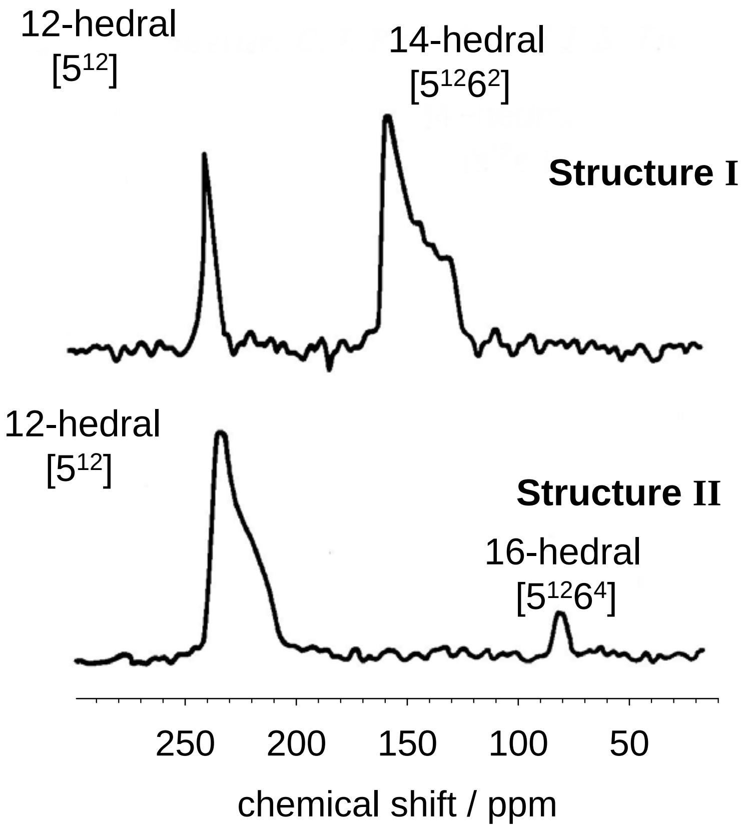
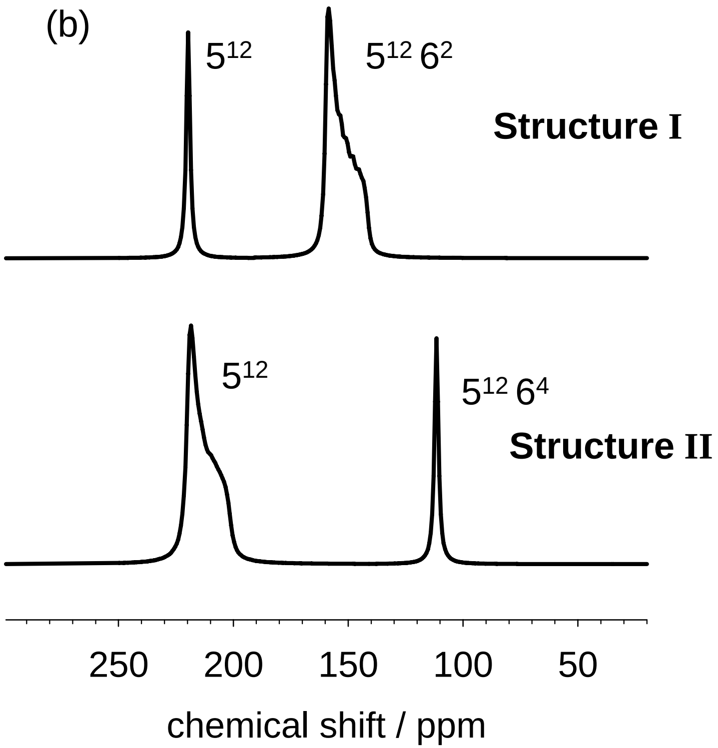
Xe chemical shift tensors in clathrate hydrates

Cynthia J. Jameson and Dirk Stueber

University of Illinois At Chicago



EXPERIMENTS



CALCULATIONS

MOTIVATION

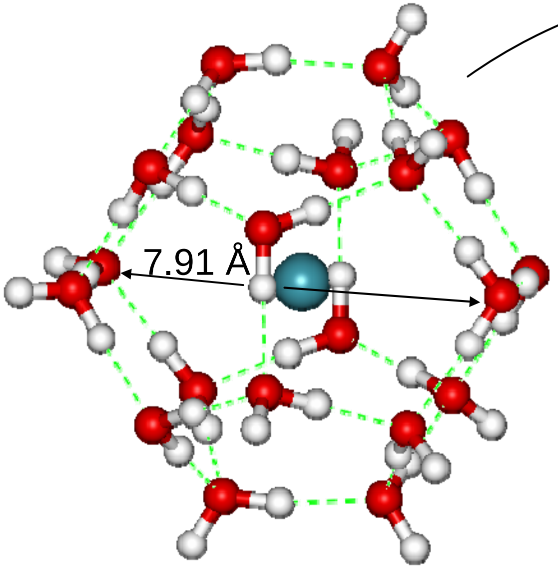
- Xe chemical shieldings and quadrupolar coupling interactions are very sensitive to void size and shape in clathrates[1,2]
- Structure of Xe clathrate hydrates of type I:

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

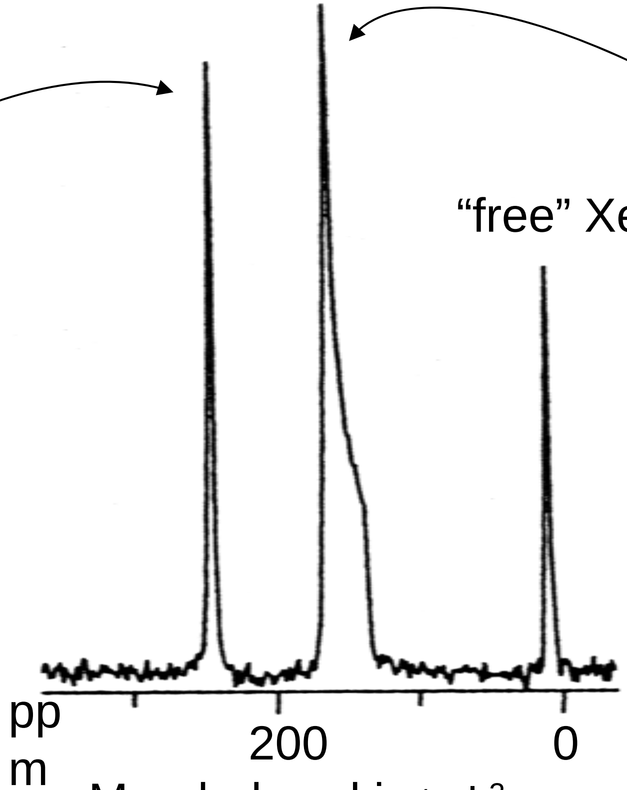
2 types of cages: 5^{12} (“small”) : $5^{12}\,6^{2}$ (“large”) = 1: 3

3-D disordered hydrogen-bonded network of H_2O molecules

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

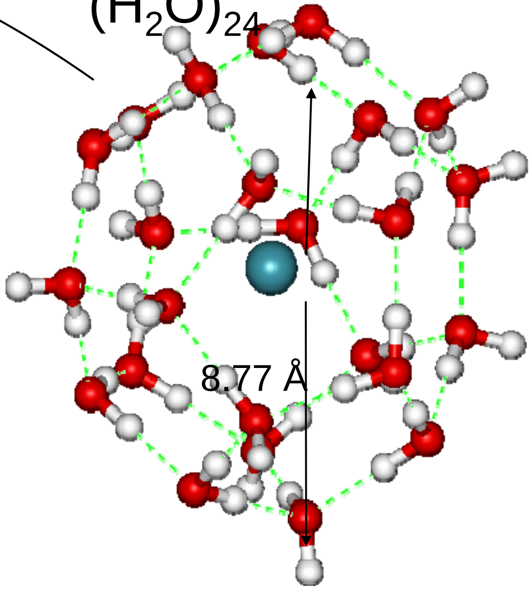


Dodecahedron of 12 pentagonal faces



Moudrakovski et al.[2]

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



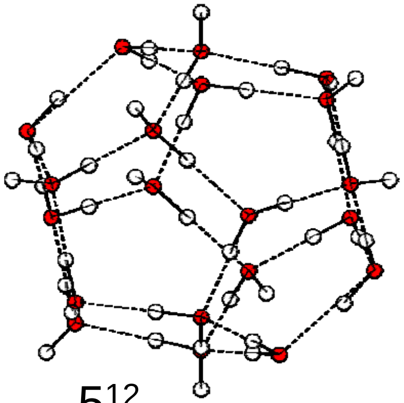
14-hedra of 12 pentagonal and two hexagonal faces

Xe in the cages of clathrate hydrates: Structures I, II, H and bromine hydrate

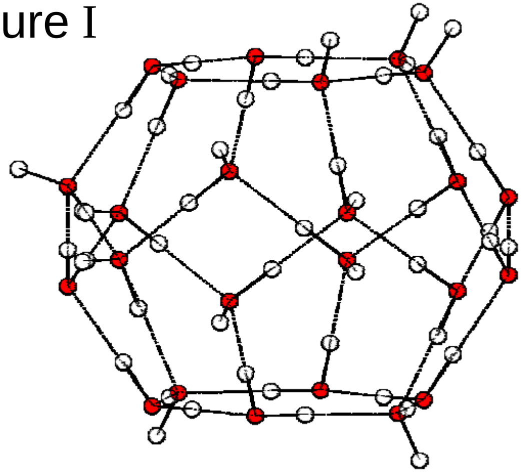
- a hydrogen-bonded network
- disordered proton configurations, yet must obey ice rules
- additive pair tensor model

the cages

Structure I

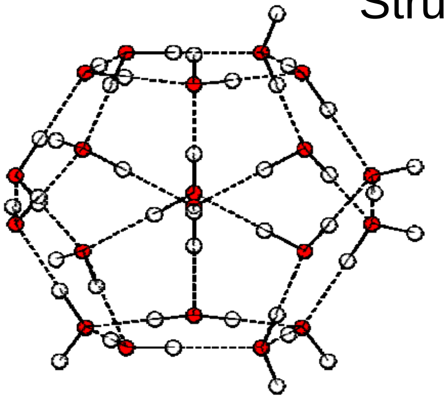


5^{12}

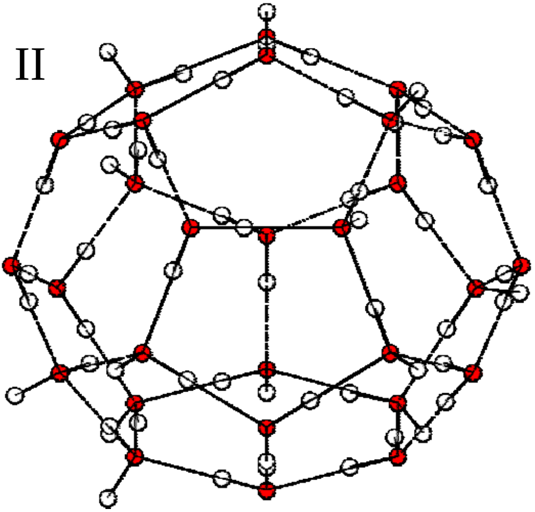


$5^{12}\,6^{2}$

Structure II



5^{12}

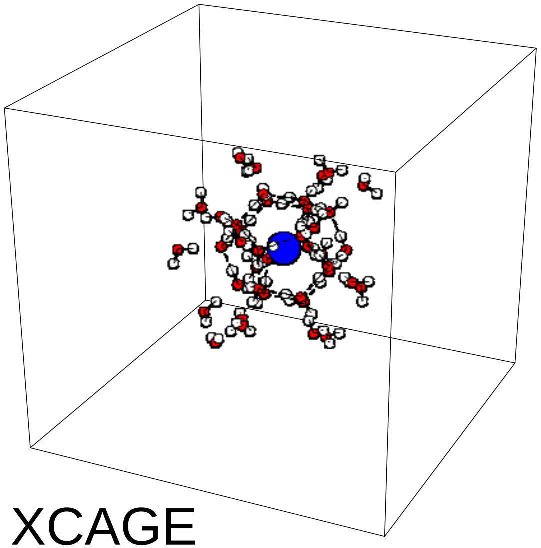


$5^{12}\,6^{4}$

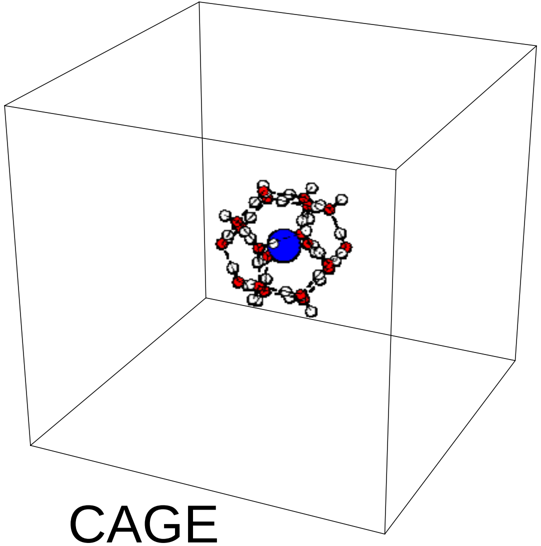
How to model a cage in a hydrogen bonded network?

- 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

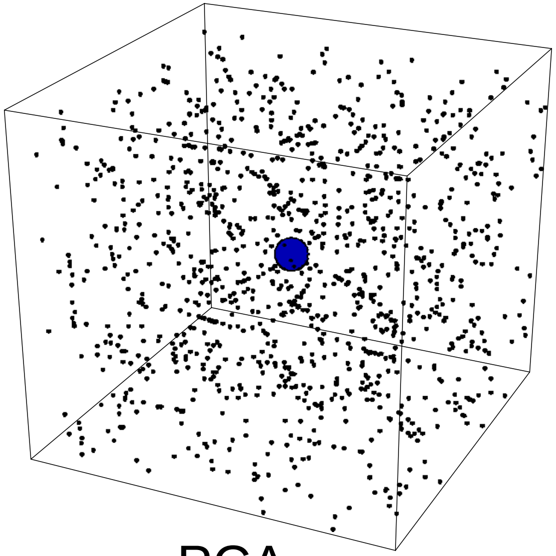
MODELS



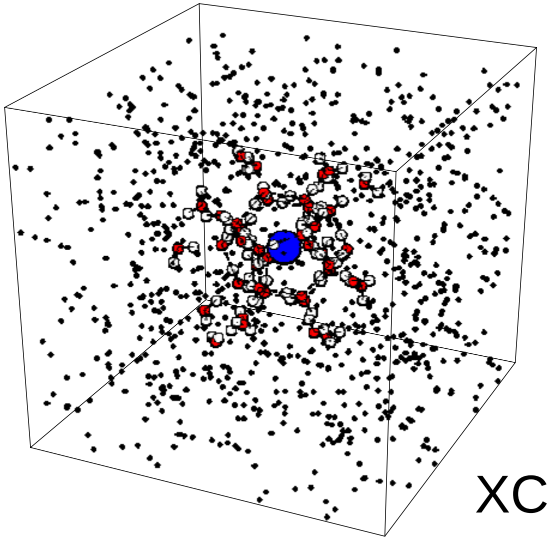
XCAGE



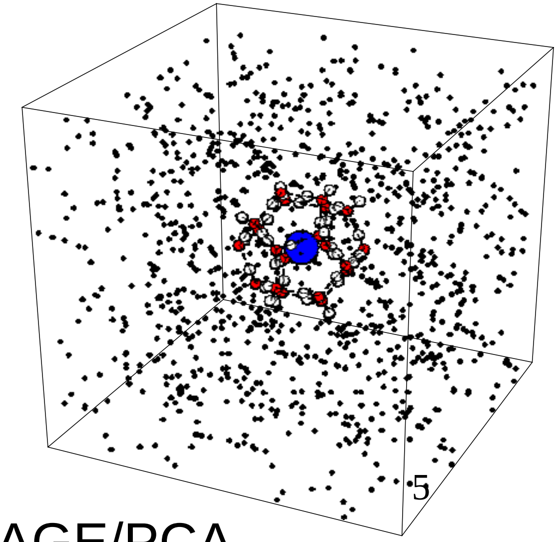
CAGE



PCA



XCAGE/PCA



CAGE/PCA

Xe shielding from electrostatics

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

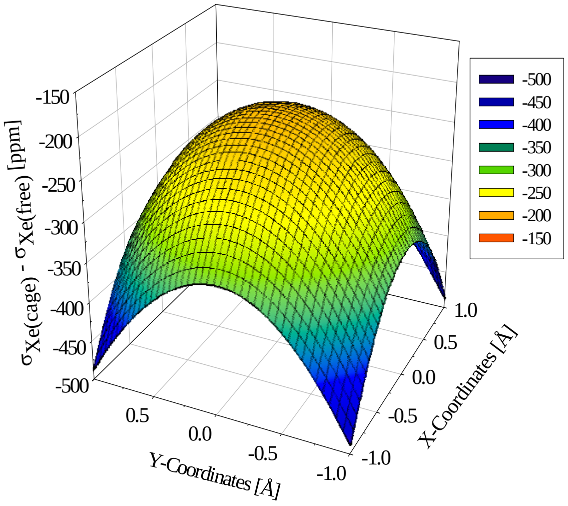
PCA	**CAGE**	**XCAGE**	**CAGE/PCA**	**XCAGE/PCA**
-0.4 ppm HF	-142.1	-138.2	-114.0	-119.4
-0.5 ppm DFT/B3LYP	-226.6	-217.0	-184.9	-199.4

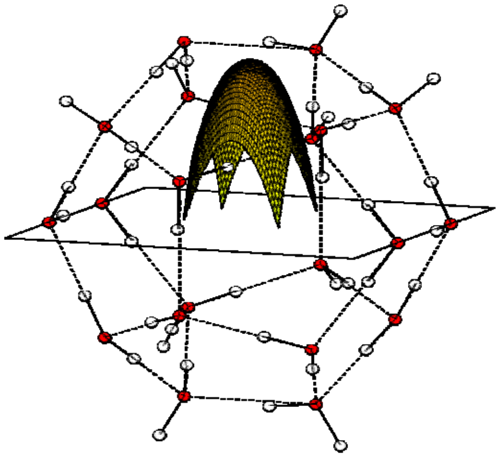
for 5^{12} cage in Structure I

purely electrostatic

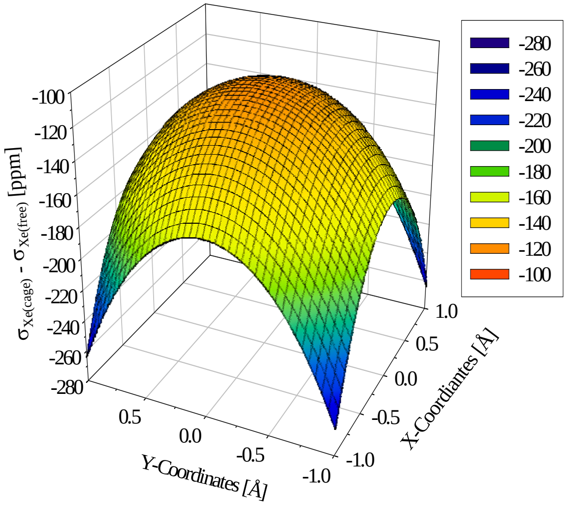
very small!

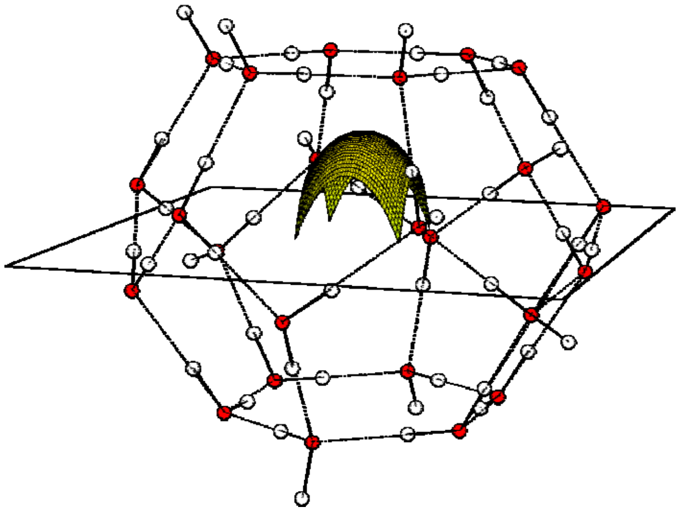
THE Xe SHIELDING SURFACES





5^{12} Cage





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

Xe shielding tensor components in clathrate hydrates

- We calculated Xe tensors in various positions inside an XCAGE/PCA model. How to combine all these calculated values into mathematical expressions so as to be able to reproduce the Xe tensor components at an arbitrary position inside the same model?

The **dimer tensor model** for Xe shielding tensor in a clathrate hydrate

The contribution to the shielding of Xe at point J due to the i_{th} O atom located at (x_i, y_i, z_i) is given by the ab initio tensor components for the XeO dimer, the functions

$\sigma_\perp(r_{XeO})$, $\sigma_{||}(r_{XeO})$.

$$\sigma_{XX} = [(x_i - x_J)/r_{iJ}]^2 \sigma_{||} + \{[(y_i - y_J)/r_{iJ}]^2 + [(z_i - z_J)/r_{iJ}]^2\} \sigma_\perp$$

$$\tfrac{1}{2}(\sigma_{XY}+\sigma_{YX}) = [(x_i - x_J)/r_{iJ}]\bullet[(y_i - y_J)/r_{iJ}](\sigma_{||} - \sigma_\perp)$$

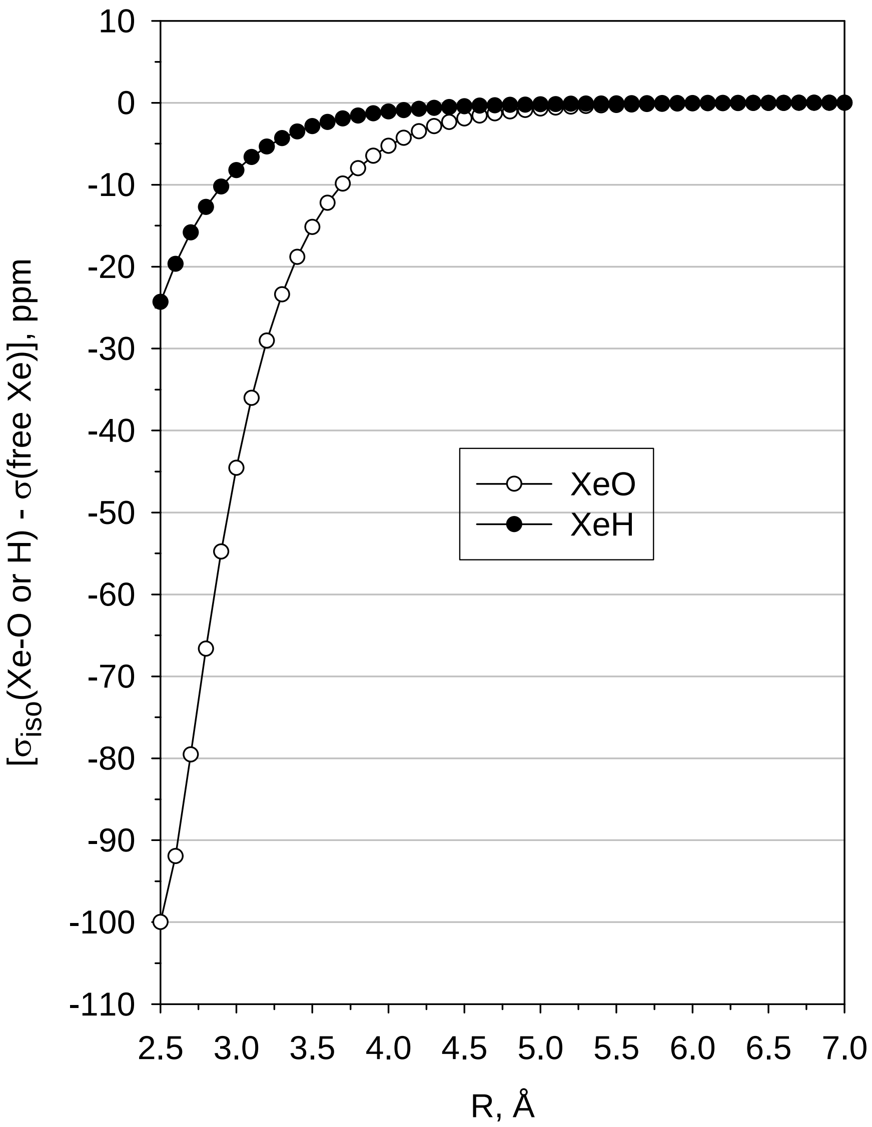
The contribution to the shielding of Xe at point J due to the $K_{\underline{th}}$ H atom located at (x_K, y_K, z_K) is given by the ab initio tensor components for the XeH dimer, the functions

$\sigma_\perp(r_{XeH})$, $\sigma_{||}(r_{XeH})$.

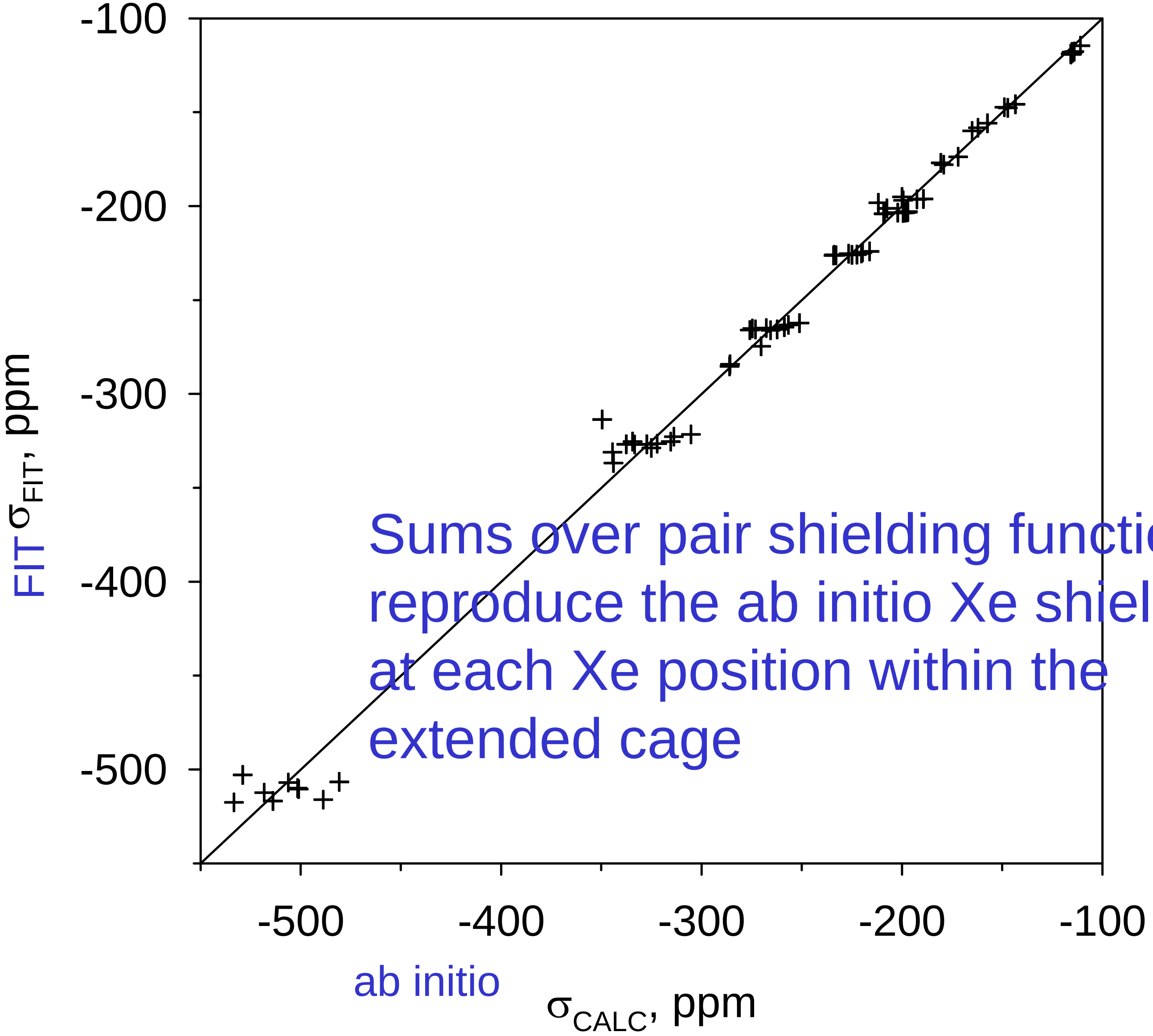
$\sigma_\perp$(rXeO), $\sigma_{||}$(rXeO), $\sigma_\perp$(rXeH), and $\sigma_{||}$(rXeH) are then expressed in terms of parameters which are found by fitting to the *ab initio* Xe shielding tensor components.

The isotropic Xe shielding can also be expressed as a sum over pairwise Xe-O and Xe-H shielding contributions

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

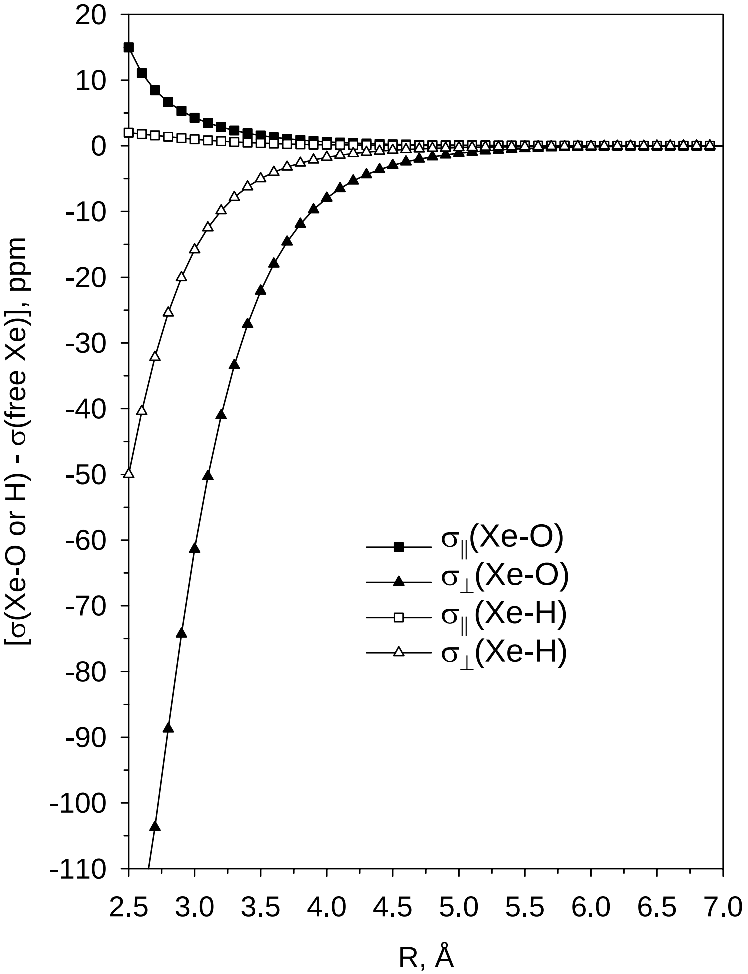


FIT to pairwise additive (Xe-O and Xe-H) isotropic shielding



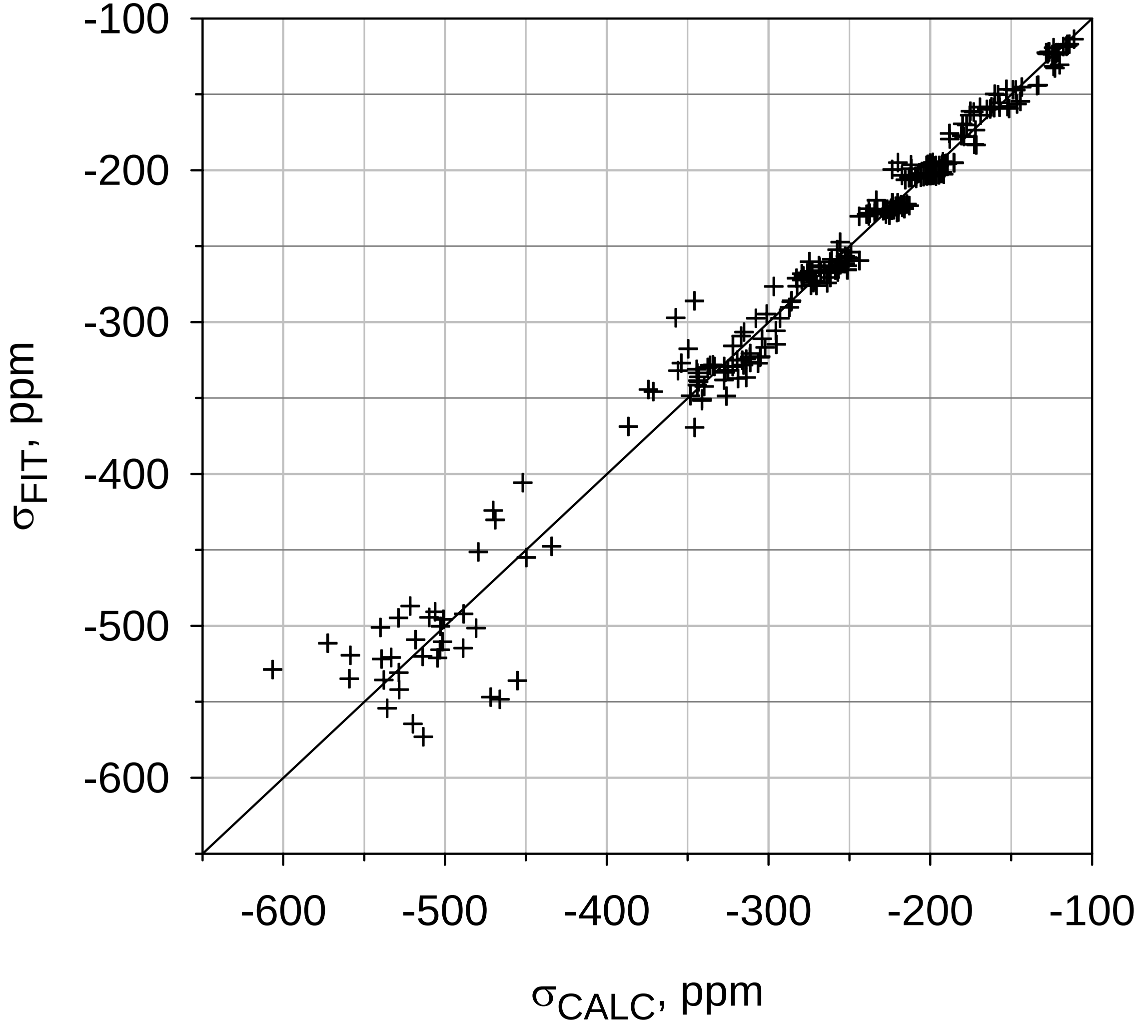
Sums over pair shielding functions reproduce the ab initio Xe shielding at each Xe position within the extended cage

The Xe-O and Xe-H shielding tensors



Sums over pair shielding functions reproduce the ab initio Xe shielding tensor at each Xe position within the extended cage

At short distances, sum over pair shielding tensors deviate from ab initio tensor components



How is information encoded into the average Xe chemical shift?

The Xe chemical shift encodes any structural or dynamic information that depends on:

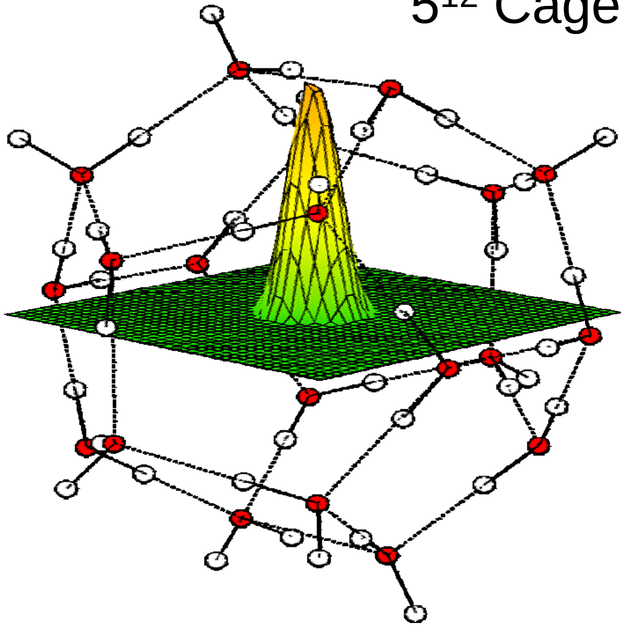
- **Electronic structure of the neighbors of the Xe atom**
- **Configurations of neighbor atoms, how many, at what distances**
- **The relative probabilities of the various configurations**

METROPOLIS MONTE CARLO SHIELDING AVERAGING

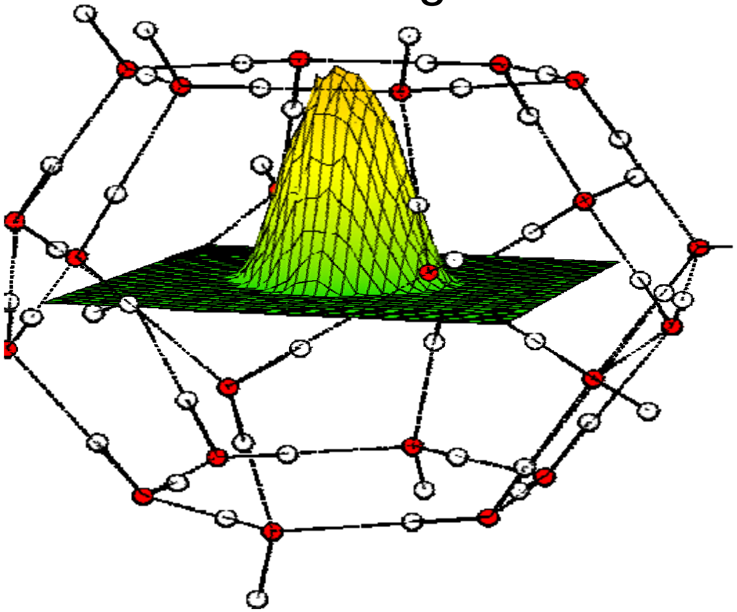
Use ab initio shielding surface and Lennard-Jones V(Xe-O)^5: r_0 = 3.700 and ε = 0.753 kJ/mol

Xe one-body distribution functions at 275 K:

5^{12} Cage

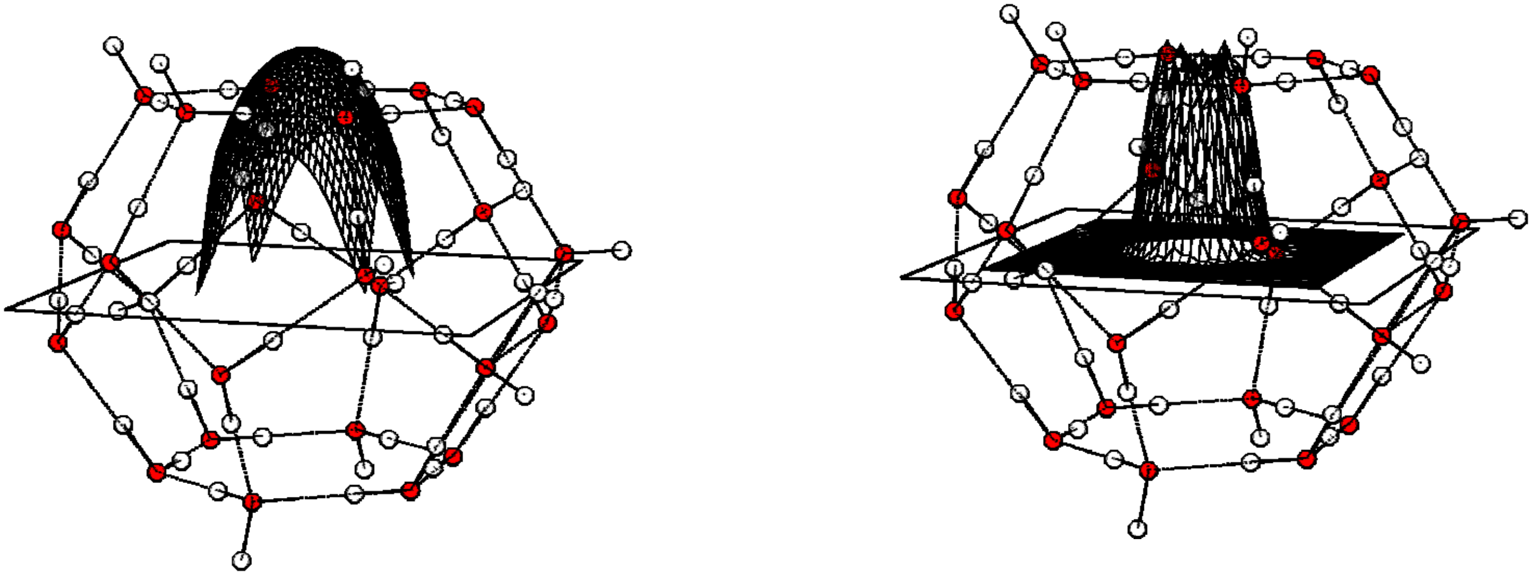


$5^{12}\,6^{2}$ Cage



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

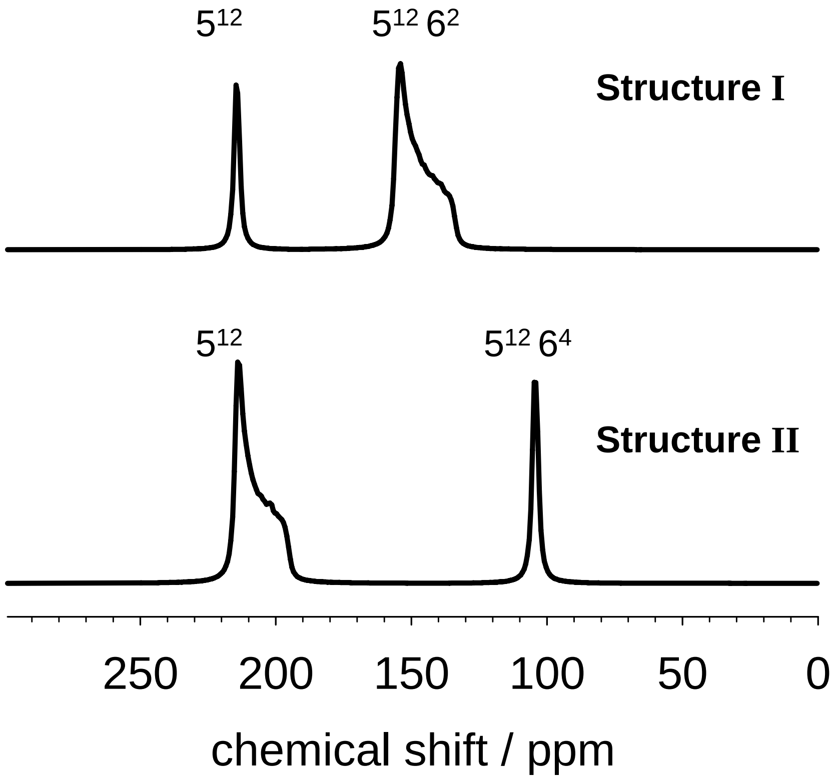
Xe in the $5^{12}6^{2}$ cage of clathrate hydrate Structure I

Xe isotropic chemical shift values, ppm

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

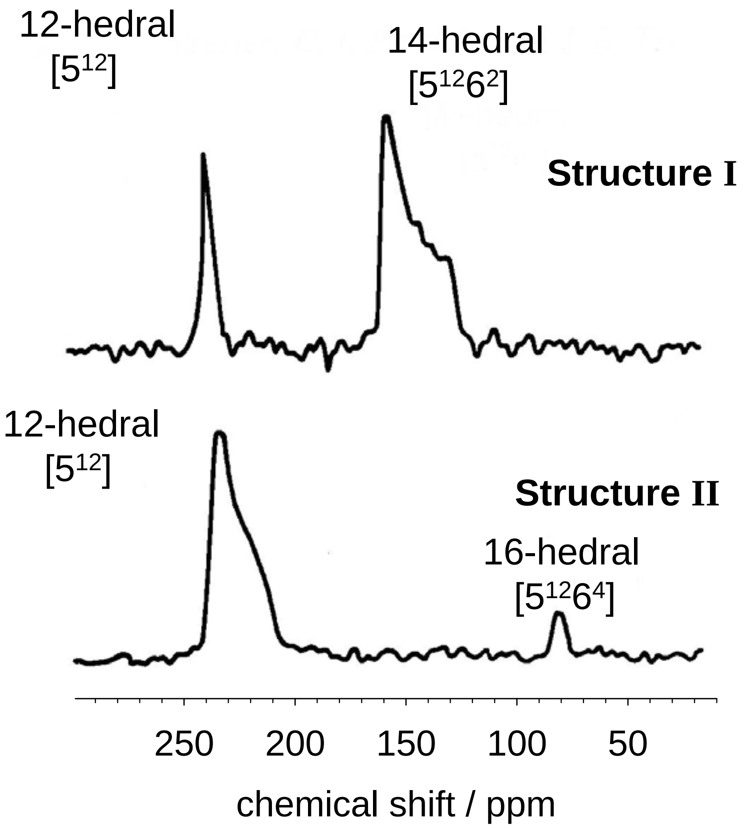
For cages of similar electronic structure,
thus the same Xe shielding function,
the averaging over Xe positions in the
smaller cage leads to a larger average
chemical shift compared to Xe in the larger cage.

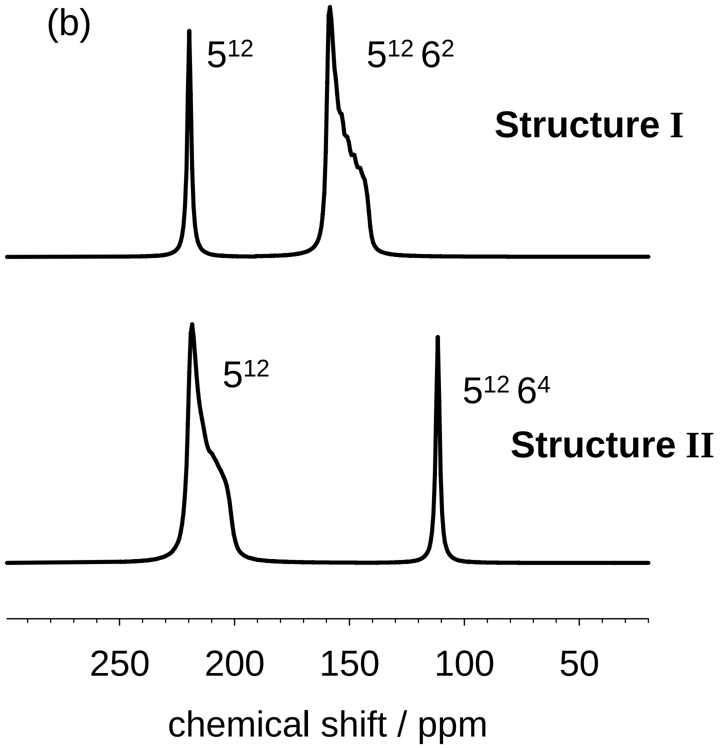
Calculated Xe NMR lineshapes from Monte Carlo simulations in single extended cages:



using
the same Xe-O and Xe-H shielding tensor functions,
the same Xe-O and Xe-H potential functions

Xe in the cages of clathrate hydrates Structure I and II





EXPERIMENTS

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

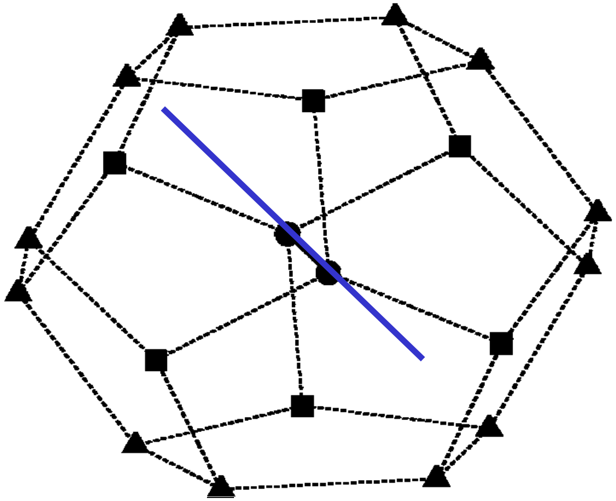
CALCULATIONS

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

Why is the Xe lineshape in the 5^{12} cage in Structure II axially anisotropic while the Xe lineshape in the 5^{12} cage in Structure I is isotropic?

(a) 5^{12} cage

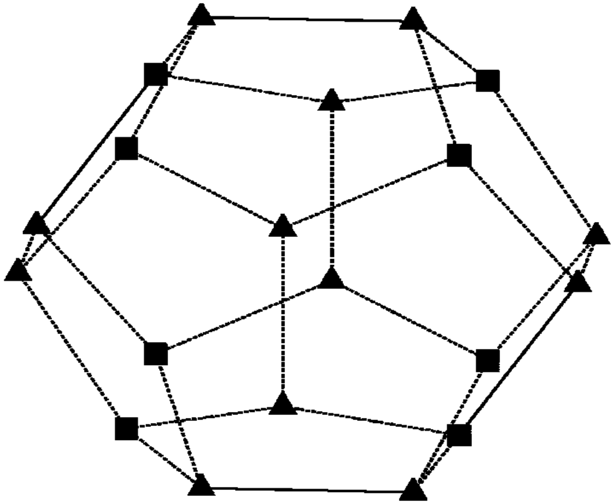
in structure II



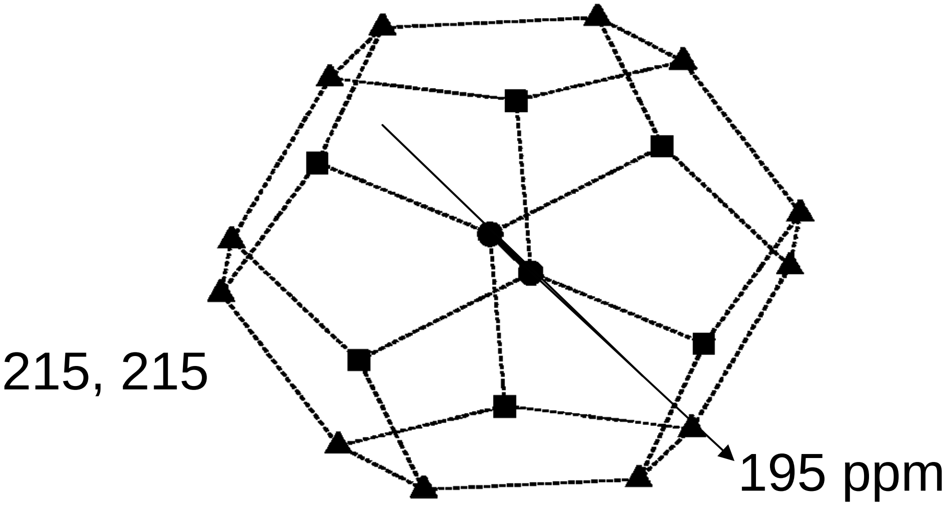
There is a unique pair
of oxygen atoms in this cage,
defining a unique axis.

(b) 5^{12} cage

in structure I



Xe chemical shift tensor in Structure II



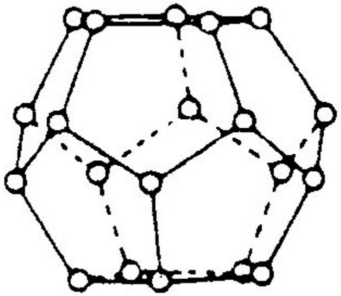
5^{12}

- number of unique components
- magnitudes
- directions of the principal axes (in the crystal frame)

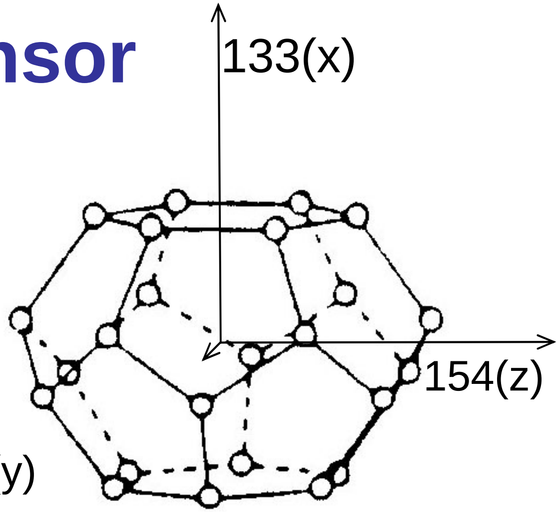
can be determined for the average Xe chemical shift tensor

Xe chemical shift tensor

isotropic 214

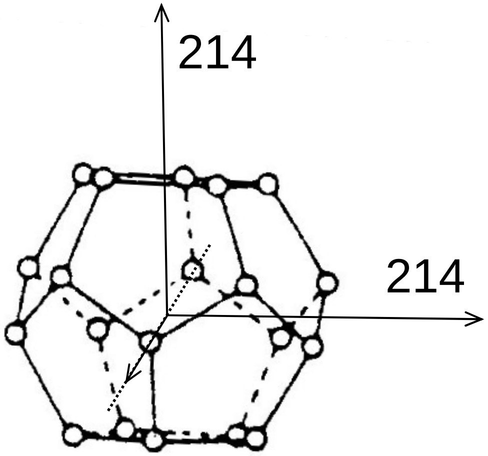


5^{12}



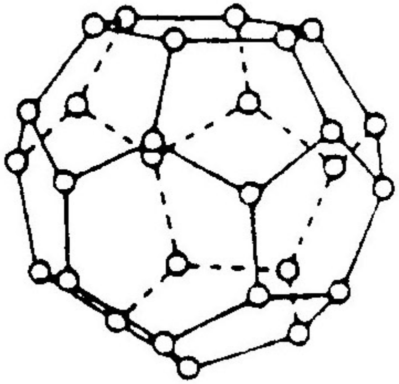
$5^{12}6^{2}$

Clathrate Structure I



5^{12}

isotropic 105

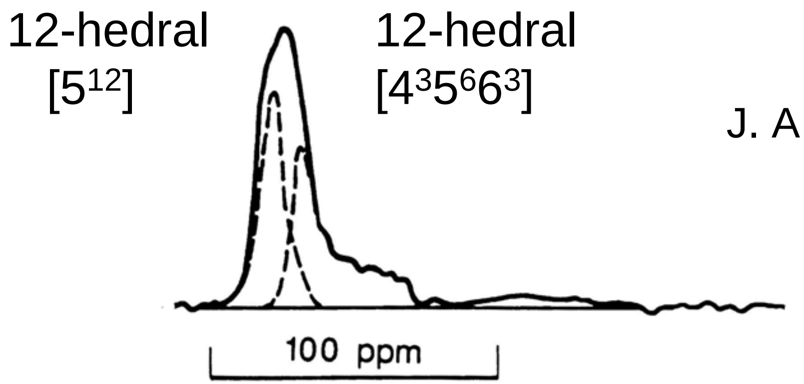


$5^{12}6^{4}$

Clathrate Structure II

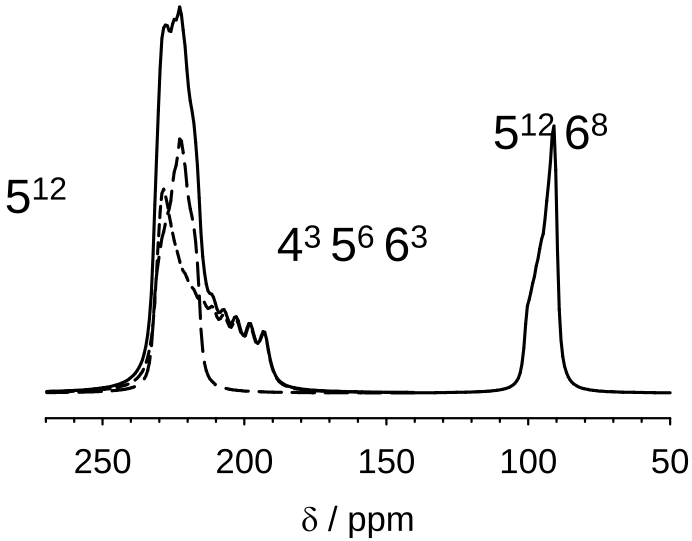
Use the same pair-wise shielding and potential functions to predict Xe tensors in other clathrate hydrates

Xe in clathrate hydrate Structure H



EXPERIMENT

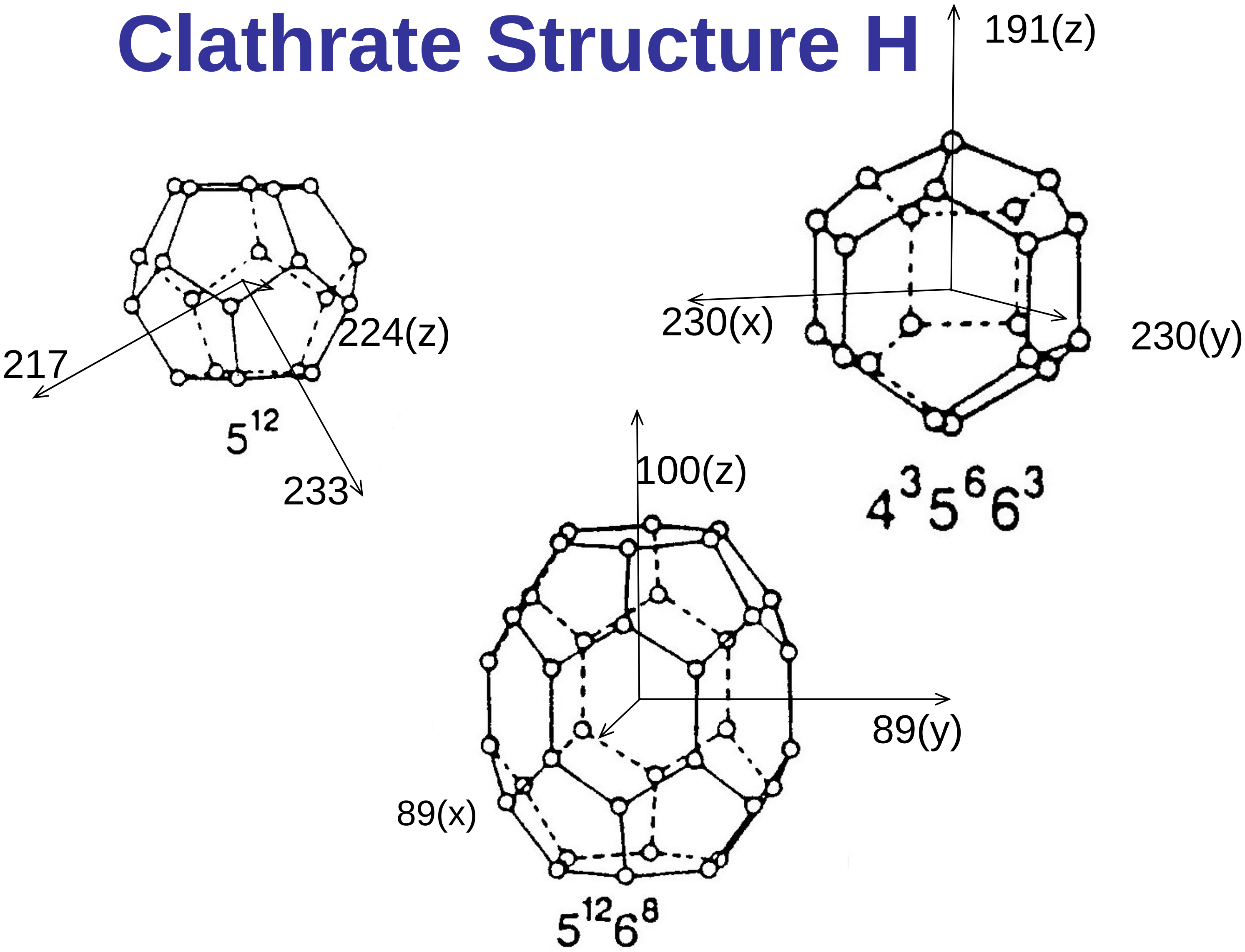
J. A. Ripmeester, C. I. Ratcliffe and J. S. Tse,
Trans. Faraday Soc. 1, 84, 3731 (1988)



CALCULATIONS

Monte Carlo simulations
C. J. Jameson & D. Stueber, 2003

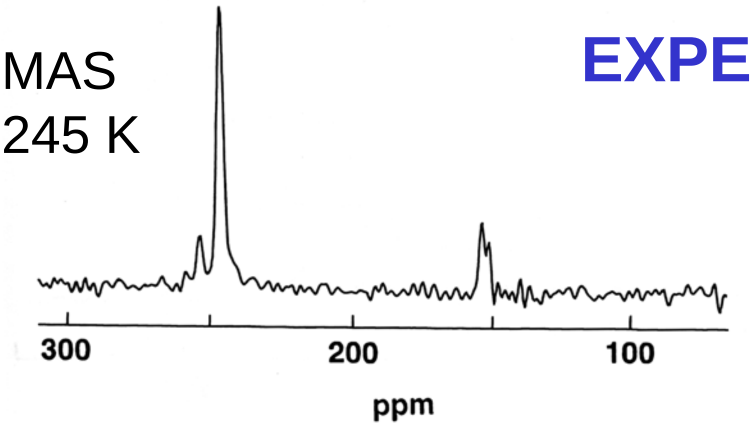
Xe tensor in Clathrate Structure H

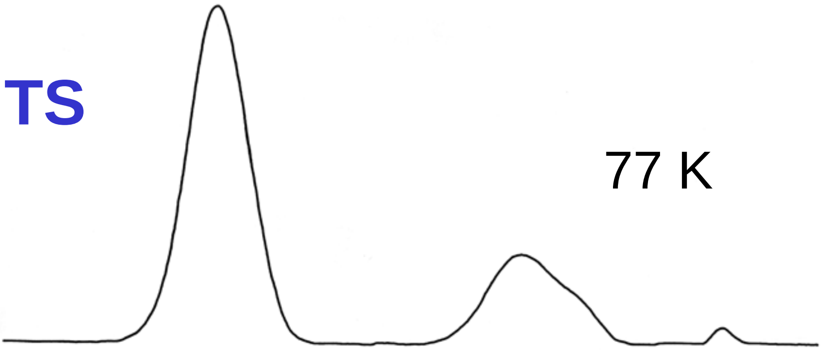


Xe in bromine hydrate

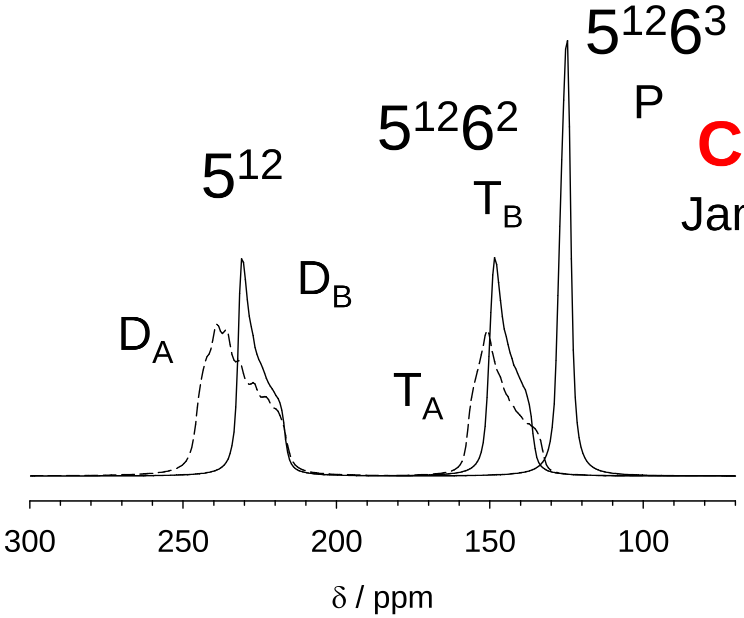
EXPERIMENTS

MAS
245 K





Udachin, Enright, Ratcliffe, Ripmeester
J. am. Chem. Soc. 119, 11481 (1997)



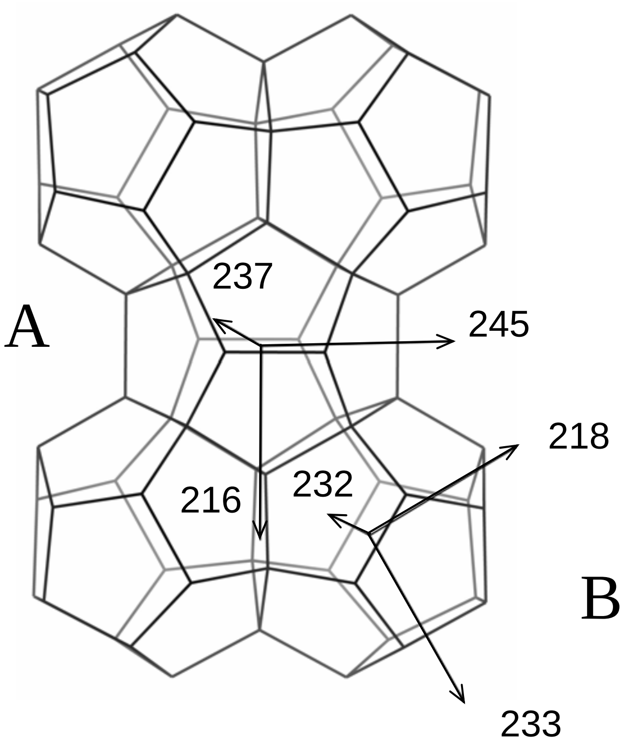
CALCULATIONS

Jameson and Stueber, 2003

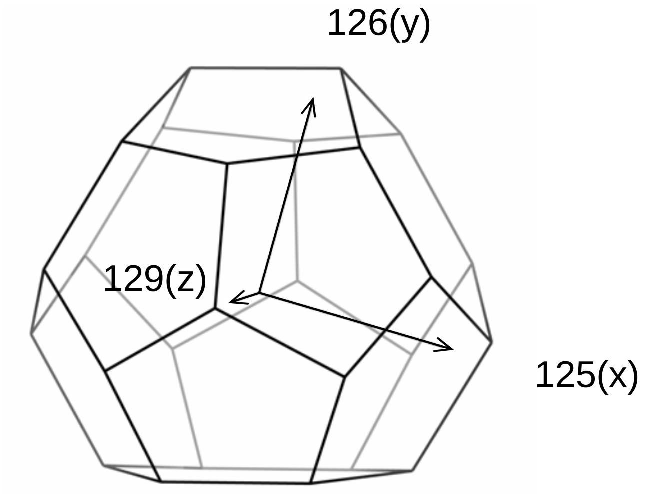
EPILOGUE: Xe in the P ($5^{12}6^{3}$) cage has Recently [*PNAS 106, 6060-6064* (1009)] been observed to be between that of Xe in the $5^{12}6^{2}$ of Struc I and $5^{12}6^{4}$ of struc II, just as we predicted here.

Xe tensors in bromine hydrate
D_A, D_B, and P cage

5^{12}

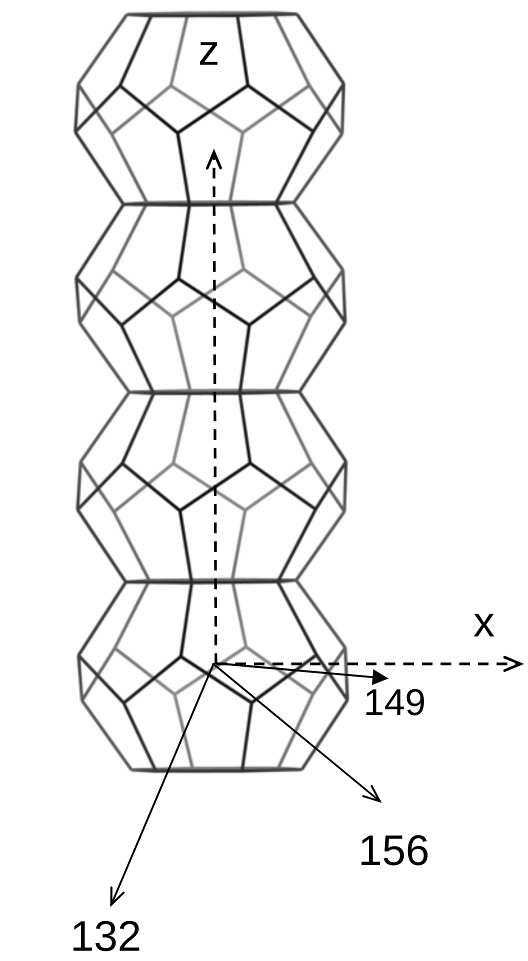


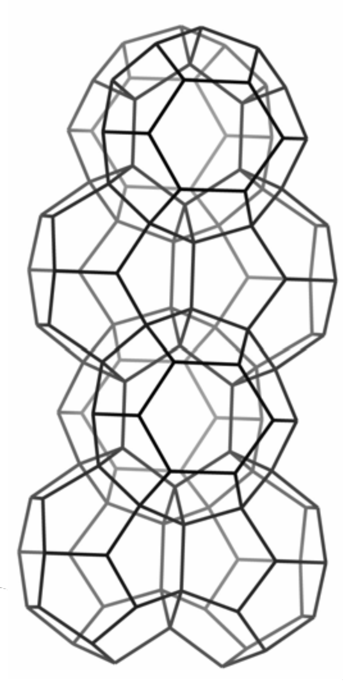
$5^{12}6^3$



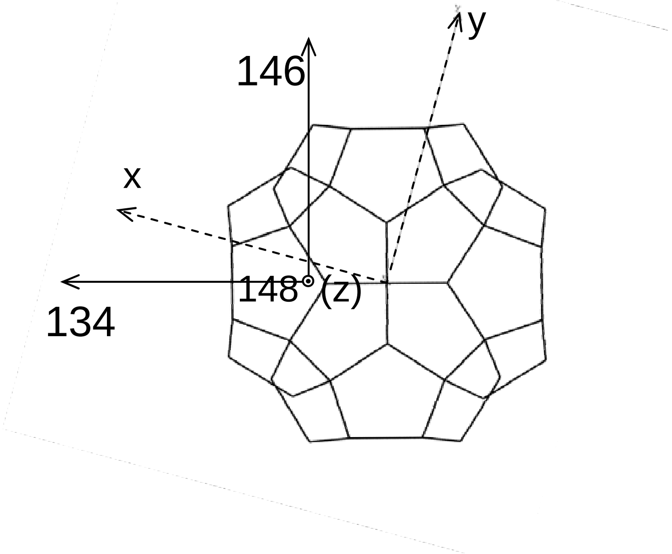
Bromine hydrate T_A and T_B cages

$5^{12}6^{2}$ - **A**





$5^{12}6^{2}$ - **B**



Unique non-vanishing tensor components found by Monte Carlo simulations for Xe in a cage is the same as expected for a spin at center of cage.

cage type	nuclear site symmetry at center of cage	unique tensor components at center, determined by symmetry*✦
5^{12} in I	T_h	1: $\sigma_{zz} = \sigma_{xx} = \sigma_{yy}$
$5^{12}6^{2}$ in I	D_{2d}	2: σ_{zz} , $\sigma_{xx} = \sigma_{yy}$
5^{12} in II	D_{3d}	2: σ_{zz} , $\sigma_{xx} = \sigma_{yy}$
$5^{12}6^{4}$ in II	T_d	1: $\sigma_{zz} = \sigma_{xx} = \sigma_{yy}$
5^{12} in H	D_{2h}	3: σ_{zz} , σ_{xx} , σ_{yy}
$4^{3}5^{6}6^{3}$ in H	D_{3h}	2: σ_{zz} , $\sigma_{xx} = \sigma_{yy}$
$5^{12}6^{8}$ in H	D_{6h}	2: σ_{zz} , $\sigma_{xx} = \sigma_{yy}$
5^{12} (D_A)	D_{2h}	3: σ_{zz} , σ_{xx} , σ_{yy}
5^{12} (D_B)	D_{2h}	3: σ_{zz} , σ_{xx} , σ_{yy}
$5^{12}6^{2}$ (T_A)	C_s	4: σ_{zz} , σ_{xx} , σ_{yy} , σ_{xz}
$5^{12}6^{2}$ $(T_{\mathbf{B}})$	C_s	4: σ_{zz} , σ_{xx} , σ_{yy} , σ_{xz}
$5^{12}6^{3}$ (P)	C_{2v}	3: σ_{zz} , σ_{xx} , σ_{yy}

*A. D. Buckingham and S. M. Malm, Mol. Phys. 22, 1127 (1975)

✦ symmetric part of tensor

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.]

Information that is encoded in observed Xe spectra:

- **structural as well as dynamic information**
- **the architecture of the cage**
- **average size of the cage**
- **average symmetry of the cage: This is reflected in the Xe tensor components that are observed in Xe lineshapes**
- **electronic structure of atoms constituting the cavity walls**

General CONCLUSIONS

- The Xe NMR chemical shift is exquisitely sensitive to the environment in which the Xe atom finds itself.
- Encoded in the ***intrinsic shielding response surface*** is the electronic structure of the system (a supermolecule or a crystal fragment) as a function of nuclear configuration.
- The ***dynamic averaging*** encodes further information about the nuclear environment into the observed chemical shift.
- It is possible to use a combination of ***quantum mechanical calculations and grand canonical Monte Carlo simulations in model systems*** in order to understand the Xe chemical shifts. From such understanding may come some insight into the encoded information in more complex, real-world systems.

ACKNOWLEDGMENTS

Funding

Inspiration

This work was inspired by the series of experiments on ^{129}Xe and ^{131}Xe in clathrate hydrates by **Ripmeester et al.**