DISCOVERY OF NEW IONIC LIQUIDS FOR CO₂ CAPTURE

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Abstract

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CO₂ concentrations in the atmosphere have been steadily increasing over the years, mainly due to CO₂ being emitted from the burning of fossil fuels. The ever increasing concentration of CO₂ is starting to have substantial effects on the global climate and the effects will continue to multiply if the problem is not addressed. While the ideal would be to have all energy sources be carbon-neutral, coal will still be a major energy source for the foreseeable future. Because of this, finding new and alternative processes for controlling CO₂ emissions becomes a vital necessity.

Post-combustion CO₂ capture is the most clear-cut and promising path to limiting carbon emissions but its implementation relies on the discovery of energy-efficient means of separating CO₂ from other flue gas components such as N₂, O₂, H₂O and other trace gases. Using the presently available amine absorption technologies, separating the CO₂ from the flue gas stream is estimated to consume more than 30% of the power produced by the plant, which is far above the theoretical minimum work needed. An alternative liquid absorbent is needed that overcomes the pitfalls of the amine absorbents, such as ionic liquids.
Ionic liquids (ILs) are low-melting salts of bulky cations and anions and are effectively non-volatile. Common ILs physically absorb CO$_2$ selectively over O$_2$ and N$_2$, but the physical solubility of CO$_2$ in the IL is too low to be practical. Therefore, to achieve the chemical absorption seen in the amine absorbents but also keep the properties of ILs, an amine group is tethered to the ionic liquid.

In this work, we use density functional theory and first principles thermodynamics to describe the ionic liquid systems. We show that by tethering an amine functional group to the anion, such as an amino acid, on an ionic liquid, we are able to achieve a one CO$_2$ to one IL reaction ratio, which is twice as much as an aqueous amine or tethering the amine functional group to the cation. This was corroborated by experimental data. Unfortunately, when amino acid based ionic liquids react with CO$_2$, their viscosity increases significantly, making them undesirable for CO$_2$ capture.

We then developed the $N$-aprotic heterocyclic anion (AHA) ionic liquids for CO$_2$ capture. They are aromatic and react with CO$_2$ with a 1:1 reaction stoichiometry. When they react with CO$_2$, no acidic proton is produced, which corresponds to the viscosity staying the same. This is supported by experimental data. We have studied the use of attaching electron withdrawing substituent groups to the AHA in order to tune its CO$_2$ reaction enthalpy ($\Delta H$). Depending on the substituent group and its location relative to the reactive nitrogen, we have been able significantly change the $\Delta H$ (-1 to -100 kJ/mol).
Finally, we developed an isotherm model, based on a Langmuir model, to predict the CO₂ isotherm of any AHA based on its ΔH. We also used this model to predict the optimal ΔH at given conditions. This will aid in the process of choosing which proposed AHAs to test experimentally. Future work should involve experimentally testing the proposed AHAs and computationally developing new AHAs that can capture CO₂ with higher reaction ratios than proposed here.
This work is dedicated to my late grandmother, Mary Lou Schilling. Although she never understood what it is that I do, she always believed I was the best at it. Her unwavering love and support helped me to always strive for my best and to never give up no matter the odds. I will always miss you.
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NOMENCLATURE

\( C_{p} \) \quad \text{Heat capacity at constant pressure}

\( C_{v} \) \quad \text{Heat capacity at constant volume}

\( \Delta \) \quad \text{Change}

\( \varepsilon \) \quad \text{Dielectric constant}

\( E \) \quad \text{Electronic energy}

\( \phi \) \quad \text{Electrostatic potential}

\( G \) \quad \text{Gibbs free energy}

\( h \) \quad \text{Henry's constant}

\( H \) \quad \text{Enthalpy}

\( \hat{H} \) \quad \text{Hamiltonian operator}

\( k_{B} \) \quad \text{Boltzmann's constant}

\( K \) \quad \text{Equilibrium constant}

\( N \) \quad \text{Number of moles}

\( P \) \quad \text{Pressure}

\( R \) \quad \text{Universal gas constant}

\( S \) \quad \text{Entropy}

\( T \) \quad \text{Temperature}

\( \nu \) \quad \text{Vibrational frequency}
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CHAPTER 1:

INTRODUCTION

1.1 Background

Greenhouse gases are gases that trap heat in the atmosphere and their relatively recent increases in concentrations are believed to have lead to global warming and climate change. Some greenhouse causes occur naturally where others are because of human activities. The main greenhouse gases that enter the atmosphere due to human activities are carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and fluorinated gases such as hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride.¹ Figure 1.1 shows a breakdown of anthropogenic greenhouse gases in 2004, where each gas is measured on a CO₂-equivalent basis.
Figure 1.1 clearly shows that CO$_2$ is the majority of greenhouse gases emitted in 2004 with it being 76.7%. In 2006, this number increased to CO$_2$ being 84.8% of all greenhouse gas emission. By far, the largest source of CO$_2$ emissions globally comes from the combustion of fossil fuels. The mitigation of CO$_2$ emissions from fossil fuel use would be a major way to affect the greenhouse gas emissions and consequently global warming and climate change.

1.2 CO$_2$ Emissions from Fossil Fuel Combustion

The main fossil fuels burned for the production of energy are petroleum, natural gas, and coal for the uses of electricity generation, industrial uses, transportation, as well as in homes and commercial buildings. Figure 1.2 shows the amount of CO$_2$ emissions, in teragrams of CO$_2$ equivalent, from fossil fuel
combustion by sector and fuel type. Electricity generation is the single largest source of CO₂ emissions in the U.S., representing 41 percent of all CO₂ emissions. The major contributor to CO₂ emissions in the process of generating electricity is coal. If we could mitigate CO₂ emissions from coal-fired power plants, we could knock out a major contributor to the emissions of CO₂.

![Graph showing relative contribution by fuel type for CO₂ emissions in the U.S.](#)

Figure 1.2: 2006 CO₂ Emissions from Fossil Fuel Combustion by Sector and Fuel Type

1.3 Coal-Fired Power Plants

There are three types of ways to capture CO₂ from coal-fired power plants: pre-combustion, oxygen combustion (oxy-combustion), and post-combustion.
1.3.1 Pre-combustion

Pre-combustion CO₂ capture occurs in coal gasification plants, where coal is converted into gaseous components in the presence of steam. CO₂ can be captured from the synthesis gas that comes from the coal gasification reactor before it is mixed with air in a combustion turbine. In pre-combustion capture, the CO₂ is at a high pressure and is in relatively high concentrations.⁴

1.3.2 Oxy-combustion

Pure oxygen diluted with recycled CO₂ or H₂O is used to combust coal in an enriched oxygen environment. The condensing water in the exhaust stream is used to capture the CO₂.⁴

1.3.3 Post-combustion

99 percent of all coal-fired power plants in the U.S. are pulverized coal plants, which burn coal in air to raise steam. CO₂ is released in the flue gas at atmospheric pressure and a concentration of 10-15 volume percent. Post-combustion CO₂ capture systems separate the CO₂ from the flue gas before it is released into the atmosphere. There are three areas of research of post-combustion CO₂ capture: solvents, sorbents, and membranes.⁵ In this work, we focus on the use of solvents for post-combustion CO₂ capture.

1.4 Solvents for Post-combustion CO₂ Capture

Currently, CO₂ capture is performed with aqueous amines, most notably monoethanolamine (MEA). MEA reacts with CO₂ with a two amines to one CO₂
reaction stoichiometry. While MEA is highly reactive with CO₂ (~80 kJ/mol), it is not cost-effective to use. Currently, amine scrubbing with CO₂ compression to 2,200 psi (line pressure) costs approximately $2,900 per kilowatt and reduces the net power plant output by 30 percent. The majority of the cost of using MEA is due to its regeneration, but other problems of MEA are its volatilization to air and corrosiveness to the equipment, both of which increase capital costs. The ideal solvent would not have these problems and therefore be cost-effective enough to actually implement on a large scale. This research focused on using ionic liquids (ILs) as a solvent for capturing CO₂.

1.4.1 Ionic Liquids for CO₂ Capture

Ionic liquids (ILs) are low-melting salts of bulky cations and anions, which also have negligible vapor pressures. Examples of the commonly used cations in ionic liquids are shown in Figure 1.3, where X- can be any number of anions, such as halides [Cl⁻, Br⁻, I⁻], nitrate [NO₃⁻], acetate [CH₃CO₂⁻], trifluoroacetate [CF₃CO₂⁻], tetrafluoroborate [BF₄⁻], hexafluorophosphate [PF₆⁻], and bis(trifluoromethylsulfonyl)imide [(CF₃SO₂)₂N⁻]. Also, the substituent R groups on the cations are typically alkyl chains but can vary.
Figure 1.3: Typical cations used in ionic liquids where $X^-$ are various anions.$^3$

Common ILs physically absorb $\text{CO}_2$ selectively over $\text{O}_2$ and $\text{N}_2$, but the physical solubility of $\text{CO}_2$ in the IL is too low to be practical. Therefore, to achieve the chemical absorption seen in the amine absorbents but also keep the properties of ILs, an amine group is tethered to the ionic liquid. The amine group can be tethered to either the cation or anion.

In this work, through first-principles computational calculation, we first investigate how different substituents attached to an amine functional group affect the $\text{CO}_2$ reaction energies of the amine. We then investigate tethering the amine functional group to either the cation or anion in the ionic liquid. We show that tethering the amine functional group to the cation results in a two IL to one $\text{CO}_2$ uptake ratio, while tethering it to an anion, such as an amino acid, results in a one IL to one $\text{CO}_2$ uptake ratio. While the uptake ratio of $\text{CO}_2$ approaches 1:1, amino acids have problems with high viscosities due to hydrogen bonding when reacted with $\text{CO}_2$. In order to eradicate the viscosity problems, we discovered a new class of ionic liquids, aprotic heterocyclic anion (AHA) ionic liquids. Our AHA ILs react with $\text{CO}_2$
with a one IL to one CO$_2$ reaction stoichiometry but without the viscosity problems. We have also developed a model to predict the CO$_2$ isotherms of any AHA IL based on its reaction enthalpy. We then employed the isotherm model to determine the optimal CO$_2$ reaction enthalpy. We have found several AHAs that fall near the optimal reaction enthalpy.
CHAPTER 2:
RESEARCH METHODOLOGY

2.1 Density Functional Theory

2.1.1 Theory

Quantum mechanics is used to describe the distribution, energy, and all other properties of electrons in atoms and molecules. The fundamental principle behind quantum mechanics is that a wave function, \( \Psi \), exists for any system and that appropriate operators acting upon \( \Psi \) return the observable properties of the system. The operator that returns the system energy, \( E \), as an eigenvalue is called the Hamiltonian operator, \( \hat{H} \). The electronic Hamiltonian for an N-electron molecule

\[
\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 + \sum_{i=1}^{N} \theta(\vec{r}_i) + \sum_{i<j} \frac{1}{\left| \vec{r}_{ij} \right|}
\]

(2.1)

where \( \theta \) describes the potential energy of the electrons due to the nuclei \( (\alpha) \)

\[
\theta(\vec{r}_i) = -\sum_{\alpha} Z_\alpha \left| \frac{1}{\vec{r}_{i\alpha}} \right|
\]

(2.2)

The electronic energies, \( E_i \), and wavefunctions, \( \Psi_i \), are then obtained by solving the Schrodinger equation

\[
\hat{H}_i \Psi_i(\vec{r}_1, \ldots, \vec{r}_N) = E_i \Psi_i(\vec{r}_1, \ldots, \vec{r}_N)
\]

(2.3)
While wavefunctions are not direct observables, they can be used to compute electron probability density,

$$\rho_0(\vec{r}) = \int \cdots \int \Psi^* (\vec{r}_1, \ldots, \vec{r}_N) \Psi(\vec{r}_1, \ldots, \vec{r}_N) \, d\vec{r}_1 \cdots d\vec{r}_N$$  \hspace{1cm} (2.4)

where \( \ast \) indicates the complex conjugate. The electron probability density is measurable and density functional theory (DFT) was built upon the concept of using the electron probability density to decrease computational cost of computing electron energies of systems with a large number of electrons. Hohenberg and Kohn were the first to develop this idea.\(^{12-14}\) They showed that the ground state energy is a unique functional of the electron probability density and that the true ground state electron probability density is the one that minimizes the total energy. From these principles, the DFT energy is

$$E_0 = \int \rho_0(\vec{r}) \theta(\vec{r}) \, d\vec{r} + T[\rho_0] + E_{ee}[\rho_0(\vec{r})] + E_{nn}$$  \hspace{1cm} (2.5)

where \( T \) is the total kinetic energy, \( E_{ee} \) is the total potential energy from electron-electron interactions and \( E_{nn} \) is the potential energy from nucleus-nucleus interactions. \( E_{nn} \) is found classically using Coulombic potentials but, \( T \) and \( E_{ee} \) are not as easy. Their forms were determined by Kohn and Sham\(^{15,16}\), who separated the problem into an interacting part and a non-interacting part

$$E_0 = \int \rho_0(\vec{r}) \theta(\vec{r}) \, d\vec{r} - \frac{1}{2} \sum_{i=1}^{N} \langle \Psi_i^* (\vec{r}) \nabla_i^2 | \Psi_i (\vec{r}) \rangle + T^{\text{int}}[\rho_0(\vec{r})] + E_{ee}^{\text{Coulomb}} + E_{xc}[\rho_0(\vec{r})] + E_{nn}$$  \hspace{1cm} (2.6)
where $\tau^{\text{int}}$ is the kinetic energy difference between the interacting and non-interacting systems and $E_{xc}$ is the potential energy difference between the actual and Coulombic electron-electron interactions. Kohn and Sham combined all of the indeterminable quantities into a single functional, the exchange-correlation energy functional $\vartheta_{xc}[\rho_0]$.

The Kohn-Sham solution gives a set of exact one-electron wavefunctions as a function of the electron probability density

$$[-1/2 \nabla^2 + \vartheta(\vec{r}_i) + E_{xc}^{\text{Coulomb}}(\vec{r}_i) + \vartheta_{xc}[\rho_0(\vec{r})]] \Psi_i = E_i \Psi_i$$

(2.7)

This provides for a much more efficient calculation of the electronic energy. As of yet, though, the true form of $\vartheta_{xc}[\rho_0]$ is unknown so the quality of the DFT calculation strongly depends on the accuracy of the approximation of $\vartheta_{xc}[\rho_0]$.

There are several possibilities of $\vartheta_{xc}[\rho_0]$ approximations available. There is a “Jacob’s ladder” of sorts of approximations. The local density approximation (LDA) uses only information about the local electron probability density to define $\vartheta_{xc}[\rho_0]$. The generalized gradient approximation (GGA) uses information about both the electron probability density and its gradients. Meta-GGA methods use the local electron density, its gradients, and its Laplacians, while hyper-GGA methods use the local electron density, its gradients, and the exact N-electron exchange energy. Hybrid functionals incorporate a part of exact exchange from the Hartree-Fock theory with the exchange and correlation from other sources. One of the most respected hybrid functionals is B3LYP. The model is defined by

$$E_{xc}^{\text{B3LYP}} = (1 - a)E_x^{\text{LSDA}} + aE_x^{\text{HF}} + b\Delta E_x^\beta + (1 - c)E_c^{\text{LSDA}} + cE_c^{\text{LYP}}$$

(2.8)
where $a$ is 0.20, $b$ is 0.72, and $c$ is 0.81. Multilevel methods, such as G3\cite{G3}, have been developed to compute very accurate energies by combining the results of several calculations, but it comes with a higher computational cost. These multilevel methods combine higher levels of theories and small basis sets with lower levels of theories and large basis sets. In this work, we mainly employ the B3LYP level of theory, but will occasionally use the G3 method for more accurate results. We use Gaussian03\cite{Gaussian03} to perform our DFT calculations.

2.1.2 Geometry Optimization and Electronic Energies

A geometry optimization is performed in order to locate stationary structures on the potential energy surface (PES). The optimization starts by first specifying an initial geometry. Its electronic energy is calculated and the forces on all of the atoms are computed by taking the gradient of the total energy. The atoms positions are then updated using these forces. Structures are iteratively relaxed in this way until the predetermined structural convergence criteria are met with the electronic energy being at a minimum. The Berny algorithm\cite{Berny} is employed in Gaussian03 as the process by which the optimization steps are taken. The geometry optimization gives us the energy associated with taking infinitely separated atoms at rest and forming a molecule, otherwise known as the internal electron energy, $\varepsilon_0$, of the molecule.

2.1.3 Vibrational Calculations/Spectrometry

A molecular potential energy curve can be approximated by a parabola near the bottom of the energy well,
\[ V = \frac{1}{2} kx^2 \]  \hspace{1cm} (2.10)

where \( V \) is the potential energy, \( k \) is the force constant, and \( x \) is the difference between the current position on the curve and the minimum of the curve. Equation 2.10, which is the equation of a parabola, is the origin of the term ‘parabolic potential energy’ for the potential energy characteristic of a harmonic oscillator.\(^{14}\)

For a diatomic molecule, the Schrodinger equation for the relative motion of two atoms of masses \( m_1 \) and \( m_2 \) with a parabolic potential energy is

\[ -\frac{\hbar^2}{2m_{\text{eff}}} \frac{d^2 \psi}{dx^2} + \frac{1}{2} kx^2 \psi = E \psi \]  \hspace{1cm} (2.11)

where \( m_{\text{eff}} \) is the effective mass

\[ m_{\text{eff}} = \frac{m_1 m_2}{m_1 + m_2} \]  \hspace{1cm} (2.12)

In solving Equation 2.11, the permitted vibrational energy levels are

\[ E_v = \left( v + \frac{1}{2} \right) \hbar \omega \]  \hspace{1cm} (2.13)

where

\[ \omega = \left( \frac{k}{m_{\text{eff}}} \right)^{1/2} \]  \hspace{1cm} (2.14)

and \( v \) is 0, 1, 2, ....

The vibrational terms of a molecule, the energies of its vibration states expressed in wavenumbers, are denoted \( G(v) \), with \( E_v = h \nu G(v) \), therefore
\[ G(v) = \left( v + \frac{1}{2} \right) \tilde{v} \]  

(2.15)

where

\[ \tilde{v} = \frac{1}{2\pi c} \left( \frac{k}{m_{\text{eff}}} \right)^{1/2} \]  

(2.16)

For a diatomic molecule, there is only one mode of vibration, the bond stretch. For a polyatomic molecule, there are several modes of vibration because all of the bond lengths and angles may change. For a nonlinear molecule consisting of N atoms, there are 3N-6 independent modes of vibration, also known as normal modes. If the molecule is linear, then there are only 3N-5 independent vibrational modes. The normal modes of polyatomic molecules are the key to describing its molecular vibrations. Each normal mode, \( q \), behaves like an independent harmonic oscillator, so each has a series of terms

\[ G_q(v) = \left( v + \frac{1}{2} \right) \tilde{v}_q \quad \tilde{v}_q = \frac{1}{2\pi c} \left( \frac{k_q}{m_q} \right)^{1/2} \]  

(2.17)

where \( \tilde{v}_q \) is the wavenumber of mode \( q \) and depends on the force constant \( k_q \) for the mode and on the effective mass \( m_q \) of the mode.\(^{14}\)

The force constants, \( k \), are the second derivatives of the potential energy, \( E(\text{ri}) \), with respect to the nuclear coordinates. In practice, we first optimize the nuclear coordinates at the B3LYP level and then perform a frequency analysis by calculating and diagonalizing the matrix of second derivatives at the same level of
theory. Reported frequencies are scaled by a factor of 0.9679 for comparison with experiment.

2.1.4 Thermochemistry

From the geometry optimizations, we have the internal electron energy but it doesn’t take into account motions of the molecule. At 0 K, the molecules have a zero-point vibrational energy (ZPE)

\[ E_0 = E\nu + ZPE \]  

(2.18)

The ZPE is calculated with the harmonic approximation according to

\[ ZPE = \sqrt{2\hbar \sum_{i=1}^{3n-6} v_i^2} \]  

(2.19)

where \( v_i \) are the 3n-6 harmonic vibrational frequencies of an \( n \) atom molecule and \( h \) is Planck’s constant. The correction to the total internal thermal energy \( E_{tot} \), at a given temperature, is described by

\[ E_{tot} = E_0 + E_{elec} + E_{vib} + E_{rot} + E_{trans} \]  

(2.20)

where \( E_{elec} \), \( E_{vib} \), \( E_{rot} \), and \( E_{trans} \) are the contributions vibrational motion, rotational motion, and translation, respectively at that temperature and pressure, which we describe using the harmonic oscillator, rigid rotor, and ideal gas approximations, respectively. The correction to the thermal enthalpy at a given temperature and pressure given by

\[ H_{corr} = E_{tot} + k_B T \]  

(2.21)
where \( k_B \) is the Boltzmann constant. The correction to the Gibbs free energy is

\[
G_{\text{corr}} = H_{\text{corr}} - TS_{\text{tot}}
\]  

(2.22)

where \( S_{\text{tot}} \) is the sum of the translational, rotational, vibrational, and electronic motion contributions to the entropy.\(^{22,23}\)

2.2 Conformational Analysis

Many species that we studied have several conformations that arise from rotation about internal bonds. We explored the conformational space of each species by systematically varying dihedral angles about all rotatable bonds and performing geometry optimizations to locate all local minima. The total number of reactant and product conformation varies from molecule to molecule but can range anywhere from four for small molecules to forty-eight or more for molecules with a large number of rotatable bonds. A Boltzmann distribution is used to average over all conformations at 298 K. The Boltzmann-weighted internal energy of species \( N \) is given by

\[
E_N = \sum_i w_i E_{0i}
\]  

(2.23)

where \( w_i \) is the Boltzmann weight defined by \( \exp(-E_{0i}/(k_B T)) \)

\[
\omega_i = \frac{e^{-E_{0i}/k_B T}}{\sum_i e^{-E_{0j}/k_B T}}
\]  

(2.24)

Reaction energies are determined by the difference between the weighted total energies of products and reactants
\[ \Delta E_{\text{ext}} = \sum_{N_{\text{product}}} E_N - \sum_{N_{\text{reactants}}} E_N \] (2.25)

2.3 Solvation Calculations

When conducting gas-phase simulations to predict and compare to liquid phase experimental data, it is wise to determine the effect of the solvent on the gas-phase energetics. There are two methods for incorporating a solvent; implicit and explicit solvation.

2.3.1 Implicit Solvation

When a molecule is submerged in a solvent, its charge distribution interacts with that of the solvent. In a continuum model, the charge distribution of the solvent is not represented explicitly but rather by a continuous electric field that represents a statistical average over all solvent degrees of freedom at thermal equilibrium.\(^{24}\) The electric field at a given point in space is the gradient of the electrostatic potential \(\phi\) at that point. All continuum solvent models rely on the Poisson equation of classical electrostatic potential as a functional of the charge density and the dielectric constant. The Poisson equation in the form of

\[ \nabla^2 \phi(r) = -\frac{4\pi\rho(r)}{\varepsilon} \] (2.26)

where \(\varepsilon\) is the electric constant of the medium, is valid for situations where a surrounding dielectric medium responds in a linear fashion to the embedding charge. Since continuum solvation involves representing the solute explicitly and the solvent implicitly, the charge distribution of the solute is thought of as being
inside a cavity that displaces an otherwise homogeneous dielectric medium. There are thus two regions, one inside and one outside the cavity, in which the Poisson equation is written as \(^{24}\)

\[ \nabla \varepsilon(r) \cdot \nabla \phi(r) = -4\pi \rho(r) \]  

(2.27)

When accounting for solvation in solving the Kohn-Sham DFT equation leads to a non-linear Schrödinger equation, it is referred to as a self-consistent reaction field (SCRF) calculation. One of the most widely used schemes for SCRF implementations of the Poisson equation is the surface area boundary element approach, which is referred to as the polarized continuum model (PCM). When the Poisson equation is solved using a boundary element approach, the charges on the molecular surface are determined in such a way to provide an equivalent representation to the electrostatic potential that is distributed throughout space when the Poisson equation is solved using a volume element approach. If the surrounding space were to be characterized by an infinite dielectric constant, for example, if the medium were conducting, then no potential exists in the medium, and instead charge develops on the conductor surface in contact with the solute. This considerably simplifies the necessary electrostatic equations for the calculation of polarization free energy. This approximation is called the conductor like screening model (COSMO).\(^{24}\)

The response of a conductor to a solute charge distribution is ‘complete’, while that of a dielectric medium is not. Therefore, in COSMO models, the more simply evaluated conductor-polarization free energy is scaled by a factor of \(2(\varepsilon-\)}
1)/(2\epsilon+1) after its computation. In the PCM formalism, conductor-like modifications have been described. To differentiate between the original (dielectric) version of PCM and the conductor-like version, the acronym CPCM is used for the latter.

When implementing a solvation model, a cavity of the solute must be described. By default, the Gaussian03 program builds up the cavity using the United Atom (UA0) model, by putting a sphere around every heavy atom in the solute. Hydrogen atoms are enclosed in the sphere of the atom to which they are bonded.

2.3.2 Explicit Solvation

For explicit solvation, solvent molecules are added around the solute. Generally, a sufficient number of solvent molecules are added around the solute to model a solvation shell. You can add as many or few solvent molecules and solvation shells as you desire.
CHAPTER 3:
NEUTRAL AMINES

3.1 Introduction

Substituted amines are a popular choice as molecules to selectively react with and separate CO₂ from gas mixtures. The physical affinity of most materials for CO₂ is too modest for practical separations, and thus to increase capture capacity, functional groups are often introduced that chemically combine with CO₂. Primary and secondary amine functional groups are the most commonly considered, as they are generally thought to react in two to one proportion with CO₂ to form carbamate anions and ammonium cations.⁶,⁷

\[
2 \text{NH}_2 + \text{CO} \rightarrow \text{NH}_2\text{CO}^- + \text{NH}_3^+ \tag{3.1}
\]

Equation 3.1 illustrates the two potential roles played by the amine, as a Lewis base combined with CO₂ and as a Brønsted base combined with a liberated proton. If the amine is a sufficiently weak Brønsted base, reaction may also stop at the formation of the carbamic acid as shown in Equation 3.2. A key opportunity for optimizing CO₂ separations is to tune these CO₂-amine equilibria.

\[
\text{NH}_2 + \text{CO} \rightarrow \text{NH}_2\text{CO}^- + \text{H}^+ \tag{3.2}
\]
Little computational work has been reported on how substituent groups affect the reaction of CO$_2$ with amines. Chakraborty and co-workers$^{26}$ used a molecular orbital approach to study substituent effects on amine-CO$_2$ interactions but only considered the effect of methyl substitution at the $\alpha$-carbon. They found that methyl substitution at the $\alpha$-carbon led to subtle but significant changes in the electronic environment of the nitrogen, resulting in the species having a lower charge at the nitrogen atom. They also found that with methyl substitution at the $\alpha$-carbon, the N-H bond of the amine is weakened.

Because of the diverse environments in which they are deployed, a clear comparison of the intrinsic reaction energies of CO$_2$ with substituted amines would be valuable. Simulations provide a reliable and unbiased way of comparing reaction energies, and allow inductive, steric, and intramolecular effects on reaction energies to be disentangled. We have used DFT calculations to compare the intrinsic CO$_2$ reaction energies of ammonia and a variety of alkyl, carbonyl, and fluoro-substituted amines (Table 3.1), selected for their range of electron donating and withdrawing effects and their relevance to CO$_2$ separations.
### TABLE 3.1:

**SUBSTITUTED AMINES INVESTIGATED**

<table>
<thead>
<tr>
<th>Alkyl Amines</th>
<th>Hydroxyl Amines</th>
<th>Amides/ Carboxyls</th>
<th>Acids/ Carboxylics</th>
<th>Fluoro Amines</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃NH₂</td>
<td>HONH₂</td>
<td>CH₃C(O)NH₂</td>
<td>NH₂C(O)OH</td>
<td>FNH₂</td>
</tr>
<tr>
<td>(CH₃)₂NH</td>
<td>HOCH₂NH₂</td>
<td>CH₃CH₂C(O)NH₂</td>
<td>NH₂CH₂C(O)OH</td>
<td>CH₂FNH₂</td>
</tr>
<tr>
<td>CH₂CH₂NH₂</td>
<td>HOCH₂CH₂NH₂</td>
<td>CH₃C(O)CH₂NH₂</td>
<td>CH₃NHC(O)OH</td>
<td>CHF₂NH₂</td>
</tr>
<tr>
<td>(CH₃CH₂)₂NH</td>
<td></td>
<td></td>
<td></td>
<td>CF₃NH₂</td>
</tr>
</tbody>
</table>

We first consider the one-to-one reactions with CO₂ to form carbamic acids,

Equation 3.2. To isolate contributions to the 2:1 reaction of Equation 3.1, we break down the overall reaction into carbamate and ammonium formation steps, Equations 3.3 and 3.4, respectively.

\[
\begin{align*}
\text{NH}_2 + \text{CO} & \rightarrow \text{NH}_{2}\text{CO}^- + \text{H}^+ \quad (3.3) \\
\text{NH}_2 + \text{H}^+ & \rightarrow \text{NH}_3^+ \quad (3.4)
\end{align*}
\]

### 3.2 Results and Discussion

#### 3.2.1 Amine-CO₂ 1:1 Reactions

Ammonia combines with CO₂ to form the parent carbamic acid, H₂NCOOH. In its lowest energy conformer (Figure 3.1a), the molecule is planar and the C(O)OH group is *cis*. The N–C bond length is 1.36 Å, intermediate between typical N–C single
and double bond lengths of 1.47 and 1.27 Å, respectively. All these results are consistent with π conjugation that extends across the entire carbamic acid molecule. The trans conformation (Figure 3.1b) is not planar, loses this π conjugation, and is 8 kcal mol⁻¹ higher in energy. The thermally averaged reaction energy is dominated by the cis conformers and is +3 kcal mol⁻¹; carbamic acid is unstable to decomposition to ammonia and CO₂, as seen in other calculations.⁶ For comparison, we calculate the reaction of water and CO₂ to form carbonic acid to be more exothermic by 6 kcal mol⁻¹.
Figure 3.1: The cis (a) and trans (b) configurations of NH$_3$ reacted 1:1 with CO$_2$, of cis (c) and trans (d) configurations of CH$_3$NH$_2$, of cis (e) and trans (f) configurations of FNH$_2$, of cis (g) and trans (h) configurations of CH$_3$NCOOH, and of cis (i) and trans (j) configurations of CH$_3$CONH$_2$. N-C(O)OH bond lengths are as follows: (a) 1.36 Å, (b) 1.38 Å, (c) 1.35 Å, (d) 1.36 Å, (e) 1.34 Å, (f) 1.36 Å, (g) 1.40 Å, (h) 1.37 Å, (i) 1.41 Å, and (j) 1.38 Å.
Other substituted carbamic acids retain the same planar core and preference for cis conformation about the C(O)OH group. We first consider alkyl-substituted amines. Figure 3.2 plots the B3LYP reaction energies at 298 K for mono- and di-substituted methyl and ethylamines relative to the NH₃ reaction energy. Electron-donating alkyls are observed to slightly increase the exothermicity of reaction with CO₂. π conjugation across the carbamic acid group introduces the possibility of isomerism about the RHN=C(O)OH bond as well. The two lowest energy conformers of the methylamine product are shown in Figure 3.1c and d and differ by 2 kcal mol⁻¹ in energy; the ethylamine products are similar. This degree of freedom is obviously not present in the symmetrically di-substituted alkylamines.

Figure 3.2: Conformationally averaged 1:1 amine-CO₂ reaction energies at 298 K, relative to NH₃.
Electron withdrawing groups have a more significant effect on carbamate stability. The FNH–CO₂⁻ bond is lengthened 0.03 Å and reaction energy decreased 12 kcal mol⁻¹ over that of H₂NCO₂⁻. The energetic effect of a CFH₂⁻ group is less significant and a CF₃⁻ group is comparable to that of the F substituent. Again the CF₂H⁻ group is an outlier, in this case having a greater enhancing effect on reaction energies than even the fully substituted CF₃⁻ group.

Hydroxyl substitution similarly increases reaction energies and introduces more interesting conformational effects. The HONH₂ reaction with CO₂ is calculated to be 13 kcal mol⁻¹ more exothermic than that of NH₃. Figure 3.4b shows that in the lowest energy product conformation, the HO group orients to allow H-bonding to one carbamate oxygen; conformations without this H bond are 0.01 kcal mol⁻¹ higher in energy. Similarly, the carbamate arising from HOCH₂NH₂ preferentially adopts a conformation in which the hydroxyl group is oriented towards the carbamate fragment (Figure 3.4c); this reaction is approximately 8 kcal mol⁻¹ more exothermic than that of CH₃NH₂. Adding one more carbon to the chain connecting hydroxyl and amine groups, as in HOCH₂CH₂NH₂ (MEA), permits conformations with even closer contacts between hydroxyl and carbamate anion fragments (Figure 3.4d). By comparison to non-H-bonded conformations, this interaction is worth approximately 7 kcal mol⁻¹. As a result the MEA reaction to carbamate is about 11 kcal mol⁻¹ more exothermic than the corresponding reaction of ethylamine. Similarly significant internal hydrogen bonding effects on carbamate formation energetics have been noted previously.\textsuperscript{27}
Carbonyl (RC(O)) functionalities introduce additional conformational effects on the carbamate reaction. Reactions of the amides CH₃C(O)NH₂ and CH₃CH₂C(O)NH₂ with CO₂ are 12 kcal mol⁻¹ more exothermic than that of NH₃. For the amides, the N is now planar with the N-C bond lengths being 1.36 Å for the N-C(O) bond and 1.50 Å for the N-C(O₂) bond. The lowest energy product conformations of the amides, CH₃CONH₂, and CH₃CH₂CONH₂, are planar and have the H-N-C=O dihedral in the cis configuration as shown in Figure 3.4e for CH₃CONH₂. For CH₃CONH₂ and CH₃CH₂CONH₂, the trans configuration is 8 and 9 kcal mol⁻¹ higher in energy, respectively. For CH₃C(O)CH₂NH₂, the reaction is more exothermic than ammonia by 11 kcal mol⁻¹. In the lowest energy conformation, the N is non-planar and the N-C(O₂) bond length is 1.46 Å. The conformation where the N is planar is 4 kcal mol⁻¹ higher in energy.

Like F, a hydroxyl substituent directly bound to an amine tends to destabilize 1:1 reaction with CO₂. Thus, the hydroxylamine (HONH₂) reaction with CO₂ is intermediate in energy between FNH₂ and NH₃. The lowest-energy reacted HONH₂ conformation is planar and the N-C bond length is 1.36 Å, similar to the NH₃ case. Cis and trans isomers about this bond are nearly isoenergetic. Unlike F, however, moving the hydroxyl substituent one carbon atom away from the amine, as in HOCH₂NH₂, nearly eliminates its effect on reaction energies with CO₂. The carbamic acid product remains planar and has an N-C bond length (1.37 Å) again consistent with partial multiple bonding. The HOCH₂NH₂ reaction energy is only about 1 kcal mol⁻¹ more endothermic than CH₃NH₂ but 5 kcal mol⁻¹ more exothermic than FCH₂NH₂. Similarly, we find the conformation-averaged 1:1 reaction of
HOCH₂CH₂NH₂ (MEA) with CO₂ to be within about 1 kcal mol⁻¹ of that of CH₃CH₂NH₂ (ethylamine). These MEA results are consistent with previous computational analysis.⁵ The inductive effects of the hydroxyl electron-withdrawing group thus have a rather short range.

Carbonyl (RC(O)) functionalities on the amine produce inductive effects similar to hydroxyl, but introduce additional conformational effects on reaction. Reactions of the amides CH₃C(O)NH₂ and CH₃CH₂C(O)NH₂ with CO₂ are 4 kcal mol⁻¹ less exothermic than that of NH₃. Conjugation extends across the C(O)NHC(O)OH core, so that the product molecules are essentially planar, as shown in Figure 3.1i and j. A variety of conformers are possible arising from rotations about the three partially double bonds. Most important is isomerization about the C(O)OH group. Unlike all the examples above, this acid group is trans in the lowest energy conformations, to allow hydrogen bonding between acid and carbonyl groups (Figure 3.1j). The N–C(O)OH bond length increases to 1.43 Å. Rotation to the cis conformation decreases this N–C distance to 1.39 Å but raises the internal energy by about 5 kcal mol⁻¹. Moving the carbonyl group one carbon away from the amine, as in CH₃C(O)CH₂NH₂, essentially eliminates its inductive effect and the conformational distortions driven by internal H bonding; reaction energies are similar to the alkyl amines, and a cis conformation about the H-N-C-O(H) group is favored over the trans by 2 kcal mol⁻¹. As above, the inductive influence of electron withdrawing is limited to those directly bound to N.

Lastly amongst the 1:1 reactions, we consider the reaction of the carbamic acids, RHNCO(O)H, with a second CO₂, to form the dicarbamic acids. In general,
formation of these di-acids is less exothermic than are the monoacids, but the close proximity of the two acid groups also has interesting conformational and energetic consequences for the products. CH$_3$NHC(O)OH reacting to CH$_3$N(C(O)OH)$_2$, Figure 3.1g and h, is representative. The dicarbamic acid core is essentially planar, reflecting conjugation that extends across the molecule. In conformations in which both C(O)OH fragments are cis, (e.g. Figure 1g), both N–C distances are similar and lengthened by 0.04 Å, to about 1.40 Å, over that in the monoacid. Reactions to form these products are 11 kcal mol$^{-1}$ less favorable than to form the monocarbamic acid. Lower in energy by about 5 kcal mol$^{-1}$, however, are conformations in which one of the C(O)OH groups is oriented trans, to facilitate hydrogen bonding with the other acid group, as shown in Figure 3.1. This rotation breaks the symmetry between the two N–C bonds; the bond to the cis acid group is 1.37 Å, similar to that in cis carbamic acid, and 1.44 Å to the trans group. The same characteristics are seen in reacted NH$_2$COOH, with just the CH$_3$ group replaced by a hydrogen atom.

3.2.2 Amine to Carbamate Reactions

We now contrast substituent effects on Equation 3.2 with those on Equation 3.3 to form carbamate anions, RNHCO$_2$$. In general, electron-withdrawing substituents stabilize the carbamate products, in contrast to their influence on the carbamic acids.

As a baseline, the parent carbamate anion H$_2$NCO$_2$ from NH$_3$ (Figure 3.4a) is pyramidalized at the N center and has an N–C bond distance of 1.47 Å, which can be compared to the 1.36 Å double bond in the carbamic acid. Unlike the carbamic acid,
conjugation between N and C is evidently lost, and rotational isomerization about
this bond becomes energetically inconsequential. The calculated gas-phase reaction
energy is, not surprisingly, very large and positive, +349 kcal mol\(^{-1}\) within the
B3LYP model, due to the large energy cost of separating the anion and proton. For
comparison, we calculate the gas-phase water reaction energy to form bicarbonate
to be a similar +344 kcal mol\(^{-1}\). In actual amine systems this positive energy is offset
by the addition of the proton to another amine (considered below) and by
electrostatic stabilization and solvation peculiar to the particular environment. For
analysis of the intrinsic substituent effects of interest here, we reference all
subsequent carbamate formation reactions to this ammonia reaction.

Most other substituted carbamate anions are similarly pyramidalized at the
N center. Figure 3.3 shows the 298 K-averaged carbamate formation energies
relative to NH\(_3\) as a function of amine substitution. Alkyl substituents have modest
effects on carbamate structure and decrease carbamate formation energies 3 to 4
cal mol\(^{-1}\). N–C bond lengths are between 1.46 and 1.47 Å.
Figure 3.1: Conformationally averaged amine to carbamate reaction energies at 298 K, relative to NH₃.

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Hydroxyl substitution similarly increases reaction energies and introduces more interesting conformational effects. The HONH₂ reaction with CO₂ is calculated to be 13 kcal mol⁻¹ more exothermic than that of NH₃. Figure 3.4b shows that in the lowest energy product conformation, the HO group orients to allow H-bonding to one carbamate oxygen; conformations without this H bond are 0.01 kcal mol⁻¹
higher in energy. Similarly, the carbamate arising from HOCH₂NH₂ preferentially adopts a conformation in which the hydroxyl group is oriented towards the carbamate fragment (Figure 3.4c); this reaction is approximately 8 kcal mol⁻¹ more exothermic than that of CH₃NH₂. Adding one more carbon to the chain connecting hydroxyl and amine groups, as in HOCH₂CH₂NH₂ (MEA), permits conformations with even closer contacts between hydroxyl and carbamate anion fragments (Figure 3.4d). By comparison to non-H-bonded conformations, this interaction is worth approximately 7 kcal mol⁻¹. As a result the MEA reaction to carbamate is about 11 kcal mol⁻¹ more exothermic than the corresponding reaction of ethylamine. Similarly significant internal hydrogen bonding effects on carbamate formation energetics have been noted previously.²⁷

Carbonyl (RC(0)) functionalities introduce additional conformational effects on the carbamate reaction. Reactions of the amides CH₃C(O)NH₂ and CH₃CH₂C(O)NH₂ with CO₂ are 12 kcal mol⁻¹ more exothermic than that of NH₃. For the amides, the N is now planar with the N-C bond lengths being 1.36 Å for the N-C(O) bond and 1.50 Å for the N-C(O₂) bond. The lowest energy product conformations of the amides, CH₃CONH₂, and CH₃CH₂CONH₂, are planar and have the H-N-C=O dihedral in the cis configuration as shown in Figure 3.4e for CH₃CONH₂. For CH₃CONH₂ and CH₃CH₂CONH₂, the trans configuration is 8 and 9 kcal mol⁻¹ higher in energy, respectively. For CH₃C(O)CH₂NH₂, the reaction is more exothermic than ammonia by 11 kcal mol⁻¹. In the lowest energy conformation, the N is non-planar and the N-C(O₂) bond length is 1.46 Å. The conformation where the N is planar is 4 kcal mol⁻¹ higher in energy.
Figure 3.4: Significant carbamate anion conformations arising from CO$_2$ reactions with (a) NH$_3$, (b) HONH$_2$, (c) HOCH$_2$NH$_2$, (d) HOCH$_2$CH$_2$NH$_2$, (e) CH$_3$C(O)NH$_2$, and (f) H$_2$NCO$_2$H.

A combination of inductive and H-bonding effects make the reactions of the carbamic acids, RHNC(O)H, to the mixed acid/carbamates to be the most energetically favored reactions of all those considered here. The lowest energy product conformations of NH$_2$COOH (Figure 3.4f) and CH$_3$NCOOH are planar, conjugated, and have reaction energies more exothermic than NH$_3$ by 25 and 23 kcal mol$^{-1}$, respectively. Separating the amine and carboxylic acid groups by a single carbon, as in NH$_2$CH$_2$COOH, destroys the extended conjugation but remains more exothermic than NH$_3$ by 25 kcal mol$^{-1}$. In all these cases, conformations are adopted that permit H-bonding between C(O)OH and CO$_2^-$ groups. Non-H-bonded conformers are 17 kcal mol$^{-1}$ higher in energy.
3.2.3 Amine Protonation

As noted above, part of the driving force for the 2:1 stoichiometric reaction between amines and CO₂ (Equation 3.1) is the energy stabilization associated with proton transfer to a second amine (Equation 3.3). The B3LYP reaction energy for NH₃ protonation to the tetrahedral NH₄⁺ cation is −203 kcal mol⁻¹. Substitutional effects on proton affinities are well known and substantial.²⁸⁻³⁴ For a consistent set of comparisons, we computed the product structures and protonation energies of all the amines in Table 3.1. These computed results can be directly compared with tabulated gas-phase amine basicities, defined as the free energy of the protonation reaction, which we take from the NIST WebBook.³² Figure 3.5 plots our conformationally averaged free energies computed from the vibrational spectra using standard statistical mechanical formulas for the amines and H₂O against available experimental data. Agreement is nearly quantitative, with maximum discrepancy of 3 kcal mol⁻¹ (HOCH₂CH₂NH₂).
Figure 3.5: Calculated versus experimental (298 K) gas-phase amine basicities.

Figure 3.6 plots the protonation energies in the same format as Figures 2 and 3, referenced to the NH$_3$ energy. As seen in the first column, electron-donating alkyl substituents progressively enhance basicity. Protonation energies relative to NH$_3$ go from $-11$ kcal mol$^{-1}$ for CH$_3$NH$_2$ to $-24$ kcal mol$^{-1}$ for (CH$_3$CH$_2$)$_2$NH. This trend with alkyl chain type and number is consistent with experimental observation.$^{17}$ Electron-withdrawing F substituents have the opposite effect on protonation energies, as shown in the last column of Figure 3.6. The CFH$_2$NH$_2$ protonation energy is approximately 15 kcal mol$^{-1}$ less exothermic than unsubstituted CH$_3$NH$_2$; addition of a second and third F substituent raises the energy a further 10 kcal mol$^{-1}$.
per F. Protonation destroys any potential for conformation-specific hyperconjugation between CF₂H⁻ and N centers, so that unlike the CO₂ reactions considered above, the CF₂HNH₂ reaction energy falls linearly between the mono- and trifluoro molecules. Protonation of FNH₂ is essentially isoenergetic with CF₃NH₂.

![Conformationally averaged amine protonation energies at 298 K, relative to ammonia.](image)

**Figure 3.6:** Conformationally averaged amine protonation energies at 298 K, relative to ammonia.

Hydroxylated amines can in principle be protonated at either the hydroxyl or amine site; in practice we find protonation at the amine is always energetically preferred. The HONH₂ protonation energy is intermediate between NH₃ and FNH₂, consistent with the CO₂ energy trends noted above. Separating the hydroxyl and amine centers with aliphatic carbons rapidly diminishes the effect: HOCH₂NH₂ is
only 5 kcal mol\(^{-1}\) less basic than CH\(_3\)NH\(_2\), and HOCH\(_2\)CH\(_2\)NH\(_2\) protonation is nearly isoenergetic with CH\(_3\)CH\(_2\)NH\(_2\). There are no internal H-bonding effects.

Electron-withdrawing amide groups might be expected to have a similar effect on protonation energies. Rather, protonation energies are somewhat more exothermic than for NH\(_3\). As illustrated in Figure 3.7d, acetamide (CH\(_3\)C(O)NH\(_2\)) is preferentially protonated at the carbonyl center rather than at the N (Figure 3.7c). The former preserves conjugation in the amide group while the latter disrupts it, contributing to the 14 kcal mol\(^{-1}\) difference between these two. The effect is characteristic of the amide group; CH\(_3\)C(O)CH\(_2\)NH\(_2\), in which the amide constituents are separated by a CH\(_2\) group, prefers to be protonated at the amine center and has a protonation energy in the range of the alkyl-substituted amines. It also shows no internal H-bonding.

![Figure 3.7: Structures of the preferentially preferred oxygen protonation over amine protonation of NH\(_2\)COOH (b), (a) and CH\(_3\)CONH\(_2\) (d), (c).](image)

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Similar to the amides, the carbamic acids $\text{H}_2\text{NC(O)OH}$ and $\text{CH}_3\text{NHC(O)OH}$ are preferentially protonated at the carbonyl centers. Figure 3.7b shows that the lowest-energy protonated carbamic acid structure is planar and conjugated; proton transfer to the N center again disrupts conjugation and is 9 kcal mol$^{-1}$ endothermic. Even with this effect, the carbamic acids are calculated to be somewhat less basic than $\text{NH}_3$. Glycine, $\text{NH}_2\text{CH}_2\text{COOH}$, prefers to be protonated at the amine center and has a basicity in line with that found for the alkyl substituents.

3.2.4 Discussion

Figures 3.2, 3.3, and 3.6 summarize the main results of this work. Figure 3.2 compares the energies of the 1:1 reaction of $\text{CO}_2$ with a variety of substituted amines to form the carbamic acids $\text{RHNC(O)OH}$, Equation 3.2. Intrinsic reaction energies span a range of approximately 12 kcal mol$^{-1}$, with alkyl groups having the greatest enhancing and fluoro groups the greatest diminishing effects on reaction energies. Electronic effects are greatest for substituents directly attached to the amines; secondary interactions, for instance through internal hydrogen bonding, have further modifying effects on equilibrium structures, for instance, biasing the C(O)OH group to a *trans* over *cis* conformation, and thereby on energetics.

Figure 3.3 compares the energies of the 1:1 reactions of $\text{CO}_2$ with the same amines to the carbamates, Equation 3.3. If the basicities of all the carbamic acids were the same, as shown in Equation 3.5, then Figures 3.2 and 3.3 would be identical.

Clearly such is not the case: substituents modify carbamate energies in distinct ways. $\text{NH}_3$ itself is calculated to be the weakest carbamate form of the
compounds studied here; all substituents induce some amount of stabilization, generally tracking with the electron withdrawing strength of the substituent and its proximity to the amine. The reaction energy range is on the order of 15 kcal mol\(^{-1}\), similar to that for the carbamic acids. Notably outside this range, and surprisingly stable, are the carbamate products of CO\(_2\) reaction with a carbamic acid, listed in the center column of Figure 3.4. These products can be conceived to result from sequential reaction of two CO\(_2\) with an amine, and are stabilized by particularly favorable internal H bonding interactions between the two carbamate groups. While we are not aware of experimental evidence for a two CO\(_2\) to one primary reaction, if promoted by a suitable environment such reactions could significantly increase the efficiency of a CO\(_2\) capture process.

Figure 3.6 reports calculated protonation energies of the same set of amines. Here substituent effects are straightforward to understand: electron donors tend to enhance and electron acceptors tend to diminish protonation energies. The range of variation across substituted amines is over 50 kcal mol\(^{-1}\), quite large relative to the effects noted above. From this work, we can conclude that the Brønsted basicity of amines is more sensitive to substituents than is the Lewis basicity as measured by reaction with CO\(_2\).

As suggested in the Introduction, the oft-observed 2:1 stoichiometry for reactions of amines with CO\(_2\) can be decomposed into the sum of Equations 3.3 and 3.4. Figure 3.8 shows a correlation plot of the energies of these two, both normalized to the corresponding NH\(_3\) reactions.
Figure 3.8: Protonation reaction versus carbamate formation reaction.

The two reaction energies for a given amine are seen to be essentially uncorrelated. Diagonal dotted lines indicate contours of constant total 2:1 reaction energy. Total reaction energies vary over nearly 50 kcal mol\(^{-1}\), and any given overall reaction energy can in principle be achieved with any number of candidate amines. For instance, despite their very different basicities and carbamate formation energies, CF\(_2\)NH\(_2\) and CF\(_2\)HNH\(_2\) are predicted to give nearly identical 2:1 reaction energies; similar conclusions apply for diethylamine and acetamide. While these are obviously all model compounds and values are based on computed gas-phase energetics, such a correlation plot could be very useful as is or parameterized with experimental data to identify and classify candidate molecules for CO\(_2\) capture.
3.3 Discussion and Conclusions

The efficiency of amine-based CO\textsubscript{2} separations depends on having an absorbant with thermodynamic characteristics tuned to the given problem. We report B3LYP calculations to characterize several reactions relevant to the amine-CO\textsubscript{2} process, as a function of amine substituent. These results indicate that reaction energies can be tuned over a substantial range and are a function both of substituent and stoichiometry.

Given the interest in aqueous amines for CO\textsubscript{2} separations, it is worthwhile to compare the reactions of H\textsubscript{2}O to those of the amines. For the amine-CO\textsubscript{2} 1:1 reaction, water reaction to form carbonic acid is less exothermic than most of the amines studied and only slightly more exothermic than the most deactivated amines, CH\textsubscript{3}NHCOOH, NH\textsubscript{2}COOH, CF\textsubscript{3}NH\textsubscript{2}, and FNH\textsubscript{2}. Compared to the amine to carbamate reaction (Equation 3.3), water reaction to form bicarbonate anion has a reaction energy similar to the alkyl amines but less exothermic than all other amines studied. Lastly, water is a weaker Brønsted base than all of the amines studied. These last two observations show that the overall 2:1 reaction, described in Equation 3.1, for water would be less exothermic than all of the amines studied here.

In order to focus on intrinsic effects on reaction energies, we report gas-phase reaction energies. The absolute magnitudes of the reported numbers are undoubtedly sensitive to the particular chemical environment in which the amine is deployed and, in aqueous systems in particular, will be modified by coupling to other aqueous reactions, such as the formation of bicarbonate just described.
Regardless of specific environment, the results here will be useful for guiding the selection of materials.
CHAPTER 4:  
AMINO ACIDS

4.1 Introduction 
In the previous chapter, we discussed attaching different substituents to an amine functional group and how they would change the energetics of the two amines to one CO$_2$ reaction and the one amine to one CO$_2$ reaction. As mentioned in the Introduction, the most commonly used amine for CO$_2$ capture is aqueous ethanolamine (MEA). Its generally accepted reaction stoichiometry is two amines to one CO$_2$. There are, however, several drawbacks to using aqueous MEA to capture CO$_2$ from flue gas. The reaction of CO$_2$ with aqueous MEA is highly reactive. The high reaction enthalpy combined with the fact that aqueous MEA is 70% water, ends up requiring more energy to regenerate the solvent. A significant portion of that regenerative energy goes into vaporizing the water. As a result, it is estimated to increase the cost of electricity by about 80%. Aqueous MEA is also volatile to the air and highly corrosive. An alternative to using aqueous amines is to tether an amine functional group to an ionic liquid.$^{35-37}$

4.2 Cation vs. Anion Tethering 
In ionic liquids, there are two possible tethering locations, on the cation or on the anion. As previously discussed with aqueous amines, the generally accepted
stoichiometry is two amines per CO₂, but with ionic liquids, there is some question as to the stoichiometry of the reaction of CO₂ with an ionic liquid. We want to compare the 1 amine to 1 CO₂ reaction versus the 2 amines to 1 CO₂ reaction. In order to accomplish this, two reactions were investigated. The first reaction, depicted by Equation 4.1, involves the combination of an amine containing molecule and CO₂ to form a carbamic acid. This would indicate a 1:1 reaction ratio.

\[
\text{NH}_2 + \text{CO} \rightarrow \text{NH} - \text{CO}^{-} \tag{1}
\]

If the complexed carbamic acid were to lose a proton, a carbamate anion would be formed and presumably, the proton would go to another amine. This would suggest a one CO₂ to two amines reaction ratio. For comparison purposes, we are not accounting for where the proton goes. Equation 4.2 depicts the deprotonation of the carbamic acid and the formation of the carbamate anion and hydrogen proton.

\[
\text{NH} - \text{CO}^{-} \rightarrow \text{NH} - \text{CO}^{-} + \text{H}^+ \tag{2}
\]

For the purpose of comparing different amine tethering strategies; two cations, aminomethyl pyridinium and amino-4-methyl pyridinium, two anions, glycine and taurine, and one neutral, ethanolamine, were investigated. The energies for each reaction are compared to the neutral ethanolamine.
4.2.1 Results

Table 4.1 shows the most stable conformers for the reactants and products of both the carbamic acid formation reaction and the deprotonation reaction. The first column of reaction energies is for the carbamic acid formation reaction and the second column is for the deprotonation reaction.
TABLE 4.1:
THE REACTANTS, PRODUCTS, AND ZERO-POINT ENERGIES FOR THE CARBAMATE FORMATION AND DEPROTONATION REACTIONS CALCULATED WITH B3LYP/6-311G**(d,p).

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Carbamic Acid Product</th>
<th>Deprotonation Product</th>
<th>(\Delta E_{\text{pwar}})</th>
<th>(\Delta E_{\text{adep}})</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Methylamino Pyridinium" /></td>
<td><img src="image2" alt="Carbamic Acid Product" /></td>
<td><img src="image3" alt="Deprotonation Product" /></td>
<td>+5 kcal/mol</td>
<td>-79 kcal/mol</td>
</tr>
<tr>
<td><img src="image4" alt="Animo-4-methyl Pyridinium" /></td>
<td><img src="image5" alt="Methylamino Pyridinium" /></td>
<td><img src="image6" alt="Animo-4-methyl Pyridinium" /></td>
<td>+3 kcal/mol</td>
<td>-84 kcal/mol</td>
</tr>
<tr>
<td><img src="image7" alt="Ethanolamine" /></td>
<td><img src="image8" alt="Ethanolamine" /></td>
<td><img src="image9" alt="Ethanolamine" /></td>
<td>0 kcal/mol</td>
<td>0 kcal/mol</td>
</tr>
<tr>
<td><img src="image10" alt="Glycine" /></td>
<td><img src="image11" alt="Glycine" /></td>
<td><img src="image12" alt="Glycine" /></td>
<td>-15 kcal/mol</td>
<td>+88 kcal/mol</td>
</tr>
<tr>
<td><img src="image13" alt="Taurine" /></td>
<td><img src="image14" alt="Taurine" /></td>
<td><img src="image15" alt="Taurine" /></td>
<td>-8 kcal/mol</td>
<td>+70 kcal/mol</td>
</tr>
</tbody>
</table>

In Table 4.1, the molecules from top to bottom are methylamino pyridinium, animo-4-methyl pyridinium, ethanolamine, glycine, and taurine. The first column of energies corresponds to the carbamic acid formation reaction relative to that for MEA, the first two columns of molecules. The second column of energies corresponds to the deprotonation reaction relative to that for MEA, the second and
third columns of molecules. For the deprotonation reaction, the hydrogen proton product is not shown as it is the same for each reaction.

4.2.1.1 Carbamic Acid Formation

Ethanolamine forms a stable product with intermolecular hydrogen bonding. Compared to ethanolamine, the anions form more stable products. For the reaction of CO$_2$ with a glycine anion, a very stable product is formed. The product that is formed has very strong hydrogen bonding with a hydrogen being shared between two carboxyl groups. For taurine, the addition of the SO$_3^-$ group promotes a stronger reaction than ethanolamine but a weaker one than glycine. Both cations form less stable products than ethanolamine and both anions.

4.2.1.2 Deprotonation

With the loss of the hydrogen proton, ethanolamine forms an even more stable product due to increased internal hydrogen bonding. In this reaction, the cations form more stable products than ethanolamine. This is due to the fact that once the cations lose a hydrogen proton, they form neutral zwitterions which are more favorable than their respective cationic carbamic acids. With deprotonation, both anions become less stable than both ethanolamine and the cations. With the loss of the hydrogen proton, the anions form dianions which are considerably less favorable than their anionic carbamic acids.
4.2.2 Discussion

In regards to stoichiometry and the results shown in Table 4.1, if carbamic acid formation is favored, it would suggest that a 1:1 reaction with CO₂ would tend to occur. Analogously, if deprotonation is favored, that would suggest that a 2:1 reaction with CO₂ would tend to occur because the hydrogen proton would most likely attach to an original reactant forming an ammonium-type molecule. Based on this and the above results, cations tend to favor deprotonation because a neutral zwitterion is formed. This suggests a tendency towards two ionic liquids per CO₂ reaction ratio, which would correspond to about a 50% molar ratio uptake capacity. On the other hand, anions tend to disfavor deprotonation because a di-anion is formed and the protonated form of the product is stable due to intermolecular hydrogen bonding. This suggests a tendency towards one ionic liquid per CO₂ reaction ratio, which corresponds to about a 100% molar ratio uptake capacity.

4.3 Methionine

We have shown that by tethering an amine functional group to an anion in an ionic liquid, we can obtain a one amine to one CO₂ stoichiometry. In doing so, we can double the uptake of CO₂ over conventional aqueous amines. We have looked at the reaction of methionine with CO₂ and its 1:1 reaction.

4.3.1 Reactant

Because of the relatively long backbone of methionine and its ability to elongate and to curl in on itself, there are numerous conformations of both the reactant and product species. For the reactant, we found 17 different stable
conformations. Using the Boltzmann distribution, we found that only 11 of the 17 reactant configurations make any significant contributions to the average reactant energy. Figure 4.1 shows these 9 conformers.

![Conformers](image)

Figure 4.1: Nine conformations of methionine that contribute the most to the overall average energy listed from most (a) to least (i)

4.3.2 Product and Reaction Enthalpy

As we showed earlier, when CO₂ reacts with the amine functional group, one of the protons transfers to the reacting CO₂. In the case of an amino acid, there are two carboxyl groups present in the reacted species, the original group seen in the reactant and the reacted CO₂. We found 46 stable conformations of the product, which can fit into three different categories based on the location of the proton.
Figure 4.2 shows examples of the three categories: shared between the carboxyl groups (a), attached to the reacted carboxyl group (b), or attached to the original carboxyl group (c).

Figure 4.2: Three categories of product conformations based on where the proton is located.

Figure 4.2a shows the most stable conformation of the reacted methionine.

Using the Boltzmann weighted average energies for both the reactant and product, the reaction enthalpy of methionine reacting with CO$_2$ is -55 kJ/mol.

4.3.3 Comparison to Experimental Data

Our experimental collaborators synthesized the ionic liquid trihexyl(tetradecyl)phosphonium methionate ([P$_{66614}$][Met]) and tested its ability to capture CO$_2$. Measurements were taken using both a stoichiometric uptake apparatus and isochorically in an IR system.$^{38}$ Figure 4.3 shows the isotherm curves that were obtained from both experimental techniques.
As can be seen from Figure 4.3, the CO₂ capacity of methionine is significantly greater than the one CO₂ to two ILs stoichiometry and approaches the 1:1 stoichiometry as predicted. This experimental data confirms the theoretical arguments that an anion tethered amine in an ionic liquid should produce a one CO₂ to one IL instead of a one CO₂ to two ILs stoichiometry. In conjunction with the uptake experiments, calorimetric measurements were employed to directly measure the heats of absorption and reaction of CO₂ with the ionic liquid [P₆₆₆₁₄][Met]. Calorimetry data produces a reaction enthalpy of -64 kJ/mol, which is good agreement with our B3LYP theoretically calculated reaction enthalpy of -55 kJ/mol.
As further evidence of a 1:1 stoichiometry, IR spectra were both measured and calculated. Figure 4.4 shows the IR spectrum of the lowest energy conformation of the unreacted methionine.

![Graph showing the computed infrared absorption spectrum of the lowest energy reactant methionine.](image)

**Figure 4.4:** The computed infrared absorption spectrum of the lowest energy reactant methionine.

Using a scaling factor of 0.9679 for B3LYP, the computed frequencies were compared to those found experimentally. In the reactant molecule, the two most important frequencies to observe would be to confirm the presence of both the NH$_2$ fragment and the COO$^-$ fragment. Table 4.2 provides a comparison between computation and experiment for these frequencies. For the computational frequencies, the lowest energy conformation of the unreacted methionine was used.
TABLE 4.2:
COMPARISON BETWEEN COMPUTATIONAL AND EXPERIMENTAL FREQUENCIES FOR UNREACTED METHIONINE.

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computational</td>
<td>Experimental</td>
</tr>
<tr>
<td>3309</td>
<td>3300</td>
</tr>
<tr>
<td>1595</td>
<td>1598</td>
</tr>
</tbody>
</table>

As can be seen from the comparison, our computational calculations are in great agreement with experimental data.

For the product molecule, the most significant frequencies to observe would be the presence of a new COOH fragment, an NH fragment and absence of an NH₂ fragment. Figure 4.5 shows the computed IR spectrum of the lowest energy conformation of the product (Figure 4.2a).

Figure 4.5: The computed infrared absorption spectrum of the lowest energy conformation of the reacted methionine.
Table 4.3 compares the calculated IR spectrum to the experimental spectrum. The experiment did not have a frequency value for the NH bend as it was at a lower frequency than the tolerance of the experimental apparatus. In both the computational and experimental IR, there is no evidence of an NH$_2$ fragment. All of these combine to affirm that the reaction of methionine with CO$_2$ is a 1:1 reaction.

**TABLE 4.3:**

**COMPARISON OF SIGNIFICANT FREQUENCIES BETWEEN COMPUTATIONAL AND EXPERIMENTAL IR SPECTRAS OF REACTED METHIONINE.**

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Computation</th>
<th>Experiment</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1704</td>
<td>1716</td>
<td>COOH stretch</td>
</tr>
<tr>
<td></td>
<td>519</td>
<td>N/A</td>
<td>NH bend</td>
</tr>
</tbody>
</table>

4.4 Proline

In addition to methionine, we have also looked at the amino acid proline. Proline is different from other amino acids, such as methionine, in that it is a five membered ring instead of a chain.

4.4.1 Reactant

Because of the ring structure of proline, there are significantly fewer conformations than methionine. For the proline reactant, there are three conformations as can be seen in Figure 4.6.
Figure 4.6: The three conformations of the reactant proline listed from lowest (a) to highest (c) energy conformation.

The main difference between the three conformations is the degree of bending of the ring. Figure 4.6a is the lowest energy conformation and contributes the majority to the overall energy of the reactant proline.

4.4.2 Product and Reaction Enthalpy

As with methionine, when proline reacts with CO$_2$, the proton can be found in three possible locations: shared between the two carboxyl groups, attached to the existing carboxyl group, or attached to the new carboxyl group. Overall, we found 13 stable conformation of reacted proline. Figure 4.7 shows the lowest energy conformation of each of the three categories.
Figure 4.7: Three categories of the reacted proline based on where the proton is located.

Figure 4.7a is the overall lowest energy conformation found where the proton is shared between the two carboxyl groups. Using the Boltzmann weighted average energies for both the reactant and product, the reaction enthalpy of proline reacting with CO$_2$ is -71 kJ/mol.

4.4.3 Compared to Experimental Results

Our experimental collaborators synthesized the ionic liquid trihexyl(tetradecyl)phosphonium prolinate ([P$_{66614}$][Pro]) and tested its ability to capture CO$_2$. It was tested using the same methods as the methionine. As can be seen from Figure 4.3, the CO$_2$ capacity of proline is significantly greater than the one CO$_2$ to two ILs stoichiometry and approaches the 1:1 stoichiometry predicted. The vast majority of the CO$_2$ uptake is due to chemical complexation, which is evidenced by the steep uptake curves at lower pressures in Figure 4.3. The steeper uptake curve of the proline, in relation to the methionine, is indicative of a higher heat of reaction. This is consistent with the computational calculations. Calorimetry found a reaction enthalpy of -80 kJ/mol$^{38}$, which is in good agreement with the
computationally calculated -71 kJ/mol and with the experimental uptake curves that show proline has a higher reaction enthalpy than methionine.

We have calculated the IR spectra of both the unreacted and reacted proline to compare to experimental results and to further confirm the 1:1 stoichiometry. Figure 4.8 shows the IR spectrum of the lowest energy conformation of unreacted proline, as illustrated in Figure 4.6a.

![Figure 4.8: Computed infrared absorption spectrum of the lowest energy conformation of unreacted proline.](image)

Table 4.4 compares the experimental and scaled computational frequencies that are the most important to observe in the reactant proline. As can be seen in the table, the computational frequencies agree quite well with the experimental data.
TABLE 4.4:

COMPARISON OF IMPORTANT FREQUENCIES OF UNREACTED PROLINE FOUND BOTH COMPUTATIONALLY AND EXPERIMENTALLY$^{38}$.

<table>
<thead>
<tr>
<th>Frequency (cm$^{-1}$)</th>
<th>Computational</th>
<th>Experimental</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3290</td>
<td>3290</td>
<td>3290</td>
<td>NH stretch</td>
</tr>
<tr>
<td>1612</td>
<td>1634</td>
<td>1634</td>
<td>COO$^-$ asymmetric stretch</td>
</tr>
</tbody>
</table>

For the reacted proline molecule, it is important to observe a new frequency associated with a COOH fragment and absence of a frequency for an NH fragment or an ammonium fragment, which would indicate a one CO$_2$ to two amine stoichiometry. The IR spectrum of the reacted proline is shown in Figure 4.9.

![Figure 4.9: Computed infrared spectrum of the lowest energy conformation of reacted proline.](image)

The new COOH fragment for the experiment occurs at 1689 cm$^{-1}$, while our scaled computational frequency occurs at 1684 cm$^{-1}$. Neither experimental nor
computational spectra had any evidence of an NH fragment or ammonium fragment, which supports the 1:1 reaction stoichiometry.\textsuperscript{38}

4.5 Conclusions

We have showed that be tethering an amine functional group to an anion in an ionic liquid, we are able to double the capacity of capturing CO\textsubscript{2} over a conventional aqueous amine system. In other words, we are able to achieve a one CO\textsubscript{2} to one IL instead of a one CO\textsubscript{2} to two amines stoichiometry. We studied the two amino acids methionine, which contains a carbon chain backbone, and proline, which contains a five membered ring. We calculated a reaction enthalpy with CO\textsubscript{2} of -71 kJ/mol and -55 kJ/mol for proline and methionine, respectively. These reaction enthalpies and the trend between the two was confirmed by both experimental CO\textsubscript{2} uptake and IR measurements.
CHAPTER 5:

AHAs

5.1 Introduction

In the previous chapter, we discussed how tethering an amine functional group to an anion in an ionic liquid would produce a 1:1 reaction stoichiometry with CO₂. We showed how CO₂ reacts with the amino acids methionine and proline and compared our calculations with experimental data. Unfortunately, the amino acids had a major drawback to using them, high viscosities. As the amino acid would react with CO₂, the viscosity of the ionic liquid would dramatically increase due to hydrogen bonding networks that formed. In order to eliminate the viscosity problems, the reaction with CO₂ should not produce acidic protons. It has been previously reported that N-heterocyclic carbenes reversibly form carboxylate adducts with CO₂ as shown in Figure 5.1a. This carbene chemistry with CO₂ suggests that the isoelectronic N-heterocyclic anions might be capable of the same, Figure 5.1b. The N-heterocyclic anions are essentially tertiary amines and therefore, eliminate the protons in the CO₂ capture process that end up causing viscosity problems through hydrogen bonding networks. There are several anions that can fall into the aprotic heterocyclic anions (AHAs) category.
Figure 5.1: Illustrations of an N-heterocyclic carbene reaction with CO$_2$ (a) and the reaction of an N-heterocyclic anion with CO$_2$ (b).\textsuperscript{41}

5.2 Parent AHAs

We have studied the reaction of CO$_2$ with five different AHAs as shown in Figure 5.2; pyrrolide (a), pyrazolide (b), imidazolide (c), indole (d), and benzimidazole (e). We looked at the nitrogen natural bond order (NBO)\textsuperscript{24} charge of the unreacted species to determine if they could be used to predict the CO$_2$ reaction enthalpy of the species. We optimized all of the structures and found their energies and enthalpies using the B3LYP method as discussed in Chapter 2.
Figure 5.2: Unreacted pyrrolide (a), pyrazolide (b), imidazolide (c), indolide (d), and benzimidazole (e).

5.2.1 Pyrrolide

The parent pyrrolide anion is both planar and aromatic with a nitrogen NBO charge of -0.604. As shown in Figure 5.3a, the pyrrolide anion reacts with CO₂ at the ring nitrogen to form a carbamate anion, similar to the reaction of CO₂ with the amino acid prolinate shown in Chapter 4. The combination of the pyrrolide anion with CO₂ results in a 298 K reaction enthalpy of -99 kJ mol⁻¹. The reaction enthalpy coupled with the N-C bond length of 1.53 Å indicate a strong affinity for CO₂, even greater than the aqueous amines. The subsequent carbamate product is planar and has a high barrier to rotation of the CO₂ of 39 kJ mol⁻¹; both which indicate the presence of π conjugation.
5.2.2 Pyrazolide

The parent pyrazolide is planar with two nitrogens next to each other in the aromatic ring. Both nitrogens have an NBO charge of -0.404. When pyrrolide is reacted with CO₂ (Figure 5.3b), it reacts with an enthalpy of -74 kJ/mol. The reacted pyrazolide is still planar and has N-C bond length of 1.57 Å, which is consistent with a more endothermic reaction than pyrrolide.

5.2.3 Imidazolide

Unreacted imidazolide is similar to pyrazolide but instead of the two nitrogens being right next to each other, they are separated by one carbon. Also similar to pyrazolide, both nitrogens have the same NBO charge, -0.613. The NBO
charge for imidazolide is more negative than pyrrolide which would suggest that imidazolide would have a CO$_2$ reaction enthalpy more exothermic than pyrrolide, but that is not the case. Imidazolide has a CO$_2$ reaction enthalpy of -78 kJ/mol. This suggests that the charge on the reacting nitrogen atom is not a good indicator of what the reaction enthalpy will be. The N-C bond length for the reacted imidazolide is 1.54 Å, which is between the bond lengths of pyrrolide and pyrazolide, and their respective reaction enthalpies.

5.2.4 Indolide

Indolide is a pyrrolide with a benzene ring attached, as seen in Figure 5.2d. The unreacted indolide nitrogen has an NBO charge of -0.607. Even though indolide is a much larger molecule than the previously mentioned AHAs, it is still planar when it reacts with CO$_2$. It has a reaction enthalpy of -72 kJ/mol and an N-C bond length of 1.53 Å. Comparing to the previous AHAs, the bond length suggests that the reaction enthalpy should be stronger, between -78 kJ/mol and -99 kJ/mol, but it is slightly less than that.

5.2.5 Benzimidazolide

Unreacted benzimidazolide is similar to indolide but contains a benzene fused to an imidazolide instead. Both of the nitrogens have the same NBO charge of -0.608. The unreacted molecule is planar and maintains planarity when reacted with CO$_2$. The CO$_2$ reaction enthalpy of the benzimidazolide is -54 kJ/mol with an N-C bond length of 1.55 Å. Both the NBO charge and N-C bond length suggest that the species should have a large reaction enthalpy, but it is quite lower than expected.
This again shows that the nitrogen NBO charge on the unreacted species is not a good indicator of reactivity with CO₂. The N-C bond length is also quite inconsistent than what has previously been observed. This along with the inconsistent indolide N-C bond length indicates that the trend between N-C bond length and CO₂ reaction enthalpy are not comparable across different species.

5.3 Addition of Functional Groups

We want to propose several possible ionic liquid AHA candidates that have a range of CO₂ reaction enthalpy between -12 kJ/mol (physical absorption) \(^{10}\) and -80 kJ/mol (chemical absorption)\(^{42}\). To meet this goal, we add electron withdrawing functional groups to the parent molecules to lower the reaction enthalpies. We have studied the use of several electron-withdrawing groups such as a cyano group in different locations around the aromatic ring of pyrrolide, pyrazolide, and imidazolide.

5.3.1 Cyano

5.3.1.1 Remote Substitution

We first investigated the effect of addition of a cyano group at a ring site remote from the reacting nitrogen center. We attached a cyano group to the pyrrolide anion in the \(\beta\) position, two carbons away from the reacting nitrogen, shown in Figure 5.4a. The cyano group is co-planar with the ring. This 3-cyanopyrrolide combines with CO₂ with an enthalpy of -59 kJ/mol. The reacted
species is planar and the N-C bond length is 1.56 Å, which would be in line with a less exothermic reaction when compared to the reacted pyrroline.

![Chemical structures](image)

**Figure 5.4**: The unreacted and CO$_2$ reacted species of 3-cyanopyrroline (a,b), 4-cyanopyrazolide (c,d), 3-cyanopyrazolide (e,f), and 4-cyanomidazolide (g,h).

For the pyrazolide anion, a cyano substituent can be placed either two carbons or one nitrogen and one carbon away from the reacting center, Figure 5.4c and e, respectively. The remote reactants and products (Figure 5.4d and f, respectively) of both 4-cyanopyrazolide and 3-cyanopyrazolide are planar. The corresponding reaction enthalpies are within 1 kJ/mol of each other, -35 and -36 kJ/mol, respectively. The new N-CO$_2$ bond lengths are within 0.01 Å apart, 1.62 Å for 4-cyanopyrazolide and 1.63 Å for 3-cyanopyrazolide. These results show that a remote CN group has a uniform effect on the reaction enthalpy.
The imidazolide anion offers one possible remote CN substitution site, two carbons from the reacting nitrogen and adjacent to the second nitrogen (Figure 5.4g). Both the reactant and product of 4-cyanoimidazolide are planar and the CO₂ reaction enthalpy is -40 kJ/mol with an N-C bond length of 1.58 Å.

Substituting a cyano group at the β position in pyrrolide, pyrazolide, and imidazolide results in less exothermic reactions with CO₂ than their unsubstituted counterparts. For both β-substituted pyrazolide and imidazolide, their CO₂ reaction enthalpies are raised by 38 kJ/mol, while for the β-substituted pyrrolide, it is raised by 40 kJ/mol. This would suggest that adding a cyano group in the β position of an unsubstituted AHA relative to the reacting nitrogen would result in the CO₂ reaction enthalpy to be raised by approximately 38-40 kJ/mol. To test this theory, the β-substituted indolide reaction with CO₂ was calculated. 3-cyanoindolide had a reaction energy of -37 kJ/mol, which is 35 kJ/mol less reactive than the unsubstituted indolide. This is consistent with the approximation proposed.

Table 5.1 summarizes the remote cyano substitution CO₂ reaction enthalpies.

**TABLE 5.1:**

**CO₂ REACTION ENTHALPIES FOR REMOTE CYANO SUBSTITUTION**

<table>
<thead>
<tr>
<th>Reactant</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-cyanopyrrolide</td>
<td>-59</td>
</tr>
<tr>
<td>4-cyanopyrazolide</td>
<td>-35</td>
</tr>
<tr>
<td>3-cyanopyrazolide</td>
<td>-36</td>
</tr>
<tr>
<td>4-cyanoimidazolide</td>
<td>-40</td>
</tr>
</tbody>
</table>
5.3.1.2 Proximal Substitution

A proximal cyano group means placing the functional group on a ring atom immediately adjacent to the reacting nitrogen. We first investigate 2-cyanopyrrolidine, Figure 5.5a. The unreacted 2-cyanopyrrolidine is planar with the cyano group being linear. After combining with CO₂, the molecule maintains its planarity but the cyano group is no longer linear, as it bends to an angle of 171°. The CO₂ reaction enthalpy is -35 kJ/mol and N-C bond length is 1.58 Å. This bond length is greater than in both the remote-substituted cyanopyrrolidine and the unsubstituted pyrrolidine, which is consistent with it having a less exothermic reaction enthalpy than either one.

Figure 5.5: Unreacted and reacted molecules of 2-cyanopyrrolidine (a,b), 5-cyanopyrazolide (c,d), 2-cyanoimidazolide (e,f), and 5-cyanoimidazolide (g,h).
The 3-substituted cyanopyrazolide, Figure 5.4/5.5c, has one proximal reaction site. Similar to 2-cyanopyrroolid, when 3-cyanopyrazolide reacts at the proximal N with CO$_2$, the cyano group bends away from CO$_2$ to an angle of 171°. CO$_2$ reacts with an enthalpy of -12 kJ/mol, which is significantly higher than reaction at a remote substituted site (-36 kJ/mol) or the unsubstituted pyrazolide (-74 kJ/mol). The N-CO$_2$ bond length is relatively long at 1.65 Å, consistent with its low reactivity and trends observed with other substitution patterns. We see that the nitrogen two carbons away from the substituent group, in this case cyano, will win out over the nitrogen right next to the substituent group as the former has a lower CO$_2$ reaction enthalpy.

In the case of imidazolide, there are two places for the cyano group to be attached proximally to the reaction center, either attached to the 2-carbon between the reacting and unreacting nitrogens, 2-cyanimidazolide (Figure 5.5e), or attached to the 4-carbon, 4-cyanimidazolide (Figure 5.4g/5.5g). Both unreacted 2- and 4-cyanimidazolide are planar with the cyano group being linear. When the N center proximal to the CN are reacted with CO$_2$, the cyano group bends to 174° in 2-cyanimidazolide and to 172° in 4-cyanimidazolide. The N-CO$_2$ bond length is 1.61 Å in both cases and the reaction enthalpies are -17 and -18 kJ/mol, respectively. Based on the reaction enthalpies, N-C bond lengths and cyano bending, a proximal cyano group has the same influence regardless of the location on the ring.

For the imidazolide, there are two nitrogens competing to react with CO$_2$. In 2-cyanopyrazolide, the nitrogens are equal to each other and there is no difference between them. In 4- cyanopyrazolide, the two nitrogens are inequivalent, where
one nitrogen is next to the cyano group and the other is two carbons away. The nitrogen that is two carbons away has a lower reaction enthalpy than the one next to the substituent group; therefore, the CO₂ will preferentially react at the remote nitrogen instead of the proximal nitrogen. This is the same trend seen in the substituted pyrazolide.

The location of the electron withdrawing functional group relative to the reacting nitrogen is key in tuning the CO₂ reaction enthalpy of an AHA molecule. An electron-withdrawing group raises the reaction energy irrespective of position; a group immediately adjacent to a reacting center has a particularly large deactivating effect. This trend was observed for all of the electron-withdrawing groups studied. A few calculations were done were two cyano groups were placed on the same AHA or a combination of two electron withdrawing groups were place on the same AHA. In each of the cases calculated, the molecule would not bind CO₂ as the multiple electron withdrawing groups lowered the reactivity of the nitrogen to below that of chemical complexation with CO₂. Therefore, the use of multiple electron withdrawing groups on a single AHA was not studied further.

Table 5.2 summarizes the proximal cyano substitution CO₂ reaction enthalpies.
TABLE 5.2:

CO₂ REACTION ENTHALPIES OF PROXIMAL CYANO SUBSTITUTION

<table>
<thead>
<tr>
<th>Reactant</th>
<th>ΔH (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-cyanopyrrolide</td>
<td>-35</td>
</tr>
<tr>
<td>3-cyanopyrazolide</td>
<td>-12</td>
</tr>
<tr>
<td>2-cyanoimidazolide</td>
<td>-17</td>
</tr>
<tr>
<td>4-cyanoimidazolide</td>
<td>-18</td>
</tr>
</tbody>
</table>

5.4 Solvation Effects

Up to this point, all of the simulations have been in the gas-phase, but the actual IL system will be in the liquid phase. We have employed both implicit and explicit solvation to determine how much the solvent will affect the CO₂ reaction enthalpies compared to the gas-phase calculations.

5.4.1 Implicit Solvation

For the implicit solvation model, we used the conductor-like polarizable continuum model (CPCM). It approximates a given solvent by a dielectric continuum, which surrounds solute molecules outside of a molecular cavity. There are several factors that define a dielectric continuum, one of them being the dielectric constant. There are several solvents already available in the Gaussian03 program, none of which are ionic liquids. Since more information than the dielectric constant would need to be known to simulate a solvent, we chose three already available solvents to calculate our liquid phase CO₂ reaction enthalpies. We chose aniline, isoquinoline and acetone, which have dielectric constants of 6.8882, 11.00, and 20.493, respectively. We ran calculations of CO₂ reactions in each of the
solvents for pyrrolide, 2-cyanopyrrolide, 3-cyanopyrrolide, 2-fluoropyrrolide, and 3-fluoropyrrolide. Table 5.1 shows the comparison of the CO₂ free energy of reaction of the five anions in the gas-phase, aniline, isoquinoline, and acetone. We are now reporting ΔG values due to the solvation calculations intrinsically consider both enthalpic and entropic contributions of the solvent. There are no analogous entropic parts in the gas phase, as there is no solvent there.

TABLE 5.1:

COMPARISON OF CO₂ REACTION FREE ENERGY FOR PYRROLIDE, 2-CYANOPYRROLIDE, 3-CYANOPYRROLIDE, 2-FLUOROPYRROLIDE, 3-FLUOROPYRROLIDE IN THE GAS-PHASE, ANILINE, ISOQUINOLINE, AND ACETONE.

ALL ENERGIES ARE IN KJ/MOL.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>ΔG_gas</th>
<th>ΔG_aniline</th>
<th>ΔG_isoquinoline</th>
<th>ΔG_acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrrolide</td>
<td>54</td>
<td>48</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>2-cyanopyrrolide</td>
<td>9</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3-cyanopyrrolide</td>
<td>-14</td>
<td>-11</td>
<td>-11</td>
<td>-12</td>
</tr>
<tr>
<td>2-fluoropyrrolide</td>
<td>-3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3-fluoropyrrolide</td>
<td>-44</td>
<td>-38</td>
<td>-37</td>
<td>-37</td>
</tr>
</tbody>
</table>

The differences between the gas-phase and the solvent reaction free energy ranges from 2-8 kJ/mol, with the average difference being 5 kJ/mol.

5.4.2 Explicit Solvation

To compare to the implicit solvation, we employ explicit solvation. In our explicit solvation calculations, we used a tetramethylphosphonium \([P_{2222}]\) cation paired with a 2-cyanopyrrolide [2-CNPyr] anion. We explored several locations of
the cation in relation to the anion. For the unreacted \([\text{P}_{2222}][2\text{-CNPy}r]\), there were four stable configurations found, all of which are shown in Figure 5.6.

![Figure 5.6: The four stable conformations of the \([\text{P}_{2222}][2\text{-CNPy}r]\) system listed from lowest energy conformation (a) to highest (d).](image)

In Figure 5.6a, c, and d, the phosphorous atom and two of the methyl groups are in the same plane as the anion, while the other two methyl groups are straddling the anion. In Figure 5.6b, the cation is not in the same plane as the anion. The same method was used to find the most stable conformations of the CO\(_2\) reacted \([\text{P}_{2222}][2\text{-CNPy}r]\) system. Again, there were four stable conformations found, which are shown in Figure 5.7. In Figures 5.7a, b, and c, the phosphorous atom and two of the methyl groups are in the same plane as the anion, while the other two methyl groups straddle the anion. In Figure 5.7d, the cation is slightly out of plane in relation to the anion and is orientated as such that three of the methyl groups are in a pyramidal shape above one of the oxygen atoms of the anion, but this is the highest energy conformation and contributes very little to the average energy.
Figure 5.7: The four stable conformations of the CO$_2$ reacted [P$_{2222}$][2-CNPyr] system listed from lowest energy conformation (a) to highest (d).

Using the Boltzmann averaged enthalpies for both the reactant and product, the CO$_2$ reaction enthalpy of the system is -40 kJ/mol, which is only a 5 kJ/mol difference from the gas-phase enthalpy of -35 kJ/mol.

Both implicit and explicit solvation have a 5 kJ/mol average difference between the solvated and gas-phase energies. These solvation calculations show that there isn’t a major difference between the solvation and gas-phase energies and the gas-phase energies are a valid approximation to use. This is because the solvation energy is relatively the same across different reactions, which doesn’t change the trends seen in the reaction energies. Also, the difference between the solvated and gas-phase energies is relatively small, so only performing the gas-phase calculations is a good approximation.
5.5 Comparison to Experimental Data

To more accurately compare our calculations to experimental data, we employed the G3 method, which is a higher order method than B3LYP, to calculate the CO$_2$ reaction enthalpy of 2-cyanopyrrolide. The B3LYP reaction enthalpy is -35 kJ/mol, but the more accurate G3 reaction enthalpy is found to be -49 kJ/mol. Experimental calorimetric measurements found the CO$_2$ reaction enthalpy of 2-cyanopyrrolide to be -53 +/- 5 kJ/mol.$^{41}$ Our G3 calculated reaction enthalpy agrees quite well with the calorimetric enthalpy. This supports our claim that our gas-phase calculated reaction enthalpies are good indicators of the liquid phase reaction enthalpy.
CHAPTER 6:
ISOTHERM MODEL

We have been able to calculate the heats of reaction with CO$_2$ for a large variety of molecules. We want to be able to develop simple isotherm models that would aide in understanding what governs the performance of an ionic liquid for capture CO$_2$ and to be able to compare our computational results with experimental results.

6.1 Model

Our experimental collaborators, the Dr. Brennecke group at Notre Dame, define the reaction of CO$_2$ with an ionic liquid as

\[ IL_0 + CO_2 \rightarrow IL + CO_2 \]

(6.1)

where IL$_0$ is a constant amount. The mole ratio of captured CO$_2$ to the amount of IL is defined as

\[ z_{CO_2} = \frac{N_{CO_2}}{N_{IL}} \]

(6.2)

We break the overall process into two steps, the physical absorption and the chemical absorption. Three different coupled equilibrium equations can be written to describe the physical and chemical reactions that are taking place in the absorption of CO$_2$. The
first reaction is the physical absorption of CO\(_2\) into the ionic liquid as shown in Figure 6.1. The second reaction is the liquid combination of CO\(_2\) and IL to form IL-CO\(_2\), which represents the complexed CO\(_2\). We can also write the chemical complexation part as reaction 3 where gas-phase CO\(_2\) combines with liquid IL to form IL-CO\(_2\).

![Diagram](image)

Figure 6.1: Schematic of the three different ways to write the physical and chemical reactions.

We chose to use reaction 3 to define the chemical complexation

\[
IL_{(l)} + CO_{2(g)} \leftrightarrow IL-CO_{2(l)}
\]  

In order to find the total mole ratio, \(z_{CO2}\), we need to find the ratio of CO\(_2\) physically absorbed versus the total amount of IL, \(N_{CO2(phys)}/N_{IL0}\), and the ratio of CO\(_2\) complexed versus the total amount, \(N_{ILCO2}/N_{IL0}\). The chemical equilibrium for the chemical complexation reaction (Equation 6.3) is

\[
K_1 = \frac{a_{IL-CO2}}{a_{IL}a_{CO2(g)}}
\]  

It is assumed that the activity coefficient is one. We want to determine the equilibrium on a molarity basis so we define the activities of each species as such.
\[ K_1 = \frac{N_{\text{IL-CO}_2}/V_L}{N_{\text{IL}}/V_L \cdot P_{\text{CO}_2}} \]  \hspace{1cm} (6.5)

\( N_{\text{IL}0} \) is the sum of \( N_{\text{IL}} \) and \( N_{\text{IL-CO}_2} \). As such, \( N_{\text{IL}} \) is equal to \( N_{\text{IL}0} - N_{\text{IL-CO}_2} \).

Substituting that into Equation 6.5 yields

\[ K_1 = \frac{N_{\text{IL-CO}_2}}{(N_{\text{IL}0} - N_{\text{IL-CO}_2})P_{\text{CO}_2}} \]  \hspace{1cm} (6.6)

Equations 6.7 and 6.8 rearrange Equation 6.6 in order to solve for \( N_{\text{ILCO}_2} \), which would give the number of moles of \( \text{CO}_2 \) complexed.

\[ K_1P_{\text{CO}_2}N_{\text{IL}} = N_{\text{ILCO}_2}(1 + K_1P_{\text{CO}_2}) \]  \hspace{1cm} (6.7)

\[ \frac{N_{\text{ILCO}_2}}{N_{\text{IL}}^*} = \frac{K_1P_{\text{CO}_2}}{1 + K_1P_{\text{CO}_2}} \]  \hspace{1cm} (6.8)

Equation 6.8 gives us the number of moles of \( \text{CO}_2 \) for chemical absorption per number of moles of \( \text{IL} \). \( K_1 \) is also be defined as

\[ K_1 = e^{-\Delta G^*/RT} = e^{-\Delta H^*/RT} e^{-\Delta S^*/RT} \]  \hspace{1cm} (6.9)

We define physical absorption as

\[ \text{CO}_2(g) \rightarrow \text{CO}_2(l) \]  \hspace{1cm} (6.10)

The chemical equilibrium for the physical absorption on a molarity basis is

\[ K_y = \frac{N_{\text{CO}_2}(l)/V_I}{P_{\text{CO}_2}} \]  \hspace{1cm} (6.11)
Based on Henry’s law, $K_B$ is equal to $1/h_{CO_2(IL)}$, where $h_{CO_2(IL)}$ is the Henry’s constant for $CO_2$ in the IL.

Since we are using an experimental value for $h_{CO_2(IL)}$, we need to use the same basis, mass rather than molar, that the experiments use. Equation 6.12 shows this relationship.

$$\frac{N_{CO_2(I)}}{N_{CO_2(I)} + N_{IL}} = \frac{P_{CO_2(g)}}{h_{CO_2(IL)}}$$  \hspace{1cm} (6.12)

Equation 6.13 is rearranged to solve for $N_{CO_2(IL)}/N_{IL}$.

$$\frac{N_{CO_2(I)}}{N_{IL}} = \frac{P_{CO_2}}{h_{CO_2(IL)} - P_{CO_2}}$$  \hspace{1cm} (6.13)

Equation 6.14 gives the total amount of $CO_2$ absorbed per amount of IL.

$$z_{CO_2} = \frac{N_{CO_2(I)}}{N_{IL}} + \frac{N_{ILCO_2}}{N_{IL}}$$  \hspace{1cm} (6.14)

Plugging Equations 6.8 and 6.13 into Equation 6.14 yields

$$z_{CO_2} = \frac{P_{CO_2}}{h_{CO_2(IL)} - P_{CO_2}} + \frac{K_1P_{CO_2}}{1 + K_1P_{CO_2}}$$  \hspace{1cm} (6.15)

In Equation 6.15, $h_{CO_2(IL)}$ and $K_1$ are parameters, while $z_{CO_2}$ is the unknown being solved for.

We will now use Equation 6.15 to determine $CO_2$ isotherms. In order to accomplish this, we need to know $h_{CO_2(IL)}$, $P_{CO_2}$, $K_1$, and Temperature. For isotherms, $P_{CO_2}$ will vary while $T$ is held constant. $T$ is typically 25°C or 40°C.
6.2 No Temperature Dependence

For the first case studied, we will consider the enthalpy, \( H \), and entropy, \( S \), of the IL to be temperature independent. The Henry’s Law constant is

\[
\ln(h_{\text{CO}_2,i}) = -\frac{\Delta S^o_1}{R} + \frac{\Delta H^o_1}{RT}
\]  

(6.16)

where both \( \Delta S^o_1 \) and \( \Delta H^o_1 \) are determined experimentally. We only studied the case where the Henry’s Law constant is taken to be consistent with the physically absorbing ionic liquid 1-n-butyl-3 methylimidazolium hexafluorophosphate. For the physically absorbing ionic liquid, \( \Delta H^o_1 \) is found to be about -11 kJ/mol, while \( \Delta S^o_1 \) is found to be about -0.0532 kJ/mol-K at 25°C.

\( \Delta S^o_3 \) is a combination of the physical and chemical losses in \( \Delta S^o \).

\[
\Delta S^o_3 = \Delta S^o_1 + \Delta S^o_2
\]  

(6.17)

The max \( \Delta S^o_3 \) is assumed to be equal to the complete loss of \( \text{CO}_2 \) translational entropy as it goes from the gas phase to the liquid phase. The exact value of \( \Delta S^o_2 \) is unknown so it will be varied according to \( \Delta S^o_2 = \alpha(\Delta S^o_{\text{trans}} - \Delta S^o_1) \)

\[
\Delta S^o_1 + \alpha(\Delta S^o_{\text{trans}} - \Delta S^o_1) \leq \Delta S^o_{\text{trans}}
\]  

(6.18)

The total translational \( \Delta S^o \) at 25°C is calculated from the Sackur-Tetrode equation,

\[
S^o_{\text{trans}} = R \ln \left( \frac{e^{\frac{5}{2}k_BT}}{PA^3} \right)
\]  

(6.19)

where
(6.20)

and \(k_B\) is Boltzmann’s constant, \(h\) is Plank’s constant, \(\beta = 1/(k_B T)\), and \(m\) is the mass of a gas particle. The \(\Delta H_{\text{rxn}}\) is calculated from first principles calculations. \(\Delta S_{\text{trans}}^o\) at 25°C is -0.15645 kJ/mol·K.

6.2.1 Results

Figure 6.2 shows isotherms at four different temperatures for a \(\Delta H\) of -55 kJ/mol and an \(\alpha\) of 1, which corresponds to the complete loss of translational entropy.

![Figure 6.2: Isotherms at 4 different temps for a \(\Delta H\) of -55 kJ/mol](image)

In order to find an optimal \(\Delta H_{\text{rxn}}\), two conditions are looked at, the absorber conditions and the desorber conditions. We assume that the absorber runs at \(P_{\text{CO}_2}\)
equal to 0.15 bar and T is 40°C, while the desorber runs at $P_{\text{CO}_2}$ equal to 1 bar and T is 140°C. Figure 6.3 depicts the change in mole ratio that is found for a $\Delta H$ of -55 kJ/mol by finding absorber and desorber conditions on the isotherms and taking the difference between them.

![Graph showing Δ mol ratio vs. $P_{\text{CO}_2}$ (bar)](image)

Figure 6.3: Absorber and desorber conditions are found on the isotherms to determine the change in the mole ratio between the two conditions, where $\alpha = 1$ and $\Delta H = -55$ kJ/mol.

By varying $\Delta H$ in order to maximize the change in the mole ratio between the two conditions, the optimal $\Delta H$ is found as shown in Figure 6.4.
Figure 6.4: Optimal $\Delta H$ that maximizes the change in mole ratio between absorber and desorber.

Figure 6.4 shows an optimal $\Delta H$ of around -60 kJ/mol. This optimal $\Delta H$ is for specific values of $\Delta S_2$ and $\Delta S_1$, which are also variables of the model. The contribution of $\Delta S_2$ is varied

$$\Delta S_{\text{trans}} \geq \Delta S_1 + \alpha(\Delta S_{\text{trans}} - \Delta S_1) \quad (6.21)$$

where $\alpha$ is varied from 0 to 1.

Figure 6.3 shows what the isotherms and $\Delta z$ would look like for a $\Delta H$ of -55 kJ/mol and an $\alpha$ of 1. Figure 6.5 shows what the isotherms and $\Delta z$ would look like keeping everything the same but using an $\alpha$ of 0.5.
Figure 6.5: Absorber and desorber conditions are found on the isotherms to determine the change in the mole ratio between the two conditions, where $\alpha = 0.5$ and $\Delta H = -55 \text{ kJ/mol}$.

Figure 6.6 shows a 3-d plot that varies both the chemical contribution of $\Delta S$ by varying $\alpha$ and $\Delta H$ with a change in temperature of 100°C (40°C to 140°C).
Figure 6.6: 3-d plot maximizing change in mole ratio while varying $\Delta S_2$ and $\Delta H_3$

For this case, the maximum change in mole ratio occurs at about a $\Delta H$ of -60 kJ/mol and an $\alpha$ of 1.

6.3 Temperature Dependence

For the second case studied, we will consider temperature dependence of $\Delta H$ and $\Delta S$. In order to include temperature dependence in the model, Equations 6.22 and 6.23 are used.

\[
\Delta H^\circ(T) = \Delta H^\circ(T_o) + \int_{T_o}^{T} \Delta C_p \, dT
\]  \hspace{1cm} (6.22)

\[
\Delta S^\circ(T) = \Delta S^\circ(T_o) + \int_{T_o}^{T} \frac{\Delta C_p}{T} \, dT
\]  \hspace{1cm} (6.23)

For step 1, the $\Delta C_p$ is estimated by Equation 6.24.
\[ \Delta C_{p_1} = -((C_v)_{gas} + R) \]  
\[ (6.24) \]

\( C_p \) of the liquid CO\(_2\) is estimated to be 0.03722 kJ/mol K at 300K.\(^3\) \( C_v \) for the gas is determined by adding the translational, electronic, rotational, and vibrational contributions to the heat capacity together. The electronic component is zero, while the translational contribution is \( 3/2 \) \( R \). Since we are determining the heat capacity of the gas phase which is essentially CO\(_2\), a linear molecule, the rotational contribution to the heat capacity is \( R \). The vibrational contribution to the heat capacity is

\[ C_{v_{vib}} = R \sum_k e^{\theta_{v,k}/T} \left( \frac{\theta_{v,k}/T}{e^{\theta_{v,k}/T} - 1} \right)^2 \]  
\[ (6.25) \]

where \( \theta_{v,k} \) is the vibrational temperature associated with each vibrational mode, \( k \).

For step 3, the \( \Delta C_p \) is estimated by

\[ \Delta C_{p_3} = -((C_v)_{gas} + R) \]  
\[ (6.26) \]

### TABLE 6.1:

<table>
<thead>
<tr>
<th>( \Delta H )</th>
<th>40°C</th>
<th>80°C</th>
<th>100°C</th>
<th>140°C</th>
</tr>
</thead>
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<tr>
<td>( \Delta H_1 )</td>
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<td>-11.11</td>
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<tr>
<td>( \Delta S_1 )</td>
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<td>( \Delta H_3 )</td>
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<td>-60.38</td>
<td>-63.50</td>
</tr>
<tr>
<td>( \Delta S_3 )</td>
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<td>-0.10620</td>
<td>-0.10720</td>
<td>-0.10894</td>
</tr>
</tbody>
</table>
6.3.1 Results

Figure 6.7 shows isotherms at four different temperatures for a $\Delta H(25^\circ C)$ of -55 kJ/mol and an $\alpha$ of 1.

![Graph showing isotherms at different temperatures]

In order to find an optimal $\Delta H_{\text{rxn}}$, two conditions are looked at, the absorber conditions and the desorber conditions. We assume that the absorber runs at $P_{\text{CO}_2}$ equal to 0.15 bar and $T$ at 40$^\circ$C, while the desorber runs at $P_{\text{CO}_2}$ equal to 1 bar and $T$ at 140$^\circ$C. Figure 6.8 depicts the change in mole ratio that is found for a $\Delta H(25^\circ C)$ of -55 kJ/mol by finding absorber and desorber conditions on the isotherms and taking the difference between them.
Figure 6.8: Absorber and desorber conditions are found on the isotherms to determine the change in the mole ratio between the two conditions, where $\alpha = 1$ and $\Delta H(25^\circ C) = -55 \text{ kJ/mol}$.

By varying $\Delta H$ in order to maximize the change in the mole ratio between the two conditions, the optimal $\Delta H$ is found as shown in Figure 6.9.
Figure 6.9: Optimal $\Delta H$ that maximizes the change in mole ratio between absorber and desorber.

The optimal $\Delta H$ that maximizes the change in mole ratio occurs around -56 kJ/mol. This is for an $\alpha$ of 1. Figure 6.10 shows what the two isotherms would look like for an $\alpha$ of 0.5.
Figure 6.10: Absorber and desorber conditions plotted on their respective isotherms to show the change in mole ratio for a \( \Delta H(25^\circ C) = -55 \text{ kJ/mol} \) and an \( \alpha \) of 0.5.

Figure 6.11 shows a 3-d plot that varies both the chemical contribution of \( \Delta S \) by varying \( \alpha \) and \( \Delta H \) with a change in temperature of 100°C (40°C to 140°C).
6.4 Conclusions

We developed simple isotherm models in order to understand what governs performance of an ionic liquid for capturing CO₂. There are several parameters that are involved in the model that can influence what the optimal ΔH of the reaction would be. These include the heat capacities associated with the physical and chemical reactions, the contribution from ΔS₂, and the desorber conditions. It was found that all of these factors are important and that they all greatly influence what the outcome of the volcano plot and 3-dimensional plot. While these factors influence the height of the curves, i.e. the change in mole ratio, the optimal ΔH₃ that
maximizes this change in mole ratio does not change very much. Also, the maximum change in mole ratio always occurs when the full translational entropy is lost.
CHAPTER 7:
CONCLUSIONS AND RECOMMENDATIONS

7.1 Summary of Conclusions

We have employed first-principle simulations to model ionic liquids for post-combustion CO$_2$ capture from coal-fired power plants. We first demonstrated tethering an amine functional group to the anion of an ionic liquid would bias the reaction towards one IL to one CO$_2$ uptake ratio instead of the two ILs to one CO$_2$ uptake ratio found when the amine is tethered to the cation. This was validated by our collaborator’s experimental data. Experimental data showed significant viscosity increases with our proposed amino acid ionic liquids when reacted with CO$_2$.\textsuperscript{41} We then proposed a new class of ionic liquids, the AHAs, that uptake CO$_2$ in a 1:1 ratio but also do not show any viscosity increases when reacted with CO$_2$. By adding various electron withdrawing groups, we were able to tune the CO$_2$ reaction enthalpy to virtually any reaction enthalpy. We also developed an isotherm model that mimicked the actual experiments and allowed us to predict what the experiments would give. Using this model at specified conditions, we were able to determine the optimal reaction enthalpy for the ionic liquid – CO$_2$ capture system.
7.2 Recommendations for Future Work

Based on the results in this dissertation, I would recommend our experimental collaborators to continue testing my discovered AHA ionic liquids. The vast database of potential AHA ionic liquids that I have compiled will give the experimental collaborators a reference of ionic liquids that will provide them with the reaction enthalpies they desire.

A few of the AHAs that I have shown in this work contain more than one nitrogen atom, imidazolide, pyrazolide, benzimidazolide. With two nitrogen atoms present, it is possible for the molecule to capture two CO$_2$s. This would double the capacity of CO$_2$ in an ionic liquid over the currently seen one IL to one CO$_2$ uptake ratio. I have run some preliminary tests on this subject but much more work is needed to find the molecule or types of molecules that promote multiple CO$_2$s to be bound to one molecule.

Another area of research that needs further attention would be to increase the uptake capacity of CO$_2$ by also functionalizing the cation in the ionic liquid. Functionalizing both the cation and the anion in the ionic liquid would also double the uptake capacity of an ionic liquid over the current 1:1 ratio. Much critical thinking and computational simulations need to be performed to figure out how to functionalize a cation without creating an acidic proton and thus a hydrogen bonding network and viscosity issues when combined with CO$_2$.
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