Centrifugal Distortion Analysis of Pure Rotational Spectra of H₂¹⁶O, H₂¹⁷O, and H₂¹⁸O

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Centrifugal distortion analyses based entirely on high-quality infrared data are carried out for the ground vibrational states of $H_2^{16}O$, $H_2^{17}O$, and $H_2^{18}O$. As a result of the analyses, the values of 27 rotation and distortion constants for each species are determined. By using these constants it was possible to improve considerably the accuracy of the literature values for rotational energy levels at high J_r , especially for $H_2^{17}O$ and $H_2^{18}O$. The experimental values for the energy levels are deduced from the observed rotational transitions constituting the fitted data.

INTRODUCTION

Several papers dealing with the centrifugal distortion analysis of H_2O have been published during the recent years. For example, De Lucia *et al.* (1, 2), De Lucia and Helminger (3, 4), and Flaud *et al.* (5, 6) have been working on the subject. The accuracy and the scope of the infrared data in these studies have varied. The situation has been better, in this respect, for $H_2^{16}O$ than for $H_2^{18}O$ or especially for $H_2^{17}O$. On the other hand, H_2O microwave data are scant and, accordingly, a need for accurate infrared spectra is obvious in the distortion analysis of H_2O .

The quality of the available infrared data, particularly the data for $H_2^{17}O$ and $H_2^{18}O$, has been considerably improved by measuring the two spectra presented in Refs. (7) and (8). Actually, this paper is a consequence of the difficulties encountered in assigning the latter spectrum, where an isotopically enriched sample was used. It turned out to be necessary to refine the existing predictions for $H_2^{17}O$ and $H_2^{18}O$ frequencies at high J_{τ} , in order to successfully complete the assignment of the spectrum. To accomplish this, a least-squares analysis program was written. By means of this program the results of the present distortion analysis have been derived. The analysis is based entirely on the infrared data available in the two spectra mentioned above.

PROGRAM AND EXPERIMENTAL DATA

The program can fit 30 rotation and distortion constants to 400 data points. The maximum J value that can be used is 15. A double-precision accuracy (three 16-bit computer words or 12 figures) was adopted for every noninteger variable. By properly programming the necessary routines, the memory space occupied by the program could be reduced to 19 kwords, which is an essential fact because the program was written for the minicomputer (Hewlett-Packard 21MXE) connected on line to our Fourier spectrometer (9). The correctness of the pro-

gram code was tested by fitting "spectra" produced computationally by different values of the rotational constants included in the program. These computations also confirmed that our minicomputer is able to handle with sufficient accuracy the large and correlated models used in the model testing.

The H₂¹⁷O and H₂¹⁸O data were prepared from the spectrum of isotopically enriched water (8). For H₂¹⁶O, both this spectrum and the spectrum of natural water (7) were utilized and a mean of the two frequencies was taken if the H₂¹⁶O line was unblended in both spectra. The numbers of lines in the three sets of data were 368, 282, and 282, respectively, for H₂¹⁶O, H₂¹⁷O, and H₂¹⁸O. Since all the blended and very weak lines were excluded, there was no need to assign different weights to the observations. Figure 1 illustrates the fitted data. As can be seen, the lines selected for the fit provide information on a wide range of rotational energy levels. Most levels are involved in several transitions of different types. The number of H₂¹⁶O lines is larger, but the essential coverage of J_{τ} values is the same in the three sets of data. To reach this obviously very advantageous situation, the doublets with $K_a = 11$ (those with the line numbers 900, 909, and 932 in Ref. (8)) were removed from the H₂¹⁶O and H₂¹⁸O data, since the corresponding H₂¹⁷O lines were not resolved. Hence the maximum value of K_a is 10 for each species.

MODEL TESTING

The data to be fitted contained several transitions at high J and K_a . Accordingly, the number of the terms in the Watson Hamiltonian which are expected to yield a significant contribution becomes large. In addition to 24 terms of the degrees 2, 4, 6 and 8, the applicability of the following terms was tested $(J_{xy}^2 = J_x^2 - J_y^2)$:

$$\begin{split} &P_{KJ}J^4J_z^6, P_{KKJ}J^2J_z^8, P_KJ_z^{10}, p_{KKJ}J^2(J_z^6J_{xy}^2 + J_{xy}^2J_z^6) \\ &p_K(J_z^8J_{xy}^2 + J_{xy}^2J_z^8) \\ &\text{and} \\ &G_{KKJ}J^2J_z^{10}, G_KJ_z^{12}, g_K(J_z^{10}J_{xy}^2 + J_{xy}^2J_z^{10}) \\ &\text{and} \\ &F_KJ_z^{14}. \end{split}$$

The first runs were performed with a model including the following 21 constants: P_K , p_K , L_K , L_{KKJ} , L_{KJ} , and l_K added to 15 constants of the degrees 2, 4 and 6. This model yields the following standard deviations¹ of observations: $\delta(H_2^{16}O) = 2.4$, $\delta(H_2^{17}O) = 2.6$, and $\delta(H_2^{18}O) = 2.5 \times 10^{-3} \text{ cm}^{-1}$. An introduction of the term $G_K P_z^{12}$ decreases the standard deviation by 20–30%, e.g., $\delta(H_2^{16}O) = 1.9 \times 10^{-3}$

¹ The standard deviation δ was defined as

$$\delta = \left(\frac{\sum_{i} (\gamma_{obs}^{(i)} - \gamma_{calc}^{(i)})^2}{(n-p)}\right)^{1/2},$$

where n is the number of lines and p is the number of parameters.



FIG. 1. The structure of the fitted data. The dots represent rotational levels and the lines connecting the dots represent transitions. J and K_a are quantum numbers. Even and odd refer to the parity of $K_a + K_c$. The plots have been drawn from H₂¹⁶O data and H₂¹⁷O data. The structure of H₂¹⁸O data is very similar to that of H₂¹⁷O data.

cm⁻¹. This is not a poor value, but the following indications of the deficiency of this model suggested the need to introduce additional terms: for several transitions even at low J the differences $\gamma_{obs} - \gamma_{calc}$ were comparatively large and to the same direction for all the isotopic species; the ability of this model to reproduce the observed microwave spectra (1-3) was not in agreement with the accuracy of the fitted data, which indicates a significant perturbation among low-order constants.

Even when the effect of a single term proved to be small, the fitting did improve gradually with inclusion of additional terms. Finally, after extensive computation, the following Hamiltonian consisting of 27 rotation and distortion terms was chosen: $(J_{xy}^2 = J_x^2 - J_y^2)$

$$\begin{split} H &= \frac{1}{2} \left(B + C \right) J^2 + \left[A - \frac{1}{2} \left(B + C \right) \right] J_z^2 + \frac{1}{2} \left(B - C \right) J_{xy}^2 - \Delta_J J^4 - \Delta_{JK} J^2 J_z^2 \\ &- \Delta_K J_z^4 - 2 \delta_J J^2 J_{xy}^2 - \delta_K (J_z^2 J_{xy}^2 + J_{xy}^2 J_z^2) + H_J J^6 + H_{JK} J^4 J_z^2 + H_{KJ} J^2 J_z^4 \\ &+ H_K J_z^6 + 2 h_J J^4 J_{xy}^2 + h_{JK} J^2 (J_z^2 J_{xy}^2 + J_{xy}^2 J_z^2) + h_K (J_z^4 J_{xy}^2 + J_{xy}^2 J_z^4) \\ &+ L_J J^8 + L_{JK} J^4 J_z^4 + L_{KKJ} J^2 J_z^6 + L_K J_z^8 + 2 l_J J^6 J_{xy}^2 + l_{JK} J^4 (J_z^2 J_{xy}^2 + J_{xy}^2 J_z^2) \\ &+ l_{KJ} J^2 (J_z^4 J_{xy}^2 + J_{xy}^2 J_z^4) + l_K (J_z^6 J_{xy}^2 + J_{xy}^2 J_z^6) + P_{KKJ} J^2 J_z^8 + P_K J_z^{10} \\ &+ p_K (J_z^8 J_{xy}^2 + J_{xy}^2 J_z^8) + G_K J_z^{12}. \end{split}$$

With this model the following standard deviations are obtained: $\delta(H_2^{16}O) = 1.3$, $\delta(H_2^{17}O) = 1.6$, and $\delta(H_2^{18}O) = 1.4 \times 10^{-3} \text{ cm}^{-1}$.

There are high correlations among many of the distortion constants which hardly can be avoided when fitting water spectra. The inclusion of the less significant terms $(L_J, l_J, l_{JK}, l_{KJ})$ increases the uncertainties of the values of the closely related constants of degree 6 by a factor of 2–4. On the other hand, with inclusion of these constants the overall appearance of the fit became closer to that obtained with smaller models by using slightly restricted J_τ range of data. For instance, removing 10% of the lines and using the model with the 21 constants mentioned above lead to $\delta = 1.1 \times 10^{-3}$ cm⁻¹ for H₂¹⁶O.

RESULTS

The final values for the rotation and distortion constants are shown in Table I. The rotational energy levels derived from these constants are listed in Table II. The agreement between observed (1-3) and calculated microwave transitions can be seen from Table III.

It was also possible to deduce the rotational energy levels from the experimental frequencies. As can be seen from Fig. 1, the calculation of the $H_2^{16}O$ levels with even $K_a + K_c$ can be initiated from the rotational ground state. The other half of the $H_2^{16}O$ levels was calculated by fixing the value of the level $1_{0,1}$ to that obtained in the fit. For $H_2^{17}O$ as well as for $H_2^{18}O$, it was necessary to fix the values of both the level $1_{0,1}$ and the level $1_{1,1}$. The propagation of the calculation was toward higher energies. Before proceeding forward from any level, a mean of the energy values resulting from all the possible routes leading to that level, was calculated. An exception to this scheme of calculation was caused by the levels which could not be reached without going downward on the energy scale. Those levels were preferably obtained by making a step toward smaller K_a within the same J value. After picking up the desired level the calculation was continued normally.

The method outlined above is still very sensitive to inaccurate data points, especially if these are located at the bases of the "trees" in Fig. 1. Therefore, it is unfortunate that in $H_2^{16}O$ spectrum of Ref. (7) there seem to be several systematic

TABLE I

	H	2	6 ₀	٢	2	70	н	18 ₀ 2
A	27.8805998	ł ±	0.00029	27.6951400	±	0.00042	27.5312371	± 0.00034
В	14.5216038	i ±	0.00014	14.5216847	±	0.00021	14.5218299	± 0.00017
с	9.2777032	±	0.00014	9.2566257	±	0.00021	9.2380164	± 0.00017
∆ر	(0.1251801	±	0.00016) • 10 ⁻²	(0.1250600	±	0.00025)•10 ⁻²	(0.1251511	± 0.00020) • 10 ⁻²
∆jk	(-0.5760005	±	0.00058) • 10 ⁻²	(-0.5727237	±	0.00080) • 10 ⁻²	(-0.5701224	± 0.00063) • 10 ⁻²
∆ĸ	(0.3244598	±	0.00020)•10 ⁻¹	(0.3202494	ŧ	0.00029)+10 ⁻¹	(0.3166570	± 0.00024)-10 ⁻¹
٥	(0.5073549	±	0.00075)•10 ⁻³	(0.5083407	±	0.0011) • 10 ⁻³	(0.5080030	± 0.00090)•10 ⁻³
^δ κ	(0.134563	ŧ	0.00060) • 10 ⁻²	(0.130837	±	0.00094) • 10 ⁻²	(0.127769	± 0.00075)•10 ⁻²
нј	(0.523416	±	0.013)•10 ⁻⁶	(0.52508	±	0.020) • 10 ⁻⁶	(0.53448	± 0.017)•10 ⁻⁶
^н јк	(-0.14047	±	0.0035)•10 ⁻⁵	(-0.14600	±	0.0050)•10 ⁻⁵	(-0.14999	± 0.0040) • 10 ⁻⁵
^н кј	(-0.171664	±	0.0020)-10 ⁻⁴	(-0.167333	±	0.0028)-10 ⁻⁴	(-0.166386	± 0.0022) • 10 ⁻⁴
н _к	(0.1243105	±	0.00089)•10 ⁻³	(0.1216752	±	0.0013) • 10 ⁻³	(0.1200590	± 0.0010) • 10 ⁻³
hj	(0.263485	±	0.0067) • 10 ⁻⁶	(0.271433	ŧ	0.010) • 10 ⁻⁶	(0.266545	± 0.0081)•10 ⁻⁶
h _{JK}	(-0.4283	±	0.072) • 10 ⁻⁶	(-0.4304	ŧ	0.12) • 10 ⁻⁶	(-0.4142	± 0.096)•10 ⁻⁶
ь _к	(0.31954	±	0.0020) • 10 ⁻⁴	(0.30951	±	0.0034) • 10 ⁻⁴	(0.30020	± 0.0024) • 10 ⁻⁴
٤ _J	(-0.24777	±	0.039) • 10 ⁻⁹	(-0.26231	ŧ	0.058)•10 ⁻⁹	(-0.27658	± 0.048) • 10 ⁻⁹
L _{JK}	(-0.64727	±	0.021) • 10 ⁻⁷	(-0.60449	±	0.039) • 10 ⁻⁷	(-0.55049	± 0.030) • 10 ⁻⁷
L _{KKJ}	(0.243074	±	0.0055)•10 ⁻⁶	(0.229103	ŧ	0.0098) • 10 ⁻⁶	(0.216647	± 0.0073)•10 ⁻⁶
L _K	(-0.732472	ŧ	0.018) • 10 ⁻⁶	(-0.709430	±	0.026) • 10 ⁻⁶	(-0.697606	± 0.022) • 10 ⁻⁶
٤J	(-0.12650	±	0.019) • 10 ⁻⁹	(-0.14797	±	0.030) • 10 ⁻⁹	(-0.13462	± 0.023) • 10 ⁻⁹
^ℓ JK	(-0.8875	ŧ	0.24) • 10 ⁻⁹	(-0.9333	±	0.20) • 10 ⁻⁹	(-0.9297	± 0.13)•10 ⁻⁹
^l kj	(-0.7096	±	0.082)•10 ⁻⁸	(-0.6808	±	0.13) • 10 ⁻⁸	(-0.5944	± 0.11)•10 ⁻⁸
٤ _K	(-0.29252	±	0.0052) • 10 ⁻⁶	(-0.27497	±	0.0092) • 10 ⁻⁶	(-0.25983	± 0.0064)•10 ⁻⁶
^Р ккј	(-0.6855	±	0.20) • 10 ⁻¹⁰	(-0.6141	±	0.28) • 10 ⁻¹⁰	(-0.7715	± 0.22) • 10 ⁻¹⁰
Рĸ	(0.245756	±	0.017) • 10 ⁻⁸	(0.241043	±	0.024) • 10 ⁻⁸	(0.243778	± 0.020) • 10 ⁻⁸
Ρ _κ	(0.5263	±	0.022) • 10 ⁻⁹	(0.4855	±	0.029)•10 ⁻⁹	(0.4794	± 0.017)•10 ⁻⁹
G _κ	(-0.52415	±	0.062) • 10 ⁻¹¹	(-0.52399	±	0.088)•10 ⁻¹¹	(-0.53464	± 0.073) • 10 ⁻¹¹

Ground-State Rotational Constants of $H_2^{16}O$, $H_2^{17}O$, and $H_2^{18}O$ (cm⁻¹). The Quoted Error Limits are 95% Confidence Intervals

measurement errors in low-J lines within the lowest wavenumber region $30-60 \text{ cm}^{-1}$. The accumulation of these errors (typically $+0.002 \text{ cm}^{-1}$) made the whole chain of experimental H₂¹⁶O levels too high when compared to the set of the levels derived from the fit. The situation was corrected by replacing our measured line positions for H₂¹⁶O lines with line numbers 1-18 in Ref. (7) by the values obtained from the energy levels given in Ref. (5). Because the results of a least-squares fit are rather insensitive to a few less accurate data points it can be expected that calculated energy levels quoted in columns H₂¹⁶O, H₂¹⁷O, and H₂¹⁸O of Table II

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TABLE II

Ground-State Rotational Levels of H216O, H217O, and H218O (cm⁻¹)

	x. ¹⁰ 0	043 0127	17		100	0.83 01.07	(()	x. ¹⁶ 0	035 2177	8.17		"` *	013 0177
16 0. 11	23.7943	.7941(01	23-1711	.1753(0)	23 7548	-7548(Q:	10(0,10)	1114.5530	-5352(14)	1112.0245	32451 03	1109.7869	-1842(-27)
11 1. 61	42-3717	5111 51	42.5441		42.0234	.02431 491	10(2, 4)	1293.0197	.0205(4)	270.2268	2252(-16)	1267.1337	2649(-13)
21 1, 2)	70.0907	.0%10(5) .4964(1) .1765(8)	70.0045	-0020(-21) -2275(9) 9708(8)	10.9213 78.9884 94 7884	4256(-17) .4901(17) .7902(18)	10(2, 8) 10(3, A) 10(3, 2)	1445.1302	.1304(2)	1443.0400	.0417(17) .0512(-38)	1440-2877	.2854(-25)
21 2. 11	154.9018	.9018(0) .1587(5)	14.1449	.1462[11) .4301[-7)	133.4750	4783[25] 1825[-6]	10[4. 7] 101 4. 51	1581.3376	.3381(5) .4553(1)	1613-9004	.6002(12) .0954(-50)	1574.4490	-4463(-27) -6499(-37)
31 a. 51	136.7617	.7617(0)	136.5367	-53611 -6)	136.3365	3348(-17) -5678[13	10(5,5)	1724.7074	.7070(-4)	1720.1833	.1798(-35)	1709.5400	.1958(-44) .4514(-34)
3(2, 2)	173.3656 206.3013	3658 21	205.4807	4801 -61	204.7555	.8025[-1) .7554[-1)	10(6, 4)	1875.4640	.4631(-9)	1060.0503	-8553(-50)	1863.0199	.0176(-23)
15.0	285.4192	.2199(-1)	283.5612	.56001-12)	282.0948	.0935(-13)	10(8, 1)	2254.2850	2871(21)	2243-5112		2233 5995	.,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
4[0, 4]	222.0524	-0549(20)	221.6196	-62021 6)	221-2330	2343(5)	10(9)	2471.2546	-2559(15) -2578(32)	2457.8321 2457.8321	-8364(43) -8375(54)	2445.9525	.9541(16)
	275.4971	4984(17)	275.1294	1289(-5)	274.8029	.8035(6) .6202(5)	10(10, 0)	2701.8897	8931(34)	2685.8404	.8414(10)	2671 - 6320	. 5104(-16)
	115.7792	.7809(17]	315.0770	.0760(-10) .0049(31	514.4588 579.2915 160.7021	-4589(1) -2916(5) -7019(-2)	+1(0,11) 11(1,11)	1327.1114	.1118(4)	1324.1207	.1223(16) .1278(2) .5166(12)	1521.4545	4576(-29) 4570(-29) 5405(-2)
41 4. 11	488.1084	1084(01	465 2082	.2080(-2) .2346(-12)	482.6437 482.6728	.6439(21 .6716(-17)	11(2,10)	1525.1569	.1382(15)	1521.7802	-7796(-6) -1056(ID)	1518.7863	4373(+12)
5 9. 23	125-3483	- 3482(-1)	124-6595	-6597(2) .8789(5)	324-C465 325-2153	.0452(-13)	11(3, 8)	1695.0709	.0715(4) .2263(21)	1810.4632	.4850(5) .6667(15) .0345(-18)	1808.3598	.2837(-27) .3599() .4641(-17)
	199-4581 416-2088	21051 153	198.8781	.41191 -2) 1252(-10)	398.3604	.3594(-101 .1678(2)		1899.0105	.0107(23	1960-1522	.4590(38) .7499(-23)	1894.1956	.1924(-32) .2922(-39)
4(2,3) 4(3,3) 4(3,2)	446-5107 503-9682 308-8121	.5115(6) .969T(15) .8126(5)	445.7917 502.1774 507.1725	.176%(-101 .175%(-101	500.1957 505.7282	.5948(-9) .7787(0)	51(6, 6) 51(6, 6)	2142-5995	.9975(0) .6006(113 .0497(18)	2135.6580	.8556(-24) .4204(20)	2129.8972	
St 4, 23	610.1151 610.5418	.1761(10) 3472(4)	607.1580 607.3961	.15651-17] .3964(1)	604.5487 604.7927	.3043(23	11(7, 5)	2325.8765	.8159(-6) .9067(-221	2312.9975	-9938(-37) -0952(-37)	2305.1954	1924(+50) - 3018(-59)
\$1.5, 01	742.0761	0770(9)	137.6219	62261 71	753.6826	.6035(•)	11 8, 11	2522.2683		2511.1671 2776.8609		2501.5416	
6(3, 6) 6(1, 6)	446.6972	.6985(13) .2539(11)	445.7177 446.2452 541.9956	.7189(12) .2440(8) .9944[-12]	444.8459 445 1458 541,1802	8469(10) .3455(-5) .1796(-5)	11(9, 2) 11(10, 2) 11(10, 1)	2740-4202 2972-8331 2972-8331	-4238(36) -8311(-20) -8291(-40)	2726.8610 2956.6427 2956.6427	.64271 0) .5416[-11)	2714.0505 2942.3129 2942.5129	-31357 6)
b(2. 5) 5(2. 4)	552.9119 602.7742	.9125(6) .7751(97	551.6075 601.9592	6074(-1) 9596(+)	550.4504 401 2574	-4496(-8)	125 0.121	1557-0434	-D462(0)	1554-2780	-22201 121	1551-2023	
	648.9791 661.5492 756.7256	.97991 07 .5503(1+) .7253(-3)	659-9847 751-7036	-9855(8) 7041(5)	658.6094	-6095(1)	12(1,11)	1774.6162	6182(20)	1770.7087	.8350(32)	1767.2230	.2212(-18)
61 4. 21 61 5. 21	757.7810	.7819(9) -5997(2)	754.8103	.8103(D) .0763(1)	752.1873 880.0761	.1875(0)	121 2,101	1960-2092	.2083(-9)	1958.2351	-23521 1) -3589(2)	1952.6784	.6755(-29) .6521(-26)
6(6, 1) 6(6, 1)	1045-0572	.0588(16) .0588(16) .0503(28)	1038-7617	7637(20)	1033 1935	.1936(1)	12(4.9)	2124.9550 2205.6561	4542(1)	2120.5151	5156(5)	2116-5635 2200-4379	-5625(-10) -4355(-24)
1(0. 2)		2452(7)	505 9795		503 - 2275	77701 -5 }	12(5, 8)	2275.3753 2300.6879 2413.8026	.3745(-8) .6865(6) .8032(6)	2270.1065	.1089(24'	2265.4367 2293.0107 2420.8633	-4346(-21) -8855(0)
1(1,6)	704.2156	.2152(-6) .6099(6)	702-5847	8544(-) 0133(-14)	701.6943	.5929(-14)	12(6, 6)	2437.5023 2612.8036	-5044(21) -8037(-1)	2430.9214	.4230(14)	2425.1209	.1177(-32) .9796(-13)
11 2. 5)	762.4112	.4111(-11	781.3754	.3755(-4)	780.4526	.4513(-11) .7617(3)	12(8, 5) 12(8, 4)	2813.5180	.5146(-34)	2002.2042	.2771(-69)	2792.3398	- 3340(-50) - 3545(-55)
16 4 41	977.7451	.74561 21	924-6401	-64021 1)	921.8958	.8940(-18) .6989(-52	12(4,4) 12(4,1)	3052.6887		1018.9854 3018.9860		1006.6505	
7(5, 5) 7(5, 2) 7(6, 2)	1059.6483	-6487(41 -8%691 -2) -19121 31	1055-2544	-0541(9) 2557(-71 8)21(1)	1050.9905	.9919(34) .2019(-15) .1597(4)	12110. 27	1266.7608	1000(10.	1250-4225		1255.4568	
71 6. 11	1216.1956	1955(D) 8150(7)	1209-8170	8167(-1) 41688 113	1204.1768	.1748(-10) .9861(-5)	13(-0,11)	1805.6705	67211 161 .67461 261 .3130(361	1802.5955		1798.9662 1798.9675 2013.7631	.9661(1)
81 0, M1	744.0649	.0652(3)	742.3977	3946(-31)	740 9120	.4110(-101	131 2.121	2042-3730 2246-8875	5757(27) 8867(-8)	2037.0495	-2114(-17)	2033.0159	.8117(-22) .0508(-36)
81 1, 8) 81 1, 7)	744.1639 882.6923	.1649(10) -89211 -21	742 4898	49281 30	740.9985	.99651-181 .4918(-281	11(5.10)	2414.7232 2426.1980	.7261(29)	2410.5367	.5301 141	2406.7669	.7690{ 21 : .7193{-29]
81 2. 61	982.9136	.9130(3)	981.4946	4936(-101	980 2219	2202(-17)	말돌릴	2555.7990 2586.5539	.7949(-41) .5317(-22)	2530.5810	.58011 -9}	2527.6901 2575.9700 2622.0118	.6075(-26) .9687[-13]
6(4, 4) 6(4, 4)	1050.1591	.1594(3) .7104(4)	1119.4867	4868(1)	1047-3281 1116-5362 1126-4394	.5269(-12) .6355(-7) .4380(-14)	13(6, 4) 13(8, 7)	2748.1040 2756.4155	.1045(5)	2741.0962 2749.9902	.9941(59)	2734.8966	34081 -71
8. 5. 41	1255-1688	.1685(-3) .9135(-4)	1250.4981	4976(-4) 2089(-18)	246.3690	.3672(-18) .2043(-24)		2927.0802	.9453(20)	2918.0360		2910.0364 2911.0598	0610 321
51 6, 31 81 6, 21 81 7, 21	1411.6442	.6145(7) .6438(~4) .6924(7)	1405.1807	1795(-17)	1399.4637	4622(-15)	151.8.50	\$127.8679	.86571-22)	3116.5064		4106.4478	.4458(-20)
91 7 11 5(0. 1)	1590.6924	.6941(17) .0447(6)	1102-1955	-1954(1574.6781	-6782() -8010(-19) -8010(-19)	141 D.141 14(1.14)	2075.5140 2075.5155 2327.0615	.0013(30)	2058.6377 2058.6363 2372.7162		2064.6743	
91 0. 91	920.1698	.1704(6)	418.1015	.1027(12)	916.2575	.2551(-24)	14(2,11)	2327.9119	.9160(41)	2545.4945	0121(-45)	2318.1362 2540.6778	
9(1,9) 9(8) 4(2,8)	920.2115	.2111(-4) .0815(0) .3872(0)	918.1400 1076-7998 1078-0191	-1350(-50 -7993(-5) -0(40(-51)	916.2932	.2904(-28) .7593(-31) .9050(-39)	140 4.113	2739.4266	4341(15)	2754.5521		2729.7658	.7632(-26) .41941 27}
9(2,7)	1201-9234	9238(4) 2352(2)	1199.4618	-9624(6) 5582(-28)	1198.1989	.1965(-24)	14(4.13) 15(0.14)	2060-0457		2076-6909		2548-2672	
91 3. 67 91 4. 61 91 4. 53	1340.8855	.8965(0) .2768(-6)	1337 4081	.4867(-14) .5552(4)	1734 - 4792	4775(-17) 1968(-27)	151 1.151	2558.3011	.2690(35)	2752.9875		2548-2475 2620-1444 2620-21	
91 5. 5) 91 5. 4]	1474.9829	. 9057(3) .7995(-3) .2480(.2)	1470.2249	.2232(-17) .6856(-9) .6925(-11)	1466-0187	.0168(-19) .6082(-45) .8936(-30)	15[2,15]	2872-2808	. 2769(- 19)	2866.1463		860.6688	
9[7,3]	1631.3857	.3860(1) .5859(-1)	1624-0423	.8416(-7) -9842(-4)	1619.0561	.0549(-12)							
91 7, 2] 9(8, 2) 9(8, 1)	1810.5906 2009.8056 2009.8055	.5911(5) .8074(21) .8062(5)	1998.9532	.9888(-9) .9571(39) .9563(30)	1794.1798 1989.3500 1989.3501	.3518(-4) .3518(18) .3511(10)							
9 4 1 9 4 0	2225 4718	4722(4)	2212.1762	1744(-18)	2200.4092	.4062(-30) .4062(-30)							

Note. The levels resulting from the fit are listed in the columns $H_2^{16}O$, $H_2^{17}O$, and $H_2^{18}O$. The levels deduced from the experimental wavenumbers are listed in the columns OBS. DIFF refers to the difference between the two sets of levels in 10^{-4} cm.

are more reliable than experimental levels listed in columns OBS. It is also seen from Table II that the standard deviations obtained for energy levels are somewhat larger than the standard deviations obtained for the fitted transitions. Columns DIFF of Table II yield: $\delta(H_2^{16}O) = 1.6$, $\delta(H_2^{17}O) = 2.1$, and $\delta(H_2^{18}O) = 2.1 \times 10^{-3} \text{ cm}^{-1}$.

DISCUSSION

It was found out during this work that the ability of the different sets of H_2O constants found in the literature to predict transitions outside the J_τ range of the original analysis is very limited. Especially if the range of K_a is extended, the pre-

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Transition	н ₂ 16	0	H2 ¹⁷	'o	н, ¹⁸ 0		
	observed	obs-calc	observed	obs-calc	observed obs-cal		
6 ₁₆ - 5 ₂₃	22235.080	-14.136	13536.02 (9/2+7/2)	-1.12	5625.147 -3.749		
3 ₁₃ - 2 ₂₀	183310.117	+9.851	194002.998 (5/2+3/2)	+23.539	203407.52 +9.89		
¹⁰ 29 - ⁹ 36	321225.644	+2.411					
⁵ 15 ^{- 4} 22	325152.919	-14.153	323825.089 (lower)	+4.592	322465.17 -4.84		
4 ₁₄ - 3 ₂₁	380197.372	-4.485	385784.860 (lower)	+12.808	390607.76 +0.43		
7 ₅₃ - 6 ₆₀	437346.667	-71.762					
6 ₄₃ - 5 ₅₀	439150.812	-29.918			520137.32 -6.51		
7 ₅₂ - 6 ₆₁	443018.295	-72.331					
4 ₂₃ - 3 ₃₀	448001.075	+25.133	469808.134 (lower)	+34.300	489054.26 +23.14		
6 ₄₂ - 5 ₅₁	470888.947	-29.785			554859.87 -6.41		
5 ₃₃ - 4 ₄₀	474689.127	+17.260			537337.57 +21.52		
6 ₂₄ - 7 ₁₇	488491.133	+5.485			517181.96 -0.89		
1 ₁₀ - 1 ₀₁	556936.002	-0.442	552020.960	-0.082	547676.44 +0.20		
5 ₃₂ - 4 ₄₁	620700.807	+21.078			692079.14 +25.00		
² ₁₁ - ² ₀₂	752033.227	+3.618	748458.254	+0.631	745320.20 +2.91		

Observed and Calculated Microwave Transitions of H216O, H217O, and H218O (MHz)

dictions soon become very poor. This remark is obviously valid for any set of rotation and distortion constants of H₂O because of the slow convergence of Watson Hamiltonian. To illustrate this, let us recall that the value obtained for G_K (term in P_z^{12}) is about -5×10^{-12} cm⁻¹. Therefore, even the smallest contribution of P_z^{2n} terms is approximately -5×10^{-12} cm⁻¹ $\times 10^{12} = -5$ cm⁻¹ for the level 10_{10,0}, and -16 cm⁻¹ and -45 cm⁻¹, respectively, for the levels 11_{11,0} and 12_{12,0}. It is not surprising that the errors in the excluded doublets with $K_a = 11$ proved to be 0.05–0.15 cm⁻¹ when calculated by the constants of Table I.

It is, however, interesting to compare the abilities of the literature constants to reproduce our spectra. The comparison is better justified if the J_{τ} range of our observations is restricted according to the analysis in question. Thus, omitting lines with J > 8 leads to $\delta(H_2^{16}O) = 3.6$, $\delta(H_2^{17}O) = 6.7$, and $\delta(H_2^{18}O) = 3.0 \times 10^{-3}$ cm⁻¹ when the present data are predicted by the constants found in Ref. (4). In this case the agreement proved to be very good, typically 0.001 cm⁻¹, at low J_{τ} but became considerably poorer toward higher K_a . A better overall agreement ($\delta = 2.0 \times 10^{-3}$ cm⁻¹) was obtained with the $H_2^{16}O$ analysis found in Ref. (5), where the J_{τ} range covers 90% of our transitions. When the 21 constants were refined according to the present data, δ was reduced to 1.1×10^{-3} cm⁻¹ and the predictions for the excluded 10% of the transitions became much more accurate.

Considering the facts that microwave data have not been included in the analysis and that the expected measurement error of the fitted infrared data is about 30 MHz, the standard deviation $\delta = 24$ MHz obtained in recalculating the 34 microwave transition frequencies shown in Table III is reasonable. This together with good fitting of high J_{τ} infrared transitions guarantee that the values of the constants given in Table I are essentially correct and that the energy levels derived from them can be safely used in practical spectroscopy.

RECEIVED: November 6, 1980

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