

Title: Molecular Basis for Carbon Dioxide Sequestration in Coal

Authors: Thomas J. Dick, Orlando Acevedo, Pranav Dalal, Jeffry D. Madura, Jeffrey D. Evanseck, and Jonathan P. Mathews#

Students: Thomas J. Dick, Orlando Acevedo, and Pranav Dalal

Institutions and Contact Information: Center for Computational Sciences, and Department of Chemistry and Biochemistry, Duquesne University, 600 Forbes Avenue, Pittsburgh, PA 15226, Voice: (412) 396-6337, FAX: (412) 396-5683, E-mail: evanseck@duq.edu; # The Energy Institute & Department of Energy & Go-Environmental Engineering, 151 Hosler Building, The Pennsylvania State University, University Park, PA 16802, Voice: (814) 863 6213, FAX: (814) 865 3248, E-mail: jmathews@psu.edu

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Abstract

Sequestration of CO₂ within coal seams that are either too deep, thin, or uneconomic has been suggested to mitigate climate change. Additionally, if there is methane present within the coal it can be replaced with the carbon dioxide, apparently at a 2:1 ratio(1) thus releasing CH₄ to help offset the sequestration cost. We have utilized computational molecular modeling to investigate the forces involved between bituminous coal structure (or idealized pores) and the molecular species CH₄ and CO₂. The molecular computations and simulations 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.

Experimental

Density functional theory, second-order Moller-Plesset theory, and classical molecular dynamics were utilized to investigate three chemical models of coal. In order of increasing model sophistication, small molecules (CH₄, CO₂, and N₂) were complexed with (a) anthracene, (b) 10, 10 nanotube, and (c) our novel bituminous coal structure. Our goal is to uncover the fundamental physical interactions between small molecules and simple aromatic structures, and use the computed information to enhance the sequestration of CO₂ in more complex coal structures.

Anthracene Model. All density functional theory calculations were carried out with the Gaussian 98 program, using a 16-node SP IBM RS/6000 super computer. The Becke three parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) with 6-31G(d) basis set has been employed. All energy optimizations and frequency analyses were carried out using the B3LYP/6-31G(d) level of theory, which has been shown to produce realistic structures and energies for weak nonbonding interactions between aromatics and small organic molecules. Vibrational frequency calculations at the same level of theory were used to confirm all stationary points as either minima or transition structures, and provide thermodynamic and zero-point energy corrections. The energy profile for CH₄, CO₂, and N₂ traversing across anthracene are investigated to determine the structure and energy of interaction as the small molecules passes over the aromatic structure.

Nanotube Model. Insight II was used to plot the energy profile of the gases within idealized pores, here treated as buckeytubes and buckyballs. In our first case, a 10,10 nanotube was constructed, as shown in Figure 2. Dummy atoms set along the centerline of the “pore” was used to define a pathway for the molecules. A strong harmonic “pushed” the guest molecule along the defined pathway and the structure allowed to minimize. To save computational expense the “pore” was rigid and did not relax or strain with the passage of the molecule. Step size along the centerline was 0.2 Å. The dummy atoms were placed several rings within the tube to reduce “end

effects". The energy of interaction between the host and guest molecule were followed. Similar techniques have been used in Zeolite simulations (2) and are well discussed there.

Bituminous Coal Model. Recent experimental and computational advances have the potential to produce a first-time reasonable constitutional model (chemical and physical structure) and enable its use. 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. Our preliminary three-dimensional model of bituminous coal structure will be described.

Results & Discussion

The relative size and shape of the three gasses: nitrogen, methane, and carbon dioxide have been considered. The sizes appear similar, although methane is bulkier. Size alone is unlikely to contribute to the significant differences between these molecules within the pores of coal. The quadrupole and octapole from the higher-level quantum mechanical computations are also used to better understand the sorption of the small molecules to aromatic surfaces. A complete discussion on the electronic properties will be presented at the conference.

To test the molecular interactions, a low level of molecular modeling was first utilized. Nitrogen as expected had the "easiest" transition through the "pore". The shape of the molecule permitted the long axis to lie perpendicular to the "pore" axis and low energetic strain indicated only slight conformational changes were required. Methane being a bulkier molecule has to undergo conformational changes to "squeeze" through the pore. Greater peaks and valleys in the plot indicate conformational changes to accommodate the passage. These conformational changes can be treated as an apparent activation energy. This apparent activation energy indicates the molecule will pass through the pore with little retention. Carbon dioxide however has a very different profile and a much higher apparent activation energy to the passage within the pore. Several local energy minima and global energy minima are present. These are sites where the interaction energy between the host and guest molecule would require significant conformational rearrangement to proceed through the pore, possibly becoming "trapped" within the pore.

The CHARMM force-field will be used in our simulation work (many will be evaluated). Constant pressure molecular dynamics will be carried out using periodic boundary conditions. Physical aspects such as porosity will be compared to experimental values to ensure a reasonable representation of our proposed large-scale coal model simulation (> 50,000 atoms). The time-scale used will be consistent with the diffusion times of the slowest diffusion rates. The results will be presented at the symposium.

Conclusions

We aim to use accurately computed atomic-level structural and dynamical information to aid in the creation of technology for optimal geological sequestration of CO₂. Our strategy is to generate a realistic and testable three-dimensional state-of-the-art molecular model of Pocahontas No. 3 coal by incorporating new structural diversity information based upon HRTEM and laser desorption data (rather than average values), while maintaining traditional analytical information (i.e., H/C aromaticity) and physical parameters (i.e., density and pore volume). Large-scale molecular dynamics simulations (> 50,000 atoms) will be carried out on this model to follow its structural changes during addition of CO₂ and removal of CH₄. The simulation work will also be used to determine the differences in sorption characteristics and diffusion rates between CO₂, H₂O, N₂ and CH₄. This significance of the proposal is that new opportunities in the optimization and gaseous management necessary for low-cost forms of CO₂ sequestration will result from this novel procedure.

References

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