

High-Resolution Fourier Transform Spectrum of the D₂O Molecule in the Region of the Second Triad of Interacting Vibrational States

Sheng-gui He,* O. N. Ulenikov,^{†,1} G. A. Onopenko,[†] E. S. Bekhtereva,[†]
Xiang-huai Wang,* Shui-ming Hu,* Hai Lin,* and Qing-shi Zhu*

*Open Laboratory of Bond Selective Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, 230026, People's Republic of China; and [†]Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, Tomsk, 634050, Russia

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The high-resolution Fourier transform spectrum of the D₂O molecule was recorded in the 3200–4200 cm⁻¹ region, where the bands of the second triad of interacting vibrational states are located. As a result of the theoretical analysis, both the rotational–vibrational structure of the (011) vibrational state was improved, and the rotational energies of the (110) and (030) vibrational states were determined for the first time up to rotational quantum numbers $J^{\max} = 15$ and 14, respectively. © 2000 Academic Press

1. INTRODUCTION

The analysis of the vibration–rotation spectra of the deuterated species of water is of great interest for many problems both of pure academic and of applied interest. Such problems, for example, are the investigation of the dynamics of molecular vibrations and rotations, the determination of the intramolecular potential function, atmospheric studies of planets, the study of the role of deuterium in interstellar molecules as an indicator of chemical reactions, the investigation of industrial pollution and of laser techniques, and so on.

The dideuterated water molecule has been the subject of several spectroscopic studies both in the microwave and in the infrared regions [see, e.g., Refs. (1–16)]. As to the second triad of interacting vibrational states (011)–(110)–(030), they were considered earlier in two papers only: in Ref. (1) the vibrational band $\nu_2 + \nu_3$ was studied with a grating spectrometer at a resolution of 0.25–0.30 cm⁻¹; in Ref. (13) the same $\nu_2 + \nu_3$ band was analyzed with a selective modulation Girard spectrometer achieving a better resolution (0.07 cm⁻¹). In the last case, few lines of the weak $\nu_1 + \nu_2$ band were also assigned.

In the present paper about 2300 transitions belonging to the D₂O absorption were measured with a high-resolution Fourier transform spectrometer in the 3200–4200 cm⁻¹ region.

2. EXPERIMENTAL DETAILS

The sample of D₂¹⁶O was purchased from PeKing Chemical Industry, Ltd. (China). The stated purity of deuterium was 99.8%.

Since HDO and H₂O have strong absorption in the 3200–4200 cm⁻¹ region in which we were interested, D₂O samples

¹To whom correspondence should be addressed. E-mail: ulenikov@phys.tsu.ru.

mixed with H₂O at different ratios (see Table 1) were used to facilitate the identification of D₂O lines. The spectra were recorded with the Bruker IFS 120HR Fourier transform interferometer at Hefei, which was equipped with a multi-pass gas cell with adjustable path length. A tungsten source, a CaF₂ beamsplitter, an optical band pass filter whose cut-off frequencies were 3200 and 4300 cm⁻¹, and a liquid-N₂-cooled InSb detector were used. The unapodized resolution was 0.008 cm⁻¹, which is comparable with the Doppler width (about 0.01 cm⁻¹) in this region. Because the absorption intensities of the $\nu_2 + \nu_3$, $\nu_1 + \nu_2$, and $3\nu_2$ bands of the D₂O were quite different, various sample pressures and path lengths have been employed, as detailed in Table 1. The pressures were measured by a pressure gauge with an accuracy better than 1 Pa. All spectra were recorded at room temperature. The signal-to-noise ratios (SNR) varied from 1800 to 3300 (see Table 1), and about 2300 lines with good SNR were supposed to belong to D₂O. The frequencies were calibrated with those of the HDO lines in that region reported by Toth and Brault (17). The wavenumber precision of not too strong, unblended lines was $2\text{--}5 \times 10^{-4}$ cm⁻¹. For illustration, two small pieces of the recorded spectra are presented in Figs. 1 and 2.

3. HAMILTONIAN MODEL

Since all three vibrational states (011), (110), and (030) of the D₂O molecule are strongly interacting, we used in the analysis the following Hamiltonian model,

$$H^{\text{eff.}} = \sum_{\nu, \nu'} |\nu\rangle \langle \nu' | H_{\nu\nu'}, \quad [1]$$

TABLE 1
Experimental Details for the Three Bands of D₂O

band	total pressure (pa)	path length (m)	percent of D ₂ ¹⁶ O	percent of HD ¹⁶ O	percent of H ₂ ¹⁶ O	number of scans	SNR
ν ₂ +ν ₃	33	15	81	18	1	505	2600
	75	15	25	50	25	600	3300
ν ₁ +ν ₂	292	51	95	5	0.06	520	1800
	860	87	98	2	0.01	500	2600
	527	15	25	50	25	400	2000
3ν ₂	1650	105	98	2	0.01	500	1800
	527	15	25	50	25	400	2000

where the diagonal operators $H_{\nu\nu}$ ($\nu = 1, 2, 3$) are the usual Watson's operators (18):

$$\begin{aligned}
 H_{\nu\nu} = & E_{\nu} + [A^{\nu} - \frac{1}{2}(B^{\nu} + C^{\nu})]J_z^2 + \frac{1}{2}(B^{\nu} + C^{\nu})J^2 \\
 & + \frac{1}{2}(B^{\nu} - C^{\nu})J_{xy}^2 - \Delta_K^{\nu}J_z^4 - \Delta_{JK}^{\nu}J_z^2J^2 - \Delta_J^{\nu}J^4 \\
 & - \delta_K^{\nu}[J_z^2, J_{xy}^2] - 2\delta_J^{\nu}J^2J_{xy}^2 + H_K^{\nu}J_z^6 \\
 & + H_{KJ}^{\nu}J_z^4J^2 + H_{JK}^{\nu}J_z^2J^4 + H_J^{\nu}J^6
 \end{aligned}$$

$$\begin{aligned}
 & + [J_{xy}^2, h_K^{\nu}J_z^4 + h_{JK}^{\nu}J^2J_z^4 + h_J^{\nu}J^4] + L_K^{\nu}J_z^8 \\
 & + L_{KKJ}^{\nu}J_z^6J^2 + L_{KJ}^{\nu}J_z^4J^4 + L_{JK}^{\nu}J_z^2J^6 + L_J^{\nu}J^6 \\
 & + [J_{xy}^2, l_K^{\nu}J_z^6 + l_{JK}^{\nu}J_z^4J^2 + l_{JK}^{\nu}J_z^2J^4 + l_J^{\nu}J^6] \\
 & + P_K^{\nu}J_z^{10} + Q_K^{\nu}J_z^{12}.
 \end{aligned} \tag{2}$$

Since the (110) and (030) states are of A₁ symmetry and the

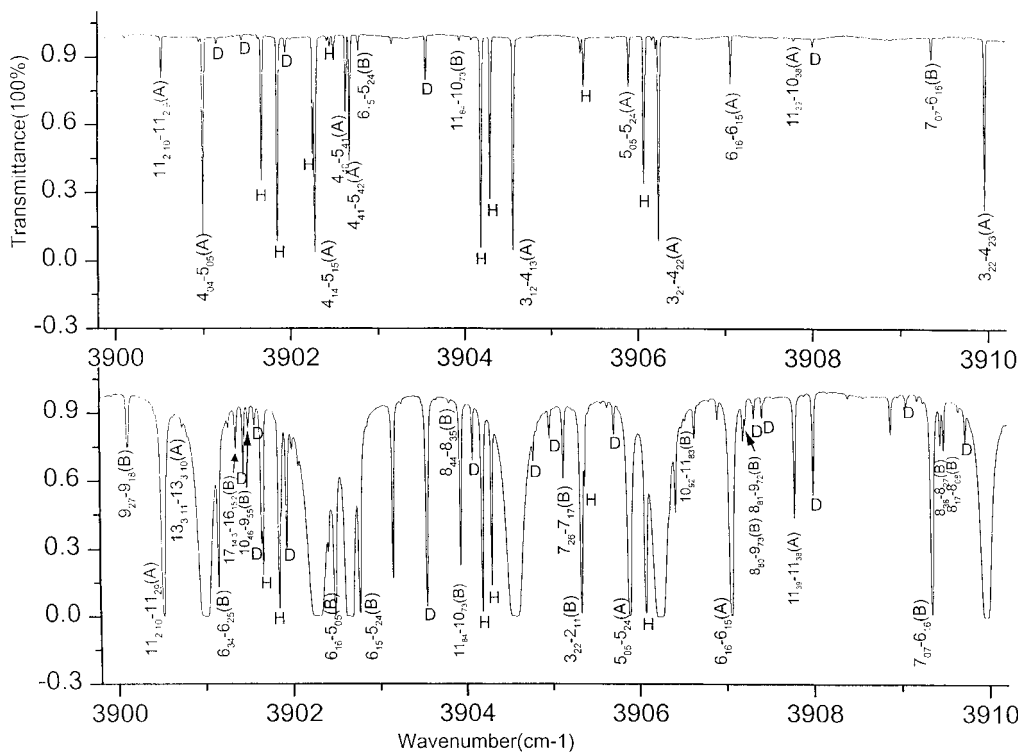


FIG. 1. A portion of the D₂¹⁶O spectrum in the region of the ν₂ + ν₃ and ν₁ + ν₂ bands. The first spectrum was measured at a total pressure of 33 Pa (about 80% of D₂O), with an absorption path length of 15 m; the second one with the conditions of 860 Pa (about 98% of D₂O) and 87 m. A and B denote the ν₂ + ν₃ and ν₁ + ν₂ bands, respectively; lines marked with D and H are absorption of HDO and H₂O in the sample, respectively.

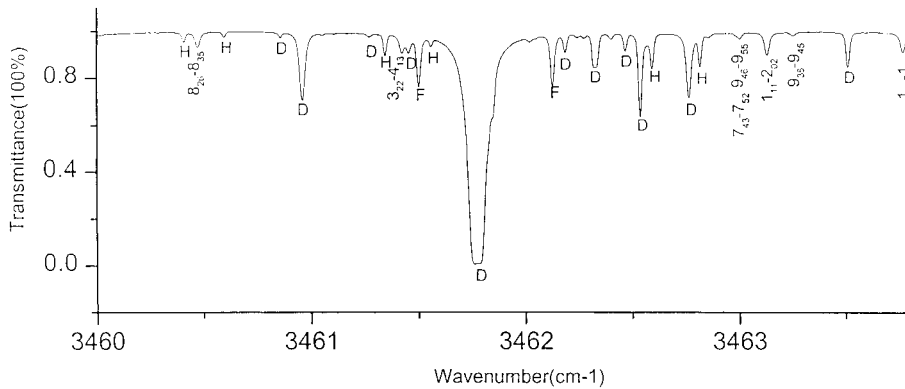


FIG. 2. A small fraction of the weak $3\nu_2$ band of the $D_2^{16}O$. The spectrum shown was measured at a total pressure of 1650 Pa (about 98% of D_2O), with an absorption path length of 105 m. Lines marked with D and H are HDO and H_2O absorptions in the sample, respectively. Two lines marked with F belong to H_2CO .

(011) state is of B_1 symmetry, resonance interaction operators $H_{\nu\nu'}$ ($\nu \neq \nu'$) were taken in the following form,

$$H_{23} = H_{32}^+ = F_0^{23} + F_J^{23}J^2 + \dots + F_{xy}^{23}J_{xy}^2 + F_{xyK}^{23}[J_{xy}^2, J_z^2]_+ + F_{xyJ}^{23}J_{xy}^2J^2 + F_{xyKK}^{23}[J_{xy}^2, J_z^4]_+ + F_{xyKL}^{23}[J_{xy}^2, J_z^2]_+J^2 + \dots \quad [3]$$

for the Fermi-type interaction between the states (110) and (030), and

$$H_{n1} = H_{1n}^+ = C_{yK}^{n1}[iJ_y, J_z^2]_+ \dots + C_{xz}^{n1}[J_x, J_z]_+ + C_{xzK}^{n1}[[J_x, J_z]_+, J_z^2]_+ + C_{xzJ}^{n1}[J_x, J_z]_+J^2 \dots + C_{xy}^{n1}[J_y, J_{xy}]_+ \dots \quad [4]$$

($n = 2$, or 3) for the Coriolis-type interactions between the states (110) or (030), on the one hand, and the (011) state, on the other hand.

In Eqs. [2]–[4] the following notations are used: $J_{xy}^2 = J_x^2 - J_y^2$ and $J^2 = \sum_{\alpha} J_{\alpha}^2$; $|1\rangle = (011)$, $|2\rangle = (110)$, and $|3\rangle = (030)$.

4. ASSIGNMENT OF TRANSITIONS AND ANALYSIS

Assignments of transitions in the recorded spectra have been made on the basis of the ground state combination differences (GSCD) method. In this case, the ground state energies were calculated on the basis of parameters from Ref. (6) (for convenience of the reader, they are reproduced in column 2 of Table 2). Thanks to the high sensitivity of the spectrometer and the possibility of using a long pathlength, we were able to assign transitions not only of the strong $\nu_2 + \nu_3$ and weaker $\nu_1 + \nu_2$ bands (see examples of the recorded spectra on Fig. 1), but also of the very weak $3\nu_2$ band (see Fig. 2) as well. As a result of the analysis, about 2000 lines in the spectra were

assigned, and values of upper state energies, which are presented in columns 2, 5, and 8 of Table 3, were determined. These latter values were determined as the mean of several individual energies obtained from P , Q , and R transitions reaching the same upper state. In this case, only “full quality” transitions were used in the determination of the mean values, namely: (1) unblended, uncovered, and not too strong (only

TABLE 2
Spectroscopic Parameters of the (011), (110), and (030) Vibrational States of the D_2O Molecule (in cm^{-1})^a

Parameter	(000) ^b	(011)	(110)	(030)
1	2	3	4	5
E		3956.014220(452)	3839.8578(958)	3475.8848(983)
A	15.4199657 ₀₀	15.989889(102)	16.36441(178)	20.05226(198)
B	7.2729744 ₁₈	7.3178833(347)	7.256958(872)	7.450325(883)
C	4.84528552 ₂₀	4.7391191(182)	4.71449(128)	4.68747(129)
$\Delta_K \times 10^3$	9.25347 ₂₁	12.39828(453)	13.5276(173)	36.1313(199)
$\Delta_{JK} \times 10^3$	-1.52324 ₂₁	-1.85209(271)	-1.87122(659)	-3.076(167)
$\Delta_J \times 10^3$	0.309983 ₇₆	0.345856(230)	0.33504(166)	0.39279(409)
$\delta_K \times 10^3$	0.34708 ₅₉	0.72717(120)	0.8048(183)	2.1610(276)
$\delta_J \times 10^3$	0.123109 ₉₃	0.140833(106)	0.139276(759)	0.162595(995)
$H_K \times 10^5$	1.8449 ₉₂	2.99237(794)	3.9059(344)	21.472(166)
$H_{KJ} \times 10^5$	-0.2457 ₄₈	-0.51294(662)	-0.3500(155)	-2.089(102)
$H_{JK} \times 10^5$	-0.02149 ₆₉	0.02717(181)	0.02896(394)	0.1918(331)
$H_J \times 10^5$	0.006513 ₈₂	0.0075058(734)	0.008207(424)	0.01212(104)
$h_K \times 10^5$	0.3790 ₈₄	0.86505(652)	1.0073(304)	3.471(191)
$h_{JK} \times 10^5$	-0.00528 ₈₇			
$h_J \times 10^5$	0.003226 ₃₀	0.0037729(318)	0.003011(243)	0.007152(659)
$L_K \times 10^7$	-0.5964 ₅₄	-0.8474(209)	-1.4367(741)	-4.653(277)
$L_{KJK} \times 10^7$	0.151 ₅₈	0.4897(324)	0.6350(901)	
$L_{KJ} \times 10^7$	-0.0384 ₈₄	-0.1256(120)	-0.2002(348)	
$L_{JJK} \times 10^7$	0.00054 ₇₆	-0.005127(530)		
$L_J \times 10^7$	-0.000168 ₂₈			
$l_K \times 10^7$	-0.173 ₆₂	-0.5458(315)	-0.6697(901)	
$l_{KJ} \times 10^7$			-0.03401(790)	
$l_{JK} \times 10^7$		-0.003375(312)		
$l_J \times 10^7$	-0.0000836 ₁₃			
$P_K \times 10^9$	0.1516 ₆₁			
$Q_K \times 10^{11}$	-0.0286 ₅₆			

^a Values in parentheses are the 1σ statistical confidence intervals.

^b Reproduced from Table IV, Ref. (6).

TABLE 3
 Experimental Rovibrational Term Values for the (011), (110), and (030) Vibrational States of the D₂O Molecule (in cm⁻¹)^a

			(011)			(110)			(030)			(011)			(110)			(030)											
<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ						
1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8	9	10
0	0	0	3956.0126		-16							8	0	8	4338.8423	3	0	4223.4252	2	-1	3861.4875	4	-6						
1	0	1	3968.0687	2	-14	3853.3996	4	7	3486.4511	2	14	8	1	8	4338.6812		13	4223.5954	3	-2	3861.9484		4						
1	1	1	3976.7349	1	-5	3862.5195	2	-2	3499.0058	4	0	8	1	7	4412.9021	6	-6	4297.4951	6	-3	3946.9196	3	4						
1	1	0	3979.3093	1	-6	3865.0471	1	-1	3501.7693	2	-5	8	2	7	4416.5553	3	8	4301.3137	5	1	3955.0485		-2						
2	0	2	3991.6786	3	-17	3876.8843	6	-1	3510.2964		8	8	2	6	4463.1209	5	-11	4347.0851	7	-12	4001.3549	4	-6						
2	1	2	3998.2782	1	-4	3883.9427	9	0	3520.5112	12	-2	8	3	6	4484.5046	3	12	4370.2034	9	2	4039.9509		-12						
2	1	1	4005.9943	1	-6	3891.5186	2	1	3528.7952	3	-3	8	3	5	4501.3948	5	1	4385.4684	7	6	4052.7906	6	-1						
2	2	1	4031.8690	1	11	3918.7457	2	-3	3566.0805	5	-7	8	4	5	4555.8575	3	14	4444.0566	5	-5	4134.0482		4						
2	2	0	4032.3615	4	5	3919.2011	2	-1	3566.4880	1	-8	8	4	4	4558.1790	2	1	4444.6860	7	3	4135.3520	4	-3						
3	0	3	4025.9611	2	-11	3911.0512	3	-1	3545.0854	2	-1	8	5	4	4631.5864	3	3	4530.0547	3	-1									
3	1	3	4030.2977	3	-5	3915.8041	2	3	3552.5200	3	3	8	5	3	4631.6559	4	5	4529.9749	4	5									
3	1	2	4045.6483	3	-1	3930.8830	3	1	3569.0252		-2	8	6	3	4738.4918	8	-9	4644.5731	4	0									
3	2	2	4068.0700	3	11	3954.6730	3	2	3602.5096	3	-3	8	6	2	4738.4956		-13	4644.4959	3	-2									
3	2	1	4070.4160	3	9	3956.8508	7	-6	3604.4827	3	-14	8	7	2	4857.2350	5	13	4761.7227	4	1									
3	3	1	4117.4623	3	2	4006.1576	6	-7	3670.5428	2	11	8	7	1	4857.2350	5	12	4761.7227	4	4									
3	3	0	4117.5235	3	7	4006.2116	8	-3	3670.5804	4	1	8	8	1	4990.0712	17		4898.5115	2	0									
4	0	4	4070.0363	4	-11	3955.0323	3	2	3589.9253		-11	8	8	0	4990.0712	17		4898.5115	2	0									
4	1	4	4072.5216	3	-2	3972.8462	2	3	3594.7851	2	1	9	0	9	4429.4052		3	4313.7342	3	-3	3952.2903		-1						
4	1	3	4097.7437	4	-10	3982.6636	4	3	3622.0417	1	-1	9	1	9	4429.4224	2	5	4313.8123	1	-5	3952.5285	2	1						
4	2	3	4115.9122	2	14	4002.1856	2	0	3650.7228	4	-7	9	1	8	4514.9218	3	-3	4399.5361	3	17	4052.2331	4	1						
4	2	2	4122.3242	5	6	4008.1926	1	-1	3656.2845	4	-8	9	2	8	4517.6104	9	-5	4401.6348	4	2	4057.2682	2	2						
4	3	2	4166.6471	3	14	4054.8284	2	-2	3719.8864	10	0	9	2	7	4577.3675	7	-9	4460.8830		-1									
4	3	1	4167.0577	5	9	4055.1965	2	-1	3720.1512	5	6	9	3	7	4592.7472	5	5	4477.7247	7	-1									
4	4	1	4233.7444	7	-18	4124.9271	11	3	3811.7590	12	16	9	3	6	4619.8733	5	-3	4502.4359	7	6									
4	4	0	4233.7499		-26	4124.9285	2	-5	3811.7590	12	-15	9	4	6	4667.2586	5	-7	4553.3765	6	-5	4245.8075	10	13						
5	0	5	4123.4728	4	-5	4008.3117	4	-1	3644.1513	1	-6	9	4	5	4672.5790	4	-3	4557.5271	3	-5									
5	1	5	4124.6940	2	-2	4009.8206	18	3	3647.0565	2	4	9	5	5	4741.0686	3	1	4640.3352	6	0									
5	1	4	4161.4836	5	-5	4046.1354	3	-2	3687.2201	2	-1	9	5	4	4741.2798	5	0	4640.2212	3	3									
5	2	4	4175.0543	5	12	4060.9693	5	6	3710.4300	6	-8	9	6	4	4848.4332	6	-7	4756.6000	4	0									
5	2	3	4188.1570	5	7	4073.3611	7	2	3722.2118	6	-6	9	6	3	4848.4529	5	-2	4756.3377	7	5									
5	3	3	4228.1593	7	15	4115.6714	7	3	3781.6404	2	4	9	7	3	4967.4428	14	20	4872.8064	14	-9									
5	3	2	4229.7108	3	19	4117.1101	2	0	3782.6589	1	0	9	7	2	4967.4428	14	15	4872.8064	14	8									
5	4	2	4295.5742	5	-9	4185.8294	5	0	3873.5617	8	3	9	8	2	5100.5669	3	27	5009.5010	5	6									
5	4	1	4295.6278	6	-9	4185.8510	4	-4	3873.5882	9	-4	9	8	1	5100.5669	3	-7	5009.5010	5	6									
5	5	1	4380.0958	57	-10	4274.2179	20	2				9	9	1	5246.8843		-26	5161.0431	14	-32									
5	5	0	4380.0958	57	-16	4274.2179	20	10				9	9	0	5246.8843		-26	5161.0431	14	-32									
6	0	6	4185.4923	3	-3	4070.7674	4	-2	3707.4839	2	0	10	0	10	4529.3460		3	4413.3943		3	4052.3515	3	-1						
6	1	6	4186.6214	1	1	4071.5244	4	0	3709.1128	2	3	10	1	10	4529.3591	2	4	4413.4287	4	0	4052.4745		4						
6	1	5	4235.8393	4	-5	4120.3548		-2	3763.7193	4	-1	10	1	9	4625.9808	1	-6	4510.5320	3	-2	4166.3585	2	-1						
6	2	5	4245.1164	4	15	4130.6621	3	5	3781.2932	2	-3	10	2	9	4635.2717	3	1	4511.6342	1	0									
6	2	4	4267.4558	3	0	4151.9734	3	-1	3802.1000	2	-3	10	2	8	4701.1281	3	-13	4584.6741	2	5	4247.3926		23						
6	3	4	4301.8377	8	18	4189.2446	4	2	3855.7114	9	7	10	3	8	4711.8149	6	-2	4595.9675	7	-1									
6	3	3	4306.0730	6	14	4192.5233	5	4	3858.5950	5	9	10	3	7	4751.1758	1	-8	4625.4746	8	1									
6	4	3	4369.8888	2	-1	4259.1418	8	3	3947.8673	9	-6	10	4	7	4790.6287	6	-13	4675.6319		-18									
6	4	2	4370.1407	5	3	4259.2664	3	3	3947.9992	5	-3	10	4	6	4801.1660	1	-5	4684.3064	5	-1									
6	5	2	4450.3807	19	-8	4347.0900	2	12				10	5	6	4863.0553	5	-17	4763.1588	2	-3									
6	5	1	4450.3838		-9	4347.0822	5	7				10	5	5	4863.5860	6	4	4763.2095		1									
6	6	1			4457.4307		-12					10	6	5	4970.7337	2	-8	4881.2431	1	7									
6	6	0			4457.4275	8	-14					10	6	4	4970.8044	9	3	4880.4827		-1									
7	0	7	4257.6289	3	-2	4142.4499	2	1	3779.9066	4	-2	10	7	4	5089.9085	17	15	4996.1605	9	-5									
7	1	7	4258.2342	10	-20	4142.8136	3	2	3780.7829	8	-2	10	7	3	5089.9085	17	-12	4996.1514	14	-16									
7	1	6	4319.8344	5	-6	4204.3604	4	1	3850.5733	3	2	10	8	3	5223.2645	3	8	5132.6893	13	-6									
7	2	6	4325.7197	5	10	4210.8927	5	4	3862.9510	8	1	10	8	2	5223.2645	3	7	5132.6893	13	-6									
7	2	5	4359.4416	3	-2	4243.2614	3	-3	3895.4039		-12	10	9	2	5369.9491	3	-16	5284.4740	5	2									
7	3	5	4387.4054	10	15	4273.8328	2	2	3941.9084	8	0	10	9	1	5369.9491	3	-16	5284.4740	5	2									
7	3	4	4396.6245	6	7	4281.9435	7	0	3948																				

TABLE 3—Continued

			(011)			(110)			(030)			(011)			(110)			(030)											
<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ	<i>J</i>	<i>K_a</i>	<i>K_c</i>	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ	<i>E</i>	Δ	δ			
1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	7	8	9	10
11	4	8	4925.6763	3	-16	4809.4777	5	-22				14	1	13	5162.3338	2	7	5045.9558	6	-20									
11	4	7	4944.0225	4	-15	4824.6703	3	2				14	2	13	5162.3625	12	0	5046.0526	2	-3									
11	5	7	4997.5194	3	1	4898.3717		-14				14	2	12	5283.7781		-5												
11	5	6	4998.6352	2	6	4899.1676	12	3				14	3	12	5284.2606		-9												
11	6	6	5105.3966	3	-6	5018.8300	1	9				14	3	11	5382.4669	3	-4	5264.9314		2									
11	6	5	5105.6069	2	-6	5016.9092	1	11				14	4	11	5402.1303	5	-5												
11	7	5	5224.6277		6	5131.7897	2	-1				14	4	10	5451.7585	4	20												
11	7	4	5224.6385		4	4131.7584	2	-1				14	5	10	5475.6772		-3												
11	8	4	5358.1374	9	-30	5268.0448	18	-2				14	5	9	5514.0515	2	9												
11	8	3	5358.1374	9	-27	5268.0448	18	1				14	6	9	5583.2029		8	5479.2115	1	4									
11	9	3	5505.1551		-7	5420.0339	17	4				14	6	8	5585.8031	6	2	5498.7666	4	-6									
11	9	2	5505.1551		-7	5420.0339	17	4				14	7	8	5702.1631	31	-18	5612.7979	4	-6									
12	0	12	4757.3588	58	8	4640.7497	7	0	4280.3060		0	14	7	7	5702.4643	18	-8	5612.0120	12	-11									
12	1	12	4757.3588	58	-26	4640.7601	12	-4	4280.3386		1	15	0	15	5169.5077	5	-9	5051.7486	6	47									
12	1	11	4875.6318		2	4759.7796	4	-16				15	1	15	5169.5077	5	-6	5051.7486	6	-14									
12	2	11	4929.8256		24	4760.1075		-5				15	1	14	5319.6080	14	16												
12	2	10	4974.9675	17	4	4858.8956	4	0				15	2	14	5319.6228	24	5												
12	3	10	4974.1516	7	-10	4863.0897	8	9				15	2	13	5451.6339	3	-1												
12	3	9	5047.7918	7	3	4875.7388	13	-4				15	3	13	5451.9123	3	-3												
12	4	9	5072.1868	5	-3							15	3	12	5562.4673	7	8												
12	4	8	5100.7022	5	6	4986.6041	4	-3				15	4	11	5643.7854	4	-12												
12	5	8	5165.5219	9	4	5045.7175		-28				15	5	11	5659.8571		4												
12	5	7	5169.8377	2	11	5048.3015	15	3				15	5	10	5707.3039	12	-23												
12	6	7	5252.4011	3	-9	5146.4129	10	3				15	6	10				5663.4955	8	-4									
12	6	6	5252.9519	4	-2	5144.4445	4	5				15	6	9	5771.5308		-11	5683.3160		-34									
12	7	6	5371.5905	9	-4	5279.7180	1	0				15	7	9	5885.6946	23		5798.3739	7	-6									
12	7	5	5371.6288	4	0	5279.6145	6	-5				15	7	8	5886.4121	19	11	5796.4827	7	24									
12	8	5	5505.1578	24	-54							16	0	16	5325.5187		-8												
12	8	4	5505.1578	24	-69							16	1	16	5325.5187		-4												
12	9	4	5652.4555	9	10	5567.6710		-1				16	1	15	5486.1502	2	2												
12	9	3	5652.4555	9	10	5567.6710		-1				16	2	15	5486.1554	3	-10												
13	0	13	4885.4088	21	11	4768.4368	30	40	4408.2128		153	16	2	14	5628.5706	9	2												
13	1	13	4885.4088	21	-5	4768.4368	30	-16	4408.2128		-26	16	3	14	5628.7358		5												
13	1	12	5014.3426	18	17							16	3	13	5750.8369		9												
13	2	12	5014.3997		9	4898.4210		20				16	5	12	5855.8152		6												
13	2	11	5124.9297	6	-12							16	7	10	6081.2833		14												
13	3	11	5125.5776	2	-14	5011.3556	8	-4				16	7	9	6082.8528		20												
13	3	10	5210.8040	10	4	5092.9150		20				17	0	17	5490.8074	14	-4												
13	4	10	5230.3889	11	11							17	1	17	5490.8074	14	2												
13	4	9	5270.3232	10	15	5152.2944	9	-3				17	1	16	5661.9498	48	21												
13	5	9	5303.8315	4	5	5204.8980	2	3				17	2	16	5661.9498	48	-14												
13	5	8	5334.8090	4	8							17	3	15	5814.6936		-19												
13	6	8	5411.6977	7	-5	5306.7279		28				17	3	14	5947.7457	15	6												
13	6	7	5412.9674	3	4	5326.1842		15				18	0	18	5665.3482	9	-12												
13	7	7	5530.7791	13	-14	5440.0079	5	-2				18	1	18	5665.3482	9	-4												
13	7	6	5530.8944		7	5439.7081	12	-9				18	1	17	5846.9780	26	-21												
13	8	6	5664.2974		-4							18	2	17	5846.9780	26	-41												
13	8	5	5664.2933	14	-103							18	2	16	6009.7962	10	-33												
13	9	5	5811.7970	6	-1							18	3	15	6153.3583		31												
13	9	4	5811.7970	6	-3							19	0	19	5849.1220		29												
14	0	14	5022.7963	11	-13	4905.4323	14	0	4545.3570		39	19	1	19	5849.1220		39												
14	1	14	5022.7963	11	13	4905.4323	14	-40	4545.3570		-50																		

unsaturated) lines; (2) since the precision of the positions of very weak lines is considerably worse than that of the lines of medium strength, the former were not taken into account in the determination of mean values appearing in columns 2, 5, and 8. The Δ value in columns 3, 6, and 9 of Table 3 is the uncertainty of the mean value determined from several such individual energies in units of 10^{-4} cm^{-1} .

The obtained upper state energies then were used as the initial data in the procedure of determining the parameters of the Hamiltonian [1]–[4]. It should be mentioned that the as-

signment of the spectral lines and the procedure of the determination of spectroscopic parameters were made at the same time. For this reason we were able to assign without a doubt even such lines in the spectrum which have no counterparts useful for the GSCD method. Such energies (determined only from one single line) are presented in Table 3 without experimental uncertainty.

To determine the spectroscopic parameters of the Hamiltonian [1]–[4], the fit of all experimentally obtained energies from Table 3 was made. In this case, in the upper state fit

TABLE 4
Parameters of Resonance Interactions for the Second Triad (in cm⁻¹)^a

Fermi		Coriolis	
Parameter	Value	Parameter	Value
$F_0^{110-030}$	23.93(167)	$C_{yK}^{110-011}10^4$	-4.585(337)
$F_f^{110-030}10^2$	1.533(587)	$C_{zz}^{110-011}10$	1.78558(362)
$F_{xy}^{110-030}10^2$	-4.713(707)	$C_{zzK}^{110-011}10^4$	-0.8333(216)
$F_{xyK}^{110-030}10^4$	8.61(122)	$C_{zz}^{030-011}10$	-0.2344(359)
$F_{xyJ}^{110-030}10^4$	1.055(178)	$C_{zzK}^{030-011}10^4$	4.189(231)
$F_{xyKK}^{110-030}10^6$	-8.898(939)	$C_{zzJ}^{030-011}10^4$	0.3425(874)
$F_{xyKJ}^{110-030}10^6$	-0.929(167)	$C_{yxy}^{030-011}10^4$	-0.3645(786)

^a See footnote to Table 2.

(determination of the parameters of the Hamiltonian) energies were used with the weights equal to $(10/\Delta)^2$ (Δ in units of 10^{-4} cm⁻¹). This means that levels with $\Delta = 10 \times 10^{-4}$ cm⁻¹ were unit-weighted. When the upper energy was obtained only from one single transition, it was given the weight of 1/100 (using the weight of 1/100 for such energies looks like a suitable procedure because the results of a fit, on the one hand, faintly depend on them and, on the other hand, indicate quality of a prediction power of a fit). The results of the fit are presented in columns 3–5 of Table 2. The values in parentheses in this table are the 1σ statistical confidence intervals for corresponding spectroscopic parameters in the last digits.

It should be mentioned that the presence of strong resonance interactions between all three bands of the second triad allowed us to determine stable values of resonance interaction parameters which are presented in Table 4. Such strong resonance interactions already appear in the spectrum for small values of the quantum number J . As an illustration, one can see an irregular rotational structure of the (110) vibrational state beginning already at a J value of $J = 6$.

We believe that the obtained parameters are correct because: (1) They reproduce the experimental energies with accuracies close to the experimental uncertainties. This statement is confirmed by the δ values in columns 4, 7, and 10 of Table 3, which are the differences between experimental energy values in units of 10^{-4} cm⁻¹ and those calculated with the parameters of Tables 3 and 4. Slightly larger than usual values of the δ for some of the $[JJ0]$ and $[JJ1]$ rotational states of the (011) vibrational state (see column 4 of Table 3) can be explained by

the fact that the corresponding energy values were obtained, as a rule, from blended lines, of the positions which are determined with a low accuracy. (2) The values of the parameters from columns 2–5 of Table 2 correlate with each other. This means that the determined parameters are physically meaningful.

5. CONCLUSION

The analysis of the high-resolution Fourier transform spectra of the D₂O molecule carried out in the framework of the Hamiltonian model which takes into account resonance interactions between the states (011), (110), and (030) allowed us to improve considerably the knowledge of the rotational vibrational structure of the (011) state. For the first time we were able to determine rotational energies of the (110) and (030) vibrational states with values of quantum number J up to 15 and 14, respectively.

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