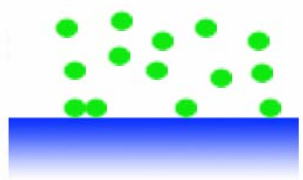
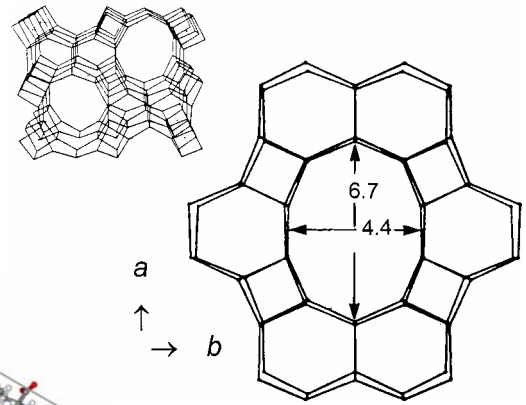
XeMAT 2009 June 7-11 Kuusamo, Finland

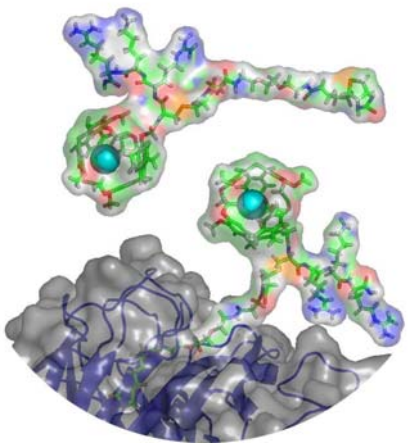
Xe chemical shifts: What do they tell us about the physical system?

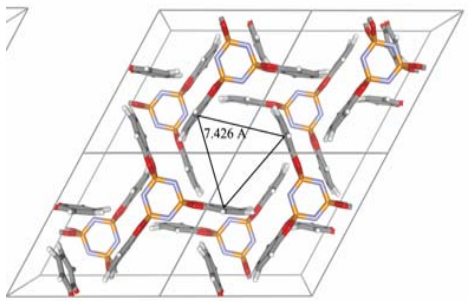


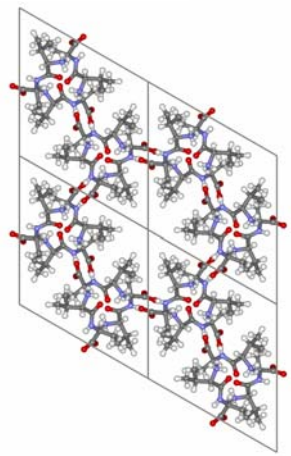
Cynthia J. Jameson

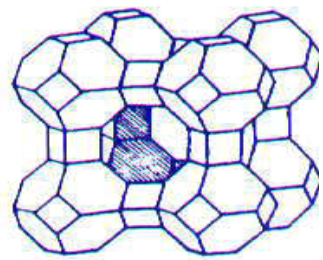
University of Illinois at Chicago







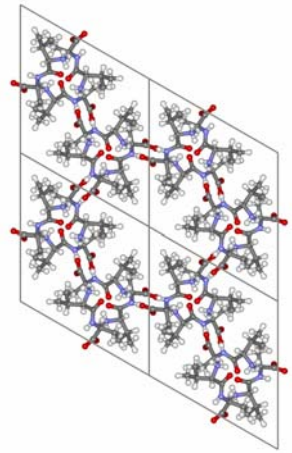


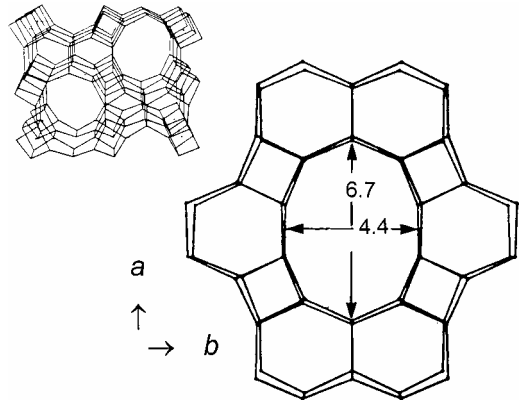


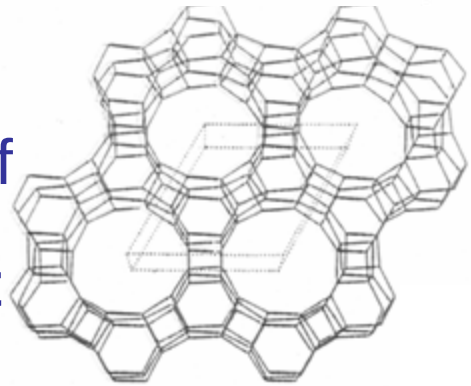
biosensor model courtesy of T. J. Lowery

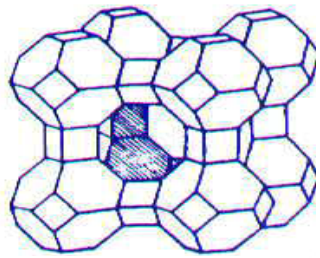
Xe intermolecular chemical shifts

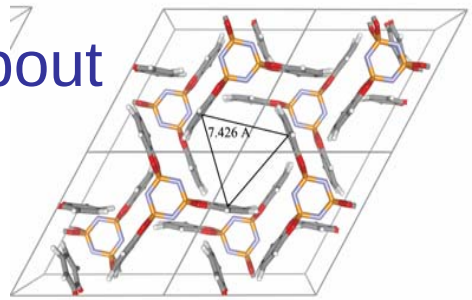
- **exquisitely sensitive** to the environment of the Xe atom
- permits the Xe nucleus to **report attributes of the physical system** in which Xe atom finds itself
- needs **understanding at a fundamental level** so as to elicit the desired detailed information about the physical system

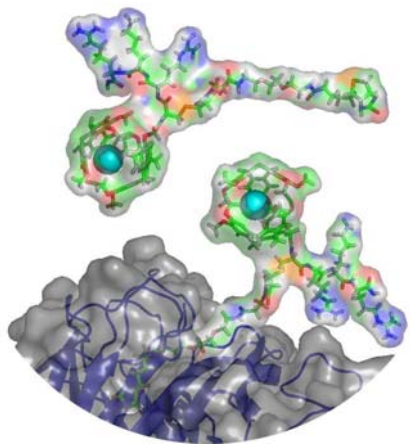


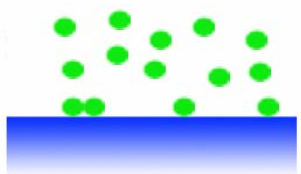












biosensor model courtesy of T. J. Lowery

The general approach:

- Use Xe and small molecules to explore **internal surfaces** of nanometer dimensions in model materials (crystalline).

- Measure average **tensor** properties of Xe, where possible, or the average isotropic property, otherwise.

- We employ a property with a **steep dependence on intermolecular distances**, a local probe

- Combine **quantum mechanical calculations of the property as a function of intermolecular separations and configurations** with **Monte Carlo grand canonical averaging or molecular dynamics simulations** to understand/reproduce what is observed.

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.

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**
-
-

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)

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.

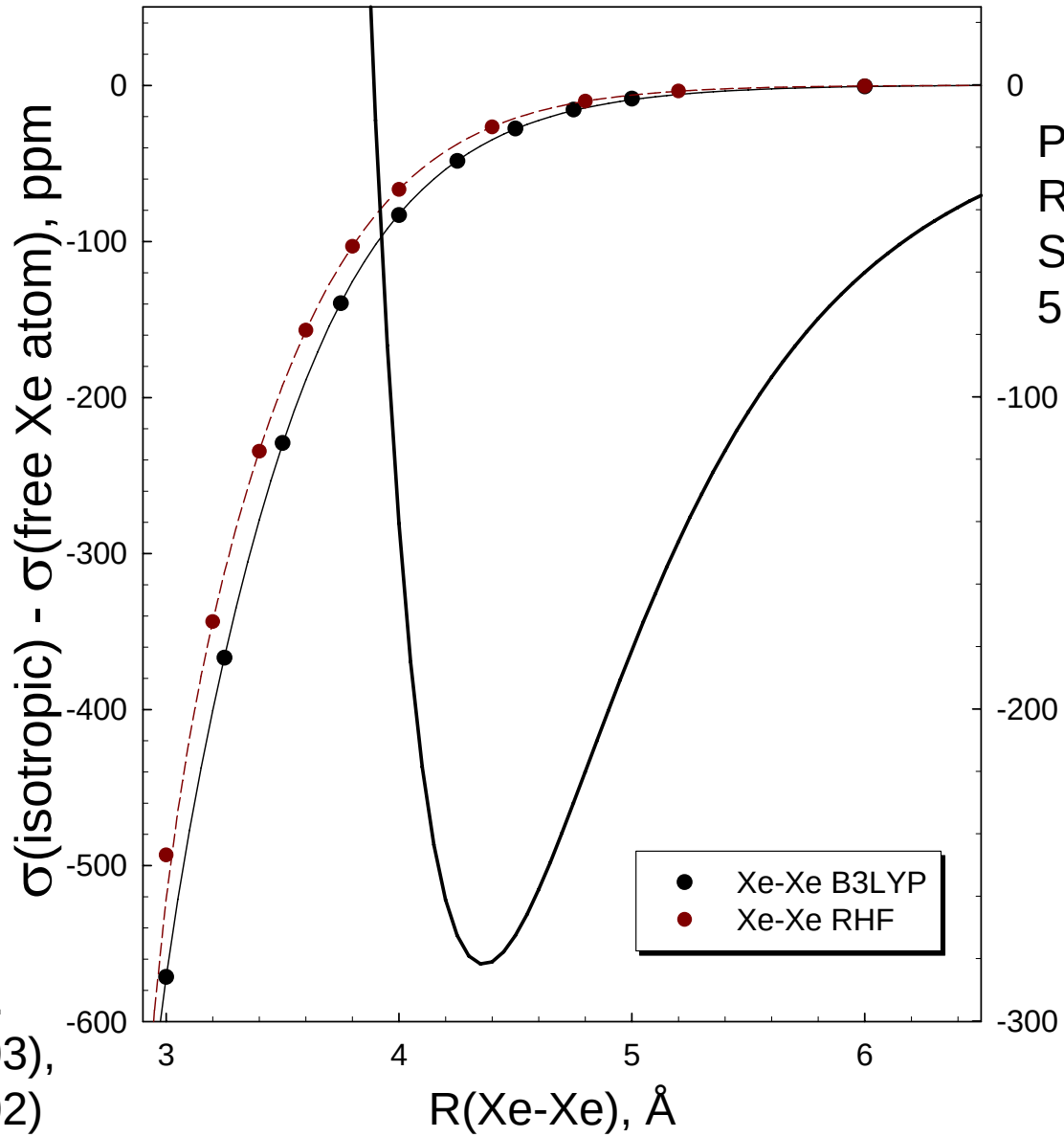
For one neighbor

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

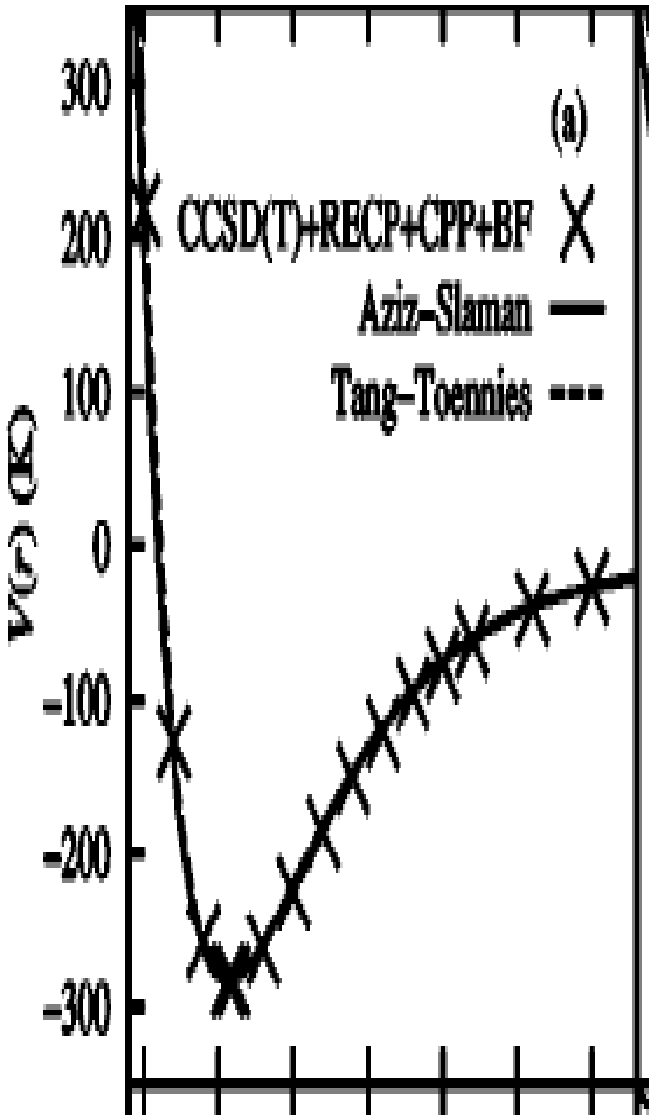
Xe isotropic shielding function σ(R) and potential function V(R) for the Xe-Xe system



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)

X Best theoretical potential energy curve for Xe_2

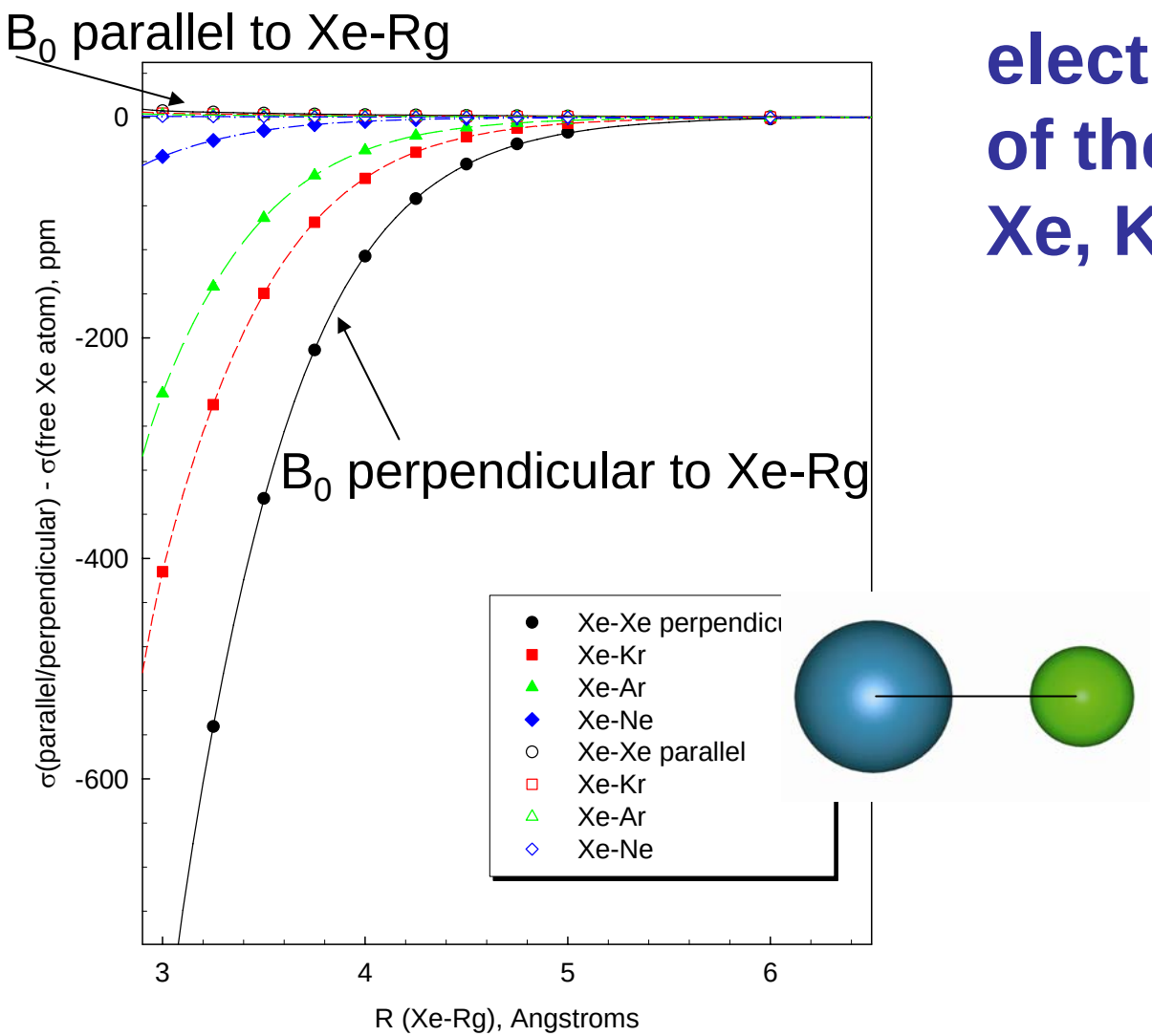


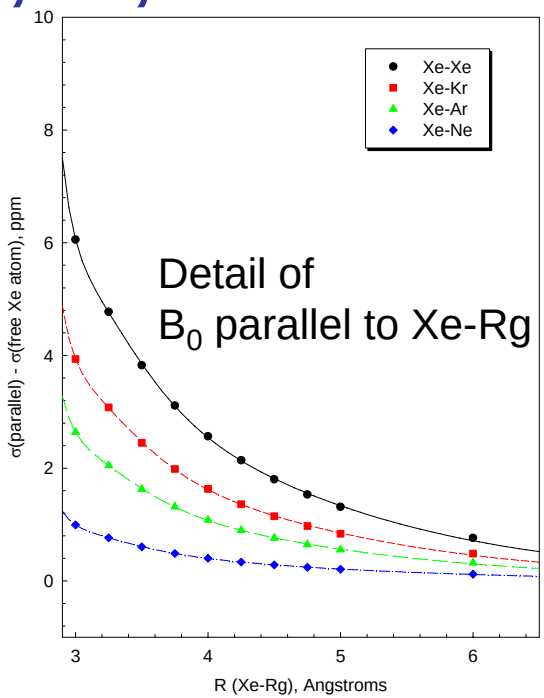
Hanni,Lantto, Nuneberg, Jokisaari, Vaara, J.Chem. Phys. 121, 5908 (2004)

The Xe SHIELDING RESPONSE

changes with magnetic field direction

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





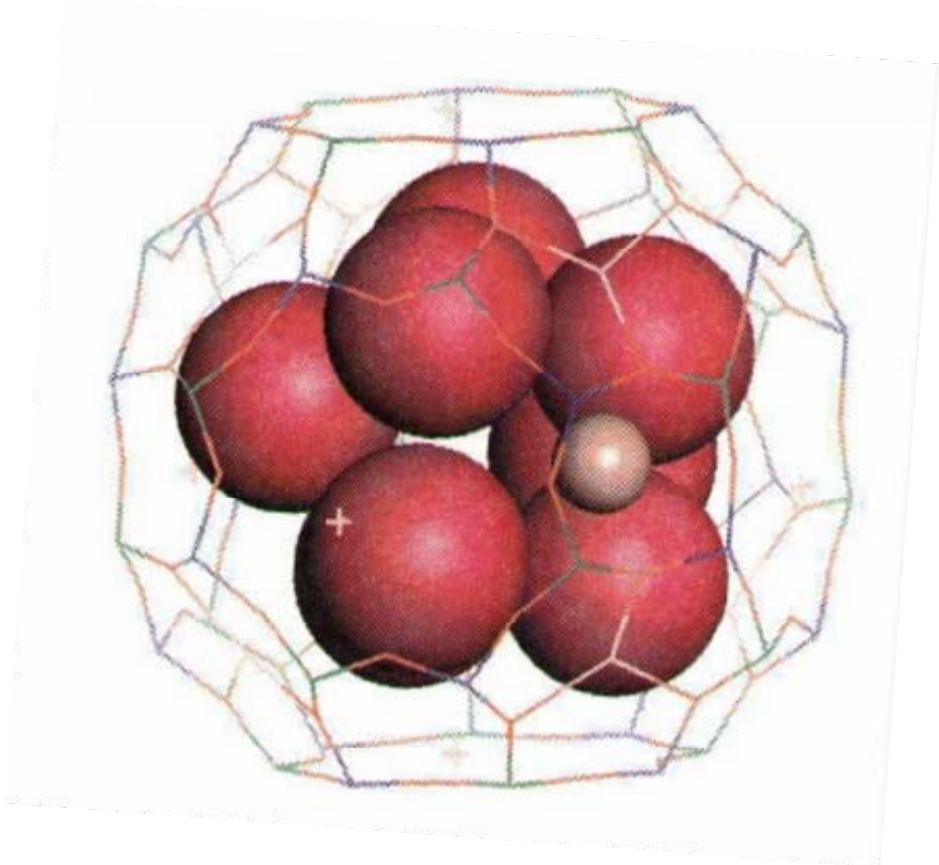
Xe shielding depends on how many neighbor atoms, at what distances

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

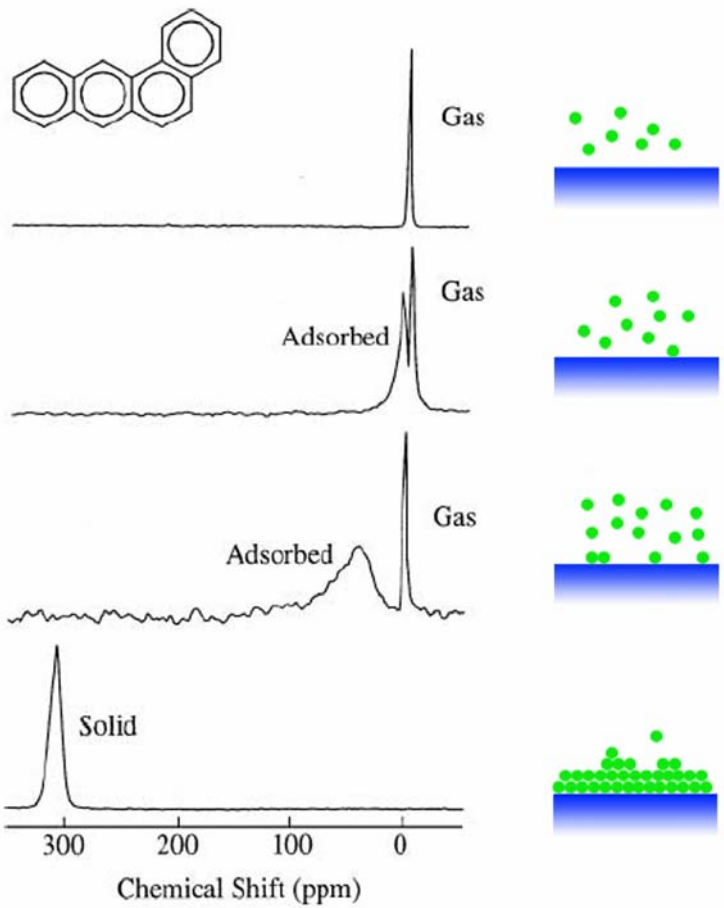
Shielding is a very local molecular property because of the r_N^{-3} part of the operator

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).

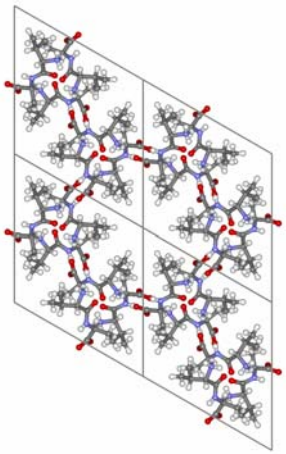
What fraction of the time a particular Xe-neighbor configuration is found

- 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.

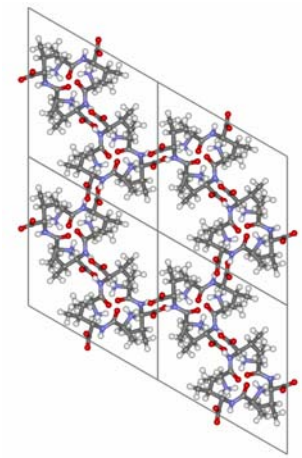
For a given solid material structure (i.e., equilibrium positions of atoms which constitute the solid), the electronic structure of the atoms which are accessible to Xe atoms determine the

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

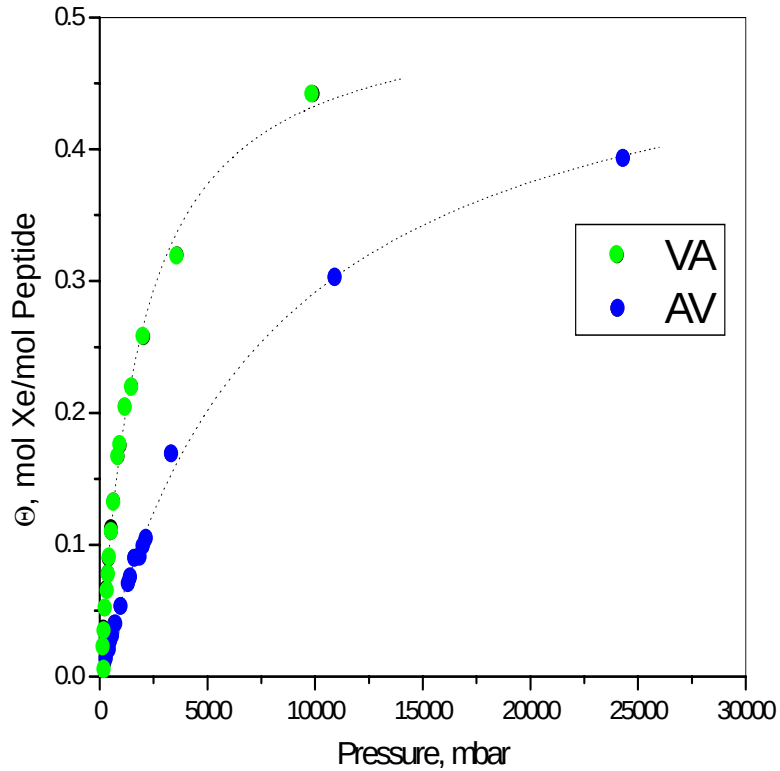
Channel structure & adsorption isotherm



L-Val-L-Ala



L-Ala-L-Val



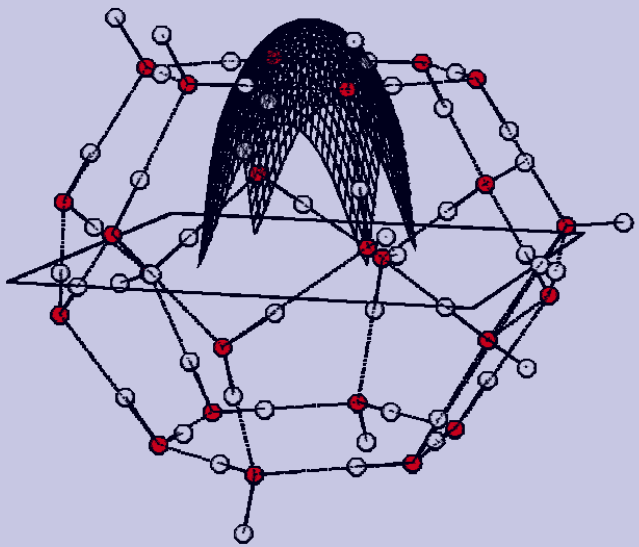
adsorption isotherm can be reproduced by simulations

Thus, we have an interesting intrinsic connection between the **Xe shielding function** for a particular configuration of atoms and the **probability of such a configuration occurring** at a particular temperature.

Intermolecular chemical shifts

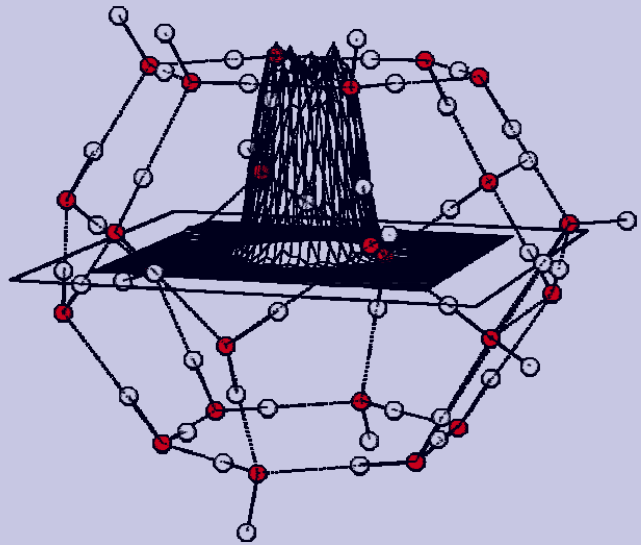
The Xe SHIELDING SURFACE: the shielding as a function of configuration (coordinates) of the system

(a) isotropic shielding surface



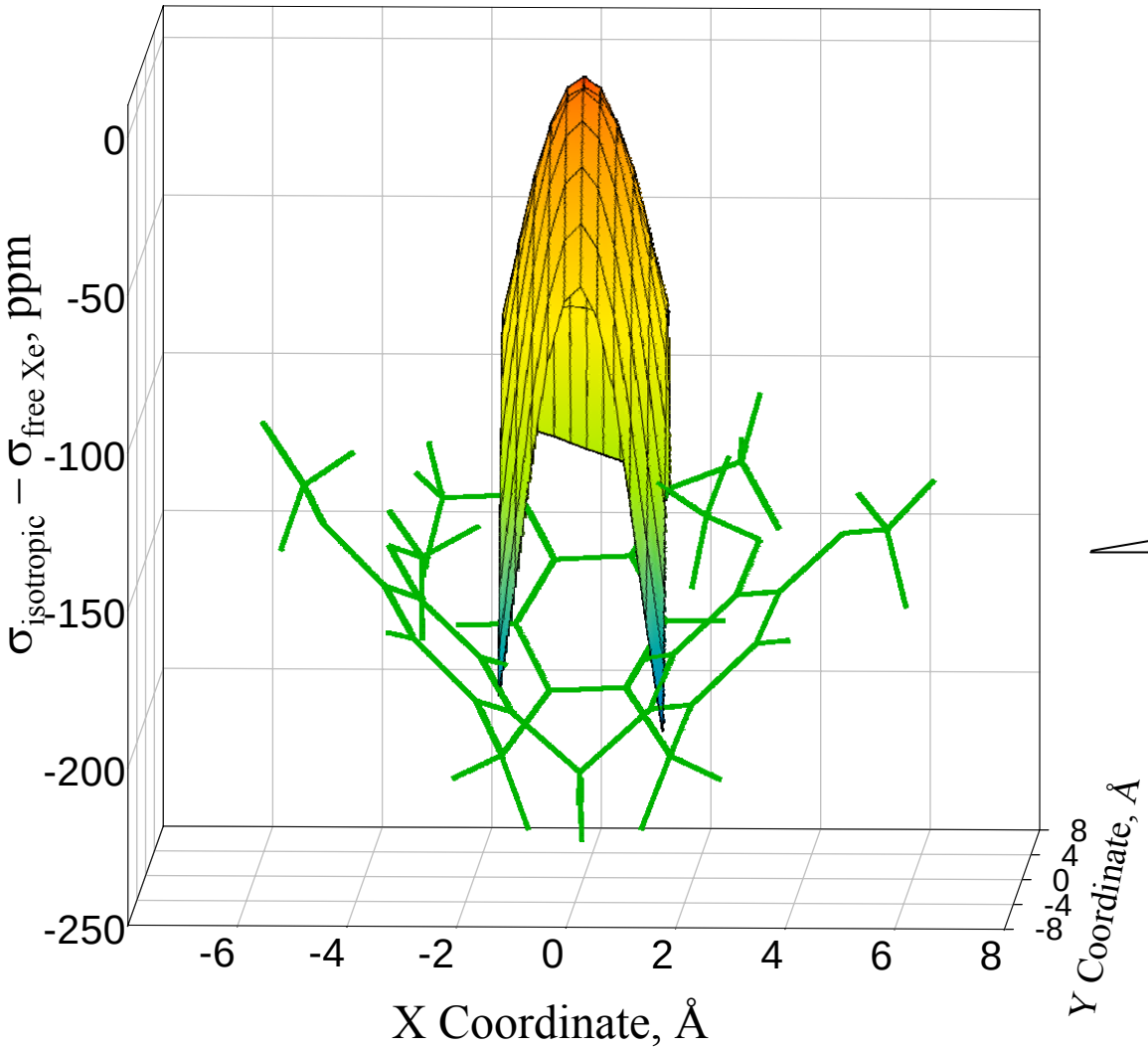
The Xe one-body distribution: the PROBABILITY of finding the system in a given configuration

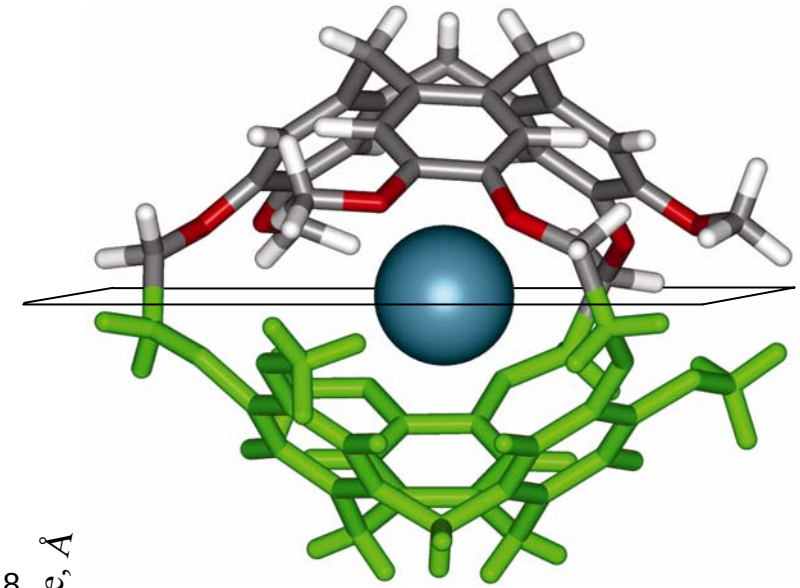
(b) one-body distribution surface



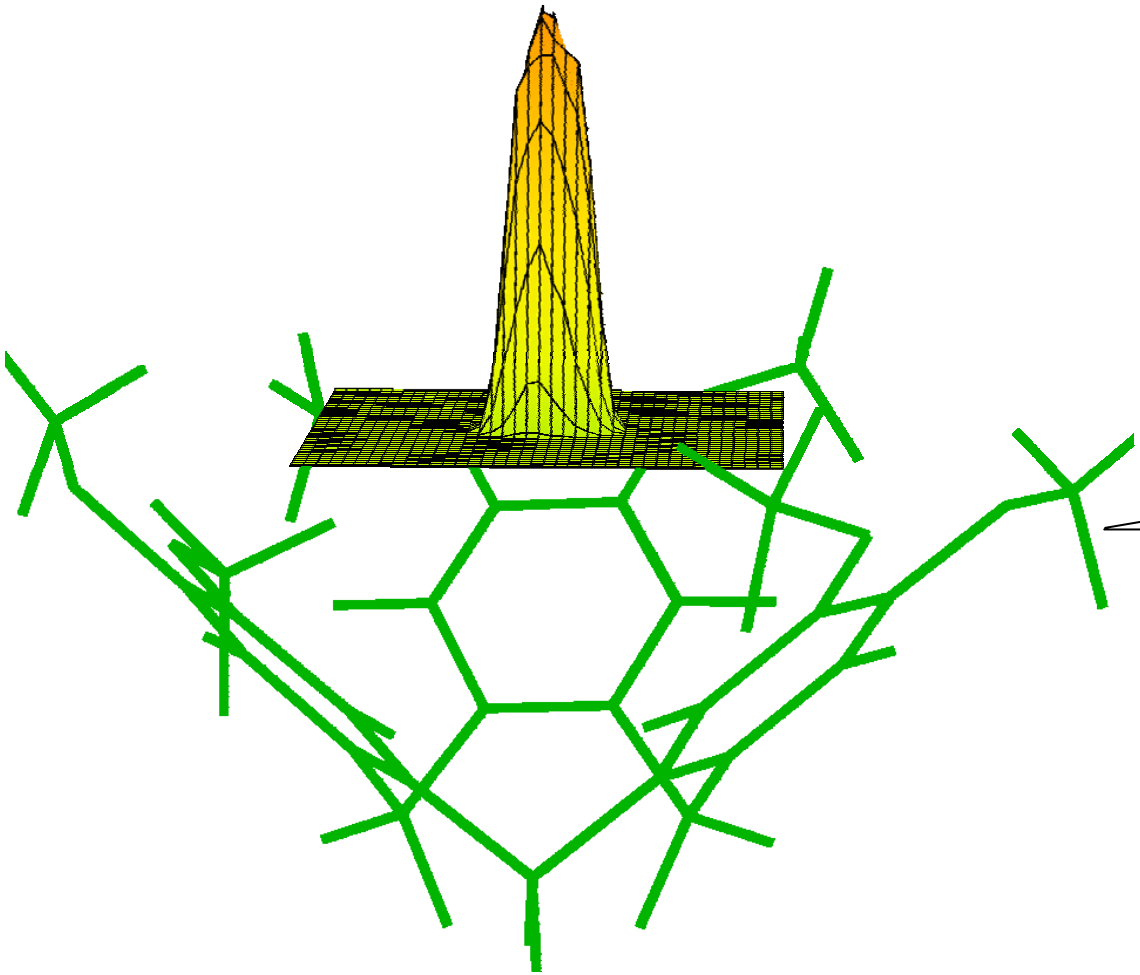
Xe in the $5^{12}6^2$ cage of clathrate hydrate Structure I

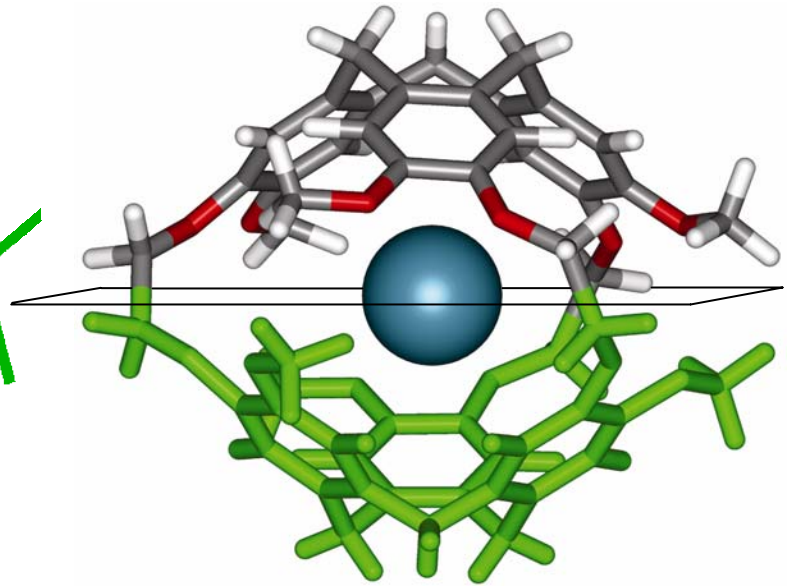
The Xe shielding surface for Xe@cryptoA



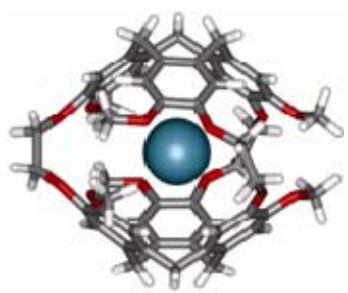


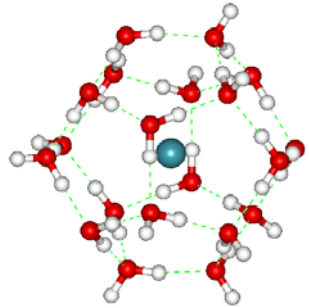
One-body distribution function for Xe@cryptoA
from Monte Carlo simulations





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

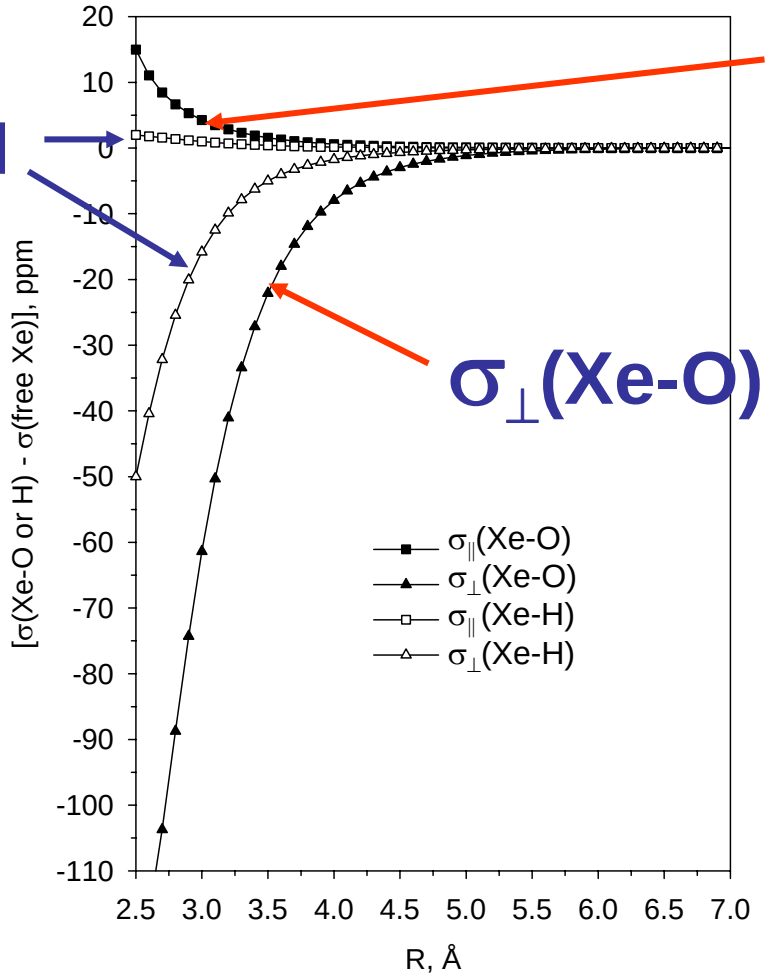
Tensor components in the laboratory frame (frame of the simulation box):

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

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

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

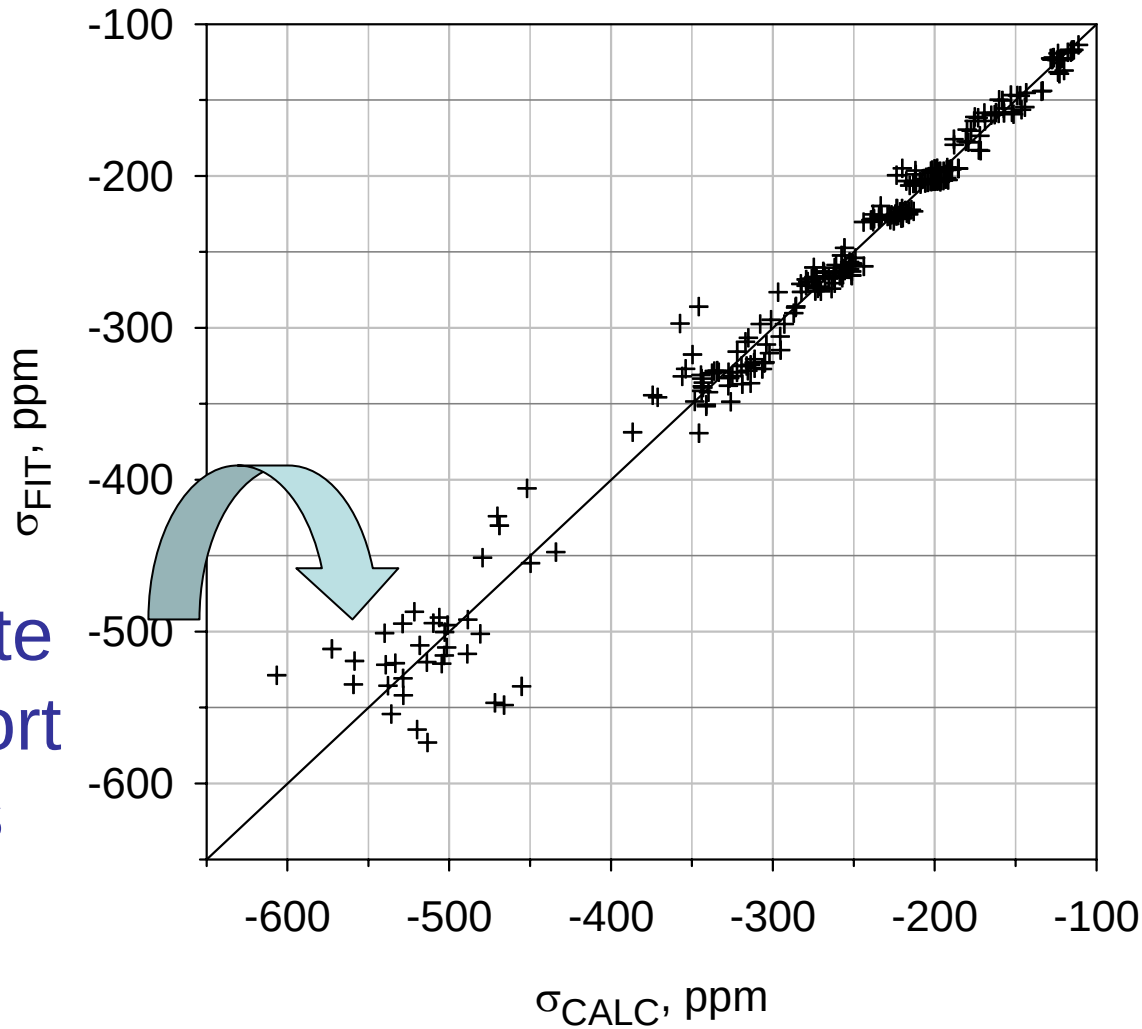
The Xe-O and Xe-H shielding tensors



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

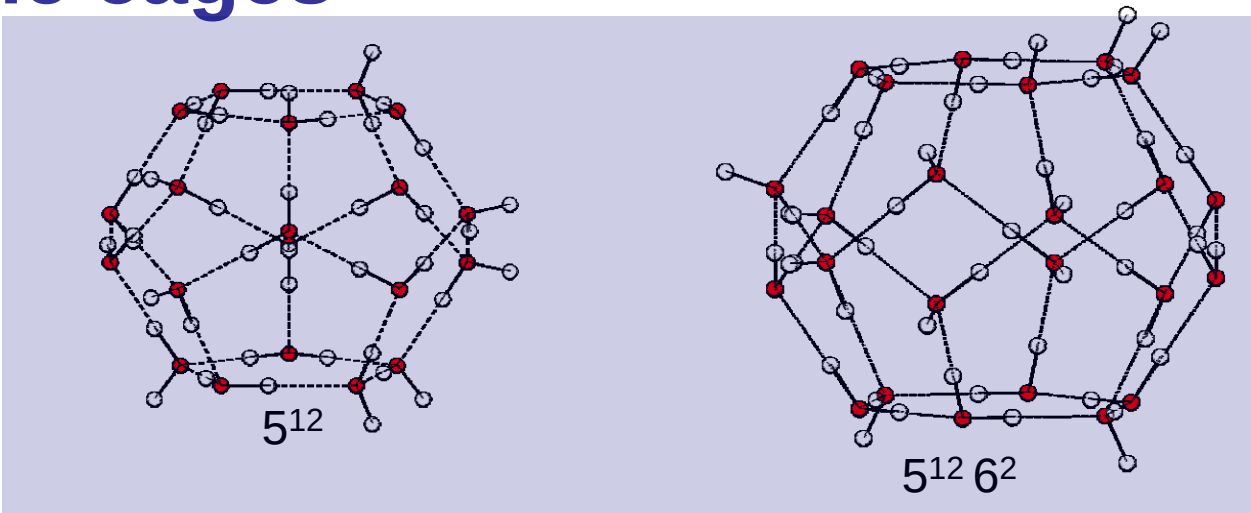


but deviate at the short distances

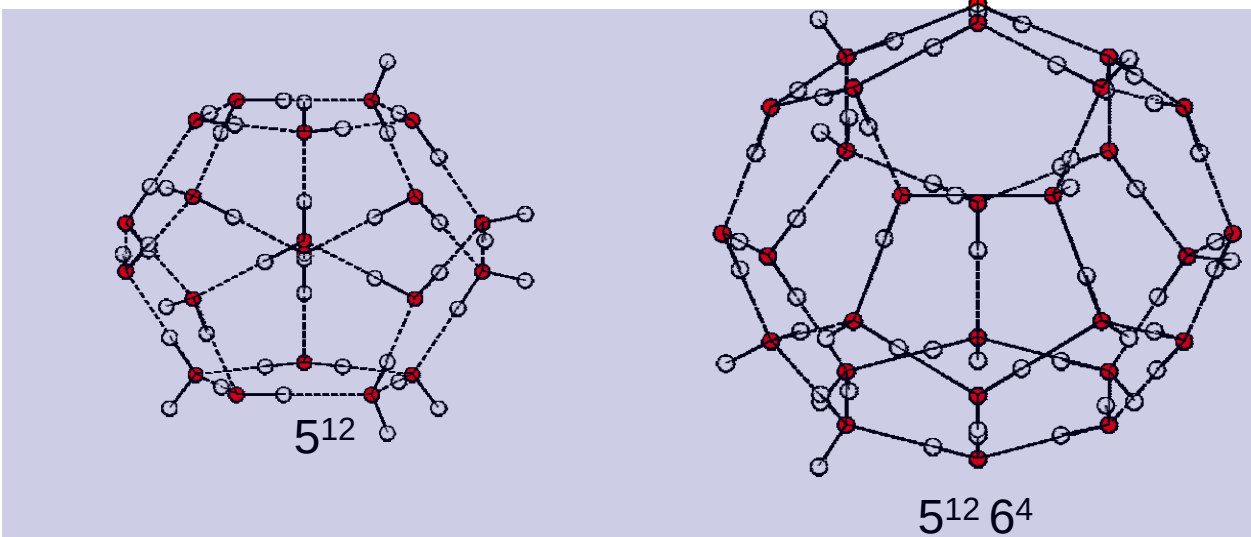
Clathrate hydrates

the cages

Structure I



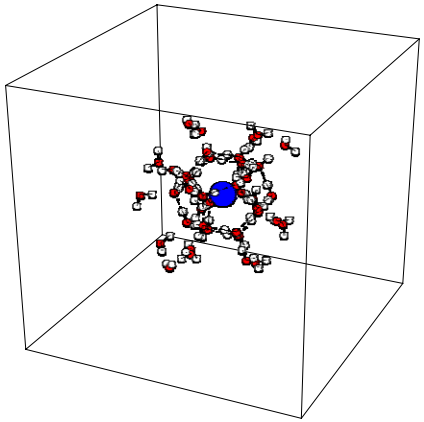
Structure II



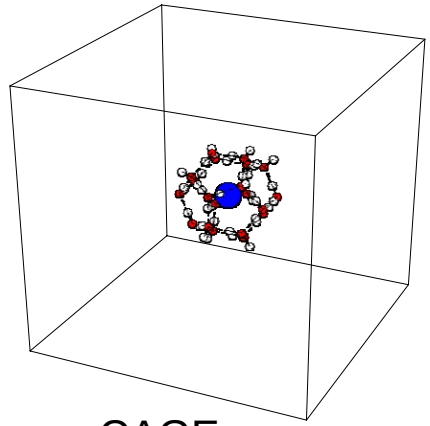
How to model a cage in a hydrogen bonded network?

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

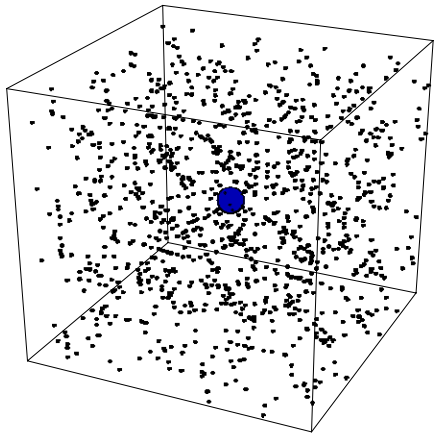
MODELS



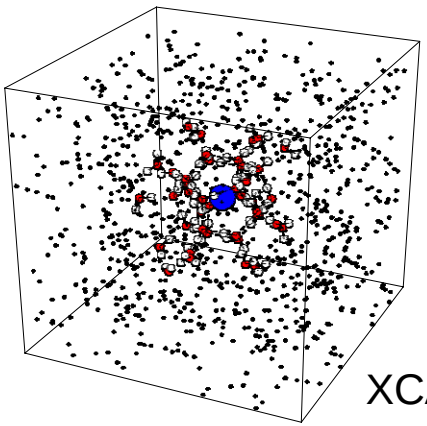
XCAGE



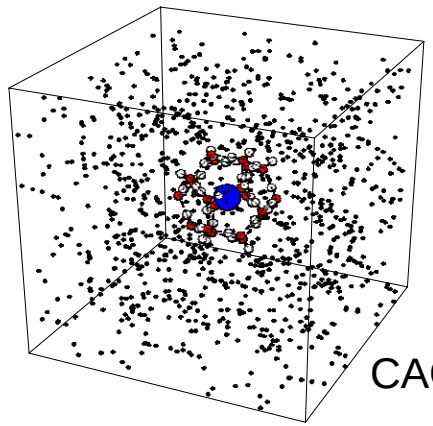
CAGE



PCA

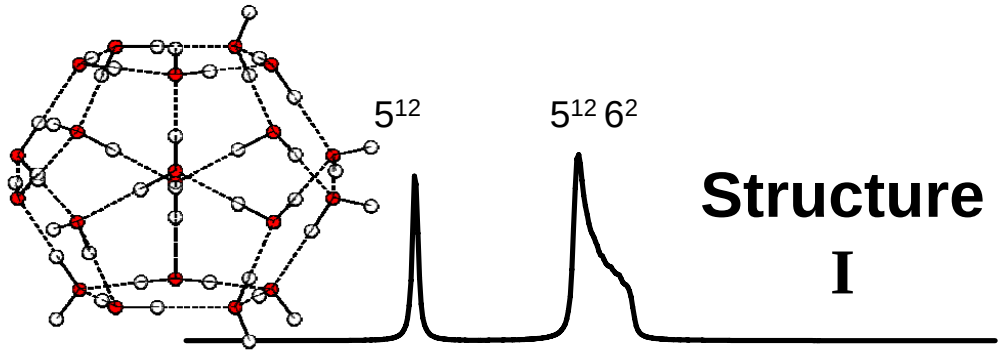


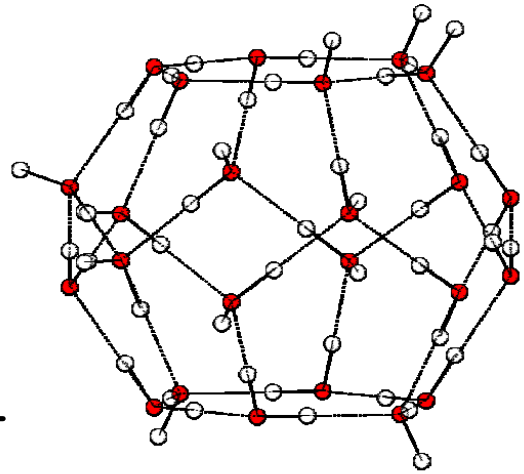
XCAGE/PCA

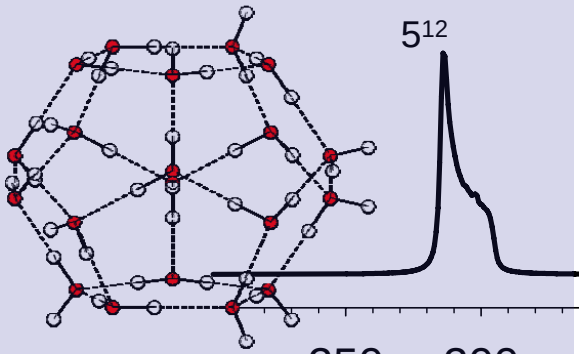


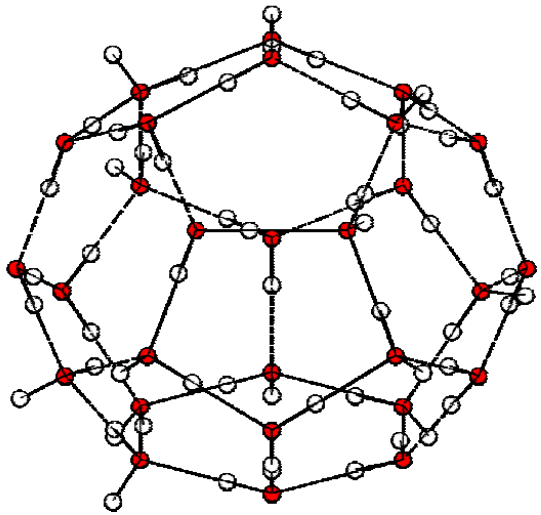
CAGE/PCA

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





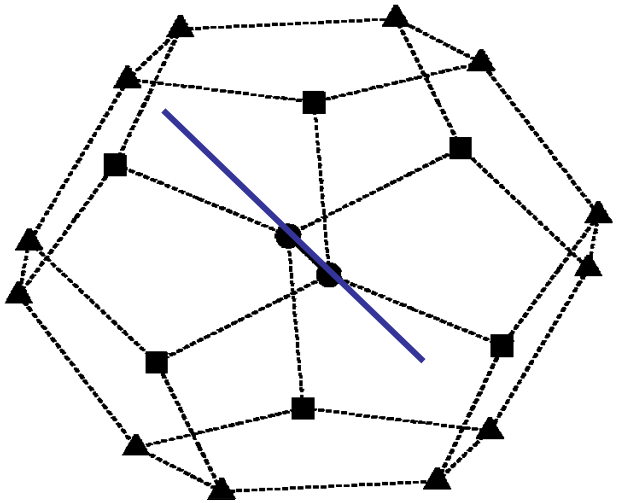




using
the same Xe-O and Xe-H shielding tensor functions,
the same Xe-O and Xe-H potential functions

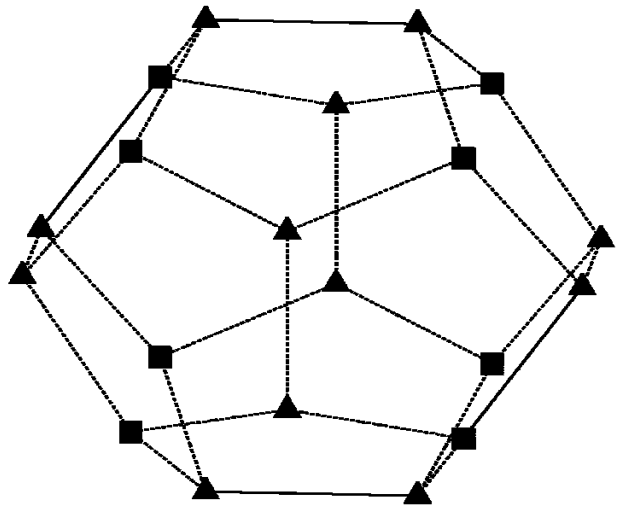
Why is the Xe lineshape in the 5^{12} cage in Structure II axially anisotropic while the Xe lineshape in the 5^{12} cage in Structure I is isotropic?

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



vs.

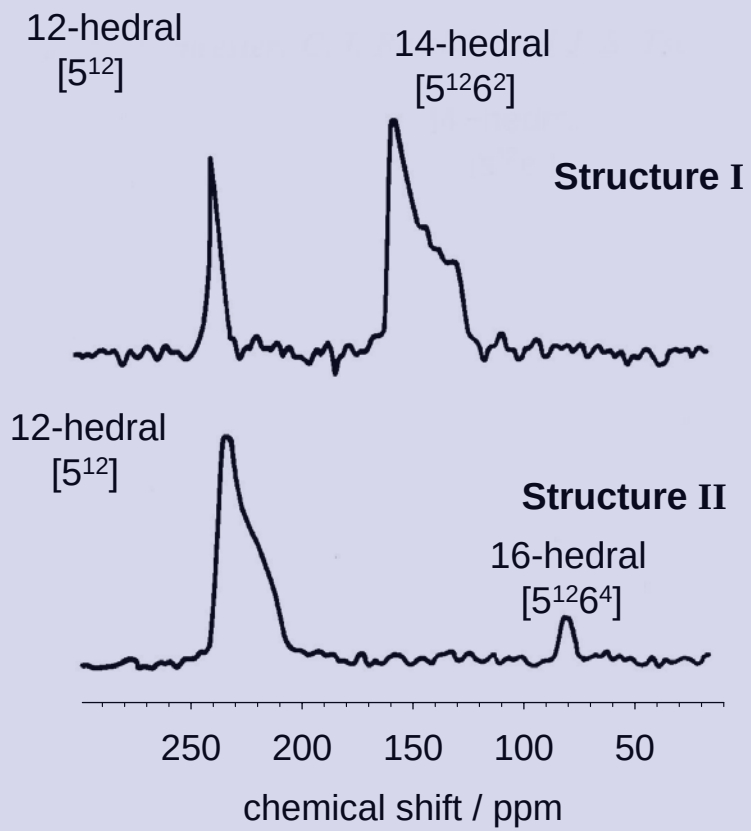
(b) 5^{12} cage in structure I



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**

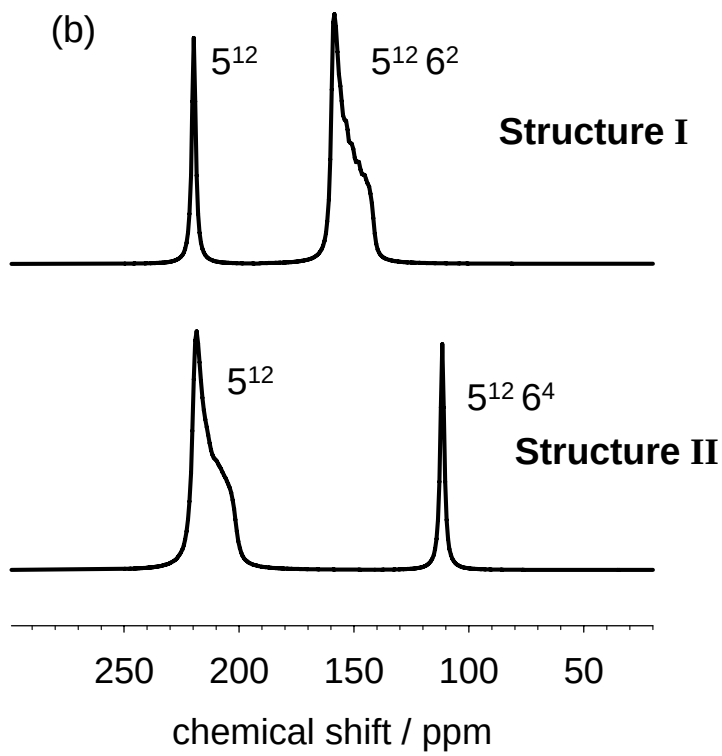
Xe can sense and report this difference!

Xe in the cages of clathrate hydrates Structure I and II



EXPERIMENTS

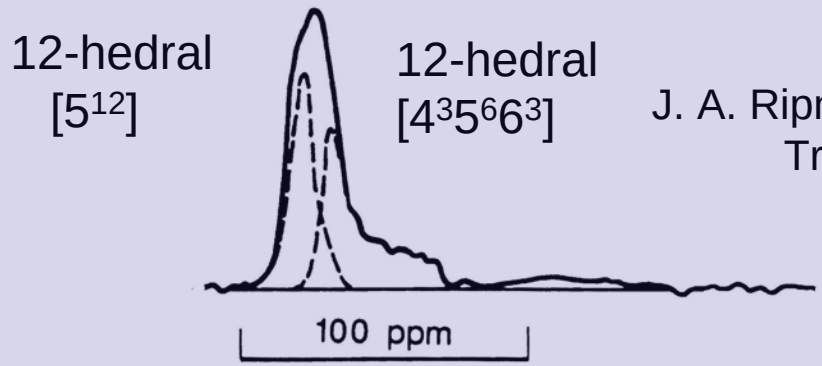
J. A. Ripmeester, C. I. Ratcliffe and J. S. Tse, Trans. Faraday Soc. 1, 84, 3731 (1988)



CALCULATIONS

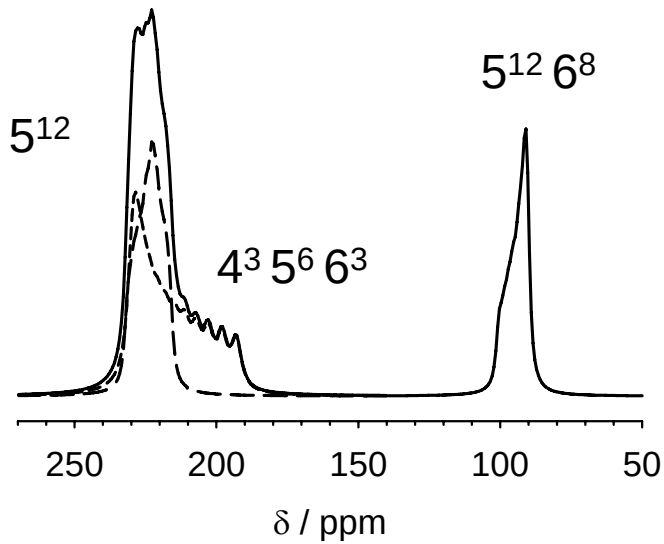
Monte Carlo simulations in a
4x4x4 supercell and 2x2x2 supercell
C. J. Jameson, D. Stueber, J Chem Phys 120, 10200 (2004)

Xe in clathrate hydrate Structure H



EXPERIMENT

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

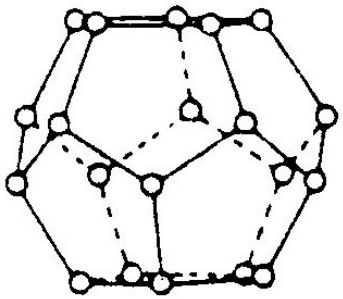


CALCULATIONS

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

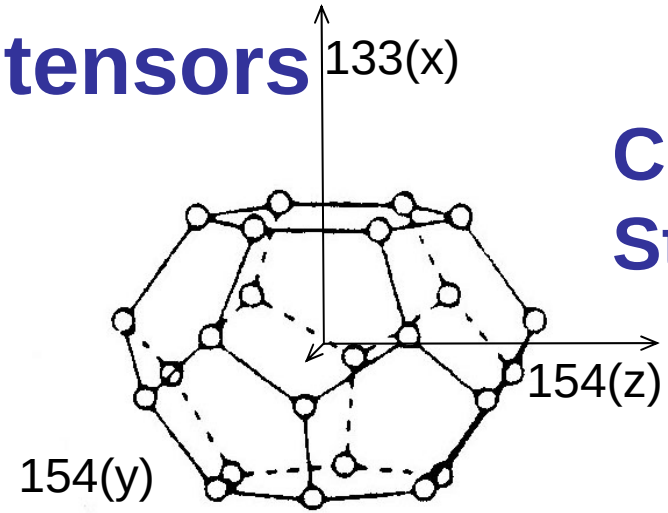
Xe chemical shift tensors

isotropic 214



5^{12}

symmetric

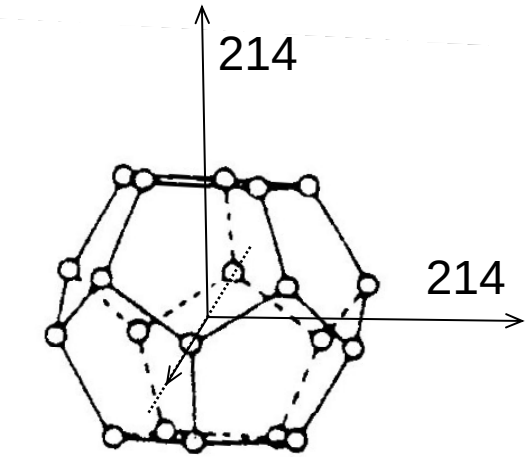


$5^{12}6^{2}$

axial, disk-like

Clathrate Structure I

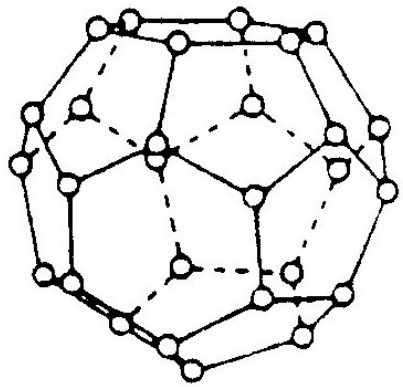
from canonical Monte Carlo simulations



5^{12}

axial

isotropic 105



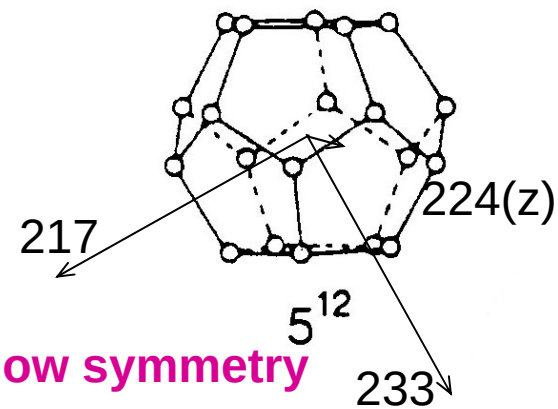
$5^{12}6^{4}$

symmetric

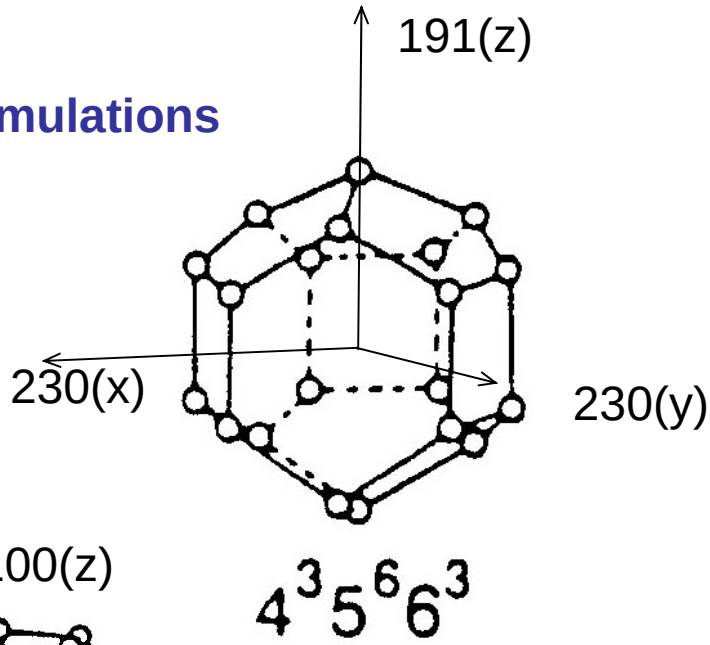
Clathrate Structure II

Xe tensors in Clathrate Structure H

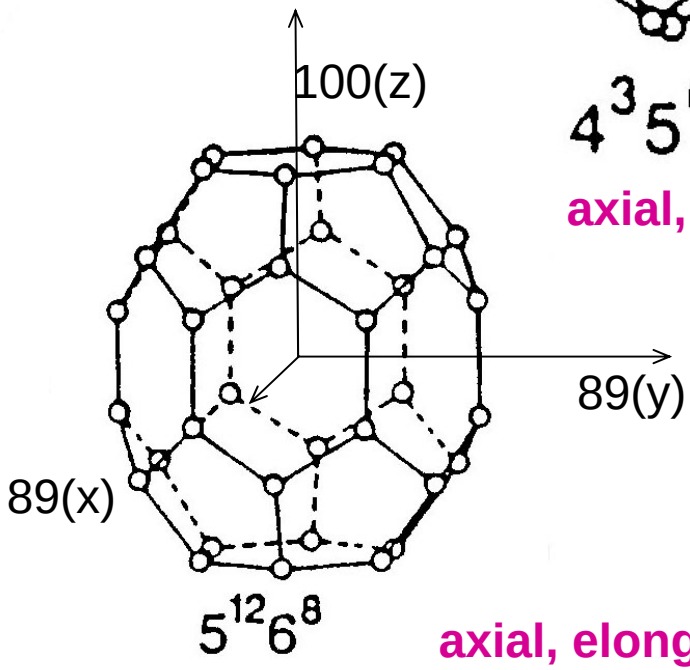
from canonical Monte Carlo simulations



low symmetry

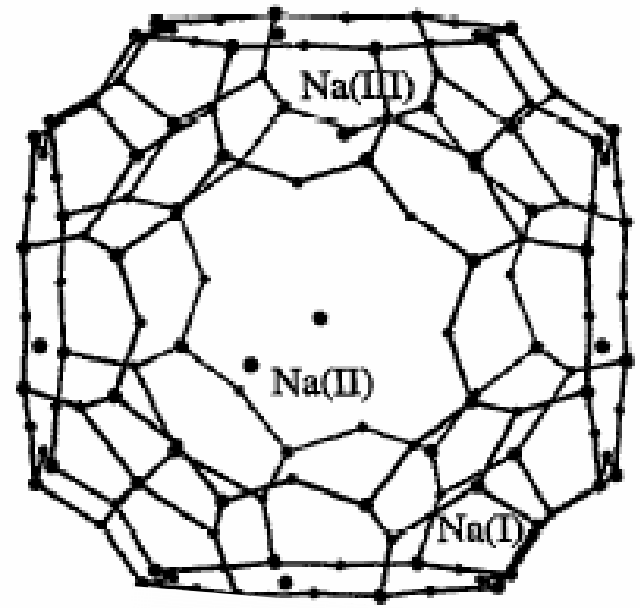


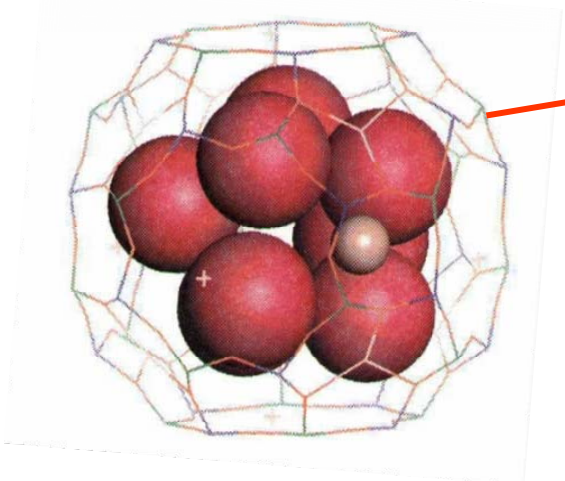
axial, squat

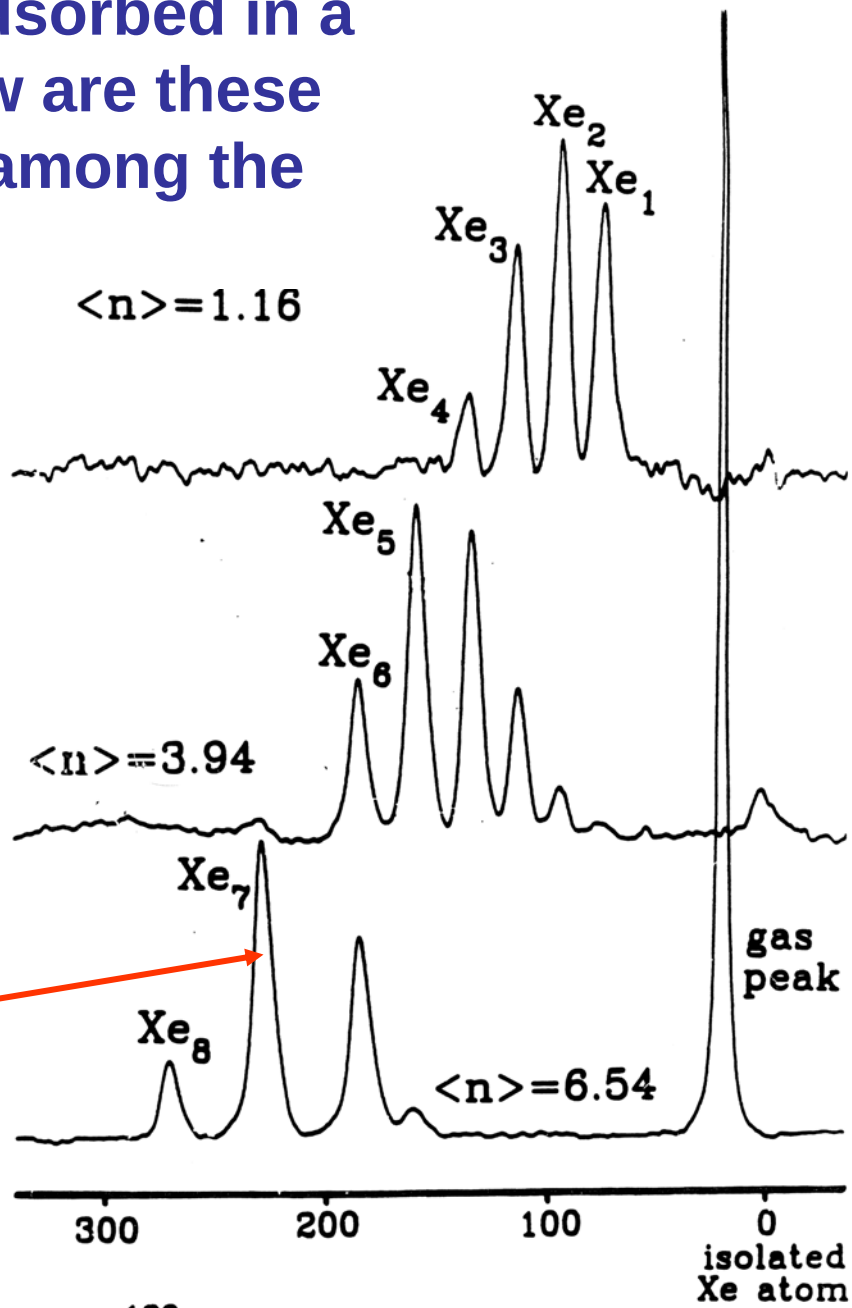


axial, elongated

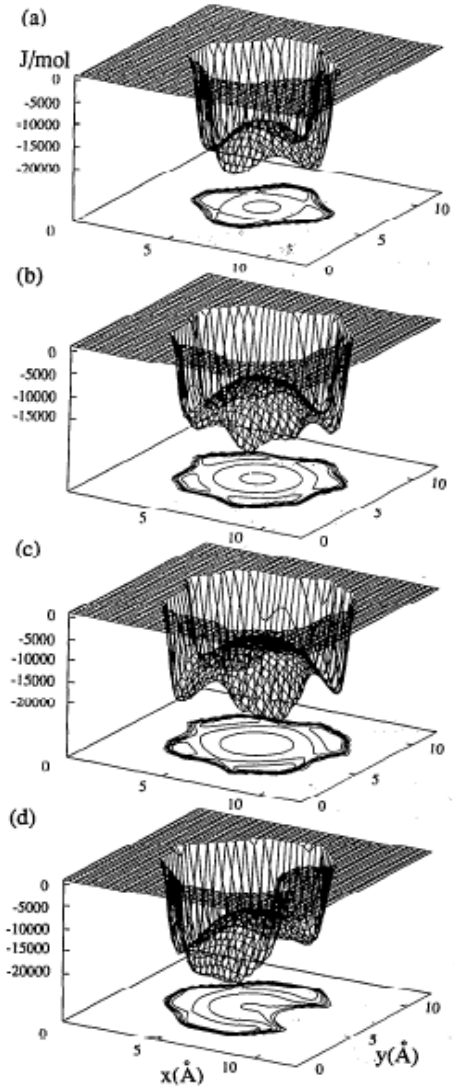
When molecules are adsorbed in a microporous solid, how are these molecules distributed among the cavities?

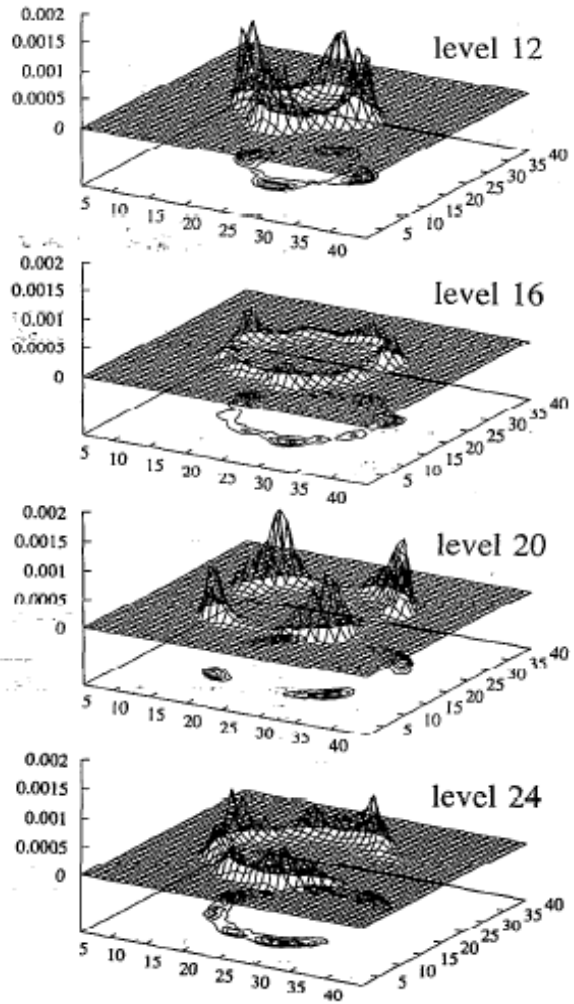


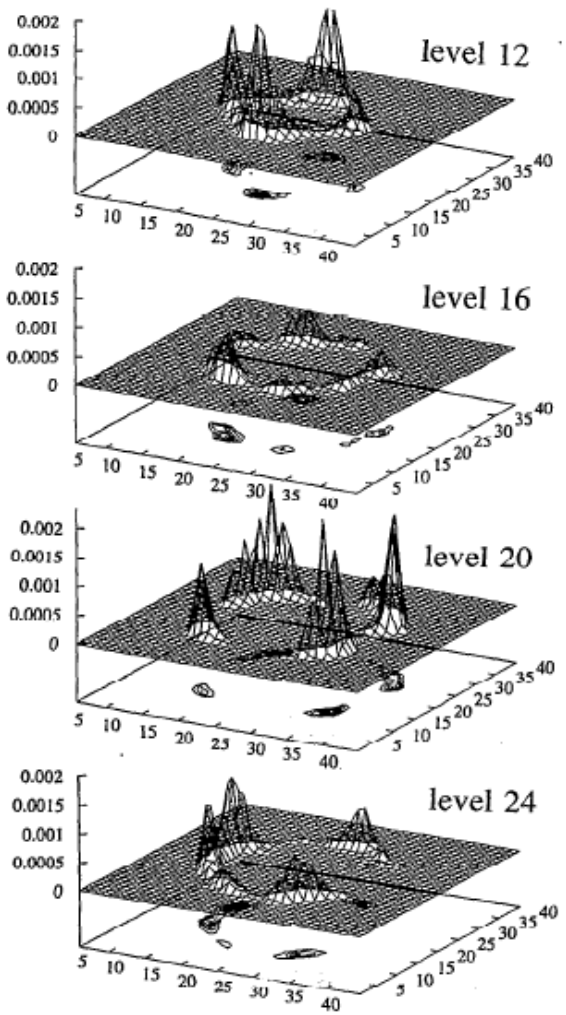




DISTRIBUTION of Xe ATOMS in a CAGE







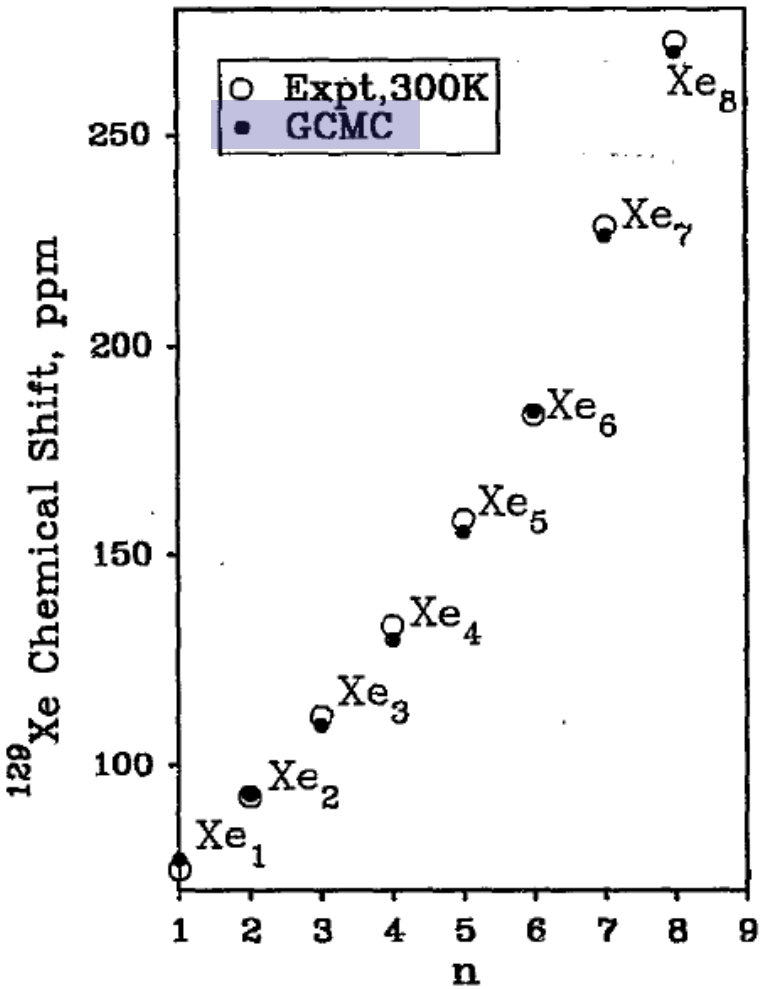
8 Xe in a cage

one Xe in a cage

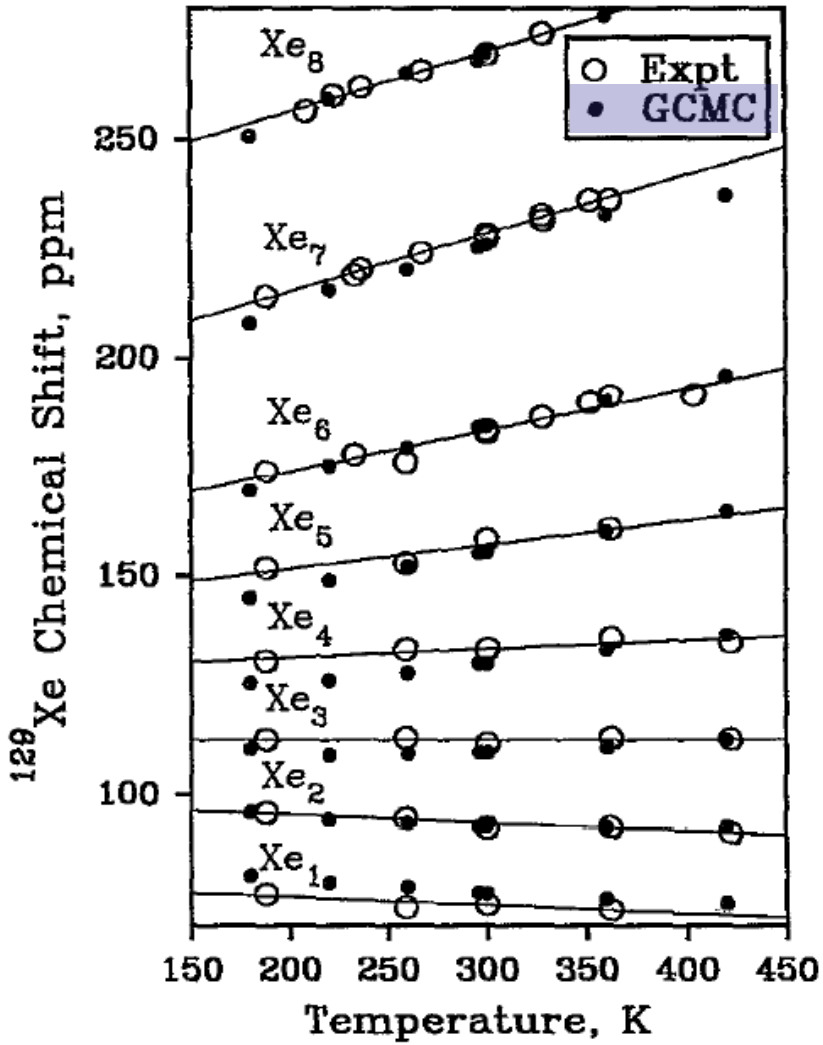
POTENTIAL ENERGY

Probability of finding a Xe on a plane in a cage

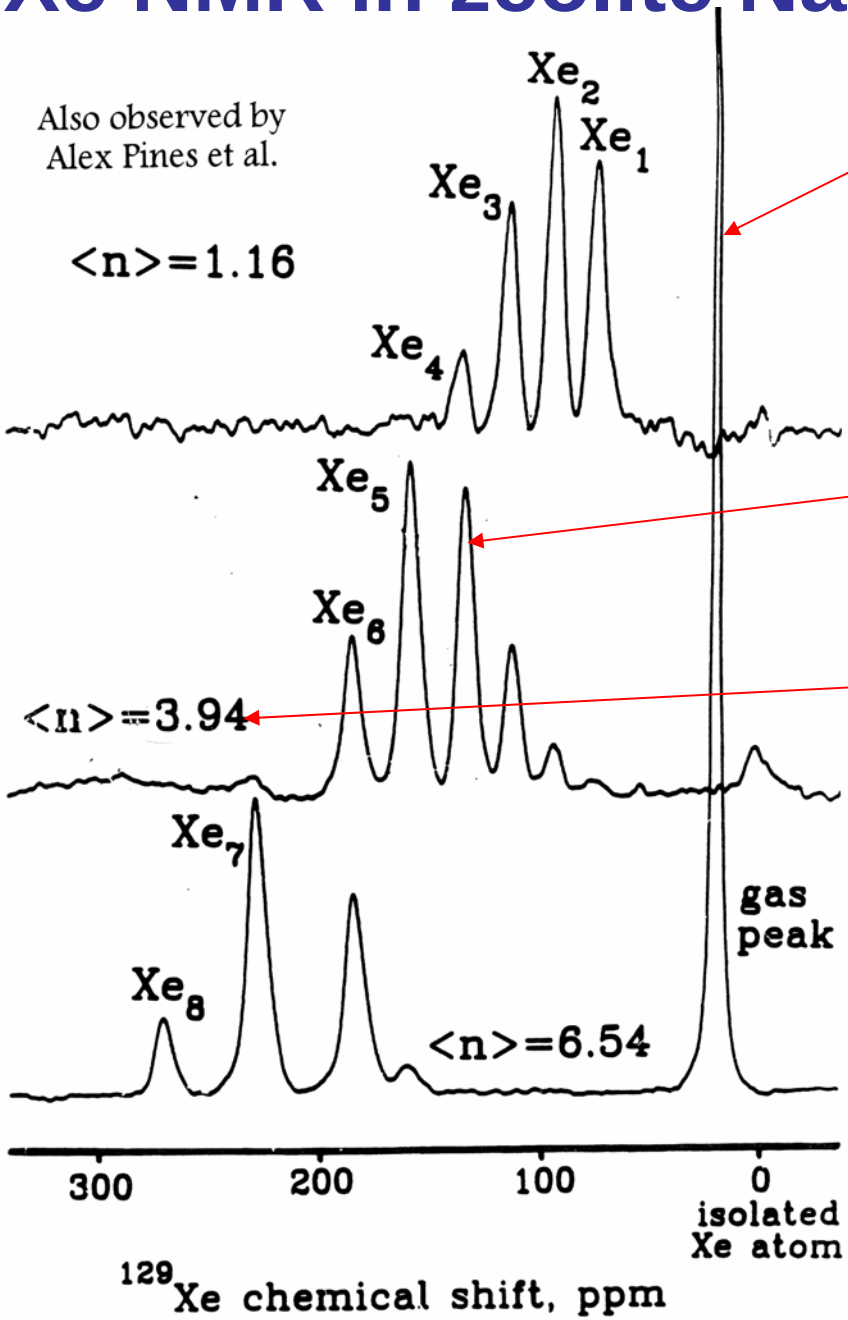
We reproduce the individual chemical shifts



and also the temperature dependence of each



Xe NMR in zeolite NaA

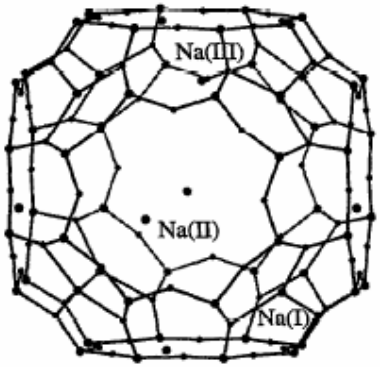


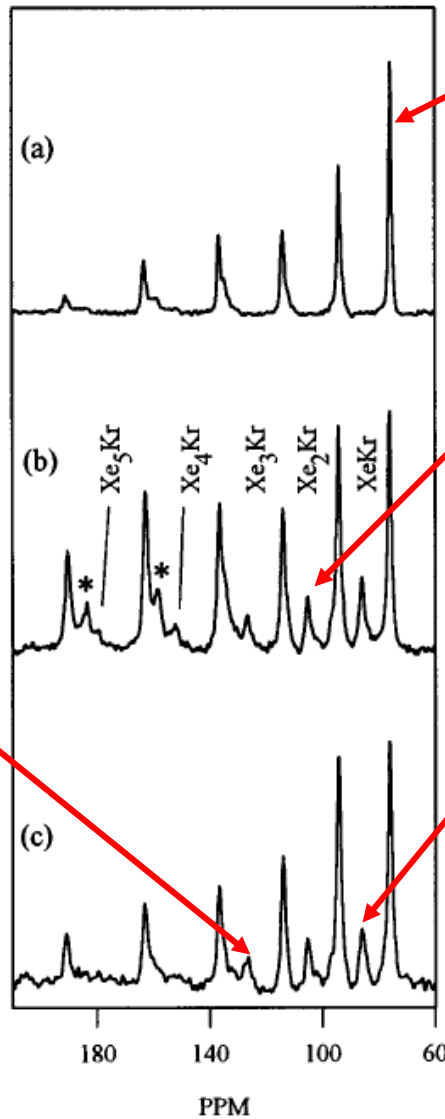
Xe chemical shift of gas peak provides ρ_{Xe} Xe density in the overhead bulk gas

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*.

Competitive Adsorption





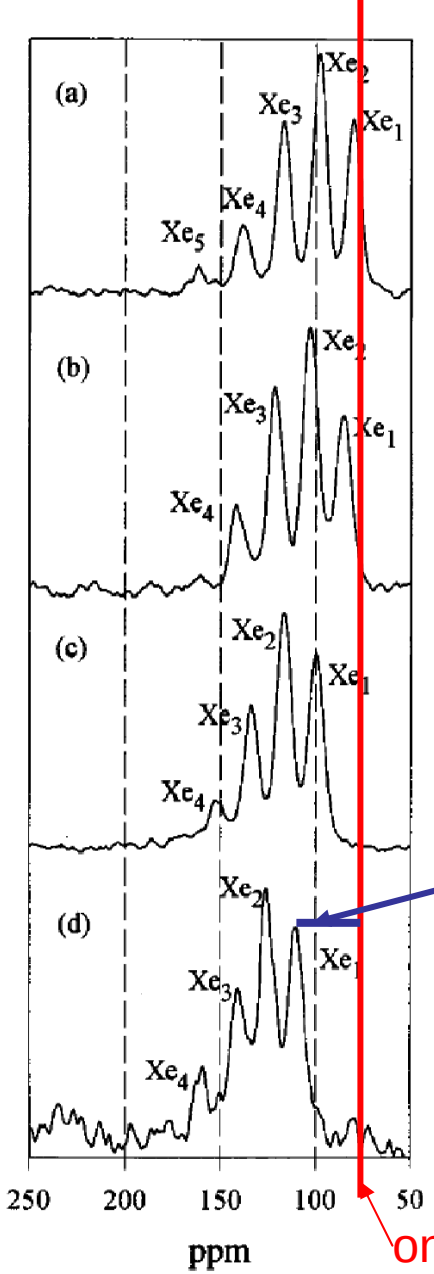
one Xe
in a cage

two Xe+one Kr
in a cage

three Xe+one Kr
in a cage

one Xe+ one Kr
in a cage

Xe NMR spectrum



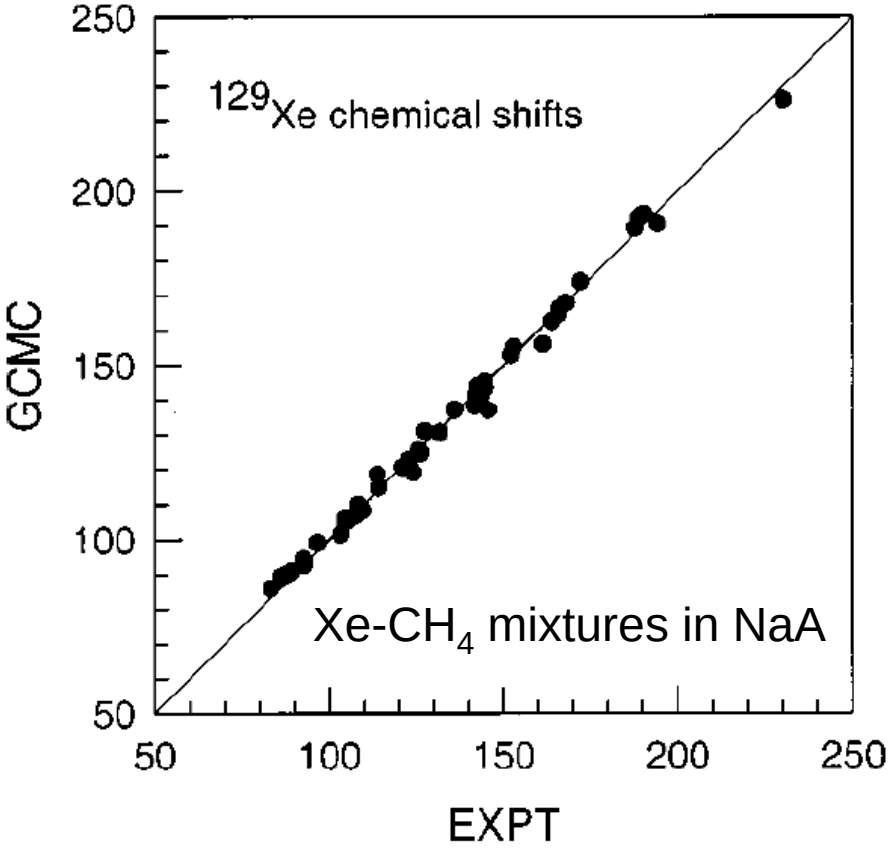
The Xe chemical shift for Xe_n depends on the average number of Ar atoms in the same cage as n Xe atoms.

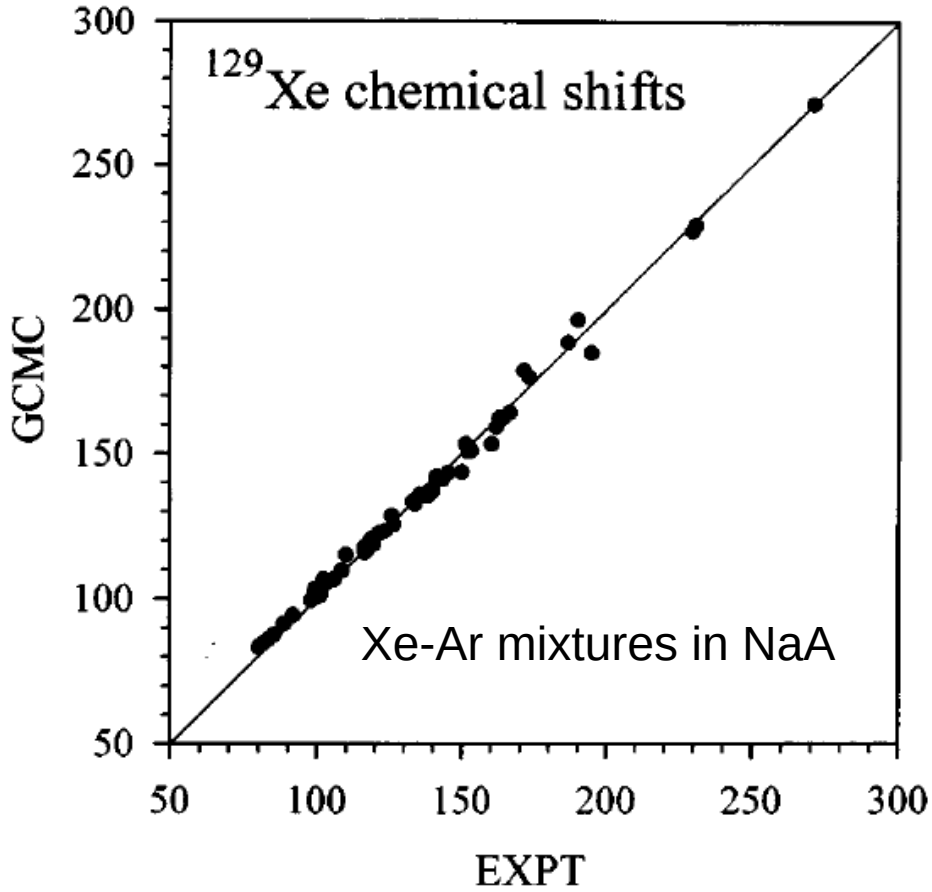
The INTENSITY of the Xe_n peak is a direct measure of the fraction of cages that have exactly *n* Xe atoms, as in pure Xe

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

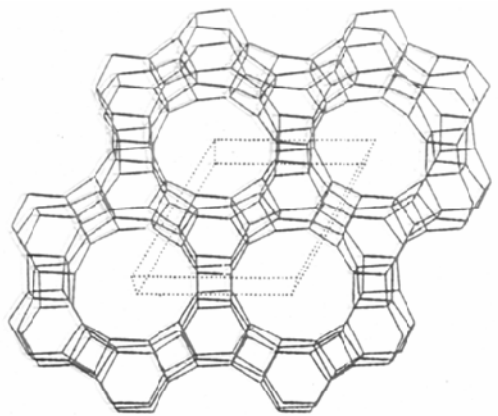
Xe NMR spectra of adsorbed Xe-Ar mixtures in zeolite NaA





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 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

Xe shielding tensor in a channel in an external magnetic field (B_0) along direction (θ,ϕ):

$$\sigma_{B0}(\theta, \phi) =$$
$$\sigma_{xx} \sin^2\theta\cos^2\phi + \sigma_{yy} \sin^2\theta\sin^2\phi + \sigma_{zz} \cos^2\theta +$$
$$\tfrac{1}{2}(\sigma_{xy}+\sigma_{yx})\sin^2\theta\sin2\phi + \tfrac{1}{2}(\sigma_{xz}+\sigma_{zx})\sin2\theta\cos\phi +$$
$$\tfrac{1}{2}(\sigma_{yz}+\sigma_{zy})\sin2\theta\sin\phi$$

one Xe tensor from interaction with ALL channel atoms

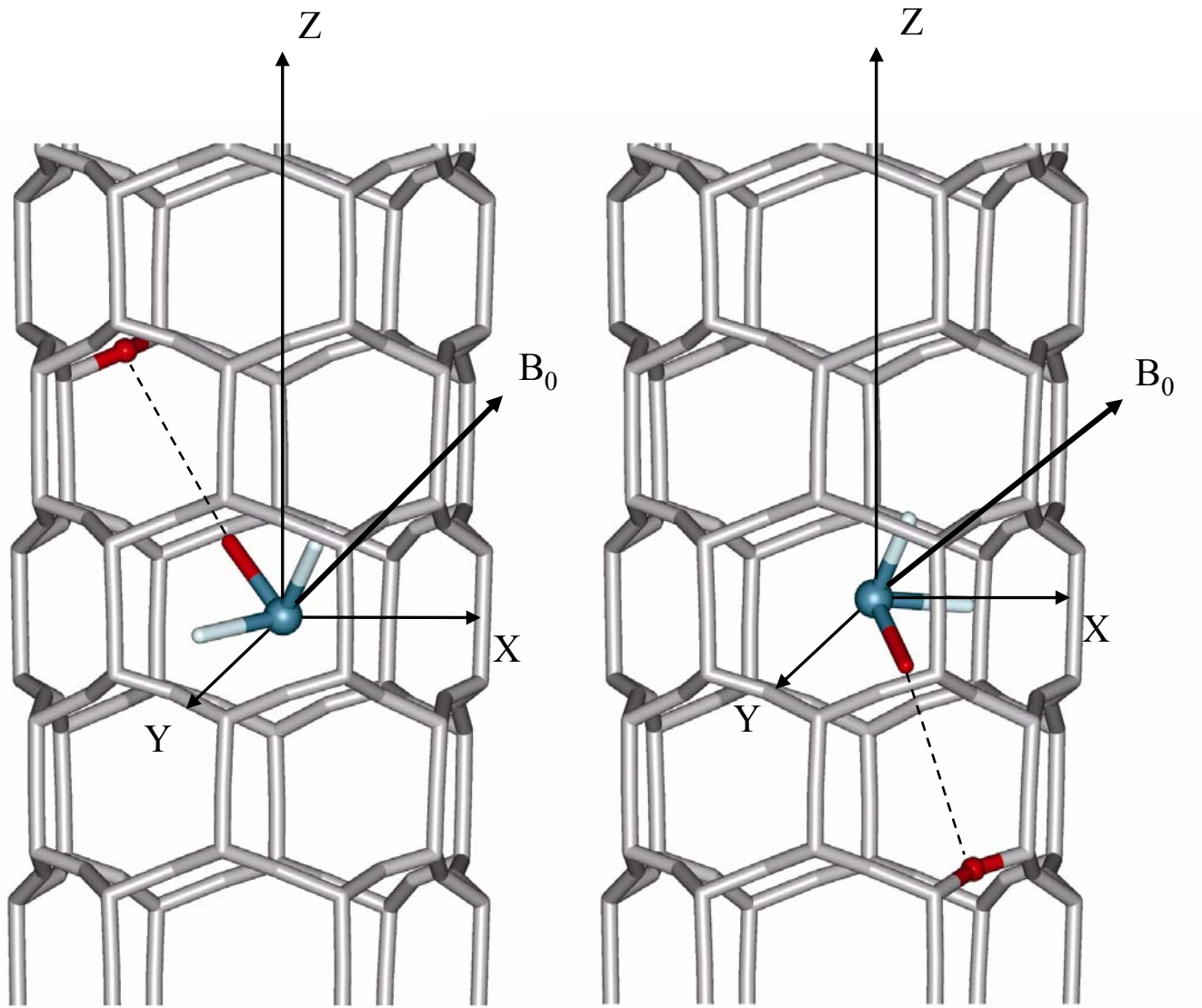
The **dimer tensor model** for Xe shielding tensor in the channel

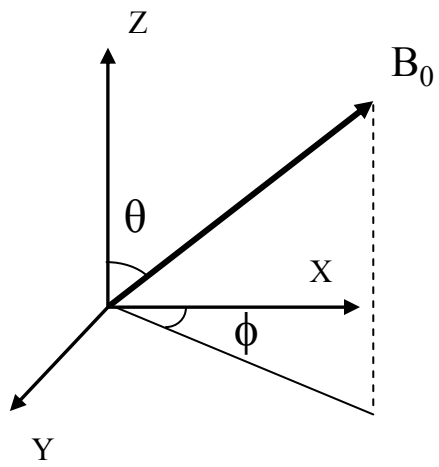
The contribution to the shielding of Xe at point J due to i_{th} C or H atom of located at (x_i, y_i, z_i) is given by the tensor components for the Xe-C or Xe-H dimer, the functions $\sigma_{\perp}(r_{XeC/H})$, $\sigma_{||}(r_{XeC/H})$.

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

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

Lineshapes by grand canonical Monte Carlo



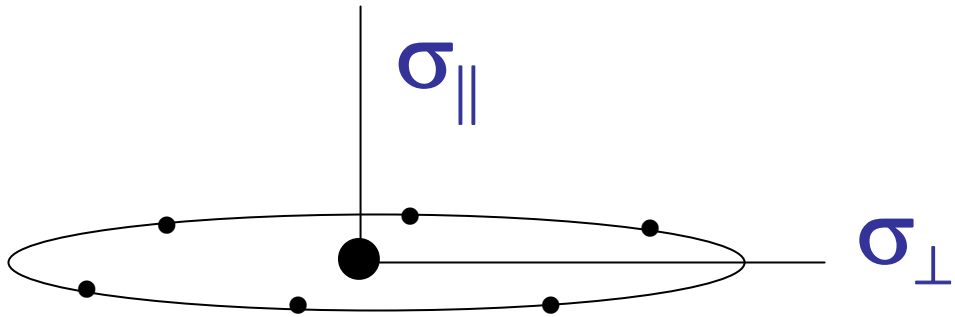


Random orientation of crystallites:
Probability that B_0 lies in any infinitesimal solid angle is
$d\zeta\, d\phi / 4\pi$, where
$\zeta = (-\cos\theta)$
Equal areas in $\zeta\phi$ plane correspond to equal probabilities

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

Are Xe shielding tensor components pairwise additive?

Example:



Xe in the center of a ring of Ne atoms

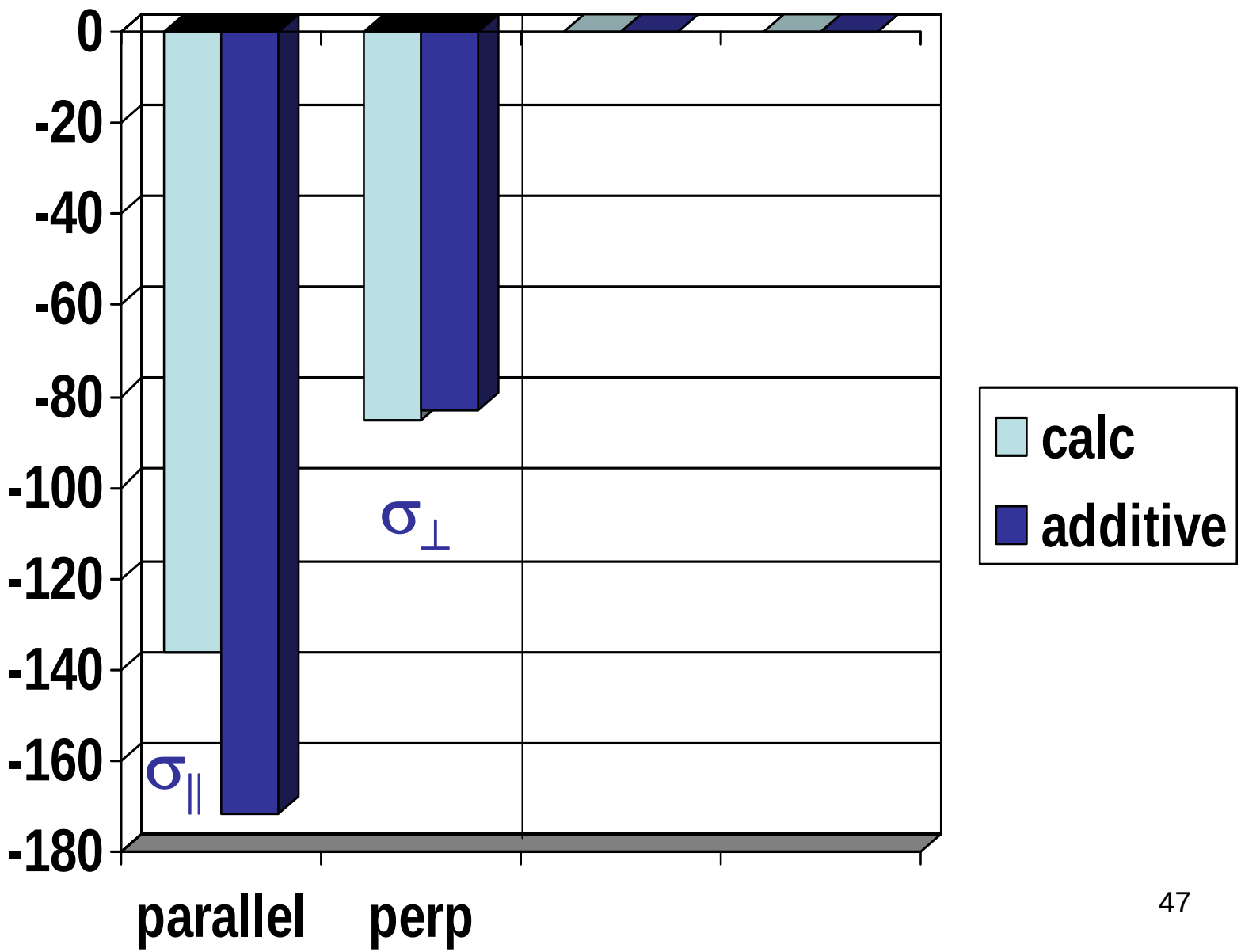
The **dimer tensor model** for Xe shielding tensor in a Ne channel

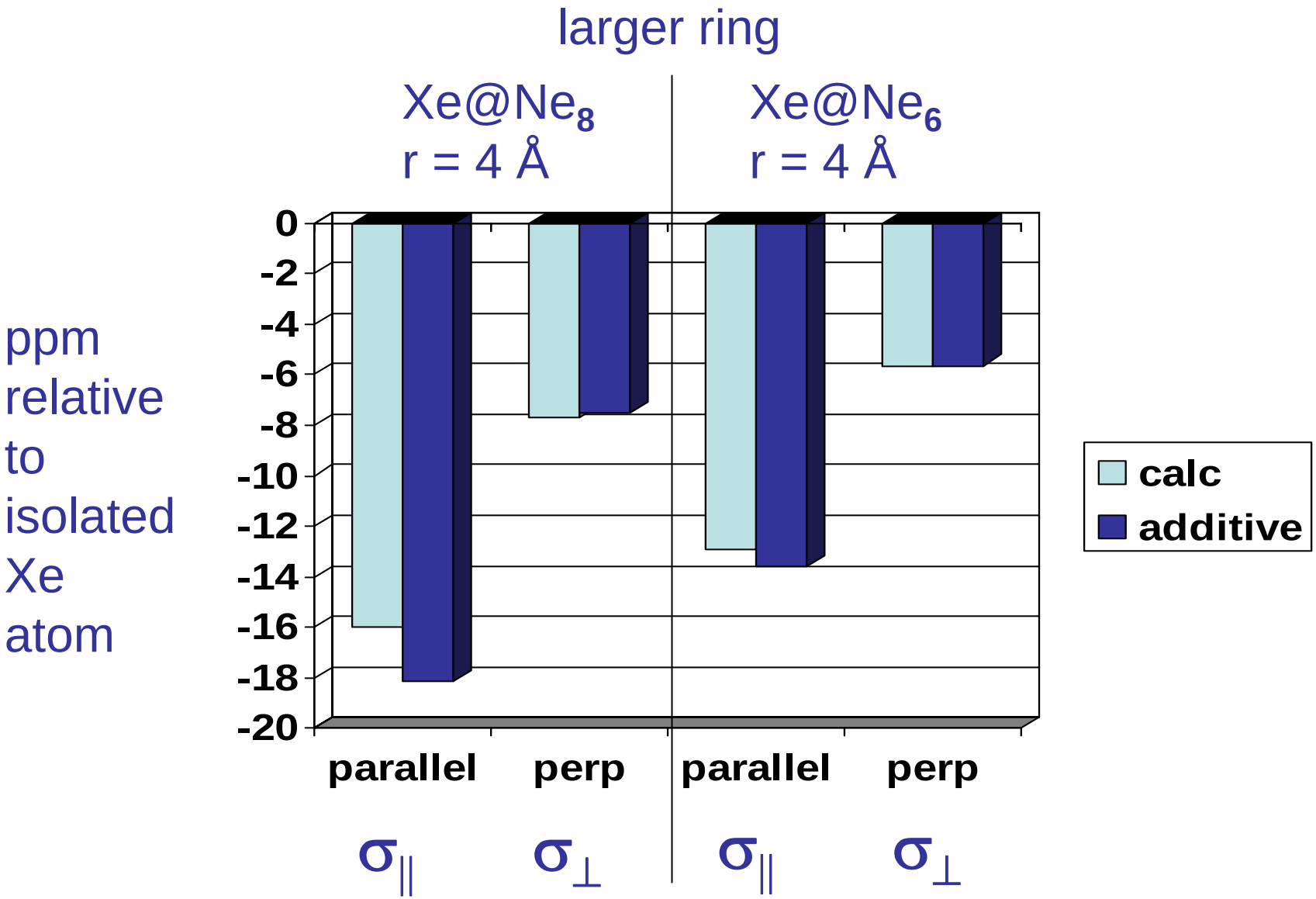
The contribution to the shielding of Xe at point J due to i_{th} Ne atom located at (x_i, y_i, z_i) is given by the ab initio tensor components for the XeNe dimer, the functions $\sigma_{\perp}(r_{XeNe})$, $\sigma_{||}(r_{XeNe})$.

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

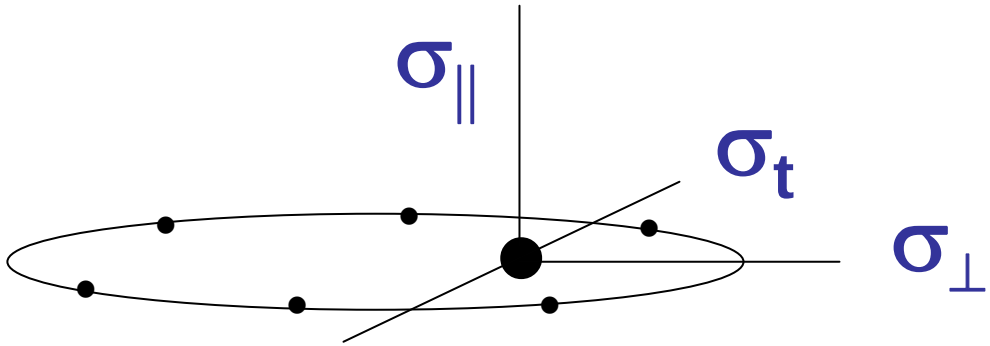
$$\tfrac{1}{2}(\sigma_{XY}+\sigma_{YX}) = [(x_i - x_J)/r_{iJ}]\bullet[(y_i - y_J)/r_{iJ}](\sigma_{||} - \sigma_{\perp})$$

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


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

Xe off-center in the larger ring of Ne atoms

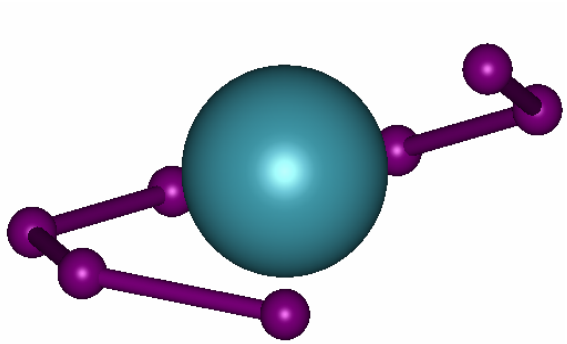


Model	r_{ring} Å	R_{Xe} Å	$\sigma_{\parallel}$	$\sigma_{\perp}$	σ_t
$Xe@Ne_6$	4.0	1.0	-40.04	-11.13	-28.86
$\sum_i^6 XeNe_i$	4.0	1.0	-43.18	-11.45	-29.00
$Xe@Ne_8$	4.0	1.0	-47.67	-18.39	-35.48
$\sum_i^8 XeNe_i$	4.0	1.0	-57.20	-18.69	-34.83

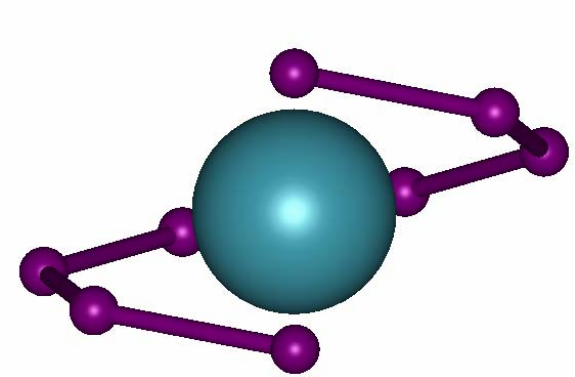
large deviation

The shielding tensor of Xe interacting with Ne helices

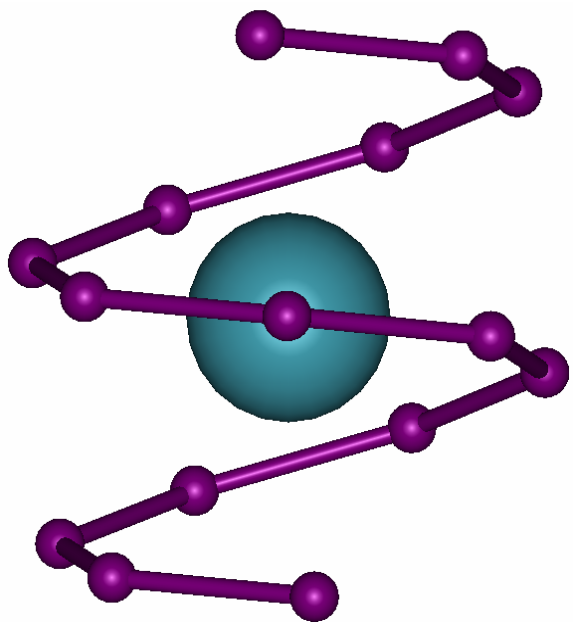
Xe in a left handed helix



Xe@Ne$_7$



Xe@Ne$_8$



Xe@Ne$_{15}$

Are Xe shielding tensor components pairwise additive?

$Xe@Ne_7(L)$	ab initio	dimer tensor model	diff
σ_{XX}	-55.4526	-55.3409	-0.11
σ_{YY}	-52.2268	-52.1340	-0.09
σ_{ZZ}	-86.6174	-98.1004	11.48
$½(\sigma_{XY} + \sigma_{YX})$	-0.0948	0.0000	-0.09
$½(\sigma_{XZ} + \sigma_{ZX})$	-2.8110	-3.2641	0.45
$½(\sigma_{YZ} + \sigma_{ZY})$	12.7147	15.4706	-2.76
σ_{iso}	-64.7656	-68.5253	3.76

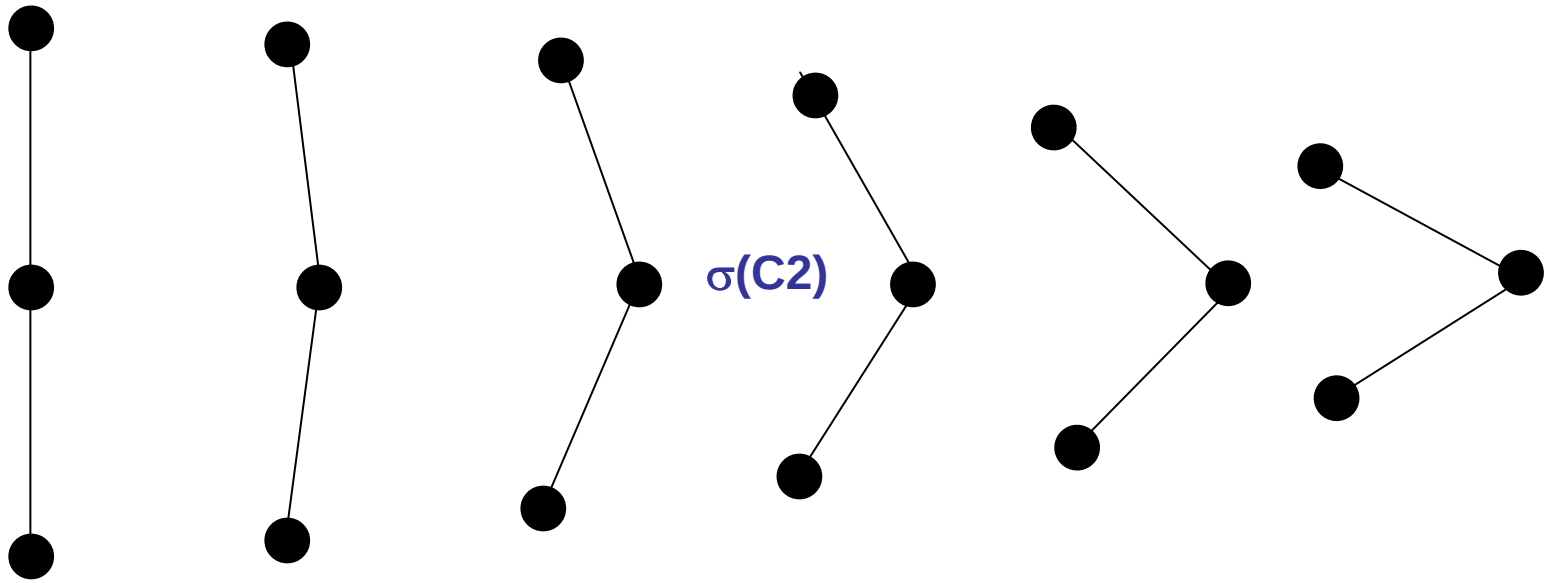
Are Xe shielding tensor components pairwise additive?

$Xe@Ne_8(L)$	ab initio	dimer tensor model	diff
σ_{XX}	-56.4270	-56.5864	0.16
σ_{YY}	-59.0700	-59.4600	0.39
σ_{ZZ}	-91.2691	-103.6742	12.41
$½(\sigma_{XY} + \sigma_{YX})$	0.0000	0.0000	0.00
$½(\sigma_{XZ} + \sigma_{ZX})$	0.0000	0.0000	0.00
$½(\sigma_{YZ} + \sigma_{ZY})$	12.5036	15.4706	-2.97
σ_{iso}	-68.9221	-73.2404	4.32

Are Xe shielding tensor components pairwise additive?

$Xe@Ne_{15}(L)$	ab initio	dimer tensor model	diff
σ_{XX}	-64.8244	-66.4863	1.66
σ_{YY}	-65.1560	-66.6497	1.49
σ_{ZZ}	-97.4705	-111.0832	13.61
$\frac{1}{2}(\sigma_{XY} + \sigma_{YX})$	-0.1955	-0.1000	-0.10
$\frac{1}{2}(\sigma_{XZ} + \sigma_{ZX})$	3.3079	4.2987	-0.99
$\frac{1}{2}(\sigma_{YZ} + \sigma_{ZY})$	6.7964	8.9260	-2.13
σ_{iso}	-75.8170	-81.4067	5.59

three Xe atoms



180 170 150 120 90 60

central Xe in Xe_3 $r_{Xe\text{-}Xe}$= 4.0 Å (shorter)

	$\sigma_{\perp}$	$\sigma_{(C2)}$	$\sigma_{(\perp \text{to } C2)}$
α = 180°	-204.72	-204.72	+5.17
if additive	*-202.38*	*-202.38*	*+5.06*
dev	***-2.3***	***-2.3***	***-0.1***
α =170°	-204.79	-203.04	+3.62
if additive	*-202.38*	*-200.80*	*+3.48*
dev	***-2.3***	***+2.2***	***-0.1***
α= 150°	-205.23	-190.17	-8.52
if additive	*-202.38*	*-188.50*	*-8.84*
dev	***+2.8***	***+2.0***	***-0.3***
α= 120°	-204.32	-151.04	-46.32
if additive	*-202.38*	*-150.52*	*-46.80*
dev	***+1.9***	***+0.5***	***-0.5***

central Xe in Xe_3 $r_{Xe\text{-}Xe}$= 4.4 Å (longer)

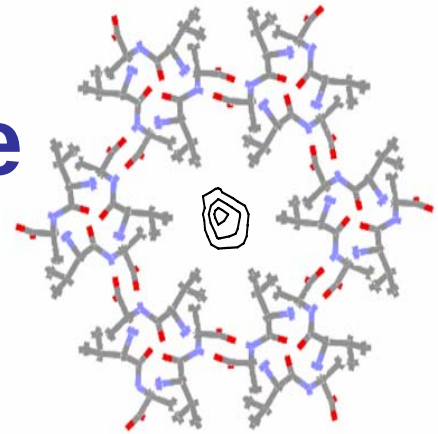
	$\sigma_{\perp}$	$\sigma_{(C2)}$	$\sigma_{(\perp to\ C2)}$
α = 180°	-81.89	-81.89	+3.88
if additive	*-81.58*	*-81.58*	*+3.88*
dev	***+0.3***	***+0.3***	***0.0***
α =170°	-81.91	-81.21	+3.23
if additive	*-81.58*	*-80.93*	*+3.23*
dev	***+0.3***	***+0.3***	***0.0***
α= 150°	-82.00	-76.04	-1.84
if additive	*-81.58*	*-75.86*	*-1.84*
dev	***+0.4***	***+0.2***	***0.0***
α= 120°	-81.81	-60.29	-17.44
if additive	*-81.58*	*-60.22*	*-17.48*
dev	***+0.2***	***+0.1***	***0.0***

central Xe in Xe_3 $r_{Xe\text{-}Xe}$= 4.4 Å

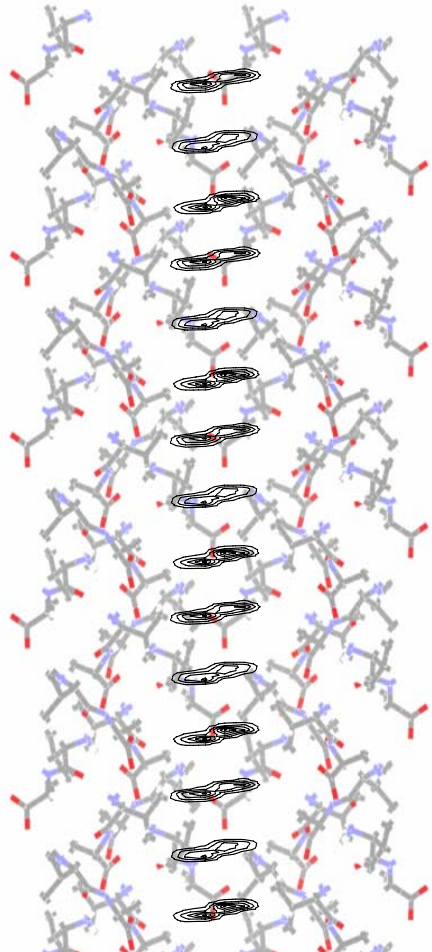
	$\sigma_{\perp}$	$\sigma_{(C2)}$	$\sigma_{(\perp to\ C2)}$
α= 90°	-79.89	-38.87	-38.87
if additive	*-81.58*	*-38.85*	*-38.85*
dev	***-1.7***	***0.0***	***0.0***
α= 60°	-70.05	-17.89	-58.51
if additive	*-81.58*	*-17.48*	*-60.22*
dev	***-11.5***	***0.4***	***-1.7***

in the molecular plane, the electrons of terminal Xe atoms interacting substantially for 60°

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

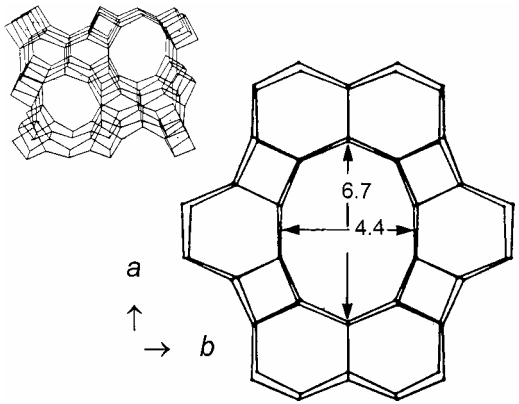


Xe in VA from GCMC simulations



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

Architecture of the channel determines the Xe lineshape

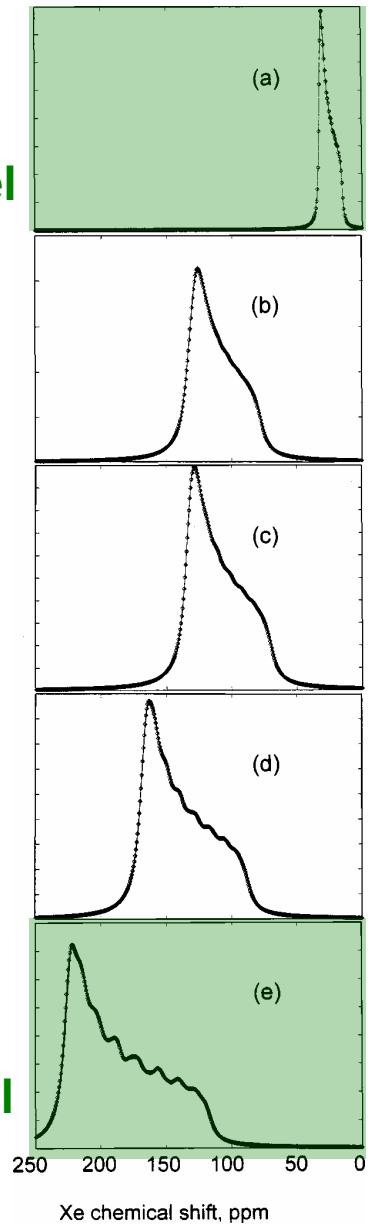


$ALPO_4$-11 architecture

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

One Xe atom in a **neon channel**

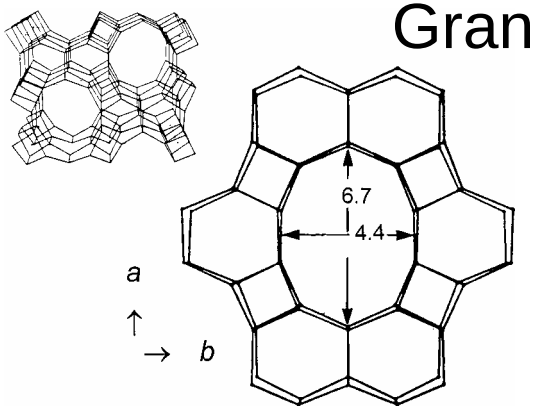
One Xe atom in an **argon channel**



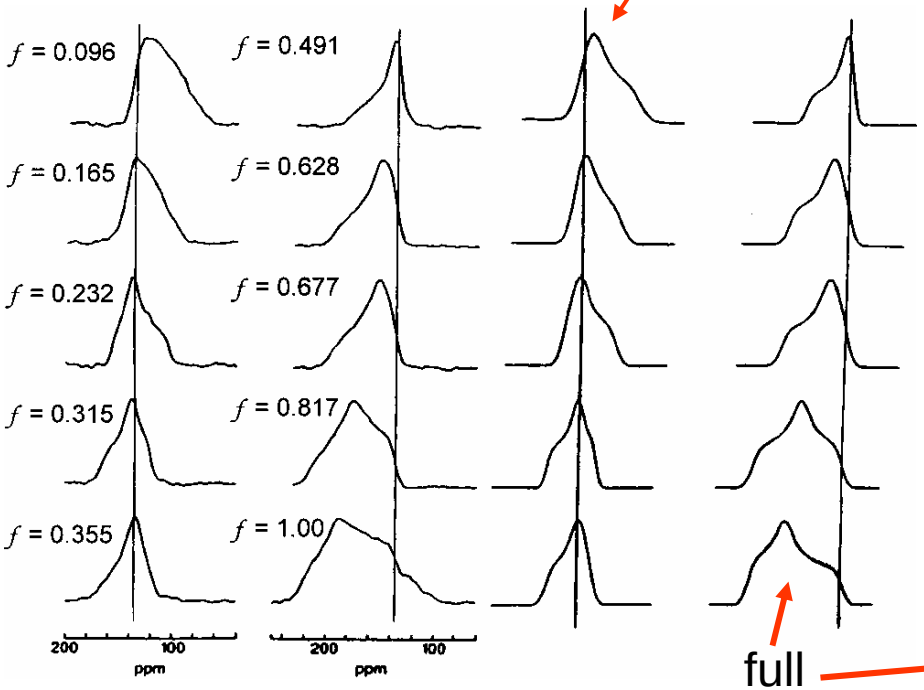
Jameson, JCP 116, 8912 (2002)

Xe in the channels of $ALPO_4$-11

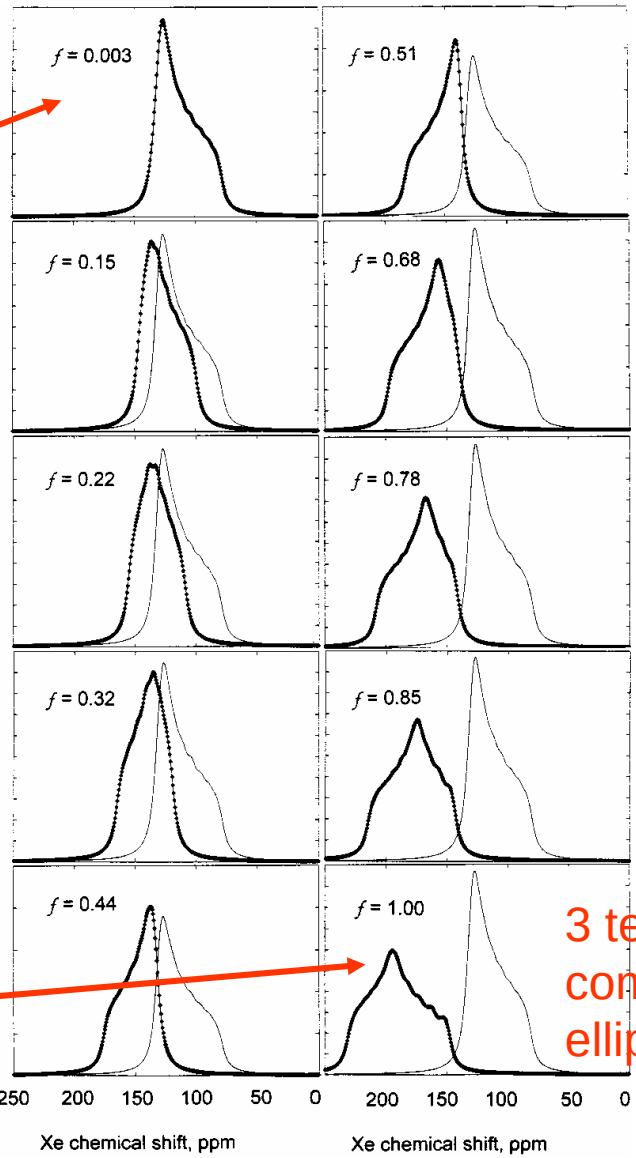
Grand Canonical Monte Carlo **SIMULATIONS**



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)

dipeptides

L-Val-L-Ala

VA

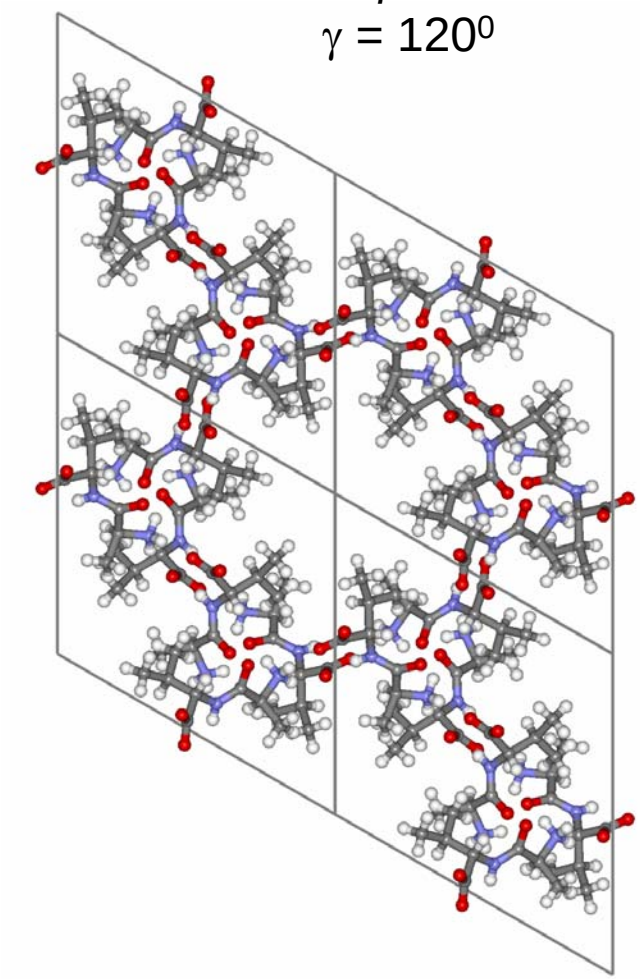
P61

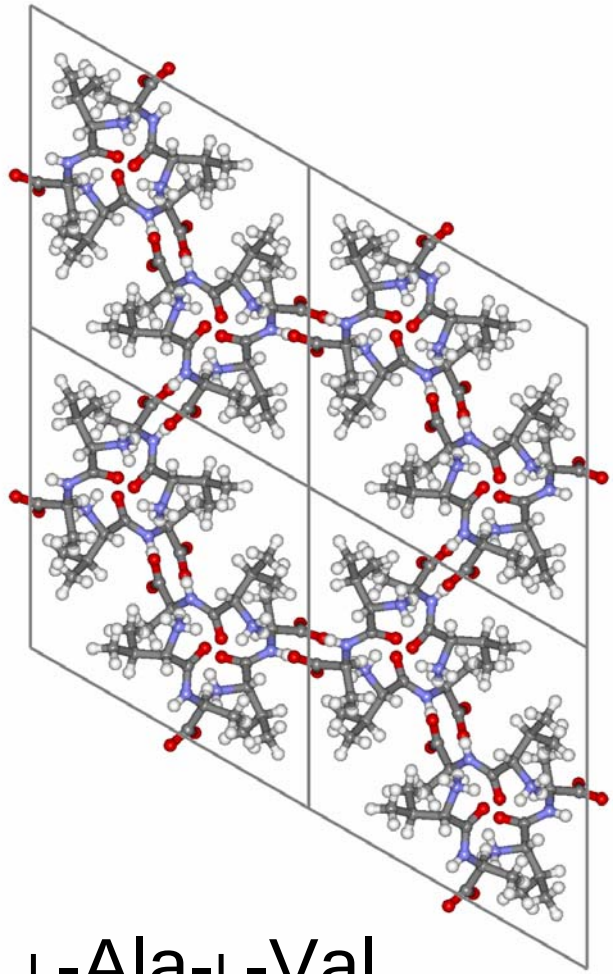
a = b= 14.461 Å

c = 10.083 Å

$\alpha = \beta = 90^0$

$\gamma = 120^0$





L-Ala-L-Val

AV

P61

a = b= 14.462 Å

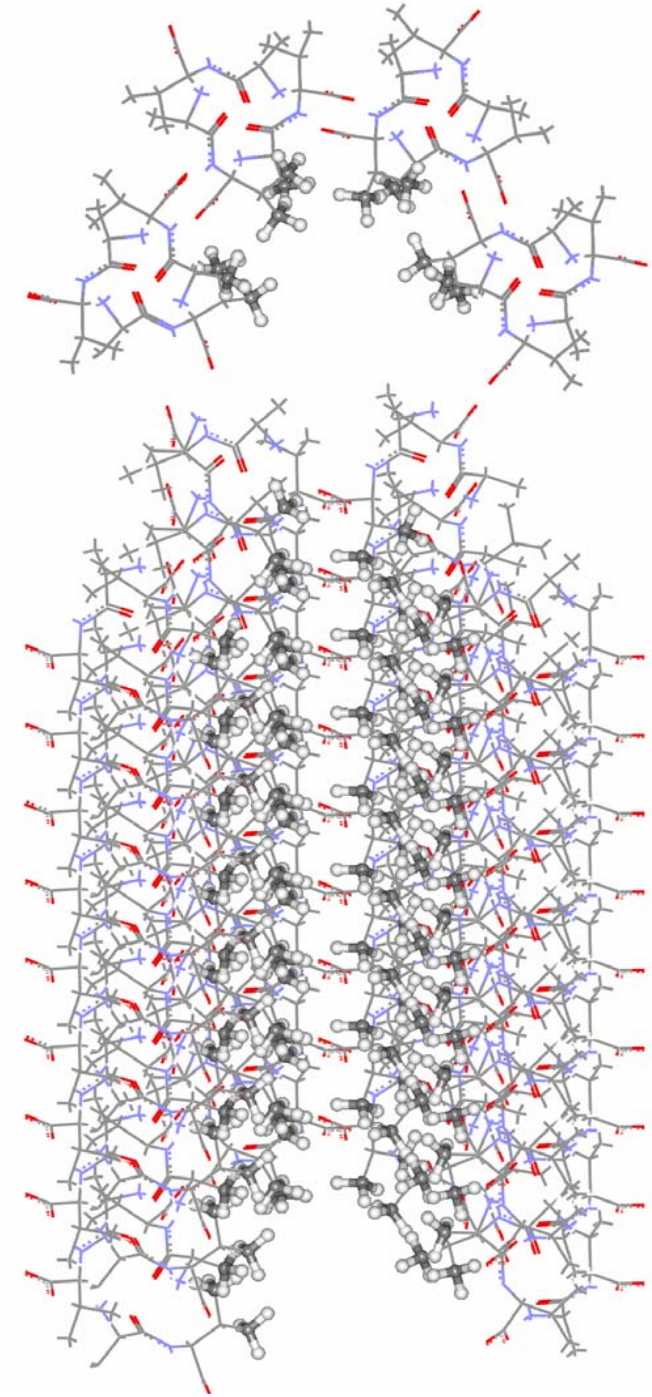
c = 10.027 Å

$\alpha = \beta = 90^0$

$\gamma = 120^0$

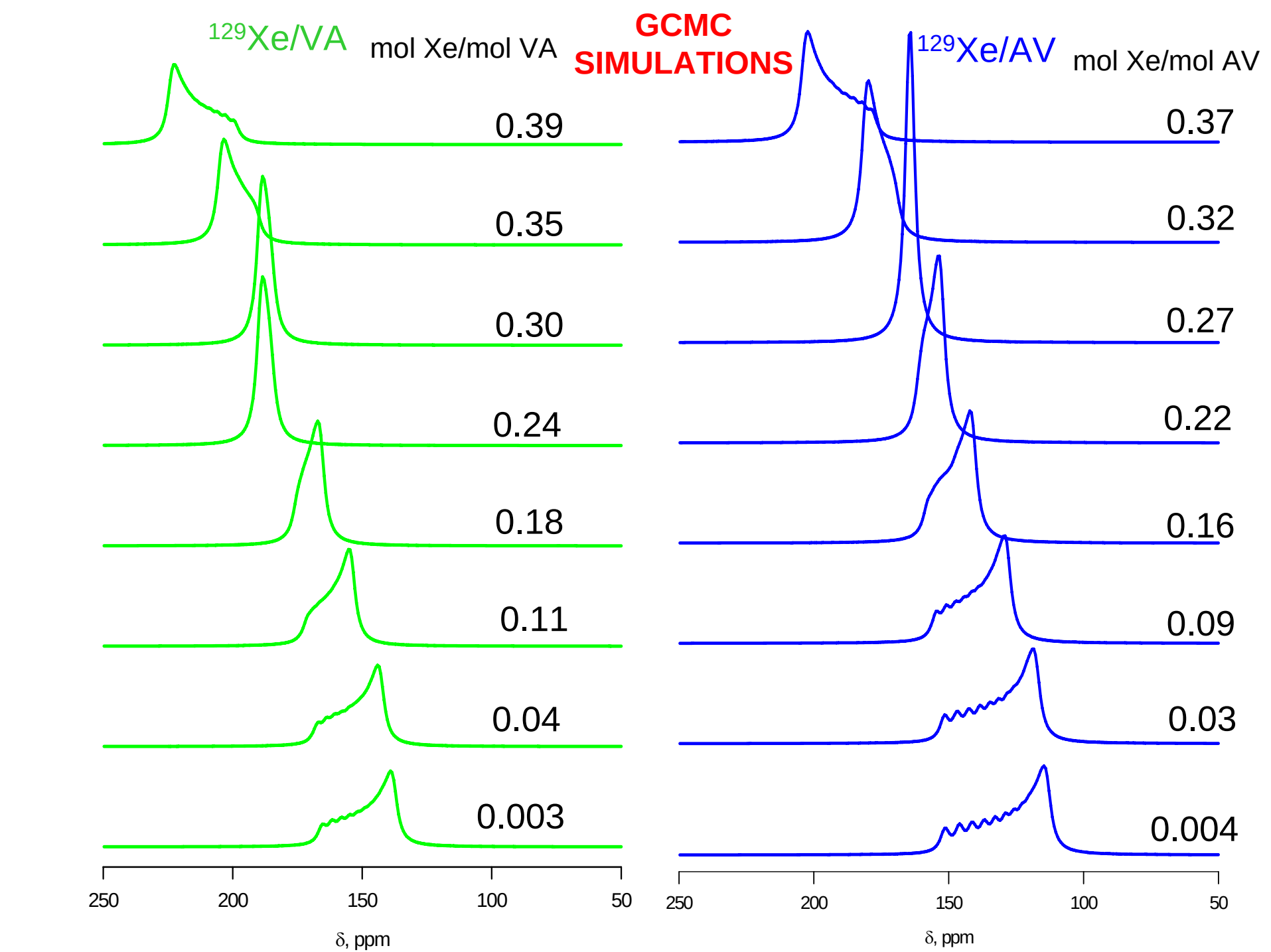
- From the perspective of the Xe only the side chain methyl groups are accessible

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

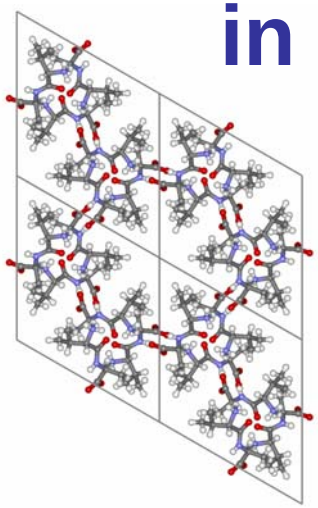


Top view

Tilted view

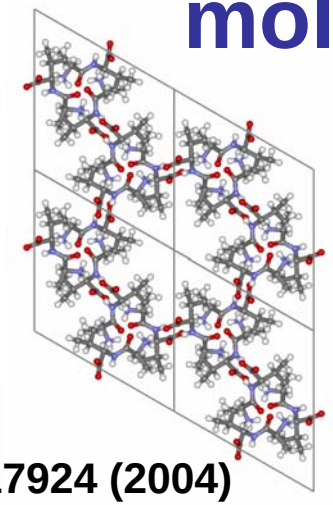

^{129}Xe/VA
mol Xe/mol VA
GCMC
SIMULATIONS
^{129}Xe/AV
mol Xe/mol AV
0.39
0.35
0.30
0.24
0.18
0.11
0.04
0.003
0.37
0.32
0.27
0.22
0.16
0.09
0.03
0.004
250
200
150
100
50
δ, ppm
250
200
150
100
50
δ, ppm

in channels of molecular crystals



L-Val-L-Ala

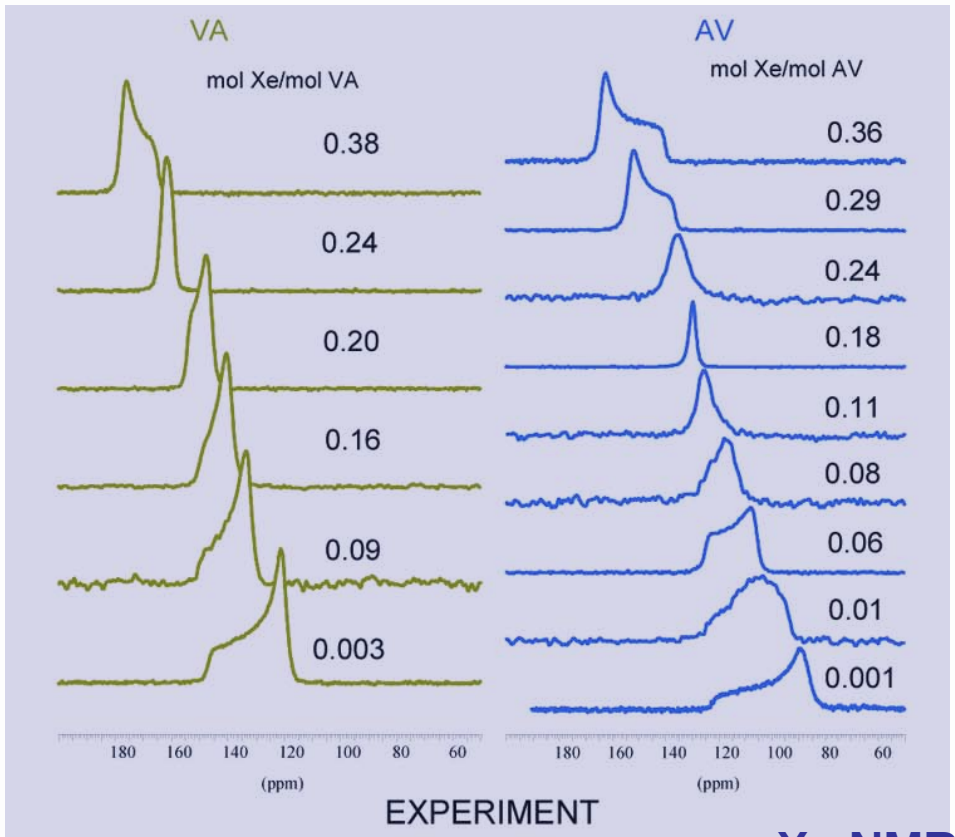
VA

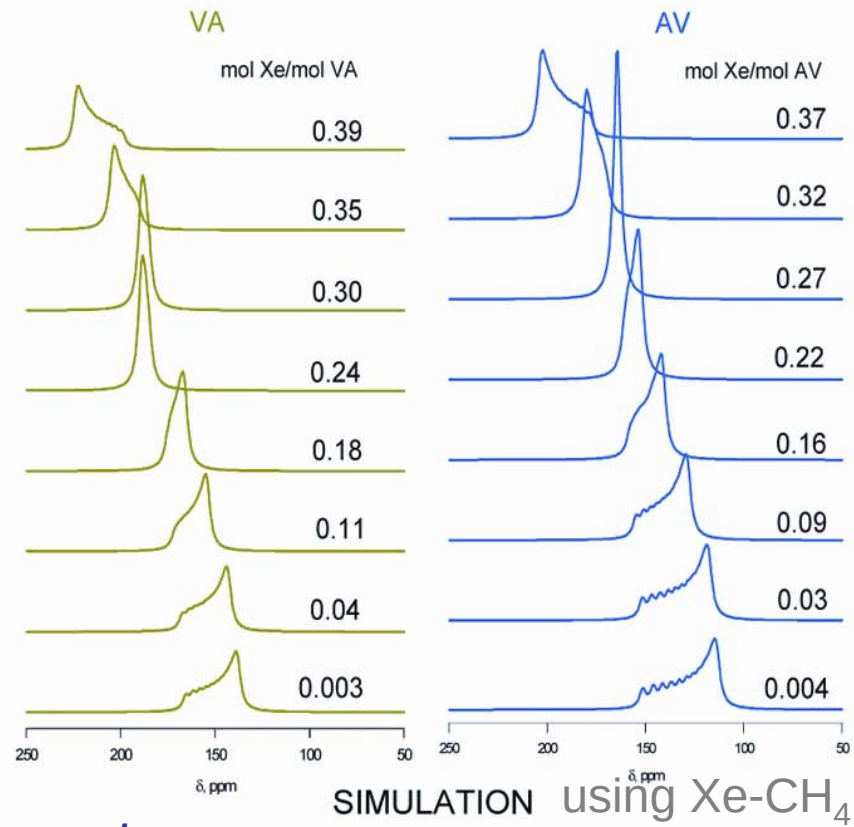


L-Ala-L-Val

AV

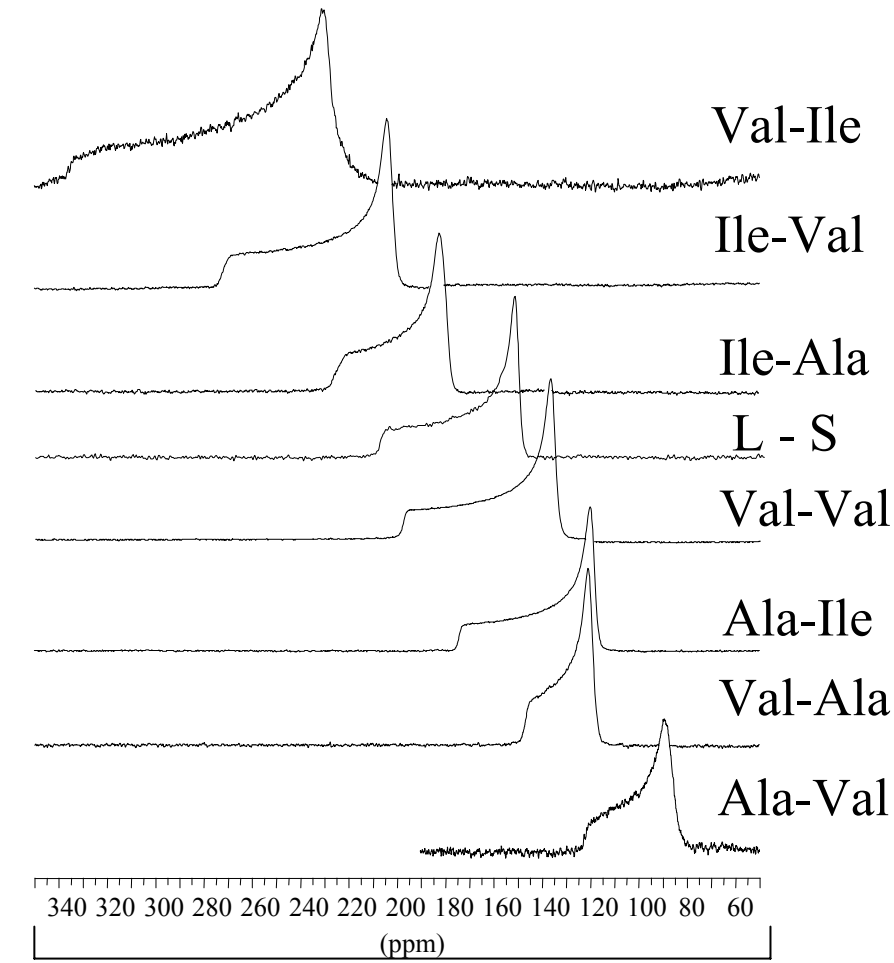
PNAS 101, 17924 (2004)





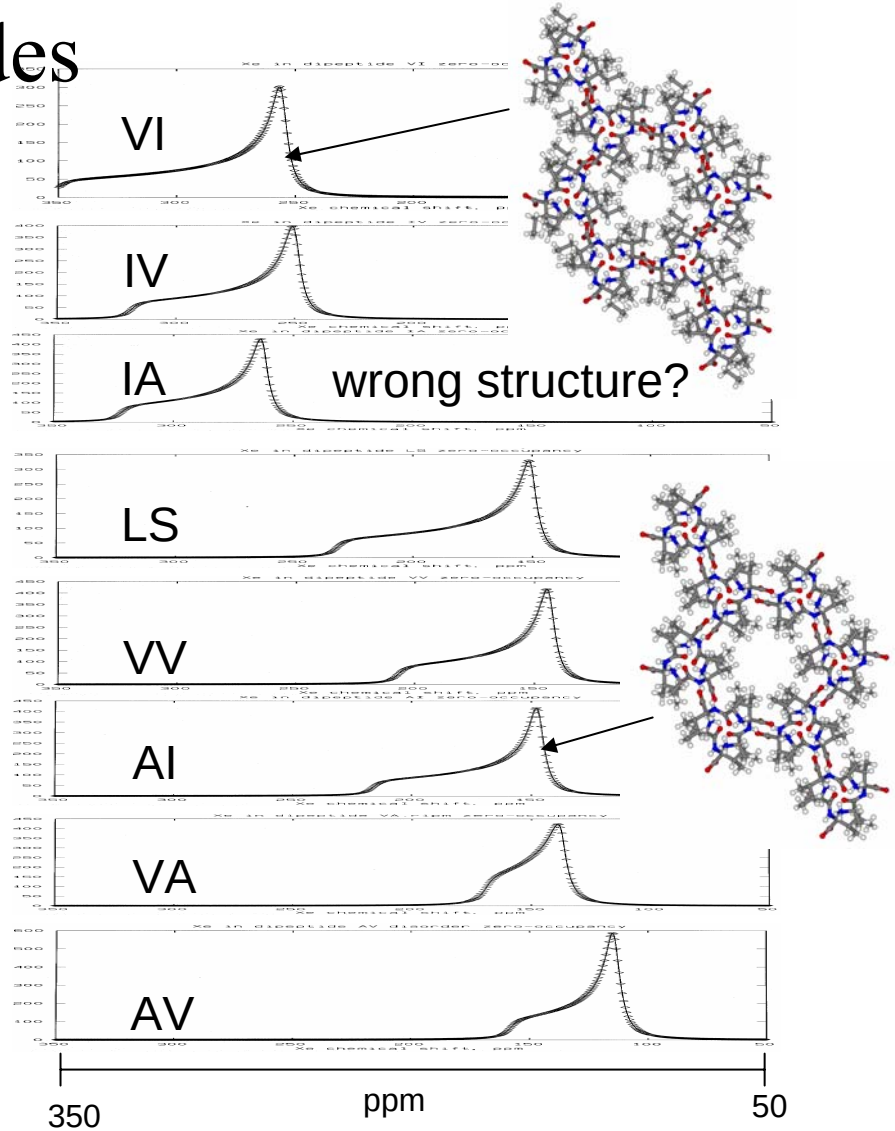
Xe NMR spectra

^{129}Xe NMR in dipeptides



350 50

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.

Xe on single crystal surfaces
EXPERIMENTS by Heinz Jänsch

- Xe at the surface of bulk xenon has a different signal than Xe in the bulk
- Xe can tell which surface it is in contact with
- Xe can tell how many other Xe are on the same surface
- The chemical shift tensor can be mapped out by rotating the single crystal in the magnetic field

Xe on model surfaces
Grand canonical Monte Carlo

- Xe on a –CO monolayer

  [using *ab initio* σ(Xe-Xe) and σ(Xe-CO) tensor functions]

- ^{129}Xe in a xenon sheet

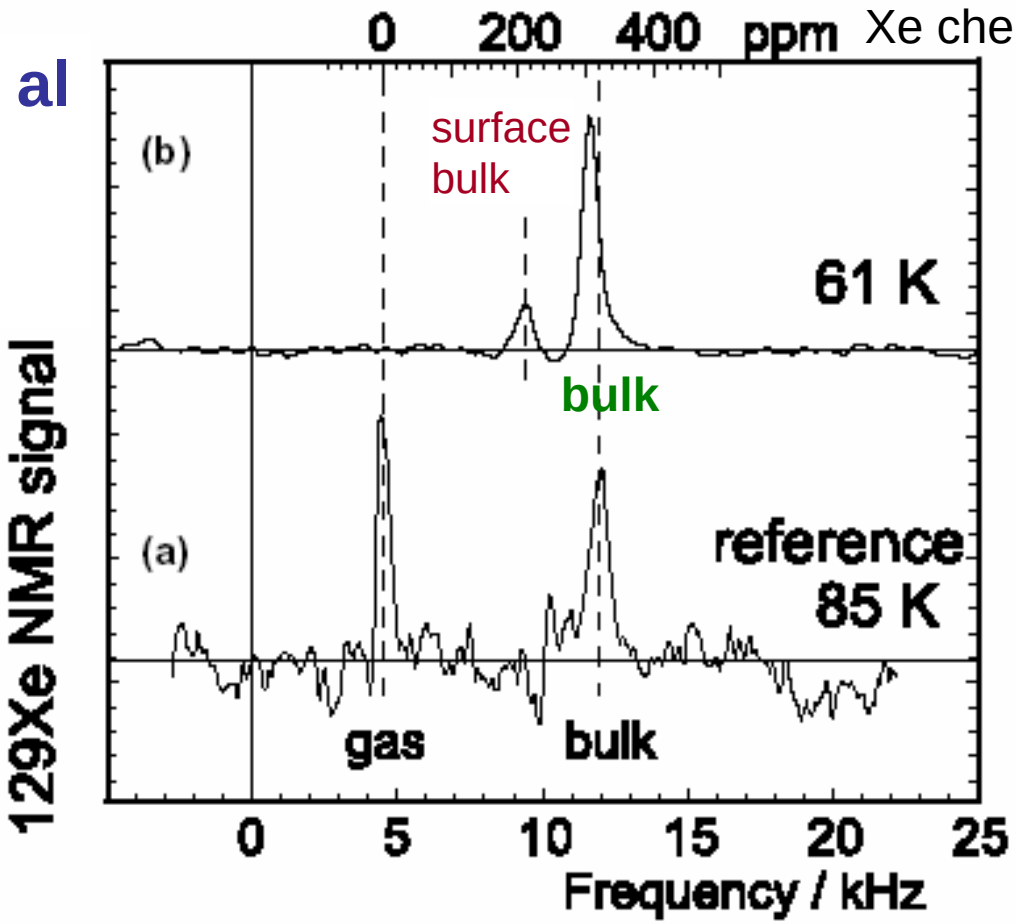
  [using *ab initio* σ(Xe-Xe) tensor function]

Deduce Xe coverage (θ_{Xe})
from observed chemical shift?

Xe on the surface of a single crystal metal surface

H.J. Jänsch et al

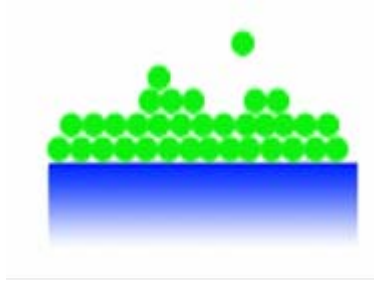
Chem. Phys. Lett.
372, 325 (2003)



The Xe atoms on the surface of the bulk Xe appear at 209 ppm while Xe in the middle of the bulk is at 321 ppm

WHY?

QUALITATIVELY



How many neighbor atoms?

- **Xe atoms on the <u>surface</u> of the bulk Xe appear at 209 ppm**

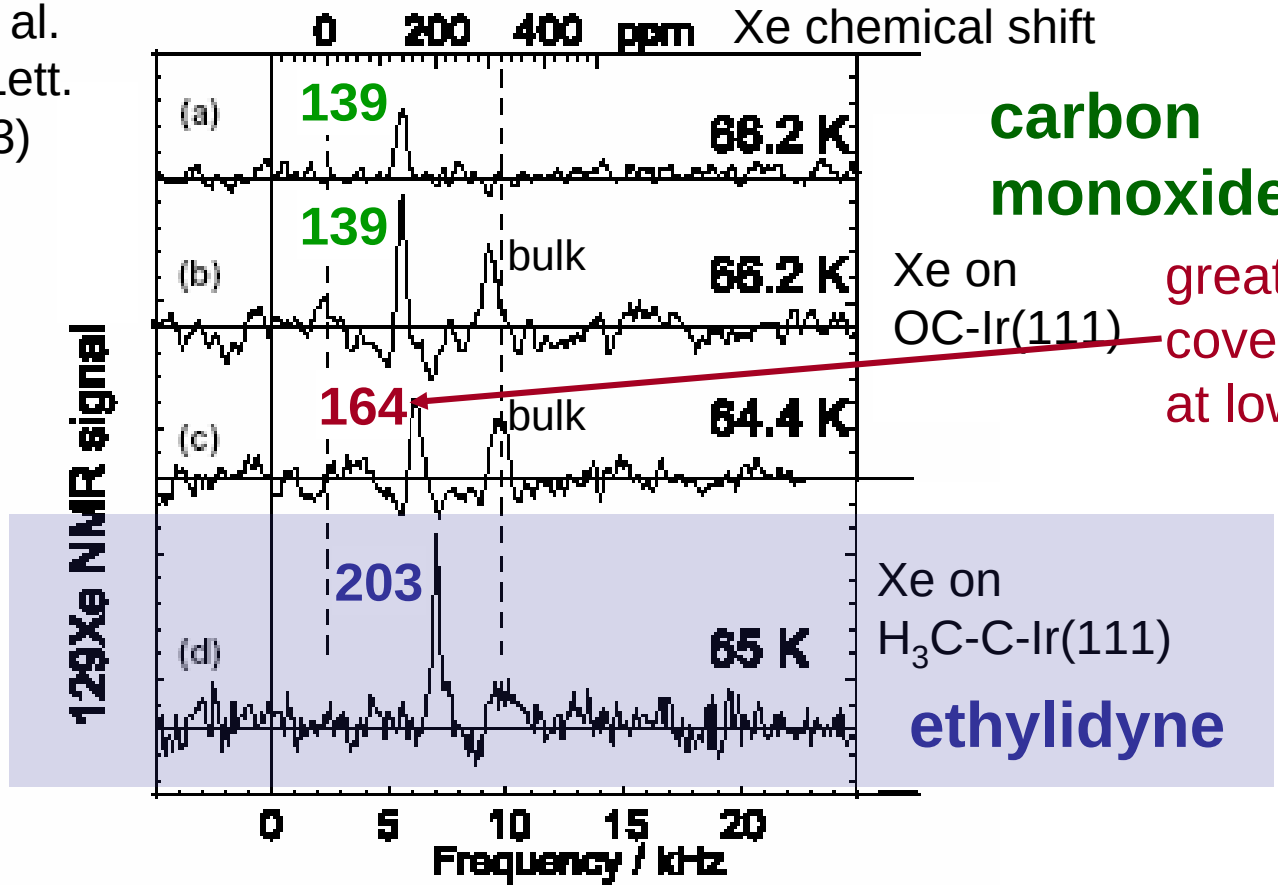
  $\sigma = \sum\sigma(r_{Xe\text{-}Xe})$ nearest (short $r_{Xe\text{-}Xe}$) neighbors are below and in same plane.

- **Xe in the middle of the bulk appear at 321 ppm**

  $\sigma = \sum\sigma(r_{Xe\text{-}Xe})$ nearest neighbors are below, <u>above</u>, and in same plane.

Xe on a chemically modified metal surface

H.J. Jänsch et al.
Chem. Phys. Lett.
372, 325 (2003)



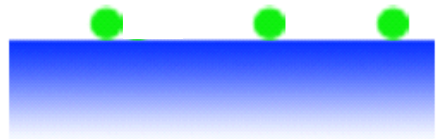
Xe can tell the difference between OC and H_3C-C surfaces.

Xe can report on surface coverage

QUALITATIVELY:

Xe @OC-Ir(111):

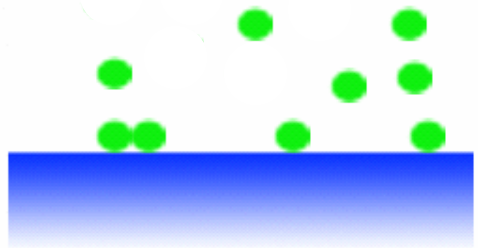
- At low Xe coverage, θ_{Xe} ,
  $\sigma = \sum\sigma(r_{Xe\text{-}O})$ only



- At lower T, larger θ_{Xe} ,

$\sigma = \sum\sigma(r_{Xe\text{-}O}) + \sum\sigma(r_{XeXe})$

once in a while, Xe runs into other Xe

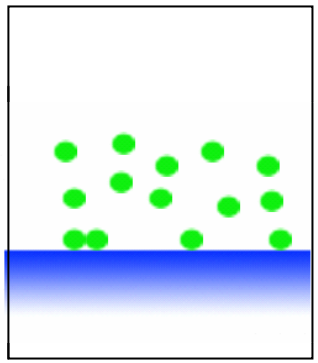


Xe can tell the difference between OC and H_3CC surfaces

- intrinsic shielding response from Xe-OC is greater than the shielding response from Xe-H_3C at same distance

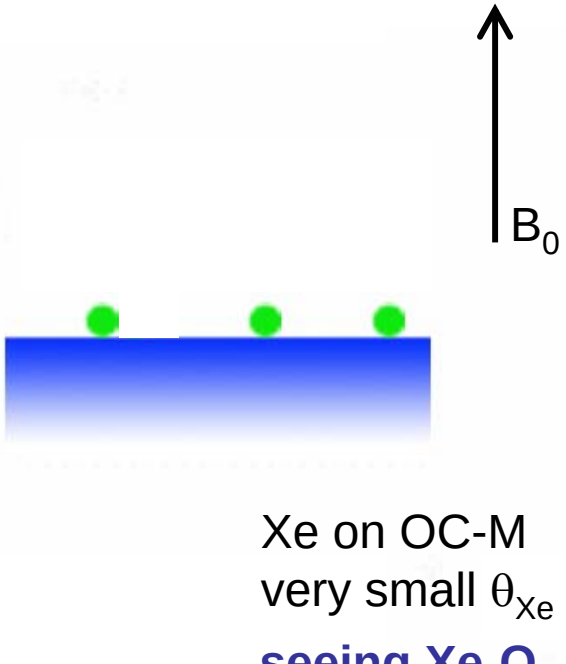
- however, potential functions permit Xe to stay closer to H_3C than OC, resulting in larger average Xe chemical shifts for the same coverage at the same temperature

GCMC simulations of Xe on surfaces



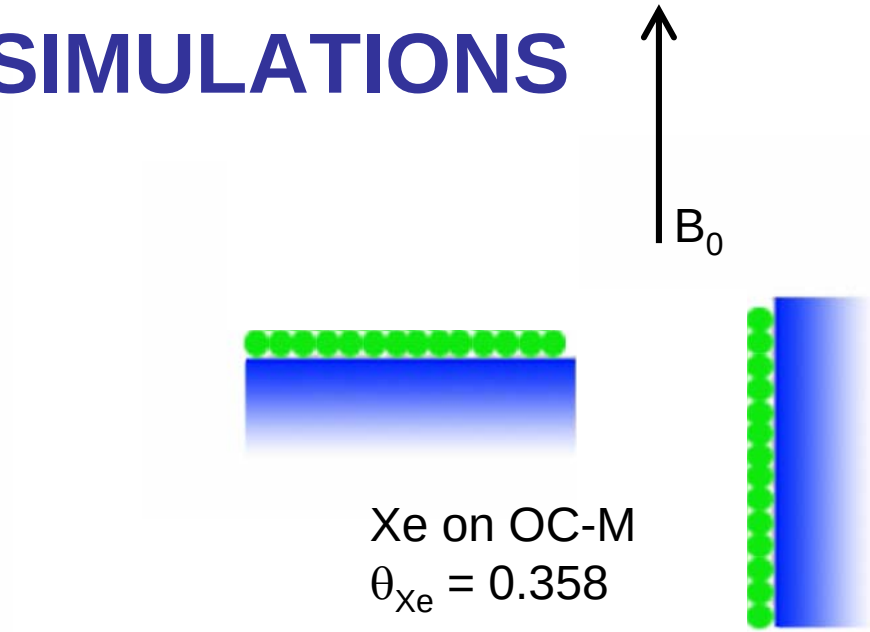
The chemical shift tensor can be mapped out by rotating the single crystal in the magnetic field

GCMC SIMULATIONS



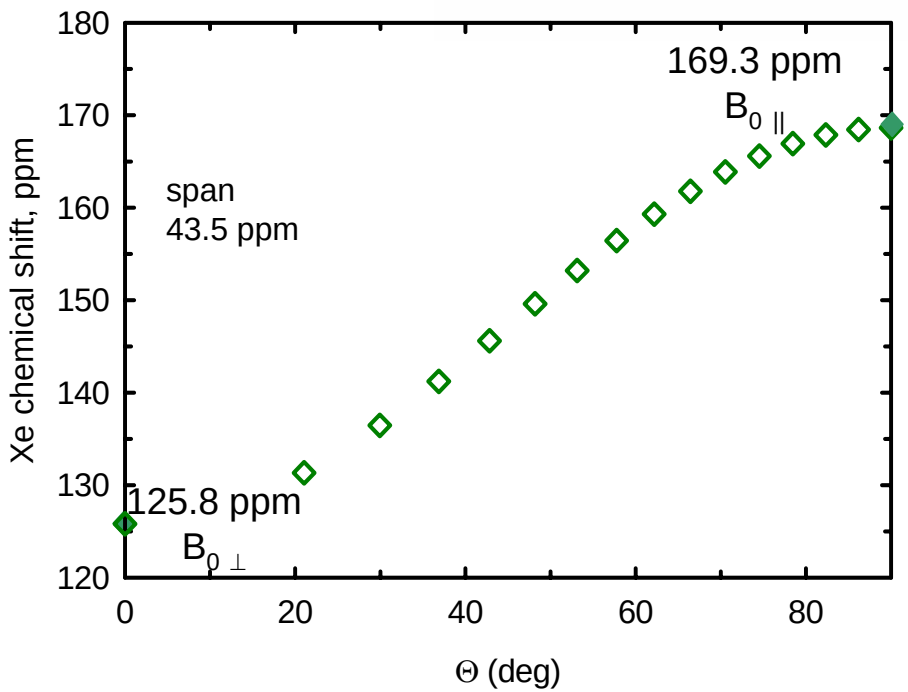
Xe on OC-M
very small θ_{Xe}

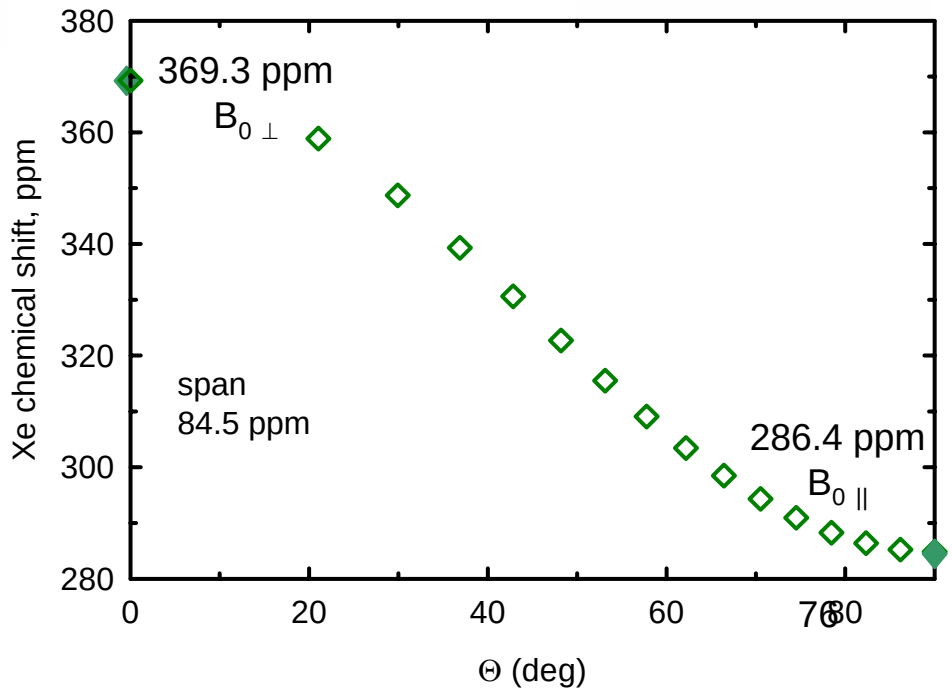
seeing Xe-O



Xe on OC-M
θ_{Xe} = 0.358

seeing Xe-O and Xe-Xe

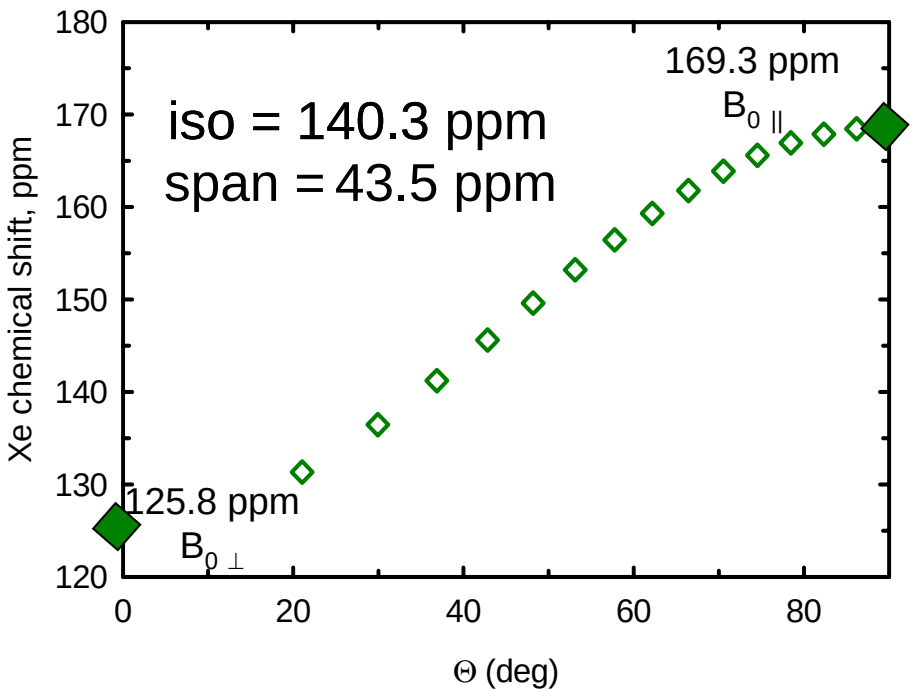




Comparison with Jänsch's experiments

Xe on OCIr(111)
very small θ_{Xe}

GCMC SIMULATIONS



Xe on OCIr(111)
small θ_{Xe}

EXPERIMENTS

iso = 165.2 ppm
span = 56.7 ppm

the same angle dependence

- The **difference between CO and ethylidyne is predictable** from isolated Xe-OC, Xe-H_3CH shielding response

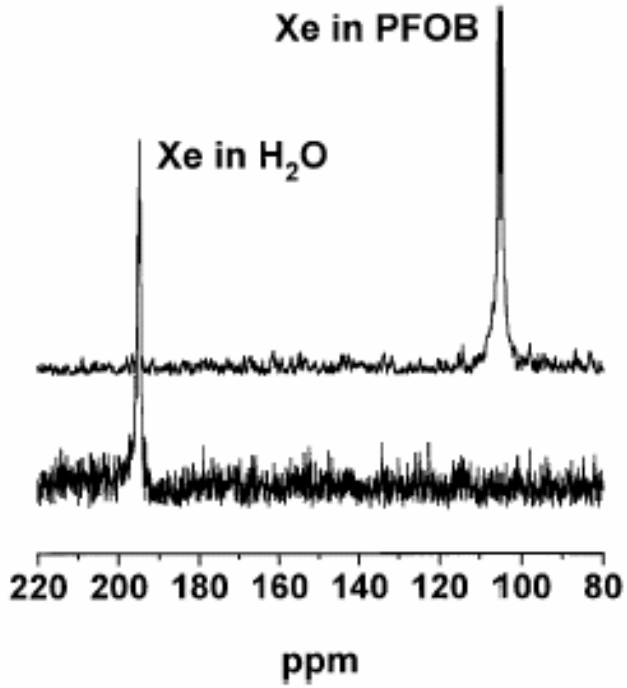
- **Dependence on crystal orientation in the field is reproduced.** For sample geometry, the dominant Xe dimer is, respectively, perpendicular (Xe-O) or parallel (Xe-Xe) to the crystal surface

- **Can deduce Xe coverage from chemical shift**, very sensitive because each Xe-Xe contribution larger than Xe-OC or Xe-H_3C

The chemical shift tensor can be mapped out by rotating the single crystal in the magnetic field

- Our GCMC simulations predict the average Xe chemical shift **tensor**
- Component along the field direction is qualitatively predictable from knowing only the numbers and types of neighbors that Xe has in the plane containing the Xe atom in question and perpendicular to the field direction

Xe in liquids



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

- instantaneous solvent cage sizes and shapes
- accurate representation can only be accomplished by molecular dynamics (MD)
- Molecular Dynamics simulations provide quick convergence of Xe chemical shift

Previous interpretations of Xe chemical shifts in liquids

- Strictly empirical (refractive index)
- Based on dispersion model of chemical shift
- No explanation for intercepts in correlation plots

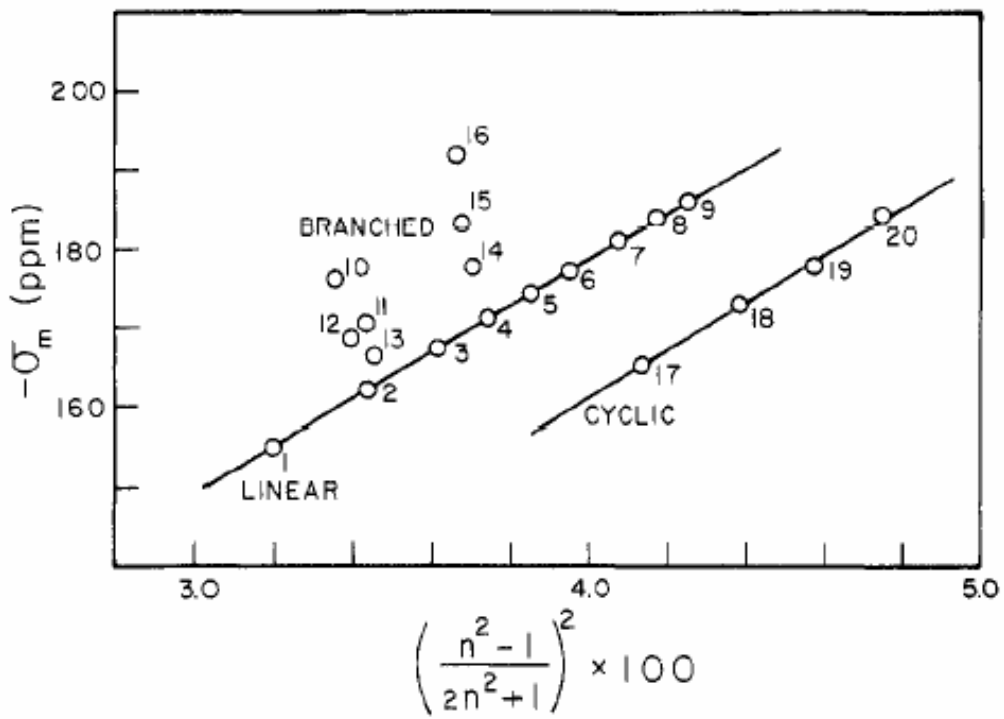
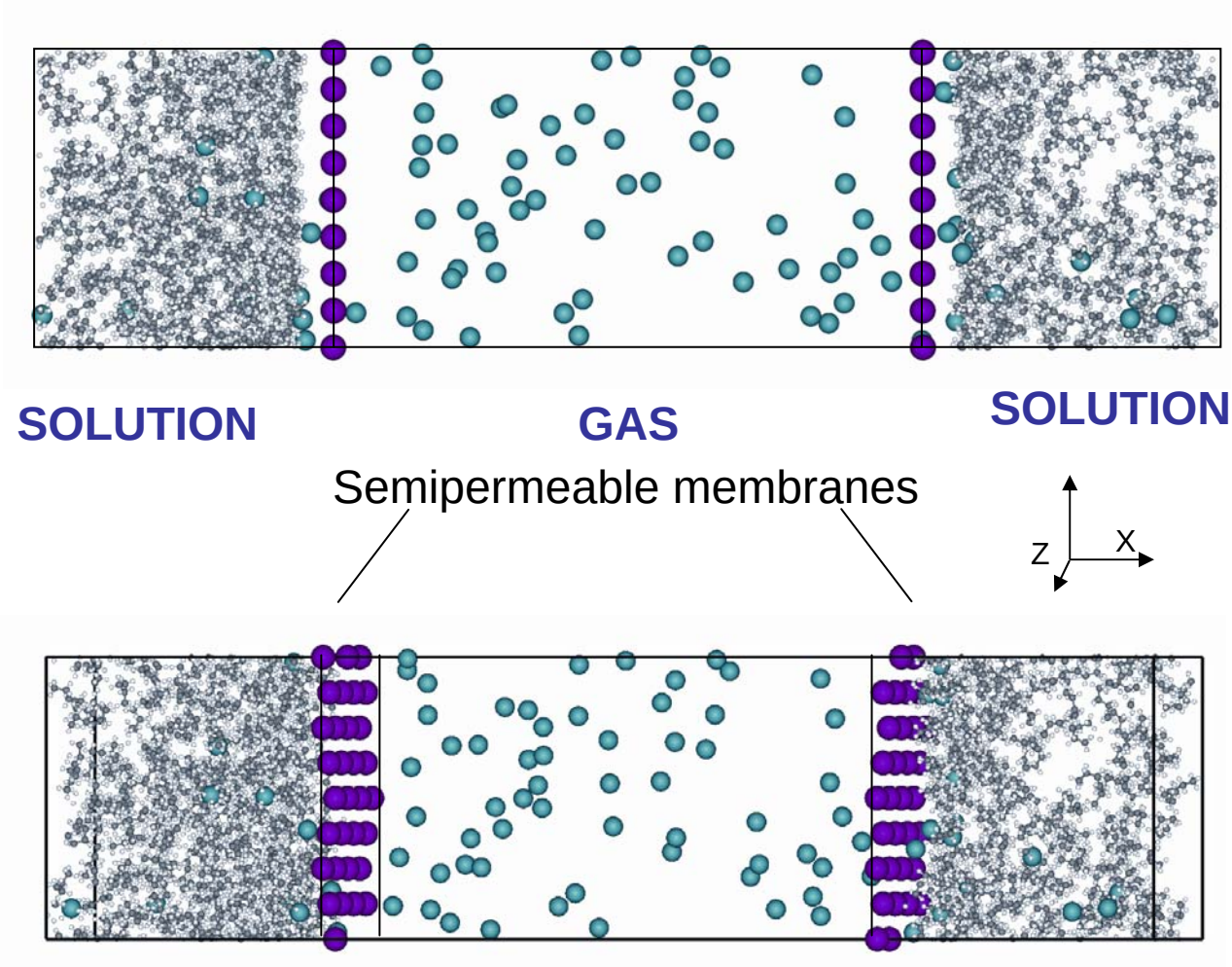
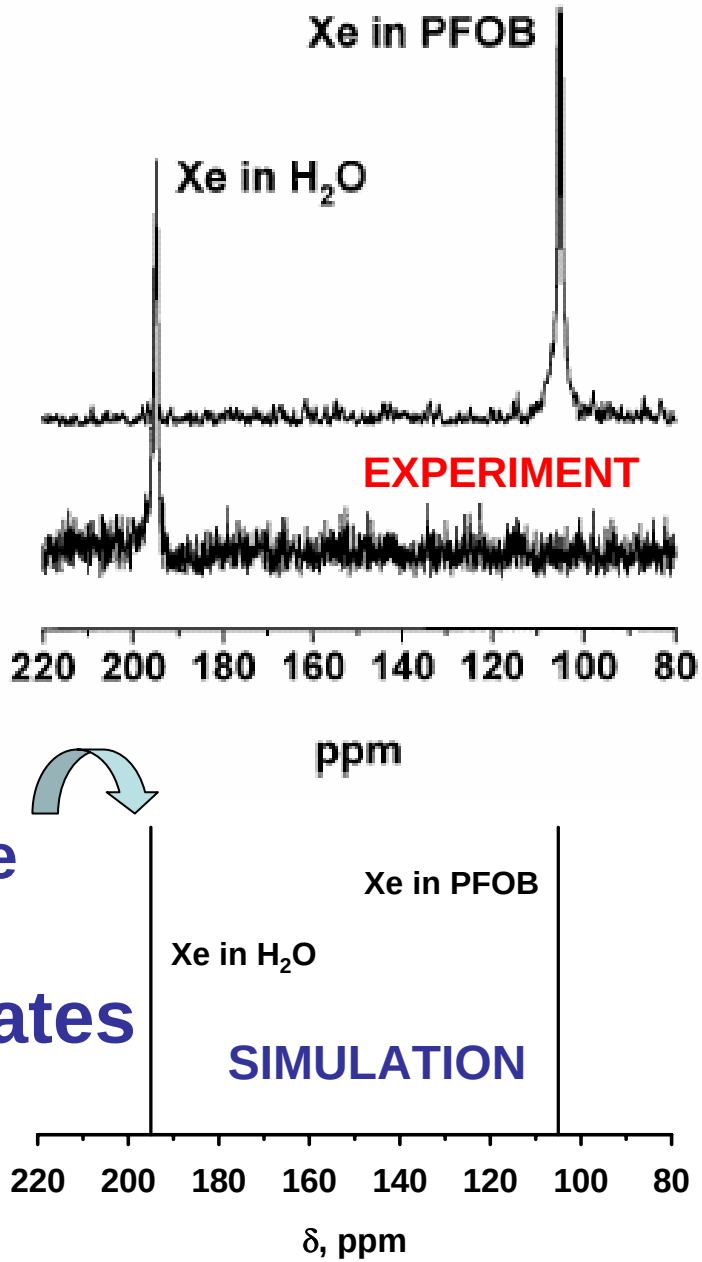


Figure taken from: Stengle et al., J. Phys. Chem. 85, 3772 (1981).

MD Simulation Box



MD Simulation box design: Murad et al, Fluid Phase Equil. 187-188, 29 (2001)
Murad et al, Chem. Phys. Lett. 319, 60 (2000)

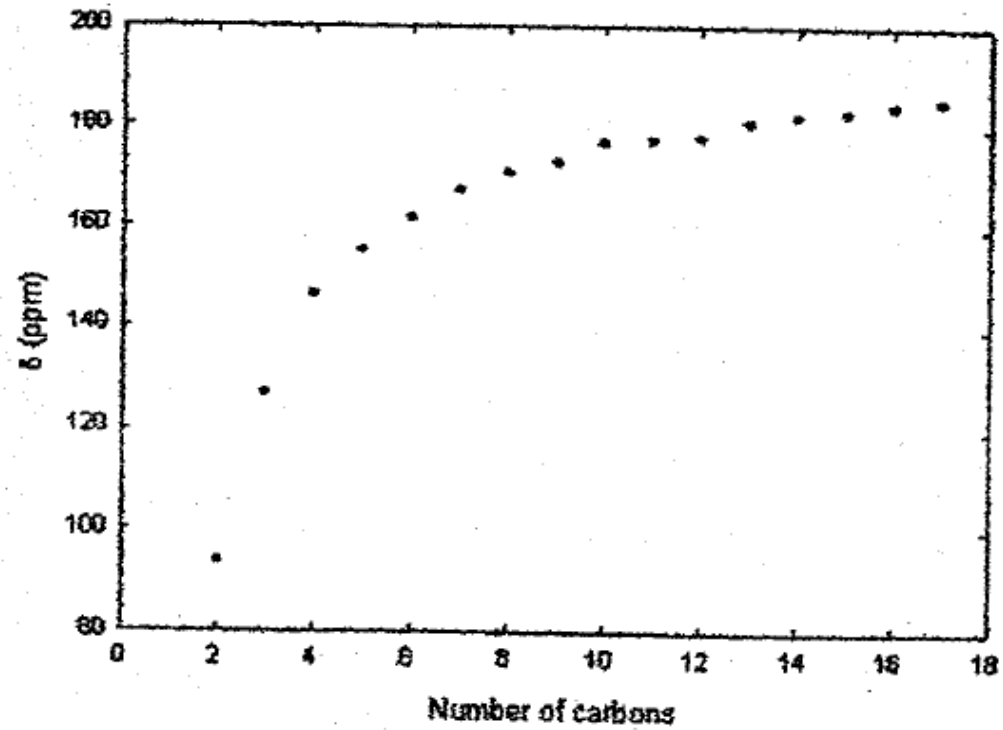


Bifone et al, Magn. Reson. Medicine 41, 442 (1999).

Using quantum mechanical Xe shielding surface calculated for clathrate hydrates

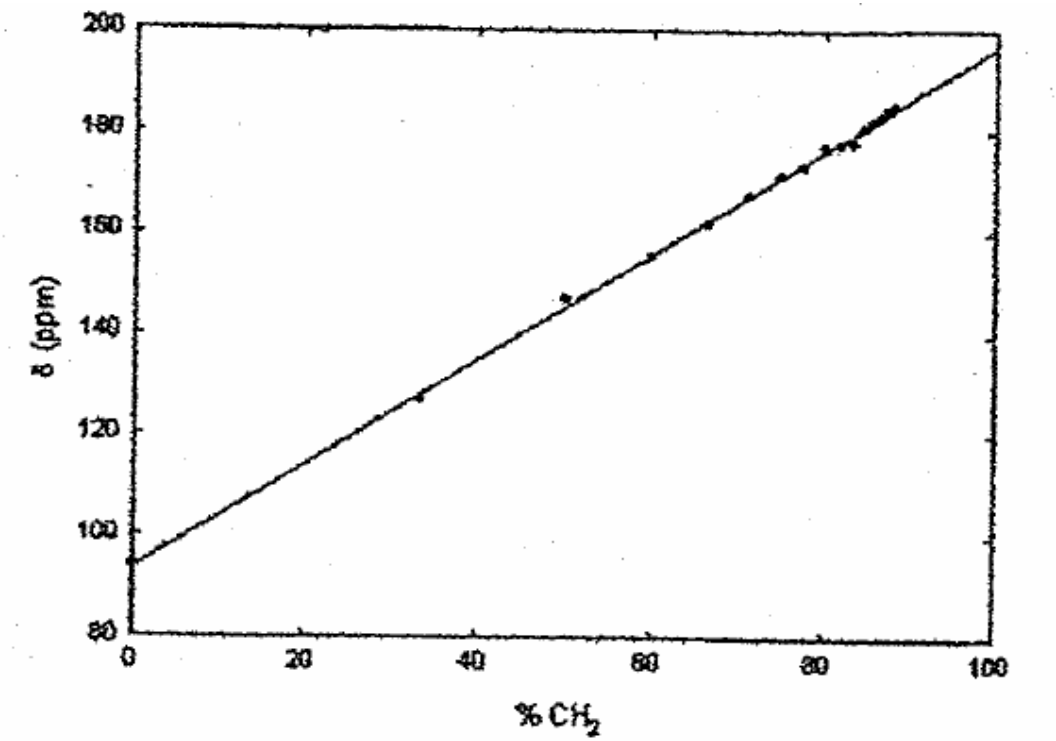
C. J. Jameson, D. N. Sears, S. Murad, J. Chem. Phys. 121, 9581 (2004)

Dependence of Xe chemical shift on number of carbons in linear alkanes



Lim et al., J. Phys. Chem. 1993

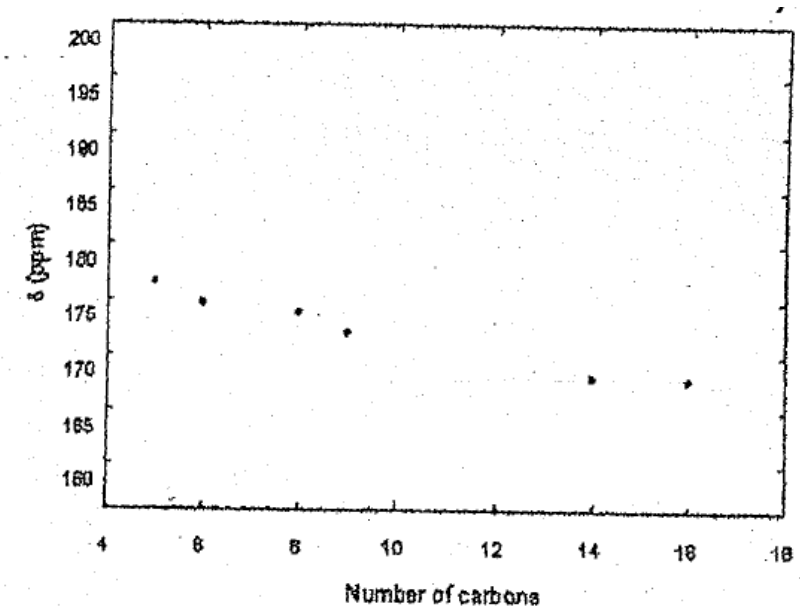
Dependence of Xe chemical shift on $\%CH_2$ in linear alkanes

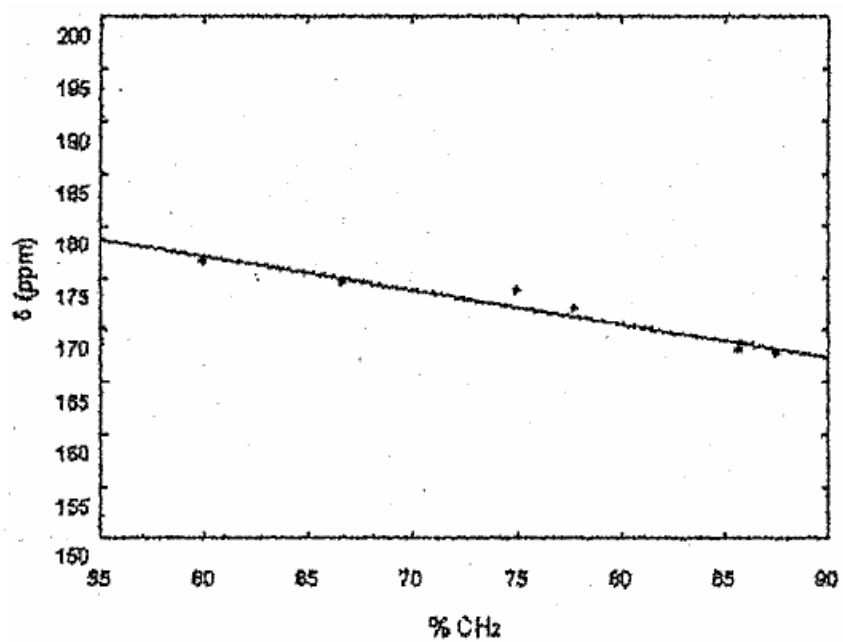


Lim et al., J. Phys. Chem. 1993

Appears counter-intuitive! What is wrong here?

R. Bonifacio & Eduardo J.M. Filipe: XeMAT 2000: Compare Xe chemical shift in the liquids at same thermodynamic state, at T* = 0.5

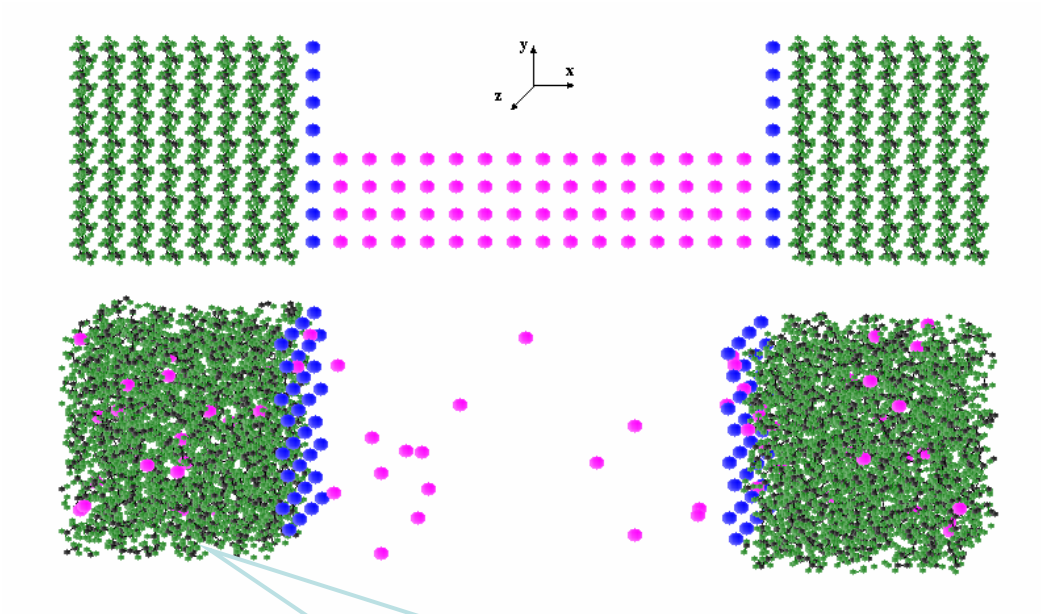




Looks more like what we should expect

Simulation System

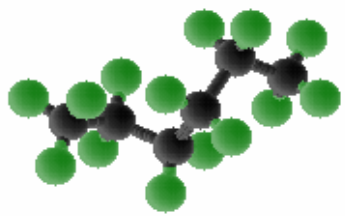
Xe and *n*-hexane



initial

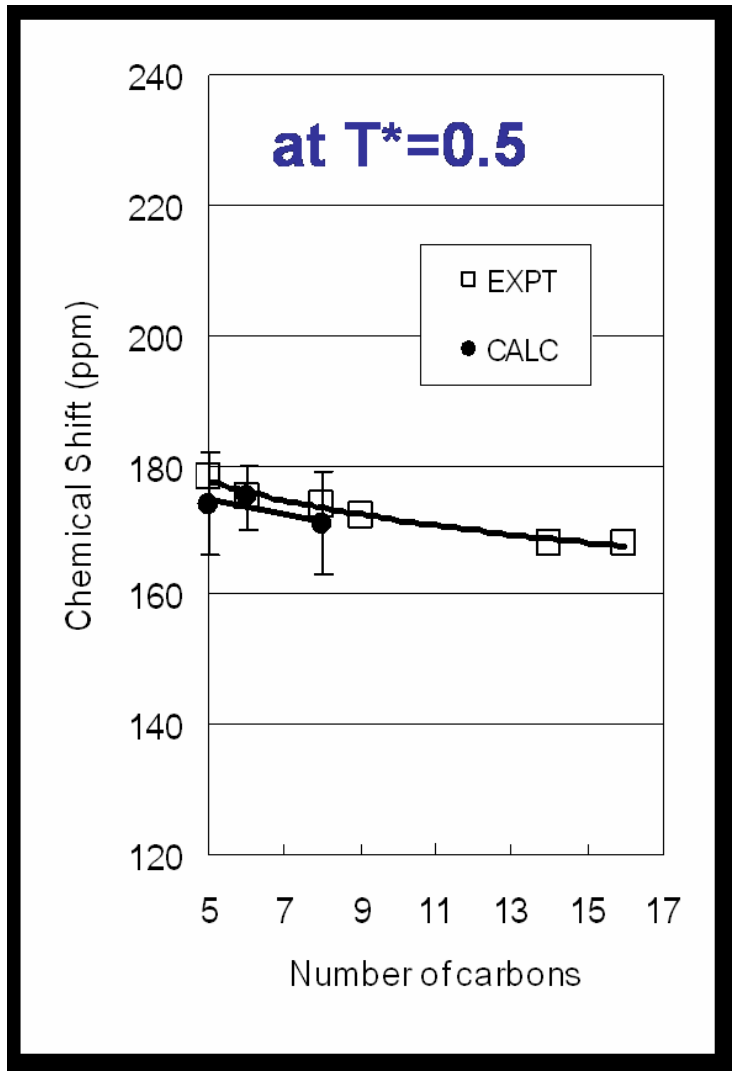
10 ns

Typical n-hexane structure:



Comparable chemical shifts in solution

Xe chemical shift at the same thermodynamic state

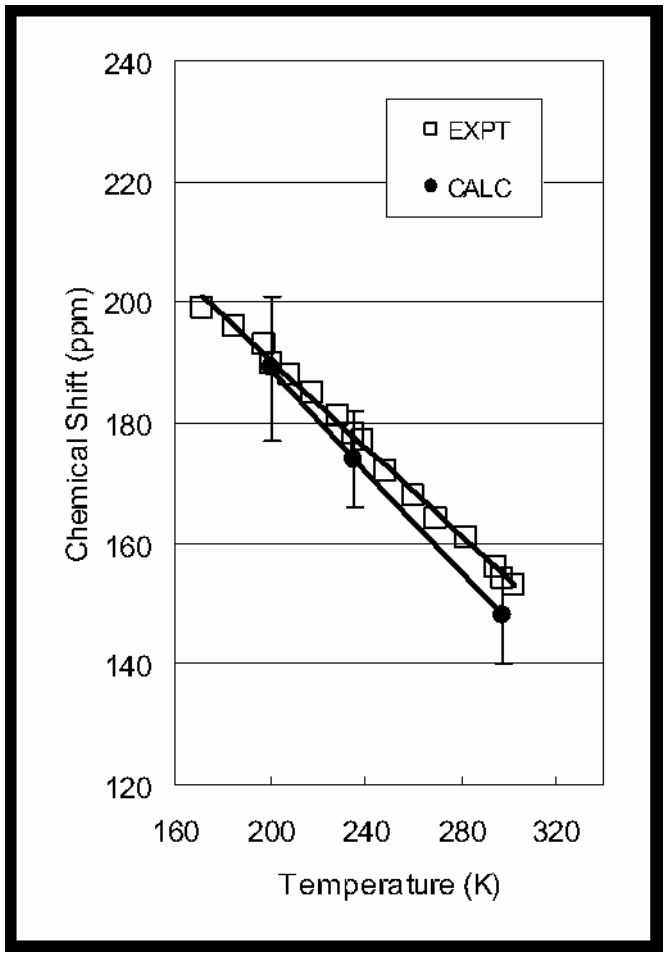


- EXPT: R. Bonifacio & E. J. M. Filipe, XeMAT 2000
- Molecular Dynamics simulations

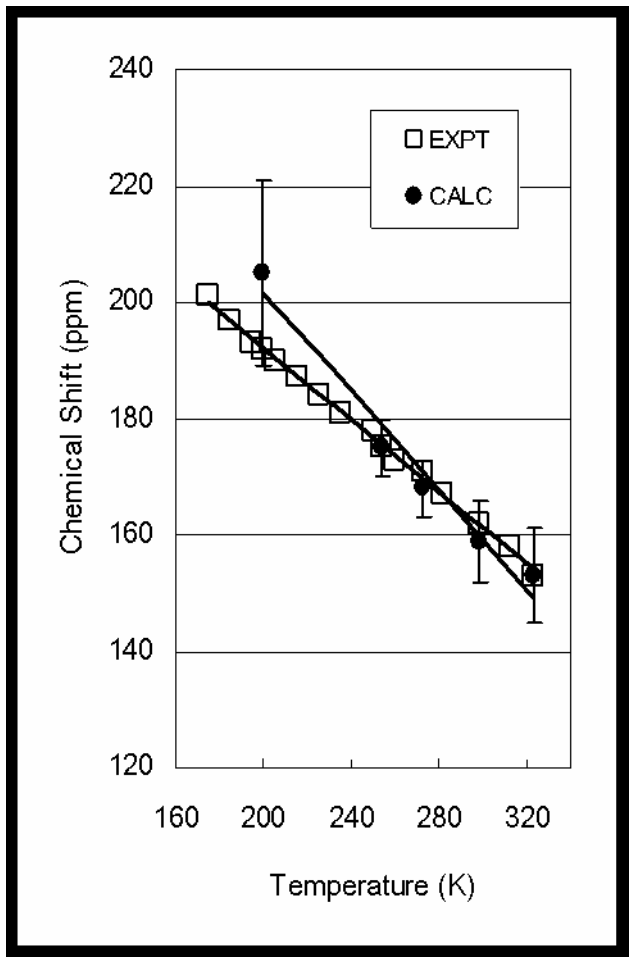
J. Phys. Chem. C, 111, 15771-15783 (2007).

Xe chemical shift temperature dependence

n-pentane :



n-hexane :

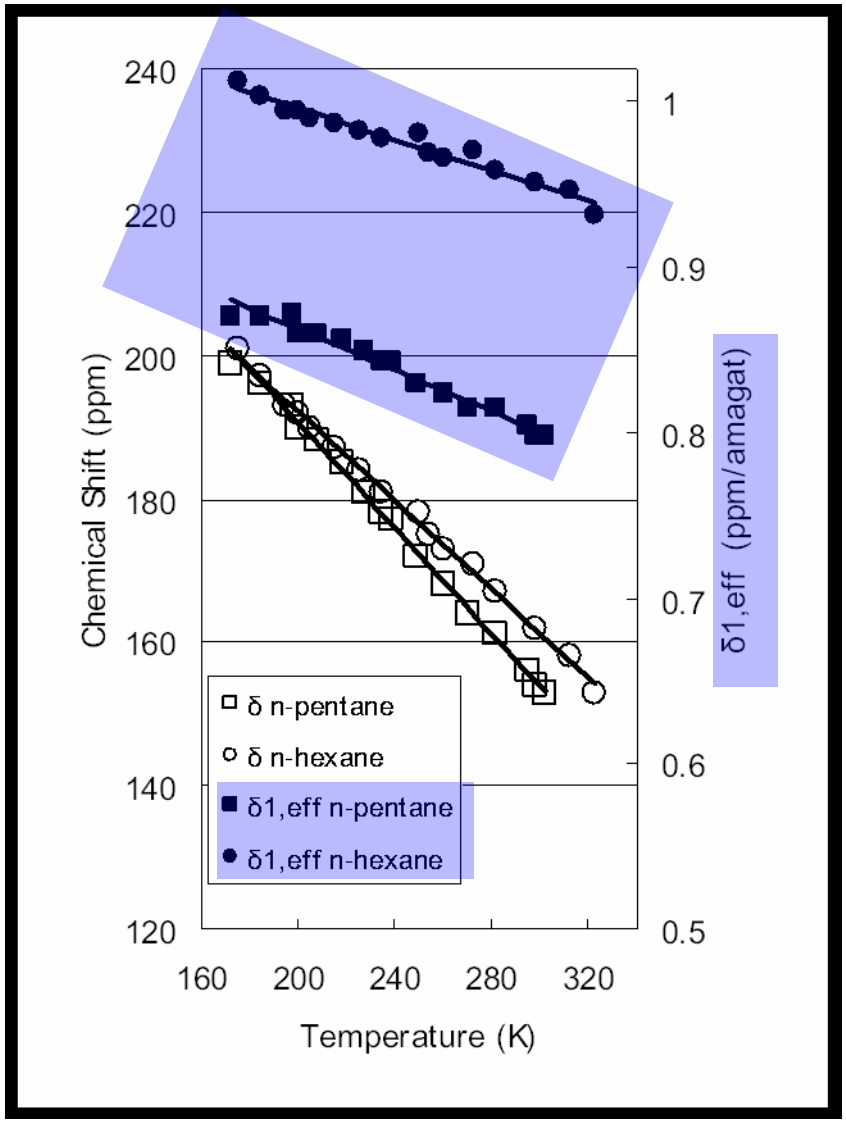


Molecular Dynamics simulations results

J. Phys. Chem. C, 111, 15771-15783 (2007).

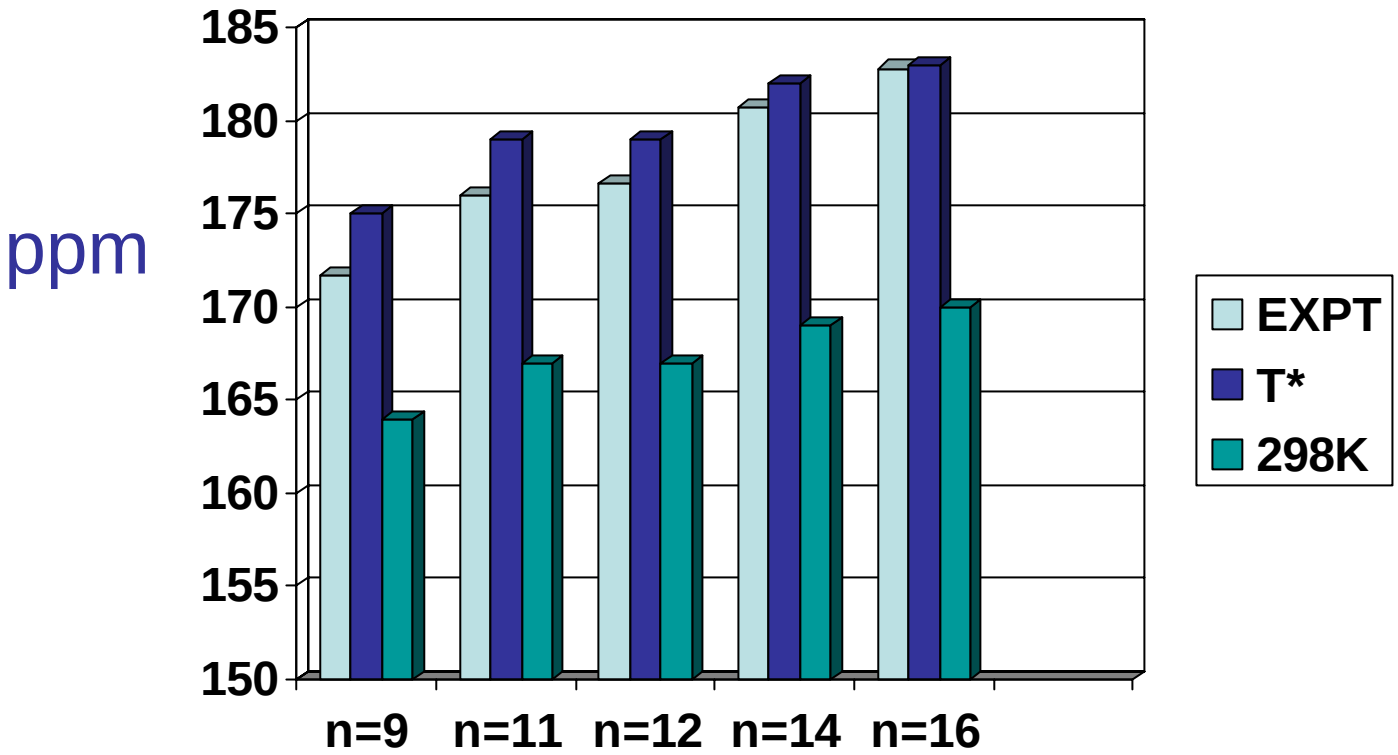
Contributions to the temperature dependence of Xe chemical shifts

T dependence of the solvent density is responsible for most of the observed steep T dependence of Xe chemical shifts in solution



divide out the density to get δ_1

Prediction of Xe chemical shifts in *n*-alkanes from constitutive contributions based on simulations for Xe in C_nH_{2n+2}, n = 4, 5, 6, 8 calculated at T*=0.5, or calculated at T=298

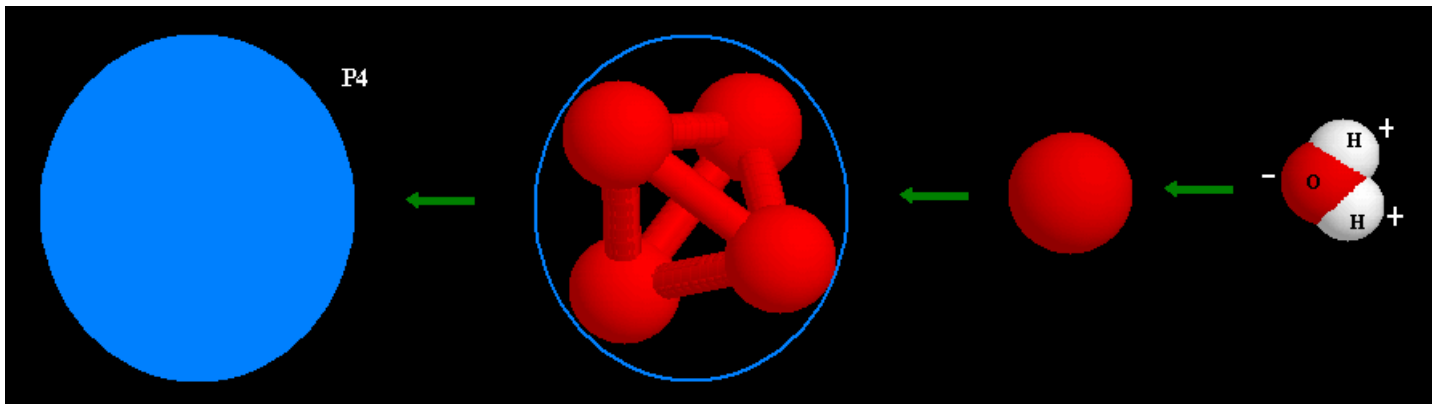


at T*=0.5: CH_2 3.1 ppm/ (mole L^{-1}) CH_3 4.7 ppm/ (mole L^{-1})

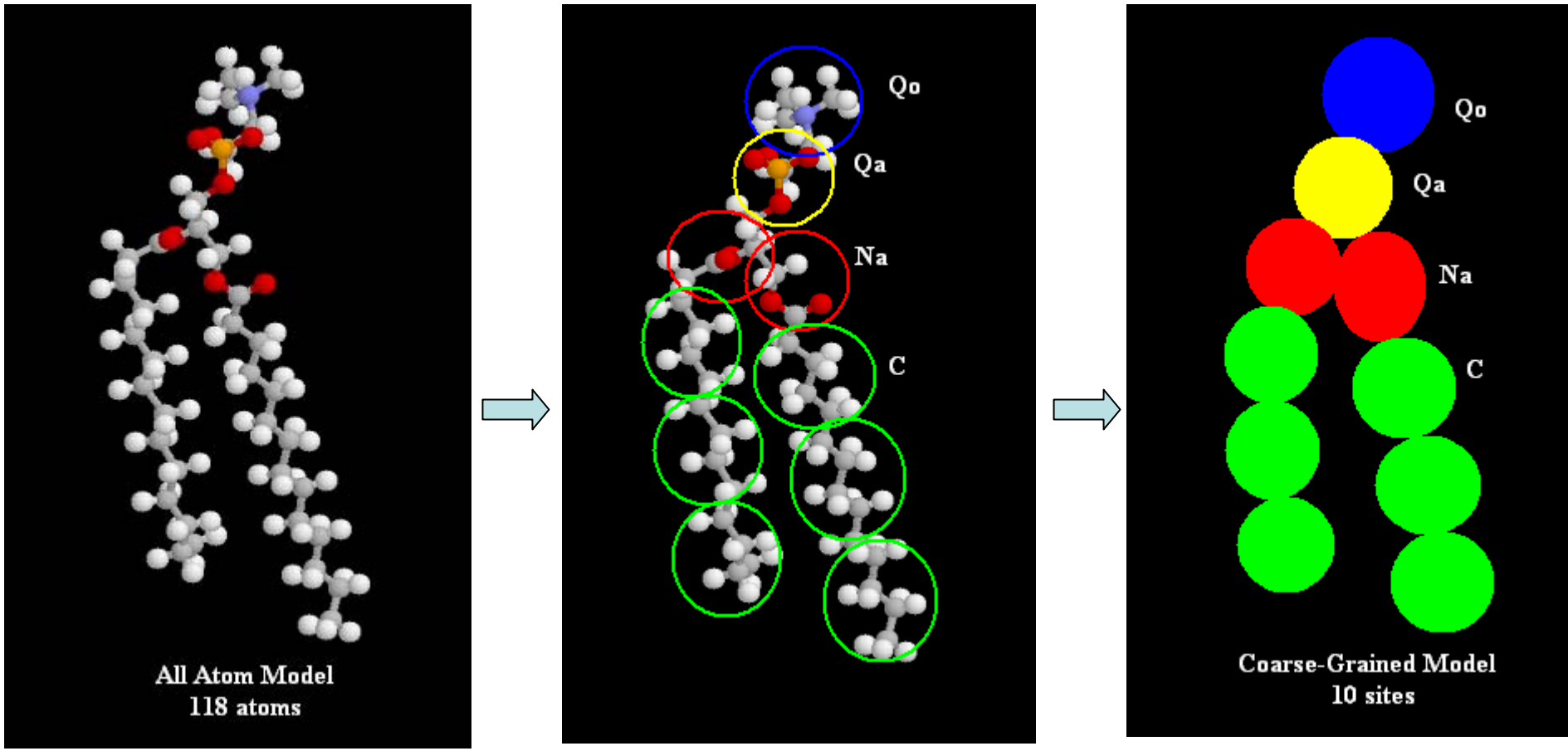
Coarse grain force field

MARTINI force field by Marrink et al J.Chem.Theory and Comput. 2008, 4, 819-834

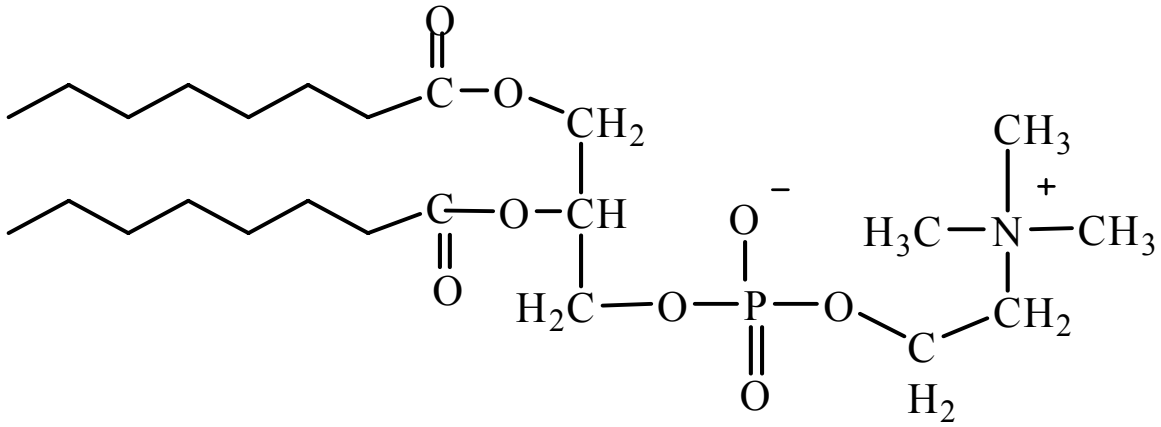
Coarse grain mapping strategy
4 → 1



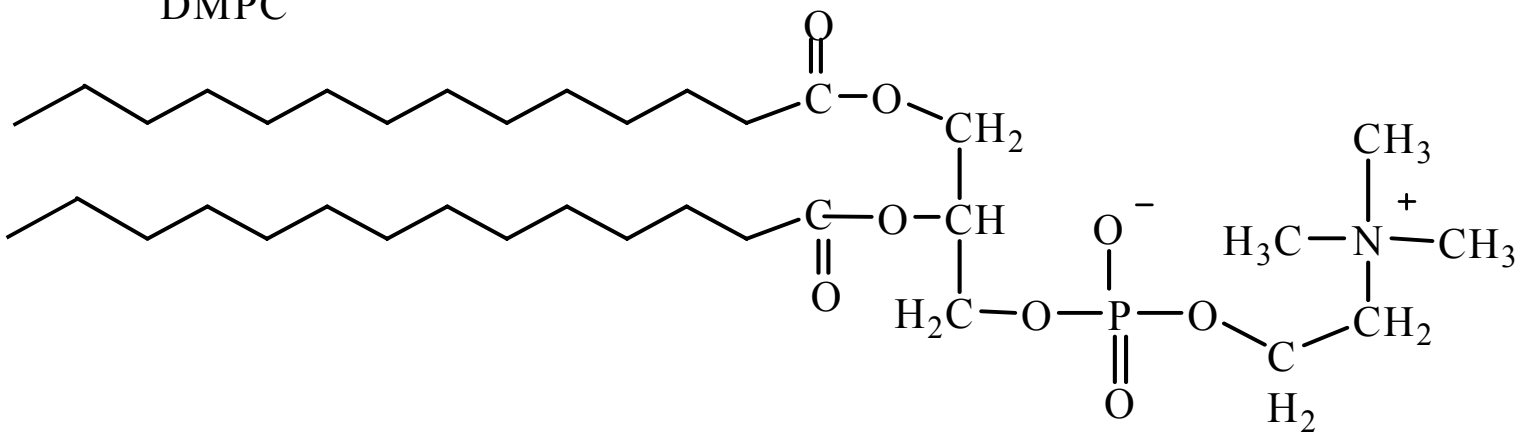
Lipid (DMPC):


All Atom Model
118 atoms
Qo
Qa
Na
C
Qo
Qa
Na
C
Coarse-Grained Model
10 sites

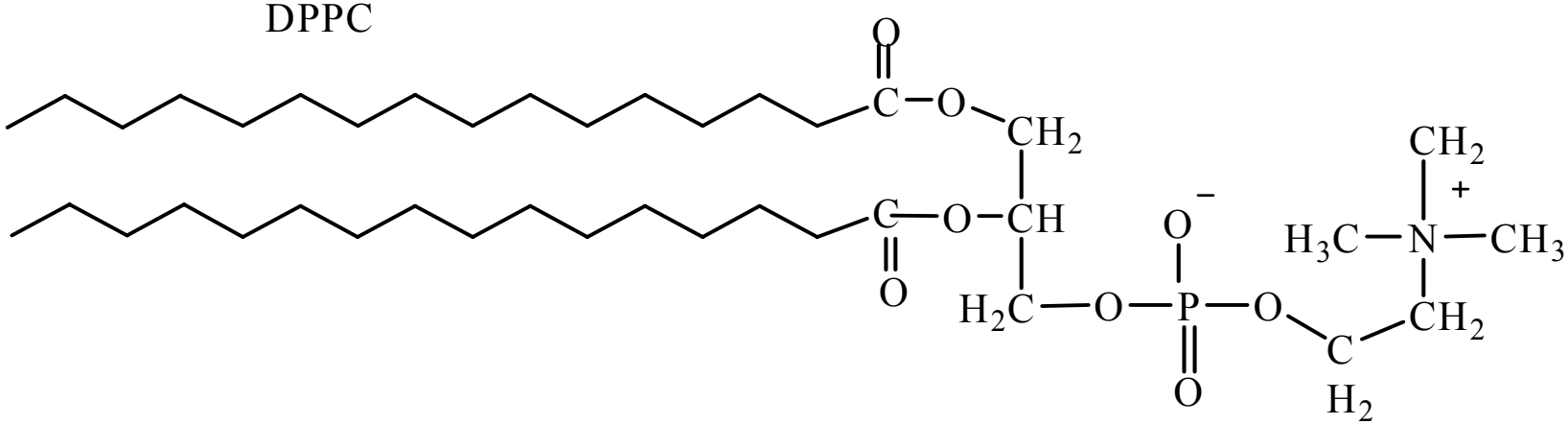
DCPC

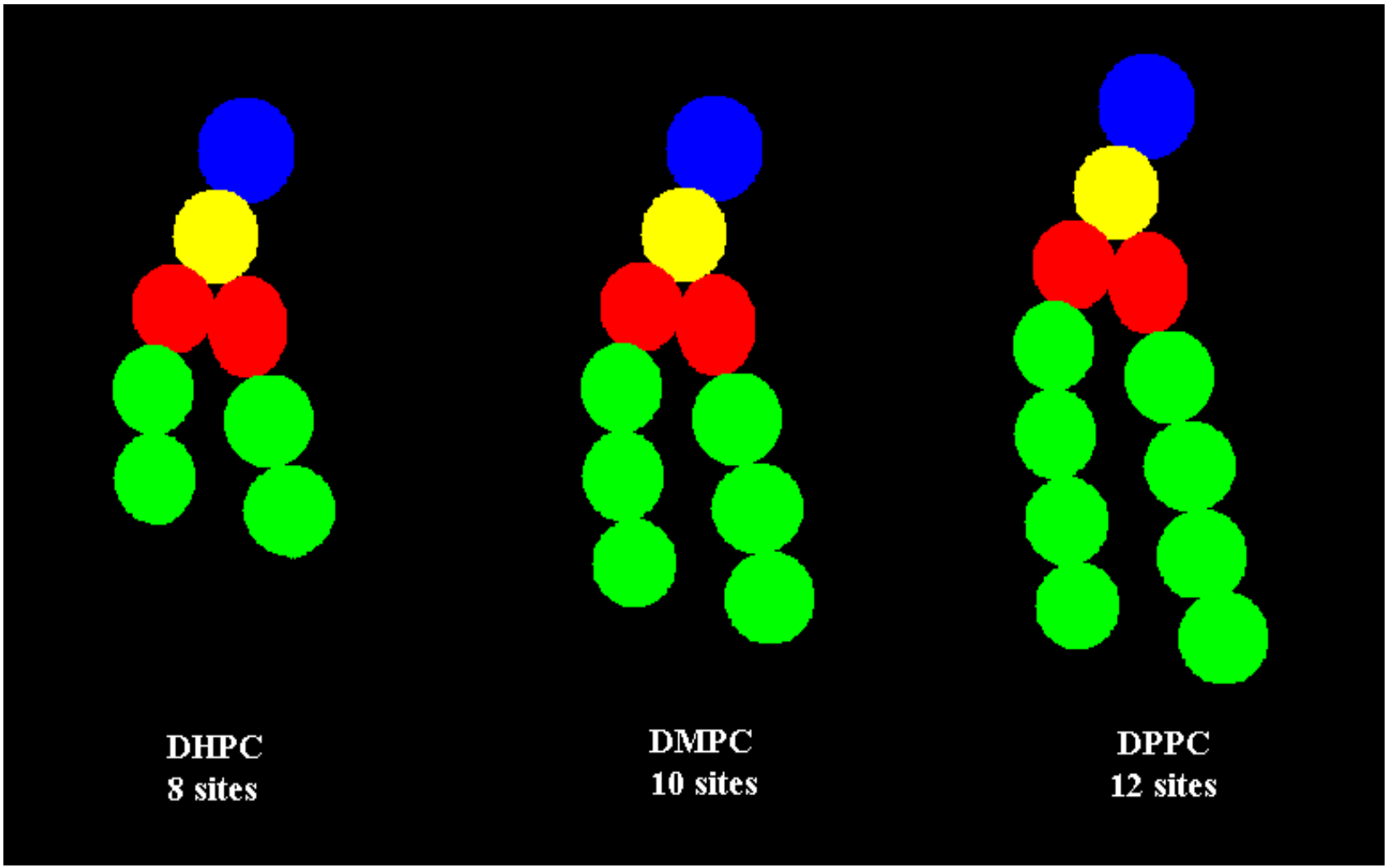


DMPC

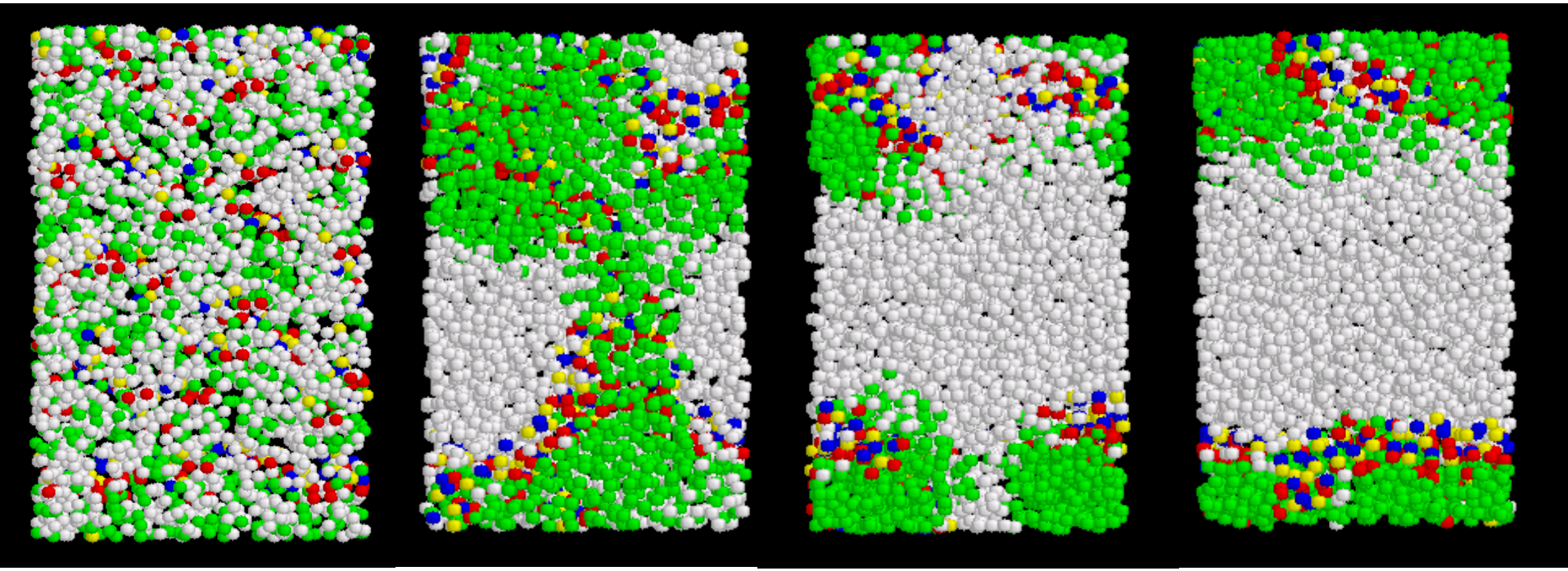


DPPC



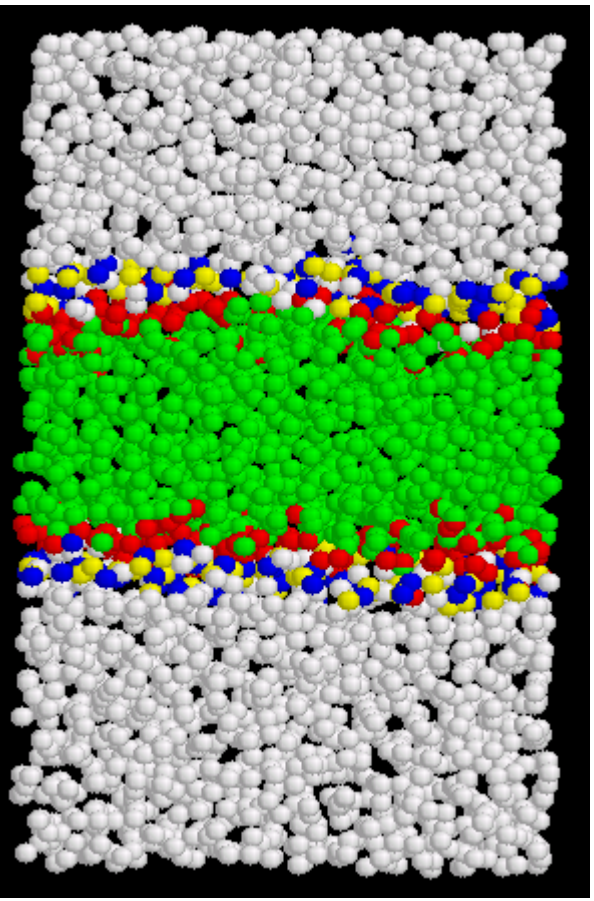

DHPC
8 sites
DMPC
10 sites
DPPC
12 sites

Self-Assembly occurs at 323K :

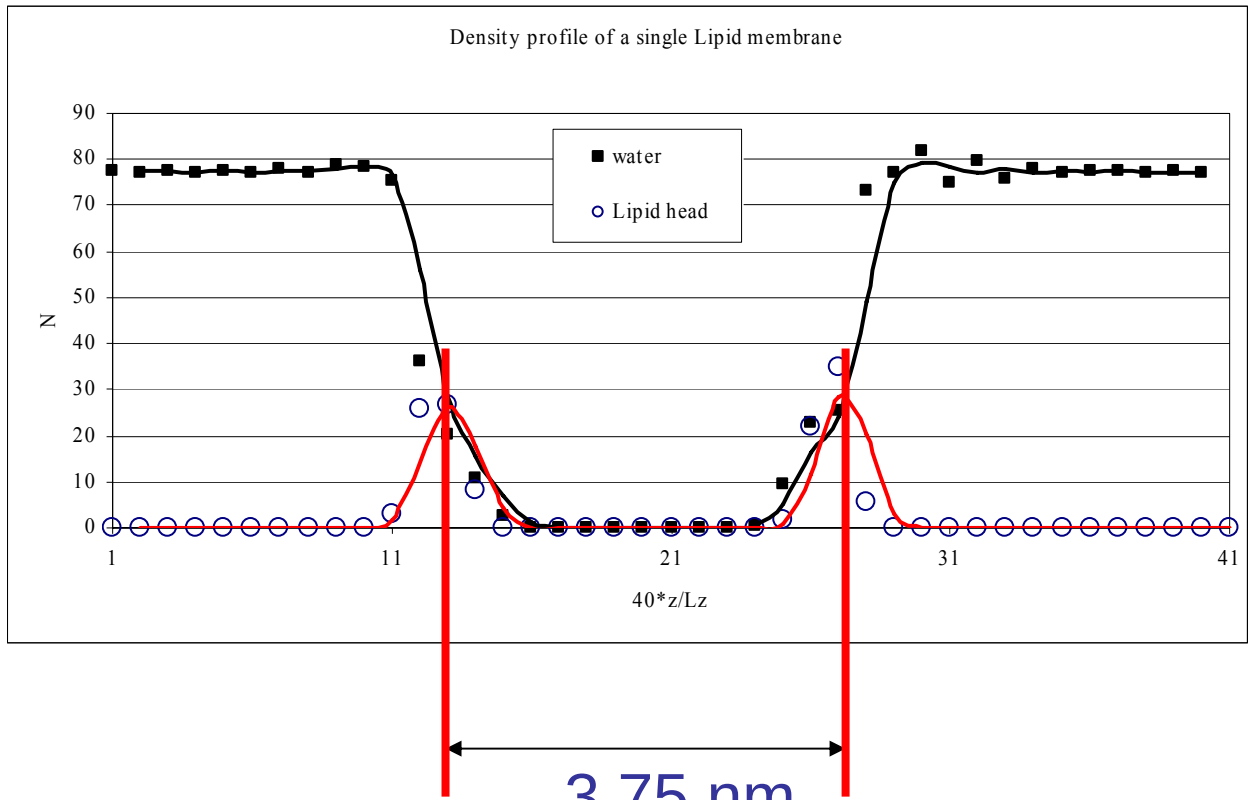


t = 0 ns t = 1 ns t = 10 ns t = 100 ns

Lipid Bilayer in water at 323K: 128DPPC+2000H_2O



Density profile at equilibrium

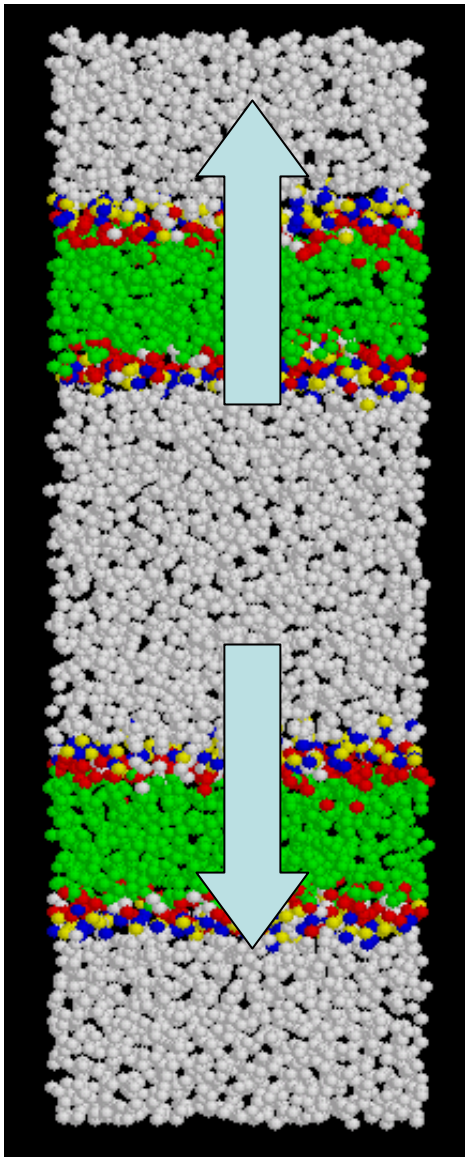


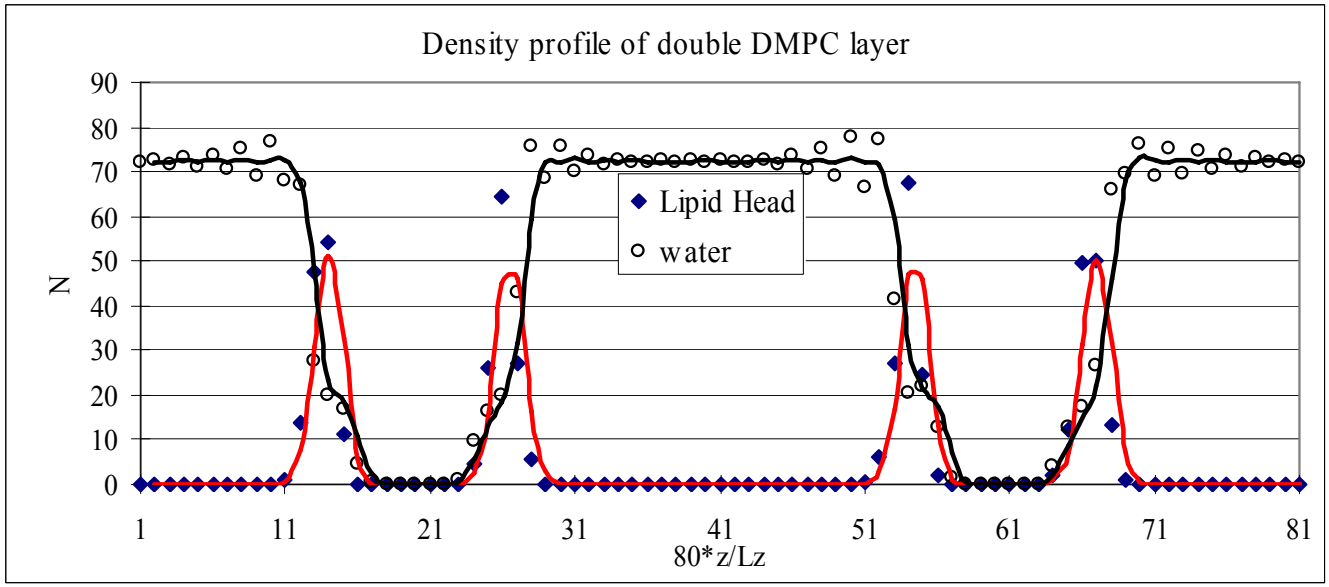
3.75 nm

Expt. 3.85 nm

Ref. Marrink et al, J.Phys.Chem B 2004, 108, 750-760

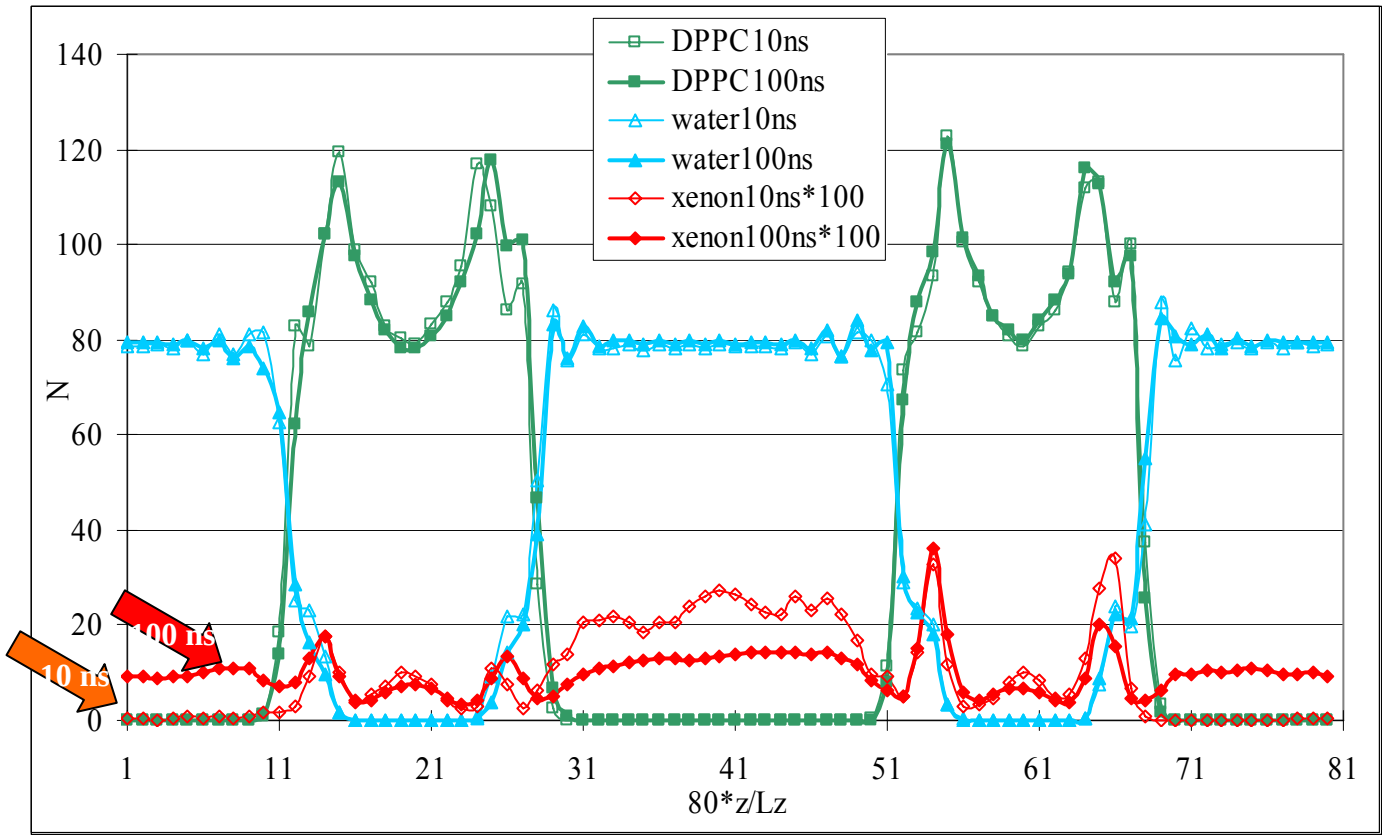
Simulation box for transport studies





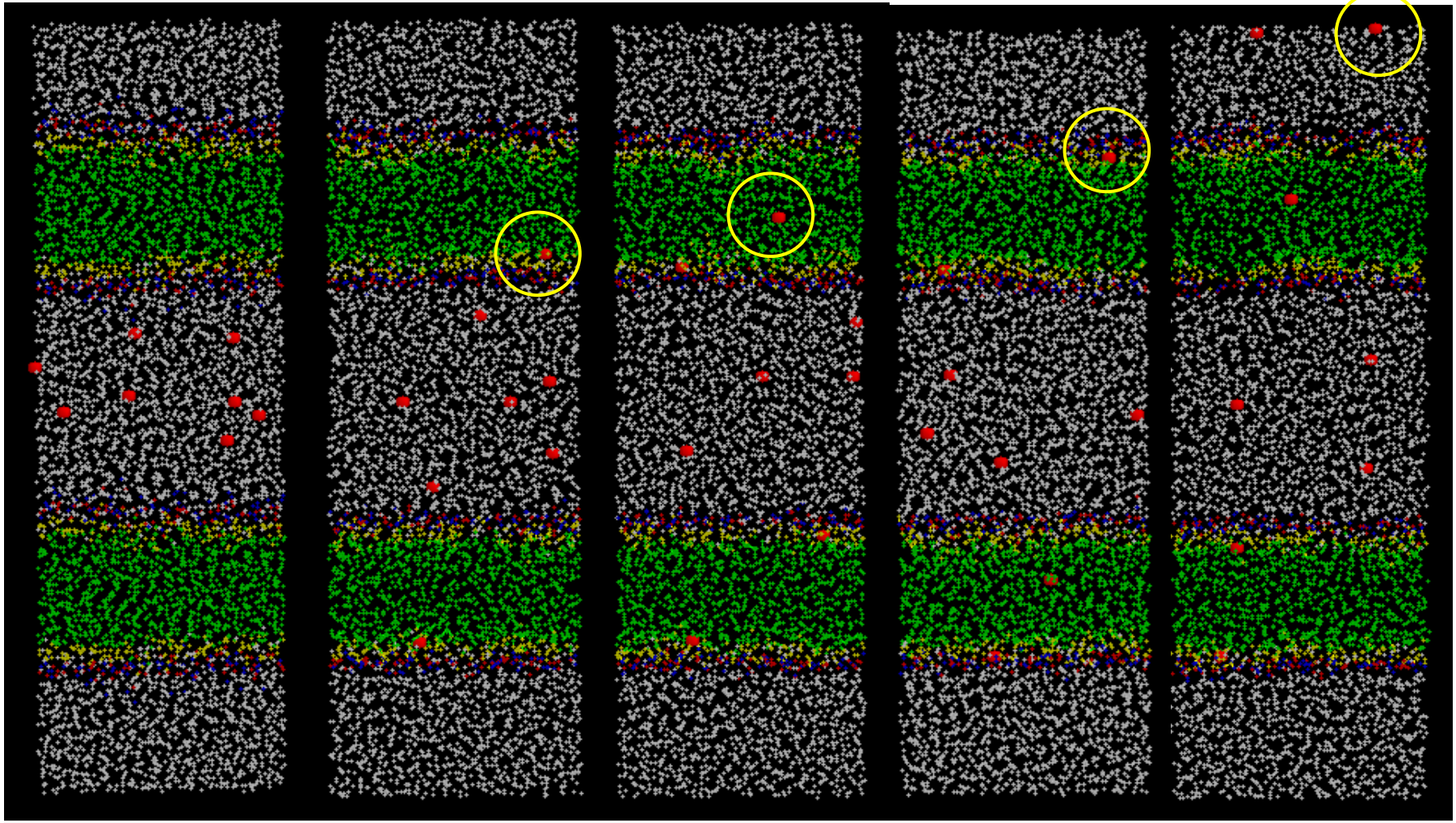
Xe placed initially in the center compartment
will diffuse through the membrane to the outside compartments

Gas permeation: **DPPC + Xe**, 323K



Empty symbol--density profile at 10 ns
Filled symbol --density profile at 100 ns

Observation of Xe atom permeation through DPPC lipid membrane



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.

Acknowledgments

Funding for CJJ's lab

Collaborators

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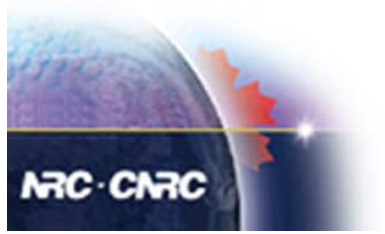
John A. Ripmeester
Chris Ratcliffe



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