

Calculation of the water vapor line intensities for rotational transitions between high-excited energy levels

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ABSTRACT

The intensities of water vapor in the range of pure rotational transitions were calculated up to high quantum numbers ($J^{\max} \sim 30$ and $K_a^{\max} \sim 25$). The diagonalization of the effective rotational Hamiltonian, approximated by Pade-Borel method, is applied to obtain the eigenvectors. The centrifugal distortion perturbations in line intensities were taken into account by the traditional equations for matrix elements of the transformed dipole moment, including eight parameters, and previously developed by authors Pade approximant. Moreover, to conduct the calculations, the rotational wavefunctions of the symmetric rotor molecule were applied. The results were compared with the known theoretical data.

Water vapor, high-temperature spectra, centrifugal distortion effects, Pade-Borel approximants, symmetric rotors

1. INTRODUCTION

At present a large amount of theoretical and experimental publications deal with water vapor (H_2O) spectra in terahertz and infrared ranges. The results of some works are presented in well-known spectroscopic databases such as HITRAN2012 [1] and HITEMP2010 [2].

The strong centrifugal distortion effects are inherent for H_2O molecule and lead to divergence of the effective rotational Hamiltonian (Watson-type Hamiltonian for asymmetric rotors). Usually the application of the Watson's Hamiltonian is restricted by transitions with maximum values of rotational quantum numbers, not greater than corresponding values of treated experimental line positions. The special methods for summation of the divergent series, based on Pade approximants, were used to improve the convergence of the Hamiltonian, for example [3, 4]. At the same time, it results in the growth of the accuracy of the prediction the high-excited energy levels with high values of projection K_a and total angular momentum J . However, the high-excited energy levels of H_2O have been better investigated both experimentally and theoretically in comparison with line intensities, produced by the transitions between such levels. A low transition probability on the high-excited levels leads to weak line intensities at normal temperature ($T \sim 300$ K). In the case of high temperatures, the absorption of these lines becomes significant. Therefore, the "hot" lines are the necessary component of the high-temperature databases.

In this work, the H_2O line intensities of the pure rotational transitions were calculated on the basis of the eigenvectors of the Watson's Hamiltonian, approximated by Pade-Borel method [3]. Similarly to Ref. [3], the operators up to the eighth order inclusive were taken into account. The set of the line position parameters for the ground (000) vibrational state was used from Ref. [5]. To take into account the centrifugal distortion perturbations in line intensities, the expansion coefficients of the transformed dipole moment were obtained. The experimental line intensities from Toth's catalog [6] were treated by means of the traditional equations for matrix elements of the transformed dipole moment [7] (traditional method - TM) and Pade-approximant from Ref. [8] (Pade). The experimental line intensities with the uncertainty of 5 % (150 lines with $J^{\max} = 19$ and $K_a^{\max} = 14$) were fitted with the root mean square deviations (RMS) of $RMS_{TM} = 2.98$ % and $RMS_{Pade} = 3.17$ %. After that the intensities of the "hot" lines with $K_a \geq 14$ and $\Delta K_a = \pm 1$ were calculated and compared with other theoretical results, taken from the HITEMP2010 and high-temperature database of Ref. [9] (Fig. 1).

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2. RESULTS AND DISCUSSION

According to the statistical analysis between 499 lines of Ref. [9] ($J^{\max} = 27$ and $K_a^{\max} = 26$) and this work results, the determined RMS values are equaled to $\text{RMS}_1 = 20.56\%$, $\text{RMS}_2 = 22.36\%$, and $\text{RMS}_3 = 16.86\%$. In the case of HITEMP's data (778 lines with $J^{\max} = 31$ and $K_a^{\max} = 28$) the following RMS values were determined: $\text{RMS}_1 = 16.56\%$, $\text{RMS}_2 = 38.75\%$, and $\text{RMS}_3 = 14.90\%$. (RMS_1 , RMS_2 , and RMS_3 – root mean square deviations for the line intensities, calculated without centrifugal distortion perturbations, taking into account centrifugal distortion perturbations by traditional method and Pade approximant of Ref. [8], respectively). The examples of the calculated line intensities in Table 1 are demonstrated.

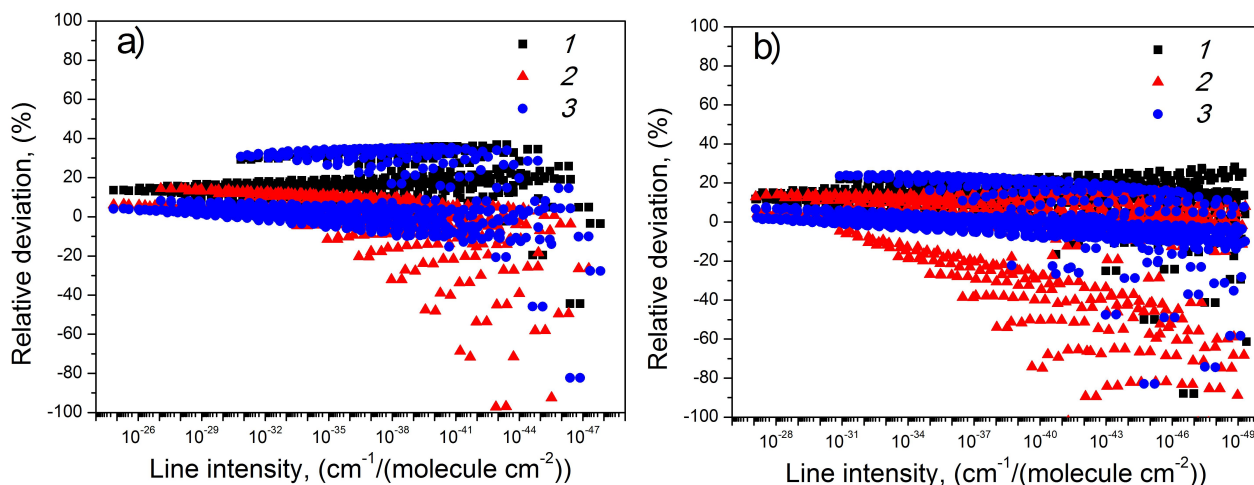


Figure 1. The relative deviations of this work line intensities for (000)-(000) band transitions with $\Delta K_a = \pm 1$ of H_2O from the results of the Ref. [9] (a) and database HITEMP2010 (b):

(1) - line intensities were calculated without centrifugal distortion perturbations; (2) and (3) – line intensities were calculated, taking into account centrifugal distortion perturbations by means of the traditional scheme and Pade-approximant of the Ref.[8] respectively.

Table 1a. The examples of the calculated intensities of the considered lines in comparison with the data of Ref. [9] at $T = 296\text{ K}$

Line intensity, $\text{cm}^{-1} / (\text{molecule} \cdot \text{cm}^{-2})$				$\delta_{a,}$ %	$\delta_{b,}$ %	$\delta_{c,}$ %	Identification					
Ref. [9]	<i>a</i>	<i>b</i>	<i>c</i>				<i>J'</i>	<i>K'_a</i>	<i>K'_c</i>	<i>J''</i>	<i>K''_a</i>	<i>K''_c</i>
$8.448 \cdot 10^{-28}$	$7.328 \cdot 10^{-28}$	$7.227 \cdot 10^{-28}$	$7.752 \cdot 10^{-28}$	13.2	14.4	8.2	14	14	1	14	13	2
$2.816 \cdot 10^{-28}$	$2.442 \cdot 10^{-28}$	$2.409 \cdot 10^{-28}$	$2.583 \cdot 10^{-28}$	13.3	14.4	8.2	14	14	0	14	13	1
$1.310 \cdot 10^{-33}$	$1.121 \cdot 10^{-33}$	$1.245 \cdot 10^{-33}$	$1.271 \cdot 10^{-33}$	14.4	5.0	3.0	22	15	7	21	14	8
$1.587 \cdot 10^{-35}$	$1.305 \cdot 10^{-35}$	$1.568 \cdot 10^{-35}$	$1.629 \cdot 10^{-35}$	17.8	1.2	2.7	22	19	4	21	18	3
$7.301 \cdot 10^{-38}$	$7.139 \cdot 10^{-38}$	$6.630 \cdot 10^{-38}$	$7.635 \cdot 10^{-38}$	2.2	9.2	4.6	24	16	9	24	15	10
$3.088 \cdot 10^{-44}$	$2.709 \cdot 10^{-44}$	$3.457 \cdot 10^{-44}$	$3.148 \cdot 10^{-44}$	12.3	11.9	1.9	24	24	0	24	23	1
$2.026 \cdot 10^{-39}$	$1.666 \cdot 10^{-39}$	$1.985 \cdot 10^{-39}$	$2.086 \cdot 10^{-39}$	17.8	2.0	3	25	19	7	24	18	6
$1.263 \cdot 10^{-45}$	$1.145 \cdot 10^{-45}$	$1.494 \cdot 10^{-45}$	$1.330 \cdot 10^{-45}$	9.3	18.3	5.3	25	25	0	25	24	1
$2.553 \cdot 10^{-44}$	$1.987 \cdot 10^{-44}$	$2.841 \cdot 10^{-44}$	$2.871 \cdot 10^{-44}$	22.2	11.3	12.4	26	26	1	25	25	0
$1.341 \cdot 10^{-41}$	$1.305 \cdot 10^{-41}$	$1.267 \cdot 10^{-41}$	$1.447 \cdot 10^{-41}$	2.7	5.5	7.9	26	18	9	26	17	10
$3.338 \cdot 10^{-42}$	$2.160 \cdot 10^{-42}$	$3.663 \cdot 10^{-42}$	$2.182 \cdot 10^{-42}$	35.3	9.7	34.6	27	16	11	26	17	10
$9.666 \cdot 10^{-41}$	$8.010 \cdot 10^{-41}$	$9.361 \cdot 10^{-41}$	$9.792 \cdot 10^{-41}$	17.1	3.1	1.3	27	18	9	26	17	10

Table 1b. The examples of the calculated intensities of the considered lines in comparison with the HITEMP2010 at $T = 296$ K

Line intensity, $\text{cm}^{-1} / (\text{molecule} \cdot \text{cm}^{-2})$				δ_a , %	δ_b , %	δ_c , %	Identification					
HITEMP	a	b	c				J'	K'_a	K'_c	J''	K''_a	K''_c
$8.303 \cdot 10^{-28}$	$7.328 \cdot 10^{-28}$	$7.227 \cdot 10^{-28}$	$7.752 \cdot 10^{-28}$	11.7	12.9	6.6	14	14	1	14	13	2
$2.797 \cdot 10^{-28}$	$2.442 \cdot 10^{-28}$	$2.409 \cdot 10^{-28}$	$2.583 \cdot 10^{-28}$	12.7	13.9	7.6	14	14	0	14	13	1
$1.279 \cdot 10^{-33}$	$1.121 \cdot 10^{-33}$	$1.245 \cdot 10^{-33}$	$1.271 \cdot 10^{-33}$	12.3	2.6	0.6	22	15	7	21	14	8
$1.576 \cdot 10^{-35}$	$1.305 \cdot 10^{-35}$	$1.568 \cdot 10^{-35}$	$1.629 \cdot 10^{-35}$	17.2	0.5	3.4	22	19	4	21	18	3
$2.648 \cdot 10^{-44}$	$1.987 \cdot 10^{-44}$	$2.841 \cdot 10^{-44}$	$2.871 \cdot 10^{-44}$	25	7.3	8.4	26	26	1	25	25	0
$1.356 \cdot 10^{-41}$	$1.305 \cdot 10^{-41}$	$1.267 \cdot 10^{-41}$	$1.447 \cdot 10^{-41}$	3.8	6.6	6.7	26	18	9	26	17	10
$2.616 \cdot 10^{-42}$	$2.160 \cdot 10^{-42}$	$3.663 \cdot 10^{-42}$	$2.182 \cdot 10^{-42}$	17.4	40.0	16.6	27	16	11	26	17	10
$4.645 \cdot 10^{-42}$	$4.767 \cdot 10^{-42}$	$3.977 \cdot 10^{-42}$	$4.928 \cdot 10^{-42}$	2.6	14.4	6.1	28	15	14	28	14	15
$2.577 \cdot 10^{-47}$	$2.395 \cdot 10^{-47}$	$2.390 \cdot 10^{-47}$	$2.750 \cdot 10^{-47}$	7.1	7.3	6.7	29	20	11	29	19	11
$5.207 \cdot 10^{-46}$	$4.727 \cdot 10^{-46}$	$8.308 \cdot 10^{-46}$	$4.791 \cdot 10^{-46}$	9.2	59.5	8.0	30	16	15	29	17	12
$6.441 \cdot 10^{-49}$	$5.917 \cdot 10^{-49}$	$6.042 \cdot 10^{-49}$	$6.921 \cdot 10^{-49}$	8.1	6.2	7.4	30	21	10	30	20	11
$5.413 \cdot 10^{-50}$	$4.666 \cdot 10^{-50}$	$9.111 \cdot 10^{-50}$	$4.993 \cdot 10^{-50}$	13.8	68.8	7.8	31	19	13	30	20	10

Note:

a - line intensities were calculated without centrifugal distortion perturbations; b and c - line intensities were calculated, taking into account centrifugal distortion perturbations by means of the traditional method and Pade-approximant of the Ref.[8] respectively; δ_a , δ_b and δ_c - the relative deviations for calculated in this work line intensities from the data of Ref. [9] and database HITEMP2010.

Thus, for prediction the line intensities of the pure rotational transitions of H_2O with $K_a \geq 14$ and $\Delta K = \pm 1$ the root mean square deviations from the theoretical data of HITEMP2010 and Ref.[9] can be decreased, if the centrifugal distortion perturbations are taken into account by means of Pade approximant [8]. The results of the statistical analysis indicate on the small centrifugal distortion perturbations in intensities of the considered lines. However, the real influence of the centrifugal distortion perturbations can be concluded after the appearance of the corresponding experimental data.

On the other hand, for H_2O molecule the degeneracy of energy levels at high values of the K_a projection of the total angular momentum J are observed. It allow considering the asymmetric rotor by nature H_2O molecule as a symmetric rotor. The rotational wavefunctions of the asymmetric rotor are the perturbed rotational wavefunctions of the symmetric rotor:

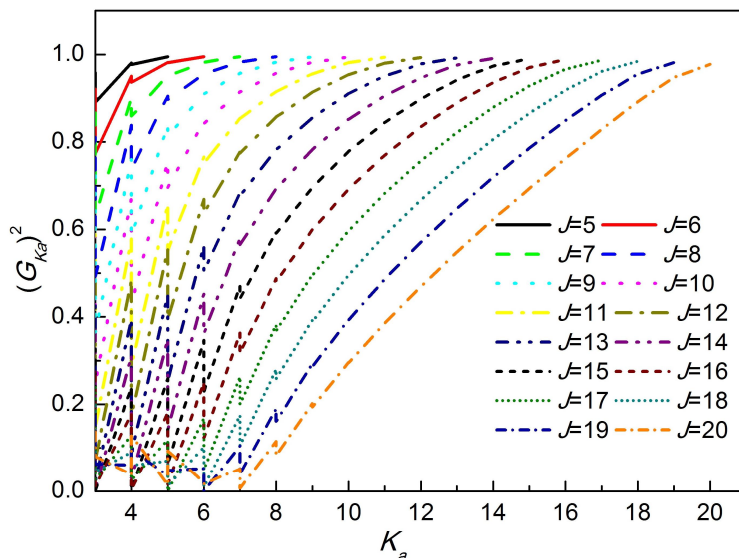


Figure 2. The square of the eigenvectors, corresponding to K_a projection for (000)-(000) band of H_2O .

$$|J, K_a, K_c\rangle = \sum_{K=-R}^R G_K^V |J, K\rangle, \quad (1)$$

where the coefficients G_K^V are obtained from the diagonalization of the effective rotational Hamiltonian. In the case of H₂O molecule, the increasing of the probability of the projection of the total angular momentum on the molecular axis a lead to decreasing the asymmetric properties and H₂O can be assumed as a prolate symmetric rotor (Fig. 2). The results, demonstrated on the Fig.2, were calculated, using the eigenvectors of the effective rotational Hamiltonian, approximated by Pade-Borel method [4] with the set of the empirical parameters from Ref. [5]. Similarly to energy levels, for eigenvectors the degeneracy also takes place, starting from the certain values of the K_a projection (Fig. 3).

The data on the Fig. 3 can be described by the following approximation equation:

$$K_a = 2.494 + 0.403 \cdot J. \quad (2)$$

Rounding the Eq. (2) at various value of J , the corresponding value of K_a is determined (see the Fig. 3 description).

Following the equations for the matrix elements of the direction cosine φ_{zx} in the case of P , Q and R [7] branches, the calculations of the pure rotational line intensities of H₂O were carried out. The transitions with $J \geq 5$ and K_a greater or equal of the right part of the Eq.(2) were taken into account. For intensity calculations, the rotational wavefunctions of the asymmetric and symmetric rotors were applied. On the Fig. 4 the relative deviations between the obtained results and the reference data are shown for lines with $\Delta K_a=1$ and $\Delta J=1$. According to statistical analysis, the root mean square deviations for line intensities calculated under symmetric rotor approximation are equaled to 9.48 % and 10.60 % in the case of Fig.4a and Fig.4b respectively. In spite of the simplicity of the symmetric rotor approximation, the obtained results are close to line intensities, calculated by accurate method: in this case, the root mean square deviations from the data of Ref. [9] and HITEMP2010 are equaled to 5.58 % and 6.10 % respectively. However, the real conclusions about the advantages of the methods cannot be made. Firstly, the comparisons were conducted with theoretical data and there are no any experimental results for line intensities, corresponding to transitions with $K_a \sim 20$. Secondly, though the Pade-Borel method are applied to approximate the effective rotational Hamiltonian, at $J \geq 20$ and $K_a \geq 20$ the quality of the eigenvectors starts to decrease, that is seen from Fig. 2.

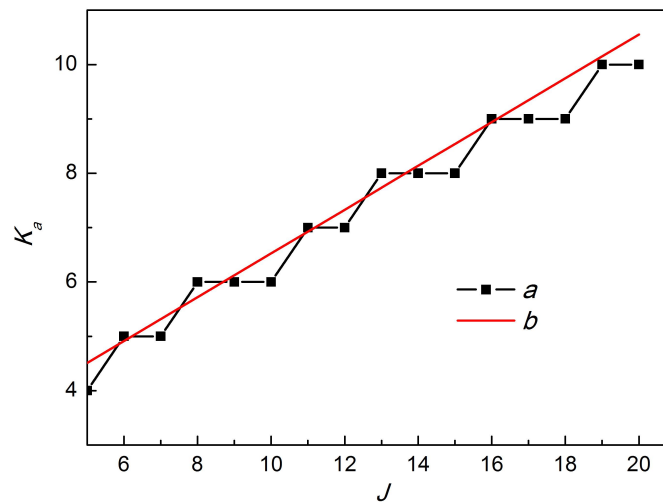


Figure 3. The minimum value of K_a projection for which the relative deviation between the eigenvectors of the rotational states $(J K_a K_c)$ and $(J K_a K_c-1)$ not greater than 1 % (plot a); plot b - the approximation curve (Eq. 2).

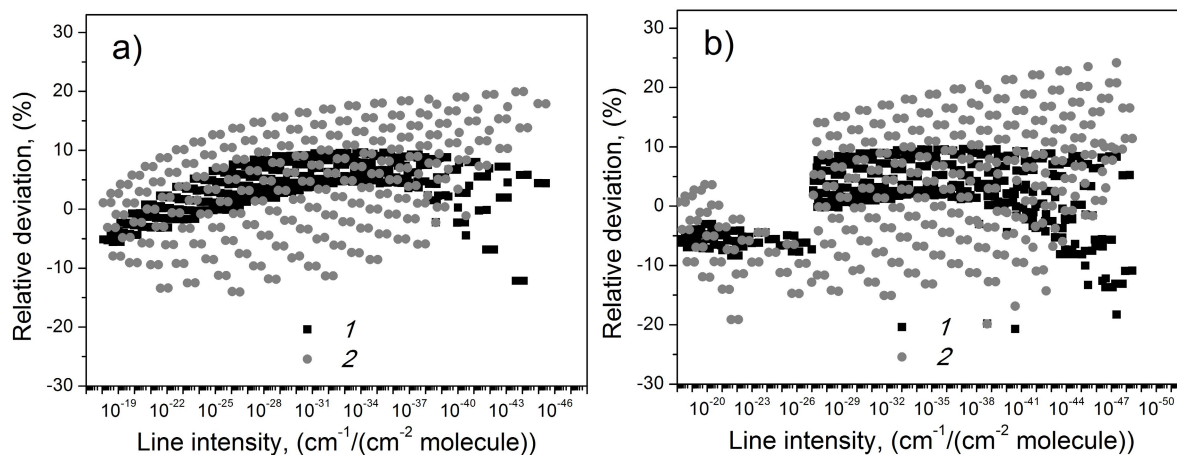


Figure 4. The relative deviations for the line intensities of (000)-(000) H₂O band, calculated on the basis of the eigenvectors of the effective rotational Hamiltonian, approximated by Pade-Borel method (1), and under symmetric rotor approximation (2) from the data of Ref. [9] (a) and database HITEMP2010 (b).

3. CONCLUSION

In this work, the intensities of water vapor in the range of pure rotational transitions were calculated up to high quantum numbers ($J^{\max} \sim 30$ and $K_a^{\max} \sim 25$), using the eigenvectors of the effective rotational Hamiltonian, approximated by Pade-Borel method. If the centrifugal distortion perturbations are taken into account by means of the previously developed by author Pade approximant, then the predicted line intensities with $K_a \geq 14$ and $\Delta K = \pm 1$ agree well with the well-known theoretical data. Although, the statistical analysis indicates on the small centrifugal distortion perturbations in intensities of the considered lines, the real influence can be concluded after the appearance of the corresponding experimental data. The symmetric rotor approximation can be applied for calculating the intensities of some pure rotational lines, produced by the transitions between the excited energy levels, and for estimating the quality of the calculated eigenvectors for such transitions.

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REFERENCES

- [1] Rothman, L. S., Gordon, I. E., Babikov, Y., Barbe, A., Chris Benner, D., Bernath, P. F., et al., "The HITRAN2012 molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transfer* 130, 4-50 (2013).
- [2] Rothman, L. S., Gordon, I. E., Barber, R. J., Dothe, H., Gamache, R. R., Goldman, A., et al., "HITEMP, the high-temperature molecular spectroscopic database," *J. Quant. Spectrosc. Radiat. Transfer* 111, 2139-2150 (2010).
- [3] Polyansky, O. L., "One-Dimensional Approximation of the Effective Rotational Hamiltonian of the Ground State of the Water Molecule," *J. Mol. Spectrosc.* 112(1), 79-87 (1985).
- [4] Burrenin, A. V., Tyuterev, Vl. G., "On the application of the Effective Rotational Pade Hamiltonian Operator of the Molecule," *J. Mol. Spectrosc.* 108(1), 153-154 (1984).
- [5] Johns, J.W.C., "High-resolution far-infrared (20-350 cm⁻¹) spectra of several isotopic species of H₂O," *J. Opt. Soc. Am. B.* 2 (8), 1340-1354 (1985).
- [6] Toth, R. A., "Linelist of water vapor parameters from 500 to 8000 cm⁻¹," <<http://mark4sun.jpl.nasa.gov/h2o.html>> (27 May 2015).

- [7] Camy-Peyret, C., Flaud, J. -M., "Line positions and intensities in the ν_2 band of H_2^{16}O ," Mol. Physics 32(2), 523-537 (1976).
- [8] Egorov, O. V., Voitsekhovskaya, O. K., "Modelling vibrational-rotational interactions in intensities of ν_2 band by Pade approximants" Proc. SPIE 9292, 929206 (2014).
- [9] Coudert, L. H., Martin-Drume, M -A., Pirali, O., "Analysis of the high-resolution water spectrum up to Second Triad and to $J=30$ " J. Mol. Spectrosc. 303, 36-41 (2014).