
INVERSE PROBLEMS OF ATMOSPHERIC
AND OCEAN OPTICS

Effective Potential Energy Surface of HD¹⁶O for Calculation of Highly Excited States of nv_3 and $v_1 + nv_3$ Types

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Abstract—A new spectroscopically determined potential energy surface (PES) for HD¹⁶O is presented, and rotational-vibrational transitions are calculated using it for low rotational quantum numbers $J \leq 4$. This surface is constructed by adjusting a high-accuracy PES by fitting to experimental energy levels of nv_3 and $v_1 + nv_3$ types. Seven hundred and forty rotational levels with energies up to 25 600 cm⁻¹ and $J \leq 8$ were used for the refinement. To improve the extrapolation properties of the empirical PES, the fitting was applied to experimental and ab initio energy levels.

Keywords: potential energy surface, HD¹⁶O, VTT

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Potential energy surfaces (PES) and dipole moment surfaces (DMS) of a molecule determine its physical and chemical properties; therefore, their retrieval from spectra is one of the most important problems of rotational-vibrational (RV) spectroscopy. In recent years, significant progress in the accuracy of variational calculations of energy levels of triatomic molecules was observed, as applied to water as one of the most studied molecules, on the basis of improved PES [1, 2].

Despite the fact that PES for different water vapor isotopologues has been studied for a long time in many works, errors of 100 cm⁻¹ were not uncommon and were typical, and an accuracy of 1 cm⁻¹ for calculated energy levels was acceptable. Partridge and Schwenke [1, 2] firstly achieved an accuracy of ~0.1 cm⁻¹ for band centers and about 10% for intensities of calculated water vapor spectra, based on an ab initio PES, optimized through fitting to experimental energy levels and an ab initio DMS. Band centers and intensities of RV transitions in [1, 2] were computed with the use of a variational method.

Transitions to nv_3 and $v_1 + nv_3$ states are the strongest in the spectrum; therefore, they are the most studied and promising for further investigations in the UV spectral range.

The first detailed analysis of the accuracy of calculation [1] for H₂¹⁶O energy levels was made in [3]. Calculation results were compared with a large amount of experimental data, including experimental levels, which were not used in the PES calculation in [1]. The

analysis confirmed high accuracy and good extrapolation properties of the calculation [1]. Later, the Partridge and Schwenke potential [1, 2] was improved in [4], where PES was used for calculation of the H₂¹⁶O line list known as BT2 (by names of authors Barber and Tennyson) [5], which is currently the fullest and includes more than 500 000 000 transitions in a range up to 30 000 cm⁻¹. Currently, work on the improvement and optimization of PES continues for the basic water vapor isotopologues (see, e.g., [6–9]).

The potential energy surface of the HD¹⁶O isotopologue has been studied much less. Following the calculation of RV energy levels by Schwenke and Partridge [1, 2], centers and intensities of RV transitions of HD¹⁶O were computed with a high accuracy by S. A. Tashkun. These results are accessible on the website (<http://spectra.iao.ru>) (see [10]). The calculations were made on the basis of PES and DMS [1, 2], but with the use of a larger basis set. Finally, in [11], a PES was described (further called HDO_07) which allowed the representation of experimental RV energy levels, included in the fitting, up to 25 000 cm⁻¹ with a rms error of 0.035 cm⁻¹ (in calculations [1, 2], the rms error was 0.45 cm⁻¹). Based on the HDO_07 PES and dipole moment [12], a HDO RV line list has been calculated known as VTT (Voronin, Tennyson, Tolchenov) [13], which is currently the fullest and the most accurate. VTT includes 697 454 528 transitions of HD¹⁶O in a range up to 25 600 cm⁻¹. The further refinement of the HDO_07 PES for calculation of the band centers and intensities of HD¹⁶O absorption lines in the UV spec-

tral range is hindered because of lack of new experimental data.

For many years, measurements of band centers and intensities for the water vapor molecule were limited to the 0–26000 cm^{-1} spectral region, which was due to the low intensity of lines in the UV range. Experimental investigations of H_2^{16}O RV states with higher energies became possible due to the use of the triple laser resonance technique. High-lying H_2^{16}O RV states were studied in triple resonance experiments on the basis of selective excitation of the levels up to dissociation energy of 41 126 cm^{-1} [14–16]. Successive interpretation of experimental high-energy H_2^{16}O RV levels became possible only after optimization of available PES [14–16] accounting for new experimental data.

The HD^{16}O molecule is of particular interest for experiments on selective excitation of high-energy RV levels, since, in contrast to H_2^{16}O , frequencies of vibrations of the OD and OH bonds in HD^{16}O (ν_1 and ν_3 vibration modes, respectively) differ significantly (2332 and 3236 cm^{-1}), which leads to different intramolecular dynamics of HD^{16}O and H_2^{16}O .

For the HD^{16}O isotopologue, measurements of the triple laser resonance were conducted [17], similar to those described in [14–16]. As a result, several levels were obtained with an energy of 41 000 cm^{-1} . When analyzing these levels, it is necessary to take into account certain significant problems [18] related to identification of experimental RV levels even in a range of energies of up to 25 000 cm^{-1} . Unjustified identification of levels included in the inverse problem of the PES retrieve can lead to a strong distortion of results. Obviously, for identification of high-energy levels [17], the currently available PES of HD^{16}O should be refined.

Thus, the interpretation of highly excited RV levels of HD^{16}O energy requires optimization of VTT, which is the best of the currently available variational calculations. In this work, a modification of the HDO_07 [11] and computation of VTT are presented, aiming at more effective retrieval and more accurate extrapolation of calculation of the HD^{16}O energy levels of $n\nu_3$ and $\nu_1 + n\nu_3$ types, which are of particular interest for experiments on selective high-energy vibration spectroscopy. When refining PES, the method proposed in [19] and described in detail in [11] was used. Briefly, the procedure of determination of the function of potential energy was the following. The ab initio CVRQD PES was written as

$$V = V_{\text{CBS}} + V_{\text{CV}} + V_{\text{MVD1}} + V_{\text{D2}} + V_{\text{Breit}} + V_{\text{QED}} + V_{\text{BODC}}, \quad (1)$$

where the first summand V_{CBS} (CBS is the complete basis set) is

$$V_{\text{CBS}}(r_1, r_2, \theta) = V^a(r_1) + V^a(r_2) + V^b(r_{\text{HH}}) + V^c(r_1, r_2, \theta), \quad (2)$$

$V^a(r_1)$, $V^a(r_2)$, and $V^b(r_{\text{HH}})$ are responsible for two-particle interaction; and the summand, responsible for three-particle interactions, is written as

$$V^c(r_1, r_2, \theta) = f_{000} + \left(\sum_{IJK}^{N_p} f_{ijk} s_1^i s_2^j s_3^k \right) e^{-\beta[(r_1-r_e)^2 + (r_2-r_e)^2]}. \quad (3)$$

Here

$$s_1 = (r_1 + r_2)/2 - r_e, \quad s_2 = (r_1 - r_2)/2, \quad s_3 = \cos\theta - \cos\theta_e; \quad (4)$$

r_1 and r_2 are lengths of bonds O–H, O–D; θ is the angle between them; and r_e and θ_e are the corresponding equilibrium values. Other terms in Eq. (1) are the minor corrections: valence V_{CV} (CV—core-valence), relativistic $V_{\text{MVD}} + V_{\text{D2}} + V_{\text{Breit}}$, Born–Oppenheimer diagonal corrections V_{BODC} , and quantum electrodynamical corrections V_{QED} . In more detail, calculation of these corrections is considered in [20]. In our case, only V_{CBS} was varied, while all other terms remained fixed to initial (ab initio) values during the fitting process.

During our fitting, 113 polynomial coefficients f_{ijk} from Eq. (3) were varied, which determine the desired effective potential. In order to improve extrapolation properties of the empirical potential, certain actions were performed. In particular, to avoid nonphysical forms of the potential during the fitting process and to solve the problem of lack of fitting data, we used the method of simultaneous fitting to experimental and ab initio energies (see [19]).

As a result, a new HD^{16}O PES was constructed starting from the ab initio PES of Polyansky et al. [4] and PES [11] through fitting experimental energy levels of $n\nu_3$ and $\nu_1 + n\nu_3$ states. In the fitting, 740 energy levels with $J < 9$ were used, up to 25 330 cm^{-1} , namely, 424 levels of vibration states of $n\nu_3$ type ($n = 0, 1–8$) and 316 levels of vibration states of $\nu_1 + n\nu_3$ type ($n = 0, 1–7$).

Based on the PES constructed (let us designate it as VTT_v3), energy levels for $J \leq 4$ were calculated, for which the program package [21] was used. The calculations were conducted at the server of Laboratory of Molecular Spectroscopy IAO SB RAS with the use of two 4-core processors controlled by OS Linux (openSUSE 12.3), 16 GB ram.

Figures 1–3 show experimental and calculated levels of HD^{16}O molecule.

After that the potential function VTT_v3 and the DMS [12] were used for finding the calculation spectrum, including more than 2 500 000 transitions. In

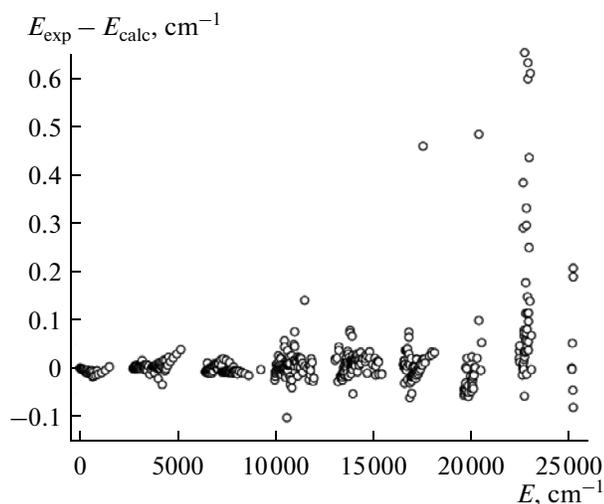


Fig. 1. Difference between calculated and experimental energy levels for nv_3 and $v_1 + nv_3$ types.

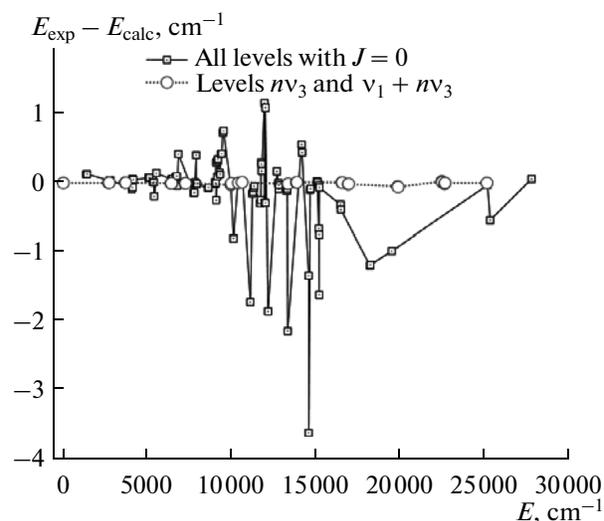


Fig. 2. Deviation of calculated vibrational levels from experimental HD¹⁶O ($J=0$): squares denote vibration levels which do not participate in the optimization, circles denote vibrational energy levels of nv_3 and $v_1 + nv_3$ types after fitting.

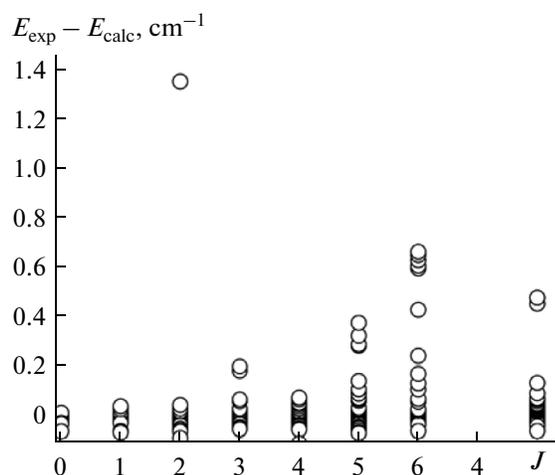


Fig. 3. Deviation of experimental energy levels from fitted ones for $v_1 + nv_3$ and v_3 states. RV states with $J=7$ were not used in the fitting. The large deviation for $J=2$ (almost 1.5 cm^{-1}) is caused by the level of state (107)–(000) and may be due to an identification error.

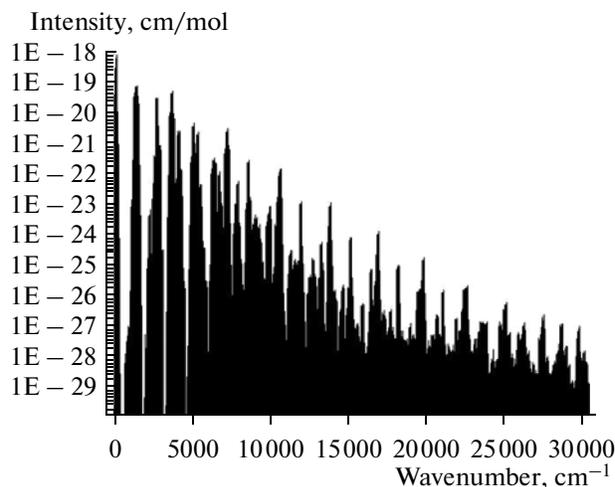


Fig. 4. General view of HD¹⁶O spectrum in the 0–30000 cm^{-1} range, calculated on the basis of new HDO_v₃ PES for transitions with quantum numbers $J=0, 1, 2, 3,$ and 4.

this case, like in calculation of VTT, the program [21] was used. Calculation results are shown in Fig. 4.

It is necessary to note that the most accurate HD¹⁶O energy levels were found from processing of IUPAC (MARVEL) experimental spectra [22]. It is interesting to compare results of our computations and IUPAC data. For nv_3 and $v_1 + nv_3$ states, 353 energy levels were selected from the IUPAC database, and 11 energy levels were added for the state (008) from [17] (in total, 364 levels). All them were compared

with the VTT calculation [13] and the calculation denoted in Tables 1–3 as $E_{\text{exp}} - E_{\text{calc}}$.

Table 1 shows that the effective potential values, which we found, agree better with experimental levels than our former VTT calculation [13].

Data on the PES obtained, calculated energy levels for $J=0, 1, 2, 3,$ and 4, their identifications, and absorption spectrum are on the website ftp://ftp.iao.ru/pub/VTT/HDO_v3/. The site includes the energy-levelsHDO_v3.dat file, which is a list of energy levels. It includes new energy levels and energy

Table 1. Comparison of calculations

Difference	Maximal positive deviation, cm^{-1}	Minimal negative deviation, cm^{-1}	Mean level difference, cm^{-1}	Standard deviation, cm^{-1}
$E_{\text{exp}} - E_{\text{VTT}}$	0.224	-0.136	0.011	0.06
$E_{\text{exp}} - E_{\text{our calc}}$	0.173	-0.082	0.003	0.02

Table 2. Known vibrational states and comparison with calculation

$E_{\text{exp}}, \text{cm}^{-1}$	$E_{\text{our calc}}, \text{cm}^{-1}$	$E_{\text{VTT}}, \text{cm}^{-1}$	ν_1	ν_2	ν_3	$E_{\text{exp}} - E_{\text{VTT}}, \text{cm}^{-1}$	$E_{\text{exp}} - E_{\text{our calc}}, \text{cm}^{-1}$
3707.46673	3707.46929	3707.47118	0	0	1	-0.00445	-0.00256
7250.51921	7250.51140	7250.49349	0	0	2	0.02572	0.00781
10631.68320	10631.69299	10631.67317	0	0	3	0.01003	-0.00979
13853.62800	13853.63456	13853.64019	0	0	4	-0.01219	-0.00656
16920.02400	16920.00375	16919.94670	0	0	5	0.07730	0.02025
19836.88280	19836.82904	19836.70427	0	0	6	0.17853	0.05376
22625.52850	22625.51708	22625.52359	0	0	7	0.00491	0.01142
25140.85000	25140.85362	25140.96323	0	0	8	-0.11323	-0.00362
6415.46062	6415.45401	6415.47381	1	0	1	-0.01318	0.00661
9967.02300	9966.99847	9966.99413	1	0	2	0.02887	0.02453
13331.60610	13331.59022	13331.59201	1	0	3	0.01409	0.01588
—	16539.04700	16539.03621	1	0	4	—	—
—	19584.51174	19584.53412	1	0	5	—	—
22454.46880	22454.49867	22454.50470	1	0	6	-0.03590	-0.02987
	25332.86921	25333.49630	1	0	7		
<i>Dispersion</i>						0.00190	0.00071

levels from VTT [13] with identification by quantum numbers $\nu_1, \nu_2, \nu_3, J, K_a,$ and K_c , a local number in a submatrix, corresponding to the given J and symmetry, and a global number between 1 and 18 200. Note that VTT energy levels higher than $29\,600\text{ cm}^{-1}$ are represented for $J=0$; they are absent in [13] and published for the first time. On the above site, h2o_ii.f, h2o_ii.par, and potv.f files include the new PES. The linelistHDO_v3.dat file is a line list, calculated using the PES obtained and DMS [20] in the $0\text{--}30\,500\text{ cm}^{-1}$ range; it includes values for the upper-

and lower-energy levels, angular momentum ($J=0, 1, 2, 3$ or 4), symmetry (0 or 1), numbers of energy level in a submatrix, and values of energy levels. In addition, frequency and line intensities for 296 K also are given there.

Table 2 shows vibrational levels for HD^{16}O energy in comparison with our and VTT calculations.

Certain statistics are given in Table 3. It shows all submatrices that were constructed up to energies of $\sim 31\,000\text{ cm}^{-1}$.

Table 3. Statistics over nine submatrices of calculated energy levels

J	S^*	E_{\max}, cm^{-1}	Number of HDO_v ₃ levels	E_{\max}, cm^{-1}	VTT	E_{\max}, cm^{-1}	VTT+
0	0	39896	1500	29665	600	39899	1500
1	1	31891	1500	25665	775	32040	1500
1	0	34900	1000	26476	420	35285	1000
2	1	32095	1500	26165	800	32305	1500
2	0	31792	2200	25773	1160	31964	2200
3	1	30931	2650	25657	1505	31043	2650
3	0	31107	2000	25622	1115	31107	2000
4	1	31032	2600	25622	1456	31149	2600
4	0	30908	3250	25625	1845	31026	3250
<i>Total</i>			18200		9676		18200

* Symmetry.

For convenience, energy levels of the VTT line list were recalculated with high values of submatrices for $J = 0, 1, 2, 3$, and 4. In Table 3, they are shown in 7th and 8th columns and are denoted as VTT+.

We hope that our calculations will be useful in investigations of highly excited states of HD¹⁶O and the strongest absorption bands in the UV range.

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