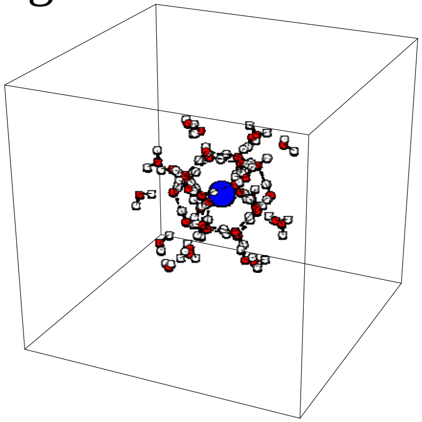
Xe in the cages of a hydrogen bonded network

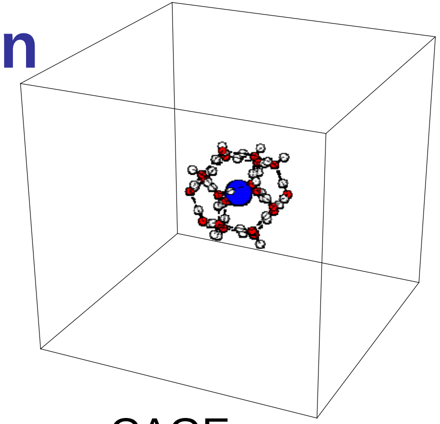
- Generate crystal fragment by replicating 1 unit cell with a valid proton configuration: 47.93 Å on the side, 4x4x4 unit cells, 2944 water molecules

Cynthia J. Jameson
and Dirk Stueber

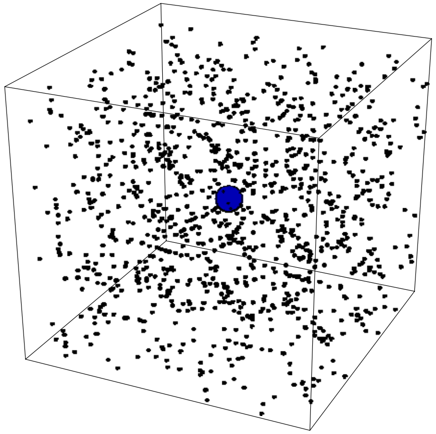
RMC 2002



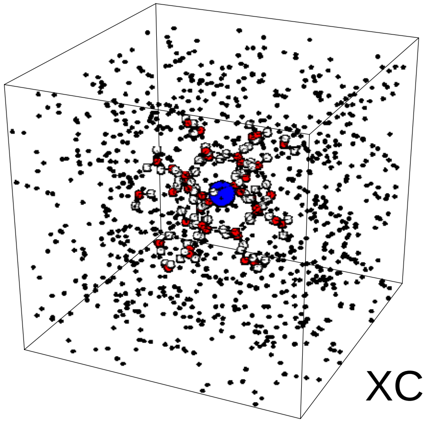
XCAGE



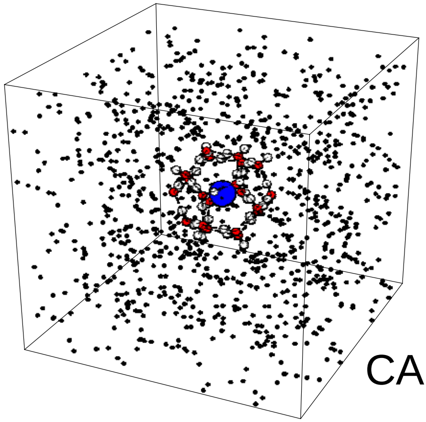
CAGE



PCA



XCAGE/PCA



CAGE/PCA

University of Illinois At Chicago

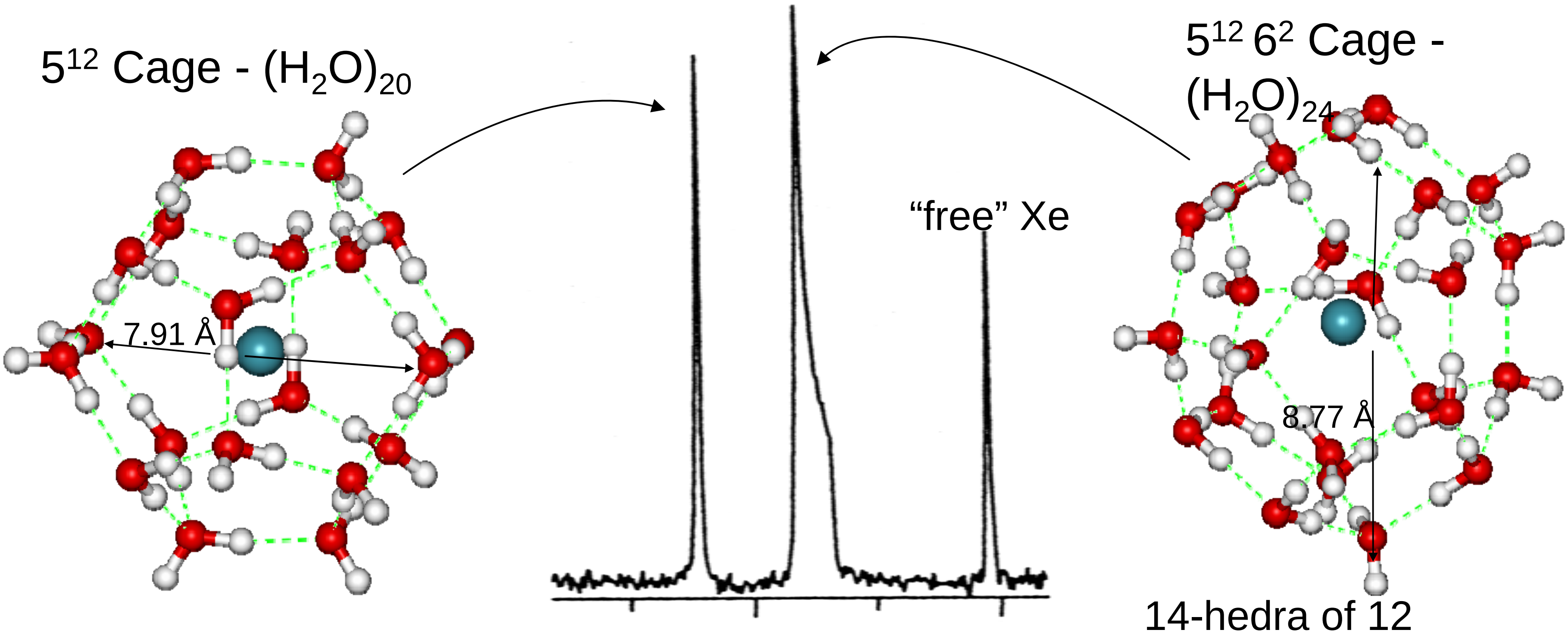
MOTIVATION

- Xe chemical shieldings and quadrupolar coupling interactions are very sensitive to void size and shape in clathrates[1,2]
- Structure of Xe clathrate hydrates of type I:

Cubic unit cell: a = 11.9825 Å, 46 water molecules

2 types of cages: 5^{12} (“small”) : $5^{12}\,6^{2}$ (“large”) = 1: 3

3-D disordered hydrogen-bonded network of H_2O molecules



5^{12} Cage - $(H_2O)_{20}$

Dodecahedron of 12 pentagonal faces

Moudrakovski et al.[2]

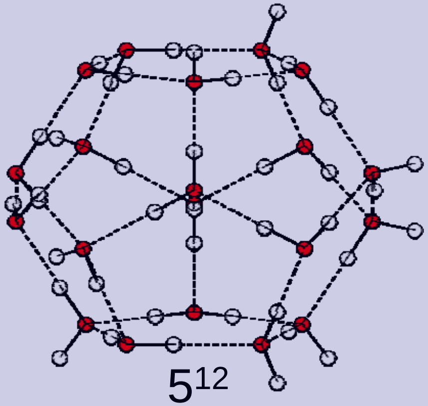
$5^{12}\,6^{2}$ Cage - $(H_2O)_{24}$

14-hedra of 12 pentagonal and two hexagonal faces

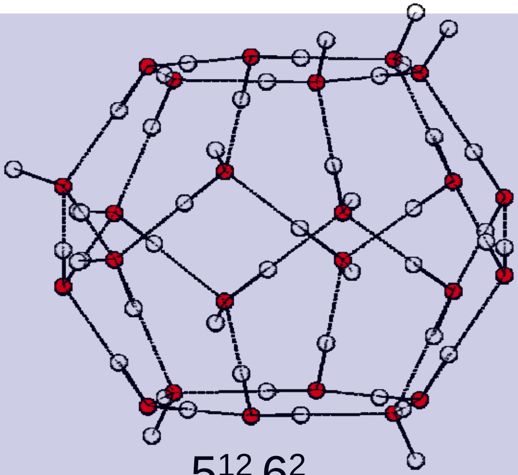
Clathrate hydrates

the cages

Structure I

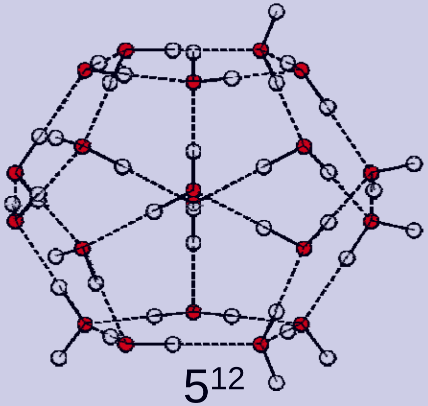


5^{12}

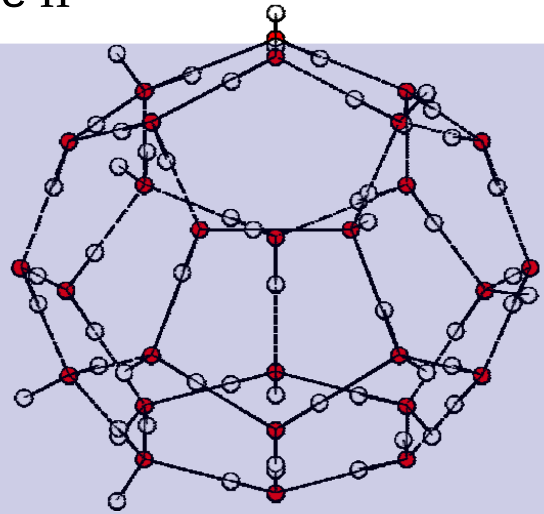


$5^{12}\ 6^{2}$

Structure II



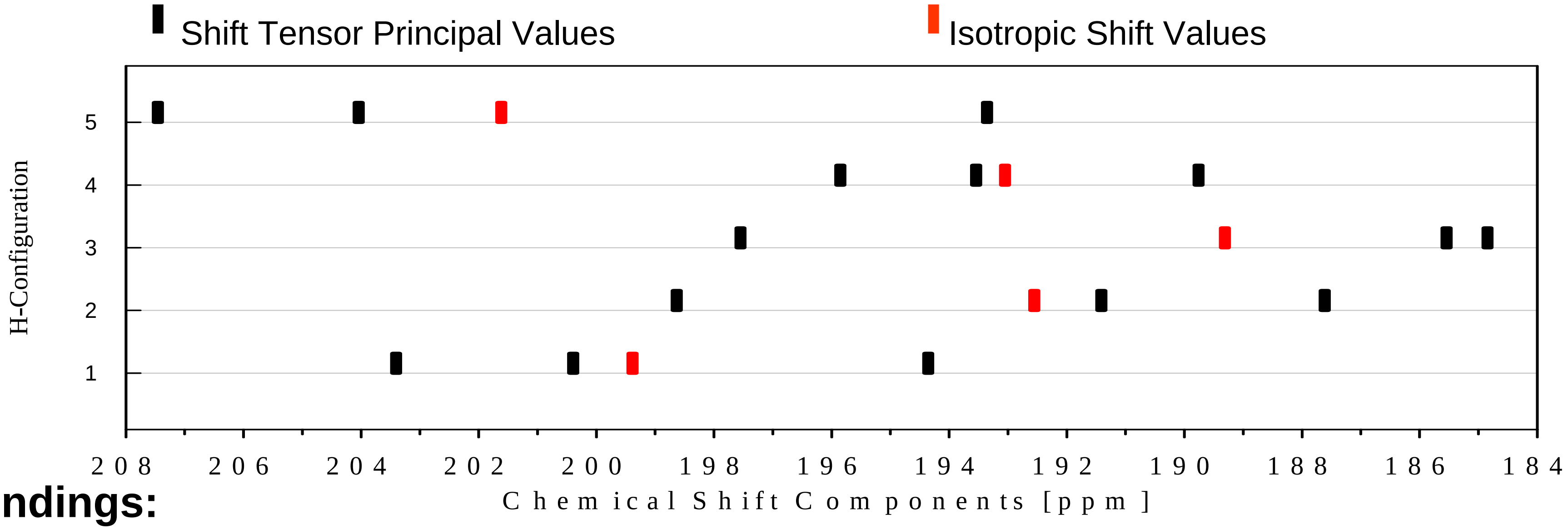
5^{12}



$5^{12}\ 6^{4}$

DIFFERENT PROTON CONFIGURATIONS

Ab initio chemical shifts for Xe at center of small cage using XCAGE/PCA model



Findings:

- Xe chemical shift values and anisotropy depend on H-configuration
- Use of single unit cell with “frozen” proton configuration to generate crystal fragments leads to “artificial” Xe chemical shift anisotropy in 5^{12} cage
- Need to somehow average over proton configurations, by having Xe occupy a variety of cages in simulation box of “supercells”. “Supercell” would contain a large enough number of unit cells such that a large number of different proton configurations is included within it. Replicate “supercells” to generate crystal fragment

Xe in the cages of clathrate hydrates Structure I and II

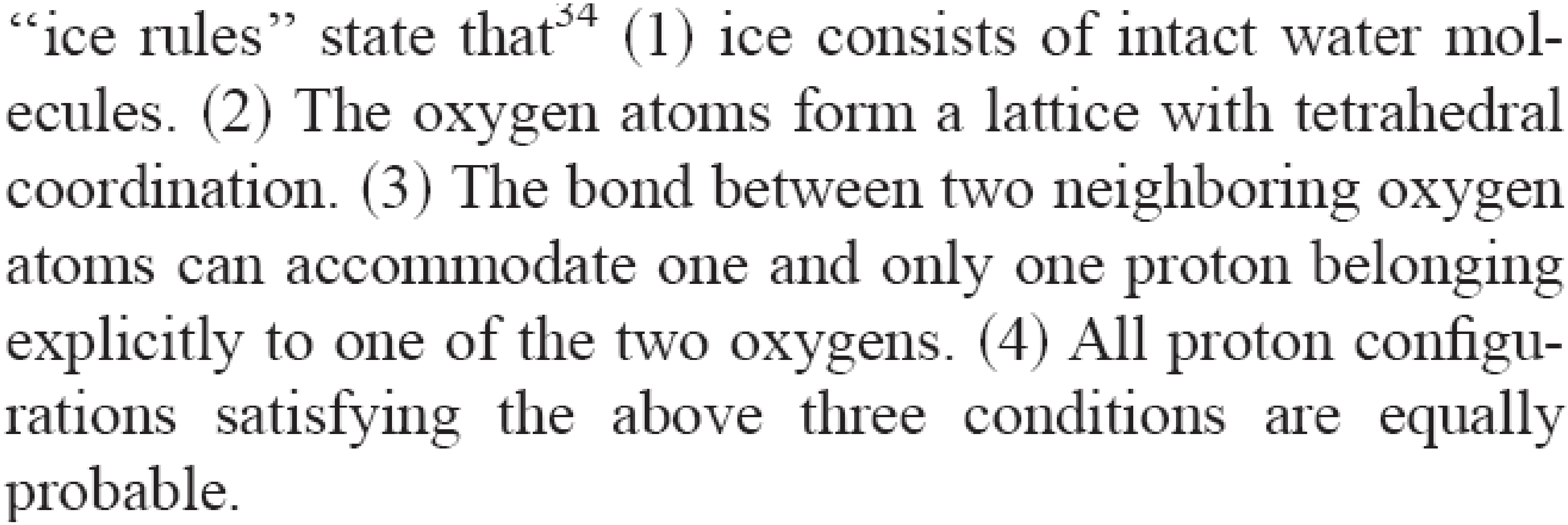
interesting as a test:

- a hydrogen-bonded network
- disordered proton configurations, yet must obey ice rules
- try out an additive pair tensor model

How to generate the coordinates of atoms in 4x4x4 unit cells of a clathrate hydrate having a valid configuration of protons?

Neutron diffraction provides all H positions, but with 1/2 populations.
What to do?

A valid configuration must obey the ice rules:



"ice rules" state that[34] (1) ice consists of intact water molecules. (2) The oxygen atoms form a lattice with tetrahedral coordination. (3) The bond between two neighboring oxygen atoms can accommodate one and only one proton belonging explicitly to one of the two oxygens. (4) All proton configurations satisfying the above three conditions are equally probable.

Monte Carlo

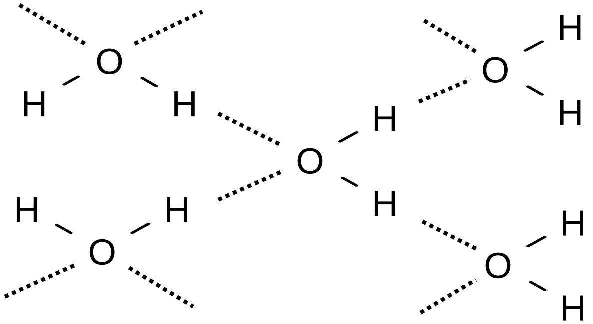
To satisfy the ice rules we need:
(1) only one H on each O-O line (in order to have the correct stoichiometry of H_2O_{cryst})
(2) each O must have two covalent H and 2 hydrogen-bonded H.

(a) random switching method:
Place one H in either of the two H positions on each O-O line. Permit H to shift to the other position on the same O-O line only, not elsewhere. This guarantees condition (1) is always satisfied. Use Monte Carlo to randomly shift various H along O-O; accept the move with probability according to the change in the total number of violations of (2).

(b) chain propagation method:
Find two problem O atoms. Shift H along a path from one to the other, no uphill steps are allowed, until both are satisfied.

PROTON DISORDER IN CLATHRATES

Obeys the Ice Rules

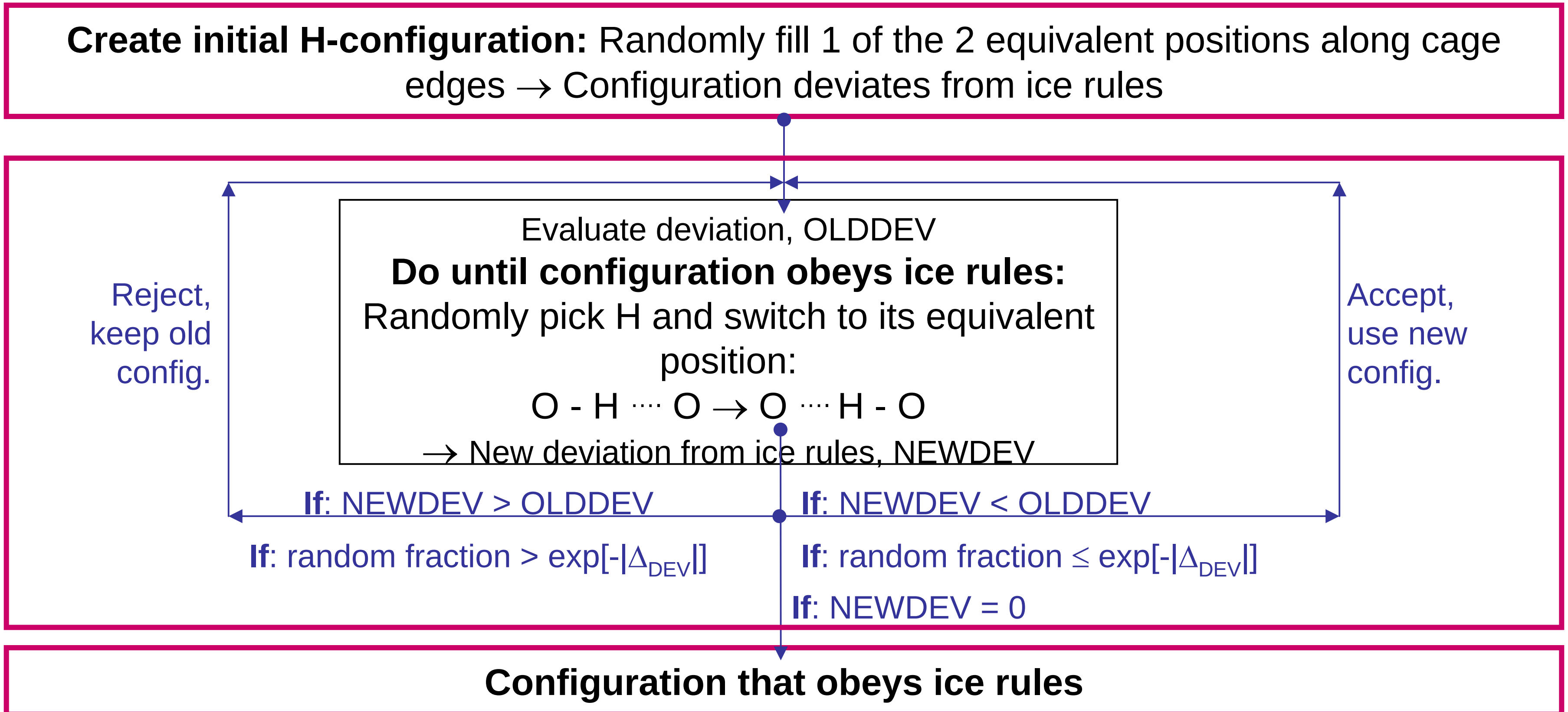


(1) Crystals contain intact water molecules
Line between two neighboring oxygens can accommodate only one proton

(2) Oxygen atoms form lattice with tetrahedral coordination

(3) Proton configurations that satisfy the above two conditions are equally probable

Generate H-Configuration for 1 unit cell in MC Simulation:



Create initial H-configuration: Randomly fill 1 of the 2 equivalent positions along cage edges → Configuration deviates from ice rules

Evaluate deviation, OLDDEV

Do until configuration obeys ice rules:

Randomly pick H and switch to its equivalent position:

O - H ···· O → O ···· H - O

→ New deviation from ice rules, NEWDEV

Reject, keep old config.

If: NEWDEV > OLDDEV

If: random fraction > $\exp[-|\Delta_{DEV}|]$

Accept, use new config.

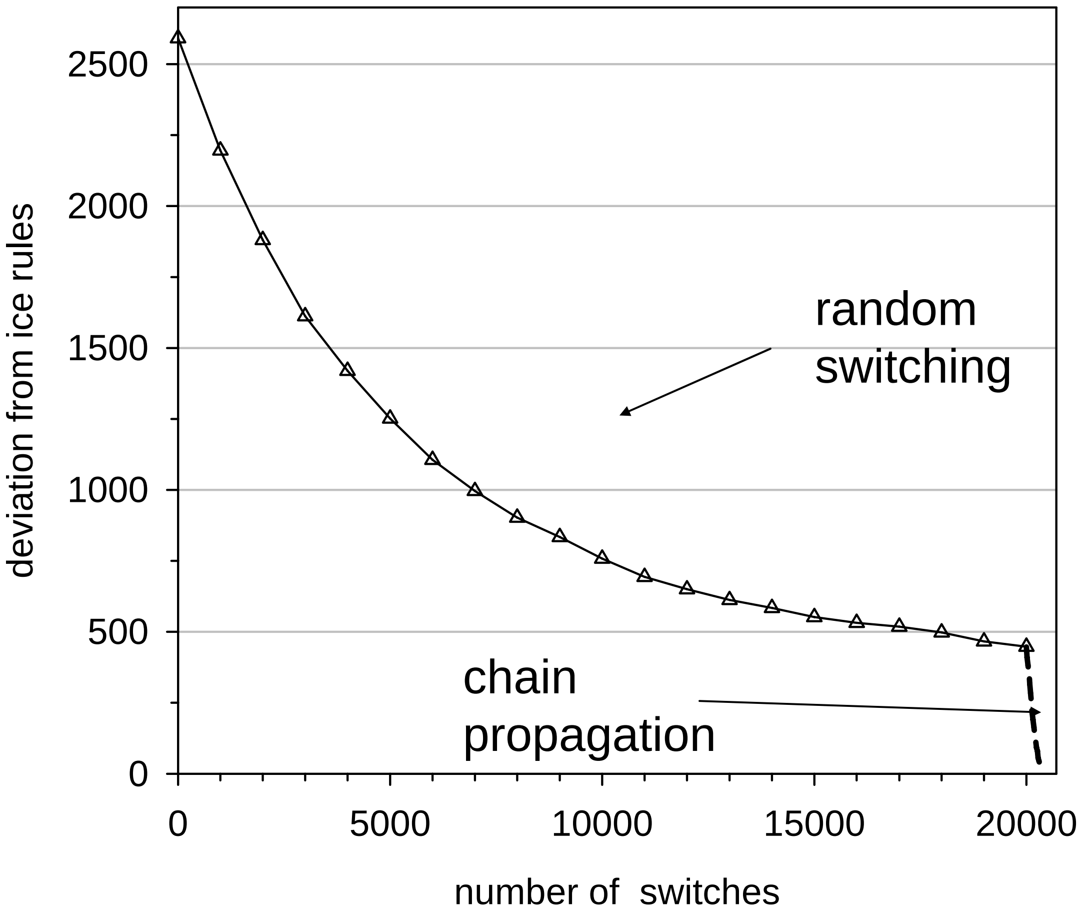
If: NEWDEV < OLDDEV

If: random fraction ≤ $\exp[-|\Delta_{DEV}|]$

If: NEWDEV = 0

Configuration that obeys ice rules

Generating proton configurations that obey the ice rules



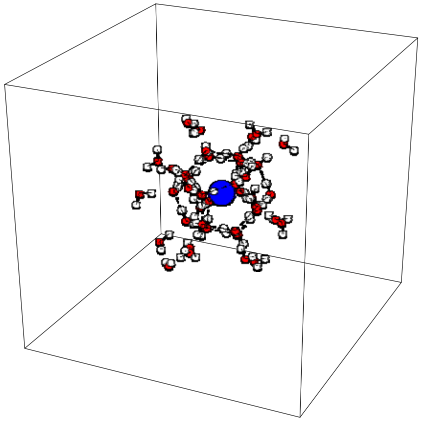
supercell of
Structure I
4x4x4 unit cell
2944 H_2O molecules

Chain propagation technique very efficient!

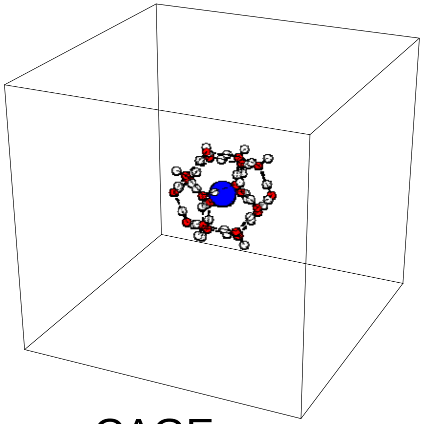
How to model a cage in a hydrogen bonded network?

Generate crystal fragment with a valid proton configuration:
47.93 Å on the side, 4x4x4 unit cells, 2944 water molecules

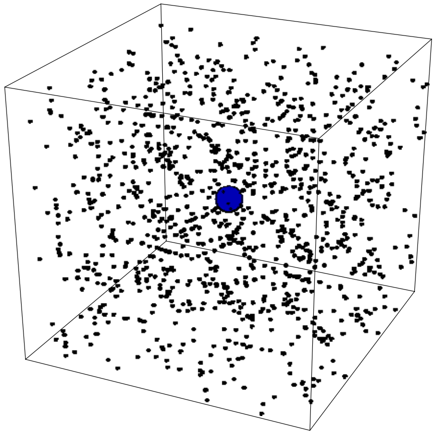
MODELS



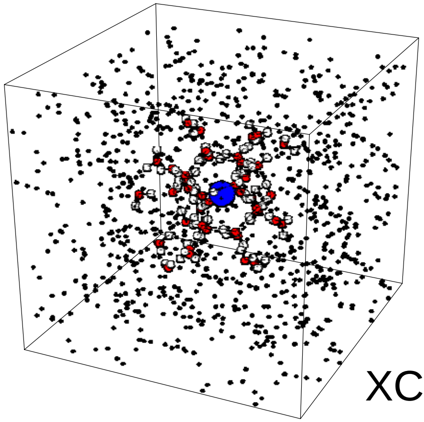
XCAGE



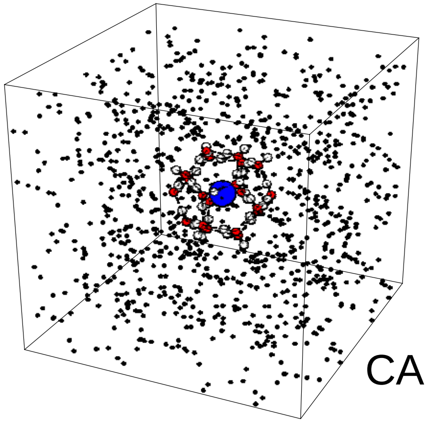
CAGE



PCA



XCAGE/PCA



CAGE/PCA

PARTIAL POINT CHARGES

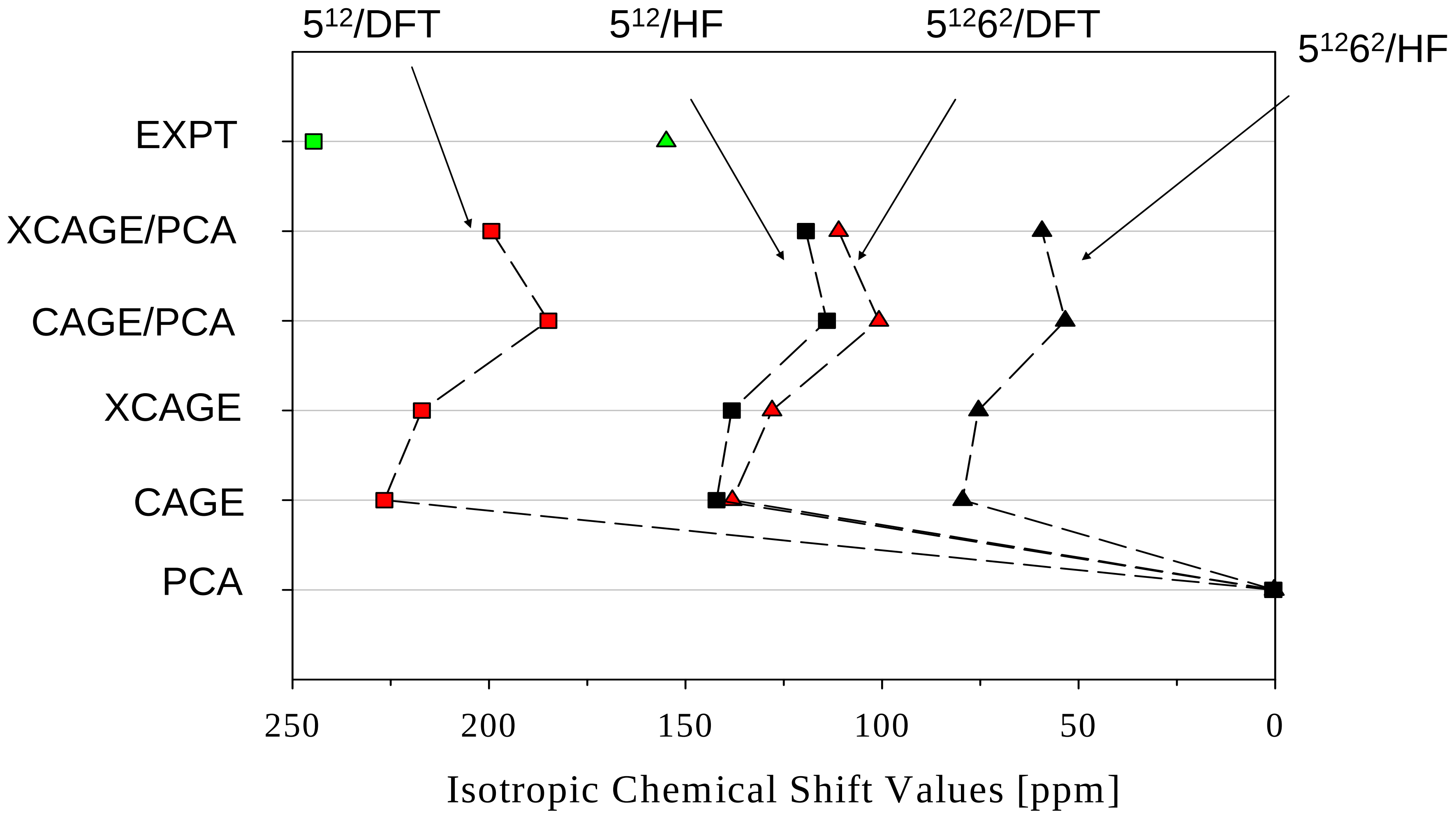
- EIM[4] approach is used to obtain partial point charges

  for each crystallographic atom position

  Point charge array simulates Madelung potential

  in defined region at center of crystal fragment

Single point isotropic shielding Xe at center of cage*



*__proton configuration 1__

Xe shielding from electrostatics

for 5^{12} cage in Structure I

σ_{iso}(Xe at center of model) -σ(free Xe atom)

PCA	**CAGE**	**XCAGE**	**CAGE/PCA**	**XCAGE/PCA**
-0.4 ppm HF	-142.1	-138.2	-114.0	-119.4
-0.5 ppm DFT/B3LYP	-226.6	-217.0	-184.9	-199.4

purely electrostatic negligible shielding response

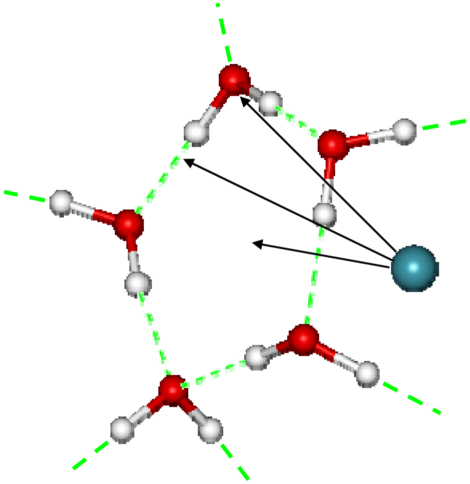
without its hydrogen-bonding partners, H_2O provides too large a response at Xe

use the more complete model, and include electron correlation

CALCULATE Xe SHIELDING SURFACES USING THE XCAGE/PCA MODEL

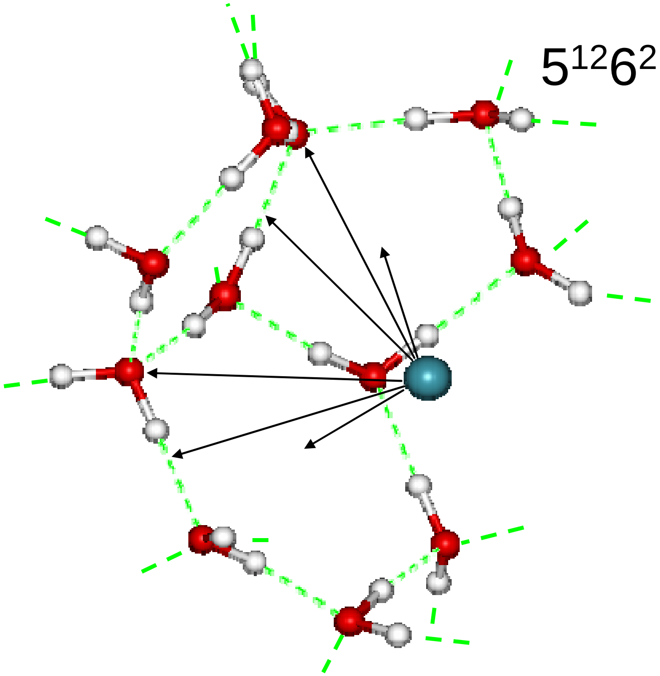
- Require Xe shieldings at other positions than center of cage to interpret experiment
- Calculate ab initio isotropic Xe shielding values at points along different approach trajectories using XCAGE/PCA model
- Use B3LYP and D95** for O, H, and 240 basis functions for Xe

5^{12} Cage



5 points along each trajectory

$5^{12}6^{2}$ Cage



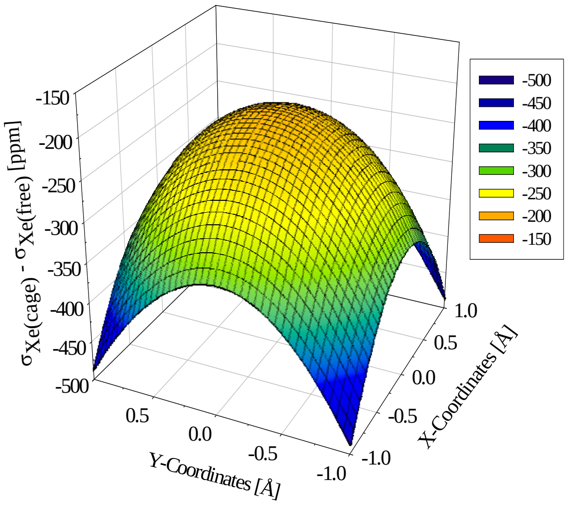
4 points along each trajectory

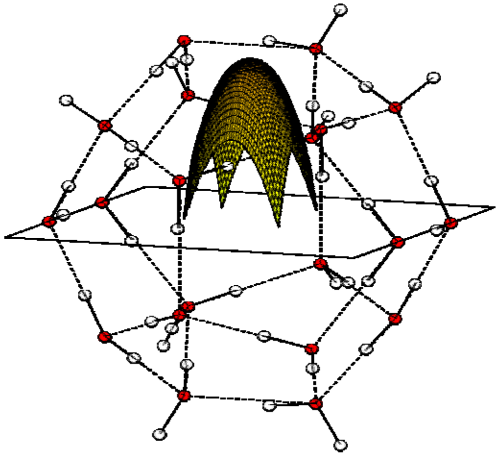
- Represent ab initio shielding values in one-site fit using function:

$$\sigma(r) = \sum_{i=1}^{NO} \frac{C_{O6}}{(r_{Xe\text{-}O_i})^{6}} + \frac{C_{O8}}{(r_{Xe\text{-}O_i})^{8}} + \frac{C_{O10}}{(r_{Xe\text{-}O_i})^{10}} + \frac{C_{O12}}{(r_{Xe\text{-}O_i})^{12}} + \frac{C_{O14}}{(r_{Xe\text{-}O_i})^{14}}$$

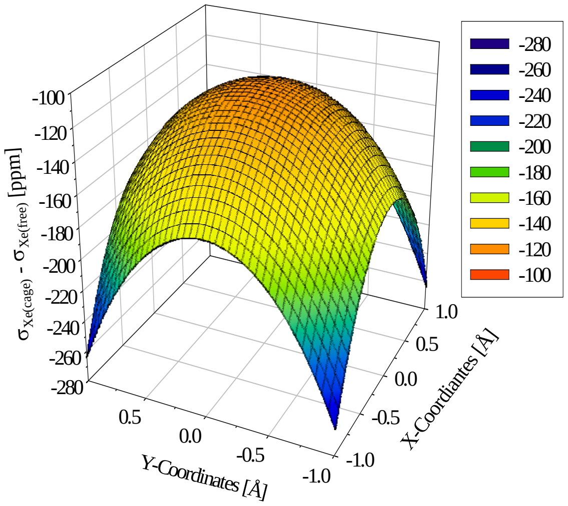
Fitting parameters: $C_{O6}, \ldots, C_{O14}$

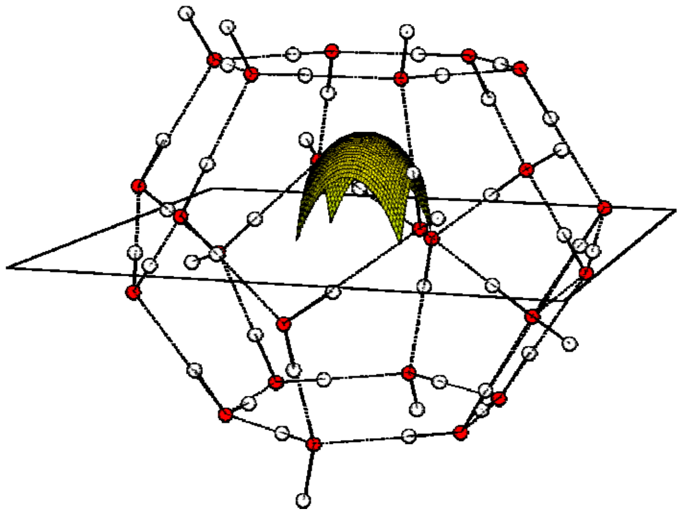
THE Xe SHIELDING SURFACES





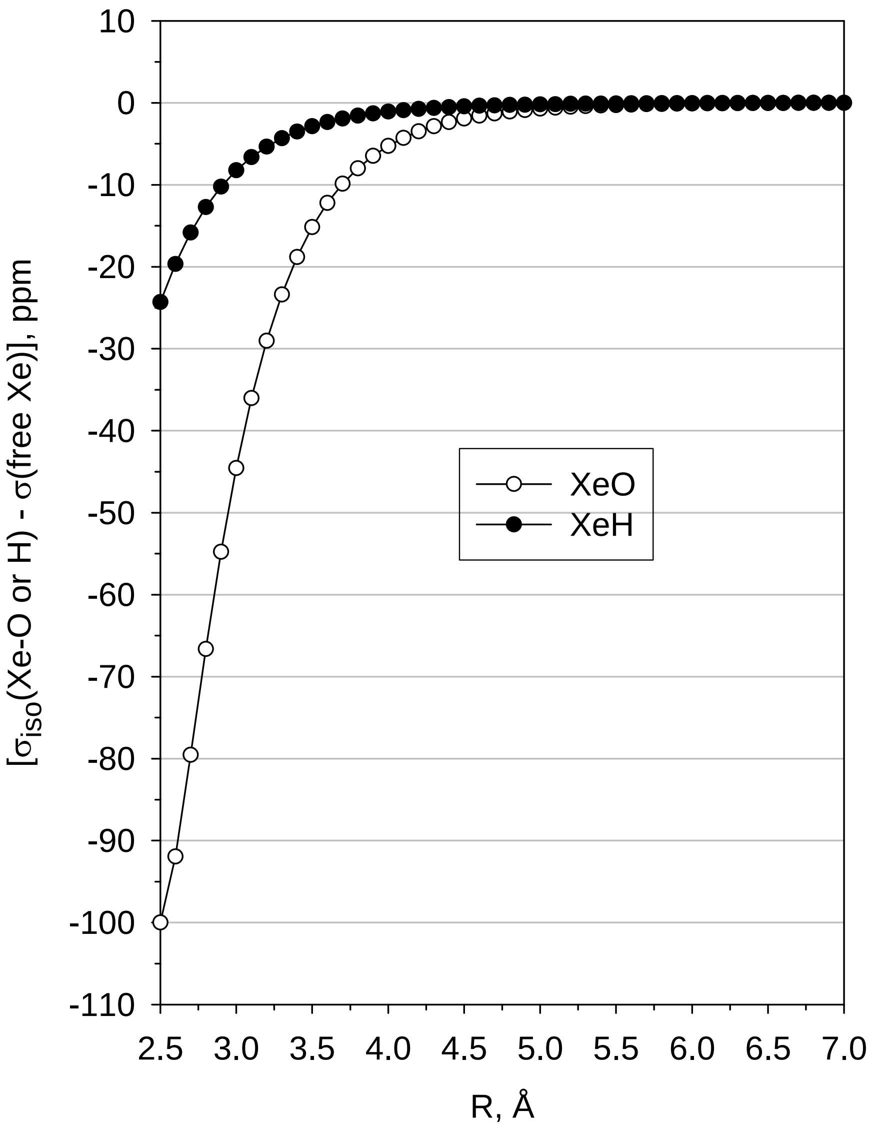
5^{12} Cage



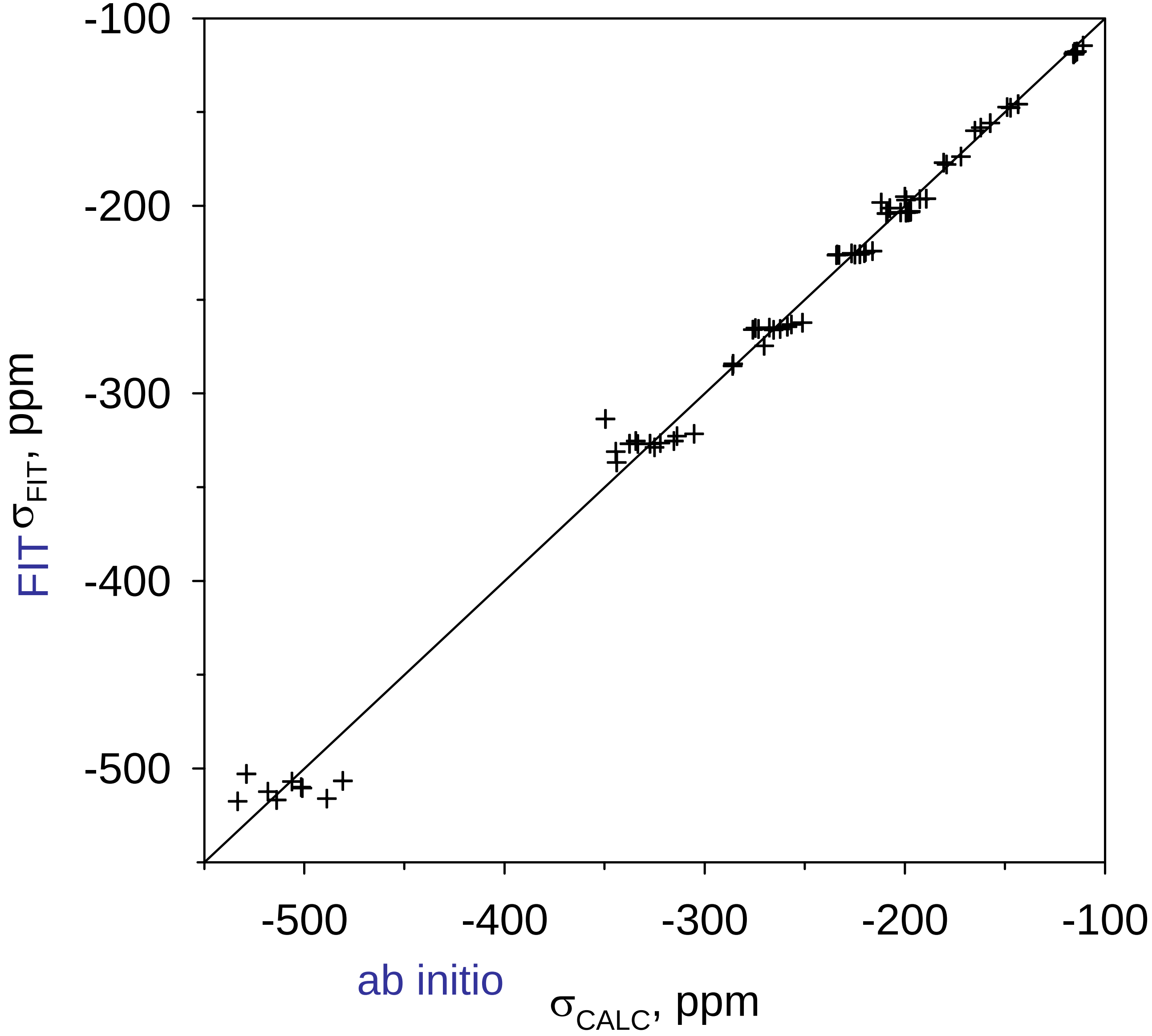


$5^{12}6^{2}$ Cage

Xe isotropic shielding functions σ(Xe-O) and σ(Xe-H)

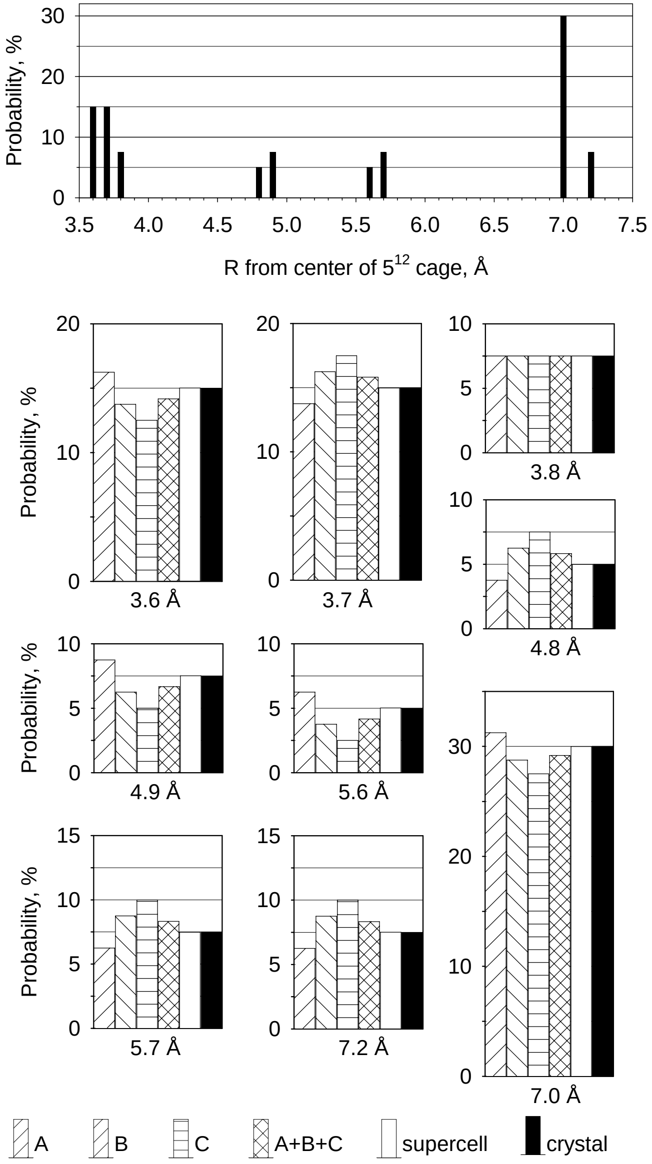


FIT to pairwise additive (Xe-O and Xe-H) isotropic shielding



- Electron correlation has to be included in QM calculations
- PCA model produces insignificant shielding response
- CAGE gives highest shielding response
- Use of point charge array to account for hydrogen-bonding of cage to <u>crystal</u> gives incomplete response
- For realistic response, need “real” H_2O molecules hydrogen-bonded to cage <u>and</u> point charge array, XCAGE/PCA model

Distribution of H positions within a cage



“mean free path” inside a zeolite is a false concept.
Xe does not move across the pore like in the gas,
but spends most of its time close to the walls,
according to the potential energy surface.

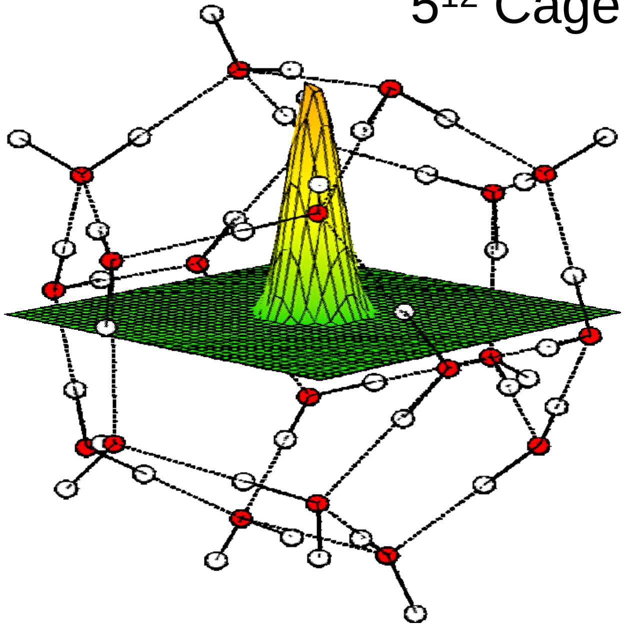
Xe is not immobilized in sites.
Although there are positions corresponding to
lowest potential energy, Xe does not sit there
unless it has very little kinetic energy (ultra-low T),
rather, there are various probabilities of finding Xe in
the pore, more localized or less according to T.

METROPOLIS MONTE CARLO SHIELDING AVERAGING

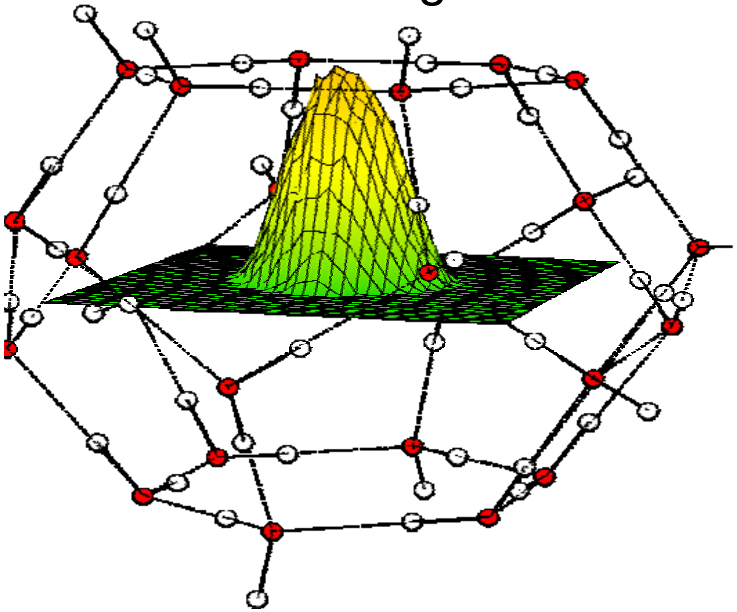
Use ab initio shielding surface and Lennard-Jones V(Xe-O)^5: r_0 = 3.700 and ε = 0.753 kJ/mol

Xe one-body distribution functions at 275 K:

5^{12} Cage

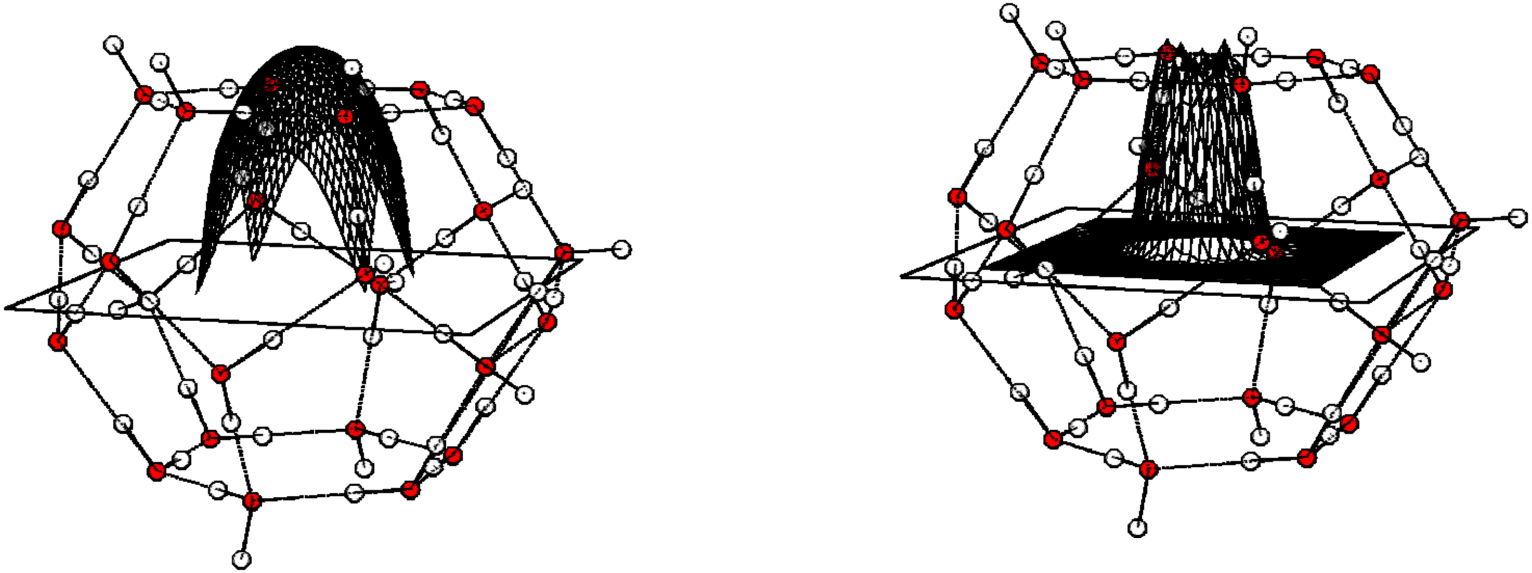


$5^{12}\,6^2$ Cage



The Xe SHIELDING SURFACE: the shielding as a function of configuration (coordinates) of the system

The Xe one-body distribution: the PROBABILITY of finding the system in a given configuration



(a) isotropic shielding surface

(b) one-body distribution surface

Xe in the $5^{12}6^{2}$ cage of clathrate hydrate Structure I

Xe isotropic chemical shift values, ppm

Method	Small Cage	Large Cage
EXPT	244.6	154.9
XCAGE/PCA	225.3	143.8

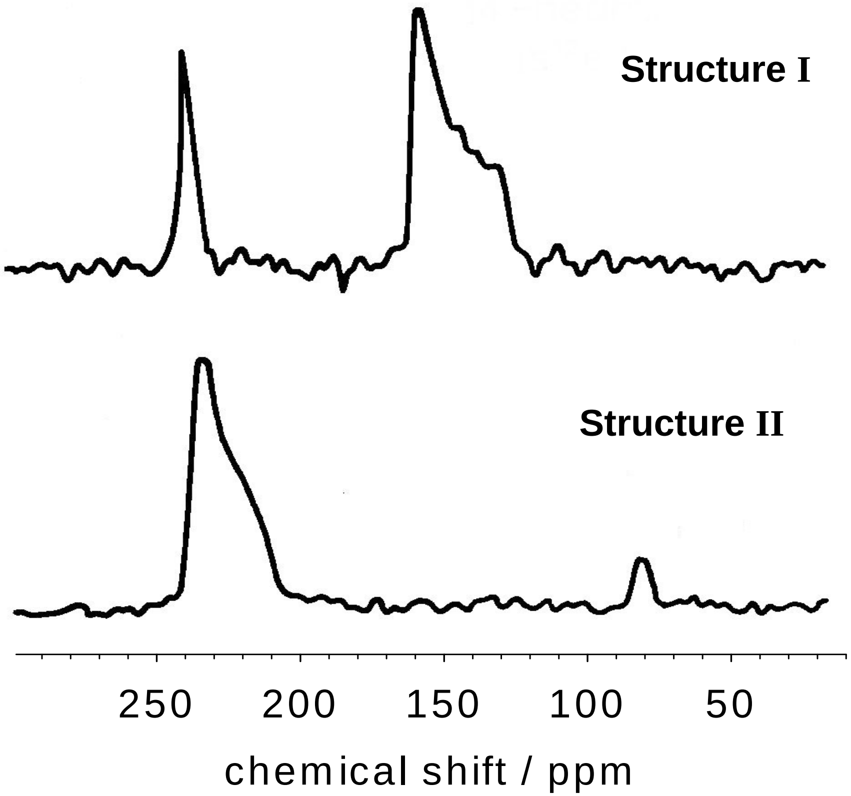
SUMMARY

- Electric polarization alone (PCA model) does not account for Xe chemical shifts
- Need at least 1 shell of “real” waters hydrogen bonded to the cage water molecules
- Proton dynamics have to be included in the average, e.g., by using a crystal fragment of supercells which have “natural” disorder of proton positions
- Xe probes electronic structure of entire crystal, although shift tensor is dominated by symmetry of the cage it is in.

Using XCAGE/PCA model and MC averaging, experimental isotropic chemical shifts of Xe trapped in small (large) cages are reproduced within 20 (10) ppm. [Better Xe-O potential may improve results.]

EPILOGUE

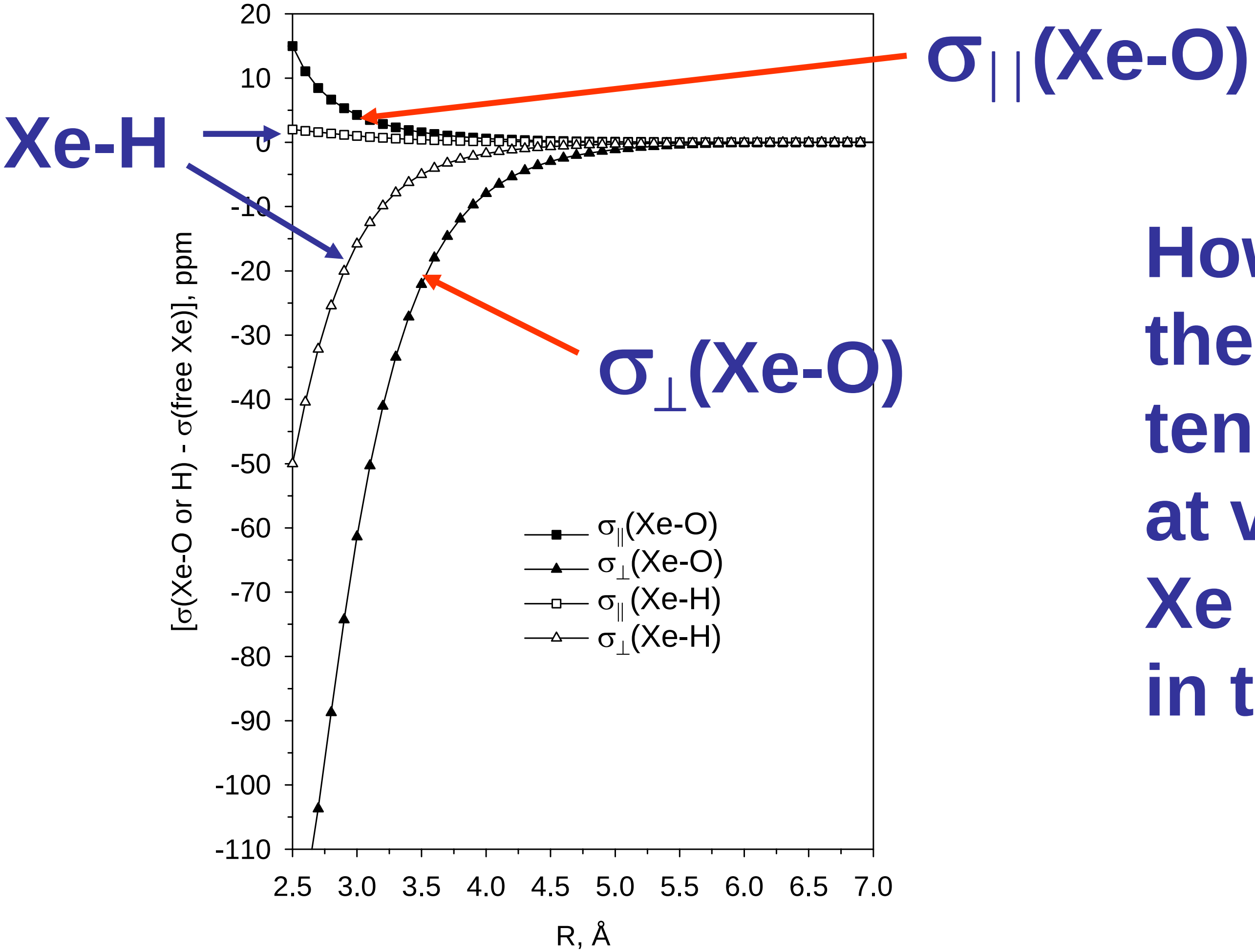
Need more than isotropic shielding



EXPERIMENTS

J. A. Ripmeester, C. I. Ratcliffe and J. S. Tse,
Trans. Faraday Soc. 1, 84, 3731 (1988)

The Xe-O and Xe-H shielding tensors



Xe-H

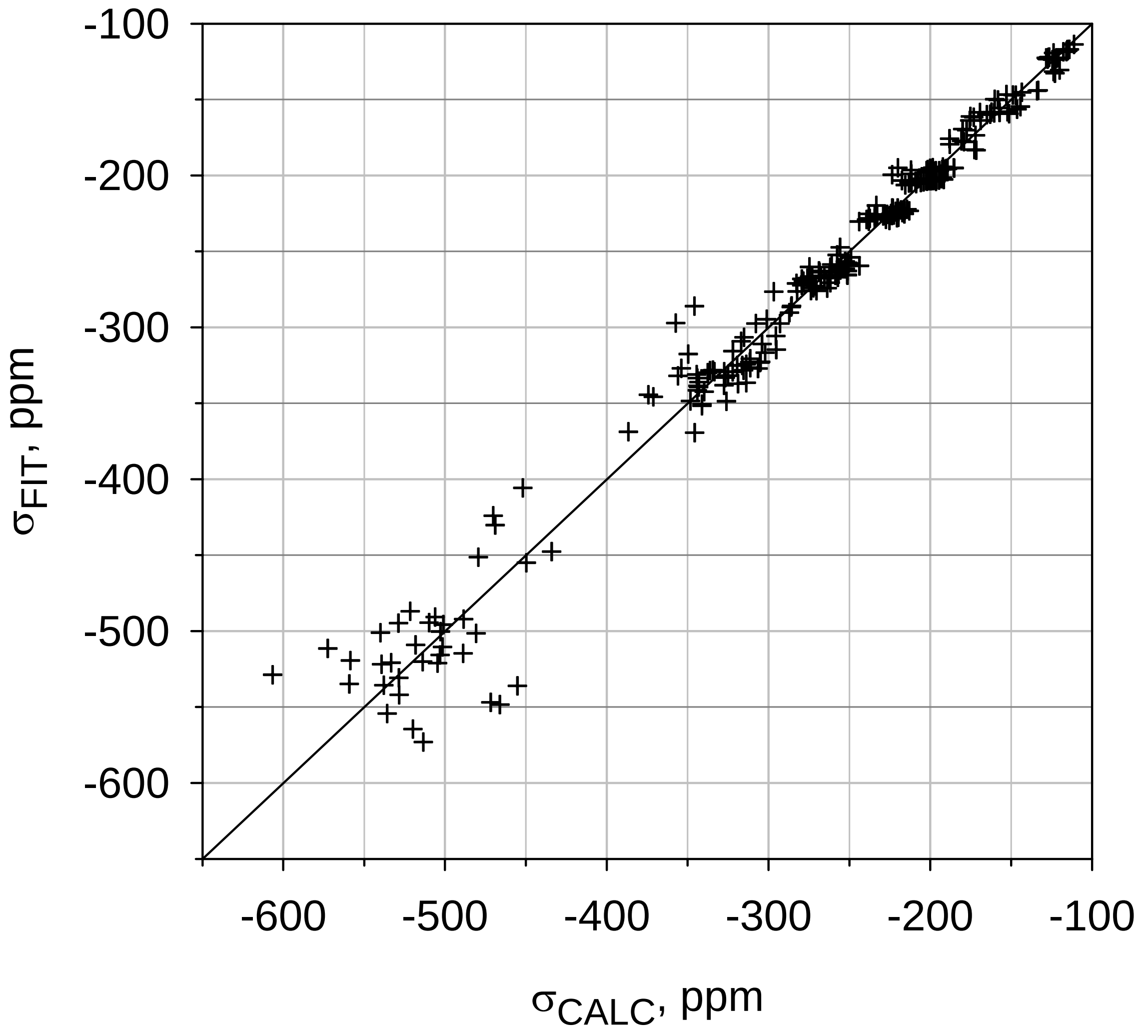
$\sigma_{||}$(Xe-O)

$\sigma_{\perp}$(Xe-O)

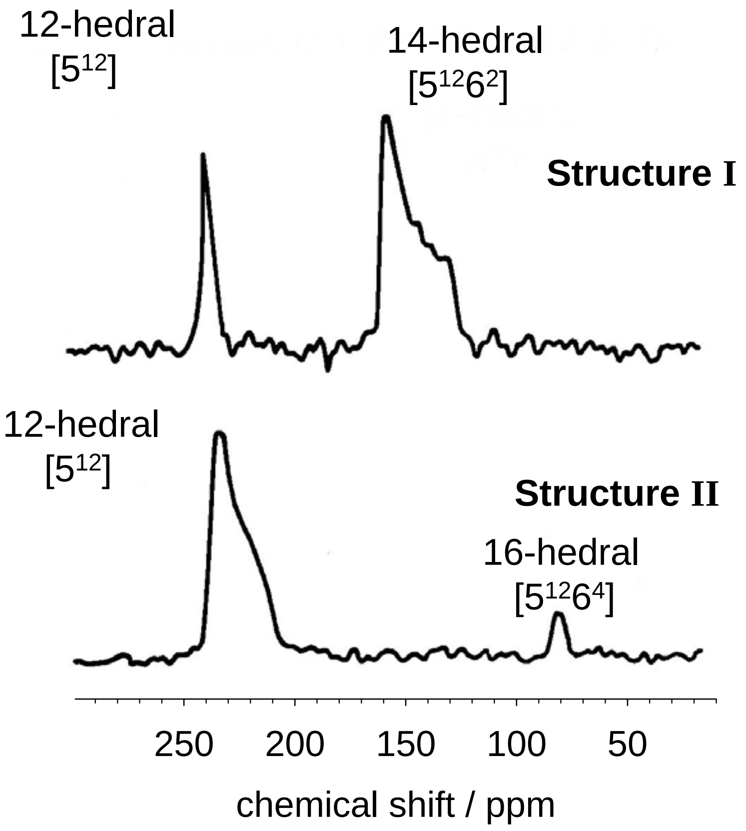
**How to describe
the ab initio
tensor values
at various
Xe positions
in the cage?**

Sums over these **pair** shielding functions
reproduce the ab initio Xe shielding tensor
at each Xe position within the cage (in model XCAGE/PCA)

Sum over pair shielding tensors deviate from ab initio tensor components



Xe in the cages of clathrate hydrates Structure I and II



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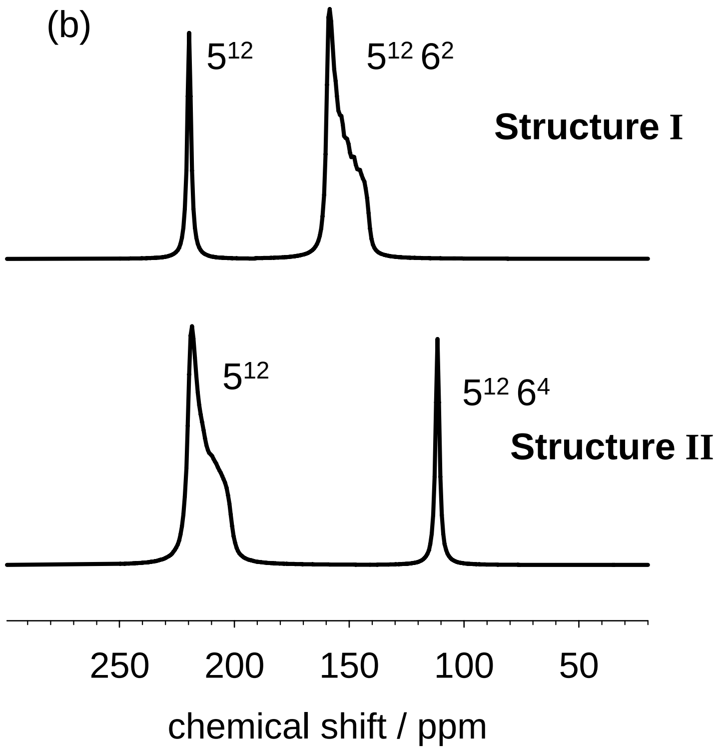
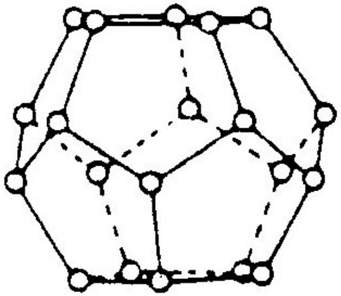


CALCULATIONS

Monte Carlo simulations in a
4x4x4 supercell and 2x2x2 supercell
D. Stueber and C. J. Jameson, 2003

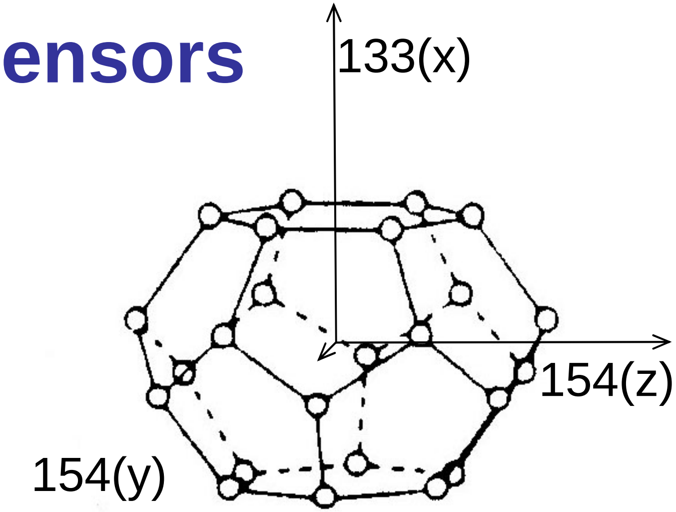
Xe chemical shift tensors

isotropic 214



5^{12}

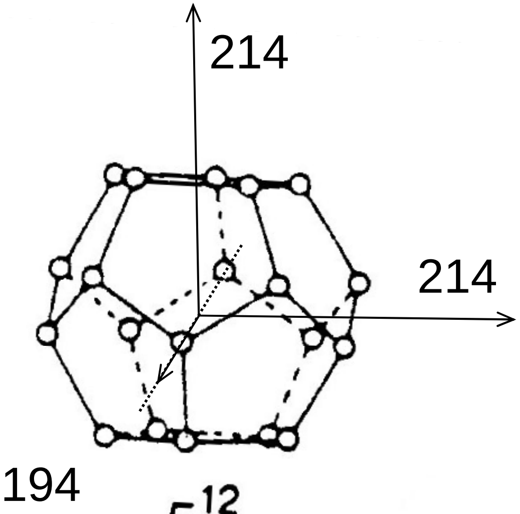
symmetric



$5^{12}6^{2}$

axial, disk-like

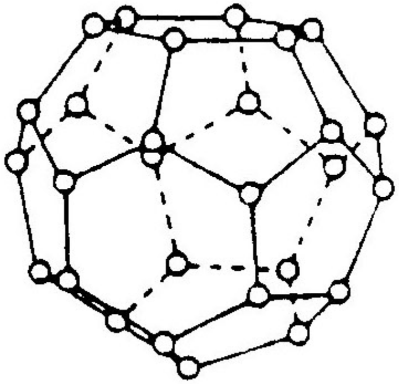
Clathrate Structure I



5^{12}

axial

isotropic 105

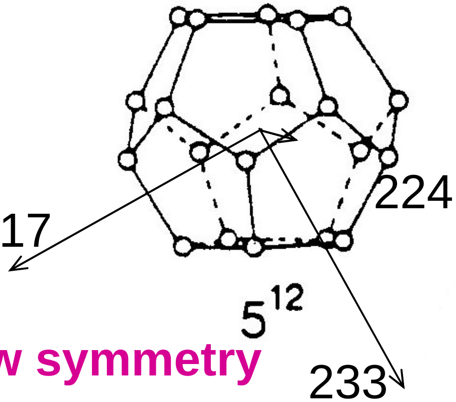


$5^{12}6^{4}$

symmetric

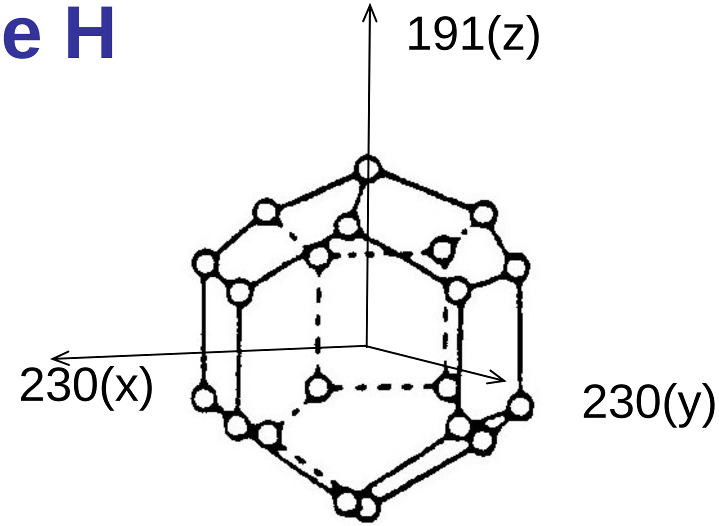
Clathrate Structure II

Xe tensors in Clathrate Structure H



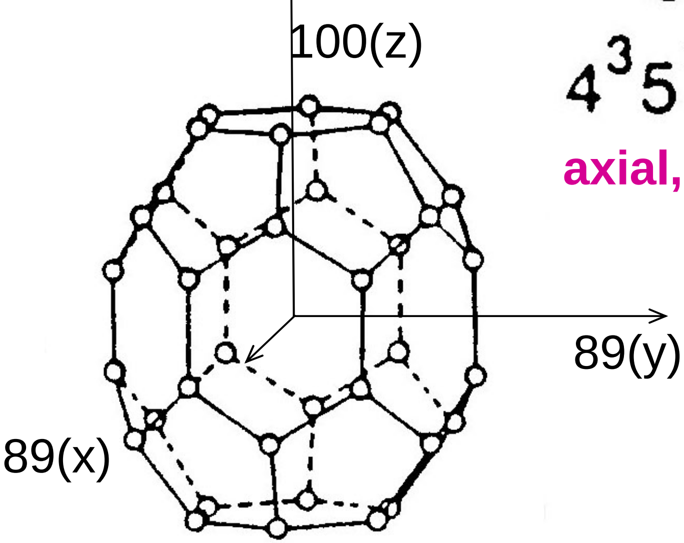
5^{12}

low symmetry



$4^3 5^6 6^3$

axial, squat



$5^{12} 6^8$

axial, elongated

ACKNOWLEDGMENT

This work was inspired by the series of experiments of John A. Ripmeester and his group which revealed for the first time that Xe can report its average tensor components in an anisotropic environment.