NEW ANALYSIS OF EXPERIMENTAL DATA FOR THE FIRST TRIAD OF H_2O MOLECULE INTERACTING STATES

V.I. Starikov

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk

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The paper describes a new approach to analysis of the experimental data for the first triad (1, 0, 0), (0, 2, 0), (0, 0, 1) of interacting vibrational states of H_2O *molecule. Analysis is carried out with the use of new models for an effective Hamiltonian of* H_2O *molecule. That enables one to significantly increase (as compared with the preceding analysis) the number of experimental energy levels (up to the rotational quantum numbers $J = 30$) to be fit and to improve the quality of this fitting. A series of highly excited rotational energy levels calculated is presented for the state (0, 2, 0) connected with a large-amplitude vibration.*

INTRODUCTION

The first triad of the H_2O molecule interacting vibrational states is formed by the states (1, 0, 0), (0, 2, 0), and (0, 0, 1) connected with the absorption bands ν_1, $2\nu_2$, and ν_3 in the 2.7 μm range. The most complete results of the experimental study in this range have been obtained in Refs. 1–6. The values of more than 1000 experimental (obtained from the experimentally measured transition wavenumbers) rotational energy levels for the considered vibrational states have been found. About 450 energy levels simultaneously for three states have been first described theoretically in Ref. 7 in 1974. The above results have been described using standard representations for the effective Hamiltonian of H_2O molecule. Theoretically, the processing of vibrational-rotational energy levels of such light molecules, as the H_2O molecule, is difficult due to the effect of strong centrifugal distortion and random resonances. The use of an effective Hamiltonian as a series of operators of angular momentum results in a poor convergence of this series. Therefore in the processing we have restricted ourselves to the experimental data with small and mean values of rotational quantum numbers J and K_a (large values of K_a correspond to highly excited rotational energy levels of H_2O molecule). In Ref. 7 the energy levels are processed with the following maximum values of the rotational quantum numbers J and K_a; $J = 14$, $K_a = 9$ for the state (1, 0, 0); $J = 15$, $K_a = 8$ for the state (0, 2, 0); $J = 16$, $K_a = 9$ for the state (0, 0, 1). For 70 per cent of the processed energy levels the error of fitting does not exceed $15\cdot10^{-3}$ cm^{-1}.

In Refs. 8–10 it was shown that the use of generating functions for the effective rotational Hamiltonian enables one to significantly improve the quality of description of the experimental data for an isolated vibrational state. Besides, the asymptotic features of these functions make it possible to involve in the processing the energy levels with large values of rotational quantum numbers ($J = 35$, $K_a = 20$ for the ground vibrational state[10]). In Ref. 11, in its turn, it was shown that a large-amplitude vibration in the molecule results in the fact that the operators H_{nm}, describing the interactions between the vibrational states (n) and (m), in the general case, cannot be reduced to the form H'_{nm}, having in the basis of the rotational wave functions $|J, K>$ of a symmetric top molecule the matrix elements $<J, K|H'_{nm}|J, K+\Delta K>$ only with $\Delta K = 0, \pm1, \pm2$, i.e., it cannot be reduced to that form which was used in Ref. 7 for describing the energy levels of the first triad of the interacting states of H_2O molecule. Generating functions G obtained for a single vibrational state,[8–10] as well as new representations of reduced forms of the operators H_{nm}, developed in Ref. 11, make good grounds for a more complete and higher-quality description of the experimental data for interacting vibrational states in the H_2O molecule.

THEORETICAL MODEL

The matrix of the effective Hamiltonian H of H_2O molecule in the basis of vibrational wave functions in the first approximation can be represented by polyads (blocks) of interacting vibrational states. The first triad was formed by the states (1) = (1, 0, 0), (2) = (0, 2, 0) and (3) = (0, 0, 1). The matrix elements $H_{nm} = <n|H|m>$, ($n, m = 1, 2, 3$) of the Hamiltonian H in the basis $|n>$, $|m>$ are the rotational operators. The diagonal matrix elements $H_{nn} = H^{(n)}$ were taken as the expansion over the G-function

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$$H^{(n)}=E_n^{(J)}+\sum_{i,j}\frac{g_{ij}^{(n)}J^{2i}G_n^j}{(1+\beta^{(n)}G_n)}+\frac{1}{2}\sum_{i,j}u_{ij}^{(n)}J^{2i}\{G_n^j,J_+^2-J_-^2\},$$

$$i,\ j = 0,\ 1,\ 2,\ \dots\ , \qquad (1)$$

which is determined by the relationship[9,12]

$$G_n = 2/\alpha^{(n)}\left(\sqrt{1+\alpha^{(n)}J_z^2}-1\right). \qquad (2)$$

In formulas (1) and (2) the parameters $E_n^{(J)}$ and $\alpha^{(n)}$ are the J-dependent parameters

$$E_n^{(J)} = E_n + g_{10}^{(n)}J^2 + g_{20}^{(n)}J^4 + \dots\ ; \qquad (3)$$

$$\alpha^{(n)} = \alpha_0^{(n)} + \alpha_1^{(n)}J^2 + \alpha_2^{(n)}J^4 + \dots\ , \qquad (4)$$

and the operators J^2, J_z, J_+, and J_- are determined by the following rules of their effect on the rotational wave function $|J,\ K>$ of a symmetric top molecule:

$$J^2|J,K> = J(J+1)|J,K>,\ J_z|J,K> = K|J,\ K>,$$

$$J_\pm|J,K> = \{J(J+1) - K(K\pm 1)\}^{1/2}|J,\ K\pm 1>. \qquad (5)$$

The relation of the parameters $g_{ij}^{(n)}$, $u_{ij}^{(n)}$ to the Watson's type parameters E_n, $A^{(n)}$ commonly used (at $\beta^{(n)} = 0$) was determined in Refs. 9, 10, and 12. The operator H_{12}, describing the interaction between the states (1) and (2), was determined as follows:

$$H_{12} = f_0 + f_{020}J_z^2 + f_{200}J^2 + \{J_+^2\Psi_2(J_z+1) +$$

$$+\Psi_2(J_z+1)J_-^2\} + \{J_+^4\Psi_4(J_z+2) + \Psi_4(J_z+2)J_-^4\}. \qquad (6)$$

The type of functions Ψ_2 and Ψ_4 can be found from Eqs. (2.17), (2.19) in Ref. 11. Processing of the experimental data was performed both with the use of series expansions of Ψ-functions over G-functions (2)

$$\Psi_{2l}(J_z+l) = \sum_{i,j,l} g_{ijl}J^{2i}G^j(J_z+l),$$

$$i,\ j = 0,\ 1,\ 2,\ \dots;\ \ l = 1,\ 2 \qquad (7)$$

(the parameters α_0, α_1, ... in the G-function were fixed to the parameters for the ground state[10]) and with the use of expansions into power (J_z+l) series of these functions:

$$\Psi_{2l}(J_z+l) = \sum_{i,j,l} \mathrm{f}_{2i2j2l}J^{2i}(J_z+l)^{2j},$$

$$i,\ j = 0,\ 1,\ 2,\ \dots;\ \ l = 1,\ 2. \qquad (8)$$

The operators H_{n3} $(n \neq 3)$, describing the interaction of the Coriolis type of the state (3) = (0, 0, 1) with the states (2) = (0, 2, 0) and (1) = (1, 0, 0), according to Ref. 11, were taken in the form

$$H_{n3} = \sum_{i,j} C_{ij1}^{(n)}J^{2i}\{J_+(J_z+1/2)^j - (-1)^j(J_z+1)^jJ_-\} +$$

$$+\{J_+^3C_3^{(n)}(J_z+3/2) - C_3^{(n)}(J_z+3/2)J_-^3\} +$$

$$+\{J_+^5C_5^{(n)}(J_z+5/2) - C_5^{(n)}(J_z+5/2)J_-^5\}, \qquad (9)$$

$$i,\ j = 0,\ 1,\ 2,\ \dots\ .$$

As for the Ψ_{2l} functions, for $C_{1+2l}^{(n)}$ functions two expansions were used: over G-functions

$$C_{1+2l}^{(n)}(J_z+l+1/2) = \sum_{i,j} g_{ij1+2l}^{(n)}J^{2i}G^j(J_z+l+1/2),$$

$$i,\ j = 0,\ 1,\ 2,\ \dots;\ \ l = 1,\ 2 \qquad (10)$$

and, with the same parameters as in the G-function from Eq. (7), over powers $(J_z+l+1/2)$

$$C_{1+2l}^{(n)}(J_z+l+1/2) = \sum_{i,j,l} C_{2ij1+2l}^{(n)}J^{2i}(J_z+l+1/2)^j \qquad (11)$$

(for odd j the sign (−) at second and third terms of formula (9) must be replaced by the sign (+)).

It is sufficient to use rules (5) to determine the matrix elements of the operators $H^{(n)}$, H_{12}, and H_{n3} in the basis of rotational wave functions $|J,\ K>$, and, therefore, it is sufficient for determining the matrix of the effective Hamiltonian H, defined by these operators, in a symmetrized basis of rotational wave functions $|J,\ K,\ \Gamma>$ generally used for the asymmetric top molecules (see, e.g., Refs. 7 and 13). From the comparison of calculated (obtained as a result of numerical diagonalization of the Hamiltonian H matrix) values E^{calc} and the experimental values E^{exp} of the vibrational-rotational energy levels we find an optimal set of the parameters g_{ij}, u_{ij}, f_{2i2j2l},..., presenting the best quality of description of experimental data, which in this paper is characterized by the value

$$\sigma = \sqrt{\sum_{i=1}^{I}(E_i^{\text{exp}} - E_i^{\text{calc}})^2/(I-L)}\ . \qquad (12)$$

In Eq. (12) I is the total number of the experimental energy levels; L is the number of the parameters varied. The value of σ is given in cm^{-1}.

RESULTS OF THE INVERSE PROBLEM SOLUTION

As the experimental data we have used the experimental rotational energy levels for the vibrational states (1, 0, 0), (0, 2, 0), and (0, 0, 1) obtained in Refs. 1–4. For the state (0, 2, 0) these data were supplemented with the highly excited energy levels from Ref. 6 (these levels are marked by asterisks in Table III).

Several series of processing for $J \le 10$, $J \le 15$, $J \le 20$, and $J \le 30$ were carried out. The values of σ, obtained as a result of the best processing, are given in Table I. Here we also show the maximum values of $K_a^{\max}$ of the quantum number K_a in the experimental energy levels used, the total number of the energy levels I, and the number L of the parameters varied. The values of σ from Table I were obtained by means of the representations (8) and (11) for the interaction operators H_{12} and H_{n3} (although the representations (7) and (10) make it possible to improve the quality of the description of the experimental data as compared to those of (8) and (10), but only slightly). Let us consider the results of some data processings.

Fitting up to $J = 10$. The energy levels are described accurate to experimental errors. The standard deviation σ, indicated in Table I, was obtained using the following models for the operators H_{nm} ($n \ne m$). In the operator H_{12}, describing the Fermi interaction, the components with the parameters f_{000} and f_{020} were used; in the operator H_{23} the components with the parameters C_{001}, C_{011}, and C_{013} were used; in the operator H_{13} the components with the parameters C_{011}, C_{021}, and C_{211} were used. Thus, already for $J \le 10$ in the interaction block H_{23} the components should be considered, which have the matrix elements with $\Delta K = \pm 3$ in the basis $|J, K>$.

Fitting up to $J = 15$. In our opinion, just for these rotational quantum numbers there exists the most complete and reliable set of data enabling one (after solution of the inverse problem) to perform extrapolation to the weak absorption lines with large K_a for the $2\nu_2$ band, connected with a large-amplitude vibration. The solution of the inverse problem is given in Table II.

The parameters derived correspond to the standard deviation $\sigma = 4.5 \cdot 10^{-3}$ cm^{-1} from Table I. A series of predicted energy levels for the state (0, 2, 0) is presented in Table III. This table also shows the errors in fitting, $\Delta E = E^{\text{exp}} - E^{\text{calc}}$, of separate energy levels (in 10^{-3} cm^{-1}). Note that the values of some predicted energy levels $[J, K_a, K_c]$ for the state (0, 2, 0) differ strongly(more than by $70 \cdot 10^{-3}$ cm^{-1}) from the values of these energy levels obtained in Ref. 5. These are the following energy levels: [11, 6, 6], [11, 7, 5], [12, 5, 7], [12, 6, 7], [13, 2, 12], [13, 3, 11], [13, 4, 10], [14, 2, 12], [14, 3, 17], [14, 6, 9]. The reason of such a disagreement can be clarified when analyzing in detail the experimental data touching upon the above energy levels.

Fitting up to $J = 20$. The results of solution of the inverse problem for $J \le 20$, being given as a table, analogous to Tables II and III, are too cumbersome and hence they are omitted here. The readers who are interested in the results, may send a request. It should only be noted that for obtaining the standard deviation $\sigma = 11.2 \cdot 10^{-3}$ cm^{-1} from Table I for the interaction block H_{12} seven parameters and Ψ_{2l} functions (8) with $l = 1, 2$ were used. For the operator H_{23} we used six parameters and C_{1+2l} functions (11) with $l = 1, 2$, and, finally, for the operator H_{13} we used nine parameters and the C_3 function (11). Besides, the series of energy levels, given in Ref. 4, was excluded from the processing, since these levels break the convergence of the inverse problem and their values, in our opinion, must be refined experimentally.

Fitting up to $J = 30$. For $20 \le J \le 30$ there are only the experimental energy levels for the states (1, 0, 0) and (0, 0, 1), moreover, starting with $J \ge 25$ only few levels with small values of the quantum number K_a are available.[4] Some energy levels (for the same reason as in the fitting up to $J = 20$) was omitted in solving the inverse problem. In the interaction blocks of H_{nm} the components were considered having in the basis of rotational wave functions $|J, K>$ the matrix elements $<J, K|H_{nm}|J, K+\Delta K>$ with $\Delta K = 0$, ± 1, ± 2, ± 3, ± 4, ± 5. In spite of the fact that for $20 \le J \le 30$ there exists only a limited set of experimental data, the result obtained is important, since it characterizes the quality of the model proposed for an effective Hamiltonian, which makes it possible to process the rotational states of a molecule with large values of rotational quantum numbers.

TABLE I. The values of σ (cm^{-1}) obtained from the best processings of the experimental energy levels from the first triad of the interacting vibrational states of H_2O molecule.

	$J \le 10$			$J \le 15$			$J \le 20$			$J \le 30$		
	(0, 2, 0)	(1, 0, 0)	(0, 0, 1)	(0, 2, 0)	(1, 0, 0)	(0, 0, 1)	(0, 2, 0)	(1, 0, 0)	(0, 0, 1)	(0, 2, 0)	(1, 0, 0)	(0, 0, 1)
$K_a^{\max}$	10	10	10	10	15	15	10	19	16	10	19	16
σ	$1.3 \cdot 10^{-3}$			$4.5 \cdot 10^{-3}$			$11.2 \cdot 10^{-3}$			$17.2 \cdot 10^{-3}$		
I*	358			639			861			1001		
L**	73			90			106			105		

*I is the number of experimental energy levels (from Refs. 1, 4, 6).

**L is the number of the parameters varied.

TABLE II. Spectroscopic parameters for the first triad of H_2O *molecule obtained in fitting the energy levels from Refs. 1, 4, 6 up to* $J = 15$ ($I = 639$)*.

State	(0, 0, 2)	(1, 0, 0)	(0, 0, 1)
α_0	0.262438E−01 (0.392E−03)	0.737821E−02 (0.241E−04)	0.709222E−02 (0.500E−04)
α_1	−0.412173E−04 (0.453E−05)	−0.105383E−04 (0.282E−06)	
α_2	0.648502E−07 (0.109E−07)	−0.989075E−08 (0.793E−09)	
E	3154.528E−00 (0.101E−00)	3654.161E−00 (0.101E−00)	3755.933E−00 (0.149E−02)
β	0.148174E−02 (0.290E−03)		
g_{10}	11.911427E−00 (0.176E−03)	11.700753E−00 (0.972E−04)	11.782531E−00 (0.111E−03)
g_{20}	−0.155392E−02 (0,278E−05)	−0.121985E−02 (0.111E−05)	−0.128462E−02 (0.193E−05)
g_{30}	0.721369E−06 (0.144E−07)	0.431144E−06 (0.272E−08)	0.577403E−06 (0.123E−07)
g_{40}			−0.302445E−09 (0.257E−10)
g_{01}	23.679196E−00 (0.910E−03)	15.428808E−00 (0.508E−03)	14.866811E−00 (0.230E−03)
g_{11}	0.108873E−01 (0.340E−04)	0.571342E−02 (0.151E−04)	0.573204E−02 (0.967E−05)
g_{21}	0.178394E−04 (0.365E−06)	−0.976526E−06 (0.634E−07)	−0.193477E−05 (0.443E−07)
g_{31}	−0.186337E−07 (0,168E−08)		
g_{02}	0.768265E−01 (0.911E−02)	−0.233530E−02 (0.111E−03)	−0.264709E−02 (0.884E−05)
g_{12}	−0.327808E−03 (0.226E−04)	−0.465859E−04 (0.111E−05)	−0.890196E−05 (0.997E−07)
g_{22}	−0.496391E−06 (0.399E−07)	−0.840450E−07 (0.418E−08)	−0.337078E−07 (0.153E−08)
g_{13}	0.412918E−05 (0.109E−06)	0.304614E−06 (0.694E−08)	0.133911E−06 (0.515E−08)
g_{33}	0.109244E−10 (0.829E−12)		
g_{04}	−0.340048E−05 (0.787E−07)	−0.198239E−06 (0.453E−08)	−0.120657E−06 (0.427E−08)
g_{24}	−0.292551E−10 (0.242E−11)		
u_{00}	1.465789E−00 (0.138E−03)	1.299527E−00 (0.126E−00)	1.323171E−00 (0.697E−04)
u_{10}	−0.643620E−03 (0.158E−05)	−0.493075E−03 (0.639E−06)	−0.523511E−03 (0.150E−05)
u_{20}	0.332046E−06 (0.734E−08)	0.214546E−06 (0.159E−08)	0.290756E−06 (0.105E−07)
u_{30}			−0.160700E−09 (0.228E−10)
u_{01}	−0.950059E−02 (0.429E−04)	−0.118478E−02 (0.807E−05)	−0.124265E−02 (0.583E−05)
u_{11}	−0.380346E−05 (0.197E−06)	−0.897478E−07 (0.455E−07)	−0.758025E−06 (0.343E−07)
u_{02}	0.429226E−03 (0.719E−05)	0.276357E−04 (0.169E−06)	0.270011E−04 (0.144E−06)
u_{03}	−0.936045E−05 (0.340E−06)	−0.171121E−06 (0.319E−08)	−0.153580E−06 (0.360E−08)
u_{13}			−0.114478E−09 (0.708E−11)
u_{04}	0.849470E−07 (0.502E−08)	0.208870E−09 (0.181E−10)	0.304128E−09 (0.806E−11)
u_{05}	−0.393372E−09 (0.305E−10)		

Interaction parameters					
Fermi interaction		Coriolis interaction			
H_{12}		H_{23}		H_{13}	
f_0	38.154E−00 (0.664E−00)	C_{001}	0.596E−00 (0.102E−01)	C_{011}	−0.326E−00 (0,598E−03)
f_{020}	−0.144E−00 (0.595E−02)	C_{211}	−0.111E−04 (0.534E−05)	C_{021}	−0.912E−02 (0.631E−03)
f_{200}	0.275E−02 (0.847E−03)	C_{023}	0.132E−04 (0,846E−06)	C_{031}	−0.951E−03 (0.751E−04)
f_{002}	0.281E−02 (0.514E−03)	C_{043}	−0.159E−06 (0.169E−07)	C_{211}	−0.276E−03 (0.225E−04)
f_{022}	−0.112E−03 (0.222E−04)			C_{213}	0.608E−06 (0.142E−06)
f_{024}	0.343E−06 (0.664E−07)			C_{033}	−0.166E−05 (0.179E−06)

*The standard deviation for the parameters are given in parenthesis.

TABLE III. The calculated (E^{calc}) energy levels for the first triad of vibrational states of H_2O *molecule as well as their deviations* $\Delta E = (E^{exp} - E^{calc})\cdot 10^3$ *from the experimental values (the values from Ref. 6 are asterisked).*

J	K_a	K_c	E^{calc}	ΔE	E^{calc}	ΔE	E^{calc}	ΔE
			(0, 2, 0)		(1, 0, 0)		(0, 0, 1)	
0	0	0	3151.6319	−1.78	3657.0580	−4.85	3755.9332	−3.60
1	0	1	3175.4429	−1.39	3680.4574	−3.80	3779.4974	−3.94
1	1	1	3196.0931	0.41	3693.2981	−4.30	3791.7035	−1.35
1	1	0	3201.9118	1.76	3698.4951	−3.38	3796.9843	−2.48
2	0	2	3221.9627	−1.18	3725.9439	−1.78	3825.2167	−2.15
2	1	2	3237.9178	−0.35	3734.8998	−2.63	3833.5789	−1.96
2	1	1	3255.3431	3.15	3750.4654	−0.58	3849.3875	−1.82
2	2	1	3316.1429	2.59	3788.6980	−3.36	3885.7364	1.60
2	2	0	3317.2080	3.03	3789.9725	−3.04	3887.1130	1.99
3	0	3	3289.2447	−1.94	3791.3725	−0.53	3890.8321	−2.48
3	1	3	3299.9923	−0.82	3796.5408	−1.23	3895.5897	−1.06
3	1	2	3334.6228	3.93	3827.3908	2.44	3926.8638	−1.36
3	2	2	3387.6783	2.68	3858.8762	−0.64	3956.6640	2.47
3	2	1	3392.7462	3.18	3864.7631	0.59	3962.9165	1.58
3	3	1	3500.5115	−0.13	3935.2149	−4.18	4030.0658	3.96
3	3	0	3500.6392	−0.04	3935.3484	−3.25	4030.3021	4.29
4	0	4	3375.3011	−2.93	3875.0165	0.64	3974.6327	−1.22
4	1	4	3381.7063	−1.86	3877.5749	0.43	3977.2621	−0.53
4	1	3	3438.5715	4.02	3927.7992	3.53	4027.8049	−0.49
4	2	3	3482.0624	2.11	3951.3137	1.37	4050.0500	2.47
4	2	2	3495.9361	3.78	3966.5557	3.60	4066.1214	1.16
4	3	2	3597.8670	−0.67	4030.8389	−0.03	4125.1483	0.56
4	3	1	3598.7281	−0.71	4031.8537	−0.38	4126.4635	−0.01
4	4	1	3746.7643	−1.30	4135.0184	−0.52	4224.8135	2.85
4	4	0	3746.7776	−1.66	4134.7995	−0.94	4224.8476	3.44
5	0	5	3478.9902	−3.36	3976.3067	1.51	4076.1442	−0.87
5	1	5	3482.4823	−1.98	3977.4550	1.50	4076.8964	−0.16
5	1	4	3565.4525	2.40	4049.5324	3.95	4149.8995	−0.24
5	2	4	3598.5140	2.06	4065.1299	1.82	4165.4704	6.66
5	2	3	3626.9204	2.14	4095.9147	5.65	4195.9701	0.88
5	3	3	3719.4940	−0.99	4150.2852	1.78	4244.3049	−0.14
5	3	2	3722.7332	−1.75	4153.9364	1.70	4248.1529	−0.63
5	4	2	3868.8745	−1.22	4257.7839	2.88	4345.2706	1.47
5	4	1	3868.9888	−1.88	4256.2383	3.03	4345.5579	1.55
5	5	1	4050.5032	0.99	4381.9076	−3.92	4468.6930	0.17
5	5	0	4050.5121	0.86	4381.9076	−3.92	4468.6976	0.50
6	0	6	3600.0554	−2.81	4095.3135	1.84	4195.4777	−0.48
6	1	6	3601.8603	−1.07	4095.8013	2.06	4195.8182	−0.18
6	1	5	3713.0819	0.37	4190.2602	2.10	4290.7571	0.41
6	2	5	3736.1690	2.02	4199.3899	1.40	4296.5630	0.65
6	2	4	3784.6795	−0.36	4249.5202	3.74	4350.6987	0.82
6	3	4	3864.9669	−0.60	4292.9081	1.81	4387.2349	−0.07
6	3	3	3873.7977	−3.75	4308.2067	5.07	4408.0278	1.41
6	4	3	4015.5168	−1.68	4394.4620	2.39	4490.0640	0.17
6	4	2	4016.0556	−2.54	4401.9375	4.32	4491.3700	−0.07
6	5	2	4197.3366	1.89	4526.7186	1.00	4613.5278	−1.18
6	5	1	4197.3591	3.49	4526.7190	1.31	4613.5747	−1.53
6	6	1	4407.0458	0.93	4677.8796	−3.53	4759.8554	−2.71
6	6	0	4407.1575	1.44	4677.8798	−3.71	4759.8560	−3.30

TABLE III. (continued).

J	K_a	K_c	$E^{\rm calc}$	ΔE	$E^{\rm calc}$	ΔE	$E^{\rm calc}$	ΔE
			(0, 2, 0)		(1, 0, 0)		(0, 0, 1)	
7	0	7	3738.6104	−1.13	4232.1926	2.30	4332.7739	0.81
7	1	7	3739.5186	0.43	4232.3822	2.24	4332.9121	0.67
7	1	6	3879.3367	0.06	4348.4153	−0.38	4448.9709	0.03
7	2	6	3894.1600	1.83	4353.2323	−0.15	4452.3524	0.66
7	2	5	3967.4904	−1.35	4426.0605	1.85	4527.9488	0.95
7	3	5	4033.6143	1.42	4457.8191	−0.30	4553.2740	−0.25
7	3	4	4052.8429	−5.99	4484.9900	2.54	4586.6837	−0.44
7	4	4	4186.5709	0.61	4363.9865	3.41	4658.9757	−0.68
7	4	3	4188.3991	−4.83	4572.4429	3.27	4663.1513	−0.15
7	5	3	4368.5440	3.27	4695.8349	1.90	4782.6647	−2.30
7	5	2	4368.6356	2.13	4695.8340	2.53	4782.9228	−2.73
7	6	2	4578.8801	5.24	4846.7714	2.94	4929.0651	−2.82
7	6	1	4578.9756	1.27	4846.7736	1.83	4929.0723	0.14
7	7	1	4812.1945	−1.25	5020.0295	−2.49	5096.2489	−3.56
7	7	0	4812.1946	−2.06	5020.0295	−2.51	5096.2489	−3.63
8	0	8	3894.7979	1.80	4387.3628	−4.29	4488.0906	0.01
8	1	8	3895.2507	2.14	4387.0609	2.47	4488.1455	0.67
8	1	7	4062.8393	−2.77	4523.5920	−2.70	4624.3036	−0.62
8	2	7	4071.7321	1.64	4525.9672	−2.39	4625.9371	0.54
8	2	6	4173.2271	−1.71	4622.9077	−1.34	4725.0618	0.80
8	3	6	4224.5848	3.99	4644.0029	−3.80	4741.0678	−0.16
8	3	5	4259.8827	−1.46	4689.3295	−0.42	4792.3411	−0.17
8	4	5	4381.7356	−1.17	4756.3937	0.53	4851.5391	−0.54
8	4	4	4386.3135	0.54	4769.0379	0.88	4861.8028	0.92
8	5	4	4564.0344	−0.77	4889.4596	−1.78	4976.0463	−2.40
8	5	3	4564.3677	0.80	4889.4040	0.88	4977.0475	−3.15
8	6	3	4774.8035	9.55	5039.6249	2.89	5122.3512	1.74
8	6	2	4775.0872	1.66	5039.6395	2.93	5122.3965	−3.62
8	7	2	5008.9629	−6.84	5213.2661	2.32	5289.9605	0.28
8	7	1	5008.9632	−7.09	5213.2665	3.75	5289.9616	0.23
8	8	1	5261.4742*	−0.23	5406.5536	−3.38	5475.7571	−0.75
8	8	0	5261.4742*	−0.23	5406.5536	−3.38	5475.7572	−0.76
9	0	9	4068.7008	3.38	4559.7063	1.22	4661.4268	0.04
9	1	9	4068.9272	3.92	4559.7504	2.59	4661.4487	0.27
9	1	8	4263.1529	−2.63	4715.9720	−4.32	4816.9925	−0.67
9	2	8	4268.2412	1.62	4717.1094	−3.49	4817.7365	−0.20
9	2	7	4399.5420	1.97	4837.7036	−3.57	4939.7942	0.84
9	3	7	4436.9385	9.71	4850.4478	−10.53	4949.0036	−0.18
9	3	6	4493.8067	−0.82	4918.2376	−2.54	5022.2811	0.93
9	4	6	4600.4947		4971.2643	−3.79	5067.0784	−1.44
9	4	5	4611.8049	−9.56	4992.1219	0.20	5087.0143	3.18
9	5	5	4783.6422		5108.3579	−8.19	5193.4601	−2.81
9	5	4	4784.6670	2.84	5107.7324	−2.51	5196.5037	−2.25
9	6	4	4994.7034		5256.3826	−0.33	5339.6445	−2.51
9	6	3	4996.3361	−3.88	5256.4490	−0.63	5339.8467	1.05
9	7	3	5229.5782	6.04	5430.1776	7.38	5507.4766	−0.62
9	7	2	5229.5799*	0.07	5430.1804	7.01	5507.4841	1.87
9	8	2	5483.3246*	1.39	5624.3849	4.65	5694.0478	1.79
9	8	1	5483.3246*	−0.63	5624.3850	4.60	5694.0480	1.64
9	9	1	5749.9185*	2.47	5836.9923	−6.30	5896.2713	−0.34
9	9	0	5749.9185*	1.47	5836.9923	−6.30	5896.2713	−0.34

TABLE III. (continued).

J	K_a	K_c	E^{calc}	ΔE	E^{calc}	ΔE	E^{calc}	ΔE
			(0, 2, 0)		(1, 0, 0)		(0, 0, 1)	
10	0	10	4260.3483		4750.3617	2.42	4852.7502	−0.46
10	1	10	4260.4629	4.24	4750.3868	1.24	4852.7569	−0.10
10	1	9	4480.3972	0.39	4925.7930	−3.38	5027.2591	−2.39
10	2	9	4483.2313	−5.08	4926.3525	−2.77	5027.5674	−6.36
10	2	8	4644.2175		5069.0932	−2.70	5171.0604	−0.08
10	3	8	4669.7373	−0.99	5076.2737	−2.91	5175.9553	0.85
10	3	7	4752.7271	16.79	5169.0409	−0.85	5273.6311	1.83
10	4	7	4842.1245	11.80	5207.8079	−5.45	5304.7293	−0.80
10	4	6	4864.3817	2.87	5246.8092	−5.69	5355.2726	−9.55
10	5	6	5027.0762	−7.51	5334.9867	1.76	5434.4854	−1.11
10	5	5	5029.8126	−2.13	5351.4142	−6.64	5442.1003	−2.40
10	6	5	5238.3875*	−1.50	5496.9863	−6.64	5580.8203	2.38
10	6	4	5237.4194*	2.62	5497.2194	−3.23	5581.5277	−3.34
10	7	4	5473.8032*	0.79	5670.6154	3.77	5748.6624	−0.04
10	7	3	5473.8121*	−10.13	5670.6297	7.39	5748.6998	−1.31
10	8	3	5728.6637*	−1.72	5865.6017	4.33	5935.8289	3.08
10	8	2	5728.6639*	−2.86	5865.6021	6.00	5935.8301	2.87
10	9	2	5996.6323*	6.71	6079.9766	−0.36	6139.3215	1.07
10	9	1	5996.6323*	6.71	6079.9766	−0.37	6139.3216	1.05
10	10	1	6318.9123*	2.73	6264.7414	−6.94	6355.7338	5.75
10	10	0	6318.9123*		6264.7414	−6.94	6355.7338	5.75
11	0	11	4469.7352	0.00	4958.9015	2.46	5062.0121	4.90
11	1	11	4469.7944	1.44	4958.9364	0.48	5062.0151	5.05
11	1	10	4714.8253	1.69	5153.1940	−2.95	5255.2084	−1.58
11	2	10	4716.3851	−1.24	5153.5390	−1.05	5255.3499	−2.84
11	2	9	4905.6620	−11.63	5316.8085	−6.14	5418.8044	−0.48
11	3	9	4922.1012		5320.8950	−3.17	5421.2676	0.68
11	3	8	5034.3723		5439.0535	4.33	5543.6341	3.32
11	4	8	5105.7188		5465.0575	−1.01	5563.4004	0.13
11	4	7	5144.4135*	−2.54	5524.5774	−5.45	5631.8432	−4.63
11	5	7	5293.7923*	0.73	5601.5341	−3.12	5698.4901	−0.88
11	5	6	5300.1872*	−8.24	5621.3408	−6.40	5714.5339	1.09
11	6	6	5505.6242*	0.84	5761.4107	−3.93	5845.6537	1.09
11	6	5	5505.1692*	5.76	5762.0651	−4.77	5847.7090	0.76
11	7	5	5741.3872*	2.77	5934.4229	−0.42	6013.3668	0.36
11	7	4	5741.4225*	5.48	5934.4802	−1.45	6013.5120	−0.72
11	8	4	5997.1779*	−1.85	6129.9826	−0.02	6200.8890	4.09
11	8	3	5997.1784*	−2.35	6129.9850	1.66	6200.8956	1.69
11	9	3	6266.3740*	−3.95	6346.1070	0.88	6405.5143	5.31
11	9	2	6266.3740*	−0.97	6346.1071	0.82	6405.5145	5.11
11	10	2	6589.3894		6534.1662	6.04	6623.6703	−0.75
11	10	1	6589.3894		6534.1662	6.04	6623.6703	−0.76
11	11	1	6867.9577		6785.6013	−0.07	6852.1648	−3.42
11	11	0	6867.9577		6785.6013	−0.07	6852.1648	−3.42
12	0	12	4696.8357		5186.3515	−12.46	5289.1544	−0.54
12	1	12	4696.8673	−11.19	5184.7346	2.83	5289.1552	−1.32
12	1	11	4966.6352	4.11	5398.2538	−5.56	5500.8600	−1.877
12	2	11	4967.4927	2.53	5399.3303	5.09	5500.9192	−1.78
12	2	10	5182.1092	−4.04	5581.1120	0.96	5683.3345	1.20
12	3	10	5193.9123		5579.4976	−5.35	5684.5310	−3.65
12	3	9	5336.3085		5726.0527	11.09	5830.2561	3.33
12	4	9	5389.5413		5742.0340	−2.91	5841.8609	2.74

TABLE III. (continued).

J	K_a	K_c	E^{calc}	ΔE	E^{calc}	ΔE	E^{calc}	ΔE
			(0, 2, 0)		(1, 0, 0)		(0, 0, 1)	
12	4	8	5450.8929		5826.1389	−2.74	5933.5465	−0.16
12	5	8	5587.5127	10.58	5887.7655	2.90	5984.6757	2.34
12	5	7	5596.4357		5918.1764	6.18	6013.4509	0.25
12	6	7	5796.1274		6049.8538	−3.61	6133.7730	−1.29
12	6	6	5796.4390		6051.2748	2.12	6138.8920	−0.54
12	7	6	6032.0662		6221.4346	0.22	6301.4081	0.16
12	7	5	6032.1830		6221.6249	−1.78	6301.8754	−3.66
12	8	5	6288.5468		6417.2998	−3.84	6489.0078	10.57
12	8	4	6288.5471		6417.3105	−9.42	6489.0359	3.91
12	9	4	6558.7687		6635.1096	1.75	6694.5761	2.85
12	9	3	6558.7688		6635.1100	1.81	6694.5773	2.81
12	10	3	6882.8778		6825.8948	−6.22	6914.3571	−0.74
12	10	2	6882.8778		6825.8948	−6.23	6914.3572	−0.78
12	11	2	7166.3668		7077.5787	−2.04	7145.1098	−5.88
12	11	1	7166.3668		7077.5787	−2.04	7145.1098	−5.88
12	12	1	7464.0856		7328.0727	9.03	7383.6792	−2.00
12	12	0	7464.0856		7328.0727	9.03	7383.6792	−2.00
13	0	13	4941.6113	4.27	5429.1198	6.08	5534.1149	−2.51
13	1	13	4941.6292		5429.1294	−12.59	5534.1140	−1.58
13	1	12	5235.9371		5662.4711	6.82	5764.1877	0.22
13	2	12	5236.4119		5660.4017	8.88	5764.2070	1.20
13	2	11	5477.0608		5862.3405	1.96	5964.9163	−2.76
13	3	11	5483.1813		5862.4703	−6.15	5965.4771	2.69
13	3	10	5654.7563		6028.8423	18.01	6132.6420	10.94
13	4	10	5695.8682		6037.8610	11.84	6139.0249	7.28
13	4	9	5781.9810		6148.6861	0.28	6256.0197	1.01
13	5	9	5896.7707		6194.2915	−3.30	6292.1205	−0.98
13	5	8	5919.0340		6241.5291	3.40	6336.0414	4.29
13	6	8	6109.5253		6363.5641	10.66	6444.6330	2.41
13	6	7	6111.4403		6365.3777	2.98	6455.7465	10.16
13	7	7	6345.5613		6531.4763	−3.05	6612.5485	2.56
13	7	6	6345.8971		6532.0163	7.86	6613.8378	−3.93
13	8	6	6602.4579		6727.3207	−5.81	6799.9543	2.02
13	8	5	6602.4496		6727.3596	−1.42	6800.0531	−0.58
13	9	5	6873.4453		6946.7012	−8.68	7006.2281	−0.43
13	9	4	6873.4460		6946.7028	−8.30	7006.2333	0.66
13	10	4	7198.9203		7139.5889	1.22	7227.4690	−4.61
13	10	3	7198.9203		7139.5889	1.18	7227.4692	−4.80
13	11	3	7486.4021		7391.6764	−2.22	7460.3580	−7.78
13	11	2	7486.4021		7391.6764	−2.22	7460.3580	−7.79
13	12	2	7789.3277		7644.4397	−3.30	7701.7427	6.58
13	12	1	7789.3277		7644.4397	−3.30	7701.7427	6.58
13	13	1	8094.2621		7901.2015	−4.50	7948.4957	0.75
13	13	0	8094.2621		7901.2015	−4.50	7948.4957	0.75
14	0	14	5204.0148		5690.8809	−2.47	5796.9436	−1.24
14	1	14	5204.0258		5690.8815	0.92	5796.8896	3.67
14	1	13	5522.7706		5940.5333	8.85	6045.1699	5.16
14	2	13	5523.0374		5940.6298	9.53	6045.1423	−1.35
14	2	12	5786.9356		6161.1436	−17.15	6263.7050	−5.02
14	3	12	5790.5184		6160.3744	3.15	6263.9249	−0.37
14	3	11	5993.2019		6347.2731		6451.0935	−10.37
14	4	11	6019.8156		6351.8265		6454.1276	0.04

TABLE III. (continued).

J	K_a	K_c	E^{calc}	ΔE	E^{calc}	ΔE	E^{calc}	ΔE
			(0, 2, 0)		(1, 0, 0)		(0, 0, 1)	
14	4	10	6134.9946		6489.6355		6596.2212	0.62
14	5	10	6229.9080		6520.5771		6619.7894	−5.60
14	5	9	6267.9664		6589.7453	1.20	6705.5889	2.84
14	6	9	6445.0898		6676.4669	3.18	6777.5267	7.14
14	6	8	6450.3877		6705.0504	−13.44	6798.7266	−8.81
14	7	8	6681.5745		6864.3844	6.64	6946.4613	0.47
14	7	7	6682.4335		6865.7171	12.05	6949.5838	−4.89
14	8	7	6938.6295		7059.8089	−4.74	7133.4787	5.76
14	8	6	6938.5765		7059.9306	8.36	7133.7785	2.00
14	9	6	7210.0456		7280.5900	5.15	7340.1867	−4.45
14	9	5	7210.0484		7280.5962	6.53	7340.2064	−6.60
14	10	5	7537.0283		7474.9445	5.70	7562.6780	−2.16
14	10	4	7537.0284		7474.9447	5.47	7562.6789	−3.11
14	11	4	7827.2040		7727.5410	−4.66	7797.5428	−0.18
14	11	3	7827.2040		7727.5410	−4.67	7797.5428	−0.21
14	12	3			7982.5102	−4.11	8041.6029	−1.36
14	12	2			7982.5102	−4.11	8041.6029	2.24
14	13	2			8242.3027	12.56	8291.7792	2.65
14	13	1			8242.3027	12.56	8291.7792	2.65
14	14	1			8505.2120	−3.14	8544.9450	−0.39
14	14	0			8505.2120	−3.14	8544.9450	−0.39
15	0	15	5483.9915		5970.2097	−0.62	6077.1141	−4.05
15	1	15	5483.9993		5970.2083	0.85	6077.1121	−1.96
15	1	14	5827.1253		6238.2050	9.99	6343.4296	14.91
15	2	14	5827.2789		6238.2305	−10.03	6342.5278	1.61
15	2	13	6113.6020		6474.7034	3.62	6578.8805	−8.80
15	3	13	6115.7484		6475.4522	−12.80	6579.7493	−5.54
15	3	12	6345.9226	1.33	6682.0096	−4.23	6784.6931	
15	4	12	6362.6040		6683.3950		6786.6822	2.80
15	4	11	6510.4647		6847.1478		6952.1886	−2.55
15	5	11	6584.4673		6865.8165		6966.5828	0.41
15	5	10	6642.1206		6960.3928	−2.62	7074.4901	
15	6	10	6803.5112		7032.7140		7131.6285	0.93
15	6	9	6813.4265		7070.6791		7167.3475	0.88
15	7	9	7039.7818		7220.1064		7302.7124	3.82
15	7	8	7041.7653		7222.9599	−3.74	7309.4753	
15	8	8	7296.8061		7414.5244		7489.2982	5.64
15	8	7	7296.6335		7414.8596	−1.62	7490.1017	−1.44
15	9	7	7568.2341		7636.4775	−4.13	7696.1628	−3.02
15	9	6	7568.2446		7636.4980	2.34	7696.2266	
15	10	6	7896.7159		7831.6882	−5.22	7919.6548	−2.61
15	10	5	7896.7164		7831.6893	−4.07	7919.6586	−0.38
15	11	5			8084.8337	5.57	8156.2994	0.79
15	11	4			8084.8338	5.53	8156.2996	0.62
15	12	4			8341.8930	−4.45	8402.8656	7.24
15	12	3			8341.8930	−4.45	8402.8656	7.24
15	13	3			8604.5943	6.91	8656.3038	−6.17
15	13	2			8604.5943	6.91	8656.3038	−6.17
15	14	2			8871.1240	−6.29	8913.5635	0.05
15	14	1			8871.1240	−6.29	8913.5635	0.05
15	15	1			9138.9570	2.11	9171.4830	−1.13
15	15	0			9138.9570	2.11	9171.4830	−1.13

CONCLUSION

In this paper we present a new analysis of the experimental data for the first triad of resonating states of H_2O molecule. The analysis has been carried out with the use of new representations for the effective Hamiltonian of H_2O molecule what has made it possible to essentially increase the number of the processed energy levels I(I = 358 for $J \le 10$, I = 639 for $J \le 15$, I = 861 for $J \le 20$, and I = 1001 for $J \le 30$) as compared to the previous analysis (in Ref. 7 I = 470 for $J \le 16$). The accuracy of the fitting of the most complete and reliable set of the experimental data (for $J \le 15$) is close to the experimental one. The values of spectroscopic constants obtained when solving the inverse problem enable one to calculate weak absorption lines in the ν_1, $2\nu_2$, ν_3 bands. In particular, for the $2\nu_2$ band the values of calculated energy levels for the (0, 2, 0) state from Table III can be used.

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