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The Higher K_{-1} States of Hydrogen Peroxide*

We previously reported (*1*) the spectrum of hydrogen peroxide between 80 and 700 GHz that originates from transitions between the $K_{-1} = 0$, 1, and 2 levels of $\tau = 1$, 2 and the $K = 0$ and 1 levels of $\tau = 3$, 4. We have also discussed the analysis of this spectrum to microwave accuracy (~0.1 MHz) by means of a centrifugal distortion Hamiltonian in which the only effect of the molecular internal rotation is the ~11-cm^{-1} splitting between the $\tau = 1$, 2 and $\tau = 3$, 4 levels. Because the data set was limited to low K_{-1}, it was not possible to calculate Δ_K, and in our analysis Δ_K was fixed to an earlier value derived from infrared studies. Since Δ_K is highly correlated with the A rotational constant and W, the torsional splitting, inaccuracies in Δ_K severely affect the values of the other two constants and make predicted line frequencies at higher values of K_{-1} much less accurate.

Higher-K_{-1} transitions are observable in the 80- to 700-GHz region, but because they are high J, relatively weak, and mixed with a dense background of lines that originate in low-lying excited torsional states, they are difficult to assign. However, we have assigned and analyzed an excellent fir Fourier transform spectrum of hydrogen peroxide provided to us by Dr. Kelley Chance of the Harvard–Smithsonian Astrophysical Observatory. The results of this analysis, combined with our earlier millimeter and submillimeter work, have made it possible to measure extensive new higher-K_{-1} data in the millimeter and submillimeter spectral range. We have now measured 101 new lines that, added to our original data set, give a total of 284 new lines in the 80- to 700-GHz region and include $K_{-1} = 0$, 1, 2, 3, 4 of $\tau = 1$, 2 and $K = 0$, 1, 2, 3 of $\tau = 3$, 4. We have performed an analysis similar to that of our earlier work.

We previously described both the experimental and theoretical techniques used for our analysis of hydrogen peroxide, and interested readers are referred to Ref. (*1*) for details. Table I shows our new data, and Fig. 1 displays the total data set in the form of a FORTRAT diagram. It can be seen that our new data are $\Delta J = \pm 1$ and that the branches originate in the terahertz region.

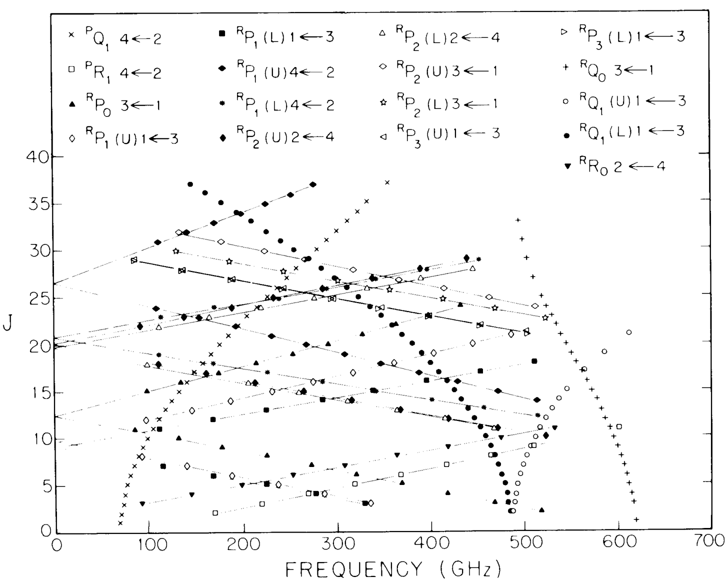

FIG. 1. FORTRAT diagram of the observed branches of HOOH.

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TABLE I

New Observed Transitions of HOOH (MHz)

R_{P_2} (Upper) Branch Transitions

Transition $\tau = 2$		$\tau = 4$	Frequency Observed
9_{37}	←	10_{29}	524 038.11
10_{38}	←	11_{210}	472 527.24
11_{39}	←	12_{211}	421 037.05
12_{310}	←	13_{212}	369 576.78
13_{311}	←	14_{213}	318 156.12
14_{312}	←	15_{214}	266 785.43
15_{313}	←	16_{215}	215 475.52
16_{314}	←	17_{216}	164 237.48
17_{315}	←	18_{217}	113 082.96
18_{316}	←	19_{218}	(62 024.01)[a]
19_{317}	←	20_{219}	(11 072.81)
20_{318}	→	21_{220}	(39 757.85)
21_{319}	→	22_{221}	90 455.10
22_{320}	→	23_{222}	141 005.86
23_{321}	→	24_{223}	191 396.73
24_{322}	→	25_{224}	241 614.15
25_{323}	→	26_{225}	291 644.55
26_{324}	→	27_{226}	341 474.11
27_{325}	→	28_{227}	391 089.33
28_{326}	→	29_{228}	440 476.17
29_{327}	→	30_{229}	489 620.96

R_{P_2} (Lower) Branch Transitions

Transition $\tau = 2$		$\tau = 4$	Frequency Observed
10_{37}	←	11_{29}	470 905.39
11_{38}	←	12_{210}	418 770.2
12_{39}	←	13_{211}	366 491.74
13_{310}	←	14_{212}	314 052.03
14_{311}	←	15_{213}	261 432.50
15_{312}	←	16_{214}	208 613.57
16_{313}	←	17_{215}	155 574.84
17_{314}	←	18_{216}	102 29[illegible].56
18_{315}	←	19_{217}	(48 7[illegible]4.89)
19_{316}	→	20_{218}	(5 068.35)
20_{317}	→	21_{219}	(59 194.63)
21_{318}	→	22_{220}	113 643.81
22_{319}	→	23_{221}	168 434.74
23_{320}	→	24_{222}	223 584.84
24_{321}	→	25_{223}	279 109.87
25_{322}	→	26_{224}	335 023.22
26_{323}	→	27_{225}	391 335.90
27_{324}	→	28_{226}	448 056.02

R_{P_1} (Upper) Branch Transitions

Transition $\tau = 4$		$\tau = 2$	Frequency Observed
12_{211}	←	13_{113}	555 548.40
13_{212}	←	14_{114}	512 539.44
14_{213}	←	15_{115}	470 178.32
15_{214}	←	16_{116}	428 474.90
16_{215}	←	17_{117}	387 438.99
17_{216}	←	18_{118}	347 080.11
18_{217}	←	19_{119}	307 408.36
19_{218}	←	20_{120}	268 434.20
20_{219}	←	21_{121}	230 167.83
21_{220}	←	22_{122}	192 619.92
22_{221}	←	23_{123}	155 801.25
23_{222}	←	24_{124}	119 722.49
24_{223}	←	25_{125}	(84 394.50)
25_{224}	←	26_{126}	(49 828.12)
26_{225}	←	27_{127}	(16 034.22)
27_{226}	→	28_{128}	(16 976.47)
28_{227}	→	29_{129}	(49 193.19)
29_{228}	→	30_{130}	(80 605.36)
30_{229}	→	31_{131}	111 202.63
31_{230}	→	32_{132}	140 974.77
32_{231}	→	33_{133}	169 911.59
33_{232}	→	34_{134}	198 003.20
34_{233}	→	35_{135}	225 240.10
35_{234}	→	36_{136}	251 612.75
36_{235}	→	37_{137}	277 112.13

R_{P_1} (Lower) Branch Transitions

Transition $\tau = 4$		$\tau = 2$	Frequency Observed
11_{29}	←	12_{111}	516 987.60
12_{210}	←	13_{112}	460 020.87
13_{211}	←	14_{113}	402 798.92
14_{212}	←	15_{114}	345 361.11
15_{213}	←	16_{115}	287 749.51
16_{214}	←	17_{116}	230 008.34
17_{215}	←	18_{117}	172 184.47
18_{216}	←	19_{118}	114 326.92
19_{217}	←	20_{119}	(56 486.84)
20_{218}	→	21_{120}	(1 282.57)
21_{219}	→	22_{121}	(58 926.70)
22_{220}	→	23_{122}	116 389.45
23_{221}	→	24_{123}	173 613.44
24_{222}	→	25_{124}	230 540.37
25_{223}	→	26_{125}	287 111.42
26_{224}	→	27_{126}	343 267.38
27_{225}	→	28_{127}	398 948.70
28_{226}	→	29_{128}	454 096.56

R_{P_2} (Upper) Branch Transitions

Transition $\tau = 3$		$\tau = 1$	Frequency Observed
23_{321}	←	24_{223}	510 225.92
24_{322}	←	25_{224}	461 893.54
25_{323}	←	26_{225}	413 861.31
26_{324}	←	27_{226}	366 148.00
27_{325}	←	28_{227}	318 772.89
28_{326}	←	29_{228}	271 755.29
29_{327}	←	30_{229}	225 115.02
30_{328}	←	31_{230}	178 872.17
31_{329}	←	32_{231}	133 047.01

R_{P_3} (Upper) Branch Transitions

Transition $\tau = 1$		$\tau = 3$	Frequency Observed
20_{417}	←	21_{319}	505 478.08
21_{418}	←	22_{320}	453 390.22
22_{419}	←	23_{321}	401 269.50
23_{420}	←	24_{322}	349 116.63
24_{421}	←	25_{323}	296 932.33
25_{422}	←	26_{324}	244 717.54
26_{423}	←	27_{325}	192 473.45
27_{424}	←	28_{326}	140 201.53
28_{425}	←	29_{327}	87 903.39

R_{P_2} (Lower) Branch Transitions

Transition $\tau = 3$		$\tau = 1$	Frequency Observed
22_{319}	←	23_{221}	523 378.52
23_{320}	←	24_{222}	468 587.22
24_{321}	←	25_{223}	413 361.72
25_{322}	←	26_{224}	357 684.42
26_{323}	←	27_{225}	301 540.89
27_{324}	←	28_{226}	244 920.57
28_{325}	←	29_{227}	187 816.91
29_{326}	←	30_{228}	130 227.97

R_{P_3} (Lower) Branch Transitions

Transition $\tau = 1$		$\tau = 3$	Frequency Observed
20_{416}	←	21_{318}	505 076.43
21_{417}	←	22_{319}	452 862.14
22_{418}	←	23_{320}	400 583.84
23_{419}	←	24_{321}	348 236.10
24_{420}	←	25_{322}	295 813.29
25_{421}	←	26_{323}	243 308.95
26_{422}	←	27_{324}	190 715.82
27_{423}	←	28_{325}	138 026.29

[a] Numbers in parenthesis are calculated from the constants of Table II.

TABLE II

Rotational Constants (MHz)

	$\tau = 1, 2$		$\tau = 3, 4$	
	value	σ	value	σ
A	301 874.205	0.037	301 586.074	0.075
B	26 212.439	0.046	26 155.639	0.036
C	25 098.604	0.046	25 186.461	0.036
Δ_J $(\cdot 10^0)$	0.105292	0.0000029	0.0996169	0.000014
Δ_{JK} $(\cdot 10^{-1})$	0.112180	0.000026	0.115275	0.000051
Δ_K $(\cdot 10^{-2})$	0.120340	0.00012	0.118558	0.00023
δ_J $(\cdot 10^3)$	-0.258456	0.0014	0.686780	0.0012
δ_K $(\cdot 10^{-1})$	0.978631	0.0027	0.638326	0.00021
H_{JK} $(\cdot 10^3)$	0.506307	0.0097	0.0594176	0.0013
H_{KJ} $(\cdot 10^2)$	-0.161735	0.0087	-0.0506399	0.0073
H_K $(\cdot 10^2)$	0.185268	0.097	-----	
h_J $(\cdot 10^7)$	0.304918	0.022	-0.515225	0.011
h_{JK} $(\cdot 10^3)$	0.172789	0.00090	0.129727	0.0011
h_K $(\cdot 10^1)$	0.440464	0.038	-0.631712	0.0028
L_{JJK} $(\cdot 10^7)$	-0.159961	0.0045	-0.105713	0.0071
L_{JK} $(\cdot 10^5)$	-0.933110	0.051	0.829787	0.0077
L_{KKJ} $(\cdot 10^4)$	0.218515	0.038	-----	
rms	0.126		0.112	
number of data points	119		141	
W		342 881.62		

The analysis of hydrogen peroxide is complex because of the effects of the torsional motion. This motion splits the ground vibrational state into two pairs of sublevels, $\tau = 1, 2$ and $\tau = 3, 4$, and gives the selection rules, $\tau = 1 \leftrightarrow 3$ and $\tau = 2 \leftrightarrow 4$, in addition to the usual asymmetric rotor restrictions. As before, we analyze the lower $\tau = 1, 2$ levels by means of combination differences connected in the $\tau = 3, 4$ state. We assume that the rotational constants in $\tau = 1$ and $\tau = 2$ are the same and find that the 119 distinct combination differences can be analyzed with an rms deviation of 0.13 MHz. The values of the constants that result from this analysis are shown in Table II. Fewer combination differences exist in $\tau = 3, 4$, so we supplement these data. Additional energy levels in $\tau = 3, 4$ are calculated from combination of the energy levels produced by the $\tau = 1, 2$ analysis with measured transition frequencies between $\tau = 1, 2$ and $\tau = 3, 4$. We are careful to use only $\tau = 1, 2$ states that we believe to be well established. The effect of this procedure is that some lines at high J (>30) are not used in the analysis because they were not part of the $\tau = 1, 2$ analysis and that these transitions may not be reproduced to microwave accuracy. While it would be possible to include them in the analysis, we feel that this is undesirable because the $\tau = 3, 4$ analysis would have to readjust its constants to cancel extrapolation errors in the $\tau = 1, 2$ analysis. The results of the $\tau = 3, 4$ analysis are also shown in Table II.

With our new measurements the characterization of the rotational–torsional spectrum of the $\tau = 1, 2, 3, 4$ states of hydrogen peroxide in the spectral region below 700 GHz is virtually complete. Most transitions between thermally populated energy levels have been directly measured and those that have not (these are mostly low-frequency lines below 100 GHz) can be calculated from our centrifugal distortion analysis with high accuracy. This work also impacts work in both the fir and ir spectral regions. In the fir the results of our analysis of microwave data predict the higher-K_{-1} data of the fir to the accuracy of those data. These analyses also provide strong ground state constraints and starting points for several very interesting (*2*, *3*) analyses of ir data now in progress.

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