

Fundamentals of Molecular Modeling of Adsorption

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2 June 2009



Outline

- Statistical mechanics of adsorption
- Examples from our work:
 - Propane on graphite
 - Acetone on graphite
 - Adsorption in MOFs
 - Adsorption on single-walled carbon nanotubes
 - Hydrogen isotopes at extremely low pressures
 - Alkanes on SWNTs, site energetics, diffusion effects
 - H₂O adsorption in SWNTs
 - CO₂ adsorption on SWNT external surfaces
 - Review of recent literature—adsorption on heterogeneous surfaces



Statistical Mechanics of Adsorption: Grand Canonical Monte Carlo

- Adsorption equilibrium is defined by

$$T^{\text{bulk}} = T^{\text{ads}}; \quad \mu_i^{\text{bulk}} = \mu_i^{\text{ads}} \quad (\text{or } f_i^{\text{bulk}} = f_i^{\text{ads}})$$

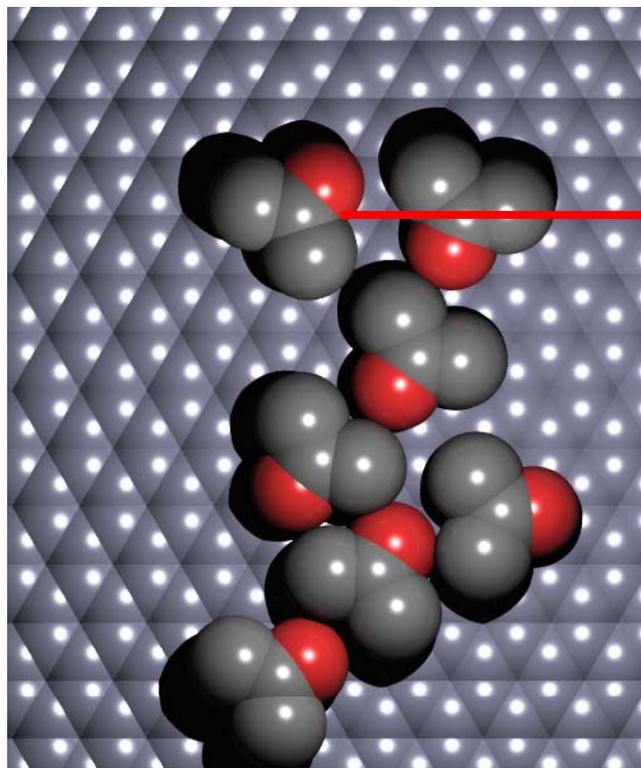
- Computer simulations can mimic this through grand canonical Monte Carlo
- The grand canonical partition function:

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} Q(N, V, T) \exp(N\mu / k_B T) = \sum_{N=0}^{\infty} Q(N, V, T) f^N$$

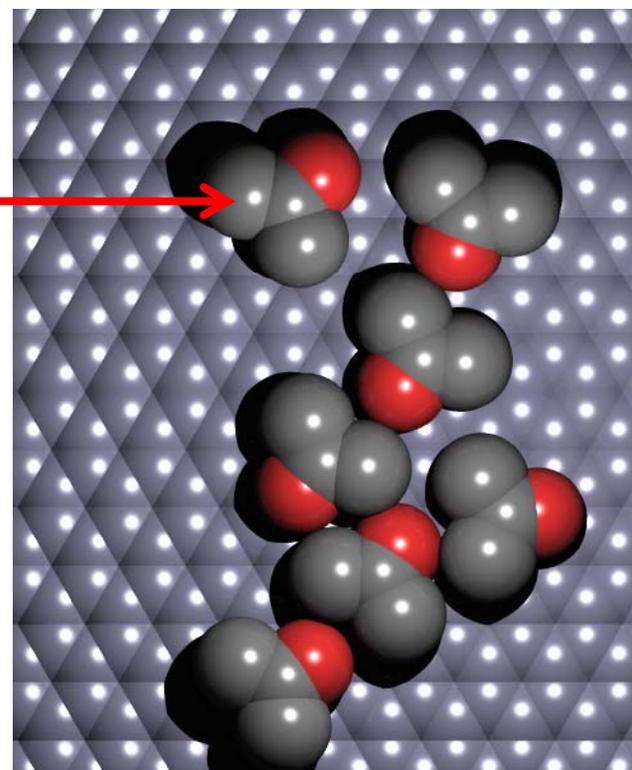
- Monte Carlo moves are attempted for **moving**, **creating** and **deleting** molecules in the system



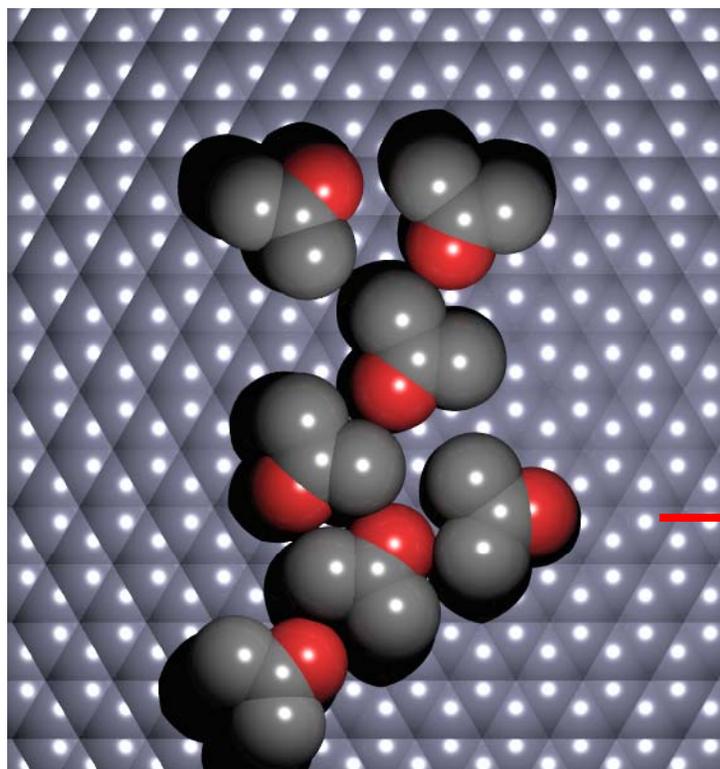
Grand Canonical Monte Carlo Moves



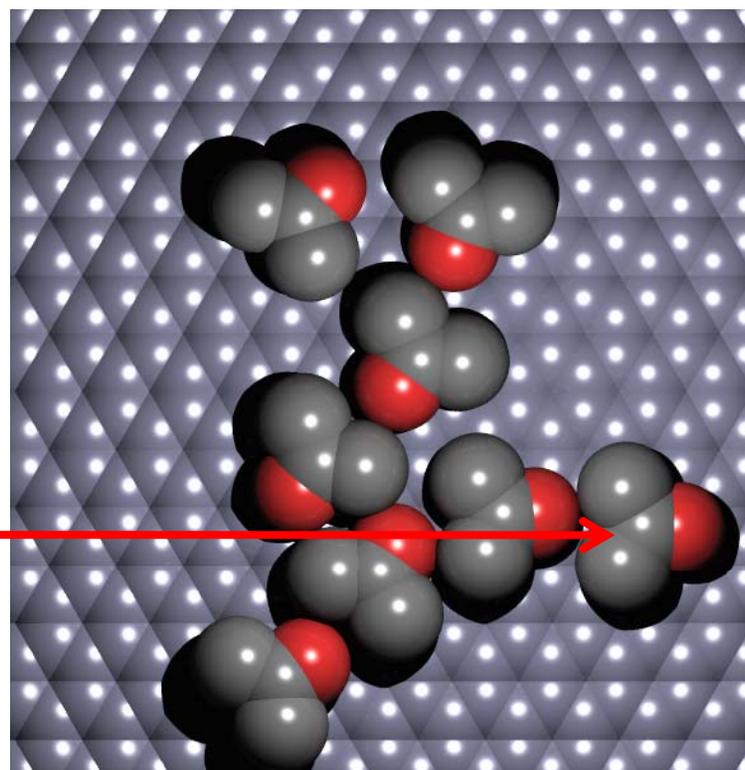
Attempted Move



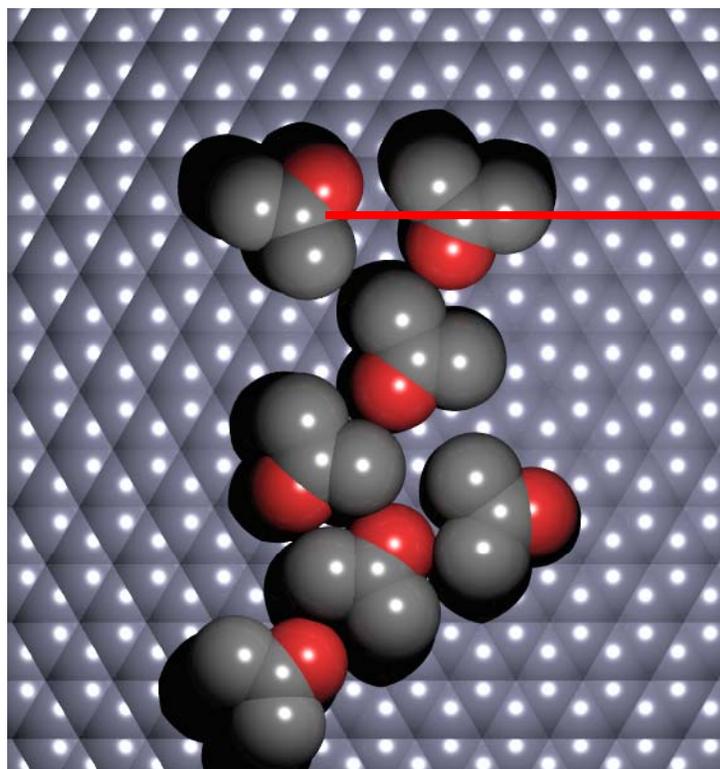
Grand Canonical Monte Carlo Moves



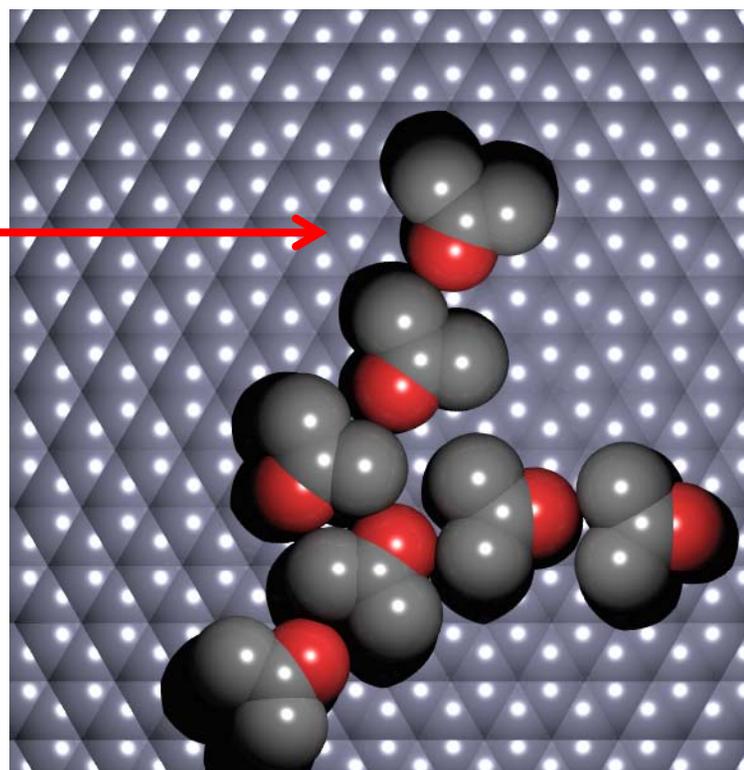
Attempted
Creation



Grand Canonical Monte Carlo Moves



Attempted
Deletion

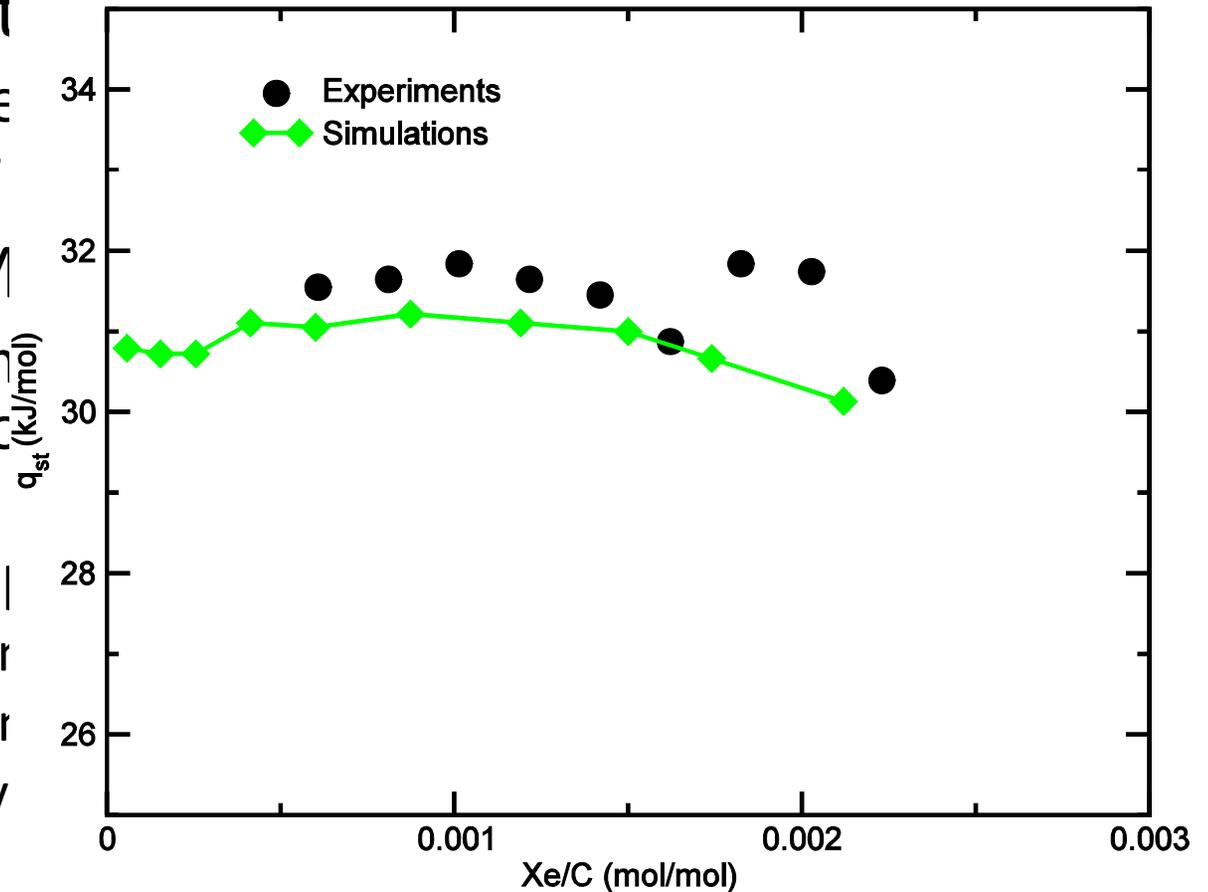


Statistical Mechanics of Adsorption: Grand Canonical Monte Carlo

- Simulation typical pressure at constant
 - Amount adsorbed
 - Isothermic heat of adsorption
- Accuracy of GCMC
 - Length of the simulation runs to reach good statistics
 - Accuracy of the potential energy
 - Fluid-fluid potential
 - Solid-fluid potential
 - Pairwise additivity

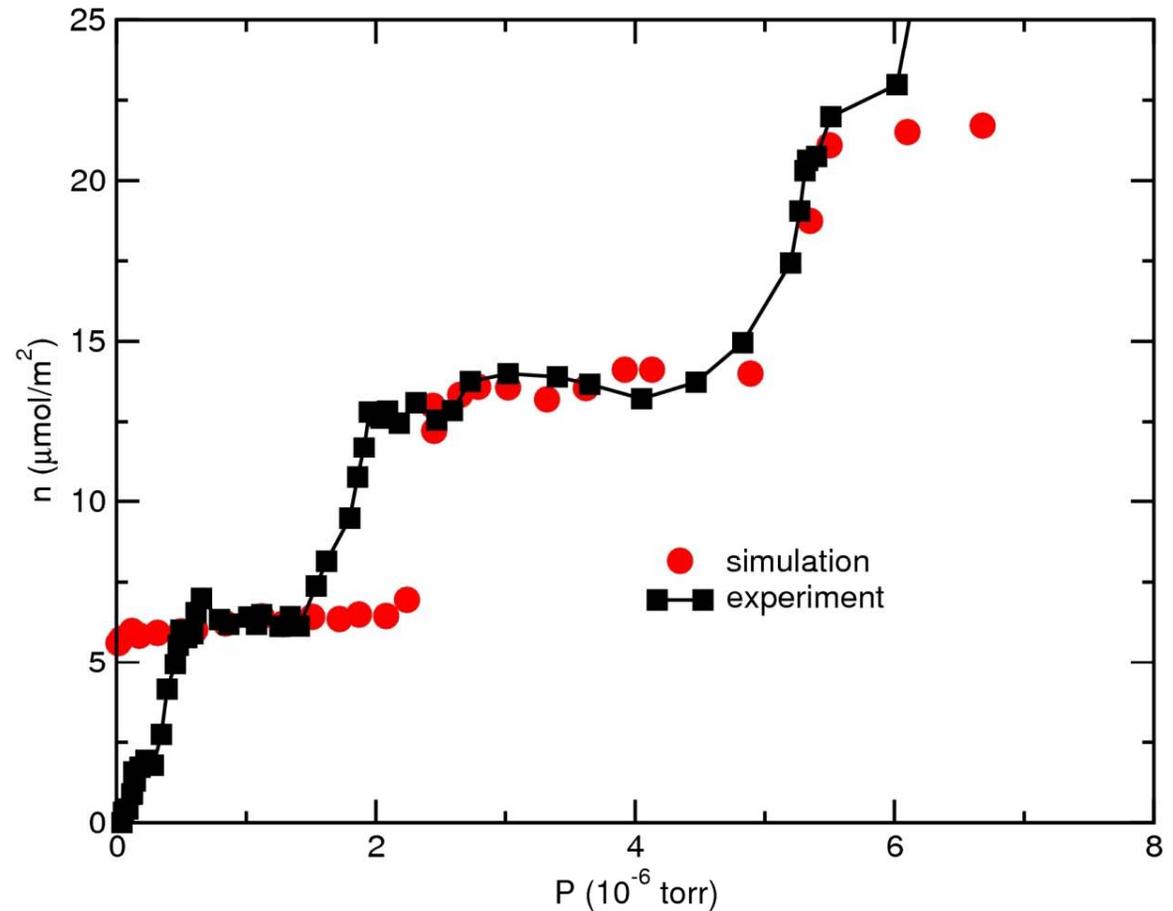
Isosteric Heat of Adsorption

Xe on carbon nanotubes



Adsorption of Propane on Graphite at $T = 91 \text{ K}$

- Computer simulations can closely match experimental data if fluid-fluid and solid-fluid potentials are accurate
- Calculated layering transitions in good agreement with experiments
- The surface is very homogeneous



Zhao et al. *J. Chem. Phys.*, **117**, 7719 (2002)

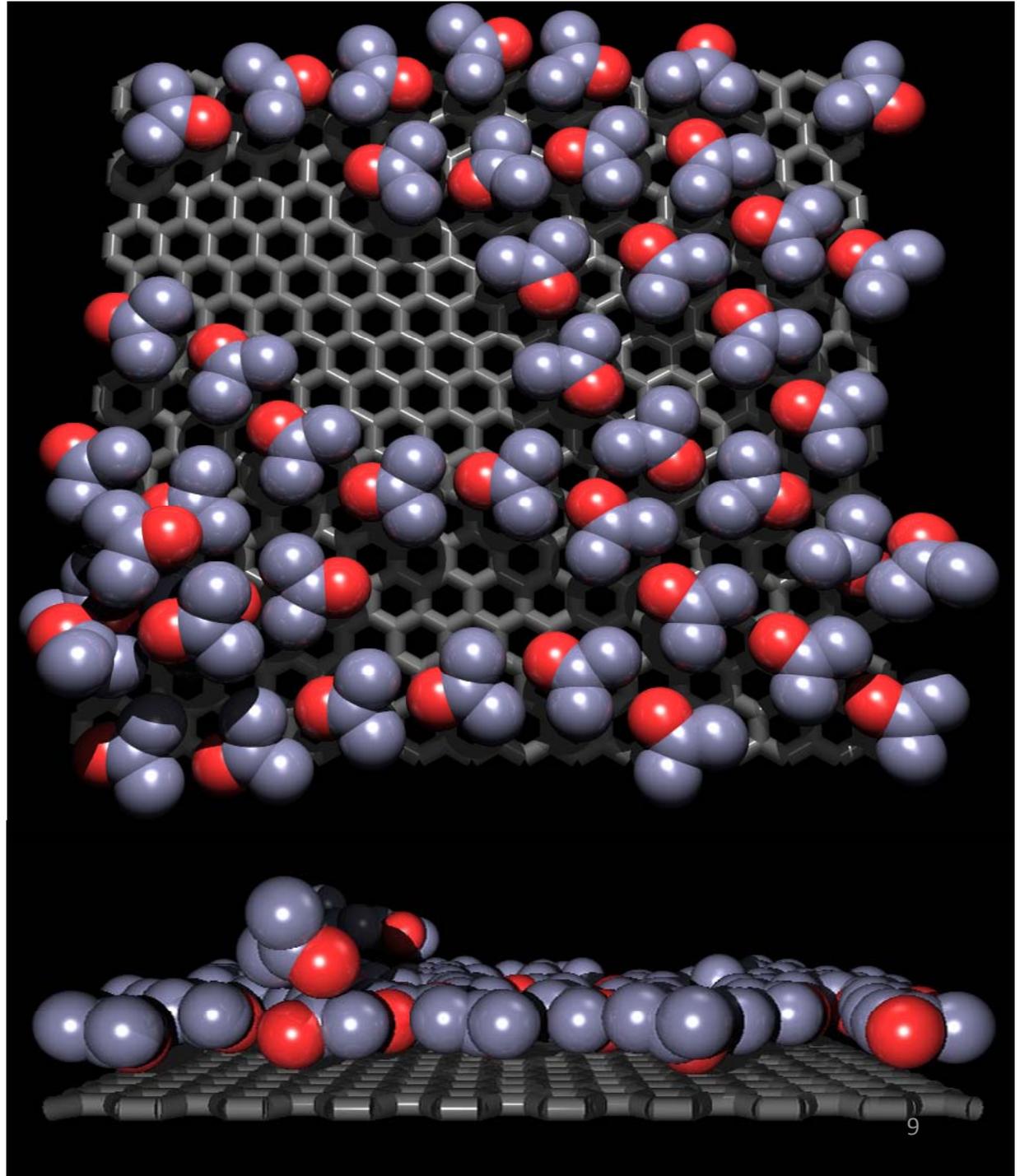


Acetone Adsorption on HOPG

Top View

- Orientational ordering is dominated by dipole-dipole interactions
- Second layer formation observed before first layer fills
- Simulations in qualitative agreement with experiments—Volmer-Weber growth

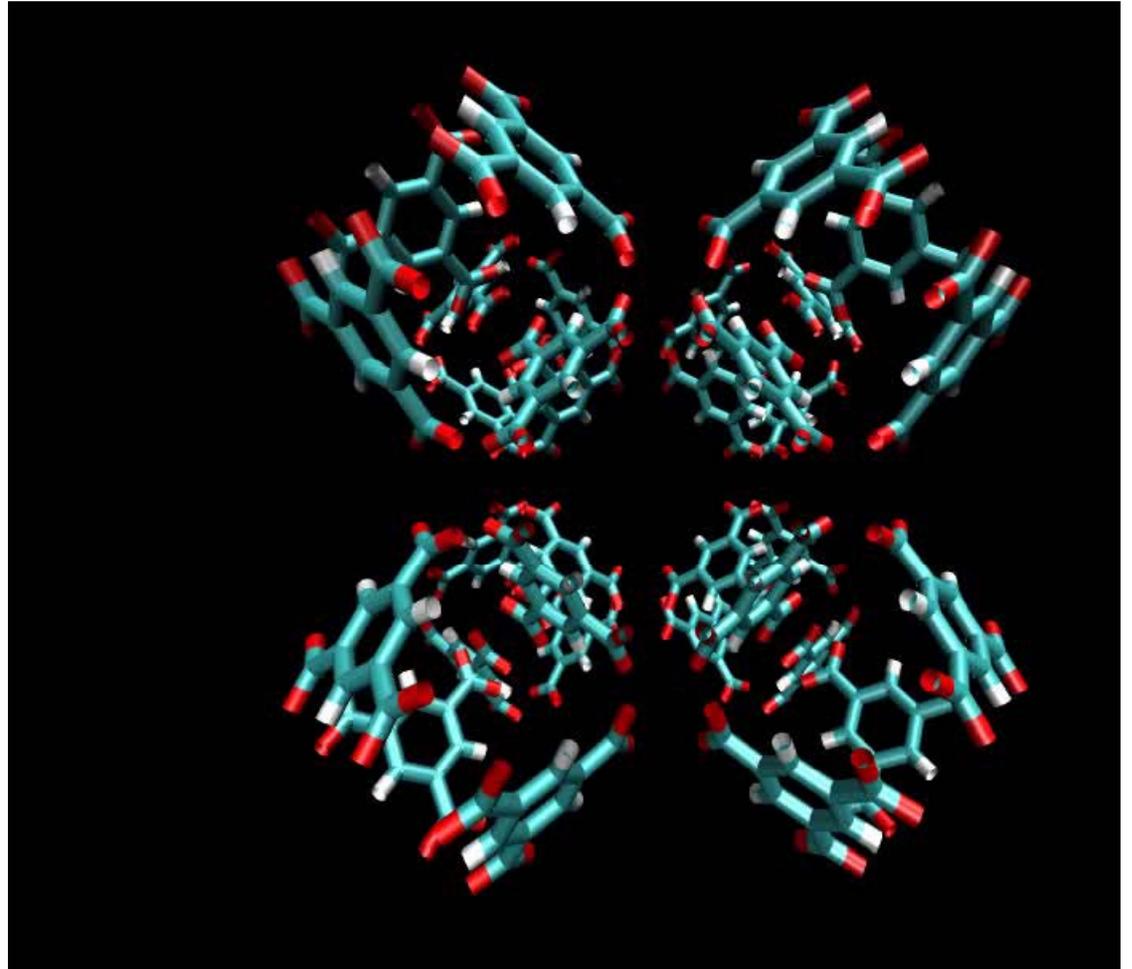
Side View



Kwon et al., *Langmuir* **18**, 2595
(2002)

Metal Organic Frameworks

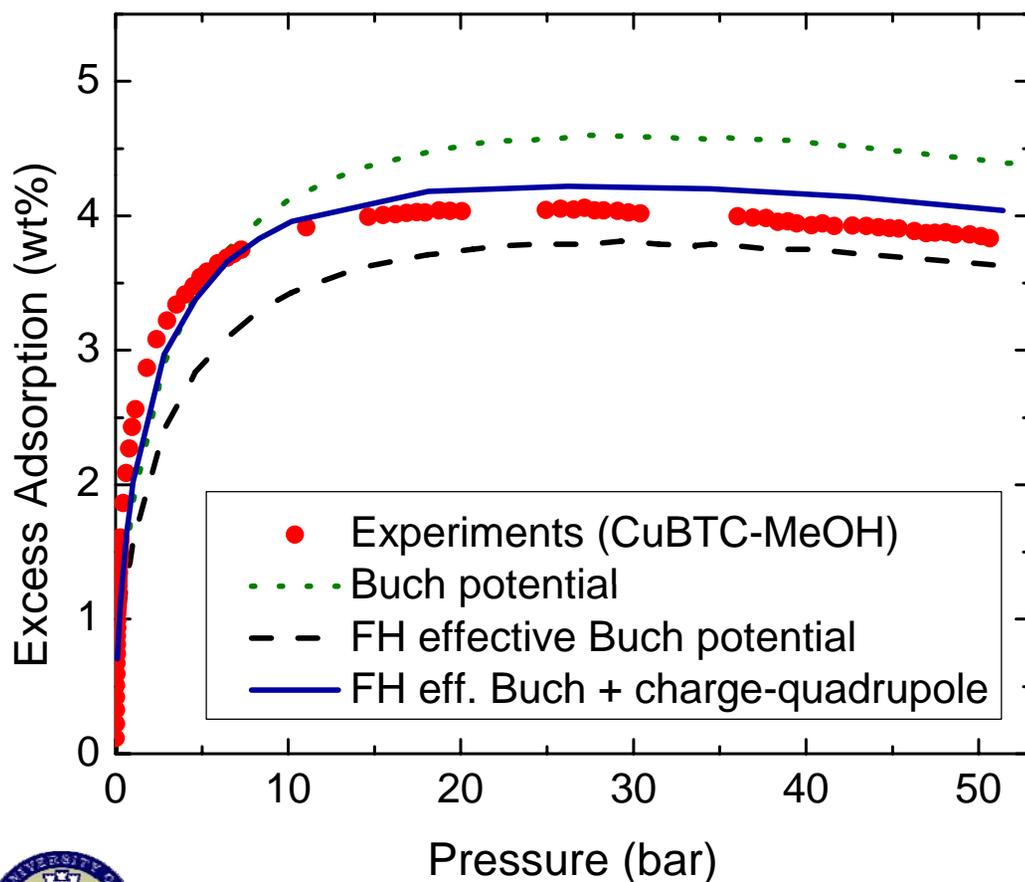
- Nanoporous materials that have been studied with experiments and simulations
- Metal-oxide vertices held together with organic linkers
- Large effective surface area and pore volume
- Can be tailored by changing metals, ligands, & organic linkers
- Have different sized pores and different binding sites due to chemical heterogeneity



Structure of CuBTC



Getting the Right Physics: Importance of Charge-Quadrupole and Quantum Effects on the H₂ Adsorption Isotherm in CuBTC at 77 K



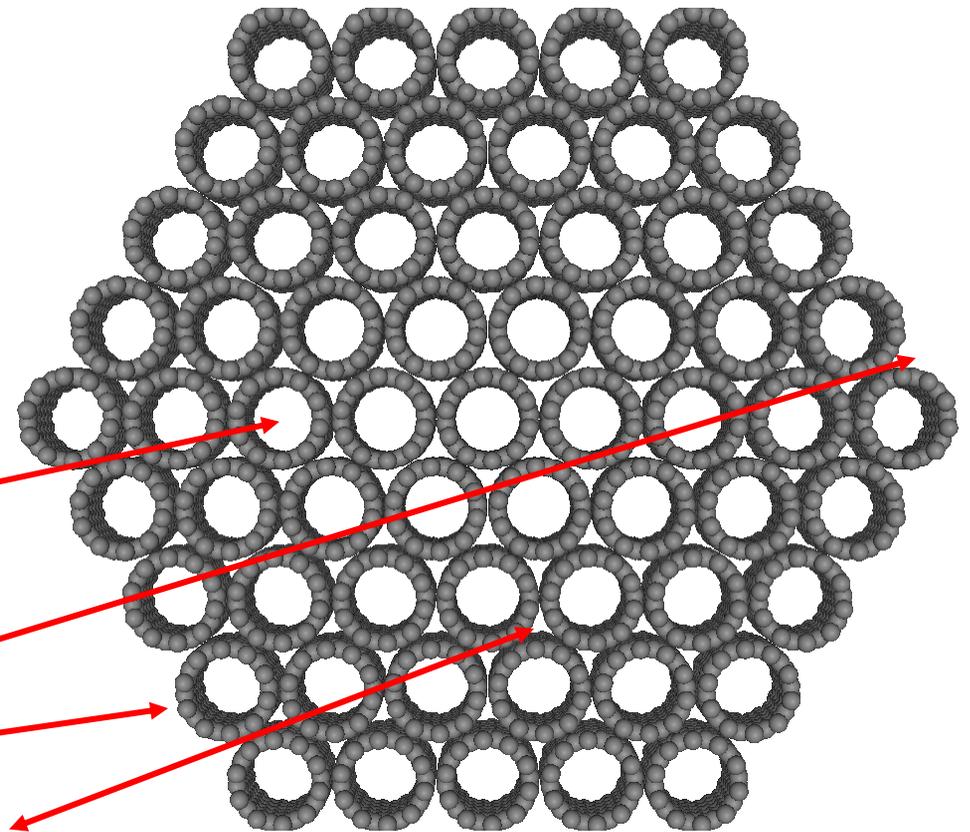
Liu et al. *Mol. Sim.*, **35**, 60 (2009)

- The classical potential w/o charge-quadrupole interactions overestimates the adsorption at high pressures
- Adding quantum effects (FH=Feynman-Hibbs) decreases the amount adsorbed too much
- Adding charge-quadrupole interactions with quantum effects gives good agreement with experiments



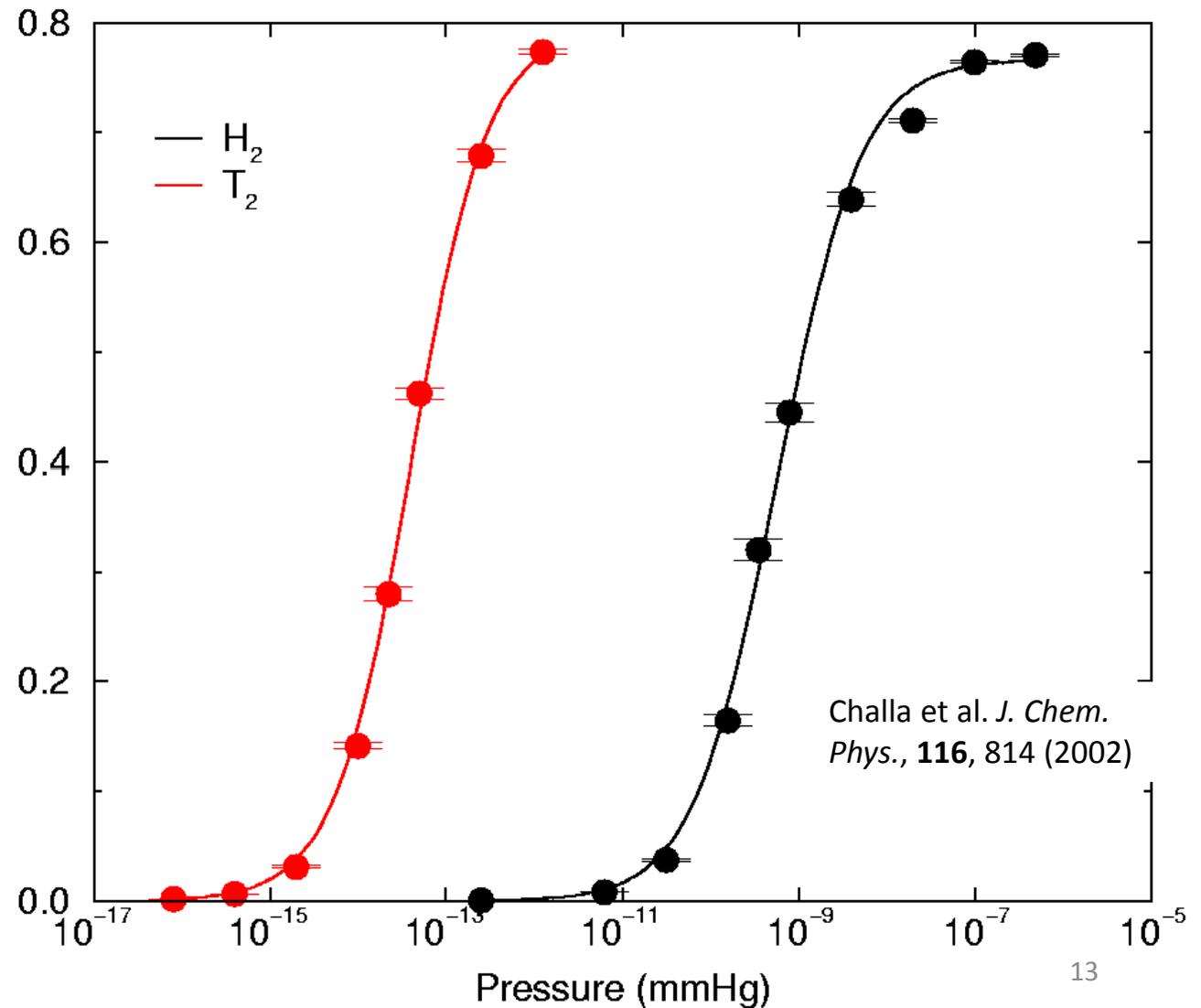
Adsorption On Carbon Nanotubes

- Single walled carbon nanotubes (SWNT) form bundles
- Gases can adsorb on many different sites on SWNT bundles
 - Internal
 - Exterior groove sites
 - Exterior surface
 - Interstitial (**very narrow**)



Pure Fluid Isotherms in the (10,10) Interstice at 20 K

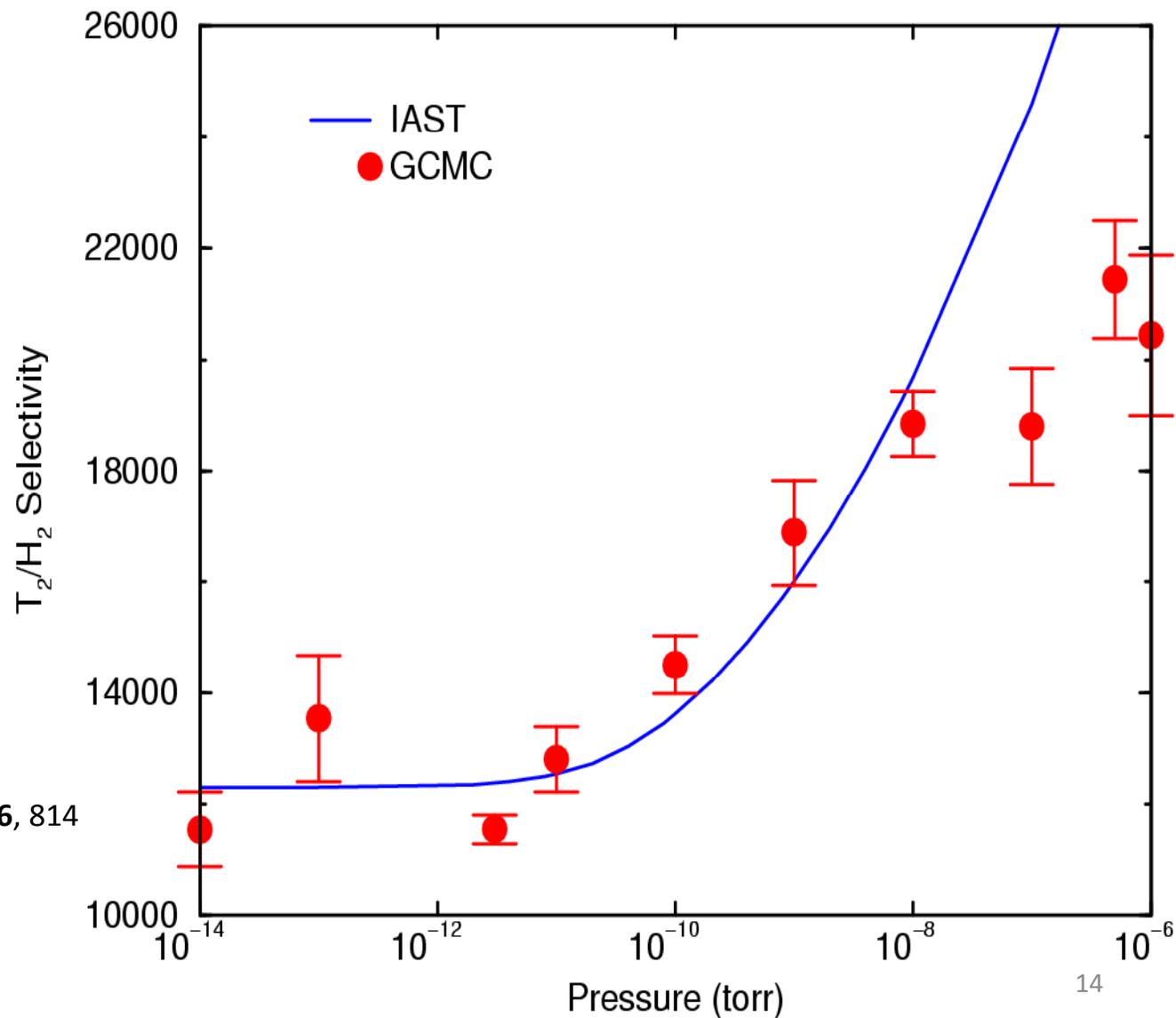
- Quantum diffraction effects (particle in a box) dictate the difference between T_2 and H_2 adsorption isotherms
- Quantum effects ρ are included through the Feynman path integral formalism
- Adsorption down to very low pressures can be easily modeled in the simulations



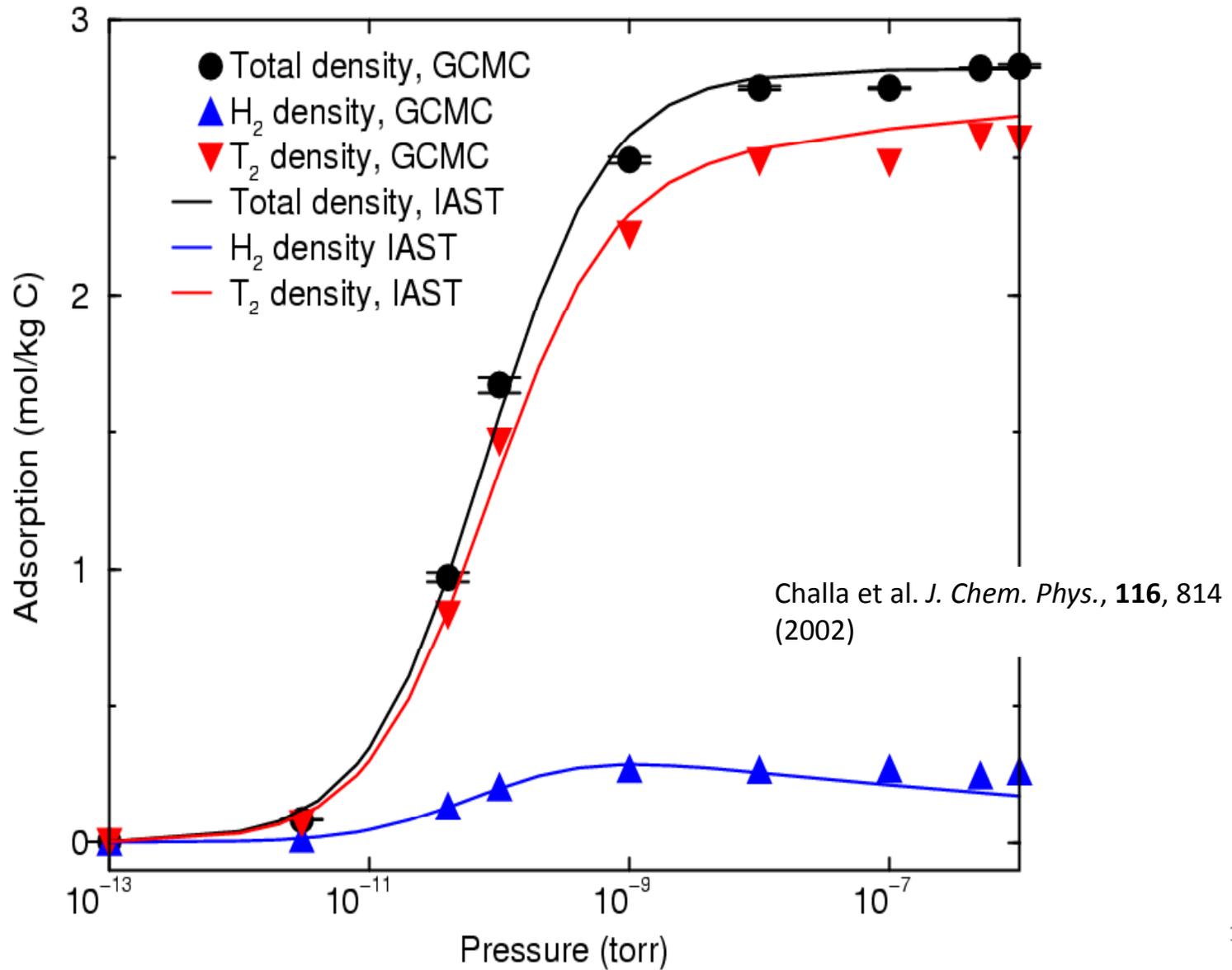
T_2/H_2 Selectivity in the (10,10) Interstice at 20 K

- The selectivity is due to quantum sieving—essentially differences in the quantum kinetic energy of the two different isotopes
- Confinement localizes the particles and hence the uncertainty in the momentum must increase, making adsorption of the light isotope energetically unfavorable

Challa et al. *J. Chem. Phys.*, **116**, 814 (2002)



T₂/H₂ densities in the (10,10) Interstice at 20 K



Modified GCMC Simulations vs. TPD Experiments

- Experiments
 - Starting from dosing a system with a known amount of alkanes.
 - The system is heated and material desorbs into vacuum.
 - Molecules that desorb are pumped away so fast that no re-adsorption can take place.
- Simulations
 - Starting from an alkane-saturated nanotube bundle.
 - Grand canonical-type moves were performed to delete alkane molecules from the system.
 - No attempt to create adsorbed molecules was made.

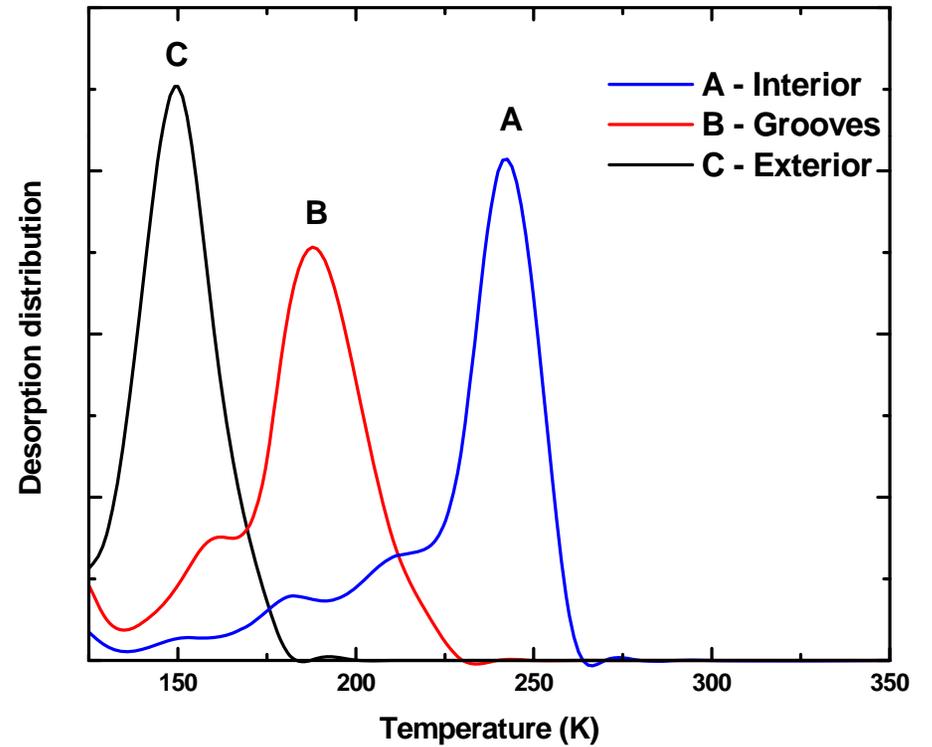
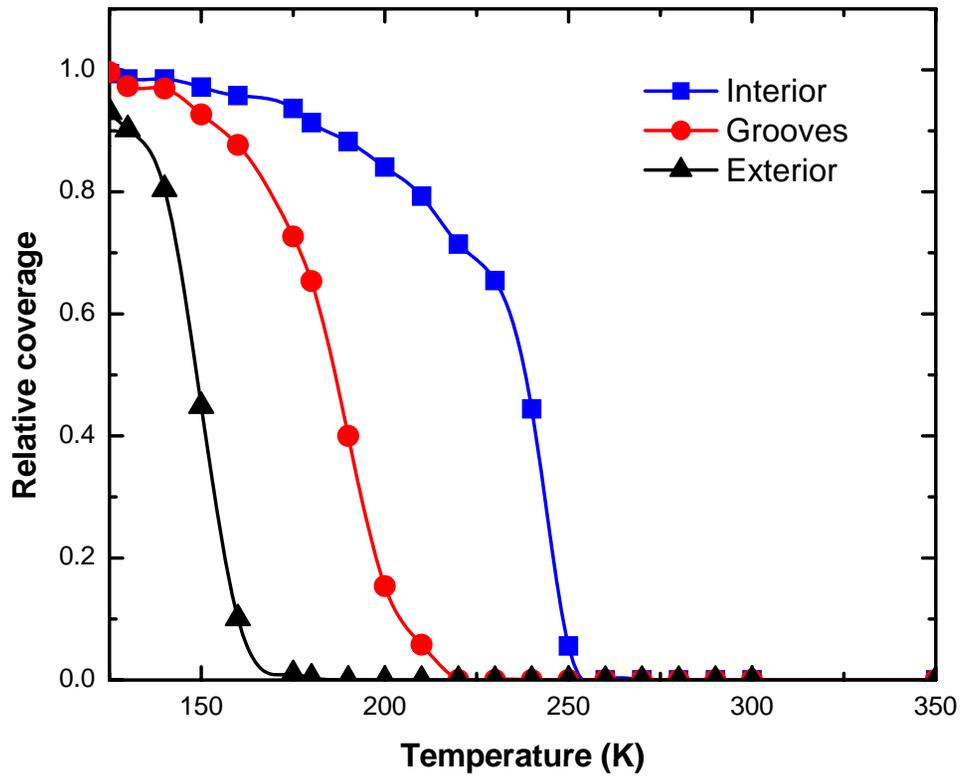


Modified GCMC Simulations vs. TPD Experiments (cont'd.)

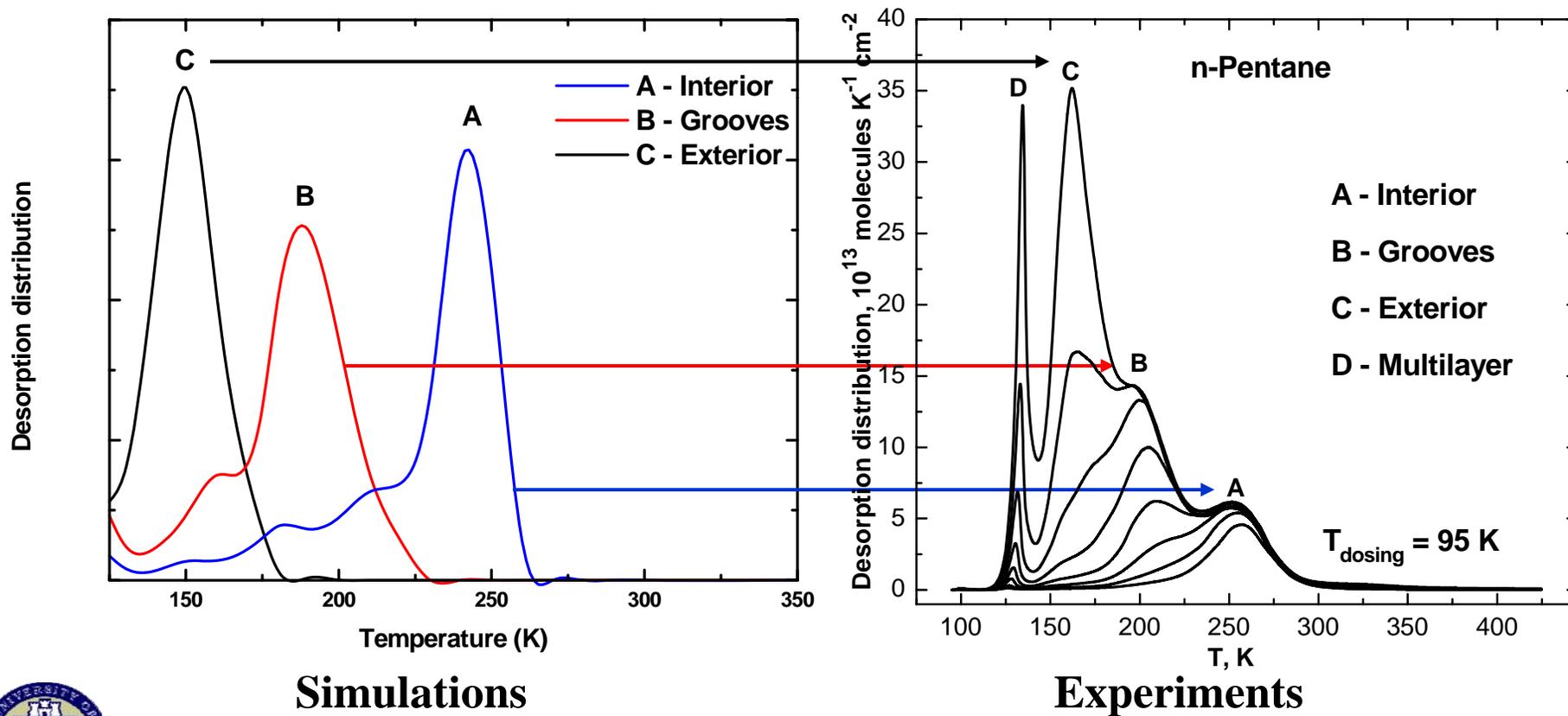
- Simulations were carried out at various temperatures, from 125 K to 350 K. Coverage data were collected after 5000 MC moves for each temperature.
- The relationship between the number of alkane molecules deleted from the system for a fixed number of MC steps and temperature is related to the desorption rates deduced from TPD experiments.
- However, the simulations do not have a real time scale. The MC data only give “pseudo-TPD” data.



Pseudo-TPD Spectra for n-Pentane



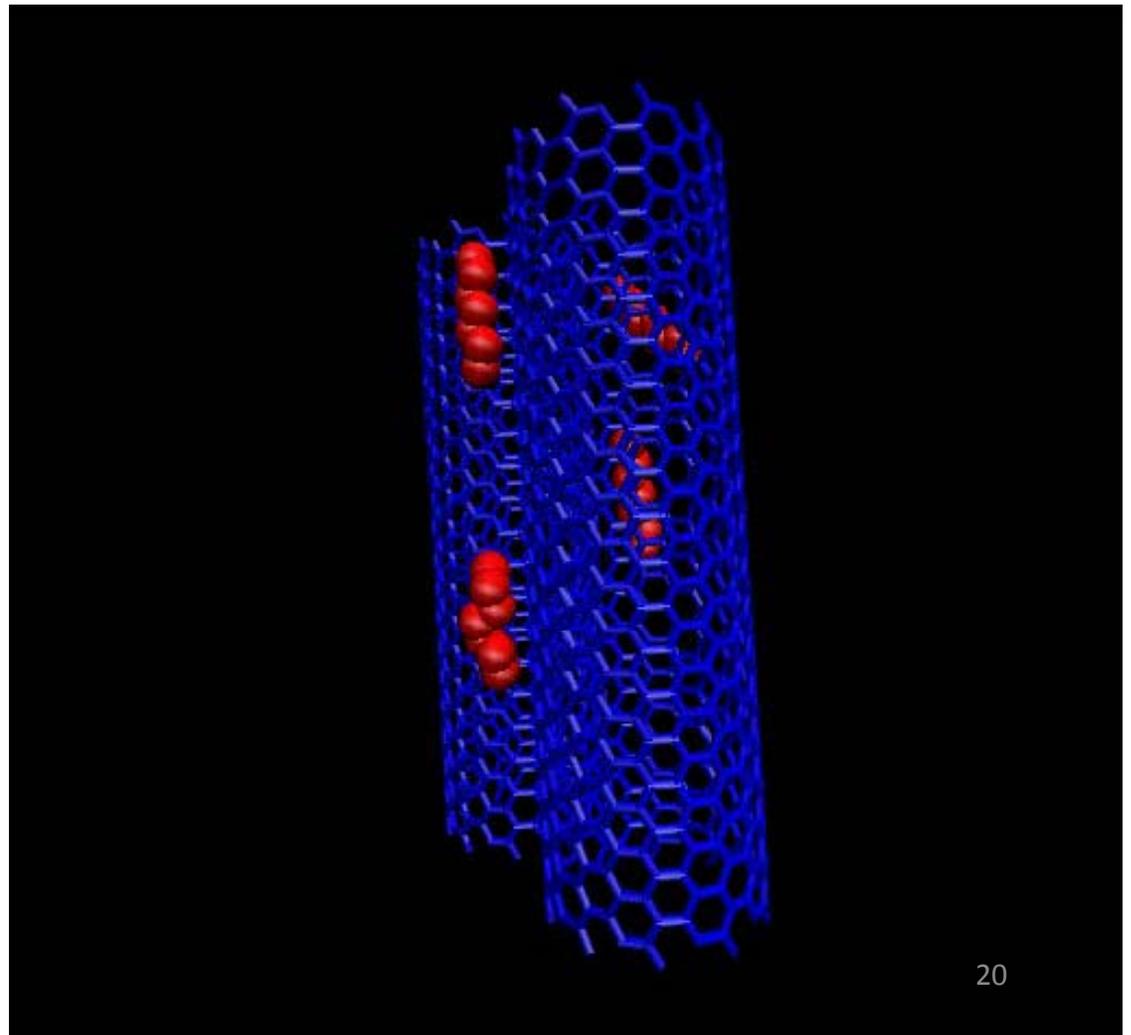
Pseudo-TPD Spectra for n-Pentane (cont'd.)



N-Heptane on a (10,10) SWNT, Low Coverage, 275 K

10 nanoseconds simulation time

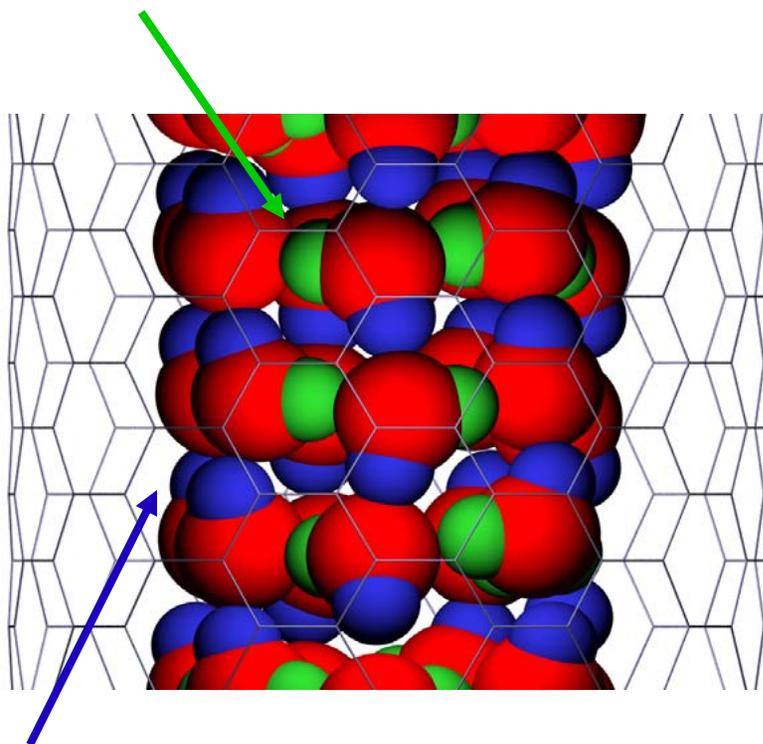
- Molecular dynamics simulations probe the kinetics of entry from the external to the internal pores
- However, simulations are limited to short times, 10 ns in this case
- Monte Carlo simulations on the same system shows all n-heptane adsorbed inside the nanotube at this coverage



Kondratyuk et al. *J. Phys. Chem. C.*,
111, 4578 (2007)

Simulations: Structure for H₂O Confined in a (10,10) Nanotube at 123 K

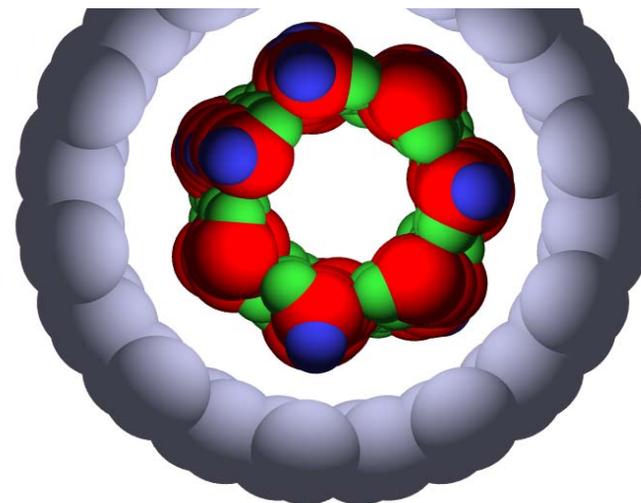
Intra-ring H-bonds—Bulk-like



Inter-ring H-bonds—Weak, gives blue-shifted IR stretch in agreement with experiments

Byl, et al., *J. Am. Chem. Soc.*, 2006, 128, 12090–12097

- These low temperature structures are difficult to find from Monte Carlo or molecular dynamics at 123 K



- We used parallel tempering to overcome free energy barriers

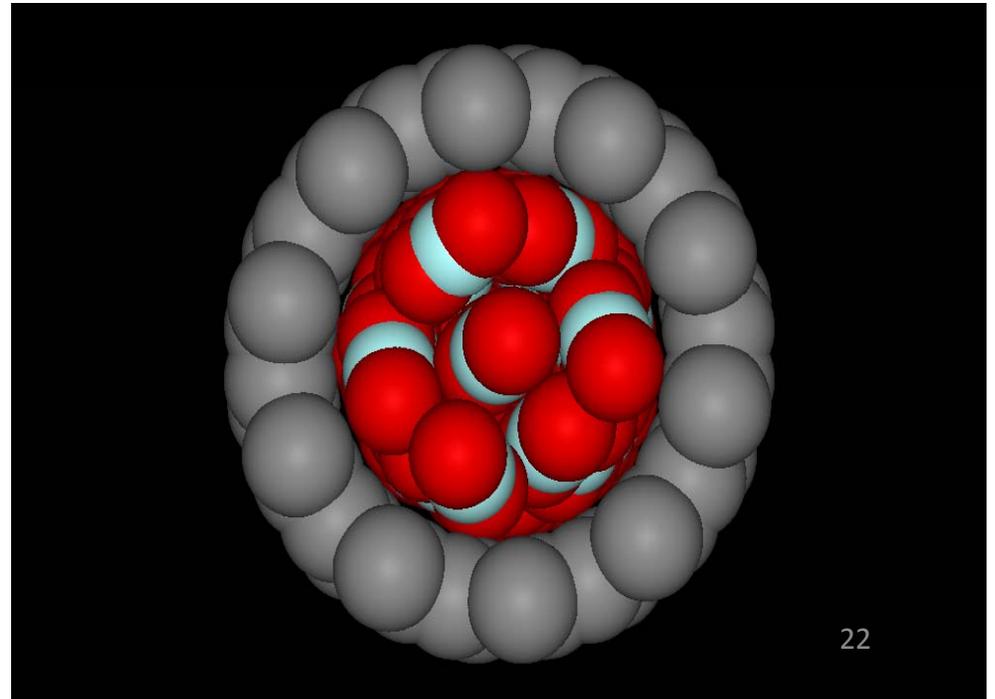
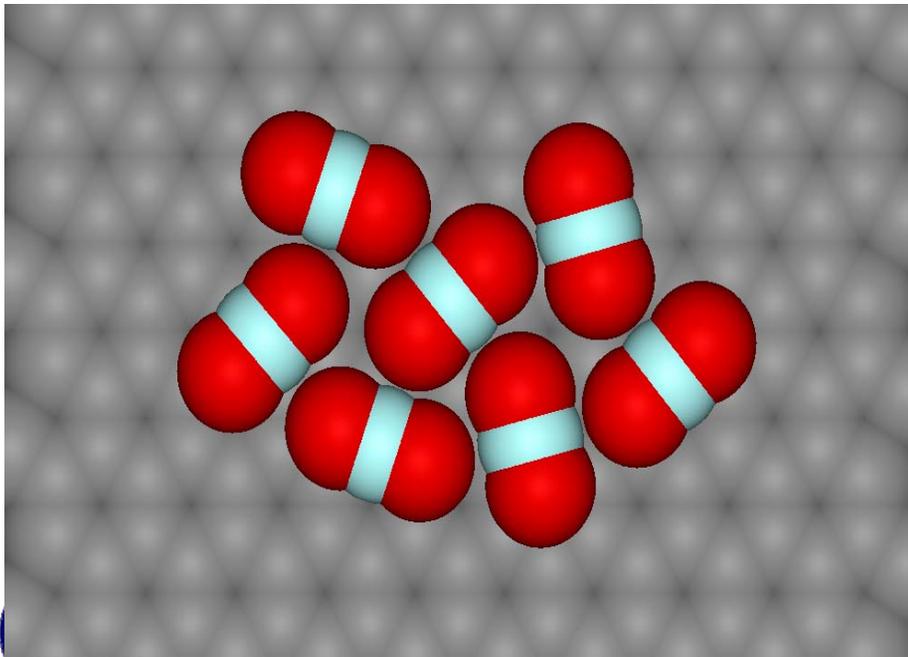


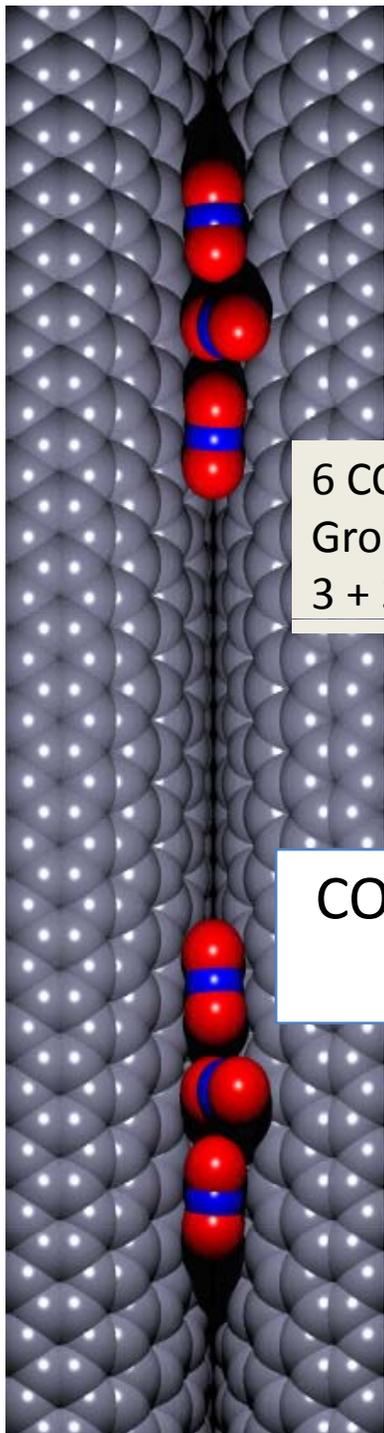
Adsorption of CO₂ on Nanotube Bundles—Effects of Dimensionality

Groove site adsorption of CO₂ is fundamentally different...

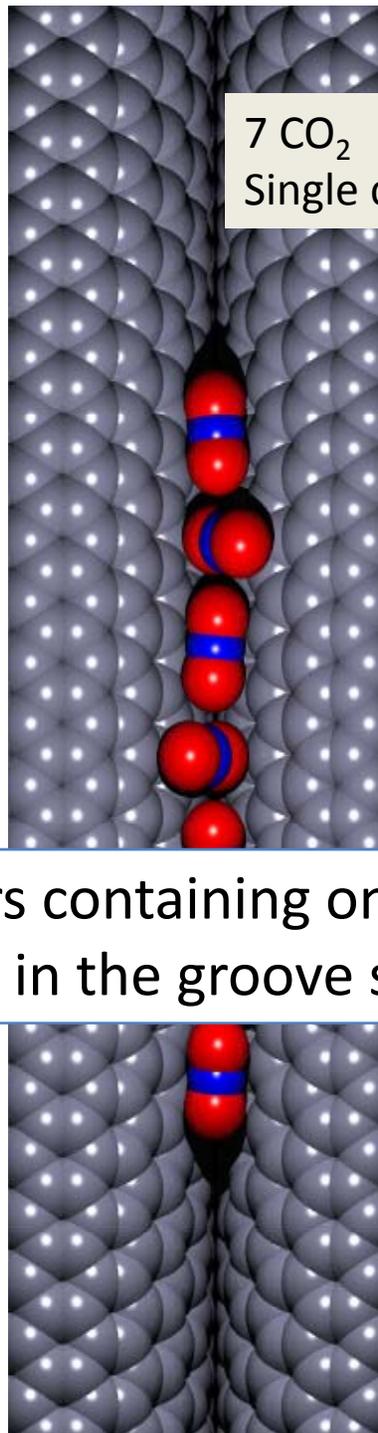
CO₂ in 2-d (on graphite)
Forms clusters of any size

CO₂ inside SWNTs
Forms clusters of any size

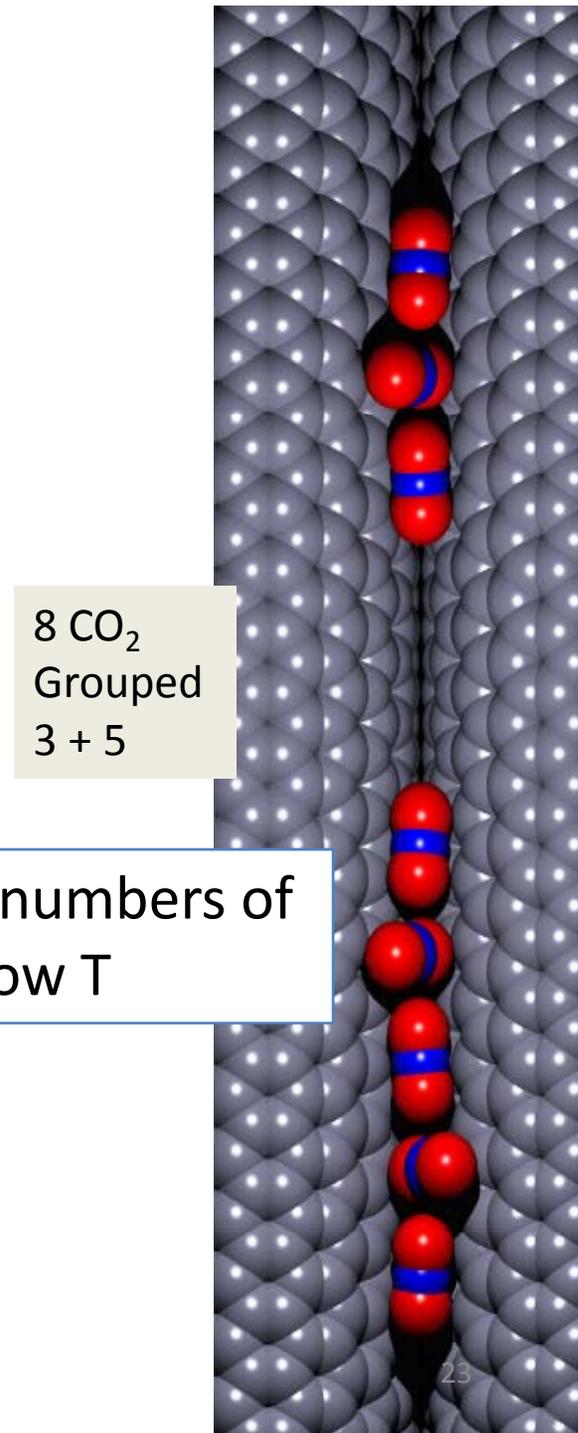




6 CO₂
Grouped
3 + 3



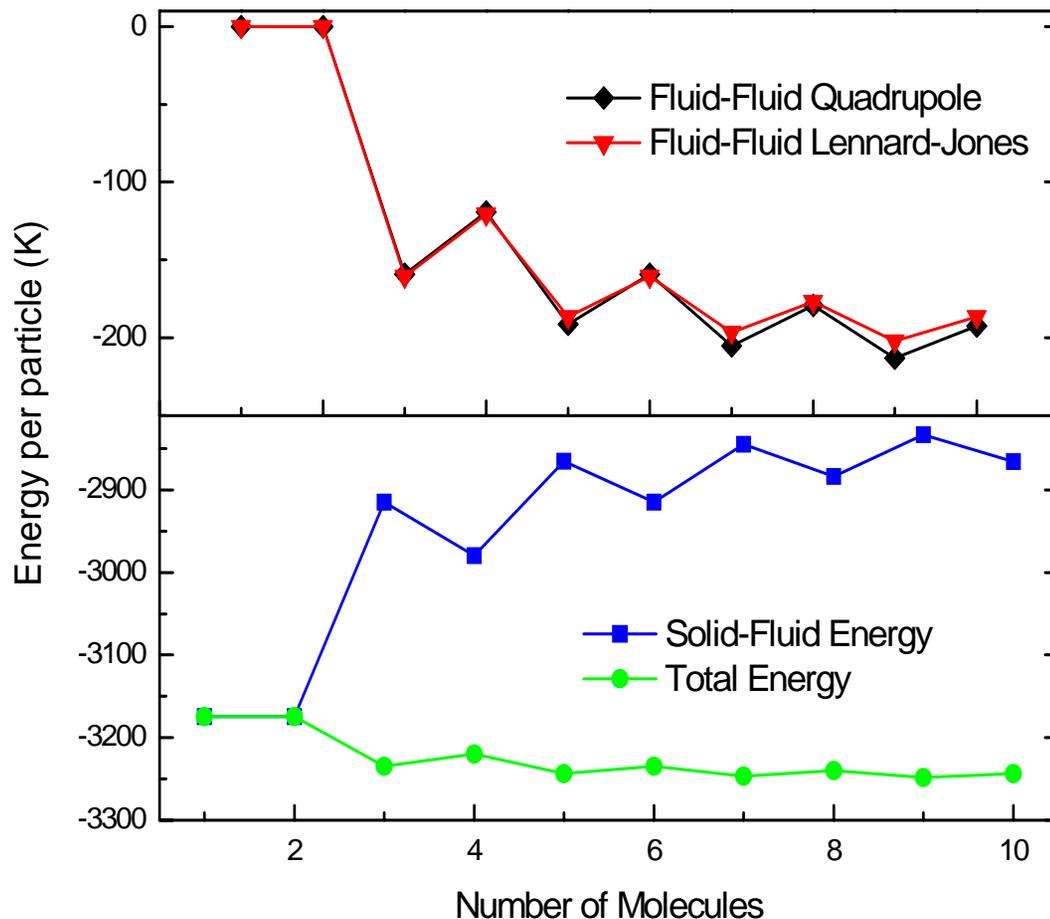
7 CO₂
Single cluster



8 CO₂
Grouped
3 + 5

CO₂ forms clusters containing only odd numbers of molecules in the groove site at low T

Reason for “Odd” Behavior: Competition Between Solid-Fluid & Fluid-Fluid Interactions



- Solid-fluid potential most favorable for CO₂ parallel to the groove
- Quadrupole-quadrupole most favorable in the “T” configuration
- Loss of solid-fluid energy is overcome for the “double T” configuration

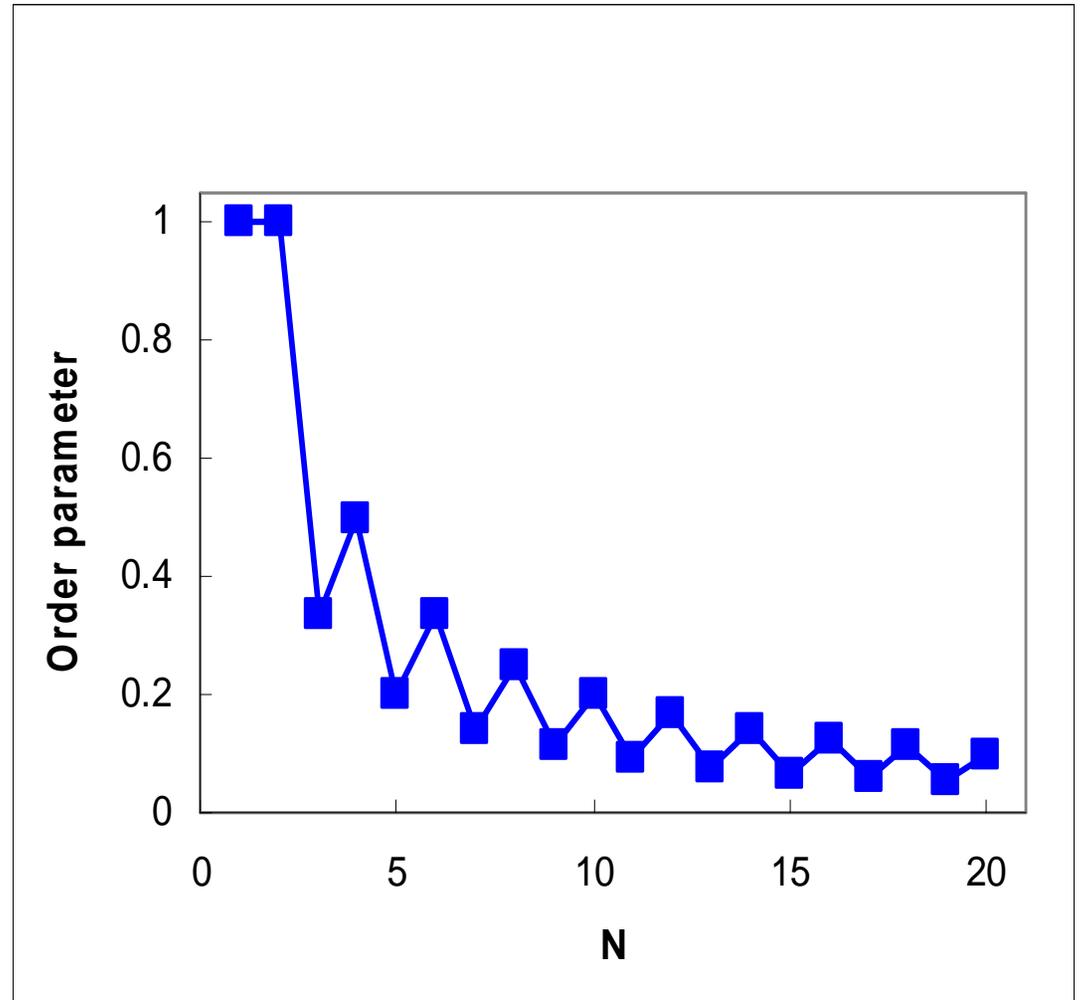
Order Parameter

$$P = \frac{2}{N} \sum_{i=1}^N \cos(\theta_i) - 1$$

$P = 1$ for all $\theta_i = 0$

$P = 0$ for 50% $\theta_i = 0$, 50% $\theta_i = 90^\circ$

$P = -1$ for all $\theta_i = 90^\circ$



Order Parameter

$$P = \frac{2}{N} \sum_{i=1}^N \cos(\theta_i) - 1$$

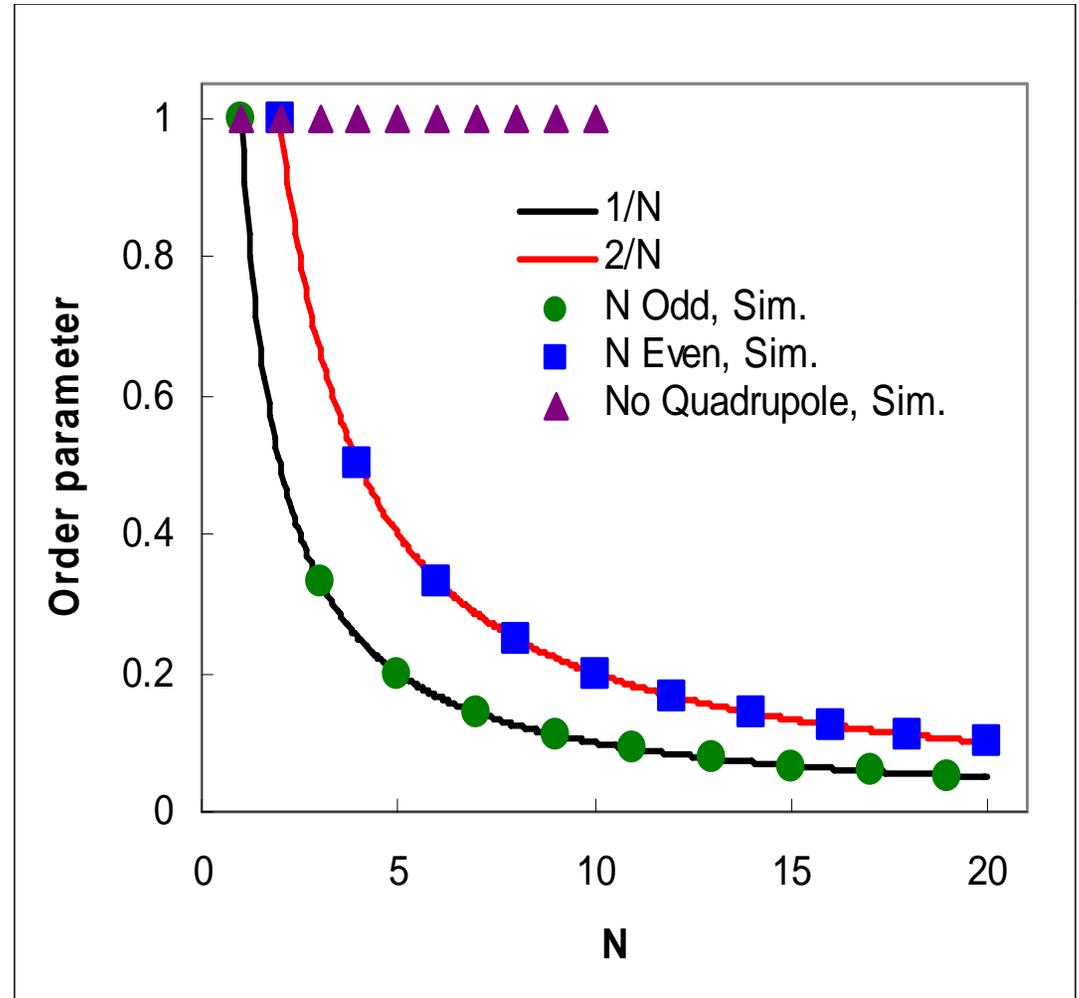
If N is odd, $\frac{N+1}{2}$ will have $\theta_i = 0$,

$\frac{N-1}{2}$ will have $\theta_i = 90^\circ$, hence

$$P(\text{odd}) = \frac{1}{N}$$

For N even we can show that

$$P(\text{even}) = \frac{2}{N}$$

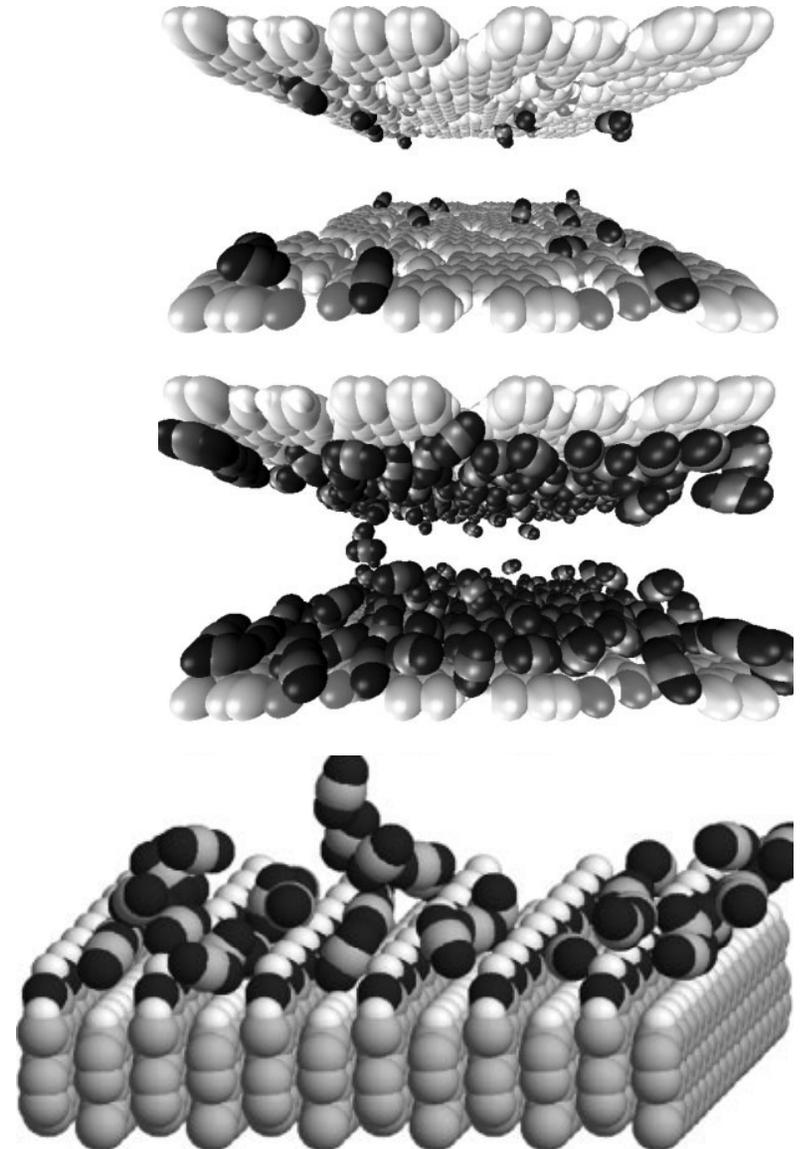


Literature Review: Adsorption on Heterogeneous Surfaces



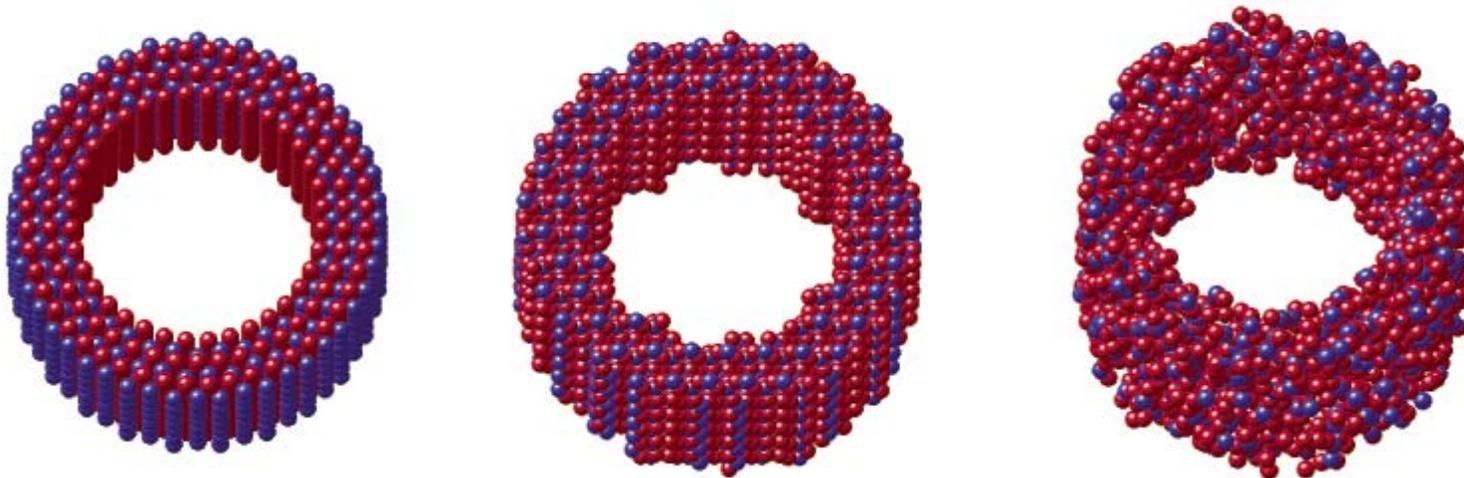
Adsorption of CO₂ on to Heterogeneous Surfaces

- Tenney & Lastoskie, *Environmental Progress*, 25, 343 (2006)
- Adsorption of CO₂ on carbonaceous sorbents
- Modeling accounted for geometric and chemical heterogeneity
- Defects in structure of the carbon
- Chemical functional groups containing oxygen and hydrogen included
- Adsorption is enhanced by defects



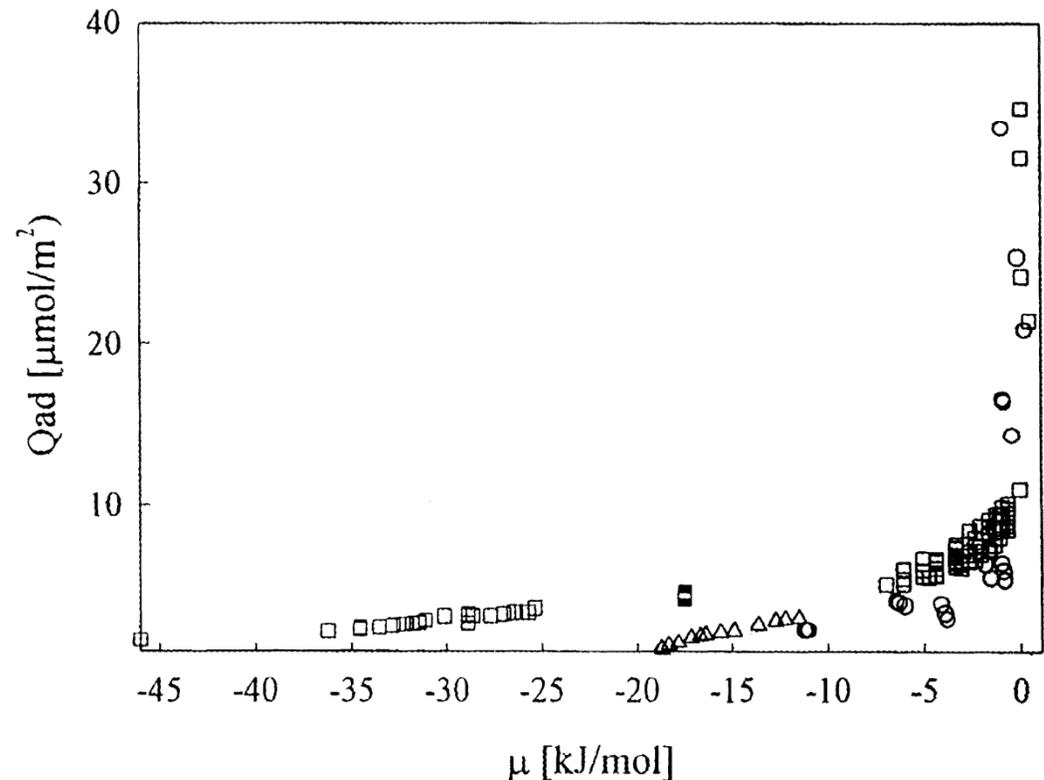
Adsorption of Ethane & CO₂ in MCM-41

- He and Seaton, *Langmuir* **19**, 10132 (2003)
- Three different models of MCM-41 used with increasing heterogeneity: Nearly homogeneous, α -quartz, energy-minimized amorphous
- Higher coverage simulation results for ethane agree with experiments on all materials
- Low coverage simulations only agree with experiments for the amorphous model
- Adsorption of CO₂ from simulations is in good agreement with experimental data only for the amorphous model



Adsorption of Phenol on Porous and Non-porous Carbons

- Bertoncini et al., *Carbon* **41**, 1101 (2003)
- GCMC used to model adsorption of phenol from the gas phase
- Compared with experiments for phenol adsorption from the liquid phase
- Solids were modeled as randomly packed spheres (Bernal's model)
- Unexpectedly good agreement between simulations and experiments

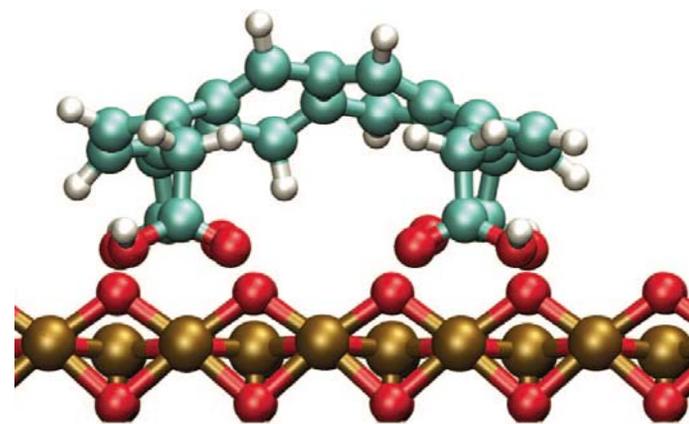


Squares, simulations. Circles & triangles, experiments.



Organic Molecules on Surfaces

- Much of the recent work in the literature on organic molecule adsorption on surfaces deals with dynamics of adsorption and diffusion—mainly molecular dynamics approaches
 - Pentacene on SiO_2 , *J. Phys. Chem. C*, **113**, 6068 (2009)
 - Organic Molecules on Calcite and Magnesite, *J. Phys. Chem. C*, **113**, 3666 (2009)
 - Organic molecules on TiO_2 , *J. Phys. Chem. C*, **112**, 19577 (2008)
 - Adsorption of small organics on TiO_2 , *Phys. Chem. Chem. Phys.* **10**, 1907 (2008)



Summary

- Grand canonical MC is a powerful tool for gaining insight into adsorption processes at a molecular level
- Good agreement with experiments can be achieved if:
 - Accurate potentials are available
 - Geometries of the sorbents can be accounted for
- Extreme temperature & pressure conditions can be modeled
- Differences in adsorption site energetics can be modeled with good agreement with experiments
- Kinetic effects must be modeled with molecular dynamics, not Monte Carlo

