Xenon Atom: The Spy Who Came in from the Cold

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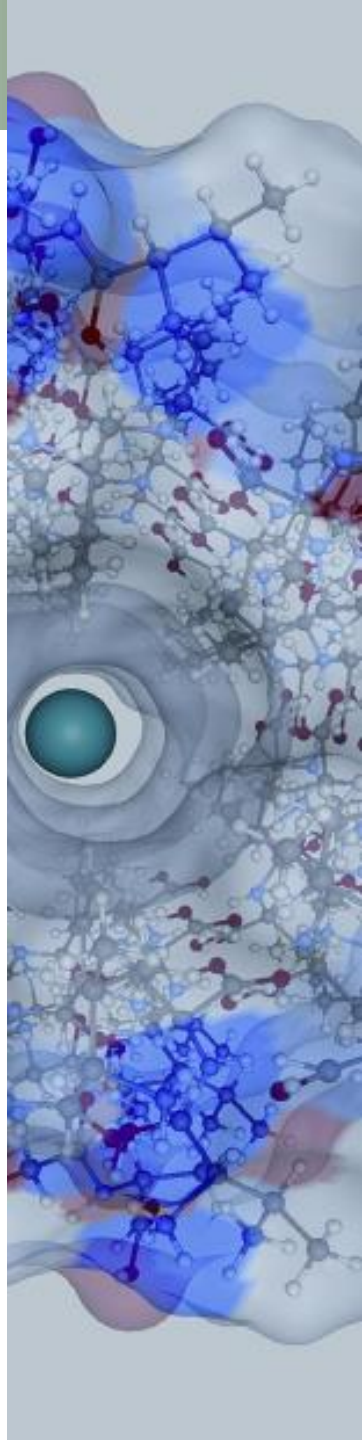


Xe spin as a spy

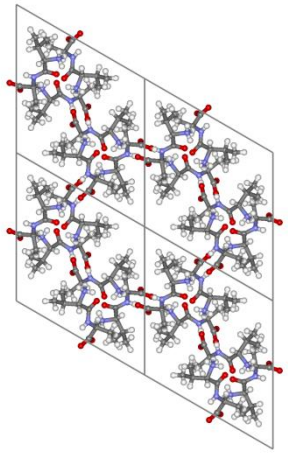
Xe atom encodes and reports a lot of information about its environment into its NMR spectrum.

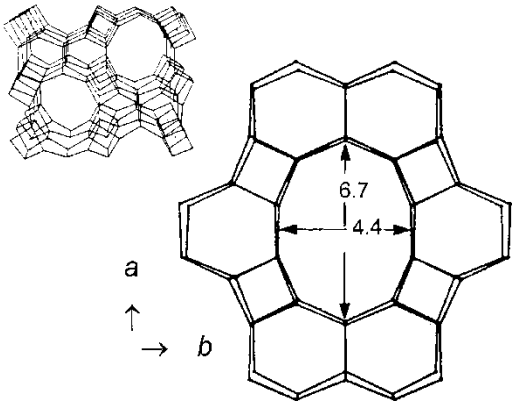
At first, we send out our spy into clear-cut scenarios where other sources can provide checks and double checks on the information, and in this process set up the encryption codes, then debriefing reveals the quality/reliability of the detailed information in those clear-cut scenarios.

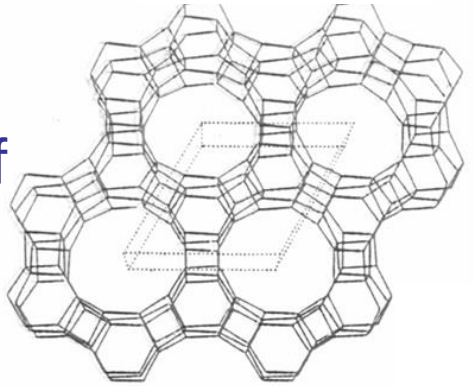
Thereafter, we can send our spy into uncharted territory where no double checks may be possible, we have our previous calibrations on the reliability of the transcription, then we can still get some useful information (situation report) from the field.

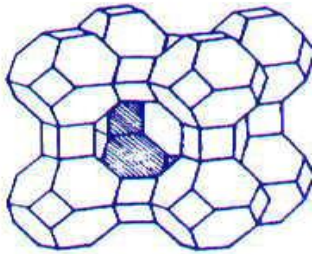
Xe intermolecular chemical shifts

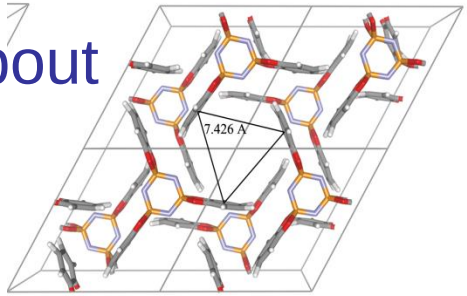
- **exquisitely sensitive** to the environment of the Xe atom
- permits the Xe nucleus to **report attributes of the physical system** in which Xe atom finds itself
- needs **understanding at a fundamental level** so as to elicit the desired detailed information about the physical system

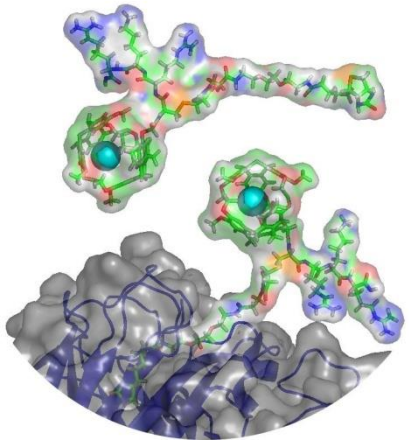


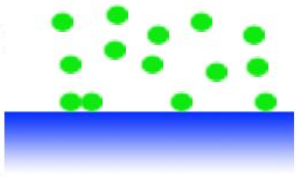












biosensor model courtesy of T. J. Lowery

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**

All these are ultimately **quantum mechanical** in origin.

Quantum-mechanical molecular level interactions determine:

(A) the sorption thermodynamics,
(B) the Xe exchange dynamics,
(C) the instantaneous shielding at a Xe nucleus arising from the electronic environment formed by all the rest of the atoms (including other Xe atoms).

The **average Xe chemical shift** is a weighted average of the Xe shielding function(C) with weighting factors determined by (A) and (B)

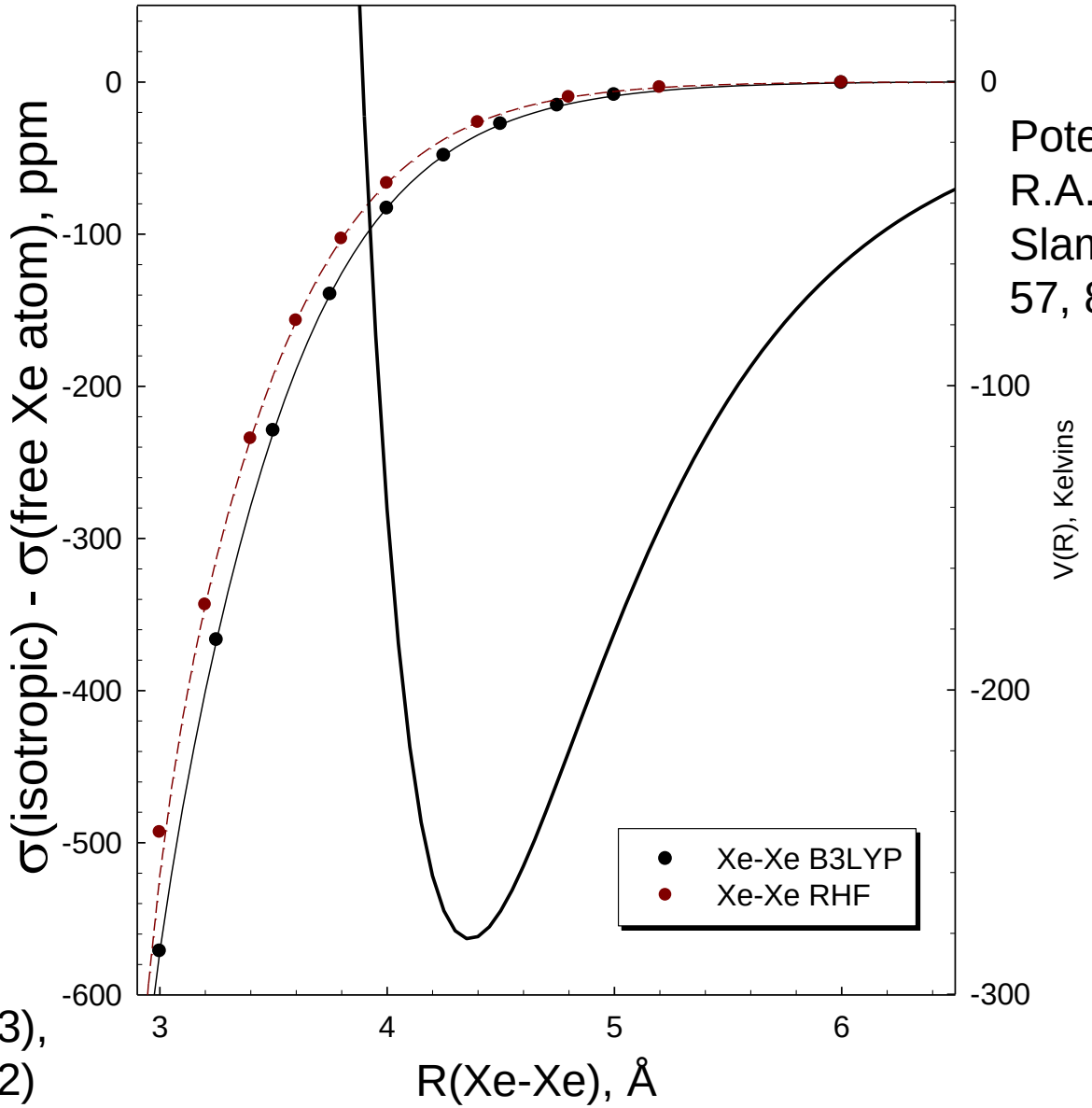
For one neighbor

Ab initio calculations show that

(1) the Xe shielding response drops off very steeply with distance of the neighbor atom

(2) the magnitude of Xe shielding response depends on the electronic structure of the neighbor atoms or molecules

Xe isotropic shielding function σ(R) and potential function V(R) for the Xe-Xe system



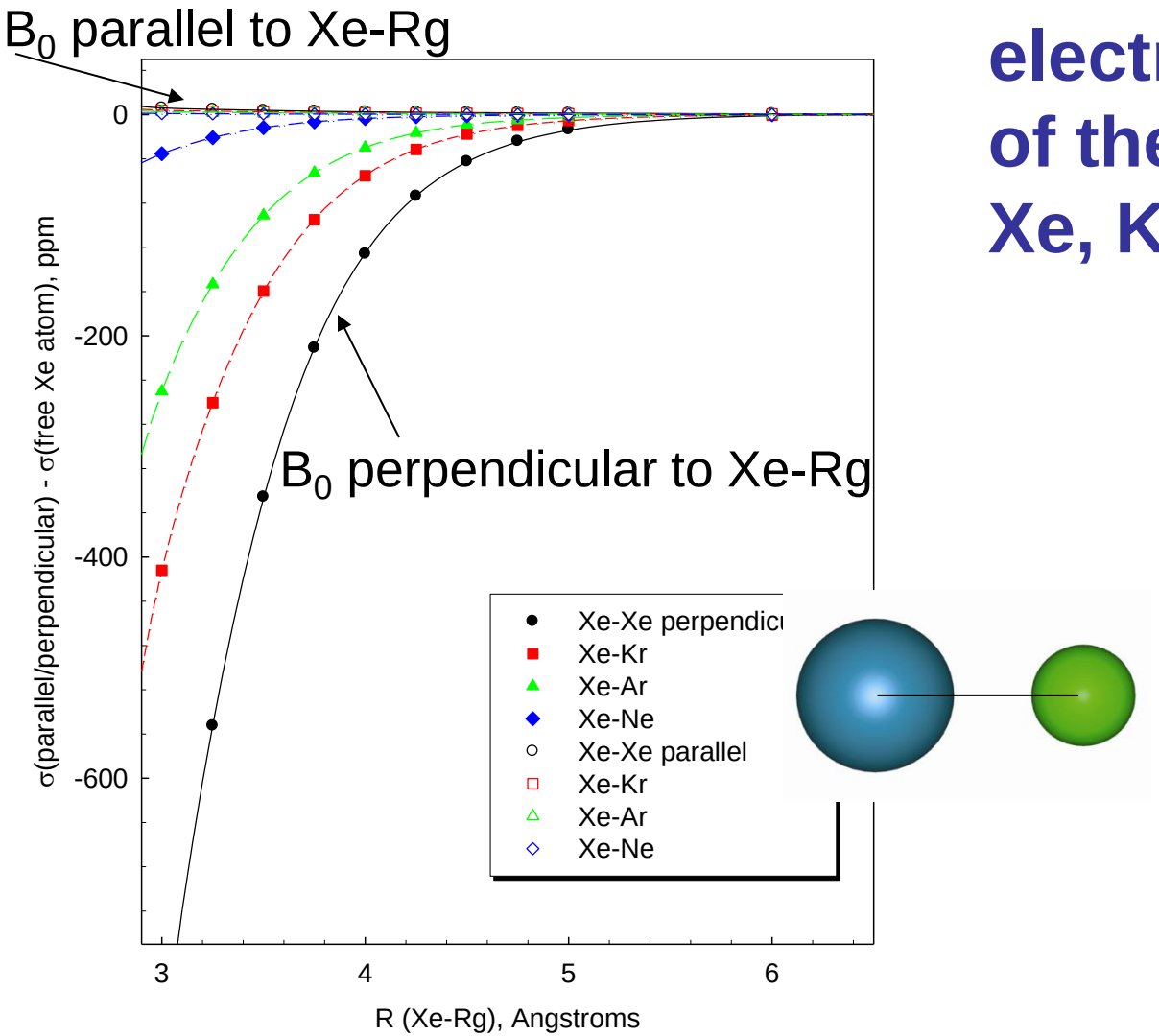
Potential function: R.A. Aziz and M.J. Slaman, Mol. Phys. 57, 825 (1986)

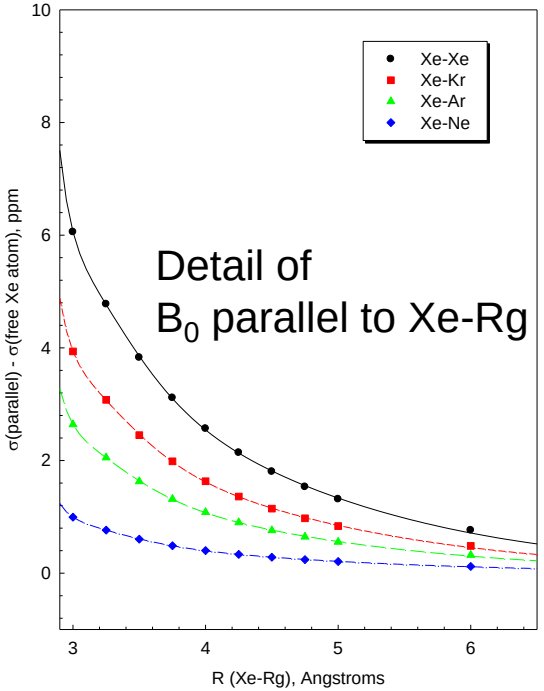
Jameson et al. J. Chem. Phys. 118, 2575 (2003), 116, 3805 (2002)

The Xe SHIELDING RESPONSE

changes with magnetic field direction

and depends on the electronic structure of the neighbor: Xe, Kr, Ar, Ne





INTERMOLECULAR CHEMICAL SHIFTS

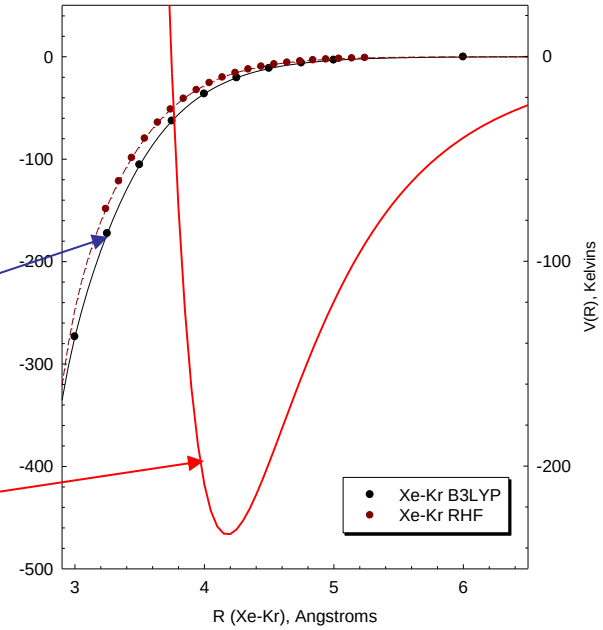
GAS phase:

$$\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \ldots$$

$$\sigma_1(T) = 2\pi \times \int\int [\sigma(r, \theta) - \sigma(\infty)] \times e[-V(r,\theta)/kT] r^2 dr \sin\theta d\theta$$

Need 2 functions:

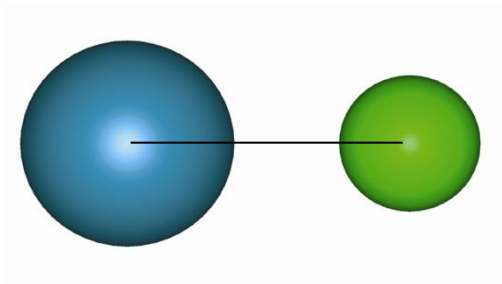
$[\sigma(r, \theta) - \sigma(\infty)]$ & $V(r,\theta)$

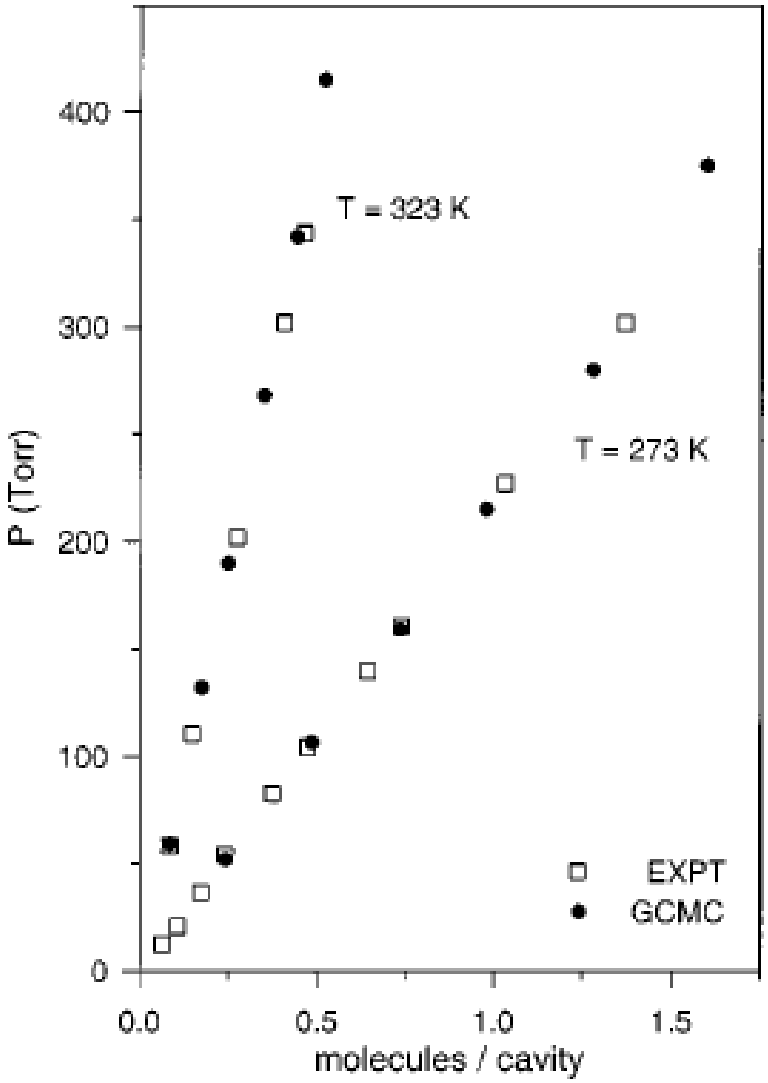


$$\delta = (\sigma_{ref} - \sigma_{sample})/(1 - \sigma_{ref})$$

with a Xe atom as reference,

$$\delta_{calc} \approx (\sigma_{Xe\ atom} - \sigma_{calc})$$





Distribution of molecules inside vs. outside

adsorption isotherm of CH_4 in zeolite NaA

Experimental vs. GCMC (Grand Canonical Monte Carlo) simulations

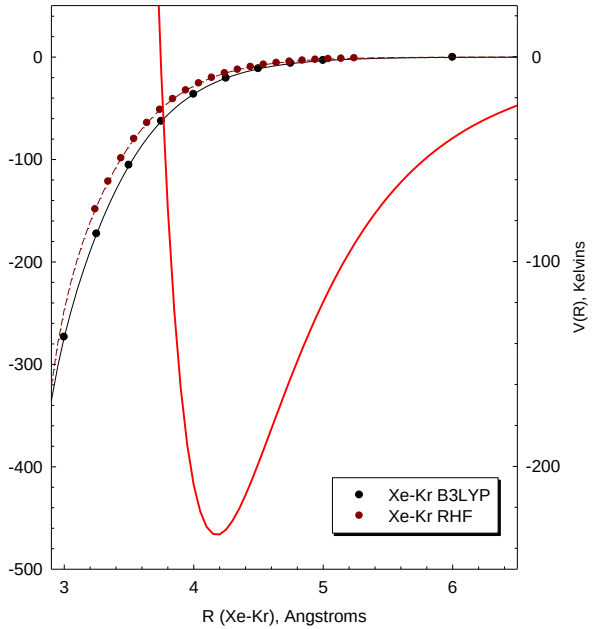
Adsorption isotherm of molecules in zeolites show that density inside (number of molecules per unit available volume) is greater than number density outside.

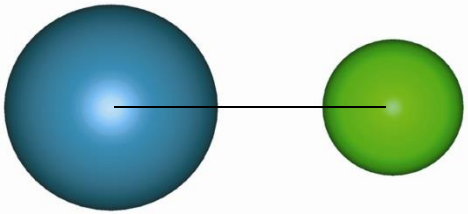
Fact: Adsorption isotherms of molecules in zeolites show that density inside is greater than outside.

QUESTION:

Why is the distribution inside the cavities different from outside, that is, why do molecules prefer to be inside the cavity rather than outside in the bulk overhead gas?

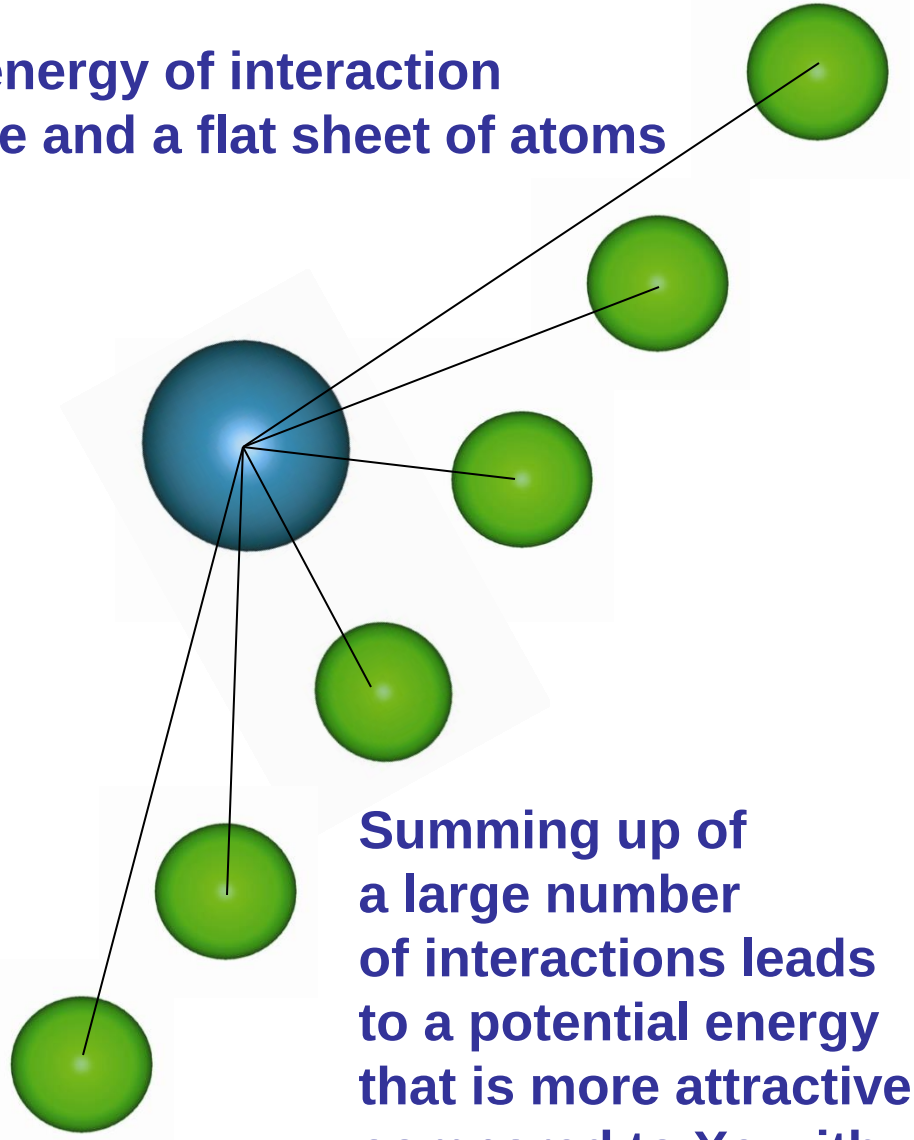
Let us consider the potential energy of interaction between Xe and other atoms



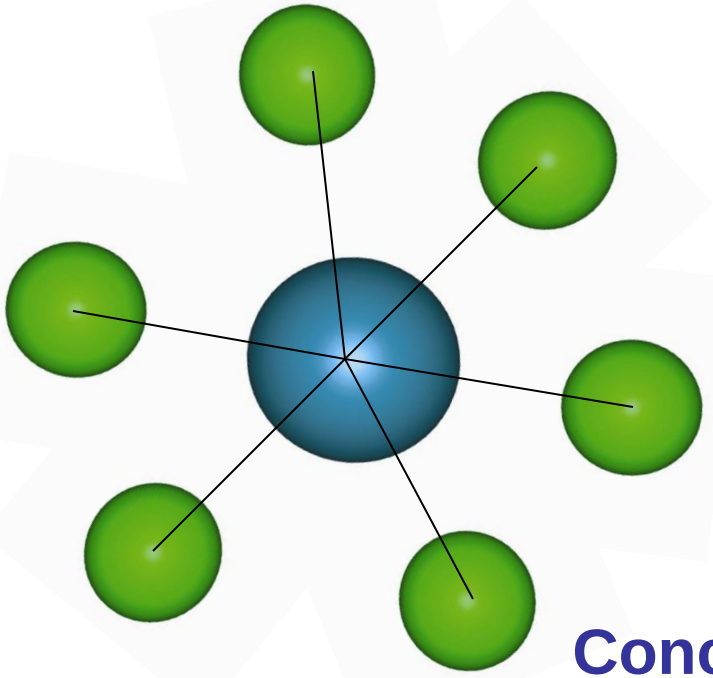


Potential energy of interaction between Xe and one atom

Potential energy of interaction between Xe and a flat sheet of atoms



Summing up of a large number of interactions leads to a potential energy that is more attractive compared to Xe with a single atom



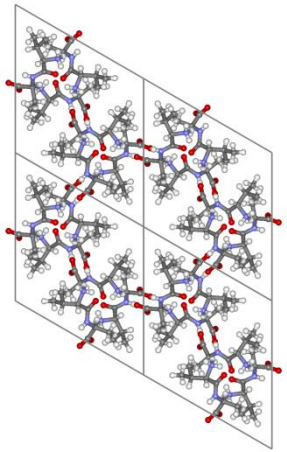
Potential energy of interaction between Xe and a curved surface of atoms

Concave curvature of the surface affords shorter distances between Xe and the other atoms, summing up to a potential energy function that is more attractive compared to a flat surface.

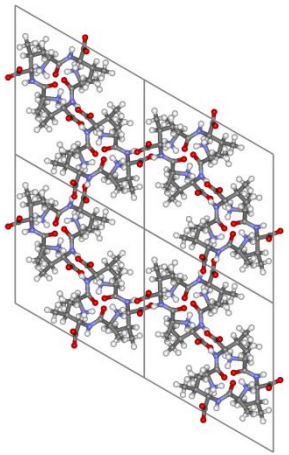
For a given solid material structure (i.e., equilibrium positions of atoms which constitute the solid), the electronic structure of the atoms which are accessible to Xe atoms determine the

- **adsorption isotherm for Xe in the material**
  i.e., the total Xe occupancy (at a given temperature and overhead Xe pressure)

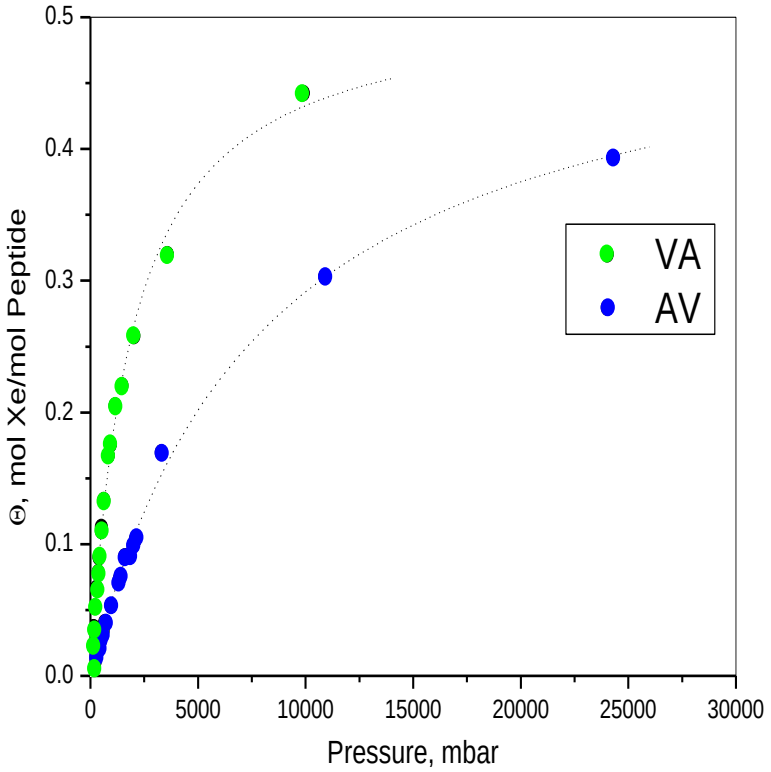
Channel structure & adsorption isotherm



L-Val-L-Ala

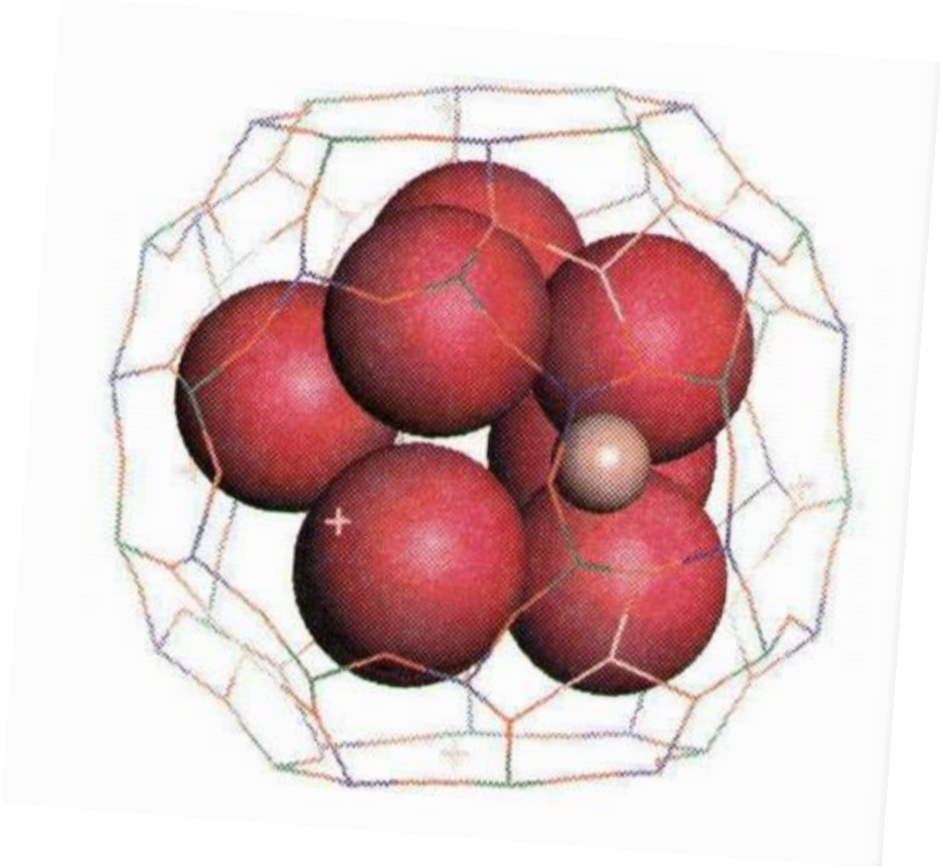


L-Ala-L-Val



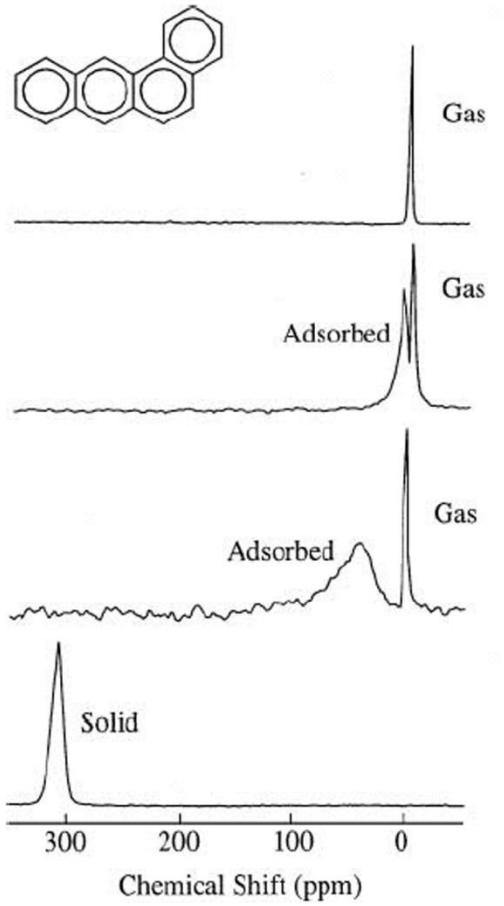
adsorption isotherm can be reproduced by simulations

How many neighbor atoms, at what distances?



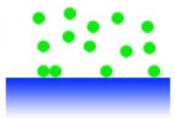
How many neighbor atoms, at what distances?

Example:

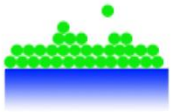


dilute Xe gas
large $r_{Xe\text{-}Xe}$,σ(Xe atom)

limiting case
one Xe on crystal
$\sigma(r_{Xe\text{-}C})$, short $r_{Xe\text{-}C}$



occasional Xe-Xe neighbors
$\sigma(r_{Xe\text{-}C})$, short $r_{Xe\text{-}C}$
$+\sigma(r_{Xe\text{-}Xe})$, short $r_{Xe\text{-}Xe}$



many Xe-Xe neighbors
$\sigma(r_{Xe\text{-}C})$, short $r_{Xe\text{-}C}$
$+\sum\sigma(r_{Xe\text{-}Xe})$, short $r_{Xe\text{-}Xe}$

D. Raftery, H. Long, T. Meersmann, P.J. Grandinetti, L. Reven, and A. Pines, Phys. Rev. Lett. **66**, 584 (1991).

Xe shielding depends on how many neighbor atoms, at what distances

For a single instantaneous configuration, the Xe shielding response is **nearly additive**.

For example, the ab initio Xe shielding for Xe surrounded by some number of Ne atoms (in circles or helices) is found to be nearly the same as the **sum** of the ab initio Xe-Ne shieldings at those Xe-Ne distances

Shielding is a very local molecular property because of the r_N^{-3} part of the operator

What fraction of the time a particular Xe-neighbor configuration is found

- Probability of finding Xe at a particular location depends on the intermolecular potential functions between Xe and the neighbor atoms. This too can be assumed to be additive and distance-dependent within a grand canonical Monte Carlo simulation.

Simulations:

1. Assume a model of the real physical system
   - Model for shielding response calculation
   - Model for the material system
2. Quantum mechanics: Calculate Xe shielding response as a function of configuration
3. Adopt potential energy of intermolecular interactions between Xe and the environment atoms
4. Choose appropriate averaging process, assuming additivity:
   - Canonical Monte Carlo
   - Grand Canonical Monte Carlo
   - Molecular Dynamics
5. **Simulations produce:**
   Xe one-body distributions: where does Xe spend time?
   Average isotropic Xe chemical shift
   Xe line shapes characterizing Xe chemical shift tensor
   Xe distribution among cages or phases, etc., etc.

INTERMOLECULAR CHEMICAL SHIFTS

in ZEOLITE: Metropolis Monte Carlo

$$\sigma(\mu, T, V) = (1/M)\sum_{i=1}^{M} \sigma_i(\mathbf{r}^N)$$

the average at a given chemical potential and T i.e. at a given overhead gas (P,T)

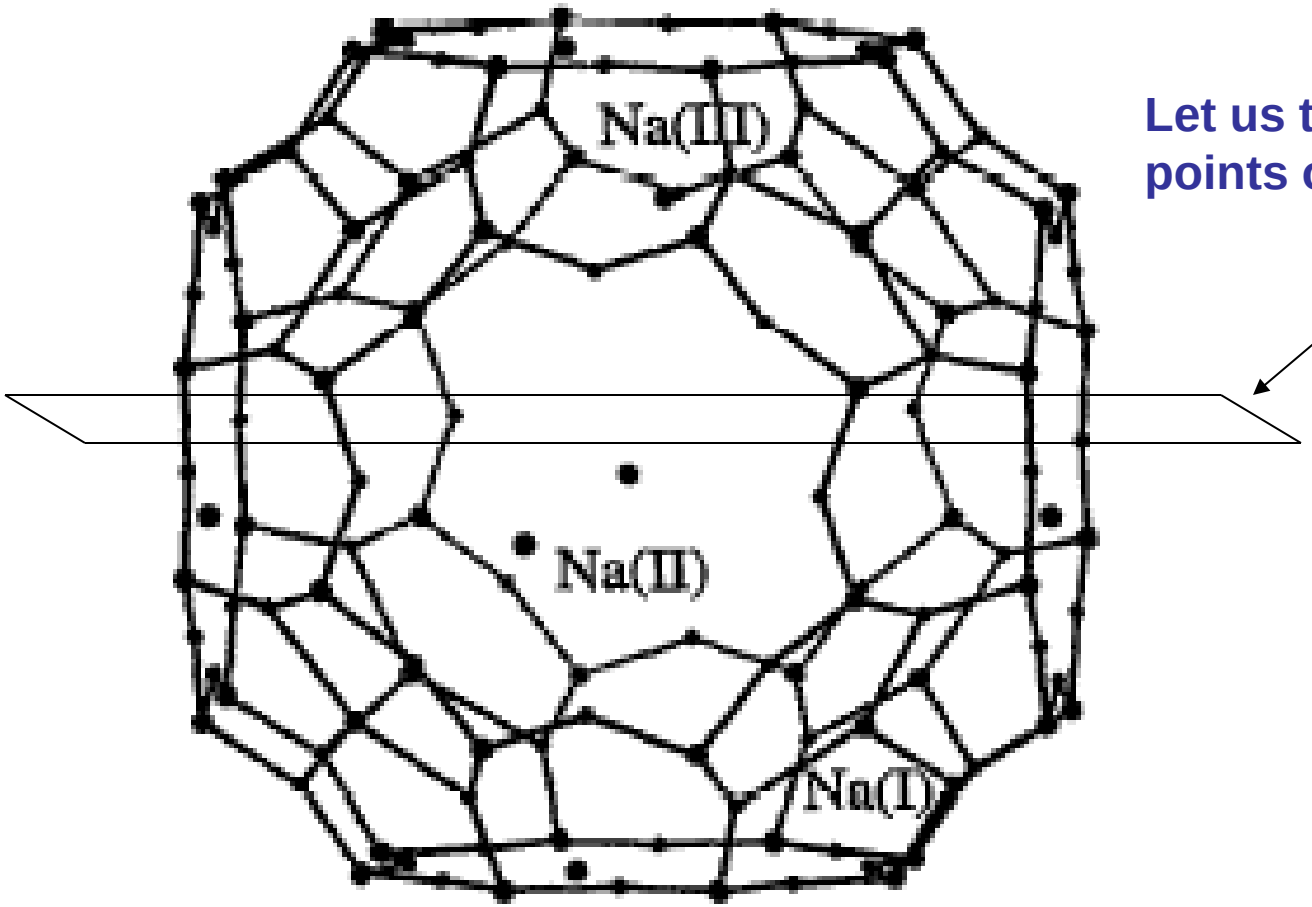
where,

$\sigma_i(r^N) = \sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4,...$in zeolite) the chemical shift function

where, the configurations *i = 1 to M*
are generated from a probability distribution,
in GCMC the probability is proportional to
$\exp\{-[\mathbf{U}(\mathbf{r}^N) - N\mu]/kT - \ln N! - 3N\ln(h^2/2\pi mkT)^{1/2} + N\ln V\}$

Need 2 functions:

$\sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4,...$in zeolite) & $\mathbf{U}(\mathbf{r}^N)$



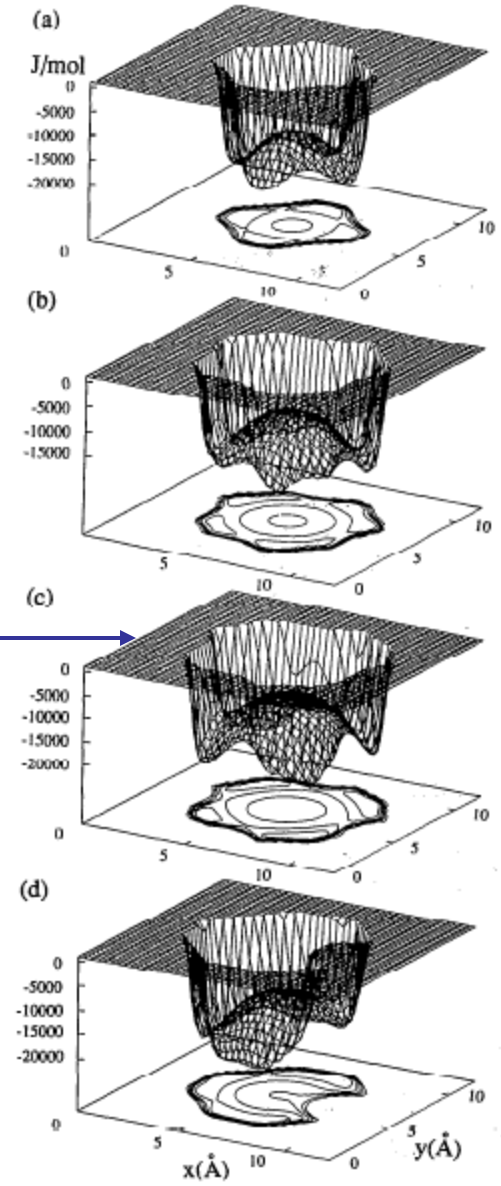
Let us take a look at points on this plane

cage of zeolite NaA

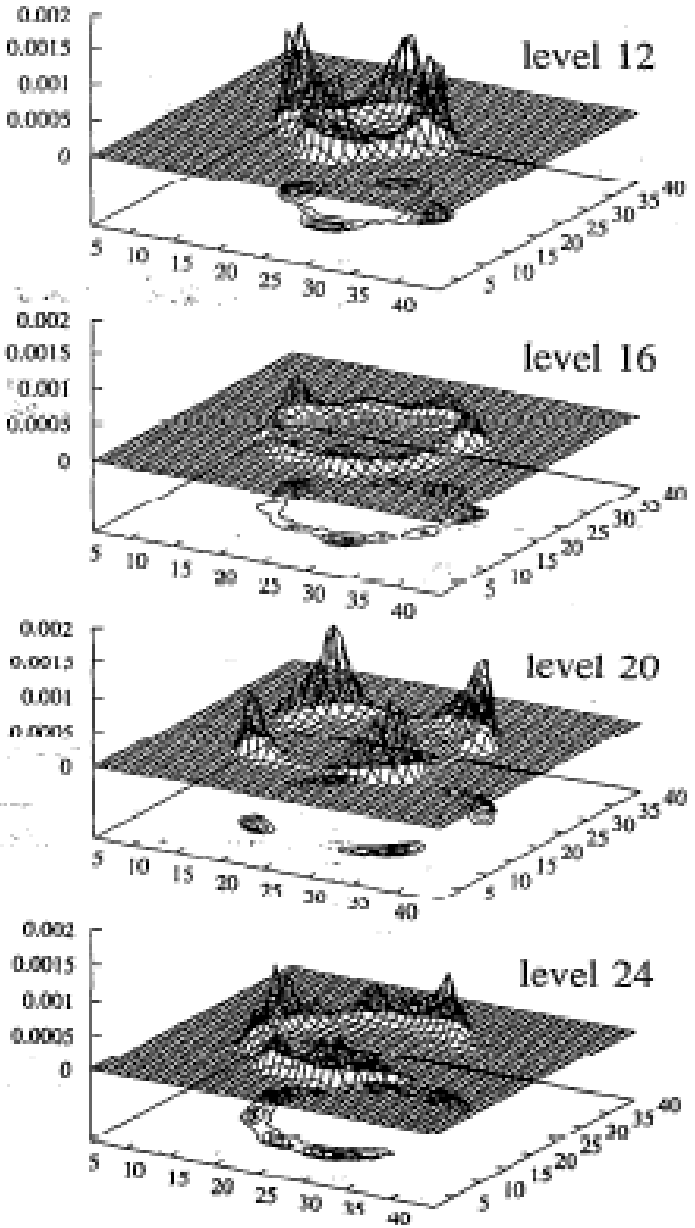
in GCMC the probability is proportional to

$\exp\{-[\mathbf{U}(\mathbf{r}^N) - N\mu]/kT - \ln N! - 3N\ln(h^2/2\pi mkT)^{1/2} + N\ln V\}$

as shown in plots ……



this plane

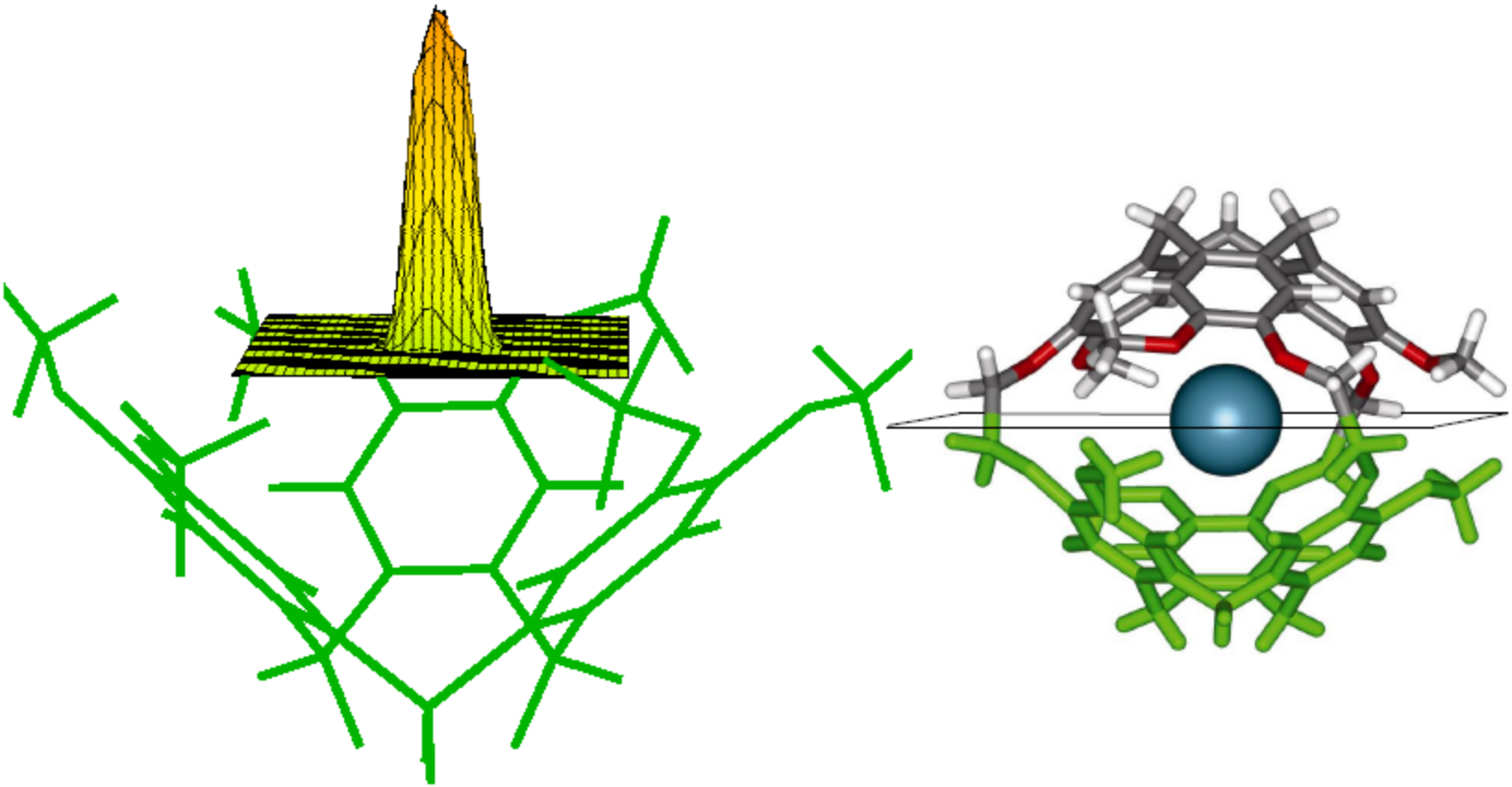


Potential energy surface $U(r^N)$ for one Xe at various planes through the zeolite cage.

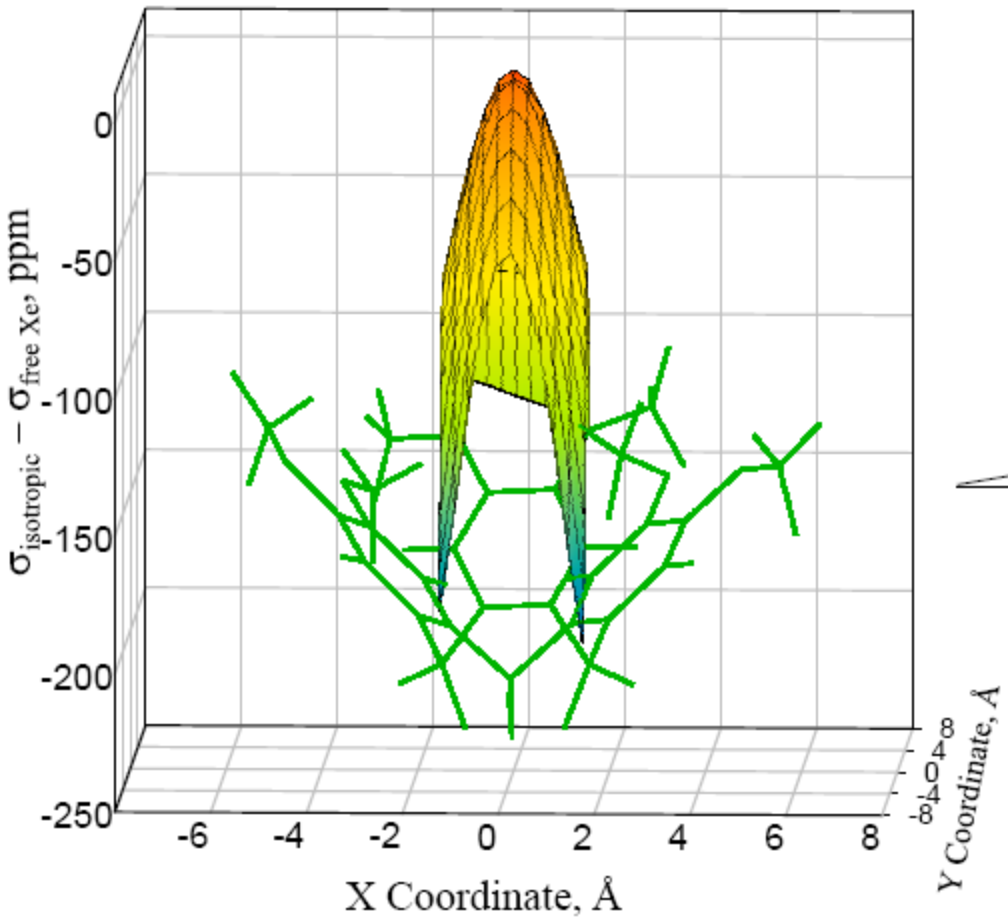
Probability distribution of Xe at those planes

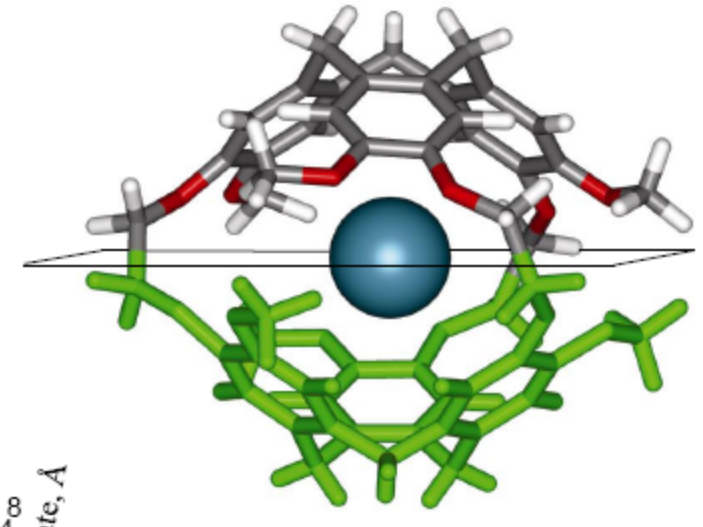
One-body distribution function for Xe@cryptoA

from Monte Carlo simulations



The Xe shielding surface for Xe@cryptoA

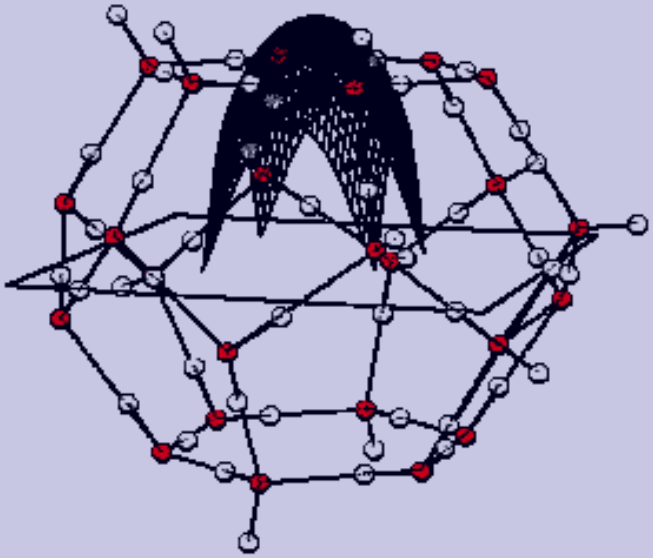




Intermolecular chemical shifts

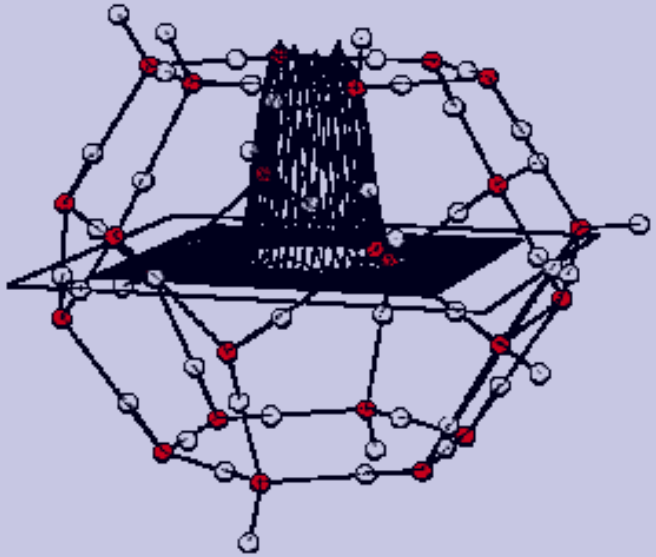
The Xe SHIELDING SURFACE: the shielding as a function of configuration (coordinates) of the system

(a) isotropic shielding surface



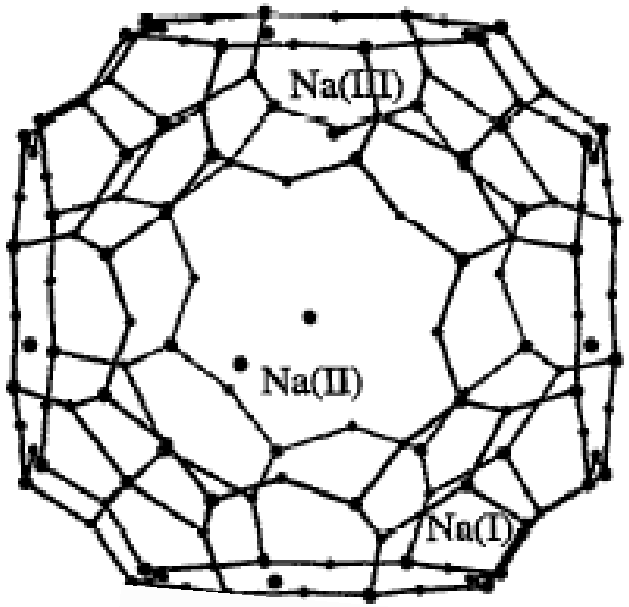
The Xe one-body distribution: the PROBABILITY of finding the system in a given configuration

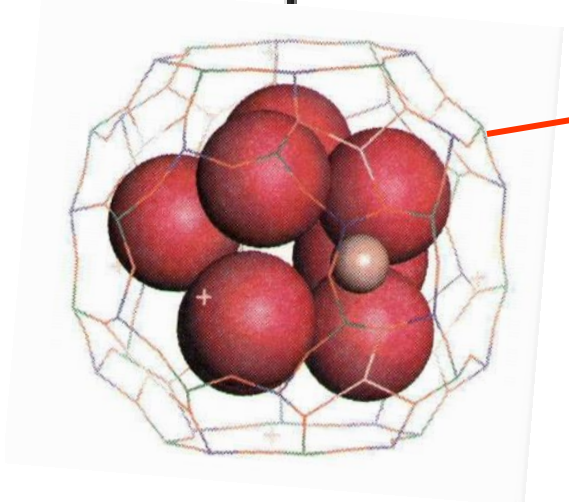
(b) one-body distribution surface

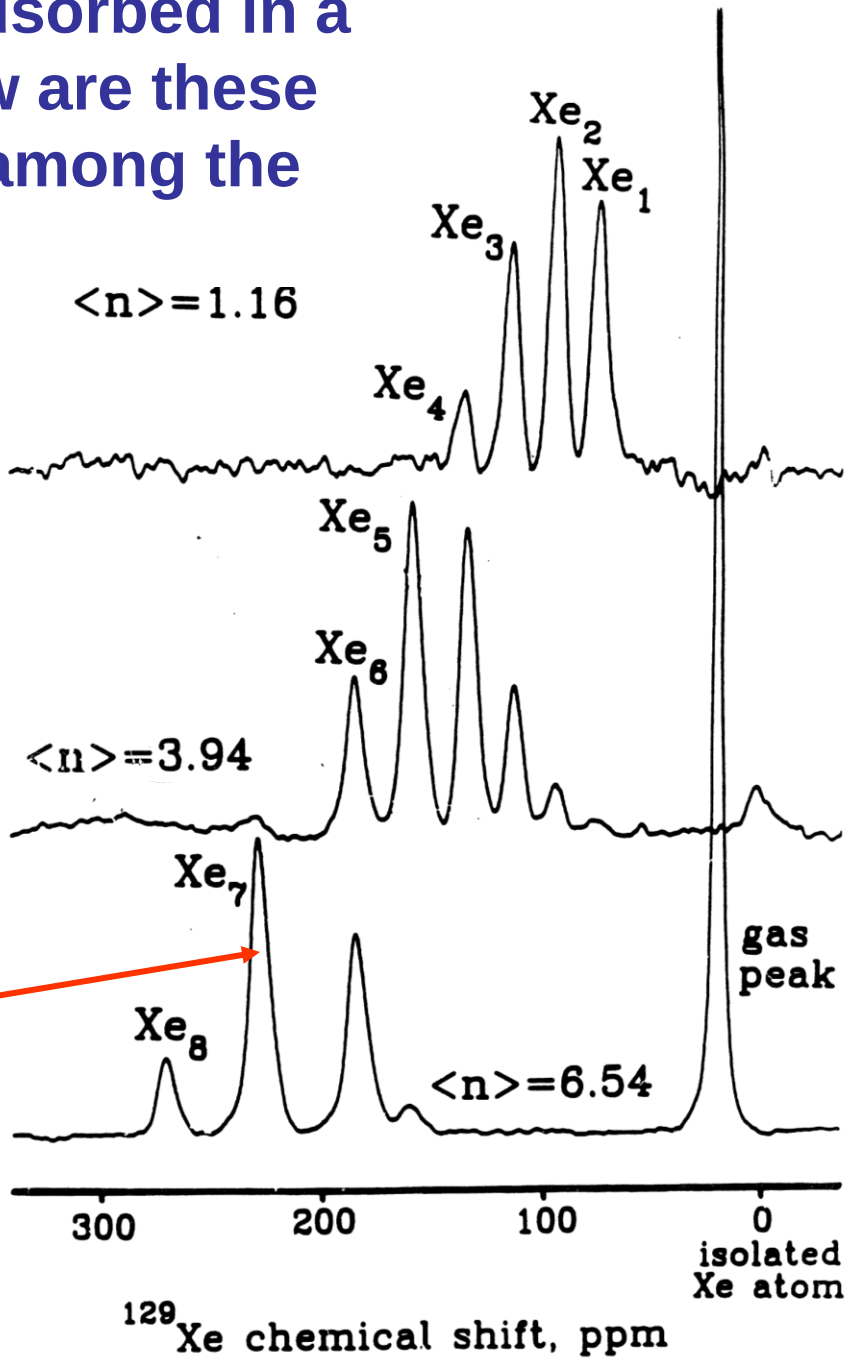


Xe in the $5^{12}6^2$ cage of clathrate hydrate Structure I

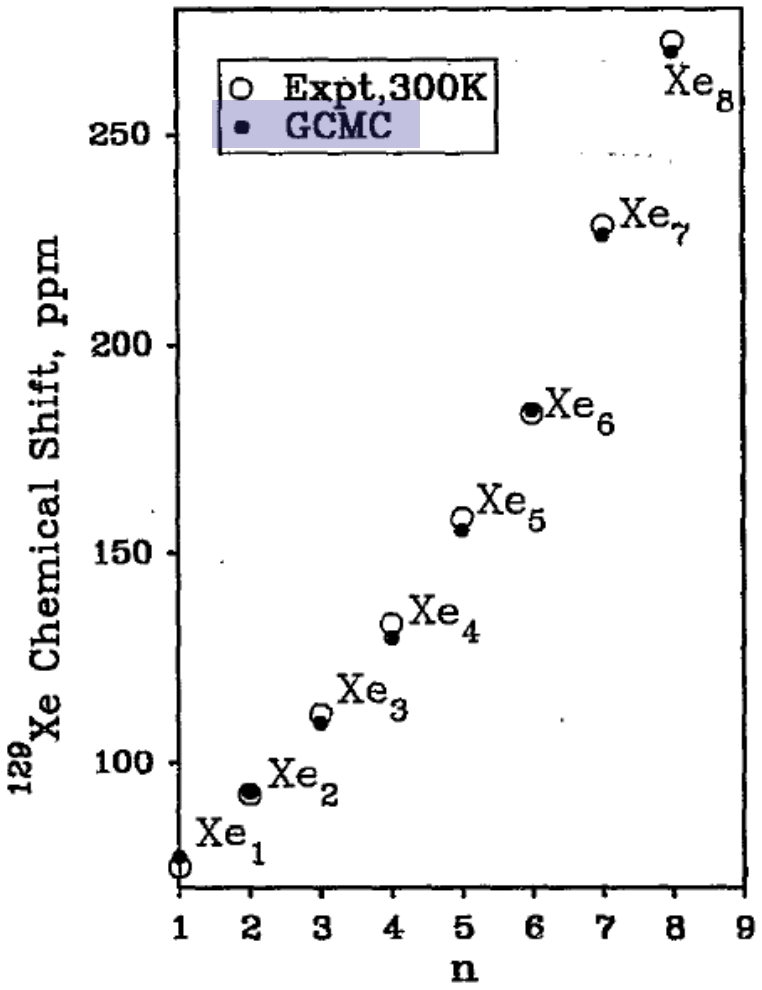
When molecules are adsorbed in a microporous solid, how are these molecules distributed among the cavities?



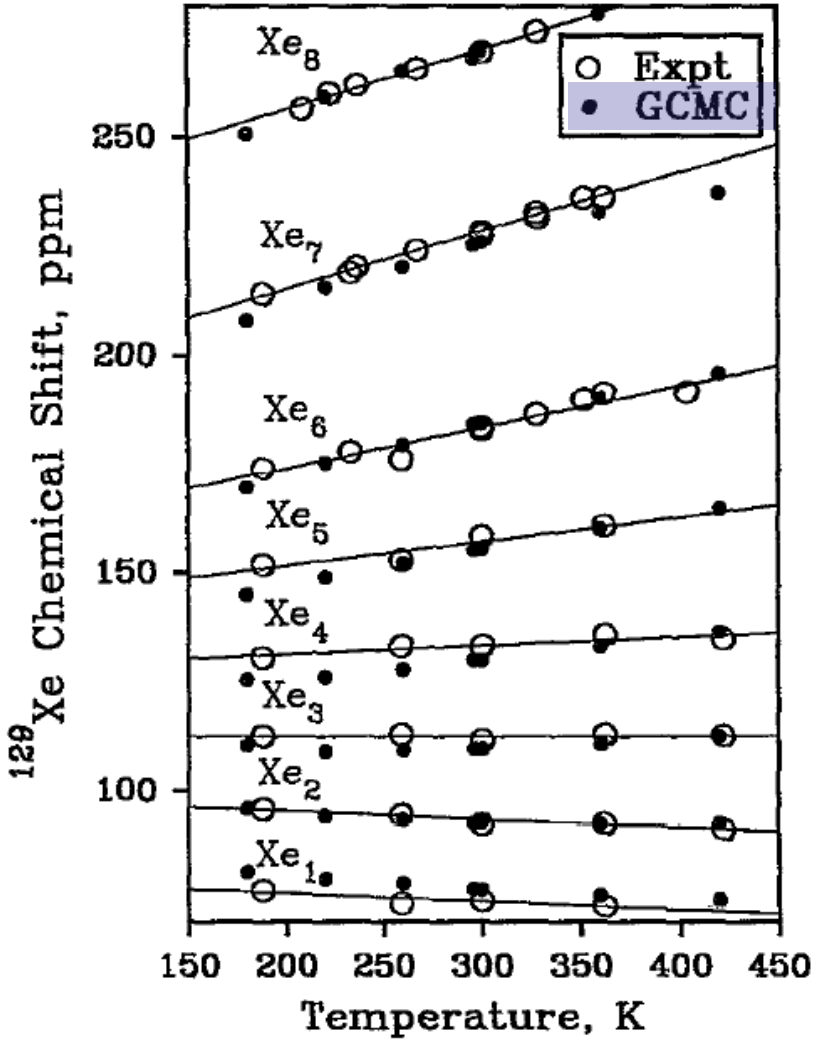




We reproduce the individual chemical shifts



and also the temperature dependence of each



Xe chemical shift of a single Xe inside a cavity depends on the average over

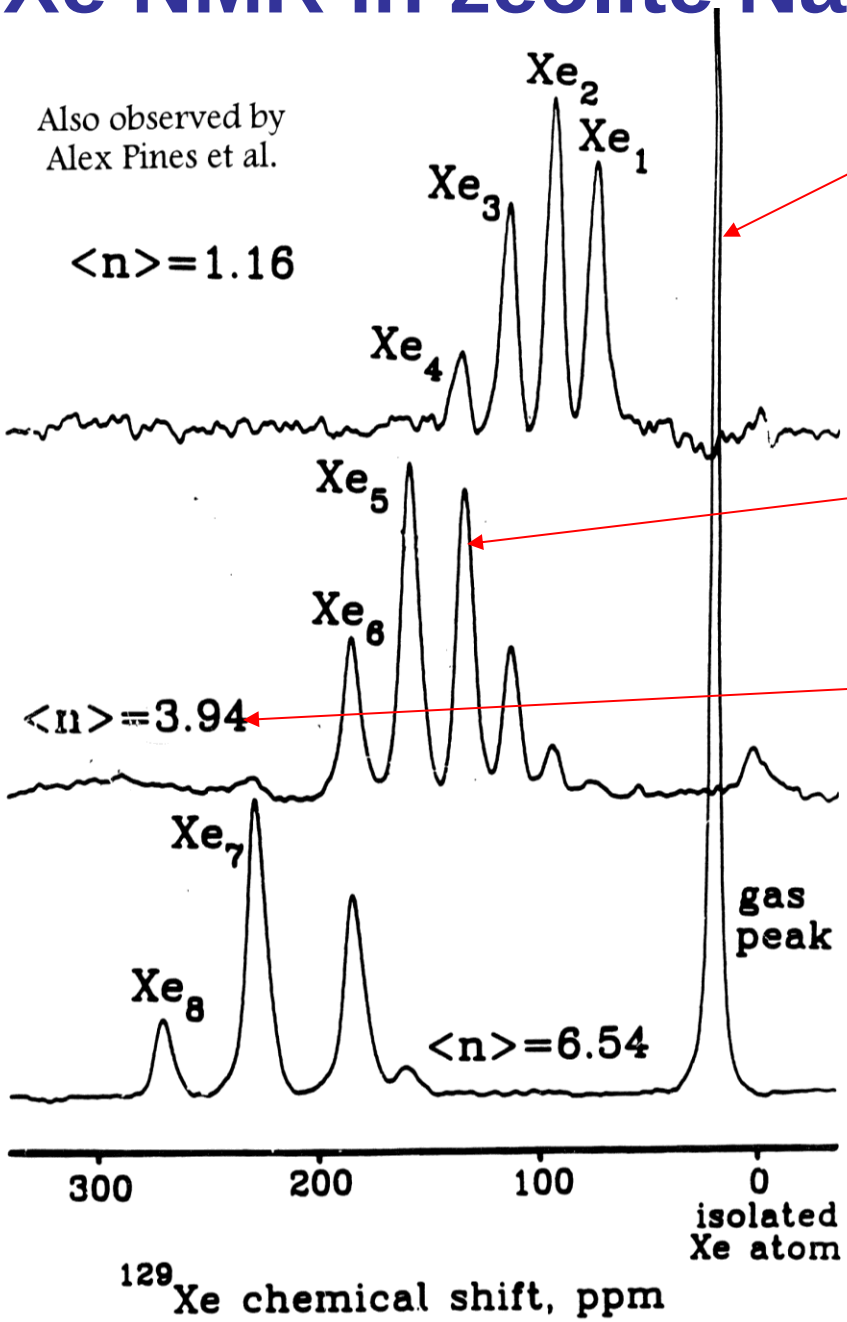
the probability of finding a Xe atom at a given position

and

the chemical shift of Xe at those distances between Xe and the atoms which constitute the cavity walls.

This means that the probability distribution of Xe within a cavity obtained by GCMC can be verified by reproducing the Xe chemical shift in that cavity.

Xe NMR in zeolite NaA



Xe chemical shift of gas peak provides ρ_{Xe} Xe density in the overhead bulk gas

Relative areas under the peaks provides the fraction of cages containing a number n of Xe atoms and also the average ⟨n⟩. Adsorption isotherm by NMR!

Chemical shift of an individual peak can verify the GCMC *distribution of n Xe atoms within the cavity*.

Adsorption of pure Xe vs. a mixture of Xe and another gas

QUESTIONS:

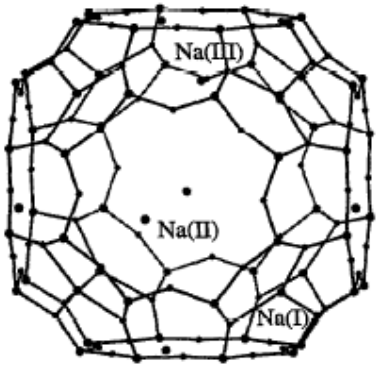
What are the consequences for Xe?

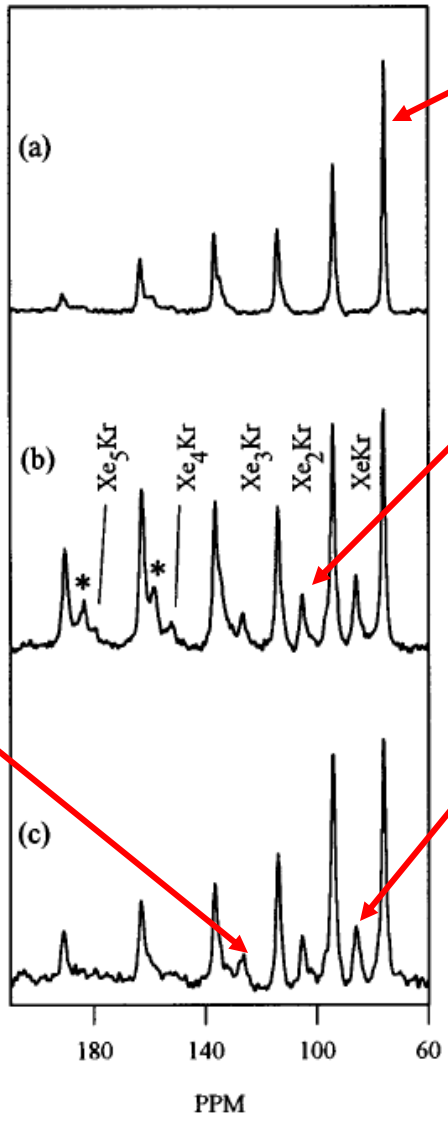
Is the distribution of Xe inside vs. outside affected?

Is the distribution of confined Xe affected?

Is the Xe chemical shift affected?

Competitive Adsorption





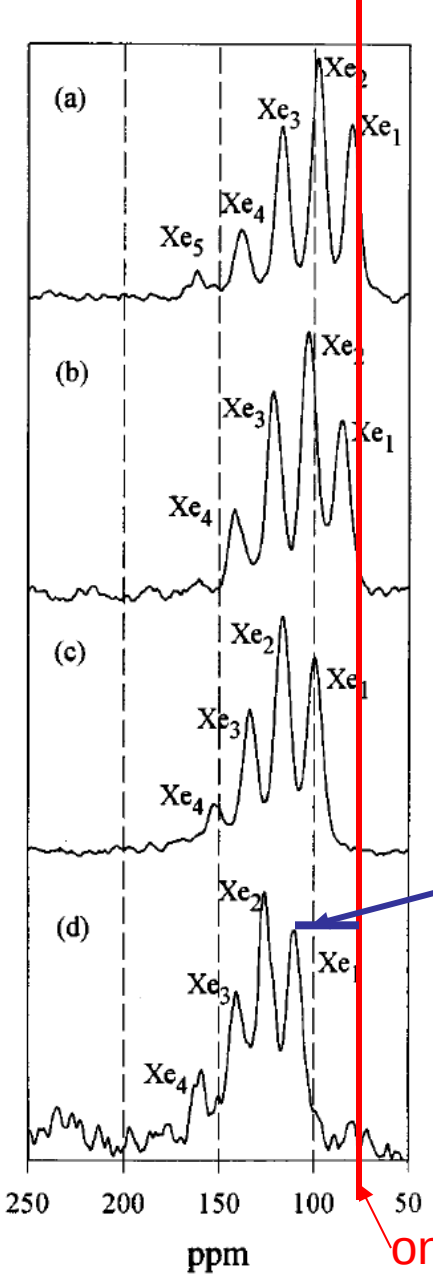
one Xe
in a cage

two Xe+one Kr
in a cage

three Xe+one Kr
in a cage

one Xe+ one Kr
in a cage

Xe NMR spectrum



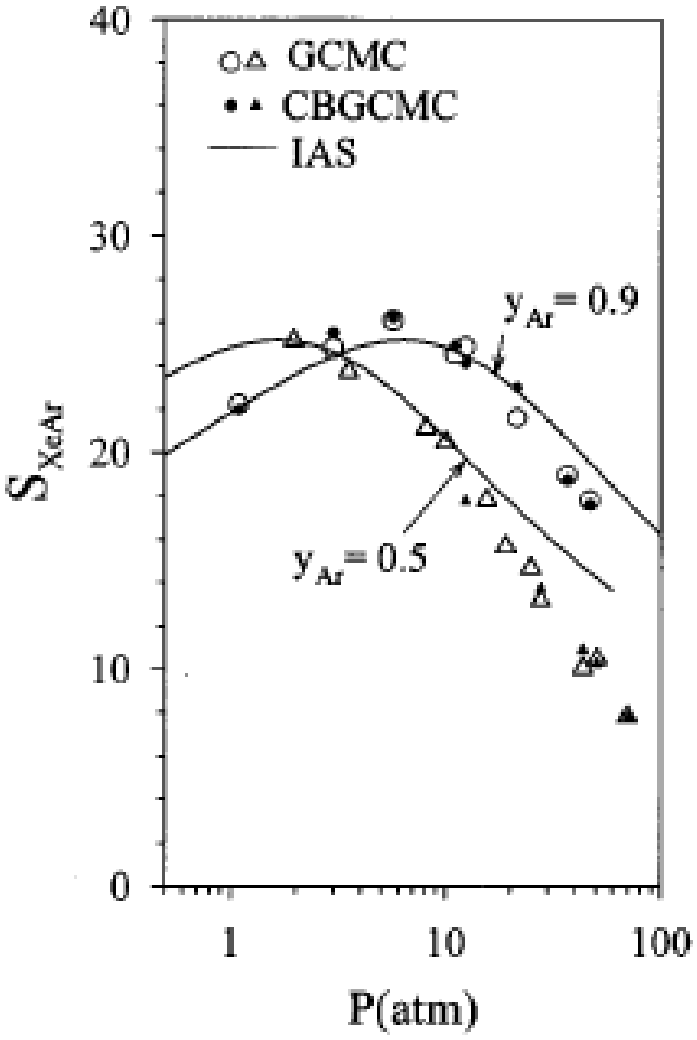
The Xe chemical shift for Xe_n depends on the average number of Ar atoms in the same cage as n Xe atoms.

The INTENSITY of the Xe_n peak is a direct measure of the fraction of cages that have exactly *n* Xe atoms, as in pure Xe

Its shift from corresp peak in pure Xe/NaA gives the average number of Ar atoms in the same cage with it!

one Xe in a cavity in pure Xe samples

Xe NMR spectra of adsorbed Xe-Ar mixtures in zeolite NaA



Selectivity coefficient of zeolite NaA for adsorption of Xe and Ar from gas mixtures at various total pressures and mole fractions

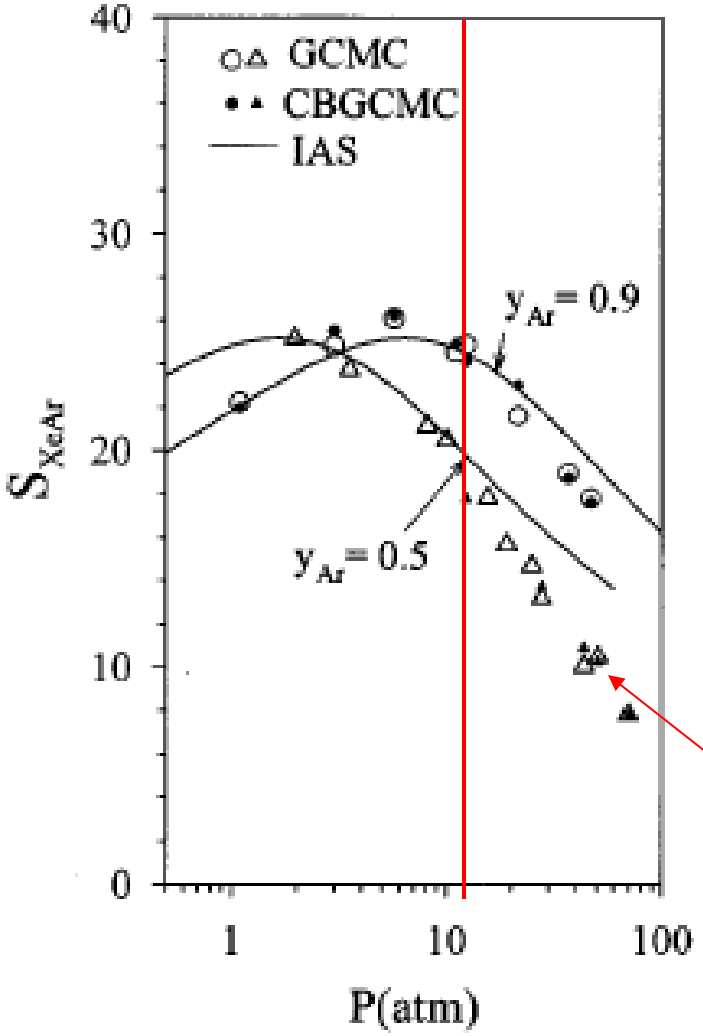
inside vs. outside

at (P_{total} , y_{CH4}) in the bulk, we get from simulations:

- the total amount of gas adsorbed,
- the composition inside ($\langle n \rangle_{Xe}$, $\langle m \rangle_{CH4}$), and
- the **separation factor** or **selectivity coefficient**

the ratio of mole fractions in the adsorbed phase and the bulk gas phase:

$$S_{Xe,Ar} = \frac{x_{Xe}/x_{Ar}}{y_{Xe}/y_{Ar}}$$



GOOD NEWS:

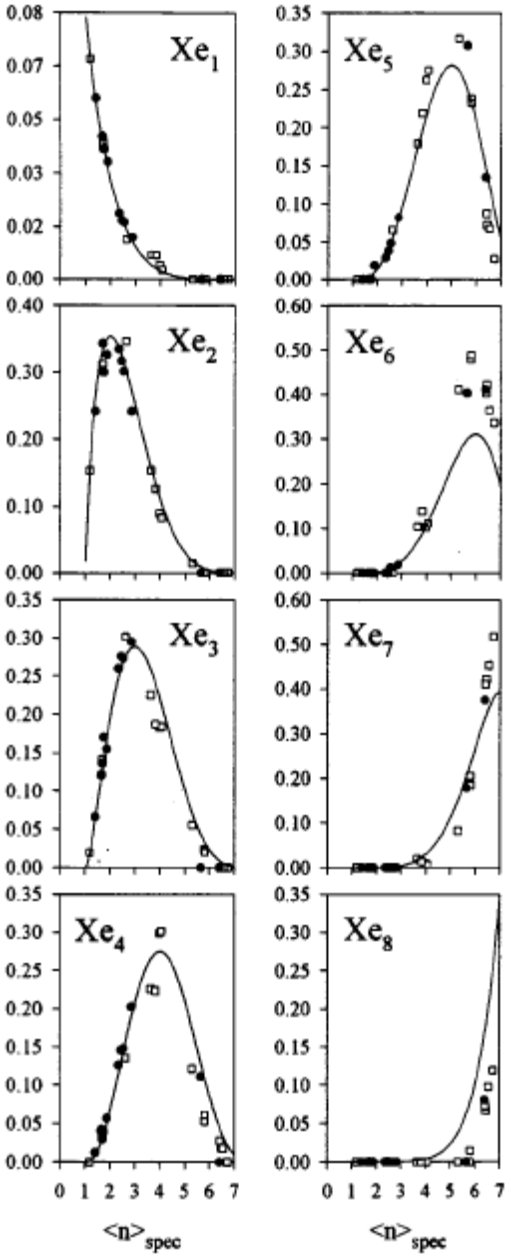
For low total pressures, the adsorption of Xe and the adsorption of the other molecule are nearly independent of each other, as predicted by Ideal Adsorbed Solution theory (IAS), analogous to Raoult's law for ideal solutions.

For high total pressures, adsorption of Xe and other molecules are no longer independent (deviations from IAS theory are larger).

In other words, at low total pressures,

the Xe distributes itself
just as it would if the other type of molecule were absent.

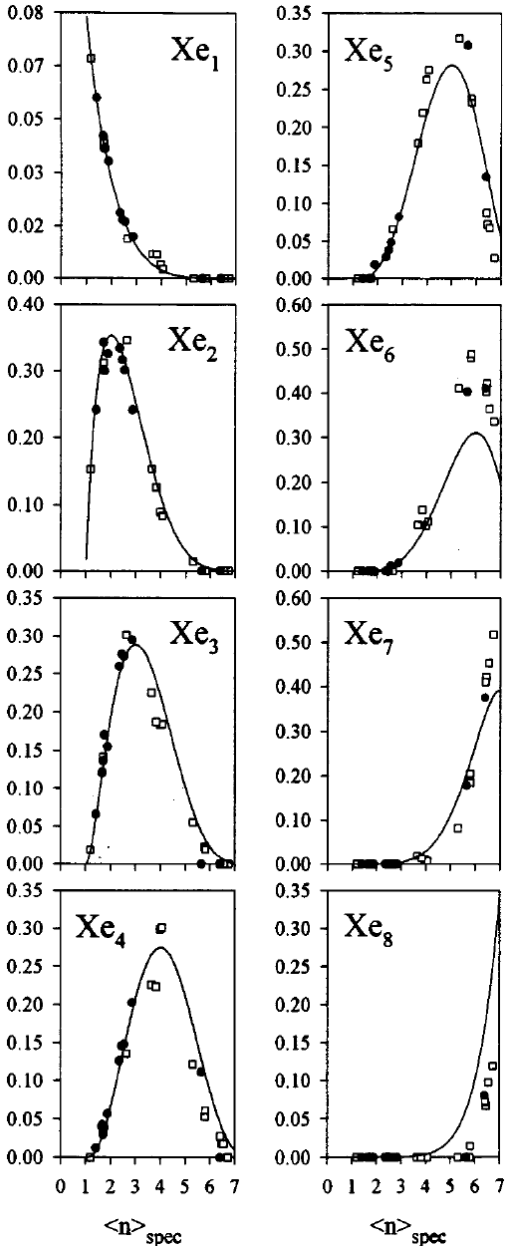
However, the mole fraction of Xe inside will be different from outside.
Separation factor is larger than one for Xe with another gas. For Xe and Ar it is 20-25 at room temperature.
For Xe and He it should be much much larger.



! ! Fraction of cages containing a specific number of Xe atoms in zeolite NaA is found to be **independent of whether pure Xe** (□) **or any mixture** (●) of Xe and Ar are overhead

pure Xe (□)
mixture (●) of Xe and Ar
are overhead

Experimental distribution of Xe among cages occupied by Xe atoms

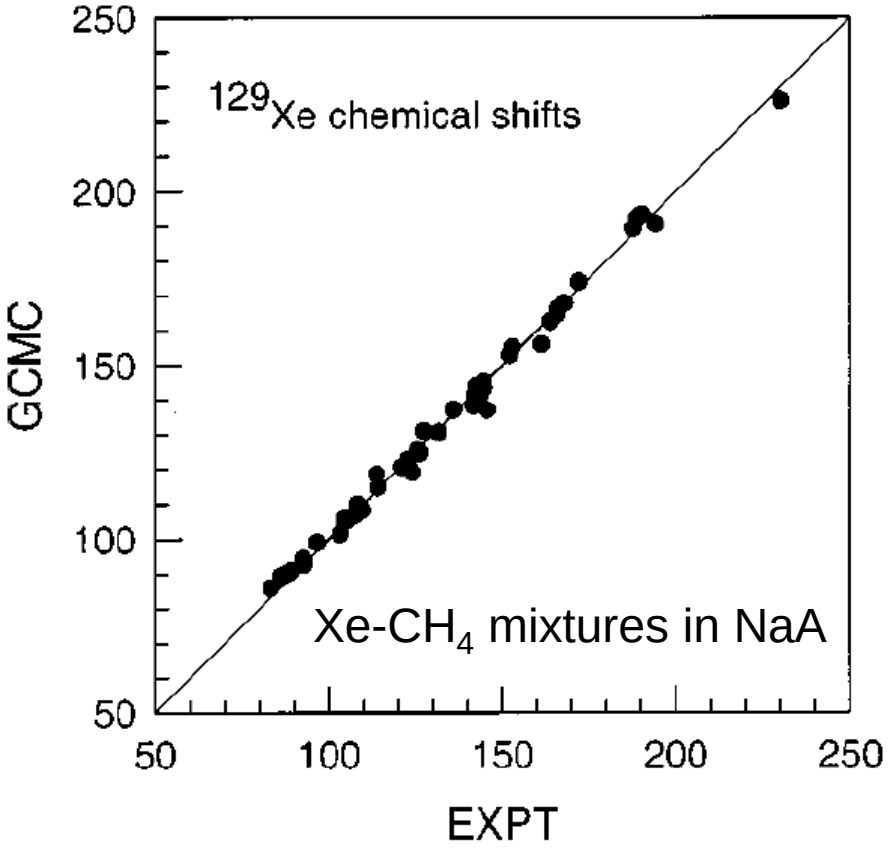


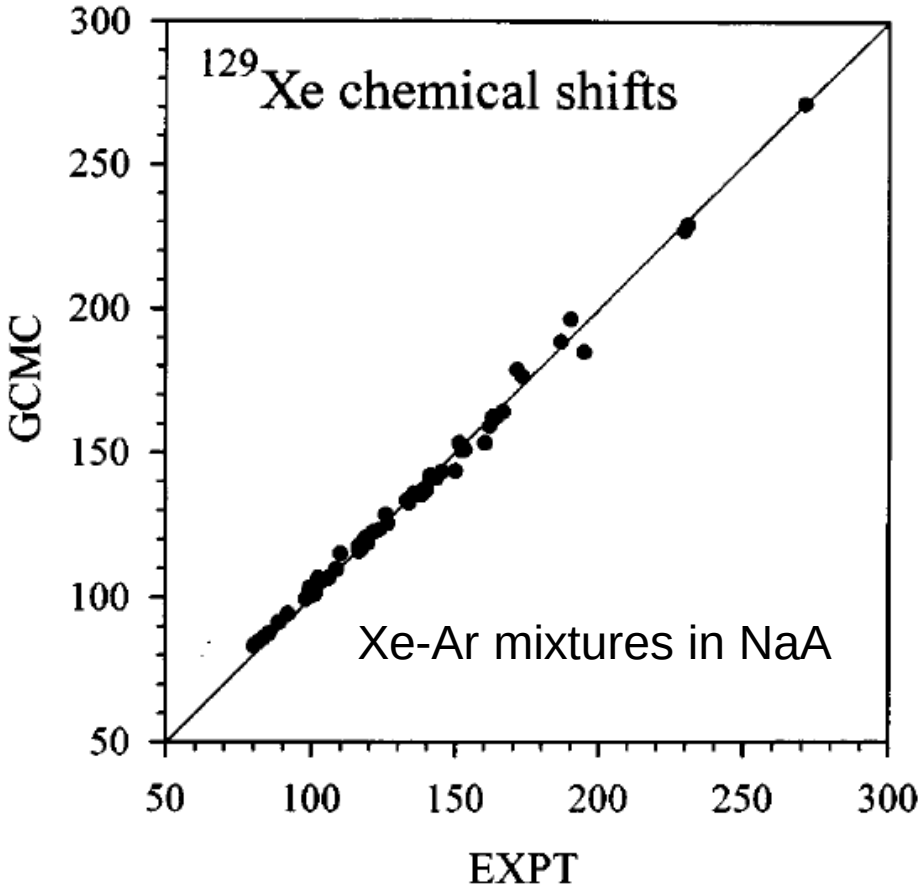
QUESTION:

Is the distribution of Xe among the cavities affected by the presence of the other gas?

! ! Fraction of cages containing a specific number of Xe atoms in zeolite NaA is found to be **independent of whether pure Xe** (□) **or any mixture** (●) of Xe and Ar are overhead

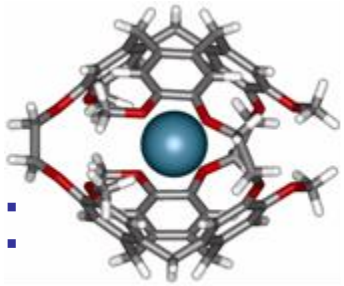
EXPERIMENTAL distribution of Xe among cages occupied by Xe atoms

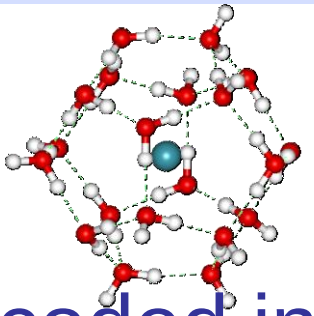




W can reproduce the Xe chemical shifts in all the samples of varying Xe- 'other' composition, thus, the average number of 'other' in the same cage as *n* Xe atoms is well represented by GCMC results.

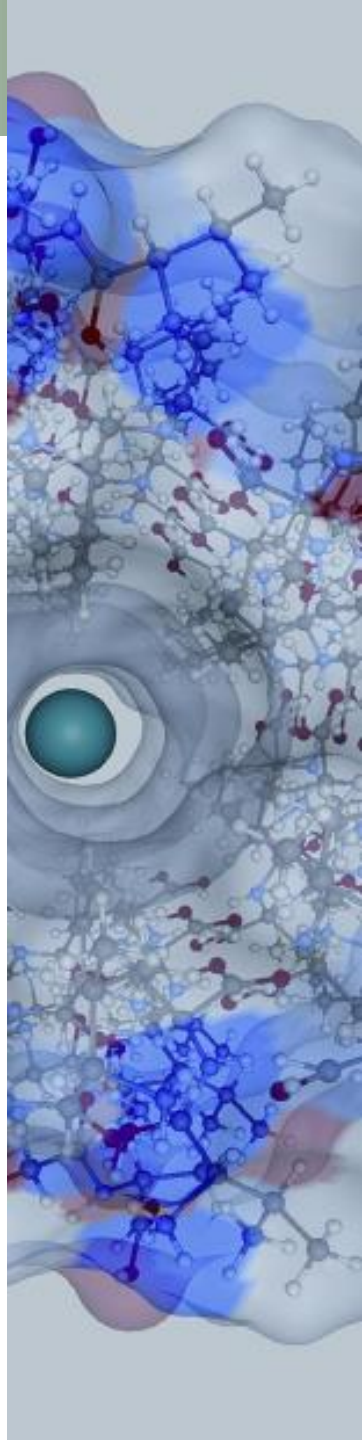
Xe in cages





QUESTION:
What information is encoded into the Xe chemical shift of a Xe atom trapped in a cage?

- architecture of the cage: size, shape
- hydrogen-bonding network
- aromatic rings
- vibrational, other dynamics of the cage atoms
- electronic structure of the cage: availability of electrons that can elicit a shielding response



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

The **dimer tensor model** for Xe shielding tensor in a cage

For example, the contribution to the shielding of Xe at point J due to 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 $\sigma_{\perp}(r_{XeO})$, $\sigma_{||}(r_{XeO})$.

Tensor components in the laboratory frame (frame of the simulation box):

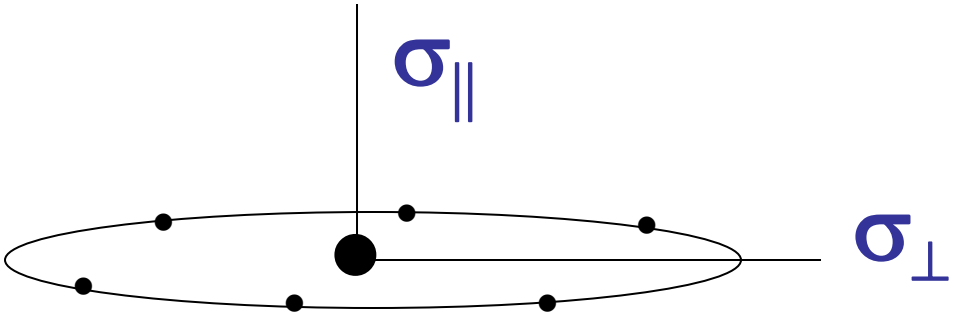
$$\sigma_{XX} = [(x_i - x_J)/r_{iJ}]^2 \sigma_{||} + \{[(y_i - y_J)/r_{iJ}]^2 + [(z_i - z_J)/r_{iJ}]^2\} \sigma_{\perp}$$

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

Sum over all such contributions from every O, every H atom.

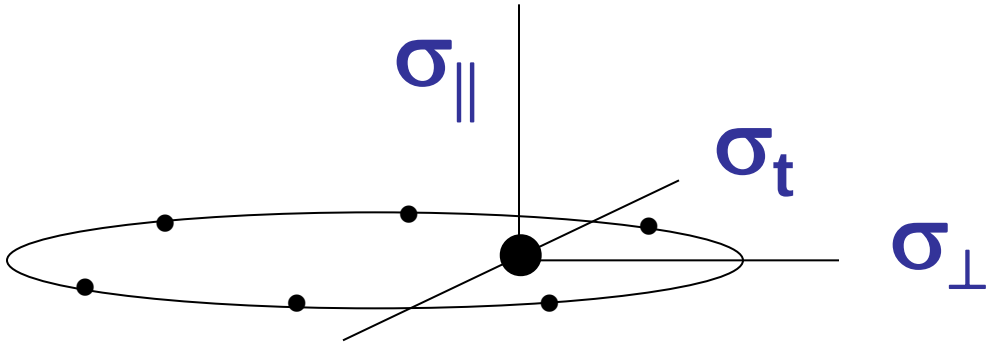
Are Xe shielding tensor components pairwise additive?

Example:



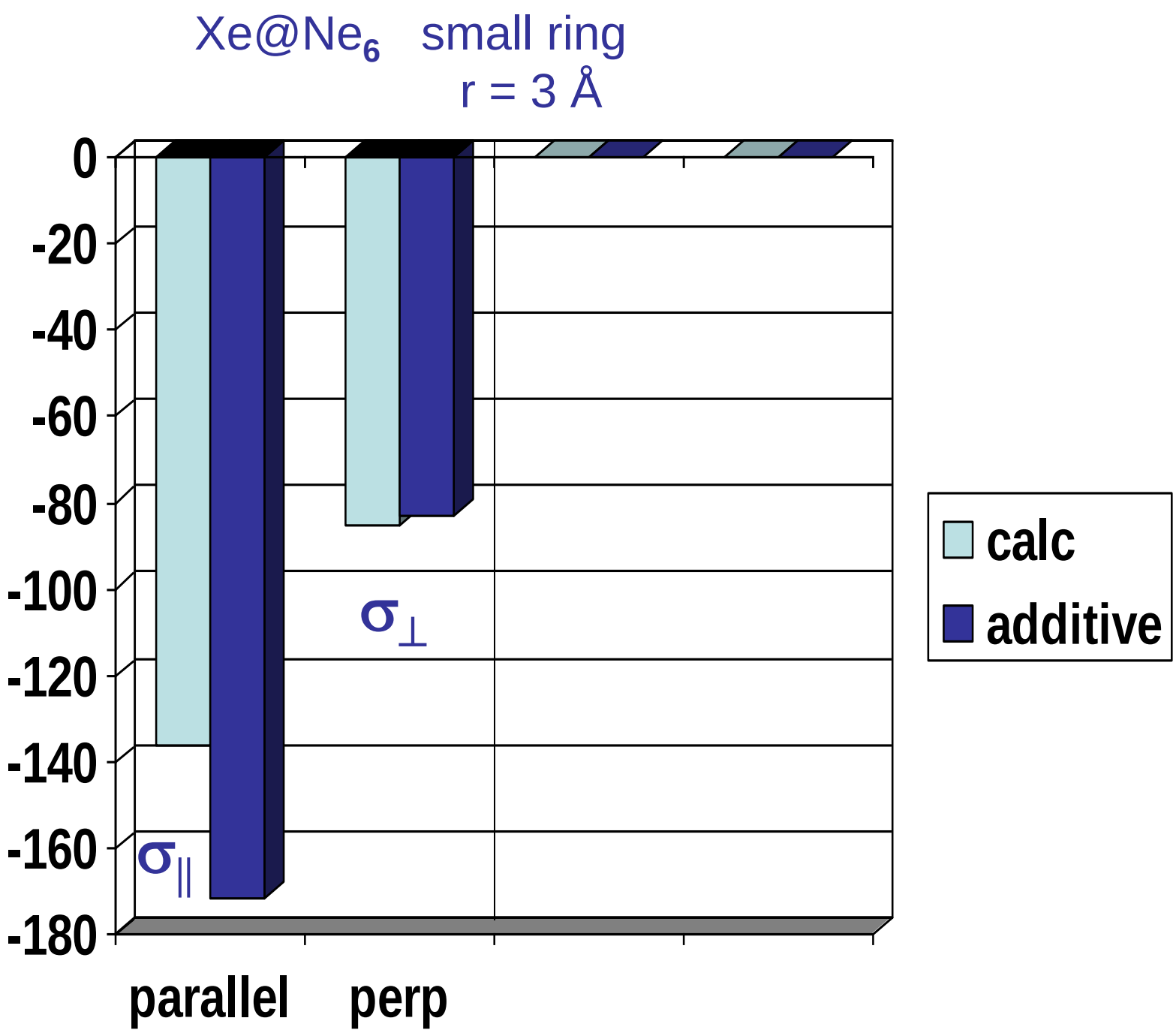
Xe in the center of a ring of Ne atoms

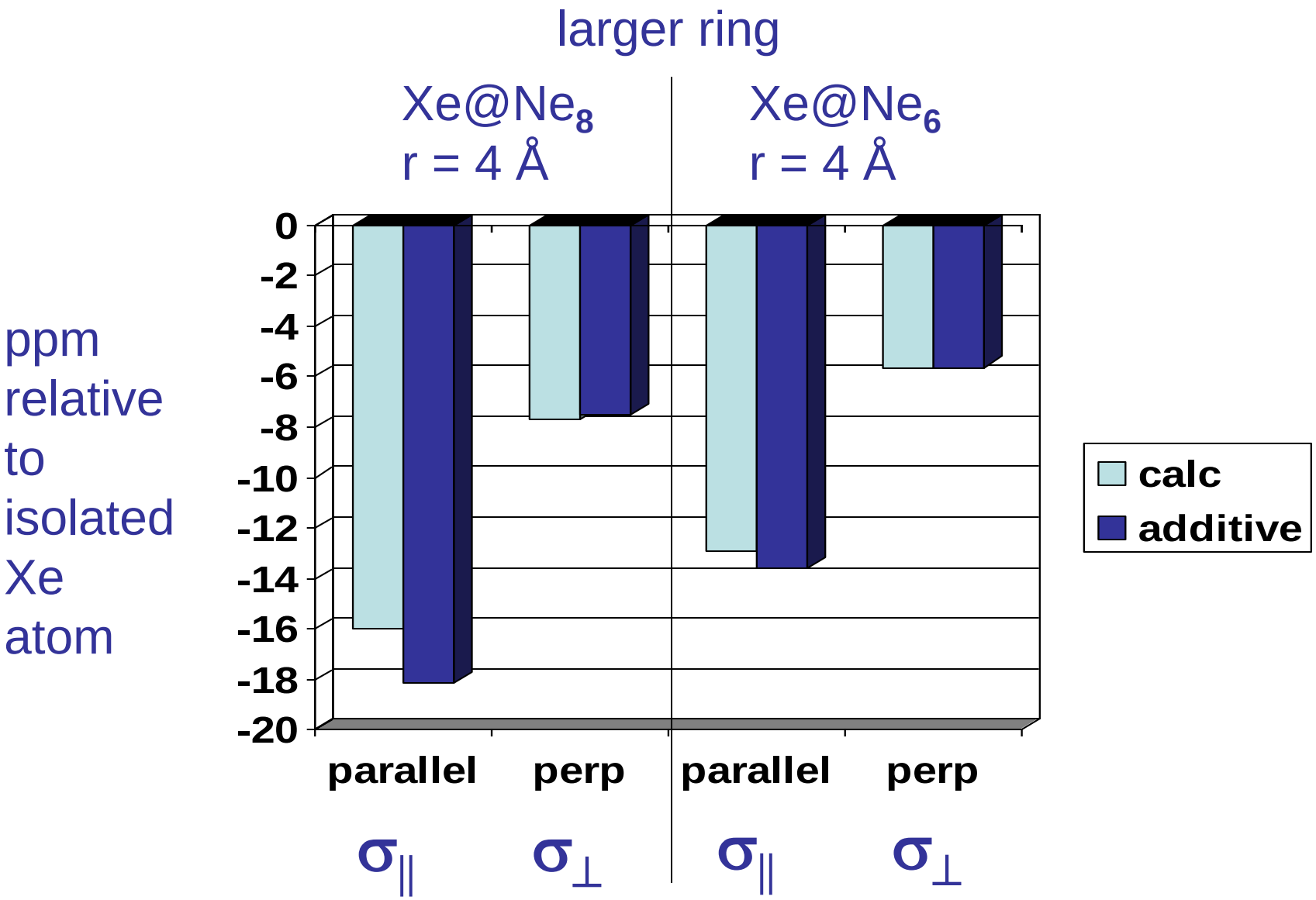
Xe off-center in the larger ring of Ne atoms



Model	r_{ring} Å	R_{Xe} Å	$\sigma_{\parallel}$	$\sigma_{\perp}$	σ_t
$Xe@Ne_6$	4.0	1.0	-40.04	-11.13	-28.86
$\sum_i^6 XeNe_i$	4.0	1.0	-43.18	-11.45	-29.00
$Xe@Ne_8$	4.0	1.0	-47.67	-18.39	-35.48
$\sum_i^8 XeNe_i$	4.0	1.0	-57.20	-18.69	-34.83

large deviation

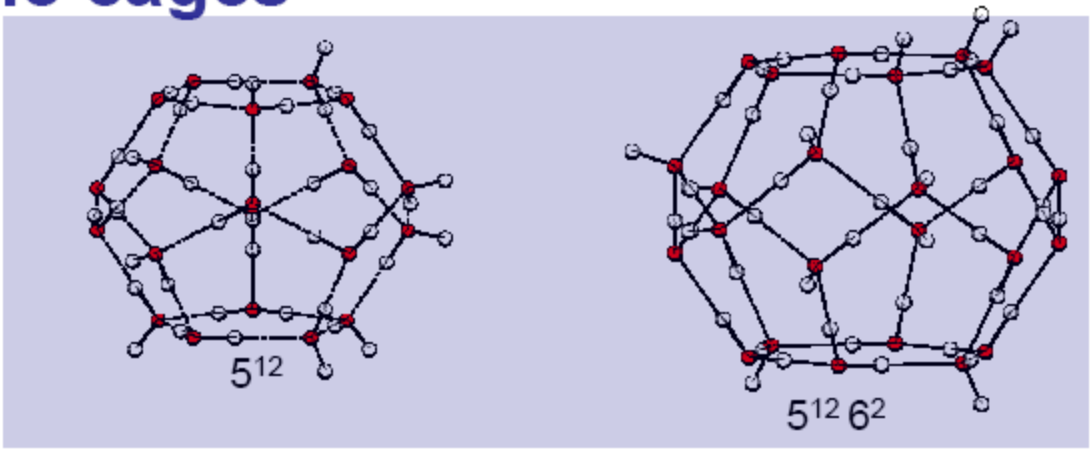

Xe@Ne6 small ring
r = 3 Å
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
σ⊥
σ||
parallel
perp
calc
additive


larger ring
Xe@Ne8
r = 4 Å
Xe@Ne6
r = 4 Å
ppm relative to isolated Xe atom
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
-20
parallel
perp
parallel
perp
σ||
σ⊥
σ||
σ⊥
calc
additive

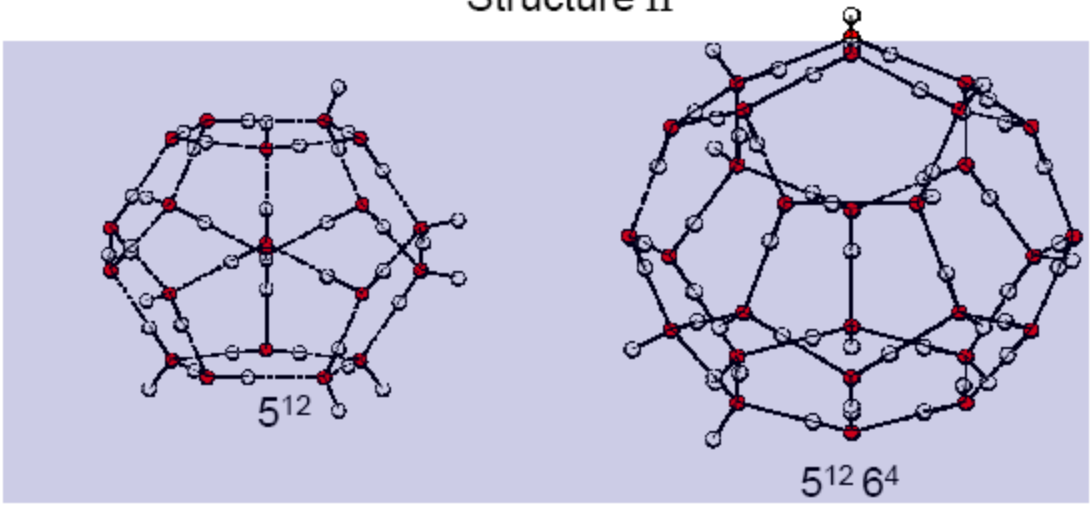
Clathrate hydrates

the cages

Structure I



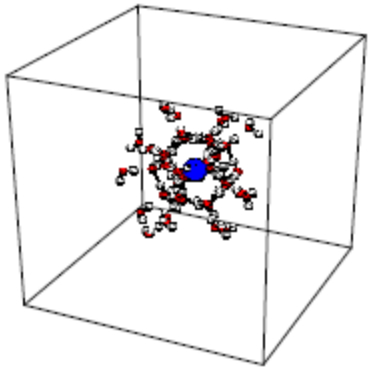
Structure II



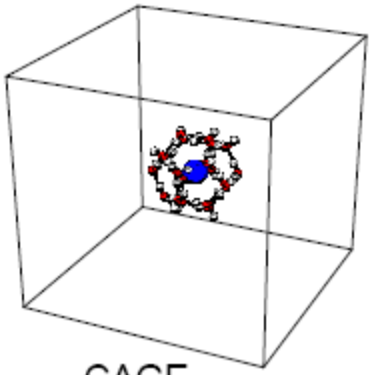
How to model a cage in a hydrogen bonded network?

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

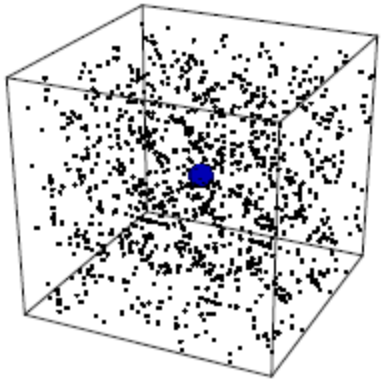
MODELS



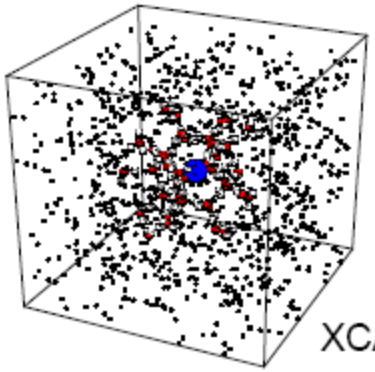
XCAGE



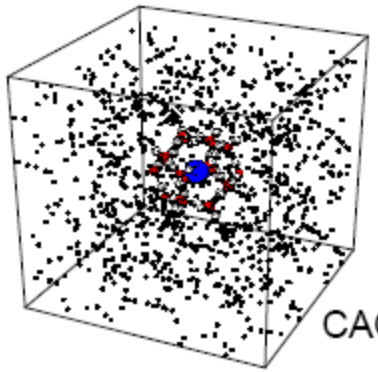
CAGE



PCA

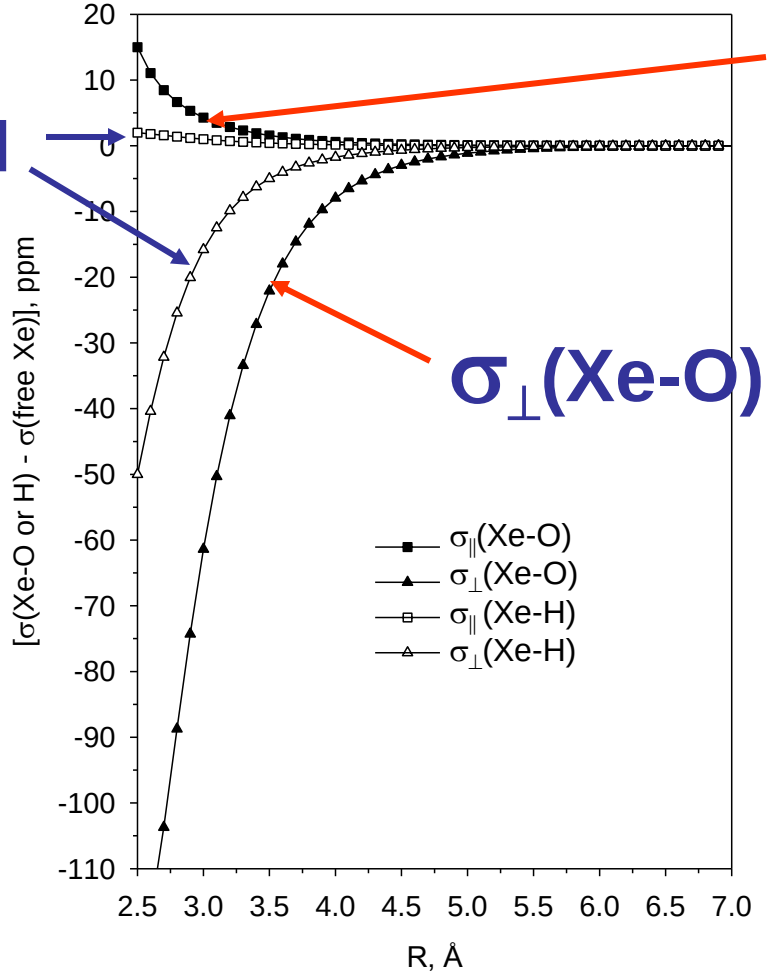


XCAGE/PCA



CAGE/PCA

The Xe-O and Xe-H shielding tensors

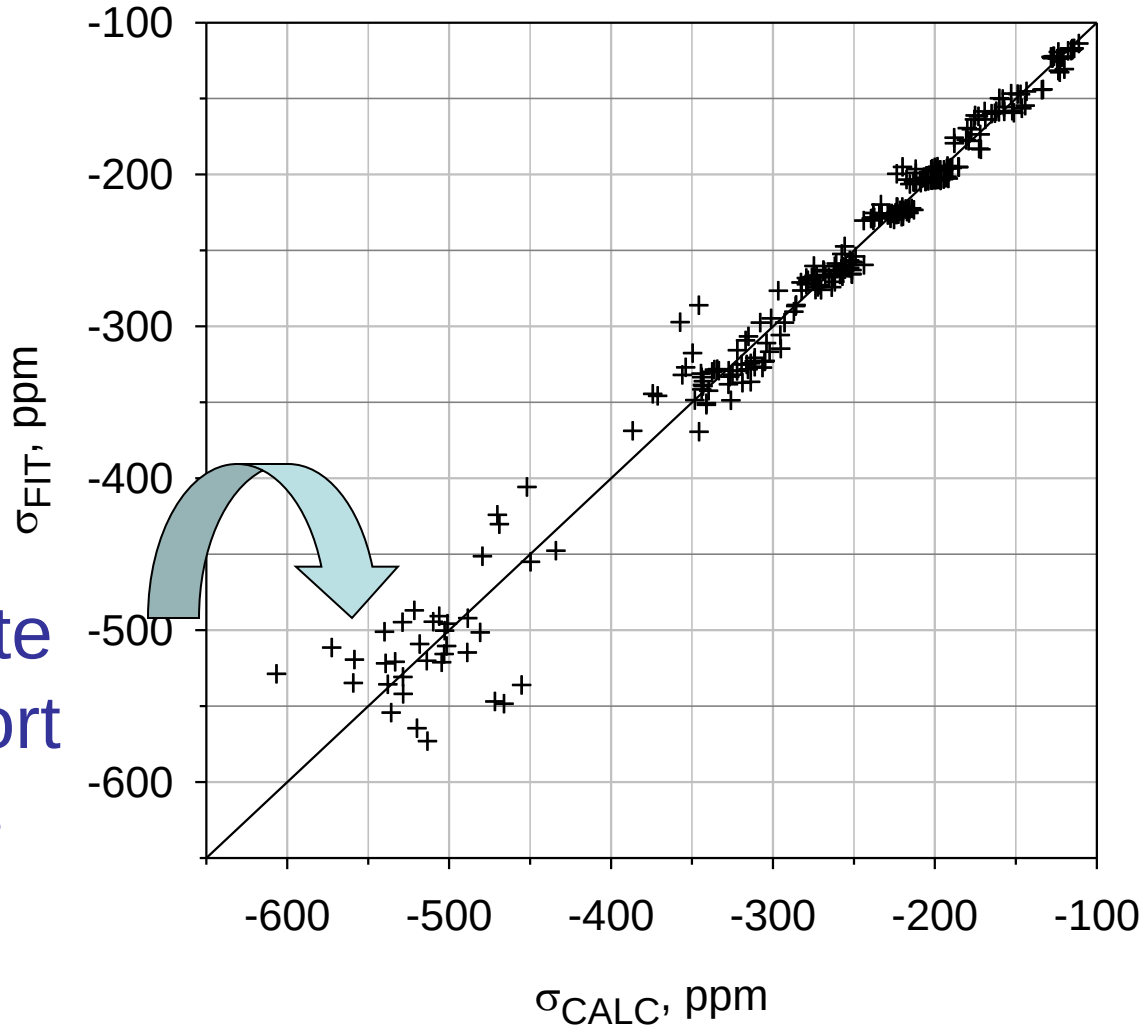


How to describe the ab initio tensor values at various Xe positions in the cage?

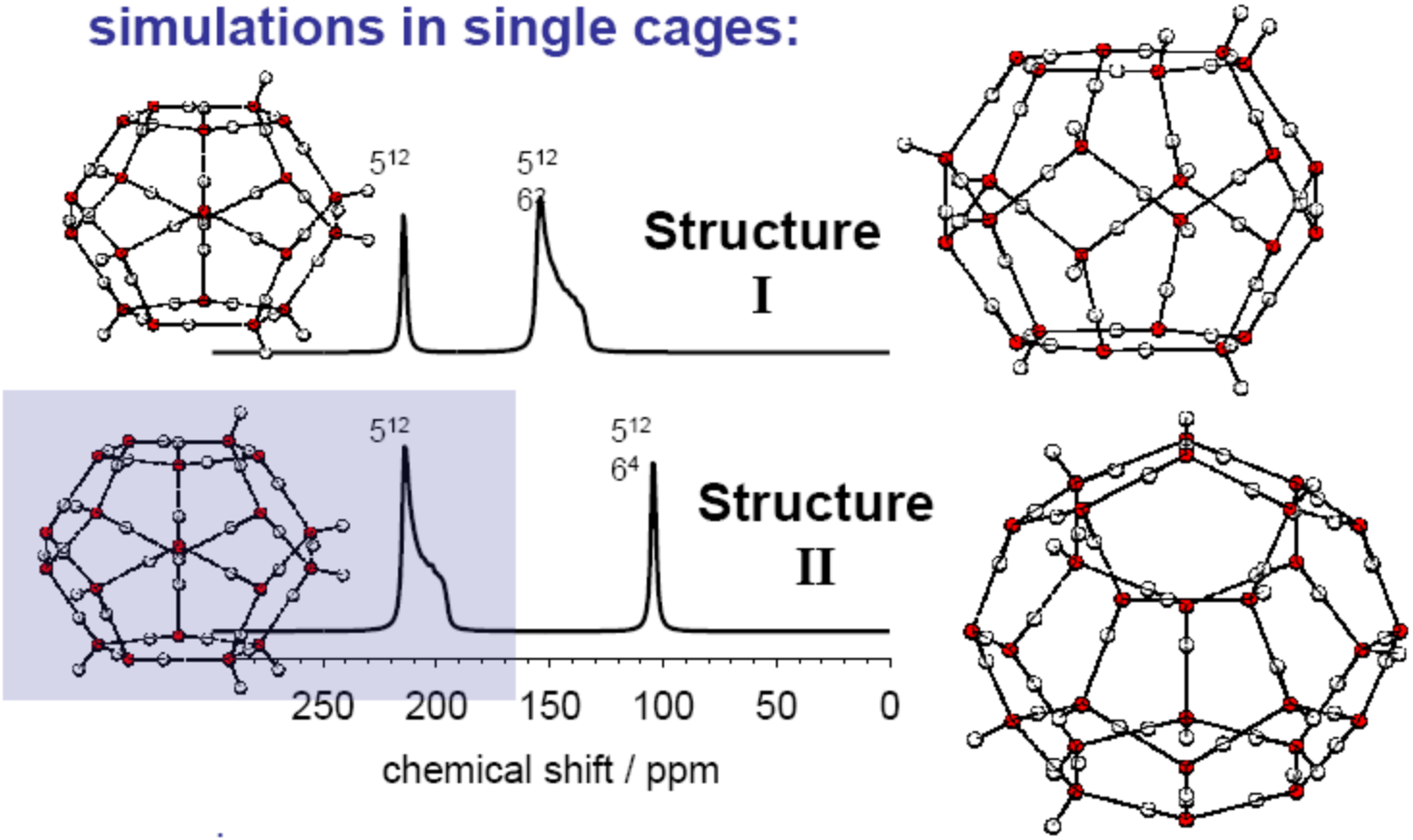
Sums over these **pair** shielding functions reproduce the ab initio Xe shielding tensor at each Xe position within the cage (in model XCAGE/PCA)

Sum over pair shielding tensors reproduce ab initio tensor components

but deviate at the short distances



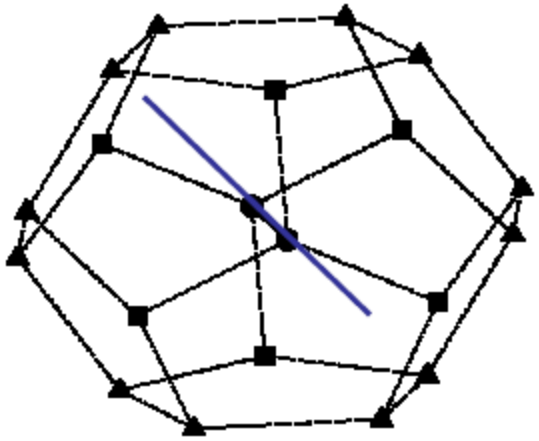
Calculated Xe NMR lineshapes from Monte Carlo simulations in single cages:



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

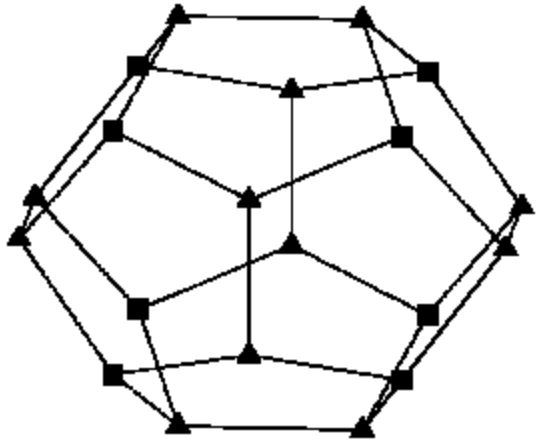
Why is the Xe lineshape in the 5^{12} cage in Structure II axially anisotropic while the Xe lineshape in the 5^{12} cage in Structure I is isotropic?

(a) 5^{12} cage in structure II



vs.

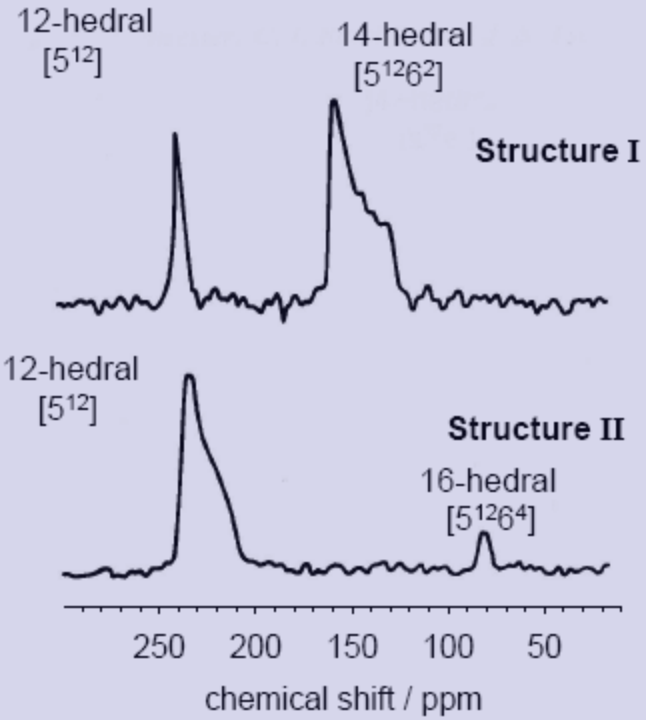
(b) 5^{12} cage in structure I



There is a unique pair of oxygen atoms in this cage, defining a unique axis. O-O distances differ from Structure I cage by **~0.11 Å**

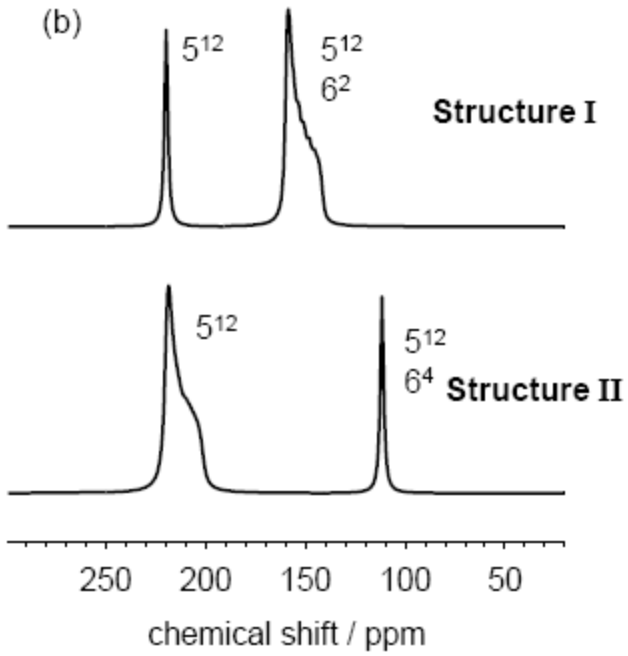
Xe can sense and report this difference!

Xe in the cages of clathrate hydrates Structure I and II



EXPERIMENTS

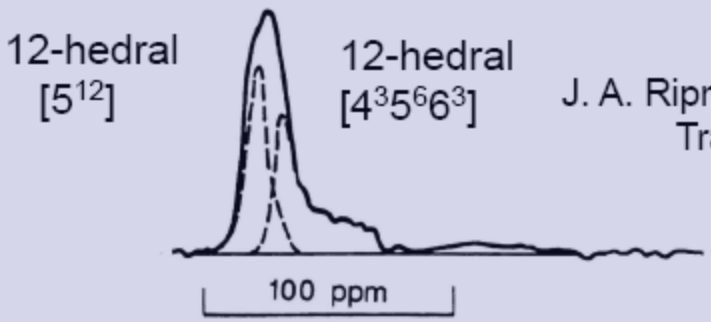
J. A. Ripmeester, C. I. Ratcliffe and J. S. Tse, Trans. Faraday Soc. 1, 84, 3731 (1988)



CALCULATIONS

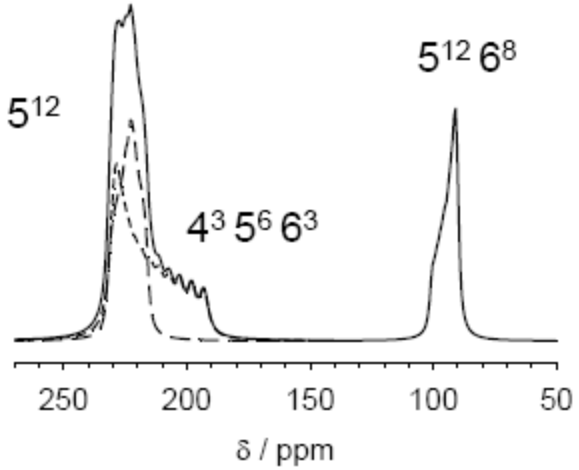
Monte Carlo simulations in a
4x4x4 supercell and 2x2x2 supercell
C. J. Jameson, D. Stueber, J Chem Phys 120, 10200 (2004)

Xe in clathrate hydrate Structure H



EXPERIMENT

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

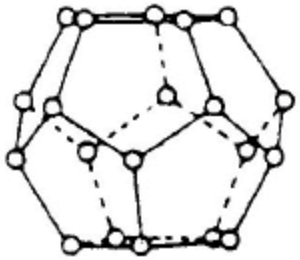


CALCULATIONS

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

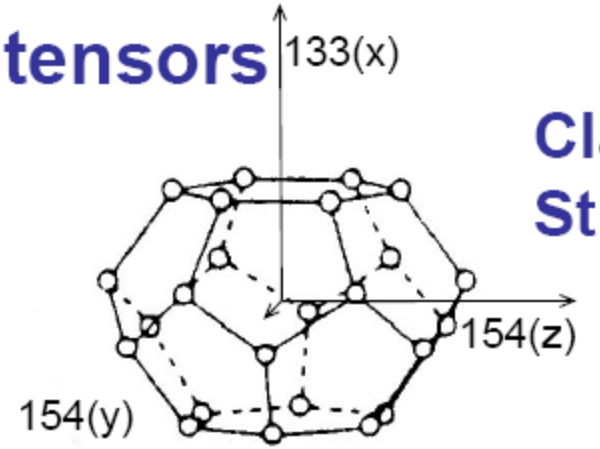
Xe chemical shift tensors

isotropic 214



5^{12}

symmetric

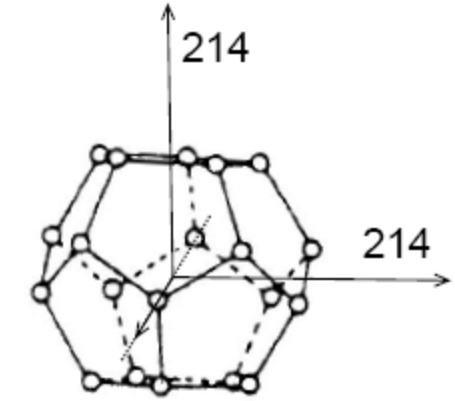


$5^{12}6^2$

axial, disk-like

Clathrate Structure I

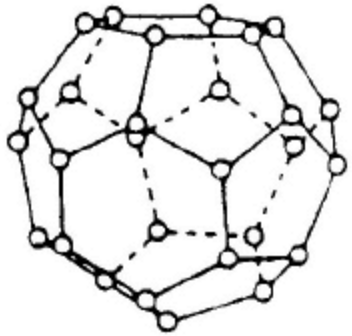
from canonical Monte Carlo simulations



5^{12}

axial

isotropic 105



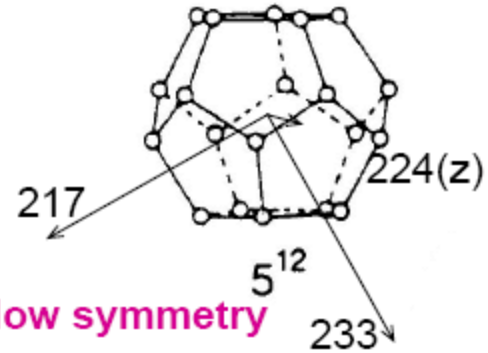
$5^{12}6^4$

symmetric

Clathrate Structure II

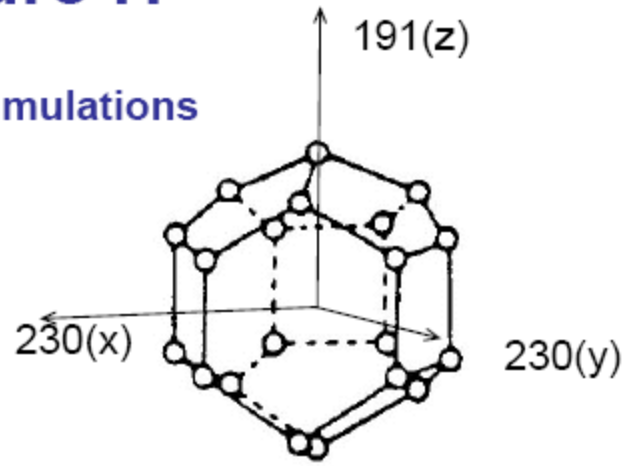
Xe tensors in Clathrate Structure H

from canonical Monte Carlo simulations



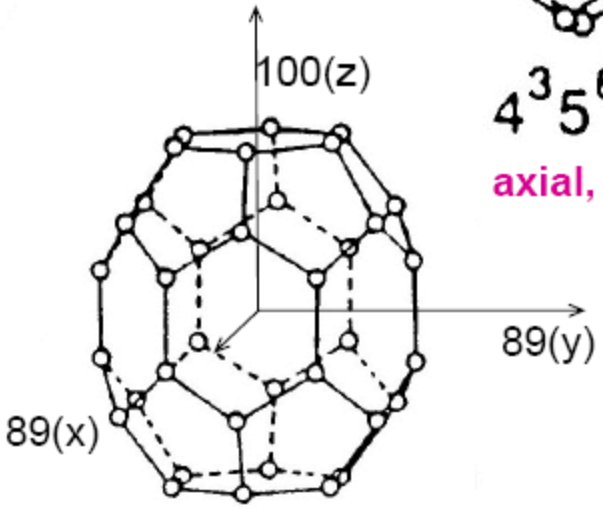
5^{12}

low symmetry



$4^3 5^6 6^3$

axial, squat

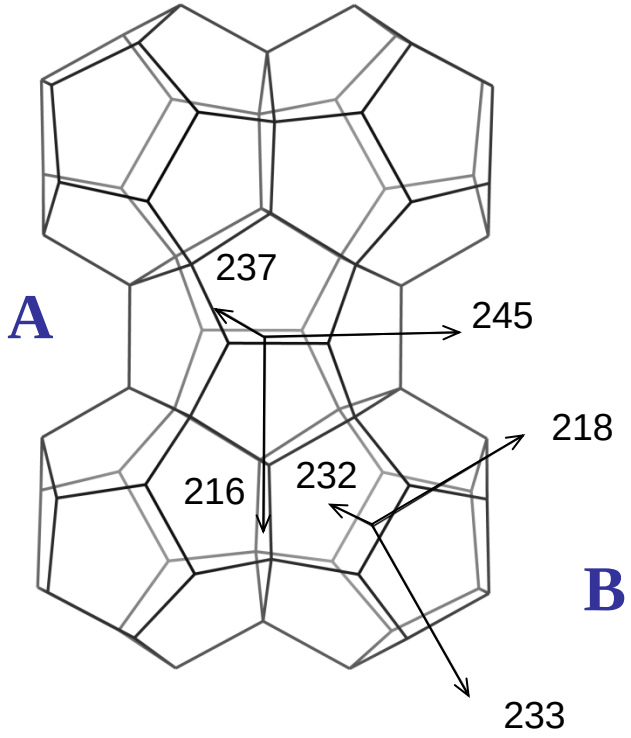


$5^{12}6^8$

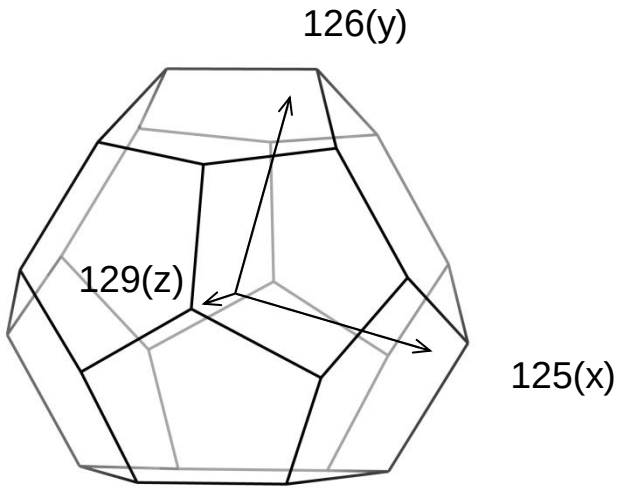
axial, elongated

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

5^{12}

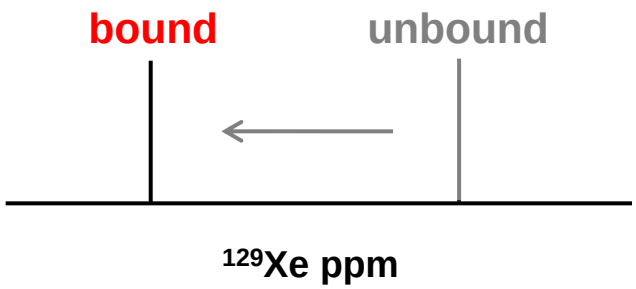


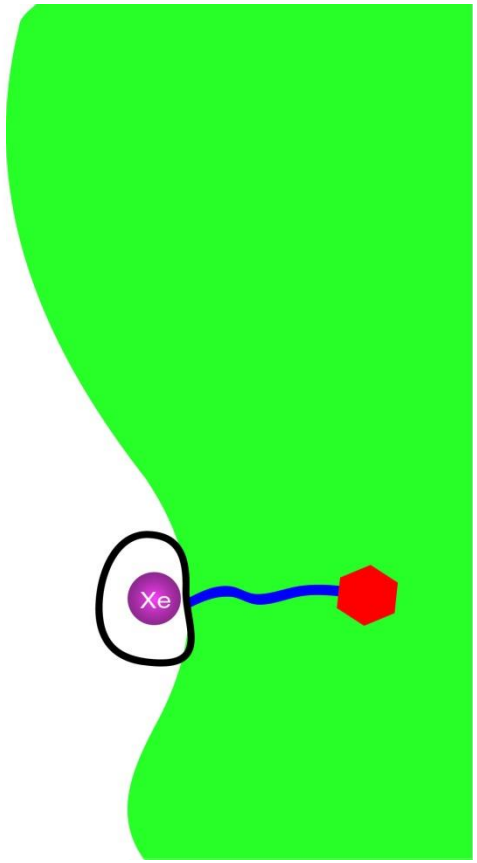
$5^{12}6^3$



Xe as a biosensor

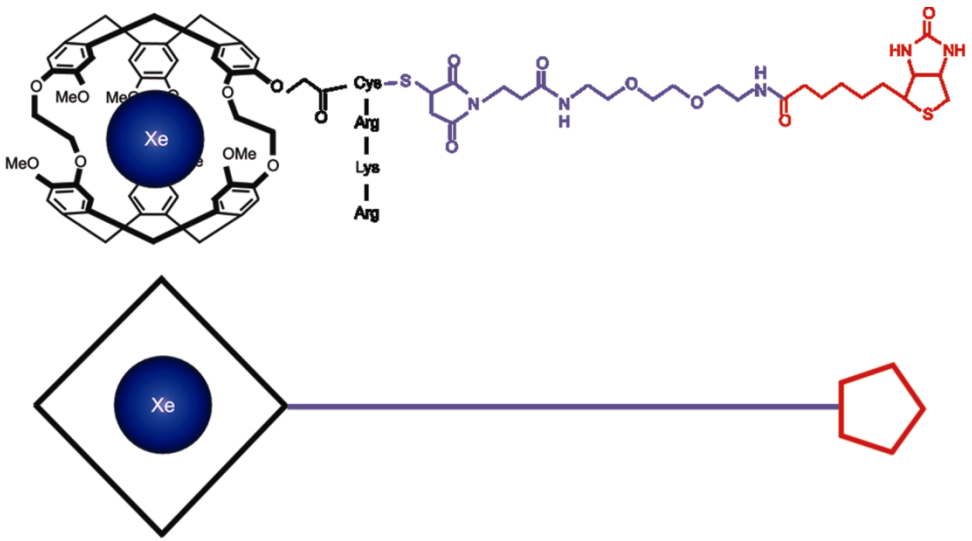
(Pines, Wemmer, et al. 2001)

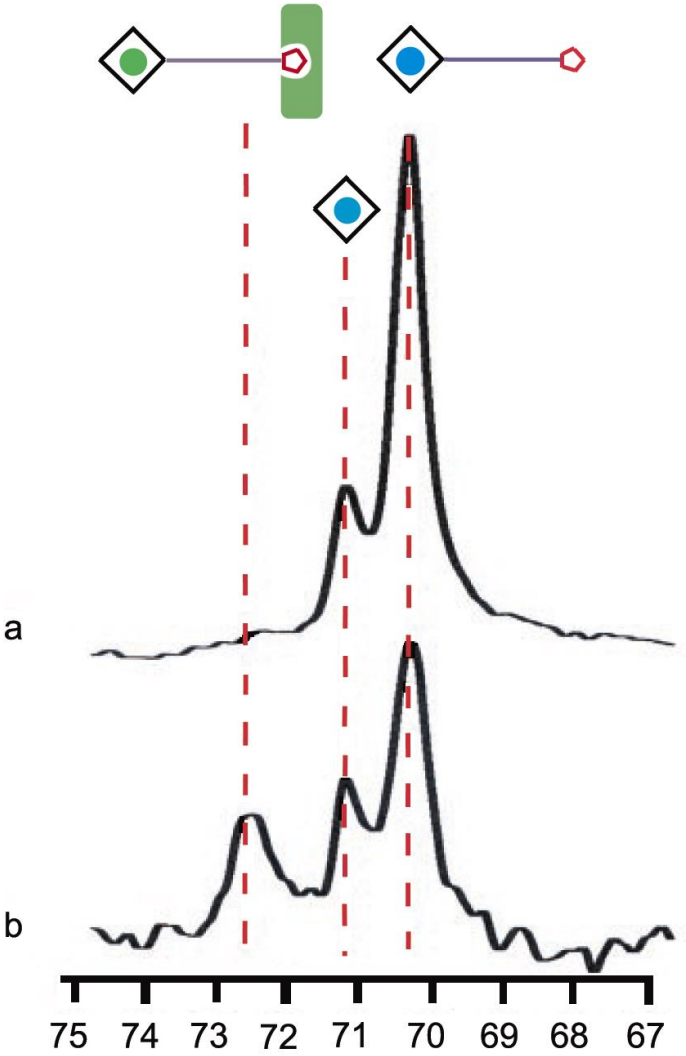




This slide courtesy of E. Janette Ruiz

MOTIVATION Xe as biosensor (Pines, Wemmer et al., 2001)



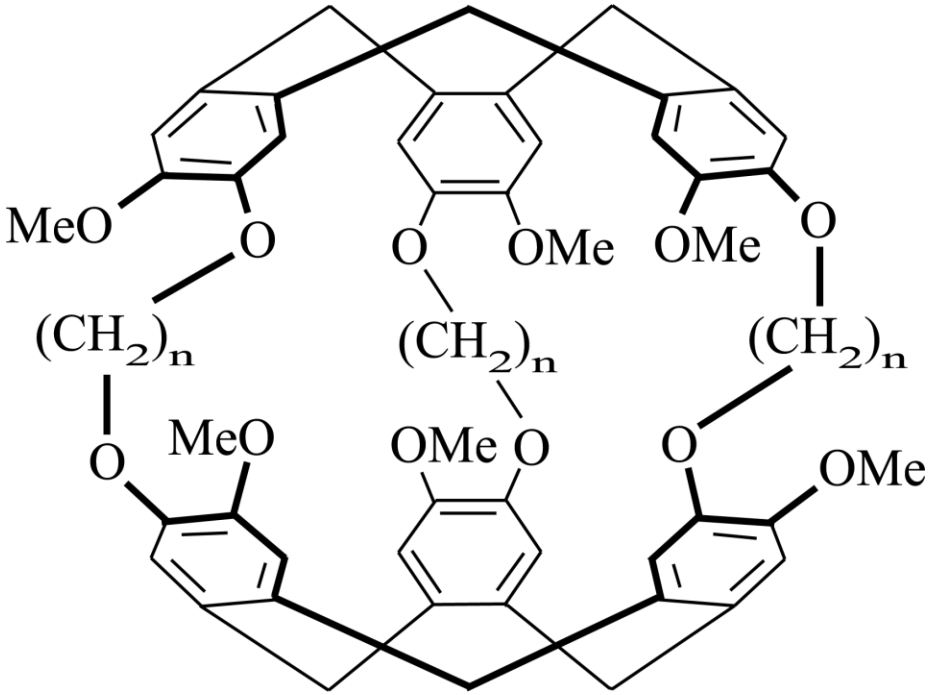


- Experiments on Xe in **cryptophane cages** provide **model systems** for comparison
- Unique cages A, 223, 332, and E
- Temperature dependence of Xe @cryptoA
- Xe isotope shifts upon deuteration of cage

M.M. Spence, S.M. Rubin, I.E. Dimitrov, E.J. Ruiz, D.E. Wemmer, A. Pines, S.Q. Yao, F. Tian, and P.G. Schultz Pro Nat. Acad. Sci. **2001**, 98, 10654-10657.

The cryptophanes

- Two cyclotriveratrylene bowls
- Connected by aliphatic linker $(CH_2)_n$
- n=2 Cryptophane-A (cryptoA)
- n=3 Cryptophane-E (cryptoE)
- n=2,2,3 Cryptophane-223
- n=2,3,3 Cryptophane-233



To calculate average Xe chemical shifts we need:

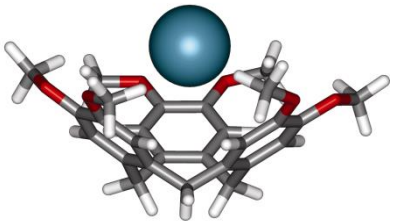
- Solution structures of cryptophanes-A, -223, -233, and -E
- Suitable fragment for *ab initio* calculations of xenon shielding surface
- Reasonable set of potential functions

X-Ray crystal structure cryptoA*

Average structural parameters of 1/3 cyclotriveratrylene

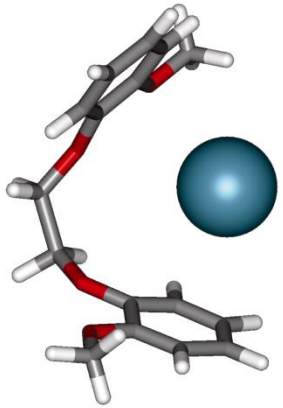
Symmetrize with GAMESS to obtain bowl structure

Optimize orientation of methoxy groups (HF & B3LYP) with Xe atom at center of bowl



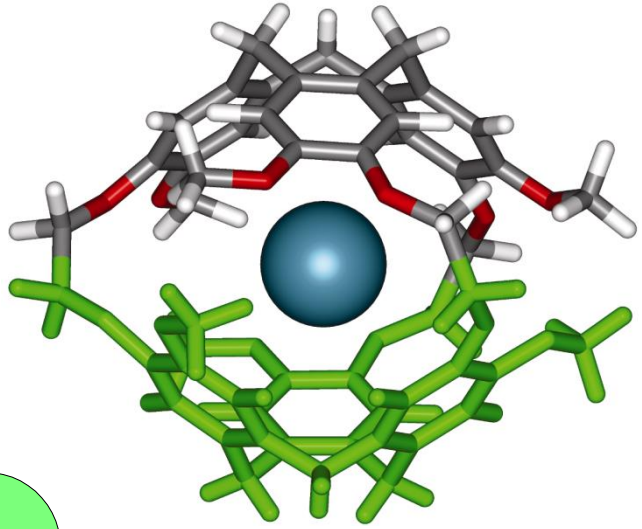
Use two bowls to form cage

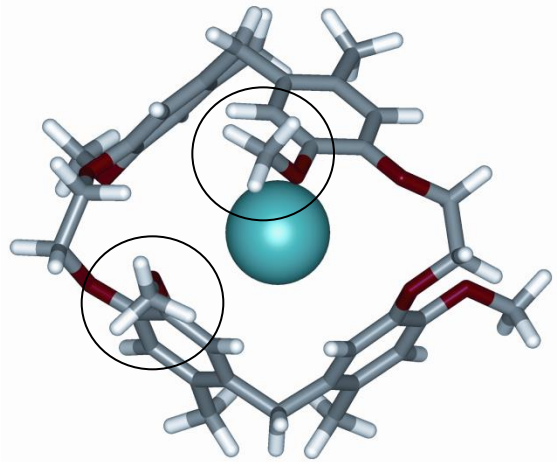
Geometry optimization of molecular fragment with Xe atom in center position
Constrain all coordinates except
$-O-CH_2-CH_2-O-$



Shielding surface calculations

Geometry optimization of molecular fragment with Xe atom in center position
Constrain all coordinates except methoxy CH_3 groups





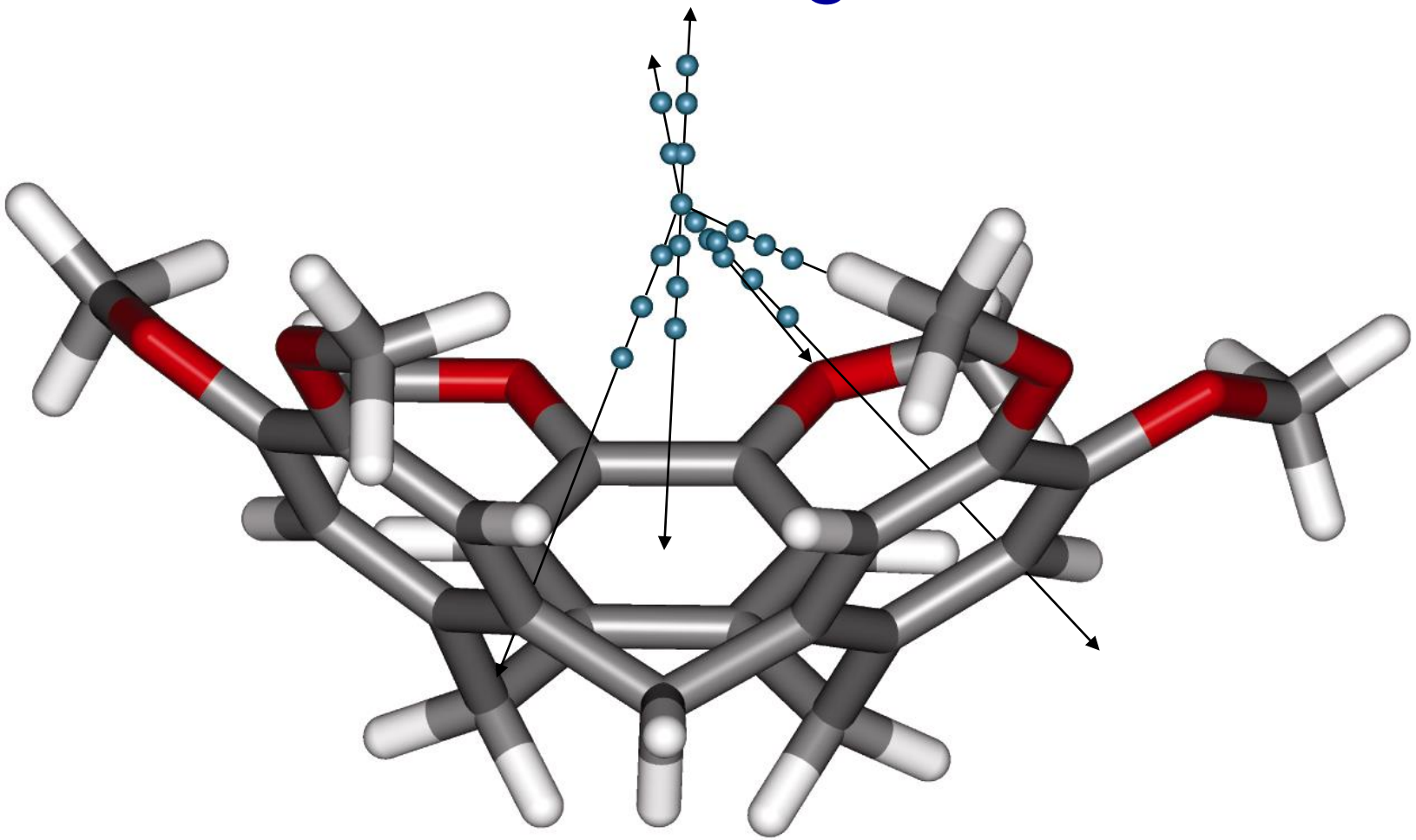
Construct full cage from optimized fragment using C_3 symmetry

Canonical Monte Carlo simulations

Average Xe Shielding

*Private Communications
J. P. Dutasta

Xe shielding surface calculations in the model fragment



- Single cyclotriveratrylene
- Hartree-Fock and DFT (B3LYP)
- 6-311G** basis set on C, O, and H atoms
- 240 basis functions on Xe atom

Representation of ab initio values by site-site shielding functions

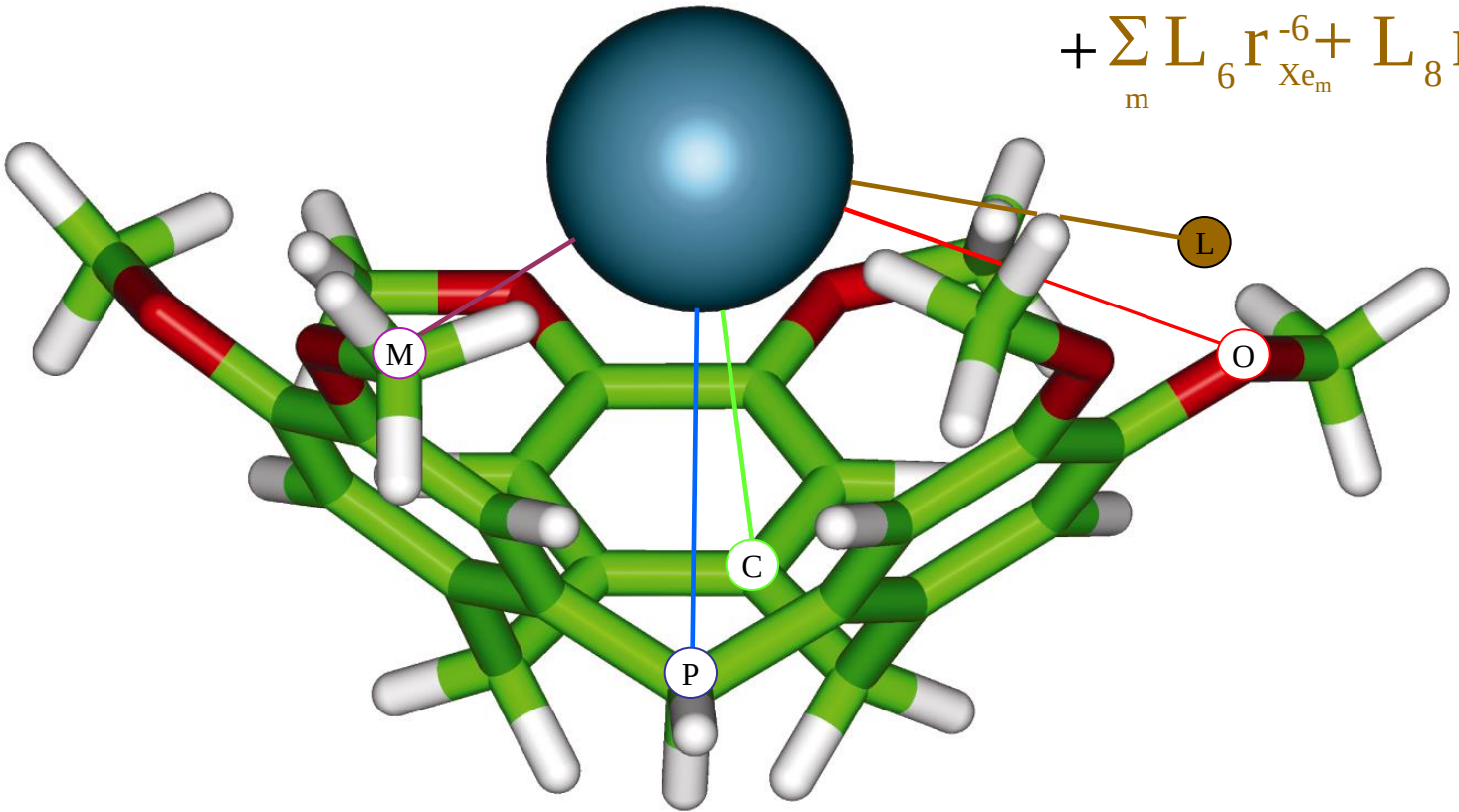
Ab initio points fit to the following site-site functional form:

$$[\sigma_{isotropic}(Xe) - \sigma(\text{free Xe})] =$$

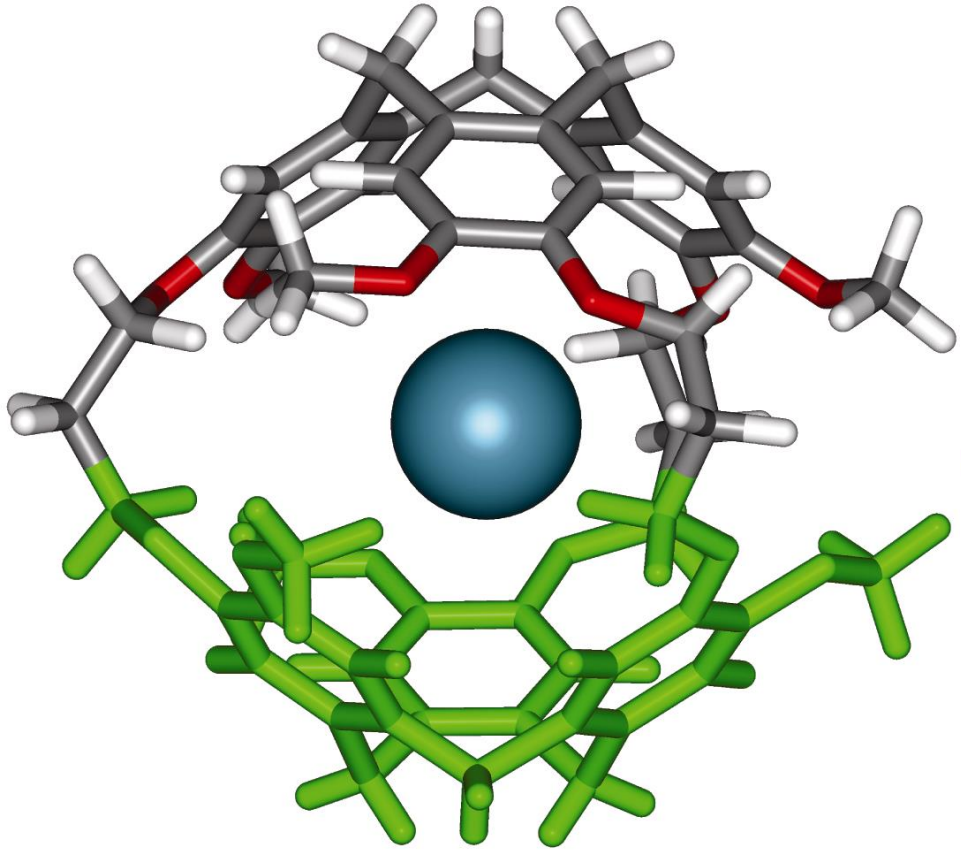
$$\sum_i O_6\, r_{Xe_i}^{-6} + O_8\, r_{Xe_i}^{-8} + O_{10}\, r_{Xe_i}^{-10} + \sum_j C_6\, r_{Xe_j}^{-6} + C_8\, r_{Xe_j}^{-8} + C_{10}\, r_{Xe_j}^{-10}$$

$$+ \sum_k M_6 r_{Xe_k}^{-6} + M_8 r_{Xe_k}^{-8} + M_{10}\, r_{Xe_k}^{-10} + \sum_n P_6\, r_{Xe_n}^{-6} + P_8 r_{Xe_n}^{-8} + P_{10}\, r_{Xe_n}^{-10}$$

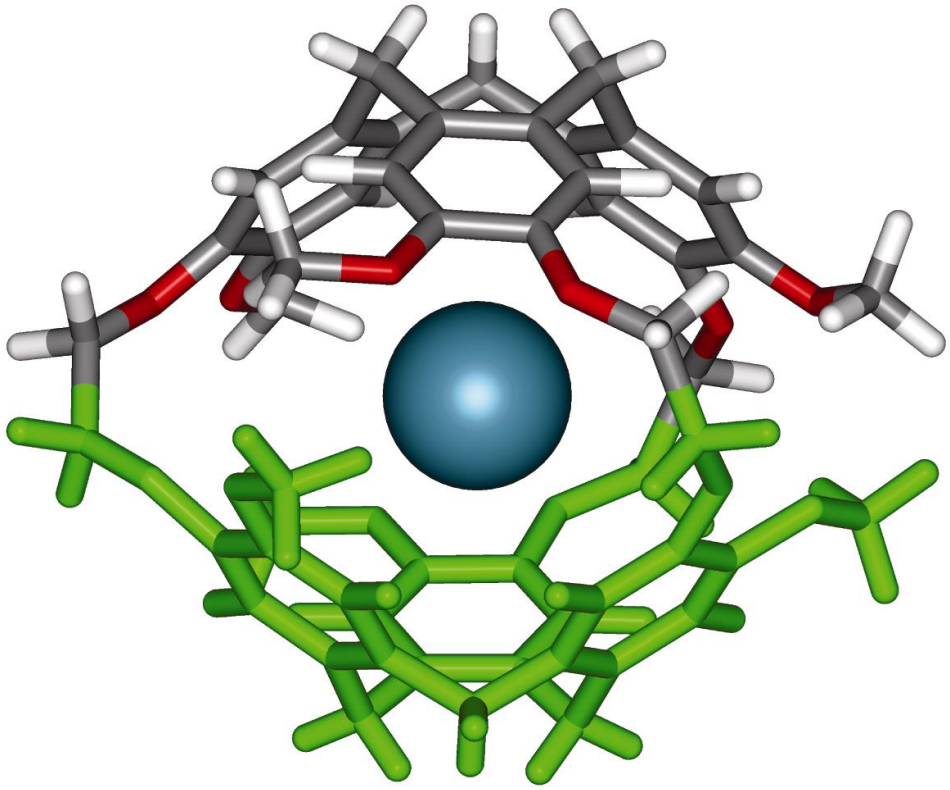
$$+ \sum_m L_6\, r_{Xe_m}^{-6} + L_8\, r_{Xe_m}^{-8} + L_{10}\, r_{Xe_m}^{-10}$$



Average structures of Xe@cryptoA and Xe@cryptoE



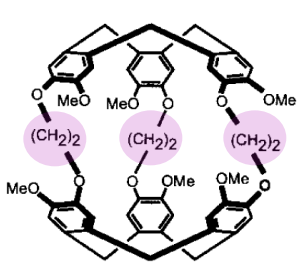
Xe@cryptoE

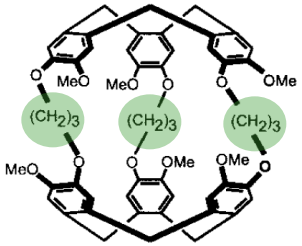


Xe@cryptoA

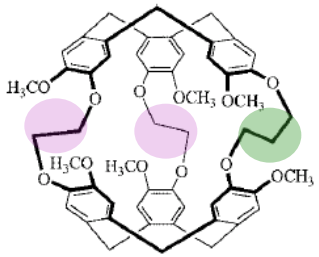
- Average structure of Xe@cryptoE arrived at using same method
- The same shielding surface can be used for both cages

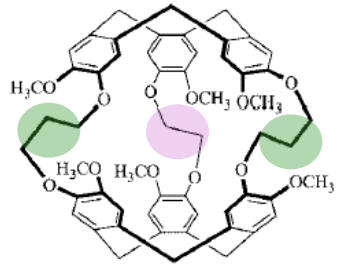
^{129}Xe@cryptophanes





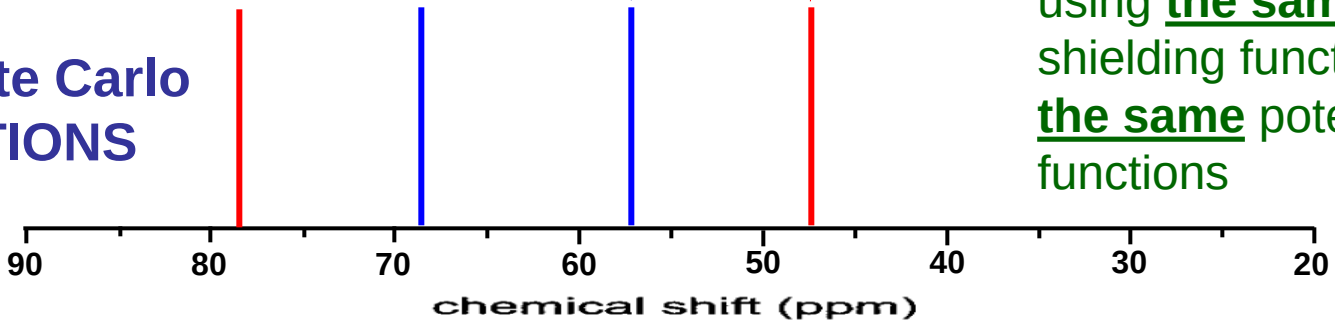
Pines et al.
Proc. Nat. Acad. Sci.
98, 10654 (2001)





Brotin et al.
Eur. J. Org. Chem.
2003, 973-984

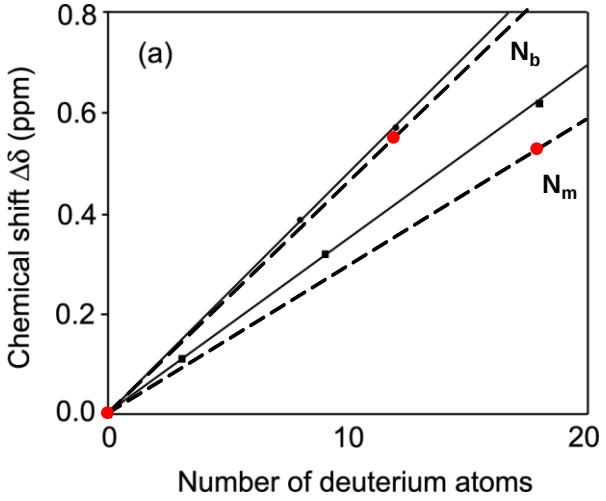
Our Monte Carlo SIMULATIONS

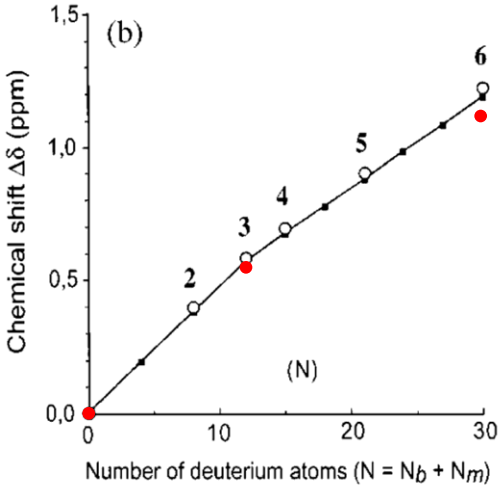


using **the same** shielding functions
the same potential functions

Xe@d_n-cryptoA

EXPERIMENT
(Brotin et al. 2000)*



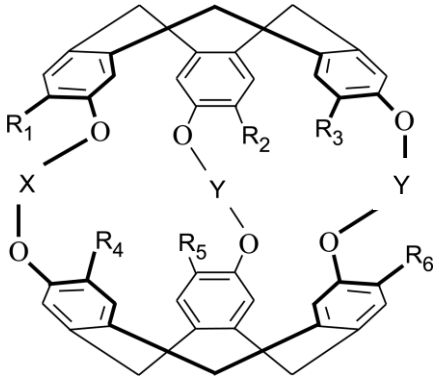


- **SIMULATIONS**

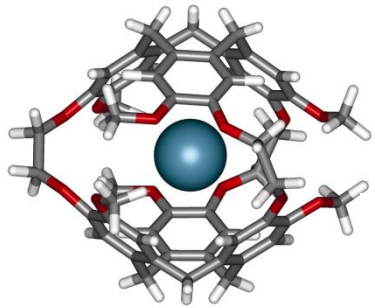
for example:

$\langle\sigma[Xe@cryptoA]\rangle_{MC} - \langle\sigma[Xe@d_{30}\ cryptoA]\rangle_{MC} = 1.118$ ppm

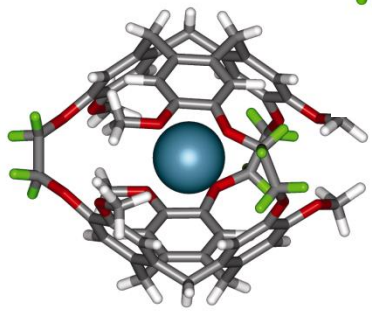
$r_0(Xe\text{-}H) - r_0(Xe\text{-}D) = 0.07$ Å



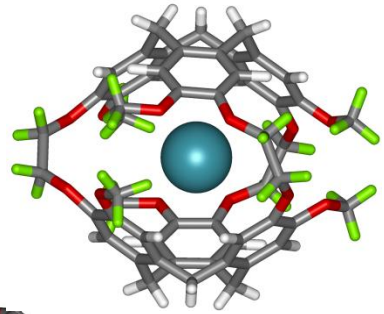
1: X = CH_2CH_2; Y = CH_2CH_2; R_1 = OCH_3; $R_2 - R_6$ = OCH_3
2: X = CH_2CH_2; Y = CD_2CD_2; R_1 = OCH_3; $R_2 - R_6$ = OCH_3
3: X = CD_2CD_2; Y = CD_2CD_2; R_1 = OCH_3; $R_2 - R_6$ = OCH_3
4: X = CD_2CD_2; Y = CD_2CD_2; R_1 = OCD_3; $R_2 - R_6$ = OCH_3
5: X = CD_2CD_2; Y = CD_2CD_2; $R_1 - R_3$ = OCD_3; $R_4 - R_6$ = OCH_3
6: X = CD_2CD_2; Y = CD_2CD_2; $R_1 - R_6$ = OCD_3



1



3



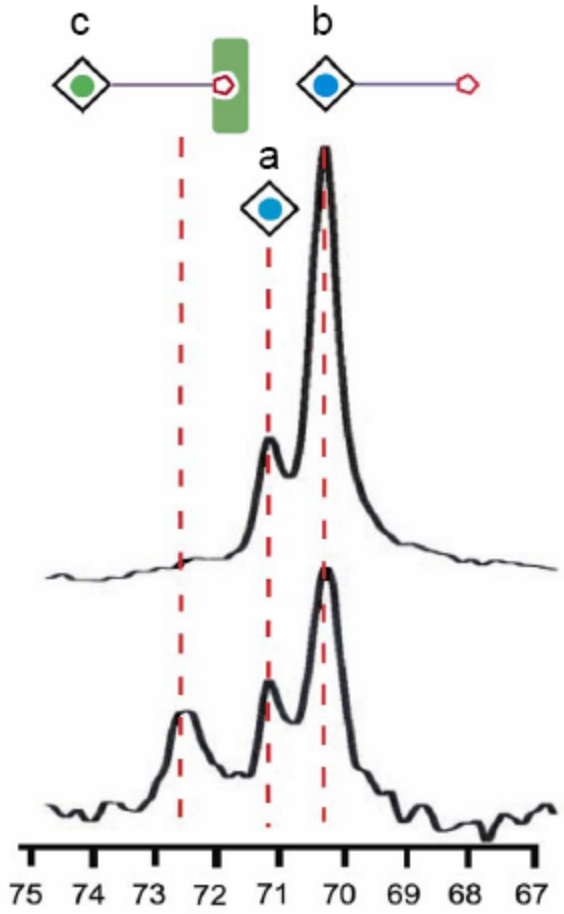
6

*T. Brotin, A. Lesage, L. Emsley, and A. Collet,
J. Am. Chem. Soc. **2000**, 122, 1171-1174

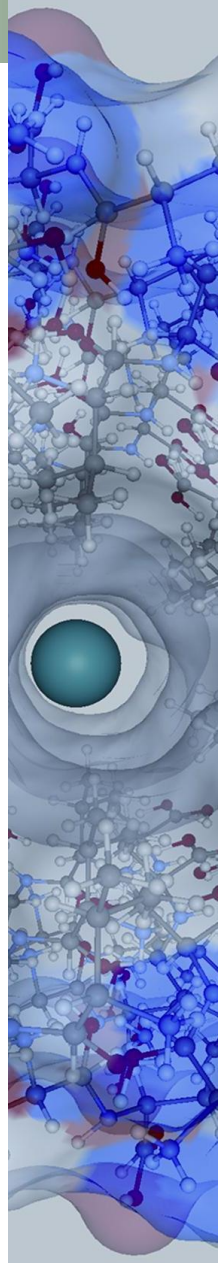
Xe in cryptophane MD simulations

Comment on the Xe biosensor

- Mechanical deformation of the cage alone can account for sensing action with no change in electronic factors
- Xe shifts to more positive chemical shift upon binding
- longer tether → smaller shift; shorter tether → larger shift

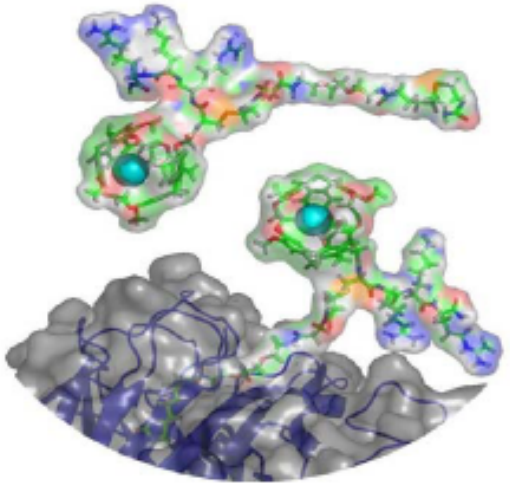


Sears



Epilogue

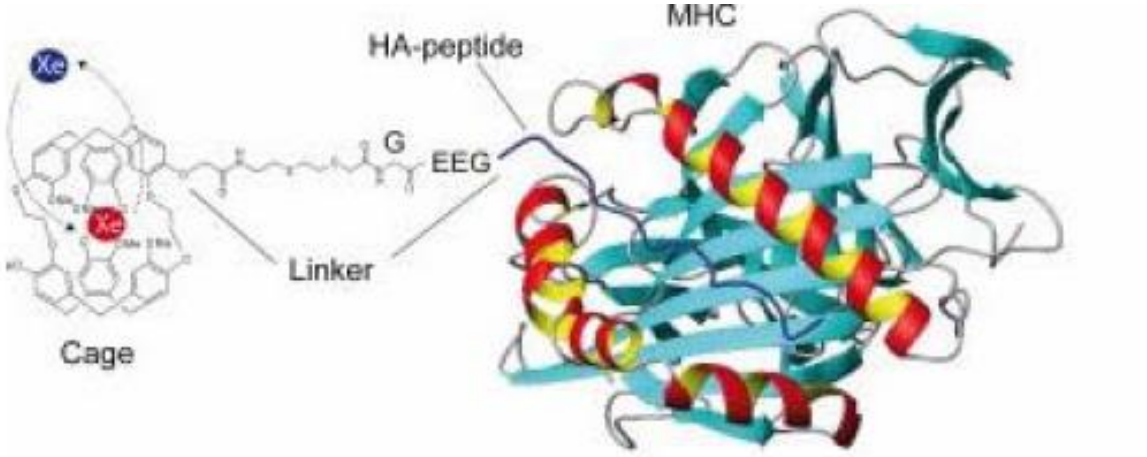
Later experiments using various tether lengths prove our **larger Xe shift for shorter tether prediction**:



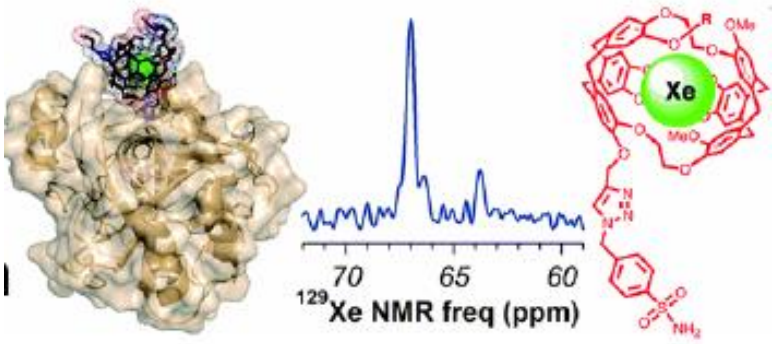
biosensor model courtesy of T. J. Lowery

Optimization of Xenon Biosensors for Detection of Protein Interactions, T. J. Lowery, S. Garcia, L. Chavez, E. J. Ruiz, T. Wu, T. Brotin, J. –P. Dutasta, D. S. King, . G. Schultz, A. Pines, D. E. Wemmer, *ChemBioChem* 7, 65-73 (2005).

Later experiments using Xe in a different functionalized crypto A binding to a different protein prove our prediction that **binding leads uniformly to a larger Xe chemical shift via the mechanical cage deformation upon binding.**



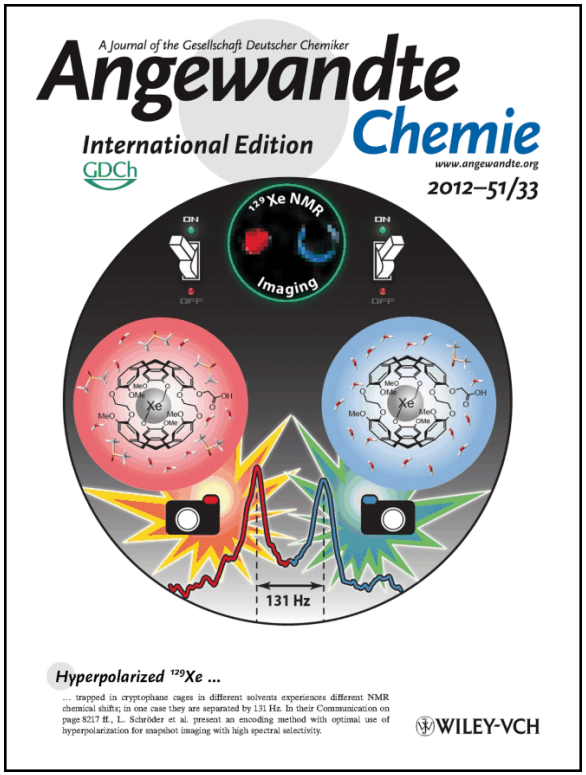
A Xe-129 Biosensor for Monitoring MHC-Peptide Interactions, A. Schlundt, W. Kilian, M.Beyermann, J. Sticht, S. Günther, S. Höpner, K. Falk, O. Roetzschke, L. Mitschang, C. Freund,Angew. Chem. Intl. Ed. 48, 4142 –4145 (2009)

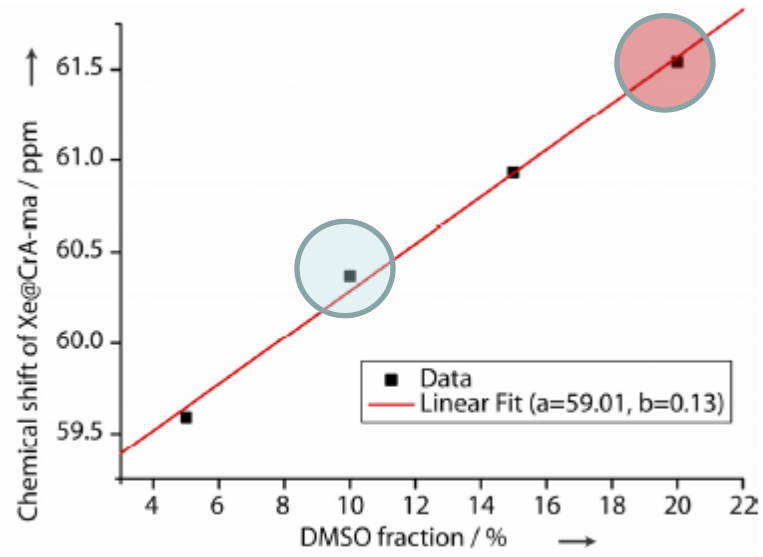


Cryptophane Xe-129 NMR Biosensors Targeting Human Carbonic Anhydrase, Dmochowski et al. J Am Chem Soc 2009, 131, 563.

The cryptophane cage enhances the sensitivity of Xe to the environment by providing a collection of atoms that ***stay at close distances*** which can evoke a shielding response that is influenced by the cage's dynamics and electronic environment.

Example: L. Schroeder et al.

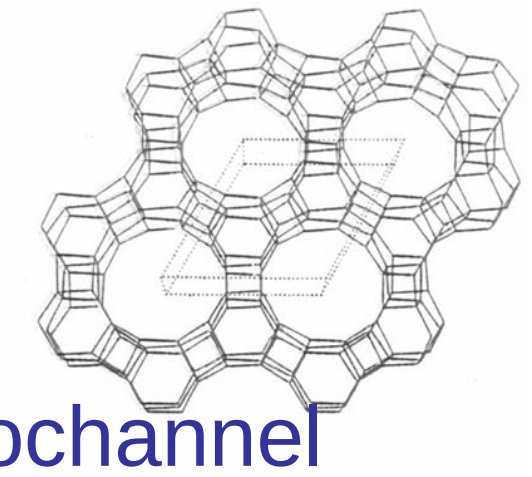




The chemical shift of Xe@CryA-ma is a function of the fraction of DMSO in H_2O

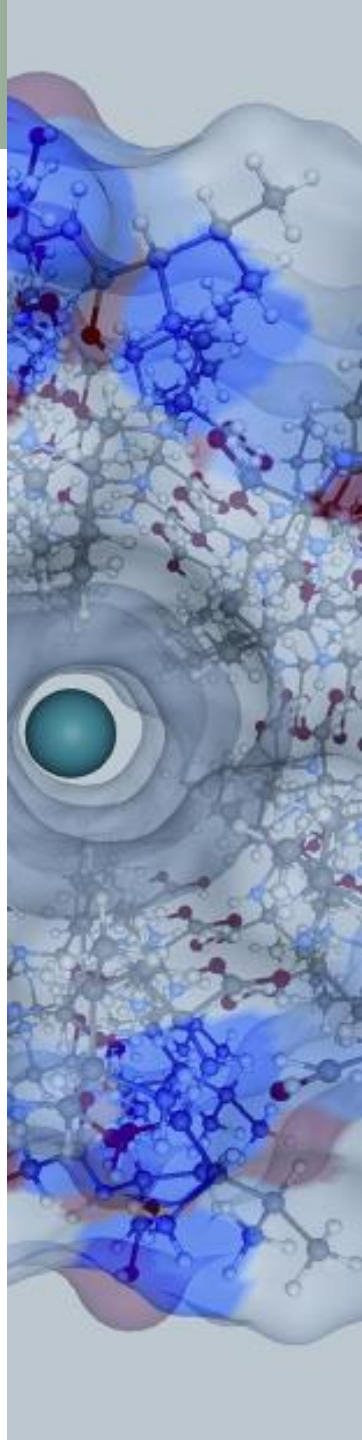
Angew. Chem. Intl. Ed. 2012, 51, 8217-8220.

Xe in nanochannels



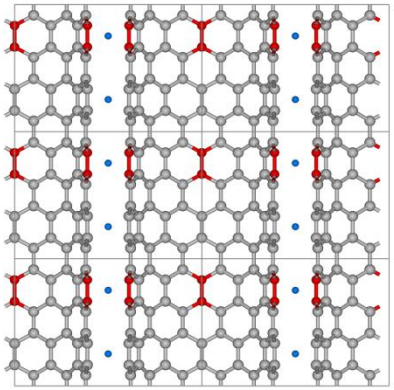
QUESTION:
Is information about the architecture and constitution of the nanochannel encoded into the Xe NMR lineshape in polycrystalline samples?

- nature of geometric confinement, i. e., size and shape of the nanochannel or cavity
- electronic structure of the channel atoms



simple atomistic model channels

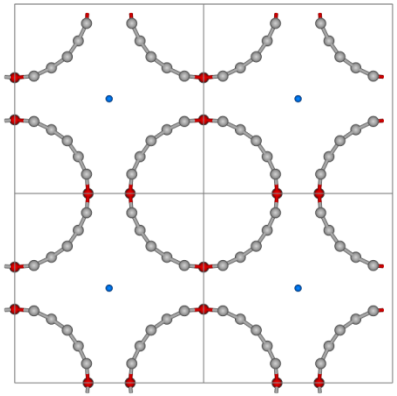
A



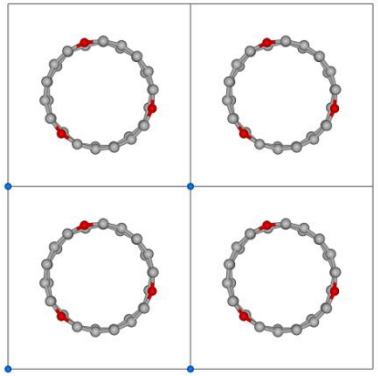
carbon nanotubes
(n,0) zigzag type

Ignore the different identity of the red atoms, used for another purpose.

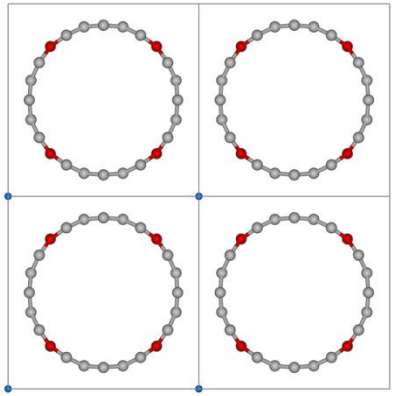
A



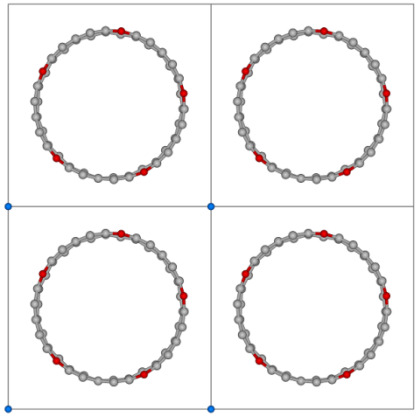
D



B



H



tube diameter in C-C distance:

D 7.1 Å

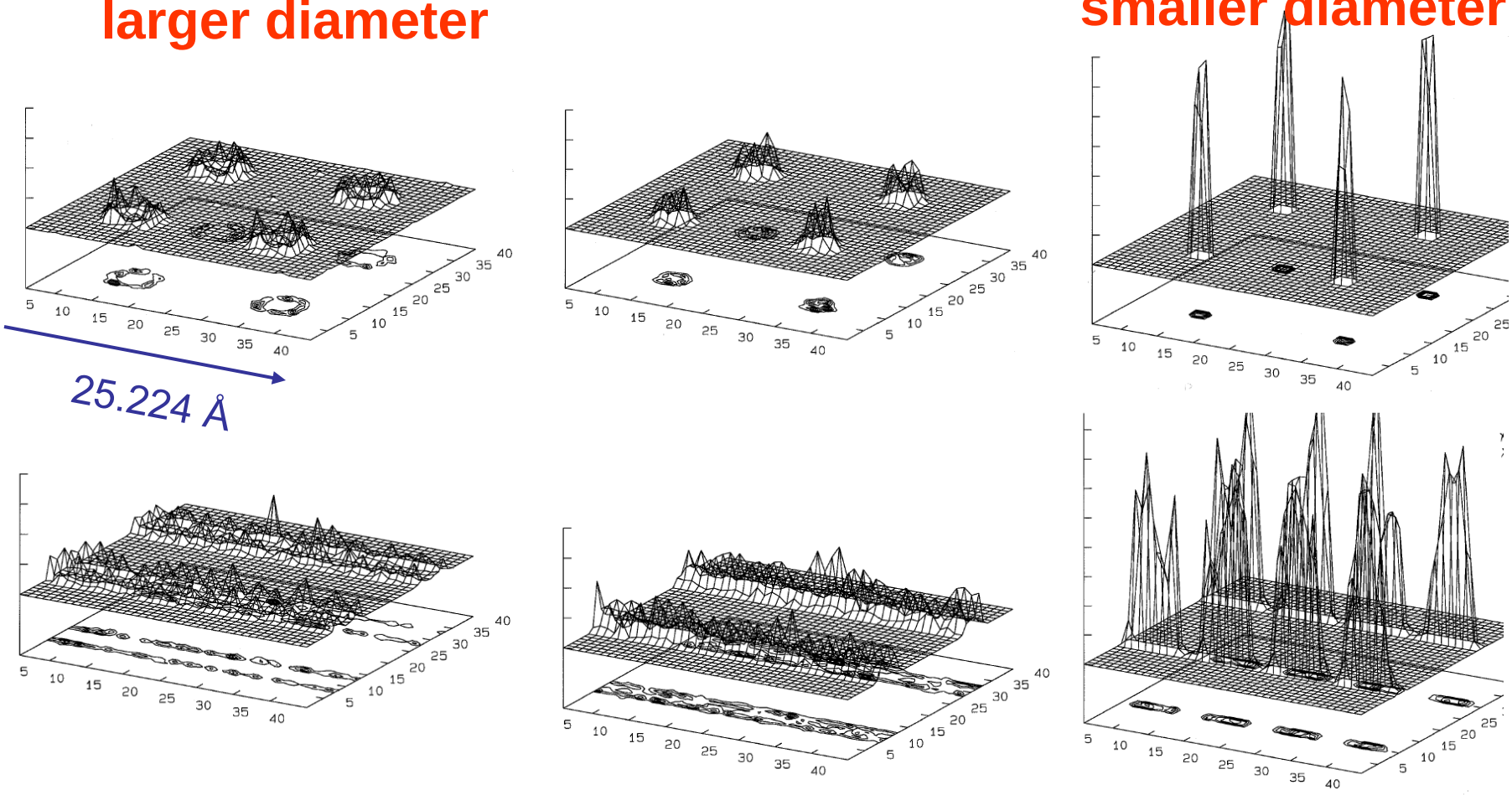
B 9.4 Å

H 11.8 Å

Model H
larger diameter

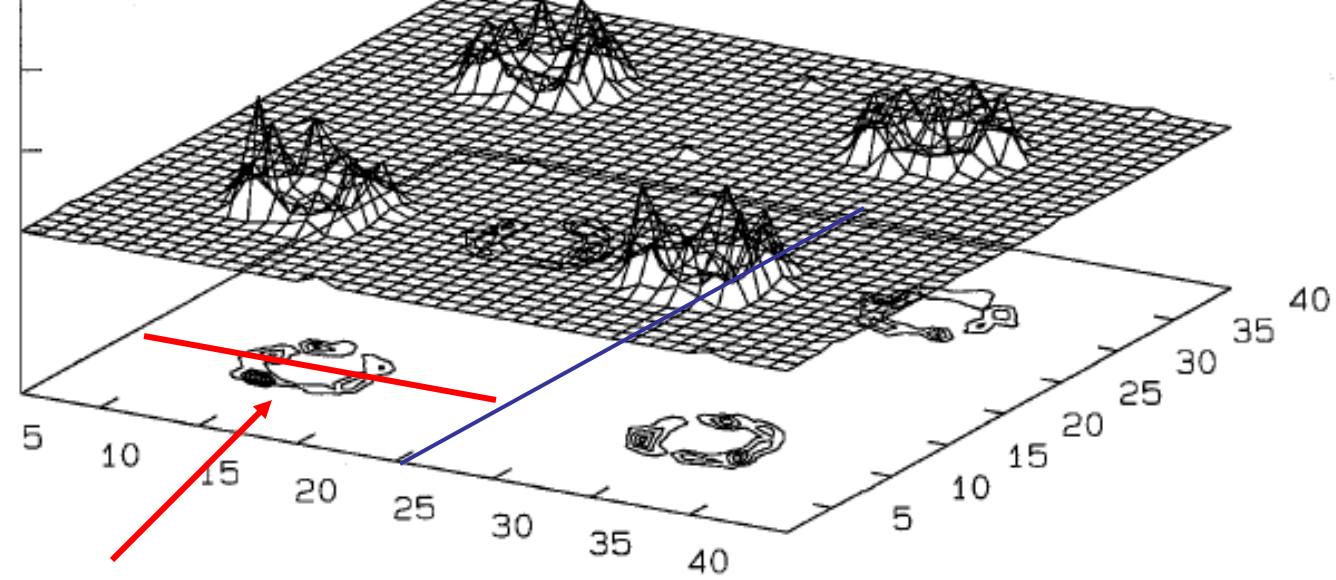
Model B

Model D
smaller diameter



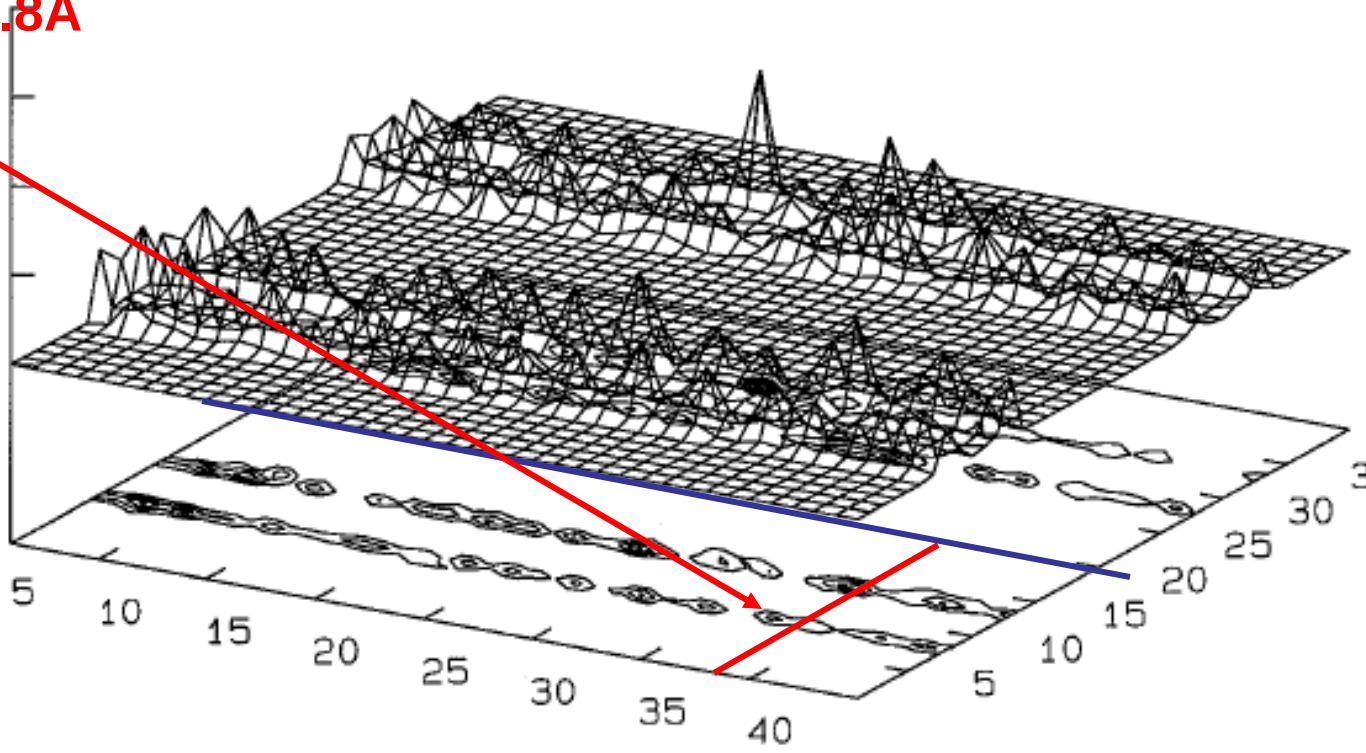
Xe one-body distribution functions in channels at 300 K

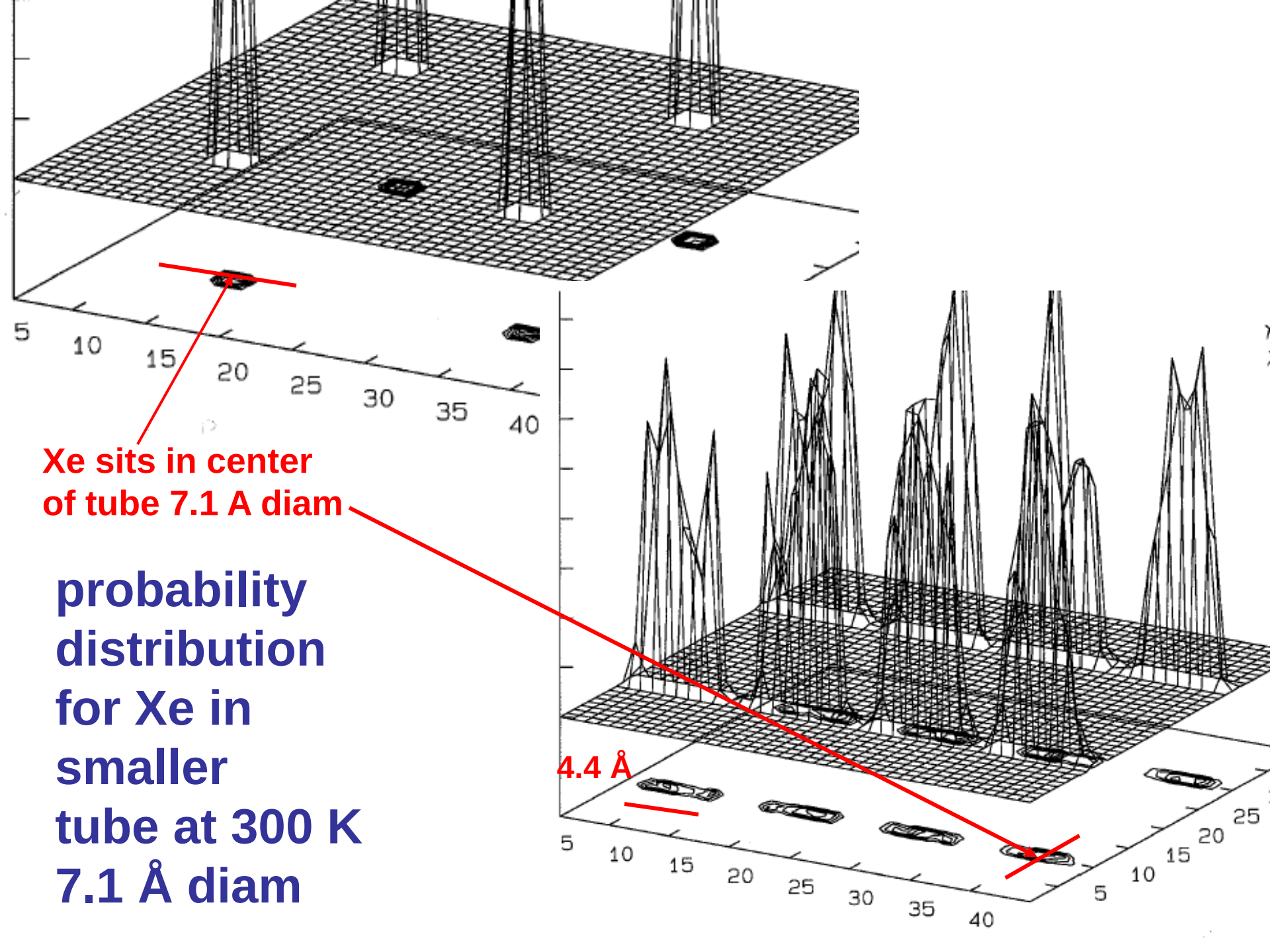
D. N. Sears, L. Vukovic, C. J. Jameson, J. Chem. Phys. 2006, 125, 114708.



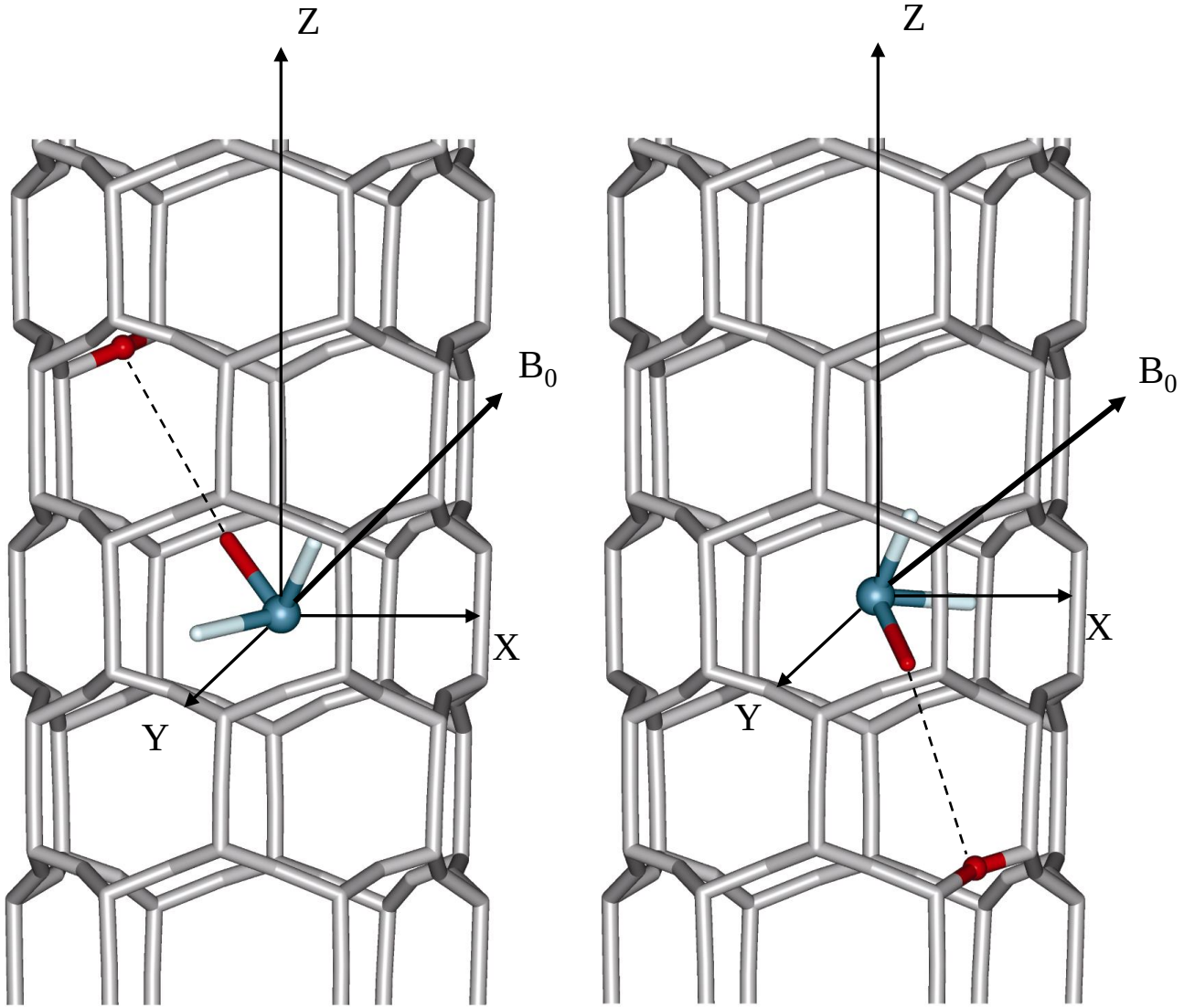
Xe stays in a cylindrical region within the 11.8Å

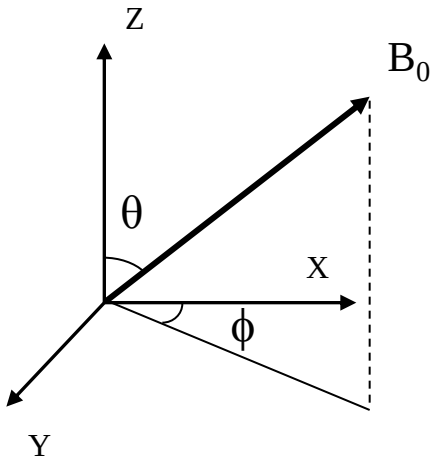
probability distribution for Xe in larger tube at 300 K




5
10
15
20
25
30
35
40
Xe sits in center
of tube 7.1 A diam
probability
distribution
for Xe in
smaller
tube at 300 K
7.1 Å diam
4.4 Å
5
10
15
20
25
30
35
40
5
10
15
20
25

Lineshapes by grand canonical Monte Carlo



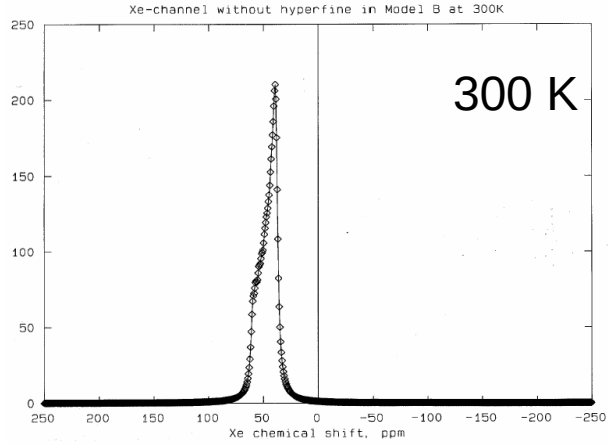


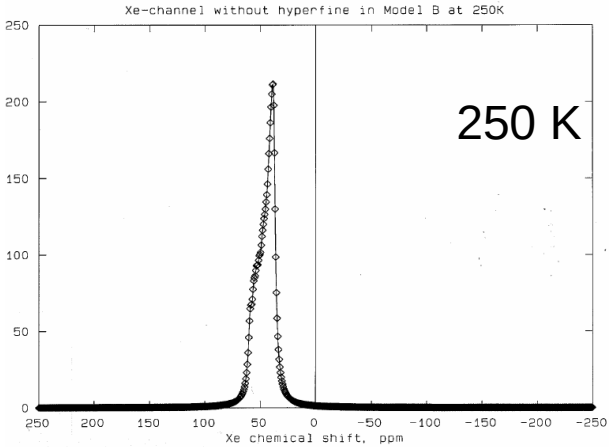
Random orientation of crystallites:
Probability that B_0 lies in any infinitesimal solid angle is
$d\zeta\, d\phi / 4\pi$, where
$\zeta = (-\cos\theta)$
Equal areas in $\zeta\phi$ plane correspond to equal probabilities

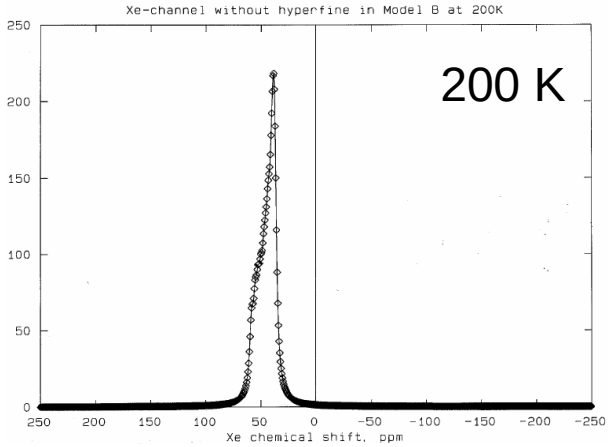
Consider one Xe-O at a time
(and one Xe-Xe at a time)

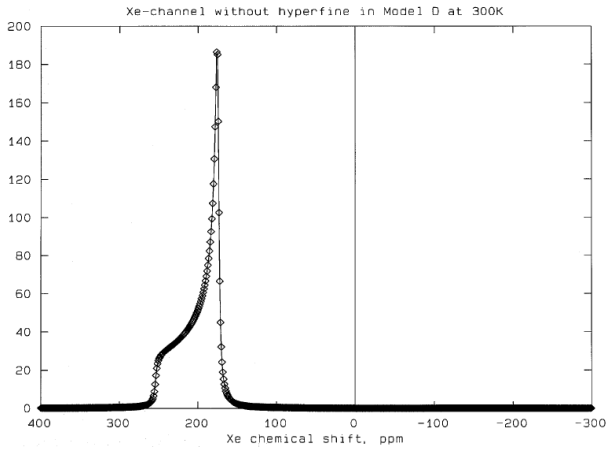
$\delta_{\parallel} > \delta_{\perp}$

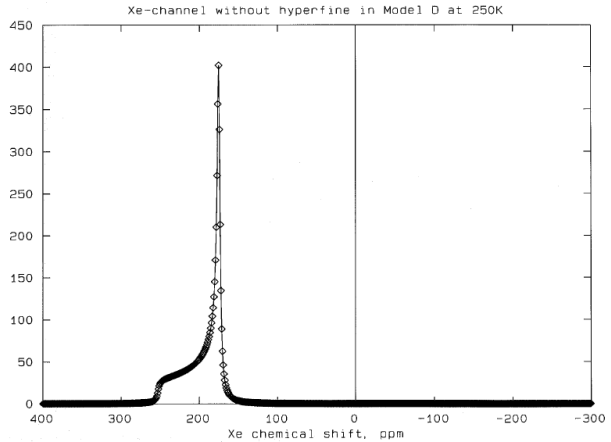
one Xe in Ne nano tube larger diam 11.8 Å

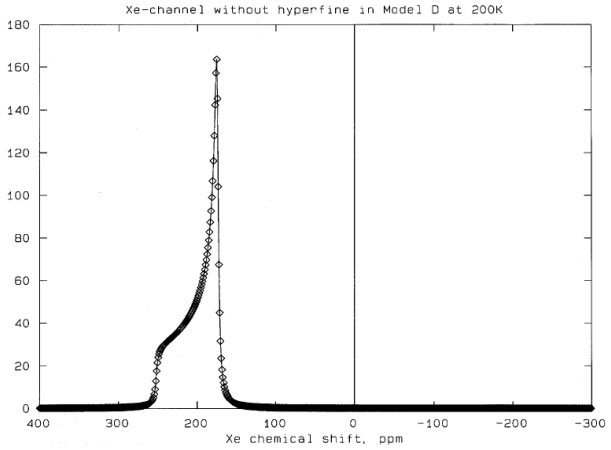








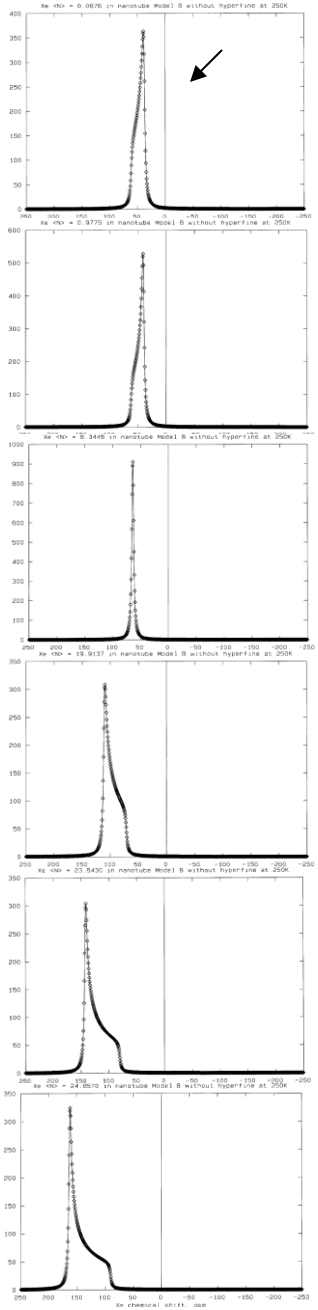




one Xe in Ne nano tube small diam 7.1 Å

$\delta_{\parallel} > \delta_{\perp}$

Line shape as a function of Xe occupancy



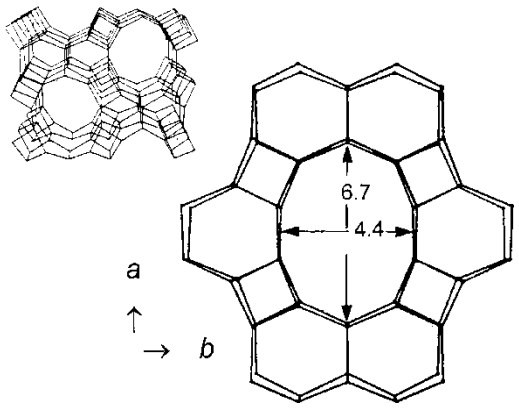
LOW <N>

HIGH <N>

Typical diamagnetic channel

NOTE the change in sign of anisotropy of Xe chemical shift tensor with increasing <N>

Architecture of the channel determines the Xe lineshape

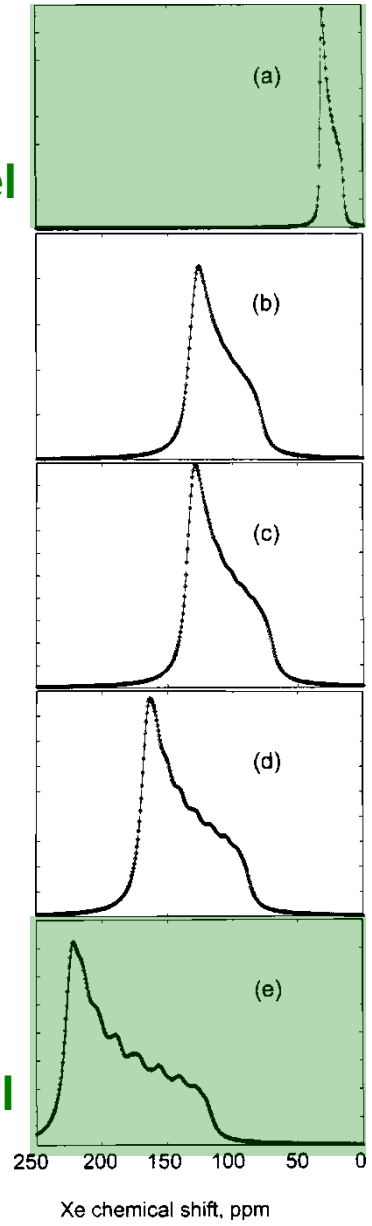


$ALPO_4$-11 architecture

Electronic structure of the channel atoms determines the isotropic chemical shift and width at zero-loading

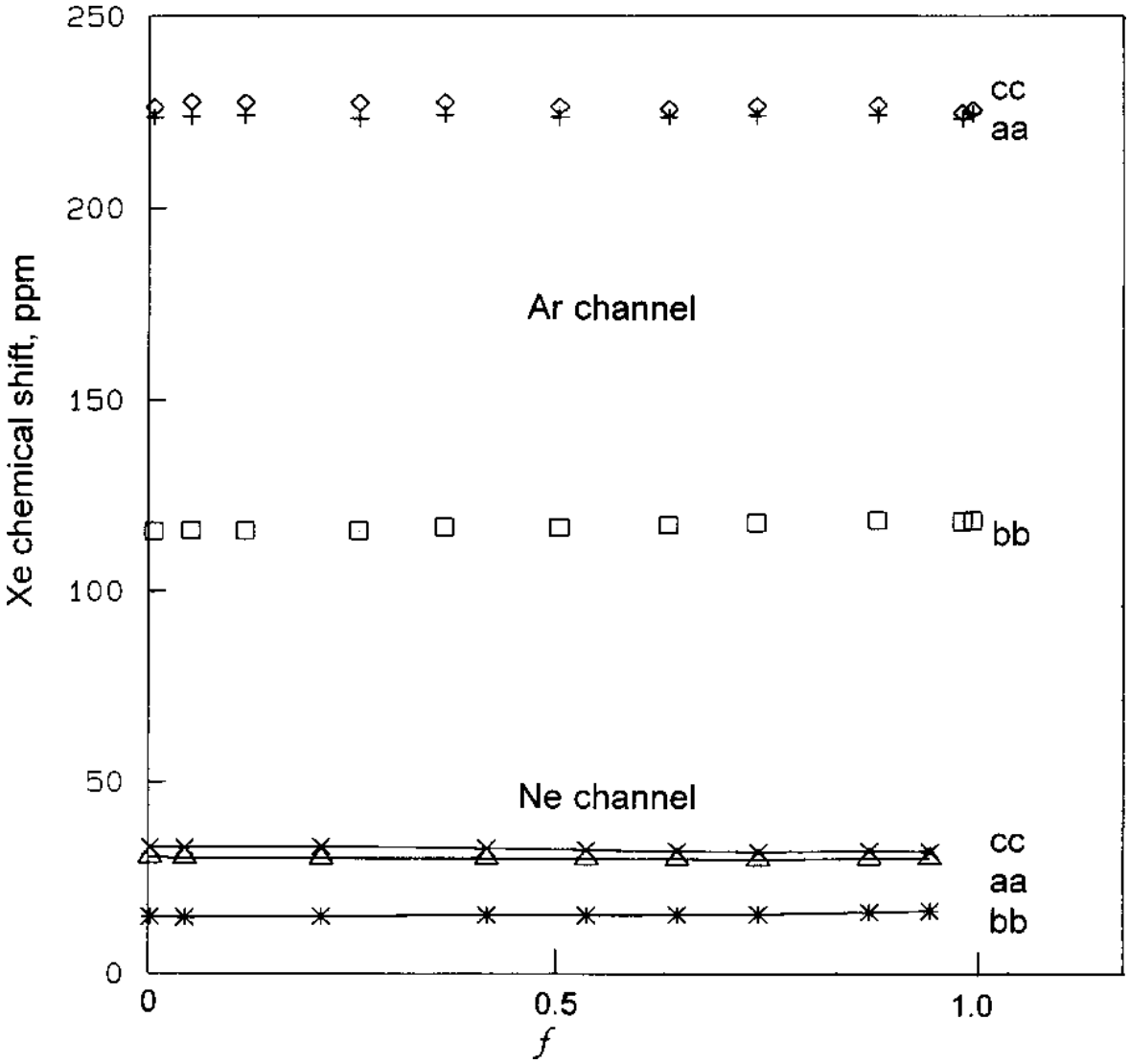
One Xe atom in a **neon channel**

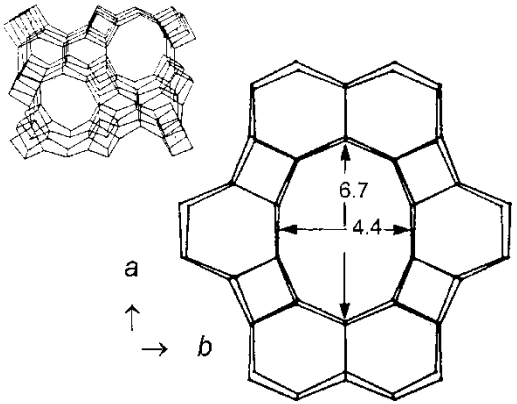
One Xe atom in an **argon channel**



Jameson, JCP 116, 8912 (2002)

signature of the channel architecture: Xe-channel contributions



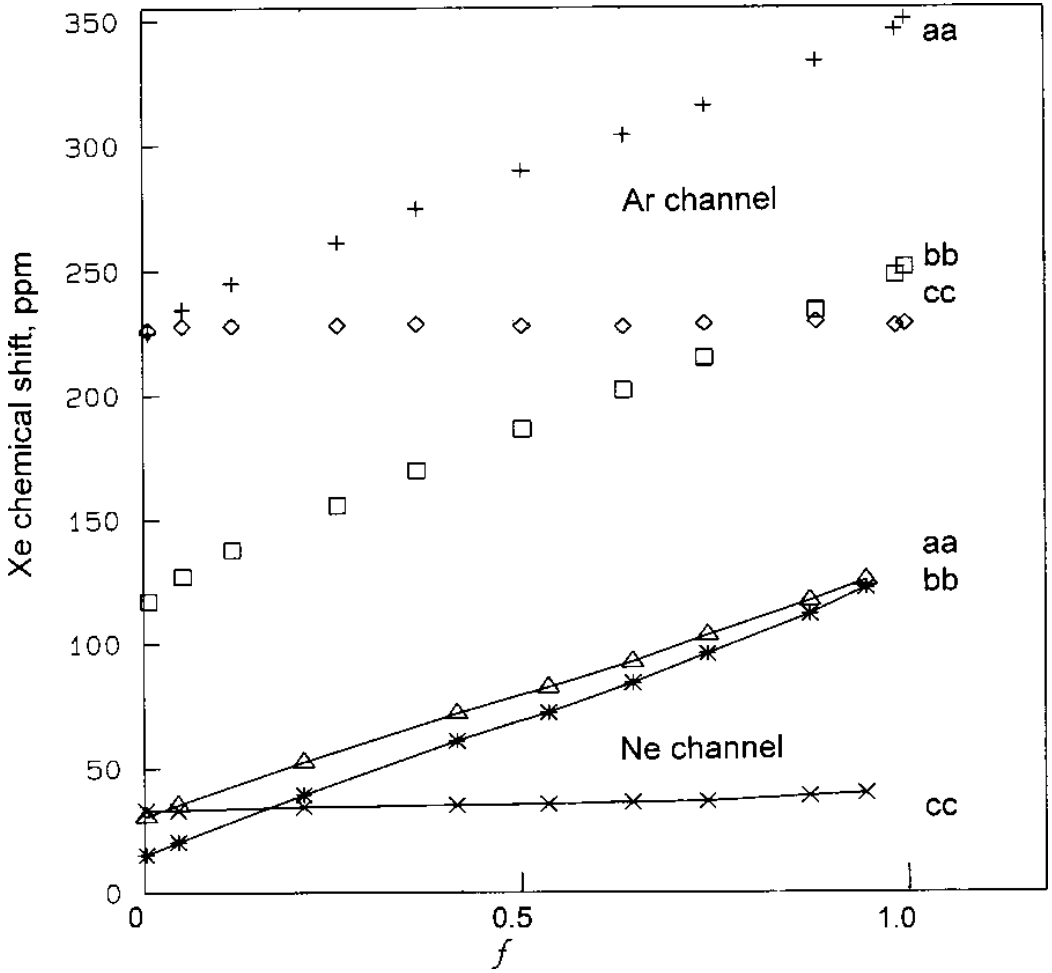


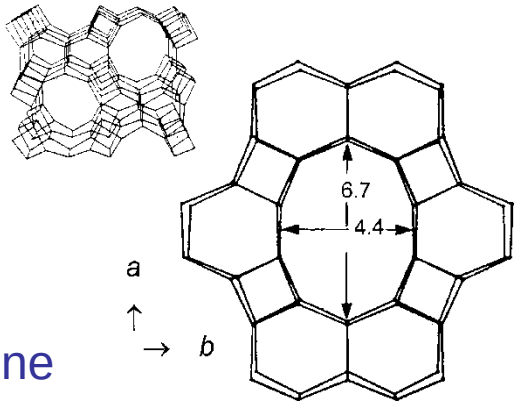
larger component is δ_{aa}

smaller is δ_{bb}, clearly not circular cross section

larger response from Ar than Ne

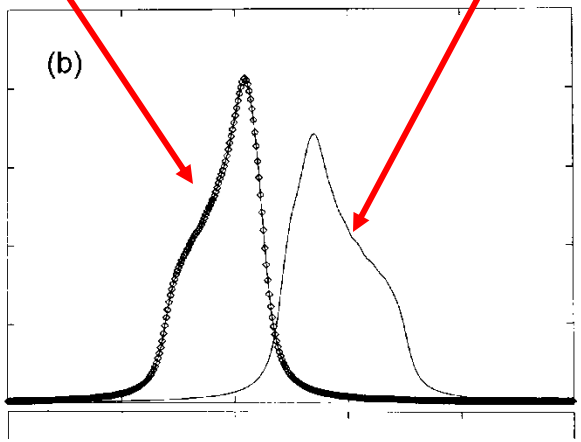
average tensor components



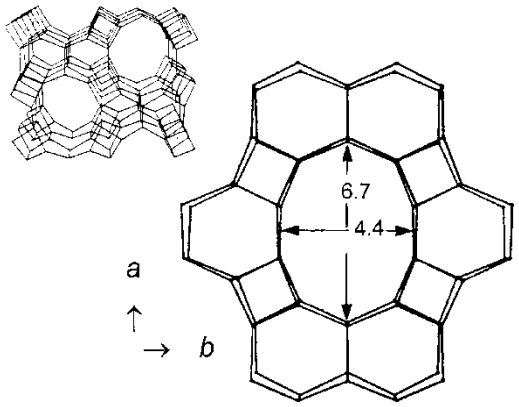


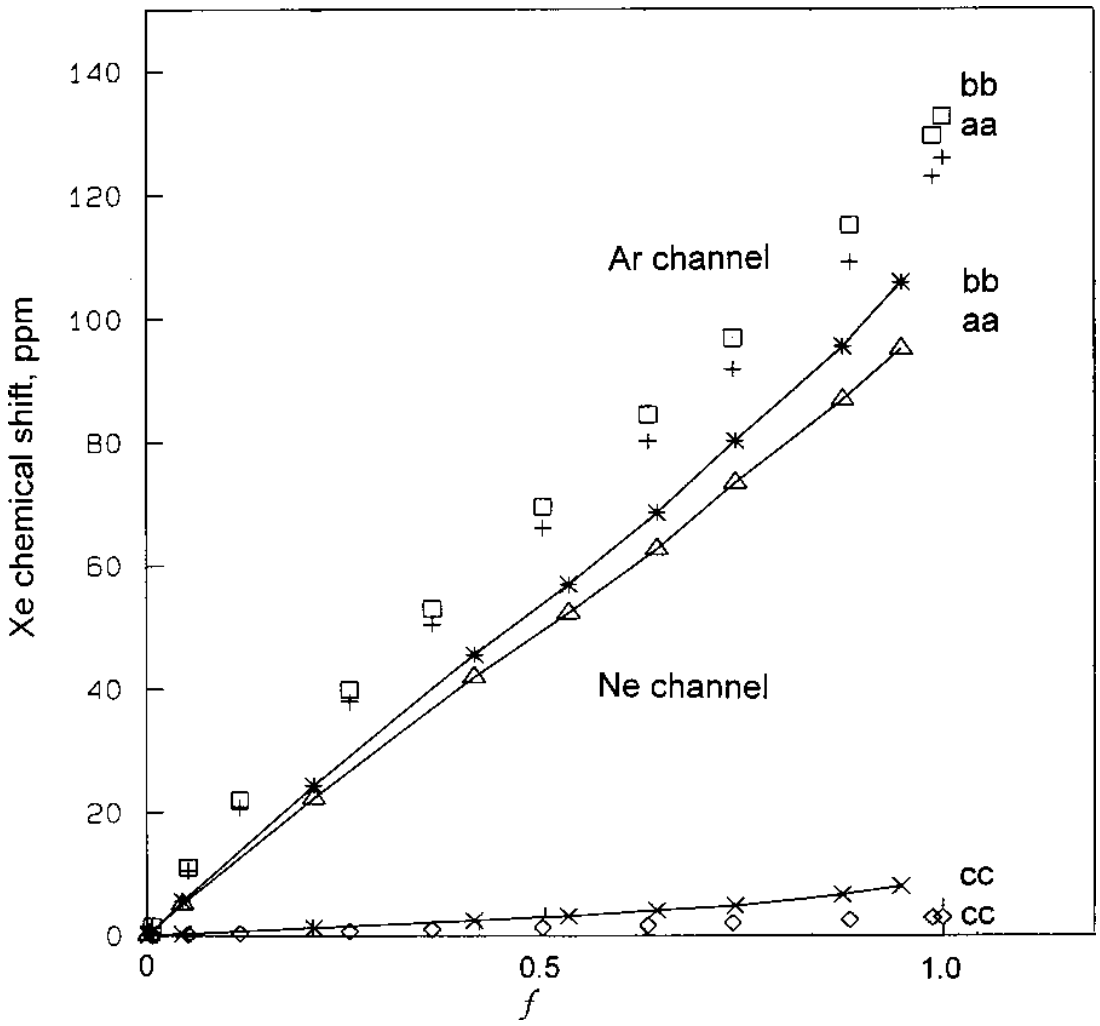
total line shape

Xe-channel contrib



signature of the channel architecture: Xe-Xe contributions





almost no δ_{cc} component, not enough space for two Xe atoms to overlap densities in one cross-sectional plane

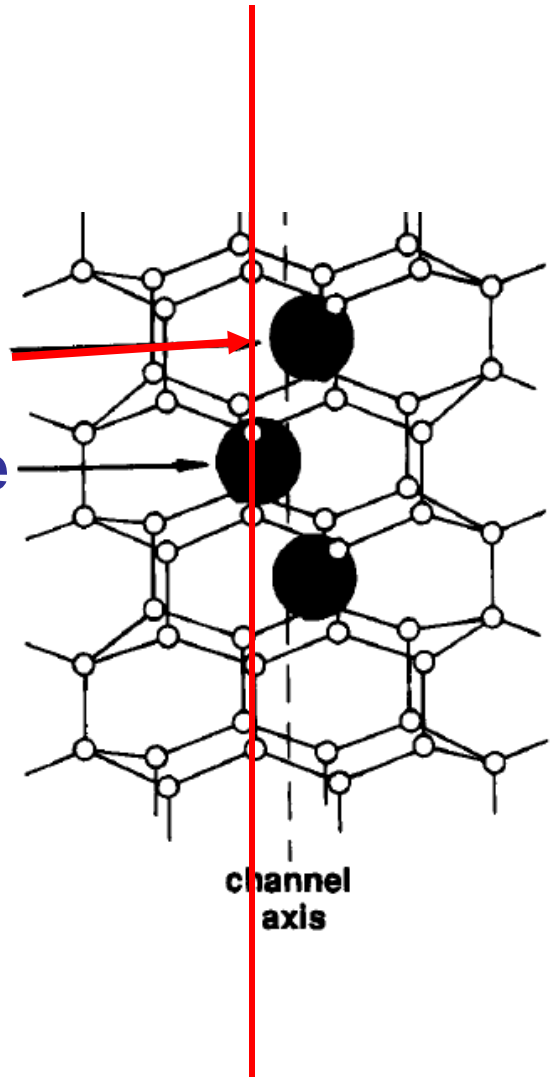
larger contribution to δ_{bb}

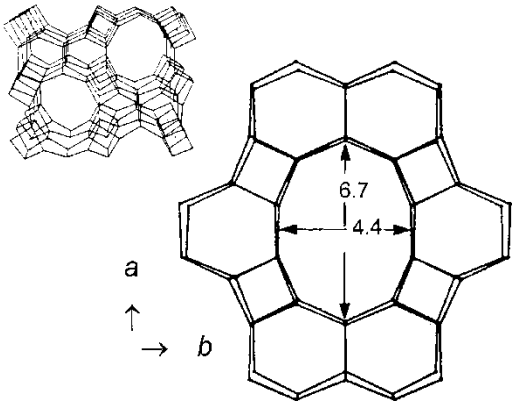
smaller to δ_{aa}

WHY?

look on the plane shown in red for electron densities which can contribute to δ_{aa}

consider the shielding of this Xe

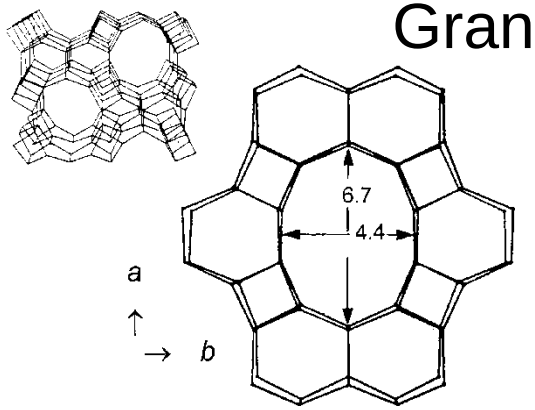




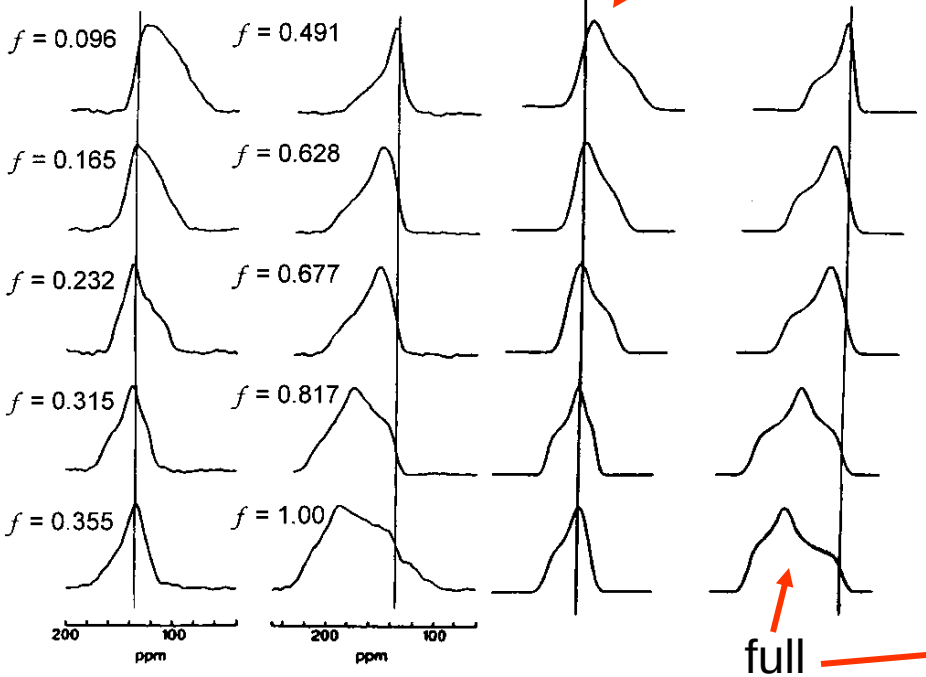
look on the plane of the screen for electron densities which can contribute to δ_{bb}

Xe in the channels of $ALPO_4$-11

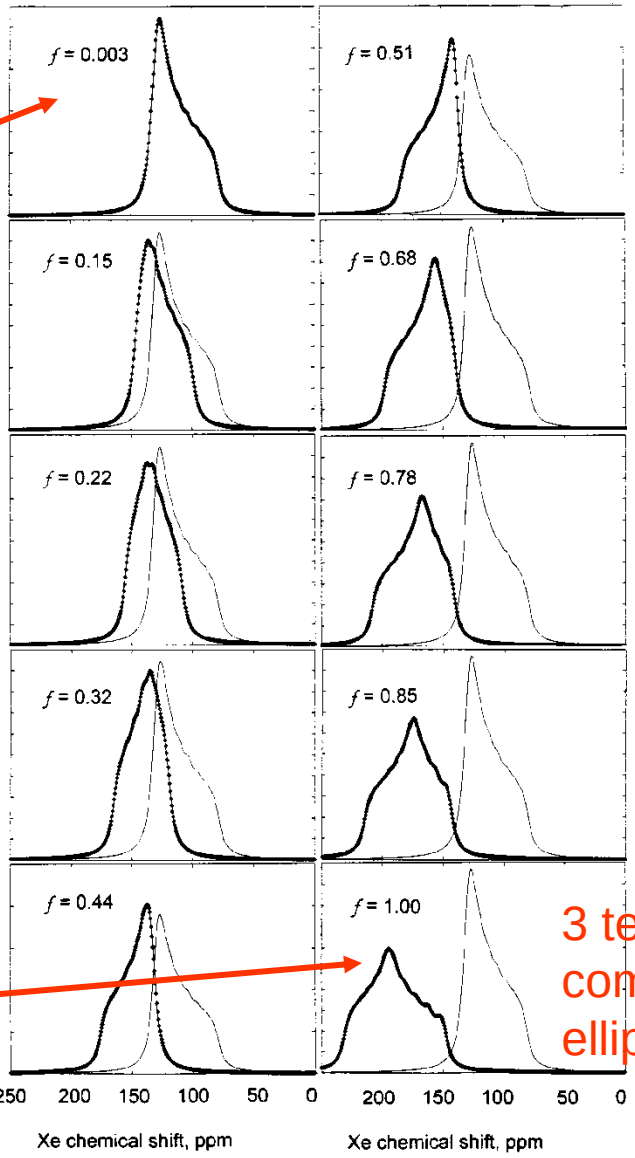
Grand Canonical Monte Carlo **SIMULATIONS**



nearly empty



full

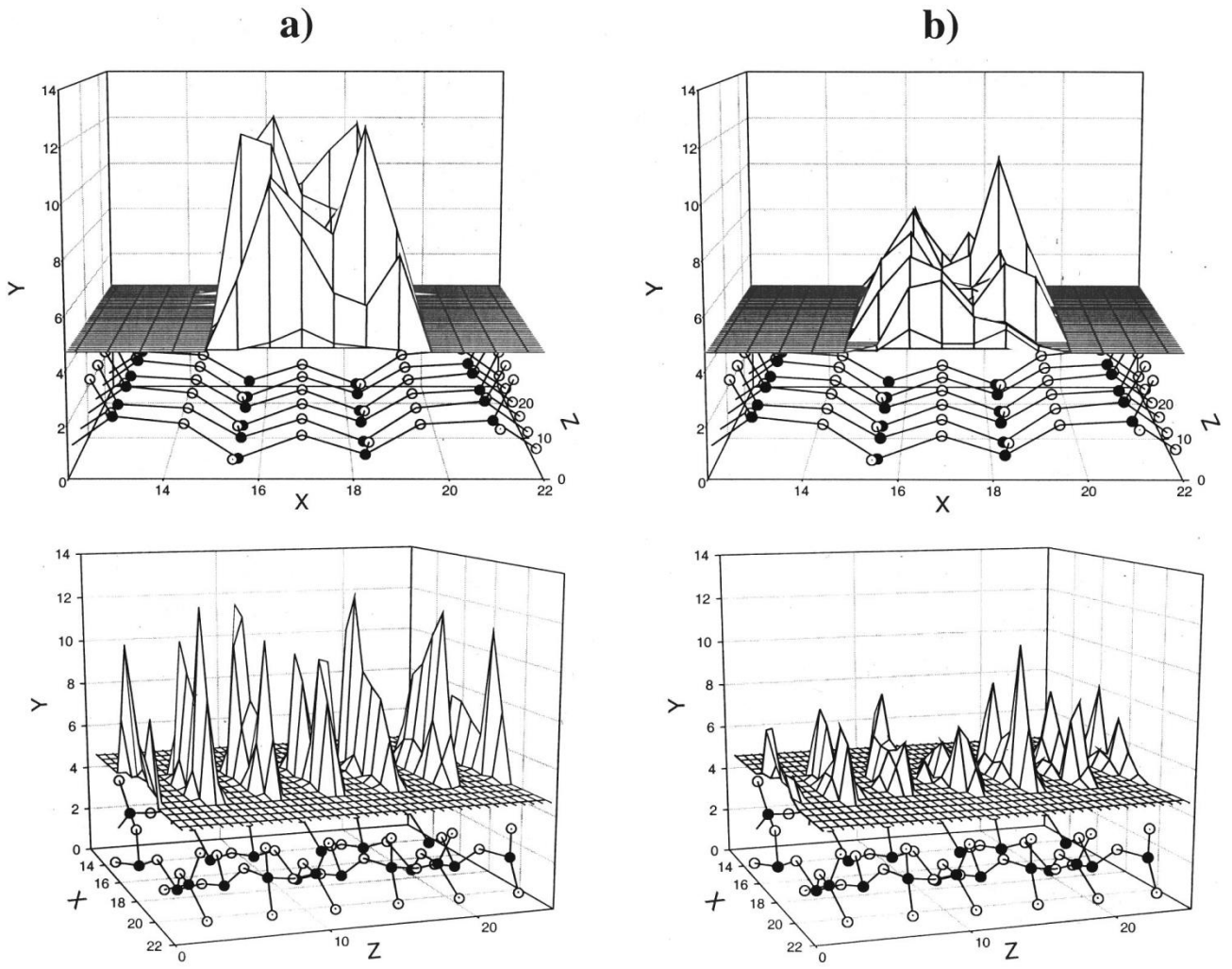


Jameson J Chem Phys 116, 8912 (2002)

3 tensor components ellipticity

EXPERIMENTS J.A. Ripmeester and C.I. Ratcliffe, J. Phys. Chem. 99, 619 (1995)

One-body distribution functions of Xe in ALPO4-11



at full loading

0.26% occupancy

Dipeptide molecular crystals form 1-D channels ideal for understanding Xe-protein interaction

L-Val-L-Ala

VA

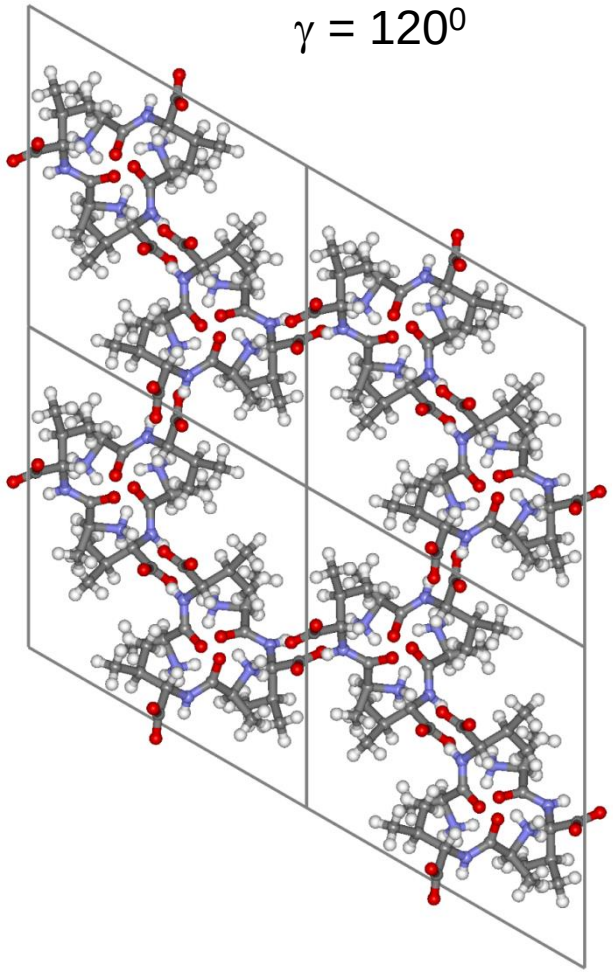
P61

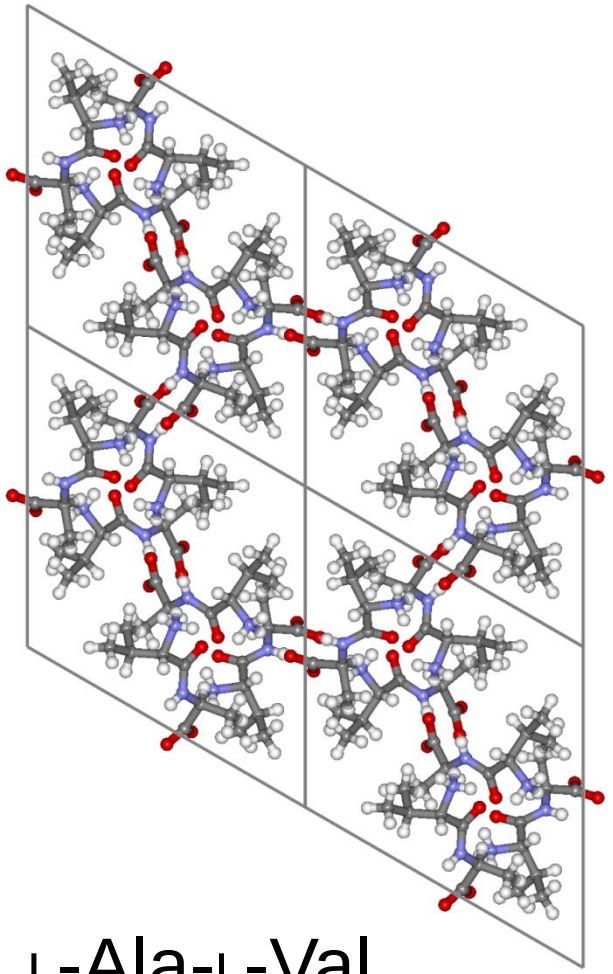
a = b= 14.461 Å

c = 10.083 Å

$\alpha = \beta = 90^0$

$\gamma = 120^0$





L-Ala-L-Val

AV

P61

a = b= 14.462 Å

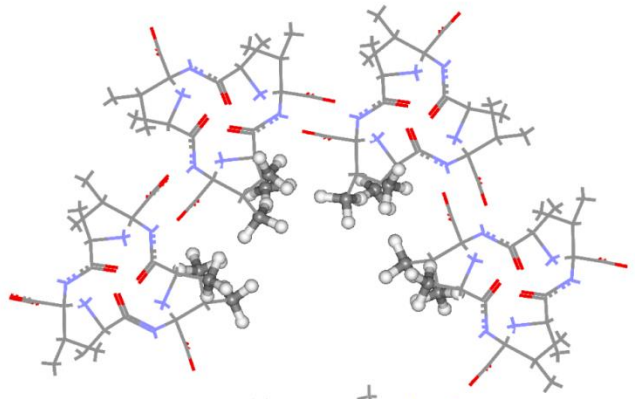
c = 10.027 Å

$\alpha = \beta = 90^0$

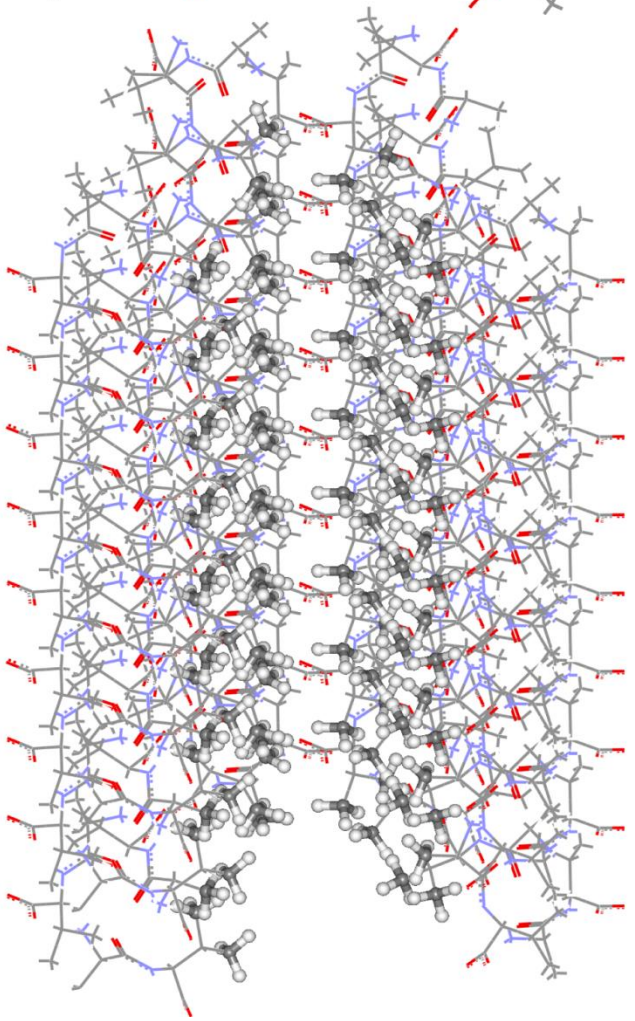
$\gamma = 120^0$

- From the perspective of the Xe only the side chain methyl groups are accessible

- **Can we use the Xe- CH_4 shielding response surface and potential energy surface** for our simulations?

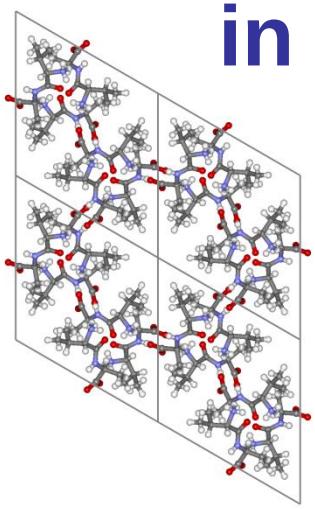


Top view



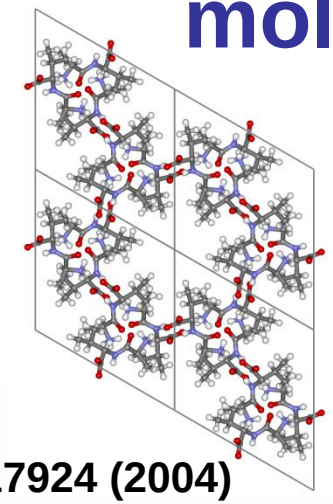
Tilted view

in channels of molecular crystals



L-Val-L-Ala

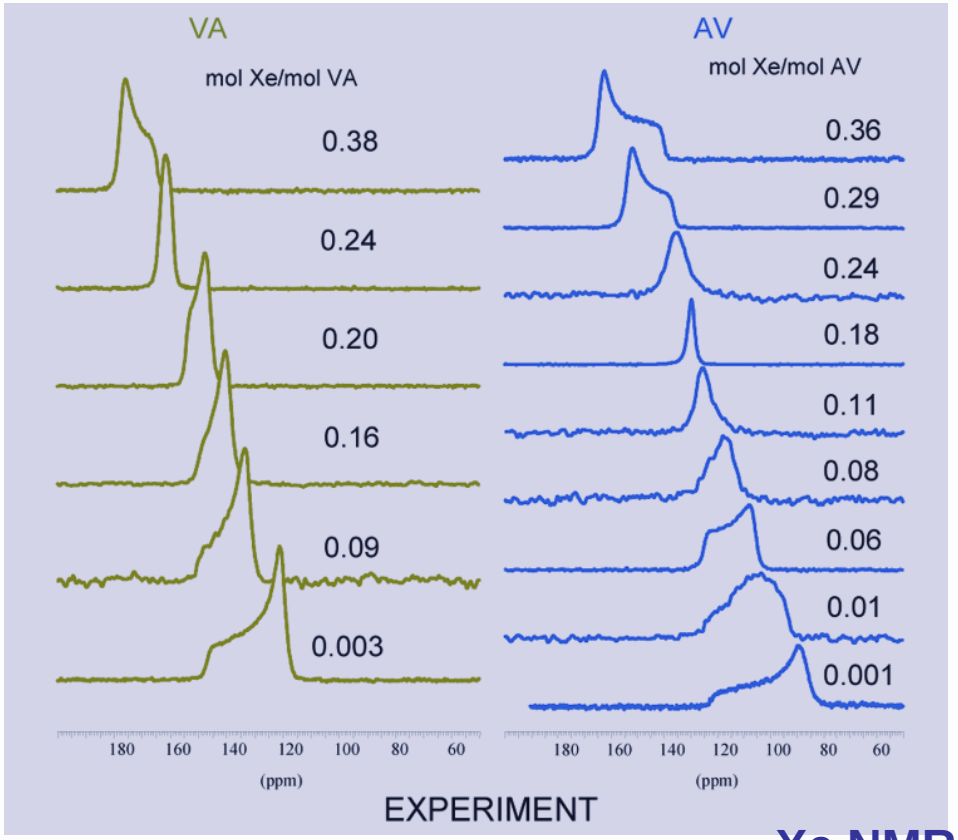
VA

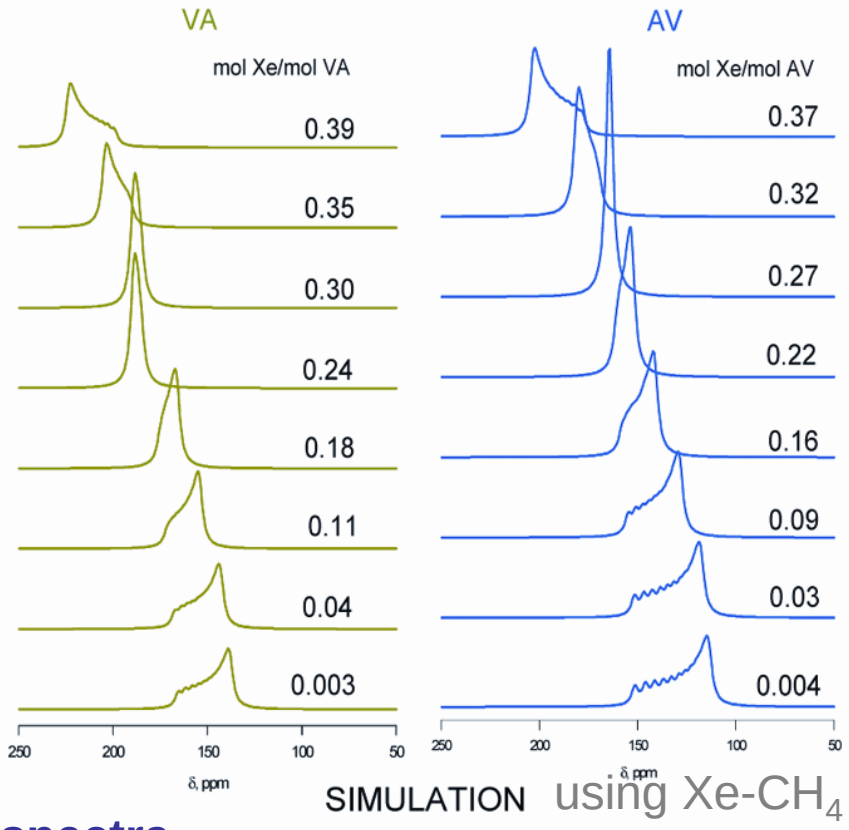


L-Ala-L-Val

AV

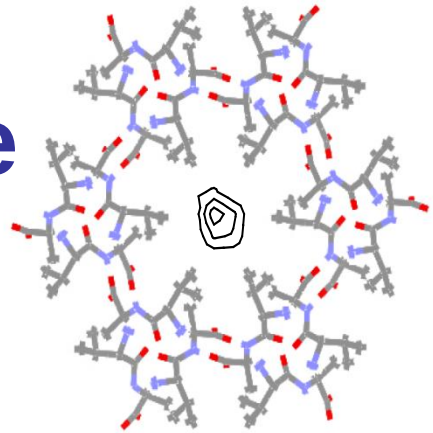
PNAS 101, 17924 (2004)





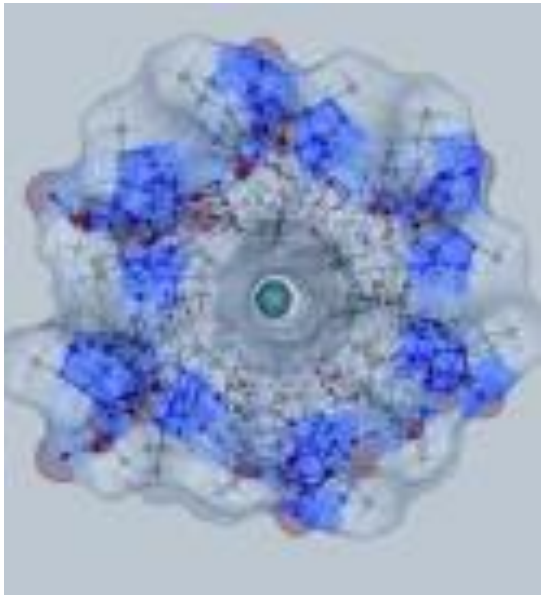
Xe NMR spectra

Xe distribution in the material, i.e., where does Xe spend time?

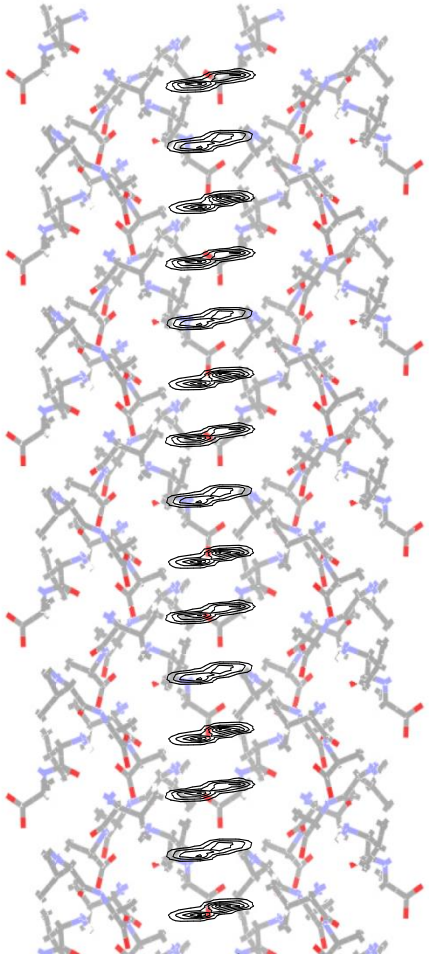


Xe in VA
from GCMC
simulations

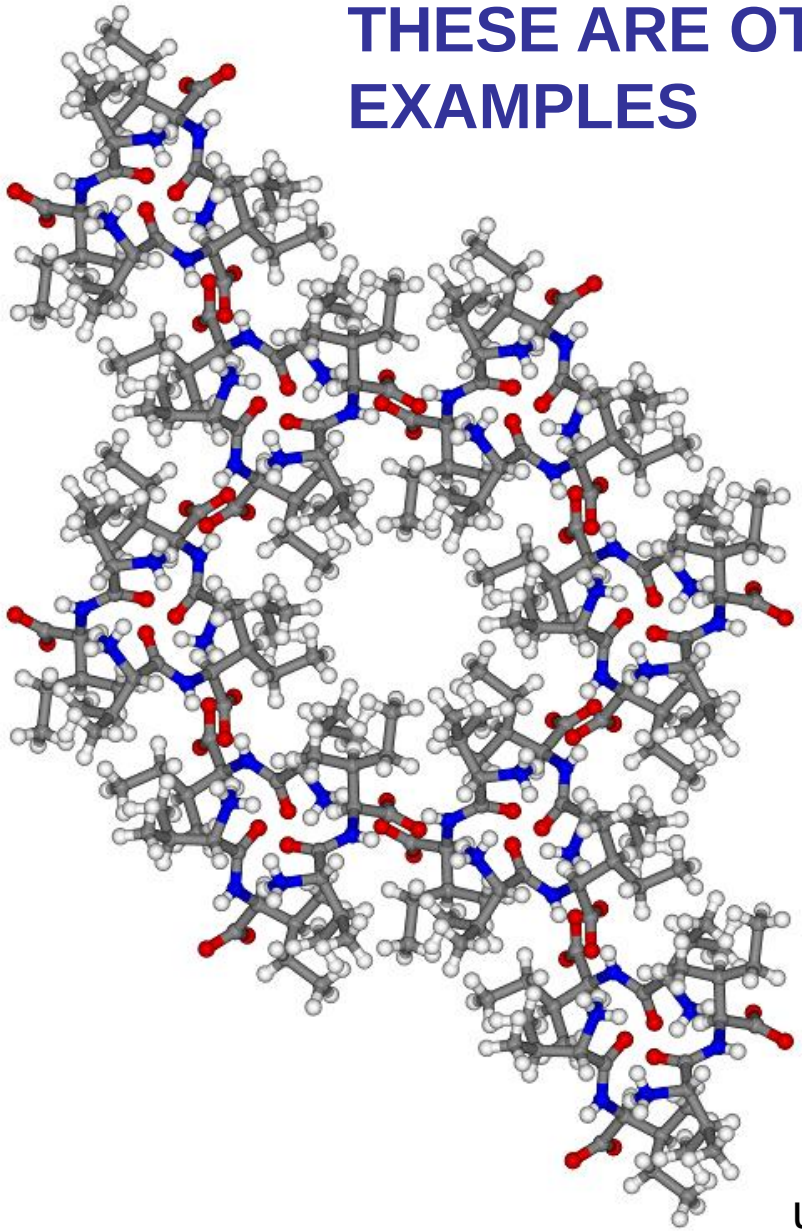
The one-body distribution function shows the probability of finding a Xe atom as a function of position within the channel

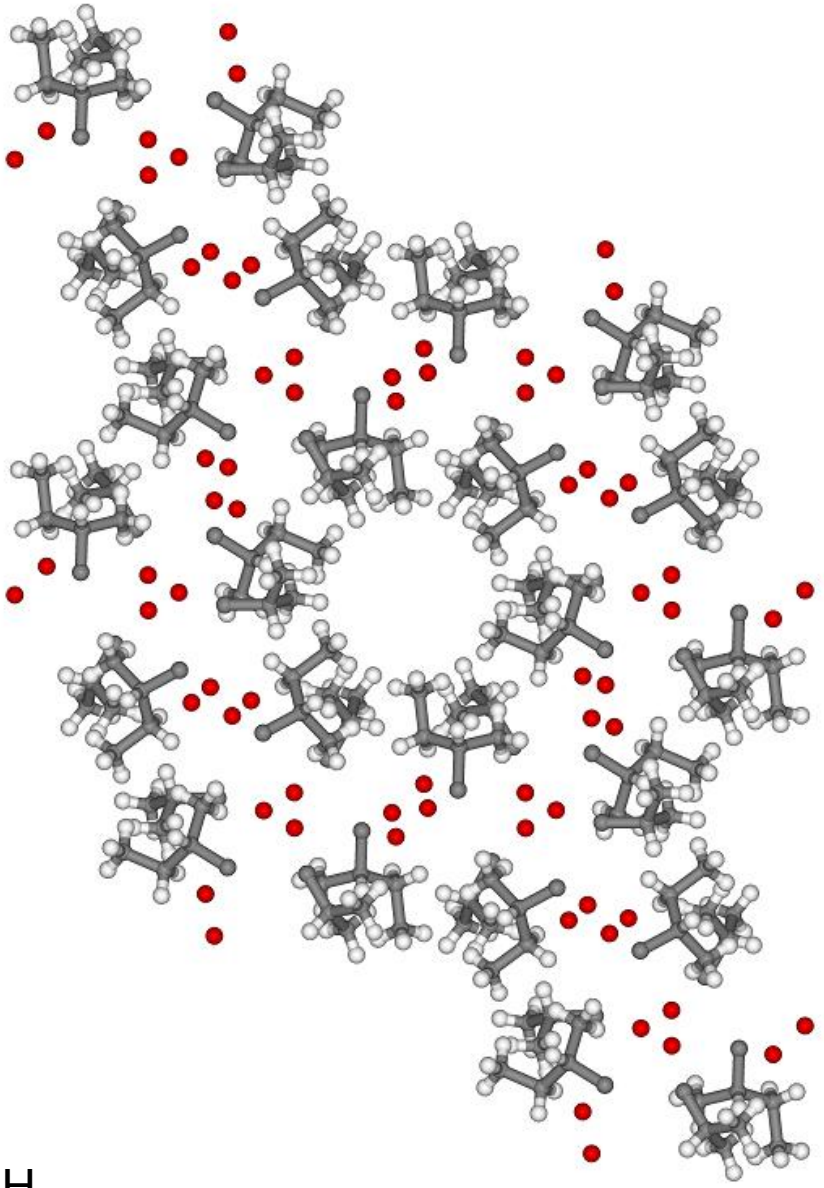


a helical channel!



THESE ARE OTHER EXAMPLES

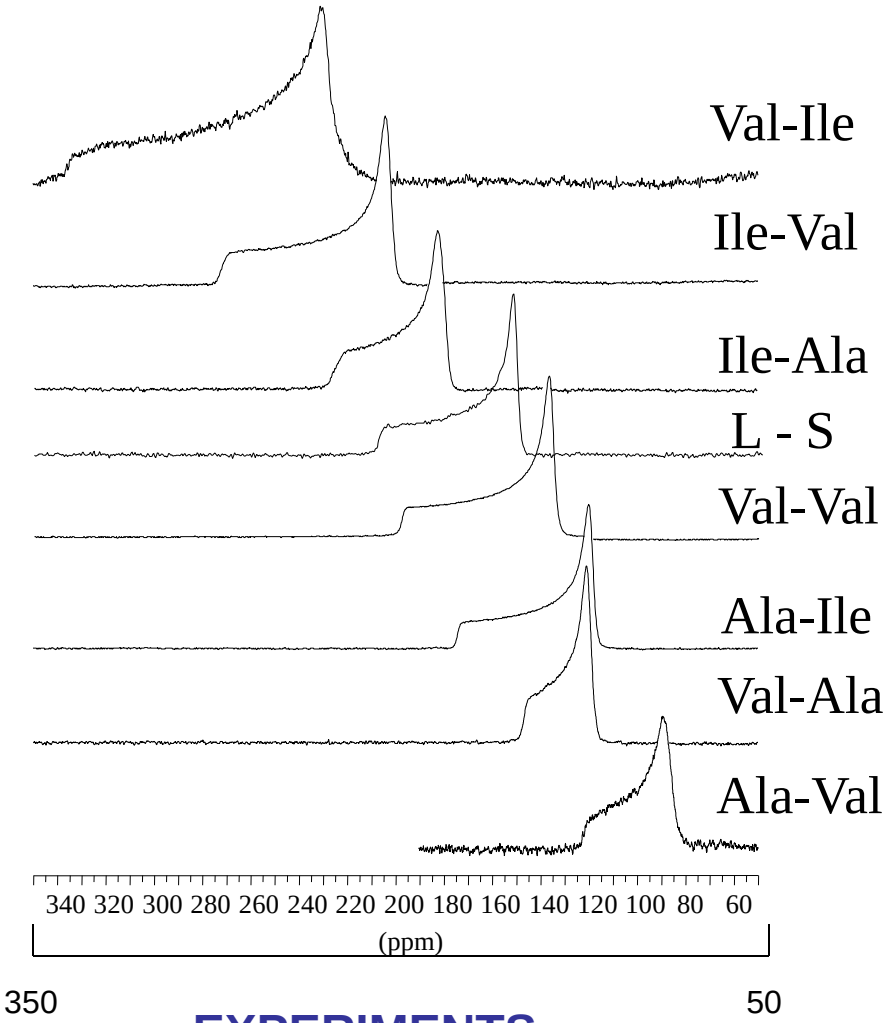


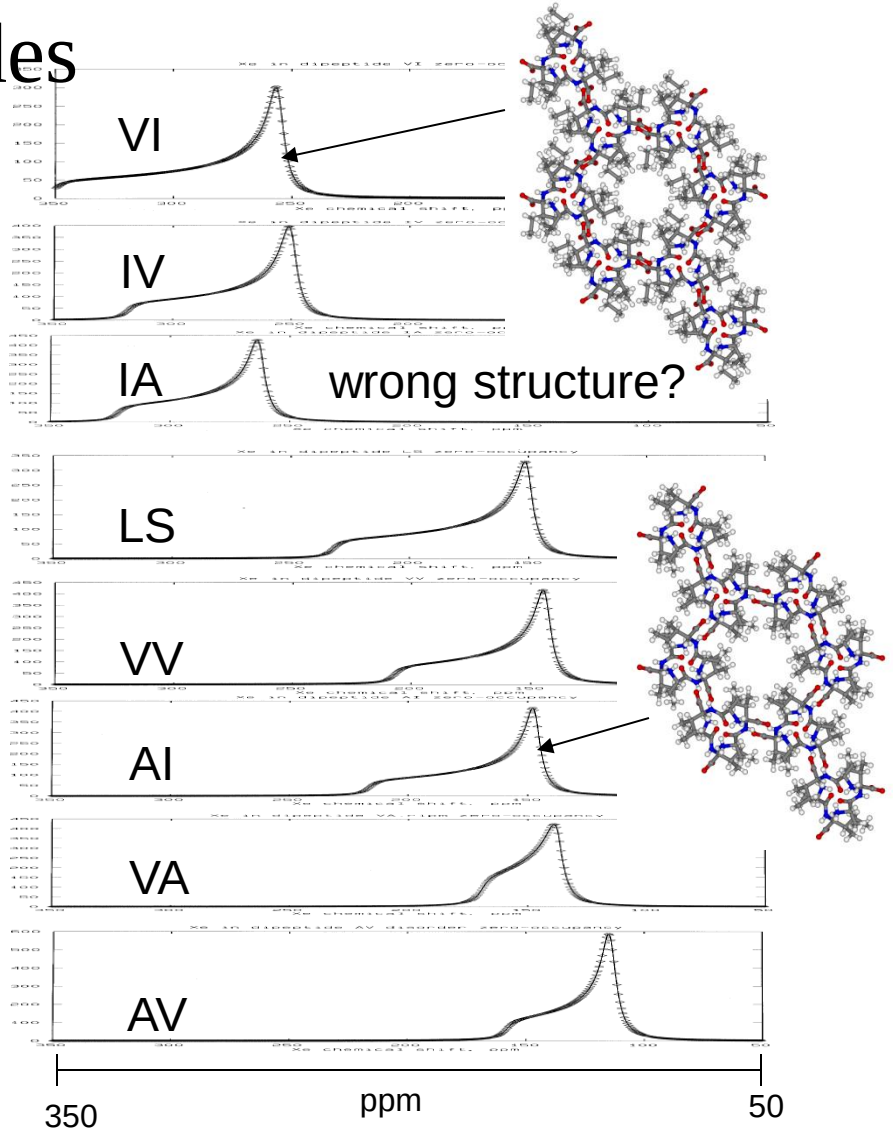


using CH_4

VI X-Ray Structure → GCMC Structure

^{129}Xe NMR in dipeptides





EXPERIMENTS

SIMULATIONS

Xe line shape signatures in diamagnetic channels

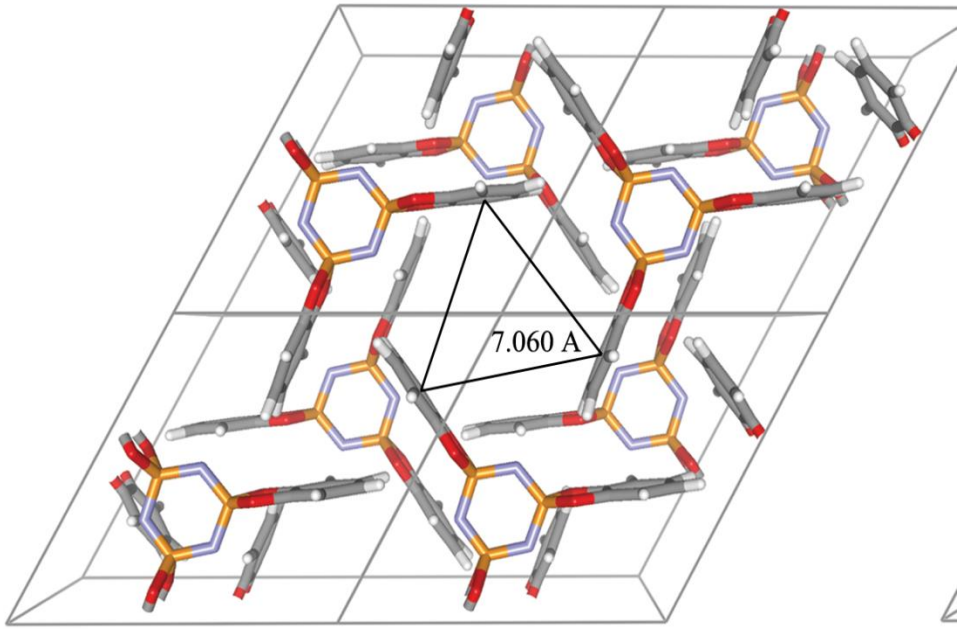
- *# singularities at high* $\langle N \rangle$ $\rightarrow$ aspect ratio of cross section (2 singularities: nearly circular; 3 singularities: elliptical)
- *1 constant tensor component with changing* $\langle N \rangle$ $\rightarrow$ channel diameter does not permit two Xe to pass each other.
- *Significant change of* $\delta_{||}$ *with* $\langle N \rangle$ $\rightarrow$ cross section large enough to permit $XeXe_2$ groupings to achieve angles smaller than 150-180°at high $\langle N \rangle$.

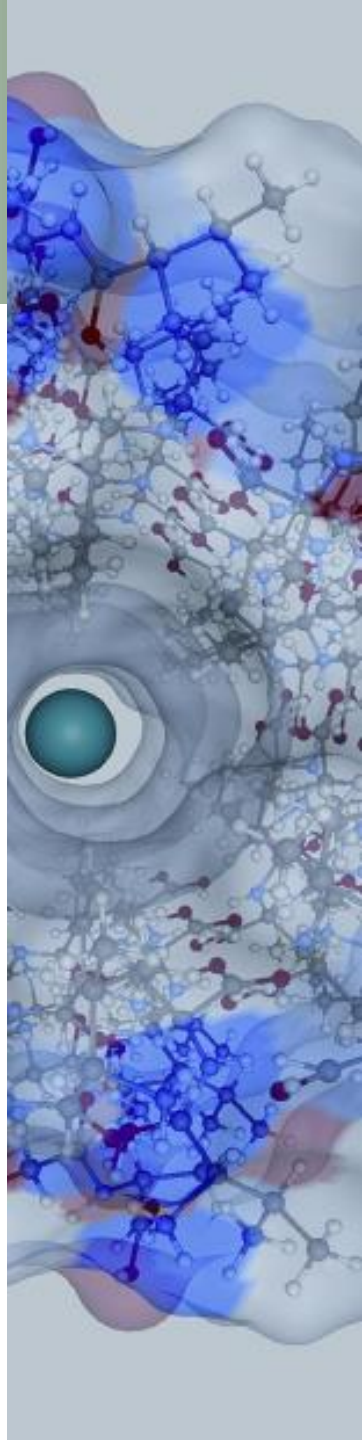
Xe line shape signatures in diamagnetic channels

- *Linear behavior of each component with* $\langle N \rangle \rightarrow$ orderly arrangement of Xe atoms in channel; Xe sits in register with sites along walls. Xe unable to do this when sites too close together

- *Non-linear behavior of tensor components with* $\langle N \rangle \rightarrow$ non-uniform channel cross section.

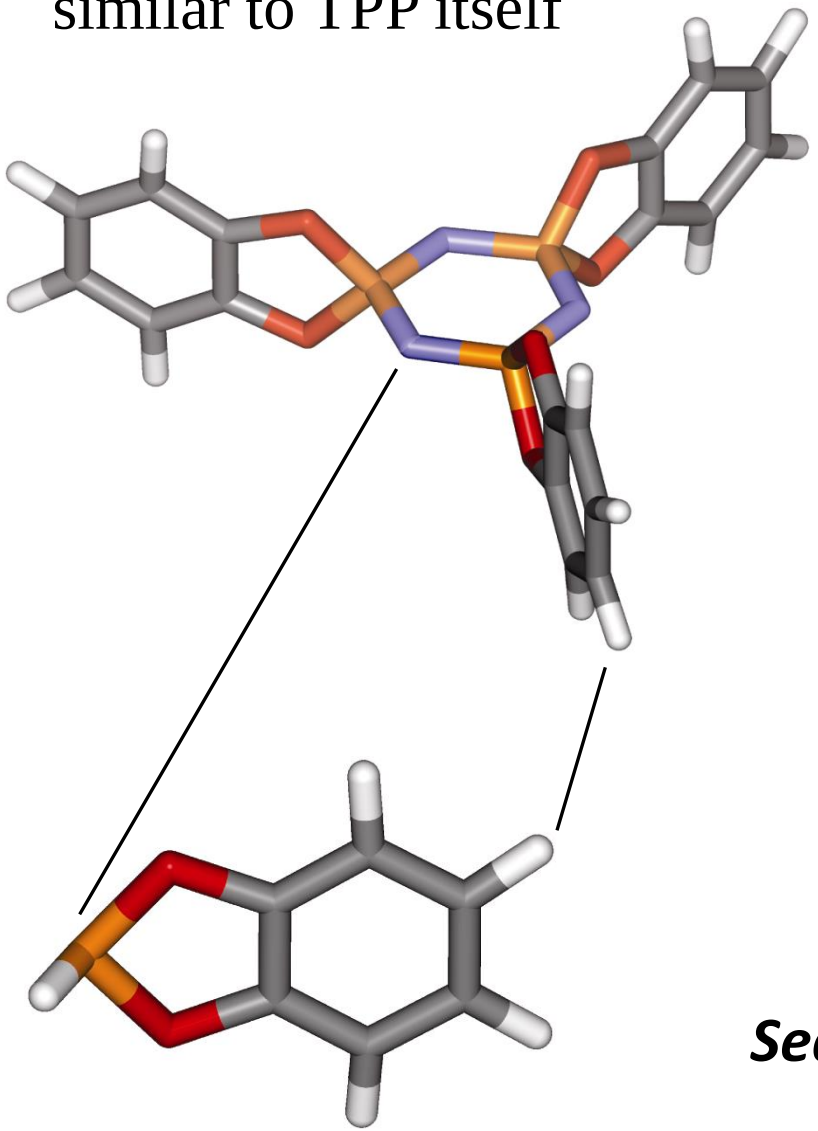
Tris(o-phenylenedioxy) cyclotriphosphazene (TPP)

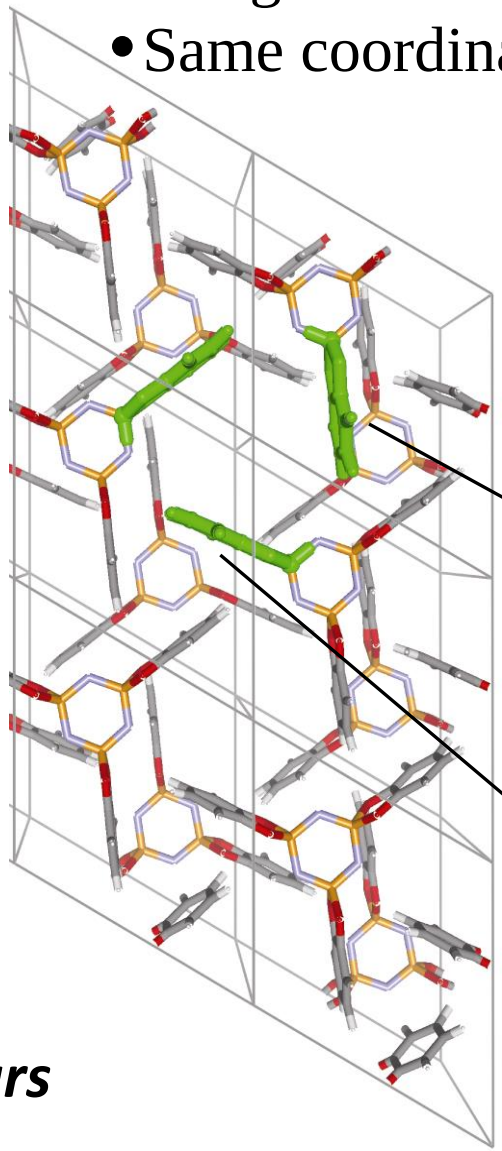


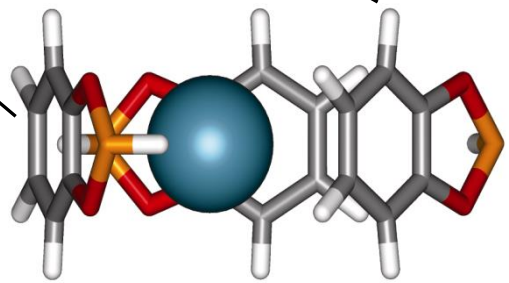


Quantum Model for TPP channel

- Suitable molecular fragment has electron density distribution similar to TPP itself
- Channel comprised of a trimer of fragments
- Same coordinate system as channel

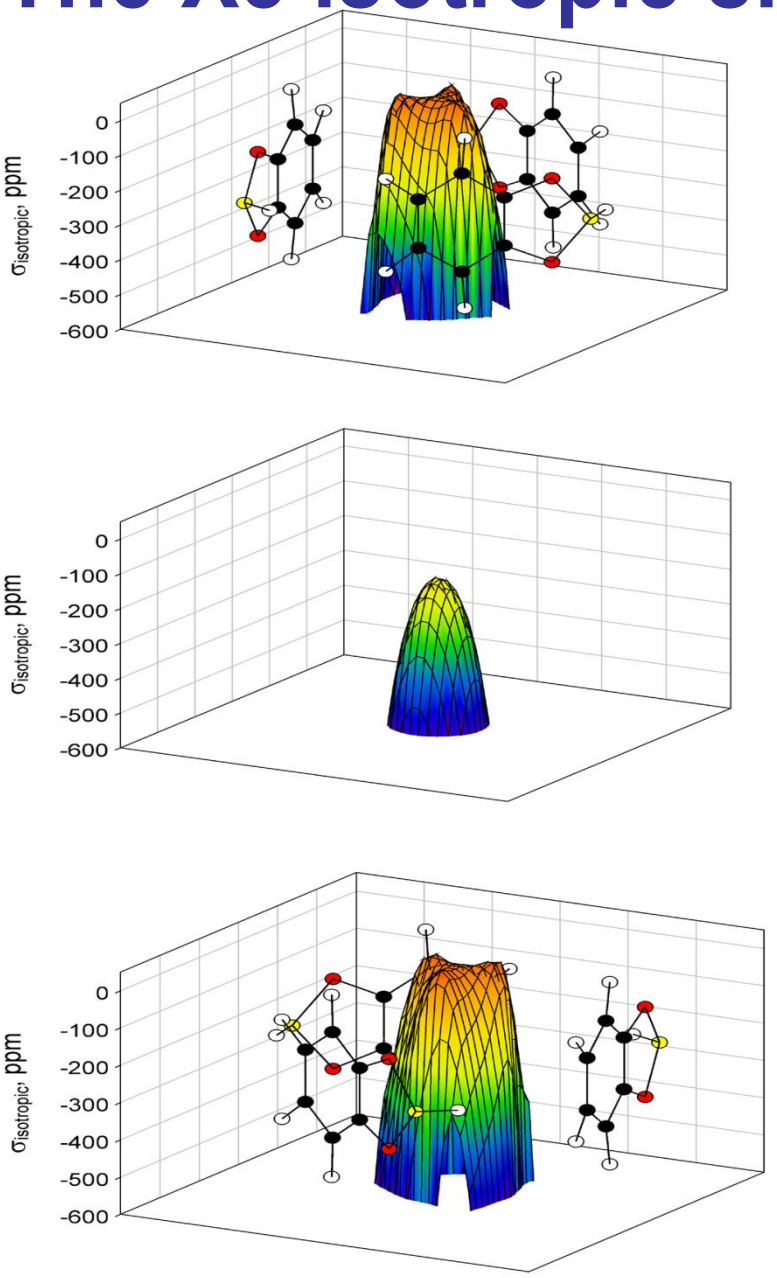


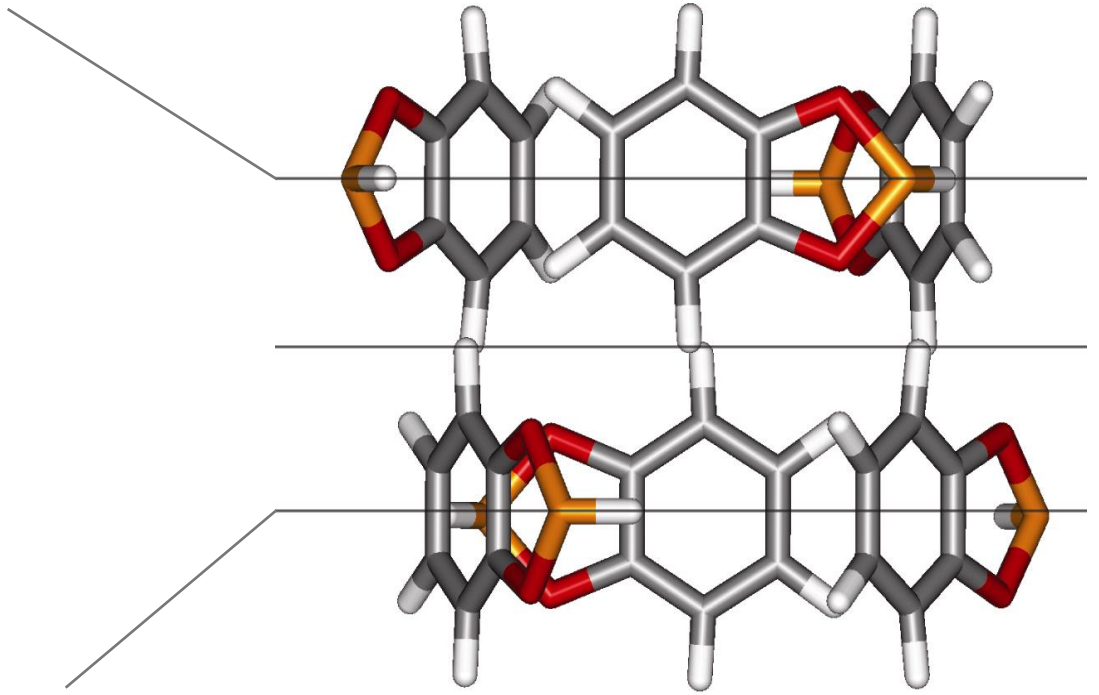




Sears

The Xe isotropic shielding surface ab initio

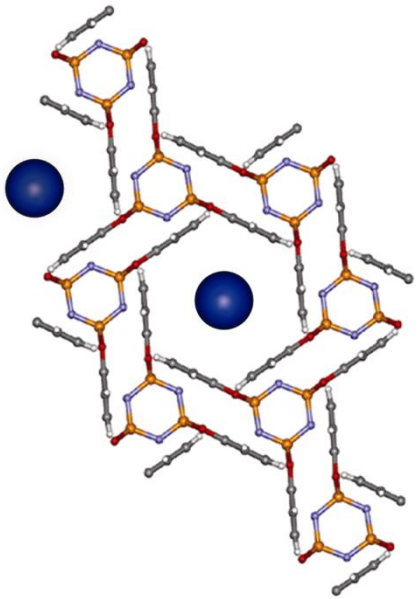




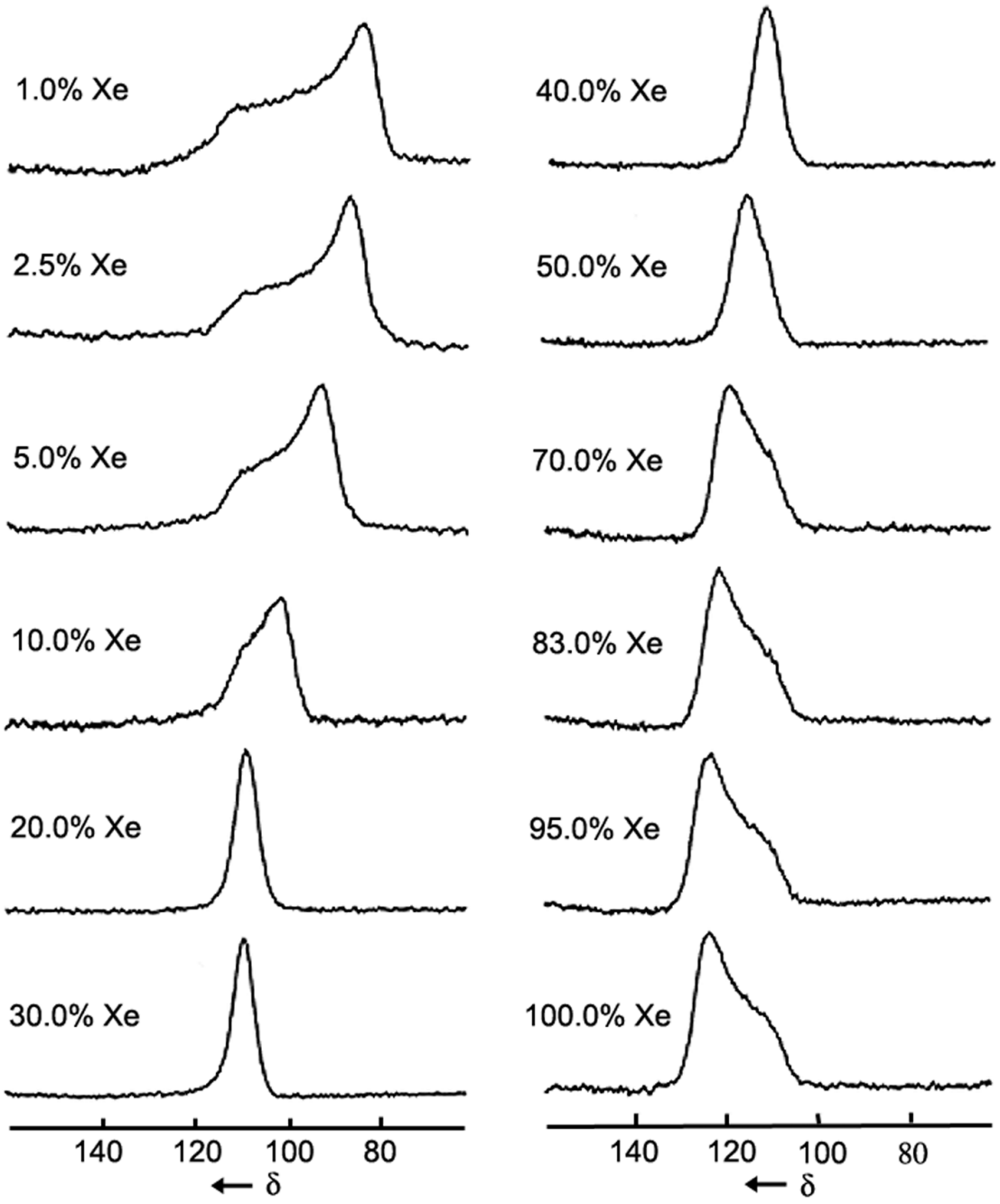
Shielding surface reflects symmetry of TPP channel

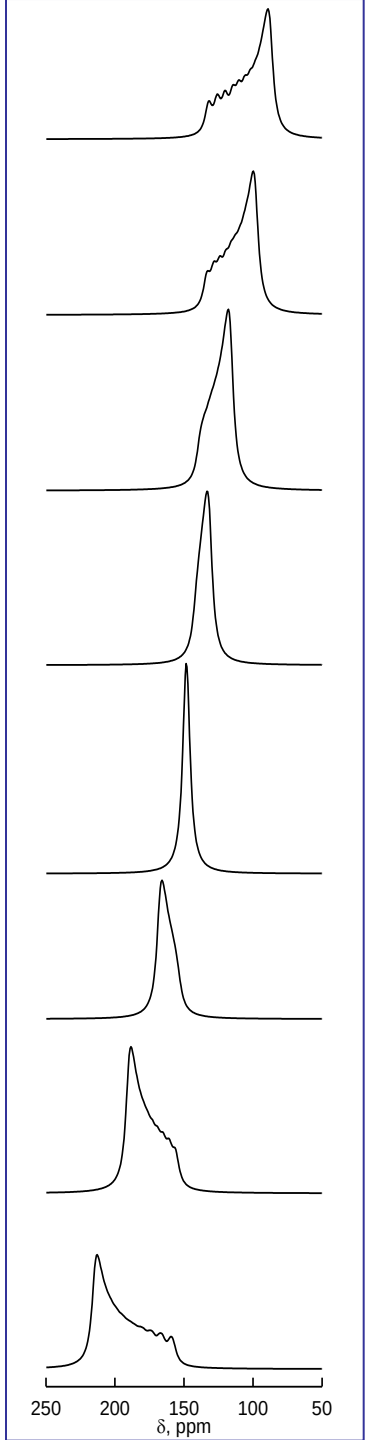
Motivation:

- Organic molecular crystals provide 1-D nanochannels with aromatic environments
- Does Xe shielding in aromatic nanochannels differ from 1-D silicate channels?
- Experimental Xe lineshapes in TPP have been observed (Sozzani et al., 2000) ⟶



P. Sozzani, A. Comotti, R. Simonutti,
T. Meersmann, J.W. Logan, A. Pines
Angew. Chem. Int. Ed. 39, 2695-2699 (2000)





⟨n⟩ = 0.063 Xe/UC

0.406

0.737

0.961

1.368

1.666

1.931

2.088

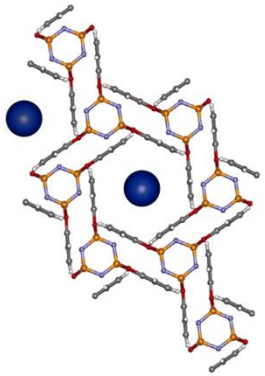
Xe lineshapes calculated using Xe shielding in QUANTUM Model and TPP crystal under Periodic Boundary Condns for Monte Carlo simulation

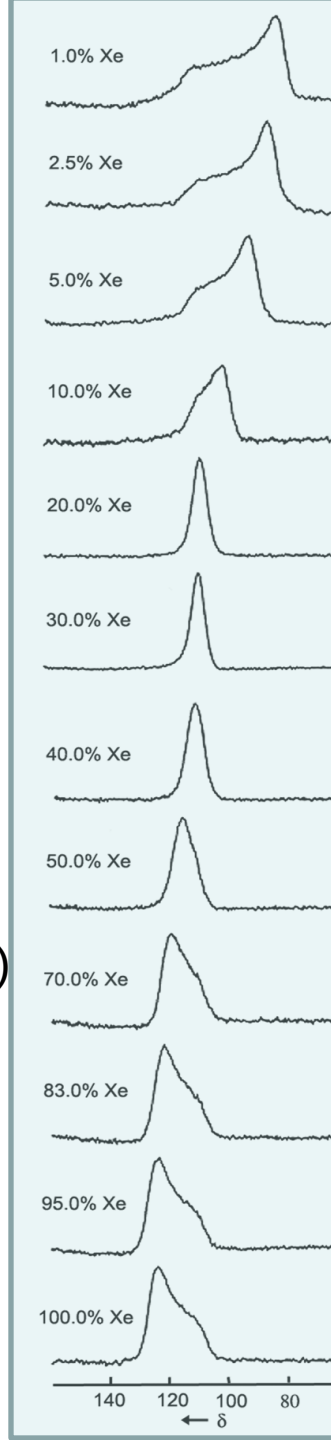
⟸ Jameson 2003

EXPERIMENTAL Xe SPECTRA

as a function of Xe mole fraction:

P. Sozzani, A. Comotti, R. Simonutti, T. Meersmann, J.W. Logan, A. Pines
Angew. Chem. Int. Ed. 39, 2695 (2000)

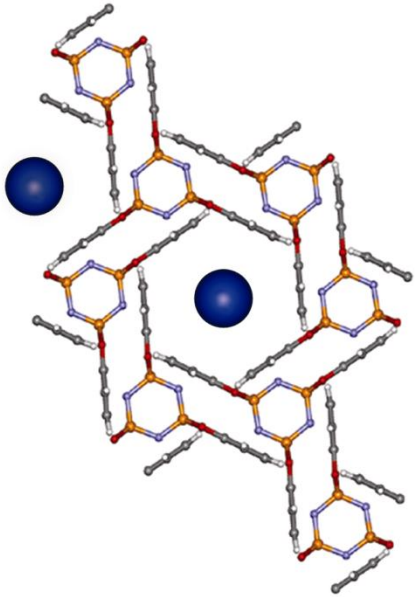




Analysis of the temperature dependence of the components of the average chemical shift tensor for Xe in a nanochannel.

The specific case of Xe in TPP

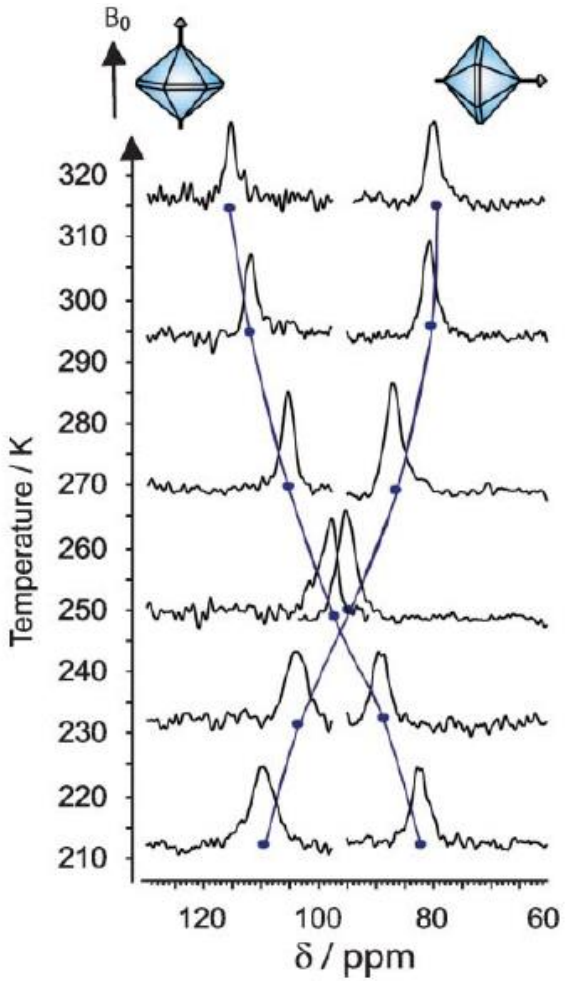
Cynthia J. Jameson
University of Illinois at Chicago



January 26, 2007
Departimento di Scienza dei Materiali
Universita' degli Studi di Milano Bicocca

Temperature dependence of the $\delta_{\perp}$ and $\delta_{||}$ components for Xe in single crystal TPP

THE EXPERIMENTAL RESULTS TO BE EXPLAINED



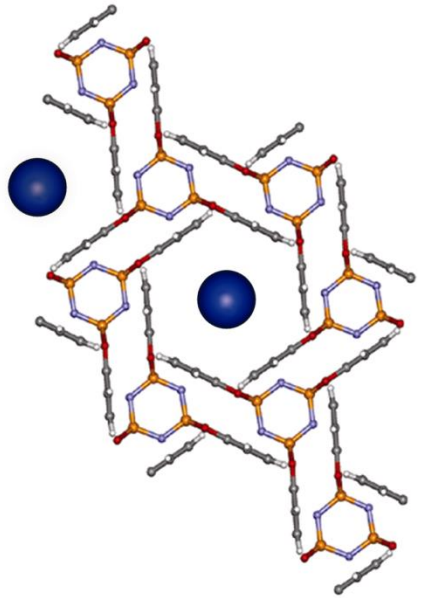
A. Comotti, S. Bracco,
L. Ferretti, M. Mauri,
R. Simonutti and P. Sozzani*
Chem. Commun. 2007, 350-353.

QUESTION:

What is the origin of the temperature dependence of $\delta_{||}$ of Xe in TPP?

GENERAL:
the electron density in the plane perpendicular to the axis of the channel

is responsible for $\delta_{||}$



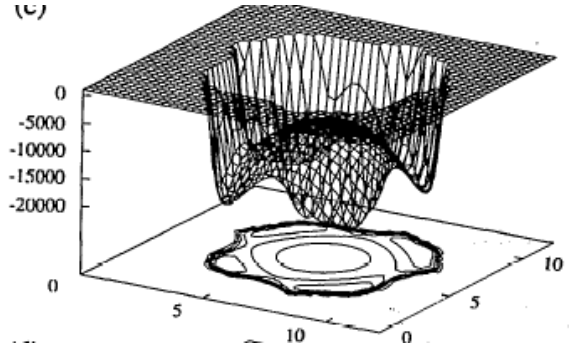
look on this plane

There are only the Xe-wall interactions to consider.

First, consider, in general,
what is the typical T dependence of
δ from Xe-wall interactions in a pore?

EXPLANATION for single Xe in a cavity

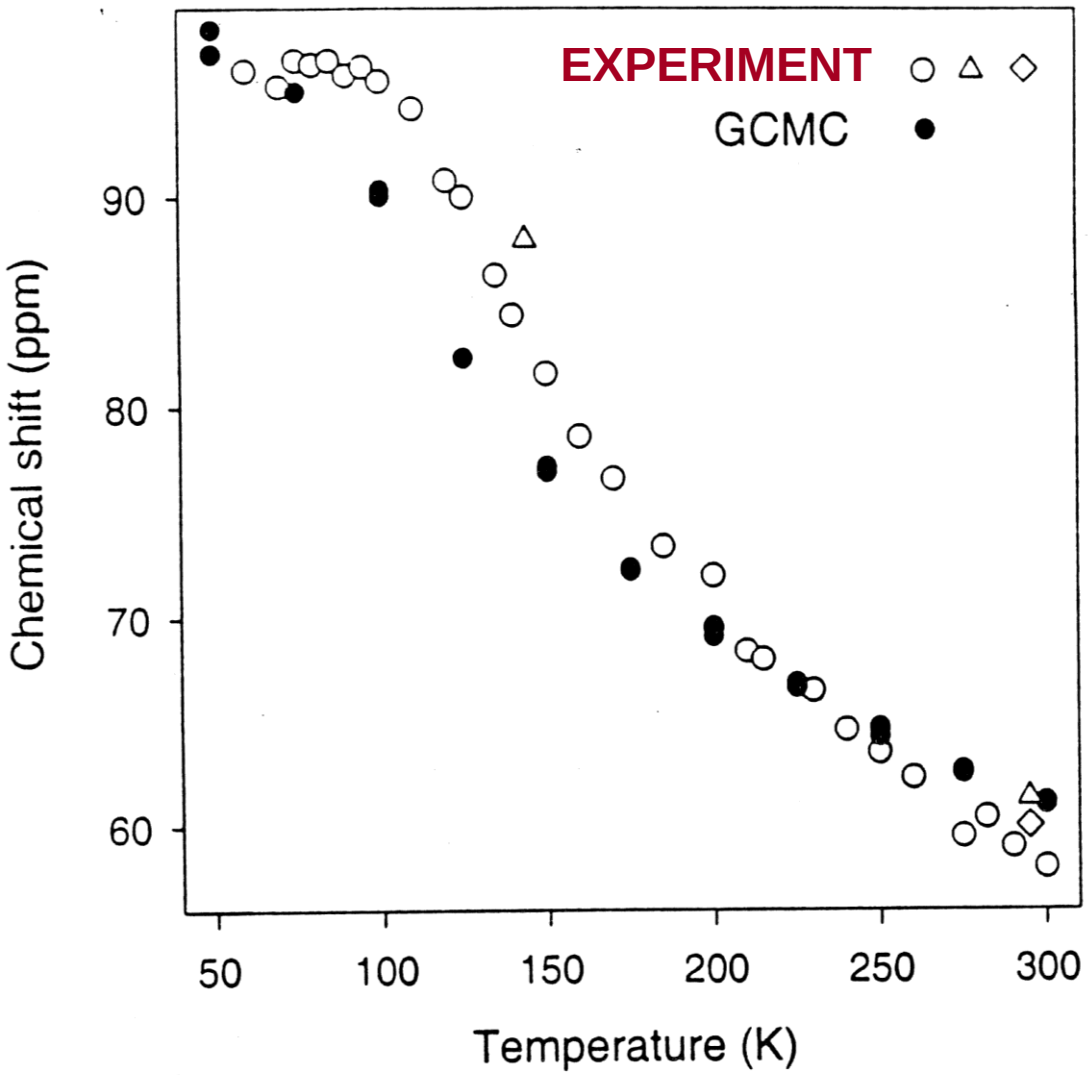
The Xe spends more time in deep potential troughs created by wall curvature at low temperatures.



At higher temperatures, Xe <u>can</u> spend more time in other areas of less favorable potential energy (farther away from the walls, toward the center of the cavity) which correspond to lower chemical shifts (because of the distance dependence of the intermolecular chemical shift).

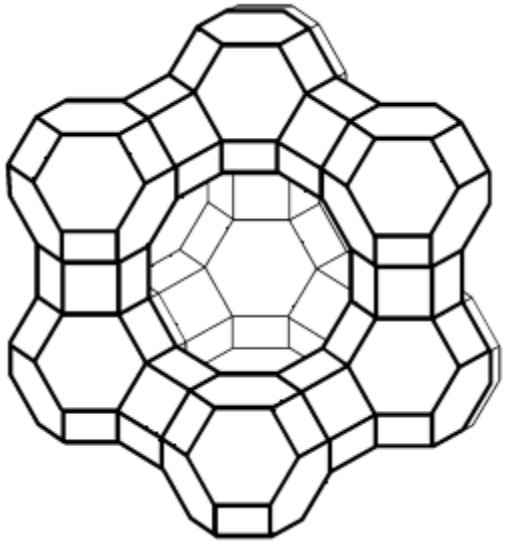
At higher temperatures the probability distribution of Xe within the cavity becomes <u>more spread out</u> compared to lower temperatures.

Temperature dependence
Xe in zeolite Na*Y* at near-zero loading



GCMC simulations

Jameson and Kostikin, 2001



❍ Expt., Pietraβ et al. 1999 $\langle n \rangle_{Xe}$ = 0.25 atoms/cage
Δ Expt., Cheung, 1988 $\langle n \rangle_{Xe}$ = 0.2 atoms/cage
◊ Expt., S. B. Liu, 1994 $\langle n \rangle_{Xe}$ = 0.2 atoms/cage
● GCMC calculations $\langle n \rangle_{Xe}$ = 0.250(5) atoms/cage

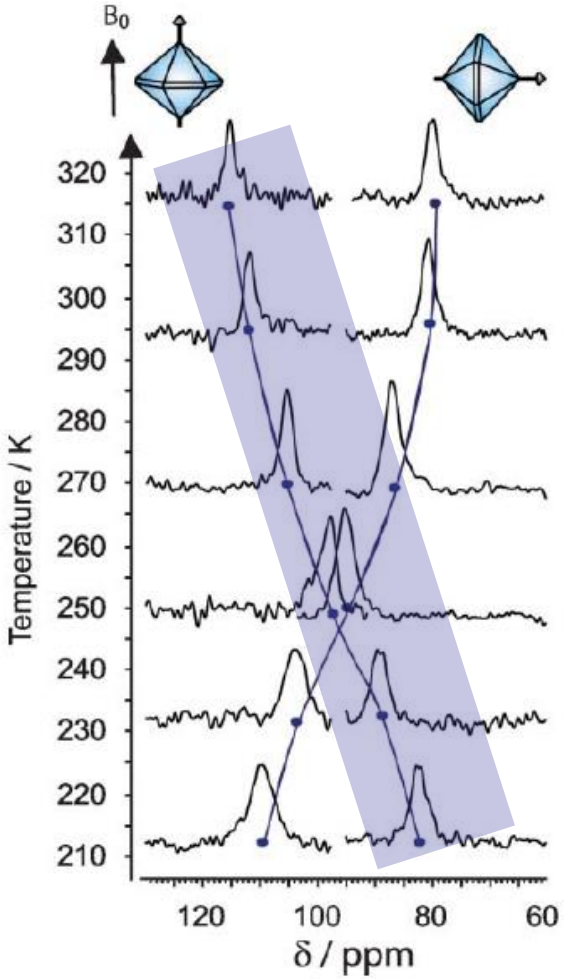
δ decreases with increasing T

Observed in TPP:

$\delta_{\parallel}$ **INCREASES with increasing T**

OPPOSITE and so large!

We have already established that this is only a Xe-wall effect.



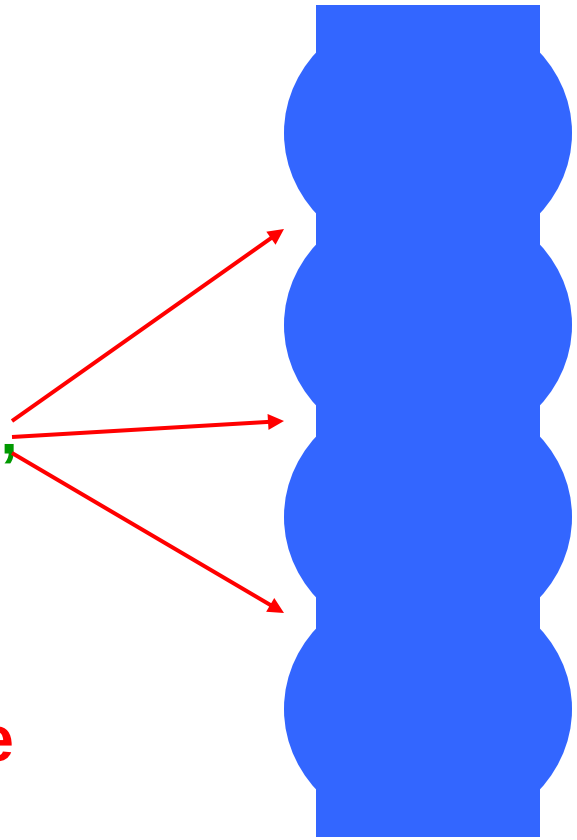
A. Comotti, S. Bracco,
L. Ferretti, M. Mauri,
R. Simonutti and P. Sozzani*
Chem. Commun. 2007, 350-353.

$\delta_{||}$ INCREASING with increasing T

means that at higher T the Xe spends more time closer to the wall atoms (which correspond to larger Xe chemical shifts)

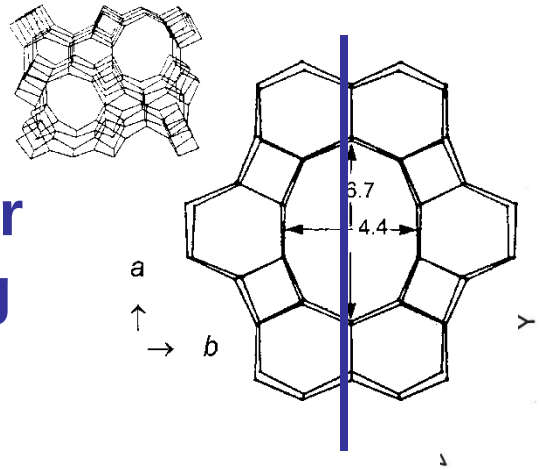
(a) Shape of the channel can provide an explanation.

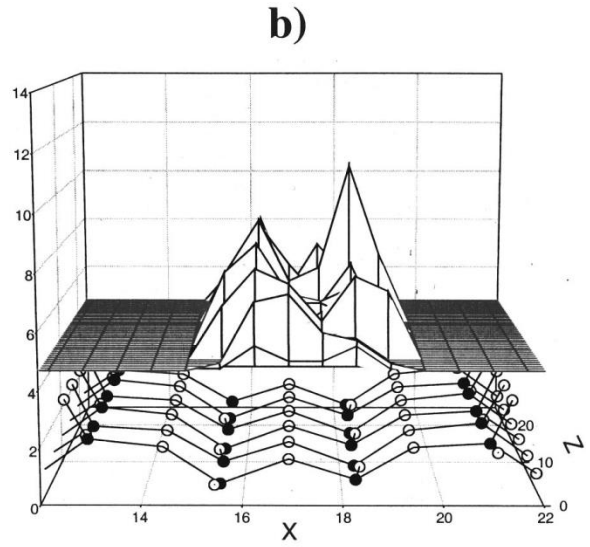
Higher potential energy regions, which Xe crosses frequently at higher temperatures, usually correspond to higher chemical shifts, because Xe is found here to have a higher shielding response at close distances



Example of Xe distribution within a channel

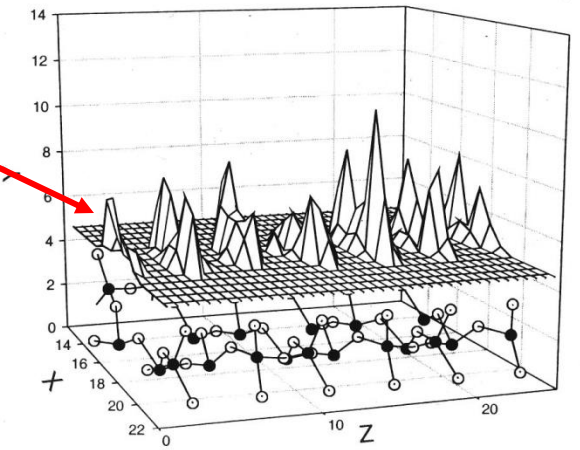
Probability distribution of Xe in ALPO4-11 *





The Xe has a higher probability of being found in the "sweet spots" with low potential energy.

As temperature increases Xe <u>can</u> also populate the regions with less favorable potential energy values.



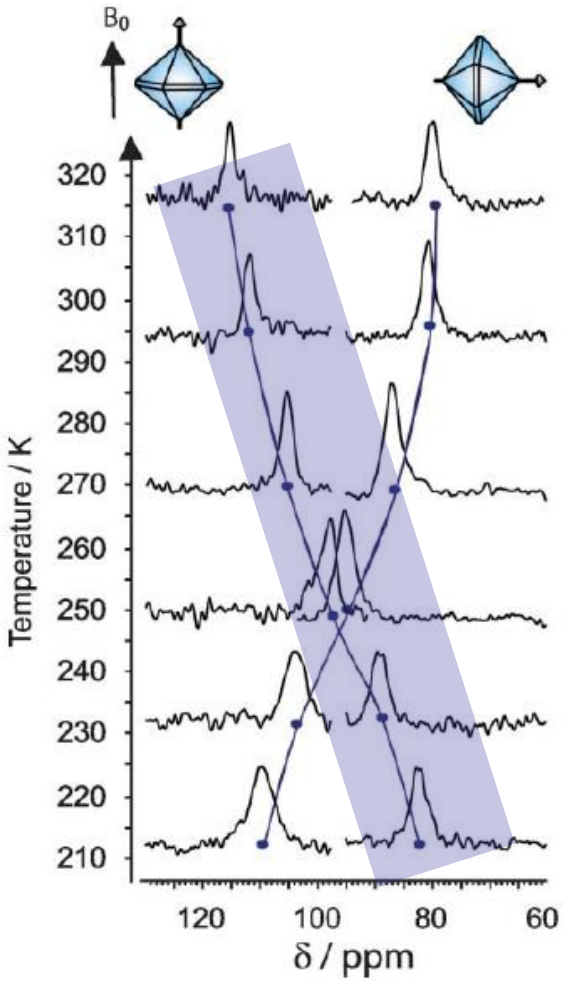
0.26% occupancy

*C. J. Jameson, J. Chem. Phys. 2002, <u>116</u>, 8912-8929.

By either argument (a) or (b),

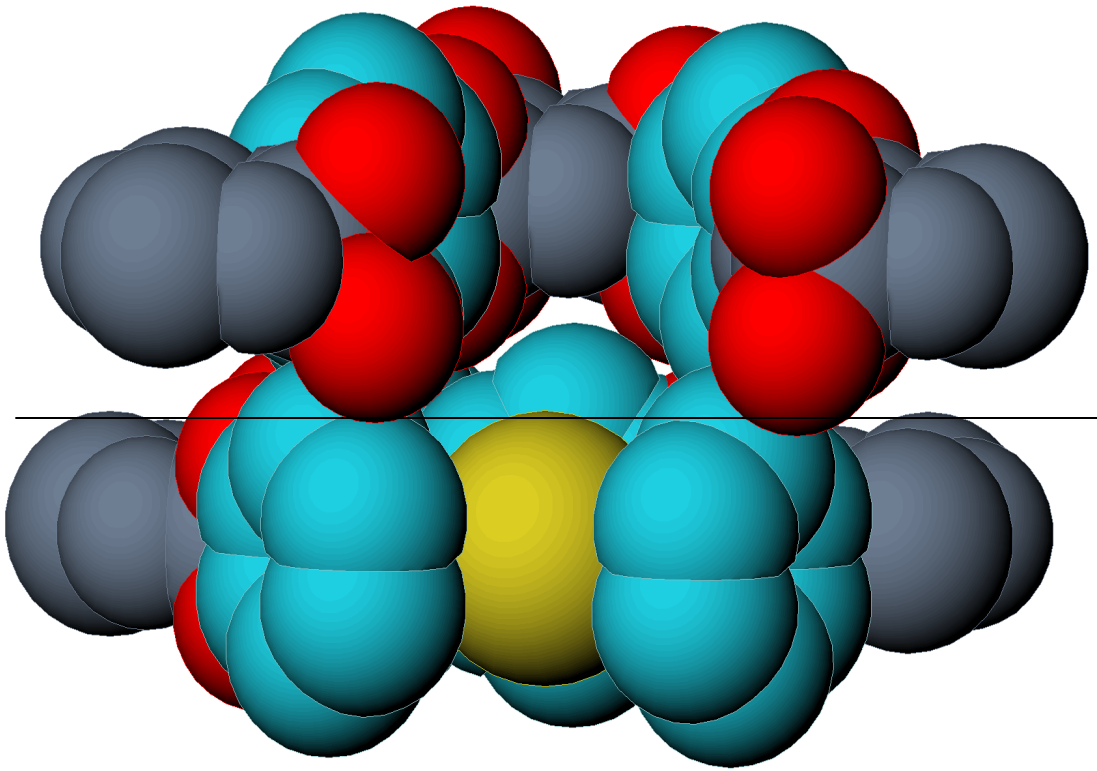
$\delta_{\|}$ INCREASES with increasing T,

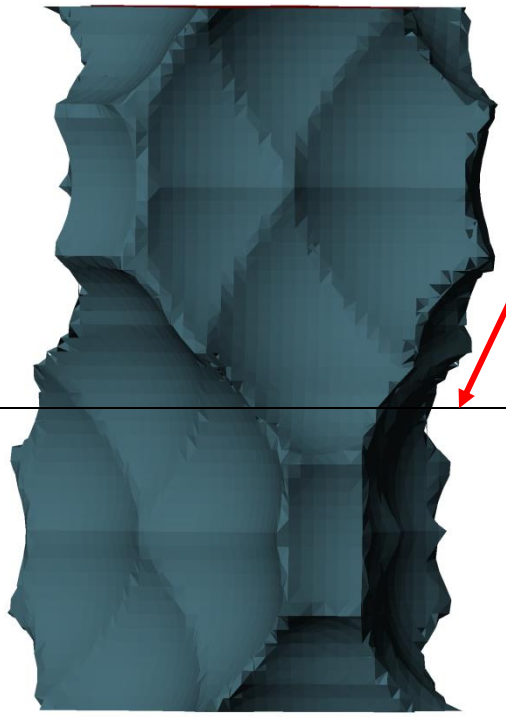
as observed in TPP single crystal data.



A.Comotti, S. Bracco, L. Ferretti, M. Mauri, R. Simonutti, P. Sozzani *Chem. Commun.* 2007, 350-353.

(a) Shape of the channel can provide an explanation in the case of Xe in TPP???



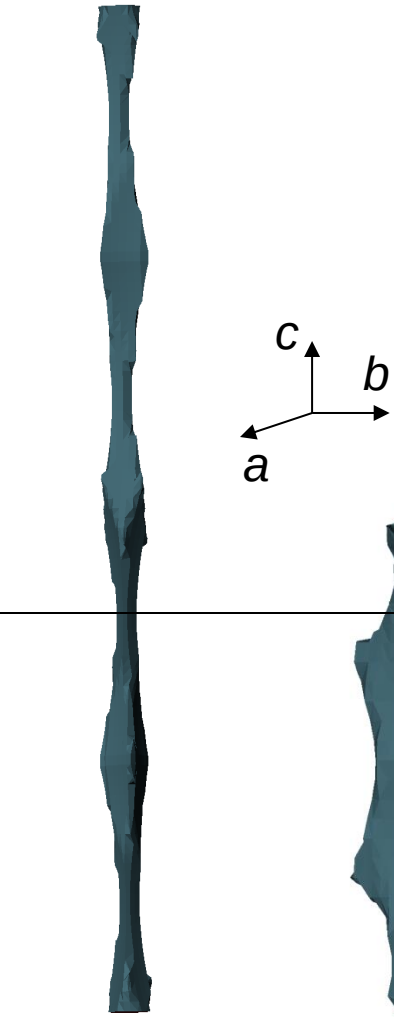


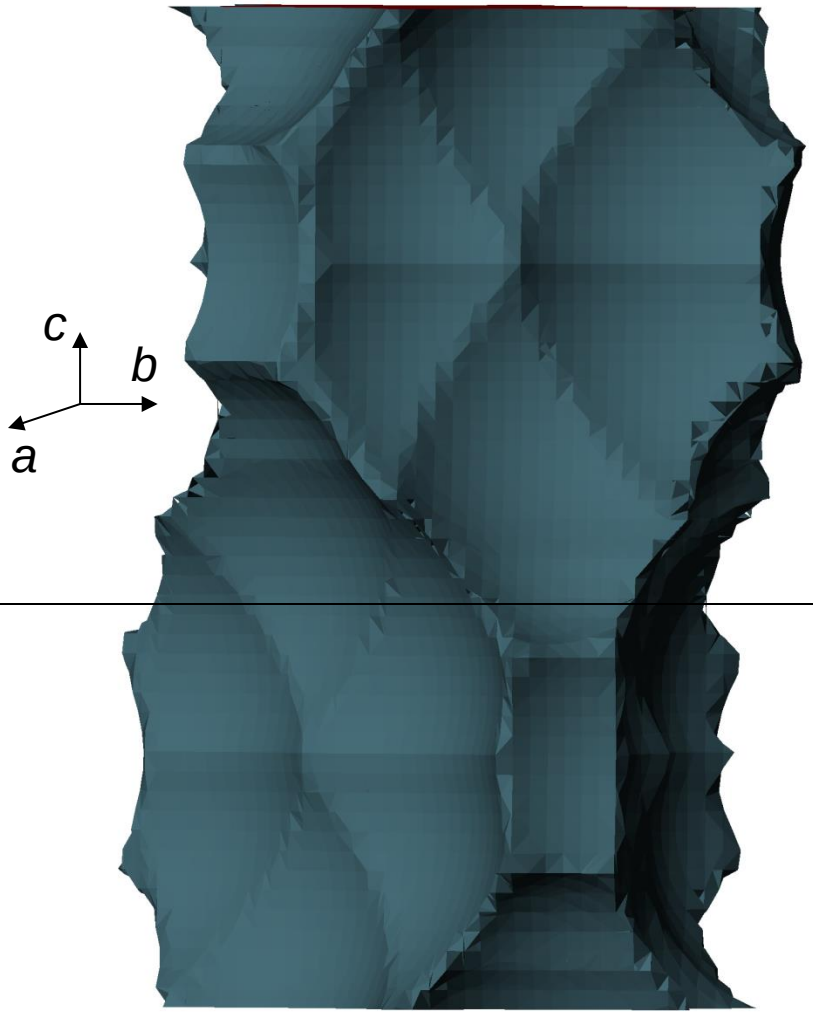
series of channel figures by Angiolina Comotti, Jan 2007

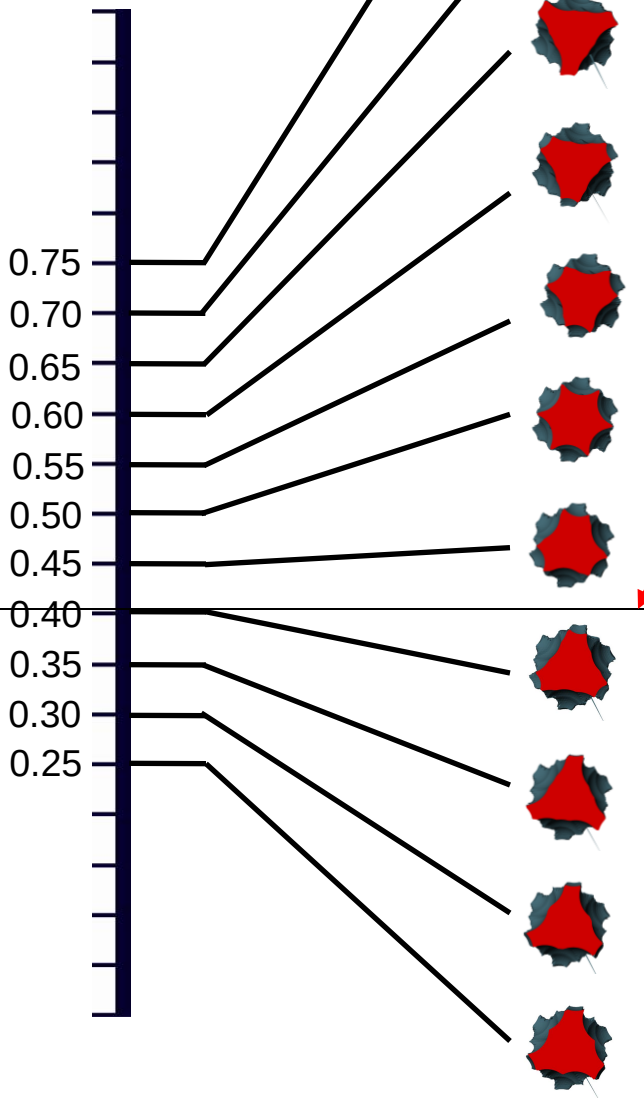
series of channel figures by Angiolina Comotti, Jan 2007

(van der Waals radii (Å): C 1.7; N 1.55; O 1.52; P 1.8; H 1.2)

c axis =10.160 Å



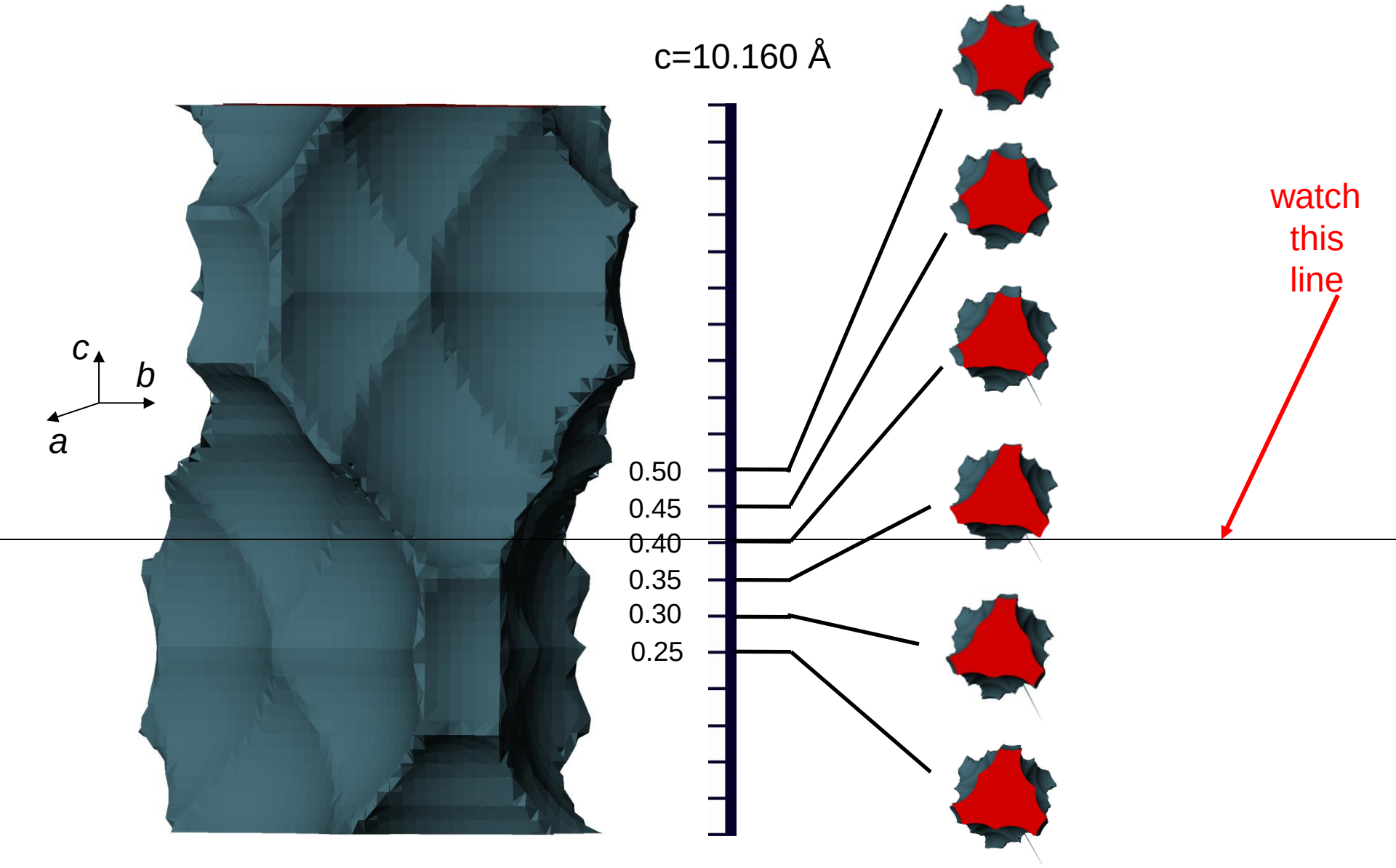


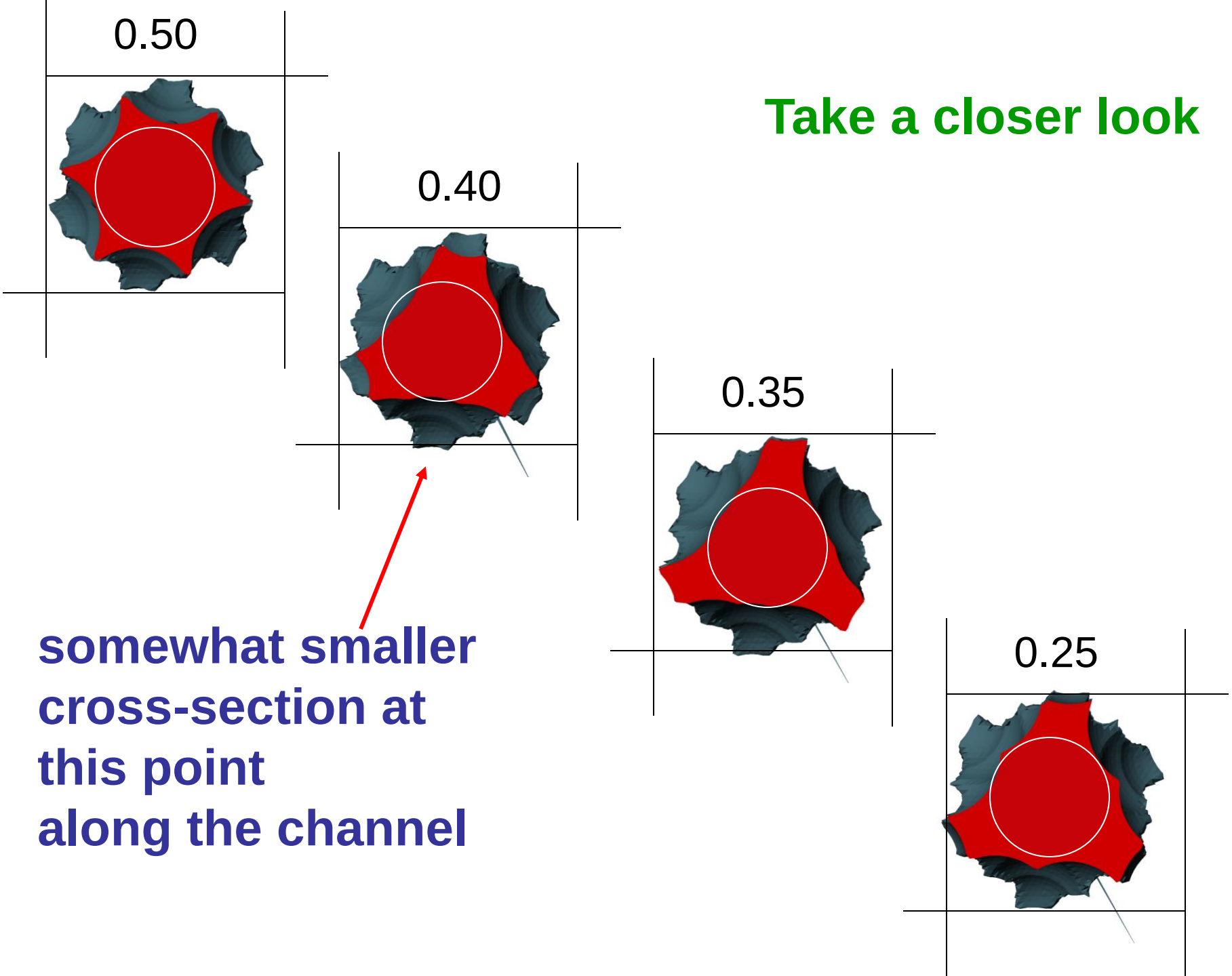


Grid=0.1
radius=2.2 Å

Grid=0.5
radius=0.2 Å

series of channel figures by Angiolina Comotti, Jan 2007



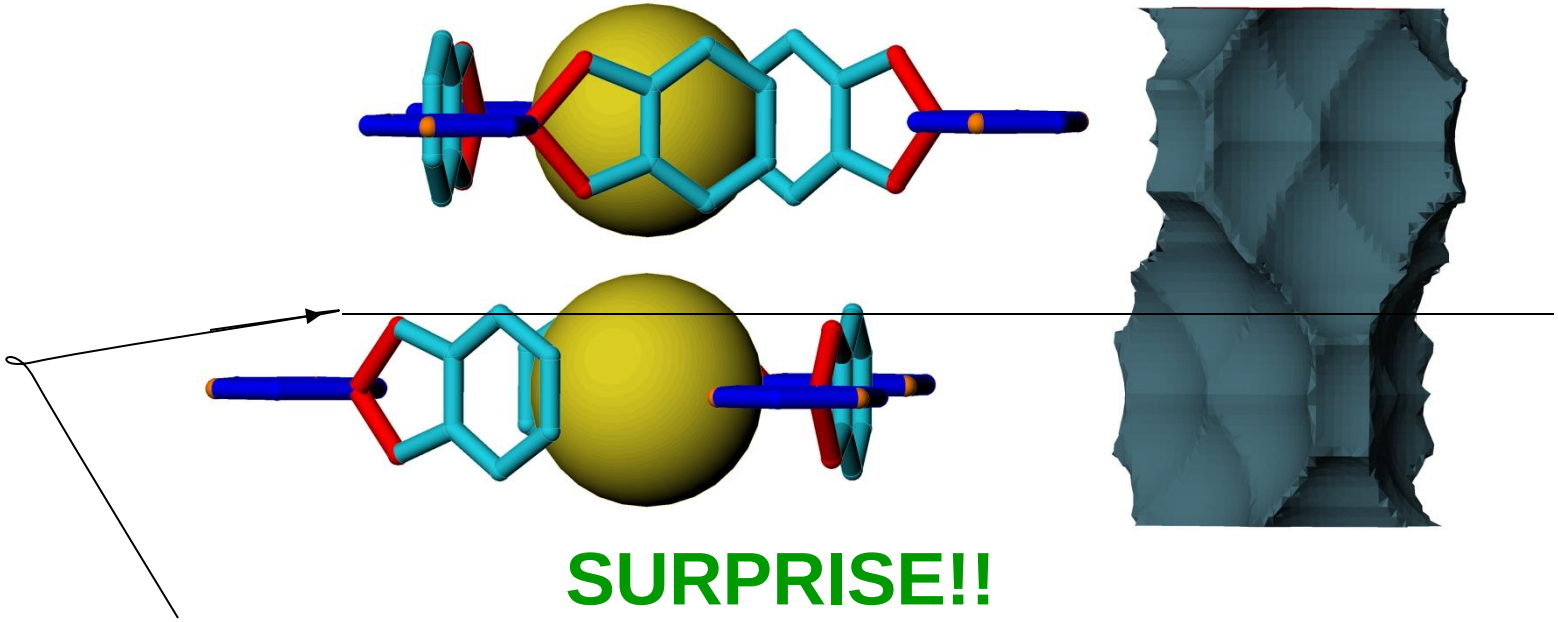


Take a closer look

somewhat smaller cross-section at this point along the channel

(a) Shape of the channel can provide an explanation in the case of Xe in TPP? YES!

series of channel figures by Angiolina Comotti, Jan 2007

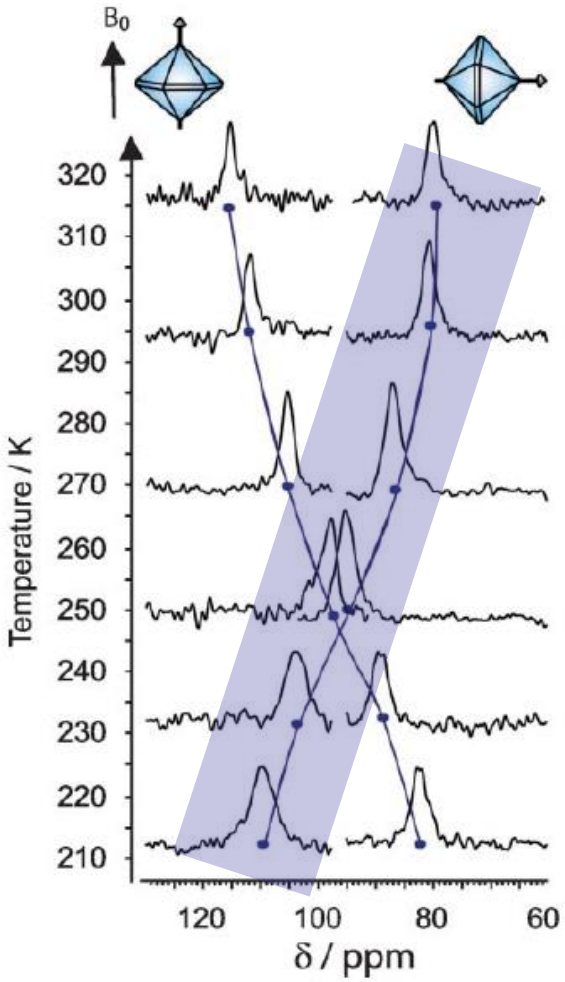


SURPRISE!!

This level, where the cross-section of the channel appears smaller, is also where the ab initio Xe deshielding was large, approximately where the oxygen lone pairs are located!!

D.N.Sears and C. J. Jameson, 2001

Temperature dependence of the $\delta_{\perp}$ components for Xe in single crystal TPP

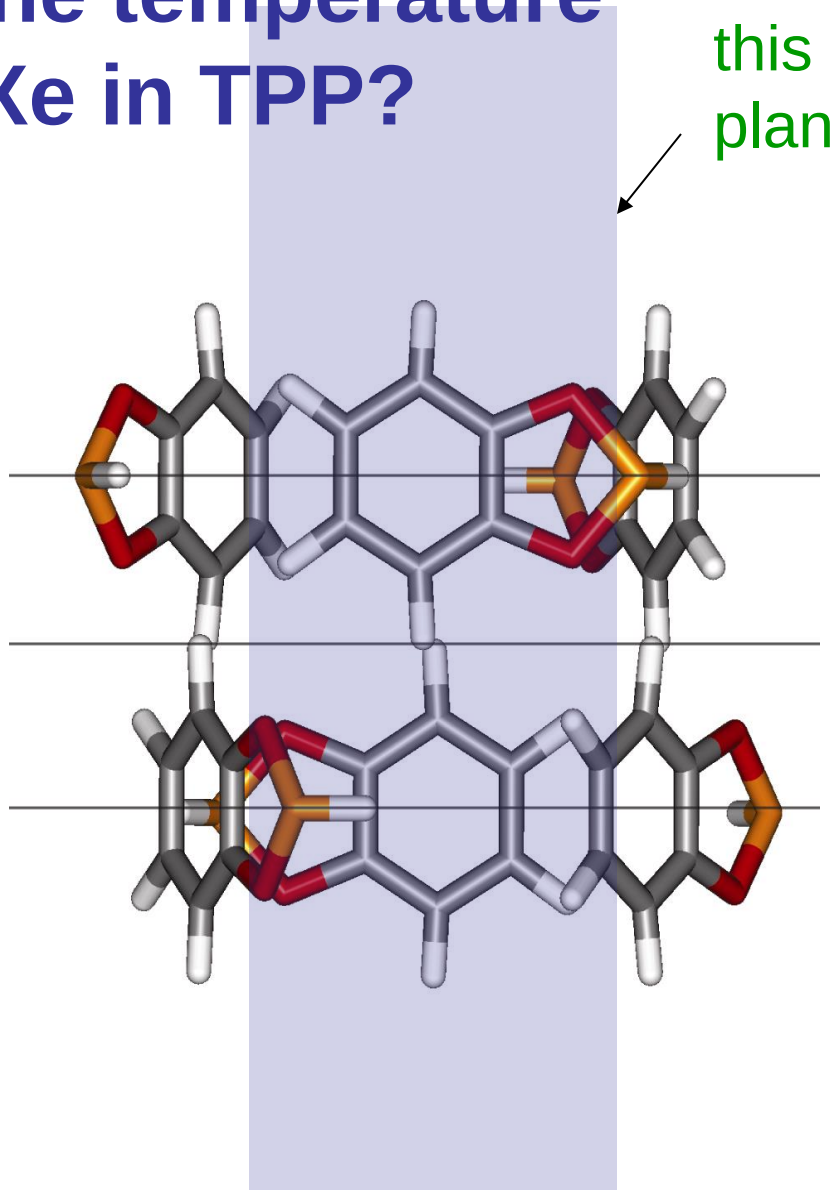


why so?

QUESTION:

What is the origin of the temperature dependence of $\delta_{\perp}$ of Xe in TPP?

this plane

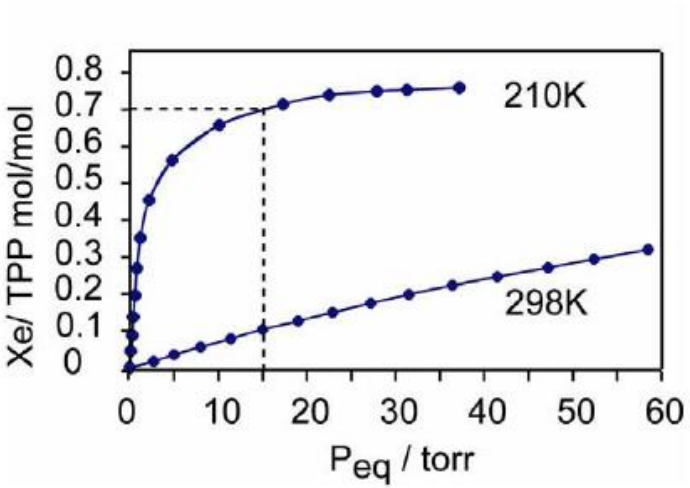


In general,
the electron density
in the plane
parallel to the axis
of the channel

is responsible for $\delta_{\perp}$

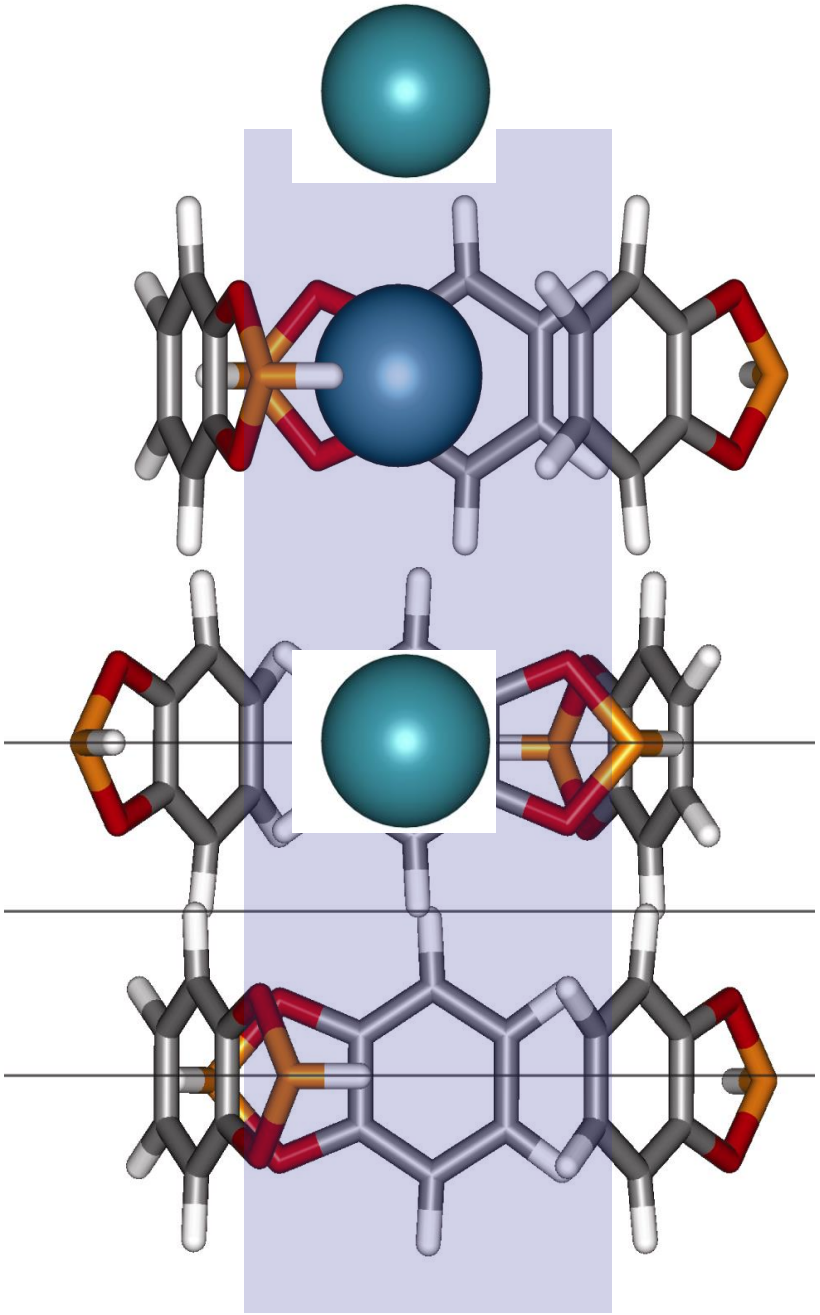
As is known from adsorption isotherms, the Xe occupancy increases with decreasing temperature in general,

and for TPP as well:



The increase in Xe-Xe contributions with increasing occupancy leads to larger average $\delta_{\perp}$ of Xe. *

***Jameson and de Dios, J. Chem. Phys. 2002, 116, 3805-3821.



HOW?

When the occupancy is higher, a particular Xe atom will more frequently have Xe neighbors above and below it,

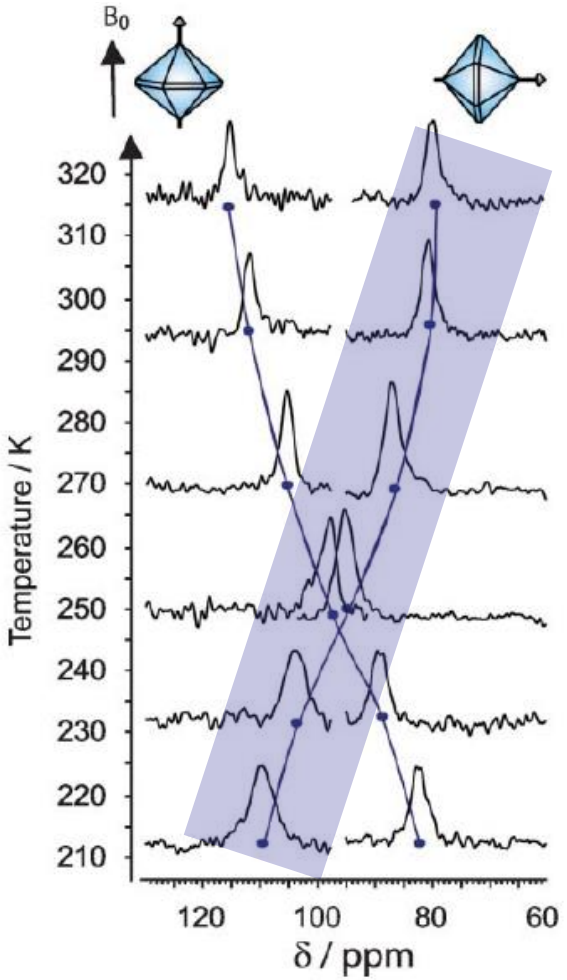
increasing electron density in the blue plane, thereby leading to a larger $\delta_\perp$ for Xe.

There is relatively no change in the Xe wall contributions.

The increase in Xe-Xe contributions to $\delta_\perp$ with increasing occupancy as T decreases, leads to larger average $\delta_\perp$ of Xe.

The increase in Xe-Xe contributions to $\delta_{\perp}$ with increasing occupancy as T decreases, leads to larger average $\delta_{\perp}$ of Xe.

This is indeed what is observed experimentally.



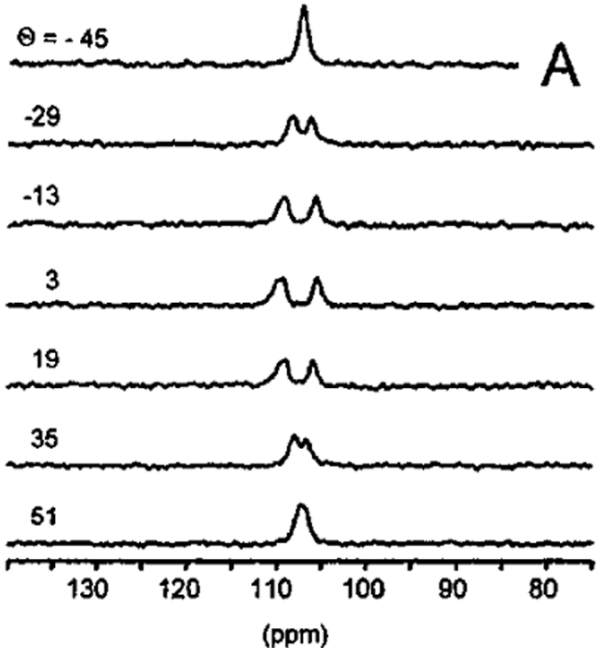
IN SUMMARY,

the opposite temperature behaviors of the $\delta_{\perp}$ and $\delta_{||}$ of Xe in TPP are completely consistent with all other known facts about adsorption and Xe chemical shifts in "narrow-bore" pipes.

In addition, for TPP specifically, there is a slightly smaller cross-section at the height at which the calculated ab initio deshielding was found to be unusually large (Sears and Jameson 2001, unpublished**).**

This means that Monte Carlo averaging, if carried out, will reproduce the observed directions of shift with temperature for both $\delta_{\perp}$ and $\delta_{||}$.

Xe in a single crystal



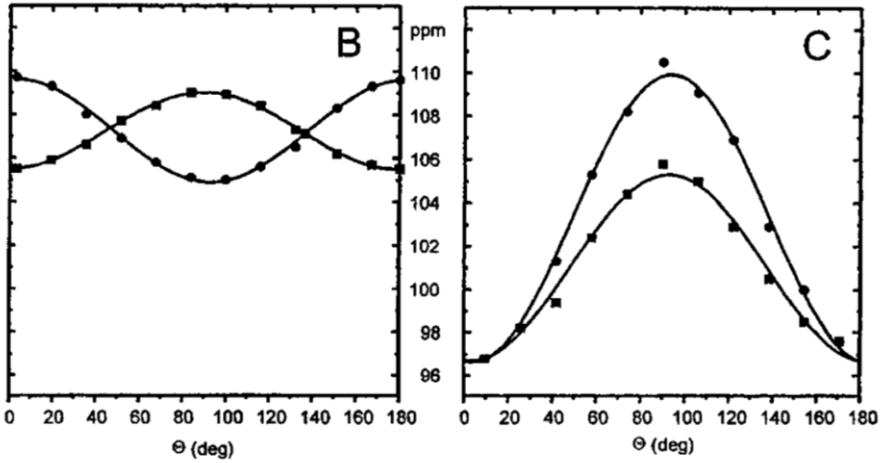
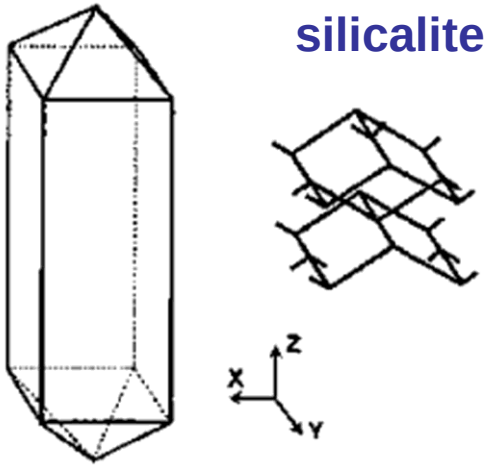
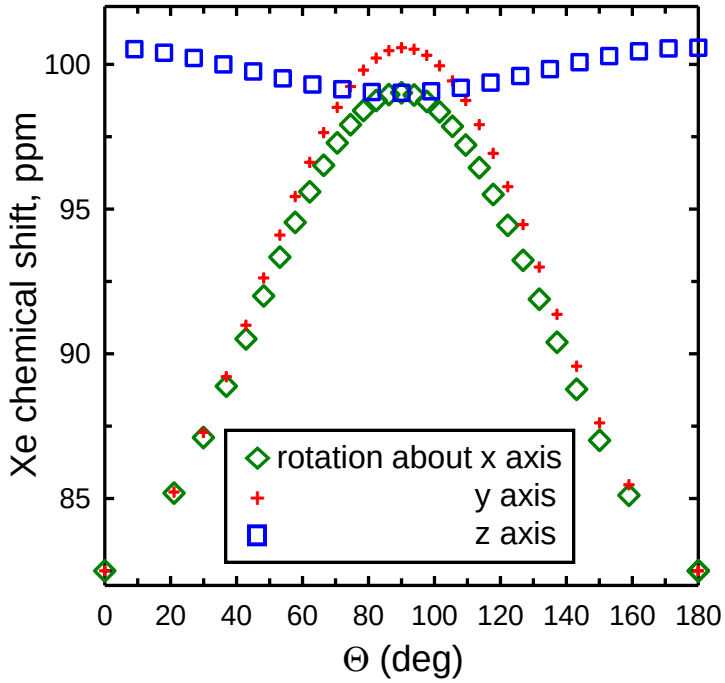


Figure 2. HP ^{129}Xe NMR results for single crystals of silicalite at 295 K: (A) spectra ($\pi/2$ pulses, 512 scans each, 5 s delay) and (B) chemical shifts versus crystal orientation, Θ, about the *z* axis, perpendicular to the magnetic field. (C) Chemical shifts versus Θ about the second orthogonal orientation. The third orthogonal orientation gave an identical pattern.

silicalite





0.285Xe/UC
at 300 K

EXPERIMENTS :

V. V. Terskikh, I. L. Moudrakovski, H. Du, C. I. Ratcliffe, and J. A. Ripmeester
J. Am. Chem. Soc. **2001**, 123, 10399-10400

GCMC SIMULATIONS JACS 2004

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 or MD 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.

Information that is encoded in observed Xe spectra:

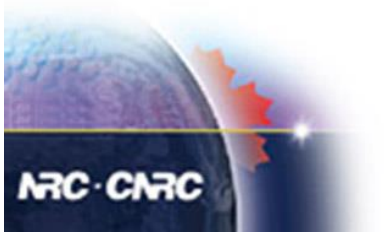
- **structural as well as dynamic information**
- **the diameter of the channel**
- **the aspect ratio of the cross section of the channel**
- **the architecture of the channel**
- **average size of the cage**
- **average symmetry of the cage**
- **number of molecules per cage**
- **electronic structure of atoms constituting the cavity walls**
- **rate of cage-to-cage jumps within the crystal**
- **coverage on a single crystal surface**
- **more…….**

Acknowledgments

Funding for CJJ's lab

Collaborators

Igor Moudrakovski
Dmitriy V. Soldatov
John A. Ripmeester
Chris Ratcliffe



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