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## ANHARMONICITY OF NORMAL VIBRATIONS AND ITS INFLUENCE ON DEVIATIONS OF O—H BOND IN H<sub>2</sub>O MOLECULE

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The inverse problem of vibrational spectroscopy for an H<sub>2</sub>O molecule in the gaseous state and liquid water has been solved. The calculations for chemical bond deviations were carried out taking the anharmonicity of vibrations into account. The potential barrier height and the inversion frequency through the linear configuration of an H<sub>2</sub>O molecule have been evaluated for a number of vibrational states.

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### 1. Introduction

Deviation of chemical bonds has been discovered for the first time in work [1] while solving an inverse spectral problem of vibrational spectroscopy for a water molecule. The deviation phenomenon was revealed, because the problem was analyzed making use of the  $3N$ -matrix method ( $N$  is the number of atoms in a molecule), in which no preliminary assumptions about the character of the molecular force field are made [2]. According to the results of work [1], the deviation angle amounts to 2° for the H<sub>2</sub>O molecule in the gaseous state and 6° in liquid water (hereafter, water molecule in the gaseous or liquid state).

In work [3], a possibility for the characteristic and noncharacteristic (translational and librational) normal vibration modes of water molecule in the liquid state to “mix” with one another was taken into consideration, which gave rise to the increase of the deviation angle up to 7.5°. The phenomenon of chemical bond deviation was demonstrated in work [4] to be the physical reason for the hydrogen bond bending, which has been found experimentally in the framework of neutron diffraction researches.

In all three works [1, 3, 4], while calculating the zero-vibration frequencies  $\omega_1$  and  $\omega_2$ , the same anharmonicity constant, as that applied for the calculation of  $\omega_3$ , was used without any substantiation. In this work, we demonstrated that there is a substantial difference between the actual values of those constants. Moreover, the calculations of the deviation angle in works [1, 3, 4] were carried out in the harmonic approximation. In this work, the deviation angle was evaluated taking the anharmonicity of vibrations into account. As a result, it has been found that the deviation angle is different in the cases of stretching or squeezing of the same bond. In addition, in this work, the potential barrier height and the inversion frequency through the linear configuration of a water molecule have been determined for a number of vibrational states.

### 2. Calculation Part

In works [1, 2], to solve the inverse spectral problem of vibrational spectroscopy, the formula

$$\hat{V} = \hat{M}\hat{L}\hat{\omega}\tilde{\hat{L}}\hat{M} \quad (1)$$

was used, where  $\hat{V}$  is the force matrix;  $\hat{M}$  the diagonal matrix which is composed of the masses of atoms that constitute the molecule; the matrix  $\hat{L}$  governs the shape of characteristic and noncharacteristic normal vibrations of the H<sub>2</sub>O molecule;  $\hat{\omega}$  the diagonal matrix of squared frequencies, both characteristic and noncharacteristic, of normal molecular vibrations; and the tilde sign means transposition operation. All the matrices are of the order of  $3N$ .

Relation (1) enables one to find the analytical expressions for all elements of the force matrix. We note that the forms of the matrix  $\hat{V}$  in Eq. (1) must be the same for different isotope modifications of the molecule. Taking this circumstance into account made it possible to insert corrections for anharmonicity into the normal vibration frequencies. For this purpose, the formula

$$\omega_{0i} = \omega_i(1 + u_i\omega_i) \quad (2)$$

was used, where  $\omega_i$  is the frequency that is determined experimentally, and  $\omega_{0i}$  is the frequency of zero vibrations.

In contrast to the previous works [1, 3, 4], the values of the anharmonicity parameters  $u_i$  were calculated separately for every normal vibration mode. With this purpose in view, we solved the system of equations composed in accordance with the following scheme. The anharmonicity parameters, which correspond to different isotope modifications of the water molecule, were considered identical. Moreover, into the force matrices that correspond to two different isotope modifications, there can be introduced such shape parameters which make those elements equal. Therefore, the anharmonicity parameters can be found by solving the system of equations for several elements of the force matrix which correspond to two isotope modifications. In our case, we used the analytical expressions for the elements  $V_{22}$ ,  $V_{33}$ ,  $V_{35}$ ,  $V_{36}$ ,  $V_{44}$ ,  $V_{58}$ , and  $V_{59}$  of the force matrix and the frequencies of normal vibrations of molecules  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . According to Eq. (2), we constructed the matrix of normal vibrations, where the correction of frequencies for anharmonicity was done.

Symmetry reasons do not determine the shapes of fully symmetric vibrations of the  $\text{H}_2\text{O}$  molecule unambiguously, but with an accuracy to the "shape parameter" which is introduced into the matrix  $\hat{L}$ . The shape parameters were considered different for different isotope modifications of the molecule. Calculations were carried on without taking the mixing of normal vibration modes into account in the case of water molecule in the liquid state.

In order to determine the deviation angle for the chemical bond, we calculated the dependence of the molecule energy on the direction of a shift of one of the hydrogen atoms and plotted a corresponding polar diagram. The amplitude of the atomic shift was taken constant, and the positions of both the second hydrogen atom and the oxygen atom were adopted unchanged.

The vector of atomic shift  $\vec{X}$  from the equilibrium position is coupled with the vector of normal coordinates  $\vec{Q}$  by the relation  $\vec{X} = \hat{L}\vec{Q}$ .

For each component of the vector  $\vec{Q}$ , the model potential  $V(Q_i)$  of the Morse function type, or another similar one, was used. The potential energy of the molecule was tried as the sum

$$V = \sum_i V(Q_i). \quad (3)$$

The dependence of the potential energy on the fully symmetric normal coordinate  $Q_1$  was simulated by the Morse function

$$V(Q_1) = D_1(1 - e^{-\sigma_1 Q_1})^2. \quad (4)$$

Using the known expression for the energy of vibrational states

$$E_{iv} = \hbar\omega_{0i}(v + \frac{1}{2}) - \hbar\omega_{0i}\chi_i(v + \frac{1}{2})^2 \quad (4a)$$

and the Morse function, we found the parameters of potential (4):

$$\omega_i = \frac{E_{i1} - E_{i0}}{\hbar}, \quad \chi_i = \frac{\omega_{0i} - \omega_i}{2\omega_{0i}},$$

$$D_i = \frac{\hbar\omega_{0i}}{4\chi_i}, \quad \sigma_i = \sqrt{2\chi_i\omega_{0i}}. \quad (5)$$

In the previous calculations of the potential energy dependence on the normal coordinate  $Q_2$ , the Morse function was used. However, from the analysis of the shape of vibrations  $\omega_2$ , it follows that, provided the amplitudes of vibrations are large enough, the inversion of the water molecule through an unstable configuration of the symmetry  $D_{\infty h}$  becomes possible, and the water molecule demonstrates the monodromy phenomenon [6]. Therefore, for the description of the vibration  $\omega_2$ , we used a double-well potential. As a model potential, the modified Manning potential [7] was suggested:

$$V(Q_2) = D_2 \left[ \frac{b_2}{2} - \frac{1}{\cosh^2(\sigma_2 z_2)} \right]^2. \quad (6)$$

Here,  $z_2 = z_0 - Q_2 \sqrt{\frac{2m}{M(M+2m)}} \sin \psi$ ;  $\psi$  is the shape parameter;  $M$  and  $m$  are the masses of oxygen and hydrogen atoms, respectively; and  $z_0$  is the coordinate of the center of mass of the molecule.

The expressions for the parameters of the Manning potential were found from the following reasons. First, the dissociation potential for the Manning curve was supposed to be not lower than that for the Morse

curve. Second, the height of the barrier located between the minima of the Manning potential has to be not larger than the value of the Morse function at the point  $z = 0$ . Third, the second derivatives of the Morse and Manning curves at their minimum points must be equal to each other. Fourth, the minimum of the Manning curve must correspond to the coordinate of the equilibrium position of oxygen atom.

A representation of the potential energy dependence on the normal coordinate, which corresponds to the antisymmetric vibration  $\omega_3$ , in the form of the Morse function also proved to be incorrect. From the analysis of the shape of this vibration, it follows that the curve describing the dependence of the potential energy on the normal coordinate  $Q_3$  should be symmetric with respect to the point  $Q_3 = 0$ . In this connection, we used the expression

$$V(Q_3) = D_3 \left[ 1 - \frac{1}{\cosh(\sqrt{2}\sigma_3 Q_3)} \right]. \quad (7)$$

Similar speculations can also be applied while selecting a potential for the description of noncharacteristic vibrations of the  $\text{H}_2\text{O}$  molecule. Therefore, the same potential, as had been used for the description of the  $\omega_3$ -vibration, was engaged in this case as well.

For the choice of the potential in form (7), formulas (5) remain valid, so that they can be applied to determine the parameters of potentials (4) and (7).

Since the Manning potential is a double-well one, the inversion of the molecule through the potential barrier that separates two minima becomes possible. We estimated the respective frequency of inversion,  $\Omega_i$ , through the potential barrier; for the  $i$ -th vibrational level of the water molecule, this quantity is calculated by the known formula

$$\Omega_i = \frac{\omega_2}{2\pi} e^I, \quad (8)$$

where  $I = -\int_{-z_i}^{z_i} \sqrt{2\mu(V(z_2) - E_{vi})} dz_2$ ;  $\mu$  is the reduced mass of the molecule;  $V(z_2)$  the Manning potential;  $E_{vi}$  the energy of the  $i$ -th vibration mode; and  $z_i$  the point, where the value of the Manning potential is equal to the energy of the  $i$ -th vibrational level.

We plotted the deviation loop following the technique described in work [1], but now, in contrast, we used relations (3)–(7) to make allowance for the anharmonicity of vibrations. The calculations were carried out for water molecule in the gaseous and liquid states. The refined data for the values of normal vibration frequencies were used.

**Table 1. Normal vibration frequencies of  $\text{H}_2\text{O}$  molecule**

$\omega_i$	$u_i, 10^{-5}$	$\omega_{ie}, \text{cm}^{-1}$ , experimental	$\omega_{in}, \text{cm}^{-1}$ , calculated with a correction for anharmonism
gaseous state			
$\omega_1$	1.814	3657.05 [8]	3899.65
$\omega_2$	1.47	1594.75 [8]	1632.14
$\omega_3$	1.3923	3755.93 [8]	3952.34
liquid state			
$\omega_1$	1.234	3420 [9]	3564.33
$\omega_2$	4.289	1640 [9]	1755.36
$\omega_3$	0.413	3490 [9]	3540.35
$\omega_t$	0.999	170 [9]	170.29
$\omega_r$	1.001	700 [9]	704.90

**Table 2. Parameters of the potential for  $\text{H}_2\text{O}$  molecule used in calculations**

$\omega_i$	$D_i$ in $\text{cm}^{-1}$ units and $\sigma_i$ in $\text{cm}^{-1/2}$ units	
	gaseous state	liquid state
$\omega_1$	$D_1 = 3.134 \cdot 10^4$ $\sigma_1 = 97.865$	$D_1 = 4.401 \cdot 10^4$ $\sigma_1 = 75.486$
$\omega_2$	$D_2 = 1.459 \cdot 10^5$ $b_2 = 1.386$ $a_2 = 346.874$	$D_2 = 8.161 \cdot 10^5$ $b_2 = 1.76$ $a_2 = 228.766$
$\omega_3$	$D_3 = 3.9767 \cdot 10^4 \text{ cm}^{-1}$ $\sigma_3 = 88.056$	$D_3 = 1.245 \cdot 10^5$ $\sigma_3 = 44.585$
$\omega_t$	–	$D_t = 0.502 \cdot 10^5$ $\sigma_t = 3.378$
$\omega_r$	–	$D_r = 0.507 \cdot 10^5 \text{ cm}^{-1}$ $\sigma_r = 13.915$

### 3. Results and Their Discussion

In Table 1, the frequency values, corrected for anharmonicity, for normal vibration modes, characteristic and noncharacteristic, of a water molecule are listed. The shape parameter equals  $\psi = 1.02$  for water molecule in the gaseous state and  $\psi = 0.824$  for that in the liquid one. To verify the found force matrices, the frequencies of normal vibrations of the  $\text{D}_2\text{O}$  molecule were calculated (it is a direct problem of vibrational spectroscopy). For water molecule in the gaseous state, the divergence parameter [1] is of the order of  $10^{-12}$ , i.e. the agreement between the experimental and calculated frequencies can be considered quite satisfactory. The numerical values of the parameters that were used for the potentials in the course of calculations are tabulated in Table 2.

Consider the results obtained for the height of the barrier of  $\text{H}_2\text{O}$  molecule linearization. Table 3 quotes the relevant data taken from the literature as well as the results obtained in this work. It is evident that the calculated value of the barrier height for the molecule

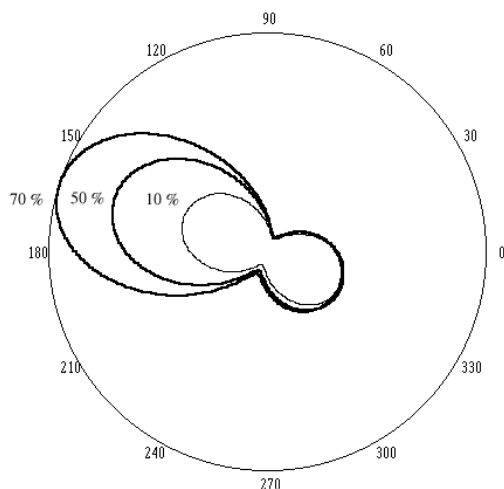


Fig. 1

linearization turned out larger than the corresponding literature data. Such a discrepancy between the results can originate from a plenty of factors. On the one hand, the barrier height for molecule linearization calculated following *ab initio* methods proved to be very sensitive to the interatomic distance in the linear configuration of the  $\text{H}_2\text{O}$  molecule. Again, those authors who used *ab initio* methods pointed out that the latter describe deformation vibrations of the water molecule insufficiently well [12].

On the other hand, we used the force matrix, the shape parameter for which had been calculated assuming the molecule to be in the equilibrium state. It could not be excluded that the magnitude of the shape parameter might depend on the vibration amplitude. Taking this fact into account would affect the height of the barrier of molecule linearization.

To summarize the aforesaid, we emphasize that the discrepancy between the arithmetic mean value calculated for the barrier heights of molecule linearization taken from the literature and the value obtained by us amounts to about 10%. Taking the difference between the methods applied into account, such a discrepancy can be considered as a satisfactory agreement.

In works [10–12], the inversion frequency for an  $\text{H}_2\text{O}$  molecule was not evaluated. Therefore, in this work, we calculated the inversion frequencies for several vibrational levels of a water molecule, making use of formula (8). The positions of the vibrational energy levels were calculated by formula (4a); their frequencies proved to be in good agreement with the experimental frequencies of vibrations [13] (see Table 4). For levels

with  $v = 7$  and 8, Table 4 gives the vibration frequencies (designated by an asterisk) that were calculated by interpolating the available data taken from work [13].

For high rotational-vibrational states, as is seen from Table 4, the inversion-induced doubling of the frequencies is appreciable. It should be noted that, if the barrier of molecule linearization is lower than that found by us, the splitting of rotational-vibrational levels should be even more notable; so that, taking the modern level of progress in spectroscopy into account, this splitting could be registered experimentally. In our opinion, the obtained results (see Table 4) can be used for the interpretation of rotational-vibrational spectra of the water molecule.

In the framework of the harmonic approximation, the orientation of the large diagonal of the deviation loop is adopted as the chemical bond direction [1, 3]. However, the results obtained in this work testify that this definition must be given more precisely.

The main difference between the results of this work and those obtained in the framework of the harmonic approximation consists in that our deviation loop turned out asymmetric. The first feature of the deviation loop, which appears in the anharmonic approximation, is the dependence of its shape on the amplitude of the shift of a selected atom. In Fig. 1, there are plotted three deviation loops for the H-atom displacement, which amounts to 10, 50, or 70% of the O–H interatomic distance. The dependences obtained were normalized by the maximum deviation value achieved in the loop that corresponds to

**Table 3. Barrier height for the linearization of  $\text{H}_2\text{O}$  molecule**

Barrier height, $\text{cm}^{-1}$	[Source] method
11 493	[10] spectroscopic empirical
11 192	[11] <i>ab initio</i>
$11\,105 \pm 5$	[12] <i>ab initio</i> corrected
13 750	this work (gaseous state)
12 790	this work (liquid state)

**Table 4. Inversion frequencies of an  $\text{H}_2\text{O}$  molecule for several vibrational states**

Vibration frequency, $\text{cm}^{-1}$	Frequency of inversion $\Omega$ , Hz	Magnitude of level splitting $\Delta\omega$ , $\text{cm}^{-1}$
1594.746	1.38	$4.605 \cdot 10^{-11}$
3151.630	189.6	$6.32 \cdot 10^{-9}$
4666.790	$1.19 \cdot 10^4$	$4.071 \cdot 10^{-6}$
6134.015	$4.9 \cdot 10^5$	$1.691 \cdot 10^{-5}$
7542.437	$1.5 \cdot 10^7$	$5.122 \cdot 10^{-4}$
8869.954	$3.62 \cdot 10^8$	0.012
11100	$6.9 \cdot 10^9$	0.232
12500*	$1.11 \cdot 10^{11}$	3.712
13820*	$1.522 \cdot 10^{12}$	50.779

the stretching of the O—H bond of an H<sub>2</sub>O molecule in the gaseous state. As is seen from the figure, the polar diagram substantially changes its form with increase in the displacement to the hydrogen atom from its equilibrium position.

Second, while analyzing the problem of chemical bond deviation in the anharmonic approximation, it has been established that the O—H bond in the H<sub>2</sub>O molecule is characterized by two deviation angles. If the problem is treated in the harmonic approximation, the deflection of the deviation loop maximum from the line connecting the hydrogen and oxygen atoms is identical at either squeezing or stretching of the O—H bond. However, when changing to the anharmonic approximation, the deflection of the deviation loop maximum from the line connecting the H and O atoms turned out different by value in the cases where the hydrogen atom becomes shifted in opposite directions.

The revealed features comprise the origin of a complicated behavior of the direction of forces that act upon each atom during the normal vibration of the molecule. This circumstance gives rise to the interaction between normal vibrations.

Figure 2 exhibits the dependences of the O—H bond deviation angle on the relative – with respect to the O—H interatomic distance – displacement of the hydrogen atom at squeezing (upper curves) or stretching (lower curves) of this bond for the water molecule in the liquid (thin curves) or gaseous (bold curves) state. If the displacement is small enough, the effect concerned does not manifest itself: the deviation angle is the same for stretching and squeezing of the O—H bond, amounting to  $\Delta = 3.8^\circ$  in the gaseous and  $7.7^\circ$  in the liquid state. Such results coincide with the values obtained if the problem is solved in the harmonic approximation, but a specific parameter of anharmonicity is used for each normal vibration. The increase of the hydrogen atom displacement brings about the difference between the deviation angles at stretching or squeezing of the bond.

The results obtained demonstrate that the deviation angle of the chemical bond is a parameter that is rather sensitive to the conditions of both real and imaginary experiments, and can be used for comparative researches of the characteristics of all 6-group hydrides.

We note that, in the case of a small amplitude of the  $\omega_1$ -vibration, the H atoms move along practically straight paths which are separated by an angle of approximately  $120^\circ$ . This value substantially exceeds the  $104.5^\circ$ -angle between O—H bond directions in the water molecule even if the deviation angle is made allowance for. These facts, on the one hand, testify to an essential

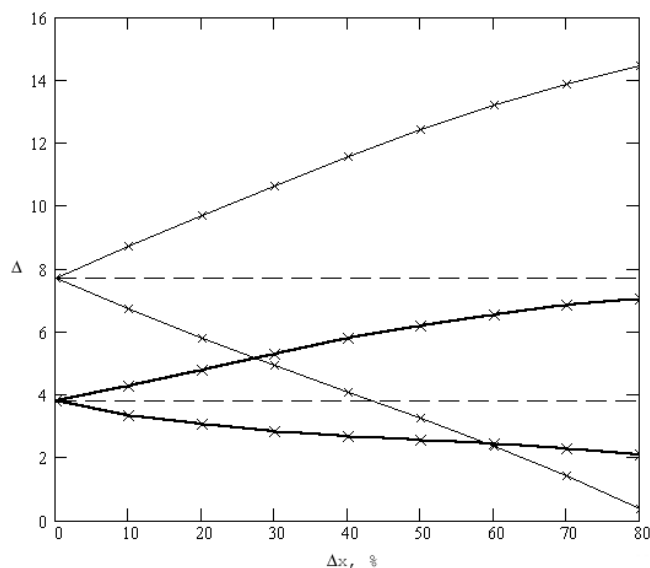


Fig. 2

role of nondiagonal elements of the force matrix; on the other hand, they indicate that not only the lengths of O—H bonds substantially change in the course of a fully symmetric valence vibration, but so does the angle between the bonds.

Since the maxima of the deviation loop sections, which are related to the squeezing or stretching of the O—H bond, do not lie on the same straight line, one can draw a conclusion that, at the excitation of  $\omega_1$ -vibration with a sufficiently large amplitude, the H atoms move along a complicated trajectory rather than along a straight interval. This result may be considered as an opportunity for the illustrative interpretation of the well-known fact that normal vibrations cannot be considered as vibrations of independent oscillators if the anharmonicity is taken into account.

Figure 3 demonstrates the dependences of the normal coordinates of an H<sub>2</sub>O molecule on the time for the initial conditions which correspond to the excitation of  $\omega_1$ -vibration only. It is evident from the figure that the excitation of  $\omega_1$ -vibration is accompanied by the excitation of  $\omega_2$ -vibration with a small constant amplitude and  $\omega_3$ -vibration, whose amplitude periodically changes; this means that the energy of vibrations becomes periodically redistributed between those modes. Such a result is in agreement with that obtained in the famous Fermi–Pasta–Ulam work, where the vibrations in the chain of atoms were examined [14].

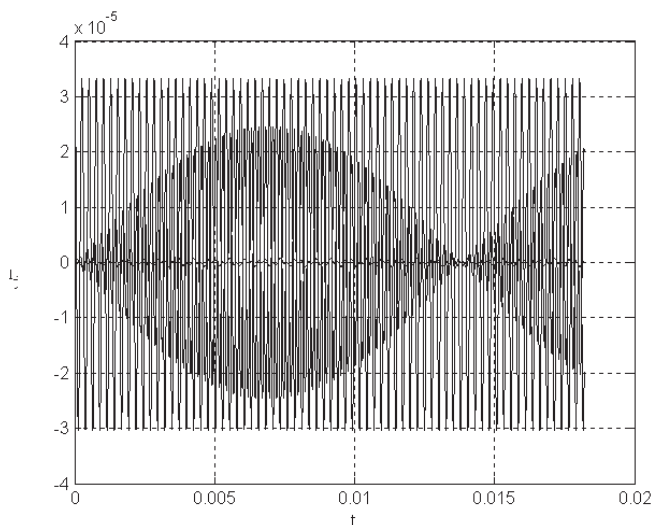


Fig. 3

#### 4. Conclusions

The deviation angle of the chemical bond has been demonstrated to have different values for the bond stretching and squeezing if the anharmonicity of vibrations is taken into account. It also depends on the amplitude of a hydrogen atom displacement from its equilibrium position. The height of the potential barrier for the  $\text{H}_2\text{O}$  molecule inversion through the linear configuration and the effect of the inversion-induced frequency doubling for a number of vibrational states of the molecule have been evaluated. In particular, the inversion of the water molecule in the ground vibrational state through the linear configuration occurs approximately once per second.

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#### ВПЛИВ АНГАРМОНІЗМУ НОРМАЛЬНИХ КОЛИВАНЬ НА ДЕВІАЦІЮ О-Н-ЗВ'ЯЗКУ МОЛЕКУЛИ $\text{H}_2\text{O}$

Б.А. Охріменко, К.С. Яблочкова

## Резюме

Розв'язана обернена спектральна задача для молекули води у газоподібному і рідкому станах. Розрахунок значень девіації хімічного зв'язку виконано з врахуванням ангармонізму коливань. Оцінено висоту потенціального бар'єра і частоту інверсії молекули води через лінійну конфігурацію для кількох коливальних станів.