THEORETICAL ANALYSIS OF THE $2\nu_3$ ABSORPTION BAND OF HD^{16}O

A.D. Bykov, O.V. Naumenko, T.M. Petrova, and L.N. Sinitsa

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk
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The absorption spectrum of the HD^{16}O *molecule in the* 1.4 μm *region [R. Toth, J. Mol. Spectrosc.* **186***, 66–89 (1997)] is theoretically analyzed. The rotational and centrifugal distortion constants for the* (002) *vibrational state and the parameters of the effective dipole moment for the* $2\nu_3$ *band are determined with the use of the least-squares method. The parameters obtained allow high-accuracy calculation of spectral line centers and intensities to be made. Comparison of the calculated results with the experimental data shows that in some cases the intensities have been measured with the errors that significantly exceed the declared ones. The calculations are based on the use of the Pade-Borel approximations and the method of effective dipole moment. It is proved that the rovibrational energy levels of the* (002) *vibrational state can be well described up to* $J < 10$ *with the model of an isolated state.*

INTRODUCTION

In this paper we continue the study of high-resolution rovibrational spectra of the water molecule and its isotopic modifications in the near IR and visible spectral regions.[1–6] The spectra in this region are due to the transitions to high-excited rovibrational states. The HD^{16}O molecule under study in this paper is an asymmetric isotopic modification of the H$_2$^{16}O molecule. It has the following harmonic oscillation frequencies: $\omega_1 = 2827\,\text{cm}^{-1}$, $\omega_2 = 1444\ \text{cm}^{-1}$, and $\omega_3 = 3893\ \text{cm}^{-1}$, which significantly differ from the corresponding values for the H$_2$^{16}O molecule: $3834\,\text{cm}^{-1}$, $1647\ \text{cm}^{-1}$, and $3940\ \text{cm}^{-1}$, respectively. As a result, the intramolecular dynamics of HD^{16}O has certain peculiarities. In particular, the vibrational states of the $(00V)$ type corresponding to excitation of the n m bond, can be considered isolated to a good approximation starting from $V = 1$ and 2 (what is demonstrated in this paper) and up to $V = 5$ (see Ref. 6).

The study of high-resolution spectra of the HD^{16}O molecule is needed for different applications in atmospheric optics, because its spectral lines are observed in atmospheric spectra. It should be noted that rovibrational spectra of HD^{16}O have been studied, more or less adequately, only in the region of low vibrational states (see, for example, Refs. 7–10). At the same time, only little is known about the HD^{16}O spectra in the region from 7000 to 16000 cm^{-1}. The spectroscopic constants (that means the rotational and centrifugal distortion constants, parameters of the effective dipole moment) of the low vibrational states have been determined in Refs. 7 and 8, while Refs. 6 and 11–14 dealt with some high-excited vibrational states with the energy up to 16000 cm^{-1}.

This paper is devoted to the study of high-resolution Fourier-transform spectrum of the HD^{16}O molecule in the 6817–7625 cm^{-1} range. The spectrum has been recorded by R. Toth.[15] In the spectral range under study there are spectral lines of the $2\nu_3$ band corresponding to excitation of two quanta of the n m bond oscillation. The aim of this study is to determine the spectroscopic constants, which could allow reconstructing the initial spectrum with the accuracy equal or close to the experimental one. The parameters obtained are then used to check the identification of the spectral lines, to test the experimental intensities, and finally to compile the reliable database on HD^{16}O absorption in this spectral range.

The necessity of doing this work is caused by the following circumstances. As known, the spectra of HDO are observed simultaneously with the spectra of H$_2$O and D$_2$O molecules. The exchange by hydrogen isotopes at collisions may lead to appearance of all the three isotopic modifications in the natural water vapor. As a result, the HD^{16}O absorption spectrum may be distorted by close spectral lines of H$_2$O and D$_2$O. This may result in errors when identifying the spectral lines and in perturbation of the observed line intensities. Other sources of errors are also possible, in particular, uncertainty in the HDO partial pressure, errors in determination of the base line, line overlapping, and others. The above circumstances often hamper adequate

assessments of the experimentally obtained intensities and the accuracy with which those have been measured.

Besides, the calculations of intensities of rovibrational lines within the framework of the effective Hamiltonian model, as a rule, provide reconstruction of the initial data and prediction of spectral line parameters with the accuracy close to the experimental one, while, simultaneously, enabling one to reveal the values, whose deviations from the exact calculations exceed the declared measurement errors. In such a case, the calculated values of intensities are preferable for use in applications.

To reconstruct and predict rovibrational line centers and intensities, we used the effective rovibrational Hamiltonian written in terms of the Pade-Borel approximations. The results of recent highly precise *ab initio* calculations[16] for the HD^{16}O molecule have also been used to support the numerical data obtained.

ANALYSIS AND RESULTS

As known, for the light non-rigid molecules, such as H$_2$^{16}O, the effective rotational Hamiltonian in its traditional form as a power series over powers of the operator of angular momentum turns out to be inapplicable. This happens because the power series become diverging with the growth of rotational and vibrational excitation. For this reason, when analyzing the rotational energy sublevels of the (002) vibrational state of the HD^{16}O molecule, we used the effective rotational Hamiltonian with the matrix elements in the form of the Pade-Borel approximations. In this case, matrix elements of the Hamiltonian in the basis of symmetric-top functions $|jk>$ are calculated by the following equations[17, 18]:

$$<jk|W_V|jk> = E_V + \int_0^\infty dt\, e^{-t} \frac{c_0 c_1 + (c_1^2 - c_0 c_2)\, t}{c_1 - c_2 t},$$

$$<jk|W_V|jk \pm 2> = <jk|J_{xy}^2|jk \pm 2> \times$$

$$\times \int_0^\infty dt\, e^{-t} \frac{b_0 b_1 + (b_1^2 - b_0 b_2)\, t}{b_1 - b_2 t}; \qquad (1)$$

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

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

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

$$+ H_j j^3 (j+1)^3 + L_k k^8 + \dots ; \qquad (2)$$

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

$$b_1 = -\delta_k [k^2 + (k \pm 2)^2] - 2\delta_j j\,(j+1), \qquad (3)$$

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

$$\times j\,(j+1) + 2h_j j^2 (j+1)^2 + \dots$$

The integrals in Eq. (1) can be calculated as follows:

$$<jk|W_V|jk> = E_v + (c_0 c_2 - c_1^2)/c_2 +$$

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

$$Ei(-x) = -\int_x^\infty e^{-t}\, t^{-1}\, dt. \qquad (4)$$

Here, $Ei(x)$ is the integral exponent; $J_{xy}^2 = J_x^2 - J_y^2$, J_x, J_y, and J_z are the operators of angular momentum; A, B, and C are the rotational constants; Δ_k, Δ_{jk}, Δ_j, δ_k, δ_j … are the centrifugal distortion constants. Equations (1)–(4) allow one to calculate the energy levels with large values of the quantum numbers J and K_a, for which the calculated results differ from those obtained using the Watson Hamiltonian. Among the advantages of the above method is that the rotational and centrifugal distortion constants obtained from fitting to the experimental data have the same meaning as in the case with the standard effective Watson Hamiltonian.

From fitting to the experimental energy levels[15] by the method of least squares, we have determined the rotational and centrifugal distortion constants (1)–(4) of the (002) vibrational state. Thus obtained values allow calculation of the line centers to 0.0016 cm^{-1} as high accuracy. Table I gives the values of parameters, the 65-% confidence intervals, and statistics of the discrepancies between the calculated and experimental values (in %).

As was assumed, the rotational energy spectrum of the (002) state of HD^{16}O is well described within the framework of the isolated-state model. At the same time, we have found that some levels of the (002) state, with $J \geq 10$, are a little bit perturbed (from 0.01 to 0.14 cm^{-1}) due to interactions with the (012), (111), (101), and (031) states. These 11 levels were excluded from fitting, because the account for resonance perturbations did not actually improve the line identification and had no effect upon calculation of the intensities of transitions to the perturbed levels. The experimental energy levels from Ref. 15 are presented in Table II along with their deviations from the calculated results. There are three experimental levels from Ref. 15 that turned out to be erratic. They deviate from our calculations by more than 1 cm^{-1}. These levels are presented in Table II separately.

The calculated energy levels of the (002) state from Ref. 16 coincide with the experimental data, on the average, within 0.1–0.15 cm^{-1}. The deviations are, as a rule, positive. They slowly decrease for the same quantum number J and increasing K_a, while increasing (up to 0.3 cm^{-1} for $J = 19$) with the increasing J.

TABLE I. *Rotational and centrifugal distortion constants of the* (002) *vibrational state of the* HDO *molecule, in* cm^{-1}.

E_v	7250.51921	H_{jk}	$0.191749(4400) \cdot 10^{-5}$
A	21.3633223(1200)	H_j	$0.465569(3400) \cdot 10^{-7}$
B	9.08115725(3900)	h_k	$0.128947(2600) \cdot 10^{-4}$
C	6.24925400(3200)	h_{jk}	$0.107760(2000) \cdot 10^{-5}$
Δ_k	$0.10495354(9600) \cdot 10^{-1}$	h_j	$0.16402(1000) \cdot 10^{-7}$
Δ_{jk}	$0.760277(3700) \cdot 10^{-3}$	L_k	$-0.5352(1200) \cdot 10^{-8}$
Δ_j	$0.3844319(1700) \cdot 10^{-3}$	L_{kj}	$-0.94737(8600) \cdot 10^{-8}$
δ_k	$0.1849169(3400) \cdot 10^{-2}$	L_{kjj}	$0.14113(1800) \cdot 10^{-8}$
δ_j	$0.1336823(2200) \cdot 10^{-3}$	L_j	$0.15015(1300) \cdot 10^{-10}$
H_k	$0.371305(2500) \cdot 10^{-4}$	p_k	$-0.84825(6300) \cdot 10^{-9}$
H_{kj}	$-0.81518(1800) \cdot 10^{-5}$	p_{kkj}	$0.42780(3000) \cdot 10^{-9}$

The number of levels 175
The number of parameters 21
RMS deviation, in cm^{-1} 0.0016

Deviation statistics

$0 < \delta E \leq 0.001$ cm^{-1}	66.86% of all levels
$0.001 < \delta E \leq 0.002$ cm^{-1}	17.14% of all levels
$0.002 < \delta E \leq 0.004$ cm^{-1}	16.00% of all levels

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

TABLE II. *Energy levels of the* (002) *vibrational state,* cm^{-1}.

J	K_a	K_c	$E_{\exp}$	$(E_e - E_c) \cdot 10^4$	J	K_a	K_c	$E_{\exp}$	$(E_e - E_c) \cdot 10^4$	J	K_a	K_c	$E_{\exp}$	$(E_e - E_c) \cdot 10^4$
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	0	0	7250.5192	0	7	7	1	8325.9906	17	11	5	7	8605.2182	40
1	0	1	7265.8482	1	7	7	0	8325.9906	17	11	5	6	8606.7908	27
1	1	1	7278.1223	−1	8	0	8	7750.4654	0	11	6	6	8744.1188	−36
1	1	0	7280.9461	1	8	1	8	7750.8215	0	11	6	5	8744.2079	−31
2	0	2	7296.0651	2	8	1	7	7836.9875	−9	11	7	5	8907.6087	43
2	1	2	7305.9476	0	8	2	7	7844.0331	−2	11	7	4	8907.6099	25
2	1	1	7314.4122	4	8	2	6	7892.5344	−6	12	0	12	8299.4140	−8
2	2	1	7351.1046	−1	8	3	6	7928.9206	2	12	1	12	8299.4302	−27
2	2	0	7351.5365	0	8	3	5	7943.0113	9	12	1	11	8440.7939	15
3	0	3	7340.3550	0	8	4	5	8023.4091	4	12	2	11	8441.4480	15
3	1	3	7347.4214	−3	8	4	4	8024.8792	8	12	2	10	8554.9805	−6
3	1	2	7364.2898	6	8	5	4	8140.3066	−10	12	3	10	8563.4975	0
3	2	2	7397.0363	0	8	5	3	8140.3710	−13	12	3	9	8632.5936	1
3	2	1	7399.1278	0	8	6	3	8282.2557	2	12	4	9	8674.2916	−3
3	3	1	7465.0669	0	8	6	2	8282.2557	−11	12	4	8	8698.1974	5
3	3	0	7465.1088	1	8	7	2	8448.3614	−1	12	5	8	8791.4471	−7
4	0	4	7397.7816	0	8	7	1	8448.3614	−2	12	5	7	*8794.9971	188
4	1	4	7402.2841	−3	8	8	1	8637.5603	−11	12	6	7	*8929.1909	−117
4	1	3	7430.1374	5	8	8	0	8637.5603	−11	12	6	6	*8929.4465	−95
4	2	3	7457.9088	0	9	0	9	7869.2437	5	12	7	6	9091.4386	0
4	2	2	7463.7942	3	9	1	9	7869.4160	5	12	7	5	9091.4449	−44
4	3	2	7526.9745	−2	9	1	8	7970.1893	−7	13	0	13	8467.3690	36
4	3	1	7527.2620	0	9	2	8	7974.3397	1	13	1	13	8467.3700	−39
4	4	1	7620.3524	−3	9	2	7	8038.8286	−11	13	1	12	8621.6291	20
4	4	0	7620.3564	3	9	3	7	8066.7605	2	13	2	12	8621.9644	12
5	0	5	7467.6630	−4	9	3	6	8090.7492	8	13	2	11	8750.3138	−36
5	1	5	7470.2672	−4	9	4	6	8163.3126	7	13	3	11	8755.4167	−9
5	1	4	7511.2850	4	9	4	5	8166.8801	12	13	3	10	8842.4405	6
5	2	4	7533.4166	0	9	5	5	8279.5845	−31	13	4	10	8873.7848	−8
5	2	3	7545.8548	5	9	5	4	8279.8029	−36	13	4	9	8910.5415	1

Continuation of Table II

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
5	3	3	7604.4570	0	9	6	4	8420.6759	3	13	5	9	8993.0792	− 13
5	3	2	7605.5704	− 1	9	6	3	8420.6826	1	13	5	8	9000.2362	− 26
5	4	2	7697.6111	− 3	9	7	3	8586.0792	0	13	6	8	*9129.8230	− 333
5	4	1	7697.6406	− 4	9	7	2	8586.0792	0	13	6	7	*9130.4434	− 619
5	5	1	7816.2712	13	9	8	2	8774.6415	− 24	14	0	14	8647.5468	5
5	5	0	7816.2712	10	9	8	1	8774.6415	− 24	14	1	14	8647.5468	− 35
6	0	6	7549.7312	− 4	9	9	1	8985.3953	7	14	1	13	8814.5405	19
6	1	6	7551.1335	− 3	9	9	0	8985.3953	7	14	2	13	8814.7091	− 5
6	1	5	7606.8188	1	10	0	10	8000.3325	9	14	2	12	8957.0030	29
6	2	5	7623.1995	− 3	10	1	10	8000.4145	9	14	3	12	8959.9335	− 13
6	2	4	7645.1069	3	10	1	9	8115.1680	− 3	14	3	11	9064.8680	0
6	3	4	7697.4250	− 1	10	2	9	8117.4889	5	14	4	11	9087.0940	− 11
6	3	3	7700.5883	2	10	2	8	8198.6778	− 17	14	5	10	9209.8358	41
6	4	3	7790.5148	− 3	10	3	8	8218.7657	2	14	6	9	*9345.9441	− 943
6	4	2	7790.6596	− 3	10	3	7	8255.5710	5	14	6	8	*9347.4030	− 1456
6	5	2	7908.7041	− 2	10	4	7	8318.6381	5	15	0	15	8839.9195	− 3
6	5	1	7908.7056	− 13	10	4	6	8326.1902	13	15	1	15	8839.9195	− 22
6	6	1	8051.8452	12	10	5	6	*8434.6014	379	15	1	14	9019.5317	2
6	6	0	8051.8452	12	10	5	5	*8435.2017	111	15	2	14	9019.6144	− 37
7	0	7	7643.9776	− 4	10	6	5	8574.6210	6	15	4	12	9313.7451	− 1
7	1	7	7644.6963	− 3	10	6	4	8574.6482	8	16	0	16	9044.4452	11
7	1	6	7715.6901	− 7	10	7	4	8739.1586	32	16	1	16	9044.4452	1
7	2	6	7726.8681	− 1	10	7	3	8739.1586	25	16	1	15	9236.5878	1
7	2	5	7760.9497	2	11	0	11	8143.7292	12	16	2	15	*9236.6226	− 92
7	3	5	7805.6805	0	11	1	11	8143.7681	16	17	0	17	9261.0778	36
7	3	4	7812.9331	5	11	1	10	8271.9995	8	17	1	17	9261.0778	41
7	4	4	7899.1150	1	11	2	10	8273.2485	9	17	1	16	9465.6764	6
7	4	3	7899.6289	1	11	2	9	8370.9882	− 16	17	2	16	*9465.7232	242
7	5	3	8016.6956	− 12	11	3	9	8384.4874	2	18	0	18	9489.7549	− 29
7	5	2	8016.7108	− 14	11	3	8	8436.5585	0	18	1	18	9489.7549	− 37
7	6	2	8159.3231	− 4	11	4	8	8489.0926	1	19	0	19	9730.4455	12
7	6	1	8159.3231	− 6	11	4	7	8503.2674	8	19	1	19	9730.4455	2

Erratic experimental levels from Ref. 15								
J	K_a	K_c	Our calculations			H. Partridgt and D. Schwenke, Ref. 16		Experiment, Ref. 15
10	8	3	8926.9626			8927.0156		8928.0343
10	8	2	8926.9626			8926.9977		8928.0343
15	2	13	9175.1653			9175.4339		9174.7987

*Asterisk denotes the levels excluded from fitting.

The wave functions obtained by solving the inverse problem for the energy levels were then used to analyze the experimental intensities of the rovibrational lines based on the commonly accepted model.[19] In this model the operator of transformed dipole moment is presented as a function of vibrational and rotational quantum numbers with eight empirically determined parameters:

$$M_Z = \sum_{v \in \Gamma} |0> \sum_k {}^v\mu'_k \, {}^v A_k <v|, \qquad (5)$$

where ${}^v\mu'_k$ are the parameters and ${}^v A_k$ are the fixed combinations of the operators of angular momentum and the direction cosines:

k	${}^v A_k$ Transitions of the A type	${}^v A_k$ Transitions of the B type
1	φ_z	φ_x
2	$\{\varphi_z, J^2\}$	$\{\varphi_x, J^2\}$
3	$\{\varphi_z, J_z^2\}$	$\{\varphi_x, J_z^2\}$
4	$\frac{1}{2}\{\varphi_x, i\,J_y\} - \frac{1}{2}\{i\,\varphi_y, J_x\}$	$\{i\,\varphi_y, J_z\}$
5	$\frac{1}{2}\{\varphi_x, \{J_x, J_z\}\} - \frac{1}{2}\{\varphi_y, \{J_y, J_z\}\}$	$\{\varphi_z, i\,J_y\}$
6	$\frac{1}{2}\{\varphi_x, i\,J_x\} + \frac{1}{2}\{i\,\varphi_y, J_x\}$	$\{\varphi_z, \{J_x, J_z\}\}$
7	$\frac{1}{2}\{\varphi_x, \{J_x, J_z\}\} + \frac{1}{2}\{i\,\varphi_y, \{J_z, J_y\}\}$	$\frac{1}{2}\{\varphi_z, J_{xy}^2\} - \frac{1}{2}\{\varphi_z, \{J_x, J_y\}\}$
8	$\{\varphi_z, J_{xy}^2\}$	$\frac{1}{2}\{\varphi_z, J_{xy}^2\} + \frac{1}{2}\{\varphi_z, \{J_x, J_y\}\}$

Here φ_x and φ_y are the direction cosines.

From fitting to 957 experimental intensities we have determined 15 parameters of the operator of dipole moment separately for the transitions of the A and b types. Thus obtained values allow reconstruction of the initial intensities to be, on the average, made with the experimental accuracy. The RMS deviation for the calculated intensities is 3.5%. Table III gives the obtained values of these parameters.

TABLE III. Parameters of the effective dipole moment for the (002) vibrational state of $HD^{16}O$.

N	Transitions of the B type	Transitions of the A type
1	$0.61331\ (120) \cdot 10^{-2}$	$0.81868\ (180) \cdot 10^{-2}$
2	$-\ 0.8102\ (630) \cdot 10^{-6}$	$0.12954\ (850) \cdot 10^{-5}$
3	$0.4301\ (270) \cdot 10^{-5}$	$-\ 0.5344\ (330) \cdot 10^{-5}$
4	$-\ 0.106956\ (960) \cdot 10^{-3}$	$-\ 0.929\ (120) \cdot 10^{-5}$
5	$0.52194\ (510) \cdot 10^{-4}$	$0.1422\ (140) \cdot 10^{-5}$
6	$-\ 0.10506\ (810) \cdot 10^{-5}$	$0.44708\ (430) \cdot 10^{-4}$
7	$0.6050\ (850) \cdot 10^{-6}$	$-\ 0.19732\ (820) \cdot 10^{-5}$
8	$0.4305\ (610) \cdot 10^{-6}$	
The number of lines	504	453
RMS deviation, %	3.69	3.25

As seen from the Table, the main parameters for transitions of the types A and b have close values, i.e., the $2\nu_3$ band is of a hybrid nature.

It was found that the calculated intensities for the 146 rovibrational lines (they were excluded from fitting) significantly (from 15 to 1000%) deviate from the experimental values. These lines, along with their quantum indices, calculated (I_{calc}) and experimental (I_{exp}) intensities, and errors in experimental values (DI_e) are presented in Table IV. For a comparison, this table also gives the calculated intensities from Ref. 16 (I_{sch}) and their deviations from the experimental values in % (DI_e).

It is seen from Table IV, that the majority of lines have large (10–15%) experimental uncertainties. Remind that R. Toth, the author of the experimental results, includes possible errors from 10 to 65% into the concept of 15-% experimental error.[15] It is easy to see that the *ab initio* calculations of the intensities by H. Partridgt and D. Schwenke (Ref. 16) are very close to our results and have the same tendencies in deviation from the experiment. Some, especially large, discrepancies between the calculated and experimental results are possibly mere misprints in Ref. 15. These values are marked in Table IV with asterisk. It should also be noted that, regardless of the discrepancies with the experimental data from Ref. 15, there are a number of lines included in fitting, in which the experimental intensity was used as a sum of two or sometimes three lines, while in Ref. 15 those have been considered as single lines.

Note also the following circumstance. The detailed comparison of calculated intensities from Ref. 16 with the experimental data has demonstrated their very close correspondence: the RMS deviation was only 4.5%. At the same time, starting from $J = 12$, the calculated intensities from Ref. 16 become strongly different (up to 96%) from the experimental values for the transitions to the levels with $K_a = 0, 1$. Table V gives some examples of such transitions. One can see that our calculations, in contrast to those in Ref. 16, closely agree with the experiment.

Based on the above-said we can assume that the calculated line intensities presented in Table IV are more accurate than the experimental ones, and they can, with high degree of confidence, be used in different applications.

Finally, we have calculated the absorption spectrum of $HD^{16}O$ in the spectral range under study. The spectrum consists of 2830 rovibrational absorption lines of HDO with the intensities $I \geq 1 \cdot 10^{-7}\ cm^{-2}/atm$. The electronic version of the data file may be presented to an interested reader on request to the authors. The integral intensity of the $2\nu_3$ band obtained as a sum of all calculated line intensities equals to 7.731 cm^{-2}/atm (5.048 and 2.682 for transitions of the A and b types, respectively). This estimate is close to that obtained in Ref. 16 – 7.526 cm^{-2}/atm.

CONCLUSIONS

Within the framework of the effective Hamiltonian of an isolated state written in terms of the Pade-Borel approximations, the absorption spectrum of the $2\nu_3$ band of the $HD^{16}O$ molecule has been theoretically analyzed in the spectral range from 6817 to 7625 cm^{-1}. The sets of spectroscopic constants have been determined. The obtained constants allow reconstruction of the spectral line centers and intensities to be made with the accuracy close or equal to the experimental one. The erratic assignments in the initial experimental data on the $2\nu_3$ band of $HD^{16}O$ have been revealed. Our calculations have allowed us to estimate the accuracy of intensity measurements presented in Ref. 15. It is shown that about 13% of the experimental values have errors from 15 to 90%. The synthetic absorption spectrum of $HD^{16}O$ molecule has been calculated for the spectral range under study.

Comparison of numerical results obtained within the framework of the effective Hamiltonian model with the high-precision *ab initio* predictions has demonstrated their close agreement. At the same time, we have found that the accuracy of *ab initio* estimates abruptly decreases for some transitions with $J \geq 12$.

Thus, simultaneous use of both these theoretical approaches is the most efficient way to create ideal data banks on absorption spectra of water vapor and its isotopic modifications.

TABLE IV. Experimental intensities of the 2ν₃ *band of* HDO *deviating by more than* 15% *from the calculated values.*

Exp. wavenumber, cm⁻¹	J	K_a	K_c	J	K_a	K_c	I_{calc}, cm⁻²/atm	I_{exp}, cm⁻²/atm	$(I_e - I_c)/I_e$, %	DI_e, %	I_{sch}, cm⁻²/atm	$(I_e - I_c)/I_e$, %
6817.2800	10	6	5	11	7	4	0.4279e −04	0.2300e −04	−86.00	10	0.4014e −04	−74.52
6817.3066	10	6	4	11	7	5	0.4278e −04	0.2610e −04	−63.90	10	0.4012e −04	−53.72
6851.6620	9	3	6	10	5	5	0.5243e −05	0.1490e −04	64.80	15	0.5561e −05	62.68
6868.1210	11	2	10	12	3	9	0.2535e −04	0.1230e −04	−106.10	15	0.2449e −04	−99.11
6879.4180	6	3	4	7	5	3	0.2254e −04	0.1880e −04	−19.90	15	0.2199e −04	−16.97
6895.2906	5	3	3	6	5	2	0.2507e −04	0.1770e −04	−41.60	15	0.2400e −04	−35.59
6896.4040	5	3	2	6	5	1	0.2494e −04	0.1720e −04	−45.00	15	0.2386e −04	−38.72
6905.1987	11	4	7	12	5	8	0.5750e −04	0.4830e −04	−19.10	15	0.5519e −04	−14.27
6918.4970	7	4	3	7	6	2	0.7446e −05	0.2060e −04	63.90	15	0.7051e −05	65.77
6940.8985	8	2	6	9	4	5	0.2260e −04	0.2770e −04	18.40	15	0.2328e −04	15.96
6943.2970	9	9	1	10	9	2	0.5177e −05	0.2940e −04	82.40	15	0.4637e −05	84.23
6943.2970	9	9	0	10	9	1	0.5177e −05	0.2940e −04	82.40	15	0.4637e −05	84.23
6954.2640	13	6	7	14	6	8	0.2102e −04	0.2660e −04	21.00	15	0.1626e −04	38.87
6954.2640	13	6	8	14	6	9	0.2102e −04	0.2660e −04	21.00	15	0.1626e −04	38.87
6972.3064	9	8	1	10	8	2	0.3362e −04	0.4040e −04	16.80	15	0.3032e −04	24.95
6972.3064	9	8	2	10	8	3	0.3362e −04	0.4040e −04	16.80	15	0.3032e −04	24.95
6975.8464	6	0	6	6	4	3	0.1496e −04	0.1780e −04	15.90	15	0.1497e −04	15.90
6975.8464	10	1	10	10	3	7	0.1496e −04	0.1780e −04	15.90	15	0.1497e −04	15.90
6982.3390	15	1	14	16	2	15	0.1634e −04	0.1390e −04	−17.50	15	0.1792e −04	−28.92
6982.4753	15	1	14	16	1	15	0.2792e −04	0.2190e −04	−27.50	15	0.2316e −04	−5.75
6983.8724	9	3	7	9	5	4	0.2508e −04	0.5770e −04	56.50	15	0.2458e −04	57.40
6986.7778	11	6	6	11	7	5	0.1917e −04	0.1550e −04	−23.70	15	0.1758e −04	−13.42
6986.9080	10	6	4	10	7	3	0.3660e −04	0.3050e −04	−20.00	15	0.3397e −04	−11.38
6988.6110	8	8	0	9	8	1	0.3661e −04	0.5260e −04	30.40	15	0.3328e −04	36.73
6988.6110	8	8	1	9	8	2	0.3661e −04	0.5260e −04	30.40	15	0.3328e −04	36.73
6994.7067	3	2	2	4	4	1	0.4422e −04	0.5690e −04	22.30	15	0.4171e −04	26.70
7000.2217	14	1	13	15	1	14	0.7671e −04	0.6420e −04	−19.50	15	0.6664e −04	−3.80
7000.3900	14	2	13	15	1	14	0.4386e −04	0.6700e −04	34.50	15	0.4579e −04	31.66
7000.4740	8	3	5	8	5	4	0.3244e −04	0.5910e −04	45.10	15	0.3134e −04	46.97
7002.8790	13	3	11	14	3	12	0.9719e −04	0.7290e −04	−33.30	15	0.8776e −04	−20.38
7007.9648	9	3	6	9	5	5	0.2643e −04	0.3600e −04	26.60	15	0.2579e −04	28.36
7009.8510	9	0	9	9	3	6	0.g673e −04	0.2940e −04	−24.90	15	0.3404e −04	−15.78
7011.7350	12	2	10	13	3	11	0.9705e −04	0.1160e −03	16.30	2	0.9588e −04	17.34
*7015.0728	7	2	6	8	3	5	0.1514e −02	0.1460e −03	−937.10	2	0.1455e −02	−896.58
7023.8680	11	2	9	12	3	10	0.2137e −04	0.2600e −04	17.80	10	0.2087e −04	19.73
7023.8820	10	5	5	11	5	6	0.3247e −03	0.2700e −03	−20.30	6	0.2972e −03	−10.07
7024.0347	10	5	6	11	5	7	0.3241e −03	0.2790e −03	−16.20	2	0.2682e −03	3.87
7034.6400	8	2	7	8	4	4	0.8032e −04	0.2400e −03	66.50	4	0.7857e −04	67.26
7038.6702	8	0	8	8	3	5	0.9443e −04	0.7700e −04	−22.60	7	0.8950e −04	−16.23
7051.7890	7	2	5	6	5	2	0.9926e −06	0.1390e −04	92.90	15	0.9364e −06	93.26
7054.3190	7	6	2	8	6	3	0.1048e −02	0.1240e −02	15.50	15	0.9754e −03	21.34
7054.3190	7	6	1	8	6	2	0.1048e −02	0.1240e −02	15.50	15	0.9754e −03	21.34
7062.1720	14	2	13	14	3	12	0.1778e −04	0.1180e −04	−50.70	15	0.1562e −04	−32.37
7065.6122	5	2	3	5	4	2	0.9297e −04	0.1120e −03	17.00	10	8801e −04	21.42
7070.7180	6	6	1	7	6	2	0.1003e −02	0.1810e −02	44.60	15	0.9378e −03	48.19
7070.7180	6	6	0	7	6	1	0.1003e −02	0.1810e −02	44.60	15	0.9378e −03	48.19
7077.8770	12	0	12	12	2	11	0.6894e −04	0.8600e −04	19.80	10	0.9381e −04	−9.08
7077.8930	12	1	12	12	2	11	0.1244e −03	0.1030e −03	−20.80	3	0.9099e −04	11.66
7078.3840	13	1	12	13	3	11	0.2515e −04	0.5270e −04	52.30	15	0.2609e −04	50.49
7079.3849	12	0	12	12	1	11	0.1246e −03	0.7800e −04	−59.70	10	0.9157e −04	−17.40
7079.4012	12	1	12	12	1	11	0.6888e −04	0.1110e −03	37.90	10	0.9389e −04	15.41
7080.5260	9	4	6	9	5	5	0.4596e −03	0.6940e −03	33.80	15	0.4401e −03	g6.59
7094.3277	12	2	11	12	3	10	0.1265e −03	0.1000e −03	−26.50	10	0.1174e −03	−17.40
7097.2945	11	1	11	11	1	10	0.1471e −03	0.2000e −03	26.40	15	0.1503e −03	24.85
7106.6069	4	1	4	4	3	1	0.1715e −03	0.1370e −03	−25.20	10	0.1631e −03	−19.05
7107.8590	7	2	5	8	2	6	0.1176e −01	0.1460e −01	19.50	7	0.1132e −01	22.47
7114.3685	3	1	3	3	3	0	0.8626e −04	0.7000e −04	−23.20	15	0.8162e −04	−16.60
7117.1840	9	3	7	9	4	6	0.9362e −03	0.1700e −02	44.90	15	0.90gge −03	46.86
7127.2769	8	3	6	9	2	7	0.9005e −03	0.1550e −02	41.90	4	0.8568e −03	44.72
7131.2661	3	1	2	3	3	1	0.1390e −03	0.1100e −03	−26.30	10	0.1317e −03	−19.73

Continuation of Table IV

Exp. wavenumbers, cm^{-1}	J	K_a	K_c	J	K_a	K_c	I_{calc}, cm^{-2}/atm	I_{exp}, cm^{-2}/atm	$(I_e - I_c)/I_e$, %	DI_e, %	I_{sch}, cm^{-2}/atm	$(I_e - I_c)/I_e$, %
7138.7445	9	4	6	10	3	7	0.174n e −0g	0.1500e −0g	−16.00	15	0.164g e −03	−9.53
7140.0970	4	4	0	5	4	1	0.5862e −02	0.8100e −02	27.60	6	0.5611e −02	30.73
7140.1096	4	4	1	5	4	2	0.5861e −02	0.8100e −02	27.60	6	0.5608e −02	30.77
7143.9130	7	5	3	6	6	0	0.4186e −04	0.4950e −04	15.40	15	0.4146e −04	16.24
7143.9130	7	5	2	6	6	1	0.4186e −04	0.4950e −04	15.40	15	0.4146e −04	16.24
7149.3190	11	3	8	11	4	7	0.2623e −03	0.3230e −03	18.80	15	0.2524e −03	21.86
7150.2658	11	7	5	11	7	4	0.1128e −03	0.4740e −03	76.20	3	0.1078e −03	77.25
7150.2658	11	7	4	11	7	5	0.1128e −03	0.4740e −03	76.20	3	0.1078e −03	77.25
7151.2250	11	7	5	12	6	6	0.2056e −05	0.2710e −04	92.40	15	0.1855e −05	93.15
7153.6633	8	1	7	7	4	4	0.2726e −04	0.3370e −04	19.10	15	0.2638e −04	21.72
7164.2310	11	2	9	11	3	8	0.3933e −03	0.2910e −03	−35.20	15	0.3794e −03	−30.38
7173.1580	12	6	6	12	6	7	0.3963e −04	0.4700e −04	15.70	15	0.3828e −04	18.55
7173.5360	9	5	4	10	4	7	0.6240e −04	0.4080e −04	−52.90	15	0.5733e −04	−40.51
7174.7792	5	1	5	4	3	2	0.6604e −04	0.1630e −03	59.50	5	0.6186e −04	62.05
7177.1820	7	1	7	6	3	4	0.8496e −04	0.5800e −04	−46.50	15	0.7959e −04	−37.22
7177.4674	6	1	6	5	3	3	0.8821e −04	0.7010e −04	−25.80	15	0.8271e −04	−17.99
*7196.6973	9	5	5	9	5	4	0.9403e −03	0.1010e −01	90.70	2	0.9057e −03	91.03
7197.0865	4	1	3	3	3	0	0.6248e −04	0.7630e −04	18.10	15	0.5874e −04	23.01
7198.7700	10	1	10	9	2	7	0.2333e −04	0.1700e −04	−37.20	15	0.2175e −04	−27.94
7199.0290	13	5	8	13	5	9	0.1843e −04	0.2430e −04	24.10	15	0.1789e −04	26.38
7201.1710	9	3	6	10	2	9	0.4956e −04	0.6280e −04	21.10	15	0.4629e −04	26.29
7206.8724	8	4	4	7	5	3	0.1319e −03	0.1050e −03	−25.70	15	0.1318e −03	−25.52
7208.1477	7	5	2	8	4	5	0.1419e −03	0.1110e −03	−27.80	5	0.1284e −03	−15.68
7240.6612	6	2	4	7	1	7	0.2096e −03	0.1700e −03	−23.30	15	0.1935e −03	−13.82
7246.6907	4	4	0	5	3	3	0.3294e −03	0.4510e −03	27.00	3	0.3042e −03	32.55
7247.0420	10	2	8	9	4	5	0.9569e −04	0.8000e −04	−19.60	15	0.8950e −04	−11.88
7248.6810	11	2	10	10	3	7	0.3679e −04	0.2520e −04	−46.00	15	0.3479e −04	−38.06
7282.1870	9	3	6	8	4	5	0.2859e −03	0.2340e −03	−22.20	15	0.2889e −03	−23.46
7293.0718	12	4	8	12	3	9	0.2203e −03	0.2660e −03	17.20	15	0.2192e −03	17.59
*7311.4706	5	2	4	5	0	5	0.1725e −02	0.1720e −01	90.00	2	0.1711e −02	90.05
7312.5500	6	3	4	6	2	5	0.8792e −02	0.7500e −02	−17.20	15	0.8602e −02	−14.69
7324.4416	10	5	5	10	4	6	0.4473e −03	0.3500e −03	−27.80	15	0.4341e −03	−24.03
7333.4440	12	2	10	12	2	11	0.4127e −04	0.3000e −04	−37.60	15	0.3814e −04	−27.13
7335.3990	9	1	8	9	1	9	0.4159e −03	0.3400e −03	−22.30	15	0.4034e −03	−18.65
7337.7960	9	6	3	9	5	4	0.3288e −03	0.6230e −03	47.20	15	0.3144e −03	49.53
7338.1657	7	3	5	6	3	4	0.2020e −01	0.4150e −01	51.30	3	0.1939e −01	53.28
7342.7244	8	8	0	8	7	1	0.6236e −04	0.5050e −04	−23.50	15	0.2782e −04	44.91
7342.7244	8	8	1	8	7	2	0.6236e −04	0.5050e −04	−23.50	15	0.2782e −04	44.91
7346.0520	10	1	9	10	1	10	0.2124e −03	0.1040e −03	−104.20	15	0.2029e −03	−95.10
7351.8162	10	5	6	9	5	5	0.1287e −02	0.1020e −02	−26.20	2	0.1072e −02	−5.10
7357.1240	11	2	10	11	1	11	0.4621e −03	0.5500e −03	16.00	10	0.4579e −03	16.75
7365.7350	12	2	11	12	0	12	0.4657e −04	0.3600e −04	−29.40	15	0.4225e −04	−17.36
7373.9765	13	2	12	13	1	13	0.8726e −04	0.1070e −03	18.40	6	0.8776e −04	17.98
7374.0585	13	6	7	12	6	6	0.6557e −04	0.5500e −04	−19.20	15	0.4669e −04	15.11
7377.1058	4	3	1	4	0	4	0.1159e −03	0.1000e −03	−15.90	6	0.1086e −03	−8.60
7381.7530	10	2	9	9	1	8	0.2078e −02	0.2470e −02	15.90	15	0.2125e −02	13.97
7387.8190	14	6	9	13	6	8	0.2778e −04	0.3360e −04	17.30	15	0.2544e −04	24.29
7389.0200	14	6	8	13	6	7	0.2756e −04	0.4240e −04	35.00	15	0.2439e −04	42.48
7391.6100	13	0	13	12	1	12	0.6303e −03	0.5200e −03	−21.20	10	0.5459e −03	−4.98
7391.6710	12	1	11	11	2	10	0.5481e −03	0.2040e −03	−168.70	15	0.5442e −03	−166.76
7394.2734	6	3	3	6	0	6	0.1383e −03	0.1000e −03	−38.30	15	0.1290e −03	−29.00
7398.9248	3	3	0	2	1	1	0.1354e −03	0.1150e −03	−17.80	4	0.1371e −03	−19.22
7400.4260	13	2	12	12	2	11	0.1290e −02	0.1000e −02	−29.00	10	0.1229e −02	−22.90
7400.4360	13	5	8	12	5	7	0.1531e −03	0.7500e −03	79.60	10	0.1448e −03	80.69
7402.1315	7	3	5	6	2	4	0.5292e −02	0.7000e −02	24.40	10	0.5447e −02	22.19
7414.4172	16	0	16	15	1	15	0.6020e −03	0.4900e −03	−22.85	10	0.5574e −03	−13.75
7414.4172	16	1	16	15	0	15	0.6020e −03	0.4900e −03	−22.85	10	0.5574e −03	−13.75
7414.4172	16	1	16	15	1	15	0.6020e −03	0.4900e −03	−22.85	10	0.5574e −03	−13.75
7414.4172	16	0	16	15	0	15	0.6020e −03	0.4900e −03	−22.85	10	0.5574e −03	−13.75
7415.1680	15	1	14	14	2	13	0.4033e −04	0.2800e −04	−44.00	15	0.3392e −04	−21.14

Continuation of Table IV

Exp. wavenumbers, cm^{-1}	J	K_a	K_c	J	K_a	K_c	I_{calc}, cm^{-2}/atm	I_{exp}, cm^{-2}/atm	$(I_e - I_c)/I_e$, %	DI_e, %	I_{sch}, cm^{-2}/atm	$(I_e - I_c)/I_e$, %
7421.3210	17	0	17	16	1	16	0.2332e−03	0.1700e−03	−37.06	10	0.2129e−03	−25.23
7421.3210	17	1	17	16	0	16	0.2332e−03	0.1700e−03	−37.06	10	0.2129e−03	−25.23
7421.3210	17	1	17	16	1	16	0.2332e−03	0.1700e−03	−37.06	10	0.2129e−03	−25.23
7421.3210	17	0	17	16	0	16	0.2332e−03	0.1700e−03	−37.06	10	0.2129e−03	−25.23
7422.0566	16	2	15	15	2	14	0.9621e−04	0.1160e−03	17.10	2	0.9695e−04	16.42
7422.2684	16	1	15	15	1	14	0.9624e−04	0.1200e−03	19.80	2	0.9695e−04	19.21
7424.2711	14	2	12	13	2	11	0.2797e−03	0.3930e−03	28.80	3	0.2655e−03	32.44
7427.8566	18	1	18	17	0	17	0.8494e−04	0.6000e−04	−41.50	15	0.7664e−04	−27.73
7427.8566	18	1	18	17	1	17	0.8494e−04	0.6000e−04	−41.50	15	0.7664e−04	−27.73
7427.8566	18	0	18	17	1	17	0.8494e−04	0.6000e−04	−41.50	15	0.7664e−04	−27.73
7427.8566	18	0	18	17	0	17	0.8494e−04	0.6000e−04	−41.50	15	0.7664e−04	−27.73
7428.9020	15	4	12	14	4	11	0.5230e−04	0.6380e−04	18.00	15	0.4934e−04	22.66
7435.6450	4	3	2	3	0	3	0.1104e−03	0.6940e−04	−59.10	15	0.1071e−03	−54.32
7459.2450	10	4	7	9	3	6	0.6224e−03	0.4100e−03	−51.80	10	0.6416e−03	−56.49
7464.9633	4	4	1	3	2	2	0.5843e−04	0.7170e−04	18.50	10	0.5958e−04	16.90
7521.3830	12	7	5	11	6	6	0.3174e−04	0.2440e−04	−30.10	15	0.3154e−04	−29.26
7530.0220	13	6	8	12	5	7	0.2117e−04	0.4520e−04	53.20	15	0.2118e−04	53.14
7534.4060	13	5	8	12	4	9	0.2562e−04	0.3340e−04	23.30	15	0.2581e−04	22.72
7549.1790	7	5	3	6	3	4	0.6908e−04	0.5790e−04	−19.30	15	0.6893e−04	−19.05
7563.4030	8	5	4	7	3	5	0.7476e−04	0.9000e−04	16.90	15	0.7413e−04	17.63
7563.8860	10	2	8	9	1	9	0.5466e−04	0.3980e−04	−37.30	15	0.5326e−04	−33.82
7585.3600	7	6	1	6	4	2	0.1684e−04	0.2400e−04	29.80	15	0.1618e−04	32.58
7585.4300	7	6	2	6	4	3	0.1683e−04	0.3270e−04	48.50	15	0.1617e−04	50.55
7593.2330	10	5	6	9	3	7	0.5311e−04	0.6380e−04	16.80	15	0.4694e−04	26.43
7602.0560	11	2	9	10	0	10	0.5173e−04	0.3930e−04	−31.60	15	0.5129e−04	−30.51
7615.3703	11	3	9	10	1	10	0.4439e−04	0.3810e−04	−16.50	15	0.4399e−04	−15.46

Erratic assignments from Ref. 15

Wavenumber, cm^{-1}	J	K_a	K_c	J	K_a	K_c	I_{calc}, cm^{-2}/atm	I_{exp}, cm^{-2}/atm	Reference
7279.0870	10	8	3	9	8	2	3.52E-05	3.23E-05	Ref. 15
	10	8	2	9	8	1	3.52E-05		Ref. 15
7428.9020	15	2	13	14	2	12	1.09E-04	6.38E-05	Ref. 15
	15	4	12	14	4	11	5.30E-05		This paper
7598.530	12	4	9	12	1	12	0	7.18E-05	Ref. 15

TABLE V. Comparison of the calculated data obtained in this paper with the ab initio predictions from Ref. 16 for the transitions to the levels with K_a = 0, 1; $J \geq 12$.

Exp. wavenumbers, cm^{-1}	J	K_a	K_c	J	K_a	K_c	I_{calc}	I_{exp} (Ref. 15)	$(I_e - I_c)/I_e$, %	DI_e, %	I_{sch} (Ref. 16)	$(I_e - I_c)/I_e$, %
6982.5483	16	0	16	17	0	17	0.2629E-04	0.2660E-04	1.2	10	0.3796E-04	−42.71
6982.5483	16	0	16	17	1	17	0.1815E-04	0.1990E-04	8.80	10	0.3315E-05	83.34
6982.5483	16	1	16	17	0	17	0.1815E-04	0.1990E-04	8.80	10	0.3320E-05	83.32
6982.5483	16	1	16	17	1	17	0.2629E-04	0.2660E-04	1.20	10	0.3799E-04	−42.82
7017.5210	14	0	14	15	0	15	0.1860E-03	0.1910E-03	2.60	10	0.1394E-03	27.02
7017.5210	14	1	14	15	1	15	0.1859E-03	0.1910E-03	2.60	10	0.1394E-03	27.02
7399.5600	14	0	14	13	1	13	0.2735E-03	0.2500E-03	−9.40	10	0.1763E-03	29.48
7399.5820	14	1	14	13	0	13	0.2735E-03	0.2500E-03	−9.40	10	0.1763E-03	29.48
7407.1623	15	0	15	14	1	14	0.1103E-03	0.1100E-03	−0.30	10	0.4106E-05	96.27
7407.1717	15	1	15	14	0	14	0.1103E-03	0.1100E-03	−0.30	10	0.4104E-05	96.27

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