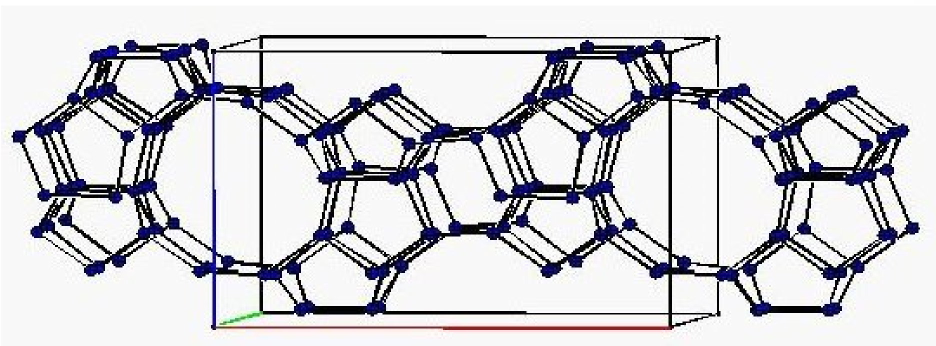
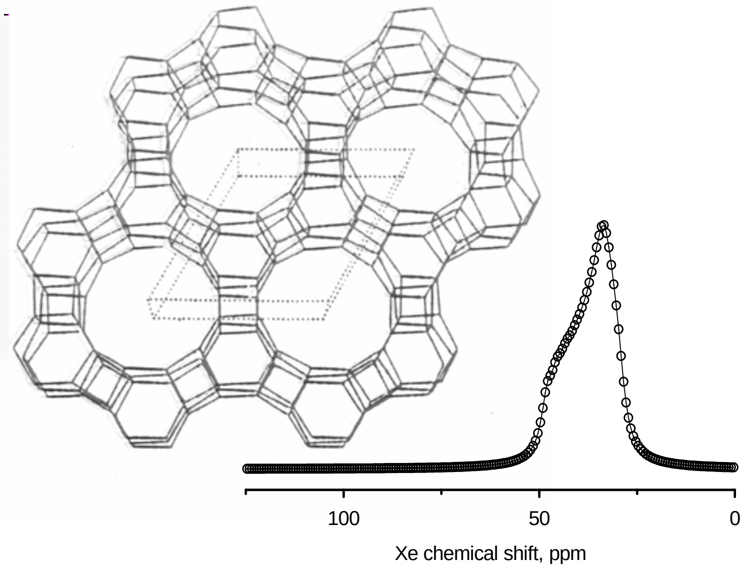
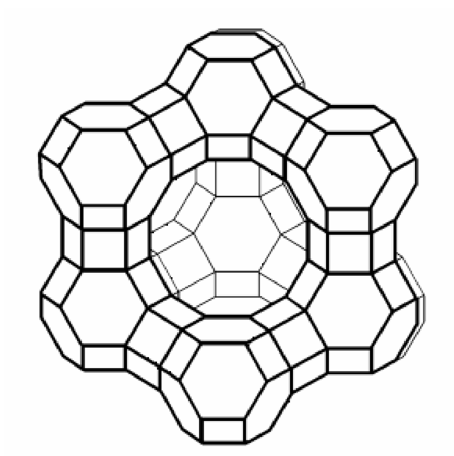
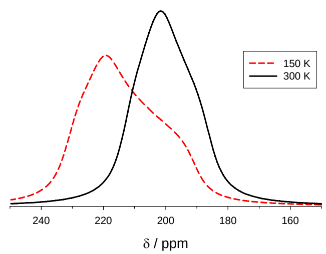
Xe in zeolitic channels

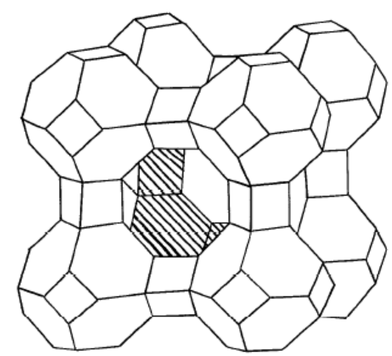








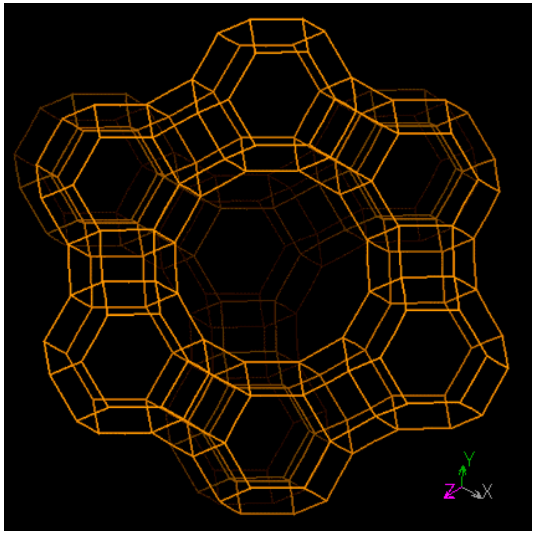
silicalite, SSZ-24, Na*Y*, Na*X*, Ca*A*



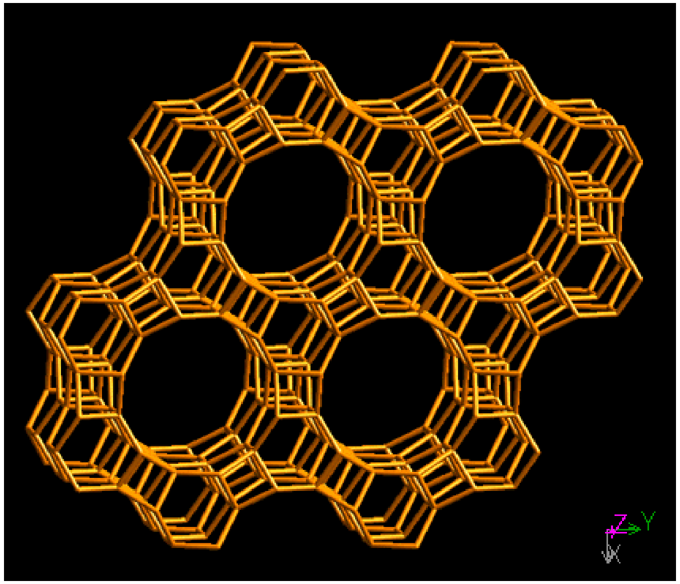
Cynthia J. Jameson

University of Illinois at Chicago

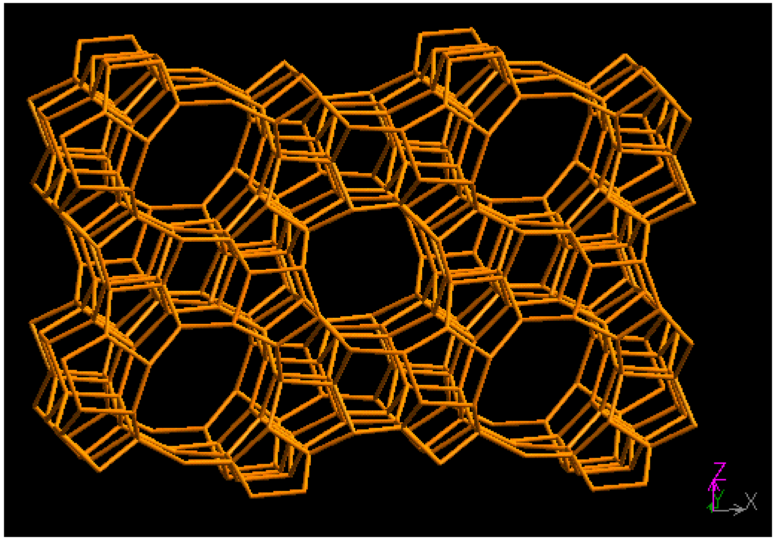
zeolite frameworks



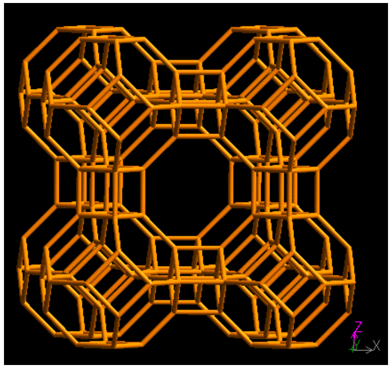
Na*Y* or Na*X* FAU



SSZ-24 AFI



silicalite MFI



Ca*A* LTA

WHY STUDY 'MICRO'POROUS SOLIDS?

- Technological applications: heterogeneous catalysis, separations, oil recovery, other industrial processes
- Applications depend on FUNDAMENTAL processes such as ADSORPTION and DIFFUSION
- ZEOLITES have well known crystalline structures. AlO_4 , SiO_4 tetrahedra form network of pores in 1, 2 or 3 dimensions, cages 3 - 13 Å diam
- Toward a FUNDAMENTAL UNDERSTANDING of sorption, DETAILED INFORMATION on adsorbate distribution, site occupancy within a cage, rates of site-to-site exchange, cage-to-cage transfer, translation and reorientation dynamics, are extremely important.

WHY ^{129}Xe NMR?

- VERY LARGE CHEMICAL SHIFTS are extremely sensitive to the environment of the Xe atom.
- SIZE about right, explores the same pores that CH_4 or larger molecules can.
- Studies in ZEOLITES at MODEST PRESSURES are particularly appropriate since these conditions are much closer to realistic catalytic conditions than ultra-high vacuum.

IN THE USUAL Xe NMR EXPERIMENT probing zeolites:

- Xe is in *fast exchange* inside $\leftrightarrow$ outside.
- In the usual *variable T or P* studies, there are changes in (a) the gas/adsorbed partitioning, (b) the distribution of occupancies among cavities, and (c) the fraction of Xe population participating in exchange with the intercrystalline environment, *all occurring at the same time*.
- Quantitative interpretation of such experiments is difficult.

Our approach has been to:

- First choose **model environments** with well-defined characteristics and which can provide detailed experimental information
- Examine the ^{129}Xe NMR chemical shifts in these model environments experimentally
- Attempt to reproduce the observed chemical shifts and distributions by grand canonical Monte Carlo simulations using *ab initio* chemical shift functions.
- Apply gained understanding and tested methods to other zeolites

From experiments with Xe in Na*A* zeolite:

we have answered the following questions about distributions

- When molecules are adsorbed in a microporous solid at a given loading, how are these molecules distributed among the cavities?
- When the average loading is 0.5 molecules/cavity, can we establish that there are any cavities with more than one molecule?
- Within a cavity, where do the molecules spend most of their time: like a snowball in the middle of the cavity? or like a thin film along the inside walls?

about competitive adsorption

- When two types of molecules are adsorbed in a microporous solid, how are these molecules distributed among the cavities?
- Does the distribution of one type of molecule affect the distribution of another?
- Is the adsorption of one type of molecule enhanced or diminished by competition with another type?
- How many molecules of type 2 can be found in those cavities that have exactly *n* molecules of type 1?

about diffusion

- How often does a molecule migrate from one cavity to another? Can we follow this migration as a function of time?
- Does the rate of migration depend on how many other molecules are in the same cavity where it is leaving from ?
- Does the rate of migration depend on how many other molecules are in the destination cavity?

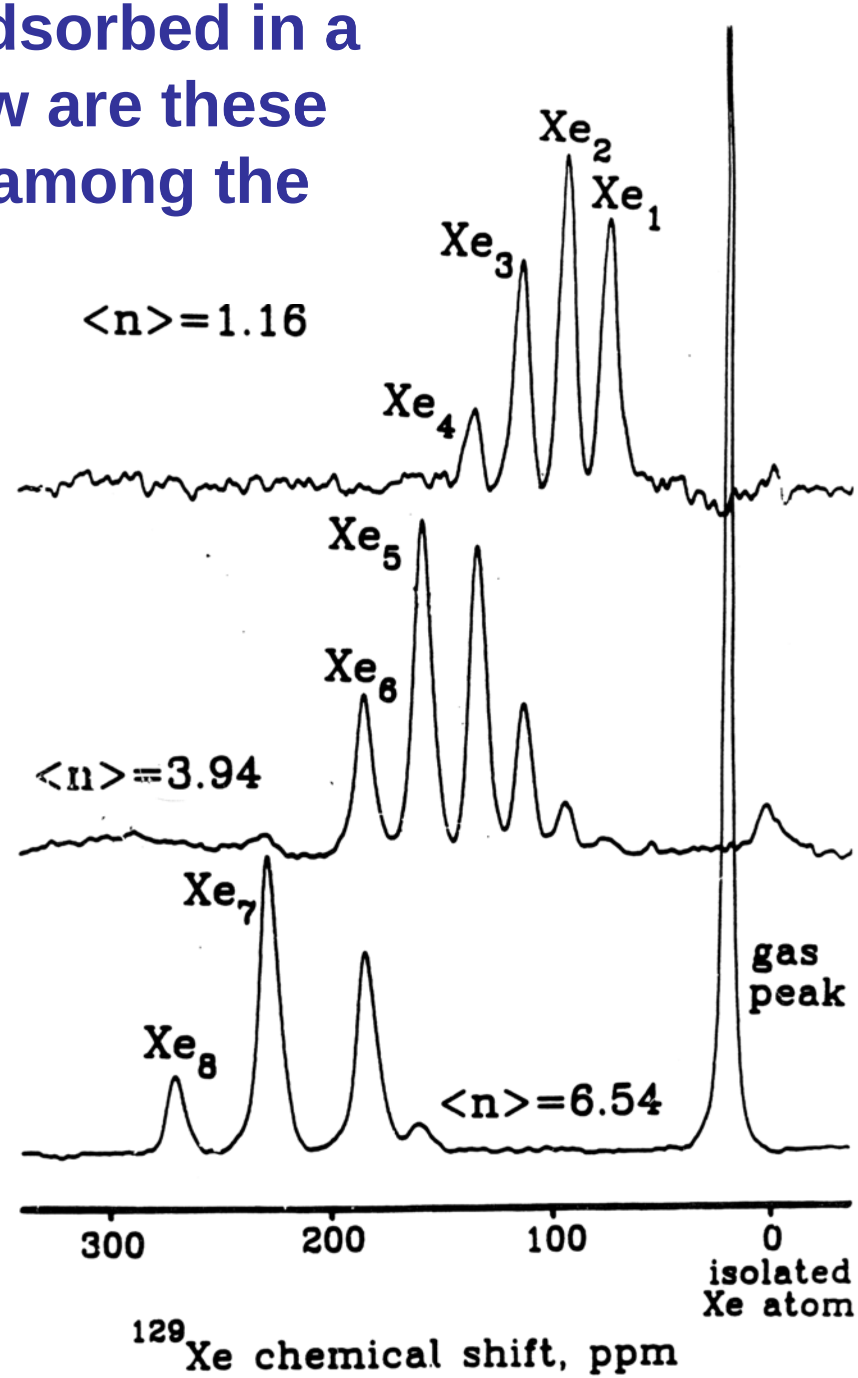
about extra-framework cations

- How do the type, size and locations of the ions affect the Xe chemical shift?
- How is the distribution of sorbates affected by the cations in a zeolite?

Examples of **well-defined environments** we have used:

- a single alpha cage (zeolite Na*A*) locations of framework atoms, cations known independently, alpha cage with a known fixed occupancy (exactly *n* Xe atoms).
- compare with single alpha cage in zeolite K*A*, exactly *n* Xe atoms. Same framework, different cation: K^+ vs. Na^+.

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



Examples of **well-defined environments** we have used: ...

- binary mixture equilibrium distribution among cavities, alpha cages with *n* Xe atoms exactly and an average number of other sorbate. Find number of co-adsorbate molecules with each Xe_n, varying mole fraction in the gas phase.

Information from Xe NMR spectrum of binary mixtures in Na*A*

The **SHIFT** of the Xe_n peak is a measure of the average number of sorbate molecules in the same cage with Xe_n

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

Examples of **well-defined environments** we have used: ...

- alpha cages (zeolite $Ca_xNa_{12-2x}A$) exactly *n* Xe atoms, in cages having 0, 1, 2 or 3 Ca^{2+} ions. Same framework, compare cages under successive replacement of $2Na^+$ by 1 Ca^{2+} ion).
- variable temperature study at fixed known occupancy: *n* Xe atoms in a single alpha cage, K^+ vs Na^+ ions.

FINDINGS

- The magnitude and the temperature dependence of the chemical shift of Xe_1 contains information about the one-body distribution function of a single Xe atom in the cage.

- The magnitude and the temperature dependence of the chemical shift difference between Xe_n and Xe_1 contains information about the pair distribution function of an Xe_n cluster, about the averaging of Xe positions within the cage
- The intensities provide direct information about the distribution of Xe atoms among the cages.

- The equilibrium distribution of the components of a binary mixture are well reproduced by the GCMC simulations.
- When the co-adsorbed species is in fast exchange, the Xe_n chemical shift provides the average number of co-sorbate molecules in the same cage as *n* Xe atoms.
- The assumption of pairwise-additive shielding contributions permits computation of average shieldings in a GCMC simulation which can be compared directly with experiment

The INTERMOLECULAR CHEMICAL SHIFT makes possible the *direct* experimental determination of:

- the **fraction of cages** which contain 1, 2, ..., *n,* up to 8, Xe atoms
- in a favorable case, the **fraction of cages** which contain exactly *n* Xe atoms and 1or 2 Kr atoms
- the **individual rate constants** for cage-to-cage migration of Xe in NaA, from a cage containing m Xe atoms to a cage containing n-1 Xe atoms.

The INTERMOLECULAR CHEMICAL SHIFTS make possible, with the help of GCMC simulations, the *indirect* experimental determination of:

- the distribution of a single Xe atom in the cage
- **the average number of co-sorbate molecules in the same cage as n Xe atoms**, for *any* overhead binary mixture of Xe and another gas, at *any* temperature, total pressure, and mole fraction,

i.e., complete information about distribution of Xe and other sorbate molecule within the zeolite.

from experiments and simulations in these model systems

- we found that we can reproduce the detailed experimental information: relative intensities (distributions) and Xe chemical shifts in adsorbed pure Xe and in adsorbed binary mixtures as a function of overhead Xe densities, mixture composition, and temperature.
- Thus armed with the understanding gained, and with confidence in our methods, we can now **investigate systems where more complete averaging occurs** such that it is no longer possible to observe individual cages with fixed numbers of Xe atoms.

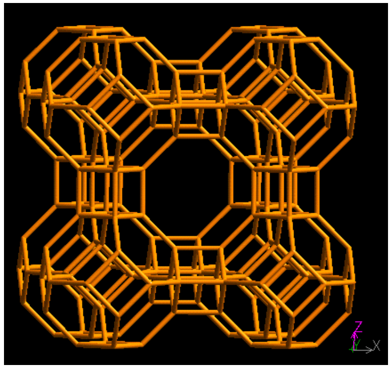
<u>Now</u> we can consider Xe in the following zeolite environments

- equilibrium distribution of Xe in the cavities/channels in a single crystal; study partitioning between gas and adsorbed phase in large crystals; variable temperature study at a fixed (full) occupancy (silicalite)
- Xe in fast exchange in one-dimensional channels with variable occupations in large crystals, revealing line shapes carrying information about average Xe chemical shift tensors (SSZ-24)

and: ...

- Xe in fast exchange in identical cavities with different occupations, in large crystals (minimize exchange with intercrystalline gas) (Ca*A*)
- Xe in fast exchange inside-outside at variable Xe loading in microcrystalline samples: changes in gas/adsorbed partitioning, distribution of occupancies among cavities, and some fraction of Xe population participating in exchange with inter-crystalline environment.
  THIS IS THE TYPICAL Xe NMR EXPERIMENT in porous solids. (Na*Y*, Na*X*)

Xe in Ca*A*



Ca*A* LTA

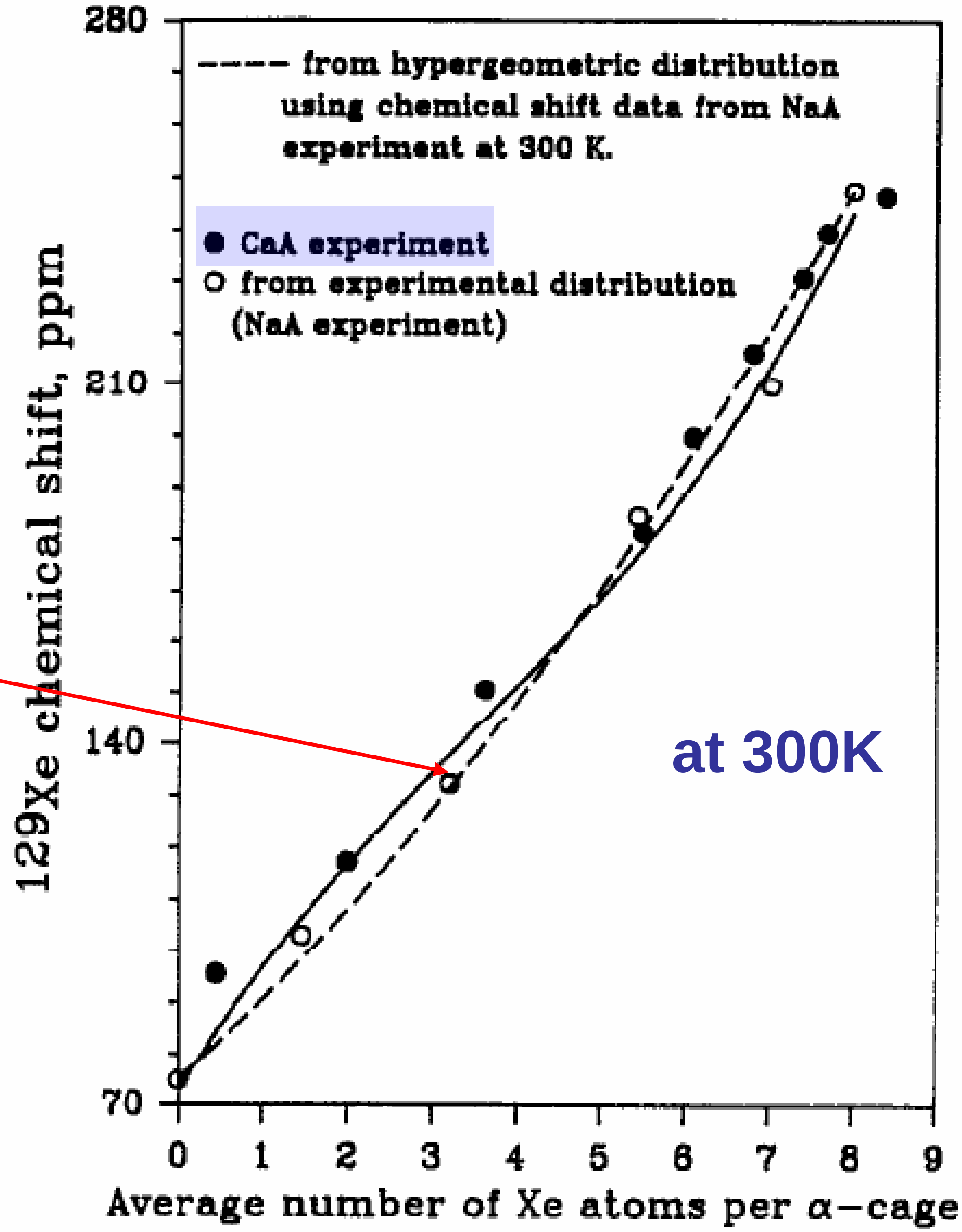
The same aluminosilicate framework as Na*A*.
The only difference is that there are half as many counterions as in Na*A*, so that all Ca^{2+} ions are entirely within the cage walls leaving no ions to block the openings to the alpha cages.
Thus, the adsorbed Xe moves freely in the three-dimensional network of alpha cages and reports a single average Xe chemical shift.

Can we use what we know from Xe in Na*A* to understand the Xe chemical shifts as a function of Xe loading in Ca*A*?

PREDICTION

(a) using same distribution of Xe atoms among the cages at 300 K

(b) using the same Xe chemical shifts for n Xe atoms in a cage at 300 K



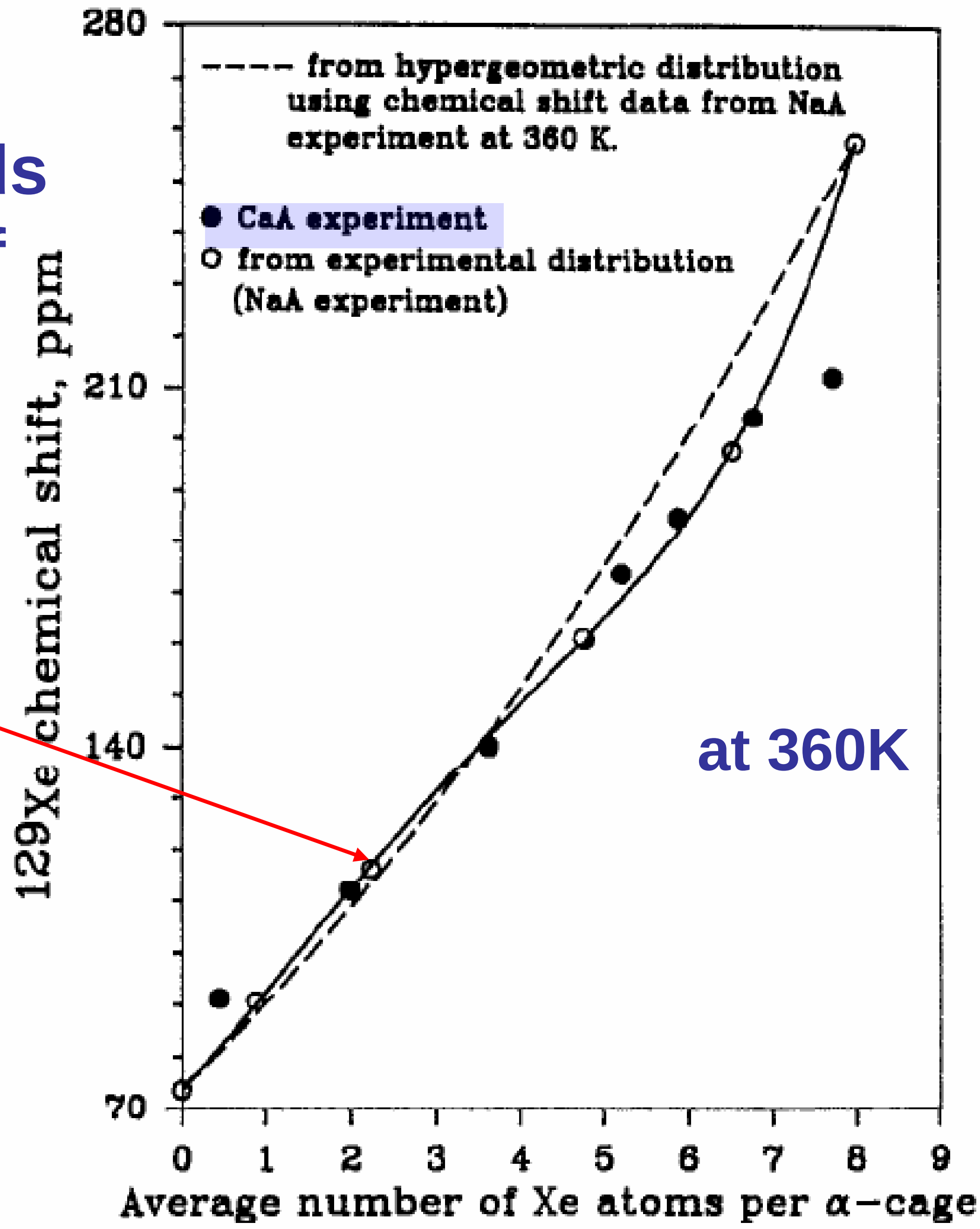
at 300K

Except at the maximum loading, NaA information leads to good prediction of Xe in Ca*A* as a function of temperature.

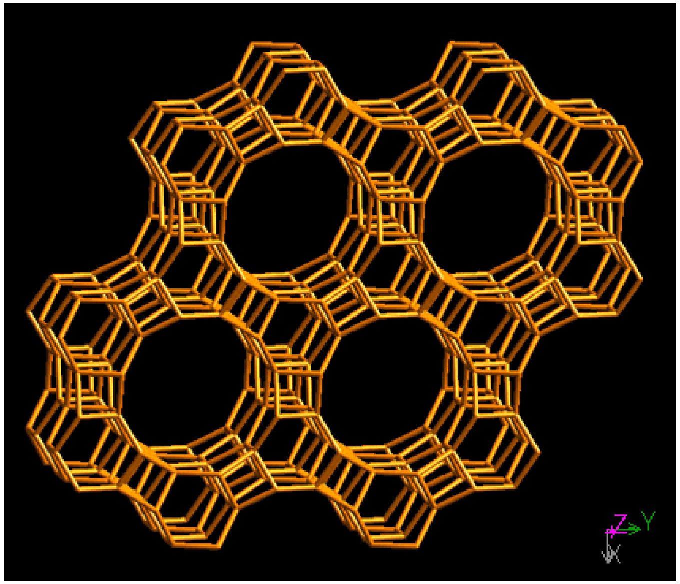
PREDICTION

(a) using same distribution of Xe atoms among the cages at 360 K

(b) using the same Xe chemical shifts for n Xe atoms in a cage at 360 K



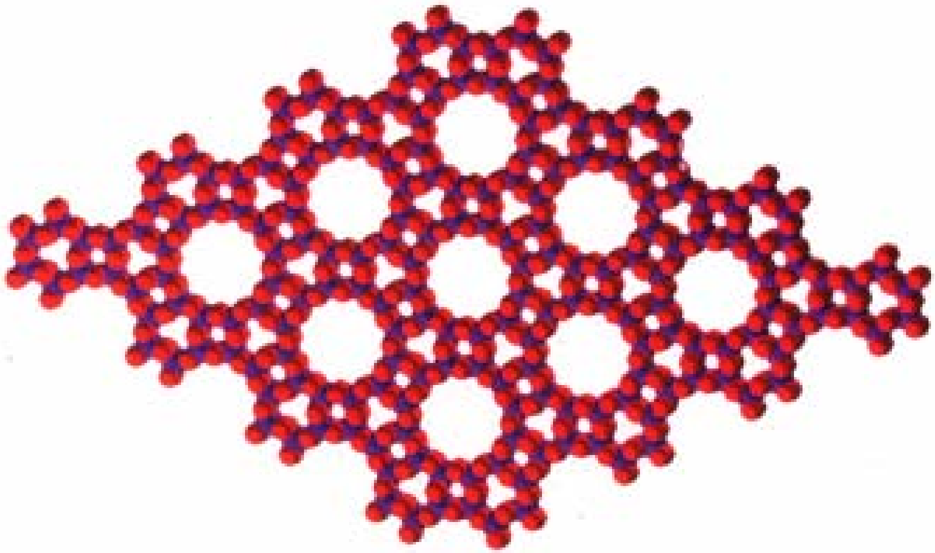
Xe in SSZ-24



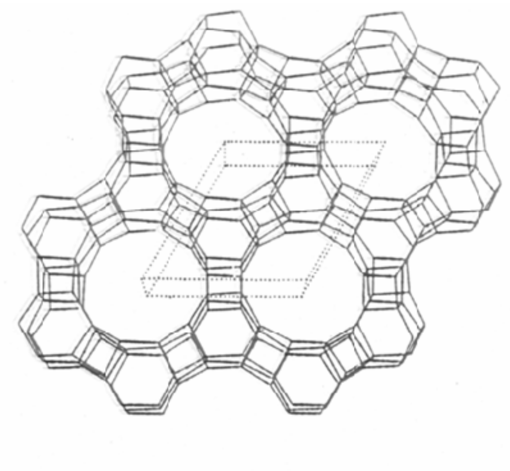
SSZ-24 AFI

In SSZ-24, the adsorbed Xe moves freely in the one-dimensional channels and reports a single average Xe chemical shift.

SSZ-24 one-dimensional channels have nearly cylindrical symmetry



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):

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

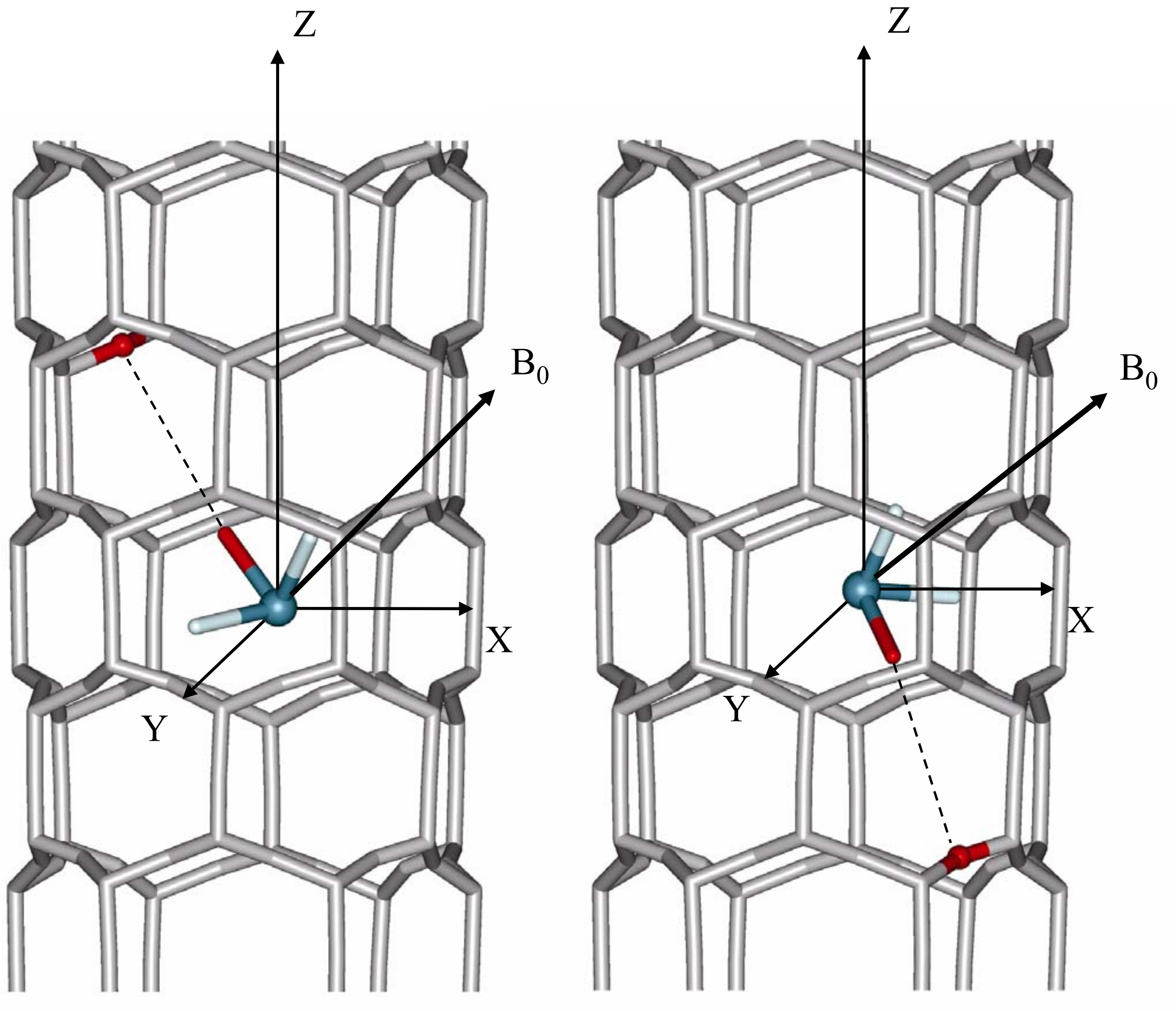
one Xe tensor from interaction with ALL channel atoms

pairwise additive Xe-channel interaction

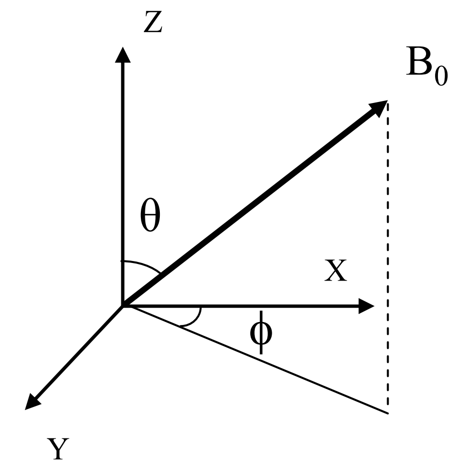
How to find σ_{xx} and other tensor components for a particular Xe atom at a particular position in a channel of O atoms?

- Assume σ_{xx} for a particular Xe atom at a particular position in the channel can be written as a sum of contributions from one Xe-O interaction at a time

Lineshapes by grand canonical Monte Carlo



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



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

The **dimer tensor model** for Xe shielding tensor in a channel lined with O atoms

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

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

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

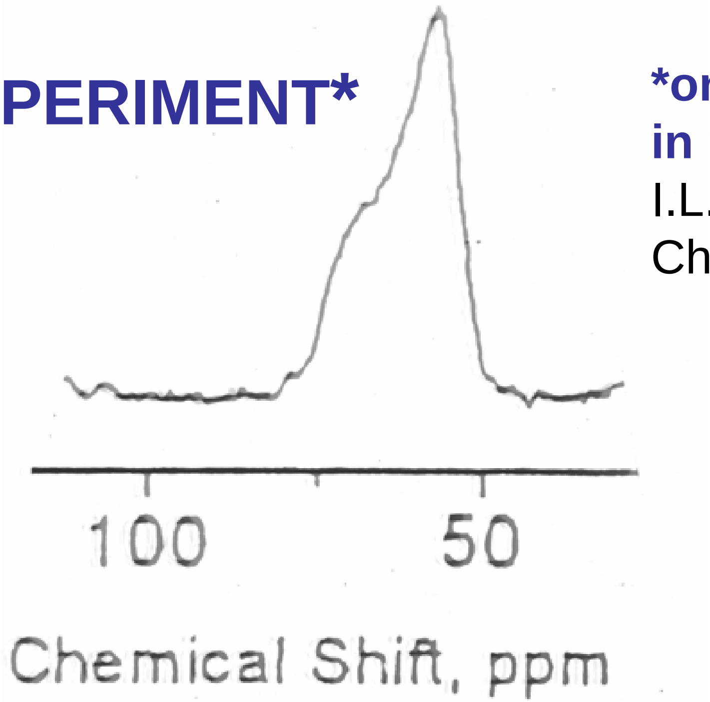
Xe-Xe contributions

The contribution to the shielding of Xe at point J due to the K_{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 $\sigma_{\perp}(r_{XeXe})$, $\sigma_{||}(r_{XeXe})$.

Grand Canonical Monte Carlo Simulations

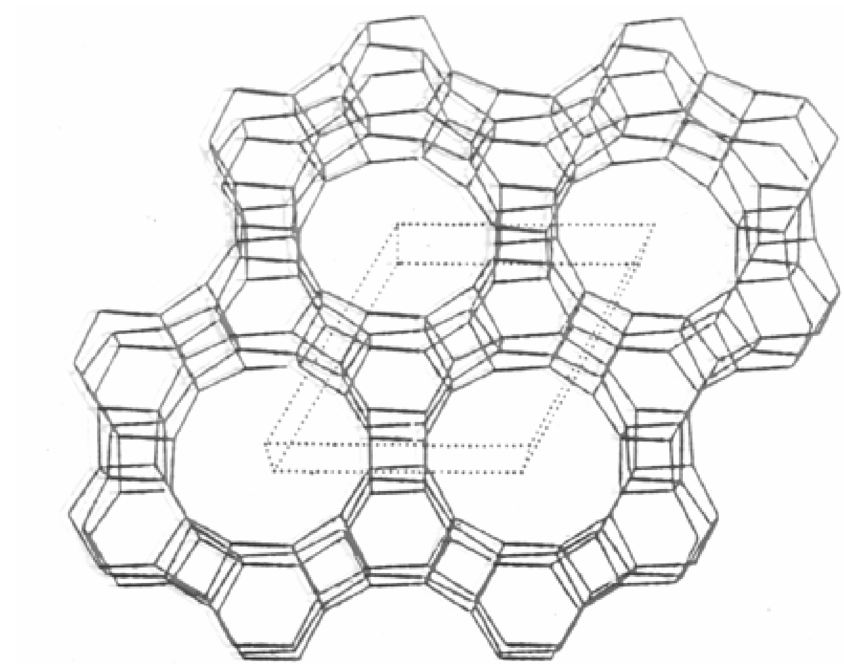
- Impose the condition that the chemical potential of Xe in the overhead bulk gas is the same as the chemical potential of Xe in the adsorbed phase (decide to create, destroy, displace Xe atoms, accordingly)
- Choose a B_0 direction, taking steps of equal probability in $\zeta\phi$ space
- Sum the tensor components along the B_0 direction from each Xe-O (or other channel atom), from each Xe-Xe

EXPERIMENT*

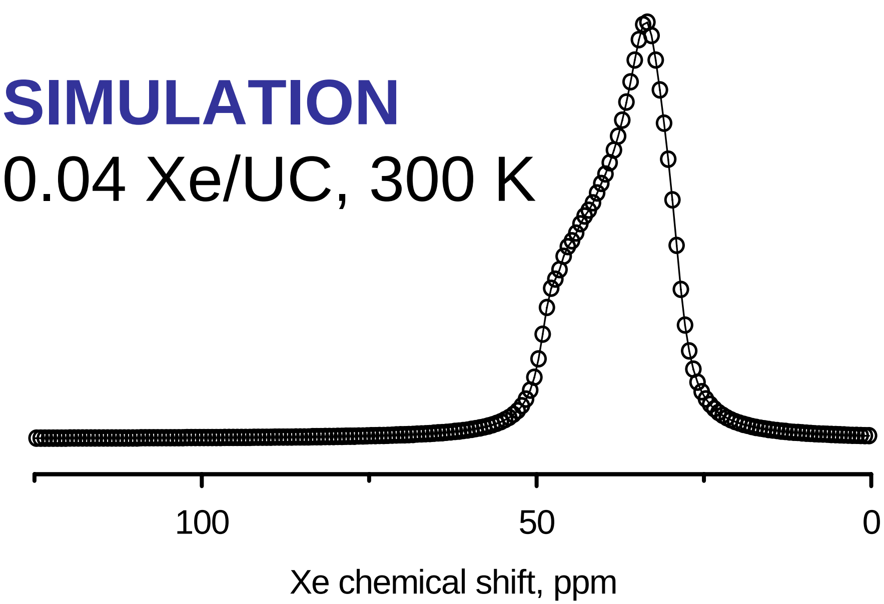


***one-scan hyperpolarized ^{129}Xe in polycrystalline SSZ-24 at 293 K**
I.L. Moudrakovski et al.
Chem. Mater. 12, 1181 (2000).

with no Xe-Xe contributions



SIMULATION
0.04 Xe/UC, 300 K

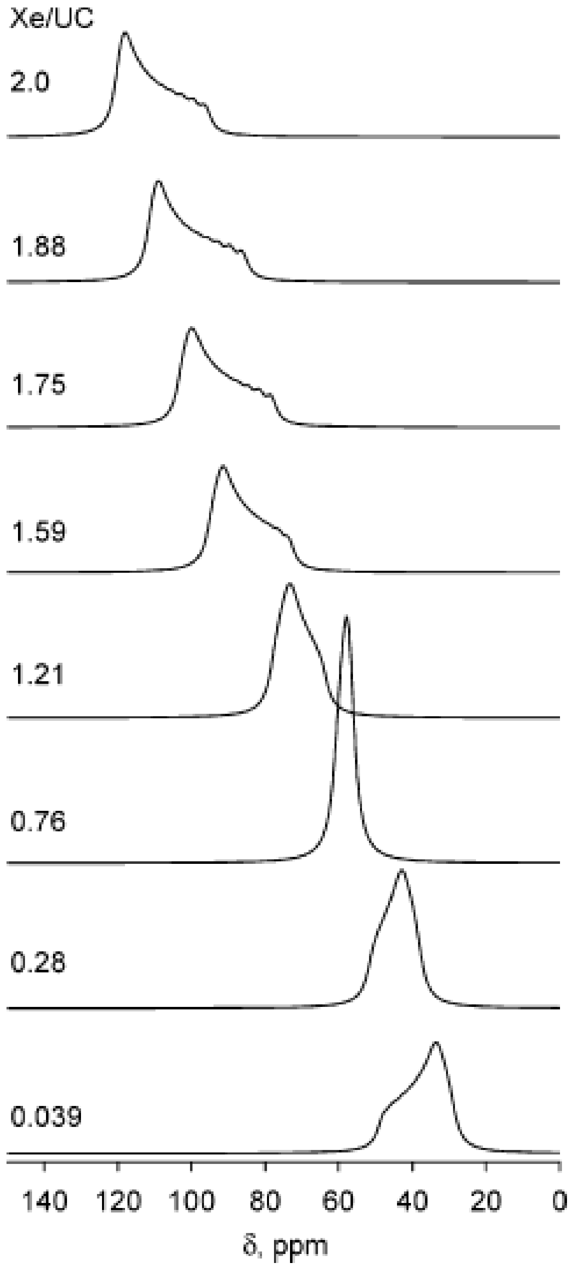


This GCMC simulation uses the same shielding and potential functions as for Xe in silicalite.
C.J. Jameson, JACS, 126, 10450 (2004)

with increasing Xe occupancy

Theoretical ^{129}Xe NMR line shapes in zeolite SSZ-24 from GCMC simulations of Xe in a simulation box of 2x2x3 unit cells under periodic boundary conditions at 300 K.

The changing axiality of the average tensor comes from increasing Xe-Xe contributions with increasing occupancy



Parallel (along the long axis of the channel) component of the Xe tensor is not a constant but increases with increasing occupancy in this case.

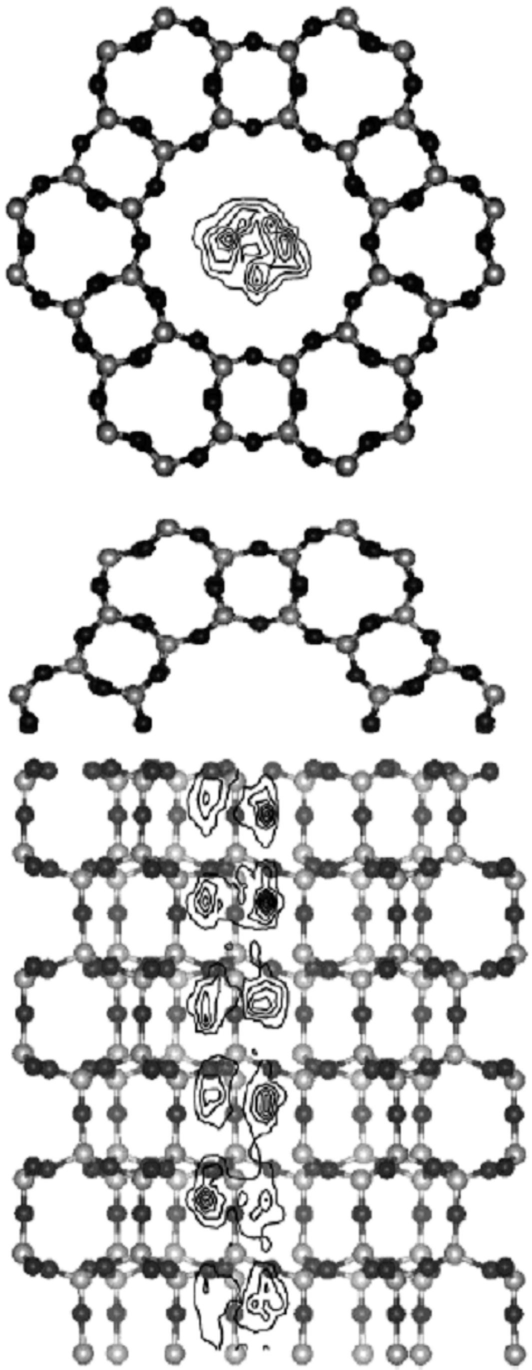
This means that on the plane perpendicular to the channel axis containing the Xe nucleus, there can be electrons of a neighbor Xe contributing to the shielding.

one-body distribution function for Xe

Probability distribution of the Xe within the channel of SSZ-24 at 300 K at 94% of maximum Xe occupancy.

(top) on a plane perpendicular to the *c* axis of the crystal, showing a cross section of a channel,

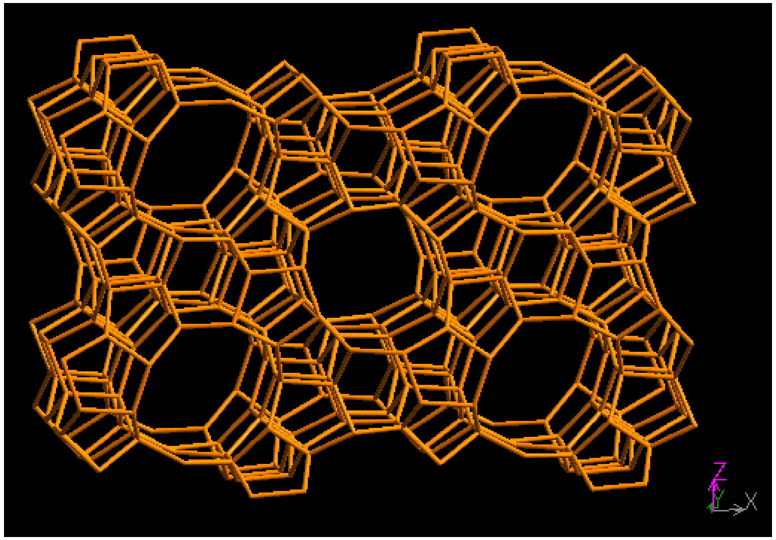
(bottom) on a plane parallel to the axis of a channel.



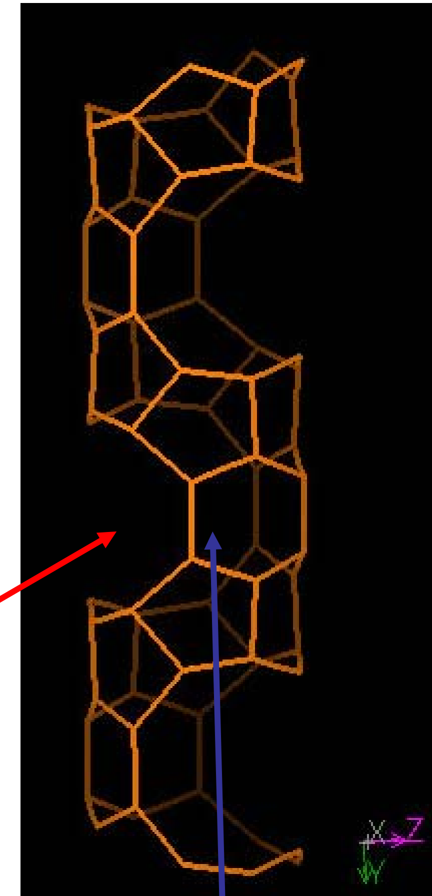
GCMC simulations of Xe under fast exchange (in large crystals) provide

- Xe chemical shifts (including line shapes) for direct comparison with experimental values at given overhead Xe densities and temperature
- Xe probability distributions within the unit cell (one body distribution function)
- Xe-Xe two-body distribution functions

Xe in silicalite

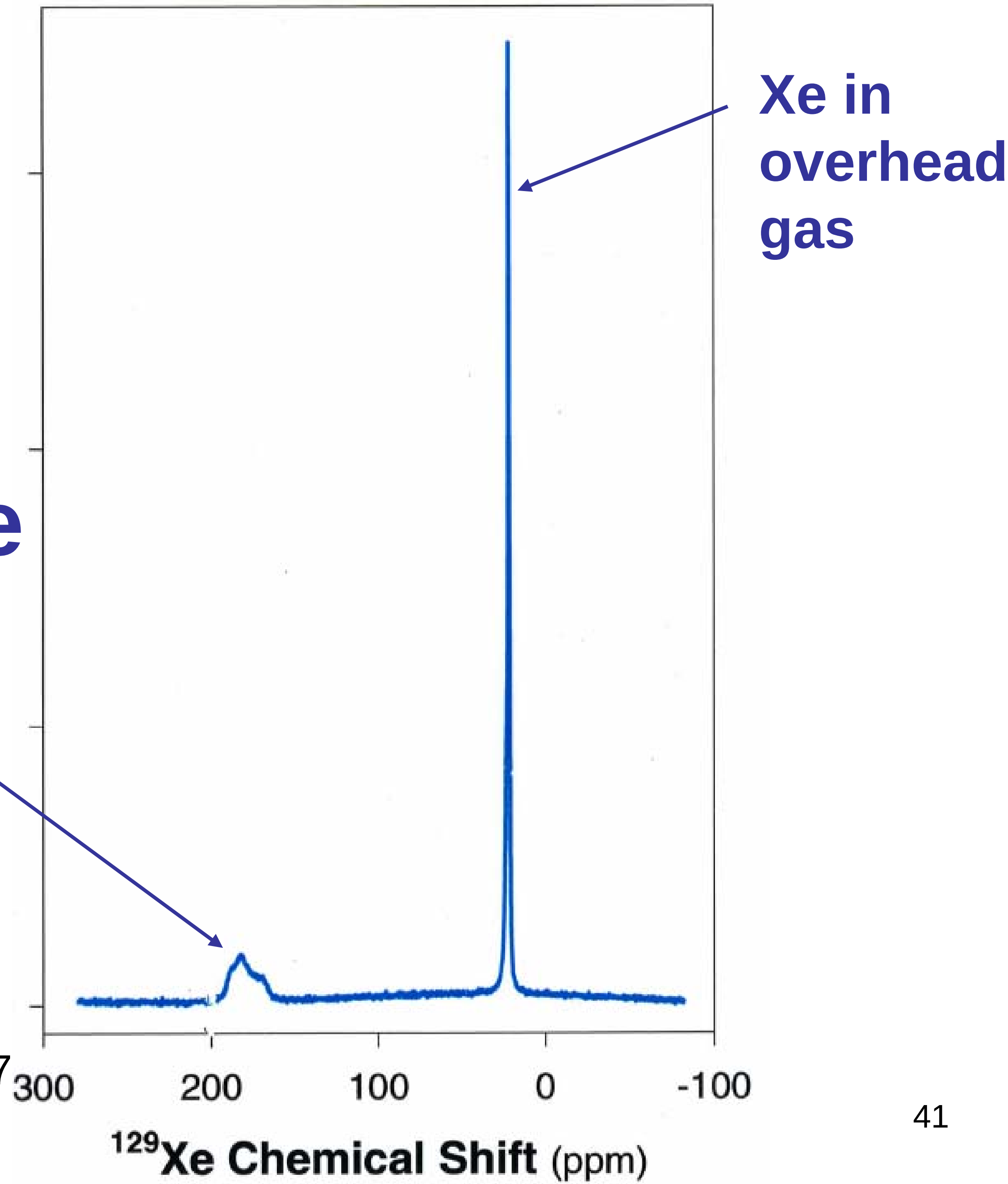


silicalite MFI



This is a three-dimensional channel system consisting of two intersecting channel systems. The larger straight channel is shown going vertically in this view. The other sinusoidal channels cross the straight ones and the intersections provide somewhat larger space for the Xe.

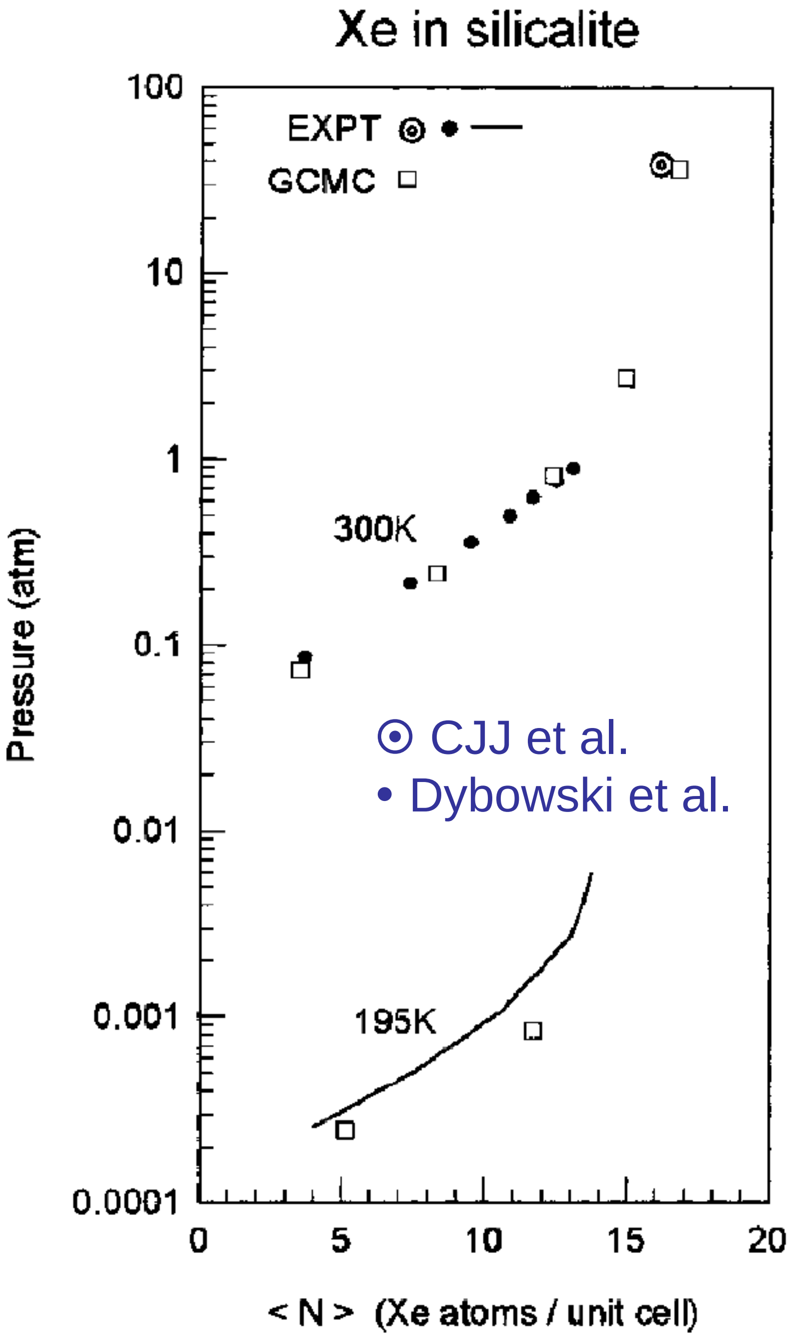
anisotropy is evident in the adsorbed Xe line shape



C. J. Jameson, A. K. Jameson, R. E. Gerald II, and H. M. Lim, **J. Phys. Chem**. 101, 8418-8437 (1997).

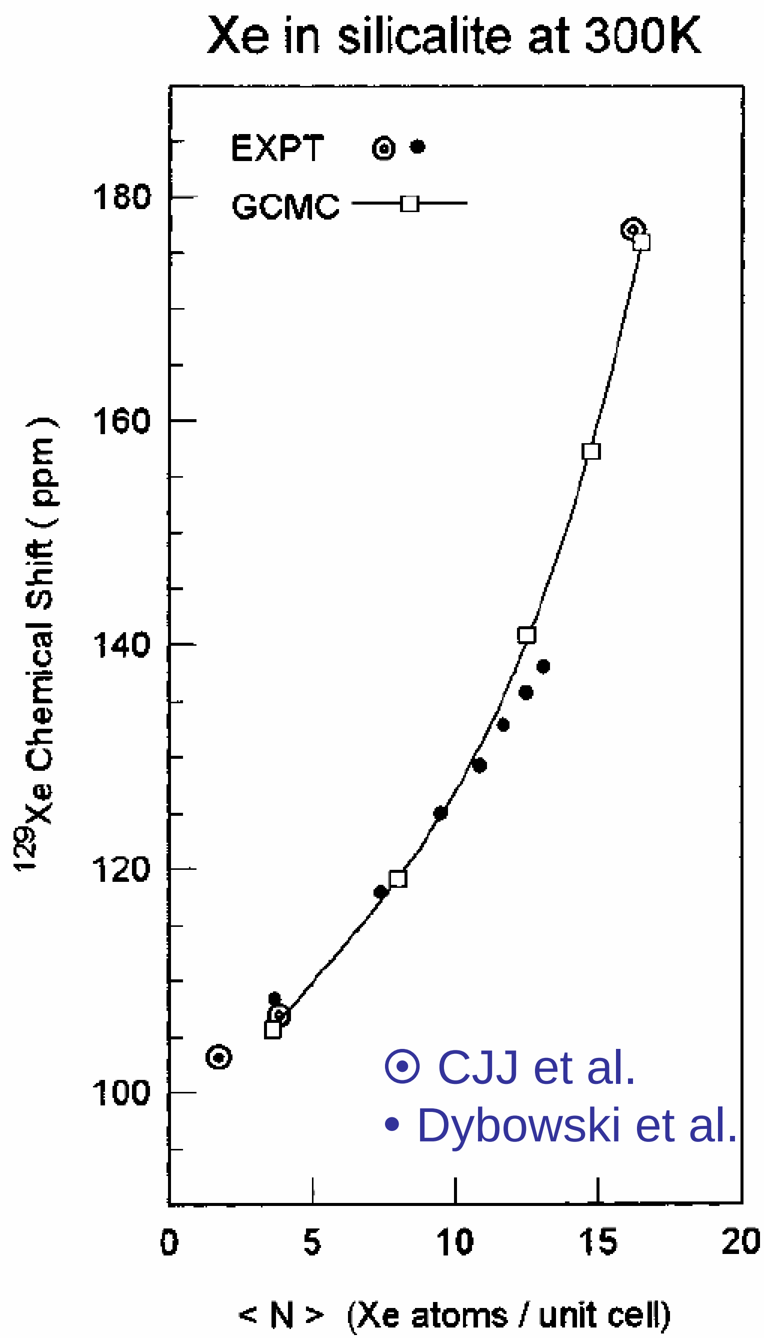
adsorption isotherm Xe in silicalite

are well-reproduced by GCMC simulations



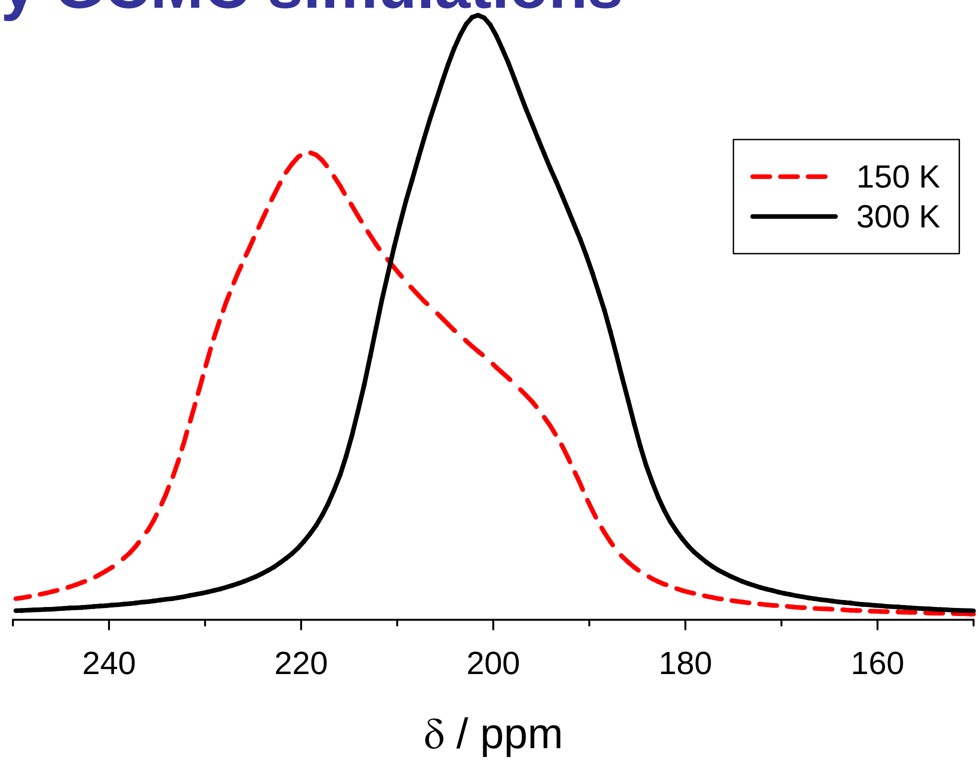
Xe chemical shifts with increasing occupancy Xe in silicalite

are well-reproduced by GCMC simulations



Xe line shapes at full occupancy

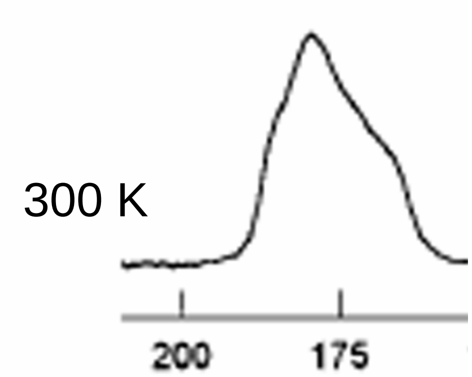
are well reproduced by GCMC simulations



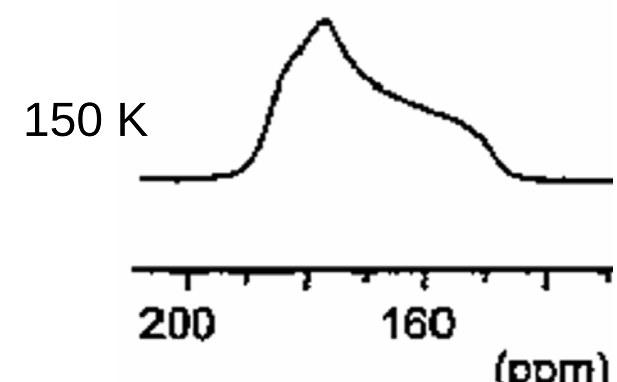
CALCULATIONS

Jameson 2003

Temperature dependence with no change in $\langle N \rangle_{Xe}$



Jameson et al.
J. Phys. Chem. B **1997,** *101,* 8418



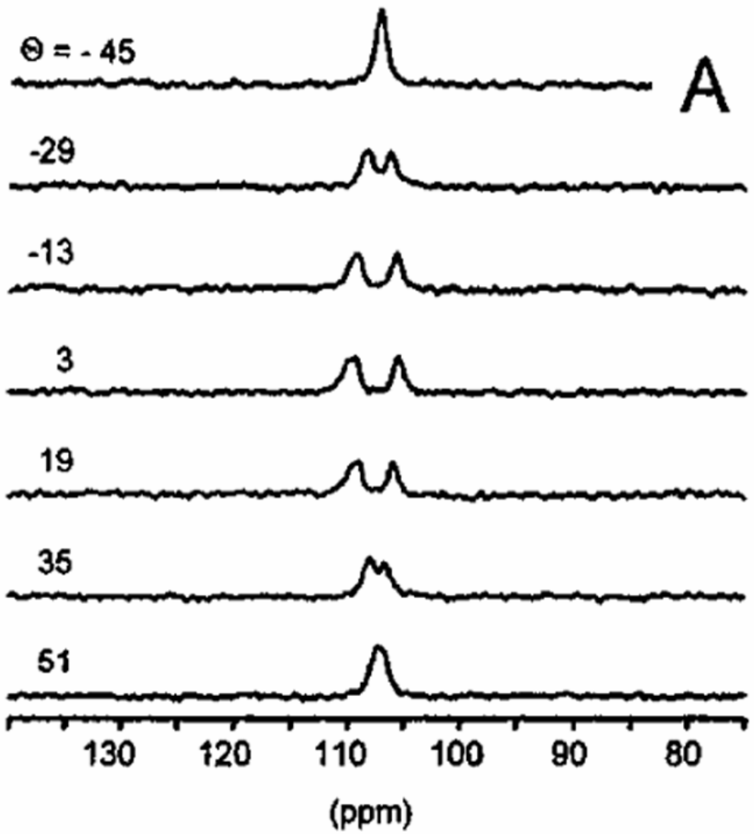
J. A. Ripmeester et al.
J. Am. Chem. Soc. **2001**, 123, 10399

EXPERIMENTS

Xe in a single crystal of silicalite

EXPERIMENTS:

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



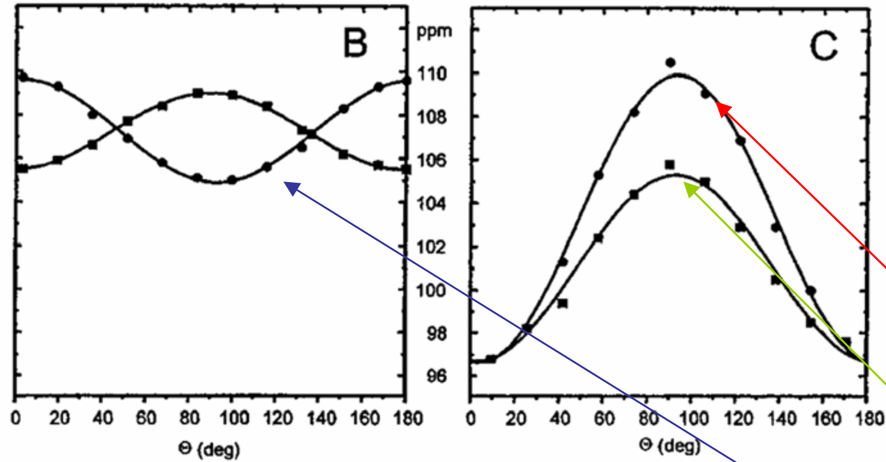
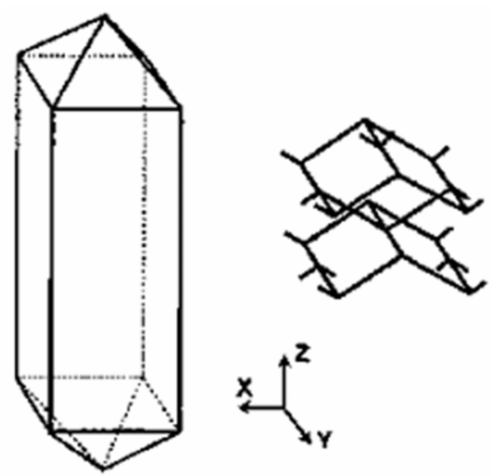
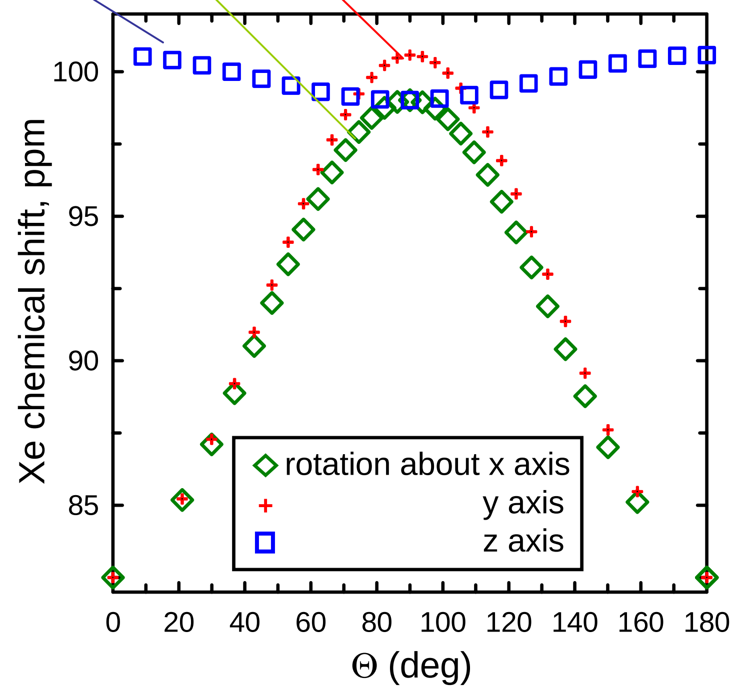


Figure 2. HP ^{129}Xe NMR results for single crystals of silicalite at 295 K: (A) spectra ($\pi/2$ pulses, 512 scans each, 5 s delay) and (B) chemical shifts versus crystal orientation, Θ, about the *z* axis, perpendicular to the magnetic field. (C) Chemical shifts versus Θ about the second orientation.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

the other set is due to the twin





0.285Xe/UC at 300 K

EXPERIMENTS :

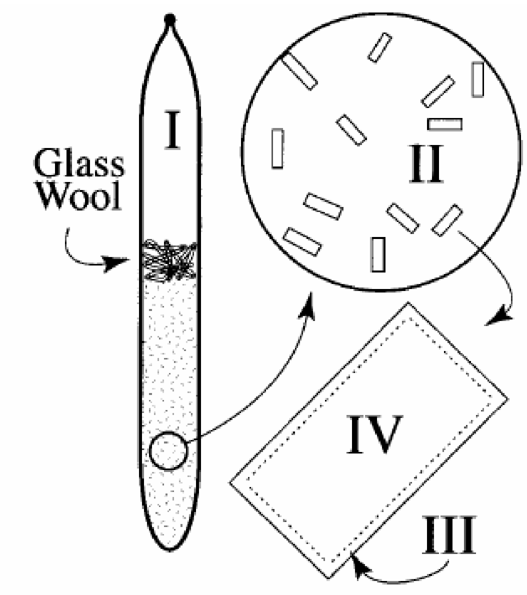
V. V. Terskikh, I. L. Moudrakovski, H. Du, C. I. Ratcliffe, and J. A. Ripmeester
J. Am. Chem. Soc. **2001**, 123, 10399-10400

GCMC SIMULATIONS Jameson 2003

Averaging under fast exchange

Various populations of Xe atoms in the sample contribute to the observed ^{129}Xe NMR spectrum:

Xe in exchange



Reservoir I Xe in overhead gas (incapable of exchanging with the Xe in IV, within the NMR time scale)
Reservoir II Xe between the crystallites (some of which may be adsorbed on outside surface of zeolite)
Reservoir III Xe inside the crystallites that are within an exchangeable layer near the outside
Reservoir IV Xe deep inside the crystallites (incapable of exchanging with the Xe outside, within the NMR time scale)

Xe in exchange

Relative volumes of these reservoirs depend on:

- morphology and size of crystallites
- crystallite packing
- overhead Xe gas pressure
- temperature

In addition to exchanges within each reservoir, mass transport in zeolites can include the following exchanges:

I $\leftrightarrow$ II $\leftrightarrow$ III $\leftrightarrow$ IV

What are the consequences of such exchanges?

When there are intercrystalline regions with pores or channels of size comparable to the inside channels or pores : microcrystalline samples

intercrystalline pore-like regions can compete with the channels for Xe population

apparent Xe occupancy is greater than that actually present inside, because significant numbers of Xe are in **II** (between the crystallites)

gives wrong occupancy number

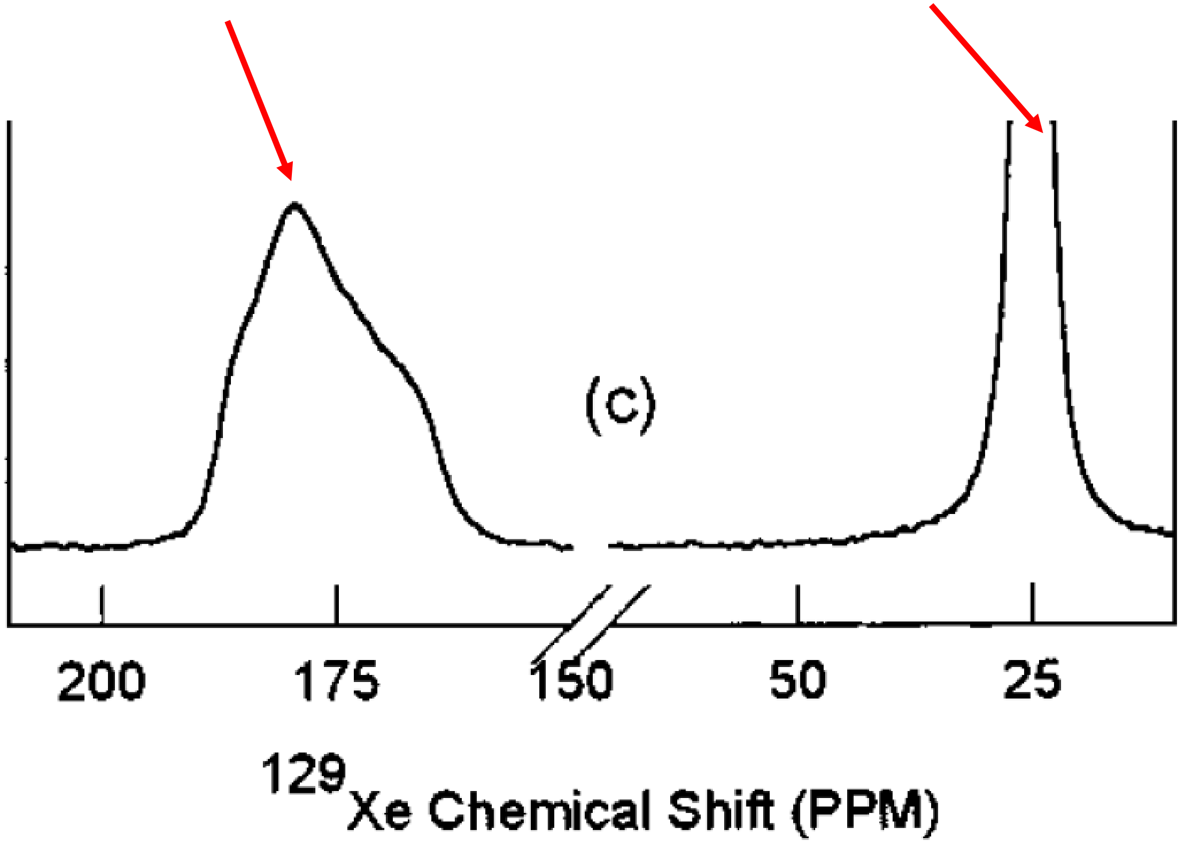
significant **II** means exchange **I**↔**II** gives **I**/**II** weighted "gas peak" chemical shift

the ratio of populations **III**/**IV** is not negligibly small; weighting factor for **IV** does not dominate

significant **III** means exchange **IV**↔**III** ↔**II** gives **IV**/**III**/**II** weighted "channel" chemical shift

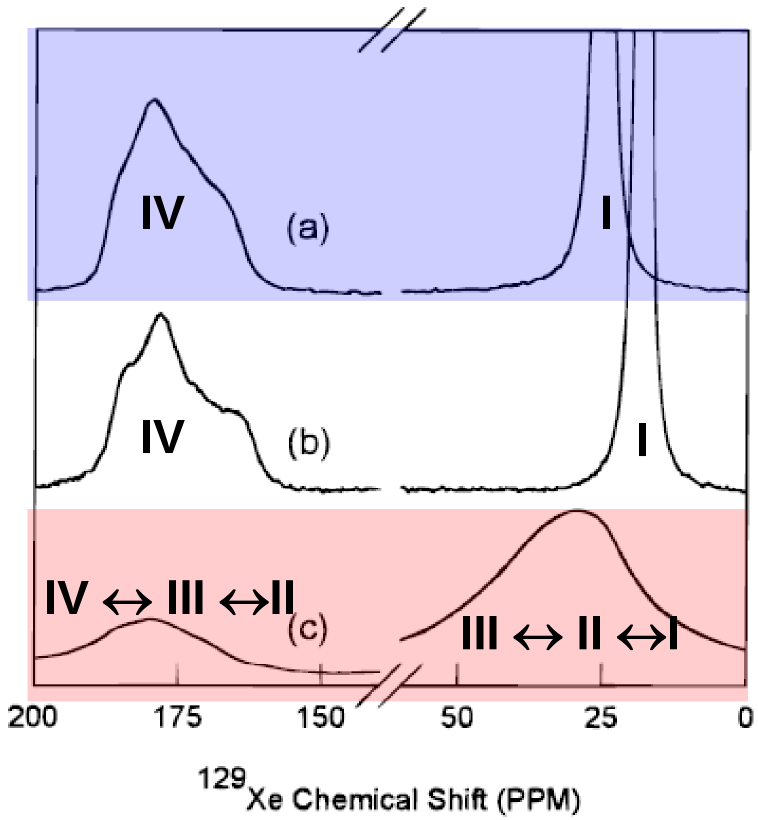
Minimize *Reservoirs II* and *III* by using large crystals

By using larger crystals we effectively have only two Xe reservoirs: *inside* the crystallite and *outside* the crystallite.



This also permits observation of the lineshapes characteristic of Xe <u>inside</u> the crystal

in microcrystalline samples, Xe exchange between Reservoirs gives rise to weighted average positions

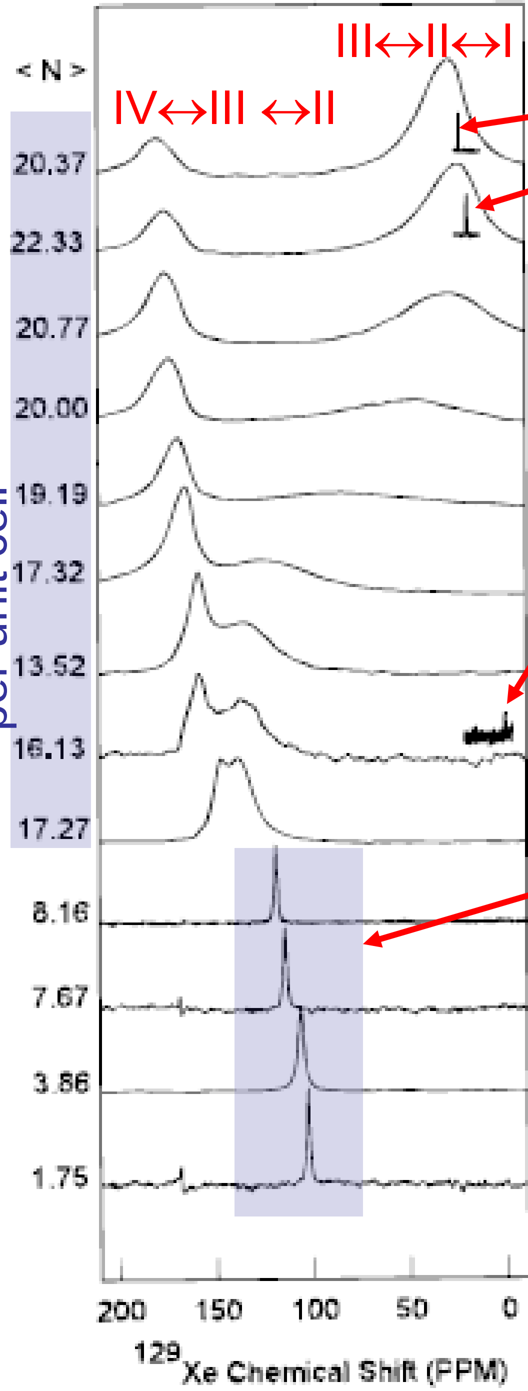


in large crystal silicalite

large crystal in a capillary observed with a microcoil

in micro-crystalline silicalite

maximum occupancy
in Reservoir IV is 16 Xe
per unit cell



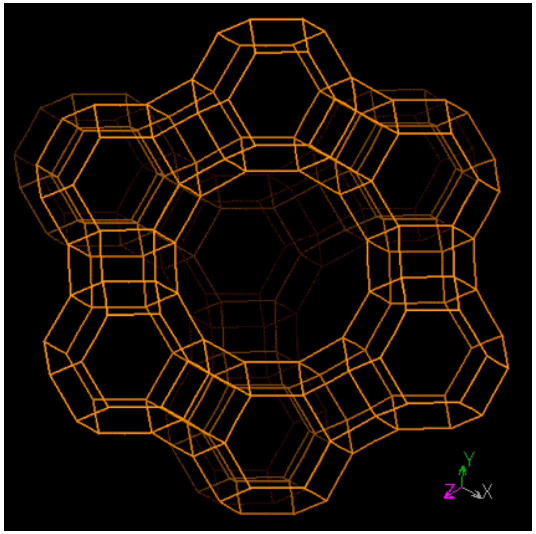
These are true chemical shifts
of Xe in bulk gas overhead
Reservoir I

all other peaks are due to exchange averaging and are not true chemical shifts, they are weighted averages of chemical shifts, weighting factors are the numbers of Xe atoms in those reservoirs which are exchanging

These are true chemical shifts
of Xe inside the channels
Reservoir IV
Exchanging with gas, too
but number of Xe in gas is nil;
weighting factor for gas is ~0

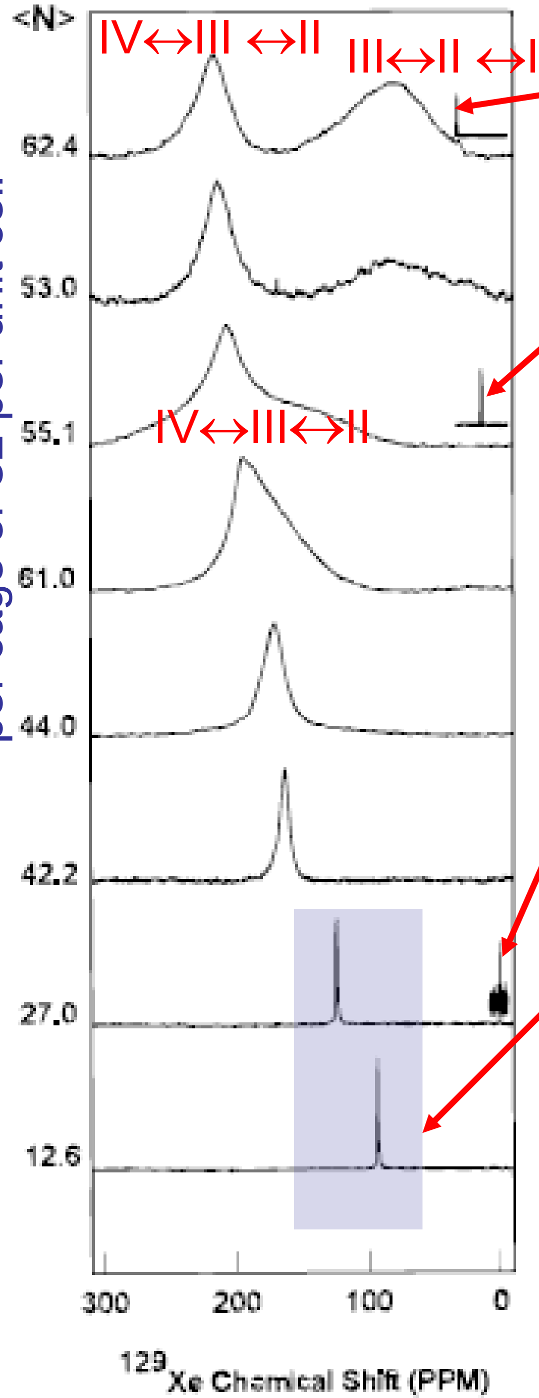
Xe in microcrystalline silicalite

Xe in zeolite Na*X* and in Na*Y*



Na*Y* or Na*X* FAU

maximum occupancy
in Reservoir IV is 12 Xe
per cage or 32 per unit cell



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These are true chemical shifts
of Xe inside the channels
Reservoir IV
Exchanging with gas, too
but number of Xe in gas is nil;
weighting factor for gas is ~0

Xe in microcrystalline Na*X*

Variable temperature studies

Changing the temperature in the typical Xe NMR experiment in porous powdered solids

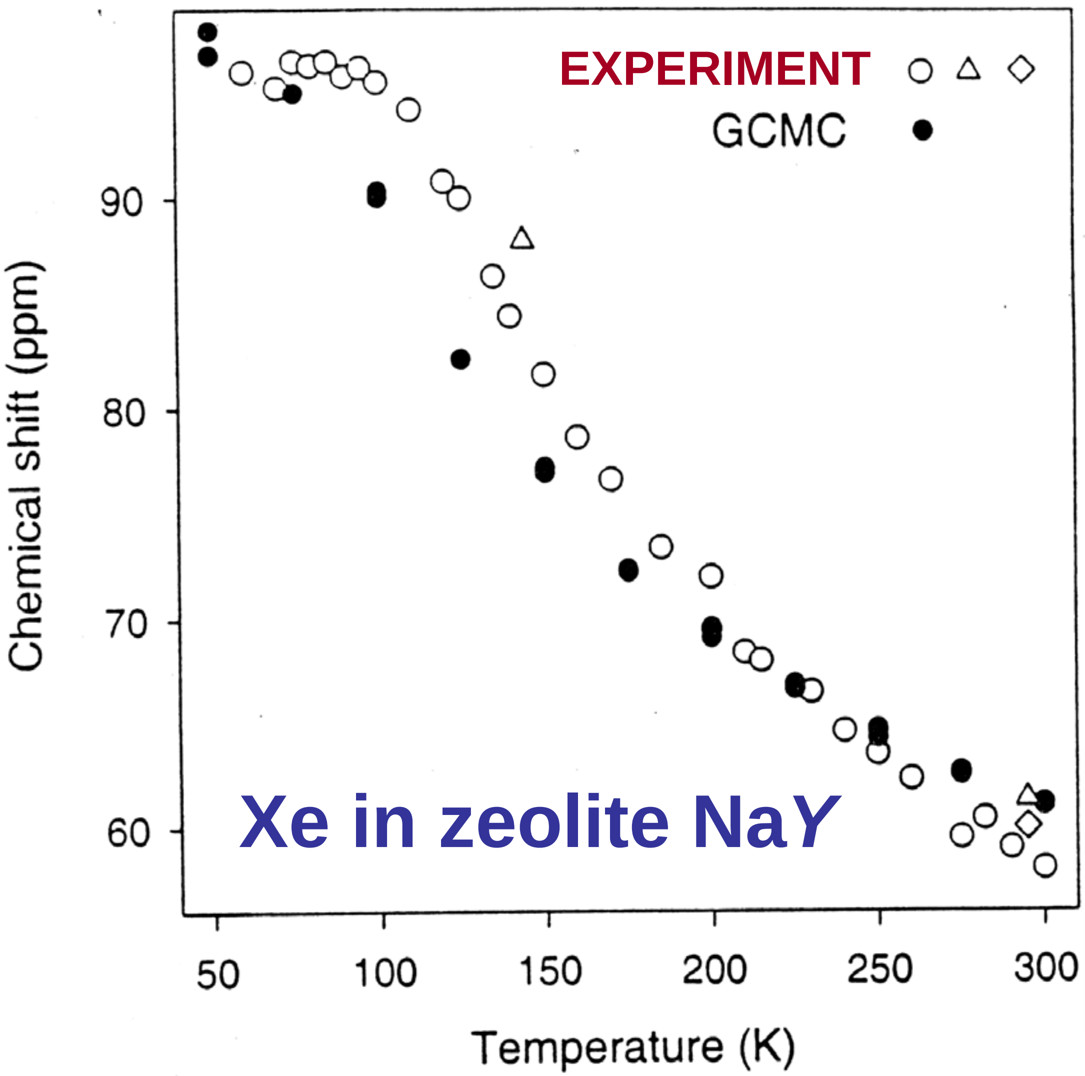
changes

- the gas/adsorbed partitioning
- the distribution of occupancies among cavities
- the fraction of Xe population participating in exchange with the inter-crystalline environment.

Temperature dependence of ^{129}Xe chemical shift at near-zero loading

GCMC simulations

Jameson and Kostikin, 2001

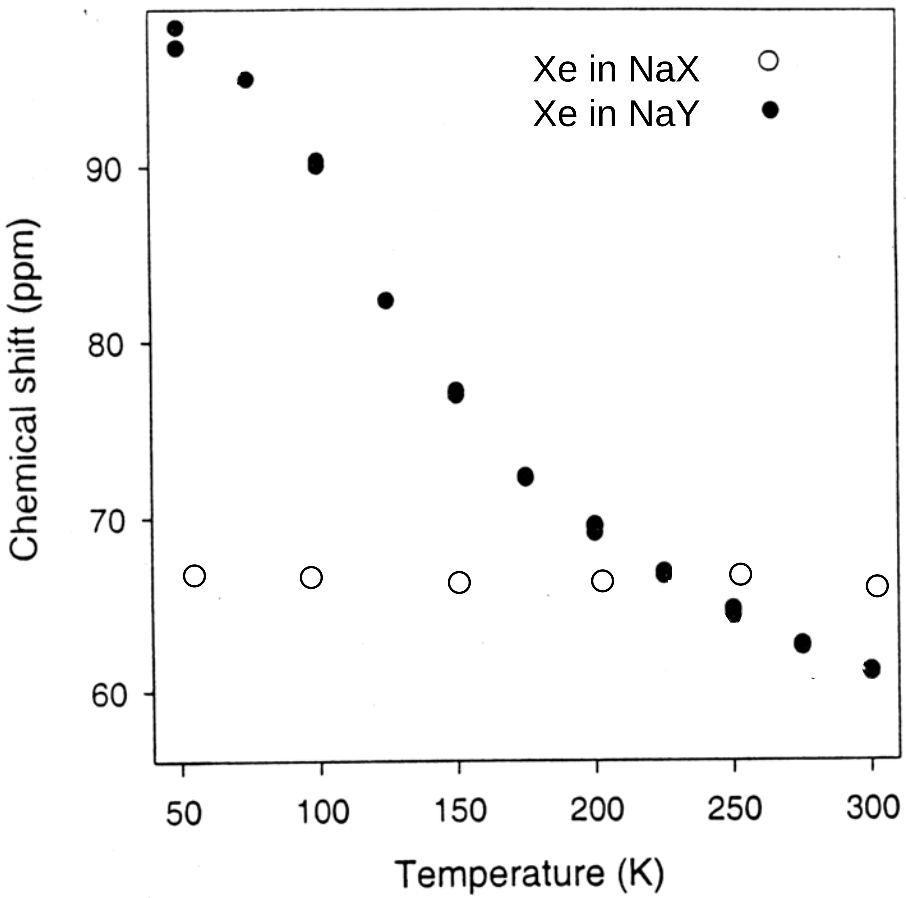


○ Expt., Pietraβ et al. 1999 $\langle n \rangle_{Xe} = 0.25$ atoms/cage
Δ Expt., Cheung, 1988 $\langle n \rangle_{Xe} = 0.2$ atoms/cage
◊ Expt., S. B. Liu, 1994 $\langle n \rangle_{Xe} = 0.2$ atoms/cage
● GCMC calculations $\langle n \rangle_{Xe} = 0.250(5)$ atoms/cage

Temperature dependence, Na*X* vs. Na*Y*

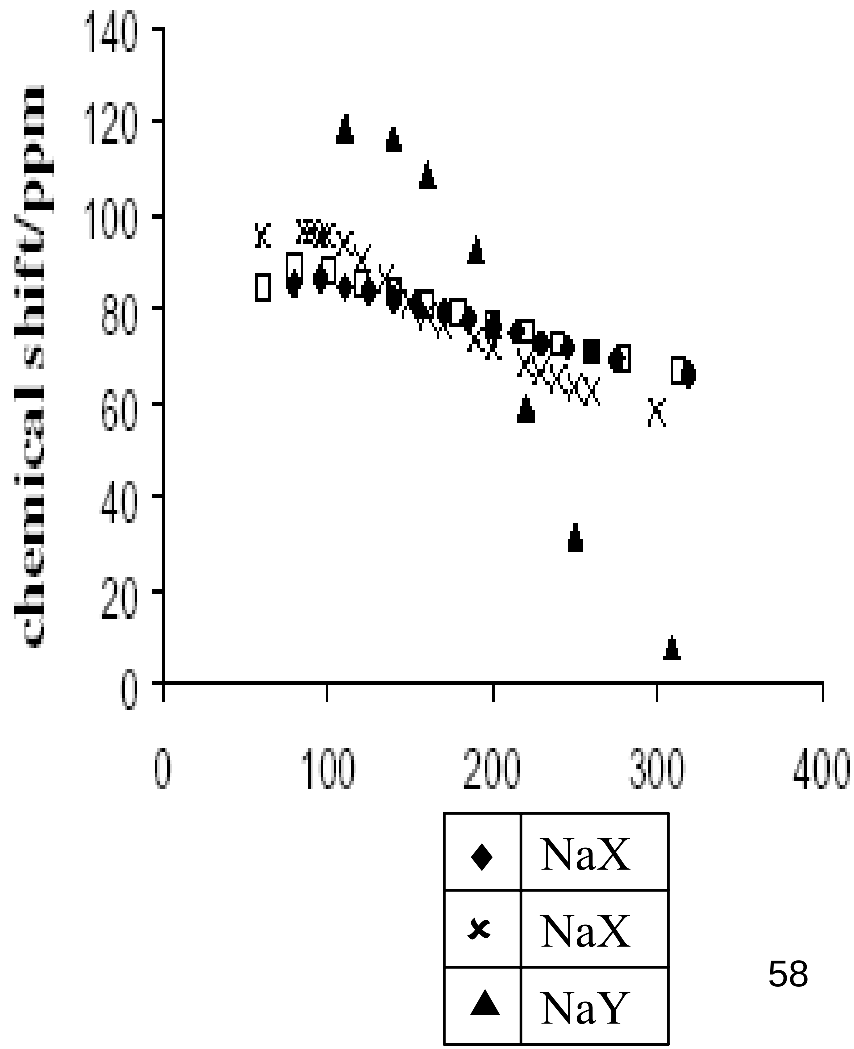
GCMC simulations

Jameson and Kostikin, 2001



Experiments

Pietrass et al. 2004



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 number of Xe atoms per unit cell
- electronic structure of atoms constituting the cavity walls

CAVEATS

- Chemical shift information from Xe in fast exchange in open networks may be compromised by averaging among the various regions populated by Xe inside and outside the zeolite. Crystallites have to be large enough to provide true “inside zeolite“ information.
- The equilibrium distribution of the Xe within the channels and cages of a zeolite is convoluted into the observed average Xe chemical shift in the adsorbed phase. This can not be accounted for especially at high loading, unless the potential functions used in the simulations test well against the Xe adsorption isotherm in that zeolite, and include polarization of the Xe atom (when cations are present).

CONCLUSIONS

NMR lineshapes in nanochannels can provide the average Xe shielding tensor in confined geometries.

- The shape of the static NMR spectrum at high Xe loading provides an indication of the anisotropy of the environment within the zeolite, even under fast inter-cavity exchange. The temperature dependence of the lineshape provides additional information (Xe in silicalite).
- Xe line shapes at full loading in real systems can be reproduced at various temperatures (Xe in silicalite).
- Single crystal rotation spectra at near zero occupancy can be reproduced by GCMC simulations (Xe in silicalite).
- Temperature dependence of Xe chemical shift at near zero occupancy (in Na*Y)* can be reproduced using the same potential and shielding functions as in silicalite.

CONCLUSIONS...

The same understanding provided by model systems applies to Xe in systems where averaging over occupancies and environments occurs

- The experimental distributions and the chemical shifts from Xe in Na*A* can predict the observed average chemical shift in the same zeolite framework (Ca*A*) where fast inter-cavity exchange permits averaging over occupancies and environments. This means that the understanding of the average Xe chemical shift in systems where fast exchange occurs is transferable from the model systems where individual peaks are observed for n Xe atoms. All the detail that we know from the model systems apply also to zeolites with 3-dimensional networks of channels.

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ANY QUESTIONS?