Theor Chem Acc (2012) 131:1110
DOI 10.1007/s00214-012-1110-5

REGULAR ARTICLE

Theoretical studies on anionic clusters of sulfate anions and carbon dioxide, $SO_4^{-1/-2}(CO_2)_n$, $n = 1-4$

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Received: 26 August 2011 / Accepted: 11 October 2011 / Published online: 10 February 2012

Abstract Geometry optimizations were performed on monoanionic and dianionic clusters of sulfate anions with carbon dioxide, $SO_4^{-1/-2}(CO_2)_n$, for $n = 1$–4, using the B3PW91 density functional method with the 6-311 + G(3*df*) basis set. Limited calculations were carried out with the CCSD(T) and MP2 methods. Binding energies, as well as adiabatic and vertical electron detachment energies, were calculated. No covalent bonding is seen for monoanionic clusters, with O_3SO–CO_2 bond distances between 2.8 and 3.0 Å. Dianionic clusters show covalent bonding of type $[O_3S–O–CO_2]^{-2}$, $[O_3S–O–C(O)O–CO_2]^{-2}$, and $[O_2C–O–S(O_2)–O–CO_2]^{-2}$, where one or two oxygens of SO_4^{-2} are shared with CO_2. Starting with $n = 2$, the dianionic clusters become adiabatically more stable than the corresponding monoanionic ones. Comparison with $SO_4^{-1/-2}(SO_2)_n$ and $CO_3^{-1/-2}(SO_2)_n$ clusters, the binding energies are smaller for the present $SO_4^{-1/-2}(CO_2)_n$ systems, while stabilization of the dianion occurs at $n = 2$ for both $SO_4^{-2}(CO_2)_n$ and $SO_4^{-2}(SO_2)_n$, but only at $n = 3$ for $CO_3^{-2}(SO_2)_n$.

Keywords Sulfate-carbon dioxide clusters · Dianions · Monoanions · Dianion stabilization · Electron detachment energies · Covalent bonding in clusters · Weakly bonded complexes · Density functional methods · Coupled cluster methods

1 Introduction

It has long been known that in gas phase the sulfate dianion SO_4^{-2} is unstable, whereas the corresponding monoanion is stable [1–3]. In a number of experimental and theoretical studies, it was shown that the sulfate dianion becomes more stable than the monoanion by addition of a sufficient number of water molecules. According to Born [4], the solvation energy of anions is proportional to the square of the electric charge, implying that dianions are more easily stabilized in solution than corresponding monoanions. It is well known that $(SO_4^{-2})_{aq}$ is more stable than $(SO_4^{-1})_{aq}$.

An electrospray study by Blades and Kebarle [5] showed a maximum band observed when twelve water molecules were attached to the sulfate dianion. The study indicated that $SO_4^{-2}(H_2O)_n$ clusters become stable in gas phase (the dianion being more stable than the monoanion) when $n = 3$. This was confirmed by Wang et al. [6–8], using photoelectron spectroscopy. Theoretical calculations performed by Wang et al. [6] on sulfate water clusters confirmed the experimental findings. Clusters of dithionate $S_2O_6^{-2}$ [5], peroxydisulfate $S_2O_8^{-2}$ [5], carbonate CO_3^{-2} [9], oxalate $C_2O_4^{-2}$ [10], and selenite SeO_3^{-2} [11] with water molecules have also been investigated.

Whereas many experimental and theoretical studies have been performed with dianions surrounded by water molecules, the principle of microscopic solvation leading to dianion stabilization is not restricted to water as solvent.

This paper is dedicated to the memory of Prof. Hermann Hartmann, the founder of Theoretical Chemistry Accounts, or Theoretica Chimica Acta, as it was originally named. Prof. Hartmann possessed a vast knowledge and superb understanding of chemistry, and also had a wide range of interests beyond science. He was an inspiring teacher, a caring person, my mentor, and friend (FG).

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Molecules other than water are also capable of stabilizing a dianion. Prior investigation by this group extended the range from water to the environmentally important gases sulfur dioxide and carbon dioxide.

In two recent papers, the stabilization of the sulfate [12] and carbonate dianions [13] by sulfur dioxide was studied by density functional theory methods. It was found that the sulfate dianion stabilizes adiabatically with the addition of a second SO_2 molecule. However, at least three SO_2 molecules are required for stabilization of the $CO_3^{-2}(SO_2)_n$ clusters. Work on clusters of carbonate with carbon dioxide has also been performed, and a publication is forthcoming.

To the best of our knowledge, prior to this work, studies of *dianionic* clusters with “solvent” molecules other than water have not been reported in the literature. On the other hand, mass spectrometric, infrared, and photoelectron work has been performed on *monoanioni*c clusters with CO_2 and SO_2 as solvents, like $O_2^{-1}(CO_2)_n$, $CO_3^{-1}(CO_2)_n$, $NO_2^{-1}(CO_2)_n$ [14], $O^{-1}(CO_2)_n$, $CO_2^{-1}(CO_2)_n$ [15], $X^{-1}(CO_2)$ with X = F, Cl, Br, I [16, 17], $I_2^{-1}(CO_2)_n$ [18], $H_2O^{-1}(CO_2)_n$ [19], and $SO_2^{-1}(SO_2)_n$ [20]. Neutral $(CO_2)_n$ clusters have also been studied [21].

Using H_2O as solvent, hydrogen bonding is the main mechanism responsible for the formation of monoanionic and dianionic clusters. On the other hand, clusters of dianions with molecules other than water, like CO_2 or SO_2, show different types of bonding, which can be classified as being either covalent or noncovalent long-range bonding. Covalent bonding is achieved by charge migration, where part of the negative charge of the anion is being transferred to the XO_2 molecules. On the other hand, noncovalent bonds are caused by electrostatic interaction between the charge on the anion and the dipole moment of SO_2, or the quadrupole moment of CO_2. While covalent bonds are stronger than hydrogen bonds, the long electrostatic bonds are very weak. Dispersion forces also play a role. It is to be expected that covalent bonding dominates at small n, whereas weak bonds are seen once the covalent pairing is saturated.

In this contribution, anionic clusters obtained by the addition of carbon dioxide to the sulfate monoanion and dianion are studied by density functional and ab initio methods. Energies and structures of the anionic clusters will be of interest. Vertical (VDE) and adiabatic electron detachment energies (ADE) will be documented to realize a reversal in stability between monoanions and dianions. Binding energies are also included to see how favorable the structure is relative to its constituents. Later in this paper, bonding characteristics of the monoanionic and dianionic clusters will be discussed.

The present study on clusters of the sulfate dianion with carbon dioxide molecules was undertaken in continuation of our previous work on sulfate–sulfur dioxide and carbonate sulfur dioxide clusters, allowing for a comparison of these related systems. Compounds formed between sulfate anions and carbon dioxide have never before been studied in a systematic manner. Both sulfates and carbon dioxide are present in the atmosphere.

2 Methods

Density functional theory (DFT) methods, coupled cluster methods with single, double (CCSD), and noniterative triple excitations (CCSD(T)), and Moller–Plesset perturbation (MP) methods, as implemented in the Gaussian 03 computational package [22], have been used for calculations on $SO_4^{-2}(CO_2)_n$ and $SO_4^{-1}(CO_2)_n$, for $n = 1$–4. DFT geometry optimizations were performed with the B3PW91 functional [23, 24] and the 6-311 + G(3*df*) basis set. MP2 geometry optimizations and single point calculations using the CCSD and CCSD(T) methods were carried out with the 6-311 + G(d) basis set on the most stable DFT optimized structures for $n = 0$–2.

Several initial starting structures were chosen for each size cluster. In Fig. 1, the structures investigated are shown from the point of view of atomic connectivity. CO_2 molecules are added to the oxygens of the sulfate monoanion or dianion, or to oxygens of previously added CO_2

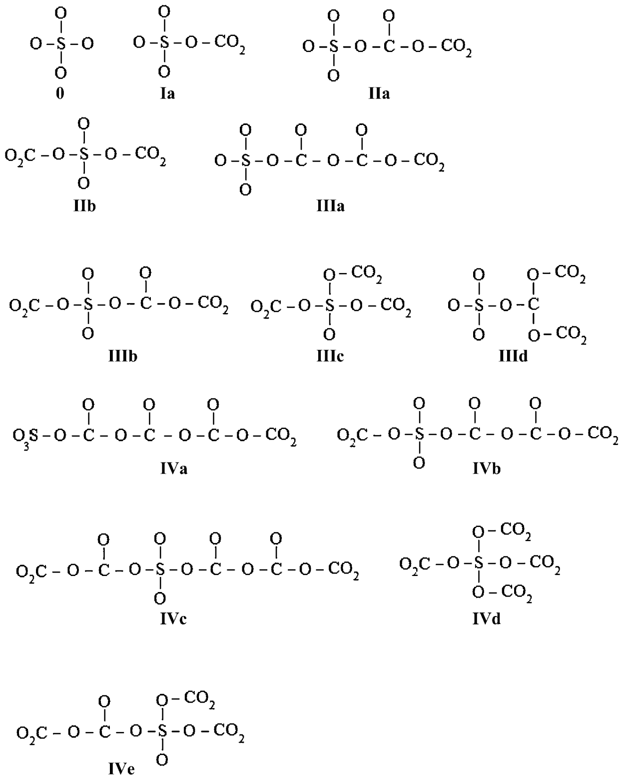


Fig. 1 Labeling of structures for $SO_4^{-1/-2}(CO_2)_n$

molecules, in all possible ways, with the restriction that none of the original S–O or C–O bonds be broken. The optimized structures do not necessarily correspond to the global minimum. The same initial structures were used for monoanions and dianions.

Frequency calculations were performed for clusters with $n = 1$ and 2. In all cases the frequencies were real, indicating that the optimized structures are potential minima. This includes the metastable structures to be discussed below.

3 Results

In Table 1, the calculated B3PW91/6-311 + G(3*df*) energies for both mono- and dianions are listed for each type of structure, together with their binding energies with respect to the separated sulfate and carbon dioxide molecules. Binding energies $\Delta E(-1)$ and $\Delta E(-2)$ are defined in Eqs. 1 and 2 as

$$\Delta E(-1) = -E\left[SO_4^{-1}(CO_2)_n\right] + E\left[SO_4^{-1}\right] + nE[CO_2] \quad (1)$$

$$\Delta E(-2) = -E\left[SO_4^{-2}(CO_2)_n\right] + E\left[SO_4^{-2}\right] + nE[CO_2], \quad (2)$$

where the E's are the total energies as calculated.

Results for the most stable structures for mono- and dianions are printed in bold. The binding energies for monoanions, while being small, increase systematically from $n = 1$ (0.11 eV) to $n = 4$ (0.56 eV). Binding energies for dianions are larger, and again increase as one goes from $n = 1$ (1.28 eV) to $n = 4$ (2.59 eV).

Table 1 Calculated B3PW91/6-311 + G(3*df*) total energies E (atomic units) for monoanions and dianions of $SO_4^{-1/-2}(CO_2)_n$, and binding energies ΔE (eV)

Molecule	Struct	Monoanion		Dianion	
		E	$\Delta E(-1)$	E	$\Delta E(-2)$
$SO_4^{-1/-2}$	0	**−699.088909**	–	**−699.024520**	–
$SO_4^{-1/-2}$ $(CO_2)_1$	Ia	**−887.675245**	**0.11**	**−887.653649**	**1.28**
$SO_4^{-1/-2}$ $(CO_2)_2$	IIa	−1076.264627	0.31	**−1076.263815**	**2.04**
	IIb	**−1076.264816**	**0.31**	−1076.246546	1.57
$SO_4^{-1/-2}$ $(CO_2)_3$	IIIa	**−1264.851484**	**0.44**	**−1264.857015**	**2.34**
	IIIb	−1264.851484	0.44	−1264.854401	2.27
	IIIc	−1264.851468	0.44	−1264.843854	1.98
	IIId	−1264.851484	0.44	−1264.855310	2.29
$SO_4^{-1/-2}$ $(CO_2)_4$	IVa	−1453.437123	0.53	−1453.445301	2.51
	IVb	**−1453.438101**	**0.56**	**−1453.448226**	**2.59**
	IVc	−1453.438099	0.56	−1453.446536	2.54
	IVd	−1453.437684	0.55	−1453.440473	2.38
	IVe	−1453.436901	0.53	−1453.436695	2.27

Energies of most stable structures are in bold

The energy of CO_2 is −188.582167 au

Adiabatic (ADE) and vertical (VDE) electron detachment energies are shown in Table 2. They are defined in Eqs. 3 and 4 with

$$ADE = E_0\left[SO_4^{-1}(CO_2)_n\right] - E_0\left[SO_4^{-2}(CO_2)_n\right] \quad (3)$$

using the calculated energies E_0 of the lowest-energy structures of the mono- and dianions, and

$$VDE = E_{vert}\left[SO_4^{-1}(CO_2)_n\right] - E_0\left[SO_4^{-2}(CO_2)_n\right], \quad (4)$$

where the energy of the anionic cluster $SO_4^{-1}(CO_2)_n$ is calculated at the optimized geometry of the lowest-energy dianion $SO_4^{-2}(CO_2)_n$ for the given n. As defined, ADE and VDE are negative if the dianion is less stable than the monoanion, and positive otherwise.

While the DFT value of ADE is −1.75 eV for the isolated sulfate ion, implying that the monoanion is more stable than the dianion by this amount, ADE for $SO_4^{-2}(CO_2)_n$ is −0.59 eV for $n = 1$, −0.03 eV for $n = 2$, and +0.15 eV for $n = 3$. Accordingly, the monoanions are more stable than the dianions for $n = 0$ to $n = 2$, but a reversal of stabilities takes place at $n = 3$, with the dianion becoming more stable than the monoanion. At $n = 2$, the monoanion is only 0.03 eV more stable than the dianion. Such a small energy difference lies within the range of computational uncertainty. VDE energies were obtained by recalculating the energy of the monoanion at the optimized geometry of the corresponding dianion. Understandably, the VDE numbers turn positive at lower n, in the present case at $n = 1$. The energy gap between VDE and ADE is only 0.24 eV for $n = 0$, but increases sharply at $n = 1$ (0.96 eV), and again at $n = 2$ (1.71 eV). After that, at $n = 3$ and 4, the gap does not increase any further.

Included in Table 2 are CCSD and CCSD(T) results for ADE and VDE at $n = 0$ to $n = 2$, calculated at the B3PW91 optimized geometries. Both ADEs and VDEs are more positive than values obtained with the DFT method, and stabilization of the dianion occurs at $n = 2$, with ADE values of 0.20 and 0.23 eV for the CCSD and CCSD(T) methods, respectively.

Table 2 Adiabatic (ADE) and vertical (VDE) electron detachment energies, in eV, for the most stable $SO_4^{-1/-2}(CO_2)_n$ structures, using B3PW91, CCSD, and CCSD(T) methods

Cluster	B3PW91		CCSD		CCSD(T)	
	ADE	VDE	ADE	VDE	ADE	VDE
$SO_4^{-1/-2}$	−1.75	−1.51	−1.57	−1.26	−1.61	−1.41
$SO_4^{-1/-2}$ $(CO_2)_1$	−0.59	0.37	−0.52	0.94	−0.56	0.78
$SO_4^{-1/-2}$ $(CO_2)_2$	−0.03	1.68	0.20	2.39	0.23	2.22
$SO_4^{-1/-2}$ $(CO_2)_3$	0.15	1.86				
$SO_4^{-1/-2}$ $(CO_2)_4$	0.28	1.97				

As will be discussed below, all of the monoanionic structures have long C–O bonds between SO_4^{-1} and CO_2, in the order of 2.8 Å, representing anionic complexes held together by weak electrostatic interactions. The reliability of the DFT results for such complexes has been checked by performing MP2 geometry optimizations for structures Ia(−1) and IIb(−1). MP2 data are shown in Table 3. For $n = 2$, the ADE and VDE energies are close to the coupled cluster values, with ADE being 0.17 eV and VDE being 2.56 eV. There are relatively larger deviations for $n = 0$ and 1. MP2 binding energies, also listed in Table 3, are close to the binding energies obtained with B3PW91.

In the following, bonding aspects of the optimized mono- and dianionic structures will be discussed. Due to the fact that in many cases long bonds are formed, the atomic connectivity as specified in the prototype input structures (Fig. 1) is not always maintained.

Figure 2 shows the optimized DFT structures of monoanions from Ia(−1) to IVd(−1), including bond distances. The monoanion SO_4^{-1} has C_{2v} symmetry, with S–O bond distances of 1.449 Å and 1.509 Å calculated at the B3PW91/6-311 + G(3*df*) level [12]. As seen in Fig. 2, all monoanionic clusters have long bonds, with O_3SO–CO_2 distances ranging from 2.8 to 3.0 Å. There is no covalent bonding of SO_4^{-1} with CO_2. As a consequence, the CO_2 moieties are linear or nearly linear. Due to transfer of a small amount of negative charge from the anion to the CO_2's (the Mullikan charges on CO_2 are about 0.02 e^-), a slight bending of the CO_2's is seen, with calculated OCO angles of 175°–176°. (The DFT optimized bond angle in CO_2^- is 138.1°). However, such bending could also be caused by electrostatic effects, as the negatively charged oxygens of CO_2 are more strongly pushed away from the anion than the carbon. By negative photoelectron spectroscopy on $X^-/(CO_2)_n$ clusters, with X being halogens, Arnold et al. [16, 17] also found that the CO_2 molecules were distorted from linearity.

Due to the lack of covalent bonding, the energies of structures with the same n are nearly identical. Structures IIIa(−1) and IIIc(−1) have two CO_2's coordinated to the same oxygen of SO_4^{-1}. The structures IIIb(−1) and IIId(−1) have been omitted from Fig. 2, as there are only minor differences to $n = 3$ ones shown. Although IVb(−1) has the lowest energy, it differs by only 0.03 eV from the least stable structure IVe(−1) (not shown). In most cases, two CO_2's are coordinated to the same oxygen of SO_4^{-1}, rather than to different oxygens.

Table 3 Adiabatic (ADE) and vertical (VDE) electron detachment energies and binding energies ΔE(−1) and ΔE(−2) in eV, from MP2 calculations with 6-31 + G(d) basis set

Cluster	ADE	VDE	ΔE(−1)	ΔE(−2)
$SO_4^{-1/-2}$	−1.24	−0.56	–	–
$SO_4^{-1/-2}(CO_2)_1$	−0.15	1.12	0.15	1.23
$SO_4^{-1/-2}(CO_2)_2$	0.17	2.56	0.53	1.93

It is interesting to note that in geometry optimizations of $SO_4^{-1}(CO_2)_n$, small O_3SO–C distances are retained when starting the geometry optimization at such distances. The resulting structures appear to have covalent bonds, but they are metastable, with an energy higher than separate $SO_4^{-1} + nCO_2$. Two examples, for $n = 1$ and $n = 2$, are shown in Fig. 3. The structures are labeled Ia*(−1) and IIa*(−1) to indicate their metastable character. Ia*(−1) is less stable than $SO_4^{-1} + CO_2$ by 0.16 eV, and IIa*(−1) is less stable than $SO_4^{-1} + 2CO_2$ by 0.70 eV. In both cases, and also in metastable structures for $n = 3$ and 4, one oxygen from SO_4^{-1} is pulled toward the neighboring CO_2, to resemble an $SO_3{\cdot}CO_3$ anionic cluster. Calculations show that Ia*(−1) is more stable than $SO_3^{-1} + CO_3$ by 4.41 eV, and more stable than $SO_3 + CO_3^{-1}$ by 1.66 eV (same method and basis set). Therefore, Ia*(−1) is stable with respect to dissociation into $SO_3 + CO_3^{-1}$ or $SO_3^{-1} + CO_3$, but unstable with respect to dissociation into $SO_4^{-1} + CO_2$.

MP2 structures for Ia(−1) and IIb(−1) are shown in Fig. 4. Of interest is a comparison of the bond distances obtained by the MP2 method with those obtained from DFT. For Ia(−1), the O–C distance in MP2 is 2.73 Å, compared with 2.84 A in DFT. For IIb(−1), the MP2 distances of 2.89 and 2.76 Å are to be compared with 2.96 and 2.92 Å, respectively, in DFT. According to these test cases, there is good agreement in the long bonds obtained by DFT and MP2 methods. In general, the MP2 distances are 0.1 to 0.2 Å shorter than corresponding DFT distances.

The optimized structures of the dianions are displayed in Fig. 5. Covalent bonding between SO_4^{-2} and CO_2 is seen for Ia(−2), IIa(−2), and IIb(−2), with O_3S–O–CO_2 bonding for Ia(−2), O_3S–O–C(O)–O–CO_2 bonding for IIa(−2), and O_2C–O–S(O_2)–O–CO_2 bonding for IIb(−2). The "a" in the structure symbol implies that SO_4^{-2} is in a terminal position, with the CO_2's attached in a chain-like fashion. Having the SO_4's not in terminal position, like IIb(−2) and IIIb(−2), results in small energy losses, about 0.5 eV for IIb(−2) and less than 0.1 eV for IIIb(−2). All $n = 3$ structures have at least one long bond. The most stable one, IIIa(−2), is of type O_3S–O–C(O)–O–CO_2 … CO_2, the dots indicating a long bond. The most stable structure for $n = 4$, IVb(−2), has two CO_2's attached by long bonds. All $n = 4$ dianionic structures except IVe(−2) have one or two CO_2's coordinated to two oxygens.

Figure 5 shows that in the dianionic systems one or several S–O bonds of SO_4^{-2} are elongated from 1.45 Å in isolated SO_4^{-2} to about 1.6 or 1.7 Å. The oxygen of the elongated bond is shared with the neighboring CO_2. A shift in bonding, from SO_4^{-2} CO_2 toward $SO_3^{-1}{\cdot}CO_3^{-1}$, is

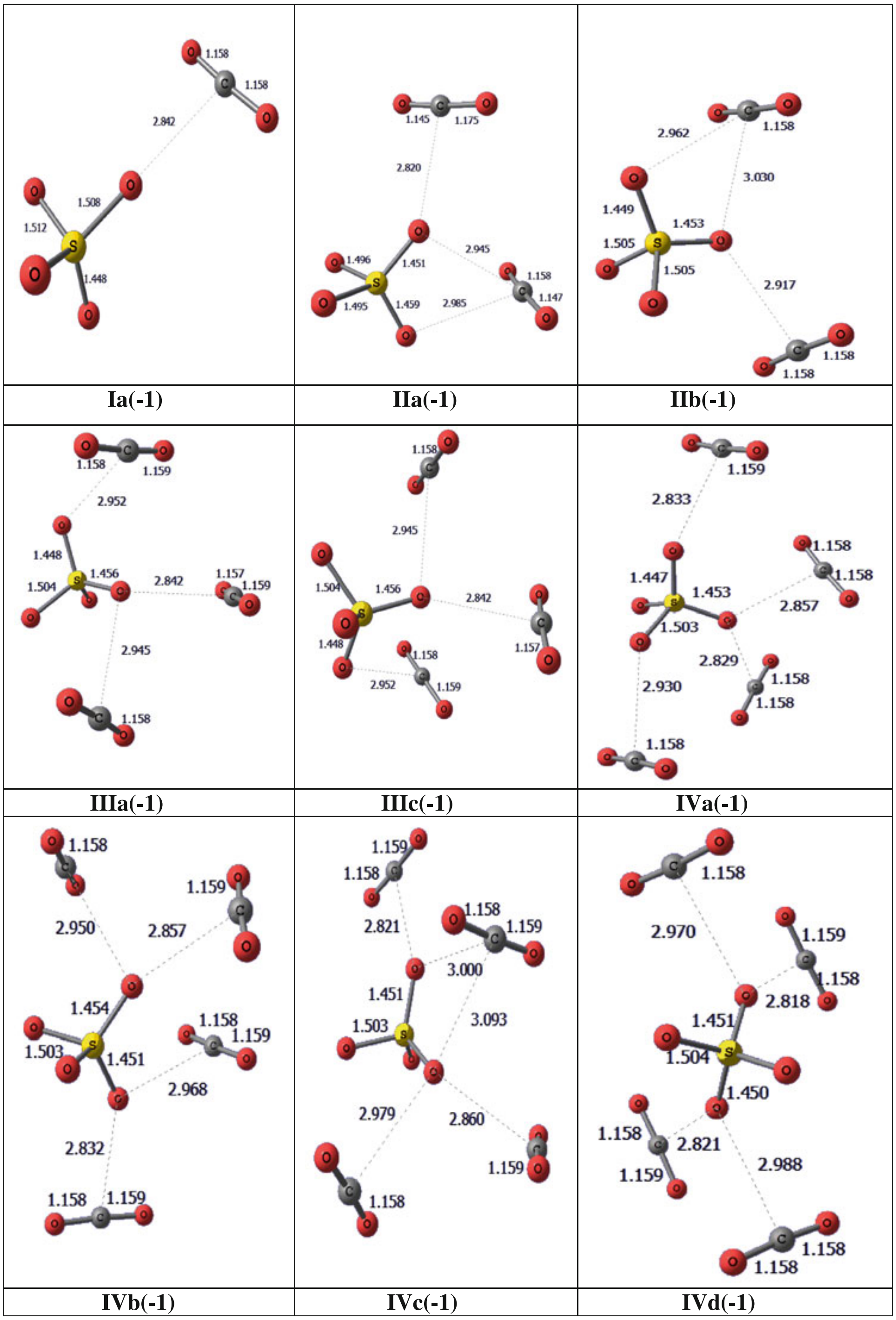


Fig. 2 DFT optimized structures of the monoanionic clusters $SO_4^{-1}(CO_2)_n$

Ia(-1) IIa(-1) IIb(-1)

IIIa(-1) IIIc(-1) IVa(-1)

IVb(-1) IVc(-1) IVd(-1)

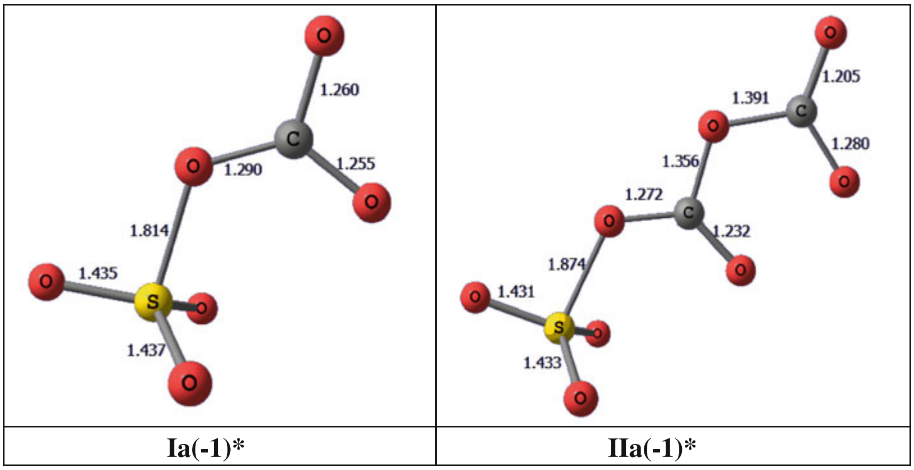
observed. By donating an oxygen to CO_2, the $SO_3^{-1}{\cdot}CO_3^{-1}$ complex stabilizes over $SO_4^{-2}{\cdot}CO_2$. Calculations show that $SO_3^{-1} + CO_3^{-1}$ is more stable than $SO_4^{-2} + CO_2$ by 2.19 eV (B3PW91/6-311 + G(3*df*) method).

In structures IIa(−2), IIIa(−2), IIIb(−2), IIId(−2), and in most structures with four additions of CO_2, $C_2O_5^{-q}$ units can be seen. In the case of IVa, the CO_2 chain extends to $C_3O_7^{-q}$. Calculations performed on dianionic $C_2O_5^{-2}$ and $C_3O_7^{-2}$ led to covalently bonded structures [25].

4 Comparison with other sulfate and carbonate clusters

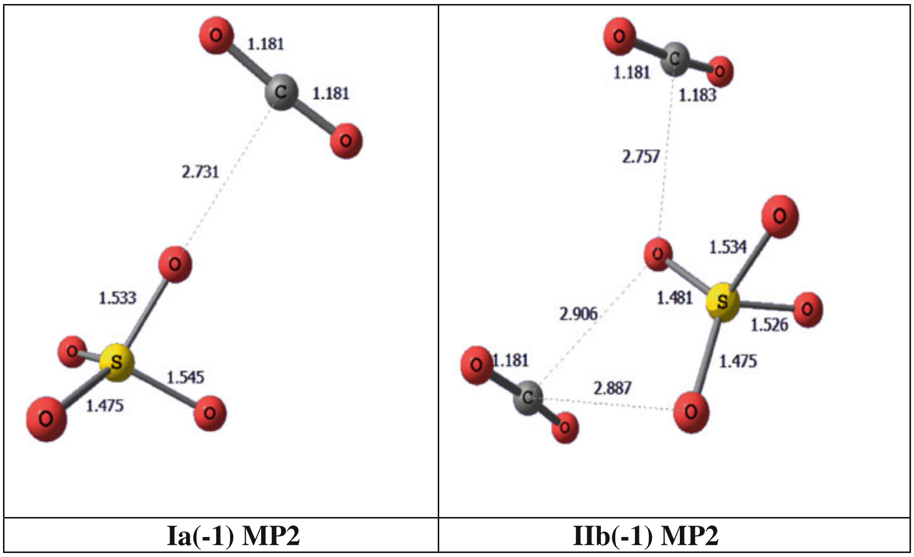
As this is the third study on anionic clusters composed of sulfate or carbonate with carbon dioxide or sulfur dioxide, a comparison of results is of interest. In Table 4, binding energies, ADE and VDE values, and bonding characteristics for the present system $SO_4^{-1/-2}(CO_2)_n$ (labeled "**A**") and the previously studied systems $SO_4^{-1/-2}(SO_2)_n$ (labeled "**B**") [12] and $CO_3^{-1/-2}(SO_2)_n$ (labeled "**C**") [13] have

Fig. 3 Structures of metastable monoanionic clusters



Ia(-1)* **IIa(-1)***

Fig. 4 MP2 optimized structures for small monoanionic clusters

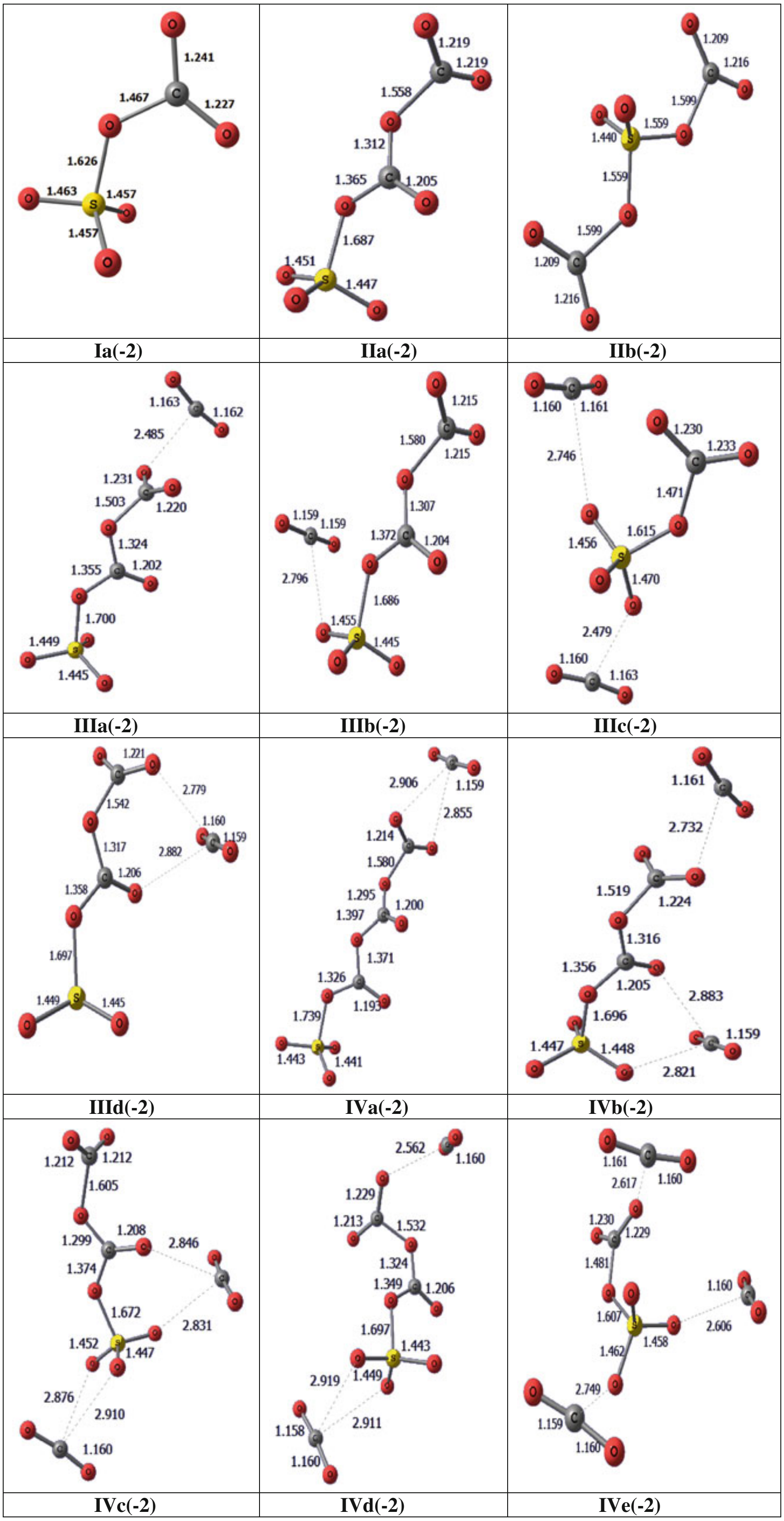


Ia(-1) MP2 **IIb(-1) MP2**

been summarized. Systems **A** and **B** have the sulfate in common, whereas systems **B** and **C** have the "solvent" molecules SO_2 in common. In all three studies, the same method and basis set, B3PW91/6-311 + G(3*df*), have been used, such that the results are comparable from a method's point of view. As shown in Table 4, the binding energies $\Delta E(-1)$ for the monoanions, for a given n, increase as one goes from **A** to **B** to **C**. The $n = 1$ values change from 0.11 to 1.04 to 1.67 eV, respectively. Similarly, the binding energies for the dianionic clusters, $\Delta E(-2)$, increase in the direction from **A** to **C**, with values for $n = 1$ of 1.28, 2.25, and 3.39 eV. Accordingly, the largest gain in energy is obtained by adding SO_2 molecules to the carbonate, better than adding to sulfate. The adiabatic electron detachment energies are negative in all three cases for $n = 1$, but at $n = 2$ they turn to zero for **A**, are distinctly positive for **B**, and still strongly negative for **C**. Even at $n = 3$, ADE is around zero for **C**. Therefore, $SO_4^{-2}(SO_2)_n$ is the easiest dianionic cluster to stabilize, whereas $CO_3^{-2}(SO_2)_n$ is the most difficult one. The VDE values confirm this trend. At $n = 1$ they are positive for **A** and **B**, but still negative for **C**.

In the last four rows of Table 4, the number of covalent (cov) and noncovalent long bonds between oxygens of sulfate or carbonate and the carbons of attached CO_2's or the sulfurs of SO_2's is listed for the monoanionic (−1) and dianionic (−2) structures. As was shown before, for the present system **A** the monoanions from $n = 1$ to $n = 4$ have long bonds only. For system **B** the monoanions have one covalent bond for all n, the other bonds are of the long type. For system **C** there is covalent bonding only for $n = 3$. The number of covalent bonds is larger for the dianions. For system **A**, all bonds of $n = 1$ and $n = 2$ are covalent, but for $n = 3$ and 4 the number of covalent bonds does not increase any further. However, the dianionic systems **B** and **C** have covalent bonds only, for all n. Overall, systems **B** and **C**, having SO_2 as ligands, are similar to each other in bonding characteristics, whereas system **A**, with CO_2 as ligand, has much weaker bonds.

Fig. 5 DFT optimized structures of the dianionic clusters $SO_4^{-2}(CO_2)_n$



Ia(-2) IIa(-2) IIb(-2)

IIIa(-2) IIIb(-2) IIIc(-2)

IIId(-2) IVa(-2) IVb(-2)

IVc(-2) IVd(-2) IVe(-2)

Table 4 Comparison of results for $SO_4^{-1/-2}(CO_2)_n$ with $SO_4^{-1/-2}(SO_2)_n$ [12] and $CO_3^{-1/-2}(SO_2)_n$ [13]

	$SO_4^{-1/-2}(CO_2)_n$ (**A**)				$SO_4^{-1/-2}$ $(SO_2)_n$ (**B**)			$CO_3^{-1/-2}$ $(SO_2)_n$ (**C**)		
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 1$	$n = 2$	$n = 3$	$n = 1$	$n = 2$	$n = 3$
ΔE(−1)	0.11	0.31	0.44	0.56	1.04	1.41	1.68	1.67	2.44	2.77
ΔE(−2)	1.28	2.04	2.34	2.59	2.25	3.54	4.41	3.39	5.25	6.43
ADE	−0.59	−0.03	0.15	0.28	−0.52	0.40	0.98	−1.96	−0.88	−0.03
VDE	0.37	1.68	1.86	1.97	0.40	1.59	2.26	−0.55	0.84	2.02
Cov(−1)	0	0	0	0	1	1	1	0	0	1
Long(−1)	1	2	3	4	0	1	2	1	2	2
Cov(−2)	1	2	2	2	1	2	3	1	2	3
Long(−2)	0	0	1	2	0	0	0	0	0	0

Adiabatic (ADE) and vertical (VDE) electron detachment energies and binding energies ΔE(−1) and ΔE(−2) in eV. Number of covalent and long noncovalent bonds for monoanions, cov(−1) and long(−1), and for dianions cov(−2) and long(−2). B3PW91/6-311 + G(3*df*) values

5 Discussion

In this section, qualitative arguments will be given to explain and contrast the results obtained in the present paper with those in the two related papers [12, 13]. Focusing on bond energies of the smaller covalently bonded dianionic clusters, we first compare system **A** with **B**, both having SO_4^{-2} as dianion, but differing in having CO_2 attached in system **A** ($SO_4^{-2}(CO_2)_n$), and SO_2 attached in system **B** ($SO_4^{-2}(SO_2)_n$). For $n = 1$, the binding energy for **A** is 1.28 eV, whereas for system **B** it is 2.25 eV.

Both isolated CO_2 and SO_2 have two double bonds. In the reaction $SO_4^{-2} + XO_2 \rightarrow [O_3S–O–XO_2]^{-2}$, X = C, S, one X–O π-bond on XO_2 gets broken, and one new O–X σ-bond is formed. Whereas the π-bond in CO_2 is $2p\pi$–$2p\pi$, with a π-bond energy of about 4.3 eV, that in SO_2 is $2p\pi$–$3p\pi$, with a π-bond energy of only about 1.7 eV (tabulated values). Assuming that the σ-bond energies are similar in the two systems, as documented in tables of bond energies, the net energy gain is much smaller for reaction **A** (CO_2) than for reaction **B** (SO_2), in agreement with our findings.

We now try to rationalize the difference in binding energies between system **B** [$SO_4^{-2}(SO_2)_n$], 2.25 eV for $n = 1$, and system **C** [$CO_3^{-2}(SO_2)_n$], 3.39 eV for $n = 1$. The formal charge on the sulfur atom in SO_4^{-2} is +2. On the other hand, it is zero on the carbon atom in CO_3^{-2} (the Mulliken charges are 1.12 on S in SO_4^{-2}, and 0.73 on C in CO_3^{-2}). It follows that SO_4^{-2} has less of a tendency to spread the (negative) charge and to form bonds than CO_3^{-2} does, in agreement with the calculated trends in bond energies. This argument is supported by the well-known fact that H_2SO_4 is a stronger acid than H_2CO_3.

It is interesting that for small values of n monoanionic clusters, despite having in general very weak bonding between the anion and SO_2 or CO_2, are still more stable than corresponding dianionic clusters having mostly covalent bonding. This implies that for small n the destabilizing effect of electron repulsion in the dianionic clusters is stronger than the stabilizing effect of covalent bonding. With increasing size of the cluster, the repelling electrons move further apart, reducing the electron repulsion, and at the same time the potential for covalent bonding increases.

6 Summary and conclusion

Anionic clusters formed by reacting sulfate mono- and dianions with one to four carbon dioxide molecules were studied by density functional and coupled cluster methods. It was found that all monoanionic clusters have noncovalent weak bonds between sulfate and CO_2, with bond distances of about 2.8–3.1 Å, whereas dianionic clusters form covalent bonds of type $[O_3S–O–CO_2]^{-2}$, $[O_3S–O–C(O)O–CO_2]^{-2}$, and $[O_2C–O–S(O_2)–O–CO_2]^{-2}$. Further additions of CO_2 occur via long bonds. In covalently bonded structures, one or two S–O bonds of the sulfate become elongated to form units closer to $SO_3^{-1}{\cdot}CO_3^{-1}$. The dianionic clusters $SO_4^{-2}CO_2$ become adiabatically more stable than the monoanionic ones starting with $n = 2$.

In comparison with $SO_4^{-1/-2}(SO_2)_n$ and $CO_3^{-1/-2}(SO_2)_n$ clusters, binding energies for $SO_4^{-1/-2}(CO_2)_n$ are the smallest, and covalent bond formation is least favored. As seen from the electron affinities of the solvent molecules, transfer of negative charge from the sulfate or carbonate anion is easier for bonding to SO_2, and more difficult for bonding to CO_2.

To round off the series of sulfate/carbonate clusters with SO_2/CO_2, a paper on anionic clusters formed by reacting carbonate with carbon dioxide is forthcoming.

Acknowledgments The authors are indebted to Drs. Jack Passmore and Pablo Bruna for reading the manuscript and providing useful comments. Thanks to Robbie Weale for helping with the structures, and to Sonya Burrill for literature studies. Financial support provided by NSERC (Canada) is gratefully acknowledged. Excellent computing facilities have been made available through ACEnet.

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