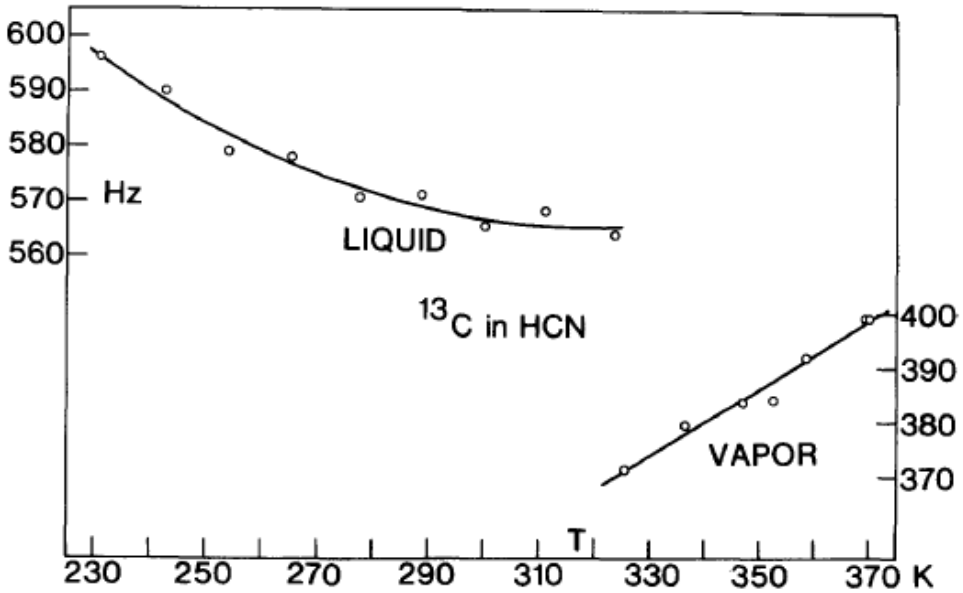
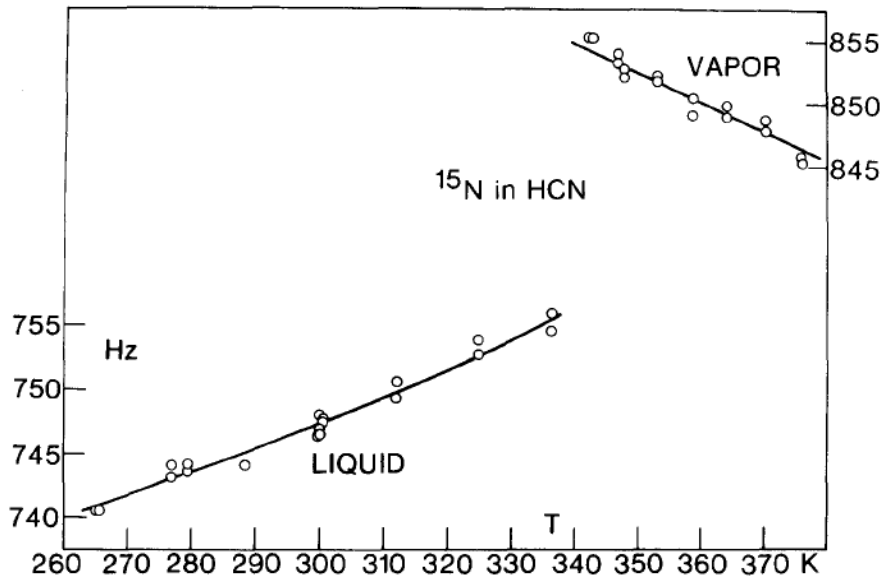
Intermolecular chemical shifts





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Intermolecular shielding depends on:

- phase, density
- number of neighbors
- electronic structure of neighbors
- “ring currents”
- size, shape of confining structure
- nuclear site in the molecule

outline

- gas phase studies
- the intermolecular shielding surface
- gas-to-liquid shifts
- nuclear site effect
- sorbate in a cage or channel in a porous solid
- solute in a liquid solvent
- constitutive contributions from chemical groups of solvent

I. Start with gas phase studies

- Gas phase is ideal system to study intermolecular chemical shifts, can do constant density experiments in the limit of binary interactions
- Density and temperature dependence of intermolecular chemical shifts can be studied separately
- Xe has largest shifts, rare gas atom is simplest structure for probe of intermolecular shielding since good potential functions are available

density dependence of the chemical shift

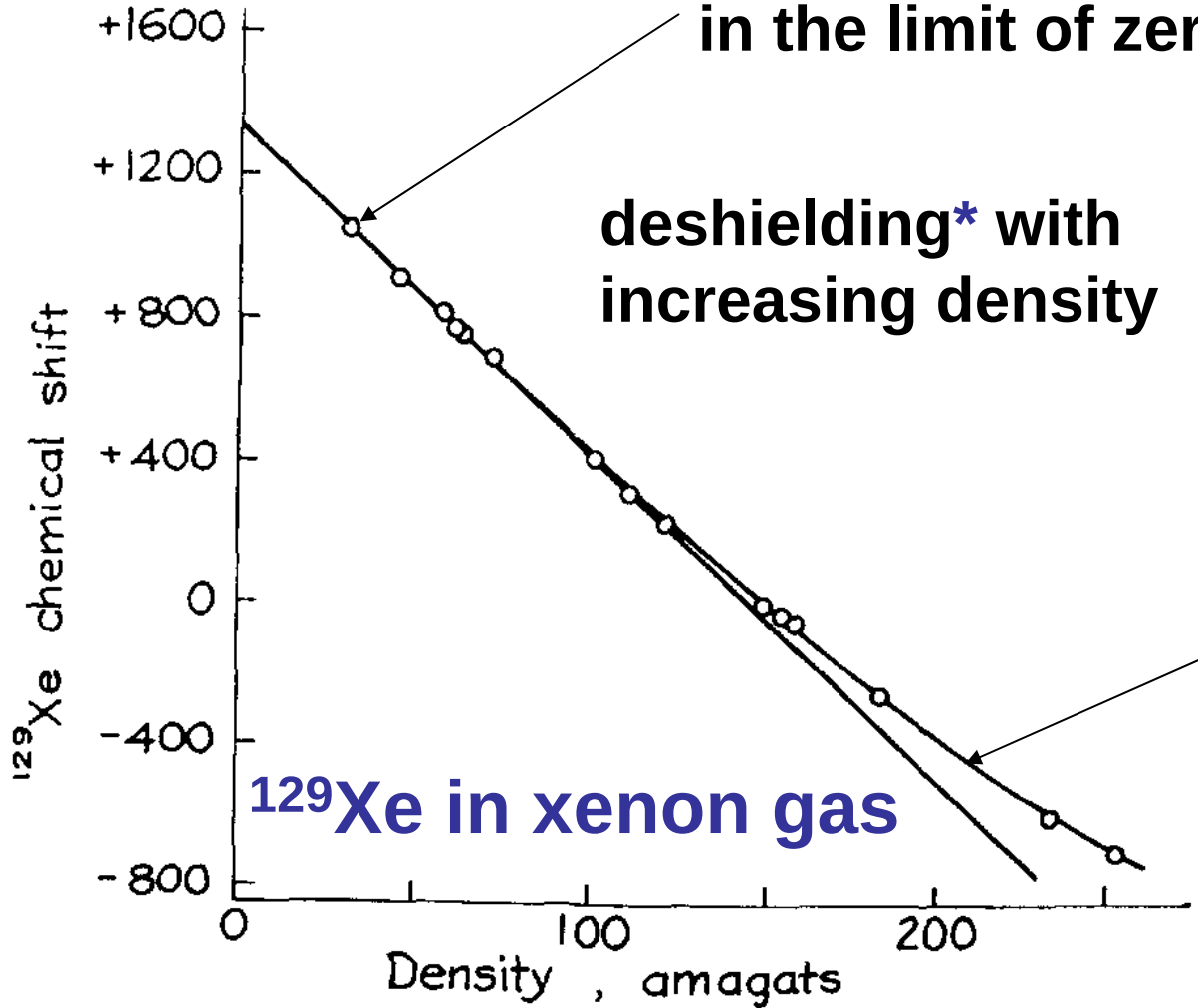
What we expect from the Buckingham-Pople analysis of intermolecular effects on molecular electronic properties as a virial expansion:

A. D. Buckingham. J. A. Pople, Discuss. Faraday Soc. 22 (1956) 17.

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

where ρ is the number density of molecules in the gas

intermolecular shift is linear with density of the gas and deshielding*



linear density dependence in the limit of zero density

deshielding* with increasing density

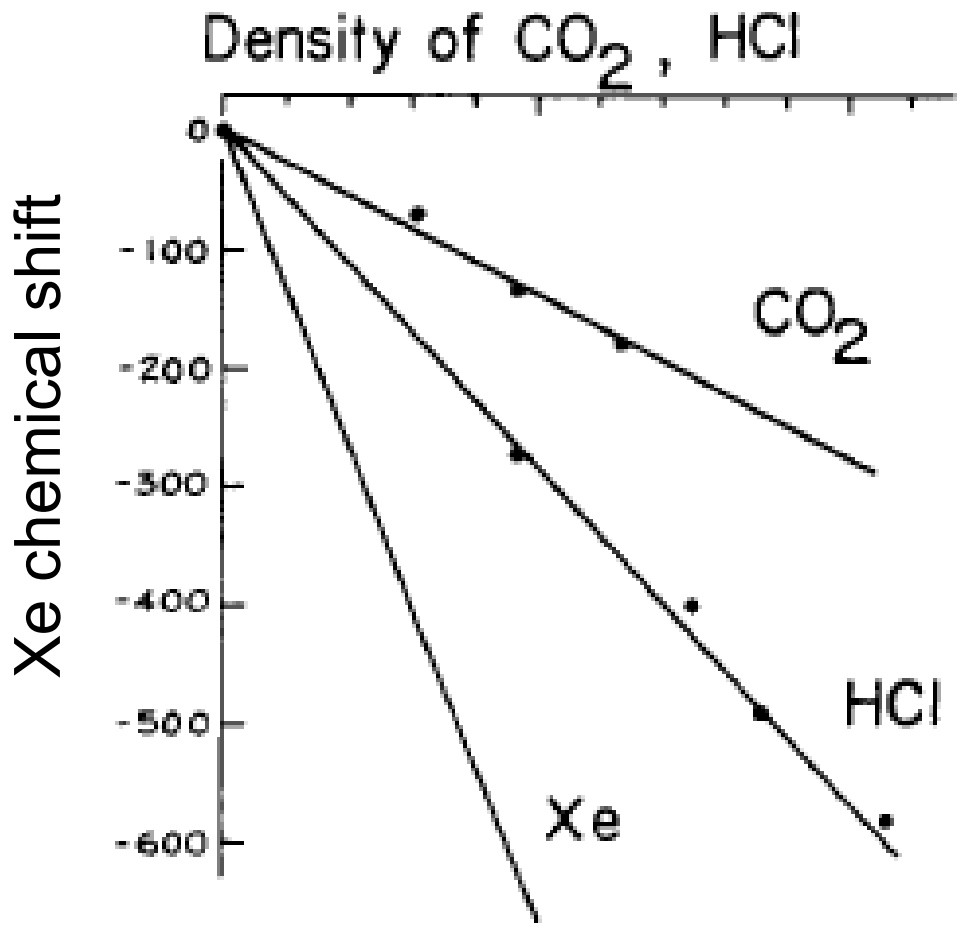
* to lower resonance frequency with increasing gas density

higher order contributions opposite sign to linear contribution

1 amagat is the number density of an ideal gas at standard T and P

Jameson et al. J. Chem. Phys. 53, 2310-2321 (1970).

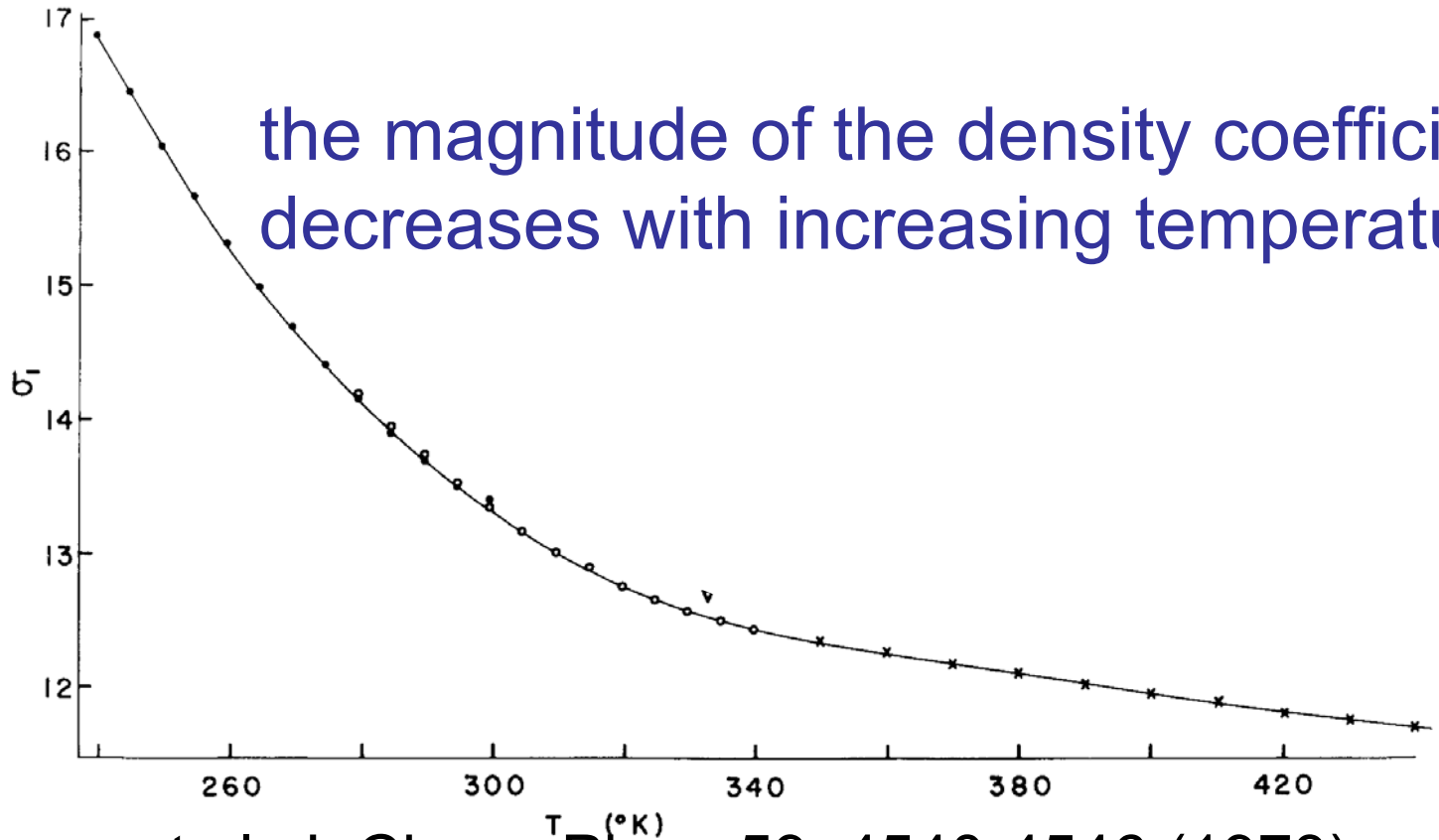
^{129}Xe chemical shift in gas mixtures



$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)_{Xe\text{-}Xe}\rho_{Xe} + \sigma_1(T)_{Xe\text{-}A}\rho_A + \ldots$$

Jameson et al. J. Chem. Phys. 53, 2310-2321 (1970).

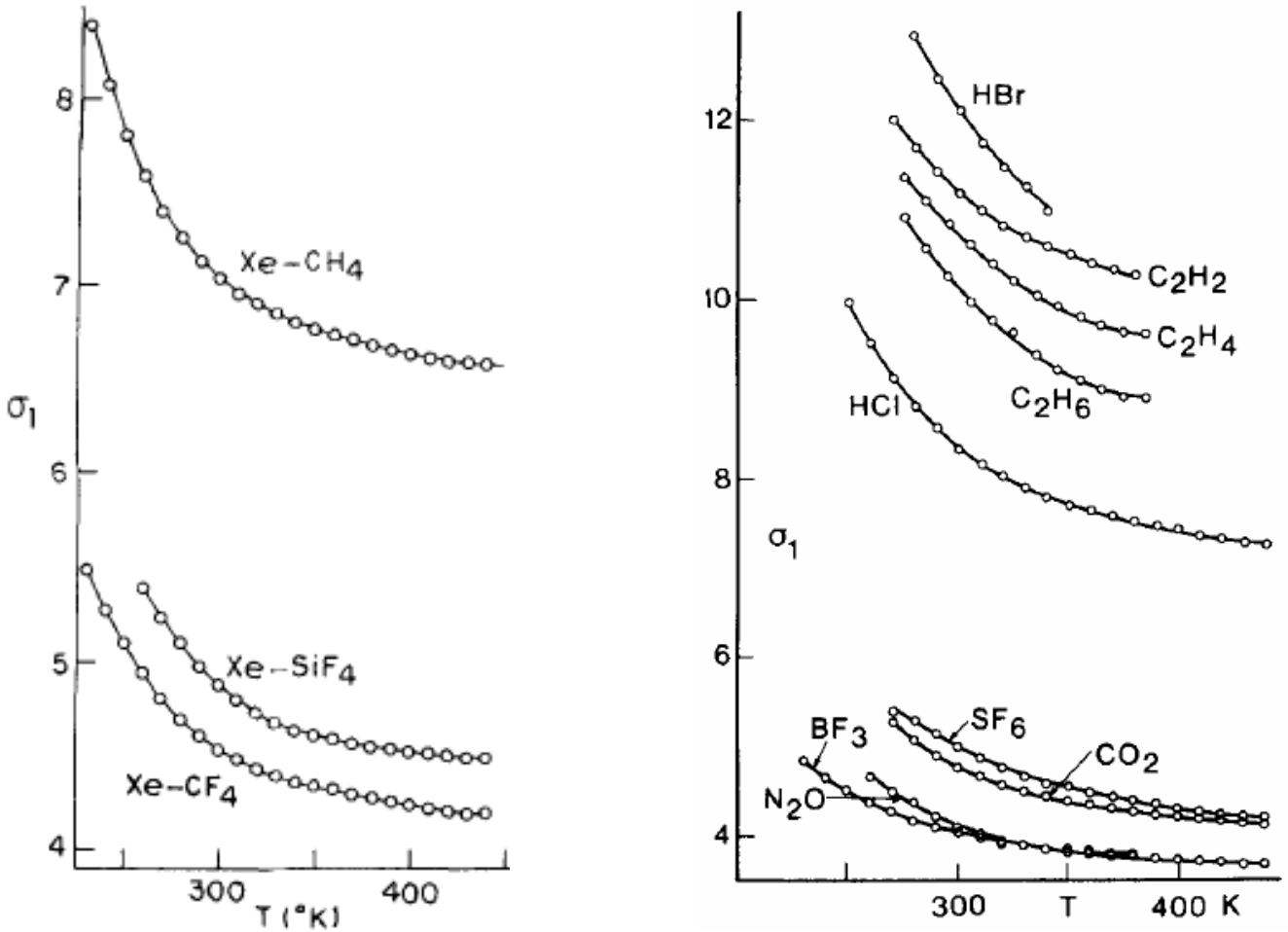
density coefficient of the ^{129}Xe chemical shift, the second virial coefficient of shielding, $\sigma_1(T)$



the magnitude of the density coefficient decreases with increasing temperature.

Jameson et al. J. Chem. Phys. 59, 4540-4546 (1973).

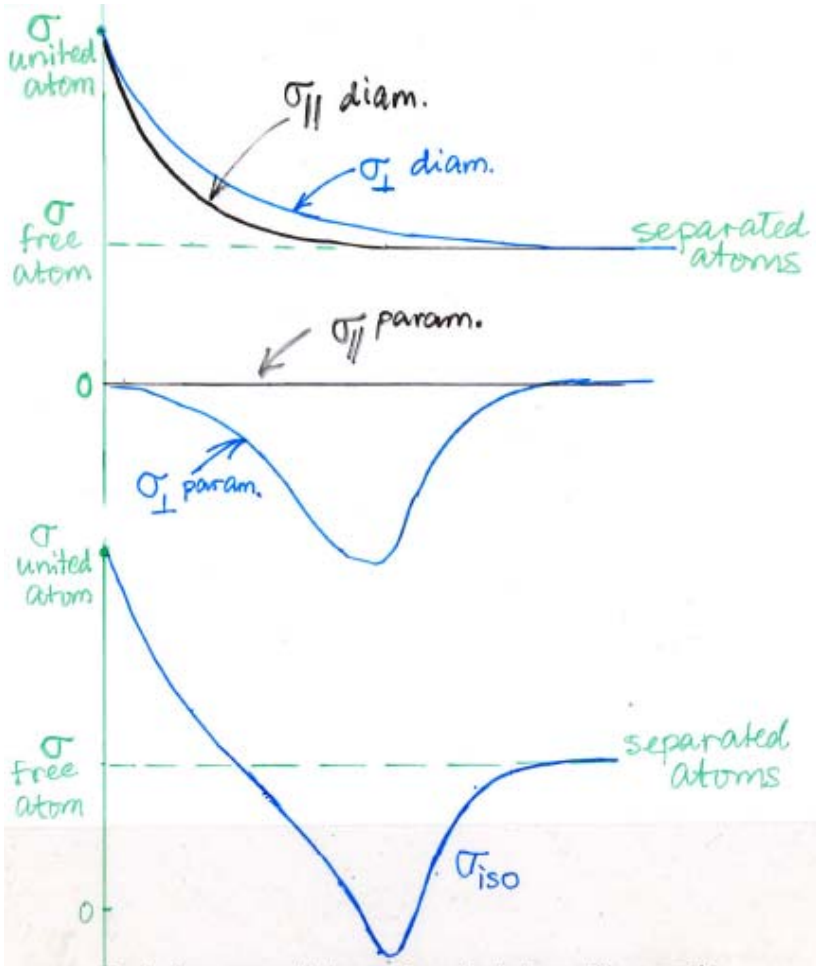
density coefficient of the ^{129}Xe chemical shift in various gases



Jameson et al. J. Chem. Phys. 65, 3401-3406 (1976); J. Chem. Phys. 66, 5226-5230 (1977).

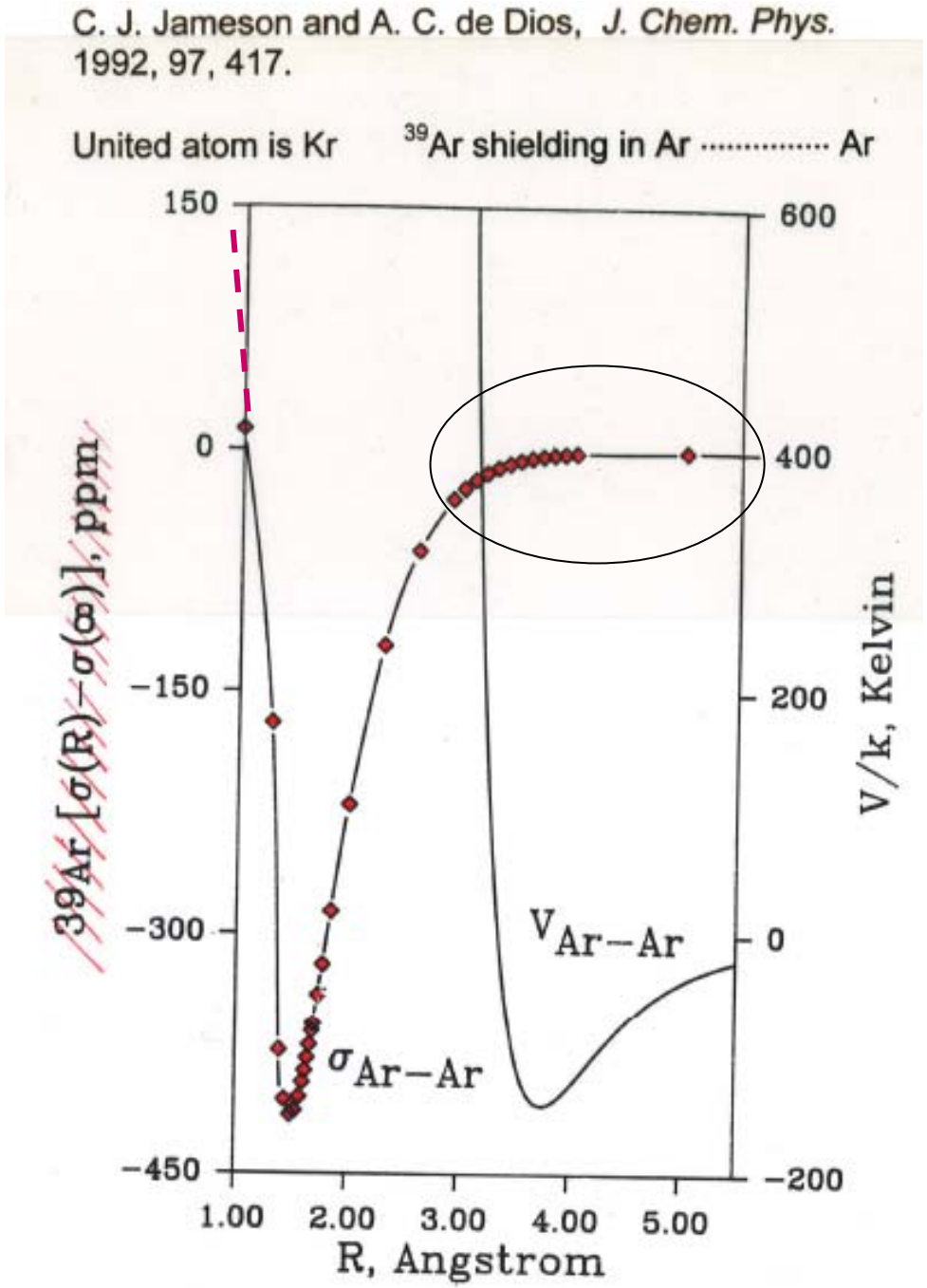
II. the intermolecular shielding function

Symmetry arguments about parallel and perpendicular components of the shielding tensor can be used to deduce the general shape of the intermolecular shielding function in going from separated rare gas atoms to the united atom.



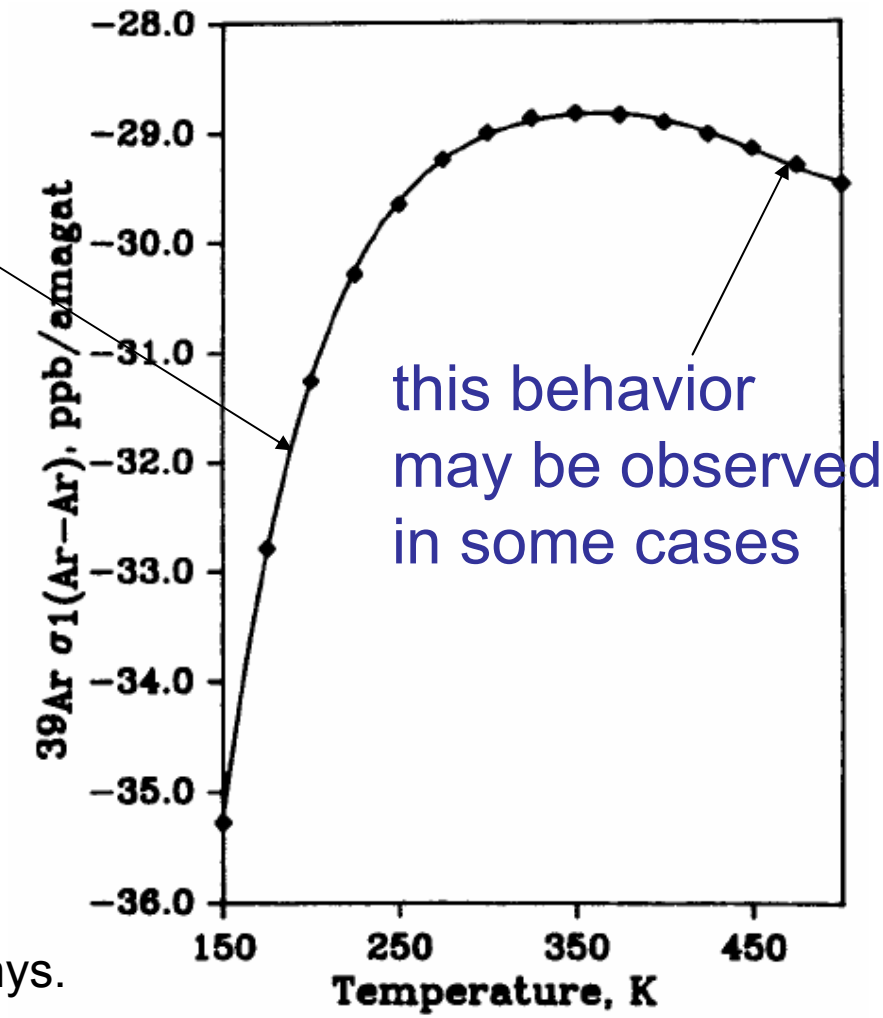
C. J. Jameson, "Intermolecular Interactions and NMR Spectroscopy", Gordon Conference on Atomic and Molecular Interactions, 1982

Quantum mechanical calculations of parallel and perpendicular components of the Ar shielding tensor (Ar_2 model system) indeed reproduce the general shape of the intermolecular shielding function in going from separated Ar atoms to the united atom Kr.



general form of the second virial coefficient of nuclear shielding

generally decreasing magnitude of the density coefficient with increasing temperature



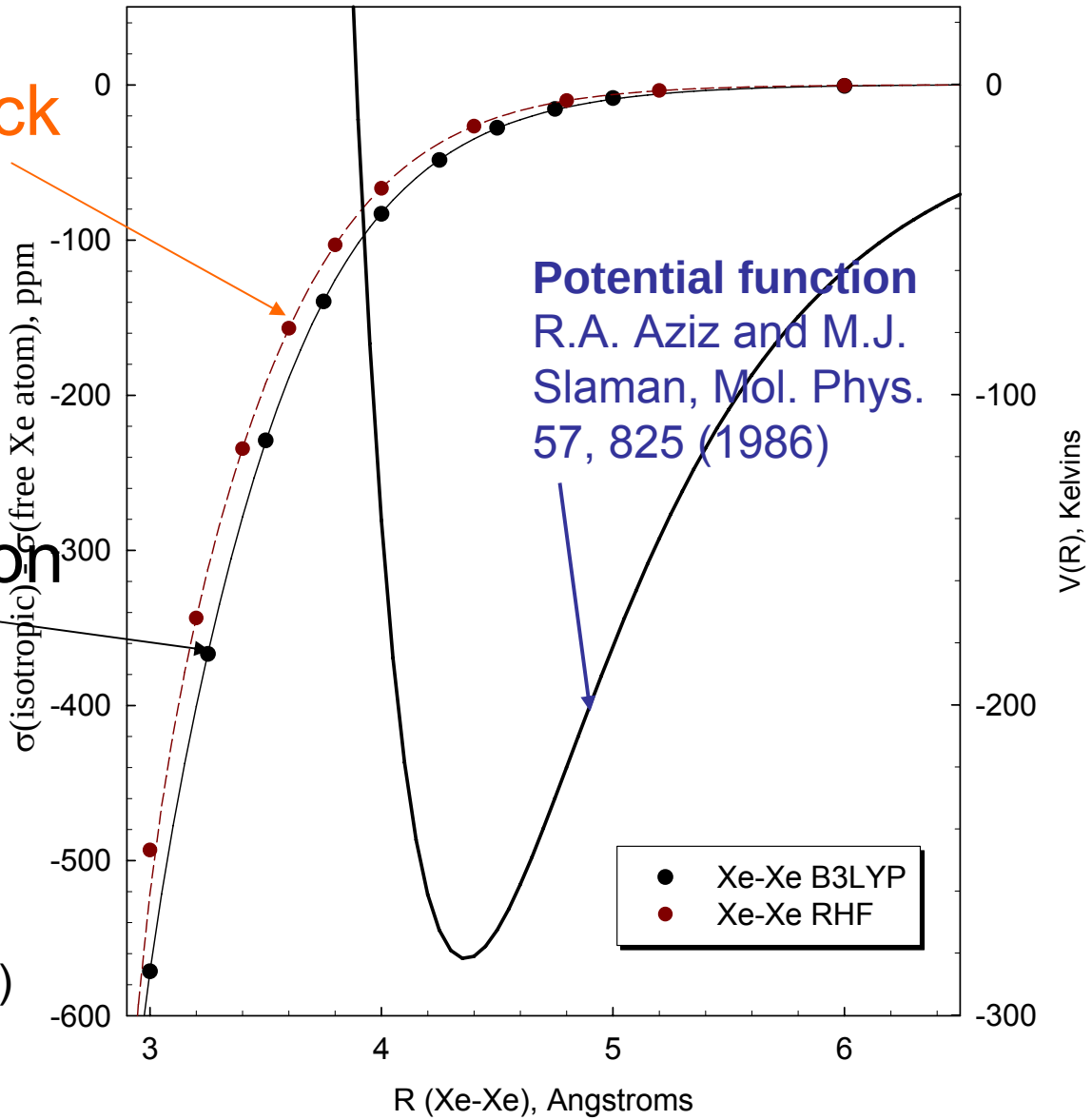
predicted: A. C. de Dios, J. Chem. Phys. 97, 417-434 (1992)

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

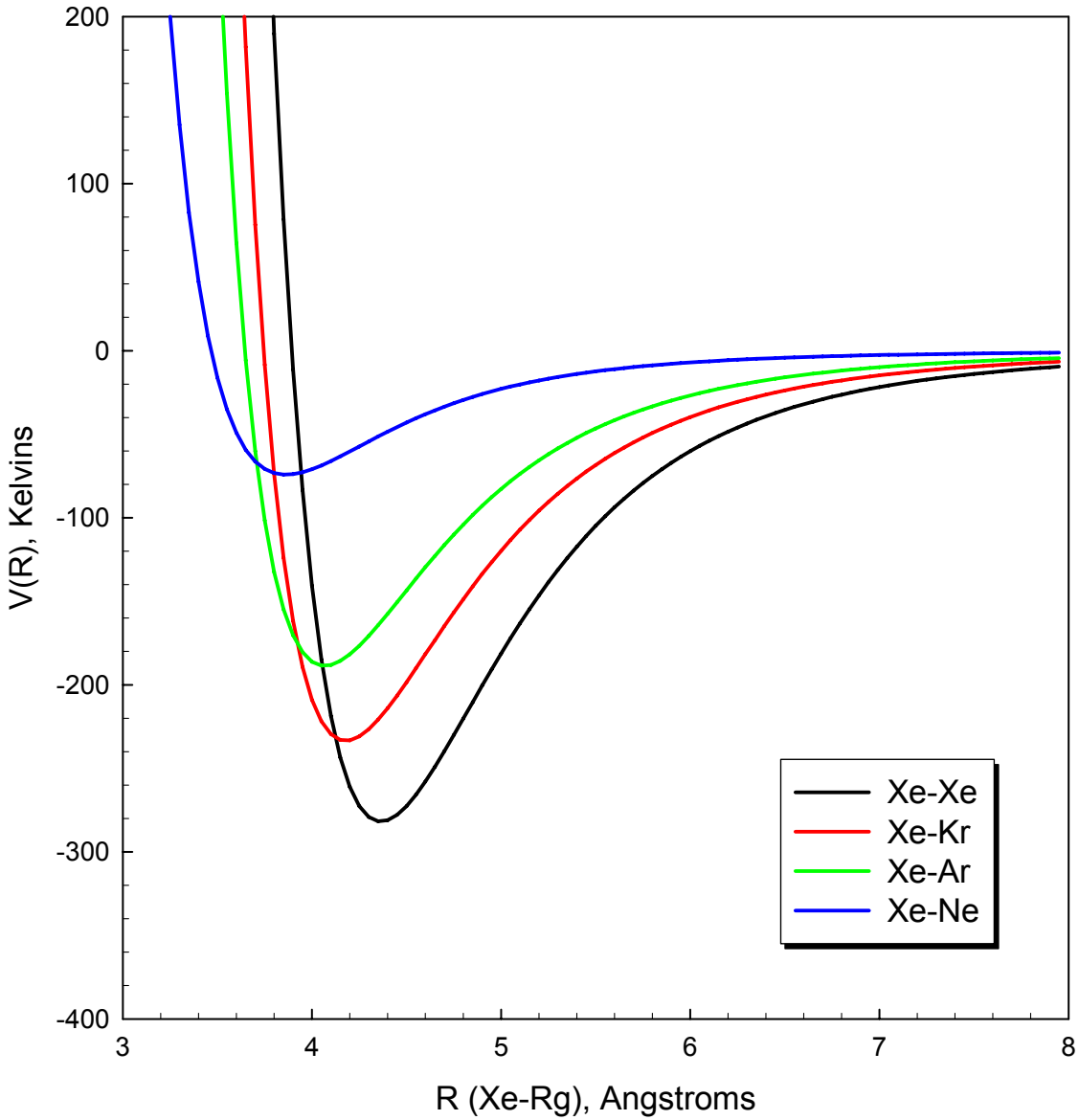
Hartree Fock

with electron correlation

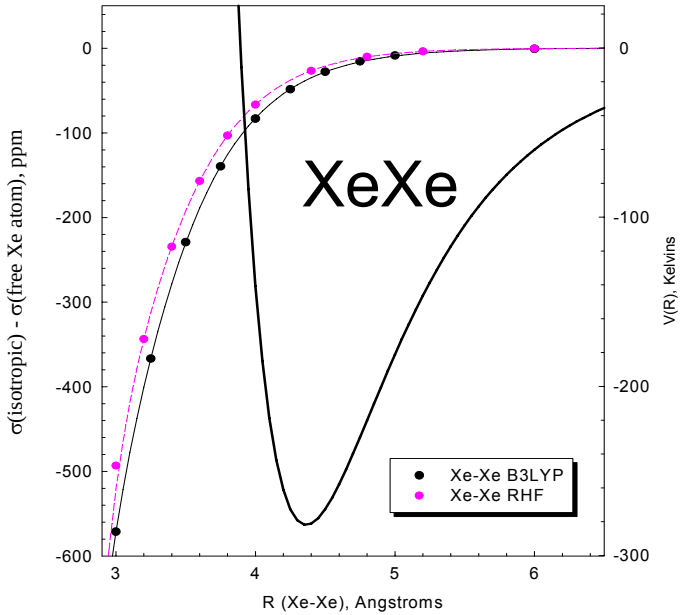
Jameson et al.
J. Chem. Phys.
118, 2575 (2003)

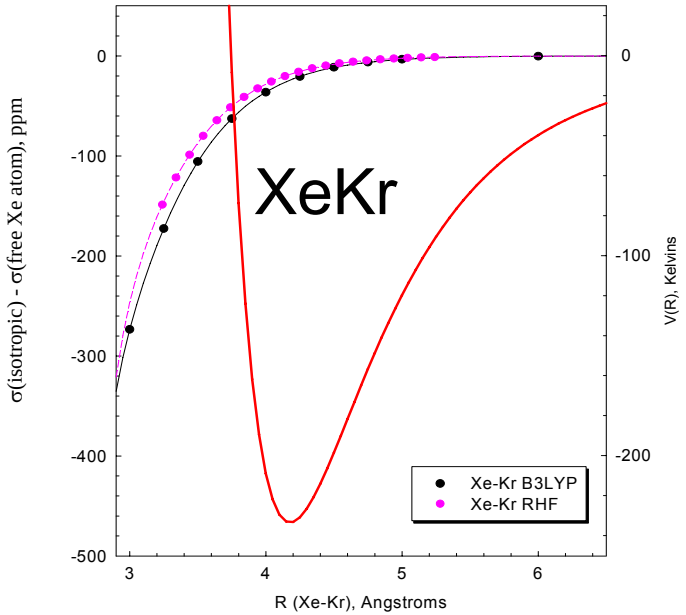


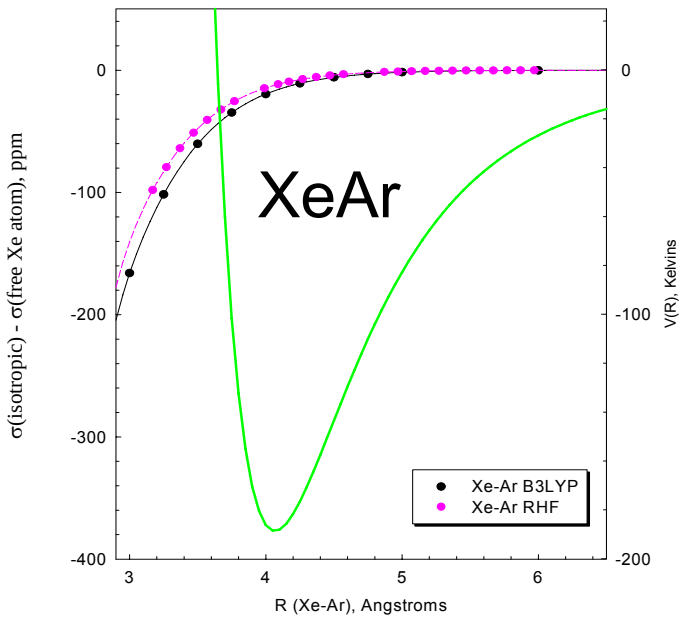
Xe - Rg Intermolecular Potentials (Aziz et al.)

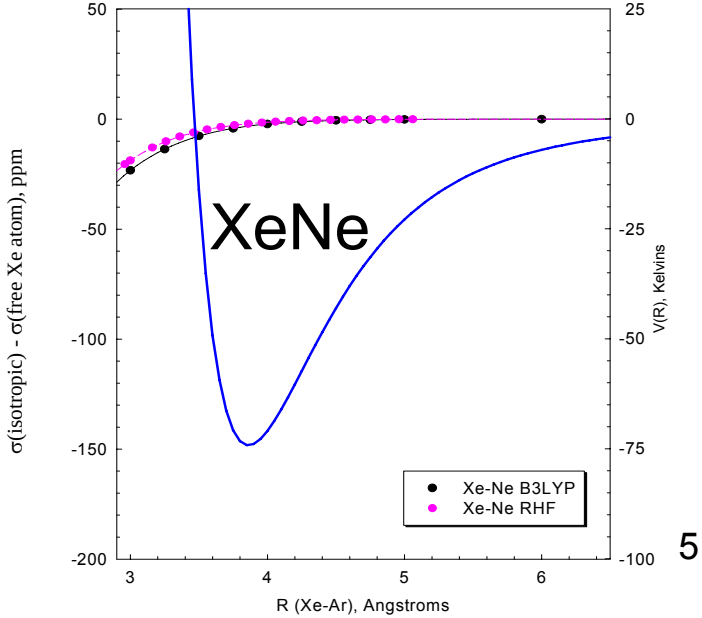


Xe shielding surface and PES for the Xe-Rare gas systems









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

Xe in gas phase mixtures:

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

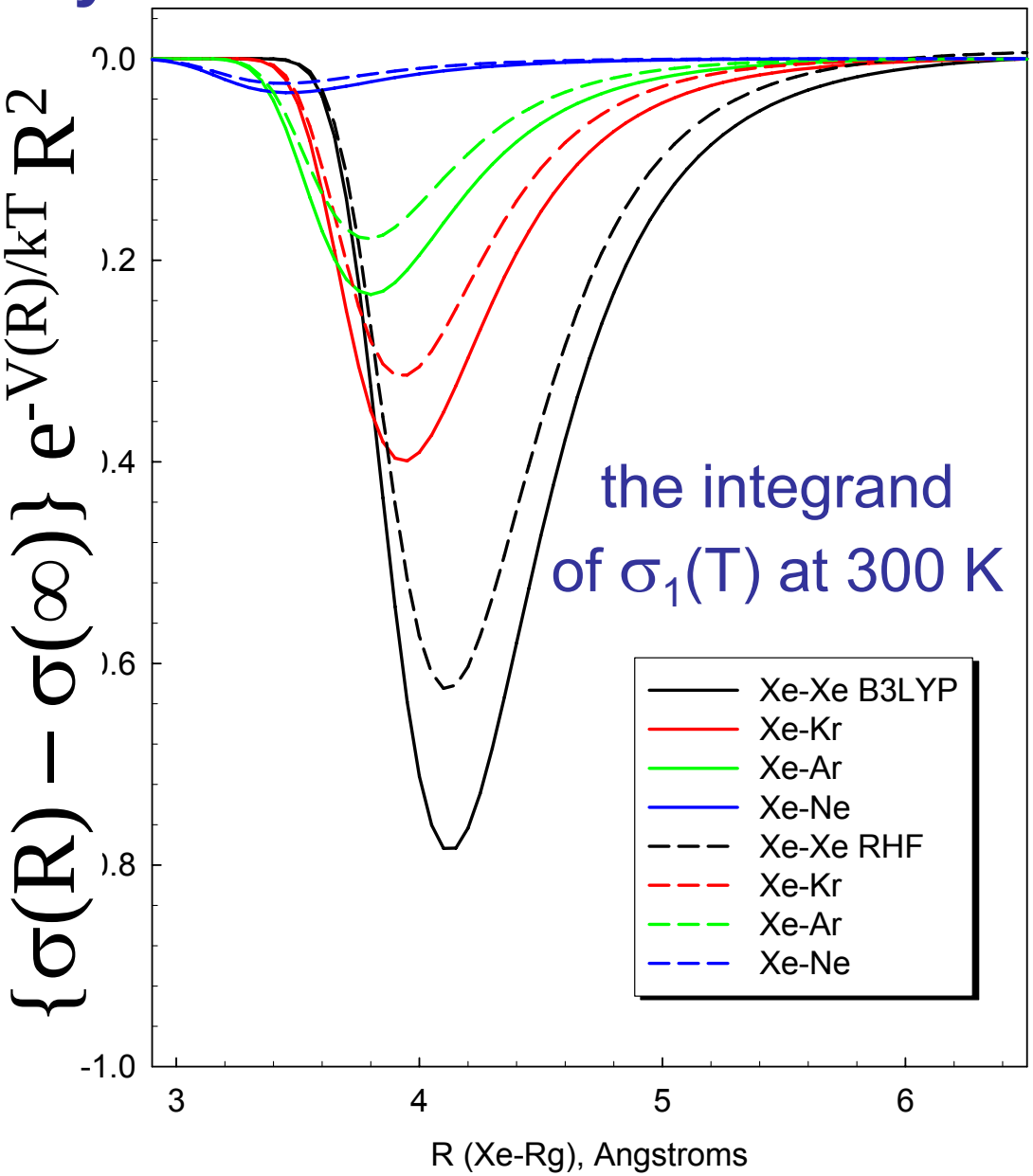
$$\sigma_1(T)_{XeRg} = 4\pi \int_0^\infty \{\sigma(R) - \sigma(\infty)\}\, e^{-V(R)/kT}\, R^2\, dR$$

SHIELDING SURFACE PROBABILITY

V(R) = Xe–rare gas potential function

Jameson et al. 1970

The range of interaction measured by the intermolecular chemical shift



or **which distances contribute to the observed density coefficient of the chemical shift?**

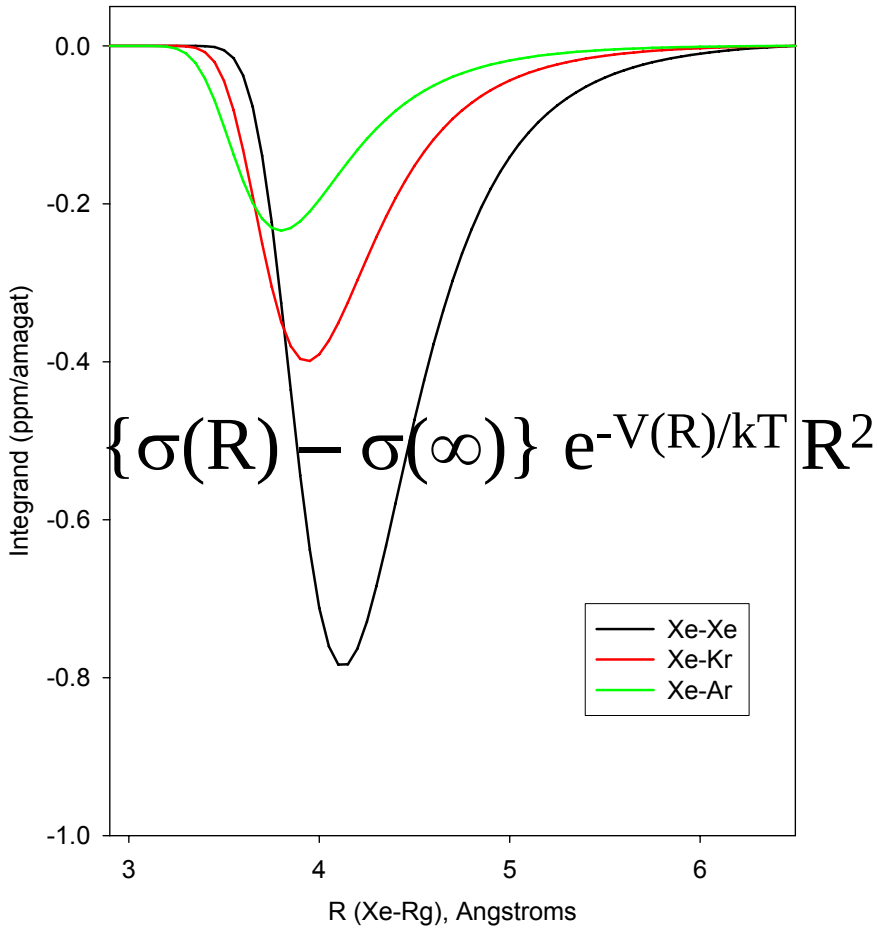
SCALING:

corresponding states

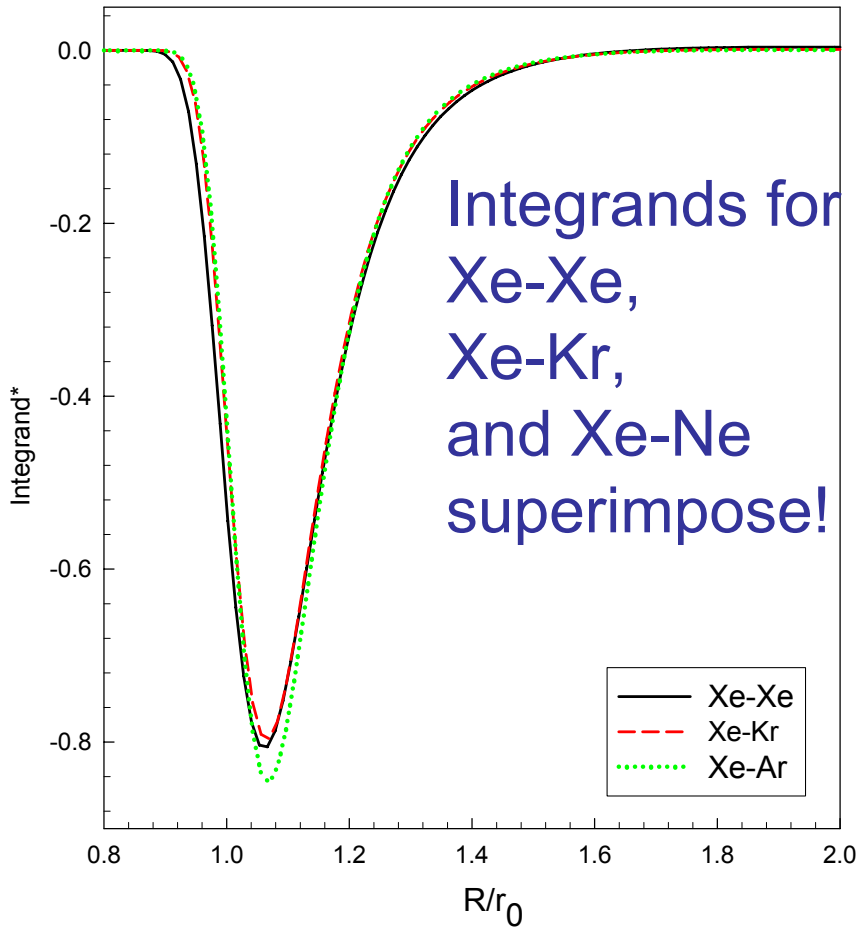
$T/T_c = 1$

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

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



$$\{\sigma(R) - \sigma(\infty)\}\, e^{-V(R)/kT}\, R^2$$

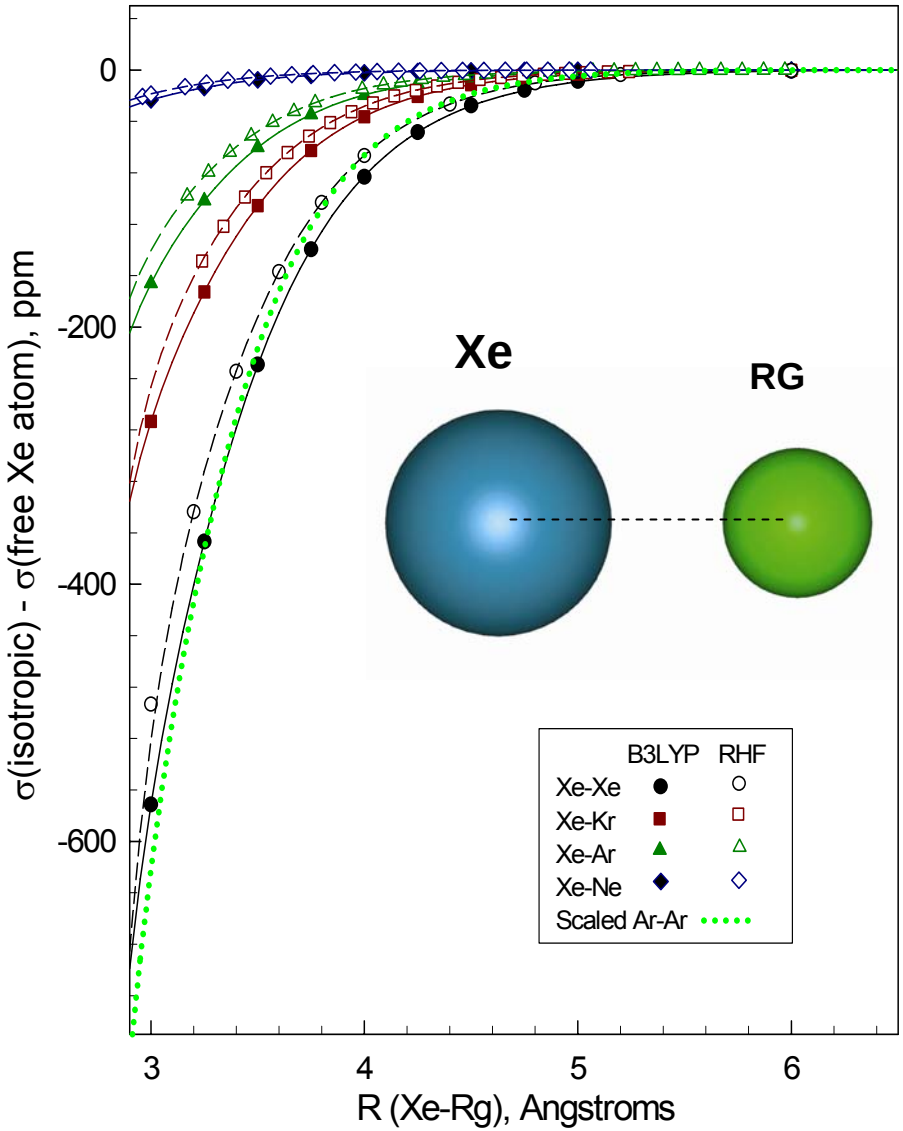


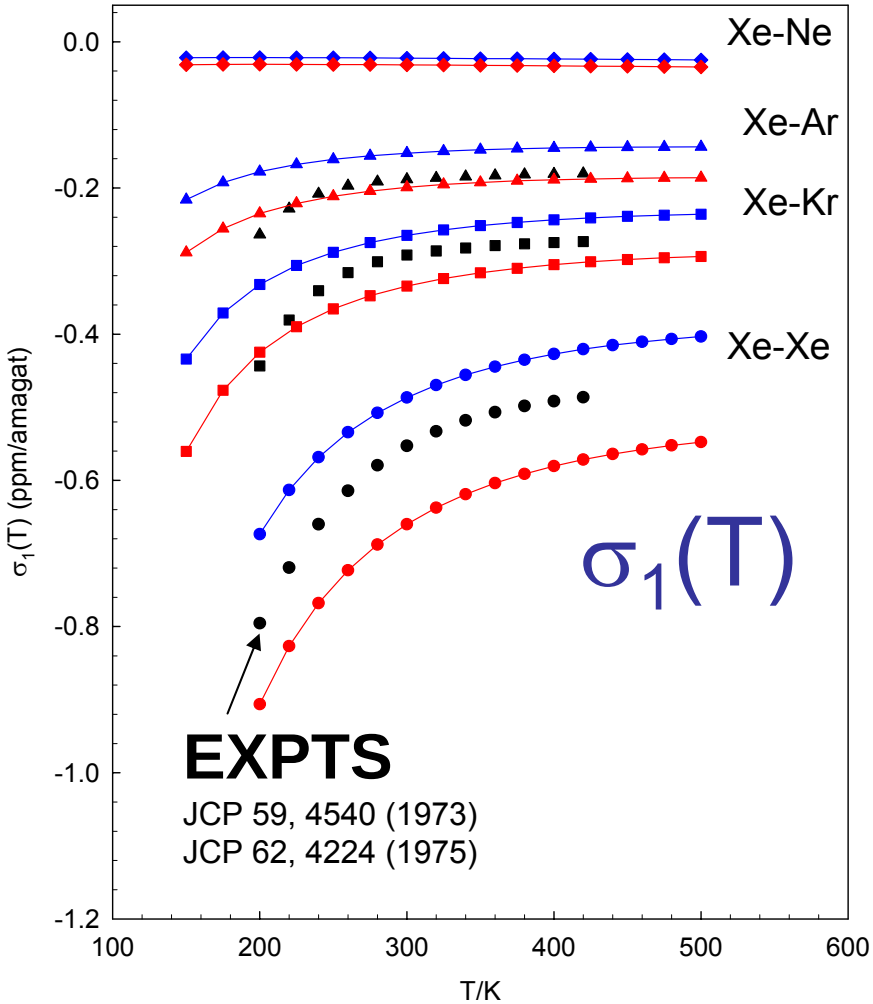
Integrands for Xe-Xe, Xe-Kr, and Xe-Ne superimpose!

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-RG shielding functions and density coeficients





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

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

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

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

quantum mechanical calculations comparison with experiment

- DFT-B3LYP has too much electron correlation contributions
- Hartree-Fock has none
- Experimental values of $\sigma_1(T)$ fall between these two calculations of second virial coefficient of nuclear shielding for Xe.

other probes

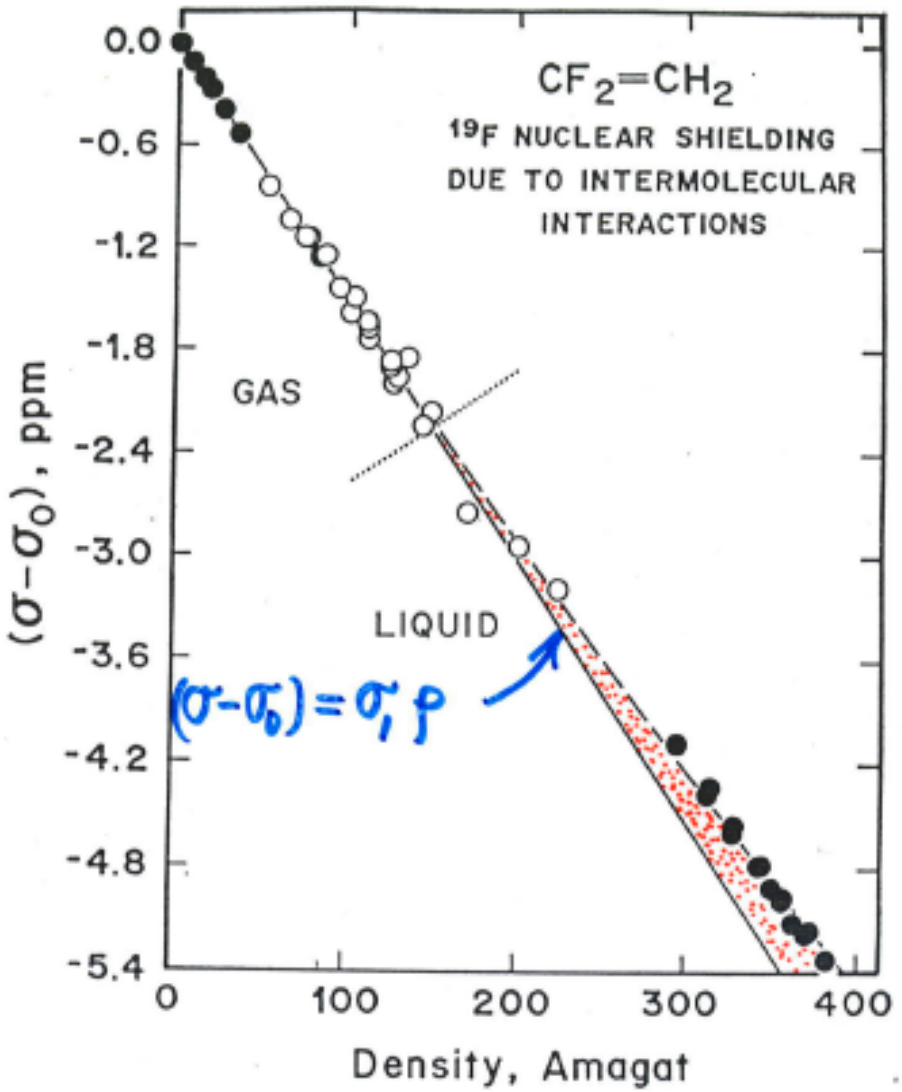
- A molecular probe can be used to study nuclear site effects
- Use ^{19}F, ^{31}P, and other high abundance high gamma spin 1/2 nuclei
- Disadvantages:
  - (a) potential functions not high quality as rare gases,
  - (b) intramolecular effects are always present and have their own temperature dependence,
  - (c) J coupling may complicate spectra and have their own temperature dependence

^{19}F intermolecular shifts

(a) intermolecular shifts are linear with density at low densities

(b) are deshielding

(c) at much higher densities, the higher order contributions to intermolecular shifts appear to be opposite in sign to the linear contribution, just as found in Xe

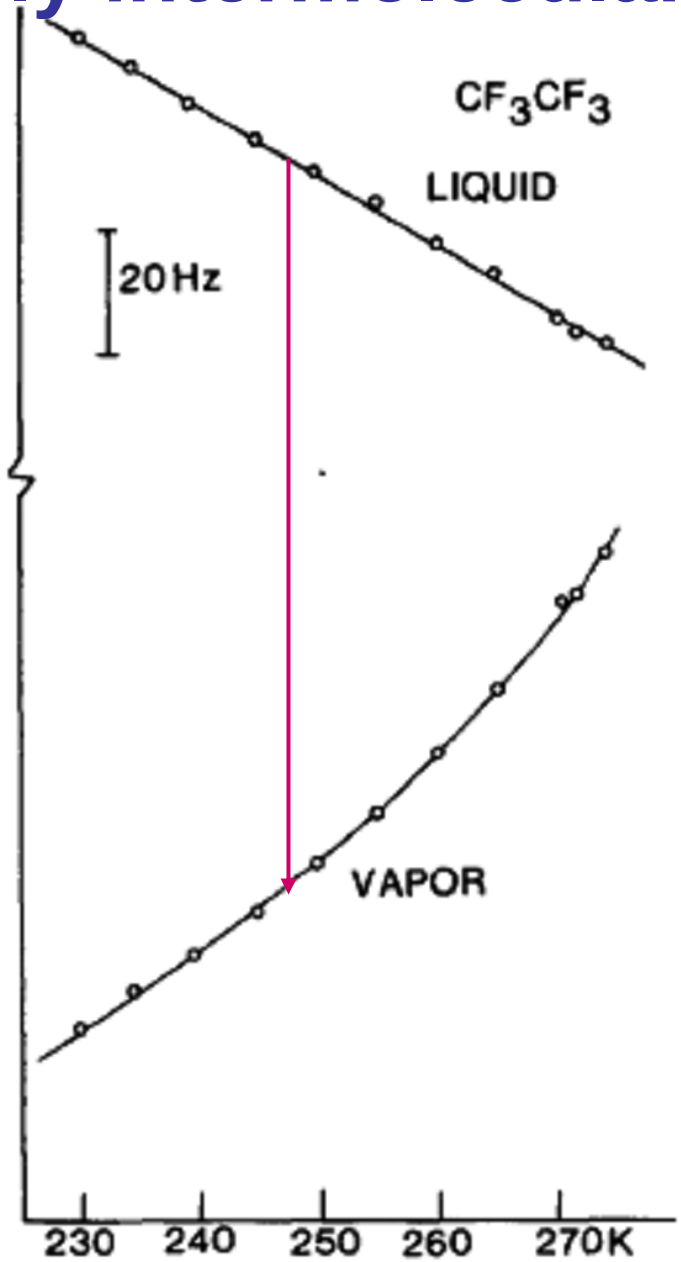


III. gas-to-liquid shifts

- for nuclei in molecules with structure, the intramolecular shielding (changes with bond length, bond angles, torsions) has a temperature dependence due to rovibrational averaging. Thus, we need to remove the latter in order to see the dependence of the intermolecular chemical shift with density and temperature.

gas-to-liquid shift is purely intermolecular

The temperature dependent **intra-molecular part** of the ^{19}F chemical shift is common to **both the liquid phase and the vapor** in equilibrium with it in the sealed sample.
Thus, the difference between the liquid and the vapor peaks in the spectrum is the **intermolecular chemical shift**, ***more deshielded (higher resonance frequency) in the liquid than in the vapor USUALLY*** and **decreasing with increasing temperature**



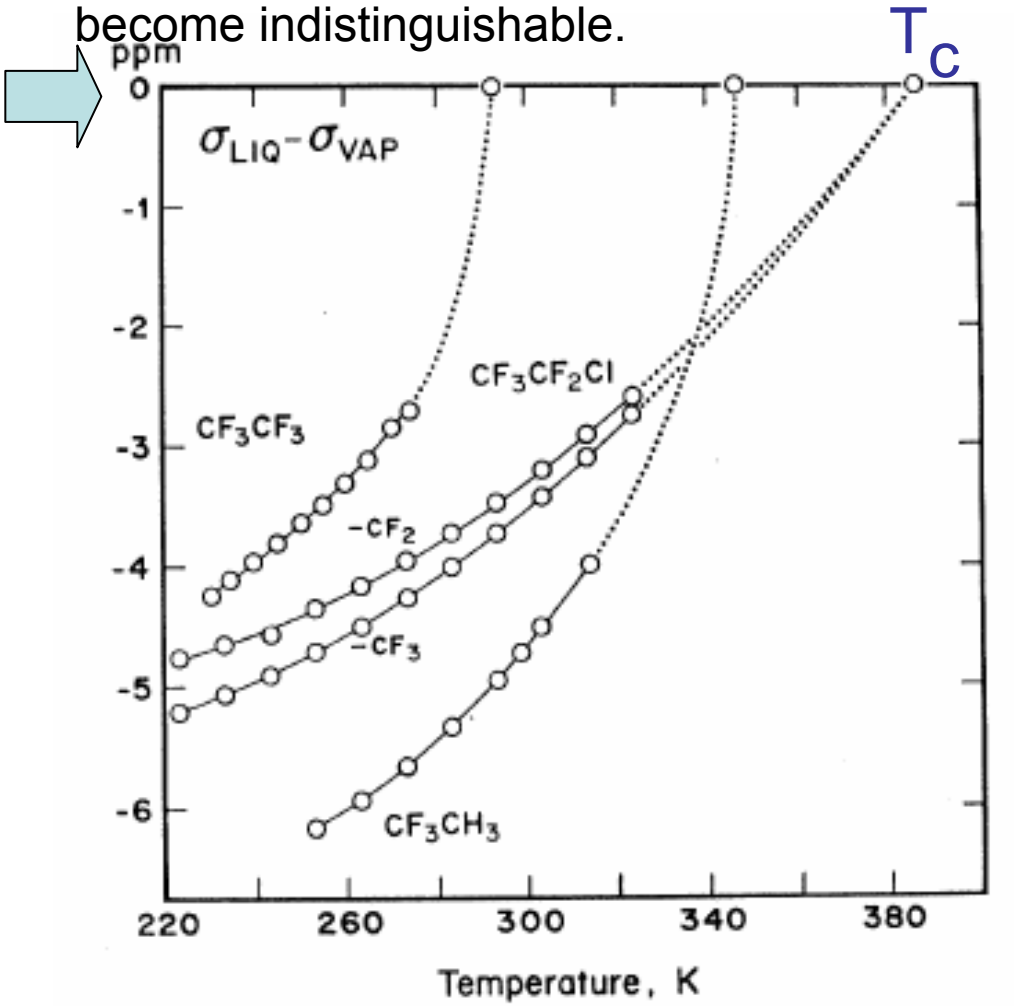
from gas to liquid shifts: $\delta(T,\rho)- \delta_0(T) \approx \delta_{1eff}(T)\, \rho_{LIQ}(T) + \ldots$

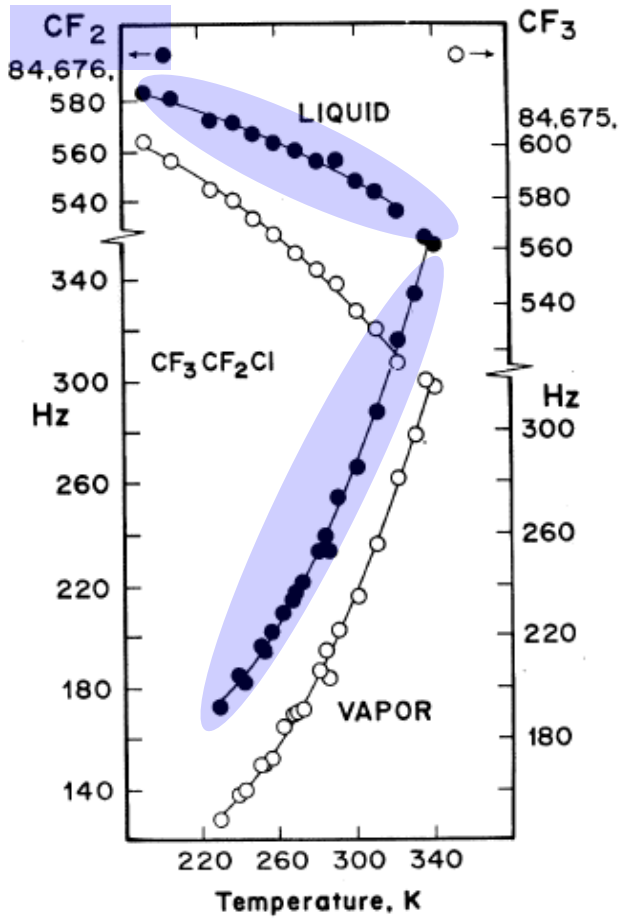
δ_{1eff} magnitudes less than δ_1 from low density gas limit

- measured density coefficient of the chemical shift in the liquid has been found to be lower in magnitude (at the same temperature) compared to the observed second virial coefficient in the low density gas
- This is consistent with the finding that many-body contributions to Xe chemical shift in high density Xe gas are opposite in sign to the two-body contributions that are obtained in the limit of vanishing density

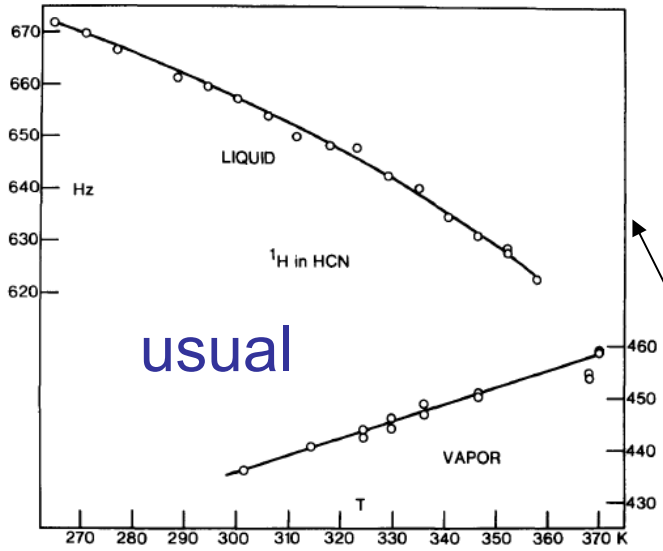
nuclei in different sites in the same molecule do not have the same intermolecular shift

The difference should go to zero at the critical temperature where liquid and vapor become indistinguishable.

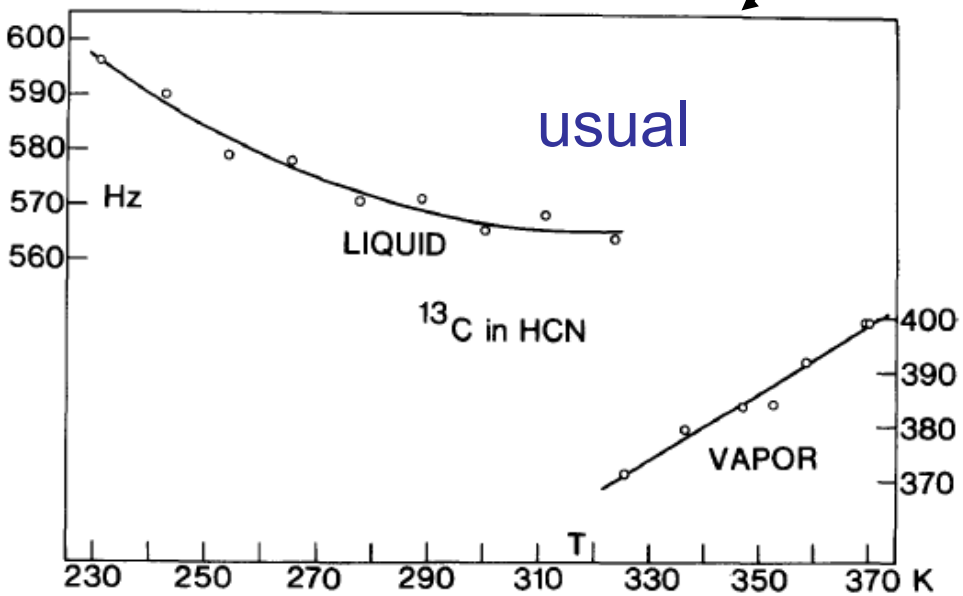


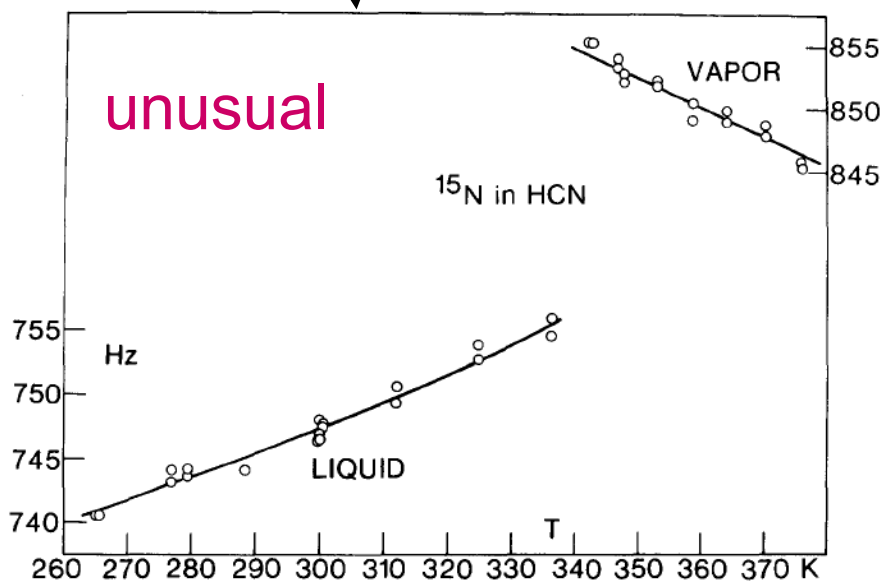


Sometimes the intermolecular chemical shift is opposite in sign to the usual.



^{1}H, ^{13}C, and ^{15}N in HCN





^{15}N in HCN

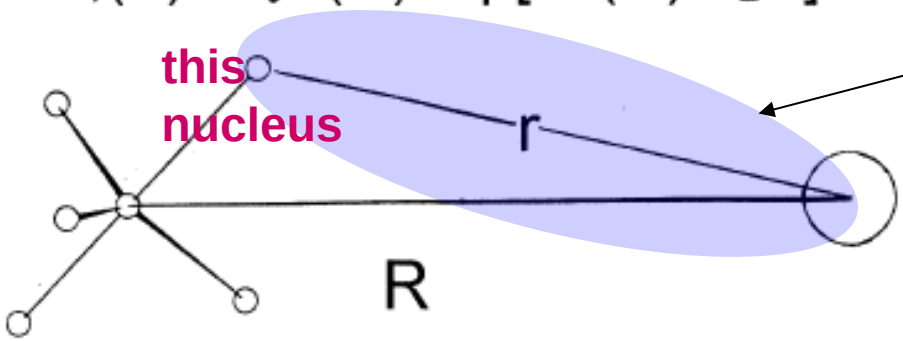
- The lone pair electrons on the N causes a shielding increase upon association of HCN molecules, since the H of one molecule forms a hydrogen bond with the N of the other molecule by sharing the lone pair. The paramagnetic part of the N shielding has a very deshielded component associated with the $n \rightarrow \pi^*$ relatively low-lying excited state. Upon association, the lone pair (n) no longer provides this very deshielded contribution. Thus association of HCN molecules leads to an unusual increase in N resonance frequency. Any effect which removes the lone pair contribution (protonation, for example) leads to this unusual intermolecular shift.

IV. the nuclear site effect

site factor

density coefficient of shielding in a gas is

$$\sigma_1(T) = \int \sigma(\mathbf{R}) \exp[-V(\mathbf{R})/k_B T] d\mathbf{R}$$



rare gas pairs: $\sigma_1(T) \sim \langle R^{-6} \rangle$

vs.

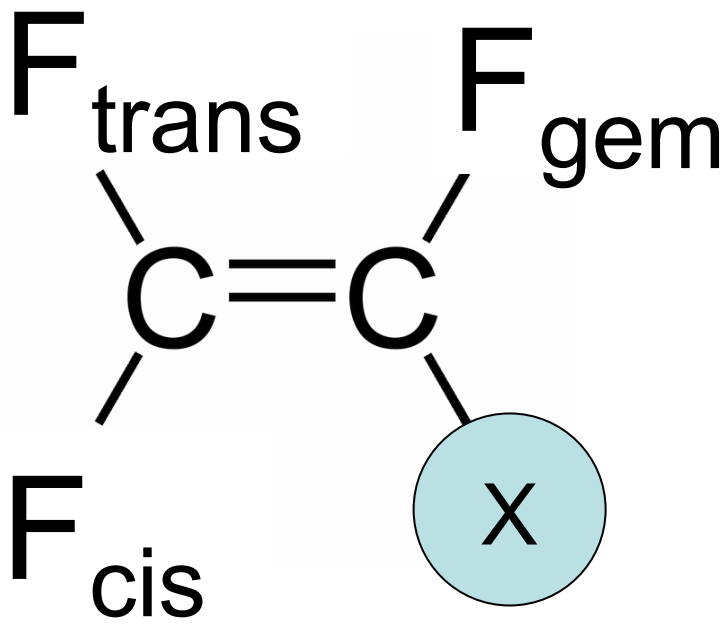
molecules with structure:

$\sigma_1(T) \sim \langle r^{-6} \rangle$ not $\langle R^{-6} \rangle$

$\sigma_1(T) \sim$ (site factor)$\langle R^{-6} \rangle$

This is the relevant distance for contributions to the intermolecular shielding since it depends on electron overlap and exchange

^{19}F nuclear site effect



In a freely rotating molecule, the distance of each F atom from the center of mass of the molecule determines the relative exposure to interactions with another molecule in comparison with the other F nuclei in the same molecule.

A quantitative measure of the nuclear site effect
C. J. Jameson, A. K. Jameson and D. Oppusunggu
J. Chem. Phys. 81, 2313-2317 (1984)

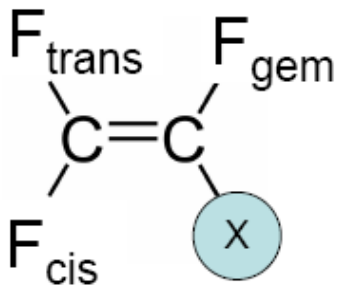
relative exposure:

trans > cis > gem when X is heavier than F

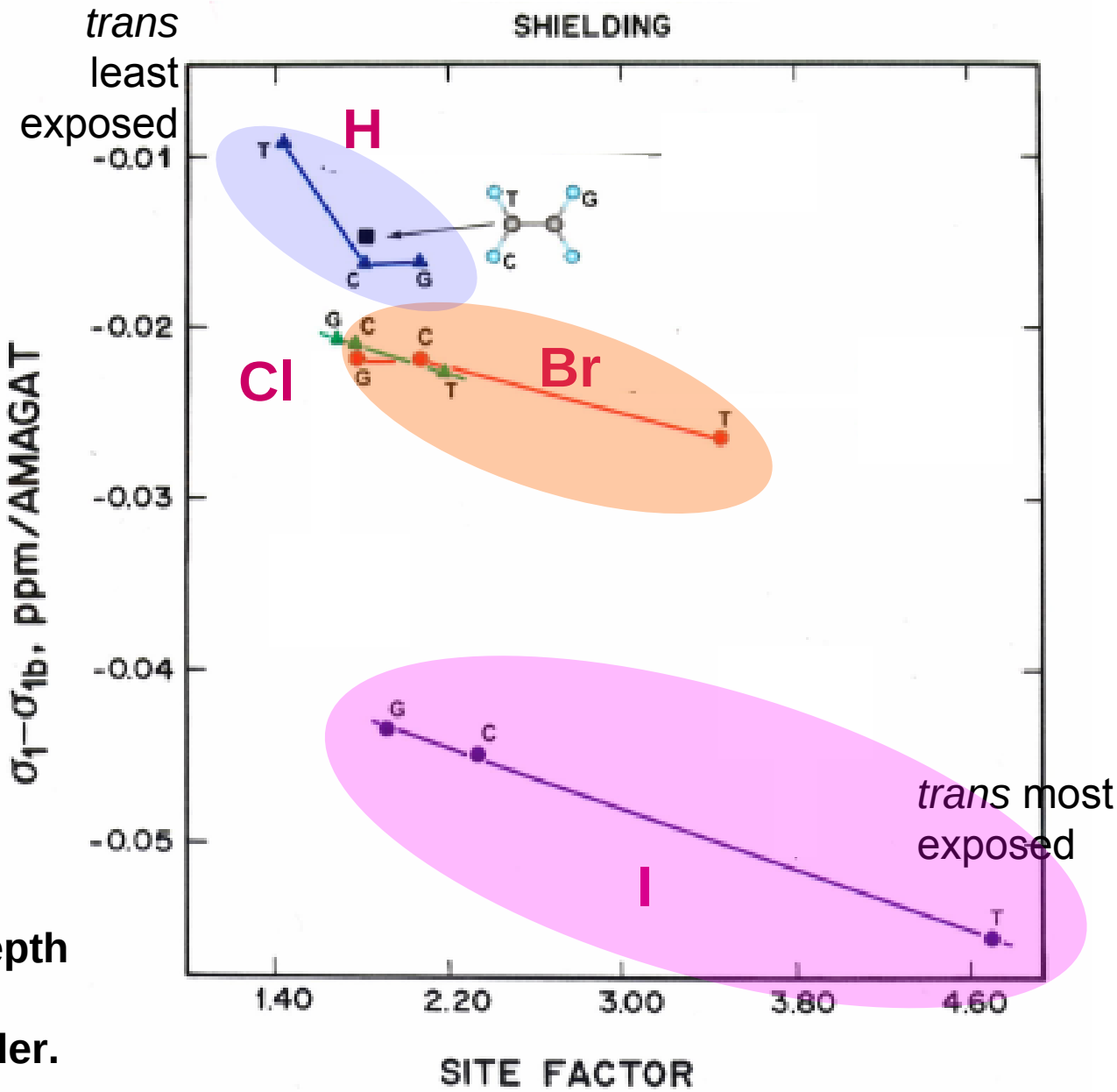
gem > cis > trans when X is lighter than F

observe the site effect in σ_1

for <u>each</u> molecule



X = H
F
Cl
Br
I



The potential functions are quite different for different molecules (deeper average well depth for molecular pairs) I, Br, Cl, F, H, in that order.

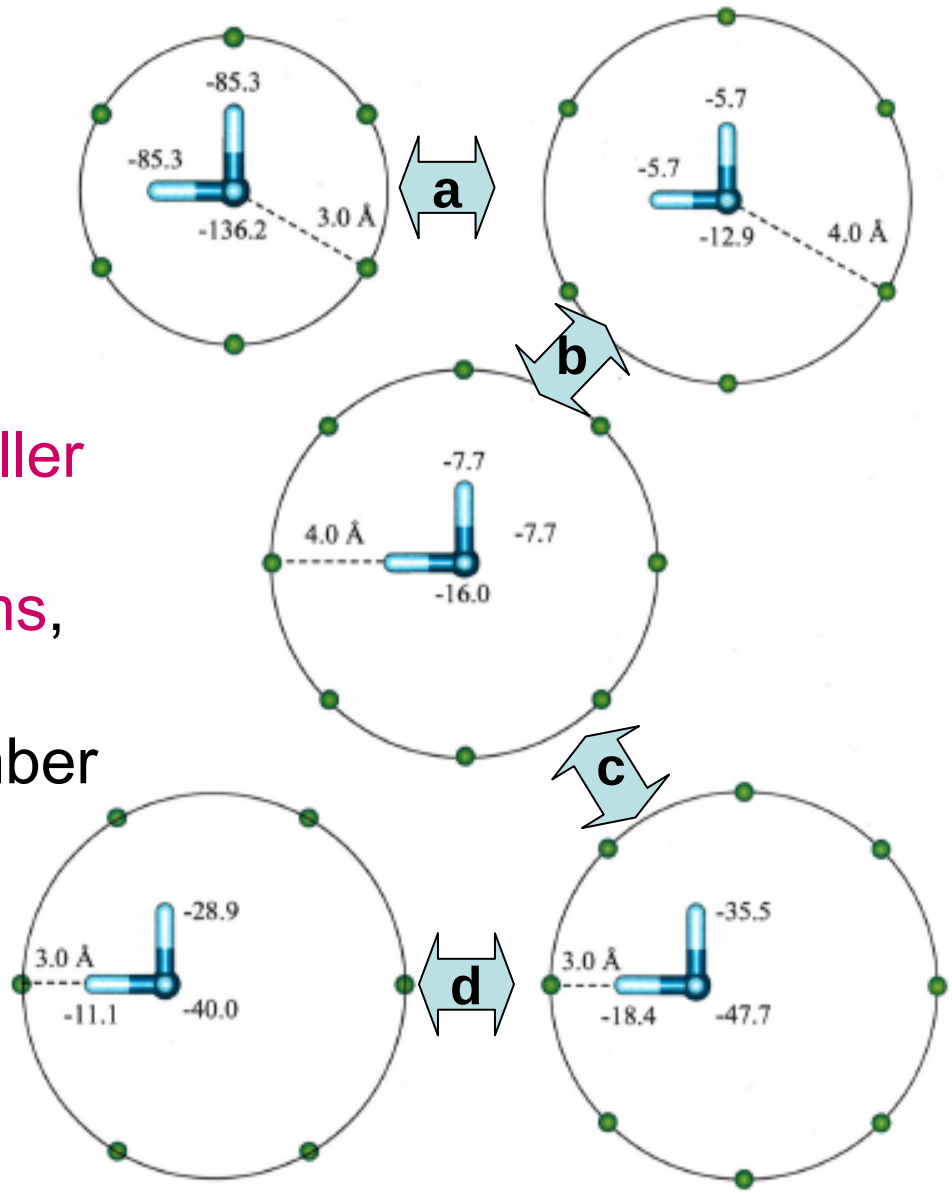
V. Xe as a model sorbate molecule in a cage or channel in a solid

- electronic structure of cage atoms
- **size of cage**
- **diameter of channel**
- **axial or off-axial siting of sorbate in channel**
- **cross section of channel (ellipticity)**
- **number density of atoms constituting cage**

all these factors arise from intermolecular shielding being a function of ‘Xe-other’ distances

- **quantum mechanical shielding for Xe at a given position**
- averaging over probabilities of Xe positions in a cage or channel, in absence of other Xe
- Xe-Xe contributions can be large and informative about structure of confining pore

calculated shielding tensor for Xe in the plane of a ring of Ne atoms



comparisons:

a. same number atoms: smaller ring, greater deshielding

b. same ring size: more atoms, greater deshielding

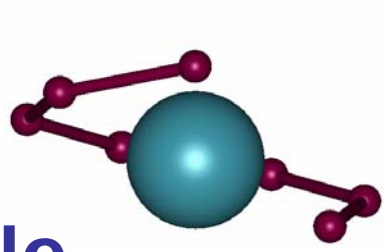
c. same ring size, same number atoms: off-center, greater deshielding

d. same ring size: more atoms, greater deshielding

ppm compared to isolated Xe atom

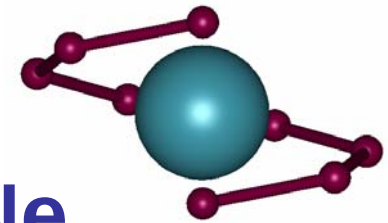
calculated shielding tensor for Xe in a helix of Ne atoms

comparisons:
same helix diameter:
more atoms,
greater intermolecular shielding values
(all are deshielding compared to isolated Xe atom)



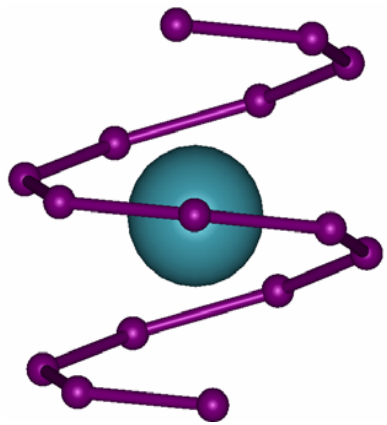
Ne_7

-55.4526
-52.2268
-86.6174



Ne_8

-56.4270
-59.0700
-91.2691

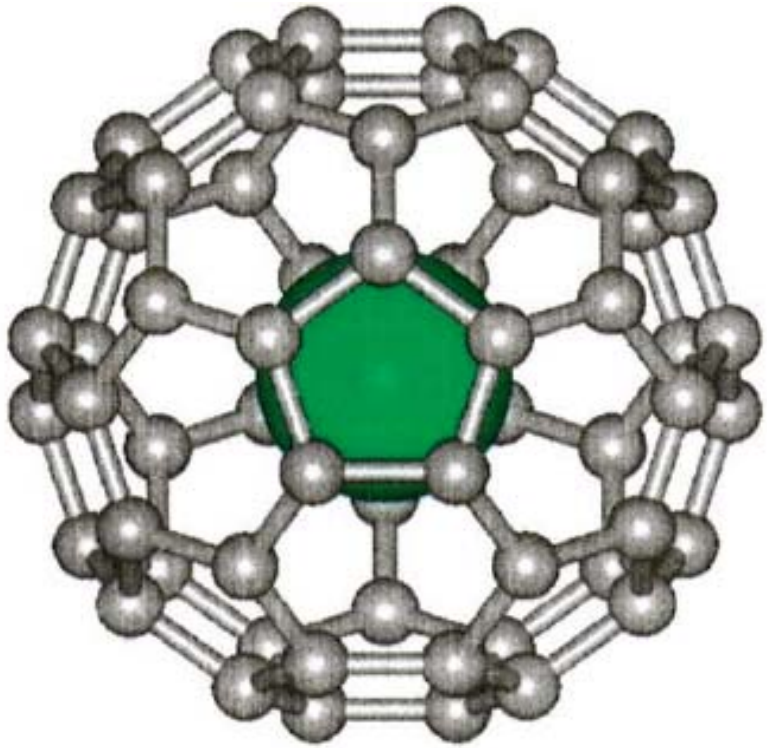


Ne_{13}

-64.8244
-65.1560
-97.4705

ppm

calculated shielding for Xe at the center of a C_{60} cage



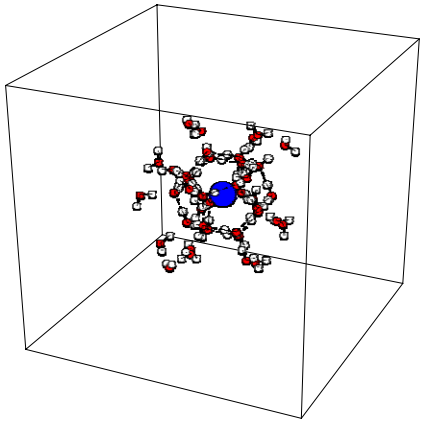
intermolecular shielding value = -181.5 ppm (deshielding compared to isolated Xe atom)

Experimental value = -179.24 ppm

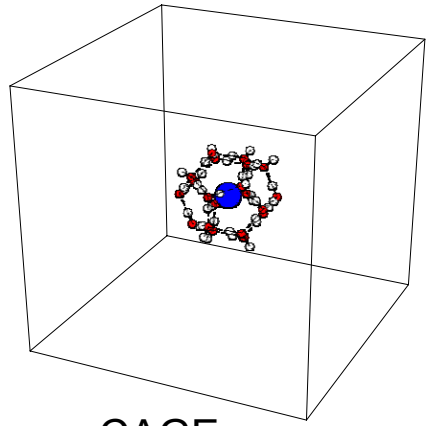
How to model a cage in a hydrogen bonded network?

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

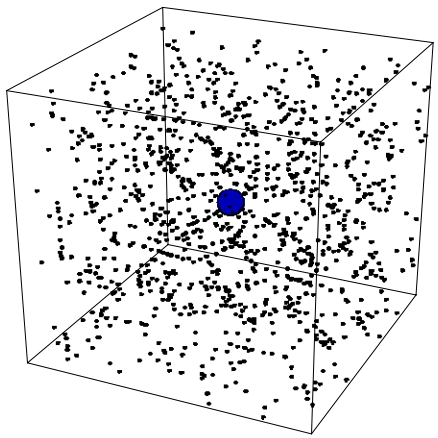
MODELS



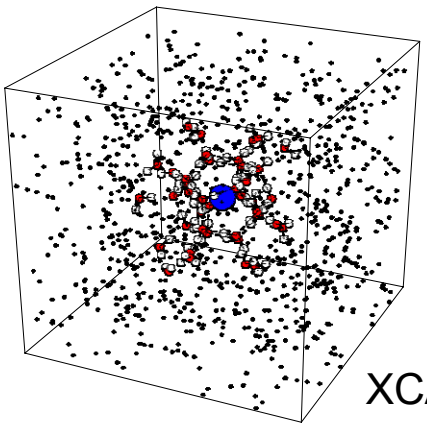
XCAGE



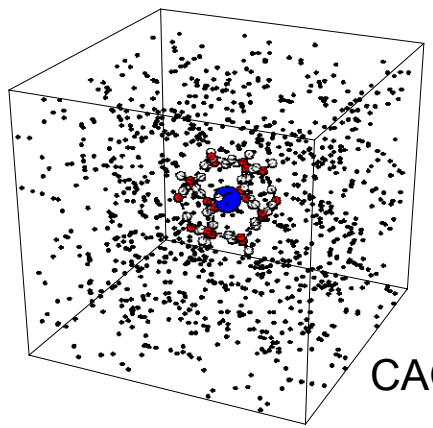
CAGE



PCA



XCAGE/PCA



CAGE/PCA

Xe shielding from electrostatics?

for 5^{12} cage in Structure I

σ_{iso}(Xe at center of model) -σ(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 negligible shielding response

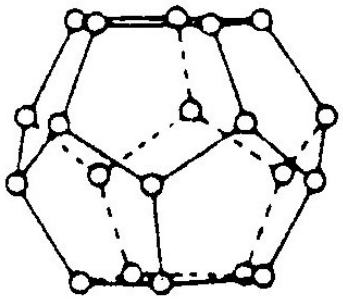
without its hydrogen-bonding partners, H_2O provides too large a response at Xe

use the more complete model, and include electron correlation

- quantum mechanical shielding for Xe at a given position
- **averaging over probabilities of Xe positions in a cage or channel, in absence of other Xe**
- Xe-Xe contributions can be large and informative about structure of confining pore

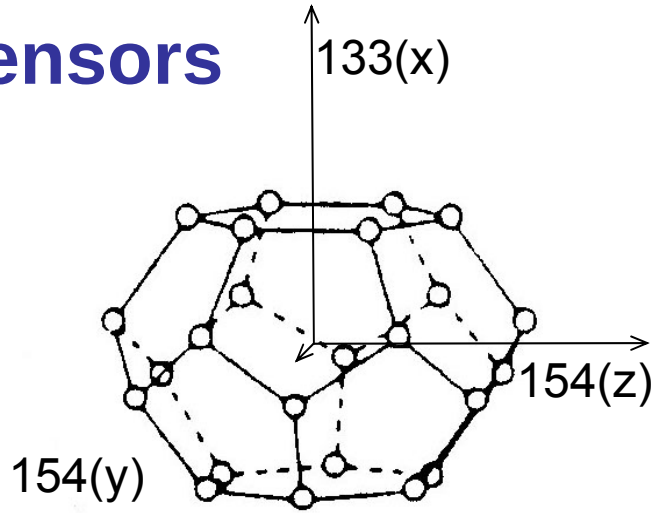
Xe chemical shift tensors

isotropic 214



5^{12}

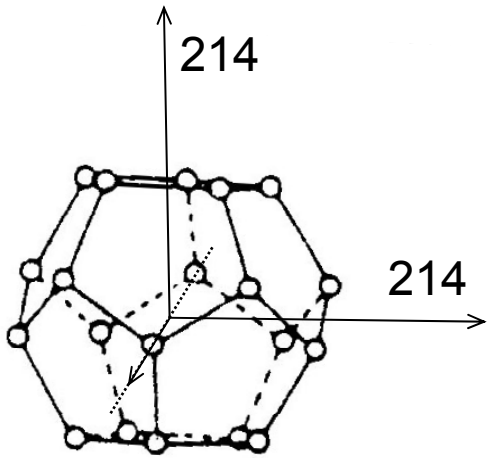
symmetric



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

axial, disk-like

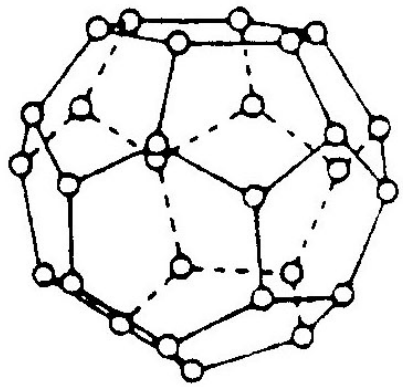
Clathrate Structure I



5^{12}

axial

isotropic 105



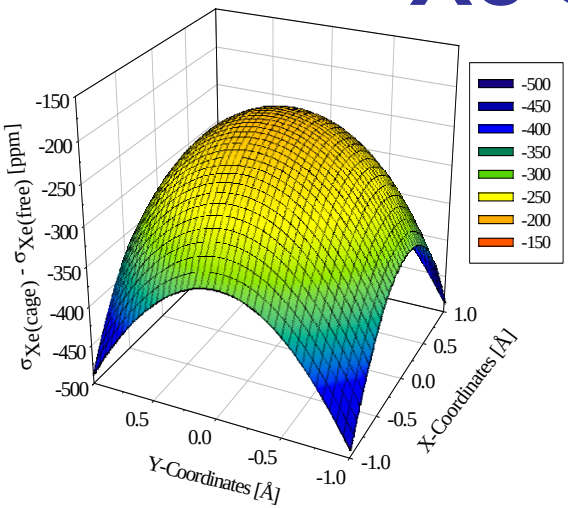
$5^{12}6^{4}$

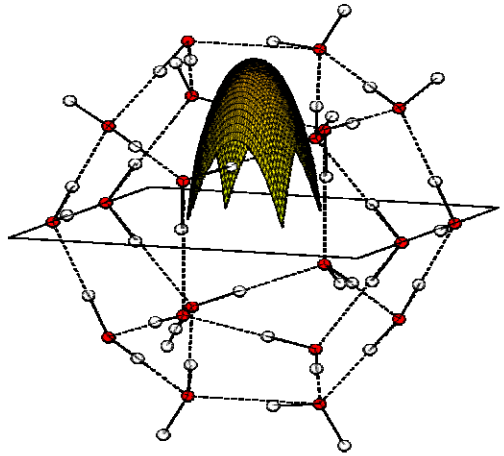
symmetric

Clathrate Structure II

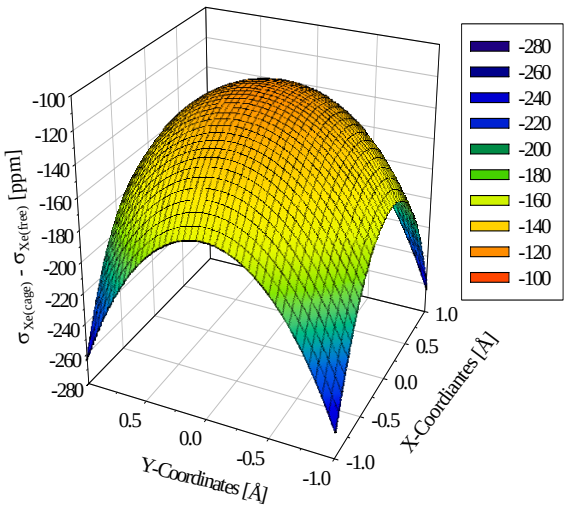
All are deshielded relative to Xe atom

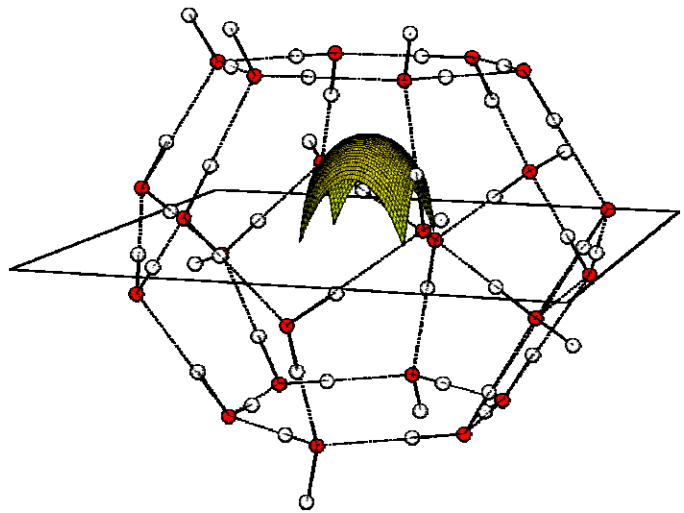
Xe SHIELDING SURFACES





5^{12} Cage

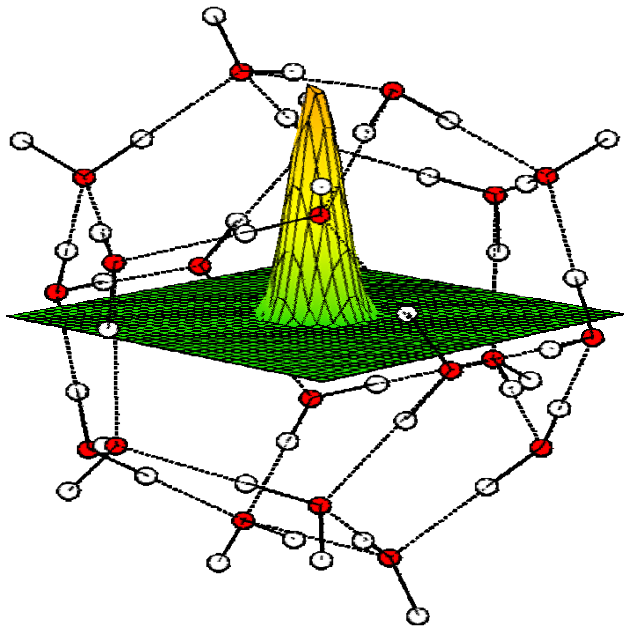




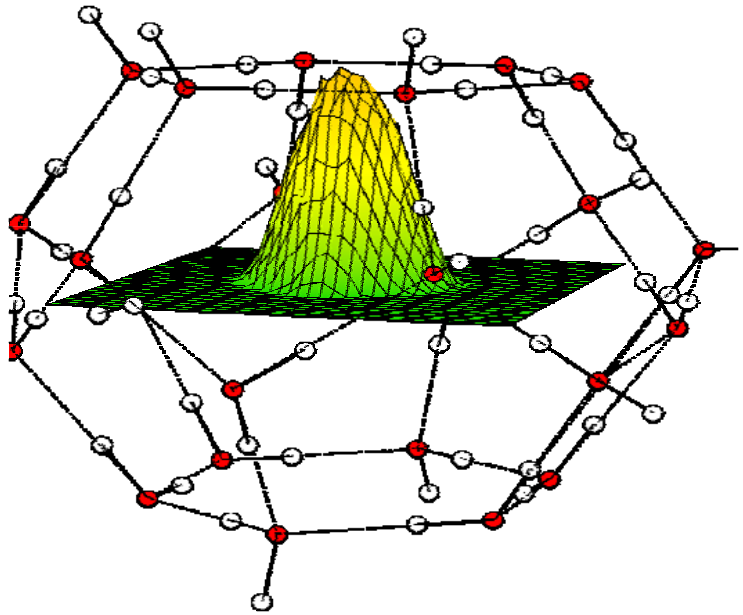
$5^{12}6^{2}$ Cage

METROPOLIS MONTE CARLO AVERAGING

Xe one-body distribution functions at 275 K:

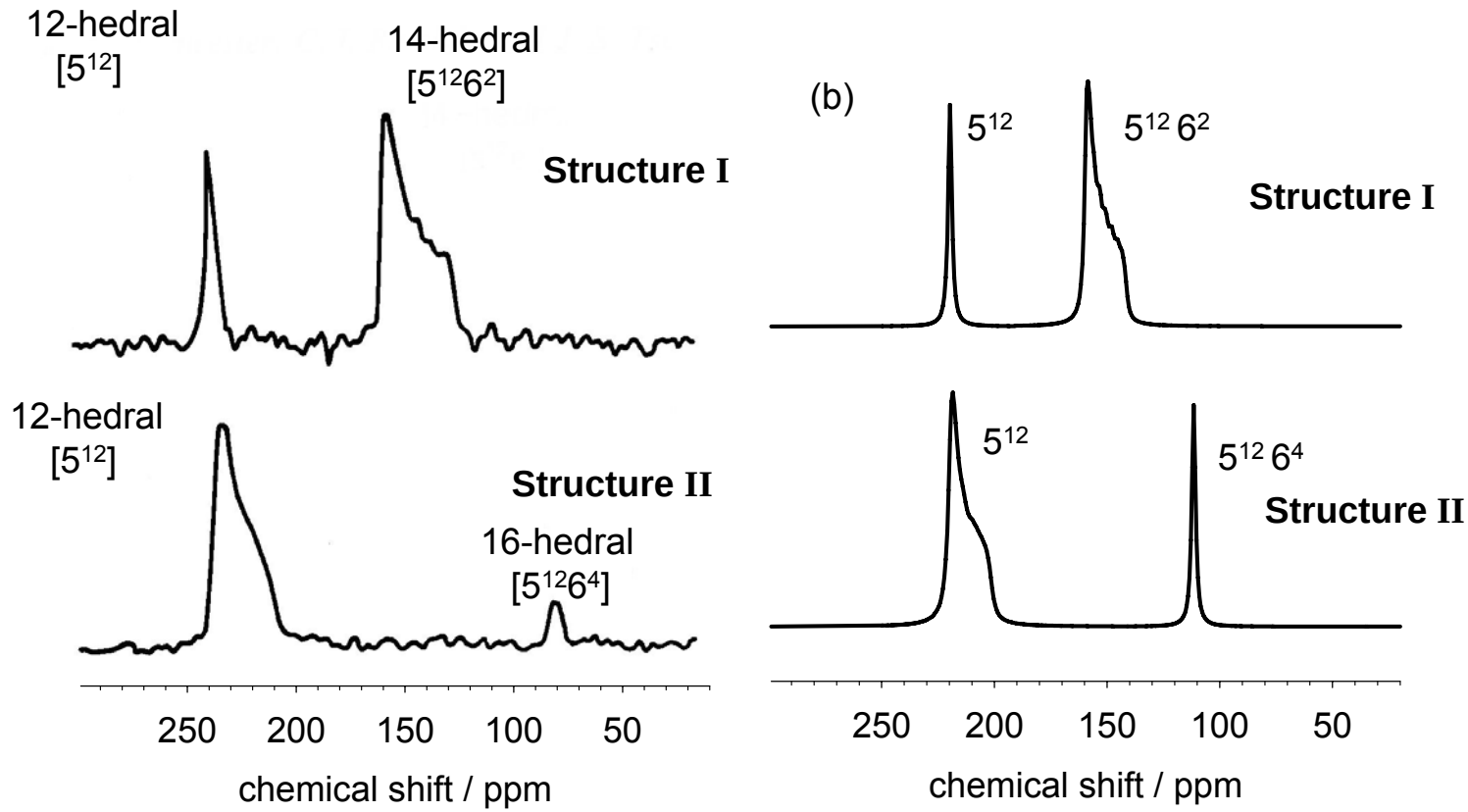


5^{12} Cage



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

Xe in the cages of clathrate hydrates Structure I & II



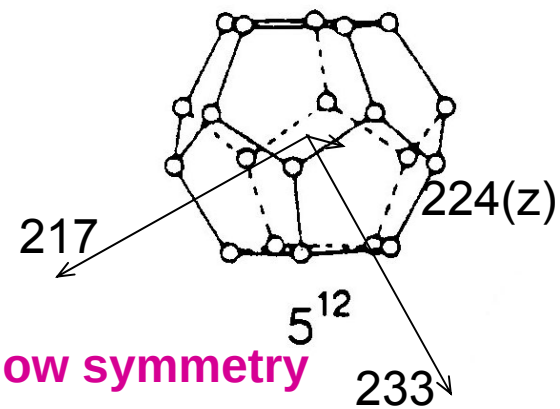
EXPERIMENTS

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

CALCULATIONS

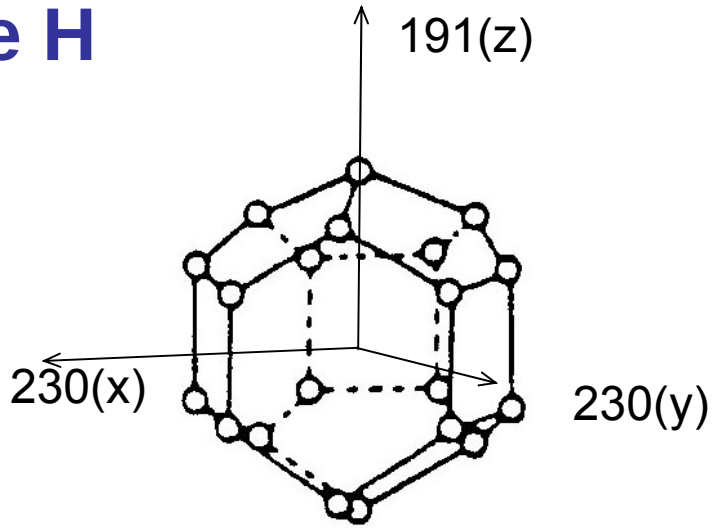
Monte Carlo simulations in a
4x4x4 supercell and 2x2x2 supercell
D. Stueber and C. J. Jameson, 2003

calculated Xe tensors in clathrate Structure H



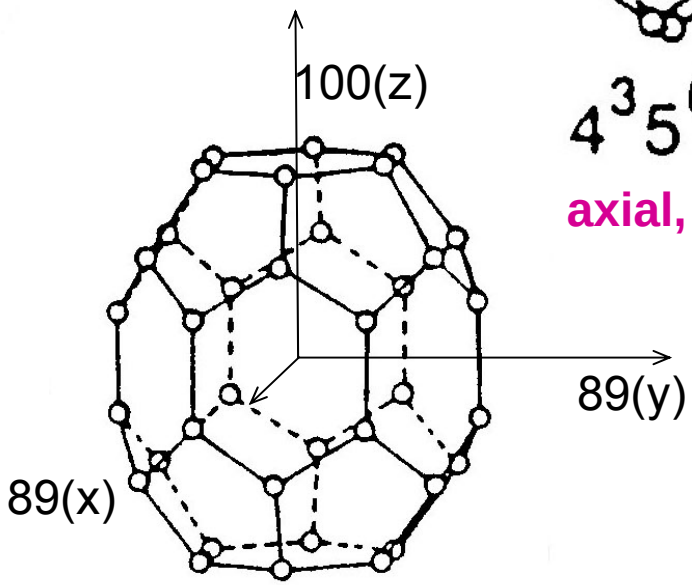
5^{12}

low symmetry



$4^3 5^6 6^3$

axial, squat

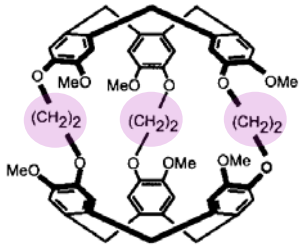


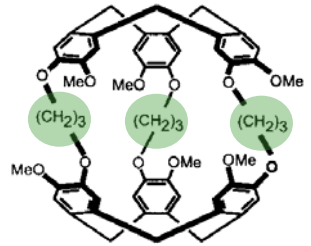
$5^{12}6^8$

axial, elongated

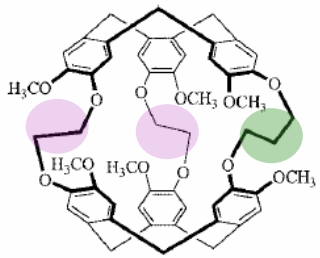
All are deshielded relative to Xe atom

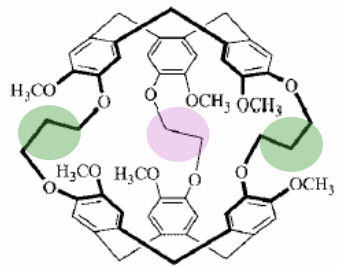
^{129}Xe@cryptophanes





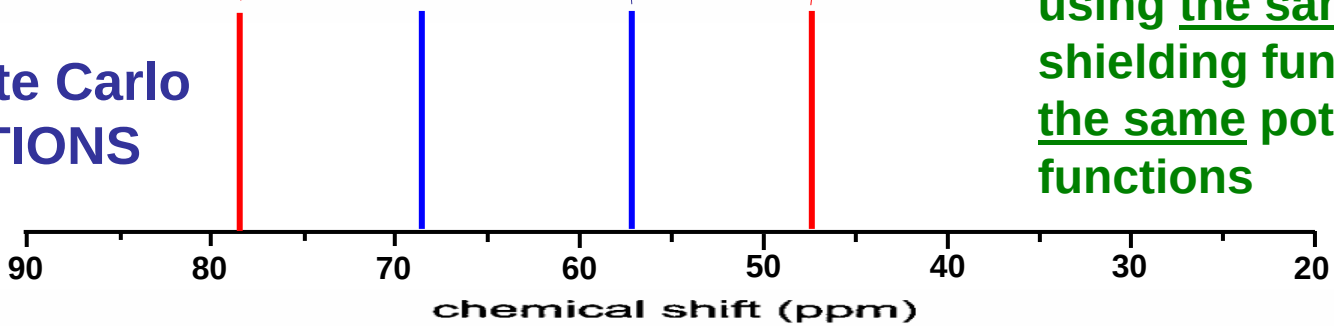
Pines et al.
Proc. Nat. Acad. Sci.
98, 10654 (2001)





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

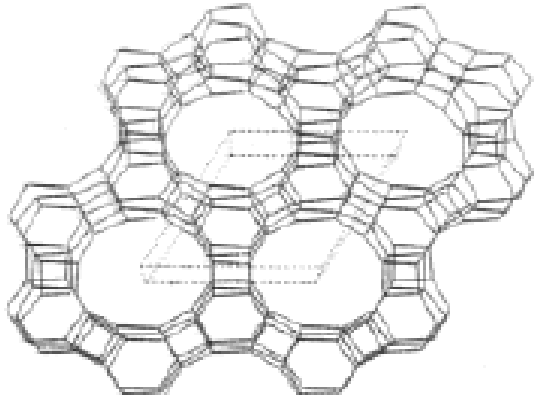
Our Monte Carlo SIMULATIONS



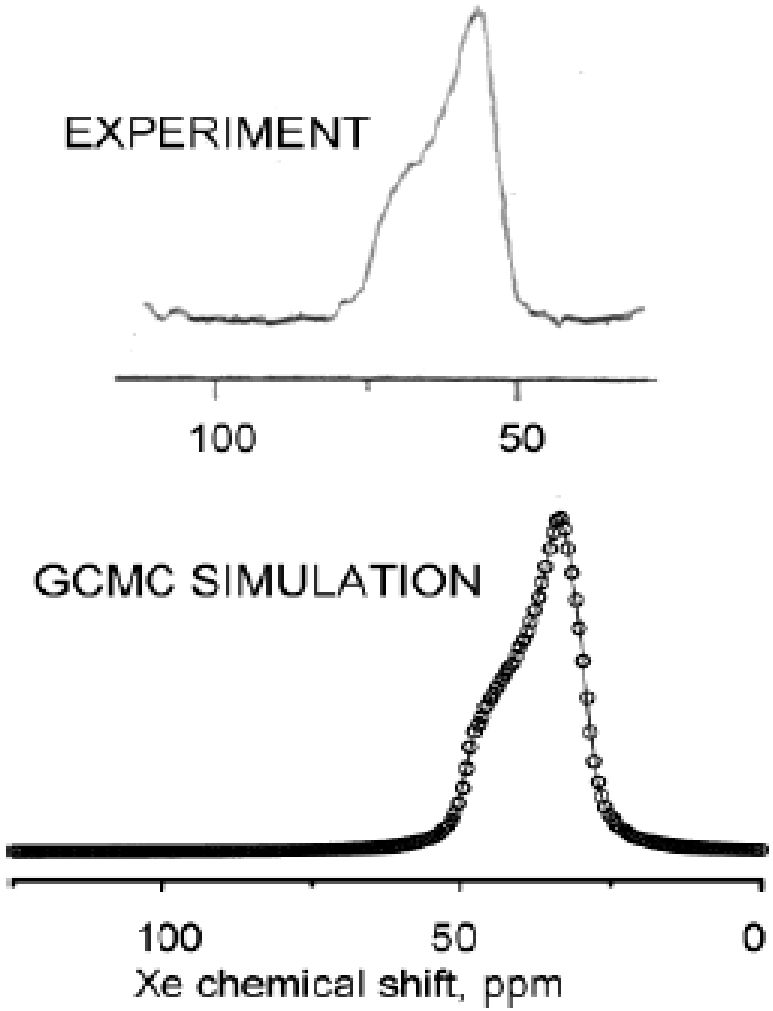
using the same shielding functions the same potential functions

- quantum mechanical shielding for Xe at a given position
- averaging over probabilities of Xe positions in a cage or channel, in absence of other Xe
- **Xe-Xe contributions can be large and informative about structure of confining pore**

Xe in a one-dimensional channel



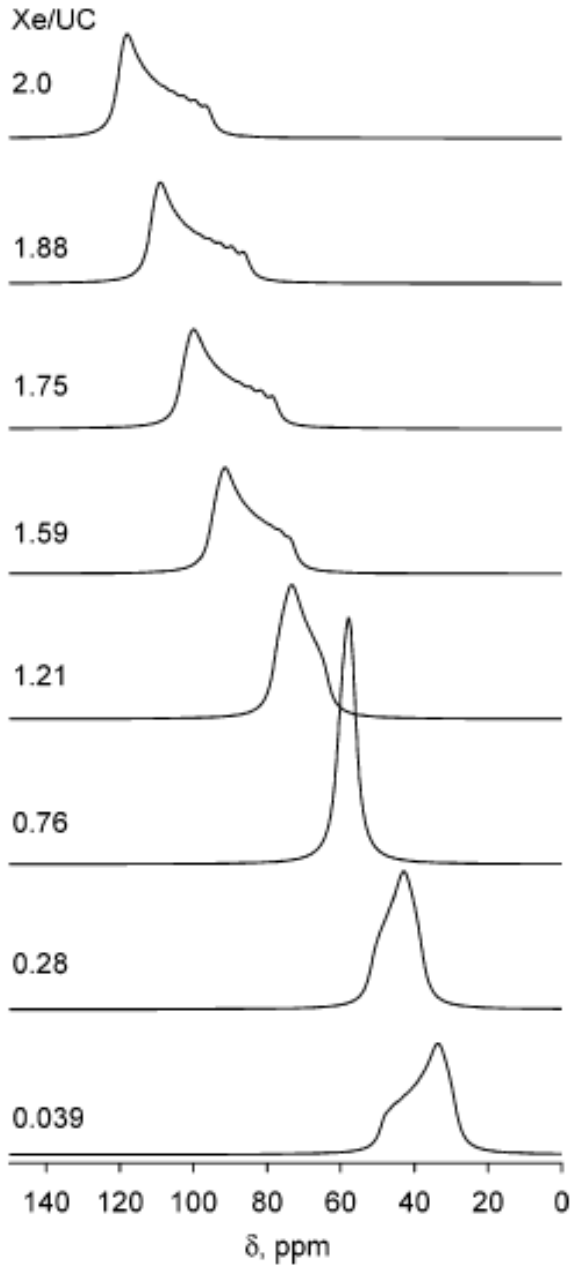
Zeolite
SSZ-24



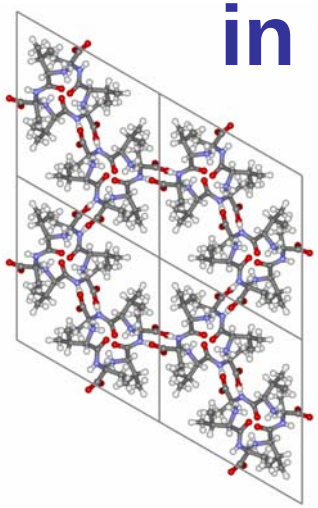
with increasing Xe occupancy

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

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

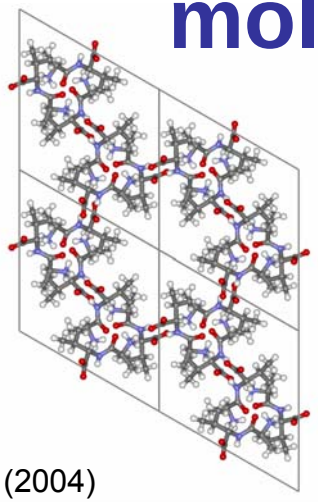


in channels of molecular crystals



L-Val-L-Ala

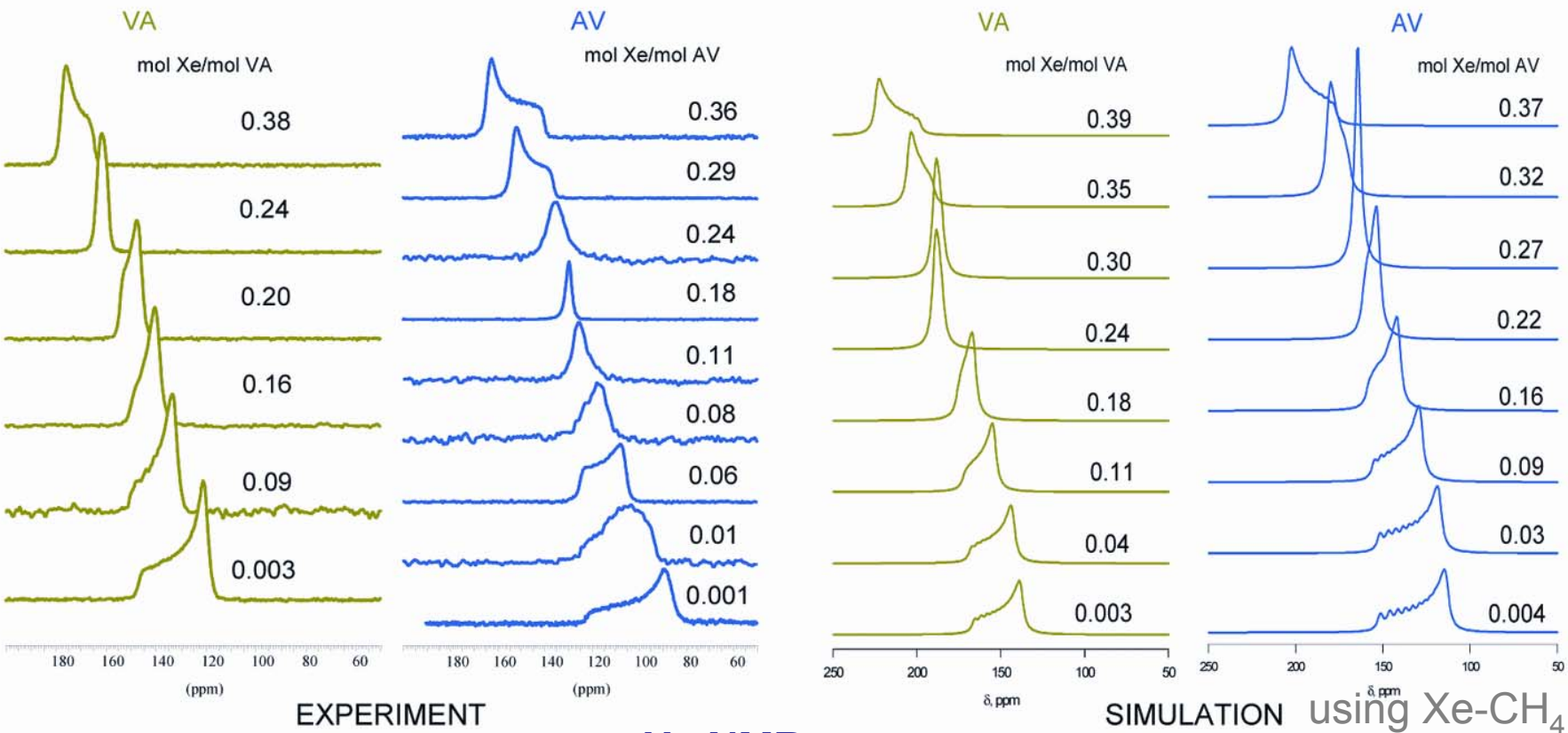
VA



L-Ala-L-Val

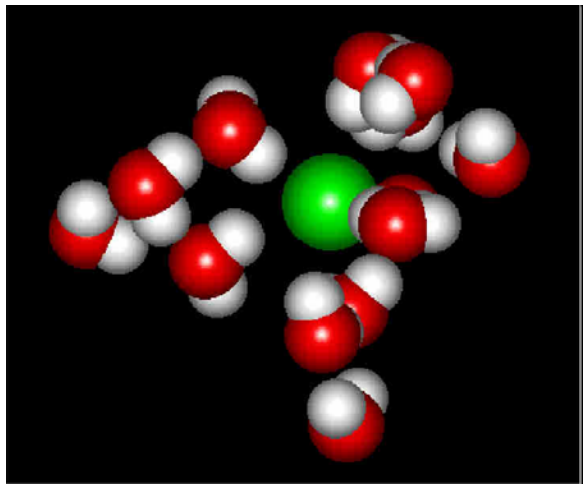
AV

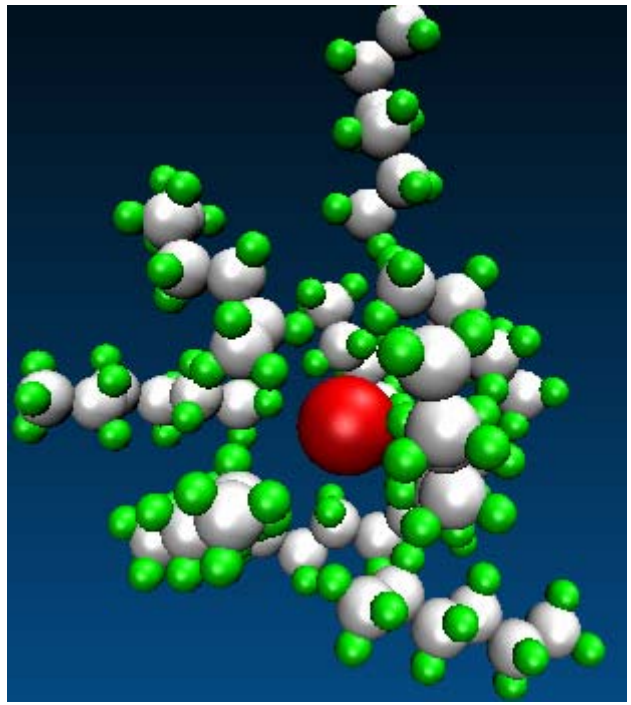
PNAS 101, 17924 (2004)



Xe NMR spectra

VI. solute in a liquid solvent

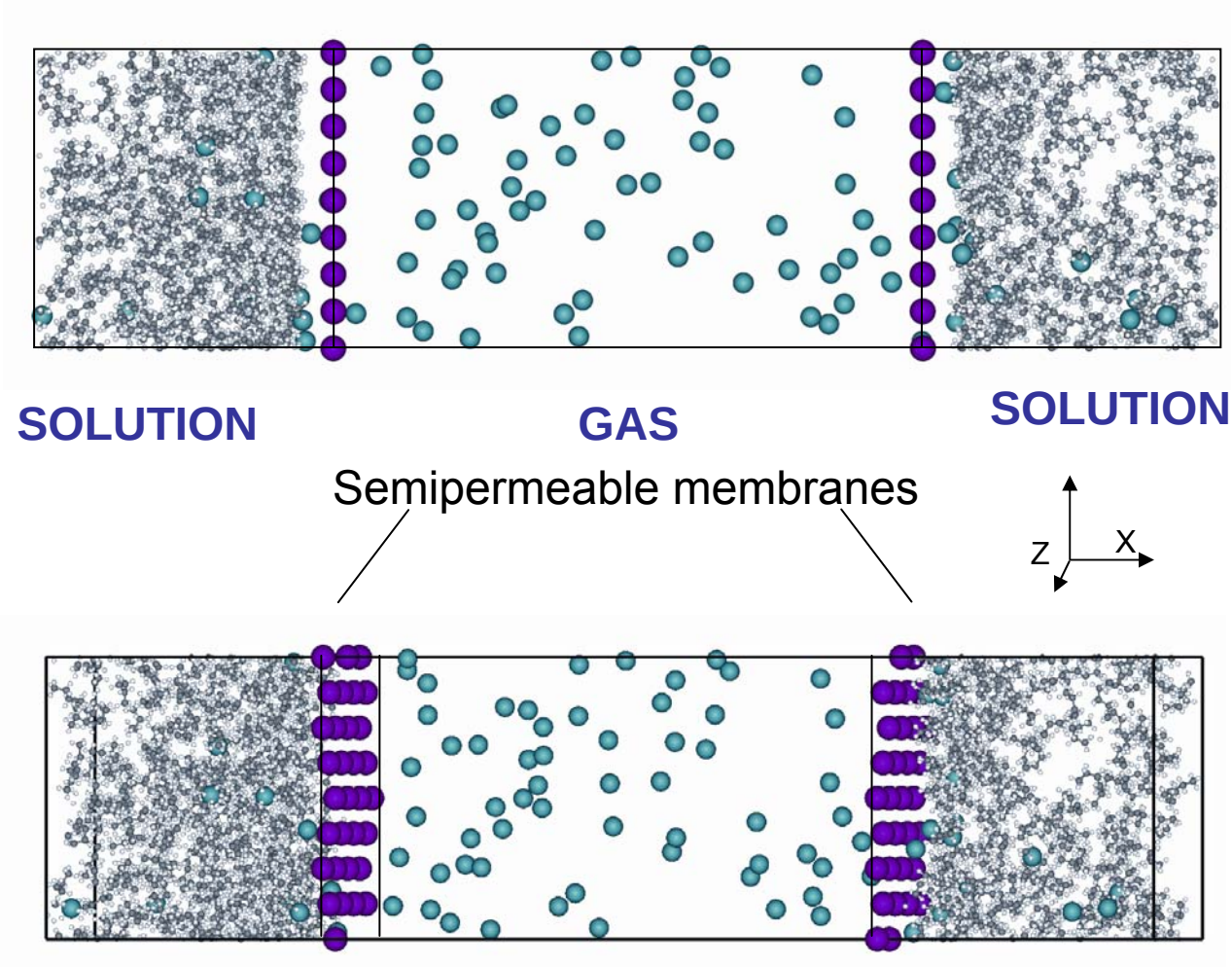




Xe in liquid H_2O

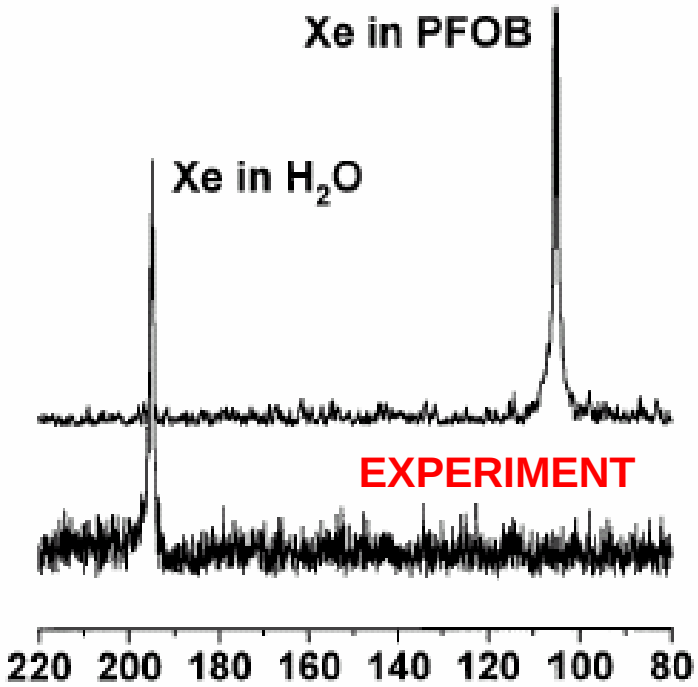
- consider this system in terms of Xe in a solvation cage of H_2O molecules. Solvation cages deform, rearrange, exchange waters with the bulk.
- Need to calculate intermolecular shielding function for Xe surrounded by a cage of H_2O molecules, express this mathematically in terms of pairwise Xe-H, Xe-O shielding functions which can then be used for Xe in liquid water.
- Need a force field that describes probability of configurations of water molecules to perform averaging of shielding functions.

MD Simulation Box



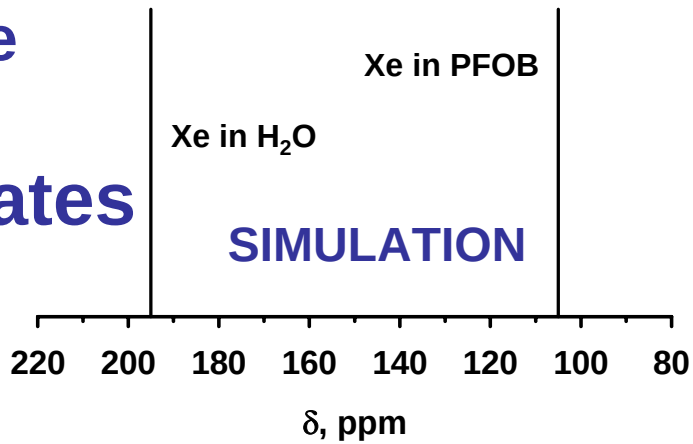
MD Simulation box design: Murad et al, Fluid Phase Equil. 187-188, 29 (2001)
Murad et al, Chem. Phys. Lett. 319, 60 (2000)

Xe in Solution



Bifone et al, Magn. Reson. Medicine 41, 442 (1999).

Using quantum mechanical Xe shielding surface calculated for clathrate hydrates



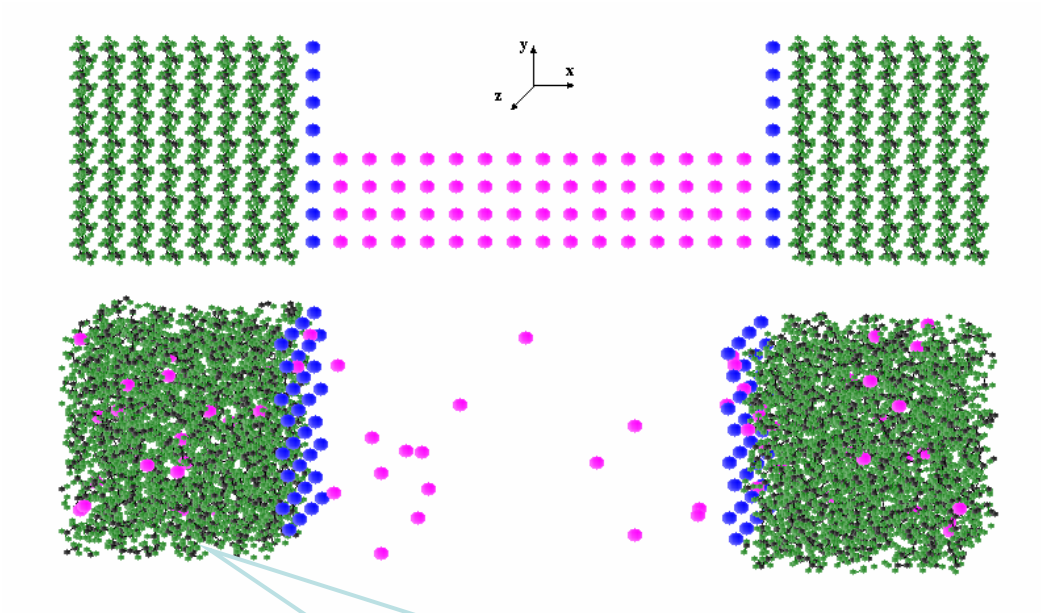
C. J. Jameson, D. N. Sears, S. Murad, J. Chem. Phys. 121, 9581 (2004)

Xe in liquid hexane

- consider this system in terms of Xe in a solvation cage of hexane molecules. Solvation cages deform, rearrange, exchange waters with the bulk.
- Need to calculate intermolecular shielding function for Xe surrounded by a cage of hexane molecules, express this mathematically in terms of pairwise Xe-H, Xe-C shielding functions which can then be used for Xe in liquid hexane. As an approximation, use Xe-C and Xe-H shielding functions calculated for Xe-CH_4.
- Need a force field that describes probability of configurations of hexane molecules to perform averaging of shielding functions.

Simulation System

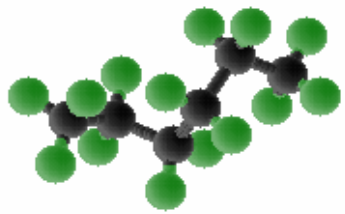
Xe and *n*-hexane



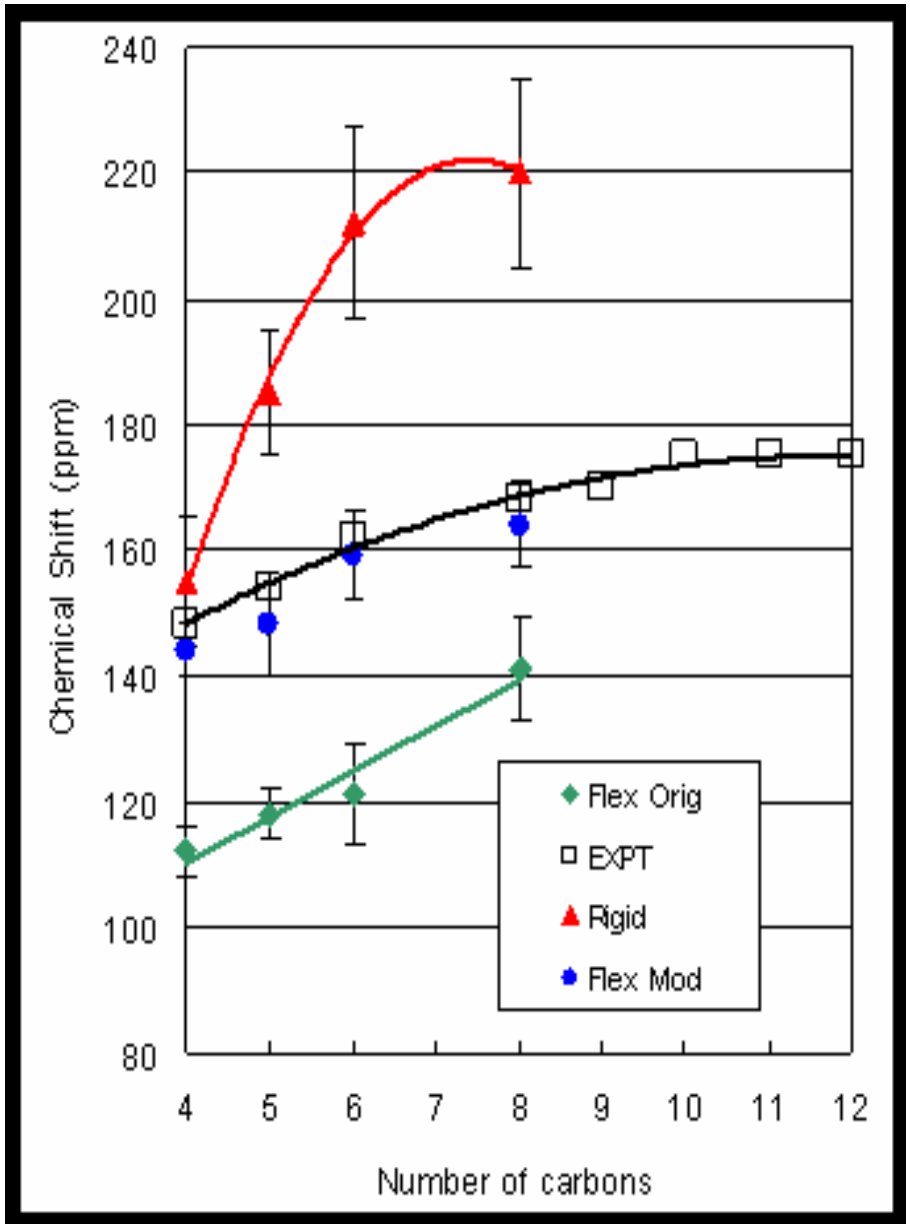
initial

10 ns

Typical n-hexane structure:



Calculate chemical shift by using different models:

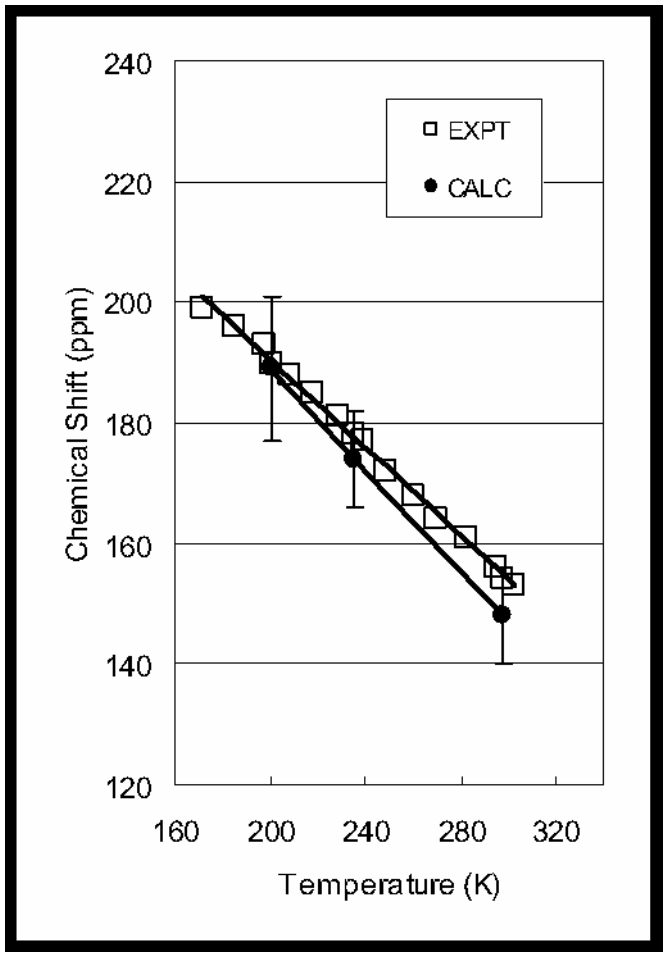


Rigid molecules permit the Xe to have greater probability of close interactions with the solvent atoms, leading to artificially steeper dependence on chain length and greater Xe chemical shifts.

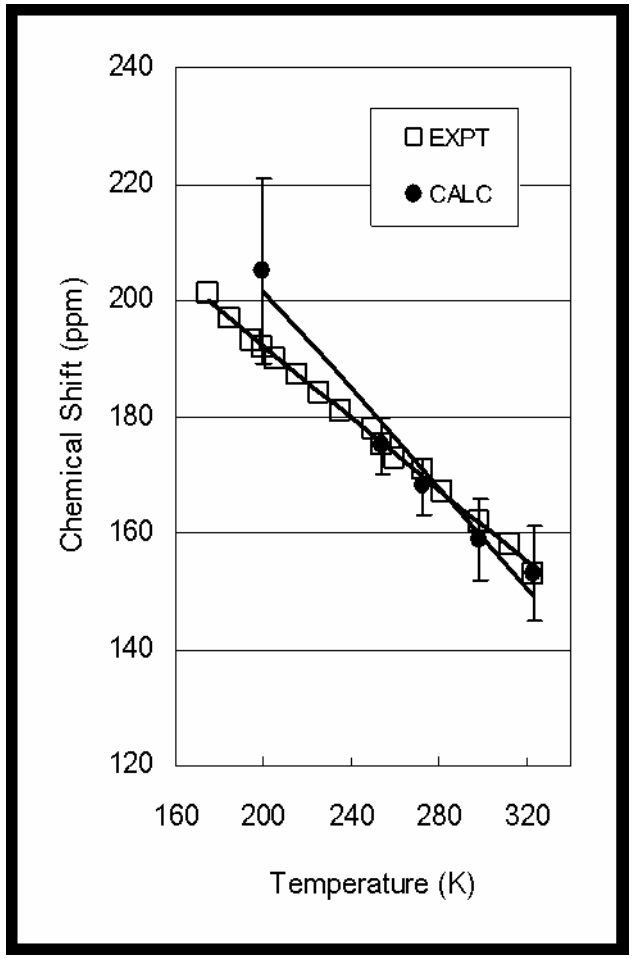
Flexible molecules give more realistic dependence on chain length.

Xe chemical shift temperature dependence

n-pentane :



n-hexane :

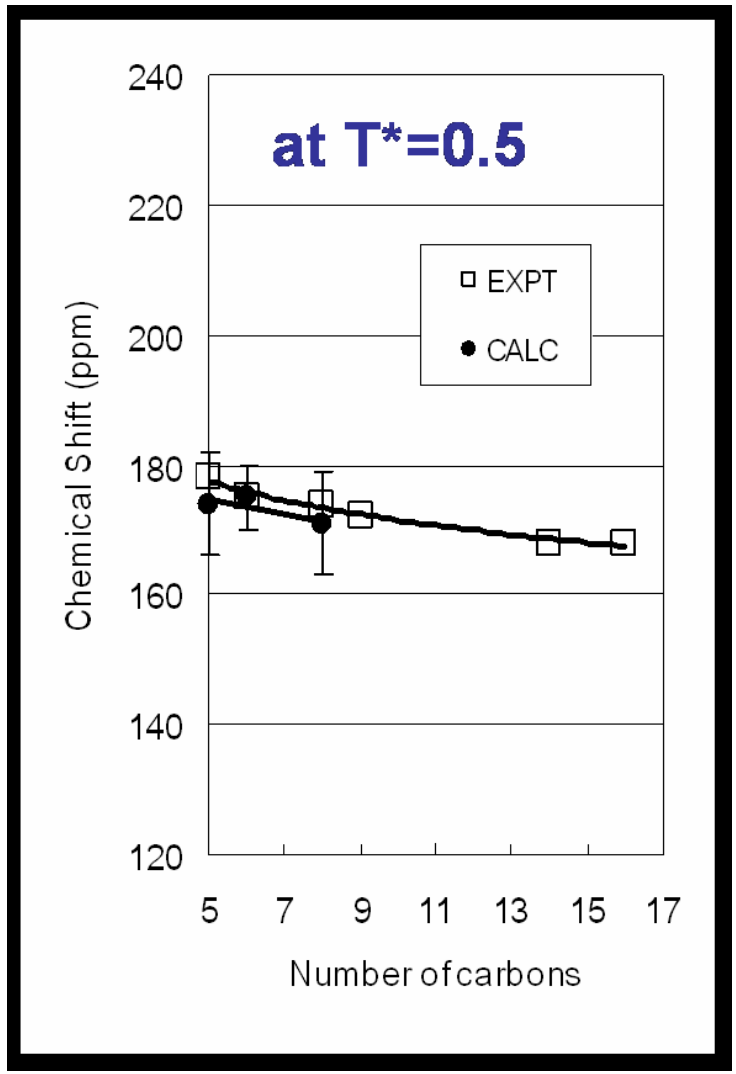


Molecular Dynamics simulations results

J. Phys. Chem. C, 111, 15771-15783 (2007).

Comparable chemical shifts in solution

Xe chemical shift at the same thermodynamic state



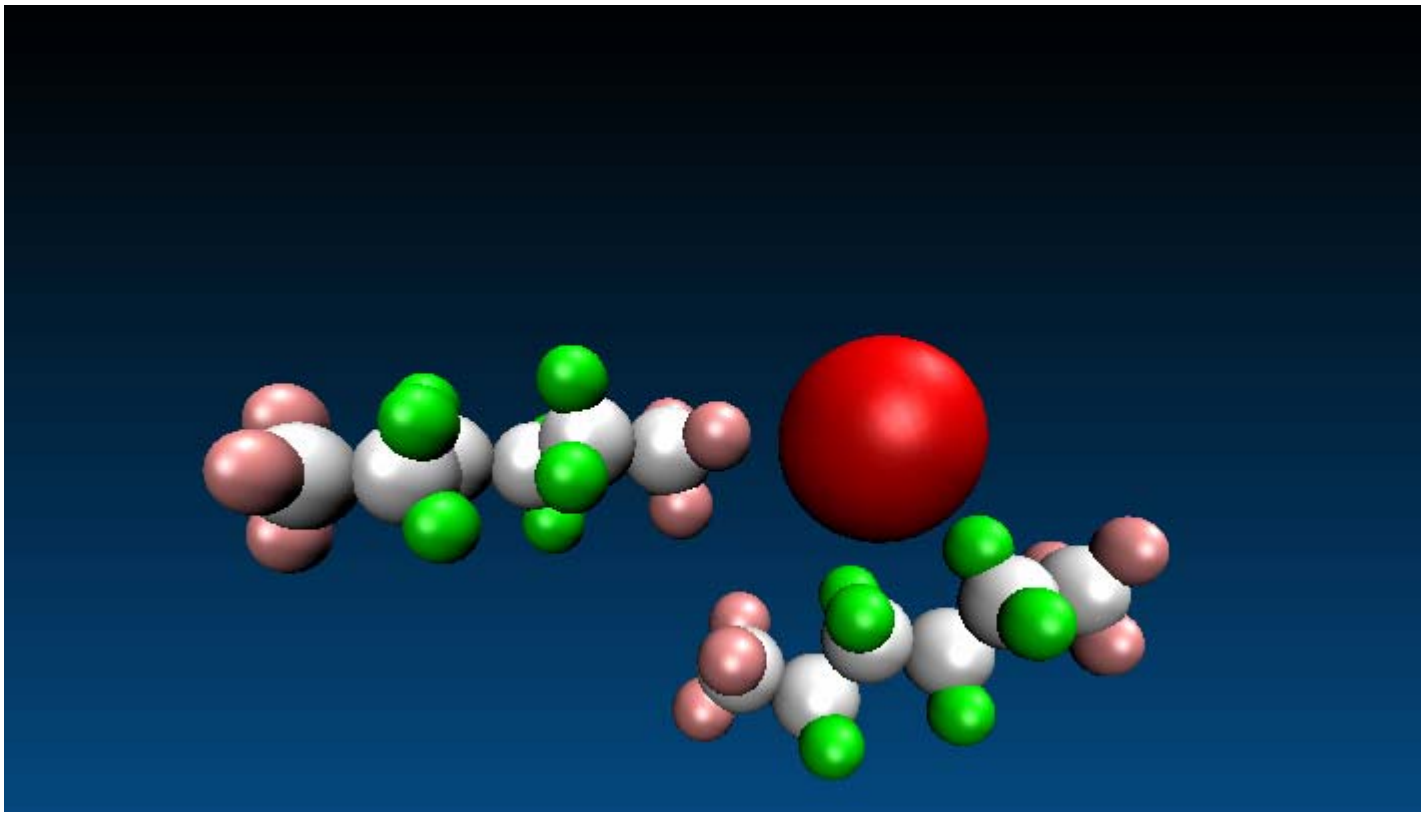
- EXPT: R. Bonifacio & E. J. M. Filipe, XeMAT 2000
- Molecular Dynamics simulations

J. Phys. Chem. C, 111, 15771-15783 (2007).

some findings

- Xe chemical shift depends on the thermodynamic state of the liquid.
- Prediction of Xe chemical shifts in linear hydrocarbons, for example, can be made if based on liquids at the same thermodynamic state (same reduced temperature, same number density), then it is possible to find constitutive contributions.

VII. constitutive contributions from chemical groups of solvent



Prediction of Xe chemical shifts in higher n-alkanes from constitutive $Xe\text{-}CH_3$ and $Xe\text{-}CH_2$ contributions to $\delta_{1effective}$ (already in same mol L^{-1} basis)

	n-nonane	*n*-undecane	*n*-dodecane	*n*-tetradecane	*n*-hexadecane
number of carbons	9	11	12	14	16
prediction using $\delta_{1effective}$ (CH_3) = 0.20 $\delta_{1effective}$ (CH_2) = 0.13 **based on MD at 298 K**	164	167	167	169	170
prediction using $\delta_{1effective}$ (CH_3) = 0.21 * $\delta_{1effective}$ (CH_2) = 0.14 **based on MD at T* = 0.5**	175	179	179	182	183
EXPERIMENT	171.7	176.0	176.6	180.7	182.8

* in units of ppm/amagat
or else, CH_3 4.7 ppm/(mole L^{-1})
CH_2 3.14 ppm/(mole L^{-1})

GOOD predictive ability from MD runs at **same thermodynamic state**

CONCLUSIONS

- Intermolecular shifts arise from overlap and exchange and also electron correlation.
- The usual intermolecular shift is deshielding (to lower resonance frequencies) although the opposite sign is sometimes found.
- The magnitude of the intermolecular shift depends on the intermolecular shielding as a function of configurations and on the probability of such configurations to occur
- Short interaction distances for a solute confined in a cage lead to large deshielding for the solute
- The site of the nucleus in the molecule affects the magnitude of the intermolecular shift
- Solvation shifts can be considered in terms of averaging over solvent cage configurations
- Constitutive contributions from functional groups can be found from density coefficient in liquids in the same thermodynamic state
- All observed intermolecular shifts can be interpreted in the same theoretical framework.

ACKNOWLEDGMENTS

Gas phase shifts:
Patricia M. Burrell
Sheila M. Cohen
Angel C. de Dios
Jila Honarbakhsh
A. Keith Jameson
Chun Luan Lee
James Moyer
Daulat Oppusunggu
Harriet Parker
Karla Schuett
Steven Wille

Shielding surfaces:
Angel C. de Dios
Hyung-Mi Lim
Devin N. Sears
Lela Vukovic

Cages & channels
Bernoli I. Baello
Angel C. de Dios
Rex E. Gerald II
A. Keith Jameson
Pavel Kostikin
Hyung-Mi Lim
Devin N. Sears
Lela Vukovic

Solutions:
Sohail Murad
Devin N. Sears
Huajun Yuan