Exploring channels, cages, and other nanopores with small molecules

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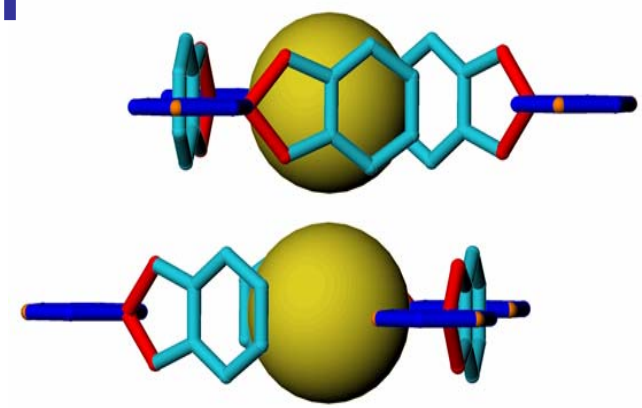
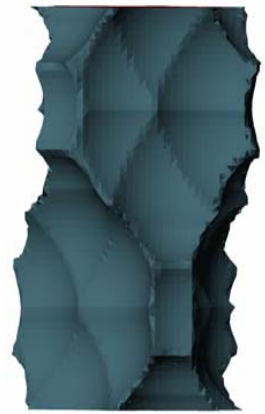




Universita' degli Studi di Milano Bicocca
February 6, 2007

The general approach:

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

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

- 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** to understand/reproduce what is observed.

Information that is encoded in observed 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**
-
-

Our probe is the Xe chemical shift which is observed in NMR spectroscopy

We can use other molecules e.g., CF_4, CH_4, benzene, but Xe is a good example.

We use only crystalline materials because we primarily wish to understand.

Others use Xe NMR in materials such as coal, metal organic frameworks, amorphous polymers, zeolites impregnated with bimetallic nanoparticles, rocks, gas-fluidized beds, clays, ...

Motivation:

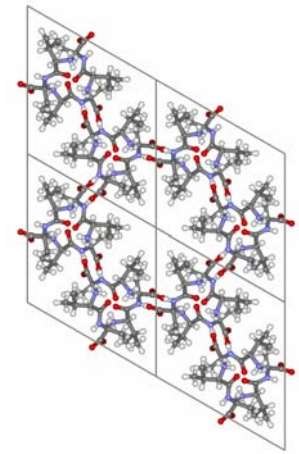
- Xe enters pore openings the size of typical small molecules
- catalysts and molecular sieves can occlude Xe
- large Xe shifts permit transport and site exchange studies in complex materials

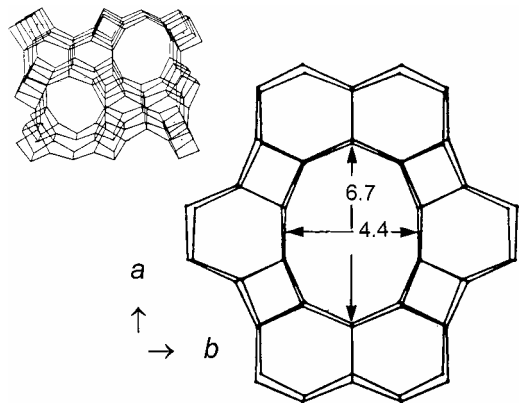
- Xe likes hydrophobic environments, can be a very good probe for soft condensed matter

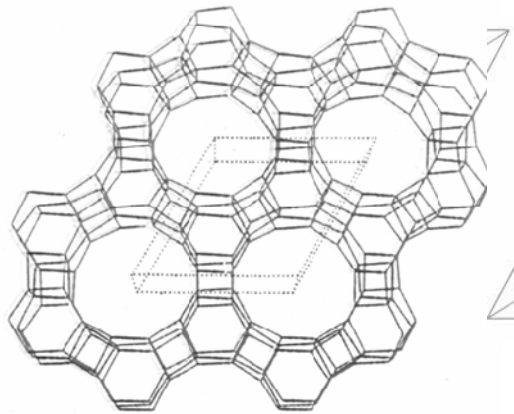
- **much more ….**

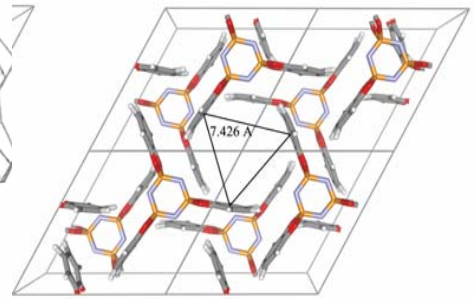
Xe intermolecular chemical shifts

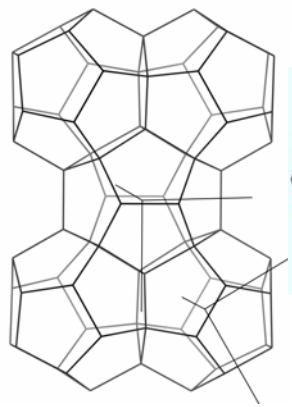
- **exquisitely sensitive** to the environment of the Xe atom
- permits the Xe nucleus to **report attributes of the physical system** in which Xe atom finds itself
- needs **understanding at a fundamental level** so as to elicit the desired detailed information about the physical system

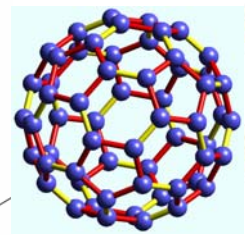


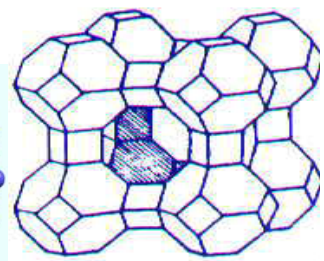


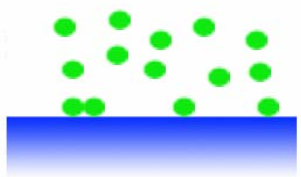




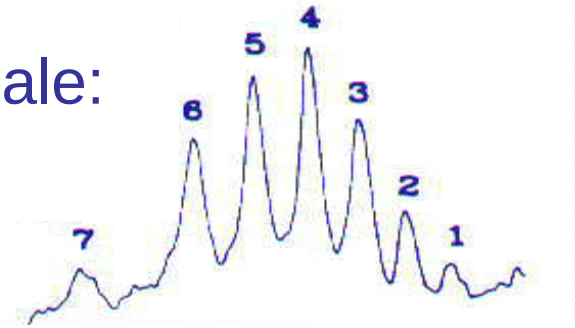


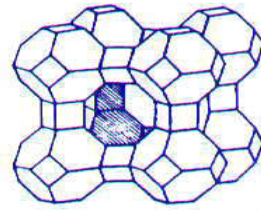




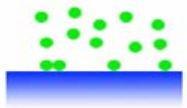


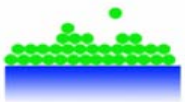
All on the same ppm scale:

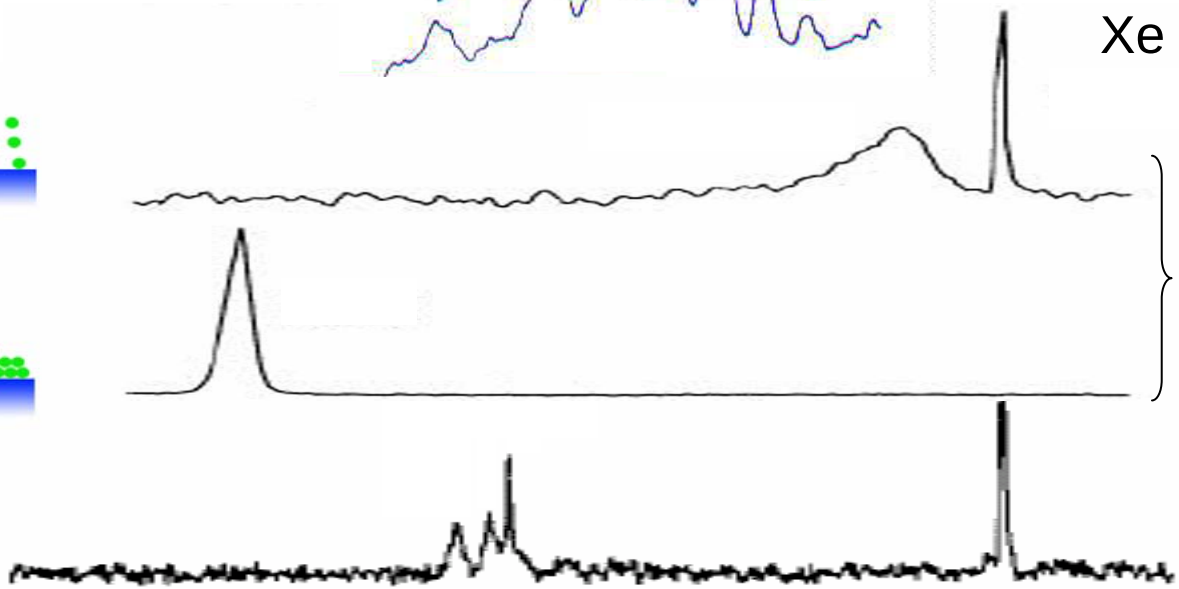




Xe in zeolite NaA







Xe on benzanthracene

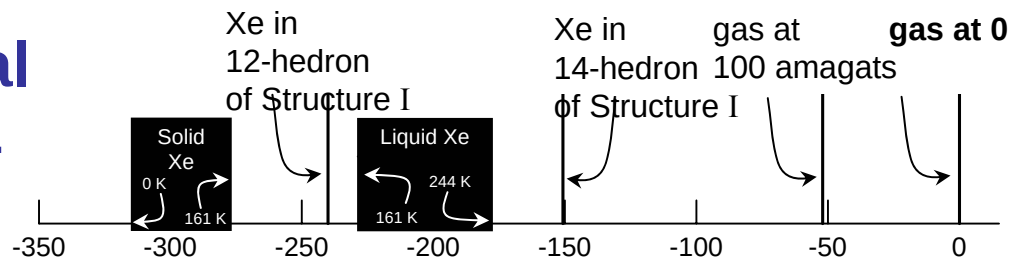
Xe in rat thorax

*K.W. Miller, N.V. Reo, A.J.M.S. Uiterkamp, D.P. Stengle, T.R. Stengle, and K.L. Williamson. P.N.A.S **78** (8), 4946-4949 (1981).

Xe in pure solvents*

Xe in liquid solvents

NMR chemical shift is $\sigma_{ref} - \sigma$



Shift in ppm with respect to dilute gas at 273 K

from J. A. Ripmeester and D. W. Davidson, J. Mol. Struct. 75, 67 (1981)

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

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

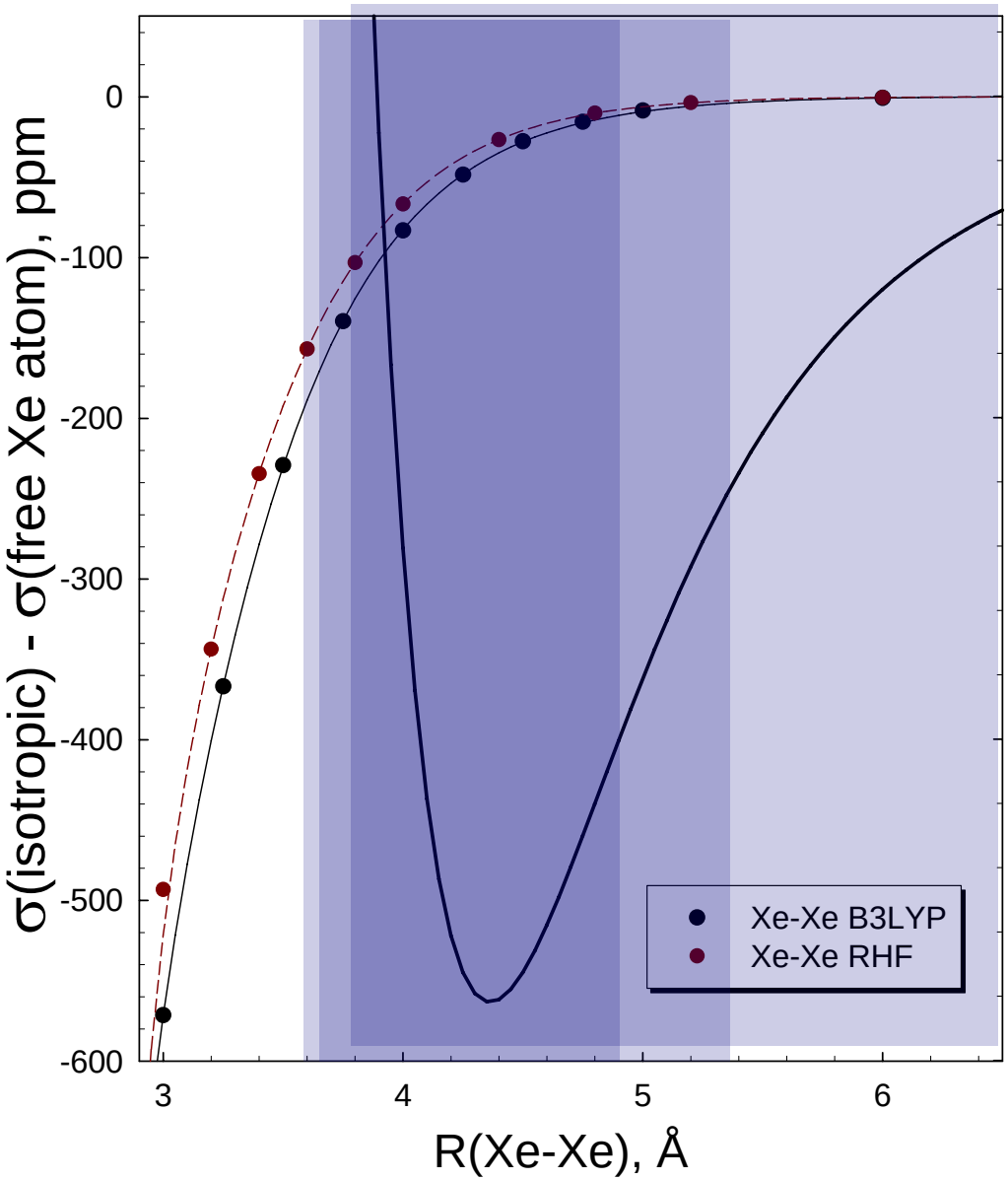
For one neighbor

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



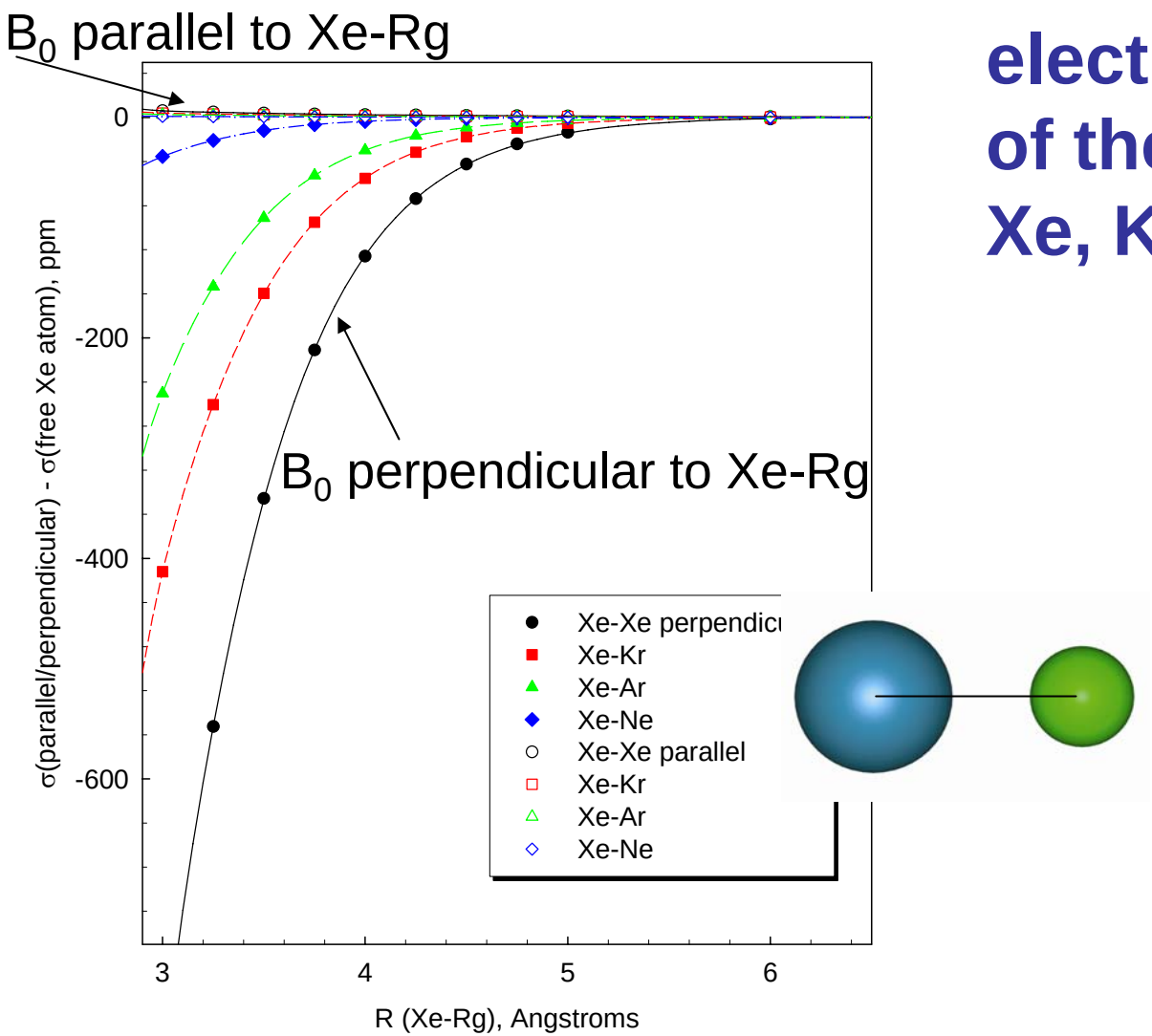
Potential function: R.A. Aziz and M.J. Slaman, Mol. Phys. 57, 825 (1986)

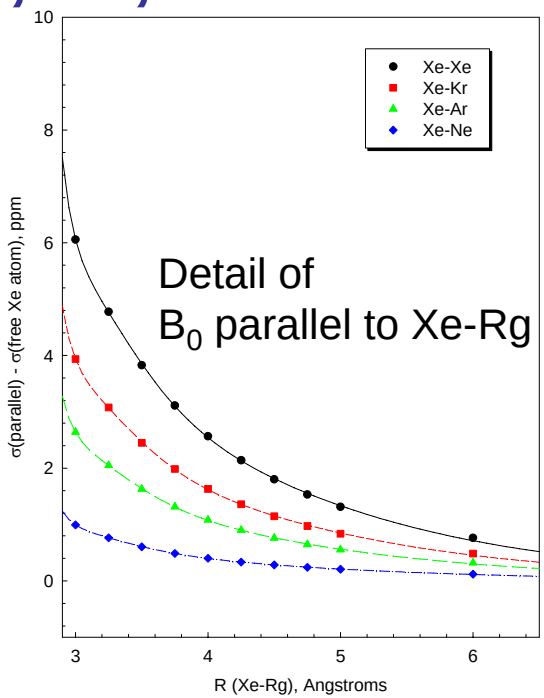
Jameson et al. J. Chem. Phys. 118, 2575 (2003)

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**.

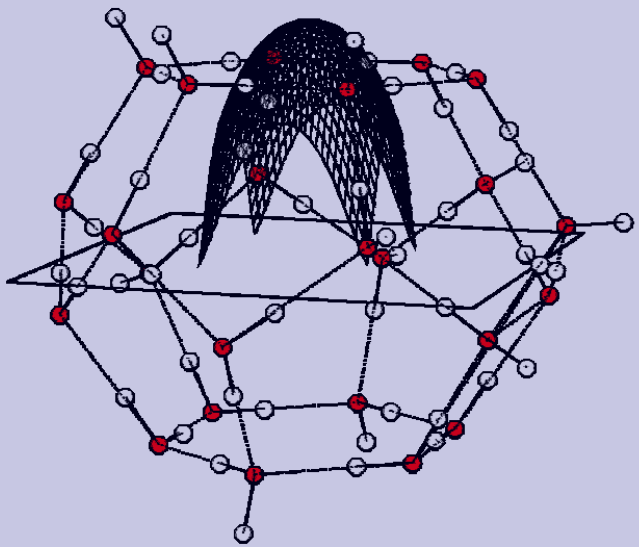
For example, the ab initio Xe shielding for Xe surrounded by some number of Ne atoms (in circles or helices) is found to be nearly the same as the **sum** of the ab initio Xe-Ne shieldings at those Xe-Ne distances

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

Intermolecular chemical shifts

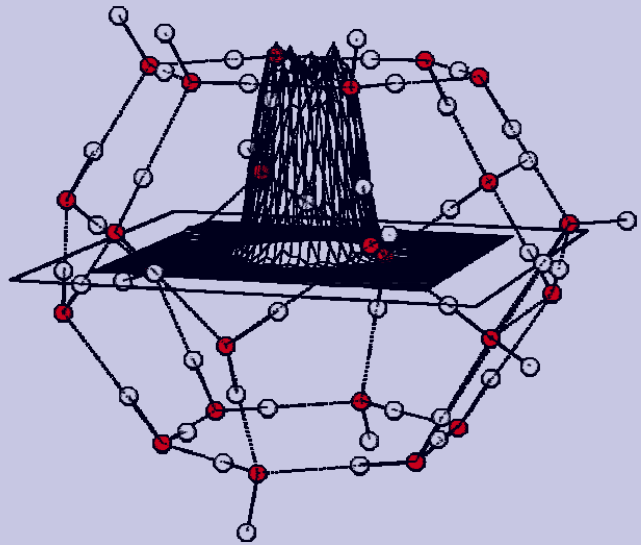
The Xe SHIELDING SURFACE: the shielding as a function of configuration (coordinates) of the system

(a) isotropic shielding surface



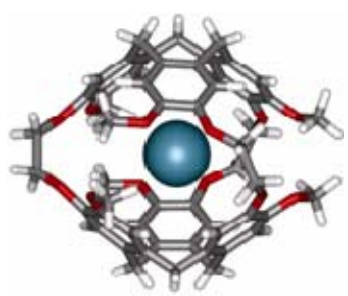
The Xe one-body distribution: the PROBABILITY of finding the system in a given configuration

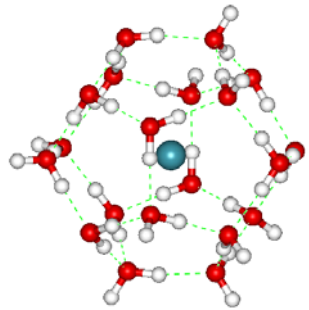
(b) one-body distribution surface



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

Xe in cages

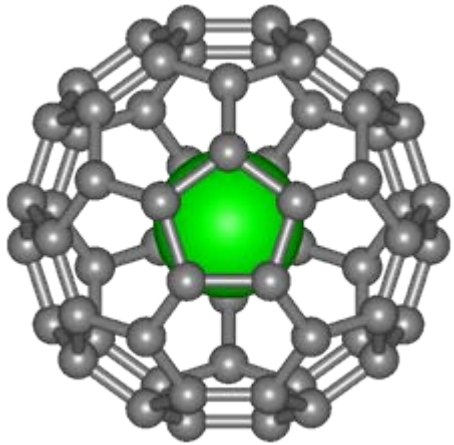




QUESTION:
What information is encoded into the Xe chemical shift of a Xe atom trapped in a cage?

- 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

Consider cages built around a Xe atom



$Xe@C_{60}$

$Xe@C_{60}$

179.24

1 atm Xe gas

0.0

M.S. Syamala,
R. J. Cross,
M. Saunders,
JACS 124, 6216
(2002)

EXPERIMENT

150 100 50

Chemical Shift (ppm)

D.N. Sears and
C.J. Jameson
J. Chem. Phys.
118, 9987(2003)

CALCULATED

181.58

0.0

Xe atom

Xe in the cages of clathrate hydrates Structure I and II

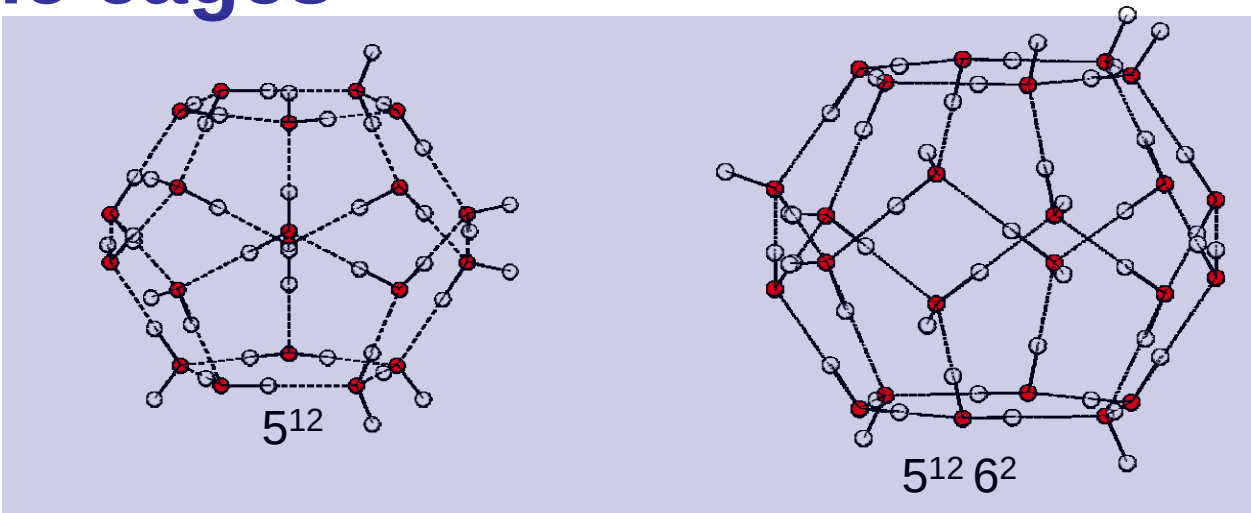
interesting as a test:

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

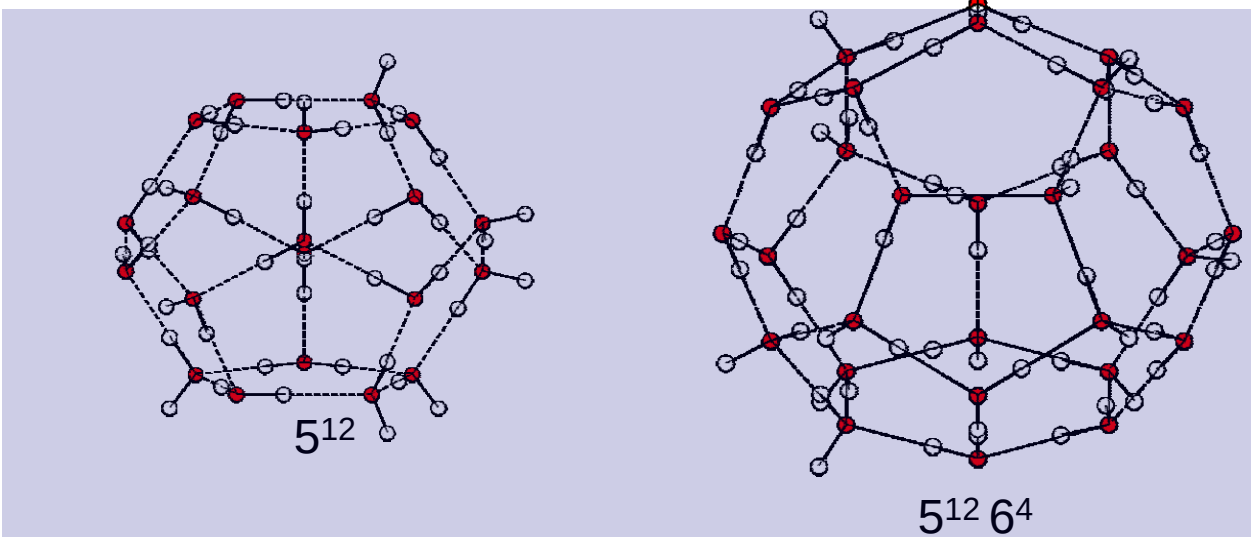
Clathrate hydrates

the cages

Structure I



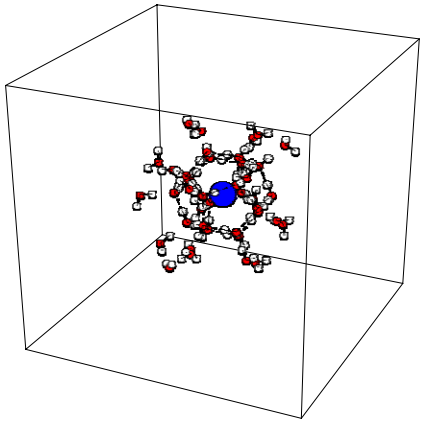
Structure II



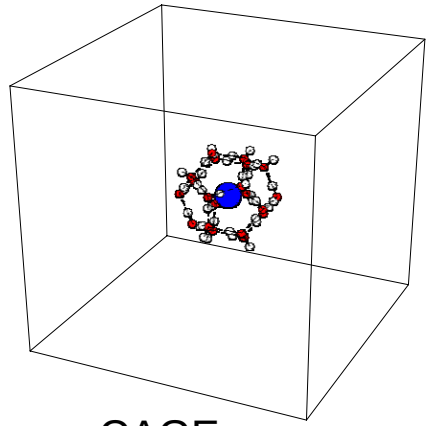
How to model a cage in a hydrogen bonded network?

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

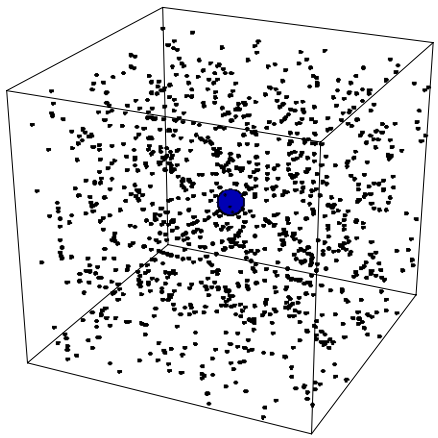
MODELS



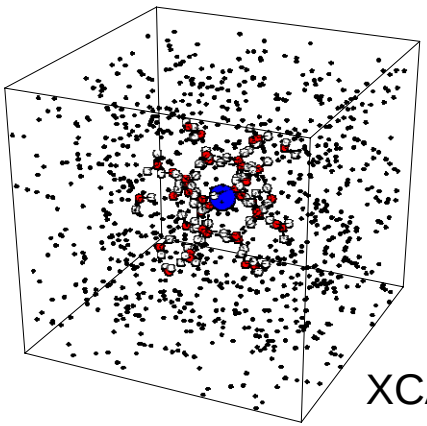
XCAGE



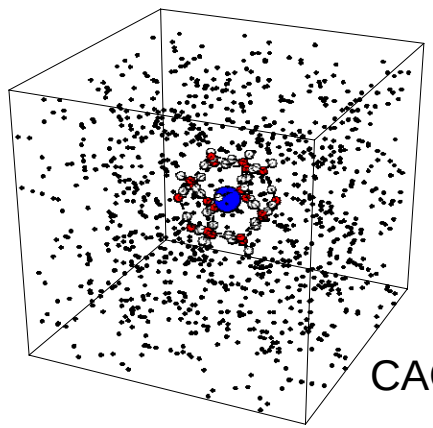
CAGE



PCA

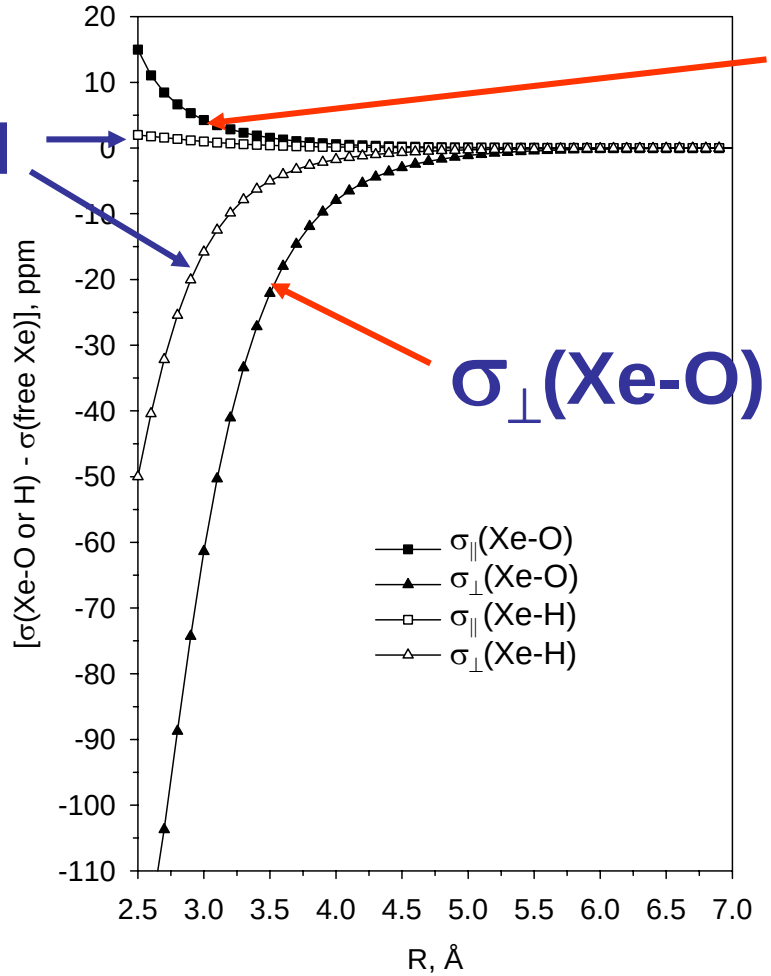


XCAGE/PCA



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)

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

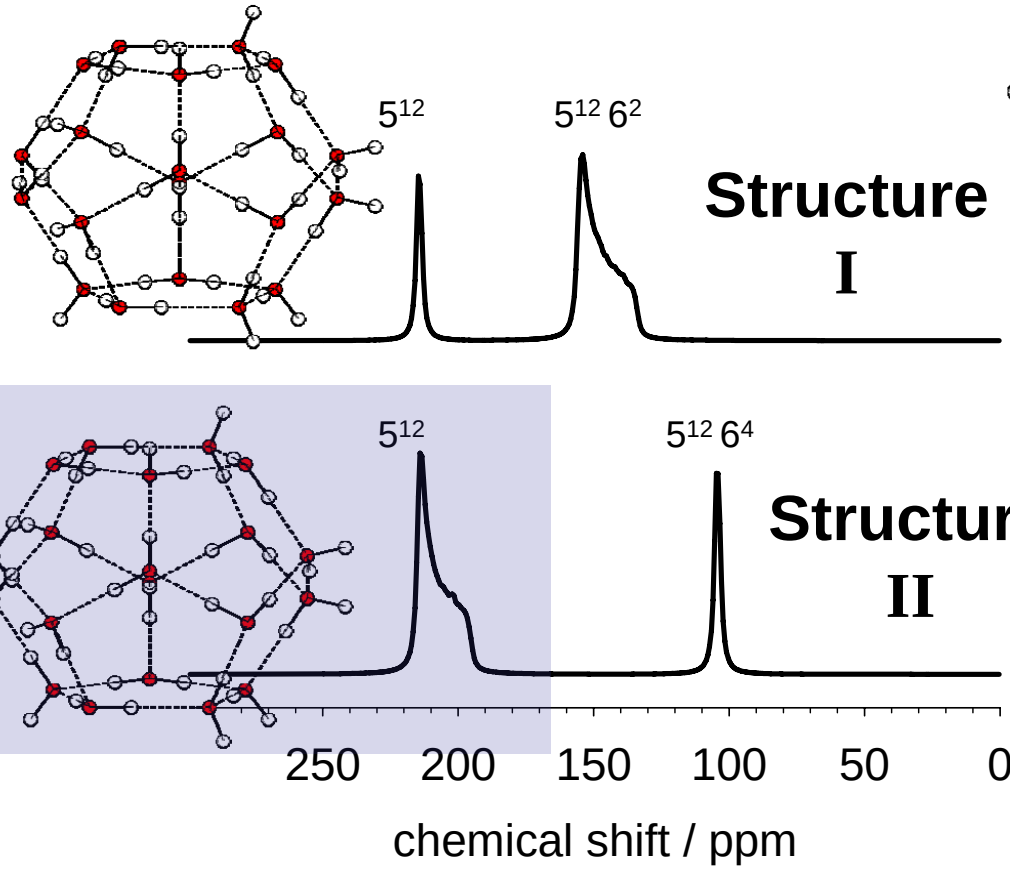
Tensor components in the laboratory frame (frame of the simulation box):

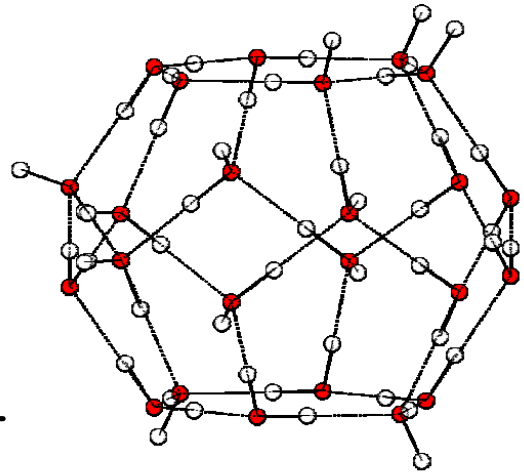
$$\sigma_{XX} = [(x_i - x_J)/r_{iJ}]^2 \sigma_{||} + \{[(y_i - y_J)/r_{iJ}]^2 + [(z_i - z_J)/r_{iJ}]^2\} \sigma_{\perp}$$

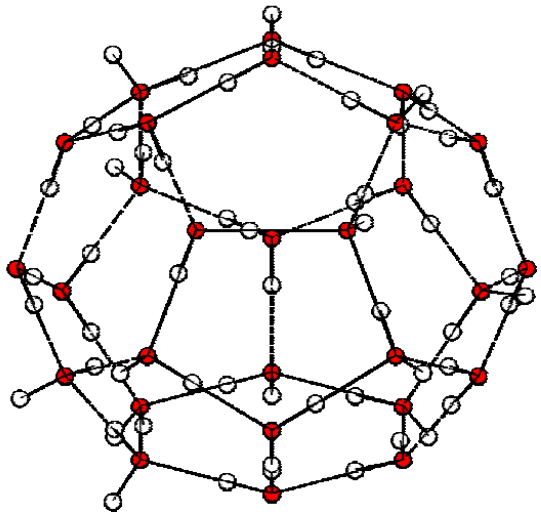
$$\tfrac{1}{2}(\sigma_{XY}+\sigma_{YX}) = [(x_i - x_J)/r_{iJ}]\bullet[(y_i - y_J)/r_{iJ}](\sigma_{||} - \sigma_{\perp})$$

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

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



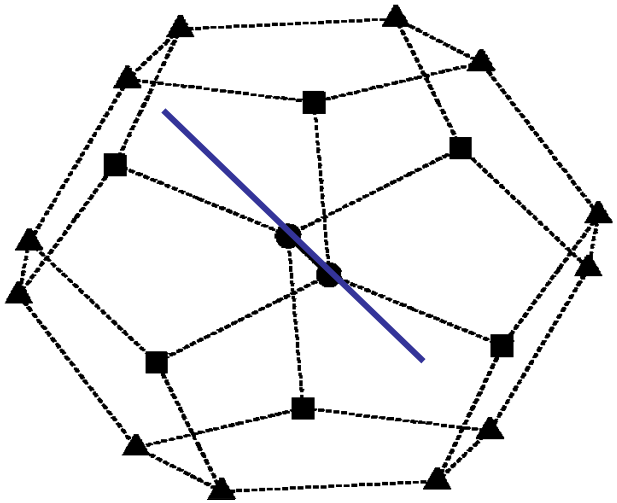




using
the same Xe-O and Xe-H shielding tensor functions,
the same Xe-O and Xe-H potential functions

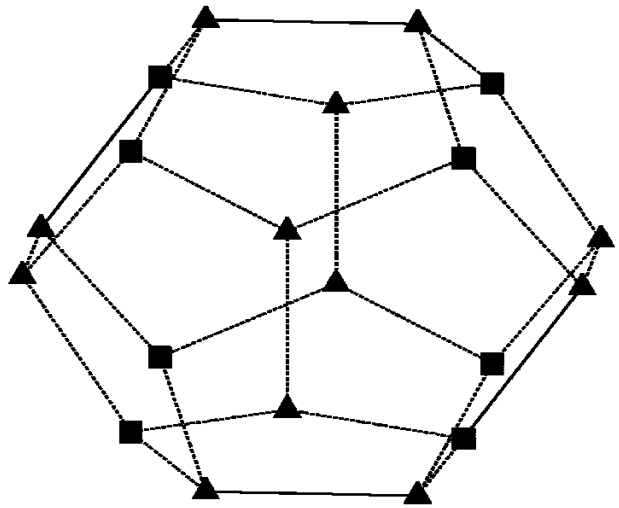
Why is the Xe lineshape in the 5^{12} cage in Structure II axially anisotropic while the Xe lineshape in the 5^{12} cage in Structure I is isotropic?

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



vs.

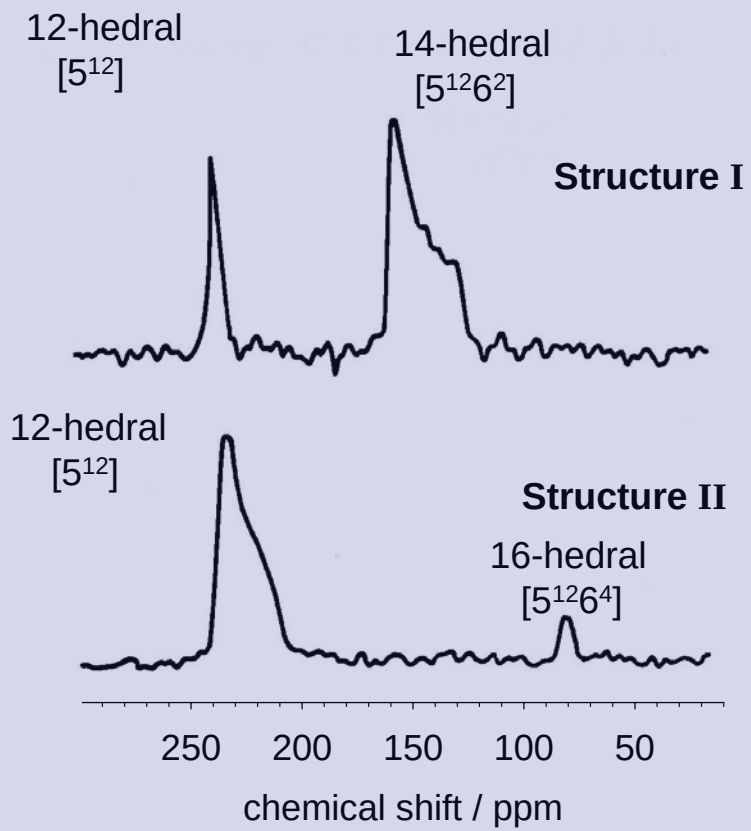
(b) 5^{12} cage in structure I



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**

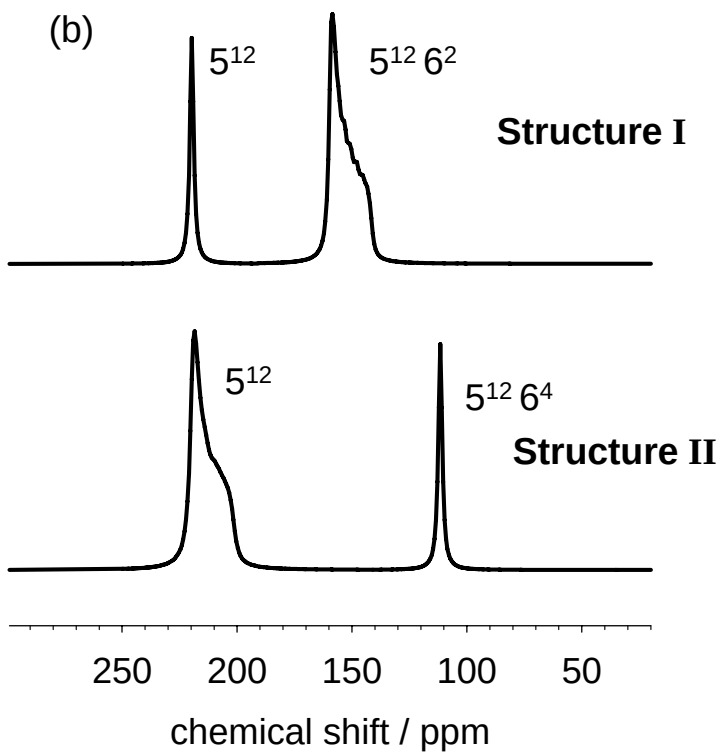
Xe can sense and report this difference!

Xe in the cages of clathrate hydrates Structure I and II



EXPERIMENTS

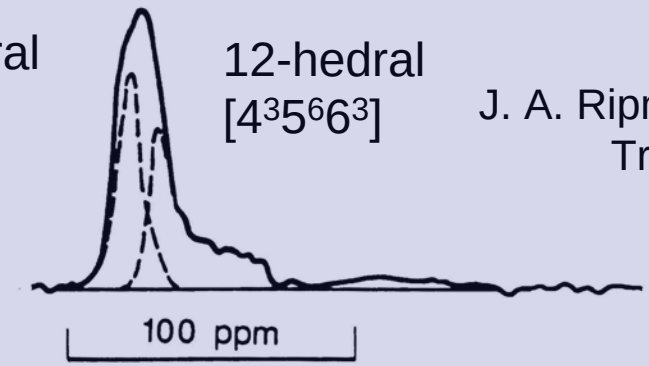
J. A. Ripmeester, C. I. Ratcliffe and J. S. Tse, Trans. Faraday Soc. 1, 84, 3731 (1988)



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



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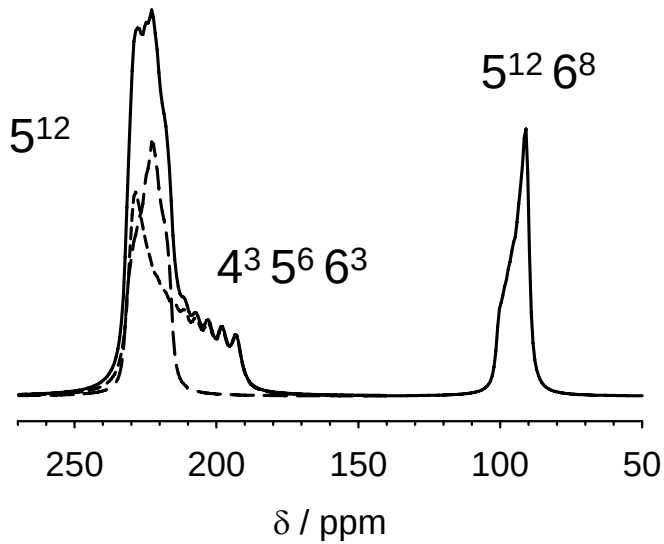
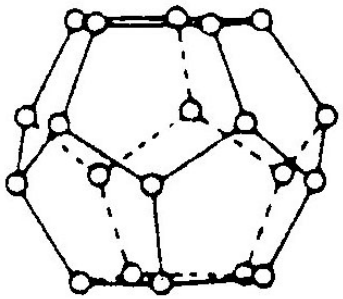


CALCULATIONS

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

Xe chemical shift tensors

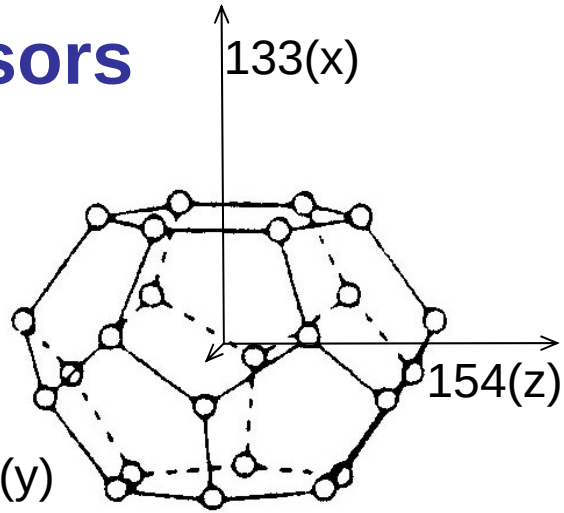
isotropic 214



5^{12}

symmetric

133(x)



154(z)

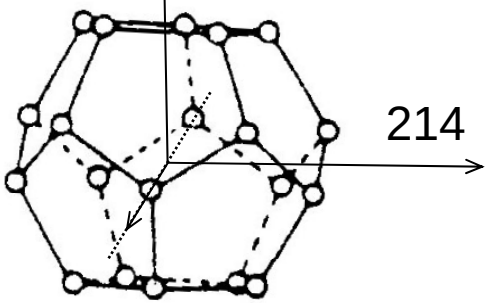
154(y)

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

axial, disk-like

Clathrate Structure I

214



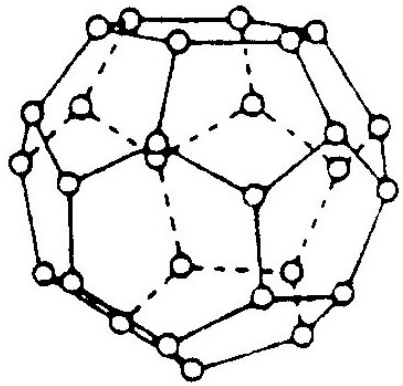
214

194

5^{12}

axial

isotropic 105

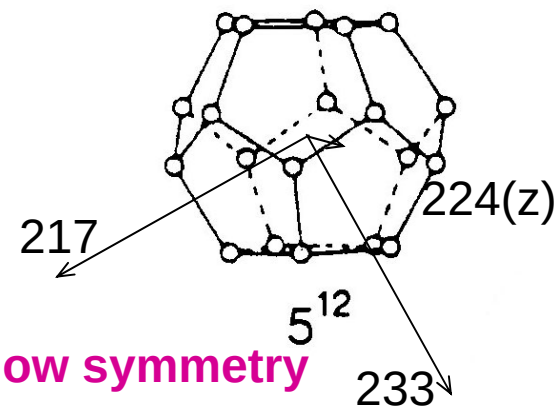


$5^{12}6^{4}$

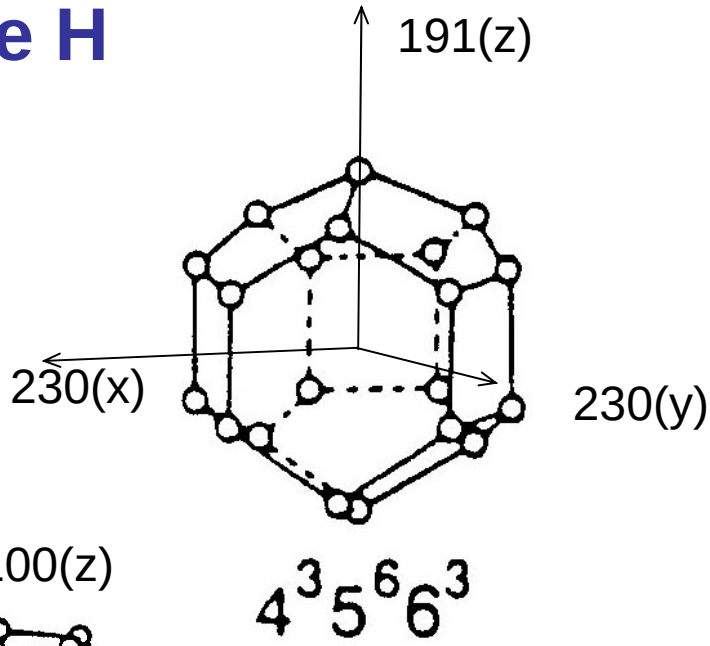
symmetric

Clathrate Structure II

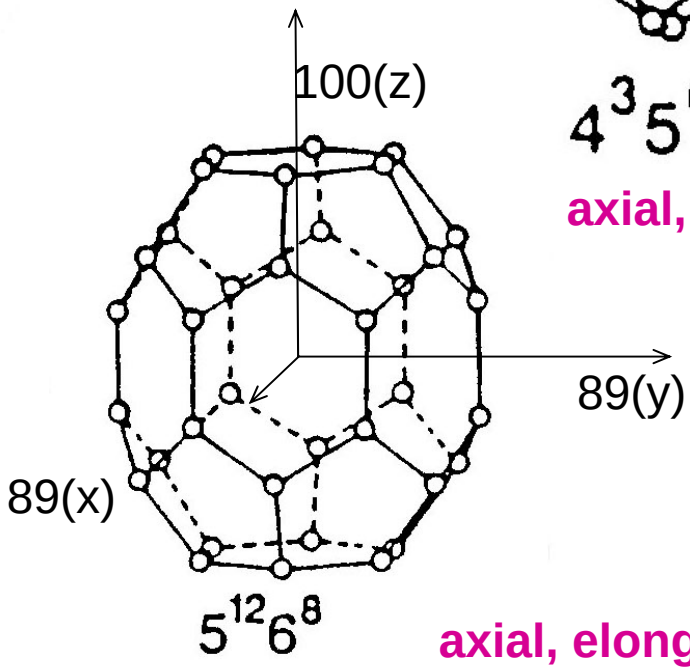
Xe tensors in Clathrate Structure H



low symmetry



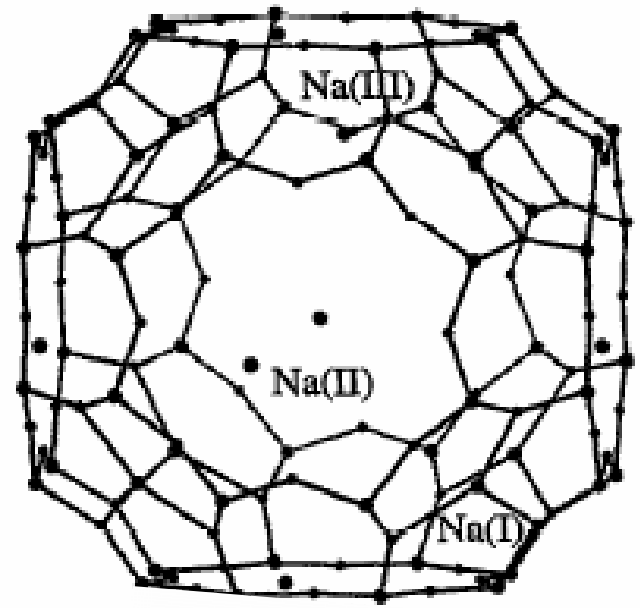
axial, squat

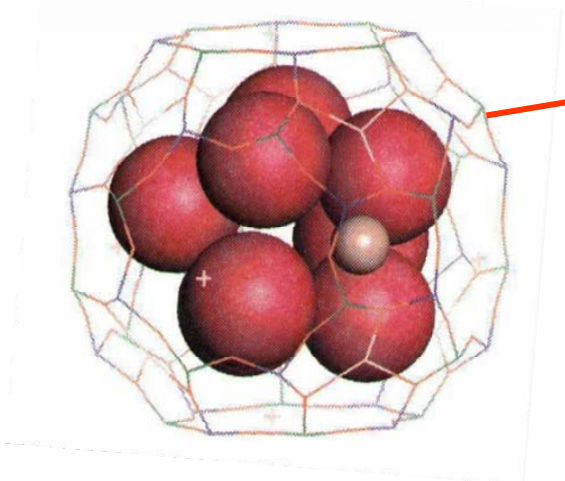


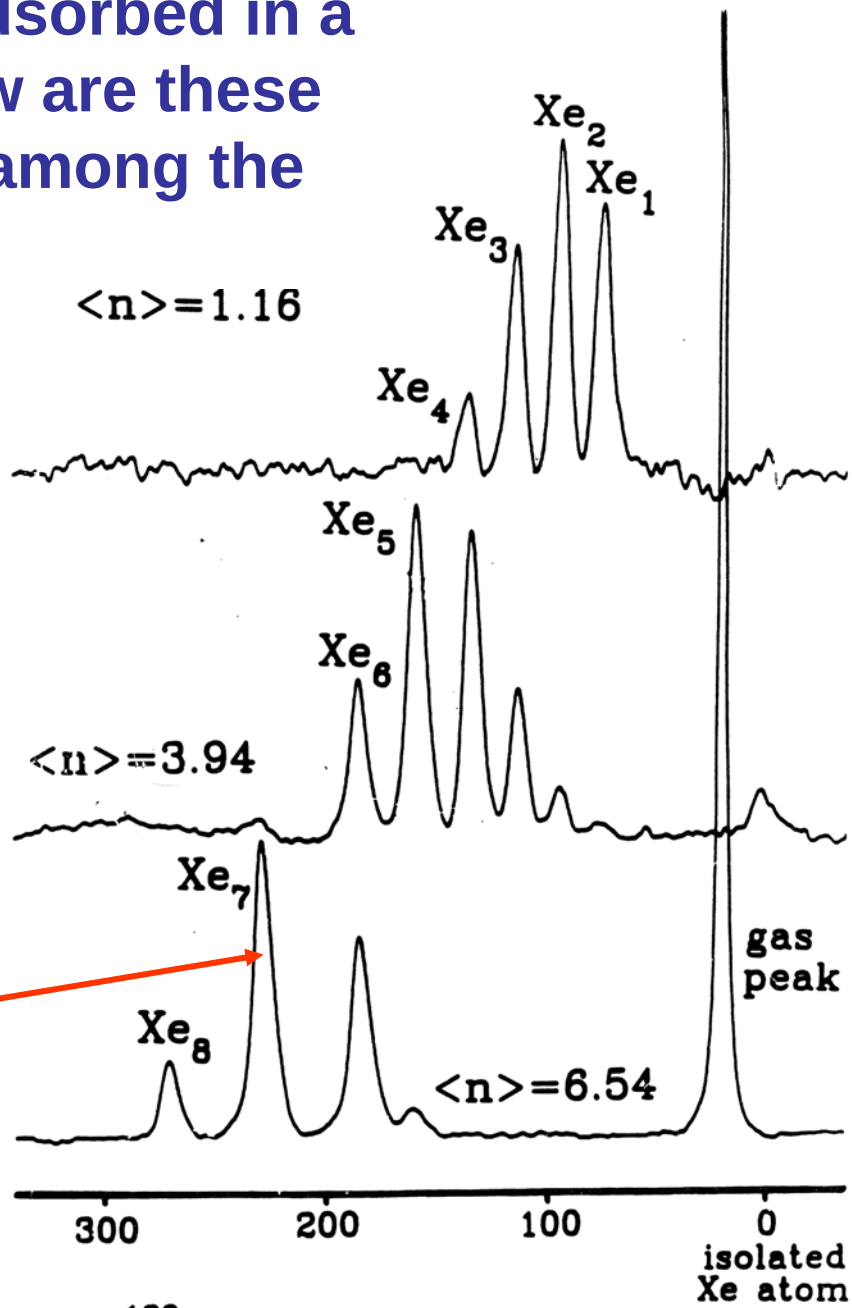
axial, elongated

What if Xe can enter and leave the cage?

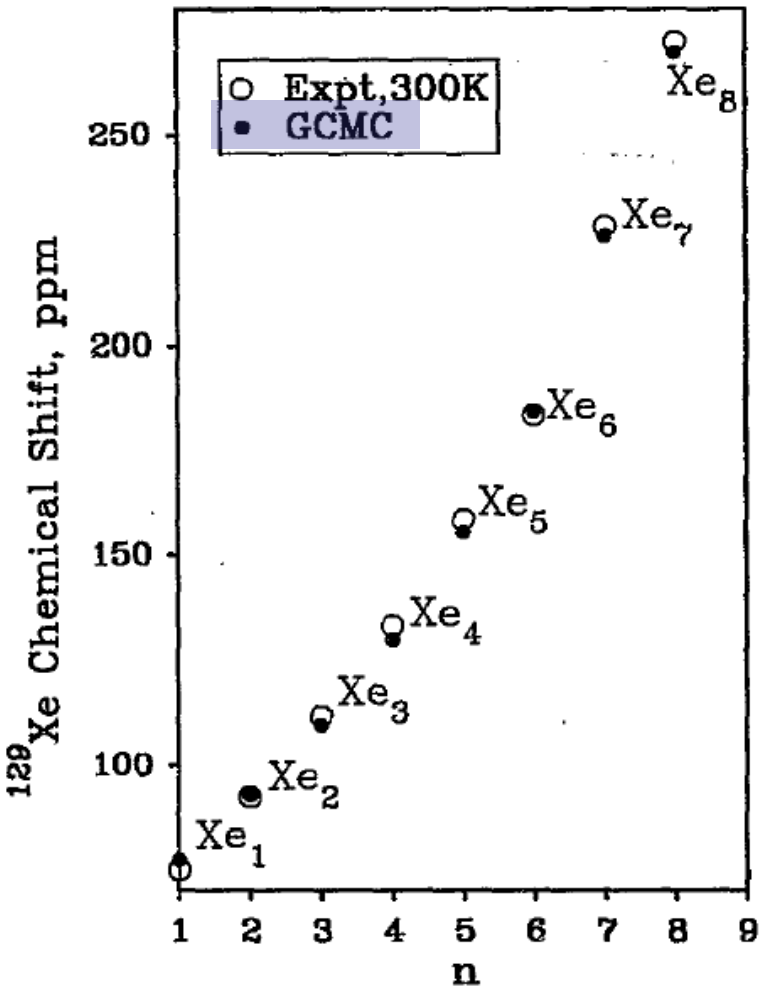
When molecules are adsorbed in a microporous solid, how are these molecules distributed among the cavities?



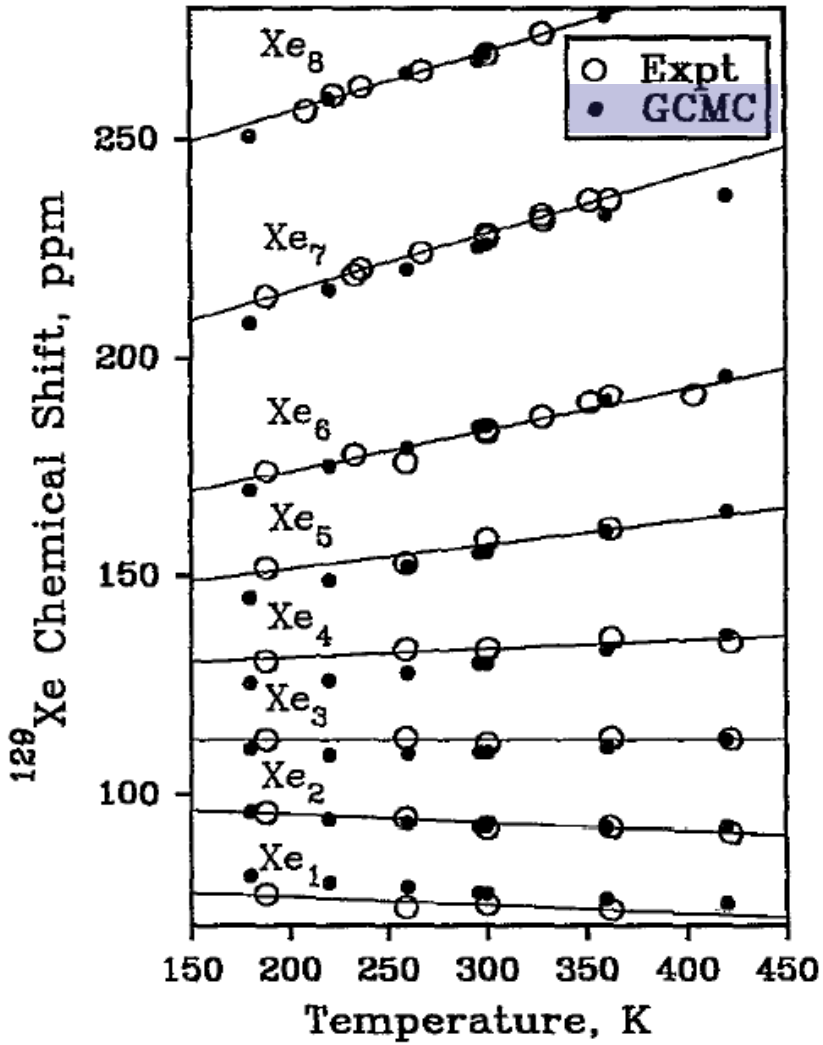




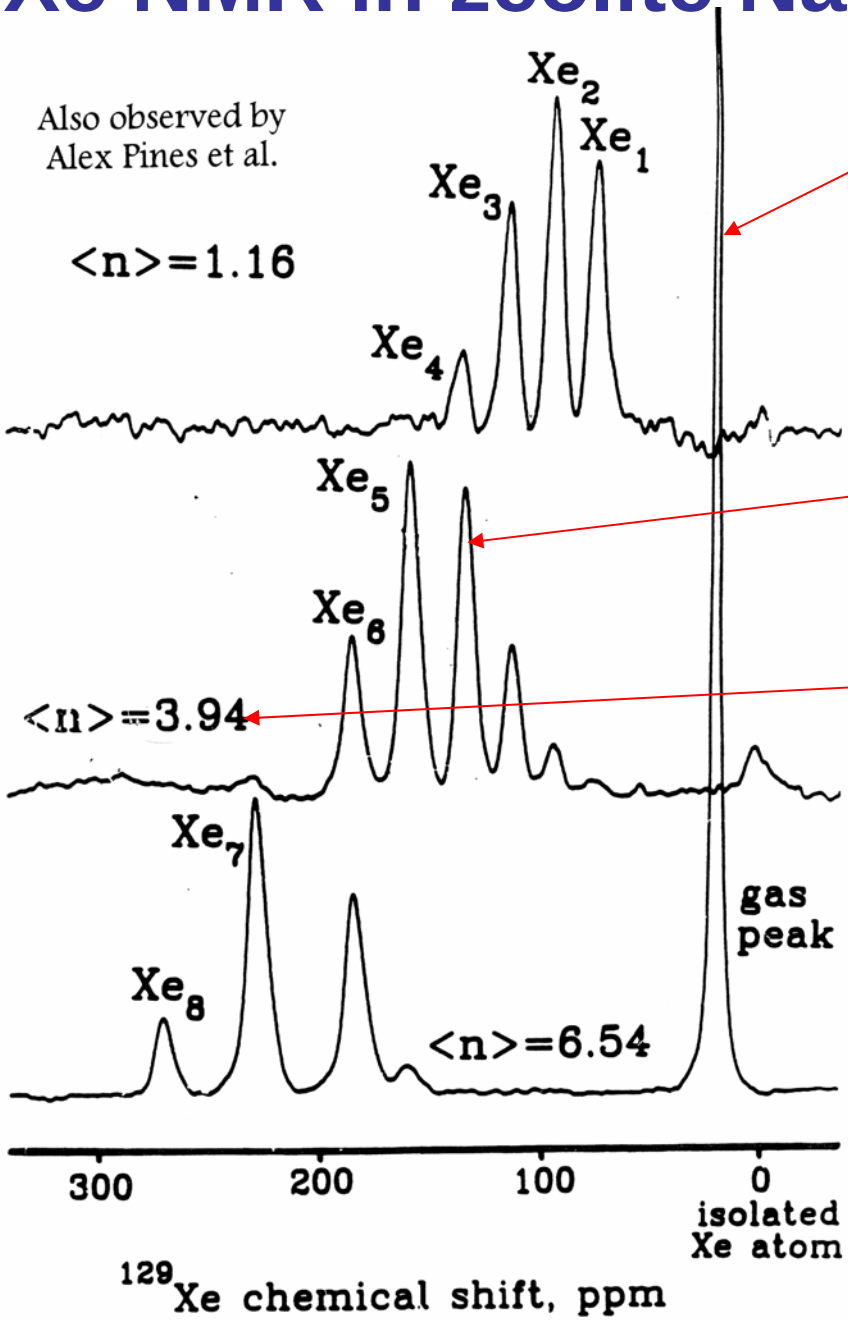
We reproduce the individual chemical shifts



and also the temperature dependence of each



Xe NMR in zeolite NaA

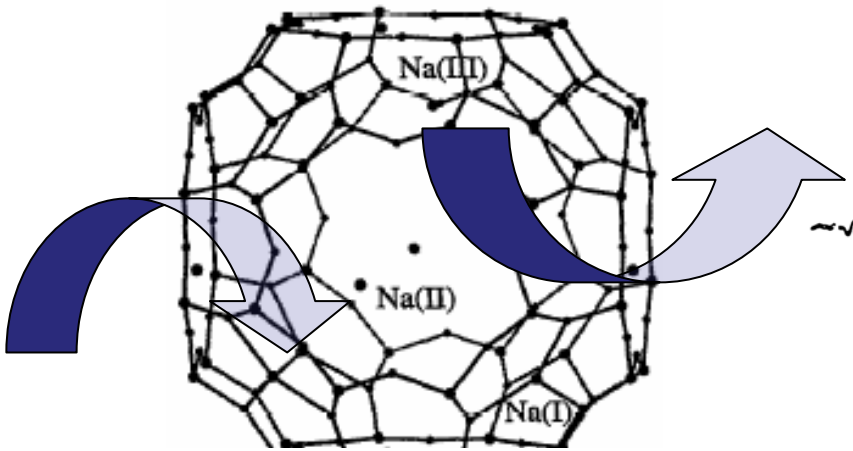


Xe chemical shift of gas peak provides ρ_{Xe} Xe density in the overhead bulk gas

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*.

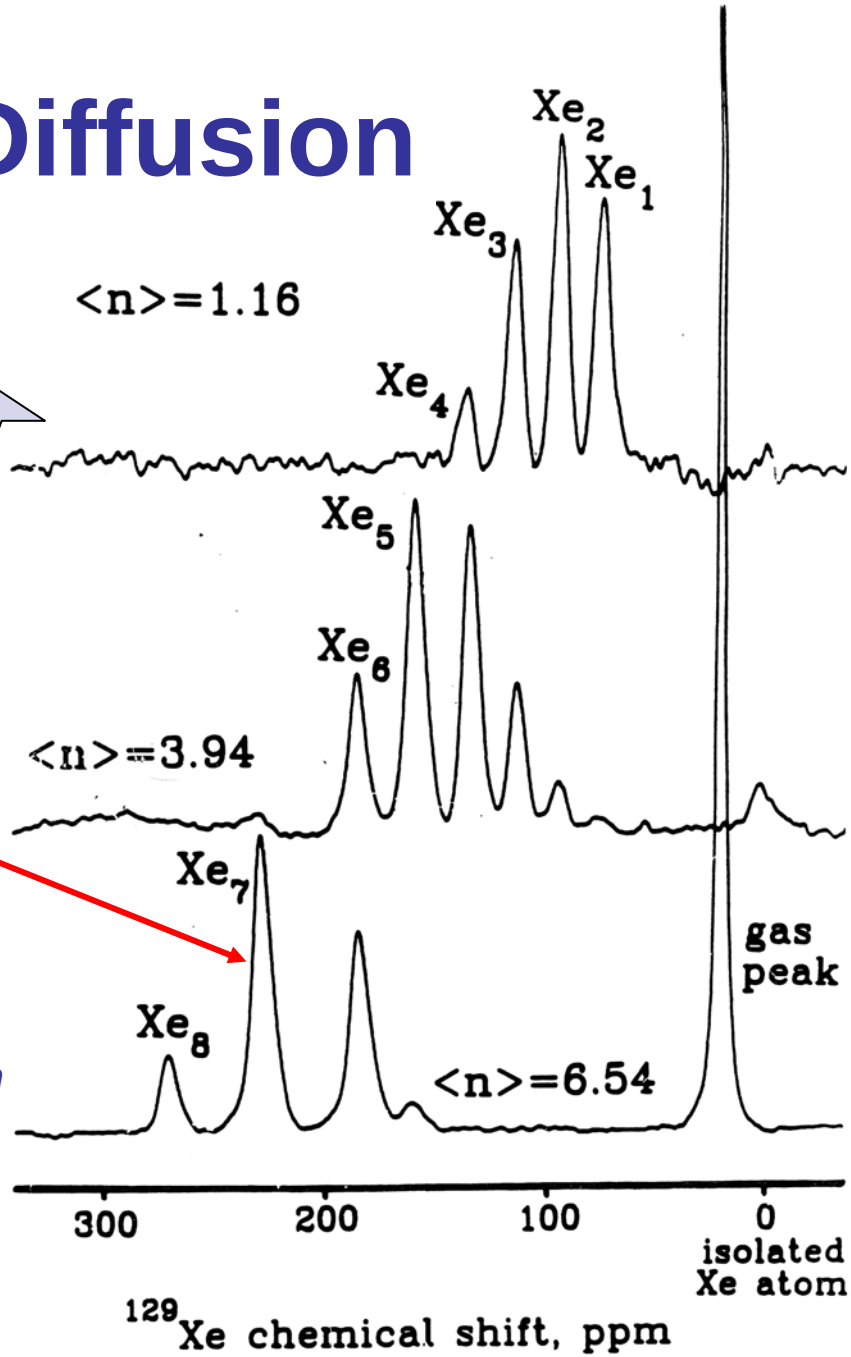
Intra-crystalline Diffusion



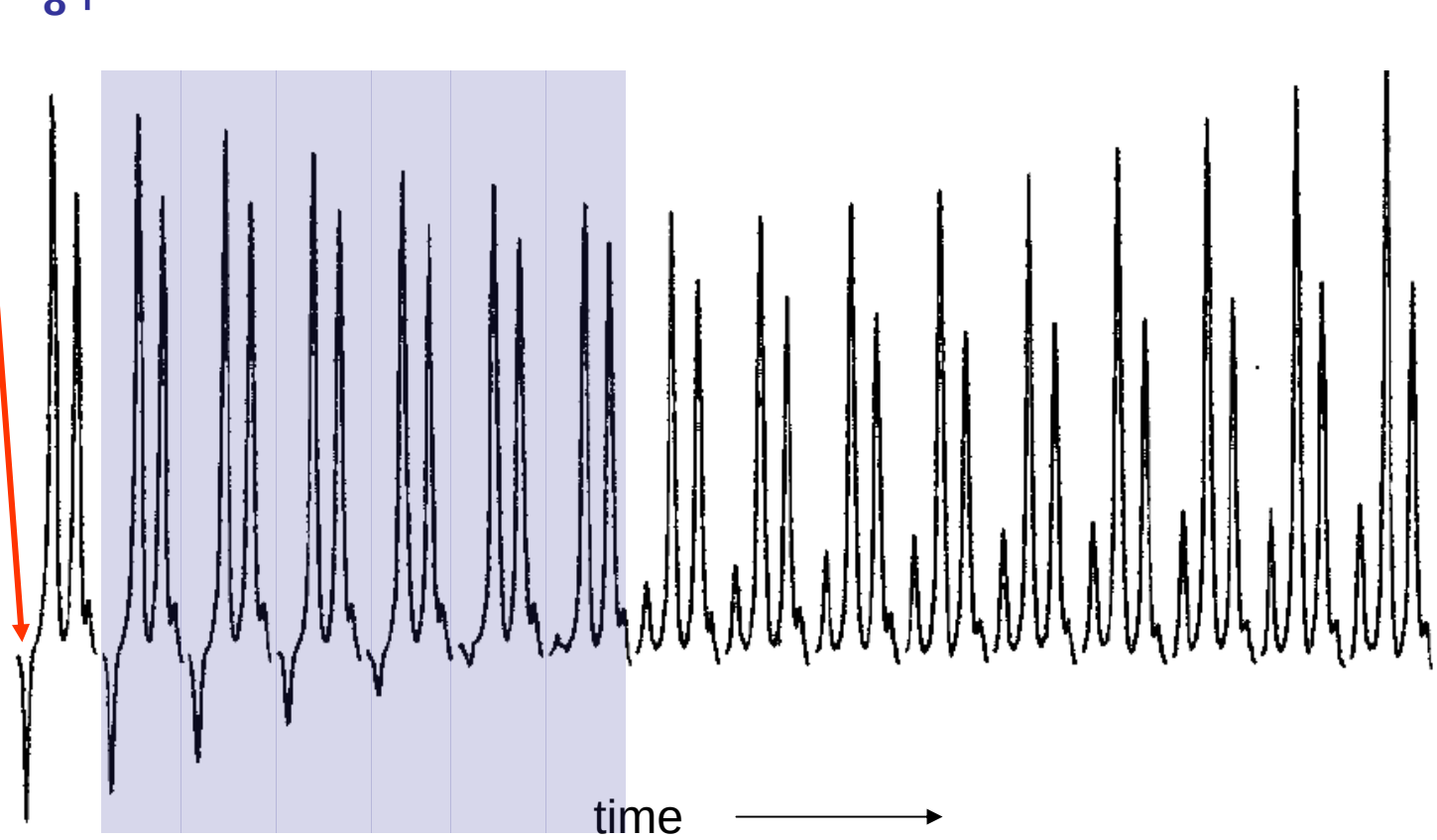
Magnetization transfer experiments on these

provide the rate constants

$$Xe_n + Xe_{m-1} \xrightarrow{k_{mn}} Xe_{n-1} + Xe_m$$



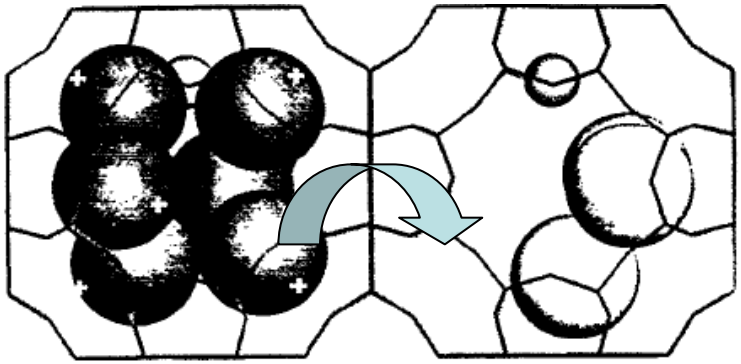
Selectively invert the magnetization of the Xe_8 peak.



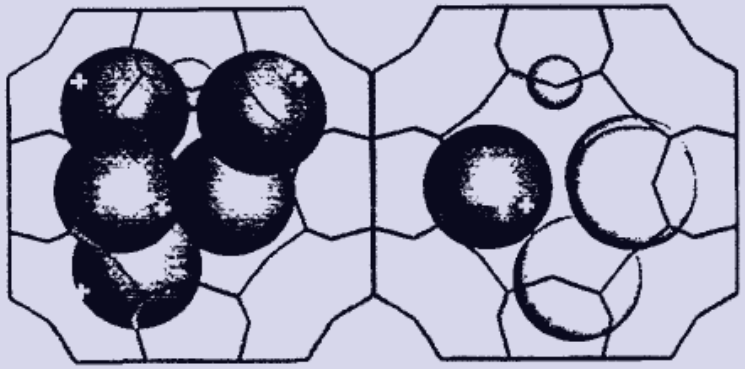
Monitor all the peak intensities as a function of time.

There are a large number of such types of experiments, using various peaks, and different samples.

before



after



time evolution of magnetization under spin relaxation and exchange

$$d\mathbf{M}/dt = \mathbf{KM} + \mathbf{M}^e,$$

$$K_{ii} = -1/T_{1i} - \Sigma_{i \neq j} K_{ji}. \qquad (2)$$

The phenomenological rate constant K_{ji} describes the pseudo-first-order exchange rate from site i to site j. The

$$K_{mn} = k_{mn} f(m-1) \quad \text{provided} \quad |n-m| > 1,$$

$$K_{m,m+1} = k_{m,m+1} f(m-1) + m \Sigma_i^8 k_{i,m+1} f(i-1),$$

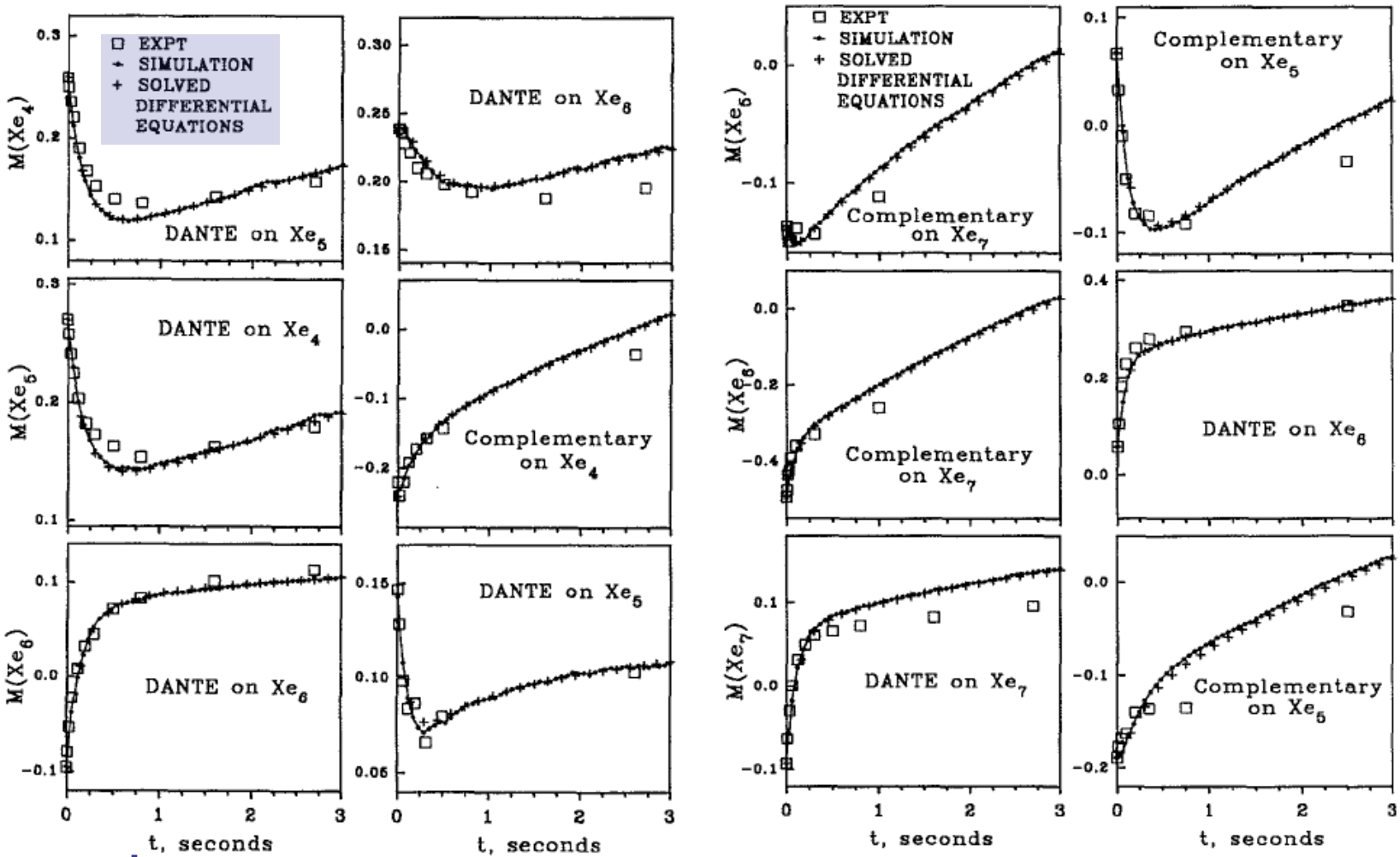
$$K_{m,m-1} = k_{m,m-1} f(m-1) + \Sigma_i^8 i k_{mi} f(i).$$

k_{46} rate constant

$Xe_6 + Xe_3 \rightarrow Xe_5 + Xe_4$ this event

This single event affects the intensities of four peaks: Xe_6, Xe_3, Xe_5, and Xe_4.

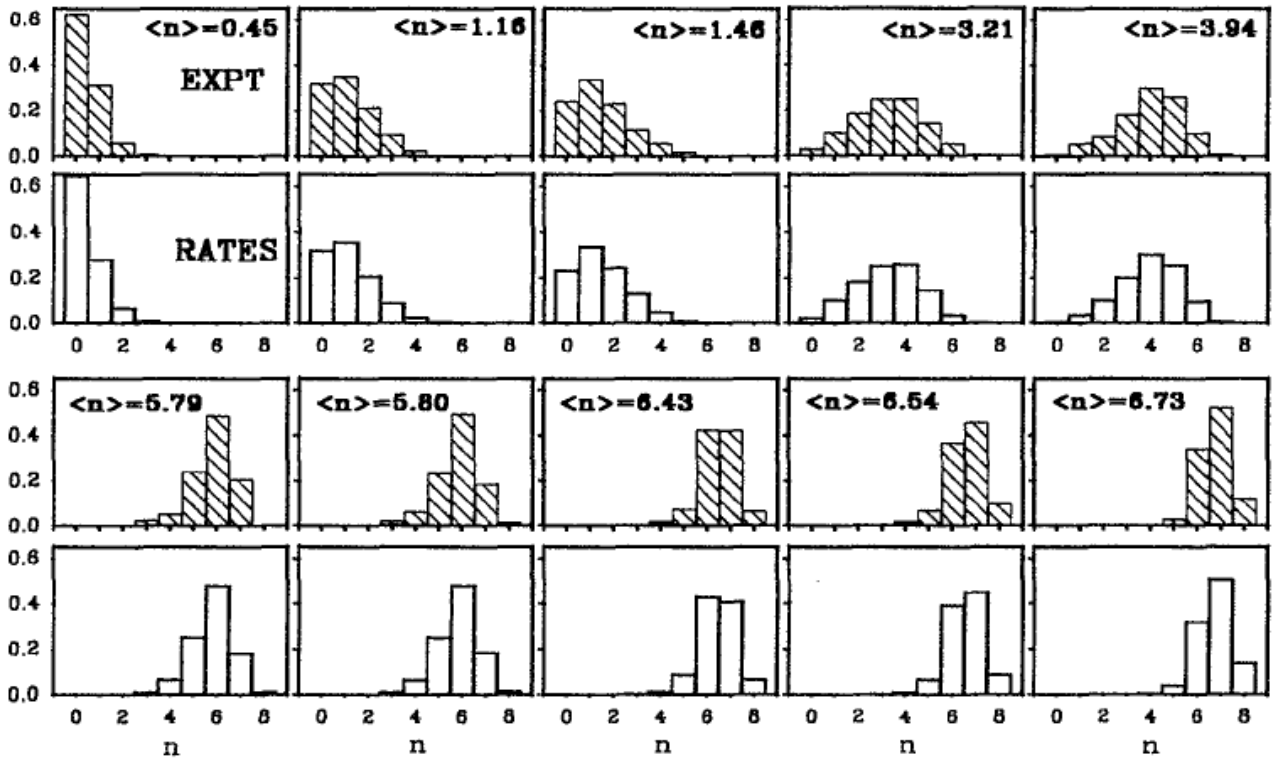
Magnetization



time

We have 138 such detailed unique curves to provide the rate constants

When the obtained rate constants are used in a Monte Carlo simulation of the cage-to-cage jumps until equilibrium is reached, they reproduce the observed distributions



Two approaches (GCMC or RATES) to the equilibrium distribution of atoms among the cavities of zeolite Na*A* lead to the same results; both agree with experiment.

Intracrystalline diffusion

How fast is the diffusion of Xe atoms within a crystallite?

We measured each one of these rate constants

$$Xe_n + Xe_{m-1} \xrightarrow{k_{mn}} Xe_{n-1} + Xe_m$$

Average rate constant for any given $\langle n \rangle$:

$$\langle k \rangle = \sum_{n=1,8} \sum_{m=1,8} P(m-1) \cdot k_{mn} \cdot P(n)$$

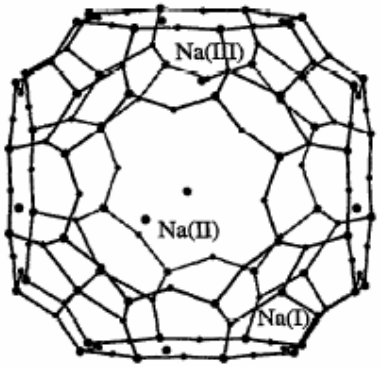
Fraction of cages having n Xe atoms

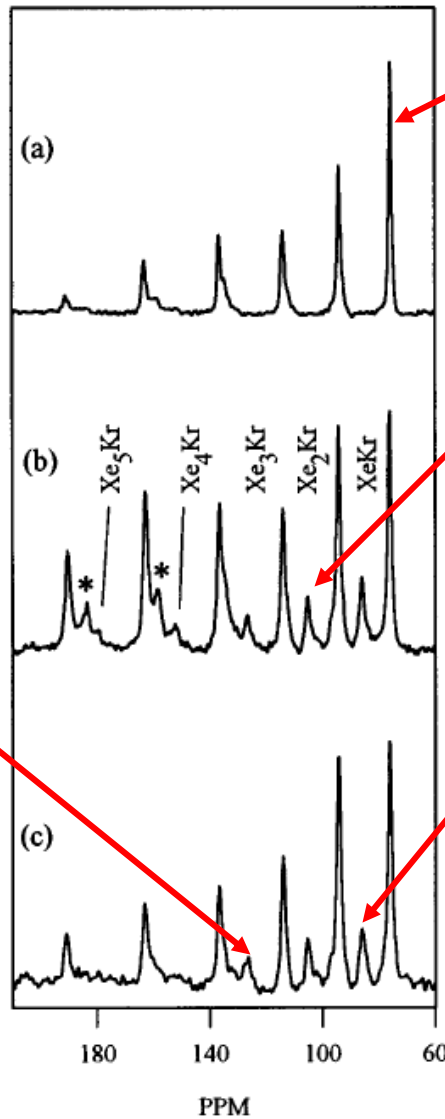
Diffusion coefficient

$D_s = \langle k \rangle \, l6$

but we have more detail!

Competitive Adsorption





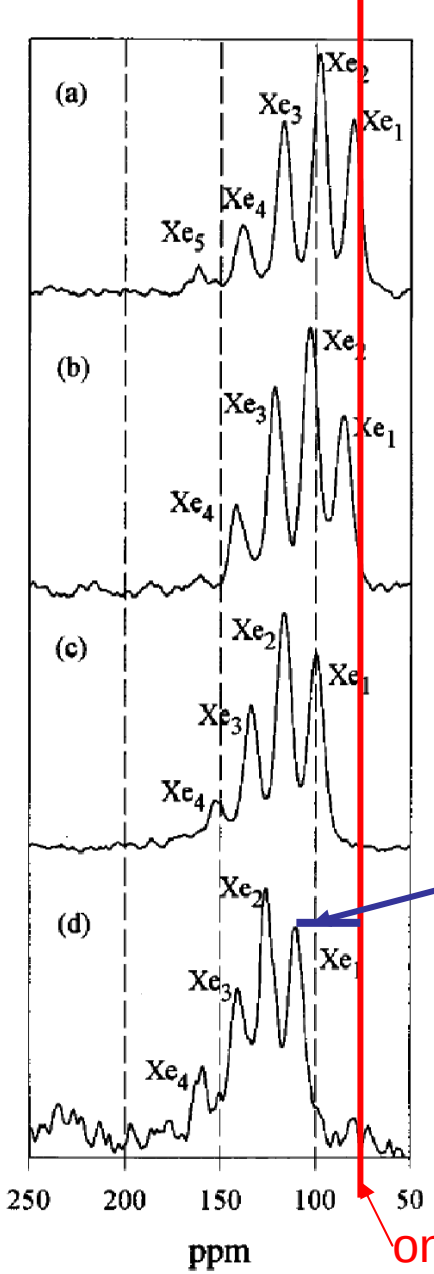
one Xe
in a cage

two Xe+one Kr
in a cage

three Xe+one Kr
in a cage

one Xe+ one Kr
in a cage

Xe NMR spectrum



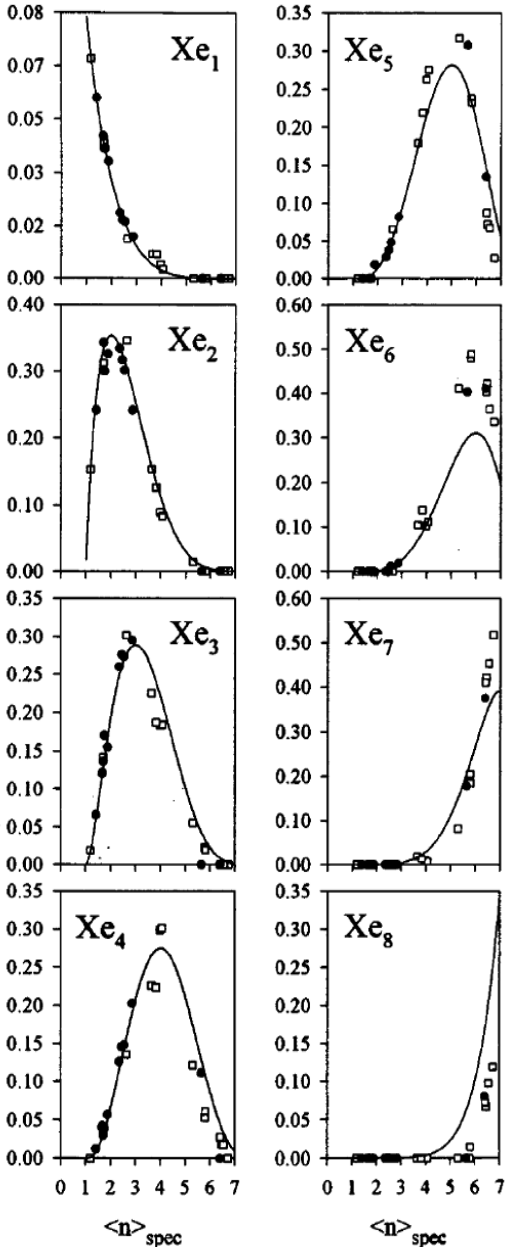
The Xe chemical shift for Xe_n depends on the average number of Ar atoms in the same cage as n Xe atoms.

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 pure Xe 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

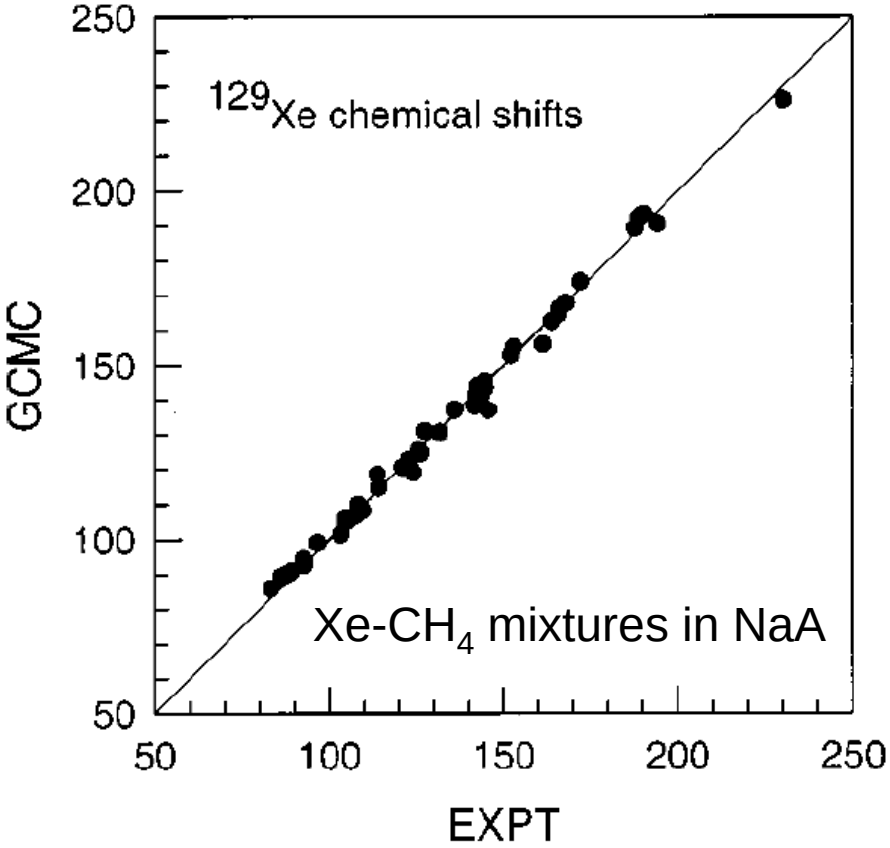


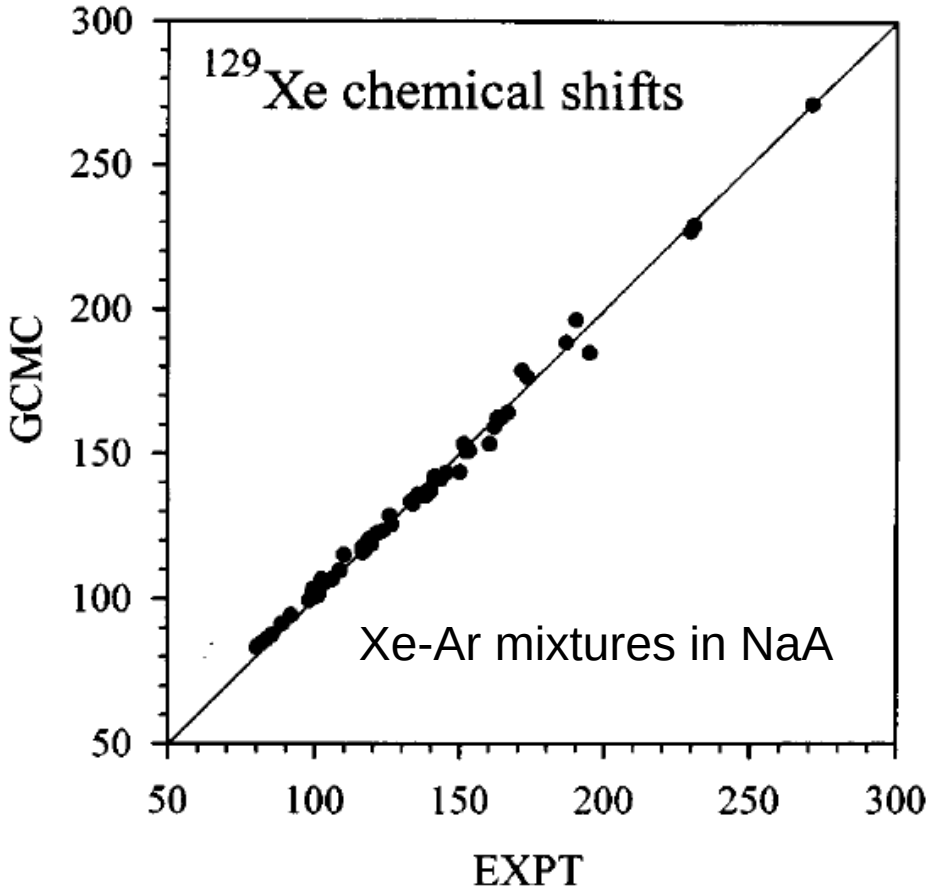
QUESTION:

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

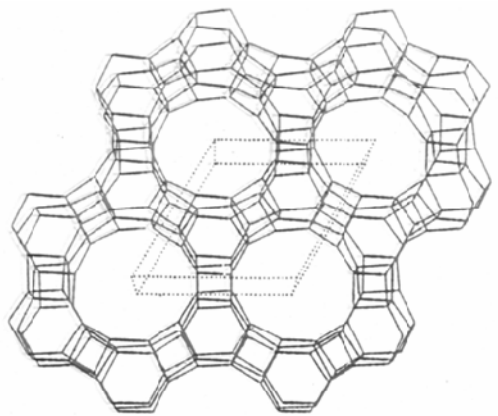
EXPERIMENTAL distribution of Xe among cages occupied by Xe atoms





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.

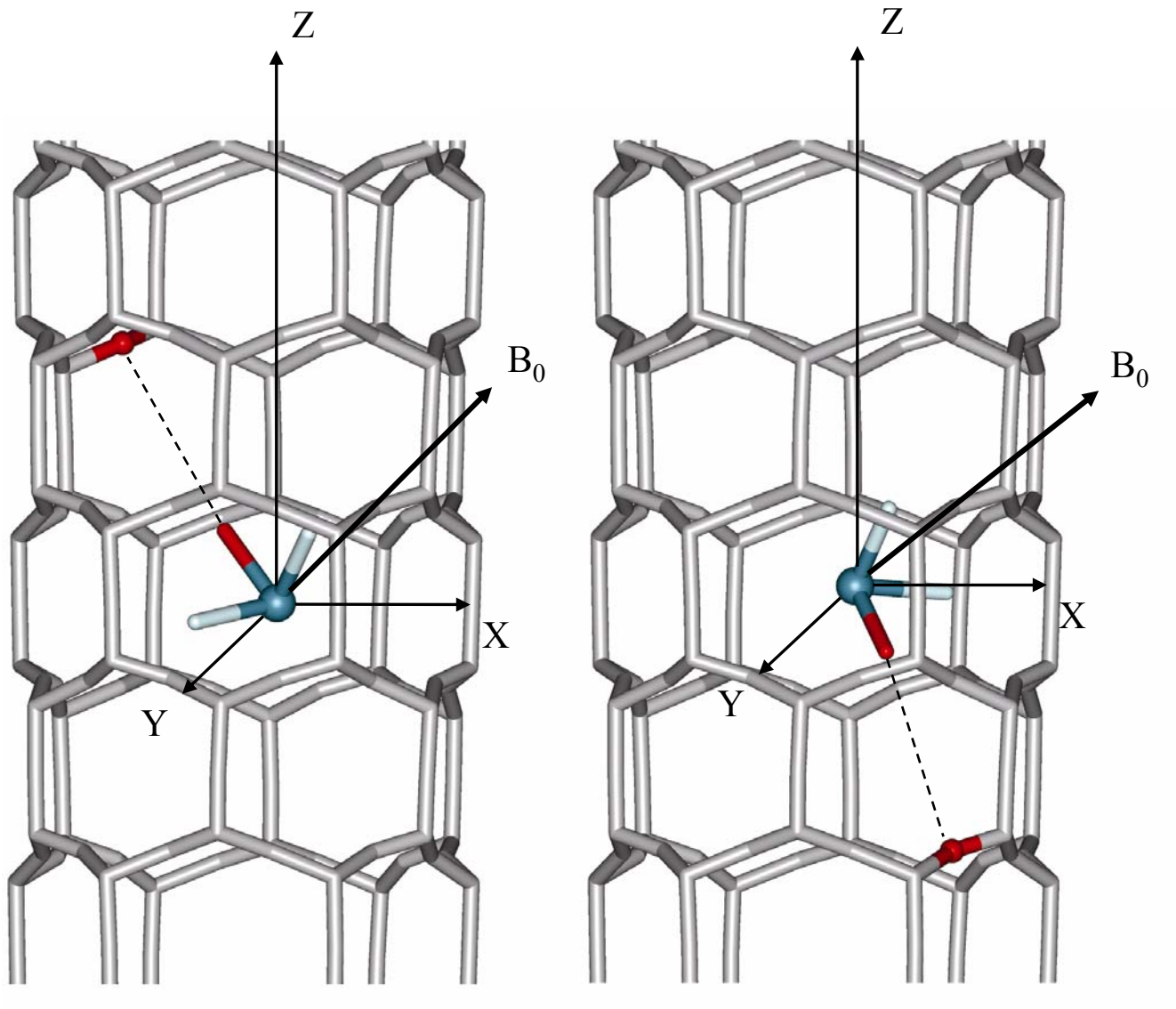
Xe in nanochannels



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

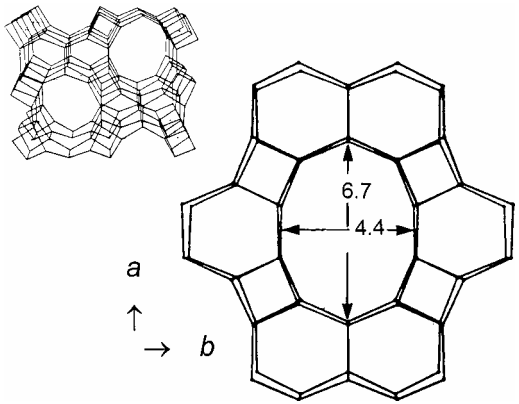
- nature of geometric confinement, i. e., size and shape of the nanochannel or cavity
- electronic structure of the channel atoms

Lineshapes by grand canonical Monte Carlo



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

Architecture of the channel determines the Xe lineshape

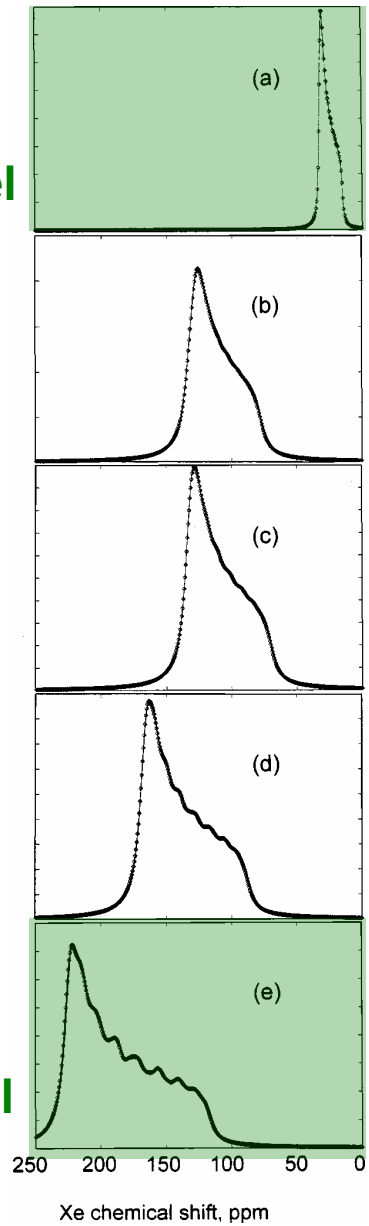


$ALPO_4$-11 architecture

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

One Xe atom in a **neon channel**

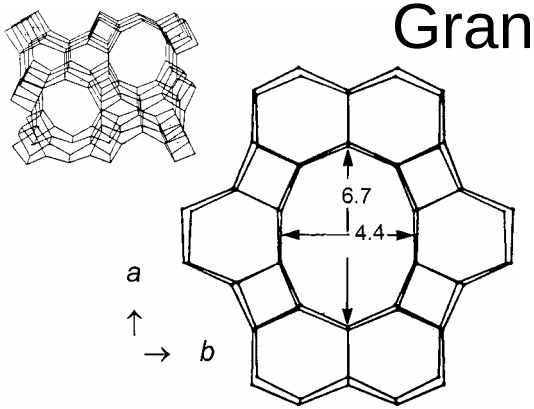
One Xe atom in an **argon channel**



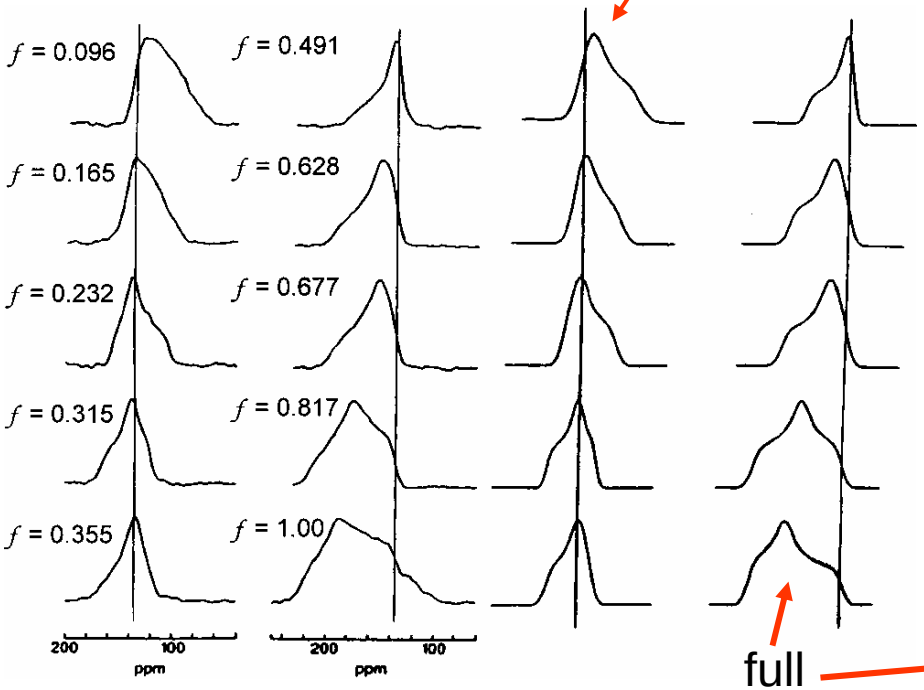
Jameson, JCP 116, 8912 (2002)

Xe in the channels of $ALPO_4$-11

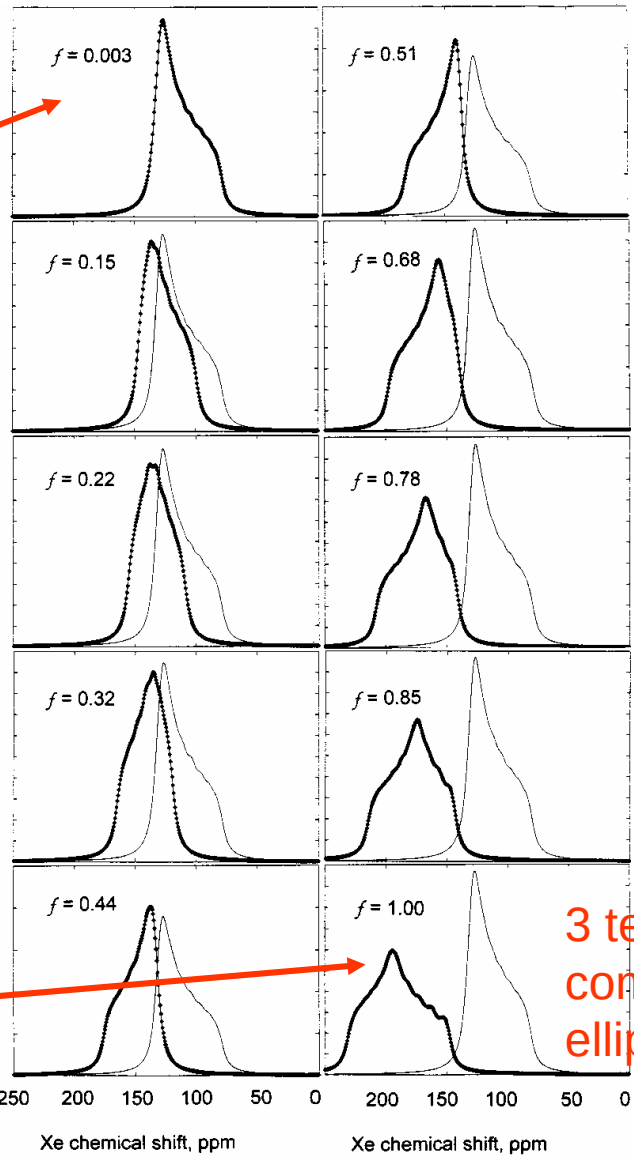
Grand Canonical Monte Carlo **SIMULATIONS**



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

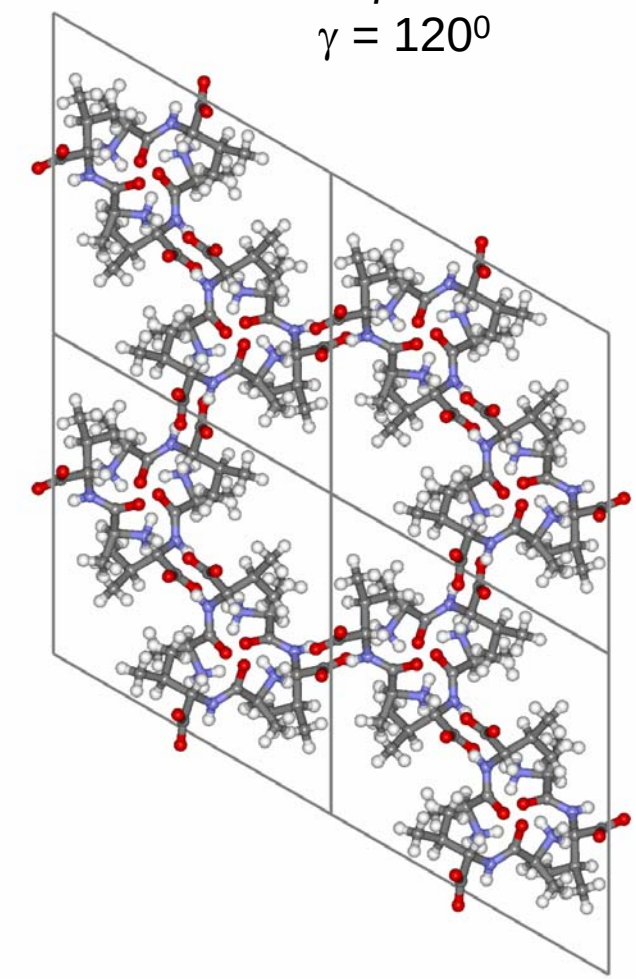
P61

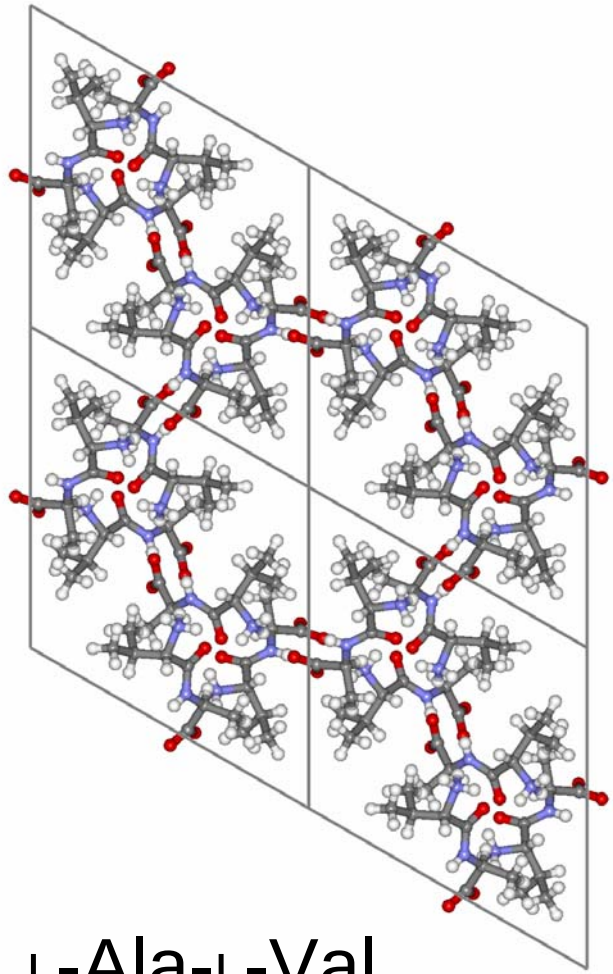
a = b= 14.461 Å

c = 10.083 Å

$\alpha = \beta = 90^0$

$\gamma = 120^0$





L-Ala-L-Val

AV

P61

a = b= 14.462 Å

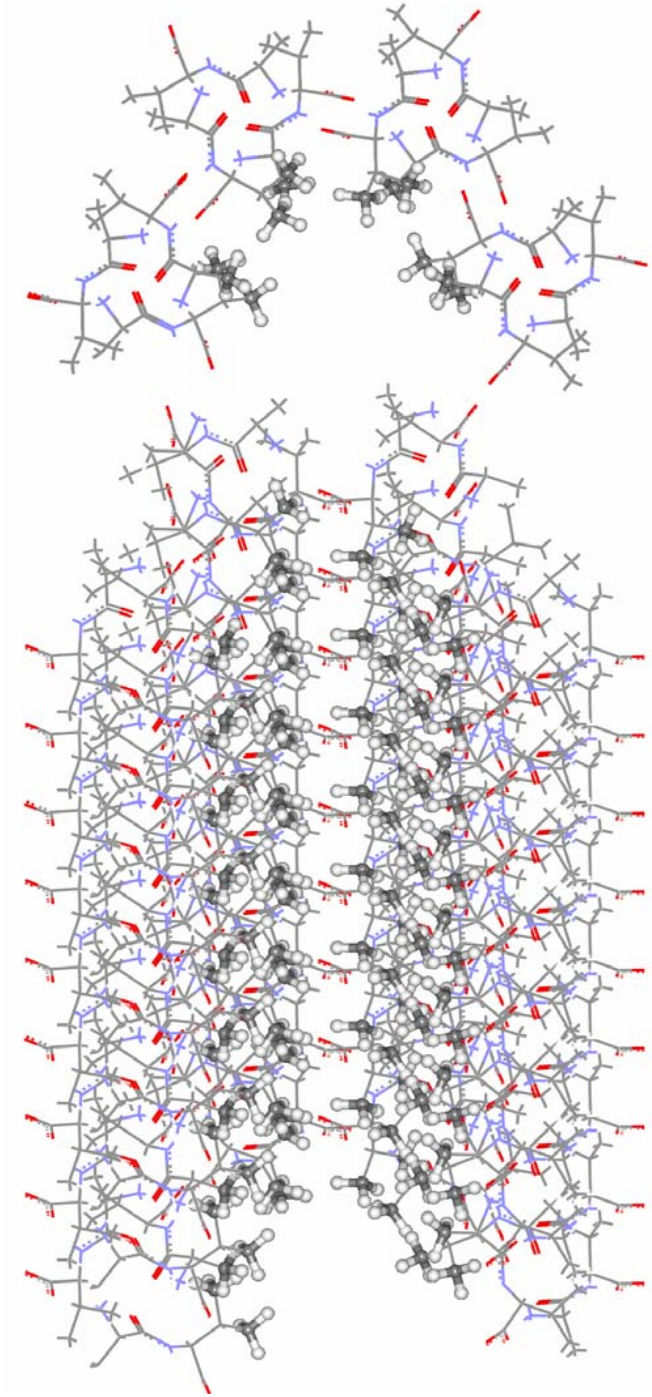
c = 10.027 Å

$\alpha = \beta = 90^0$

$\gamma = 120^0$

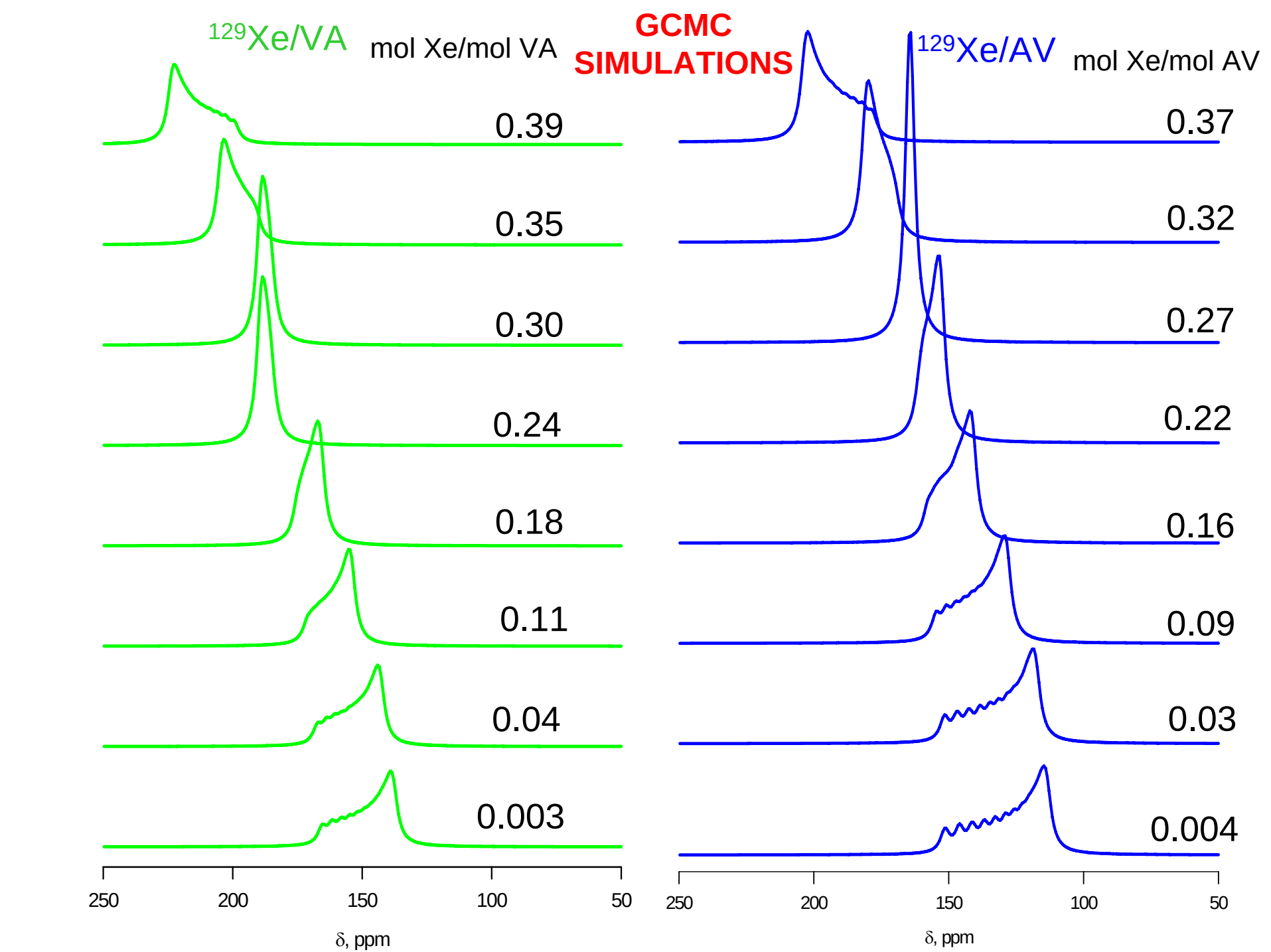
- From the perspective of the Xe only the side chain methyl groups are accessible

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

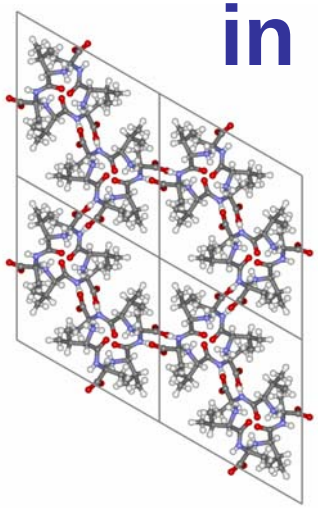


Top view

Tilted view

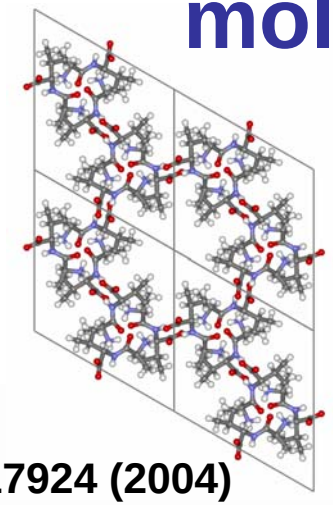

^{129}Xe/VA
mol Xe/mol VA
GCMC
SIMULATIONS
^{129}Xe/AV
mol Xe/mol AV
0.39
0.35
0.30
0.24
0.18
0.11
0.04
0.003
0.37
0.32
0.27
0.22
0.16
0.09
0.03
0.004
250
200
150
100
50
δ, ppm
250
200
150
100
50
δ, ppm

in channels of molecular crystals



L-Val-L-Ala

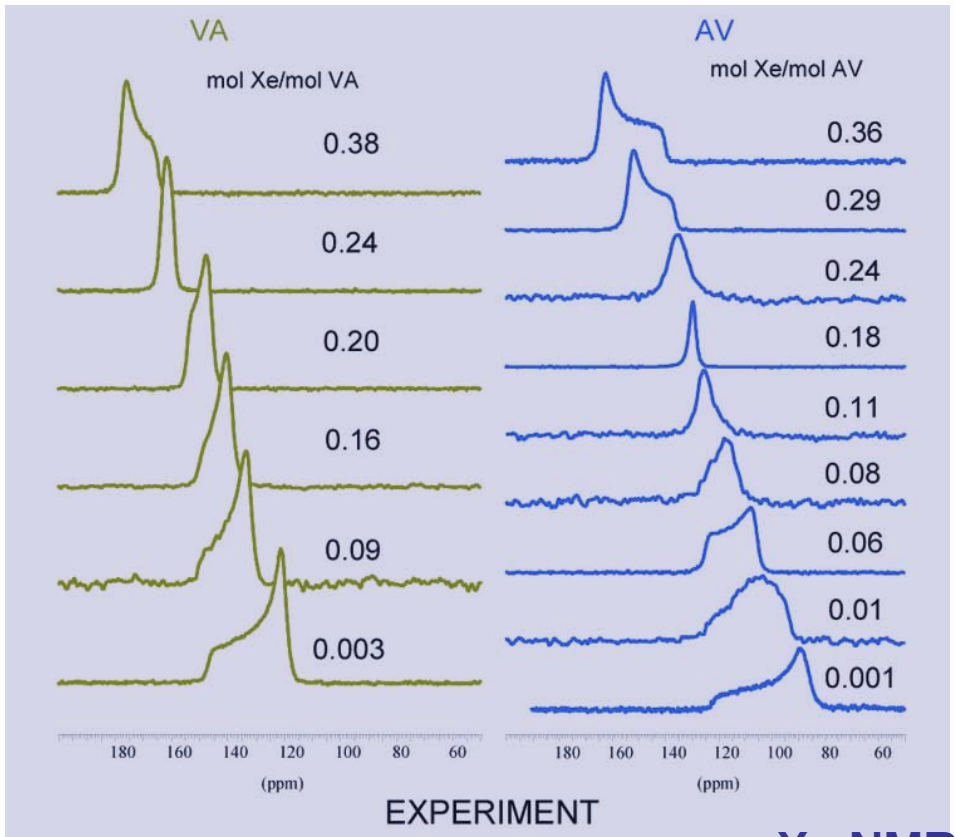
VA

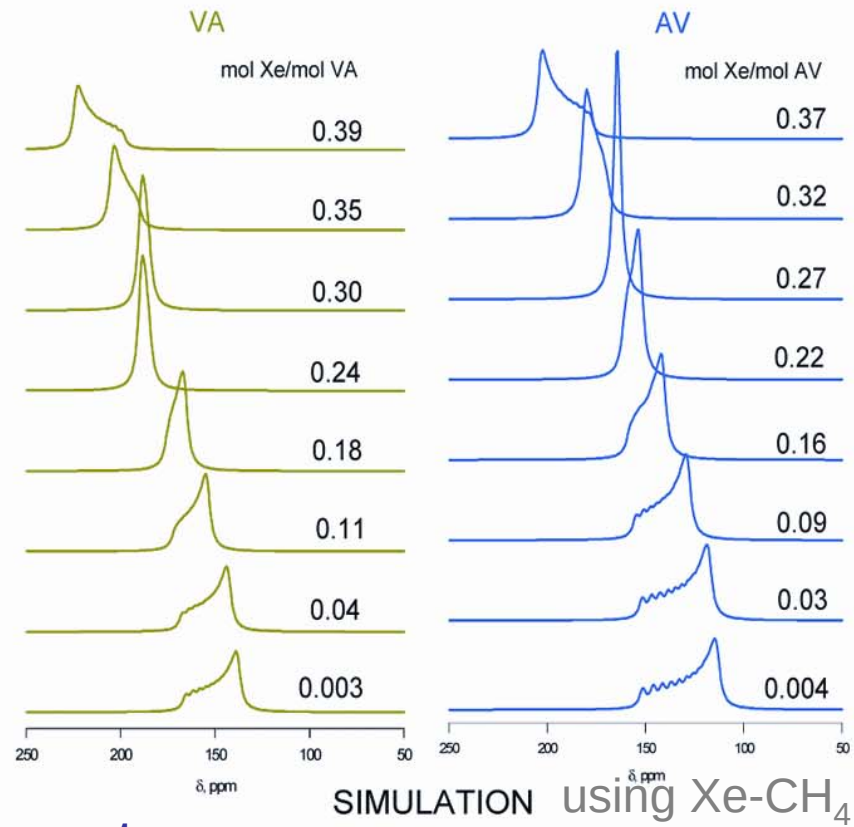


L-Ala-L-Val

AV

PNAS 101, 17924 (2004)



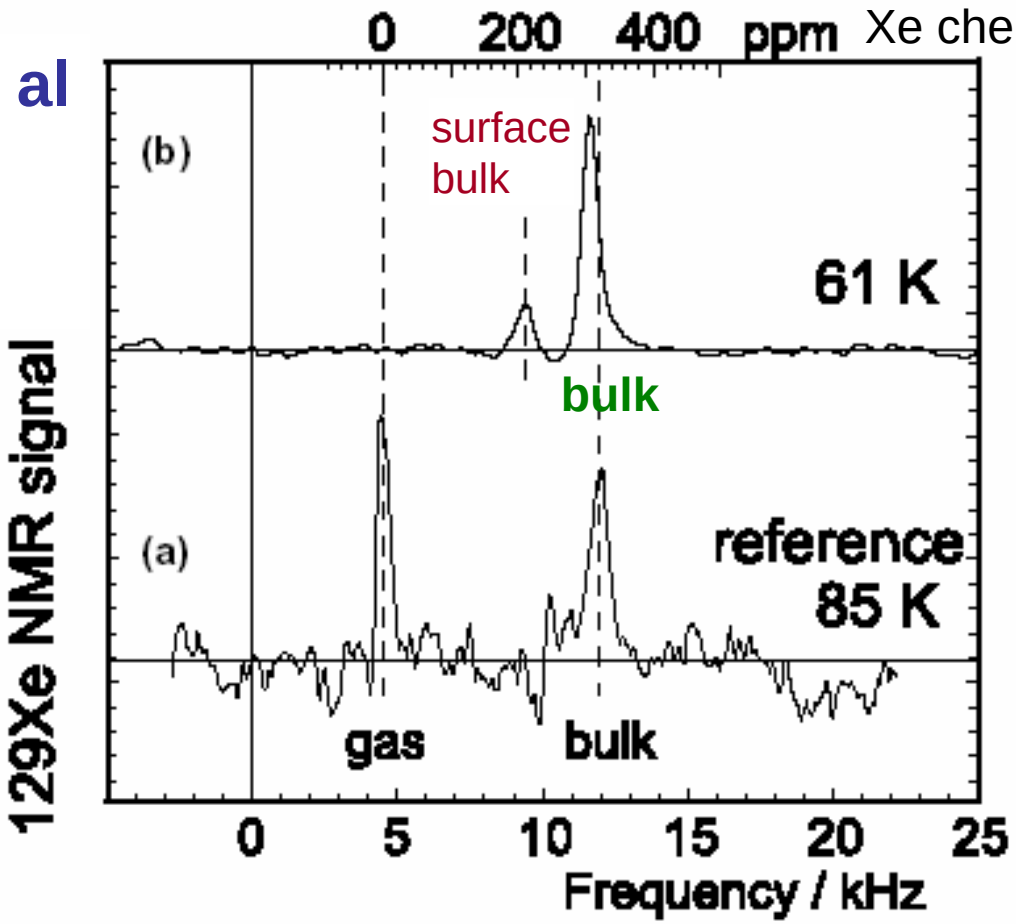


Xe NMR spectra

Xe on the surface of a single crystal metal surface

H.J. Jänsch et al

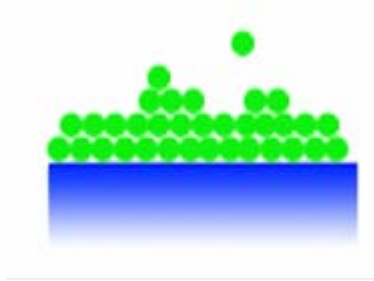
Chem. Phys. Lett.
372, 325 (2003)



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



Consider number of neighbor atoms:

- **Xe atoms on the surface of the bulk Xe appear at 209 ppm**

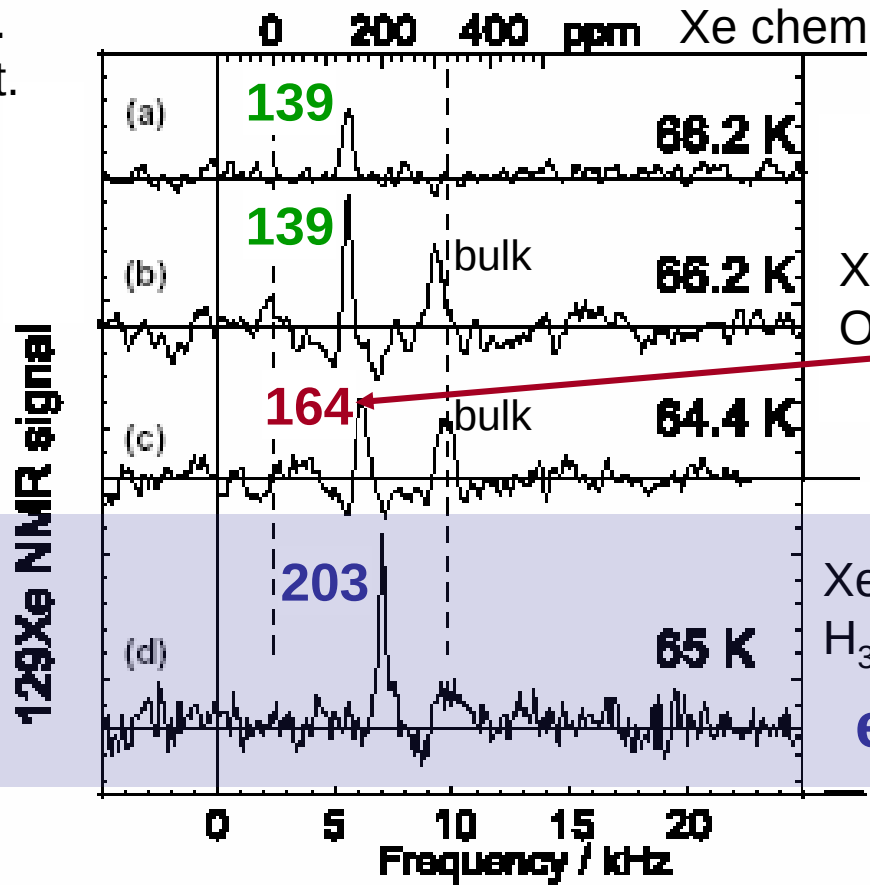
  nearest (short $r_{Xe\text{-}Xe}$) neighbors are below and in same plane.

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

  nearest neighbors are below, above, and in same plane.

Xe on a chemically modified metal surface

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



carbon monoxide

Xe on OC-Ir(111)

greater Xe coverage at lower T

Xe on H_3C-C-Ir(111)

ethylidyne

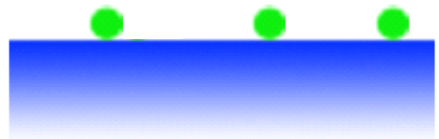
Xe can tell the difference between OC and H_3C-C surfaces.

Xe can report on surface coverage

QUALITATIVELY:

Xe @OC-Ir(111):

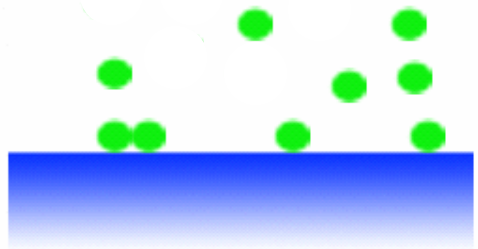
- At low Xe coverage, θ_{Xe} ,
  $\sigma = \sum\sigma(r_{Xe\text{-}O})$ only



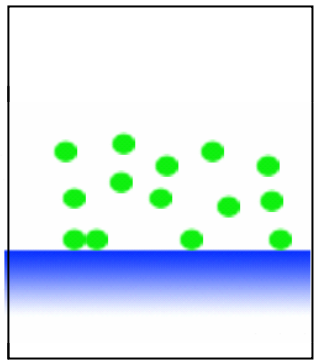
- At lower T, larger θ_{Xe} ,

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

once in a while, Xe runs into other Xe



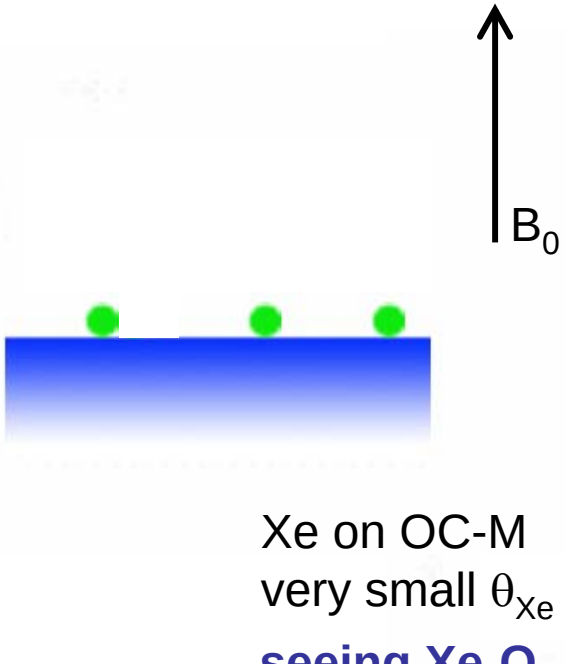
GCMC simulations of Xe on surfaces



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

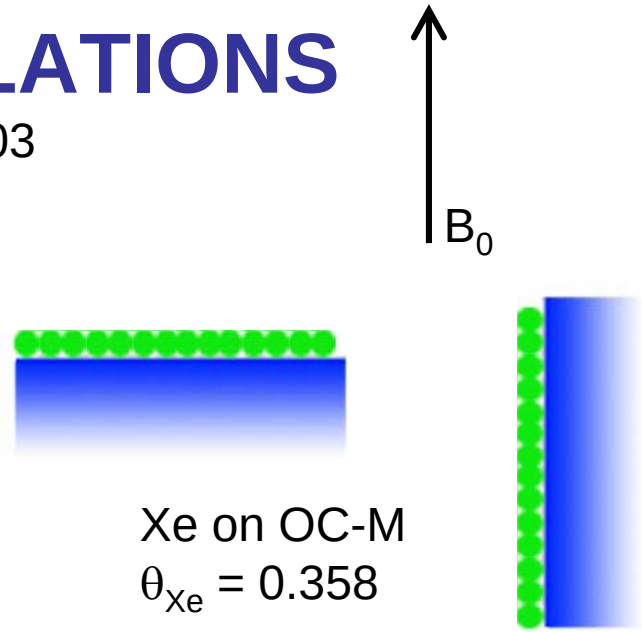
GCMC SIMULATIONS

Jameson, 2003



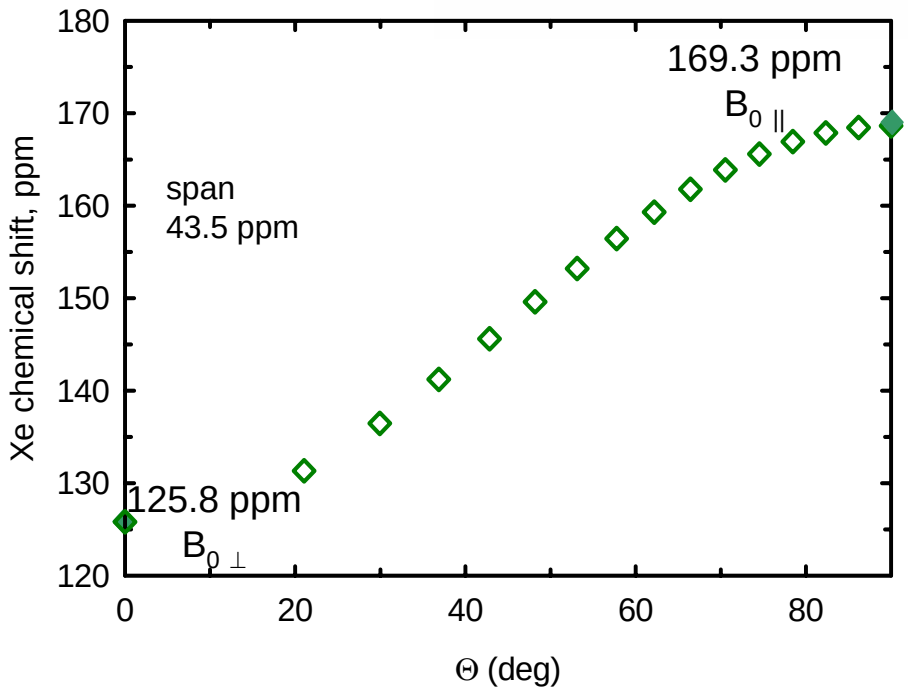
Xe on OC-M
very small θ_{Xe}

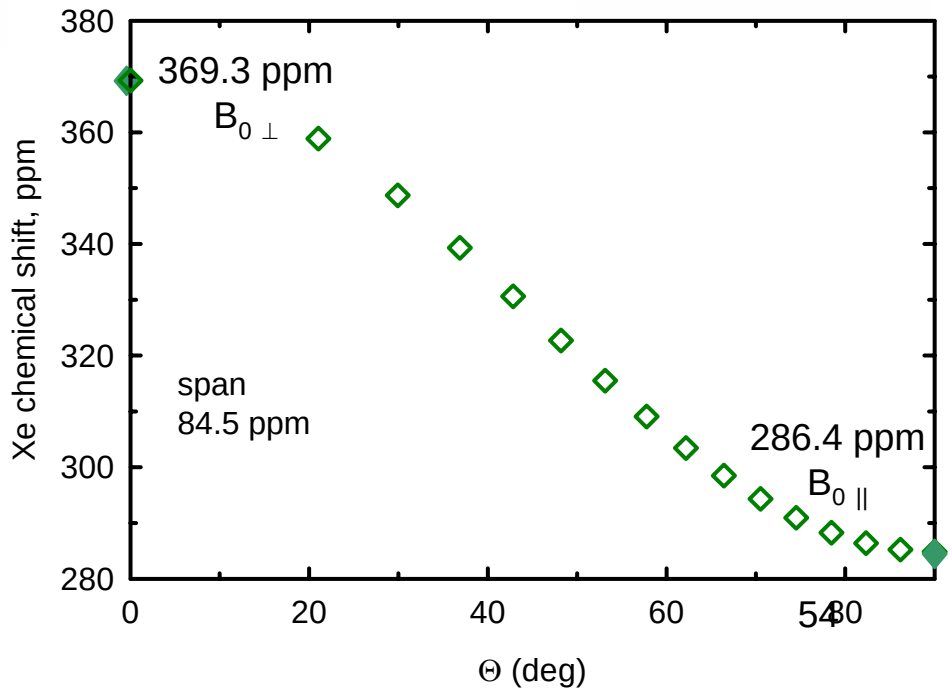
seeing Xe-O



Xe on OC-M
θ_{Xe} = 0.358

seeing Xe-O and Xe-Xe

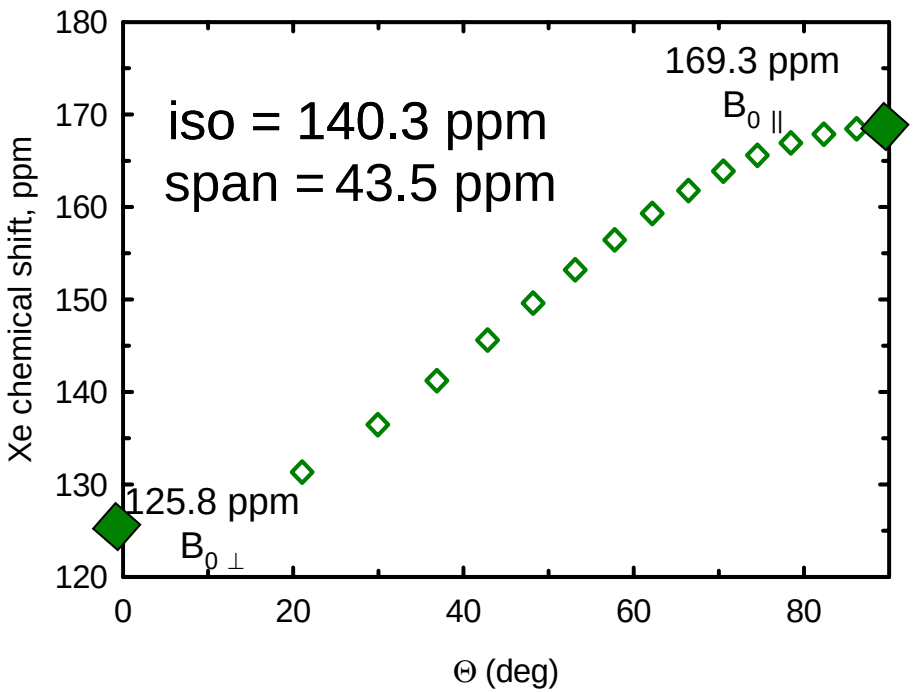




Comparison with Jänsch's experiments

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

CONCLUSIONS

The Xe NMR chemical shift is exquisitely sensitive to the environment in which the Xe atom finds itself.

The ***Xe NMR experiments*** can provide detailed information about distributions (adsorbed vs. in bulk phase, among cages in the crystal, within the cage, also in adsorption of mixtures), rates of exchange between environments, and some structural features of materials (symmetry of the cage, aspect ratio of an axially symmetric cage, aspect ratio of the channel cross-section).

It is possible to use a combination of ***quantum mechanical calculations and grand canonical Monte Carlo simulations in model systems*** in order to understand the Xe chemical shifts. From such understanding may come some insight into the encoded information in complex materials.

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Collaborators

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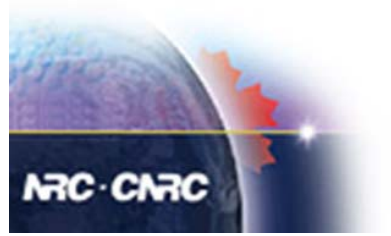

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