The Harry Emmett Gunning Lecture Series
October 2-4, 2002
Department of Chemistry
The University of Alberta
Edmonton, Alberta

Lecture 2

Adsorption and Diffusion in Nanopores

Cynthia J. Jameson
University of Illinois at Chicago

- Surfaces have the ability to select one or more components from a mixture by adsorbing some more strongly than others.
- Pores and slits have attracted a great deal of attention because of their theoretical and industrial importance.
- In these systems fluids are under extreme conditions of non-uniformity, as a result of the molecule-surface interactions.

Xe NMR has been used to study surfaces, carbon nanotubes, molecular sieves such as zeolites, metal oxide catalysts, solutions, polymers, rat brains, etc.

- Industrial adsorption processes involve adsorption from streams which have multiple components, and applications of microporous solids in separations depend on competitive adsorption.
- Thus, fundamental studies of binary and more complex mixtures in microporous solids is extremely relevant.
- Selectivity coefficients have been found to be strongly dependent on the composition of the fluid phase.
- A molecular level understanding requires microscopic detail.

Some questions we would like answers to:

- 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 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?
- 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?
- When two or more types of molecules are adsorbed in a microporous solid, how does the distribution of one type of molecule affect the distribution of another?
- How many molecules of type 2 can be found in those cavities that have exactly n molecules of type 1?

What we need are experiments that can be used to test simulations and simple models.

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 Monte Carlo simulations using ab initio chemical shift functions.

Intermolecular Chemical Shifts

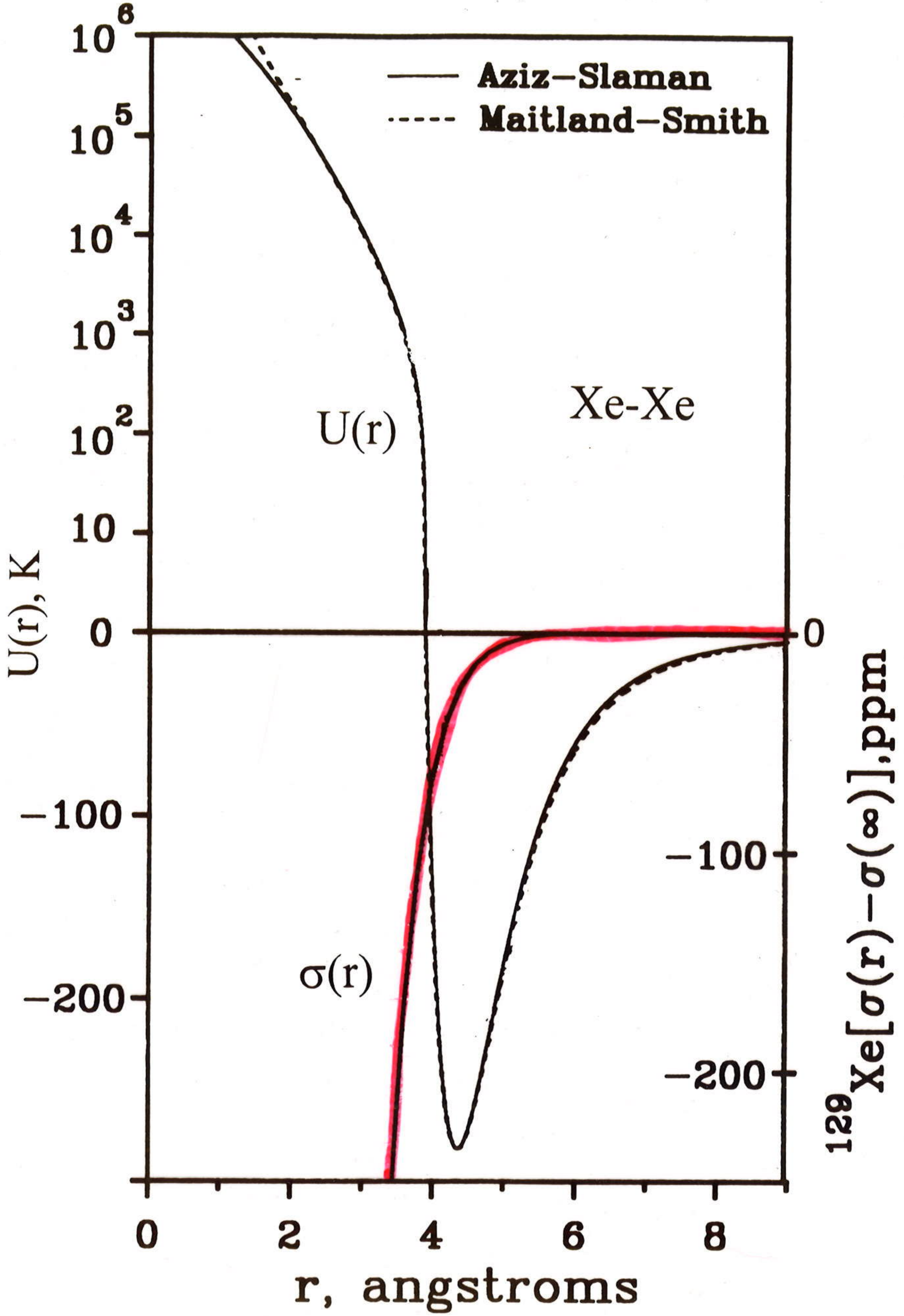
GAS phase:

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

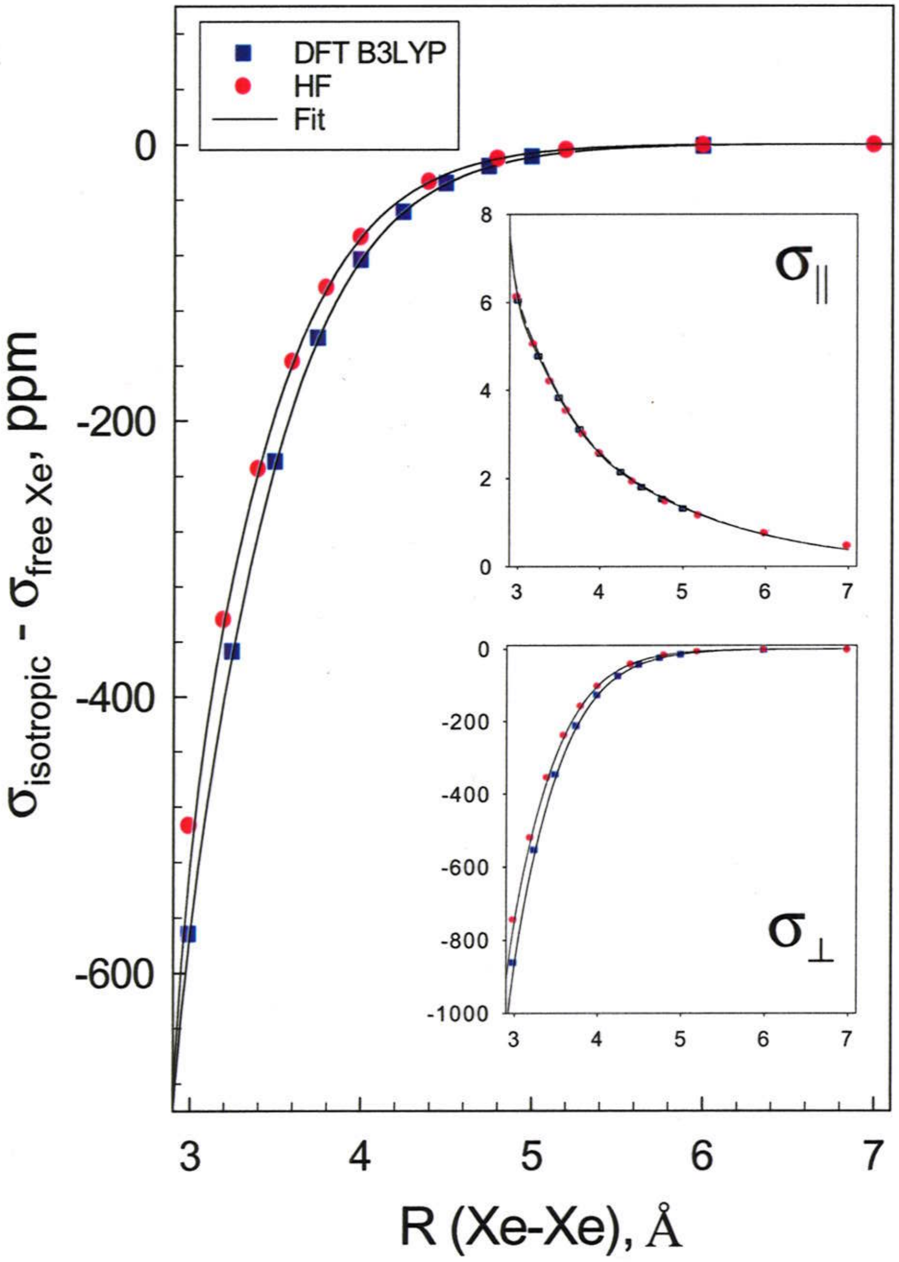
$$\sigma_1(T) = 2\pi \times \iint [\sigma(r, \theta) - \sigma(\infty)] \times e[-V(r,\theta)/kT] r^2 dr \sin\theta d\theta$$

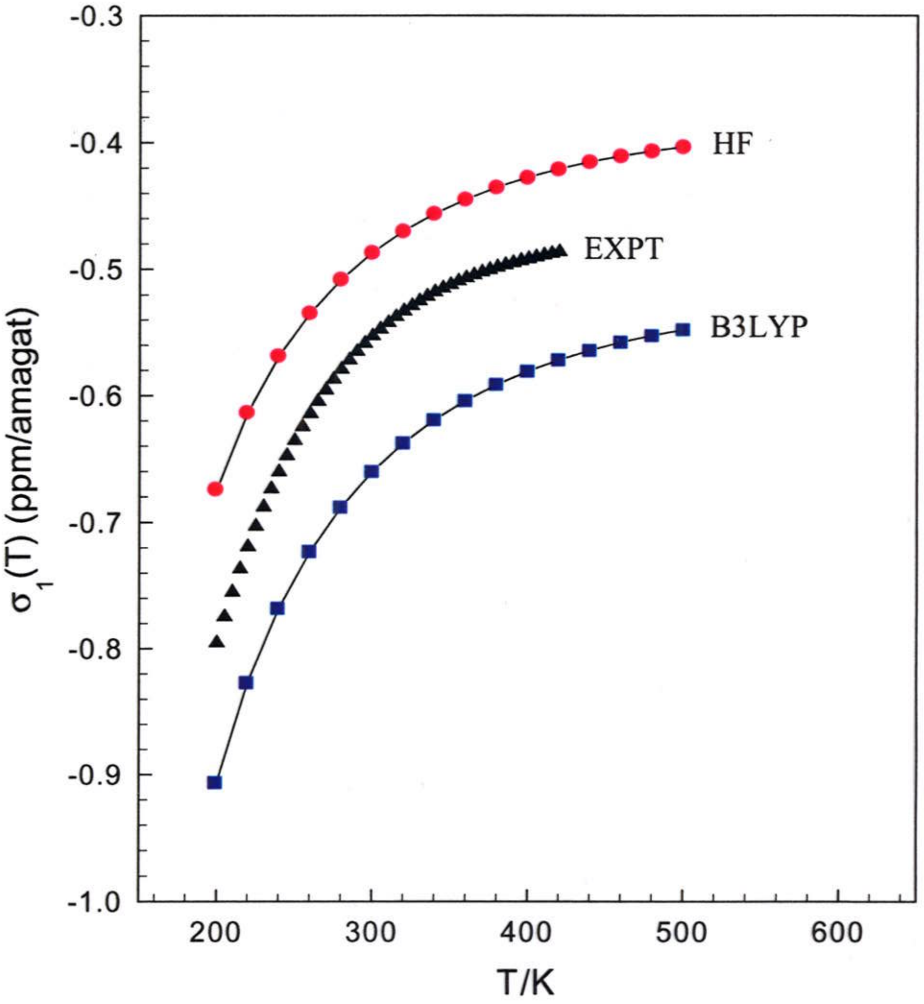
Need 2 functions:

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


10^6
10^5
10^4
10^3
10^2
10
0
−100
−200
U(r), K
Aziz–Slaman
Maitland–Smith
U(r)
Xe-Xe
σ(r)
0
−100
−200
129Xe[σ(r)−σ(∞)],ppm
0
2
4
6
8
r, angstroms

Xe-Xe diatomic molecule shielding





$$\sigma_1(T) = \int_0^\infty [\sigma_{Xe-Xe} - \sigma_{freeXe}] e^{\frac{-V(R)_{Xe-Xe}}{kT}} R^2 dR$$

$V(R)_{Xe-Xe}$ Aziz-Slaman Potential[3]

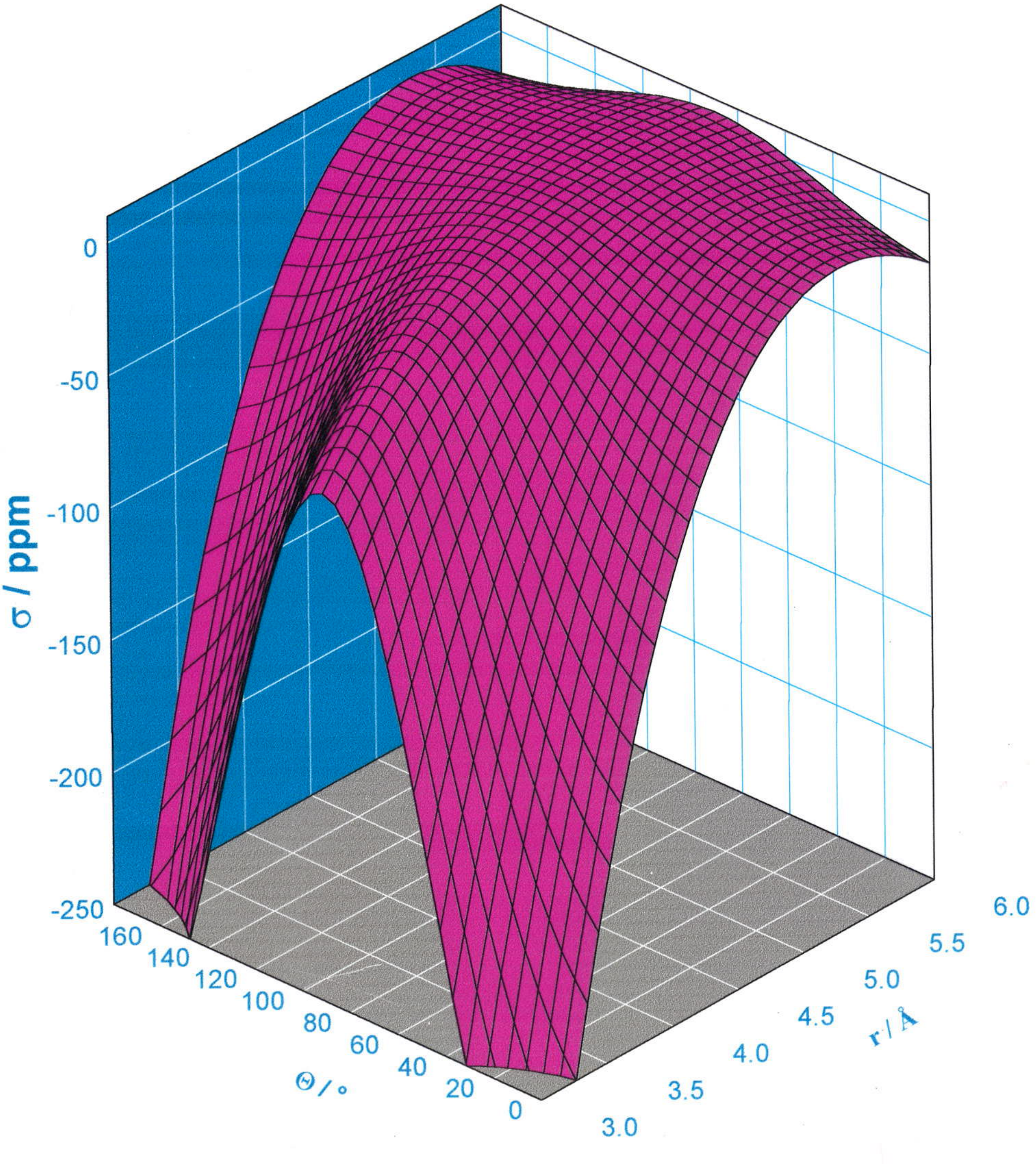
For Xe interacting with a polyatomic molecule, the shielding function and the potential energy surface depend on distance and orientation

Xe 240 basis functions
(uncontracted 29s 21p 17d 9f).
The core (25s 18p 13d) was taken from Partridge and Faegri, this was augmented by 3s 2p 4d and 9f orbitals with exponents from D. Bishop.
Large enough so that the counterpoise correction to the ^{129}Xe shielding function is negligible in every case, ~ +0.03 ppm where the intermolecular shielding is -63.35 ppm (0.05%)and less (<0.01%) at longer distances.

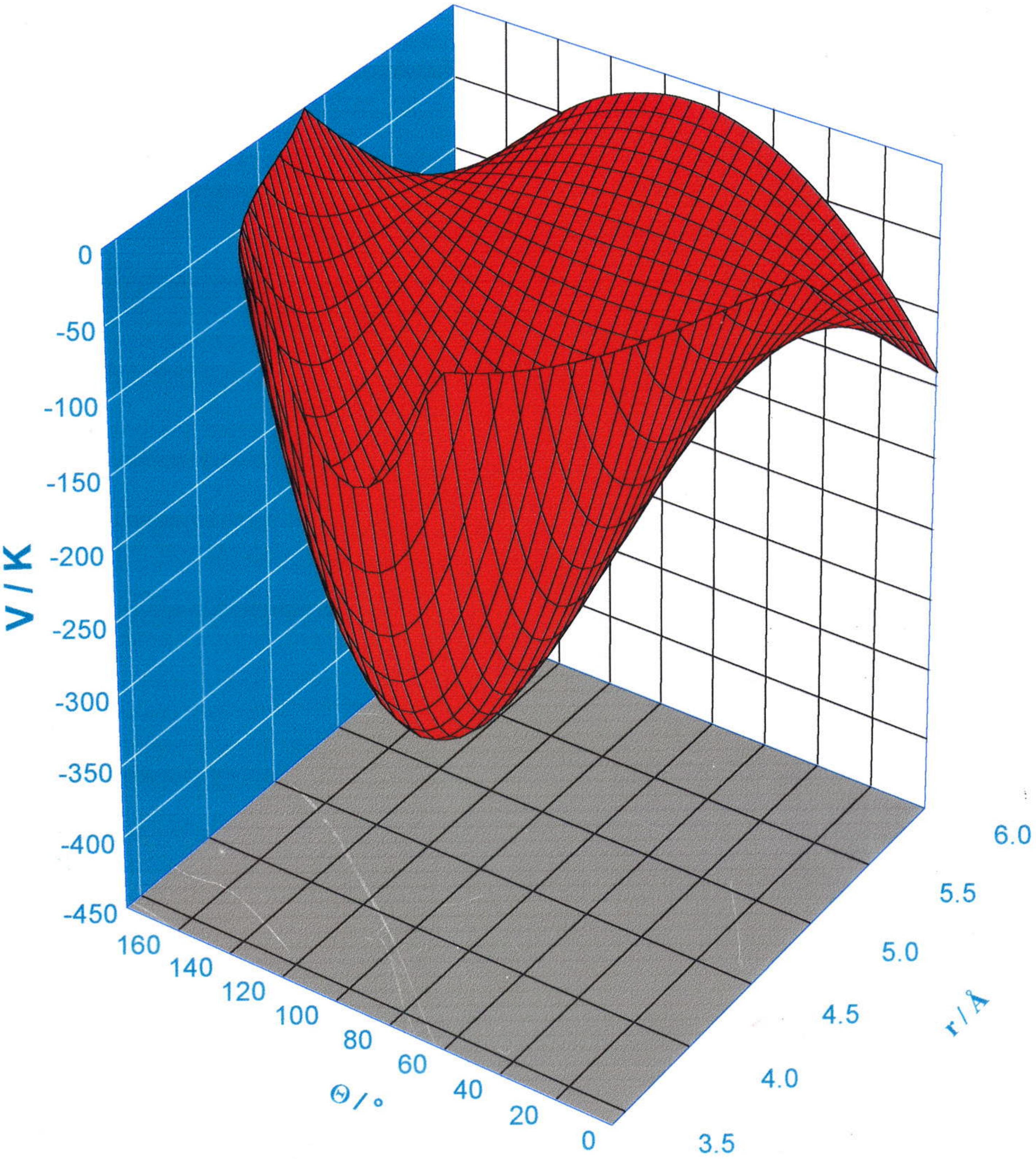
Values of σ were calculated at 70 (R,θ) points for Xe-CO_2 and 130 (R, θ) points for Xe-CO using GIAO in Gaussian94.

with Angel de Dios

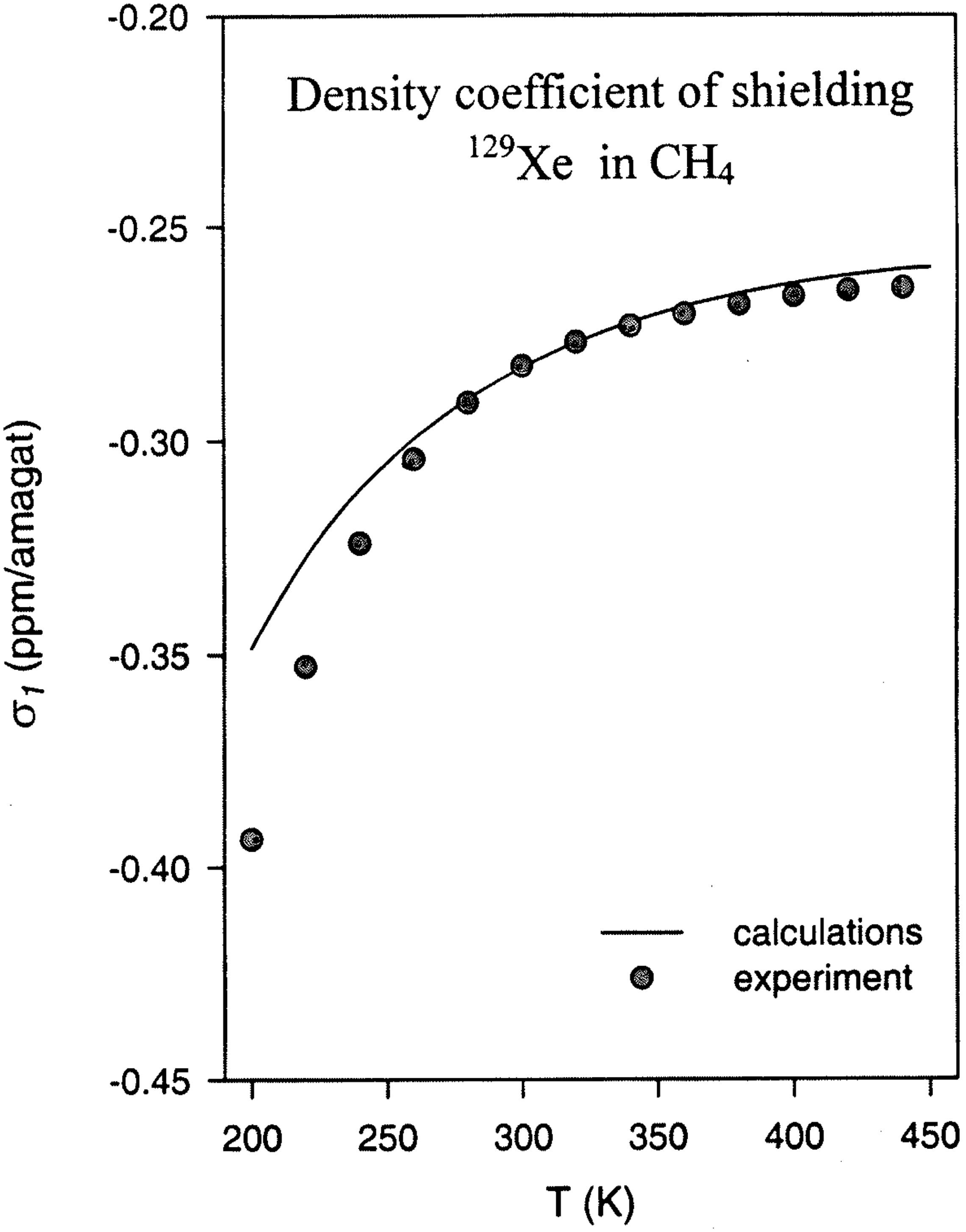
Shielding Surface for Xe - CO_2



Buck Potential Surface for Xe - CO_2



$$\sigma_1(T) = \iint \{\sigma(r_{Xe\text{-}C}, r_{Xe\text{-}H1}, r_{Xe\text{-}H2},..) - \sigma(\infty)\} \times \exp[-V(r_{Xe\text{-}C}, r_{Xe\text{-}H1}, r_{Xe\text{-}H2},..)/kT]\, d\tau$$



The description of adsorption in molecular sieves in statistical terms by means of a grand canonical ensemble:

The approach starts from the conception that the adsorption space of molecular sieves is formed by quasi-independent cavities and/or channels which interchange molecules among themselves and with the bulk phase.

Our model:

- pore is not a homogeneous cavity; atoms and ions of the cavity are individually represented
- adsorbate is not a hard sphere; sorbate-sorbate interactions use realistic intermolecular potentials
- adsorbates are not restricted to specific adsorption sites
- Xe chemical shifts provide detailed observations for testing the ensemble averages; use ab initio quantum mechanical intermolecular anisotropic Xe-sorbate shielding surfaces

in ZEOLITE: **Metropolis Monte Carlo**

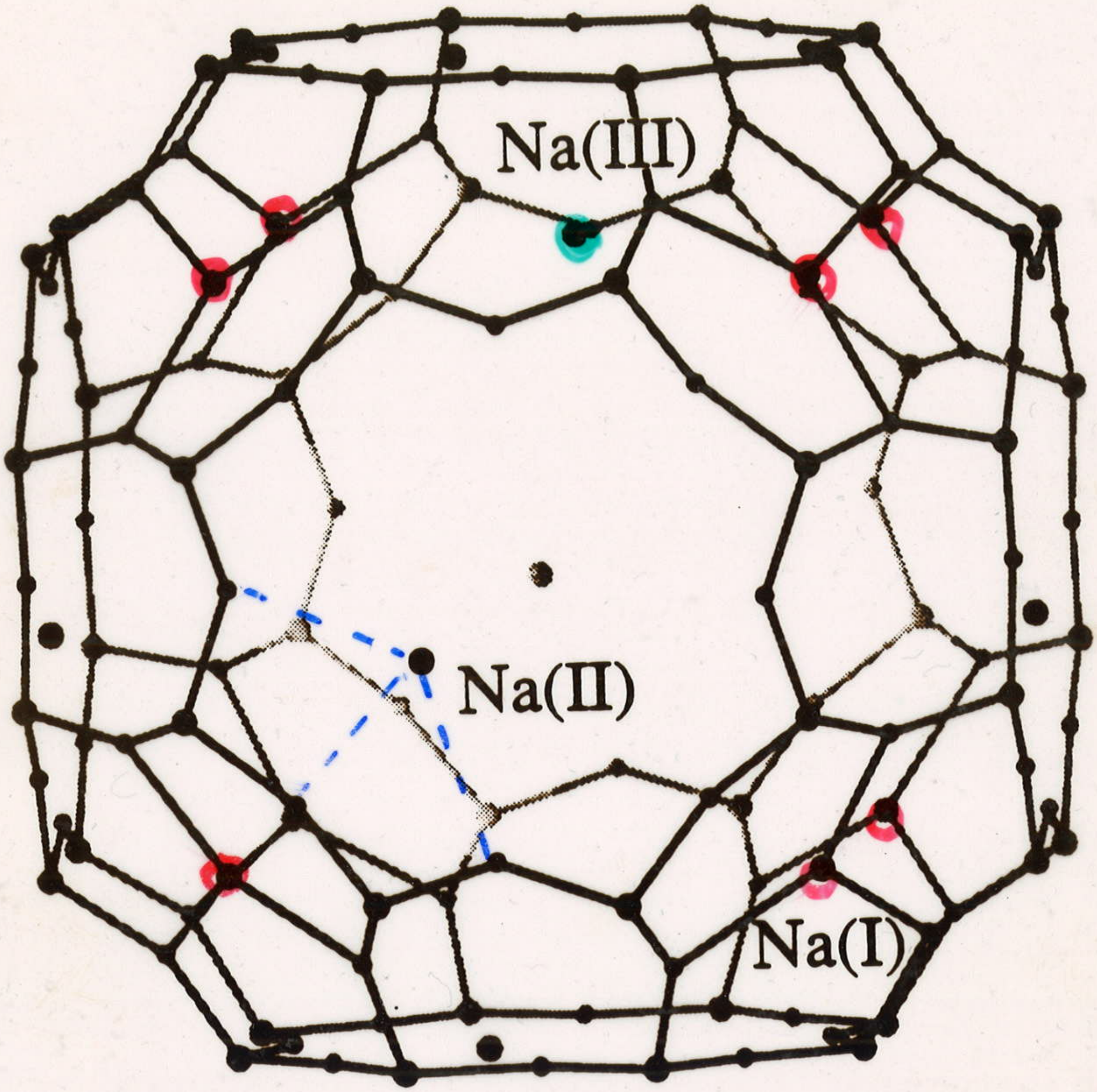
$$\sigma(\mu, T, V) = (1/M)\sum_{i=1}^{M} \sigma_i(\mathbf{r}^N)$$

$\sigma_i(r^N) = \sigma(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \ldots$in zeolite$)$ where the configurations *i = 1 to M* are generated from a probability distribution, in GCMC the distribution is proportional to

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

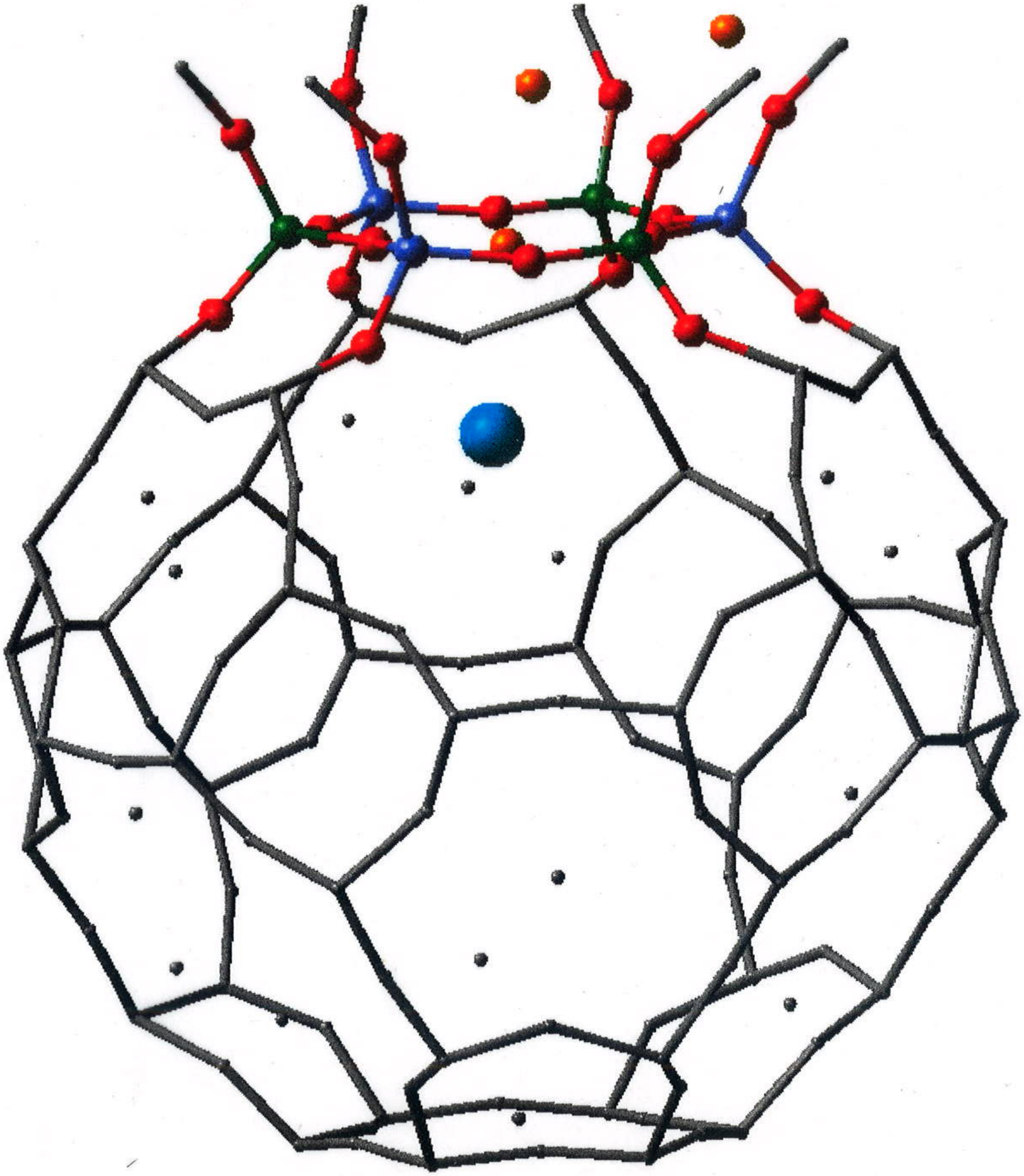
Need 2 functions:

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

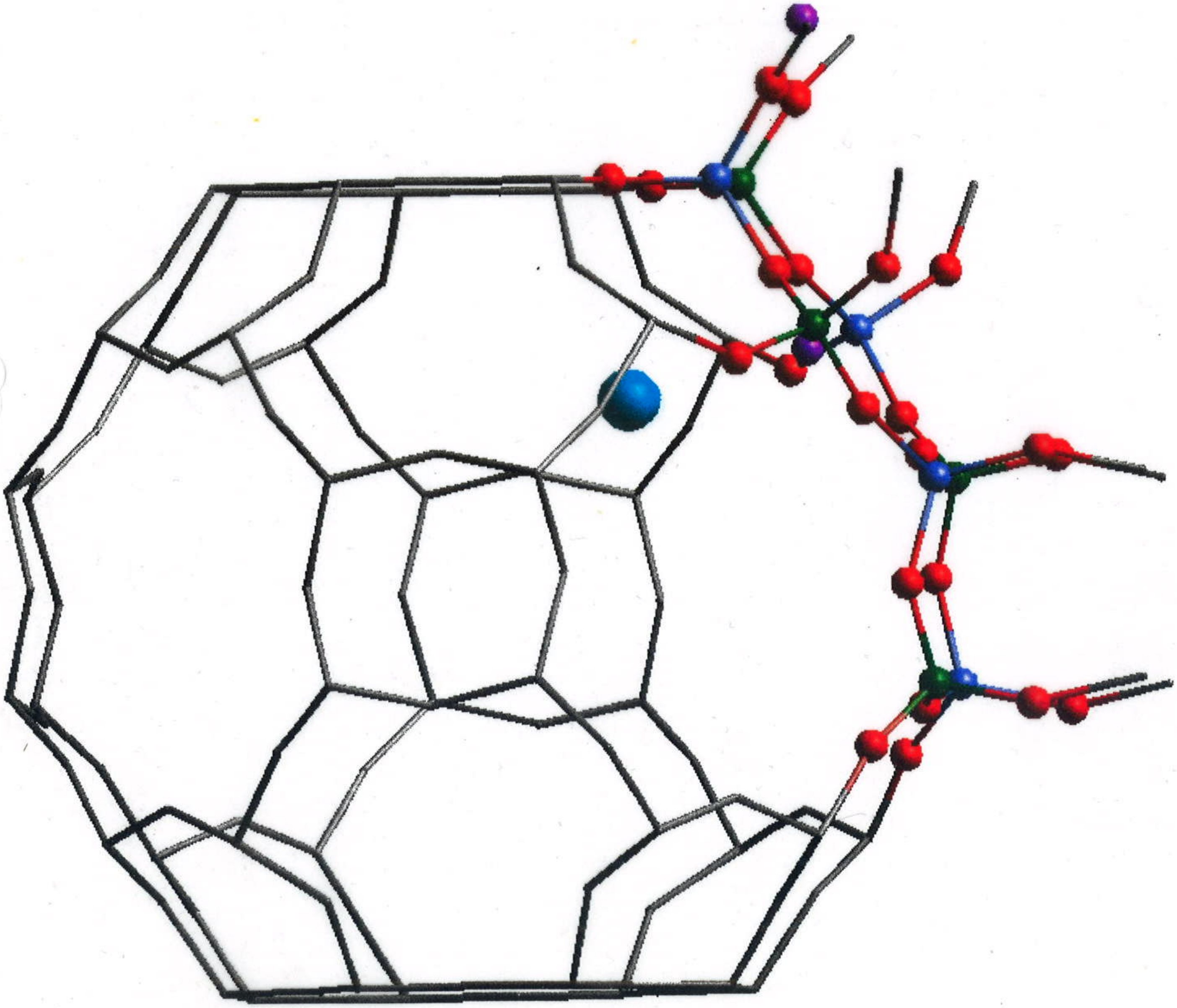


zeolite cage (Na*A*)

Portion of the Na*A* zeolite cage represented by a neutral fragment a 6-ring: $[Si_3Al_3O_6(OH)_{12}]^{3-} Na^{+}_{3}$



Portion of the Ca*A* zeolite cage represented by neutral fragment: $[Si_4Al_4O_9(OH)_{14}]^{4-}\ Ca^{2+}{}_2$



GRAND CANONICAL MONTE CARLO
Constant μ, V, T

Norman-Filinov

equal probability for 3 moves:
2[create/annihilate] + displace

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

create $\Delta E = \Delta U_{ji}(\mathbf{r}^N) + k_B T \ln\left(\dfrac{N+1}{V\rho^0}\right) - \mu$

annih. $\Delta E = \Delta U_{ji}(\mathbf{r}^N) - k_B T \ln\left(\dfrac{N}{V\rho^0}\right) + \mu$

displ. $\Delta E = \Delta U_{ji}(\mathbf{r}^N)$

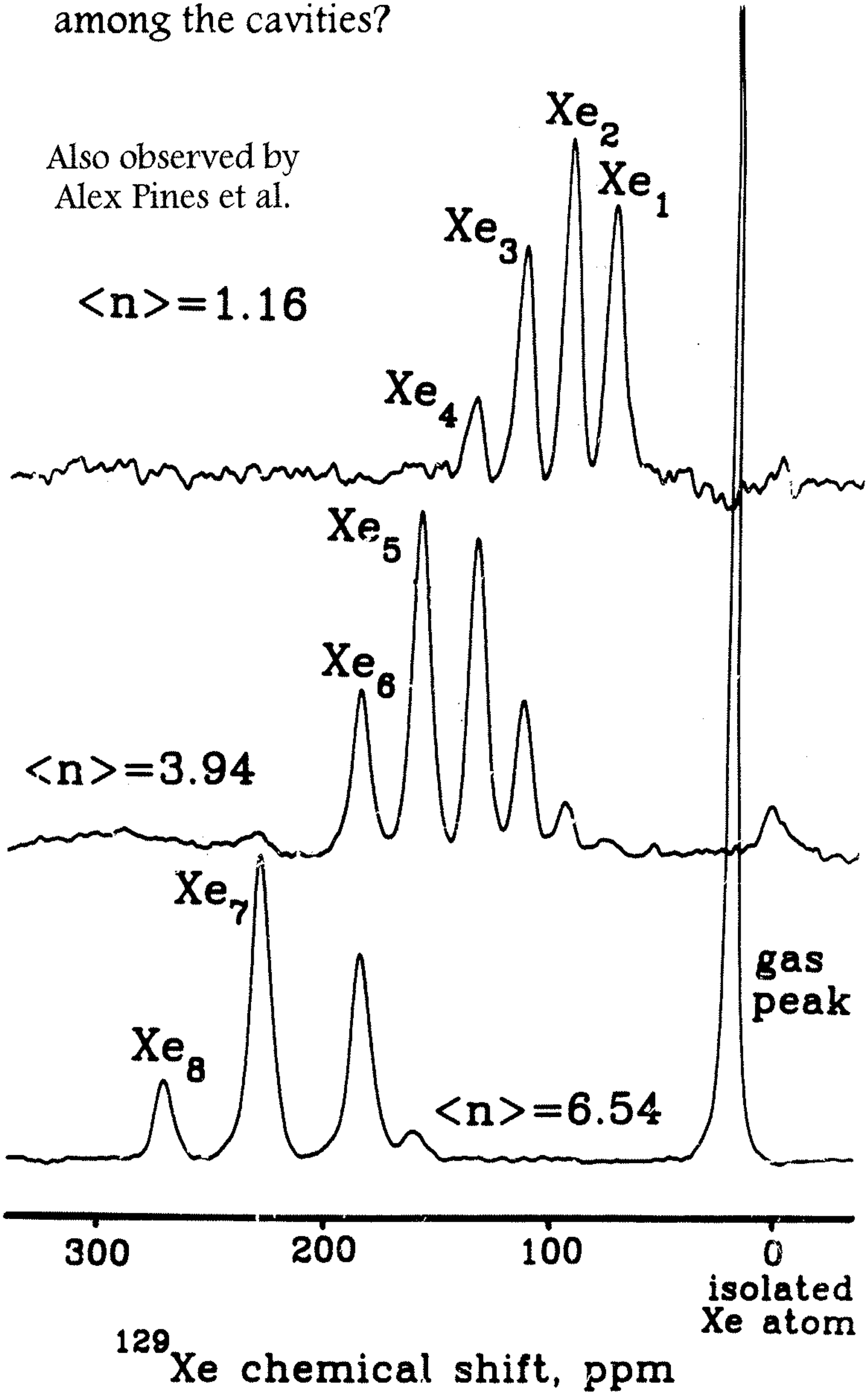
$$\Delta U_{ji}(\mathbf{r}^N) = \underset{\text{NEW}}{U_j(\mathbf{r}^N)} - \underset{\text{OLD}}{U_i(\mathbf{r}^N)}$$

ASSUME PAIRWISE ADDITIVE!

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

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

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

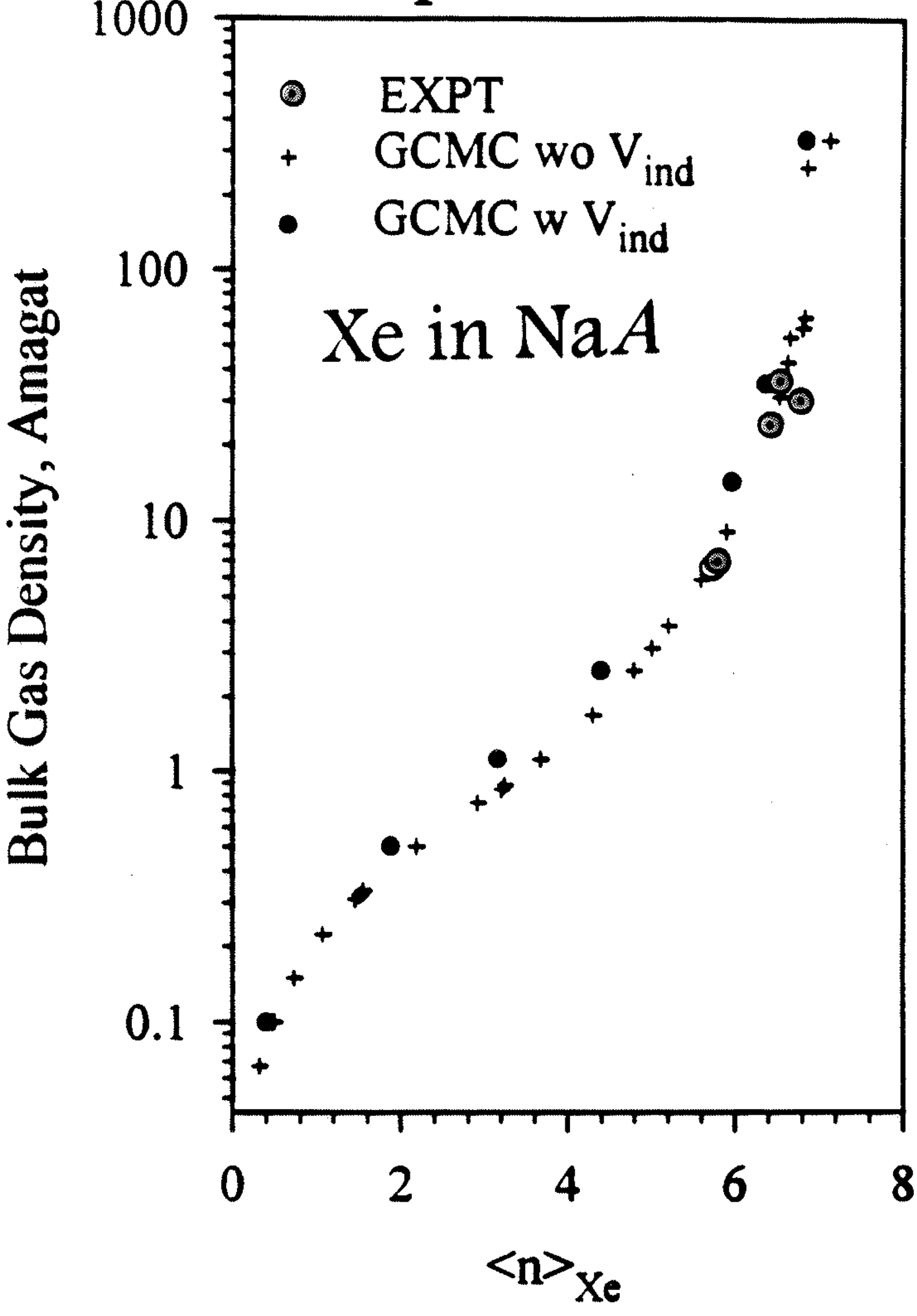


Also observed by Alex Pines et al.

Distribution

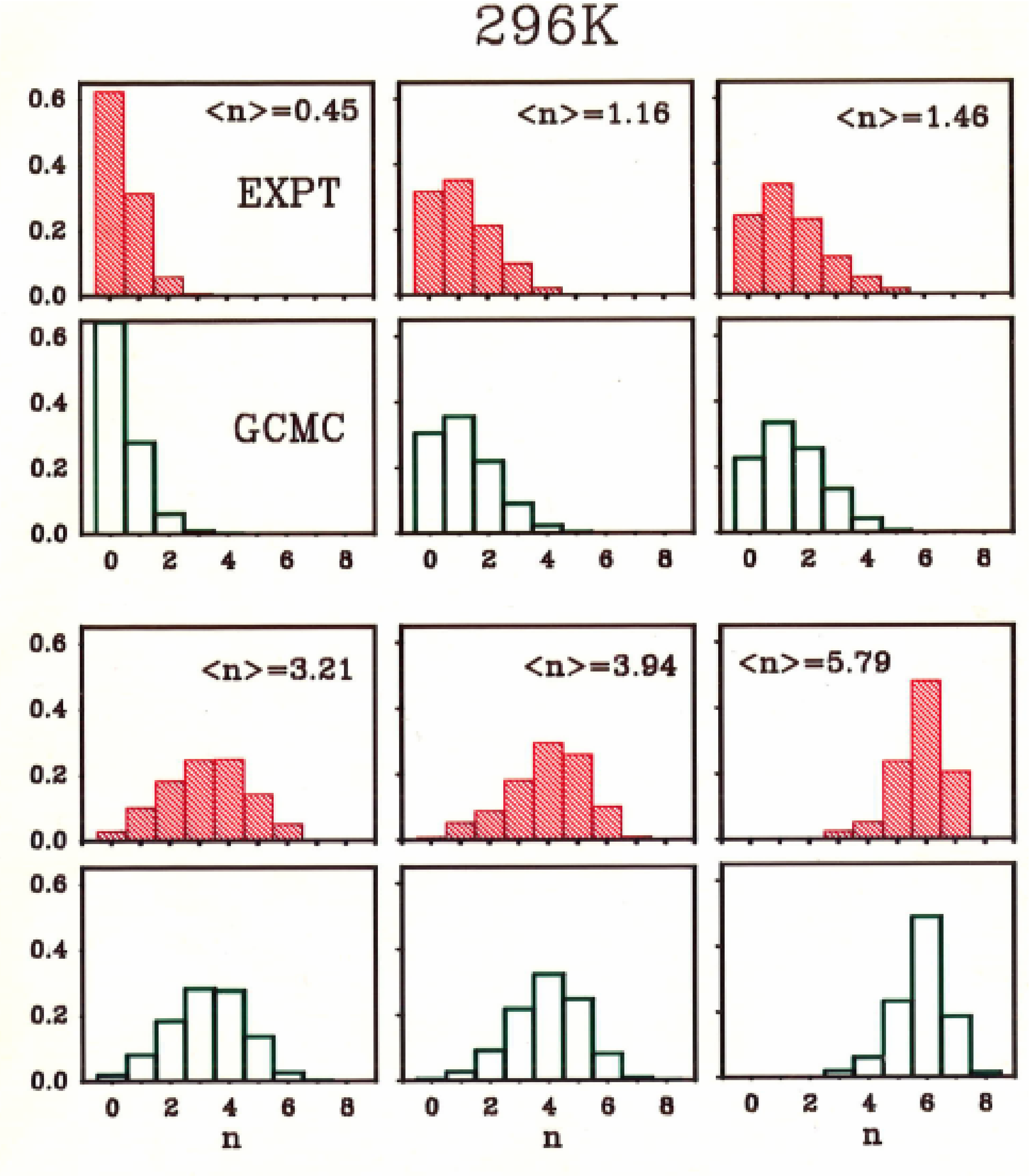
between
the bulk phase
and
the adsorbed phase

Adsorption isotherm

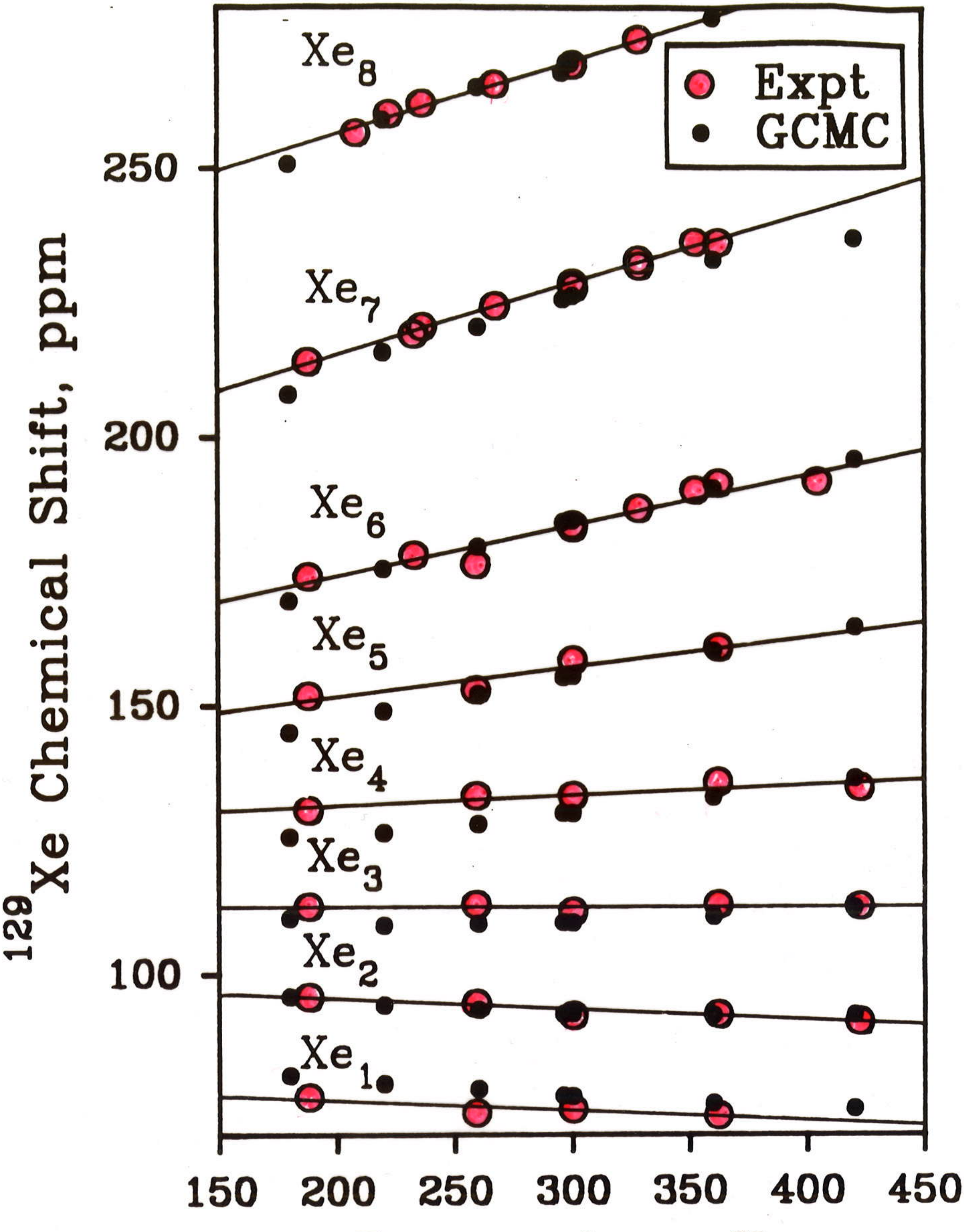


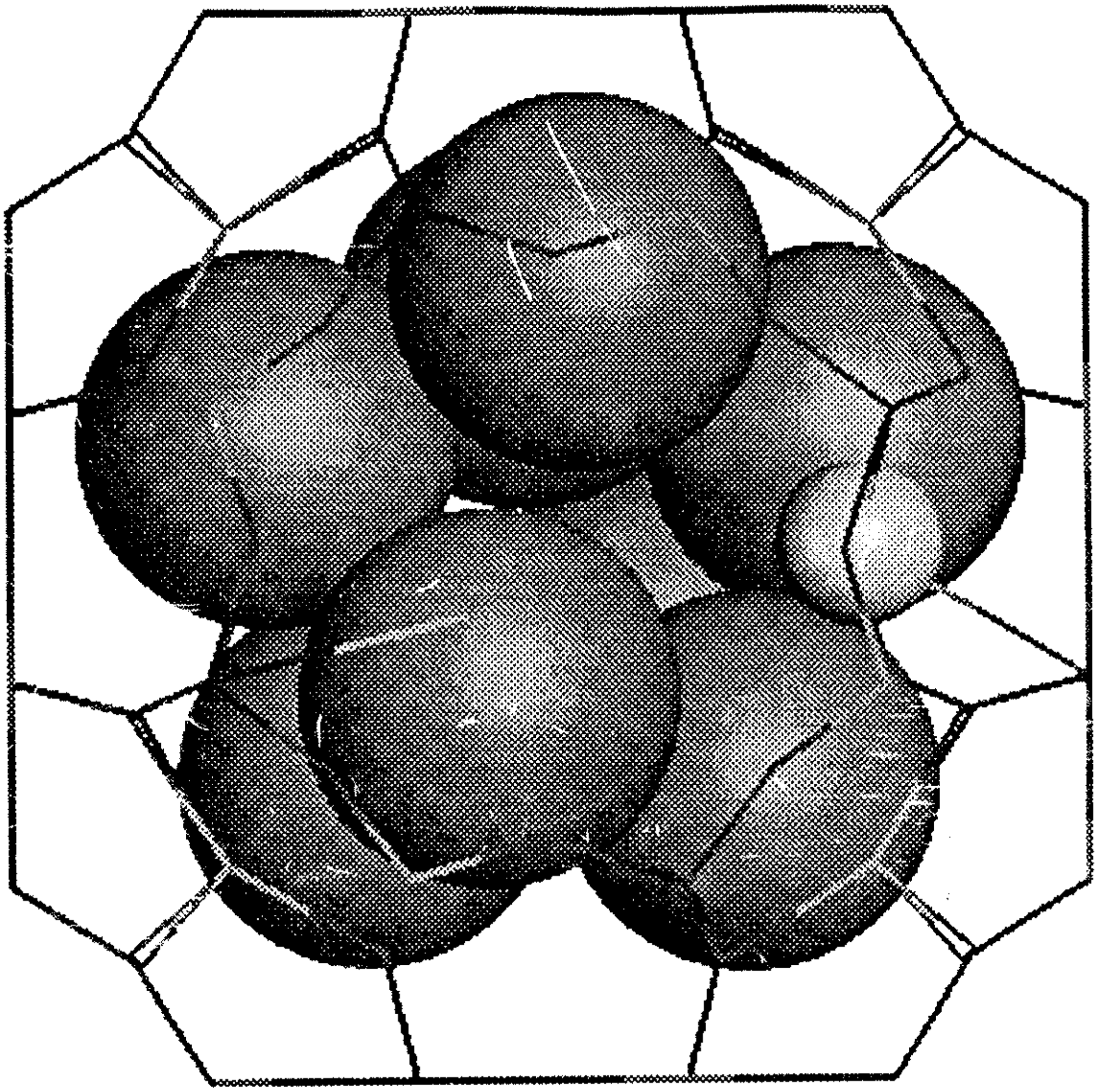
Distribution
among
cages

When the average loading is 0.5 molecules per cavity, can we establish that there are cavities with more than one molecule?



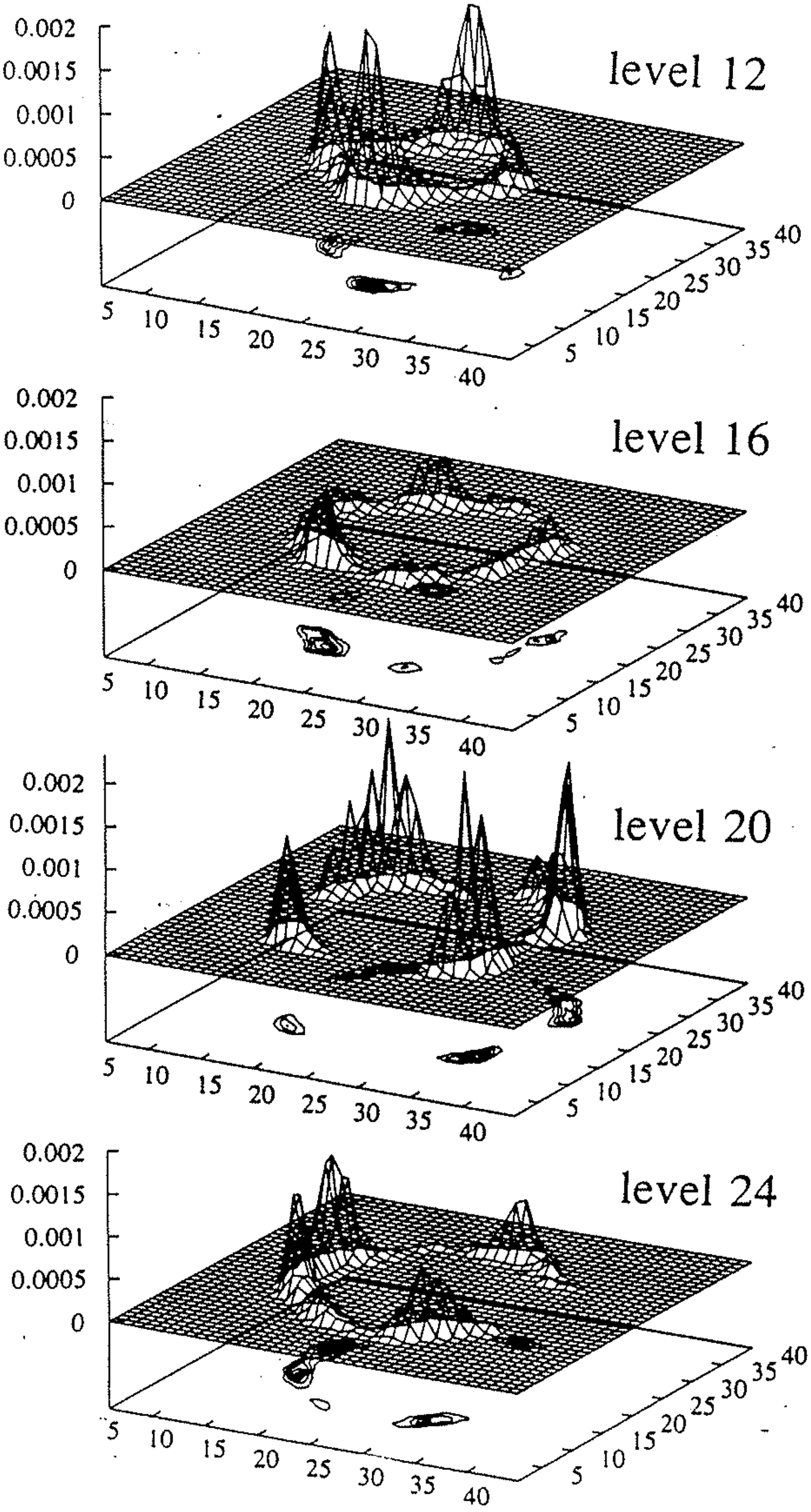
Distribution
within
the cavity


Xe8
Xe7
Xe6
Xe5
Xe4
Xe3
Xe2
Xe1
Expt
GCMC
250
200
150
100
^{129}Xe Chemical Shift, ppm
150
200
250
300
350
400
450
Temperature, K



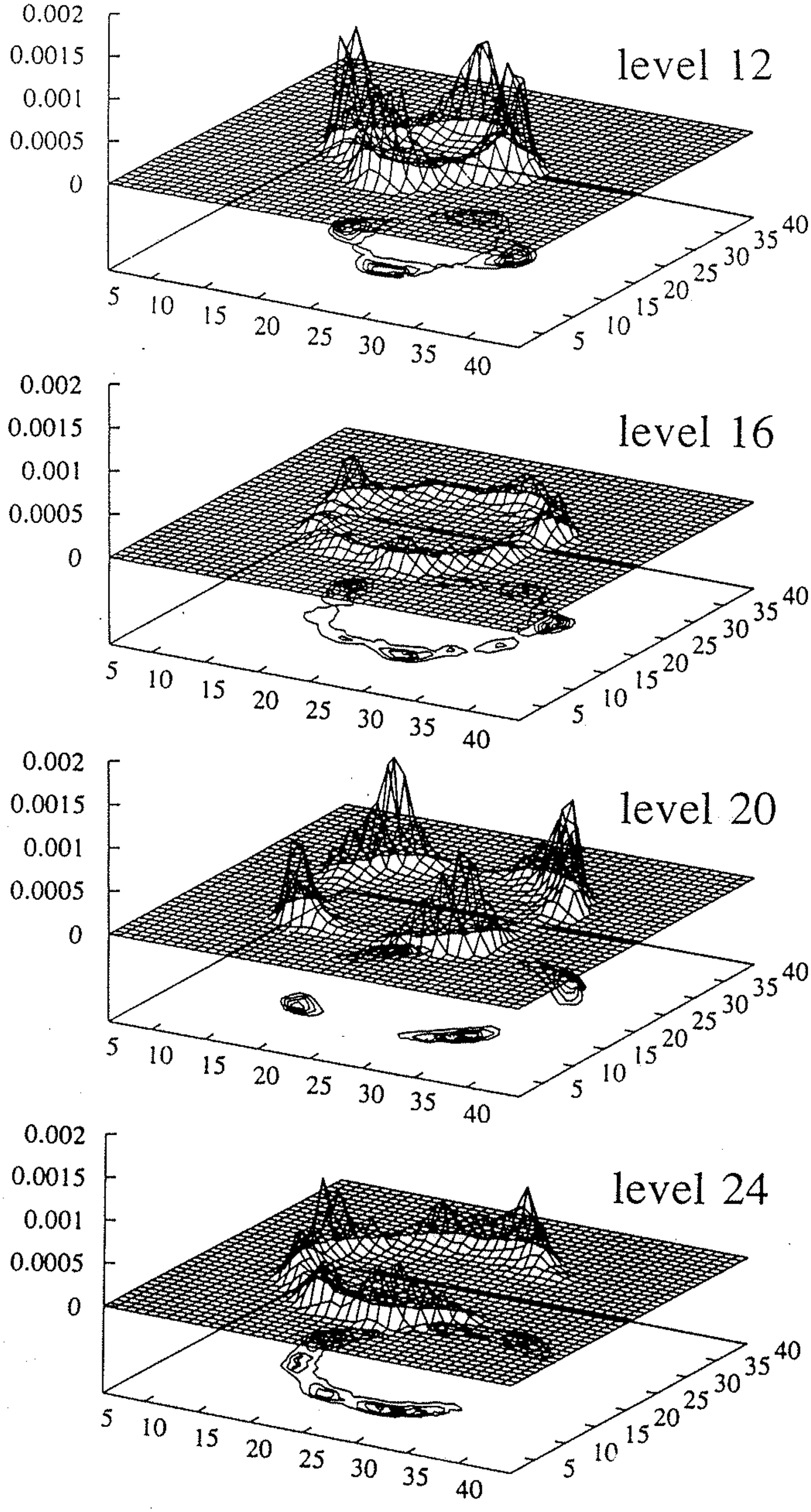
n = 8

- 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?



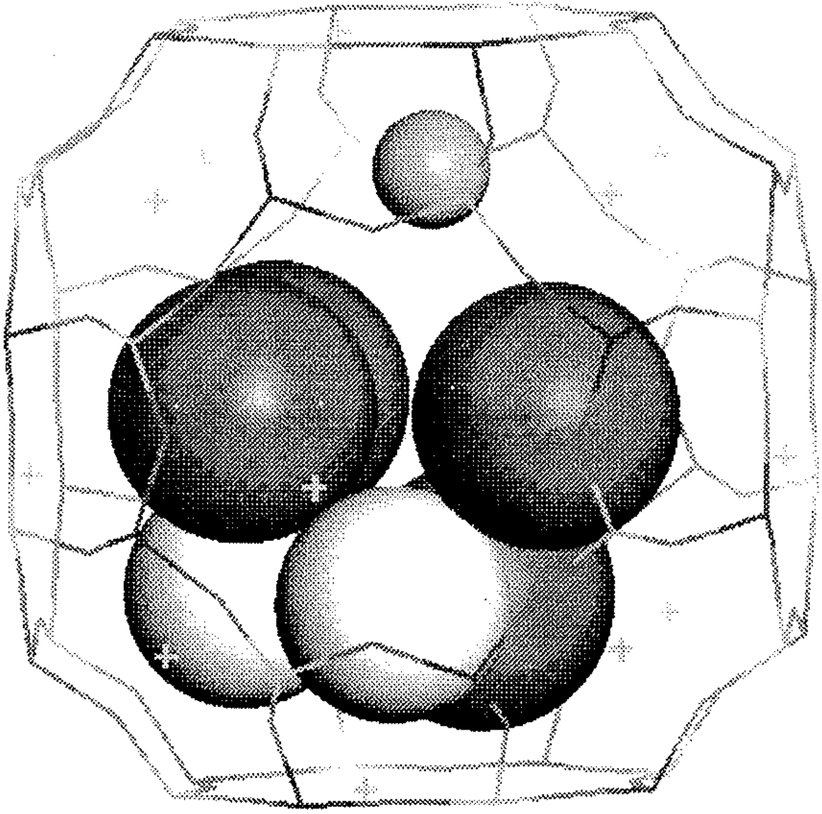
Cluster of Xe_8

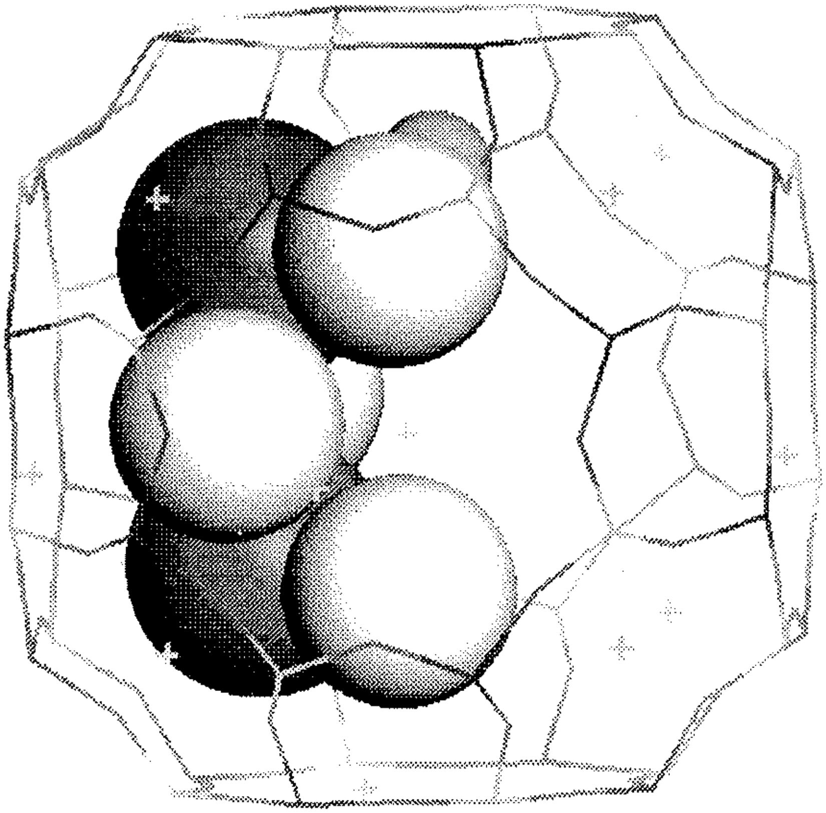
Single Xe



level 12
level 16
level 20
level 24
0.002
0.0015
0.001
0.0005
0
5
10
15
20
25
30
35
40

- When two or more types of molecules are adsorbed in a microporous solid, 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?





Distribution of two components

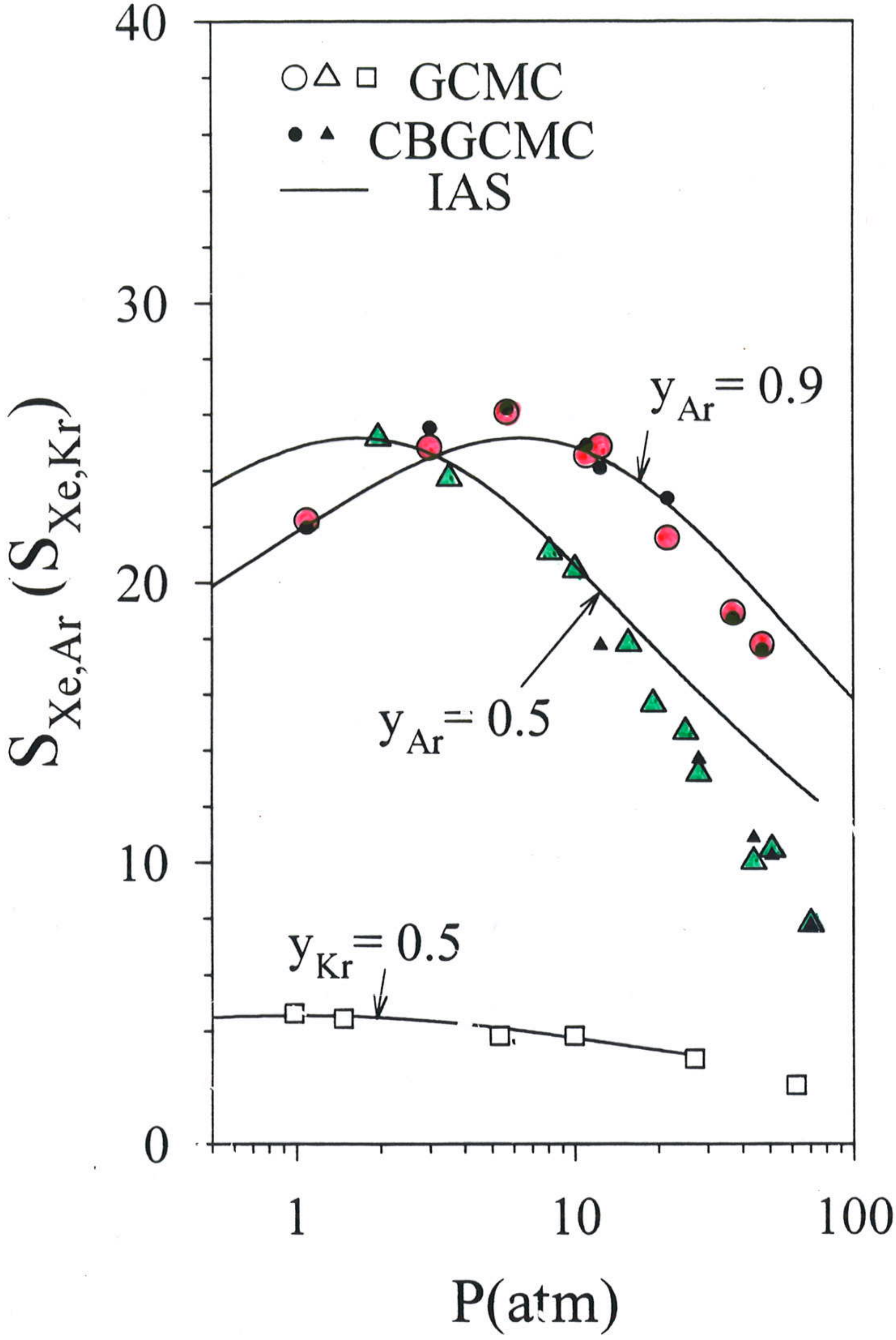
Separation factor

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

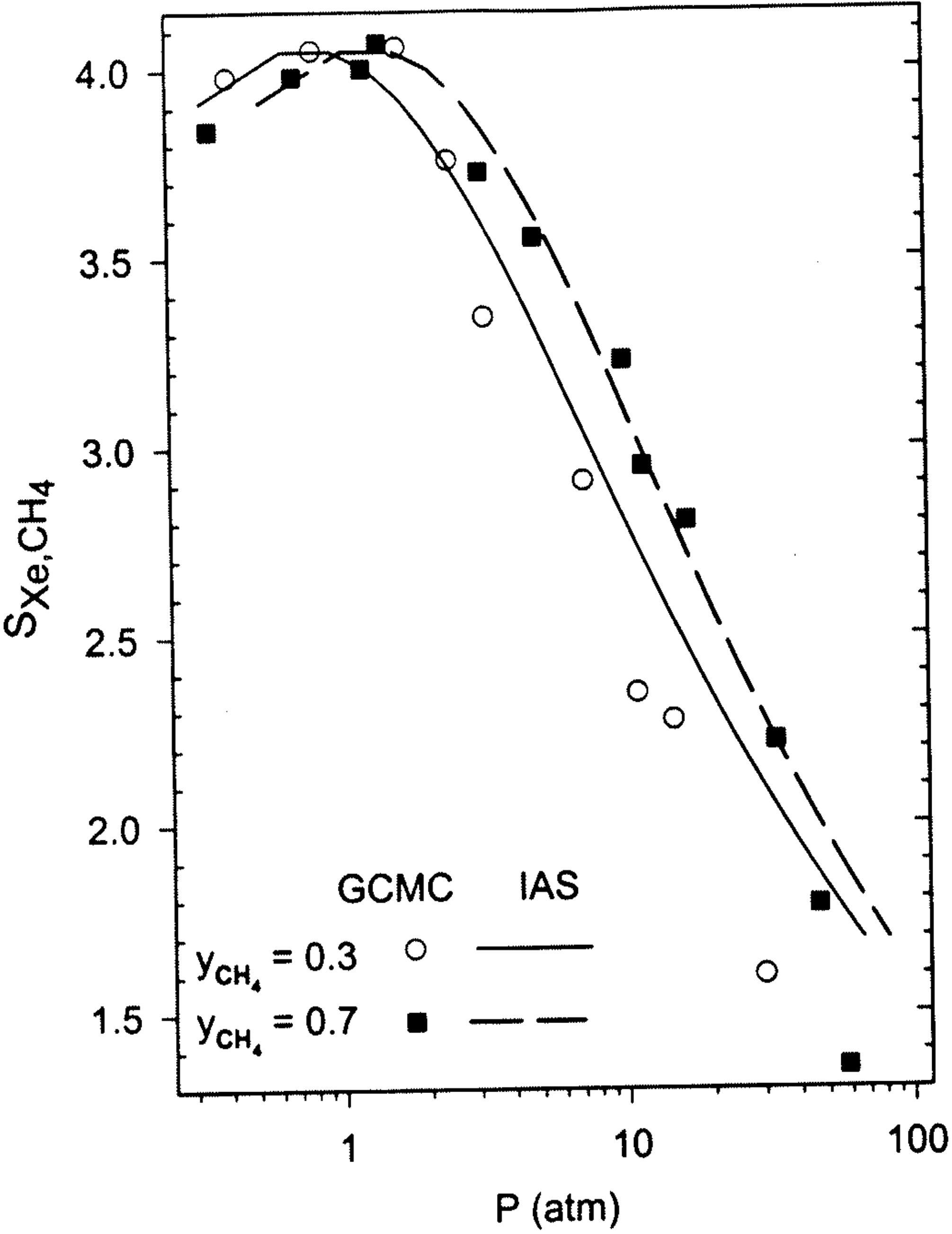
$$S_{Xe,Ar} = \frac{x_{Xe}/x_{Ar}}{y_{Xe}/y_{Ar}}$$

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*). Examples:

$S_{Xe,Ar}$ $S_{Xe,Kr}$, 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.


○△□ GCMC
●▲ CBGCMC
IAS
$y_{Ar} = 0.9$
$y_{Ar} = 0.5$
$y_{Kr} = 0.5$
$S_{Xe,Ar}$ ($S_{Xe,Kr}$)
P(atm)
0
10
20
30
40
1
10
100

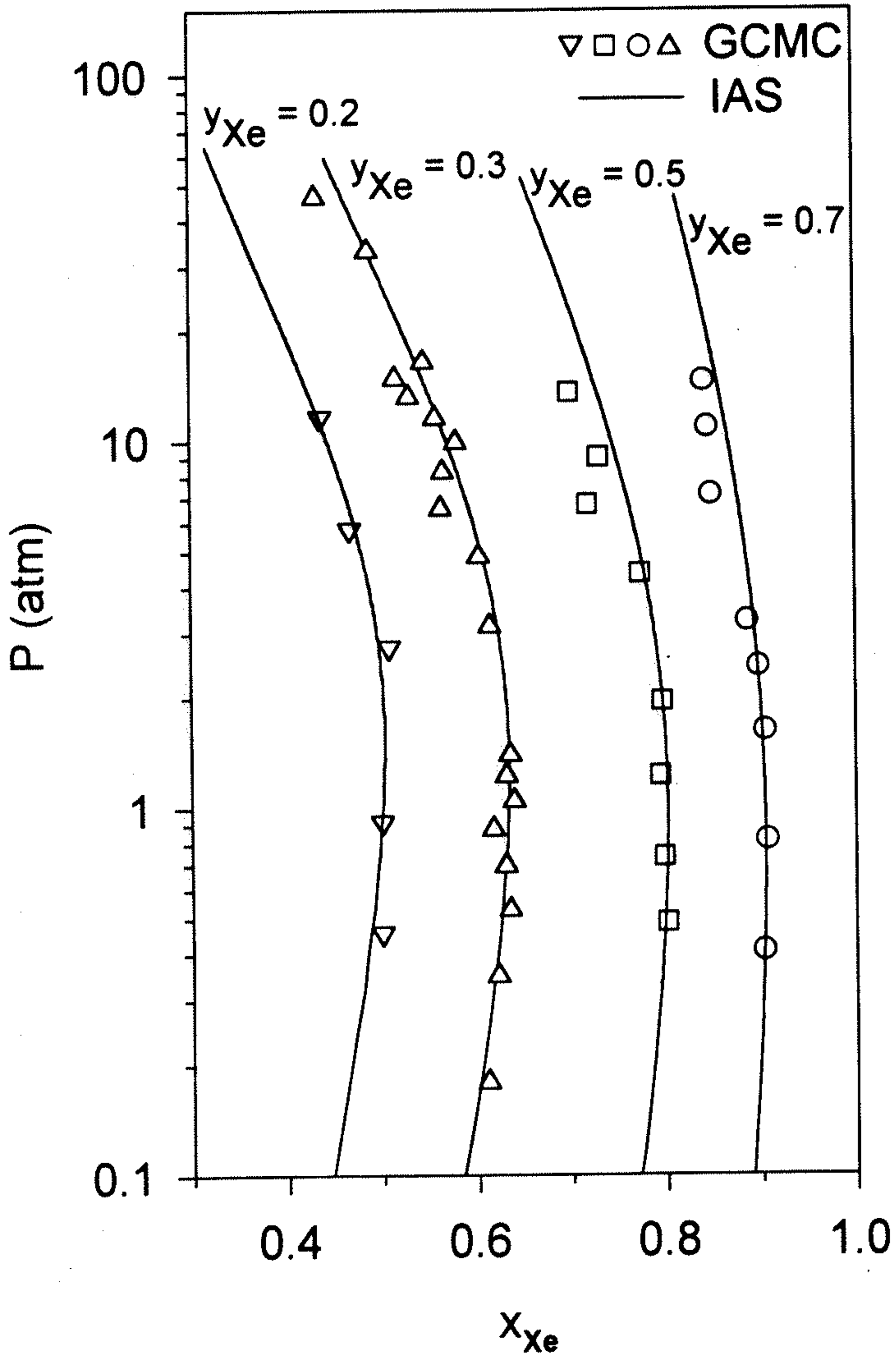
Separation Factor for Xe/CH_4 in NaA:



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

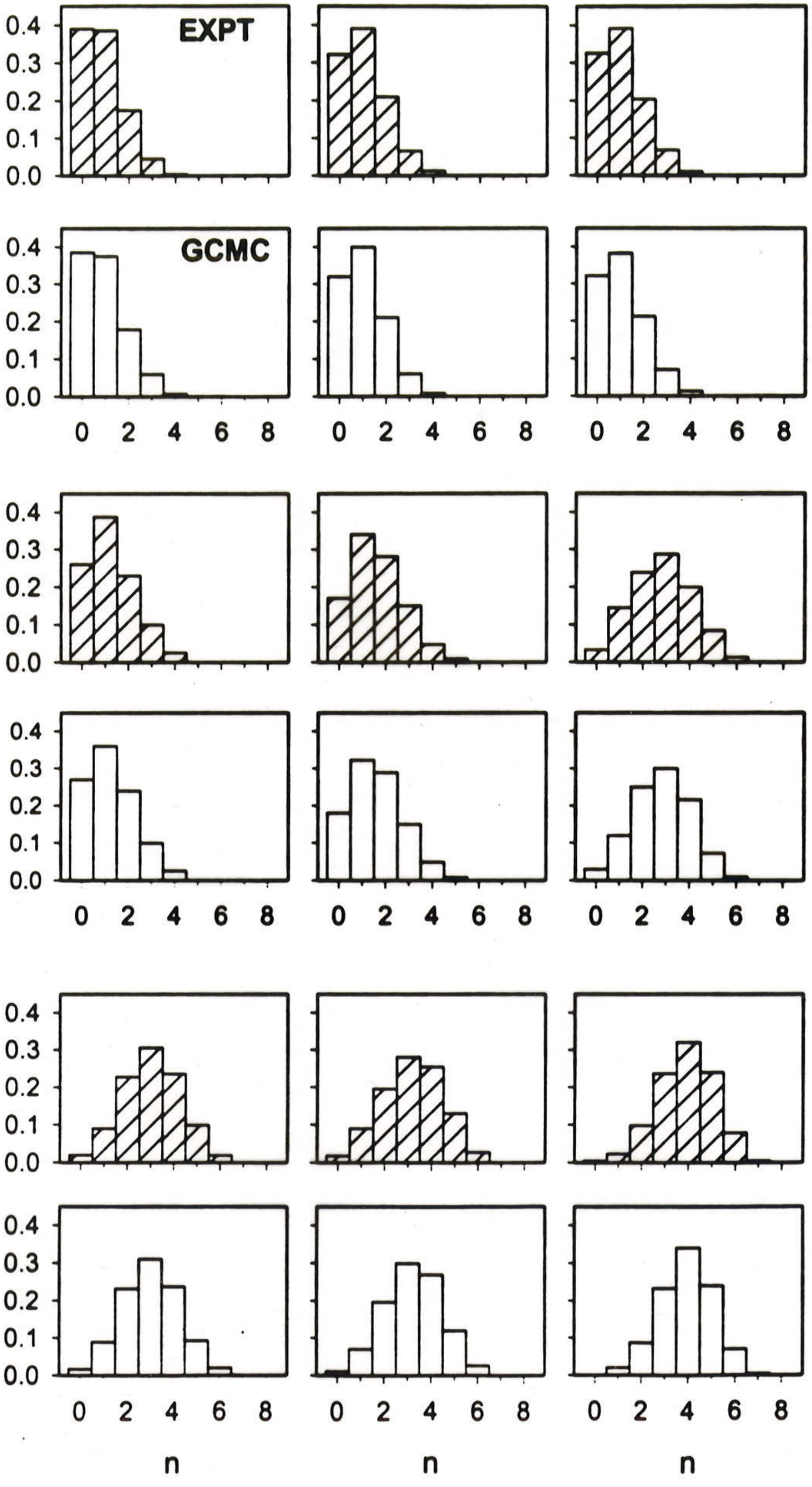
- by increasing the mole fraction of CH_4 in the bulk phase (good only for P < 1 atm).
- by increasing the total pressure (at any bulk composition).

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



- When two or more types of molecules are adsorbed in a microporous solid, how does the distribution of one type of molecule affect the distribution of another?
- How many molecules of type 2 can be found in those cavities that have exactly n molecules of type 1?

DISTRIBUTION of Xe in zeolite Na*A*



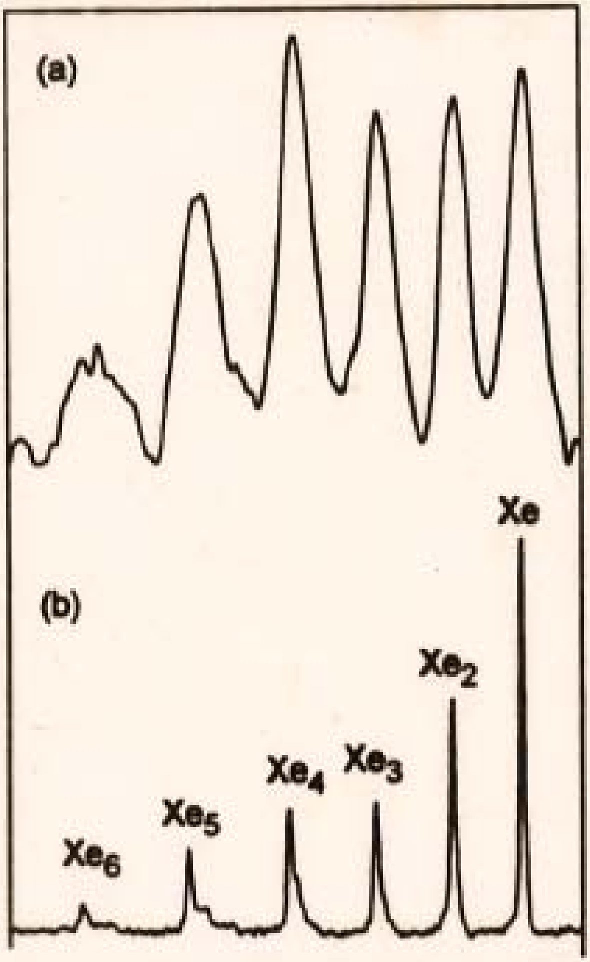
COMPARISON
OF
GCMC
SIMULATIONS
AND
EXPERIMENT
Xe-CH_4
Mixtures

These are P_n
the
fractions
of cages
containing
n Xe atoms,
from either
intensities
or GCMC

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

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

^{129}Xe MAS NMR spectra of a sample of Xe in dehydrated NaA

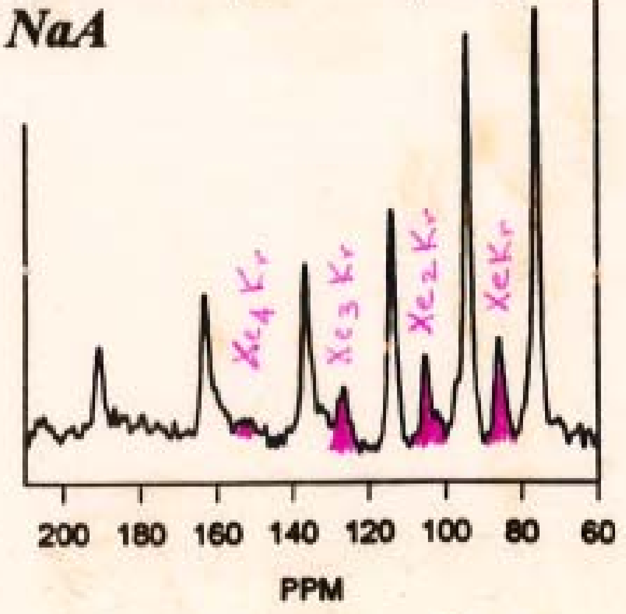


static

MAS

^{129}Xe MAS NMR spectrum of a sample of Xe and Kr in dehydrated NaA

making it possible to observe mixed clusters



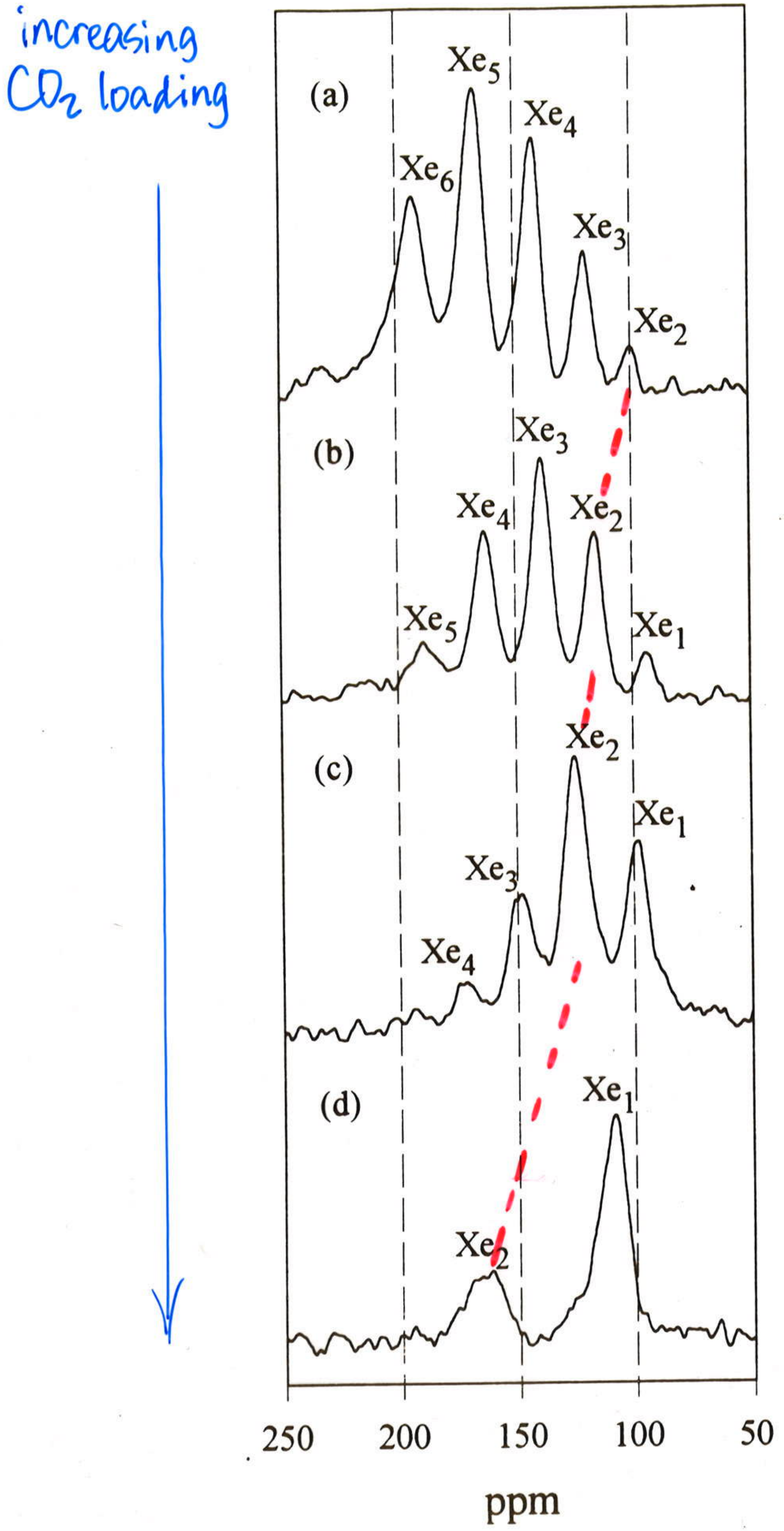
Co-adsorption of Xe and Kr in NaA

- 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.

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

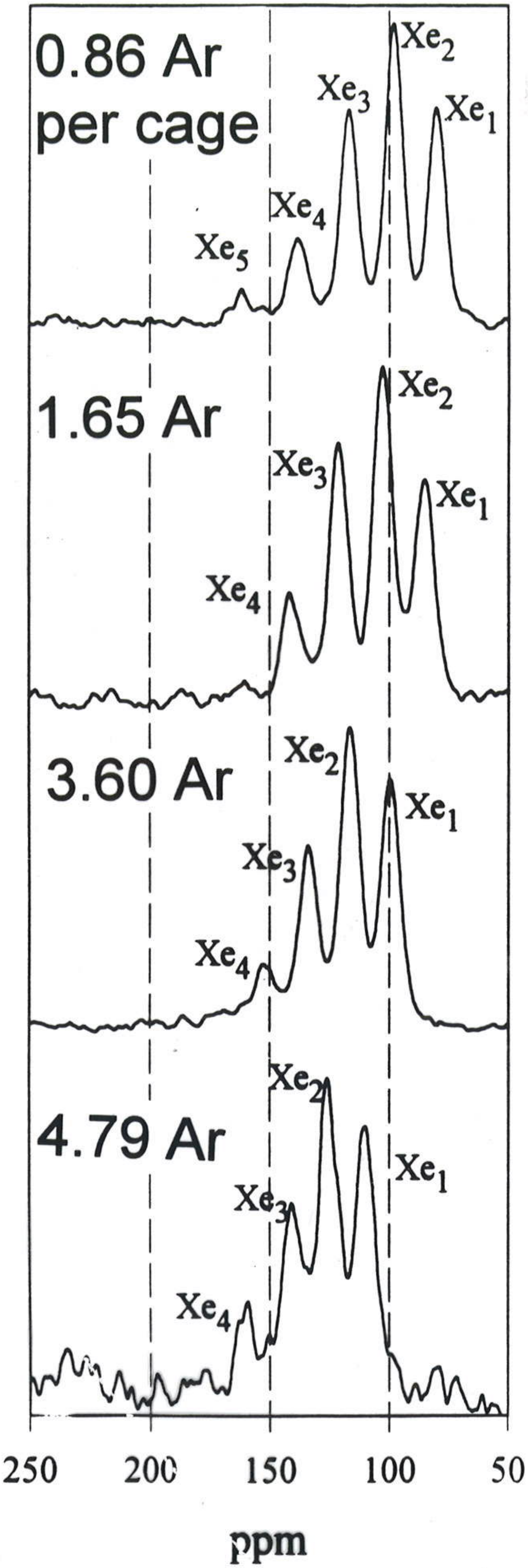
Cluster	$\delta(Xe_nKr)$		$\delta(Xe_nKr) - \delta(Xe_n)$	
	OBSD	GCMC	OBSD	GCMC
Xe_1Kr	84.7	86.6	9.9	8.9
Xe_2Kr	103.3	101.5	11.0	8.8
Xe_3Kr	124.5	121.4	12.8	11.3
Xe_4Kr	148.9	144.6	15.7	16.0
Xe_5Kr	174.7	173.3	16.3	18.7
Xe_6Kr	209.9	208.6	26.5	24.7

Xe-CO_2


increasing CO_2 loading
(a)
Xe_5
Xe_4
Xe_6
Xe_3
Xe_2
(b)
Xe_3
Xe_4
Xe_2
Xe_5
Xe_1
(c)
Xe_2
Xe_1
Xe_3
Xe_4
(d)
Xe_1
Xe_2
250
200
150
100
50
ppm

At the same temperature, the Xe_3 peak (for example) appears at the same ^{129}Xe chemical shift in samples at different loadings of pure Xe in NaA zeolite. This indicates that the Xe_3 have the same chemical shift, independent of the high or low occupancy of neighboring cavities.

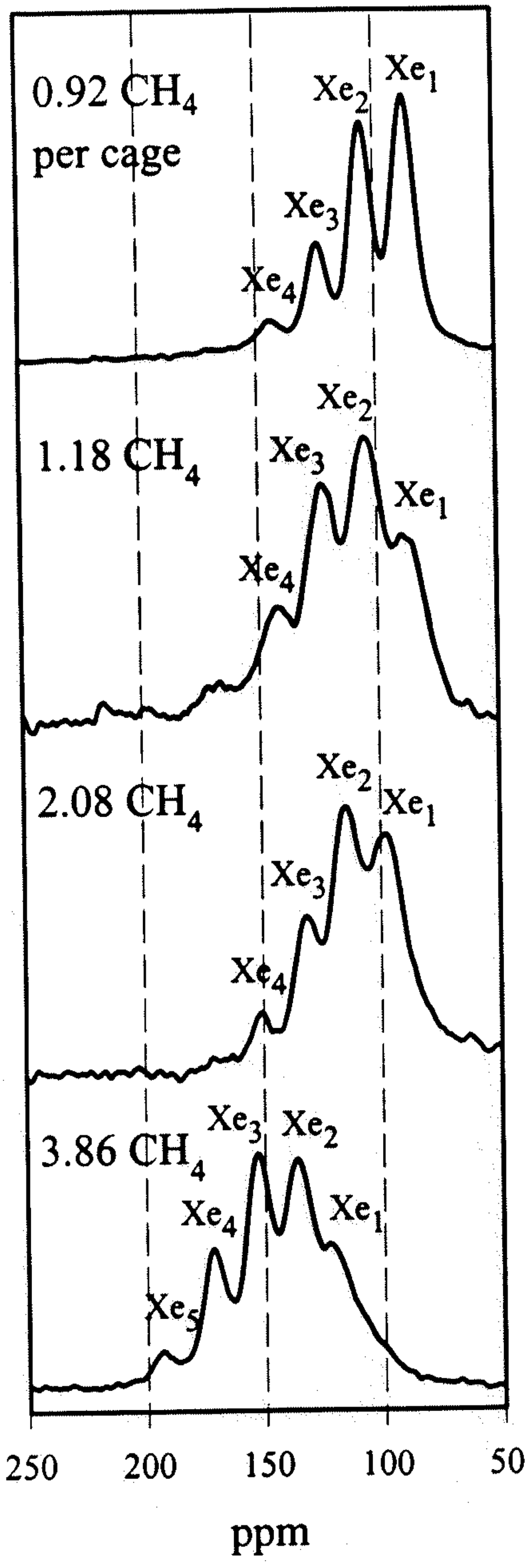
- On one hand, this is an affirmation of the local nature of the NMR shielding, thus, the individual Xe_n chemical shifts can not be used to infer information about cooperativity of distributions.
- On the other hand, Mother Nature giveth as she taketh away. The change in the Xe_3 chemical shift in the same zeolite, in the presence of other sorbates can therefore be used to infer the presence of some average number of visiting sorbate molecules in the same cage as the Xe_3.



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

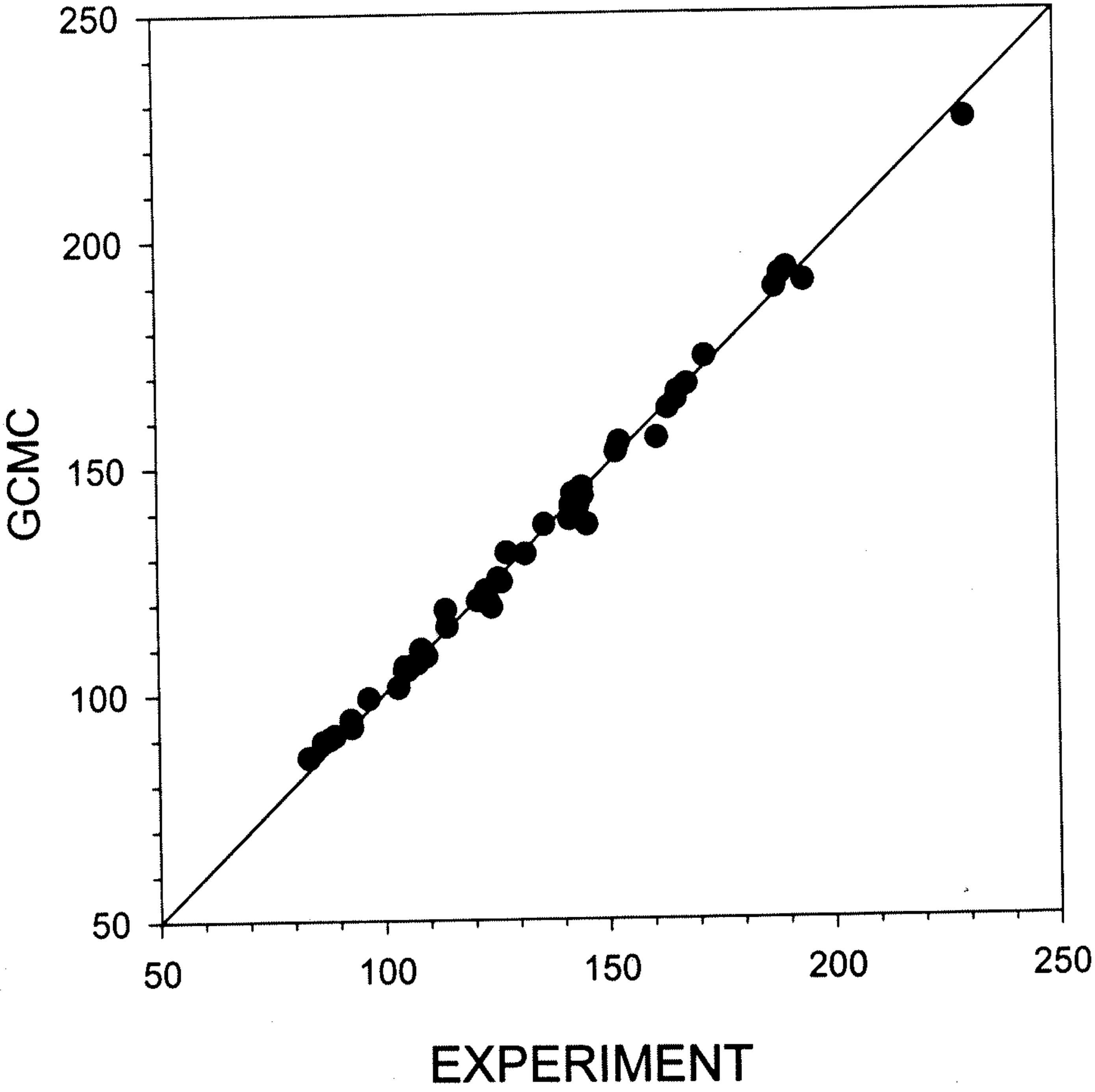
✓ The INTENSITY of the Xe_n peak is a direct measure of the fraction of cages that have exactly *n* Xe atoms.



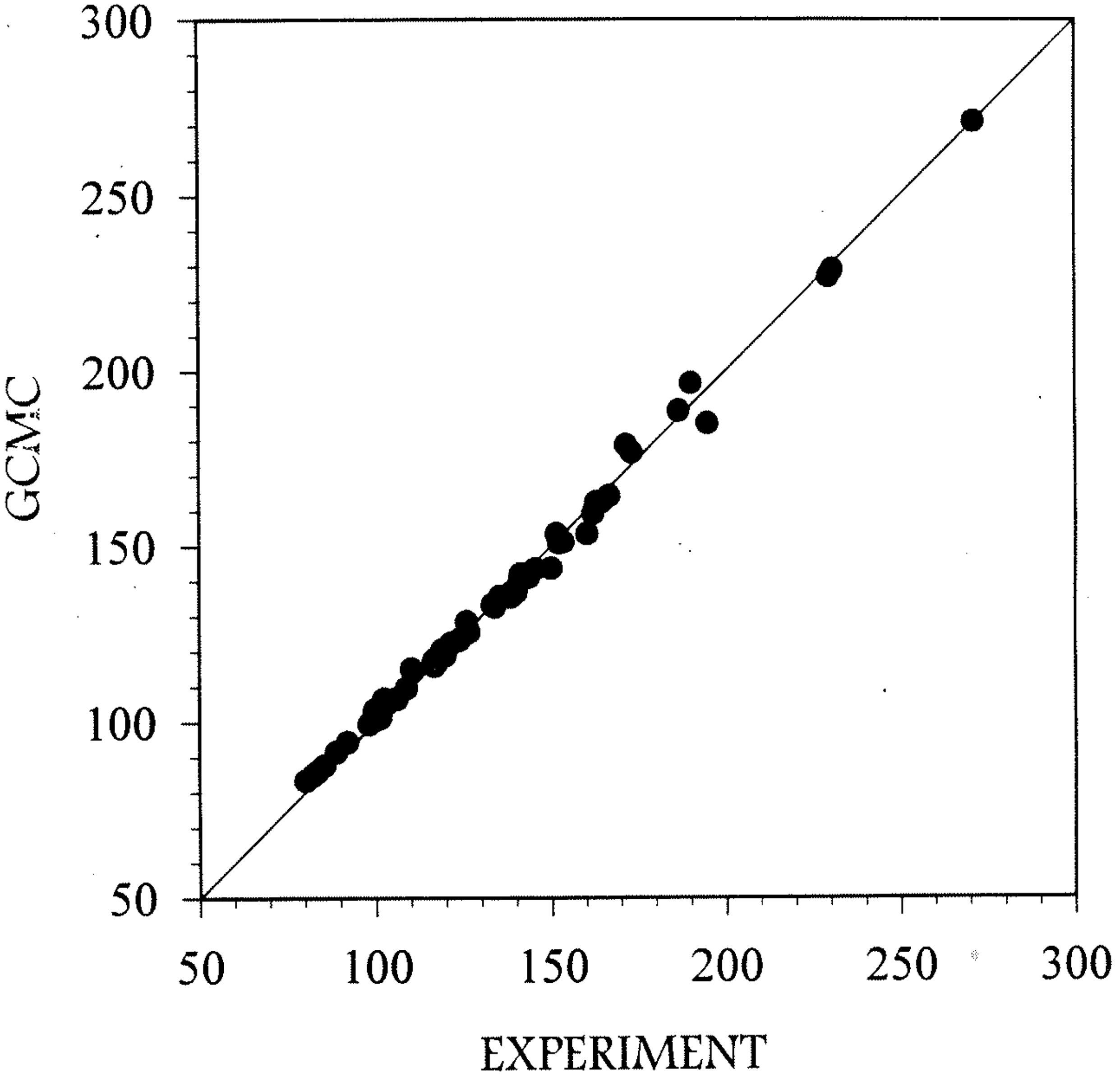
The SHIFT of a Xe_n peak is a measure of the average number of sorbate molecules in the same cage with Xe_n

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

^{129}Xe CHEMICAL SHIFT of Xe$_n$ in
Xe-CH$_4$ MIXTURES in ZEOLITE Na*A*
ppm from isolated Xe atom



^{129}Xe CHEMICAL SHIFT of Xe_n in Xe-Ar MIXTURES in ZEOLITE NaA



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.
- 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 Xe and 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.

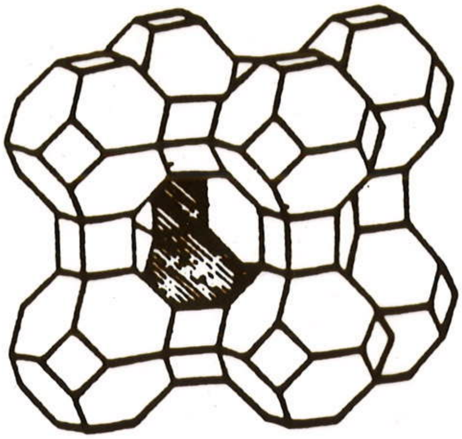
We have details for testing GCMC simulations

- The assumption of pairwise-additive shielding contributions permits computation of average shieldings in a Grand Canonical Monte Carlo 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 Xe and CH_4) in competitive adsorption.
- The equilibrium distribution of the components of a binary mixture are well reproduced by the GCMC simulations.

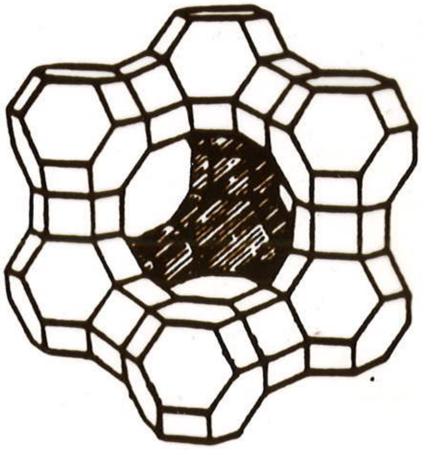
Mass Transport in Zeolites at the Molecular Level

Xe under fast exchange in open zeolite networks

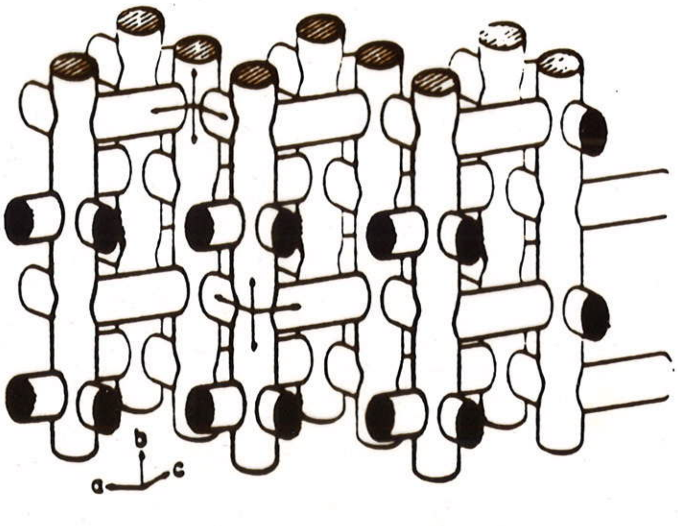
- Ca*A*



- faujasites Na*X* and Na *Y*



- silicalite

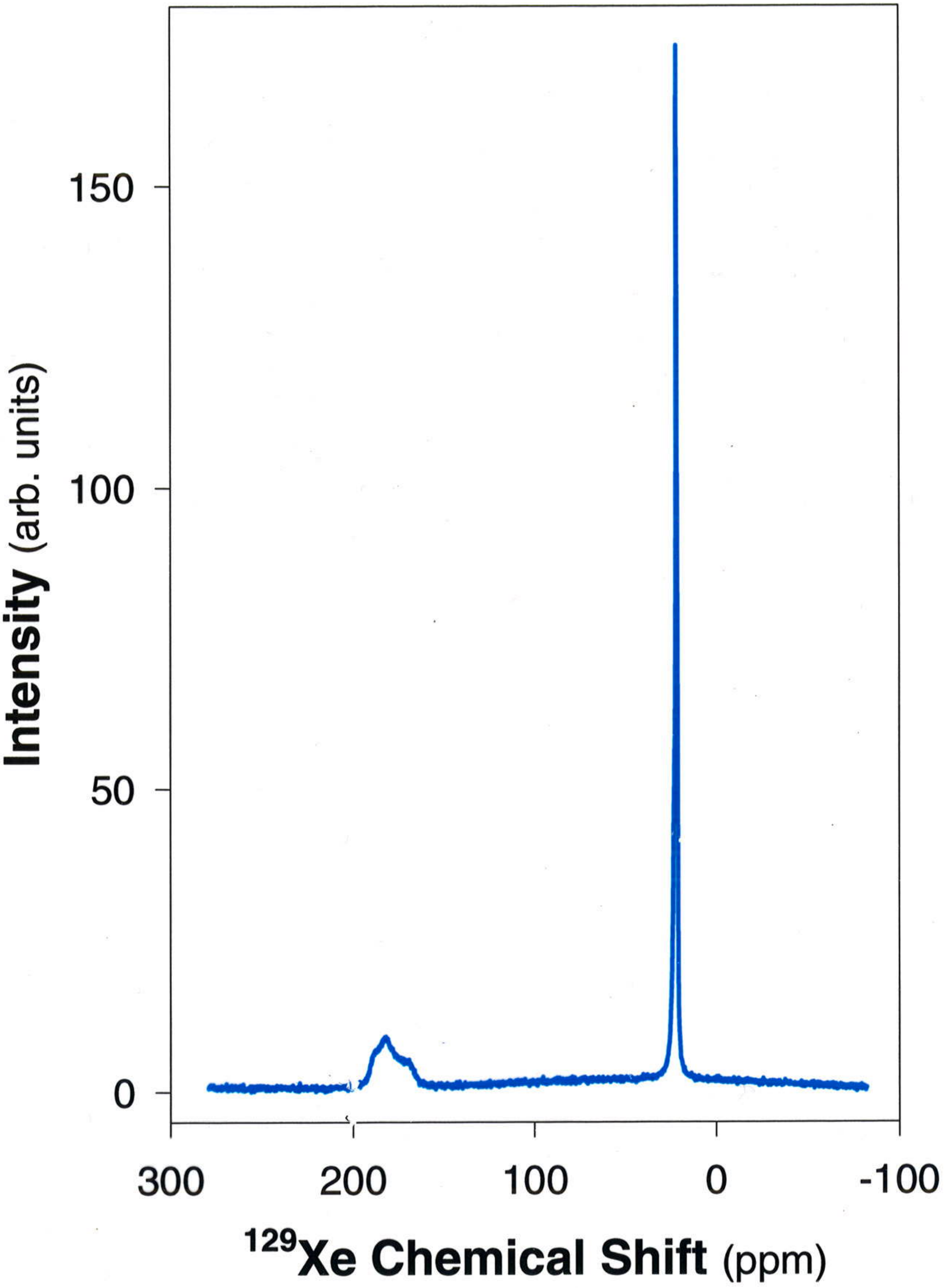


How fast is the exchange between Xe atoms inside the crystallite and Xe atoms outside the crystallite?

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

Now measure the rate constants for the processes:

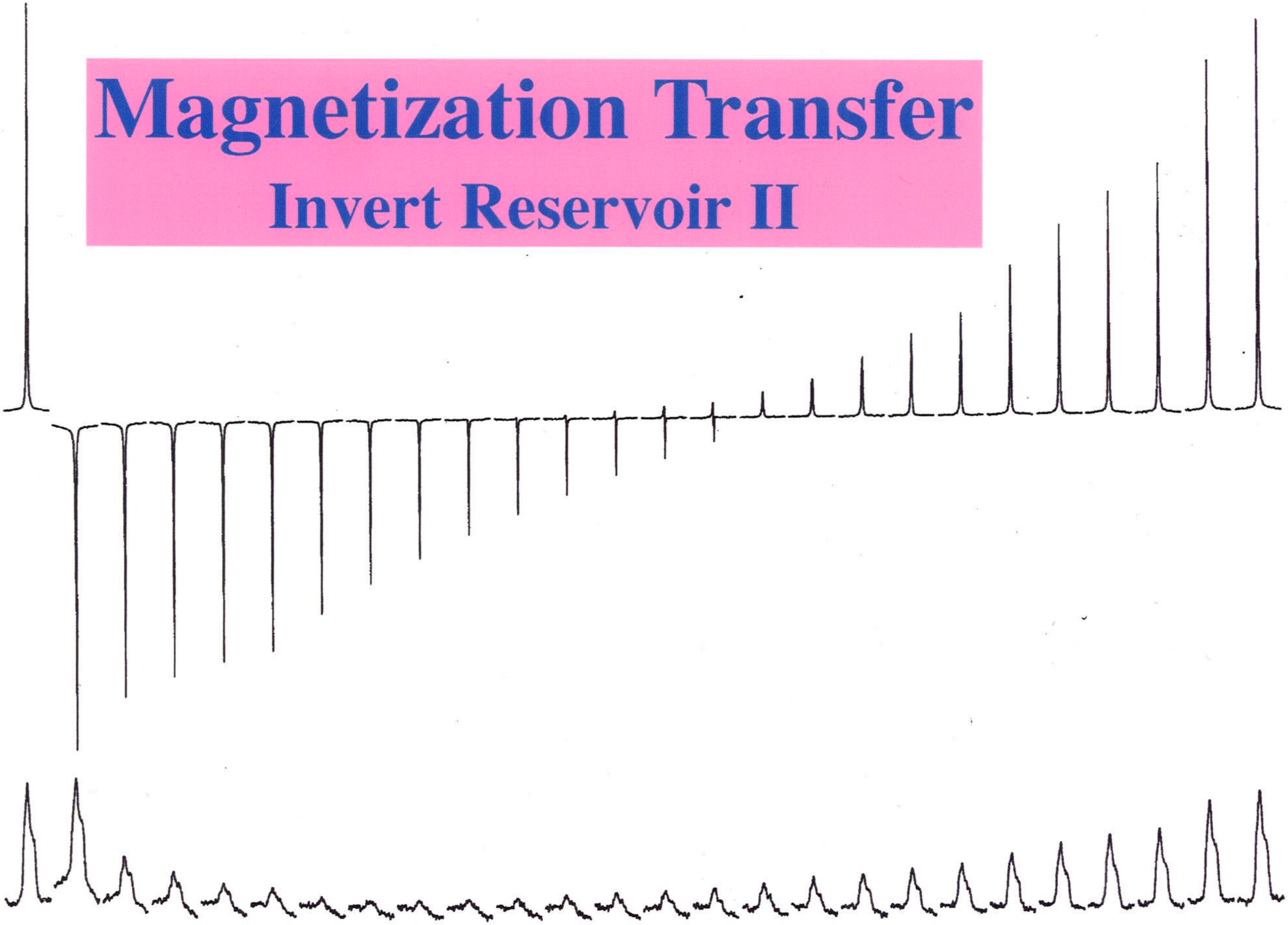
$$\text{Xe(adsorbed)} \rightarrow \text{Xe(bulk)}$$
$$\text{Xe(adsorbed)} \leftarrow \text{Xe(bulk)}$$



150
100
50
0
Intensity (arb. units)
300
200
100
0
-100
^{129}Xe Chemical Shift (ppm)

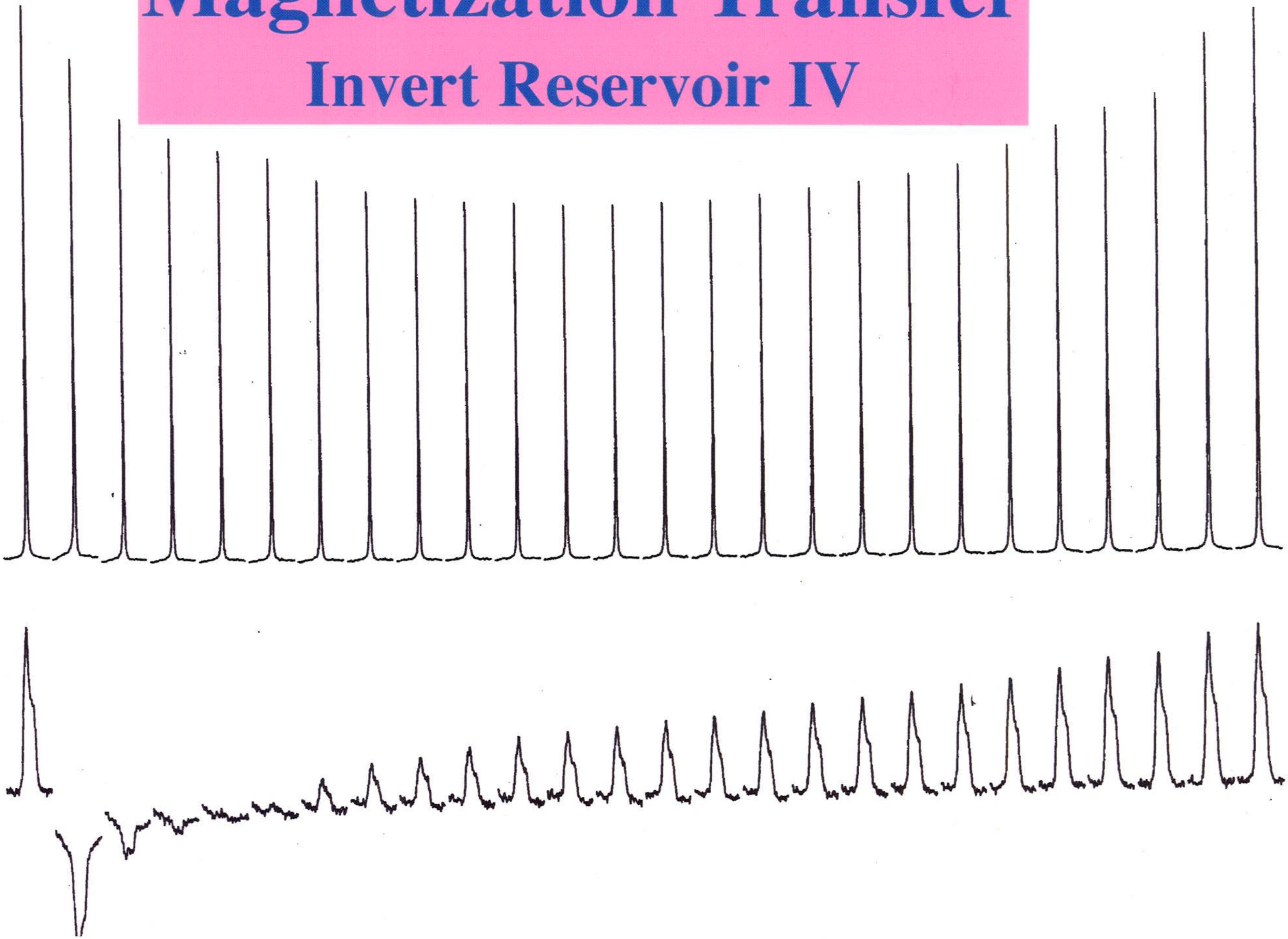
Magnetization Transfer

Invert Reservoir II

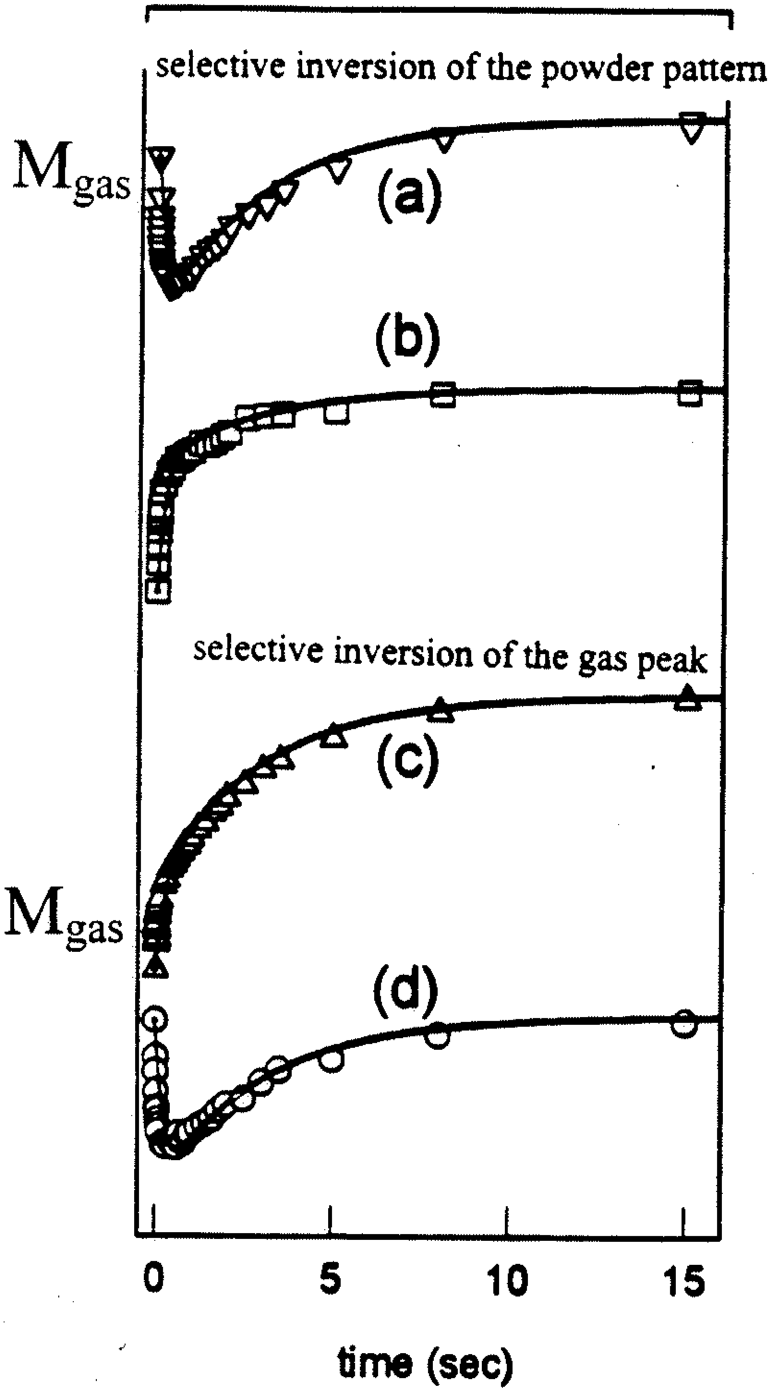


Magnetization Transfer

Invert Reservoir IV



Magnetization transfer
Xe in large crystals of silicalite



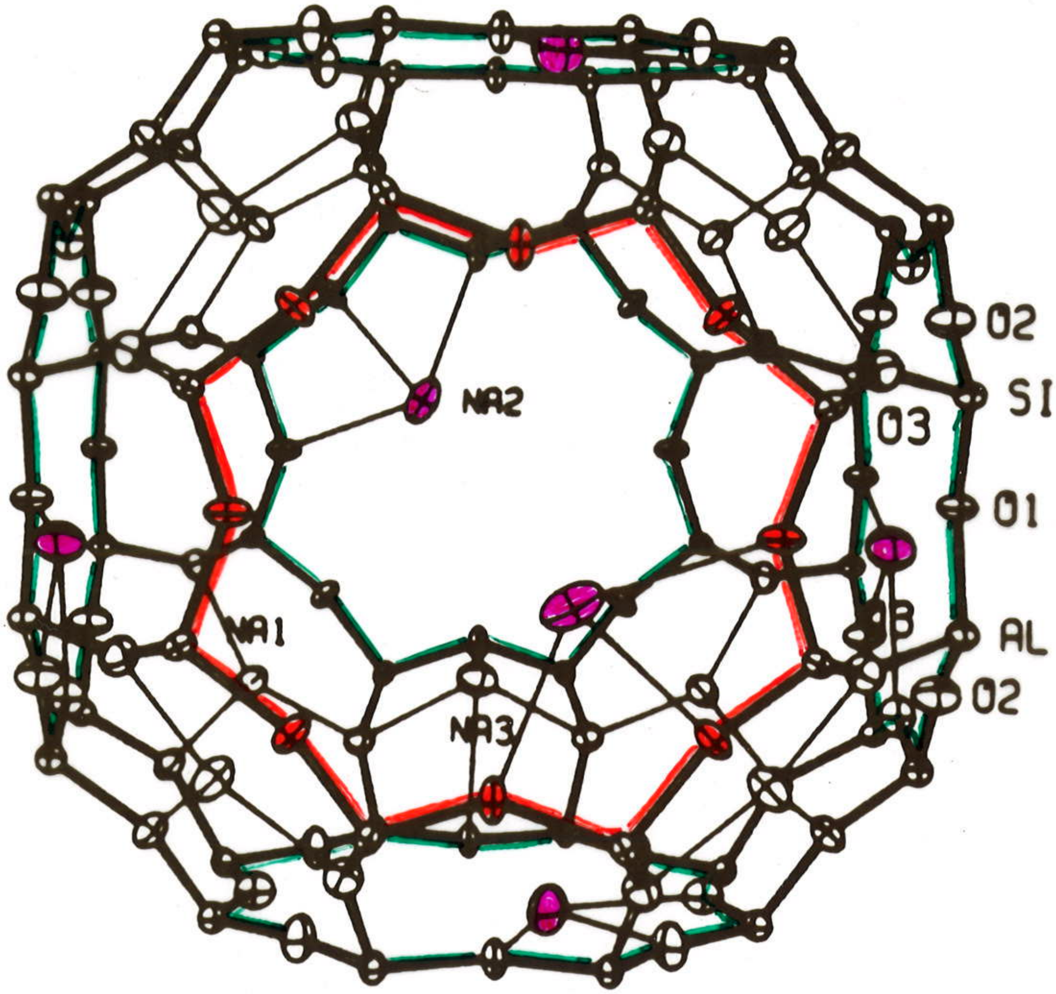
$k=3.0\ s^{-1}\rightarrow$
adsorbed ↔ gas
$\leftarrow k=1.39\ s^{-1}$

The rate constants for the exchange processes at 300 K in large crystals of silicalite at full loading of Xe:

$$\mathrm{Xe(adsorbed)} \xrightarrow{k = 3.0\ \mathrm{s}^{-1}} \mathrm{Xe(bulk)}$$

$$\mathrm{Xe(adsorbed)} \xleftarrow[k = 1.39\ \mathrm{s}^{-1}]{} \mathrm{Xe(bulk)}$$

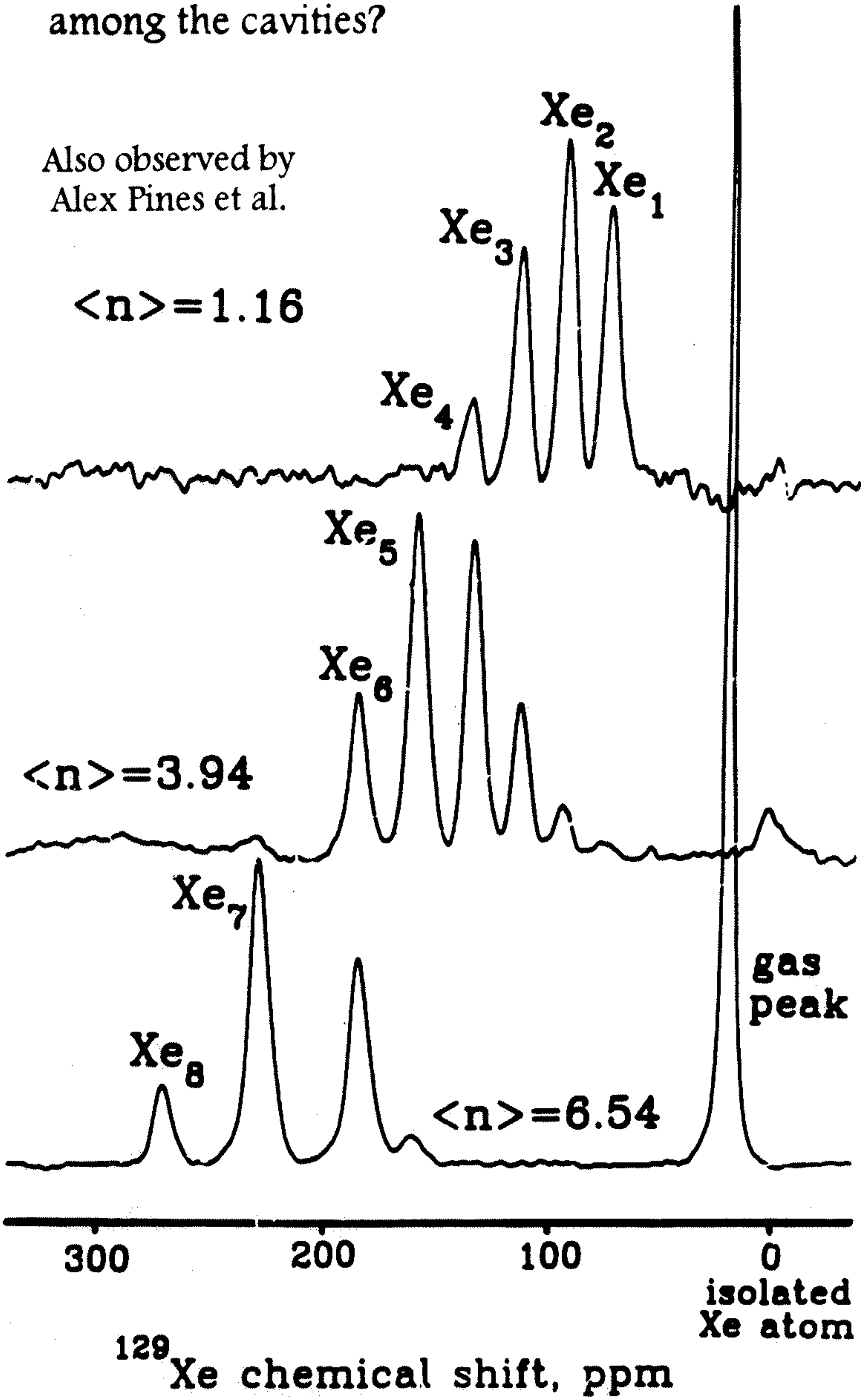
- How often does a molecule migrate from one cavity to another? Can we follow this migration as a function of time?
- Does the rate of migration depend on how many other molecules are in the same cavity where it is leaving from? on how many molecules are in the cavity it is jumping to?



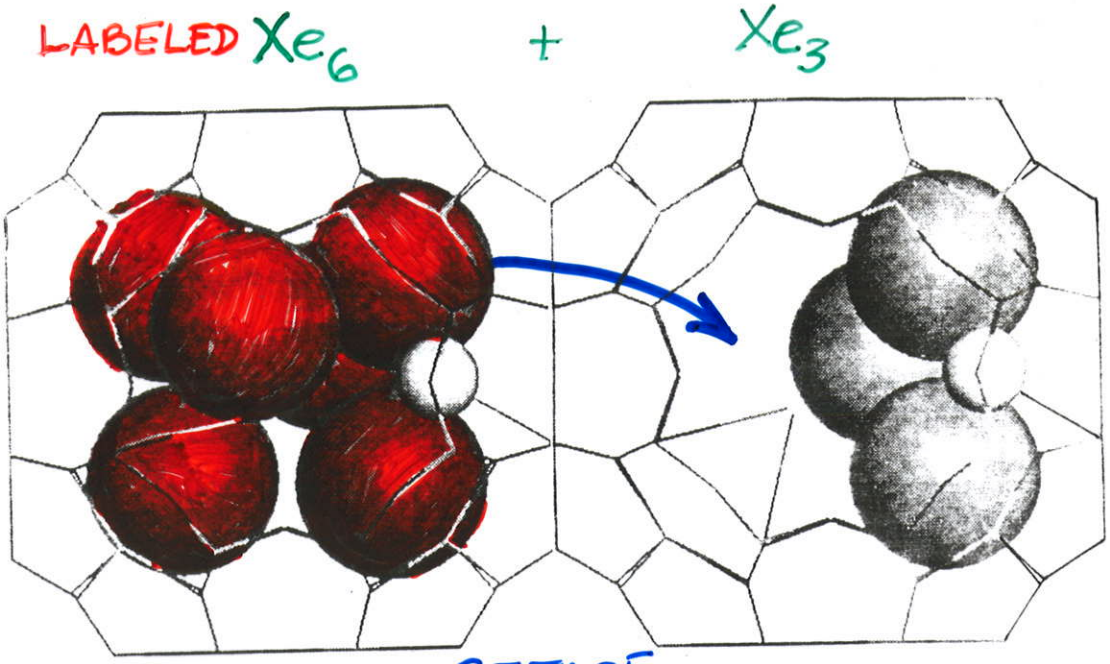
dehydrated zeolite Na-A.

J. J. Pluth & J.V. Smith
J. Am. Chem. Soc. 102,
4104(1980)

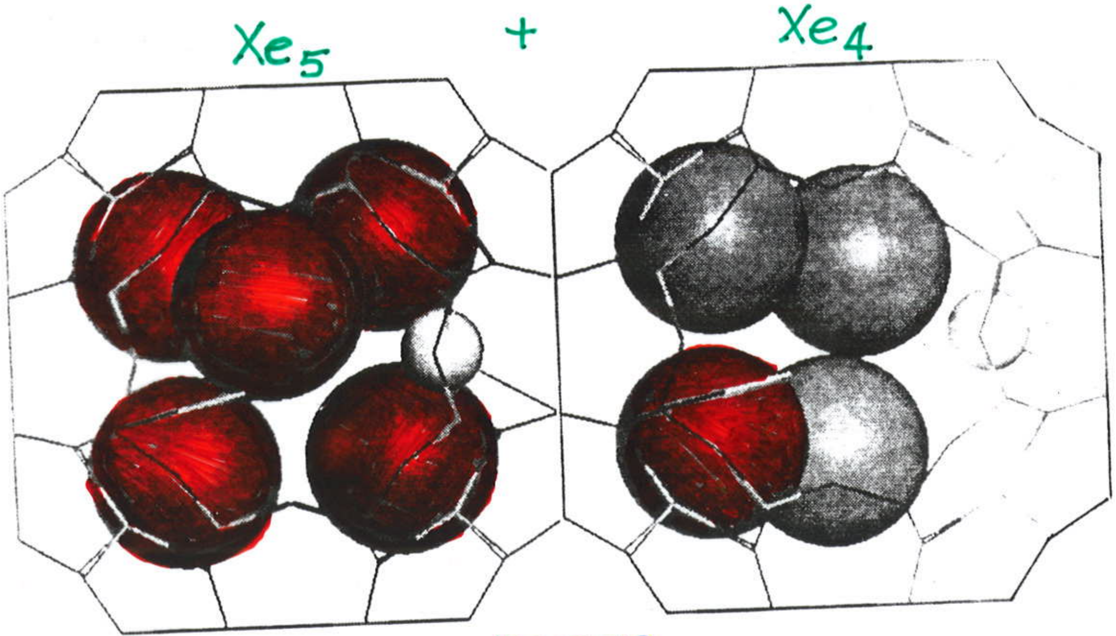
- When molecules are adsorbed in a microporous solid at a given loading, how are these molecules distributed among the cavities?



Also observed by Alex Pines et al.



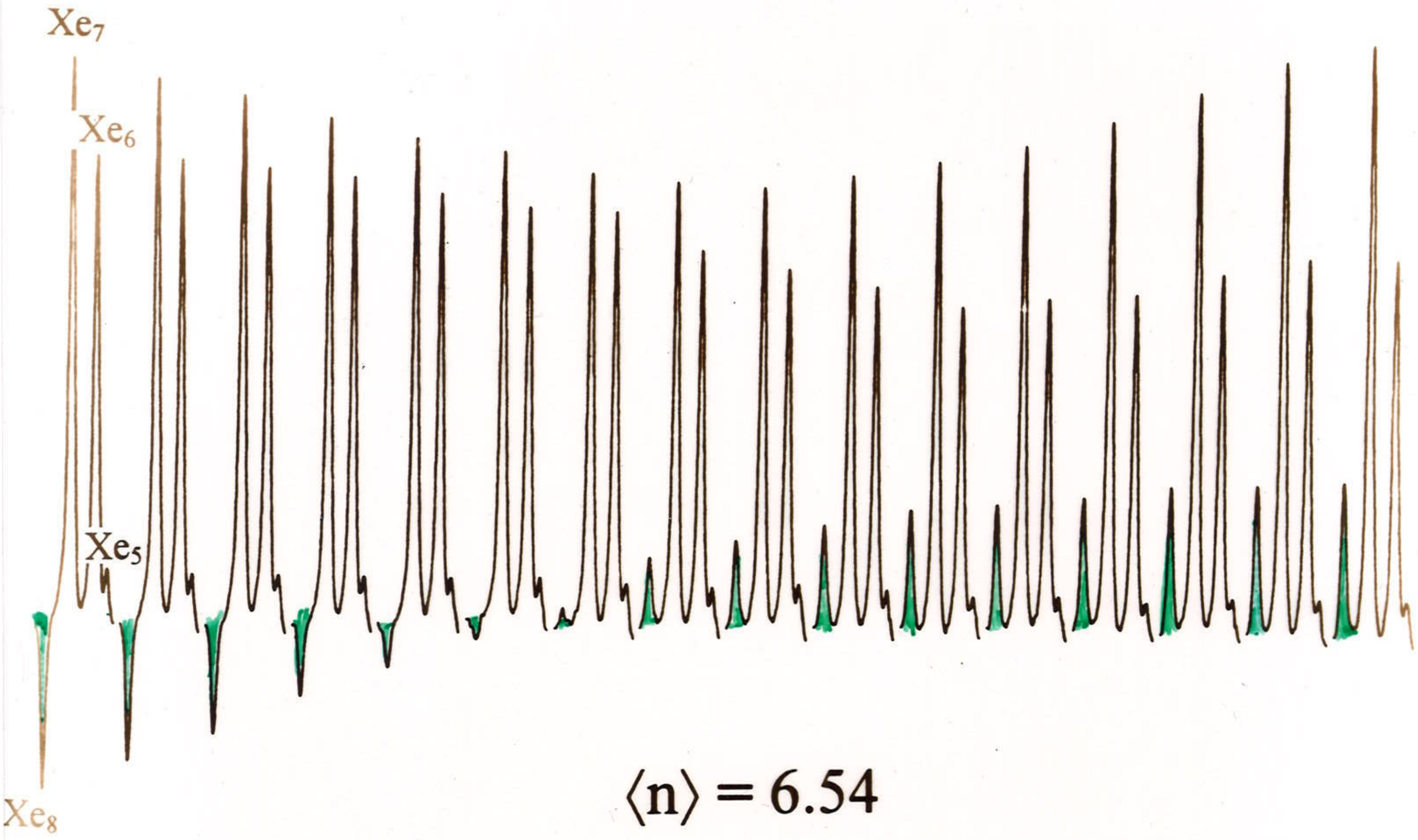
BEFORE



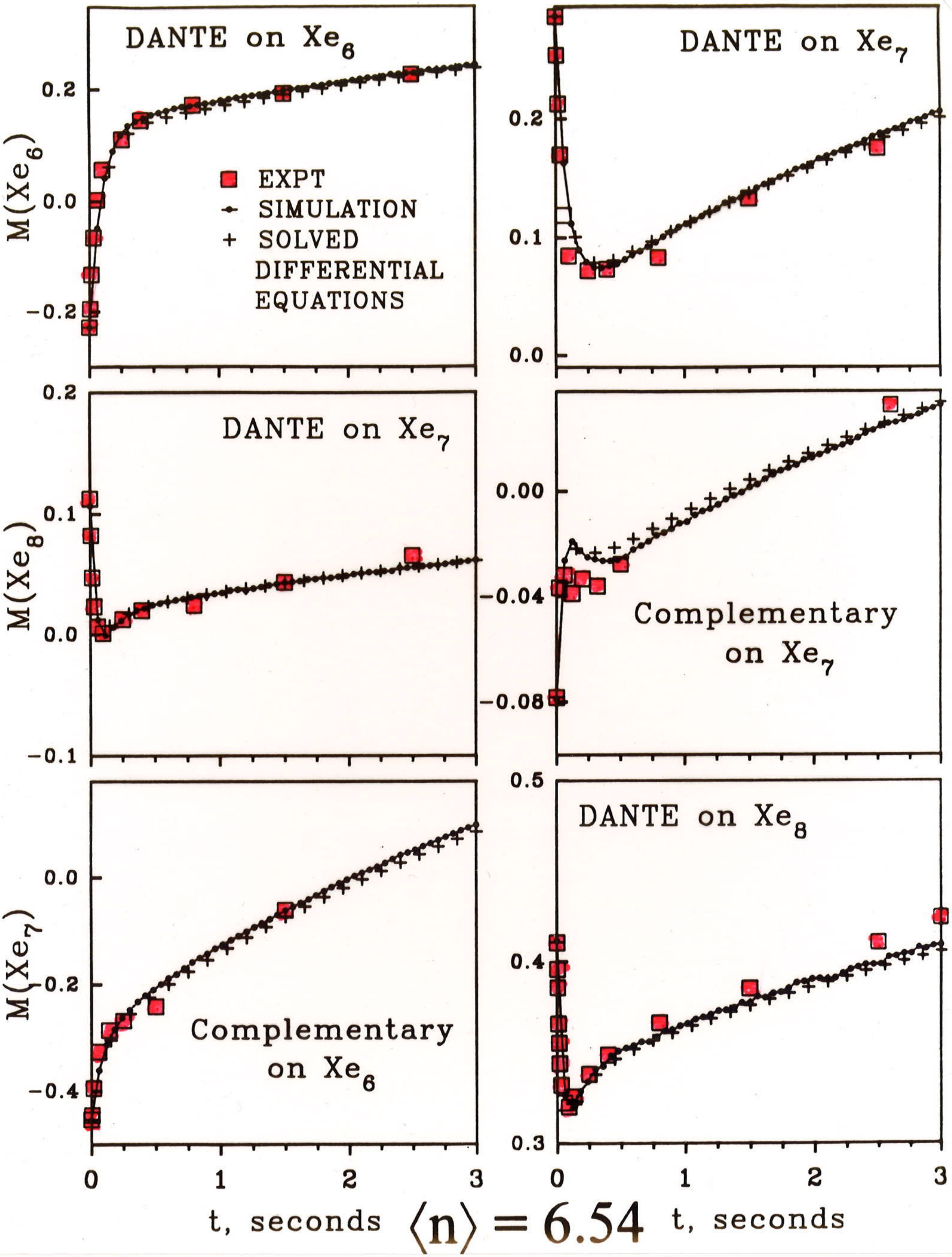
AFTER

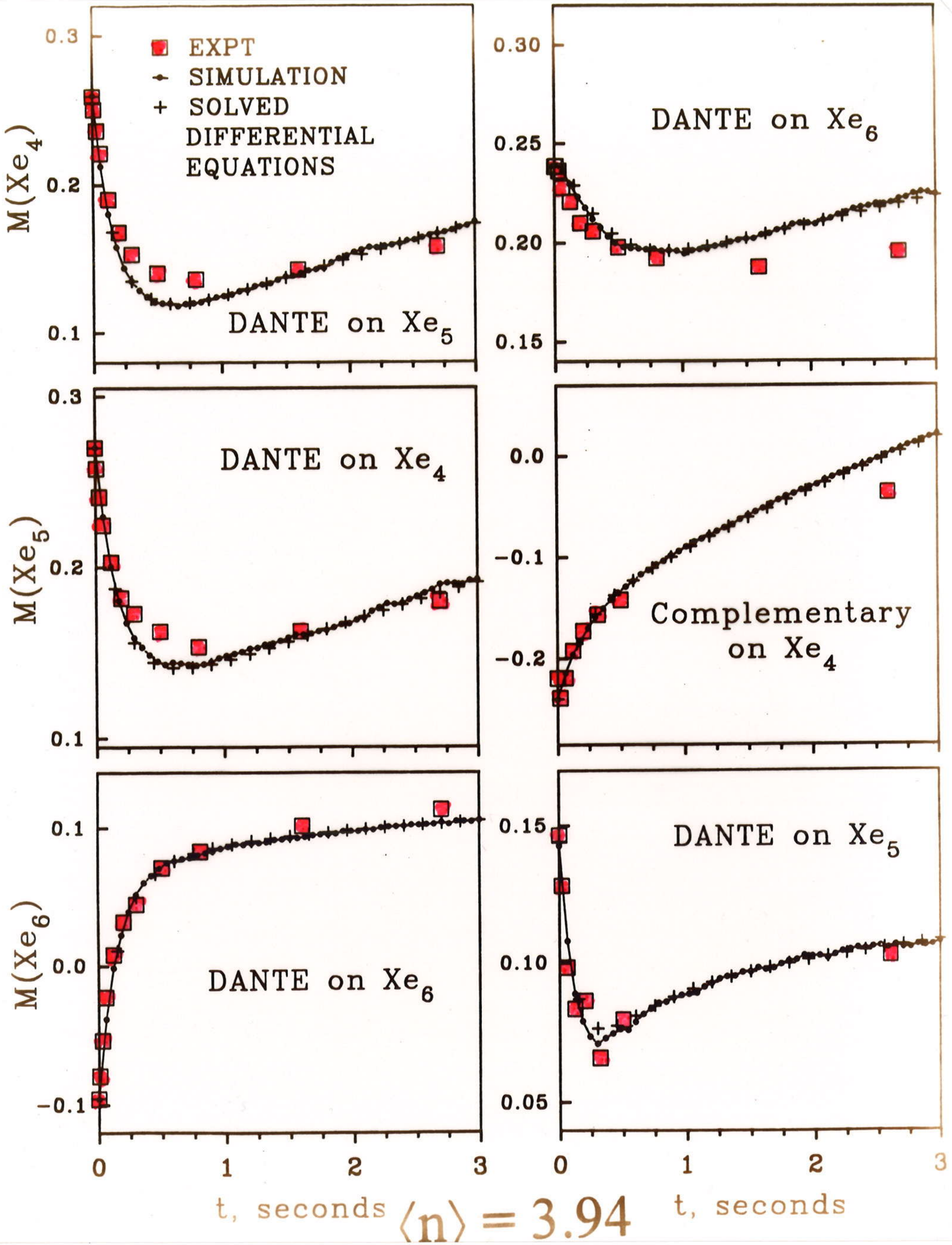
$$Xe_6 + Xe_3 \xrightarrow{k_{46}} Xe_5 + Xe_4$$

How often does a molecule migrate from one cavity to another? Can we follow this migration as a function of time? (Also addressed by Alex Pines et al. using 2D-EXSY)

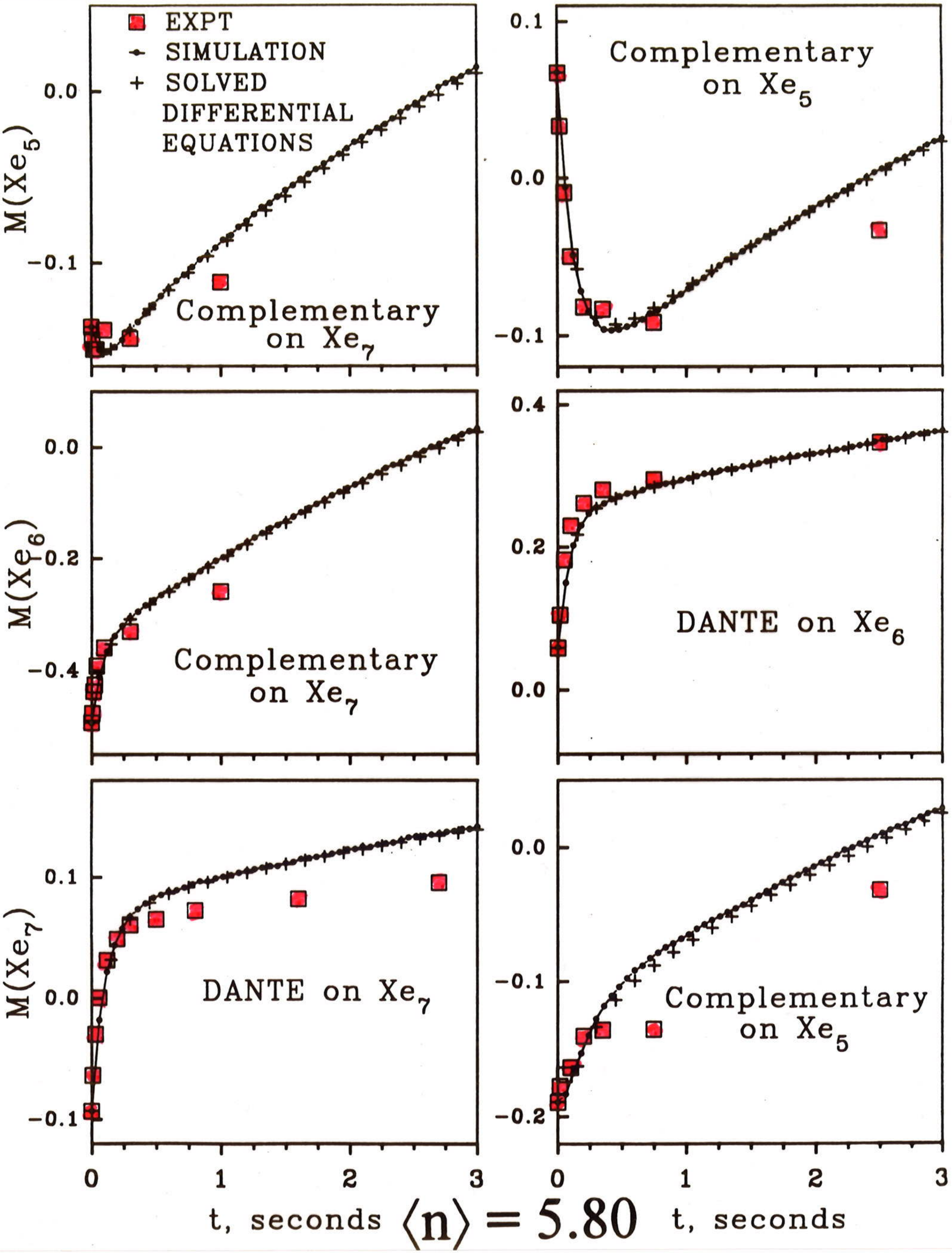


A typical magnetization experiment. This is a Dante experiment on Xe_8 in a sample with $\langle n \rangle = 6.54$ Xe atoms per alpha cage of zeolite NaA at 300 K. The delay times are (from left to right): 0, 2, 5, 10, 15, 20, 30, 60, 90, 130, 250, 400, 800, 1500, 2500, 3000 ms.


DANTE on Xe_6
EXPT
SIMULATION
SOLVED DIFFERENTIAL EQUATIONS
$M(Xe_6)$
0.2
0.0
-0.2
DANTE on Xe_7
0.2
0.1
0.0
DANTE on Xe_7
$M(Xe_8)$
0.2
0.1
0.0
-0.1
Complementary on Xe_7
0.00
-0.04
-0.08
Complementary on Xe_6
$M(Xe_7)$
0.0
-0.2
-0.4
DANTE on Xe_8
0.5
0.4
0.3
0
1
2
3
t, seconds
$\langle n \rangle = 6.54$
t, seconds


EXPT
SIMULATION
SOLVED DIFFERENTIAL EQUATIONS
M(Xe$_4$)
DANTE on Xe$_5$
0.3
0.2
0.1
DANTE on Xe$_6$
0.30
0.25
0.20
0.15
M(Xe$_5$)
DANTE on Xe$_4$
Complementary on Xe$_4$
0.0
-0.1
-0.2
M(Xe$_6$)
DANTE on Xe$_6$
DANTE on Xe$_5$
0.15
0.10
0.05
0
1
2
3
t, seconds
t, seconds

⟨n⟩ = 3.94

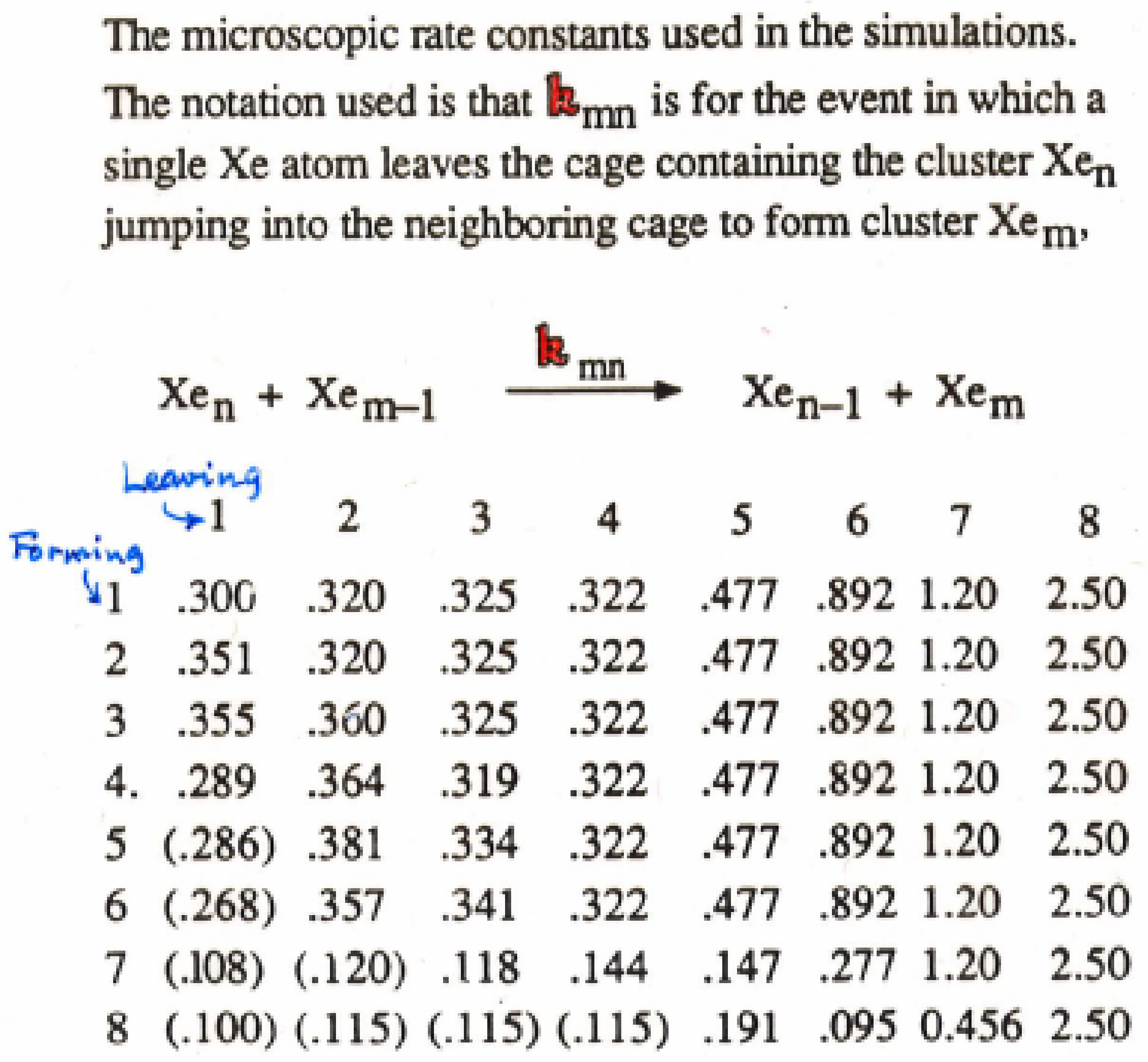


$\langle n \rangle = 5.80$

Simulations use k_{mn} to define the intrinsic probability of making a jump.

- 5000 cages—as many Xe atoms as needed for $\langle n \rangle$
- Start with uniform distribution
- 2000 equilibration steps
- Prepare initial labels (alpha and beta spins)
- Random hops as in equilibration but keep track of labels, 100 time steps
- Signal average over 25 “scans”

Does the rate of migration depend on how many other molecules are in the same cavity where it is leaving from?

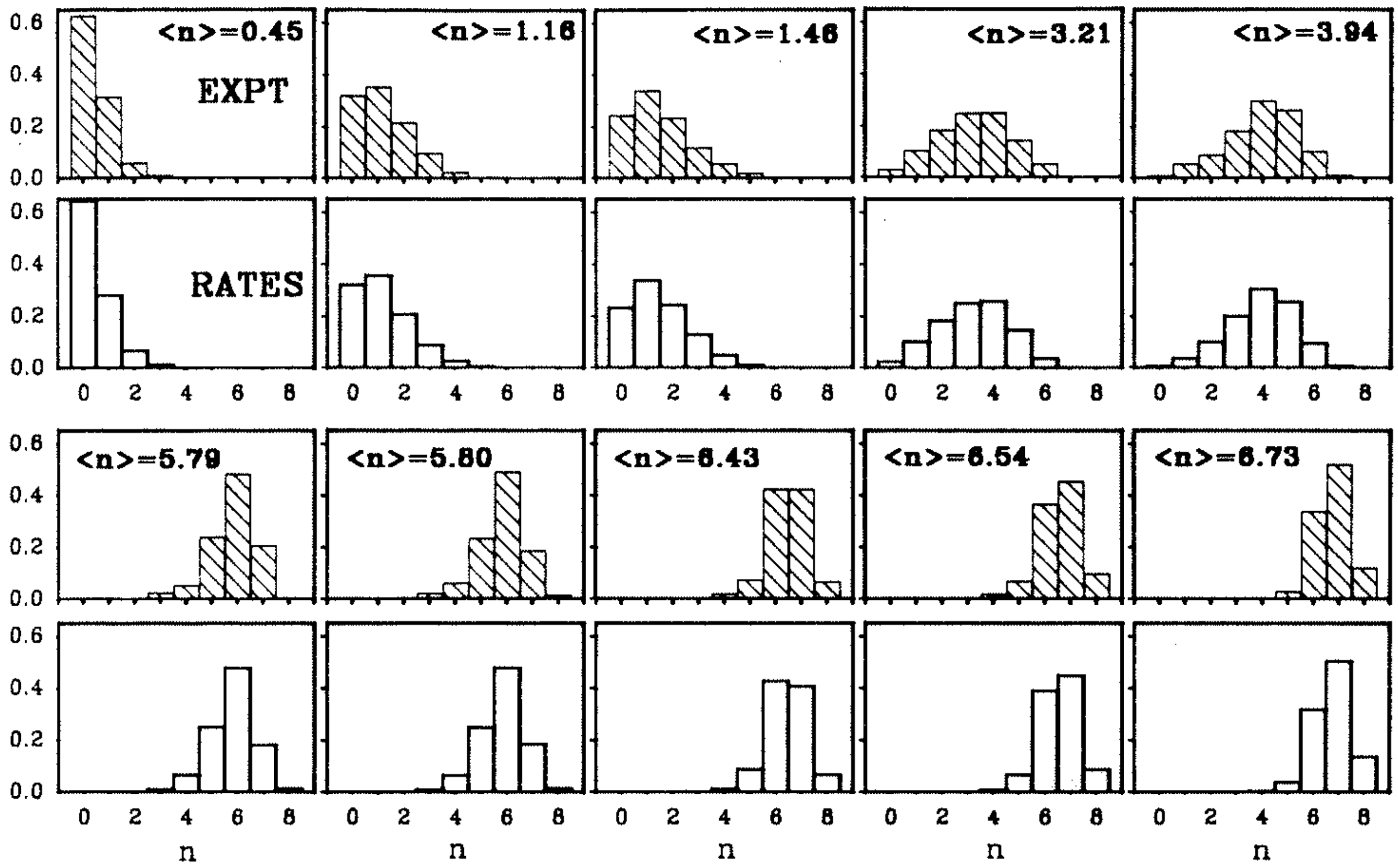


The microscopic rate constants used in the simulations. The notation used is that k_{mn} is for the event in which a single Xe atom leaves the cage containing the cluster Xe_n jumping into the neighboring cage to form cluster Xe_m.

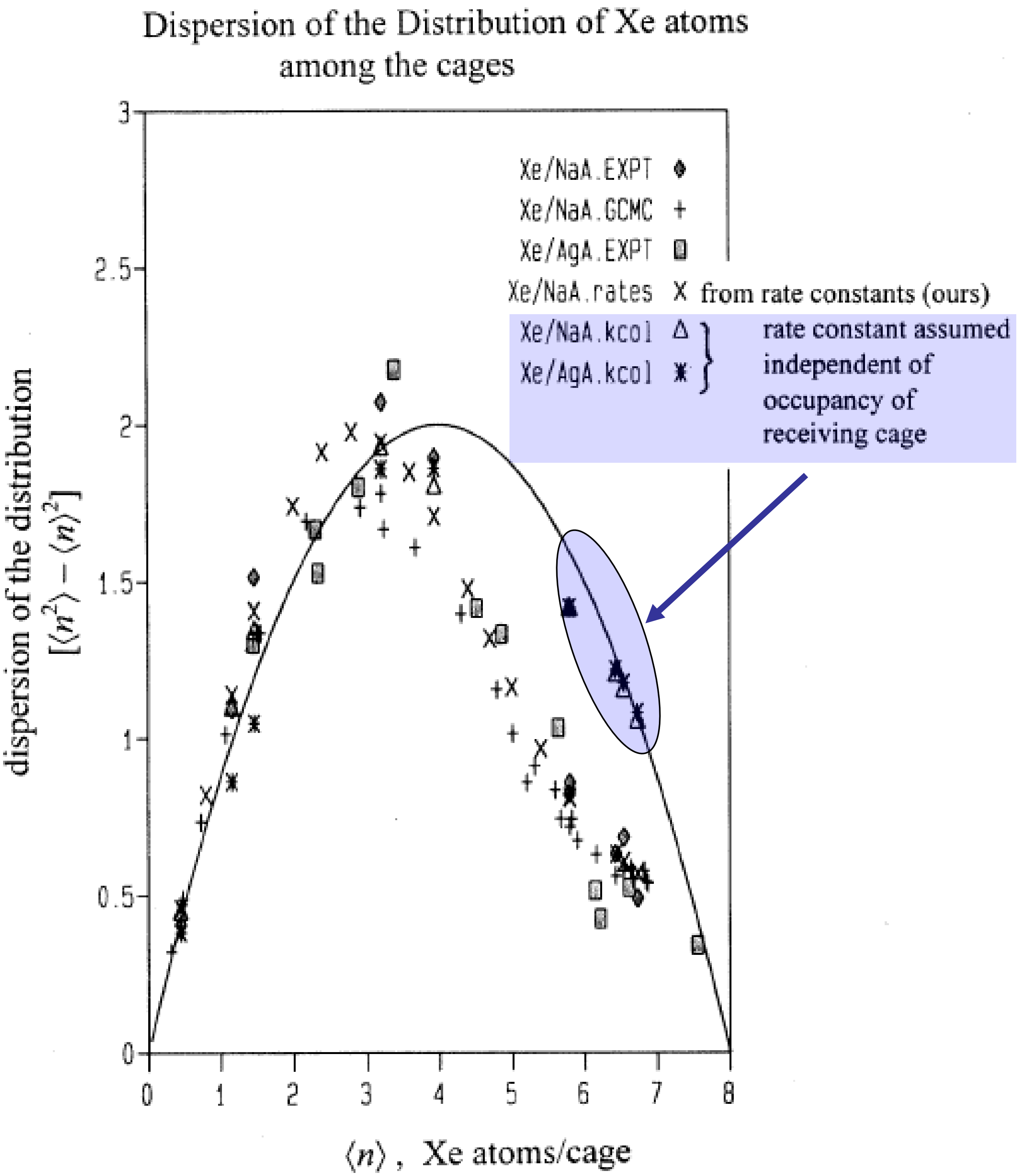
$$Xe_n + Xe_{m-1} \xrightarrow{k_{mn}} Xe_{n-1} + Xe_m$$

Forming ↘	Leaving ↳1	2	3	4	5	6	7	8
1	.300	.320	.325	.322	.477	.892	1.20	2.50
2	.351	.320	.325	.322	.477	.892	1.20	2.50
3	.355	.360	.325	.322	.477	.892	1.20	2.50
4.	.289	.364	.319	.322	.477	.892	1.20	2.50
5	(.286)	.381	.334	.322	.477	.892	1.20	2.50
6	(.268)	.357	.341	.322	.477	.892	1.20	2.50
7	(.108)	(.120)	.118	.144	.147	.277	1.20	2.50
8	(.100)	(.115)	(.115)	(.115)	.191	.095	0.456	2.50

The “best” set of rate constants at 300 K lead to the following equilibrium distributions:



Does the rate constant depend on the occupancy of the receiving cage?


Dispersion of the Distribution of Xe atoms among the cages

from rate constants (ours)

rate constant assumed independent of occupancy of receiving cage

- Simulations provide a means of understanding the magnetization transfer experiments, and verify derived relationships between the elementary rate constants k_{mn} (a single atom hopping from a cage to another cage) and the phenomenological rate constants $\boldsymbol{K}$ associated with the magnetization transfer experiment.
- Labeling the Xe allows us to observe dynamics and measure rates in a system which is at equilibrium.
- The individual cage-to-cage migration rate constants depend largely on the occupancy of the cage from which the Xe is leaving, except that rate constants are significantly smaller when the Xe is going into a cage with high occupancy.
- Two approaches to the equilibrium distribution of atoms among the cavities of zeolite Na*A* lead to the same results, that agree with experiment.

$$k_{mn} \xrightarrow{\text{RATES}} \text{equilibrium } P(n)$$

$$\text{PES} \xrightarrow{\text{GCMC}} \text{equilibrium } P(n)$$

Intracrystalline diffusion

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

$$\mathrm{Xe}_n + \mathrm{Xe}_{m-1} \xrightarrow{k_{mn}} \mathrm{Xe}_{n-1} + \mathrm{Xe}_m$$

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

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

Diffusion coefficient

$$D_s = \langle k \rangle / 6$$

CONCLUSIONS

We have detailed information about slow diffusion

- We can follow the diffusion of Xe atoms from inside the zeolite crystallite to outside the zeolite and obtain the average rate constants for the two processes, Xe(adsorbed) ↔ Xe(bulk gas). The ratio of these rate constants is related to the adsorption isotherm.
- We can follow the cage-to-cage migration of Xe atoms within a crystallite, and obtain the individual rate constants. These provide a truly molecular level picture of the intracrystalline diffusion process. These rate constants reproduce the observed equilibrium distributions.

Acknowledgment

A. Keith Jameson
Angel C. de Dios
Rex E. Gerald II
Hyung-Mi Lim
Pavel Kostikin

NSF