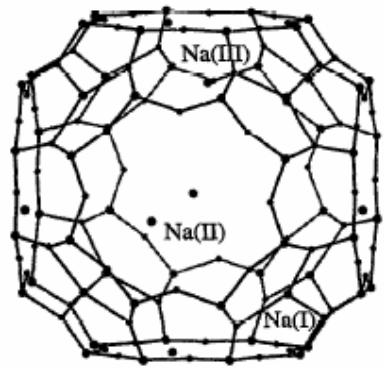
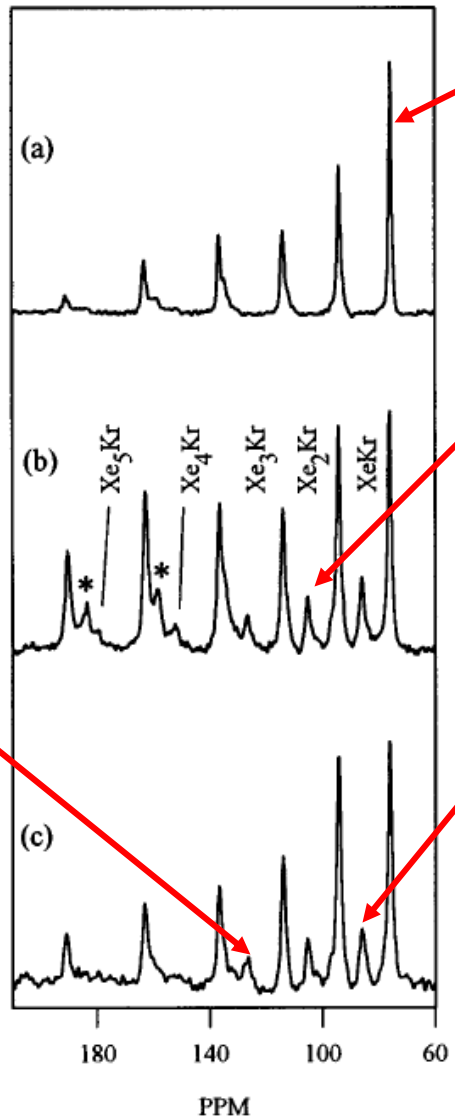
Adsorption of one or more gases into cavities. Zeolite Na*A* model system



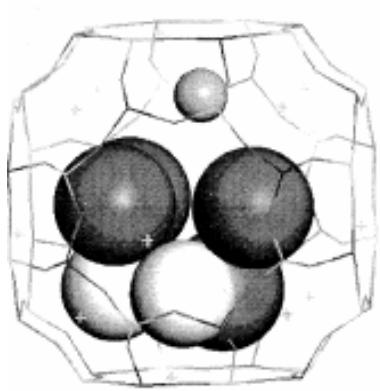


one Xe
in a cage

two Xe+one Kr
in a cage

three Xe+one Kr
in a cage

one Xe+ one Kr
in a cage



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outline

1. Motivation
2. We seek answers to these questions
3. Our approach/strategy
4. Distributions
5. Cation effects
6. Competitive adsorption
7. What is wrong with previous models?
8. Conclusions

I. MOTIVATION

- Why do we need to know about adsorption?
- Why use Xe NMR?
- Consider only ADSORPTION in this talk, DIFFUSION is another story

INTRODUCTION

- **The processes of adsorption and diffusion are fundamental to many technological applications of zeolites.**
- **^{129}Xe nuclear magnetic resonance spectroscopy has been used as a probe of cavity size, siting of metal atoms or ions or other details of structure. Although this had been a useful empirical tool, a fundamental understanding of the Xe NMR in zeolites had been lacking.**
- **Our studies combine NMR spectroscopy and computer simulations to provide a molecular level understanding of the fundamental processes of adsorption and diffusion.**
- **NMR spectroscopy provides very detailed information for testing computer simulations.**

WHY "MICROPOROUS" SOLIDS?

- **Technological applications: heterogeneous catalysis, separations, oil recovery, various industrial processes**
- **These applications depend on fundamental processes such as ADSORPTION and DIFFUSION**
- **ZEOLITES have well known crystalline structures. AlO_4 and SiO_4 tetrahedra linked together to form cages of 3 - 13 Å diameter, a network of pores in 1, 2 or 3 dimensions.**
- **Toward a FUNDAMENTAL UNDERSTANDING of sorption in "micropores" (actually the pores are nanoscale), 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.

II. we seek answers to these QUESTIONS

Some questions we would like answers to:

- When molecules are adsorbed in a microporous solid at a given loading, what is the distribution of these molecules among the cavities?
- When the average loading is 0.5 molecules per 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?

Some questions we would like answers to:

- When two types of molecules are adsorbed in a microporous solid, how are these two types of molecules distributed among the cavities?
- How many molecules of type 2 can be found in those cavities that have exactly *n* molecules of type 1?
- 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?
- Is the selectivity of a zeolite for a specific component modified by the presence of other components in the system?

Defer DIFFUSION QUESTIONS

- 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? on how many molecules are in the cavity it is jumping to?

III. OUR APPROACH/STRATEGY

Our approach

- choose model environments with well-defined characteristics
- examine the ^{129}Xe NMR chemical shifts in these model environments experimentally
- attempt to reproduce the observed chemical shifts by grand canonical Monte Carlo simulations using *ab initio* chemical shift functions

Simulations STRATEGY

- Get coordinates of zeolite framework and cations from x-ray data. Calculate induction energy of a single Xe atom at various positions in the zeolite using a fine grid, to be used in GCMC simulations by interpolation
- GCMC simulations of Xe in the zeolite. Test Xe-zeolite potential against adsorption isotherms of Xe in the zeolite
- Shielding functions for Xe-Xe and Xe-zeolite in GCMC simulations provide Xe chemical shifts at various loadings, compare with experiment

Examples of **well-defined environments** we have used to study distributions:

- a single alpha cage (Na*A*) with exactly *n* Xe atoms
- variable temperature study at fixed known occupancy: *n* Xe atoms in a single alpha cage
- equilibrium distribution of Xe among cavities in a single crystallite; variable temperature, study partitioning between gas and adsorbed phase, the distribution among cavities

Examples of **well-defined environments** we have used to study cation effects:

- a single alpha cage (zeolite Na*A*), locations of framework atoms and cations known independently, alpha cage has 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^+
- 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 (successive replacement of $2Na^+$ by 1 Ca^{2+} ion)

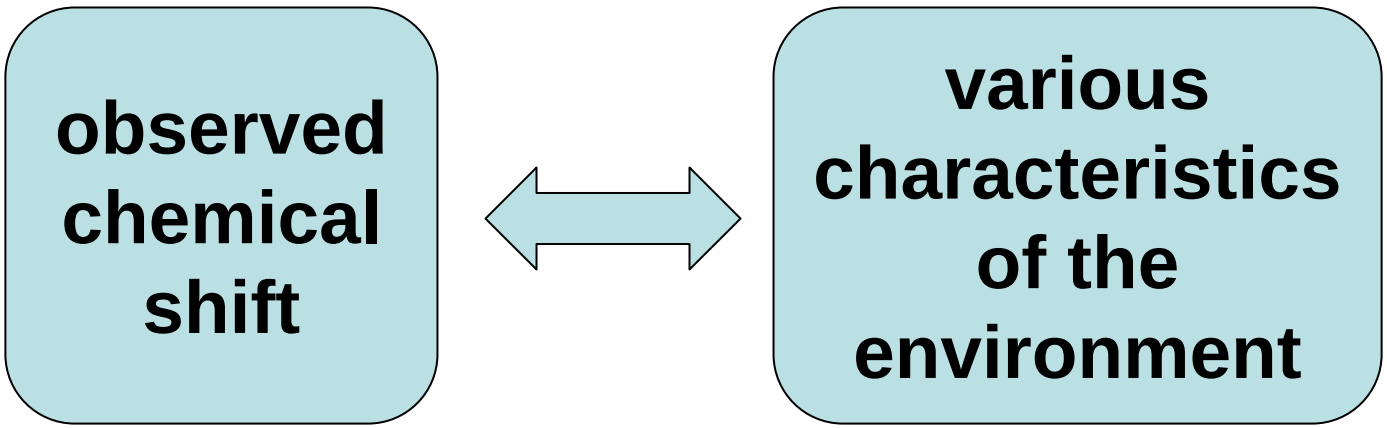
Examples of **well-defined environments** we have used to study competitive adsorption:

- a single alpha cage (Na*A*) with exactly *n* Xe atoms and *m* Kr atoms
- binary mixture equilibrium distribution among cavities, alpha cages *n* Xe atoms exactly and an average number of other sorbate. Find number of co-adsorbate molecules with each Xe_n, varying the mole fraction and total pressure in the gas phase

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

- Xe in fast exchange in identical cavities of different occupations, in very large crystals (minimize exchange with *inter-crystalline* gas)
- Xe in fast exchange inside↔outside. Variable *T* studies: changes the gas/adsorbed partitioning, the distribution of occupancies among cavities, and the fraction of Xe population participating in exchange with the inter-crystalline environment. This is the typical Xe NMR experiment in porous powdered solids**.**

need the connection:



the shielding surface

- The nuclear magnetic shielding as a mathematical function of nuclear coordinates of a molecule.
- What is observed experimentally is a dynamic average over this surface. The average arises from the shielding value at each point on the shielding surface being weighted according to the probability of finding the molecular system at that nuclear configuration.

types of averages leading to observed chemical shifts

- a) INTRAmolecular averages over all nuclear displacements, governed by the intramolecular potential surface
- INTRAmolecular averages lead to *isotope shifts and temperature-dependent chemical shifts of a molecule in the zero-pressure limit*.

- **b) INTERmolecular averages over the intermolecular potential functions include the effects of neighbor atoms**
- **INTERmolecular averages lead to dependence of chemical shifts on number density, temperature, geometry and electronic structure of the confining space**

We will consider INTERmolecular averages.

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**

For one neighbor atom

Ab initio calculations show the Xe shielding response depends on the distance of the neighbor atom.

A mathematical description of a large number of ab initio values as a function of R(Xe-A) is: (for A = Xe or Kr or Ar or Ne)

$$\sigma_{Xe}(r_{Xe\text{-}A}) = a_6 r^{-6} + a_8 r^{-8} + a_{10} r^{-10} + a_{12} r^{-12}$$

the shielding response drops off very steeply with distance

Electronic structure of the neighbors of the Xe atom

Ab initio calculations show that

at corresponding distances,

the magnitude of Xe shielding response

from a neighbor atom drops off in the order:

Xe > Kr > Ar > Ne

Xe > O > H

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

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.

- The INTERmolecular chemical shift of ^{129}Xe is the difference between the shielding of ^{129}Xe in an isolated Xe atom and the average shielding of a Xe atom in a supermolecule averaged over all the various configurations.
- The averages are done in a Grand Canonical ensemble using a Monte Carlo method (GCMC).
- Both the potential surface and the shielding surface are assumed to be pairwise additive functions.

INTERMOLECULAR CHEMICAL SHIFTS

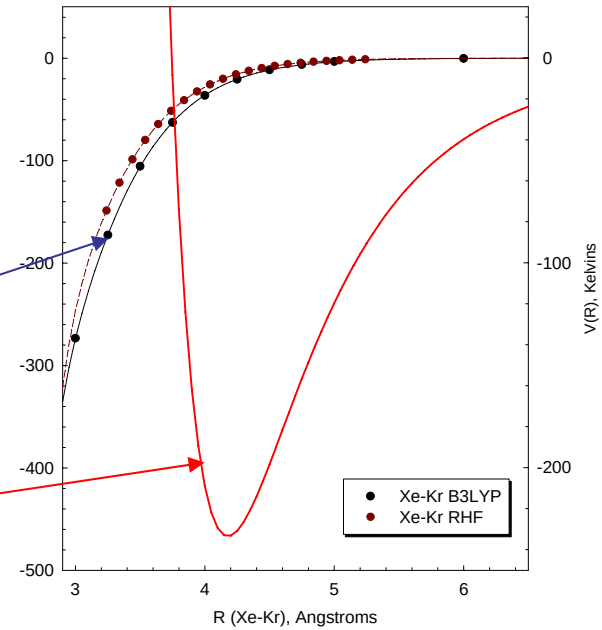
GAS phase:

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

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

Need 2 functions:

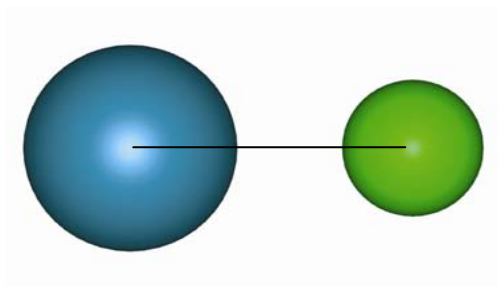
$[\sigma(r, \theta) - \sigma(\infty)]$ & $U(r,\theta)$



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

with a Xe atom as reference,

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



INTERMOLECULAR CHEMICAL SHIFTS

in ZEOLITE: Metropolis Monte Carlo

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

the average at a given chemical potential and T

i.e., at a given overhead gas (P,T)

where,

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

where, the configurations *i = 1 to M*
are generated from a probability distribution.
in GCMC the probability is proportional to

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

Need 2 functions:

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

GRAND CANONICAL MONTE CARLO

Constant μ, V, T Norman-Filinov

Equal probability for 3 moves:

2[create/annihilate] + displace

$$P_{acc} = \begin{cases} \min [1, \exp(-\Delta E/k_B T)] & \Delta E/k_B T \leq 180 \\ 0 & > 180 \end{cases}$$

create $\quad \Delta E = \Delta U_{ji}(r^N) + k_B T \ln[N+1)/V\rho^0] - \mu$

annihilate $\quad \Delta E = \Delta U_{ji}(r^N) - k_B T \ln(N/V\rho^0) + \mu$

displace $\quad \Delta E = \Delta U_{ji}(r^N)$

$$\Delta U_{ji}(r^N) = U_{ji}(r^N)_{NEW} - U_{ji}(r^N)_{OLD}$$

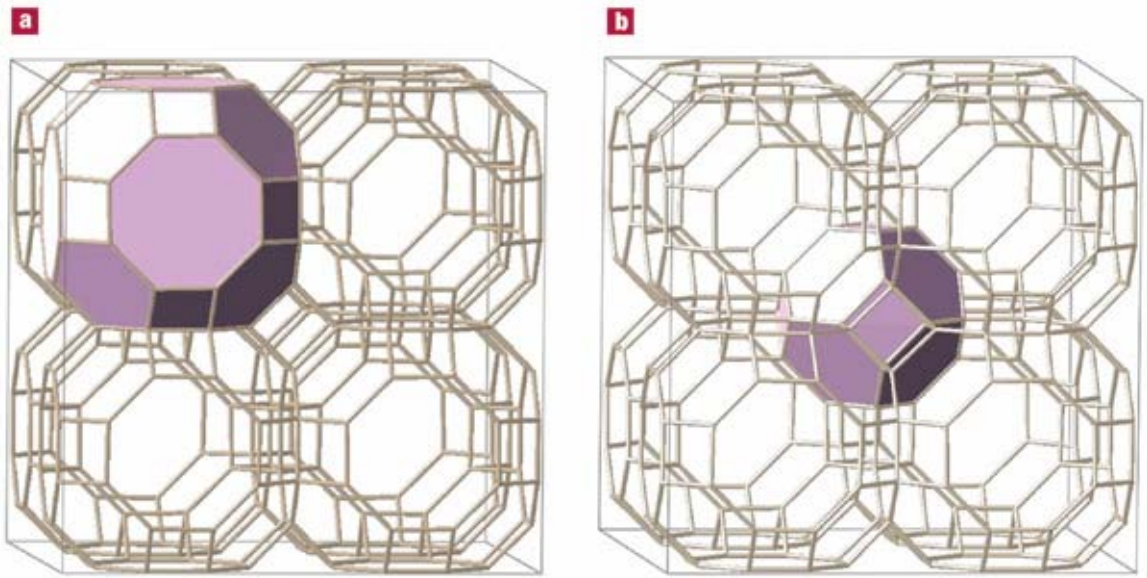
ASSUME PAIRWISE ADDITIVE!

$$\langle \mu \rangle_{GCMC} = \mu_{bulk\ gas}$$

$$\mu_{bulk\ gas} = RT \ln (\rho/\rho^0) + RT(Z-1) + \int_0^\rho d\rho [P-RT\rho]/\rho^2$$

Xe in zeolite Na*A*: a model system

There is only one type of cage that is the Xe environment, the alpha cage; the beta cages are not accessed by Xe.

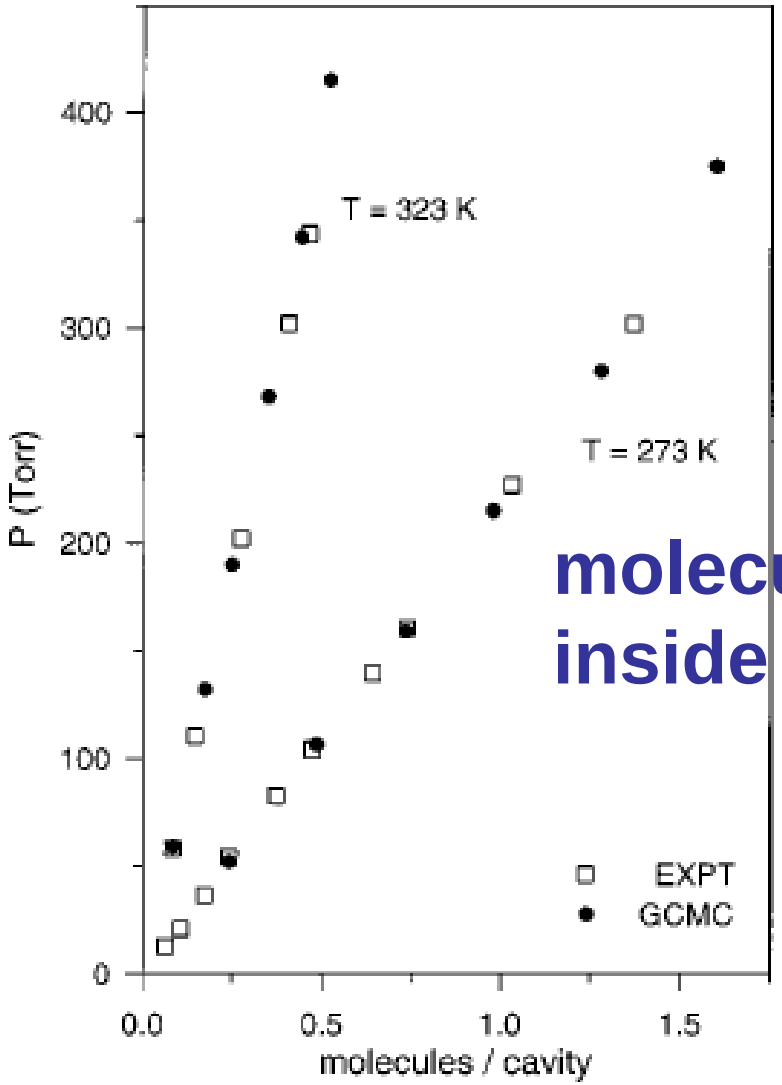


***a**, The alpha cage. **b**, The beta cage.*
The alpha cages, joined by eight-rings, form the three perpendicular sets of channels, the beta cages joined by double four-rings are relatively impermeable.

Image from Andrew M. Walker, Ben Slater, Julian D. Gale & Kate Wright
Nature Materials 3, 715 - 720 (2004)

- The great sensitivity of Xe NMR chemical shift to neighbor atoms provides well separated peaks that enable detailed information to be obtained directly from the spectra
- The long residence times of Xe in the alpha cages of this zeolite permit the ***direct observation of the distribution of Xe among the cages*** and the ***direct observation of the average occupancy*** of the cages (except in the limit of low loading where the probability of zero occupancy is not negligible)
- Sealed samples permit experiments as a function of temperature without changing the total number of Xe in the sample
- Xe density in the gas phase in equilibrium with the adsorbed phase can be obtained from the gas peak chemical shift.
- This density and the known total amount of Xe, known volume of the container, known volume of free space (outside of zeolite cages), together with the spectroscopic measure of distribution, permit a complete description of the physical system using mass balance.

IV. DISTRIBUTIONS



Distribution

between the bulk phase
and
the adsorbed phase

molecules
inside vs. outside

adsorption isotherm of CH_4 in zeolite NaA

Experimental vs. GCMC (Grand Canonical Monte Carlo) simulations

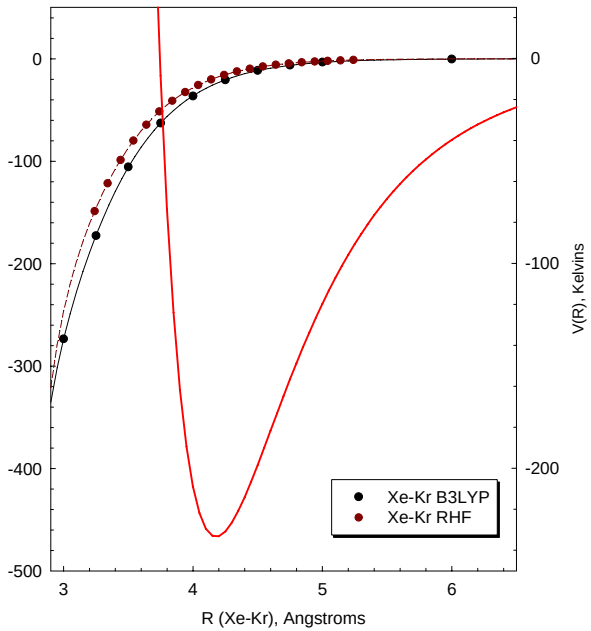
Adsorption isotherm of molecules in zeolites show that density inside (number of molecules per unit available volume) is greater than number density outside.

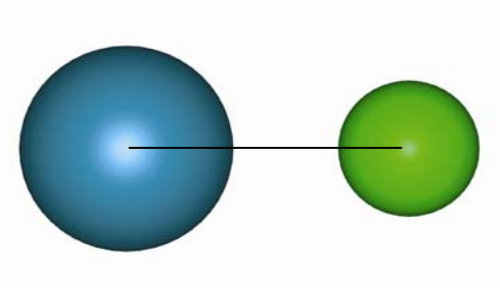
Fact: Adsorption isotherms of molecules in zeolites show that density inside is greater than outside.

QUESTION:

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

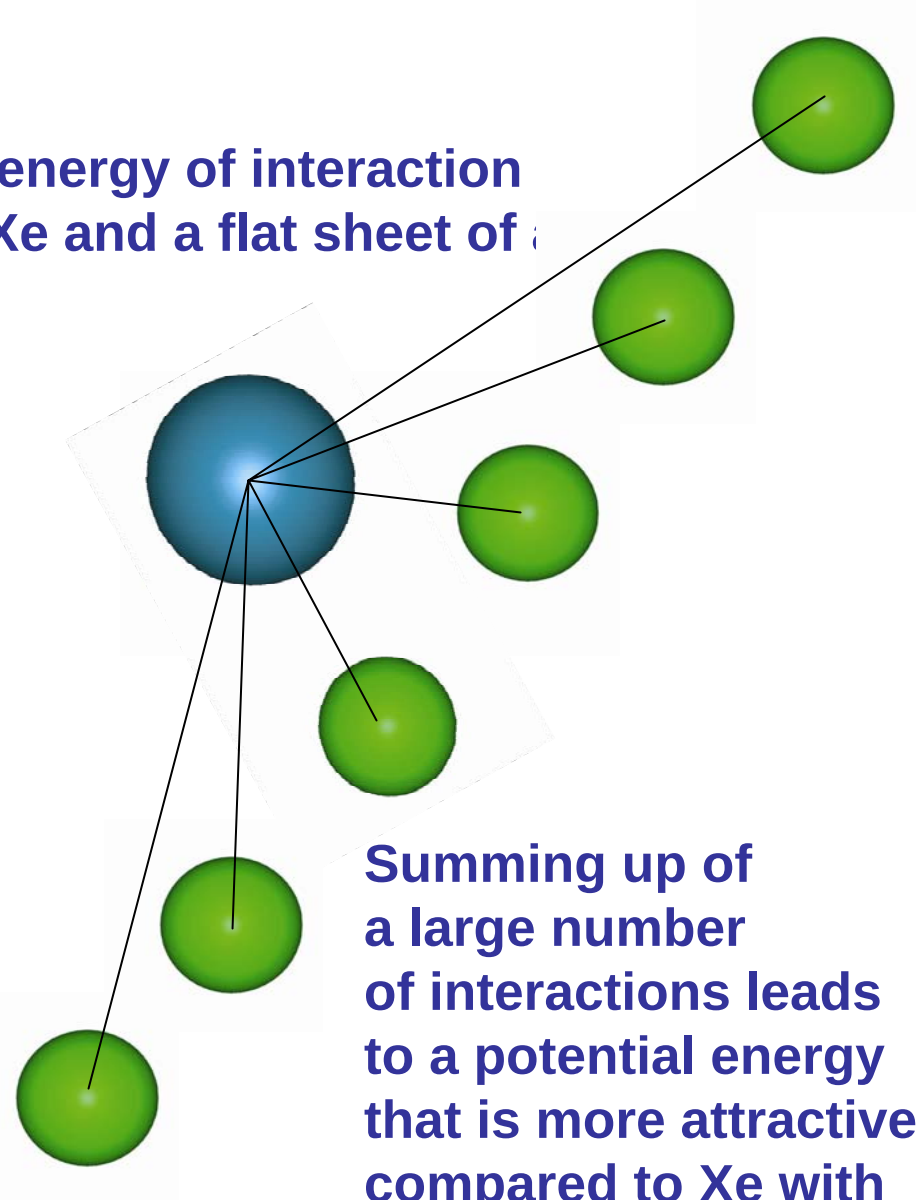
Let us consider the potential energy of interaction between Xe and other atoms



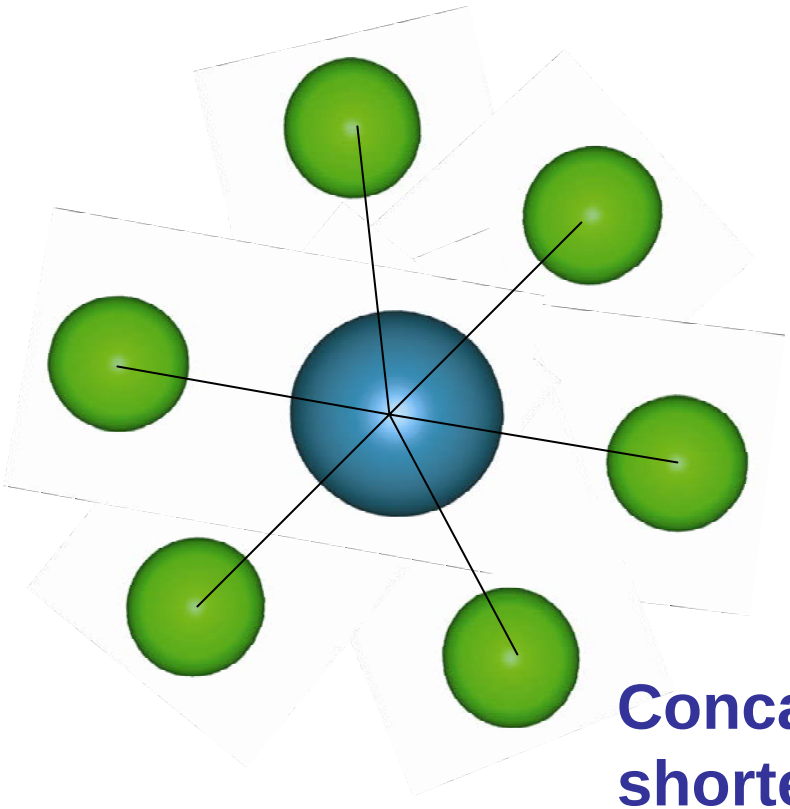


Potential energy of interaction between Xe and one atom

Potential energy of interaction between Xe and a flat sheet of



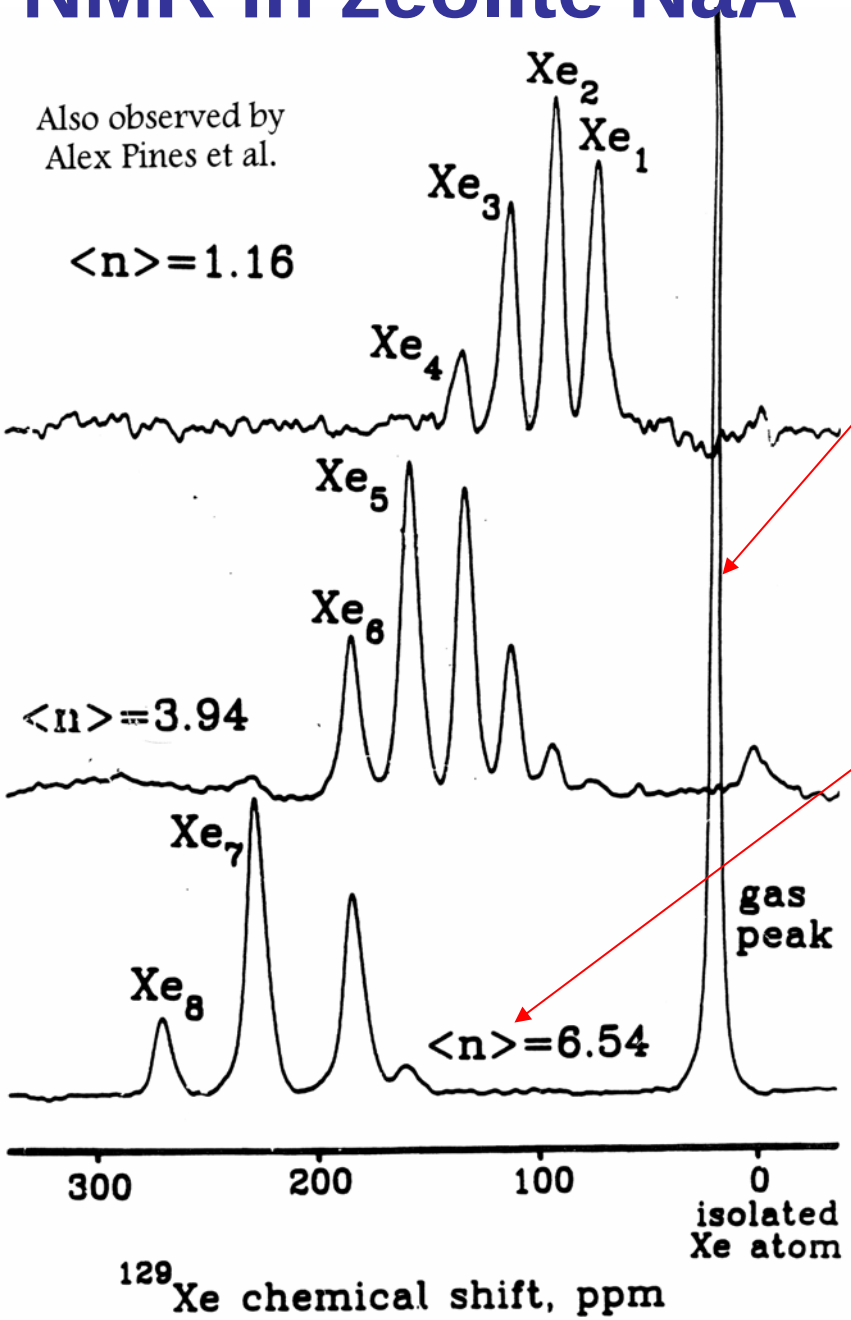
Summing up of a large number of interactions leads to a potential energy that is more attractive compared to Xe with a single atom



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

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

Xe NMR in zeolite NaA



Distribution

between the bulk phase and the adsorbed phase

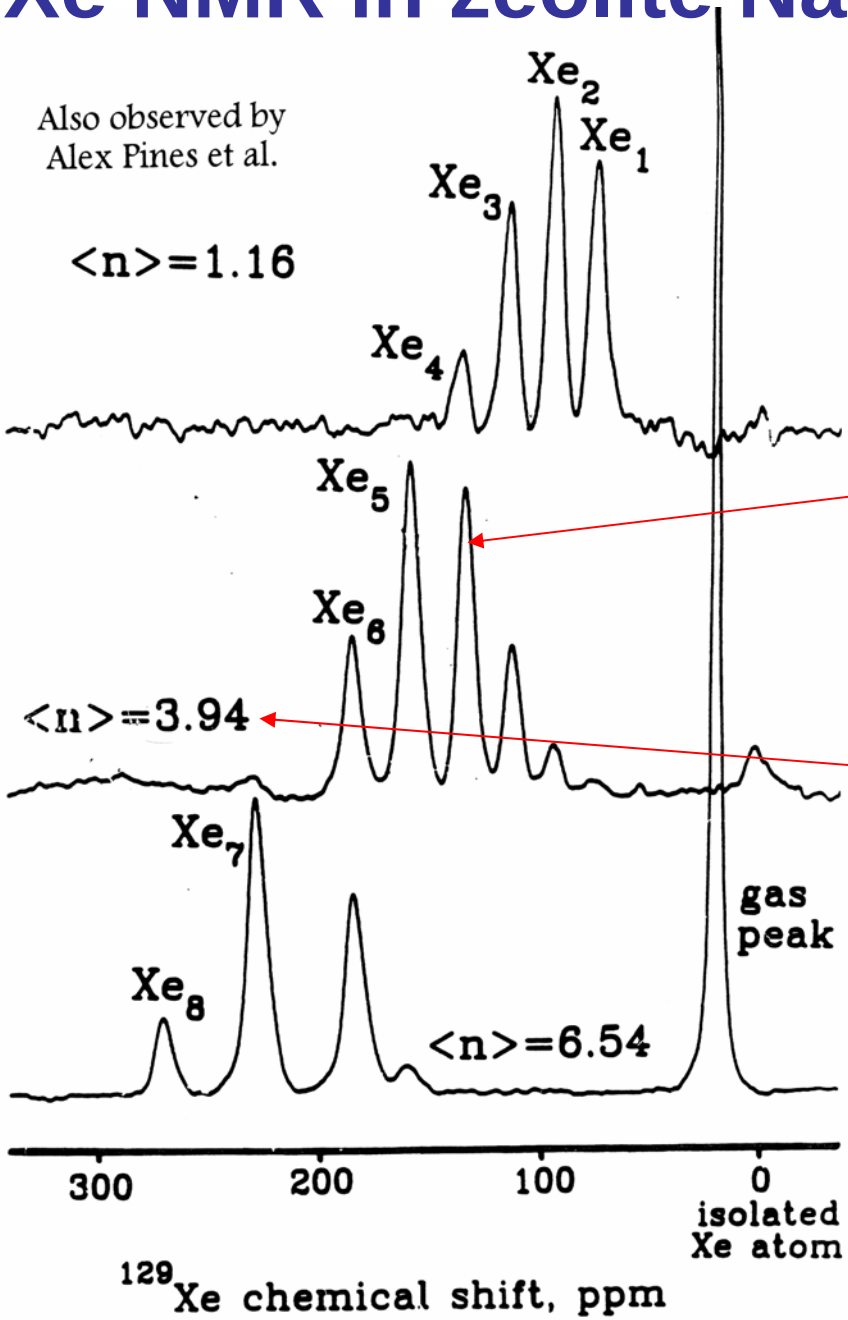
Xe chemical shift of gas peak provides ρ_{Xe} Xe density in the overhead bulk gas

relative intensities provide ⟨n⟩ average number of Xe per cage

ρ_{Xe} and ⟨n⟩ together provide the adsorption isotherm

Distribution of Xe among the cages

Xe NMR in zeolite NaA

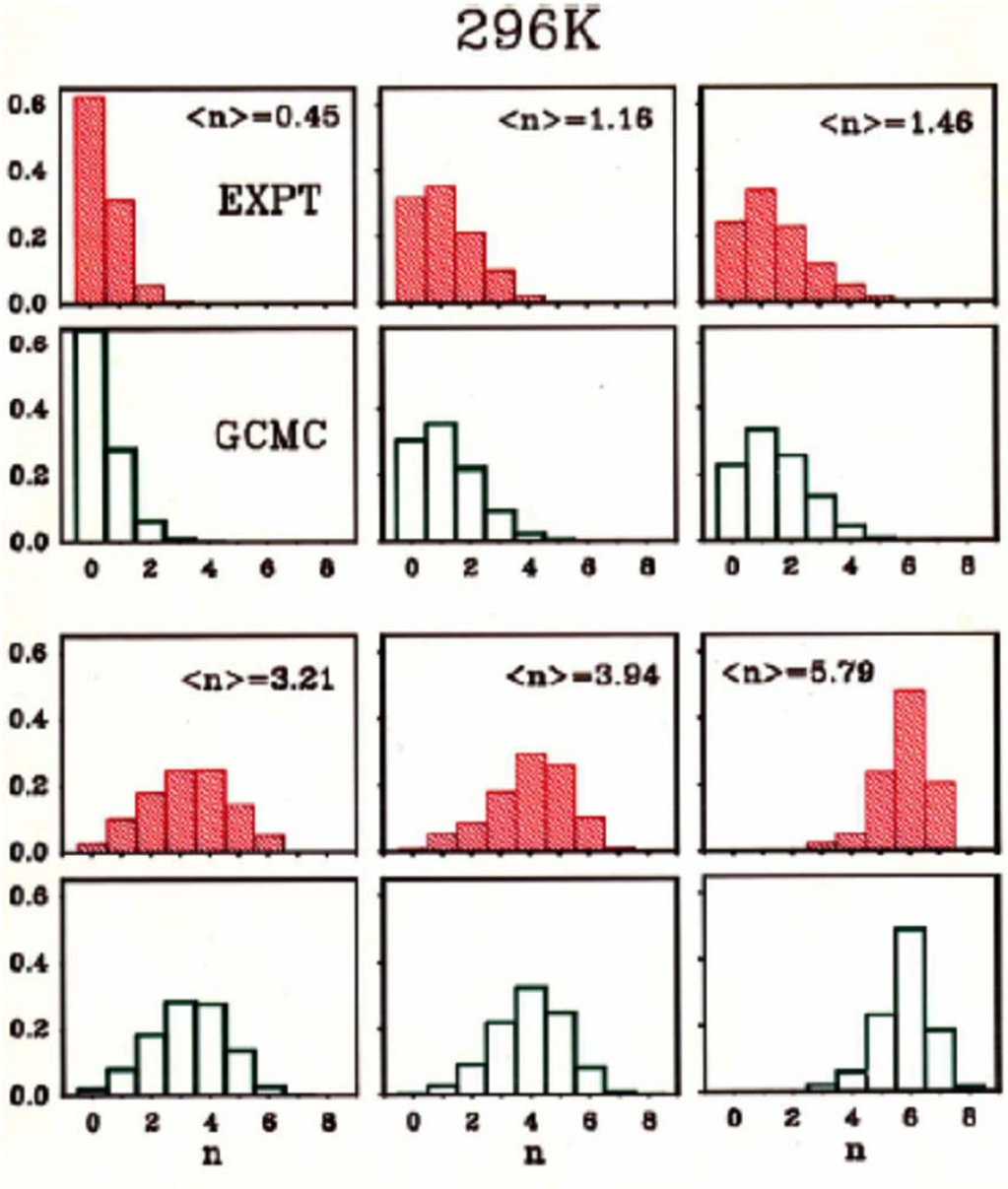


Relative areas under the peaks provides the fraction of cages containing a number n of Xe atoms

and also the average ⟨n⟩.

Distribution of Xe among the cages

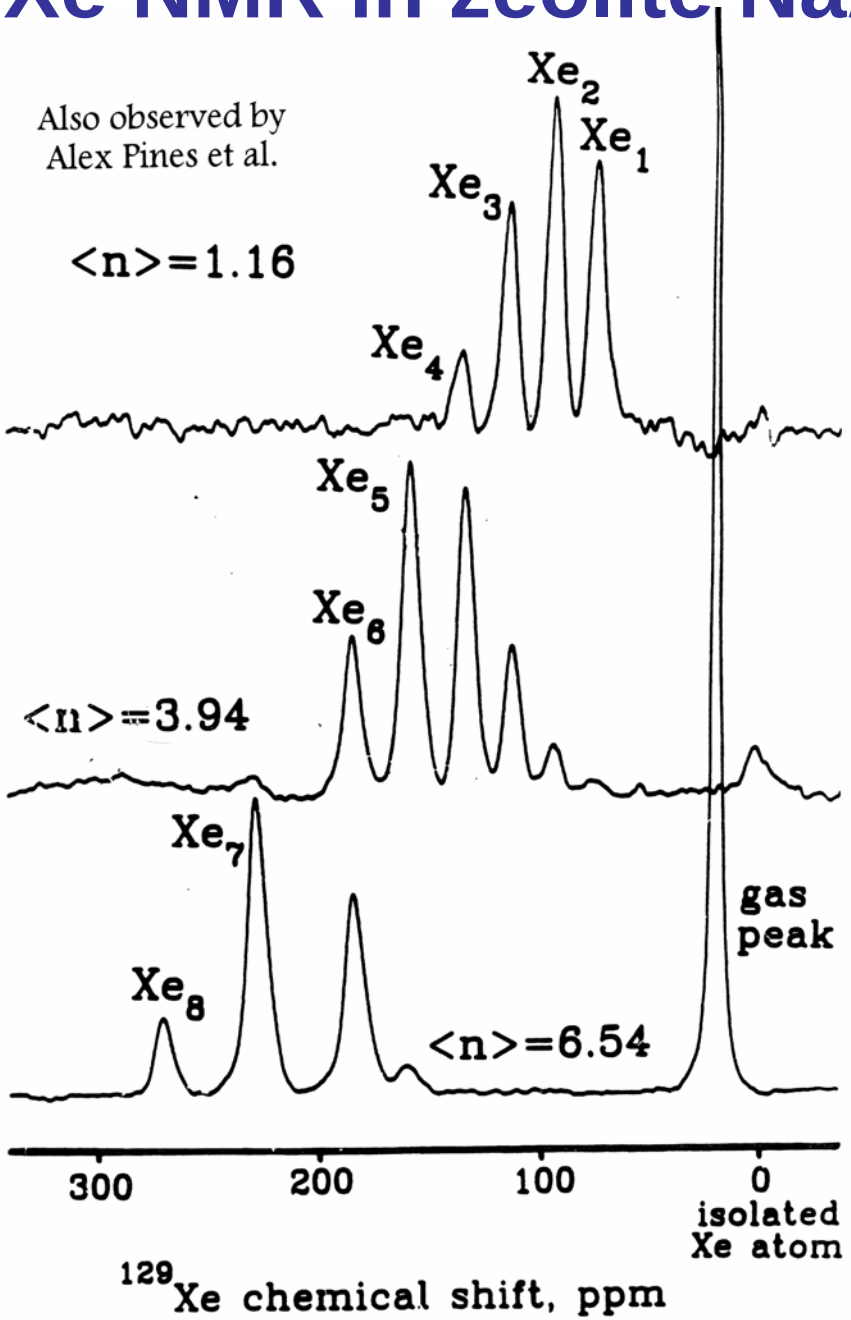
from relative intensities



Distribution within the cavity

How are the Xe atoms distributed within a cage?
like a snowball in the middle of the cage?
or like a thin film on the walls?

Xe NMR in zeolite NaA



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

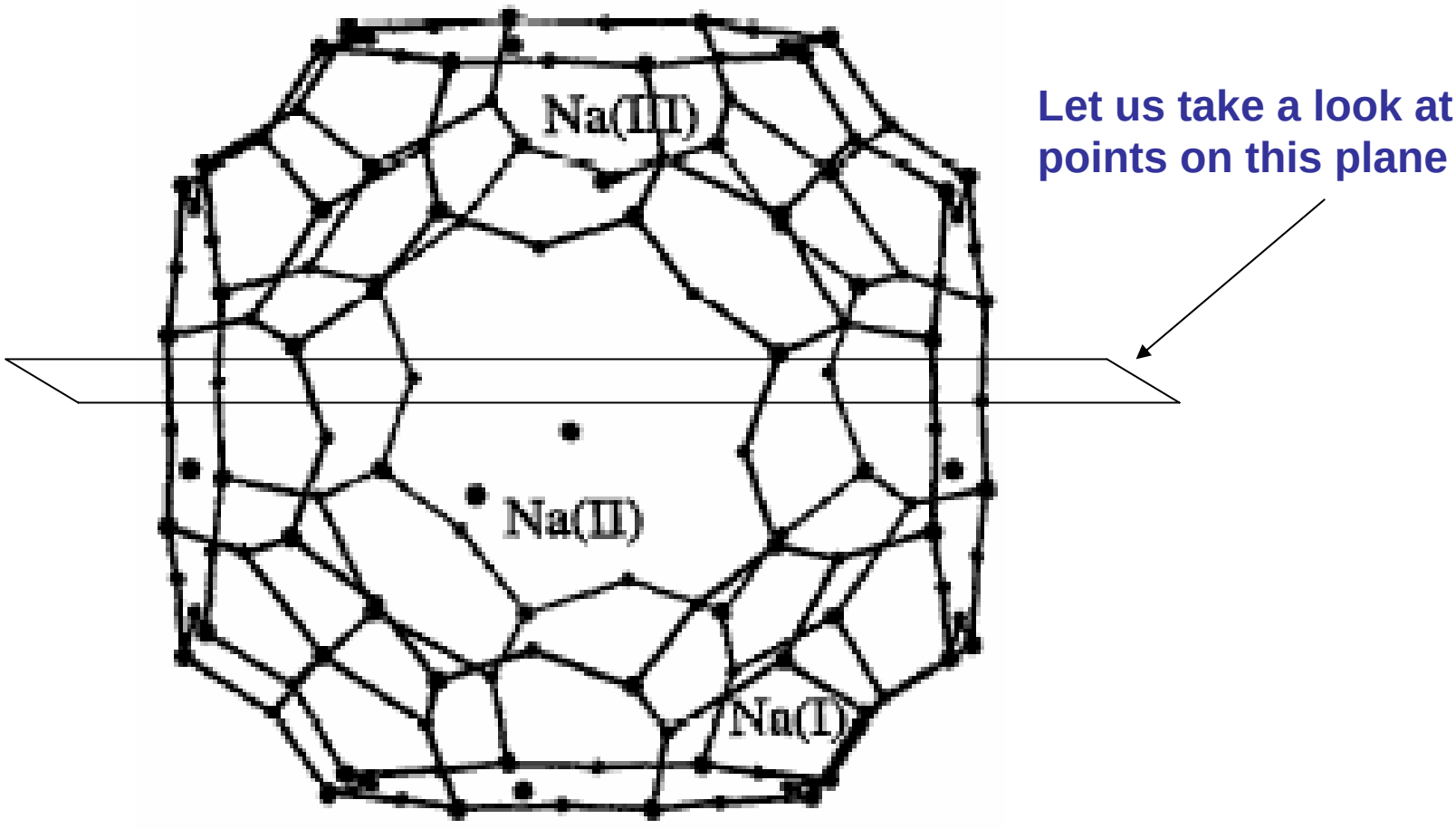
Xe chemical shift of a single Xe inside a cavity depends on the average over

the probability of finding a Xe atom at a given position

and

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

This means that the probability distribution of Xe within a cavity obtained by Grand Canonical Monte Carlo simulations can be verified by reproducing the Xe chemical shift in that cavity.

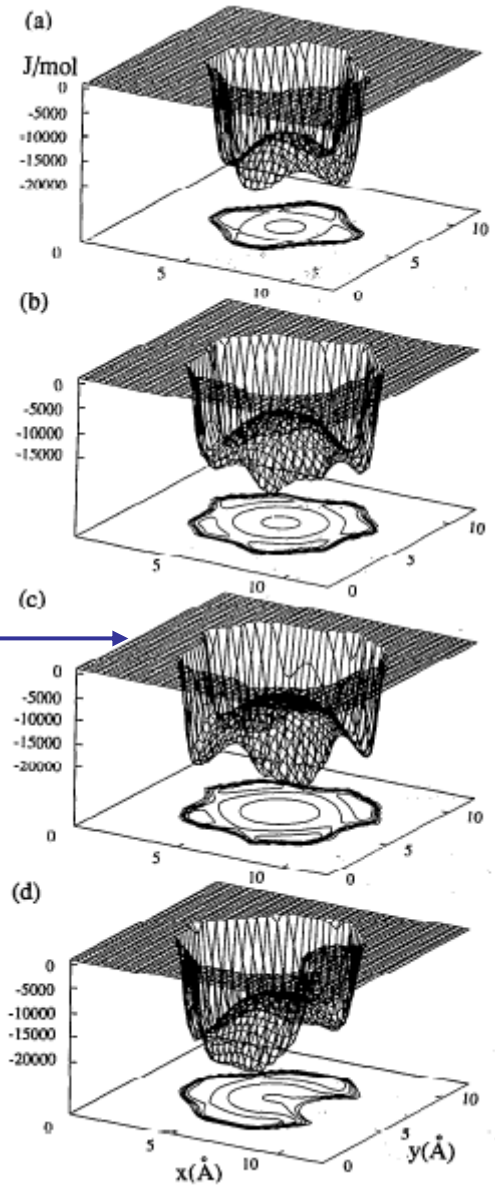


cage of zeolite NaA

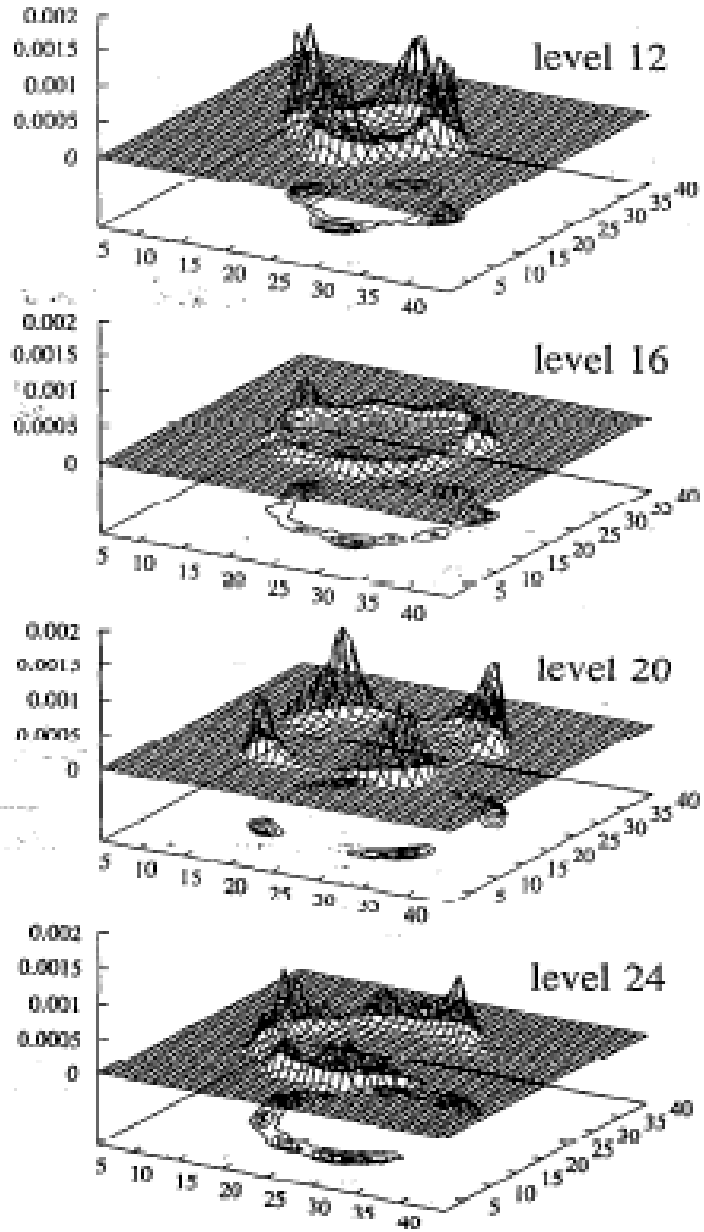
in GCMC the probability is proportional to

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

as shown in plots ……



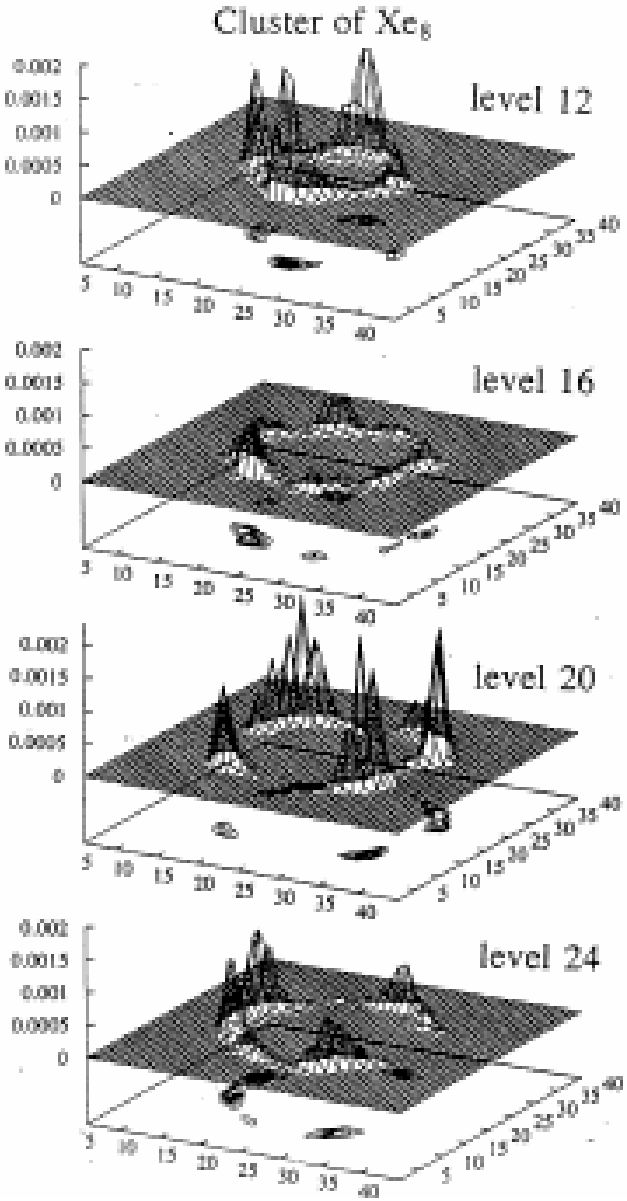
this plane

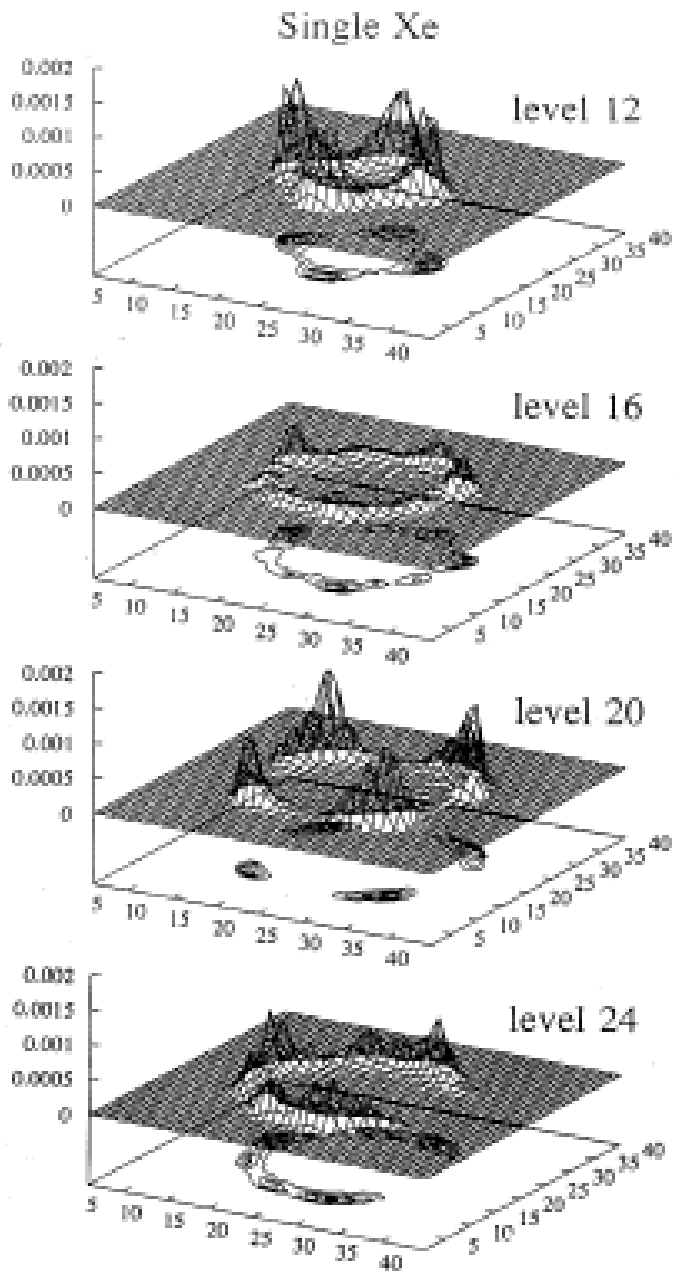


Potential energy surface $U(r^N)$ for one Xe at various planes through the zeolite cage.

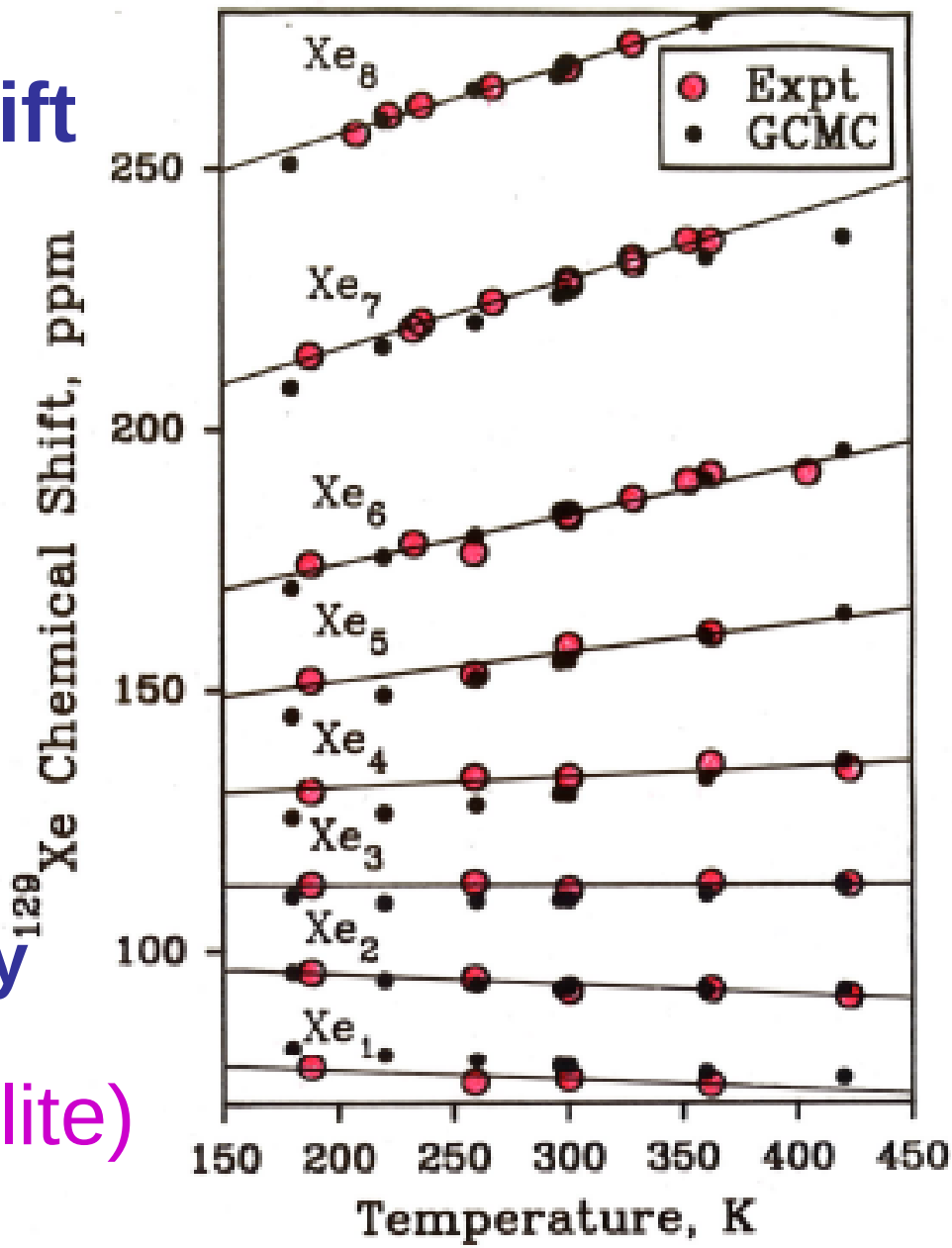
Probability distribution of Xe at those planes

- 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?





We reproduce the Xe chemical shift as a function of temperature.



This tests the reliability of the functions used:

$\sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots$ in zeolite)

& $\mathbf{U}(\mathbf{r}^N)$

V. CATION effects

- Use the same zeolite framework, only with different cation to balance the charge
- Find the differences between Xe NMR in the two systems

What part of the differences in chemical shifts upon ion substitution is due to *differences in:*

- Xe-M^+ contributions to the Xe chemical shift? V(Xe-M^+)? σ(Xe-M^+)?
- Xe-zeolite framework contributions to the Xe chemical shift?
- Xe-Xe contributions to the shifts?
- Xe distribution within a cavity?
- excluded volume?
- occupancy distributions of Xe among the cavities?

Xe in zeolite K*A* versus Na*A*

^{129}Xe chemical shifts of Xe_n clusters in K*A*, compared with Na*A* (at 300 K)

n		1	2	3	4	5	6	7	8
K*A*	$\delta(Xe_n)$	79.5	98.4	119.7	145.4	180.5			
	$\delta(Xe_n) - \delta(Xe_{n-1})$		18.9	21.3	25.7	35.1			
Na*A*	$\delta(Xe_n)$	74.8	92.3	111.7	133.2	158.4	183.5	228.3	272.3
	$\delta(Xe_n) - \delta(Xe_{n-1})$		17.5	19.4	21.5	25.2	25.1	44.8	44.0
K*A* – Na*A*	$\delta(Xe_n)_{KA} - \delta(Xe_n)_{NaA}$	4.7	6.1	8	12.2	22.1			

- Absolute shielding is uniformly greater in zeolite K*A* than in Na*A* for all Xe_n

Xe in zeolite K*A* versus Na*A*

^{129}Xe chemical shifts of Xe_n clusters in K*A*, compared with Na*A* (at 300 K)

- Chemical shift increments (for each additional Xe) are uniformly larger in zeolite K*A* than in Na*A*.

n		1	2	3	4	5	6	7	8
K*A*	$\delta(Xe_n)$	79.5	98.4	119.7	145.4	180.5			
K*A*	$\delta(Xe_n) - \delta(Xe_{n-1})$		18.9	21.3	25.7	35.1			
Na*A*	$\delta(Xe_n)$	74.8	92.3	111.7	133.2	158.4	183.5	228.3	272.3
Na*A*	$\delta(Xe_n) - \delta(Xe_{n-1})$		17.5	19.4	21.5	25.2	25.1	44.8	44.0
K*A* – Na*A*	$\delta(Xe_n)_{KA} - \delta(Xe_n)_{NaA}$	4.7	6.1	8	12.2	22.1			

Contributions to the Xe_n chemical shifts in a **Na*A*** cage, from GCMC averaging using the shielding functions (ppm at 300 K)

		Xe-O	Xe-cation	Xe-Xe	Total	Expt
	Xe_1	58.4	17.9	-	76.2	74.8
	Xe_2	58.8	18.0	15.2	92.0	92.3
	Xe_3	59.7	18.1	31.7	109.4	111.7
	Xe_4	61.0	18.3	50.4	129.8	133.2
	Xe_5	64.8	18.6	73.2	156.6	158.4
	Xe_6	68.3	18.9	98.1	185.2	183.4
	Xe_7	76.6	19.4	132.7	228.7	228.3
	Xe_8	83.1	19.8	170.3	273.7	272.3

Contributions to the Xe_n chemical shifts in a ***KA*** cage, from GCMC averaging using the same shielding functions. (ppm at 300 K)

The differences between K*A* and Na*A* cages are also shown

	Xe-O contrib	diff K*A* - Na*A*	Xe-K contrib	diff K*A* - Na*A*	Xe·Xe contrib	diff K*A* - Na*A*	Total K*A*	Expt K*A*
Xe_1	52.2	-6.2	26.5	8.6	-		78.7	79.5
Xe_2	48.6	-10.2	30.6	12.6	19.6	4.4	98.8	98.4
Xe_3	46.6	-13.1	35.0	16.9	40.8	9.1	122.4	119.7
Xe_4	46.0	-15.0	39.3	21.0	63.3	12.9	148.6	145.4
Xe_5	50.7	-14.1	45.4	26.8	96.9	23.7	192.9	180.5
Xe_6	55.7	-12.6	50.5	31.6	136.8	38.7	243.0	

What is the Xe chemical shift in zeolites telling us about the distribution and siting of cations?

- To answer this question, we need to be able to answer the following question:

  What is the effect of extra-framework cations on the Xe chemical shift in zeolites? How do the type, size, and locations of the ions affect the Xe chemical shift?

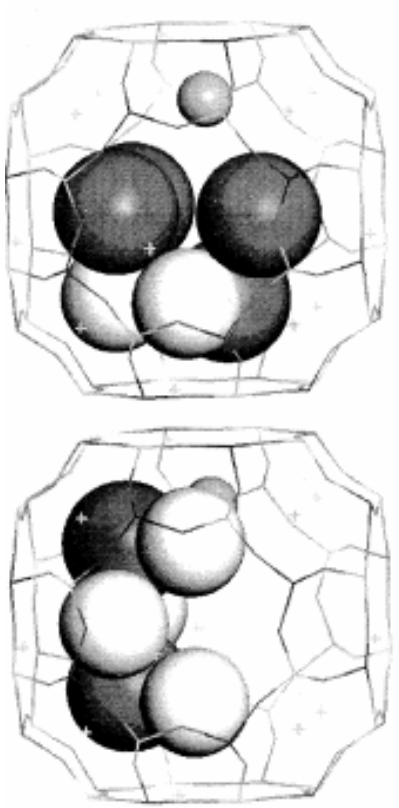
Influence of cation size on the ^{129}Xe chemical shifts

in the limit of zero loading:

- trend: increase in δ(Xe) with increasing cation size
- origin: the combination of the much more deshielding $\sigma(r_{Xe\text{-}M})$ shielding function and deeper potential well for the larger more polarizable cation leads to larger values of the Xe_n cluster shifts where the larger cations leave a smaller effective volume for the Xe-Xe pairs to average over

VI. COMPETITIVE ADSORPTION

Competitive adsorption



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

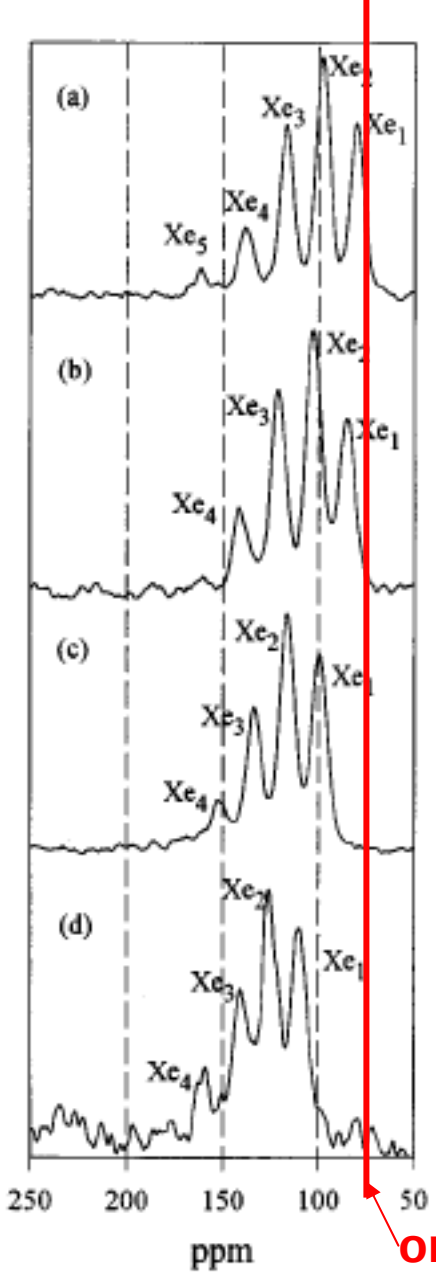
QUESTIONS:

What are the consequences for Xe?

Is the distribution of Xe inside vs. outside affected?

Is the distribution of confined Xe affected?

Is the Xe chemical shift affected?



The Xe chemical shift for a specific number of Xe

- is different from that when the overhead gas is pure Xe, and
- depends on the average number of Ar in the same cage as the Xe.

	$\langle n \rangle_{Xe}$	$\langle m \rangle_{Ar}$
(a)	1.54	0.86
(b)	1.36	1.65
(c)	1.22	3.60
(d)	1.23	4.79

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

one Xe in a cavity in pure Xe samples

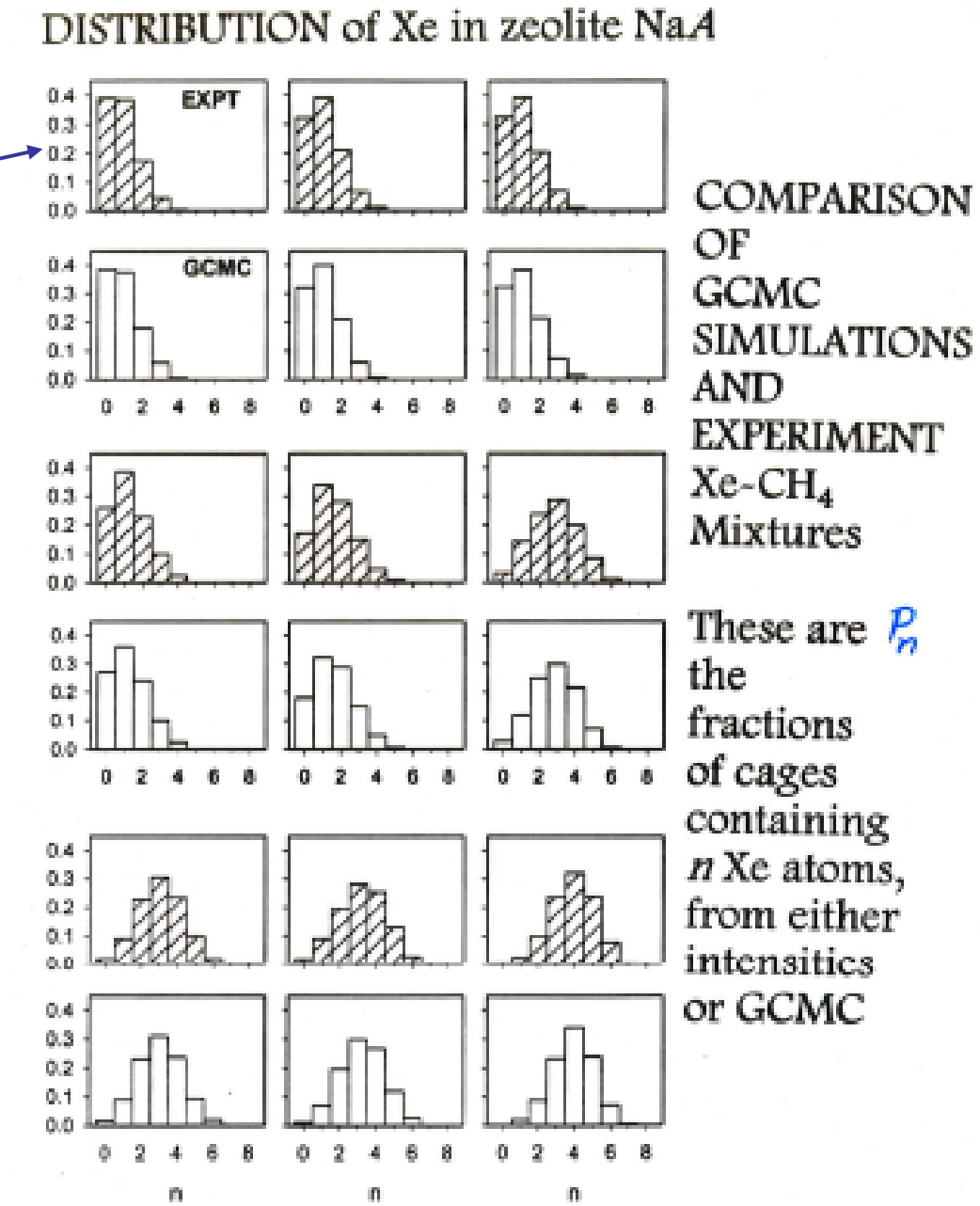
Xe NMR spectra of adsorbed Xe-Ar mixtures in zeolite NaA

Simulation STRATEGY for mixtures

- Use ab initio shielding functions of ^{129}Xe in Xe-CO_2, test against gas phase experiments using anisotropic potential surface
- GCMC simulations of CO_2 in Na*A*. Test CO_2-CO_2 potential and CO_2-zeolite potential against adsorption isotherm of pure CO_2 in Na*A*
- *GCMC simulations of Xe-CO_2 mixtures, get distributions and mixture adsorption isotherms, compare with ideal adsorbed solution theory*
- GCMC simulations provide Xe_n chemical shifts in mixtures, compare with experiment

DISTRIBUTION of Xe:

from the NMR spectrum we still obtain the distribution of Xe among the cavities from the relative intensities



Distribution of two components inside and outside

from the Monte Carlo simulations

at a given (P_{total} , y_{CH4}) in the bulk, we obtain

- the total amount of gas adsorbed
- the composition inside: $\langle n \rangle_{Xe}$, $\langle m \rangle_{CH4}$

Separation factor

the ratio of mole fractions in the adsorbed phase (***x***) and the bulk gas phase (***y***):

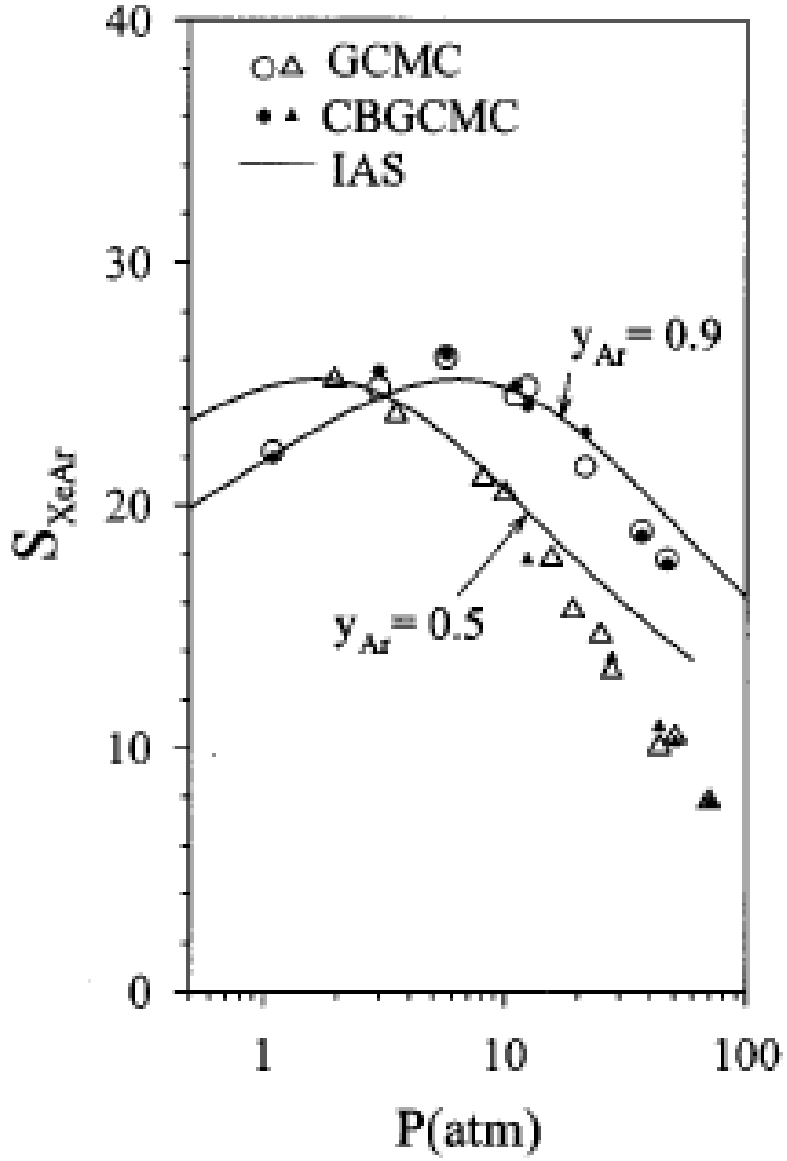
$$S_{Xe,Ar} = \frac{x_{Xe}/x_{Ar}}{y_{Xe}/y_{Ar}}$$

Separation factor

or

Selectivity coefficient

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

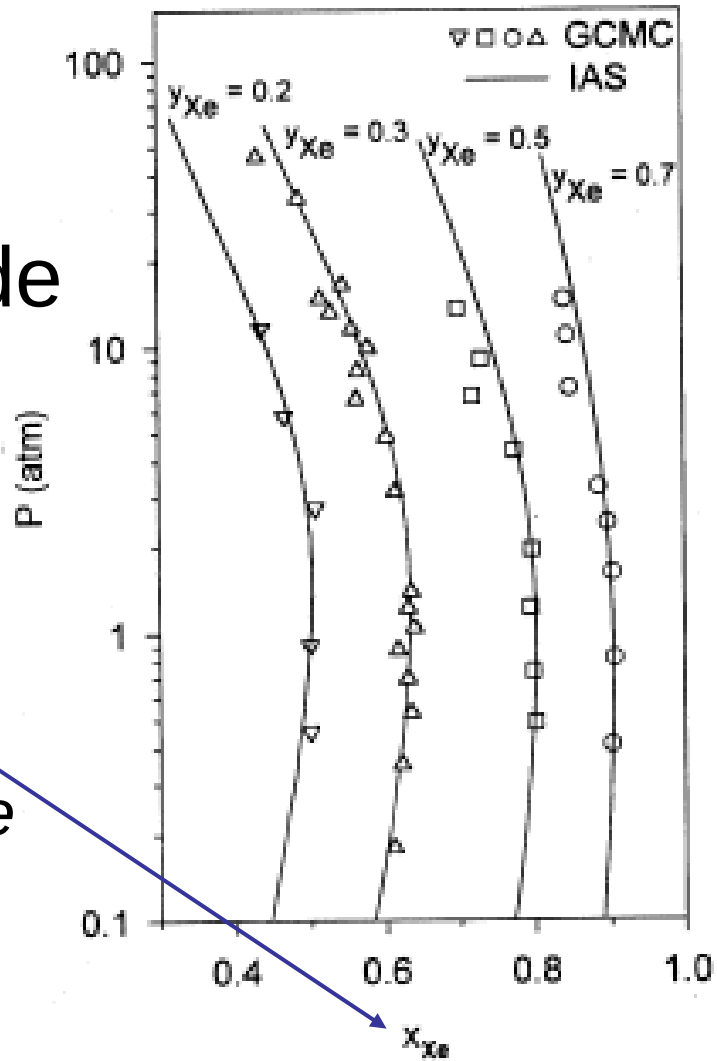


Distribution of two components inside and outside

given P_{total} , y_{Xe} outside
GCMC simulations provide
x_{Xe} inside

for competitive adsorption of Xe and CH_4

Separation of the components of Xe-CH_4 mixture: mole fraction y_{Xe} in the bulk gas, in equilibrium with x_{Xe} in the adsorbed phase at total pressure P



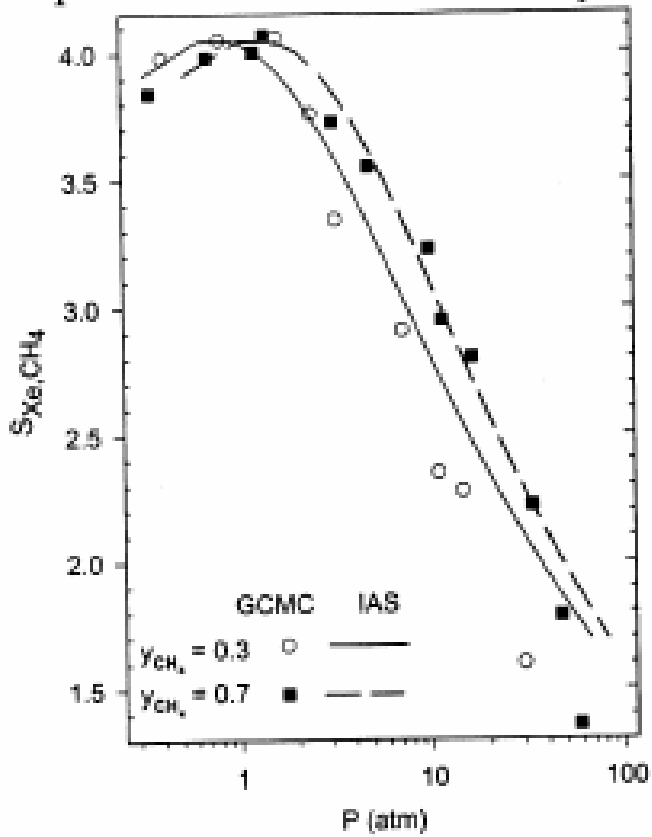
Separation factor

or

Selectivity coefficient

of zeolite NaA
for adsorption
of Xe and CH_4
from gas mixtures
at various
total pressures
and mole fractions

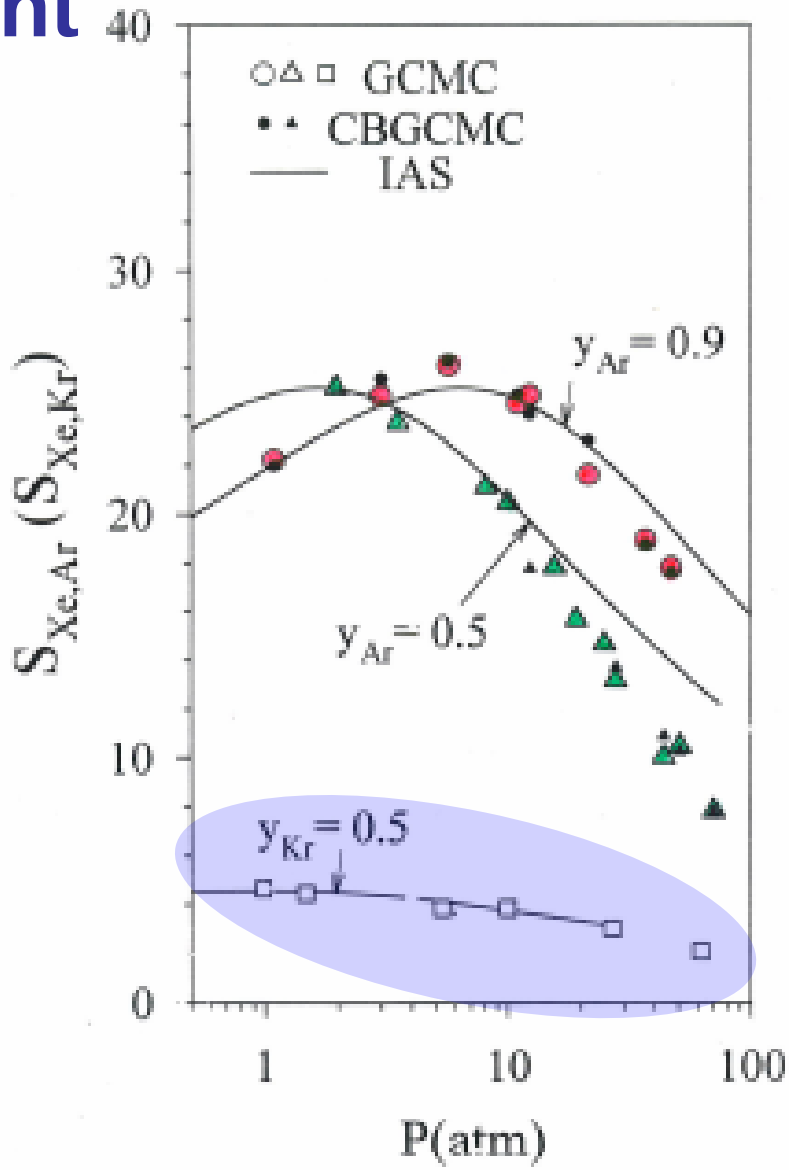
Separation Factor for Xe/CH_4 in NaA:



Ideal solution model good for P < 10 atm.
The preferential adsorption of Xe is decreased somewhat

- by increasing the mole fraction of CH_4 in the bulk phase (good only for P < 1 atm).
- by increasing the total pressure (at any bulk composition).

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



Is the distribution of Xe inside vs. outside affected by the second gas?

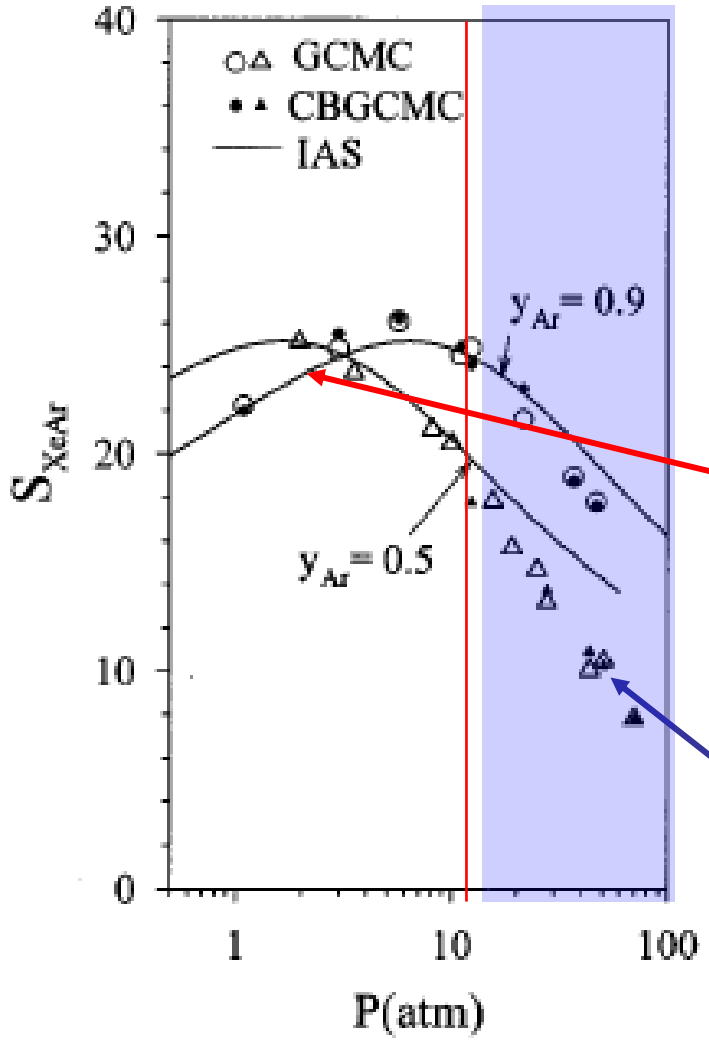
Both molecules adsorb, but have different pure adsorption isotherms because of different potential energies of interaction with the atoms of the cavity.

QUESTION:

Is the adsorption isotherm for a mixture the same as that predicted from the individual pure adsorption isotherms?

Ideal Adsorbed Solution theory (IAS) is analogous to Raoult's law for ideal solutions.

The separation factors obtained from GCMC simulations in the binary mixture can be compared with the theoretical separation factors that may be obtained from the individual single component adsorption isotherms (if each component adsorbed independently of one another in an *ideal adsorbed solution*).



GOOD NEWS:

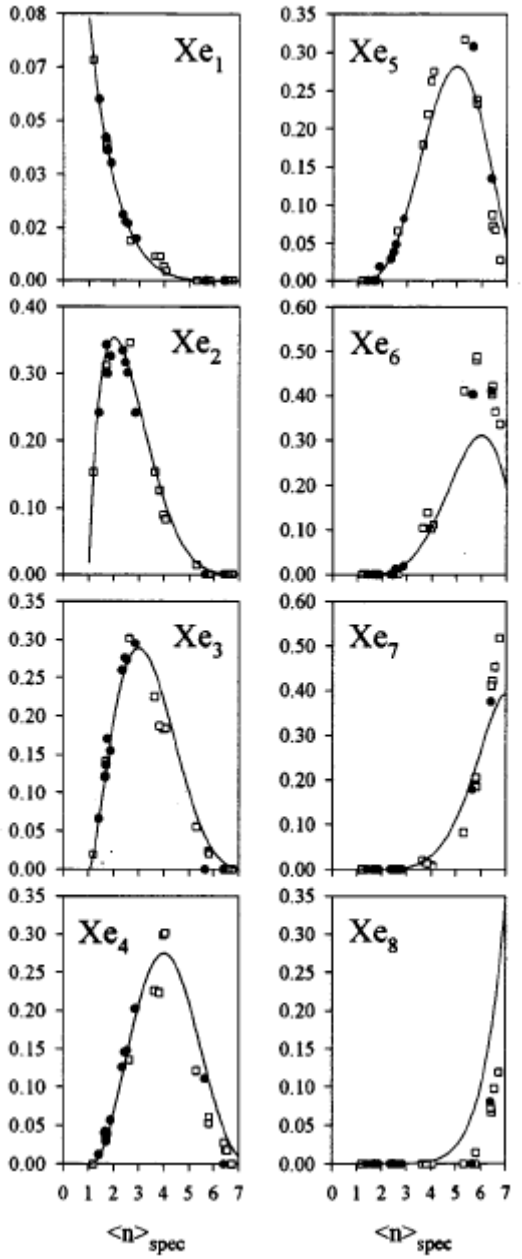
For low total pressures, the adsorption of Xe and the adsorption of the other molecule are nearly independent of each other, as predicted by Ideal Adsorbed Solution theory (IAS), analogous to Raoult's law for ideal solutions.

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

$S_{Xe,Ar}$, $S_{Xe,Kr}$, and $S_{Xe,CH4}$ are all greater than 1.0, showing that Xe is preferentially adsorbed, and GCMC simulations show that realistic separation behavior deviates from ideal at higher gas pressures.

QUESTION:

Is the distribution of confined Xe affected?



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

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

Experimental distribution of Xe among cages occupied by Xe atoms

In other words,

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

Caveat: we can not say the same for the other molecule.

QUESTION:

Does the Xe distribution within the cage change when other molecules are in the cage with it?

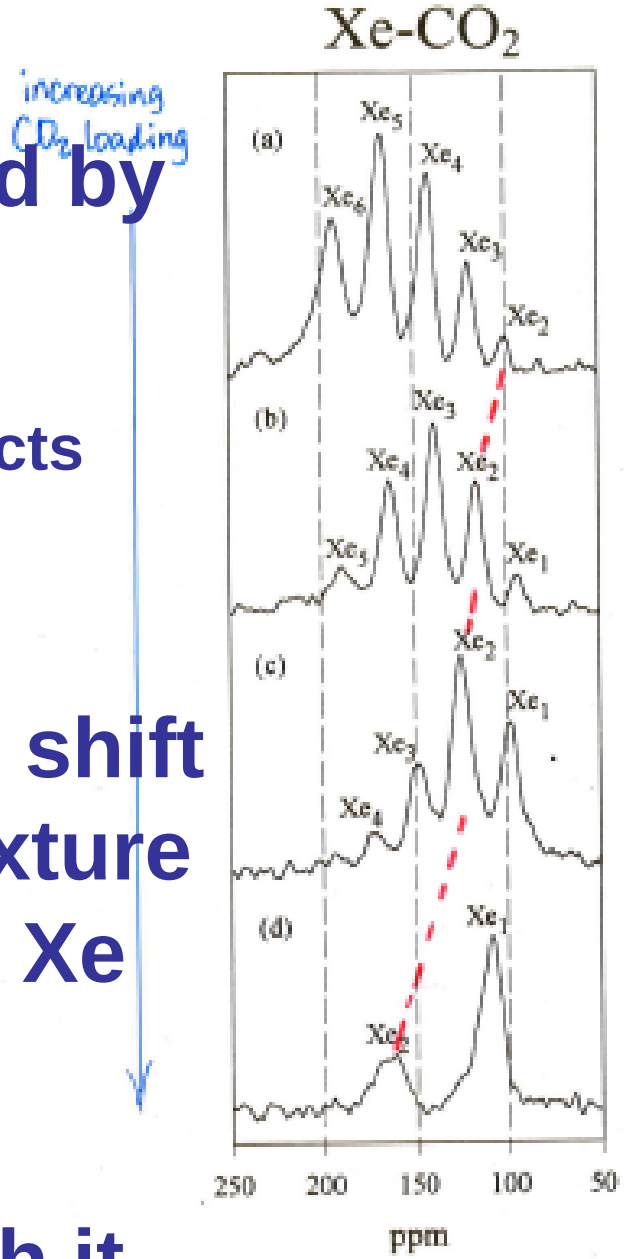
YES, for any Xe_n the available volume within the cage depends on the number of Ar (or other) with it.

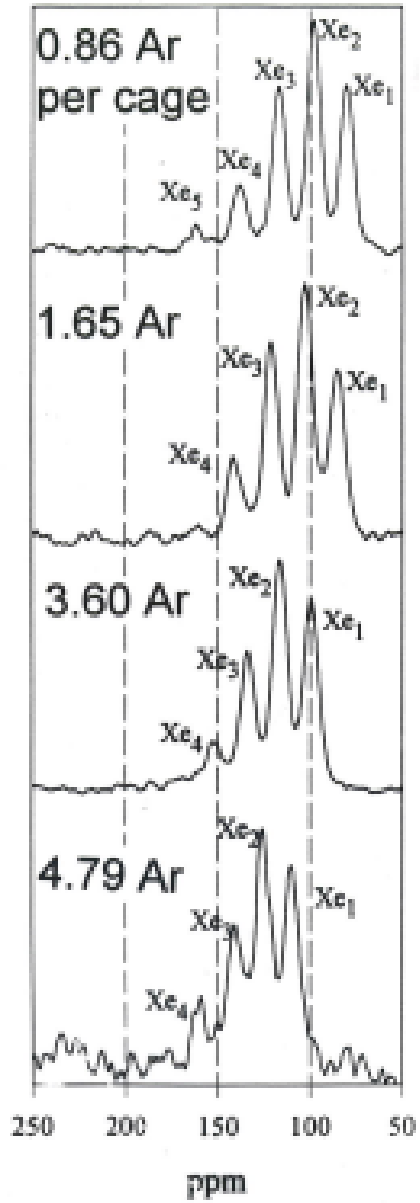
QUESTION:

Is the Xe chemical shift affected by the presence of the other gas?

- **Yes, found experimentally, and also by simulations [because the Xe interacts with additional molecules inside the confined space].**

This means that the observed shift in Xe_n peak position in the mixture compared to Xe_n peak in pure Xe can be used to deduce the average number of the other molecules inside the cage with it.

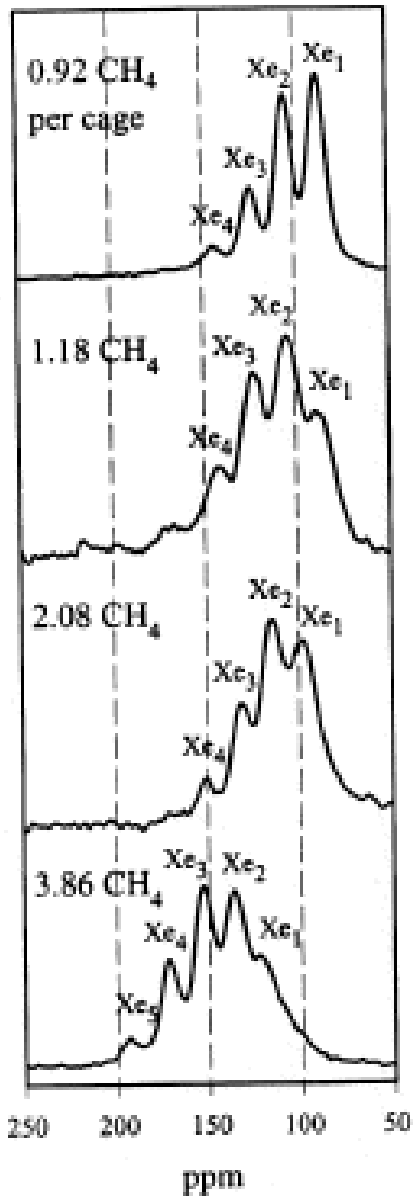




PROPOSE:

The SHIFT of a Xe_n peak is a measure of the average number of Ar atoms 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.



The SHIFT of a 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

QUESTION:

Is it possible to observe $\delta(Xe_nAr_m)$ directly?

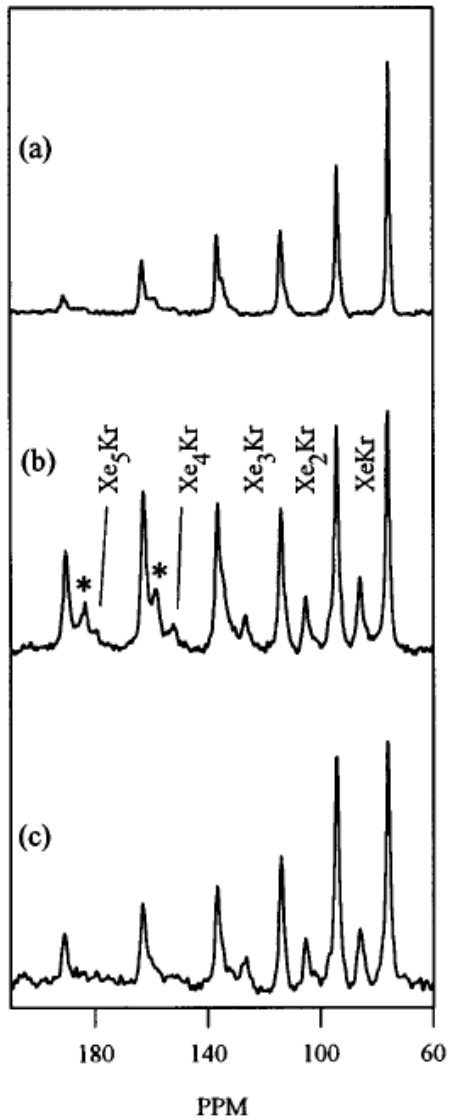
$\delta(Xe_nAr_m)$ would be the peak position, i.e., Xe chemical shift relative to an isolated Xe atom) observed for Xe in a cage containing exactly nXe atoms and m Ar atoms. But we can not observe such peaks directly. Because the Ar atoms are freely visiting many cages, only the average for nXe and $\langle m \rangle$Ar is observed.

Is it possible to observe *f*(Xe_nAr_m) directly?

This would be the relative intensity of the peak at $\delta(Xe_nAr_m)$. **NOT for Ar**

Co-adsorption of Xe and Kr in Na*A*

Peaks which can be directly assigned to XeKr, Xe_2Kr, Xe_3Kr, Xe_4Kr, Xe_5Kr are observed



^{129}Xe chemical shifts of the mixed 'clusters' Xe_nKr in the alpha cages of zeolite NaA (ppm)

Cluster	$\delta(Xe_nKr)$		$\delta(Xe_nKr) - \delta(Xe_n)$	
	OBSD	GCMC	**OBSD**	GCMC
Xe_1Kr	84.7	86.6	9.9	8.9
Xe_2Kr	103.3	101.5	11.0	8.8
Xe_3Kr	124.5	121.4	12.8	11.3
Xe_4Kr	148.9	144.6	15.7	16.0
Xe_5Kr	174.7	173.3	16.3	18.7
Xe_6Kr	209.9	208.6	26.5	24.7

Co-adsorption of Xe and Kr in Na*A*

Observations:

- Peaks which can be directly assigned to mixed clusters are observed.
- ^{129}Xe chemical shift increments upon addition of a Kr atom to the cluster are increasing with cluster size.

- **The magnitude of the increments can be predicted from the known gas phase shifts in mixtures of Xe and Kr and from the Xe_n cluster shift increments?**

The answer is yes.

The increments in the chemical shifts of the Xe_n cluster upon addition of one Xe or Kr or Ar are related in the same ratio as the observed density coefficients of the Xe chemical shift in the gas phase:

δ_1(Xe-Kr) /δ_1(Xe-Xe) = 0.53 cf 0.57-0.65

δ_1(Xe-CH_4) /δ_1(Xe-Xe) = 0.51 cf 0.44-0.64

δ_1(Xe-Ar) /δ_1(Xe-Xe) = 0.34 cf 0.34-0.46

i.e., when the Xe-Xe increment is known in the cavity, the Xe-A increment can be estimated well from gas phase density coefficient data in Xe-A mixtures. Estimate gets better with smaller A.

Plot density coefficient at same T or (T/T_{crit}) for Xe-Xe, Xe-Kr, Xe-Ar vs. number of electrons; extrapolate to Xe-Ne, Xe-He to find estimate for Xe-He.

The increments in the chemical shifts of the Xe_n cluster upon addition of one Xe (or Kr or Ar) are related in the same ratio as the second virial coefficients of the Xe chemical shift in the gas

σ_1(Xe-Kr) /σ_1(Xe-Xe) = **0.53** σ_1(Xe-Ar) /σ_1(Xe-Xe) = **0.3**

	$\sigma(Xe_n)$	$\sigma(Xe_{n+1})$ - $\sigma(Xe_n)$ EXPT	$\sigma(Xe_nKr)$ - $\sigma(Xe_n)$ EXPT	ratio to Xe-Xe	$\sigma(Xe_nAr)$- $\sigma(Xe_n)$ CALC	ratio to Xe-Xe
Xe_1	-74.8					
Xe_2	-92.3	17.5	9.9	0.57	5.9	0.34
Xe_3	-111.7	19.4	11.0	0.57	6.7	0.34
Xe_4	-133.2	21.5	12.8	0.60	8.1	0.38
Xe_5	-158.4	25.2	15.7	0.62	10.0	0.40
Xe_6	-183.4	25.1	16.3	0.65	11.6	0.46
Xe_7	-228.3	45.1	26.5	0.59	16.6	0.37
Xe_8	-272.3	43.7				

^{129}Xe chemical shifts of the mixed clusters Xe_nCH_4 in the alpha cages of zeolite NaA are comparable with Xe_nKr

Cluster	$\delta(Xe_nKr)$		Cluster	$\delta(Xe_nCH_4)$
	OBSD	GCMC		GCMC
Xe_1Kr	84.7	86.6	Xe_1CH_4	86.5
Xe_2Kr	103.3	101.5	Xe_2CH_4	102.6
Xe_3Kr	124.5	121.4	Xe_3CH_4	121.0
Xe_4Kr	148.9	144.6	Xe_4CH_4	143.3
Xe_5Kr	174.7	173.3	Xe_5CH_4	170.9
Xe_6Kr	209.9	208.6	Xe_6CH_4	204.4

Distribution of two components among cages

P_n = the fraction of cages that have n molecules of type A

$$P_n = \sum_{m=0} f(n,m)$$

f(n,m) = the fraction of cages that have exactly *n* molecules of type A and *m* molecules of type B

simple statistical model

distribution of molecules in cages having 8 mutually exclusive sites

fraction of cages containing i molecules:

$H_i = \langle i \rangle_i (8 - \langle i \rangle)(8-i)8! / 8^8 i!(8-i)!$

(the hypergeometric distribution)

2 types of molecules compete for same mutually exclusive sites in each cage

fraction of cages containing n of one and m of the other

$$f(n,m) = \frac{H_i \langle n \rangle^n \langle m \rangle^m}{\sum_{n} n!m! \sum_{k=0} [\langle n \rangle^k \langle m \rangle^{i-k} / k!(i-k)!]}$$

What did we find out about competitive adsorption in zeolites from Xe NMR expts?

for any chosen sample (various bulk gas compositions):

- $\langle n \rangle_{Xe}$ (Xe adsorption isotherm in Xe/CH_4 mixture)
- P_n (fraction of cavities having exactly *n* Xe atoms)
- $\delta(Xe_n)$ (average Xe_n chemical shift)

What did we find out about competitive adsorption in zeolites from chemical shift calcns?

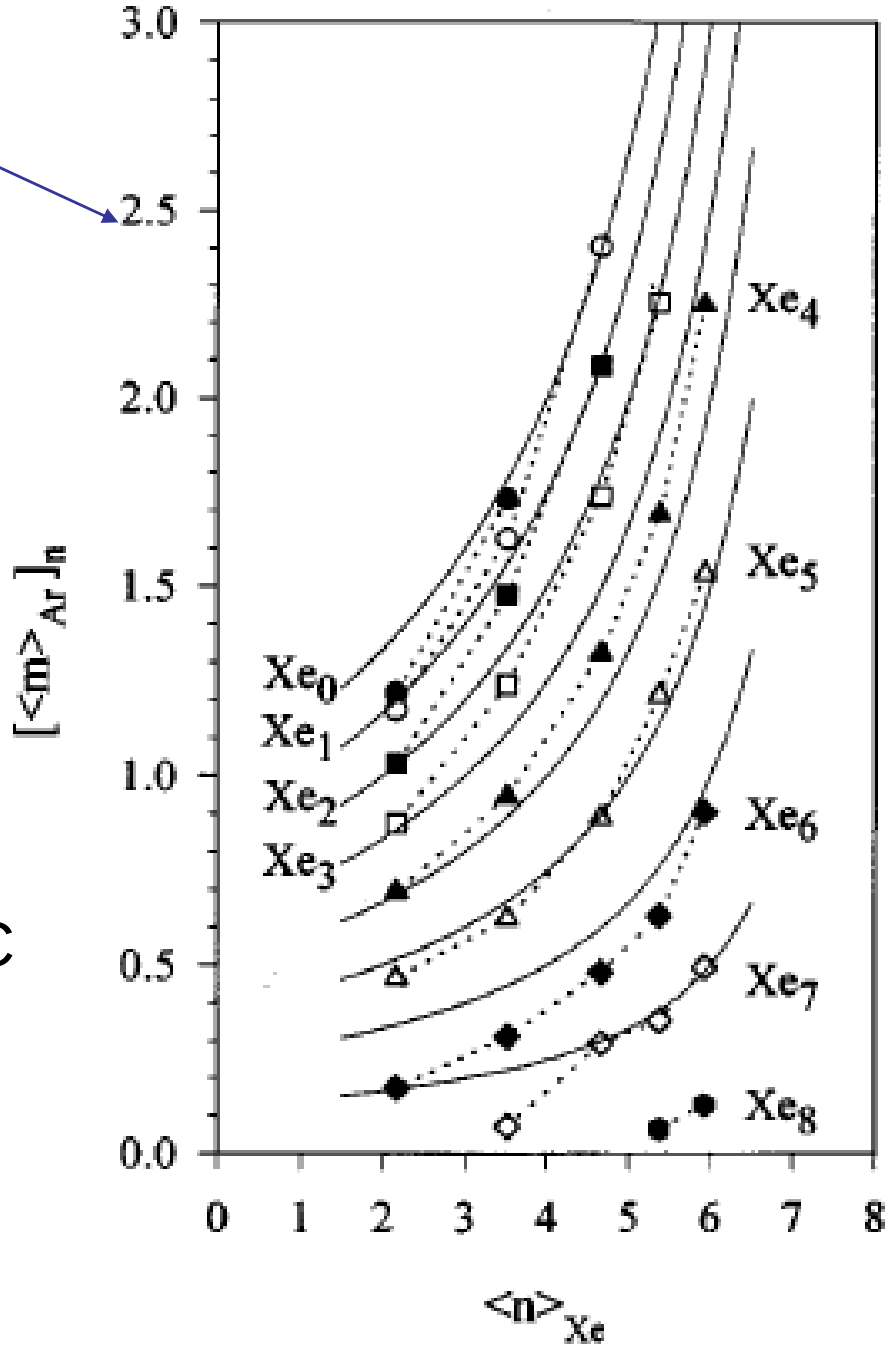
for any chosen sample (various bulk gas composition)

- average ^{129}Xe chemical shift for $Xe_n(CH_4)_m$ in NaA
- average number of CH_4 in same cavity as *n* Xe atoms for any chosen sample (various bulk gas compositions).

at (P_{total} , y_{CH4}) in the bulk,

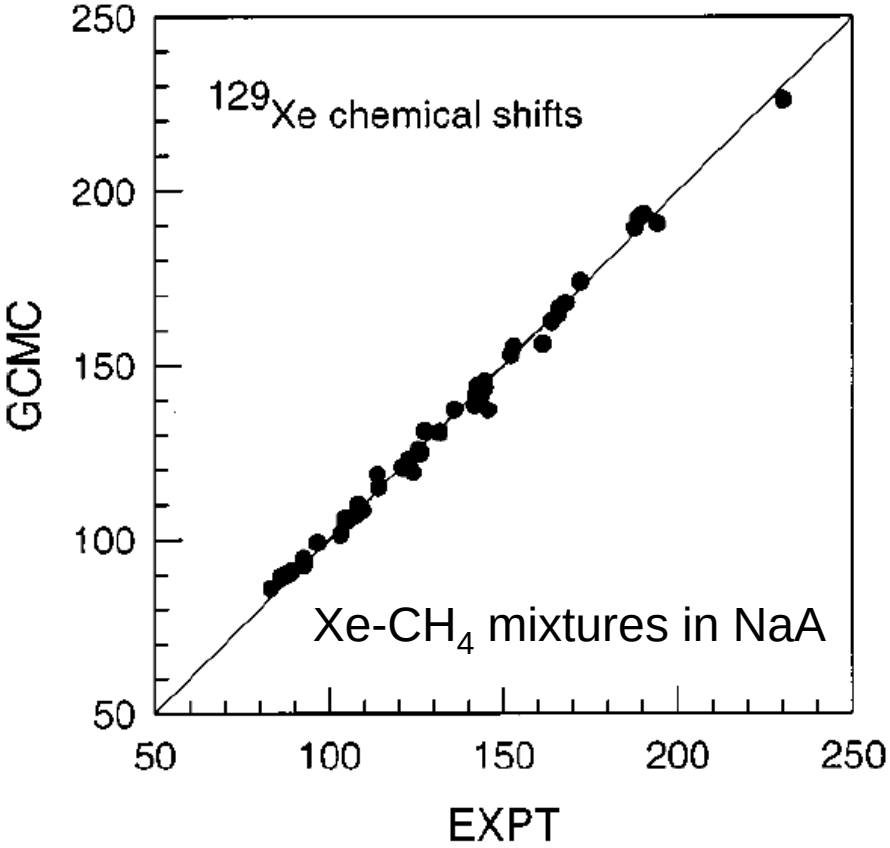
- the total amount of gas adsorbed,
- the composition inside ($\langle n \rangle_{Xe}$, $\langle m \rangle_{CH4}$),
- the separation factor within the zeolite: *f(m,n)* fraction of cages with n_{Xe}, m_{CH4}
- the average number of CH_4 found in the same cage as n_{Xe}, while CH_4 are in fast exchange within a single cage
- the thermal average distribution of the atoms: i.e., the probability of finding a Xe at any specific position in the cage, the probability of finding a Xe at 5Å from a Xe, C, H.

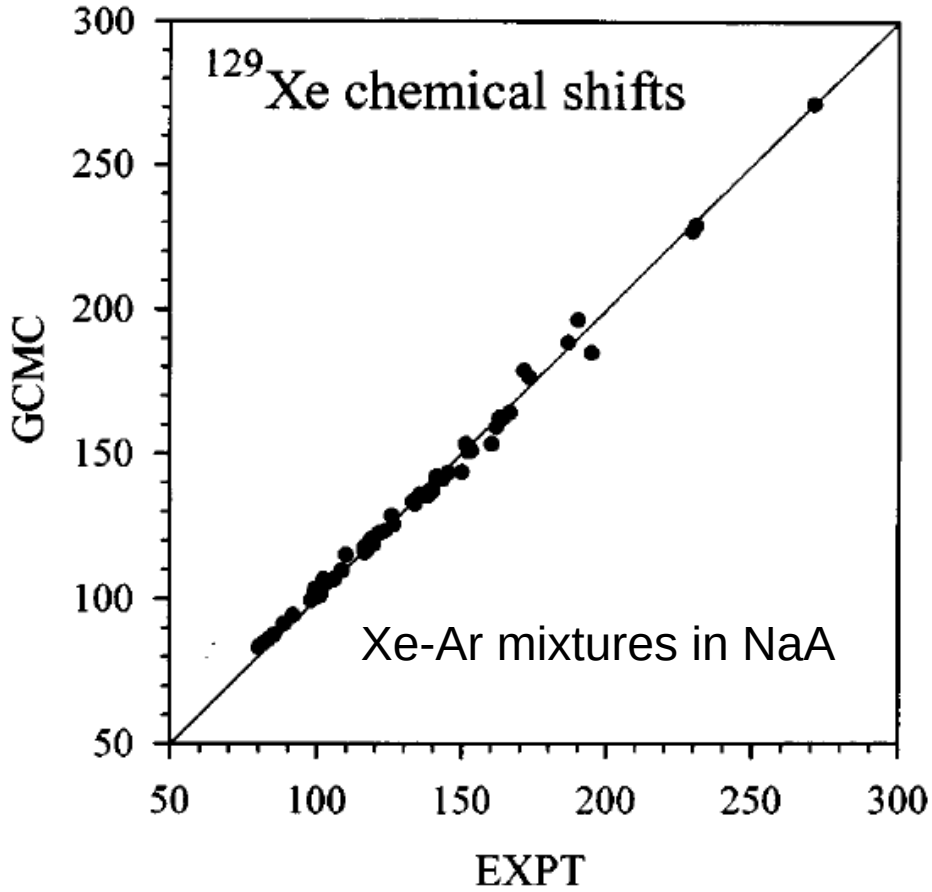
Average number of Ar atoms in the same cage as Xe_n



-------- EXPT & GCMC

———————— using hypergeometric distribution model





Since we can reproduce the Xe chemical shifts in all the samples of varying Xe-other composition, then the average number of other in the same cage as n Xe atoms is probably well represented by the GCMC results.

VII. What is wrong with previous models?

Models for interpretation of ^{129}Xe chemical shifts

- **Raynes, Buckingham and Bernstein model**

$$\sigma = \sigma_0 + \sigma_{\text{bulk susc}} + \sigma_{\text{Electric}} + \sigma_{\text{magn aniso}} + \sigma_{\text{vdW}}$$

$\sigma_{vdW} = B\langle F^2(r)\rangle$, fluctuating electric fields associated with dispersion forces

$$\langle F^2(r)\rangle = (3/2)\, \alpha_b(0) r^{-6}\, U_X U_b/(_{UX+Ub}).$$

- **Reaction field model**

cavity in a uniform continuous medium

$$\sigma = \sigma_0 + B[f(\epsilon)]^2$$

$$f(\epsilon) = [(n^2-1)/(2n^2+1)] \quad \text{(Linder, Rummens)}$$

dielectric constant *refractive index*

- **Fraissard model**

$$\sigma = \sigma_0 + \sigma_{surface} + \sigma_{Electric} + \sigma_{Xe\text{-}Xe}$$

Xe is assumed to behave as a gas with a definable “mean free path” λ.

- **Cheung model**

$$\sigma = \sigma_0 + \boldsymbol{c}\ \varepsilon\ \{1 + F \exp\,[-\varepsilon/kBT]\}^{-1}$$

F related to Fraissard's mean free path λ

- **Two site model**, Raftery et al.

$$\sigma = \sigma_0 + [\sigma_{surf} - \sigma_0] \bullet P_s + [\sigma_g - \sigma_0] \bullet P_g$$

surface site gas site

$$P_s = \tau_{surf}/(\tau_{surf} + \tau_\nu)$$

τ_{surf} = sticking time of Xe on the surface

$= \tau_0 \exp[\varepsilon/k_B T]$

Fraissard model

$$\sigma = \sigma_{surf} + \sigma_{Xe\text{-}Xe} + \sigma_{elec}$$

- σ_{surf} was thought to be a constant equal to the shielding at the zero-loading limit
- $\sigma_{Xe\text{-}Xe}$ was assumed to be proportional to the number of Xe atoms
- σ_{elec} was the shielding contribution from electric fields generated by the cations

Our results establish that

- σ_{surf} is not a constant for a given framework but depends on the cation and on the cage occupancy
- $\sigma_{Xe\text{-}Xe}$ is not proportional to the number of Xe atoms in the cage, it is not a constant for a given occupancy for a given framework, but depends on the cation
- σ_{elec} contribution from electrostatics is nil

  shielding calculated for Xe in the presence of point charges in an overall neutral system is negligibly small

The **Xe-zeolite contribution** to the ^{129}Xe chemical shift (Fraissard's σ_{surf}) **is not a constant**; it depends on occupancy

	Xe-zeol Xe in Na*A*	Xe-zeol Xe in K*A*
Xe_1	76.2	78.7
Xe_2	76.8	79.2
Xe_3	77.8	81.6
Xe_4	79.3	85.3
Xe_5	83.4	96.0
Xe_6	87.2	106.2
Xe_7	96.0	
Xe_8	102.9	

The **Xe-Xe contribution** to the ^{129}Xe chemical shift is **not proportional to the number** of other Xe atoms in the cage:

	Xe-Xe in Na*A*		Xe-Xe in K*A*	
	calcd GCMC	If $\propto$ (n-1)	calcd GCMC	if $\propto$ (n-1)
δXe_2-δXe_1	15.2	15.2	19.6	19.6
δXe_3-δXe_1	31.7	30.4	40.8	39.2
δXe_4-δXe_1	50.4	45.6	63.3	58.8
δXe_5-δXe_1	73.2	60.8	96.9	78.4
δXe_6-δXe_1	98.1	76.0	136.8	98.0
δXe_7-δXe_1	132.7	91.2		
δXe_8-δXe_1	170.3	106.4		

While simple models have their place in *a posteriori* interpretation, they usually can not be made consistent with other physical observables of the system, and have little predictive value.

What we need is a calculation as close to first principles as possible.

VIII. CONCLUSIONS

SUMMARY

- ^{129}Xe nuclear magnetic resonance spectroscopy has been used as a probe of cavity size, siting of metal atoms or ions or other details of structure. Although this had been a useful empirical tool, a fundamental understanding of the Xe NMR in zeolites had been lacking.
- Our studies combine NMR spectroscopy and computer simulations to provide a molecular level understanding of the fundamental processes of adsorption and diffusion.
- NMR spectroscopy provides very detailed information for testing computer simulations.

CONCLUSIONS

We obtain detailed distributions

- We obtain from intensities directly the distribution of Xe atoms among the cages.
- 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.

CONCLUSIONS ...

We obtain detailed distributions ....

- The magnitude and the temperature dependence of the chemical shift difference between Xe_n and Xe_1 contains information about the averaging over the various configurations of Xe_n within the cage or the pair distribution function of an Xe_n cluster.
- The Xe_n chemical shift in a mixture of Xe and Ar (or CH_4) provides a direct measure of the average number of Ar atoms (or CH_4 molecules) in the same cage as *n* Xe atoms, for a given loading or composition.

CONCLUSIONS ...

We have details for testing GCMC simulations

- Assumption of pairwise-additive shielding contributions permits computation of average shieldings in a GCMC simulation which can be compared directly with experiment, for Xe_n clusters as a function of temperature in pure xenon in Na*A*, for individual Xe_nKr mixed clusters, and for Xe_n observed in various loadings of Xe and Ar (or CH_4) in competitive adsorption.

CONCLUSIONS ...

We have details for testing GCMC simulations...

- The detailed distributions of both components of a Xe-other gas binary mixture into the cages of a zeolite provide a good test of GCMC simulations

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