
Understanding Interaction Capacity of CO₂ with Organic Compounds at Molecular Level: A Theoretical Approach

Pham Ngoc Khanh and Nguyen Tien Trung

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<http://dx.doi.org/10.5772/intechopen.71878>

Abstract

In this chapter, interactions of CO₂ with a number of organic compounds at molecular level are discussed in detail. The naked and substituted hydrocarbons along with compounds functionalized by hydroxyl, carbonyl, thiocarbonyl, carboxyl, sulfonyl, and amide groups have attracted much attention as CO₂-philic agents. In general, interaction capacity between the functionalized organic compounds with CO₂ is stronger than the hydrocarbon and its derivatives. An addition of more CO₂ molecules into the interaction system formed by the functionalized organic compounds and CO₂ leads to an increase in the stability of the complexes. The obtained results indicate that $\pi\cdots\pi$ linkages between CO₂ and aromatic rings can significantly contribute to the interactions between CO₂ and MOF/ZIF materials. Formic acid (HCOOH) is likely to be the most soluble compound as compared to the remaining host molecules (CH₃OH, CH₃NH₂, HCHO, HCOOCH₃, and CH₃COCH₃) when dissolved in CO₂. The carbonyl (>C=O, >C=S) and sulfonyl (>S=O, >S=S) compounds have presented a higher stability, as compared to other functionalized groups, when they interact with CO₂. Therefore, they can be valuable candidates in the design of CO₂-philic materials and in the search of materials to adsorb CO₂.

Keywords: supercritical carbon dioxide, Lewis acid-base, hydrogen bond, weak interaction

1. Introduction

Carbon dioxide (CO₂) causes negative effect on global climate due to its “greenhouse effect” property multiplying by its high level in the atmosphere. Currently, its concentration is increasing due to the fossil fuels combustion process by human activities [1]. Nevertheless,

it is usually regarded as an environmentally benign solvent because of its less hazardous property. Furthermore, it is an attractive solvent owing to the ease of its removal capacity, abundance, inexpensive, and flexibility of the solvent parameters [2]. Consequently, supercritical CO₂ (sc-CO₂) is well known as an efficient solvent over conventional organic ones in many chemical processes, and is expected to be useful in many applications of green chemistry such as extraction, separation, chemical reaction, and material processes [3–6]. Recently, sc-CO₂ has been employed in direct sol-gel reactions for the synthesis of oxide nanomaterials, oligomers, and polymers, etc. [7–10]. It is noteworthy that due to a lack of polarity, sc-CO₂ is a very feeble solvent for most polar solutes [11]. Nevertheless, due to the possession of a substantial quadrupole moment and a polar C=O bond, the majority of materials attached by carbonyl functional or fluoride groups are soluble in sc-CO₂. In the context, continuing efforts have been reported for the purpose of enhancement in applicability of sc-CO₂ solvent through the use of “CO₂-philes”, which makes insoluble or poorly soluble materials becoming more soluble in sc-CO₂ at an acceptable level of low temperature and pressure conditions [3, 12]. Experimental works have aimed at better understanding of behavior of the sc-CO₂ as solvent for organic compounds [13–18]. It might be assumed that CO₂ is a green yet feeble solvent because its full potential could not be realized without a thorough understanding of its solvent behavior at molecular level. Accordingly, numerous results on the CO₂-philes have been reported during the 1990s [19, 20]. These CO₂-philes are less favorable and effective both economically and environmentally because most of them are fluorinated polymers. Thus, in attempts to avoid expensive cost and environmental impacts of the fluorinated materials, during the last three decades, large-scale studies have focused on the design of nonfluorinated CO₂-philes, specifically hydrocarbon-based and oxygenated hydrocarbon-based polymers [21, 22]. In 1996, Kazarian et al. discovered the formation of Lewis acid-base (LA-LB) type of interaction between CO₂ with the O atom of a number of carbonyl compounds (>C=O) for the first time [23]. Soon later, Beckman et al. successfully synthesized copolymer of nonfluorinated carbonate in sc-CO₂ at low pressure [21]. Interaction of CO₂ with delocalized π aromatic systems in the gas phase have been theoretically studied for the purpose of ranking in a database of a large variety of organic ligands, which would be valuable candidates for designing new metal-organic framework materials with enhanced affinity for CO₂ adsorption at low pressure. Accordingly, some extensive studies have been reported on the interactions of CO₂ with π -systems at level of theory and experiment [24–29]. In recent years, interactions of simple functionalized organic molecules, including CH₃OH, CH₃CH₂OH [30–32], CH₃OCH₃, CH₃OCH₂CH₂OCH₃ [33–35], HCHO, CH₃CHO, CH₃COOCH₃, CH₃COCH₃, CH₃COOH [36–41], and XCHZ (X = CH₃, H, F, Cl, Br; Z = O, S) [42] CH₃SZCH₃ (Z = O, S) [43] with CO₂ have been carried out using quantum chemical methods. Today, the interest in CO₂ computational chemistry is the interaction capacity of a solute molecule surrounded by a number of CO₂ molecules. Despite the fact that numerous studies have been performed, a full understanding of the CO₂ characteristics as a solvent remains a challenging task [1]. It is therefore clear that we need more systematic studies to gain a better understanding on the nature of the interactions involved, rather than considering the origin for a few disparate systems. Furthermore, there is also a great interest in deep understanding of the origin of the interactions between different types of organic compounds with CO₂ at molecular level for an effective use of CO₂ in different states.

This chapter focuses on evaluating interaction capacity of CO₂ with model organic compounds at level of molecule using theoretical approaches. Section 2 provides us with a brief summary of theoretical methods and computational techniques. Section 3 reviews the remarkable results of the investigation of interactions between CO₂ with organic compounds and is divided into two parts: (3.1) interactions of CO₂ with selected models of saturated and unsaturated hydrocarbons and their substituted derivatives, and modeled aromatic hydrocarbons; (3.2) interactions of CO₂ and modeled organic compounds with different functional groups and their substituted derivatives. Obtained results presented in Section 4 support for the enhancement of sc-CO₂ solvent used as a replacement for toxic classical organic solvents in industrial applications. In addition, the functional groups that present the more stable interaction with CO₂ at molecular level are revealed, which could be attached on the surface of materials to absorb and store CO₂ gas.

2. Computational details

Geometrical parameters of all the considered structures including monomers and complexes are optimized using suitable quantum-chemical methods such as the molecular orbital theory (MO) and density functional theory (DFT) and large basis sets, depending on investigated systems, such as 6-311++G(2d,2p), 6-311++G(3df,2pd), aug-cc-pVDZ, aug-cc-pVTZ, which have succeeded in investigating noncovalent interactions, especially hydrogen bonds [44, 45]. Harmonic vibrational frequencies are subsequently calculated at investigated level of theory to ensure that the optimized structures are local minima on the potential energy surfaces, and to estimate their zero-point energy (ZPE). The stabilization energy of each complex is calculated using the supermolecular method as the difference in total energies between that of each complex and the sum of the relevant monomers at the selected level of theory. The interaction energy is corrected by zero-point energy (ZPE) and basis set superposition errors (BSSE). The latter is computed using the function counterpoise procedure of Boys and Bernardi [46]. The “atoms-in-molecules” (AIM) [47] analyses are applied to identify critical points and to calculate their characteristics including electron density ($\rho(r)$), Laplacian, electron potential and kinetic energy density, and total energy density. The GenNBO 5.G program [48] is used to perform NBO calculations, which is extensively applied to investigate chemical essences of hydrogen bonds and other weak interaction, and can provide information about natural hybrid orbitals, natural bond orbitals, natural population, occupancies in NBOs, hyperconjugation energies, rehybridization, and repolarization.

3. Interaction capacity of CO₂ with organic compounds

3.1. Interaction of CO₂ with model hydrocarbons

3.1.1. Interaction of CO₂ with saturated hydrocarbons and their substituted derivatives

Saturated hydrocarbons are a primary energy source for our civilization. Fluorocarbons have been currently used as CO₂-philic functionalities in many potential applications of chemistry utilizing liquid and supercritical CO₂ as a “green” alternative to conventional organic solvents

for chemical processes [20, 49–52]. The miscibility and dissolution of organic molecules in sc-CO₂ generally increase when the hydrogen atoms in molecules are substituted by fluorine atoms [49, 53]. It is crucial, therefore, to investigate interaction of CO₂ with saturated hydrocarbons and its substituted derivatives. A study [54] on density-dependent ¹H and ¹⁹F NMR chemical shift of hydrocarbons and fluorocarbons in sc-CO₂ pointed out that there is a distinct difference in the chemical shift changes, as a function of density, for the two nuclei. In addition, the authors suggested a specific interaction of type “solute-solvent” in the system formed by the fluorocarbons and CO₂, and a site specificity for the ¹⁹F shifts due to the surface accessibility of the individual fluorine atoms. In 1996, interactions between CO₂ with ethane (C₂H₆) and hexafluoroethane (C₂F₆), in particular the (CO₂)_n⋯C₂H₆ and (CO₂)_n⋯C₂F₆ interactions, with n = 1–4, were examined using restricted Hartree-Fock method [55]. The interaction energy for the CO₂⋯C₂F₆ complex was calculated to be -3.35 kJ.mol⁻¹, while it was -1.26 kJ.mol⁻¹ for the CO₂⋯C₂H₆ complex, indicating that the interaction of CO₂ with C₂F₆ is stronger than that with C₂H₆. The obtained results showed key differences between the interaction of hydrocarbons and fluorocarbons with CO₂. The interaction of the fluorocarbon with CO₂ is predominantly electrostatic in nature. Thus, the positively charged carbon atom in CO₂ has a strong attraction with the negatively charged fluorine atoms of the fluorocarbons, resulting in a favorable binding energy of 3.14–3.35 kJ.mol⁻¹ for each CO₂ molecule in the first solvent shell. The interaction of CO₂ with hydrocarbons is quite weak due to the noble nature of the hydrocarbons molecule. Nevertheless, Han and Jeong [56] pointed out that the results in Ref. [55] were incorrect because the calculations for interaction energy of the complexes were not corrected by the basis set superposition error.

In 1998, interactions of CO₂ with small hydrocarbons (CH₄ and C₂H₆) and fluorocarbons (CF₄ and C₂F₆) were reinvestigated using second-order many-body perturbation theory (MP2) methods by Diep et al. [57]. These authors surprisingly did not find any enhanced attraction between CO₂ and perfluorocarbons relative to the analogous hydrocarbons as in the publication of Cece et al. [55]. On the contrary, interaction energies of the obtained complexes range from -3.31 to -4.90 kJ.mol⁻¹, in which the interaction energies are slightly more negative for the CO₂-hydrocarbon complexes than for the corresponding CO₂-perfluorocarbon ones, suggesting that the interaction capacity of CO₂ and hydrocarbons is stronger than that of fluorocarbons and CO₂. Yonker and Palmer [58] studied the nuclear shielding of ¹H and ¹⁹F nuclei in CH₃F and CHF₃ by NMR and molecular dynamics simulations. Obtained results showed that there is no distinct or specific interaction between fluoromethane and CO₂. A various work by Yee et al. [59] reported that the polarizability of CF₄ and C₂F₆, which is derived from dielectric constant measurement, is larger than that of CH₄ and C₂H₆, and noted that this reason should result in a proportional difference in the magnitude of the interaction between the induced dipoles. Consequently, they suggested that the repulsion of CO₂ is greater for CF₄ than for CH₄. However, Diep et al. [57] argued that only the electronic component of the total polarizability cited by Yee et al. [59] is the adequate reason for the induced dipole-induced dipole interactions between the molecules. They showed that the electronic polarizability is comparable between the perfluorocarbons and the alike hydrocarbons. The CO₂-philicity of fluorinated compounds with varying numbers of fluorine atoms in the system was investigated by Wallen et al. [60]. By using correlated ab-initio

calculations and studying effect of stepwise substitution of H atom of methane by fluorine, the authors explored origin of fluorocarbon and hydrocarbon interactions with CO₂. The results suggested an optimum density of fluorine atoms that can be viewed as a maximum CO₂-philicity, and CO₂ molecule plays both weak Lewis acid and base in these systems. In this work, the authors suggested the fundamentally different nature of interaction between CO₂-fluorocarbon and CO₂-hydrocarbon, in spite of comparable interaction energy. For complexes formed by fluorocarbons and CO₂, their stability is contributed by interaction of carbon in CO₂ and fluorine in fluorocarbons, while the stability of complexes of hydrocarbons and CO₂ is thanks to two oxygen of CO₂. It should be noteworthy that the stability of complex is also contributed by the C–H...O weak hydrogen. In summary, these molecular modeling computations have shed some light on the interaction of hydrocarbons and fluorocarbons with CO₂, which may help to explain the difference in solubility of various saturated hydrocarbons and their substituted derivatives in sc-CO₂.

3.1.2. Interaction of CO₂ with unsaturated hydrocarbons and its substituted derivatives

Unsaturated hydrocarbons is one of the most important classes of materials for synthesizing polymers; and sc-CO₂ has been seen as a good solvent for this kind of synthesis. In 2009, interaction between C₂H₂ with CO₂ was investigated by Alkorta et al. [61] and interaction energy was evaluated to be *ca.* -4.70 kJ.mol⁻¹ at M05-2x/6-311++G(d,p) and -5.99 kJ.mol⁻¹ at MP2/aug-cc-pVTZ, implying that the complex C₂H₂...CO₂ is stable on the potential energy surface. The stability of complex is determined by weak C...C interaction and is confirmed by AIM and NBO analyses. Indeed, AIM analysis shows the presence of this intermolecular contact owing to the values of electron density ($\rho(r)$) and Laplacian ($\nabla^2\rho(r)$) at its BCP to be 0.0067 and 0.0246 au. Furthermore, the NBO analysis also indicates that upon complexation the electron-rich carbon atom of CO₂ transfers electrons to the anti-bonding orbital of C₂H₂ having electron-poor carbon atoms. In order to understand deeply origin of interaction of unsaturated hydrocarbons with CO₂, the complexes of C₂H₄ and CO₂ were investigated by our group in 2016 [1]. It is remarkable that the interaction energies corrected by both ZPE and BSSE for the C₂H₄...CO₂ complexes are in the range from -1.1 to -4.9 kJ.mol⁻¹. The most stable structure of C₂H₄...CO₂ is in line with the report by Miller et al. that CO₂'s main axis parallels the plane of C₂H₄, but is not parallel to its C–C axis [62]. Obtained results showed that the p... π^* and π ... π^* interactions play more important role than the C–H...O hydrogen bond in stabilizing the C₂H₄...CO₂ complexes. Remarkably, contribution of the π ... π^* interaction to stabilization of the complex formed by CO₂-philic compounds and CO₂ has been observed for the first time in this literature. The stability of complex C₂H₄...CO₂ (-4.9 kJ.mol⁻¹) is more stable than the complexes of interaction between CO₂ with hydrocarbons and fluorinated hydrocarbons such as CH₄, C₂H₆, CF₄, C₂F₆ (from -3.7 to -4.9 kJ.mol⁻¹ at the MP2/aug-cc-pVDZ) [56, 57, 61]. This review indicates that interaction capacity of CO₂ with unsaturated hydrocarbons is stronger than that of CO₂ with saturated hydrocarbons.

Our group [1] continued to investigate the interactions of the 1,2-dihalogenated derivatives of ethylene (XCH=CHX) with CO₂ in order to evaluate the substituent effects on the interactions. Six stable shapes of the optimized structures of XCH=CHX...CO₂ (X = F, Cl and Br) at the MP2/

aug-cc-pVDZ level are showed in **Figure 1**, which are denoted hereafter by **C1X**, **C2X** and **C3X** for *cis*-XCH=CHX \cdots CO₂ pairs, and **T1X**, **T2X** and **T3X** for *trans*-XCH=CHX \cdots CO₂ pairs.

The obtained results showed that stability of the complexes **C1X** and **C3X** is determined by the C–H \cdots O hydrogen bonded interaction, whereas the presence of both the C–H \cdots O hydrogen bond and C–X \cdots C Lewis acid-base interaction leads to stabilization of the complexes **C2X**, **T1X** and **T2X**. For **T3X**, their stability is induced by a p \cdots π^* interaction from the lone pair n(O) to the $\pi^*(C=C)$ orbital and a $\pi\cdots\pi^*$ interaction from MO- $\pi(C=O)$ to MO- $\pi^*(C=C)$ orbital. The two H atoms in C₂H₄ substituted by two alike halogen atoms X results in an additional presence of C–X \cdots C Lewis acid-base interaction, thus contributing supplementary to the stabilization of the investigated complexes. In general, the *cis*-XCH=CHX \cdots CO₂ complexes are more stable than the *trans* counterparts. In addition, CH₂CH₂ \cdots CO₂ is less stable than both *trans*-XCH=CHX \cdots CO₂ and *cis*-XCH=CHX \cdots CO₂. Thus, the interaction energies with both ZPE and BSSE corrections are calculated to be from -1.7 to -7.5 kJ.mol⁻¹ for *cis*-XCH=CHX \cdots CO₂ and from -4.4 to -6.8 kJ.mol⁻¹ for *trans*-XCH=CHX \cdots CO₂. Hence replacement of the two H atoms in CH₂=CH₂ by the same halogen atoms actually increases the stability of complexes formed by interaction of XCH=CHX with CO₂ and causes a decrease of the role of the $\pi\cdots\pi^*$ interaction in stabilization of the parent C₂H₄ \cdots CO₂ complex in comparison with the XCH=CHX \cdots CO₂ ones.

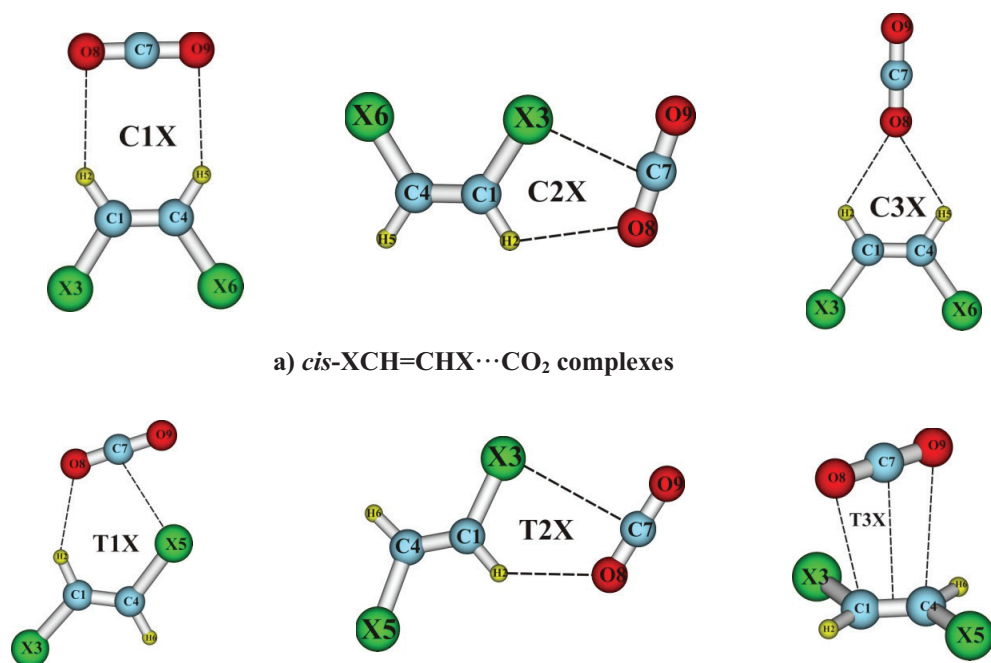


Figure 1. The stable geometries of the complexes of CO₂ and XCH=CHX derivatives (X = F, Cl, and Br). (a) *cis*-XCH=CHX \cdots CO₂ complexes, (b) *trans*-XCH=CHX \cdots CO₂ complexes.

3.1.3. Interaction of CO₂ with some model aromatic hydrocarbons

Key aromatic hydrocarbons of commercial interests such as benzene, toluene, and xylene play a key role in the biochemistry of all living things. They are used to produce a range of important chemicals and polymers. In 2009, interactions between CO₂ and a large number of functionalized aromatic molecules were investigated by means of using density functional theory by Torrisi et al. [24] with the aim of ranking a large variety of organic ligands in a database, which could be suitable candidates for designing new metal organic framework materials with enhanced CO₂ adsorption capacity at ambient pressure. Two groups of substituted benzene derivatives including the electron-withdrawing halogen groups (tetrafluoro-, chloro-, bromo-, and dibromobenzene) and methyl electron donor (mono-, di-, and tetramethylbenzene) were considered since these substituents are very common components of aromatic ligands in MOF₅. The results of interaction energy showed that halogen substitution causes relatively strong destabilization of complexes formed, which is increased with number of substituting groups, and thus reduces the magnitude of the aromatic ring adsorption toward CO₂. Nevertheless, a decrease of electron density of the aromatic ring induces an increase in acidity for some of the aromatic hydrogen atoms, which helps weak hydrogen bond-like interactions of these hydrogen atoms with oxygen atom of CO₂ formed. On the other hand, substitution of hydrogen atom in aromatic ring by methyl group clearly strengthens its interaction capacity with CO₂, which is usually very accessible on the internal surface of a MOF cavity, and hence it can be seen as a promising way to enhance the CO₂ affinity of the MOF, in which tetramethyl substitution manifests a maximum advantage of this particular class of ligand.

In 2013, Chen et al., by using high-level *ab initio* methods, suggested the $\pi\cdots\pi$ interaction between CO₂ and three aromatic molecules, namely benzene (C₆H₆), pyridine (C₅H₅N), and pyrrole (C₄H₅N), which serve as common functional groups in metal-organic/zeoliticimidazolate framework materials [63]. The interaction energies for the complexes of CO₂ with aromatic hydrocarbons calculated at MP2/aug-cc-pVTZ are in the range from -11.9 to -15.4 kJ.mol⁻¹, which are twice more negative than the most stable complex of the C₂H₄...CO₂ system (-4.9 kJ.mol⁻¹ at CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ level). This result implies that interaction capacity of CO₂ with aromatic hydrocarbons is stronger than that of CO₂ with unsaturated hydrocarbons. These authors also optimized the side-on structures of all possible complexes to compare the interaction strength of side-on configurations and $\pi\cdots\pi$ top-on configurations. This work obtained the three most-stable side-on configurations, specifically S-C₆H₆...CO₂, S-C₅H₅N...CO₂, and S-C₄H₅N...CO₂, as illustrated in **Figure 2**.

The side-on interaction is significantly weaker than the $\pi\cdots\pi$ interaction in C₆H₆...CO₂ and C₄H₅N...CO₂ pairs. On the contrary, for the C₅H₅N...CO₂ pair the $\pi\cdots\pi$ interaction [-11.6 kJ.mol⁻¹ for T-C₅H₅N...CO₂(N) and -11.5 kJ.mol⁻¹ for TC₅H₅N...CO₂(C)] is weaker than the side-on interaction (-18.0 kJ.mol⁻¹). The obtained results showed that the EDA-type interactions are not available in real MOF/ZIF materials because the central cationic metal of MOF/ZIF materials is linked to the exposed aromatic N atom of the EDA-type interaction in S-C₅H₅N...CO₂. In short, the results indicate that $\pi\cdots\pi$ interaction between CO₂ and aromatic rings can significantly contribute to the interactions between CO₂ and MOFs/ZIFs.

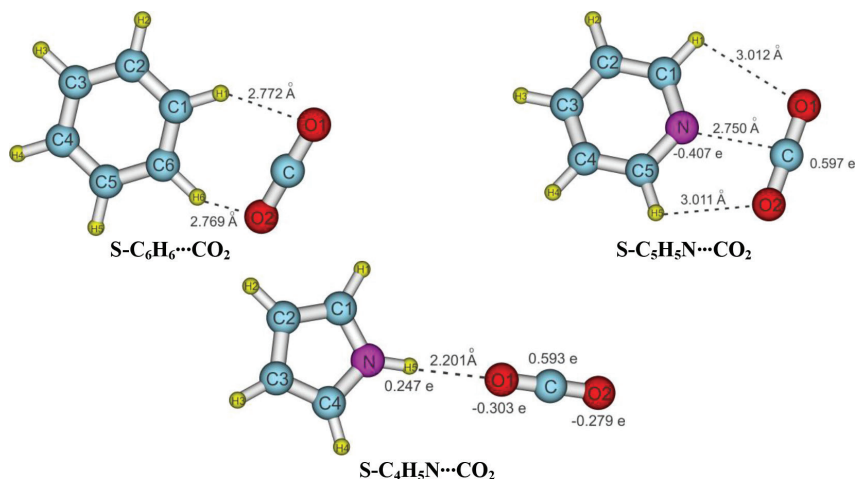


Figure 2. Optimized structures of $\text{S-C}_6\text{H}_6\cdots\text{CO}_2$, $\text{S-C}_5\text{H}_5\text{N}\cdots\text{CO}_2$, and $\text{S-C}_4\text{H}_5\text{N}\cdots\text{CO}_2$.

3.1.4. Concluding remarks on interaction of CO_2 with model hydrocarbons

Interactions of CO_2 with model hydrocarbons including saturated, unsaturated, aromatic hydrocarbons and their substituted derivatives were investigated using high-level *ab initio* methods. In general, the strength of the complexes increases in going from the interaction of the saturated hydrocarbons with carbon dioxide to unsaturated hydrocarbons with carbon dioxide and finally to the parent aromatic hydrocarbons with carbon dioxide. The stability of the obtained complexes is determined by the $\text{C-H}\cdots\text{O}$ hydrogen bonded interaction, $\text{C-X}\cdots\text{C}$ Lewis acid-base interaction, $\pi\cdots\pi$, $p\cdots\pi^*$ and $\pi\cdots\pi^*$ interactions. The contribution of the $\pi\cdots\pi^*$ interaction to the formation of the complexes between CO_2 -philic compounds and CO_2 has been observed. The $\pi\cdots\pi$ interactions were significantly stronger than the side-on hydrogen-bond interactions but weaker than EDA-type interaction. The $\pi\cdots\pi$ interactions can significantly contribute to adsorption of CO_2 in practical applications. Consequently, approach to the increase in the aromaticity of the linker should be an effective way with purpose of increasing the CO_2 adsorption in MOF/ZIF materials.

3.2. Interaction of CO_2 with model functionalized organic compounds and their substituted derivatives

3.2.1. Interaction of CO_2 with model functionalized organic compounds

Up to now, a large number of complexes for interactions of CO_2 with simple functionalized organic molecules have been studied using quantum chemical methods [33–43]. In more recent investigations, the Lewis acid-base interaction between CO_2 and some carbonyl-functionalized compounds has been reported [34, 44, 64–67]. The existence of the $\text{C-H}\cdots\text{O}$ hydrogen bond in complexes was confirmed clearly by Wallen et al. [38, 39, 60]. However, it is necessary to perform systematic studies to elucidate the nature of the

interactions formed in complexes, rather than considering the results obtained from few specific systems. We investigated complexes of CO₂ and some typically functionalized organic molecules such as methanol (CH₃OH), methylamine (CH₃NH₂), formaldehyde (HCHO), formic acid (HCOOH), dimethylether (CH₃OCH₃), acetone (CH₃COCH₃) and methyl formate (HCOOCH₃) [40]. Obtained results showed that the Lewis acid-base interaction such as C–N...C(CO₂), C=O...C(CO₂) plays a more dominant role compared to the C–H...O blue-shifting hydrogen bond in stabilizing most of the complexes. However, the stability of the HCOOH...CO₂ pair is mainly determined by O–H...O red-shifting hydrogen bond. All interaction energies are significantly negative, indicating that obtained complexes are quite stable. Particularly, the interaction energies with both ZPE and BSSE corrections are in the range from –3.3 to –14.2 kJ.mol⁻¹, in which the HCOOH...CO₂ pair is the most stable, whereas the weakest one is the HCHO...CO₂ pair. As a consequence, solubility of HCOOH in sc-CO₂ is likely to be the largest in all the considered compounds. The interaction energies of some considered complexes are more negative than the values reported in the previous works [35, 64]. Thus, for the pair (CH₃OH, CO₂), its interaction energy of –13.3 kJ.mol⁻¹ with only ZPE correction, and –11.4 kJ.mol⁻¹ with both ZPE and BSSE corrections is more negative than that of –11.3 kJ.mol⁻¹ obtained with only BSSE correction at the MP2/aug-cc-pVTZ level [64]. Another example is that the BSSE corrected interaction energy of the CH₃OCH₃...CO₂ pair was computed to be –13.1 kJ.mol⁻¹ at the MP2/6-311++G(2d,2p)//MP2/6-311++G(d,p) level [35] while it is –13.7 kJ.mol⁻¹ with ZPE and BSSE corrections, and –16.3 kJ.mol⁻¹ with only ZPE correction in the present work.

In 2011, our group investigated the interactions of CO₂ with substituted derivatives of formaldehyde and thioformaldehyde [42]. The interaction energies (with ZPE and BSSE corrections) of –10.5 kJ.mol⁻¹ for CH₃CHO...CO₂ and –9.1 kJ.mol⁻¹ for CH₃CHS...CO₂ are more negative than for complexes of HCHO...CO₂ and HCHS...CO₂, respectively. The obtained results supported that both O and S atoms act as Lewis bases and the >C=X (X = O, S) groups should be considered as potential candidates for the design of CO₂-philic materials. The interactions between carbonyl compounds and CO₂ are stronger than those of fluorocarbons and fluorocarbonyl compounds. Obtained results suggested that the Lewis acid-base and hydrogen bonded interactions should be the key factors in governing the solubility of isolated monomers in sc-CO₂, in which the crucial role of the former is suggested. The function of these interactions in the solvation of >C=O and >C=S compounds in sc-CO₂ may be important in terms of the specific solute-solvent.

In 2014, we investigated the interactions between some carbonyl compounds including acetone (CH₃COCH₃) with CO₂ [41]. Interaction energies of obtained complexes which are denoted by **H1**, **H2**, **H3**, and **H4** at the CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p) level are gathered in **Table 1**. The results indicate that the stability of studied complexes is contributed by both Lewis acid-base and hydrogen bonded interactions. As shown in **Table 1**, the interaction energy for **H1** (–10.3 kJ.mol⁻¹) is less negative than that reported in Ref. [40] (–11.1 kJ.mol⁻¹) at CCSD(T)/aug-cc-pVTZ but is more negative than that in Ref. [64] (–8.8 kJ.mol⁻¹) at MP2/aug-cc-pVDZ. Notably, complex **H3** is less stable than **H1** in this work, which is different from the results reported by Ruiz-Lopez et al [68]. By using the levels of theory MP2/aug-cc-pVDZ and CCSD(T)/aug-cc-pVDZ, the authors suggested

	H1	H2	H3	H4
ΔE	-12.7	-11.3	-12.7	-4.7
ΔE^*	-10.3	-9.4	-9.2	-2.4

Source: Dai et al. [41].

Table 1. Interaction energies ($\text{kJ}\cdot\text{mol}^{-1}$) corrected for only ZPE and for both ZPE and BSSE of the complexes.

that **H1** is *ca.* $1.0 \text{ kJ}\cdot\text{mol}^{-1}$ higher in interaction energy than **H3**. These authors conclusively suggested that the $>\text{C}=\text{O}$ group can be a valuable candidate in the design of CO_2 -philic and adsorbent materials.

Further, interactions of CO_2 with CH_3SZCH_3 ($Z = \text{O}, \text{S}$) were also investigated by our group [43]. Three stable shapes of the complexes at MP2/6-311++G(2d,2p) are presented in **Figure 3**, denoted hereafter by **T1**, **T2** and **T3**. Interaction energies of complexes at two different levels of theory are also given in the **Table 2**.

The $\text{CH}_3\text{SZCH}_3\cdots\text{CO}_2$ ($Z = \text{O}, \text{S}$) complexes are in general stabilized by the Lewis acid-base, chalcogen-chalcogen and hydrogen bonded interactions. However, the crucial role contributing to the overall stabilization energy should be the Lewis acid-base interaction. The obtained results pointed out a slight difference in the interaction energies between the two employed levels of theory. Thus, the interaction energies of the examined complexes range from -13.8 to -17.2 and -9.8 to $-14.4 \text{ kJ}\cdot\text{mol}^{-1}$ (at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p)), and -13.6 to -17.7 and -9.6 to $-14.5 \text{ kJ}\cdot\text{mol}^{-1}$ (at CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p)) for only ZPE correction and for both ZPE and BSSE corrections, respectively (*cf.* **Table 2**). The results indicate that the formed complexes are significantly stable, and more stable than the complexes of the $>\text{C}=\text{O}$ or $>\text{C}=\text{S}$ functionalized compounds with CO_2 reported in Refs. [38, 40, 42]. This implies a stronger interaction of CO_2 with the $>\text{S}=\text{O}$ and $>\text{S}=\text{S}$ functional groups relative to the $>\text{C}=\text{O}$ and $>\text{C}=\text{S}$ counterparts. In addition, we

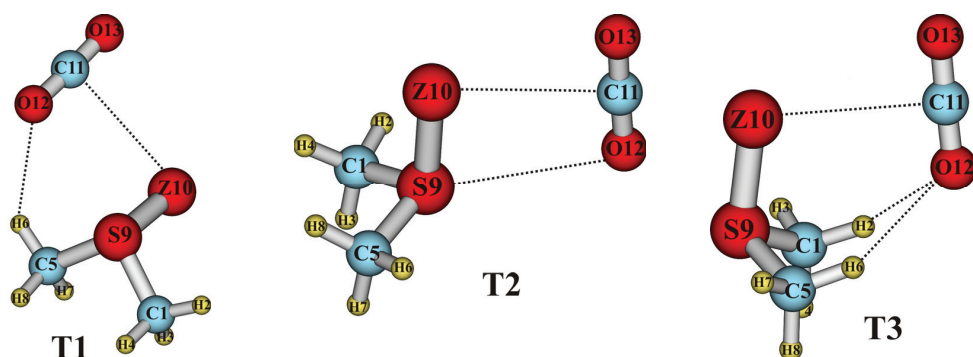


Figure 3. Stable shapes of complexes between CH_3SZCH_3 ($Z = \text{O}, \text{S}$) and CO_2 .

Structures	Z = O			Z = S		
	T1	T2	T3	T1	T2	T3
ΔE ^a	-17.2	-14.3	-17.4	-17.1	-13.8	-16.9
ΔE ^b	-17.6	-14.8	-17.7	-16.8	-13.6	-16.4
ΔE ^{*a}	-14.4	-10.9	-13.7	-14.2	-9.8	-13.2
ΔE ^{*b}	-14.5	-11.3	-14.0	-13.5	-9.6	-12.0

^aTaken from MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p).

^bTaken from CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p).

Source: Phuong et al. [43].

Table 2. Interaction energies corrected for ZPE (ΔE⁰, in kJ.mol⁻¹) and for ZPE and BSSE (ΔE*, in kJ.mol⁻¹) of obtained complexes.

also suggested a stronger interaction of CO₂ with the >S=O moiety compared to the >S=S one, and they both should be candidates for designing CO₂-philic materials, CO₂ adsorption and storage materials in the future.

For the CH₃SOCH₃...CO₂ complexes, the strength of **T3** is close to that of **T1** reported by Wallen et al. [38]. Thus, the interaction energies of **T1** in this work are -14.4 kJ.mol⁻¹ at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) and -14.5 kJ.mol⁻¹ at CCSD(T)/6-311++G(3df,2pd)//MP2/6-311++G(2d,2p), which are in consistent with the value of -14.3 kJ.mol⁻¹ at MP2/aug-cc-pVDZ//MP2/6-31+G(d) reported in Ref. [38].

3.2.2. Effect of various substituted groups to strength the complexes formed by interaction of CO₂ with model functionalized organic compounds

We now continue to discuss in some details the effects of substitution to the overall interaction energy in obtained complexes between CO₂ with model functionalized organic compounds. The complexes of the interactions of CO₂ with CH₃SZCHX₂ (X = H, CH₃, F, Cl, Br; Z = O, S) were studied by our group and reported in Ref. [43]. In general, the CH₃SOCHX₂...CO₂ complexes are more stable than the CH₃SSCHX₂...CO₂ complexes. This firmly indicates that the >S=O, as compared to the >S=S, has a stronger interaction with CO₂, which originates from a contribution of a larger attractive electrostatic interaction of the former than the latter in stabilizing the examined complexes. For the CH₃SOCHX₂...CO₂ complexes, the strength is enhanced by the X substitution in the order from H *via* F to Cl to Br and finally to CH₃. Therefore, the substitution of two H atoms in a CH₃ group of CH₃SOCH₃ by two alike X groups significantly influences the strength of CH₃SOCHX₂...CO₂ complexes relative to CH₃SOCH₃...CO₂ complexes. The replacement also leads to a slight enhancement of stability of the CH₃SSCHX₂...CO₂ complexes in the sequence from F, H, Cl, Br to CH₃. In Ref. [41], we replaced two H atoms in a CH₃ group of CH₃COCH₃ by two alike CH₃, F, Cl and Br groups, and the results showed that interaction energies of complexes are in the range from -9.2 to -10.7 kJ.mol⁻¹ with both ZPE and BSSE

corrections, which are more negative than that of interactions of CO_2 with hydrocarbons and fluorocarbons. Thus, the interaction energies range from -3.7 to -4.9 $\text{kJ}\cdot\text{mol}^{-1}$ for the complexes of CO_2 with the hydrocarbons such as CH_4 , C_2H_6 , CF_4 , C_2F_6 ; and from -2.4 to -7.8 $\text{kJ}\cdot\text{mol}^{-1}$ for the complexes of CO_2 with $\text{CH}_{4-n}\text{F}_n$ ($n = 0 \div 4$) [57, 60] at the MP2/aug-cc-pVDZ level. These results are in line with the suggestion on larger stability of carbonyl relative to fluorocarbons and other functionalized compounds in interacting with CO_2 . Generally, the strength of $\text{CH}_3\text{COCHR}_2\cdots\text{CO}_2$ complexes is gently increased when $\text{R} = \text{CH}_3$ as compared to $\text{CH}_3\text{COCH}_3\cdots\text{CO}_2$, while it is slightly decreased with $\text{R} = \text{F}$, Cl and Br .

3.2.3. Interaction of $n\text{CO}_2$ ($n = 1:3$) with model functionalized organic compounds

It is important to investigate the strength of interactions between CO_2 and carbonyl-containing molecules, as well as the underlying their chemical nature. Due to a strong interest in CO_2 as a solvent, it is imperative to consider aggregates in which a solute molecule is surrounded by a number of CO_2 molecules, an unexplored area at present [69]. Expansion of the system by adding more CO_2 molecules shows how the geometry and bonding in the heterodimer is affected by placement of the solute in an environment. This would make our simulation more akin to solvation phenomenon, and particularly the magnitude of cooperative effects. The complexes formed by H_2CO , CH_3CHO , and $(\text{CH}_3)_2\text{CO}$ with two and three molecules of CO_2 are studied using *ab initio* calculations by Scheniner et al. [69]. There are a host of different geometries adopted by the complexes of the carbonyl with two or three CO_2 molecules, with small energy differences. The bonding features of the heterodimers are generally carried over to these larger heterotrimers and tetramers, although the linear $\text{C}=\text{O}\cdots\text{C}$ arrangement of the binary complexes is largely absent. The $\text{O}\cdots\text{O}$ chalcogen bonds, absent in the heterodimers, play a major role in many of the larger complexes. The degree of cooperativity in these oligomers is generally rather small, with a maximal positive cooperativity of only 1.1 kJ/mol . The binding energies of heterotetramers complexes range from -39.0 to -50.7 $\text{kJ}\cdot\text{mol}^{-1}$, which are more negative than heterodimers (-8.8 to -12.5 $\text{kJ}\cdot\text{mol}^{-1}$) and trimers complexes (-23.1 to -34.2 $\text{kJ}\cdot\text{mol}^{-1}$). These results suggest that the addition of more carbon dioxide molecules into systems leads to a larger increase in stability of complexes.

3.2.4. Concluding remarks on interaction capacity of CO_2 with model functionalized organic compounds

The organic compounds functionalized by hydroxyl, carbonyl, thiocarbonyl, carboxyl and amide groups have been paid much attention as CO_2 -philic compounds. The carbonyl and thiocarbonyl compounds have presented a higher stability, as compared to other functionalized ones, when they interact with CO_2 . This durability has been assigned to a main contribution of the $>\text{C}=\text{Z}\cdots\text{C}$ ($\text{Z} = \text{O}, \text{S}$) Lewis acid-base interaction and/or an additional cooperation of the $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonded interaction, except for the case of the $\text{HCOOH}\cdots\text{CO}_2$ complex, where the role of the $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond was found to be more important than the $>\text{C}=\text{O}\cdots\text{C}$ Lewis acid-base interaction. We have also found that there is a stronger interaction of CO_2 with the $>\text{S}=\text{O}$ and $>\text{S}=\text{S}$ containing compounds

relative to the >C=O and >C=S counterparts, and therefore it should be suggested that they would be potential groups attached on the surface of materials to adsorb CO₂ and used to design CO₂-philic materials.

4. Concluding remarks

From the contents mentioned above, we can draw some key conclusions for this chapter:

- i. Interaction capacity of CO₂ with various organic compounds including hydrocarbons and functionalized organic compounds along with its derivatives were investigated by using *ab initio* calculations. The obtained results show that interaction capacity between functionalized organic compounds with CO₂ is stronger than that of model hydrocarbons with CO₂. For interactions of CO₂ with model hydrocarbons, the larger stability of complexes is found for interaction of aromatic relative to saturated and unsaturated hydrocarbons with carbon dioxide. In the case of interactions between functionalized organic compounds with CO₂, interaction capacity of the carbonyl and sulfonyl compounds with CO₂ is stronger than that of other functionalized compounds. Obtained results on interaction of nCO₂ (n = 1–3) with functionalized organic compounds indicate that the addition of more CO₂ into systems leads to an increase in the stability of complexes formed.
- ii. The stability of examined complexes is determined by weakly noncovalent interaction including C–H...O, O–H...O of hydrogen bonds, X...C Lewis acid-base interaction, O...O chalcogen-chalcogen, $\pi\cdots\pi$, $p\cdots\pi^*$, and $\pi\cdots\pi^*$ interactions. Remarkably, contribution of the $\pi\cdots\pi^*$ interaction to the complex formed between CO₂-philic compounds and CO₂ has been revealed in our work. The $\pi\cdots\pi$ interactions can significantly contribute to the adsorption of CO₂ in MOF/ZIF materials. Obtained results show the strength of intermolecular interaction tends to decrease in going from >C=S...C via >C=O...C to >C=X...C (X = F, Cl, Br). This observation points out enormous applicability of CO₂-philic materials based on thiocarbonyls.
- iii. It is found that the functional groups such as carbonyl and sulfonyl give a more stable interaction with CO₂ than other functionalized groups, in which a stronger interaction of CO₂ with the >S=O and >S=S counterparts relative to the >C=O and >C=S ones is revealed, and they should be valuable candidates for synthesizing CO₂-philic materials and finding new materials to adsorb CO₂.

Author details

Pham Ngoc Khanh and Nguyen Tien Trung*

*Address all correspondence to: nguyentienchung@qnu.edu.vn

Department of Chemistry, Laboratory of Computational Chemistry and Modelling, Quy Nhon University, Quy Nhon, Binh Dinh, Vietnam

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