INFLUENCE OF SO_2 MOLECULE DEFORMATION ON THE MANIFESTATION OF S–O BOND DEVIATION

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The influence of a preliminary deformation of SO_2 molecule by shifting either of the oxygen atoms from its equilibrium position on the manifestation of S–O bond deviation has been studied. The indicated deformation at a fixed position of the sulfur atom is shown to be accompanied by a variation in the equilibrium position of the other oxygen atom. The increase in the distance between the sulfur atom and either of oxygen ones gives rise to a reduction of the O–S–O angle.

The phenomenon of chemical bond deviation consists in that the direction of the bond between two atoms in a multiatomic molecule, which are usually considered to be chemically coupled with each other, does not coincide, generally speaking, with that of a straight line connecting the nuclei of those atoms. For instance, the direction of a chemical bond O–H in H_2O molecule for water in the liquid state deviates from the direction of the straight line O–H by an angle of 7.5° [1]. The angle between two indicated directions was called the "deviation angle", and the term "chemical bond deviation" was proposed for this phenomenon as a whole.

Hence, there is a notable difference between those two directions. Therefore, it is necessary to specify the meaning of the term "chemical bond direction", which characterizes the relation between a certain atom and the multiatomic molecule. Below, we refer to the chemical bond direction as a direction, in which the potential energy gradient for the atom shifted from its equilibrium position in the molecule is maximal.

The chemical bond deviation is observed for both free molecules and molecules in a condensed medium. From this viewpoint, the known fact of the hydrogen bond bending between water molecules in the condensed state can be regarded as a specific example of the more general phenomenon, the chemical bond deviation. Further researches in this domain revealed the chemical bond deviation in molecules belonging to both the C_{2v} and C_{2v} symmetry groups. Relevant references can be found in work [2], in which the deviation phenomenon in a non-deformed SO_2 molecule was studied both in the harmonic approximation and with regard for the anharmonicity of normal vibrations. Certain peculiarities in the manifestation of the deviation phenomenon were revealed for a non-deformed SO_2 molecule in comparison with hydrides of atoms belonging to the sixth group in the Periodic table of elements. This circumstance stimulated further researches of the force field of this molecule.

As was shown in work [3], additional information concerning the molecular force field can be obtained by studying the influence of a molecule deformation on manifestations of the deviation phenomenon. In this work, a preliminary deformation of the SO_2 molecule is carried out by shifting the left oxygen atom (see Figure) in the plane of the molecule. The displacement vector can be presented in the form

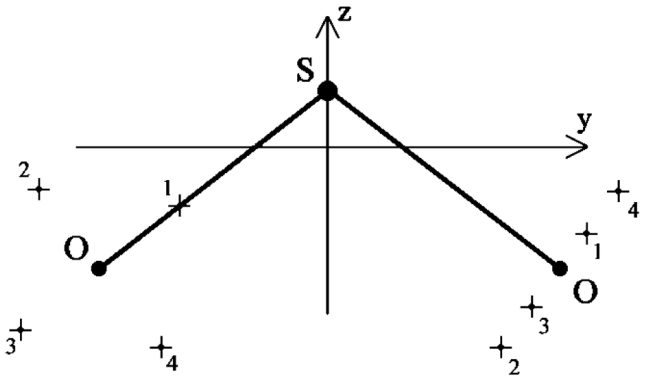
$$\tilde{\boldsymbol{\upsilon}}_L(\psi_i) = \left[\begin{array}{ccccccccc} 0 & 0 & 0 & 0 & y(\psi_i) & z(\psi_i) & 0 & 0 & 0 \end{array}\right],$$

where $y(\psi_i) = r_d \sin(\psi_i)$, $z(\psi_i) = r_d \cos(\psi_i)$, r_d is a multiplier that equals the magnitude of displacement from the equilibrium position for the left oxygen atom, and the angle ψ_i corresponds to the direction of the left oxygen atom shift at a preliminary deformation of the molecule. The number of components of the $\boldsymbol{\upsilon}_L(\psi_i)$ vector corresponds to the force matrix order.

The researches of the deviation loop for a deformed SO_2 molecule showed that the direction toward the deviation loop maximum is rather a sensitive parameter, which responds to both the direction and the magnitude

T a b l e

Position of left oxygen atom in the deformed molecule (Figure)	Deviation angles Δ_d for two values of parameter r_d		Displacement of equilibrium position for the right oxygen atom (Figure)
	$\Delta_d(r_d = 0.01)$	$\Delta_d(r_d = 0.005)$	
1	2.142	1.642	$r_d/5$
2	−4.158	−1.508	$-r_d$
3	−0.008	0.542	$-r_d/5$
4	6.092	3.592	r_d



Arrangement of atoms in SO_2 molecule with respect to the coordinate axes. The symbols "+" to the left from the ordinate axis correspond to the consecutive, marked by figures, positions of the left oxygen atom, which point to the character of a molecule deformation in the gaseous state; the symbols "+" and the figures to the right from the ordinate axis mark the corresponding new equilibrium positions of the right oxygen atom

of left oxygen atom displacement that bring about the molecule deformation. The meaning of the term "deviation loop" was explained in works [1–3].

It turned out that the molecule deformation induced by a displacement of the left oxygen atom, provided that the position of the sulfur atom is fixed, is accompanied not only by a variation of the deviation angle, but also a variation in the equilibrium position of the right oxygen atom (Figure). The shifts of the left oxygen atom designated by figures "2" and "4" were studied to test the calculation procedure, because, in those cases, the shifts of the equilibrium position of the right atom correspond to simple rotations of the molecule.

The increase (decrease) in the left O–S distance was found to be accompanied by a decrease (increase) of the O–S–O angle, with the right O–S distance being practically unchanged. The results obtained correlate with an assumption [2] that the internal electrons of oxygen and sulfur atoms affect the character of the force field acting on each atom of the molecule.

The main results of our researches are quoted in Table.

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ВПЛИВ ДЕФОРМАЦІЇ МОЛЕКУЛИ SO_2 НА ПРОЯВ ДЕВІАЦІЇ S–O-ЗВ'ЯЗКУ

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Р е з ю м е

Вивчено вплив попередньої деформації молекули за рахунок зміщення одного з атомів кисню з положення рівноваги на прояв явища девіації. Помічено, що деформація молекули за рахунок зміщення одного з атомів кисню при незмінному положенні атома сірки, супроводжується зміною рівноважного положення іншого атома кисню. Збільшення довжини одного із відрізків O–S супроводжується зменшенням кута між відрізками O–S.