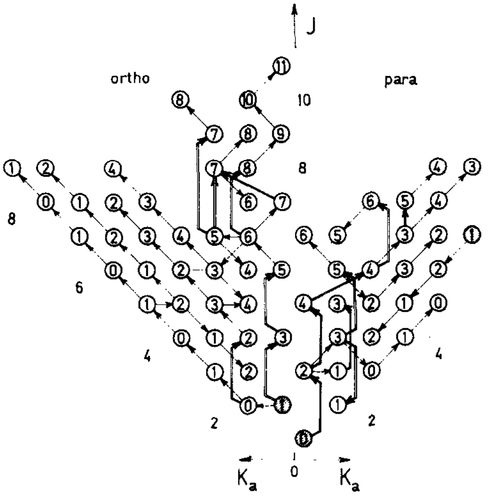

FIG. 3. Schematic representation of the ground-state rotational levels and far infrared transitions of $H_2{}^{17}O$ (see caption of Fig. 2).

Table III

Ground State Energy Levels of $H_2^{18}O$ and $H_2^{17}O$ in cm^{-1}

			$H_2^{18}O$		$H_2^{17}O$	
J	K_a	K_c	This Work	Ref. (13)	This Work	Ref. (12)
0	0	0	0.000	0.000	0.000	0.000
1	0	1	23.755	23.756	23.773	23.773
1	1	1	36.720	36.750	36.930	36.931
1	1	0	42.023	42.024	42.187	42.187
2	0	2	69.911	69.930	70.006	70.004
2	1	2	78.975	78.995	79.210	79.226
2	1	1	94.788	94.790	94.972	94.970
2	2	1	133.473	133.480	134.145	134.144
2	2	0	134.783	134.785	135.427	135.430
3	0	3	136.341	136.344	136.537	136.536
3	1	3	141.568	141.577	141.899	141.901
3	1	2	172.885	172.888	173.109	173.109
3	2	2	204.761	204.763	205.451	205.479
3	2	1	210.808	210.800	211.414	211.434
3	3	1	282.093	282.093	283.536	283.559
3	3	0	282.306	282.304	283.768	283.765
4	0	4	221.233	221.237	221.624	221.618
4	1	4	223.832	223.830	224.282	224.302
4	1	3	274.811	274.793	275.130	275.128
4	2	3	298.624	298.629	299.444	299.436
4	2	2	314.468	314.460	315.075	315.076
4	3	2	379.298	379.293	380.797	380.804
4	3	1	380.705	380.700	382.156	382.174
4	4	1	482.644	482.632	485.211	485.209
4	4	0	482.671	482.660	485.219	485.237
5	0	5	324.043	324.044	324.661	324.658
5	1	5	325.217	325.216	325.876	325.878
5	1	4	398.367	398.372	398.895	398.877
5	2	4	414.173	414.177	415.130	415.126
5	2	3	445.160	445.160	445.785	445.792
5	3	3	500.603	500.595	502.182	502.179
8	2	7	881.925	881.900	883.630	883.664
8	2	6	980.236	980.230		981.504
8	3	6	1001.688	1001.709		1003.791
8	3	5	1047.340	1047.317		1048.662
8	4	5	1116.644	1116.620		1119.484
8	4	4	1126.455	1126.480	1128.965	1128.935
8	5	4	1246.379	1246.369	1250.499	1250.505
8	5	3	1247.167	1247.20	1251.310	1251.298
8	6	3	1399.444	1399.74		
8	6	2	1399.465			
8	7	2	1574.716		1582.226	
8	8	1	1768.823		1778.292	
9	0	9	916.265	916.250	918.090	
9	1	9	916.298	916.300		
9	1	8	1074.777	1074.779	1076.788	
9	2	8	1075.909	1075.920		
9	2	7	1198.195	1198.190	1199.982	
9	3	7	1211.195			
9	3	6	1279.821	1279.800		
9	4	6	1334.476	1334.68		
9	4	5	1355.171	1355.19		
9	5	5	1466.029			
9	5	4	1468.615			
9	6	4	1618.867			
9	6	3	1619.057			
9	7	2	1794.400			
9	8	1	1989.389			
9	9	0	2198.615			
10	0	10		1109.808		
10	1	10	1109.809	1109.770	1112.046	
10	1	9	1287.722	1287.727		
10	2	9	1288.276	1288.264		

TABLE III—*Continued*

5	3	2	505.736	505.727	507.187	507.174
5	4	2	604.555	604.550	607.151	607.165
5	4	1	604.799	604.796	607.395	607.403
5	5	1		733.673		737.629
5	5	0	733.690	733.678	737.620	737.632
6	0	6	444.848	444.860	445.737	445.717
6	1	6	445.347	445.355	446.237	446.243
6	1	5	541.182	541.183	542.048	541.996
6	2	5	550.457	550.447	551.620	551.610
6	2	4	601.251	601.246		601.961
6	3	4	645.377	645.387	647.062	647.074
6	3	3	658.565	658.623	660.010	659.988
5	4	3	751.043	751.040	753.713	753.712
6	4	2	752.186	752.195	754.809	754.819
6	5	2	880.087	880.079	884.076	884.104
6	5	1	880.134	880.121	884.112	884.140
6	6	1	1033.203	1033.195	1038.761	1038.934
6	6	0		1033.195		1038.934
7	0	7	583.781	583.767	584.921	584.941
7	1	7	583.981	583.972		585.162
7	1	6	701.707	701.697	702.869	702.888
7	2	6	706.608	706.608	708.036	708.022
7	2	5	780.433	780.440		781.381
7	3	5	812.770	812.753	814.630	814.616
7	3	4	839.557	839.561		840.868
7	4	4	921.865	921.910	924.673	924.647
7	4	3	925.705	925.698	928.296	928.301
7	5	3	1050.970	1050.990		1055.082
7	5	2	1051.216	1051.210	1055.285	1055.283
7	6	2		1204.172		
7	6	1	1204.209	1204.186	1209.856	
7	7	1		1378.98		
7	7	0	1379.006	1378.98	1386.418	
8	0	8	740.914	740.930		742.401
8	1	8	741.003	741.000	742.481	742.494
8	1	7	879.486	879.481		881.108
10	2	8		1433.061		
10	3	8	1440.304	1440.295		1443.051
10	3	7		1534.368		
10	4	7	1574.484			
10	5	5	1716.259			
10	6	5	1862.455			
10	7	4	2037.787			
11	0	11	1321.471	1321.44		1324.149
11	1	10	1518.564	1518.55		
11	3	8	1808.473			
11	4	7	1894.242			
11	5	6	1990.835			
11	7	4	2305.272			
12	1	12	1551.221	1551.19		
12	4	9	2116.663			

The underlined levels have been used as basis for the calculation, as explained in the text.

as used here because the slit width dependence was left out, but the frequency corrections of Tables I and II are so small (generally ≤ 0.01 cm^{-1}) that the residual errors are less than the precision of the line positions. Exceptions are the lines of $H_2{}^{18}O$ $7_{44} \leftarrow 6_{33}$ (corr. 0.025 cm^{-1}) and $7_{70} \leftarrow 6_{61}$ (corr. 0.038 cm^{-1}), where the error of the correction may be as high as 50%. For $H_2{}^{16}O$, doublet separations such as, for instance, between $6_{61} \leftarrow 5_{50}$ and $6_{60} \leftarrow 5_{51}$ are well known (*5*). The calculated separations for the corresponding $H_2{}^{18}O$ and $H_2{}^{17}O$ doublets (*19*, *12*) are almost unchanged from those of $H_2{}^{16}O$ so that the correction method described above may be applied with confidence, even where the absolute level height for $H_2{}^{18}O$ and $H_2{}^{17}O$ is uncertain. In Tables I and II the corrected frequencies are given in brackets below the observed ones.

The calculated frequencies of Table I are from Ref. (*19*). For those of Table II the empirical expression $\nu_{17} = (1 - 0.529)\nu_{16} + 0.529\ \nu_{18}$ given in Ref. (*14*) has been used. (The indices of the expression refer to the corresponding oxygen isotope.) ν_{16}'s have been obtained from the levels of Ref. (*5*) and ν_{18}'s were taken from this work. The empirical expression was used for calculating the line positions of Table II because it yields precise predictions and because high *J* levels are missing from the list of Ref. (*12*). Where both calculation methods were applicable, the agreement is within the experimental error, except for the $6_{61} \leftarrow 5_{50}$ transition. The line is predicted from Ref. (*12*) to be at 301.302 cm^{-1}, whereas the empirical expression gives 301.147 cm^{-1}, much nearer the observed line at 301.157 (corr. 301.141) cm^{-1}.

The intensities (Int.) listed in Tables I and II in units of 10^{-23} cm^{-1}/molecules·cm^{-2} have been obtained from the intensities of the corresponding $H_2{}^{16}O$ lines as given in Ref. (*20*), multiplied by the isotopic ratios. For overlapping lines the positions (Pos.) have been taken from this work in the case of $H_2{}^{18}O$ or $H_2{}^{17}O$ lines, from Ref. (*20*) for HDO lines, and from Ref. (*5*) for $H_2{}^{16}O$ or $H_2{}^{16}O(010)$ lines. Where instead the separations (Sep.) of narrow doublets are given in brackets, they have been obtained from Ref. (*19*) or (*12*). The sign convention for the doublet separation is: Positive, when the main component is at lower frequency than the overlapping one. The approximate intensity ratio of the line of interest and overlapping lines is given in the last column

Table IV

Comparison of Energy Levels (cm^{-1}) Used for Table III

			$H_2{}^{18}O$				$H_2{}^{17}O$
J	K_a	K_c	Ref. (14)	Ref. (15)	Ref. (13)	Ref. (19)	Ref. (12)
1	0	1	23.756	23.759	23.756	$\underline{23.7548}$	23.773
1	1	0	42.024	42.023	42.024	$\underline{42.0233}$	
2	2	0	134.785	134.784	134.785	$\underline{134.7832}$	
3	1	3	141.576	141.581	141.577	$\underline{141.5682}$	
6	5	1	- difference to level 6_{52}				0.036
7	2	6	706.608	706.603	$\underline{706.608}$	706.6032	

The underlined levels have been used in this work - see text.

Table V

Additional Data (in cm^{-1}) Used for Table III

Isotopic Species	Upper Level				Ground State Levels						Combination Difference	Lit. Ref.
	$v_1v_2v_3$	J	K_a	K_c	J'	K_a'	K_c'	J"	K_a''	K_c''		
$H_2^{18}O$	(0 0 1)	2	1	2	3	1	3	2	1	1	46.7803	(16)
	(0 0 1)	4	2	3	5	2	4	3	2	2	209.4120	(16)
	(0 0 1)	6	4	2	7	4	3	5	4	1	320.9064	(16)
	(0 0 1)	7	0	7	8	0	8	6	0	6	296.0663	(16)
	(1 0 0)	8	4	5	9	5	4	7	3	4	629.058	(13,14)*
	(0 0 1)	9	1	9	10	1	10	8	1	8	368.8065	(16)
	Microwave line:				6	1	6	5	2	3	0.1876	(11)
$H_2^{17}O$	(0 0 1)	1	0	1	2	0	2	0	0	0	70.006	(16)
	(0 0 1)	2	0	2	3	0	3	1	0	1	112.7640	(16)
	(0 0 1)	2	1	2	3	1	3	1	1	1	104.969	(16)
	(0 0 1)	2	1	1	3	1	2	1	1	0	130.9222	(16)
	(0 0 1)	3	0	3	4	0	4	2	0	2	151.6183	(16)
	(0 0 1)	3	1	2	4	1	3	2	1	1	180.1589	(16)
	(0 0 1)	4	0	4	5	0	5	3	0	3	188.1236	(16)
	(0 0 1)	4	1	4	5	1	5	3	1	3	183.9777	(16)
	(0 1 0)	5	1	5	5	2	4	4	0	4	193.506	(15)**
	(0 0 1)	6	2	5	7	2	6	5	2	4	292.906	(14)
	(0 1 0)	6	2	4	7	3	5	6	3	3	154.620	(15)†
	(0 0 1)	7	1	7	8	1	8	6	1	6	296.2446	(16)††
	(0 1 0)	7	1	6	8	2	7	6	2	5	332.036	(15)§
	(0 1 0)	7	1	6	8	2	7	7	0	7	298.684	
	(0 0 1)	8	2	6	9	2	7	7	2	5	418.601	(14)§§
	(0 0 1)	6	2	4	7	2	5	6	2	5	229.761	
	Microwave Lines:				1	1	0	1	0	1	18.4134	(12)
					2	1	1	2	0	2	24.9659	(12)
					3	1	3	2	2	0	6.4712	(12)
					5	1	5	4	2	2	10.8017	(12)
					6	1	6	5	2	3	0.4515	(12)

* Calculated from line 183 (*13*) and line 158 (*14*). Lines 960 and 1010 (*14*) also have (100) 8_{45} as the upper level, but seem to be misassigned.

** The assignment of the (010) $5_{15} \leftarrow$ (000) 5_{24} line has been changed from 1503.739 to 1503.533 cm^{-1}, because the combination difference differed 0.2 cm^{-1} from the calculated value (*12*).

† The assignment of the (010) $6_{24} \leftarrow$ (000) 7_{35} line has been changed from 1392.250 to 1392.147 cm^{-1}, because of disagreement with the calculated combination difference (*12*). The change is confirmed by the combination difference $7_{35} \leftarrow 6_{15}$ (from line 540 (*15*)).

†† The assignment of the (001) $7_{17} \leftarrow$ (000) 8_{18} line has been changed from 3581.89324 to 3581.54970 cm^{-1} because of disagreement with the calculated combination difference (*12*).

§ The mean of the values 883.656 and 883.605 cm^{-1} has been used for the 8_{27} level of Table III.

§§ The sum of the combination differences has been used for the 9_{27} level of Table III.

(Int. Rat.) of Tables I and II, in this order. For triplets, a (Σ) together with one of the figures indicates that the total intensity of a narrow doublet relative to the third component is given. Again, the intensities have been taken from Ref. (*20*).

Table VI

Comparison of Energy Level Differences (in cm^{-1})

$H_2^{18}O$

Upper Level			Ground State Levels						Combination	This Work
J	K_a	K_c	J'	K'_a	K'_c	J"	K''_a	K''_c	Difference	− Comb.Dif.
1	0	1	2	0	2	0	0	0	69.9272	-0.017
1	0	1*	2	1	2	1	1	0	36.9649	-0.013
1	1	1	2	1	2	1	1	0	36.963	
2	0	2	3	0	3	1	0	1	112.5828	0.004
2	1	2	3	1	3	1	1	1	104.8194	0.029
2	1	1	3	1	2	1	1	0	130.8596	0.003
2	1	1	3	1	2	2	1	2	93.8943	0.016
2	2	1	3	2	2	2	2	0	69.9728	0.005
2	2	0	3	2	1	2	2	1	77.3233	0.012
3	0	3	4	0	4	2	0	2	151.3068	0.016
3	1	3	4	1	4	2	1	2	144.8396	0.017
3	1	3	4	1	4	3	1	2	50.9454	0.001
3	1	2	4	1	3	2	1	1	180.0144	0.009
3	2	2	4	2	3	2	2	1	165.1446	0.006
3	2	2	4	2	3	3	0	3	162.2830	-0.001
3	2	2	4	2	3	3	2	1	87.8209	-0.006
3	2	1	4	2	2	2	2	0	179.6756	0.009
3	2	1	4	2	2	3	2	2	109.7034	0.004
3	3	1	4	3	2	3	3	0	96.9842	0.008
3	3	0	4	3	1	3	3	1	98.6068	0.006
4	0	4	5	0	5	3	0	3	187.7100	-0.009
4	1	4	5	1	5	3	1	3	183.648	0.000
4	1	3	5	1	4	3	1	2	225.4779	0.004
4	1	3	5	1	4	4	1	4	174.5318	0.004
4	2	2	5	2	3	3	0	3	308.8226	-0.004
4	2	2	5	2	3	3	2	1	234.3596	-0.008
4	2	2	5	2	3	4	2	3	146.5383	-0.002
4	3	2	5	3	3	3	3	1	218.5040	0.006
4	3	1	5	3	2	3	3	0	223.4214	0.009
4	3	1	5	3	2	4	3	2	126.4369	0.001

RESULTS

The number of observed rotational lines of $H_2^{18}O$ and $H_2^{17}O$ was in both cases almost equal to the number of energy levels to be determined. Thus the levels listed in Table III were built up as illustrated in Figs. 2 and 3 from the line frequencies of this work and a minimum number of additional data of comparable accuracy from the literature. In Table IV different values of the levels which were used as starting points in the calculation are compared. These levels are hatched in Figs. 2 and 3 and the direction of arrows shows how the energy level scheme was developed. For $H_2^{17}O$ it was appropriate to connect two series of transitions by the calculated separation of levels 6_{51} and 6_{52} (*12*). It should be noted that generally the values in Tables I to VII have been calculated to four figures after the decimal point, but just three are given in the Tables. This may lead to insignificant numerical discrepancies.

Table V contains the additional information used for calculating Table III, mainly ground-state combination differences from Ref. (*16*). Some lines from $H_2^{17}O$ rotation–vibration bands had to be reassigned as specified in the footnotes of Table V. No systematic search for dubious assignments has been made, but the number of reassigned

TABLE VI—*Continued*

4	4	0	5	4	1	4	4	1	122.1482	0.007
5	0	5	6	0	6	4	0	4	223.6131	0.002
5	1	5	6	1	6	4	1	4	221.5181	-0.003
5	2	4	6	2	5	4	2	3	251.8309	0.002
5	3	2*	6	2	5	4	2	3	251.8314	
5	2	4	6	2	5	5	0	5	226.4074	0.007
5	2	4	6	2	5	5	2	3	105.2942	0.003
5	2	3	6	2	4	4	2	2	286.7783	0.005
5	3	3	6	3	4	4	3	2	266.0911	-0.013
5	3	3	6	3	4	5	3	2	139.6531	-0.013
6	3	3	6	3	4	5	3	2	139.6542	
5	4	2	6	4	3	4	4	1	268.3916	0.008
5	4	2	6	4	3	5	4	1	146.2429	0.001
6	5	1	6	5	2	5	5	0	146.3740	0.023
6	0	6	7	0	7	5	0	5	259.7313	0.007
6	1	5	7	1	6	5	1	4	303.3339	0.006
6	2	5	7	2	6	5	2	4	292.4290	0.006
6	2	4	7	2	5	5	2	3	335.2946	-0.021
6	2	4	7	2	5	6	2	5	230.0002	-0.025
7	4	4	7	4	3	6	4	3	174.6668	-0.004
7	1	7	8	1	8	6	1	6	295.6525	0.003
7	2	6	8	2	7	6	2	5	331.4632	0.005
8	0	8	9	0	9	7	0	7	332.4789	0.006
Microwave Lines										
			2	1	1	2	0	2	24.8612	0.016
			4	1	4	3	2	1	13.0293	-0.006
			4	2	3	3	3	0	16.3131	0.004
			5	1	5	4	2	2	10.7563	-0.008
			5	3	3	4	4	0	17.9237	0.009
			5	3	2	4	4	1	23.0853	0.007
			6	2	4	7	1	7	17.2513	0.018
			6	4	3	5	5	0	17.3499	0.002
FIR Lines										
			1	1	1	0	0	0	36.7450	-0.026
			3	1	2	2	2	1	39.4083	0.004
			3	2	1	3	1	2	37.9127	0.010
			4	2	2	4	1	3	39.5518	0.005

Near infrared data from Ref. (*16*), microwave lines from Ref. (*11*), and far infrared lines from Ref. (*10*).
* Upper-level (100) vibrational state, all other upper levels (001) state.

$H_2{}^{17}O$ lines indicates that the rotation–vibration bands of this species should be reinvestigated.

To test the accuracy and internal consistency of the energy levels obtained in this work a comparison was made between combination differences calculated from the levels of Table III and ground-state combination differences from such lines of Ref. (*16*), which have not been evaluated so far. The results are given as Tables VI and VII, also including some comparisons with microwave and far infrared lines which have not been used in the energy level calculation. It is seen that most of the deviations for $H_2{}^{18}O$ are less than 0.01 cm^{-1} (rms deviation = 0.010 cm^{-1}), whereas for $H_2{}^{17}O$ the scattering is larger, corresponding to the weakness of the lines of this isotopic species. It is also interesting to note that the average value of a selection of 46 deviations less than 0.01 cm^{-1} from Table VI is slightly positive: 0.0028 cm^{-1}. This is equivalent to 1/27 of the resolution used in this work and indicates that errors due to unsymmetrical line profiles have not been eliminated completely.

Table VII

Comparison of Energy Level Differences (in cm^{-1})

$H_2^{17}O$

Upper Level			Ground State Levels						Combination	This Work
J	K_a	K_c	J'	K_a'	K_c'	J''	K_a''	K_c''	Difference	- Comb.Dif.
1	1	1	2	1	2	1	1	0	37.0420	-0.019
2	1	1	3	1	2	2	1	2	93.8831	0.016
3	1	3	3	1	2	2	1	2	93.8830	
3	1	3	4	1	4	2	1	2	145.0767	-0.004
3	1	3	4	1	4	3	1	2	51.1937	-0.021
3	2	2	4	2	3	2	2	1	165.2935	0.005
3	2	2	4	2	3	3	2	1	88.0043	0.026
4	3	1	4	3	2	3	3	0	97.0388	-0.010
4	1	3	5	1	4	3	1	2	225.7687	0.017
4	2	2	5	2	3	3	2	1	234.3572	0.014
4	2	2	5	2	3	4	2	3	146.354	-0.013
6	0	6	7	0	7	5	0	5	260.2797	-0.019
Microwave Lines										
			4	1	4	3	2	1	12.8685	0.000
			4	2	3	3	3	0	15.6712	0.004
FIR Line										
			3	2	1	3	1	2	38.323	-0.018

Near infrared data from Ref. (*16*), all upper levels are from the (001) vibrational state. Microwave lines from Ref. (*12*). The far infrared line is from (*10*).

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