THE $\nu_2 + \nu_3$ BAND OF $HD^{16}O$

A.D. Bykov, O.V. Zotov, V.S. Makarov, and O.V. Naumenko

Institute of Atmospheric Optics
Siberian Branch of the Academy of Sciences of the USSR, Tomsk
Received August 26, 1991

Using a UFS–02 Fourier–transform spectrometer the absorption spectrum for the isotope–substituted modification of water vapor $HD^{16}O$ *has been recorded in the region* 5087–5279 cm^{-1} *with spectral resolution* 0.0098 cm^{-1} *and accuracy in the determination of line positions better than* 0.005 cm^{-1}. 103 *lines of the band formed by the transition to the vibrational state* (011) *have been interpreted, and* 72 *energy levels up to* $J \le 11$ *and* $K_a \le 6$ *have been deduced. A set of rotational and centrifugal constants reproducing the experimental data with a mean accuracy of* 0.0034 cm^{-1} *has been reconstructed from this spectrum.*

The study of rovibrational spectra of isotopic modification of the H_2O molecule is needed for determining constants of intramolecular potential function and the function of dipole moment, for calculating contribution of a weak absorption line to the atmospheric transmission function in the microwindows of relative transparency.

The $\nu_2 + \nu_3$ band is one of the strongest absorption band of the $HD^{16}O$ molecule in the 2 μm region. This band has been studied previously[1] using a classical grating spectrometer with a spectral resolution of 0.1–0.2 cm^{-1}.

In this paper we present experimentally recorded and theoretically analyzed absorption spectrum of $HD^{16}O$ near 1.9 μm as well as rovibrational energy levels and rotational and centrifugal constants of the vibrational state (011) determined using this spectrum.

The spectrum was recorded using a UFS–02 Fourier spectrometer with a resolution of 0.0098 cm^{-1}. In addition to the Fourier spectrometer, the experimental setup includes a White multipass gas cell with a baselength of 125 cm and a IVK–8 measuring–computating complex. Total pressure of the water vapor isotopic modifications in the cell was controlled with an oil–filled manometer. The pressure did not exceed 14 Torr, the optical path length in the cell was 1005 cm, and the accuracy of determining the line position was better than 0.005 cm^{-1}.

The Fourier spectrometer housing was not evacuated, therefore the narrow absorption lines of a gas sample were observed on the background of wide atmospheric absorption lines. Since the absorption by the atmosphere in the 2 μm region is mainly caused by water vapor, simultaneously observed lines of the mixture under study and those of the atmosphere made it possible a reliable identification of the absorption lines of the basic isotopic modification $H_2^{16}O$. In addition, the results from Ref. 1 were used in determining the HDO lines.

During the analysis 136 isolated lines were related to the HDO absorption lines, they are listed in Table I. The positions of line centres (cm^{-1}) are given in the first column, the absorption measured at line peaks (per cent) is shown in the second column, and in the last two columns are given the rotational quantum numbers J, K_a, and K_c. The asterisk denotes the lines not used in determining the energy levels.

The line identification has been performed using both the data from Ref. 1 and the method of combination differences. For the lines with $K_a > 4$ we also used the calculational results on the centers and relative intensities, after the inverse problem was solved (determination of rotational and centrifugal constants). Finally, 103 lines were related to rovibrational transitions in the $\nu_2 + \nu_3$ band and 15 lines – the $2\nu_1$ band.

TABLE I Absorption lines of the $\nu_2 + \nu_3$ *band of the* $HD^{16}O$ *molecule near* 1.9 μm.

ν, cm^{-1}	S	J'	K_a'	K_c'	J''	K_a''	K_c''
5087.583	0.90	1	1	1	1	1	0
5087.882	0.60	4	2	3	4	2	2
5091.169	0.60	3	2	2	3	2	1
5092.602	1.00	2	2	1	2	2	0
5093.246	0.80	1	1	0	1	1	1
5093.402	0.80	–	–	–	–	–	–
5094.628	0.20	6	3	4	6	3	3
5094.784	0.70	3	2	1	3	2	2
5096.085	0.50	5	3	3	5	3	2
5096.675	0.60	4	3	2	4	3	1
5096.859	0.90	3	3	1	3	3	0
5096.930	0.80	3	3	0	3	3	1
5097.094	0.70	4	3	1	4	3	2
5097.727	0.40	5	3	2	5	3	3
5098.184	0.60	4	2	2	4	2	3
5098.828	0.30*	2	1	1	2	1	2
5101.495	0.15	7	4	4	7	4	3
5101.696	0.30	6	4	3	6	4	2
5101.781	0.30	5	4	2	5	4	1
5101.826	0.90	4	4	1	4	4	0
		4	4	0	4	4	1
5105.022	0.70	1	0	1	0	0	0
5107.142	0.20*	3	1	2	3	1	3
5107.192	0.10	8	5	4	8	5	3
5107.266	0.50	6	5	2	6	5	1
		6	5	1	6	5	2
5107.308	0.60	5	5	1	5	5	0
		5	5	0	5	5	1
5112.903	0.30	6	6	1	6	6	0
		6	6	0	6	6	1
5113.153	0.30	6	2	4	6	2	5
5116.198	0.30	3	1	2	3	0	3
5118.234	0.70	2	1	2	1	1	1

0235-6880/91/11 807-04 $02.00

ν, cm^{-1}	S	J'	K'_a	K'_c	J''	K''_a	K''_c
5120.057	1.00	2	0	2	1	0	1
5124.194	0.20	4	1	3	4	0	4
5124.467	0.90	2	1	1	1	1	0
5131.617	1.00	3	1	3	2	1	2
5132.241	0.15	4	2	2	4	1	3
5132.531	0.15	2	1	2	1	0	1
5132.622	0.15	5	2	3	5	1	4
5133.711	0.15	3	2	1	3	1	2
5134.235	1.00	3	0	3	2	0	2
5138.237	0.20	4	0	4	3	1	3
5139.307	0.80	3	2	2	2	2	1
5140.901	0.60	3	2	1	2	2	0
5141.340	1.00	3	1	2	2	1	1
5143.573	0.10	3	1	3	2	0	2
5144.543	1.00	4	1	4	3	1	3
5146.137	0.15						
5146.906	0.15						
5147.300	1.00	4	0	4	3	0	3
5147.843	0.20	3	2	2	3	1	3
5153.076	0.15	5	0	5	4	1	4
5153.607	0.15	4	1	4	3	0	3
5154.328	0.90	4	2	3	3	2	2
5157.890	0.90	4	1	3	3	1	2
5158.161	0.80	4	2	2	3	2	1
5159.310	0.90	5	0	5	4	0	4
5159.529	0.40	4	3	1	3	3	0
5159.550	0.10						
5163.197	0.20	5	1	5	4	0	4
5166.636	0.20	6	0	6	5	1	5
5168.885	0.90	6	1	6	5	1	5
5168.983	0.85	5	2	4	4	2	3
5172.461	0.10	2	2	0	1	1	1
5172.805	0.20	6	1	6	5	0	5
5173.846	1.00	5	1	4	4	1	3
5175.005	0.60	5	3	3	4	3	2
5175.311	0.15	4	3	2	4	2	3
5175.711	0.60	5	3	2	4	3	1
5176.023	0.70	5	2	3	4	2	2
5179.714	0.30	5	4	2	4	4	1
5180.307	0.80	7	1	7	6	1	6
5181.378	0.90	7	0	7	6	0	6
5182.052	0.35	3	2	2	2	1	1
5183.189	0.90	6	2	5	5	2	4
5188.910	0.50	6	1	5	5	5	4
5190.628	0.70	6	3	4	5	3	3
5191.276	0.80	8	1	8	7	1	7
5191.844	0.30						
5191.908	0.90	8	0	8	7	0	7
5192.463	0.70	6	3	3	5	3	2
5194.031	0.80	6	2	4	5	2	3
5195.428	0.30	6	4	3	5	4	2
5195.512	0.35	6	4	2	5	4	1
5200.468	0.15	6	5	2	5	5	1
		6	5	1	5	5	0
5201.824	0.70	9	1	9	8	1	8
5202.181	0.60	9	0	9	8	0	8
5202.777	0.80	7	1	6	6	1	5
5209.964	0.70	8	2	7	7	2	6
5211.217	0.30	7	4	4	6	4	3
5211.495	0.15	7	4	3	6	4	2
5211.704	0.60	7	2	5	6	2	4
5211.990	0.50	10	1	10	9	1	9
5212.178	0.40	10	0	10	9	0	9
5214.830	0.15	4	2	2	3	1	3
5215.346	0.60	8	1	7	7	1	6
5215.404	0.15*	9	1	8	8	2	7
5221.235	0.40	8	3	6	7	3	5
5221.789	0.45	11	1	11	10	1	10
5221.887	0.45	11	0	11	10	0	10
5222.472	0.30	9	2	8	8	2	7
5222.593	0.25						
5226.798	0.40	9	1	8	8	1	7
5227.039	0.30	8	4	5	7	4	4
5228.184	0.45	8	3	5	7	3	4
5228.675	0.40*	8	2	6	7	2	5
5233.276	0.30 *a*	6	2	4	7	2	5
5234.393	0.30	10	2	9	9	2	8
5235.207	0.15						
5235.282	0.20	4	3	2	3	2	1
5235.537	0.10						
5235.558	0.50						
5237.506	0.30	10	1	9	9	1	8
5239.512	0.50 *a*	6	1	5	7	1	6
5240.925	0.40 *a*	7	0	7	8	0	8
5241.624	0.40 *a*	7	1	7	8	1	8
5245.754	0.50 *a*	6	2	5	7	2	6
5246.831	0.20	9	3	6	8	3	5
5253.576	0.30						
5256.610	0.50 *a*	6	0	6	7	0	7
5257.115	0.40 *a*	5	1	4	6	1	5
5257.771	0.40 *a*	6	1	6	7	1	7
5258.909	0.40						
5259.187	0.40 *a*	5	3	3	6	3	4
5259.347	0.20 *a*	3	1	2	4	2	3
5260.040	0.60						
5263.320	0.50	5	2	4	6	2	5
5271.112	0.35	4	4	1	3	3	0
5271.137	0.40	4	4	0	3	3	1
5271.467	0.50						
5271.859	0.60 *a*	5	0	5	6	0	6
5271.909	0.50						
5271.966	0.30						
5273.647	0.70 *a*	5	1	5	6	1	6
5273.827	0.30						
5274.763	0.50 *a*	4	2	2	5	2	3
5275.137	0.50						
5275.165	0.20 *a*	4	1	3	5	1	4
5278.926	0.50						

Note. The letter *a* denotes the lines attributed to the $2\nu_1$ band.

The $\nu_2 + \nu_3$ absorption band is hybrid, that is, the transitions of both *a* and *b* types were observed in it. The analysis of the spectrum has shown that the *b*–type transitions were much weaker than those of the *a* type, and the integral intensities for them were related as 13/100. These results are in good agreement with the data presented in Ref. 1.

We have determined 72 rotational energy levels for the state (011) with $J \le 11$ and $K_a \le 6$ based on the results of line identification. The levels of the ground vibrational state were calculated with an account of rotational and centrifugal constants.[2] The experimental levels of the state (011) were used as the initial data for solving the inverse problem.

TABLE II. Rotational and centrifugal constants of the (011) *state of* $HD^{16}O$ (cm^{-1}).

$E_V = 5089.5491_8 \pm 0.0012$

$A = 24.30220_4 \pm 0.00035$ $B = 9.23234_2 \pm 0.00012$

$C = 6.244093_4 \pm 0.000069$

$\Delta_k = (2.1097_4 \pm 0.0028) \cdot 10^{-2}$ $\Delta_{jk} = (7.856_2 \pm 0.044) \cdot 10^{-4}$

$\Delta_j = (4.1905_9 \pm 0.0079) \cdot 10^{-4}$ $\delta_k = (2.8899_2 \pm 0.0074) \cdot 10^{-3}$

$\delta_j = (1.5213_9 \pm 0.0046) \cdot 10^{-4}$

$H_k = (8.916_9 \pm 0.053) \cdot 10^{-5}$

$L_k = -3.1 \cdot 10^{-7}$

$P_k = 1.5 \cdot 10^{-9}$

Note. Standard deviation $\sigma = 0.0034$ cm^{-1}.

The vibrational state (011) with the energy 5089 cm^{-1} can surely be considered as an isolated state (not interfering with other states) because the closest to it levels (200) and (030) have energies of 5363 cm^{-1} and 4145 cm^{-1}, respectively. This fact allows one to use the effective rotational Hamiltonian by Watson, when calculting energy levels and wave functions.

The spectroscopic constants of the state (011) derived from the fitting by the method of least squares are listed in the Table 2 together with the 68% confidence intervals. The parameters without the confidence intervals were fixed in the fitting. This set of parameters provides the reconstruction of the initial levels with a mean accuracy of 0.0034 cm^{-1}. The statistical analysis of deviations of the experimental data from the calculated ones is given below:

$\Delta = |E_{exp} - E_{calc}|$;
$\Delta \le 0.003$ 71% of levels
$0.003 < \Delta \le 0.005$ 19% of levels
$0.005 < \Delta \le 0.007$ 7% of levels
$0.007 < \Delta \le 0.012$ 3% of levels.

The parameters from Table II were then used for calculating the energy levels of the (011) state up to $J \le 12$ and $K_a \le 8$. They are listed in Table III, where $\Delta = E_{exp} - E_{cal}$ and N is the number of lines based on which this level was determined. The 68% confidence intervals for the calculated levels are given in parentheses. The experimentally determined levels of the state (011) are more accurate than those found in Ref. 1. As the comparison of different data shows the experimental levels from Ref. 2 usually exceed our values by from +0.05 to +0.60 cm^{-1}.

Table III makes it possible to judge on the predictability of the obtained spectroscopic constants, since it also tabulates the calculated values of the levels not involved in the fitting. It can also be seen that the maximum estimate the calculational error for all of the levels does not exceed 0.05 cm^{-1}.

TABLE III. Rotational energy levels of the (011) *state of* HDO *for* $J \le 12$ *and* $K_a \le 8$ (cm^{-1}).

J	K_a	K_c	E_{calc}	$\Delta E \cdot 10^4$	N
0	0	0	5089.5491 (12)	–	–
1	0	1	5105.0239 (12)	–19	1
1	1	1	5120.0776 (10)	14	1
1	1	0	5123.0530 (10)	19	1
2	0	2	5135.5665 (10)	–6	1
2	1	2	5148.0421 (9)	–16	2
2	1	1	5156.9612 (9)	18	1
2	2	1	5201.8685 (9)	34	1
2	2	0	5202.2654 (9)	46	1
3	0	3	5180.4125 (9)	–35	1
3	1	3	5189.7438 (8)	6	2
3	1	2	5207.5268 (9)	–9	2
3	2	2	5248.2337 (8)	0	4
3	2	1	5250.1687 (7)	26	3
3	3	1	5329.9216 (11)	–116	1
3	3	0	5329.9549 (11)	–19	1
4	0	4	5238.6315 (8)	–31	2
4	1	4	5244.9350 (8)	0	2
4	1	3	5274.3501 (10)	3	2
4	2	3	5309.7120 (7)	39	2
4	2	2	5315.2241 (7)	6	4
4	3	2	5392.3501 (9)	–11	3
4	3	1	5392.5801 (9)	8	2
4	4	1	5504.1588 (12)	6	2
4	4	0	5504.1612 (12)	–36	2
5	0	5	5309.4581 (8)	38	2
5	1	5	5313.3513 (8)	17	1
5	1	4	5356.8307 (11)	–17	1
5	2	4	5386.0195 (7)	44	1
5	2	3	5397.8594 (10)	–14	2
5	3	3	5470.4940 (9)	–10	2
5	3	2	5471.3909 (9)	–9	2
5	4	2	5582.0395	14	2
5	4	1	5582.0601 (9)	–	–
5	5	1	5723.2708 (17)	61	1
5	5	0	5723.2710 (17)	60	1
6	0	6	5392.5047 (9)	–37	1
6	1	6	5394.7480 (10)	15	2
6	1	5	5454.1426 (12)	23	1
6	2	5	5476.8185 (8)	64	1
6	2	4	5498.0283 (12)	–3	1
6	3	4	5564.2942 (9)	–21	2
6	3	3	5566.8716 (9)	3	1
6	4	3	5675.6695 (9)	–15	2
6	4	2	5675.7701 (9)	–1	1
6	5	2	5816.4351 (13)	–1	2
6	5	1	5816.4366 (13)	–16	2
6	6	1	5985.6944 (24)	–4	1
6	6	0	5985.6944 (24)	–4	1
7	0	7	5487.6924 (11)	5	1
7	1	7	5488.9224 (11)	–4	1
7	1	6	5565.2845 (11)	–16	1
7	2	6	5581.7361 (9)		
7	2	5	5615.2602 (14)	–52	1
7	3	5	5673.5946 (9)		

J	K_a	K_c	$E_{\rm calc}$	$\Delta E\cdot 10^4$	N
7	3	4	5679.6164 (10)		
7	4	4	5785.1030 (11)	24	2
7	4	3	5785.4616 (11)	33	1
7	5	3	5925.2491 (16)		
7	5	2	5925.2582 (16)		
7	6	2	6094.0076 (28)		
7	6	1	6094.0077 (28)		
7	7	1	6289.9240 (145)		
7	7	0	6289.9240 (145)		
8	0	8	5595.0693 (11)	–4	1
8	1	8	5595.7209 (12)	1	1
8	1	7	5689.2652 (11)	–22	1
8	2	7	5700.3897 (10)	12	1
8	2	6	5748.8138 (18)		
8	3	6	5798.1415 (10)	–25	1
8	3	5	5810.1419 (15)	30	1
8	4	5	5910.3566 (15)	53	1
8	4	4	5911.3909 (14)		
8	5	4	6049.7606 (24)	–76	1
8	5	3	6049.7992 (23)		
8	6	3	6217.8547 (44)		
8	6	2	6217.8554 (41)		
8	7	2	6413.2291 (154)		
8	7	1	6413.2292 (154)		
8	8	1	6634.7751 (513)		
8	8	0	6634.7751 (513)		
9	0	9	5714.6958 (11)	1	1
9	1	9	5715.0327 (11)	–27	1
9	1	8	5825.3613 (13)	–13	1
9	2	8	5832.4140 (13)	40	1
9	2	7	5897.7638 (26)		
9	3	7	5937.5965 (14)		
9	3	6	5958.6233 (29)	17	1
9	4	6	6051.3843 (21)		
9	4	5	6053.9295 (24)		
9	5	5	6190.0128 (34)		
9	5	4	6190.1438 (34)		
9	6	4	6357.2553 (58)		
9	6	3	6357.2588 (59)		
9	7	3	6551.9463 (168)		
9	7	2	6551.9463 (168)		
9	8	2	6772.8894 (525)		
9	8	1	6772.8894 (525)		
10	0	10	5846.6081 (12)	–31	1
10	1	10	5846.7793 (12)	6	1
10	1	9	5973.2449 (19)	–49	1
10	2	9	5977.4857(19)	32	1
10	2	8	6061.0415 (41)		
10	3	8	6091.5618 (24)		
10	3	7	6124.7549 (55)		
10	4	7	6208.0562 (35)		
10	8	3	6926.2845 (541)		
10	8	2	6926.2845 (541)		
10	0	11	5990.8162 (20)	–2	1
10	1	11	5990.9022 (20)	27	1
10	4	6	6213.5613 (43)		
10	5	6	6346.0338 (50)		
10	5	5	6346.4110 (51)		
10	6	5	6512.2284 (79)		
10	6	4	6512.2420 (79)		
11	7	4	6706.0702 (189)		
11	7	3	6706.0705 (189)		
11	1	10	6132.8890 (31)		
11	2	10	6135.3384 (31)		
11	2	9	6237.5240 (60)		
11	3	9	6259.6084 (41)		
11	3	8	6307.8249 (92)		
11	4	8	6380.1490 (56)		
11	4	7	6390.7950 (78)		
11	5	7	6517.8212 (73)		
11	5	6	6518.7764 (75)		
11	6	6	6682.7897 (106)		
11	6	5	6682.8341 (106)		
11	7	5	6875.5928 (216)		
11	7	4	6875.5940 (216)		
12	8	4	7094.0343 (563)		
12	8	3	7094.9343 (563)		
12	0	12	6147.3114 (37)		
12	1	12	6147.3543 (37)		
12	1	11	6304.3915 (48)		
12	2	11	6305.7549 (48)		
12	2	10	6426.2202 (83)		
12	3	10	6441.3073 (65)		
12	3	9	6506.8694 (141)		
12	4	9	6567.3489 (87)		
12	4	8	6585.9675 (134)		
12	5	8	6705.3237 (107)		
12	5	7	6707.4967 (113)		
12	6	7	6868.9472 (141)		
12	6	6	6869.0747 (141)		
12	7	6	7060.5021 (250)		
12	7	5	7060.5065 (250)		
12	8	5	7278.8073 (593)		
12	8	4	7278.8074 (593)		

REFERENCES

1. W.S. Benedict, N. Gailar, and E.K. Plyler, J. Chem. Phys. 24, 1139 (1956).

2. N. Papineau, C. Camy–Peyret, J.M. Flaud, and G. Guelachvili, J. Mol. Spectrosc. **92**, 451 (1982).