High-Resolution Study of the First Hexad of D₂O

Xiang-huai Wang,* O. N. Ulenikov,†,1 G. A. Onopenko,† E. S. Bekhtereva,† Sheng-gui He,*
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

The high-resolution Fourier transform spectra of the D₂O molecule have been recorded and assigned in the 4200–5700 cm⁻¹
region where the vibration–rotation bands $2\nu_1$, $2\nu_3$, $\nu_1 + \nu_3$, $\nu_1 + 2\nu_2$, $2\nu_2 + \nu_3$, and $4\nu_2$ are located. The presence of numerous
and very strong accidental perturbations between the states of the hexad makes it necessary to take into account not only
ordinary resonance interactions of the Fermi, Darling-Dennison, and/or Coriolis types, but interactions between the states
$(\nu_1\nu_2\nu_3)$ and $(\nu_1 \mp 2\nu_2 \pm 2\nu_3 \pm 1)$ as well. Parameters of all six vibrational states of the hexad were obtained from the fit of
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1. INTRODUCTION

Recently (*1*) we analyzed the high-resolution Fourier transform spectrum of the D₂O molecule in the region 3200–4200 cm⁻¹, where the bands of the second triad of interacting vibrational states are located. The present paper is a continuation of that study and is devoted to the analysis of the Fourier transformed spectra of D₂O in the shorter wavelength region where the strongly interacting states of the first hexad are located.

Earlier only three bands of that hexad (namely, (101), (200), and (120)) were studied in Ref. (*2*) with a low resolution. Rotational structures of the (021) and (002) bands were recorded and analyzed in the present study for the first time.

2. EXPERIMENTAL DETAILS

The sample of D₂ ¹⁶O was purchased from PeKing Chemical Industry, Ltd. (China). The stated abundance of deuterium was 99.8%. The spectra were recorded at room temperature with the Bruker IFS 120HR Fourier transform interferometer (Hefei, China), which is equipped with a multipass gas cell with adjustable path length, a tungsten source, a CaF₂ beam-splitter, and a liquid-N₂-cooled InSb detector. To cover the whole studied region, two optical filters were used, whose cut off frequencies are 4080/4980 and 5040/6170 cm⁻¹, respectively. The unapodized resolution was 0.01 cm⁻¹, and the apodization function was Blackman-Harris 3-Term.

Since in the region under study there are many absorption lines due to H₂O and HDO, we mixed D₂O with H₂O at different ratios in order to identify D₂O lines without doubts.

The ratios were estimated by the recorded spectra. Since the strengths of the D₂O absorption bands vary quite a lot, different sample pressures and path lengths were used to record both the strong and weak lines, as detailed in Table 1. The total pressures were measured by a pressure gauge whose accuracy was better than 1 Pa. The signal-to-noise ratios (SNR) of the measured spectra varied from 800 to 4500. The frequency was calibrated with HDO lines in this region reported by Toth (*3*). The estimated precision in positions of not very weak, not very strong unblended lines was 2–5 × 10⁻⁴ cm⁻¹. For illustration, a small piece of one of the recorded spectra is presented in Fig. 1.

3. HAMILTONIAN MODEL

As the analysis shows, all six vibrational states of the first hexad are strongly interacting with each other. For this reason, the effective Hamiltonian in the most general form was used in the present study:

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

Here the diagonal operators H_{vv} ($v = 1, 2, 3, 4, 5, 6$) are the usual Watson operators (*4*),

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

TABLE 1
Experimental Details

Region, cm^{-1}	Total pressure, Pa	Path length, m	D$_2$O ratio, %	HDO ratio, %	H$_2$O ratio, %	Number of scans	SNR
4200 - 5250	527	15	25	50	25	166	800
4800 - 5710	527	15	25	50	25	300	2400
4800 - 5710	106	15	25	50	25	200	4500
5248 - 5485	113	15	81	18	1	200	2100
4928 - 5250	253	15	81	18	1	200	3600
5200 - 5710	503	87	81	18	1	600	1400
4800 - 5200	1540	105	98	2	0.01	250	2600
4200 - 5200	1540	105	98	2	0.01	235	1700

$$+ [J_{xy}^2, h_K^v J_z^4 + h_{JK}^v J^2 J_z^4 + h_J^v J^4] + L_K^v J_z^8$$
$$+ L_{KJ}^v J_z^6 J^2 + L_{KJK}^v J_z^4 J^4 + L_{JK}^v J_z^2 J^6 + L_J^v J^6$$
$$+ [J_{xy}^2, l_K^v J_z^6 + l_{KJ}^v J_z^4 J^2 + l_{JK}^v J_z^2 J^4 + l_J^v J^6]$$
$$+ P_K^v J_z^{10} + Q_K^v J_z^{12}; \qquad [2]$$

$|1\rangle = (200)$, $|2\rangle = (002)$, $|3\rangle = (120)$, $|4\rangle = (040)$, $|5\rangle = (101)$, and $|6\rangle = (021)$. The $H_{vv'} = H_{v'v}^+$ ($v \neq v'$) account for the operators of different kinds of resonance interactions. In this case, the operators $H_{vv'}$ which describe interactions between the states of the same symmetries have the form:

$$H_{vv'} = H_{v'v}^+ = F_0^{vv'} + F_J^{vv'} J^2 + F_{KK}^{vv'} J_z^4 + F_{JK}^{vv'} J^2 J_z^2$$
$$+ F_{KKK}^{vv'} J_z^6 + \cdots + F_{xy}^{vv'} J_{xy}^2 + F_{xyK}^{vv'} [J_{xy}^2, J_z^2]_+ \qquad [3]$$
$$+ F_{xyJ}^{vv'} J_{xy}^2 J^2 + \cdots F_{xyxy}^{vv'} J_{xy}^4 + F_{xyxyJ}^{vv'} J_{xy}^4 J^2 + \cdots .$$

In turn, the operators which describe interactions between the states of different symmetries (A_1 and B_1) have the form:

$$H_{vv'} = H_{v'v}^+ = C_{yK}^{vv'} [iJ_y, J_z^2]_+ \ldots$$
$$+ C_{xz}^{vv'} [J_x, J_z]_+ + C_{xzK}^{vv'} [[J_x, J_z]_+, J_z^2]_+ \qquad [4]$$
$$+ C_{xzJ}^{vv'} [J_x, J_z]_+ J^2 \cdots + C_{yxy}^{vv'} [J_y, J_{xy}]_+ \ldots .$$

In Eqs. [2]–[4] the following notations are used: $J_{xy}^2 = J_x^2 - J_y^2$, and $J^2 = \sum_\alpha J_\alpha^2$.

As the analysis shows, the rotational–vibrational energies determined on the basis of experimentally recorded spectra cannot be reproduced with satisfactory accuracy if one takes into account only ordinary resonance interactions of the Fermi, Darling-Dennison, or Coriolis types. Even adding numerous extra terms to those three types of interaction operators preserves large discrepancies between experimental and calculated values of some of the rotation–vibration energies. On the

other hand, the addition of the operator $H_{(200)(021)}$ to the Hamiltonian [1] improves the situation immediately.

The importance of including the resonance interactions of the $H_{(200)(021)}$ type in the Hamiltonian model, Eq. [1], can be understood from the following simple considerations. It is clear that any of the operator matrix elements $H_{vv'}$ of the Hamiltonian [1] can be derived from the vibration–rotation Hamiltonian of a molecule (5),

$$(hc)^{-1} H = \frac{1}{2} \sum_\lambda w_\lambda (p_\lambda^2 + q_\lambda^2)$$
$$+ \frac{1}{2} \sum_{\alpha\beta} \mu_{\alpha\beta} (J_\alpha - G_\alpha)(J_\beta - G_\beta) \qquad [5]$$
$$- \frac{\hbar^2}{8} \sum_\alpha \mu_{\alpha\alpha} + V_{anh}(k_{\lambda\ldots\mu}; q_\lambda \cdots q_\mu),$$

by using the results and formulas of the operator perturbation theory (in the form of contact transformation, e.g., Refs. (6–7), or projector formulation of operator perturbation theory, e.g., Refs. (8–9)). In any case, if one remembers that the vibration–rotation operator [5] can be expressed in the form of a series expansion of terms of different order of the small Born–Oppenheimer parameter κ, then it can be easily shown that the terms of the form

$$\sim \frac{\langle q_3 (J_x J_z + J_z J_x) \rangle \langle k_{1122} q_1^2 q_2^2 \rangle}{\omega_3 (2\omega_2 - 2\omega_1)} \qquad [6]$$

and

$$\sim \frac{\langle G_y J_y \rangle \langle k_{112} q_1^2 q_2 \rangle}{(\omega_3 + \omega_2)(\omega_2 - 2\omega_1)} \qquad [7]$$
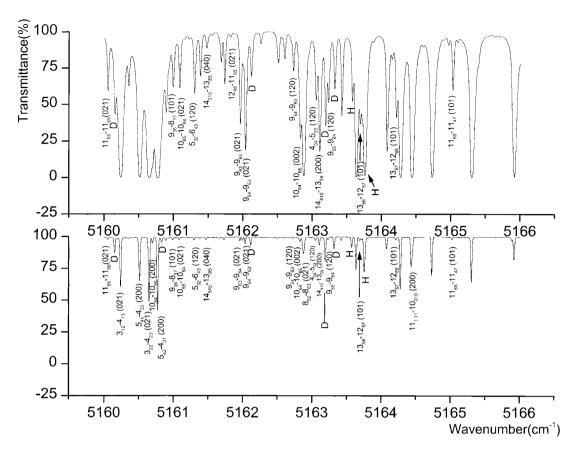
FIG. 1. A portion of the D$_2$O spectra in the region of the first hexad of interacting vibrational states. The upper spectrum was measured at a total pressure of 1540 Pa (about 98% of D$_2$O), with an absorption path length of 105 m; the lower one was measured at a total pressure of 253 Pa and an absorption path length of 15 m. The lines marked by D and H belong to HDO and H$_2$O, respectively.

will be generated in the $H_{(v_1 v_2 v_3)(v_1 \mp 2v_2 \pm 2v_3 \pm 1)}$ elements of the effective Hamiltonian, Eq. [1]. In this case, in accordance with the statements of ordinary vibration–rotation theory, Eq. [6] has to be a value of the order κ^3 in comparison to the values of the rotational constants (compare with the values C_{xz} of the ordinary Coriolis resonance interactions $C_{xz}(J_x J_z + J_z J_x)$ which have the order κ^2 in comparison with the values of the rotational constants (7)). On the other hand, it is clear that the expression in Eq. [7] has a value on the order of κ^1 (the analogous term $C_{xz} J_x$ in the ordinary Coriolis resonance block $H_{(v_1 v_2 v_3)(v_1 \mp 1 v_2 v_3 \pm 1)}$ has a value of the same order of magnitude as the rotational parameters (7)). The presented arguments explain and confirm the important role of the $(V_1 V_2 V_3) - (V_1 \mp 2V_2 \pm 2V_3 \pm 1)$-type interactions in a description of high-resolution vibration–rotation spectra.

4. ASSIGNMENT OF TRANSITIONS

Thanks to the high sensitivity of the spectrometer and the possibility of using long path lengths, on the one hand, and the presence of strong accidental resonance interactions between all six vibrational states of the hexad, on the other hand, we were able to assign transitions of the five vibration–rotation bands: $v_1 + v_3$, $2v_2 + v_1$, $2v_1$, $2v_3$, and $v_1 + 2v_2$. The ground

TABLE 2
Statistical Information on Bands of the D$_2$O Molecule (First Hexad)

Band	Band center, in cm^{-1}	J^{max}	K^{max}	Number of lines	Number of upper energies
1	2	3	4	5	6
$4v_2$	4588.6568				
$2v_2 + v_3$	5105.3845	18	7	450	142
$v_1 + 2v_2$	4990.8260	14	6	350	102
$2v_1$	5291.7221	16	7	680	168
$v_1 + v_3$	5373.9022	20	9	820	211
$2v_3$	5529.4372	17	7	370	75

TABLE 3
Experimental Rovibrational Term Values for the (101), (021), and (200) Vibrational States of the D_2O Molecule (in cm^{-1})[a]

J	K_a	K_c	(200) E	Δ	δ	(101) E	Δ	δ	(021) E	Δ	δ
0	0	0	5291.7226		28	5373.9026		12	5105.3850		-11
1	0	1	5303.5285	1	-4	5385.7881	10	4	5117.4514		-9
1	1	1	5311.3688	1	-3	5393.2852	1	7	5127.3907	1	3
1	1	0	5313.7573	1	-3	5395.7175	14	5	5130.0845	1	1
2	0	2	5326.6734	1	-3	5409.0513	4	14	5141.0974	1	-10
2	1	2	5332.5955	1	-2	5414.6364	12	-6	5148.8369	1	2
2	1	1	5339.7548	2	1	5421.9270	2	9	5156.9101	2	-3
2	2	1	5363.1887	3	-1	5444.3336	12	-11	5186.5311	2	13
2	2	0	5363.6526	2	1	5444.8366	10	1	5187.0077	1	10
3	0	3	5360.3199	2	-2	5442.6396	14	-17	5175.4596	5	-6
3	1	3	5364.1603	2	0	5446.3685	1	1	5180.7185	1	-1
3	1	2	5378.4009	1	0	5460.8539	9	-3	5196.7871	2	-3
3	2	2	5398.5914	1	1	5480.0768	2	-2	5222.7752	2	10
3	2	1	5400.7973	2	0	5482.4409	14	-7	5225.0570	2	10
3	3	1	5443.7282	2	1	5523.4490	10	-2	5278.4618	3	-8
3	3	0	5443.6150	2	-2	5523.5153		-7	5278.5163	1	-5
4	0	4	5403.6397	1	0	5486.0662	5	3	5219.6959	2	-15
4	1	4	5405.8079	3	0	5488.2121		-18	5222.7653	5	-3
4	1	3	5429.2026	3	4	5511.9550	5	2	5249.2128	2	-7
4	2	3	5445.4068	3	3	5527.2974	10	-9	5270.6866	2	11
4	2	2	5451.4250	3	5	5533.6754	8	6	5276.9826	3	7
4	3	2	5491.6405	2	-1	5572.2554	3	-8	5327.7253	2	0
4	3	1	5491.8465	1	0	5572.6943	3	-5	5328.0923	2	-1
4	4	1	5552.6373		-2	5630.9824		-4	5403.1737		-45
4	4	0	5552.6272		-1	5630.9888		-7	5403.1790		-44
5	0	5	5456.1945	3	0	5538.6953	1	-1	5272.8164	1	4
5	1	5	5457.2978	4	1	5539.9526	4	-2	5274.7187	1	-1
5	1	4	5491.4065	3	3	5574.3955	16	-9	5313.4291	3	-4
5	2	4	5503.3181	3	4	5585.6644	4	-1	5329.9324	4	6
5	2	3	5515.5622	2	3	5598.5087	2	-4	5342.9395	2	5
5	3	3	5551.6632	5	0	5633.2076	3	-5	5389.3440	3	-1
5	3	2	5552.8607	1	0	5634.8131	2	-1	5390.7358	1	6
5	4	2	5612.3706	4	-1	5687.2126	4	9	5465.5763	1	-18
5	4	1	5612.3083	4	2	5687.2419	3	6	5465.6176	3	-13
5	5	1	5695.2460	3	2	5766.5662	16	-21	5559.6791		-40
5	5	0	5695.3371	5	-2	5766.5662	16	1	5559.6791		-44
6	0	6	5517.9159	1	2	5600.5324	4	-5	5335.3339	2	-1
6	1	6	5518.4395	7	-2	5601.6620	2	-4	5336.3793	1	0
6	1	5	5564.0521	1	4	5647.1425	2	4	5388.4410	1	-5
6	2	5	5571.9647	3	4	5654.8320	5	-5	5400.1401	3	3
6	2	4	5592.5029	2	6	5676.4226	3	3	5422.5468	4	2
6	3	4	5623.6049	3	3	5706.1217	2	-2	5463.1759	3	4
6	3	3	5627.2080	7	6	5710.3845	1	0	5467.0103	1	6
6	4	3	5684.4865	2	-4	5769.6601	3	0	5540.3208	3	2
6	4	2	5684.3241	2	-5	5769.8432	2	-3	5540.5057	3	2
6	5	2	5758.0985	3	0	5837.7740	2	6	5632.7750	17	-4
6	5	1	5757.8300	5	1	5837.7277	2	7	5632.7750	17	-49
6	6	1	5858.3835	11	8	5929.5571	3	3	5746.6854	4	-5
6	6	0	5858.3835	11	17	5929.5571	3	4	5746.6854	4	-6
7	0	7	5588.8657	4	0	5671.6448	3	-8	5406.9460	1	2
7	1	7	5589.1043	1	3	5671.4772	3	-5	5407.7841	2	-1
7	1	6	5646.2298	1	1	5729.2873	3	-2	5473.2294	1	0
7	2	6	5650.9793	2	4	5734.5920	3	-1	5480.9373	4	0
7	2	5	5683.2453	2	3	5766.5922	2	4	5515.0785	2	4
7	3	5	5707.1995	3	4	5790.7400	2	2	5548.9682	1	-3
7	3	4	5715.1822	9	8	5799.7862	3	4	5557.4397	3	3
7	4	4	5769.0455	3	-2	5841.0629	5	-3	5627.4400	3	12
7	4	3	5768.9108	2	-9	5841.5844	2	2	5628.0619	3	13
7	5	3	5856.4391	2	-2	5920.7551	4	12	5718.2377	4	5
7	5	2	5855.8399	3	2	5921.1789	3	6	5718.2622	4	-3
7	6	2	5943.9959	1	0	6013.0210	4	-2	5832.4865	18	13
7	6	1	5944.0058	4	3	6013.0210	4	10	5832.4865	18	1
7	7	1	6051.1780	4	-7	6119.1839	3	-5	5962.8070	2	7
7	7	0	6051.1780	4	-9	6119.1839	3	-5	5962.8070	2	7
8	0	8	5669.1043	2	1	5752.0861	13	-8	5487.7607	5	0
8	1	8	5669.2095	4	0	5752.0861	13	-7	5487.8152	2	1
8	1	7	5737.4103	6	-2	5820.4082	5	-1	5567.0865	3	-5
8	2	7	5740.0267	7	-2	5825.8692	3	0	5572.0360	2	0
8	2	6	5784.0843	3	-3	5867.9714	3	2	5619.5912	6	0
8	3	6	5802.0933	5	1	5886.7874	5	3	5646.3936	4	-5
8	3	5	5815.5244	3	-1	5902.9509	7	-1	5662.1905	5	3
8	4	5	5865.8935	2	-1	5936.7871	2	-3	5726.9045	4	12
8	4	4	5866.3480	2	-6	5938.0749	5	-5	5728.6147	2	9
8	5	4	5955.6577	4	1	6016.5753	3	5	5816.1068		-3
8	5	3	5953.9771	5	-1	6017.0356	5	-2	5816.2043	2	-1
8	6	3	6041.7341	7	-3	6108.6713		-1	5930.5978	8	16
8	6	2	6041.7865	3	2	6108.6658		5			
8	7	2	6148.5475	4	20	6214.6082	3	-3	6061.1473	4	-13
8	7	1	6148.5475	4	-8	6214.6082	3	1	6061.1473	4	-13
9	0	9	5758.6628	6	5	5841.8621	4	-1	5577.8297	2	6
9	1	9	5758.7071	4	-1	5841.8860	5	0	5577.8884	2	2
9	1	8	5837.4853	3	-2	5920.4716	3	-2	5669.7680	3	3
9	2	8	5838.8371	4	-1	5935.9692	5	4	5673.8026	2	27
9	2	7	5895.5093	5	-4	5979.3389	7	3	5734.9918	4	10
9	3	7	5907.8820	5	6	5993.7497	3	0	5755.1035	2	-11
9	3	6	5920.1477	3	1	6019.2913	8	-3	5780.9043	4	0
9	4	6	5974.7454	7	5	6044.9772	5	-1	5838.6106	4	2
9	4	5	5976.6987	2	1	6047.5288	5	0	5842.6474	9	-1
9	5	5	6068.0344	6	5	6124.5461	4	2	5926.4021	2	-1
9	5	4	6063.9015	5	11	6125.4649	4	-3	5926.7258	7	-12
9	6	4	6151.6513	4	-1	6216.5843	5	-7	6041.0081	3	5
9	6	3	6151.8169	1	2	6216.5601	3	1	6041.0651	5	12
9	7	3	6257.9515	1	-1	6322.1875	19	-17			
9	7	2	6257.9686		-3	6322.1875	19	3			
9	8	2				6441.5055	2	2	6317.4607	3	4
9	8	1				6441.5055	2	3	6317.4607	3	-4
9	9	1				6573.2605	11	0			
9	9	0				6573.2605	11	0			
10	0	10	5857.5554	7	15	5941.0307		1	5677.1727		2
10	1	10	5857.5616	3	-10	5941.0345	2	0	5677.2040	5	4
10	1	9	5946.5837	7	3	6029.6282	4	3	5781.3194	6	-1
10	2	9	5947.2120	6	-4	6029.6796	4	-1	5781.7766	7	-14
10	2	8	6016.3442	4	-1	6102.1011	4	0	5860.1810	5	22
10	3	8	6024.1517	6	7	6115.1385	6	17	5874.8861	2	-10
10	3	7	6063.2142	4	6	6147.8141	8	-5	5912.8031	2	-8
10	4	7	6095.2671	4	3	6165.7070	3	4	5943.8223		4
10	4	6	6096.9721	4	13	6169.6991	9	1			
10	5	6	6194.1082	5	1	6244.7191	6	-1	6049.1066		-9
10	5	5				6246.7088	7	-5	6049.9418	6	1
10	6	5	6273.8348	7	-5	6336.8603	6	-7	6163.5813	4	-8
10	6	4	6274.1144	9	2	6336.7797	2	2	6163.8901	3	3
10	7	4	6379.4039	13	9						
10	7	3	6379.4699	3	-4						
10	8	3				6560.8195	3	12	6440.5421	14	1
10	8	2	6503.5680		-10	6560.8195	3	20	6440.5421	14	0
10	9	2				6691.5695	9	-16			
10	9	1				6691.5695	9	-15			
11	0	11	5965.7502	6	-10	6049.5343	4	5			
11	1	11	5965.7598	9	-12	6049.5373	7	14			
11	1	10	6064.6805		3	6147.9601	4	4			
11	2	10	6065.0228	7	0	6148.0094	8	9			
11	2	9	6145.9451	3	1	6230.0151	1	2	5994.3073	4	11
11	3	9	6150.5224	9	-3	6230.0323	1	12	6006.4518	7	11
11	3	8	6202.5445	3	-9	6287.0288	6	-5			
11	4	8	6227.0918	6	8	6297.1371	7	-1			
11	4	7	6250.6559	8	0	6334.0283	2	1	6113.2160	2	0
11	5	7	6304.0812	6	11	6376.8345	8	-7			
11	5	6	6305.8660	10	-2	6381.0670	1	-2	6186.0329	6	3

[a] In Table 3 Δ is the experimental uncertainty of the energy value, equal to one standard deviation in units of 10^{-4} cm^{-1}; δ is the difference $E^{exp} - E^{calc}$, also in units of 10^{-4} cm^{-1}; Δ is not quoted when the energy value was obtained from only one transition (corresponding energies were used in the fit with the weight 1/100).

TABLE 3—*Continued*

			(200)			(101)			(021)						(200)			(101)			(021)		
J	K_a	K_c	E	Δ	δ	E	Δ	δ	E	Δ	δ	J	K_a	K_c	E	Δ	δ	E	Δ	δ	E	Δ	δ
	1		2	3	4	5	6	7	8	9	10		1		2	3	4	5	6	7	8	9	10
11	6	6	6408.4392	8	-3	6469.6364	4	-1	6299.5280	14	5	14	1	13	6474.3059	11	5	6558.4783	5	-7	6318.3242	5	0
11	6	5	6408.5640	9	1	6469.4244	1	4	6299.1155	8	-6	14	2	13	6474.3673	2	1	6557.7560	5	8	6318.3938	6	28
11	7	5	6512.9109	3	11	6573.9595	14	-14				14	2	12	6586.5108	5	-13	6670.5678	6	5			
11	7	4	6513.1075	7	5	6573.9315	5	7				14	3	12	6590.3574		-27	6670.7238	6	6			
11	8	4				6692.3421	5	-12	6575.7840	20	8	14	3	11	6679.0440	3	8	6764.5479		2			
11	8	3	6638.4168	6	5	6692.3386	1	-14	6575.7840	20	-7	14	4	11				6765.6355	2	-4			
11	9	3				6822.5331	8	7				14	4	10	6744.2021	1	4	6827.5494	7	18			
11	9	2				6822.5331	8	10				14	5	10				6850.3289	11	4			
12	0	12	6083.2743	21	45	6167.3796	11	24	5903.6901		0	14	5	9				6890.0559	4	15			
12	1	12	6083.2743	21	-11	6167.3796	11	-12	5903.6979		0	14	6	9	6862.2080	5	4	6942.3844	11	-2			
12	1	11	6192.0121	10	0	6275.5242	4	10	6031.5158	9	7	14	6	8	6884.5674	5	-2	6943.8341	6	9			
12	2	11	6192.1756	6	-1	6275.5542	5	9	6031.7600	5	8	14	7	8	6985.7934	3	-6	7043.8219	5	1			
12	2	10	6284.1355	2	7	6367.9329	4	9	6163.9883		-6	14	7	7	6987.0910	2	-1	7043.4739	17	4			
12	3	10	6286.6807	2	2	6368.2411	6	12				14	8	7	7116.3043	6	23	7160.0282		23			
12	3	9	6352.3315	4	2	6430.4549	3	1	6211.9427	1	-8	14	8	6				7159.9222	2	-8			
12	4	9	6369.8142	6	-2	6444.0104	4	1	6245.5023	6	-2	15	0	15							6312.8891	6	-2
12	4	8	6402.1256	4	-5	6450.2646	3	-6				15	1	15							6312.8891	6	4
12	5	8	6446.7403	14	1	6519.7970	2	-5				15	1	14	6629.3371	15	9	6713.6302	15	-10			
12	5	7	6447.1464	2	3	6528.7282	2	0				15	2	14				6713.6421	4	-27			
12	6	7	6555.7342	3	2	6615.0197	2	3				15	2	13	6751.5224	2	2	6835.4813	6	-7			
12	6	6	6555.0932	7	7	6614.6460	5	7	6487.5764	4	2	15	3	13				6835.2970	3	6			
12	7	6				6718.2334	5	1				15	3	12				6939.0763	4	6			
12	7	5	6658.9293	6	-4	6718.1504	2	6				15	4	12				6940.4405	4	-7			
12	8	5				6836.0577	3	-19				15	5	11				7030.3799		-10			
12	8	4	6785.7657	1	-2							15	6	10				7123.5123	4	-2			
12	9	4				6965.8468	7	-6				15	6	9				7128.3859	10	0			
12	9	3				6965.8468	7	6				16	0	16				6731.7514	20	-4	6467.7379	3	-3
13	0	13	6210.0895	12	17	6294.5723	20	45	6030.8495	11	16	16	1	16	6646.0697	8	23	6731.7514	20	-9	6467.7379	3	3
13	1	13	6210.0895	12	-10	6294.5723	20	-48	6030.8495	11	-29	16	2	14				7009.1402	17	2			
13	1	12	6328.5472		-6				6170.3240		3	16	3	14				7009.2943	4	12			
13	2	12	6328.6330	5	-2				6170.4533	2	5	16	3	13	7281.5286	3	-10	7124.0235	2	5			
13	2	11	6430.9997	15	-3	6514.7533	4	- 1	6288.1820	2	-15	16	4	13				7124.0984	9	2			
13	3	11	6432.3704	5	6	6567.2271		-12	6289.9288	3	-8	17	0	17				6896.0003	12	21	6631.7804	2	-5
13	3	10	6511.4160	2	-2	6597.7116	6	-2	6376.8656	7	7	17	1	17				6896.0003	12	9	6631.7804	2	5
13	4	10				6599.8396	6	-2				17	1	16				7051.8851	13	0			
13	4	9				6652.2926	2	-7				17	2	16				7051.8851	13	-11			
13	5	9				6682.5286	5	-3				17	2	15				7192.3264	6	-3			
13	5	8				6716.1449	4	0				17	3	15				7192.3462	4	23			
13	6	8	6689.4184	4	-5							17	3	14				7317.3136	6	1			
13	6	7	6713.7213	5	-4	6772.6784	4	6				17	4	14				7316.6405	3	-18			
13	7	7	6816.1031	3	4	6874.8345	2	-6				18	0	18							6804.9973	10	12
13	7	6				6874.6438	11	1				18	1	18				7069.4669	13	4	6804.9973	10	5
13	8	6	6944.8113	3	0	6991.9553	3	10				18	1	17				7234.7734	10	-12			
13	8	5				6991.9157	7	4				18	2	17				7234.7734	10	22			
14	0	14	6346.2005	7	40	6430.9856	10	11	6167.2435	13	-5	20	0	20				7443.8711	10	6			
14	1	14	6346.2005	7	-23	6430.9856	10	-1	6167.2435	13	-5	20	1	20				7443.8711	10	-10			

state combination difference method was used for the assignments, and the data from Ref. (*10*) were taken as the ground state rotational energies. In this case, about 820 transitions with the value $J^{\text{max.}} = 20$ were assigned to the strongest band $\nu_1 + \nu_3$. Statistical information on this and the other bands studied is presented in Table 2.

In the second step of the analysis, the assigned lines were used for determining the values of upper vibration–rotation energies "*E*," which are presented in columns 2, 5, and 8 of Table 3 and columns 2 and 5 of Table 4. These last values were determined as the mean values of several individual energies

obtained from the *P*, *Q*, and *R* transitions with the same upper state. In the present case, only "full quality" transitions were used in the determination of mean values, namely: (1) unblended, uncovered, and not too strong (only 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 was not taken into account in the determination of mean values *E* appearing in Tables 3 and 4. The value Δ in these tables is the experimental uncertainty of the mean value determined from several such individual energies in units of 10^{-4} cm^{-1}. Energies determined only from the one single line

TABLE 4

Experimental Rovibrational Term Values for the (002) and (120) Vibrational States of the D$_2$O Molecule (in cm^{-1})^a

J	K_a	K_c	(002) E	Δ	δ	(120) E	Δ	δ	J	K_a	K_c	(002) E	Δ	δ	(120) E	Δ	δ
			2	3	4	5	6	7				2	3	4	5	6	7
0	0	0				4990.8266		-13	7	4	3	6004.5442	4	5	5516.4682	4	-10
1	0	1				5002.8102	4	-4	7	5	3	6075.5477	7	-19	5613.6409	5	-3
1	1	1				5013.3260	4	2	7	5	2				5613.5227	4	-7
1	1	0				5015.9665	8	-19	7	6	2				5735.8827	5	3
2	0	2	5564.7705		2	5026.3291	4	-6	7	6	1	6162.6199		14			
2	1	2				5034.6516	4	2	8	0	8	5909.1180		4	5372.5341	3	1
2	1	1	5577.4259		0	5042.5709	3	-7	8	1	8	5909.0909	7	-3	5372.7976	3	6
2	2	1				5073.8998		-6	8	1	7	5977.5794	4	0	5451.8117	2	-14
2	2	0				5074.3379		6	8	2	7	5979.3098	2	-3	5457.1654	2	-5
3	0	3	5598.6347		0	5060.5727		-20	8	2	6	6025.5202	1	-1	5503.5679	6	12
3	1	3	5601.8961	1	2	5066.3761	7	11	8	3	6	6040.2051	5	-1	5532.7777	14	10
3	1	2	5616.5895	2	0	5082.1465	3	-8	8	3	5	6059.0781		13	5546.8562	11	1
3	2	2				5109.8596	4	3	8	4	5	6101.5851		2	5615.3070	8	-9
3	2	1				5111.9636		14	8	4	4	6104.8411		7	5615.5289	4	-13
3	3	1				5168.1841	3	-14	8	5	4	6173.9796	10	-2	5711.3881	3	-1
3	3	0				5168.2360		-10	8	5	3	6174.1996	5	-6	5711.0694	5	3
4	0	4	5642.1415		1	5104.6562	2	-5	8	6	2	6260.7951	8	-9			
4	1	4	5643.8913	8	2	5108.2455	2	17	9	0	9	5999.9359	3	7	5462.4080	3	-2
4	1	3	5667.9577	5	-5	5134.2412	1	-10	9	1	9	5999.3129	1	0	5462.5332	3	-10
4	2	3				5157.4297	4	13	9	1	8	6078.3151		-2	5554.6252	10	-6
4	2	2				5163.2838	1	5	9	2	8	6078.7546	6	-4	5557.7194	9	-1
4	3	2				5216.8087	4	4	9	2	7	6137.3905		5	5618.6103		33
4	3	1				5217.2138	10	-6	9	3	7	6146.9993		2	5640.6536	3	1
4	4	1				5296.0665		-21	9	3	6				5663.4230	9	-3
4	4	0				5296.0694		-5	9	4	6	6211.8748		5	5724.7901	10	1
5	0	5	5694.9171	3	4	5157.9895		6	9	4	5				5727.9709	7	9
5	1	5	5695.8925	4	6	5160.0070	5	18	9	5	5	6284.8598	12	-3	5821.8063	10	24
5	1	4	5730.6631	1	-4	5198.1695	5	-29	9	5	4	6285.5602		-5	5821.1579	3	9
5	2	4	5740.7393	5	2	5216.3022	3	5	9	6	4	6370.9719	8	5	5946.0404	5	-15
5	2	3	5754.2773	4	-1	5228.5187	13	-5	9	6	3				5945.9905	3	-10
5	3	3	5786.5667	5	2	5278.0377	4	-1	10	0	10				5561.5257	2	-9
5	3	2	5788.4465		5				10	1	10	6096.7164	12	3	5561.5819	6	-3
6	0	6	5756.9471		6	5220.3868		9	10	1	9	6183.6984	2	-14	5666.2605	6	5
6	1	6	5757.1951	4	4	5221.4489		25	10	2	9	6187.8800	1	-9			
6	1	5	5803.6586		-4	5273.0282	7	-12	10	2	8				5743.8165		30
6	2	5	5810.0208	3	-5	5286.1285		19	10	3	8				5759.3542	3	-12
6	2	4	5832.6735	1	2	5307.3658	7	4	10	4	7				5847.2981	3	11
6	3	4	5859.5654	8	-1	5351.1015		2	10	4	6				5854.0569	6	21
6	3	3	5864.5869		4	5354.3226	4	16	10	6	5				6069.7685		-9
6	4	3	5917.3560	5	0	5430.3081		-8	10	6	4				6069.5919	1	9
6	4	2	5917.7138	18	7	5430.3935		-23	11	0	11				5669.9429		11
6	5	1				5528.4737	10	7	11	1	11				5669.9123		-7
6	6	1				5649.3418	2	4	11	2	10				5787.6880		-3
6	6	0				5649.3418	2	6	11	3	9				5901.8686	8	9
7	0	7	5828.3156	6	8	5291.8777	8	6	11	3	8				5902.2978	6	-10
7	1	7	5828.4327	1	5	5292.4132	7	8	11	5	7				6080.3012	16	-6
7	1	6	5886.0827	7	0	5357.8291	11	-18	11	5	6				6079.2853	12	-1
7	2	6	5889.6542	7	-1	5366.5328	10	2	11	6	6				6206.0999	3	-4
7	2	5	5923.7895		-8	5398.9916	12	-5	11	6	5				6205.5580	7	13
7	3	5	5944.2482	6	5	5436.1319	3	4	12	0	12				5787.4789	3	-14
7	3	4	5954.8723		8	5443.5230	6	4	12	1	12				5787.5075	3	22
7	4	4	6003.3318		1	5516.0960	7	-2	12	1	11	6432.1868	3	1			

^{a} See footnote to Table 2.

TABLE 4—*Continued*

			(002)			(120)						(002)			(120)		
J	K_a	K_c	E	Δ	δ	E	Δ	δ	J	K_a	K_c	E	Δ	δ	E	Δ	δ
	1		2	3	4	5	6	7		1		2	3	4	5	6	7
12	2	11				5916.8138	5	2	14	3	12	6838.6211		-4			
12	2	10	6528.8158		3	6021.2347	4	19	14	3	11	6921.1701	2	-6			
12	3	10	6528.8001	10	1				14	4	10	6991.4651		-22			
13	2	12				6055.2570	10	3	15	0	15	6736.2686	12	-1			
13	2	11	6670.2614	7	-6				15	1	15	6736.2686	12	-1			
13	3	10	6772.7890	2	0				15	4	11	7179.0641	3	18			
14	0	14	6590.3087		19				16	0	16	6891.8684	6	1			
14	2	12	6827.5492	7	16				16	1	16	6891.8684	6	-3			

are presented in Tables 3 and 4 without experimental uncertainty.

5. DETERMINATION OF THE HAMILTONIAN PARAMETERS AND DISCUSSION

To determine the spectroscopic parameters of the Hamiltonian [1], the fit of all experimentally obtained energies from Tables 3 and 4 was made. In this case, because of the presence of numerous resonance interactions, the problem of a correct choice of initial values for the largest and most important spectroscopic parameters was solved first. This is important because the greater the number of interacting states, the more different correlations between band centers, rotational, and centrifugal distortion parameters, from the one hand, and resonance interaction parameters, from the other hand, occur. Under similar conditions, a fit of experimental data can lead to physically meaningless results, and the best way to avoid such a situation is to achieve a correct estimate of the values of the most important spectroscopic parameters.

In our case, the initial values of the parameters of the (200), (101), (002), and of the (120) and (021) states were fixed to the values of the corresponding parameters of the (000) and (020) states, respectively, from Ref. (*10*). Initial values of the parameters of the (040) state were estimated from interpolation of the values of corresponding parameters of the states (000), Ref. (*10*); (010), Ref. (*11*); (020), Ref. (*10*); and (030), Ref. (*1*). Initial values of the Fermi and Darling-Dennison $F_0^{vv'}$ parameters were estimated from the global vibrational–rotational fit of 23 bands belonging to the $v = 0, \frac{1}{2}, 1, 2, \frac{3}{2}, 2, 3, 4,$ and 5 polyads (here $v = v_1 + (v_2/2) + v_3$; v_1, v_2, and v_3 are the vibrational quantum numbers) (*12*). Initial values of all Coriolis type parameters were fixed to zero.

Energies from Tables 3 and 4 were then introduced into the fit procedure for the determination of the more exact values of the spectroscopic parameters. For this purpose, energies were used with weights equal to $(10/\Delta)^2$. This means that levels with $\Delta = 10$ (in units of 10^{-4} cm^{-1}) were unit-weighted. When the upper state energy was obtained from only one single transition, it was given the weight of 1/100. Results of the fit are presented in Tables 5 and 6. Values in parentheses in these tables are the 1σ statistical confidence intervals for corresponding spectroscopic parameters in the last digits. Parameters which are given without confidence intervals were fixed to their initial values. To confirm the physical meaningfulness of the determined parameters, columns δ of Tables 3 and 4 present differences between experimental energy values and the corresponding ones as calculated on the basis of the parameters from the energy values of Tables 5 and 6 (in units of 10^{-4} cm^{-1}).

The following important circumstance should be mentioned here. In spite of the absence of transitions which could be assigned to the $4\nu_2$ band, the (040) state perturbs the rotational structures of the states (120) and (021) so strongly that a correct reproduction of rotational–vibrational energies of these states is impossible already for quantum number $J \sim 6$ without taking into account the influence of the (040) state. As a consequence, at least two parameters (band center and A rotational constant) of the (040) state are determined with confidence from the fit, as can be seen in Table 5.

6. CONCLUSION

The analysis of the high-resolution Fourier transform spectra of the D₂O molecule carried out in the framework of a Hamiltonian model taking into account resonance interactions between the states (200), (002), (120), (040), (101), and (021) (both ordinary Fermi, Darling-Dennison, Coriolis interactions, and the new-type interaction between the state $(v_1 v_2 v_3)$ and $(v_1 \mp 2v_2 \pm 2v_3 \pm 1)$) enable us not only to

TABLE 5
Spectroscopic Parameters of the (200), (002), (120), (040), (101), and (021) Vibrational States of the D_2O Molecule (in cm^{-1})[a]

Parameter	(200)	(002)	(101)
E	5299.26300(40)	5521.05920(60)	5373.67980(50)
A	14.972630(800)	14.368240(800)	14.671797(500)
B	7.126590(800)	7.190201(800)	7.1630060(800)
C	4.707028(800)	4.749818(700)	4.7279049(600)
$\Delta_K \times 10^3$	8.3865(300)	7.7060(100)	8.2521(100)
$\Delta_{JK} \times 10^3$	-1.58563(400)	-1.40699(600)	-1.50300(400)
$\Delta_J \times 10^3$	0.294577(500)	0.334956(600)	0.321042(500)
$\delta_K \times 10^3$	0.22746(200)	0.46218(200)	0.28458(200)
$\delta_J \times 10^3$	0.117644(600)	0.136598(800)	0.125856(200)
$H_K \times 10^5$	1.4494(500)	1.3017(300)	1.5956(200)
$H_{KJ} \times 10^5$	- 0.18189(800)	-0.1530(100)	-0.25215(800)
$H_{JK} \times 10^5$	- 0.03683(200)	-0.03001(400)	-0.01424(100)
$H_J \times 10^5$	0.006667(200)	0.007328(200)	0.005884(100)
$h_K \times 10^5$	0.40219(700)	0.3153(100)	0.35436(500)
$h_{JK} \times 10^5$	- 0.00528	-0.00528	-0.008656(900)
$h_J \times 10^5$	0.0032894(700)	0.0037531(800)	0.0034163(800)
$L_K \times 10^7$	-0.4888(400)	-0.5964	-0.7258(300)
$L_{KJK} \times 10^7$	0.151	0.151	0.2659(200)
$L_{KJ} \times 10^7$	-0.0384	-0.0384	-0.05529(400)
$L_{JJK} \times 10^7$	0.000540	0.000540	0.000540
$L_J \times 10^7$	-0.000168	-0.000168	-0.0001839(200)
$l_K \times 10^7$	-0.173	-0.173	-0.173
$l_{KJ} \times 10^7$			
$l_{JK} \times 10^7$			
$l_J \times 10^7$	-0.0000836	-0.0000836	-0.0000836
$P_K \times 10^9$	0.1516	0.1516	0.1516

Parameter	(120)	(021)	(040)
E	4987.8152(30)	5105.60770(40)	4591.9696(100)
A	17.804742(400)	17.323660(400)	22.572807(900)
B	7.314352(300)	7.3822300(700)	7.52
C	4.663874(300)	4.6823020(600)	4.63
$\Delta_K \times 10^3$	21.4004(400)	18.8913(200)	64.1
$\Delta_{JK} \times 10^3$	-2.32128(900)	-2.22914(700)	-4.03
$\Delta_J \times 10^3$	0.35909(100)	0.376837(500)	0.421
$\delta_K \times 10^3$	1.29539(800)	1.36790(500)	3.18
$\delta_J \times 10^3$	0.150936(500)	0.155281(200)	0.183
$H_K \times 10^5$	8.5960(100)	6.5023(300)	44.7
$H_{KJ} \times 10^5$	- 0.9183(200)	-0.8291	-3.64
$H_{JK} \times 10^5$	0.0713(100)	0.14998(400)	0.276
$H_J \times 10^5$	0.007856(500)	0.010976(200)	0.01505
$h_K \times 10^5$	1.8196(400)	1.7061(200)	6.11
$h_{JK} \times 10^5$	0.02718(500)	0.05386(200)	0.00508
$h_J \times 10^5$	0.004125(300)	0.004654(100)	0.00735
$L_K \times 10^7$	-2.721(200)	-1.6095(300)	-3.45
$L_{KJK} \times 10^7$			
$L_{KJ} \times 10^7$			
$L_{JJK} \times 10^7$	0.02511(400)		
$L_J \times 10^7$			
$l_K \times 10^7$			
$l_{KJ} \times 10^7$			
$l_{JK} \times 10^7$			
$l_J \times 10^7$			
$P_K \times 10^9$			

[a] Values in parentheses are the 1σ statistical confidence intervals. Parameters presented without confidence intervals were fixed to their initial values (see text for details).

TABLE 6
Parameters of Resonance Interactions for the First Hexad of D_2O (in cm^{-1})[a]

Fermi and Darling-Dennison Type Interactions

Parameter	Value	Parameter	Value	Parameter	Value
$F_0^{200-002}$	-43.87	$F_J^{200-002}10^2$	-3.113(200)		
$F_{xy}^{200-002}10^2$	-4.0848(200)	$F_{xyK}^{200-002}10^4$	-0.6388(300)	$F_{xyJ}^{200-002}10^4$	-0.1354(200)
$F_0^{200-120}$	16.00	$F_J^{200-002}10^2$	-2.347(300)	$F_{KK}^{200-002}10^4$	-26.97(200)
$F_{JK}^{200-120}10^4$	-3.269(300)	$F_{KKK}^{200-002}10^6$	31.83(200)	$F_{xyK}^{200-002}10^4$	2.394(200)
$F_0^{120-040}$	39.20	$F_{xy}^{120-040}10^2$	-0.8937(200)		
$F_{xyxy}^{120-040}10^4$	0.1643(400)	$F_{xyxyJ}^{120-040}10^6$	-0.1433(300)		
$F_0^{101-021}$	7.71	$F_K^{101-021}10^2$	-17.214(600)	$F_J^{101-021}10^2$	-3.569(100)
$F_{xyK}^{101-021}10^4$	-1.096(200)	$F_{xyxy}^{101-021}10^4$	-0.01914(500)		

Ordinary Coriolis Type Interactions

Parameter	Value	Parameter	Value	Parameter	Value
$C_{yK}^{200-101}10^2$	-0.00898(400)	$C_{yJ}^{200-101}10^2$	-0.10600(900)		
$C_{(xz)}^{200-101}$	0.304488(100)	$C_{zzJ}^{200-101}10^3$	-0.09802(700)		
$C_{(xz)}^{002-101}$	-0.149473(200)	$C_{zzJ}^{002-101}10^3$	0.22812(300)	$C_{zzJJ}^{002-101}10^6$	-0.6309(500)
$C_{(xz)}^{120-101}$	0.03669(100)	$C_{yxyK}^{120-101}10^6$	10.166(400)	$C_{yxyJ}^{120-101}10^6$	-0.3496(100)
$C_{(xz)}^{002-021}$	0.05522(600)	$C_{xzK}^{002-021}10^3$	-0.4961(500)		
$C_{yK}^{120-021}10^2$	0.1615(300)	$C_{yJK}^{120-021}10^4$	-0.1790(100)	$C_{yKKJ}^{120-021}10^6$	0.1860(100)
$C_{(xz)}^{120-021}$	0.16574(100)	$C_{zzK}^{002-021}10^3$	0.0953(100)		
$C_{(xz)}^{040-021}$	0.20595(600)	$C_{zzK}^{040-021}10^3$	-2.4282(600)	$C_{xzJ}^{040-021}10^3$	-0.2730(300)
$C_{xzKK}^{040-021}10^6$	19.477(800)	$C_{xzJK}^{040-021}10^6$	3.970(300)		

New Coriolis Type Interaction

Parameter	Value	Parameter	Value	Parameter	Value
$C_y^{200-021}$	0.4802(900)	$C_{yJ}^{200-021}10^2$	-0.1702(100)	$C_{yJK}^{200-021}10^6$	6.82(100)
$C_{xz}^{200-021}10^2$	-3.603(100)	$C_{zzK}^{200-021}10^4$	-2.151(100)	$C_{xzJ}^{200-021}10^4$	-0.7733(900)
$C_{xzJJ}^{200-021}10^6$	0.1656(300)				

[a] See footnote to Table 5.

improve considerably the knowledge of the rotational–vibrational structures of the (101), (200), and (021) vibrational states, but for the first time also to determine rotational energies of the (002) and (210) vibrational states. The band centers and the A rotational constant of the (040) vibrational state were also estimated.

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