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Measurement and analysis of precision data on the vibrational and vibrational-rotational spectra of a molecule. The ground and 010 states of $H_2^{18}O$

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The frequencies of nine rotational transitions in the 000 and 010 vibrational states of the $H_2^{18}O$ molecule have been measured in the 250–650-GHz range with an RAD spectrometer. Because of the weak intensity of the transitions, the line shift due to pressure was not checked, with the exception of the $1_{01}-1_{10}$ transition of the 010 state, for which this shift is the most appreciable. With the aid of the Borel variant of the 1-D approximation of Watson's effective rotational Hamiltonian, an analysis was made of microwave (MW) and precision IR data on the purely rotational spectrum of the ground state and ~ 300 lines of the fundamental band ν_2 . Two sets of 24 rotational and centrifugal constants for the ground and 010 states were obtained which reproduced the MW and IR data to experimental accuracy.

INTRODUCTION

The study of the vibrational-rotational and purely rotational spectra of the $H_2^{18}O$ molecule in different vibrational states is of considerable interest from the standpoint of the development of the theory of vibrational-rotational interaction in light molecules and the theory of isotope substitution in light molecules. This spectrum is also of interest from the standpoint of various applications. Thus far, only 12 microwave (MW) lines (see Ref. 1 and references therein) of the purely rotational spectrum of $H_2^{18}O$ in the ground vibrational state are known, and to our knowledge, there have been no measurements of the transition frequencies of the rotational spectrum in the 010 state. In addition, the extensive set of precision data on the fundamental band ν_2 obtained by Guelachvili,² has not been analyzed.

This paper reports on a measurement of the frequencies of six lines of the rotational spectrum of the ground state and three lines in the 010 state and on a combined analysis of MW data¹ and data obtained in the present study with precision IR data on the purely rotational spectrum in the ground state,¹ (140 lines, measured by Johns to an accuracy of ~ 6 MHz) and 300 lines of the ν_2 fundamental band in the model of the 1-D approximation of Watson's Hamiltonian, proposed in Ref. 3. Analysis of the enumerated data produced two sets of 24 rotational constants for the ground and 010 states, which reproduce the experimental data to the experimental accuracy.

EXPERIMENT

In the 250–650-GHz range the frequencies of nine lines of the 000 and 010 states were measured at pressures from

0.3 to 0.6 Torr with an RAD spectrometer.⁴ The measurements used a sample enriched with water isotopes, in which $H_2^{18}O$ amounted to $\sim 20\%$. The shift of the lines by pressure was not checked, with the exception of the $1_{01}-1_{10}$ line of the 010 state, for which this shift is the most significant. The value of this frequency was measured at 0.6 Torr and amounted to 647 214.348 MHz. We proceeded from the fact that the shifts of this line in the ground and 010 states of the main and isotopic water were fairly close,⁵ and the shift parameter of the $1_{01}-1_{10}$ line of the ground state of $H_2^{18}O$ was used for an approximate extrapolation of the frequency value to zero pressure, which led to a frequency value of 647 215.80 MHz. Since the pressure shifts for the remaining lines were not checked, they were given a weight corresponding to 500 kHz during the fitting, but because the shifts of lines with higher values of J and K than in the $1_{01}-1_{10}$ line are substantially smaller, the precision of determination of the centers of these lines may turn out to be higher than 500 kHz. Table II lists the values of the MW transition frequencies (the asterisk denotes the frequencies which we measured).

ANALYSIS

In the water molecule the effects of centrifugal distortion are very strong, causing poor convergence and even divergence of Watson's Hamiltonian.³ Reference 3 proposed the method of 1-D approximation in the smallness parameter; this made it possible, with the aid of different kinds of approximations (Pade, Borel, etc.), to obtain fairly rapidly converging expressions which include the same rotational constants as does Watson's Hamiltonian of the corresponding order. In the present paper, a Hamiltonian of the follow-

TABLE I. Rotational and centrifugal constants of $H_2^{18}O$ in the 000 and 010 vibrational states (in MHz).

Constants	000	010	Constants	000	010
A	825 866.3837(441)	921 250.7021(502)	$h_{JK} \cdot 10^4$	-0.2943 (440)	-0.4022 (303)
B	435 353.073 (559)	440 239.9917 (734)	h_K	0.8839 (655)	3.1745 (475)
C	276 950.533 (559)	272 546.811 (734)	$L_J \cdot 10^4$	-0.809 (174)	-2.011 (118)
Δ_J	57.5213 (143)	41.8831 (109)	$L_{JK} \cdot 10^4$	1.548 (835)	-0.504 (440)
Δ_{JK}	-474.5948 (752)	-230.8098 (805)	$L_{KKJ} \cdot 10^2$	-0.1469 (376)	-0.4560 (510)
Δ_K	950.7324 (918)	1704.516 (125)	$L_{KJ} \cdot 10^2$	0.6966 (902)	2.683 (128)
δ_J	15.22728 (624)	17.30083 (756)	$L_K \cdot 10^4$	-0.2669 (684)	-1.4841 (810)
δ_K	37.484 (299)	110.287 (256)	$L_K \cdot 10^4$	-0.4781 (335)	-1.1229 (789)
$H_J \cdot 10$	0.15689 (158)	0.21547 (475)	$I_J \cdot 10^4$	0.1453 (516)	0.447 (177)
$H_{JK} \cdot 10$	-0.6496 (371)	0.7762 (343)	$I_{JK} \cdot 10^4$	0.8876 (556)	1.120 (476)
H_{KK}	$\frac{h}{2} - 0.5089 (140)$	$-4.7004 (139)$	$I_{KJ} \cdot 10^4$	-0.9091 (287)	-5.252 (204)
$h_J \cdot 10^2$	8.7153 (287)	12.1488 (145)	$I_K \cdot 10^2$		
	0.81331 (808)	1.09247 (903)			

ing form was used to analyze the experimental data:

$$H = {}^S H_{diag}^{(8)} + \frac{1}{2} {}^P H_{off-diag}^{(8)} (J_x^2 - J_y^2) + \frac{1}{2} (J_x^2 - J_y^2) {}^P H_{off-diag}^{(8)}, \quad (1)$$

${}^P H_{off-diag}^{(8)}$

$$= \int_0^\infty e^{-x} \frac{U_0^2 U_2 - U_1^2 U_0 + (2U_0 U_1 U_2 - U_0^2 U_3 - U_1^2) x}{U_0 U_2 - U_1^2 + (U_0 U_1 - U_0 U_3) x + (U_1 U_3 - U_0^2) x^2} dx,$$

$${}^P H_{off-diag}^{(8)} = b_0 + \frac{b_1 (b_2 b_2 - b_3^2) - b_0 (b_2 b_1 - b_3^2)}{b_0 b_2 - b_1^2 + b_2 b_1 - b_0 b_3 + b_1 b_3 - b_2^2},$$

$$U_n = \frac{C_n}{n!},$$

$$C_n = \frac{B+C}{2} J^2 + \left(A - \frac{B+C}{2}\right) J_x^2,$$

$$C_1 = -\Delta_J J^4 - \Delta_{JK} J^2 J_x^2 - \Delta_K J_x^4,$$

$$C_2 = H_J J^8 + H_{JK} J^4 J_x^2 + H_{KK} J^2 J_x^4 + H_K J_x^8,$$

$$\bar{C}_3 = L_J J^8 + L_{JK} J^4 J_x^2 + L_{KK} J^4 J_x^4 + L_{KJ} J^4 J_x^4, \quad b_0 = (B-C)/2,$$

$$b_1/2 = -b_J J^2 - b_K J_x^2,$$

$$b_2/2 = h_J J^4 + h_{JK} J^2 J_x^2 + h_K J_x^4,$$

$$b_3/2 = l_J J^4 + l_{JK} J^4 J_x^2 + l_{KK} J^2 J_x^4 + l_K J_x^8.$$

This Hamiltonian differs from Eq. (6) of Ref. 3 in the fact that in the derivation of the formulas of the Borel approximation, the coefficients U_n are expressed in terms of the coefficients C_n as $U_n = C_n / n!$ not $U_n = C_n / (n+1)!$, as in Eq. (4) of Ref. 3. As was shown by calculations, this change leads to a high rate of convergence of the approximation. In Ref. 3, the integration was performed numerically. In calculations of the frequencies during the fitting, the Hamiltonian (1) in the present work was expressed in terms of the specific function $E_1(x)$ —an integral exponential function for which are known the Chebyshev approximants, which make it possible to calculate the values of this function to an accuracy better than 10^{-15} from the equations of Ref. 6, and this led to an appreciable reduction of the computer time required for the analysis. Thanks to the fact that Eq. (1) was expressed in terms of specific functions, the expenditure of computer time was comparable to that involved in the use of the traditional Hamiltonian.

Let us now examine the question of the weights assigned to different frequencies during the fitting. In accordance with the experimental error for IR data,¹ the latter were given weights corresponding to a precision of 6 MHz. For data on the v_2 fundamental band, Ref. 2 indicated an accuracy up to 1.5 MHz, but analysis of the combination differences showed that the discrepancies between the same combina-

TABLE II. M/W transition frequencies of the $H_2^{18}O$ molecule in the 000 and 010 states (in MHz).

Transition	ν_{exp}	$\nu_{exp} - \nu_{theor}$			Transition	ν_{exp}	$\nu_{exp} - \nu_{theor}$		
		Taylor	Pade	Borel			Taylor	Pade	Borel
000 State					7 5 2-6 6 4	539 598.85 *	-1.9	0.5	-0.4
6 1 6-5 2 3	5 625.147	1.8	0.2	-0.05	4 1 0-1 0 1	547 675.44	17.4	2.1	0.2
3 1 8-2 2 0	203 407.52	-0.8	0.3	0.06	6 4 2-5 5 1	554 850.87	-0.4	-1.0	0.07
10 2 9-9 3 6	253 913.4 *	-0.08	0.1	0.2	8 6 3-7 7 0	612 824.5 *	10.9	0.8	0.7
5 1 5-4 2 2	322 465.17	1.7	0.1	0.06	8 6 2-7 7 1	613 888.93 *	-4.2	-0.4	-0.3
4 1 4-3 2 1	380 607.76	-3.2	-0.7	-0.07	5 3 2-4 4 1	692 075.14	4.3	0.9	0.1
10 3 7-11 2 10	467 058.51 *	0.9	-0.5	0.1	2 1 1-2 0 2	745 320.2	-8.9	-1.7	-0.5
4 2 3-3 3 0	489 054.26	0.05	-1.0	0.1	010 State				
6 2 4-7 1 7	517 451.06	0.9	0.07	-0.04					
6 4 3-5 5 0	520 157.32	-12.5	-2.3	0.09					
7 5 3-6 6 0	533 502.57 *	8.1	1.3	0.6	4 2 2-3 3 1	522 480.79 *	0.03	-0.01	-0.08
5 3 3-4 4 0	537 337.57	8.2	2.5	-0.3	5 2 4-4 3 1	587 107.98 *	-0.2	0.3	0.2
					1 1 0-1 0 1	647 215.93 *	0.07	-0.02	-0.02

TABLE III. Energy of rotational levels of the 000 and 010 vibrational states of $H_2^{18}O$ molecule (in cm^{-1}).

<i>J</i>	<i>K_a</i>	<i>K_c</i>	000	010	<i>J</i>	<i>K_a</i>	<i>K_c</i>	000	010
1	0	1	23.7549	23.7704	8	2	7	884.9146	896.6019
1	1	1	36.7486	39.7845	8	2	6	960.2228	998.3531
1	4	0	42.0234	45.3592	8	3	6	1001.7059	1030.6466
2	0	2	69.9274	70.0585	8	3	5	1047.3287	1072.7289
2	4	2	78.9886	81.7647	8	4	5	1118.6365	1153.1431
2	1	1	94.7887	98.4580	8	4	4	1128.4397	1170.0389
2	2	1	153.4758	145.9432	8	5	4	1246.3685	1315.0540
2	2	2	154.7838	147.1825	8	5	3	1247.2064	1315.6118
3	0	3	136.8867	136.7417	8	6	3	1399.4280	1402.9256
3	1	3	141.5684	143.9876	8	6	2	1399.4634	1402.9470
3	1	2	172.8830	177.4229	8	7	2	1574.5789	1604.0587
3	2	2	204.7560	217.3016	8	7	1	1574.5797	1604.0692
3	2	1	210.7994	223.0455	8	8	1	1768.8044	1914.3250
3	3	1	232.0948	209.1780	8	8	0	1768.8045	1914.3250
3	3	0	232.8073	309.8524	9	0	0	916.2587	913.6550
4	0	4	221.2342	221.9124	9	1	9	916.2941	913.7658
4	1	4	223.8287	225.8424	9	1	8	1074.7829	1069.0080
4	1	3	274.5034	279.9791	9	2	8	1075.9097	1091.2580
4	2	3	288.8404	311.3344	9	2	7	1198.1996	1220.0050
4	2	2	314.4598	326.6064	9	3	7	1211.1554	1241.2574
4	3	2	370.2920	408.4286	9	3	6	1279.7972	1306.4287
4	3	1	380.7029	407.5655	9	4	6	1334.4793	1381.4462
4	4	1	432.6441	528.7340	9	4	5	1355.1999	1387.9382
4	4	0	432.6732	528.7552	9	5	5	1466.0189	1534.6954
5	0	5	324.0474	324.7479	9	5	4	1468.8138	1538.4452
5	1	5	325.2464	326.6587	9	6	4	1618.8972	1712.5110
5	1	4	398.3609	405.0024	9	6	3	1619.0569	1712.6075
5	2	4	414.1658	427.1783	9	7	3	1794.3783	1914.1480
5	2	3	445.1594	457.0481	9	7	2	1794.3539	1914.4512
5	3	3	500.5968	527.8638	9	8	2	1959.3643	2135.5348
5	3	2	505.7294	532.1800	9	8	1	1959.3644	2135.5349
5	4	2	604.5448	550.7008	9	9	1	2200.4197	2372.6087
5	4	1	604.7935	650.5825	9	9	0	2200.4197	2372.6087
5	5	1	733.6799	802.0791	10	0	10	1109.7883	1105.6823
5	5	0	733.6838	802.0816	10	1	10	1109.8028	1105.7182
6	0	6	444.5467	445.2441	10	1	8	2387.7353	1303.0846
6	1	6	445.3468	448.1023	10	2	9	1288.2664	1304.2163
6	1	5	541.8072	549.8142	10	2	8	1433.0277	1458.8207
6	2	5	550.4514	563.9074	10	3	8	1440.2882	1471.8344
6	2	4	601.2388	614.7452	10	3	7	1534.3674	1563.5200
6	3	4	645.8833	672.9427	10	4	7	1574.4484	1622.2291
6	3	3	658.8108	684.8716	10	4	6	1811.6548	1653.2166
6	4	3	751.0335	797.2386	10	5	6	1709.5438	1778.2494
6	4	2	752.1580	798.0913	10	5	4	1716.2051	1732.8371
6	5	2	880.0767	948.6350	10	6	5	1862.4596	1956.0608
6	6	1	880.1150	948.6602	10	6	4	1868.0253	1956.4046
6	6	1	1023.1942	1126.1890	10	7	4	2037.9420	2137.9551
6	8	0	1023.1946	1126.1893	10	7	3	2037.9701	2157.9808
7	0	7	533.7785	583.4662	10	8	3	2233.6200	2380.3381
7	1	7	583.0871	583.8686	10	8	2	2233.6200	2380.3385
7	1	6	701.6948	712.4997	10	9	2	2445.9875	2619.0392
7	2	6	708.5984	720.6311	10	9	1	2445.9875	2619.0392
7	2	5	780.4535	795.7672	10	10	1	2874.6722	2870.1802
7	3	5	812.7823	840.8001	10	10	0	2874.6722	2870.1802
7	3	4	859.5500	884.7831	11	0	11	1321.4855	1315.5703
7	4	4	921.8963	968.1867	11	1	11	1321.4828	1315.5880
7	4	3	925.7003	971.0395	11	1	10	1518.5454	1524.6676
7	5	3	1050.0908	1119.6465	11	2	10	1518.7874	1555.2310
7	5	2	1051.2033	1119.7873	11	2	9	1684.1378	1743.0695
7	6	2	1204.1694	1297.4426	11	3	9	1658.2382	1721.4868
7	6	1	1204.1749	1297.4400	11	3	8	1808.3623	1841.4445
7	7	1	1578.9864	1497.9410	11	4	8	1835.4867	1884.4891
7	7	0	1578.9864	1497.9410	11	4	7	1894.1992	1955.4684
8	0	8	740.9134	739.6106	11	5	7	1976.3065	2045.1953
8	1	8	740.9892	739.7913	11	5	6	1990.8702	2055.5489
8	1	7	879.4950	892.2307	11	6	6	2129.9133	2223.3792
11	6	5	2131.5834	2224.4042	12	4	9	2116.5717	2167.2127
11	7	5	2305.2155	2425.3271	12	5	8	2200.4487	2242.8358
11	7	4	2305.3255	2425.3892	12	5	8	2265.4555	2324.8095
11	8	4	2501.3685	2648.4738	12	5	7	2223.0259	2355.2680
11	8	3	2501.3732	2648.4763	12	6	7	2420.9223	2514.1753
11	9	3	2744.9163	2888.6692	12	6	6	2425.1658	2516.5205
11	9	2	2744.9465	2888.6693	12	7	6	2506.0198	2716.0260
11	10	1	2942.3965	3141.9857	12	7	5	2556.8833	2716.2306
11	11	1	3180.4976	3404.5785	12	8	4	2792.4434	2639.7028
11	11	0	3180.4976	3404.5785	12	9	4	3006.9943	3181.1835
12	0	12	1551.2075	1543.3026	12	9	3	3006.5551	3181.1839
12	1	12	1551.2414	1543.3099	12	10	3	3236.0955	3436.5354
12	1	11	1767.2335	1783.6657	12	10	2	3236.0953	3436.5354
12	2	11	1787.3414	1784.4435	12	11	2	3476.5243	3702.0060
12	2	10	1952.6847	1985.4414	12	11	1	3476.5245	3702.0060
12	3	10	1954.6570	1989.6266	12	12	1	3724.9415	3973.6547
12	3	9	2099.6637	2137.6939	12	12	0	3724.9415	3973.6547

tion differences obtained from different frequencies can be as large as 10 MHz, and therefore, the data of Ref. 2 were assigned a weight corresponding to an experimental accuracy of 10 MHz.

Table I lists the rotational and centrifugal constants of the $H_2^{18}O$ molecule obtained by fitting the data enumerated earlier. The MW frequencies and their differences between the calculation and the experiment are listed in Table II, and the energy levels up to $J = 12$ of the ground and excited O10 states, obtained by calculation using Eq. (1) and the constants of Table I, are listed in Table III. The calculated values of the frequencies being processed can be obtained by means of these levels. The standard deviation of the fitting

was 1.3. To analyze a less extensive set of data from the ground state in the traditional approach, it was necessary to use 34 constants and terms of the Hamiltonian up to $J = 12$, and the use of the Hamiltonian (1) made it possible to do this in a model consisting of 24 parameters up to $J = 8$.

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Effect of external factors on the shape of the polarized CARS spectrum of the Raman band of stretching vibrations of water

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The effect of temperature and concentration of a dissolved salt (LiI) on the shape of polarized CARS spectra of the band of stretching O–H vibrations of liquid water has been studied. The spectra were decomposed into individual components by fitting by computer, and the temperature changes of the spectroscopic parameters of the components of the decomposition were studied. The experimental conditions under which the band structure is manifested most clearly in the CARS spectra have been determined. The possible accuracy of measurement of water temperature and concentration of dissolved salt based on polarized CARS is estimated.

One of the most important problems in modern optical spectroscopy is the study of the molecular interaction in condensed media. In particular, considerable attention has been focused on systems with hydrogen bonds, the most important of which is liquid water.^{1–3} The complex internal structure of liquid water, due to the presence of hydrogen-bonded complexes, is manifested in the vibrational spectra, including the inhomogeneous broadening of the band of stretching O–H vibrations, and therefore, this band is being intensively studied in different states of aggregation of water by methods of spontaneous Raman scattering (RS),^{4–6} IR predissociation,⁷ and coherent anti-Stokes Raman spectra (CARS).^{8–10} The latter method (in its polarization variant) makes it possible to observe the spectral structure of the band of liquid water not manifested in RS or IR absorption, and therefore, it is of interest to study the deformation of the polarized CARS spectra of water subjected to various external factors (temperature change, dissolution of salt). Moreover, by analogy with Raman studies,^{4,6} it is important not only to follow the temperature deformation of the CARS spectrum as a whole, but also, after decomposing the spectrum into individual components by computer, to study the temperature dependence of the spectroscopic parameters of these components. The influence of certain salts (in particu-

lar, alkali metal halides) on the RS spectrum of a band was studied in Refs. 11–13, which showed that as the concentration of dissolved salt increases, an increase takes place in the intensity of the RS signal of the bands of stretching (ν_{OH}) and deformation (δ_{OH}) vibrations, the spectrum of ν_{OH} is distorted, the characteristic low-frequency shoulder disappears, and a maximum is formed. When the LiI concentration of the solution is 0.2 M, the RS spectrum of ν_{OH} assumes a symmetric shape,^{11,12} which in Ref. 12 was interpreted as resulting from the complete destruction of hydrogen bonds and formation of complexes of O–H groups of H_2O molecules with I^- ions. One of the aims of the present work was to study the changes in the structure of the ν_{OH} band, manifested in the polarization CARS spectra when alkali metal halides are dissolved in water.

In addition, it is of practical interest to compare quantitatively the relative temperature and salt deformations of spectra of RS and polarized CARS, since the latter method can be used comparatively easily under natural conditions for contactless and nondestructive testing of the temperature and salinity of seawater samples in oceanographic studies.

The experiments involved the use of the method of polarized CARS (described in detail in Ref. 14) with an auto-