ABSORPTION SPECTRUM OF HD^{16}O IN 0.7 μm REGION

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The absorption spectrum of HD^{16}O *has been investigated in the* 12700–12900 cm^{-1} *region with the photo-acoustic spectrometer built using the Ti-Sapphire laser with the threshold absorption sensitivity of* 10^{-8} cm^{-1}. *The absorption lines of the* $5\nu_1$ *band of* HD^{16}O *have been assigned for the first time. Fifty four energy levels of the highly excited vibrational state* (500) *have been obtained with the uncertainty from* 0.0003 *to* 0.0066 cm^{-1}. *A set of the rotational and centrifugal distortion constants has been determined by solving the inverse problem with the least squares method.*

Investigation of the intramolecular interactions in the water vapor molecule requires knowledge of the energy level structure of its isotopic species, in particular, of the nonsymmetrical isotope HDO. The HDO absorption spectra are important for atmospheric applications as well, since the water isotopic species may contribute into atmospheric absorption, especially in transparency windows and microwindows, and influence the propagation of laser radiation through the atmosphere.[3] Rovibrational structure of the HD^{16}O energy spectrum is poorly known, especially in the high energy region. Up to now information about only 15 vibrational states is available in the literature (see Ref. 1 and references therein). The $3\nu_3$ and $4\nu_3$ bands have been investigated in recently published Ref. 2 in addition to above-mentioned states. The lack of the data limits to a large extent the possibilities to study influence of intramolecular interactions on formation of the molecular spectrum, especially in the short-wave region.

In this paper, the results of the HD^{16}O absorption spectrum analysis in the 0.7 μm region are presented.

The absorption spectrum of the H$_2^{16}$O, D$_2^{16}$O and HD^{16}O mixture was recorded in the 12700–12900 cm^{-1} region using photo-acoustic spectrometer based on the single-mode tunable Ti-Sapphire laser Coherent 899–29 with the generation linewidth of 50 kHz and the tuning step of 50 MHz. The spectrometer permits investigation of weak absorption lines in the 11300–13000 cm^{-1} region and has the threshold sensitivity over the absorption coefficient of 10^{-8} cm^{-1} that corresponds to 1% beam attenuation in a 10-km cell for the classical spectrophotometry. The detailed description of the spectrometer can be found in Ref. 4.

The measurements were carried out at mixture pressure of 17 Torr and temperature of 300 K. The mixture (H$_2^{16}$O, D$_2^{16}$O, HD^{16}O) was prepared in such a way that the relative content of HD^{16}O was 50%, whereas H$_2^{16}$O and D$_2^{16}$O comprised 25% each. The recorded spectrum contains about 200 absorption lines.

The 23 absorption lines of the main isotopic species of water were found in the analyzed region, these lines were identified using data of Ref. 6 and used later on as reference lines, relative to which the positions of the HD^{16}O absorption lines were determined. The D$_2^{16}$O absorption lines were not found that, in the whole, correlates with the concept that transitions of this molecule in the near IR and visible regions are of low probability.

The special computer program[5] exploiting the pattern recognition theory has been used for line identification. Use of the recognition methods considerably facilitated and simplified the procedure of line identification in the spectrum. The lower-state combination differences method and estimations of rotational and centrifugal distortion constants were used as well.

The line identification procedure included: (a) estimation of the absorption line positions and relative intensities; (b) use of the combination difference method; (c) fitting of the rotational and centrifugal distortion constants followed by prediction calculations of the absorption lines parameters (line centers and intensities) for large values of the rotational quantum number J.

As a result of the spectrum analysis, 120 spectral lines of the $5\nu_1$ band of HD^{16}O have been assigned (see Table I), 54 energy levels with $J \leq 9$ and $K_a \leq 4$ (Table II) have been derived. In the identification process, only the absorption lines of HD^{16}O nonoverlapping with the main isotope lines were used.

Determination of the rotational and centrifugal distortion constants has been performed using the Watson-type Hamiltonian that corresponds to the isolated vibrational state case:

$$H = E_\nu + \left(A^\nu - \frac{B^\nu + C^\nu}{2}\right) J_z^2 + \frac{B^\nu + C^\nu}{2} J^2 +$$

$$+ \frac{B^\nu - C^\nu}{2} J_{xy}^2 - \Delta_k^\nu J_z^4 - \Delta_{jk}^\nu J_z^2 J^2 - \Delta_j^\nu J^4 -$$

$$- \delta_k^\nu \{J_z^2, J_{xy}^2\} - 2\delta_j^\nu J_{xy}^2 J^2 + H_k^\nu J_z^6 + H_{kj}^\nu J_z^4 J^2 + \dots ;$$

$$J^2 = J_x^2 + J_y^2 + J_z^2 , \quad J_{xy}^2 = J_x^2 - J_y^2 ;$$

$$\{A, B\} = AB + BA ,$$

where J_x, J_y, and J_z are the angular momentum operators; E_ν is the vibrational energy; A, B, C are the rotational constants, and Δ_k, Δ_{jk}, Δ_j, δ_k, δ_j ... are the centrifugal distortion constants.

Some of the levels seemed to be perturbed, and they were excluded from the fitting of the Hamiltonian parameters (for example (110) level). We believe that these levels are perturbed due to strong resonance interactions of the (500) state with the (420), (340), (260), and (071) states, which were neglected in our calculations. The parameters obtained as a result of the inverse problem solution, as well as their 68% confidential intervals are presented in Table III. It is seen from Table II that the agreement between the calculated energy levels and the levels derived from the spectrum (the 5th column of Table II) is quite satisfactory with rms deviation being only 0.013 cm^{-1}. In the whole, the reproduction of the experimental energy levels is characterized by the following relations:

$\delta < 0.005$ 23.7% of all levels

$0.005 \le \delta < 0.01$ 25.4% ,

$0.010 \le \delta < 0.03$ 37.3% ,

$0.030 \le \delta < 0.05$ 13.6% ,

where $\delta = |E_{calc} - E_{exp}|$.

TABLE I. Absorption spectrum of HD^{16}O in the 0.7 μm region.

Wave-number, cm^{-1}	$J'K_a'K_c'$	$J''K_a''K_c''$	Wave-number, cm^{-1}	$J'K_a'K_c'$	$J''K_a''K_c''$	Wave-number, cm^{-1}	$J'K_a'K_c'$	$J''K_a''K_c''$	Wave-number, cm^{-1}	$J'K_a'K_c'$	$J''K_a''K_c''$
12720.5472	2 1 2	3 1 3	12772.7615	3 1 2	3 1 3	12813.7465	4 2 2	3 2 1	12833.8797	8 1 8	7 1 7
12721.2192	4 0 4	4 1 3	12777.9519	4 1 3	3 2 2	–"–	5 0 5	4 1 4	12834.2731	8 0 8	7 0 7
12725.8531	6 4 3	6 4 2	12781.2188	1 0 1	0 0 0	12816.8857	4 1 3	3 1 2	12834.7930	8 2 7	7 2 6
12728.1255	6 3 4	6 3 3	12781.5383	1 1 0	1 0 1	12817.3020	5 3 3	4 3 2	12835.1602	8 1 8	7 0 7
12730.8547	1 1 0	2 1 1	12781.8233	3 1 2	3 0 3	12817.6086	5 3 2	4 3 1	12835.5137	7 1 6	6 1 5
12731.7035	6 3 3	6 3 4	12783.1962	4 1 3	4 0 4	12818.1152	5 1 5	4 1 4	12836.5902	7 2 5	6 2 4
12734.8795	5 4 1	5 4 2	12785.9842	5 1 4	5 0 5	12819.4807	4 1 4	3 0 3	12836.3781	9 0 9	8 1 8
12735.0413	1 0 1	2 0 2	12791.1310	2 1 2	1 1 1	12819.5848	6 4 3	5 4 2	12836.4990	2 2 1	1 1 0
12736.9029	1 1 1	2 1 2	12792.2027	3 0 3	2 1 2	12819.7789	5 2 4	4 2 3	12836.8447	9 1 9	8 1 8
12738.3730	5 3 3	5 3 2	12793.6161	2 0 2	1 0 1	12819.9789	5 0 5	4 0 4	12836.9694	9 2 8	8 2 7
12739.6175	5 3 2	5 3 3	12795.0477	1 1 1	0 0 0	12821.6832	8 1 7	7 2 6	12837.0625	9 0 9	8 0 8
12742.3111	4 4 0	4 4 1	12795.2066	2 1 1	1 1 0	12821.8539	6 0 6	5 1 5	12837.5413	9 1 9	8 0 8
12745.3351	4 2 3	4 2 2	12795.9679	3 2 1	3 1 2	12822.9371	5 2 3	4 2 2	12838.1977	8 1 7	7 1 6
12746.3279	4 3 2	4 3 1	12801.3997	3 1 3	2 1 2	12824.1165	6 3 4	5 3 3	12839.4486	2 2 0	1 1 1
12746.6392	4 3 1	4 3 2	12802.2423	3 2 2	2 2 1	12824.3441	5 1 5	4 0 4	12839.6437	8 2 6	7 2 5
12748.7137	1 0 1	1 1 0	12802.7338	6 1 5	5 2 4	12824.5497	6 1 6	5 1 5	12844.9819	3 2 2	2 1 1
12751.1344	5 2 3	5 2 4	12803.0735	2 2 0	2 1 1	12824.8092	6 3 3	5 3 2	12848.3602	9 2 8	8 1 7
12751.6177	0 0 0	1 0 1	12803.1554	3 2 1	2 2 0	12824.9499	5 1 4	4 1 3	12850.7111	4 2 3	3 1 2
12752.3956	3 3 1	3 3 0	12803.8135	4 0 4	3 1 3	12825.7815	6 0 6	5 0 5	12851.3158	8 2 7	7 1 6
12752.4248	3 3 0	3 3 1	12804.1597	3 0 3	2 0 2	12826.2421	6 2 5	5 2 4	12853.6066	7 2 6	6 1 5
12753.7653	4 2 2	4 2 3	12805.4342	2 1 2	1 0 1	12828.2117	7 0 7	6 1 6	12853.8311	5 2 4	4 1 3
12754.1048	3 2 2	3 2 1	12806.9617	3 1 2	2 1 1	12828.4661	6 1 6	5 0 5	12854.3049	3 2 1	2 1 2
12754.7511	2 1 2	2 1 1	12808.9775	4 3 2	3 3 1	12829.3679	7 3 5	6 3 4	12854.6544	6 2 5	5 1 4
12757.0433	3 2 1	3 2 2	12810.4180	4 1 4	3 1 3	12829.7871	7 1 7	6 1 6	12876.1688	3 3 1	2 2 0
12759.7305	2 2 1	2 2 0	12810.7975	4 2 3	4 1 4	12830.4440	6 2 4	5 2 3	12876.5356	3 3 0	2 2 1
12760.3343	2 2 0	2 2 1	12811.7810	4 2 3	3 2 2	12830.5151	7 0 7	6 0 6	12886.7420	4 3 1	3 2 2
12762.5379	1 1 1	1 1 0	12812.7936	5 4 1	4 4 0	12831.1428	6 1 5	5 1 4	12888.3894	5 2 3	4 1 4
12767.2369	1 1 0	1 1 1	12812.8783	4 0 4	3 0 3	12831.2312	7 2 6	6 2 5	12890.9482	5 3 3	4 2 2
12769.5857	2 1 1	2 1 2	12813.1377	7 1 6	6 2 5	12832.0930	7 1 7	6 0 6	12893.3220	7 3 5	6 2 4
12771.9285	6 2 4	6 1 5	12813.3554	3 1 3	2 0 2	12832.9920	8 0 8	7 1 7	12896.2428	5 3 2	4 2 3
									12911.6071	4 4 0	3 3 1

TABLE II. Energy levels of vibrational state (500) *of* HD^{16}O.

$J\,K_a\,K_c$	E_{exp}, cm^{-1}	rms, 10^{-3} cm^{-1}	N	δ, 10^{-3} cm^{-1}	E_{calc}, cm^{-1} (Ref. 7)	Δ, cm^{-1}
0 0 0	12767.1259	–	1	2.5	12766.7205	0.4053
1 0 1	12781.2144	3.53	3	−4.3	12780.8005	0.4141
1 1 1	12795.0320	2.24	2	−7.6	12794.6343	0.3975
1 1 0	12797.0437	3.21	3	–	12796.7760	0.2676
2 0 2	12809.1243	–	1	−14.3	12808.6972	0.4268
2 1 2	12820.9389	2.47	4	−36.1	12820.5610	0.3779
2 1 1	12827.7078	4.79	2	6.3	12827.2926	0.4150
2 2 1	12868.9975	2.12	2	1.7	12868.6219	0.3750
2 2 0	12869.2586	1.42	3	1.23	12868.8778	0.3809
3 0 3	12850.3312	1.64	2	−8.2	12849.9071	0.4238
3 1 3	12859.5276	0.93	2	3.1	12859.1213	0.4062
3 1 2	12873.1507	3.21	3	−1.6	12872.7246	0.4258
3 2 2	12911.1681	1.31	3	14.8	12910.7847	0.3828
3 2 1	12912.4295	3.09	4	11.0	12912.0414	0.3887
3 3 1	12985.4424	4.46	2	−8.2	12985.1068	0.3359
3 3 0	12985.4552	6.67	2	−3.1	12985.1236	0.3311
4 0 4	12904.2052	2.45	3	−7.1	12903.7797	0.4258
4 1 4	12910.8099	0.98	2	12.5	12910.3966	0.4131
4 1 3	12933.3468	4.72	3	0.1	12932.9160	0.4307
4 2 3	12967.1733	3.79	4	9.6	12966.7795	0.3936
4 2 2	12970.8092	2.02	2	5.3	12970.4087	0.4004
4 3 2	13042.0033	2.06	2	−6.0	13041.6631	0.3398
4 3 1	13042.1287	2.27	2	−6.0	13041.7843	0.3447
4 4 0	13144.6355	4.73	2	−0.6	13144.3690	0.2666
5 0 5	12970.1319	3.22	2	−5.0	12969.7109	0.4209
5 1 5	12974.4989	1.44	2	8.7	12974.0855	0.4131
5 1 4	13007.9319	1.61	2	−2.5	13007.4912	0.4404
5 2 4	13036.8177	3.07	2	8.9	13036.4174	0.4004
5 2 3	13044.7720	0.96	3	4.4	13044.3629	0.4092
5 3 3	13112.7855	2.71	3	−0.8	13112.4443	0.3408
5 3 2	13113.2847	1.13	3	−1.8	13112.9275	0.3574
5 4 1	13215.1234	1.21	2	11.8	13214.8410	0.2822
6 0 6	13047.7232	4.43	2	50.0	13047.3112	0.4121
6 1 6	13050.4133	1.19	2	8.7	13050.0106	0.4023
6 1 5	13096.3747	4.34	2	−2.6	13095.9294	0.4453
6 2 5	13119.8846	5.99	2	2.1	13119.4764	0.4082
6 2 4	13134.4373	1.58	2	−7.1	13134.0159	0.4219
6 3 4	13197.7857	3.39	2	−9.7	13197.4366	0.3496
6 3 3	13199.2186	0.54	2	−11.6	13198.8497	0.3691
6 4 3	13299.8256	1.91	2	−0.4	13299.5239	0.3018
7 0 7	13136.8286	1.22	2	−6.9	13136.4148	0.4131
7 1 7	13138.4053	2.48	2	1.2	13137.9959	0.4092
7 1 6	13198.0171	3.76	2	−8.5	13197.5652	0.4521
7 2 6	13216.1103	3.49	2	−5.2	13215.6969	0.4131
7 2 5	13239.5663	–	1	1.6	13239.1408	0.4258
7 3 5	13296.8768	5.1	2	1.5	13296.5349	0.3319
8 0 8	13237.4361	1.53	2	−7.7	13237.0428	0.3936
8 1 8	13238.3235	1.86	2	−1.2	13237.9319	0.3916
8 1 7	13312.1130	4.45	2	1.8	13311.6632	0.498
8 2 7	13325.2269	6.55	2	−21.0	13324.8104	0.4160
8 2 6	13359.7672	–	1	−13.6	13359.3265	0.4414
9 0 9	13349.5818	3.46	2	−9.8	13349.1925	0.3896
9 1 9	13350.0545	2.63	2	7.5	13349.6646	0.3896
9 2 8	13446.9196	3.66	2	−9.1	13446.5110	0.4086

TABLE III. Band center, rotational and centrifugal distortion constants of vibrational state (500) *of* $HD^{16}O$ *molecule (in* cm^{-1}*).*

Parameter	Value	Parameter	Value
E	12767.1201(60)	$\Delta_{jk}10^3$	2.299(30)
A	22.0137(17)	Δ_j10^4	3.275(28)
B	8.18388(57)	δ_k10^3	2.465(43)
C	5.90020(46)	δ_j10^4	1.018(28)
Δ_k10^2	1.1502(94)	H_k10^4	1.88

The band center was derived through two transitions to (000) level and found to be $\nu_0 = 12767.1259 \pm 0.0060$ cm^{-1}.

Recently the high-accuracy calculations of the energy structure and transitions probabilities of water isotopic species by Partridge and Schwenke have been published.[7] It is interesting to compare the rovibrational energy levels of the (500) state obtained in this work with that predicted in Ref. 7. The calculations in Ref. 7 were made by the variational method using *ab initio* calculated potential energy function, which was later on corrected over the data from HITRAN–92 spectral database. In Ref. 7, it is stated that the difference between the calculated line positions and that presented in the HITRAN database comprised, on average, 0.021 cm^{-1}. Differences between rovibrational energy levels calculated in Ref. 7 and that derived from the spectrum in this work are presented in the last column of Table II. For a number of levels this difference amounts up to 0.4 cm^{-1} (with the calculated values from Ref. 7 being larger than the experimental levels) decreasing up to 0.2 cm^{-1} (at $K_a = 4$) as the K_a quantum number increases. It may be suggested that the error in the vibrational energy ($J = 0$) calculation gives the main contribution into errors of the data from Ref. 7 for (500) state of $HD^{16}O$, therefore introduction of the corresponding correction to the rotational energy sublevels ($J > 0$) provides quite satisfactory agreement with the experimental data. The experimental energy levels presented in this paper can be used for correction of the potential energy function published in Ref. 7.

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