

High-resolution ro-vibrational spectroscopy of HDO in the region of 8900–9600 cm^{-1}

O.N. Ulenikov^{a,b}, S.-M. Hu^{a,*}, E.S. Bekhtereva^{a,b}, Q.-S. Zhu^a

^a Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics,
University of Science and Technology of China, Hefei 230026, China

^b Laboratory of Molecular Spectroscopy, Physics Department, Tomsk State University, Tomsk 634050, Russia

Received 8 July 2004; in revised form 22 December 2004

Abstract

The high-resolution absorption spectrum of the HDO molecule was recorded with a Fourier-transform interferometer in the region of 8900–9600 cm^{-1} , where the strongly interacted bands $2\nu_1 + \nu_3$, $3\nu_1 + \nu_2$, $\nu_1 + 2\nu_2 + \nu_3$, $2\nu_1 + 3\nu_2$, $4\nu_2 + \nu_3$, $\nu_1 + 5\nu_2$, and $7\nu_2$ are located. About 1000 transitions were assigned to these seven bands based on the ab initio predictions [J. Chem. Phys. 106 (1997) 4618]. Altogether, 375 upper energy levels were determined, including 24 energy levels of the highly excited bending (070) state. On that basis, the necessity of the “Effective Hamiltonian” concept in the spectroscopic analysis is discussed.
© 2005 Elsevier Inc. All rights reserved.

Keywords: Vibration–rotation spectra; HDO molecule; Water absorption

1. Introduction

The high-resolution spectroscopy of water molecule and its different isotopic species is of great interest in many fields of physics and chemistry. The water molecule is one of the simplest polyatomic molecules. However, numerous intra-molecular interactions are evidenced in the complicated high-resolution spectra of water vapor. The water molecule can be considered as a good “touchstone” to test miscellaneous methods derived in chemical physics. A more basic motivation for the study of high-resolution spectra of water vapor is stimulated by numerous applications, in atmospheric science for instance, since water vapor is the main absorber of solar radiation. Extensive theoretical and experimental efforts in the study of high-resolution water vapor spectra, which have been undertaken during recent years, led to great progress (see, e.g., recent reviews

in [1–3] and references therein). In spite of this, the necessity to have more and more precise quantitative information leads to unabated interest in the spectra analysis of water vapor.

The HDO molecule is one of the H_2O isotopic species which high-resolution spectra were extensively analyzed and discussed during last few years, especially in the near IR region, with ICLAS (intra-cavity laser absorption spectroscopy) [4–10] and Fourier transform spectroscopy (FTS) [11–14] techniques. In the present contribution, we report the results of high-resolution vibration–rotation analysis of the HDO spectrum in the region of 8900–9600 cm^{-1} , which was analyzed earlier in [15] with lower resolution. Here, the better performance of the equipment allowed us to reach more transitions with better precision in the same region. The presence of an excellent theoretical prediction of the upper ro-vibrational energy values, [17], also allowed us to assign a considerably larger number of transitions belonging to the seven vibrational bands (only two bands in [15]) of the HDO molecule in this region.

* Corresponding author. Fax: +86 551 3602969.
E-mail address: smhu@ustc.edu.cn (S.-M. Hu).

The details of our experiment are given in Section 2. Section 3 presents the description of the spectrum and results of assignments of the recorded transitions.

One of the key points in the modern chemical physics is the knowledge of the correct multi-dimensional potential energy surface (PES) of the lowest electronic state of a molecule which is a base for the study of intra-molecular dynamics, chemical reactions, etc. Up to now, the most efficient and precise method to derive a PES is by the high-resolution analysis of vibration–rotation spectra under the framework of the “Effective Hamiltonian” model (EH). The procedure in the present work, with the assignments and further analysis of the derived upper energy values, stimulated us to some consideration on the role of the EH concept which is presented in Section 4.

2. Experimental details

The sample of D₂O was purchased from PeKing Chemical Industry (China). The stated purity of deuterium was 99.8%. The HDO sample was prepared by mixing D₂O and H₂O with a ratio of 1:1. The spectra were recorded at room temperature (296 K) with a Bruker IFS 120HR Fourier-transform interferometer (Hefei, China), which is equipped with a path length adjustable multi-pass gas cell (base length 1.5 m), a tungsten source, a CaF₂ beam-splitter, and a Si diode detector. The sample pressure was 18.4 hPa measured by a capacitance manometer with a stated accuracy of 20 Pa. The total path length was 123 m. The unapodized resolution was 0.02 cm⁻¹, and no apodization function was used (Boxcar function). The spectrum was cali-

brated with H₂O lines in this region listed in the HITRAN database [16]. The positions accuracy of those unblended and not-very-weak lines was estimated better than 1×10^{-3} cm⁻¹. Six thousand co-added scans provide a signal-to-noise ratio around 400.

Since there are many absorption lines due to H₂O and D₂O in the region under study, the spectrum of “pure” D₂O was also recorded to identify the absorption lines of HDO. For illustration, an overview of the spectrum is given in Fig. 1. Note that strong absorption lines of H₂O appear in the longer wavelength region of the figure. The predicted HDO band centers in this region are also given in the same figure. Two small pieces of the recorded spectra are also presented as Figs. 2 and 3.

We also tried to give rough values of the observed line strengths. To obtain the absolute line strengths, first, a PC-based program “Intwin” written in C++ was applied to obtain line parameters from the profile fitting. Voigt profile was adopted for each line. The Gaussian width of the Voigt profile was fixed at the Doppler width. The position and the intensity of each line can be obtained from the fitting procedure. Then, if we assume that the percentage of HDO in the nearly 1:1 D₂O/H₂O mixture was 50%, absolute line strength of each line can be derived from the fitting results. The observed line strengths are given in the [Supplementary material](#). The precision of the line-to-line relative intensity values is estimated to be around 10% for isolated lines. But the accuracy of absolute values can be worse because of the difficulties in obtaining an accurate number density of the HDO molecules in the sample. This may introduce a systematic deviation about 5–10% in the absolute line strengths. We admitted that the accuracy can be improved if we would try to record more

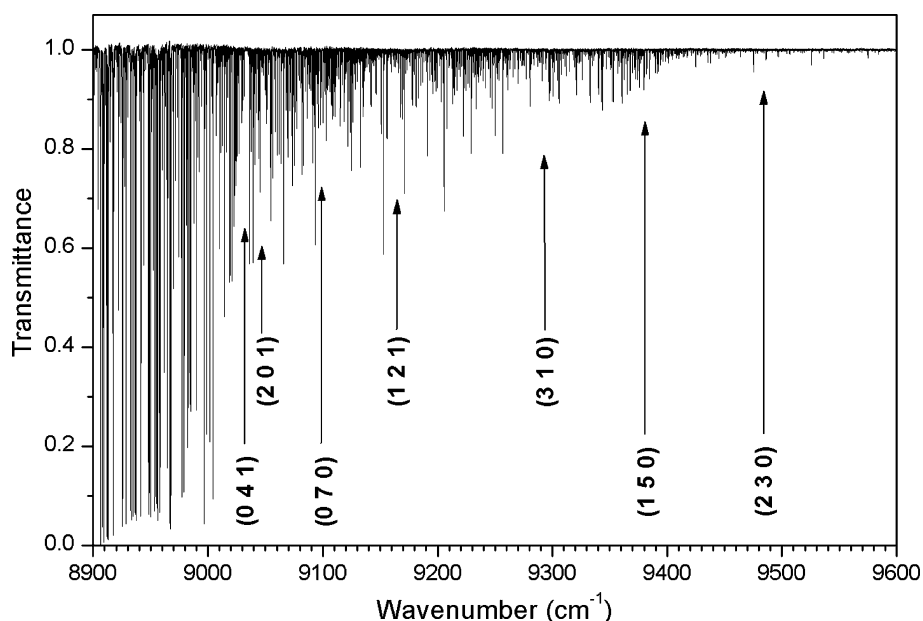


Fig. 1. Survey spectrum of HDO in the region of 8900–9600 cm⁻¹. Centers of bands located in this region are marked with arrows.

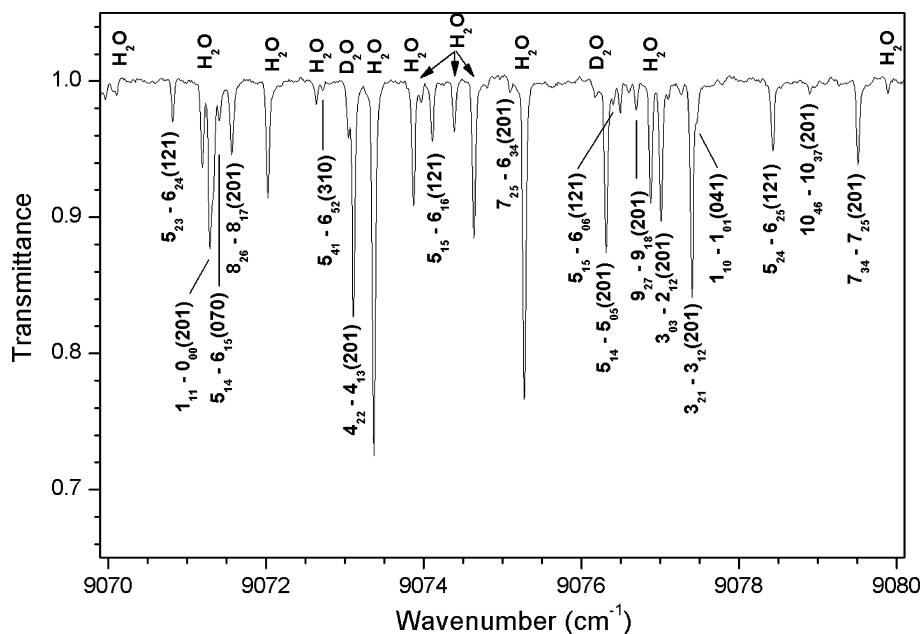


Fig. 2. A small part of the high-resolution spectrum of HDO in the Q-branch region of the $2\nu_1 + \nu_3$ band. Some P-branch transitions of the $\nu_1 + 2\nu_2 + \nu_3$, $7\nu_2$, $3\nu_1 + \nu_2$, and $4\nu_2 + \nu_3$ bands can be seen also.

spectra with different sample pressures and/or different absorption path lengths, but the absorption bands under present study are so weak that we just recorded the spectrum with almost maximal partial pressure of HDO and maximal path length as we could reach in our laboratory.

3. Description of the spectrum and assignments of transitions

Assignments of the recorded transitions were made on the basis of the knowledge of the calculated upper ro-vibrational energies of the HDO molecule from the high quality ab initio potential energy surface given in [17]. As the analysis shows, seven vibrational bands of the HDO molecule are located in the studied region. They are $2\nu_1 + \nu_3$, $3\nu_1 + \nu_2$, $\nu_1 + 2\nu_2 + \nu_3$, $2\nu_1 + 3\nu_2$, $4\nu_2 + \nu_3$, $\nu_1 + 5\nu_2$, and $7\nu_2$ bands, using the notation ν_1 for OD stretching mode, ν_2 for the bending mode and ν_3 for the OH stretching mode. It should be mentioned that, owing to the high accuracy of the predicted upper energy values, the procedure of assignments based on the ground state combination differences (GSCD) was straightforward. The ground state rotational energies were taken from [18]. As the analysis showed, the accuracy is $0.04\text{--}0.10\text{ cm}^{-1}$ for most of the predicted upper energy values. In some cases, the accuracy reduced to $0.20\text{--}0.30\text{ cm}^{-1}$, but the difference between the observed and predicted positions behaves regularly.

The absorption of HDO in the analyzed region is very weak (for illustration, two fragments of the

recorded spectrum are shown in Figs. 2 and 3). We assigned altogether about 800 lines for three strongest bands, $2\nu_1 + \nu_3$, $3\nu_1 + \nu_2$, and $\nu_1 + 2\nu_2 + \nu_3$. And the existence of the strong resonance interactions between the states $2\nu_1 + \nu_3/3\nu_1 + \nu_2/\nu_1 + 2\nu_2 + \nu_3$ and the $2\nu_1 + 3\nu_2/4\nu_2 + \nu_3/\nu_1 + 5\nu_2/7\nu_2$ states allowed us to assign 46, 46, 39, and 68 transitions to the last four bands, respectively. Table 1 gives the numbers of assigned transitions, J^{\max} and K_a^{\max} for each band. The list of assigned transitions is attached to this paper as Supplementary material. The sets of experimental upper energies for the vibrational states (201), (310), and (121) derived from the assigned line positions are given in Table 1. Upper ro-vibrational energies of the states (230), (041), (150), and (070) are given in Table 3. N , the number of experimental transitions which connect to the same upper energy level, and Δ , the experimental uncertainties (one standard deviation in units of 10^{-4} cm^{-1}) for those $N \geq 2$ energy levels, are also given for each energy level in those two tables. The value $\delta = E^{\text{exp}} - E^{\text{predict}}$ is the difference between the upper “experimental” energy value and the predicted values from [17]. Table 1 shows the excellent correspondence between the ab initio predictions and the experimental values.¹

¹ It should be mentioned that the values ($\nu^{\text{exp}} - \nu^{\text{predict}}$) in the last column of Supplementary material differ a little bit from corresponding values $\delta = E^{\text{exp}} - E^{\text{predict}}$ of Tables 2 and 3. The reason is in the fact that the value E^{exp} in Tables 2 and 3 is the mean value of an upper energy level obtained from some different transitions, while the value in the last column of Supplementary material is connected with one concrete transition.

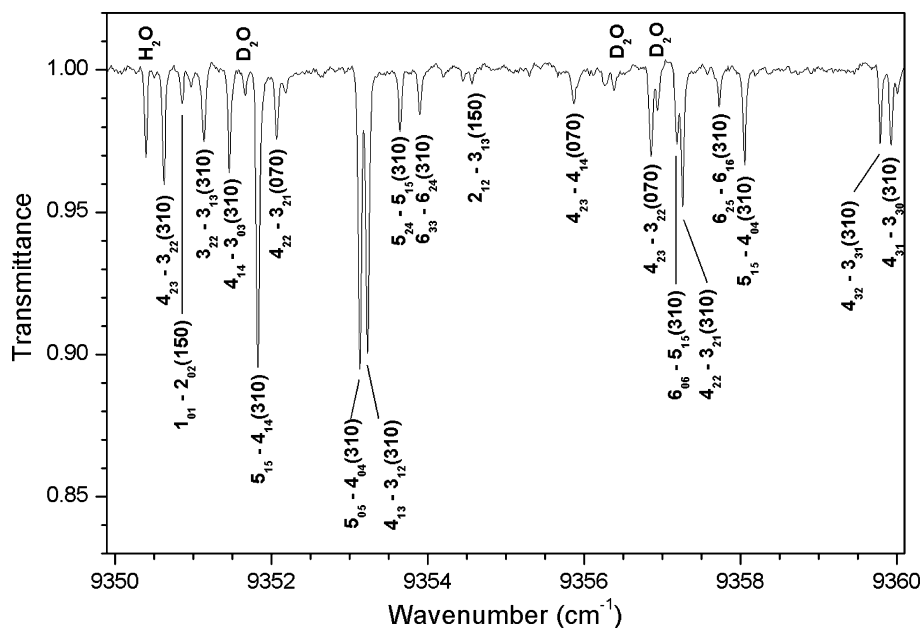


Fig. 3. HDO spectrum in the region of 9350–9360 cm^{-1} . This spectrum is mainly due to the $3\nu_1 + \nu_2$ band. Some transitions belonging to the $7\nu_2$ and $\nu_1 + 5\nu_2$ bands can be seen also.

Table 1

Statistics of the assigned transitions of the seven bands in the 8900–9600 cm^{-1} region

ν_1	ν_2	ν_3	$\nu_{\text{PS}}^{\text{a}}$	N^{b}	J^{max}	K_a^{max}
0	4	1	9032.41	46	8	4
2	0	1	9047.10	307	13	7
0	7	0	9086.42	68	7	2
1	2	1	9155.80	130	9	6
3	1	0	9293.02	364	14	6
1	5	0	9381.59	39	6	2
2	3	0	9488.13	46	8	2

^a Predicted band centers from [17].

^b Number of the lines assigned.

The assignments are confirmed by several lines of evidence given below. First is the combination differences for most of the upper levels given in Tables 2 and 3. The second is, as a rule, the values $\delta = E^{\text{exp}} - E^{\text{predict}}$ of levels $[J K_a K_c](\nu_1 \nu_2 \nu_3)$ change “smoothly” with the quantum number J at a given K_a value. The only two exceptions to this statement can be seen in Table 3. One of them is for the $E_{[J-1 J-1]}$ levels of (121) and (070) states. As one can see, the δ -value changes greatly at $J = 5$. It should be noted that the notation for the energy levels in Tables 2 and 3 correspond to the notation given in [17]. From a comparison of the δ -values for the ro-vibrational levels $[J-1 J-1]$ ($J \geq 5$) of the vibrational states (121) and (070), it is clear that the above mentioned discrepancy is actually a consequence of transposition of the vibrational notation. The second exception is in the $E_{[J-2 J-1]}$ and $E_{[J-2 J-2]}$ levels of states (230) and (150), respectively. The situation is totally analogous to the above discussed one. It means that the vibrational

notation for the $E_{[J-2 J-1]}$ and $E_{[J-2 J-2]}$ levels of (230) and (150) states should be switched in comparison with the notation of [17]. To illustrate the “smooth” behavior of the δ -values, Fig. 4 presents some examples of the dependence of δ -values on the quantum number J for some sets of ro-vibrational energies of four vibrational states: (310), (230), (041), and (070). In case of plot IV in this figure, which is for the $[J-1 J-1]$ levels of the (070) state, the above discussed “transpositions” of the corresponding ro-vibrational levels of (121) and (070) states have been taken into account.

If one extracts any set of transitions with $[J K_a K_c](\nu_1 \nu_2 \nu_3) \leftarrow [J' K'_a K'_c](0 0 0)$ and/or $[J K_a K_c](\nu_1 \nu_2 \nu_3) \leftarrow [J \pm 1 K'_a K'_c](0 0 0)$ (K_a and K'_a fixed) from the line list given in Supplementary material, it is possible to see that the line strengths change “smoothly” in such set. This fact also can be considered as a confirmation of the assignments.

4. Discussion

As in general treatments, after (and sometimes together with) the spectral assignment, the next step should be a fitting procedure to determine some spectroscopic parameters from the experimental data (Tables 2 and 3, in our case). There are mainly two goals in such a fitting procedure: (1) to produce a set of “physically suitable” rotational, centrifugal distortion, and resonance interaction parameters of a polyad, which can be further used in the determination of the fundamental characteristics of a molecule; (2) to create a basis for further assignments of new experimentally recorded transitions

Table 2

Experimental ro-vibrational term values for the (201), (310), and (121) vibrational states of the HDO molecule (in cm^{-1})^a

J	K_a	K_c	(201)				(310)				(121)			
			E^{exp}	N	Δ	δ	E^{exp}	N	Δ	δ	E^{exp}	N	Δ	δ
1			2	3	4	5	6	7	8	9	10	11	12	13
0	0	0	9047.0685	1		-370	9293.0016	2	22	-239				
1	0	1	9062.0176	2	20	-584	9307.6947	4	6	-213	9170.9753	1		-113
1	1	1	9071.2899	3	21	146	9323.6500	4	7	-321	9192.5675	2	33	388
1	1	0	9074.0407	2	2	172	9326.3661	4	7	-312	9195.9421	3	20	403
2	0	2	9091.5835	3	9	-571	9336.7510	5	3	-192	9200.8996	2	2	-129
2	1	2	9098.4456	4	25	125	9350.3032	7	12	-309	9220.0803	3	12	404
2	1	1	9106.6215	2	5	206	9358.4446	6	8	-281	9230.2091	3	21	429
2	2	1	9147.6282	4	10	256	9406.7342	4	7	-607	9279.7414	2	1	-222
2	2	0	9147.9764	3	2	248	9406.9969	4	5	-600	9280.1065	1		-220
3	0	3	9135.1428	3	2	-798	9379.5485	5	12	-177	9245.9402	3	5	52
3	1	3	9139.0860	4	18	115	9390.0872	5	10	-280	9261.1900	4	16	421
3	1	2	9155.1470	3	4	254	9406.3254	7	8	-235	9281.4249	3	7	381
3	2	2	9192.1631	5	9	245	9451.5272	5	10	-515	9325.9028	2	17	-223
3	2	1	9193.8659	5	5	254	9452.6210	8	7	-523	9327.6882	3	15	-212
3	3	1	9264.7782	2	4	108	9533.7054	4	12	-810	9428.6308	2	26	-199
3	3	0	9264.8072	2	2	121	9533.7277	4	22	-824				
4	0	4	9191.3242	5	8	-518	9435.2969	5	7	-166	9304.2837	2	7	128
4	1	4	9193.8323	6	6	-720	9442.7953	8	6	-280	9316.5073	3	2	223
4	1	3	9219.2069	2	6	226	9469.6931	7	7	-181	9349.4023	2	12	303
4	2	3	9251.2608	4	8	242	9506.0186	5	11	-26	9387.1663	3	28	-178
4	2	2	9256.0975	5	21	260	9514.3255	6	10	-368	9392.2759	3	3	-216
4	3	2	9324.6390	4	10	89	9592.8150	7	11	-784	9490.9149	2	2	-279
4	3	1	9324.8409	5	45	106	9592.9823	6	8	-768	9491.0968	2	20	-195
4	4	1	9423.9780	4	17	-86	9708.2098	4	12	-1204	9565.7036	2	17	-124
4	4	0	9423.9732	3	25	-47	9708.2094	3	9	-1223	9565.7036	2	17	-146
5	0	5	9252.7416	4	9	-1037	9503.2884	3	2	-173	9374.9318	3	7	157
5	1	5	9258.4265	4	11	-3	9508.2120	5	8	-265	9382.7256	3	10	389
5	1	4	9298.2655	3	2	311	9548.0800	4	13	-115	9417.5563	2	1	-1590
5	2	4	9324.5749	3	7	231	9579.5165	6	27	-218	9463.3064	2	2	-223
5	2	3	9335.0509	4	6	263	9591.4835	5	3	-38	9474.3702	3	3	-224
5	3	3	9399.5800	3	8	95	9666.8150	4	5	-72	9568.9370	2	10	-295
5	3	2	9400.3539	5	8	113	9667.5546	5	10	-552	9569.6204	2	3	-306
5	4	2	9498.6291	2	5	-89	9781.8789	2	6	-1175	9642.6493	2	70	-149
5	4	1	9498.6453	2	1	-86	9781.8904	4	36	-1187	9642.6666	2	30	-166
5	5	1	9624.6773	2	98	-286	9928.0373	3	8	-1661	9806.4151	1		-312
5	5	0	9624.6773	2	98	-287	9928.0373	3	8	-1661	9806.4151	1		-312
6	0	6	9334.6321	3	26	-507	9583.0545	5	18	-168	9457.5087	4	11	172
6	1	6	9337.6830	3	4	87	9586.1013	6	26	-236	9463.3543	3	6	436
6	1	5	9391.5671	4	7	316	9640.8369	3	7	-68	9516.8825	2	25	-1387
6	2	5	9411.9471	4	6	232	9666.3485	7	14	-246	9554.2045	1		-153
6	2	4	9430.6882	4	5	282	9684.0465	4	4	-13	9574.0410	2	3	-257
6	3	4	9489.4931	3	5	76	9755.6779	4	11	-652	9662.6316	2	5	-336
6	3	3	9491.7759	2	4	120	9757.4479	5	6	-600	9664.6421	2	10	-323
6	4	3	9588.3530	3	24	-119	9870.4502	6	26	-1086				
6	4	2	9588.4428	3	27	-113	9870.5117	3	4	-1096				
6	5	2	9713.9188	5	9	-275	10016.4494	3	6	-1481	9898.1728	3	14	-314
6	5	1	9713.9188	5	9	-288	10016.4494	3	6	-1488	9898.1728	3	14	-324
6	6	1	9865.8809	2	23	-444	10190.9374	3	5	-2150	10087.2964	1		-507
6	6	0	9865.8809	2	23	-447	10190.9374	3	5	-2152	10087.2964	1		-514
7	0	7	9427.7870	4	19	-94	9674.4815	5	11	-175	9551.8579	4	16	163
7	1	7	9429.3299	4	20	124	9676.2647	5	13	-234	9556.8035	4	8	435
7	1	6	9498.2327	4	30	310	9747.1530	6	16	-41	9629.9911	2	5	-1102
7	2	6	9512.9681	4	10	217	9766.5575	6	14	-229	9660.6349	2	20	-127
7	2	5	9542.6122	3	24	308	9794.7930	3	14	27	9690.9676	2	4	-279
7	3	5	9594.3120	6	46	54	9859.3068	5	18	-596				
7	3	4	9599.6377	2	1	123	9863.5940	5	16	-499	9709.4354	1		-241
7	4	4	9693.2216	5	28	-88	9973.9809	3	11	-998	9843.2468	2	13	-231
7	4	3	9693.5398	4	20	-87	9974.2070	5	3	-991				
7	5	3	9818.1456	2	8	-338	10117.3168	3	22	-989	10005.3465	1		-256
7	5	2	9818.1554	1		-325	10117.3175	3	25	-1049	10005.3465	1		-342

(continued on next page)

Table 2 (continued)

J	K _a	K _c	(201)				(310)				(121)			
			E ^{exp}	N	Δ	δ	E ^{exp}	N	Δ	δ	E ^{exp}	N	Δ	δ
1			2	3	4	5	6	7	8	9	10	11	12	13
7	6	2	9969.5373	2	12	-516	10293.1898	3	52	-2085	10193.8346	1		-584
7	6	1	9969.5373	2	12	-538	10293.1898	2	52	-2087	10193.8346	1		-565
7	7	1	10146.5791	1		-719								
7	7	0	10146.5791	1		-717								
8	0	8	9532.5175	4	15	31	9777.5831	3	16	-206				
8	1	8	9533.2720	3	15	121	9778.6119	4	17	-215				
8	1	7	9617.3814	3	17	279	9866.1527	3	16	-80	9755.8365	2	13	-841
8	2	7	9627.3041	4	3	170	9879.9659	3	24	-169				
8	2	6	9670.1302	3	6	295	9921.5075	3	22	116	9823.9411	2	15	-288
8	3	6	9713.7874	2	7	68	9977.5426	3	8	-513	9828.9014	2	7	-180
8	3	5	9724.4128	1		193	9986.3016	4	18	-342	9838.9006	1		-118
8	4	5	9813.2416	2	13	-124	10092.5120	4	22	-935				
8	4	4	9814.1622	2	32	-50	10093.1899	3	13	-876				
8	5	4	9937.4160	2	2	-347	10235.8037	3	26	-1371				
8	5	3	9937.4553	1		-346	10235.8224	3	36	-1403				
8	6	3	10088.0648	1		-562	10410.1088	4	39	-2050				
8	6	2	10088.0842	1		-514	10410.1088	4	39	-2056				
8	7	2	10264.5354	1		-765								
8	7	1	10264.5354	1		-768								
9	0	9	9649.0633	2	2	66	9892.2922	3	6	-196				
9	1	9	9649.4164	1		85	9892.9855	4	22	-206				
9	1	8	9748.3701	3	6	235	9997.1534	2	12	-48	9893.7406	3	12	-654
9	2	8	9754.6283	2	17	184	10006.2798	4	32	-179	9907.3401	4	20	-377
9	2	7	9812.4321	2	1	269	10063.2430	3	9	205				
9	3	7	9847.6145	2	1	89	10110.4460	4	93	-507				
9	3	6	9866.2506	2	11	183								
9	4	6	9948.3875	2	5	-113	10226.0521	2	4	-856				
9	4	5	9950.6510	2	8	-97	10227.4632	3	33	-706				
9	5	5	10071.7764	2	2	-350	10368.4923	1		-1375				
9	5	4	10071.9017	2	12	-351	10368.5675	1		-1353				
9	6	4	10221.4729	2	19	-556	10541.7189	1		-2026				
9	6	3	10221.5151	3	41	-576	10541.7189	1		-2047				
9	7	3	10397.2768	2	45	-794								
9	7	2	10397.2768	2	45	-789								
10	0	10	9777.5399	3	30	73	10018.9254	3	48	-151				
10	1	10	9777.7021	3	73	68	10019.3200	4	43	-230				
10	1	9	9890.9085	3	19	193	10139.3302	2	45	7				
10	2	9	9894.6437	2	8	139	10145.1429	2	25	-129				
10	2	8	9968.5643	3	47	232								
10	3	8	9995.4237	2	49	102								
10	3	7	10024.8974	1		217								
10	4	7	10098.5315	1		-122								
10	4	6	10103.4655	2	1	-59								
10	5	6	10221.2492	2	3	-391								
11	0	11	9917.9803	3	8	-38	10157.3065	1		-220				
11	1	11	9918.0500	1		87	10158.2483	2	12	-174				
11	1	10	10044.9700	3	65	106								
11	2	10	10047.1167	1		155	10296.5075	1		-172				
11	2	9	10137.4945	2	36	248								
11	3	9	10156.1446	2	6	172								
11	3	8	10199.7047	1		183								
12	0	12	10070.4559	1		57								
12	1	12	10070.4161	1		-15	10307.4906	1		-215				
12	1	11	10210.7287	1		159	10451.4434	1		-135				
12	2	11					10460.0629	1		-159				
12	2	10	10318.5347	1		173								
13	0	13	10234.8603	1		58	10469.2230	1		-206				
13	1	13	10234.8127	1		-138	10469.3827	1		-203				
13	1	12					10633.9669	1		-73				
14	1	14					10643.0419	1		-221				

^a In this table, Δ is the experimental uncertainty of the energy value, equals to one standard deviation in 10⁻⁴ cm⁻¹; Δ is not quoted when the energy value was obtained from only one transition; δ = E^{exp} - E^{predict}, E^{predict} from [17], also in 10⁻⁴ cm⁻¹.

Table 3

Experimental ro-vibrational term values for the (230), (041), (150), and (070) vibrational states of the HDO molecule (in cm^{-1})^a

<i>J</i>	<i>K_a</i>	<i>K_c</i>	(230)				(041)				(150)				(070)			
			<i>E^{exp}</i>	<i>N</i>	<i>Δ</i>	<i>δ</i>	<i>E^{exp}</i>	<i>N</i>	<i>Δ</i>	<i>δ</i>	<i>E^{exp}</i>	<i>N</i>	<i>Δ</i>	<i>δ</i>	<i>E^{exp}</i>	<i>N</i>	<i>Δ</i>	<i>δ</i>
1			2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
0	0	0	9487.9153	1		−2180					9381.7861	1		1960				
1	0	1	9503.2870	3	12	−2123					9397.0312	1		1935				
1	1	1	9528.8006	1		−2319	9089.1683	2	17	−1212	9427.9579	1		1978	9174.2619	2	7	−1665
1	1	0	9532.0412	2	43	−2338	9092.9770	2	2	−1214	9431.4240	2	34	1975	9177.7149	1		−1811
2	0	2	9533.6506	1		−2090					9427.2906	2	1	1980				
2	1	2	9556.3630	2	14	−2238	9116.2354	3	18	−1201	9454.9589	2	10	1989	9203.8168	4	20	−970
2	1	1	9566.0737	2	17	−2336	9127.3949	1		−1218	9465.3412	2	48	2000	9212.7625	3	4	−1745
2	2	1	9549.3426	1		1575								9399.1335	2	4	198	
2	2	0	9549.6972	1		1583					9645.7489	2	24	−2637	9399.2695	2	16	295
3	0	3	9578.3412	2	9	−2012					9472.1227	1		2008				
3	1	3					9156.9426	1		−1201	9495.2708	3	5	1948	9240.8755	3	35	−1578
3	1	2	9616.9023	1		−2253	9178.8294	2	2	−1237	9515.9726	3	9	2062	9264.7102	3	16	−1748
3	2	2	9594.8817	2	9	1599	9245.7636	1		−579				9445.5682	6	15	172	
3	2	1	9596.5589	2	5	1593	9250.0251	3	29	−544				9446.3477	4	16	190	
4	0	4	9636.6243	2	11	−1887					9531.1100	3	9	1921				
4	1	4	9651.9980	3	22	−2145	9211.1040	3	19	−1177	9548.7062	2	14	1920	9295.8292	2	4	−1693
4	1	3	9684.2247	1		−2166	9246.9550	2	25	−1277	9582.9935	2	25	2130	9333.1815	3	7	−1691
4	2	3	9655.3414	2	7	1540					9753.6375	2	6	−2578	9512.2518	5	16	−258
4	2	2	9660.1131	2	4	1564	9313.3002	3	22	−270				9509.1318	4	23	146	
4	4	1					9641.8586	2	78	−138								
4	4	0					9641.8586	2	78	−189								
5	0	5	9707.8809	2	11	−1824												
5	1	5	9719.6470	1		−1976	9279.4664	1		−995	9604.7903	3	12	1506	9363.8541	3	8	−1722
5	1	4	9767.6052	1		−2149	9331.3856	2	9	−1123	9615.0508	2	38	1924	9433.9196	2	2	136
5	2	4	9730.5432	2	16	1555					9665.8444	2	19	1999	9589.5153	4	18	22
5	2	3	9740.6113	1		1639								9587.5685	4	20	275	
5	4	2					9720.2320	1		−177								
5	4	1					9720.2909	4	16	−265								
6	0	6	9791.6292	1		−1744												
6	1	6	9800.2316	2	1	−1915	9358.7035	5	9	−1045	9694.0638	2	19	1782	9444.8720	3	6	−1699
6	1	5												9534.6860	2	13	−191	
6	2	5	9820.3332	1		1445								9682.6083	1		66	
6	2	4	9838.2776	2	12	1743												
6	4	3					9814.2768	2	4	−134								
6	4	2					9814.5579	2	6	−235								
7	0	7	9887.5440	2	14	−1595												
7	1	7					9451.6121	3	38	−1126				9538.7015	3	28	−1681	
7	1	6												9650.4619	2	20	−617	
7	2	5												9808.5517	1		111	
7	4	3					9924.8271	1		−236								
8	0	8	9995.5458	1		−1399												
8	1	8					9556.9620	1		−1116								

^a See footnote to Table 2.

(e.g., transitions belonging to the same polyad, but with higher values of the quantum numbers *J* and *K*) and for a quantitative description of a spectrum. This is the so-called EH method and different modifications have been carried out based on this idea, see, e.g., [19–23]. However, in spite of the widespread use of the EH method

in vibration–rotation spectroscopy, this concept suffers from several serious defects. Some problems can be mentioned which are the most complicated and the most frequently discussed in high-resolution molecular spectroscopy. One of them is the ambiguities in spectroscopic parameters of the effective Hamiltonians

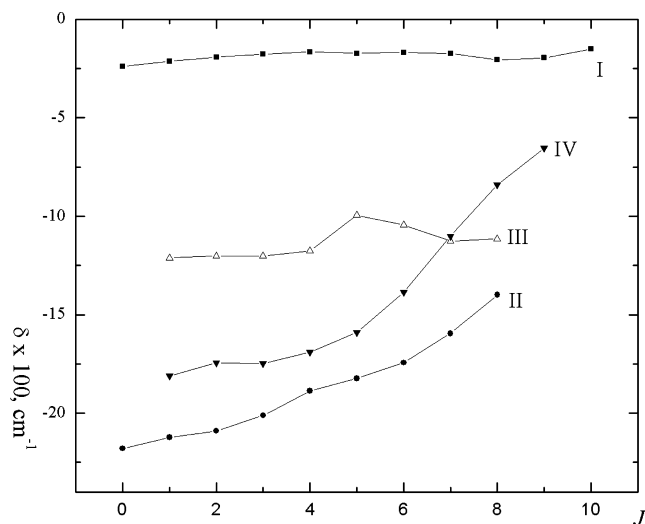


Fig. 4. Dependence of the value $\delta = E^{\text{exp}} - E^{\text{predict}}$ on the value of quantum number J for some sets of upper energy levels $E_{[J, K_a, K_c](v_1, v_2, v_3)}$: I, $(v_1, v_2, v_3) = (310)$, $K_a = 0$, $K_c = J$; II, $(v_1, v_2, v_3) = (230)$, $K_a = 0$, $K_c = J$; III, $(v_1, v_2, v_3) = (041)$, $K_a = 1$, $K_c = J$; and IV, $(v_1, v_2, v_3) = (070)$, $K_a = 1$, $K_c = J - 1$.

derived from experimental data and the connected problem of the reduction of the effective Hamiltonian. Another problem is resonance interactions. We always attempt to give some reasonable physical understanding to these interactions, but very often we have to accept that such understanding is either doubtful or of little interest. An additional disadvantage of the EH approach is the fact that, even with the knowledge of an extensive set of spectroscopic parameters for one vibrational polyad, it is often impossible, to directly extrapolate to other polyads with satisfied accuracy. The complicated spectrum of water vapor stands as an example of these problems mentioned above.

There are numerous spectroscopic references where these problem are discussed as applied to different kinds of molecules, particularly in the analysis of high-resolution vibration–rotation spectra of polyatomic molecules. At the same time, if one examines the procedure of the construction of the effective Hamiltonian [19–23], it can be seen that the resonance interaction problem is a mathematical consequence of using perturbation theory. Namely, it is a mathematical consequence of the choice of the zeroth order approximation for the vibrational part of the Hamiltonian which leads to the appearance of resonance denominators in formulas of the perturbation theory operators. The problem of the ambiguities in EH spectroscopic parameters derived from experimental data, also has a mathematical nature, rather than a “physical” one. Namely, the effective Hamiltonian is determined to the accuracy of an arbitrary unitary transformation. Then the rest problems with the EH model are the problem of the ambiguity of spectroscopic parameters and, closely connected with it, the problem

of deriving the “physically suitable” values of the effective spectroscopic parameters, [22–27]. But the most important information which can be produced within the framework of the EH approach, is not the spectroscopic parameters, but the energy values. The most important requirement for the fitted parameters in EH approaches is that they must be able to reproduce the input data, and to predict new spectroscopic data with a proper accuracy as well.

During recent years, especially in view of the rapid increase in computer power, more and more attention has been paid to find other approaches which would be free from the defects mentioned above. They are the methods without the EH concept. The Morse oscillator rigid bender internal dynamics (MORBID) method can be mentioned in this respect. It reproduces the experimental ro-vibrational energies by pure quantum mechanical calculations with the vibration–rotation Hamiltonian [28–35]. We would like to mention especially another approach which is mainly based on the ab initio calculation of the molecular potential energy surface (PES) and its further adjustment according to the known experimental ro-vibrational energy levels, e.g., [2,17,36–40] and references in the last two ones. Now this approach has the possibility to reach an accuracy better than 1 cm^{-1} for light three or four atom molecules. The excellent predictions of the upper state energy levels for water in [17] prove the power of the method. The accuracy is again demonstrated in our present analysis of the high-resolution spectrum of HDO. Then there is no need to do any more fitting of the spectroscopic parameters in the traditional EH approach unless this fitting can not only reproduce the input data but also predict new spectra with a better accuracy than the PES approach can give.

As an illustration of this statement, the present high-resolution analysis of the HDO spectrum can be mentioned. The experimental information presented in Tables 2 and 3 can be used in a fitting procedure, as in the previous high-resolution studies of HDO, [4–8,11–14,10], with the effective Hamiltonian $H^{v-r} = \sum_{v,v'} H^{vv'}$ $|v\rangle\langle v'|$, where the summation, in this case, is over the seven vibrational states in the present study. The diagonal blocks H^{vv} in this equation have the form of the usual Watson type operators [24], and the non-diagonal operators $H^{vv'}$, ($v \neq v'$), describe resonance interactions between the states $|v\rangle$ and $|v'\rangle$.

Numerous fits with different sets of parameters have been completed. In this case, the above-mentioned mathematical peculiarities of the EH approach led to an extremely complicated picture of resonance interactions between each pair of the seven vibrational states. As a consequence, a satisfactory accuracy of fits (with a rms deviation of $0.005\text{--}0.007 \text{ cm}^{-1}$ for most energy levels) could only be achieved with the use of an excessively large number of fitted effective parameters. Moreover, the values of parameters obtained from fits seemed

to be far from the physically suitable values. Otherwise, if we try to limit the number of effective parameters, the derived rms deviation (in the order of $0.1\text{--}1.0\text{ cm}^{-1}$ for different fits) would be even worse than the predictions from [17] (see columns “ δ ” of Tables 2 and 3). In our opinion, the EH study of water spectra corresponding to highly excited vibrational states has no advantages compared with the results obtained from [17], particularly when a large number of strongly interacting vibrational states are involved in the spectrum.

Acknowledgments

This work was supported by the National Project for the Development of Key Fundamental Sciences in China, the National Natural Science Foundation of China (20103007, 20473079, and 20210102154), and Chinese Academy of Science. O. Ulenikov and E. Bekhtereva thank the University of Science and Technology of China for guest professorships in 2003–2004.

Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect (www.sciencedirect.com) and as part of the Ohio State University Molecular Spectroscopy Archives (http://msa.lib.ohio-state.edu/jmsa_hp.htm).

References

- [1] P.F. Bernath, *Phys. Chem. Chem. Phys.* 4 (2000) 1501–1509.
- [2] O.L. Polyansky, A.G. Császár, S.V. Shirin, N.F. Sobov, P. Barletta, J. Tennyson, D.W. Schwenke, P.J. Knowles, *Science* 299 (2003) 539–542.
- [3] T. Parekunnel, P.F. Bernath, N.F. Sobov, S. Shirin, O.L. Polyansky, J. Tennyson, *J. Mol. Spectrosc.* 210 (2001) 28–40.
- [4] O. Naumenko, E. Bertseva, A. Campargue, *J. Mol. Spectrosc.* 197 (1999) 122–132.
- [5] S. Hu, H. Lin, S. He, J. Cheng, Q. Zhu, *Phys. Chem. Chem. Phys.* 1 (1999) 3727–3730.
- [6] O. Naumenko, A. Campargue, *J. Mol. Spectrosc.* 199 (2000) 59–72.
- [7] O. Naumenko, E. Bertseva, A. Campargue, D. Schwenke, *J. Mol. Spectrosc.* 201 (2000) 297–309.
- [8] E. Bertseva, O. Naumenko, A. Campargue, *J. Mol. Spectrosc.* 203 (2000) 28–36.
- [9] E. Bertseva, O. Naumenko, A. Campargue, *J. Mol. Spectrosc.* 204 (2000) 94–105.
- [10] E. Bertseva, O. Naumenko, A. Campargue, *J. Mol. Spectrosc.* 221 (2003) 38–46.
- [11] S.-M. Hu, O.N. Ulenikov, G.A. Onopenko, E.S. Bekhtereva, S.-G. He, X.-H. Wang, H. Lin, Q.-S. Zhu, *J. Mol. Spectrosc.* 203 (2000) 228–234.
- [12] X.-H. Wang, S.-G. He, S.-M. Hu, J.-J. Zheng, Q.-S. Zhu, *Chin. Phys.* 9(12) (2000) 885–891.
- [13] O.N. Ulenikov, S.-M. Hu, E.S. Bekhtereva, G.A. Onopenko, X.-H. Wang, S.-G. He, J.-J. Zheng, Q.-S. Zhu, *J. Mol. Spectrosc.* 208 (2001) 224–235.
- [14] A. Jenouvrier, M.F. Merienne, M. Carleer, R. Colin, A.-C. Vandaele, P.F. Bernath, O.L. Polyansky, J. Tennyson, *J. Mol. Spectrosc.* 209 (2001) 165–168.
- [15] A.D. Bykov, V.P. Lopasov, Yu.S. Makushkin, L.N. Sinitisa, O.N. Ulenikov, *J. Mol. Spectrosc.* 94 (1982) 1–27.
- [16] L.S. Rothman, A. Barbe, D. Chris Benner, L.R. Brown, C. Camy-Peyret, M.R. Carleer, K. Chance, C. Clerbaux, V. Dana, V.M. Devi, A. Fayt, J.-M. Flaud, R.R. Gamache, A. Goldman, D. Jacquemart, K.W. Jucks, W.J. Lafferty, J.-Y. Mandin, S.T. Massie, V. Nemtchinov, D.A. Newnham, A. Perrin, C.P. Rinsland, J. Schroeder, K.M. Smith, M.A.H. Smith, K. Tang, R.A. Toth, J. Vander Auwera, P. Varanasi, K. Yoshino, *J. Quant. Spectrosc. Radiat. Transfer* 82 (2003) 5–44.
- [17] H. Partridge, D.W. Schwenke, *J. Chem. Phys.* 106 (1997) 4618–4639.
- [18] N. Papineau, C. Camy-Peyret, J.-M. Flaud, G. Guelachvili, *J. Mol. Spectrosc.* 92 (1982) 451–468.
- [19] H.H. Nielsen, *Rev. Mod. Phys.* 23 (1951) 90–136.
- [20] G. Amat, H.H. Nielsen, G. Tarrago, *Rotation–Vibration of Polyatomic Molecules*, Marcel Dekker, New York, 1971.
- [21] F. Jørgensen, T. Pedersen, *Mol. Phys.* 27 (1974) 33–47; *Mol. Phys.* 27 (1974) 959–971; *Mol. Phys.* 29 (1975) 1137–1164.
- [22] D. Papousek, M.R. Aliev, *The Molecular Vibration–Rotation Spectra*, Elsevier, Amsterdam, Oxford, New York, 1982.
- [23] Y.S. Makushkin, O.N. Ulenikov, *Sov. J. Phys. N3* (1975) 11–16.
- [24] J.K.G. Watson, *J. Chem. Phys.* 46 (1967) 1935–1949; *J. Chem. Phys.* 48 (1968) 181–185; *J. Chem. Phys.* 48 (1968) 4517–4524.
- [25] E.I. Lobodenko, O.N. Sulakshina, V.I. Perevalov, V.G. Tyuterev, *J. Mol. Spectrosc.* 126 (1987) 159–170.
- [26] K. Sarka, H. Harder, *J. Mol. Spectrosc.* 197 (1999) 254–261.
- [27] O.N. Ulenikov, *J. Mol. Spectrosc.* 119 (1986) 144–152.
- [28] P. Jensen, *J. Chem. Soc. Faraday Trans. 2* (128) (1988) 478–501.
- [29] P. Jensen, *J. Mol. Spectrosc.* 128 (1988) 478–501.
- [30] P. Jensen, in: S. Wilson, G.H.F. Diercksen (Eds.), *Methods in Computational Molecular Physics*, Plenum Press, New York, 1992.
- [31] P. Jensen, I.N. Kozin, *J. Mol. Spectrosc.* 160 (1993) 39–57.
- [32] I.N. Kozin, P. Jensen, *J. Mol. Spectrosc.* 161 (1993) 186–207.
- [33] I.N. Kozin, P. Jensen, *J. Mol. Spectrosc.* 163 (1994) 483–509.
- [34] O.L. Polyansky, P. Jensen, J. Tennyson, *J. Chem. Phys.* 101 (1994) 7651–7657; *J. Chem. Phys.* 105 (1996) 6490–6497; *J. Chem. Phys.* 178 (1996) 184–188.
- [35] O.N. Ulenikov, E.S. Bekhtereva, N.A. Sanzharov, P. Jensen, *J. Mol. Spectrosc.* 227 (2004) 1–12.
- [36] D.W. Schwenke, H. Partridge, *J. Chem. Phys.* 113 (2000) 6597–6952.
- [37] T. Cours, P. Rosmus, V.G. Tyuterev, *J. Chem. Phys.* 117 (2002) 5192–5208.
- [38] H. Lin, W. Thiel, S.N. Yurchenko, M. Carvajal, P. Jensen, *J. Chem. Phys.* 117 (2002) 11265–11276.
- [39] S.V. Shirin, O.L. Polyansky, N.F. Zobov, P. Barletta, J. Tennyson, *J. Chem. Phys.* 118 (2003) 2124–2129.
- [40] T. Rajamäki, A. Miani, L. Halonen, *J. Chem. Phys.* 118 (2003) 6358–6369.