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Computational Geochemistry at Sandia National Labs: Gas Hydrates and Other Applications

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Funding

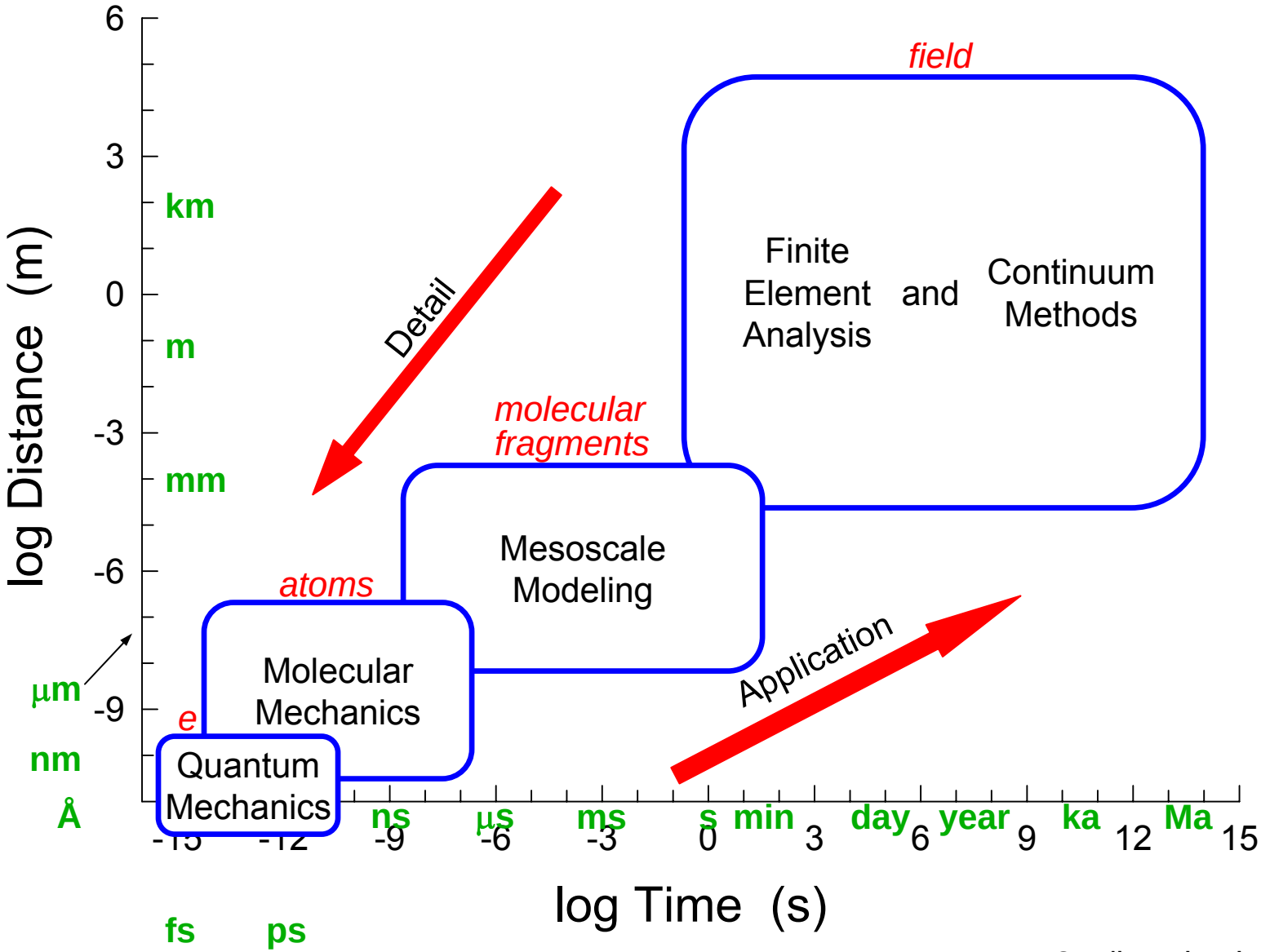
Laboratory Directed Research & Development

DOE Basic Energy Sciences

Outline

- **Atomistic simulations**
- **Methane Hydrate**
- **HCFC Hydrates**
- **Other Molecular Simulation Projects**

Time and Length Scales



Molecular Modeling Methods

Experiment
Ab initio

Forcefield

+

Structure

Structure

Molecular Mechanics

$F = ma$

Energy Minimization

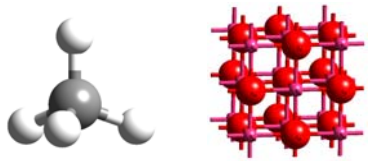
Conformational Analysis

Lattice Dynamics

Molecular Dynamics

Monte Carlo

Molecular Model



Cluster Periodic

Quantum Mechanics

$H\psi = E\psi$

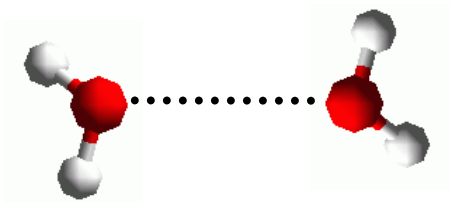
Hartree-Fock and DFT

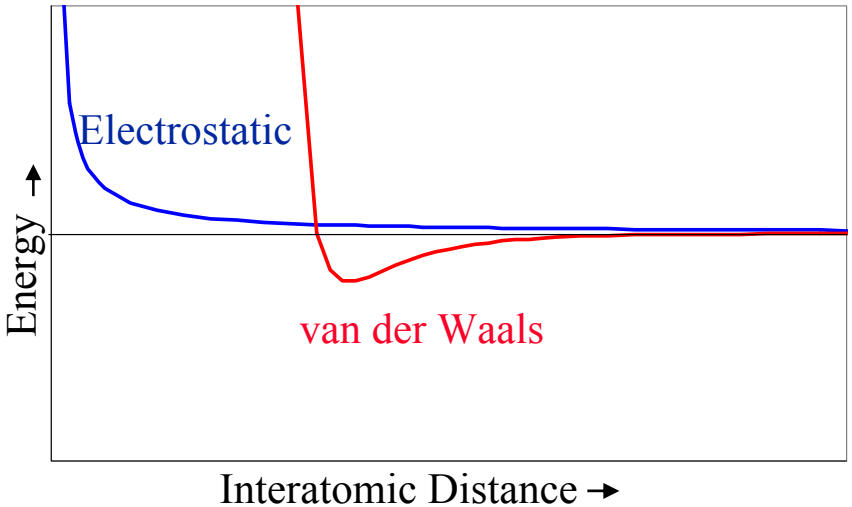
EM, CA, MD

Structure
Physical properties
Thermodynamics
Kinetics
Spectroscopy
.

Potential Parameters

Intermolecular Terms (rigid or flexible models)



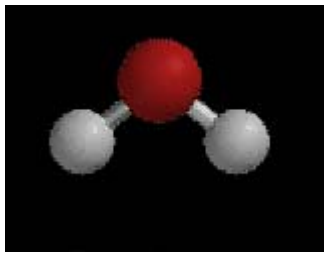


$$U_{ij} = \frac{q_i q_j}{r} + 4\varepsilon\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right]$$

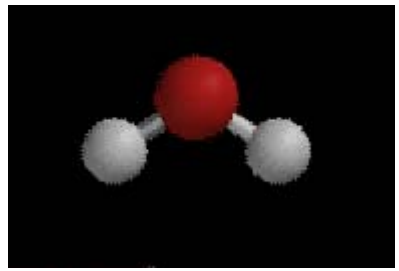
Long-range electrostatics handled in reciprocal space by **Ewald sum** or **particle mesh** techniques

Potential Parameters

Intramolecular Terms (flexible models)

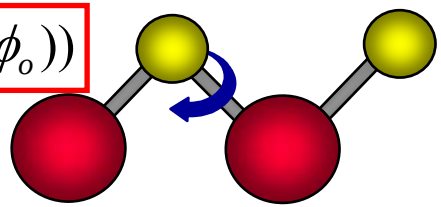


Bond Stretch $E = K\left(r - r_0\right)^2$

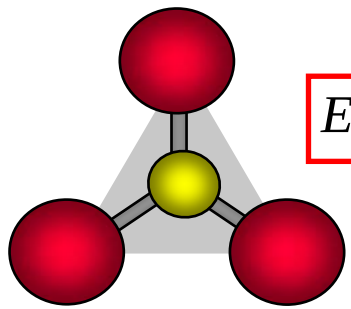


Angle Bend $E = K\left(\theta - \theta_0\right)^2$

$$E = k(1 + \cos(n\phi - \phi_o))$$



Torsion



$$E = k(1 + \cos(n\chi - \chi_o))$$

Out-of-Plane Stretch

Simulation vs Experiment

Property	Simulation	Experiment
Unit cell data	Lattice constants (constant P simulation)	Diffraction
Local atomic coordination	Radial distribution functions	EXAFS
Interfacial structure	Atomic density profiles	X-Ray Scattering
Vibrational motion	Power spectra	IR/Raman

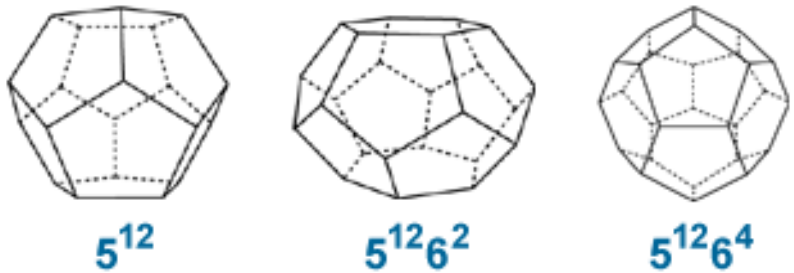
Outline

- Atomistic simulations
- **Methane Hydrate**
- HCFC Hydrates
- Other Molecular Simulation Projects

Natural Gas Hydrates

Components

- **Water in various cage sizes (host)**
- **Gas-phase guest molecules**



Natural Gas Hydrates

Components

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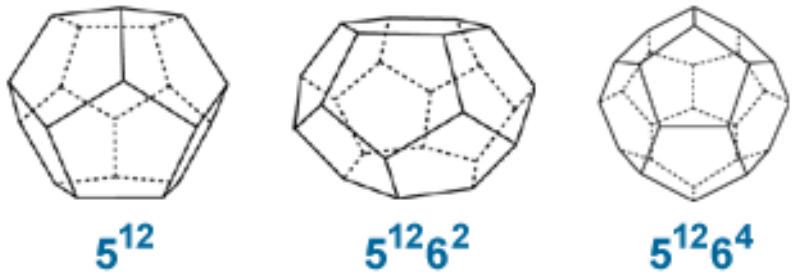
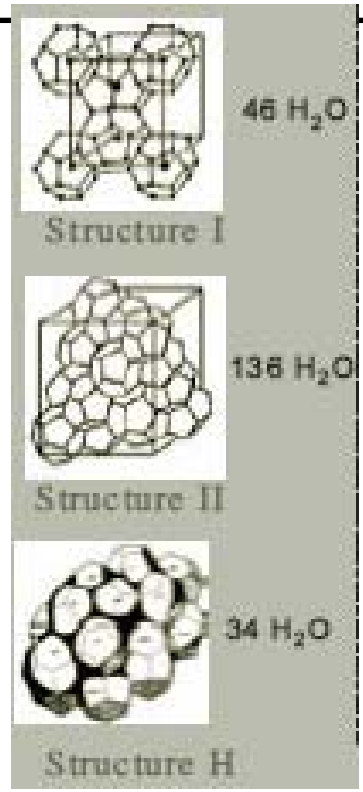
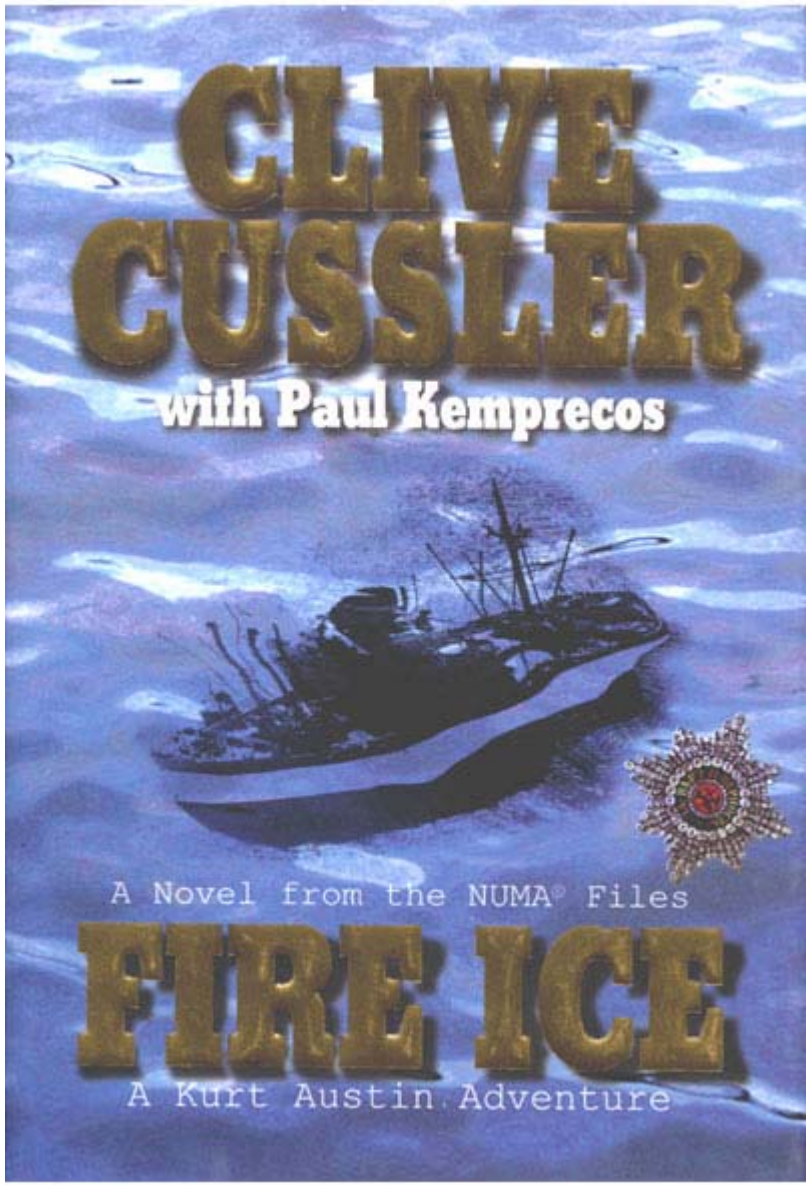




Hydrate Crystal Structure	I (12.0 Å)		II (17.1 Å)		H (a=12.3 Å, c=10.2 Å)		
Cavity	Small 5^{12}	Large $5^{12}6^{2}$	Small 5^{12}	Large $5^{12}6^{4}$	Small 5^{12}	Large $4^{3}5^{6}6^{3}$	Large $5^{12}6^{8}$
# per unit cell	2	6	16	8	3	2	1
Coordination #	20	24	20	28	20	20	36

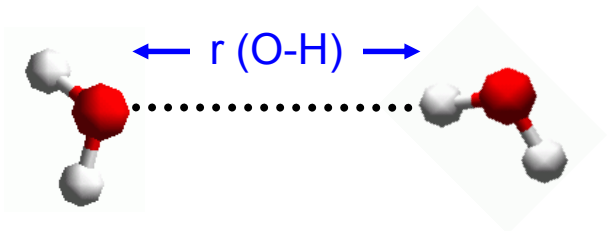
Sloan, 1998

www.netl.doe.gov, National Methane Hydrate R&D Program

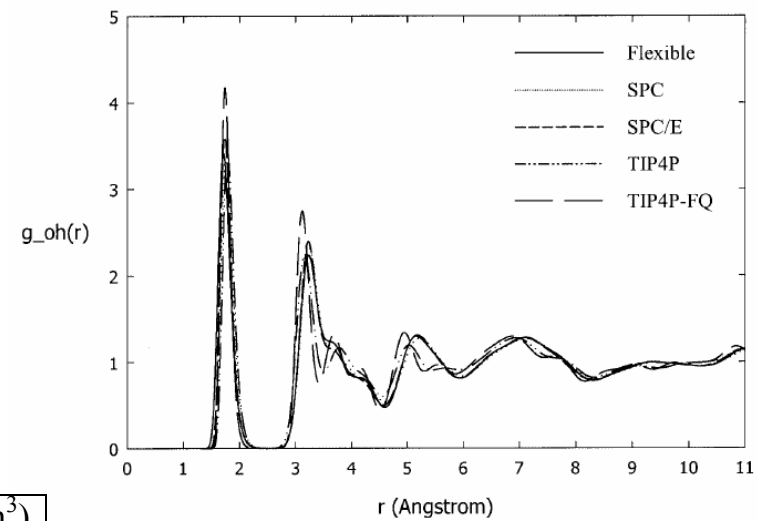

CLIVE
CUSSLER
with Paul Kemprecos
A Novel from the NUMA® Files
FIRE ICE
A Kurt Austin Adventure

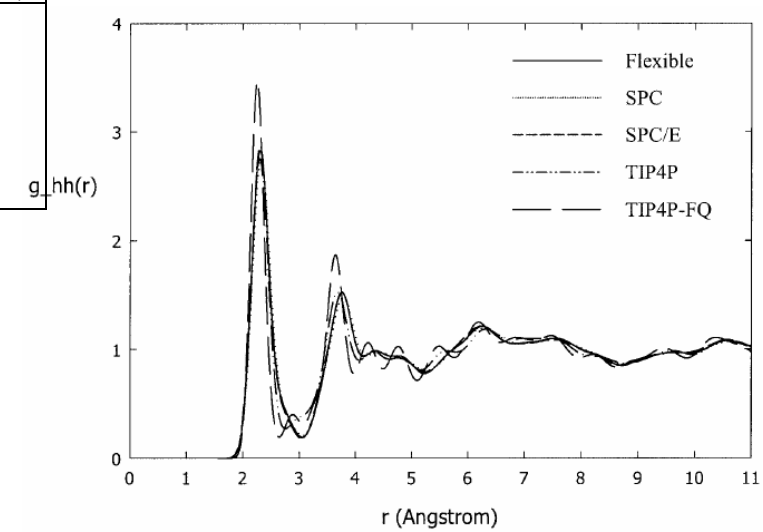
Effect of Water Potential

Methane Hydrate (sI), 200 K, 20 bar



g = Radial Distribution Function

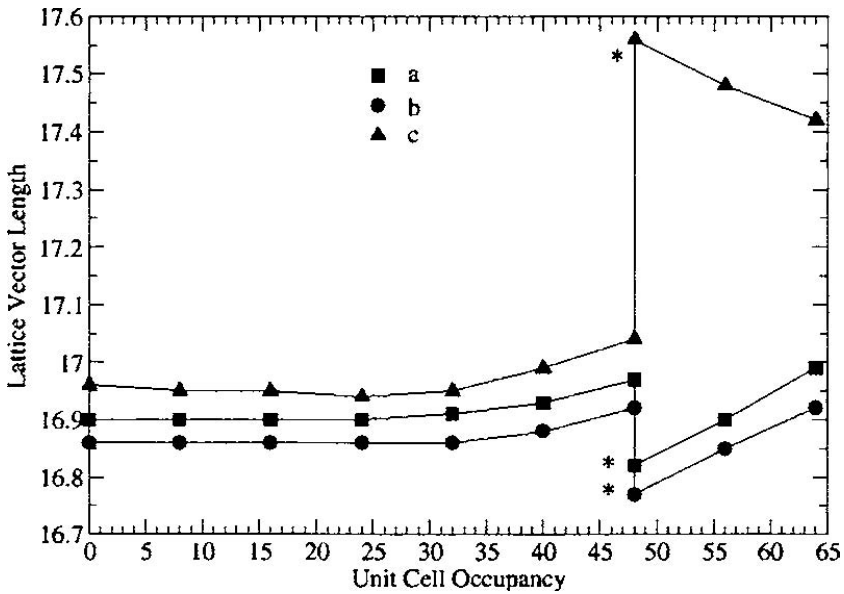


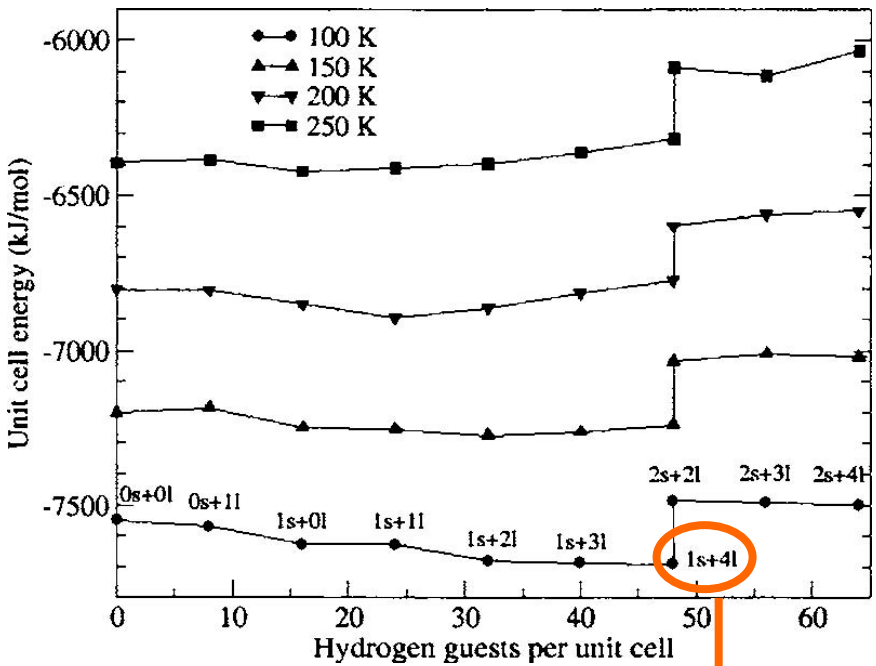


	Water Dipole Moment (D)	Bulk Density (kg·m^3)
SPC	2.274	945 ± 2
SPC/E	2.351	966 ± 2
TIP4P	2.177	961 ± 2
Polarizable TIP4P	3.15 ± 0.14	999 ± 2
Flexible SPC	2.44 ± 0.10	955 ± 2
Bulk Water	1.85	997

English and MacElroy, *J. Comp. Chem.* **2003**

MD Simulations of H_2 Hydrate





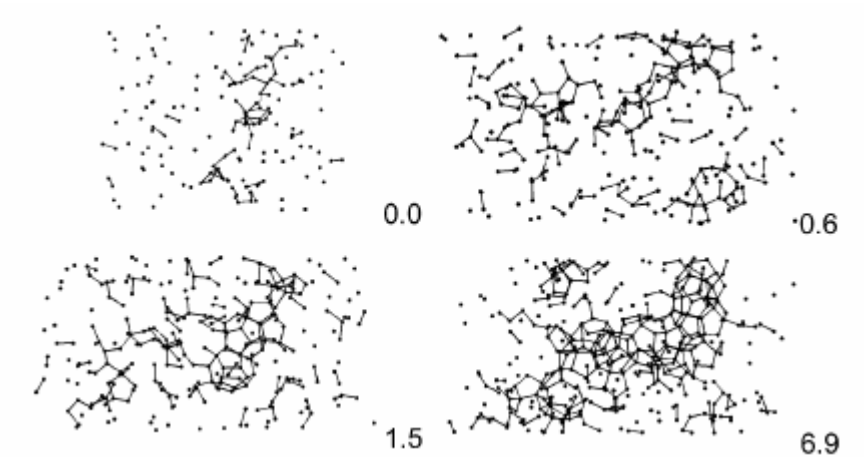
Drastic change in structure when # H_2/unit cell > 48

1 H_2/small cage
4 H2/large cage

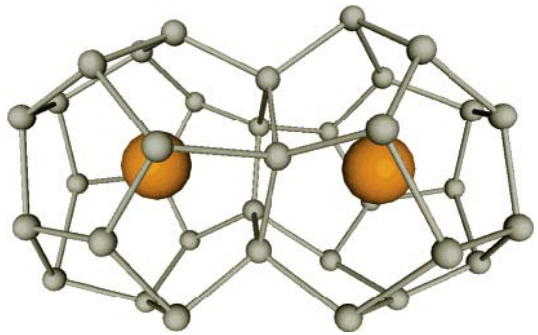
Alavi et al, *J. Chem. Phys.*, **2005**

Methane Hydrate Formation

Methane Hydrate (sI), 300 K, 30 bar, rigid SPC water



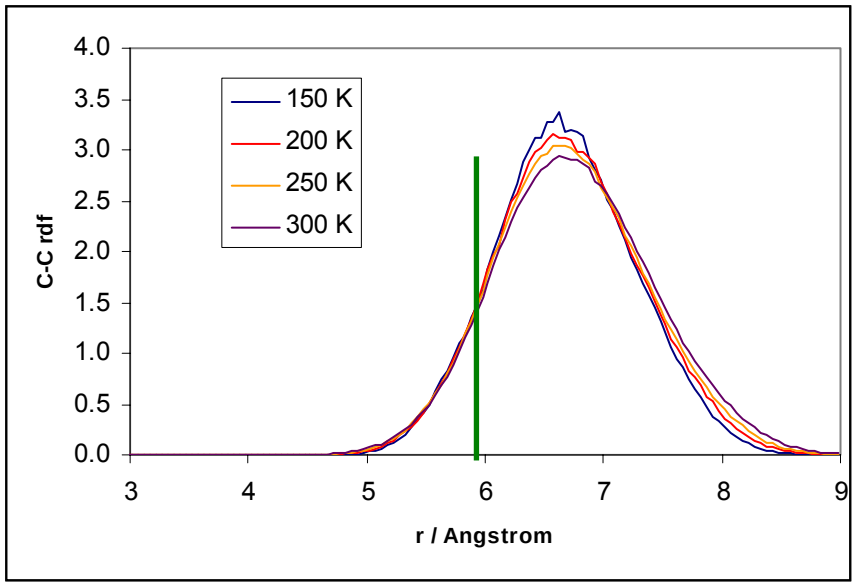
Hydrate cluster formation at 6.9 ns

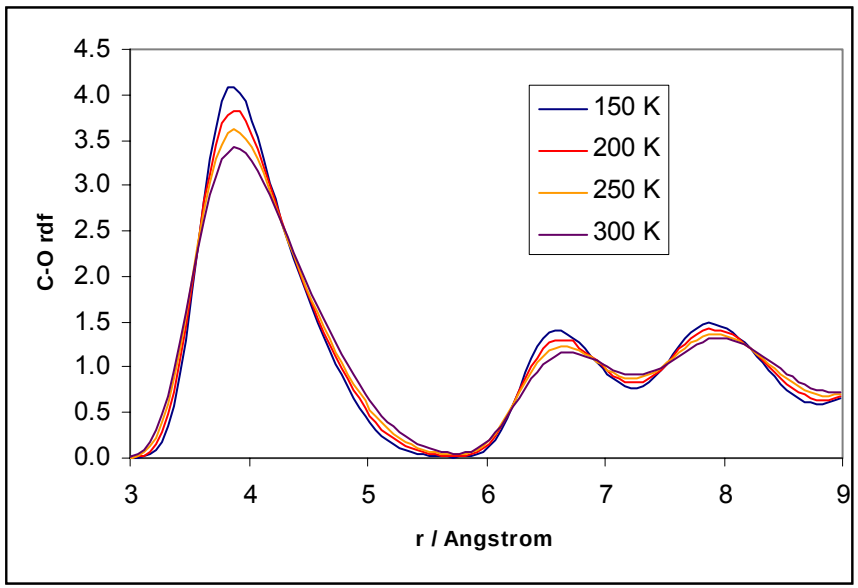


Face-sharing 5^{12} dimer (sII)

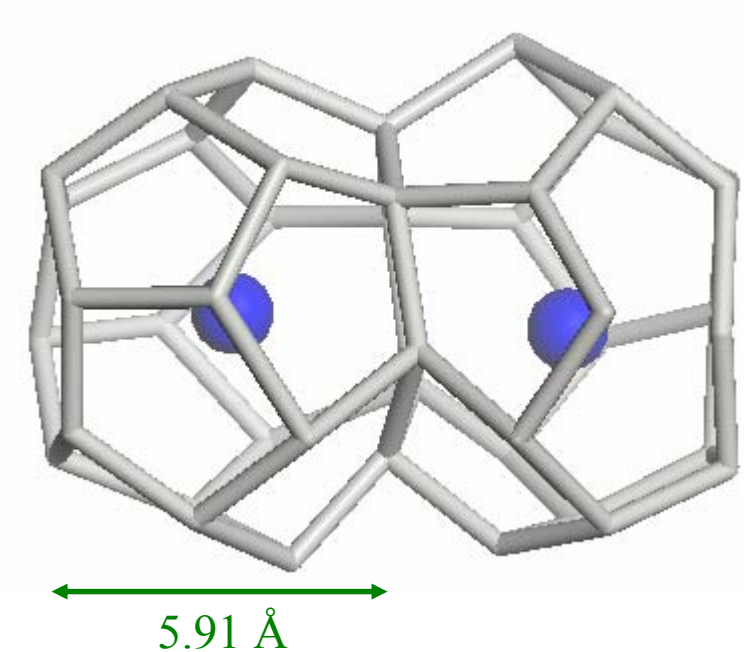
Moon et al, *J. Am. Chem. Soc.*, **2003**

Methane sI, Cage Structure



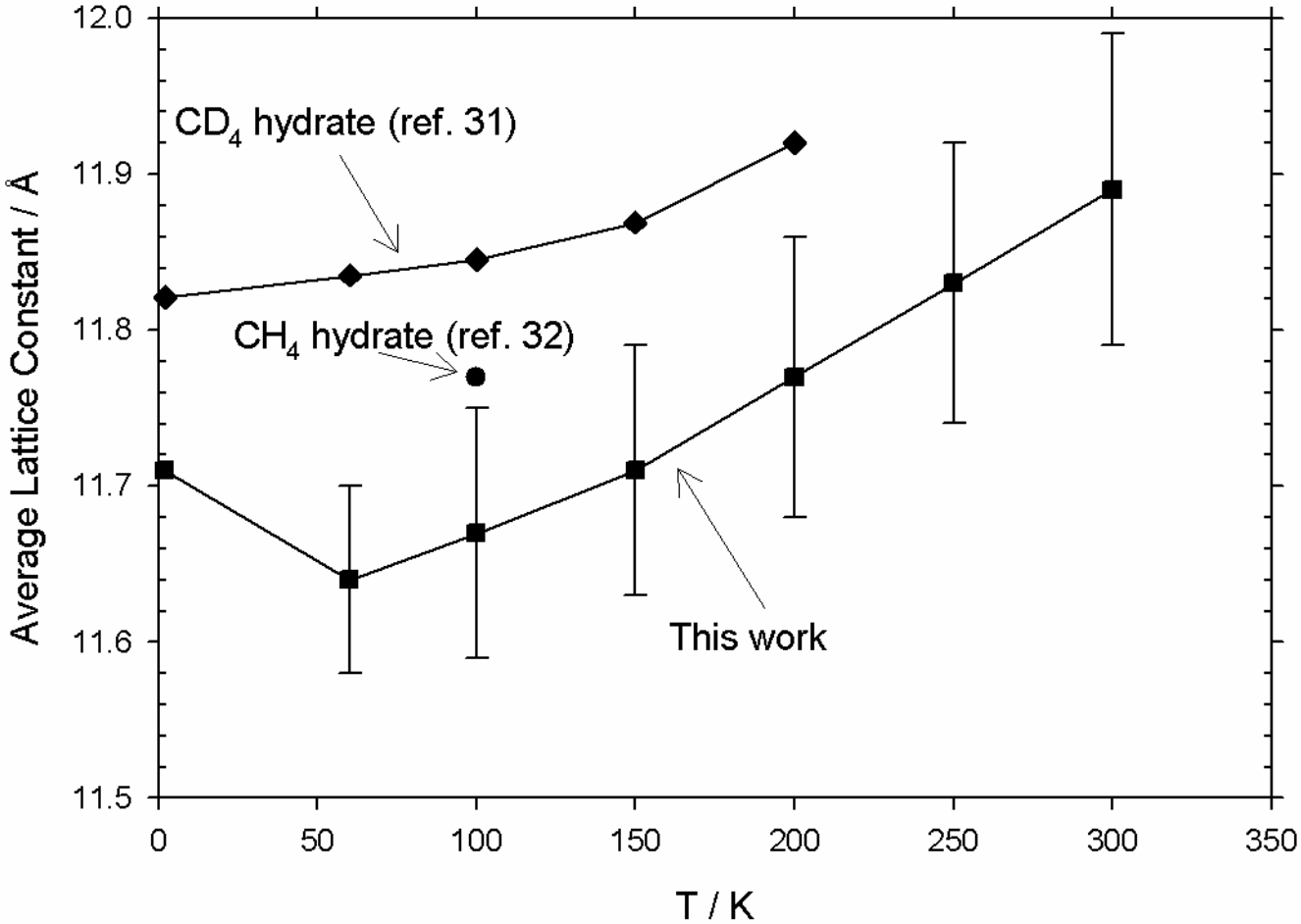


Methane-Methane
Coordination # = 13.5



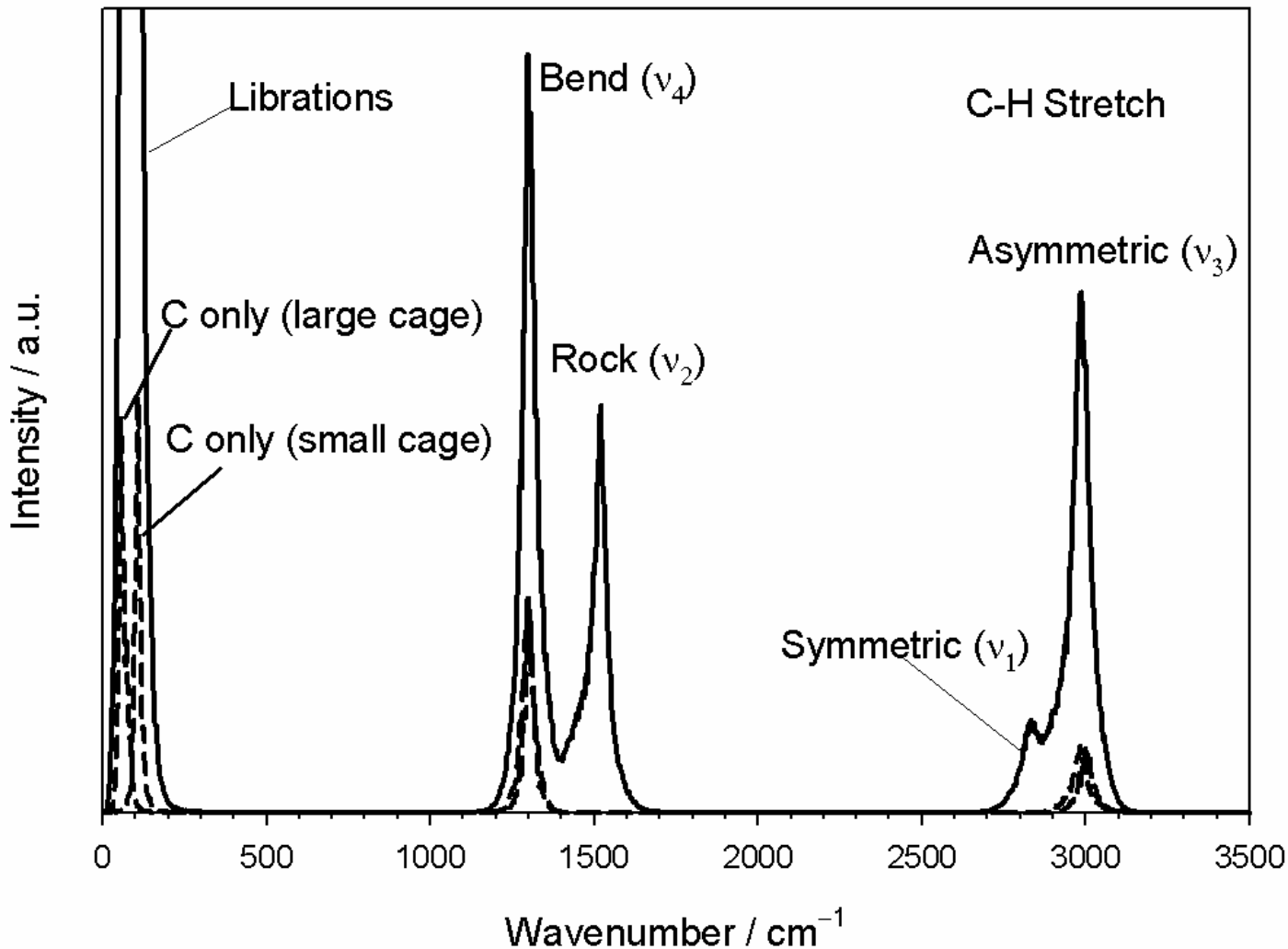
Methane-Water
Coordination # = 23 (first peak)

Methane Hydrate Thermal Expansion



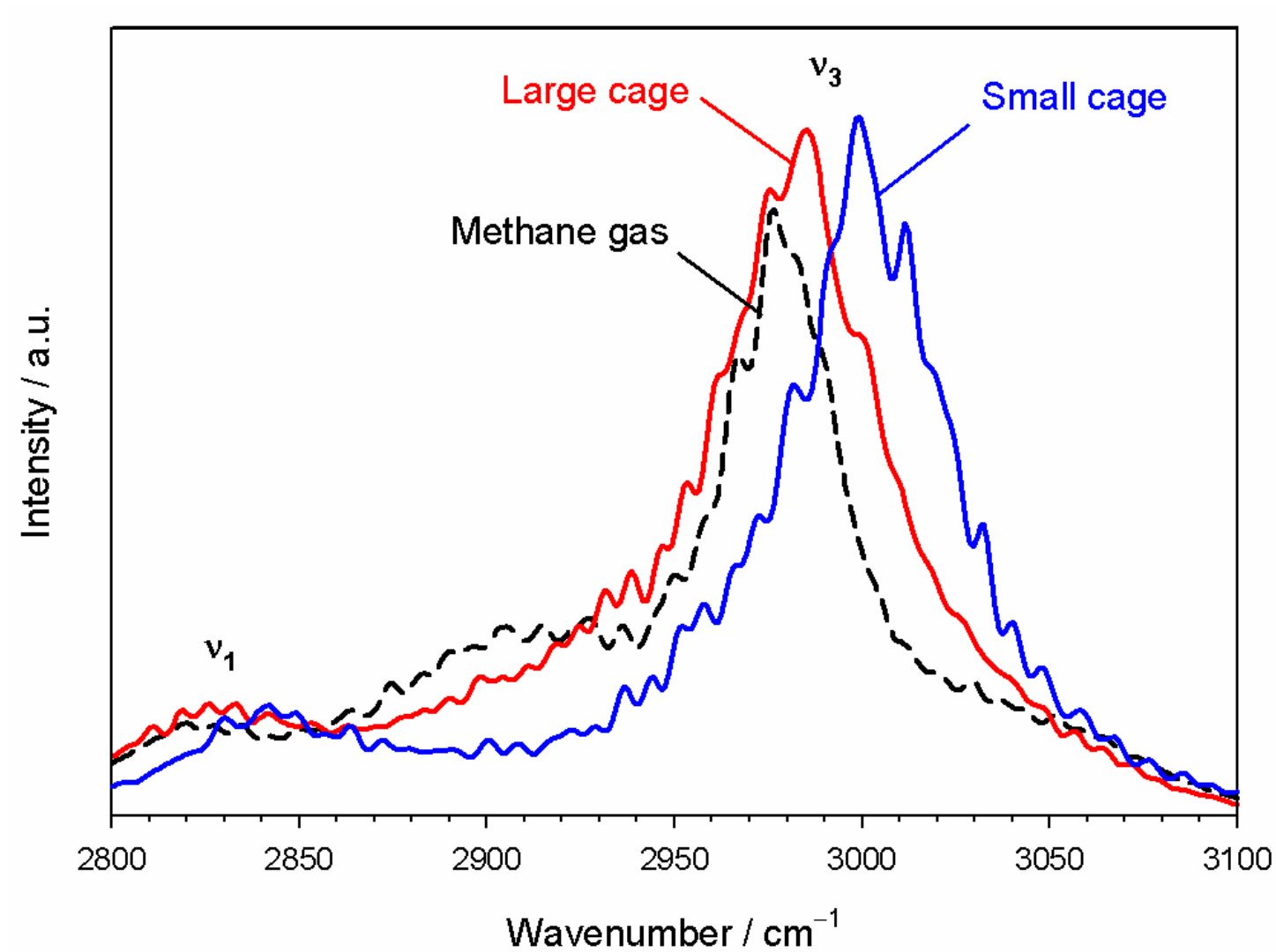
Greathouse et al, *J. Phys.Chem. B* **2006**, *110*, 6428-6431

Methane Hydrate Power Spectrum



Greathouse et al, *J. Phys.Chem. B* **2006**, *110*, 6428-6431

Methane Hydrate Thermal Expansion

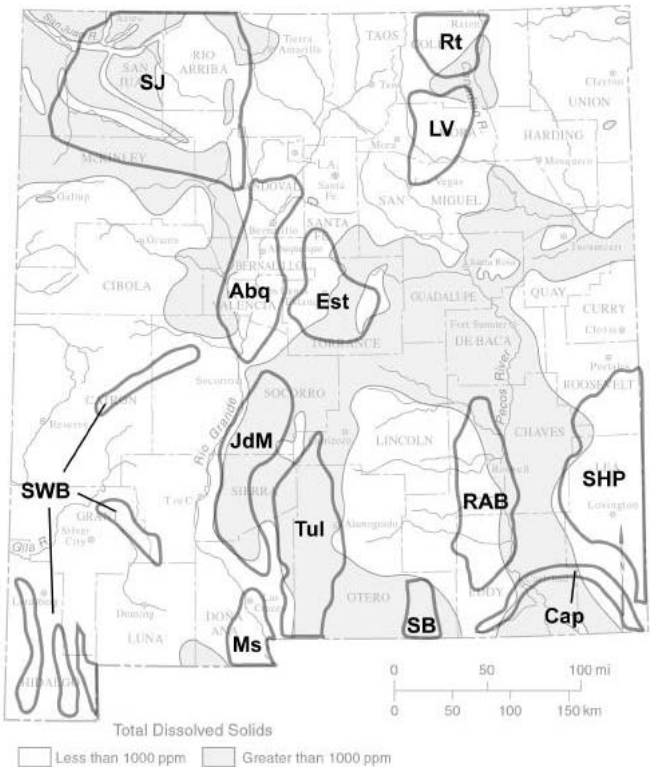


Normal modes from methane in large cage similar to methane gas

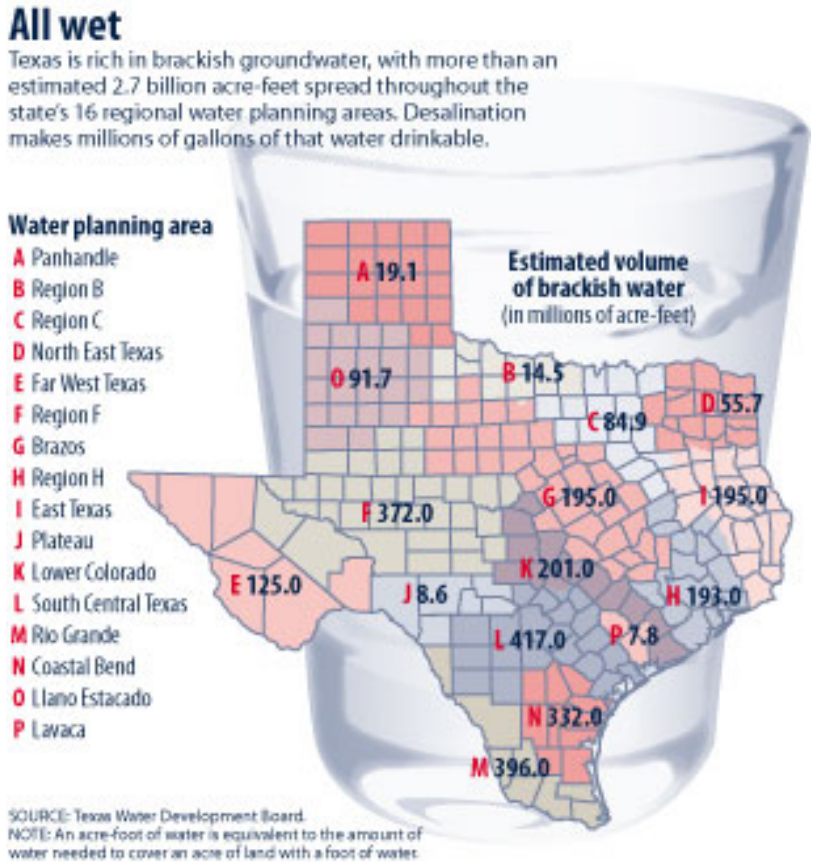
Outline

- Atomistic simulations
- Methane Hydrate
- **HCFC Hydrates**
- Other Molecular Simulation Projects

Desalination of Brackish Water



http://wrri.nmsu.edu/



Drinking water…..< 1k mg/L

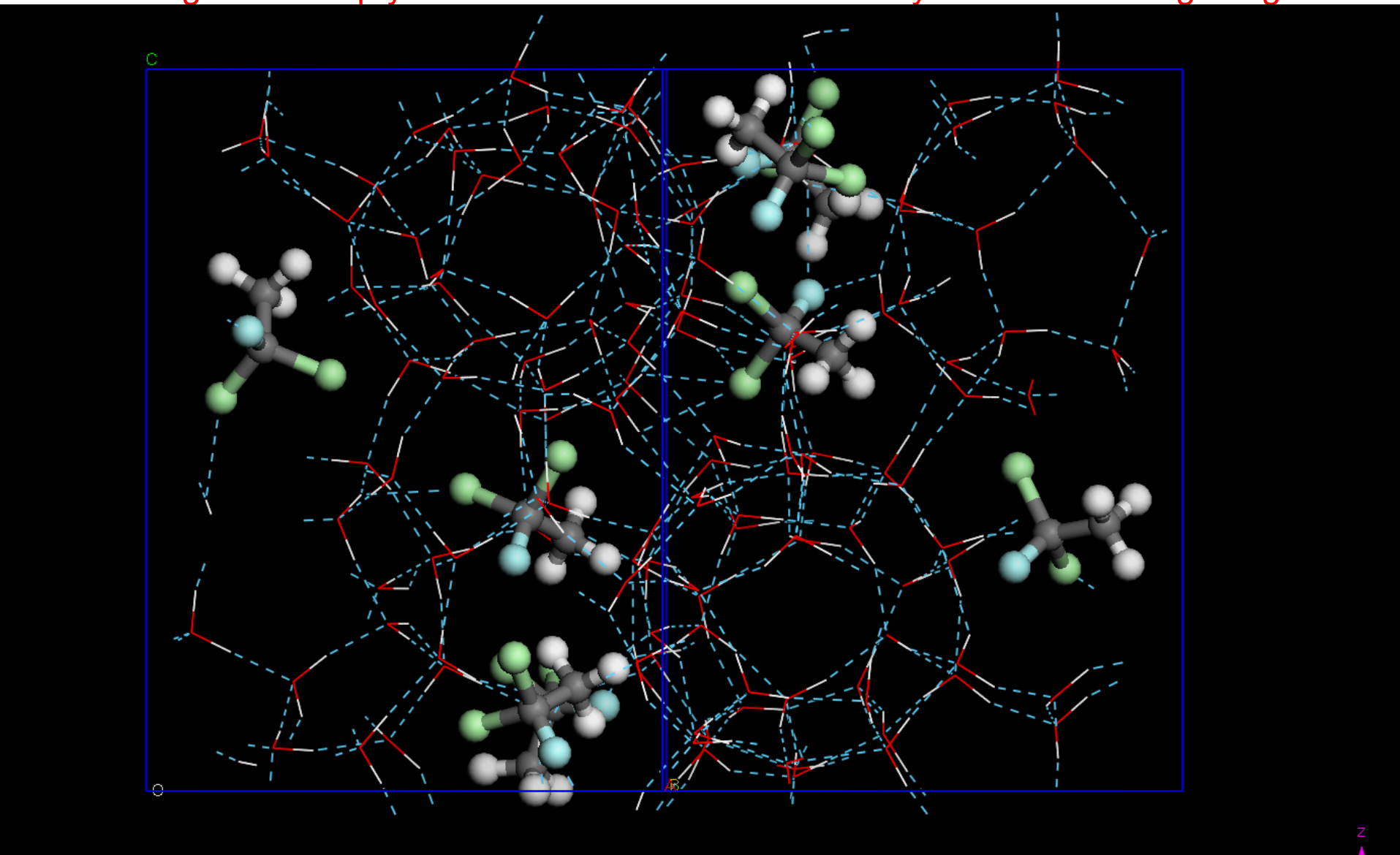
Brackish water…..1k-10k mg/L

Seawater……> 30k mg/L

R141b-Hydrate, Structure II

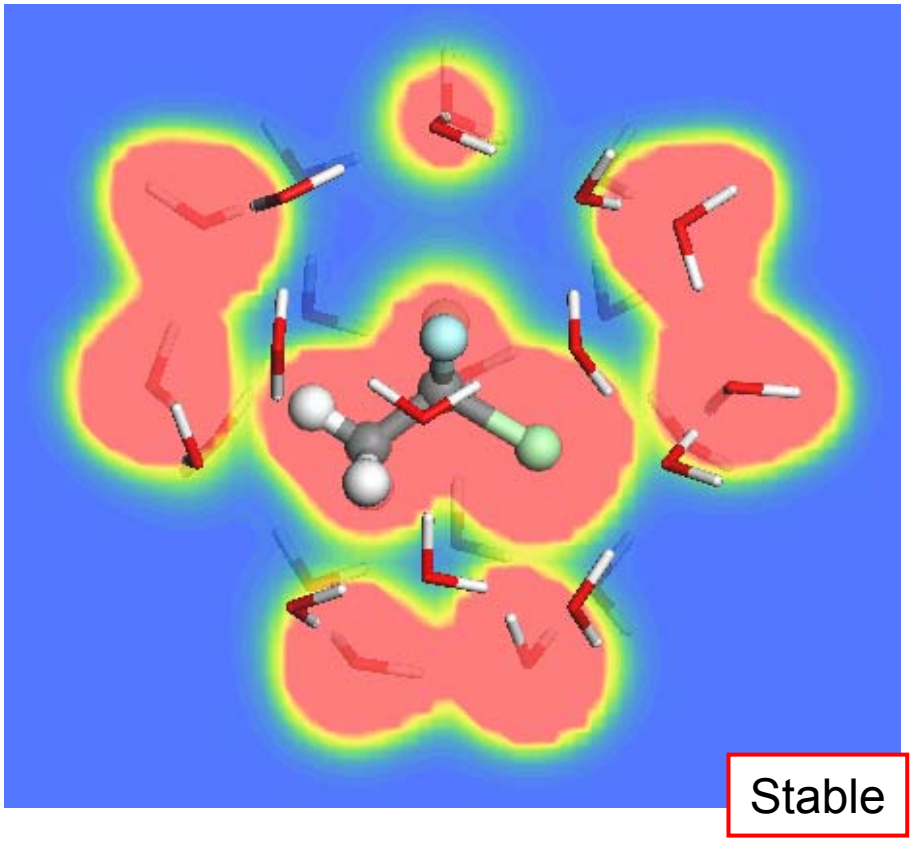
(R141b = 1,1-dichloro-1-fluoroethane, 265 K)

Small cages are empty. R141b molecules freely rotate within large cages.



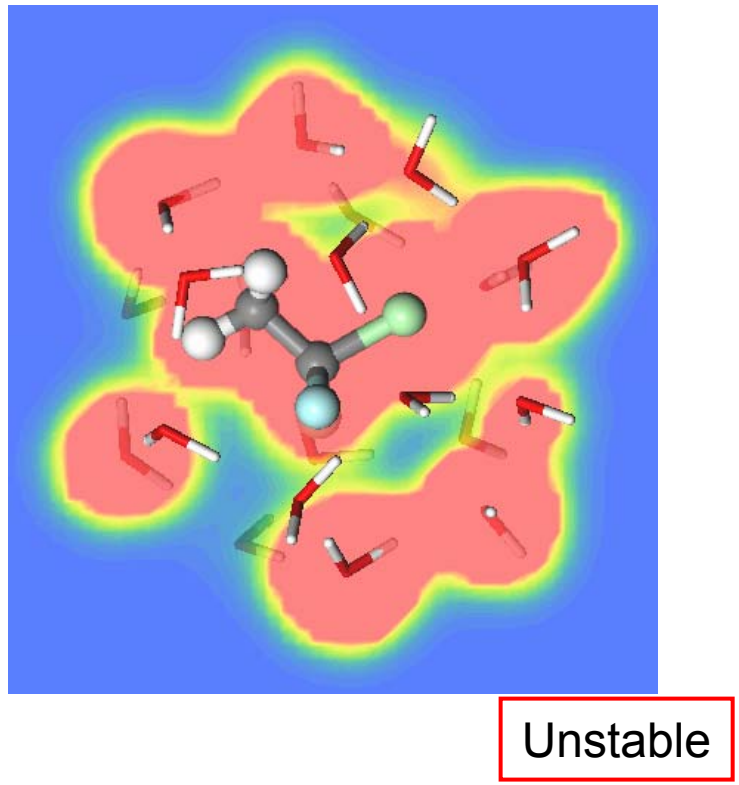
Density Functional Theory (DFT)

Cluster model of R141b in LARGE cage



$\Delta E_{formation}$ = -49.9 kcal/mol

Cluster model of R141b in SMALL cage

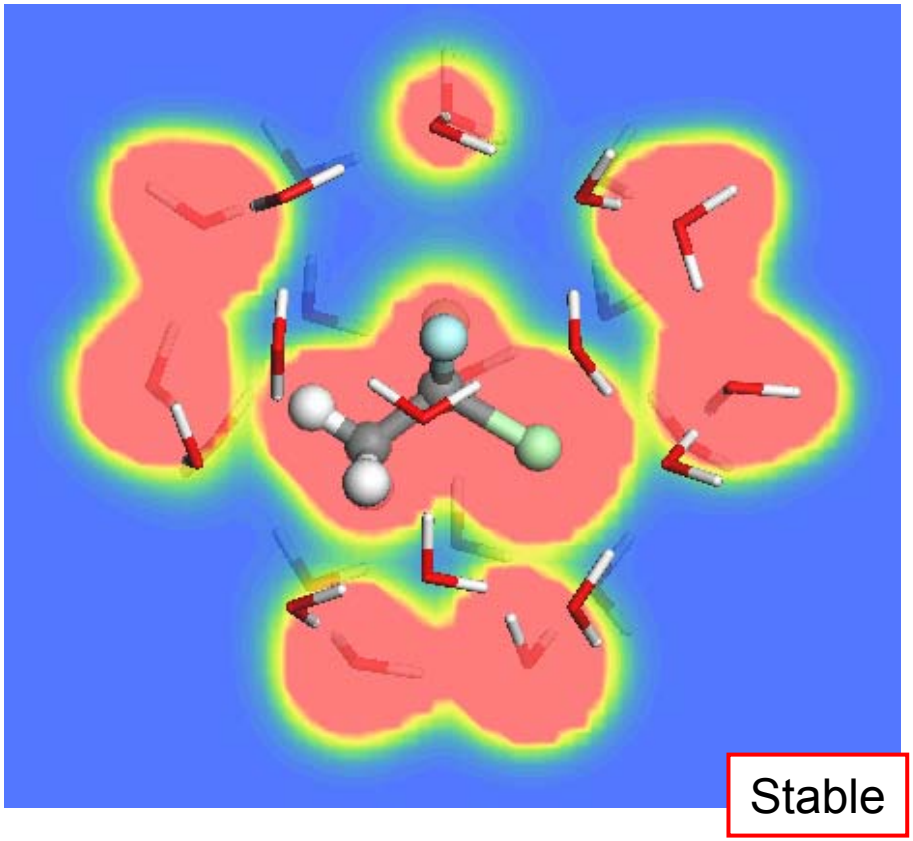


$\Delta E_{formation}$ = +38.6 kcal/mol

- Strong interactions between guest molecule and cage waters lead to destabilization of the hydrate; R141b is not expected to occupy the small cage

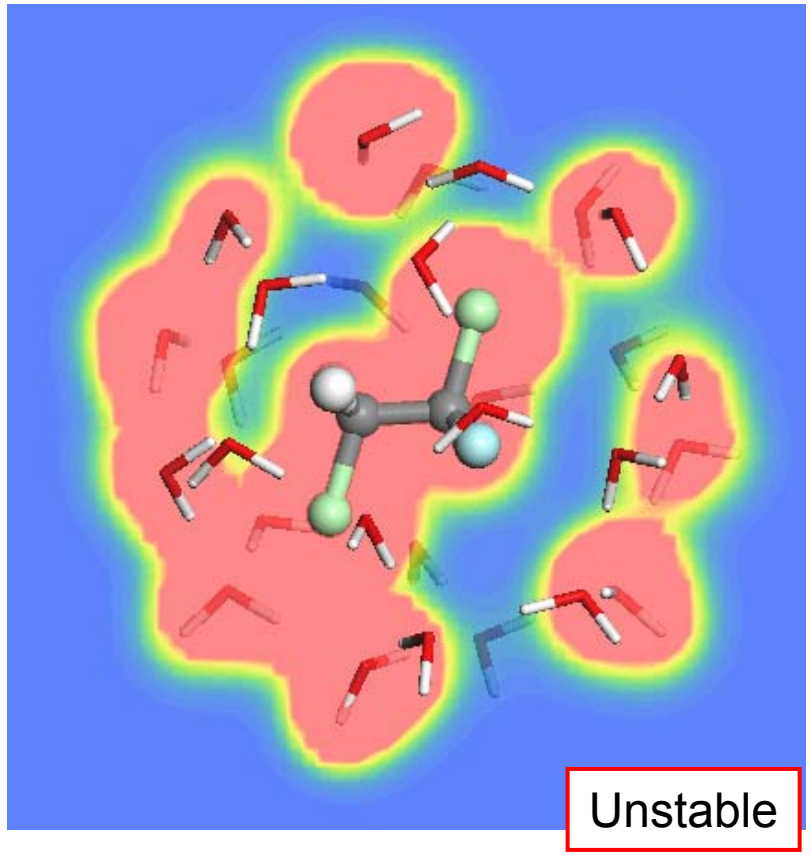
R141b Isomer Instability

Cluster model of R141b in LARGE cage



$\Delta E_{formation}$ = -49.9 kcal/mol

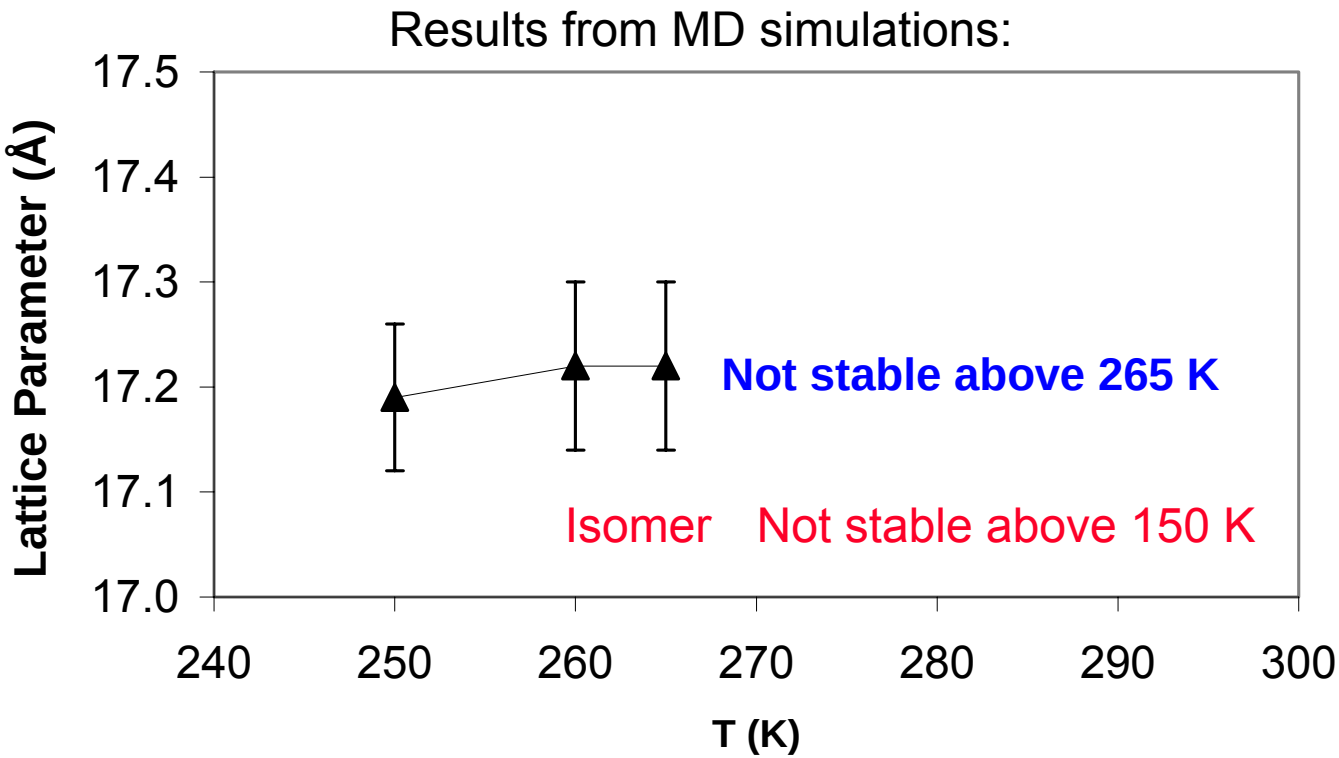
Isomer (1,2-dichloro-1-fluoroethane)



$\Delta E_{formation}$ = -43.9 kcal/mol

- Electron density map (through C-C-Cl plane) for isomer in large cage exhibits strong interaction between isomer and water molecules as indicated by sharing of electrons

R141b Hydrate Thermal Expansion



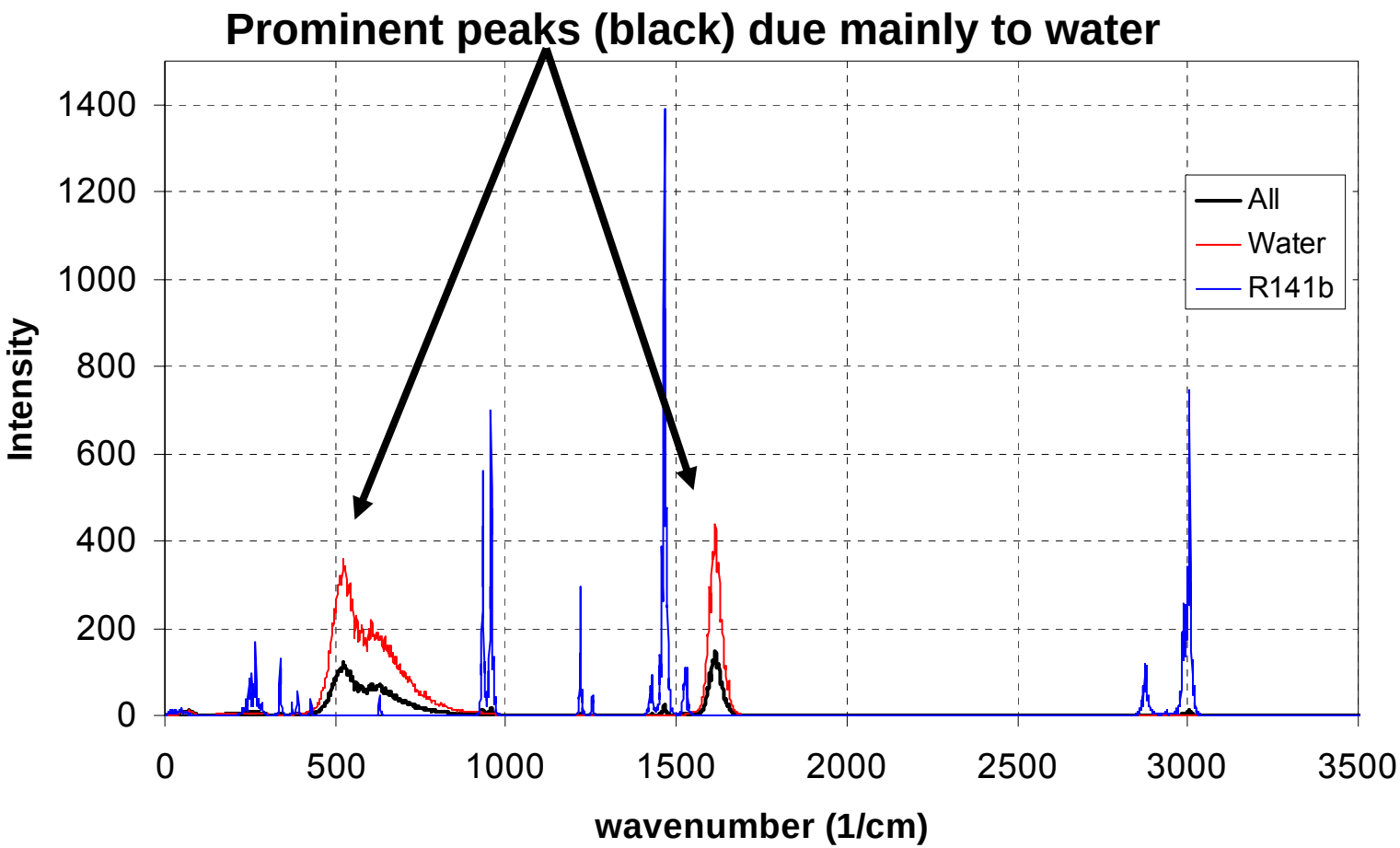
Experimental forming conditions:

R141b 280 K, 1 atm pressure

Isomer No formation seen at 273 K, 1 atm

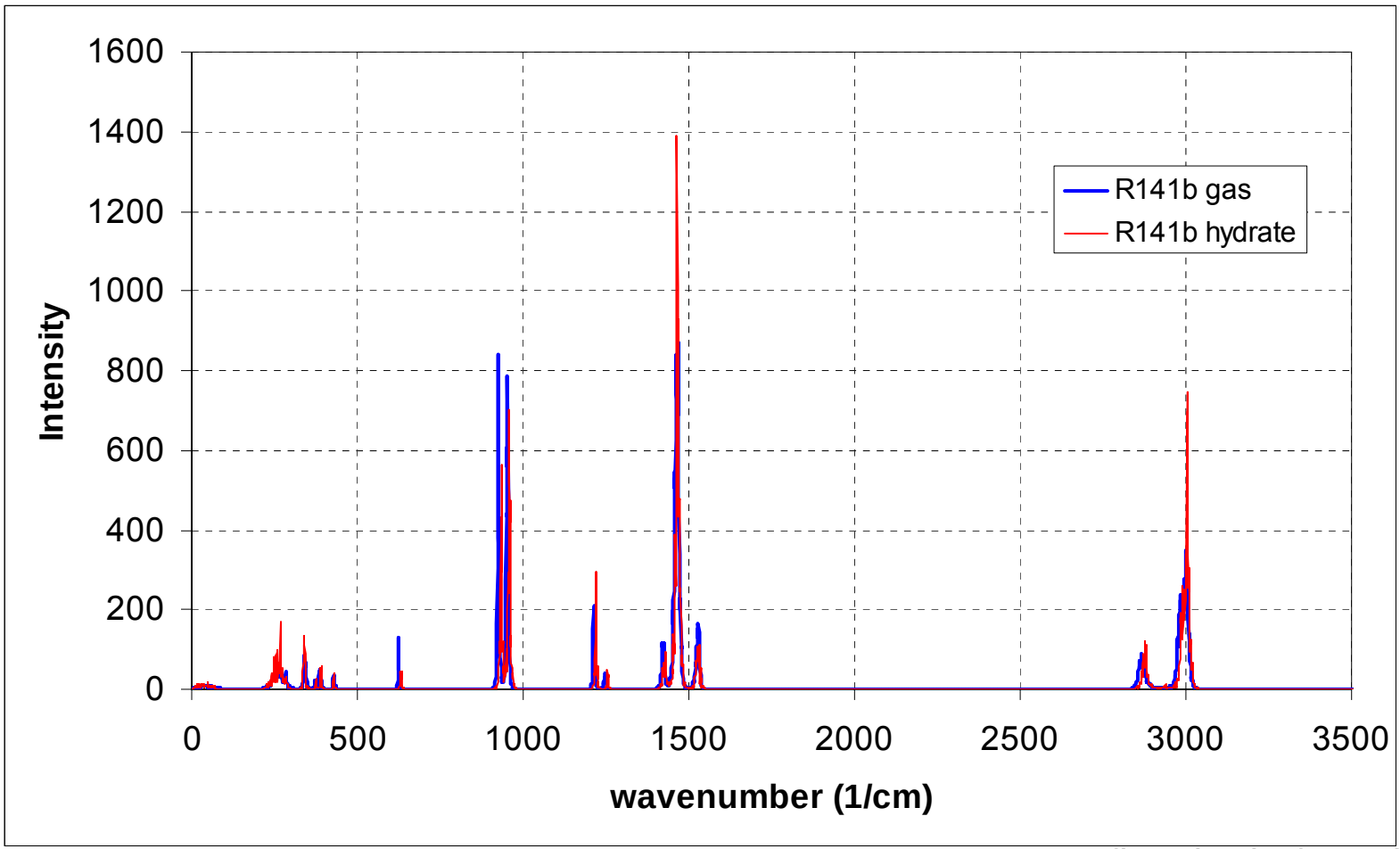
Greathouse et al, *J. Phys.Chem. C* **2007**, *submitted.*

R141b Hydrate Power Spectrum

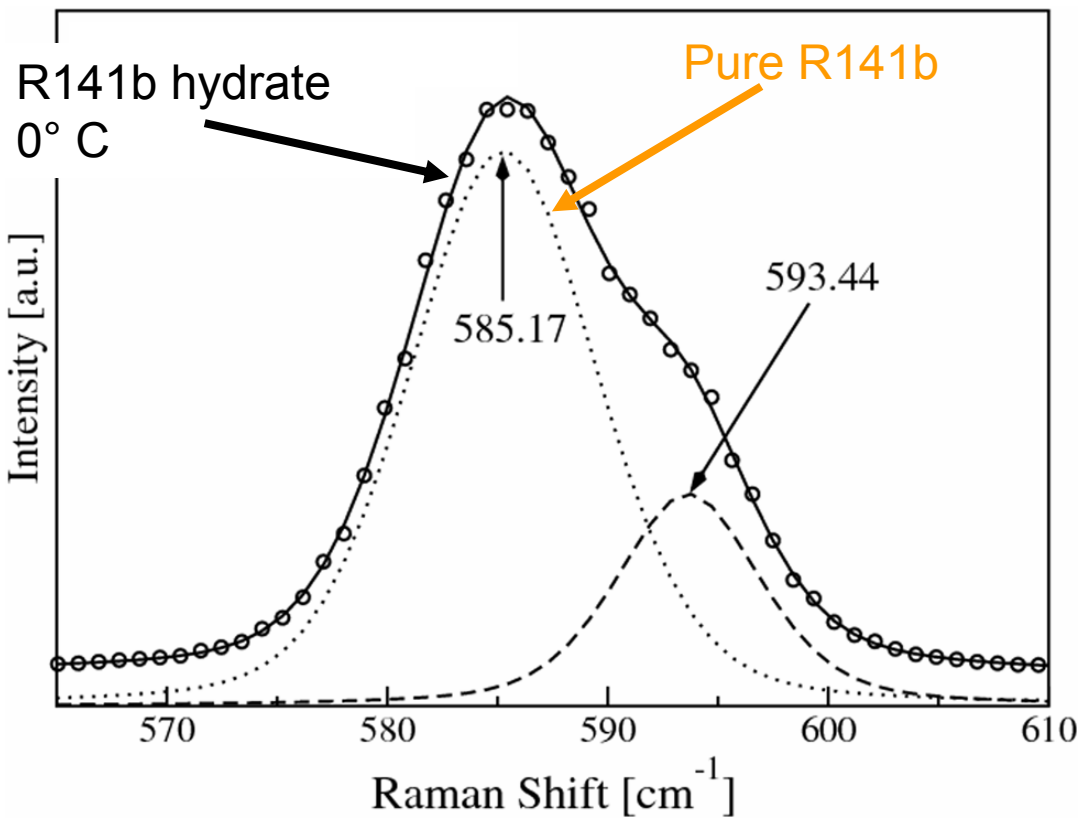


R141b Peak Comparison

Slight shift (5-10 cm^{-1}) in C-Cl and C-F stretch modes between pure gas and hydrate phases



Experimental Raman Spectrum



Gas Hydrate Summary and Conclusions

- **Conclusions**
  - Flexible atomistic forcefield (CVFF) is able to predict hydrate structure and aid in interpretation of Rama spectra
  - Quantum calculations are useful in refining guest/cage diameters
- **Future work**
  - Monte Carlo simulations to determine cage occupancies
  - Kinetic Monte Carlo simulations to study hydrate nucleation and growth
  - Effect of mineral surfaces on hydrate nucleation

Outline

- Atomistic simulations
- Methane Hydrate
- HCFC Hydrates
- **Other Molecular Simulation Projects**

UO_2-Clay Simulations

- **Montmorillonite (octahedral charge), Beidellite (tetrahedral charge), and Pyrophyllite (no charge)**

- **Simulation specifics:**
  - Monte Carlo and Molecular Dynamics Simulations
  - Nonbonded interactions only (rigid-body)
  - Constant pressure interlayer simulations
  - Constant volume adsorption simulations (external surface)

- **Goal:** examine equilibrium water content and layer spacing, sorption tendencies of:

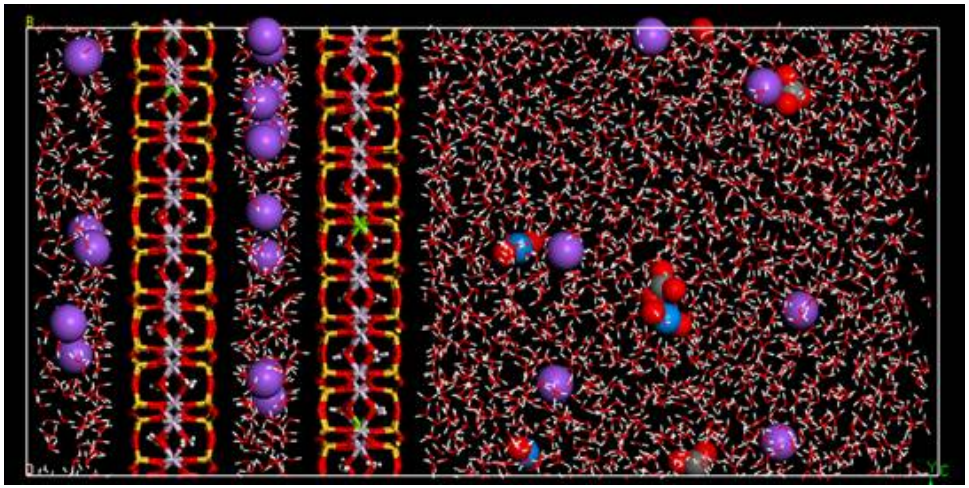
  $UO_2(H_2O)_5^{2+}$

  $UO_2(H_2O)_3(CO_3^{2-})^0$

  $UO_2(H_2O)(CO_3^{2-})_2^{2-}$

  UO_2 oligomers

Large-Scale Simulations of Uranyl Adsorption



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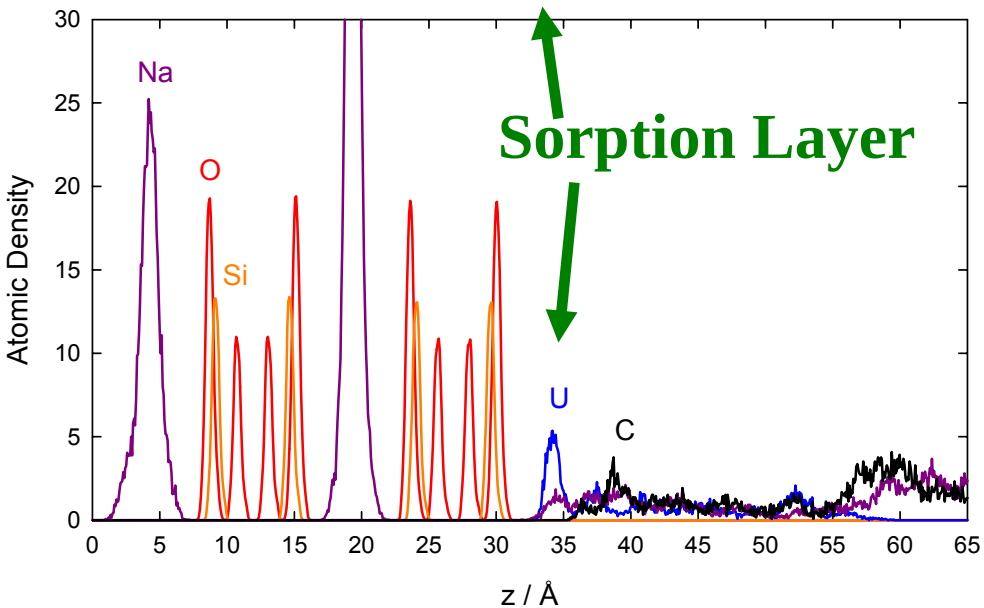
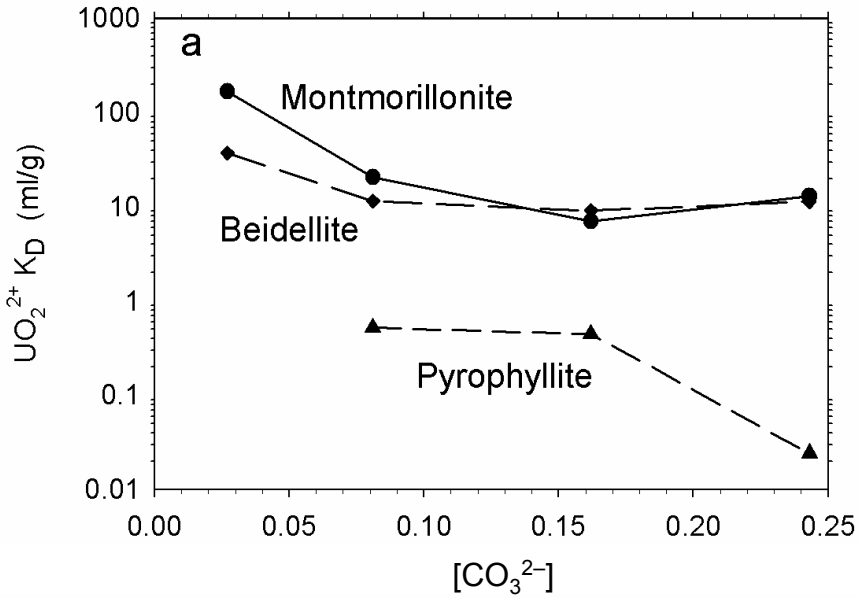


Integrate density peaks to obtain percent sorbed

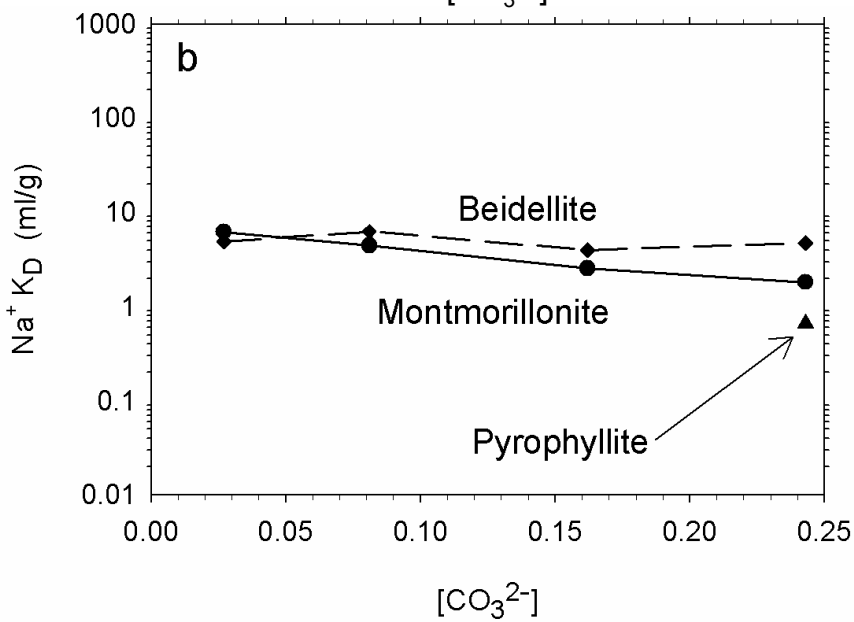
UO_2 + clay → UO_2-clay

$$K = \frac{\%U_{sorbed}}{\%U_{aqueous}} = \frac{\text{area sorbed}}{\text{area aqueous}}$$

Sorption Equilibria (K_D)



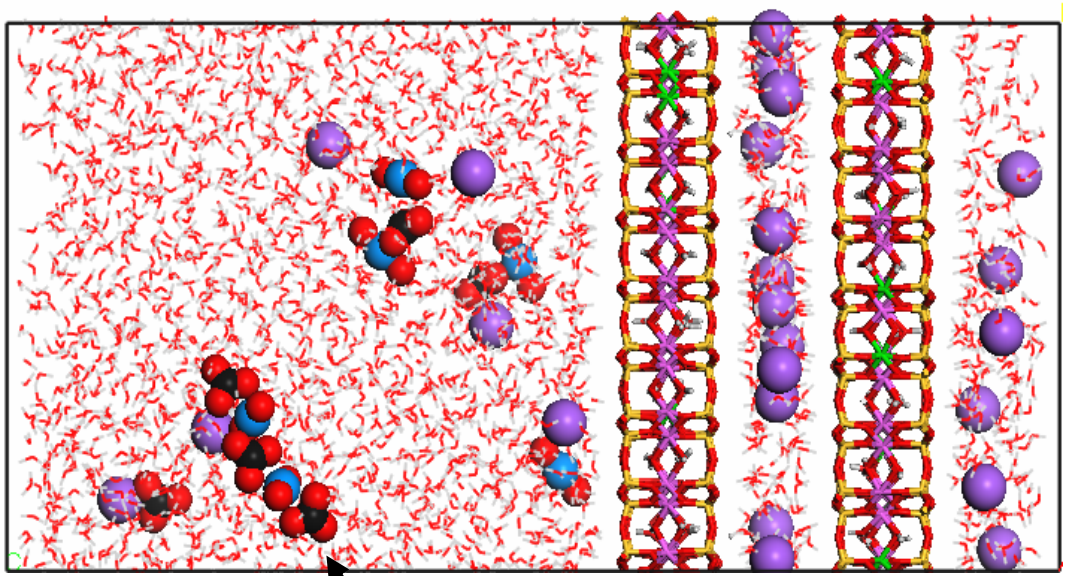
UO_2^{2+} sorption is influenced by solution concentration



Na^+ sorption is unaffected by solution concentration

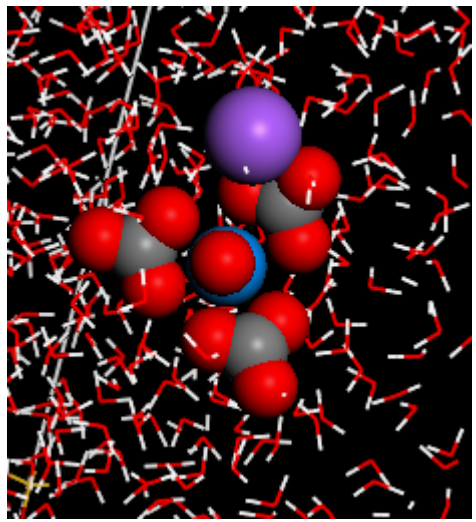
Greathouse and Cygan, *ES&T*, in press

Carbonato Complexes and Oligomers



$[(UO_2)_2(CO_3)_3]^{2-}$

$[UO_2(CO_3)_3]^{4-}$



High carbonate concentration hinders uranyl sorption

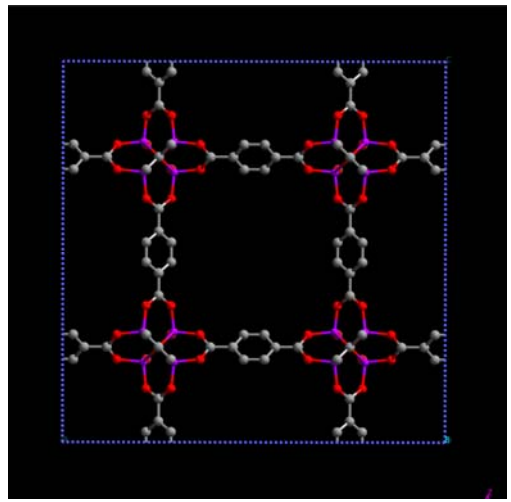
Curtis et al, *App. Geochem.* **2004**; Fuller et al, *ES&T* **2003**.

Zinc-based metal organic frameworks (MOFs): nanoporous materials with exceptional properties

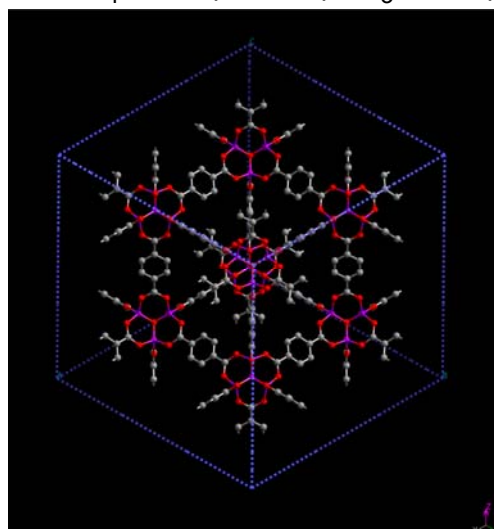
- MOFs are inorganic complexes linked by coordinated organic ligands
- Crystalline nanoporous materials
  - **Homogeneous, periodic pores**
  - **~4 - 19 Å aperture diameter; 13-29 Å Van der Waals diameter (calculated)**
  - **Extremely high surface areas (up to 4,500 m^2/g)**
  - **Very low density**

➡ Tunable pore environment for applications

➡ Rational design possible because crystallinity enables first-principles modeling



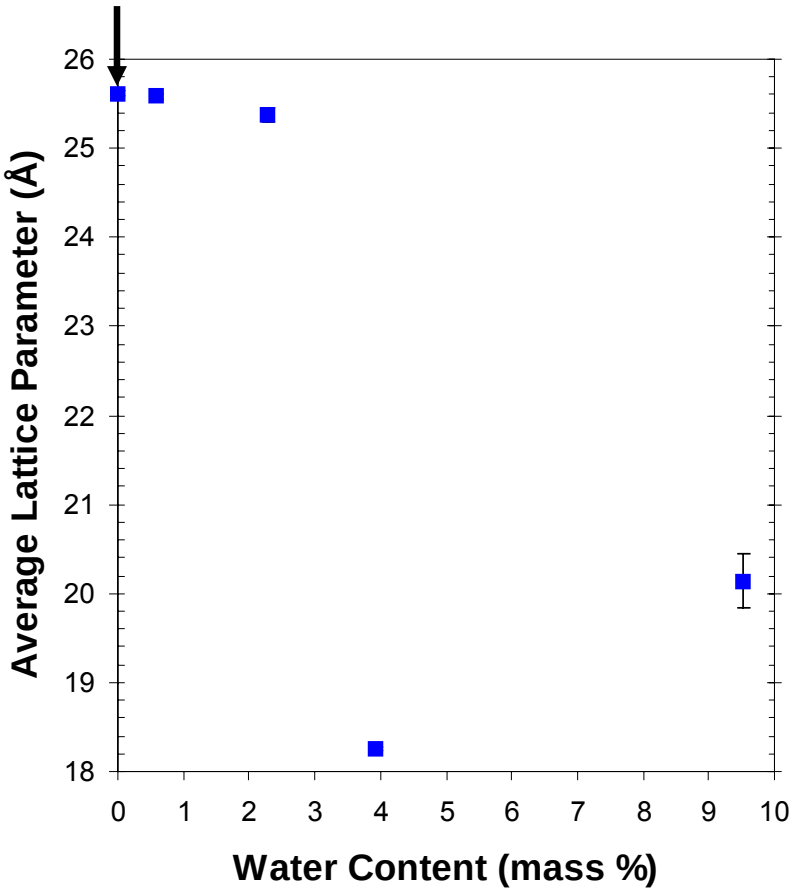
IRMOF-1: C_4 axis (above); C_3 axis (below)

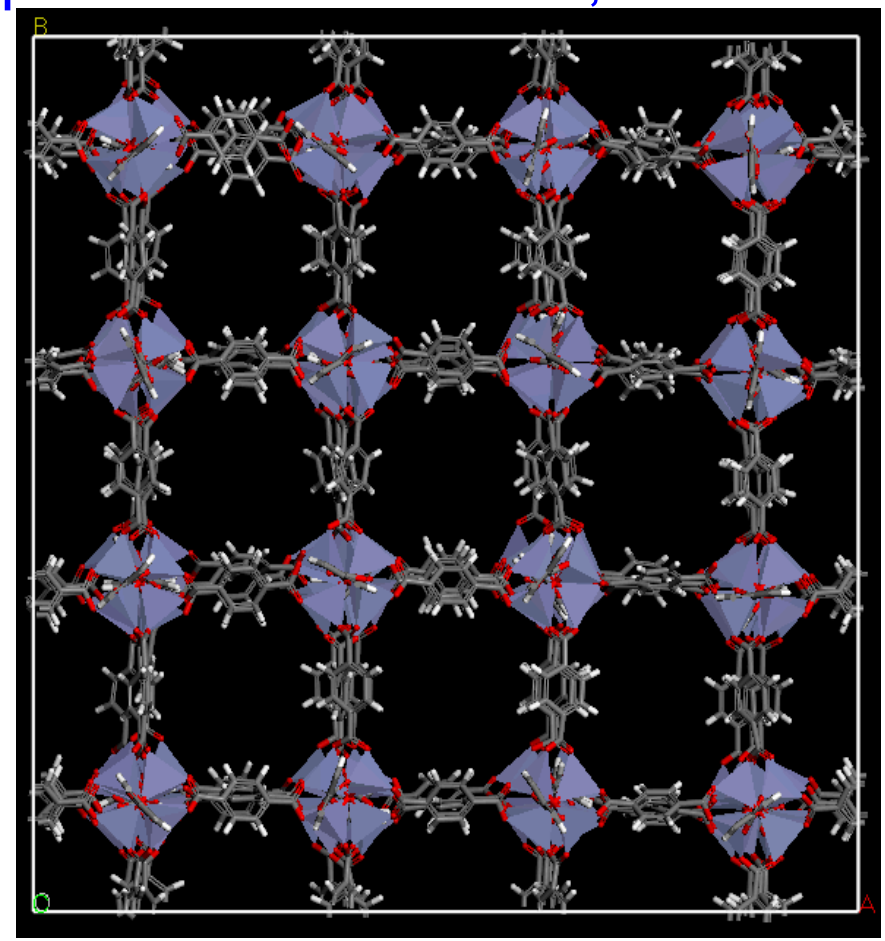


MOF5 (IRMOF-1): Zn_4O tetrahedra linked by benzene dicarboxylate linkers

MD simulations reveal substantial molecular motion by the solvent-free MOF5 lattice

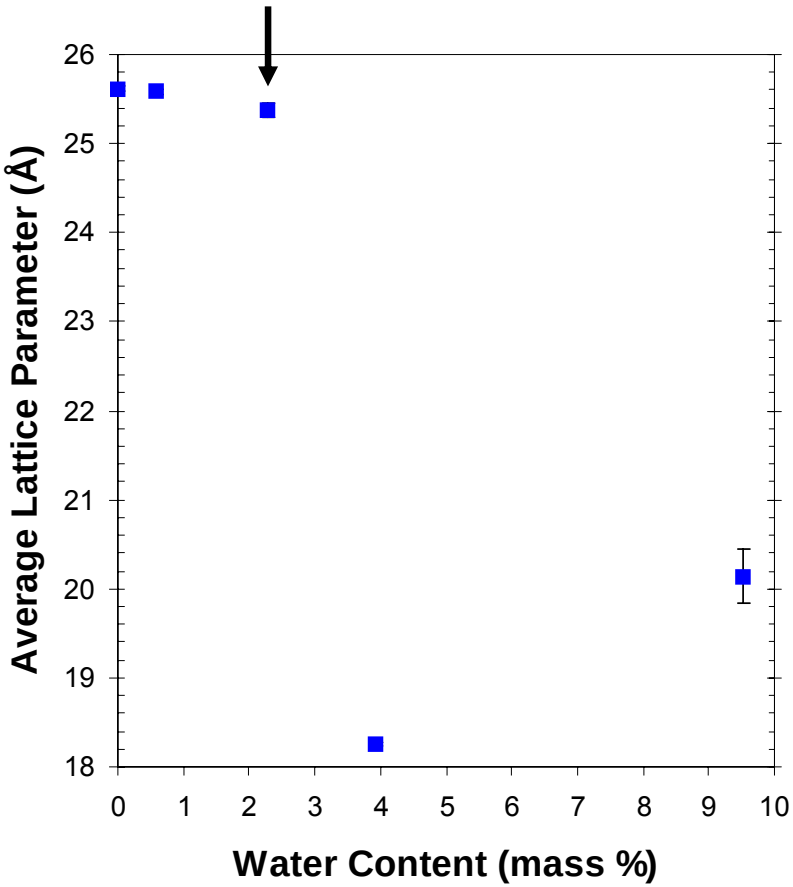
0.0% Water, lattice parameter = 25.61 Å, 300 K

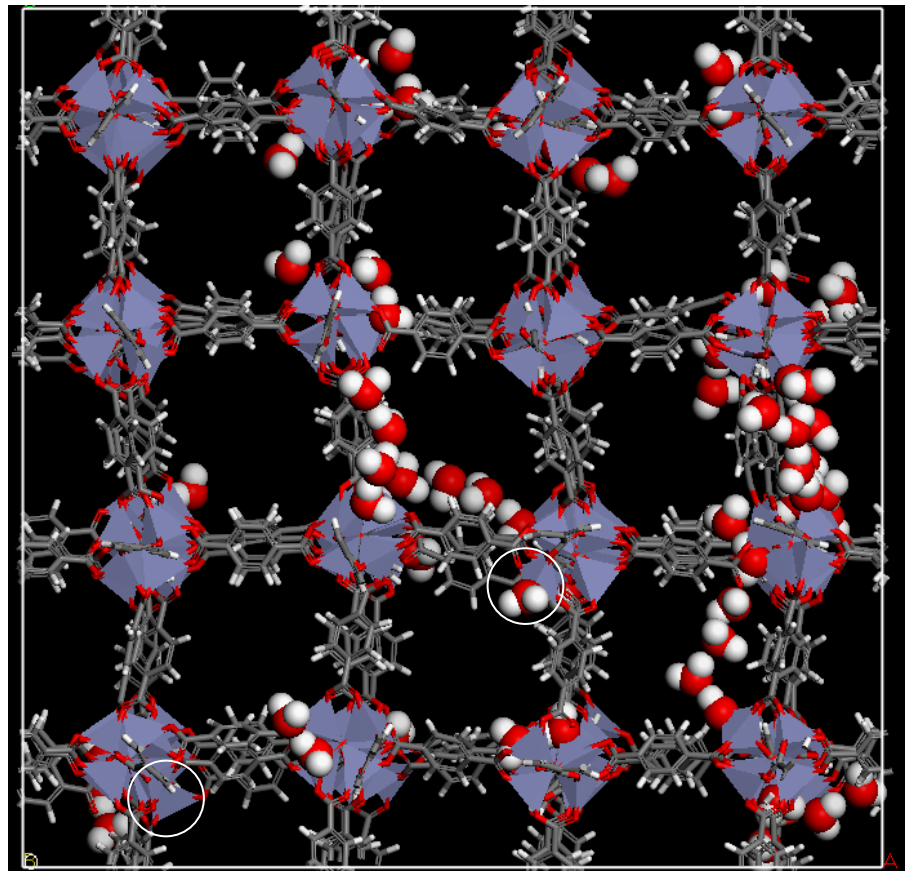




Increasing the amount of H_2O results in chains of hydrogen-bonded water molecules

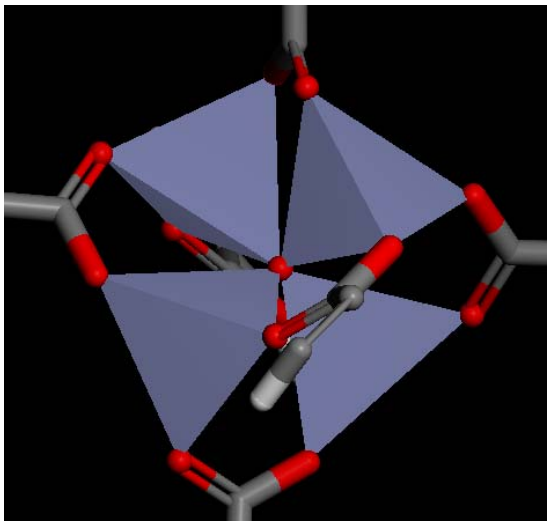
2.3% Water (9 H_2O/unit cell), 25.37 Å, 300 K



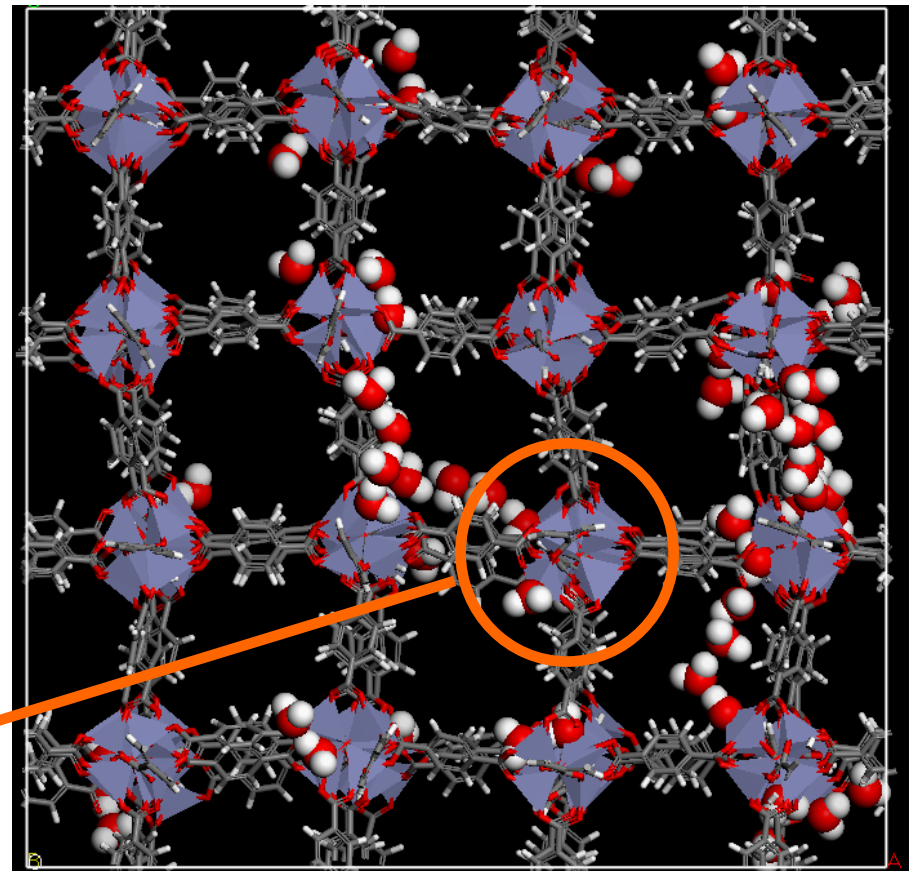


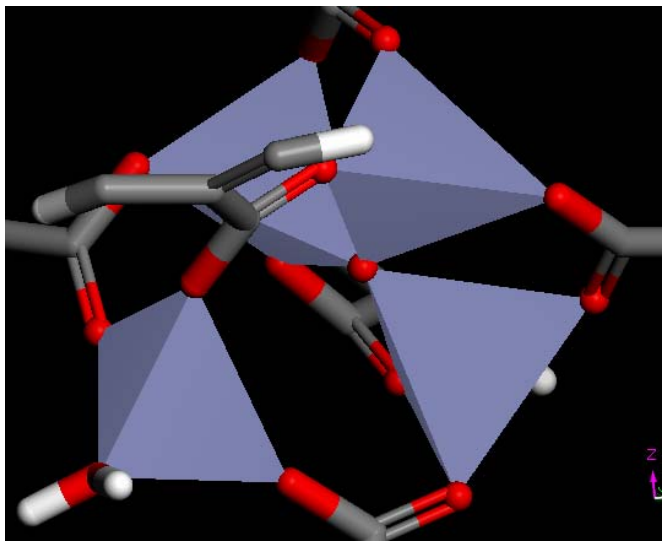
Water molecules gradually replace framework O atoms. Zn-O_{water} distance ≈ 1.9 Å.

Close examination indicates that H_2O disrupts the tetrahedral geometry of the Zn_4O cluster



Equilibrium structure, no H_2O





MOF5 structural collapse

9.5% Water (36 H_2O/unit cell), 20.14 Å, 300