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

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Abstract

A 3-dimensional coal structural model for the Argonne Premium Coal Pocahontas No. 3 has been generated. The model was constructed based on the wealth of structural information available in the literature with the enhancement that the structural diversity within the structure was represented implicitly (for the first time) based on image analysis of HRTEM in combination with LDMS data. The complex and large structural model (>10,000 carbon atoms) will serve as a basis for examining the interaction of gases within this low volatile bituminous coal. Simulations are of interest to permit reasonable simulations of the host-guest interactions with regard to carbon dioxide sequestration within coal and methane displacement from coal. The molecular structure will also prove useful in examining other coal related behavior such as solvent swelling, liquefaction and other properties. Molecular models of CO_2 have been evaluated with water to analyze which classical molecular force-field parameters are the most reasonable to predict the interactions of CO_2 with water. The comparison of the molecular force field models was for a single CO_2-H_2O complex and was compared against first principles quantum mechanical calculations. The interaction energies and the electrostatic interaction distances were used as criteria in the comparison. The *ab initio* calculations included Hartree-Fock, B3LYP, and Möller-Plesset 2nd, 3rd, and 4th order perturbation theories with basis sets up to the aug-cc-pvtz basis set. The Steele model was the best literature model, when compared to the *ab initio* data, however, our new CO_2 model reproduces the QM data significantly better than the Steele force-field model.

Introduction

Coal exists as a complex organic rock[1]. The coal structure is very diverse with the term "rank" being used as a pseudo maturation guide to distinguish the various sub-classifications of coal. Of interest here, is the rank of coal that is likely to produce substantial quantities of methane to offset the cost of carbon dioxide sequestration. Significant capacity for carbon dioxide is also desirable. Low volatile bituminous coal is hence a likely contender for meeting these criteria. An added bonus from the modeling standpoint is the high rank of the coal significantly simplifies the structural diversity with regard to the heteroatoms, and the structural diversity associated with (and within) the maceral groups. For a high rank coal, as the coalification process continues tends to form increasingly larger prominently aromatic hydrocarbon "rafts." The difficulty in analyzing these high rank coals is related to these large structural entities. They are not amenable to standard analytical practices such as GCMS, hence the majority of the information is related to the average properties of the coal. While this is very useful information, the average values, such as the aromaticity or for another example the atomic hydrogen to carbon ratio, can be achieved via many approaches by simply varying the frequency and diversity of the structural sizes. Such an approach is clearly limited if the desire is a reasonable representation of the structure such that it would be useful in a predictive manner.

Three recent advances during the last decade have shed light on this issue:

1) The adaptation of the oxidation/decarboxylation of coals to produce carboxylic acids that on reduction produces mostly GC amenable aromatic structures. This approach has been reported in the literature with an excellent paper dedicated to the structural features of Pocahontas No. 3 Coal by Stock and Obeng[2]. This technique permitted analysis of approximately 25% of the aromatic carbons to be retained (and presumably most of this material can be analyzed). This paper follows the also excellent review article of the structural features of this coal[3]. The technology here is old but it is the advances in GCMS technology that has enhanced the identification process.

2) High Resolution Transmission Electron Microscopy was successfully applied to the edges of small coal particles[4]. The significant advancement that followed was the use of image processing techniques to extract the lattice fringes out of the micrograph[5, 6]. This permitted a direct "observation" of the structural diversity to be quantified for the first time on the length basis of the fringe. Lattice stacking[5-7] and orientation[8] issues can also be addressed.

3) Laser desorption mass spectroscopy (LDMS) is also able to quantify the structural diversity on a mass basis.

The utilization of the combination of HRTEM and LDMS has been discussed previously by the author[8]. This permits the 2D (lattice fringes) and the 3D (molecular weight distribution from presumably cross-linked fringes) to be combined to yield a measure of the structural diversity. This provides a molecular basis for the structural representation that has a basis in multiple analytical techniques and provides a superior starting point for the molecular construction.

The Emerging “Picture” of the Structure of Pocahontas No. 3 Coal

Figure 1 reports the key traditional structural features of the coal. This elemental analysis provides a quantitative analysis of the building blocks of the final structure. Solid state ^{13}C NMR (single pulse, CRAMPS and dipolar dephasing) provides the aromaticity of the coal and the degree to which the aromatic carbons are protonated. As the molecular size of the aromatic raft increases the protonated fraction of aromatic carbons is reduced. A similar reduction can be obtained via increasing the crosslink density of the coal. Hence although these are key clues to the construction of the molecular representation their sole reliance is prone to investigator bias in the final representation. The structural “map” has various inconsistencies that are not uncommon when comparing multiple analytical techniques for coal structural analyses. For example with only 1.1 oxygen atoms per 100 carbon atoms it is not possible to have 5.3 phenolic carbon atoms (from the Utah groups NMR analysis[9]). Other inconsistencies exist, hence the data is a basic ingredient list for what the structure should contain.

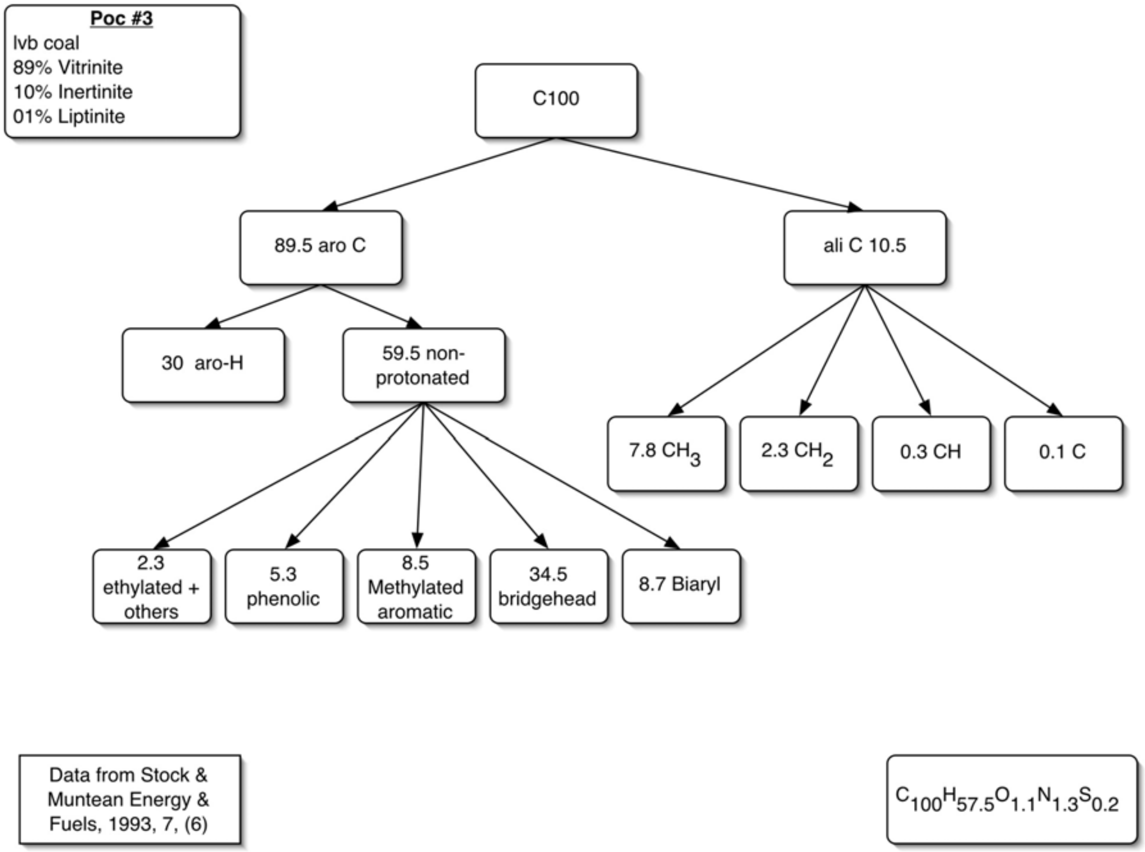


Figure 1. Structural parameters used in constructing the molecular representation

The HRTEM micrographs with false color representation is shown in Figure 2. There are several important observations from this and other micrographs: considerable fringe length diversity is evident, the structure is orientated (with a bias to 120°'), and many of the fringes exhibit curvature. The diversity within the length of the fringes is presented in Table 1. With assumptions on the shape of the fringe the distribution of the structural entities can be estimated. Stacking of fringes is also evident.

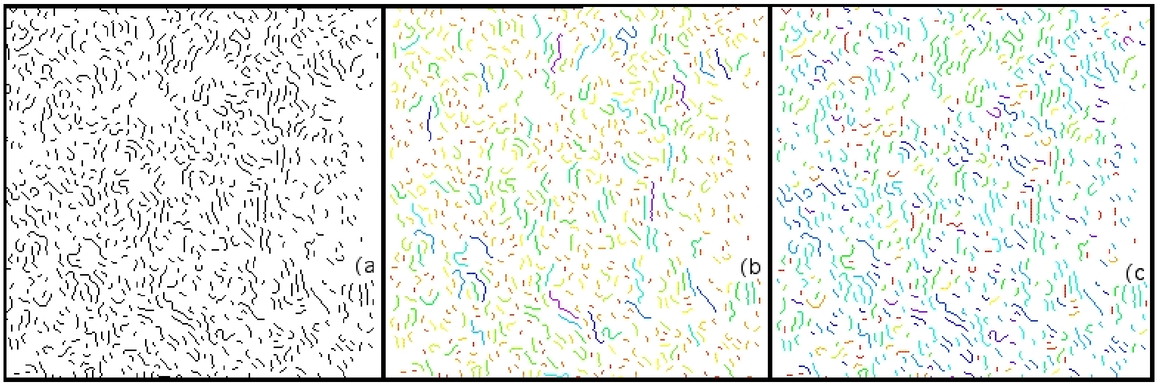


Figure 2. a) HRTEM Lattice Fringe Image, and False Colored Images by b) Length, and c) Angle. From[8]

The shape of the large aromatic "rafts" was assumed to be parallelogram in shape. The shape assumption and the assignment of the molecules and raft sizes is discussed in detail here[8]. An interesting distribution in size is presented in Table 1. The diverse distribution, and frequency of the molecular sizes shown in the micrograph is demonstrated (Table 1).

Table 1. Structural assignments based on image analysis of HRTEM fringes.

Assignment	Frequency
Benzene	40
Naphthalene	336
<3x3	199
<4x4	109
<5x5	56
<6x6	23
<7x7	6
<8x8	5
<9x9	3
Total	1,000

The assignment of a molecule called "3x3" would be a dibenzocorronene such that it formed a parallelogram shape (3 rings across by 3 rings down). 2x2 if listed would be pyrene.

Admittedly considerable uncertainty exists over the assignments shown but this approach does offer an excellent starting point for the assignment of structural models. Indeed, the first structural representation obtained was simply for the aromatic portion of the structure. The SIGNATURE program[10-13] was used to reveal if this would be an acceptable “gross” structure in keeping with the atomic H/C ratio and protonated aromatic fraction. This program looks at the connectivity and hybridization of the atoms and given pieces (molecular structures) attempts to elucidate a structure that is consistent with the supplied analytical data. In essence, it is a macromolecular jigsaw maker with the pieces of the jigsaw being supplied along with the connectivity (allowable bonds or cross-links) to make a picture (a macromolecular model) in keeping with the pictures description (the structural parameters). The traditional construction approach is to add all the potential molecular structure building blocks and simply see what ratios would meet the desired data. The approach utilized here of basing the distribution of the molecules on the frequency of the lattices from the HRTEM proved to be very useful in speeding the construction approach, removing some of the structural uncertainty (what might the largest structure be?) and reduced the impact of the structural biases of the molecular construction worker/architect. Given this basis the SIGNATURE program was limited to very little (if any) flexibility in the allocation of the structural (fragments) frequency and was simply charged to see how many cross-links would be required to meet the appropriate crosslink frequency (based on reaching the protonated aromatic frequency). When this was successful the basic SIGNATURE of the structure is known: the carbon and hydrogen atoms and their environment within the model (for example is the aromatic carbon attached to two other aromatic carbons AND a hydrogen). Following the increase in molecular weight following each of these cross-links permitted the *molecular weight distribution* to be determined.

The molecular weight distribution can also be determined from the LDMS analysis. An example of the molecular weight distribution of the Pocahontas coal is shown in Figure 3. A wide distribution of molecular weights is evident, with the peak frequency being approximately 1,000 amu. The highest mass observed is hard to distinguish in the noise of the tail. The highest molecular weight based on an unconnected (not crosslinked) lattice fringe from the HRTEM technique is 2,414 amu which is still within the “envelope” of the LDMS curve. This is discussed further later in the report.

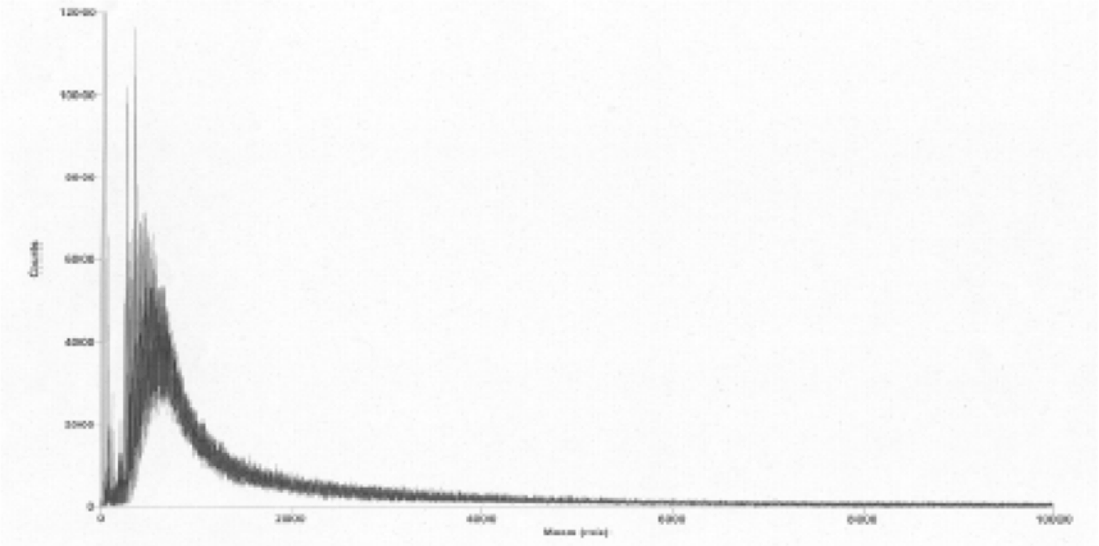


Figure 3. Laser Desorption Mass Spectroscopy data showing the molecular weight distribution.

The basic structure discussed above would be too basic for actual use as the diversity of the complex coal structure is highly limited with 9 structural types. Hence the challenge is to keep the relative abundances of the molecular sizes while increasing the structural diversity based on the Stock and Obeng structural assignments[2]. They list 150 compounds detected. To show all these structures with appropriate frequency (relative abundance) would require an enormous structural model that would easily exceed the useful size needed for the future computational experiments. Most coal molecular models are small (<600 carbon atoms)[14] the expectation here was to far exceed existing models by generating a model that is >10,000 atoms. This given the distribution of molecular sizes requires the construction molecules to be approximately 460 in number being comprised of >50 structural entities.

Table 2. Structural Assignments of the most abundant decarboxylated carboxylic acids from the oxidation of Pocahontas No. 3 Coal

Structural Assignment	Relative Abundance
Naphthalene	Very large
Biphenyl	Very large
Phenanthrene	Very large
Anthracene	*Very small*
Fluoranthene	Very large
Pyrene	Very large
Methylterphenyl	Very large
Benzo(a)anthracene	Large
Chrysene	Very large
Phenylanthracene	Large
Benzo(j)fluoranthene	Very large
Perylene	Very large
Dibenzofluorene	Large
Dibenzofluorene	Large
Benzo(g)chrysene	Large
Data from[2]	

Note: this technique essentially oxidizes the coal and the pendant alky groups. Aromatic rings can also be "opened" and oxidized hence the dibenzo and benzo derivatives would also have been present in some cases.

The advantage to the modeling approach used here, as well as the challenge, is the balancing of the information regarding the chemically determined relative structural abundance of Table 2 with the observed fringe frequency (HRTEM) and subsequent structural assignments of Table 1. This delicate balancing act requires that for each new structural inclusion the frequency of the existing base molecules (2x2, 3x3, 4x4) be reduced. Phenanthrene was found to be far more abundant than anthracene[2], a very surprising and interesting observation. Hence, phenanthrene is far more abundant in the structural model than anthracene. The structural features observed from the Stock and

Obeng paper[2] can be summarized as polycyclic aromatic hydrocarbons with 4,5, & 6 rings. The HRTEM analysis can be summarized (interpreted) as polycyclic aromatic hydrocarbons from benzene (low frequency) to structures as large as 9x9 aromatic raft (very low frequency). However, due to the large fringe length, and the assumption of a similar depth 9x9 is a very large molecule containing: 198 carbon and 38 hydrogen atoms, with a molecular weight of 2,414 amu, and an atomic H to C ratio of 0.19. Hence the structural model needs to have (structural) molecules as small as benzene, and structures as large as a 9x9 aromatic sheet, with the appropriate frequency of each and all the structural entities in-between.

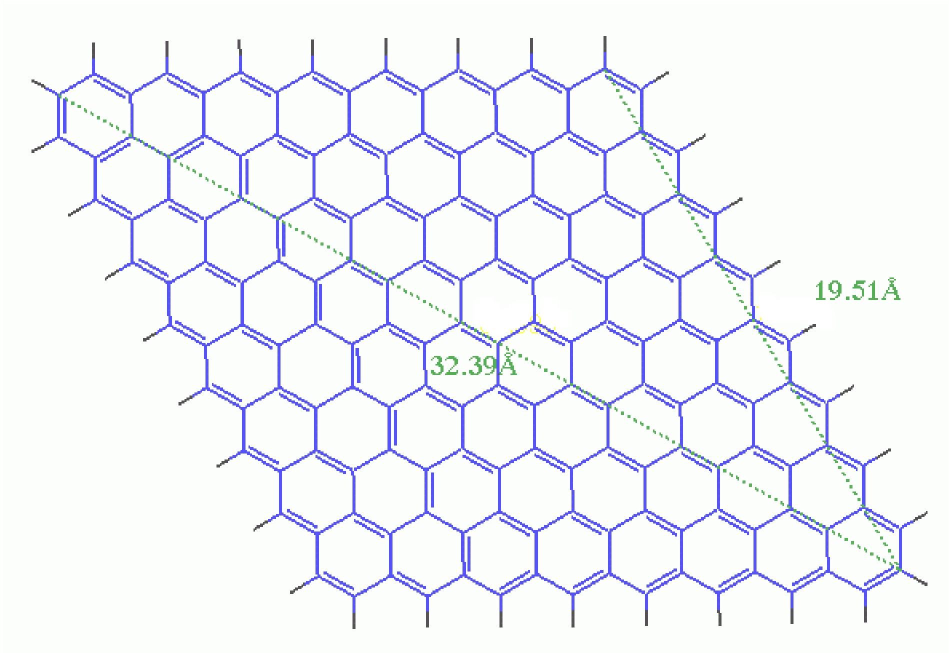


Figure 4. Assumed aromatic "sheet" (or "raft") shape. Sheet 8x8 is shown.

Physical Evaluation

The goal is to produce a reasonable molecular representation of Pocahontas No. 3 coal. For this to be achieved accurately representing the chemical structure (and the diversity within the structure) alone is not sufficient. The physical structure also needs to be a reasonable representation. Helium density is one such measurement. As the Helium molecule is small (and has enough energy to overcome many of the activated diffusion issues into the coal) it can penetrate all or nearly all of the pore space. From the known mass of the coal and the pressure change of the helium on exposure to an evacuated sample the helium density can be calculated. The experimental helium density of Pocahontas No. 3 coal is reported[15] as 1.38 g/cm^3 on a mineral matter free basis. A virtual measurement is also possible via the POR[11, 16] program (an accompanying program with the SIGNATURE[10, 17, 18] program). This technique determines the atomic occupied space of a 1 Å^3 cell, and the accessible and inaccessible space. From these values and the known molecular weight the simulated helium density can be determined. Values for the structural models generated here are within the appropriate range. As the model continues to grow, diversity within the pore space is an issue. The appropriate sub-micro, micropore, and macropores need to be present. Micropores are already present within the structural representation(s) from the necessarily imperfect stacking of the various shaped and sized structural fragments. Large pores can be introduced via simple deleting structural fragments or by "doping" the model during the construction process with atoms such as silica that have been "redefined" as to their van der Waals radius. Simply changing the default van der Waals value to represent the transitional sized pores or mesopores and macropores produces the necessary pore size distribution within large molecular structures. Interconnecting these various atoms via bonds or simply assessing the random placement of these atoms can produce spherical "shaped" pores. However give the dominance of aromatic sheets in structures of this rank range (low volatile bituminous) slit shaped or pyramid shaped pores are probably better representations. As we enter phase II of this project issues such as this can be addressed. Figure 5 shows an attempt at predicting pore size distribution from a HRTEM micrograph. It is important to point out that it is unknown as to the legitimacy of this approach. Many factors influence the lattice fringe "extraction" process. But it is a potentially intriguing approach.

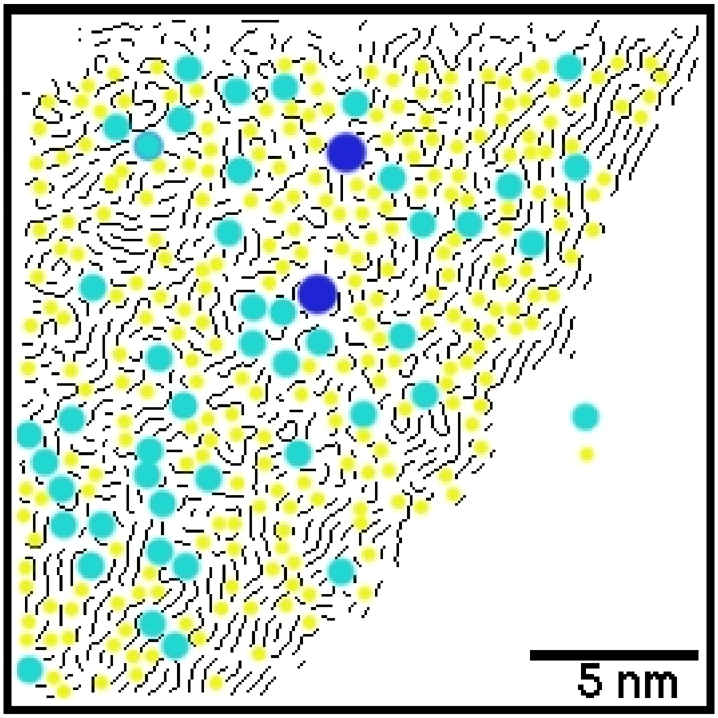


Figure 5. HRTEM micrograph showing "potential" pore space(s) and frequency.

Alignment Issues

The various HRTEM micrographs show there is structural alignment with Pocahontas No. 3 coal. This is to be expected for mature coals, with the direction of preferred orientation being parallel to the original bedding plane (subsequent uplifting and tectonic motion cal orient the coal seam to 60° angles an above as in the Pennsylvania anthracite region). The alignment is produced by overburden pressure over millions of years in mature coals (presence of aromatic sheets influence this process). This structural alignment can place considerable stresses on the coal. Solvent swelling anisotropy is well known for high rank bituminous coals, with the coal volume doubling in good solvents with greater swelling parallel with the bedding plane[19]. This physical behavior can not be explained by structural models that only consists of a single interconnected macromolecular structure[14]. Hence alignment issues are important in representing the physical structure of the coal. Optical anisotropy in plane-polarized reflected light levels (from rotating vitrinite polished surfaces) is also evident at this rank[20].

Accurately portraying orientation issues within the model(s) continues to be challenging. Random arrangements of structural fragments did not produce the desired alignment, although this can be somewhat achieved by using amorphous builders (part of the MSI Cerius^2 software suite) when requiring much higher than reasonable densities, but this approach require additional study. Placing the structural model(s) within non-periodic cells and minimizing the model with simulated directional stress (for example y-y) was very effective at aligning *all* the structural entities. Some combination of various construction techniques, and effective stressing of the structures will probably yield the required orientation.

Curvature Issues

It is also evident from the HRTEM micrographs (Figures 1 & 5) that there is considerable curvature within the lattice fringes. The impact of this is unclear but undoubtedly impacts the shapes of the (micro)pores and the interactions of small molecules within the structure. From the structural assignments of Stock and Obeng[2] there is no obvious curvature in those compounds. Rather the molecules are all "flat". A very slight puckering is introduced into some of the structures due to the steric hindrance of close proximity hydrogen's. Benzene(a)(e)pyrene is a good example of this steric strain. With much larger molecules the "puckering" becomes more apparent. Within the aromatic sheets the presence of 5-membered rings produces the well-known Buckyball effect of curvature. Corranulene is a bowl-shaped molecule with a 5-membered ring surrounded by aromatic rings, it was added as a structural fragment. Similar curvature is evident in the HRTEM. HRTEM simulations on Corranule produced an authentic looking curved lattice almost identical to the fringes observed experimentally within the coal structure. Some very highly curved structures observed with the HRTEM could not be reproduced and are likely a result of unconnected fringes "overlapping." Increasing the presence of 5-membered (and 5-membered in combination with 7-membered) rings will increase the degree of curvature and permit further fine-tuning of the structural representation. The condensation of chair and zig-zag carbon edge sites produce such 5- and 7-membered rings. Internal condensation of Benzo(j)fluoranthene also produced adjacent 5-membered rings and may contribute to the high extent of curvature in the fringes if such structure are components of the large structures.

Molecular Representations

A very large solution to the SIGNATURE program was produced containing >12,000 carbon atoms. A smaller sub-model is shown in Figure 6. The model shown is approximately 1/3 size (number of atoms.) This combination of crosslinked structural entities produces >30 separate molecular weights. The model *overall* contains $C_{3,538}H_{2,061}O_{32}N_{45}S_6$. This is entirely consistent with relative abundance of the elemental analysis. This structure is 90% aromatic (NMR value is 89.5%). The aliphatic carbons consist of CH_3 and CH_2 in approximately a 4:1 ratio. The majority of the nitrogen is present within the aromatic sheets (quaternary) with some occupancy at the edge sites in pyrrole and pyrdine structures. Oxygen functionalities are present in naphthofurans with some furans. The relative low abundance of the oxygen gave accurate representation of this heteroatom a low priority. However, the oxygen as presented needs to be better integrated into the structures. Sulfur is present at such low quantities (0.2 atoms per 100 carbon atoms) that a few thiophenes isomers of 5, 6 and 7 rings[2] where enough to satisfy the appropriate sulphur content.

The molecular weight distribution of the structure shown in Figure 6 is shown in Figure 7. There is good agreement between the distribution range shown from the LDMS (Figure 3) and the structure considering that the frequency of the molecular weight fragments is small given the size of the model. As we increase the molecular size the diversity will also increase.

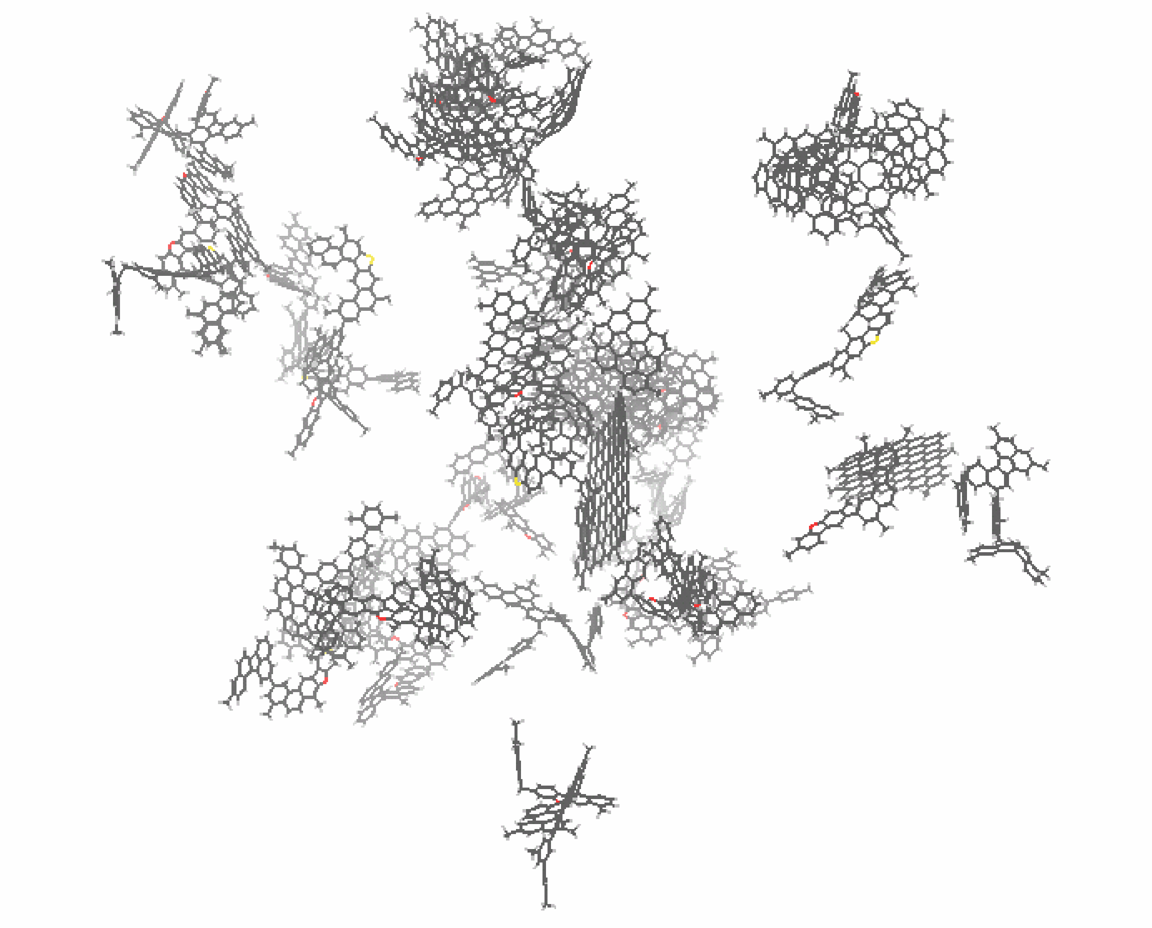


Figure 6. Image of a structural representation of Pocahontas No. 3 coal.

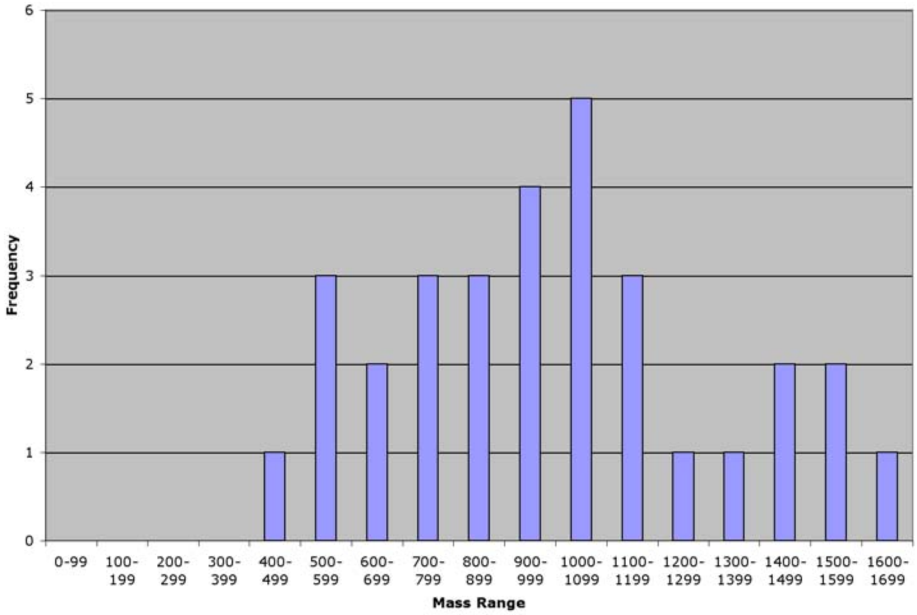


Figure 7. The molecular weight distribution of the model shown in Figure 6.

Use of the Model

The model agrees well with the analytical data and is consistent with much of its (Pocahontas No. 3) known coal chemistry. However, "the proof of the pudding is in the eating" is an apt phrase for it is in the *use* of the model that its contribution can be made. Future work will continue to refine the structure. Particularly in the area of size, structural alignment, degree of curvature, oxygen placement, and pore size distribution. The exciting use of the model however will be in the simulation of sequestration related interactions. This is the direction of the continuation of our Innovative concepts interaction between Duquesne and Penn State.

Computational Considerations

Development of carbon dioxide models that reproduce the properties of carbon dioxide in solution is critical for understanding the processes involved in mineral trapping, in particular the dissolution of CO_2 into aqueous solution. In this work, we develop and evaluate molecular models for carbon dioxide that can be used to study the structural and energetic properties of carbon dioxide with water.

Ab Initio

First principle quantum mechanics methods were used in all calculations. A thorough evaluation of the CO_2-H_2O complex was achieved by using different theory and basis sets. Hartree-Fock (HF), Möller-Plesset perturbation theory (MPPT), and density functional theory (DFT) 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 with the Lee, Yang, and Parr corrections. These levels of theory chosen were based on the treatment of electron correlation and computational cost. All of the *ab initio* calculations were done using Gaussian98.

The CO_2-H_2O complex was investigated with the varying levels of basis sets to observe the convergence in interaction energies with the addition of basis functions. The smallest basis used was the 3-21G basis set yielding in.12 basis functions (bf) on the core electrons, 36 contracted bf on the valence electrons, and 18 diffuse bf on the valence electrons for the CO_2-H_2O complex. For the complete QM study of the complex, the use of polarized valence basis sets was also used to allow the molecular orbitals to change shape by adding basis functions to higher than ground state levels to increase angular momentum.

All of the zero point energy calculations were done releasing the constraints of the system until all degrees of freedom were obtained. The minima were obtained and frequency calculations were completed and evaluated with every level of theory 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 Sadlej *et. al.* had done and frequency calculations on the minimized structure for comparison.

The *ab initio* calculations were completed for single CO_2 molecule, a single water molecule, and the CO_2-H_2O complex for every level of theory and basis set 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 CO_2 and water molecules. This can be shown as:

$$\Delta E = E\left(AB\right) - E\left(A\right) - E\left(B\right)$$

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 CO_2 and water molecules.

Molecular Mechanics

A classical force field was used to model the CO_2-H_2O interactions. The potential energy function of the force field is given as follows.

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

where the

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

and the

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

where the 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 coulombic terms between molecules was observed. The mixing rules can be shown as:

$$\sigma_{AB} = \tfrac{\sigma_{AA}+\sigma_{BB}}{2} \quad \text{and} \quad \varepsilon_{AB} = \sqrt{\varepsilon_{AA}\varepsilon_{BB}}$$

The Dynamo program was used to perform the molecular mechanics calculations.

Parameters

The force-field parameters used in the molecular mechanics calculations were taken from the literature and developed here. For the water molecule, the TIP3P water molecule from Jorgensen *et. al*. was used. Several CO_2 model from the literature were studied along with a newly developed model, the TJDM1 model. The intermolecular terms for the various CO_2 models are presented in Table 3.

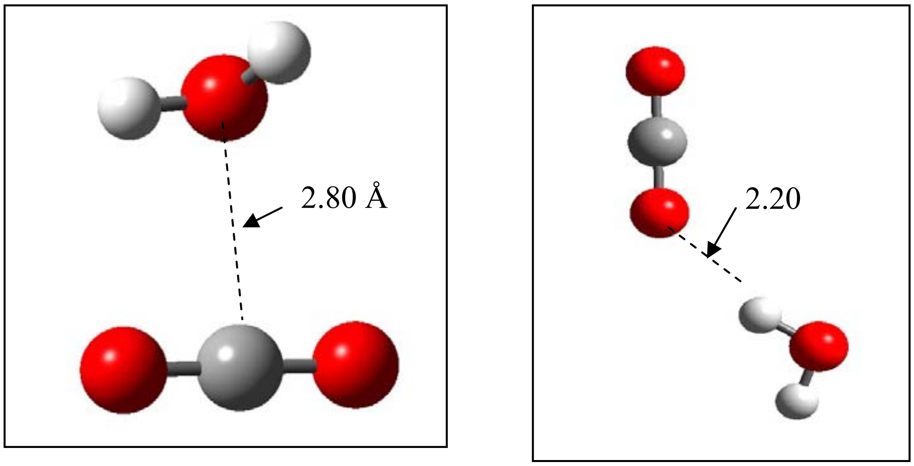
Carbon dioxide model		ε	σ	q
Harris	**C**	0.057627	2.785	0.6645
	O	0.164933	3.064	-0.33225
Murthy	**C**	0.057629	2.785	0.596
	O	0.165138	3.014	-0.298
Steele	**C**	0.057629	2.652	0.596
	O	0.165138	2.870	-0.298
Harris2	**C**	0.055898	2.757	0.6512
	O	0.159985	3.033	-0.3256
TJDM1	**C**	0.087630	2.152	0.720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

Table 3: The CO_2 molecular forcefield parameters from the literature and the developed TJDM1 model.

All the CO_2 models used in the calculations are 3-point models with the charges centered on the atom centers as well as the 12-6 Lennard-Jones terms.

Previous calculation of the CO2-H_2O complex were been done by Sadlej *et. al.* The energetic minima found, the T-structure and H-structure, were similar to the structures found in this study, with one exception. Sadlej *et. al.* had the T-structure to a constrained to C_2V symmetry based on assumptions from experimental microwave data. This study also 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 in this study, were done with no symmetry constraints on the complex.

Using *ab initio* quantum chemical calculations, two energy minima were located for the CO_2-H_2O complex. The two energetic minima for the CO_2-H_2O complex is in agreement with previous work done by Sadlej *et. al.*, where these minima were called the H-structure and the T-structure based on the geometry of the atoms in the complex. Shown in Figures 8 and 9 are the T-structure and the H-structure, respectively.



Figures 8 and 9: 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.

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 4 and 5 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 due to assumptions made in interpreting the experimental microwave work done by Peterson and Klemperer.

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

Table 4: Interaction energies of the T-structure, energies given in kcal/mol.

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

Table 5: Geometry of T-Structure: The distance between the C(CO_2) and the O(H_2O), distances in Å **.**

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 CO_2 molecule. Shown in Tables 6 and 7 are the interaction energies and geometric distances between the CO_2 and the water molecule.

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

Table 6: Interaction energies of the H-structure; energies given in kcal/mol.

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

Table 7: Geometry of H-Structure: The distance between the O(CO_2) and the H(H_2O), distances in Å.

As seen in the T-structure *ab initio* data, the H-structure *ab initio* data also converges 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.

For the molecular forcefield models from the literature, the Steele model matches the *ab initio* data the best 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 CO_2 models from the *ab initio* data led to the development of the TJDM1 force field model.

The TJDM1 forcefield 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 forcefield model's interaction energies and interaction distances can be seen in Tables 8 and 9.

	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 8: The interaction energies of the four literature CO_2 models and the developed TJDM1 model with water 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	2.934	-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

Table 9: The geometric distances of the four literature CO_2 models and the developed TJDM1 model with water and comparison to the ab initio calculations. Distances given in Å.

Conclusions

The combination of traditional coal structural information (elemental analysis, and various NMR techniques) with modern structural elucidation techniques (oxidation and decarboxylation and analysis by GCMS) in conjunction with the *combination* of laser desorption mass spectroscopy with image analysis of HRTEM lattice fringes provided the necessary information regarding the extent of structural diversity within the coal. A large structural model was generated to represent this structural diversity. This model is superior in both the degree of diversity, and size to previous structural models. Inclusion of the physical parameters permitted the constitution of the coal to be represented. It is expected that this model will prove useful in simulation and understanding the interaction that occur between small molecules within the coal structure. These interactions are of interest if we wish to pursue carbon dioxide sequestration within coal. The structural model is also likely to prove beneficial for other areas of coal science such as solvent swelling, liquefaction, combustion and other physical properities.

Two minima were found for the interaction of a CO_2 molecule with a water molecule called the T-structure and the H-structure by Sadlej *et. al.* From the *ab initio* calculations, the T-structure was found to have an interaction energy of –3.0 kcal/mol with a distance between the molecules of 2.80 Å and was found to be the global minimum. The H-structure, a local minimum, was found to have an interaction energy of –2.1 kcal/mol and a distance of 2.20 Å between the molecules. The Steele model was found to be the best 3-point literature CO_2 model, however the new TJDM1 model matches the *ab initio* data better than the Steele model. For the TJDM1 forcefield model the interaction energies for the T-structure and H-structure were found to be –2.65 kcal/mol and –2.08 kcal/mol respectively and the distance were found to be 2.81 Å and 2.01 Å for the T-structure and H-structure respectively.

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