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Density Functional Theory Study of the Hydrogen Bonding Interaction of Complexes of Dimethyl Sulfoxide with Water

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The hydrogen bonding of complexes formed between dimethyl sulfoxide and water molecule have been investigated in the present study using density functional theory and second-order moller-plesset perturbation (MP2) method at varied basis set levels from 6-31g to 6-311++g (2d,2p). Two reasonable geometries on the potential energy hypersurface of DMSO and H_2O system are considered. The solution phase studies are also carried out using the Onsager reaction field model with a range of dielectric constants at the B3LYP/6-311++g (d,p) level.

Key Words: Density functional theory, Hydrogen bond, DMSO-H_2O.

INTRODUCTION

Aqueous dimethyl sulfoxide (DMSO) solutions are used in a wide variety of biological and medical application[1]. Dimethyl sulfoxide penetrates most membranes and human skin without permanent disruption of the local structure. The behaviour of aqueous DMSO has attracted the interest of many researchers. For the simple mixtures of DMSO and H_2O, a combination of strong hydrogen bonding interactions and hydrophobic leads to remarkable non-ideal physical properties, such as decreased density, longer rotational reorientation relaxation times, lower diffusion coefficients and negative changes in molar enthalpy and volume[2,3]. The mechanism of the unusual physical properties of DMSO-H_2O mixtures is closely related to the hydrogen bond interactions and the hydrophobic associations between molecules. Some extensive theoretical and experimental works have been carried out to explore the roles of them for DMSO-H_2O systems in gas and condense phases[4-6].

While there is sufficient evidence[7] that density functional theory (DFT) provides an accurate description of the electronic and structural properties of solids, interfaces and small molecules. Relatively little is known about the systematic performance of DFT application to molecular associates. To further access the reliability of DFT application to this field of chemistry, in this paper, we discuss the structure and bonding of the 1:1 DMSO-H_2O complex between DMSO and H_2O as obtained by high level *ab initio* calculations. We thus report geometry optimization and calculated bonding energies between DMSO and H_2O for a variety of theoretical models and basis sets. The stable structure found for complex is not entirely now and in fact, it has been obtained previously by explicit calculations. However, in the present paper, we put forward what we believe is now the most accurate results for the hydrogen bond interaction between DMSO and H_2O, as obtained from high-level calculations and systematic analysis of the theoretical results obtained.

In the second part, as compared with the isolated gas phase results, we pay some attention to the influence of solvent effects in both structure and stability of these hydrogen-bonded systems.

EXPERIMENTAL

In the present paper, a variety of theoretical methods have been used in the research, including the Hartree-Fock (HF), the second-order Moller-Plesset theory (MP2) as well as the hybrid density functional methods (B3LYP) in order to test the reliability of these methods to the hydrogen bonding systems.

For hydrogen bonding, it is expected that both diffuse and polarization functions may be necessary in the basis sets, we thus analyze the separate influence of the diffuse and polarization functions, the geometry optimization of DMSO-H_2O has been carried out using SCF, MP2 and B3LYP correlation methods with the 6-31g, 6-31g(d), 6-31+g (d), 6-311++g(d,p) and 6-311++g(2d,2p) basis sets along with analytic vibrational frequency calculations.

Interaction energies (ΔE_{int}) are calculated for the DMSO-H_2O hydrogen bond by taking the energy difference between the fragments and the complex.

The corrected E_{int} is given by

$$\Delta E = \Delta E_{int} + \Delta E_{bsse} + \Delta E_{zpe} \qquad (1)$$

ΔE_{zpe} is the zero point energy (ZPE) correction at the B3LYP/6-311++g(d,p) level and ΔE_{bsse} is the basis set superposition error (BSSE) correction estimated at the same level using the standard counterpoise method implemented in Gaussian 03[8].

RESULTS AND DISCUSSION

The structures of the super molecule will depend on the structures calculated for the DMSO and H_2O monomers. DMSO is a polyfunctional molecule with a highly polar S=O group and two hydrophobic CH_3 groups.

The calculated structures of DMSO and H_2O using DFT method at 6-311++g(d,p) and 6-311++g(2d,2p) basis sets are presented in Table-1. For comparison, results of MP2, HF at 6-311++(d,p) level and the experimentally determined structures are also given in Table-1. For simplicity, the results with 6-31g, 6-31g(d) and 6-31+g(d) are not listed.

A general observation from comparing the calculated and the experimental structural parameters is that all HF bond distances are slightly shorter than the experimental results. This may be due to the result of the neglect of the electron correction by HF theory. Considering all geometric parameters obtained with different theoretical model at varied basis sets, as expected, the 6-31g predicted the bond length in relatively in poor agreement with the experimental values. When polarization and diffuse functions are added, the results are improved. MP2 and B3LYP at 6-311++g(d,p) basis set level reproduced the experimental values most satisfactorily for the DMSO. For example, the bond lengths of the S-C and S=O bond are 1.835 and 1.514 Å calculated at the B3LYP/6-311++g(d,p) level, 1.807 and 1.508 Å at MP2/6-311++g(d,p) level and 1.502 Å at B3LYP/6-311++g(2d,2p) level and the corresponding experimental values[9] are 1.82 and 1.47 Å. As shown in Table-1, the Hartee-Fock bond distances are slightly shorter than experimental ones. When the basis set are enlarged to 6-311++g(2d,2p), the difference between the B3LYP calculated and experimental results may be negligible.

At all the *ab initio* and DFT (B3LYP) levels employed here, two structures for the complex were optimized. The structures optimized at B3LYP/6-311++g(d,p) level of both the complexes are shown in Fig. 1 and the most interesting geometrical parameters are listed in Table-2.

DW1

DW2
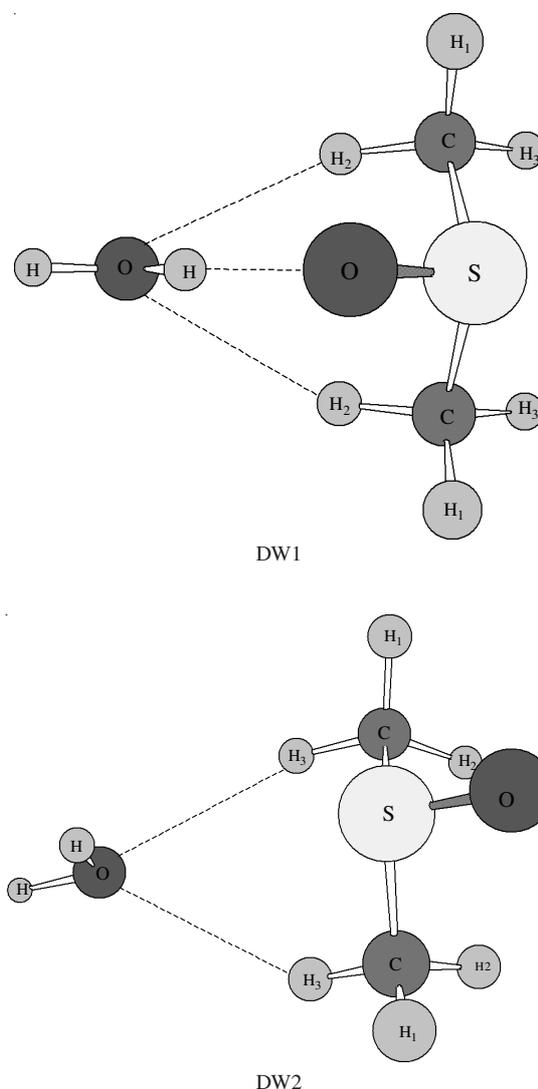
Fig. 1. Optimized DMSO-H_2O complexes in gas phase at the B3LYP/6-311++g(d,p) level

Parameters	B3LYP/6-311++g(d,p)	B3LYP/6-311++g(2d,2p)	HF/6-311++g(d,p)	MP2/6-311++g(d,p)	Expt[24]
		DMSO			
R_{S-C}	1.835	1.830	1.797	1.807	1.82
R_{C-H1}	1.090	1.087	1.082	1.091	1.08
R_{C-H2}	1.091	1.088	1.083	1.093	1.08
R_{C-H3}	1.092	1.089	1.084	1.093	1.08
$R_{S=O}$	1.514	1.502	1.486	1.508	1.47
$\angle H_1CS$	106.5	106.5	107.0	107.0	107.5
$\angle H_2CS$	109.1	108.8	109.3	108.7	107.5
$\angle H_3CS$	109.6	109.6	109.8	110.0	107.5
$\angle CSO$	106.8	106.7	106.3	106.7	106.7
		H_2O			
R_{O-H}	0.962	0.961	0.941	0.960	0.957
$\angle HOH$	105.0	105.1	106.2	103.9	104.5

TABLE-1
STRUCTURAL PARAMETERS CALCULATED FOR DMSO AND H_2O

TABLE-2
OPTIMIZED GEOMETRIC PARAMETERS OF THE DMSO-H₂O COMPLEX USING
DIFFERENT THEORETICAL MODELS (DISTANCES IN Å, ANGLES IN DEGREE)*

Method	DW1				DW2	
	R_{OD-HW}	R_{OW-HD}	α	β1	R_{OW-HD}	β2
B3LYP/6-31g	1.688	2.243	157.9	135.2	2.378	147.1
B3LYP/6-31g(d)	1.833	2.433	158.0	134.0	2.464	148.8
B3LYP/6-31+g(d)	1.827	2.536	156.5	131.2	2.659	126.3
B3LYP/6-311++g(d,p)	1.821	2.542	155.0	131.3	2.595	131.8
B3LYP/6-311++g(2d,2p)	1.845	2.575	158.9	131.8	2.875	119.4
HF/6-311++g(d,p)	1.911	2.753	156.1	130.5	2.724	130.3
MP2/6-311++g(d,p)	1.810	2.484	154.6	131.3	2.566	128.2

*OD-HW means O of DMSO hydrogen-bonded to H of water, OW-HD means O of water hydrogen-bonded to H of DMSO. α is O_DHO, β1 and β2 is CHO_W.

Surveying the calculated results for the different methods at different basis set levels is that changes in the monomer geometries upon complexation are relatively minor. The S-C bond length slightly shorten while S=O bond length increased a little. Other bond lengths involved in the hydrogen bonding slightly lengthen. The maximum bond length change is less than 0.015 Å at the two large basis set levels.

As shown in Fig. 1, for the cyclic structure of DW1, water forms a hydrogen bond to the sulfoxide oxygen and receives a hydrogen bond from a methyl hydrogen of each of the two methyl, resulting in three relatively strong hydrogen bonds. R_{OW-HD} (the hydrogen bond distance between the oxygen of water and hydrogen of DMSO) is 2.484, 2.542 and 2.575 Å for MP2/6-311++g(d,p), B3LYP/6-311++g(d,p) and B3LYP/ 6-311++g(2d,2p) level, the R_{OD-HW} is 1.810, 1.821 and 1.845 Å, respectively. Hartee-Fock method gives longer hydrogen bond due to its neglect of dispersion energy (2.753 and 1.911 Å). And the MP2/6-311++g(d,p) calculations, which yield the O···H-O angle of 154.6º and C-H···O angle of 131.3º, are in good agreement with the B3LYP values of 155.0 and 131.3º.

For DW2, water molecule accepts a hydrogen bond from each of the methyl, the bond distance is 2.595 Å (B3LYP/6-311++g(d,p) level), slightly longer than the hydrogen-bond distances of DW1. Therefore, interaction energy of this structure will be less than DW1, which is in accordance with the data in Table-3.

To analyze in more detail the role of basis set size effects on the binding energy between DMSO and H₂O, we use Table-3 that gives a detailed analysis of the binding energy obtained with several different theoretical models. As expected, basis set sensitivity exists. The interaction energies computed with B3LYP using the minimal basis set 6-31g are much higher.

With increasing basis set size, the computed values decrease and converge smoothly. All the ZPE-corrected energies are smaller than uncorrected ones and all of the ZPE-corrected energies calculated at 6-31+g (d), 6-311++g(d,p) and 6-311++g(2d,2p) levels are smaller than the BSSE-corrected ones at the same basis levels. Moreover, at 6-31+g(d), 6-311++g(d,p) and 6-311++g(2d,2p) levels the correction is not sensitive to the basis sets. From the table we can see that the magnitude of BSSE decreases with the basis sets enlarged, when the diffusion and polarization functions are considered, especially for the 6-311++g(d,p) and 6-311++g(2d,2p) basis sets using the B3LYP method, the inclusion of BSSE correction has minor importance to the bonding energy.

From Table-3, we can see that the relative stability order of the two structures is DW1 > DW2. It is easy to understand the relative stability of order, for DW1, it is a cyclic structure, water forms a hydrogen bond to the sulfoxide oxygen and forms a hydrogen bond from a methyl hydrogen of each of the two methyl, resulting in three relatively strong hydrogen bonds (the shorter hydrogen bond distance).

The interaction of H₂O with DMSO has also been studied in solution phase at the B3LYP/6-311++g(d,p) level of the theory. The Onsager reaction field model has been used to treat solvent effects. In this work, we focus our attention first on results obtained using C_6H_{12}, Me₂CO, DMSO and H₂O as the solvent which dielectric constant is 2.023, 20.7, 46.7 and 78.39, respectively. However, we will also present a study of the energy changes of the systems as the dielectric constants are varied.

The most interesting parameters in solvents are listed in Table-4. For comparing, we also list the results in gas phase (B3LYP/6-311++g(d,p)) in the Table-4. From Table-4, we have

TABLE-3
INTERACTION ENERGIES OF DMSO-H₂O COMPLEXES (KJ/mol) IN GAS PHASE

Method	DW1				DW2		
	ΔE_{int}	$\Delta E_{int} + \Delta E_{zpe}$	$\Delta E_{int} + \Delta E_{bsse}$	$\Delta E_{int} + \Delta E_{zpe} + \Delta E_{bsse}$	ΔE_{int}	$\Delta E_{int} + \Delta E_{zpe}$	$\Delta E_{int} + \Delta E_{bsse}$	$\Delta E_{int} + \Delta E_{zpe} + \Delta E_{bsse}$
B3LYP/6-31g	-80.3	-68.5	-64.5	-52.7	-25.5	-19.6	-17.5	-11.6
B3LYP/6-31g(d)	-53.7	-43.5	-35.3	-25.1	-19.0	-14.6	-16.4	-12.0
B3LYP/6-31+g(d)	-42.0	-32.4	-39.9	-30.3	-14.4	-9.2	-12.1	-6.9
B3LYP/6-311++g(d,p)	-42.9	-33.5	-39.7	-30.3	-16.7	-11.0	-11.8	-6.1
B3LYP/6-311++g(2d,2p)	-35.8	-26.6	-35.3	-26.1	-11.7	-6.90	-11.6	-6.8
HF/6-311++g(d,p)	-37.8	-28.7	-35.6	-26.5	-15.3	-9.70	-12.1	-6.5
MP2/6-311++g(d,p)	-47.8	*	-36.8	*	-22.6	*	-13.7	*

*Frequency calculated at MP2/6-311++g(d,p) level is not successful.

TABLE-4
OPTIMIZED GEOMETRIC PARAMETERS OF DW1 AND DW2 IN SOLUTIONS CALCULATED AT THE
B3LYP/6-311++g(d,p) LEVEL (DISTANCES IN Å, ANGLES IN DEGREE)*

Solvent	ε	DW1				DW2	
		R_{OD-HW}	R_{OW-HD}	α	$\beta1$	R_{OW-HD}	$\beta2$
In gas	–	1.821	2.542	155.0	131.3	2.595	131.8
In cyclohexane	2.023	1.809	2.568	156.2	131.0	2.476	151.5
In acetone	20.7	1.791	2.644	159.3	130.1	2.431	152.4
In DMSO	46.7	1.789	2.655	159.7	130.0	2.429	152.3
In water	78.39	1.788	2.659	159.8	129.9	2.428	152.3

*OD-HW means O of DMSO hydrogen-bonded to H of water, OW-HD means O of water hydrogen-bonded to H of DMSO. α is O_DHO, $\beta1$ and $\beta2$ is CHO_W.

found that the solvent can appreciably modified the geometries of hydrogen-bonded systems.

With respect to DW1, the most notable differences between the gas and solution phase are that the R_{OD-HW} length is reduced (1.821 Å in gas phase, 1.809, 1.791, 1.789 and 1.788 Å in the four solvents, respectively), but R_{OW-HD} distances are increased from 2.542 Å in gas phase to 2.568, 2.644, 2.655 and 2.659 Å in the four solvents. At the same time, $\angle O_DHO$ is changed (gas phase: 155.0º, solution phase: 156.2, 159.3, 159.7 and 159.8º, respectively) and differences in $\angle CHO_W$ are less than 2º.

For DW2, the most dramatic changes induced by the solvent is the angle $\angle CHO_W$ varied from 131.8º in gas phase to 151.5, 152.4, 152.3 and 152.3º in the four solvents, respectively The R_{OW-HD} distance is about 0.167 Å in water shorter than in the gas phase value. The changes can be explained by the large variation of the dipole moments from 5.86 in gas phase to 8.85 D in water. The changes of the geometries of hydrogen-bonded systems and the dipole moments are made by the change of polarity of the solvents, the dielectric constant of cyclohexane is 2.023 and the polarity is small, but the polarity of the other three solvents is stronger. The R_{OW-HD} distances and the angles $\angle CHO_W$ we calculated in acetone, DMSO and H_2O are similar, which indicates the effect of the change of the polarity to the geometries of hydrogen-bonded systems is no more notable when the dipole moment comes to a fixed value.

A summary of the relative energies of the DW1 and DW2 in solution is also presented in Table-5. The energies are measured relative to the energies of separated H_2O and DMSO in solution. From the table it is observed that there exits a large influence of solvent polarization on hydrogen bond energies. The energy of DW2 in water and at the gas phase is -26.1 and -16.7 KJ/mol, respectively. For DW1, the energy is -25.4 and -42.9 KJ/mol. Therefore it is clear that DW1 is more stable at

gas phase, while the energies of DW1 and DW2 are similar in water.

Finally, we have also investigated the effect of varying the dielectric constant on the energies and geometries of the DMSO-H_2O interaction. Calculations at the B3LYP/6-311++g(d,p) level of theory employing the onsager reaction field model have been carried out for a range of dielectric constant. The binding energies in various solutions of DW1 and DW2 are presented in Fig. 2. As one would expect, the inversion of the relative stability of the studied isomer is observed for polar and nonpolar solvents. The more polar the solvent, the more stable is the conformation with large polarity (DW2) which is characterized by the larger dipole moment. DW2 is more stable than DW1 not only in pure DMSO but also in pure water.
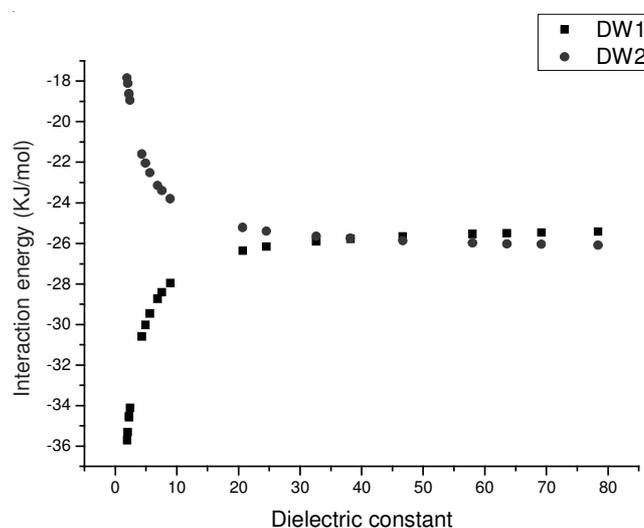
Fig. 2. Variation of the interaction energy of DW1 and DW2 with dielectric constant

TABLE-5
INTERACTION ENERGIES OF DMSO-H_2O COMPLEXES IN SOLUTIONS
CALCULATED AT THE B3LYP/6-311++g(d,p) LEVEL (KJ/mol)

Solvent	ε	DW1				DW2			
		ΔE_{int}	$\Delta E_{int} + \Delta E_{zpe}$	$\Delta E_{int} + \Delta E_{bsse}$	$\Delta E_{int} + \Delta E_{zpe} + \Delta E_{bsse}$	ΔE_{int}	$\Delta E_{int} + \Delta E_{zpe}$	$\Delta E_{int} + \Delta E_{bsse}$	$\Delta E_{int} + \Delta E_{zpe} + \Delta E_{bsse}$
In gas	–	-42.9	-33.5	-39.7	-30.3	-16.7	-11.0	-11.8	-6.1
In cyclohexane	2.023	-35.3	-25.8	-37.0	-27.5	-18.1	-11.9	-18.5	-13.1
In acetone	20.70	-26.4	-17.2	-33.4	-24.2	-25.2	-16.0	-28.5	-19.3
In DMSO	46.70	-25.7	-16.6	-33.1	-24.0	-25.9	-19.1	-28.9	-22.1
In water	78.39	-25.4	-16.3	-33.1	-24.0	-26.1	-19.3	-29.7	-22.9

Conclusion

The hydrogen bond interaction of 1:1 complex between DMSO and H_2O has been analyzed by HF, MP2 and B3LYP methods employing different basis set levels. Two structures are considered. DW1 is slightly more energetically favourably than DW2 in gas phase. Finally, the study of the solvent effect on the potential energy surface of DMSO-H_2O complex has been performed. It is found that DW2 is more stable than DW1 in solution phase and the geometry and the stability of the system are appreciably modified by the solvent.

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