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First-principles-guided design of ionic liquids for CO₂ capture†

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The identification of sorbents that combine selectively and reversibly with CO₂ is essential for efficient and economical abatement of ever-increasing CO₂ emissions. Room temperature ionic liquids (ILs) are a promising class of potential absorbents, especially when modified to chemically combine with CO₂. In this perspective we describe the evolution of IL-based CO₂ capture chemistries over the last ten years and in particular the important role that first principles simulations have played in helping guide those developments. Current anion-functionalized ILs achieve high CO₂ capture efficiencies tailorable to a wide range of separation conditions and avoid the viscosity problems that plagued the earliest amine-functionalized, CO₂-reactive ILs. Further progress is needed to develop ILs able to meet all the requirements of a CO₂ separation system, and simulations will play a central role in those developments.

1 Introduction

Because they are cheap and abundant, fossil fuels will continue to be the primary source of energy for society for the foreseeable future, and combustion of those fossil fuels will thus

continue to produce large amounts of CO₂.¹ Carbon capture and sequestration (CCS) is a viable strategy for limiting emissions of CO₂ to the atmosphere, but cost-effective CCS depends on the discovery of optimal CO₂ sorbents.^{2–5} Large stationary CO₂ emitters (*e.g.* power plants) are the most likely targets for CCS.⁶ Stationary-source flue gas typically contains on the order of 10% CO₂ at ambient pressure and near-ambient pressure. The affinity of common organic physical absorbents for CO₂ is too modest for practical separations under these conditions,⁵ so that liquid sorbents are generally sought that exhibit some chemical reactivity towards CO₂.

The practical relevance of CO₂ binding to the performance of a CO₂ capture system is easy to understand. Imagine a

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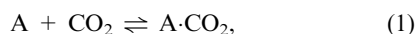
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hypothetical adsorbent A that reacts reversibly and selectively with CO₂ and follows a Langmuir-type isotherm:



$$K(T) = e^{-\Delta G^\circ(T)/RT} \approx \frac{x_A \text{CO}_2}{x_A P_{\text{CO}_2}} \quad (2)$$

CO₂ separations can be affected by swinging this equilibrium to the right and left by modulating the temperature T and pressure P_{CO_2} . For example, consider a temperature-swing absorption cycle in which CO₂ is selectively absorbed from a flue gas at 0.13 bar and 40 °C and desorbed at 1.0 bar and 110 °C.⁷ Fig. 1 compares the performance of three hypothetical sorbents A with identical standard entropies of absorption and enthalpies of absorption of -70 , -55 , and -40 kJ mol⁻¹. The -70 kJ mol⁻¹ sorbent is not an efficient separating agent under these conditions: the sorbent is saturated with one mole of CO₂ for each mole of sorbent under the absorber condition, but this ratio decreases only to 0.9 under the desorber condition, so that only 0.1 mole of CO₂ is transferred for each mole of sorbent (Fig. 1b). The -40 kJ mol⁻¹ sorbent has the opposite problem: the mole ratio of CO₂ to sorbent is small both under the absorber and desorber conditions, and again the effectiveness of the sorbent in transporting CO₂ between the two conditions is low. An intermediate binding sorbent fairs much better. The -55 kJ mol⁻¹ sorbent takes up approximately 0.5 mole of CO₂ per mole of sorbent under the absorber condition, decreasing to a ratio of 0.1 under the desorber condition, for a net effectiveness of 0.4 mole of CO₂ per mole of sorbent. Fig. 1b shows that this effectiveness of the sorbent in transferring CO₂ for the conditions considered here is maximized at an adsorption enthalpy of about -60 kJ mol⁻¹.

Clearly, many other features of a liquid sorbent play into its suitability as a CO₂ separating agent: high selectivity against other majority and minority gases, rapid kinetics of uptake and release, favorable physical properties, low volatility, low corrosivity, *etc.* And the ultimate performance measure is the overall energy efficiency of separation, for which the equilibrium CO₂ transfer efficiency shown in Fig. 1b is only an approximate surrogate. These issues notwithstanding, the basic absorption

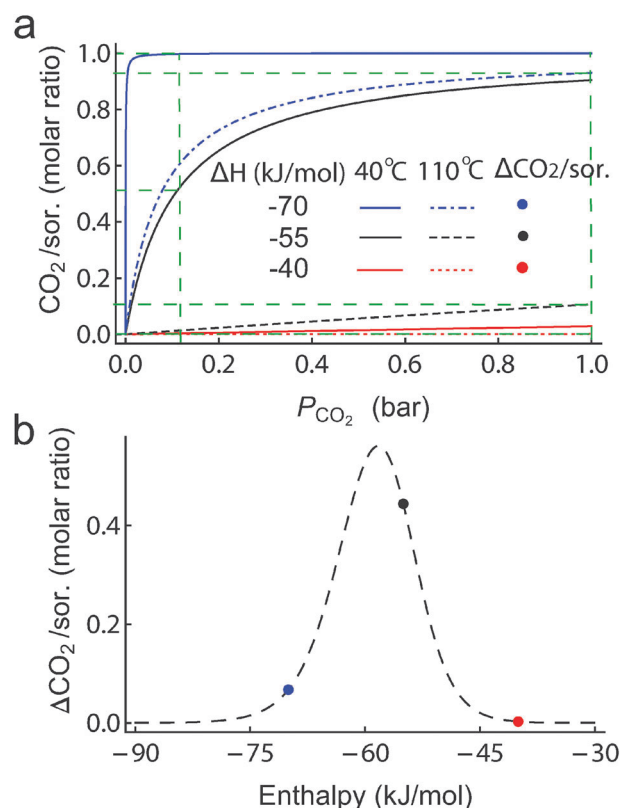


Fig. 1 Langmuir absorption isotherms and their consequences for CO₂ separations. (a) 40° and 110° isotherms of three hypothetical sorbents with CO₂ reaction enthalpies of -70 , -55 , and -40 kJ mol⁻¹. Vertical green dashed lines indicate representative adsorber and desorber pressures. Horizontal green dashed lines indicate the absorption molar ratio at the corresponding pressures. (b) Net CO₂ transfer efficiency vs. reaction enthalpy.

chemistry of CO₂ is central to effective CO₂ separations, and the ability to control this chemistry is the key to optimal separation systems. In fact, process simulations suggest that the “volcano” behavior shown in Fig. 1b persists even when optimizing the energy efficiency of the entire separation process.⁸

Room temperature ionic liquids (ILs) are a promising platform for developing highly controllable CO₂ sorbents.^{7,9–18} ILs are salts of bulky cations and/or anions that have melting points below ambient.^{10,19} ILs intrinsically have very low volatility,^{10,19} high thermostability, and low corrosivity. This low corrosivity can be compromised by the release of decomposition products (*e.g.* sulfuric acid, phosphoric acid) resulting from reactions of H₂O with ILs.²⁰ Nonetheless, this can be avoided by choosing proper cations and anions. Further, because ILs can be prepared from a wide range of cations and anions, they provide a virtually unlimited space for designer solvents, in particular for CO₂ separations.⁷ This vast design space presents both an opportunity for identifying high performing sorbents and a challenge in searching for them.

Common ILs do preferentially absorb CO₂ over N₂ and O₂, similar to that of other physical sorbents.^{11,21–23} However, the CO₂ solubility in these ILs is low under ambient conditions, as only physical absorption takes place. For instance, a typical pre-combustion CO₂ sorbent, 1-hexyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide absorbs a 3% mole ratio of



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CO₂ at ~1 bar and room temperature.²² Thus high solubility under flue gas conditions can only be achieved using chemical absorption. ILs specifically tailored to chemically combine with CO₂ were first described in 2002²⁴ and since that time significant advances have been made in viable IL-based sorbents. Computational chemistry methods have proved to be invaluable in guiding the search and in understanding CO₂-IL chemistry.^{25–29} In this perspective, we describe the role that simulation has played in some of the significant milestones in this discovery process, from the first “task specific” ionic liquids inspired by analogous aqueous amine chemistry to the Aprotic Heterocyclic Anions (AHAs) ILs sorbent. We also discuss issues that impact practical applications of ILs. Finally, we envision the next generation ILs for CO₂ capture.

2 Simulations in the IL–CO₂ system

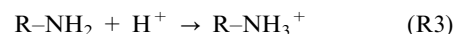
Classical atomistic simulations can provide fast and reliable thermodynamic and kinetic property predictions as well as mechanistic insights into the physical interactions of ionic liquids with gases. Monte Carlo (MC) simulations based on classical force fields have been shown to accurately reproduce the physical solubility of gases in IL sorbents over wide ranges of temperature and pressure.²⁵ Molecular dynamics (MD) simulations show that CO₂ tends to interact most strongly with the anions, which thus have the largest impact on solubility.^{21,30–34} Similar simulations of the liquid–vapor interface show that a CO₂ layer first accumulates at the IL surface due to favorable trade-offs between anion binding with CO₂ and with cations. Surface-accumulated CO₂ molecules then diffuse into the bulk.³⁵ While these classical simulations provide many valuable insights, new force fields must be parameterized for each new IL–gas pair. Further, common functional forms do not lend themselves to describing chemical bond formation or breaking. Rapid progress is being made in “reactive” force fields, but these require even more extensive parameterizations to the specific type of reaction.^{36,37}

Ab initio electronic structure calculations provide the most directly predictive description of chemically reactive systems.^{38–40} With the input only of the atoms that make up the system, molecular structure, spectroscopy, reaction energies, and even reaction rates can today be determined quite accurately for isolated systems. Condensed-phase problems, such as CO₂ combining with a reactive IL, can be described inexpensively using continuum solvation models^{29,41,42} or at greater cost through various *ab initio* and hybrid explicit solvation models. As we have shown, considerable progress in reactive IL design can be made even when neglecting these solvation effects.^{26,28,29}

3 Amine-inspired reactive ionic liquids

CO₂ is a Lewis acid, and thus chemically reactive absorbents (A in eqn (1)) are typically basic. Aqueous alkanolamines, in particular monoethanolamine (MEA),^{43–47} are the most widely studied and used chemical CO₂ absorbents. CO₂ can combine with an amine lone pair to form an N–C bond; to preserve the preferred valency on all atoms, an amine proton is transferred to CO₂ to form a carbamic acid (R1). Depending on the surrounding environment, this carbamic acid may prefer to

deprotonate to a carbamate (R2), protonating another amine in the absence of any other Brønsted base (R3).



If all reactions go to completion, then, the overall amine-to-CO₂ stoichiometry is two to one:



Details vary from amine to amine and with specific reaction conditions.^{3,43–47} The promise of improving upon this chemistry, by increasing the uptake of CO₂ per functional group, eliminating the volatile aqueous solvent, and providing direct control over the reaction equilibria, has inspired the search for reactive ILs.

Davis *et al.*²⁴ were the first to modify ILs with a pendant amine group in an attempt to introduce chemical reactivity with CO₂. An IL in which an amine group was tethered to the butyl chain of an imidazolium-based cation absorbed nearly 0.5 mole of CO₂ per functional group when equilibrated with dry CO₂ at 1 atm and room temperature, consistent with the stoichiometry of R4. Vibrational spectroscopy confirmed the formation of a carbamate. CO₂ could be released by heating to 80–100 °C under vacuum, and multiple cycles did not reduce the CO₂ uptake capacity. Subsequent work by Galansanchez *et al.* further showed that a primary amine functional group was more effective than a tertiary amine or hydroxyl group in enhancing CO₂ uptake.⁴⁸ Later Zhang and co-workers coated amino-acid based ILs on a porous silica gel support and found efficient and reversible CO₂ uptake to >0.5 molar ratio.⁴⁹ The high viscosity of the product makes it difficult to achieve the equilibrium CO₂ uptake unless water is added to relieve the situation.⁵⁰

These early functionalized ILs can be viewed as primary amines RNH₂ with anionic or cationic substituents R. To what extent do variations in R influence the strength of the amine–CO₂ chemical bond and thus the theoretical CO₂ uptake? *Ab initio* calculations are well suited to answering such questions in a systematic way. We used an *ab initio* variant, hybrid density functional theory (DFT), to determine the relative energies of R1–R3 for neutral R groups including alkyl, hydroxyl, carbonyl, carboxyl, and fluoro, including appropriate averaging over conformational degrees of freedom and inclusion of finite temperature corrections.²⁷ For example, the structure of acetamide (CH₃CONH₂) and its carbamic acid products with CO₂ (R1) were calculated at the B3LYP^{51,52} level using a 6-311+ + G(d,p) basis set⁵³ (Fig. 2).²⁷ The CH₃CONHCOOH product exhibits two major stable conformers that differ in the orientation of the carbamic acid OH group. Carbamic acid formation is overall endothermic, less so in the *cis* isomer (29 kJ mol^{–1}) than the *trans* (54 kJ mol^{–1}).²⁷

These results are typical of the primary amines in R1. The most stable conformers have a planar carbamic acid group to maximize conjugation across the newly formed N–C bond. Intramolecular hydrogen bonding provides additional stability. In Fig. 2, both the *cis* and *trans* conformers exhibit some degree of π conjugation, but the 25 kJ mol^{–1} greater stability

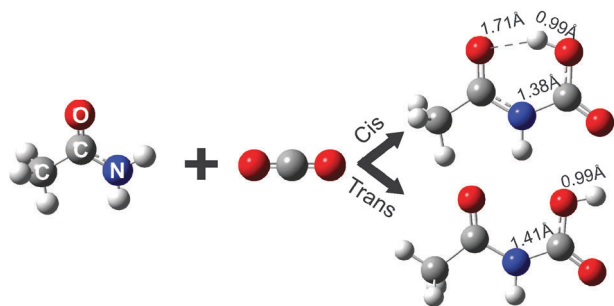


Fig. 2 DFT-calculated structures of acetamide and its reaction products with CO_2 .²⁷

of the *cis* conformer is reflected in a shorter N–C bond (1.38 Å vs. 1.41 Å). These distances are slightly shorter than typical C–N single bonds (~ 1.47 Å in amines) and are a little bit longer than double bonds (~ 1.28 Å in imines), which confirms the conjugation across the N–C bond. The intramolecular hydrogen bond (1.71 Å, dashed line) completes a six-membered ring in the *cis* conformer. The B3LYP calculations show that electron-donating R groups, such as alkyls, make the carbamic acid reaction more exothermic and that electron-withdrawing groups, such as halogens, make it more endothermic. Overall reaction energies span 50 kJ mol^{-1} .

In contrast to the carbamic acid formation reaction (R1), electron-withdrawing groups tend to promote acid deprotonation (R2). Deprotonation energies span a window of about 60 kJ mol^{-1} , similar to R1. Amine protonation R3 is even more sensitive to functional groups; the computed range of reaction energies is about 200 kJ mol^{-1} . Again, electron donors enhance the reactivity and electron acceptors reduce it. In fact, the calculations suggest that the Brønsted basicity (R3) and Lewis basicity (R1) are nearly independent, and that these two could be tuned independently to control the overall reaction energy (R4). Variations in the R group thus primarily influence reaction energies through local, inductive effects and intra (or inter) molecular hydrogen bonding. Absolute reaction energies in a functionalized IL will depend sensitively on the balance of reaction products and on their interactions with the IL solvent. The complexity of this primary amine chemistry is a disadvantage in its application in ILs. Similar observations of the substitution effect on the CO_2 reaction were made by Johnson *et al.* both by simulations and experiments.⁴² In their study, the amine– CO_2 reaction energy to form carbamate and carbamic acid was correlated with the corresponding Brønsted basicity of the amine. Due to the different sensitivity in the basicity–reactivity dependence of the two species, by adjusting functional groups, for amines with very weak basicity, carbamic acid formation may be favored over the carbamate and therefore a 1 : 1 reaction ratio could be achieved.

The choice to amine-functionalize the cation or the anion portion of an ionic liquid is a design degree of freedom unique to ionic liquids. Does this choice have an influence on reaction products? To address this question, we contrasted the computed carbamate formation (R1) and deprotonation (R2) energies of two amine-functionalized cations and anions with that of MEA.²⁶ Results are summarized in Fig. 3, and reaction

	carbamic acid formation energy (kJ/mol)	deprotonation energy (kJ/mol)
1-aminomethylpyridinium	21	-330
4-aminomethylpyridinium	13	-351
MEA	0	0
glycine anion	-63	368
taurine anion	-33	293

Fig. 3 The carbamic formation reaction (R1) and the deprotonation reaction (R2) of selected amine-functionalized IL ions. Boltzmann-averaged 298 K reaction energies referenced to MEA are shown between structures.²⁶

energies are reported relative to MEA. All of these species are primary amines bound to a RCH_2 fragment, and this chemical similarity causes the carbamic acid formation energy to span a relatively narrow range of about 84 kJ mol^{-1} . The anions tend to bind the carbamic acid product more strongly than the cations, especially in cases in which intramolecular hydrogen bonding is possible. In contrast, the deprotonation energies span a very wide range of about 720 kJ mol^{-1} . The cations are strongly biased towards deprotonation due to the electrostatic stability of the product zwitterion. The anions are strongly biased against deprotonation, due to the instability of the product dianion. The results suggest that anion-functionalized ILs will be biased towards a 1 : 1 amine : CO_2 stoichiometry through reaction R1, while cation-functionalized ones are biased towards the 2 : 1 stoichiometry arising from reactions R2 and R3.

These gas-phase calculations surely exaggerate the importance of electrostatics in controlling product selectivity, but nonetheless the predictions are borne out by experiment. The CO_2 uptake isotherms of the two anion-functionalized ionic liquids trihexyl(tetradecyl)phosphonium proline ([P66614][Pro]) and methionate ([P66614][Met]) (Fig. 4) approach 1 : 1 CO_2 uptake at room temperature and about 1 bar.²⁸ The B3LYP/6-311G++(d,p) calculations predict proline and methionate reaction enthalpies with CO_2 (reaction R1) under standard conditions of -71 and -55 kJ mol^{-1} . More sophisticated G3⁵⁴ and G4⁵⁵ calculations predict slightly more exothermic reactions. Calorimetric enthalpies at 25°C and 2–3 bar CO_2 were measured to be -80 and -64 kJ mol^{-1} , in surprisingly good agreement with the calculations, both in terms of relative and absolute values. This good agreement reflects a reaction that is dominated by an anion chemistry that is well represented by its gas-phase counterpart. The cation only has a secondary effect^{25,30} on CO_2 absorption,

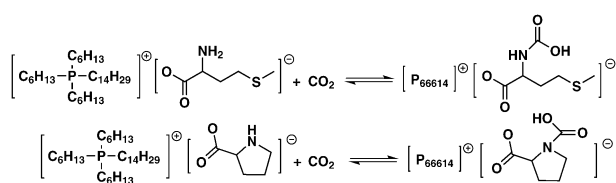


Fig. 4 Reaction schematics for CO_2 with [P66614][methionate] (top) and [P66614][proline] (bottom).²⁸

influencing uptake per mass basis, viscosity and other physical properties. Furthermore, even in the non-reactive ILs cation–CO₂ distances are about 1 Å longer than anion–CO₂ ones.³¹

Similar uptake behavior has since been reported for a larger number of anion-functionalized amino acid ILs.⁵⁰ An unfortunate side-product of the reaction of virtually all amine-functionalized ILs with CO₂ is a precipitous increase in viscosity, so much so that some amino acid ILs actually become solids upon CO₂ absorption.^{24,49,50} Molecular dynamics simulations of a cation-functionalized IL show the presence of an extensive network of hydrogen bonds between amine functionalities that depresses dynamics and increases viscosity.^{56,57} Adding CO₂ exacerbates the slowing of dynamics by one to two orders of magnitude as even more and stronger hydrogen bonds are formed between carbamates and ammoniums. Reducing the number of available hydrogen bonding sites can diminish this viscosity effect. The proline anion has a secondary amine group and thus half as many protons available to participate in hydrogen bonding. As a result, the ([P66614][Pro]) IL exhibits only a small increase in viscosity when combined with CO₂.⁵⁰ Controlling hydrogen bonding is crucial to designing functionalized ILs useful for CO₂ capture.

4 Aprotic heterocyclic anion ILs

More recently, simulations have contributed to the development of a new class of ILs with physical properties and systematically tunable chemical properties more suitable to CO₂ capture. Many of the complications in understanding and difficulty in controlling the amine-based ILs for CO₂ separations stem from the mix of reactions R1–R3. A more desirable chemistry would involve a simple, clean, and reversible 1 : 1 reaction between absorbent and CO₂, like that embodied in reaction R1, and take advantage of the intrinsic basicity of an anion. To avoid the changes in physical properties associated with acidic protons described above, the base should be aprotic, and ideally should contain chemical handles that introduce tunability into the reaction equilibrium. A 1 : 1 acid–base reaction should in principle also promote rapid reaction kinetics.

Common IL anions such as BF₄[−], PF₆[−], *etc.*¹⁶ in general interact weakly with CO₂ to form non-specific physical bonds. Carboxylic anions, like acetates (CH₃CO₂[−]), associate more strongly with CO₂ but offer limited chemical handles for tunability.^{23,58} Another class of ILs originally designed by Jessop *et al.*⁵⁹ showed that organic bases like DBU (1,8-diazabicyclo-[5.4.0]-undec-7-ene) can form ILs with alcohols and the deprotonated alcohol anions react with CO₂. The overall process is reversed when the system is heated or CO₂ is removed. The Dai group extends this idea and achieves over a 1 : 1 absorbent-to-CO₂ molar absorption ratio.^{13,14,60} Strong bases are used to deprotonate alcohols (usually fluorinated) and the alkoxides serve as Lewis bases for bonding with CO₂ (Fig. 5). Calculations by Teague *et al.*⁴¹ show that the binding energy of RO[−]CO₂ chemistry spans a large range, indicating the good reaction tunability. However the use of strong base hinders the application of this oxygen chemistry to CO₂ capture.

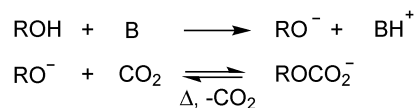


Fig. 5 Reversible CO₂ capture utilizing oxygen chemistry.

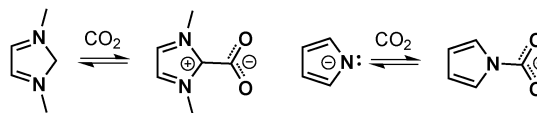


Fig. 6 *N*-heterocyclic carbene (NHC) and aprotic heterocyclic anion reactions with CO₂.²⁹

The neutral nitrogen-heterocyclic carbenes (NHCs) provide inspiration for an alternative IL–CO₂ chemistry that meets the criteria above. As illustrated in Fig. 6, imidazolium-based carbenes were reported in 2004 to react stoichiometrically and reversibly with CO₂ through the carbene center to form a carboxylate.^{61,62} A pyrrolide is an isoelectronic but anionic analog of an NHC (Fig. 6) in which the reactive lone pair is nitrogen-centered, and one might imagine a similar CO₂ chemistry for the two. Calculations confirm this hypothesis. DFT calculations at the B3LYP/6-311G++(d,p) level show that both complexes adopt planar conformations with NHC–CO₂ and pyrrolide–CO₂ bond lengths of 1.55 and 1.53 Å, respectively. The computed pyrrolide–CO₂ bond energy of −99 kJ mol^{−1} is 60 kJ mol^{−1} stronger than the NHC–CO₂ one in gas-phase simulations.

The pyrrolide is essentially a tertiary amine incorporated into an aprotic heterocyclic anion (AHA). The potential advantages of ILs based on the AHA construct include low molecular weight, aprotic CO₂ absorption sites to control viscosity changes, a delocalized aromatic π network that conjugates into adsorbed CO₂, and a ring structure that provides opportunities to control reactivity through substitutions that tune both steric and electronic interactions. Accurate G3 calculations predict that a cyano substituent in the 3 position decreases the CO₂ binding energy from −109 to −70 kJ mol^{−1} due to electronic deactivation through the ring; substitution in the 2 position further decreases the computed binding energy to −49 kJ mol^{−1} due to additional steric blocking of the reactive site reflected in the bending of the cyano group.²⁹ In all cases calculations predict the CO₂ moiety to maintain planarity with the pyrrolide ring to preserve π conjugation, as in the NHC system.²⁹ A tetraalkyl phosphonium 2-cyanopyrrolide [P66614][2-CNpyr] IL was synthesized and CO₂ uptake isotherms were observed over 22–100 °C temperature range. The reaction enthalpy measured by differential calorimetry was −53 ± 5 kJ mol^{−1}, in very good agreement with the G3-computed binding energy of −49 kJ mol^{−1}. Notably, the viscosity of the [P66614][2-CNpyr] IL is nearly independent of CO₂ uptake over a wide temperature range, consistent with the behavior expected in the absence of acidic protons.²⁹

The rather surprisingly good agreement between the gas-phase calculations and observed CO₂ uptake in the condensed phase can be traced to a fortuitous cancellation in the solvation energies of the unreacted and reacted ions.²⁹ Test calculations suggest the difference between these to be on the order of 5 kJ mol^{−1}.

Direct condensed-phase solubility calculations are an important area of future opportunity.

Other nitrogen-containing heterocycles lend themselves to the same type of AHA chemistry. In addition to the 2-CN pyrrolide IL, Brennecke *et al.* prepared and reported CO₂ uptakes for a 3-trifluoromethyl pyrazolide ([CF₃Pyr][−]) IL.²⁹ Calculations show that the pyrazolide offers two potential binding sites with energies -54 and -27 kJ mol^{−1} (G3 values, standard condition) for the unblocked and sterically hindered sites, respectively. Experimental observations suggest that both sites contribute to the CO₂ uptake and both lead to the weaker CO₂ binding energy for ([CF₃Pyr][−]). Dai *et al.* reported an example of this chemistry with an imidazolide anion.¹³ Later the same group of researchers showed a series of ILs consists of pyrrole and indole backbones but with di-, tri-, and tetra-nitrogen atoms to be effective CO₂ sorbents.¹⁴ They also found a good correlation between the measured Brønsted basicity of the anions and the calculated reaction enthalpy and suggested that basicity can be used as a knob for fine tuning the CO₂ uptake.

To further explore generalizations of the AHA chemistry, we summarize in Fig. 7 the results of 70 calculations on a wider variety of AHA candidates, including the parent pyrrolide (Pyr), indolide (Indo), pyrazolide (Pyra), imidazolide (Im), and benzimidazolide (BnIm) with substituents including CH₃, F, CF₃, CN, COH, OCH₃, and COOCH₃ encompassing electron withdrawing, neutral, and donating groups (for details, see ESI†). All are found to bind CO₂ in the same planar conformation. The unsubstituted parent molecules have binding energies that range from -99 kJ mol^{−1} for pyrrolide to -52 kJ mol^{−1} for benzimidazolide (Fig. 7, R = H, black solid symbols linked by a dashed line). Parent pyrrolide binds CO₂ most strongly, and multiple nitrogens and fused aromatic rings both lead to a weaker bond. In cases in which an anion presents multiple CO₂ binding sites, the less steric hindered one is generally favored. Extra delocalization of electrons to additional rings reduces the electron donating

ability of the N, and multiple nitrogens compete with each other for electron density, which makes it harder for them to give up electrons to CO₂. Naturally, the combination of the two (benzimidazolide, BnIm) has the weakest reaction energy.

Substitutions of different functional groups and at different positions can induce large changes in reaction energy. We put single electron withdrawing groups such as CF₃, CN, *etc.* at all possible positions and computed CO₂ binding energies. Notice the labeling of position numbers are relative to the nitrogen binding with CO₂. Only the chemical bond forming reactions are reported in Fig. 7. By adding electron withdrawing groups, the reaction energy can be tuned in a range of about 70 kJ mol^{−1} for pyrrolide and indolide families and in smaller ranges for other groups. The weakest reaction energies of the five families are highlighted by the open symbols linked with a dotted-dashed line, which contain either CF₃ or CN substitutions, the strongest electron withdrawing groups tested here. Except for the benzimidazolide family, these substitutions (open symbols) are all at R1, while for benzimidazolide, CF₃ or CN at R1 allows only CO₂ physical interaction at the binding N site and the open symbol represents the R2 substitution. In general, the farther away from the CO₂ binding site, the weaker the substitution effect. For indolide, except R1 and R6, all other positions show ~ -50 kJ mol^{−1} reaction energy for CF₃ and CN. CN substitution usually leads to a stronger binding compared to CF₃, as the latter imposes a bigger steric effect.

To illustrate the above statements, we take a closer look at the Im family with F and CF₃ electron withdrawing groups (Fig. 8). The unsubstituted Im binds with CO₂ with a reaction energy of -73.9 kJ mol^{−1}, more exothermic than all the electron withdrawing substituted molecules. F and CF₃ groups are chosen to contrast steric effects of substitutions. For F groups (Fig. 8a–c), the binding enthalpies are stronger (more negative) than CF₃ groups (d, e, and f) at the same position of substitutions. The difference is about 15 to 20 kJ mol^{−1} with the bulkier CF₃ leading to weaker bonding, which can be seen from the N(AHA)–C(CO₂) distance. For example, Fig. 8b and d indicate N–C distances of 1.55 and 1.57 Å, respectively.

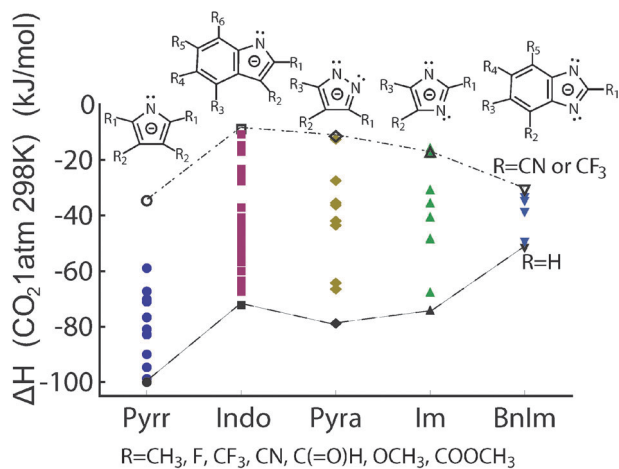


Fig. 7 Comparison of AHA–CO₂ binding enthalpies, based on B3LYP/6-311++G(d,p) calculated structures under the standard conditions. Each point represents a different substitution pattern. The dashed and dotted-dashed lines mark the computed lower and upper limits of reaction enthalpies. For details, see ESI.†

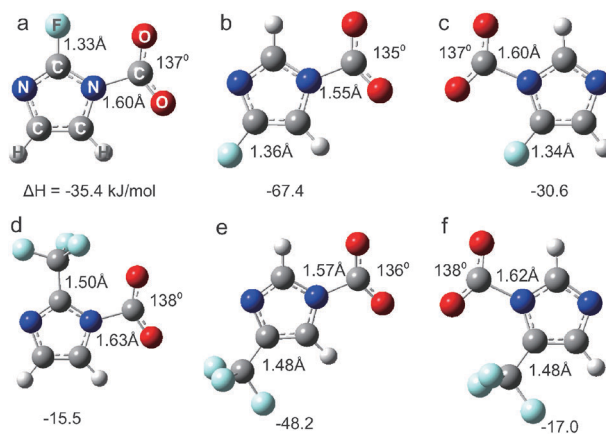


Fig. 8 Selected imidazolide-based structures complexing with CO₂. B3LYP/6-311++G(d,p)-level geometry optimizations show that CO₂ binds to imidazolide N-heteroatom. Optimizations are checked with following frequency calculations and the binding enthalpy ΔH is calculated under the standard conditions.

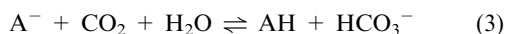
CO₂ binds more strongly when F or CF₃ is the farthest from CO₂ (Fig. 8b and e *versus* other substitutions). The steric effect due to different relative positions of substitution groups is about 30 kJ mol⁻¹ (e.g. Fig. 8a *versus* b). This again exemplifies how computational design can play an important role in pinpointing the most promising candidate ILs on a quantitative basis.

5 Future challenges and opportunities

The Perspective here highlights the healthy interplay between experiment and simulation that has led to the evolution of CO₂-reactive ILs from the simple analogs of aqueous MEA chemistry to anions with directly tunable reactivity. Simulations provide reliable indicators of CO₂ reactivity and guide synthesis towards promising candidate ILs. Experiments inform and guide the development of more reliable reactivity descriptors. Together they advance both understanding and development of new materials at a more rapid pace than could possibly happen without each other.

While highly useful, the vast majority of first-principles models used to screen CO₂-reactive ILs to date have described single anions in isolation. More molecularly realistic models, likely to be based on periodic supercell models of many cation/anion pairs, are needed to better understand the liquid structure of these materials, how this detailed structure influences equilibrium CO₂ uptake, and the extent to which this CO₂ chemistry is sensitive to the extent of reaction. Computed spectroscopies in realistic environments are needed to correlate with observation. Further, little is known about the kinetics or mechanism of CO₂ reactions with bulk ILs. Simulations again are needed to provide a window into this reactivity, to understand the compositional factors that limit achievement of equilibrium. CO₂ uptake will ultimately occur through the IL-gas interface, and here too first-principles simulations have a role in describing the structure of the interface and how it modifies reactivity from the bulk.

Much of the discussion here has focused on the IL-CO₂ chemistry in isolation. Practical applications will have to address the influence and potential interference of other flue gas constituents on this chemistry. SO₂ is much more acidic than CO₂ and will undoubtedly interfere with the CO₂ chemistry described here. In fact, experiments and calculations suggest that AHA anions bind SO₂ effectively at multiple sites.⁶³ The most important (albeit weakly) acidic component of flue gas is water. Even nominally hydrophobic ILs will absorb ample H₂O to potentially interfere with CO₂ uptake chemistry. Experiments have shown that small amounts of water (0.1 to 7.1 wt% at room temperature) can actually speed absorption by reducing amino acid IL viscosity.⁵⁰ In the AHA ILs, preliminary experiments indicate that H₂O does not interfere with the AHA-CO₂ chemistry.²⁹ More sophisticated first-principles models are needed to understand the influence and potential participation of H₂O in CO₂ chemistry, for instance through formation of bicarbonate:



Predicting the behavior of multiple coupled equilibrium in the liquid phase from first principles is a very challenging task; here again, creative combinations of qualitative and quantitative

models will be necessary to understand, predict, and guide the design of optimal materials.

Of course the most exciting opportunities are the IL-CO₂ chemistries yet to be discovered: the ionic liquids with dramatically higher capacities than those known today, that exhibit more energy efficient cooperative adsorption, that couple phase-change with CO₂ uptake, or that can be triggered to adsorb or desorb CO₂ in novel ways. Undoubtedly simulation will continue to play a critical role in these advances.

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