Spectroscopic constants of the (011), (200), (120), and (040) states of the $HD^{16}O$ molecule

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The method of effective Hamiltonian was applied to determine the rotational, centrifugal distortion, and resonance coupling constants for the four vibrational states: (011), (200), (120), and (040) of the $HD^{16}O$ molecule by fitting to the experimental energy levels reported recently by R. Toth [J. Mol. Spectrosc. **186**, 276–292 (1997)]. The effective Hamiltonian included all the possible resonances between close energy levels. The Pade–Borel approximations were used to take into account the strong centrifugal distortion effect. The fit of 62 spectroscopic constants has shown good agreement with the experimental energy levels (the rms deviation of 0.0030 cm^{-1} for the total of 407 energy levels). The set of spectroscopic constants obtained allows one to calculate the synthetic spectrum with the accuracy close to the experimental one.

1. Introduction

A detailed knowledge of the rovibrational absorption spectra of the water molecule, as well as its isotopic species, is necessary for solution of atmospheric spectroscopy problems. Absorption at the $HD^{16}O$ lines can give essential corrections both in the case of narrow-band laser measurements of the atmospheric transmittance and in the case of measurements in a wide spectral region.

As is well known, the semi-empirical method of effective Hamiltonians is a powerful tool for obtaining spectroscopic information, since it allows one to calculate line positions and intensities even in the case of weak or overlapping lines with an accuracy comparable with the measurement error. However, the reliability of results obtained by the method of effective Hamiltonian depends on whether and what intramolecular interactions are taken into account, as well as on the employed scheme of accidental (Fermi, Coriolis, Darling–Dennison, etc.) resonances, which perturb positions and intensities of spectral lines.

The HDO molecule along with the main isotopic modification $H_2{}^{16}O$ falls in the class of atmospheric molecules, and its spectral line parameters are included in the well-known HITRAN and GEISA databases. The rotational structure of the $HD^{16}O$ excited vibrational states is considerably poorer investigated both experimentally and theoretically as compared to $H_2{}^{16}O$ (for more information see Ref. 1 and references therein). The rovibrational dynamics of the $HD^{16}O$ molecule differs from that of the main isotopic specie because of the asymmetric isotopic substitution reducing the molecular symmetry, as well as because of a large relative change in the mass of the substituted atom and different, as compared to H_2O, ratio between the frequencies of normal vibrations. As a consequence, the scheme of accidental resonances is different too.

It is shown in Refs. 2 and 3 that only the Fermi-type resonance caused by exchange of one quantum of the stretching vibration (ν_1) and two quanta of the bending vibration ($2\nu_2$) should be taken into account for low-lying vibrational states of $HD^{16}O$. The rotational sublevels of the (101) and (021) vibrational states were analyzed in Ref. 4 with only the above resonance taken into account. It was found in Refs. 1 and 5–7 that the ($00v_3$) states corresponding to the vibrations of the OH bond can be considered as isolated, whereas in Ref. 8 it is shown that the high-order resonance between the (210) and (050) vibrational states leads to strong mixing of wave functions of these states. As a result, numerous lines of the weak $5\nu_2$ band with $J \le 8$ and $K_a \le 2$ are observed in the spectrum due to borrowing the intensity from the strong line-partners of the $2\nu_1 + \nu_2$ band. It should be noted that the direct Fermi resonance between the (210) and (130) vibrational states proved to be too weak to cause the resonance intensity redistribution and strengthening of lines of the $\nu_1 + 3\nu_2$ band. Let us also note that in the case of the H_2O molecule the (050) state is only slightly perturbed, and under ordinary conditions the lines of the $5\nu_2$ band are practically absent in the spectrum.

On the other hand, the resonances corresponding to the interaction of the stretching ν_1 and ν_3 vibrations are weak in HDO due to the 1000 cm^{-1} difference between ω_1 and ω_3 harmonic frequencies. The weak mixing of the rotational sublevels with $J > 10$ of the (002) state with those of the (012), (111), (101), (031) states was found in Ref. 1.

Thus, there is no clear pattern of resonance interactions in HDO even for low-lying vibrational states, not to mention highly excited states. In this paper the interacting (011), (200), (120), and (040) states, which are the upper states for the transitions forming the HDO absorption spectrum in the 4719–

5843 cm^{-1} region, are theoretically analyzed. The line positions and intensities from Ref. 9 were used as initial experimental information. The subject of this paper is to study the resonance interactions between highly excited vibrational states of HDO, as well as to estimate rotational, centrifugal distortion, and resonance coupling constants of the states under study. These constants would allow one to calculate the initial rovibrational energy levels and to predict yet unstudied levels with high accuracy. The parameters obtained are supposed to be further applied to analysis of experimental intensities and to retrieval of dipole moment constants needed for compiling the database of HDO absorption lines nearby 2 μm.

2. Effective Hamiltonian

The ν_2+ν_3 band is the strongest one in the 2 μm region. The (200), (120), and (040) states with vibrational energy levels of 5089, 5363, 5419, and 5506 cm^{-1}, respectively, are close in energy to the (011) vibrational state. The (110) and (101) vibrational states with the energy of 4145 and 6415 cm^{-1} are rather far in energy from the states under study, therefore we used the effective Hamiltonian including the (011), (200), (120), and (040) states only, as well as all the possible resonances between them:

$$H = \sum_{v,v' \in \Gamma} |v\rangle\, h^{[vv']}\, \langle v'| , \qquad (1)$$

where Γ = (011), (200), (120), (040); $h^{[vv]}$ are the diagonal operators corresponding to the rotational and centrifugal distortion energy, while $h^{[vv']}$ with $v \neq v'$ are resonance operators.

As in the previous paper[1] dealing with the $2\nu_3$ band, the operators $h^{[vv]}$ in the form of Pade–Borel approximations were used for calculation of the energy levels of highly excited states. In this case the matrix elements of the Hamiltonian in the basis of symmetric-top wave functions $|jk\rangle$ are calculated in accordance with formulas from Ref. 10 (for a given vibrational state v):

$$\langle\, jk \mid h^{[vv]} \mid jk\rangle = E_v + \int_0^\infty \mathrm{d}t\; \mathrm{e}^{-t}\, \frac{c_0\, c_1 + (c_1^2 - c_0\, c_2)\, t}{c_1 - c_2\, t} ,$$

$$\langle\, jk \mid h^{[vv]} \mid jk \pm 2\rangle = \langle\, jk \mid J^2_{xy} \mid jk \pm 2\rangle \times$$

$$\times \int_0^\infty \mathrm{d}t\; \mathrm{e}^{-t}\, \frac{b_0\, b_1 + (b_1^2 - b_0\, b_2)\, t}{b_1 - b_2\, t} , \qquad (2)$$

where

$$c_0 = \left[A - \frac{B+C}{2}\right] k^2 + \frac{B+C}{2}\, j(j+1);$$

$$c_1 = -\,\Delta_k\, k^4 - \Delta_{jk}\, k^2\, j(j+1) - \Delta_j\, j^2\, (j+1)^2;$$

$$2c_2 = H_k\, k^6 + H_{kj}\, k^4\, j(j+1) + H_{jk}\, k^2\, j^2 (j+1)^2 +$$

$$+ H_j\, j^3 (j+1)^3 + L_k\, k^8 + \ldots ; \qquad (3)$$

$$b_0 = [B - C]/2;$$

$$b_1 = -\,\delta_k\, [k^2 + (k \pm 2)^2] - 2\delta_j\, j(j+1);$$

$$2b_2 = h_k\, [k^4 + (k \pm 2)^4] + h_{jk}\, [k^2 + (k \pm 2)^2] \times$$

$$\times\, j(j+1) + 2h_j\, j^2 (j+1)^2 + \ldots . \qquad (4)$$

The integrals in Eq. (2) can be calculated as follows:

$$\langle\, jk \mid W_v \mid jk\rangle = E_v + (c_0\, c_2 - c_1^2)/c_2 +$$

$$+ c_1\, Ei(c_1/c_2)\, c_1^2/c_2^2\, \exp\,(-c_1/c_2);$$

$$Ei(-x) = -\int_x^\infty \mathrm{e}^{-t}\, t^{-1}\, \mathrm{d}t, \qquad (5)$$

Here E_v is the vibrational energy; A, B, and C are the rotational constants; Δ_k, Δ_{jk}, Δ_j, ... are the centrifugal distortion constants; $Ei(x)$ is the exponential integral; $J^2_{xy} = J^2_x - J^2_y$, J_x, J_y, and J_z are the angular momentum operators. Equation (5) is also valid for off-diagonal matrix elements (replacing c_n by b_n and omitting E_v). The resonance operators have the form

$$h^{[vv']} = F_0^{[vv']} + C_y^{[vv']}\, J_y + C_{xz}^{[vv']}\, \{J_x, J_z\} +$$

$$+ F_k^{[vv']}\, J_z^2 + F_j^{[vv']}\, J^2\, F_{xy}^{[vv']}\, J^2_{xy}. \qquad (6)$$

Since the HDO molecule belongs to the C_s symmetry group, the resonance operators simultaneously include both the Fermi-type $F_0^{[vv']}$, $F_k^{[vv']} J_z^2$, $F_j^{[vv']} J^2$, $F_{xy}^{[vv']} J^2_{xy}$, and Coriolis-type $C_y^{[vv']} J_y$, $C_{xz}^{[vv']} \{J_x, J_z\}$ terms.

An initial approximation for the spectroscopic constants in Eqs. (1)–(4) was obtained by interpolation of the corresponding parameters of the (010), (002), and (020) states. The parameters for the highly excited bending (040) state, experimental energy levels for which are not found and which, consequently, is a dark state in our analysis, were evaluated from fitting to the levels calculated in Ref. 11.

3. Results and discussion

As a result of the analysis performed, the set of 62 spectroscopic parameters was determined which reproduces 407 initial experimental energy levels with the accuracy as high as 0.0032 cm^{-1}. These parameters are presented in Table 1 together with the 65% confidence intervals. Note that the rotational and centrifugal distortion constants obtained agree well with the predicted ones and closely correspond to the constants obtained earlier for the lower states. In particular, the negative value of the Δ_{jk} centrifugal distortion constant of the (040) state is due to the influence of vibrational excitation ($\Delta_{jk} > 0$ for the (000) and (010) states), what is confirmed by the negative values of this constant for the (030) (Ref. 3) and (050) (Ref. 8) states.

The experimental energy levels from Ref. 9 together with their deviations $DE = (E_{\text{exp}} - E_{\text{calc}}) \cdot 10^{-4}$ cm^{-1} from those calculated using the effective Hamiltonian (1)–(6) are presented in Table 2. Levels marked by asterisks (six levels) were excluded from fitting. Besides, for eleven energy levels the experimental values assumed in Ref. 9 proved to be incorrect, that is confirmed both by our calculation and by the high-accuracy *ab initio* estimations.[11] These energy levels are given in Table 3 together with the values calculated by us and in Ref. 11. It can be seen that the differences achieve 34 cm^{-1} clearly confirming the incorrect assignment of these levels in Ref. 9.

Table 1. Spectroscopic constants of the (011), (200), (120), and (040) states of the HDO molecule (in cm^{-1})

		(011)	(200)	(120)	(040)
E_v		5089.5398	5364.340111(8700)	5505.941741(1700)	5420.69216(7600)
A		24.3043179(2100)	22.8570859(9300)	28.777236(1900)	36.22869(1700)
B		9.2328918(1100)	8.7463452(1100)	9.2567264(2400)	9.538556(1500)
C		6.2458968(4600)	6.1970096(2200)	6.16479811(9300)	6.065
Δ_k	10^{-1}	0.2139333(1800)	0.1041618(5000)	0.28876(1100)	2.272009(7200)
Δ_{jk}	10^{-3}	0.827888(5000)	15.60579(9300)	0.360	–0.129
Δ_j	10^{-3}	0.419845(1000)	0.3362975(4100)	0.542037(2700)	0.563
δ_k	10^{-2}	0.313781(1100)	0.225374(1900)	0.405868(7100)	1.18
δ_j	10^{-3}	0.1558577(4400)	0.1161624(2500)	0.173359(1700)	0.254
H_k	10^{-3}	0.1203509(5600)	0.0392674(8500)	1.44244(5100)	5.00
Hkj	10^{-4}	–0.133141(1900)	–0.054790(2900)	–1.24198(5100)	
H_{jk}	10^{-5}	0.427936(6000)	0.143008(6300)		
H_j	10^{-7}	0.71887(3300)	0.43145(1000)		
h_k	10^{-4}	0.405418(6300)	0.19565(1200)	0.450	0.700
h_{kj}	10^{-5}	0.107040(4300)	0.171913(5800)		
h_j	10^{-7}	0.28203(1800)	0.164		
L_k	10^{-7}	–0.211339(2200)	–0.0540	–1.30	–220.0
L_{kkj}	10^{-7}	–0.589			
L_{kj}	10^{-7}	–0.302	–0.0947		
L_{kjj}	10^{-8}	0.124	0.141		
l_k	10^{-6}		–0.12843(1200)		
l_{jk}	10^{-8}	0.516			
P_{kkj}	10^{-9}	0.178			
p_k	10^{-8}	–0.19465(1200)	–0.0848		
p_{kj}	10^{-8}	0.236109(8300)	0.0427		
p_{kjj}	10^{-9}	–0.264			

Resonance constants

	F_0	F_k	F_j	F_{xy}	C_y
200–011		–0.043140(1200)			–0.095837(2300)
120–011				0.042594(2100)	0.83242(9000)
120–200		–0.59082(1200)		–0.0326297(7500)	
040–011				–0.038337(1000)	
040–200	5.40466(5000)		0.0105909(8500)	–0.0086273(3100)	
040–120	–4.478(1300)	–2.46766(1000)	–0.1023567(2800)	–0.0304156(7300)	

Statistics of deviations:

407 levels, 62 (48 diagonal and 14 resonance) parameters ;
RMS = 0.0030 cm^{-1};
$0 < \delta E \leq 0.002$ 71.99%
$0.002 < \delta E \leq 0.004$ 16.71%
$0.004 < \delta E \leq 0.0136$ 11.30%
$\delta E = |E_{\text{exp}} - E_{\text{calc}}|$, in cm^{-1};

Table 2. Experimental energy levels (in cm^{-1}) of the (011), (200), and (120) states of HDO from Ref. 9 and the deviations

J K_a K_c	(011)	DE	(200)	DE	(120)	DE	J K_a K_c	(011)	DE	(200)	DE	(120)	DE
1	2	3	4	5	6	7	8	9	10	11	12	13	14
0 0 0	5089.5398	0	5363.8245	–6			7 7 0	6289.7195	8	6508.1382	26		
1 0 1	5105.0147	–2	5378.7684	–6			8 0 8	5595.0634	–7	5859.1913	17	6014.2569	45
1 1 1	5120.0705	5	5392.9600	–14	5541.5132	0	8 1 8	5595.7159	–5	5859.9507	1	6016.0493	–64
1 1 0	5123.0461	5	5395.5072	–14	5544.6002	–23	8 1 7	5689.2571	–10	5941.4304	–5	6117.8550	83
2 0 2	5135.5579	–3	5408.3370	2	5552.1556	67	8 2 7	5700.3928	17	5953.3569	–7	6142.1268	53
2 1 2	5148.0355	5	5420.2870	–10	5569.3288	–16	8 2 6	5748.7939	–6	5993.4803	–2	*6186.8228	–342
2 1 1	5156.9550	6	5427.9229	–10	5578.5895	–36	8 3 6	5798.1345	10	6042.4668	2	6275.7612	–18
2 2 1	5201.8645	15	5470.2049	4	5639.7500	43	8 3 5	5810.1414	7	6051.5450	–16	6283.0716	108
2 2 0	5202.2610	13	5470.5176	–1	5640.0723	37	8 4 5	5910.3586	–6	6147.3600	–6	6447.0220	–46
3 0 3	5180.4043	–6	5451.9209	6	5597.1042	33	8 4 4	5911.3983	–8	6148.0572	0	6447.4111	43
3 1 3	5189.7376	1	5461.0830	–5	5610.8462	–11	8 5 4	6049.7701	–12	6279.1667	94		
3 1 2	5207.5213	5	5476.3132	–7	5629.3301	–46	8 5 3	6049.7959	8	6279.1787	–19		
3 2 2	5248.2306	15	5514.9607	2	5686.2591	22	8 6 3	6217.8242	–7	6439.2132	5		
3 2 1	5250.1646	12	5516.4914	–13	5687.8415	–9	8 6 2	6217.8252	–4	6439.2132	1		
3 3 1	5329.9146	2	5591.3286	24	5802.9271	13	8 7 2	6412.9821	–3	6626.5608	–1		
3 3 0	5329.9479	1	5591.3526	25	5802.9458	12	8 7 1	6412.9821	–3	6626.5608	–1		
4 0 4	5238.6240	–7	5508.7572	15	5655.6415	–3	8 8 1	6633.7249	–4	6840.2745	–18		
4 1 4	5244.9293	0	5515.1474	0	5665.8463	–5	8 8 0	6633.7249	–4	6840.2745	–18		
4 1 3	5274.3450	4	5540.3671	–2	5696.5038	–32	9 0 9	5714.6897	–7	5977.0771	10	6134.1314	59
4 2 3	5309.7101	15	5574.3655	0	5747.9974	15	9 1 9	5715.0276	–5	5977.4821	–3	6135.2116	–93
4 2 2	5315.2198	11	5578.7515	–10	5752.5768	–52	9 1 8	5825.3524	–14	6074.0808	–12	6257.5608	–8
4 3 2	5392.3437	3	5651.4476	14	5865.8874	–1	9 2 8	5832.4168	13	6081.9243	–8	6275.9428	1
4 3 1	5392.5738	4	5651.6136	14	5866.0174	–1	9 2 7	5897.7322	–17	6136.6009	–17		
4 4 1	5504.1505	–8	5756.5658	9	6036.3022	5	9 3 7	5937.5820	7	6177.1163	8	6417.1625	–122
4 4 0	5504.1525	–11	5756.5675	11	6036.3036	10	9 3 6	5958.6247	5	6193.2926	20	6430.6149	135
5 0 5	5309.4510	–10	5578.1701	20	5727.0075	–10	9 4 6	6051.3915	–10	*6283.0130	–125	6589.4574	59
5 1 5	5313.3459	–4	5582.2612	2	5734.0881	–3	9 4 5	6053.9791	2	6284.7683	24	*6590.4309	299
5 1 4	5356.8256	4	5619.6188		5779.6442	18	9 5 5	6190.0399	–17	6414.0100	–9		
5 2 4	5386.0191	16	5648.1935	–3	5824.7380	31	9 5 4	6190.1611	4	6414.0916	–6		
5 2 3	5397.8542	11	5657.7014	–3	5834.8083	–81	9 6 4	6357.2332	–18	6573.2211	23		
5 3 3	5470.4887	7	5726.6935	7	5944.6967	–24	9 6 3	6357.2404	–10	6573.2213	5		
5 3 2	5471.3857	7	5727.3443	8	5945.2058	–20	9 7 3	6551.6769	–15	6759.8106	–18		
5 4 2	5582.0310	–6	5831.5228	–4	6115.1530	24	9 7 2	6551.6776	–8	6759.8106	–18		
5 4 1	5582.0511	–10	5831.5359	–5	6115.1607	26	9 8 2	6771.7518	6	6972.7883	25		
5 5 1	5723.2712	–1	5965.1413	0			9 8 1	6771.7518	6	6972.7883	25		
5 5 0	5723.2712	–3	5965.1413	0			9 9 1	7016.0730	–18	7211.2593	–10		
6 0 6	5392.4980	–12	5659.7696	21	5810.6894	7	9 9 0	7016.0730	–18	7211.2593	–10		
6 1 6	5394.7430	–4	5662.2140	5	5815.3349	9	10 0 10	5846.6024	–3	6107.1265	–1	6266.1203	21
6 1 5	5454.1368	0	5713.4238	2			10 1 10	5846.7745	–2	6107.3388	–19	6266.7681	–81
6 2 5	5476.8196	17	5736.1739	–4	5916.2098	58	10 1 9	5973.2355	–13	6218.5308	–7	6409.7521	–91
6 2 4	5498.0202	5	5753.3895	1	5934.7532	–76	10 2 9	5977.4880	9	6223.4155	–3	6423.2677	–27
6 3 4	5564.2896	8	5817.0393	–16	6039.3431	–28	10 2 8	6060.9922	–22	6294.0070	–12	6504.8078	3
6 3 3	5566.8678	8	5818.9198	5	6040.8223	–17	10 3 8	6091.5312	12	6325.9790	16	*6573.6629	–504
6 4 3	5675.6626	–4	5921.6117	–13	6209.8697	–12	10 3 7	6124.7582	6	6351.9551	–32	6596.1336	–58
6 4 2	5675.7637	–4	5921.6782	–10	6209.9067	–8	10 4 7	6208.0645	–11	6433.7999	17		
6 5 2	5816.4241	–9	6054.7610	–19			10 4 6	6213.6128	–9				
6 5 1	5816.4311	–7	6054.7614	–25			10 5 6	6346.0891	–14	6564.0166	–2		
6 6 1	5985.6848	22	6216.0350	–10			10 5 5	6346.4590	–31	6564.2544	11		
6 6 0	5985.6848	22	6216.0350	–10			10 6 5	6512.2396	–16	6722.2028	27		
7 0 7	5487.6860	–11	5753.4374	19	5906.4541	33	10 6 4	6512.2540	–46	6722.2102	22		
7 1 7	5488.9175	–5	5754.8252	5	5909.3795	–31	10 7 4	6705.8070	6	6907.8872	–49		
7 1 6	5565.2777	–3	5820.9779	0	5991.1309	116	10 7 3	6705.8070	3	6907.8874	–49		
7 2 6	5581.7386	18	5838.0012	–11	6022.1120	78	10 8 3	6925.0932	–4				
7 2 5	5615.2475	0	5865.5025	2	6052.2452	–108	10 8 2	6925.0932	–4				
7 3 5	5673.5902	10	5922.3498	2	6149.7481	–14	10 9 2	7168.6240	28				
7 3 4	5679.6142	8	5926.8281	2	6153.2841	30	10 9 1	7168.6240	28				
7 4 4	5785.0997	–4	6026.8822	–14	6320.4893	–60	11 0 11	5990.8119	2	6249.3482	–18	6410.2597	62
7 4 3	5785.4601	–5	6027.1217	–7	6320.6218	–37	11 1 11	5990.8986	0	6249.4544	–5	6410.6437	–3
7 5 3	5925.2509	–8	6159.4187	–27			11 1 10	6132.8803	–4	6374.6602	–3	6574.1589	–39
7 5 2	5925.2497	–2	6159.4235	–34			11 2 10	6135.3400	0	6377.5454	2	6583.8435	83
7 6 2	6093.9817	5	6320.1566	1			11 2 9	6237.4448	–11	6464.7587	–15		
7 6 1	6093.9817	4	6320.1566	–6			11 3 9	6259.5564	–23	6488.6985	25		
7 7 1	6289.7195	8	6508.1382	26			11 3 8	6307.8292	9	6527.1207	44		

Table 2 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
11 4 8	6380.1903	–5	6599.5237	6			13 0 13	6316.0769	15		
11 4 7	6390.8806	–17	6607.0174	19			13 1 13	6316.0981	0	6570.2853	–30
11 5 7	6517.9149	1	6729.1861	–23			13 1 12	6487.8568	22	6722.2704	28
11 5 6	6518.8811	16	6729.7948	–11			13 2 12	6488.6177	–16	6723.1535	2
11 6 6	6682.8584	20	6886.1835	17			13 2 11	6626.2825	38	6842.8387	–4
11 6 5	6682.8907	–8	6886.2092	15			13 3 11	*6636.0320	–365	6854.2340	12
11 7 5	6875.3650	32					13 3 10	6720.6736	26	6923.8191	–4
11 7 4	6875.3677	46					13 4 10	6769.2353	3		
11 8 4	7093.7333	–15					13 4 9	6799.2591	–11		
11 8 3	7093.7333	–16					13 6 8	7070.9461	–7		
12 0 12	6147.3104	12	6403.7299	–7			13 6 7	7071.2844	–69		
12 1 12	6147.3542	9	6403.7863	–19			14 0 14	6497.0848	19	6748.9000	34
12 1 11	6304.3845	1	6542.5256	5			14 1 14	6497.0958	12	*6748.9000	–121
12 2 11	6305.7670	–8	6544.1984	7			14 1 13	6683.3693	51	6913.7414	–24
12 2 10	6426.1023	–22	6647.9414	–7			14 2 13	6683.7805	–32	6914.2645	–10
12 3 10	6441.2085	–28	6664.9033	21			14 2 12	6837.8829	6		
12 3 9	6506.8678	14	6718.0356	21			14 4 10	7029.7785	–21		
12 4 9	6567.3511	9	6779.9658	–17			15 0 15	6690.2970	–2	6939.6142	61
12 4 8	6586.1277	2	6793.4289	–17			15 1 15	6690.3020	–17	6939.6142	–24
12 5 8	6705.4643	43	6909.4984	–91			15 1 14	6890.9540	48		
12 5 7	6707.6737	15	6910.9164	–5			15 2 14	6891.1724	–78		
12 6 7	6869.0985	53	7065.2024	23			16 0 16	6895.6866	47	7142.3534	8
12 6 6	6869.2254	26	7065.2786	37			16 1 16	6895.6866	1	7142.3534	–33
12 7 6	7060.3277	43					17 0 17	7113.1913	–55	7357.0843	9
12 7 5	7060.3284	8					17 1 17	7113.1913	–74	7357.0843	–9
12 8 5	7277.6508	–27					18 0 18	7342.8036	36		
12 8 4	7277.6508	–29					18 1 18	7342.8036	27		

Table 3. Incorrect energy levels from Ref. 9 (in cm^{-1})

v_1 v_2 v_3	J K_a K_c	Our calculation	Calculation (Ref. 11)	Experiment (Ref. 9)	Exp. – our calc.
0 1 1	13 5 9	6908.603	6908.679	6905.5077	–3.095
	13 5 8	6913.201	6913.255	6908.5151	–4.685
	14 3 12	6843.959	6844.022	6844.5123	0.553
	14 3 11	6948.300	6948.398	6940.9060	–7.394
	14 4 11	6985.381	6985.448	6985.1053	–0.276
2 0 0	10 4 6	6437.811	6437.918	6437.4670	–0.344
	13 0 13	6570.259	6570.263	6570.2862	0.027
1 2 0	5 5 1	6330.681	6330.454	6365.1098	34.429
	5 5 0	6330.681	6330.453	6365.1098	34.429
	6 5 2	6425.136	6424.879	6459.0422	33.906
	6 5 1	6425.136	6424.879	6459.0422	33.906

The analysis of the resonance interactions is of special interest.

1. The (011) state proved to be perturbed only slightly, since its vibrational energy E_v = 5089.5398 cm^{-1} is more than 270 cm^{-1} away from the nearest value E_v = 5363.8244 cm^{-1} for the (200) state. The mixing coefficients of wave functions for the (011) state are about fractions of percent, exceeding 1% only in some cases for the interaction with (200) and (040) and achieving the maximum of 6% for the [13 3 10] level at 6720.6736 cm^{-1} which is close to the [13 1 12] level of the (200) state at 6722.2704 cm^{-1}. Nevertheless, the resonance interaction between the (011) and (200) states, although being weak on the whole, causes considerable (up to ten times) strengthening of the intensity of transitions reaching the perturbed levels of the $2\nu_1$ band. This is a usual phenomenon of interaction between strong and weak bands. As this takes place, intensities of lines of the strong band change only slightly, often within the experimental accuracy, while the intensities of line-partners in the weak band undergo considerable change. Existence of the weak resonance mixing between the (011) and (200) states has been confirmed by the special calculation of line intensities.

2. The energy levels of the (200) state, besides the above-mentioned local interaction with the (011) state, are regularly perturbed by the resonance interaction with the (040) (low values of K_a) and (120) (high values of K_a) states with the mixing coefficients of 0.3 to 0.7%. Despite relatively weak resonance mixing of the wave functions, reconstruction of energy levels of the (200) vibrational state proved impossible without varying the corresponding resonance parameters (see Table 1).

The resonance between the (200) and (040) states differs from the (210)–(050) resonance investigated in Ref. 8 by the fact that vibrational energy E_v = 5420.6921 cm^{-1} for the (040) state turns out to be 56 cm^{-1} higher than E_v for the (200) vibrational state, while E_v for the (050) (6707.62 cm^{-1}) proves to be 44 cm^{-1} lower than E_v for the (210) (6751.14 cm^{-1}). Taking into account that the rotational constants A for the (040), (050), (200), and (210) states are 36.22, 46.72, 22.85, and 24.58 cm^{-1}, respectively, it is easily seen that the differences between levels of the (040) and (200) states, which can be involved into resonance interaction, increase as the rotational quantum number K_a grows. To the contrary, in the case of the (050)–(210) resonance the corresponding levels for small K_a are close in energy, and the resonance interaction is large. Despite the mixing coefficients of the (200) and (040) wave functions do not exceed 1%, the resonance can be large enough to cause the lines of the $4\nu_2$ band to manifest themselves in the spectrum, since the intensities of the $2\nu_1$ band line-partners are as high as $6.4\cdot10^{-2}$ cm^{-2}/atm.

3. The (120)–(040) resonance proved to be the strongest. The vibrational energy of the (040) state is 86 cm^{-1} less than that of the (120) state. This difference decreases because of more rapid growth of energy of the (040) levels caused by excitation of two additional quanta of the large-amplitude bending vibration. As a result, the mixing coefficients of the (120) and (040) wave functions reach 30% already for the levels with $J = 3$ and $K_a = 3$ and then grow up to 48%. It is obvious that the vibrational assignment of these levels is ambiguous. In particular, in the Partridge and Schwenke's variational calculation[11] some (120) levels are assigned as belonging to (040).

As in the case of the resonance interaction with the (200) state, the mixing coefficients of the (120) and (040) wave functions give strong grounds to believe that the lines of the $4\nu_2$ band must appear in the spectrum, since the line-partners of the $\nu_1 + 2\nu_2$ band are strong enough (line intensities up to $6.6\cdot10^{-4}$ cm^{-2}/atm). Note that Toth[9] points out the existence of weak unassigned lines which may belong to the $4\nu_2$ band. In the absence of combination differences, it is probable that considerable errors were made in Ref. 9 in assignment of the transitions to the (120) [551], [552], [652], [651] highly excited levels which are strongly (up to 32% according to our calculations) perturbed by the interaction with the (040) state.

It is of interest to compare the accuracy of calculation achieved in the method of effective Hamiltonian with that provided by the variational calculation.[11] The comparison was made for all the experimental energy levels of the polyad under study. It has shown that the variational calculation[11] reproduces the experiment with the RMS deviation of 0.04 cm^{-1}, the maximum deviation being 0.19 cm^{-1}.

A detailed comparison of the calculated intensities[11] with the experimental data was also performed. The RMS deviation amounted to 8.5%. The agreement between the calculation and experiment was quite close for the line intensities of the $2\nu_1$ band, poorer for the $\nu_2 + \nu_3$ band, and worst for the $\nu_1 + 2\nu_2$ band. The maximum errors reached 45%. It should be noted that using the method of effective Hamiltonian it is possible, as a rule, to reconstruct the initial intensities at the level of their declared accuracy (usually it ranges, on average, from 3 to 5%). The reconstruction of intensities of the HDO rovibrational lines is the subject of a forthcoming publication.

4. Conclusion

The detailed theoretical analysis of the HDO (011), (200), (120), and (040) interacting vibrational states based on the use of the suitable theoretical models in terms of the effective Hamiltonian has made it possible to determine the set of the spectroscopic constants reproducing the experimental energy levels with the accuracy close to the experimental uncertainty. It was found that eleven energy levels were assigned incorrectly in Ref. 9.

The high accuracy achieved in calculation of the energy levels suggests that the scheme of resonance interactions between the states under study has been correctly chosen. Three of six levels excluded from the fit were obtained experimentally with large uncertainties, and relatively large (from 0.03 to 0.05 cm^{-1}) deviations took place only for three strongly perturbed energy levels of the (120) vibrational state, what is likely the consequence of the resonance shift.

The performed consideration of the resonance interactions shows that there is the resonance intensity redistribution from the lines of the $\nu_2 + \nu_3$ and $2\nu_1$ bands to the line-partners of the $4\nu_2$ band. This effect is strong enough for the latter to be observed experimentally.

The set of parameters obtained will be further used for modeling calculation of line intensities and the HDO absorption spectrum in the 4719–5843 cm^{-1} region. These parameters can also be used in other areas of spectroscopy, in particular, for calculation of shift and broadening of HDO spectral lines by air pressure.

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