

## Hydrogen-bonded systems of water with dimethyl and diethyl sulfoxides. Theoretical study of structures, stability and vibrational spectra

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The structural and vibrational characteristics (vibrational frequencies and infrared intensities) of the hydrogen-bonded systems dimethylsulfoxide (DMSO)–water (1:1, 1:2) and diethylsulfoxide (DESO)–water (1:1, 1:2) have been investigated employing *ab initio* and DFT calculations at different basis sets. The calculations show that the optimised structures of the studied systems 1:2 are cyclic while the optimised structures of the hydrogen-bonded systems 1:1 are linear. The corrected values of the dissociation energy for the hydrogen-bonded systems have been calculated by *ab initio* and DFT calculations at different basis sets in order to estimate their stability. It was established that the hydrogen-bonded systems DESO–water (1:1, 1:2) are more stable than the systems DMSO–water (1:1, 1:2). The influence of the hydrogen bonding on the properties of the monomers (H<sub>2</sub>O, DMSO and DESO) has been investigated. The hydrogen bonding between H<sub>2</sub>O and DMSO, and DESO leads to changes in the vibrational characteristics of the monomers. The predicted vibrational characteristics for the studied hydrogen-bonded systems are in very good agreement with the experimentally observed.

**Key words:** hydrogen-bonding; DMSO:H<sub>2</sub>O and DESO:H<sub>2</sub>O complexes; structures; vibrational spectra; *ab initio*; DFT.

### INTRODUCTION

Hydrogen bonding is of fundamental importance in chemistry, physics and biology. Computational methods based on quantum theory and developed for the treatment of chemical bonding, intermolecular forces, reactivity and interactions with electromagnetic radiation can reproduce or predict the measurable characterizing the hydrogen bonds. A large number of theoretical studies on the structures, stability and vibrational spectra employing *ab initio* and DFT calculations have been undertaken in recent years for the hydrogen-bonded complexes [1–8].

In many industrial and biomedical fields dialkyl sulfoxides (DASO) have found applications because of their unusual physicochemical properties. DMSO and DESO are used as industrial solvents for polar and ionic substances in chemistry, biology and medicine. DESO exhibits strong self-associative effects, even stronger than in DMSO. To this purpose, vibrational spectroscopy (Raman and IR) has been widely used [9–14] for studying the vibrational features of DMSO and DESO both pure and in aqueous solutions. The biomedical significance of DESO has been reported also [15]. Thermodynamic measurements of DESO–water mixtures (heat of fusion and solidification, melting and freezing temperature) suggested very strong

deviations from ideality, like in DMSO–water solutions, but to a greater extent [16].

The objects of the present study are the hydrogen-bonded systems DMSO–H<sub>2</sub>O (1:1, 1:2) and DESO–H<sub>2</sub>O (1:1, 1:2). The aim of the study is first, to establish the most stable structures of the hydrogen-bonded systems, secondly, to study the nature of the hydrogen bonding and finally to estimate the changes in the vibrational characteristics upon hydrogen bonding.

### METHODS

The structures, stability and vibrational characteristics of the hydrogen-bonded systems dimethylsulfoxide (DMSO)–water (1:1, 1:2) and diethylsulfoxide (DESO)–water (1:1, 1:2) are studied extensively in this work by *ab initio* and DFT calculations with various basis sets using the GAUSSIAN 98 series of programs [17]. Full geometry optimisation of the studied hydrogen-bonded complexes was performed. On Figs. 1 and 2 are presented the optimized structures with B3LYP/6-311++G (d,p) calculations for the DMSO–H<sub>2</sub>O (1:1, 1:2) and DESO–H<sub>2</sub>O (1:1, 1:2), complexes **1** and **2**. The optimized values of the hydrogen-bonded parameters (bond lengths and angles) obtained with B3LYP/6-311++G (d,p) calculations for the complexes studied are shown on Figs. 1 and 2.

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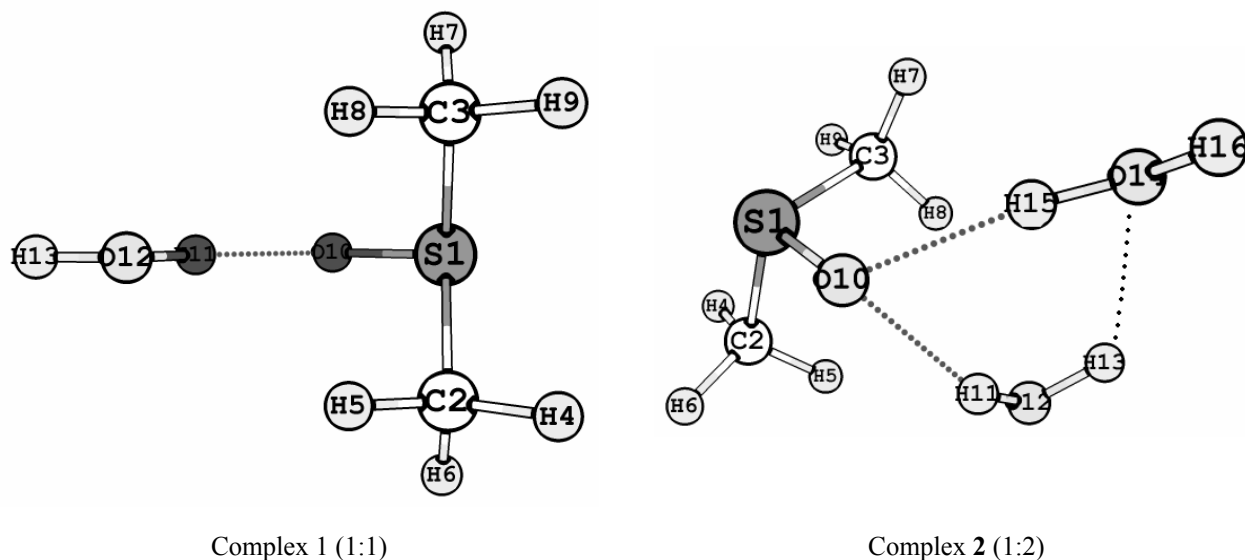


Fig. 1. Optimized structures with B3LYP/6-311++G(d,p) calculations for the hydrogen-bonded: DMSO and one molecule H<sub>2</sub>O (Complex 1); DMSO and two molecules H<sub>2</sub>O (Complex 2):

Complex 1:  $R_{O_{10}\dots H_{11}}=1.822$  Å; Angles (°):  $H_{11}\dots O_{10}S_1=41.3$ ;  $O_{10}\dots H_{11}O_{12}=8.7$ .

Complex 2:  $R_{O_{10}\dots H_{15}}=1.851$  Å;  $R_{O_{10}\dots H_{11}}=1.981$  Å;  $R_{O_{14}\dots H_{13}}=2.436$  Å; Angles (°):  $H_{15}\dots O_{10}\dots H_{11}=72.7$ ;  $O_{10}\dots H_{15}O_{14}=161.2$ ;  $O_{10}\dots H_{11}O_{12}=152.7$ ;  $O_{14}\dots H_{13}O_{12}=122.1$ ;  $H_{15}\dots O_{10}S_1=124.0$ ;  $H_{11}\dots O_{10}S_1=40.1$ .

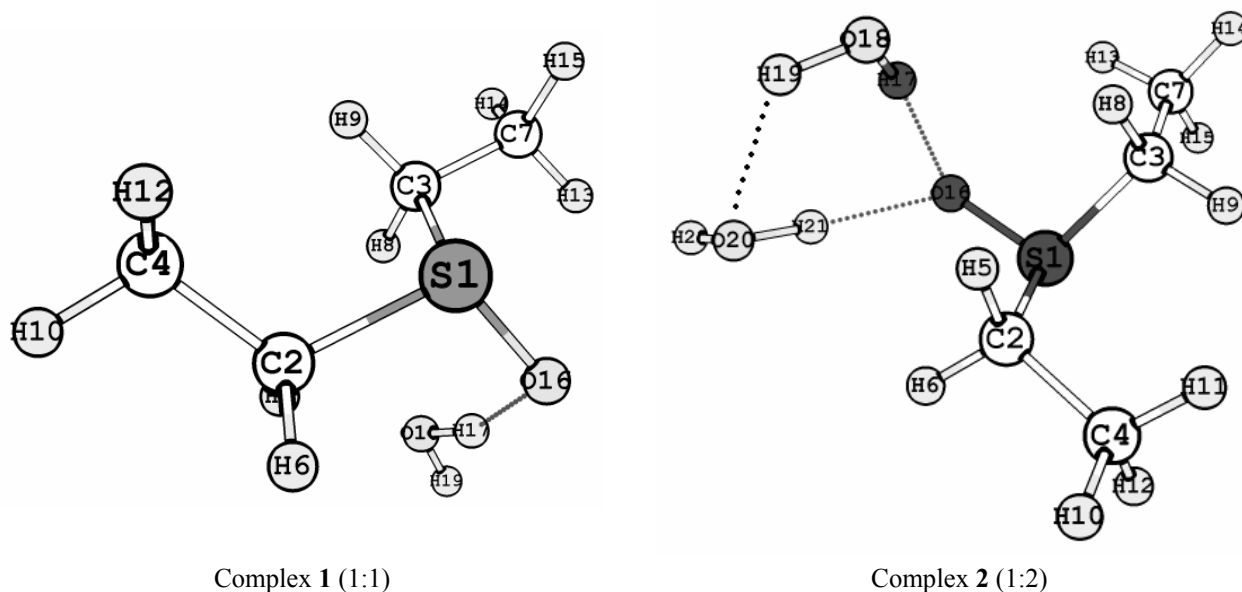


Fig. 2. Optimized structures with B3LYP/6-311++G(d,p) calculations for the hydrogen-bonded: DESO and one molecule H<sub>2</sub>O (Complex 1); DESO and two molecules H<sub>2</sub>O (Complex 2):

Complex 1:  $R_{O_{16}\dots H_{17}}=1.811$  Å; Angles (°):  $H_{17}\dots O_{16}S_1=31.1$ ;  $O_{16}\dots H_{17}O_{18}=158.3$ .

Complex 2:  $R_{O_{16}\dots H_{17}}=1.961$  Å;  $R_{O_{16}\dots H_{21}}=1.842$  Å;  $R_{O_{20}\dots H_{19}}=2.460$  Å; Angles (°):  $H_{19}\dots O_{20}H_{21}=83.7$ ;  $H_{19}O_{18}\dots O_{20}=123.0$ ;  $H_{17}\dots O_{16}\dots H_{21}=73.8$ ;  $O_{18}H_{17}\dots O_{16}=156.3$ ;  $O_{16}\dots H_{21}O_{20}=161.9$ ;  $H_{17}\dots O_{16}S_1=29.9$ ;  $H_{21}\dots O_{16}S_1=31.3$ .

The density functional (DFT) calculations in this work were carried out in the framework of Kohn-Sham density-functional theory [18] (DFT) with the nonlocal three-parameter gradient-corrected exchange-correlation functional of Becke and Lee, Yang and Parr including partially exact HF-exchange (B3LYP) [19].

The dissociation energy is used for the estimation of the stability of the hydrogen-bonded systems between two and more partners. The supermolecular variation method determines dissociation energy ( $\Delta E$ ) as a difference between the energy of the complex and the energies of the isolated molecules:

$$\Delta E = E_{\text{com.}} - (E_1 + E_2 + E_3 \dots) \quad (1)$$

where  $E_1, E_2, E_3 \dots$  are the energies of the isolated monomers in their own basis set and  $E_{\text{com.}}$  is the energy of the complex.

The supermolecular approach is theoretically able to provide dissociation energy at any accuracy, however, only if a sufficiently large basis set and a sufficiently high level of correlation is used. For the exact determination of the interaction energy in the supermolecular approach the consideration of the zero-point energies is very important.

The zero-point vibrational energy correction for the studied complexes can be defined as a difference between the calculated zero-point vibrational energy of the complex and the zero-point energies of the monomers:

$$\Delta E_{\text{zp vib}} = E_{\text{zp vib.}}(\text{com.}) - (E_{\text{zp vib}}(1) + E_{\text{zp vib}}(2) + E_{\text{zp vib}}(3) \dots) \quad (2)$$

The dissociation energies, uncorrected and corrected with zero-point energy differences are calculated by *ab initio* and DFT calculations with different basis sets.

The MP2 method for different basis sets (6-31G(d,p); 6-311++G(d,p)) is used in this study in order to estimate the MP2 correlation contribution to the dissociation energy for the hydrogen-bonded systems dimethylsulfoxide (DMSO)–water (1:1, 1:2) and diethylsulfoxide (DESO)–water (1:1, 1:2) (See Figs. 1 and 2). The MP2 correlation contribution  $\delta E(\text{MP2})$  to MP2 dissociation energy is:

$$\delta E(\text{MP2}) = \Delta E(\text{MP2}) - \Delta E(\text{SCF}) \quad (3)$$

where  $\Delta E(\text{MP2})$  is the dissociation energy, calculated at the MP2 level, and  $\Delta E(\text{SCF})$  is the dissociation energy, calculated at the SCF level.

## RESULTS AND DISCUSSION

### *Structures and stability*

In order to establish the most stable structures of the hydrogen-bonded hydrogen-bonded systems dimethylsulfoxide (DMSO)–water (1:1, 1:2) and diethylsulfoxide (DESO)–water (1:1, 1:2) full geometry optimization have been performed by *ab initio* and DFT (B3LYP) calculations with basis sets: 6-31G(d,p) and 6-311++G(d,p) using the GAUSSIAN 98 series of programs [17]. On Figs. 1 and 2 are shown the optimized structures of the complexes **1** and **2** with B3LYP/6-311++G(d,p) calculations. As can be seen the hydrogen bonding between two water molecules and DMSO, and DESO molecules leads to the formation of cyclic structures (Figs. 1 and 2, complexes **2**), while the

hydrogen-bonded systems of one water molecule with DMSO and DESO are open (Figs. 1 and 2, complexes **1**).

The dissociation energies, uncorrected and corrected with zero-point energy differences for the studied hydrogen-bonded systems of one and two water molecules with DMSO and DESO (complexes 1:1 and 1:2) are calculated by *ab initio* and DFT calculations with different basis sets. The results from the calculations are presented in Table 1. As can be seen from the data of  $\Delta E$  (uncorrected and corrected with  $\Delta E(\text{zp vib})$ ) the values of the dissociation energy calculated with *ab initio* SCF and MP2 level are different. The main cause for this effect is the MP2 correlation contribution to the dissociation energy ( $\delta E(\text{MP2})$ ). The calculated values of the dissociation energy as well as of the MP2 correlation contribution to the dissociation energy for the hydrogen-bonded complexes of two water molecules with DMSO and DESO molecules (complexes 1:2) are approximately twice as much in comparison with the values calculated at the same basis set for the hydrogen-bonded complexes 1:1. In all cases, the complexes of water with DESO are more stable than the complexes of water with DMSO. On Figs. 1 and 2 is given the description of the full characteristics of hydrogen bonds with lengths and angles of all hydrogen-bonded bridges (distance between donor and acceptor of proton).

### *Vibrational spectra*

It is known from previous studies [1–8] on the hydrogen-bonded complexes that the hydrogen bonding leads to the substantial changes in the vibrational characteristics of the stretching vibrations for the monomer bonds involved in the hydrogen bonding.

The changes in the vibrational frequencies and infrared intensities of the monomers characterizing their interactions have been evaluated by *ab initio* and DFT calculations employing the GAUSSIAN 98 series of programs [17].

The predicted values of the vibrational characteristics are presented in Tables 2 and 3 together with the detailed description of the normal modes based on the potential energy distribution (PED) obtained from MP2/6-311++G(d,p) calculations.

The changes in the vibrational characteristics arising from the hydrogen bonding of DMSO and DESO molecules with one and two water molecules have been estimated. The predicted frequency shift is:

$$\Delta \nu_i = \nu_i^{\text{complex}} - \nu_i^{\text{monomer}} \quad (4)$$

The changes in the infrared intensities ( $\Delta A_i$ ) upon hydrogen bond formation are also estimated using

ab initio and DFT calculations.

$$\Delta A_i = A_i^{\text{complex}} - A_i^{\text{monomer}} \quad (5)$$

The predicted changes in the vibrational frequencies and infrared intensities are shown in Tables 2 and 3. As it was noted the hydrogen bonding leads to the substantial changes in the vibrational characteristics of the stretching vibrations for the monomer

bonds involved in the hydrogen bonding. The data presented in Tables 2 and 3 show that for the complexes studied the hydrogen bonds are formed between O–H group from water molecule and S=O group from DMSO and DESO molecules. For the complexes of two water molecules with DMSO and DESO the weak hydrogen bonds are predicted between water molecules: O<sub>14</sub>...H<sub>13</sub> and O<sub>20</sub>...H<sub>19</sub>.

**Table 1.** Dissociation energies  $\Delta E$  (uncorrected and corrected), MP2 correlation contribution to the dissociation energy  $\delta E(\text{MP2})$  and zero-point energy differences  $\Delta E_{\text{zpv}}$  in kcal/mol for the hydrogen-bonded complexes DMSO–H<sub>2</sub>O (1:1; 1:2) and DESO–H<sub>2</sub>O (1:1; 1:2).

Basis set	$\Delta E_{\text{uncorr}}$		$\Delta E_{\text{zpv}}$		$\Delta E_{\text{corr}}$		$\delta E^{\text{MP2}}$	
	DMSO–H <sub>2</sub> O (1:1) <sup>a</sup> , (1:2) <sup>b</sup>	DESO–H <sub>2</sub> O (1:1) <sup>a</sup> , (1:2) <sup>b</sup>	DMSO–H <sub>2</sub> O (1:1) <sup>a</sup> , (1:2) <sup>b</sup>	DESO–H <sub>2</sub> O (1:1) <sup>a</sup> , (1:2) <sup>b</sup>	DMSO–H <sub>2</sub> O (1:1) <sup>a</sup> , (1:2) <sup>b</sup>	DESO–H <sub>2</sub> O (1:1) <sup>a</sup> , (1:2) <sup>b</sup>	DMSO–H <sub>2</sub> O (1:1) <sup>a</sup> , (1:2) <sup>b</sup>	DESO–H <sub>2</sub> O (1:1) <sup>a</sup> , (1:2) <sup>b</sup>
SCF/	–10.20965 <sup>a</sup>	–10.37462 <sup>a</sup>	2.26955 <sup>a</sup>	2.21640 <sup>a</sup>	–7.94005 <sup>a</sup>	–8.15822 <sup>a</sup>	-	-
6-31G(d,p)	–19.15788 <sup>b</sup>	–19.33295 <sup>b</sup>	4.65554 <sup>b</sup>	4.50172 <sup>b</sup>	–14.50234 <sup>b</sup>	–14.83123 <sup>b</sup>	-	-
MP2/	–13.30635 <sup>a</sup>	–13.64866 <sup>a</sup>	2.22666 <sup>a</sup>	2.35560 <sup>a</sup>	–11.07969 <sup>a</sup>	–11.29306 <sup>a</sup>	–3.13960 <sup>a</sup>	–3.27404 <sup>a</sup>
6-31G(d,p)	–25.39533 <sup>b</sup>	–25.83961 <sup>b</sup>	5.17173 <sup>b</sup>	4.78348 <sup>b</sup>	–20.22360 <sup>b</sup>	–21.05613 <sup>b</sup>	–6.23745 <sup>b</sup>	–6.50665 <sup>b</sup>
B3LYP/	–12.89533 <sup>a</sup>	–12.94699 <sup>a</sup>	2.49229 <sup>a</sup>	2.10752 <sup>a</sup>	–10.40304 <sup>a</sup>	–10.83947 <sup>a</sup>	-	-
6-31G(d,p)	–24.40386 <sup>b</sup>	–24.71574 <sup>b</sup>	5.30508 <sup>b</sup>	5.19523 <sup>b</sup>	–19.09878 <sup>b</sup>	–19.52051 <sup>b</sup>	-	-
SCF/	–8.76556 <sup>a</sup>	–8.92809 <sup>a</sup>	2.2064 <sup>a</sup>	2.03070 <sup>a</sup>	–6.55916 <sup>a</sup>	–6.89739 <sup>a</sup>	-	-
6-311++G(d,p)	–15.92620 <sup>b</sup>	–16.25602 <sup>b</sup>	4.31929 <sup>b</sup>	4.13148 <sup>b</sup>	–11.60691 <sup>b</sup>	–12.12454 <sup>b</sup>	-	-
MP2/	–11.17922 <sup>a</sup>	–11.31106 <sup>a</sup>	2.27932 <sup>a</sup>	2.22151 <sup>a</sup>	–8.89990 <sup>a</sup>	–9.08955 <sup>a</sup>	–2.41366 <sup>a</sup>	–2.38297 <sup>a</sup>
6-311++G(d,p)	–20.21712 <sup>b</sup>	–20.54988 <sup>b</sup>	4.49494 <sup>b</sup>	4.35326 <sup>b</sup>	–15.72218 <sup>b</sup>	–16.19662 <sup>b</sup>	–4.29092 <sup>b</sup>	–4.29386 <sup>b</sup>
B3LYP/	–9.92093 <sup>a</sup>	–9.94363 <sup>a</sup>	2.30743 <sup>a</sup>	2.09343 <sup>a</sup>	–7.61350 <sup>a</sup>	–7.85020 <sup>a</sup>	-	-
6-311++G(d,p)	–17.36322 <sup>b</sup>	–17.52736 <sup>b</sup>	4.47088 <sup>b</sup>	4.41286 <sup>b</sup>	–12.89234 <sup>b</sup>	–13.11450 <sup>b</sup>	-	-

a - Complexes (1:1); b - Complexes (1:2).

**Table 2.** Calculated vibrational characteristics ( $\nu$  in cm<sup>–1</sup>,  $A$  in km·mol<sup>–1</sup>) and changes in the vibrational characteristics ( $\Delta\nu$  in cm<sup>–1</sup>,  $\Delta A$  in km·mol<sup>–1</sup>) from monomers to a complex for the hydrogen-bonded systems DMSO–H<sub>2</sub>O (1:1) and DMSO-2H<sub>2</sub>O (1:2).

Mode	MP2/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
	1:1		1:2		1:1		1:2	
	$\nu_i^{\text{compl.}}/\Delta\nu_i$	$A_i^{\text{compl.}}/\Delta A_i$	$\nu_i^{\text{compl.}}/\Delta\nu_i$	$A_i^{\text{compl.}}/\Delta A_i$	$\nu_i^{\text{compl.}}/\Delta\nu_i$	$A_i^{\text{compl.}}/\Delta A_i$	$\nu_i^{\text{compl.}}/\Delta\nu_i$	$A_i^{\text{compl.}}/\Delta A_i$
$\nu(\text{O}_{12}\text{--H}_{11})$	3591/–282	443.9/430.8	3747/–126	221.3/208.2	3498/–319	483/473.9	3680/–137	243.8/234.6
$\nu(\text{O}_{12}\text{--H}_{13})$	3983/–12	72.6/23.6	3930/–65	103.8/42.9	3892/–31	60.4/3.4	3831/–95	110.6/53.5
$\nu(\text{O}_{14}\text{--H}_{15})$	-	-	3648/–225	446.1/432.9	-	-	3596/–221	432.9/423.7
$\nu(\text{O}_{14}\text{--H}_{16})$	-	-	3962/–33	98.8/37.9	-	-	3889/–34	87.9/30.8
59 $\nu(\text{C}_2\text{--H}_6)$ +41 $\nu(\text{C}_2\text{--H}_5)$	3213/22	1.1/–0.6	3216/25	1.0/–0.6	3150/15	0.9/0.8	3153/18	0.4/0.3
69 $\nu(\text{C}_3\text{--H}_8)$ +26 $\nu(\text{C}_3\text{--H}_7)$	3203/0	0.9/–0.7	3208/5	0.8/–0.8	3149/1	1.3/–0.2	3155/7	0.9/–0.5
49 $\nu(\text{C}_2\text{--H}_4)$ +29 $\nu(\text{C}_2\text{--H}_5)$ +19 $\nu(\text{C}_2\text{--H}_6)$	3191/112	1.3/–4.4	3190/111	1.2/–4.4	3142/104	4.4/–0.7	3145/107	2.4/–2.7
49 $\nu(\text{C}_3\text{--H}_9)$ +45 $\nu(\text{C}_3\text{--H}_7)$	3183/–12	1.5/–4.7	3188/–17	0.4/–5.8	3139/–9	0.6/–2.8	3141/–7	0.4/–2.9
48 $\nu(\text{C}_2\text{--H}_4)$ +28 $\nu(\text{C}_2\text{--H}_5)$ +21 $\nu(\text{C}_2\text{--H}_6)$	3078/–23	9.9/9.1	3078/–23	9.4/8.7	3041/–98	12.6/1.6	3044/–95	11.1/0.1
43 $\nu(\text{C}_3\text{--H}_9)$ +27 $\nu(\text{C}_3\text{--H}_7)$ +26 $\nu(\text{C}_3\text{--H}_8)$	3071/–14	6.7/0.4	3073/–12	4.2/–2.0	3038/–2	4.6/–4.8	3041/1	2.7/–6.5
$\nu(\text{S--O})$	1071/–24	112.1/6.7	1053/–41	133.6/35.2	1030/–21	112.1/3.8	1024/–27	92.8/43.2
$\nu(\text{S--C})$	701/–19	4.9/–12.8	704/–16	5.5/–12.3	631/8	4.9/–4.0	667/44	7.2/–1.7
$\tau(\text{O}_{12}\text{H}_{11}\dots\text{O}_{10}\text{S}_1)$	704	69.5	719	114.1	698	107.5	698	145.3
$\delta(\text{O}_{12}\text{H}_{11}\dots\text{O}_{10})$	442	134.3	462	70.1	478	158.8	452	56.6
$\tau(\text{O}_{14}\dots\text{H}_{13}\text{O}_{12}\text{H}_{11})$	-	-	356	61.1	-	-	341	61.3
$\delta(\text{H}_{15}\text{O}_{14}\dots\text{H}_{13})$	-	-	247	55.7	-	-	198	46.7
$\nu(\text{O}_{10}\dots\text{H}_{11})$	212	17.8	203	23.8	209	11.3	195	12.6
$\nu(\text{O}_{10}\dots\text{H}_{15})$	-	-	178	1.1	-	-	151	1.4
$\delta(\text{H}_{11}\dots\text{O}_{10}\text{S}_1)$	106	28.8	101	24.9	98	24.7	88	22.4
$\nu(\text{O}_{14}\dots\text{H}_{13})$	-	-	85	3.8	-	-	62	4.6

**Table 3.** Calculated vibrational characteristics ( $\nu$  in  $\text{cm}^{-1}$ ,  $A$  in  $\text{km}\cdot\text{mol}^{-1}$ ) and changes in the vibrational characteristics ( $\Delta\nu$  in  $\text{cm}^{-1}$ ,  $\Delta A$  in  $\text{km}\cdot\text{mol}^{-1}$ ) from monomers to a complex for the hydrogen-bonded systems DESO–H<sub>2</sub>O (1:1) and DESO–2H<sub>2</sub>O (1:2).

Mode	MP2/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
	1:1		1:2		1:1		1:2	
	$\nu_i^{\text{compl}}/\Delta\nu_i$	$A_i^{\text{compl}}/\Delta A_i$	$\nu_i^{\text{compl}}/\Delta\nu_i$	$A_i^{\text{compl}}/\Delta A_i$	$\nu_i^{\text{compl}}/\Delta\nu_i$	$A_i^{\text{compl}}/\Delta A_i$	$\nu_i^{\text{compl}}/\Delta\nu_i$	$A_i^{\text{compl}}/\Delta A_i$
$\nu(\text{O}_{18}\text{--H}_{17})$	3583/–290	471.7/458.6	3753/–120	228.4/215.3	3479/–338	537.1/527.8	3669/–148	293.3/284.1
$\nu(\text{O}_{18}\text{--H}_{19})$	3933/–62	80.2/19.3	3890/–105	134.3/73.4	3890/–33	59.4/2.3	3832/–91	109.9/52.9
$\nu(\text{O}_{20}\text{--H}_{21})$	-	-	3670/–203	444.7/431.6	-	-	3579/–238	476.3/467.1
$\nu(\text{O}_{20}\text{--H}_{22})$	-	-	3951/–44	109.9/19.0	-	-	3887/–36	87.1/30.1
$56\nu(\text{C}_7\text{--H}_{13})+27\nu(\text{C}_1\text{--H}_{15})$	3181/–9	8.1/3.5	3183/–6	7.4/2.8	3122/3	12.3/–2.2	3124/5	8.9/–5.6
$48\nu(\text{C}_4\text{--H}_{11})+12\nu(\text{C}_4\text{--H}_{12})$	3174/–3	13.2/–1.2	3179/2	10.8/–3.6	3118/2	9.2/–11.3	3123/9	7.6/–12.8
$59\nu(\text{C}_4\text{--H}_{10})+38\nu(\text{C}_4\text{--H}_{12})$	3168/102	9.6/–3.2	3173/107	9.6/–3.2	3108/76	0.8/–15.3	3108/76	1.1/–15.0
$56\nu(\text{C}_7\text{--H}_{14})+31\nu(\text{C}_7\text{--H}_{15})$	3164/–3	10.2/–10.8	3161/–6	4.4/–16.6	3098/64	17.1/–8.1	3102/68	17.7/–7.5
$41\nu(\text{C}_3\text{--H}_9)+21\nu(\text{C}_3\text{--H}_8)$	3157/–19	2.9/–11.1	3157/–19	6.5/–7.4	3094/54	13.0/–4.7	3097/57	17.7/0.1
$31\nu(\text{C}_2\text{--H}_6)+18\nu(\text{C}_2\text{--H}_5)$	3153/51	2.5/–3.7	3155/53	1.8/–4.5	3092/39	10.4/–3.2	3096/43	2.3/–4.2
$+26\nu(\text{C}_4\text{--H}_{11})$								
$61\nu(\text{C}_2\text{--H}_5)+36\nu(\text{C}_2\text{--H}_6)$	3089/–80	2.8/–7.6	3091/–78	1.2/–9.2	3057/–44	1.9/–12.8	3062/–39	0.0/–14.6
$52\nu(\text{C}_3\text{--H}_8)+38\nu(\text{C}_3\text{--H}_9)$	3079/–66	19.3/18	3081/–64	17.2/16.0	3047/–43	14.6/12.8	3047/–43	10.8/8.9
$30\nu(\text{C}_4\text{--H}_{12})+28\nu(\text{C}_4\text{--H}_{11})$	3077/–73	5.3/–9.3	3079/–71	12.8/–1.7	3035/–57	23.7/5.0	3037/–55	20.8/6.1
$+26\nu(\text{C}_4\text{--H}_{10})$								
$40\nu(\text{C}_7\text{--H}_{14})+33\nu(\text{C}_7\text{--H}_{15})$	3075/–82	19.4/6.9	3077/–80	10.1/–2.4	3032/–62	17.8/2.4	3036/–58	17.6/2.23
$+26\nu(\text{C}_7\text{--H}_{13})$								
$\nu(\text{S--O})$	1032/–28	104.9/34.0	989/–71	133.1/62.3	984/–30	60.8/–10.1	955/–59	158.5/87.5
$\nu(\text{S--C})$	724/63	45.6/36.8	727/66	58.1/49.2	657/5	33.7/11.5	702/50	46.8/27.6
$\tau(\text{O}_{18}\text{H}_{17}\dots\text{O}_{16}\text{S}_1)$	692	61.3	459	55.7	697	102.7	442	63.0
$\delta(\text{H}_{21}\text{O}_{20}\dots\text{H}_{19})$	-	-	695	118.1	-	-	702	175.2
$\delta(\text{O}_{16}\dots\text{H}_{17}\text{O}_{18})$	458	110.6	616	204.1	458	153.5	649	194.7
$\tau(\text{O}_{20}\dots\text{H}_{19}\text{O}_{18}\text{H}_{17})$	-	-	398	95.9	-	-	367	112.1
$\tau(\text{O}_{16}\dots\text{H}_{21}\text{O}_{20}\text{H}_{22})$	-	-	356	61.1	-	-	341	61.3
$\nu(\text{O}_{16}\dots\text{H}_{21})$	-	-	304	28.1	-	-	335	24.8
$\tau(\text{H}_{19}\text{O}_{18}\text{H}_{17}\dots\text{O}_{16})$	272	114.4	150	91.1	253	111.1	156	125.3
$\nu(\text{O}_{16}\dots\text{H}_{17})$	240	31.5	202	30.1	243	20.2	257	24.1
$\delta(\text{S}_1\text{O}_{16}\dots\text{H}_{17})$	109	13.1	137	8.1	91	18.4	146	10.5
$\delta(\text{O}_{20}\dots\text{H}_{19}\text{O}_{18})$	-	-	133	3.4	-	-	138	10.5
$\nu(\text{O}_{20}\dots\text{H}_{19})$	-	-	73	3.4	-	-	146	0.5

### Changes in the vibrational characteristics of the stretching O–H modes

As can be seen from the results in Tables 2 and 3, the predicted changes in the vibrational characteristics of the stretching O–H vibrations are the most considerable. For the complexes of DMSO with one and two water molecules (Table 2) the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) calculations predict considerable changes in the vibrational frequencies and IR intensities for the stretching vibrations  $\nu(\text{O}_{12}\text{--H}_{11})$  and  $\nu(\text{O}_{14}\text{--H}_{15})$ . The predicted frequency shifts for the stretching vibrations  $\nu(\text{O}_{12}\text{--H}_{11})$  in the complex **1** (1:1) are in the range of  $-282\text{ cm}^{-1}$  to  $-319\text{ cm}^{-1}$  and for  $\nu(\text{O}_{14}\text{--H}_{15})$  in the complex **2** (1:2) are from  $-225$  to  $-221\text{ cm}^{-1}$ . The IR intensity of these vibrations increases dramatically upon hydrogen bonding. In the same time the changes in the vibrational characteristics for the vibrations  $\nu(\text{O}_{12}\text{--H}_{13})$  and  $\nu(\text{O}_{14}\text{--H}_{16})$  are negligibly. Bearing in mind these results it could be concluded that the stretching vibrations  $\nu(\text{O}_{12}\text{--H}_{11})$

and  $\nu(\text{O}_{14}\text{--H}_{15})$  (in the complex 1:2) taking part in the hydrogen bonding with DMSO, while the vibrations  $\nu(\text{O}_{12}\text{--H}_{13})$  (in the complex 1:1) and  $\nu(\text{O}_{14}\text{--H}_{16})$  (in the complex 1:2) are free from the hydrogen bonding.

For the hydrogen-bonded complexes of one and two water molecules with DESO the predicted changes in the vibrational characteristics for the stretching O–H vibrations show that the bonds  $\text{O}_{18}\text{--H}_{17}$  and  $\text{O}_{20}\text{--H}_{21}$  are taking part in the hydrogen bonding. Their frequencies are shifted to lower values more than  $-200\text{ cm}^{-1}$ . The IR intensities of these vibrations increase dramatically in the complexes. In the same time the vibrational characteristics of the modes  $\nu(\text{O}_{18}\text{--H}_{19})$  (in the complex 1:1) and  $\nu(\text{O}_{20}\text{--H}_{22})$  (in the complex 1:2) are changed negligibly. These vibrations are free from the hydrogen bonding.

### Changes in the vibrational characteristics of the stretching S=O modes

As can be seen from the optimized structures of

the hydrogen-bonded systems between one and two water molecules with DMSO and DESO, shown on Figs. 1 and 2, the hydrogen bonds are formed between O–H group from water molecules and S=O group from DMSO and DESO. The experimental evidences based on the Raman and FT IR ATR studies of these hydrogen-bonded systems [16] also confirm that the S=O group is taking part in the hydrogen bonding: “The lower frequency peak near  $1010\text{ cm}^{-1}$  both in the Raman and IR spectra, whose intensity of which increases with dilution with a simultaneous shift to lower frequency, is attributed to the  $\nu(\text{SO})$  directly involved in H-bonds with water molecules only”. Bearing in mind this statement the changes in the S=O stretching vibrations upon hydrogen bonding are studied here by *ab initio* and DFT calculations with 6-311++G(d,p) basis set.

It was established for the hydrogen-bonded systems between one and two water molecules and DMSO (see Table 2) that the stretching vibration  $\nu(\text{S=O})$  is shifted in the complexes (1:1; 1:2) to lower frequencies of about  $24\text{ cm}^{-1}$  for the complex **1** (1:1) and of about  $41\text{ cm}^{-1}$  for the complex **2** (1:2). The experimentally observed frequency shift [11] for this vibration is  $8\text{ cm}^{-1}$ . The calculations show that the IR intensity of the stretching vibration  $\nu(\text{S=O})$  increases in the complexes. As a consequence the double character of the S=O bond decreases, becoming more polar:  $\text{S=O} \leftrightarrow \text{S}^+ - \text{O}^-$ .

For the hydrogen-bonded systems of one and two water molecules with DESO (see Table 3) the observed appearances are the same as for the systems DMSO–H<sub>2</sub>O (1:1; 1:2) only at higher extent. The predicted frequencies shifts by *ab initio* and DFT calculations at 6-311++G(d,p) basis set of the stretching vibration  $\nu(\text{S=O})$  for the hydrogen-bonded systems DESO–H<sub>2</sub>O (1:1; 1:2) are larger and the IR intensity increases in these complexes at higher extent. It can conclude that the water-sulfur dioxide interactions in the hydrogen-bonded systems DESO–H<sub>2</sub>O (1:1; 1:2) are stronger than in the DMSO–H<sub>2</sub>O (1:1; 1:2) systems.

#### *Changes in the vibrational characteristics of the stretching C–H modes*

The predicted values of the vibrational characteristics for the hydrogen-bonded systems of one and two water molecules with DMSO and DESO, presented in Tables 2 and 3 show that for the stretching C–H modes they are also sensitive to the complexations.

The potential energy distribution (PED), based on the MP2/6-311++G(d,p) calculations shows that for the hydrogen-bonded systems DMSO–H<sub>2</sub>O (1:1; 1:2) the  $\nu(\text{C}_2\text{–H})$  vibrations are more sensitive to the

complexation than the  $\nu(\text{C}_3\text{–H})$  vibrations. In agreement with the experiment [16] the  $\nu(\text{C}_2\text{–H})$  vibrations are shifted to higher frequency more than  $100\text{ cm}^{-1}$  by water dilution and their IR intensities are changed negligibly.

The similar changes are observed for the stretching vibrations  $\nu(\text{C}_2\text{–H})$  and  $\nu(\text{C}_4\text{–H})$  of the hydrogen-bonded systems DESO–H<sub>2</sub>O (1:1; 1:2) (see Table 3). Bearing in mind the experimental results from Raman and FT IR ATR spectra of these hydrogen-bonded systems the authors [16] supposed, “This effect could be due to the breaking of the hydrogen bonds CH...OS, the existence of which has been evidenced in both pure liquid DMSO and DESO”.

The  $\nu(\text{C}_3\text{–H})$  vibrations for the hydrogen-bonded systems DMSO–H<sub>2</sub>O (1:1; 1:2) and  $\nu(\text{C}_3\text{–H})$ , and  $\nu(\text{C}_7\text{–H})$  for the hydrogen-bonded systems DESO–H<sub>2</sub>O (1:1; 1:2) are shifted to lower frequency in the complexes. These bonds become weaker upon hydrogen bonding.

#### *Intermolecular vibrations*

The results from potential energy distribution (PED), obtained from MP2/6-311++G(d,p) calculations show that the hydrogen bonding of one and two water molecules with DMSO and DESO molecules leads to arising of the intermolecular vibrations (see Tables 2 and 3).

The stretching intermolecular vibrations for the hydrogen-bonded system water–DMSO (1:1; 1:2) are predicted with B3LYP/6-311++G(d,p) calculations in the range: from  $62\text{ cm}^{-1}$  to  $195\text{ cm}^{-1}$  (see Table 2). For the complexes water–DESO (1:1; 1:2) the predicted stretching  $\nu(\text{O...H})$  vibrations are: from  $146\text{ cm}^{-1}$  to  $335\text{ cm}^{-1}$  (see Table 3). The calculated IR intensities of the stretching intermolecular vibrations for the complexes DMSO–H<sub>2</sub>O (1:1; 1:2) and DESO–H<sub>2</sub>O (1:1; 1:2) are low.

Having in mind the PED distribution, the torsional intermolecular vibrations for the studied hydrogen-bonded systems are in the range  $156\text{--}698\text{ cm}^{-1}$  with medium IR intensities.

The predicted frequencies for the deformation vibrations are at lower wavenumbers in comparison with the frequencies of the torsional intermolecular vibrations. Their IR intensities are higher in comparison with the IR intensities of the torsional intermolecular vibrations for the studied hydrogen-bonded systems.

## CONCLUSIONS

The structures, stability and vibrational spectra of the hydrogen-bonded complexes of one and two

water molecules with DMSO and DESO molecules have been studied using *ab initio* MP2 and DFT calculations. The main results of the study are:

- The hydrogen bonding of two water molecules with DMSO and DESO molecules leads to the formation of cyclic structures, while the hydrogen-bonded systems of one water molecule with DMSO and DESO are open.

- It was established that the hydrogen-bonded systems DESO–water (1:1, 1:2) are more stable than the systems DMSO–water (1:1, 1:2).

- The predicted changes in the vibrational characteristics for the stretching S=O and C–H vibrations in the complexes DMSO–H<sub>2</sub>O (1:1; 1:2) and DESO–H<sub>2</sub>O (1:1; 1:2) are in good agreement with the experiment. Having in mind this result, it could be concluded that the optimized structures are reliable.

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ВОДОРОДНО-СВЪРЗАНИ СИСТЕМИ НА ВОДА С ДИМЕТИЛ- И ДИЕТИЛСУЛФОКСИДИ.  
ТЕОРЕТИЧНО ИЗСЛЕДВАНЕ НА СТРУКТУРИ, СТАБИЛНОСТ И ВИБРАЦИОННИ СПЕКТРИ

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(Резюме)

Изследвани са структурните и вибрационните характеристики на водородно-свързаните системи диметил-сулфоксид (ДМСО)–вода (1:1, 1:2) и диетилсулфоксид (ДЕСО)–вода (1:1, 1:2) посредством *ab initio* и ТФП пресмятания с различни базисни набори. Пресмятанията показват, че оптимизираните структури на изследваните системи 1:2 са циклични, докато оптимизираните структури на водородно-свързаните системи 1:1 са линейни. Коригираните стойности на енергията на свързване за водородно-свързаните системи са изчислени посредством *ab initio* и ТФП пресмятания с различни базисни набори с цел да се оцени тяхната стабилност. Установено е, че водородно-свързаните системи ДЕСО–вода (1:1, 1:2) са по-стабилни от системите ДМСО–вода (1:1, 1:2). Изследвано е влиянието на водородното свързване върху свойствата на мономерите (H<sub>2</sub>O, ДМСО и ДЕСО). Установено е, че водородното свързване води до промени във вибрационните характеристики (вибрационни честоти и интензивности на ивиците) на мономерите. Предсказаните вибрационни характеристики за изследваните водородно-свързаните системи са в много добро съгласие с експериментално наблюдаваните.