



High resolution vibration–rotation spectrum of the D₂O molecule in the region near the $2\nu_1 + \nu_2 + \nu_3$ absorption band

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The high resolution Fourier transform spectrum of the D₂O ($\nu = \nu_1 + \nu_2/2 + \nu_3 = 3.5$) polyad was analysed within the framework of the Hamiltonian model taking into account resonance interactions between the seven states (310), (211), (112), (013), (230), (131) and (032). Transitions belonging to the $2\nu_1 + \nu_2 + \nu_3$, $3\nu_1 + \nu_2$ and $3\nu_2 + 2\nu_3$ bands were assigned in the experimentally recorded spectrum. This provided the possibility of obtaining spectroscopic parameters of the ‘visible’ states (211), (310) and (032) and of estimating the band centres, and the rotational and resonance interaction parameters of the ‘dark’ states (112) and (131).

1. Introduction

The D₂O molecule, together with the HDO species and the parent H₂O, are a subject of great interest because of their important role in many problems, such as e.g. investigation of the dynamics of molecular vibrations and rotations, determination of the intramolecular potential function, studies of planetary atmospheres, study of the role of deuterium in interstellar molecules as an indicator of chemical reactions, investigation of industrial pollution, laser engineering, and so on.

The dideuterated water molecule has been the subject of several spectroscopic investigations (a short review of earlier studies of D₂O spectra can be found in [1]). The present contribution, being the continuation of our recent analysis [1–3], of the $\nu = 1.5$, 2, and 3 ($\nu = \nu_1 + \nu_2/2 + \nu_3$) polyads of the D₂O molecule, is devoted to consideration of the $\nu = 3.5$ polyad. Up until now there were no available studies of the high resolution vibration–rotation bands of this polyad. On the other hand, because of extreme weakness of the recorded bands (the usual Bruker IFS 120HR Fourier transform interferometer was used), only lines of the strongest $2\nu_1 + \nu_2 + \nu_3$ band of the $\nu = 3.5$ polyad were expected to appear in the spectrum. However, some transitions caused by resonance interactions and belonging to the $3\nu_1 + \nu_2$ and $3\nu_2 + 2\nu_3$ bands were assigned as well.

2. Experimental details

A sample of D₂O was purchased from PeKing Chemical Industry, Ltd. (China). The stated abundance of deuterium was 99.8%. The sample pressure was 1600 Pa. The spectra were recorded at room temperature with the Bruker IFS 120HR Fourier transform spectrometer (Hefei), which was equipped with a multipass gas cell with a path length of 105 m, a tungsten source, a CaF₂ beamsplitter, and a Ge diode detector. The unpodized resolution was 0.015 cm⁻¹, and the apodization function was the Blackman–Harris 3-term function.

In order to identify D₂O lines without doubt, another sample prepared by mixing ‘pure’ H₂O and D₂O in a 1:1 ratio was investigated under the same experimental conditions.

The line positions were calibrated with those of H₂O from the HITRAN96 base data. The accuracy of the positions of unblended lines was estimated to be no worse than 0.003 cm⁻¹, and a small part of the recorded spectrum is shown in figure 1.

3. Hamiltonian model and initial approximation for the parameters

As an analysis showed, in spite of the extreme weakness and the absence (with some exceptions) of lines belonging to the other rovibrational bands in the recorded spectrum, the rotational structure of the $2\nu_1 + \nu_2 + \nu_3$ band cannot be understood and described successfully if one neglects numerous resonance inter-

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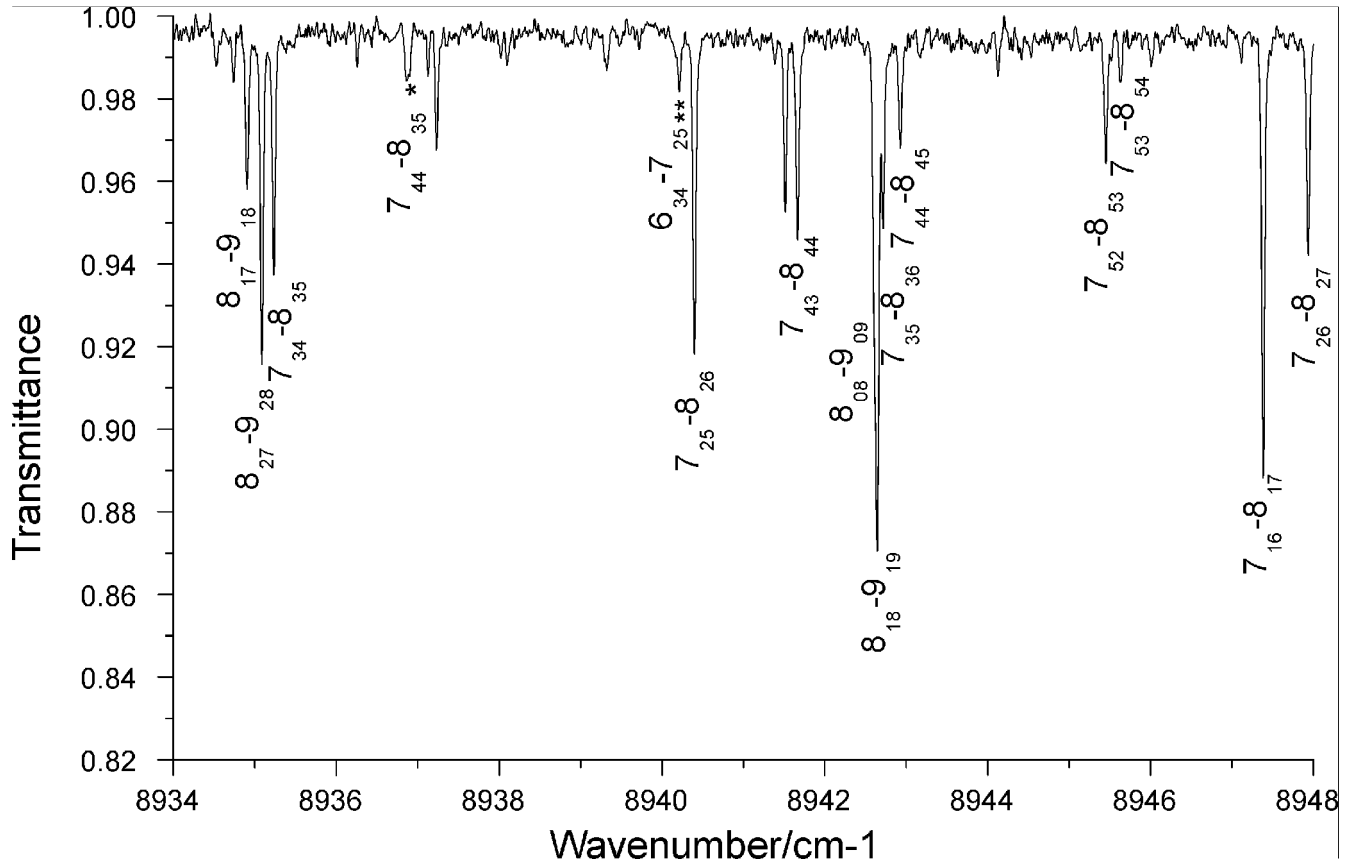


Figure 1. A small part of the region of location of the $2\nu_1 + \nu_2 + \nu_3$ band. Two weak lines can be seen (marked by * and **) belonging to the $3\nu_2 + 2\nu_3$ and $3\nu_1 + \nu_2$ bands, respectively. Experimental conditions: room temperature; pressure and absorption path length are 1600 Pa and 105 m, respectively.

actions between the (211) state, on the one hand, and the other vibrational states of the $\nu = 3.5$ polyad, on the other. For this reason, in a further theoretical description of the spectrum we took the Hamiltonian model with seven interacting vibrational states. We believe that the influence of the three lowest vibrational states, (070), (150) and (051), on the rotational structure of the (211) state can be neglected. This assumption is based on the fact that the (070), (150) and (051) states influence the (211) state not directly but via the states (230), (032) and (131) only.

Thus, the Hamiltonian used in our analysis has the form

$$H^{\text{eff}} = \sum_{i,j} |i\rangle\langle j|H^{ij}, \quad (1)$$

where $i, j = 1-7$, and the following notations are used: $|1\rangle = (310)$, $|2\rangle = (112)$, $|3\rangle = (230)$, $|4\rangle = (032)$, $|5\rangle = (211)$, $|6\rangle = (0,13)$ and $|7\rangle = (131)$. ‘Diagonal’ operators H^{ii} ($i = 1, 2, 3, 4, 5, 6, 7$) are the usual Watson’s operators [4]:

$$\begin{aligned} H^{ii} = & E^i + [A^i - \frac{1}{2}(B^i + C^i)]J_z^2 + \frac{1}{2}(B^i + C^i)J^2 \\ & + \frac{1}{2}(B^i - C^i)J_{xy}^2 - \Delta_K^i J_z^4 - \Delta_{JK}^i J_z^2 J^2 - \Delta_{Jz}^i J^4 \\ & - \delta_K^i [J_z^2, J_{xy}^2] - 2\delta_{Jz}^i J^2 J_{xy}^2 + H_{Kz}^i J_z^6 + H_{KJz}^i J_z^4 J^2 \\ & + H_{JKz}^i J_z^2 J^4 + H_{Jz}^i J^6 + [J_{xy}^2, h_{Kz}^i J_z^4 + h_{JKz}^i J_z^2 J^2 + h_{Jz}^i J^4] \\ & + L_K^i J_z^8 + L_{KKJz}^i J_z^2 J^2 + L_{JKz}^i J_z^4 J^4 + L_{JJz}^i J_z^2 J^6 \\ & + L_{Jz}^i J^6 + [J_{xy}^2, l_{Kz}^i J_z^6 + l_{KJz}^i J_z^4 J^2 + l_{JKz}^i J_z^2 J^4 + l_{Jz}^i J^6]. \end{aligned} \quad (2)$$

$H^{ij} = H^{ji+}$ ($i \neq j$) are operators of resonance interaction of different kinds. In this case, the operators H^{ij} which describe interactions between the states of the same symmetry have the form

$$\begin{aligned} H^{ij} = H^{ji+} = & F_0^{ij} + F_{Kz}^{ij} J_z^2 + F_{Jz}^{ij} J^2 + F_{KKz}^{ij} J_z^4 + F_{JKz}^{ij} J_z^2 J^2 \\ & + \dots + F_{xy}^{ij} J_{xy}^2 + F_{xyK}^{ij} [J_{xy}^2, J_x^2] + \dots \end{aligned} \quad (3)$$

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

$$\begin{aligned}
 H^{ij} = H^{i+} = & C_{y^i J_y}^{ij} + C_{y^i K}^{ij} [iJ_y, J_z^2] + C_{y^i J}^{ij} iJ_y J^2 \\
 & + C_{y^i K K}^{ij} [iJ_y, J_z^4]_{+\dots} + C_{x^i z}^{ij} [J_x, J_z]_{+} \\
 & + C_{x^i z K}^{ij} [[J_x, J_z]_{+}, J_z^2]_{+\dots}. \quad (4)
 \end{aligned}$$

In equations (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 in [2], an analysis of the situation shows that the rovibrational energies of the (211) state cannot be reproduced with satisfactory accuracy if one neglects extra

Table 1. Values of some band centres of the $\nu = 3.5$ polyad of D₂O (in cm⁻¹).

(1)	Centre ^a	
	(from prediction) (2)	(from the fit) (3)
3ν ₁ + ν ₂	9005.60	9005.35
2ν ₁ + ν ₂ + ν ₃	9050.41	9050.36
ν ₁ + ν ₂ + 2ν ₃	9199.98	9201.90
ν ₂ + 3ν ₃	9365.41	9365.46
2ν ₁ + 3ν ₂	8713.63	8713.31
ν ₁ + 3ν ₂ + ν ₃	8793.88	8788.60
3ν ₂ + 2ν ₃	8947.19	8934.60

^a See text for details.

Table 2. Experimental rovibrational term values for the (211) vibrational state of the D₂O molecule (in cm⁻¹).^a

J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ	J	K_a	K_c	E	Δ	δ
	(1)	(2)	(2)	(3)	(4)		(1)	(2)	(2)	(3)	(4)		(1)	(2)	(2)	(3)	(4)
1	0	1	9062.128	1	-6	5	5	1	9462.395	2	-2	8	3	5	9577.660	2	0
1	1	1	9070.449	1	-3	5	5	0	9462.395	2	-2	8	4	5	9629.572	2	-5
1	1	0	9073.003	1	-3	6	0	6	9274.042	2	-3	8	4	4	9632.526	4	-4
2	0	2	9085.168	3	-4	6	1	6	9274.385	1	0	8	5	4	9712.497	3	17
2	1	2	9091.601	1	-3	6	1	5	9323.509	5	7	8	5	3	9712.313	1	0
2	1	1	9099.184	1	0	6	2	5	9329.873	1	0	8	6	3	9811.133	4	3
2	2	1	9123.982	1	5	6	2	4	9356.173	2	5	8	6	2	9811.133	4	7
2	2	0	9124.485	1	6	6	3	4	9384.624	3	-9	9	0	9	9510.796	2	8
3	0	3	9118.556	2	-3	6	3	3	9388.853	3	-17	9	1	9	9510.825	3	-1
3	1	3	9123.326	2	-7	6	4	3	9450.692	1	-3	9	1	8	9594.806	3	0
3	1	2	9138.009	2	2	6	4	2	9451.037	1	0	9	2	8	9595.618		-10
3	2	2	9158.230	2	6	6	5	2	9533.527	6	-1	9	4	6	9736.484	3	8
3	2	1	9160.225	1	6	6	5	1	9533.527	6	4	9	4	5	9743.385	2	-4
3	3	1	9207.090	1	5	6	6	1	9633.354	3	-2	9	5	4	9820.293	2	-14
3	3	0	9207.154	1	6	6	6	0	9633.354	3	-2	9	6	4	9918.227	3	-15
4	0	4	9161.399	1	-4	7	0	7	9343.867	6	-8	9	6	3	9918.208	3	-1
4	1	4	9162.515	2	6	7	1	7	9344.006	2	1	10	0	10	9607.968	26	-15
4	1	3	9188.920	1	6	7	1	6	9405.204	5	6	10	1	10	9607.968	26	-12
4	2	3	9204.134	1	6	7	2	6	9408.703	1	-9	10	2	9	9703.175	3	4
4	2	2	9216.124	3	2	7	2	5	9445.450	2	-14	10	3	8	9783.519	2	0
4	3	2	9254.351	1	5	7	3	5	9467.327	3	-8	10	4	7	9852.165	3	-2
4	3	1	9254.775	3	4	7	3	4	9476.117	2	3	10	4	6	9868.115		8
4	4	1	9320.061	5	-2	7	4	4	9534.148	2	-3	10	5	6	9941.666	1	-1
4	4	0	9320.061	5	-18	7	4	3	9535.252	1	0	10	6	5	10037.623	2	6
5	0	5	9213.246	2	-3	7	5	3	9616.824	1	7	11	0	11	9714.263	12	17
5	1	5	9213.990	2	3	7	5	2	9616.788	2	6	11	1	11	9714.263	12	-5
5	1	4	9251.100	6	10	7	6	2	9716.200	4	-2	11	1	10	9819.645	4	-16
5	2	4	9261.485	1	5	7	6	1	9716.200	4	-1	11	2	10	9819.833	3	3
5	2	3	9279.446	1	7	8	0	8	9422.732	4	3	11	2	9	9906.727	1	-2
5	3	3	9313.565	1	-4	8	1	8	9422.830	4	1	11	6	5	10169.159	3	-1
5	3	2	9315.150	1	-12	8	1	7	9495.662	1	5	12	1	11	9945.567	4	8
5	4	2	9379.333	2	-3	8	2	7	9497.405	4	4	13	0	13	9954.027	5	4
5	4	1	9379.419	1	-1	8	3	6	9561.306	3	10	13	1	13	9954.027	5	-8

^a Δ is the experimental uncertainty of the energy value, equal to one standard deviation in units of 10⁻³ cm⁻¹; δ is the difference $E^{\text{exp}} - E^{\text{calc}}$, also in units of 10⁻³ cm⁻¹; Δ is not quoted when the energy value was obtained from only one transition.

Table 3. Transitions assigned to the $3\nu_1 + \nu_2$ and $3\nu_1 + 2\nu_3$ bands of D₂O.

Upper			Lower			Line position	Transmit.	Upper energy	Mean value	Calc.	Band	
J'	K'_a (1)	K'_c	J	K_a (2)	K_c	cm^{-1} (3)	% (4)	cm^{-1} (5)	cm^{-1} (6)	cm^{-1} (7)		
7	4	4	6	3	3	9132.339	97	9477.786	9477.786	9477.786	$3\nu_2 + 2\nu_3$	
			8	3	5	8936.904	99	9477.785				
3	2	1	2	1	2	9074.815	98	9116.884	9116.881	9116.861	$3\nu_1 + \nu_2$	
			4	1	4	8999.565	98	9116.877				
3	3	1	2	2	0	9092.138	96	9166.280	9166.280	9166.281	$3\nu_1 + \nu_2$	
			3	2	2	9056.245	96	9166.279				
			4	2	2	9002.103	96	9166.280				
3	3	0	2	2	1	9092.259	98	9165.936	9165.936	9165.938	$3\nu_1 + \nu_2$	
4	2	2	3	1	3	9094.568	93	9169.074	9169.074	9169.097	$3\nu_1 + \nu_2$	
			5	1	5	8998.830	95	9169.073				
4	3	2	3	2	1	9096.482	94	9208.733	9208.732	9208.731	$3\nu_1 + \nu_2$	
			5	2	3	8978.739	95	9208.731				
4	3	1	3	2	2	9104.526	95	9214.561	9214.563	9214.567	$3\nu_1 + \nu_2$	
			5	2	4	8996.981	96	9214.566				
5	3	3	4	2	2	9105.160	93	9269.338	9269.339	9269.345	$3\nu_1 + \nu_2$	
			5	2	4	9051.754	98	9269.339				
			6	2	4	8960.074	94	9269.339				
6	3	4	5	2	3	9111.487	98	9341.479	9341.478	9341.485	$3\nu_1 + \nu_2$	
			7	2	5	8940.214	98	9341.477				
6	3	3	5	2	4	9131.571	96	9349.156	9349.154	9349.147	$3\nu_1 + \nu_2$	
			7	2	6	8979.886	98	9349.152				
7	3	5	6	2	4	9115.660	98	9424.925	9424.924	9424.919	$3\nu_1 + \nu_2$	
			8	2	6	8919.875	98	9424.924				

resonance interaction of the $(\nu_1 \nu_2 \nu_3) - (\nu_1 \mp 2 \nu_2 \mp 2 \nu_3 \pm 1)$ type which differs from the usual Fermi, Darling–Dennison, and Coriolis ones (its nature was discussed in detail in [2], so, we omit it here). For this reason, nonzero interactions between the (211) and (032) states are included in the Hamiltonian model.

Since only lines of the $2\nu_1 + \nu_2 + \nu_3$ band (and only some lines of the other bands) can be assigned in the spectrum, the problem of correct choice of the initial approximations for the parameters of the Hamiltonian (equations (1)–(4)) is very important. In this study, the initial values for parameters were estimated from the following considerations.

(1) The vibrational energies E^i of all the seven vibrational states and purely vibrational interaction parameters F_0^{ij} were estimated from the pre-fit of the known band centres of the D₂O molecule. In this case, as follows from equation (3), the Darling–Dennison $F_0^{\nu_1 \nu_2 \nu_3, \nu_1-2 \nu_2 \nu_3+2}$ parameters are proportional to $[\nu_1(\nu_1-1)(\nu_3+1)(\nu_3+2)]^{1/2}$. In the estimations, we used the following band centres: $\nu_2 = 1178.38 \text{ cm}^{-1}$ [5]; $\nu_1 = 2671.65 \text{ cm}^{-1}$, $2\nu_2 = 2336.84 \text{ cm}^{-1}$ and $\nu_3 = 2787.72 \text{ cm}^{-1}$ [6]; $\nu_1 + \nu_2 = 3841.42 \text{ cm}^{-1}$, $\nu_2 + \nu_3 = 3956.01 \text{ cm}^{-1}$ and $3\nu_2 = 3474.32 \text{ cm}^{-1}$ [1]; $2\nu_1 = 5291.72 \text{ cm}^{-1}$, $\nu_1 + \nu_3 = 5373.90 \text{ cm}^{-1}$, $2\nu_3 =$

5529.44 cm^{-1} , $\nu_1 + 2\nu_2 = 4990.83 \text{ cm}^{-1}$ and $2\nu_2 + \nu_3 = 5105.38 \text{ cm}^{-1}$ [2]; $2\nu_1 + \nu_2 = 6452.98 \text{ cm}^{-1}$, $\nu_1 + \nu_2 + \nu_3 = 6533.24 \text{ cm}^{-1}$, $\nu_2 + 2\nu_3 = 6687.00 \text{ cm}^{-1}$, $\nu_1 + 3\nu_2 = 6119.04 \text{ cm}^{-1}$ and $3\nu_2 + \nu_3 = 6235.08 \text{ cm}^{-1}$ [7]; $3\nu_1 = 7852.93 \text{ cm}^{-1}$, $2\nu_1 + \nu_3 = 7899.82 \text{ cm}^{-1}$, $\nu_1 + 2\nu_3 = 8054.06 \text{ cm}^{-1}$, $3\nu_3 = 8220.18 \text{ cm}^{-1}$, $2\nu_1 + 2\nu_2 = 7593.12 \text{ cm}^{-1}$, $\nu_1 + 2\nu_2 + \nu_3 = 7672.92 \text{ cm}^{-1}$ and $2\nu_2 + 2\nu_3 = 7825.37 \text{ cm}^{-1}$ [3]. It should be mentioned that the first step of the fit gave large statistical confidence intervals for the Fermi interaction parameters $F_0^{\nu_1 \nu_2 \nu_3, \nu_1 \mp 1 \nu_2 \pm 2 \nu_3}$. For this reason, the Fermi interaction parameters $F_0^{\nu_1 \nu_2 \nu_3, \nu_1 \mp 1 \nu_2 \pm 2 \nu_3}$ were omitted at the final step. The estimated values of the band centres of the $\nu = 3.5$ polyad are presented in column 2 of table 1.

(2) The rotational parameters A^i , B^i and C^i of the (310), (211), (112), (013), (230), (131) and (032) states were estimated by the equation

$$P^{\nu_1 \nu_2 \nu_3} = P^{0\nu_2 0} + \nu_1(P^{100} - P^{000}) + \nu_3(P^{001} - P^{000}),$$

where P denotes any of the parameters A^i , B^i or C^i ; the values of the parameters of the (000), (100), (001), (010) and (030) vibrational states were taken from [1], [5], and [6].

(3) All the values of the centrifugal distortion coefficients of the $(\nu_1 1 \nu_3)$ states were estimated as the mean

Table 4. Spectroscopic parameters of the (310), (211), (112), (013), (230), (131) and (032) vibrational states of the D₂O molecule (in cm⁻¹).^a

Parameter	(310)	(211)	(112)	(013)
E	9033.548(78)	9066.221 8(41)	9173.70(46)	9349.6
A	15.938 25(259)	15.621	15.328	15.035
B	7.085 47(235)	7.149 969(769)	7.2252(121)	7.256
C	4.622 67(490)	4.582 53(438)	4.619	4.631
$\Delta_K 10^3$	12.96	12.96	12.96	12.96
$\Delta_{JK} 10^3$	-1.86	-1.86	-1.86	-1.86
$\Delta_J 10^3$	0.34	0.462 8(153)	0.34	0.34
$\delta_K 10^3$	0.76	1.190 1(390)	0.76	0.76
$\delta_J 10^3$	0.14	0.196 38(597)	0.14	0.14
$H_K 10^5$	3.45	3.45	3.45	3.45
$H_{KJ} 10^5$	-5.30	-5.30	-5.30	-5.30
$H_{JK} 10^5$	0.028	0.028	0.028	0.028
$H_J 10^5$	0.007 9	0.007 9	0.007 9	0.007 9
$h_K 10^5$	0.94	0.94	0.94	0.94
$h_J 10^5$	0.003 4	0.003 4	0.003 4	0.003 4
$L_K 10^7$	-1.14	-1.14	-1.14	-1.14
$L_{KKJ} 10^7$	0.56	0.56	0.56	0.56
$L_{KJ} 10^7$	-0.016	-0.016	-0.016	-0.016
$L_{JJK} 10^7$	-0.002 6	-0.002 6	-0.002 6	-0.002 6
$l_K 10^7$	-0.61	-0.61	-0.61	-0.61
$l_{KJ} 10^7$	-0.017	-0.017	-0.017	-0.017
$l_{JK} 10^7$	-0.001 7	-0.001 7	-0.001 7	-0.001 7

Parameter	(230)	(131)	(032)
E	8719.3	8788.6(14)	8928.61(23)
A	19.573	19.280	18.986
B	7.265	7.330	7.506 08(837)
C	4.557	4.569	4.582
$\Delta_K 10^3$	36.13	36.13	36.13
$\Delta_{JK} 10^3$	-3.08	-3.08	-3.08
$\Delta_J 10^3$	0.39	0.39	0.39
$\delta_K 10^3$	2.16	2.16	2.16
$\delta_J 10^3$	0.16	0.16	0.16
$H_K 10^5$	21.47	21.47	21.47
$H_{KJ} 10^5$	-2.10	-2.10	-2.10
$H_{JK} 10^5$	0.192	0.192	0.192
$H_J 10^5$	0.0121	0.0121	0.012 1
$h_K 10^5$	3.47	3.47	3.47
$h_J 10^5$	0.007 2	0.007 2	0.007 2
$L_K 10^7$	-4.65	-4.65	-4.65

^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).

values of the corresponding parameters of the states (110) and (011) from [1]. The centrifugal distortion coefficients of the (ν₁ 3 ν₃) states were taken to be equal to the values of the corresponding coefficients of the (030) state from [1] as well.

(4) All the initial values of Coriolis type parameters were taken to be zero.

4. Assignment of transitions and analysis

In spite of the extreme weakness of the 2ν₁ + ν₂ + ν₃ band, we assigned 266 transitions with $J^{\max} = 13$ and $K_a^{\max} = 6$ (a small fragment of the spectrum of the 2ν₁ + ν₂ + ν₃ band is shown in figure 1). Assignment was based on the ground state combination differences method, and the ground state rotational energies were

Table 5. Parameters of resonance interactions between the states of the $\nu_1 + \nu_2/2 + \nu_3 = 3.5$ polyad of the D_2O molecule (in cm^{-1}).^a

Parameter	Value	Parameter	Value	Parameter	Value
Fermi-type interactions					
$F_0^{310-112}$	-68.9				
$F_0^{230-032}$	-35.9				
$F_0^{211-013}$	-68.9	$F_K^{211-013}$	-0.201 56(349)	$F_{KK}^{211-013} 10^2$	0.417 3(277)
$F_{JK}^{211-013} 10^2$	-0.171 0(249)				
$F_K^{211-131}$	0.494 1(176)	$F_J^{211-131}$	0.183 11(885)		
$F_{xy}^{211-131}$	0.073 10(621)	$F_{xyK}^{211-131} 10^2$	0.179 4(180)		
Coriolis-type interactions					
$C_y^{310-211}$	-1.102 (109)	$C_{yJ}^{310-211} 10^2$	0.104 6(106)	$C_{xz}^{310-211}$	0.318 9(166)
$C_{xz}^{112-211}$	0.164 7(117)	$C_{xzK}^{112-211} 10^2$	0.074 3(105)	$C_{xz}^{230-211}$	0.029 92(529)
$C_{yK}^{032-211} 10^2$	-6.186 (322)	$C_{yKK}^{032-211} 10^4$	8.133 (886)		
$C_{xz}^{032-211}$	-0.155 1(134)	$C_{xzK}^{032-211} 10^2$	-0.060 4(299)		

^a See footnote *a* to table 4.

calculated on the basis of the parameters from [6]. The above-mentioned 266 line positions produced 99 rotational energies of the upper vibrational state. These energies are presented in column 2 of table 2. Column 3 shows their experimental uncertainties Δ .

Because of strong resonance interaction between the closely located $2\nu_1 + \nu_2 + \nu_3$ and $3\nu_1 + \nu_2$ bands, some sets of transitions (with quantum numbers $K_a^{\text{upper}} = 2$ and 3) were assigned to the latter. Moreover, two transitions belonging to the $3\nu_2 + 2\nu_3$ band and enriching the [$J = 7K_a = 4K_c = 4$] upper state were assigned as well. The rotational energies of the (310) and (032) vibrational states determined on this basis are given in columns 5 and 6 of table 3.

In the next step of the analysis, all the upper energies obtained were involved in the fit procedure with the Hamiltonian from equations (1)–(4). As a result of the fit, the parameters presented in tables 4 and 5 were obtained. In these tables, the values presented with the confidence intervals (shown in parentheses) were varied in the fit procedure. The values presented without confidence intervals were fixed to their initial values (see the above discussion). One can see that the values of both the fixed and fitted spectroscopic parameters are physically suitable and correlate with each other. It should be mentioned that the presence of strong resonance interactions gave the possibility of estimating the values of the band centres and rotational parameters for some of the ‘dark’ states of the considered polyad from the fit. To compare the results of the fit with the values of the band centres presented in column 2 of table 1, column 3 of table 5 presents the fitted values of corresponding

band centres. One can see the satisfactory agreement between the two sets of values.

To show the reproductive power of the parameters from tables 4 and 5, column 3 of table 2 and column 7 of table 3 present the values $\delta = E^{\text{exp}} - E^{\text{calc}}$ which are the differences between the ‘experimental’ energies and those calculated with the parameters from tables 4 and 5. In this case, 49 energies are reproduced with an accuracy no worse than 0.004 cm^{-1} (44.2% of the obtained upper energies); for 47 energies $0.004 \leq \delta \text{ cm}^{-1} \leq 0.010 \text{ cm}^{-1}$ (42.3%); and for 15 energies $0.010 \leq \delta \text{ cm}^{-1}$ (13.5%).

5. Conclusion

The high resolution Fourier transform spectrum of the $D_2O \nu = 3.5$ polyad was analysed within the framework of the Hamiltonian model taking into account resonance interactions between the seven states (310), (211), (112), (013), (23), (131) and (032). Transitions belonging to the $2\nu_1 + \nu_2 + \nu_3$, $3\nu_1 + \nu_2$ and $3\nu_2 + 2\nu_3$ bands were assigned from the experimentally recorded spectrum. This gave us the possibility of obtaining spectroscopic parameters of the ‘visible’ states (211), (310) and (032) and of estimating band centres, and rotational and resonance interaction parameters of the ‘dark’ states (112) and (131).

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