THE INFLUENCE OF H_2O DEFORMATION ON A DEVIATION ON O–H CHEMICAL BOND

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A deviation loop is plotted in the harmonic approximation of molecular vibrations. The loop acts as a sensitive indicator reacting to the initial deformation of a water molecule due to the displacement of H atom from its equilibrium position. The deformation of the molecule leads to a displacement of the second hydrogen atom. The dependence of the corresponding Lagrangian on the orientation of the coordination plane has been determined.

1. Introduction

The inverse spectral problem of vibrational spectroscopy allows one to determine the force matrix of a molecule. In order to solve this problem, the valence-force model is used. In such model, the bonds existing between chemically bonded atoms and the angles between the chemical bonds are characterized by elasticity constants. It is usually implied that the forces between two chemically bonded atoms are directed along the segments connecting the nuclei of these atoms. Such approach is justified only if the valence-force field is fully realized in the system.

Certain factors imply that such approach must be somewhat corrected. Consider, for instance, a water molecule. According to available data, the location of the “center-of-mass” of molecule’s electron shell does not coincide with that of the oxygen atom, being displaced toward H–H segments. Such displacement appears to be rather natural in view of the effective positive charge of hydrogen atoms. As a result, the direction of the Coulomb force between the hydrogen atom and the electron shell’s “center of mass” will not coincide with the direction of the segment connecting the nuclei of hydrogen and oxygen. We consider the direction of the net force to be the same as a direction of the maximum gradient of the potential energy, characterizing a displacement of the hydrogen atom from the equilibrium position. Such speculations lead to the conclusion that the direction of the resulting bond between the oxygen and hydrogen atoms may deviate from the directions of segments connecting the nuclei of these atoms.

The angle between such directions is referred as the chemical bond deviation angle. To our knowledge, [1] was the first paper to identify the chemical bond deviation phenomenon in H_2O molecule. The term deviation was introduced in [2], where certain properties of the deviation phenomenon have been discussed for water in the condensed state. According to [1–3], the deviation angle for a free water molecule constitutes about 2° and 7.5° for water in the condensed state. The deviation angle of water in the liquid state identified in [3] correlates with the neutronographic studies demonstrating the twisting of the hydrogen bonds by 10°.

The deviation phenomenon [1] is demonstrated as a result of solving the inverse spectral problem of vibrational spectroscopy with the help of a relatively new $3N$-matrix method, which requires no presuppositions, unlike many other methods, about the shape of molecule’s force field and can be used for free molecules and molecules of the condensed state.

The further studies in this field resulted in discovering the deviation phenomenon in molecules of symmetries C_{2v} [5–11] and C_{3v} [12–15]. The phenomenon was demonstrated to be present for free molecules and molecules in the condensed state. Bearing this in mind, the twisting of hydrogen bonds should be considered as a special case of the broader phenomenon of the chemical bond deviation.

Most of the works cited earlier studied molecules that contain hydrogen atoms. Nevertheless, the chemical bond deviation was also discovered for molecule SO_2 [16], both atoms of which belong to the 6-th group of Periodic Table of elements. The latter finding allowed one to make certain assumptions about the role of inner electrons of sulfur and oxygen atoms.

The above-described facts allowed one to advance the studies of the chemical bond deviation as a characteristic of molecule’s force field. According to [17], the additional information about molecule’s force field can be obtained by studying the influence of molecule’s deformation on the deviation angle.

2. Deviation Loop of a Deformed Molecule

The term "deviation loop" is an short name for the polar graph of molecule's potential energy as a function of the constant finite displacement of one of its atoms, when all other atoms are kept in their respective equilibrium positions. In order to plot such graph, the force matrix of the molecule must be constructed.

Force matrices $\hat{V}$ (Table 1) of H_2O molecule in the gas and liquid states were calculated in [3]. The matrix $\hat{V}$ has the following characteristics. The columns and rows of a water molecule in the gas-state matrix, that correspond to x coordinates of each atom of a molecule, contain zeros. This is due to the fact that a relatively small displacement of an atom along the axis x hardly changes its distance from other atoms and is equivalent to a rotation of the tri-atomic molecule. Such operation does not change free molecule's potential energy. Further calculations in the present paper are carried out in the approximation of harmonic vibrations.

Deviation loop is defined as the energy characterizing a displacement of one of the atoms in the coordinate plane yz of the Cartesian system of coordinates. The locations of other atoms remain unchanged. When molecule H_2O is studied, the right hydrogen atom is displaced by

$$\tilde{\mathbf{v}}_R(\varphi) = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & y(\varphi) & z(\varphi) \end{bmatrix}, \qquad (1)$$

where the tilde signifies a transposed matrix, $y(\varphi) = r_0 \sin(\varphi)$, $z(\varphi) = r_0 \cos(\varphi)$, r_0 is the factor determining the right atom's displacement (Fig. 1) and the angle φ determines the direction of a displacement.

T a b l e 1. Elements of the force matrix $\hat{V} \times 10^{-5}$ of H_2O in the gas state (top values) and the liquid state (bottom values)

0	0	0	0	0	0	0	0	0
0.89	0	0	–0.31	0	0	–0.31	0	0
0	18.26	0	0	–9.13	–7.07	0	–9.13	7.07
0	11.04	0	0	–6.66	–4	0	–6.66	4
0	0	11.43	0	–5.31	–5.72	0	5.31	–5.72
0	0	9.85	0	–5.45	–3.41	0	5.45	–3.41
0	0	0	0	0	0	0	0	0
–0.31	0	0	0.48	0	0	–0.01	0	0
0	–9.13	–5.31	0	10.14	6.19	0	–1	–0.88
0	–6.66	–5.45	0	9.72	3.71	0	–1.25	–1.49
0	–7.07	–5.72	0	6.19	5.6	0	0.88	0.12
0	–4	–3.41	0	3.71	3.5	0	1.49	–0.35
0	0	0	0	0	0	0	0	0
–0.31	0	0	–0.01	0	0	0.48	0	0
0	–9.13	5.31	0	–1	0.88	0	10.14	–6.19
0	–6.66	5.45	0	–1.25	1.49	0	9.72	–3.71
0	7.07	–5.72	0	–0.88	0.12	0	–6.19	5.6
0	4	–3.41	0	–1.49	–0.35	0	–3.71	3.5

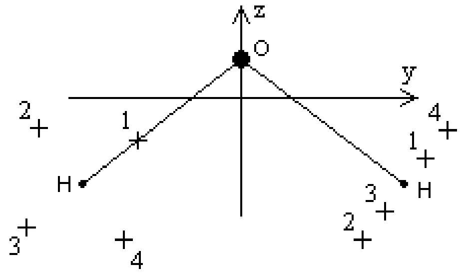

Fig. 1. The positions of H_2O atoms and the orientation of the coordinate system. Four consecutive positions of the left hydrogen atom, which correspond to the prior deformation of the molecule in the gas state, and the new positions of the right hydrogen atom are denoted by crosses. Deformation denoted by "i" corresponds to the new equilibrium position of the right hydrogen atom of the same number

For a non-deformed molecule, the deviation loop is determined by the dependence of molecule's potential energy on the angle φ

$$V(\varphi) = \frac{1}{2} \tilde{\mathbf{v}}_R(\varphi) \hat{V} \mathbf{v}_R(\varphi). \qquad (2)$$

According to the problem formulated earlier, a prior deformation of a molecule is made. It is carried out by means of a displacement of the left hydrogen atom, whose vector of displacement is given by

$$\tilde{\mathbf{v}}_L(\psi_i) = \begin{bmatrix} 0 & 0 & 0 & 0 & y(\psi_i) & z(\psi_i) & 0 & 0 & 0 \end{bmatrix}, \qquad (3)$$

where $y(\psi_i) = r_d \sin(\psi_i)$, $z(\psi_i) = r_d \cos(\psi_i)$, r_d is a factor determining the left atom's displacement from the equilibrium position, and the angle ψ_i gives the direction of the left atom's displacement.

For a deformed molecule, the deviation loop is determined by the dependence of molecule's potential energy on the angle φ

$$V_i(\varphi) = \frac{1}{2} \tilde{\mathbf{v}}_i(\varphi) \hat{V} \mathbf{v}_i(\varphi), \qquad (4)$$

where $\mathbf{v}_i(\varphi) = \mathbf{v}_R(\varphi) + \mathbf{v}_L(\psi_i)$.

In order to determine how the deviation loop depends on a prior deformation, we chose the angles $\psi_i = 0, \pi/2, \pi$, and $3\pi/2$ for $i = 1, 2, 3, 4$. The angle ψ_i is counterclockwise, such that its zero value corresponds to the direction of the segment connecting the left hydrogen atom with the oxygen atom. Hence, the values

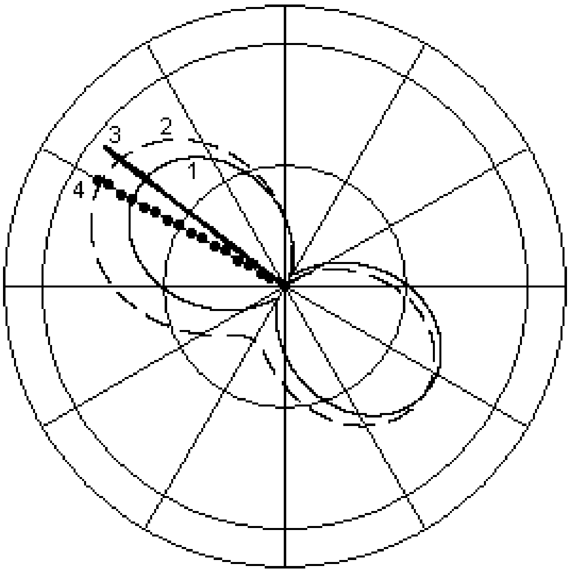

Fig. 2. Deviation loop of non-deformed (*1*) and deformed (*2*) water molecules in the gas state. Deformation is due to a displacement of the left hydrogen atom from the equilibrium position into position "4" in Fig. 2. Dots (*4*) show the direction of the maximum of (*2*). Segment (*3*) shows the direction of O–H

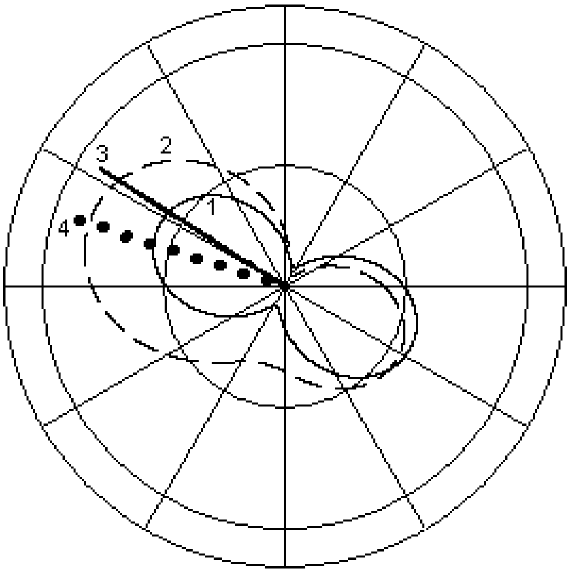

Fig. 3. Deviation loop of non-deformed (*1*) and deformed (*2*) water molecules in the liquid state. Deformation is due to a displacement of the left hydrogen atom from the equilibrium position into position "4" in Fig. 2. Dots (*4*) show the direction of the maximum of (*2*). Segment (*3*) shows the direction of O–H

$i = 1, 3$ correspond to the compression and the elongation of O–H segment, and values $i = 2, 4$ correspond to an increase and a decrease of the angle $\angle$HOH.

The magnitude of displacement is chosen at $r_d = 0.01$, which corresponds to 30% of O–H segment. Such value is chosen in order to make the changes in the deviation loop easily noticeable.

The above-mentioned four positions of the left hydrogen atom are shown in Fig. 1. The prior deformation of the molecule appears to result in visible changes of the deviation loop. These changes are shown, for instance, in Fig. 2, where the deviation loops for the non-deformed and deformed (left hydrogen atom in position "4") free water molecules are shown simultaneously. Figure 3 shows the deviation loops for non-deformed and deformed (left hydrogen atom in position "4") water molecules in the liquid state. Figure 3 suggests that, although the plane of the deviation loop does not change significantly, the loop itself becomes asymmetric, as the deviation angle increases. Similar changes occur when the left hydrogen atom is displaced in position "2", which corresponds to an increase of the angle between O–H segments, although the deviation angle becomes negative in this case.

The results of the deviation loop analysis are shown in Table 2, where the term "deviation angle" is shown in quotation marks. This is due to the fact that the further research revealed that a deformation of the molecule results in a displacement of the right hydrogen atom from the equilibrium position. When the right hydrogen atom is displaced, along with the left one, the direction of deviation loop's maximum, strictly speaking, does not determine the chemical bond direction. This question is further discussed in the next chapter.

3. Displacement of the Right Hydrogen Atom

A prior deformation of the molecule is carried out by means of a displacement of the left hydrogen atom, as shown in Fig. 1. It is natural to suggest that, due to a displacement of the left hydrogen atom, while the oxygen atom is fixed, the right hydrogen atom must change its equilibrium position as well.

Table 2. "Deviation angle" for the deviation loop for H_2O deformed due to a displacement of the left hydrogen atom

Position of the left H atom (Fig. 1)	"Deviation angle" of water molecule	
	in gas state	in liquid state
1	5.7	15.6
2	–3	–2.35
3	0	0.2
4	8.05	14.65

The rotation of the molecule by a certain angle results in molecule's new symmetry axis not coinciding with the coordinate axis z. Consequently, the previously calculated force matrix $\hat{V}$ cannot be applied to the rotated molecule. The clockwise rotation of a molecule around the axis x is known to be equivalent to a rotation of the coordinate system around the axis x by the same angle, but in the opposite direction. Such consideration allow us to calculate the new force matrix $\hat{V}'(\phi)$ of a non-deformed molecule rotated by a certain angle. We denote the matrix determining the transformation of the coordination system due to its rotation around the axis x by an angle ϕ as $\hat{c}_\phi$. The matrix $\hat{V}'(\phi)$ can be found from the relation

$$\hat{V}'(\phi) = \hat{C}_\phi \hat{V} \hat{C}_\phi^{-1}, \tag{5}$$

where

$$\hat{C}_\phi = \begin{bmatrix} \hat{c}_\phi & \hat{0} & \hat{0} \\ \hat{0} & \hat{c}_\phi & \hat{0} \\ \hat{0} & \hat{0} & \hat{c}_\phi \end{bmatrix}, \tag{6}$$

and $\hat{0}$ is the 3×3 zero matrix.

In order to check the described speculations, the deviation loop of a non-deformed rotated molecule was plotted using matrix (6) for $\phi = 20°$. Instead of (4), we take

$$V(\varphi, \phi) = \frac{1}{2} \tilde{\mathbf{v}}_R(\varphi) \hat{V}'(\phi) \mathbf{v}_R(\varphi). \tag{7}$$

As was expected, the maximum of the deviation loop corresponds to the angle $\triangle_d = \phi + \triangle = 20° + 3.8°$, where $\triangle = 3.8°$ – deviation angle of the O–H bond in H_2O in its initial position [5].

In the case of deformation "2" or "4" (Fig. 1), the new equilibrium position of the right hydrogen atom shifts from the initial equilibrium position by the same distance, as the left hydrogen atom does. When the right hydrogen atom is displaced into a new equilibrium position, the potential energy of the molecule decreases from 100%, to zero. As a result, the displacement of the right hydrogen atom into a new equilibrium position helps the molecule to restore its geometry.

In the case of deformation "1" or "3" (Fig. 1), the energy of the molecule increases tenfold, as compared with that at deformation "2" or "4". The new displacement of the right hydrogen atom is about five times smaller than that of the left atom. When the right atom is displaced into the new equilibrium position "1" or "3", the potential energy of the molecule decreases by only 0.3%, and the initial geometry of the molecule is not restored. For deformation "1", the distance O–H for the left hydrogen atom is smaller than that for the right hydrogen atom, whereas the angle between the direction O–H increases with respect to the non-deformed molecule.

4. Discussion of Results and Conclusions

The study of the deviation loop of a deformed H_2O molecule shows that the direction of the deviation loop maximum is a sensitive parameter reacting to both the direction and the magnitude of a displacement of the left hydrogen atom, which determines the deformation of the molecule. The deformation of the molecule due to a displacement of the left hydrogen atom with the oxygen atom fixed is shown to result in a change of the equilibrium position of the right hydrogen atom.

An increase (decrease) of the left O–H segment length is accompanied by a corresponding decrease (increase) of the angle between segments O–H.

A deformation of the molecule due to a change of the angle between segments O–H leads to an unforeseen change in the equilibrium position of the right hydrogen atom. Shifting the right hydrogen atom into a new position corresponds to the rotation of the molecule by a certain angle. Since, after such rotation, there is no deformation of the molecule, molecule's force matrix should be expected to remain constant. It is demonstrated that such conclusion is wrong. As a result of molecule's rotation, its symmetry axis does not correspond to any axis of the Cartesian coordinate system. The new force matrix can be easily obtained with the use of the conformity transformation, which changes the elements of the force matrix, but does not change its eigenvalues. In order to test the properties of the new matrix (6), the deviation loop of the rotated molecule has been plotted. The results obtained through (7) conform to the predicted values.

A change in the coordinate system orientation with respect to the molecule is accompanied by a change in the elements of the force matrix. Such reflection illustrates expression (7), which hints at the dependence of the potential energy on coordinate system' angle of rotation ϕ around x. It must be noted that

$$\frac{\partial V(\varphi, \phi)}{\partial \phi} \neq 0 \tag{8}$$

including case $\phi = 0$.

The expressed dependence of the potential energy (7) on the angle ϕ may have effect on a Lagrangian, which characterizes vibrations of H_2O and contains expression

(7). It follows from (8) that such Lagrange function is not invariant with respect to the rotation of the coordinate system by a small angle. According to Noether's theorem, in such case, the conservation of the angular momentum cannot be applied to either H_2O molecule or any other multiatomic molecule. This conclusion supports the results of [18], where these questions were considered in more details.

1. M.U. Bilyu and B.A. Okhrimenko, Ukr. Fiz. Zh. **44**, 326 (1999).
2. M.U. Bilyu, G.I. Gaididei, and B.A. Okhrimenko, Funct. Mater. **7**, 543 (2000).
3. B.A. Okhrimenko and G.I. Gaididay, Ukr. Fiz. Zh. **48**, 739 (2003).
4. M.U. Bilyu, B.A. Okhrimenko, and S.M. Yablochkov, Izv. Vuzov SSSR, Fiz. **4**, 52 (1987).
5. B.A. Okhrimenko and K.S. Yablochkova, Ukr. J. Phys. **52**, 558 (2007).
6. M.U. Bilyy and B.A. Okhrimenko, Ukr. Fiz. Zh. **46**, 825 (2001).
7. G.I. Gaididay and B.A. Okhrimenko, Visnyk KNU, Phys. **4**, 22 (2002).
8. B.A. Okhrimenko, G.I. Gaididei, and D.M. Samoilenko, Proc. SPIE **5507**, 184 (2002).
9. M.U. Bilyy, G.I. Gaididay, B.A. Okhrimenko, V.P. Sakun, and D.M. Samoilenko, Ukr. Fiz. Zh. **12**, 1256 (2001).
10. G.I. Gaididay, B.A. Okhrimenko, M.V. Shelehova, and K.S. Yablochkova, Visnyk KNU, Phys. **5**, 16 (2003).
11. B.A. Okhrimenko and K.S. Yablochkova, Visnyk KNU, Phys. **4**, 449 (2006).
12. M.U. Bilyu and B.A. Okhrimenko, Ukr. Fiz. Zh. **4**, 466 (2001).
13. B.A. Okhrimenko and D.M. Samoilenko, Visnyk KNU, Phys. **4**, 45 (2002).
14. B.A. Okhrimenko, G.I. Gaididei, and D.M. Samoilenko, Funct. Mater. **1**, 136 (2004).
15. B.A. Okhrimenko and D.M. Samoilenko, Ukr. J. Phys. **6**, 544 (2005).
16. B.A. Okhrimenko and O.A. Yushko, Optics Spectr. **2**, 211 (2011).
17. O.V. Matyash and B.A. Okhrimenko, Ukr. J. Phys. **12**, 1167 (2009).
18. B.A. Okhrimenko, Ukr. Fiz. Zh. **5**, 500 (2002).

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ВПЛИВ ДЕФОРМАЦІЇ МОЛЕКУЛИ H_2O НА ДЕВІАЦІЮ ХІМІЧНОГО ЗВ'ЯЗКУ О–Н

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Резюме

У наближенні гармонічних коливань побудовано петлю девіації молекули. Вона є чутливим індикатором, що реагує на попередню деформацію молекули, яку здійснено зсувом одного з атомів водню від початкового положення рівноваги. Деформація молекули супроводжується зміщенням положення рівноваги іншого атома водню. Виявлено характер залежності відповідної функції Лагранжа від орієнтації системи координат.