

High-Resolution Study of Strongly Interacting Vibrational Bands of HDO in the Region 7600–8100 cm⁻¹

Shui-Ming Hu,* O. N. Ulenikov,† G. A. Onopenko,† E. S. Bekhtereva,† Sheng-Gui He,*
Xiang-Huai Wang,* Hai Lin,* and Qing-Shi Zhu*

*Open Laboratory of Bond-Selective Chemistry and High Institute for Advanced Research, 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 HDO molecule was recorded and analyzed in the region 7600–8100 cm⁻¹ where the weak vibration–rotation bands $3\nu_1$ and $\nu_1 + \nu_2 + \nu_3$ are located. Because of the presence of strong local resonance interactions, transitions belonging to the $3\nu_2 + \nu_3$ and $6\nu_2$ bands were assigned as well. Spectroscopic parameters of all four bands were estimated, which reproduce initial line positions with accuracy close to experimental uncertainties.

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1. INTRODUCTION

Because of the large amount both of pure academic (e.g., as the partner of the H₂O and D₂O molecules in solving the problem of studying fundamental properties of water-type molecules) and applied (absorption by HDO is easily detectable in Earth's atmosphere spectra) interests, the HDO infrared spectra were the subject of extensive study for a long period of time beginning with contributions by Benedict *et al.* (1). The most extensive study was conducted by Toth and co-authors [Refs. (2–7)], who discussed HDO high-resolution spectra in the regions 970–1890 cm⁻¹ (2); 600–3100 cm⁻¹ (3); 2400–3300 cm⁻¹ (4); 3290–4370 cm⁻¹ (5); 4720–5840 cm⁻¹ (6); and 6000–7700 cm⁻¹ (7), respectively. The ν_2 and $\nu_1/2\nu_2$ bands were studied by Guelachvili (8) and Papineau *et al.* (9), respectively. Ohshima and Sasada (10) used DFB semiconductor laser spectroscopy for recording HDO spectrum in the region 6380–6600 cm⁻¹. Spectra in the regions with wavenumbers shorter than 8500 cm⁻¹ were considered in Refs. (11–16). Up until today there has been no discussion of the vibrational–rotational spectrum between 7700 and 8500 cm⁻¹.

Therefore, the goal of the present study is to discuss the experimentally recorded high-resolution spectrum of HDO in the region 7600–8100 cm⁻¹. Experimental details and results of assignments of recorded spectral lines are presented in Sections 2 and 3, respectively. Theoretical analysis of assigned transitions and obtained results are discussed in Section 4.

2. EXPERIMENTAL DETAILS

The sample of D₂¹⁶O was purchased from PeKing Chemical Industry, Ltd. (China). The stated purity of deuterium was 99.8%. The sample of HDO was prepared by mixing the D₂O and H₂O in a ratio of 1:1. The spectra were recorded at room

temperature with a Bruker IFS 120HR Fourier transform interferometer (Hefei, China), which was equipped with a path length adjustable multipass gas cell, a tungsten source, a CaF₂ beam splitter, and a Ge-diode detector. The unapodized resolution was 0.02 cm⁻¹, and the apodization function was a Blackman–Harris 3-Term. The sample pressure was 1500 Pa, which was measured by a manometer with a stated accuracy of 20 Pa. The total path length was 105 m.

Since in the region under study there are many absorption lines due to the H₂O and D₂O, the spectrum of “pure” D₂O was also recorded to identify the absorption lines of HDO. The frequency was calibrated with H₂O lines in this region listed in the HITRAN96 database. The estimated precision of positions of unblended lines was 2×10^{-3} cm⁻¹. For illustration, a small piece of one of the recorded spectra is presented in Fig. 1.

3. ASSIGNMENT OF THE SPECTRA AND THEORETICAL BACKGROUND

The HDO is a prolate asymmetric-top molecule of C_v-type symmetry. As a consequence, any of its vibrational–rotational bands contain absorption lines arising from transitions of the two types (both A and B).

Absorption spectrum in the studied region is caused by the two weak bands: by the second stretching overtone $3\nu_1$ and by the considerably weaker combination band $\nu_1 + \nu_2 + \nu_3$. Lines were assigned on the basis of the ground state combination differences method. In this case, ground state rotational energies were calculated on the basis of parameters from Ref. (9).

As a result of analysis, we were able to assign undoubtedly 215 transitions with quantum numbers $J^{\max} = 11$ and $K_a^{\max} = 5$ to the $3\nu_1$ band and 86 transitions with quantum numbers $J^{\max} = 10$ and $K_a^{\max} = 3$ to the $\nu_1 + \nu_2 + \nu_3$ band. On this basis, 83 and 37 upper energies belonging to the (300) and (111)

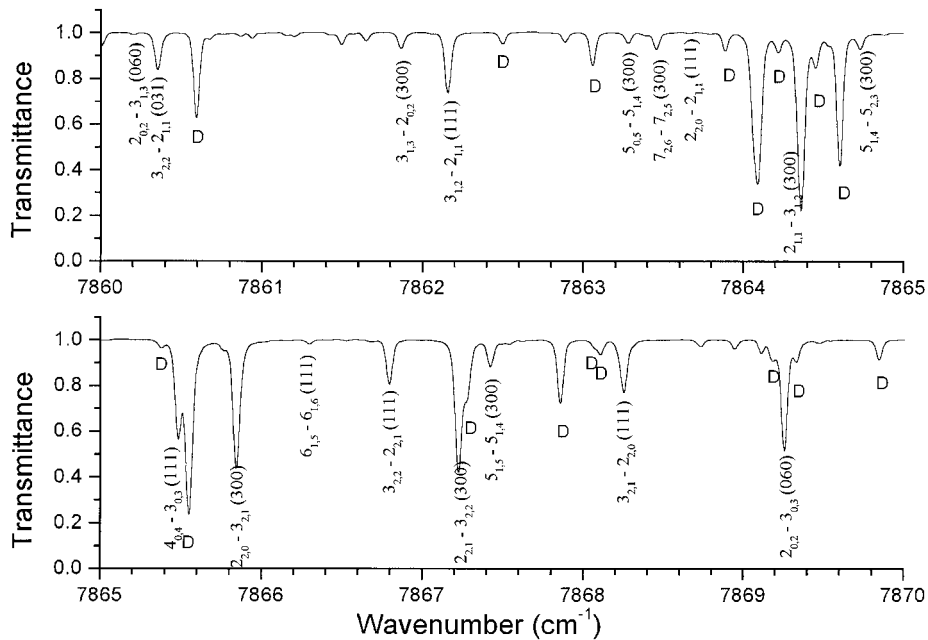


FIG. 1. Part of the spectrum of the HDO molecule in the region 7600–8100 cm^{-1} . The spectrum was recorded by a Bruker IFS 120HR FT spectrometer, with a 1:1 mixed sample of H_2O and D_2O ; pressure and optical path length were 1500 Pa and 105 m, respectively. Assignments of HDO are given; lines marked by “D” belong to D_2O .

vibrational states, respectively, were determined. One can see the mentioned energy values in columns 2 and 5 of Table 1. Δ values in columns 3 and 6 indicate the experimental uncertain-

ties of the energy values, equal to one standard deviation in units of 10^{-3} cm^{-1} .

As follows from Ref. (17), there are two additional vi-

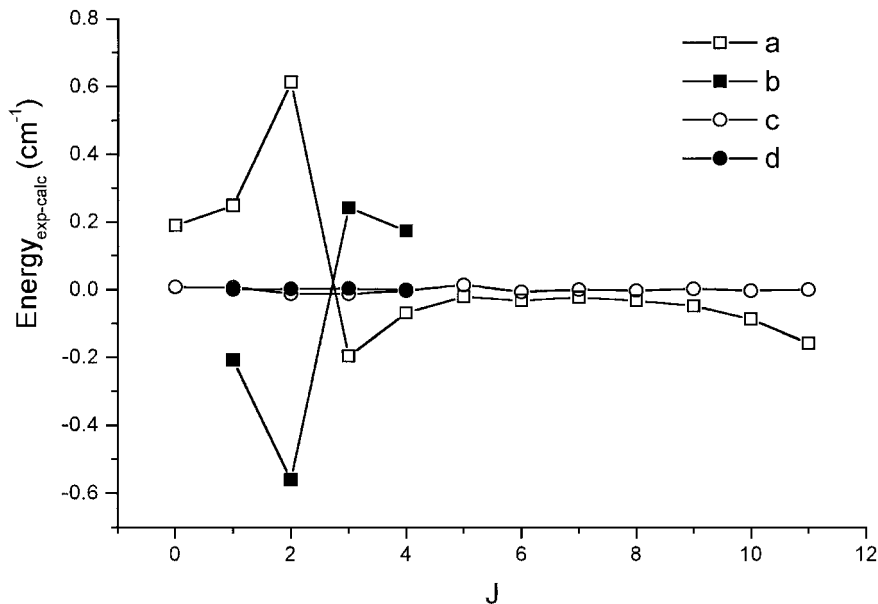


FIG. 2. Illustration of strong local resonance interaction in the (300) and (060) vibrational states of HDO. (a, b) Differences between experimental and calculated $J_{0,J}$ rovibrational energy values of the (300) band (marked with open squares) and of the (060) band (marked with solid squares), respectively. The calculated values were obtained when each band was analyzed separately and no resonance interactions with other bands were taken into account. (c, d) Values of corresponding differences of (300) band (marked with open circles) and of (060) band (marked with solid circles) when all four bands were analyzed together and the resonance interactions were included in the Hamiltonian model.

TABLE 1
Experimental Rovibrational Term Values for the (300), (111), (031), and (060) Vibrational States of the HDO Molecule (in cm^{-1})^a

(300)			(111)			(031)			(060)			(300)			(111)			(031)			(060)																			
<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	<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	11	12	13	1	2	3	4	5	6	7	8	9	10	11	12	13	1	2	3	4	5	6	7	8	9	10	11	12	13		
0	0	0	7918.172		13										6	1	5	8260.764	1	-2	8174.915	2	2																	
1	0	1	7932.887	1	11	7824.105	3	5		7929.567	1	-1		6	2	5	8283.604	2	0	8204.051	1	11																		
1	1	1	7946.614	1	4	7840.931	1	-1						6	2	4	8299.982	2	-2																					
1	1	0	7949.071	1	4	7843.993	1	-11						6	3	4									8309.142	1	-13													
2	0	2	7962.264	1	-12	7854.417	1	10		7960.594	3	6		6	3	3	8365.152	2	0																					
2	1	2	7973.462	2	3	7868.585	1	-2						6	4	3	8466.960	2	3																					
2	1	1	7980.826	1	1	7877.751	6	-16						6	4	2	8467.021	3	-1																					
2	2	1	8022.622	3	-2	7929.477	2	-6	7880.767	1	0			6	5	2	8598.815	6	13																					
2	2	0	8022.915	3	-4	7929.847	2	-7	7881.128	2	3			6	5	1	8598.815	6	13																					
3	0	3	8004.249	2	-10	7898.951	2	11		8007.463	1	2		7	0	7	8300.917	1	1	8204.288	6	-5																		
3	1	3	8013.550	2	2	7909.840	3	-2						7	1	7	8302.348	2	-1	8206.016	2	-6																		
3	1	2	8028.240	2	-1	7928.344		-19						7	1	6	8366.381	4	4	8286.575	4	-2																		
3	2	2	8066.518	1	0	7975.725	0	2	7926.538	1	-4			7	2	6	8383.581	2	0																					
3	2	1	8067.959	2	0	7977.527	2	12	7928.583	2	4			7	2	5	8409.821	2	-3																					
3	3	1	8142.018	1	-3									7	3	5	8466.571	2	-17																					
3	3	0	8142.038	2	-5									7	3	4	8471.128	1	-2																					
4	0	4	8060.223	3	-4	7956.815	3	13		8066.892		3		7	4	4	8570.236	2	21																					
4	1	4	8066.686	3	0	7964.460	1	-2						7	4	3	8570.450	1	8																					
4	1	3	8091.021	2	-2	7994.962	2	-15						7	5	3	8701.403	4	9																					
4	2	3	8124.799	3	2	8037.079	4	3	7987.545	1	-1			7	5	2	8701.403	4	5																					
4	2	2	8128.942	1	0	8042.240	5	29	7993.006	2	1			8	0	8	8404.950	2	0	8310.789	5	-1																		
4	3	2	8200.972	1	-2									8	1	8	8405.738	1	-2	8311.760	14	-4																		
4	3	1	8201.124	2	-1									8	1	7	8484.632	3	0	8411.458	2	0																		
4	4	1	8305.112	4	-2									8	2	7	8496.882	2	11																					
4	4	0	8305.112	4	-2									8	2	6	8535.261	3	-1																					
5	0	5	8128.520	3	-5	8027.231	5	6						8	3	6	8584.419	3	-4																					
5	1	5	8132.663	3	-3	8032.186	0	-3						8	3	5	8592.551	1	3																					
5	1	4	8168.729	2	-3	8077.415	1	-2						8	4	5	8688.722	3	-9					8685.554	2	5														
5	2	4	8197.246	1	0	8113.292	2	7	8063.156	1	1			8	4	4	8689.292	1	6																					
5	2	3	8206.262	2	-1	8124.382	3	-15	8074.850	1	0			8	5	4	8818.765	3	-4																					
5	3	3	8274.782	9	-6				8214.976	3	0			8	5	3	8818.781	1	-10																					
5	3	2	8275.368	2	5									9	0	9	8520.923	-	1	8429.325	1	16																		
5	4	2	8378.612	1	-2									9	1	9	8521.345	2	1	8429.844	1	-19																		
5	4	1	8378.625	1	-2									9	1	8	8615.064	1	7																					
5	5	1	8510.957	1	9									9	2	8	8623.155	1	-9																					
5	5	0	8510.957	1	7									9	2	7	8675.625	1	2																					
6	0	6	8208.767	2	1	8109.773	1	2						9	3	7	8716.557	2	14																					
6	1	6	8211.273	1	0	8112.773	2	-4						10	0	10	8648.859	1	0	8559.858		1																		

^a In Table 1, 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 1—Continued

			(300)			(111)			(031)			(060)						(300)			(111)			(031)			(060)			
<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	<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	11	12	13	1	2	3	4	5	6	7	8	9	10	11	12	13	1	2	3	4	
10	1	10	8649.082	2	1	8560.221	2	3							11	1	11	8788.884	2	1										
10	1	9	8757.106	2	6										11	1	10	8910.652	1	-2										
10	2	9	8762.191	2	-2										11	2	10	8913.705	2	-3										
11	0	11	8788.770	1	-1										11	2	9	8997.850	1	-3										

brational bands, $3\nu_2 + \nu_3$ and $6\nu_2$, which are located very close (according to Ref. (17), their band centers are $6\nu_2 = 7906.8$ cm⁻¹ and $3\nu_2 + \nu_3 = 7754.3$ cm⁻¹) to the discussed bands (from (17): $3\nu_1 = 7919.7$ cm⁻¹ and $\nu_1 + \nu_2 + \nu_3 = 7808.6$ cm⁻¹). These two additional bands can strongly perturb rotational structures of the bands $3\nu_1$ and $\nu_1 + \nu_2 + \nu_3$ by means of possible local resonance interactions. For this reason, in our further theoretical analysis we used the Hamiltonian model which takes into account four interacting vibrational states:

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

Here the diagonal operators H^{vv} ($v = 1, 2, 3, 4$) are the usual Watson's operators, Ref. (18):

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

$|1\rangle = (300)$, $|2\rangle = (111)$, $|3\rangle = (031)$, $|4\rangle = (060)$. The $H^{vv'} = (v \neq v')$ account for the operators of resonance interactions. In this case, resonance operators $H^{vv'}$ should be written in the form of the sum of two terms

$$H^{vv'} = H_F^{vv'} + H_C^{vv'}, \quad [3]$$

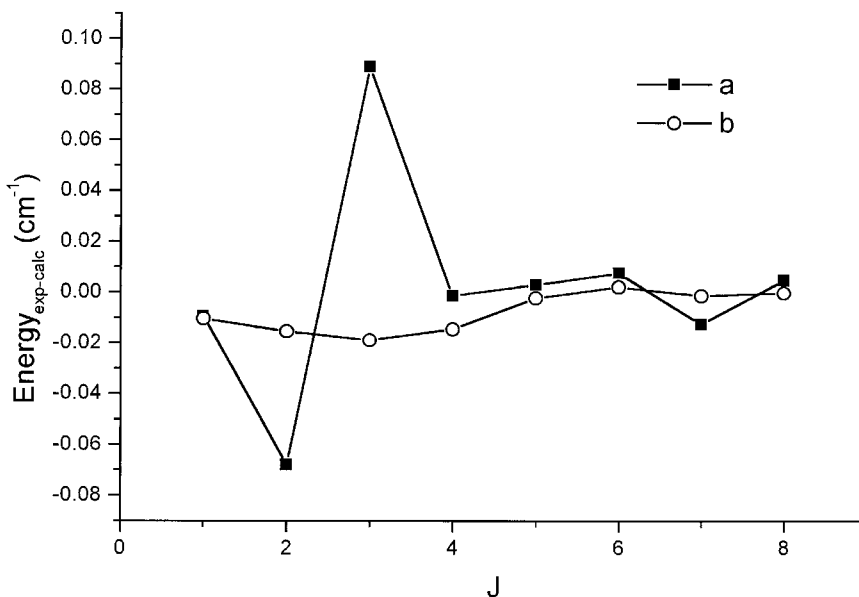


FIG. 3. Illustration of strong local resonance interaction in the (111) vibrational state of HDO. (a) Differences between experimental and calculated energy values of the $J_{1,J-1}$ (111) rovibrational states when the band was analyzed separately and no resonance interactions with other bands were taken into account. (b) Values of corresponding differences when all four bands were analyzed together and the resonance interactions were included in the Hamiltonian model.

TABLE 2
List of Transitions Belonging to the $6\nu_2$ Band of HDO

Upper			Lower			Line position,	Transmit.,	Upper energy,	Mean value,
J'	K'_a	K'_c	J	K_a	K_c	in cm^{-1}	in per cent	in cm^{-1}	in cm^{-1}
1			2			3	4	5	6
1	0	1	2	0	2	7883.3940	79.5	7929.5671	7929.5671
2	0	2	1	0	1	7945.0847	55.7	7960.5929	7960.5935
			3	0	3	7869.2618	51.4	7960.5920	
			1	1	1	7930.7839	98.6	7960.5925	
3	0	3	2	0	2	7961.2903	82.1	8007.4633	8007.4630
			4	0	4	7857.3063	87.7	8007.4624	
			2	1	2	7949.3363	99.3	8007.4632	
4	0	4	4	1	3	7883.9083	99.0	8066.8917	8066.8917

which describe resonance interactions of the Fermi-type

$$H^{vv'} = F_0^{vv'} + F_K^{vv'} J_z^2 + F_J^{vv'} J^2 + \dots + F_{xy}^{vv'} J_{xy}^2 + F_{xyK}^{vv'} [J_{xy}^2, J_z^2]_+ + \dots, \quad [4]$$

and Coriolis-type

$$H^{vv'} = C_{yK}^{vv'} [iJ_y, J_z^2]_+ + \dots + C_{xz}^{vv'} [J_x, J_z]_+ + C_{xzJ}^{vv'} [J_x, J_z]_+ J^2 + \dots, \quad [5]$$

respectively. In Eqs. [2]–[5] the following notations are used: $J_{xy}^2 = J_x^2 - J_y^2$, and $J^2 = \sum_{\alpha} J_{\alpha}^2$.

4. ANALYSIS AND DISCUSSION

The analysis began with the (300) vibrational state which corresponds to the strongest absorption band $3\nu_1$. In this case, as the analysis showed, numerous local resonance interactions do not allow one to satisfactorily reproduce rovibrational energies even for smallest values of the quantum number K_a . In particular, even an attempt to fit energies of the rovibrational states [$J, K_a = 0, K_c = J$] leads to anomalous behavior of value of the difference $E_{JK_a=0K_c=J}^{\text{exp}} - E_{JK_a=0K_c=J}^{\text{calc}}$ against the value of quantum number J (see open squares in Fig. 2). As further analysis showed, such anomalous behavior can be explained only on the basis of the Fermi-type resonance

TABLE 3
List of Transitions Belonging to the $3\nu_2 + \nu_3$ Band of HDO

Upper			Lower			Line position,	Transmit.,	Upper energy,	Mean value,	Upper			Lower			Line position,	Transmit.,	Upper energy,	Mean value,
J'	K'_a	K'_c	J	K_a	K_c	in cm^{-1}	in per cent	in cm^{-1}	in cm^{-1}	J'	K'_a	K'_c	J	K_a	K_c	in cm^{-1}	in per cent	in cm^{-1}	in cm^{-1}
1			2			3	4	5	6	1			2			3	4	5	6
2	2	1	1	1	0	7848.2705	95.1	7880.7669	7880.7670				4	1	3	7810.0235	90.3	7993.0069	
			2	1	2	7822.6402	93.9	7880.7671					4	2	3	7775.9625	99.3	7993.0043	
			3	1	2	7764.3058	96.9	7880.7671					5	3	3	7619.3416	96.7	7993.0073	
2	2	0	1	1	1	7851.3207	94.0	7881.1292	7881.1282	5	2	4	4	1	3	7880.1725	96.0	8063.1559	8063.1560
			2	1	1	7814.9442	93.5	7881.1286					5	3	3	7689.4912	98.7	8063.1569	
			2	2	1	7772.2013	97.3	7881.1275					6	1	5	7700.6479	97.4	8063.1548	
			3	3	1	7648.1037	95.2	7881.1273					6	2	5	7678.2811	98.5	8063.1564	
3	2	2	2	1	1	7860.3535	84.0	7926.5379	7926.5376	5	2	3	4	1	4	7918.4681	98.8	8074.8503	8074.8502
			3	2	1	7769.4730	99.5	7926.5377					5	1	4	7809.6132	91.4	8074.8492	
			4	2	3	7709.4961	99.1	7926.5380					5	3	2	7700.4404	98.6	8074.8502	
			4	3	1	7630.8595	96.2	7926.5368					6	2	4	7671.3037	98.2	8074.8525	
3	2	1	2	1	2	7870.4566	96.1	7928.5835	7926.5831				6	3	4	7607.3343	98.1	8074.8486	
			2	2	0	7819.3144	99.6	7928.5835		5	3	3	5	2	4	7921.3404	99.7	8214.9768	8214.9764
			3	1	2	7812.1211	90.4	7928.5824					5	3	2	7840.5661	90.6	8214.9759	
			3	2	2	7773.1937	99.4	7928.5827		6	3	4	5	3	3	7935.4756	85.0	8309.1413	8309.1415
			4	3	2	7633.0960	96.1	7928.5832					6	3	3	7839.4782	94.8	8309.1415	
4	2	3	4	1	4	7831.1629	33.5	7987.5451	7987.5452				7	3	5	7732.2374	93.3	8309.1417	
			5	1	4	7722.3098	98.2	7987.5457		8	4	5	7	3	4	8103.5922	99.1	8685.5538	8685.5544
			5	3	2	7613.1349	97.5	7987.5447					7	5	2	7867.5435	99.4	8685.5563	
4	2	2	3	1	3	7892.6134	97.0	7993.0043	7993.0057				9	4	6	7735.9772	96.7	8685.5534	

TABLE 4
Spectroscopic Parameters of the (300), (111), (031), and (060)
Vibrational States of the HDO Molecule (in cm⁻¹)^a

	(300)	(111)	(031)	(060)
1	2	3	4	5
E	7917.709(128)	7801.366(629)	7760.030(649)	7913.8760(142)
A	22.55269(489)	24.6140(400)	30.4665 (416)	42.492(896)
B	8.56585(139)	9.12372(398)	9.51708(316)	9.8788(596)
C	6.094889(510)	6.09340(380)	6.07558(254)	6.058(186)
$\Delta_K \times 10^2$	1.04106(648)	4.012(143)	8.5461 ^{b)}	16.7 ^{d)}
$\Delta_{JK} \times 10^2$	0.15978(175)	0.1290(135)	-0.0117 ^{b)}	-0.4 ^{d)}
$\Delta_J \times 10^2$	0.033581(287)	0.09782(305)	0.0596 ^{b)}	0.4843(932)
$\delta_K \times 10^2$	0.25977(683)	1.5560(807)	0.7941 ^{b)}	0.7941 ^{c)}
$\delta_J \times 10^2$	0.010686(163)	0.04035(158)	0.0211 ^{b)}	0.0211 ^{c)}
$H_K \times 10^5$	4.9519 ^{c)}	7.9484 ^{b)}	61.2612 ^{b)}	260.0 ^{d)}
$H_{KJ} \times 10^5$	-0.9269 ^{c)}	-0.9269 ^{b)}		-0.9269 ^{c)}
$H_{JK} \times 10^5$	0.2404 ^{c)}	0.2404 ^{b)}		0.2404 ^{c)}
$H_J \times 10^5$	0.003996 ^{c)}	0.003996 ^{b)}	0.00836 ^{b)}	0.003996 ^{c)}
$h_K \times 10^5$	0.890(353)	2.6179 ^{b)}		1.8366 ^{c)}
$h_{JK} \times 10^5$	0.1016 ^{c)}	0.3095 ^{b)}		0.1016 ^{c)}
$h_J \times 10^5$	0.002085 ^{c)}	0.002085 ^{b)}		0.002085 ^{c)}

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

^b Fixed to the values of parameters of the (110)/(030) diad (see text for details).

^c Fixed to the values of corresponding parameters of the ground vibrational state from Ref. (9).

^d Estimated on the basis of quadratic interpolation of corresponding parameters of the (300), (111), and (031) states.

interaction between the states [$J, K_a = 0, K_c = J$] of the (300) vibrational state and the corresponding [$J, K_a = 0, K_c = J$] states of the highly excited (060) vibrational state. On the other hand, one can expect in this case an appearance of transitions caused by the strong resonance interaction and belonging to the fifth bending overtone $6\nu_2$. Really, we were able to reliably assigned the set of such transitions, listed in Table 2. Thus, obtained rotational energies of the (060) vibrational state (see column 11 of Table 1) easily explain the anomalous behavior of the $E_{JK_a=0K_c=J}^{\text{exp}} - E_{JK_a=0K_c=J}^{\text{calc}}$ differences (see open circles in Fig. 2). Analogous analysis of the other sets of states [J, K_a, K_c] (300) with the fixed value of quantum number K_a ($K_a = 1-5$) and different values of quantum number $K_c = J - K_a$ or $K_c = J - K_a + 1$ lead to the conclusion on the presence of strong local resonances of both Fermi- and Coriolis-type between the (300) and (111) vibrational states.

Analysis of the $\nu_1 + \nu_2 + \nu_3$ band showed that, besides strong local interactions with the $3\nu_1$ band, the $\nu_1 + \nu_2 + \nu_3$ band is strongly perturbed by the $3\nu_2 + \nu_3$ band. In particular,

the set of states [$J, K_a = 1, K_c = J - 1$] (111) shows the behavior of the $E_{JK_a=1K_c=J-1}^{\text{exp}} - E_{JK_a=1K_c=J-1}^{\text{calc}}$ differences (see Fig. 3) which is very similar to the behavior of the corresponding differences in Fig. 2. In this case, it is clear (it can be seen, e.g., from comparison of energy values in columns 2 and 5 of Table 1) that the (300) vibrational state cannot cause such a behavior. The only possible reason for such strong perturbations can be in the (031) vibrational state which is close to the (111) state. In this case (similar to the pair of the (300)/(060) states), one can expect an appearance of the transitions caused by such local resonance interactions and belonging to the $3\nu_2 + \nu_3$ band. The set of such transitions assigned to the $3\nu_2 + \nu_3$ band can be seen in Table 3. The corresponding rovibrational energies of the (031) vibrational state, which were determined from the assigned transitions, are presented in column 8 of Table 1.

As a final part of analysis, energies from Table 1 were used as the input data in the fit with the Hamiltonian, Eqs. [1]–[5]. Results of the fit are given in Tables 4 and 5. In these tables, the values in parentheses are the 1 σ statistical confidence intervals. Parameters presented without confidence intervals were fixed to their initial values. In this case, the initial values of parameters of the (111) and (031) states, which are marked in Table 4 by ^{b)}, were estimated in the following way: As is clear from general physical considerations [see e.g., (19)], (a) the values of rotational constants and centrifugal distortion coefficients of the states (111) and (031) should be close to the values of the corresponding parameters of the (110) and (030) states, respectively; (b) values of the parameters of resonance interaction between the states (111) and (031) also should be close to the values of corresponding parameters describing interaction between the states (110) and (030). From this point of view, it would be suitable to take parameters of the (110) and (030) states from (20) and then use them as the initial approximations in our analysis. However, in our opinion,

TABLE 5
Parameters of Resonance Interactions Between the States (300), (111), (031), and (060) of the HDO Molecule (in cm⁻¹)^a

Parameter	Value	Parameter	Value	Parameter	Value
Fermi Type Interactions					
$F_0^{111-031}$	19.046(686)	$F_K^{111-031}$	-0.7884(853)	$F_y^{111-031}10$	-0.6396(431)
$F_{xy}^{111-031}10$	0.1679(405)	$F_{xyK}^{111-031}10^2$	0.2085(586)		
$F_{xy}^{111-300}10$	0.1231(145)				
$F_0^{031-300}$	-6.63(149)	$F_K^{031-300}$	-0.2153(647)	$F_J^{031-300}10$	-0.2223(612)
$F_{xy}^{031-300}10$	0.3564(511)	$F_{xyK}^{031-300}10^2$	-0.2872(319)		
$F_0^{300-060}$	0.8437(118)	$F_K^{300-060}$	0.3153(770)	$F_J^{300-060}10^2$	0.446(147)
Coriolis Type Interactions					
$C_{yK}^{111-031}10$	0.8846(293)	$C_{xz}^{111-031}$	-0.1394(153)	$C_{xzJ}^{111-031}10^2$	0.6505(336)
				$C_{xzJ}^{111-300}10^3$	-0.2984(665)
$C_{yK}^{031-300}10$	0.4727(612)				

^aSee footnote (a) to Table 4.

the set of parameters of Ref. (20) which, on the one hand, correctly reproduces the initial experimental data from Ref. (5), on the other hand, contains some physically unsuitable data. It concerns, first of all, some of sextic centrifugal distortion coefficients of the (110) and (030) states which are differentiated from each other and from the corresponding parameters of the ground vibrational state (9), not only by the orders of magnitude, but also by the sign. Because at the first step of our main analysis we did not need the exact values of parameters of the (111)/(031) vibrational states (but in as physically suitable, as possible, their approximate values), we refitted the experimental rovibrational energies of the (110) and (030) vibrational states from (5). In this case, we did not take into account energy values marked by "b" in Table I of Ref. (5) (energies which were not confirmed by the presence of combination differences) and sacrificed the accuracy of reproduction of the initial experimental energy values in favor of reduction of the number of used parameters. Thus, obtained values of the parameters were then used as the initial approximations for the corresponding parameters of the (111) and (031) vibrational states.

So, the parameters of the states (111) and (031) marked by (^b) in Table 3 just were fixed to the values determined from the fit of energies of the (110) and (030) vibrational states. The parameters of the state (300) marked by (^c) in Table 3 were fixed to the values of the corresponding parameters of the ground vibrational state from Ref. (9). Values of the parameters Δ_K , Δ_{JK} , and H_K of the (060) vibrational state were estimated on the basis of quadratic interpolation of the corresponding parameters of the (300), (111), and (031) states and then fixed; δ_K and δ_J parameters were fixed to the values of the corresponding parameters of the (031) state; the rest of the H - and h -type constants were fixed to the values of the corresponding parameters of the ground vibrational state (9).

The sets of parameters obtained from the fit and given in Tables 4 and 5 look like physically suitable ones because (1) they satisfactorily reproduce the initial experimental energy values (see columns 4, 7, 10, and 13 of Table 1 where the value $\delta = E^{\text{exp}} - E^{\text{calc}}$ is presented); (2) values of parameters of Table 4 correlate both with each other and with the values of the corresponding parameters of the ground vibrational state [Ref. (9)].

5. CONCLUSION

The analysis of the high-resolution Fourier transform spectra of the HDO molecule which was recorded in the region 7600–

8100 cm^{-1} allowed us not only to obtain information about the weak absorption bands $3\nu_1$ and $\nu_1 + \nu_2 + \nu_3$, but to assign for the first time the set of transitions to the "exotic" bands $6\nu_2$ and $3\nu_2 + \nu_3$. The appearance of the latter bands is caused by the strong local resonance interactions between all four vibrational states.

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