

Quantifying cooperative intermolecular interactions for improved carbon dioxide capture materials

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We have optimized the geometry and calculated interaction energies for over 100 different complexes of CO₂ with various combinations of electron accepting (Lewis acid) and electron donating (Lewis base) molecules. We have used the recently developed explicitly correlated coupled cluster singles doubles and perturbative triples [CCSD(T)-F12] methods and the associated VXZ-F12 (where X = D,T,Q) basis sets. We observe only modest changes in the geometric parameters of CO₂ upon complexation, which suggests that the geometry of CO₂ adsorbed in a nanoporous material should be similar to that of CO₂ in gas phase. When CO₂ forms a complex with two Lewis acids via the two electron rich terminal oxygen atoms, the interaction energy is less than twice what would be expected for the same complex involving a single Lewis acid. We consider a series of complexes that exhibit simultaneous CO₂-Lewis acid and CO₂-Lewis base intermolecular interactions, with total interaction energies spanning 14.1–105.9 kJ mol⁻¹. For these cooperative complexes, we find that the total interaction energy is greater than the sum of the interaction energies of the constituent complexes. Furthermore, the intermolecular distances of the cooperative complexes are contracted as compared to the constituent complexes. We suggest that metal-organic-framework or similar nanoporous materials could be designed with adsorption sites specifically tailored for CO₂ to allow cooperative intermolecular interactions, facilitating enhanced CO₂ adsorption. © 2011 American Institute of Physics. [doi:10.1063/1.3624363]

INTRODUCTION

Any serious effort to reduce anthropogenic carbon dioxide (CO₂) emissions must contend with the geopolitical and economic reality that fossil fuels will continue to make a dominant contribution to the world's energy supply for decades to come.¹ This makes development of scalable, cost-effective CO₂ capture technologies of equal importance to innovations in renewable energy resources over the near future.² Furthermore, captured CO₂ is potentially a cheap and green carbon source that can be converted into a variety of valuable organic molecules.^{3–5}

Metal organic framework (MOF) materials are a relatively new class of nanoporous crystalline compounds that demonstrate promising ability as physical adsorbents for the separation of gases, including CO₂ (see, for example, Refs. 6–9). However, current MOF materials do not yet show the necessary selectivity for CO₂ from combustion exhaust gas mixtures.¹⁰ In particular, very little is known about adsorption of CO₂ in the presence of H₂O, the co-product of combustion.^{1,11} CO₂ has previously been found to bind to MOF materials at either electron deficient open metal adsorption sites via the electron rich terminal oxygen atom^{12–14} or to electron rich adsorption sites via the electron deficient central carbon atom.^{9,15,16} We propose that MOF adsorption sites which allow simultaneous interaction of the electron rich terminal oxygen atoms and the electron deficient central carbon atom of CO₂ could be designed to exploit so-called cooper-

ative intermolecular interactions, increasing the total adsorption strength.

The use of supercritical CO₂ as a “green solvent” for industrial processes has resulted in a number of recent experimental^{17–21} and theoretical^{18–24} investigations concerning the fundamental intermolecular interactions of CO₂. For molecules containing carbonyl functional groups, CO₂ demonstrates simultaneous Lewis acid–Lewis base R₂C=O···CO₂ and hydrogen bonding interactions CH···O=C=O.^{17,20,21,24} These two simultaneous intermolecular interactions work cooperatively to strengthen the total interaction.¹⁷ Similar cooperative intermolecular interactions have also been observed for CO₂ complexes with dimethyl ether and 1,2-dimethoxyethane [(CH₃)₂O···CO₂ and CH₃···O=C=O],^{19,21} small fluorinated alkanes (RF···CO₂ and CH···O=C=O),²² and various nitrogen containing Lewis bases (N···CO₂ and CH···O=C=O).^{25,26} These previous works conclusively demonstrate that CO₂ is able to form cooperative intermolecular interactions but they do not quantify the strength of the individual Lewis acid–Lewis base or hydrogen bonding interactions. As a consequence, it is not yet known how strongly cooperative interactions affect the total interaction energy and intermolecular distance(s) of CO₂ complexes.

In the present work, we investigate over 100 different complexes involving CO₂ with various combinations of electron accepting (Lewis acid) and electron donating (Lewis base) molecules. We consider a range of different donor and acceptor molecules of various strengths that contain first and second row elements. We optimize the geometry and

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calculate the interaction energy for each complex using explicitly correlated coupled cluster methods. We impose a few minor geometric constraints on the complexes to simplify interpretation of the intermolecular interactions and to allow more systematic investigation of the nature of cooperative interactions involving CO₂. Our primary objective is to quantify the effect of cooperative interactions on the adsorption strength and optimal intermolecular distance(s) for CO₂ complexes to ultimately facilitate a more rational design of MOF materials with adsorption sites specifically tailored for CO₂. The present work complements some recent DFT and MP2 studies that have investigated the interactions of CO₂ with potential organic framework linker molecules.^{26–28}

THEORETICAL METHODS

We have optimized the geometries of all complexes and their constituent monomers using the explicitly correlated CCSD(T)-F12 methods as implemented in MOLPRO 2010.1 (Refs. 29 and 30) and the VXZ-F12 (where X = D,T,Q) orbital basis sets.³¹ Recently, we showed that interaction energies and intermolecular distances of weakly bound complexes obtained with this approach are in excellent agreement with the CCSD(T)/CBS limit.^{32,33}

Density fitting approximations^{34,35} and the resolution of the identity approximation were utilized in all explicitly correlated calculations with the default auxiliary basis sets^{36–38} for all atoms except Li. For Li, the def2-TZVPP/JKFIT auxiliary basis set was used. The default complementary auxiliary basis set singles correction was applied,²⁹ which substantially improves the accuracy of the Hartree-Fock (HF) contributions particularly with smaller orbital basis sets.³⁹ The diagonal, fixed amplitude 3C(FIX) *ansatz* was used, which is orbital invariant, size consistent, and free of geminal basis set superposition error.^{40–42} The default CCSD-F12 correlation factor $[(1/\beta)e^{-\beta r_{12}}$, where $\beta = 1$] was used in all explicitly correlated calculations. We have not scaled the triples contribution in our CCSD(T)-F12 calculations.

Unless specified all coupled cluster calculations assume a frozen core (B:1s, C:1s; N:1s; O:1s; F:1s; P:1s,2s,2p; S:1s,2s,2p; Cl:1s,2s,2p) and were performed using MOLPRO 2010.1.³⁰ The optimization threshold criteria were set to: gradient = 1×10^{-6} a.u., stepsize = 1×10^{-6} a.u., energy = 1×10^{-8} a.u. All single point energies were converged to 1×10^{-9} a.u.

We calculate atomic charges using the natural bond orbital (NBO) analysis in GAUSSIAN 09 with the B3LYP/aug-cc-pVTZ method using the CCSD(T)-F12a/VDZ-F12 optimized geometries.⁴³

RESULTS AND DISCUSSION

As shown in Fig. 1, CO₂ is able to form simultaneous intermolecular interactions via the electron rich terminal oxygen atoms (O···X) and the electron deficient central carbon atom (C···Y). These simultaneous interactions work cooperatively such that the total interaction energy of a complex is different to the sum of the individual parts. Within this context, we define the magnitude of the coop-

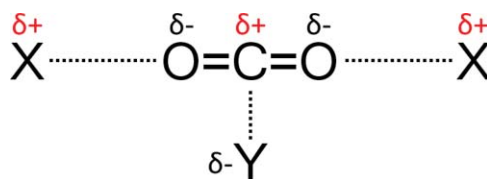


FIG. 1. A simplified model of simultaneous intermolecular interactions in X₂-CO₂-Y complexes.

erative interaction as being the difference (either positive or negative) between the interaction energy of the total complex and the interaction energy of the constituent individual complexes. For example, if the interaction energy of X₂-CO₂-Y was 40 kJ mol⁻¹ and the interaction energies of X₂-CO₂ and CO₂-Y were 20 and 15 kJ mol⁻¹, respectively, the magnitude of the cooperative interaction would be +5 kJ mol⁻¹. It is important to note that our definition of cooperative interaction assumes that the effect of basis set superposition error (BSSE) is negligible. While this requirement can not be satisfied with any finite basis set, the magnitude of BSSE obtained with explicitly correlated CCSD(T)-F12 methods is much smaller than with conventional CCSD(T).³³ For example, the difference between the interaction energy of H₂O-CO₂ obtained with and without counterpoise correction is 0.8 kJ mol⁻¹ for CCSD(T)-F12a/VDZ-F12 and 3.2 kJ mol⁻¹ for CCSD(T)/aug-cc-pVDZ. The difference in the corresponding optimized intermolecular distance of H₂O-CO₂ obtained with and without counterpoise correction is 0.013 Å for CCSD(T)-F12a/VDZ-F12 and 0.089 Å for CCSD(T)/aug-cc-pVDZ. Furthermore, the absolute values of the non-counterpoise corrected CCSD(T)-F12a/VDZ-F12 interaction energy (12.4 kJ mol⁻¹) and intermolecular distance (2.761 Å) for H₂O-CO₂ are in better agreement with the CCSD(T)/CBS limits (12.2 kJ mol⁻¹ and 2.755 Å) than the counterpoise corrected values (11.5 kJ mol⁻¹ and 2.774 Å).³³ Finally, it should also be noted that the magnitude of the cooperative interaction in the electronic energy of our model adsorption site will not necessarily be the same as the magnitude of the cooperative interaction for the enthalpy of adsorption (ΔH_{ads}) of a bulk MOF material that incorporates the same adsorption site. This work, therefore, is a “proof of concept” that cooperative intermolecular interactions may facilitate enhanced CO₂ adsorption in MOF or similar nanoporous materials.

(HF)_n-CO₂

We begin by investigating the suitability of the CCSD(T)-F12 methods to accurately calculate interaction energies and hence the magnitude of cooperative interactions in a model system consisting of (HF)_n-CO₂ (where n = 1-4,6). We consider two CO₂-Lewis acid complexes with either 1 or 2 HF molecules forming hydrogen bond(s) with the electron rich terminal oxygen atom(s) of CO₂ and three CO₂-Lewis base complexes with either 1, 2, or 4 HF molecules interacting via the electron rich fluorine atom(s) and the electron deficient central carbon atom of CO₂. We also consider three cooperative complexes in which two HF molecules form hydrogen

TABLE I. CCSD(T)-F12 interaction energies (in kJ mol^{-1}) for $(\text{HF})_n\text{-CO}_2$.^a

	VDZ-F12		VTZ-F12		VQZ-F12	
	F12a	F12b	F12a	F12b	F12a	F12b
CO ₂ -Lewis acid complexes: ^b						
(HF)-CO ₂	12.11	12.00	12.22	12.24	12.16	12.19
(HF) ₂ -CO ₂	20.18	20.00	20.39	20.43	20.26	20.32
CO ₂ -Lewis base complexes: ^c						
(HF)-CO ₂	5.60	5.50	5.51	5.49	5.47	5.47
(HF) ₂ -CO ₂	9.60	9.42	9.39	9.36	9.34	9.33
(HF) ₄ -CO ₂	10.99	10.67	10.55	10.51	10.50	10.50
Cooperative complexes:						
(HF) ₃ -CO ₂	32.62	32.29	32.77	32.80	32.60	32.65
(HF) ₄ -CO ₂	43.24	42.78	43.30	43.30	43.10	43.15
(HF) ₆ -CO ₂	57.12	56.43				
Cooperative interaction ^d						
(HF) ₃ -CO ₂	+6.83	+6.79	+6.88	+6.87	+6.87	+6.87
(HF) ₄ -CO ₂	+13.45	+13.36	+13.52	+13.52	+13.51	+13.51
(HF) ₆ -CO ₂	+25.94	+25.76				

^aAll interaction energies are determined at the corresponding optimized geometry.

^bComplexes where CO₂ acts as an electron donor.

^cComplexes where CO₂ acts as an electron acceptor.

^dDifference between the interaction energy of a cooperative complex and the interaction energy of the constituent CO₂-Lewis acid and CO₂-Lewis base complexes. See text for details.

bonds to the two oxygen atoms of CO₂ and either 1, 2, or 4 HF molecules interact via the fluorine atom(s) with the central carbon atom of CO₂. Representative images of all $(\text{HF})_n\text{-CO}_2$ (where $n = 1\text{-}4,6$) complexes optimized with the CCSD(T)-F12a/VDZ-F12 method are included in Fig. S1 of the supplementary material.⁴⁴

In Table I, we present CCSD(T)-F12a and CCSD(T)-F12b interaction energies for $(\text{HF})_n\text{-CO}_2$ (where $n = 1\text{-}4,6$) obtained with the VDZ-F12, VTZ-F12 and VQZ-F12 basis sets. We have previously found that CCSD(T)-F12b/VQZ-F12 interaction energies are in exceptionally good agreement with the CCSD(T)/CBS limit so we consider this the benchmark for comparison.^{32,33} Overall, we find that the calculated interaction energies converge as the cardinal number of the basis set increases from VDZ-F12 to VQZ-F12, although there is some small oscillation in some of the results. We find there to be relatively small differences between the CCSD(T)-F12a and CCSD(T)-F12b interaction energies obtained with a given basis set and not surprisingly these differences are largest for the VDZ-F12 basis set and smallest for the VQZ-F12 basis set. As some of the complexes considered in the subsequent subsections are relatively large, we are, however, restricted to use of the VDZ-F12 basis set. We find that interaction energies of the CO₂-Lewis acid complexes are slightly underestimated with the VDZ-F12 basis set whereas interaction energies of the CO₂-Lewis base complexes are slightly overestimated. For both types of complexes, these discrepancies become larger as the number of HF molecules increases. Interestingly, the CCSD(T)-F12a method appears to better describe the CO₂-Lewis acid complexes and the CCSD(T)-F12b method appears to better describe the CO₂-Lewis base complexes with the VDZ-F12 basis set. For the

cooperative complexes where both types of intermolecular interactions are present, the CCSD(T)-F12a/VDZ-F12 interaction energies are appreciably closer to the CCSD(T)-F12b/VQZ-F12b results as compared to the CCSD(T)-F12b/VDZ-F12 interaction energies. As a consequence, we find that the magnitude of the cooperative interaction determined with CCSD(T)-F12a/VDZ-F12 method is slightly ($<0.1 \text{ kJ mol}^{-1}$ difference) more accurate than if determined with the CCSD(T)-F12b/VDZ-F12 method. This result is consistent with other theoretical investigations that recommend use of the CCSD(T)-F12a method with smaller VDZ-F12 and VTZ-F12 basis sets and use of the CCSD(T)-F12b method with the larger VQZ-F12 basis set.^{32,45} It follows that all geometry optimizations and interaction energies in the rest of this investigation are determined using the CCSD(T)-F12a/VDZ-F12 method. This method is expected to give interaction energies for all three types of complexes and the magnitude of the cooperative interaction to within a few tenths of a kJ mol^{-1} of the CCSD(T)-F12b/VQZ-F12 result.

CO₂-Lewis acid complexes

In Table II, we present CCSD(T)-F12a/VDZ-F12 interaction energies, optimized intermolecular distances, and the magnitude of the cooperative interaction for a series of $X_n\text{-CO}_2$ (where $n = 1$ or 2) complexes. We consider 20 Lewis acid molecules that bind to CO₂ via $\text{O}\cdots\text{X}$ interactions involving four different electron deficient atoms (H, Li, B, Al). In Fig. 2, we show a representative image of the $(\text{H}_2\text{O})_2\text{-CO}_2$ complex with the optimized geometries of all other $X\text{-CO}_2$ and $X_2\text{-CO}_2$ complexes given in Figs. S2-S4 of the supplementary material.⁴⁴ As our primary motivation is to ascertain the effect of “cooperative interactions” on CO₂, we have introduced some minor geometric constraints to simplify this interpretation. We assume that all diatomic and linear molecules bind CO₂ in a linear fashion with either $C_{\infty v}$ ($X=1$) or $D_{\infty h}$ ($X=2$) symmetry. For the polyatomic hydrogen bonding molecules, we restrict the hydrogen bond to be linear [e.g., $\theta(\text{C}=\text{O}\cdots\text{H})$ and $\theta(\text{O}\cdots\text{HO})$ of $\text{H}_2\text{O}\text{-CO}_2$ are 180°] and orientate the two X molecules to be on the opposite side to each other to minimize any potential $\text{X}\cdots\text{X}$ interactions. For the boron and aluminum hydrides and halides, we assume that the $\theta(\text{C}=\text{O}\cdots\text{B})$ or $\theta(\text{C}=\text{O}\cdots\text{Al})$ angle is linear and that the two electron deficient groups are in a staggered orientation (D_{3h} symmetry). All other geometric parameters are optimized.

As expected, there are only modest differences between the geometric parameters of CO₂ as a monomer and in the $X\text{-CO}_2$ and $X_2\text{-CO}_2$ complexes. For $X\text{-CO}_2$, we find that the bonded $\text{R}(\text{C}=\text{O})_b$ distance is slightly elongated and the free $\text{R}(\text{C}=\text{O})_f$ distance is slightly contracted, as compared to $\text{R}(\text{C}=\text{O})$ in CO₂ monomer. Furthermore, there is a strong correlation between the interaction energy of a complex and the values of both $\text{R}(\text{C}=\text{O})_b$ and $\text{R}(\text{C}=\text{O})_f$ (Figs. S5 and S6 of the supplementary material).⁴⁴ These results are consistent with the Lewis acid essentially polarizing the CO₂ molecule so that electron density moves from a non-bonding orbital of the free C=O group into an anti-bonding orbital of the bonded C=O group (Table S1 of the supplementary material).⁴⁴ In

TABLE II. CCSD(T)-F12a/VDZ-F12 interaction energies (in kJ mol⁻¹) and selected geometric parameters (in Å) for a series of CO₂-Lewis acid complexes.

Molecule	X-CO ₂		X ₂ -CO ₂			Coop. Int. ^c
	Int. energy	R(O···X) ^a	Int. energy	R(O···X) ^a	R(X···X) ^b	
HNC	12.4	2.058	19.6	2.123	6.568	-5.1
HF	12.1	1.981	20.2	2.037	6.395	-4.0
HCOOH	10.5	2.071	18.7	2.114	6.551	-2.3
C ₄ H ₅ N	8.6	2.217	15.2	2.255	6.835	-2.1
HCN	8.3	2.269	13.5	2.324	6.973	-3.1
OH	8.2	2.182	14.2	2.228	6.779	-2.2
HCl	7.9	2.217	14.2	2.256	6.836	-1.6
CH ₃ OH	7.4	2.200	13.6	2.252	6.786	-1.3
H ₂ O	7.0	2.221	12.5	2.252	6.828	-1.4
C ₆ H ₆	3.1	2.603	6.1	2.605	7.536	-0.0
CH ₄	1.7	2.743	3.4	2.744	7.815	-0.0
LiCl	37.2	1.990	43.3	2.093	6.504	-31.1
LiH	32.4	2.008	39.8	2.104	6.526	-25.1
LiF	31.4	2.028	37.7	2.127	6.572	-25.1
BF ₃	9.9	2.674	18.5	2.706	7.736	-1.3
BH ₃	8.4	2.518	16.0	2.550	7.423	-0.8
BCl ₃	7.3	3.042	14.7	3.044	8.413	+0.1
AlF ₃	50.8	2.027	67.8	2.167	6.646	-33.7
AlCl ₃	37.2	2.065	47.4	2.290	6.896	-27.1
AlH ₃	24.5	2.229	36.7	2.385	7.088	-12.3

^aDistance from the electron rich oxygen atom of CO₂ to the electron deficient atom of the acceptor molecule.

^bDistance between the electron deficient atoms of the two acceptor molecules.

^cInteraction energy of X₂-CO₂ subtract interaction energy of two times the X-CO₂ interaction energy.

contrast we find that the R(C=O)_b distance for X₂-CO₂ is actually contracted as compared to R(C=O) in CO₂ monomer. We attribute this result to electron density transfer from the non-bonding orbitals of CO₂ to the electron deficient atom of the Lewis acid (Table S1 of the supplementary material).⁴⁴ The value of R(C=O)_b for X₂-CO₂ is again very well correlated with the interaction energy of the complex and is shortest for strongly bonded complexes (Fig. S7 of the supplementary material).⁴⁴

With exception of the BCl₃ results, we find that the cooperative interaction of all X₂-CO₂ complexes is negative. That is the total interaction energy is less than two times the interaction energy of the X-CO₂ complex. This result can be rationalized by considering the atomic charges of oxygen atoms of CO₂ from NBO analysis (Table S1 of the supplementary material).⁴⁴ Upon forming the X-CO₂ complex, the non-bonded oxygen atom of CO₂ becomes less electron rich and is hence less attractive to the electron deficient atom of the second X molecule in X₂-CO₂. The magnitude of the cooperative interaction is well correlated with the interaction energy of X-CO₂ and is large for strongly bound complexes such as (AlF₃)₂-CO₂ and small for weakly bound complexes such

as (CH₄)₂-CO₂ (Fig. S8 of the supplementary material).⁴⁴ We find that the R(O···X) intermolecular distance for X₂-CO₂ is longer than for X-CO₂ and this difference can be thought of as the primary geometric effect of the cooperative interactions. The difference between R(O···X) for X₂-CO₂ and X-CO₂ correlates reasonably well with the magnitude of the cooperative interaction (Fig. S9 of the supplementary material).⁴⁴ This correlation is more pronounced if the results of the very strongly bonded lithium and aluminum hydrides and halides are excluded (Fig. S10 of the supplementary material).⁴⁴

The optimized R(X···X) distances for X₂-CO₂ shown in Table II represent the optimal dimensions for a CO₂ adsorption site based on two equivalent electron deficient atoms through O···X intermolecular interactions. We find that there is considerable variation in the R(X···X) distance even for the same atom type (H, Li, B, Al) and hence it is not reasonable to generalize the optimal dimensions of an adsorption site based purely on the immediate atom of interaction O···X. For example, R(X···X) is 6.395 Å for HF₂-CO₂ and 7.815 Å for (CH₄)₂-CO₂ despite both molecules binding through an electron deficient hydrogen atom.

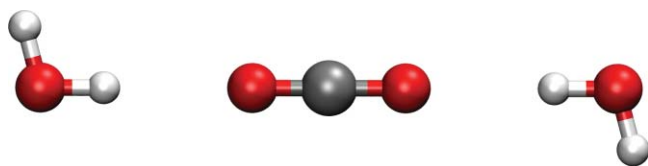


FIG. 2. The CCSD(T)-F12a/VDZ-F12 optimized geometry of (H₂O)₂-CO₂.

CO₂-Lewis base complexes

In Table III, we present CCSD(T)-F12a/VDZ-F12 interaction energies, optimized intermolecular distances and the OCO angle of CO₂ for a series of CO₂-Y complexes. We consider 29 different Lewis base molecules that bind to CO₂ via C···Y interactions involving seven different electron rich atoms (C, N, O, F, P, S, and Cl). Each complex adopts

TABLE III. CCSD(T)-F12a/VDZ-F12 interaction energies (in kJ mol^{-1}) and selected geometric parameters (in \AA and degrees) for a series of CO_2 -Lewis base complexes.

Molecule	Int. energy	$R(\text{C}\cdots\text{Y})^a$	$\theta(\text{OCO})$	Molecule	Int. energy	$R(\text{C}\cdots\text{Y})^a$	$\theta(\text{OCO})$
C-donor							
$\text{C}_3\text{H}_4\text{N}_2^b$	19.2	2.900	175.6				
HNC	8.7	3.117	178.5				
N-donor				P-donor			
$\text{C}_5\text{H}_5\text{N}^b$	18.5	2.751	176.3				
$\text{N}(\text{CH}_3)_3^b$	18.3	2.778	176.3				
$\text{C}_4\text{H}_4\text{N}_2^b$	16.6	2.787	177.3				
NH_3^b	12.8	2.926	177.5	PH ₃	6.3	3.536	179.2
CH_3CN	10.6	2.936	178.1	HCP	2.3	3.670	180.1
HNC	8.9	2.976	178.5				
FCN	8.4	2.981	178.7				
CH_2N_2	7.6	2.967	179.1				
O-donor				S-donor			
$\text{O}(\text{CH}_3)_2^b$	17.2	2.660	177.6				
OPH_3	13.6	2.756	177.6	$\text{C}_4\text{H}_4\text{S}^a$	6.3	3.536	179.7
$\text{C}_4\text{H}_4\text{O}^b$	12.5	2.760	178.8				
H_2O	12.4	2.761	178.2	CH_2S	2.3	3.387	179.9
$(\text{CH}_3)_2\text{CO}$	12.1	2.765	178.2				
CH_2O	9.8	2.811	178.6				
OPF_3	9.4	2.843	178.6				
CF_2O	7.0	2.891	179.2				
CH_2CO	6.8	2.901	179.2				
F-donor				Cl-donor			
LiF	20.6	2.565	175.5	LiCl	10.7	3.228	178.0
CH_3F	7.1	2.825	179.0	CH_3Cl	3.2	3.430	179.8
HF	5.6	2.874	179.2	HCl	1.8	3.527	180.1

^aDistance from the electron deficient carbon atom of CO_2 to the electron rich atom of the donor molecule.

^bHydrogen atoms adjacent to the primary interaction site permit additional hydrogen bonding interactions to the oxygen atoms of CO_2 .

either a symmetric “t-shape” structure with both $\text{C}=\text{O}$ bonds of CO_2 equivalent (e.g., $\text{C}_3\text{H}_4\text{N}_2$) or an asymmetric “t-shape” structure with the two $\text{C}=\text{O}$ bonds approximately equivalent [e.g., $\text{N}(\text{CH}_3)_3$]. In Fig. 3, we show a representative image of the CO_2 - $\text{C}_5\text{H}_5\text{N}$ complex with the optimized geometries of all other CO_2 -Y complexes given in Figs. S11-S13 of the supplementary material.⁴⁴

It is worth noting that many of the complexes that have large interaction energies already exhibit cooperative intermolecular interactions via hydrogen bonding ($\text{OCO}\cdots\text{H}$) to hydrogen atoms adjacent to the electron rich atom. For example, $\text{C}_3\text{H}_4\text{N}_2$, $\text{C}_5\text{H}_5\text{N}$, $\text{N}(\text{CH}_3)_3$, NH_3 , $\text{C}_4\text{H}_4\text{N}_2$, $\text{O}(\text{CH}_3)_2$, and $\text{C}_4\text{H}_4\text{O}$. This perhaps complicates the interpretation of the strength of the “cooperative interactions” in Table IV (*vide infra*) as the net effect of simultaneous $\text{OCO}\cdots\text{H}$ and $\text{O}\cdots\text{X}$ interactions will likely result in a small positive cooperative effect (Table II). As expected, we find that the interaction energies of the complexes involving second row electron rich atoms (P, S, Cl) are generally not as strong as their first row equivalents. This suggests that first row electron rich atoms are a better choice for design of an adsorption site that strongly binds CO_2 via the electron deficient central carbon atom.

Overall, there are modest changes in the geometric parameters of CO_2 upon formation of the CO_2 -Y complexes.

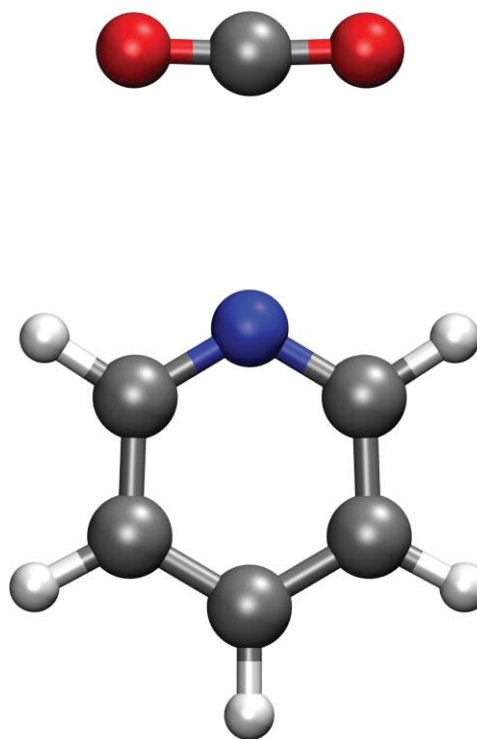


FIG. 3. The CCSD(T)-F12a/VDZ-F12 optimized geometry of CO_2 - $\text{C}_5\text{H}_5\text{N}$.

TABLE IV. CCSD(T)-F12a/VDZ-F12 interaction energies (in kJ mol⁻¹) and selected geometric parameters (in Å) for cooperatively bonded complexes of the (HF)₂-CO₂-Y.

Molecule	Int. energy	Coop. int. ^a	Enhancement ^b	ΔR (O···H) ^c	ΔR (C···Y) ^d
LiF	66.3	+25.5	63%	-0.137	-0.148
C ₃ H ₄ N ₂	58.8	+19.3	49%	-0.142	-0.175
C ₅ H ₅ N	52.1	+13.4	34%	-0.109	-0.110
LiCl	48.4	+17.5	57%	-0.080	-0.171
O(CH ₃) ₂	47.7	+10.3	28%	-0.090	-0.072
C ₄ H ₄ N ₂	46.9	+10.1	27%	-0.098	-0.086
(CH ₃) ₂ CO	45.4	+13.1	41%	-0.078	-0.115
H ₂ O	42.4	+9.8	30%	-0.072	-0.078
CH ₂ O	40.1	+10.1	34%	-0.063	-0.104
HCN	39.5	+10.4	36%	-0.061	-0.121
HNC	39.0	+10.2	35%	-0.060	-0.123
C ₄ H ₄ O	38.8	+6.1	19%	-0.067	-0.054
FCN	37.9	+9.3	33%	-0.058	-0.116
CH ₂ N ₂	34.6	+8.6	33%	-0.047	-0.096
CF ₂ O	33.3	+6.1	22%	-0.044	-0.091
CH ₂ CO	33.2	+7.3	28%	-0.042	-0.098
HF	32.6	+6.8	26%	-0.041	-0.109
C ₄ H ₄ S	29.9	+3.4	13%	-0.032	-0.247
HCl	23.8	+1.8	8%	-0.004	-0.111
HCP	22.8	+0.4	2%	-0.003	-0.034

^aThe interaction energy of (HF)₂-CO₂-Y subtract the interaction energy of (HF)₂-CO₂ and CO₂-Y.

^bPercentage increase in the interaction energy of (HF)₂-CO₂-Y compared with the interaction energy of CO₂-Y.

^cR(O···H) of (HF)₂-CO₂-Y subtract R(O···H) of (HF)₂-CO₂.

^dR(C···Y) of (HF)₂-CO₂-Y subtract R(C···Y) of CO₂-Y.

We find that the R(C=O) bond distance becomes slightly elongated and this is attributed to electron density from the Lewis base transferring into anti-bonding CO₂ orbitals (Table S2 of the supplementary material).⁴⁴ With exception of CO₂-HCP and CO₂-HCl, we find that the obtuse angle (< 180°) of CO₂ is orientated on the opposite side of CO₂ to Y. Even for the strongest Lewis bases, we find that θ(OCO) is > 175°, which indicates that CO₂ should remain largely linear upon adsorption in MOF materials via C···Y interactions. This result corroborates recent findings by Wu *et al.* that large apparent variations in the value of θ(OCO) for MOF materials with CO₂ adsorbed are due to the high orientational disorder of CO₂ in the crystal structures rather than any actual chemical changes in CO₂.⁴⁶ We find that the θ(OCO) angle exhibits a clear correlation with the interaction energy, whereas the R(C=O) bond distance exhibits a weaker correlation (Figs. S14 and S15 of the supplementary material).⁴⁴

Similar to what was observed in Table II, there is significant variation in the intermolecular distance R(C···Y) for a given electron rich atom. For example, R(C···Y) is 2.660 Å for CO₂-O(CH₃)₂ and 2.901 Å for CO₂-CH₂CO despite both molecules binding through an electron rich oxygen atom. It follows that the optimal R(C···Y) distance for constructing a CO₂ adsorption site cannot be generalized based on the immediate atom of interaction.

TABLE V. CCSD(T)-F12a/VDZ-F12 interaction energies (in kJ mol⁻¹) and selected geometric parameters (in Å) for cooperatively bonded complexes of the type X₂-CO₂-CH₂O.

Molecule	Int. energy	Coop. int. ^a	Enhancement ^b	ΔR (O···X) ^c	ΔR (C···O) ^d
AlF ₃	105.9	+28.3	37%	-0.056	-0.291
LiCl	83.7	+30.7	58%	-0.062	-0.211
LiH	76.5	+26.9	54%	-0.059	-0.198
LiF	74.4	+26.9	57%	-0.062	-0.192
AlH ₃	64.0	+17.5	38%	-0.108	-0.211
HNC	41.1	+11.7	40%	-0.073	-0.101
HF	40.1	+10.1	34%	-0.063	-0.104
HCOOH	35.3	+6.7	24%	-0.062	-0.061
BF ₃	34.6	+6.3	22%	-0.066	-0.085
HCN	32.5	+9.2	39%	-0.082	-0.072
OH	31.7	+7.6	32%	-0.071	-0.073
BH ₃	31.0	+5.2	20%	-0.085	-0.080
HCl	31.0	+7.0	29%	-0.073	-0.073
CH ₃ OH	29.8	+6.6	28%	-0.059	-0.082
H ₂ O	28.9	+6.6	29%	-0.062	-0.080
CH ₄	14.1	+0.9	7%	-0.050	-0.013

^aThe interaction energy of X₂-CO₂-CH₂O subtract the interaction energy of X₂-CO₂ and CO₂-CH₂O.

^bPercentage increase in the interaction energy of X₂-CO₂-CH₂O compared with the interaction energy of X₂CO₂.

^cR(O···X) of X₂-CO₂-CH₂O subtract R(O···X) of X₂-CO₂.

^dR(C···O) of X₂-CO₂-CH₂O subtract R(C···O) of CO₂-CH₂O.

Cooperative complexes

In Tables IV and V, we present CCSD(T)-F12a/VDZ-F12 results for two sets of cooperative complexes, namely, (HF)₂-CO₂-Y and X₂-CO₂-CH₂O. It is not computationally practicable to evaluate all possible combinations of X and Y considered in this investigation with the CCSD(T)-F12a/VDZ-F12 method. Hence, to illustrate the effects of cooperative intermolecular interactions we consider just one electron acceptor (HF) with various electron donors and one electron donor (CH₂O) with various electron acceptors. The linear structure of the (HF)₂-CO₂ complex and the perpendicular orientation of CH₂O relative to the “t-shape” plane of the CO₂-CH₂O complex, minimize potentially confounding X···Y intermolecular interactions. The geometry of (HF)₂-CO₂-CH₂O is shown in Fig. 4 to illustrate the general structure of the cooperative complexes considered with the optimized geometries of all other X₂-CO₂-CH₂O and (HF)₂-CO₂-Y complexes given in Figs. S16-S20 of the supplementary material.⁴⁴

To limit the computational expense of the (HF)₂-CO₂-Y calculations, we consider only electron donor molecules that permit C_{2v} symmetry for the cooperative complex. We find that the total interaction energy of these complexes varies from 66.3 kJ mol⁻¹ with the strong electron donor LiF to 22.8 kJ mol⁻¹ with the weak electron donor HCP. This wide range is important as it shows that the adsorption energy for a X₂-CO₂-Y type adsorption site can be readily tuned for optimal adsorption/desorption processes by varying the electron donor functional group. We find that the cooperative interactions of all (HF)₂-CO₂-Y complexes are positive, with the total interaction energy larger than the sum of the individual

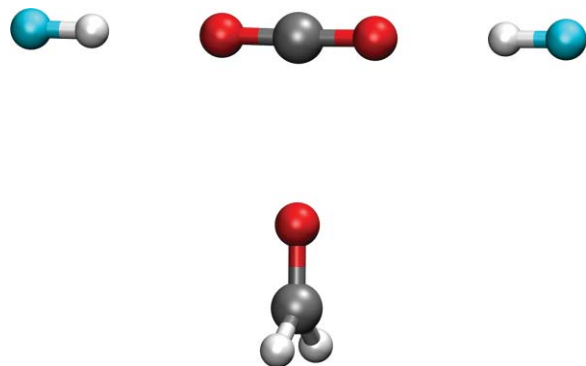


FIG. 4. The CCSD(T)-F12a/VDZ-F12 optimized geometry of $(\text{HF})_2\text{-CO}_2\text{-CH}_2\text{O}$.

interaction energies of the electron donor ($\text{CO}_2\text{-Y}$) and electron acceptor $[(\text{HF})_2\text{-CO}_2]$ complexes. Again, we rationalize this result by considering the NBO atomic charges on CO_2 (Table S3 of the supplementary material).⁴⁴ The central carbon atom of $(\text{HF})_2\text{-CO}_2$ is more electron deficient than in CO_2 monomer and hence is more attractive to the electron rich atom of Y. Correspondingly, the terminal oxygen atoms of the $\text{CO}_2\text{-Y}$ complex are more electron rich than in CO_2 and hence are more attractive to the electron deficient hydrogen atoms of HF.

In general, we find that the magnitude of the cooperative interactions for $(\text{HF})_2\text{-CO}_2\text{-Y}$ is well correlated with total interaction energy and is large for the more strongly bound complexes and small for the more weakly bound complexes (Fig. S21 of the supplementary material).⁴⁴ The primary geometric effects of these cooperative interactions is to decrease both the $R(\text{O}\cdots\text{H})$ and $R(\text{C}\cdots\text{Y})$ intermolecular distances for $(\text{HF})_2\text{-CO}_2\text{-Y}$ as compared to the respective $(\text{HF})_2\text{-CO}_2$ and $\text{CO}_2\text{-Y}$ complexes. We find that $\Delta R(\text{O}\cdots\text{H})$ correlates strongly with the magnitude of the cooperative interactions, whereas the correlation between $\Delta R(\text{C}\cdots\text{Y})$ is much weaker (Figs. S22-S24 of the supplementary material).⁴⁴

For the $\text{X}_2\text{-CO}_2\text{-CH}_2\text{O}$ complexes, we consider all electron acceptors from Table II except for $\text{C}_4\text{H}_5\text{N}$, C_6H_6 , BCl_3 , and AlCl_3 as these were too computationally demanding with our present resources with the CCSD(T)-F12a/VDZ-F12 method. We again assume that the diatomic and linear X molecules bind CO_2 in a linear fashion with $\theta(\text{C}=\text{O}\cdots\text{X})$ equal to 180° . For the polyatomic hydrogen bonding molecules, we also restrict the hydrogen bond to be linear and orientate the two X molecules to be on the opposite side to the Y molecule. Note that in this orientation, the two X molecules are on the same side as each other; whereas in Table II, the two X molecules were on opposite sides. For the boron and aluminum hydrides and halides, the $\theta(\text{C}=\text{O}\cdots\text{B})$ or $\theta(\text{C}=\text{O}\cdots\text{Al})$ angle is also restricted to be linear with the two electron deficient groups orientated in an eclipsed position with the in-plane hydrogen or halide *trans* to the CH_2O group to minimize potentially confounding $\text{X}\cdots\text{Y}$ intermolecular interactions. We have reoptimized the geometries of these “same side” and “eclipsed” $\text{X}_2\text{-CO}_2$ complexes and use these reoptimized results when determining the magnitude of the cooperative interactions and change in $R(\text{O}\cdots\text{X})$ and $R(\text{C}\cdots\text{Y})$ for $\text{X}_2\text{-CO}_2\text{-CH}_2\text{O}$.

We find that the total interaction energy of the $\text{X}_2\text{-CO}_2\text{-CH}_2\text{O}$ complexes varies from 105.9 kJ mol^{-1} with the strong electron acceptor AlF_3 to 14.1 kJ mol^{-1} with the weak electron acceptor CH_4 . The cooperative interactions of all $\text{X}_2\text{-CO}_2\text{-CH}_2\text{O}$ complexes are positive, with the total interaction energy larger than the sum of the interaction energies of the constituent complexes. Similar to the $(\text{HF})_2\text{-CO}_2\text{-Y}$ results, the strength of the cooperative interactions for the $\text{X}_2\text{-CO}_2\text{-CH}_2\text{O}$ complexes also appears well correlated with the total interaction energy (Fig. S25 of the supplementary material).⁴⁴ These two results are together important as it shows that the magnitude of cooperative interactions affecting CO_2 binding in a potential adsorption site can be tuned via modification of either the electron poor (X) or the electron rich (Y) atoms. Again, the primary effect of these cooperative interactions on the geometry of $\text{X}_2\text{-CO}_2\text{-CH}_2\text{O}$ is to decrease both the $R(\text{O}\cdots\text{X})$ and $R(\text{C}\cdots\text{O})$ intermolecular distances as compared to the respective $\text{X}_2\text{-CO}_2$ and $\text{CO}_2\text{-CH}_2\text{O}$ complexes. Interestingly, we find that there is essentially no correlation between $\Delta R(\text{O}\cdots\text{X})$ and the magnitude of the cooperative interactions whereas the correlation between $\Delta R(\text{C}\cdots\text{O})$ is strong (Figs. S26 and S27 of the supplementary material).⁴⁴

If we consider the intermolecular distances of the $(\text{HF})_2\text{-CO}_2\text{-Y}$ and $\text{X}_2\text{-CO}_2\text{-CH}_2\text{O}$ results collectively, we observe significant variation in the optimal $R(\text{O}\cdots\text{X})$ and $R(\text{C}\cdots\text{Y})$ distances for the different combinations of X and Y. This, in turn, suggests that when designing the optimal adsorption site for CO_2 it is important to consider the effect that cooperative interactions will have on the optimal dimensions of that site. It is worth noting that even if an adsorption site is not deliberately designed to exploit “cooperative interactions” these may still be present from adjacent atoms with potentially unwanted effects.

CONCLUSIONS

We have calculated the optimized geometry and interaction energy for over 100 different complexes containing CO_2 with various combinations of Lewis acids and bases using the explicitly correlated CCSD(T)-F12a/VDZ-F12 method. Our initial calculations on the model complexes $(\text{HF})_n\text{-CO}_2$ (where $n = 1\text{-}4,6$) showed that this method generally gave interaction energies and the magnitude of the cooperative effect to within a few tenths of a kJ mol^{-1} of the CCSD(T)-F12b/VQZ-F12 results.

Overall, we observe only modest changes in the geometric parameters of CO_2 upon formation of the various complexes considered in this work. This result indicates that the geometry of CO_2 adsorbed in a MOF material should be similar to that of CO_2 monomer. We find that when CO_2 interacts with a single electron deficient atom via one of the terminal oxygen atoms (X-CO_2), the bonded $R(\text{C}=\text{O}_b)$ distance slightly elongates and the free $R(\text{C}=\text{O}_f)$ distance slightly contracts. However, when CO_2 interacts simultaneously with two electron deficient atoms via both terminal oxygen atoms ($\text{X}_2\text{-CO}_2$), the two bonded $R(\text{C}=\text{O}_b)$ distances slightly contract. For the $\text{CO}_2\text{-Lewis base}$ complexes, we find that complexation causes a slight increase in the CO_2 bond distances

and a minor deviation from linearity ($< 5^\circ$) in the $\theta(\text{OCO})$ angle.

The interaction energy of the $\text{X}_2\text{-CO}_2$ complex is found to be less than twice the interaction energy of the X-CO_2 complex. In addition, the $\text{R}(\text{O}\cdots\text{X})$ intermolecular distance for $\text{X}_2\text{-CO}_2$ is found to be longer than for X-CO_2 . These results are attributed to a decrease in the electron density of the non-bonded oxygen atom of X-CO_2 as compared to CO_2 monomer, which in turn makes the non-bonded oxygen atom less attractive to a second Lewis acid molecule.

We investigated two series of cooperative complexes [$(\text{HF})_2\text{-CO}_2\text{-Y}$ and $\text{X}_2\text{-CO}_2\text{-CH}_2\text{O}$] that exhibit simultaneous $\text{CO}_2\text{-Lewis acid} (\text{O}\cdots\text{X})$ and $\text{CO}_2\text{-Lewis base} (\text{C}\cdots\text{Y})$ intermolecular interactions. The interaction energy of these cooperative complexes was found to be larger than the sum of the interaction energies of the constituent $\text{X}_2\text{-CO}_2$ and $\text{CO}_2\text{-Y}$ complexes. Furthermore, the $\text{R}(\text{O}\cdots\text{X})$ and $\text{R}(\text{C}\cdots\text{Y})$ intermolecular distances of the cooperative complexes were found to be shorter than the corresponding intermolecular distances of the constituent complexes. We rationalize these results by considering that formation of $(\text{HF})_2\text{-CO}_2$ reduces the electron density on the central carbon atom of CO_2 making it more attractive to a Lewis base, whereas formation of $\text{CO}_2\text{-CH}_2\text{O}$ increases the electron density on the terminal oxygen atoms of CO_2 making them more attractive to a Lewis acid. We find that the magnitude of this cooperative enhancement of the interaction energy and contraction of the intermolecular distances are correlated to the strength of the various Lewis acids and Lewis bases involved. It follows that the total adsorption strength and optimal dimensions of a MOF CO_2 binding site can in principle be tuned via modification of either electron deficient (X) or electron rich (Y) atoms.

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