# Frequency Measurement of Pure Rotational Transitions of $H_2^{17}O$ and $H_2^{18}O$ from 0.5 to 5 THz

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Frequencies of pure rotational transitions of isotopic species of water,  $H_2^{17}O$ , and  $H_2^{18}O$  were measured in the 1–5 THz region with a high-precision far-infrared spectrometer using a tunable radiation source. Measured frequencies of more than 100 spectral lines for each species provide an excellent frequency standard for the far-infrared region. Molecular parameters based on a Watson-type Hamiltonian have been obtained to reproduce the observed frequencies. © 1999 Academic Press

*Key Words:* tunable far-infrared; rotational spectra;  $H_2^{17}O$ ;  $H_2^{18}O$ .

## 1. INTRODUCTION

The rotational spectrum of water vapor falls in the farinfrared (FIR) region where new spectroscopic techniques have been developed in the last decades. The rotational spectrum of water vapor is so strong and dense in the FIR region that the line frequencies can be used as conventional calibration standards for spectrometers in the region. From the point of view of molecular theory, the H<sub>2</sub>O molecule is a good example of a light rotator with large centrifugal distortion effects which make the calculation of highly excited rotational levels so difficult. Spectroscopists are attempting to analyze the spectrum using new theories to obtain better fitting. Accurate measurement of the transition frequencies is desired to provide a reliable data set for testing the theories. In our previous work (1), we measured the frequencies of rotational transitions of  $H_2^{16}O$  from 0.5 to 5 THz using a tunable FIR spectrometer based on the difference frequency generation of two CO<sub>2</sub> laser lines. This work is extended to the rotational spectra of  $H_2^{17}O$ and  $H_2^{18}O$  in the present work.

Historically, in 1970s, several low-frequency rotational lines of  $H_2^{17}O(2)$  and  $H_2^{18}O(2-4)$  were measured by microwave spectroscopic technique and molecular parameters in the ground vibrational state were obtained for  $H_2^{17}O(5)$  and  $H_2^{18}O(4-6)$ . Rotational lines of  $H_2^{18}O$  were observed from 10 to 40 cm<sup>-1</sup> with a Fourier-transform (FT) spectrometer by Fleming and Gibson (7) in 1976. Then, a number of rotational lines of  $H_2^{17}O$  and  $H_2^{18}O$  were observed in natural abundance using FT spectrometers (8, 9). In 1980, Kauppinen and Kyrö (10) precisely measured rotational lines of  $H_2^{17}O$  and  $H_2^{18}O$ from 50 to 730 cm<sup>-1</sup> using a FT spectrometer. Measurement of more than 280 lines for each species with an accuracy of 0.001 cm<sup>-1</sup> resulted in a revision of molecular parameters for these species (11). Partridge measured rotational lines of these two species from 10 to 47 cm<sup>-1</sup> by using a FT spectrometer with an accuracy of 0.0006 cm<sup>-1</sup> (*12*). Johns measured the FT spectrum of  $H_2^{18}O$  from 33 to 280 cm<sup>-1</sup> with an accuracy of 0.0002 cm<sup>-1</sup> and improved the molecular parameters for  $H_2^{18}O$  (*13*).

In the present work, frequencies of pure rotational transitions of  $H_2^{17}O$  and  $H_2^{18}O$  have been measured in the range from 0.5 to more than 5.2 THz (16–173 cm<sup>-1</sup>) with accuracies better than 100 kHz (3 × 10<sup>-6</sup> cm<sup>-1</sup>). Molecular parameters of a Watson-type Hamiltonian have been determined to reproduce the observed frequencies.

## 2. EXPERIMENTAL

Our FIR spectrometer is based on a tunable FIR (referred to as TuFIR) technique developed by Evenson and coworkers (14). Because detailed descriptions of the spectrometer can be found in our previous papers (1, 15, 16), only a brief description is given here. As shown in Fig. 1, FIR radiation of high spectral purity is generated as a difference of two CO<sub>2</sub> laser radiations which are mixed in a metal-insulator-metal (MIM) diode. Microwave radiation tunable up to 18 GHz is added to generate tunable sidebands. Power of the sideband radiation is typically about 100 nW. With an appropriate choice of the pair of normal CO<sub>2</sub> laser lines, tunable FIR radiation up to 5.7 THz is generated. The frequency of each CO<sub>2</sub> laser is stabilized to the saturated fluorescence signal at 4.3  $\mu$ m from CO<sub>2</sub> in an external cell. A laser frequency modulation at 1 kHz which is used to stabilize the laser frequency results in a source modulation of FIR radiation at 1 kHz. The FIR radiation detected by a liquid helium-cooled silicon composite bolometer is phase sensitively detected at 1 kHz to obtain absorption lines.

The sample cell is a Pyrex glass tube of 0.5 m in length and 30 mm in diameter with polypropylene windows at each end. Because rotational lines of  $H_2^{17}O$  or  $H_2^{18}O$  are close in frequency to the corresponding lines of normal  $H_2O$ , the path of





FIG. 1. Block diagram of the tunable far-infrared spectrometer.

the FIR radiation outside of the sample cell was made as short as possible and was purged with nitrogen gas to prevent the absorption of FIR radiation by atmospheric water vapor. Though some of the strong lines of  $H_2^{18}O$  were measured using normal  $H_2O$  sample in natural abundance (0.2%), most of the lines were measured with an isotope-enriched sample. A 10% enriched sample of  $H_2^{17}O$  and a 96% enriched sample of  $H_2^{18}O$  were used.

#### 3. RESULTS

Prior to the present measurement, the most accurate frequency table covering the frequency range of our spectrometer (0.5-5.3 THz) had been given by Kauppinen and Kyrö (10), Kyrö (11), and Partridge (12) for H<sub>2</sub><sup>17</sup>O and by Johns (13) for H<sub>2</sub><sup>18</sup>O. So we chose spectral lines below 5.3 THz from tables in these references and remeasured them.

As for  $H_2^{17}O$ , several lines below 50 cm<sup>-1</sup> are missing in the table of Partridge (12). Therefore, we measured the lines higher than 50 cm<sup>-1</sup> first, then obtained a preliminary set of molecular parameters and searched for spectral lines below 50 cm<sup>-1</sup> around calculated frequencies using the parameters. About 130 rotational lines of  $H_2^{17}O$  and 120 lines of  $H_2^{18}O$ were measured. Each spectral lineshape, whose width is dominated by Doppler broadening, was fitted by a least squares program (17) to a theoretical Voigt profile to determine the line center. Measured and calculated center frequencies of  $H_2^{17}O$ and  $H_2^{18}O$  are shown in Tables 1 and 3, respectively.

### 4. ANALYSIS

Analysis of the rotational energy levels of  $H_2O$  has been a challenging task for spectroscopists because the molecule

shows an extremely large centrifugal distortion effect and the calculation based on the Taylor-series Hamiltonian in the Watson form (18) leads to large errors for highly excited rotational levels. A number of extensive studies with new theories have been reported to analyze the water molecule (19-26).

For the levels with low rotational quantum numbers like those observed in the present work, however, a calculation based on a Watson-type Hamiltonian is still a convenient method for giving precise energy values as shown in Refs. *1* and *13*. Therefore, the observed frequencies were analyzed using a Watson-type *A*-reduced Hamiltonian as follows:

$$\begin{split} H &= (B + C)/2J^{2} + \{A - (B + C)/2\}J_{z}^{2} + (B - C)/2J_{xy}^{2} \\ &- \Delta_{J}(J^{2})^{2} - \Delta_{JK}J^{2}J_{z}^{2} - \Delta_{K}J_{z}^{4} - 2\delta_{J}J^{2}J_{xy} - \delta_{K}\{J_{z}^{2}, J_{xy}^{2}\} \\ &+ H_{J}(J^{2})^{3} + H_{JK}(J^{2})^{2}J_{z}^{2} + H_{KJ}J^{2}J_{z}^{4} + H_{K}J_{z}^{6} \\ &+ 2h_{J}(J^{2})^{2}J_{xy}^{2} + h_{JK}J^{2}\{J_{z}^{2}, J_{xy}^{2}\} + h_{K}\{J_{z}^{4}, J_{xy}^{2}\} \\ &+ L_{J}(J^{2})^{4} + L_{JJK}(J^{2})^{3}J_{z}^{2} + L_{JK}(J^{2})^{2}J_{z}^{4} + L_{KKJ}J^{2}J_{z}^{6} \\ &+ L_{K}J_{z}^{8} - 2l_{J}(J^{2})^{3}J_{xy}^{2} + l_{JK}(J^{2})^{2}\{J_{z}^{2}, J_{xy}^{2}\} \end{split}$$

$$\begin{aligned} &+ l_{KJ}J^{2}\{J_{z}^{4}, J_{xy}^{2}\} + l_{K}\{J_{z}^{6}, J_{xy}^{2}\} + P_{J}(J^{2})^{5} + P_{JJK}(J^{2})^{4}J_{z}^{2} \\ &+ P_{JK}(J^{2})^{3}J_{z}^{4} + P_{KJ}(J^{2})^{2}J_{z}^{6} + P_{KKJ}J^{2}J_{z}^{8} + P_{K}J_{z}^{10} \\ &+ p_{JJK}(J^{2})^{3}\{J_{z}^{2}, J_{xy}^{2}\} + p_{KKJ}J^{2}\{J_{z}^{6}, J_{xy}^{2}\} + p_{K}\{J_{z}^{8}, J_{xy}^{2}\} \\ &+ T_{JJK}(J^{2})^{4}J_{z}^{4} + T_{KKJ}(J^{2})^{2}J_{z}^{8} + T_{KKKJ}J^{2}J_{z}^{10} + T_{K}J_{z}^{12}, \end{aligned}$$

where  $J_{xy}^2 = J_x^2 - J_y^2$ , and  $\{A, B\} = AB + BA$ .

Data obtained by microwave spectroscopy and FT spectroscopy were also included in the best fit analysis. As for  $H_2^{17}O$ , lines lower than 400 GHz were from microwave data by Steenbeckeliers (2). The total number of lines for  $H_2^{17}O$  was 127. As for  $H_2^{18}O$ , lines lower than 550 GHz were from microwave data by De Lucia *et al.* (4), where the three highest frequency lines,  $6_{42} \leftarrow 5_{51}$ ,  $5_{32} \leftarrow 4_{41}$ , and  $2_{11} \leftarrow 2_{02}$ , were remeasured in the present work. Because the experimental errors for these three lines were smaller in our measurement, we used our data. The data from 5.25 to 8.4 THz were from those by Johns (13). The total number of lines for  $H_2^{18}O$ was 165.

The weights in the best fit analysis were set to be proportional to the inverse squares of the experimental uncertainties. The obtained molecular parameters for  $H_2^{17}O$  and  $H_2^{18}O$  are listed in Tables 2 and 4, respectively. The transition frequencies calculated with these parameters are shown in Tables 1 and 3 together with their observed – calculated (O – C) values.

<b>FABLE 1</b>
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Measured and Calculated Frequencies<sup>a</sup> (in MHz) of Pure Rotational Transitions of H<sub>2</sub><sup>17</sup>O

Γ Ka' Kc' ← J' Ka'' Kc"	Obs.	Calc,	0-C	J' Ka' Kc'	← J" Ka" Kc"	Obs.	Calc.	0-C
6 1 6 5 2 3 13	535.510 *	13 535.459	0.051	542	533	3 147 209.261 ( 36)	3 147 209.405	-0.144
3 1 3 2 2 0 194	002.290 <sup>b</sup>	194 002.240	0.050	625	616	3 158 746.404 ( 36)	3 158 746.457	-0.053
4 2 3 3 3 0 469	809.339 (351) 4	69 809.928	-0.589	735	726	3 195 616.643 ( 38)	3 195 616.527	0.116
1 1 0 1 0 1 552	021.075 (38) 5	552 021.065	0.010	643	634	3 196 773.182 ( 36)	3 196 773.249	-0.067
5 3 2 4 4 1 658	504.180 (149)	558 504.540	-0.360	744	735	3 298 639.736 ( 56)	3 298 639.692	0.044
2 1 1 2 0 2 748	458.779 (42) 7	748 458.617	0.162	322	2 1 1	3 313 043.876 ( 46)	3 313 044.054	-0.178
4 2 2 3 3 1 944	853.071 (42) 9	44 853.091	-0.020	845	836	3 468 801.961 ( 38)	3 468 801.906	0.055
524431 987	879.876 (39) 9	987 880.027	-0.151	954	945	3 451 481.974 (428)	3 451 480.059	1.915
202111 991	519.683 (36) 9	991 519.679	0.004	7 1 6	707	3 535 900.842 (39)	3 535 900.415	0.427
3 1 2 3 0 3 1 096	415.186 (36) 1 (	096 415.076	0.110	606	515	3 592 683.645 ( 39)	3 592 683.914	-0.269
	166.987 (36) 1	107 166.896	0.091	836	827	3 601 383.801 (51)	3 601 383.846	-0.045
3 2 1 3 1 2 1 148	9/4.962 (36) 1:	148 9/4.939	0.023	010	505	3 644 995.072 ( 39)	3 644 995.009	0.063
	419 971 (38) 1	106 135.091	0.009	0 0 0 0	044 747	3 663 663 666 (30)	3 008 047.555	0.13/
4 2 2 4 1 2 1 107	410.0/1 (36) 1	109 410.027	0.044	120	310	3 787 242 695 ( 44)	3 787 242 849	-0.154
3 2 4 3 1 1 1 2 1 2	009.027 (30) 1	137 009.104	-0.096	<del>1</del> 23	5 2 4	3 803 428 532 (77)	3 903 428 606	-0.074
744651 1212	. 991 983 (51) 1 1	212 979.404	0.218	6 5 1	642	3 876 375 114 ( 85)	3 876 375 039	0.075
8 2 7 7 3 4 1 282	726 792 (42) 1 2	082 726 776	0.016	5 5 0	541	3 904 093 322 (156)	3 904 093.300	0.022
7436521325	632,503 (38) 1.3	325 632 564	-0.061	652	643	3 908 469 423 ( 53)	3 908 469.475	-0.052
6 2 5 5 3 2 1 332	129,386 (38) 1 3	332 129,269	0.117	753	744	3 909 669,422 ( 80)	3 909 669.931	-0.509
5 2 3 5 1 4 1 406	448.955 (38) 1 4	406 448.808	0.147	5 5 1	542	3 911 126.846 ( 60)	3 911 126.647	0.199
6 3 3 5 4 2 1 583	727.403 (38) 1 5	583 727.371	0.032	725	634	4 026 370.245 ( 48)	4 026 370.195	0.050
7 2 6 6 3 3 1 439	891.568 (149) 1 4	39 891.680	-0.112	10 4 7	10 3 8	4 036 624.943 (46)	4 036 624.910	0.033
4 1 3 4 0 4 1 604	180.557 (38) 1 6	504 180.590	-0.033	937	928	4 063 443.292 ( 56)	4 063 443.407	-0.115
2 2 1 2 1 2 1 646	398.143 (39) 1 6	546 398.129	0.014	10 5 6	10 4 7	4 082 007.509 ( 64)	4 082 007.664	-0.155
2 1 2 1 0 1 1 662	464.158 (36) 1 6	662 464.094	0.064	707	6 1 6	4 158 000.015 ( 77)	4 158 000.188	-0.173
303212 1718	118.736 (38) 17	18 118.743	-0.007	7 1 7	606	4 180 385.495 (48)	4 180 385.642	-0.147
6336241739	572.000 (36) 17	739 571.948	0.052	524	413	4 197 019.729 ( 42)	4 197 019.549	0.180
7 3 4 7 2 5 1 783	388.025 (36) 1 7	783 388.077	-0.052	827	8 1 8	4 231 907.193 ( 39)	4 231 907.270	-0.077
532 523 1840	152.668 (36) 1 8	340 152.647	0.021	10 2 8	10 1 9	4 351 161.455 ( 48)	4 351 161.813	-0.358
3 2 2 3 1 3 1 906	062.231 (36) 1 9	906 062. <b>380</b>	-0.149	330	303	4 413 848.064 ( 42)	4 413 847.998	0.066
5 2 3 4 3 2 1 948	277.941 (36) 1 9	948 277.796	0.145	331	220	4 440 837.832 ( 80)	4 440 837.802	0.030
4 3 1 4 2 2 2 011	529.712 (36) 2 (	011 529.818 ·	-0.106	330	221	4 485 568.539 (44)	4 485 568.612	-0.073
8 3 5 8 2 6 2 013	437.033 (51) 2 (	013 437.517	-0.484	716	625	4 535 154.497 ( 56)	4 535 154.145	0.352
4 1 3 3 2 2 2 088	016.649 (36) 2 (	088 016.569	0.080	963	954	4 561 561.243 ( 53)	4 561 560.770	0.473
3 1 3 2 0 2 2 155	440.437 (36) 21	155 440.291	0.146	10 3 8	10 2 9	4 564 109.765 (39)	4 564 109.609	0.156
3 3 0 3 2 1 2 168	(457.888 (38) 21	168 457.982	-0.094	862	853	4 613 500.984 (680)	4 613 502.610	-1.626
514 505 2225	010.637 (39) 2 2	225 010.742	-0.105	904	900	4 030 033.514 (810)	4 030 031.424	2.090
4 2 3 4 1 4 2 232	(401.120 (30) 2. (002.276 (46) 2.	232 401,327	-0.139	7 6 1	7 5 9	4 575 730.854 ( 00) A 633 697 667 (103)	4 515 130.124	0.003
0 3 0 7 4 3 2 202 0 4 5 0 3 6 2 287	034 489 (51) 2 1	202 333.000	0.153	863	854	4 636 270 403 (71)	4 636 271 668	-1 265
3 3 1 3 2 2 3 3 40	773 242 (38) 2	340 773 182	0.060	6 6 0	651	4 636 336 821 (224)	4 636 337 375	-0.554
7 2 5 7 1 6 2 353	116.027 (38) 2	353 116.101	-0.074	6 6 1	652	4 637 408.255 ( 53)	4 637 408.666	-0.411
404 313 2389	898.207 (38) 2 3	389 898.359	-0.152	762	753	4 639 564.820 (71)	4 639 563.609	1.211
844 835 2406	767.120 (38) 2	406 766.943	0.177	808	7 1 7	4 713 837.243 (214)	4 713 837.049	0.194
936 927 2437	474.985 (59) 2	437 474.784	0.201	8 1 8	707	4 723 224.243 ( 85)	4 723 224.099	0.144
4 3 2 4 2 3 2 4 3 9	319.592 (38) 2	439 319.607	-0.015	918	909	4 757 672.856 (46)	4 757 672.966	-0.110
5 3 3 5 2 4 2 609	740.484 (36) 2 (	609 740.514	-0.030	928	919	4 793 077.382 ( 64)	4 793 077.560	-0.178
734 643 2612	2 984.953 (51) 2 (	512 985.023	-0.070	431	404	4 813 320.420 ( 69)	4 813 320.112	0.308
7437342621	117.184 (39) 2	621 117.015	0.169	936	845	4 850 055.006 (44)	4 850 054.668	0.338
4 1 4 3 0 3 2 631	176.821 (46) 2	631 176.598	0.223	11 2 9	11 1 10	4 972 521.517 ( 99)	4 972 521.379	0.138
5 2 4 5 1 5 2 675	5 583.371 (39) 2 (	675 583.526	-0.155	726	615	4 977 140.283 ( 53)	4 977 140.364	-0.081
2 2 1 1 1 0 2 756	3 841.024 (39) 2 1	756 841.157	-0.133	826	735	5 003 094.161 ( 59)	5 003 094.128	0.033
6426332842	2 780.905 (42) 2	842 781.095	-0.190	432	321	5 077 587.318 ( 90)	5 077 587.517	-0.199
6346252861	1900.086 (36) 2	861 900.052	0.034	817	726	5 188 886.526 ( 39)	5 188 886.490	0.036
6 1 5 6 0 6 2886	5 328.247 (36) 2	886 328.218	0.029	4 2 2	313	5 191 688.836 (44)	5 191 688.653	0.183
2 2 0 1 1 1 2 952	2 957.663 (38) 2	952 957.730	-0.067	909	8 1 8	5 264 693.665 (42)	5 264 694.082	-0.417
5 1 4 4 2 3 2 981	148.445 (36) 2	981 148.595	-0.150	919	808	5 268 608.573 (48)	5 268 608.460	0.113
624 533 2991	1 364.726 (36) 2	991 364.828	-0.102	770	761	5 294 347.567 (42)	5 294 347.528	0.039
505414 3008	3 619.064 (39) 3	008 619.180	-0.116	4 3 1	322	5 297 156.277 ( 56)	5 297 156.091	0.186
8 2 6 8 1 7 3 009	9 824.350 (71) 3	009 824.165	0.185	871	862	5 306 809.792 ( 90)	5 306 810.186	-0.394
4 4 0 4 3 1 3 089	9 086.890 (38) 3	089 686.814	0.0/6	872	863	5 307 775.850 ( 51)	a JU/ //6.001	-0.011
5 1 5 4 0 4 3 125	<b>5 6 16</b> . / <b>17</b> ( <b>36</b> ) <b>3</b>	125 616.612	0.105	972	э 6 3	a 310 (60.945 (156)	0 310 700.318	0.62/
441432 3129	a azo. 903 (42) 3	129 925.903	0.000					

<sup>*a*</sup> The  $1\sigma$  uncertainties in the last quoted digits are shown in parentheses.

<sup>b</sup> Lines taken from Ref. 2.

TABLE 2Molecular Parameters (in MHz) of H2170

A	830283.720 (43)	$l_J$	-5.159 (40) $\times 10^{-6}$
В	435350.739 (26)	l <sub>JK</sub>	-7.88 (83) ×10 <sup>-6</sup>
С	277511.307 (22)	l <sub>KJ</sub>	4.61 (15) ×10 <sup>-4</sup>
$\Delta_J$	37.5724 (13)	l <sub>K</sub>	$-1.1611$ (50) $\times 10^{-2}$
$\Delta_{J\!K}$	-172.3431 (56)	$P_J$	9.0 (23) $\times 10^{-9}$
$\Delta_{K}$	961.8478 (81)	P <sub>JJK</sub>	$-3.02$ (21) $\times 10^{-7}$
$\delta_J$	15.22729 (35)	P <sub>JK</sub>	2.49 (26) $\times 10^{-6}$
$\delta_{\!K}$	38.8045 (43)	P <sub>KJ</sub>	1.268 (90) $\times 10^{-5}$
$H_J$	1.6563 (39) $\times 10^{-2}$	P <sub>KKJ</sub>	$-6.82$ (20) $\times 10^{-5}$
$H_{J\!K}$	-5.705 (28) $\times 10^{-2}$	P <sub>K</sub>	1.844 (15) ×10 <sup>-4</sup>
H <sub>KJ</sub>	-5.1874 (51) $\times 10^{-1}$	<i>Р</i> <sub>JJK</sub>	0.0 (fixed)
H <sub>K</sub>	3.78193 (87)	Р <sub>КК</sub> Ј	-4.32 (44) $\times 10^{-6}$
$h_J$	$8.2289$ (71) $\times 10^{-3}$	<i>P</i> <sub>K</sub>	7.06 (12) $\times 10^{-5}$
h <sub>JK</sub>	$-2.536$ (10) $\times 10^{-2}$	T <sub>JJK</sub>	-5.41 (70) ×10 <sup>-9</sup>
h <sub>K</sub>	9.4430 (85) ×10 <sup>-1</sup>	T <sub>KKJ</sub>	$2.271$ (45) $\times 10^{-7}$
$L_J$	$-1.216$ (50) $\times 10^{-5}$	T <sub>KKKJ</sub>	-4.023 (75) $\times 10^{-7}$
L <sub>JJK</sub>	$1.194$ (45) $\times 10^{-4}$	T <sub>K</sub>	$-3.484$ (68) $\times 10^{-7}$
L <sub>JK</sub>	-2.337 (22) $\times 10^{-3}$		
T	_2		
LKKJ	9.143 (52) ×10 <sup>-5</sup>		
L <sub>KKJ</sub> L <sub>K</sub>	9.143 (52) $\times 10^{-3}$ -2.6793 (51) $\times 10^{-2}$		

## 5. DISCUSSION

The uncertainty of the synthesized FIR frequency of the present spectrometer is typically about 10 kHz (*30*). The uncertainties of measured frequencies of line positions, which are several tens of kilohertz in most cases, mainly come from determination of center frequencies of deformed lineshapes. The sample in the absorption cell is optically thick for strong absorption. The optical thickness results in the line deformation. The sample pressure must be kept below 0.1 Pa in most measurements to remove the deformation. Difficulty in maintaining a constant pressure during the measurement caused a slight deformation of the lineshape and brought about some uncertainty in determining the line center.

For some lines, experimental uncertainties exceed 100 kHz. In the neighborhood of a strong absorption line of atmospheric water vapor, not only the signal to noise ratio of a spectral line is degraded but also its baseline is deformed. These effects result in large uncertainties in determining center frequencies of the spectral lines.

In a preliminary experiment using a molecular beam sample (27), we observed hyperfine splitting due to the quadrupole moment of <sup>17</sup>O nucleus in low-*J* lines of  $H_2^{17}O$ . In the Doppler-broadened line profile observed in the present work, the hyperfine components were not resolved. For low-*J* and low frequency rotational lines, the effect of hyperfine structure brings about larger uncertainties in the determination of center frequencies. The large experimental uncertainty of  $4_{23} \leftarrow 3_{30}$  line can be attributed to this effect. In most measurements, however, the effect of hyperfine structure was not considered to be the main source of experimental error.

Molecular parameters in the ground vibrational state of  $H_2^{17}O$  and  $H_2^{18}O$  have been also obtained through the measurements of vibration–rotation transitions in the infrared region (28, 29). Measurements of pure rotational transitions with FT spectrometers (11, 13) improved the accuracy of the parameters obtained from infrared spectroscopy. However, calculated values using those parameters scattered

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TABLE 3
Measured and Calculated Frequencies <sup>a</sup> (in MHz) of Pure Rotational Transitions of H <sub>2</sub> <sup>18</sup> O

J' Ka' Kc' ← J' Ka'' Kc''	Obs.	Calc.	0-C	<b>Г Ка' н</b>	(c' ← J" Ka" Kc"	Obs.	Cak.	0-C
616 523	5 625,147 b	5 625,138	0.009	6 2	4 5 3 3	3 017 158.833 ( 36)	3 017 158.904	-0.071
3 1 3 2 2 0	203 407.520 *	203 407.267	0.253	82	6 8 1 7	3 019 734.029 ( 38)	3 019 734.269	-0.240
515422	322 465.170	322 465.146	0.024	44	0 4 3 1	3 056 987.150 (42)	3 056 986.787	0.363
414 321	390 607.760 <sup>b</sup>	390 607.752	0.008	44	1 4 3 2	3 098 412.349 (38)	3 098 412.270	0.079
423 330	489 054.260 °	489 054.201	0.059	54.	2 5 3 3 5 5 4 0 4	3 116 280.344 (38)	3 116 200.004	-0.340
624 / 1 /	517 181.900 520 137 320 <sup>b</sup>	520 136.948	0.372	6 2	5 6 1 6	3 150 956.912 (38)	3 150 956.843	0.069
533440	537 337.570 b	537 337.654	-0.084	64	3 6 3 4	3 167 316.921 ( 46)	3 167 317.132	-0.211
1 1 0 1 0 1	547 676.440 <sup>b</sup>	547 676.548	-0.108	73	5726	3 182 712.688 ( 36)	3 182 712.463	0.225
642 551	554 859.748 ( 60)	554 859.647	0.101	74	4 7 3 5	3 271 757.942 (38)	3 271 757.831	0.111
532441	692 079.347 (36)	692 079.888	-0.541	32	2 2 1 1	3 296 734.387 (39)	3 296 734.421	-0.034
211 202	745 320.142 (36) 970 276 659 (36)	745 320.014 970 276 789	-0.130	84	4 943 5 836	3 445 526,204 (36)	3 445 525.384	0.820
202 111	994 674.431 ( 36)	994 674.261	0.170	71	6 7 0 7	3 535 045.216 ( 38)	3 535 045.258	-0.042
3 1 2 3 0 3	1 095 628.955 ( 36)	1 095 628.647	0.308	60	6 5 1 5	3 586 431.043 ( 44)	3 586 431.398	-0.355
111 000	1 101 697.036 ( 36)	1 101 697.194	-0.158	83	6 8 2 7	3 591 263.266 ( 56)	3 591 263.190	0.076
321 312	1 136 703.041 ( 36)	1 136 703.059	-0.018	8 5	3 8 4 4	3 620 500.441 (42)	3 620 500.736	-0.295
3 1 2 2 2 1	1 181 396.004 ( 36)	1 181 395.675	0.329	6 1 7 0	6 5 0 5	3 535 465.380 (44)	3 636 400.000	-0.164
422 413	1 188 864.647 (36)	1 188 804.048	~0.291	94	6 9 3 7	3 696 249.232 (38)	3 696 248.898	0.334
634 541	1 216 849.584 (36)	1 216 849.113	0.471	92	7 9 1 8	3 700 536.122 ( 93)	3 700 536.622	-0.500
744 651	1 252 570.303 ( 39)	1 252 570.535	-0.232	83	5 7 4 4	3 760 381.332 ( 39)	3 760 381.456	-0.124
8 2 7 7 3 4	1 270 059.914 ( 36)	1 270 060.559	-0.645	75	2 7 4 3	3 762 496.201 ( 64)	3 762 495.162	1.039
6 2 5 5 3 2	1 340 733.590 ( 36)	1 340 733.173	0.417	42	3 3 1 2	3 769 506.447 (46)	3 769 506.419	0.028
743652	1 367 758.352 ( 36)	1 367 758.686	-0.334	6 1	5 5 2 4	3 807 723.582 (277)	3 807 723.996	-0.414
523 514	1 402 970.791 (36)	1 402 970.688	0.103	55	0 541	3 864 028.946 (36)	3 868 620.715	0.497
413 404	1 408 633.938 (38)	1 605 963.435	0.217	75	3 7 4 4	3 870 153.180 (39)	3 870 152.834	0.346
633 542	1 620 855.257 (42)	1 620 855.427	-0.170	55	1 5 4 2	3 871 373.851 (46)	3 871 374.306	~0.455
221 212	1 633 482.650 ( 36)	1 633 482.830	-0.180	85	4 8 4 5	3 889 278.593 (38)	3 889 279.534	-0.941
212101	1 655 865.959 (36)	1 655 866.129	-0.170	10 4	7 10 3 8	4 022 058.648 (277)	4 022 059.761	-1.113
432 505	1 656 197.895 (42)	1 656 197.598	0.297	72	5 6 3 4	4 049 304.037 (103)	4 049 304.049	-0.012
3 0 3 2 1 2	1 719 249.729 ( 36)	1 719 249.859	-0.130	93	7 9 2 8	4 055 475.586 (39)	4 150 075.594	-0.134
633624	1 719 976.985 (36)	1 719 977.406	-0.421	8 1	7 8 0 8	4 154 598.933 (77)	4 154 598.840	0.093
624 615	1 800 483 386 (36)	1 800 483.271	0.115	7 1	7606	4 171 320.223 ( 64)	4 171 320.123	0.100
532 523	1 815 848.526 (36)	1 815 848.809	-0.283	52	4 4 1 3	4 178 056.034 ( 51)	4 178 055.859	0.175
322 313	1 894 322.824 ( 36)	1 894 322.823	0.001	82	7 8 1 8	4 224 538.935 (103)	4 224 539.912	-0.977
7 3 5 6 4 2	1 815 970.280 ( 36)	1 815 969.806	0.474	33	0 3 0 3	4 376 081.039 (46)	4 376 080.864	0.175
523432	1 974 643.232 ( 36)	1 974 643.349	-0.117	33	1 2 2 0	4 410 284.094 (44)	4 415 203.010	0.2/8
431422	1 985 915.025 (35)	1 985 915.233	-0.208	96	3 9 5 4	4 510 186.958 ( 64)	4 510 186.819	0.139
413 322	2 099 900.044 (30)	2 143 749.158	0.068	7 1	6 6 2 5	4 534 163.808 (75)	4 534 164.009	-0.201
3 1 3 2 0 2	2 147 731.770 ( 36)	2 147 731.611	0.159	10 3	8 10 2 9	4 557 466.890 ( 51)	4 557 466.399	0.491
514 505	2 227 870.337 (36)	2 227 870.260	0.077	62	5 5 1 4	4 559 552.927 ( 65)	4 559 552.670	0.257
423414	2 242 195.713 ( 39)	2 242 195.608	0.105	86	2 8 5 3	4 564 558.314 ( 99)	4 564 558.606	-0.292
331 322	2 318 553.879 ( 36)	2 318 553.726	0.153	66	1 6 5 2	4 590 355.444 (680)	4 590 354.641	-1 692
725716	2 361 122.444 ( 36)	2 361 122.232	0.212	86	3 8 5 4	4 588 605.610 (149)	4 588 604.346	1.264
404 313	2 388 325.067 (36)	2 308 323.303	-0.213	6 6	0 6 5 1	4 589 221.268 ( 99)	4 589 220.286	0.982
936 927	2 446 246.202 (38)	2 446 246.312	-0.110	76	2 7 5 3	4 592 194.400 (625)	4 592 194.988	-0.588
743734	2 582 720.292 ( 36)	2 582 720.178	0.114	8 0	8 7 1 7	4 704 517.673 ( 39)	4 704 517.602	0.071
533 524	2 591 048.043 ( 36)	2 591 048.362	-0.319	8 1	8 7 0 7	4 713 360.504 (133)	4 713 360.444	0.060
414 303	2 622 939.667 (42)	2 622 939.458	0.209	91	8 9 0 9	4 751 869.061 (194)	4 751 867.523	-0.057
734 643	2 653 659.320 (44)	2 653 659.224	0.096	4 J G 9	8 9 1 9	4 785 166.445 (44)	4 785 166.422	0.023
524 515	2 666 726.307 ( 59)	2 000 720.103	-0.126	93	6 8 4 5	4 891 457.231 (107)	4 891 456.955	0.276
642633	2 805 378.378 (36)	2 805 378.526	-0.148	72	6 6 1 5	4 959 096.406 ( 80)	4 959 096.546	-0.140
634 625	2 845 982.199 ( 36)	2 845 982.192	0.007	82	6735	5 020 343.166 (123)	5 020 343.062	0.104
615606	2 888 018.719 ( 77)	2 888 018.763	-0.044	43	2 3 2 1	5 051 272.514 ( 80)	5 051 272.609	-0.095
220 111	2 938 998.549 (36)	2 938 998.605	-0.056	42	2 3 1 3	5 183 153.399 (110)	5 183 153.338	0.061
541532	2 969 866.143 (38)	2 969 866.252	-0.109	81	7 7 2 6	5 183 321.763 (48)	5 183 321.255	0.508
514 423	2 990 141.426 (44)	2 950 141.910	-0.426	77	v 761	0 240 (14.940 (02)	0 240 114.304	0.019
505414	J 001 100.003 ( 00)							

 $^a$  The  $1\sigma$  uncertainties in the last quoted digits are shown in parentheses.

<sup>b</sup> Lines taken from Ref. 4.

TABLE 4Molecular Parameters (in MHz) of H2180

A	825367.428 (67)	$l_J$	-4.929 (72) $\times 10^{-6}$
В	435353.585 (38)	l <sub>JK</sub>	$1.6 \times 10^{-5}$ (fixed)
С	276950.565 (29)	l <sub>KJ</sub>	2.95 (19) $\times 10^{-4}$
$arDelta_J$	37.5492 (13)	l <sub>K</sub>	-9.773 (92) $\times 10^{-3}$
$\Delta_{J\!K}$	-171.4038 (49)	$P_J$	$3.29 \times 10^{-9}$ (fixed)
$\Delta_{K}$	950.788 (13)	P <sub>JJK</sub>	$-1.07$ (32) $\times 10^{-7}$
$\delta_J$	15.22848 (54)	P <sub>JK</sub>	-1.34 ×10 <sup>-6</sup> (fixed)
$\delta_{K}$	37.8207 (59)	P <sub>KJ</sub>	1.21 (16) $\times 10^{-5}$
$H_J$	$1.6420$ (24) $\times 10^{-2}$	P <sub>KKJ</sub>	-3.23 (36) ×10 <sup>-5</sup>
H <sub>JK</sub>	-5.492 (31) $\times 10^{-2}$	P <sub>K</sub>	$1.463$ (22) $\times 10^{-4}$
H <sub>KJ</sub>	-5.0975 (95) ×10 <sup>-1</sup>	Р <sub>ЈЈК</sub>	-1.5 ×10 <sup>-7</sup> (fixed)
H <sub>K</sub>	3.7125 (15)	р <sub>ККЈ</sub>	-5.85 (34) ×10 <sup>-6</sup>
$h_J$	8.171 (11) $\times 10^{-3}$	p <sub>K</sub>	$3.84(22) \times 10^{-5}$
$h_{JK}$	$-2.577$ (13) $\times 10^{-2}$	T <sub>JJK</sub>	0.0 (fixed)
h <sub>K</sub>	9.101 (12) ×10 <sup>-1</sup>	T <sub>KKJ</sub>	0.0 (fixed)
$L_J$	-1.076 (13) ×10 <sup>-5</sup>	T <sub>KKKJ</sub>	0.0 (fixed)
L <sub>JJK</sub>	6.93 (63) ×10 <sup>-5</sup>	T <sub>K</sub>	$-4.85$ (10) $\times 10^{-7}$
L <sub>JK</sub>	-1.976 (22) ×10 <sup>-3</sup>		
L <sub>KKJ</sub>	7.989 (36) ×10 <sup>-3</sup>		
L <sub>K</sub>	$-2.5496$ (71) $\times 10^{-2}$		

typically by several megahertz from frequencies observed in the present work. This large deviation reflects the accuracy of the FT spectroscopic measurements. As shown in Tables 1 and 3, the new sets of molecular parameters obtained in the present work reproduce most of the measured frequencies within 1 MHz.

For diatomic species studied so far using TuFIR spectrometers, the calculation using fitted parameters yielded frequencies three to four times more accurate than the measured values (*30*). However, the theory for the water molecule is not nearly accurate, and the experimental values are more accurate.

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#### REFERENCES

- F. Matsushima, H. Odashima, T. Iwasaki, S. Tsunekawa, and K. Takagi, J. Mol. Struct. 352/353, 371–378 (1995).
- 2. G. Steenbeckeliers and J. Bellet, *Compt. Rend.* **273B**, 471–474 (1971).
- 3. F. X. Powell and D. R. Johnson, Phys. Rev. Lett. 24, 637 (1970).
- F. C. De Lucia, P. Helminger, R. L. Cook, and W. Gordy, *Phys. Rev.* A6, 1324–1326 (1972).
- 5. P. Helminger and F. C. De Lucia, J. Mol. Spectrosc. 70, 263–269 (1978).
- F. C. De Lucia, P. Helminger, and W. H. Kirchhoff, J. Phys. Chem. Ref. Data 3, 211–219 (1974).
- 7. J. W. Fleming and M. J. Gibson, J. Mol. Spectrosc. 62, 326-337 (1976).
- 8. F. Winter, J. Mol. Spectrosc. 65, 405-419 (1977).
- J. Kauppinen, T. Kärkkäinen, and E. Kyrö, J. Mol. Spectrosc. 71, 15–45 (1978).
- 10. J. Kauppinen and E. Kyrö, J. Mol. Spectrosc. 84, 405-423 (1980).
- 11. E. Kyrö, J. Mol. Spectrosc. 88, 167-174 (1981).
- 12. R. H. Partridge, J. Mol. Spectrosc. 87, 429-437 (1981).
- 13. J. W. C. Johns, J. Opt. Soc. Am. B 2, 1340-1354 (1985).

- 14. K. M. Evenson, D. A. Jennings, and F. R. Petersen, Appl. Phys. Lett. 44, 576–578 (1984).
- F. Matsushima, H. Odashima, D. Wang, S. Tsunekawa, and K. Takagi, Jpn. J. Appl. Phys. 33, 315–318 (1994).
- 16. F. Matsushima, T. Oka, and K. Takagi, Phys. Rev. Lett. 78, 1664–1666 (1997).
- K. V. Chance, D. A. Jennings, K. M. Evenson, M. D. Vanek, I. G. Nolt, J. V. Radostitz, and K. Park, *J. Mol. Spectrosc.* **146**, 375–380 (1991).
- J. K. G. Watson, in "Vibrational Spectra and Structure" (J. R. Durig, Ed.), Vol. 6, Elsevier, Amsterdam, 1997.
- A. V. Burenin, T. M. Fevral'skikh, E. N. Karyakin, O. L. Polyansky, and S. M. Shapin, J. Mol. Spectrosc. 100, 182–192 (1993).
- 20. A. V. Burenin and VI. G. Tyuterev, J. Mol. Spectrosc. 108, 153-154 (1984).
- 21. O. L. Polyansky, J. Mol. Spectrosc. 112, 79-87 (1985).

- S. P. Belov, I. N. Kozin, O. L. Polyansky, M. Yu. Tret'yakov, and N. F. Zobov, *J. Mol. Spectrosc.* **126**, 113–117 (1987).
- 23. V. I. Starikov, S. A. Tashkun, and Vl. G. Tyuterev, J. Mol. Spectrosc. 151, 130–147 (1992).
- 24. P. Jensen, J. Mol. Spectrosc. 133, 438-460 (1989).
- 25. Vl. G. Tyuterev, J. Mol. Spectrosc. 151, 97-129 (1992).
- 26. L. H. Coudert, J. Mol. Spectrosc., J. Mol. Spectrosc. 154, 427-442 (1992).
- F. Matsushima, H. Odashima, S. Tsunekawa, and K. Takagi, *in* "Laser Spectroscopy" (M. Inguscio *et al.*, Eds.), pp. 259–260, World Scientific Publishing Co., Singapore, 1996.
- J.-M. Flaud, C. Camy-Peyret, and R. A. Toth, J. Mol. Spectrosc. 68, 280–287 (1977).
- 29. R. Toth, J. Opt. Soc. Am. B 9, 462–482 (1992).
- 30. T. Varberg and K. M. Evenson, Astrophys. J. 385, 763-765 (1992).