Understanding Xe chemical shifts

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University of Illinois at Chicago

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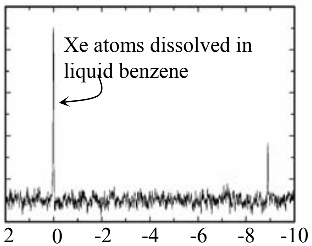
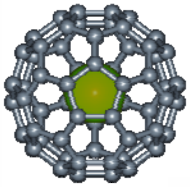
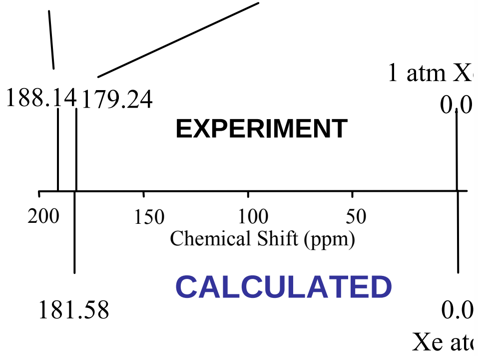
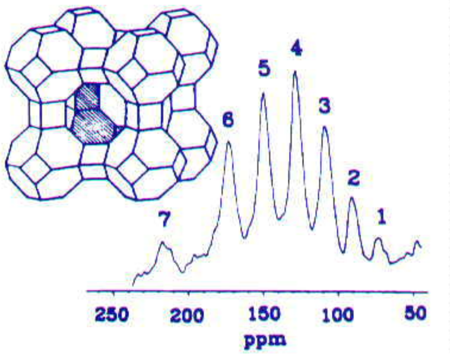
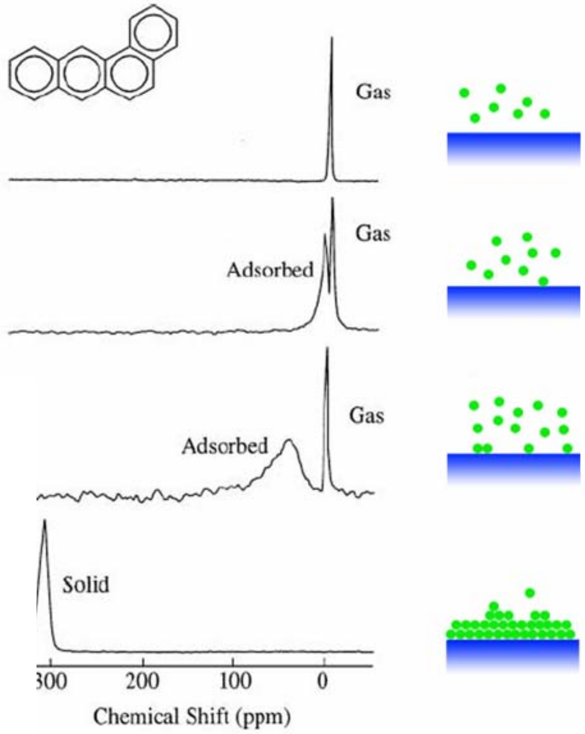
La Colle sur Loup, FRANCE

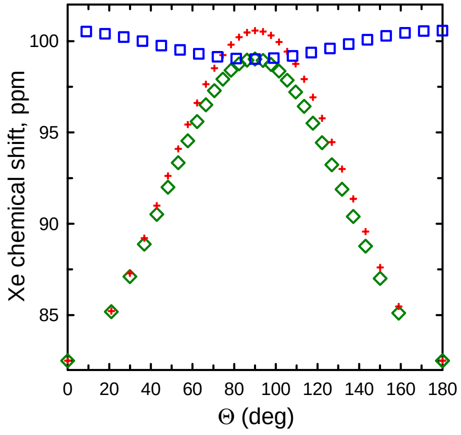


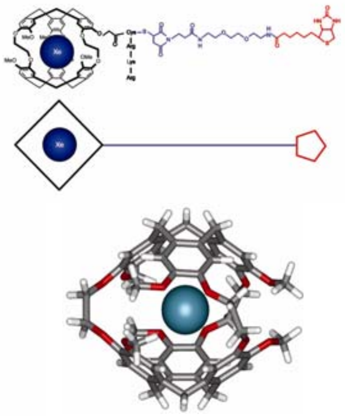


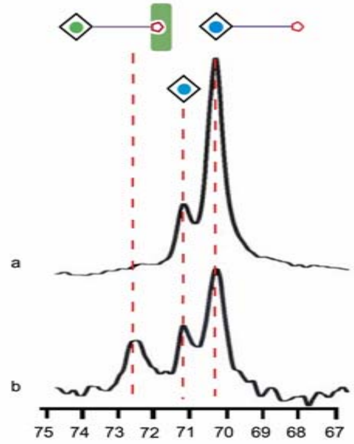




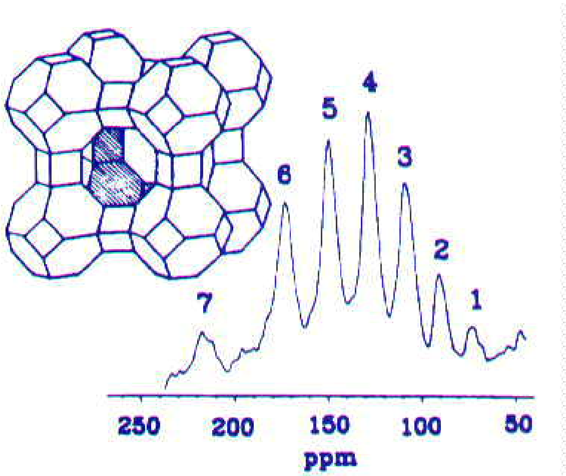




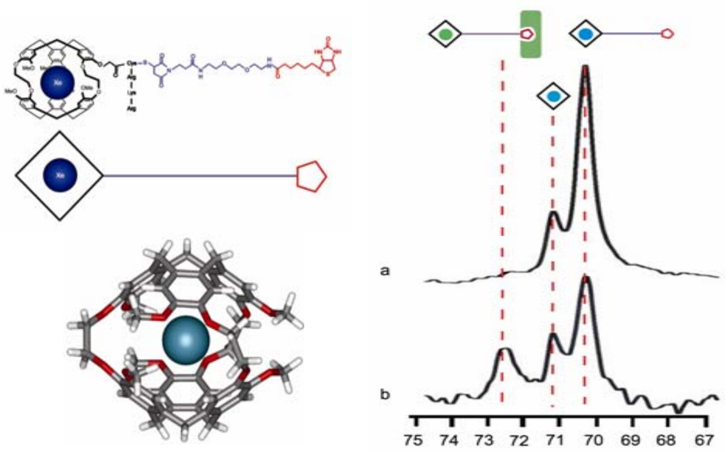




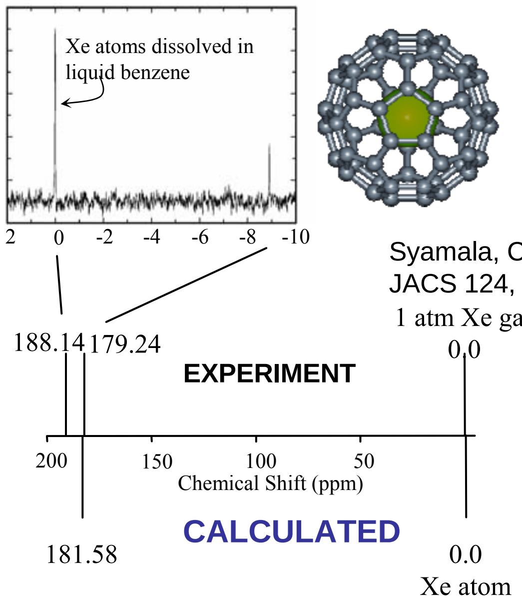
Applications of Xe NMR



C. J. Jameson, A. K. Jameson, R. Gerald, A. C. de Dios, J. Chem. Phys. 97, 417 (1992).

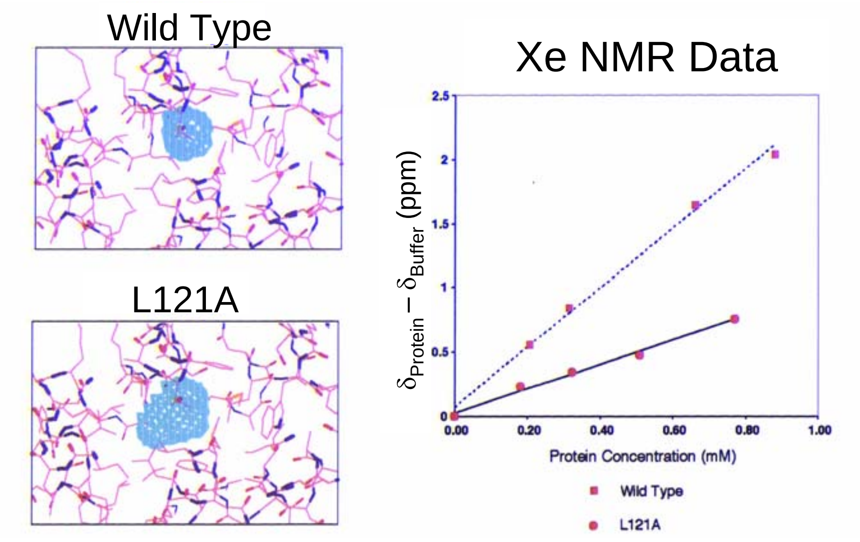


M.M. Spence, S.M. Rubin, I.E. Dimitrov, E.J. Ruiz, D.E. Wemmer, A. Pines, S.Q. Yao, F. Tian, and P.G. Schultz Proc. Nat. Acad. Sci. 98, 10654-10657 (2001)

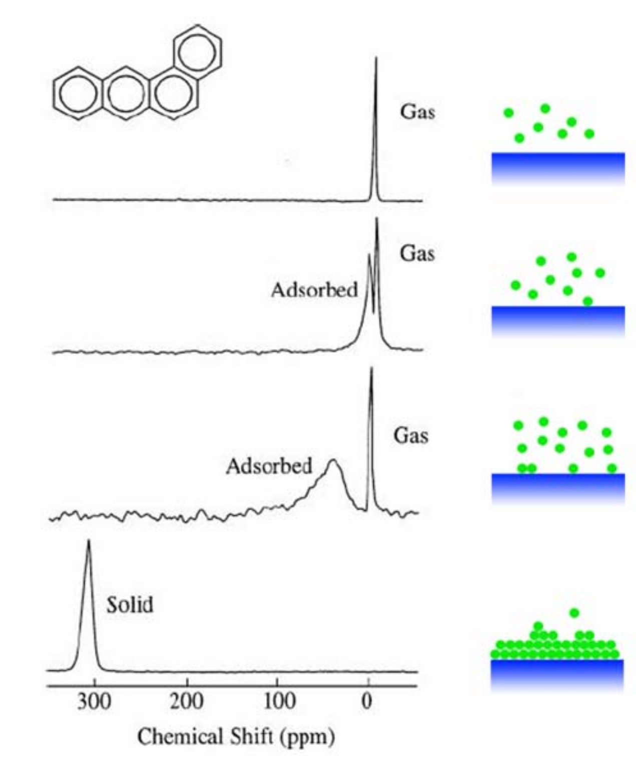


Syamala, Cross, Saunders
JACS 124, 6216 (2002)

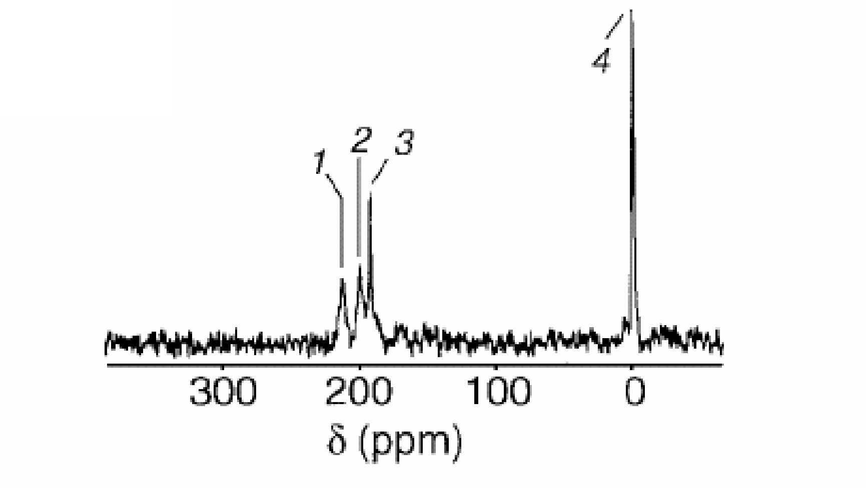
D. N. Sears and C. J. Jameson
J. Chem. Phys. **118** (23) Jun 15 (2003)



S.M. Rubin, M.M. Spence, B.M. Goodson, D.E. Wemmer, A. Pines.
Proc. Natl. Acad. Sci. **97** (17) 9472-9475 (2000)



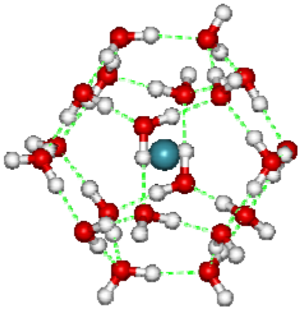
D. Raftery, H. Long, T. Meersmann, P.J. Grandinetti, L. Raven, and A. Pines. Phys. Rev. Lett. **66**, 584 (1991).



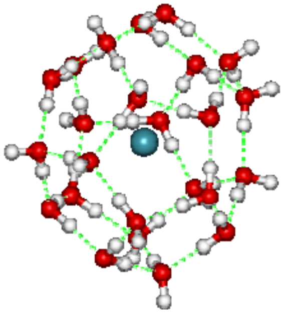
^{129}Xe NMR spectrum from the thorax of an anesthetized rat

1) red blood cells
2) lung tissue
3) blood plasma/ adipose tissue
4) Xe gas

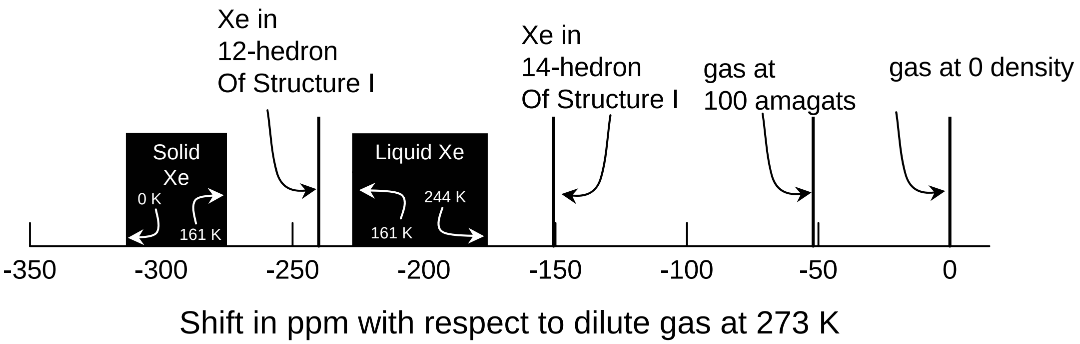
K. Sakai, A.M. Bilek, E. Oteiza, R.L. Walsworth, D. Balamore, F. Jolesz, and M.S. Albert. J. Magn. Reson. B **111**, 300-304 (1996).



Xe in
12-hedron
Of Structure I

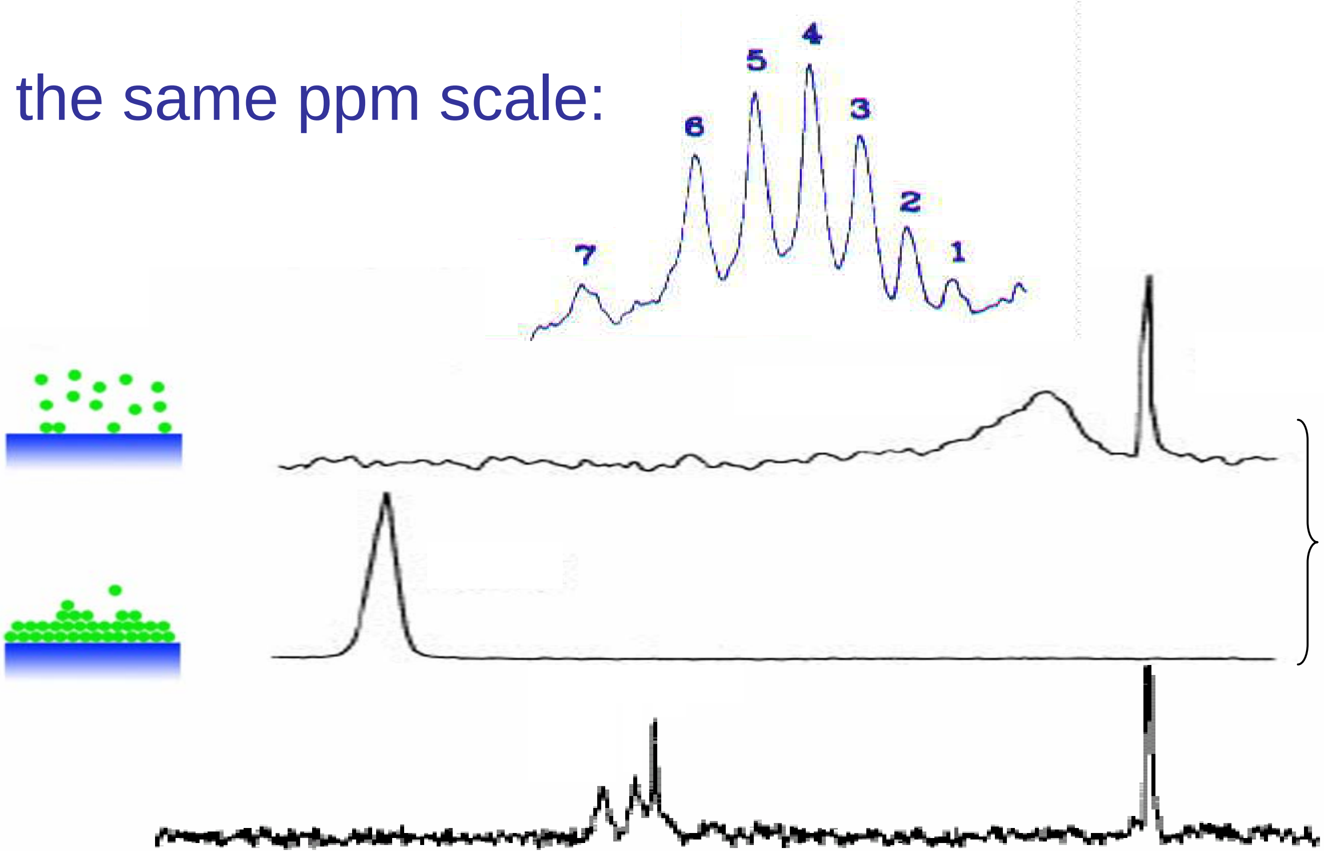


Xe in
14-hedron
Of Structure I



J. A. Ripmeester and D. W. Davidson
J. Mol. Struct. **75** 67-72 (1981)

All on the same ppm scale:



Xe in zeolite NaA

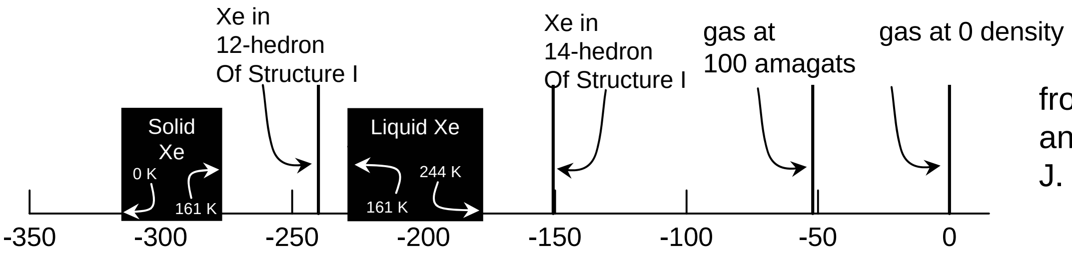
Xe on
benzanthracene

Xe in
rat thorax

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

Xe in pure solvents*

Xe in liquid solvents



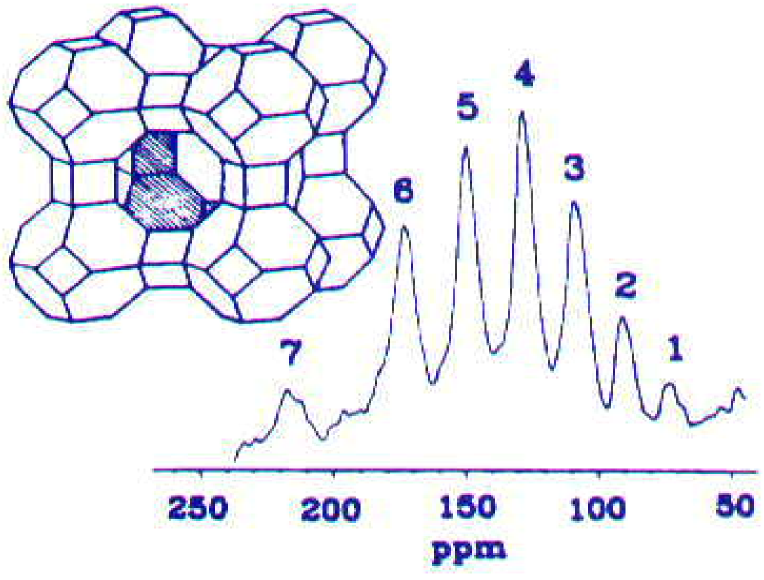
Shift in ppm with respect to dilute gas at 273 K

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

Understanding Xe chemical shifts in various environments

- Xe in mixtures of gases
- Xe in cages: C_{60}, cryptophanes
- Xe in helices: a model of induced chirality
- Xe in hydrogen-bonded networks: clathrate hydrates
- Xe in nanochannels: $ALPO_4$-11, SSZ-24, TPP
- Xe in a single crystal of silicalite
- Xe on model surfaces
- Future work

Intermolecular chemical shifts



- The SHIELDING SURFACE: the shielding as a function of configuration (coordinates) of the system
- The PROBABILITY of finding the system in a given configuration

Xe in mixtures of gases

The model system is the same as the physical system. Direct comparison with experiment is possible when the potential function is well known from

molecular beam scattering,
van der Waals spectroscopy,
and thermophysical properties.

EXAMPLES:

- Xe-Xe, Kr, Ar
- Xe-CO_2

Second Virial Coefficient of Shielding, $\sigma_1(T)$

Xe in gas phase mixtures:

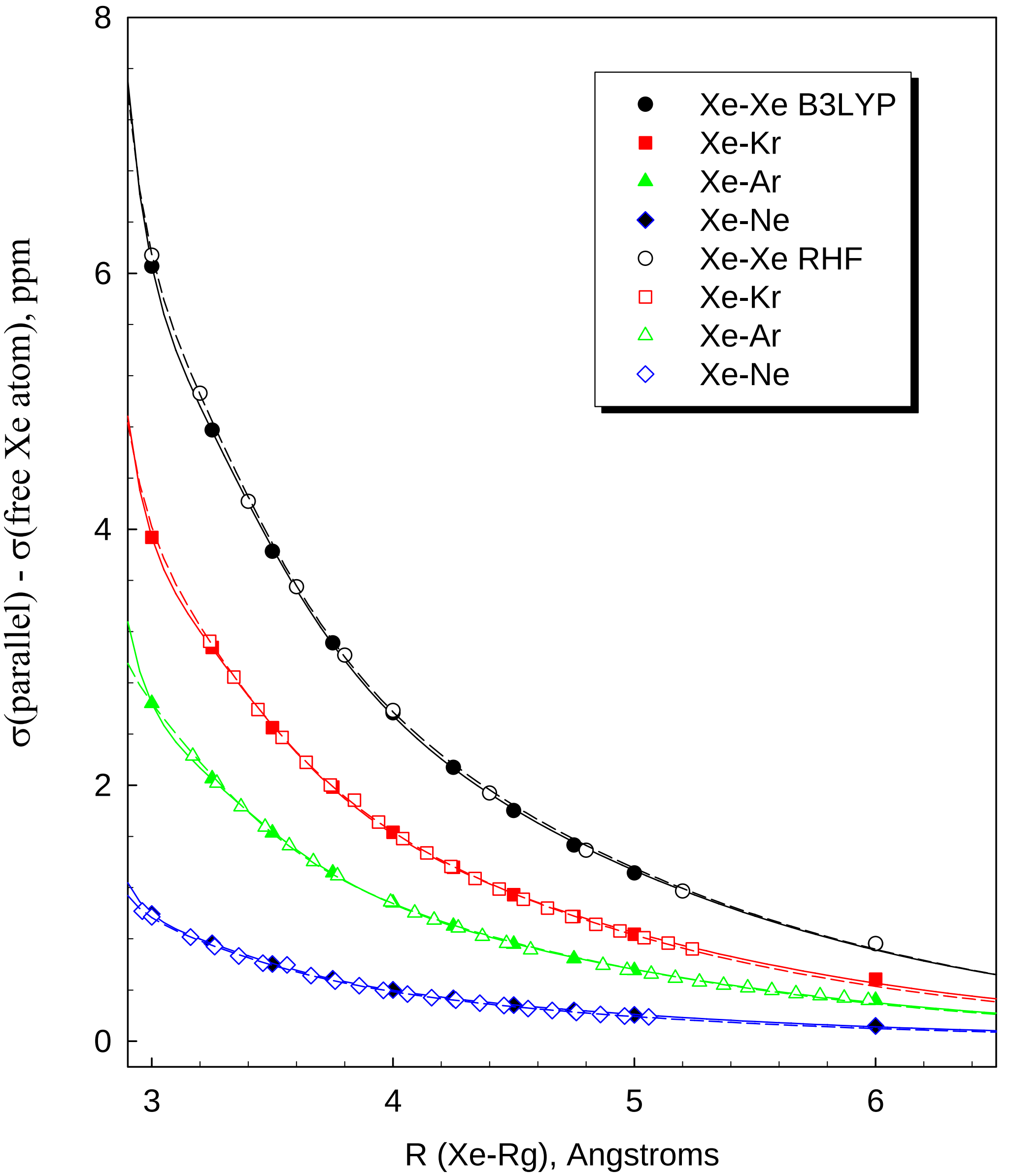
$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)_{\mathrm{XeXe}}\rho_{\mathrm{Xe}} + \sigma_1(T)_{\mathrm{XeRg}}\,\rho_{\mathrm{Rg}} + \sigma_2(T)_{\mathrm{XeXe}}\rho_{\mathrm{Xe}}^2 + \ldots$$

$$\sigma_1(T)_{\mathrm{XeRg}} = 4\pi \int_0^\infty \underbrace{\{\sigma(R) - \sigma(\infty)\}}_{\text{SHIELDING SURFACE}}\ \underbrace{e^{-V(R)/kT}}_{\text{PROBABILITY}}\, R^2\, dR$$

$V(R)$ = Xe–rare gas potential function

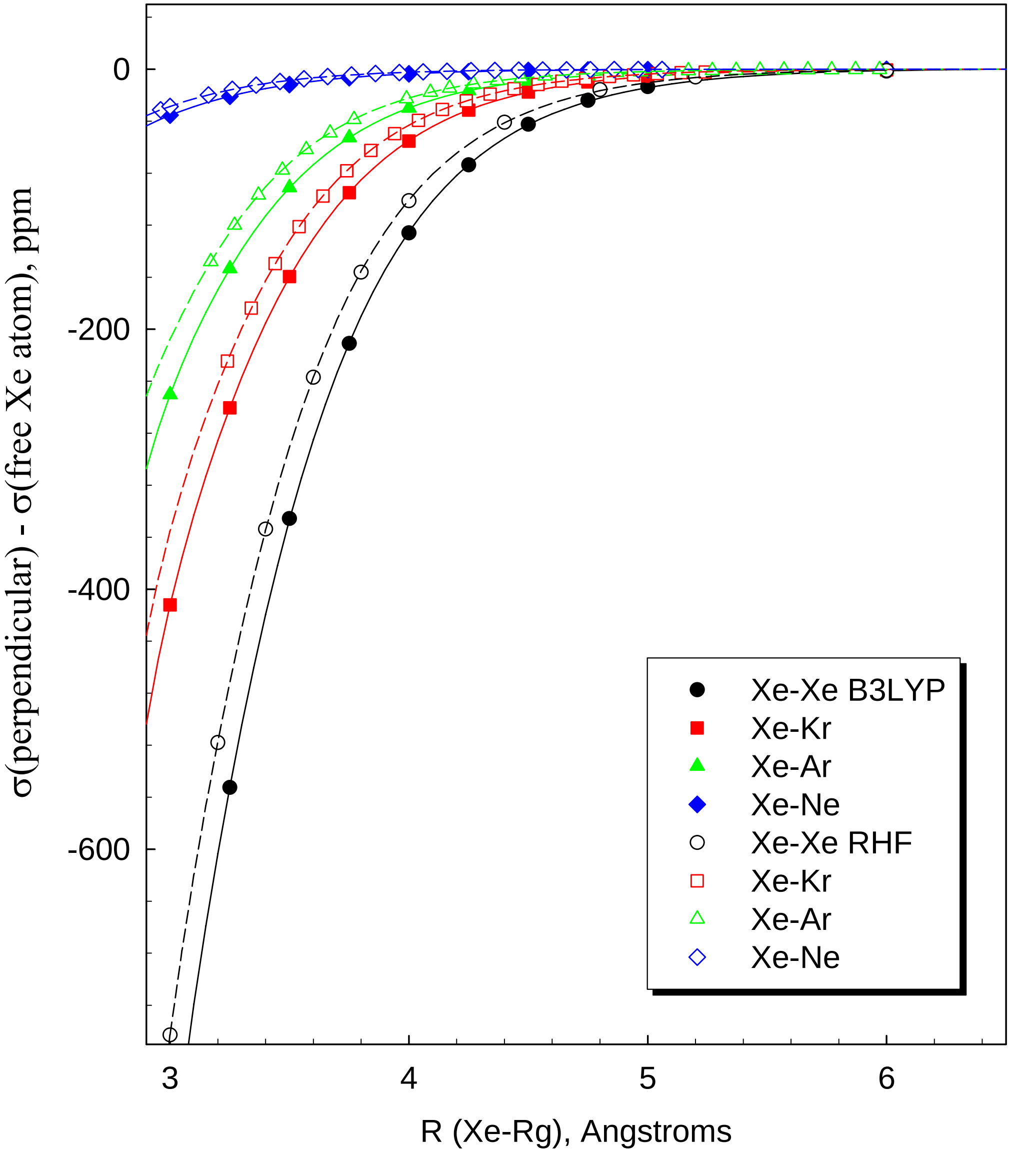
Jameson et al. 1970

Xe Shielding Tensors: Parallel Components



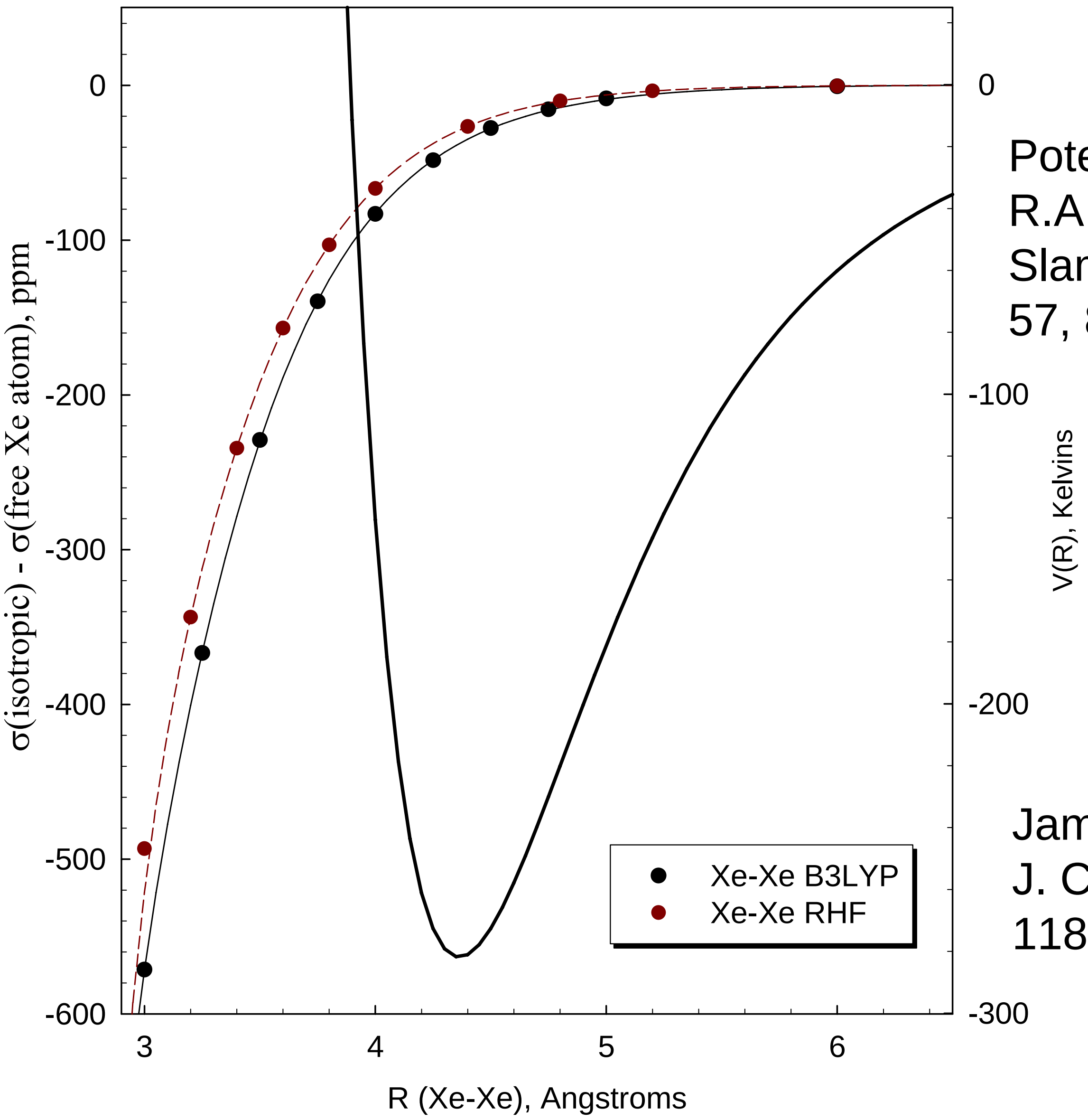
Jameson et al.
J. Chem. Phys.
118, 2575 (2003)

Xe Shielding Tensors: Perpendicular Components



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

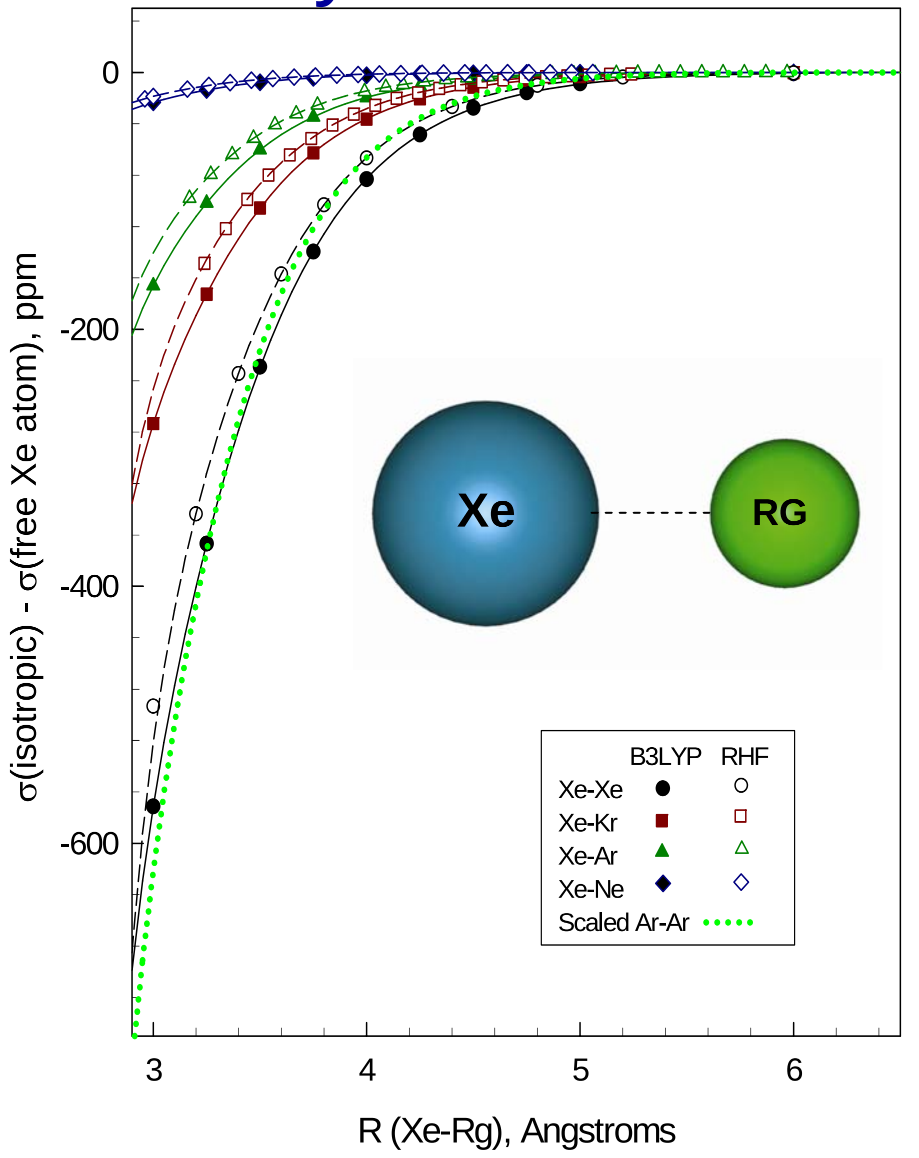
Xe Shielding Function σ(R) and Potential Function V(R) for the Xe-Xe System

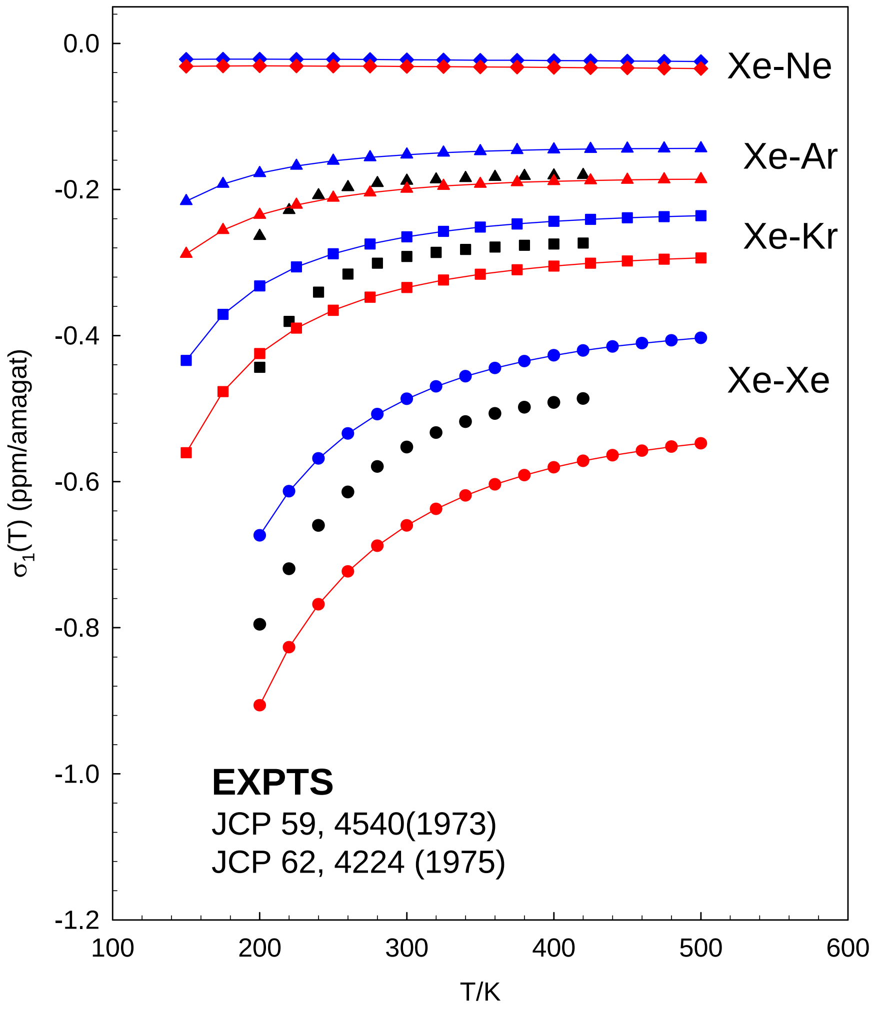


Potential function:
R.A. Aziz and M.J. Slaman, Mol. Phys. 57, 825 (1986)

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

Density coefficients of Xe-Rare gas shielding





$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\ \rho + \sigma_2(T)\ \rho^2 + \text{✪}$$

$$\sigma_1(T) = 4\square\int_0^{\infty} \{\sigma(R) - \sigma(\text{◎})\}\ e^{-V(R)/kT}\ R^2 dR$$

Calculations: Jameson et al, JCP 118, 2575 (2003)

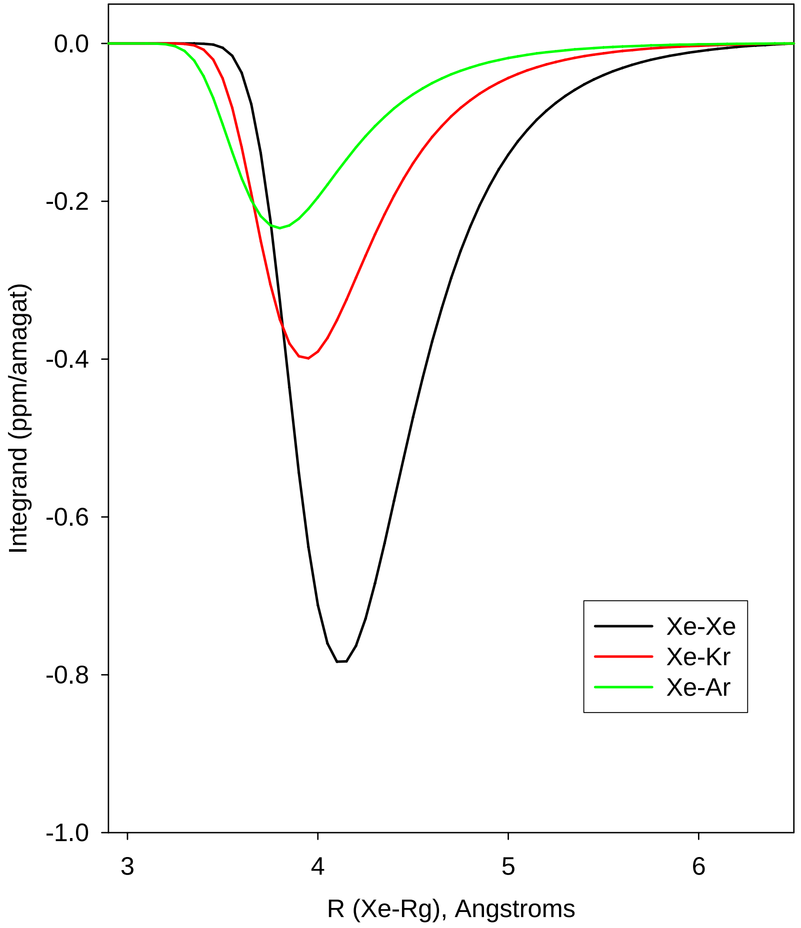
Scaling: Jameson and de Dios, JCP 97, 417 (1992)

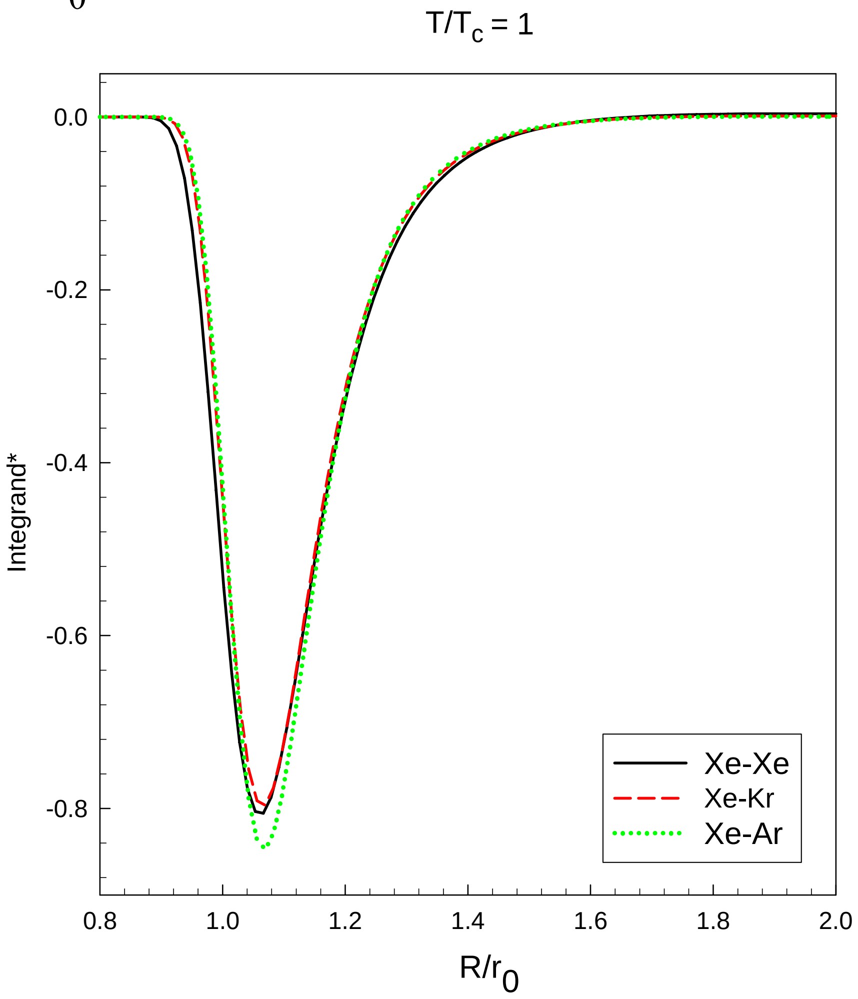
$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\,\rho + \sigma_2(T)\,\rho^2 + \text{✪}$$

SCALING:

corresponding states

$$\sigma_1(T) = 4\square\int_0^\infty \{\sigma(r) - \sigma(\circledcirc)\}\, e^{-V(r)/kT}\, r^2\, dr$$





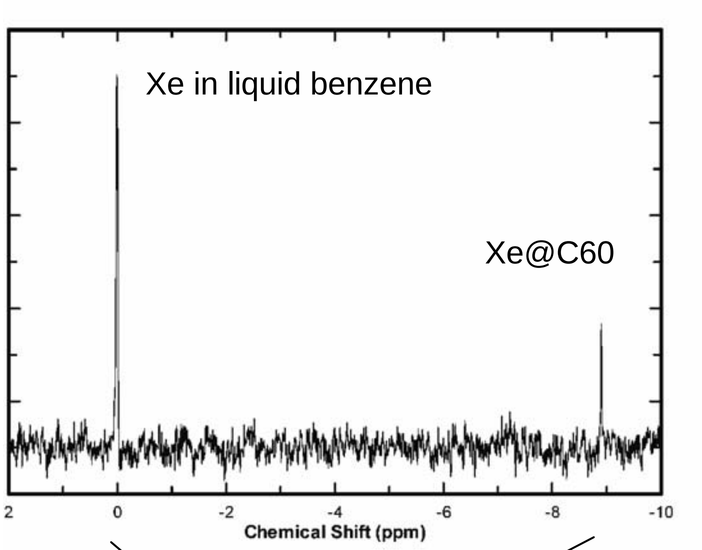
Integrand* stands for scaled values using the scaling factor $\{[\alpha_{Xe}(0)/\alpha_{Rg}(0)]\bullet[IP_{Xe}/IP_{Rg}]\bullet[(IP_{Xe}+IP_{Rg})/2IP_{Xe}]\}^*\sigma(r)$

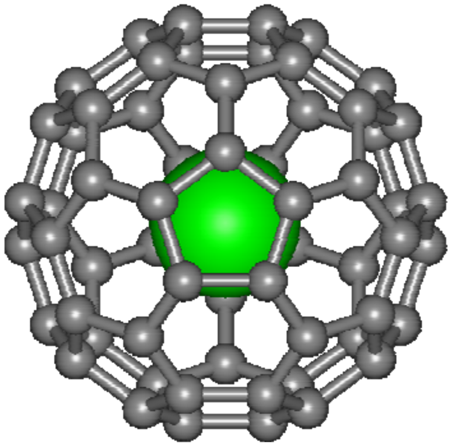
Xe in cages

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

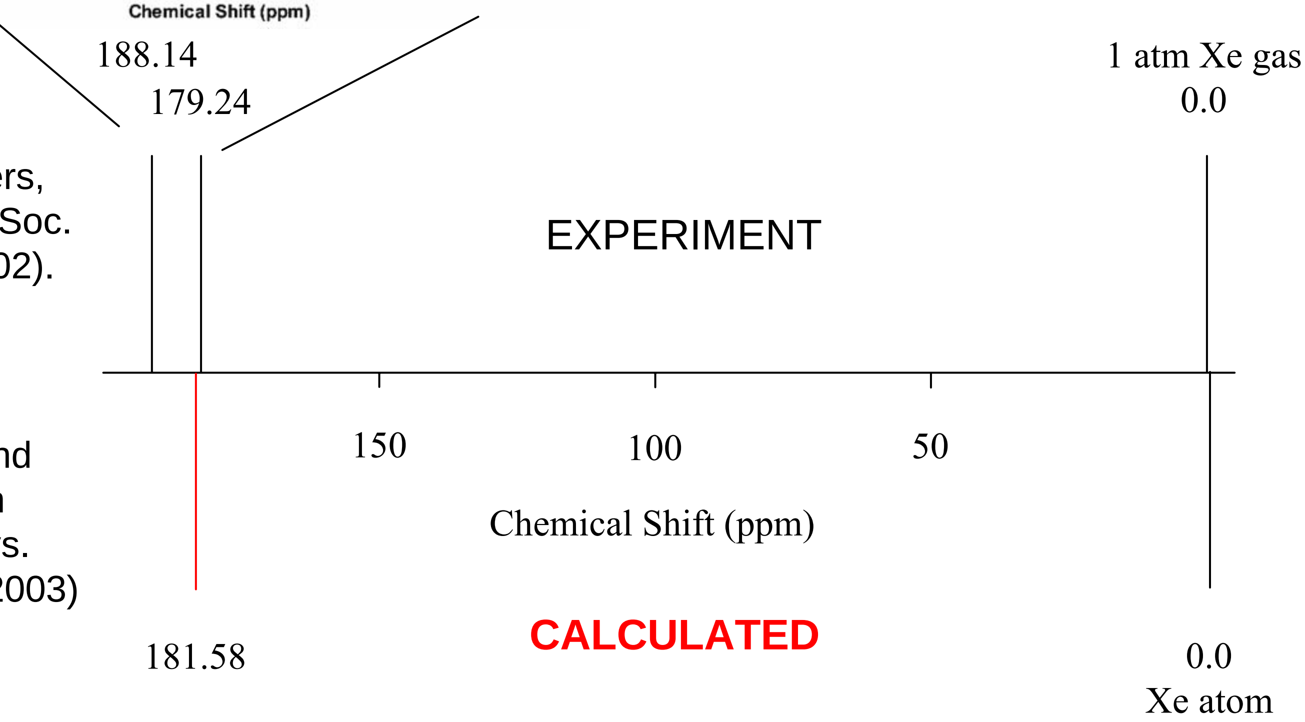
- architecture of the cage: size, shape
- hydrogen-bonding network
- Madelung potential of the crystal
- aromatic rings
- vibrational, other dynamics of the cage atoms
- electronic structure of the cage: availability of electrons that can elicit a shielding response

Xe@C_{60}





M.S.Syamala,
R.J.Cross,
and M.Saunders,
J. Am. Chem. Soc.
124, 6216 (2002).



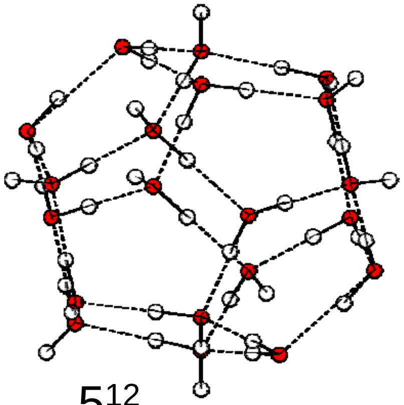
D.N. Sears and
C.J. Jameson
J. Chem. Phys.
118 (23)xxx(2003)

Xe in the cages of clathrate hydrates Structure I and II

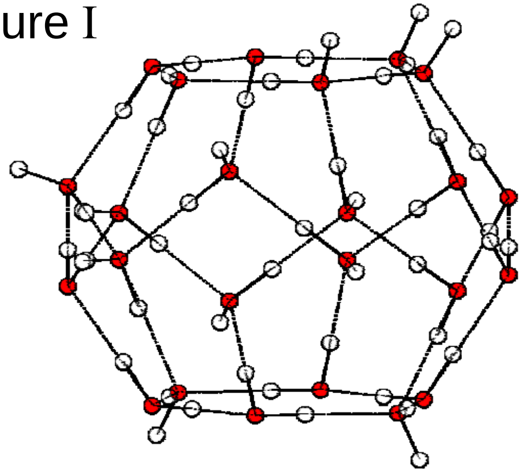
- a hydrogen-bonded network
- disordered proton configurations, yet must obey ice rules
- additive pair tensor model

the cages

Structure I

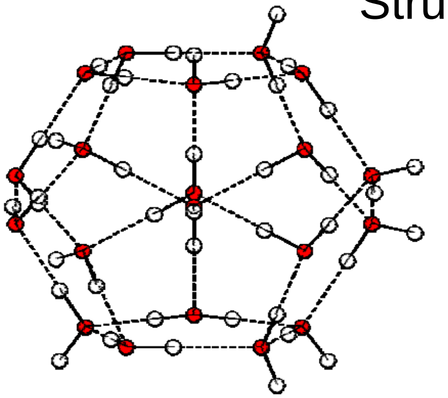


5^{12}

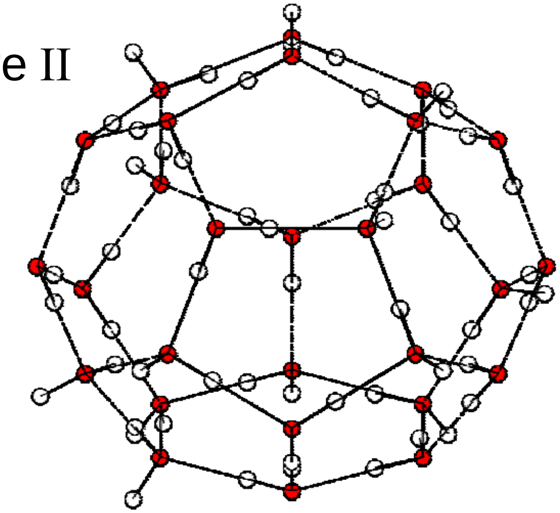


$5^{12}\,6^{2}$

Structure II



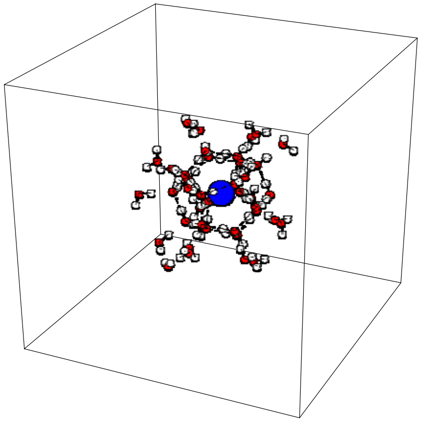
5^{12}



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

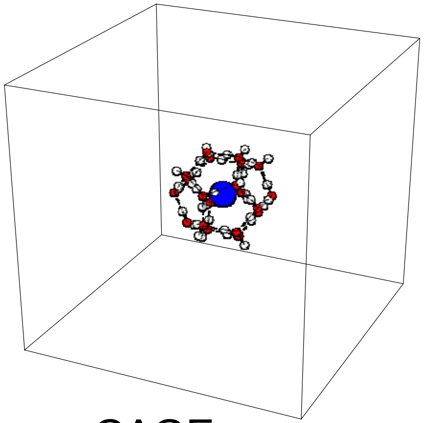
How to model a cage in a hydrogen bonded network?

- Generate crystal fragment by replicating 1 unit cell with a valid proton configuration: 47.93 Å on the side, 4x4x4 unit cells, 2944 water molecules

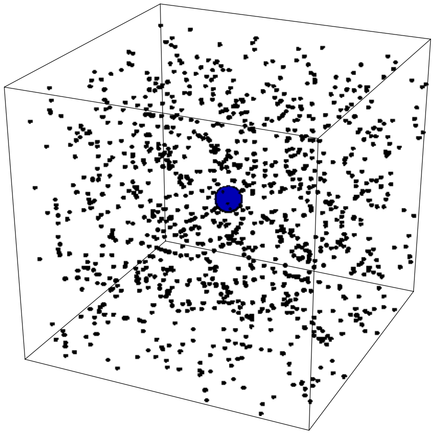


XCAGE

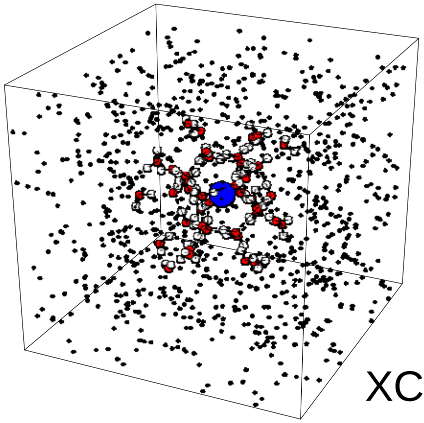
MODELS



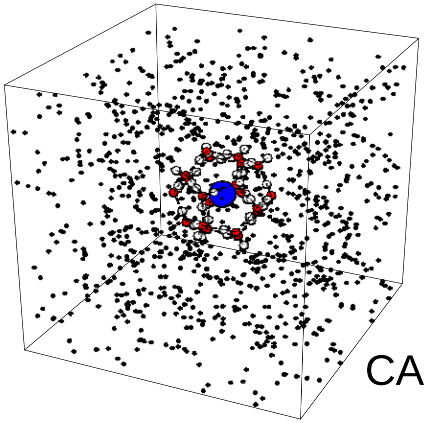
CAGE



PCA



XCAGE/PCA



CAGE/PCA

Xe shielding from electrostatics

σ_{iso}(Xe at center of model) $-\sigma$(free Xe atom)

PCA	**CAGE**	**XCAGE**	**CAGE/PCA**	**XCAGE/PCA**
-0.4 ppm HF	-142.1	-138.2	-114.0	-119.4
-0.5 ppm DFT/B3LYP	-226.6	-217.0	-184.9	-199.4

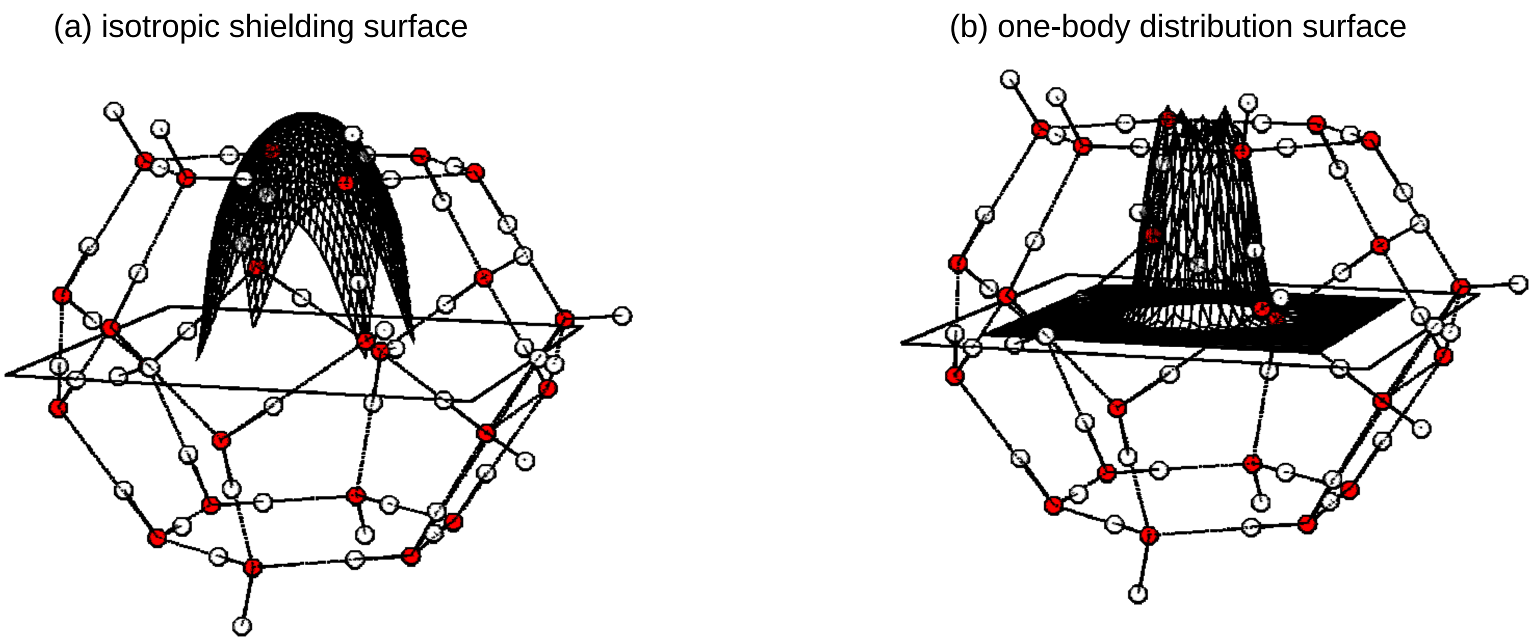
↑

purely electrostatic

for 5^{12} cage in Structure I

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

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

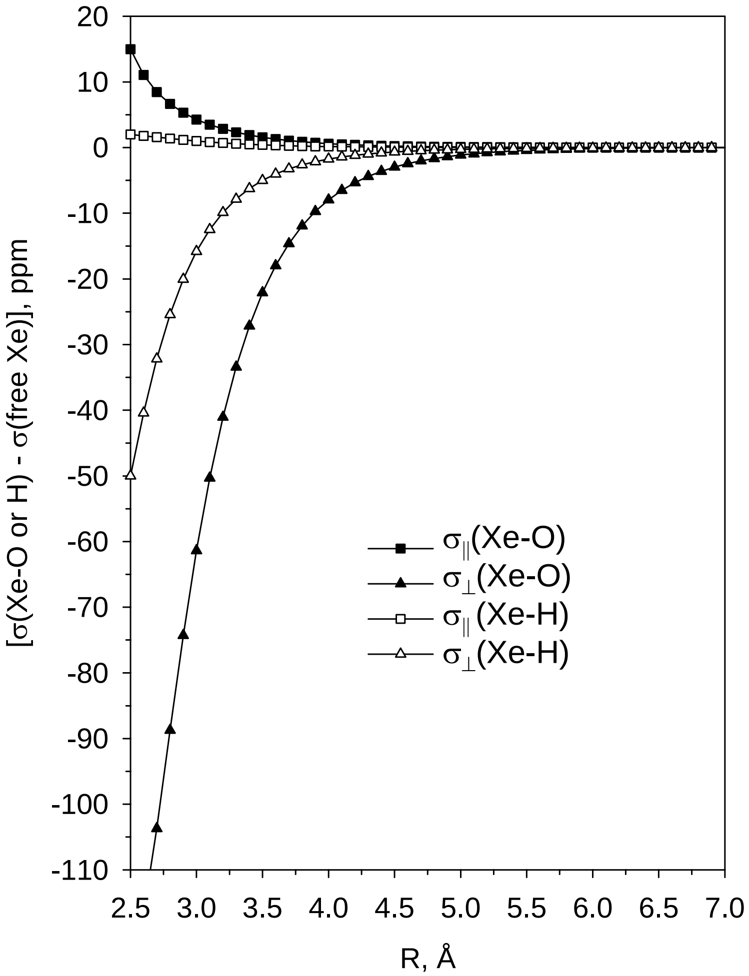


(a) isotropic shielding surface

(b) one-body distribution surface

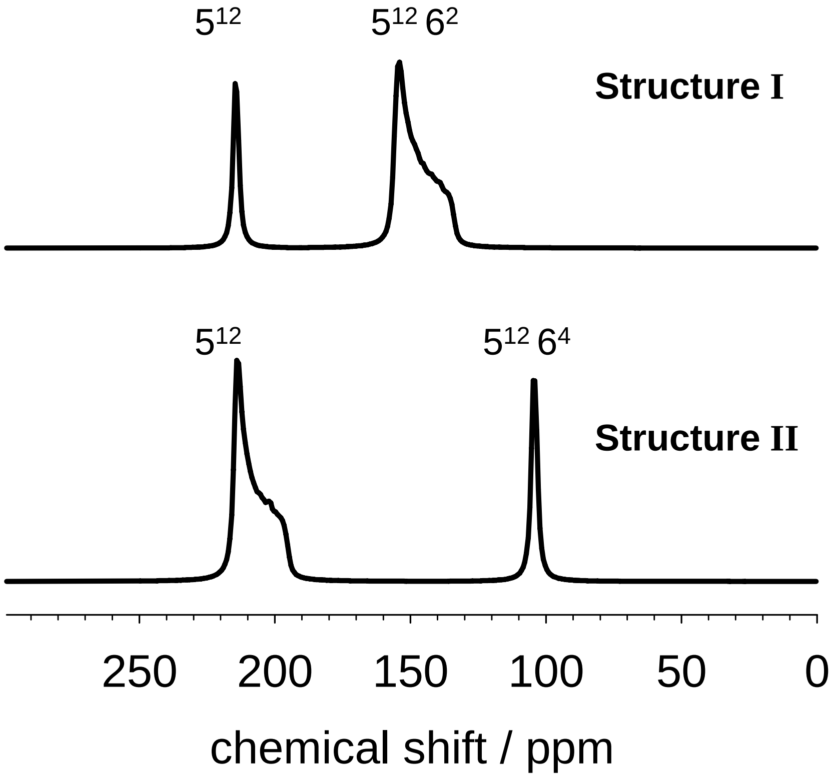
Xe in the $5^{12}6^{2}$ cage of clathrate hydrate Structure I

The Xe-O and Xe-H shielding tensors



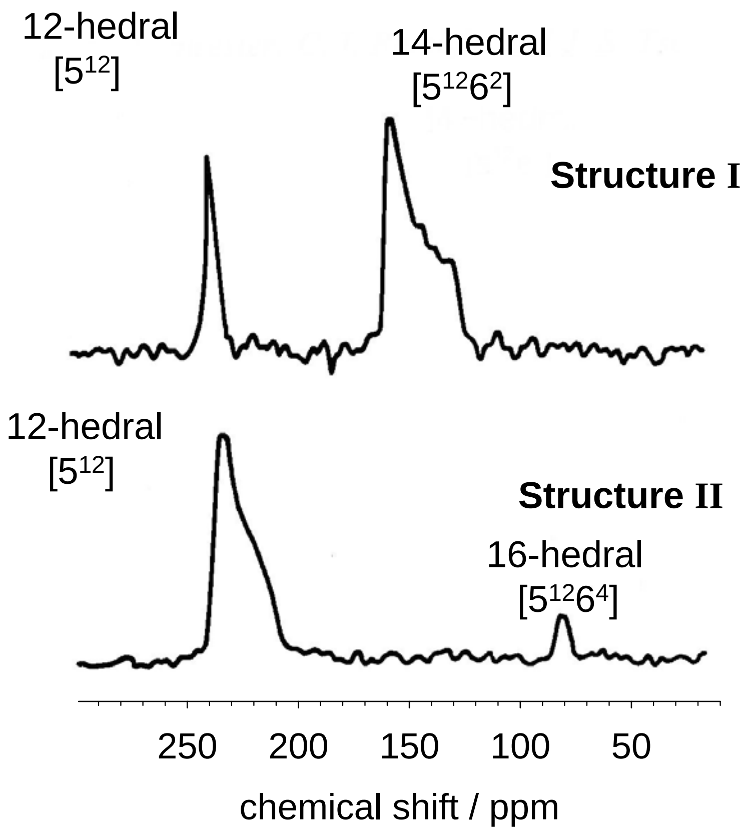
Sums over pair shielding functions
reproduce the ab initio Xe shielding tensor
at each Xe position within the extended cage

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



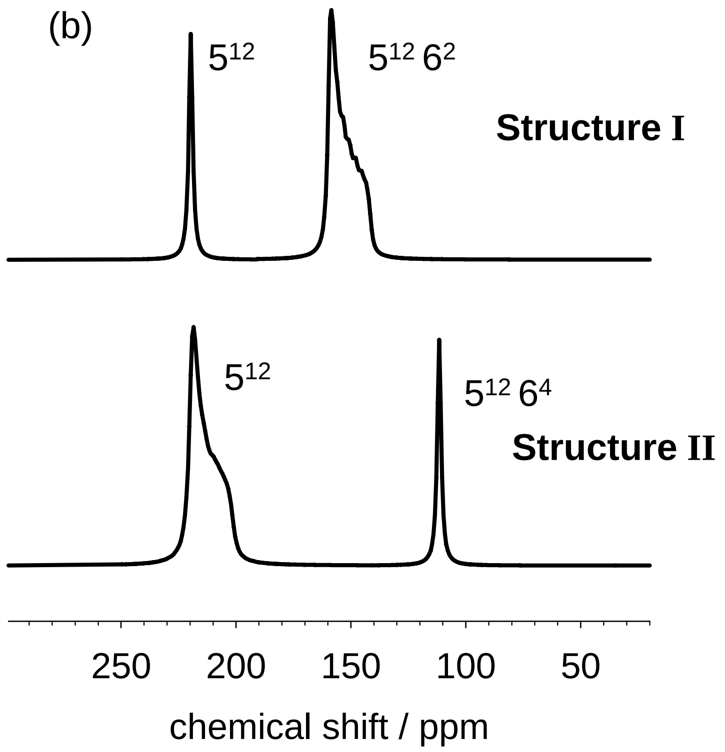
using
the same Xe-O and Xe-H shielding tensor functions,
the same Xe-O and Xe-H potential functions

Xe in the cages of clathrate hydrates Structure I and II



EXPERIMENTS

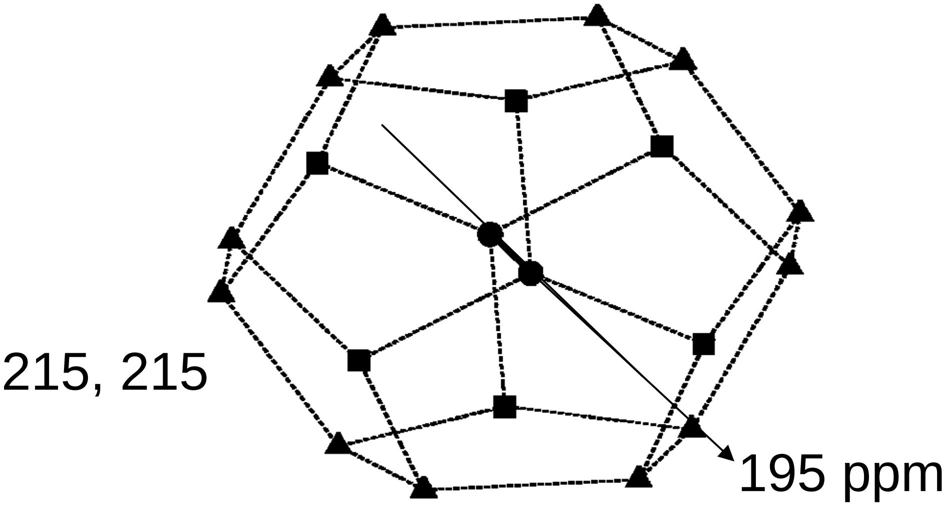
J. A. Ripmeester, C. I. Ratcliffe and J. S. Tse, Trans. Faraday Soc. 1, 84, 3731 (1988)



CALCULATIONS

Monte Carlo simulations in a
4x4x4 supercell and 2x2x2 supercell
D. Stueber and C. J. Jameson, 2003

Xe chemical shift tensor in Structure II



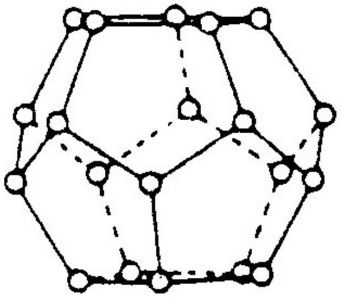
5^{12}

- number of unique components
- magnitudes
- directions of the principal axes (in the crystal frame)

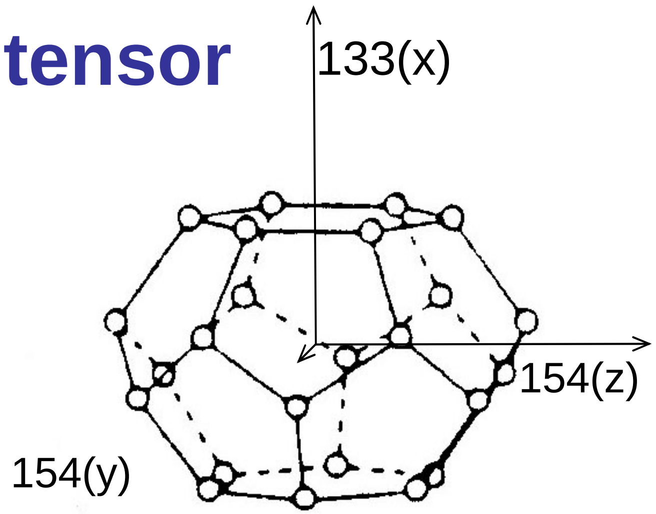
can be determined for the average Xe chemical shift tensor

Xe chemical shift tensor

isotropic 214

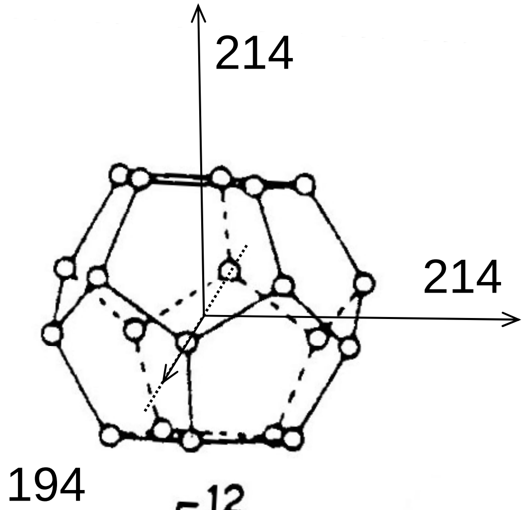


5^{12}



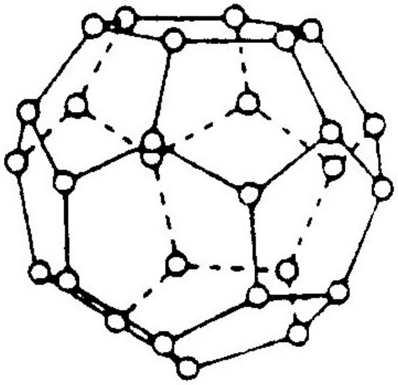
$5^{12}6^{2}$

Clathrate Structure I



5^{12}

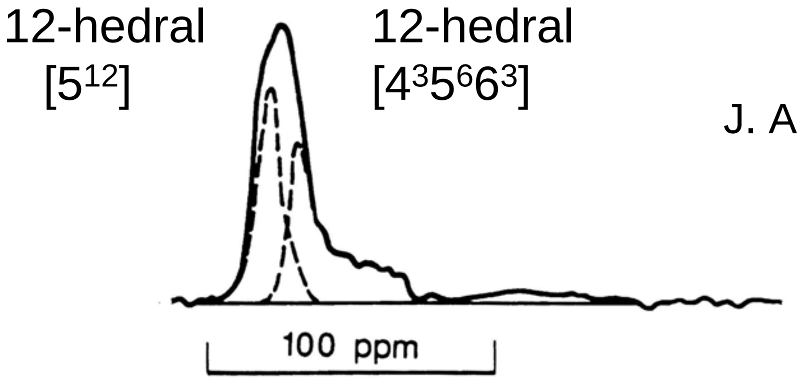
isotropic 105



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

Clathrate Structure II

Xe in clathrate hydrate Structure H



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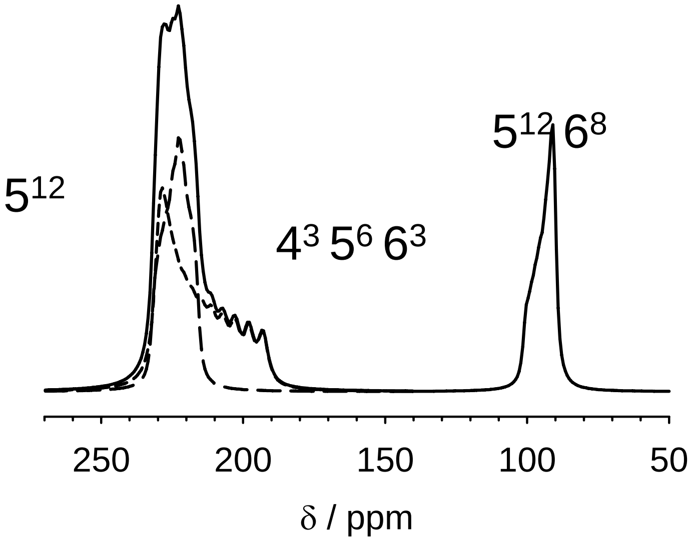
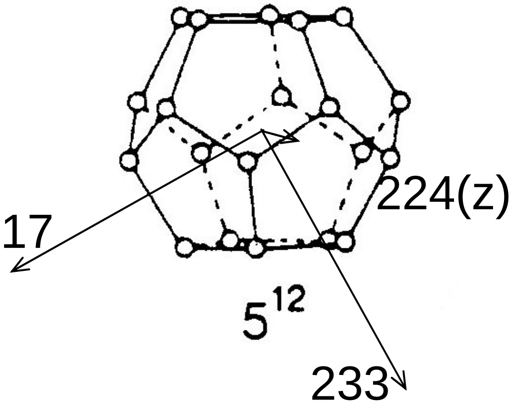
J. A. Ripmeester, C. I. Ratcliffe and J. S. Tse,
Trans. Faraday Soc. 1, 84, 3731 (1988)



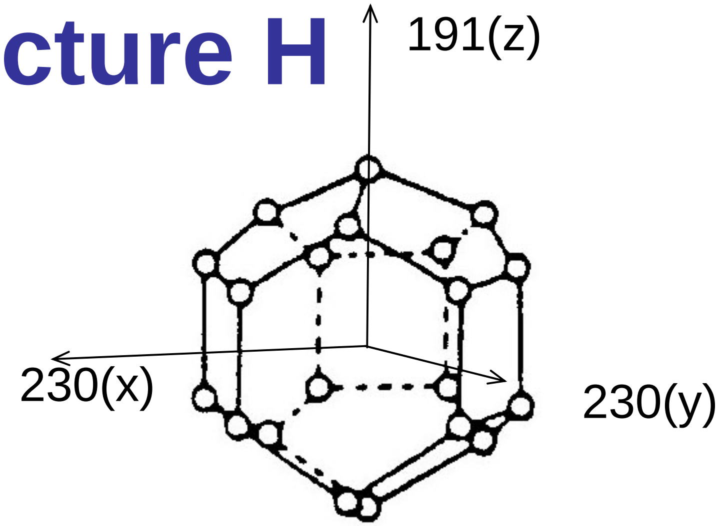
CALCULATIONS

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

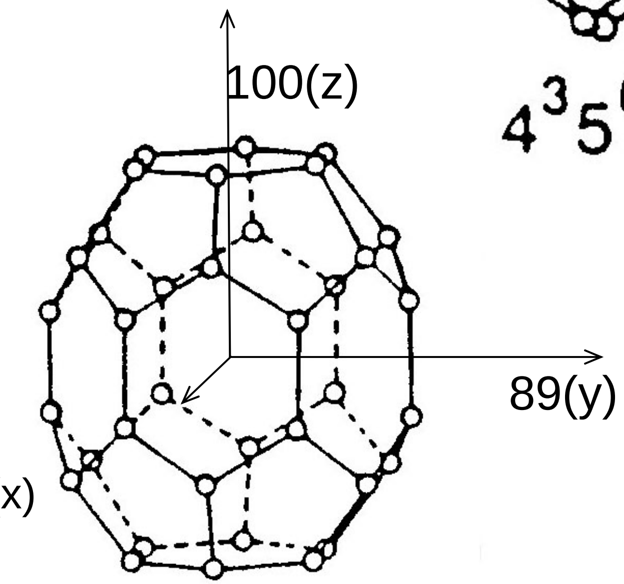
Xe tensor in Clathrate Structure H



5^{12}



$4^3 5^6 6^3$

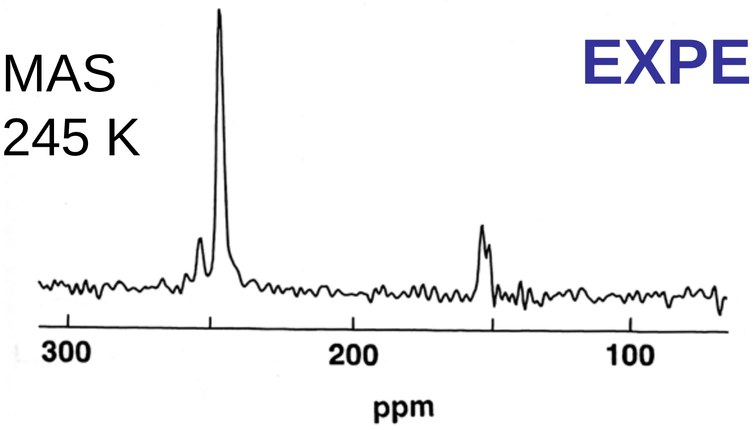


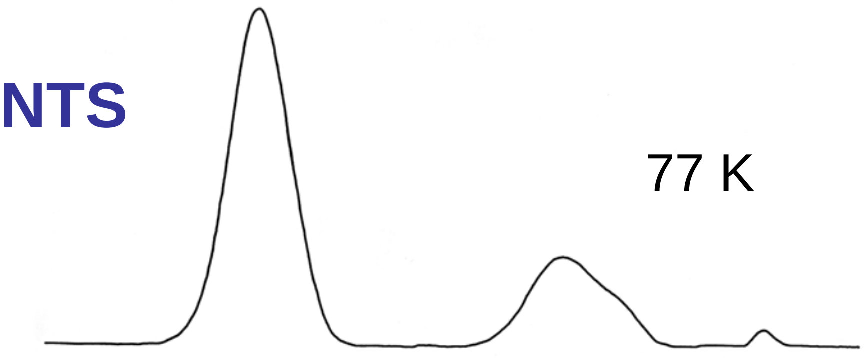
$5^{12} 6^8$

Xe in bromine hydrate

EXPERIMENTS

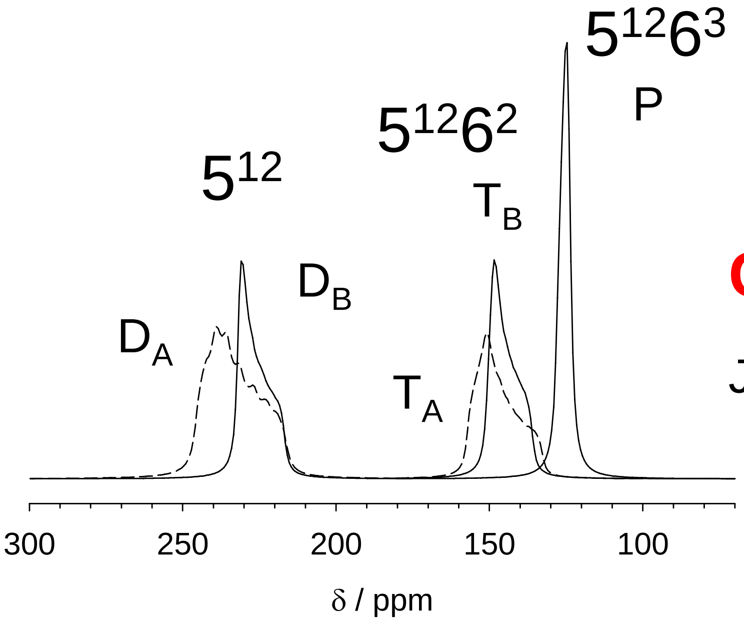
MAS
245 K





77 K

Udachin, Enright, Ratcliffe, Ripmeester
J. am. Chem. Soc. 119, 11481 (1997)

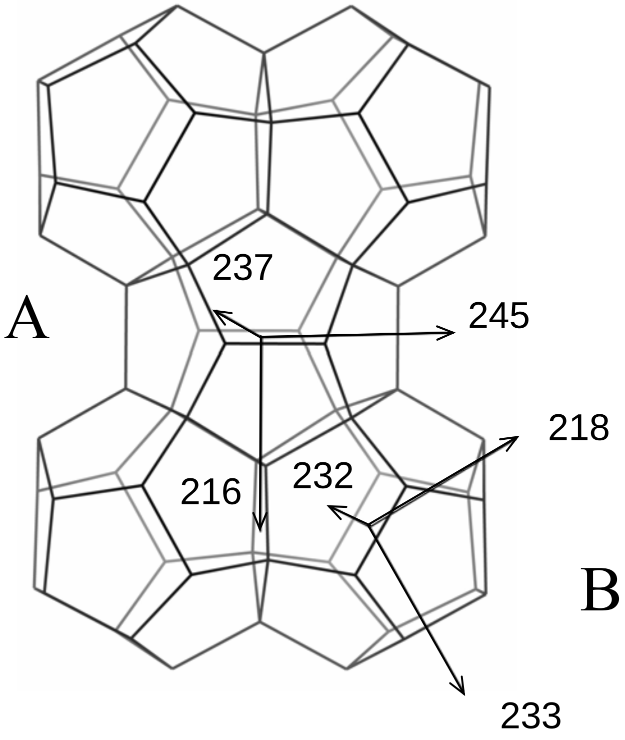


CALCULATIONS

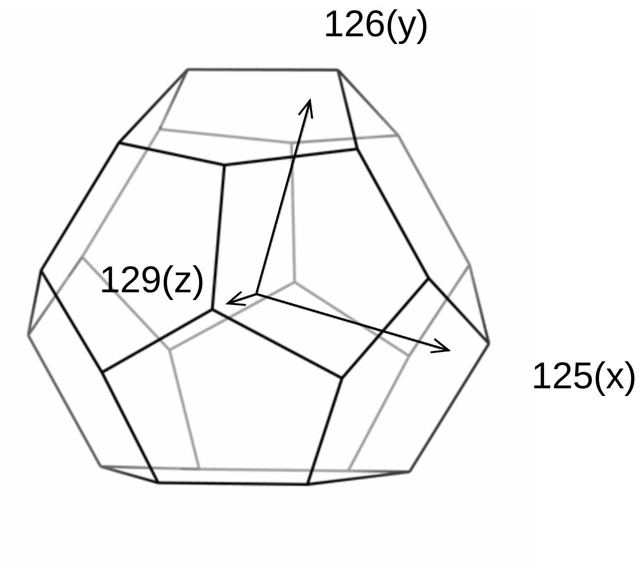
Jameson and Stueber, 2003

Xe tensors in bromine hydrate D_A, D_B, and P cage

5^{12}

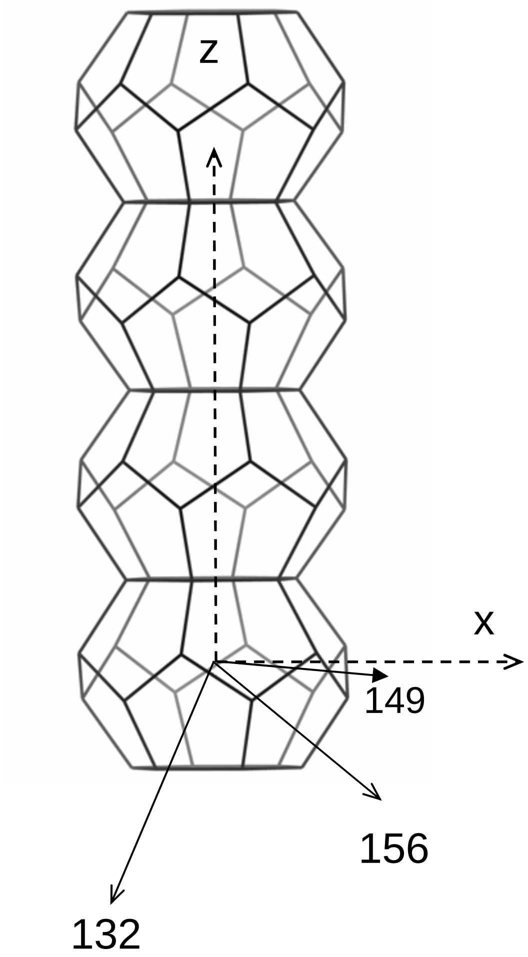


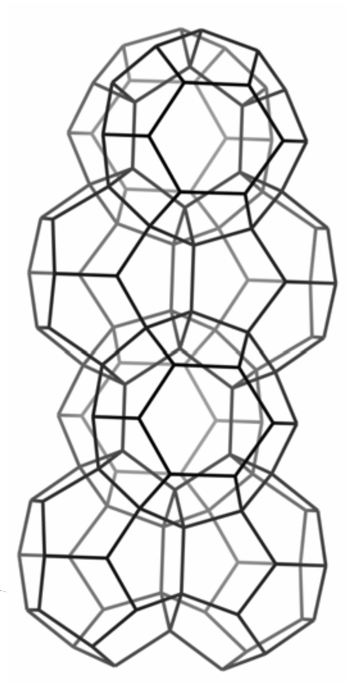
$5^{12}6^{3}$



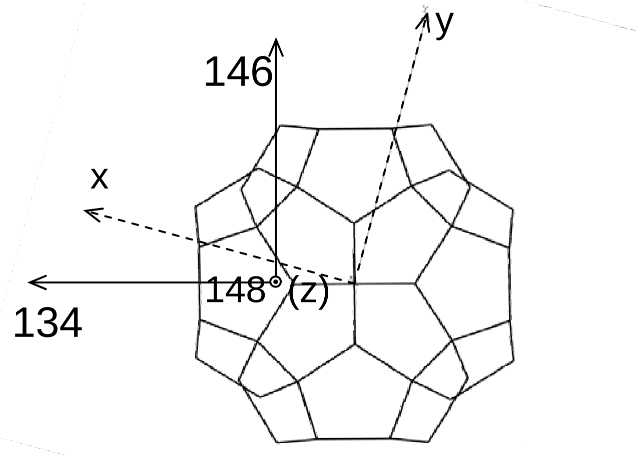
Bromine hydrate T_A and T_B cages

$5^{12}6^{2}$ - **A**



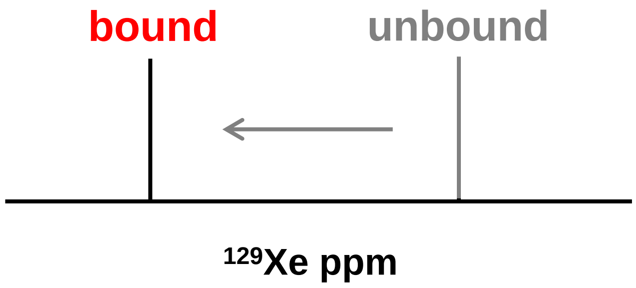


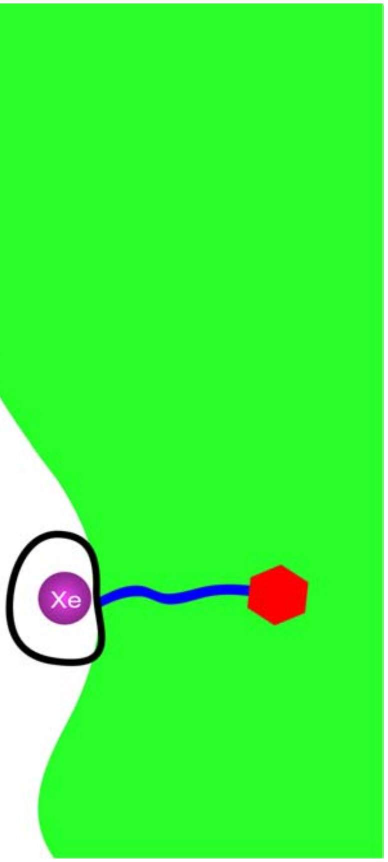
$5^{12}6^{2}$ - **B**



Xe as a biosensor

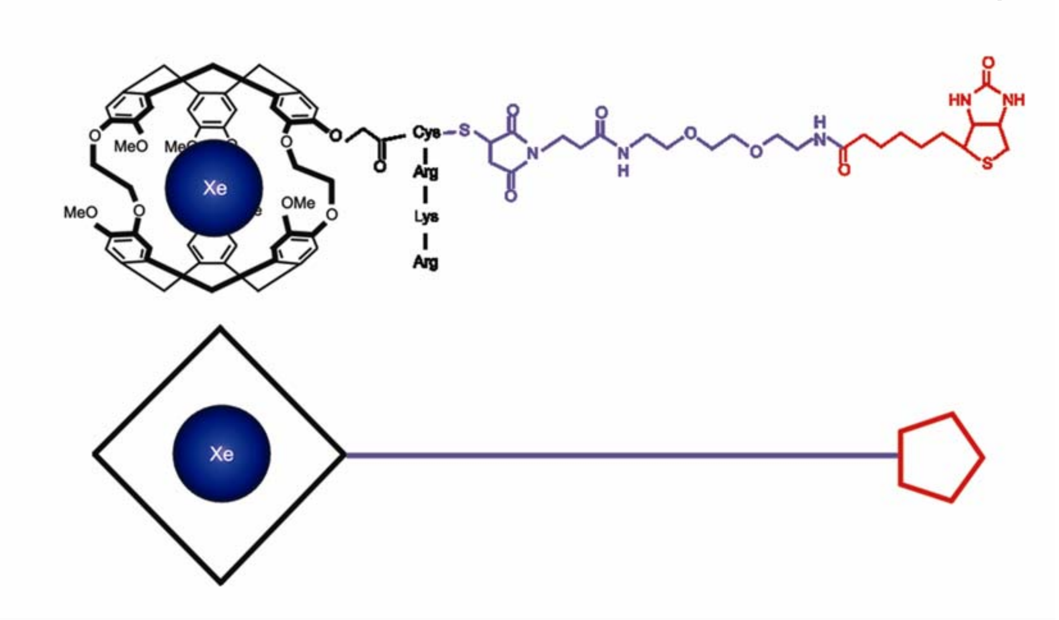
(Pines, Wemmer, et al. 2001)

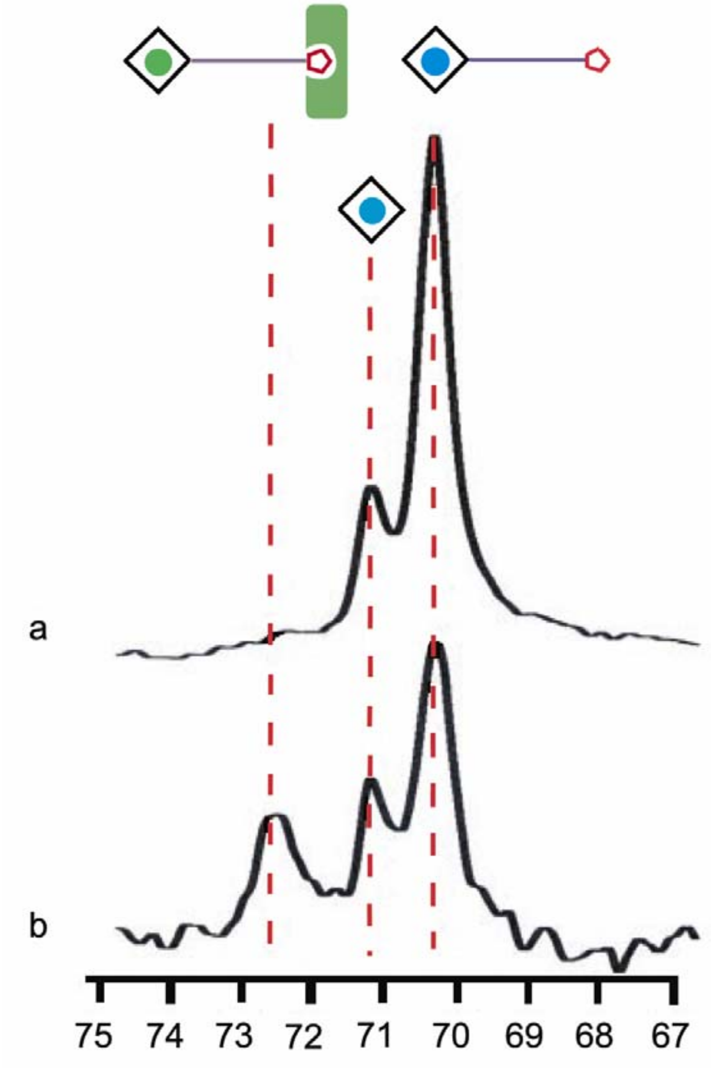




This slide courtesy of E. Janette Ruiz

MOTIVATION Xe as biosensor (Pines, Wemmer et al., 2001)



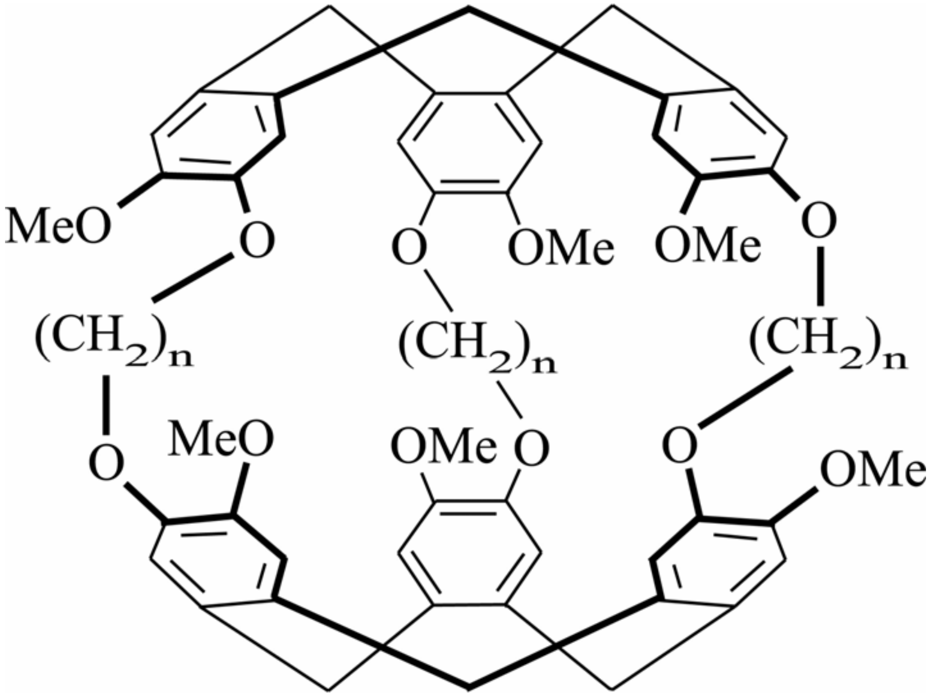


- Experiments on Xe in **cryptophane cages** provide **model systems** for comparison
- Unique cages A, 223, 332, and E
- Temperature dependence of Xe @cryptoA
- Xe isotope shifts upon deuteration of cage

M.M. Spence, S.M. Rubin, I.E. Dimitrov, E.J. Ruiz, D.E. Wemmer, A. Pines, S.Q. Yao, F. Tian, and P.G. Schultz Proc. Nat. Acad. Sci. **2001**, 98, 10654-10657.

The cryptophanes

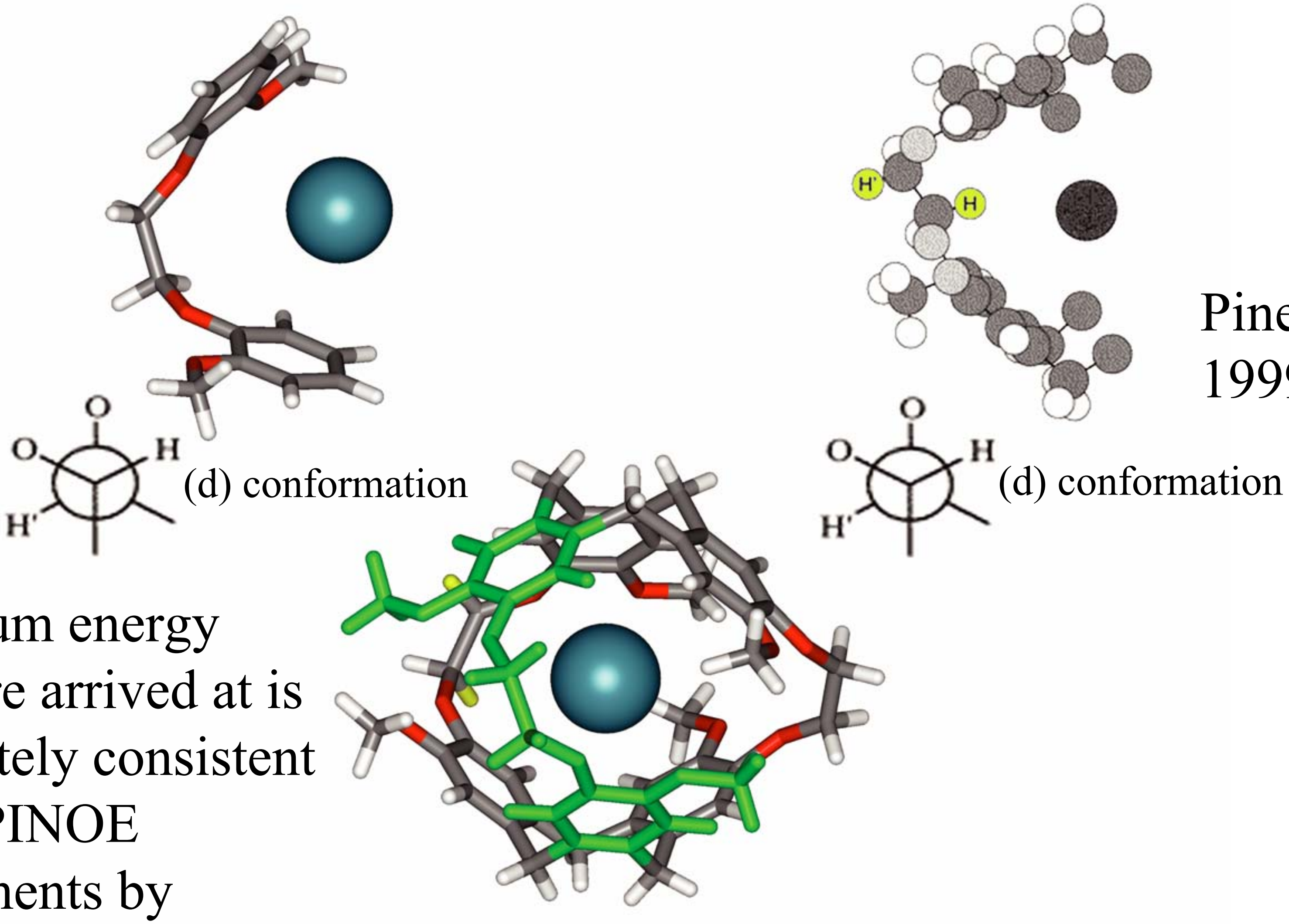
- Two cyclotriveratrylene bowls
- Connected by aliphatic linker $(CH_2)_n$
- n=2 Cryptophane-A (cryptoA)
- n=3 Cryptophane-E (cryptoE)
- n=2,2,3 Cryptophane-223
- n=2,3,3 Cryptophane-233



To calculate average Xe chemical shifts we need:

- Solution structures of cryptophanes-A, -223, -233, and -E
- Suitable fragment for *ab initio* calculations of xenon shielding surface
- Reasonable set of potential functions

The average structure of Xe@cryptoA to be used for Monte Carlo simulations

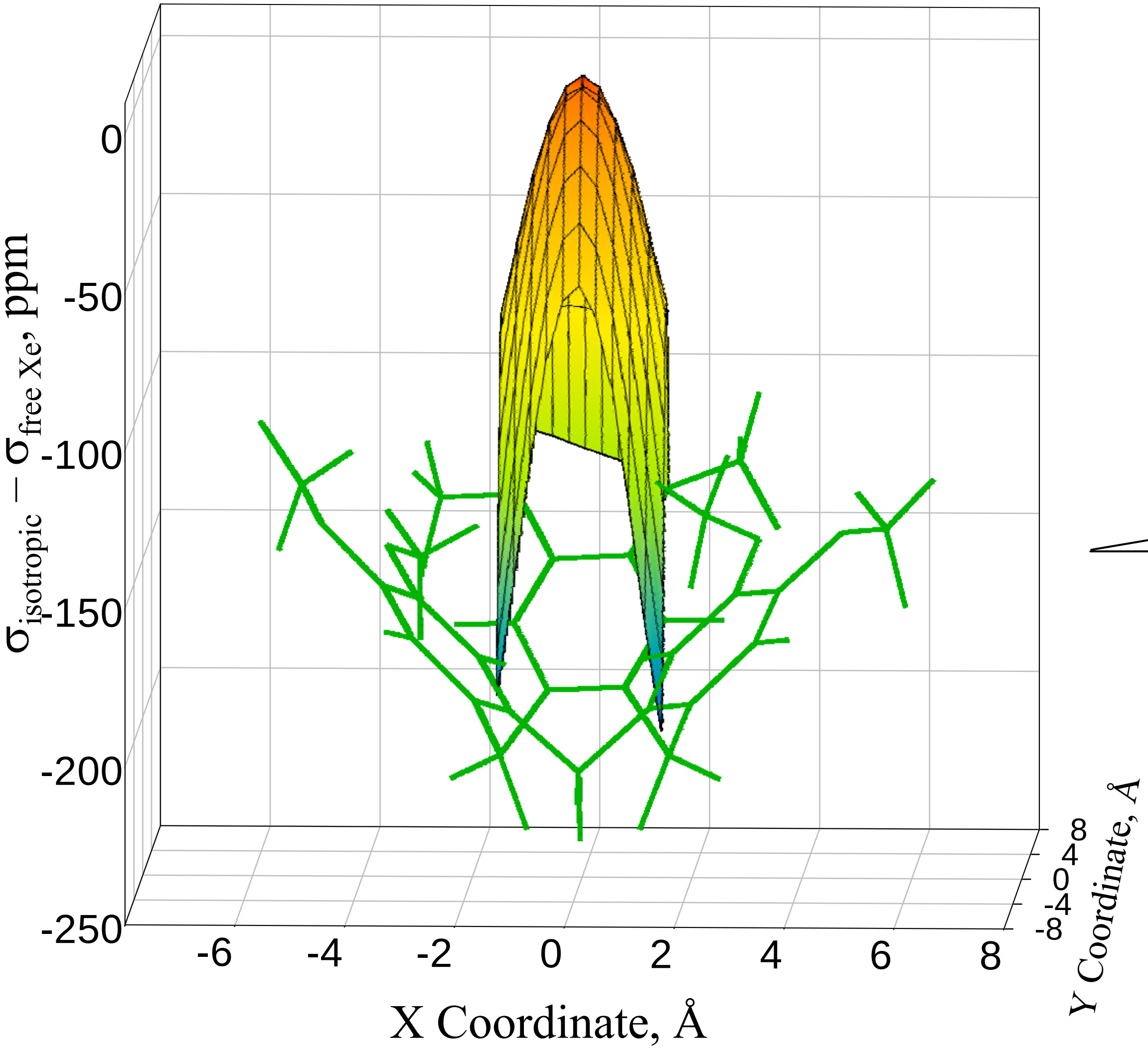


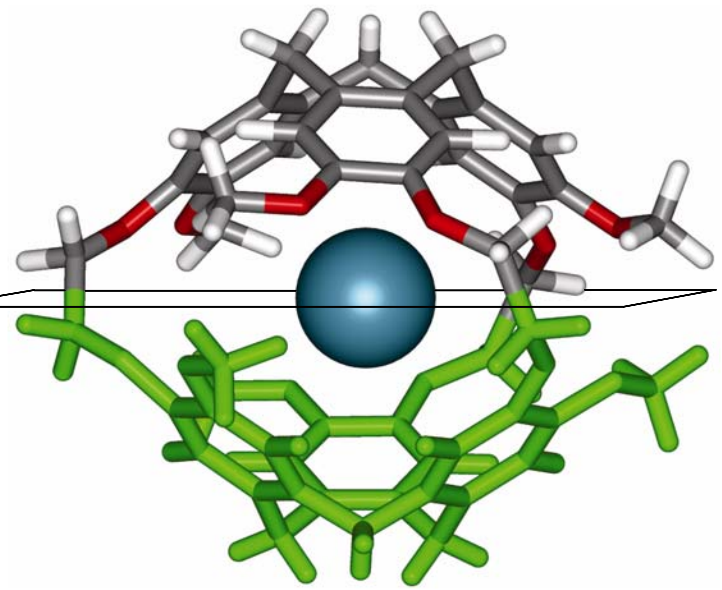
Pines et al. 1999*

Minimum energy structure arrived at is completely consistent with SPINOE experiments by Pines et al!

* M., Luhmer, B. M. Goodson, Y. Q. Song, D. D. Laws, L. Kaiser, M. C. Cyrier, and A. Pines J. Am. Chem. Soc. **1999**, 121, 3503.

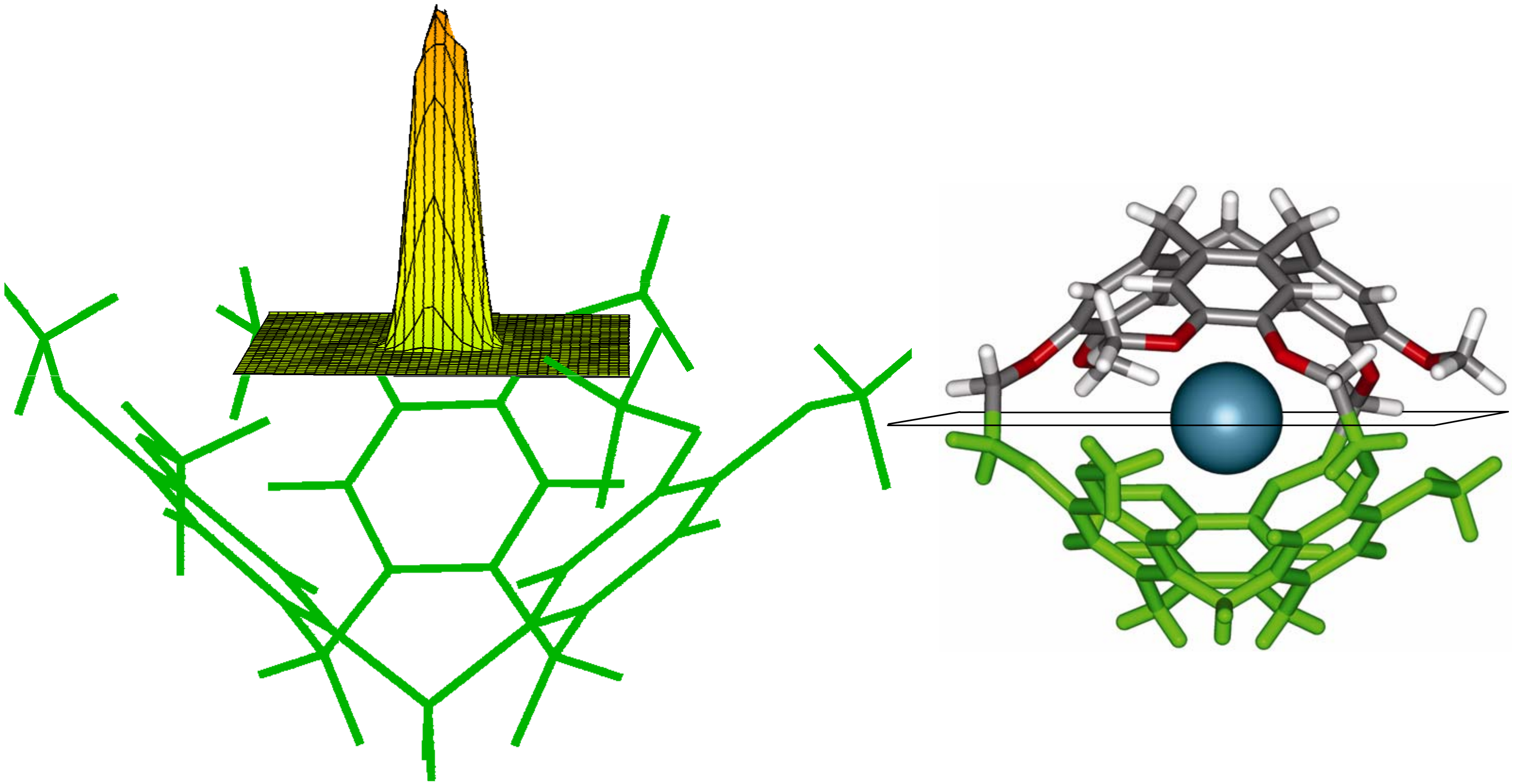
The Xe shielding surface for Xe@cryptoA





One-body distribution function for Xe@cryptoA

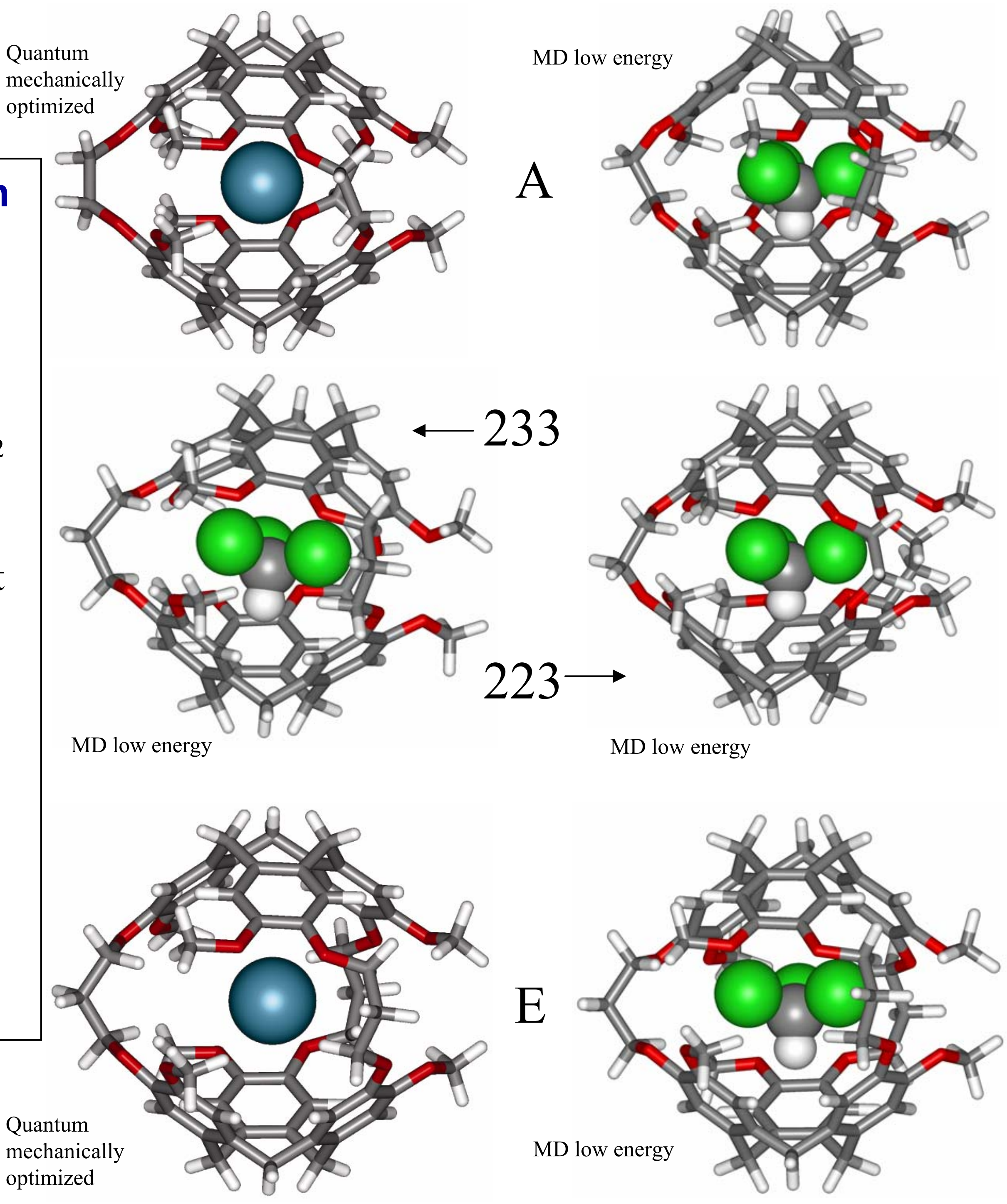
from Monte Carlo simulations



Determination of the solution structures of cryptophanes-223, and -233 by molecular dynamics simulations:

- Equilibration of solvent $(CHCl_2)_2$ at room temperature (120 molecules)
- Introduce cryptophane with guest to replace 5 $(CHCl_2)_2$ molecules
- Relax solvent around solute
- Simulated all-atom annealing
- MD to find low energy structure

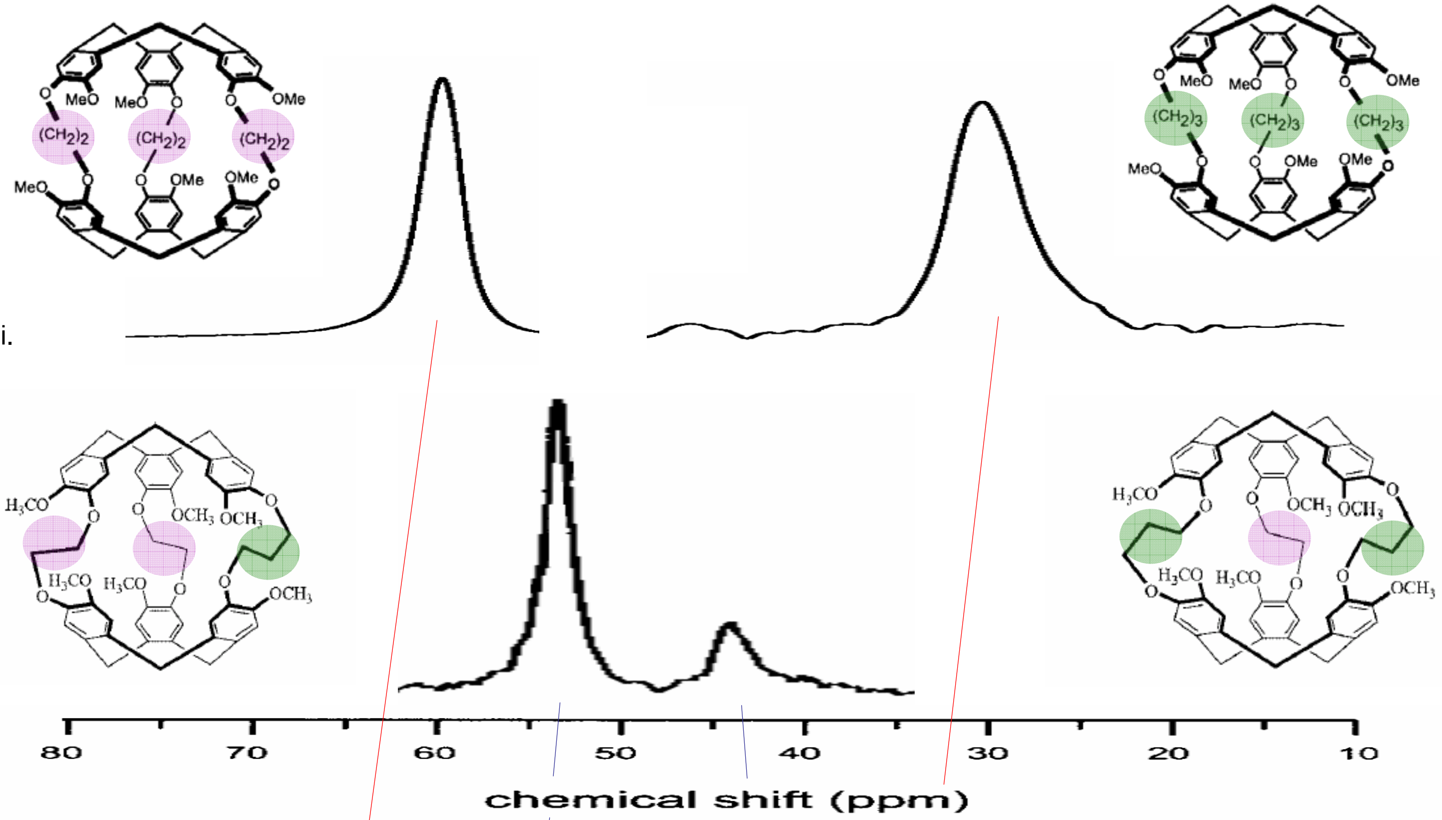
Quantum-mechanically optimized cryptophane-A and –E structures are used to calibrate the method using guests: CH_4, $CHCl_3$, CCl_4



^{129}Xe@cryptophanes

A

E



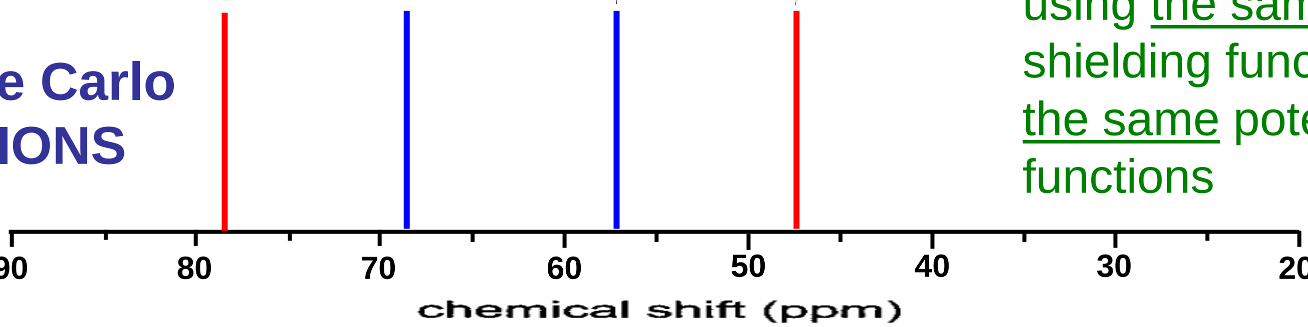
223

233

Pines et al.
Proc. Nat. Acad. Sci.
98, 10654 (2001)

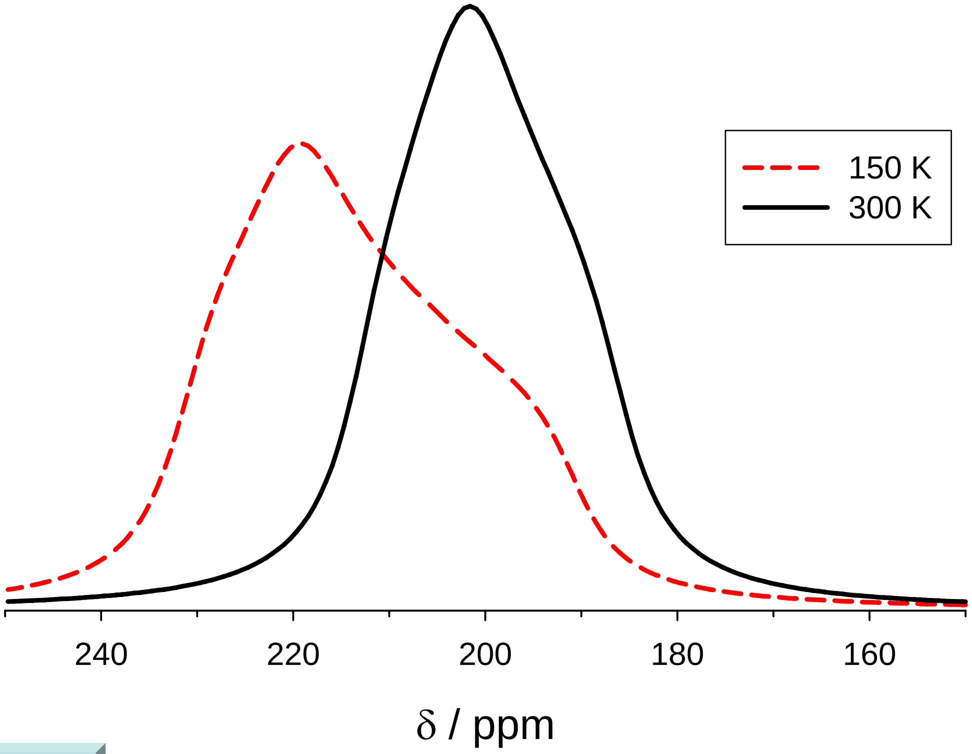
Brotin et al.
Eur. J. Org. Chem.
2003, 973-984

Our Monte Carlo SIMULATIONS

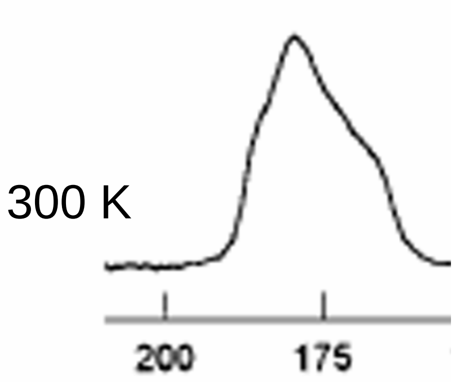


using <u>the same</u> shielding functions <u>the same</u> potential functions

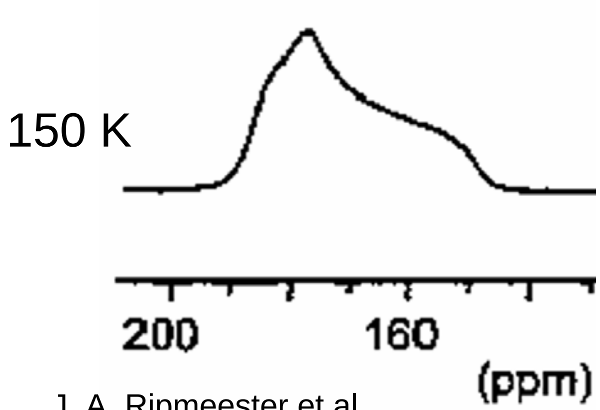
Temperature dependence
Xe in silicalite at full loading



CALCULATIONS



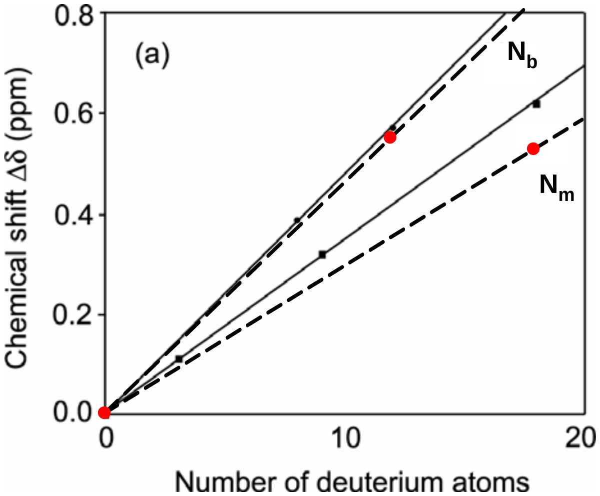
Jameson et al.
J. Phys. Chem. B **1997,** *101,* 8418



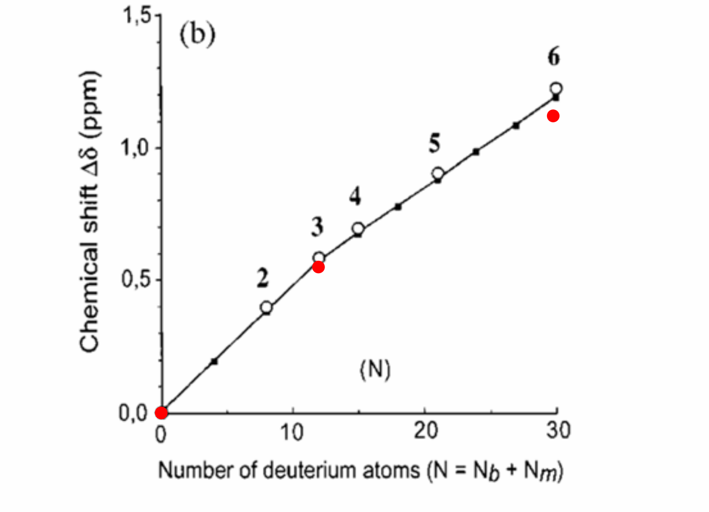
J. A. Ripmeester et al.
J. Am. Chem. Soc. **2001**, 123, 10399

EXPERIMENT

Xe@d$_n$-cryptoA



EXPERIMENT
(Brotin et al. 2000)*

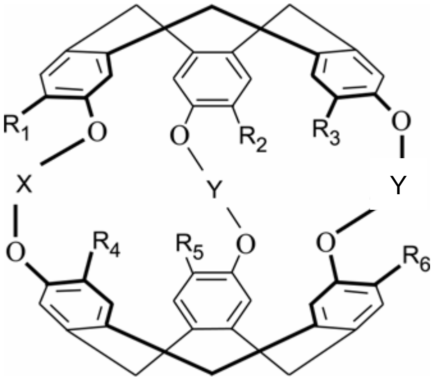


- **SIMULATIONS**

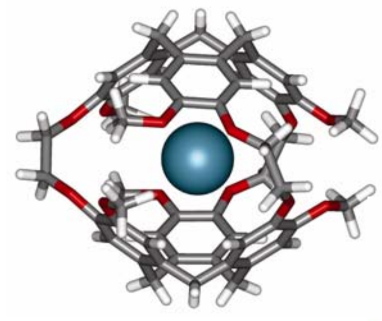
for example:

$\langle\sigma[\text{Xe@cryptoA}]\rangle_{MC} - \langle\sigma[\text{Xe@}d_{30}\text{ cryptoA}]\rangle_{MC} = 1.118$ ppm

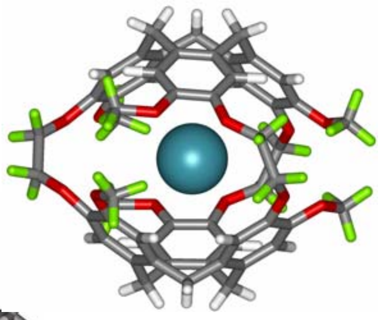
$r_0(\text{Xe-H}) - r_0(\text{Xe-D}) = 0.07$ Å



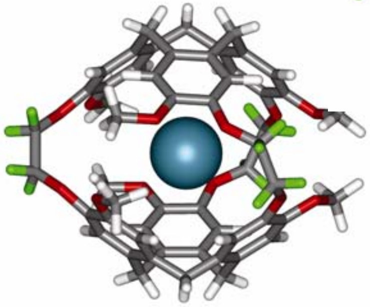
1: X = CH_2CH_2; Y = CH_2CH_2; $R_1 = OCH_3$; $R_2 - R_6 = OCH_3$
2: X = CH_2CH_2; Y = CD_2CD_2; $R_1 = OCH_3$; $R_2 - R_6 = OCH_3$
3: X = CD_2CD_2; Y = CD_2CD_2; $R_1 = OCH_3$; $R_2 - R_6 = OCH_3$
4: X = CD_2CD_2; Y = CD_2CD_2; $R_1 = OCD_3$; $R_2 - R_6 = OCH_3$
5: X = CD_2CD_2; Y = CD_2CD_2; $R_1 - R_3 = OCD_3$; $R_4 - R_6 = OCH_3$
6: X = CD_2CD_2; Y = CD_2CD_2; $R_1 - R_6 = OCD_3$



1



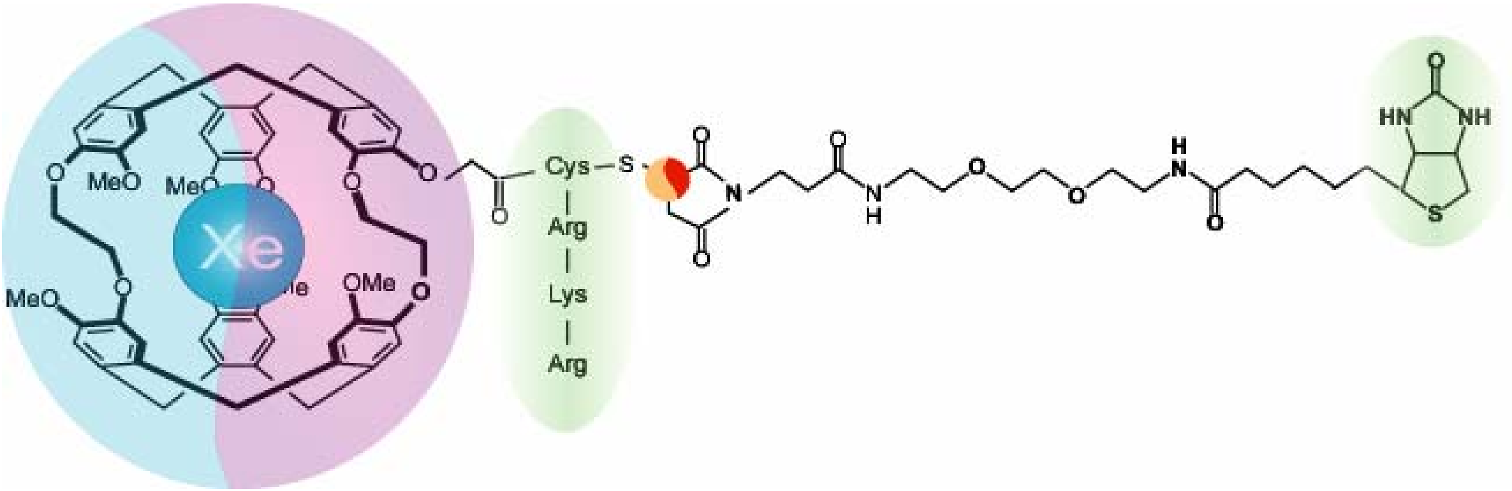
6

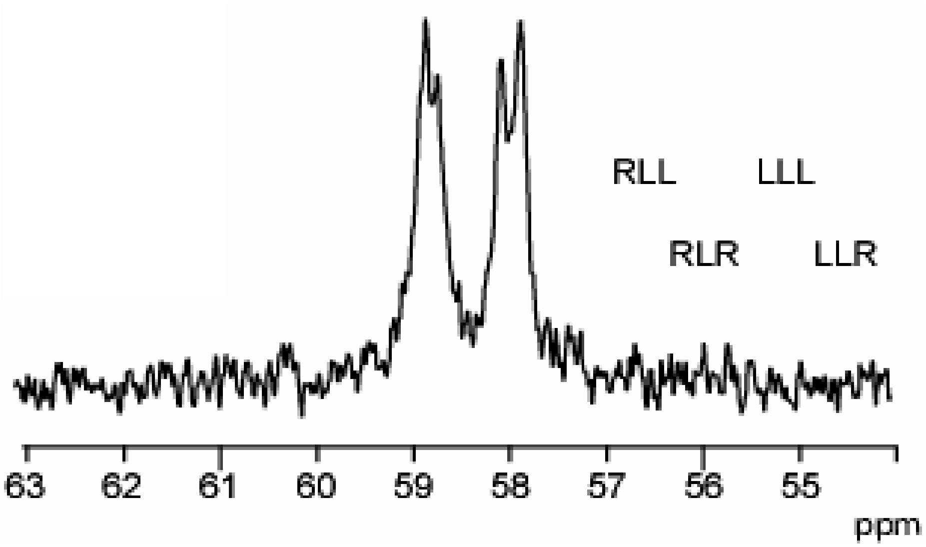


3

*T. Brotin, A. Lesage, L. Emsley, and A. Collet,
J. Am. Chem. Soc. **2000**, 122, 1171-1174

Chiralization of Xe





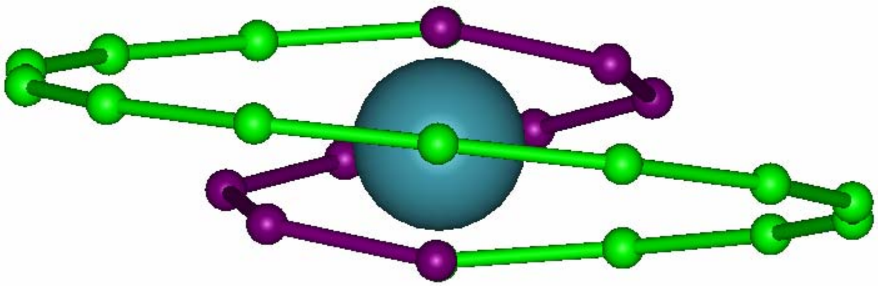
Chiral Center	Configuration			
Cage	L	L	R	R
Peptide	L	L	L	L
Asymmetric Carbon	L	R	L	R
Ligand	D	D	D	D

This slide courtesy of E. Janette Ruiz

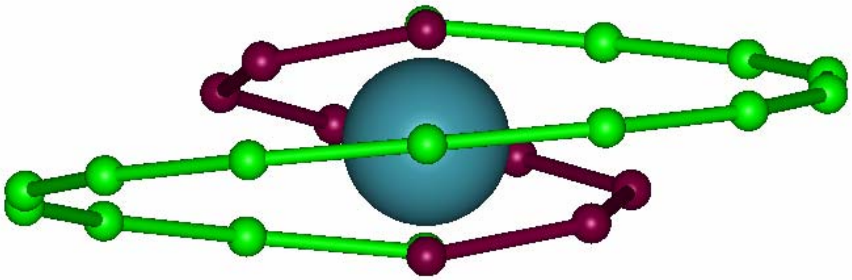
E. Ruiz, M.M. Spence, D. E. Wemmer, A. Pines

Model Chiral Systems: Xe@Ne$_8$(+q)$_{15}$

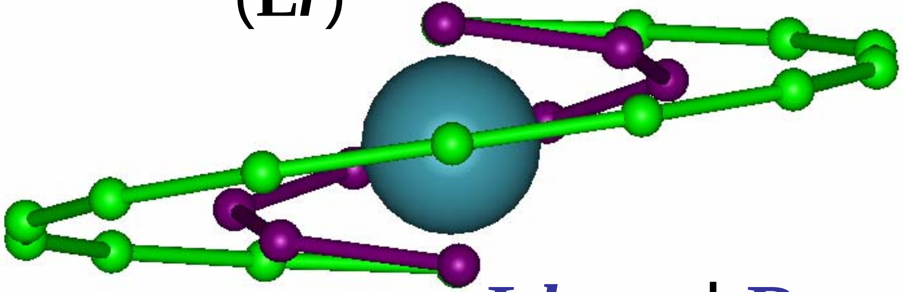
(**L*l***)



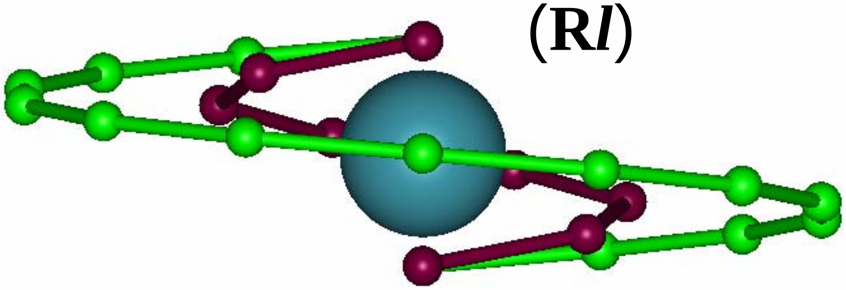
(**R*r***)



(**L*r***)



(**R*l***)

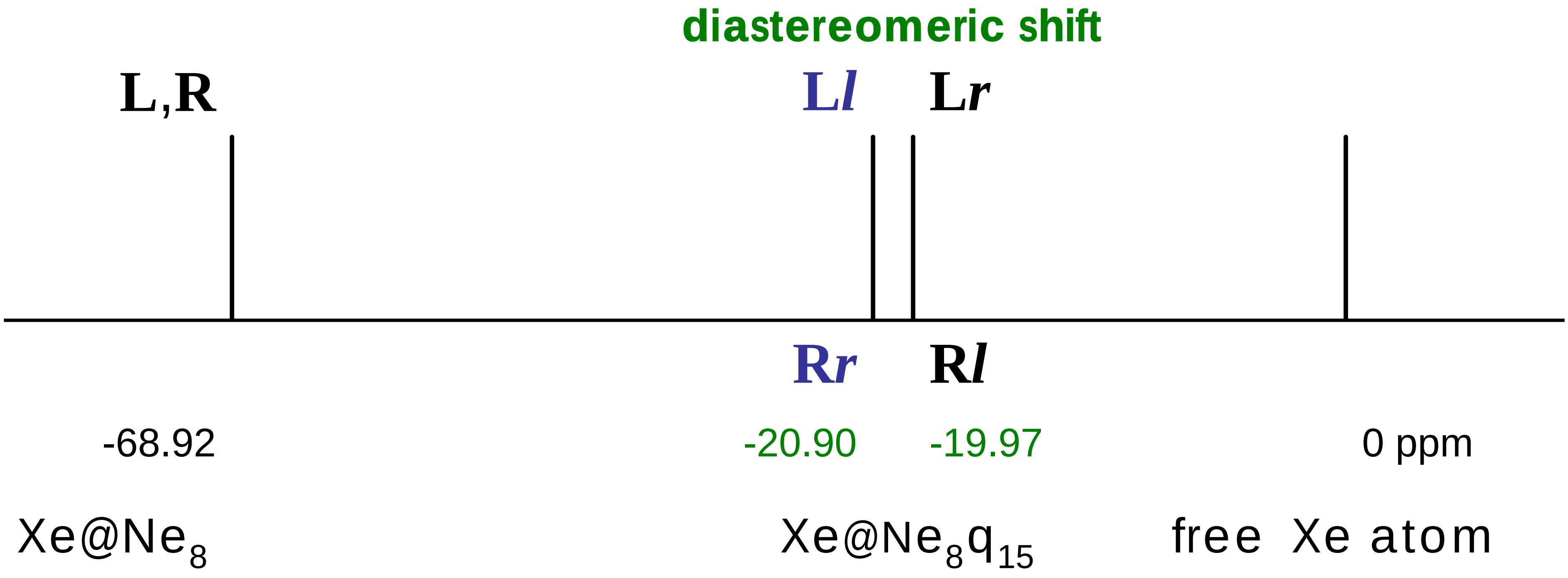


L*l* and **R*r*** are mirror images

L*r* and **R*l*** are mirror images

L*l* and **L*r*** are diastereomers

^{129}Xe NMR spectrum of Xe in Ne helices



diastereomeric shift

L,R **L*l*** **L*r***

R*r* **R*l***

-68.92 -20.90 -19.97 0 ppm

Xe@Ne$_8$ Xe@Ne$_8$q$_{15}$ free Xe atom

D.N. Sears, C. J. Jameson, R. A. Harris, JCP Aug 1, 2003

Xe in nanochannels

QUESTION:

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

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

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

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

one Xe tensor from interaction with ALL channel atoms

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

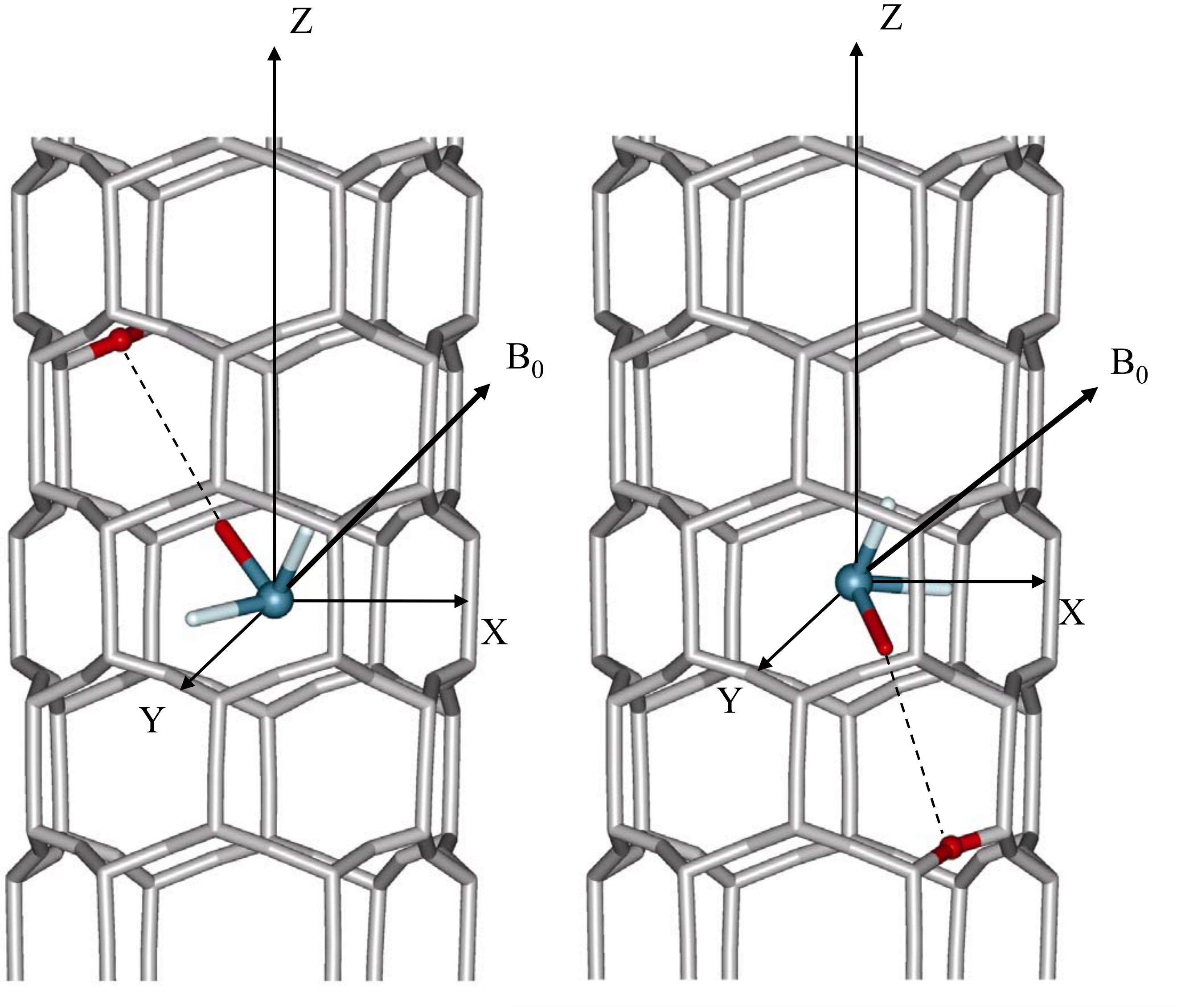
The contribution to the shielding of Xe at point J due to i_{th} Ne atom located at (x_i, y_i, z_i) is given by the ab initio tensor components for the XeNe dimer, the functions $\sigma_{\perp}(r_{XeNe})$, $\sigma_{||}(r_{XeNe})$.

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

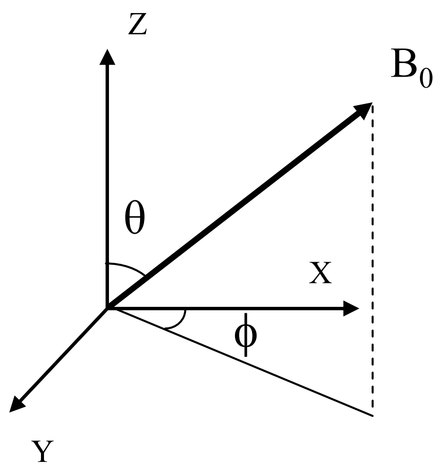
$$\tfrac{1}{2}(\sigma_{XY}+\sigma_{YX}) = [(x_i - x_J)/r_{iJ}] \bullet [(y_i - y_J)/r_{iJ}](\sigma_{||} - \sigma_{\perp})$$

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

Lineshapes by grand canonical Monte Carlo



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

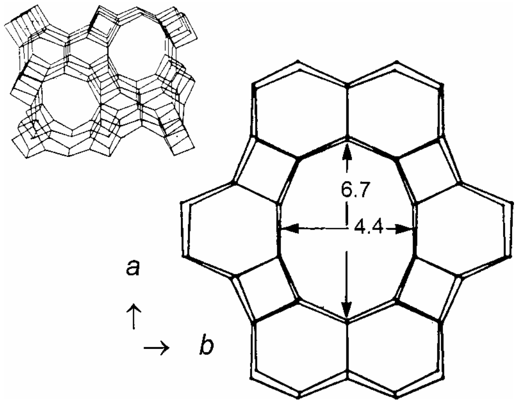


Random orientation of crystallites:
Probability that B_0 lies in any infinitesimal solid angle is $d\zeta\ d\phi\ /\ 4\pi$, where $\zeta = (-\cos\theta)$
Equal areas in $\zeta\phi$ plane correspond to equal probabilities

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 tensor components along the B_0 direction from each Xe-O (or other channel atom), from each Xe-Xe

Architecture of the channel determines the lineshape

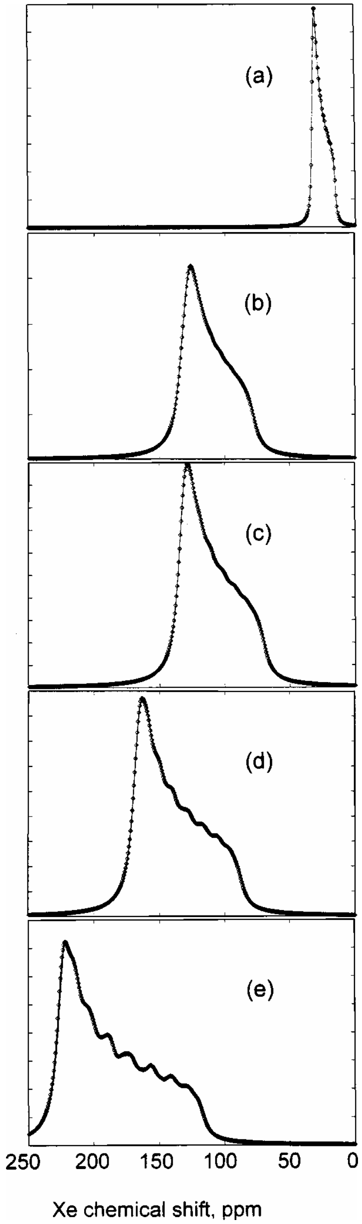


ALPO$_4$-11
architecture

One Xe atom
in a neon channel

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

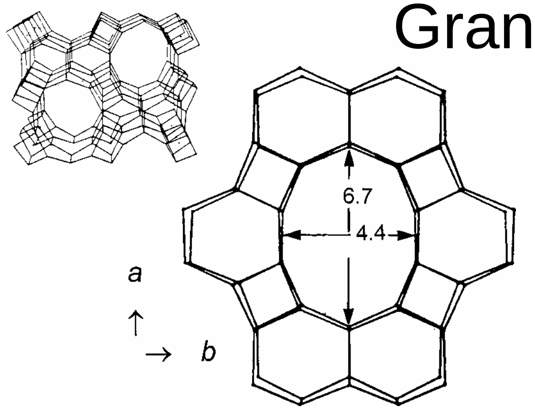
One Xe atom
in an argon channel

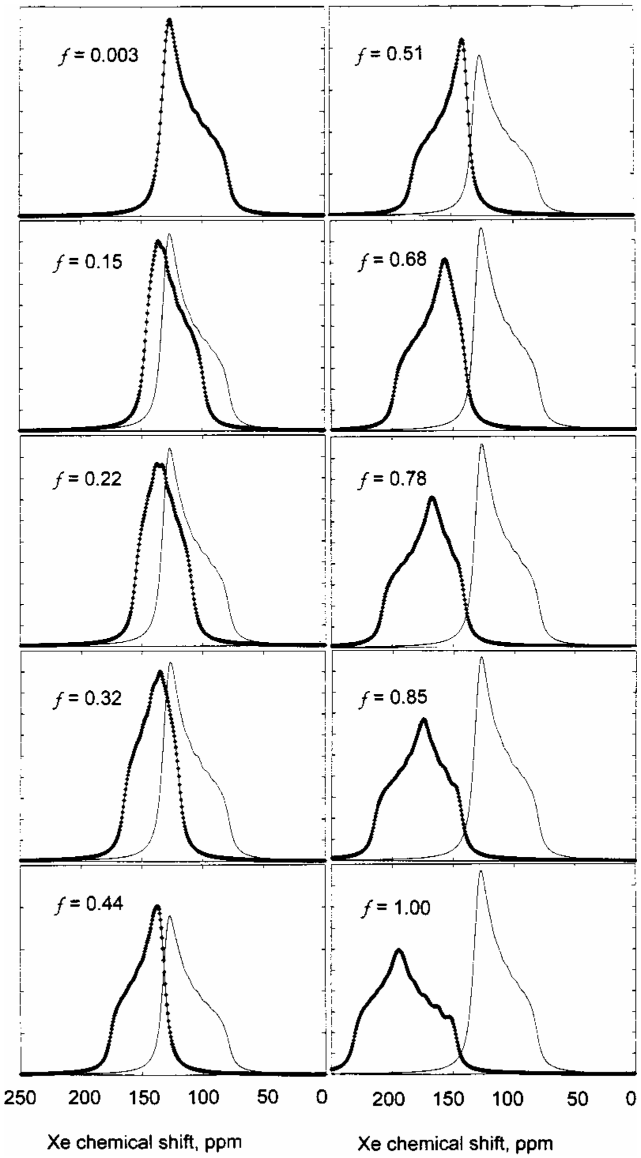


Jameson,
JCP 116,
8912 (2002)

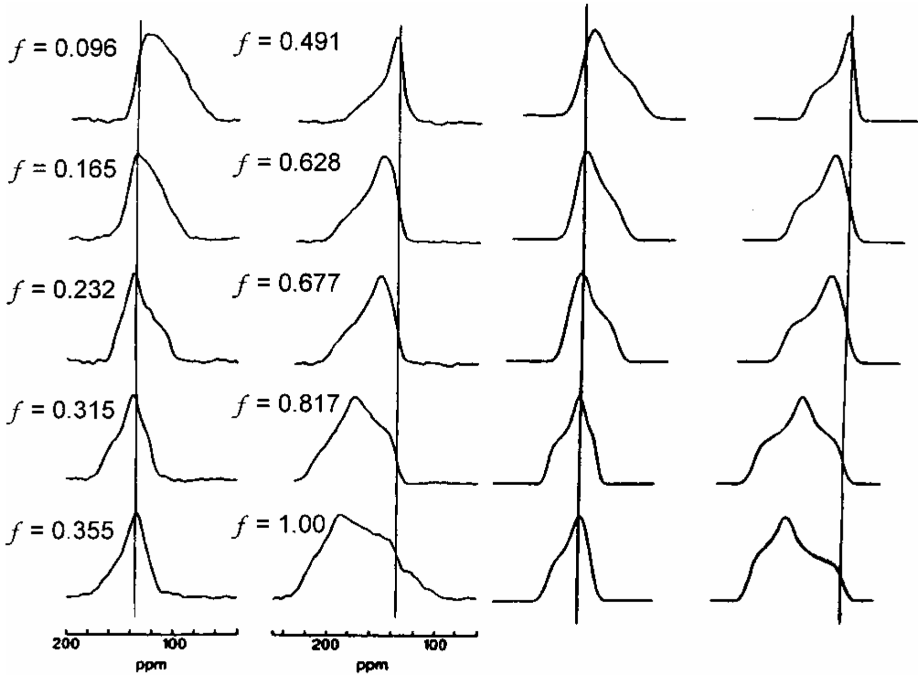
Xe in the channels of ALPO$_4$-11

Grand Canonical Monte Carlo **SIMULATIONS**



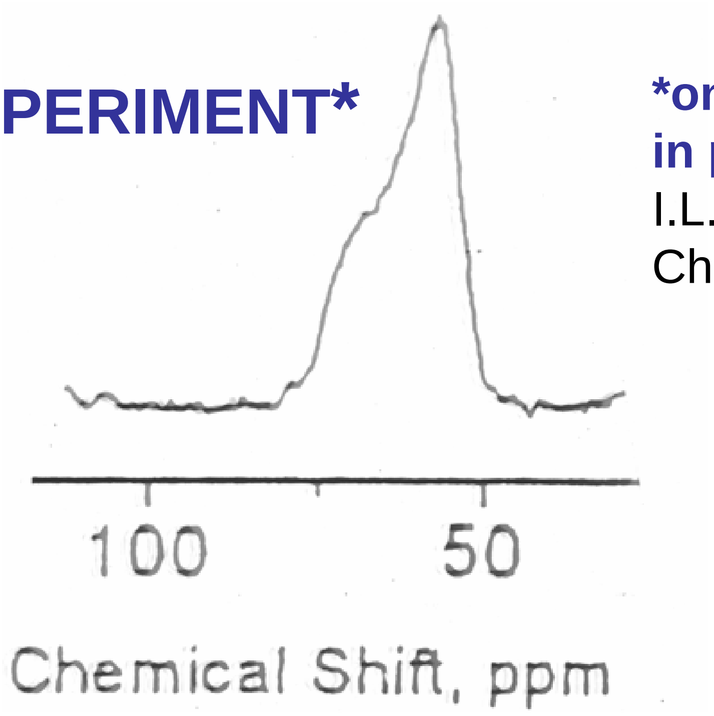


Jameson
J Chem
Phys 116,
8912
(2002)

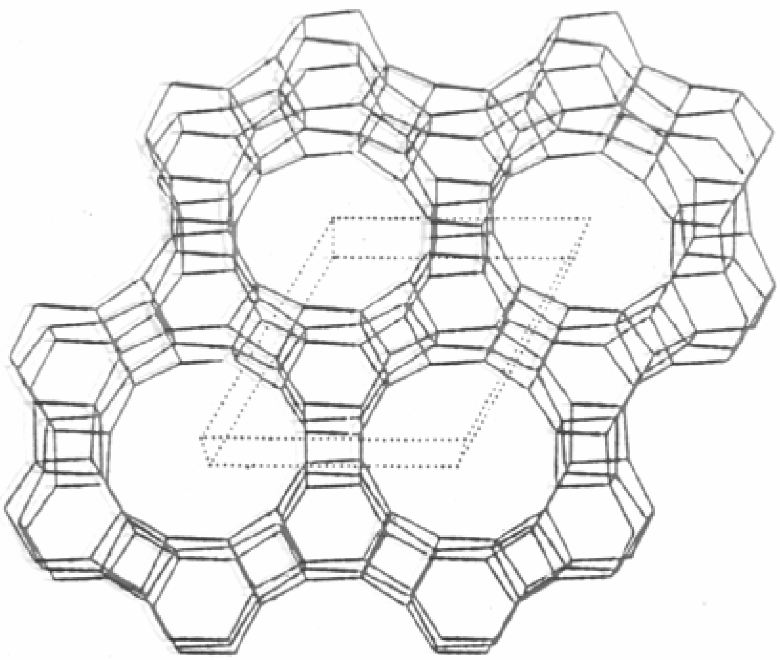


EXPERIMENTS J.A. Ripmeester and C.I. Ratcliffe, J. Phys. Chem. 99, 619 (1995)

EXPERIMENT*

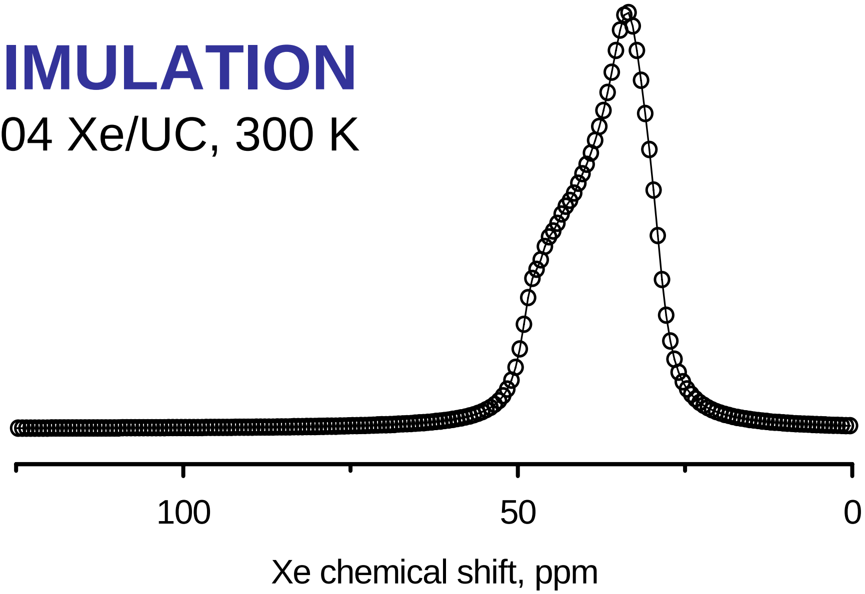


***one-scan hyperpolarized ^{129}Xe in polycrystalline SSZ-24 at 293 K**
I.L. Moudrakovski et al.
Chem. Mater. 12, 1181 (2000).



SIMULATION

0.04 Xe/UC, 300 K

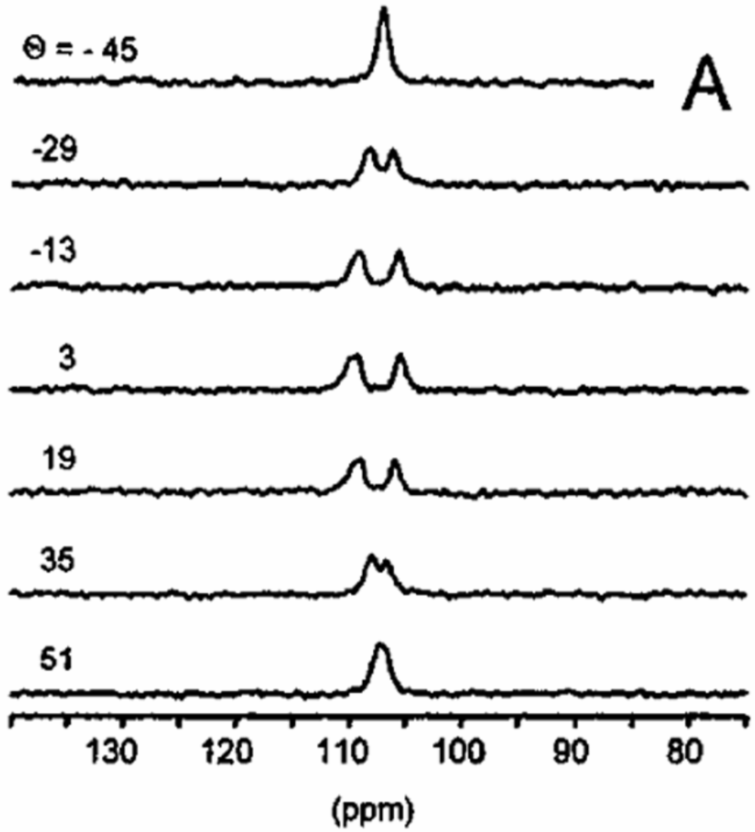


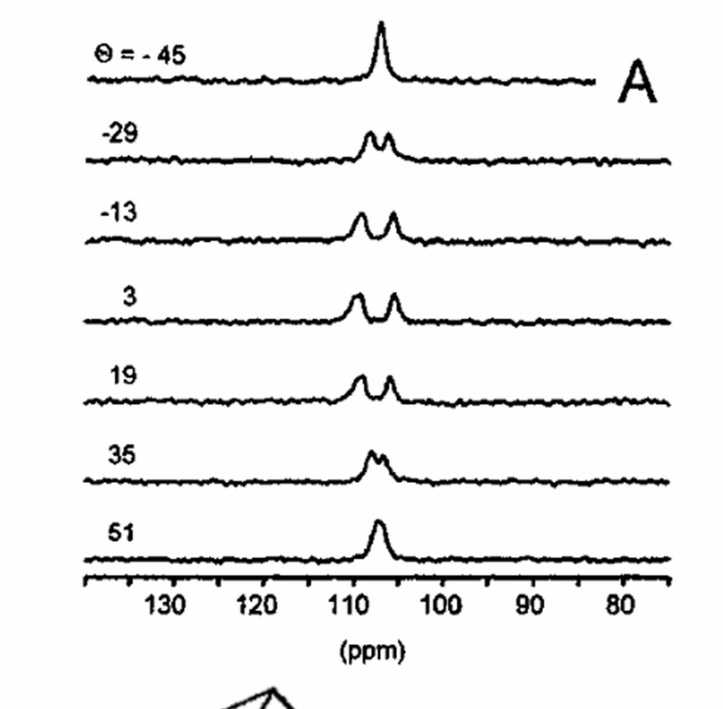
This GCMC simulation uses the same shielding and potential functions as for Xe in silicalite.
C.J. Jameson, 2003

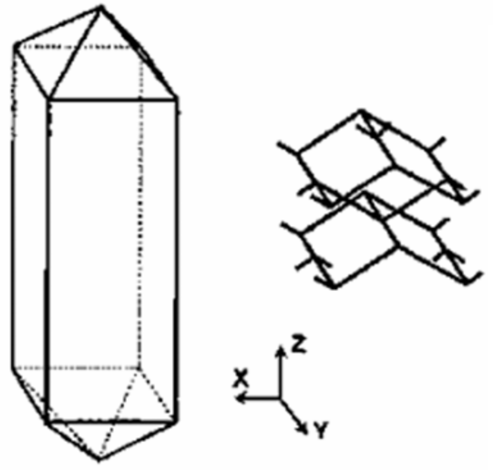
Xe in a single crystal of silicalite

EXPERIMENTS:

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







EXPERIMENTS :

V. V. Terskikh, I. L. Moudrakovski, H. Du, C. I. Ratcliffe, and J. A. Ripmeester

J. Am. Chem. Soc. **2001**, 123, 10399-10400

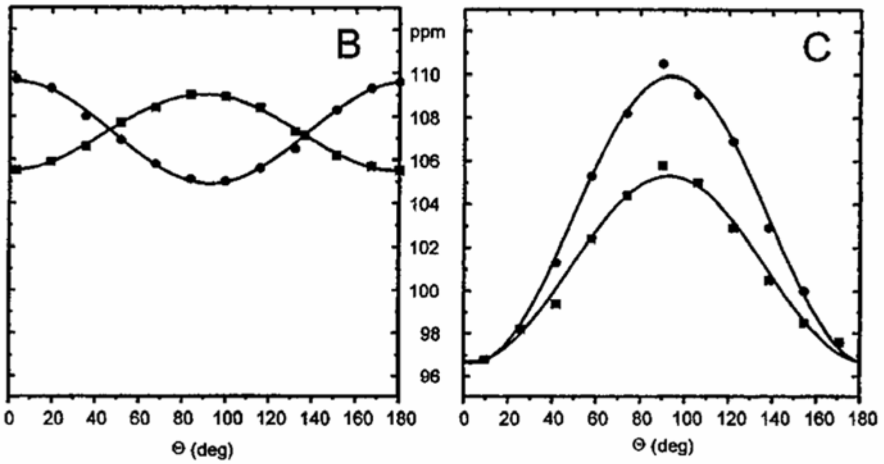
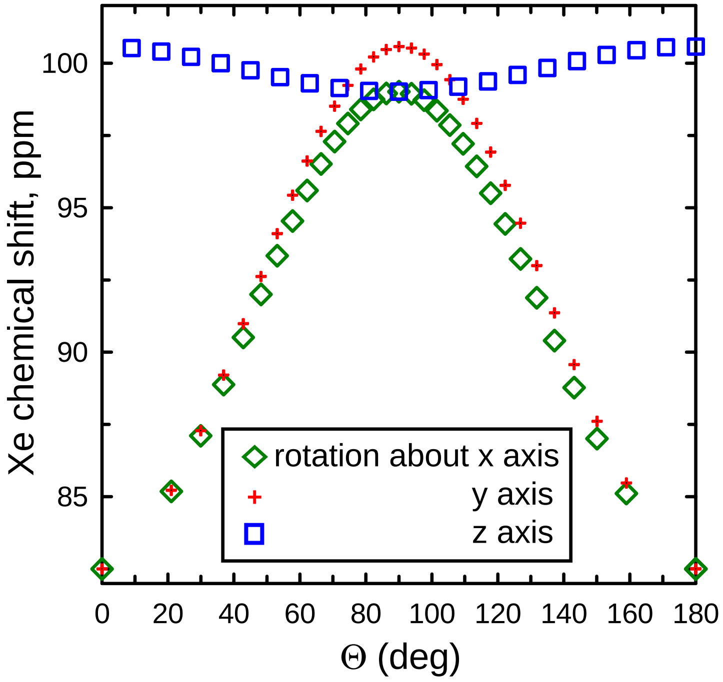


Figure 2. HP ^{129}Xe NMR results for single crystals of silicalite at 295 K: (A) spectra ($\pi/2$ pulses, 512 scans each, 5 s delay) and (B) chemical shifts versus crystal orientation, Θ, about the *z* axis, perpendicular to the magnetic field. (C) Chemical shifts versus Θ about the second orthogonal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

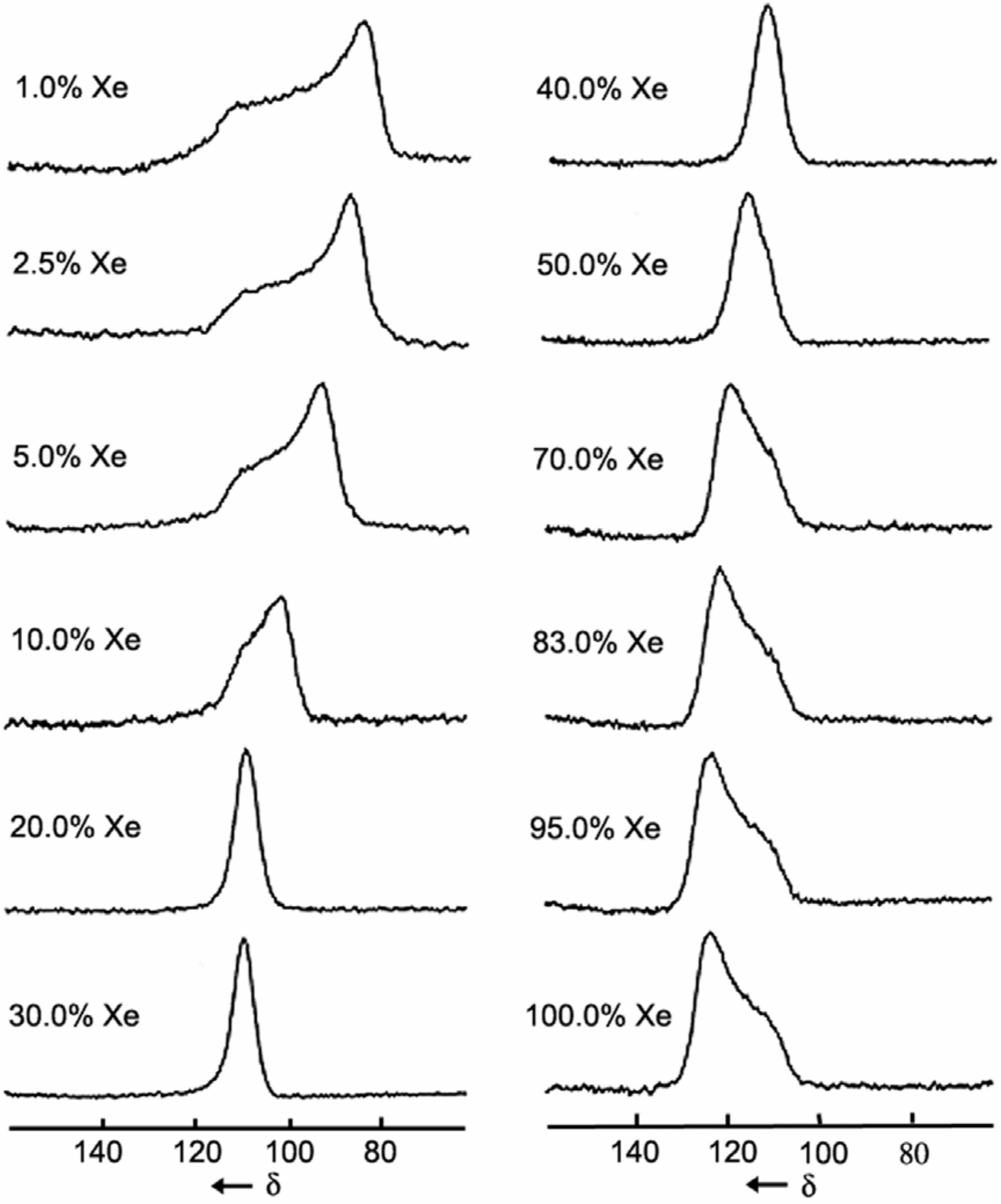


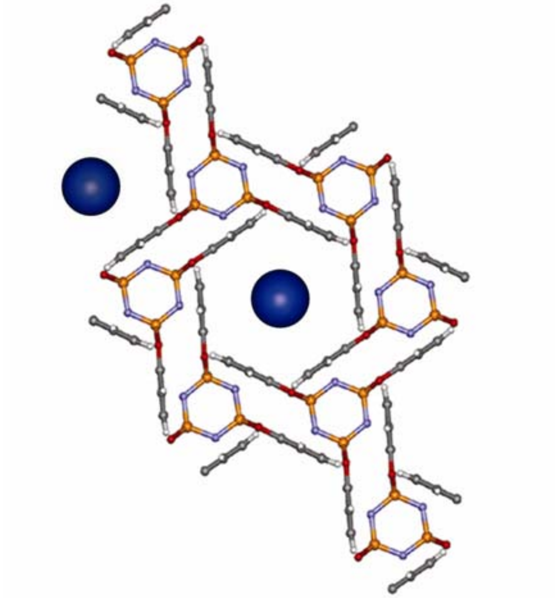
0.285Xe/UC
at 300 K

GCMC SIMULATIONS Jameson 2003

Motivation:

- Organic molecular crystals provide 1-D nanochannels with aromatic environments
- Does Xe shielding in aromatic nanochannels differ from 1-D silicate channels?
- Experimental Xe lineshapes in TPP have been observed (Sozzani et al., 2000)



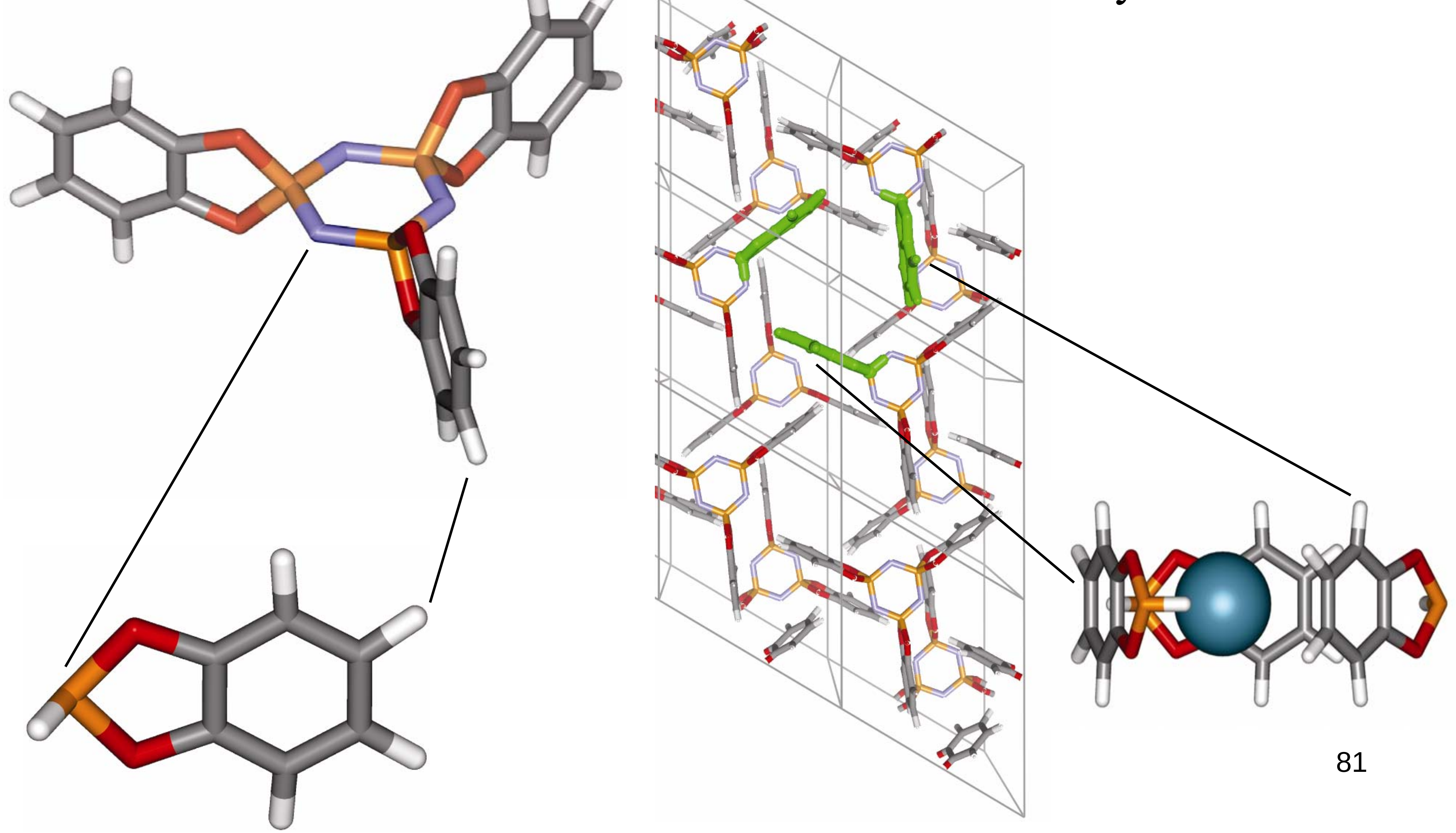


P. Sozzani, A. Comotti, R. Simonutti,
T. Meersmann, J.W. Logan, A. Pines
Angew. Chem. Int. Ed. 39, 2695-2699 (2000)

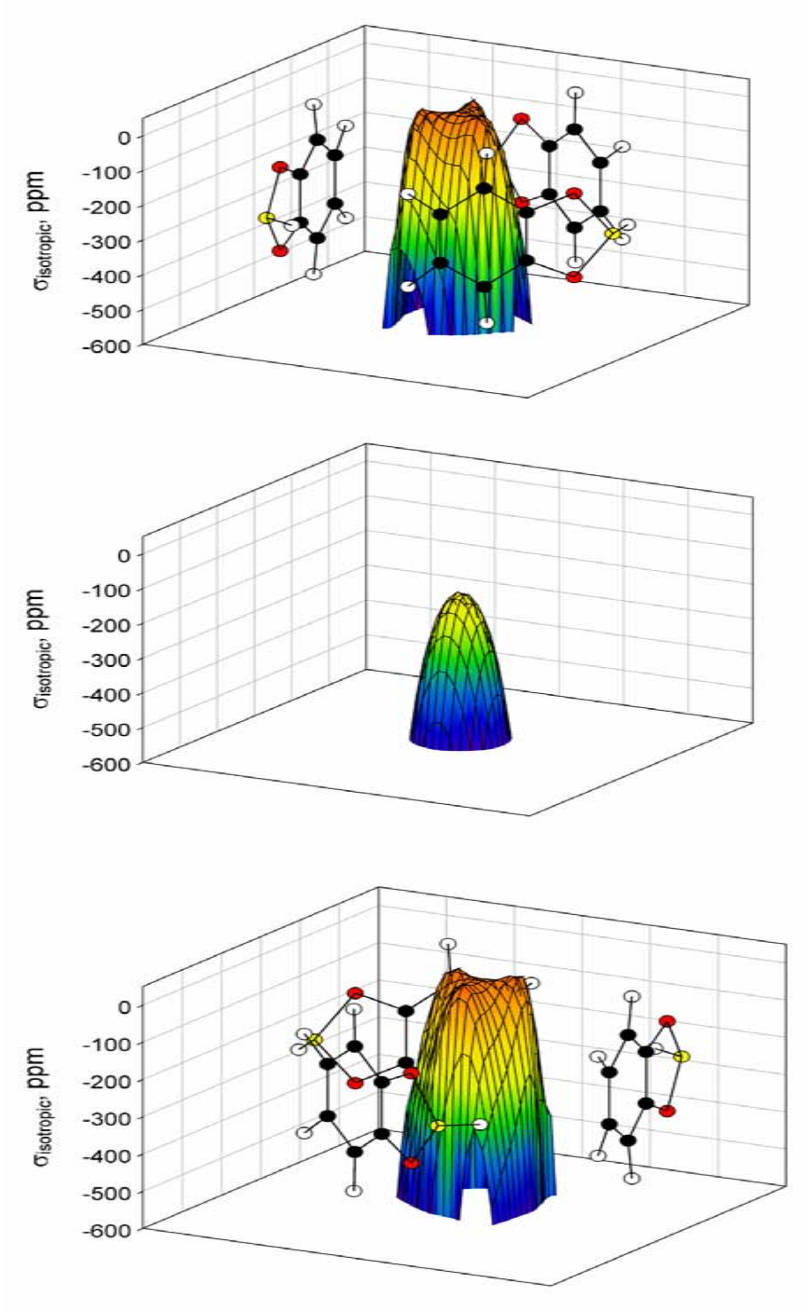
Model for TPP channel

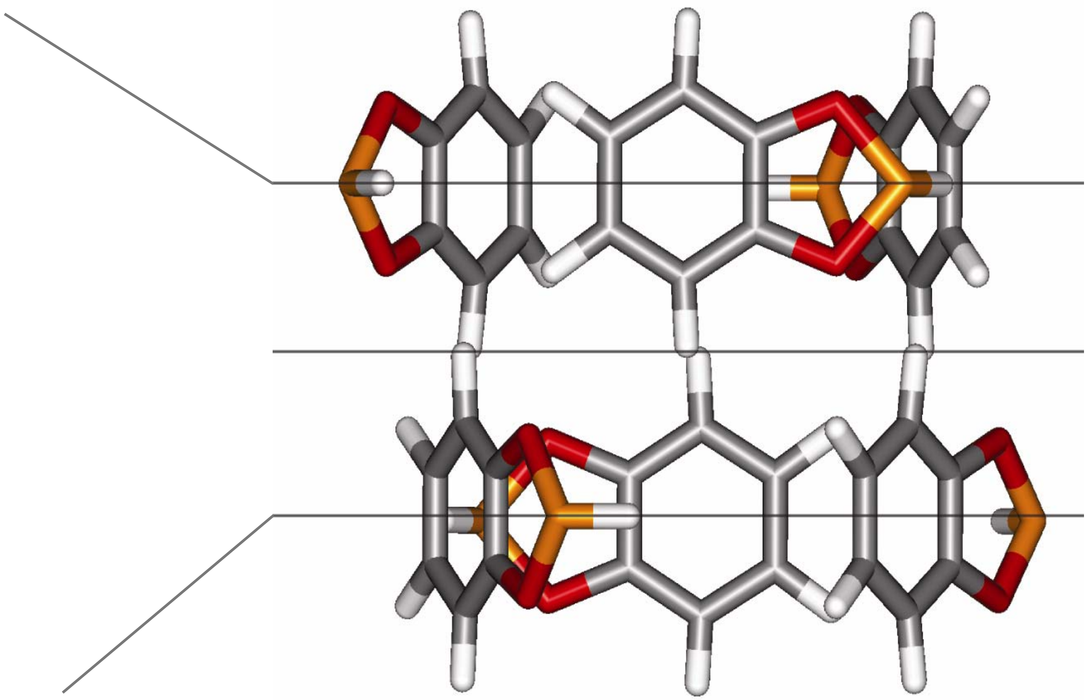
- Suitable molecular fragment has electron density distribution similar to TPP itself

- Channel comprised of a trimer of fragments
- Same coordinate system as channel

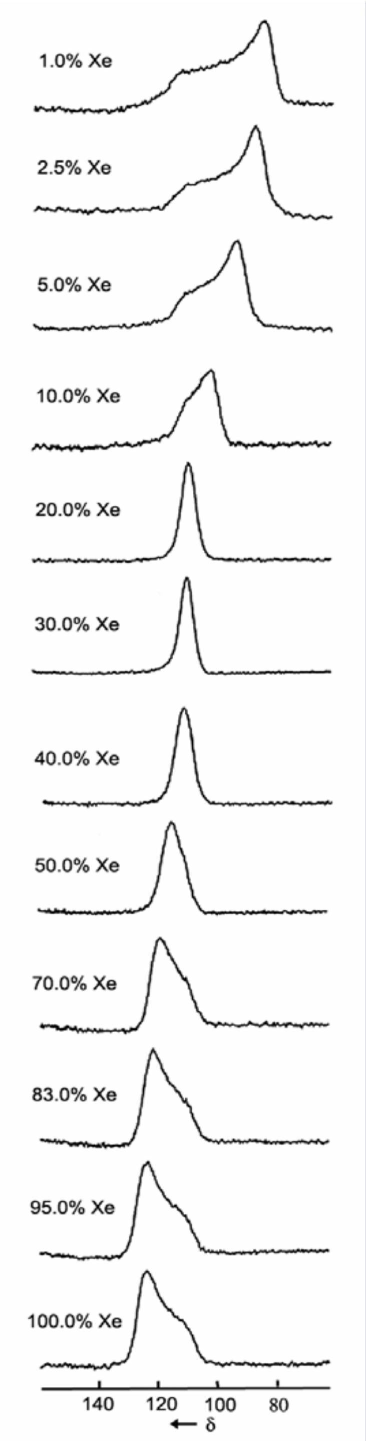


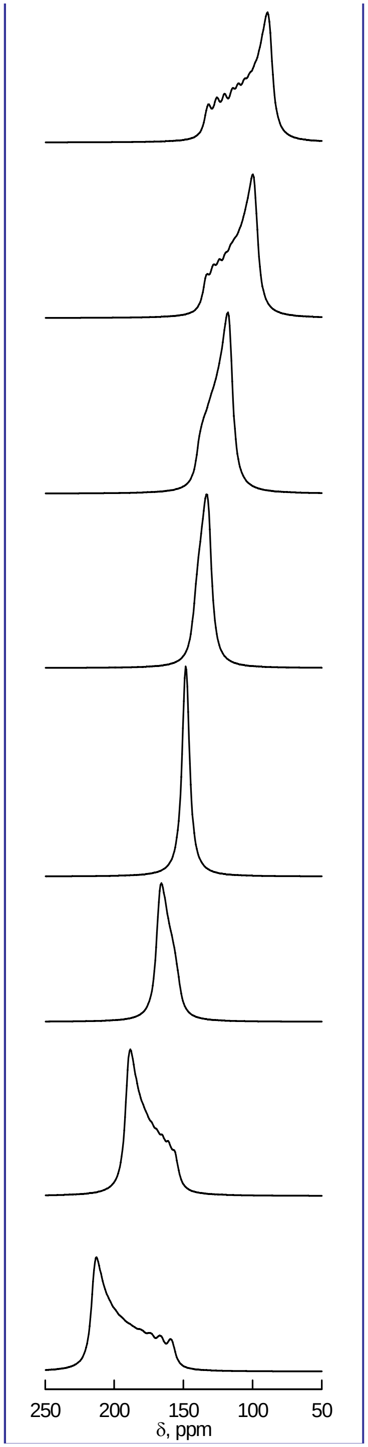
The Xe isotropic shielding surface in model channel of 2 trimers





Shielding surface reflects symmetry of TPP channel





⟨n⟩ = 0.063 Xe/UC

0.406

0.737

0.961

1.368

1.666

1.931

2.088

GCMC SIMULATIONS

trial functions

Jameson 2003

EXPERIMENTAL SPECTRA
as a function of Xe mole fraction:
P. Sozzani, A. Comotti, R. Simonutti,
T. Meersmann, J.W. Logan, A. Pines
Angew. Chem. Int. Ed. 39, 2695 (2000)

NMR lineshapes in nanochannels and nanocavities 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.

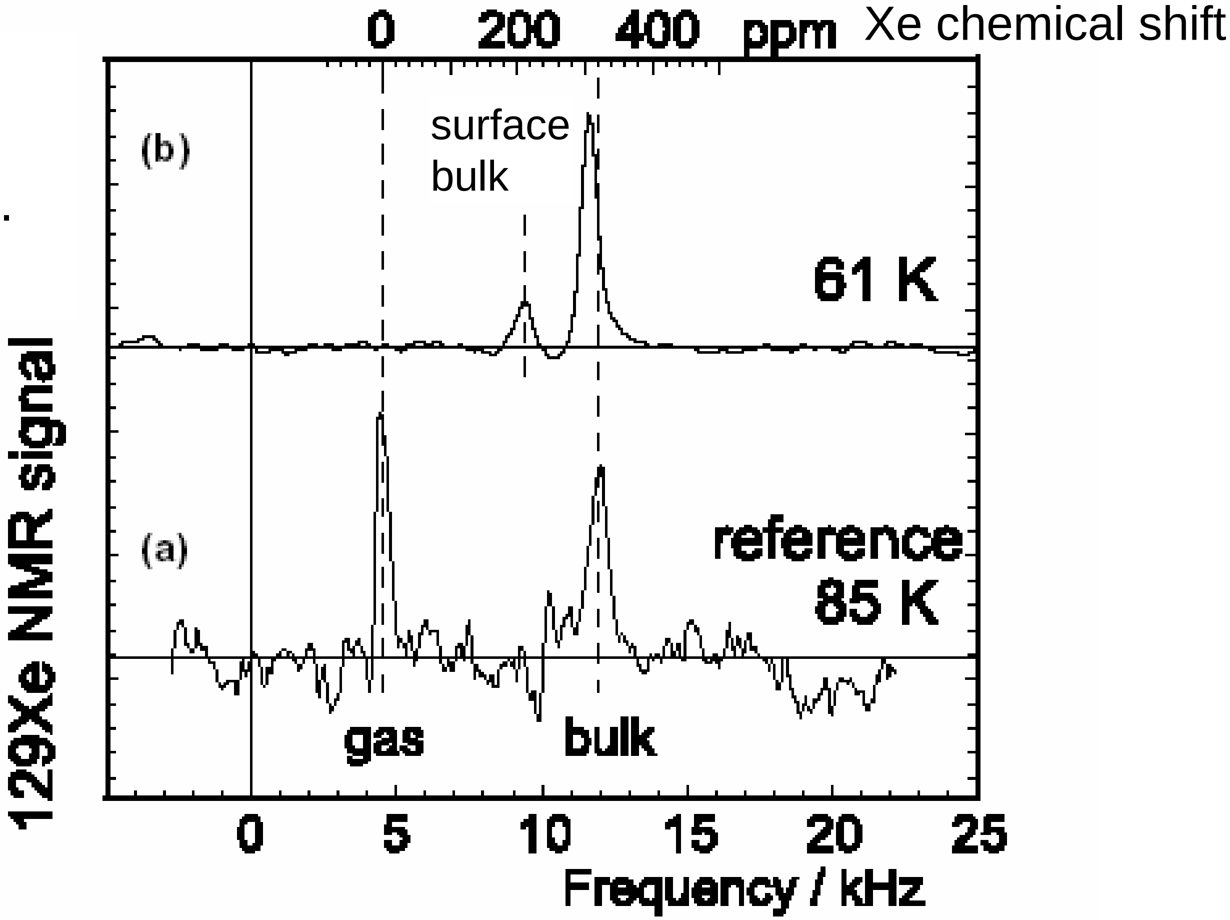
Xe on single crystal surfaces

EXPERIMENTS by Heinz Jänsch

- Xe at the surface of bulk xenon has a different signal than Xe in the bulk
- Xe can tell which surface it is in contact with
- Xe can tell how many other Xe are on the same surface
- The chemical shift tensor can be mapped out by rotating the single crystal in the magnetic field

Xe on the surface of a single crystal metal surface Ir(111)

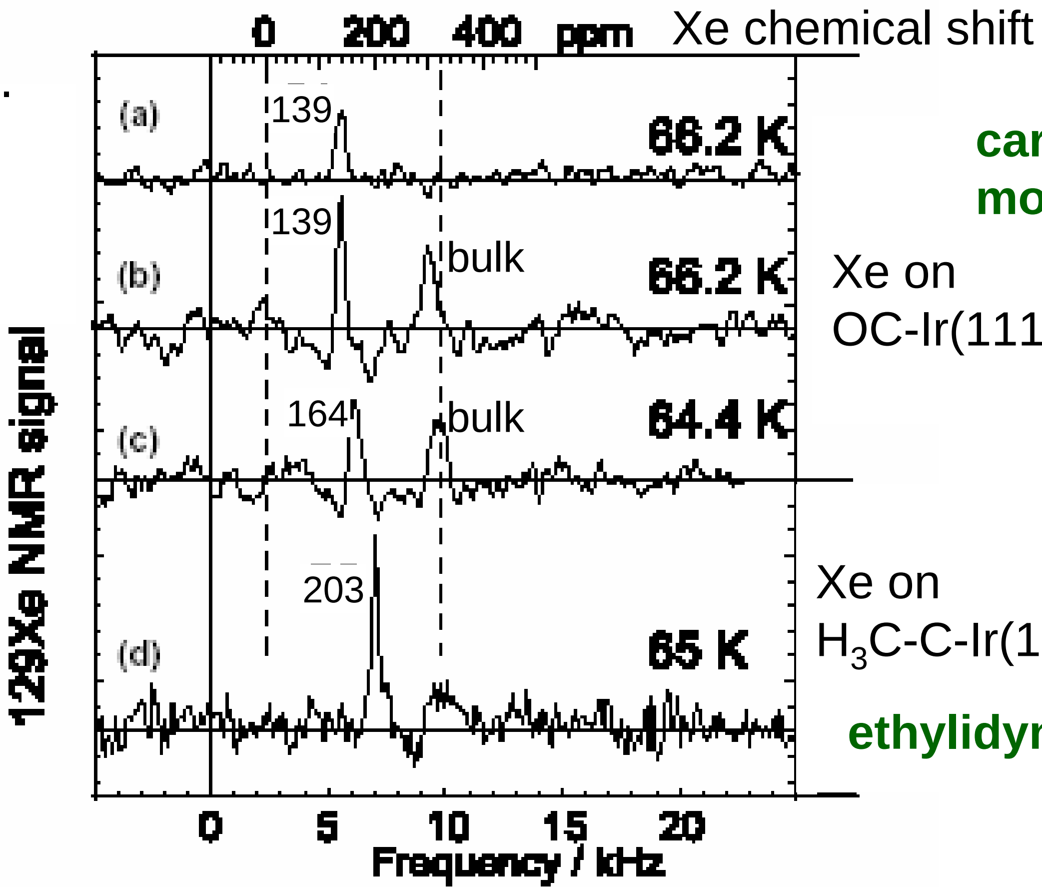
H.J. Jänsch et al.
Chem. Phys. Lett.
372, 325 (2003)



The Xe atoms on the surface of the bulk Xe appear at 209 ppm while Xe in the middle of the bulk is at 321 ppm

Xe on a chemically modified metal surface

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



carbon monoxide

Xe on OC-Ir(111)

greater Xe coverage at lower T

Xe on H_3C-C-Ir(111)

ethylidyne

Xe can tell the difference between OC and H_3C-C surfaces.
Xe can tell how many other Xe atoms are on the same surface.

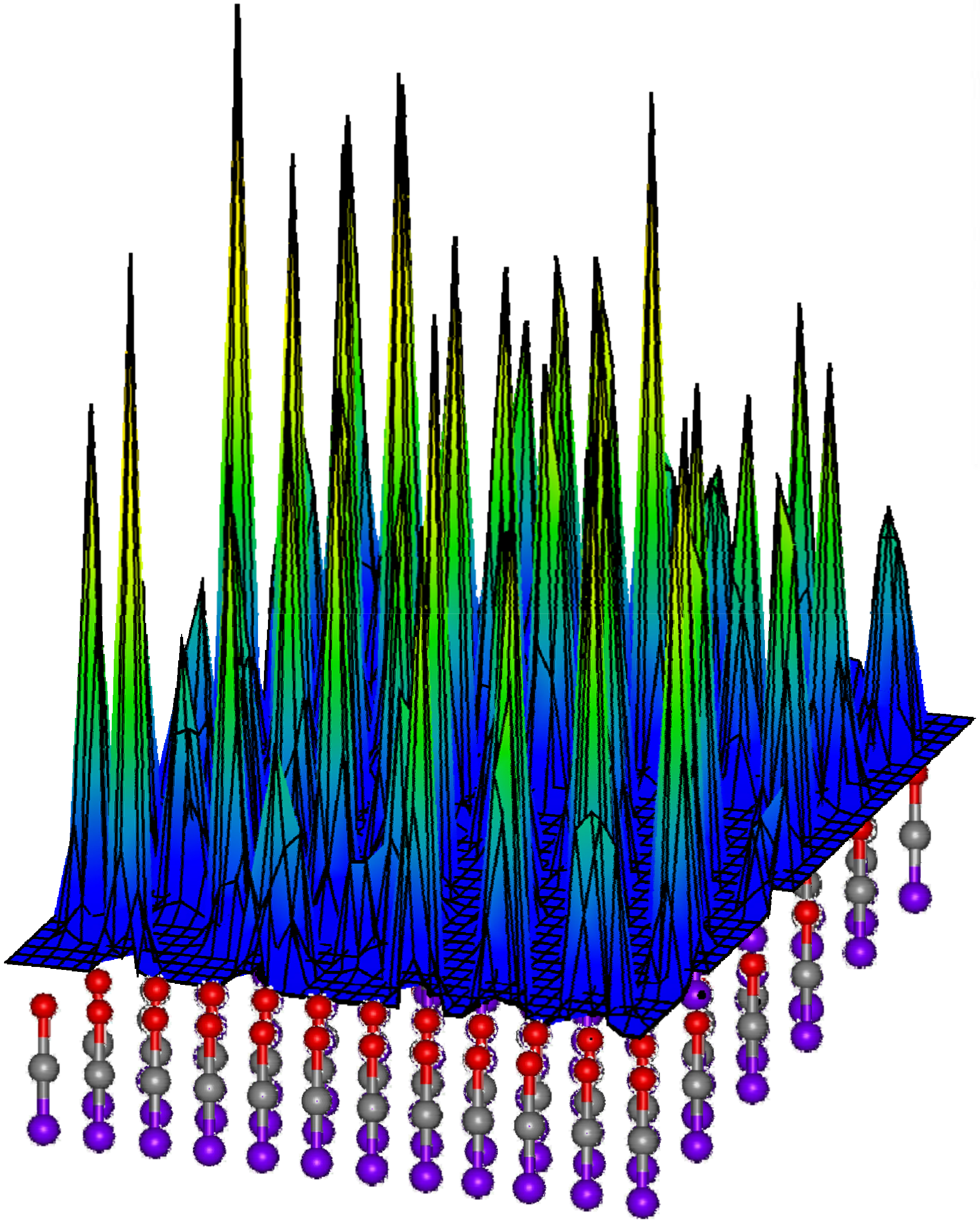
Calculations Xe chemical shift tensor on model surfaces

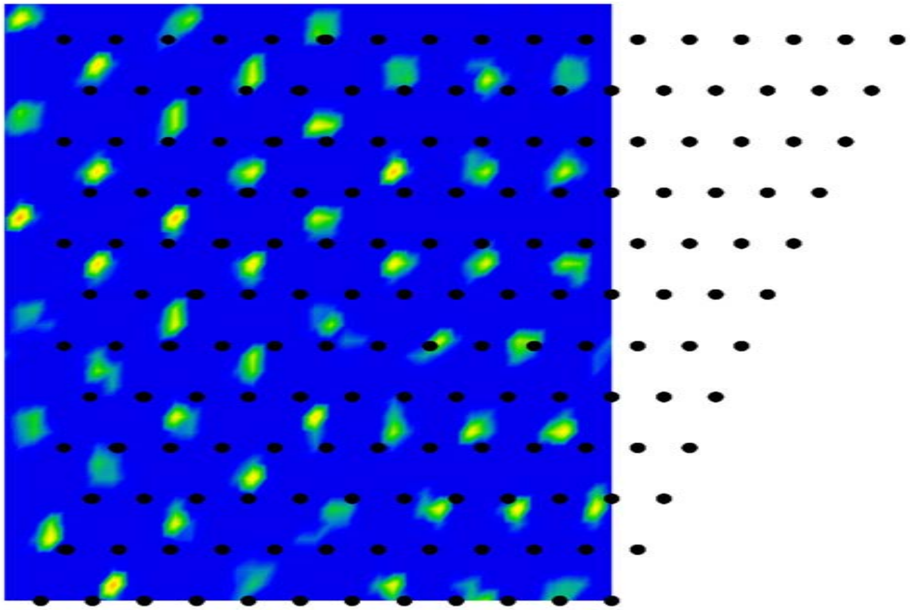
- ^{129}Xe in a xenon sheet

  [using *ab initio* σ(Xe-Xe) tensor function]
- Xe on a –CO monolayer

  [using *ab initio* σ(Xe-Xe) and σ(Xe-CO) tensor functions]

PROBABILITY of finding Xe at various locations



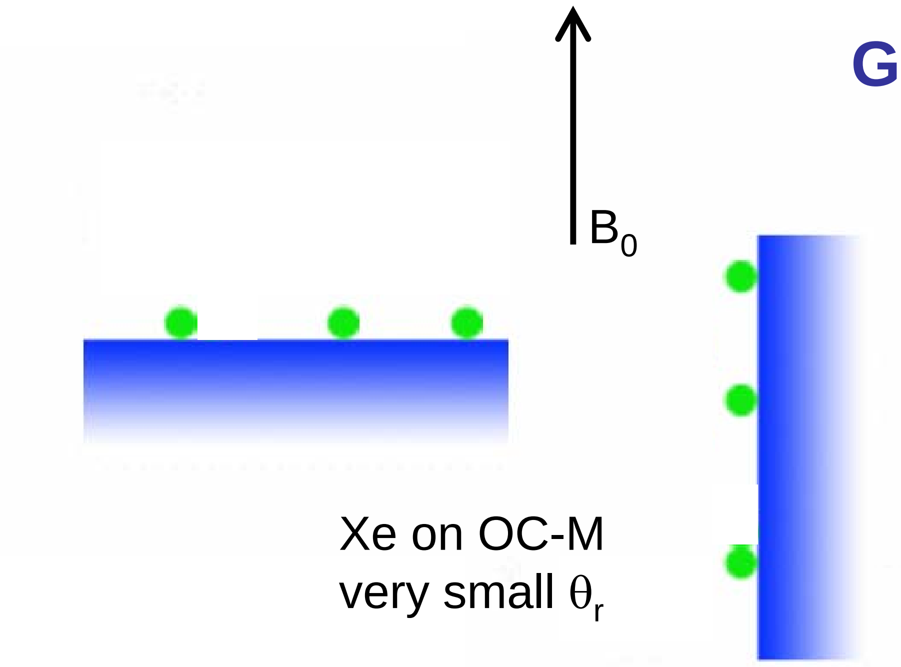


One-body distribution function for Xe@CO monolayer $\theta_r = 1.0$ on Ir(111) from grand canonical Monte Carlo simulations

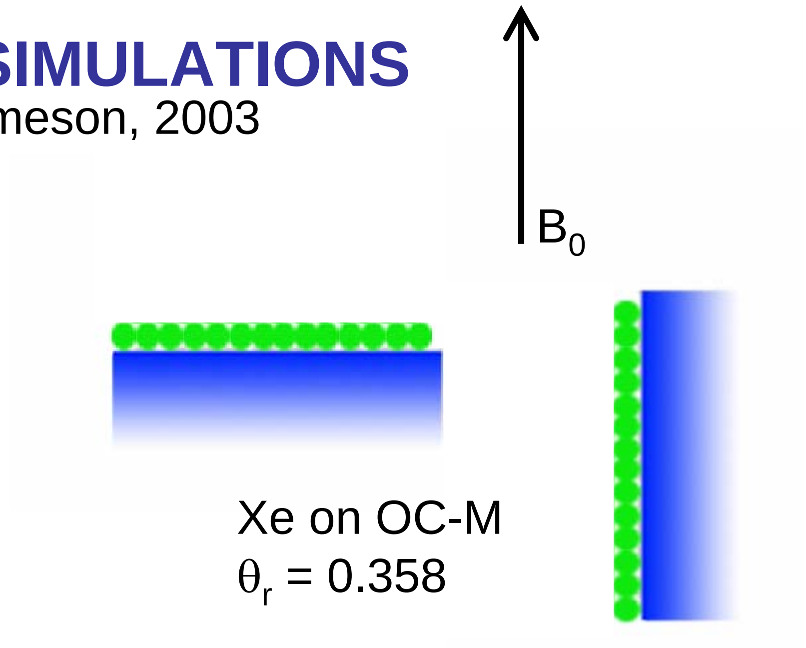
Jameson, 2003

GCMC SIMULATIONS

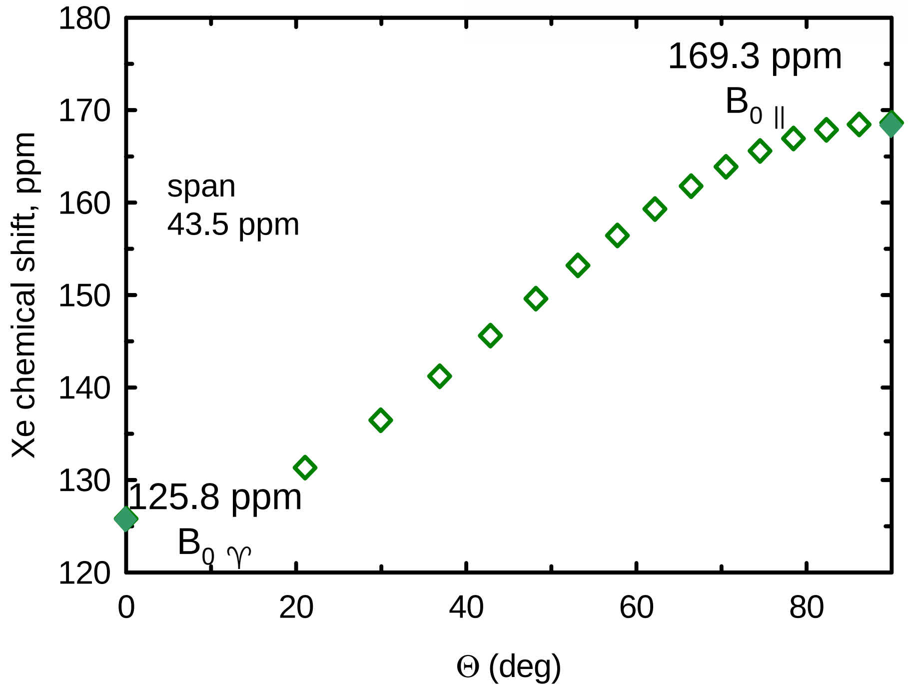
Jameson, 2003

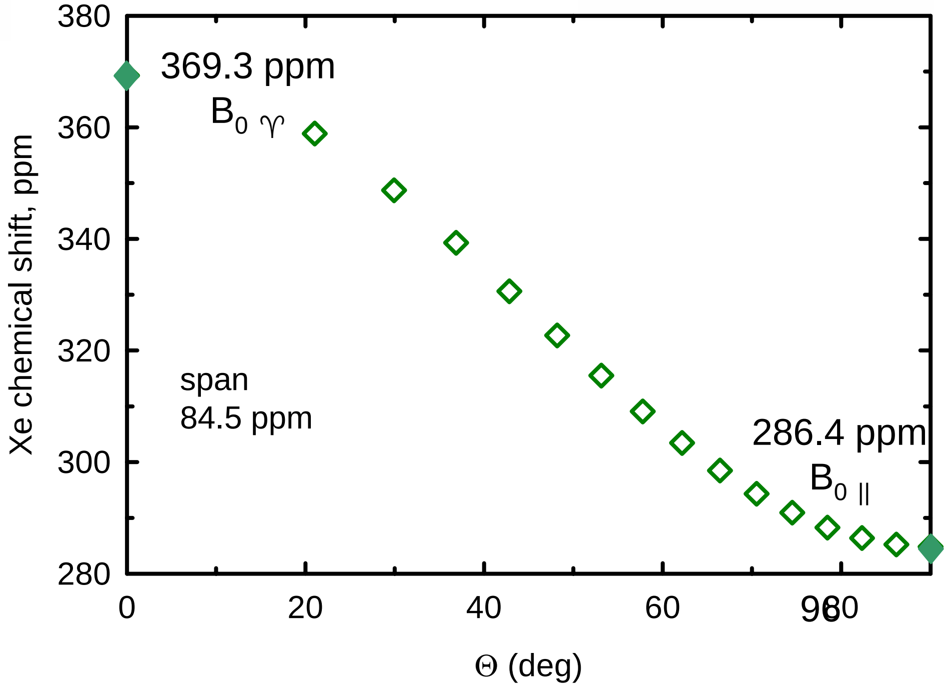


Xe on OC-M
very small θ_r



Xe on OC-M
θ_r = 0.358





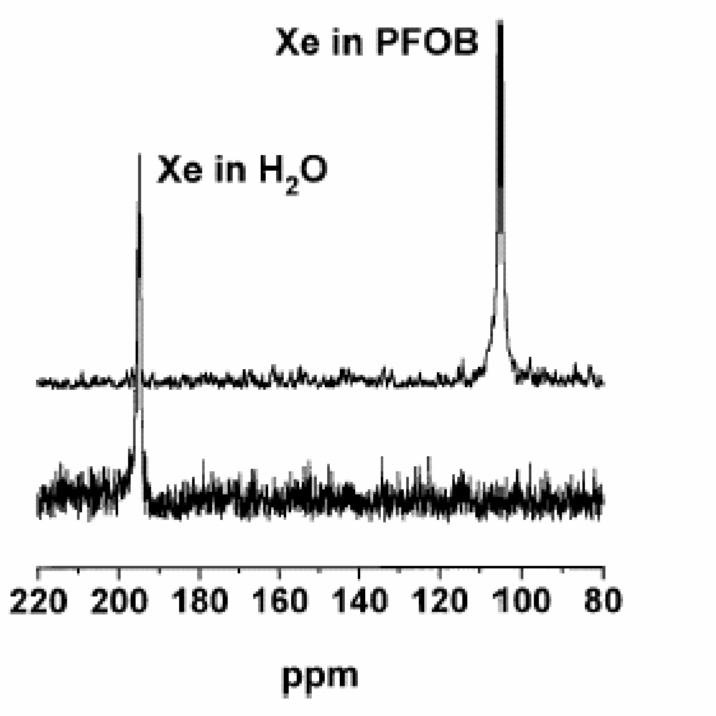
CONCLUSIONS

- The Xe NMR chemical shift is <u>exquisitely sensitive</u> to the environment in which the Xe atom finds itself.
- Encoded in the ***intrinsic shielding response surface*** is the electronic structure of the system (a supermolecule or a crystal fragment) as a function of nuclear configuration.
- The ***dynamic averaging*** encodes further information about the nuclear environment into the observed chemical shift.
- It is possible to use a combination of ***quantum mechanical calculations and grand canonical Monte Carlo simulations in model systems*** in order to understand the Xe chemical shifts. From such understanding may come some insight into the encoded information in more complex, real-world systems.

Future work:
beyond Monte Carlo Molecular Dynamics Simulations

- Xe in **liquids**
    - H_2O
    - perfluorooctyl bromide
    - benzene

- Xe in **models** of polymer voids and protein pockets



J. Wolber, I.J. Rowland, M.O. Leach, and A. Bifone.
Magn. Reson. in Med. **41**, 442-449 (1999).

ACKNOWLEDGMENTS

- with **Devin Sears**:
  Xe in Xe-Rg
  Xe in cryptophane cages
  chirality & shielding
  Xe@C_{60}
  Xe in TPP channel

- with **Robert Harris**:
  chirality & shielding

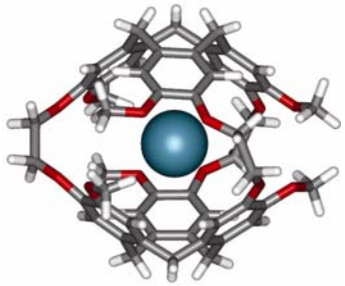
- with **Dirk Stueber**:
  Xe in clathrate hydrates

- **National Science Foundation**

Understanding Xe chemical shifts

additional information:

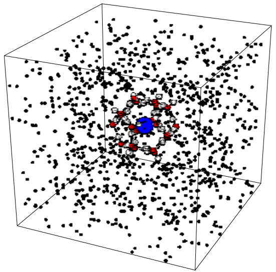
ⓘ additivity



ⓘ crypto QM opt geom

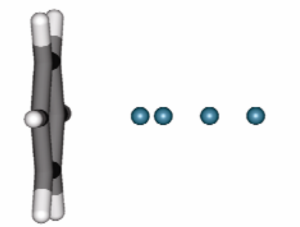
ⓘ crypto fit

ⓘ temp dep

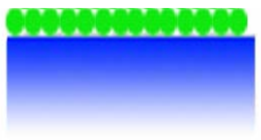


ⓘ proton configs

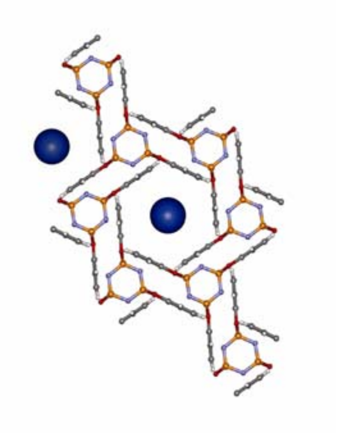
ⓘ clath fit



ⓘ aromatic HF/DFT



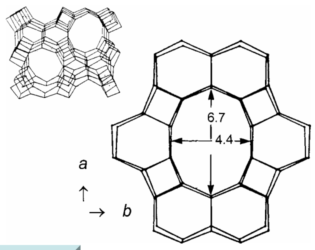
ⓘ Xe sheet



ⓘ TPP ab initio

ⓘ TPP peo/bz

ⓘ Ramsey



ⓘ alpo-11