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Absorption Spectrum of $H_2{}^{18}O$ in the Range 12 400–14 520 cm^{-1}

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Fourier transform spectra recorded using (a) natural abundance water vapor, (b) $H_2{}^{18}O$-enriched water vapor, and (c) $H_2{}^{17}O$-enriched water vapor are analyzed. The ratio of intensities in three spectra is used to identify 927 lines due to absorption by $H_2{}^{18}O$. Intensities and self-broadening parameters are derived for these lines. Using theoretical linelists, comparisons with previously assigned $H_2{}^{16}O$ spectra, and automatic searches for combination differences, 747 lines are assigned. These lines belong to 14 vibrational states in the $3\nu + \delta$ and 4ν polyads. Newly determined $H_2{}^{18}O$ vibrational band origins include $4\nu_1$ at 13 793.09 cm^{-1}, $3\nu_1 + \nu_3$ at 13 795.40 cm^{-1}, $2\nu_1 + 2\nu_3$ at 14 188.82 cm^{-1}, $\nu_1 + 3\nu_3$ at 14 276.34 cm^{-1}, and $2\nu_2 + 2\nu_2 + \nu_3$ at 13 612.71 cm^{-1}. These results are compared with data in HITRAN. © 2002 Elsevier Science (USA)

1. INTRODUCTION

Water is well known as the major absorber of sunlight in the Earth's atmosphere. Indeed water is so important that its second most abundant isotopomer, $H_2{}^{18}O$, is considered to be the fifth most important absorber of solar radiation. Despite its importance the near-infrared and optical spectrum of $H_2{}^{18}O$, key regions for atmospheric studies, remain poorly determined.

In the early 1980s Chevillard and co-workers used the McMath Fourier transform spectrometer at the National Solar Observatory (Kitt Peak, AZ) to record spectra of isotopically enriched water over a wide frequency range. This experimental work resulted in a series of papers analyzing the spectrum of $H_2{}^{18}O$ in the range 4 400–11 500 cm^{-1} (*1–3*). More recently this analysis has been extended up to 13 600 cm^{-1} by Bykov *et al.* (*4*). In this work we extend the frequency range for which the $H_2{}^{18}O$ spectra are analyzed up to 14 520 cm^{-1} so that the $3\nu + \delta$ and 4ν polyads are completely covered.

Spectra of natural abundance water in the near-infrared and visible have been extensively studied (*5–15*). Recently Schermaul *et al.* (*16*) remeasured the spectrum of normal water using a long-path-length Fourier transform spectrometer belonging to the Molecular Structure Facility at Rutherford Appleton Laboratory (UK) over the range 6 500–16 400 cm^{-1}. For much of this range they probed significantly deeper than previous studies. In this work we use the spectra of Schermaul *et al.* to aid the identification of different isotopomers.

2. EXPERIMENT DATA

As reported previously (*1–3*) Chevillard *et al.* measured the spectrum of two isotopically enriched samples of water using the McMath Fourier transform spectrometer. The first sample contained $H_2{}^{18}O$ at 73 ± 1% (*2*), refered to as "^{18}O" below, and the second sample, "^{17}O" below, contained enhanced $H_2{}^{17}O$ and $H_2{}^{18}O$ (*3*). These spectra, which achieved a typical uncertainty of 0.001 cm^{-1} (*4*) in their line positions, are publicly available via the Kitt Peak electronic archive. The ^{18}O spectrum was recorded using 927 scans and a pathlength of 434.0 m with a vapor pressure of 361.1 Pa. Lines in both spectra were fitted in the range 12 400–14 520 cm^{-1} using the GREMLIN program (Brault, unpublished). The exact isotopic composition of these spectra is considered in detail below.

To aid analysis of the isotopically enriched spectra we used the natural abundance, "^{16}O" below, Fourier Transform spectrum of Schermaul *et al.* (*16*). For the frequency range 12 400–14 520 cm^{-1} the ^{16}O, ^{18}O, and ^{17}O spectra were read into a spreadsheet and lines of the same frequency were aligned. The intensities of these were ratioed, giving characteristic patterns which, for most lines and particularly for those appearing in all three spectra, facilitated their identification as belonging to $H_2{}^{16}O$, $H_2{}^{17}O$, or $H_2{}^{18}O$. In this fashion 927 lines were definitely identified as belonging to $H_2{}^{18}O$. Parameters for these lines were then extracted from the ^{18}O spectrum and used for theoretical analysis. A complete list of these lines including intensities, scaled to natural abundance (see below), and self-broadening parameters are given in the electronic archive.

The exact isotopic composition of the ^{18}O spectrum is of course crucial for determining accurate transition intensities. In this work we used the comparison between the three spectra to determine the factor by which the lines of $H_2{}^{18}O$ are enhanced in the ^{18}O spectrum. To do this we used the following information: the total number of water molecules per cm^{-2} in each sample, the abundance of each species in the ^{16}O spectrum (assumed to be natural abundance), the ratio of $H_2{}^{16}O$ linestrengths

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in the ^{17}O and ^{18}O spectra relative to the ^{16}O spectrum, and the ratio of $H_2{}^{17}O$ and $H_2{}^{18}O$ linestrengths in the ^{17}O and ^{18}O spectra. This procedure gives the ratio of $H_2{}^{18}O$ linestrengths in the ^{18}O to the ^{16}O spectrum as 31.0 with an estimated error of 0.5. It also shows that the abundance of $H_2{}^{17}O$ in the ^{17}O spectrum, which has yet to be analyzed, is fairly small, at only about 3% of the total water content. Our result is consistent with the previous analysis of Chevillard *et al.* (*2*) whose published results can be used to give an enhancement of 30.7 with an error of 0.5. The linestrengths given in the electronic archive have therefore been divided by 31.0 to scale them to natural abundance.

3. ANALYSIS

Significant advances have been made in the analysis of optical spectra of water using variational calculations (*12, 13, 17, 18*). In this work a variety of strategies were adopted to analyze the spectra. At lower frequencies some transitions, all belonging to the $3\nu + \delta$ polyad, had previously been assigned by Bykov *et al.* (*4*), who studied $H_2{}^{18}O$ up to 13 600 cm^{-1}. Further "trivial" assignments, ones linking energy levels previously determined experimentally, could be made using the upper energy levels so generated.

Initial assignments to new upper levels were then made by comparison with the variational $H_2{}^{18}O$ line list generated by Partridge and Schwenke (*17*). Although we were able to confirm many of these assignments by combination differences, it became apparent by comparison with known levels of $H_2{}^{16}O$ (*19*) that in many cases the vibrational labels taken from the line list were not correct. The transitions were therefore relabeled to obtain a consistent set of $H_2{}^{18}O$ energy levels. Particularly helpful in this regard was the ratio of $H_2{}^{18}O$ to $H_2{}^{16}O$ energy levels, which was found to be almost constant within a vibrational band and to vary only slightly between bands. The structure of the $H_2{}^{18}O$ levels in the region of the $3\nu + \delta$ and 4ν polyad having been established, further assignments were made by searching for combination differences using a small computer program. This analysis led to the assignment of 747 of the 927 $H_2{}^{18}O$ lines. These assignments are given with the lines in the electronic archive.

Lines are assigned to 14 different upper vibrational levels. Three of these, (013), (112), and (211), were already extensively studied by Bykov *et al.* (*4*). The other states have not been previously observed for $H_2{}^{18}O$. Our new assignments can be used to characterize further $H_2{}^{18}O$ energy levels. Table 1 gives newly derived energy levels for vibrational states (221), (400), (301), (202), and (103), which cover most of the new data. For these states, vibrational band origins have been determined at 13 612.71, 13 793.09, 13 795.40, 14 188.82, and 14 276.34 cm^{-1}, respectively. The small splitting between the (400) and (301) band origins shows, as has been noted previously (*12*), that stretching states in the 4ν polyad for water are local-mode-like. Table 1 therefore labels the vibrational states using both normal and local mode notations. All our levels, including 11 for (023), 9 for (122), 3 for (004), and one each for (141) and (042), are given in the electronic archive.

TABLE 1
$H_2{}^{18}O$ Energy Levels in cm^{-1}: Also Given Are the Number of Transitions Assigned to Each Level

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	13612.71029	1	13793.09263	1	13795.39829	1	14188.82279	1	14276.33594	1
1	0	1	13635.20035	1	13815.59986	1	13817.70342	2	14210.32317	2	14298.91140	2
1	1	1	13651.98268	2	13826.21088	1	13828.30932	2	14221.01936	2	14308.78586	2
1	1	0	13657.84428	2	13829.96903	1	13833.44816	2	14226.20768	2	14314.08100	2
2	0	2	13679.55793	2	13858.82353	2	13860.81739	3	14253.48141	2	14342.39912	3
2	1	2	13691.79112	3	13865.89005	4	13867.80525	3	14260.48337	3	14348.71126	3
2	1	1	13709.27878	3			13883.19049	4	14276.00949	1	14364.54358	3
2	2	1	13757.79133	2	13912.95811	3	13914.90280	2	14307.88613	3	14393.96665	2
2	2	0	13759.09973	2			13916.36102	2	14309.32461	1	14395.59132	3
3	0	3			13920.64162	2	13922.46923	3	14315.15534	3	14404.30826	2
3	1	3	13750.40525	3	13924.60916	3	13926.26742	4	14318.83042	3	14407.71132	3
3	1	2	13785.36505	2	13954.59924	3	13956.63031	3	14349.54377	3	14438.85672	3
3	2	2	13826.22733	4	13980.00173	3	13981.85151	3	14374.78800	1	14462.30154	4
3	2	1	13832.33231	3	13986.48666	2	13988.46754	3	14381.30031	4	14469.35834	4
3	3	1	13919.95254	4	14045.80809	1	14047.93090	4	14440.77476	2	14524.26011	2
3	3	0	13920.17986	2	14046.38039	2	14048.20104	3	14440.79902	3	14524.59279	2
4	0	4	13824.20313	3	13999.43072	2	14001.79765	4	14393.73465	3	14483.13081	3
4	1	4	13827.77120	2	14000.37909	3	14002.83899	3	14395.37957	3	14486.10948	2
4	1	3	13884.62104	3	14050.15086	3	14052.07040	5	14445.05599	1	14535.04019	3
4	2	3	13916.52921	2	14068.12697	5	14069.83089	3	14462.74970	4	14552.07242	2
4	2	2	13932.60604	4	14084.79832	3	14086.74964	4	14478.34927	2	14569.38969	3
4	3	2	14013.56819	4	14137.80518	5	14139.53803	4	14532.19471	2	14625.15782	2
4	3	1	14014.70784	3	14139.47837	2	14141.32217	3	14532.92982	1	14625.85421	3

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TABLE 1—*Continued*

J	K_a	K_c	(221) or $30^{-}2$		(400) or $40^{+}0$		(301) or $40^{-}0$		(202) or $31^{+}0$		(103) or $31^{-}0$	
4	4	1	14137.05362	1	14226.98082	3			14614.41463	3	14700.01980	2
4	4	0	14137.08575	3	14227.02664	1	14228.77416	3	14612.98367	2	14700.11566	2
5	0	5	13921.24395	2			14097.01368	3	14488.92057	3	14578.70516	4
5	1	5	13922.96724	3			14097.34284	3	14489.59465	1	14578.84244	3
5	1	4	14004.81826	3	14165.40969	3	14167.13472	3	14560.10049	4	14650.39783	2
5	2	4			14176.38066	1	14177.89117	4	14570.80649	1	14663.40709	2
5	2	3	14059.51085	3	14208.15462	3	14210.25362	1	14604.02424	2		
5	3	3	14130.17703	3	14252.12466	1	14253.79683	4	14648.90231	2		
5	3	2	14134.65727	3	14258.18064	4	14260.08003	4	14649.28398	3		
5	4	2	14254.30174	3	14342.22011	1	14343.90916	3	14729.97901	1	14814.53462	3
5	4	1			14342.56759	3	14344.42896	1			14815.00955	1
5	5	1	14403.02356	2	14464.79057	2	14461.44404	1			14920.61971	1
6	0	6	14034.75914	2	14208.94433	1	14208.93576	1				
6	1	6	14035.65941	2	14208.49650	3	14209.41305	3	14601.15128	2		
6	1	5	14143.37873	2	14298.24448	1	14299.75174	3			14782.66823	2
6	2	5	14155.69990	2					14697.99098	2		
6	2	4	14212.57896	3	14355.01469	1					14842.62953	1
6	3	4	14269.31666	2	14388.38620	3						
6	3	3	14281.02374	2	14403.07298	2			14802.09627	1	14892.38763	3
6	4	3	14395.09222	2	14480.74460	2			14869.82308	2	14952.44196	2
6	4	2	14396.32699	4							14954.73741	1
6	5	2			14598.93038	2						
6	5	1	14543.06111	3	14599.78596	1						
6	6	1			14699.06576	1						
6	6	0					14710.55900	2				
7	0	7	14164.98360	2							14821.23573	1
7	1	7	14166.15979	2	14338.16022	3	14338.19745	3			14821.60027	1
7	1	6	14299.34340	2							14931.20436	1
7	2	6	14305.54084	2	14446.07989	1	14452.00200	1			14932.02700	1
7	3	5	14430.31292	2								
7	3	4									15065.09786	1
7	4	4	14559.95017	3								
7	4	3										
7	5	3							15153.45004	2		
7	6	1										
8	0	8	14312.78125	2								
8	1	8	14310.23219	1	14484.28735	2	14485.37538	1			14967.90933	2
8	1	7	14470.93016	2			14611.06029	1				
8	2	7			14613.41220	4						
8	3	6					14724.89019	2				
8	3	5	14656.46424	2			14774.02630	1				
8	4	5	14746.52326	1			14828.21233	1				
8	4	4	14755.67830	2			14841.35660	1				
8	5	4	14951.01156	1								
8	5	3	14951.53235	1								
8	6	3	14987.05511	1								
9	1	9	14475.02134	1								
9	1	8	14658.71978	1								
9	2	8	14658.61190	2								
9	2	7	14804.09979	2								
9	3	7	14812.55634	1								
9	4	5	14974.81540	1								
9	7	3					15401.70313	1				
10	0	10										
10	1	10	14654.10173	1								
10	3	7	15126.11924	1								
11	2	10	15086.39666	1								

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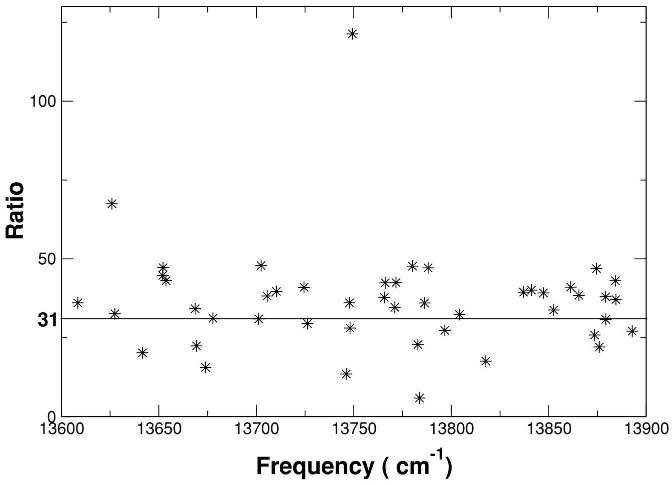

FIG. 1. Ratio of $H_2{}^{18}O$ line intensities obtained in this work (unscaled for isotopic enrichment) to those given in HITRAN (*20*).

4. DISCUSSION AND CONCLUSIONS

A major reason for analyzing the $H_2{}^{18}O$ spectra presented here is so that the data can be included in databases for use in atmospheric and other models. HITRAN (*20*) contains 47 transitions assigned to $H_2{}^{18}O$ in the region studied here, which are confined to the frequency range 13 608–13 893 cm^{-1}. The source of these data is unknown to us. Our analysis confirms the assignments given in HITRAN, the only exceptions being the line at 13 847.279 cm^{-1}, which we assign to 3_{13}–2_{12} 301–000 but whose assignment is mistyped in HITRAN, and the 4_{14}–5_{15} line from the same band, which we find at 13 677.624 cm^{-1} as opposed to 13 677.131 cm^{-1} in HITRAN.

Figure 1 compares the intensities given in HITRAN with those derived here. For ease of analysis we plot the intensities from the ^{18}O spectrum directly without scaling for enhanced $H_2{}^{18}O$ abundance. The ratio of our intensities to those in HITRAN is 36.5 ± 17.3. This result is consistent with our result of 31.0 ± 0.5. The almost 50% error is well outside our error estimates, even when allowance is made for the errors in the individual lines, and it would appear therefore that the larger uncertainty must be inherent in the HITRAN data.

In this work we have used three separate long-path-length Fourier transform spectra, recorded using water with different isotopic composition, to identify lines belonging to $H_2{}^{18}O$. We have identified 927 lines and assigned 747 of them using a variety of techniques. Comparison with known data for $H_2{}^{16}O$ aided this process. The spectra analyzed here include one containing enhanced $H_2{}^{17}O$. It should be possible to apply the techniques used here to this spectrum.

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