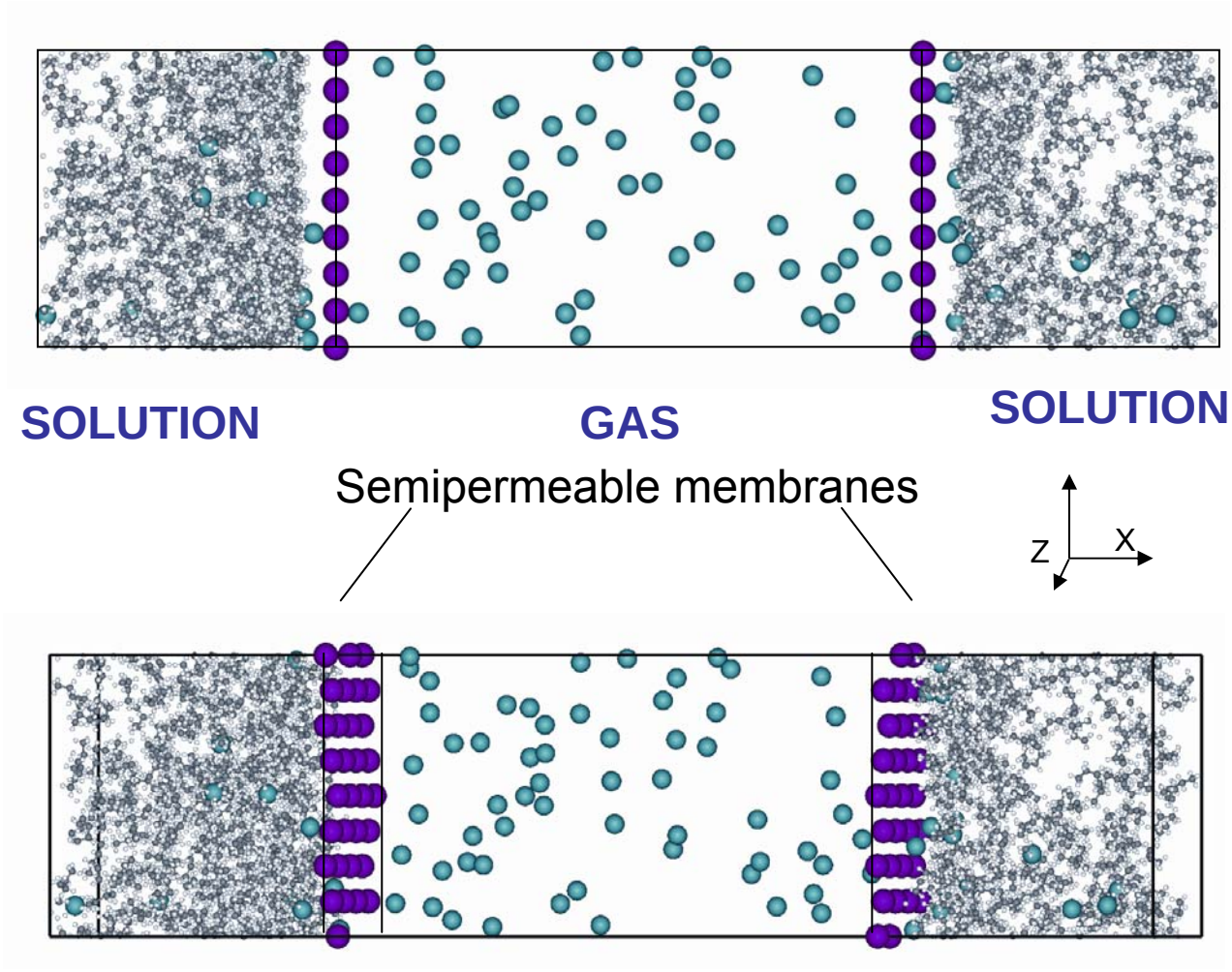
Xe in Solutions



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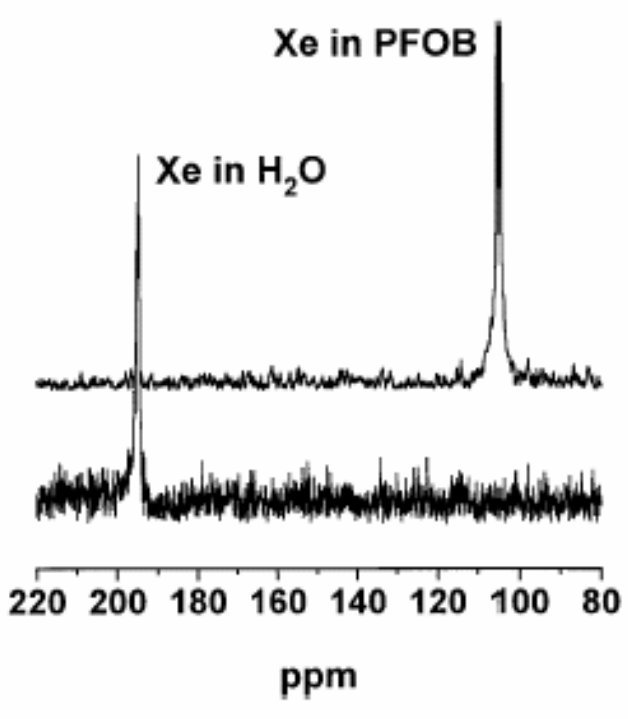
Xe in liquids



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

- instantaneous solvent cage sizes and shapes
- accurate representation can only be accomplished by molecular dynamics (MD)
- Molecular Dynamics simulations provide quick convergence of Xe chemical shift

Previous interpretations of Xe chemical shifts in liquids

- Strictly empirical (refractive index)
- Based on dispersion model of intermolecular chemical shifts
- No explanation for intercepts in correlation plots

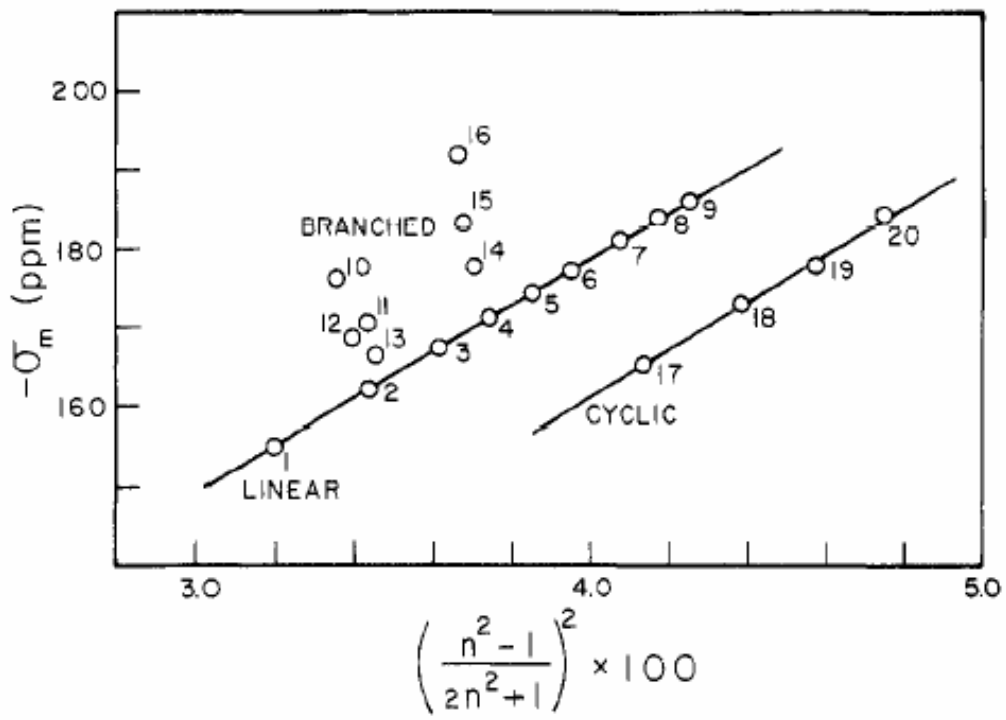


Figure taken from: Stengle et al., J. Phys. Chem. 85, 3772 (1981).

Quantum-mechanical molecular level interactions determine:

(A) the solvation thermodynamics,
(B) the instantaneous shielding at a Xe nucleus arising from the electronic environment formed by all the rest of the atoms (including other Xe atoms).

The **average Xe chemical shift** is a weighted average of the Xe shielding function(B) with weighting factors determined by (A)

How is information encoded into the average Xe chemical shift?

The Xe chemical shift encodes any structural or dynamic information that depends on:

- **Electronic structure of the neighbors of the Xe atom**
- **Configurations of neighbor atoms, how many, at what distances**
- **The relative probabilities of the various configurations**

All these are ultimately **quantum mechanical** in origin.

For one neighbor

Ab initio calculations show that

(1) the Xe shielding response drops off very steeply with distance of the neighbor atom

(2) the magnitude of Xe shielding response depends on the electronic structure of the neighbor atoms or molecules

What fraction of the time a particular Xe-neighbor configuration is found

- Probability of finding Xe at a particular location depends on the intermolecular potential functions between Xe and the neighbor atoms. This too can be assumed to be additive and distance-dependent within a molecular dynamics simulation.

Simulations:

1. Assume a model of the real physical system
   - Model for shielding response calculation
   - Model for the material system
2. Quantum mechanics: Calculate Xe shielding response as a function of configuration
3. Adopt potential energy of intermolecular interactions between Xe and the environment atoms
4. Choose appropriate averaging process, assuming additivity:
   - MOLECULAR DYNAMICS
5. **Simulations produce average isotropic Xe chemical shifts**

This is the same approach we have used for Xe in zeolites, except that instead of grand canonical Monte Carlo, we use MOLECULAR DYNAMICS SIMULATIONS

this talk:

Xe chemical shifts in solution

- Xe in liquid water
- Xe in normal alkanes, dependence on number of carbons
- Comparable chemical shifts in solution: when liquids are in the same thermodynamic state
- Constitutive contributions to the Xe chemical shift in a solvent
- Xe in cyclo alkanes

Best case scenario

- (a) We have a function which describes the Xe shielding in an arbitrary configuration of solvent molecules around the Xe atom
- (b) We have a method of finding the probability of finding an arbitrary configuration of solvent molecules around the Xe atom

To model Xe shielding in liquid water

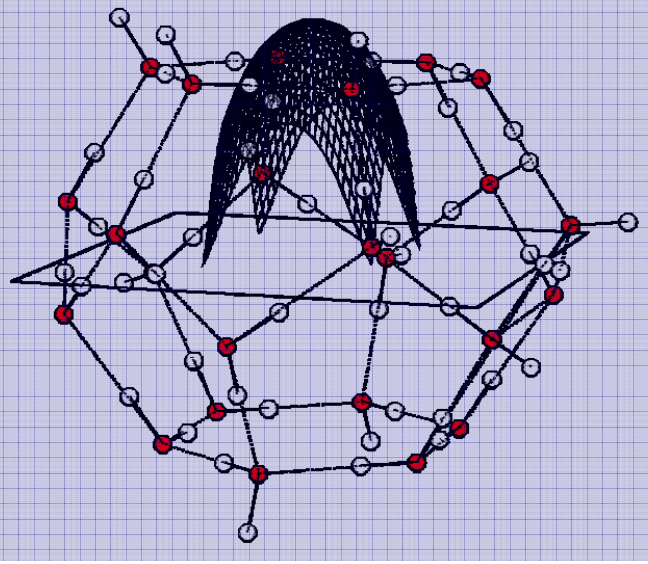
Part (a) we can get from quantum mechanical calculations of Xe surrounded by water in a crystalline clathrate, provided we can mathematically describe the QM results in terms of additive terms which are functions of Xe-H distance and Xe-O distance

Part (b) we can get from a classical molecular dynamics simulation, provided we have a reasonably good intermolecular potential in terms of Xe-H and Xe-O distances and a good potential model description for liquid water itself.

Intermolecular chemical shifts

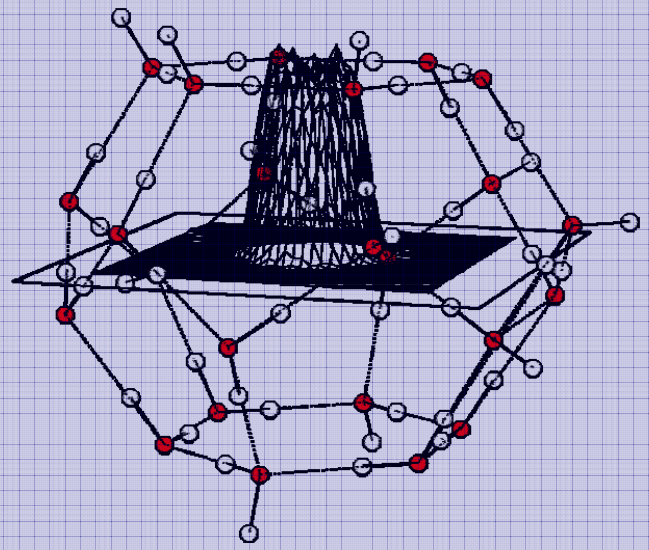
The Xe SHIELDING SURFACE: the shielding as a function of configuration (coordinates) of the system

(a) isotropic shielding surface



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

(b) one-body distribution surface



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

Xe in the cages of clathrate hydrates Structure I and II

interesting as a test:

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

The **dimer tensor model** for Xe shielding tensor in a cage

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

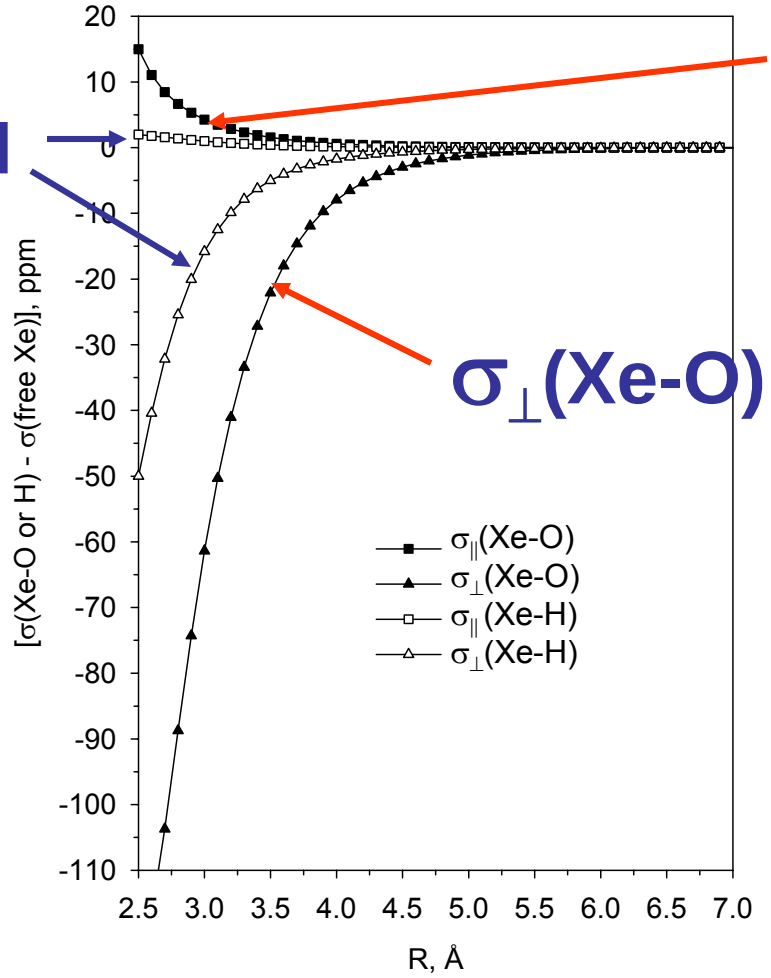
Tensor components in the laboratory frame (frame of the simulation box):

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

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

Sum over all such contributions from every O, every H atom.

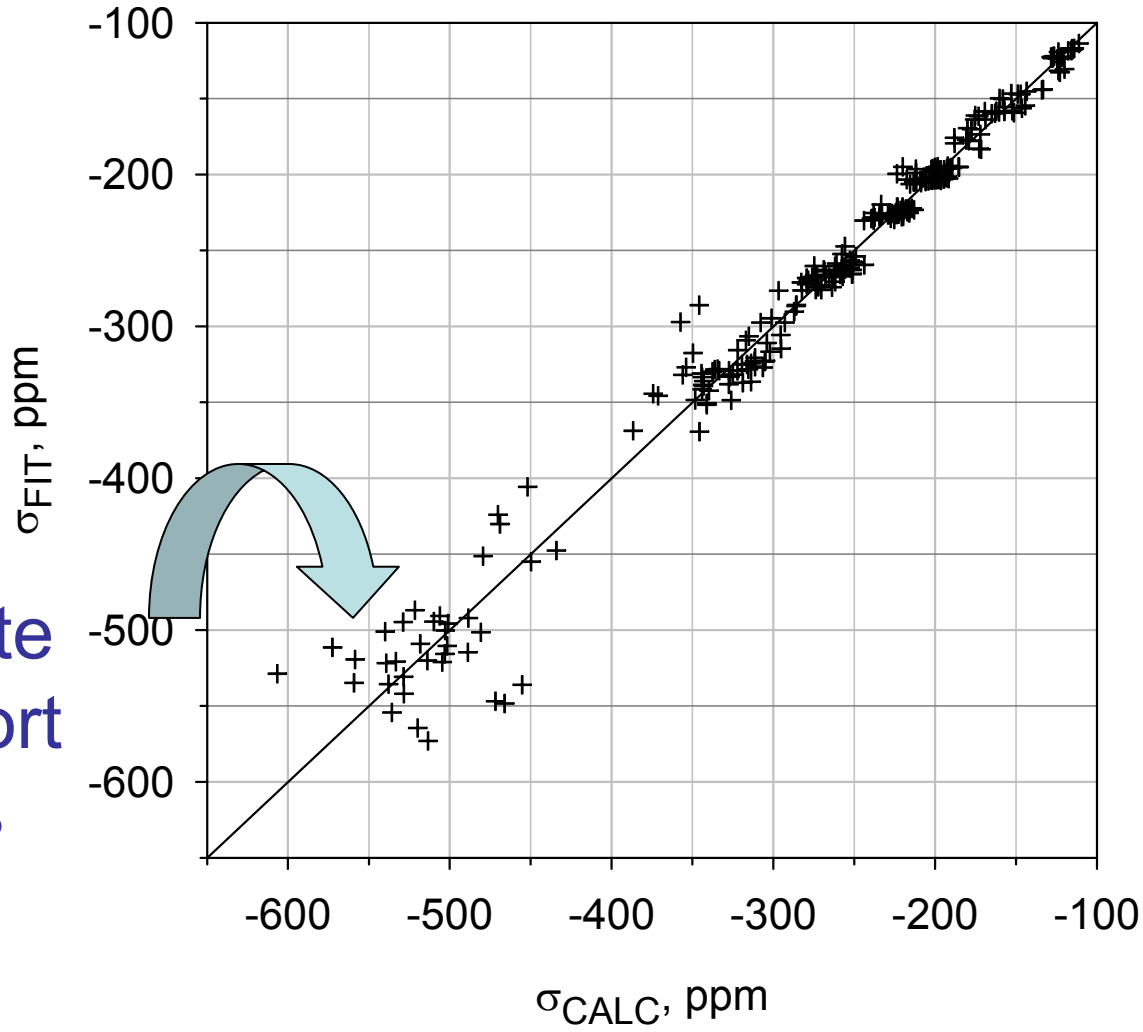
The Xe-O and Xe-H shielding tensors



How to describe the ab initio tensor values at various Xe positions in the cage?

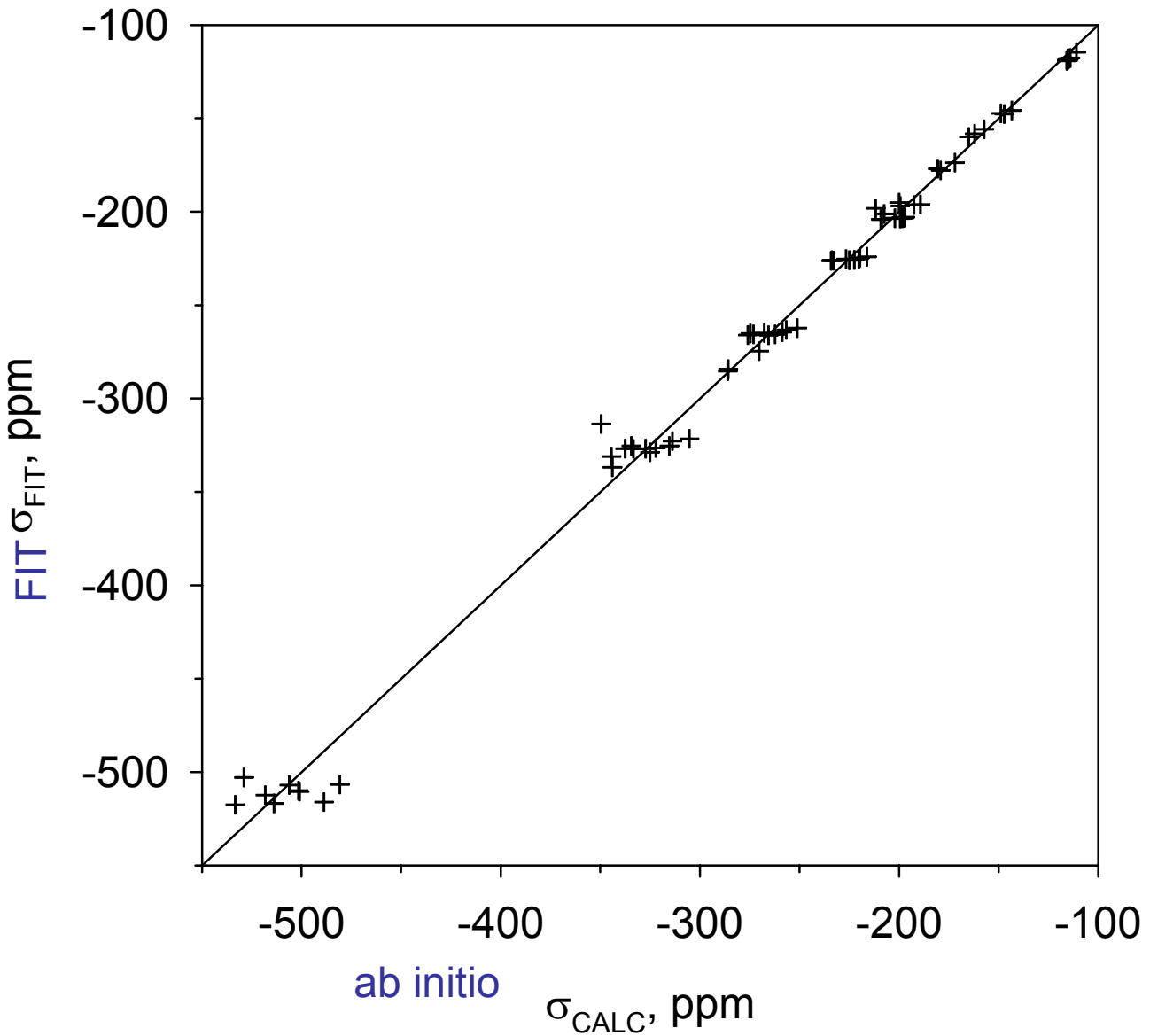
Sums over these **pair** shielding functions
reproduce the ab initio Xe shielding tensor
at each Xe position within the cage (in model XCAGE/PCA)

Sum over pair shielding tensors reproduce ab initio tensor components



but deviate at the short distances

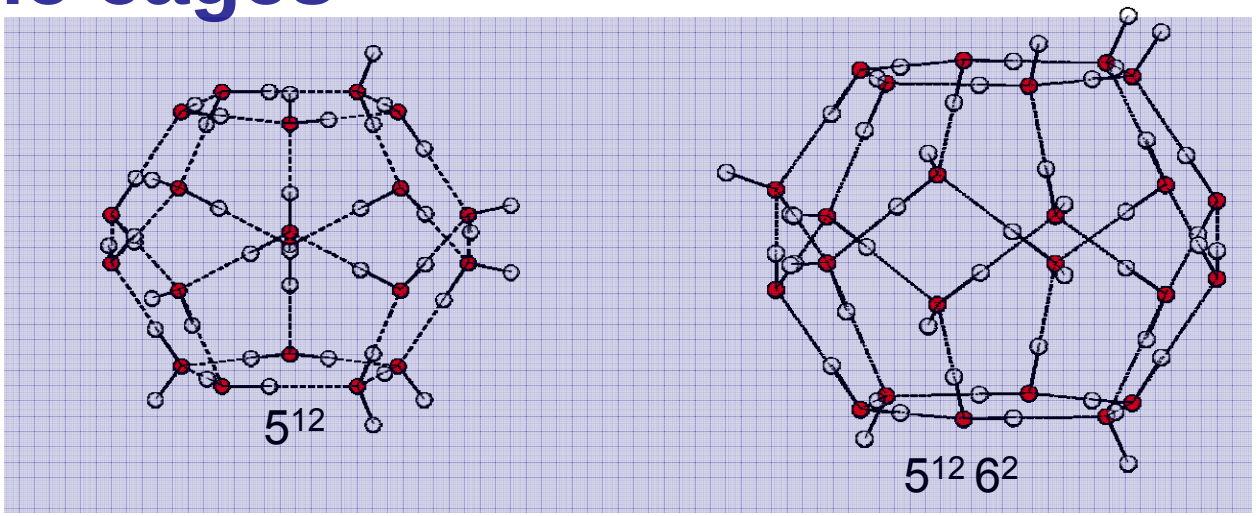
Sum over (Xe-O and Xe-H) **isotropic** shielding reproduce ab initio shielding values very well



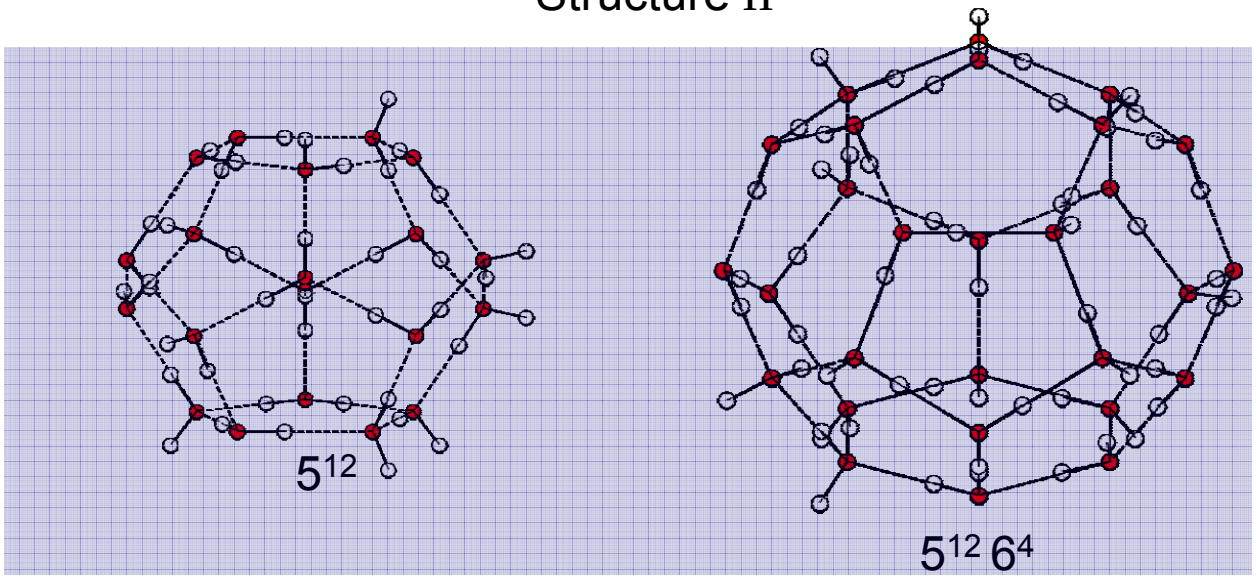
Clathrate hydrates

the cages

Structure I



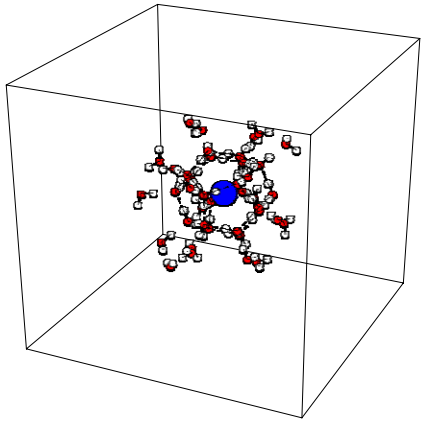
Structure II



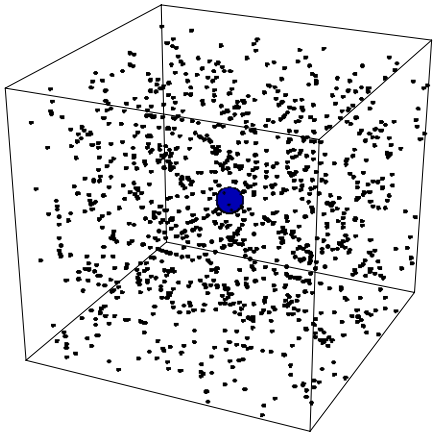
How to model a cage in a hydrogen bonded network?

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

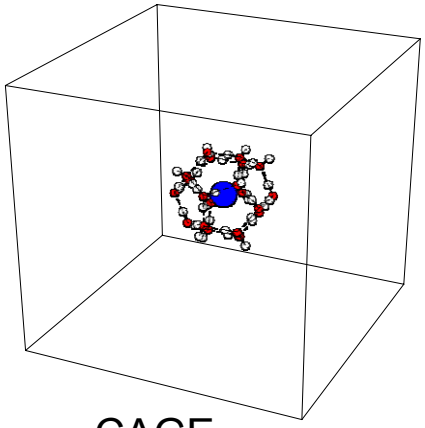
MODELS



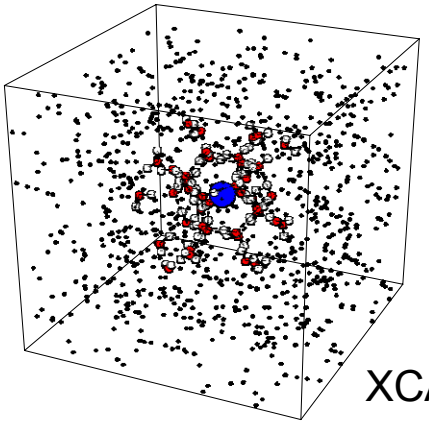
XCAGE



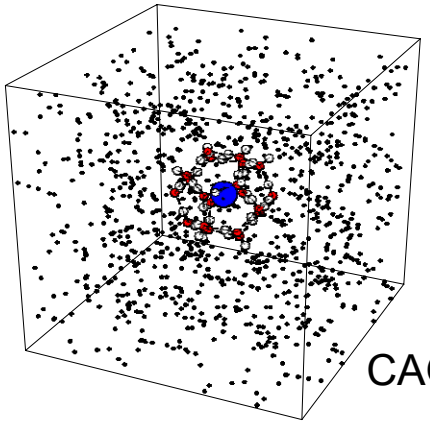
PCA



CAGE

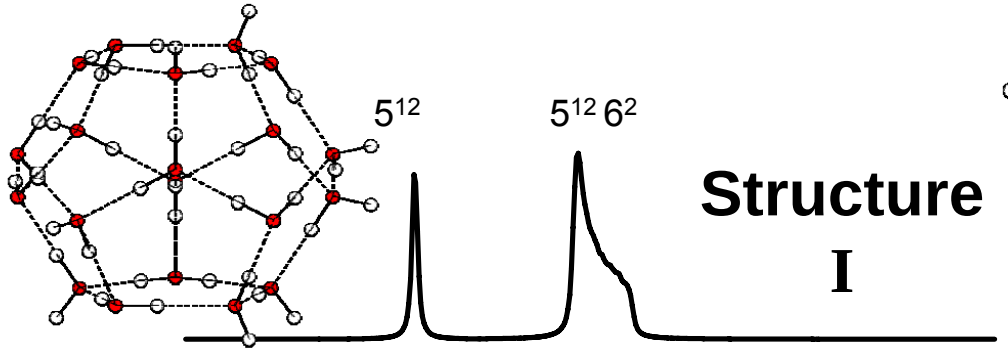


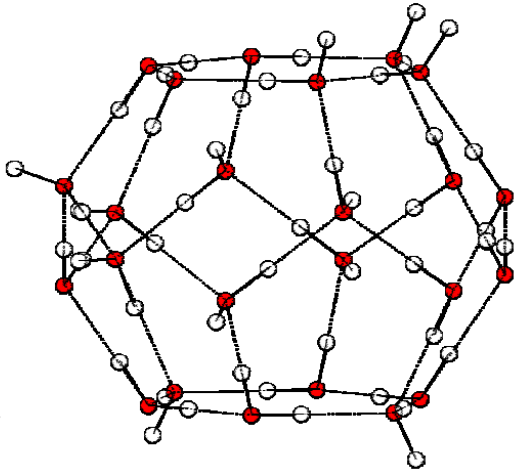
XCAGE/PCA

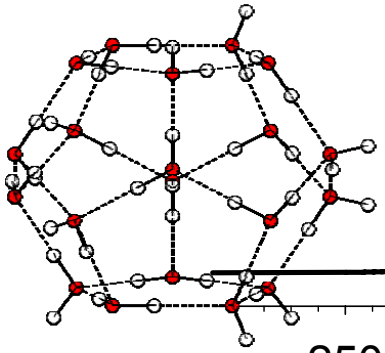


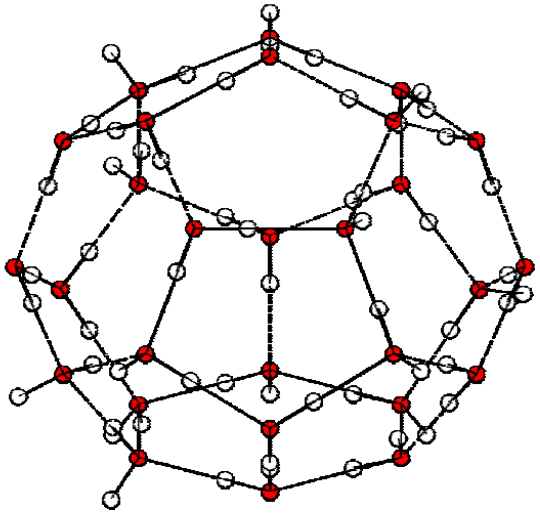
CAGE/PCA

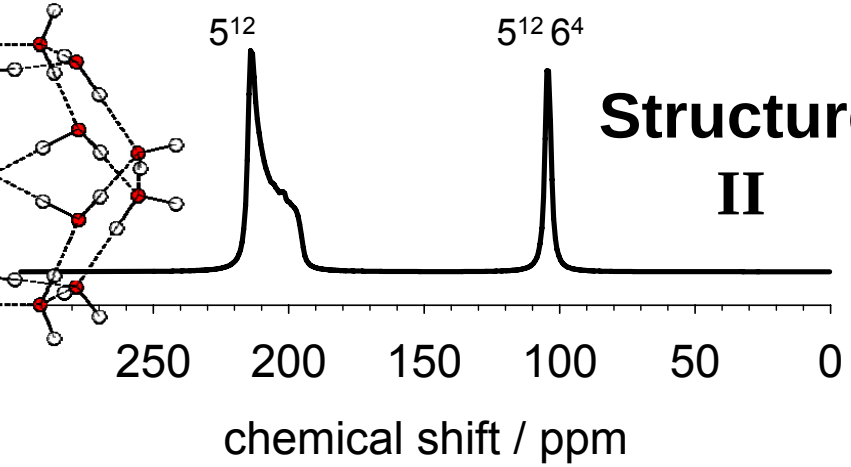
Calculated Xe NMR lineshapes from Monte Carlo simulations in single cages:









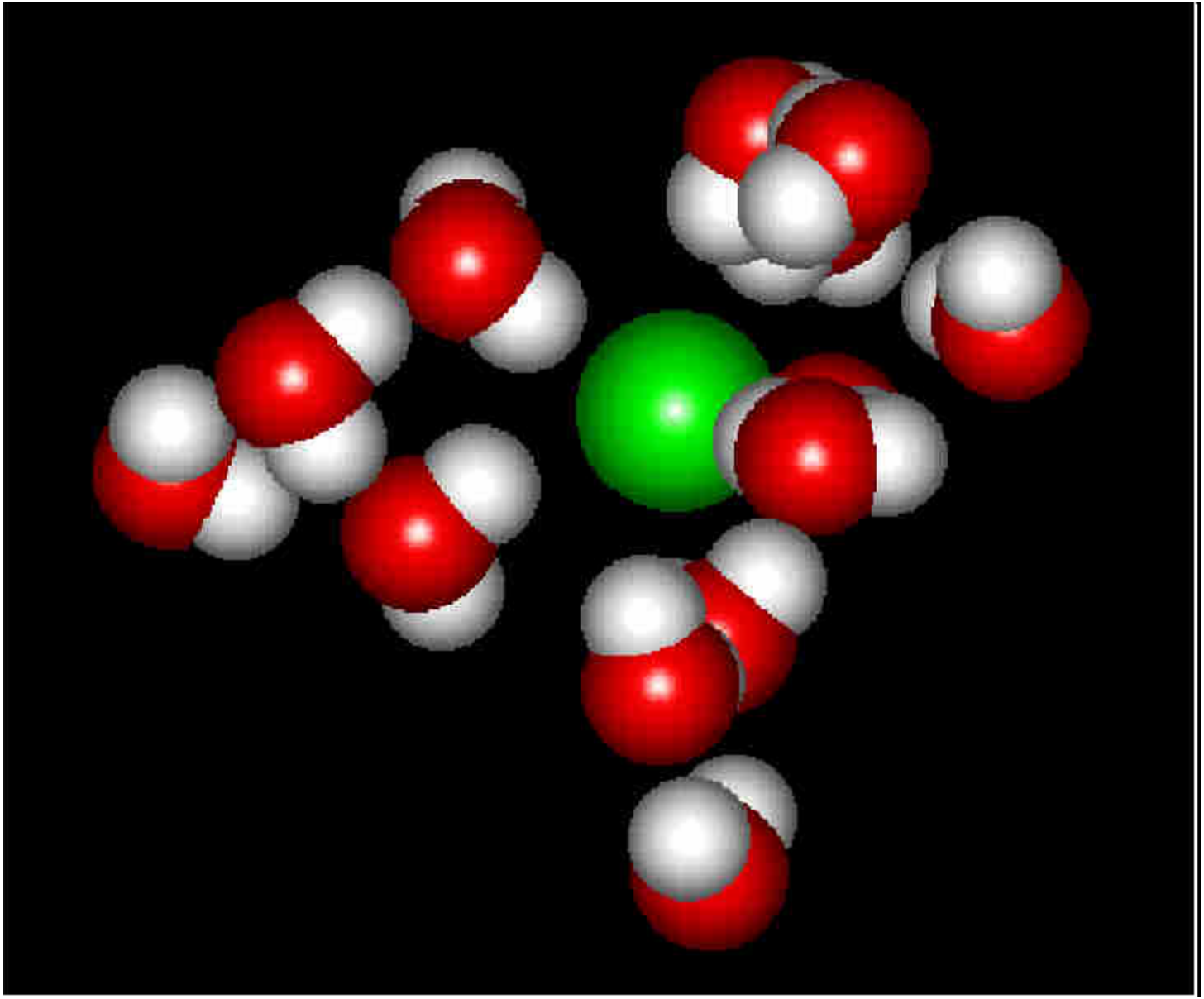


using
the same Xe-O and Xe-H shielding tensor functions,
the same Xe-O and Xe-H potential functions

Check transferability to other Xe clathrate hydrates

- Using **the same** Xe-H and Xe-O shielding functions, and *the same* Xe-H and Xe-O potential energy functions for all, **we reproduce Xe tensor components for Xe** in all cages of clathrate Structure I, Structure II, clathrate H, and also in bromine hydrate Xe clathrate.

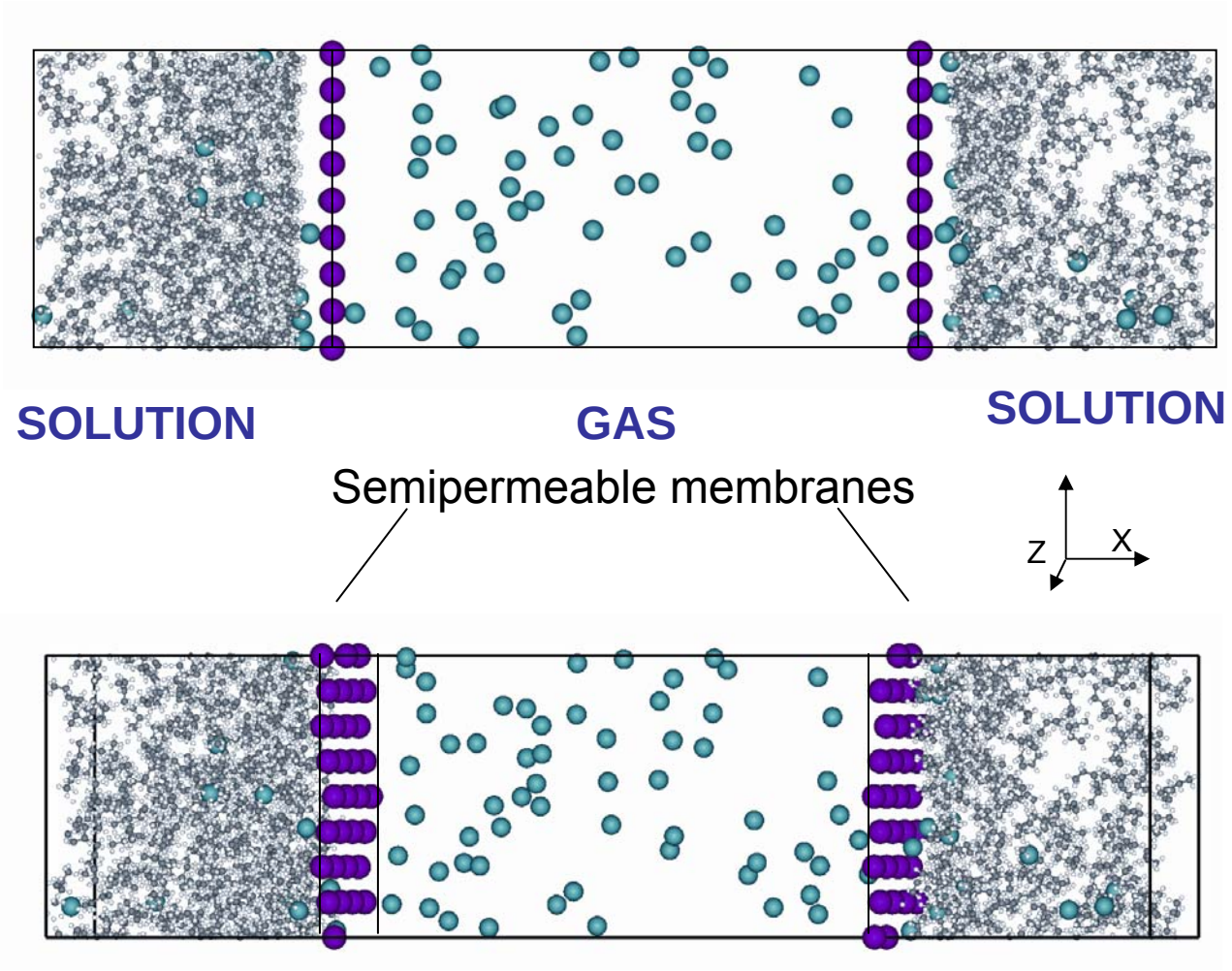
Xe in liquid water



Transferability to Xe in liquid water

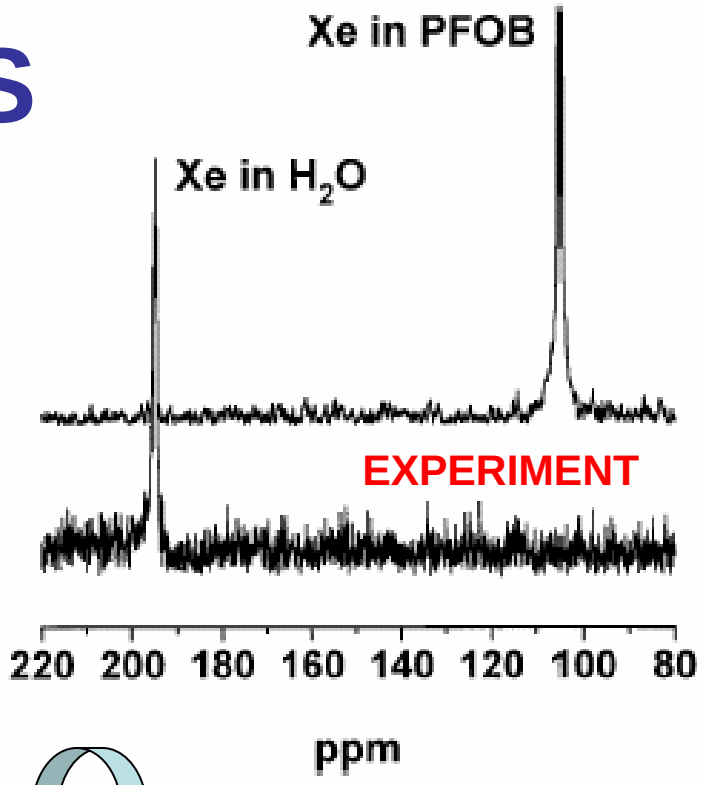
- Use **the same** Xe-H and Xe-O shielding functions, and *the same* Xe-H and Xe-O potential energy functions
- Use an acceptable potential for the structure of liquid water
- Carry out molecular dynamics simulations in a simulation box which is equivalent to the grand canonical Monte Carlo scheme

MD Simulation Box



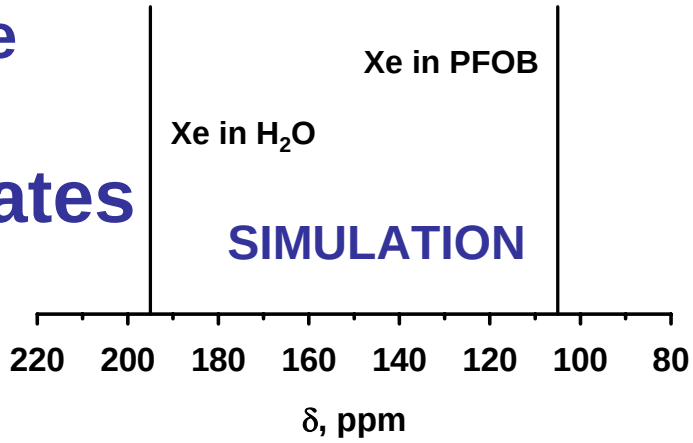
MD Simulation box design: Murad et al, Fluid Phase Equil. 187-188, 29 (2001)
Murad et al, Chem. Phys. Lett. 319, 60 (2000)

RESULTS



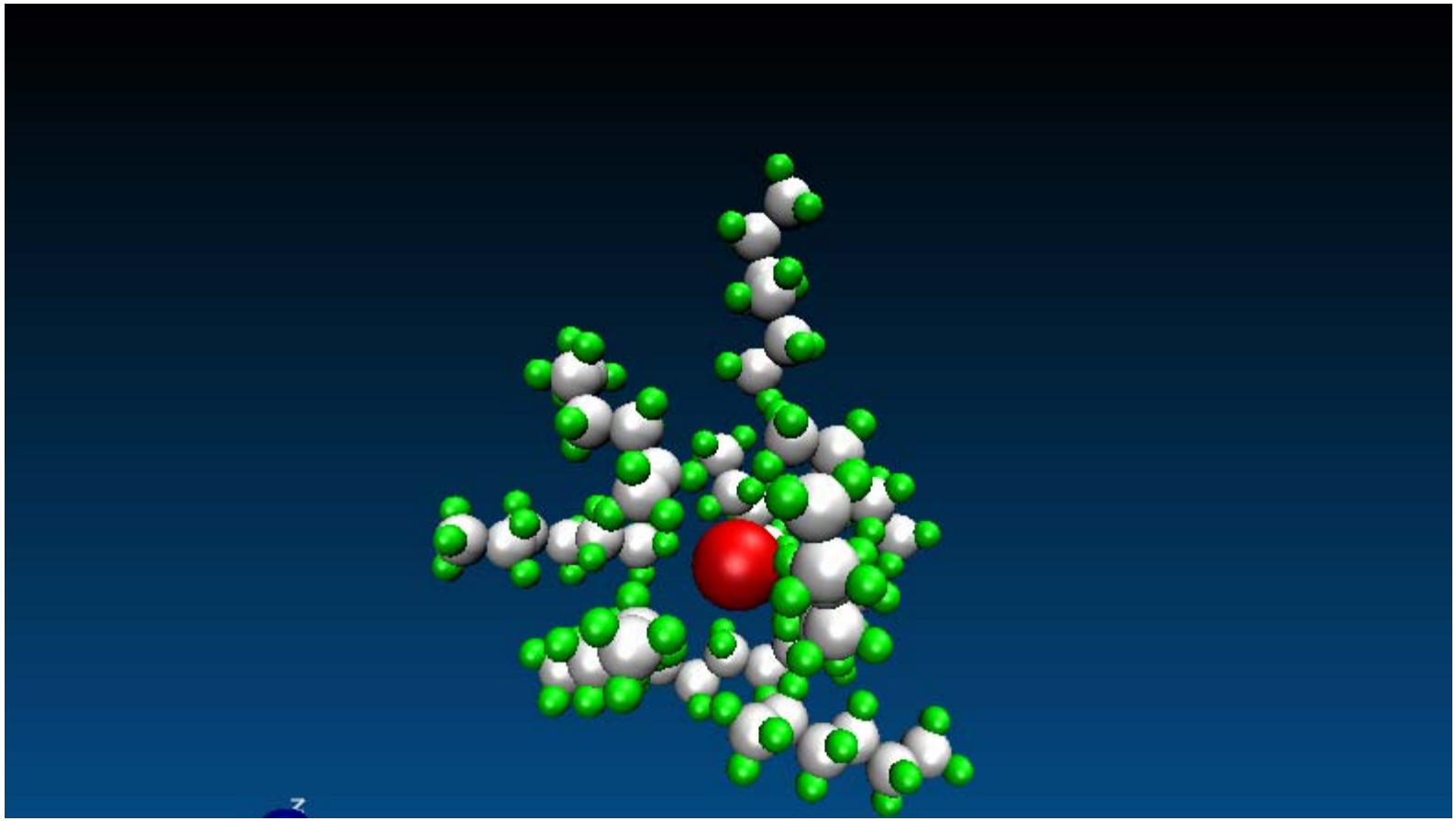
Bifone et al, Magn. Reson. Medicine 41, 442 (1999).

Using quantum mechanical Xe shielding surface calculated for clathrate hydrates

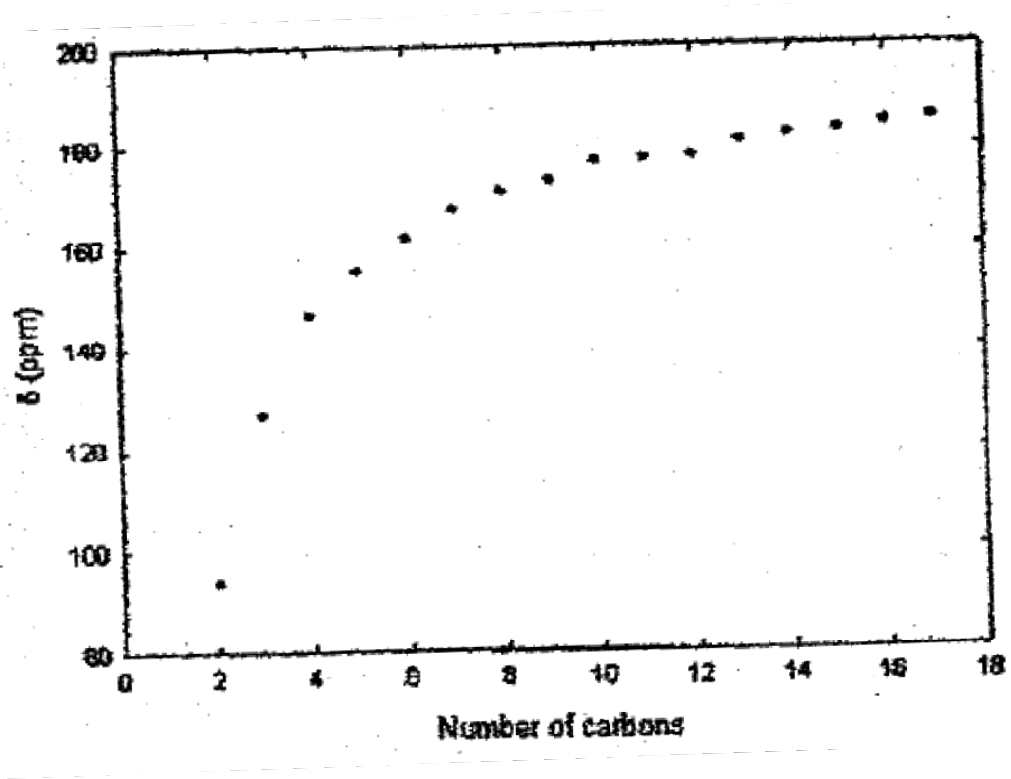


C. J. Jameson, D. N. Sears, S. Murad, J. Chem. Phys. 121, 9581 (2004)

Xe in normal alkanes, dependence on number of carbons

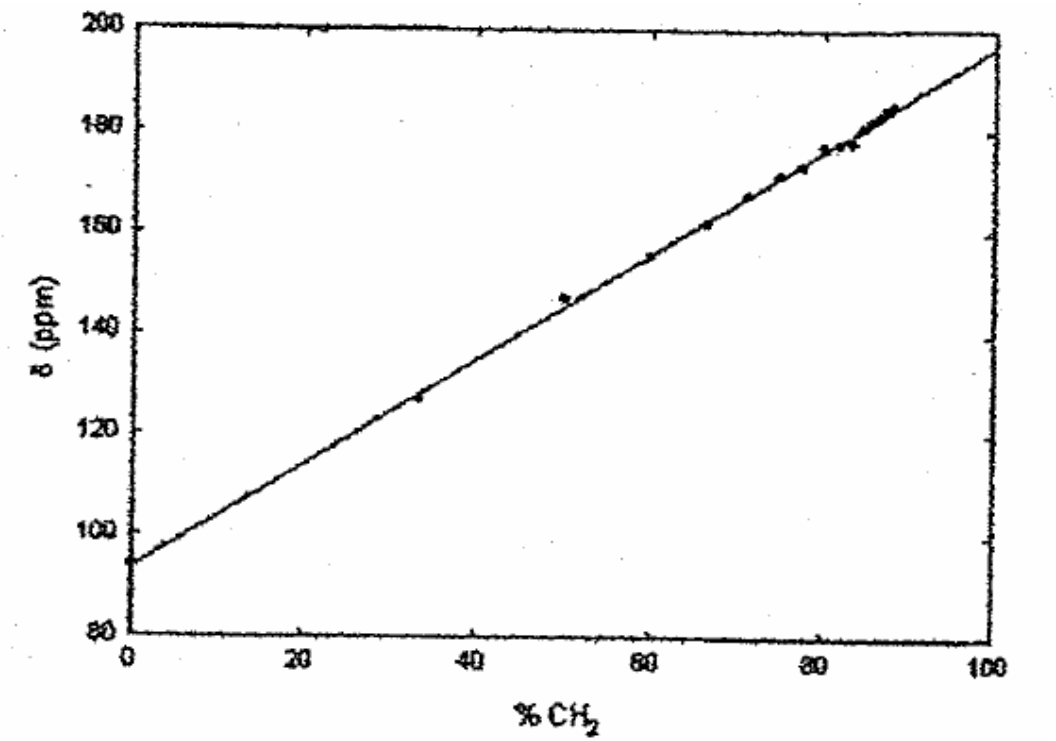


Dependence of Xe chemical shift on number of carbons in linear alkanes



Lim et al., J. Phys. Chem. 1993

Dependence of Xe chemical shift on $\%CH_2$ in linear alkanes



Lim et al., J. Phys. Chem. 1993

Appears counter-intuitive! What is wrong?

To model Xe shielding in liquid hydrocarbons

- (a) Need a function which describes the Xe shielding in an arbitrary configuration of hydrocarbon molecules around the Xe atom
- (b) Need a function which describes the probability of finding that arbitrary configuration

Part (a) we can estimate from quantum mechanical calculations of Xe interacting with CH_4 molecule, provided we can mathematically describe the QM results in terms of additive terms which are functions of Xe-H distance and Xe-C distance

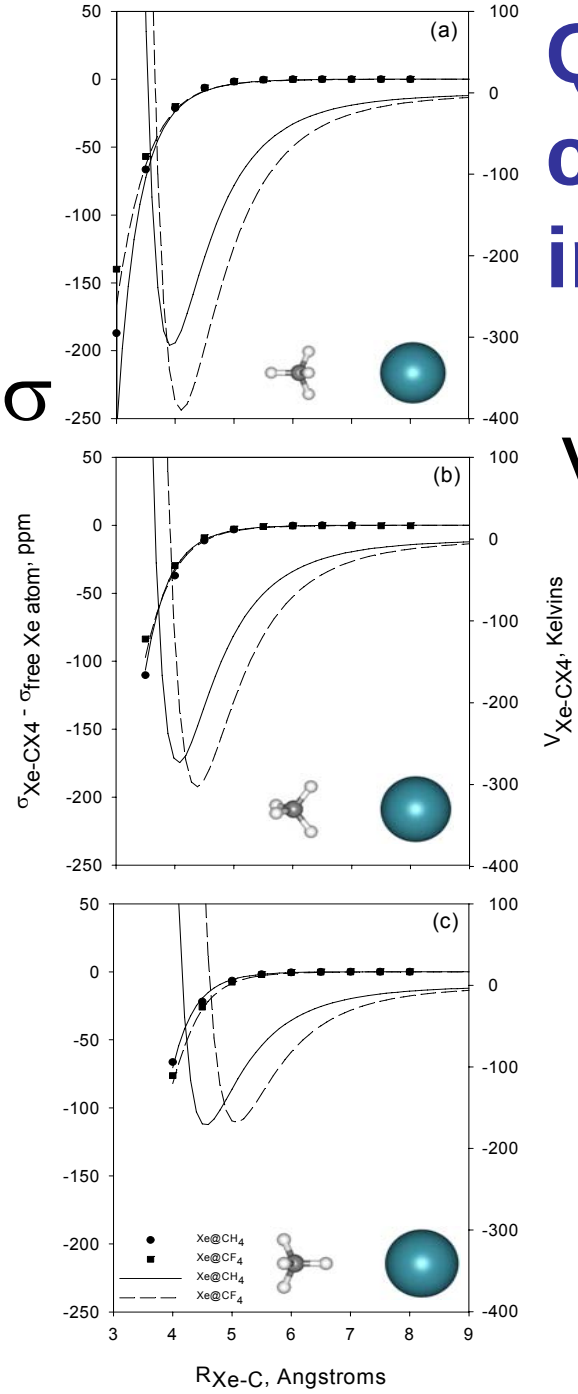
Part (b) we can get from a classical molecular dynamics simulation, provided we have a reasonably good intermolecular potential in terms of Xe-H and Xe-C distances and a good potential model description for liquid hydrocarbon itself.

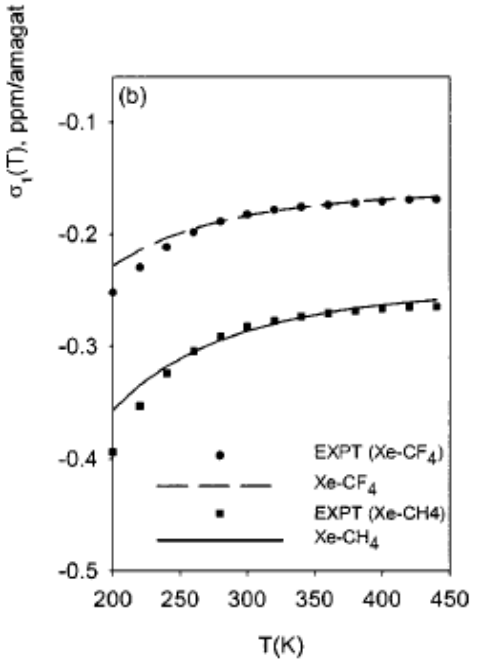
Quantum mechanical calculations of Xe-CH_4 intermolecular shielding

Use σ and V functions to test against Xe chemical shifts in CH_4 gas (and in CF_4)

σ

V





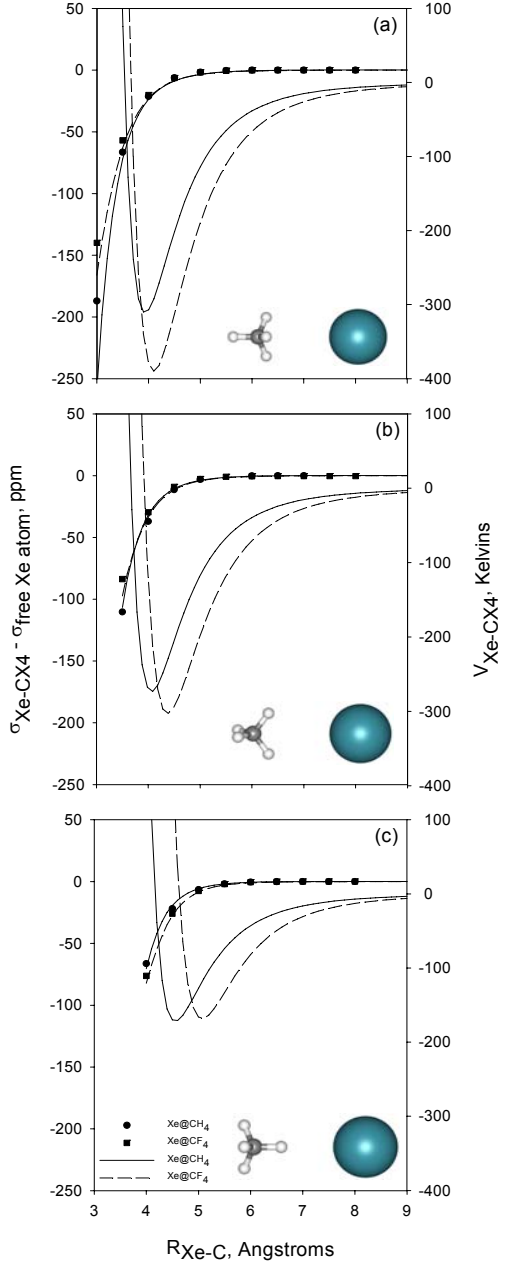
Xe chemical shift function :

Comparison of
$\sigma(Xe\text{-}CH_4)$
vs. $\sigma(Xe\text{-}CF_4)$

and $V(Xe\text{-}CH_4)$
vs. $V(Xe\text{-}CF_4)$

along 3
trajectories.

$V(Xe\text{-}CF_4)$
keeps Xe from
sampling
highly deshielded
σ values at
shorter distances



$$\delta = \frac{[\sigma(\text{free Xe atom}) - \sigma(\text{Xe in infinitely dilute solution})]}{[1 - \sigma(\text{free Xe atom})]}$$

Xe chemical shift function:

$$\delta = \sum_{H(j)} \sum_{n=6}^{14} h_n r_{Xe-H(j)}^{-n} + \sum_{C(k)} \sum_{n=6}^{14} c_n r_{Xe-C(k)}^{-n}$$

n	6	8	10	12	14
c_n (Å^{-n})	-1.48211×10^5	1.045×10^7	-1.90132×10^8	1.38433×10^9	-3.45561×10^9
h_n (Å^{-n})	8.58334×10^3	6.55733×10^5	1.42131×10^7	-6.34747×10^7	4.20088×10^7

Fitted to quantum mechanical calculations on Xe-CH_4 supermolecule, using large basis sets

Xe-solvent potential

$$u_{Xe-i} = \sum_i \varepsilon_{Xe-i} \left\{ \left(\frac{6}{\alpha_{Xe-i} - 6} \right) \exp[\alpha_{Xe-i}(1 - \bar{r})] - \left(\frac{\alpha_{Xe-i}}{\alpha_{Xe-i} - 6} \right) \bar{r}^{-6} \right\}$$

where $\bar{r} = \dfrac{r_{Xe-i}}{r_{\min, Xe-i}}$

i = C or H with parameter values fitted to best Xe-CH_4 potential function that reproduces crossed beam scattering results

Potential function for liquid *n*-alkanes

OPLS - All Atom Potential Model

$$u_{ij} = \sum_{i}^{a}\sum_{j}^{b}\left\{4\varepsilon_{ij}\left[\left(\frac{r_{ij}}{\sigma_{ij}}\right)^{-12} - \left(\frac{r_{ij}}{\sigma_{ij}}\right)^{-6}\right] + q_i q_j / r_{ij}\right\} f_{ij}$$

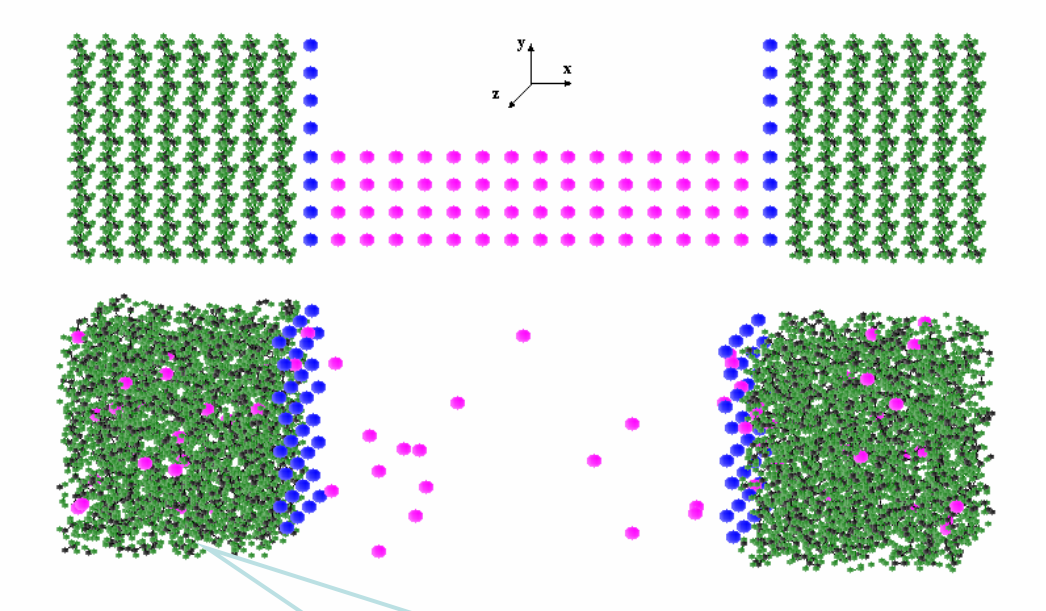
bond stretch: $V_{\text{bond}}(R) = \frac{1}{2} K_{\text{bond}}(R - R_{\text{bond}})^2$

angle bend: $V_{\text{angle}}(\theta) = \frac{1}{2} K_{\text{angle}}\{\cos(\theta) - \cos(\theta_0)\}^2$

torsion: $V_{\text{torsion}}(\varphi) = k_1(1+\cos\varphi)/2 + k_2(1-\cos 2\varphi)/2 + k3(1+\cos 3\varphi)/2$

Simulation System

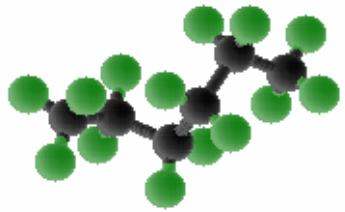
Xe and *n*-hexane



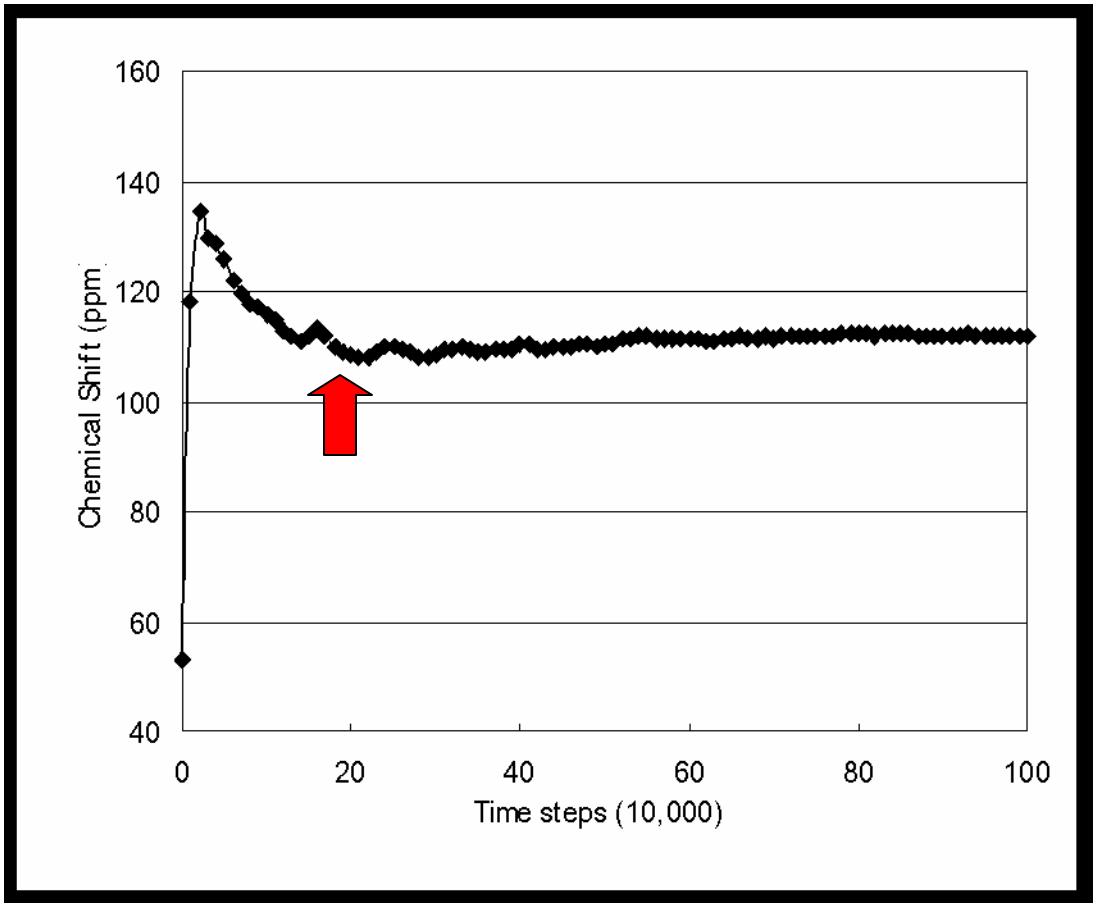
initial

10 ns

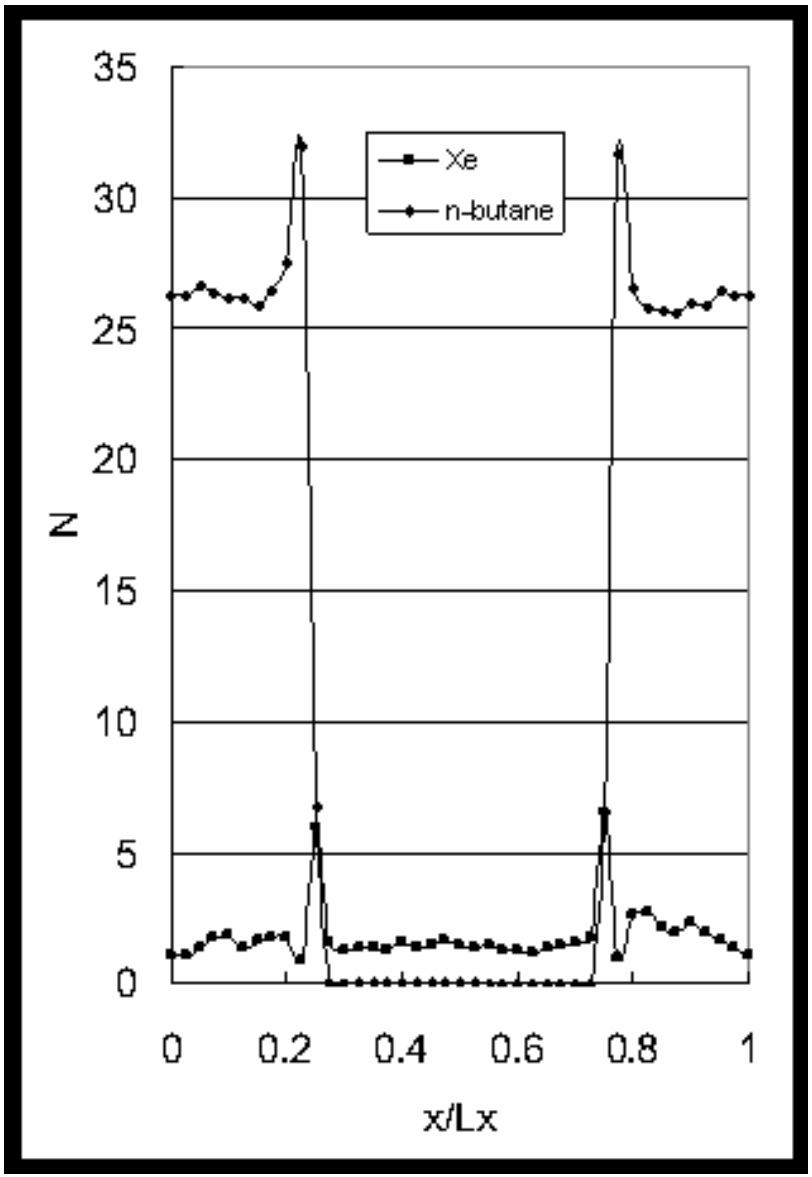
Typical n-hexane structure:



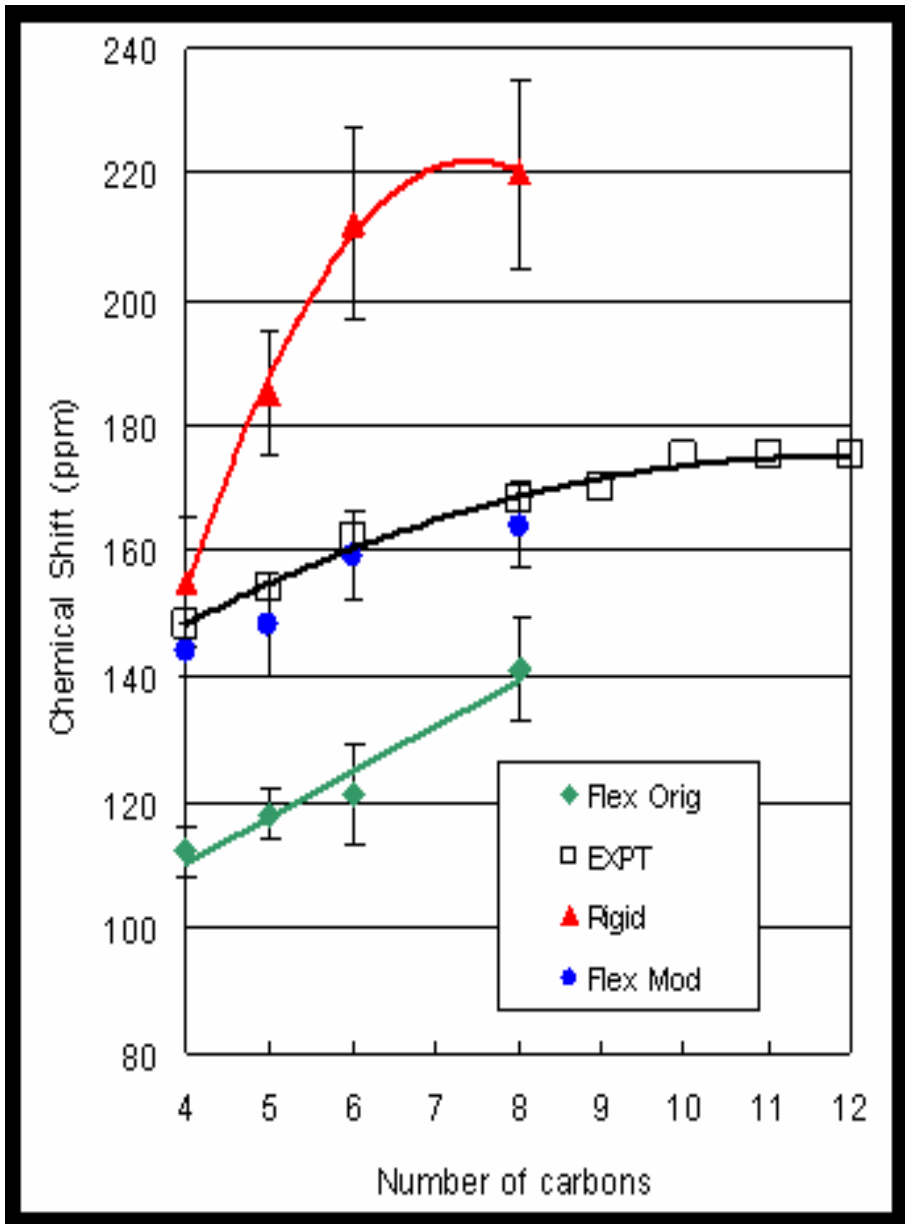
A typical Xe chemical shift calculation run:



Density profile for Xe-alkane system:



Calculate chemical shift by using different models:

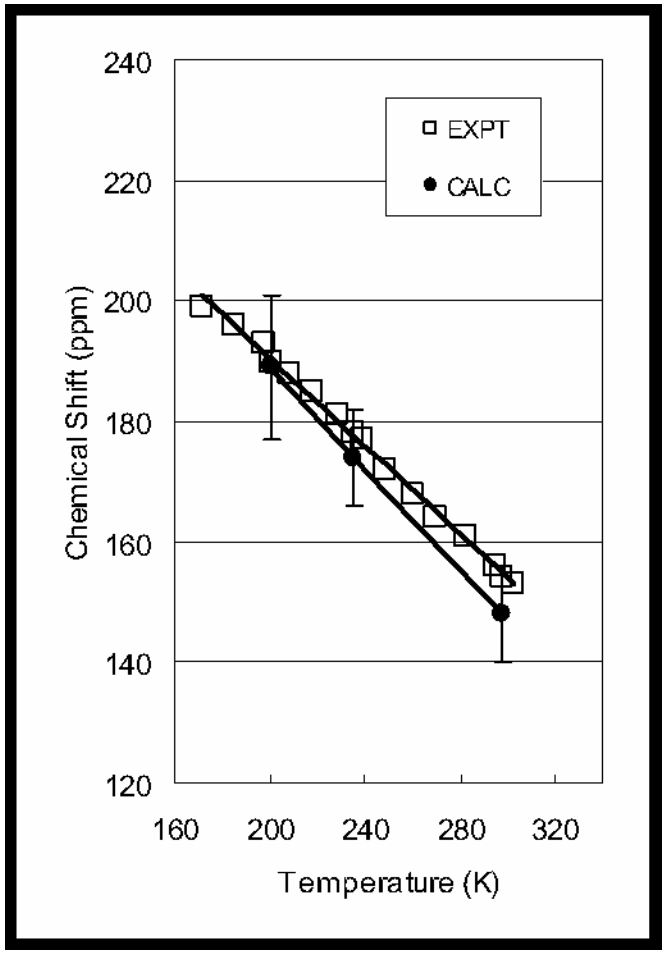


Rigid molecules permit the Xe to have greater probability of close interactions with the solvent atoms, leading to artificially steeper dependence on chain length and greater Xe chemical shifts.

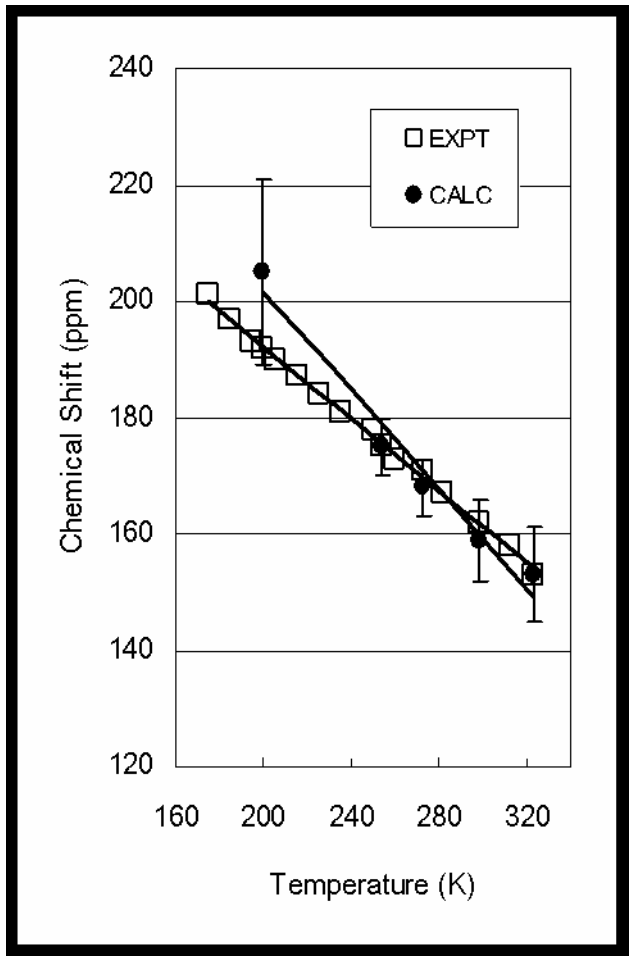
Flexible molecules give more realistic dependence on chain length.

Xe chemical shift temperature dependence

n-pentane :



n-hexane :



Molecular Dynamics simulations results

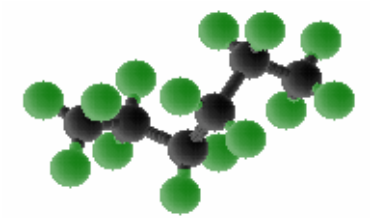
J. Phys. Chem. C, 111, 15771-15783 (2007).

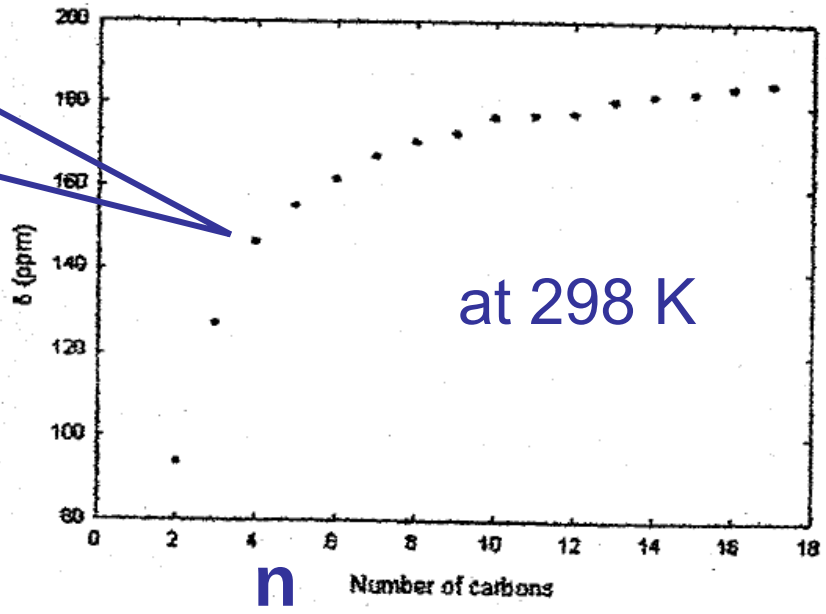
Comparable Xe chemical shifts in solution?

when liquids are not in the same thermodynamic state

Lim et al., J. Phys. Chem. 1993

hexane





C_nH_{2n+2}

Must not compare Xe chemical shifts for liquids in different thermodynamic states

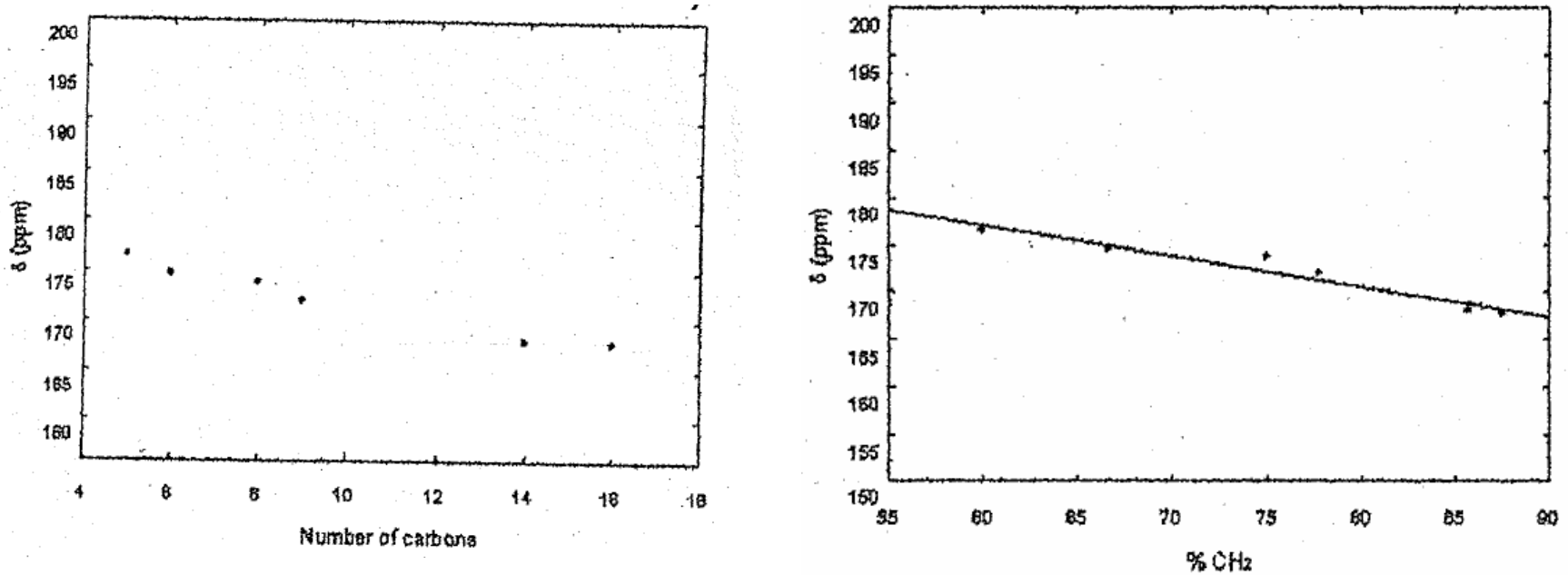
- Compare liquids at the same reduced temperature, for example

or

- Compare liquids at the same density M L^{-1}

R. Bonifacio & Eduardo J.M. Filipe experiments, XeMAT2000:

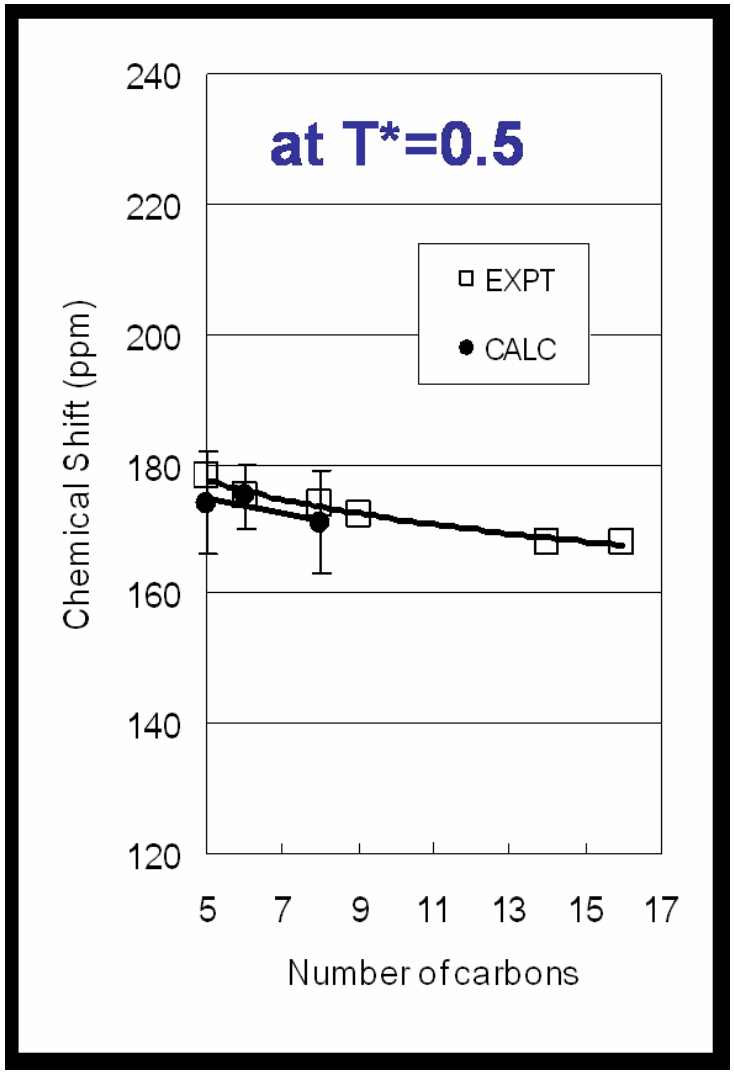
Compare experimental Xe chemical shifts in the liquids at the same thermodynamic state, at T* = 0.5



Xe chemical shift in various liquid alkanes. Looks more like what we should expect

Comparable chemical shifts in solution

Xe chemical shift at the same thermodynamic state

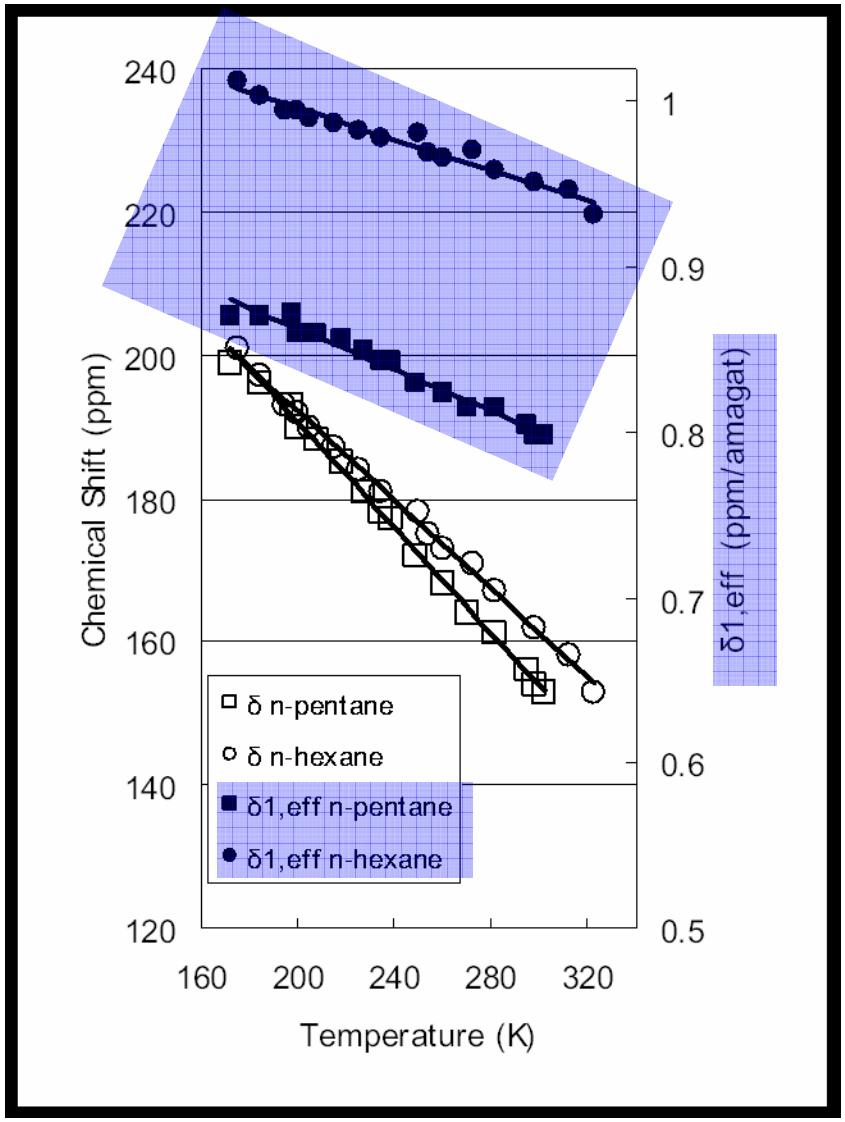


- EXPT: R. Bonifacio & E. J. M. Filipe, XeMAT 2000
- Molecular Dynamics simulations

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

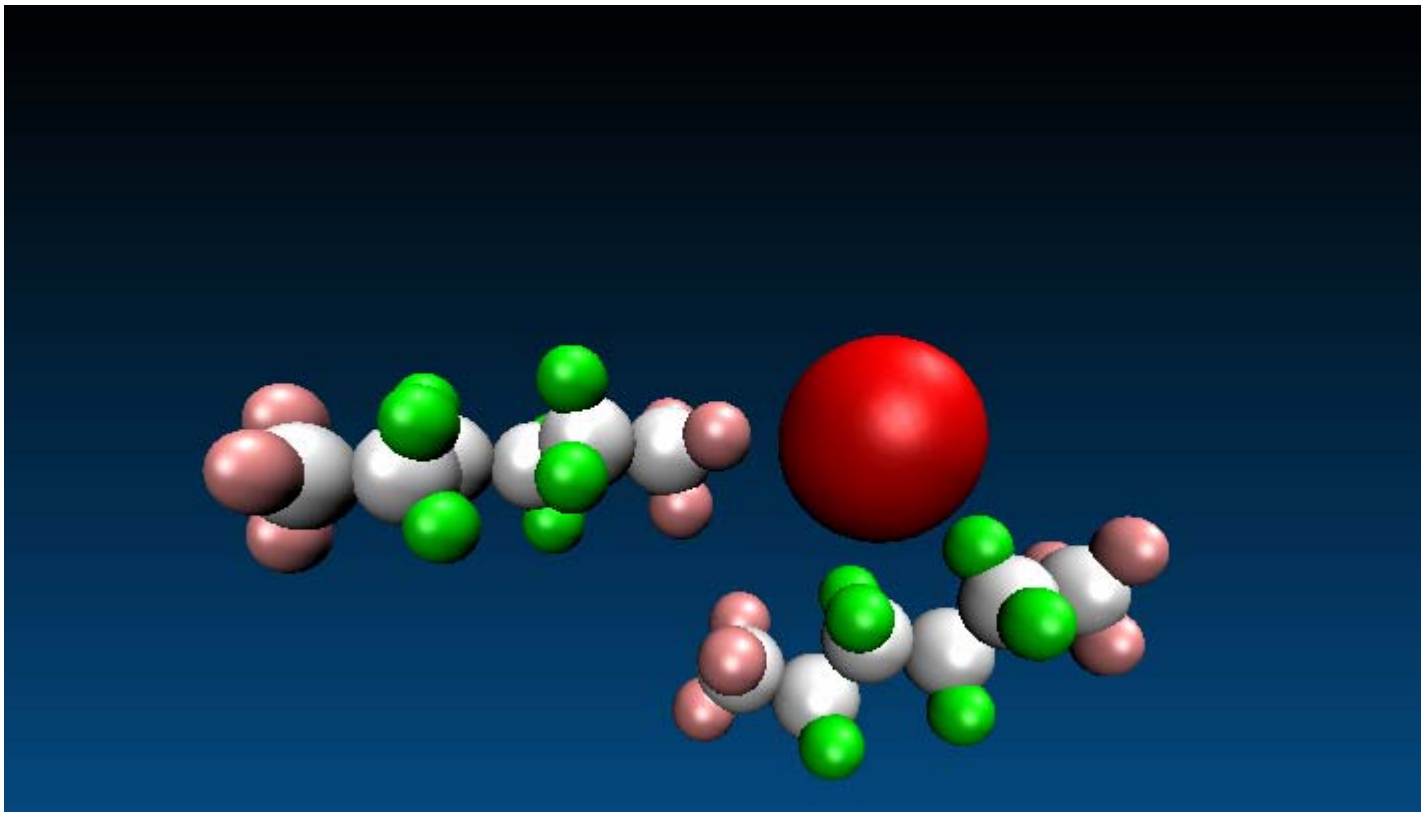
Contributions to the temperature dependence of Xe chemical shifts

T dependence of the solvent density is responsible for most of the observed steep T dependence of Xe chemical shifts in solution



divide out the density to get δ_1

Constitutive contributions to the Xe chemical shift in a solvent



Advantage of MD simulations

- Can separately sum up the contributions of Xe-CH_2 and Xe-CH_3 interactions to the average Xe chemical shift in the solution and compare against each other.
- We find that per Xe-CH_3 contributions are greater than per Xe-CH_2 contributions in a given liquid hydrocarbon.
- Can devise a method for finding “constitutive” Xe-CH_3 and Xe-CH_2 contributions for the prediction of average Xe chemical shift in other liquid hydrocarbons.

Definition of constitutive Xe-CH_3 and Xe-CH_2 contributions to Xe chemical shift in liquid hydrocarbons

We can determine individually the Xe-CH_3 and the Xe-CH_2 contributions in MD since we are calculating pair-wise contributions during the MD runs to obtain the average.

Define the constitutive contributions to $\delta_{1effective}$, i.e., the Xe chemical shift divided by the number density of the liquid

Xe-CH_3 vs Xe-CH_2 contributions to Xe chemical shift (ppm) in *n* – alkanes from MD simulations

	at T = 298 K				at T* = 0.5			
	n-butane	*n*-pentane	*n*-hexane	*n*-octane	*n*-butane	*n*-pentane	*n*-hexane	*n*-octane
n	4	5	6	8	4	5	6	8
CH_3	42.2	39.4	33.1	30.1	53.1	46.1	39.7	30.5
CH_2	28.9	26	21.7	18.1	37.7	30.2	24.7	19.7
ratio	1.46	1.51	1.52	1.66	**1.41**	**1.53**	**1.61**	**1.55**

How to find constitutive contributions to Xe chemical shift (ppm) that can be applied for all *n*-alkanes?

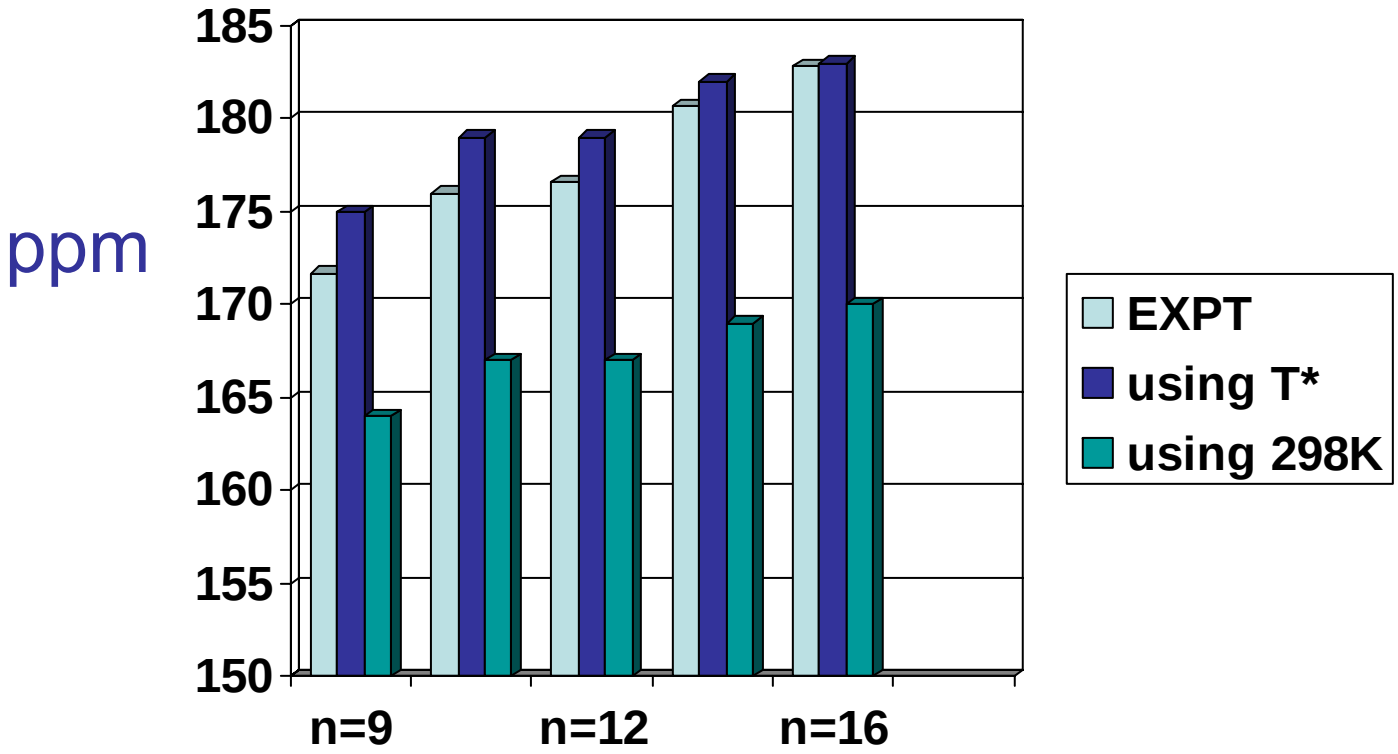
Prediction of Xe chemical shifts in higher n-alkanes from constitutive Xe-CH_3 and Xe-CH_2 contributions to $\delta_{1effective}$ (already in same mol L^{-1} basis)

	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**

Prediction of Xe chemical shifts in higher *n*-alkanes from constitutive contributions based on simulations for Xe in C_nH_{2n+2}, n = 4, 5, 6, 8 calculated at T=298, or calculated at T*=0.5



at T*=0.5: CH_2 3.1 ppm/ (mole L^{-1}) CH_3 4.7 ppm/ (mole L^{-1})

Prediction of Solubility

- Solubility
  - depends on the interaction between solute and solvent.

- Average Chemical Shift
  - depends on the free volume associated with the liquid structure of the solvent and solute-solvent intermolecular interactions

Prediction of gas solubility, Henry's constant

- understand the molecular basis for xenon chemical shift in liquids
- explain at the fundamental molecular level why the chemical shift is closely related to the solute-solvent interaction potential
- use this information to develop strategies for better design of solute-solvent interaction potential, and provide a better estimation of Henry's constant

Strategy for gas solubility calculations

- use molecular simulation to model the chemical shift of xe in *n*-alkanes
- determine the key parameters of solute-solvent interaction potential that influence the chemical shift calculation.
- use molecular simulation for chemical shift calculation as a quick screening tool for improving the gas solubility calculation.

Calculation of Henry's constant

$$H_{1,2} = \lim_{x_1 \to 0} \left\{ \frac{P_1 \phi_1}{x_1 \exp[(P_2 - P_2^{sat})\overline{V}_1^{\infty} / RT]} \right\}$$

Here the gas pressure:

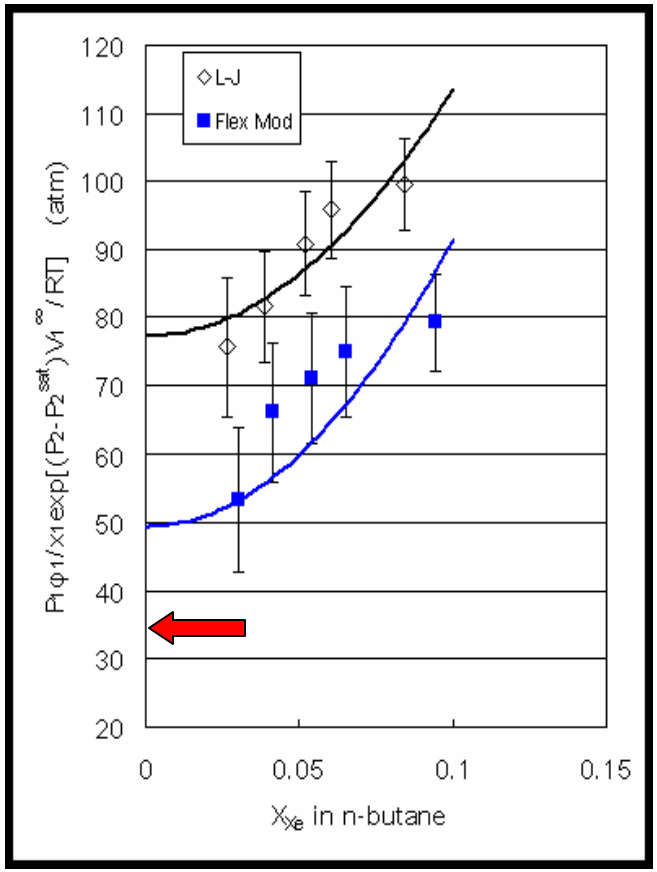
$$P_1 = (1 + B\rho)\rho RT$$

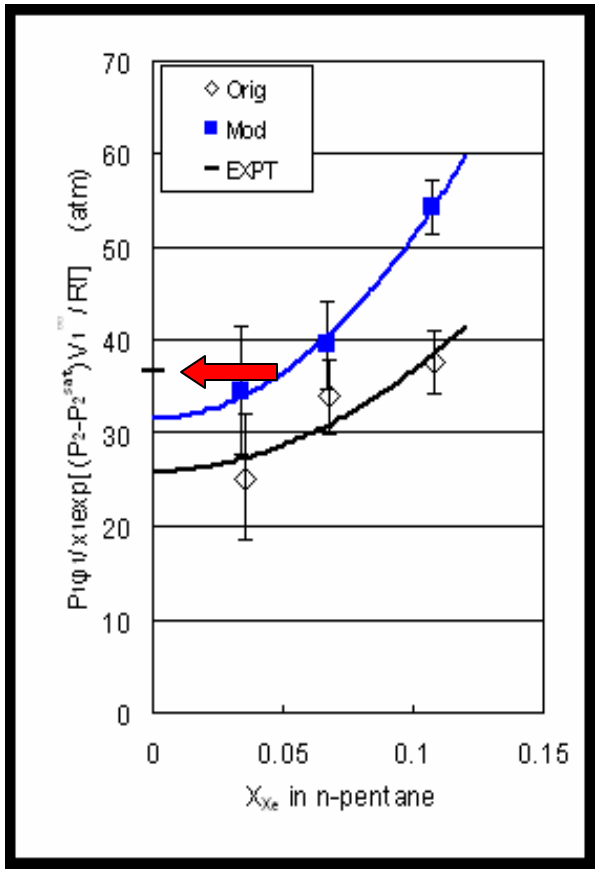
Gas fugacity coefficient:

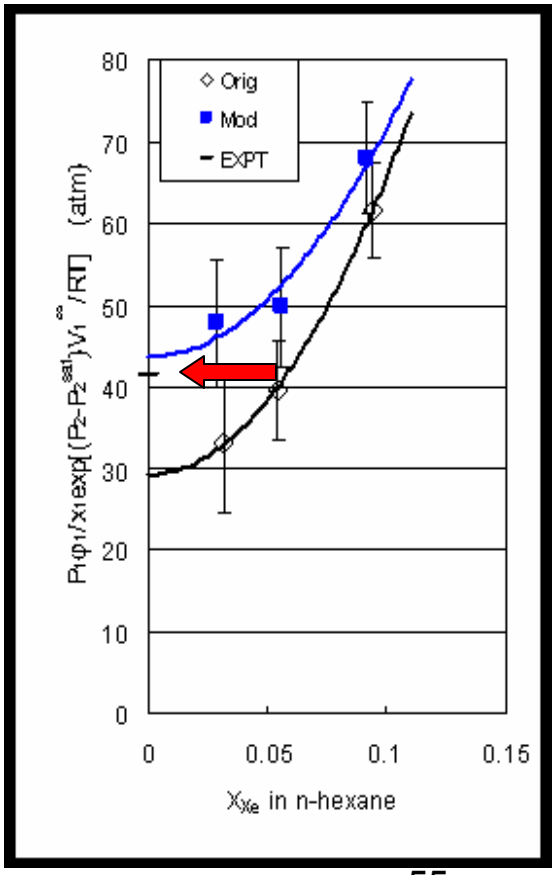
$$\ln \phi = 2\rho B - \ln (P/\rho RT)$$

Henry's Constant from MD simulations:

Henry's Constant Calculation Using Different Potential Models:

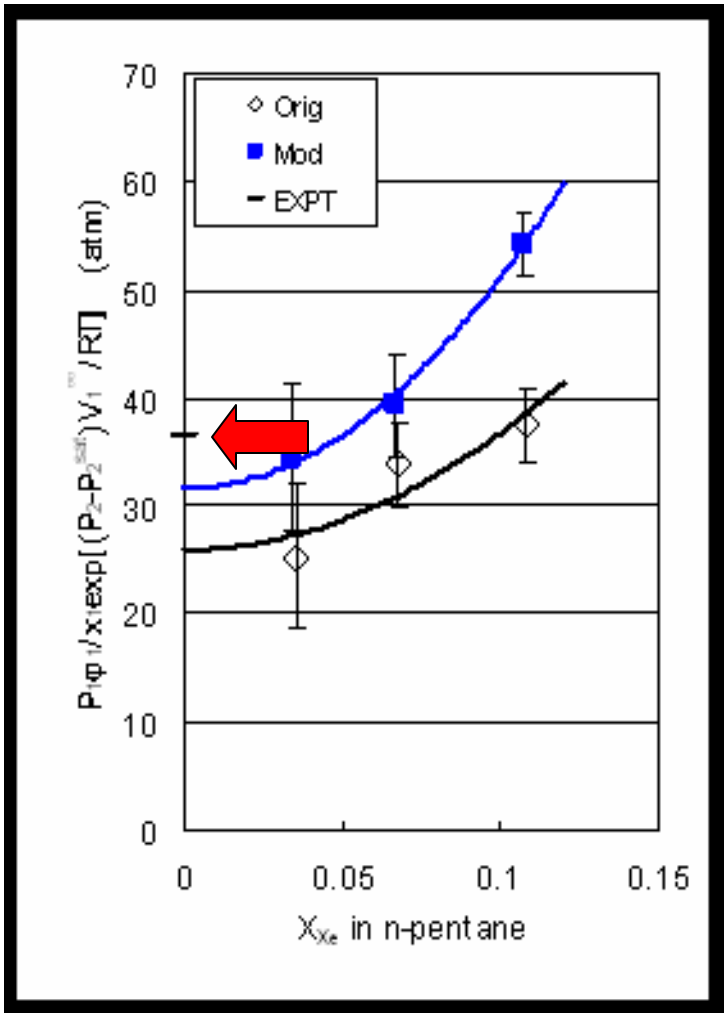


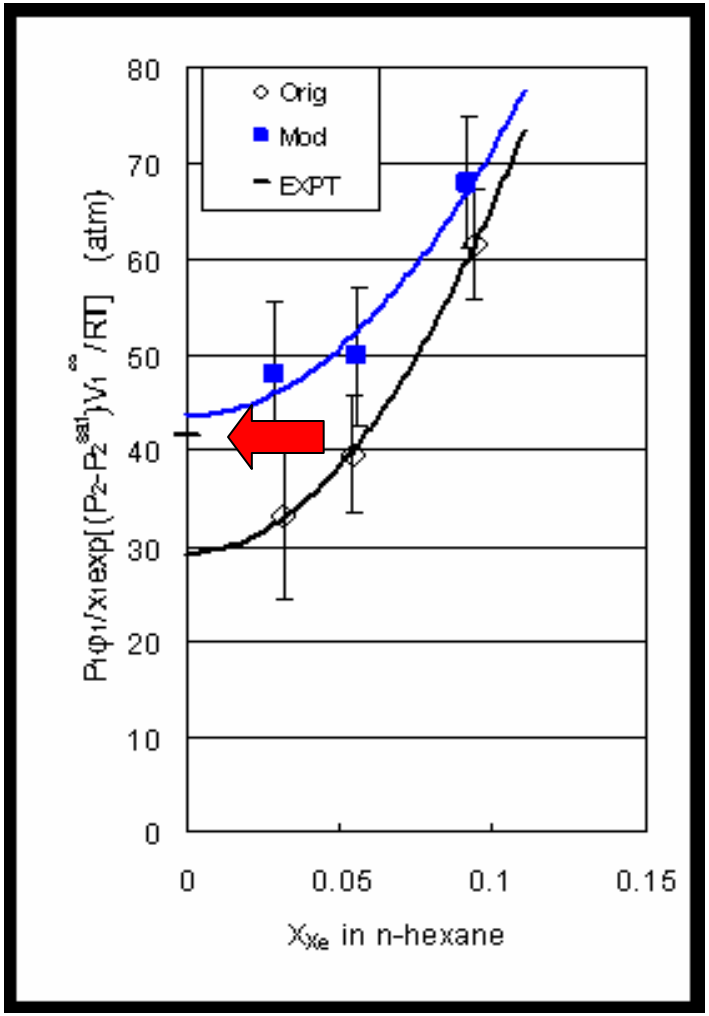




Henry's Constant from MD simulations:

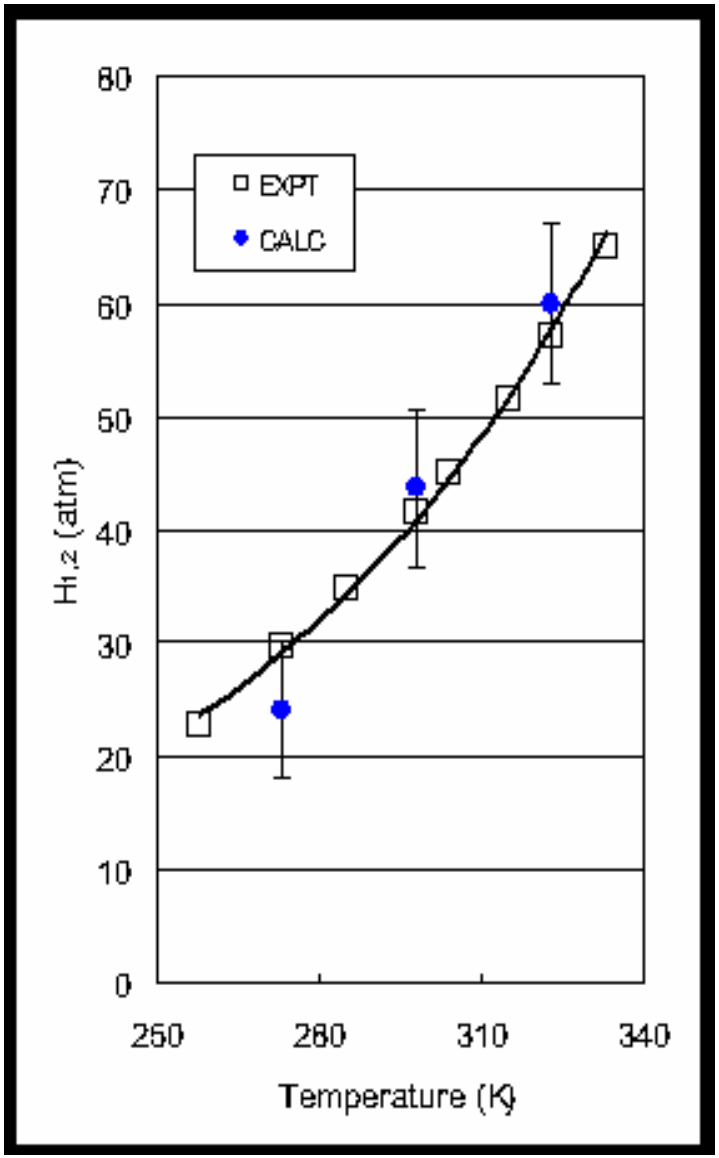
Henry's Constant Calculation Using Different Potential Models:





Temperature dependence of Henry's Constant

Xe in *n*-hexane



Good agreement with experiment

SUMMARY

- modeled the *n*-alkanes with explicit carbon and hydrogen atoms; compared with former simulations
- improved the solute-solvent potential for better agreement with Xe chemical shifts
- obtained meaningful insight into the chemical shift temperature dependence
- calculated the gas solubility of xenon in different *n*-alkanes
- showed that improved agreement with chemical shift resulted in better solubility results

CONCLUSIONS

- Xe chemical shifts in solutions can be interpreted at the molecular level using the same approach as for Xe in cavities of a porous solid.
- Flexible solvent molecules provide smaller Xe chemical shifts, whereas rigid models provide higher probabilities for close approach and unrealistically higher Xe chemical shifts.
- Adequate potential functions for the liquid structure in an MD simulation and using quantum mechanical Xe shielding functions can reproduce experimental chemical shifts and their temperature dependence.
- Comparing the liquids at the same thermodynamic state permits insight into constitutive contributions to Xe chemical shifts in these liquids.

EPILOGUE

- The $\delta_{1effective}$ (Xe–CH_2) ~2.69 ppm/ mol L^{-1} per CH_2 for Xe **in cyclo alkanes is smaller** than the corresponding values (~3.14 ppm/ mol L^{-1} per CH_2 at T*=0.5) found in the linear alkanes, illustrating the dependence of the Xe chemical shift on the accessibility of the atoms providing electronic response which gives rise to the chemical shift.
- End (CH_3) groups have a distinct advantage in contributing to the Xe chemical shift because of the site effect. Likewise, we should expect that the constraints associated with the cyclic geometry will keep the CH_2 from getting as close to the Xe atom as does the CH_2 in a linear chain.

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Acknowledgments

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