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STUDY ON STABILITY AND NATURE OF INTERACTIONS OF FUNCTIONAL ORGANIC MOLECULES WITH CO_2 AND H_2O BY USING QUANTUM CHEMICAL METHODS

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INTRODUCTION

1. Research introduction

Air pollution is one of the hottest topics which attracts a lot of attention. Increasing amount of carbon dioxide (CO_2) in the air is the main factor that affects significantly the greenhouse effect. The enhancing applications of supercritical CO_2 ($scCO_2$) in manufacturing industries help to partially solve emission problems, while also saving other resources. $ScCO_2$ has attracted much attention due to its environmentally friendly applications, as compared to conventional organic solvents. $ScCO_2$ has indeed been widely used as a solvent for extraction purposes or in organic solvent elimination/purification processes, also as an antisolvent in polymerization of some organic molecules and precipitation of polymers. Therefore, it is essential to clarify interactions between CO_2 and functional organic compounds and their electronic characteristics at molecular level.

Up to now, various experimental researches on the interactions between solutes and $scCO_2$ solvent have been undertaken to better investigate the solubility in $scCO_2$. Furthermore, the use of polarized compounds as H_2O, small alcohols as cosolvents was reported to affect the thermodynamic and even kinetic properties of reactions involving CO_2. Addition of H_2O into $scCO_2$ solvent also helps to increase the solubility and extraction yield of organic compounds. Therefore, systematically theoretical research on interactions between CO_2, H_2O and organic functional compounds will open the doors to the nature and role of formed interactions, the effect of cooperativity in the solvent – cosolvent – solute system. The achieved results are hopefully to provide a more comprehensive look at $scCO_2$ applications and also contribute to the understanding of the intrinsic characteristics of weak noncovalent interactions.

2. Object and scope of the research

- Research object: Geometrical structure, strength of complexes, and stability, characteristic of noncovalent interactions including tetrel bond and hydrogen bond.

- Scopes: complexes of functional organic compounds including dimethyl sulfoxide, acetone, thioacetone, methanol, ethanol, ethanthiol, dimethyl ether and its halogen/methyl substitution with some molecules of CO_2 and/or H_2O.

3. Novelty and scientific significance

This work represents the stability and properties of noncovalent interactions in complexes of functional organic compounds with CO_2 and/or H_2O. Remarkably, the geometric trend of complexes with mentioned organic compounds and CO_2 and/or H_2O is determined. The bonding features of complexes with CO_2 and/or H_2O are also analysed in detail. The O–H···O HBs contribute largely into the cooperativity among other weak interactions including C···O/S TtBs, C–H···O HBs and O···O ChBs. Especially, it is found the growth pattern in complexes of ethanol with 1-5 CO_2 molecules which is expected to be useful for understanding the ethanol solvation in $scCO_2$.

The achieved results provide useful information for the development of promising functionalized materials for CO_2 capture/sequestration and increase the knowledge in noncovalent interactions. It is an important reference for future works on $scCO_2$ and benchmark of noncovalent interactions.

Chapter 1. DISSERTATION OVERVIEW

1.1. Overview of the research

Fluorocarbons, fluoropolymers, and carbonyl-based compounds are previously considered as CO_2-philic functional groups. While high cost and toxicity are the limitations of the first two compounds, carbonyl-based compounds have been paid much attention thanks to their simple synthesis process and lower cost. The addition of a small amount of cosolvents into the $scCO_2$ solvent resulted in an increase in the solubility of the solutes. In particular, some alkanes were added to $scCO_2$ to dissolve the nonpolar compounds, whereas functional organic compounds or H_2O were used for the polar ones. Alcohols including methanol, ethanol, and propanol were extensively used as cosolvents to improve both solubility and selectivity processes. The addition of H_2O into $scCO_2$ solvent was reported to induce an increase in the solubility and extraction yield of organic compounds.

From the theoretical viewpoint, it is important to elucidate the interactions, stability and structures of complexes between organic compounds and CO_2 with/without H_2O at molecular level. The intrinsic strength of the noncovalent interactions between CO_2 and adsorbents is determined as a key to demanded captured abilities.

The molecules containing carbonyl group have been paid much attention by series of experimental and theoretical works. The structures of complexes and strengths of intermolecular interactions have been reported through numerous studies on systems bound by CO_2 and various organic compounds. The C⋯O tetrel was addressed as the bonding feature of many complexes involving CO_2. Different with the great attention of carbonyl compounds, thiocarbonyl ones have been rarely studied in searching for an effective cosolvent in $scCO_2$. Thiocarbonyl compounds have been used in syntheses and have provided several unique organocatalysts thanks to their higher reactivity and less polarity in comparison with carbonyl ones. Accordingly, understanding of interactions of thioacetone (acs) with popular solvents

and cosolvents used in synthesis, extraction, separation processes such as $scCO_2$ and/or H_2O is required.

Up to now, most of studies concentrated on the geometries, stability and interactions of binary complexes involving CO_2. Nevertheless, the aggregation and growth mechanism of complexes with more CO_2 molecules, which are important to understand the absorption processes and their properties, have not been reported yet. Besides, the solvation structures and stability of complexes formed by interactions of organic compounds with a small number of CO_2 and H_2O molecules have not yet been discovered.

1.2. Objectives of the research

1. To determine stable structures and to compare the strength of the complexes formed by interaction of basic organic compounds functionalized by various groups with CO_2 and H_2O molecules.

2. To specify the existence and the role of noncovalent interactions in stabilizing the complexes, to unravel their cooperativity. Furthermore, this research was investigated to clarify role of H_2O in stabilization of noncovalent interactions and complexes.

3. To investigate the effect of different substitution groups including halogen and methyl on the geometry and stability of complexes of functionalized organic compounds with CO_2 and/or H_2O.

4. To discover the trend of geometrical structures and characteristic of noncovalent interactions when increasing number of CO_2/H_2O molecules.

1.3. Research content

The complexes of functional organic molecules including $(CH_3)_2SO$, $(CH_3)_2CO$, $(CH_3)_2CS$, CH_3OCHX_2 (X=F,Cl, Br, H, CH_3) $(CH_3)_2S$, CH_3OH, C_2H_5OH, C_2H_5SH with nCO_2 and/or nH_2O (n=1-2) were investigated. With those systems, the following contents were performed:

- Choosing the computational methods along with basis sets which are suitable.

- Finding the stable geometries with minima of energy on potential energy surfaces.

- Identifying the electronic properties of noncovalent interactions formed.

- Evaluate the interaction energy of complexes, and comparing their strength. Besides, the contribution of physical energetic components to the complex stabilisation was also estimated.

- Evaluating the cooperative effect between noncovalent interactions in complexes. The effect of addition of another CO_2 or H_2O molecule into complexes was explored.

1.4. Research methodology

Optimization and vibrational frequency calculations were done at MP2/6-6-311++G(2d,2p). Single point energies with the geometries optimized at MP2/6-311++G(2d,2p) were computed at CCSD(T)/6-311++G(2d,2p) or MP2/aug-cc-pVTZ. Interaction energies and cooperative energies are corrected for ZPE and the BSSE. The depth of intermolecular interactions *via* AIM was discovered at MP2/6-311++G(2d,2p) or MP2/aug-cc-pVTZ. NBO analyses with ωB97X-D or MP2 method was used to quantitatively determine the charge-transfer effects and the characteristics of noncovalent interactions. To further identify the noncovalent behaviors, interactions between carbon dioxide and ethanol were assessed with NCIplot at MP2/6-311++G(2d,2p). MEP of isolated monomers was plotted at MP2/aug-cc-pVTZ. All quantum calculations mentioned above were carried out *via* the Gaussian09 package. The SAPT2+ analysis executed by PSI4 programs was applied to decompose the interaction energy into physically meaningful components.

Chapter 2. THEORETICAL BACKGROUNDS AND COMPUTATIONAL METHODS

2.1. Theoretical background of computational chemistry

This section introduces the basic understanding of the theory behind the methods using the dissertation, including the Hartree-Fock method, the post Hartree-Fock methods, density functional theory and basis set.

2.2. Computational approaches to noncovalent interactions

In this section, detailed descriptions of quantum chemical approaches using in the dissertation are given.

2.3. Noncovalent interactions

Noncovalent interactions have a constitutive role in the science of intermolecular relationships. In nature, these interactions are the foundation of the life process itself, the ultimate function articulation, both mechanical and cognitive. In synthetic chemistry, interactions between rationally designed molecular subunits drive the assembly of nanoscopic aggregates with targeted functions.

The definition, properties and overview of noncovalent interactions including tetrel, hydrogen, halogen, chalcogen bonds are described.

2.4. Computational methods of the research

A detailed description of quantum chemical methods using in this dissertation is presented. In particular, geometries and harmonic vibrational frequencies of the monomers and complexes are obtained by MP2 in combination with high basis sets 6-311++G(2d,2p). The interaction energy of each complex is determined by using the supramolecular approach at MP2/aug-cc-pVTZ or CCSD(T)/6-311++G(2d,2p). The electron analysed including AIM, NBO, MEP, NCIplot are applied to give an insight to the noncovalent interactions formed. SAPT2+ calculations are performed with density-fitted integrals with the standard aug-cc-pVDZ basis set to investigate the contribution of physical components.

Chapter 3. RESULTS AND DISCUSSION

3.1. Interactions of dimethyl sulfoxide with nCO_2 and nH_2O (n=1-2)

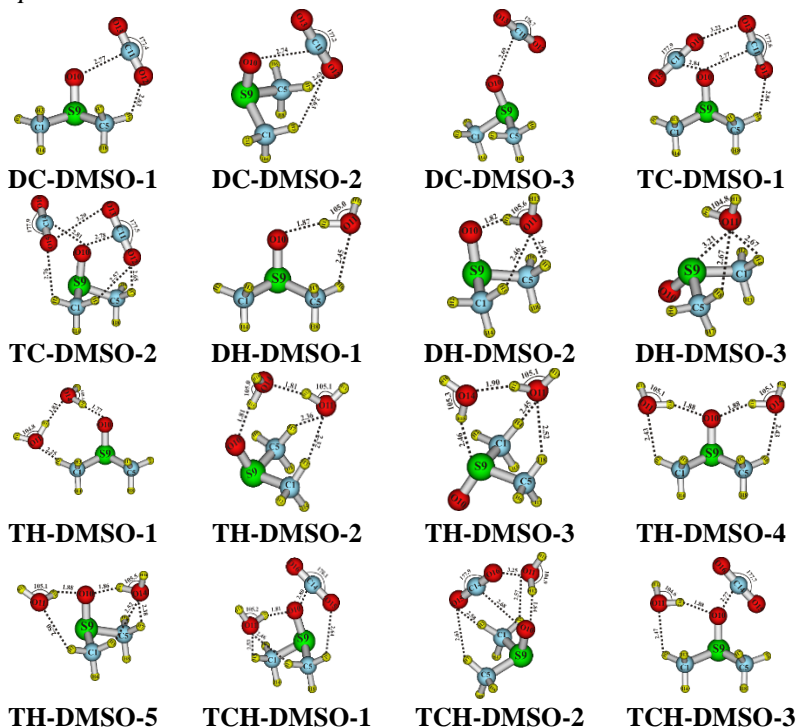*3.1.1. Geometries, AIM analysis and stability of intermolecular complexes*

DC-DMSO-1   **DC-DMSO-2**   **DC-DMSO-3**   **TC-DMSO-1**

TC-DMSO-2   **DH-DMSO-1**   **DH-DMSO-2**   **DH-DMSO-3**

TH-DMSO-1   **TH-DMSO-2**   **TH-DMSO-3**   **TH-DMSO-4**

TH-DMSO-5   **TCH-DMSO-1**   **TCH-DMSO-2**   **TCH-DMSO-3**

Figure 3.1. Geometries of stable complexes formed by interactions of DMSO with CO_2 and H_2O (MP2/6-311++G(2d,2p))

- The S(O)···O and C···O intermolecular contacts are named as ChB and TtB, respectively. The positive values of both $\nabla^2\rho(r)$ (0.021−0.055 au) and $H(r)$ (0.0009−0.0014 au) for the S(O)···O and S=O···C interactions at these BCPs suggest that these intermolecular contacts are weak noncovalent interactions.

- There is an increase in electron density at the BCPs of the interactions in the order of O···O < C−H···O ≈ S···O < S=O···C < O−H···O(S). Accordingly, the S=O···C TtB appears to play a more important role than the C−H···O HB and O···O ChB in stabilizing DMSO···1,2CO_2,

while complexes of DMSO···1,2H_2O are mainly stabilized by O−H···O(S) HBs along with an additional role of C−H···O HB and S···O ChB. In the case of DMSO···1CO_2···1H_2O, the magnitude of interactions contributing to their stability increases in the ordering going from O···O ChB to C−H···O HB to S=O···C TtB and finally to O−H···O HB.

3.1.2. Interaction and cooperative energies and energy component

- Interaction energies of DMSO···1H_2O are more negative than that for DMSO···1CO_2, showing that DMSO interacts with H_2O more strongly than with CO_2.

- Interaction energies for DMSO···2H_2O and DMSO···2CO_2 are more negative than those compared to corresponding binary systems by 1−43 kJ.mol^{-1} and 10−16 kJ.mol^{-1}.

- The addition of CO_2 and H_2O molecules into binary complexes leads to an increase in stability of ternary complexes, in which the increasing magnitude is larger for the addition of H_2O than that for CO_2.

- The cooperative energies are more negative for DMSO···2H_2O than for DMSO···2CO_2 by 9−22 kJ.mol^{-1} and DMSO···1CO_2···1H_2O by 5−18 kJ.mol^{-1}. This implies a good correlation between both cooperative and interaction energies of the investigated systems.

Table 3.1. Interaction energy and cooperative energy of complexes of DMSO with CO_2 and/or H_2O at CCSD(T)/6-311++G(2d,2p)//MP2/6-311++G(2d,2p), kJ.mol^{-1}

Complex	E_{int}	Complex	E_{int}	E_{coop}
DC-DMSO-1	-12.5	**TC-DMSO-1**	-23.7	-1.4
DC-DMSO-2	-13.3	**TC-DMSO-2**	-25.6	-1.0
DC-DMSO-3	-9.5	**TH-DMSO-1**	-46.6	-20.3
DH-DMSO-1	-22.8	**TH-DMSO-2**	-51.7	-22.7
DH-DMSO-2	-27.1	**TH-DMSO-3**	-28.5	-13.1
DH-DMSO-3	-9.2	**TH-DMSO-4**	-44.2	-10.3
		TH-DMSO-5	-47.4	-9.5
		TCH-DMSO-1	-39.0	-5.4
		TCH-DMSO-2	-36.4	-5.5
		TCH-DMSO-3	-34.3	-5.2

3.1.3. Bonding vibrational modes and NBO analysis

- The existence of C−H···O HB, O−H···O HB and S=O···C TtB in the complexes is confirmed here by means of EDT from n(O) to σ*(C−H),

n(O) to σ*(O−H) and n(O) to π*(C=O) with the $E^{(2)}$ values of 0.3−14 kJ.mol^{-1}, 36−107 kJ.mol^{-1} and 6−16 kJ.mol^{-1}, respectively.

- The C−H···O HBs belong to the blue-shifting HB type, while the O−H···O(S) HBs are red-shifting.

3.1.4. Remarks

Addition of H_2O or CO_2 molecules into binary complexes leads to an increase in the stability of the resulting ternary complexes. It is remarkable that a greater cooperativity of relevant interactions in DMSO···$2H_2O$ was observed, as compared to those in DMSO···$1CO_2$···$1H_2O$ and DMSO···$2CO_2$.

The stability of DMSO···$1,2CO_2$ complexes is contributed by the crucial role of the S=O···C TtB, while the O−H···O HB plays a more important role than other weak interactions in stabilizing DMSO···$1,2H_2O$ and DMSO···$1CO_2$···$1H_2O$.

In general, the magnitude of the red shift in O−H stretching frequency of O−H···O bond is enhanced, whereas the extent in stretching frequency blue shift of the C−H bond in the C−H···O bonds is weakened when a cooperativity happens.

3.2. Interactions of acetone/thioacetone with nCO_2 and nH_2O

3.2.1. Geometric structures

- Three types of aco···CO_2 geometries are observed as previously investigated, in which **Oc-1** was reported as global minimum with the cooperativity of C···O TtB and C−H···O HB, as typical or conventional structure.

- It is noteworthy that in case of acs complexes, the non-conventional geometry **Sc-2** is also found, however, the T-shape one is not observed on the potential surface. This absence is probably explained by the decreasing negative charge from O to S atom, which cause the electrostatic nature of C···O/S TtB.

- Complexes with the attendance of $1,2H_2O$ are mainly characterized by two types of HBs including O−H···O/S and C−H···O. The coexistence of C···O/S TtBs and O−H···O/S HBs is found in the combinations of aco/acs and CO_2 and H_2O.
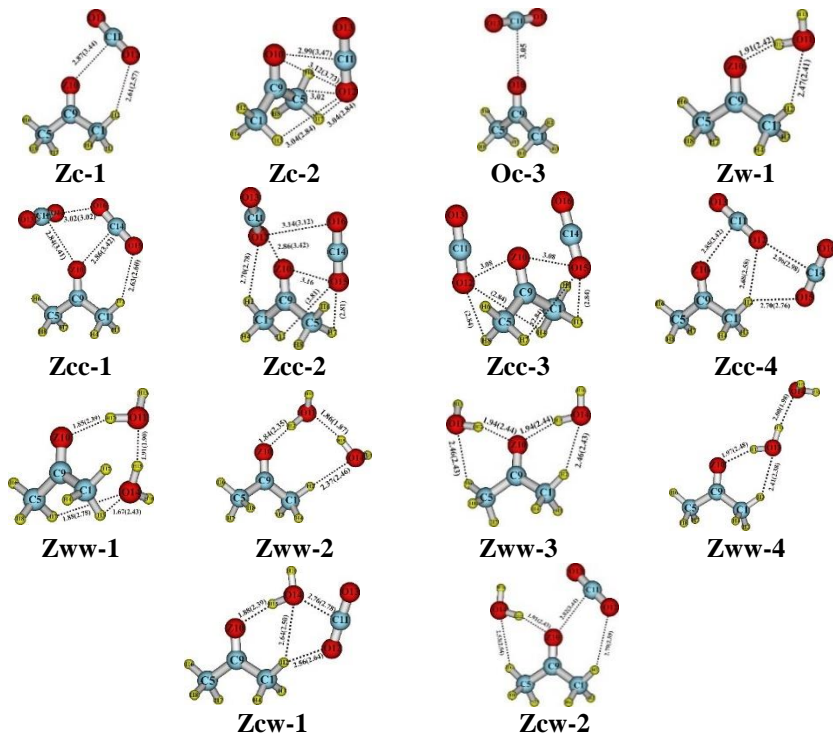
Figure 3.3. Stable structures of complexes formed by interactions of $(CH_3)_2CZ$ with CO_2 and H_2O (Z=O, S) (the values in parentheses are for complexes of $(CH_3)_2CS$)
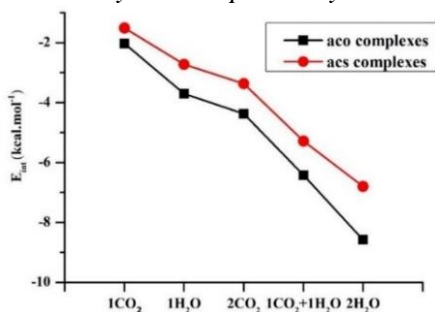
3.2.2. Stability and cooperativity

Figure 3.4. The correlation in interaction energies of the most energetically favorable structures in six systems at CCSD(T)/6-311++G(2d,2p)//MP2/6-311++G(2d,2p)

- The negative values of E_{coop} support the positive cooperative effect in ternary systems. The cooperative energies of aco complexes are more negative than the corresponding ones of acs by 0.1-1.3 kcal.mol^{-1}.

3.2.3. NBO analysis, and hydrogen bonds

- The results suggest a stronger electron transfer from aco/acs to H_2O relative to CO_2.
- From binary to ternary complexes, the second-order energies of these interactions change insignificant, consistent with the quite slight positive cooperativity between them.

3.2.4. Remarks

The complexes of CO_2 and/or H_2O with aco are more stable than those with acs. The solubility of aco and acs in $scCO_2$ with the presence of water as cosolvent is promising to be better than that that in pure $scCO_2$. The stabilities of considered complexes are contributed mainly by electrostatic energy. The complexes of $1,2CO_2$ with aco are primarily stabilized by C···O TtBs while those with acs are balanced by multiple weak interactions. For complexes relevant H_2O, the O−H···O/S plays a decisive role in stabilizing the complexes.

All O−H···O HBs in the systems investigated belong to red-shifting HBs, which is caused by an increase of electron occupation of $\sigma^*(O-H)$ antibonding orbital overcoming an increase of s-character of O hybridized atom. The blue-shift of C−H···O HBs in CO_2 complexes is apparently governed by an increase of *s*-character percentage in C−hybridized atom.

3.3. Interactions of methanol with CO_2 and H_2O

3.3.1. Structures and AIM analysis

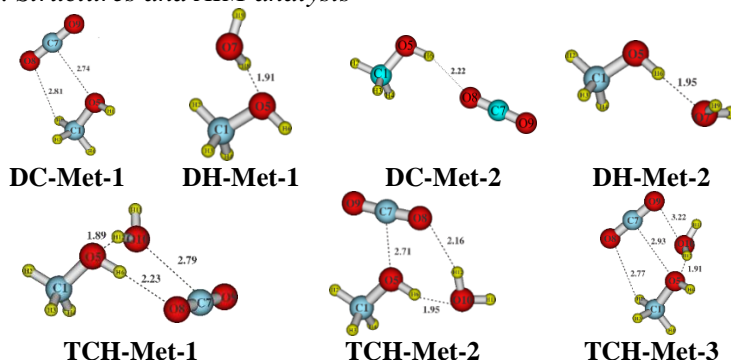**DC-Met-1** **DH-Met-1** **DC-Met-2** **DH-Met-2**

TCH-Met-1 **TCH-Met-2** **TCH-Met-3**

Figure 3.6. Stable geometries of complexes formed by interaction of CH_3OH with CO_2 and H_2O at MP2/6-311++G(2d,2p)

3.3.2. Interaction and cooperative energies

- Interaction energy of $CH_3OH \cdots CO_2 \cdots H_2O$ complexes is much more negative than binary ones by 12.7-24.5 $kJ.mol^{-1}$, suggesting that the addition of a CO_2 or H_2O molecule leads to an increase in the stability of the formed trimers, in which the increasing magnitude is higher for the adding of H_2O than the CO_2 counterpart.

- All values of E_{coop} of ternary complexes are negative in ranging from -3.8 to -8.9 $kJ.mol^{-1}$, indicating that the formed interactions work in concert and enhance the complex stability.

3.3.3. Vibrational and NBO analyses

For $CH_3OH \cdots CO_2$ system, the $E^{(2)}$ of $n(O5) \rightarrow \pi^*(C7=O8)$ in **DC-Met-1** is higher than that of $n(O8) \rightarrow \sigma^*(O5-H6)$ in **DC-Met-2** by *ca.* 4.39 $kJ.mol^{-1}$, indicating that the stability of **DC-Met-1** is larger than **DC-Met-2** and the $O \cdots C=O$ TtB plays a decisive role in stabilization of $CH_3OH \cdots CO_2$ complexes. For complexes involving H_2O, $E^{(2)}$ values of $n(O) \rightarrow \sigma^*(O-H)$ are remarkably higher than those of the remaining interactions. These results show a considerable role of the $O-H \cdots O$ HB in stabilizing the complexes.

- The $O-H \cdots O$ and $C-H \cdots O$ contacts in most examined complexes generally belong to the red-shifting HB which are determined by an increase in the electron density at the $\sigma^*(O(C)-H)$ orbital.

3.3.4. Remarks

The interaction of CH_3OH with H_2O is stronger than that with CO_2. For ternary complexes, the addition of a CO_2 or H_2O guest molecule into binary structures leads to an increase in the stability of complexes.

There is a large cooperativity (ranging from 3.8 to 8.9 $kJ.mol^{-1}$) between HBs and TtBs in stabilizing the ternary complexes. The $O-H \cdots O$ and $C-H \cdots O$ contacts in examined complexes generally belong to the red-shifting HB, except for the $C1-H2 \cdots O9$ in **TCH-Met-3** which belongs to the blue-shifting HB.

3.4. Interactions of ethanethiol with CO_2 and H_2O
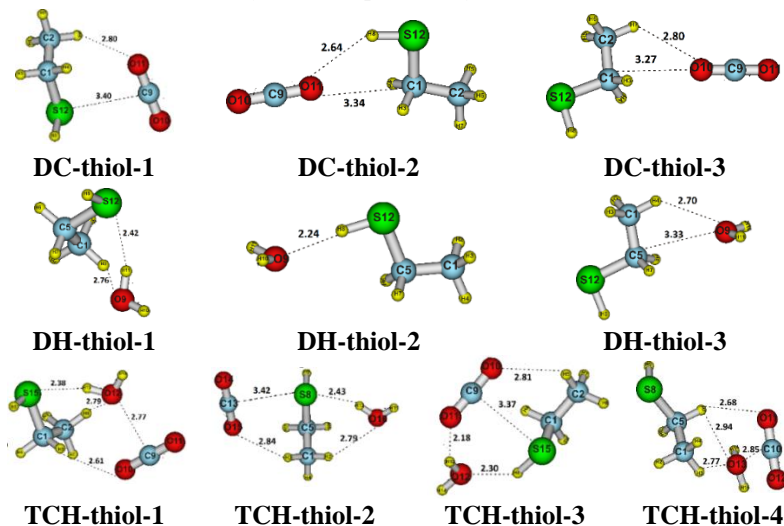
3.4.1. Structure, stability and cooperativity

DC-thiol-1	DC-thiol-2	DC-thiol-3
DH-thiol-1	DH-thiol-2	DH-thiol-3
TCH-thiol-1	TCH-thiol-2	TCH-thiol-3	TCH-thiol-4

Figure 3.7. Stable geometries of complexes formed by interactions of C_2H_5SH with CO_2 and H_2O at MP2/6-311++G(2d,2p)

3.4.2. Vibrational and NBO analyses

- Amount of electron transfers from the C_2H_5SH molecule (acts as electron donor) to the CO_2 and H_2O molecules (as electron acceptors).

- NBO results confirm the primary role of S···C=O tetrel interaction in C_2H_5SH···CO_2 complexes. For complexes with the presence of H_2O, the strength of HBs increasing in the ordering: C−H···O < O−H···O < S−H···O < O−H···S.

3.4.3. Remarks

The interaction energies of C_2H_5SH···$1CO_2$···$1H_2O$ are more stable than C_2H_5SH···$1CO_2$ and C_2H_5SH···$1H_2O$ by 8.4 - 9.7 kJ.mol^{-1} and 6.0 - 11.5 kJ.mol^{-1}, respectively. The stability of C_2H_5SH···$1CO_2$ is due to the crucial role of the >C=O···S TtB and an additional cooperation from C−H···O HBs. The C_2H_5SH···$1H_2O$ and C_2H_5SH···$1CO_2$···$1H_2O$ are significantly stabilized by O−H···S strong hydrogen bonded interaction and a complementary of C−H···O, O−H···O interactions.

Generally, all C−H···O are characterized as blue-shifting HBs while

O−H⋯S interactions belong to red-shifting HBs. The behavior of S−H⋯O HB depends on the guest molecule. Their character changes from blue to red shift when the guest molecule goes from CO_2 to H_2O.

3.5. Interactions of CH_3OCHX_2 with nCO_2 and nH_2O (n=1,2)

3.5.1. Interactions of CH_3OCHX_2 with $1CO_2$

- The interactions of CO_2 with CH_3OCHX_2 (X = H, F, Cl, Br, CH_3) induce two geometries including **DC1-DME-X** and **DC2-DME-X** at MP2/6-311++G(2d,2p).
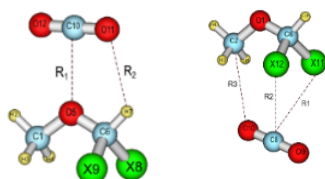

Figure 3.8. Stable structures of CH_3OCHX_2⋯$1CO_2$ complexes

DC1-DME   **DC2-DME**

- The interaction energies with both ZPE and BSSE of these complexes range from -2.8 kJ.mol^{-1} to -15.1 kJ.mol^{-1} at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) level of theory.
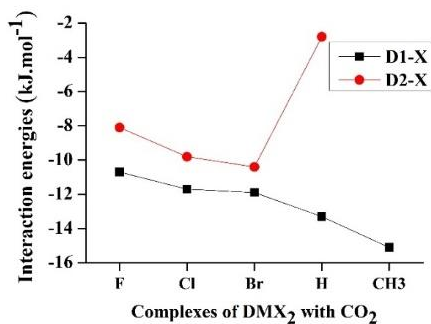

Figure 3.9. The difference in interaction energies (with ZPE and BSSE) of CH_3OCHX_2⋯$1CO_2$ complexes

- **DC1-DME** is found to be energetic-favored structure as compared to **DC2-DME** one. The halogenated-substituted derivatives cause a decrease in the complex strength while methyl-substituted one leads to a stabilization enhancement.

- The C⋯O tetrel bond plays the main contribution into the stability of complexes with the complement of C−H⋯O hydrogen bond.

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3.5.2. Interactions of CH₃OCHX₂ with 2CO₂

TC-DME-H **TC-DME-F** **T-DME-Cl** **TC-DME-Br** **TC-DME-CH₃**
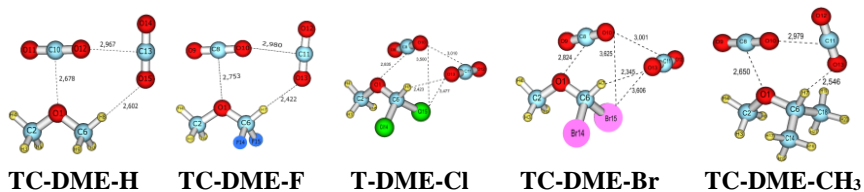
Figure 3.11. Stable structures of complexes $CH_3OCHX_2\cdots2CO_2$

- The addition of CO_2 molecule into binary complexes leads to the rearrangement of geometries, where three molecules interact mutual creating a ring or a cage.

- The appearance of new TtB between two CO_2 molecules is predicted to strengthen the ternary complexes.

- The stability of $CH_3OCHX_2\cdots2CO_2$ increases in order of F < H < CH₃ < Cl < Br, which is different with the binary complexes. It is due to the formation of Cl/Br···C=O interactions in **TC-DME-Cl** and **TC-DME-Br** strengthens the complex stability.

3.5.3. Interactions of CH₃OCHX₂ with nH₂O (n=1-2)

DH-DME-H **DH-DME-CH₃** **DH-DME-F** **DH-DME-Cl** **DH-DME-Br**

TH-DME-H **TH-DME-CH₃** **TH-DME-F** **TH-DME-Cl** **TH-DME-Br**
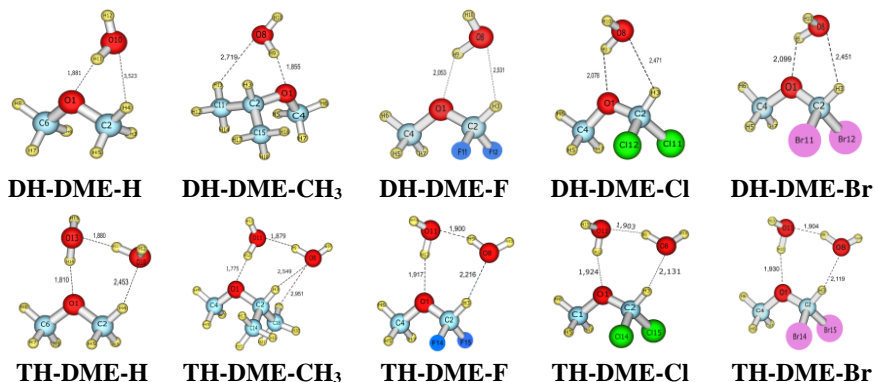
Figure 3.12. The stable structures of $CH_3OCHX_2\cdots nH_2O$ complexes
(n =1-2; X = H, F, Cl, Br, CH₃)

- All geometry of all **DH-DME-X** is stabilized by one O−H···O and one C−H···O HB. For complexes with $2H_2O$, it creates a heptagon in all structural shapes where three molecules connect mutual.

- It is found that the substitution of halogen atom into dimethyl ether results to a decrease in strength of O−H···O HB while the CH₃

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substituent makes that interaction becomes stronger. It is in agreement with the results found in complexes $CH_3OCHX_2 \cdots CO_2$.

- The O$\cdots$H−O is the main driver in stabilizing complexes besides the additional role of the remaining interactions.

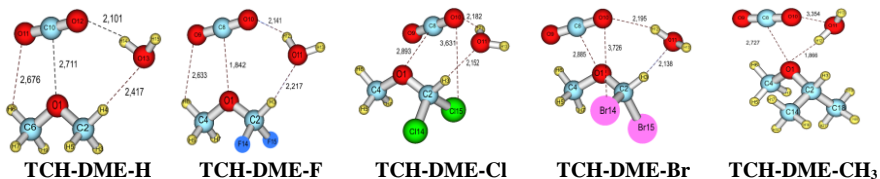### 3.5.4. Interactions of CH_3OCHX_2 with $1CO_2$ and $1H_2O$

| TCH-DME-H | TCH-DME-F | TCH-DME-Cl | TCH-DME-Br | TCH-DME-CH₃ |

Figure 3.13. Stable structures of complexes $CH_3OCHX_2 \cdots 1CO_2 \cdots 1H_2O$
(X = H, F, Cl, Br, CH_3)

- It exists the C−Cl/Br$\cdots$O halogen bond in **TCH-DME-Cl/Br** complexes.

- The **TCH-DME-H/CH₃** is mainly stabilized by the O−H$\cdots$O HB and O$\cdots$C while C−H$\cdots$O HB plays the main role in the **TCH-DME-F/Cl/Br** among multiple weak noncovalent interactions.

- The stability of ternary complexes with the same X is followed the order: **$2H_2O$ > $1CO_2+1H_2O$ > $2CO_2$**. This trend also is also observed for complexes with the substitution of halogen and methyl group into 2H in DME.

3.5.5. Remarks

For binary complexes $CH_3OCHX_2 \cdots 1CO_2/H_2O$, the stability is increased as order of substitution as F < Cl < Br < H < CH_3. The upward trend of stability for ternary complexes is different, due to the existence of the Cl/Br$\cdots$C=O TtB and Cl/Br$\cdots$O interactions. In general, the halogenated-substituted derivatives cause a decrease in the complex strength while methyl-substituted one leads to a stabilization enhancement.

For the same X, the addition of H_2O contributes a large amount to the complex stabilization, as compared to the addition of CO_2. AIM results found that all intermolecular interactions are weakly noncovalent interactions. The O−H$\cdots$O HBs are found to contribute to the positive cooperative effect leading to the greater cooperativity in

$CH_3OCHX_2\cdots2H_2O$ in comparison with in $CH_3OCHX_2\cdots2CO_2$.

The attractive electrostatic energy is the main contribution overcoming other energetic components in stabilizing the complexes.

3.6. Interactions of dimethyl sulfide with nCO_2 (n=1-2)
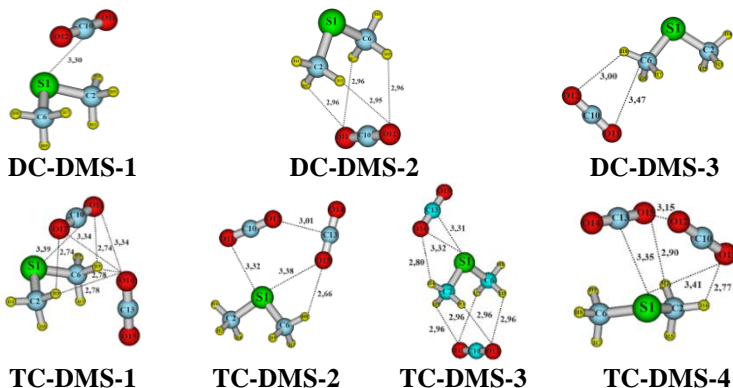
3.6.1. Geometric structures and AIM analysis

DC-DMS-1   **DC-DMS-2**   **DC-DMS-3**

TC-DMS-1   **TC-DMS-2**   **TC-DMS-3**   **TC-DMS-4**

Figure 3.14. Optimized structures of $(CH_3)_2S$ and nCO_2 (n = 1-2)

- The stability of complexes between DMS and nCO_2 (n = 1-2) is mainly contributed by S···C=O TtB with an additional complement from C−H···O HB and S(O)···O ChB. This observation is consistent with that taken from the complexes of dimethyl ether and CO_2.

3.6.2. Interaction and cooperativity energy and energetic components

Table 3.26. Interaction energies and cooperative energies of complexes DMS···nCO_2

Complex	E_{int}	Complex	E_{int}	E_{coop}
DC-DMS-1	-9.9	**TC-DMS-1**	-15.2	-1.0
DC-DMS-2	-3.9	**TC-DMS-2**	-16.9	-0.6
DC-DMS-3	-2.7	**TC-DMS-3**	-12.5	-0.4
		TC-DMS-4	-22.0	-0.8

All values are in kJ.mol^{-1}.

- For the binary system, the E_{int} is more negative for **DC-DMS-1** than for **DC-DMS-2** and **DC-DMS-3** by *ca.* 6.0 and 7.2 kJ.mol^{-1}, respectively. This indicates a decrease in the stability of complexes in going from **DC-DMS-1** to **DC-DMS-2** and then to **DC-DMS-3**.

- The stability of ternary complexes decreases in the trend of **TC-DMS-4** > **TC-DMS-2** > **TC-DMS-1** > **TC-DMS-3**, which is in good

agreement with the obtained AIM results.

- The stability of DMS⋯CO_2 is contributed mainly by induction component as compared to other energetic components.

3.6.3. Vibrational and NBO analyses

- 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.
- The S⋯C=O TtB plays a primary role into the stability of DMS⋯nCO_2 complexes while the other interactions act as an additional component.

3.6.4. Remarks

The interaction energies of DMS⋯nCO_2 (n=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)⋯C=O TtB overcoming the O(S)⋯O ChB and C−H⋯O HB.

When a CO_2 molecule is added to DMS⋯$1CO_2$ 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⋯nCO_2 complexes.

3.7. Growth pattern of the C_2H_5OH⋯nCO_2 complexes (n=1-5)

3.7.1. Structural pattern of the C_2H_5OH⋯nCO_2 complexes (n=1-5)

- Our predicted rotational spectra of **1A**-anti fit well with the experimental data, as previous studies did.
- **2A-**anti and **2A-**gauche are the rearrangements of C_2H_5OH corresponding conformers and two CO_2 molecules *via* two O8⋯C TtB and C−H⋯O HBs.
- It is worth noting that two CO_2 in **2A** are oriented to associate with two electron lone pairs of the oxygen atom O8 in C_2H_5OH. This result confirms the geometrical arrangements reported previously using molecular dynamic simulation.
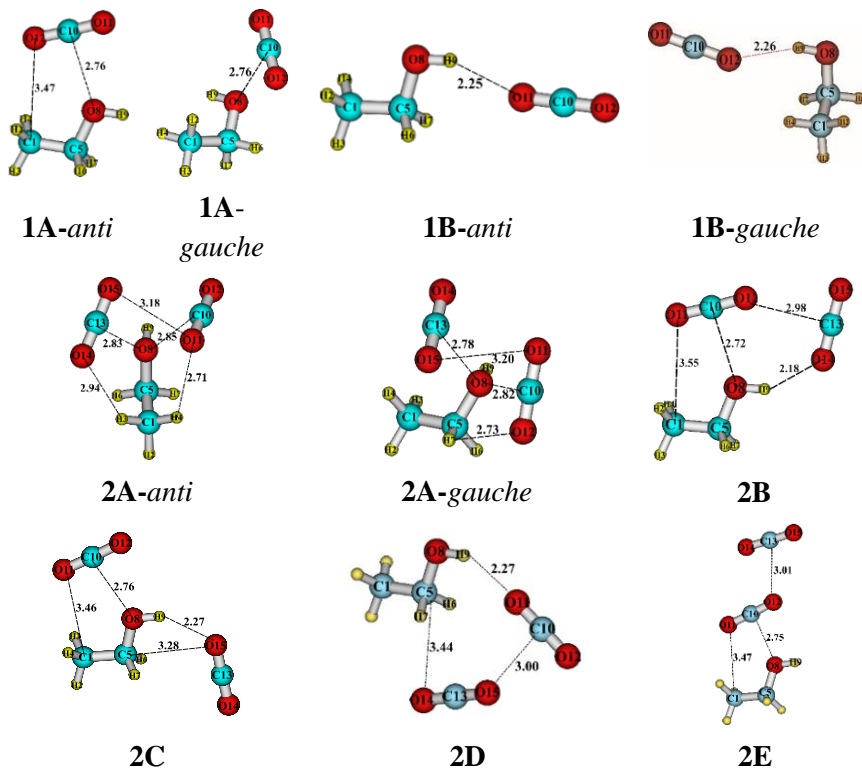
Figure 3.15a. Optimized structures of $C_2H_5OH \cdots nCO_2$ (n=1-2)

- The complexes with $3CO_2$ are obtained from the corresponding **2A-**anti or **2A-**gauche geometries with different positions of the third CO_2.

- For the conformers containing four CO_2 molecules, the fourth CO_2 molecule is likely to connect to neighbour CO_2 molecules rather than the C_2H_5OH as observed in the smaller complexes with $\leq 3CO_2$ molecules.

- The stable geometries of larger complexes with n=3-5 are discovered for the first time.

- Complexes of ethanol with nCO_2 (n=1−5) seem to be similar to other carbonyl-containing molecules, in which CO_2 molecules surround the functional groups (=O, >C=O, and –OH) of the host molecules.

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3A   **3B**   **3C**

4A   **4B**

5A   **5B**
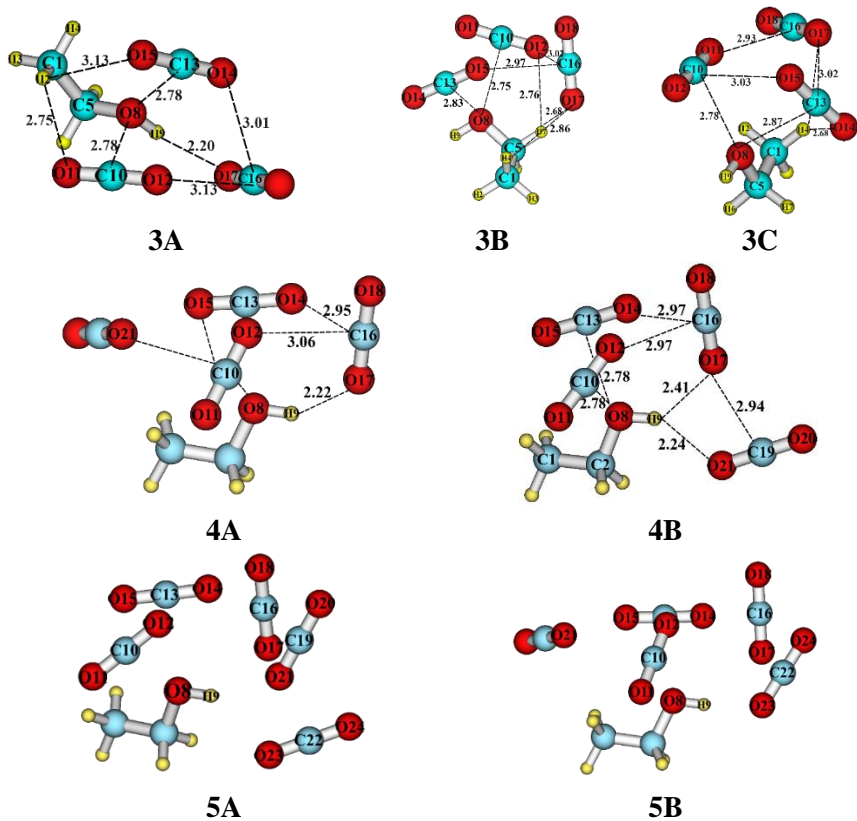
Figure 3.15b. Optimized structures of $C_2H_5OH \cdots nCO_2$ (n=3-5)

3.7.2. Complex stability, and changes of OH stretching frequency and intensity under variation of CO_2 molecules

- Their stabilities rise in the order $1CO_2 < 2CO_2 < 3CO_2 < 4CO_2 < 5CO_2$. It is proposed that the addition of CO_2 molecules leads to the stability enhancement of investigated complexes.

- The slightly higher stability of **1A**-anti as compared to **1A**-gauche is due to an additional role of C=O⋯C1 TtB.

- With the aim of CO_2 capture, the interaction capacity of CO_2 with ethanol is weaker than that of carbonyl/sulfoxide compounds, compatible with that of methanol, methylamine, and obviously stronger than alkanes such as methane, ethane and ethylene.
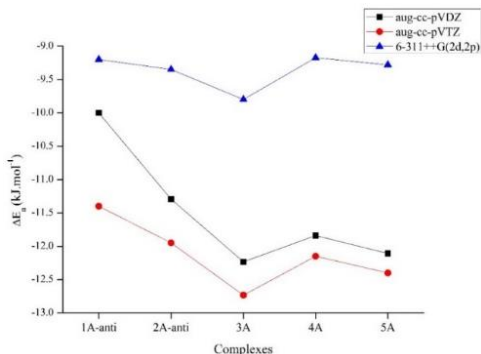
Figure 3.16. The binding energies per carbon dioxide

- In solvent perspective, the concentration ratio of 1:3 between ethanol and $scCO_2$ is predicted to be a potential ratio for the good solubility.

3.7.3. Intermolecular interaction analysis

- The 2Dplot of **1A-**anti has a peak in negative site of $(\lambda_2).\rho(r)$ with the electron density of about 0.01 au, confirming again the noncovalent attractive nature of O8···C TtB which also obtained from AIM analysis. The larger volume of gradient isosurface of **1A-**anti describes a stronger strength of O8···C TtB as compared to the O−H···O hydrogen one of **1B-**anti.

- From n=1 to n=3, the spikes expand in the negative site of $sign(\lambda_2).\rho(r)$, indicating the increasing of the attractive interactions contributing to the stabilization of the corresponding complexes). However, at n=4−5, it is observed the unchanged of the attractive spike as compared to complexes of $3CO_2$. It confirms the stronger interactions of complexes with $3CO_2$ in the sequence of 1-5 CO_2.

- The NBO analysis emphasizes the dominant role of C···O8 TtB relative to O8−H9···O11 HB in stabilizing the complexes investigated.

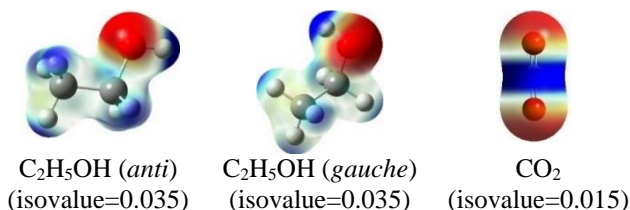### 3.7.4. Role of physical energetic components

C₂H₅OH (*anti*)
(isovalue=0.035)

C₂H₅OH (*gauche*)
(isovalue=0.035)

CO₂
(isovalue=0.015)

Figure 3.18. MEP surface of monomers including C_2H_5OH and CO_2 at MP2/aug-cc-pVTZ

- A significantly large role of attractive electrostatic is observed in comparison with induction and dispersion terms.

3.7.5. Remarks

For $C_2H_5OH\cdots nCO_2$ complexes (n=1-5), CO_2 molecules preferentially solvate around -OH of ethanol as the solvation site. A growth pattern in geometry is found that the stable complexes are formed based on the structures of (n-1) CO_2 ones when adding CO_2 molecule, with an exception of n=5.

It is noted that the binding of C_2H_5OH with 3 CO_2 molecules has a remarkable stability, which is expected for the good solubility of ethanol in $scCO_2$ solvent at ratio 1:3.

It is found that the positive cooperativity between the noncovalent interactions in $C_2H_5OH\cdots 2CO_2$ is slightly weaker than that of $(CO_2)_3$ pure systems. With the addition of CO_2 molecules, the $C\cdots O$ TtB overwhelming the C/O−H$\cdots$O HBs is maintained as the bonding characteristics and mainly contributes to the strength of $C_2H_5OH\cdots nCO_2$ complexes. These findings are expected to be useful for understanding the ethanol solvation in $scCO_2$.

CONCLUSIONS

The systematic investigation on complexes of functional organic molecules with CO_2 and/or H_2O using appropriate high level of theory is studied. These following results are hoped to contribute to the thorough understanding of the solvation process of organic functional molecules (including dimethyl sulfoxide, acetone, thioacetone, methanol, ethanol, ethanethiol, dimethyl ether and its halogen/methyl substitution) by carbon dioxide with and without the presence of water, the stability and bonding features of mentioned systems in aspect of theoretical viewpoint.

- The geometrical structures of complexes between dimethyl sulfoxide, acetone, thioacetone, dimethyl ether and its halogen/methyl-substituted derivatives, methanol, ethanethiol, dimethyl sulfide with $1,2CO_2$ and/or $1,2H_2O$ molecules are figured out that the guess CO_2/H_2O molecules preferentially solvate around the functional group of organic compounds, as the solvation site. The complexes of organic compounds with CO_2 molecules prefer the formations of C···O TtBs, while those with the presence of H_2O are stabilized by O–H···O/S HBs.

- Dimethyl sulfoxide, acetone, dimethyl ether is recognized to be more effective than ethanol, methanol, ethanethiol, thioacetone, dimethyl sulfide in aiming of carbon dioxide capture. The halogenated-substituted derivatives cause a decrease in the complex strength while methyl-substituted one leads to a stabilization enhancement. Remarkably, it is found that the interactions of CO_2 and/or H_2O with functional groups containing oxygen are more stable than those containing sulfur atom, and the larger positive cooperativity of ternary complexes is estimated in the complexes with O-containing organic molecules relative to S-containing ones.

- The addition of CO_2 or H_2O molecules into binary complexes leads to an increase in the stability of the resulting complexes, and it is significantly larger for the H_2O than CO_2 addition.

- The positive cooperative effect is found in all investigated systems indicating the mutual influence of intermolecular interactions in complexes of organic compounds with CO_2 and/or H_2O. It is interesting that the O−H···O HBs contribute largely into the cooperativity among other weak interactions including C···O/S TtBs, C-H···O HBs and O···O ChBs. A larger positive cooperativity is also found in case of H_2O relative to CO_2 addition.

- The complexes of 1,2CO_2 are primarily stabilized by C···O tetrel bonds. For complexes relevant H_2O, the O−H···O/S dominating other weak interaction plays a decisive role in stabilizing the complexes. The stabilities of investigated complexes are contributed mainly by electrostatic energy, and a smaller contribution of dispersion and induction term.

- For complexes C_2H_5OH···nCO_2 (n=1-5), a growth pattern in geometry is found that the stable complexes are formed based on the structures of (n-1) CO_2 ones when adding CO_2 molecule, with the exception of n=5. With the addition of CO_2 molecules, the C···O TtB overwhelming the C/O−H···O HBs is maintained as the bonding characteristics and mainly contributes to the strength of C_2H_5OH···nCO_2 complexes.

- All O−H···O HBs in the systems investigated belong to red-shifting HBs while the characteristic of C−H···O HBs is complicated. In most case, the C−H···O HBs is blue-shifting, however, their magnitude depends on the strength of C−H···O HBs.

List of publications contributing to the dissertation

1) The growth pattern, stability and properties of complexes of C_2H_5OH and nCO_2 (n = 1-5) molecules: a theoretical study
   Cam-Tu Dang Phan, Nguyen Thi Ai Nhung, Nguyen Tien Trung, *ACS Omega*, **2020**, 5, 14408-14416.

2) General trends in structure, stability and role of interactions in the complexes of acetone and thioacetone with carbon dioxide and water
   Phan Dang Cam-Tu, Vu Thi Ngan, Nguyen Tien Trung, *Chemical Physics*, **2020**, 530, 110580.

3) Insights into the cooperativity between multiple interactions of dimethyl sulfoxide with carbon dioxide and water
   Khanh Pham Ngoc, **Phan Dang Cam-Tu**, Dai Quoc Ho, Quan Van Vo, Vu Thi Ngan, Minh Tho Nguyen, Nguyen Tien Trung, *Journal of Computational Chemistry*, **2019**, 40, 464-474.

4) Interaction of ethanethiol with carbon dioxide and water: structure, stability and cooperativity
   Phan Dang Cam Tu, Le Minh Trong, Nguyen Le Tuan, Vu Thi Ngan, Nguyen Thi Ai Nhung, Nguyen Tien Trung, *Vietnam Journal of Chemistry*, **2018**, 56(6E2), 318-324.

5) A theoretical study on structure, stability and behavior of complexes containing CH_3OH, CO_2 and H_2O
   Phan Dang Cam Tu, Nguyen Thi Duong, Nguyen Ngoc Tri, Nguyen Tien Trung, *Vietnam Journal of Chemistry*, **2018**, 56(6E2), 245-250.

6) Effects of substituents on intermolecular interaction and stability of complexes of CO_2 and CH_3OCHX_2 (X = H, F, Cl, Br, CH_3)
   Pham Thi Hoa, **Phan Dang Cam Tu**, Nguyen Tien Trung, *Journal of Science - Quy Nhon University,* **2019**, *13*(5), 75-83.

7) A theoretical study on interaction and stability of complexes between dimethyl sulfide and carbon dioxide
   Truong Tan Trung, **Phan Dang Cam-Tu**, Ho Quoc Dai, Nguyen Phi Hung, Nguyen Tien Trung, *Journal of Science - Quynhon University* **2019**, 13(1), 95-105.