Assignment of quantum numbers to calculated highly excited energy levels of water molecule

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We propose a new technique for assignment of quantum numbers of the calculated energy levels of water molecule that has been developed based on extrapolation of the monotonic dependence of energy levels on quantum numbers. As compared with the standard technique based on the analysis of the wave function of a quantum state, the proposed technique allows much better assignment of the levels with the energies higher than 15000 cm^{-1}. Prospects of this technique are demonstrated as applied to improvement of theoretical calculations of water vapor spectra. The possibility of using the improved variation calculations for simulation of the Earth's radiative budget is discussed.

Introduction

Water vapor is one of the main atmospheric constituents responsible for absorption of solar radiation in the atmosphere and Earth's radiative budget. The amount of incoming solar radiation must be in balance with the thermal radiation of the planet.[1] Regardless of the more than 100 years long study of the Earth's radiative budget, no exact mathematical description has yet been developed.[2] Existing models describe the absorption very roughly even for clear skies at even only small effect of clouds. The majority of the investigators agree that the current atmospheric models underestimate absorption in the visible spectral region by about 25%. To explain the excess absorption in the so-called atmospheric windows, such mechanisms as continuum absorption are being discussed.[3,4] Meanwhile, the first step toward better description is to account for the absorption caused by a great number of weak spectral lines of the water vapor molecule. The absence of a correct model of the radiative budget is a serious obstacle in the further progress in the science about the atmosphere. In particular, prediction of such effects as global warming involves the change of atmospheric absorption by less than 1%.

The most part of solar radiation falls on the UV, visible, and near infrared spectral regions. Weak absorption bands of water vapor, oxygen, and ozone determine the amount of energy that reaches the Earth's surface.[1] For simulating atmospheric absorption of solar radiation, the HITRAN database[5] is now commonly used. It contains information on tens thousands of measured transitions of the water vapor molecule and molecules of other atmospheric gases. However, even this number proves to be insufficient. As was shown in Ref. 6, calculation of the absorption by water vapor for astronomic applications requires millions of weak lines to be taken into account. The neglect of a great number of weak, experimentally undetermined lines of water vapor leads to significant errors in simulation of the radiative budget.[4] It is impossible to measure all these weak lines. They can be taken into account only using theoretical calculations. In this paper, we consider the possibility of improving the calculations with a new technique of assignment of theoretical energy levels.

1. Statement of the problem

In quantum mechanics, the Born-Oppenheimer approximation is used for studying the properties of molecules.[7] In this approximation, the motion of electrons is considered to occur in the field of fixed nuclei. The electron energy depending on the nuclei coordinates as parameters is then used as a potential surface in the equation of nuclei motion. The latter equation is solved by variational methods, and it yields the energy levels of a molecule. Variational calculations, in contrast to calculation by the method of effective Hamiltonians based on the theory of perturbations, allow determination of all energy levels and frequencies of the transitions between them.

The accuracy of variational calculations is significantly affected by the method of obtaining the potential energy surface. There are two methods for determining the potential energy surface of electron motion: the method of quantum chemistry (*ab initio*) and the semiempirical method.

The former method consists in numerical solution of the Schrödinger equation for motion of electrons in the field of fixed nuclei. The direct solution of the Schrödinger equation even by numerical methods using modern supercomputers is impossible for almost any molecule. Therefore, one has to apply approximate methods using molecular orbitals, self-consistent field, and configuration interactions.[8]

The latter method is semiempirical, i.e., it uses experimental data. In this approach, the potential surface is set as some analytical function, whose parameters are determined by the criterion of the closest agreement with the experimental data in variational calculations. The semiempirical method provides for higher accuracy in calculating the molecular spectra, but in a limited region determined by the experimental data used for the determination of the potential energy surface. The extrapolation capabilities of this method are limited.

The most accurate *ab initio* potential surface has been obtained by Partridge and Schwenke.[9] They used it as the starting point for fitting an empirical potential. The set of lines calculated based on this potential reconstructs the experimental spectra of water vapor with the highest accuracy in the microwave and infrared spectral regions. In Ref. 9, all the calculated energy levels have been assigned, i.e., a complete set of vibrational and rotational quantum numbers has been defined. To determine the quantum numbers, Partridge and Schwenke used the standard technique of counting the nodes obtained in calculation of wave functions. Their assignment contains some errors, especially for strongly interacting levels. The authors themselves acknowledge this. As known, there exists strong interaction between levels of the water vapor molecule with the constant sum $v_1 + v_3$. With the increasing energy, the number of interacting levels increases too. Thus, the assignment proposed in Ref. 9 becomes increasingly unreliable, as the energy of the levels grows. In the previous studies,[10,11] it was found that about one third of the energy levels belonging to the $4v$ and $4v + \delta$ polyads are assigned incorrectly. Most of the levels belonging to the (103) vibrational state are assigned in Ref. 9 to the state (301). Similarly, the levels of (122) are usually assigned to the state (320), and the levels of (113) are assigned to (311). In the visible and UV regions, the assignment becomes practically useless.[10,12]

Poor extrapolation capabilities of the variational calculations based on semiempirical potentials do not allow their application to analysis of new experimental data. Therefore, starting from 1996 the spectrum of water vapor has been calculated[13] with the use of high-accuracy *ab initio* potential energy surface.[9] Adiabatic effects distorting the Born-Oppenheimer approximation (these effects are significant for the rotationally excited levels with high K_a) were taken into account in the form of an addition to the *ab initio* surface. Non-adiabatic effects were taken into account approximately with the help of the effective hydrogen masses.[13] The calculated spectrum allowed assignment of a huge (about 15 000) number of transitions of hot water vapor in the absorption spectrum of sun spots (3300 K) and in the emission spectra under laboratory (1800 K) conditions (Ref. 14). This yielded several thousands of new levels determined experimentally. The spectra of cold water vapor in the IR and visible regions were successfully analyzed as well,[10–12] and 25 new vibrational states were found.

Variational calculations[14] were conducted using the total symmetry of the system. Thus, "good"[15] quantum numbers (the total angular momentum J and evenness of rotational-vibrational levels) were automatically assigned to the calculated energy levels. The rest quantum numbers v_1, v_2, v_3, K_a, and K_c, which are approximate, remained unassigned. This complicates analysis of new experimental data, because all quantum numbers of the upper and lower levels of a transition should be known for assignment of a line.

Since the assignment made in Ref. 9 is inapplicable to high energy levels, there is a need in the development of a new, more accurate technique of assignment. In contrast to the standard method used in Ref. 9, we propose a technique that is based on analysis of the dependence of energy levels on quantum numbers.

2. New technique of assignment

The problem of assignment of theoretical energy levels of the water vapor molecules[12] was solved in two stages. Fist, vibrational quantum numbers were assigned to the calculated energy levels with $J = 0$, i.e., purely vibrational levels. The vibrational motion of nuclei is determined by the potential energy calculated using the methods of quantum chemistry. In assignment, we used the fact that the potential surface near a minimum can be presented as a quadratic form. Owing to transition to normal coordinates, it can be written as a potential energy of a 3D harmonic oscillator. The energy levels of the harmonic oscillator are well known.[8] They are determined by fundamental frequencies. Although the anharmonicity terms are present in the potential surface of the water vapor molecule, their influence can be taken into account. Let us consider, for example, a series of vibrational energy levels $(n, 0, 0)$, where $n = 0, 1, 2, \dots$. This series is given in Table 1.

One can see that the energy difference ΔE decreases monotonically. The energy increment to the levels decreases, because the actual potential surface is wider than the potential of the harmonic oscillator. The energy increment changes smoothly from level to level. Based on the above-said, we can try to predict the next vibrational levels based on the preceding ones.

Table 1. Energies E of the vibrational states (n, 0, 0)

Vibrational state	(000)	(100)	(200)	(300)	(400)	(500)	(600)	(700)	(800)
E, cm^{-1}	0	3658	7203	10601	13828	16897	19780	22523	25112
ΔE, cm^{-1}	–	3658	3545	3398	3227	3069	2883	2743	2589

The initial data for assignment are three fundamental vibrational bands of the water vapor molecule and the set of calculated vibrational energy levels.[12] The fundamental vibrational frequencies of the water vapor molecule are the frequencies of transition from the ground state to $(100) - 3656$ cm^{-1}, $(010) - 1594$ cm^{-1}, and $(001) - 3755$ cm^{-1} (Ref. 5). All possible vibrational quantum numbers were exhausted starting from the ground state (000) by increasing each number by unity. The energy of a level (n_1, n_2, n_3) was calculated as

$$E = n_1\nu_1 + n_2\nu_2 + n_3\nu_3,$$

where n_1, n_2, and n_3 are vibrational quantum numbers, and ν_1, ν_2, and ν_3 are fundamental frequencies. In the set of calculated vibrational levels, we found the level closest to E, and the corresponding quantum numbers were assigned to this level.

The correctness of the assignment was checked by comparing with the experimental data.[5,10,12] As is seen from Table 1, the energy differences between the vibrational states (i.e., effective ν_1, ν_2, and ν_3) do not remain constant. This change was taken into account and then used for calculation of the next energy levels. As a result, we have assigned all calculated vibrational levels with $J = 0$. The region from 0 to 26 000 cm^{-1} includes about 270 vibrational levels of the water molecule. Because of the limited volume of this paper, we cannot present here the table of all these levels with their assignments, but it is available on request via e-mail zobov@appl.sci-nnov.ru.

The second stage was assignment of rotational and vibrational quantum numbers to the levels with the total angular momentum $J \neq 0$. The total energy of a level is the sum of vibrational and rotational energies. The energies of the levels with the same set of rotational quantum numbers in different vibrational states differ widely. However, the pure rotational energy of such levels is almost the same. Let us consider, for example, the total and rotational energies of the levels with $J_{K_aK_c} = 4_{04}$ in some vibrational states. They are given in Table 2.

Table 2. Total E_t and rotational E_{rot} energies of the levels with $J_{K_aK_c} = 4_{04}$

Vibrational state	(400)	(500)	(600)	(700)	(800)
E_t, cm^{-1}	14035	17102	19979	22722	25309
E_{rot}, cm^{-1}	207	204	198	194	189

The data of Table 2 are indicative of the smooth change in the rotational energy as a function of vibrational quantum numbers. This allows predicting the rotational levels based on the known preceding levels. Then the assumed total energy of a level is calculated, and the value closest to it is sought in the list of the theoretical energy levels. The corresponding quantum numbers are assigned to this level.

The results of assignment are not given here, but are available on request via e-mail.

3. Analysis of the obtained results

The results of this study have improved the quality of assignment of the energy levels of the water vapor molecule. This is confirmed by the comparison with the experimental data.[5,10–12] Thus, in the region up to 15000 cm^{-1} the assignment almost coincides with the experimental data. In the region from 15000 to 21000 cm^{-1}, some insignificant differences with the experiment are observed. In the region from 21000 to 26000 cm^{-1} (boundary of the experimental data), the number of errors increases. The assignment is most difficult for the rotational states with high K_a and for highly excited bending vibrational states.

Let us explain the appearance of these errors using, as an example, the rotational levels 4_{04}, 4_{22}, and 4_{40} in the ground and first excited vibrational states. It is seen from Table 3 that the difference between the rotational energies of the level 4_{04} in these vibrational states is less than the difference between the rotational energies of the level 4_{22} (~5 and ~30 cm^{-1}, respectively). In the state 4_{04}, the difference between the states (000) and (020) is ~100 cm^{-1} as high.

Table 3. Rotational energies in first vibrational states

Vibrational state	Rotational energy, cm^{-1}		
	4_{04}	4_{22}	4_{40}
(000)	222.05	315.78	488.13
(010)	222.76	328.21	534.97
(100)	218.04	309.58	477.86
(001)	218.76	310.25	469.02
(020)	223.45	340.65	581.89

Since the energy levels were predicted based on the preceding ones, the difference between the initial energies increases with the growth of K_a, and accurate prediction of the next energy levels becomes problematic. Consequently, errors are possible in assignment of the levels with close calculated energies.

The obtained results were compared with the results by Partridge and Schwenke (P.–Sch.) from Ref. 9. Table 4 gives a fragment of assignment for the rotational state 4_{22}.

The experimental energy is given in the Table only for the known levels. The states assigned incorrectly in Ref. 9 are marked with the minus sign. The asterisk marks the vibrational quantum numbers assigned in Ref. 9 to different energy levels (this is naturally incorrect). The exclamation sign marks the levels belonging to other polyads, whose energies must differ by several thousands wavenumbers.

As is seen from Table 4, seven of the ten experimentally known levels are assigned incorrectly in Ref. 9. This is explained by the fact that assignment in

Ref. 9 was conducted by the method of counting the nodes of wave functions, and the errors even by unity significantly distorted the general pattern. If the entire spectral region is considered, then it should be noted that the assignment up to the energy about 10000 cm^{-1} in Ref. 9 are correct and coincide with our results. At higher energies, about 50% levels in Ref. 9 are assigned incorrectly, and at the energy higher than 20000 cm^{-1} up to 90% levels have wrong assignments.

The technique proposed here makes it impossible to assign the same quantum numbers to different energy levels. The error of prediction of energy levels in only some cases exceeded 10 cm^{-1}. For the entire spectral region, the number of incorrectly assigned levels for 4_{04} was 2%, and for 4_{40} this number was 20% (first errors at 21526 and 12614 cm^{-1}, respectively). The errors are presented for the levels with the lowest and highest K_a at a given J.

Table 4. Comparison of assignments made in this study and in Ref. 9 in the region of 16900−18600 cm^{-1}

Vibrational state	Energy of level, cm^{-1}	Energy of level (P.−Sch.) Ref. 9, cm^{-1}	Vibrational state (P.−Sch.) Ref. 9	Experimental energy Ref. 10, cm^{-1}
(340)	16900.207	16898.721	(340)*	
(241)	16909.442	16908.059	(241)	16907.973
(142)	17171.003	17168.754	(340)-*	−
(321)	17130.924	17130.438	(321)	17130.822
(420)	17127.978	17127.424	(322)-!	17127.757
(500)	17192.014	17191.983	(402)-!	17192.271
(401)	17191.740	17191.756	(303)-!	17192.143
(043)	17337.813	17324.070	(043)	−
(270)	17889.236	17835.702	(270)	−
(222)	17581.977	17543.976	(420)-*	17544.190
(171)	17919.953	17872.545	(171)	−
(123)	17624.038	17621.558	(420)-*	17621.805
(302)	17748.363	17746.286	(500)-*	17746.409
(203)	17782.936	17781.236	(401)-	17781.308
(024)	17842.796	17840.543	(024)	−
(104)	18038.822	18036.418	(500)-*	−
(350)	18320.185	18318.811	(350)*	−
(251)	18355.003	18329.188	(251)	−
(152)	18595.076	18585.358	(350)-*	−
(331)	18590.641	18590.376	(331)	18590.199
(430)	18586.234	18596.875	(350)-*	−

Some difference between the obtained assignment and the experimental one is connected with the interaction between the levels that cannot be taken into account in this technique. It should be noted that the errors in our assignment of energy levels do not usually exceed several cm^{-1}.

Conclusion

A new technique of assignment of calculated energy levels has been developed and implemented. The technique is based on extrapolation of the monotonic dependence of the energies on quantum numbers. It significantly improves the quality of assignment as compared with the standard technique based on the analysis of wave function of a quantum state. Our technique is applicable in the entire region of the experimental data from 0 to 26000 cm^{-1}. In the region up to 15000 cm^{-1} our assignment coincides with the experimental data. Above 15000 cm^{-1} some errors appear. Only in some cases, these errors exceed 10 cm^{-1}. It is worthy to note here that the standard technique is inapplicable in this spectral region.

In the future, we plan to apply our technique to achieve improvement of theoretical calculations of water vapor spectrum in the IR, visible, and UV regions. The use of theoretical spectra available now allowed assignment of only 50% of weak experimental lines in these spectral regions.[10,12] The improved theoretical calculation of the water vapor spectrum will allow assignment of the majority of measured weak lines. This, in its turn, will allow these lines to be included in the databases of known transitions of the water vapor molecule. Such databases are now the main source of the data for simulation of the radiative budget of the Earth's atmosphere. The calculation of absorption by water vapor for astronomic applications demonstrated that millions weak lines should be taken into account.[6] The technique proposed in this paper also improves the calculation of experimentally invisible lines that, nevertheless, should also be taken into account in simulating the radiative budget.

The proposed technique can be used for assignment of the energy levels of other polyatomic molecules as well.

Acknowledgments

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