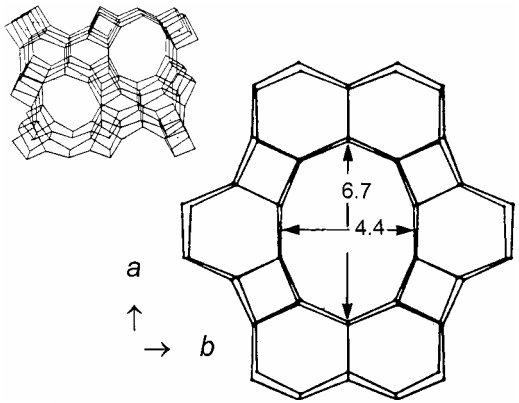
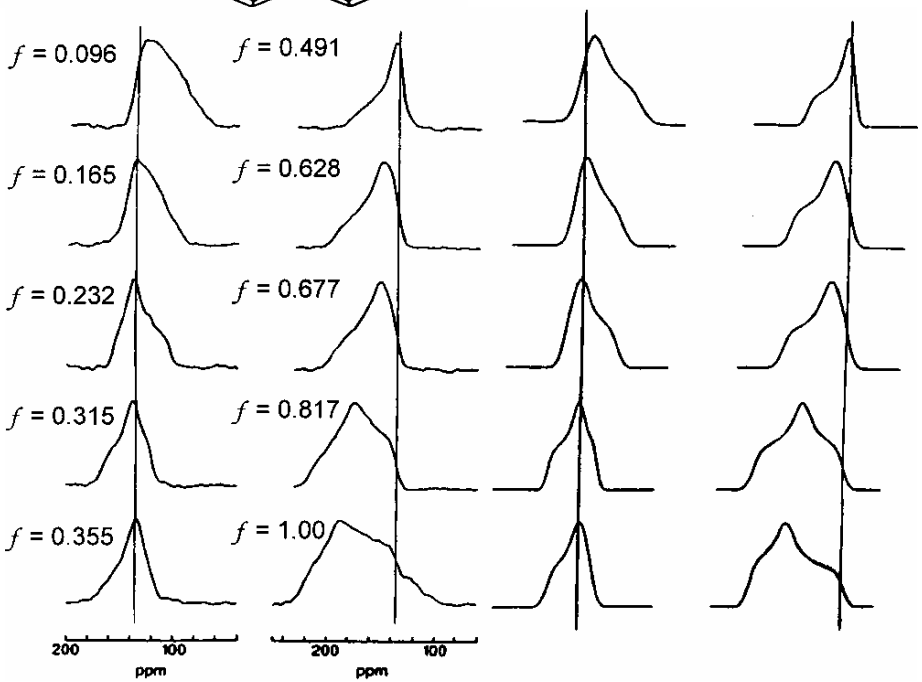
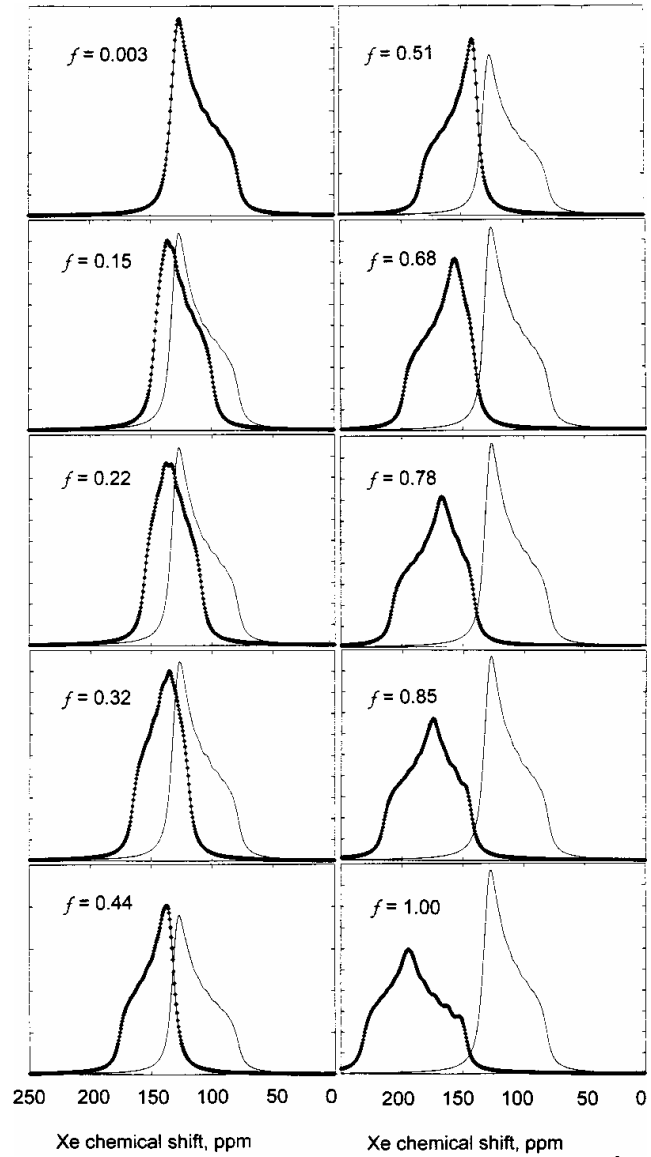
Xe in the channels of $ALPO_4$-11



Cynthia J. Jameson
University of Illinois at Chicago

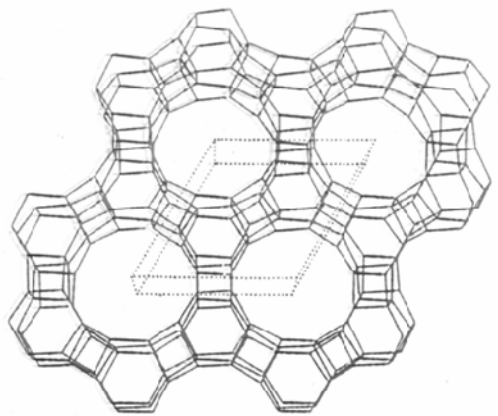


EXPERIMENTS J.A. Ripmeester and C.I. Ratcliffe, J. Phys. Chem. 99, 619 (1995)



SIMULATIONS

Xe in nanochannels



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

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

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

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

one Xe tensor from interaction with ALL channel atoms

The **dimer tensor model** for Xe shielding tensor in a clathrate hydrate

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

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

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

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

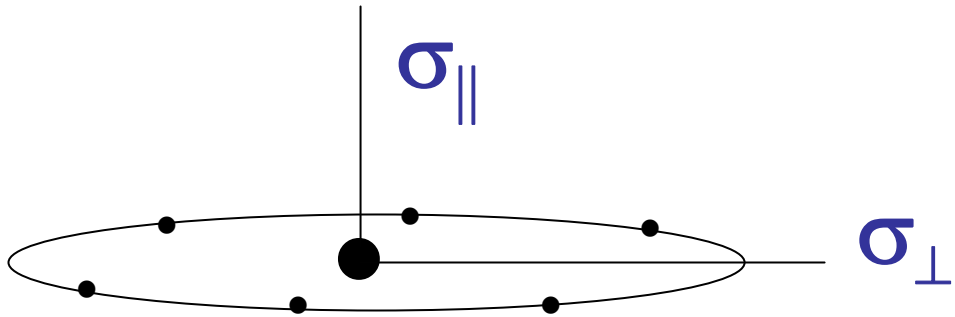
The $\sigma_{\perp}$(rXeO), $\sigma_{||}$(rXeO), $\sigma_{\perp}$(rXeH), and $\sigma_{||}$(rXeH) functions are expressed in terms of parameters which are found by fitting to the *ab initio* Xe shielding tensor components calculated for Xe in the clathrate hydrate.

Similarly, for Xe in a Ne channel

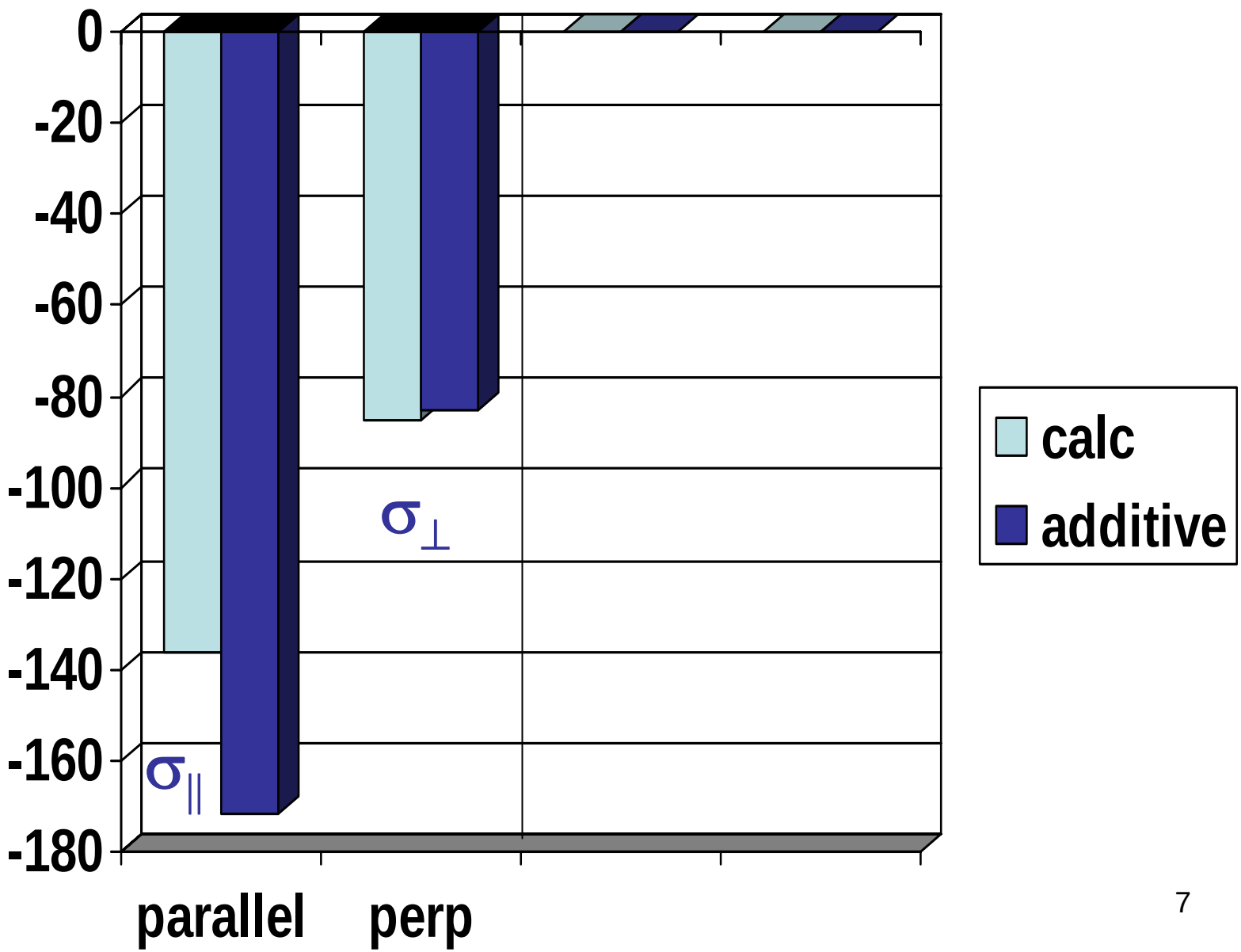
- We propose that the contribution to the shielding of Xe at point J due to the ith Ne atom located at (x_i, y_i, z_i) is given by the *ab initio* tensor components for the XeNe dimer, the functions $\sigma_{\perp}(r_{XeNe})$, $\sigma_{||}(r_{XeNe})$ which are known from our previous quantum mechanical calculations.
- Let us test this proposed additivity by comparing with calculations of Xe in various arrangements of Ne atoms.

Are Xe shielding tensor components pairwise additive?

Example:

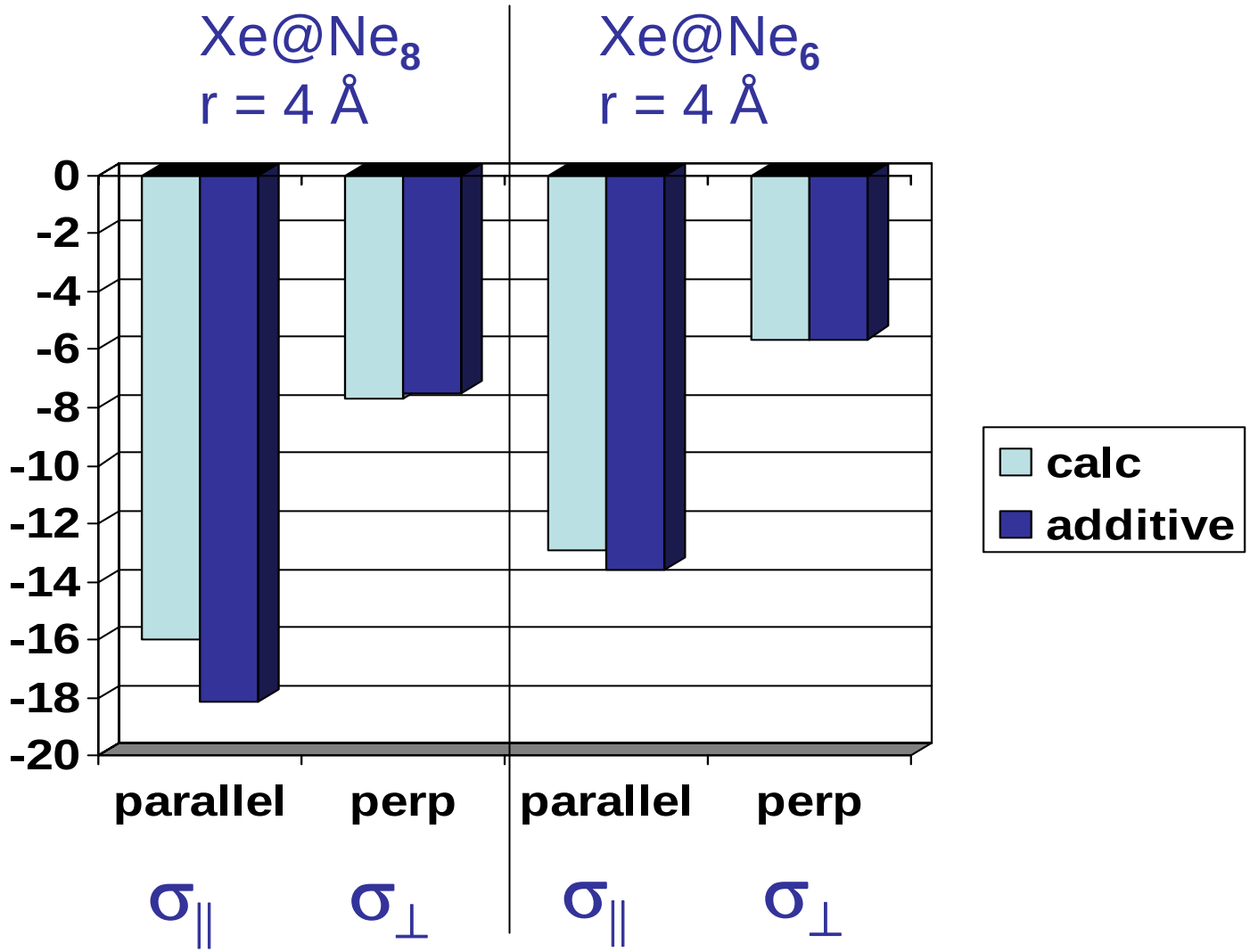


Xe in the center of a ring of Ne atoms

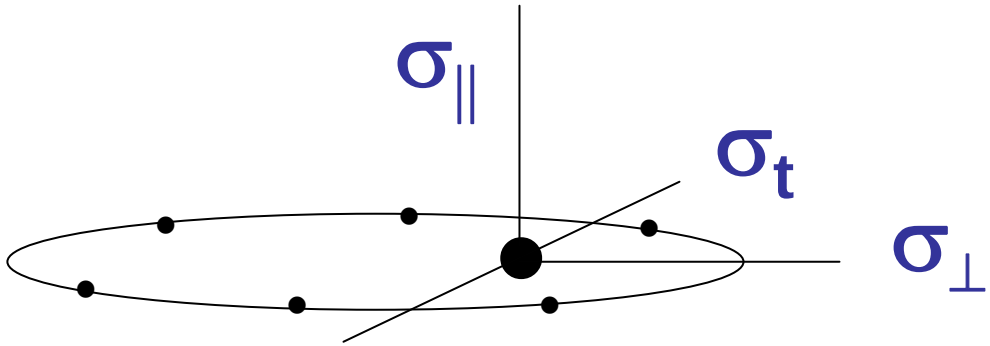

Xe@Ne6 small ring
r = 3 Å
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
σ⊥
σ||
parallel
perp
calc
additive

larger ring

ppm relative to isolated Xe atom



Xe off-center in the larger ring of Ne atoms

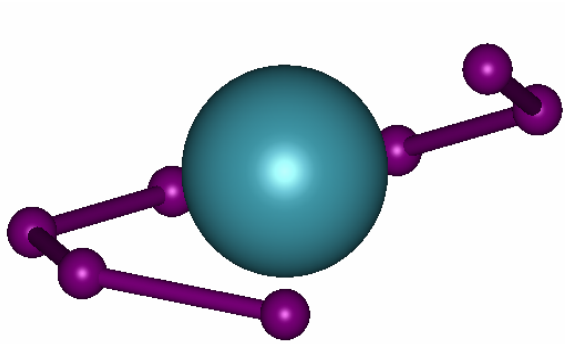


Model	r_{ring} Å	R_{Xe} Å	$\sigma_{\parallel}$	$\sigma_{\perp}$	σ_t
$Xe@Ne_6$	4.0	1.0	-40.04	-11.13	-28.86
$\sum_i^6 XeNe_i$	4.0	1.0	-43.18	-11.45	-29.00
$Xe@Ne_8$	4.0	1.0	-47.67	-18.39	-35.48
$\sum_i^8 XeNe_i$	4.0	1.0	-57.20	-18.69	-34.83

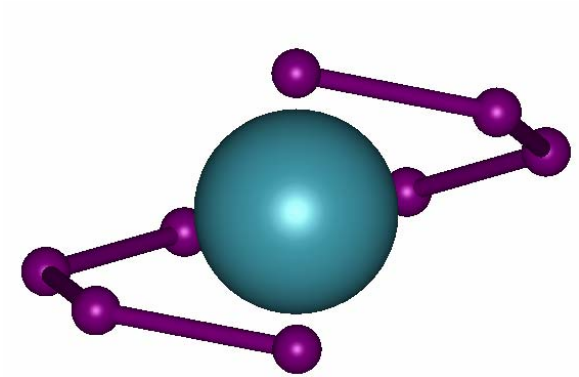
large deviation in $\sigma_{\parallel}$

The shielding tensor of Xe interacting with Ne helices

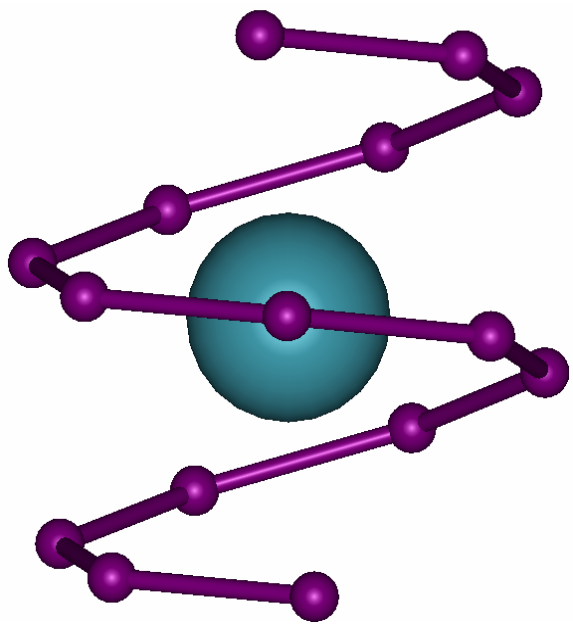
Xe in a left handed helix



Xe@Ne$_7$



Xe@Ne$_8$



Xe@Ne$_{15}$

Are Xe shielding tensor components pairwise additive?

Z direction along the axis of the Ne_7 helix

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

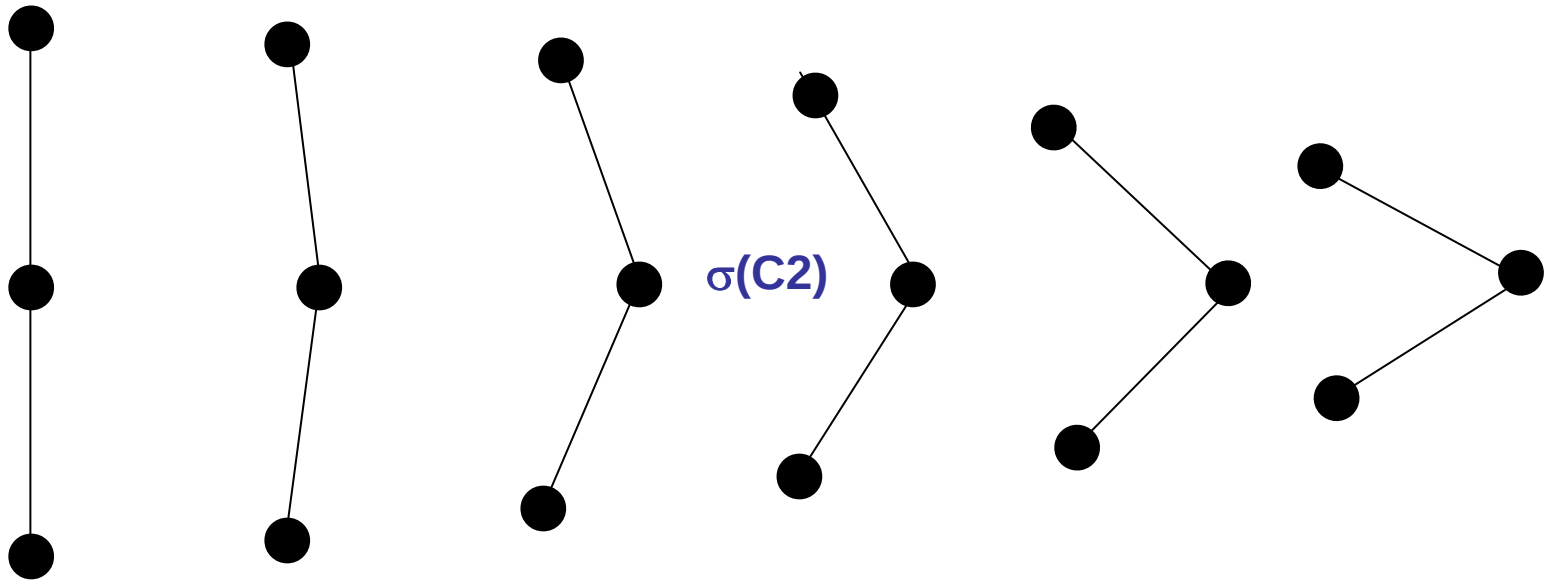
Are Xe shielding tensor components pairwise additive?

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

Are Xe shielding tensor components pairwise additive?

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

Are Xe shielding tensors arising from Xe neighbors pair-wise additive?



180° 170° 150° 120° 90° 60°

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

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

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

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

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

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

Worst case: in the molecular plane, the electrons of terminal Xe atoms are interacting substantially for 60°

conclusion

- Pairwise additivity is a good approximation for intermolecular shielding tensor components of Xe

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

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

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

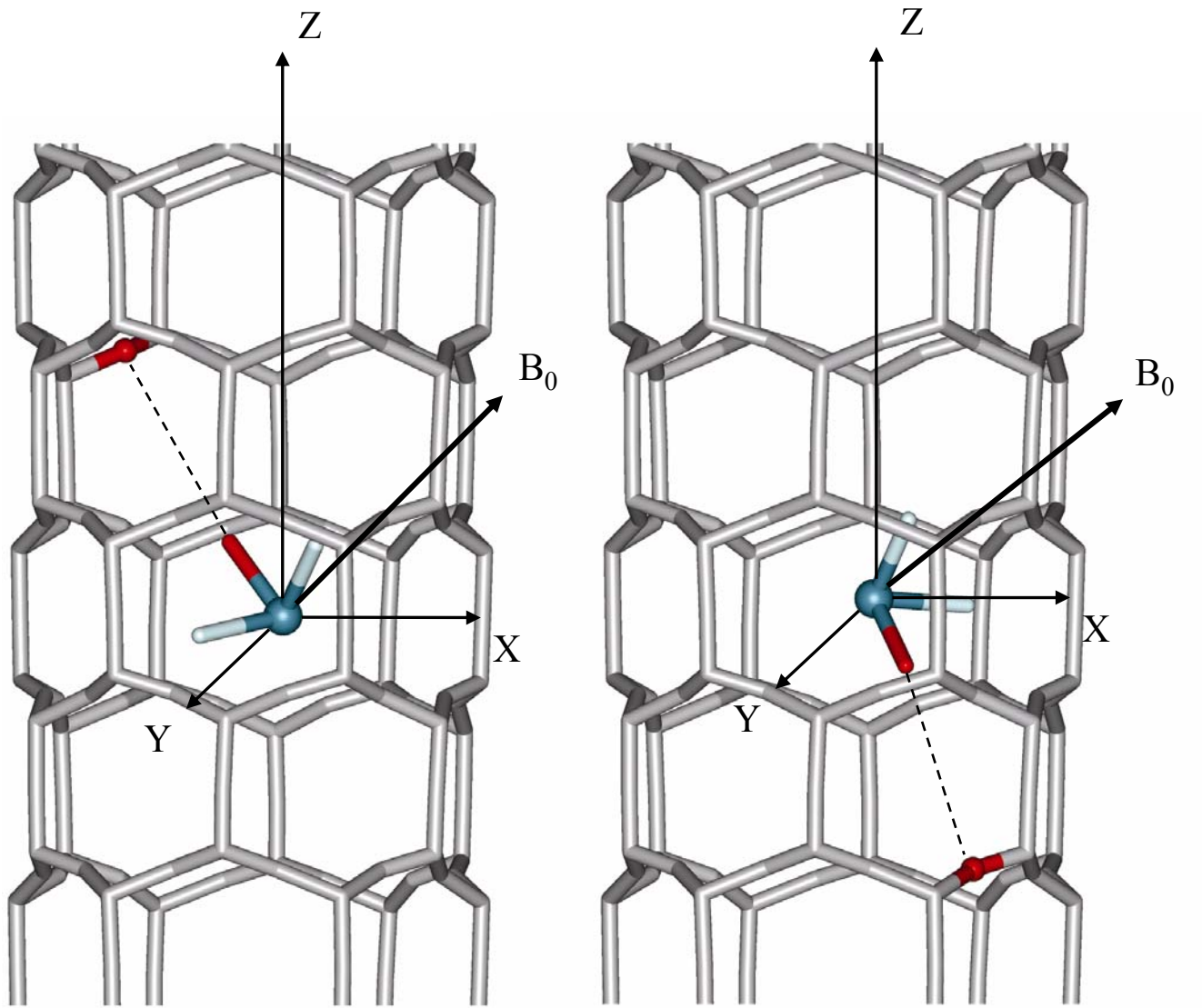
$$\tfrac{1}{2}(\sigma_{XY}+\sigma_{YX}) = [(x_i - x_J)/r_{iJ}]\bullet[(y_i - y_J)/r_{iJ}](\sigma_{||} - \sigma_{\perp})$$

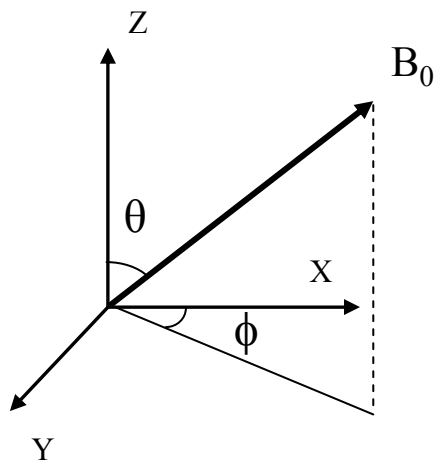
The contribution to the shielding of Xe at point J due to the $K_{\underline{th}}$ Xe atom located at (x_K, y_K, z_K) is given by the ab initio tensor components for the XeXe dimer, the functions $\sigma_{\perp}(r_{XeXe})$, $\sigma_{||}(r_{XeXe})$.

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

Lineshapes by grand canonical Monte Carlo

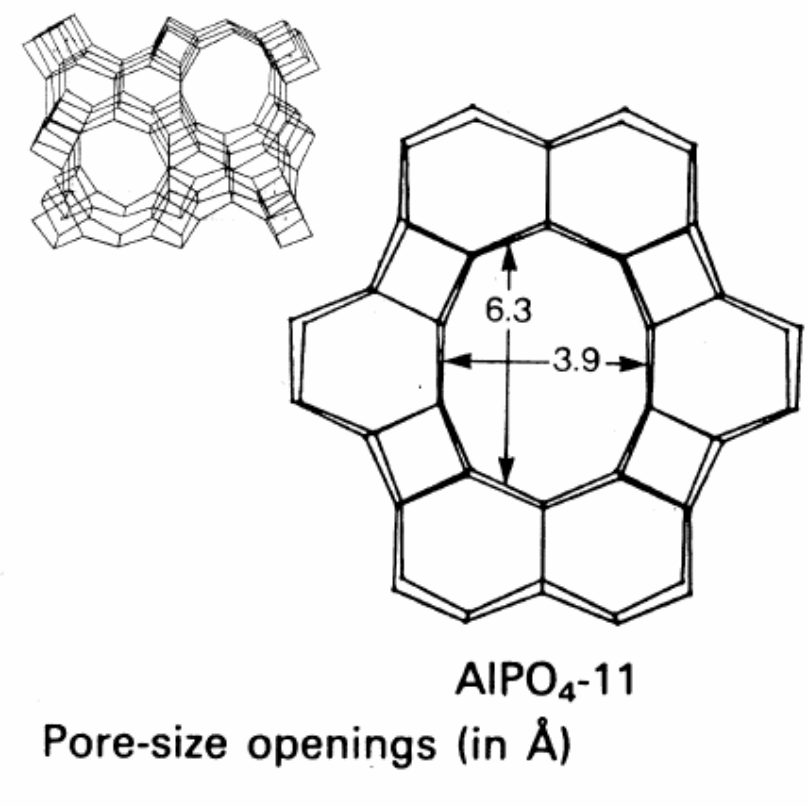




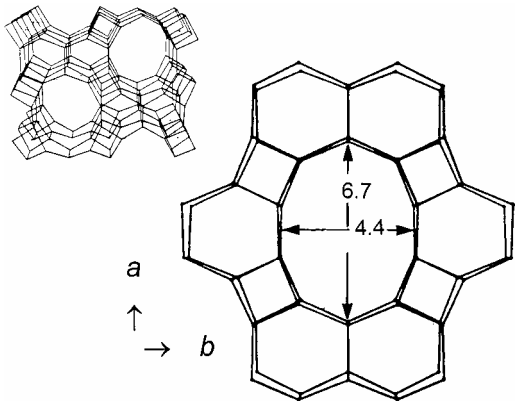
Random orientation of crystallites:
Probability that B_0 lies in any infinitesimal solid angle is
$d\zeta\, d\phi / 4\pi$, where
$\zeta = (-\cos\theta)$
Equal areas in $\zeta\phi$ plane correspond to equal probabilities

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

dimensions of the $AlPO_4$-11 channel



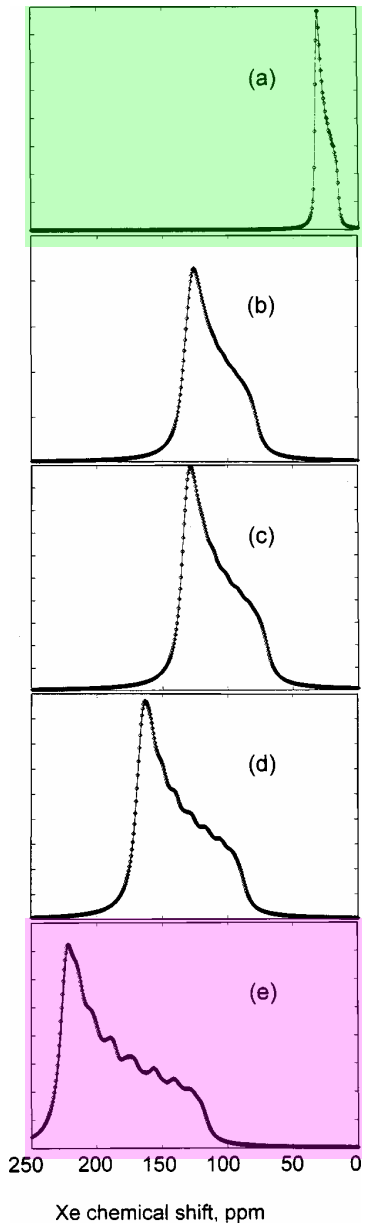
Architecture of the channel determines the lineshape



$ALPO_4$-11 architecture

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

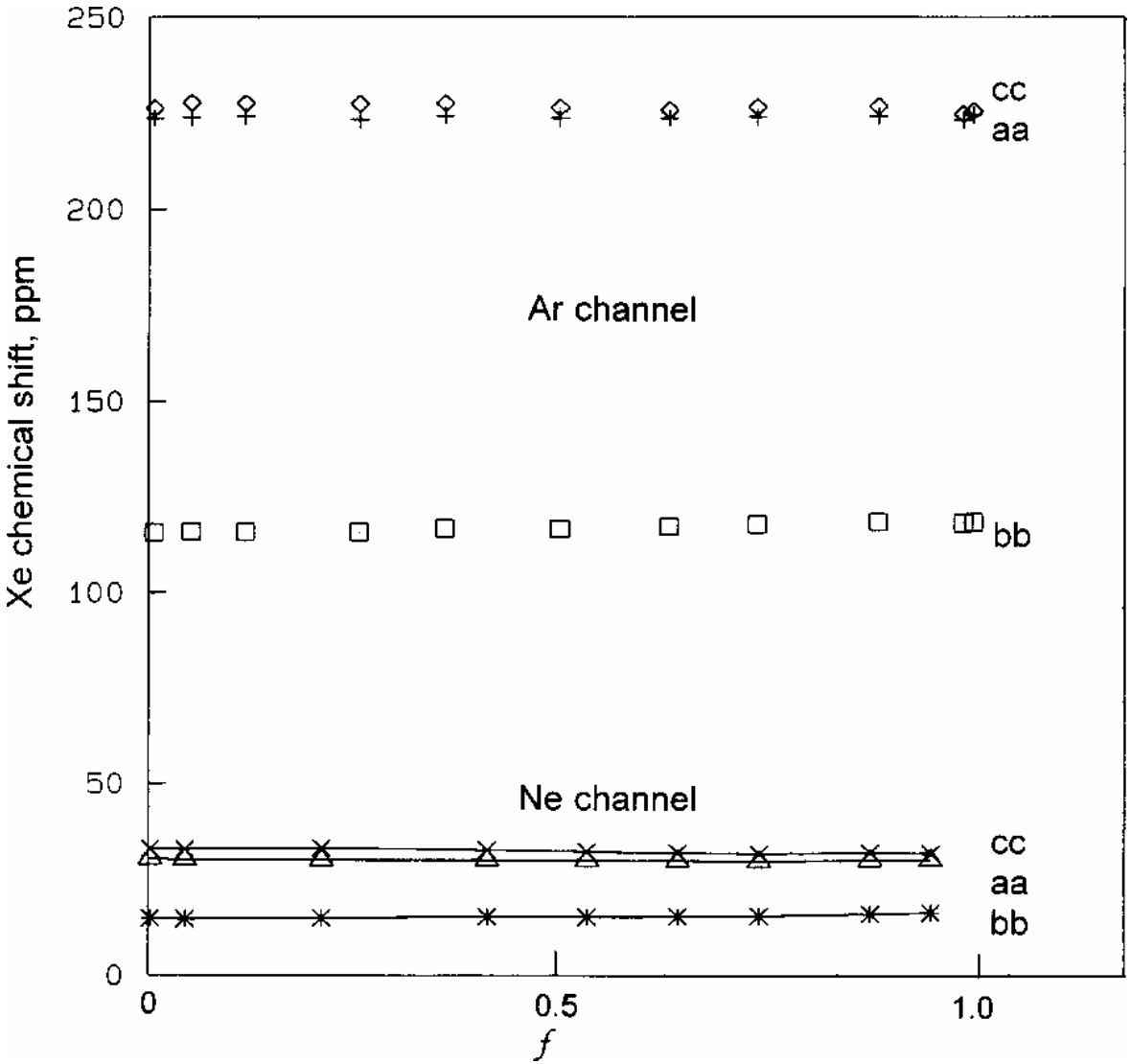
One Xe atom in a neon channel

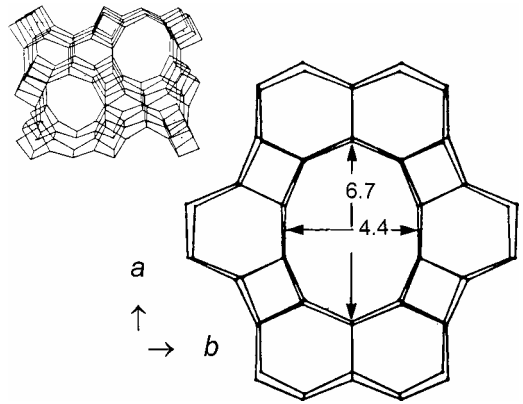


One Xe atom in an argon channel

Jameson, JCP 116, 8912 (2002)

signature of the channel architecture: Xe-channel contributions





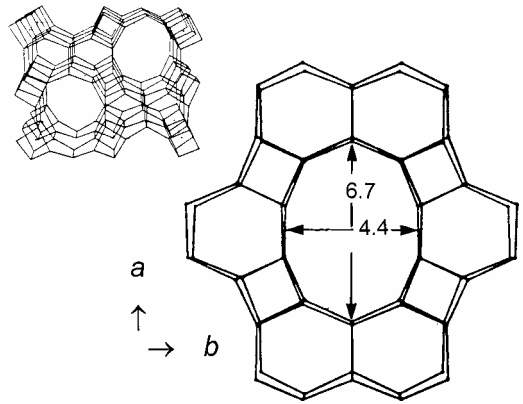
MODEL CHANNELS
ALPO4-11 coordinates
all Ne or all Ar

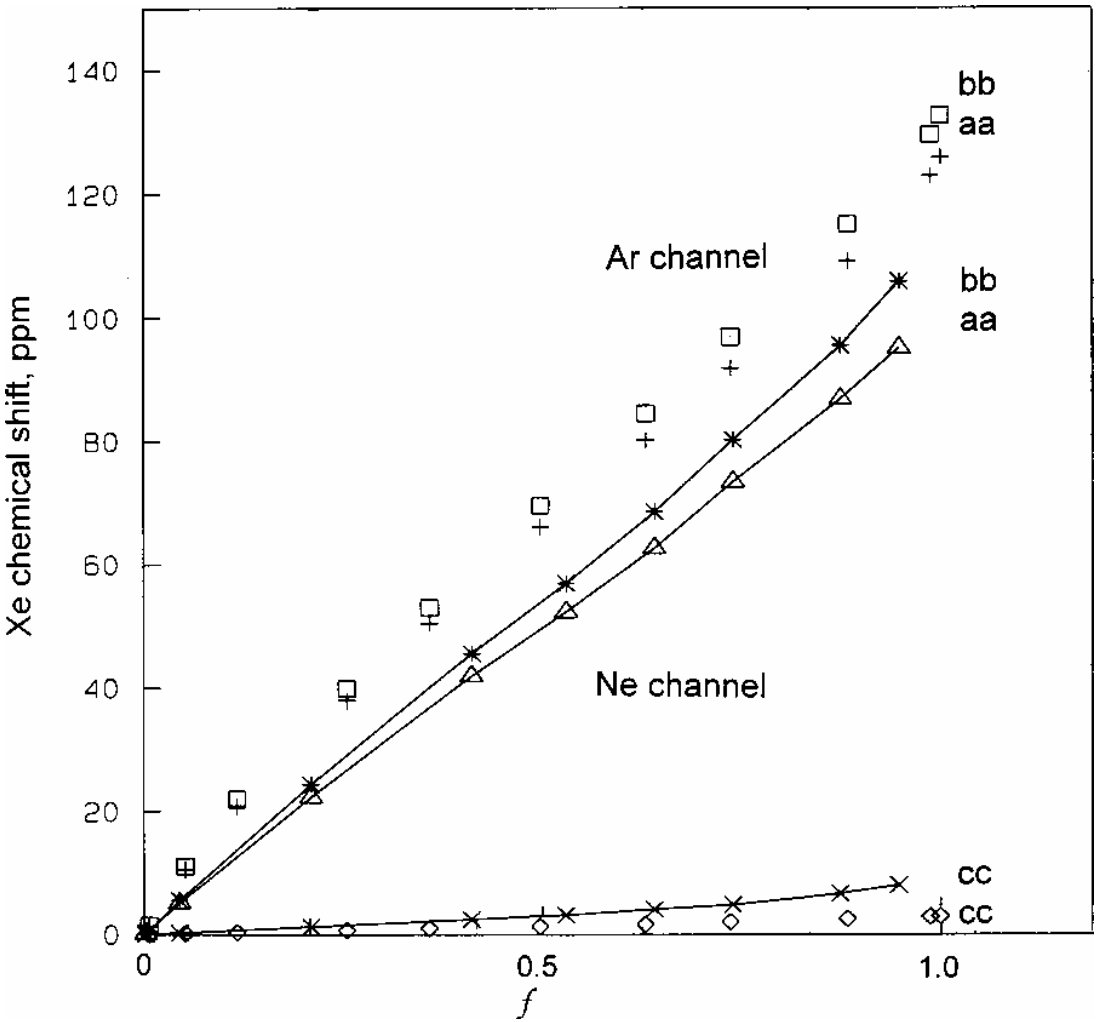
larger component is δ_{aa}

smaller is δ_{bb}, clearly not circular cross section

LARGER response from Ar than Ne

signature of the channel architecture: Xe-Xe contributions





almost no δ_{cc} component, not enough space for two Xe atoms to overlap densities in one cross-sectional plane

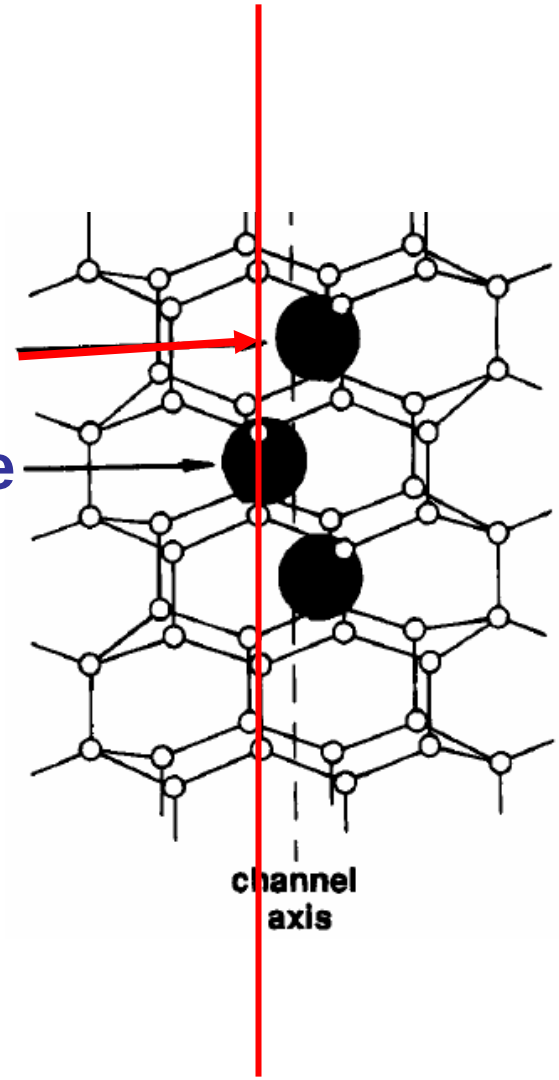
larger contribution to δ_{bb}

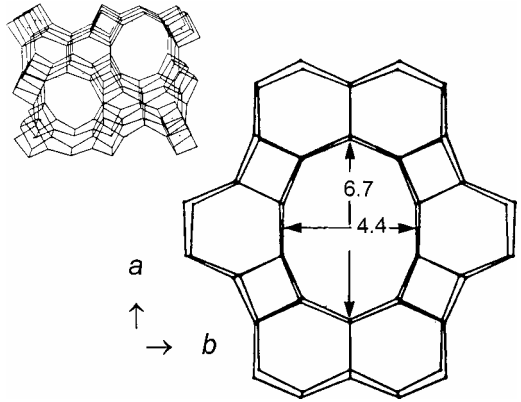
smaller to δ_{aa}

WHY?

look on the plane shown in red for electron densities which can contribute to δ_{aa}

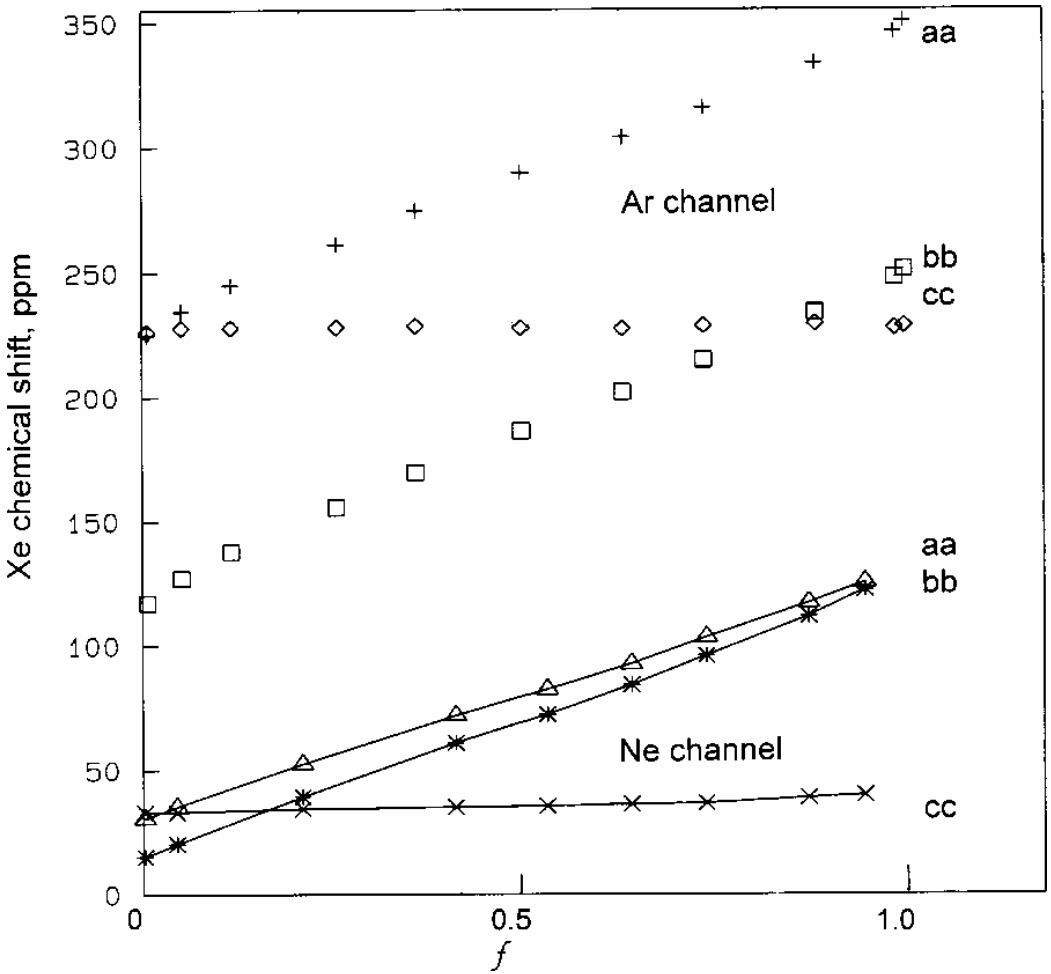
consider the shielding of this Xe

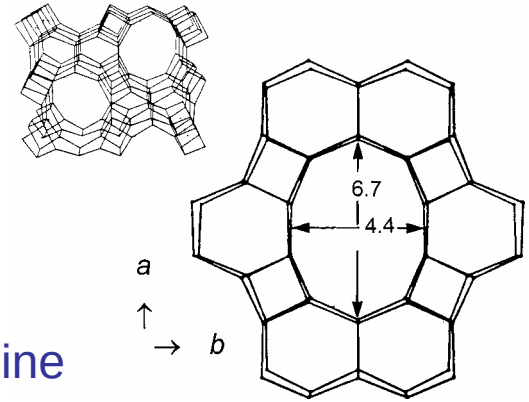




look on the plane of the screen for electron densities which can contribute to δ_{bb}

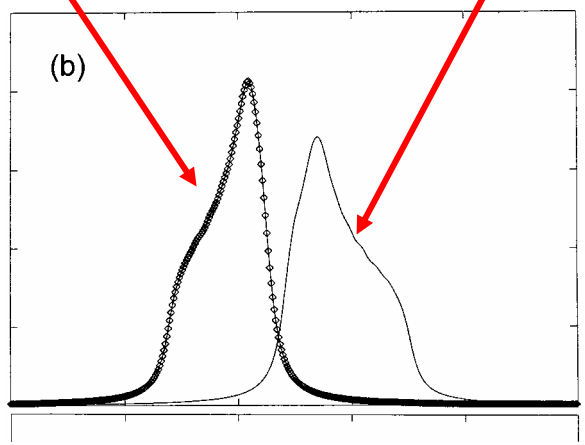
average tensor components





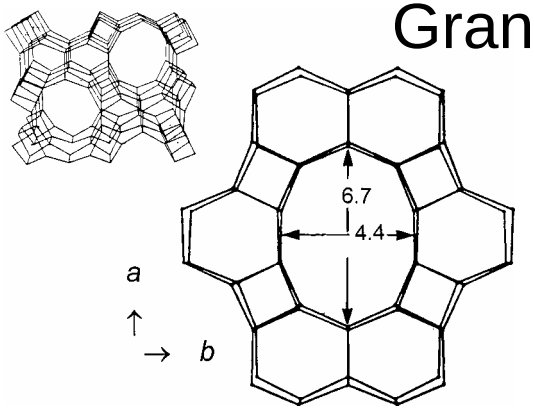
total line shape

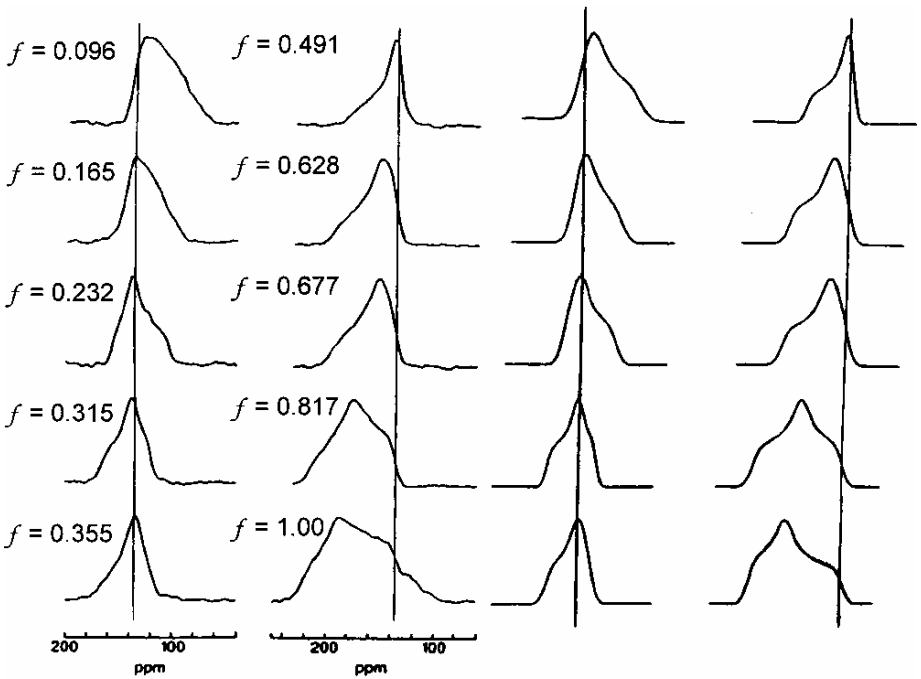
Xe-channel contrib

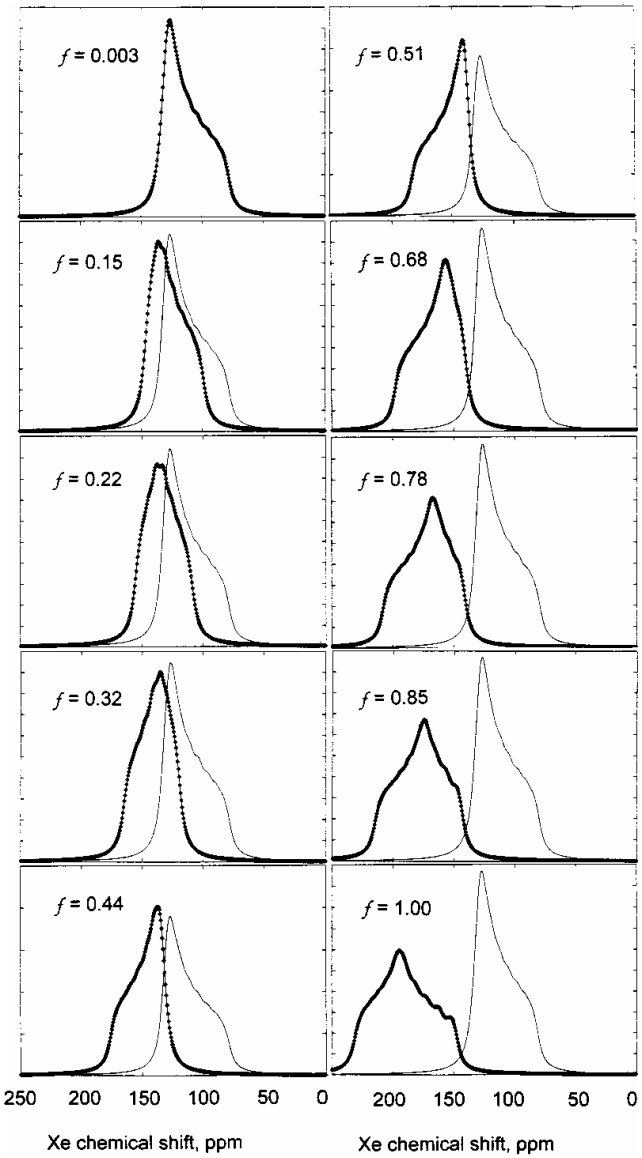


Xe in the channels of $ALPO_4$-11

Grand Canonical Monte Carlo **SIMULATIONS**



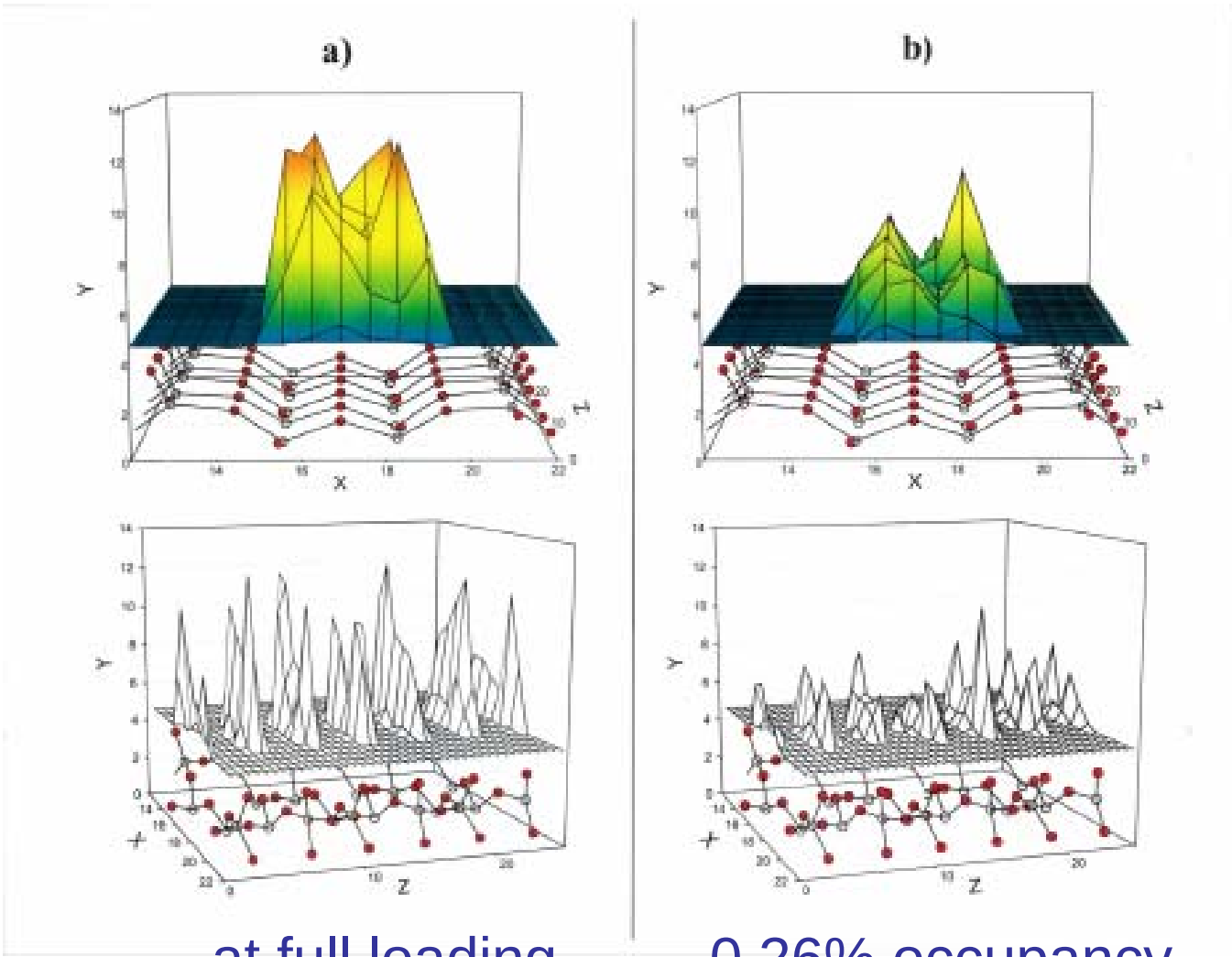




Jameson J Chem Phys 116, 8912 (2002)

EXPERIMENTS J.A. Ripmeester and C.I. Ratcliffe, J. Phys. Chem. 99, 619 (1995)

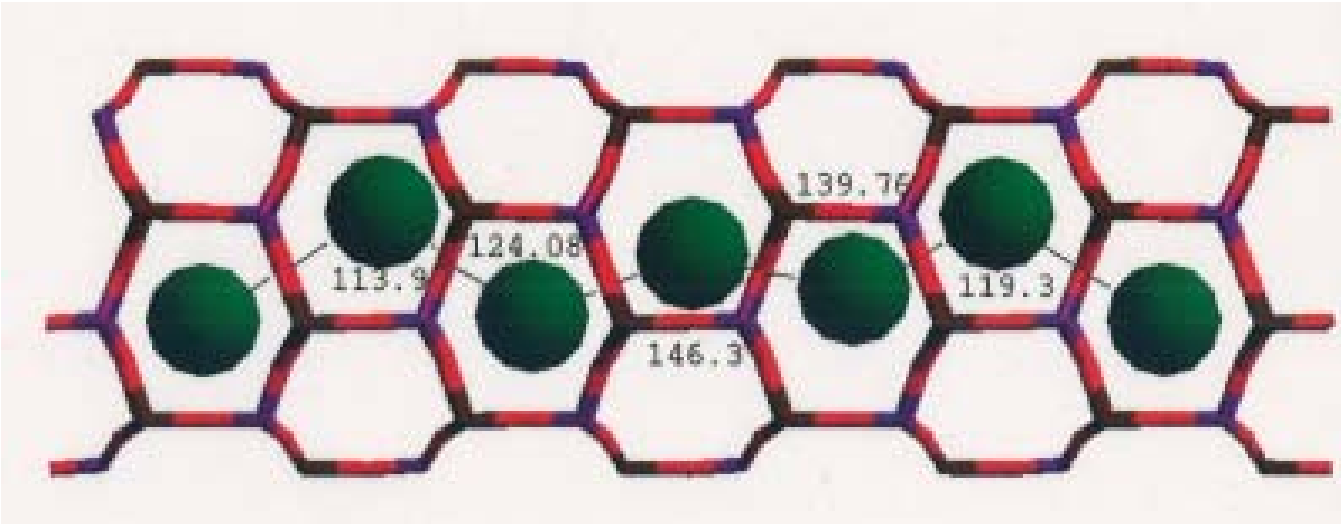
One-body distribution functions of Xe in $ALPO_4$-11



at full loading 0.26% occupancy

Orderly arrangement of Xe atoms in channel: Xe sits in register with sites along walls. Xe unable to do this when sites too close together

MD simulation snapshot



Information that is encoded in observed Xe spectra:

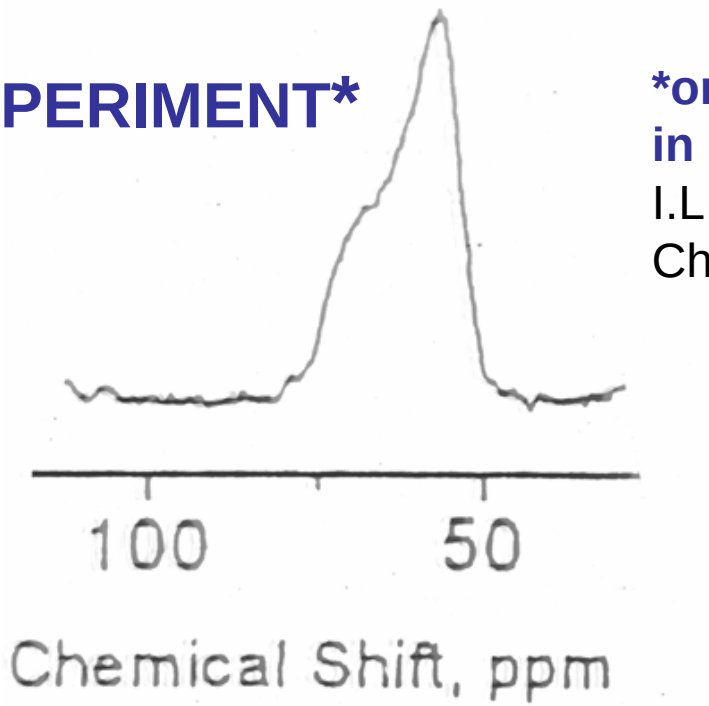
- structural as well as dynamic information
- the diameter of the channel
- the aspect ratio of the cross section of the channel
- the architecture of the channel
- average number of Xe atoms per unit cell
- electronic structure of atoms constituting the cavity walls

other simulations of Xe in nanochannels in zeolites

- Xe in SSZ-24 C.J. Jameson, JACS, 126, 10450 (2004) (Experiments by I.L. Moudrakovski et al. Chem. Mater. 12, 1181 (2000))

- Xe in ZSM-12 C.J. Jameson, unpublished work (Experiments by I. L. Moudrakovski, C. I. Ratcliffe and J. A. Ripmeester Appl. Magn. Reson. 10, 559 (1996))

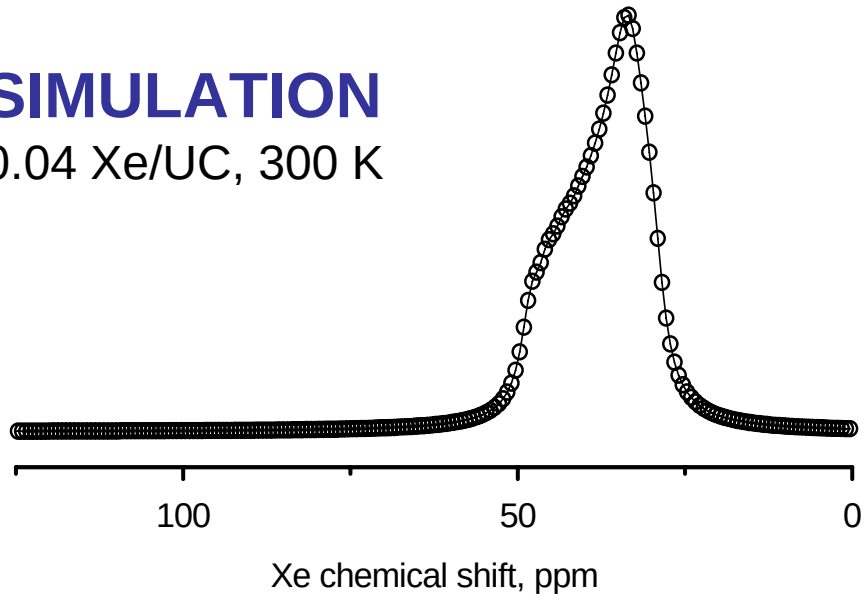
EXPERIMENT*

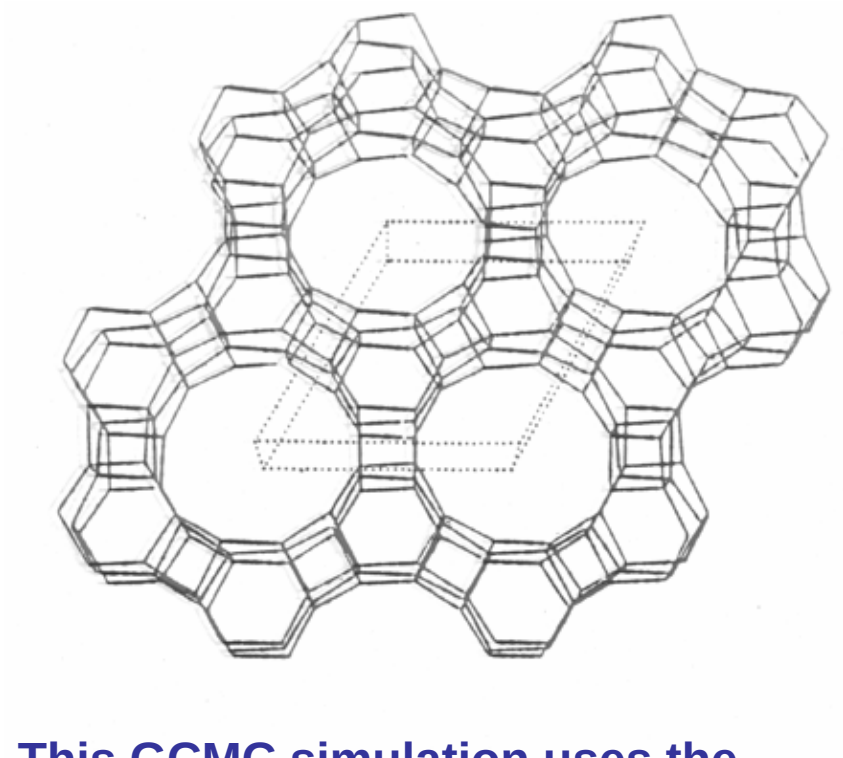


***one-scan hyperpolarized ^{129}Xe in polycrystalline SSZ-24 at 293 K**
I.L. Moudrakovski et al.
Chem. Mater. 12, 1181 (2000).

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)

Xe line shape signatures in diamagnetic channels

- *# singularities at high* $\langle N \rangle$ $\rightarrow$ aspect ratio of cross section (2 singularities: nearly circular; 3 singularities: elliptical)
- *1 constant tensor component with changing* $\langle N \rangle$ $\rightarrow$ channel diameter does not permit two Xe to pass each other.
- *Significant change of* $\delta_{||}$ *with* $\langle N \rangle$ $\rightarrow$ cross section large enough to permit $XeXe_2$ groupings to achieve angles smaller than 150-180°at high $\langle N \rangle$.

Xe line shape signatures...

- *Linear behavior of each component with* $\langle N \rangle \rightarrow$ orderly arrangement of Xe atoms in channel; Xe sits in register with sites along walls. Xe unable to do this when sites too close together
- *Non-linear behavior of tensor components with* $\langle N \rangle \rightarrow$ non-uniform channel cross section.
- *crossing of tensor components with* $\langle N \rangle \rightarrow$ Xe-Xe interactions occur, i.e., Xe see each other in open channels, not cells.

CONCLUSIONS

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

- Simulations demonstrate separately which part of the observed NMR lineshape characteristics provides the signature of the channel architecture, and which part provides information on the electronic structure of the atoms constituting the channel.
- The variation in lineshape as a function of loading in real systems can be reproduced.
- The additive dimer tensor model can work well in channels and cavities of arbitrary size and shape.

ACKNOWLEDGMENT

This work was inspired by the series of experiments of John A. Ripmeester and his group which revealed for the first time that Xe can report its average tensor components in an anisotropic environment.