

SPECTROSCOPY OF ATOMS AND MOLECULES

The Assignment of Quantum Numbers in the Theoretical Spectra of the H_2^{16}O , H_2^{17}O , and H_2^{18}O Molecules Calculated by Variational Methods in the Region 0–26000 cm^{-1}

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Abstract—Quantum numbers have been assigned in the theoretical spectra of three isotopologues of the water molecule: H_2^{16}O , H_2^{17}O , and H_2^{18}O . The spectra were calculated by variational methods in the region 0–26000 cm^{-1} at a temperature of 296 K. For each molecule, the quantum numbers are assigned to more than 28000 levels. The quantum numbers are assigned to 216766, 210679, and 211073 spectral lines of the H_2^{16}O , H_2^{17}O , H_2^{18}O molecules, respectively. The theoretical spectra with the assigned quantum numbers are available in the Internet.

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INTRODUCTION

The investigation of the water molecule is one of the priority problems of spectroscopy. Water vapor plays the key role in the absorption of electromagnetic waves both in the Earth's atmosphere and in the atmospheres of cold stars. To calculate this absorption, it is necessary to know the spectrum of water vapor with a high accuracy.

The fundamental frequencies of the symmetric and antisymmetric stretching vibrations of the water molecule are close to each other and are roughly equal to the doubled frequency of the bending vibration. As a result, many vibrational–rotational levels are located closely and interact with each other. Therefore, the spectrum of the water molecule has a complex polyad structure. The traditional method of investigation of the vibrational–rotational molecular spectra, which is based on the use of effective Hamiltonians of centrifugal distortion, has led to considerable progress in the theoretical analysis of the spectra of a huge number of molecules. Now it is the main method used to study the spectra of molecules in a small number of vibrational states. However, the traditional approach faces difficulties in attempts at the global description of the molecular spectrum of water. Some states, not observed in the spectrum, can perturb the observed bands. So, they should be taken into account in the determination of the spectroscopic constants of the studied levels; that is, the information about all the interacting vibrational states is needed. Therefore, variational methods have gained wide use for the calculation of the vibrational–rotational spectra of the water molecule. The use of variational calculations

has allowed the analysis of a large number of experimental spectra of water vapor, for example, the study of the absorption spectrum in sunspots at a temperature of 3000 K [1] and the spectrum of H_2O at room temperature in the IR and visible regions [2].

VARIATIONAL CALCULATIONS

To solve the Schrödinger equation of a molecule, the motion of its nuclei is considered in specialized internal coordinates, in which the operators of the kinetic and potential energies are expressed. The wave functions of the molecule are represented as an expansion in terms of the set of basis functions, and the Hamiltonian of the system is written in the matrix form in the same basis of the wave functions. In such a representation, the Schrödinger equation is a matrix equation. Varying the wave functions, it is possible to reduce the Hamiltonian matrix to a diagonal form, thus obtaining the energies and wave functions of the stationary states of the molecule.

The equation for the operator of the kinetic energy of the nuclei in the internal coordinates of a triatomic molecule in the Born–Oppenheimer approximation was derived exactly in [3]. The accuracy of spectral calculations depends on the quality of the potential energy surface. At the first stage, this surface is determined from the solution of the Schrödinger equation for the motion of electrons (the *ab initio* surface). However, the electron Schrödinger equation for the water molecule can be solved only with the aid of some approximations, the surface obtained has a quality insufficient for

spectral calculations with accuracy close to the experimental accuracy. To improve the accuracy of the calculations, the surface is optimized through the fitting of the potential parameters for the best description of the experimental data. This allows one to considerably improve the calculation of all the energy levels, both involved and not involved in the optimization.

The spectra assigned in this work were calculated with the use of the potential energy surface obtained in [4] from the optimization of the ab initio surface from [5], and the DVR3D program suit [6]. The optimization was performed with the use of 1788 experimental energy levels of the molecules H_2^{16}O , H_2^{17}O , and H_2^{18}O with $J = 0, 2$, and 5 , as well as 26 fitted parameters. As a result of the optimization, the standard deviation of the calculated energy levels from the experimental ones was 0.079 cm^{-1} . It should be noted here that the mean experimental uncertainty was $0.01\text{--}0.02 \text{ cm}^{-1}$.

The potential energy surface is represented in the form:

$$V_{\text{fit}}(r_1, r_2, \theta) = f_{\text{morp}}(r_1, r_2, \theta) V_{\text{ai}}(r_1, r_2, \theta),$$

where V_{ai} is the ab initio surface from [5], f_{morp} is the morphing function described in [4]. The morphing function is represented as a power series in the Jensen coordinates [7]:

$$s_1 = (r_1 + r_2)/2 - r_e,$$

$$s_2 = \cos \theta - \cos \theta_e,$$

$$s_3 = (r_1 - r_2)/2,$$

$$f_{\text{morp}} = c_{000} + \sum_{i,j,k} c_{i,j,k} s_1^i s_2^j s_3^k, \quad 2 \leq i + j + k \leq N.$$

Here, r_e and θ_e are the equilibrium distance and angle; N is the maximal power of the parameters involved in the optimization; $c_{i,j,k}$ are the parameters, determined in the optimization by the least-squares method from the condition of the best description of the experimental data.

The spectra were calculated with the use of the DVR3D program suit [6]. As input data, these programs used the surfaces of the potential energy (the optimized surface described above) and of the dipole moment (ab initio), as well as the nuclear masses. The DVR3D programs allow the calculation of the vibrational–rotational energy levels and the corresponding wave functions and intensities of transitions.

The calculations were carried out at the Joint Super-Computer Center of the Russian Academy of Sciences on a MVS 15000M supercomputer. Its peak productivity is 8.13 Tflops with 1848 GB RAM. The calculations on a personal computer face difficulties, because the wave functions for three water vapor molecules take more than 300 GB, the calculations require 2 GB RAM,

and the calculation of small spectra takes up to a month of computer time.

The motions of the nuclei were calculated in the Radau coordinates with the x axis bisecting the bond angle and the z axis lying in the molecular plane [3, 8]. The DVR3D program suite [6] used 29 radial grid points for the Morse basis functions and 40 angular grid points based on the Legendre polynomials. For the rotational problem, the Hamiltonian matrices had the dimension $300(J + 1 - p)$, where J is the total angular momentum, and p is the parity. In all the calculations, the nuclear masses were used.

The frequencies of the lines were calculated from the data about the energy levels taking into account the selection rules. The wave functions and the surface of the dipole moment were used to calculate the line strengths and the transition dipole moments. In the calculations, we used the Schwenke–Partridge ab initio surface of the dipole moment [9].

The intensity of an emission, as well as of an absorption transition, depends on the line strength and on the population of the levels taking part in the transition. Therefore, the spectrum, corresponding to particular physical conditions, depends on the temperature and the concentration of water vapor.

The spectra of the water isotopologues H_2^{16}O , H_2^{17}O , and H_2^{18}O were calculated for a temperature of 296 K and for the transitions between the energy levels up to 26000 cm^{-1} and $J \leq 10$.

ASSIGNMENT OF QUANTUM NUMBERS

The quantum numbers serve to identify the energy levels and lines in the spectra. Every state of any of the three molecules H_2^{16}O , H_2^{17}O , and H_2^{18}O can be described by the complete set of the quantum numbers J , responsible for the symmetry of the wave function and the number of a level in a block (at a particular J and the symmetry of the level). These quantum numbers are automatically assigned to energy levels by the DVR3D programs [6]. However, it is commonly accepted to use another complete set of quantum numbers: J , K_a , K_c , v_1 , v_2 , and v_3 , which is based on the notions of a harmonic oscillator and a rigid top. These quantum numbers are more informative from the viewpoint of the physics of transitions from one level to another. The quantum numbers K_a , K_c , v_1 , v_2 , and v_3 are approximate, and the assignment of these numbers to energy levels by different methods may be ambiguous in some cases and depend on the method used. This is connected with the fact that approximate quantum numbers, in contrast to the exact ones, are not defined in the states with the determined energy. The assignment of approximate quantum numbers is a separate problem, unsolvable by the DVR3D program suite, and it is a subject of this paper. Since the structures of the energy levels of the water molecules with different oxy-

gen isotopes are similar, we will consider first the assignment of quantum numbers to the energy levels of the H_2^{16}O molecule.

The main method used in this work to assign the quantum numbers is based on the analysis of the dependence of the energy levels on the quantum numbers [10, 11]. The assignment by this method is carried out in two stages. At the first stage, to assign the quantum numbers to particular vibrational energy levels ($J = 0$), we used the quasi-harmonicity of the molecule. For a harmonic oscillator with the three degrees of freedom, the energy can be expressed as

$$E = \nu_1 \omega_1 + \nu_2 \omega_2 + \nu_3 \omega_3,$$

where ν_1 , ν_2 , and ν_3 are the vibrational quantum numbers, and ω_1 , ω_2 , and ω_3 are the fundamental frequencies. The energy here is measured from the energy of the ground state.

However, the real molecule is not a harmonic oscillator. Therefore, our assignment method dealt with the effective fundamental frequencies:

$$\omega_1^{\text{eff}} = E(\nu_1, \nu_2, \nu_3) - E(\nu_1 - 1, \nu_2, \nu_3),$$

$$\omega_2^{\text{eff}} = E(\nu_1, \nu_2, \nu_3) - E(\nu_1, \nu_2 - 1, \nu_3),$$

$$\omega_3^{\text{eff}} = E(\nu_1, \nu_2, \nu_3) - E(\nu_1, \nu_2, \nu_3 - 1).$$

The effective frequencies themselves are functions of ν_1 , ν_2 , and ν_3 . These functions vary smoothly, and they are the key functions for the prediction of the energy levels from the previous, already predicted levels. Every energy level $E(\nu_1, \nu_2, \nu_3)$ was predicted on the basis of the three previous levels: $E(\nu_1 - 1, \nu_2, \nu_3)$, $E(\nu_1, \nu_2 - 1, \nu_3)$, and $E(\nu_1, \nu_2, \nu_3 - 1)$ taking into account the current values of the effective frequencies. Certainly, if some $\nu_i = 0$ ($i = 1, 2, 3$), then the number of the previous levels is smaller than three. To increase the accuracy of the assignment in some cases, the experimental values were used as predictions. Then, for every predicted level, one of the closest calculated energy levels with the symmetry identical to that of the predicted level was selected. The quantum numbers ν_1 , ν_2 , ν_3 were assigned to this calculated level, and then new effective frequencies were calculated.

At the second stage, the quantum numbers were assigned to the vibrational-rotational energy levels ($J \neq 0$). The total energy of a level can be conditionally represented as a sum of the vibrational and rotational energies. At the second stage, we used the following empiric regularities: (i) the rotational energy weakly depends on the vibrational quantum numbers and (ii) at the constant rotational quantum numbers and the smooth change of the vibrational quantum numbers, the rotational part of the energy changes smoothly.

To eliminate the ambiguity in the selection of the calculated level corresponding to the given set of quantum numbers, the following considerations were used.

For a particular energy level, the properly assigned set of the quantum numbers is that corresponding to the set obtained from the analysis of experimental data (if the level has the experimentally determined energy value), or, otherwise, for which the absolute value of the difference between the predicted and calculated values is smaller.

The accurate assignment of the quantum numbers at the first stage of the basic method (the energy levels with $J = 0$) is more important than at the second stage, since, at the second stage, the results of the first stage are used, and the error in the assignment of the vibrational quantum numbers at the first stage will entail new errors in the assignment of the quantum numbers to levels with $J \neq 0$. Therefore, in this work, each of 275 vibrational levels with an energy up to 26000 cm^{-1} was assigned manually. In addition, other methods were used to eliminate the ambiguity at the first stage of the basic method and to check the ultimate assignment. One of these methods is based on the analysis of wave functions [12]. The vibrations of the molecule near the equilibrium (small vibrations) can be divided into independent vibrations along the normal coordinates. The Hamiltonian of a multidimensional harmonic oscillator in the normal coordinates is a sum of one-dimensional Hamiltonians, and the multidimensional wave function is a product of one-dimensional wave functions. For the normal coordinates, the diagonal element of the matrix of any square coordinate can be expressed through the degree of excitation along only this coordinate [13]:

$$\langle X_v^2 \rangle = \left(v + \frac{1}{2} \right) (\hbar / \mu \omega).$$

The diagonal matrix elements were calculated by the numerical integration of the corresponding wave functions. Since the wave functions in the vibrational states (000), (100), (010), and (001) can be easily identified, we determined from these states the normalization coefficients $(\hbar / \mu \omega)_i$ for each normal coordinate. Then,

using the matrix elements $\langle X_v^2 \rangle$, we calculated the vibrational quantum numbers, which were then rounded. The Jensen coordinates [7], which are close to the normal ones, were used. This method is not so accurate as the basic one, but it is important to remove the ambiguity in the assignment of quantum numbers.

The assignment of the vibrational quantum numbers to levels with large values of the quantum number ν_2 , corresponding to the bending vibrations, is the most doubtful. Therefore, we used one more method to analyze the value of this quantum number by adding a term to the potential that depends only on the angle [14]. The artificial addition of this term to the potential energy surface in the calculations shifts energy levels, and the larger the value of ν_2 , the larger this shift. Therefore, the comparison of the results of two calculations—with and without the additional term—allows us to estimate

Table 1. Example of a transition from the theoretical spectrum of the H_2^{18}O molecule

Column number	1	2	3	4	5	6	7	8	9	10	11	12	13	14										
Value	1	5	0	153	5	1	1	14253.83	398.36	13855.47	2.92×10^{-8}	4.8×10^{-25}	3.0×10^{-7}	2.22×10^{-3}										
Column number	15		16		17		18		19		20		21		22		23		24		25		26	
Value	5		3		3		3		0		1		5		1		4		0		0		0	

Table 2. Explanation of the format of theoretical spectra

Column number	Explanation to the content of this column
1	Vibrational symmetry of levels: 0 corresponds to symmetric states, 1 is for antisymmetric states
2	Quantum number J of the upper level
3	Rotational symmetry of the upper level (0 or 1)
4	Number of the upper level in the given block
5	Quantum number J of the lower level
6	Rotational symmetry of the lower level (0 or 1)
7	Number of the lower level in the given block
8	Energy of the upper level, cm^{-1}
9	Energy of the lower level, cm^{-1}
10	Transition frequency, cm^{-1}
11	Square of the transition dipole moment
12	Absolute intensity of the line, showing the absorption per one molecule, cm molecule^{-1}
13	Relative intensity of the transition (the maximal absolute intensity of this calculation is taken to be unity)
14	Einstein coefficient, s^{-1}
15	Quantum number J of the upper level
16	Quantum number K_a of the upper level
17	Quantum number K_c of the upper level
18	Quantum number v_1 of the upper level
19	Quantum number v_2 of the upper level
20	Quantum number v_3 of the upper level
21	Quantum number J of the lower level
22	Quantum number K_a of the lower level
23	Quantum number K_c of the lower level
24	Quantum number v_1 of the lower level
25	Quantum number v_2 of the lower level
26	Quantum number v_3 of the lower level

v_2 . This method also has an error, but the combination of different methods provides a more accurate assignment of the quantum numbers than in the case of only one method.

The assignment of the quantum numbers to energy levels of the molecules H_2^{17}O and H_2^{18}O by the method similar to that used for H_2^{16}O appears to be less efficient. For these molecules, few experimental data,

needed for the permanent refinement of the effective frequencies, are known. Without this refinement, inaccuracies in the prediction process are accumulated fast, and this can significantly increase the number of misassigned levels.

In the structure of their energy levels, the H_2^{17}O and H_2^{18}O molecules are more similar to H_2^{16}O than D_2^{16}O . This is connected with the fact that the oxygen nucleus lies near the center of mass of the molecule and the relatively small changes of its mass weakly influence the changes of the principal moments of inertia and, consequently, the rotational energies. The addition of neutrons to the oxygen nucleus much more weakly affects the structure of energy levels than the addition of neutrons to the hydrogen nucleus.

For the molecules H_2^{17}O and H_2^{18}O , the quantum numbers were assigned on the basis of the quantum numbers already assigned to the energy levels of the molecule H_2^{16}O . Since each set of energy levels is divided into blocks (all the levels of the same block have identical quantum numbers of the angular momentum and the same symmetry), and the levels of each block are put in increasing order of their energy, it is easy to set the correspondence between the levels of H_2^{16}O and two other isotopologues, H_2^{17}O and H_2^{18}O . In most cases, this correspondence means the coinciding quantum numbers. Unfortunately, the assignment of the quantum numbers with the aid of direct correspondence is incorrect in some cases. Such errors were corrected by other assignment methods and with the aid of the notion that the energy levels change smoothly with varying quantum numbers.

To check the quality of the transfer of the quantum numbers assigned to the energy levels of H_2^{16}O to H_2^{17}O and H_2^{18}O , we have compared the assigned quantum numbers with the quantum numbers of the already known experimental levels. For H_2^{17}O , the quantum numbers coincide in 89% of the cases, and, for H_2^{18}O , they coincide in 86% of the cases. Once the misassignments were corrected through the analysis of the wave functions, the quantum numbers coincided in about 93% of the cases for both H_2^{17}O and H_2^{18}O . The notion about smooth changes of the energy levels with varying quantum numbers has allowed us to correct some misassignments even for the H_2^{16}O molecule.

The assigned quantum numbers do not coincide with the experimental ones in vibrational states with a strong interaction between levels. In the cases where, for example, the contribution of each of two vibrational states is close to 50%, the assignment of the quantum numbers may depend on the method of assignment.

RESULTS AND CONCLUSIONS

This paper presents the assignment of quantum numbers to the earlier calculated theoretical spectra of

three isotopologues of the water molecule. The assignment was performed with the use of different methods, which complement each other and allow a more accurate assignment. The quantum numbers have been assigned to the theoretical spectra of three isotopomers of the water molecule, calculated in [4] in the range of 0–26000 cm^{-1} at a temperature of 296 K. For each molecule, 28233 energy levels have been assigned. The quantum numbers have been assigned to 216766 lines of the theoretical spectrum for the H_2^{16}O molecule, 210679 lines for the H_2^{17}O molecule, and 211073 lines for the H_2^{18}O molecule. The spectra of H_2^{17}O and H_2^{18}O have been assigned for the first time in such a wide frequency region. The spectrum of H_2^{16}O already has been assigned in [15] by counting the nodes of wave functions. The assignments coincide completely in the energy range up to 10000 cm^{-1} . Up to 20000 cm^{-1} , the assignment of [15] is unreliable, and, above 20000 cm^{-1} , almost all levels are misassigned. These mistakes are connected with the fact that the wave functions of high energy levels are mixed much more significantly than the energy levels. In addition, in [15], the same set of quantum numbers is often assigned to two different energy levels, which is not a case in our paper.

The theoretical spectra will be used in the analysis of experimental spectra, especially, for the molecules H_2^{17}O and H_2^{18}O , for which only 1400 and 2600 experimental energy levels, respectively, are known.

We have tried to retain the format of the theoretical spectra close to the commonly accepted DVR3D format [6]. For each line from the spectrum of [4], 12 quantum numbers were added (by six numbers for each level). The theoretical spectra are available either at <http://saga.atmos.appl.sci-nnov.ru/fis3/> or, in the case of no access, directly from the authors (for example, on request by e-mail: zobov@appl.sci-nnov.ru). Let us explain the format of the theoretical spectra in a more detail. Table 1 presents one of transitions of the H_2^{18}O molecule. The upper row gives the serial number of the columns, and the second row gives the particular value in the given transition. A brief explanation of every column is given in Table 2.

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