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A Polarizable and Transferable Carbon Dioxide Potential for Materials Simulation

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A Polarizable and Transferable Carbon Dioxide Potential for Materials Simulation

by

Ashley Lynn Mullen

A thesis submitted in partial fulfillment
Of the requirements for the degree of
Master’s of Science
with a concentration in Computational Chemistry
Department of Chemistry
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# TABLE OF CONTENTS

List of Tables .................................................................................................................................. ii

List of Figures ................................................................................................................................ iii

Abstract .......................................................................................................................................... iv

Introduction ...................................................................................................................................... 1

Methods.......................................................................................................................................... 5
   Electronic Structure Calculations .............................................................................................. 5
   Many-Body Polarization ............................................................................................................. 6
   Intermolecular Potential Energy Function ................................................................................ 8
   Model Validation ......................................................................................................................... 9
      Carbon Dioxide Simulations ................................................................................................. 9
      Simulations in MOFs .............................................................................................................. 9

Results and Discussion .................................................................................................................. 10
   Electronic Structure Calculations ............................................................................................. 10
   Model Validation ....................................................................................................................... 13
      Pressure-density isotherms ................................................................................................... 13
      Simulations in MOFs ............................................................................................................ 18

Conclusion ..................................................................................................................................... 26

References...................................................................................................................................... 28
LIST OF TABLES

Table 1: CO₂ Molecular Polarizability Tensor Calculated via Time-Dependent Hartree-Fock along with its Rescaled Components .....................................................10

Table 2: Parameters for PHASTq, PHAST, and TraPPE³ Models a,b .................................................................10
LIST OF FIGURES

Figure 1: Orientations of CO2 dimer chosen for electronic structure calculations .................5
Figure 2: Ab initio curves and potential energy curves of carbon dioxide dimers .....................12
Figure 3: Ab initio curves and potential energy curves of carbon dioxide dimers ......................13
Figure 4: Pressure-density plot of carbon dioxide at 298.15 K ..................................................14
Figure 5: Pressure-density plot of carbon dioxide at 350.15 K ...................................................15
Figure 6: Pressure-density plot of carbon dioxide at 500.15 K ...................................................15
Figure 7: Radial distribution function, g(r), for dense gaseous bulk carbon dioxide at 298.15 K and 10 atm .............................................................................................................16
Figure 8: Radial distribution function, g(r), for bulk carbon dioxide at 298.1 K and 100 atm .................................................................................................................................17
Figure 9: Radial distribution function, g(r), for liquid bulk carbon dioxide at 298.15 K and 500 atm .................................................................................................................................17
Figure 10: Carbon dioxide uptake in MOF-5 at 298.15 K ............................................................19
Figure 11: CO2 sorption isotherms in [Cu(dpa)2SiF6-i] at 298 K and pressures up to 1.0 atm .................................................................20
Figure 12: CO2 sorption isotherms in PCN-61 at 298 K and pressures up to 1.0 atm .................22
Figure 13: Radial distribution function, g(r), about the exterior Cu ion in PCN-61 at 298 K and 0.20 atm .................................................................................................................................24
Figure 14: 3D histogram of CO2 occupancy (blue) in PCN-61 using the CO2-PHAST* model .................................................................................................................................25
Figure 15: 3D histogram of CO2 occupancy (blue) in PCN-61 using the TraPPE model .................................................................................................................................25
ABSTRACT

Intermolecular potential energy functions for CO\textsubscript{2} have been developed from first principles for use in heterogeneous systems, including one with explicit polarization. The intermolecular potentials have been expressed in a transferable form and parameterized from nearly exact electronic structure calculations. Models with and without explicit many-body polarization effects, known to be important in simulation of interfacial processes, are constructed. The models have been validated on pressure-density isotherms of bulk CO\textsubscript{2} and adsorption in three metal-organic framework (MOF) materials. The present models appear to offer advantages over high quality fluid/liquid state potentials in describing CO\textsubscript{2} interactions in interfacial environments where sorbates adopt orientations not commonly explored in bulk fluids. Thus, the nonpolar CO\textsubscript{2}-PHAST and polarizable CO\textsubscript{2}-PHAST* potentials are recommended for materials/interfacial simulations.
INTRODUCTION

Carbon dioxide is a greenhouse gas, meaning it absorbs infrared radiation from the planet’s surface and emits it back, elevating the temperature of the surface. Carbon dioxide levels in the earth's atmosphere have risen since the industrial revolution, and the current global average was 390 ppmv in 2010.\textsuperscript{1,2} Amongst all the greenhouse gases, CO\textsubscript{2} is the largest contributor, contributing 60% of the global warming effects, and the highest contributor to CO\textsubscript{2} in the atmosphere is the anthropogenic CO\textsubscript{2} emission sources. The Intergovernmental Panel on Climate Change warns that an increase in atmospheric CO\textsubscript{2} could lead to a rise in mean global temperature, a rise in ocean levels, acidification of the planet’s oceans, and possible species extinction.\textsuperscript{1,3}

There are three main approaches to reduce CO\textsubscript{2} emissions: obtain more energy for the same amount of fossil fuel, find fuels or energy sources that do not produce CO\textsubscript{2} as a byproduct, or capture and sequester it. Existing CO\textsubscript{2} capture methods include extraction with an aqueous amine solution, separation and capture with membranes, and adsorption within activated charcoal, zeolites, and metal-organic framework (MOF) materials.\textsuperscript{1,2} The focus of this work is on carbon dioxide capture in MOFs.

Metal organic frameworks, MOFs, are metal-organic coordination polymers that have tunable pore sizes and shapes. By choosing organic linker molecules and metal ions, materials with various adsorption specific properties (e. g. surface area and free volume) can be designed.\textsuperscript{4} Capturing CO\textsubscript{2} by adsorbent materials can be viable if they have a high CO\textsubscript{2} capacity/affinity and CO\textsubscript{2} uptake is also fully reversible. The current benchmarks zeolites 13X and MAXSORB can
adsorb 7.4 mmol/g (at 32 bar) and 25 mmol/g (at 35 bar) respectively at room temperature. It has been found by the Yaghi group that a metal organic framework, MOF-177 with chemical formula Zn₄O(1,3,5-benzenetribenzoate)₂, can adsorb 35 mmol/g carbon dioxide (at 35 bar) at the same temperature.⁵ Therefore, the possibility of MOFs enhancing CO₂ capture is promising.

To expedite the design and testing of new materials for such applications, many chemists are using the computational techniques of electronic structure calculations, Molecular Dynamics, and Monte Carlo simulations to model gas adsorption and separation.²,⁶,⁷,⁸,⁹ These computational tools allow a scientist to gather information that cannot be measured in an experiment, and they can be used on materials that do not exist yet. Electronic structure calculations, either *ab initio* or DFT methods, can provide information about the potential energy surface of the sorbate and the sorbent, and especially with *ab initio* methods, can give information about the binding sites and energy of the sorbate-sorbent interaction.⁹ Molecular Dynamic simulations can give insight into the diffusion of a single species or gas mixtures, through the sorbent.⁷ Monte Carlo simulations, most importantly, Grand Canonical Monte Carlo (GCMC) simulations can provide information about the gas uptake and heats of adsorption of a single species gas or a gas mixture.²,⁶,⁹

The most critical component of a Molecular Dynamics or Monte Carlo simulation is the potential energy function or force field. Some popular force fields used today are universal force field (UFF),¹⁰ DREIDING,¹¹ and optimized potential for liquid simulations- all atom (OPLS-AA).¹² These force fields have been parameterized for many elements, and do well to capture intramolecular forces, but they do not always capture the intermolecular forces well, specifically the electrostatic energy contribution. Often MD or GCMC simulations treat the gaseous species with one potential energy function while the sorbent is modeled with a separate one.²
Intermolecular potentials for CO\(_2\) have been constructed from fitting to experimental data such as solid CO\(_2\) lattice parameters and lattice energies,\(^{13,14,15,16}\) liquid densities, and vapor-liquid equilibria.\(^{17,18,19,20,21,22}\) One of the first CO\(_2\) intermolecular potentials was developed by Walmsley and Pople to investigate the low-frequency lattice vibrations of solid CO\(_2\). Their potential energy function used the Lennard-Jones 6-12 form to describe the repulsion and dispersion terms, and included a quadrupole-quadrupole interaction term.\(^{13}\) Murthy et al. parameterized a pair potential from the lattice energy of solid CO\(_2\) and proved the model was sufficient via MD simulations in the liquid region as well.\(^{15}\) Other CO\(_2\) models were developed from computer simulations and VLE data and of those, the TraPPE model by Potoff and the EMP model by Harris are the models most used today. Both potentials use the Lennard-Jones function for the repulsion and dispersion forces, however, they use the distributed multipole analysis (DMA) of Buckingham and Fowler for the electrostatic term.\(^{23}\) Reasonably simple pair potentials of this type, especially those with Lennard-Jones functions representing van der Waals interactions, have the capability of being used in simulations of heterogeneous media because of mixing rule conventions. The limitations of these models parameterized from bulk thermodynamic properties are that experimental measurements can cover only a limited region of the potential energy surface represented in the fluid and limited information about the anisotropy of the potential is given.

With advances in electronic structure methods\(^ {24}\) and computer hardware, electronic structure calculations can provide information for a wide range of separation distances and many dimer configurations, both of which lead to a fuller understanding of the potential energy surface. Many CO\(_2\) potentials have been developed using \textit{ab initio} calculations\(^ {25,26,27,28,29,30,31,32}\) dating back to Bohn and Aldrich in 1984.\(^ {25}\) Some potentials had to be refined with thermodynamic data such as the second virial coefficient\(^ {25}\) or experimental liquid properties data\(^ {33}\). High quality intermolecular
potentials of this type are often chosen as complex functional forms with many parameters and damping coefficients. These potential energy functions produce high fidelity analytic representations which require many parameters and are thus limited to model only pure CO$_2$.

Existing potential energy surfaces to molecularly model CO$_2$ are parameterized for neat simulation and may not accurately capture highly anisotropic and complex many-body interactions. Thus, a transferable and accurate carbon dioxide potential that includes anisotropy and polarization is desirable for modeling adsorption in heterogeneous and dense systems. The potential energy form, of this work, is chosen to capture intermolecular interactions with a minimum of terms that reflect the essential physical interactions to maintain transferability of the surface. The resulting potential form is a compromise in that it cannot exactly reproduce the \textit{ab initio} dimer potentials for carbon dioxide because of the limited, compact description. However, it does a reasonable job for all geometries (including those important in sorption but not in bulk fluids) and includes polarization, thus making the potential suitable for simulations with strong interactions. Therefore, the resulting potential, while effective for bulk simulations, is also efficacious in modeling CO$_2$ in heterogeneous environments and at extreme conditions.
METHODS

**Electronic Structure Calculations**

The carbon dioxide molecule was approximated as linear and rigid with a C-O bond length of 1.162 Å, as determined by rotational spectra.\(^{34}\) Five distinct orientations (Figure 1) were chosen as a subspace of the complete CO\(_2\)-CO\(_2\) Born-Oppenheimer surface, and the interaction energy was calculated over the domain of center-of-mass separation for the monomers from 2.5 to 8.0 Å in 0.1 Å increments.\(^{31,35}\) All *ab initio* calculations were performed using Molpro\(^{24}\) at the CCSD(T)\(^{36}\) level of theory, with basis functions of Dunning et al, (aug-cc-PVTZ/QZ).\(^{37,38,39}\) The total energy was extrapolated to the complete basis set limit\(^{40}\) and basis set superposition error was corrected by the counterpoise method.\(^{41}\)

![Figure 1](image.png)

**Figure 1.** Orientations of CO\(_2\) dimer chosen for electronic structure calculations.
The \textit{ab initio} quadrupole tensor was calculated at the CCSD(T)/aug-cc-pV5Z level of theory, via the finite-field method with a homogeneous field strength of 0.005 $\text{e}^{-1}\text{a}_0^{-1}\text{E}_h$.\textsuperscript{42} For a linear molecule, the permanent molecular electric quadrupole moment is $\Theta = \Theta_{zz} = -2\Theta_{yy} = -2\Theta_{xx}$ was found to be $\Theta = -4.284 \text{DÅ}$, a value comparable to experimental and electronic structure results.\textsuperscript{43,44,45}

The molecular polarizability tensor of carbon dioxide was computed at the Time-Dependent Hartree Fock\textsuperscript{46} TDHF/aug-cc-pVQZ level of theory. The tensor values were rescaled so that the isotropic polarizability matched the experimental result of $2.507 \text{Å}^3$ and kept the ratio of $XX$ to $ZZ$ fixed. Values for the \textit{ab initio} polarizability tensor and the rescaled tensor are given in Table 1.

\textbf{Many-Body Polarization}

The interest of this work is to develop an intermolecular potential energy function effective in charged and polar heterogeneous environments. Such a model requires inclusion of induction effects that are essentially many-body; the Thole-Applequist atomic point polarizability model was adopted to capture these interactions. A brief description of the polarization model as applied here is presented, and a more thorough description can be found elsewhere.\textsuperscript{35,47,48} For any atom, the atomic point dipole is

\begin{equation}
\mathbf{m}_i = \alpha_i \left( E^m_i + E^m_i \right)
\end{equation}

\begin{equation}
\mathbf{m}_i = \alpha_i \left( E^m_i - \sum_{j,n} T_{ij}^{mn} n_j \right)
\end{equation}

where $\alpha_i$ is the atomic site polarizability, $E^m_i$ is the static contribution, and $E^m_i$ is the induced contribution to the electrostatic field vector. The induced contribution can be written in terms of the dipole field tensor, $T_{ij}$, which can be constructed from the positions and scalar point polarizabilities of the system.
\[ T_{ii}^{mm} = 0 \]  \hspace{1cm} (3)

\[ T_{ij}^{mn} = \frac{\delta_{mn}}{r_{ij}^3} - \frac{3r_{ij}^m r_{ij}^n}{r_{ij}^5} \]  \hspace{1cm} (4)

However, equation (4) needs to be corrected for non-physical results at small distances. The exponential damping function given in equation (5) was utilized.\(^{48}\)

\[ T_{ij}^{mn} = \frac{\delta_{mn}}{r_{ij}^3} \left( 1 - \left( \frac{\lambda^2 r_{ij}^2}{2} + \lambda r_{ij} + 1 \right) e^{-\lambda r_{ij}} \right) - \frac{3r_{ij}^m r_{ij}^n}{r_{ij}^5} \left( 1 - \left( \frac{\lambda^2 r_{ij}^2}{6} + \frac{\lambda^2 r_{ij}^2}{2} + \lambda r_{ij} + 1 \right) e^{-\lambda r_{ij}} \right) \]  \hspace{1cm} (5)

From equation (2) one can construct block-matrices (6) and solve (7)

\[
\tilde{\mathbf{A}} \equiv \begin{pmatrix}
\frac{1}{\alpha_0} & [T_{0,1}] & \cdots & [T_{0,N-1}] \\
[T_{1,0}] & \frac{1}{\alpha_1} & \cdots & [T_{1,N-1}] \\
\vdots & \vdots & \ddots & \vdots \\
[T_{N-1,0}] & [T_{N-1,1}] & \cdots & \frac{1}{\alpha_{N-1}}
\end{pmatrix}
\]  \hspace{1cm} (6)

\[ \tilde{\mathbf{A}} \tilde{\mathbf{\mu}} = \tilde{\mathbf{E}} \]  \hspace{1cm} (7)

which has solutions by either matrix inversion or iterative methods; the latter was the method employed herein. Long-range corrections were handled using an implementation of the Wolf field method.\(^{49,50,51}\) The polarizability model has the advantage that it can include polarizable sites from any other species that is similarly parameterized without further assumptions, thus keeping the entire potential energy in a transferable form. The ostensible disadvantage is the cost of evaluating the many-body function. However, this can be largely offset by iterating efficiently and porting these operations to GPUs.
Intermolecular Potential Energy Function

For this research, PHAST (Potentials with High Accuracy, Speed, and Transferability) models, CO$_2$-PHAST and CO$_2$-PHAST*, where * denotes the inclusion of explicit polarization were created. The total non-bonded potential energy, $U$, has contributions from electrostatic interactions $U_{es}$, repulsion and dispersion interactions $U_{rd}$, and polarization interactions $U_{pol}$ as shown in equation 8.

$$U = U_{es} + U_{rd} + U_{pol}$$  \hspace{1cm} (8)

The polarization contribution $U_{pol}$ of the carbon dioxide model was developed according to the Thole-Applequist polarizability model as explained above. A trial polarizability tensor was created according to the Thole model with exponential damping from scalar point polarizabilities at the atomic coordinates and with the molecule aligned along the Z axis. This trial polarizability tensor was compared with the scaled \textit{ab initio} tensor. The scalar point polarizabilities were varied until the difference between the two tensors was minimized, and the final values are listed in Table 2.

After the point polarizabilities were determined, the parameters of $U_{es}$ and $U_{rd}$ were fit simultaneously \textit{via} simulated annealing to give a minimum ($U-U_{BO}$), where $U_{BO}$ is the \textit{ab initio} Born-Oppenheimer surface. Similarly to Steinebrunner and Vogel,$^{31,52}$ a five-site model was employed to describe the carbon dioxide molecule. The point charges are fixed on the atomic sites while, in a departure from most previous studies, the Lennard-Jones sites are allowed to vary along the bond vector, along with magnitudes for a best fit. This modification is critical in producing a simple potential that captures the correct anisotropy.$^{35}$ Four models were parameterized for this investigation. The PHASTq models were fit to the \textit{ab initio} data points with energy below 2500 K and have fixed atomic partial charges that reproduce the quadrupole of -4.287 DÅ. The PHAST
models were fit to data points with energy below 5000 K and parameterized by allowing the atomic partial charges to fluctuate as well, allowing the charges to not reproduce the first non-vanishing electric moment results in a better potential energy function.

**Model Validation**

*Carbon Dioxide Simulations*

For model validation, Monte Carlo simulations, with the isothermal-isobaric ensemble, of CO$_2$ at various temperatures and pressures were performed with the software Massively Parallel Monte Carlo (MPMC). System sizes ranged from 100 to 150 CO$_2$ molecules and include averages from 700,000 correlation times, with an additional 700,000 correlation times for state points near a vapor-liquid transition.

*Simulations in MOFs*

Simulations of CO$_2$ adsorption in MOFs were performed via Grand Canonical Monte Carlo. The probability of molecule insertion/deletion was set to 0.3. The chemical potential of CO$_2$ was mapped to the pressure by the Peng-Robinson equation of state. Three MOFs were chosen to simulate CO$_2$ sorption: Zn$_4$O(1,4-benzenedicarboxylate)$_3$ (MOF-5), [Cu(4,4’-dipyridylacetylene)$_2$SiF$_6$-i],(also known as SIFSIX-2-Cu-i) and [Cu(H$_2$O)$_3$(5,5’,5”-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalate)) (PCN-61). All metal-organic frameworks were modeled as rigid frameworks. The MOF-5 potential parameters used in GCMC simulations were that of Belof et al. [Cu(dpa)$_2$SiF$_6$-i] and PCN-61 were established according to previous work. Simulations with MOF-5 were run for 300,000 correlation times, and simulations with [Cu(dpa)$_2$SiF$_6$-i] and PCN-61 were run for $10^6$ correlation times.
RESULTS AND DISCUSSION

Electronic Structure Calculations

Table 1. CO₂ Molecular Polarizability Tensor Calculated via Time-Dependent Hartree-Fock along with its Rescaled Components.

<table>
<thead>
<tr>
<th>Component</th>
<th>TDHF/ Å³</th>
<th>rescaled/ Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX</td>
<td>1.7727</td>
<td>1.8885</td>
</tr>
<tr>
<td>YY</td>
<td>1.7727</td>
<td>1.8885</td>
</tr>
<tr>
<td>ZZ</td>
<td>3.5146</td>
<td>3.7441</td>
</tr>
<tr>
<td>isotropic</td>
<td>2.3533</td>
<td>2.507</td>
</tr>
</tbody>
</table>

Table 2. Parameters for PHASTq, PHAST, and TraPPE c Models a, b

<table>
<thead>
<tr>
<th></th>
<th>lₐ₋₀ (Å)</th>
<th>lₐ₋ₓ (Å)</th>
<th>qₓ (e)</th>
<th>εₓ (K)</th>
<th>εₐ (K)</th>
<th>σₓ (Å)</th>
<th>σₐ (Å)</th>
<th>αₓ (Å³)</th>
<th>αₐ (Å³)</th>
<th>Θₓₓ DÅ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂-PHASTq</td>
<td>1.162</td>
<td>1.178</td>
<td>0.6613</td>
<td>24.014</td>
<td>85.817</td>
<td>3.168</td>
<td>2.734</td>
<td></td>
<td></td>
<td>-4.289</td>
</tr>
<tr>
<td>CO₂-PHASTq*</td>
<td>1.162</td>
<td>1.187</td>
<td>0.6613</td>
<td>26.894</td>
<td>70.244</td>
<td>3.180</td>
<td>2.755</td>
<td>1.228</td>
<td>0.739</td>
<td>-4.289</td>
</tr>
<tr>
<td>CO₂-PHAST</td>
<td>1.162</td>
<td>1.091</td>
<td>0.7710</td>
<td>8.522</td>
<td>76.767</td>
<td>3.055</td>
<td>2.945</td>
<td></td>
<td></td>
<td>-5.003</td>
</tr>
<tr>
<td>CO₂-PHAST*</td>
<td>1.162</td>
<td>1.114</td>
<td>0.7714</td>
<td>19.618</td>
<td>46.475</td>
<td>3.034</td>
<td>2.994</td>
<td>1.228</td>
<td>0.739</td>
<td>-5.003</td>
</tr>
<tr>
<td>TraPPE 18</td>
<td>1.161</td>
<td>0.7</td>
<td>27.0</td>
<td>79.0</td>
<td>2.8</td>
<td>3.05</td>
<td></td>
<td></td>
<td></td>
<td>-4.532</td>
</tr>
</tbody>
</table>

aX denotes the Lennard-Jones sites along the bond vector.
bThere are two equal negative charges, q₀, on each oxygen center so that the net charge of the molecule is zero.
c Quadrupole from Chetty et al -4.29 DÅ. 45

While other models of this type that have been explored reproduced the quadrupole when the charges were allowed to vary, 48,42 this was not the case for the best fit parameters for CO₂. The origin of this effect is not obvious but may be the result of the limitations of the potential form or the nature of the interactions at intermediate distances, where, for example, dispersion may not have yet
achieved its asymptotic inverse sixth form. This result suggests that including other physically motivated terms such as other inverse distance powers (presumably between 1/r and 1/r^6 and not higher order inverse powers characteristic of the asymptotic dispersion expansion) might capture the correct functional form of the interactions and would result in the fits giving the true quadrupole as was found in H_2 and N_2.\textsuperscript{58,42} Currently, the parameters for the attractive van der Waals and point electrostatics have to compensate to "best fit" the intermediate behavior, resulting in a more accurate potential but incorrect asymptotic behavior. The compact transferable form that was chosen is a compromise to keep the potential simple and suitable for heterogeneous simulation.

These four models and, for comparison, the TraPPE\textsuperscript{18} model parameters are given in Table 2. The TraPPE model is given because it is a highly effective bulk potential fit to reproduce phase coexistence that has been extensively and successfully employed. It will also be shown below, that although it is not fit to any \textit{ab initio} data, it nearly exactly reproduces the dimer curves that are well represented in liquid configurations and misrepresents others not important for bulk structure. Note, the TraPPE potential also has a quadrupole larger than the experimental value.

Figure 1 gives the \textit{ab initio} interaction energy curves for five carbon dioxide dimers. The largest interaction energy is from the slipped parallel (S) configuration, which is 5% larger than that reported by previous authors, and at similar dimer separation distances.\textsuperscript{28,31,59} The interaction energy of the T configuration is 3% larger than previous reports while the separation distance is consistent with such reports.

Figures 1 and 2 also show the intermolecular potential models compared to the \textit{ab initio} curves. Note, only the models without explicit polarization are plotted. The CO_2-PHASTq* and CO_2-PHAST* curves are excluded because they lie on top of CO_2-PHASTq and CO_2-PHAST results, respectively. All PHAST and PHASTq models have better fits to the repulsive region of all
ab initio curves as compared to the TraPPE model. The TraPPE model fits the attractive region of the X, P, and S dimer interaction curves well. This trend is expected since the TraPPE parameters were fitted from vapor-liquid equilibria data, and liquids inherently minimize repulsive configurations. Furthermore, the PHASTq and PHAST models fit closer to the ab initio curve for the E configuration, which is unsurprising since the E configuration is highly repulsive and would have a low occurrence in the liquid state. Due to the simplicity of the functional form and the anisotropy of the potential energy surface, neither the TraPPE, PHASTq, nor the PHAST models predict the S configuration to be the minimum energy dimer structure.

Comparing the PHAST and PHASTq models, the PHASTq models fit better to the ab initio curves for configurations E, T, and X, but worse for the P configuration. Conversely, the PHAST models underestimate the minimum energy for the X configuration. These differences can be attributed to the larger partial charges of the PHAST models compared to the PHASTq models.

Figure 2. Ab initio curves and potential energy curves of carbon dioxide dimers. Graph (a) compares TraPPE and CO2-PHASTq to ab initio. Note, the polarizable PHASTq* curves are visually identical to the nonpolar PHASTq curves shown here.
Figure 3. *Ab initio* curves and potential energy curves of carbon dioxide dimers. Graph (b) compares TraPPE and CO$_2$-PHAST to *ab initio*. Note, the polarizable PHAST* curves are visually identical to the nonpolar PHAST curves shown here.

**Model Validation**

*Pressure-density isotherms*

Each model was used in NPT Monte Carlo simulations of CO$_2$ at various temperatures and pressures and compared to experimental data from IUPAC.$^{60}$ Figures 4, 5, and 6 give the pressure-density isotherms at the temperatures 298.15 K, 350.15 K, and 500.15 K respectively. At 298.15K (Figure 4), the TraPPE model produces the correct density for all pressures from 0.5 atm to 500 atm. The two PHASTq models give a density 10% larger in the liquid region. The CO$_2$-PHAST* model correctly produces gas phase densities from 0.5 atm to 40 atm and liquid phase densities from 300 atm to 500 atm. Radial distribution function plots were created for three state points below the critical temperature in order to compare the fluid structures, and they are shown in Figures7-9.
Figure 4. Pressure-density plot of carbon dioxide at 298.15 K. Inset graph is from 0 to 50 atm.

Above the critical point, at 350.15 K, all models do well from 0.5 atm to 75 atm. The CO$_2$-PHAST* model underestimates the densities in the pressure range 100 to 400 atm, while the CO$_2$-PHASTq models overestimate the density from 200 atm to 500 atm. As with the 298.15 K isotherms, the TraPPE model produces an isotherm that is in excellent agreement with experiment at 350.15 K for the pressure range considered.

At 500 K, Figure 6, the CO$_2$-PHAST and CO$_2$-PHAST* models reproduce the experimental densities reasonably well from 0.5 to 500 atm. The CO$_2$-PHAST* model underestimates the density by 8% in the range of 300-500 atm. Note, the TraPPE model is accurate in this region as well.
Figure 5. Pressure-density plot of carbon dioxide at 350.15 K.

Figure 6. Pressure-density plot of carbon dioxide at 500.15 K.
Note CO$_2$-PHASTq and CO$_2$-PHASTq* models have similar charges, epsilons, and sigmas as the TraPPE model, however CO$_2$-PHAST and CO$_2$-PHAST* do not. This parameter set represents a different compromise between the limited functional form allowed in the compact description of CO$_2$ interactions. To investigate the structural origins of the differing densities plotted in Figure 4, the radial distribution function, g(r), was plotted for three state points and is shown in Figures 7-9. The fluid structures of the PHAST and PHASTq models are quite similar to that of the TraPPE model at pressures 10 atm and 500 atm at 298 K. The CO$_2$-PHAST* model shows a less structured fluid than the others at 298K and 100 atm (Figure 8). All models agree with the recent publication by Neuefeind et al. that gives a C-C pair distribution function maximum at 3.95 Å for liquid CO$_2$ at 298 K and 66 bar.$^{61}$ Thus, it appears that a large number of potentials of this form can reproduce bulk structure and thermodynamics, making the choice of potential parameters underdetermined. More work is needed to establish better compact transferable forms where this uncertainty may be resolved.

**Figure 7.** Radial distribution function, g(r), for dense gaseous bulk carbon dioxide at 298.15 K and 10 atm. The distance is taken from the center-of-mass of each molecule.
Figure 8. Radial distribution function, g(r), for bulk carbon dioxide at 298.15 K and 100 atm. The distance is taken from the center-of-mass of each molecule.

Figure 9. Radial distribution function, g(r), for liquid bulk carbon dioxide at 298.15 K and 500 atm. The distance is taken from the center-of-mass of each molecule.
The energetics of solid CO$_2$ were examined using the PHAST and PHASTq models and the minimum energy structure gave lattice parameters of 5.32 to 5.34 Å for the Pa3 face-centered cubic crystal. Literature values for the lattice parameter for the same thermal crystal range from 5.624 to 5.494 Å. The proposed potentials are reasonable bulk models albeit not as effective as e.g. TraPPE; however, this appears to be the compromise in order to produce a potential that can better function in non-bulk environments as will be demonstrated next.

**Simulations in MOFs**

Monte Carlo simulations with the $\mu$VT ensemble were performed with the PHAST, PHASTq, and TraPPE potentials. Figure 10 shows the excess CO$_2$ uptake in MOF-5 at 298.15 K. The isotherms from simulation were corrected for the latest Brunauer-Emmett-Teller (BET) surface area calculation of 3800 m$^2$/g. Specifically, the original isotherms were scaled by the factor 2,833/3,800, as the crystal structure of MOF-5 used in this work has a surface area of 2,833 m$^2$/g as reported by Millward et al. MOF-5 is a network of 1,4-benzenedicarboxylate (BDC) linked to zinc tetramers with very little charge separation on the framework, it is expected that polarization effects would be negligible. As determined from the simulations, polarization accounts for 6% and 11% of the total energy for the CO$_2$-PHASTq* and the CO$_2$-PHAST* models, respectively. Previous GCMC simulations of CO$_2$ adsorption in MOF-5 by Skoulidas et al used the EPM2 potential for CO$_2$ and Lennard-Jones parameters from UFF for the MOF-5 framework. Only Lennard-Jones interactions were considered, and the resulting uptakes were higher than experiment. The GCMC simulation of CO$_2$ sorption in MOF-5 performed by Babarao et al was an improvement, as the framework was assigned atomic partial charges to reproduce the electrostatic potential surface; however the uptakes are also higher than experiment. The PHASTq models have comparable Lennard-Jones values to the TraPPE and EPM2 models and produced higher uptakes as
well. The PHAST models have reduced epsilon values and predict uptakes that are in best agreement with experiment. The TraPPE model is an adequate potential, as expected, and underestimates the maximum loading by only 8%; however, it does not do well for modeling low pressure CO$_2$ uptake.

![Graph of CO$_2$ uptake in MOF-5 at 298.15 K. Inset graph is from 0 to 5 atm.]

**Figure 10.** Carbon dioxide uptake in MOF-5 at 298.15 K. Inset graph is from 0 to 5 atm.

The [Cu(dpa)$_2$SiF$_6$-i] square-pillared metal-organic material (MOM) is water stable and shows promise for applications in CO$_2$ sorption and separation. This structure is highly polar with SiF$_6^{2-}$ moieties, but recent theoretical studies on this compound demonstrate that polarization effects are negligible due to the narrow pore size.$^{51}$ Sorption in [Cu(dpa)$_2$SiF$_6$-i] is dominated by van der Waals interactions. All CO$_2$ models (TraPPE, PHASTq, and PHAST) were tested in this MOM and compared to experimental results. It can be observed that the PHAST models produce isotherms that
are in very good agreement with the experimental data (Figure 11). The CO$_2$-PHAST* model provides the best agreement with experiment while the CO$_2$-PHAST model produces slightly higher uptakes. This is due to the fact that polarization causes a favorable sorbate ordering of CO$_2$ molecules in the MOM, which decreases overall sorption. In general, the PHASTq models produce higher uptakes than the PHAST models in the compound; this can be attributed to the greater potential well depth of the T configuration associated with the PHAST models. Note, polarization accounts for 9-10% in both polar PHAST/PHASTq models. Similarly to the isotherms for MOF-5, the TraPPE model overestimates the experimental isotherm at low pressure CO$_2$ sorption and underestimates at higher pressures.

![Figure 11. CO$_2$ sorption isotherms in [Cu(dpa)$_2$SiF$_6$-i] at 298 K and pressures up to 1.0 atm.](image)

Simulation of CO$_2$ sorption was performed using the TraPPE, PHASTq, and PHAST models in PCN-61. This is a prototypical polar rht-MOF that was chosen for baseline computational studies.
Previous work involving H₂ sorption in PCN-61 showed that many-body polarization interactions were essential to capture the correct sorption behavior in the MOF. GCMC simulations of CO₂ sorption were performed using the PCN-61 force field that was developed by Forrest et al. Figure 12 shows the low-pressure excess sorption isotherms at 298 K for the five models compared to experimental data. It can be seen that the CO₂-PHAST model undersorbs the experimental data across all loadings, while the CO₂-PHAST* model produced an isotherm that is in excellent agreement with the experiment. The difference between the CO₂-PHAST and CO₂-PHAST* isotherms in PCN-61 demonstrate the importance of explicit polarization for the modeling of gas sorption in a polar MOF with high surface area and open metal sites. The isotherm generated by the CO₂-PHASTq model is higher than that of the CO₂-PHAST models, which is a direct consequence of the larger epsilon parameters for the former. It is important to note that the CO₂-PHASTq* model produces an isotherm that is much higher than experiment across all loadings in PCN-61, despite having the correct quadrupole, the inclusion of polarization, and slightly smaller epsilon values that the TraPPE model. From this, it can be deduced that simulations using the CO₂-PHASTq* model in PCN-61 result in sorption to regions that are dominated by van der Waals and electrostatic interactions as well as induction simultaneously. In contrast, van der Waals interactions contribute much less to the sorption structure for the CO₂-PHAST model. At 1.0 atm, polarization accounts for 15.9% (CO₂-PHASTq*) and 16.7% (CO₂-PHAST*) of the total energy. The TraPPE model slightly undersorbs the experimental isotherm at initial loading, but comes into agreement at pressures approaching 1.0 atm.
Although, the TraPPE model can be seen agreeing well with the experimental isotherm with respect to raw uptake, it inadequately captures the most prominent MOF-sorbate interaction. Figure 13 shows the radial distribution functions of CO$_2$ molecules about the exterior Cu$^{2+}$ ions (the ions projecting into the cuboctahedral cage of the MOF) for all five models at low loading. The radial distribution functions are normalized to a total magnitude of unity over the distance examined. This was chosen to obtain a direct comparison between the relative magnitudes for each model. The CO$_2$-PHASTq* and CO$_2$-PHAST* models produced a large peak at ca. 3.25 Å, which corresponds to a significant population of CO$_2$ molecules sorbing onto the open-metal site. Note, this peak is consistent to the observed CO$_2$-Cu distance in HKUST-1, a prototypical MOF containing 1,3,5-benzenetricarboxylate linkers coordinated to Cu$^{2+}$ ions, as determined from neutron powder diffraction and *ab initio* studies. A reasonable peak can also be seen for the CO$_2$-PHAST model at that distance, although the magnitude is approximately half that of the CO$_2$-PHAST* model. The
CO$_2$-PHASTq model produces a smaller peak at 3.25 Å than the CO$_2$-PHAST model, which can be explained by the smaller partial charges for the former. Thus, while the isotherm for the CO$_2$-PHASTq model is higher than the CO$_2$-PHAST model in PCN-61, the radial distribution functions demonstrate that the occupancy about the metal centers for the CO$_2$-PHASTq model is not comparable to those for the CO$_2$-PHAST model. The TraPPE model produced the smallest peak of the five models at 3.25 Å, which signifies that there is little occupation of CO$_2$ molecules about the open-metal site. These results demonstrate that, although the CO$_2$-PHAST* and TraPPE model produced similar uptakes in PCN-61, only the polarizable model captures the critical interaction between the CO$_2$ molecules and the open-metal sites. Note, however, the nonpolar PHAST/PHASTq models give a far more reasonable structure than the TraPPE model, which does not capture the sorbate-metal interaction peak. The majority of TraPPE CO$_2$ molecules can be seen sorbing into regions that are dominated by van der Waals and electrostatic interactions in PCN-61, such as the corners of the truncated tetrahedral cages (see below). Other than the difference in magnitudes of the 3.25 Å radial distribution peak, the distribution of CO$_2$ molecules between all five models are similar with increasing distance from the metal ion. It is important to note the CO$_2$-Cu interaction in PCN-61 is characterized as physisorption, not chemisorption. Evaluation of the binding energy for a CO$_2$ molecule sorbed onto the Cu$^{2+}$ ion via calculation of the isosteric heat of adsorption, $Q_{st}$, in experiment and simulation revealed that the adsorption energy ranges from 20 to 30 kJ/mol. Although the CO$_2$ molecule sorbs onto the open-metal sites using the PHAST/PHASTq models, the inclusion of explicit polarization results in a much stronger CO$_2$-Cu interaction, and thus, a larger nearest-neighbor peak is seen for the CO$_2$-PHAST* and CO$_2$-PHASTq* models.
Figure 13. Radial distribution function $g(r)$, about the exterior Cu ion in PCN-61 at 298 K and 0.20 atm.

Figures 14 and 15 show the 3D histograms revealing the most frequent sites of CO$_2$ occupancy in PCN-61 at low loading for both the CO$_2$-PHAST* and TraPPE models, respectively. For the polarizable model, there is significant sorption onto the exterior Cu$^{2+}$ ions of the copper paddlewheels at low loading. Thus, as expected, sorption onto the open-metal sites is captured using this potential. In contrast, for the TraPPE model, the CO$_2$ molecules mostly coordinate to the corners of the truncated tetrahedral cage at initial loading. This region is dominated by van der Waals and electrostatic interactions, which is where the majority of CO$_2$ molecules sorb to using the TraPPE model. Note, significant sorption onto metals is not seen for the TraPPE model.
**Figure 14.** 3D histogram of CO$_2$ occupancy (blue) in PCN-61 using the CO$_2$-PHAST* model.

**Figure 15.** 3D histogram of CO$_2$ occupancy (blue) in PCN-61 using the TraPPE model.
CONCLUSION

This work introduced the PHAST potentials that were parameterized from electronic structure data and include explicit polarization terms. They are a compromise between exactly reproducing the ab initio dimer curves for carbon dioxide and having a limited, compact description. The PHAST models were compared to the excellent bulk TraPPE potential. Interestingly, the TraPPE CO$_2$ model was shown to reproduce the ab initio dimer curves for configurations occurring most often in the liquid state (even though not fit to them), but is less effective in capturing configurations not frequently occurring in the bulk.

The proposed PHAST models perform well for all geometries (including those that are absent in bulk fluids, yet important in sorption) and include polarization, which makes the potential suitable for simulations with induced-dipole interactions. The resulting potentials have been shown to be reasonably effective for bulk simulations and very efficient for modeling CO$_2$ at charged/polar interfaces. The PHAST models, compared to PHASTq models, have larger partial charges and reduced Lennard-Jones well depths, shifting the energy composition to more electrostatic in nature, with less emphasis on van der Waals interactions. This shift accounts for the improved CO$_2$ initial uptake in MOFs, since it directs the CO$_2$ molecules to metal centers first. The PHAST models are recommended for materials simulation.

For the three MOFs in which simulations of CO$_2$ sorption were investigated herein, the CO$_2$-PHAST* model provided the best agreement with experimental data. The maximum calculated errors for the CO$_2$-PHAST* model in MOF-5, [Cu(dpa)$_2$SiF$_6$-i], and PCN-61 are ±0.33 mmol/g, ±0.11 mmol/g, and ±0.07 mmol/g, respectively. The CO$_2$-PHAST model produced an isotherm that
is in good agreement with experiment in MOF-5 and [Cu(dpa)$_2$SiF$_6$-i]; however, the lack of explicit polarization causes this model to undersorb the experimental isotherm in PCN-61. The CO$_2$-PHASTq model oversorbs in MOF-5 and [Cu(dpa)$_2$SiF$_6$-i], but undersorbing slightly in PCN-61. The isotherms generated by the CO$_2$-PHASTq* model significantly oversorbed the experimental results for all three MOFs. For simulations using the TraPPE model in MOF-5 and [Cu(dpa)$_2$SiF$_6$-i], the generated isotherm oversorbed experiment at low pressures and then undersorbs at higher pressures. Further, although the TraPPE model produces an isotherm that is in good agreement with experiment in PCN-61, it is clear from Figure 8b that the TraPPE CO$_2$ molecules are farther away from the Cu$^{2+}$ ions, which is in contrast to the experimentally observed CO$_2$-Cu$^{2+}$ interaction.

Future work will include using PHAST models for simulations of CO$_2$ sorption in other MOFs. These models will also be adapted for use in Molecular Dynamics studies of the diffusion of CO$_2$ through MOFs. Finally, it would be useful to perform simulations of mixed gas separation using the PHAST models.
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