A THEORETICAL STUDY ON INTERACTION AND STABILITY OF COMPLEXES BETWEEN DIMETHYL SULFIDE AND CARBON DIOXIDE

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ABSTRACT

Interactions of dimethyl sulfide with CO_2 are investigated using MP2 method with the 6-311++G(2d,2p) basis set. Nine stable geometries are observed, in which DMS···$2CO_2$ is found to be more stable than DMS···$1CO_2$. Interaction energies for all the compexes with ZPE and BSSE corrections at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) range from -2.7 to -22.0 kJ.mol^{-1}. The AIM and NBO results show that the stability of DMS···xCO_2 complexes (x=1,2) are determined by S···C=O Lewis acid-base interaction and an additional contribution of C−H···O hydrogen bond and S(O)···O chalcogen-chalcogen interaction. Remarkably, the SAPT2+ analysis indicates that the contribution of induction term to the total stabilization energy is more important than other energetic components.

Keywords: Dimethyl sulfide, carbon dioxide, blue/red-shifting hydrogen bond, NBO, SAPT analysis.

TÓM TẮT

Nghiên cứu tương tác của $(CH_3)_2$S với CO_2 bằng phương phương pháp hóa học lượng tử

Tương tác giữa dimethyl sulfide với xCO_2 (x = 1,2) được nghiên cứu tại mức lý thuyết MP2/6-311++G(2d,2p). Kết quả tối ưu thu được chín phức bền, trong đó phức DMS···$2CO_2$ bền hơn phức DMS···$1CO_2$. Năng lượng tương tác hiệu chỉnh ZPE và BSSE của tất cả các phức tại MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) trong khoảng từ -2,7 đến -22,0 kJ.mol^{-1}. Kết quả phân tích AIM và NBO cho thấy độ bền của phức giữa DMS với xCO_2 (x=1,2) được quyết định bởi tương tác acid-base Lewis với sự bổ trợ của liên kết hydro C−H···O và tương tác chalcogen S(O)···O. Đáng chú ý, kết quả phân tích SAPT2+ cho thấy hợp phần cảm ứng đóng góp chính vào sự bền hóa của phức so với các hợp phần năng lượng khác.

Từ khóa: $(CH_3)_2$S, CO_2, liên kết hydro chuyển dời xanh/đỏ, phân tích NBO, phân tích SAPT.

1. Introduction

There are many greenhouse gases including carbon dioxide, sulfur dioxide, methane, etc in which carbon dioxide is one of the main agents among the remaining gases. Its concentration is still increasing in the atmosphere and causing environmental problems which are challenging not only scientists but also human survival. During the last decades, many researches on applications of CO_2 have been published [1]. Especially, supercritical carbon dioxide (scCO_2) has attracted more attention for the development of "green chemistry" processes. It is becoming an important

commercial and industrial solvent because it has no environmentally hazardous impact, low cost and tunability of solvent parameters [2]. Therefore, $scCO_2$ has been widely used in several chemical processes such as extraction, separation, chemical synthesis and material processing [3], [4], [5]. Recently, direct sol-gel reaction in $scCO_2$ has also been used in the synthesis of oxide nanomaterials [6], oligomers, polymer [7] and copolymer [8]. However, the usage of $scCO_2$ as a solvent has serious limitations due to the poor solubility of a majority of polar or ionic materials. Therefore, searching and designing CO_2-philic materials to increase the solubility of organic solvents in $scCO_2$ attract more interest of scientists. To do this, investigations on origin and stability of interactions between organic molecules and CO_2 at the molecular level are necessary in order to use CO_2 effectively wih different purposes [1].

Noncovalent interactions play an important role in crystal packing, molecular recognition, and reaction selectivity [9]. Among them, A−H···B hydrogen bonds have a significant impact in many fields of chemistry and biochemistry [10], [11] as they determine structures and properties of liquids, molecular crystals and biological molecules [12]. Accordingly, a study of hydrogen bond to unravel its characteristic is necessary. Dimethyl sulfide (DMS) is used in organic synthesis as a reducing agent in ozonolysis reaction. Particularly, DMS can be oxidized to dimethyl sulfoxide (DMSO) which is an organic solvent frequently used in chemistry, biological and medicinal studies. To the best of our knowledge, a systematic investigation into interactions between DMS and CO_2 has not been reported yet in the literature. In the present work, the complexes between DMS and CO_2 are investigated at molecular level by theoretical method based on quantum chemistry. We are going to reveal the interactions and stability of complexes formed by DMS and CO_2 and hope to provide an insight into the origin of the hydrogen bonds.

2. Computational methods

Geometry optimizations for monomers and complexes were carried out at the second-order Moller-Plesset perturbation theory (MP2) level with the 6-311++G(2d,2p) basis set. Vibrational frequencies were calculated at the same level of theory to ensure that the optimized structures were minima on potential energy surface and to estimate zero-point energy (ZPE). Single point energy and basis set superposition error (BSSE) were done using MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p). Interaction energies corrected ZPE or both ZPE and BSSE were obtained as the differences in total energy between complexes and relevant monomers. All calculations were carried out using the GAUSSIAN 09 program [13]. Topological parameters such as electron density ($\rho(r)$) and Laplacian of electron density ($\nabla^2(\rho(r))$), electron kinetic energy density ($G(r)$) and electron potential energy density ($V(r)$) at bond critical points (BCPs) of intermolecular interactions were indentified using AIM2000 software [14] on the basis of Bader's Atom in Molecules theory. In addition, electronic properties of monomers and complexes were also examined utilizing NBO analysis executed in the GenNBO 5.G program [15] at MP2/6-311++G(2d,2p) level. Finally, in order to quantify contribution of energetic components to overall stability of interactions, SAPT2+ calculations were performed based on the symmetry-adapted perturbation theory [16] using the PSI4 program at MP2/6-311++G(2d,2p).

3.   Results and discussion

3.1.   Geometric structures and AIM analysis

The geometric shapes and topolographies of nine stable complexes formed by interactions between DMS and CO_2 (DMS···xCO_2) (x = 1,2) at MP2/6-311++G(2d,2p) are shown in Figure 1, which are denoted by **D-n,** and **T-n**, where **D**, **T** are labled for dimer and trimer, respectively; *n* = 1, 2, 3,... are numerical orders of isomers.

Figure 1 shows that the distances of the O···H, S···C, C···O, S···O và O···O contacts are in the ranges of 2.66−3.04, 3.30−3.39, 3.01−3.47, 3.32−3.52 and 3.10−3.34 Å, respectively; which are smaller than the sum of van der Waals radii of the two atoms involving interactions (being 2.72, 3.22, 3.55, 3.37 and 3.04 Å for the corresponding pairs of H and O, S and C, C and O, S and O, O and O atoms). The DMS···xCO_2 (x = 1,2) complexes are formed by the intermolecular contacts which are hydrogen bonds and/or Lewis acid-base interactions and/or chalcogen-chalcogen interactions.
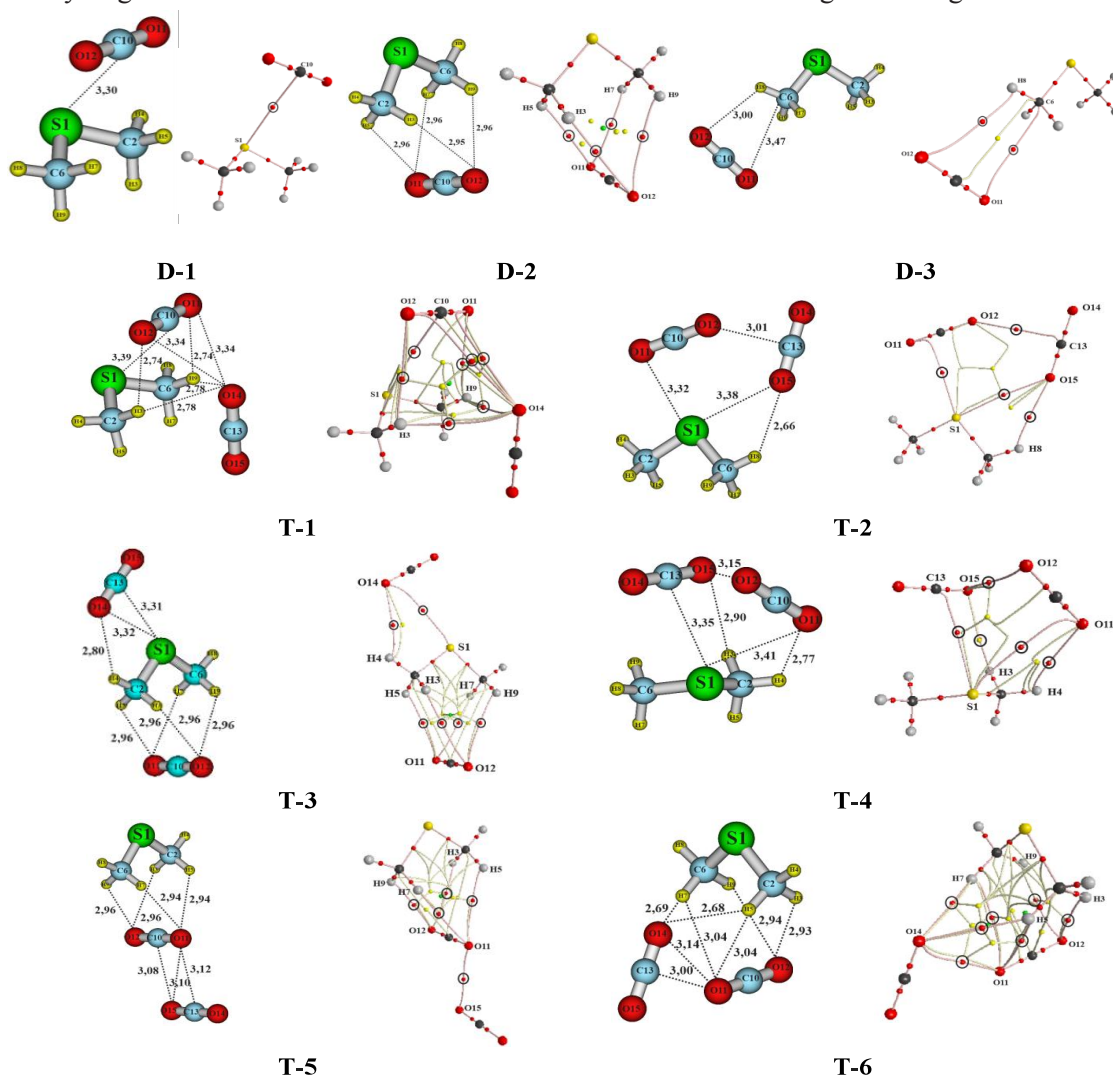

Figure 1. Optimized structures and topological geometries of $(CH_3)_2S$ and xCO_2 (x=1,2) at MP2/6-311++G(2d,2p) (all distances are in Å)

The obtained results from AIM analysis are collected in Table 1. All the values of $\rho(r)$, $\nabla^2\rho(r)$, $H(r)$, and the ratio $G/|V(r)|$ at BCPs of all interactions are in the ranges of 0.003-0.008 au, 0.013-0.022 au, 0.0007-0.0015 au and 1.195-1.477, respectively. These values fall within the critical limits for the formation of weak and non-covalent interaction in nature (0.002-0.035 au and 0.02-0.15 au for $\rho(r)$ and $\nabla^2\rho(r)$, respectively; $H(r) > 0$ and the ratio $G/|V(r)| > 1$) [17]. Accordingly, all intermolecular contacts in the complexes are non-covalent weak interactions. For DMS$\cdots CO_2$ binary complexes, the value of $\rho(r)$ at the BCP of S$\cdots$C=O Lewis acid-base interaction in **D-1** is *ca.* 0.0004 au larger than that of other interactions in **D-2** and **D-3**. These results imply a larger strength of the S$\cdots$C=O Lewis acid-base interaction relative to the C$-$H$\cdots$O hydrogen bond. As a consequence, it is roughly predicted that **D-1** is the most stable complex of DMS$\cdots CO_2$. There are four C$-$H$\cdots$O hydrogen bonds in **D-2** while **D-3** is formed by only one C$-$H$\cdots$O hydrogen bond and one C$\cdots$O interaction with the comparable values of electron densities at BCPs of the contacts. As a result, the stability of DMS$\cdots CO_2$ binary complexes decreases in the ordering of **D-1 > D-2 > D-3**.

Table 1. *Selected parameters at the BCPs of intermolecular contacts of $(CH_3)_2S\cdots xCO_2$ (x=1,2)*

Complex	Contacts	$\rho(r)$ (au)	$\nabla^2\rho(r)$ (au)	$G/|V(r)|$	$H(r)$ (au)
D-1	S1$\cdots$C10$-$O12	0.008	0.030	1.339	0.0015
D-2	C2$-$H5$\cdots$O11	0.004	0.015	1.327	0.0007
	C6$-$H7$\cdots$O11	0.004	0.015	1.326	0.0007
	C2$-$H3$\cdots$O12	0.004	0.015	1.321	0.0007
	C6$-$H9$\cdots$O12	0.004	0.015	1.323	0.0007
D-3	C6$-$H8$\cdots$O12	0.004	0.015	1.354	0.0008
	O11$\cdots$C6	0.004	0.016	1.477	0.0010
T-1	S1$\cdots$C10$-$O12	0.006	0.026	1.409	0.0014
	C2$-$H3$\cdots$O12	0.006	0.022	1.251	0.0009
	C6$-$H9$\cdots$O11	0.006	0.022	1.251	0.0009
	C2$-$H3$\cdots$O14	0.005	0.020	1.256	0.0009
	C6$-$H9$\cdots$O14	0.005	0.020	1.256	0.0009
	O11$\cdots$O14	0.004	0.020	1.375	0.0011
	O12$\cdots$O14	0.004	0.020	1.375	0.0011
T-2	S1$\cdots$O11	0.007	0.029	1.279	0.0013
	O12$\cdots$C13$-$O14	0.006	0.027	1.332	0.0013
	C6$-$H8$\cdots$O15	0.005	0.021	1.290	0.0010
	S1$\cdots$O15	0.004	0.018	1.269	0.0008
T-3	C2$-$H5$\cdots$O11	0.004	0.015	1.298	0.0007
	C2$-$H3$\cdots$O12	0.004	0.015	1.297	0.0007
	C6$-$H7$\cdots$O11	0.004	0.015	1.299	0.0007
	C6$-$H9$\cdots$O12	0.004	0.015	1.299	0.0007
	C2$-$H4$\cdots$O14	0.005	0.018	1.248	0.0007
	S1$\cdots$O14	0.007	0.026	1.251	0.0011

	S1···O11	0.007	0.025	1.285	0.0011
	S1···C13−O14	0.008	0.027	1.292	0.0013
T-4	O12···O15	0.007	0.028	1.226	0.0011
	C2−H4···O11	0.005	0.020	1.252	0.0008
	C2−H3···O15	0.004	0.016	1.308	0.0008
	C2−H5···O11	0.004	0.016	1.314	0.0008
	C2−H3···O12	0.004	0.015	1.329	0.0007
T-5	C6−H7···O11	0.004	0.016	1.312	0.0008
	C6−H9···O12	0.004	0.015	1.324	0.0007
	O11···O15	0.007	0.019	1.195	0.0010
	C2−H3···O12	0.004	0.016	1.309	0.0007
	C2−H5···O11	0.003	0.013	1.365	0.0007
	C2−H5···O14	0.005	0.019	1.228	0.0008
T-6	O11···O14	0.006	0.015	1.238	0.0010
	C6−H7···O11	0.003	0.013	1.367	0.0007
	C6−H7···O14	0.005	0.019	1.230	0.0007
	C6−H9···O12	0.004	0.015	1.314	0.0007

In going from DMS···CO_2 binary to DMS···$2CO_2$ ternary complexes, S(O)···O chalcogen-chalcogen interactions are found along with conventional Lewis acid-base interactions and hydrogen bonds mentioned above. For DMS···$2CO_2$ system, S···C=O Lewis acid-base interaction in **T-4** dominates the remaining intermolecular contacts which is due to the highest value of electron density at its BCP (0.008 au). It is clear that there is a slight increase of $\rho(r)$ at the BCPs of intermolecular interactions in sequence from C−H···O to S(O)···O, O···C=O and then to S···C=O, implying a strengthing increase in this trend. In a word, the stability of complexes between DMS and xCO_2 (x = 1,2) is mainly contributed by S···C=O Lewis acid-base interaction with an additional complement from C−H···O hydrogen bond and S(O)···O chalcogen-chalcogen interaction. This observation is quite consistent with that taken from the complexes of dimethyl ether (DME) and CO_2 in which the Lewis acid-base interaction overwhelming the C−H···O hydrogen bond has a significant impact on the stability of complex [18].

3.2. Interaction and cooperativity energy and energetic components

Interaction and cooperativity energies of binary and ternary complexes at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) are tabulated in Table 2. The interaction energies of the complexes are negative and range from -2.7 to -22.0 kJ.mol^{-1} (with both ZPE and BSSE corrections) and from -4.1 to -27.8 kJ.mol^{-1} (with ZPE correction only), indicating that the complexes investigated are quite stable. The ternary complexes are *ca.* 5.6-12.1 kJ.mol^{-1} more stable than the binary ones. This suggests that an addition of one CO_2 molecule to DMS···CO_2 leads to an increase in stability of complex.

Table 2*. Interaction energies (ΔE, kJ.mol^{-1}) and cooperativity energies (E$_{coop}$, kJ.mol^{-1})*

Complex	ΔE	ΔE$_{AB}$	E$_{AC}$	ΔE$_{BC}$	E$_{coop}$
D-1	-12.4(-9.9)	-	-	-	-
D-2	-6.3(-3.9)	-	-	-	-
D-3	-4.1(-2.7)	-	-	-	-
T-1	-21.3(-15.2)	-11.3(-8.7)	-4.8(-2.4)	-4.1(-3.1)	-1.1(-1.0)
T-2	-21.7(-16.9)	-10.2(-8.4)	-6.2(-4.3)	-4.8(-3.6)	-0.5(-0.6)
T-3	-16.8(-12.5)	-10.3(-8.4)	-6.3(-3.9)	0.1(0.2)	-0.3(-0.4)
T-4	-27.8(-22.0)	-10.4(-8.5)	-12.3(-9.8)	-4.2(-2.9)	-0.9(-0.8)
T-5	-12.4(-8.3)	-6.2(-3.8)	0.1(0.2)	-5.5(-4.2)	-0.8(-0.5)
T-6	-16.0(-10.5)	-6.3(-4.0)	-4.3(-2.3)	-4.8(-3.5)	-0.6(-0.5)

Values in brackets are for both ZPE and BSSE corrections, A = DMS, B = CO$_2$, C = CO$_2$

For the binary system, the interaction energy is more negative for **D-1** than for **D-2** and **D-3** by *ca.* 6.0 and 7.2 kJ.mol^{-1}, respectively. This indicates a decrease in the stability of complexes in going from **D-1** to **D-2** and then to **D-3**, which is consistent with AIM analysis above. In comparison with other organic molecules, the interaction energy of **D-1** is less negative that that of $(CH_3)_2O \cdots 1CO_2$ and $(CH_3)_2CO \cdots 1CO_2$ by *ca.* 3.8 and 1.2 kJ.mol^{-1}. It is predicted that the solubility of DME and DMSO in scCO2 is slightly better than DMS [19]. For ternary complexes, **T-4** has the most negative interaction energy with -22.0 kJ.mol^{-1} while **T-5** is the least stable complex with an energetic value of -8.3 kJ. mol^{-1}. As shown in Table 2, the stability of ternary complexes decreases in the trend of **T-4** > **T-2** > **T-1** > **T-3** > **T-6** > **T-5**, which is in good agreement with the obtained results from AIM analysis above.

The cooperative energy (E$_{coop}$) in ternary system is calculated from the following expression:
E$_{coop}$ = ΔE$_{ABC}$ − ΔE$_{AB}$ − ΔE$_{BC}$ − ΔE$_{AC}$, Where A= DMS, B = CO$_2$, C = CO$_2$; ΔE$_{ABC}$ is the interaction energy of the trimer formed from A B and C; ΔE$_{AB}$, ΔE$_{BC}$, ΔE$_{AC}$ are the interaction energies of the dimers A and B, B and C, A and C, respectively. The values of E$_{coop}$ with ZPE and BSSE corrections of trimer are also given in the Table 2. All E$_{coop}$ values are slightly negative and fall within the range of -0.5 to -1.0 kJ.mol^{-1}, indicating that the cooperativiy of intermolecular interactions takes place in complexes and leads to an enhance in the strength of ternary complexes.

SAPT2+ analysis is used to evaluate contribution of different energertic components to total sabilization energy of the binary complexes, which include electrostatic (E$_{elest}$), exchange energy (E$_{exch}$), induction (E$_{ind}$), dispersion (E$_{disp}$) and the second and high order level correlation energy ($\delta E_{int,r}^{HF}$).

Table 3. Contributions of different energetic components into stabilization energy using SAPT2 + approach (kJ.mol^{-1})

Complex	E_{elest}	E_{exch}	E_{ind}	E_{disp}	$\delta E_{int,r}^{HF}$
D-1	-15.3(30.1)	46.3	-21.3(42.1)	-13.1(25.9)	-1.0(1.9)
D-2	-0.6(4.1)	14.1	-4.2(29.3)	-9.3(64.3)	-0.3(2.2)
D-3	-1.0(11.3)	7.5	-2.2(24.4)	-5.5(62.3)	-0.2(1.9)

Values in brackets are the percentages (%) of corresponding energertic components contributing to total stabilization energy.

Table 3 shows that there are three mainly energetic components contributing to stability of DMS⋯CO_2 complexes. A larger role of induction term (42.1%) as compared to both electrostatic (30.1%) and dispersion (25.9%) terms is found for **D-1**, while **D-2** and **D-3** are mainly determined by dispersion term of 62.3−64.3% overwhelming induction (24.4-29.3%) and electrostatic (4.1-11.3%) term. Contribution of the second and high order level correlation energy to stabilization of binary complexes is quite small. Therefore, the stability of DMS⋯CO_2 is contributed mainly by induction component as compared to other energetic component.

3.3. Vibrational and NBO analyses

Stretching vibrational frequency and NBO analyses for DMS⋯xCO_2 complexes (x=1,2) and relevant monomers are performed at MP2/6-311++G(2d,2p). Electron density transfer (EDT), electron transfer process and donor-acceptor stabilization energy (E_{inter}) are gathered in Table 4.

The obtained results from NBO analysis show that there are different directions of electron density transfer between CO_2 and DMS upon complexation. The EDT values of DMS in **D-1**, **T-1**, **T-2**, **T-3**, **T-4** and **T-5** are positive while those values in the remaining complexes are negative. These results show that electron density is transfered from DMS to CO_2 in **D-1**, **T-1**, **T-2**, **T-3**, **T-4** and **T-5** and an inverse trend occurs in the rest of complexes. The presence of electron transfer processes from n(O) to σ*(C−H) anti-bonding orbitals and from n(S), n(O) to π*(C=O) anti-bonding orbitals confirm the formation of C−H⋯O hydrogen bonds and >C=O⋯S(O) Lewis acid-base interactions in the complexes investigated. Moreover, π(C−O)→σ*(S−C) and n(O)→σ*(S−C) processes are found to be represented for S⋯O chalcogen-chalcogen interactions. For binary complexes, the E_{inter} value of n(S)→π*(C=O) in **D-1** is 7.2 kJ.mol^{-1}, while they are *ca.* 0.3 kJ.mol^{-1} for electron transfer from n(O) to σ*(C−H) in **D-2** and **D-3**. This affirms that the stability of DMS⋯$1CO_2$ complexes increases in the sequence: **D-3** < **D-2** < **D-1**. The same tendency is also obtained for DMS⋯$2CO_2$ ternary complexes. The >C=O⋯S(O) Lewis acid-base interactions dominate the other interactions in stabilization of complexes (*cf.* Table 4). Four >C=O⋯S(O) Lewis acid-base interactions are found in **T-4** with the largest E_{inter} value of 5.5 kJ.mol^{-1}, showing that **T-4** is the most stable complex for DMS⋯$2CO_2$ ternary system. The n(S)→π*(C=O) processes are observed in **T-1**, **T-2** and **T-3** but not found in **T-5** and **T-6**. Thus, **T-1** and **T-2** are stabilized mainly by two S(O)⋯C=O Lewis acid-base interactions with the E_{inter} values ranging from 2.0 to 4.9 kJ.mol^{-1}. Meanwhile, **T-3** is only formed by S⋯C=O and other weak interactions (E_{inter} values of 0.2-0.8

kJ.mol^{-1}). There are three electron transfer processes contributing considerably to the strength of **T-6** (E_{inter} values of 1.9-2.5 kJ.mol^{-1}) and only two O···C=O interactions determining **T-5** stability (E_{inter} values of 2.6-3.3 kJ.mol^{-1}). Accordingly, the stability of ternary complexes decreases in the ordering **T-4** > **T-2** > **T-1** > **T-3** > **T-6** > **T-5**, which is consistent with the results of interaction energy in Table 2. These results also show that intermolecular interactions have increasing order of stability in going from C−H···O to S···O to O···C=O and then to S···C=O.

Table 4. Selected results of vibrational and NBO analysis at MP2/6-311++G(2d,2p)

Complex	EDT (e)	Electron donor-acceptor process	E_{inter} (kJ.mol^{-1})	Δr_{C-H} (Å)	Δv_{X-H} (cm^{-1})
D-1	0.0085[a]	n(S1)→π*(C10=O12)	7.2	-	-
D-2	-0.0004[a]	n(O11)→σ*(C2−H5)	0.2	0.0005	-3.5
		n(O11)→σ*(C6−H7)	0.2	0.0004	-3.0
		n(O12)→σ*(C2−H3)	0.3	0.0004	-2.7
		n(O12)→σ*(C6−H9)	0.3	0.0004	-3.0
D-3	-0.0006[a]	n(O12)σ*(C6−H8)	0.2	-0.0002	-6.6
T-1	0.0048[a] -0.0060[b] 0.0012[c]	n(S1)π*(C10=O11)	4.9	-	-
		n(O12)→σ*(C2−H3)	0.5	-0.0005	9.9
		n(O11)→σ*(C6−H9)	0.5	-0.0005	10.1
		n(O14)→σ*(C2−H3)	0.7	-0.0005	9.9
		n(O14)→σ*(C6−H9)	0.7	-0.0005	10.1
		n(O14)→π*(C10=O11)	2.0	-	-
T-2	0.0028[a] -0.0023[b] -0.0005[c]	n(S1)→π*(C10=O11)	3.2	-	-
		π(C10−O11)→σ*(S1−C6)	1.7	-	-
		n(O12)→π*(C13=O14)	2.8	-	-
		n(O15)→σ*(C6−H8)	1.0	-0.0015	11.5
		n(O15)→π*(S1−C2)	1.5	-	-
T-3	0.0031[a] -0.0028[b] -0.0003[c]	π(C10−O11)→σ*(C2−H5)	0.3	0.0003	-1.3
		π(C10−O12)→σ*(C2−H3)	0.2	0.0003	-1.3
		π(C10−O11)→σ*(C6−H7)	0.3	0.0003	-1.0
		π(C10−O12)→σ*(C6−H9)	0.2	0.0003	-1.0
		n(O14)→σ*(C2−H4)	0.8	-0.0009	3.1
		n(O11)→π*(C6−S1)	0.8	-	-
		n(S1)→π*(C13=O15)	2.5	-	-
T-4	0.0108[a] -0.0034[b] -0.0074[c]	n(S1)→π*(C10=O11)	3.6	-	-
		n(S1)→π*(C13=O14)	5.5	-	-
		n(O12)→π*(C13=O14)	3.6	-	-
		n(O15)→π*(C10=O11)	1.6	-	-
		n(O11)→σ*(C2−H4)	0.3	-0.0012	6.7
		n(O15)→σ*(C2−H3)	0.3	0.0002	1.1

T-5	0.0002[a] -0.0007[b] 0.0005[c]	$n(O11) \rightarrow \sigma^*(C2−H5)$	0.4	0.0004	-2.6
		$\pi(C10−O12) \rightarrow \sigma^*(C2−H3)$	0.3	0.0005	-3.4
		$n(O11) \rightarrow \sigma^*(C6−H7)$	0.3	0.0004	-2.9
		$n(O11) \rightarrow \pi^*(C13=O14)$	2.6	-	-
		$n(O15) \rightarrow \pi^*(C10=O12)$	3.3	-	-
T-6	-0.0014[a] 0.0009[b] 0.0005[c]	$n(O11) \rightarrow \pi^*(C13=O15)$	2.5	-	-
		$\pi(C10−O12) \rightarrow \sigma^*(C2−H3)$	0.3	0.0006	-5.3
		$n(O11) \rightarrow \sigma^*(C2−H5)$	0.2	0	6.0
		$n(O14) \rightarrow \sigma^*(C2−H5)$	2.0	0	6.0
		$n(O11) \rightarrow \sigma^*(C6−H7)$	0.2	0.0001	5.0
		$n(O14) \rightarrow \sigma^*(C6−H7)$	1.9	0.0001	5.0
		$\pi(C10−O12) \rightarrow \sigma^*(C6−H9)$	0.3	0.0007	-6.0

[a), b), c)] *for charge of DMS, CO_2, CO_2*

When adding one CO_2 molecule to DMS$\cdots$1CO_2, the stabilization energy of $n(S) \rightarrow \pi^*(C=O)$ processes are lowers by 1.7-4.7 kJ.mol^{-1} and that of $n(O) \rightarrow \sigma^*(C−H)$ processes rise slightly by 0-1.7 kJ.mol^{-1}. This indicates that when the cooperativity of intermolecular interactions happens, the strength of >C=O$\cdots$S Lewis acid-base interactions decrease while it is increased for C−H$\cdots$O hydrogen bonds. In summary, NBO results confirm again that the S$\cdots$C=O Lewis acid-base interaction plays a primary role into the stability of DMS$\cdots$xCO_2 complexes while the other interactions act as an additional component.

The characteristics of the C−H$\cdots$O hydrogen bond are investigated via the changes of C-H bond length and its stretching frequency in complexes compared to relevant monomers, as described in Table 4. In general, the C−H bond lengths in **T-1**, **T-2**, **T-3** and **T-4** are shortened by 0.0002−0.0015 Å and accompanied by an increase in stretching frequency of 3.1−11.5 cm^{-1}. In addition, a small elongation of C−H bond length of 0.0001−0.0007 Å and a decrease of its corresponding stretching frequency of 1.0−6.0 cm^{-1} in **D-2**, **D-3**, **T-5** and **T6** are estimated. Nevertheless, both changes of C-H bond lengths and stretching frequencies are quite small and do not rule, causing difficulty in assigning exactly to kind of C−H$\cdots$O hydrogen bond in the systems. This assignment will be explored in our next work on the basis of deeper investigations.

4. Concluding remarks

The theoretical investigation on interactions between DMS and CO_2 induce nine stable structures in which three for DMS$\cdots$1CO_2 binary and six for DMS$\cdots$2CO_2 ternary complexes. The interaction energies of DMS$\cdots$xCO_2 (x=1, 2) complexes range from -8.3 to -22.0 kJ.mol^{-1} at the MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) level. The complex stabilization is mainly determined by S(O)$\cdots$C=O Lewis acid-base interaction overcoming the O(S)$\cdots$O chalcogen-chalcogen and C−H$\cdots$O hydrogen bonded interaction. When a CO_2 molecule is added to DMS$\cdots$1CO_2 dimer, the stability of complexes is enhanced due to the slighly cooperative effect of intermolecular

interactions. The SAPT2+ analysis shows a dominating contribution of induction term as compared to other energetic terms to the overall stabilization energy of DMS···xCO$_2$ complexes. The obtained results suggest that classfication of C−H···O hydrogen bond in the DMS···xCO$_2$ complexes (x=1,2) is complicated, and will be solved in the next study.

ACKNOWLEDGMENT

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