Full paper/Mémoire

Ab initio analysis of the interaction of CO_2 with acetylated D-glucopyranose derivatives

Honghong Chang [a], Congcong Yang [a], Xing Li [a], Wenchao Gao [a], Wenlong Wei [a], Gang Liu [a], Xianyong Pang [a,**], Yan Qiao [b,*]

[a] College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, Shanxi, PR China
[b] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Shanxi, PR China

ARTICLE INFO

ABSTRACT

Peracetylated D-glucopyranose has a high solubility in CO_2 and can be a promising phase-change physical solvent or absorbent for CO_2, as reported recently. However, peracetylated D-glucopyranose is unstable under acidic atmospheres, especially in sulfur-containing waste gases, and the possibly major decomposition products are 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose, 1-thiol-D-glucopyranose tetraacetate, and 1-mercaptoethyl-D-glucopyranose tetraacetate. Therefore, it is highly interesting to investigate the interaction between CO_2 and these three compounds using ab initio calculations, including geometry optimizations with HF/3-21G, B3LYP/6-31+G** and single-point energy calibration with MP2/aug-cc-pVDZ. The results indicate that the electrostatic interactions between the substrates and CO_2 are mainly influenced by the interaction distance and the numbers of negative charge donors or the interacting pairs involved in the complex. It is furthermore found that ΔE increases significantly if S and O atoms could interact with CO_2 simultaneously. The binding energy is irrelevant if one considers the chemical environment of the O atom (i.e. O_{Ac}, O_E or O_S) or the S atom (i.e. SEt or SH), and the electronegativity difference between the S and O atoms. The three substrates studied are still excellent CO_2-philes, although their average ΔE (–20 kJ/mol) is slightly lower than that of peracetylated D-glucose (–22 kJ/mol), which has one more O atom that can interact with CO_2. Therefore, the applications of carbohydrates can be expanded to include adsorbents for CO_2, SO_2 or both, and the functional groups attached to the carbohydrate can vary from those to the acetyl groups.

© 2015 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Symbol description:

- The two oxygen atoms of CO_2 are referred to as O_1 and O_2, respectively. The carbon atom is designated as C.
- The oxygen atom in the glucose ring is referred to as O_S, the hydrogen atoms in the sugar as H_S and the hydrogen atom in the methylene as H_{S2}.
- The oxygen atom adjacent to the carbonyl group is labeled as O_E, while the carbonyl oxygen atom is labeled as O_{AC}. The hydrogen atom in methyl group was expressed by H_{Ac}.

- The oxygen atom in OH is referred to as O_{Hy}, the hydrogen atom as H_{Hy}.
- The sulfur atom in SH is referred to as S_{Su}, the hydrogen atom as H_{Su}.
- The sulfur atom in SEt is referred to as S_{Et}, the hydrogen atom as H_{Su}, the hydrogen atom in the methyl group as H_{Et3}, the hydrogen atom as H_{Et2}.

1. Introduction

Carbon dioxide (CO_2) has two faces: it is both a greenhouse gas and also a valuable carbon resource and solvent owing to its abundance, low cost and non-toxicity [1–8]. For example, supercritical carbon dioxide (scCO$_2$) can be used as a solvent for extraction, separation, and other chemical processes, including chemical reactions and material handling [9–12]. However, many polar compounds, high molecular-weight substances and organometallic complexes usually exhibit poor solubility in scCO$_2$, which seriously limits its industrial applications [13–16]. Therefore, much effort has been made to look for CO_2-philes that can enhance the solubility of insoluble compounds in CO_2 or as a potential phase-change physical solvent for CO_2 [17]. Compared to the existing CO_2-philes, such as fluorinated compounds or silicone polymers, hydrocarbons, especially carbohydrates with carbonyl groups, are one of the most attractive CO_2-philic materials owing to their low cost, as well as their easy-modification and environmentally friendly properties [6,17–20]. Therefore, several CO_2-phile carbohydrates have been prepared. One of the major classes is peracetylated sugar, such as peracetylated D-glucopyranose (Fig. 1, compound 1). However, peracetylated D-glucopyranose is unstable under acidic conditions, particularly in the presence of sulfur-containing waste

gases that released during coal combustion. The exposure to acidic atmosphere leads to 2,3,4,6-tetra-O-acetyl-D-glucopyranose (Fig. 1, compound 2), 1-thiol-D-glucopyranose tetraacetate (Fig. 1, compound 3), and 1-mercaptoethyl-D-glucopyranose tetraacetate (Fig. 1, 4).

As reported, carbohydrate based CO_2-philes should have CO_2-philic functional groups, such as acetyls, with high free volume and flexibility, displaying weak self-interactions, but relatively strong interactions with CO_2. The high solubility of hydrocarbon carbonyl systems in CO_2 has been attributed to the Lewis acid (LA)–Lewis base (LB) interactions between CO_2 and CO_2-philic Lewis base functionalities, such as carbonyl groups [21–23]. Our recent ab initio calculations established that the interactions of compound 1 with CO_2 are distance related, and should be of electrostatic origin (point charge effects) and not only LA–LB and hydrogen bond interactions [24]. Accordingly, it is necessary for us to get a deeper insight into the interaction properties of compounds 2, 3 and 4 with CO_2 at the molecular level. If the affinity of the thiol (–SH in compound 3) or mercaptoethyl (–SEt in compound 4) group with CO_2 were to be clear, the adsorption of CO_2 and the conversion of sulfur gas would occur simultaneously and the application of carbohydrates could be widened.

2. Computational models and methods

On the basis of previous work, it was found that one CO_2 molecule could only interact with two adjacent Ac groups in peracetylated D-glucopyranose by weak binding and complex formation through the 1,2-di-O-acetyl-D-glucopyranose model [24]. The following substrates were designed: 2-O-acetyl-α-D-glucopyranose (A–OH in Fig. 2), 2-O-acetyl-β-D-glucopyranose (B–OH in Fig. 2),

Compound 2
D-Glucopyranose, 2, 3, 4, 6-tetraacetate

Compound 1
Peracetylated D-glucopyranose

Compound 3
1-thio-D-glucopyranose tetraacetate

Compound 4
1-mercaptoethy-D-glucopyranose tetraacetate
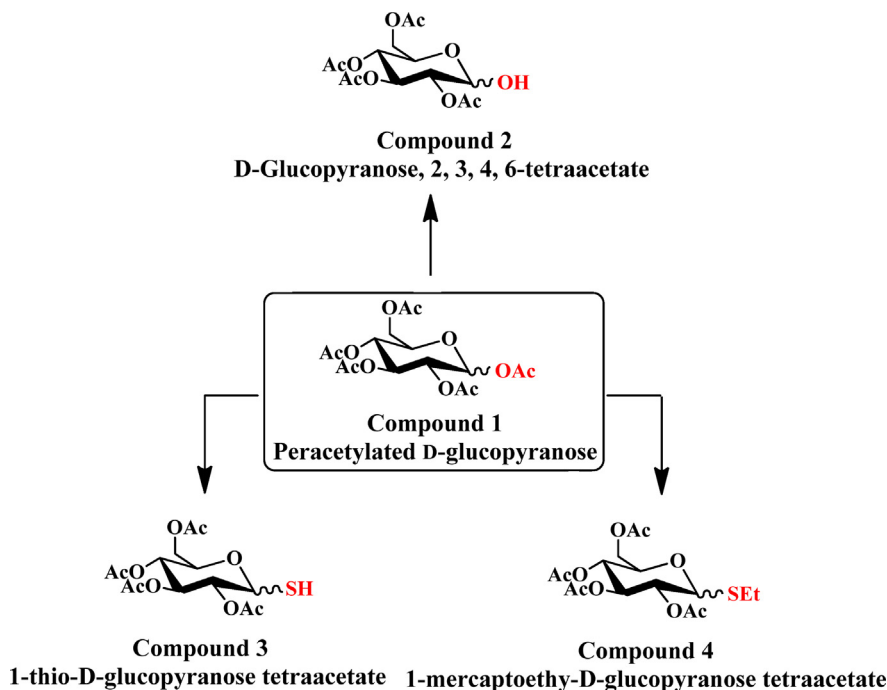
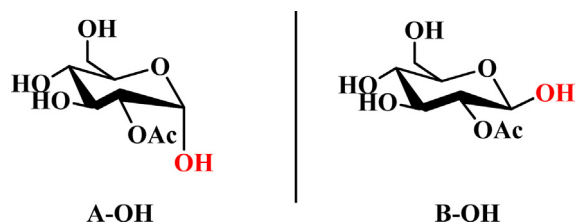Fig. 1. (Color online.) The transformation process from 1–OAc of D-glucose pentaacetate to 1–OH, 1–SH, 1–SEt group.

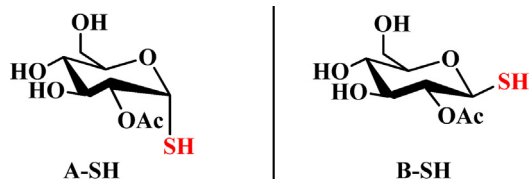**Fig. 2.** (Color online.) The structures of 2-O-acetyl-α-D-glucopyranose (A–OH) and 2-O-acetyl-β-D-glucopyranose (B–OH).

Fig. 3. (Color online.) The structures of 2-O-acetyl-1-thio-α-D-glucopyranose (A–SH) and 2-O-acetyl-1-thio-β-D-glucopyranose (B–SH).

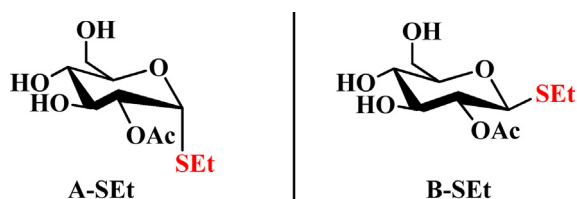**Fig. 4.** (Color online.) The structures of 1-mercaptoethyl-2-O-acetyl-α-D-glucopyranose (A–SEt) and 1-mercaptoethyl-2-O-acetyl-β-D-glucopyranose (B–SEt).

2-O-acetyl-1-thio-α-D-glucopyranose (A–SH in Fig. 3), 2-O-acetyl-1-thio-β-D-glucopyranose (B–SH in Fig. 3), 1-mercaptoethyl-2-O-acetyl-α-D-glucopyranose (A–SEt in Fig. 4), and 1-mercaptoethyl-2-O-acetyl-β-D-glucopyranose (B–SEt in Fig. 4) instead of their tetraacetated derivatives, as shown in Fig. 1.

Ab initio calculations for the interactions of CO_2 with the D-glucopyranose derivatives were performed on a 1:1 complex. Preliminary geometry optimizations were carried out at the Hartree–Fock (HF/3-21G) level. In order to determine the configuration property provided within weak interactions, more precise geometry and vibrational frequency calculations were then performed at the B3LYP/6-31+G** level. Single-point energy calculation was carried out at the MP2/aug-cc-pVDZ level, including the zero-point energy (ZPE) to obtain more accurate

interaction energies, as shown in our previous work [24]. All the calculations were performed using Gaussian 09. The interaction energies (ΔE) of these complexes were calculated using the "supermolecule" method:

$$\Delta E = E_{AB} - (E_A + E_B)$$

where E_{AB} is the energy of optimized D-glucopyranose derivatives–CO_2 complexes, E_A is the energy of the optimized CO_2 molecule, and E_B is the energy of the optimized D-glucopyranose derivatives molecule.

3. Results and discussion

3.1. The interaction between compound 2 and a CO_2 molecule

As mentioned above, the interactions between 2-O-acetyl-α-**D**-glucopyranose (C1–OH group in axial direction, A–OH in Fig. 2) or its anomer 2-O-acetyl-β-D-glucopyranose (C1–OH group in the equatorial plane, B–OH in Fig. 2) and CO_2 are achieved by the formation of a complex.

3.1.1. A–OH–CO_2

With the anomeric OH group of A–OH in the axial position, and C2–OAc in the equatorial plane, three configurations (Fig. 5) can be formed. These structures are numbered from **I** to **III** based on their calculated energies, from the highest to the lowest. If the energy of **I** is assigned to be zero, the relative energies are −5.6 kJ/mol and −27.9 kJ/mol for **II** and **III**, respectively. Even though their energies are different, due to the tiny difference between them (less than 30 kJ/mol), these configurations would all exist in real conditions.

The three configurations of A–OH (Fig. 5) can bind with one CO_2 molecule to yield five binding models, as shown in Fig. 6. Owing to its quadrupole properties, one CO_2 molecule may interact with A–OH through its carbonyl oxygen atom (O_{Ac}), its ester oxygen atom (O_E), its oxygen atom in the sugar ring (O_S), its hydroxyl oxygen atom (O_{Hy}), the hydrogen atoms of its Ac group (H_{Ac}), the hydrogen atom of its hydroxyl group (H_{Hy}), and/or the hydrogen atoms attached on the sugar ring (H_S). Each A–OH–CO_2 complex structure was optimized and found to have different binding energies (ΔE) from those of the other ones, as detailed in Table 1.

As shown in Fig. 6 and Table 1, structure **IIb** has one O_{Hy} while **IIIb** has one O_{Ac} involved in the interaction, without changing the ΔE. The interaction between CO_2 and O_{Hy} was as strong as that with O_{Ac}, i.e. the chemical environment of the oxygen atom (O_{Hy} or O_{Ac}) has only minor influence on

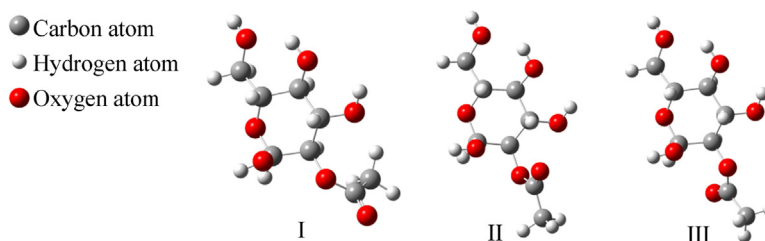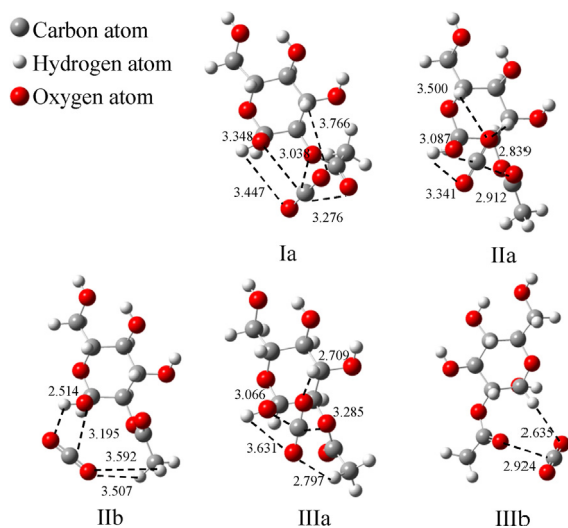**Fig. 5.** (Color online.) Three optimized structures of 2-O-acetyl-α-D-glucopyranose (A–OH).

Fig. 6. (Color online.) The optimized binding models for A–OH–CO_2. (The dashed lines indicate the interaction points between the two molecules. The values represent the distances between two atoms, and the unit is 1 Å).

the ΔE value of the A–OH–CO_2 complex. Consequently, the data in Table 1 also revealed that ΔE increased if more oxygen atoms were joined in the binding model (i.e. **IIa**). Hydrogen atoms could interact with oxygen atoms as presented in all structures in Fig. 6, but this interaction has no saturation and directional features, as expected from a hydrogen bond. Therefore, it should be attributed to the point charge interaction rather than to the hydrogen bond.

3.1.2. B–OH–CO_2

B–OH can display three different configurations, as shown in Fig. 7. The energy of structure A was assigned to

be zero and the others are –15.2 kJ/mol and –18.9 kJ/mol for structures B and C, respectively (like with 3.1.1).

The three configurations of B–OH (Fig. 7) could bind with one CO_2 molecule to yield five binding models (Fig. 8). As shown in Fig. 8 and Table 2, four binding models (A1, B1, B2, C2) display one O atom involved in the interaction. For example, structures A1 or B1 had one O_{Hy}, structure B2 had one O_{Ac}, while C2 had one O_E involved in the interaction, but their ΔEs were all around –19 kJ/mol. The interaction between CO_2 and O_{Ac} was as strong as that with O_E and O_{Hy}; the chemical environmental of oxygen atom had no obvious influence on ΔE of B–OH–CO_2 complex.

From Table 1 and Table 2, the average ΔE of A–OH–CO_2 (–20.7 kJ/mol) is similar to that of B–OH–CO_2 (–19.7 kJ/mol), which means that the interaction between CO_2 and α-D-glucopyranose tetraacetate is almost strong as that with its β-anomer. In addition, because compound **2** has less carbonyl groups than compound **1**, the average ΔE values of compound **2**–CO_2 complexes are lower than those of compound **1**–CO_2 complexes (–24.2 and –22 kJ/mol). Therefore, the numbers of negative charges are important in such a carbohydrate–CO_2 system.

3.2. The interaction between compound **3** and a CO_2 molecule

The α- and β-1-thio-D-glucopyranose tetraacetate (compound **3**) had one anomeric–SH group and four Ac groups. 2-O-acetyl-1-thio-α-D-glucopyranose (A–SH in Fig. 3) and 2-O-acetyl-1-thio-β-D-glucopyranose (B–SH in Fig. 3) were used as models. One CO_2 molecule may interact with A–SH or B–SH through its carbonyl oxygen atom (O_{Ac}), an ester oxygen atom (O_E), an oxygen atom in the sugar ring (O_S), a sulfur atom (S_{Su}) and/or hydrogen atoms, including H_{Su} and H_{Ac}.

Table 1
Interaction energies of CO_2 with A–OH.

Structures	Interaction pairs	Distances of two atoms (Å)	Interaction pairs number	Binding energy (ΔE^*, kJ/mol)	Gibbers free energy (ΔG^*, kJ/mol)
Ia	C–O_{Hy}	3.348	3	–23.4	5.4
	C–O_E	3.038			
	C–O_{Ac}	3.276			
	O_1–H_S	3.766	2		
	O_2–H_{Hy}	3.447			
IIa	C–O_{Hy}	3.087	2	–24.3	7.3
	C–O_{Ac}	2.839			
	O_1–H_{Hy}	3.341	3		
	O_2–H_S	3.500			
	O_2–H_S	2.839			
IIb	C–O_{Hy}	3.195	1	–16.3	8.1
	O_1–H_{Hy}	2.514	3		
	O_2–H_{Ac}	3.592			
	O_2–H_{Ac}	3.507			
IIIa	C–O_E	3.285	2	–22.7	9.5
	C–O_{Hy}	3.066			
	O_1–H_S	2.709	3		
	O_2–H_{Ac}	2.797			
	O_2–H_{Hy}	3.631			
IIIb	C–O_{Ac}	2.924	1	–17.0	9.7
	O_1–H_S	2.635	1		
Average binding energy (kJ/mol)				–20.7	8.0

$^*\Delta E$ is the binding energy after zero-point energy calibration (ZPE); ΔG is the binding energy after thermal adjustment for the Gibbs free energy.
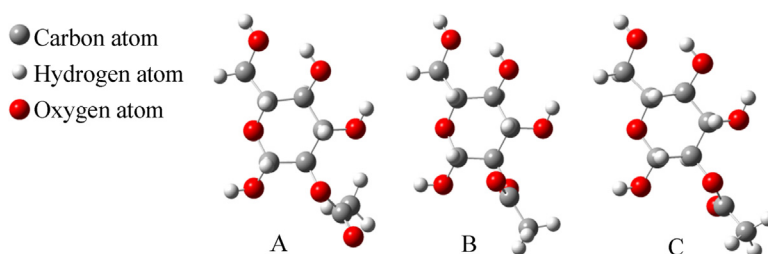
Fig. 7. (Color online.) Three optimized structures of 2-*O*-acetyl-β-ᴅ-glucopyranose (B–OH).
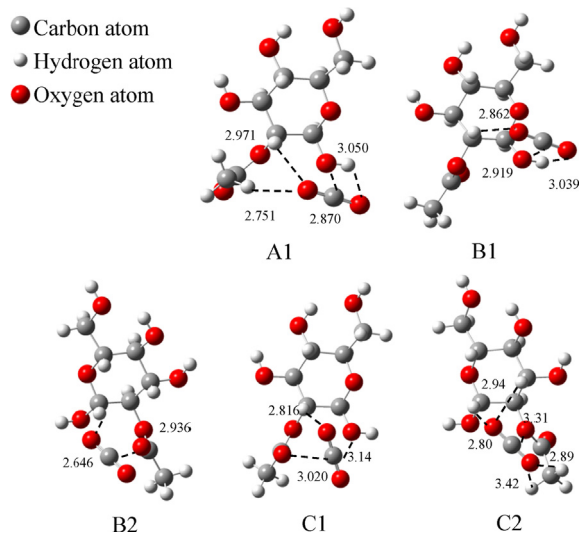

Fig. 8. (Color online.) The optimized binding models for B–OH–CO_2. (The dashed lines indicate the interaction points between the two molecules. The values represent the distances between two atoms, and the unit is 1 Å).

3.2.1. A–SH–CO_2

The anomeric–SH group of A–SH is in axial position, whereas C2–OAc is in the equatorial plane, and these two groups can create some rotation conformers, as shown in

Fig. 9. The structures are numbered from **I** to **III** based on the calculated energies, from the highest to the lowest. If the energy of **I** is assigned to be zero, the relative energies are –10.5 kJ/mol, and –31.4 kJ/mol for configurations **II** and **III**, respectively (similar to 3.1.1).

The three configurations of A–SH (Fig. 9) can bind with one CO_2 molecule to yield four binding models, as shown in Fig. 10. Compared with others (**IIa**, **IIb** and **IIIa** in Fig. 10), structure **Ia** had one more sulfur atom besides the oxygen atoms (O_{Ac} and O_E) that can interact with the CO_2 molecule and therefore gives a higher ΔE (–22.4 kJ/mol, Table 3). Moreover, the distance between the CO_2 molecule and the –SH group ($>$S$\cdots$C, 3.8 Å) is slightly longer than in the case of **1**–OH (around 3 Å, Fig. 6); this may be the cause of a weaker electrostatic interaction between A–SH and CO_2 and thereby of a lower average ΔE value (18.8 kJ/mol for A–SH in Table 3, –20.7 kJ/mol for A–OH in Table 1).

3.2.2. B–SH–CO_2

B–SH has one equatorial anomeric–SH group and one C2–OAc group similar to that of A–SH, and can create three rotation conformers, as shown in Fig. 11. The structures are numbered from A to C based on the calculated energies from the highest to the lowest, i.e. the energy of A was assigned to be zero, which gives –19.0 kJ/mol for B and –22.8 kJ/mol for C. There are four binding models with three configurations of B–SH binding with one CO_2 molecule (Fig. 12), and the ΔEs of these models are listed in Table 4.

Table 2
Interaction energies of CO_2 with B–OH.

Structures	Interaction pairs	Distances of two atoms (Å)	Interaction pairs number	Binding energy (ΔE^*, kJ/mol)	Gibbs free energy (ΔG^*, kJ/mol)
A1	C–O_{Hy}	2.870	1	–19.5	8.7
	O_1–H_{Hy}	3.050	3		
	O_2–H_S	2.971			
	O_2–H_{Ac}	2.751			
B1	C–O_{Hy}	2.919	1	–19.0	6.8
	O_1–H_{Hy}	3.039	2		
	O_2–H_s	2.862			
B2	C–O_{Ac}	2.936	1	–18.9	5.4
	O_1–H_S	2.646	1		
C1	C–O_{Ac}	3.020	2	–22.7	8.4
	C–O_{Hy}	3.140			
	O_1–H_S	2.816	1		
C2	C–O_E	3.310	1	–18.6	10.4
	O_1–H_S	2.940	4		
	O_1–H_S	2.800			
	O_2–H_{Ac}	2.890			
	O_2–H_{Ac}	3.420			
Average binding energy (kJ/mol)				–19.7	8.0

$^*\Delta E$ is the binding energy after zero-point energy calibration (ZPE); ΔG is the binding after thermal adjustment for the Gibbs free energy.
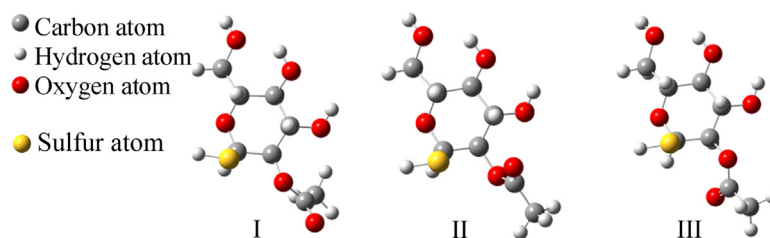
Fig. 9. (Color online.) Three optimized structures of 2-O-acetyl-1-thio-α-D-glucopyranose (A–SH).
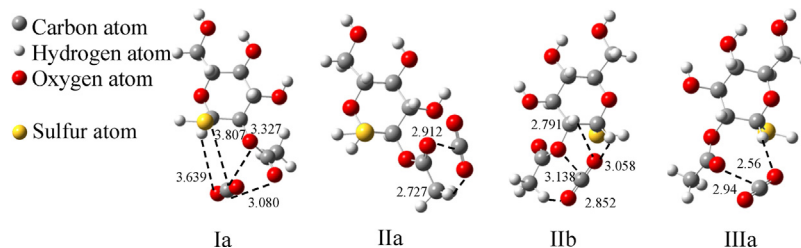

Fig. 10. The optimized binding models for A–SH–CO_2. (The dashed lines indicate the interaction points between the two molecules. The values represent the distances between two atoms, and the unit is 1 Å).

Except A1, which has one more S atom, all the other structures have only one O atom interacting with CO_2. Correspondingly, the ΔE value of A1 is higher (–21.1 kJ/mol, Table 4) than that of the others, which indicates that ΔE increases when a more negative charge is involved in the complex. In addition, the ΔE values of B1, C1 and C2 are similar, even though there are four O⋯H interactions existing in the C2 complex (two in B1 and C1), i.e. the number of O⋯H bonds has no significant influence on ΔE. The average binding energy of CO_2 with B–SH is the same as that with B–OH, but the latter has more binding modes with CO_2.

3.3. The interaction between compound 4 and the CO_2 molecule

1-Mercaptoethy-D-glucopyranose tetraacetate has one anomeric SEt group and four Ac groups. 1-Mercaptoethyl-2-O-acetyl-α-D-glucopyranose (A–SEt)

and 1-mercaptoethyl-2-O-acetyl-β-D-glucopyranose (B–SEt) are preferred as the final models, as shown in Fig. 4.

3.3.1. A–SEt–CO_2

The anomeric SEt group of A–SEt is in the axial position, whereas C2–OAc is in the equatorial plane, and these two groups can create three rotational conformers, as shown in Fig. 13. The structures are numbered from **I** to **III** based on the calculated energies, from the highest to the lowest. If the energy of **I** was assigned to be zero, the relative energies were –10.1 kJ/mol and –32.0 kJ/mol for configurations **II** and **III**, respectively (similar with 3.1.1). There are five binding models by three configurations of A–SEt binding with one CO_2 molecule (Fig. 14). The ΔE values of the binding models are listed in Table 5.

As shown in Fig. 14, one CO_2 molecule may interact with A–SEt through its carbonyl oxygen atom (O_{Ac}), ester oxygen atom (O_E), oxygen atom in the sugar ring (O_S),

Table 3
Interaction energies of CO_2 with A–SH.

Structures	Interaction pairs	Distances of two atoms (Å)	Interaction pairs number	Binding energy (ΔE^*, kJ/mol)	Gibbers free energy (ΔG^*, kJ/mol)
Ia	C–S_{Su}	3.807	1	–22.4	7.4
	C–O_E	3.327	2		
	C–O_{Ac}	3.080			
	O_1–H_S	3.639	1		
IIa	C–O_{Ac}	2.912	1	–16.5	10.4
	O_1–H_{Ac}	2.727	1		
IIb	C–O_E	3.138	1	–18.8	9.6
	O_1–H_S	3.058	3		
	O_1–H_S	2.791			
	O_2–H_{Ac}	2.852			
IIIa	C–O_{Ac}	2.940	1	–17.5	9.0
	O_1–H_S	2.560	1		
Average binding energy (kJ/mol)				–18.8	9.1

$^*\Delta E$ is the binding energy after zero-point energy calibration (ZPE); ΔG is the binding after thermal adjustment for the Gibbs free energy.
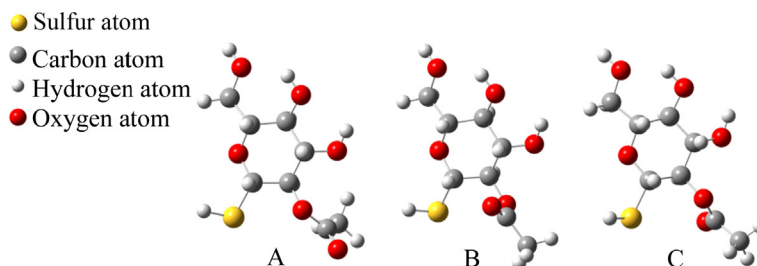
Fig. 11. Three optimized structures of the 2-*O*-acetyl-1-thio-β-D-glucopyranose (B–SH).
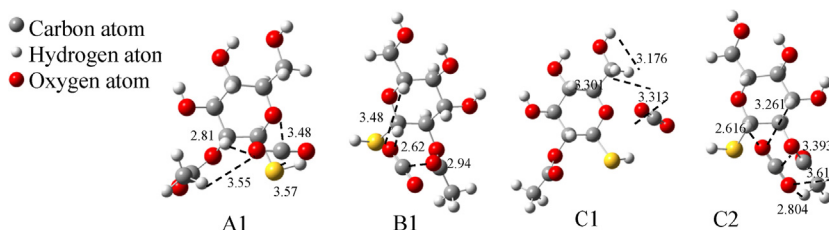

Fig. 12. The optimized binding models for B–SH–CO_2. (The dashed lines indicate the interaction points between two molecules. The values represent the distances between two atoms, and the unit is 1 Å).

sulfur atom of SEt group (S_{Et}) and/or hydrogen atoms. Both **Ia** and **IIIb** have S_E in the complex, but two additional O atoms in **Ia** instead of two H atoms in **IIIb** interacted with CO_2. Meanwhile, the other three models (Fig. 14) have only one O atom and no S atom to interact with CO_2, and **Ia** has the highest ΔE value (–25.2 kJ/mol), as shown in Table 5. So it can be deduced that ΔE will increase if a more negative point charge induced by oxygen or sulfur atoms is added in the binding model (three negative charges in **Ia**), i.e. if the interaction between A–SEt and CO_2 is electrostatic.

All the structures, **IIa**, **IIIa** and **IIIc**, have only one O atom, but different numbers of H atoms to interact with CO_2. **IIa** has only hydrogen atom interacting with the CO_2 molecule, and its ΔE is –16.9 kJ/mol, three hydrogen atoms of **IIIa** and two hydrogen atoms of **IIIc** form a H···O=C=O bond and give a ΔE around –19.1 kJ/mol. The interaction of

H with CO_2 is complicated. It could be a hydrogen bond (interaction distance is around 2 Å) or a point charge interaction, which could be influenced by distance, charge density, and so on. From the distance of H···O=C=O, it appeared that the contribution of H···O interactions to ΔE is larger if the distance is shorter (i.e. 2.6 and 3.2 Å in **IIIc**) but it could be negligible if the distance is too long (i.e. 3.7 Å in **IIIc**).

It is notable that the ΔE of **IIIb** is the lowest (–14.5 kJ/mol, Table 5), and this might be caused by a difference in electronegativity between O and S atom (compared with **IIIc**) and a longer distance from sulfur to CO_2 (about 3.8 Å).

3.3.2. B–SEt–CO_2

There are three rotation conformers of B–SEt, as shown in Fig. 15. The structures are numbered from A to C based

Table 4
Interaction energies of CO_2 with B–SH.

Structures	Interaction pairs	Distances of two atoms (Å)	Interaction pairs number	Binding energy (ΔE^*, kJ/mol)	Gibbs free energy (ΔG^*, kJ/mol)
A1	C–S_{Su}	3.570	1	–21.1	7.8
	C–O_s	3.480	1		
	O_1–H_S	2.810	2		
	O_1–H_{Ac}	3.550			
B1	C–O_{Ac}	2.940	1	–19.1	8.2
	O_1–H_S	2.620	2		
	O_1–H_S	3.480			
C1	C–O_S	3.301	1	–18.2	7.1
	O_1–H_{Su}	3.313	2		
	O_1–H_{S2}	3.176			
C2	C–O_E	3.393	1	–18.8	6.6
	O_1–H_{Ac}	3.611	4		
	O_1–H_{Ac}	2.804			
	O_2–H_S	3.261			
	O_2–H_S	2.616			
Average binding energy (kJ/mol)				–19.3	7.4

$^*\Delta E$ is the binding energy after zero-point energy calibration (ZPE); ΔG is the binding after thermal adjustment for the Gibbs free energy.
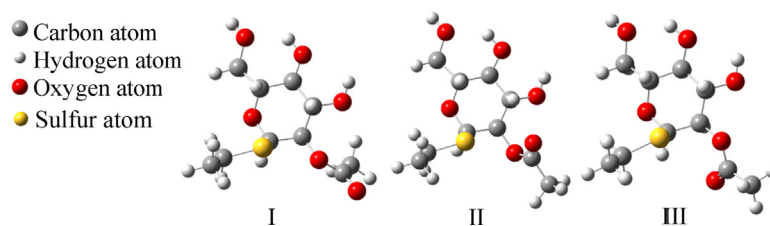
Fig. 13. Three optimized structures of 1-mercaptoethyl-2-O-acetyl-α-D-glucopyranose (A–SEt).
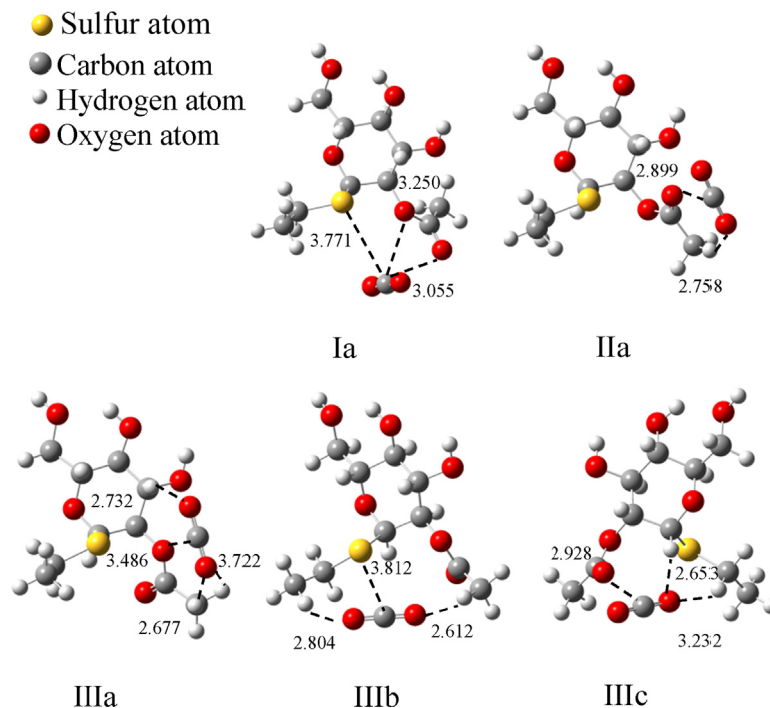

Fig. 14. The optimized binding models for A–SEt–CO_2. (The dashed lines indicate the interaction points between the two molecules. The values represent the distances between two atoms, and the unit is 1 Å).

Table 5
Interaction energies of CO_2 with A–SEt.

Structures	Interaction pairs	Distances of two atoms (Å)	Interaction pairs number	Binding energy (ΔE^*, kJ/mol)	Gibbs free energy (ΔG^*, kJ/mol)
Ia	C–S_{Su}	3771	1	−25.2	2.0
	C–O_E	3.250	2		
	C–O_{Ac}	3.055			
IIa	C–O_{Ac}	2.899	1	−16.9	9.2
	O_1–H_{Ac}	2.758	1		
IIIa	C–O_E	3.486	1	−19.1	11.1
	O_1–H_S	2.732	3		
	O_2–H_{Ac}	2.677			
	O_2–H_{Ac}	3.722			
IIIb	C–S_{Su}	3.812	1	−14.5	13.4
	O_1–H_{Et3}	2.804	2		
	O_2–H_{Ac}	2.612			
IIIc	C–O_{Ac}	2.928	1	−19.1	7.3
	O_1–H_S	2.653	2		
	O_1–H_{Et2}	3.232			
Average binding energy (kJ/mol)				−18.9	8.6

*ΔE is the binding energy after zero-point energy calibration (ZPE); ΔG is the binding after thermal adjustment for the Gibbs free energy.
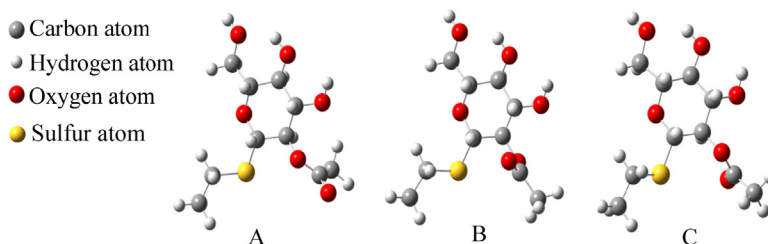
Fig. 15. Three optimized structures of ethyl 2-*O*-acetyl-1-thio-β-D-glucopyranose (B–SEt).
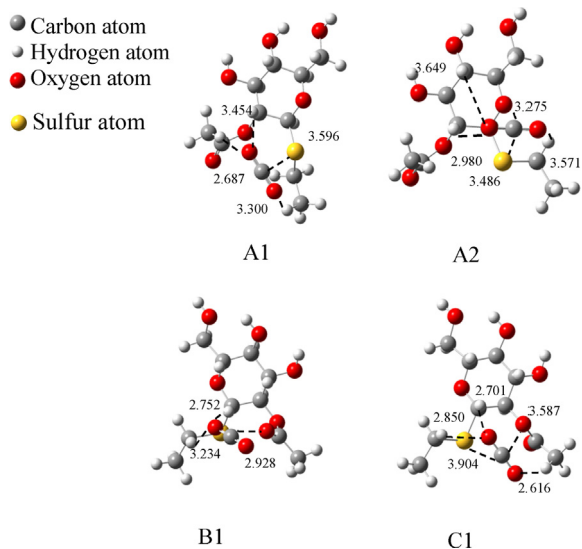

Fig. 16. The optimized binding models for B–SEt–CO_2. (The dashed lines indicate the interaction points between the two molecules. The values represent the distances between two atoms, and the unit is 1 Å).

on the calculated energies, from the highest to the lowest. If the energy of A is assigned to be zero, the relative energies are –19.1 kJ/mol and –22.4 kJ/mol for configurations B and C, respectively. There three configurations of B–SEt could bind with a CO_2 molecule through four binding modes (Fig. 16). The ΔE values of the above binding models are listed in Table 6.

A1 shows the lowest binding energy (–16.1 kJ/mol) because it has only one S atom, which interacts with CO_2, and ΔE is increased to –20.9 kJ/mol if the S atom is replaced by an O atom (B1) because the O atom could donate a more negative charge. ΔE will be even higher if one S plus an O atom can interact with CO_2 (–26.5 kJ/mol for A2, –22 kJ/mol for C1). Moreover, the ΔE value of C1 is lower than A2 because the distance of S and O with CO_2 is shorter (i.e. 3.275 Å for S–CO_2 and 3.486 Å for O–CO_2 in A2; 3.587 Å for S–CO_2 and 3.904 Å of O–CO_2 in C1).

From Tables 5 and 6, the average binding energy of A–SEt is slightly lower than B–SEt, but A–SEt had one more binding mode than B–SEt. Compared with compound **3**, the ethyl group in compound **4** makes the S atom more negative and thereby there are more H atoms in the binding site, but these factors did not affect the ΔE value of compound **4** (data shown in Tables 3–6).

Table 6
Interaction energies of CO_2 with B–SEt.

Structures	Interaction pairs	Distances of two atoms (Å)	Interaction pairs number	Binding energy (ΔE^*, kJ/mol)	Gibbs free energy (ΔG^*, kJ/mol)
A1	C–S_{Su}	3.596	1	–16.1	20.9
	O_1–H_{Et3}	3.300	3		
	O_2–H_S	3.454			
	O_2–H_{Ac}	2.687			
A2	C–S_{Su}	3.486	1	–26.5	3.1
	C–O_S	3.275	1		
	O_1–H_{Et2}	3.571	3		
	O_2–H_S	3.649			
	O_2–H_S	2.980			
B1	C–O_{Ac}	2.928	1	–20.9	7.3
	O_1–H_{Et2}	3.234	2		
	O_1–H_S	2.752			
C1	C–S_{Su}	3.904	1	–22.0	7.4
	C–O_E	3.587	1		
	O_1–H_{Ac}	2.616	3		
	O_2–H_{Et2}	2.850			
	O_2–H_S	2.701			
Average binding energy (kJ/mol)				–21.4	9.7

$^*\Delta E$ is the binding energy after zero-point energy calibration (ZPE); ΔG is the binding after thermal correction for the Gibbs free energy.

4. Conclusion

In order to study the interaction properties of D-glucopyranose-2,3,4,6-tetraacetate, 1-thio-D-glucopyranose tetraacetate, 1-mercaptoethyl-D-glucopyranose tetraacetate with CO_2, their analogous models (2-O-acetyl derivatives) were selected as substrates, and the complex model was one CO_2 molecule combined with one sugar substrate (1:1). Ab initio calculations of these six systems were accomplished including geometry optimizations with HF/3-21G, B3LYP/6-31+G**, and single-point energy calibration with MP2/aug-cc-pVDZ. The results indicated that the electrostatic interactions between substrates with CO_2 are mainly influenced by interaction distance, numbers of donors of negative charge, or interacting pairs involved in the complex. ΔE increased greatly if S and O atoms could interact with CO_2 simultaneously. The binding was to be strengthened if CO_2 could interact with S, O, and H atoms at shorter distance. The binding energy is not highly related to the chemical environment of the oxygen atom (i.e. O_{Ac}, O_E, or O_S) or sulfur atom (i.e. SEt or SH), and to the differences in electronegativity between S and O atoms. The average ΔE value of these three substrates were all around –20 kJ/mol, even though their C-1 (anomeric) functional groups were different (i.e. **1**–OH, **1**–SH and **1**–SEt), but this energy is slightly lower than that of peracetylated D-glucose (–22 kJ/mol), which has one more oxygen atom that could interact with CO_2.

Acknowledgements

References

[1] C.A. Eckert, B.L. Knutson, P.G. Debenedetti, Nature 383 (1996) 313–318.
[2] S.L. Wells, J. DeSimone, Angew. Chem. Int. Ed. 40 (2001) 518–527.
[3] A.J. Mesiano, E.J. Beckman, A.J. Russell, Chem. Rev. 99 (1999) 623–634.
[4] J.M. DeSimone, Z. Guan, C.S. Elsbernd, Science 257 (1992) 945–947.
[5] K.P. Johnston, K.L. Harrison, M.J. Clarke, S.M. Howdle, M.P. Heitz, F.V. Bright, C. Carlier, T.W. Randolph, Science 271 (1996) 624–626.
[6] T. Sarbu, T. Styranec, E.J. Beckman, Nature 405 (2000) 165–168.
[7] H.M. Woods, M.M.C.G. Silva, C. Nouvel, K.M. Shakesheff, S.M. Howdle, J. Mater. Chem. 14 (2004) 1663–1678.
[8] S. Cummings, K. Trickett, R. Enick, J. Eastoe, Phys. Chem. Chem. Phys. 13 (2011) 1276–1289.
[9] K.P. Johnston, P.S. Shah, Science 303 (2004) 482–483.
[10] Y. Kachi, T. Tsukahara, Y. Kayaki, T. Ikariya, J. Sato, Y. Ikeda, J. Supercrit. Fluids 40 (2007) 20–26.
[11] N. Levit, G. Tepper, J. Supercrit. Fluids 31 (2004) 329–333.
[12] C.F. Kirby, M.A. McHugh, Chem. Rev. 99 (1999) 565–602.
[13] L. Reynolds, J.A. Gardecki, S.J.V. Frankland, M.L. Horng, M. Maroncelli, J. Phys. Chem. 100 (1996) 10337–10354.
[14] J.F. Kauffman, J. Phys. Chem. A105 (2001) 3433–3442.
[15] M.A. Blatchford, P. Raveendran, S.L. Wallen, J. Am. Chem. Soc. 124 (2002) 14818–14819.
[16] E.J. Beckman, Chem. Commun. 17 (2004) 1885–1888.
[17] M.B. Miller, B. Wei, D.R. Luebke, R.M. Enick, J. Supercrit. Fluids 61 (2012) 212–220.
[18] K. Chen, L. Liang, B. Tan, Prog. Chem. 21 (2009) 2199–2204.
[19] S.G. Kazarian, M.F. Vincent, F.V. Bright, L.L. Charles, A.E. Charles, J. Am. Chem. Soc. 118 (1996) 1729–1736.
[20] M.R. Nelson, R.F. Borkman, J. Phys. Chem. A 102 (1998) 7860–7863.
[21] P. Raveendran, S.L. Wallen, J. Am. Chem. Soc. 124 (2002) 7274–7275.
[22] V.K. Potluri, J.H. Xu, R. Enick, E. Beckman, A.D. Hamilton, Org. Lett. 4 (2002) 2333–2335.
[23] L. Ma Sh, Y.T. Wu, M.L. Hurrey, S.L. Wallen, C.S. Grant, J. Phys. Chem. B 114 (2010) 3809–3817.
[24] H.H. Chang, C.C. Yang, X. Li, W.L. Wei, X.Y. Pang, Y. Qiao, J. Mol. Model 20 (2014) 2259–2268.