

# Molecular orbital versus DFT calculations in CO<sub>2</sub>-sequestration reactions with anions: Basis set extrapolation and solvent effects

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## Abstract

The emission of carbon dioxide in large amounts is commonly believed to be the main cause of global climate changes. Development of CO<sub>2</sub> capture processes is still a big current challenge. Some anions have been studied for the gas sequestration process due their great affinity to CO<sub>2</sub>. In this work, electronic structure calculations were performed at the MP2/aug-cc-pvtz level to compute the interaction between 20 anions and CO<sub>2</sub>. A CBS scheme, using extrapolated energies, was also employed for both gas phase and solvent calculations. The reactions between the anions and CO<sub>2</sub> were therefore studied in four different conditions (gas phase, toluene, tetrahydrofuran and water). The trends observed for the reaction thermodynamics with the MP2 method is similar to that observed previously with the B3LYP-D3 and M06-2X functionals. The reactions in the gas phase are highly exothermic and do not involve any activation energy. The solvent effect reduces the exothermicity and induces an intrinsic activation barrier. The negative charge is dispersed in the adduct, leading to a weaker interaction in a polar solvent. Then, increasing the medium polarity, the energy difference between the adduct and the reactants decreases. We also observed a limit for solvent stabilization in the low dielectric constant range. For example, the results obtained with tetrahydrofuran are closer to those obtained with water than to those obtained with toluene. Considering both the thermodynamics of the reaction and the differential solvent effects, we were able to indicate anions derived from alkyl sulfides as the most convenient for CO<sub>2</sub> sequestration among the set here considered.

## Introduction

The demand for energy has increased continuously in the last decades due to the world economic development and population growth. In this context, large quantities of greenhouse gases have been emitted, reflecting on global climate changes.<sup>1</sup> Carbon dioxide (CO<sub>2</sub>) is one of the main gases emitted by anthropogenic activities such as burning of fossil fuels and other raw materials and may be associated with global warming and acidification of the oceans.<sup>2-4</sup> Despite several attempts for sustainable development and agreements to reduce CO<sub>2</sub> concentration, the emitted quantity of this polluting gas continues to increase.<sup>5,6</sup> CO<sub>2</sub> capture and storage emerges therefore as a way to control gas emission through various technologies. The captured CO<sub>2</sub> may subsequently be used as material for manufacturing value-added products such as methanol, urea and formic acid, among others.<sup>7</sup>

Although technologies for CO<sub>2</sub> capture have advanced, their development still poses a great challenge nowadays and several issues remain.<sup>8</sup> Currently, chemical filtration using amine solvents, like monoethanolamine (MEA), is among the most employed processes to separate CO<sub>2</sub>.<sup>9</sup> However, it still shows some problems such as corrosion of equipment and high cost for regeneration.<sup>9</sup> Some alternatives have emerged, aiming to improve the CO<sub>2</sub> capture process. Microporous metal-organic frameworks (MOFs),<sup>10</sup> porous solids,<sup>11</sup> ionic

liquids,<sup>12,13</sup> and membranes<sup>14</sup> are among the materials that have been tested for carbon capture. In all cases, regardless of the structure and form of utilization, some interaction between CO<sub>2</sub> and the employed material is required.

Recent studies have focused on the interaction mechanism of different chemical absorbents with carbon dioxide using both Density Functional Theory (DFT) and wavefunction-based approaches.<sup>15,16</sup> Carneiro et al. studied the reaction between CO<sub>2</sub> and amines using the CAM-B3LYP and  $\omega$ B97X-D functionals and the MP2 method with the aug-cc-pVTZ basis sets.<sup>15</sup> All energies were subsequently extrapolated to the complete basis set limit using Truhlar’s procedure.<sup>17</sup> They have shown that the interaction energy and stabilization of the zwitterion intermediate show high correlation with the basicity of the amines.<sup>15</sup> Different kinds of basic species, such as amines<sup>9,16</sup> and benzyl-chalcogenides<sup>18</sup> were also investigated by theoretical procedures, trying to quantify their capacity to react with CO<sub>2</sub>. Along the same lines, Varandas<sup>19</sup> and Sucarrat and Varandas<sup>20</sup> studied the capture of a CO<sub>2</sub> molecule by Li<sub>3</sub>N and Li<sub>3</sub>N<sub>3</sub>. Moreover, they investigated the interaction of 26 anions with CO<sub>2</sub> in the gas phase and in three distinct solvents<sup>21</sup> using the B3LYP-D3 and M06-2X functionals with the aug-cc-pVTZ basis set. From this study, it has been shown that alkoxylate and thiolate anions are promising candidates for the capture process due to their reaction reversibility, in spite of the fact that the solvent has some influence on the stability of the formed anion-CO<sub>2</sub> adduct.

Although the above pioneering study<sup>21</sup> has shed some light upon the thermodynamics of the reaction, some questions still remain, particularly on the effect of the solvent on the whole process. The reaction in gas phase is usually barrierless, while in a solvent of high dielectric constant it is less spontaneous and exothermic, involving the formation of a transition state. The thermodynamic results were rationalized in terms of the stabilization of the anions in the polar solvents that decreases their reactivity.<sup>21</sup> Furthermore, more recent studies suggest that the energies computed using the M06-2X/aug-cc-pVTZ method may underestimate the barrier energies, thus motivating the present work.<sup>22,23</sup>

In the present study, we compute the stationary points on the pathways for reaction of a set of oxygen, sulfur, phosphorous and nitrogen anions with CO<sub>2</sub>. Electronic energies, zero-point vibrational energies (ZPVE) and thermal corrections are also computed for all species, leading to enthalpies and Gibbs free energies at 298 K and 1 atm. The computational approach is the same as that used in the previous DFT study.<sup>21</sup> The CBS extrapolation was used to enhance the results accuracy and confirm the trends reported by Sucarrat and Varandas in their DFT calculations for anions reacting with CO<sub>2</sub>.<sup>21</sup>

## Computational details

In the present study we have computed pre-reactive complexes, transition states (TS) and adducts for the reaction of each anion with CO<sub>2</sub>. The solvent effects were accounted for by using the Integral Equation Formalism Polarizable Continuum solvation Model (IEFPCM).<sup>24</sup> Three solvents with varying dielectric constant were employed: water (w,  $\epsilon = 78.35$ ), tetrahydrofuran (thf,  $\epsilon = 7.42$ ) and toluene (t,  $\epsilon = 2.37$ ). All geometries of the three stationary points (pre-reactive complex, transition state, and adduct) were fully optimized using the MP2<sup>25</sup> method and the aug-cc-pvtz basis set.<sup>26-28</sup> The energies were extrapolated to the complete basis set (CBS) limit using the Varandas-Pansini<sup>29-33</sup> scheme. This approach<sup>22,29-34</sup>, has been reported as a successful procedure to compute the total energy of a plethora of systems, with CBS extrapolation eliminating the basis set superposition error which is inherent to cases where two or more species are converted to a single one along a reaction path.<sup>22,34</sup> According to the Varandas-Pansini work, the extrapolated CBS energies (equation 1) are given by a sum of Hartree-Fock ( $E_{\infty}^{\text{HF}}$ ) and correlation energies ( $E_{\infty}^{\text{cor}}$ ), as given in equations 2 and 3:<sup>29,30</sup>

$$E^{\text{CBS}} = E_{\infty}^{\text{cor}} + E_{\infty}^{\text{HF}}$$

$$E_{\infty}^{\text{HF}} = \frac{E_{x_i} e^{\beta x_i} - E_{x_j} e^{\beta x_j}}{e^{\beta x_i} - e^{\beta x_j}}$$

$$E_{x_i}^{\text{cor}} = E_{\infty}^{\text{cor}} + \frac{A}{x_i^3}$$

where the  $\beta$  value is 1.62,  $E_x^{\text{cor}}$  is the correlation energy obtained from MP2 calculations using the aug-cc-

pVXZ ( $X = D$  or  $T$ ) basis set,  $X_D = 2.13$  and  $2.08$ , and  $X_T = 2.90$  and  $2.96$  for MP2 and Hartree-Fock methods, respectively, see elsewhere<sup>33</sup> for a review.

The nature of each stationary point was confirmed via standard harmonic vibrational analysis. Thence, local minima were identified as having all eigenvalues positive in the hessian matrix, while transition states have just one negative eigenvalue. Thermal corrections at 298 K were computed from the partition functions. Therefore, the total energy ( $E_{\text{tot}}$ ) of the system results from the sum of four terms: translational ( $E_t$ ), rotational ( $E_r$ ), vibrational ( $E_v$ ) and electronic energies ( $E_e$ ). To find the extrapolated Gibbs Free energy ( $G^{\text{CBS}}$ ) and enthalpy ( $H^{\text{CBS}}$ ) we have considered the electronic energies extrapolated to the complete basis set limit plus the thermal correction obtained at the same level of theory used to optimize the geometries (equations 4 and 5).

$$G^{\text{CBS}} = E^{\text{CBS}} + e_g$$

$$H^{\text{CBS}} = E^{\text{CBS}} + e_h$$

where  $e_g$  and  $e_h$  are the thermal corrections for the Gibbs free energy and enthalpy, respectively, and  $E^{\text{CBS}}$  is the extrapolated energy. All systems were optimized both in the gas phase and in presence of three solvents: water, tetrahydrofuran, and toluene.

The Gas-Phase Basicity (GPB) for each anion was also computed. It is the negative of the Gibbs free energy for a base protonation (equation 6) and can be calculated according to equation 7. The value of  $-6.28$  kcal mol<sup>-1</sup> was used for  $G_{H^+}$ .<sup>35</sup>



$$GPB = \text{selectlanguagegreek} - G_T = -[G_{HB} - (G_{H^+} + G_{B^-})]$$

All calculations were performed using the Gaussian 09<sup>36</sup> program.

## Results and discussion

In the first step, we have computed the enthalpy and Gibbs free energy changes for the reaction of each anion with  $\text{CO}_2$  in the gas phase. Our discussion is based on the values computed with the MP2/aug-cc-pvtz method. The MP2 results are also compared to the B3LYP-D3 and M06-2X results from Sucarrat and Varandas.<sup>21</sup> Additional data such as cartesian coordinates of the optimized species, electronic energies, zero point energies and all reaction profiles are given in the supporting information.

The general trends here observed with the MP2 results are similar to those found previously.<sup>21</sup> In the gas phase most anions react spontaneously and without any apparent activation barrier. As it will be shown below, changes in the Gibbs free energy are about 8 kcal mol<sup>-1</sup> less negative than changes in the enthalpy. This is a consequence of reducing the degrees of freedom from the reactants ( $\text{CO}_2 + \text{anion}$ ) to the products (adduct). In this process, the entropy decreases, with a consequent effect in the Gibbs free energy. The solvent effect is more pronounced for solvents with higher dielectric constants.

### Thermodynamics of the anions/ $\text{CO}_2$ reactions in the gas phase

The approach adopted to quantify the energies for each reaction is represented in equation 8, where the anion ( $A^-$ ) reacts with  $\text{CO}_2$  to form the adduct  $[A-\text{CO}_2]^-$ .

$$X = (X_{[A-\text{CO}_2]^-}) - (X_{A^-} + X_{\text{CO}_2})$$

with X being the enthalpy (H) or Gibbs free energy (G).

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Table 1 gives the  $\Delta G$  results obtained with the MP2 and CBS scheme for the reactions in the gas phase, as well as the gas-phase basicity (GPB) of the anions (organized by decreasing values, based on the MP2/aug-cc-pvtz results). For comparison we also include in Table 1 the previous results obtained with the M06-2X and B3LYP-D3 functionals.<sup>21</sup> The trends found for changes in the Gibbs free energy and enthalpy are the same. This is indicated by the high correlation between these properties, as shown in Figure 1. The average difference between the Gibbs free energy and the enthalpy is around 8 kcal mol<sup>-1</sup> at 298 K. As noted above, the entropy change is negative because the reaction leads to a more organized system, thence with reduction in the number of degrees of freedom.

**Figure 1.** Gibbs free energy *versus* enthalpy for A<sup>-</sup> + CO<sub>2</sub> reactions with different methods.

The B3LYP-D3, MP2 and CBS results are close to each other, with differences smaller than 3.4 kcal mol<sup>-1</sup>. On the other hand, the Gibbs free energies computed with the M06-2X are more negative than those obtained with the MP2 method, particularly for OH<sup>-</sup>, CH<sub>3</sub>O<sup>-</sup>, C<sub>2</sub>H<sub>3</sub>NH<sup>-</sup>, F<sup>-</sup>, C<sub>2</sub>H<sub>3</sub>O<sup>-</sup> and NH<sub>2</sub><sup>-</sup>, where it is on average 7 kcal mol<sup>-1</sup> smaller. As expected, the base strength, quantified by the gas-phase basicity, shows a high correlation with the Gibbs free energy for the A<sup>-</sup> + CO<sub>2</sub> reactions (Figure 2). The more negative Gibbs free energies are found for stronger bases, which can donate electron density more easily.<sup>15</sup>

**Table 1.** Gibbs Free energies in the gas phase for the A<sup>-</sup> + CO<sub>2</sub> reactions (eq. 8) and gas-phase basicity (GPB) of the anions, calculated with the MP2/aug-cc-pvtz method. All values are in kcal mol<sup>-1</sup>

Reactions	$\Delta G_{M062x}^{(a)}$	$\Delta G_{B3LYP-D3}^{(a)}$	$\Delta G_{MP2}$
CH <sub>3</sub> <sup>-</sup> + CO <sub>2</sub> → [CH <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup>	-53.4	-49.5	-50.9
H <sup>-</sup> + CO <sub>2</sub> → [HCO <sub>2</sub> ] <sup>-</sup>	-50.4	-46.3	-48.6
CH <sub>3</sub> NH <sup>-</sup> + CO <sub>2</sub> → [CH <sub>3</sub> NHCO <sub>2</sub> ] <sup>-</sup>	-51.7	-45.3	-45.8
NH <sub>2</sub> <sup>-</sup> + CO <sub>2</sub> → [NH <sub>2</sub> CO <sub>2</sub> ] <sup>-</sup>	-50.7	-44.2	-42.4
OH <sup>-</sup> + CO <sub>2</sub> → [OHCO <sub>2</sub> ] <sup>-</sup>	-44.2	-36.1	-34.0
CH <sub>3</sub> O <sup>-</sup> + CO <sub>2</sub> → [CH <sub>3</sub> OCO <sub>2</sub> ] <sup>-</sup>	-35.3	-27.2	-29.3
C <sub>2</sub> H <sub>3</sub> NH <sup>-</sup> + CO <sub>2</sub> → [C <sub>2</sub> H <sub>3</sub> NHCO <sub>2</sub> ] <sup>-</sup>	-31.2	-26.3	-25.4
F <sup>-</sup> + CO <sub>2</sub> → [FCO <sub>2</sub> ] <sup>-</sup>	-31.3	-24.3	-22.0
CH <sub>3</sub> PH <sup>-</sup> + CO <sub>2</sub> → [CH <sub>3</sub> PHCO <sub>2</sub> ] <sup>-</sup>	-20.2	-18.8	-19.1
SiH <sub>3</sub> <sup>-</sup> + CO <sub>2</sub> → [SiH <sub>3</sub> CO <sub>2</sub> ] <sup>-</sup>	-19.0	-17.0	-19.0
PH <sub>2</sub> <sup>-</sup> + CO <sub>2</sub> → [PH <sub>2</sub> CO <sub>2</sub> ] <sup>-</sup>	-13.9	-12.4	-12.0
CH <sub>3</sub> S <sup>-</sup> + CO <sub>2</sub> → [CH <sub>3</sub> SCO <sub>2</sub> ] <sup>-</sup>	-12.5	-9.8	-10.2
CN <sup>-</sup> + CO <sub>2</sub> → [CNCO <sub>2</sub> ] <sup>-</sup>	-9.7	-8.9	-9.1
C <sub>2</sub> H <sub>3</sub> O <sup>-</sup> + CO <sub>2</sub> → [C <sub>2</sub> H <sub>3</sub> OCO <sub>2</sub> ] <sup>-</sup>	-14.0	-9.1	-8.1
C <sub>2</sub> H <sub>5</sub> S <sup>-</sup> + CO <sub>2</sub> → [C <sub>2</sub> H <sub>5</sub> SCO <sub>2</sub> ] <sup>-</sup>	-9.6	-7.5	-8.1
C <sub>2</sub> H <sub>3</sub> PH <sup>-</sup> + CO <sub>2</sub> → [C <sub>2</sub> H <sub>3</sub> PHCO <sub>2</sub> ] <sup>-</sup>	-8.7	-7.1	-7.3
HS <sup>-</sup> + CO <sub>2</sub> → [SHCO <sub>2</sub> ] <sup>-</sup>	-6.4	-4.0	-3.3
Cl <sup>-</sup> + CO <sub>2</sub> → [ClCO <sub>2</sub> ] <sup>-</sup>	-3.3	-2.3	-2.3
C <sub>2</sub> H <sub>3</sub> S <sup>-</sup> + CO <sub>2</sub> → [C <sub>2</sub> H <sub>3</sub> SCO <sub>2</sub> ] <sup>-</sup>	-4.4	-2.4	-2.1
Br <sup>-</sup> + CO <sub>2</sub> → [BrCO <sub>2</sub> ] <sup>-</sup>	-1.9	-1.2	-1.8
(a) Data from Reference 21.	(a) Data from Reference 21.	(a) Data from Reference 21.	(a) Data from Reference 21.

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**Figure 2.** Correlation between changes in the Gibbs free energy ( $\Delta G$ ) for the  $A^- + CO_2$  reactions in the gas phase and the gas phase basicity (GPB) of the anions. Also indicated is the square of the residuals.

The nature of the atom that interacts with  $CO_2$  determines the changes in the Gibbs free energies (figure 3). Specifically, the reactions with anions containing nitrogen atoms are found to be more spontaneous than those with analog anions containing oxygen, followed by those containing phosphorous and then sulfur atoms (Figure 3). The anions  $CH_3^-$ ,  $H^-$ ,  $NH_2^-$  and  $OH^-$ , which do not have any special stabilization effect and are small species, are among those leading to the most negative change in the Gibbs free energy.

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**Figure 3.** Effect of the nature of the atom that interacts with  $CO_2$  in the Gibbs free energy.

For the set  $CH_3X^-$  ( $X = NH, O, PH$  or  $S$ ), the changes in the Gibbs-free energy are -45.8, -29.3, -19.1 and -10.2 kcal mol<sup>-1</sup>, respectively. For the set  $C_2H_3X^-$  the corresponding changes are smaller, namely -25.4, -8.1, -7.3 and -2.1 kcal mol<sup>-1</sup>, respectively. Clearly, the conjugation with the vicinal double bond helps to stabilize the negative charge. However, this stabilization is much higher in the nitrogenated and oxygenated cases than in the anions containing phosphorous or sulfur atoms. In these anions, charge delocalization through the double bond is not so effective, therefore having a smaller effect. Although the methyl group can act either as electron donor or as electron acceptor,<sup>37</sup> its insertion in  $NH_2^-$ ,  $PH_2^-$  and in  $SH^-$  makes the Gibbs free energy more negative than in the corresponding anion without the methyl group. Conversely, for oxygenated species, the insertion of a methyl group ( $OH^- \times CH_3O^-$ , for example) reduces the changes in the Gibbs free energy. We associated this fact with the stabilization of the adduct, which helps to decrease the charge localization. For example,  $CH_3NH^-$  and  $NH_2^-$  have essentially the same GPB (Table 1), although  $CH_3NH^-$  leads to a more spontaneous reaction. For  $CH_3PH^-$  and  $PH_2^-$  both the GPB and the Gibbs free energy are more negative for the methylated species.

In the reaction of the anions with  $CO_2$ , in addition to the structural changes in the geometry of the  $CO_2$  molecule, which goes from a linear to a bent structure, there is a strong charge transfer from the anions to  $CO_2$ . This charge transfer leads to charge redistribution, with consequent stabilization of the whole system. Thus, the amount of charge transferred between the two reactants may have some correlation with the relative stability of the adduct. Table 2 gives the natural population (NPA) electronic charge on the  $CO_2$  moiety in the adduct ( $Q_{CO_2\_adduct}$ ), the distance between the interacting atom and the carbon atom of  $CO_2$  ( $d_{A\_CO_2}$ ) and the OCO angle. As the isolated  $CO_2$  molecule is neutral, the charge on this moiety in the adduct is a measure of the amount of charge transferred from the anion to  $CO_2$ . Also, from the geometrical point of view, a larger OCO angle is expected for a stronger interaction between  $CO_2$  and the anions, because of the rehybridization that takes place in the carbon atom. These electronic and geometrical parameters have been reported to correlate with the anion/ $CO_2$  bond strength.<sup>38,39</sup>

**Table 2 .** Total NPA charge (in  $e^-$ ) on the  $CO_2$  moiety in the anion/ $CO_2$  adduct ( $Q_{CO_2\_adduct}$ ), distance between the interacting atom and the carbon atom in the adduct ( $d_{A\_CO_2}$ , in Å) and the OCO angle ( $\angle_{OCO\_MP2}$ , in degrees).

Anions	$Q_{CO_2\_adduct}$ ( $e$ )	$d_{A\_CO_2}$ (Å)	$\angle_{OCO}$ ( $^\circ$ )
$CH_3S^-$	-0.755	1.954	135.77
$C_2H_5S^-$	-0.758	1.954	135.91
$SH^-$	-0.681	2.006	137.73
$C_2H_3S^-$	-0.666	2.017	138.46
$OH^-$	-0.618	1.445	132.61
$CH_3O^-$	-0.588	1.453	132.94

Anions	$Q_{\text{CO}_2\text{-adduct}}$ ( $e$ )	$d_{\text{A-CO}_2}$ ( $\text{\AA}$ )	$\angle_{\text{OCO}}$ ( $^\circ$ )
$\text{C}_2\text{H}_3\text{O}^-$	-0.495	1.537	136.37
$\text{CH}_3\text{PH}^-$	-0.991	1.931	132.12
$\text{PH}_2^-$	-0.947	1.949	132.89
$\text{C}_2\text{H}_3\text{PH}^-$	-0.944	1.950	133.38
$\text{CH}_3\text{NH}^-$	-0.740	1.454	130.30
$\text{NH}_2^-$	-0.747	1.459	130.42
$\text{C}_2\text{H}_3\text{NH}^-$	-0.683	1.464	132.05
$\text{F}^-$	-0.447	1.485	137.26
$\text{Cl}^-$	-0.021	2.906	170.95
$\text{Br}^-$	-0.017	3.111	172.49
$\text{SiH}_3^-$	-1.129	1.940	130.50
$\text{H}^-$	-0.956	1.126	130.20
$\text{CH}_3^-$	-0.854	1.550	128.80
$\text{CN}^-$	-0.760	1.530	133.00

The amount of charge transferred from the anion to  $\text{CO}_2$  strongly depends on the nature of the atom bonding to the carbon atom. As a general trend, the amount of charge transfer occurs in the following order:  $\text{P} > \text{S} \sim \text{N} > \text{O}$ , reflecting the reverse of the atomic electronegativity. Within a given group, the trends for charge transfer is the same as that of the relative stability of the adduct, with a larger transferred charge leading to more stable adducts. The same trend is observed for the geometrical parameters. Although the  $d_{\text{A-CO}_2}$  distance is strongly influenced by the atomic radius, within a given group (P, S, N or O), this distance and the OCO angle are smaller for the more strongly bonded anions, although in the last case the effects are indeed small.

### Solvent effect on the relative Gibbs free energy for the $\text{A}^- + \text{CO}_2$ reactions

The solvent effect was computed with the IEFPCM model for the solvents water, tetrahydrofuran and toluene. These solvents are the same as those investigated in the previous work by Sucarrat and Varandas.<sup>21</sup> The results are given in Table 3. The solvent effect ( $\rho$ ) was quantified in terms of the difference between the Gibbs free energy in the gas phase ( $\Delta G_{\text{gp}}$ ) and in the solvent ( $\Delta G_{\text{solv}}$ ), namely

$$\rho = \Delta G_{\text{solv}} - \Delta G_{\text{gp}} \text{ Eq. 9}$$

**Table 3.** Solvent effect and Gibbs free energy (in  $\text{kcal mol}^{-1}$ ) for the reactions in toluene ( $\rho_{\text{to-gp}}$ ), tetrahydrofuran ( $\rho_{\text{thf-gp}}$ ) and water ( $\rho_{\text{w-gp}}$ ).

Reactions	$\rho_{\text{to-gp}}$	$\rho_{\text{thf-gp}}$	$\rho_{\text{w-gp}}$	$\Delta G_{\text{MP2,to}}$	$\Delta G_{\text{MP2,thf}}$	$\Delta G_{\text{MP2,w}}$
$\text{F}^- + \text{CO}_2 \rightarrow [\text{FCO}_2]^-$	13.5	21.0	24.0	-8.5	-1.0	2.0
$\text{H}^- + \text{CO}_2 \rightarrow [\text{HCO}_2]^-$	7.4	12.9	15.3	-41.2	-35.7	-33.3
$\text{OH}^- + \text{CO}_2 \rightarrow [\text{OHCO}_2]^-$	9.9	14.8	17.1	-24.1	-19.2	-16.9
$\text{HS}^- + \text{CO}_2 \rightarrow [\text{SHCO}_2]^-$	6.6	9.6	11.5	3.3	6.3	8.2
$\text{CN}^- + \text{CO}_2 \rightarrow [\text{CNC}_2]^-$	6.9	10.4	11.8	-2.2	1.3	2.7
$\text{CH}_3\text{S}^- + \text{CO}_2 \rightarrow [\text{CH}_3\text{SCO}_2]^-$	6.3	8.8	9.8	-3.9	-1.4	-0.4
$\text{NH}_2^- + \text{CO}_2 \rightarrow [\text{NH}_2\text{CO}_2]^-$	5.5	8.2	9.3	-36.9	-34.2	-33.1
$\text{CH}_3\text{O}^- + \text{CO}_2 \rightarrow [\text{CH}_3\text{OCO}_2]^-$	5.4	8.1	9.3	-23.9	-21.2	-20.0
$\text{C}_2\text{H}_5\text{S}^- + \text{CO}_2 \rightarrow [\text{C}_2\text{H}_5\text{SCO}_2]^-$	3.9	6.6	8.0	-4.2	-1.5	-0.1
$\text{C}_2\text{H}_3\text{S}^- + \text{CO}_2 \rightarrow [\text{C}_2\text{H}_3\text{SCO}_2]^-$	3.6	5.3	7.7	1.5	3.2	5.6
$\text{C}_2\text{H}_3\text{O}^- + \text{CO}_2 \rightarrow [\text{C}_2\text{H}_3\text{OCO}_2]^-$	3.6	5.7	6.7	-4.5	-2.4	-1.4
$\text{CH}_3^- + \text{CO}_2 \rightarrow [\text{CH}_3\text{CO}_2]^-$	4.0	5.8	6.4	-46.9	-45.1	-44.5
$\text{PH}_2^- + \text{CO}_2 \rightarrow [\text{PH}_2\text{CO}_2]^-$	3.3	5.0	5.6	-8.7	-7.0	-6.4

Reactions	$\rho_{\text{to-gp}}$	$\rho_{\text{thf-gp}}$	$\rho_{\text{w-gp}}$	$\Delta G_{\text{MP2\_to}}$	$\Delta G_{\text{MP2\_thf}}$	$\Delta G_{\text{MP2\_w}}$
$\text{CH}_3\text{NH}^- + \text{CO}_2 \rightarrow [\text{CH}_3\text{NHCO}_2]^-$	2.9	4.1	4.7	-42.9	-41.7	-41.1
$\text{CH}_3\text{PH}^- + \text{CO}_2 \rightarrow [\text{CH}_3\text{PHCO}_2]^-$	1.3	3.5	3.5	-17.8	-15.6	-15.6
$\text{C}_2\text{H}_3\text{NH}^- + \text{CO}_2 \rightarrow [\text{C}_2\text{H}_3\text{NHCO}_2]^-$	0.3	1.7	2.3	-25.1	-23.7	-23.1
$\text{SiH}_3^- + \text{CO}_2 \rightarrow [\text{SiH}_3\text{CO}_2]^-$	1.5	1.7	1.4	-17.5	-17.3	-17.6
$\text{C}_2\text{H}_3\text{PH}^- + \text{CO}_2 \rightarrow [\text{C}_2\text{H}_3\text{PHCO}_2]^-$	1.3	1.3	1.0	-6.0	-6.0	-6.3

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Figure 4 shows a representation of the solvent effect. The dielectric constant of the solvent has a direct influence on the reaction spontaneity, with water having a higher effect, followed by tetrahydrofuran and then toluene. Although this would be expected, considering the values of the dielectric constant for these solvents, it is interesting to observe that although the tetrahydrofuran dielectric constant is closer to that of toluene than to the dielectric constant of water, the effect of tetrahydrofuran on the reaction Gibbs free energy is closer to that of water than to that of toluene. Additionally, the effect is higher for the smaller anions, which are capable of polarizing the solvent more strongly than the bigger ones.

**Figure 4.** Solvent effect on the Gibbs free energy for the  $\text{A}^- + \text{CO}_2$  reactions. The solvent effect is the difference between the Gibbs free energy in the solvent and the corresponding one in the gas-phase.

The interaction with the solvent decreases the basicity and, consequently, the reactivity of the anions. The free anions are therefore more strongly stabilized by the solvent than the adducts, resulting in a less spontaneous reaction. In turn, the solvent effect is higher for smaller anions such as  $\text{F}^-$ ,  $\text{H}^-$  and  $\text{OH}^-$  because they have a more concentrated charge density, increasing polarization of the solvent. However, the reactions are still exergonic in all solvents, except for  $\text{C}_2\text{H}_3\text{S}^-$  and  $\text{SH}^-$  which are the weakest bases.

The Gibbs free energy changes for the  $\text{SiH}_3^-$ ,  $\text{C}_2\text{H}_3\text{NH}^-$ ,  $\text{C}_2\text{H}_3\text{PH}^-$  and  $\text{CH}_3\text{PH}^-$  anions are the less strongly influenced by the solvent. For  $\text{C}_2\text{H}_3\text{NH}^-$ ,  $\text{C}_2\text{H}_3\text{PH}^-$  and  $\text{CH}_3\text{PH}^-$ , as the charge is already dispersed in the free anion, both the anion and the adduct are equally stabilized by the solvent. For  $\text{SiH}_3^-$  in toluene the free anion and the adduct are equally stabilized while in water the adduct is slightly more stabilized than the anion.

## Energy barriers

In a subsequent step we have computed both the structures and energies of the transition states for the formation of the adducts in the solvents. Table 4 gives the relative Gibbs free energy for the transition structures computed for the direct reaction (in this case the values are computed relative to the reagents) and for the reverse reaction (in this case the values are computed relative to the adducts). The existence of a barrier for the direct reaction is highly dependent on the solvent. Solvents with higher dielectric constant, water in this case, may induce an activation barrier.

**Table 4.** Gibbs free energy activation barrier to the direct and reverse reactions (in kcal mol<sup>-1</sup>).

Transition state	Direct reaction	Direct reaction	Reverse reaction	Reverse reaction
	MP2	CBS	MP2	CBS
$\text{H}^-_{\text{w}}$	7.5	7.1	40.8	41.4
$\text{H}^-_{\text{thf}}$	5.8	5.6	41.5	42.4
$\text{SiH}_3^-_{\text{w}}$	10.4	10.1	28.0	28.9
$\text{SiH}_3^-_{\text{thf}}$	9.4	9.0	26.7	27.5

Transition state	Direct reaction	Direct reaction	Reverse reaction	Reverse reaction
SiH <sub>3</sub> <sup>-</sup> _to	6.4	6.1	23.9	24.8
PH <sub>2</sub> <sup>-</sup> _w	8.6	8.3	15.0	15.4
PH <sub>2</sub> _thf	7.7	7.3	14.7	15.1
PH <sub>2</sub> <sup>-</sup> _to	4.8	4.6	13.5	14.1
CH <sub>2</sub> =CHPH <sup>-</sup> _w	8.3	8.0	14.6	15.2
CH <sub>2</sub> =CHPH <sup>-</sup> _thf	8.1	7.8	14.1	15.6
CH <sub>2</sub> =CHPH <sup>-</sup> _to	6.0	5.7	12.0	12.6
CH <sub>2</sub> =CHPH <sup>-</sup> _gp	1.2	1.0	8.5	9.3
CH <sub>3</sub> S <sup>-</sup> _w	8.1	7.5	8.5	9.1
CH <sub>3</sub> S <sup>-</sup> _thf	6.1	5.6	7.6	8.2
CN <sup>-</sup> _w	12.7	12.0	10.0	10.3
CN <sup>-</sup> _thf	11.5	10.9	10.2	10.6
CN <sup>-</sup> _to	7.7	7.0	9.9	10.2
CN <sup>-</sup> _gp	0.5	0.0	9.6	10.2
CH <sub>2</sub> =CHO <sup>-</sup> _w	6.9	6.6	8.3	9.2
CH <sub>3</sub> CH <sub>2</sub> S <sup>-</sup> _w	8.7	7.7	8.8	8.9
CH <sub>3</sub> CH <sub>2</sub> S <sup>-</sup> _thf	6.8	6.4	8.3	9.0
F <sup>-</sup> _w	6.3	5.7	4.3	5.2
CH <sub>2</sub> =CHS <sup>-</sup> _w	9.8	9.1	4.2	4.7
CH <sub>2</sub> =CHS <sup>-</sup> _thf	8.2	7.6	5.0	5.6
HS <sup>-</sup> _w	11.1	10.4	2.9	3.2
HS <sup>-</sup> _thf	9.3	8.6	3.0	2.8
HS <sup>-</sup> _to	5.6	5.0	2.3	2.7

As shown in Table 4, the activation barriers are small for the direct reaction, even in the most polar solvent (smaller than 13 kcal mol<sup>-1</sup>). Therefore, all reactions must show a fast kinetics. From the viewpoint of CO<sub>2</sub> recovering after capture, it is desirable that the reverse reactions also have a small activation barrier. In this way, the thermodynamics of the reaction is the determinant parameter for the feasibility of the capture process. By selecting from Table 3 the anions with negative value for the Gibbs free energy change (in any solvent) and activation barrier for either the direct or the reverse reaction around 10 kcal mol<sup>-1</sup> or below (Table 4), which would then combine kinetics and thermodynamics features favoring the reaction and its reverse, the following species show up: CH<sub>3</sub>S<sup>-</sup>, C<sub>2</sub>H<sub>5</sub>S<sup>-</sup>, F<sup>-</sup> and CN<sup>-</sup>.

Additionally, important cases are those where changing the solvent dielectric constant changes the spontaneity of the reaction. This was found for F<sup>-</sup>, CN<sup>-</sup>, CH<sub>3</sub>S<sup>-</sup> and C<sub>2</sub>H<sub>5</sub>S<sup>-</sup>. In these cases, we could think of a capture process in a less polar solvent and thus CO<sub>2</sub> recovering in a more polar one. Therefore, some solvent gradient could be designed to combine the two processes, capture and regeneration.

As an example of such a behavior, Figure 5 shows the profile for the reaction between CN<sup>-</sup> and CO<sub>2</sub>. Among all systems studied, CN<sup>-</sup> is the one which shows a clear dependency of the transition state energy with the solvent polarity. Curiously, as observed before, the effects of THF on the energy values are closer to the effects of water than to those of toluene. In this case, we additionally computed the effect of chloroform, a solvent with a dielectric constant ( $\epsilon = 4.81$ ) intermediary between that of THF and toluene. The results are also shown in Figure 6. The values for chloroform are between those of THF and toluene, but closer to THF.

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**Figure 5** . (a) Enthalpy and (b) Gibbs free energy profiles for the  $\text{CN}^- + \text{CO}_2 \rightarrow [\text{CNCO}_2]^-$  reaction in gas phase, toluene, chloroform, tetrahydrofuran and water. All the electronic energies were computed with MP2/aug-cc-pvtz.

## CBS extrapolation

In this section we discuss the performance of the electronic structure methods taking as reference the extrapolated and corrected Gibbs free energy and enthalpy for all the reactions in gas phase and in the solvents as well as for the activation energies (when it exists). Varandas *et al*<sup>23</sup> reported that MP2/CBS theory tends to overestimate barrier heights while M06-2X underestimate them in isomerization processes.

Figure 6 shows the difference for the Gibbs free energy obtained with the CBS extrapolation procedure and the MP2/aug-cc-pvtz, M06-2X/aug-cc-pvtz and B3LYP-D3/aug-cc-pvtz methods. While the MP2/aug-cc-pvtz results show an almost linear correlation with the extrapolated results, both DFT methods diverge significantly. The MP2/aug-cc-pvtz, M06-2X/aug-cc-pvtz and B3LYP-D3/aug-cc-pvtz results differ from the extrapolated ones by  $-0.99 \pm 0.28 \text{ kcal mol}^{-1}$ ,  $2.56 \pm 1.00 \text{ kcal mol}^{-1}$  and  $-1.05 \pm 1.27 \text{ kcal mol}^{-1}$  (on average), respectively. Among the DFT methods, the B3LYP-D3 is closer to the CBS results, with most DFT values more positive than the CBS ones. The differences between the M06-2X/aug-cc-pvtz and the CBS values are even larger, although in this case with the DFT values more negative than the CBS ones. These differences may be observed in Figure 6.

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**Figure 6** . Gibbs free energy in gas phase obtained with different theory levels versus CBS extrapolation.

This picture does not change when including solvents effects. The reactivity order is maintained but, in some cases ( $\text{OH}^-$ ,  $\text{CH}_3\text{O}^-$ ,  $\text{C}_2\text{H}_3\text{NH}^-$ ,  $\text{F}^-$ ,  $\text{C}_2\text{H}_3\text{O}^-$  and  $\text{NH}_2^-$ ) the M06-2X functional overestimates the energy values. As show in Figure 1, the enthalpy shows a linear correlation with the Gibbs free energy and the error associated with the functional is almost the same.

Most reactions do not show a transition state either in the gas phase or in the solvent. When a transition state exists, the activation energy calculated with MP2/aug-cc-pvtz underestimate the CBS values (on average) by  $0.5 \text{ kcal mol}^{-1}$  and  $0.6 \text{ kcal mol}^{-1}$  for the direct and the reverse reactions, respectively. The values computed with the DFT functionals do not diverge too significantly, although the M06-2X functional shows two values that diverge from the CBS values ( $\text{PH}_2^-_{\text{to}}$  and  $\text{H}^-_{\text{thf}}$ ). When we remove these two cases, the average deviation is  $0.9 \text{ kcal mol}^{-1}$  for the direct reaction. The differences for the reverse reaction are larger because, as already mentioned for the calculation of the reaction energy, the M06-2X functional overestimates the Gibbs free energy in some cases. Therefore, the activation energy for the reverse reaction is also affected. The B3LYP-D3 results are close to the CBS values in both directions, with maximum difference values of  $3.1 \text{ kcal mol}^{-1}$  ( $\text{SiH}_3^-_{\text{w}}$ ) for the direct reaction.

## Conclusion

The reactions of  $\text{CO}_2$  with 20 anions were computed with the wavefunction MP2/aug-cc-pvtz method. To test for convergence of the results, we also employed an extrapolation procedure using the CBS approach, as reported in previous studies. Solvent effects were computed using the IEFPCM method with water, tetrahydrofuran and toluene as solvents. In the gas-phase the computed reactions are exergonic without

any activation energy. In the condensed phase the anions are more stabilized than the adducts, reducing the reaction spontaneity and inducing an activation barrier for some systems. Interestingly, although the dielectric constant of tetrahydrofuran is closer to that of toluene than to the dielectric constant of water, results obtained with tetrahydrofuran are closer to results obtained with water than with toluene. For some anions we observe a change in the reaction spontaneity in the different solvents, allowing to think of a medium where CO<sub>2</sub> sequestration and regeneration could be done depending only on the medium composition. Alkyl sulfide anions emerge as an interesting candidate for CO<sub>2</sub> sequestration because they combine suitable thermodynamics with low activation barrier for both the direct and the reverse reactions.

When comparing the trends obtained with the different methods, we observe that the MP2 and CBS approaches yield results that are close to each other within 3 kcal mol<sup>-1</sup>. Comparing to results obtained previously with the B3LYP-D3 and M06-2X functionals we found that B3LYP-D3 follows the same trends as MP2, while M06-2X tends to diverge from the wavefunction results.

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