REVISED ANALYSIS OF EXPERIMENTAL DATA ON THE SECOND TRIAD OF THE H₂O MOLECULE RESONANCE STATES

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We present here some results of revised analysis of the experimental data on the second triad (1, 1, 0), (0, 3, 0), and (0, 1, 1) of interacting vibrational states of the H₂O *molecule. To do this, we used new models of centrifugal distortion Hamiltonian of a molecule. It enabled one to increase the number of the fitted energy levels and to improve the quality of the fitting. The following values of the standard deviation* σ *were obtained for the experimental energy levels: at J ≤ 10, σ = 3.6·10⁻³ cm⁻¹, at J ≤ 15, σ = 6.2·10⁻³ cm⁻¹, and at J ≤ 20, σ = 9.5·10⁻³ cm⁻¹.*

INTRODUCTION

The second triad of the H₂O molecule resonance vibrational states includes the states (1, 1, 0), (0, 3, 0) and (0, 1, 1) connected with the absorption bands $\nu_1 + \nu_2$, $3\nu_2$ and $\nu_2 + \nu_3$ in the near infrared spectral range. More than 600 experimental rotational energy levels obtained from the experimental frequencies of transitions are known to date for the vibrational states considered. The greatest number of these levels (up to the rotational quantum numbers $J = 30$ and $K_a = 14$) has been obtained for the state (0, 1, 1) with which the most intense band $\nu_2 + \nu_3$ is connected. Tables of experimental energy levels can be found in Refs. 1–4. About 380 energy levels have been first described theoretically for the three states simultaneously in Ref. 5. The above levels have been described using the standard representations for an effective Hamiltonian of a molecule. In that case included into the processing were energy levels with the following maximum values of rotational quantum numbers J and K_a: $J = 14$, $K_a = 7$ for the state (1, 1, 0); $J = 12$, $K_a = 6$ for the state (0, 3, 0); $J = 15$, $K_a = 9$ for the state (0, 1, 1). For 73% of the energy levels processed the reconstruction error did not exceed $40 \cdot 10^{-3}$ cm⁻¹.

In this paper we use a new approach to description of the experimental data on the H₂O molecule. Details of this approach are presented in Refs. 6 and 7 and its brief description is given in the next section.

It should be noted that the use of this approach in Ref. 7 to analyze experimental data on the first triad of resonant vibrational states of a molecule has made it possible to essentially increase the amount of experimental data suitable for reconstruction (up to the energy levels with $J = 30$) as well as to improve the quality of such a reconstruction.

THEORETICAL MODEL

We briefly describe here the theoretical model used for analyzing the experimental data. The effective Hamiltonian H of the H₂O molecule for the three states (1) = (1, 1, 0), (2) = (0, 3, 0) and (3) = (0, 1, 1) in the basis of vibrational wave functions $|n>$, $|m>$ (n, m = 1, 2, 3) is presented in the form of a 3×3 matrix. The matrix elements $H_{nm} = <n|H|m>$ of the Hamiltonian H in the basis $|n>$, $|m>$ are the rotational operators. The diagonal matrix elements $H_{nn} = H^{(n)}$ were taken as a series expansion over G-function[8,9]:

$$H^{(n)} = E_n^{(J)} + \sum_{i,j \neq 0} g_{ij}^{(n)} J^{2i} G_n^j / (1 + \beta^{(n)} G_n) +$$

$$+ \frac{1}{2} \sum_{i,j} u_{ij}^{(n)} J^{2i} \{G_n^j, J_+^2 + J_-^2\} ; \quad i, j = 0, 1, 2, ..., \quad (1)$$

which is determined by the relationship[9–11]

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

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

$$E_n^{(J)} = E_n + g_{10}^{(n)} J^2 + g_{20}^{(n)} J^4 + ... ,$$

$$\alpha^{(n)} = \alpha_0^{(n)} + \alpha_1^{(n)} J^2 + \alpha_2^{(n)} J^4 + .. ,. \quad (3)$$

$$\beta^{(n)} = \beta_0^{(n)} + \beta_1^{(n)} J^2 + \beta_2^{(n)} J^4 + ... \quad (4)$$

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

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

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

The association of the parameters $g_{ij}^{(n)}$, $u_{ij}^{(n)}$ with the common Watson-type parameters E_n and $A^{(n)}$ (at $\beta^{(n)} = 0$) has been determined in Refs. 9, 10, and 12. The operator H_{12} describing the interaction between the states (1) and (2) has been defined as follows:

$$H_{12} = \sum_{i,j} f_{2i2j0} J^{2i} J_z^{2j} + \{J_+^2 \Psi_2 (J_z + 1) +$$

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

$$i, j = 0, 1, 2, \dots . \quad (6)$$

In this formula f_{2i2j0} are the numerical coefficients, and $\Psi_{2l}(l = 1, 2)$ are the functions of the operators J_2 and J_z. In Ref. 7, when analyzing the experimental data on the first triad of H_2O, we used the following representations for Ψ_{2l}–functions. First, the expansion of these functions into a series over G–functions, i.e., the representation

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

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

(the parameters α_0, $\alpha_1,\dots$ in the G-function were fixed to accord with the parameters of the ground state[12]). Second, the expansion of these functions into a power series over $(J_z + 1)$ is:

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

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

The operators $H_{n3}(n \neq 3)$ describing the Coriolis interaction of state (3) = (0, 1, 1) with the states (2) = (0, 3, 0) and (1) = (1, 1, 0) were taken as

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

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

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

$$n = 1, 2; \quad i, j = 0, 1, 2, \dots .$$

As in the case with Ψ_{2l}-functions, for $C_{1+2l}^{(n)}$ functions we used two expansions, namely, the expansion over G-functions

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

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

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

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

$$i, j = 0, 1, 2, \dots ; \quad l = 0, 1 \quad (11)$$

(at an odd j the $(-)$ sign in the second and third terms of Eq. (9) should be replaced by the $(+)$ sign).

The rules (5) would suffice to determine the matrix elements of the operators $H^{(n)}$, H_{12} and H_{n3} in the basis of the rotational wave functions $|J, K>$ and, hence, it is sufficient to determine the matrix of the effective Hamiltonian H, determined by these operators in the symmetrized basis of rotational wave functions $|J, K, \Gamma>$ commonly used for the asymmetric top molecules (see, for example, Ref. 13). From the comparison of the calculated (obtained as a result of numerical diagonalization of the Hamiltonian H matrix), E^{calc}, and experimental, E^{exp}, vibrational-rotational energy levels, an optimal set of the parameters $g_{ij}^{(n)}$, $u_{ij}^{(n)}$, f_{2i2j2l}, ..., has been found, which provided the best quality of a description of the experimental data, characterized in our paper by the value:

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

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

RESULTS OF SOLUTION OF THE INVERSE PROBLEM

As the experimental data we have used the following experimental rotational energy levels: for vibrational states (1, 1, 0) − from Ref. 1, for the state (0, 3, 0) − from Ref. 2, and for the vibrational state (0, 1, 1) − from Ref. 4 (for the rotational quantum number $J > 15$ the experimental data are available only for one state (0, 1, 1)). Some series of processings have been carried out up to the rotational quantum numbers $J = 10$, $J = 15$ and $J = 20$. The values of σ, obtained from most successful processings, are given in

Table I. Here we present maximum values K_a^{max} of the quantum number K_a of the experimental energy levels used, the total number of energy levels I and the number of varied parameters L. The values of σ in the table were obtained with the use of the representations (8) and (11) for the operators of interaction H_{12} and H_{n3} (representations (7) and (10) were used for analyzing the experimental data on the first triad of the molecule; in this case we have clarified that although they make it possible to improve the quality of description of the experimental data as compared with the representations (8) and (11) but only insignificantly). Let us now consider the results of processings.

TABLE I. *Quality* σ *(in* cm^{-1}*) of reconstruction of the rotational energy levels of the second triad of the vibrational states of the* H_2O *molecule.**

	$J \le 10$			$J \le 15$			$J \le 20$		
	(0, 3, 0)	(1, 1, 0)	(0, 1, 1)	(0, 3, 0)	(1, 1, 0)	(0, 1, 1)	(0, 3, 0)	(1, 1, 0)	(0, 1, 1)
K_a^{max}	6	8	10	6	8	14	6	8	14
σ	$3.6 \cdot 10^{-3}$			$6.2 \cdot 10^{-3}$			$9.5 \cdot 10^{-3}$		
I	295			445			541		
L	74			90			98		

*K_a^{max} is the maximum value of the rotational quantum number K_a of the energy levels used in fitting; I is the total number of these energy levels; L is the number of the parameters varied.

TABLE II. *Spectroscopic parameters obtained for the second triad of vibrational states* (0, 3, 0), (1, 1, 0) *and* (0, 1, 1) *of* H_2O *molecule.*

State	(0, 3, 0)	(1, 1, 0)	(0, 1, 1)
α_0	0.817370E−01 (0.569E−02)	0.117813E−01 (0.638E−04)	0.194231E−01 (0.110E−02)
α_1	− 0.144195E−03 (0.251E−04)	0.297013E−05 (0.597E−06)	0.384398E−04 (0.482E−05)
α_2			0.366330E−07 (0.317E−08)
E	4673.042E−00 (0.163E+01)	5228.725E−00 (0.403E−02)	5331.274E−00 (0.231E−02)
β_0	0.776573E−02 (0.101E−02)		− 0.713346E−02 (0.491E−03)
g_{10}	11.901781E−00 (0.318E−03)	11.712986E−00 (0.199E−03)	11.802349E−00 (0.176E−03)
g_{20}	− 0.180177E−02 (0.788E−05)	− 0.138096E−02 (0.432E−05)	− 0.144532E−02 (0.169E−05)
g_{30}	0.169058E−05 (0.681E−07)	0.655906E−06 (0.299E−07)	0.448901E−06 (0.109E−07)
g_{01}	29.953801E−00 (0.134E−01)	18.749010E−00 (0.135E−01)	17.729842E−00 (0.883E−03)
g_{11}	0.170701E−01 (0.112E−03)	0.603275E−02 (0.603E−04)	0.778686E−02 (0.227E−04)
g_{21}	0.556362E−04 (0.165E−05)	0.922033E−05 (0.805E−06)	0.197472E−05 (0.176E−06)
g_{31}		− 0.322549E−07 (0.499E−08)	
g_{32}		0.199077E−09 (0.620E−10)	
g_{02}	0.587242E−00 (0.717E−01)		− 0.907904E−01 (0.126E−01)
g_{12}	− 0.104371E−02 (0.152E−03)		0.100571E−03 (0.195E−04)
g_{22}	− 0.132563E−05 (0.112E−06)		0.457977E−07 (0.104E−07)
g_{03}	− 0.835677E−03 (0.891E−04)	0.329293E−04 (0.198E−05)	− 0.423934E−03 (0.470E−04)
g_{13}		− 0.543644E−06 (0.612E−07)	− 0.156141E−05 (0.257E−06)
g_{23}			− 0.371603E−09 (0.894E−10)
g_{04}			0.128367E−05 (0.154E−06)
g_{14}	0.918488E−07 (0.953E−08)	0.7919367E−08 (0.669E−09)	0.279262E−08 (0.690E−09)
u_{00}	1.544290E−00 (0.188E−03)	1.379653E−00 (0.975E−04)	1.404858E−00 (0.669E−04)
u_{10}	− 0.779820E−03 (0.503E−05)	− 0.573701E−03 (0.198E−05)	− 0.599548E−03 (0.121E−05)
u_{20}	0.103327E−05 (0.362E−07)		0.365178E−06 (0.806E−08)
u_{01}	− 0.251154E−01 (0.145E−03)	− 0.264993E−02 (0.451E−04)	− 0.333743E−02 (0.126E−04)
u_{11}	0.102636E−04 (0.946E−06)		− 0.191337E−05 (0.131E−06)
u_{02}	0.128665E−02 (0.184E−04)	0.836386E−04 (0.181E−05)	0.807749E−04 (0.199E−05)
u_{21}		− 0.114805E−07 (0.952E−09)	
u_{22}			0.9139156E−10 (0.102E−10)
u_{03}	− 0.157468E−04 (0.542E−06)		− 0.805471E−06 (0.582E−07)
u_{04}			0.386822E−08 (0.443E−09)

	Parameters of interaction		
	Fermi-interaction	Coriolis interaction	
	H_{12}	H_{23}	H_{13}
f_{000} 59.269E−00 (0.146E−01)	C_{001} 0.413E−00 (0.380E−01)	C_{011} −0.313E−00 (0.956E−03)
f_{020} − 1.514E−00 (0.614E−01)	C_{011} −0.181E−01 (0.516E−02)	C_{201} 0.256E−02 (0.957E−04)
f_{040} 0.127E−01 (0.826E−03)	C_{033} 0.362E−05 (0.339E−06)	C_{031} −0.440E−03 (0.846E−04)
f_{220} 0.650E−02 (0.263E−03)	C_{025} 0.724E−07 (0.914E−08)	C_{211} −0.806E−03 (0.338E−04)
f_{022} − 0.384E−02 (0.132E−03)		C_{203} − 0.534E−06 (0.548E−07)
f_{240} − 0.725E−04 (0.440E−05)		C_{231} 0.296E−05 (0.512E−06)
f_{402} 0.818E−06 (0.371E−07)		C_{033} −0.992E−05 (0.634E−06)
f_{242} 0.144E−06 (0.123E−07)		C_{025} 0.299E−07 (0.997E−08)
f_{224} − 0.306E−07 (0.287E−08)		

The parameters have been obtained for the energy levels with $J \le 15$.

TABLE III. Calculated (in cm^{-1}*) energy levels and differences, DE (in* 10^{-3} cm^{-1}*), for the second triad of the* H$_2$O *vibrational states.*

J	K_a	K_c	(0, 3, 0) E^{calc}	DE	(1, 1, 0) E^{calc}	DE	(0, 1, 1) E^{calc}	DE
0	0	0	4666.7908	2.30	5234.9765	1.04	5331.2743	− 5.23
1	0	1	4690.5820	− 1.21	5258.4006	0.06	5354.8763	− 3.03
1	1	1	4717.4719	− 1.63	5274.1611	− 1.34	5369.7691	− 5.49
1	1	0	4723.5441	0.59	5279.6733	− 1.35	5375.3693	− 4.31
2	0	2	4737.2057	− 2.16	5304.0078	0.68	5400.7397	− 0.61
2	1	2	4759.0201	2.78	5315.5033	− 1.44	5411.4160	− 1.92
2	1	1	4777.2000	0.59	5332.0110	2.12	5428.1740	0.22
2	2	1	4855.3022	− 1.89	5378.7491	− 2.29	5472.3572	− 4.20
2	2	0	4856.2181	− 1.42	5379.9432	− 2.09	5473.6620	− 4.62
3	0	3	4804.9165	− 3.64	5369.6946	− 1.08	5466.6352	1.51
3	1	3	4820.7582	4.81	5376.7882	− 1.27	5473.1468	− 0.83
3	1	2	4856.9177	− 0.89	5409.5466	2.47	5506.3096	4.73
3	2	2	4926.8636	1.09	5449.0320	− 1.56	5544.2508	0.23
3	2	1	4931.2722	− 0.49	5454.5978	0.07	5549.7031	1.51
3	3	1	5065.3641	− 0.80	5539.2560	− 2.32	5629.9488	− 4.22
3	3	0	5065.4557	0.70	5538.8069	− 2.87	5630.1483	− 2.77
4	0	4	4891.7460	− 4.35	5453.5738	− 3.00	5550.6712	1.73
4	1	4	4902.1260	3.70	5457.3734	− 1.74	5552.9805	− 1.99
4	1	3	4961.6860	− 2.58	5510.9193	3.39	5608.2814	5.39
4	2	3	5021.3927	− 1.02	5541.6642	0.88	5633.3945	− 0.19
4	2	2	5033.7075	1.79	5557.8490	5.22	5653.0244	3.68
4	3	2	5162.6435	− 1.54	5635.0148	1.88	5726.2573	− 0.01
4	3	1	5163.2643	− 0.11	5639.7288	3.80	5727.5732	− 0.08
4	4	1	5342.1889	1.88	5756.6610	− 1.66	5842.0060	− 1.99
4	4	0	5342.1971	− 2.21	5756.6692	0.30	5842.0319	− 1.96
5	0	5	4996.2863	− 1.78	5554.8380	− 2.79	5652.1393	3.37
5	1	5	5002.5650	3.08	5556.6882	− 0.69	5653.5643	1.56
5	1	4	5090.0367	2.00	5634.1212	2.00	5731.9112	7.99
5	2	4	5138.1900	− 4.03	5655.7968	4.55	5749.6636	1.64
5	2	3	5164.0267	3.54	5686.1813	0.01	5783.4007	4.46
5	3	3	5284.1983	4.44	5754.7426	2.56	5846.5119	1.73
5	3	2	5286.5604	2.47	5761.0281	1.98	5851.2690	1.68
5	4	2	5464.2656	2.83	5877.3269	0.13	5962.9654	− 0.32
5	4	1	5464.3363	− 2.13	5877.3929	1.52	5963.1861	− 0.07
5	5	1	5678.7256	8.57	6026.5801	− 5.17	6106.2978	0.13
5	5	0	5678.7278	1.67	6026.5818	− 4.67	6106.3009	− 0.02
6	0	6	5117.9890	− 0.44	5673.4608	− 10.03	5771.0740	2.26
6	1	6	5121.5988	2.27	5674.3122	0.18	5771.7168	1.76
6	1	5	5240.0666	2.85	5776.7909	1.89	5874.7426	5.59
6	2	5	5276.4681	− 2.16	5790.5091	4.06	5885.7345	4.24
6	2	4	5321.6518	6.05	5840.9503	3.61	5939.3360	2.75
6	3	4	5429.6934	0.38	5897.8022	2.19	5990.1794	2.41
6	3	3	5436.2718	4.21	5910.3253	− 4.28	6002.2918	2.06
6	4	3	5610.7659	0.17	6022.5477	1.13	6108.3149	1.88
6	4	2	5611.1013	− 13.10	6022.7866	− 0.29	6109.3376	0.03
6	5	2	5825.6322	− 3.03	6171.3353	0.03	6251.6831	1.21
6	5	1	5825.6483	− 2.33	6171.3529		6251.7156	− 0.29
6	6	1	6068.4970	− 2.45	6347.2492	− 1.30	6420.0557	3.49
6	6	0	6068.4973	− 2.79	6347.2494	− 1.51	6420.0561	3.21

TABLE III. （continued）.

J	K_a	K_c	(0, 3, 0)		(1, 1, 0)		(0, 1, 1)	
			E^{calc}	DE	E^{calc}	DE	E^{calc}	DE
7	0	7	5256.8452	1.00	5809.6113	4.44	5907.6374	1.99
7	1	7	5258.8687	− 0.97	5809.9762	0.84	5907.9174	0.24
7	1	6	5409.6954	− 0.54	5937.0351	5.25	6034.9868	5.19
7	2	6	5435.4171	− 10.57	5944.9235	4.24	6041.0698	4.04
7	2	5	5505.2157	− 11.31	6019.3885	1.85	6118.6371	0.39
7	3	5	5598.5763	3.52	6063.3849	2.84	6156.5031	1.47
7	3	4	5613.3677	2.74	6087.8627	− 10.85	6179.8394	0.07
7	4	4	5781.5738		6193.3675	− 2.77	6277.8635	2.57
7	4	3	5782.7157	− 12.96	6193.3728	− 3.80	6281.2363	− 0.50
7	5	3	5996.7629		6340.2387	13.41	6421.3610	0.06
7	5	2	5996.8420	0.76	6340.3369	11.05	6421.5410	− 1.80
7	6	2	6240.4825		6516.4062	7.76	6589.9708	0.61
7	6	1	6240.4864	5.48	6516.4087	5.28	6589.9753	− 2.72
7	7	1	6505.8218		6716.1783	− 4.82	6780.4212	− 0.90
7	7	0	6505.8218		6716.1783		6780.4212	− 0.94
8	0	8	5413.0021	1.31	5963.2701	− 9.45	6061.9229	− 0.88
8	1	8	5414.1290	− 0.75	5963.5199	2.10	6062.0445	− 1.28
8	1	7	5597.1806	4.54	6114.0505	8.94	6212.0378	4.19
8	2	7	5614.2756	8.68	6118.3045	8.75	6215.1620	2.61
8	2	6	5712.9075		6219.0519		6318.7221	− 2.72
8	3	6	5790.1133	− 0.77	6250.5546	3.01	6344.5403	1.27
8	3	5	5818.3561		6292.7250	− 10.97	6394.2542	− 7.72
8	4	5	5976.4371	18.16	6378.0241	− 2.56	6471.1667	− 1.29
8	4	4	5976.7229		6389.9978	− 12.96	6479.8981	− 3.12
8	5	4	6191.9619	8.60	6533.2615	− 3.85	6615.2651	1.08
8	5	3	6192.2419		6533.6465	− 4.35	6615.9712	0.82
8	6	3	6436.5374		6709.4444	4.82	6783.9266	6.52
8	6	2	6436.5615		6709.4604	− 5.35	6783.9554	− 7.31
8	7	2	6702.8929		6910.0389		6974.9885	0.51
8	7	1	6702.8931		6910.0393		6974.9891	0.89
8	8	1			7131.9214	1.18	7184.6054	− 4.71
8	8	0			7131.9214	0.48	7184.6054	− 4.71
9	0	9	5586.5903	1.18	6134.7266	− 4.10	6233.9552	− 4.63
9	1	9	5587.2218	1.89	6134.8494	− 0.63	6234.0121	− 5.15
9	1	8	5801.5498	0.37	6307.8587	3.09	6406.0223	4.19
9	2	8	5812.3901	− 6.19	6310.1123	4.12	6407.5020	4.64
9	2	7	5942.6468		6437.4757	− 0.58	6537.0987	− 11.22
9	3	7	6003.4537		6458.3738	− 7.51	6553.1996	1.04
9	3	6	6050.8493		6523.0634	4.23	6624.5630	− 9.78
9	4	6	6194.9285		6594.7801	− 3.31	6687.5335	0.17
9	4	5	6202.4841		6613.6082	11.23	6706.1048	− 7.01
9	5	5	6410.9886		6750.3492	1.93	6833.2059	0.53
9	5	4	6411.8868	− 10.92	6751.5228	1.13	6835.3918	− 2.33
9	6	4	6656.4768		6926.2563		7001.8177	− 0.26
9	6	3	6656.5843		6926.3283	− 11.31	7001.9468	3.12
9	7	3	6923.8309		7127.4897	− 1.86	7193.3259	0.93
9	7	2	6923.8323		7127.4920	− 3.27	7193.3303	5.41
9	8	2			7350.9137		7404.0398	− 1.74
9	8	1			7350.9137		7404.0399	− 1.83
9	9	1			7595.4783		7629.9617	− 2.37
9	9	0			7595.4783		7629.9617	− 2.37

TABLE III. (continued).

J	K_a	K_c	(0, 3, 0)		(1, 1, 0)		(0, 1, 1)	
			E^{calc}	DE	E^{calc}	DE	E^{calc}	DE
10	0	10	5777.6899	2.17	6323.8139	2.29	6423.7186	− 8.82
10	1	10	5778.0484	− 8.49	6323.9150		6423.7339	− 9.66
10	1	9	6022.5794	− 1.99	6518.7266	− 3.60	6617.2093	2.30
10	2	9	6029.2498	− 6.53	6520.0090		6617.9292	1.76
10	2	8	6192.2421		6672.8071	− 21.11	6772.1085	0.63
10	3	8	6237.6952		6686.1218	10.13	6781.4054	3.74
10	3	7	6309.5637		6776.5293		6878.4803	− 7.31
10	4	7	6436.4183		6832.5099	− 6.32	6926.0915	− 5.14
10	4	6	6451.9340		6864.4862	14.71	6959.4322	− 10.39
10	4	6	6653.3836		6991.5659	1.32	7074.8146	0.28
10	5	5	6655.6969		6994.4154	− 10.38	7080.4464	− 3.25
10	6	5	6900.1072		7166.7091	4.89	7243.4981	3.32
10	6	4	6900.4996		7166.9644		7243.9533	1.23
10	7	4	7168.4332		7368.3542		7435.2359	0.14
10	7	3	7168.4404		7368.3657		7435.2579	− 2.10
10	8	3			7593.1830		7646.8921	1.26
10	8	2			7593.1833		7646.8928	0.59
10	9	2			7840.0482		7874.3941	− 3.72
10	9	1			7840.0482		7874.3941	− 3.72
10	10	1					8114.0223	9.33
10	10	0					8114.0223	9.33
11	0	11	5986.3401	− 6.36	6530.5786	− 3.95	6631.1758	− 1.79
11	1	11	5986.5453	9.11	6530.7775	8.49	6631.1822	− 6.87
11	1	10	6260.4532	8.48	6746.8764	− 22.60	6845.7818	1.95
11	2	10	6264.4944		6747.9063		6846.1125	− 3.01
11	2	9	6459.6742		6924.2526		7023.2246	− 1.22
11	3	9	6491.8713		6934.3595		7028.2924	3.75
11	3	8	6592.6223		7050.5767	− 9.65	7152.4395	6.50
11	4	8	6700.0011		7091.0992		7185.8574	− 5.05
11	4	7	6728.4721		7141.4978	0.15	7236.8823	2.67
11	5	7	6917.4547		7258.0828	− 1.79	7339.5162	1.15
11	5	6	6924.0349		7263.0026	9.40	7351.9321	− 0.54
11	6	6	7167.2301		7430.6327		7508.7493	1.34
11	6	5	7168.5173		7431.3857	6.48	7510.0886	7.93
11	7	5	7436.5290		7632.4387		7700.5145	− 1.66
11	7	4	7436.5579		7632.4838		7700.6006	− 7.12
11	8	4			7858.5019		7912.9089	3.72
11	8	3			7858.5035		7912.9125	4.47
11	9	3			8107.6332		8141.8717	1.65
11	9	2			8107.6332		8141.8718	1.55
11	10	2					8383.6021	0.08
11	10	1					8383.6021	0.08
11	11	1					8634.5135	− 1.01
11	11	0					8634.5135	− 1.01
12	0	12	6212.5520		6755.7892		6856.2807	− 1.52
12	1	12	6212.6672	− 0.29	6753.5275		6856.2791	0.13
12	1	11	6515.4658		6992.4621		7091.8276	0.00
12	2	11	6517.8995		6995.9806		7091.9608	− 5.12
12	2	10	6742.7477		7191.8408	34.23	7290.6204	7.52
12	3	10	6767.0821		7192.2326		7293.2579	7.41
12	3	9	6897.7993		7342.7763		7443.8810	0.43
12	4	9	6982.4693		7369.7994		7465.7909	− 5.08

TABLE III. (continued).

J	K_a	K_c	(0, 3, 0)		(1, 1, 0)		(0, 1, 1)	
			E^{calc}	DE	E^{calc}	DE	E^{calc}	DE
12	4	8	7031.9914		7441.8313		7554.3015	− 4.31
12	5	8	7212.9773		7531.1440	− 13.61	7626.5489	− 4.06
12	5	7	7217.3020		7557.9883		7650.3455	3.12
12	6	7	7457.5471		7717.8169	− 0.91	7797.2398	4.52
12	6	6	7461.5888		7719.7271		7800.6433	6.27
12	7	6			7919.5216		7988.9367	4.39
12	7	5			7919.6679		7989.2172	− 3.12
12	8	5			8146.6272		8201.8264	− 1.87
12	8	4			8146.6341		8201.8419	− 1.36
12	9	4					8432.0802	2.82
12	9	3					8432.0808	3.22
12	10	3					8675.7997	− 5.54
12	10	2					8675.7998	− 5.55
12	11	2					8929.3767	− 1.60
12	11	1					8929.3767	− 1.60
12	12	1					9189.3464	− 2.08
12	12	0					9189.3464	− 2.08
13	0	13	6456.3141		6996.1815	7.76	7099.0100	15.56
13	1	13	6456.3719		6996.2621		7098.9853	13.87
13	1	12	6787.8907		7255.9578		7355.3924	− 8.22
13	2	12	6789.3523		7254.0931		7355.3928	− 11.71
13	2	11	7044.0462		7475.8927	− 7.67	7574.6526	− 0.25
13	3	11	7058.5329		7476.0293		7575.9094	2.93
13	3	10	7222.3262		7651.2896		7751.3439	2.45
13	4	10	7292.8915		7667.8021		7764.8774	− 1.92
13	4	9	7361.4929		7761.9566		7878.2077	4.47
13	5	9	7522.5893		7840.7907		7935.0209	4.10
13	5	8	7536.1133		7879.6015		7975.1828	18.08
13	6	8			8028.0658		8108.4911	− 1.37
13	6	7			8032.2958		8116.1151	0.17
13	7	7					8300.2376	− 2.77
13	7	6					8301.0275	− 1.95
13	8	6					8513.3687	0.22
13	8	5					8513.4234	− 21.59
13	9	5					8744.6958	4.07
13	9	4					8744.6986	4.44
13	10	4					8990.2484	1.98
13	10	3					8990.2485	1.88
13	11	3					9246.3652	− 6.50
13	11	2					9246.3652	− 6.50
13	12	2					9509.6006	− 2.61
13	12	1					9509.6006	− 2.61
13	13	1					9776.5815	0.32
13	13	0					9776.5815	0.32
14	0	14	6717.5852		7255.6749	− 4.86	7358.6210	8.65
14	2	13	6717.6021		7255.7147		7357.2406	
14	1	13	7077.9524		7533.9497		7636.7906	11.70
14	2	13	7078.8217		7534.6753		7636.3766	− 7.96
14	2	12	7361.6104	− 3.34	7776.7791		7875.8604	− 1.73
14	3	12	7369.6788		7776.0680		7875.9984	− 6.79
14	3	11	7567.3171		7975.1772		8074.2159	− 4.36
14	4	11	7617.4862		7984.3275		8082.2463	2.42

TABLE III. (continued).

J	K_a	K_c	(0, 3, 0) E^{calc}	DE	(1, 1, 0) E^{calc}	DE	(0, 1, 1) E^{calc}	DE
14	4	10	7715.1206		8124.5219		8222.8386	2.89
14	5	10			8169.2010		8263.9757	− 3.78
14	5	9			8227.1535		8324.3505	3.44
14	6	9			8361.5109		8441.8670	− 0.80
14	6	8			8369.5849		8457.0949	8.67
14	7	8					8634.0881	− 0.41
14	7	7					8636.0597	− 10.63
14	8	7					8847.2450	− 3.19
14	8	6					8847.4120	− 3.88
14	9	6					9079.3877	6.43
14	9	5					9079.3980	1.13
14	10	5					9326.5784	2.11
14	10	4					9326.5789	1.63
14	11	4					9585.0733	2.79
14	11	3					9585.0733	2.77
14	12	3					9851.4289	7.26
14	12	2					9851.4289	7.26
14	13	2					10122.3496	− 1.02
14	13	1					10122.3496	− 1.02
14	14	1					10394.4420	− 0.98
14	14	0					10394.4420	− 0.98
15	0	15	6996.2718		7532.5822		7636.6240	− 6.11
15	1	15	6996.2571		7532.6291		7636.6256	− 7.70
15	1	14	7385.8234		7831.9153		7934.0484	3.42
15	2	14	7386.3229		7832.1022		7935.8114	2.68
15	2	13	7691.7879		8085.8387		8191.8117	1.11
15	3	13	7697.8974		8092.9032		8193.3768	− 14.53
15	3	12	7924.4569		8314.2228		8412.5320	− 1.71
15	4	12	7962.8811		8318.5737		8417.2411	4.51
15	4	11	8099.3837		8487.8173		8584.5919	− 6.27
15	5	11			8516.6218		8612.4404	10.02
15	5	10			8599.0835		8693.1216	
15	6	10			8719.9497		8796.5976	− 14.79
15	6	9			8732.1763		8823.9061	− 9.43
15	7	9					8990.0732	8.78
15	7	8					8994.5069	− 2.38
15	8	8					9203.1470	16.69
15	8	7					9203.5993	4.09
15	9	7					9435.8228	5.85
15	9	6					9435.8564	− 15.95
15	10	6					9684.4238	2.21
15	10	5					9684.4257	0.30
15	11	5					9945.1157	− 3.81
15	11	4					9945.1158	− 3.89
15	12	4					10214.4101	− 0.24
15	12	3					10214.4101	− 0.24
15	13	3					10489.0595	− 1.17
15	13	2					10489.0595	− 1.17
15	14	2					10765.8661	− 1.04
15	14	1					10765.8661	− 1.04
15	15	1					11037.6879	
15	15	0					11037.6879	

Fitting up to J = 10. The standard deviation σ, given in Table I, was obtained with the use of the following models for operators $H_{nm}(n \neq m)$. In the operator H_{12}, describing the Fermi-interaction, 11 components were used containing the parameters f_{000}, f_{020}, f_{200}, f_{002}, f_{040}, f_{220}, f_{022}, f_{042}, f_{242}, f_{422}, f_{044}, in the operator H_{23} three components were used with the parameters C_{001}, C_{023} and C_{033}, and, finally, in the operator H_{13} four components with the parameters C_{011}, C_{021}, C_{031} and C_{211} were used. For the dimensionless standard deviation χ, determined by the relationship:

$$\chi = \{[\sum_{i}^{I} (E_i^{exp} - E_i^{calc})/w_i]^2/(I - L)\}^{1/2}, \qquad (13)$$

where w_i are the errors of determining the experimental energy levels, this model gives the value χ = 1.3. Hence, the energy levels are described practically with the experimental accuracy. It should be noted that the model used in the interaction blocks $H_{nm}(n \neq m)$ contained the components having, in the basis $|J, K>$, the matrix elements $<J, K,| H_{nm} |J, K + \Delta K>$ with $\Delta K = \pm 4$ for the operator H_{12} and the matrix elements with $\Delta K = \pm 3$ for the operator H_{23}.

Fitting up to J = 15. Solution of the inverse problem for such a set of experimental data is given in Table II. The parameters obtained correspond to the standard deviation $\sigma = 6.2 \cdot 10^{-3}$ cm^{-1} of the Table I. The calculated energy levels for the three states considered are given in Table III. This table shows the fitting errors $DE = (E^{exp} - E^{calc})$ for some energy levels (10^{-3} cm^{-1}). In analyzing, 12 energy levels $[J, K_a, K_c]$ were omitted for the state (1, 1, 0) as well as 3 energy levels for the state (0, 1, 1) because they gave a large error of fitting, DE. For the state (1, 1, 0) these energy levels are [8 2 6], [8 7 2], [8 7 1], [9 6 4], [10 1 10], [10 3 7], [11 2 10], [11 2 9], [11 4 8], [11 6 6], [13 1 13] and [13 1 12]. For the state (0, 1, 1) these levels are the following: [14 1 14], [15 3 13] and [15 5 10].

The large error of fitting of these energy levels, in our opinion, is due to the errors in determining their experimental values. For the «weighted» standard deviation χ (13) the model used for an effective Hamiltonian H gives the value χ = 2.5. By this is meant that the energy levels are fitted with an accuracy close to the experimental one.

Fitting up to J = 20. The results of solution of the inverse problems for $J \leq 20$, given in the tables, similar to Tables II and III, take a great deal of space and therefore are not given here. (The above data can be presented to all persons who are interested in.) It should be noted that for obtaining the standard deviation $\sigma = 9.5 \cdot 10^{-3}$ cm^{-1} from the Table I, for the interaction operator H_{12} 13 parameters are used, for $H_{23} - 5$ parameters, and for $H_{13} - 8$ parameters are used. The operator H_{12} has the matrix elements $<J, K,| H_{12} |J, K + \Delta K>$ with $\Delta K = 0; \pm 2, \pm 4$; the operator $H_{n3}(n = 1,2)$ have the matrix elements $<J, K,| H_{n3} |J, K + \Delta K>$ with $\Delta K = \pm 1 \pm 3, \pm 5$. Besides, 34 energy levels, given in Refs. 1 and 4, are eliminated from the processing, because these levels hamper good convergence of the inverse problem; and their values, in our opinion, should be determined more accurately.

CONCLUSION

This paper presents a new analysis of the experimental data on the second triad of the resonant states of H_2O molecule. The analysis has been performed with the use of new representations for the effective Hamiltonian of the molecule. This made it possible to increase the number of energy levels I suitable for processing ($I = 295$ for $J \leq 10$, $I = 445$ for $J \leq 15$, $I = 541$ for $J \leq 20$) as compared with the preceding analysis (in Ref. 7 $I = 382$ for $J \leq 15$). The accuracy of fitting of the data (for $J \leq 10$ and for $J \leq 15$) is close to the experimental one. The values of spectroscopic constants obtained when solving the inverse problem, as well as calculated energy levels given in Table III for the three states considered have made it possible to calculate weak adsorption lines in the bands $\nu_1 + \nu_2$, $3\nu_2$ and $\nu_2 + \nu_3$.

REFERENCES

1. C. Camy-Peyret, J.M. Flaud, Thesis, University Pierre and Marie Curie, Paris, 1975.
2. J.M. Flaud, C. Camy-Peyret, J.P. Maillard, and G. Guelachvili, J. Mol. Spectrosc. **65,** 219–228 (1977).
3. S.A. Pugh, K. Narahari Rao, J. Mol. Spectrosc. **47**, 403–408 (1973).
4. J.M. Flaud, C. Camy-Peyret, and J.P. Maillard, Mol. Physics **2**, 499–521 (1976).
5. C. Camy-Peyret and J.M. Flaud, J. Mol. Spectrosc. **59**, 327–337 (1976).
6. V.I. Starikov, Atmos. Oceanic Opt. **9**, No. 1, 67–74 (1996).
7. V.I. Starikov, Atmos. Oceanic Opt. **9**, No. 3, 189–194 (1996).
8. V.I. Starikov and S.N. Mikhailenko, Atmos. Oceanic Opt. **5**, No. 9, 615–621 (1992).
9. V.I. Starikov, S.A. Tashkun, and Vl.G. Tyuterev, J. Mol. Spectrosc. **151**, 130–147 (1992).
10. Vl.G. Tyuterev, V.I. Starikov, and V.I. Tolmachev, Dokl. Akad. Nauk SSSR, Fizika **297**, 345–349 (1987).
11. Vl.G. Tyuterev, J. Mol. Spectrosc. **151**, 97–129 (1992).
12. Vl.G. Tyuterev, V.I. Starikov, S.A. Tashkun, and S.N. Mikhailenko, J. Mol. Spectrosc. **170**, 38–58 (1995).
13. Y.Y. Kwan, J. Mol. Spectrosc. **71**, 260–280 (1978).