

TITLE: Use of Molecular modeling to determine the interaction and competition of gases within coal for carbon dioxide sequestration

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ABSTRACT

We have utilized computational molecular modeling to generate a state-of-the-art large scale structural representation of a bituminous coal of lower bituminous rank. This structure(s) has been used to investigate the molecular forces between the bituminous coal structure (or idealized pores) and the molecular species CH_4 and CO_2 . We have created a new force field for these simulations and are currently carrying out molecular dynamics simulations. An initial step performed is to help define the issues with sequestration utilizing the molecular modeling approach. Once defined advanced molecular modeling techniques can be utilized in investigating sorbent and host behavior.

TABLE OF CONTENTS

	Page No.
Abstract.....	3
List of Graphical Materials.....	5
Introduction.....	6
Executive Summary.....	6
Experimental.....	7
Results and Discussion.....	7
Conclusion.....	16
References.....	17
Bibliography.....	18
List of Acronyms and Abbreviations.....	18

LIST OF GRAPHICAL MATERIAL

	Page No.
Figures 1 and 2. The T-structure and the H-structure respectively. These energetic minima structures were similar to those found by Sadlej <i>et. al.</i> The interaction energies were found to be -3.0 kcal/mol at a distance of 2.80 Å for the T-structure and -2.1 kcal/mol at a distance of 2.20 Å for the H-structure.	10
Figure 3. Adsorption Isotherm for Methane and Carbon Dioxide on Pocahontas No. 3 coal. Adsorption data is taken from the literature.	14
Figure 4. Representation showing how much methane (shown at STP) can be obtained (on average) from 10 g of Pocahontas No. 3 coal.	14
Figure 5. Representation showing the relationship between micropores (small red spheres), mesopores (yellow sphere—head) and macropore (white sphere—body).	14
Figure 6. Representation of a micropore and a molecule of CO_2	15
Figure 7. Dispersed model structural representation of Pocahontas coal showing a stack of 32 methane molecules that such a structure should contain (average value) and the 64 carbon dioxide molecules that should be able to displace the methane molecules.	16

INTRODUCTION

Sequestration of CO₂ within coal seams that are too deep, thin, or uneconomic has been suggested to slow the rate of climate change. Additionally, coal can hold twice as much CO₂, (from sorption isotherm studies) as it can hold methane(1). Sequestered CO₂ also displaces CH₄ within coal, a valuable fossil fuel, to help offset the sequestration cost. The objective is to carry out first time molecular dynamics simulations to provide useful information on accessible pore volumes, energy of interactions between host and guest molecules, self-diffusion coefficients, identification of likely sorption sites, impact of carbon dioxide sorption/methane exchange upon the coal matrix (expansion/contraction), and competitive adsorption isotherms. The molecular modeling approach essentially permits us to investigate the complex interactions at the molecular level to define and explain the issues relating to sequestration of CO₂ within coal. The structural model is being revised to better represent the structural alignment in a coal of this rank which has implications for the shape of pores, diffusion, and swelling anisotropy. The objective is to construct a reasonable molecular representation of Pocahontas No. 3 coal which is representative of both the physical and chemical composition, *and behavior* of this low volatile bituminous coal.

EXECUTIVE SUMMARY

Recent experimental and computational advances have the potential to produce a first-time reasonable constitutional model (chemical and physical structure) and enable its use. We have utilized computational molecular modeling to generate a state-of-the-art large scale structural representation of a bituminous coal of lower bituminous rank. First, structural diversity may be incorporated through the combination of high-resolution transmission electron microscopy (HRTEM) and laser desorption mass spectroscopy, which has not been previously included into a three-dimensional structural model of coal. Secondly, methodological advances in molecular simulations that have been successfully applied to biomolecular systems and new engineering materials coupled with available high capacity and high speed parallel super computers make the modeling of CO₂ sequestration by coal realistic and practical. A major focus of the presented research is in the modification and creation of appropriate force field parameters to model accurately the structure and properties of coal with small molecules such as CO₂ and CH₄. Molecular models of CO₂ have been evaluated with water to analyze which classical molecular force-field parameters are the most reasonable to predict CO₂ interactions with water. The molecular force field models for a single CO₂-H₂O complex were compared against quantum mechanical calculations, to develop a reasonable aqueous force field model for CO₂. All of the structural calculations show that two structures exist for the interaction of a CO₂ with a water molecule, called the H-structure and T-structure. It was found that the Steele model was the best literature model with respect to reproducing both structures from the *ab initio* data; the newly developed TJDM1 CO₂ model reproduced the interaction energies and geometries significantly better than the Steele force field model. The newly development three-dimensional structure(s) has been used to investigate the molecular forces between the bituminous coal structure (or idealized pores) and the molecular species CH₄ and CO₂ using the newly developed force field. We

have created a new force field for these simulations and are currently carrying out molecular dynamics simulations. An initial step performed is to help define the issues with sequestration utilizing the molecular modeling approach. Once defined advanced molecular modeling techniques can be utilized in investigating sorbent and host behavior of CO₂ and CH₄.

EXPERIMENTAL

Twenty 1.8-3.2 GHz Pentium IV computers with molecular computation and data processing software were utilized. In terms of super computing facilities, IBM RISC System/6000 SP Supercomputer Model 3A8 (four nodes @ 160 MHz each w/256 Mb ECC memory, twelve nodes @ 120 MHz each w/1 GB ECC memory); 2 IBM RISC System/6000 (77 MHz and 66 MHz w/512 Mb ECC memory); and 2 Dec Alpha Beowulf Clusters containing Master-node (600 MHz w/512 MB ECC memory and 24 GB of disk space) and 16 nodes (600 MHz w/256 MB ECC memory) were utilized.

RESULTS AND DISCUSSION

Data Reduction

The *ab initio* calculations were completed for a CO₂ molecule, a single water molecule, and the CO₂-H₂O complex for multiple levels of theory and basis sets in order to calculate the interaction energy of the complex. For the interaction energies, they were calculated as the energy of the complex minus the energies of the individual CO₂ and water molecules. This can be shown as:

$$\Delta E = E(AB) - E(A) - E(B) \quad (1)$$

where delta E is the energy of interaction, E(AB) is the energy of the complex, and E(A) and E(B) are the energies of the CO₂ and water molecules[1].

A thorough evaluation of the CO₂-H₂O complex was achieved by using different theory and basis sets. Hartree-Fock (HF), density functional theory (DFT), Möller-Plesset perturbation theory (MPPT), and coupled clusters with single and double excitations (CCSD) were used with the following basis sets: 3-21G, 6-31G, 6-31G(d), aug-cc-pvdz, and aug-cc-pvtz. The density functional theory used in the calculations was the Becke3 exchange functional with the Lee, Yang, and Parr non-local functional corrections [2, 3]. For the most complete QM study of the complex, the use of polarized split-valence basis sets were employed to allow the molecular orbitals to change shape by adding basis functions to higher than ground state levels to increase angular momentum and efforts were made to keep a balanced basis set in the calculations [1, 4]. The investigation with the increasing levels of theory was in an attempt to converge the interaction energies and the *ab initio* calculations were done using Gaussian98 and Gaussian03 [5, 6].

The zero point energy calculations were obtained by releasing the constraints of the system until all degrees of freedom were free. The minima were obtained and frequency calculations were completed and evaluated with all of the above mentioned

methods and basis sets. The energetic minima were found to have no negative frequencies, concluding that the true minimum was found for both the T-structure and the H-structure of the complex. The T-structure was also constrained to C_{2V} symmetry, as had been done in previous *ab initio* calculations and frequency calculations on the minimized structure for comparison [7].

For the classical simulations, including both the MM minimizations and MC simulations, a classical force field was used to model the CO_2 - H_2O interactions; the waters in the bulk phase simulations were modeled in the same fashion. The potential energy function of the force field is given as follows [8].

$$U(R) = U(R)_{bonded} + U(R)_{non-bonded} \quad (2)$$

where

$$U(R)_{bonded} = \sum_{bonds} K_b (b - b_0)^2 + \sum_{angles} K_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} K_\chi [1 + \cos(n\chi - \sigma)] \quad (3)$$

and

$$U(R)_{non-bonded} = \sum_{\substack{non-bonded \\ pairs}} \left(\epsilon_{ij} \left[\left(\frac{R_{min.ij}}{r_{ij}} \right)^{12} - \left(\frac{R_{min.ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{\epsilon_D r_{ij}} \right) \quad (4)$$

where $U(R)$ is the potential energy of the system. For the CO_2 - H_2O complexes, the only parameters that will be evaluated will be the non-bonded terms, since the CO_2 and water will be treated as rigid molecules. The standard mixing rules for the mixing of the LJ terms between molecules was observed [4]. The mixing rules can be shown as:

$$\sigma_{AB} = \frac{\sigma_{AA} + \sigma_{BB}}{2} \quad (5) \quad \text{and} \quad \epsilon_{AB} = \sqrt{\epsilon_{AA} \epsilon_{BB}} \quad (6)$$

The DYNAMO program was used to perform the MM minimizations and BOSS was used in the MC simulations [9, 10]. The MM minimizations were done using several steps of steepest decent followed by conjugate gradient, in order to find the lowest energy structures; the complexes interaction energies were calculated using the same methods in the *ab initio* calculations shown in *Equation 1*. The MC simulations were standard done using the standard acceptance/rejection ratio of 0.40/0.60, which has been shown to give reasonable sampling in simulations [4].

The force-field parameters used in the molecular mechanics calculations were taken from the literature and developed here. The water molecules used in the simulations the TIP3P and TIP4P water models from Jorgensen *et. al.* [11, 12]. Several CO₂ models from the literature were studied along with a newly developed model, the TJDM1 model (named from the authors initials) [13-15]. All the CO₂ models used in the calculations are 3-site electrostatic models with the charges and LJ 12-6 terms centered on the atoms. The intermolecular terms for the various CO₂ models are presented in *Table 1*.

Experimental and Operational Data

Molecular models of CO₂ have been evaluated with water to analyze which classical molecular force-field parameters are the most reasonable to predict CO₂ interactions with water. The molecular force field models for a single CO₂-H₂O complex were compared against quantum mechanical calculations, to develop a reasonable aqueous force field model for CO₂. All of the structural calculations show that two structures exist for the interaction of a CO₂ with a water, called the H-structure and T-structure. It was found that the Steele model was the best literature model with respect to reproducing both structures from the *ab initio* data; the newly developed TJDM1 CO₂ model reproduced the interaction energies and geometries significantly better than the Steele force field model.

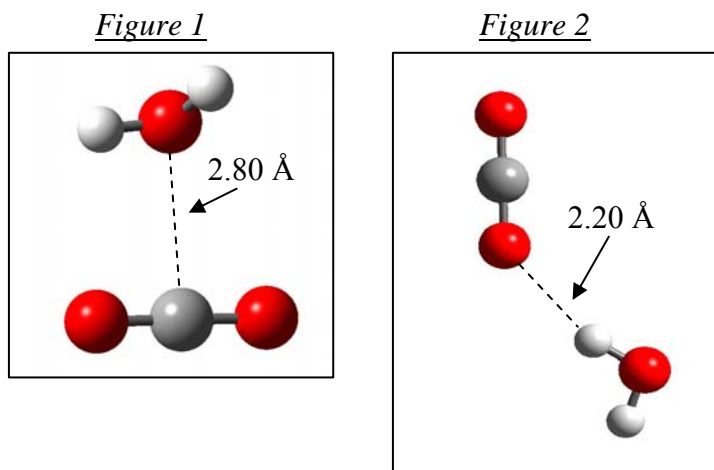
Table1: The CO₂ force field parameters from the literature and the developed TJDM1 model [13-15].

Carbon dioxide model		ϵ	σ	q
Harris (EPM)	C	0.057627	2.785	0.6645
	O	0.164933	3.064	-0.33225
Murthy	C	0.057629	2.785	0.596
	O	0.165138	3.014	-0.298
Steele	C	0.057629	2.652	0.596
	O	0.165138	2.870	-0.298
Harris2 (EPM2)	C	0.055898	2.757	0.6512
	O	0.159985	3.033	-0.3256
TJDM1	C	0.087630	2.152	0.720
	O	0.13714	3.080	-0.360

Using *ab initio* quantum chemical calculations, two energy minima were located for the CO₂-H₂O complex. The two energetic minima for the CO₂-H₂O complex are in agreement with previous work done by Sadlej *et. al.*, with one noted exception, where these minima were called the H-structure and the T-structure based on the geometry of the atoms in the complex[7]. Shown in *Figures 1 and 2* are the T-structure and the H-structure, respectively.

The noted exception from the previous work done by Sadlej *et. al.* held the T-structure to a constrained to C_{2v} symmetry based on assumptions from experimental microwave data [16]. This current study did frequency calculations on constrained T-structures minimized at several levels of theory and basis sets and found that negative frequencies existed in every case of the constrained structure. The first principle quantum mechanical calculations shown in this study were done with no symmetry constraints on the complex. Calculation of the frequencies with all degrees of freedom released showed that true energy minima were obtained.

The T-structure is the global minimum for the CO_2-H_2O complex in all the levels of theory and basis sets. It exhibits 2 electrostatic interactions between the carbon dioxide and the water, one between the oxygen of the water with the carbon of the CO_2 and the second between a hydrogen of the water and an oxygen of the CO_2 . Shown in *Tables 2 and 3* are the interaction energies and geometric distances between the CO_2 and water for the T-structure. This is in disagreement with the reported T-structure from Sadlej, where he held the CO_2-H_2O T-structure complex in C_{2v} symmetry, which would prevent the second electrostatic interaction between the molecules from forming.



Figures 1 and 2: The T-structure and the H-structure respectively. These energetic minima structures were similar to those found by Sadlej *et. al.* The interaction energies were found to be -3.0 kcal/mol at a distance of 2.80 Å for the T-structure and -2.1 kcal/mol at a distance of 2.20 Å for the H-structure.

Table 2: Interaction energies of the T-structure; energies given in kcal/mol.

b.s. / method	B3LYP	HF	MP2	MP3	MP4	CCSD
3-21G	-8.30	-7.97	-6.64	-7.45	-6.91	-7.16
6-31G	-5.18	-5.81	-4.46	-5.48	-4.96	-5.45
6-31G(d)	-3.41	-3.10	-3.69	-3.82	-3.68	-3.72
aug-cc-pvdz	-1.95	-2.67	-2.99	-2.95	-3.00	
aug-cc-pvtz	-1.79	-2.56	-2.81			

Table 3: Geometry of T-Structure: The distance between the C(CO₂) and the O(H₂O), in Å .

b.s. / method	B3LYP	HF	MP2	MP3	MP4	CCSD
3-21G	2.514	2.592	2.616	2.525	2.583	2.562
6-31G	2.576	2.586	2.696	2.619	2.659	2.647
6-31G(d)	2.772	2.774	2.749	2.723	2.721	2.730
aug-cc-pvdz	2.847	2.841	2.783	2.816	2.785	
aug-cc-pvtz	2.869	2.858	2.777			

From the T-structure *ab initio* data it is observable that the energies of interaction and the distances between the molecules converge going across and down the tables, converging in both the levels of theory and in number of basis sets respectively. The convergence of the methods and basis sets reached a limiting value of -3.0 kcal/mol for the interaction energy and 2.80 Å for the distance between the molecules. These are the values that will be used in the comparison with the molecular mechanics values.

The second minima found was for the H-structure, which was similar to that found by Sadlej. The H-structure exhibits hydrogen bonding between a hydrogen of the water molecule and an oxygen of the CO₂ molecule. Shown in *Tables 4 and 5* are the interaction energies and geometric distances between the CO₂ and the water molecule. As seen in the T-structure *ab initio* data, the H-structure *ab initio* data also converge going across and down the tables, converging in both the levels of theory and in number of basis sets respectively. The convergence of these values reaches a limiting value of -2.1 kcal/mol for the interaction energy and 2.20 Å for the distance between the molecules. As before, these are the values that will be used in the comparison with the molecular mechanics values.

Table 4: Interaction energies of the H-structure; energies given in kcal/mol.

b.s. / method	B3LYP	HF	MP2	MP3	MP4	CCSD
3-21G	-4.38	-4.16	-4.34	-4.29	-4.34	-4.32
6-31G	-3.03	-2.91	-2.74	-2.92	-2.89	-3.19
6-31G(d)	-2.07	-1.77	-2.25	2.21	-2.21	-2.19
aug-cc-pvdz	-1.36	-1.33	-2.11	-2.10	-2.08	
aug-cc-pvtz	-1.35	-1.24	-2.05			

The development of the force field parameters was achieved by minimizing the error of both the MM calculated H-structure and the T-structure against the QM convergence structures. To start the development, the ϵ , σ , and q were all adjusted $\pm 15\%$

of the original values, which were started from the Steele structure, and the difference in the energetics and structure were noted. From this, it was found that the charge was the contributing the most in the energetics and structure deviation, followed by σ , and then the well depth, ϵ . To minimize the change in the original parameters, the charge was optimized followed, by the σ , and then ϵ . Several other trials were attempted using other error minimization processes, but it was found that the previously mentioned one was the closest to the original parameters. These parameters were used in the initial solubility calculations, but were modified to the parameters noted in *Table 1* to achieve the correct solubility; the difference between the original development described here and the final was found to be $< 1\%$, and thus the original parameters are omitted, but noted to give slightly better structural properties by $< 2\%$.

Table 5: Geometry of H-Structure: The distance between the O(CO₂) and the H(H₂O), in Å.

b.s. / method	B3LYP	HF	MP2	MP3	MP4	CCSD
3-21G	1.997	2.061	2.055	2.059	2.056	2.060
6-31G	2.082	2.136	2.161	2.147	2.161	2.160
6-31G(d)	2.195	2.301	2.216	2.228	2.233	2.261
aug-cc-pvdz	2.234	2.355	2.182	2.196	2.203	
aug-cc-pvtz	2.266	2.382	2.187			

The MM minimizations were performed using a variety of minimization steps, in order to insure the finding of the lowest energy structure with some degree of accuracy. It was found that no improvement was gained by going over 100 steps of steepest decent, followed by 200 steps of conjugate gradient minimization steps in the minimization process, when starting from a reasonable starting structure. It is also noted that the tolerance for the minimization method were kept low, in order that the barrier from the T-structure to the H-structure was not cross in the process.

Table 6: The interaction energies of the four literature CO₂ models and the developed TJDM1 model with TIP4P water model and comparison to the *ab initio* calculations; interaction energies given in kcal/mol.

	T-Structure		H-Structure	
	MM	Δ (QM –MM)	MM	Δ (QM –MM)
Harris	-2.26	-0.74	-1.93	-0.17
Murthy	-2.08	-0.92	-1.73	-0.37
Steele	-2.27	-0.73	-1.98	-0.12
Harris2	-2.26	-0.74	-1.94	-0.16
TJDM1	-2.65	-0.35	-2.08	-0.02

Table 7: The geometric distances of the four literature CO₂ models and the developed TJDM1 model with TIP4P water model and comparison to the *ab initio* calculations; distances given in Å.

	T-Structure		H-Structure	
	MM	Δ (QM –MM)	MM	Δ (QM –MM)
Harris	2.934	-0.134	2.010	-0.190
Murthy	2.935	-0.135	2.038	-0.162
Steele	2.838	-0.038	1.880	-0.320
Harris2	2.914	-0.114	1.993	-0.207
TJDM1	2.808	+0.008	2.008	-0.192

Among the molecular force field models found in the literature, the Steele model provides the best match with the *ab initio* data, with an interaction energy and distance of -2.27 kcal/mol and 2.84 Å respectively for the T-structure and -1.98 kcal/mol and 1.88 Å respectively for the H-structure. This yielded a difference, when compared to the *ab initio*, of -0.73 kcal/mol and -0.04 Å for the T-structure and -0.12 kcal/mol and -0.32 Å for the H-structure. The deviations of the literature CO₂ models from the *ab initio* data are noted to be not within reason agreement and therefore would not be accurate in aqueous simulations. The developed TJDM1 force field model yields dramatic improvements over the Steele model, when compared to the *ab initio* data. The interaction energies and distances of the T-structure were found to be -2.65 kcal/mol and 2.81 Å respectively and the H-structure yielded results of -2.08 kcal/mol and 2.01 Å respectively. The differences between the TJDM1 model and the *ab initio* are -0.35 kcal/mol and 0.01 Å for the T-structure and -0.02 kcal/mol and -0.19 Å for the H-structure. This shows much improvement over the Steele and all of the other compared models. A comparison of the molecular force field model's interaction energies and interaction distances can be seen in *Tables 6 and 7*.

A representation of an adsorption isotherm for Pocahontas No. 3 is shown in Figure 3. Clearly the 2:1 ratio is pressure dependent. The Pocahontas coal is also very rich in methane content as shown in Figure 4.

Adsorption Isotherms for Carbon Dioxide and Methane

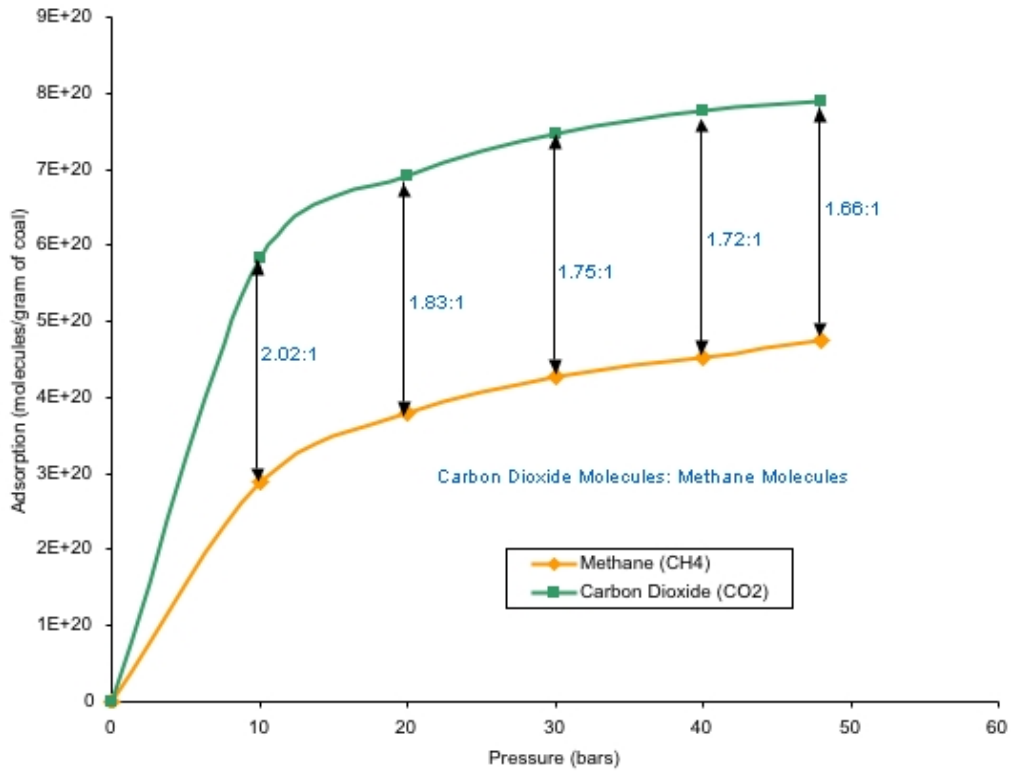


Figure 3. Adsorption Isotherm for Methane and Carbon Dioxide on Pocahontas No. 3 coal. Adsorption data is taken from the literature.

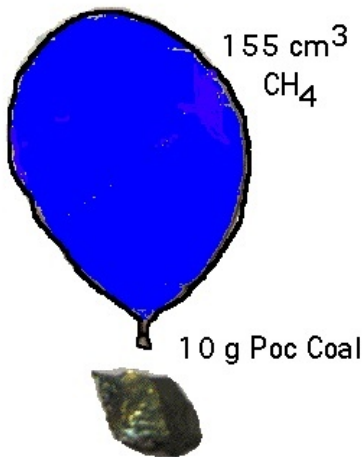


Figure 4. Representation showing how much methane (shown at STP) can be obtained (on average) from 10 g of Pocahontas No. 3 coal.

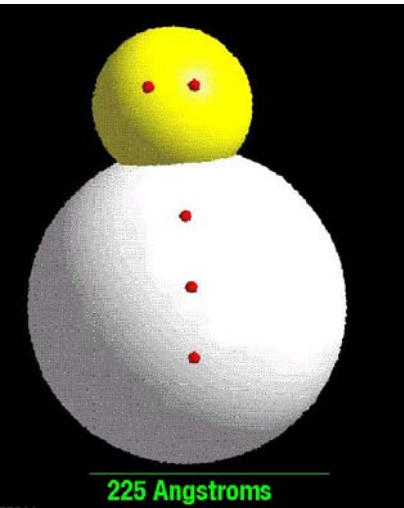


Figure 5. Representation showing the relationship between micropores (small red spheres), mesopores (yellow sphere—head) and macropore (white sphere—body).

The complex interconnection, distribution, and shapes of the pores are the controlling features with regard to capacity and kinetics of uptake. Figure 5 shows the representation of the relative scale of macro, meso, and micropores, (shown as spheres.) The dual porosity nature of the coal means for the most part that mesoporosity is limited. Shown in Figure 6 is the relative scale of a micropore (shown as sphere) and a CO₂ molecule. We believe that the distribution, size and shape of the micropores limits access to the methane molecules while permitting carbon dioxide to enter (molecular sieving). Shown in Figure 7 is a “blow-up” structural model with the fragments dispersed in space to aid in viewing. Also shown are the 32 molecules of methane that a structure of this size should contain (based on average methane content values for this coalseam) and the 64 carbon dioxide molecules that can displace the methane (assuming 2:1 ratio).

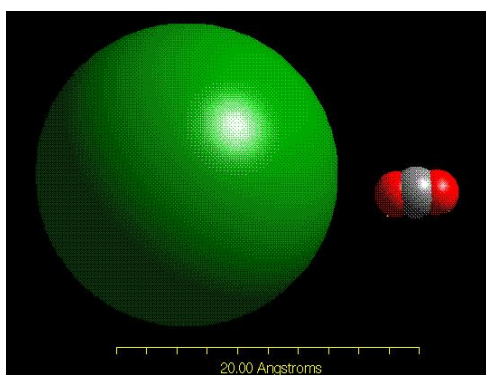


Figure 6. Representation of a micropore and a molecule of CO₂

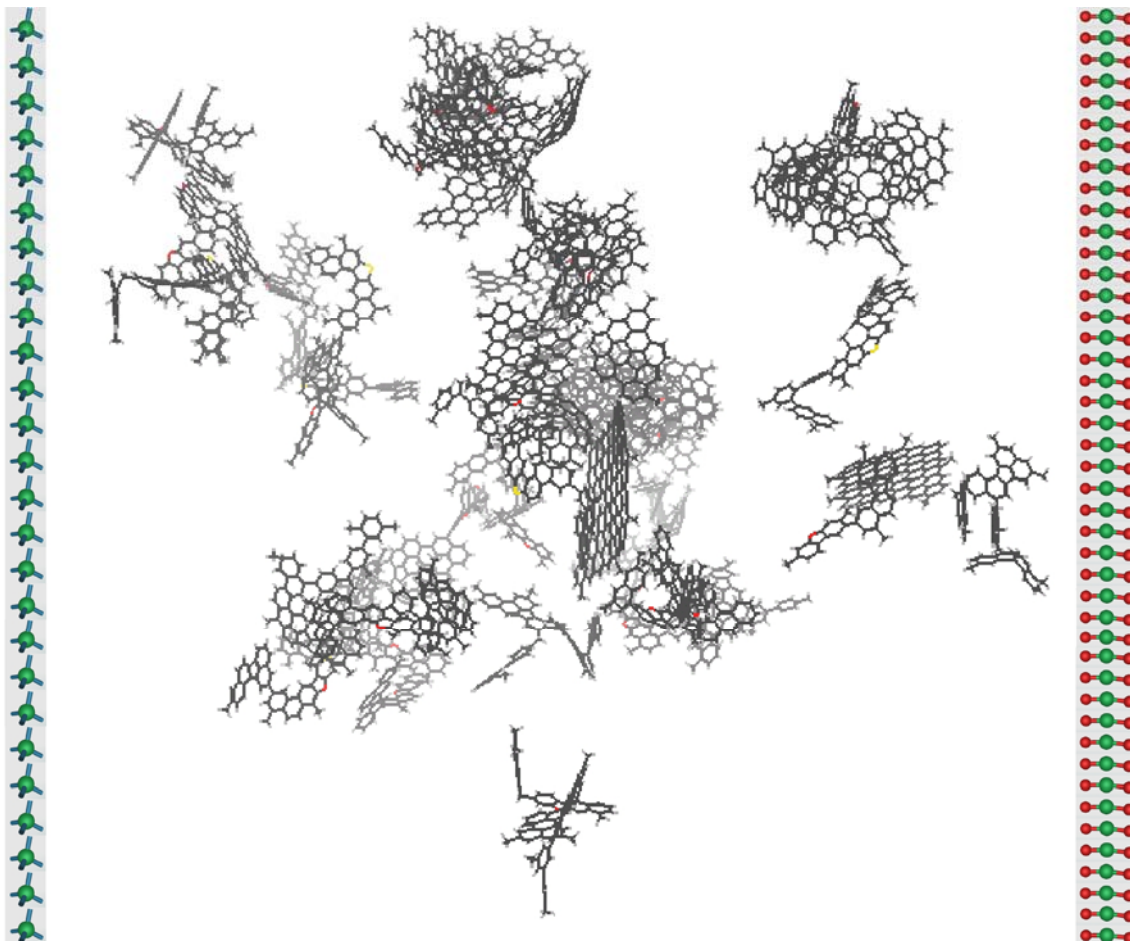


Figure 7. Dispersed model structural representation of Pocahontas coal showing a stack of 32 methane molecules that such a structure should contain (average value) and the 64 carbon dioxide molecules that should be able to displace the methane molecules.

CONCLUSIONS

We have utilized computational molecular modeling to generate a state-of-the-art large scale structural representation of a bituminous coal of lower bituminous rank. This structure(s) has been used to investigate the molecular forces between the bituminous coal structure (or idealized pores) and the molecular species CH_4 and CO_2 . We have created a new force field for these simulations and are currently carrying out molecular dynamics simulations. An initial step performed is to help define the issues with sequestration utilizing the molecular modeling approach. Once defined advanced molecular modeling techniques can be utilized in investigating sorbent and host behavior.

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LIST OF ACRONYMS AND ABBREVIATIONS

CCSD	coupled clusters with single and double excitations
DFT	density functional theory
HF	Hartree-Fock
HRTEM	high-resolution transmission electron microscopy
MC	Monte Carlo
MM	Molecular Mechanical
MPPT	Möller-Plesset perturbation theory
QM	Quantum Mechanical
TJDM1	Tom Jeffrey David Madura 1 water model