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# Understanding Interaction Capacity of CO<sub>2</sub> with Organic Compounds at Molecular Level: A Theoretical Approach

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## Abstract

In this chapter, interactions of CO<sub>2</sub> 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 CO<sub>2</sub>-philic agents. In general, interaction capacity between the functionalized organic compounds with CO<sub>2</sub> is stronger than the hydrocarbon and its derivatives. An addition of more CO<sub>2</sub> molecules into the interaction system formed by the functionalized organic compounds and CO<sub>2</sub> leads to an increase in the stability of the complexes. The obtained results indicate that  $\pi\cdots\pi$  linkages between CO<sub>2</sub> and aromatic rings can significantly contribute to the interactions between CO<sub>2</sub> and MOF/ZIF materials. Formic acid (HCOOH) is likely to be the most soluble compound as compared to the remaining host molecules (CH<sub>3</sub>OH, CH<sub>3</sub>NH<sub>2</sub>, HCHO, HCOOCH<sub>3</sub>, and CH<sub>3</sub>COCH<sub>3</sub>) when dissolved in CO<sub>2</sub>. 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 CO<sub>2</sub>. Therefore, they can be valuable candidates in the design of CO<sub>2</sub>-philic materials and in the search of materials to adsorb CO<sub>2</sub>.

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

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## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) 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 CO<sub>2</sub> (sc-CO<sub>2</sub>) 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-CO<sub>2</sub> 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-CO<sub>2</sub> 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-CO<sub>2</sub>. In the context, continuing efforts have been reported for the purpose of enhancement in applicability of sc-CO<sub>2</sub> solvent through the use of “CO<sub>2</sub>-philes”, which makes insoluble or poorly soluble materials becoming more soluble in sc-CO<sub>2</sub> at an acceptable level of low temperature and pressure conditions [3, 12]. Experimental works have aimed at better understanding of behavior of the sc-CO<sub>2</sub> as solvent for organic compounds [13–18]. It might be assumed that CO<sub>2</sub> 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 CO<sub>2</sub>-philes have been reported during the 1990s [19, 20]. These CO<sub>2</sub>-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 CO<sub>2</sub>-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 CO<sub>2</sub> 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-ete-carbonate in sc-CO<sub>2</sub> at low pressure [21]. Interaction of CO<sub>2</sub> with delocalized  $\pi$  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 CO<sub>2</sub> adsorption at low pressure. Accordingly, some extensive studies have been reported on the interactions of CO<sub>2</sub> with  $\pi$ -systems at level of theory and experiment [24–29]. In recent years, interactions of simple functionalized organic molecules, including CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH [30–32], CH<sub>3</sub>OCH<sub>3</sub>, CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> [33–35], HCHO, CH<sub>3</sub>CHO, CH<sub>3</sub>COOCH<sub>3</sub>, CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>COOH [36–41], and XCHZ (X = CH<sub>3</sub>, H, F, Cl, Br; Z = O, S) [42] CH<sub>3</sub>SZCH<sub>3</sub> (Z = O, S) [43] with CO<sub>2</sub> have been carried out using quantum chemical methods. Today, the interest in CO<sub>2</sub> computational chemistry is the interaction capacity of a solute molecule surrounded by a number of CO<sub>2</sub> molecules. Despite the fact that numerous studies have been performed, a full understanding of the CO<sub>2</sub> 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 CO<sub>2</sub> at molecular level for an effective use of CO<sub>2</sub> in different states.

This chapter focuses on evaluating interaction capacity of CO<sub>2</sub> 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 CO<sub>2</sub> with organic compounds and is divided into two parts: (3.1) interactions of CO<sub>2</sub> with selected models of saturated and unsaturated hydrocarbons and their substituted derivatives, and modeled aromatic hydrocarbons; (3.2) interactions of CO<sub>2</sub> and modeled organic compounds with different functional groups and their substituted derivatives. Obtained results presented in Section 4 support for the enhancement of sc-CO<sub>2</sub> 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 CO<sub>2</sub> at molecular level are revealed, which could be attached on the surface of materials to absorb and store CO<sub>2</sub> 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 CO<sub>2</sub> with organic compounds

### 3.1. Interaction of CO<sub>2</sub> with model hydrocarbons

#### 3.1.1. Interaction of CO<sub>2</sub> with saturated hydrocarbons and their substituted derivatives

Saturated hydrocarbons are a primary energy source for our civilization. Fluorocarbons have been currently used as CO<sub>2</sub>-philic functionalities in many potential applications of chemistry utilizing liquid and supercritical CO<sub>2</sub> as a “green” alternative to conventional organic solvents

for chemical processes [20, 49–52]. The miscibility and dissolution of organic molecules in sc-CO<sub>2</sub> generally increase when the hydrogen atoms in molecules are substituted by fluorine atoms [49, 53]. It is crucial, therefore, to investigate interaction of CO<sub>2</sub> with saturated hydrocarbons and its substituted derivatives. A study [54] on density-dependent <sup>1</sup>H and <sup>19</sup>F NMR chemical shift of hydrocarbons and fluorocarbons in sc-CO<sub>2</sub> 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 CO<sub>2</sub>, and a site specificity for the <sup>19</sup>F shifts due to the surface accessibility of the individual fluorine atoms. In 1996, interactions between CO<sub>2</sub> with ethane (C<sub>2</sub>H<sub>6</sub>) and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>), in particular the (CO<sub>2</sub>)<sub>n</sub>⋯C<sub>2</sub>H<sub>6</sub> and (CO<sub>2</sub>)<sub>n</sub>⋯C<sub>2</sub>F<sub>6</sub> interactions, with n = 1–4, were examined using restricted Hartree-Fock method [55]. The interaction energy for the CO<sub>2</sub>⋯C<sub>2</sub>F<sub>6</sub> complex was calculated to be -3.35 kJ.mol<sup>-1</sup>, while it was -1.26 kJ.mol<sup>-1</sup> for the CO<sub>2</sub>⋯C<sub>2</sub>H<sub>6</sub> complex, indicating that the interaction of CO<sub>2</sub> with C<sub>2</sub>F<sub>6</sub> is stronger than that with C<sub>2</sub>H<sub>6</sub>. The obtained results showed key differences between the interaction of hydrocarbons and fluorocarbons with CO<sub>2</sub>. The interaction of the fluorocarbon with CO<sub>2</sub> is predominantly electrostatic in nature. Thus, the positively charged carbon atom in CO<sub>2</sub> 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<sup>-1</sup> for each CO<sub>2</sub> molecule in the first solvent shell. The interaction of CO<sub>2</sub> 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 CO<sub>2</sub> with small hydrocarbons (CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) and fluorocarbons (CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>) 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 CO<sub>2</sub> 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<sup>-1</sup>, in which the interaction energies are slightly more negative for the CO<sub>2</sub>-hydrocarbon complexes than for the corresponding CO<sub>2</sub>-perfluorocarbon ones, suggesting that the interaction capacity of CO<sub>2</sub> and hydrocarbons is stronger than that of fluorocarbons and CO<sub>2</sub>. Yonker and Palmer [58] studied the nuclear shielding of <sup>1</sup>H and <sup>19</sup>F nuclei in CH<sub>3</sub>F and CHF<sub>3</sub> by NMR and molecular dynamics simulations. Obtained results showed that there is no distinct or specific interaction between fluoromethane and CO<sub>2</sub>. A various work by Yee et al. [59] reported that the polarizability of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>, which is derived from dielectric constant measurement, is larger than that of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, 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 CO<sub>2</sub> is greater for CF<sub>4</sub> than for CH<sub>4</sub>. 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 CO<sub>2</sub>-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 CO<sub>2</sub>. The results suggested an optimum density of fluorine atoms that can be viewed as a maximum CO<sub>2</sub>-philicity, and CO<sub>2</sub> molecule plays both weak Lewis acid and base in these systems. In this work, the authors suggested the fundamentally different nature of interaction between CO<sub>2</sub>-fluorocarbon and CO<sub>2</sub>-hydrocarbon, in spite of comparable interaction energy. For complexes formed by fluorocarbons and CO<sub>2</sub>, their stability is contributed by interaction of carbon in CO<sub>2</sub> and fluorine in fluorocarbons, while the stability of complexes of hydrocarbons and CO<sub>2</sub> is thanks to two oxygen of CO<sub>2</sub>. 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 CO<sub>2</sub>, which may help to explain the difference in solubility of various saturated hydrocarbons and their substituted derivatives in sc-CO<sub>2</sub>.

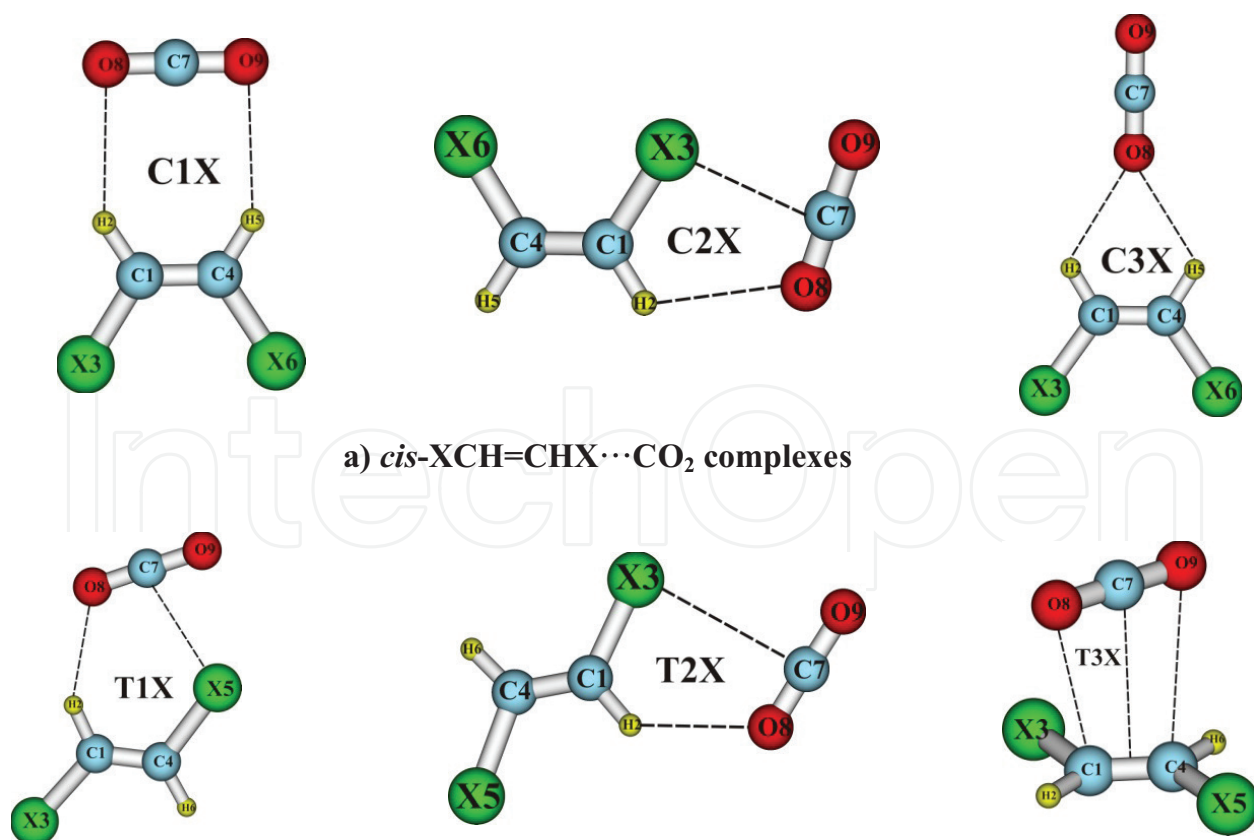
### 3.1.2. Interaction of CO<sub>2</sub> with unsaturated hydrocarbons and its substituted derivatives

Unsaturated hydrocarbons is one of the most important classes of materials for synthesizing polymers; and sc-CO<sub>2</sub> has been seen as a good solvent for this kind of synthesis. In 2009, interaction between C<sub>2</sub>H<sub>2</sub> with CO<sub>2</sub> was investigated by Alkorta et al. [61] and interaction energy was evaluated to be *ca.* -4.70 kJ.mol<sup>-1</sup> at M05-2x/6-311++G(d,p) and -5.99 kJ.mol<sup>-1</sup> at MP2/aug-cc-pVTZ, implying that the complex C<sub>2</sub>H<sub>2</sub>...CO<sub>2</sub> 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 (ρ(r)) and Laplacian (∇<sup>2</sup>ρ(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 CO<sub>2</sub> transfers electrons to the anti-bonding orbital of C<sub>2</sub>H<sub>2</sub> having electron-poor carbon atoms. In order to understand deeply origin of interaction of unsaturated hydrocarbons with CO<sub>2</sub>, the complexes of C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub> were investigated by our group in 2016 [1]. It is remarkable that the interaction energies corrected by both ZPE and BSSE for the C<sub>2</sub>H<sub>4</sub>...CO<sub>2</sub> complexes are in the range from -1.1 to -4.9 kJ.mol<sup>-1</sup>. The most stable structure of C<sub>2</sub>H<sub>4</sub>...CO<sub>2</sub> is in line with the report by Miller et al. that CO<sub>2</sub>'s main axis parallels the plane of C<sub>2</sub>H<sub>4</sub>, 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 C<sub>2</sub>H<sub>4</sub>...CO<sub>2</sub> complexes. Remarkably, contribution of the π...π\* interaction to stabilization of the complex formed by CO<sub>2</sub>-philic compounds and CO<sub>2</sub> has been observed for the first time in this literature. The stability of complex C<sub>2</sub>H<sub>4</sub>...CO<sub>2</sub> (-4.9 kJ.mol<sup>-1</sup>) is more stable than the complexes of interaction between CO<sub>2</sub> with hydrocarbons and fluorinated hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> (from -3.7 to -4.9 kJ.mol<sup>-1</sup> at the MP2/aug-cc-pVDZ) [56, 57, 61]. This review indicates that interaction capacity of CO<sub>2</sub> with unsaturated hydrocarbons is stronger than that of CO<sub>2</sub> with saturated hydrocarbons.

Our group [1] continued to investigate the interactions of the 1,2-dihalogenated derivatives of ethylene (XCH=CHX) with CO<sub>2</sub> in order to evaluate the substituent effects on the interactions. Six stable shapes of the optimized structures of XCH=CHX...CO<sub>2</sub> (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 $\cdots$ CO<sub>2</sub> pairs, and **T1X**, **T2X** and **T3X** for *trans*-XCH=CHX $\cdots$ CO<sub>2</sub> 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 $\cdots$  $\pi^*$  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 C<sub>2</sub>H<sub>4</sub> 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 $\cdots$ CO<sub>2</sub> complexes are more stable than the *trans* counterparts. In addition, CH<sub>2</sub>CH<sub>2</sub> $\cdots$ CO<sub>2</sub> is less stable than both *trans*-XCH=CHX $\cdots$ CO<sub>2</sub> and *cis*-XCH=CHX $\cdots$ CO<sub>2</sub>. Thus, the interaction energies with both ZPE and BSSE corrections are calculated to be from -1.7 to -7.5 kJ.mol<sup>-1</sup> for *cis*-XCH=CHX $\cdots$ CO<sub>2</sub> and from -4.4 to -6.8 kJ.mol<sup>-1</sup> for *trans*-XCH=CHX $\cdots$ CO<sub>2</sub>. Hence replacement of the two H atoms in CH<sub>2</sub>=CH<sub>2</sub> by the same halogen atoms actually increases the stability of complexes formed by interaction of XCH=CHX with CO<sub>2</sub> and causes a decrease of the role of the  $\pi\cdots\pi^*$  interaction in stabilization of the parent C<sub>2</sub>H<sub>4</sub> $\cdots$ CO<sub>2</sub> complex in comparison with the XCH=CHX $\cdots$ CO<sub>2</sub> ones.



**Figure 1.** The stable geometries of the complexes of CO<sub>2</sub> and XCH=CHX derivatives (X = F, Cl, and Br). (a) *cis*-XCH=CHX $\cdots$ CO<sub>2</sub> complexes, (b) *trans*-XCH=CHX $\cdots$ CO<sub>2</sub> complexes.

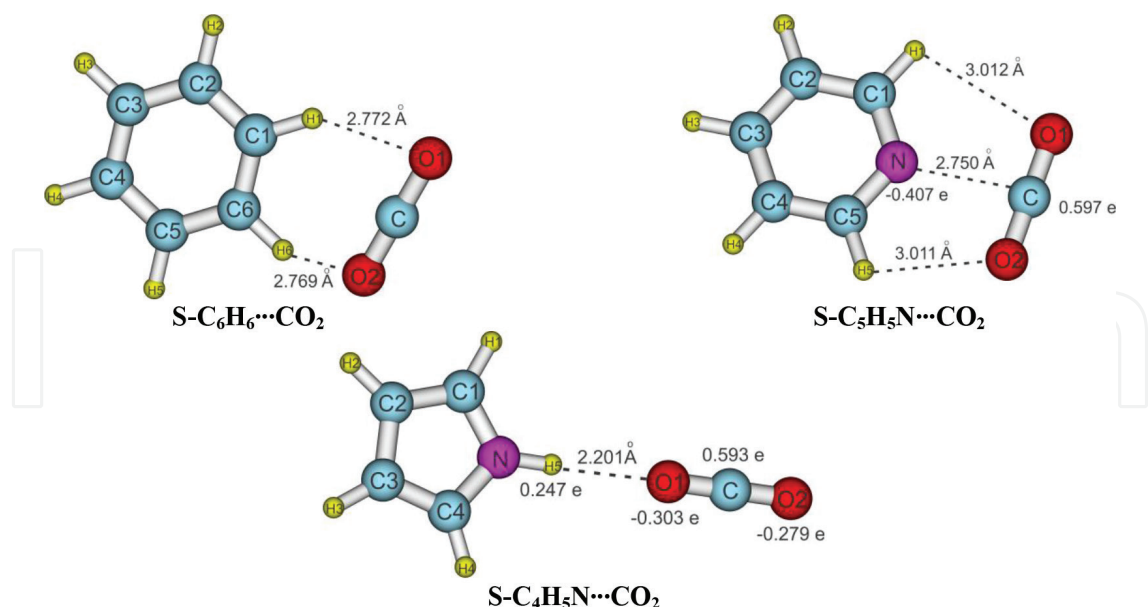
### 3.1.3. Interaction of CO<sub>2</sub> with some model aromatic hydrocarbons

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 CO<sub>2</sub> 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 CO<sub>2</sub> 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 MOFs. 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 CO<sub>2</sub>. 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 CO<sub>2</sub> formed. On the other hand, substitution of hydrogen atom in aromatic ring by methyl group clearly strengthens its interaction capacity with CO<sub>2</sub>, 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 CO<sub>2</sub> 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 CO<sub>2</sub> and three aromatic molecules, namely benzene (C<sub>6</sub>H<sub>6</sub>), pyridine (C<sub>5</sub>H<sub>5</sub>N), and pyrrole (C<sub>4</sub>H<sub>5</sub>N), which serve as common functional groups in metal-organic/zeoliticimidazolate framework materials [63]. The interaction energies for the complexes of CO<sub>2</sub> with aromatic hydrocarbons calculated at MP2/aug-cc-pVTZ are in the range from -11.9 to -15.4 kJ.mol<sup>-1</sup>, which are twice more negative than the most stable complex of the C<sub>2</sub>H<sub>4</sub>...CO<sub>2</sub> system (-4.9 kJ.mol<sup>-1</sup> at CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ level). This result implies that interaction capacity of CO<sub>2</sub> with aromatic hydrocarbons is stronger than that of CO<sub>2</sub> 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-C<sub>6</sub>H<sub>6</sub>...CO<sub>2</sub>, S-C<sub>5</sub>H<sub>5</sub>N...CO<sub>2</sub>, and S-C<sub>4</sub>H<sub>5</sub>N...CO<sub>2</sub>, as illustrated in **Figure 2**.

The side-on interaction is significantly weaker than the  $\pi\cdots\pi$  interaction in C<sub>6</sub>H<sub>6</sub>...CO<sub>2</sub> and C<sub>4</sub>H<sub>5</sub>N...CO<sub>2</sub> pairs. On the contrary, for the C<sub>5</sub>H<sub>5</sub>N...CO<sub>2</sub> pair the  $\pi\cdots\pi$  interaction [-11.6 kJ.mol<sup>-1</sup> for T-C<sub>5</sub>H<sub>5</sub>N...CO<sub>2</sub>(N) and -11.5 kJ.mol<sup>-1</sup> for TC<sub>5</sub>H<sub>5</sub>N...CO<sub>2</sub>(C)] is weaker than the side-on interaction (-18.0 kJ.mol<sup>-1</sup>). 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-C<sub>5</sub>H<sub>5</sub>N...CO<sub>2</sub>. In short, the results indicate that  $\pi\cdots\pi$  interaction between CO<sub>2</sub> and aromatic rings can significantly contribute to the interactions between CO<sub>2</sub> and MOFs/ZIFs.





**Figure 2.** Optimized structures of S-C<sub>6</sub>H<sub>6</sub>...CO<sub>2</sub>, S-C<sub>5</sub>H<sub>5</sub>N...CO<sub>2</sub>, and S-C<sub>4</sub>H<sub>5</sub>N...CO<sub>2</sub>.

### 3.1.4. Concluding remarks on interaction of CO<sub>2</sub> with model hydrocarbons

Interactions of CO<sub>2</sub> 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 C–H...O hydrogen bonded interaction, C–X...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<sub>2</sub>-philic compounds and CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> adsorption in MOF/ZIF materials.

## 3.2. Interaction of CO<sub>2</sub> with model functionalized organic compounds and their substituted derivatives

### 3.2.1. Interaction of CO<sub>2</sub> with model functionalized organic compounds

Up to now, a large number of complexes for interactions of CO<sub>2</sub> 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<sub>2</sub> and some carbonyl-functionalized compounds has been reported [34, 44, 64–67]. The existence of the C–H...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 CO<sub>2</sub> and some typically functionalized organic molecules such as methanol (CH<sub>3</sub>OH), methylamine (CH<sub>3</sub>NH<sub>2</sub>), formaldehyde (HCHO), formic acid (HCOOH), dimethylether (CH<sub>3</sub>OCH<sub>3</sub>), acetone (CH<sub>3</sub>COCH<sub>3</sub>) and methyl formate (HCOOCH<sub>3</sub>) [40]. Obtained results showed that the Lewis acid-base interaction such as C–N···C(CO<sub>2</sub>), C=O···C(CO<sub>2</sub>) 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···CO<sub>2</sub> 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<sup>–1</sup>, in which the HCOOH···CO<sub>2</sub> pair is the most stable, whereas the weakest one is the HCHO···CO<sub>2</sub> pair. As a consequence, solubility of HCOOH in sc-CO<sub>2</sub> 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 (CH<sub>3</sub>OH, CO<sub>2</sub>), its interaction energy of –13.3 kJ.mol<sup>–1</sup> with only ZPE correction, and –11.4 kJ.mol<sup>–1</sup> with both ZPE and BSSE corrections is more negative than that of –11.3 kJ.mol<sup>–1</sup> obtained with only BSSE correction at the MP2/aug-cc-pVTZ level [64]. Another example is that the BSSE corrected interaction energy of the CH<sub>3</sub>OCH<sub>3</sub>···CO<sub>2</sub> pair was computed to be –13.1 kJ.mol<sup>–1</sup> at the MP2/6-311++G(2d,2p)//MP2/6-311++G(d,p) level [35] while it is –13.7 kJ.mol<sup>–1</sup> with ZPE and BSSE corrections, and –16.3 kJ.mol<sup>–1</sup> with only ZPE correction in the present work.

In 2011, our group investigated the interactions of CO<sub>2</sub> with substituted derivatives of formaldehyde and thioformaldehyde [42]. The interaction energies (with ZPE and BSSE corrections) of –10.5 kJ.mol<sup>–1</sup> for CH<sub>3</sub>CHO···CO<sub>2</sub> and –9.1 kJ.mol<sup>–1</sup> for CH<sub>3</sub>CHS···CO<sub>2</sub> are more negative than for complexes of HCHO···CO<sub>2</sub> and HCHS···CO<sub>2</sub>, 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 CO<sub>2</sub>-philic materials. The interactions between carbonyl compounds and CO<sub>2</sub> 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-CO<sub>2</sub>, 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-CO<sub>2</sub> may be important in terms of the specific solute-solvent.

In 2014, we investigated the interactions between some carbonyl compounds including acetone (CH<sub>3</sub>COCH<sub>3</sub>) with CO<sub>2</sub> [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<sup>–1</sup>) is less negative than that reported in Ref. [40] (–11.1 kJ.mol<sup>–1</sup>) at CCSD(T)/aug-cc-pVTZ but is more negative than that in Ref. [64] (–8.8 kJ.mol<sup>–1</sup>) 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
$\Delta E$	-12.7	-11.3	-12.7	-4.7
$\Delta E^*$	-10.3	-9.4	-9.2	-2.4

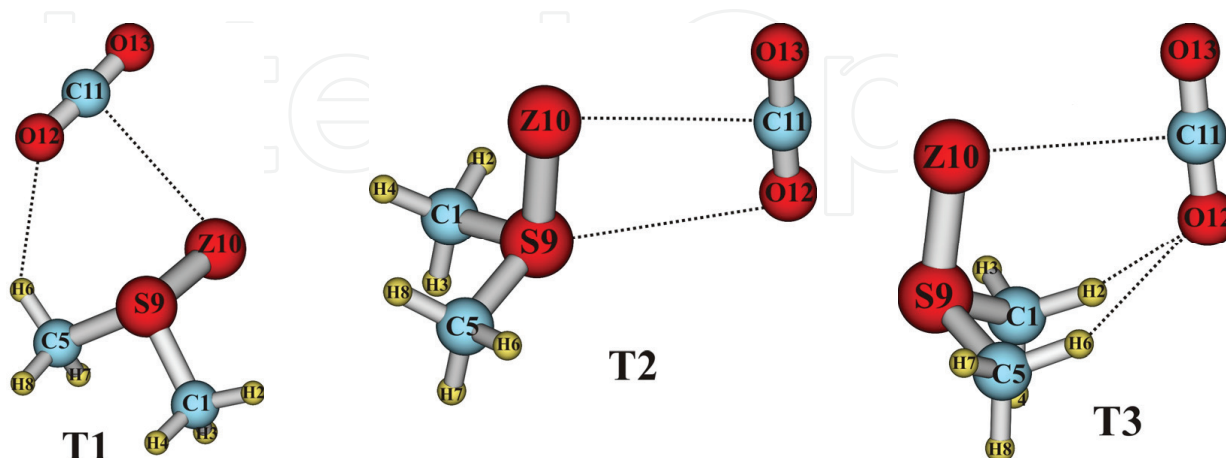
Source: Dai et al. [41].

**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  $\text{CO}_2$ -philic and adsorbent materials.

Further, interactions of  $\text{CO}_2$  with  $\text{CH}_3\text{SZCH}_3$  ( $Z = \text{O}, \text{S}$ ) 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  $\text{CO}_2$  reported in Refs. [38, 40, 42]. This implies a stronger interaction of  $\text{CO}_2$  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  $\text{CH}_3\text{SZCH}_3$  ( $Z = \text{O}, \text{S}$ ) and  $\text{CO}_2$ .

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

<sup>a</sup>Taken from MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p).  
<sup>b</sup>Taken 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 (ΔE<sup>0</sup>, in kJ.mol<sup>-1</sup>) and for ZPE and BSSE (ΔE\*, in kJ.mol<sup>-1</sup>) of obtained complexes.

also suggested a stronger interaction of CO<sub>2</sub> with the >S=O moiety compared to the >S=S one, and they both should be candidates for designing CO<sub>2</sub>-philic materials, CO<sub>2</sub> adsorption and storage materials in the future.

For the CH<sub>3</sub>SOCH<sub>3</sub>...CO<sub>2</sub> 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<sup>-1</sup> at MP2/aug-cc-pVTZ//MP2/6-311++G(2d,2p) and -14.5 kJ.mol<sup>-1</sup> 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<sup>-1</sup> 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 CO<sub>2</sub> 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 CO<sub>2</sub> with model functionalized organic compounds. The complexes of the interactions of CO<sub>2</sub> with CH<sub>3</sub>SZCHX<sub>2</sub> (X = H, CH<sub>3</sub>, F, Cl, Br; Z = O, S) were studied by our group and reported in Ref. [43]. In general, the CH<sub>3</sub>SOCHX<sub>2</sub>...CO<sub>2</sub> complexes are more stable than the CH<sub>3</sub>SSCHX<sub>2</sub>...CO<sub>2</sub> complexes. This firmly indicates that the >S=O, as compared to the >S=S, has a stronger interaction with CO<sub>2</sub>, which originates from a contribution of a larger attractive electrostatic interaction of the former than the latter in stabilizing the examined complexes. For the CH<sub>3</sub>SOCHX<sub>2</sub>...CO<sub>2</sub> complexes, the strength is enhanced by the X substitution in the order from H *via* F to Cl to Br and finally to CH<sub>3</sub>. Therefore, the substitution of two H atoms in a CH<sub>3</sub> group of CH<sub>3</sub>SOCH<sub>3</sub> by two alike X groups significantly influences the strength of CH<sub>3</sub>SOCHX<sub>2</sub>...CO<sub>2</sub> complexes relative to CH<sub>3</sub>SOCH<sub>3</sub>...CO<sub>2</sub> complexes. The replacement also leads to a slight enhancement of stability of the CH<sub>3</sub>SSCHX<sub>2</sub>...CO<sub>2</sub> complexes in the sequence from F, H, Cl, Br to CH<sub>3</sub>. In Ref. [41], we replaced two H atoms in a CH<sub>3</sub> group of CH<sub>3</sub>COCH<sub>3</sub> by two alike CH<sub>3</sub>, 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<sup>-1</sup> with both ZPE and BSSE

corrections, which are more negative than that of interactions of CO<sub>2</sub> with hydrocarbons and fluorocarbons. Thus, the interaction energies range from -3.7 to -4.9 kJ.mol<sup>-1</sup> for the complexes of CO<sub>2</sub> with the hydrocarbons such as CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>; and from -2.4 to -7.8 kJ.mol<sup>-1</sup> for the complexes of CO<sub>2</sub> with CH<sub>4-n</sub>F<sub>n</sub> (n = 0 ÷ 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<sub>2</sub>. Generally, the strength of CH<sub>3</sub>COCHR<sub>2</sub>...CO<sub>2</sub> complexes is gently increased when R = CH<sub>3</sub> as compared to CH<sub>3</sub>COCH<sub>3</sub>...CO<sub>2</sub>, while it is slightly decreased with R = F, Cl and Br.

### 3.2.3. Interaction of nCO<sub>2</sub> (n = 1:3) with model functionalized organic compounds

It is important to investigate the strength of interactions between CO<sub>2</sub> and carbonyl-containing molecules, as well as the underlying their chemical nature. Due to a strong interest in CO<sub>2</sub> as a solvent, it is imperative to consider aggregates in which a solute molecule is surrounded by a number of CO<sub>2</sub> molecules, an unexplored area at present [69]. Expansion of the system by adding more CO<sub>2</sub> 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<sub>2</sub>CO, CH<sub>3</sub>CHO, and (CH<sub>3</sub>)<sub>2</sub>CO with two and three molecules of CO<sub>2</sub> 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<sub>2</sub> molecules, with small energy differences. The bonding features of the heterodimers are generally carried over to these larger heterotrimers and tetramers, although the linear C=O...C arrangement of the binary complexes is largely absent. The O...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 kJ.mol<sup>-1</sup>, which are more negative than heterodimers (-8.8 to -12.5 kJ.mol<sup>-1</sup>) and trimers complexes (-23.1 to -34.2 kJ.mol<sup>-1</sup>). 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<sub>2</sub> with model functionalized organic compounds

The organic compounds functionalized by hydroxyl, carbonyl, thiocarbonyl, carboxyl and amide groups have been paid much attention as CO<sub>2</sub>-philic compounds. The carbonyl and thiocarbonyl compounds have presented a higher stability, as compared to other functionalized ones, when they interact with CO<sub>2</sub>. This durability has been assigned to a main contribution of the >C=Z...C (Z = O, S) Lewis acid-base interaction and/or an additional cooperation of the C-H...O hydrogen bonded interaction, except for the case of the HCOOH...CO<sub>2</sub> complex, where the role of the O-H...O hydrogen bond was found to be more important than the >C=O...C Lewis acid-base interaction. We have also found that there is a stronger interaction of CO<sub>2</sub> with the >S=O and >S=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 CO<sub>2</sub> and used to design CO<sub>2</sub>-philic materials.

#### 4. Concluding remarks

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

- i. Interaction capacity of CO<sub>2</sub> 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 CO<sub>2</sub> is stronger than that of model hydrocarbons with CO<sub>2</sub>. For interactions of CO<sub>2</sub> 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 CO<sub>2</sub>, interaction capacity of the carbonyl and sulfonyl compounds with CO<sub>2</sub> is stronger than that of other functionalized compounds. Obtained results on interaction of nCO<sub>2</sub> (n = 1–3) with functionalized organic compounds indicate that the addition of more CO<sub>2</sub> 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 CO<sub>2</sub>-philic compounds and CO<sub>2</sub> has been revealed in our work. The  $\pi\cdots\pi$  interactions can significantly contribute to the adsorption of CO<sub>2</sub> 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 CO<sub>2</sub>-philic materials based on thiocarbonyls.
- iii. It is found that the functional groups such as carbonyl and sulfonyl give a more stable interaction with CO<sub>2</sub> than other functionalized groups, in which a stronger interaction of CO<sub>2</sub> 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 CO<sub>2</sub>-philic materials and finding new materials to adsorb CO<sub>2</sub>.

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