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Spectroscopic and theoretical evidence for the cooperativity between red-shift hydrogen bond and blue-shift hydrogen bond in DMSO aqueous solutions

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Abstract

The cooperativity between red-shifted hydrogen bond and blue-shifting hydrogen bond in dimethyl sulfoxide aqueous solutions was studied by methods of quantum chemical calculations and infrared spectroscopy. The water molecule plays a different role in two types of hydrogen bonds: proton–donor in red-shifted hydrogen bond and proton–acceptor in blue-shifting hydrogen bond. The cooperativity is not prominent if the ring structure is formed through the O—H···O=S H-bond and C—H···O_w H-bond. However, if the methyl groups in the above ring structure participate in second C—H···O_w H-bond, the cooperativity is increased. The second C—H···O_w H-bond enhances O—H···O=S H-bond and weakens the first C—H···O_w H-bond.

Keywords: Cooperativity; Hydrogen bond; *Ab initio*; FT-IR spectroscopy; Dimethyl sulfoxide

1. Introduction

More than half a century has elapsed since Pauling proposed his idea about the cooperativity of the hydrogen bond in his landmark book [1]. It implies that a first H-bond A—H···B between a proton–donor group A—H and a proton–acceptor group or molecule B will become stronger when a second H-bond is formed between a further A—H group and the A—H group already involved in the first bond, i.e., A—H···A—H···B. It is known that cooperative interactions are important for the stability of many H-bonded systems [2]. The occurrence of the cooperativity among the subunits in hydrogen bonding system is accompanied with changes in the dynamics of the structures, for example, in DNA duplexes [3]. The cooperativity is also important in the formation of non-covalently bound aggregates of synthetic materials [4]. Therefore, researchers paid more attention to the cooperativity of hydrogen bond [5–7].

The X—H stretching vibration moves to low frequency in infrared spectra if H-bond is formed. However, recent experimental [8–10] and theoretical [11,12] studies indicated that there is another type of H-bond that is different from the conventional H-bond in infrared spectra. Hobza named this type of H-bond as improper, blue-shifting H-bond [11], and thought their nature is different. Kar and Scheiner [5] have investigated the cooperativity in the C—H···O blue-shifting H-bonds. Since there is the cooperativity in both H-bonds, how about is the cooperativity between conventional H-bond and blue-shifting H-bond?

The aqueous solutions of dimethyl sulfoxide have been extensively studied for their unique biological and physicochemical properties [13]. Kirchner and Reiher [12] classified interactions between DMSO and water into O—H···O=S red-shifted H-bond and C—H···O_w blue-shifting hydrogen contact, and the C—H···O_w hydrogen bond in DMSO aqueous solutions has been substantiated [14–16]. So in this paper we investigated this mixture by means of quantum chemical calculations and infrared spectra to illuminate the cooperativity between two types of hydrogen bonds. Since both types of hydrogen bonds have a great difference in strength and nature, it is hoped that there appears some new cooperativity between them.

2. Experimental and computational details

Dimethyl sulfoxide (99.5%, SP) was purchased from the Beijing Chemical Plant (Beijing, China). It was stored over 4 A

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molecular sieves before use. The water was distilled-deionized water. All solutions were prepared by weighing. Caution was taken to prevent evaporation during preparation of solutions and measurement.

The ATR-FT-IR spectra over the range from 4000 to 650 cm^{-1} were collected using a Perkin-Elmer spectrometer (Spectrum GX, England), with a resolution 2 cm^{-1} and 16 parallel scans. The ATR cell was made of trapezoidal ZnSe crystal with an incident angle of 45° and 12 reflections. Three parallel measurements for each sample were performed at room temperature. The analyzed spectrum was obtained by ATR correction for the measured spectrum.

According to previous studies on the interaction between DMSO and water [11,14], the optimized structures of various hydrogen-bonded complexes were again calculated using MP2/6-31++G** theoretical method. Harmonic vibrational frequencies were computed to confirm that these structures are local minima on the energy surfaces. The interaction energies ΔE were corrected with zero-point vibrational energies and basis set superposition errors. All calculations were carried out using the GAUSSIAN 98 program package [17].

3. Results and discussion

The O–H···O=S H-bond is formed between S=O group in DMSO and OH group in H_2O. The formation results in a decrease of S=O electron density in DMSO and an increase of OH electron density in water. This increase of negative charge will make OH group in DMSO/H_2O complex a better proton acceptor. Analogous reasoning would make the CH_3 group in the complex a more powerful proton donor, in comparison to the isolated DMSO molecule. Therefore, the O atom in water is prone to form C–H···O_w H-bond with the H atom in DMSO if the O–H···O=S H-bond is formed.

Since the O–H···O=S H-bond plays a promotive role in the formation of the C–H···O_w H-bond in DMSO–H_2O complex, the C–H···O_w H-bond may be formed simultaneously with the O–H···O=S H-bond. Therefore, we propose the formation of a bifunctionally hydrogen-bonding hydration complex seen in Fig. 1C and D, in which water molecules play the roles of both a proton donor in conventional O–H···O=S H-bond and an acceptor in blue-shifting C–H···O_w H-bond simultaneously. Thus it provides a model to study the cooperativity between both H-bonds in such ring structure, like in the linear H-bonded structure.

Table 1
Interaction energies (in kJ/mol) and geometrical changes (in Å) of DMSO–H_2O complexes

Complexes[a]	ΔE_{corr}	$R(O_D–H_w)$[b]	$R(O_w–H_D)$[c]
A	−20.41	1.8561	
B	−8.58		2.5541 (2.5531)
C	−24.77	1.8722	2.4571
D	−28.28	1.8334	2.4582 (2.4598)
E	−47.92	1.8685	2.4688
F	−34.51	1.8545	2.5129
G	−38.53	1.8149	2.4960 (2.5370)
H	−58.23	1.8461	2.5305

[a] Structure illustrated in Figs. 1–3.

[b] The O_D and H_w represent oxygen atom of DMSO and hydrogen atom of water, respectively.

[c] The O_w and H_D represent oxygen atom of water and hydrogen atom of DMSO, respectively.

The non-additivity characteristic in energy is the most persuasive evidence for the cooperativity of hydrogen bonds. For DMSO–1H_2O complexes, four dimers were obtained at the MP2/6-31++G** level and shown in Fig. 1. Their interaction energies were given in Table 1. The energies were corrected for zero-point vibrational energy and basis set superposition error. The interaction energy is −20.41 kJ/mol in complex A, where only an O–H···O=S H-bond is present, so the interaction energy of O–H···O=S H-bond is −20.41 kJ/mol. The interaction energy is −8.58 kJ/mol in complex B, where there are two C–H···O_w H-bonds, so the mean interaction energy of C–H···O_w H-bond is −4.29 kJ/mol. The intensity of O–H···O=S H-bond is almost four times to C–H···O_w H-bond. For complex C, where the water simultaneously combines with the S=O group and one CH_3 group and forms a ring containing six atoms, its interaction energy (−24.77 kJ/mol) is almost equal to the sum of both interactions. The similar result is found in structure D, where water simultaneously S=O group and two methyl groups and two similar rings are formed. Therefore, the cooperativity of two type hydrogen bonds is very small in such ring structures. In spite of this, the ring structures C and D are energetically favorable in DMSO–1H_2O complex.

For DMSO–2H_2O complexes, three trimers were optimized at the same theoretical level; and their structures are illustrated in Fig. 2. Following the interaction energies in Table 1, structure E, where there are two hexacyclic structures, is more stable than structure F and G. The interaction energy of complex E is less two times than that of complex C. The main reason is that oxygen

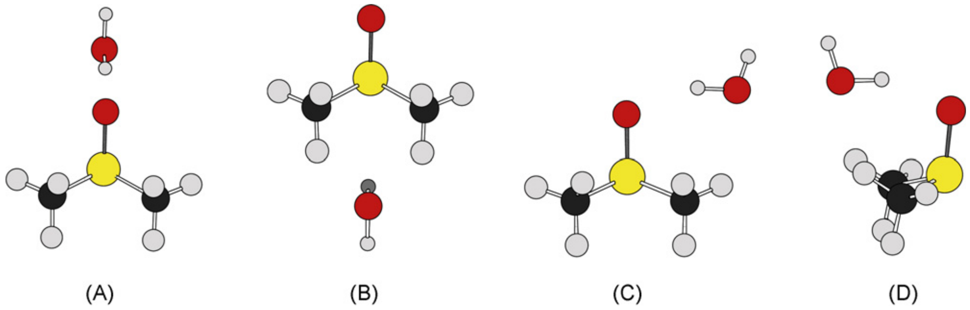

Fig. 1. The geometrical structures of DMSO–1H_2O complexes optimized at the MP2/6-31++G** level.

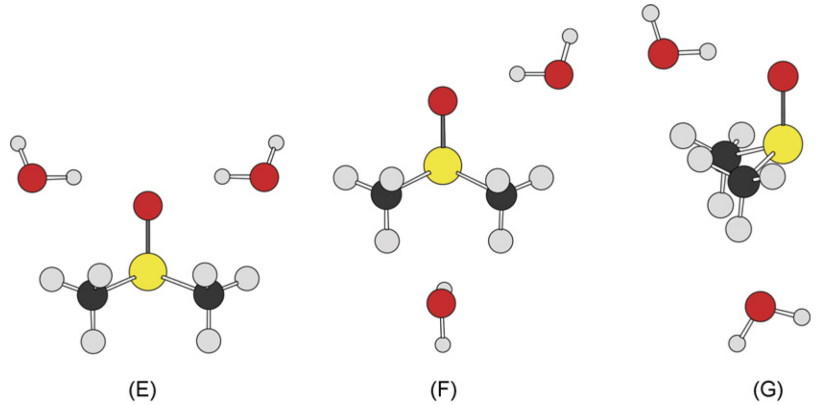

Fig. 2. The geometrical structures of DMSO–$2H_2O$ complexes optimized at the MP2/6-31++G** level.

atom in DMSO participates formation of two hydrogen bonds. For complex F, which can be looked as an addition of complex B and C, the calculated energies are −8.58 kJ/mol for complex B, −24.77 kJ/mol for complex C, and −34.51 kJ/mol for complex F. Numerically, the energy gain in structure F due to cooperativity corresponds to 3% of the total interaction energy. Clearly, it is indicative of some positive cooperativity (1.16 kJ/mol), but not a large effect. Similar positive cooperativity (1.67 kJ/mol) is also found in complex G.

For DMSO–$3H_2O$ complex, one tetramer was optimized at the same theoretical level; and its structure is depicted in Fig. 3. Complex H illustrates that two waters hydrate the S=O group whereas the third one is placed between both methyl groups. The difference in structure between H and E is the third water hydrates two methyl groups of DMSO. However, the energy of the cooperativity in complex H is positive (1.73 kJ/mol), whilst that is negative (−1.62 kJ/mol) in complex E. It is evident that the second C–H$\cdots$$O_w$ interaction leads to such different change of cooperativity.

In order to probe the effect of two types of hydrogen bonds in the cooperativity, the changes of H-bond lengths were analyzed. The results are also listed in Table 1. The $R(O_D–H_w)$ in complex C is elongated 0.0161 Å against that in complex A, whilst the $R(O_w–H_D)$ is contracted 0.0965 Å in comparison with that in complex B. Similar results are found in complex D. These geometrical changes show that both types of interactions are changed differently when the cooperativity happens. The O–H$\cdots$O=S H-bond is weakened, whilst the C–H$\cdots$$O_w$ H-bond is enhanced. Furthermore, the enhanced result of the C–H$\cdots$$O_w$ H-bond is larger than the decreased result of the O–H$\cdots$O=S H-bond. This can be explained as follows: the O–H$\cdots$O=S H-bond is much stronger than the C–H$\cdots$$O_w$ H-bond, so the effect of the strong interaction on the weak one is much big whereas the effect of the weak interaction on the strong one is a little. Two results counteract, so the cooperativity is not distinct in complex C and D. Such cooperativity may be attributed to different nature of both hydrogen bonds.

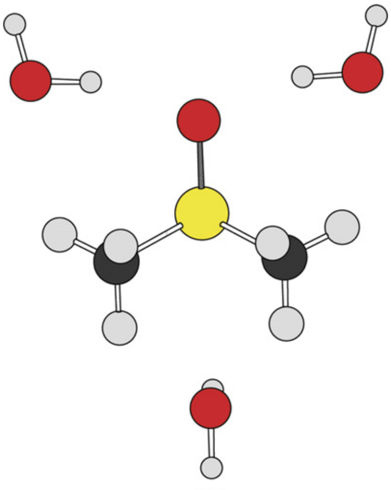

Fig. 3. The geometrical structures of DMSO–$3H_2O$ complex optimized at the MP2/6-31++G** level.

Compared with complex C, the $R(O_D–H_w)$ is shortened 0.0177 Å in complex F, whilst the $R(O_w–H_D)$ is elongated 0.0558 Å. To compare complex H and E or complex G and D, similar results are also found. These geometric changes mean the O–H$\cdots$O=S H-bond is enhanced and the C–H$\cdots$$O_w$ H-bond is decreased. Because their distinction lies in the second C–H$\cdots$$O_w$ H-bond, the added water is responsible for these changes. It is usually energetically unfavorable for a molecule to act as a double proton donor in classical hydrogen bond [2]. This rule is also suitable for blue-shifting hydrogen bond.

Cooperative effects are also usually mirrored in the frequency shifts undergone by the CH stretching vibration [18,19]. The O–H$\cdots$O=S H-bond and the C–H$\cdots$$O_w$ H-bond can all cause blue-shift of the CH stretching vibration [15,20]. Consequently, an alternative way of describing the cooperativity is by the difference, $\Delta v = v - v_0$, where v and v_0 represent CH stretching vibration frequency in DMSO solution and pure DMSO. Fig. 4 shows the frequency shift of the CH_3 asymmetric stretching vibration in DMSO with the increase of X_{water}. With the increase of X_{water}, the frequency shift of the CH_3 stretching vibration is also increased. This is common result of two interactions. Interestedly, the change of Δv at $X_{water} > 0.5$ is faster than that at $X_{water} < 0.5$. We attribute it to the cooperativity between two types of hydrogen bonds.

Table 2
C–H stretching vibration frequencies of DMSO and corresponding frequency shifts upon complexation[a]

Species	1A″	1A′	2A″	2A′	3A″	3A′
DMSO	3120 (4.3)[b]	3121 (8.8)	3238 (0.0)	3241 (7.8)	3253 (0.8)	3253 (2.2)
A	+3 (2.6)	+3 (7.8)	+4 (0.0)	+4 (5.2)	+3 (0.1)	+4 (1.2)
B	+5 (6.1)	+4 (6.6)	+6 (1.0)	+4 (5.2)	+6 (0.9)	+8 (0.1)
C	+0 (7.3)	+2 (7.3)	+1 (1.6)	+3 (4.7)	+3 (1.2)	+4 (3.7)
D	+1 (4.7)	+1 (13.4)	+4 (0.3)	+4 (2.5)	+1 (0.7)	+1 (1.8)
E	+2 (0.1)	+2 (14.1)	+4 (0.0)	+3 (4.4)	+7 (1.2)	+7 (1.2)
F	+5 (5.5)	+6 (5.4)	+8 (1.8)	+7 (2.8)	+9 (0.3)	+10 (1.9)
G	+7 (6.9)	+6 (1.7)	+11 (1.6)	+9 (0.9)	+6 (0.3)	+8 (1.9)
H	+8 (6.7)	+8 (0.1)	+13 (1.3)	+10 (1.9)	+13 (2.2)	+14 (2.5)

[a] Structure illustrated in Figs. 1–3.
[b] The data in parenthesis are absorption intensities.

In order to further illustrate the above frequency change, we obtained harmonic vibrational frequencies of isomers calculated at the MP2/6-31++G** level. The results are listed in Table 2. No scale was used for the calculated frequencies. As revealed in Table 2, the prominent CH_3 stretching frequencies (absorption intensities) of DMSO located at 3120 (4.3), 3121 (8.8), and 3241 (7.8). It is found that the hydration of DMSO leads to blue-shift of CH_3 stretching frequencies in all structures. The shift resulting from two C–H···O_w interactions in B is larger than that from one O–H···O=S H-bond in A. Interestly, the shifts are decreased once two types of hydrogen bonds are formed simultaneously in C and D. We attribute it to the different origin of blue-shift in two types of hydrogen bonds: the electrostatic repulsion force in C–H···O_w interaction and the electrostatic attraction force in O–H···O=S hydrogen bond [21]. When they were combined together, they weaken each other. Thus their common interaction results may be smaller than the single interaction results. Even so, the blue-shifts were found in C and D species, in comparison with the isolated DMSO molecule. However, comparing the shifts in C and F, it is found that the shifts in F are great bigger than those in C. For example, the shift of 1A′ stretching mode in F is three times as large as that in C. The same results are found in D and G, E and H pairs. Their distinctions are that there is a water molecule between two methyl groups in E, F, and G. Here two H atoms of the methyl group participate in the formation of C–H···O_w hydrogen bond. This water molecule weakens the cooperativity between C–H···O_w interaction and O–H···O=S hydrogen bond, so the shifts are increased. As revealed in Table 2, there is a strong correlation between the experimental results in Fig. 4 and the structures from the Gaussian calculations, i.e., Figs. 1–3. Nevertheless, it is instructive to note that *ab initio* calculations may only provide qualitative support for the cooperativity between two types of hydrogen bonds, since the calculations are based on gas phase structures.

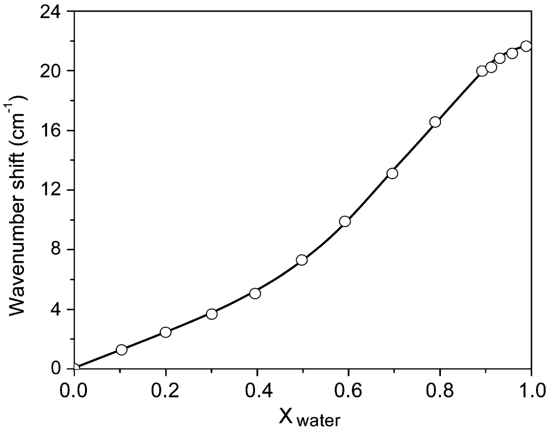

Fig. 4. Frequency shift of CH_3 asymmetrical stretching vibration in DMSO–water mixtures.

4. Conclusions

Both spectroscopic results and quantum chemical calculation results show that there is the cooperativity between both types of hydrogen bonds. Due to the discrimination in strength and nature, their cooperativity shows some new characteristics. In ring structure of DMSO–H_2O complex, the enhancement of C–H···O_w H-bond is a price of the weakening O–H···O=S H-bond, making total cooperativity not evident. However, with the increase of water concentration, the positive cooperativity is increased, leading to the enhancement of O–H···O=S H-bond and weakening of C–H···O_w H-bond in the above ring structure.

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