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Centrifugal Distortion Analysis of the Ground Vibrational States of $H_2{}^{17}O$ and $H_2{}^{18}O$[1]

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Centrifugal distortion analyses of combined infrared-microwave data sets for $H_2{}^{17}O$ and $H_2{}^{18}O$ have been performed. These analyses make possible critical evaluation of data points and results in substantially improved energy levels. The Fraley-Rao interpolation rule for the prediction of $H_2{}^{17}O$ energy levels is examined and extended.

INTRODUCTION

Several years ago we published centrifugal distortion analyses for a number of isotopic species of water. Except for the $H_2{}^{16}O$ (*1*), $H_2{}^{17}O$ (*2*), and $H_2{}^{18}O$ (*3*) species these were based entirely upon microwave data. Because for these species it was not possible to measure enough microwave lines, it was necessary to include infrared data in our calculations. Although at the time of our analyses extensive $H_2{}^{16}O$ infrared data was available, only a modest amount of $H_2{}^{18}O$ data (*4, 5*) and virtually no $H_2{}^{17}O$ data had been published. In this paper we report new analyses of $H_2{}^{17}O$ and $H_2{}^{18}O$ that include substantial amounts of new infrared data in addition to our earlier microwave data.

Because a centrifugal distortion analysis has substantially fewer degrees of freedom than a purely algebraic combination difference analysis and because the former are more sensitive to "bad" data points which can be eliminated,[3] more accurate and reliable energy levels can be obtained. In addition, the independent analyses of the three isotopic species make possible a critical evaluation and refinement of the Fraley-Rao interpolation rule for the prediction of $H_2{}^{17}O$ energy levels.

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[2] Travel to Duke University supported by Southern Regional Educational Board.

[3] For an enlightening discussion of a mathematician's view on the rejection of data, see F. J. Anscombe and J. W. Tukey, Technometrics 5, 141 (1963).

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$H_2{}^{17}O$ ANALYSIS

We have combined 46 of the far-infrared lines reported by Winther (*6*), 31 combination differences calculated from the data of Toth *et al.* (*8*), 20 combination differences calculated from the data of Camy-Peyret *et al.* (*9*), and our seven microwave lines (*2*) in a weighted Watson analysis.[4] The assigned weights were inversely proportional to the square of the expected uncertainty and ranged from 10^7 for the microwave lines to one for Winther's weakest lines. In order to carefully screen the data, each of the 104 data points was removed (in groups) from the analysis and predicted on the basis of the remaining data. With the exception of a few lines at high J_τ, the uncertainty in each of the predictions was $< \pm 0.01$ cm^{-1} and most were much better. For all the lines contained in the data set, the agreement between the calculated uncertainty in the prediction and the expected experimental uncertainty was satisfactory except for the data points listed in Table I. While only one of these data points is dramatically bad (the rest are off by about 0.05 cm^{-1}), they are all substantially worse than the data retained in the analysis. The spectral constants which result from our analysis are shown in Table II and the energy levels calculated from them in Table III. Four places are retained in the energy levels because it has been found that the analyses successfully predict unanalyzed microwave lines to this accuracy.

$H_2{}^{16}O$ AND $H_2{}^{18}O$ ANALYSES

The $H_2{}^{18}O$ energy levels shown in Table III result from an analysis very similar to the $H_2{}^{17}O$ analysis discussed above except that each of the data subsets is larger and a total of 240 data points were analyzed. At the highest J_τ it was not possible to establish with certainty the reliability of the infrared data points because of the scattered nature of the data. However, at lower J_τ the deviations of several points from the fit were inconsistent with their assigned weights and they were eliminated from the fit. These are shown in Table IV.

The $H_2{}^{16}O$ energy levels listed in Table III are those which result from the original analysis (*1*) of 15 microwave lines and the infrared data available to us at that time.

TABLE I

Data Points Removed from $H_2{}^{17}O$ Analysis

Levels	Obs-Calc (cm^{-1})	Ref.
$5_{32} - 5_{23}$	0.054	6
$4_{23} - 4_{14}$	0.049	6
$5_{41} - 6_{43}$	-0.567	9[a]

[a] The reassignment by Winther (Ref. 6) of one of the transitions of Ref. 9 which leads to the $6_{16} - 8_{18}$ combination difference seems to be correct and is included in our analysis.

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[4] For a detailed discussion of our analysis technique, see Ref. (*1*)

TABLE II

Rotation and Distortion Constants of the Ground Vibrational State of Water (MHz)

Constant	$H_2{}^{16}O$		$H_2{}^{17}O$		$H_2{}^{18}O$	
	Value[a]	σ	Value[a]	σ	Value[a]	σ
a	835 840.288	0.50	830 282.791	1.6	825 366.844	1.0
b	435 351.717	0.45	435 357.289	2.6	435 356.685	0.8
c	278 138.700	0.45	277 505.735	2.6	276 948.998	0.8
Δ_J	37.59422	0.02	37.59414	0.09	37.54579	0.017
Δ_{JK}	-172.9128	0.17	-171.8532	0.3	-171.1683	0.13
Δ_K	973.29052	0.10	960.46634	0.5	949.88229	0.2
δ_J	15.21040	0.010	15.34663	0.04	15.23181	0.011
δ_K	41.0502	0.15	41.4538	1.2	38.8850	0.2
$H_J \cdot (10^2)$	1.56556	0.020	1.82110	0.12	1.53906	0.019
$H_{JK} \cdot (10^2)$	-4.2081	0.6			-3.1738	0.4
$H_{KJ} \cdot (10^1)$	-5.09508	0.10	-6.42468	2.6	-5.21898	0.12
$H_K \cdot (10^0)$	3.733028	0.008	3.745123	0.06	3.624767	0.017
$h_J \cdot (10^3)$	7.79579	0.09	10.18803	0.6	8.04641	0.14
$h_{JK} \cdot (10^2)$	-2.5165	0.11	3.7859	2.4	-2.4187	0.25
$h_K \cdot (10^0)$	1.0971	0.03	1.1495	0.13	1.0488	0.04
$L_{JK} \cdot (10^3)$	-3.0647	0.46			-4.6449	0.6
$L_{KKJ} \cdot (10^2)$	1.02952	0.12			1.46700	0.16
$L_K \cdot (10^2)$	-2.340138	0.08	-1.517327	0.17	-2.617359	0.11
$\ell_J \cdot (10^6)$					-2.59	0.8
$\ell_{JK} \cdot (10^4)$			-4.257	2.6		
$\ell_K \cdot (10^2)$	-1.3546	0.10	-0.326	0.2	-1.32008	0.13
$P_K \cdot (10^5)$	5.19841	0.07	4.71660	1.5	5.72244	0.4
$p_K \cdot (10^5)$	3.7603	1.0				

[a] The large number of digits retained in the higher order constants is required in order to reproduce the energy levels to experimental uncertainty.

More recent energy levels *(10)*, based upon the high resolution experimental data of Guelachvili (and apparently upon our microwave data, too), result in essentially the same energy levels over the J_τ range of the original analysis.

FRALEY-RAO INTERPOLATION RULE

The Fraley-Rao *(4)* interpolation rule can be stated as

$$\frac{\nu_{17} - \nu_{16}}{\nu_{18} - \nu_{16}} = k \tag{1}$$

Table V shows the result of the application of this rule to the observed microwave transitions of $H_2{}^{17}O$. It is obvious that large deviations exist. A similar effect has been observed for microwave transitions of D_2O *(11)*. However, critical inspection of the

TABLE III

Energy Levels of the Ground Vibrational States of Water (cm^{-1})

	$H_2{}^{16}O$	$H_2{}^{17}O$	$H_2{}^{18}O$
1_{01}	23.7945	23.7735	23.7550
1_{11}	37.1372	36.9311	36.7487
1_{10}	42.3718	42.1870	42.0235
2_{02}	70.0911	70.0047	69.9276
2_{12}	79.4965	79.2273	78.9887
2_{11}	95.1762	94.9706	94.7888
2_{21}	134.9019	134.1453	133.4759
2_{20}	136.1642	135.4312	134.7833
3_{03}	136.7622	136.5378	136.3369
3_{13}	142.2788	141.9024	141.5682
3_{12}	173.3665	173.1102	172.8832
3_{22}	206.3019	205.4820	204.7561
3_{21}	212.1568	211.4359	210.7995
3_{31}	285.2199	283.5615	282.0950
3_{30}	285.4191	283.7677	282.3075
4_{04}	222.0536	221.6212	221.2344
4_{14}	224.8388	224.3043	223.8288
4_{13}	275.4981	275.1305	274.8037
4_{23}	300.3628	299.4389	298.6206
4_{22}	315.7801	315.0786	314.4599
4_{32}	382.5177	380.8068	379.2924
4_{31}	383.8433	382.1772	380.7033
4_{41}	488.1083	485.2082	482.6445
4_{40}	488.1348	485.2361	482.6736
5_{05}	325.3489	324.6613	324.0472
5_{15}	326.6261	325.8803	325.2161
5_{14}	399.4591	398.8787	398.3612
5_{24}	416.2094	415.1269	414.1689
5_{23}	446.5114	445.7931	445.1591
5_{33}	503.9687	502.1802	500.5973
5_{32}	508.8127	507.1764	505.7298
5_{42}	610.1160	607.1629	604.5461
5_{41}	610.3428	607.4014	604.7948
5_{51}	742.0744	737.6190	733.6817
5_{50}	742.0777	737.6225	733.6854
6_{06}	446.6976	445.7193	444.8467
6_{16}	447.2531	446.2446	445.3467
6_{15}	542.9078	541.9946	541.1810
6_{25}	552.9121	551.6058	550.4519
6_{24}	602.7743	601.9598	601.2382
6_{34}	648.9786	647.0694	645.3837
6_{33}	661.5489	659.9894	658.6111
6_{43}	756.7262	753.7094	751.0354
6_{42}	757.7816	754.8182	752.1899
6_{52}	888.6029	884.0865	880.0806
6_{51}	888.6368	884.1228	880.1189
6_{61}	1045.0623	1038.7644	1033.1986
6_{60}	1045.0627	1038.7648	1033.1991
7_{07}	586.2446	584.9403	583.7782
7_{17}	586.4800	585.1610	583.9869
7_{16}	704.2166	702.8811	701.6952
7_{26}	709.6092	708.0092	706.5992
7_{25}	782.4110	781.3750	780.4530
7_{35}	816.6931	814.6007	812.7628
7_{34}	842.3560	840.8691	839.5505
7_{44}	927.7438	924.6402	921.8983
7_{43}	931.2371	928.3024	925.7023
7_{53}	1059.6510	1055.0641	1050.9958
7_{52}	1059.8398	1055.2667	1051.2086
7_{62}	1216.1996	1209.8270	1204.1766
7_{61}	1216.2043	1209.8322	1204.1821
7_{71}	1394.8190	1386.4179	1378.9899
7_{70}	1394.8191	1386.4179	1378.9899

TABLE III—*Continued*

	$H_2{}^{16}O$	$H_2{}^{17}O$	$H_2{}^{18}O$
8_{08}	744.0648	742.3976	740.9125
8_{18}	744.1636	742.4895	740.9989
8_{17}	882.8934	881.0929	879.4956
8_{27}	885.6017	883.6428	881.9156
8_{26}	982.9139	981.4921	980.2218
8_{36}	1006.1139	1003.7614	1001.7065
8_{35}	1050.1580	1048.6671	1047.3304
8_{45}	1122.7063	1119.4733	1116.6389
8_{44}	1131.7742	1128.9465	1126.4425
8_{54}	1255.1689	1250.4961	1246.3755
8_{53}	1255.9137	1251.2943	1247.2128
8_{63}	1411.6216	1405.1541	1399.4402
8_{62}	1411.6520	1405.1877	1399.4754
8_{72}	1590.7053	1582.1979	1574.6833
8_{71}	1590.7059	1582.1986	1574.6840
8_{81}	1789.0395	1778.2960	1768.8142
8_{80}	1789.0395	1778.2960	1768.8142

energy levels of Table III show that they obey the rule

$$\frac{E_{17} - E_{16}}{E_{18} - E_{16}} = k \tag{2}$$

where $k = 0.5307 \rightarrow 0.5275$. This results directly from

$$\frac{A_{17} - A_{16}}{A_{18} - A_{16}} = 0.5307 \qquad \text{and} \qquad \frac{C_{17} - C_{16}}{C_{18} - C_{16}} = 0.5275$$

with the change in rotational energy due to isotopic substitution given by

$$\Delta E = \frac{\partial E}{\partial A} \Delta A + \frac{\partial E}{\partial B} \Delta B + \frac{\partial E}{\partial C} \Delta C \tag{3}$$

and $\Delta B \approx 0$ for an on axis isotopic substitution. As a result at high K_{-1} where

TABLE IV

Data Points Removed from $H_2{}^{18}O$ Analysis

Levels	Obs-Calc (cm^{-1})	Ref.
$2_{20} - 1_{11}$	0.029	6
$5_{24} - 4_{13}$	0.040	6
$6_{33} - 5_{24}$	-0.049	6
$7_{44} - 7_{35}$	0.040	6
$8_{54} - 7_{25}$	-0.041	6
$8_{27} - 8_{18}$	0.042	6
$7_{25} - 6_{25}$	0.047	8
$6_{52} - 5_{50}$	-0.021	9
$7_{25} - 6_{25}$	-0.884	9
$8_{27} - 7_{25}$	0.883	9

TABLE V

Values of the Fraley-Rao Constant for Observed Microwave Transitions

Transition	k
$1_{10}-1_{01}$	0.530807
$2_{11}-2_{02}$	0.532543
$3_{13}-2_{20}$	0.532021
$4_{14}-3_{21}$	0.536887
$4_{23}-3_{30}$	0.531228
$5_{15}-4_{22}$	0.493528
$6_{16}-5_{23}$	0.523757

$\partial E/\partial A = \langle P_a^2\rangle$ is large and $\partial E/\partial C = \langle P_c^2\rangle$ is small, $k \approx 0.5307$. Conversely at low K_{-1}, $k \approx 0.5275$.

Equation (2) can be rewritten for transitions as

$$\frac{\nu_{17}-\nu_{16}}{\nu_{18}-\nu_{16}} = k^l + (k^u - k^l)\frac{E_{18}{}^u - E_{16}{}^u}{\nu_{18}-\nu_{16}} \tag{4}$$

where the superscripts refer to the upper and lower energy levels of the transition. The correction term is large in regions where the dominant terms of Eq. (3) are changing, especially for transitions whose frequency changes little upon isotopic substitution. The lines of Table V which show the greatest deviations from Eq. (1) are the same lines that Eq. (4) predicts to have these variations.

COMPARISON WITH OTHER ENERGY LEVELS AND CONCLUSIONS

Our original $H_2{}^{17}O$ analysis was based upon our measured microwave data and distortion constants calculated from the $H_2{}^{16}O$ and $H_2{}^{18}O$ analyses. A comparison between the energy levels which resulted from this and those of Table III show exceedingly close agreement (typically 0.002 cm^{-1}) up to the 5_{41} level. At higher J_τ the agreement is still good (typically 0.002 cm^{-1} at low K_{-1} up to 0.02 cm^{-1} at high K_{-1}) except for the 6_{61} and 6_{60} levels. These are lower by 0.17 cm^{-1} in our latest analysis. This is because our earlier analysis of $H_2{}^{18}O$ was perturbed by infrared energy levels for 6_{60} and 6_{61} which were high by 0.30 cm^{-1} compared to the $H_2{}^{18}O$

TABLE VI

Comparison of Observed Energy Levels with those Calculated from Eq. (2) (cm^{-1})

State	Observed	Calculated	Difference
1_{10}	42.1870	42.1870	0.0000
2_{20}	135.4312	135.4313	-0.0001
3_{30}	283.7677	283.7678	-0.0001
4_{40}	485.2361	485.2365	-0.0004
5_{50}	737.6225	737.6239	-0.0014
6_{60}	1038.7648	1038.7667	-0.0019
7_{70}	1386.4179	1386.4186	-0.0007
8_{80}	1778.2960	1778.3059	-0.0099

energy levels shown in Table III. For medium values of J_τ the energy levels of Refs. (*6*) and (*8*) differ from the levels of Table III by substantially more (typically 0.01 cm^{-1}) than do our earlier energy levels. The energy levels of Ref. (*6*), which extend to higher J_τ than those of Ref. (*8*), deteriorate somewhat relative to the values of Table III, but all agree to within 0.05 cm^{-1} or better.

It is to be expected that our latest analysis is better than previous analyses because it contains the earlier data sets as subsets and because our analysis technique makes possible rather sensitive tests for bad data points and substantially reduces the degrees of freedom. It is perhaps somewhat surprising that our earlier analysis was so good.

Since all of the energy levels of the three isotopes were calculated independently, one check of their accuracy and also of the accuracy of Eq. (2) can be accomplished by the use of the $H_2{}^{16}O$ and $H_2{}^{18}O$ energy levels in this equation to calculate the energy levels of $H_2{}^{17}O$. Since it is most difficult to get good energy levels at high K_{-1} and since the isotopic splittings of the energy levels are also greatest there, the most stringent test would be the J_{J0} levels. The close argument shown in Table VI between the energy levels calculated directly from the $H_2{}^{17}O$ data and the levels calculated via Eq. (2) confirms both the accuracy of this relation and the quality of the energy levels for all three species.

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Note added in proof. The problems in our earlier analysis of $H_2{}^{18}O$ have recently been attributed (J.-M. Flaud, C. Camy-Peyret, and R. A. Toth, *J. Mol. Spectrosc.* **65**, 219 (1977)) to the heavy weights assigned the microwave data in that analysis. In fact, as shown above, the errors in the literature of 0.30 cm^{-1} in the infrared energies of 6_{60} and 6_{61} perturbed several of the higher order distortion constants and some of the energy levels closely associated with 6_{60} and 6_{61}. All analyses reported in this paper contain heavily weighted microwave data, and, as demonstrated above, excellent agreement among the isotopes result. All checks of isotopic agreement were performed after each isotopic analysis was final, and no adjustments at subjective points in the data analysis were carried out with isotopic agreement as an objective.

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