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Microwave Spectrum and Ground State Energy Levels of $H_2{}^{17}O$

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The rotational spectrum of $H_2{}^{17}O$ in the ground vibrational state has been investigated by means of high-resolution microwave spectroscopy. Fifteen transitions in the 2.0–0.4 mm wavelength region have been measured. Both the quadrupole and spin–rotation molecular hyperfine tensors for the ^{17}O nucleus are calculated from the observed hyperfine splittings of the rotational transitions. In addition, several of the low-J lines are of significance in the atmospheric absorption of electromagnetic radiation in the microwave region. The observed microwave transitions are combined with our earlier analyses of $H_2{}^{16}O$ and $H_2{}^{18}O$ to calculate the ground state energy levels of $H_2{}^{17}O$.

I. INTRODUCTION

Although isotopic species of water have been extensively studied for many years in the infrared and more recently in the microwave region (*1*), little work has been reported on $H_2{}^{17}O$. Infrared studies have been difficult because of the overlapping bands of $H_2{}^{16}O$ and $H_2{}^{18}O$ which result from the high concentration of these species in isotopically enriched samples of $H_2{}^{17}O$. The microwave spectrum of $H_2{}^{17}O$ consists of only two rotational transitions at wavelengths longer than 1 mm, at 13 GHz and at 194 GHz (*2*). We have observed the latter under high resolution and with good signal-to-noise and have resolved seven hyperfine components which result from the quadrupole moment of the ^{17}O nucleus. In addition, we have observed the hyperfine components of five submillimeter transitions. These measurements are now possible because of both a significant increase in the spectral region accessible to our microwave spectrometer and a corresponding order of magnitude increase in sensitivity in the region of the submillimeter spectrum previously available to us (*3*). Among the newly observed lines are several low-J transitions which make significant contributions to the atmospheric absorption in the submillimeter region even though the natural abundance of ^{17}O is only 0.04%. These measurements, when combined with the results of our previous analyses of $H_2{}^{16}O$ (*4*) and $H_2{}^{18}O$ (*5*), make possible the analysis of $H_2{}^{17}O$ without the explicit inclusion of $H_2{}^{17}O$ infrared data. The energy levels which result from this analysis are in good agreement with combination differences which can be calculated from lines of $H_2{}^{17}O$ observed by Fraley, Rao, and Jones (*6*) and by Williamson and Rao (*7*) as impurities in infrared $H_2{}^{18}O$ spectra.

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Table I. Hyperfine Interaction Constants for ^{17}O in $H_2{}^{17}O$.

Spectral Constants

	3_{13}	2_{20}
eQq_J	4.258 ± .020 MHz	−3.000 ± .020 MHz
C	−0.012 ± .003 MHz	−0.017 ± .003 MHz

Molecular Constants

Quadrupole	Spin-Rotation ($\times 10^9$)
V_{aa} = −8.899 MHz	Λ_{aa} = 63.4
V_{bb} = −1.269 MHz	Λ_{bb} = 29.1
V_{cc} = 10.169 MHz	Λ_{cc} = 30.6

II. EXPERIMENTAL DETAILS

The millimeter and submillimeter spectrometer used for this work has been described previously (*8*). Briefly, a crystal harmonic generator is driven by a phase-locked OKI 55V11 klystron to produce tunable microwave power in the 100–800 GHz region. This power is directed with tapered horn and teflon lens optics through a 1-m quasifree space absorption cell and detected by a 1.5K InSb photodetector. All frequency measurements are referenced to WWVB. The absorption cell was typically filled to 50 μm with a sample isotopically enriched to 30% $H_2{}^{17}O$. This sample was kindly supplied by Drs. H. W. Morgan and P. A. Staats of Oak Ridge National Laboratory.

Fraley, Rao, and Jones (*6*) have proposed the empirical relation

$$[\nu(H_2{}^{16}O) - \nu(H_2{}^{17}O)]/[\nu(H_2{}^{16}O) - \nu(H_2{}^{18}O)] = 0.529. \qquad (1)$$

This relation and the results of our previous work on $H_2{}^{16}O$ and $H_2{}^{18}O$ were used to initially locate the 1_{10}–1_{01} and 2_{11}–2_{02} transitions of $H_2{}^{17}O$ at 552 and 748 GHz, respectively. These transitions, the two previously observed microwave transitions, and distortion constants calculated from the other species made possible the calculation of an initial set of rotational constants $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, as well as the accurate prediction of the remaining microwave lines.

III. HYPERFINE ANALYSIS

Each of the rotational transitions of $H_2{}^{17}O$ is split into a number of components because of the interaction of the quadrupole moment of the ^{17}O nucleus and the gradient of the molecular electric field. Under the assumption that the difference between the equilibrium hyperfine constants and the hyperfine constants of the ground vibrational state is small, the quadrupole eQq_J and spin–rotation C constants are related to the fundamental molecular tensors $\mathbf{V}$ and $\mathbf{\Lambda}$ by

$$q_J = \frac{2}{(J+1)(2J+3)} \sum_g V_{gg} \langle P_g{}^2 \rangle, \qquad (2)$$

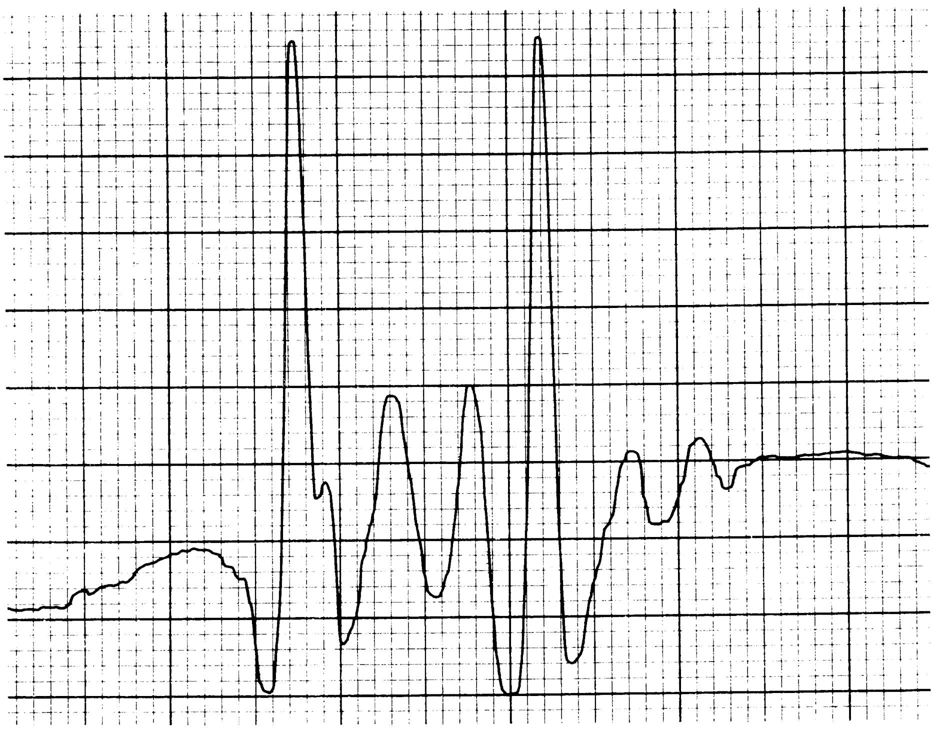

FIG. 1. Observed hyperfine structure of the 3_{13}–2_{20} transition of $H_2{}^{17}O$.

$$C = g_I \frac{1}{J(J+1)} \sum_g A_{gg} B_g \langle P_g{}^2 \rangle, \tag{3}$$

where g refers to the principal axes of the moment of inertia tensor, P_g is the component

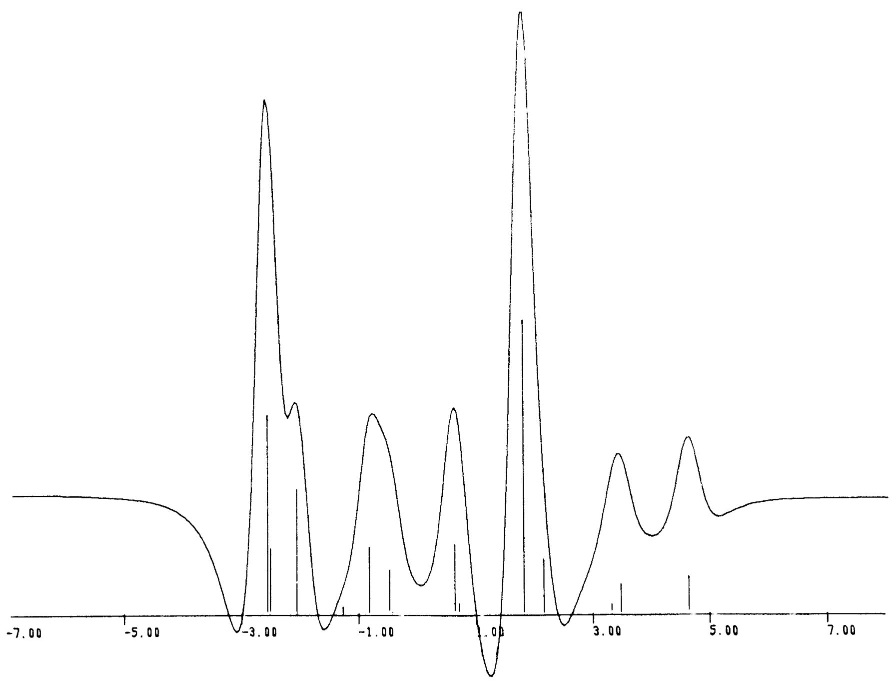

FIG. 2. Theoretical hyperfine structure of the 3_{13}–2_{20} transition of $H_2{}^{17}O$. Units are in MHz.

Table II. Observed Microwave Spectrum of $H_2{}^{17}O$ (MHz).

Transition ($F' \leftarrow F$)	Observed	Calculated	Obs-Cal
$1_{10} \leftarrow 1_{01}$	552020.960	552020.765	0.195
$2_{11} \leftarrow 2_{02}$	748458.254	748458.368	-0.114
$3_{13} \leftarrow 2_{20}$			
9/2 ← 7/2 7/2 ← 7/2	193999.796	193999.790	0.006
7/2 ← 5/2	194000.310	194000.274	0.036
5/2 ← 5/2 9/2 ← 9/2	194001.675	194001.656	0.019
5/2 ← 3/2	194002.998	194002.981	0.017
11/2 ← 9/2 3/2 ← 3/2	194004.172	194004.151	0.021
3/2 ← 1/2	194005.835	194005.815	0.020
1/2 ← 1/2	194007.002	194006.987	0.015
$4_{14} \leftarrow 3_{21}$			
lower	385784.860	385785.234	-0.374
upper	385788.189	385788.326	-0.137
$4_{23} \leftarrow 3_{30}$			
lower	469808.134	469808.170	-0.036
upper	469811.064	469811.045	0.019
$5_{15} \leftarrow 4_{22}$			
lower	323825.089	323824.944	0.145
upper	323827.873	323827.748	0.125
$6_{16} \leftarrow 5_{23}$ [a]			
13/2 ← 11/2	13533.79	13533.83	-0.04
15/2 ← 13/2 11/2 ← 9/2	13534.41	13534.50	-0.09
9/2 ← 7/2	13536.02	13536.10	-0.08
17/2 ← 15/2	13537.06	13537.09	-0.03
7/2 ← 5/2	13537.97	13538.00	-0.03

[a] Ref. 2.

of the rotational angular momentum along the g axis, B_g is the rotational constant for the g-axis, and g_I is the nuclear g factor. The products $g_I \Lambda_{gg} B_g$ are the diagonal elements of the spin–rotation tensor C_{gg}.

A precise molecular beam maser measurement of the hyperfine structure of the 2_{20}–2_{21} transition of $HD^{17}O$ has resulted in accurate values of $(eQq_J)_{^{17}O}$ and $(C)_{^{17}O}$ for these states (*9*). Because of the molecular symmetry of the ^{17}O site, only the diagonal elements of **V** and **Λ** are nonzero. Although the Λ_{ii} cannot be calculated from these data, the V_{ii} can be by the inclusion of the Laplace condition $\Sigma V_{ii} = 0$.

Since the contribution of the spin–rotation interaction is small for most of the transitions reported here, Eq. (2) and the V_{ii} of (*9*) make possible a good approximation to most of the hyperfine structure observed in this work. However, an analysis of the extensive hyperfine structure of the 3_{13}–2_{20} transition requires a consideration of spin–rotation effects. The hyperfine constants which result from this analysis are shown in Table I and the spectrum calculated from these constants is compared to the experimental spectrum in Figs. 1 and 2. These hyperfine constants can be combined with those of (*9*) to calculate both the V_{ii} and Λ_{ii} which are also shown in Table I. These elements of the molecular tensors will reproduce the hyperfine constants of both experiments to within their quoted error limits.

Table III. Rotational Constants of $H_2{}^{17}O$ (MHz).

$A = 830282.838 \pm 8.7$[a,b]	$B = 435341.662 \pm 8.0$	$C = 277510.396 \pm 8.0$
$\Delta_J = 37.44401$[c]	$\Delta_{JK} = -171.5584$	$\Delta_K = 965.7665 \pm 2.3$
$\delta_J = 15.22675$	$\delta_K = 36.2566$	
$H_J = 1.48878 \times 10^{-2}$	$H_{JK} = -2.10405 \times 10^{-2}$	$H_{KJ} = -4.81054 \times 10^{-1}$
$H_K = 4.409069 \times 10^{0}$	$h_J = 7.844745 \times 10^{-3}$	$h_{JK} = -2.11625 \times 10^{-2}$
	$h_K = 5.4855 \times 10^{-1}$	
$L_{JK} = 1.53235 \times 10^{-3}$	$L_{KKJ} = 5.1476 \times 10^{-3}$	$L_K = -5.966754 \times 10^{-2}$
	$l_K = 4.982 \times 10^{-3}$	
$P_K = 7.50542 \times 10^{-4}$	$p_K = 1.88015 \times 10^{-5}$	

a. Errors quoted are twice the statistical standard deviation and reflect uncertainties in and correlations among the distortion constants calculated from $H_2{}^{16}O$ and $H_2{}^{18}O$ data.

b. The number of places quoted are required to reproduce the observed microwave lines. Because of the correlation among the distortion constants this number can be substantially larger than the uncertainty for many of the higher order constants.

c. All distortion constants except Δ_K are calculated from $H_2{}^{16}O$ and $H_2{}^{18}O$ data.

IV. ROTATIONAL ANALYSIS

It has been shown that it is possible to characterize the spectra of light asymmetric rotors to within the expected experimental uncertainty of microwave measurements (~0.1 MHz) (*10, 11*) by use of Watson's formulation (*12, 13, 14*) of a reduced centrifugal distortion Hamiltonian. For $H_2{}^{16}O$ this Hamiltonian has the form

$$\mathcal{H} = \mathcal{H}_r + \mathcal{H}_d^{(4)} + \mathcal{H}_d^{(6)} + \mathcal{H}_d^{(8)} + \mathcal{H}_d^{(10)}, \tag{4}$$

$$\mathcal{H}_r = \tfrac{1}{2}(\mathcal{B} + \mathcal{C})P^2 + [\mathcal{A} - \tfrac{1}{2}(\mathcal{B} + \mathcal{C})](P_z^2 - b_p P_-^2), \tag{4a}$$

$$\mathcal{H}_d^{(4)} = -\Delta_J P^4 - \Delta_{JK} P^2 P_z^2 - \Delta_K P_z^4 - 2\delta_J P^2 P_-^2 - \delta_K (P_z^2 P_-^2 + P_-^2 P_z^2), \tag{4b}$$

$$\mathcal{H}_d^{(6)} = H_J P^6 + H_{JK} P^4 P_z^2 + H_{KJ} P^2 P_z^4 + H_K P_z^6 + 2h_J P^4 P_-^2 + h_{JK} P^2 (P_z^2 P_-^2 + P_-^2 P_z^2) + h_K (P_z^4 P_-^2 + P_-^2 P_z^4), \tag{4c}$$

$$\mathcal{H}_d^{(8)} = L_{JK} P^4 P_z^4 + L_{KKJ} P^2 P_z^6 + L_K P_z^8 + l_K (P_z^6 P_-^2 + P_-^2 P_z^6), \tag{4d}$$

$$\mathcal{H}_d^{(10)} = P_K P_z^{10} + p_K (P_z^8 P_-^2 + P_-^2 P_z^8), \tag{4e}$$

where $P^2 = (P_x^2 + P_y^2 + P_z^2)$, $P_-^2 = (P_x^2 - P_y^2)$, and $b_p = (\mathcal{C} - \mathcal{B})/(2\mathcal{A} - \mathcal{B} - \mathcal{C})$ is Wang's asymmetry parameter appropriate for a prolate top. A similar Hamiltonian is appropriate for $H_2{}^{18}O$. For both of these species, the number of adjustable parameters exceeds the number of observed microwave transitions. As a result, the rather extensive body of infrared data for these species was used in a weighted least-squares analysis with the microwave data (*4, 5*).

The infrared work on $H_2{}^{17}O$ is significantly less extensive and other techniques are required. Although the observed microwave transition frequencies of particular transitions of $H_2{}^{16}O$ and $H_2{}^{18}O$ differ by as much as 100 GHz, the distortion constants of the two species are very similar. In many cases the difference between the constants is sufficiently small that their uncertainties overlap. Since the different data sets which were used in the two analyses resulted in the inclusion of somewhat different Hamiltonian terms and since these terms are highly correlated, the similarity between the distortion in the two species is probably even greater than indicated by this comparison. Therefore, all or most of the distortion parameters can be fixed at the average of their values for the $H_2{}^{16}O$ and $H_1{}^{18}O$ species.

Table II shows the measured frequencies of the $H_2{}^{17}O$ microwave transitions. Extensive hyperfine structure was resolved for the 3_{13}–2_{20} and 6_{16}–5_{23} transitions, three of the other *R*-branch transitions were observed as doublets, and the *Q*-branch transitions were observed as unresolved singlets. Unsplit rotational frequencies were calculated for the multiplet transitions by the subtraction of the hyperfine contributions from the observed frequencies. It was found that these frequencies could be fit to within the expected uncertainties of the microwave measurements by use of the Hamiltonian of Eq. (4) with Δ_K and $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ as adjustable parameters. The remaining parameters were fixed at the values calculated from our earlier analyses of $H_2{}^{16}O$ and $H_2{}^{18}O$. These parameters are shown in Table III. Since the values of these constants depend upon the distortion constants of $H_2{}^{16}O$ and $H_2{}^{18}O$, the uncertainty in these constants can be no smaller than the uncertainty in the corresponding constants of $H_2{}^{16}O$ and $H_2{}^{18}O$. Since the rotation–distortion parameters of $H_2{}^{18}O$ are somewhat less certain than those of $H_2{}^{16}O$, the uncertainties in the $H_2{}^{17}O$ parameters are taken to be those of $H_2{}^{18}O$.

The rotational constants $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$ of the Watson formulation contain contributions from the distortion term R_6 and thereby differ from the A, B, C of Kivelson and Wilson (*15*). Similarly, the A, B, C of Kivelson and Wilson contain contributions from other distortion terms. The removal of these contributions results in A', B', C' which are simply related to the moments of inertia by $I_a = h/8\,\pi^2\,A'$, etc. The relations among these constants are discussed in (*16*) and Table IV shows their values for $H_2{}^{17}O$.

V. ENERGY LEVELS

Because of the large number of resolvable lines in the infrared spectra of light asymmetric molecules, their energy levels are usually constructed by a bootstrap technique which builds upon the ground state by use of measured energy differences. This approach is not possible for $H_2{}^{17}O$ because of the small number of infrared measurements reported

Table IV. Rotational Constants of $H_2{}^{17}O$ (MHz).

A: B: C:	830282.8	435341.7	277510.4
A: B: C:	830338.4	435146.5	277650.1
A':B':C'	830273.6	435081.7	277747.3

Table V. Energy Levels of $H_2{}^{17}O$ (cm^{-1}).

1_{01}	23.773	5_{05}	324.658	7_{07}	584.941
1_{11}	36.931	5_{15}	325.878	7_{17}	585.162
1_{10}	42.187	5_{14}	398.877	7_{16}	702.888
2_{02}	70.004	5_{24}	415.126	7_{26}	708.022
2_{12}	79.226	5_{23}	445.792	7_{25}	781.381
2_{11}	94.970	5_{33}	502.179	7_{35}	814.616
2_{21}	134.144	5_{32}	507.174	7_{34}	840.868
2_{20}	135.430	5_{42}	607.165	7_{44}	924.647
3_{03}	136.536	5_{41}	607.403	7_{43}	928.301
3_{13}	141.901	5_{51}	737.629	7_{53}	1055.082
3_{12}	173.109	5_{50}	737.632	7_{52}	1055.283
3_{22}	205.479	6_{06}	445.717	8_{08}	742.401
3_{21}	211.434	6_{16}	446.243	8_{18}	742.494
3_{31}	283.559	6_{15}	541.996	8_{17}	881.108
3_{30}	283.765	6_{25}	551.610	8_{27}	883.664
4_{04}	221.618	6_{24}	601.961	8_{26}	981.504
4_{14}	224.302	6_{34}	647.074	8_{36}	1003.791
4_{13}	275.128	6_{33}	659.988	8_{35}	1048.662
4_{23}	299.436	6_{43}	753.712	8_{45}	1119.484
4_{22}	315.076	6_{42}	754.819	8_{44}	1128.935
4_{32}	380.804	6_{52}	884.104	8_{54}	1250.505
4_{31}	382.174	6_{51}	884.140	8_{53}	1251.298
4_{41}	485.209	6_{61}	1038.934		
4_{40}	485.237	6_{60}	1038.934		

in the literature. On the other hand, use of a theoretical model makes possible the introduction of information from other isotopic species and the analysis discussed above. The spectral constants which result from this analysis make possible the calculation of the set of energy levels shown in Table V.

One test of the accuracy of these energy levels is a comparison of them with combination difference energies calculated from the $H_2{}^{17}O$ lines which were observed by Fraley, Rao, and Jones (*6*) and by Williamson and Rao (*7*). With the exception of a small number of combination differences, the agreement is excellent and comparable with the experimental uncertainty of the infrared data ($\sim$0.01 cm^{-1}). Most of these exceptions can be shown to be internally inconsistent with the other $H_2{}^{17}O$ combination differences. In addition, there is no systematic deterioration in the agreement between the energy levels of Table V and the infrared combination differences over the range of J_τ states covered by the combination differences. These results indicate that the uncertainties in the $H_2{}^{17}O$ energy levels are similar to those derived for $H_2{}^{16}O$ (*17*) and $H_2{}^{18}O$ (*6, 7*). Since the accuracy of these levels depends upon the information contents transferred to the $H_2{}^{17}O$ analysis from $H_2{}^{16}O$ and $H_2{}^{18}O$ analyses in the form of distortion constants, Table V includes only those energy levels for which the corresponding levels in $H_2{}^{16}O$ and $H_2{}^{18}O$ are well established.

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