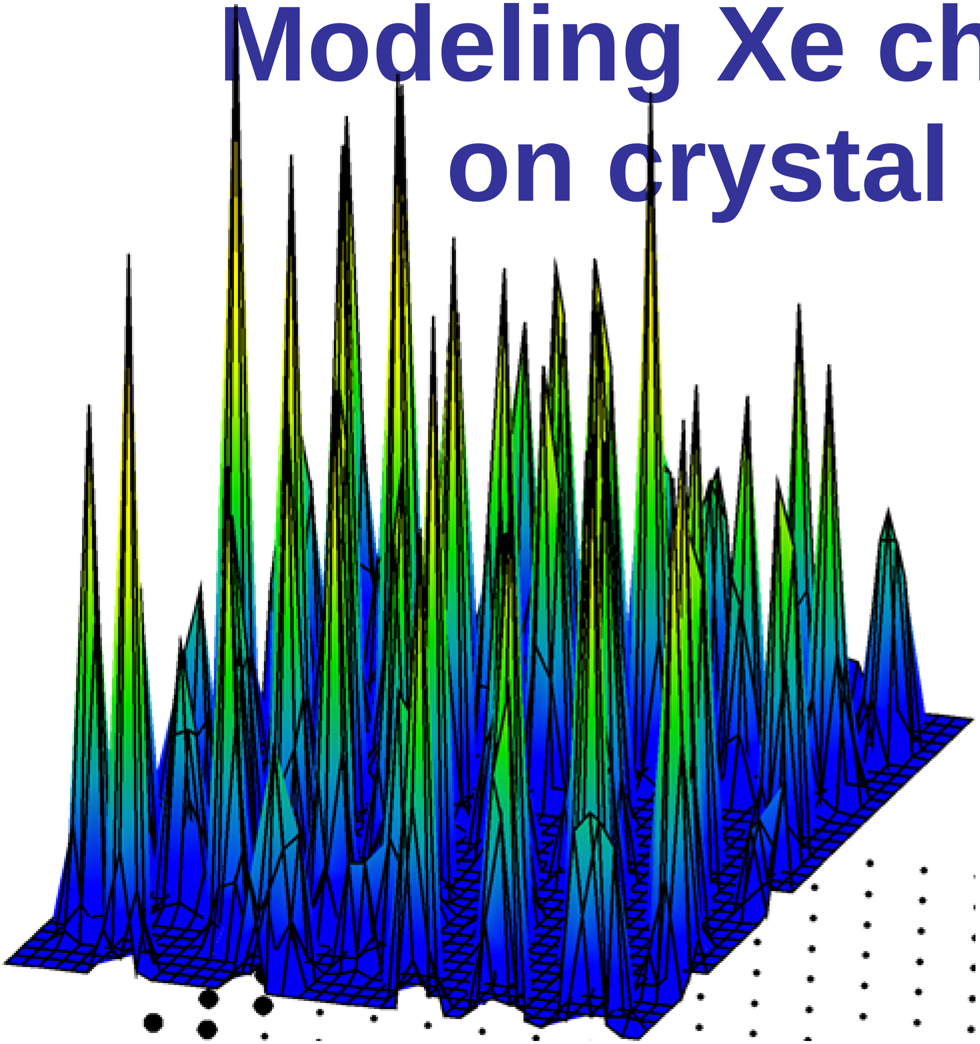
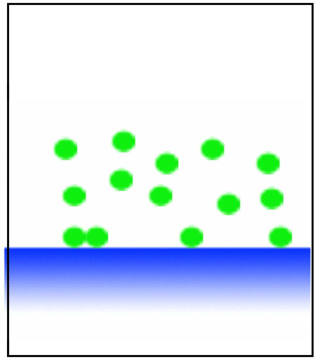
Modeling Xe chemical shifts on crystal surfaces





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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 with which the Xe is in contact**
- **How many neighbor atoms, at what distances**
- **How long the Xe atom stays in contact**

Electronic structure of neighbors with which the Xe is in contact

At the corresponding distances,
ab initio calculations show that
the magnitude of Xe shielding response
drops off with polarizability in the order:

Xe > Kr > Ar > Ne

Xe > C > H

Xe > O > H

For one neighbor atom

Ab initio calculations show the Xe shielding response depends on the distance of the neighbor atom.

A mathematical description of a large number of ab initio values as a function of R(Xe-A) is: (for A = Xe or Kr or Ar or Ne)

$$\sigma_{Xe}\,(r_{Xe\text{-}A}) = a_6 r^{-6} + a_8 r^{-8} + a_{10} r^{-10} + a_{12}\, r^{-12}$$

the shielding response drops off very steeply with distance

How many neighbor atoms, at what distances?

For a single instantaneous configuration, the Xe shielding response is **nearly additive**.

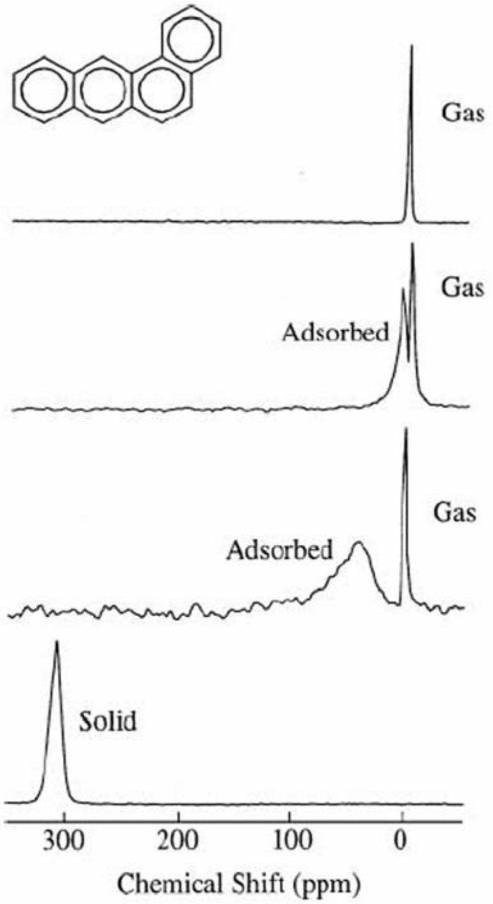
For example, the ab initio Xe shielding for Xe surrounded by some number of Ne atoms (in circles or helices) is found to be nearly the same as the **sum** of the ab initio Xe-Ne shieldings at those Xe-Ne distances

How long the Xe atom stays in contact, i.e., 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 grand canonical Monte Carlo simulation.

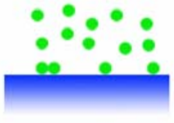
How many neighbor atoms, at what distances?

Example:



dilute Xe gas
large $r_{Xe\text{-}Xe}$,σ(Xe atom)

limiting case
one Xe on crystal
$\sigma(r_{Xe\text{-}C})$, short $r_{Xe\text{-}C}$



occasional Xe-Xe neighbors
$\sigma(r_{Xe\text{-}C})$, short $r_{Xe\text{-}C}$
$+\sigma(r_{Xe\text{-}Xe})$, short $r_{Xe\text{-}Xe}$

many Xe-Xe neighbors
$\sigma(r_{Xe\text{-}C})$, short $r_{Xe\text{-}C}$
$+\sum\sigma(r_{Xe\text{-}Xe})$, short $r_{Xe\text{-}Xe}$

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

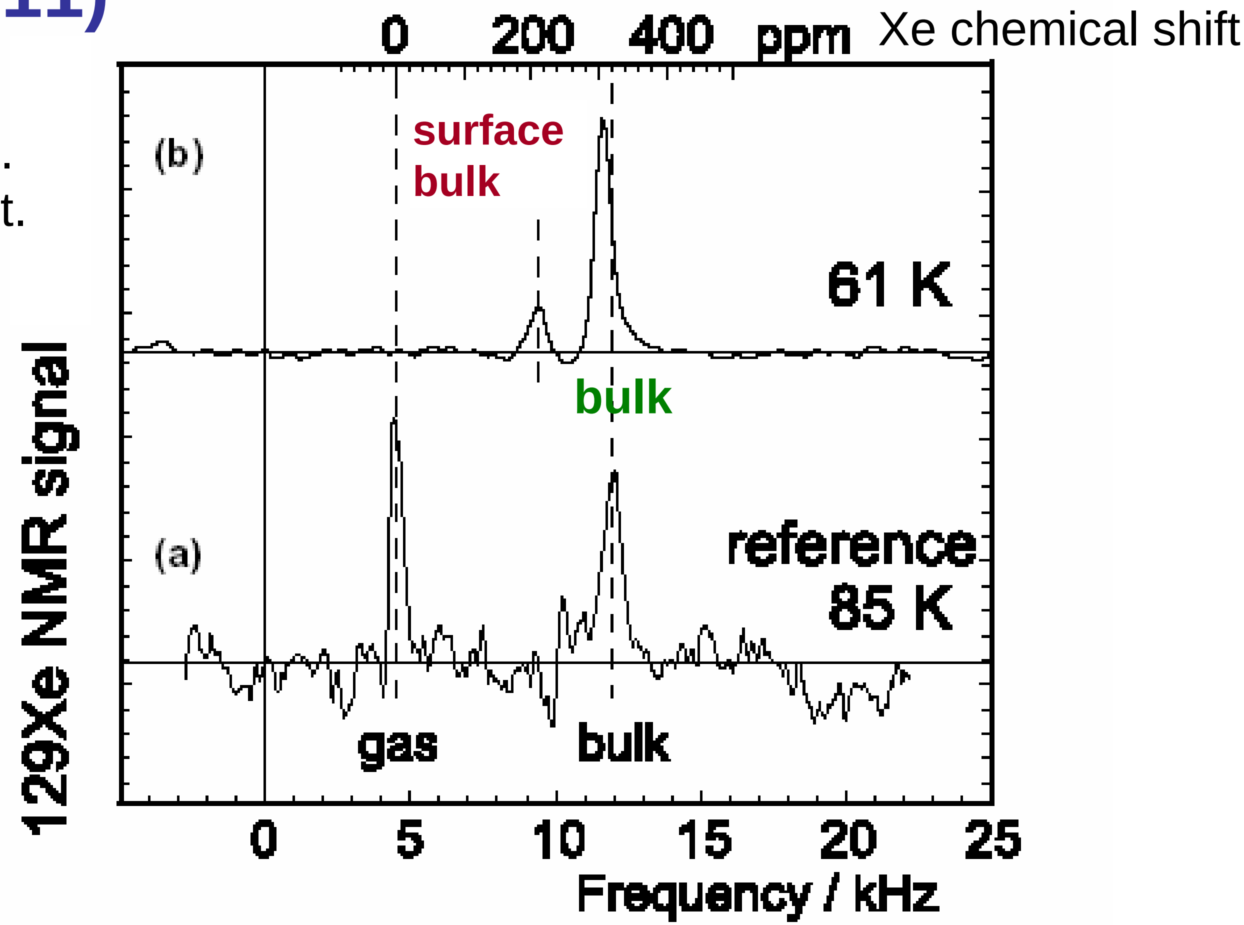
Xe on single crystal surfaces

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

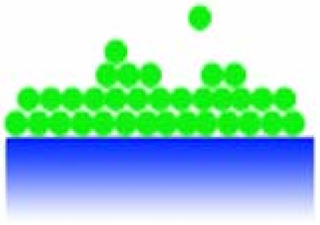
Bulk Xe on the surface of a single crystal metal surface Ir(111)

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

QUALITATIVELY



How many neighbor atoms?

- **Xe atoms on the <u>surface</u> of the bulk Xe appear at 209 ppm**

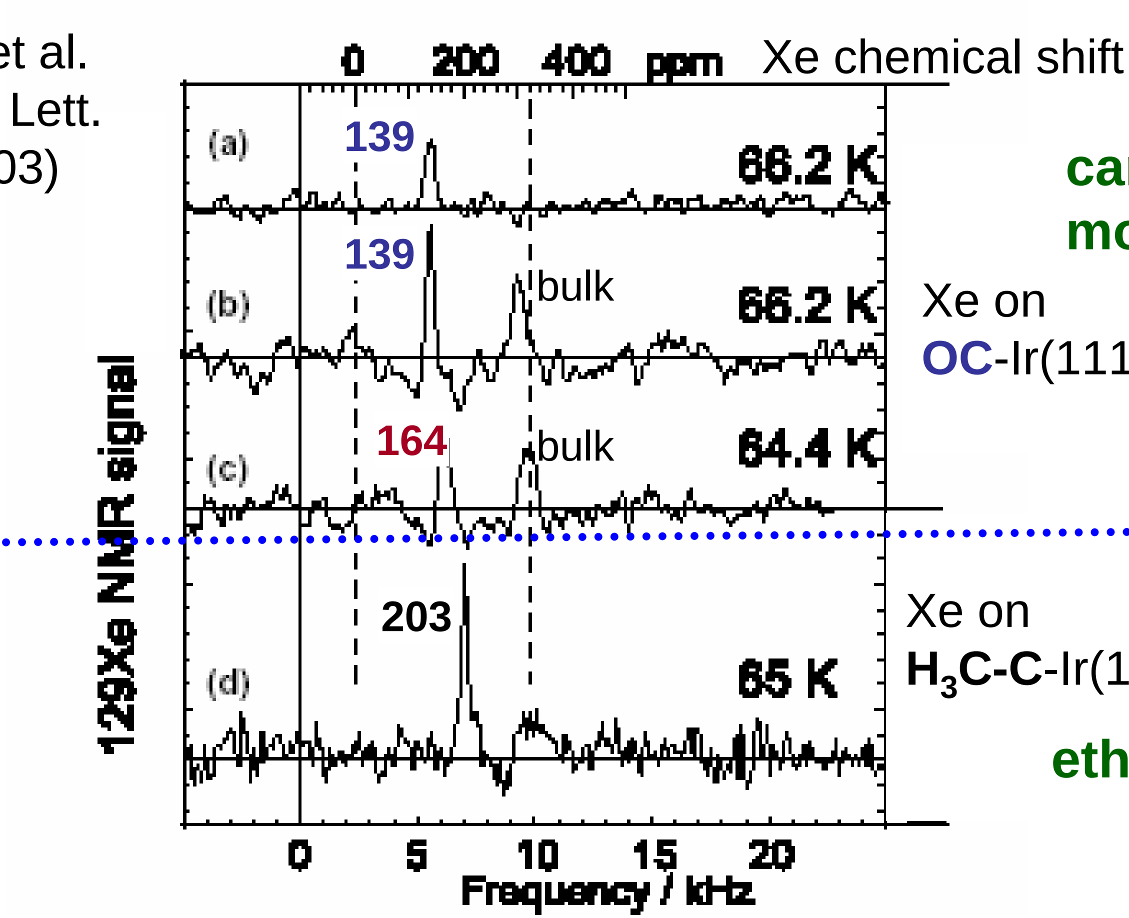
  $\sigma = \sum \sigma(r_{Xe\text{-}Xe})$ nearest (short $r_{Xe\text{-}Xe}$) neighbors are below and in same plane.

- **Xe in the middle of the bulk appear at 321 ppm**

  $\sigma = \sum \sigma(r_{Xe\text{-}Xe})$ nearest neighbors are below, <u>above</u>, and in same plane.

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

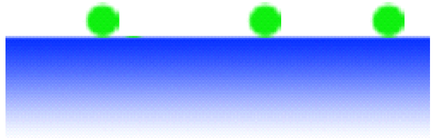
Xe can tell the difference between OC and H_3C-C surfaces.
Xe can tell how many other Xe atoms are on the same surface.

QUALITATIVELY

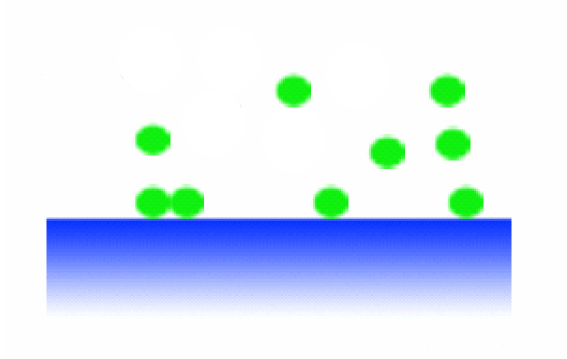
Xe can tell how many other Xe atoms are on the same surface

Xe @OC-Ir(111):

- At low Xe coverage, $\sigma = \sum\sigma(r_{Xe\text{-}O})$ only



- At lower T, larger θ_{Xe}, $\sigma = \sum\sigma(r_{Xe\text{-}O}) + \sum\sigma(r_{XeXe})$ once in a while, Xe runs into other Xe



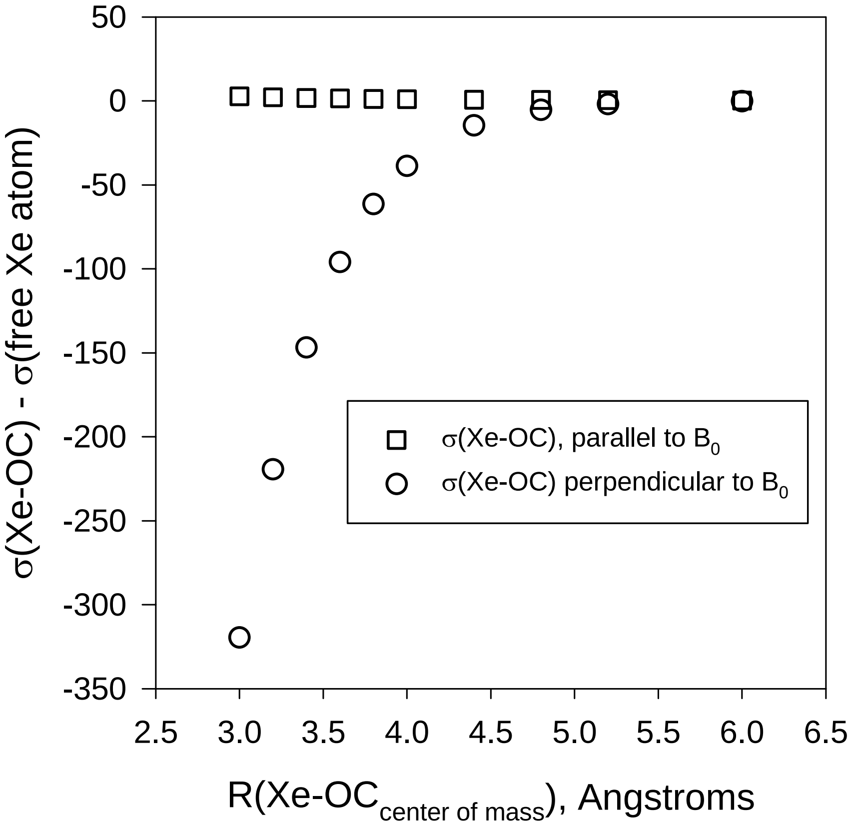
Xe can tell the difference between OC and H_3CC surfaces

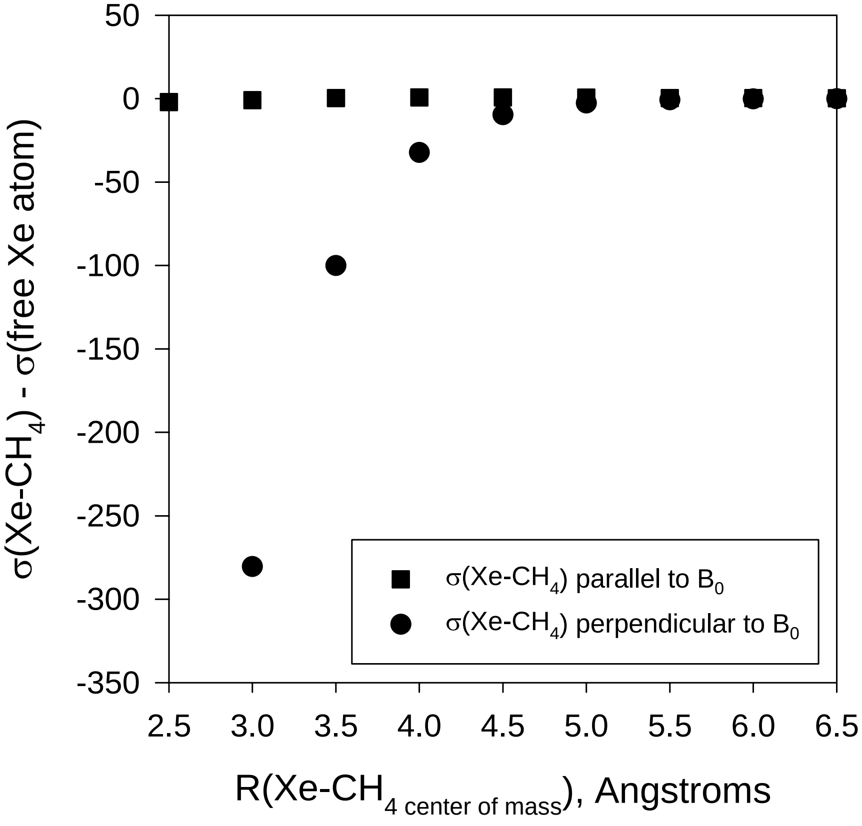
- At low Xe coverage, $\sigma = \sum \sigma(r_{Xe\text{-}O})$
- or $\sigma = \sum \sigma(r_{Xe\text{-}H3C})$
- intrinsic shielding response from Xe-OC is greater than the shielding response from Xe-H_3C at same distance
- however, potential functions permit Xe to stay closer to H_3C than OC, resulting in larger average Xe chemical shifts for the same coverage at the same temperature

Xe SHIELDING RESPONSE

At same Xe-C distance, shielding response from Xe-OC interaction is greater than shielding response from Xe-H_3C

$\sigma(\mathrm{Xe}\cdots\mathrm{OC})$ and $\sigma(\mathrm{Xe}\cdots\mathrm{H_3CH})$, $B_0 \perp$ and $||$



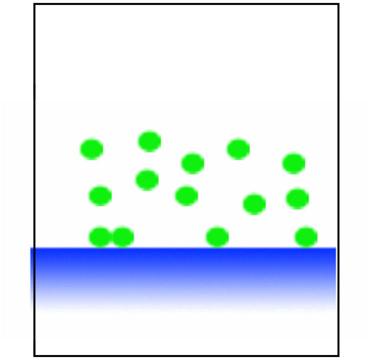


Xe POTENTIAL FUNCTIONS

- Potential functions permit Xe to stay closer in the configuration Xe···H_3CH (r_{min}=4.05 Å, ε/k_B = 282 K) compared to Xe···OC (r_{min}=4.25 Å, ε/k_B = 177 K)
- Xe-Xe pair distribution function determined by r_{min} = 4.36 Å ε/k_B = 282 K

**Shielding response
and interaction potential
both favor larger chemical shifts
for Xe on ethylidyne-
compared to CO-covered surface**

GCMC simulations of Xe on surfaces



Xe on model surfaces
Grand canonical Monte Carlo

- Xe on a –CO monolayer

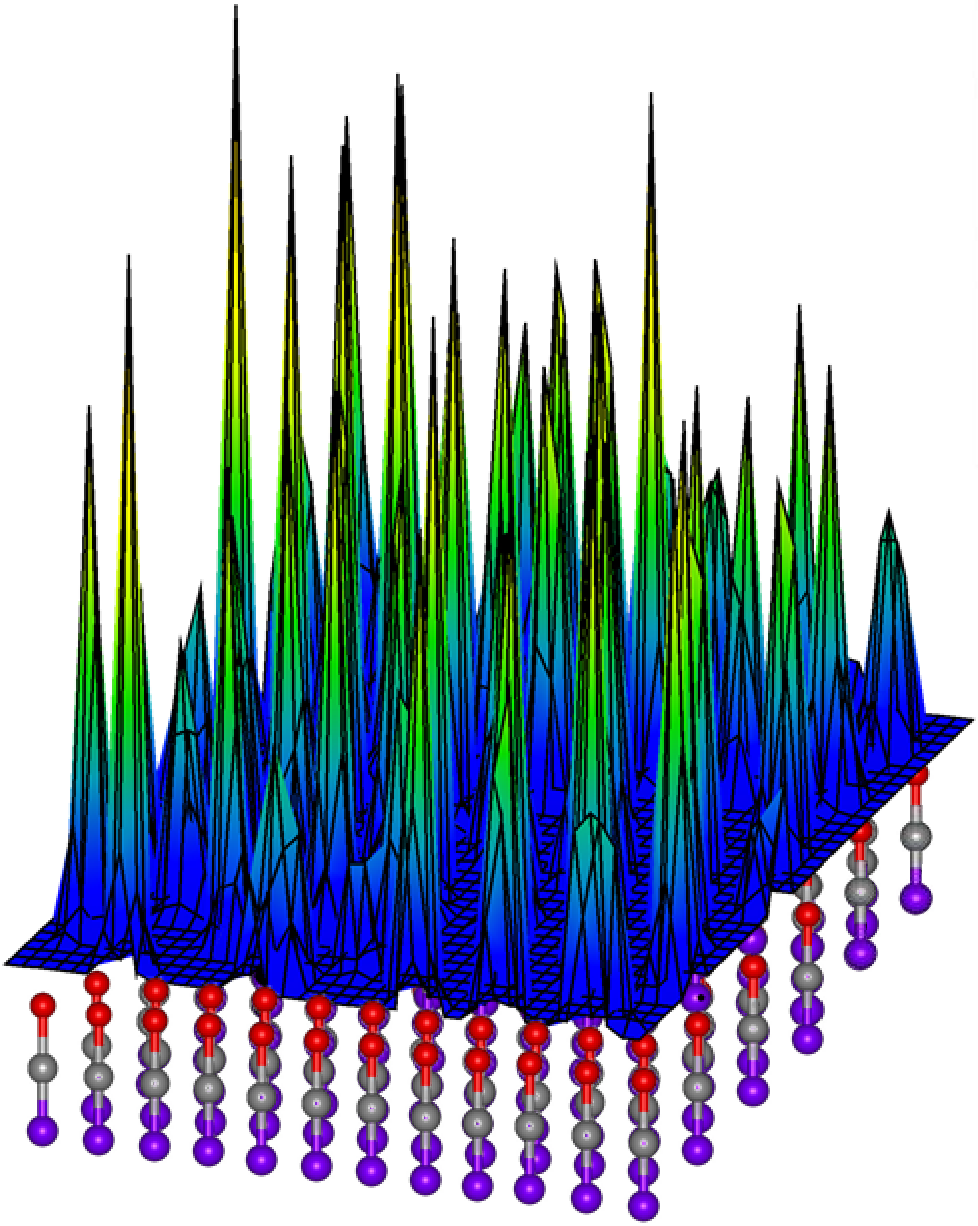
  [using *ab initio* σ(Xe-Xe) and σ(Xe-CO)
  tensor functions]

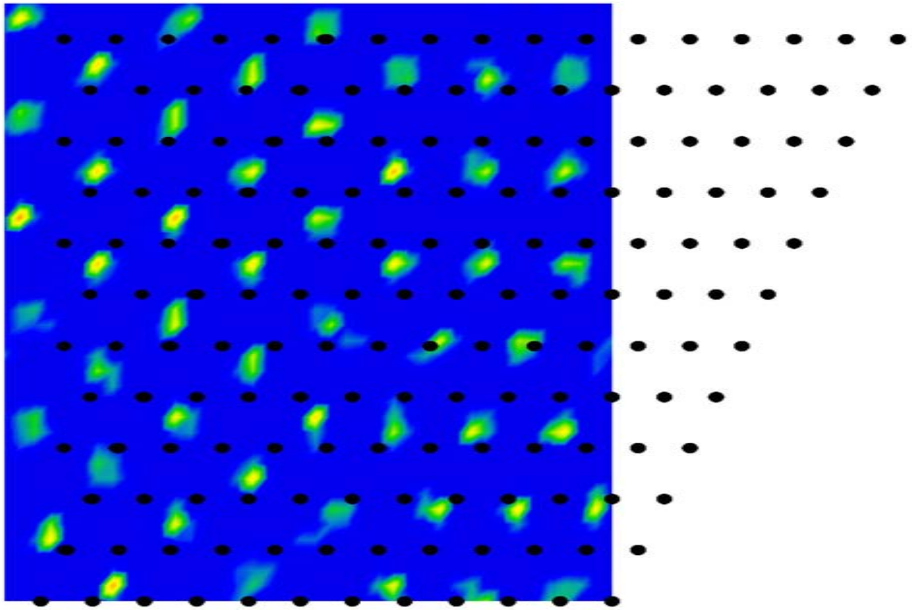
- ^{129}Xe in a xenon sheet

  [using *ab initio* σ(Xe-Xe) tensor function]

Deduce Xe coverage (θ_{Xe})
from observed chemical shift?

PROBABILITY of finding Xe at various locations



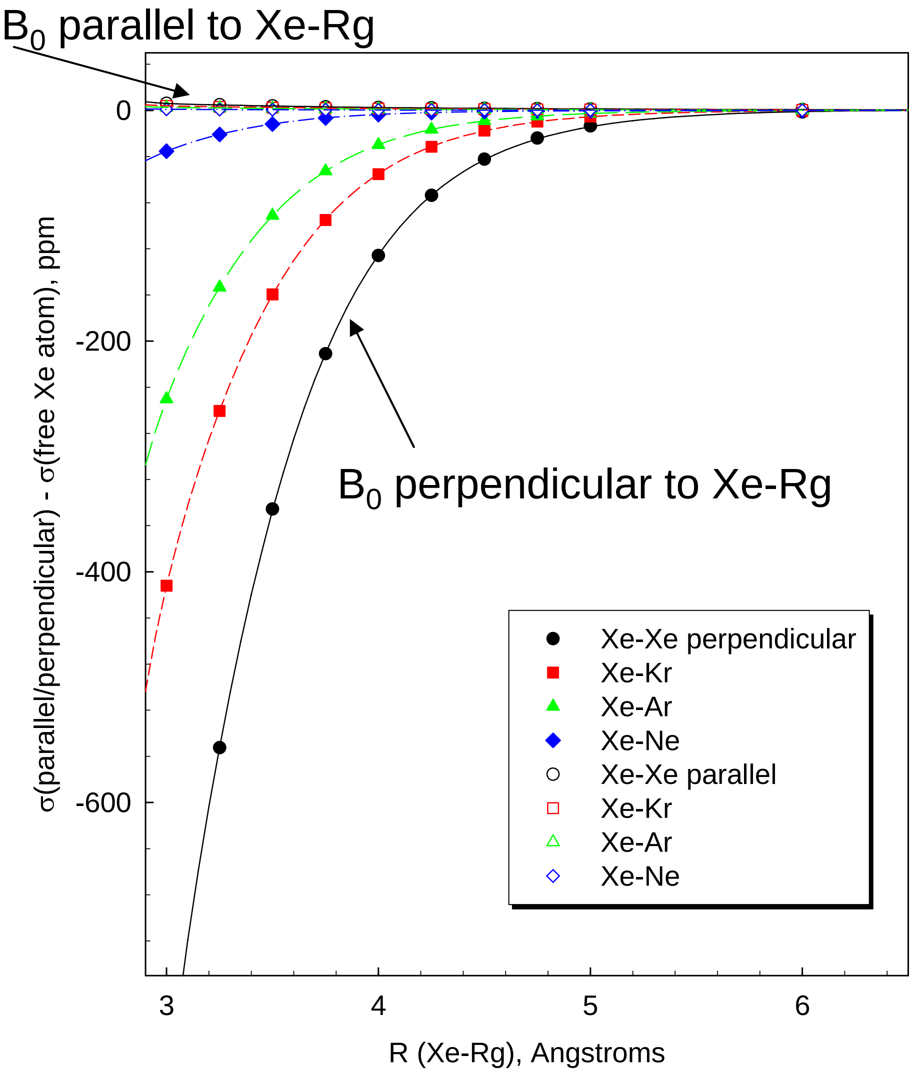


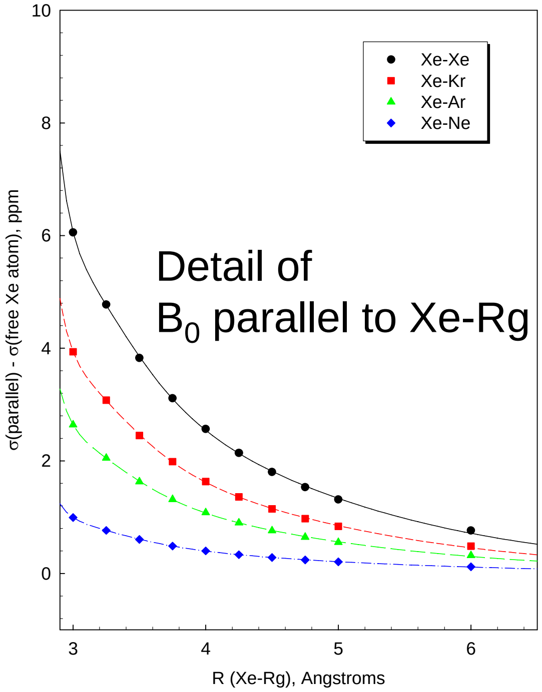
One-body distribution function for Xe@CO monolayer $\theta_r = 1.0$ on Ir(111) from grand canonical Monte Carlo simulations

Jameson, 2003

The Xe SHIELDING RESPONSE

changes with magnetic field direction

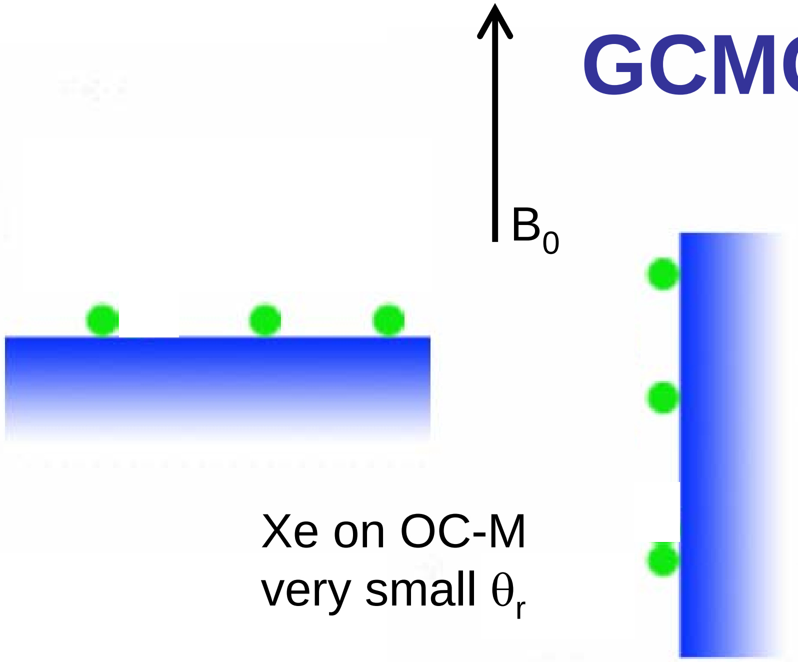




The chemical shift tensor can be mapped out by rotating the single crystal in the magnetic field

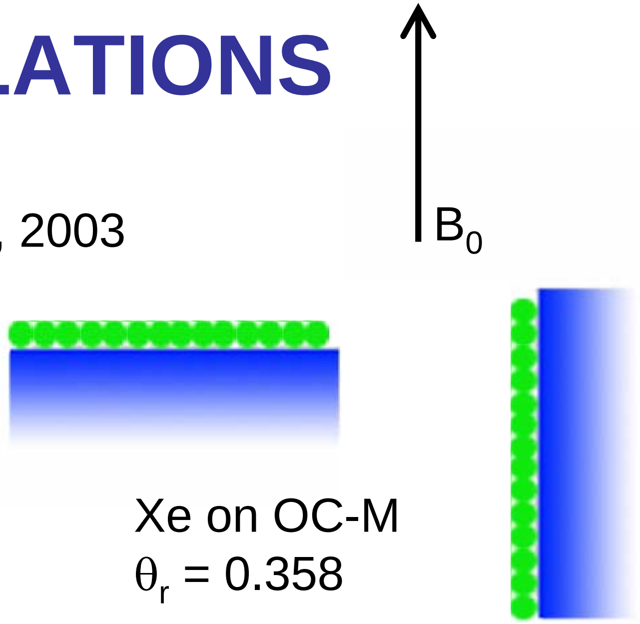
- Our GCMC simulations predict the average Xe chemical shift **tensor**
- Component along the field direction is qualitatively predictable from knowing only the numbers and types of neighbors that Xe has in the plane containing the Xe atom in question and perpendicular to the field direction

GCMC SIMULATIONS

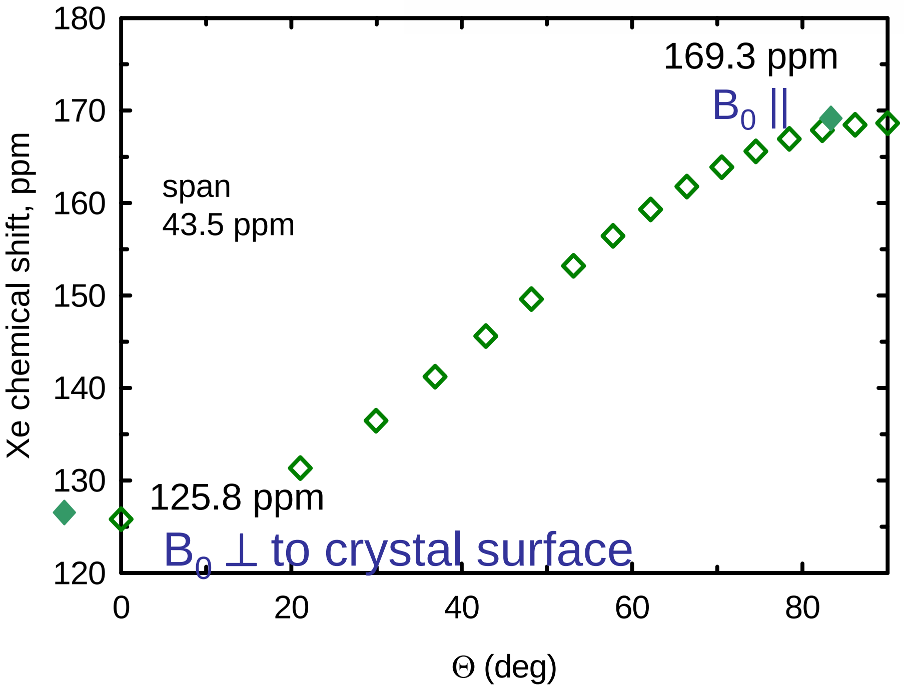


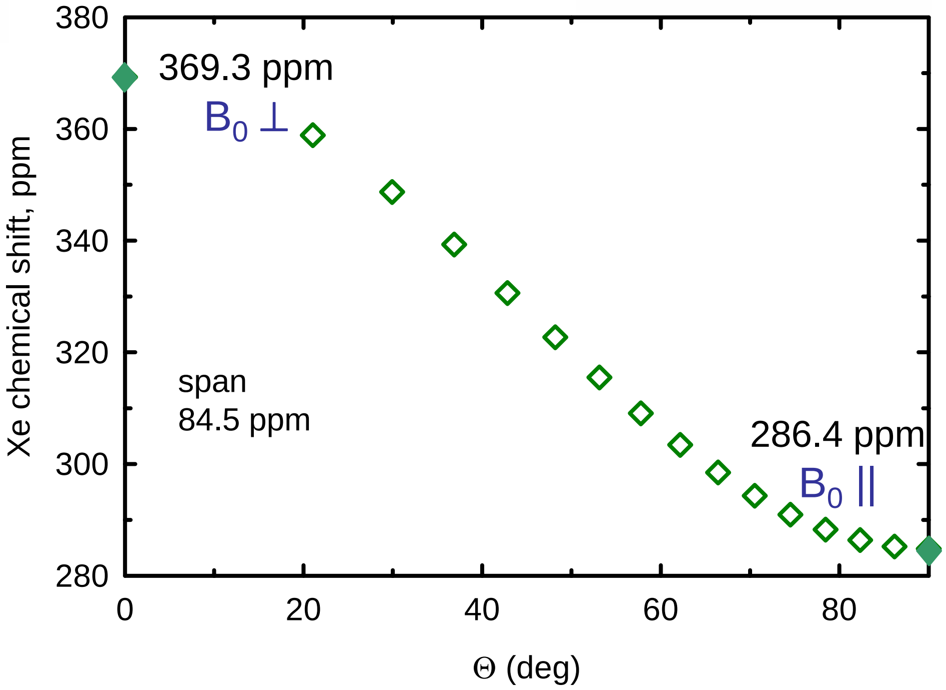
Xe on OC-M
very small θ_r

Jameson, 2003

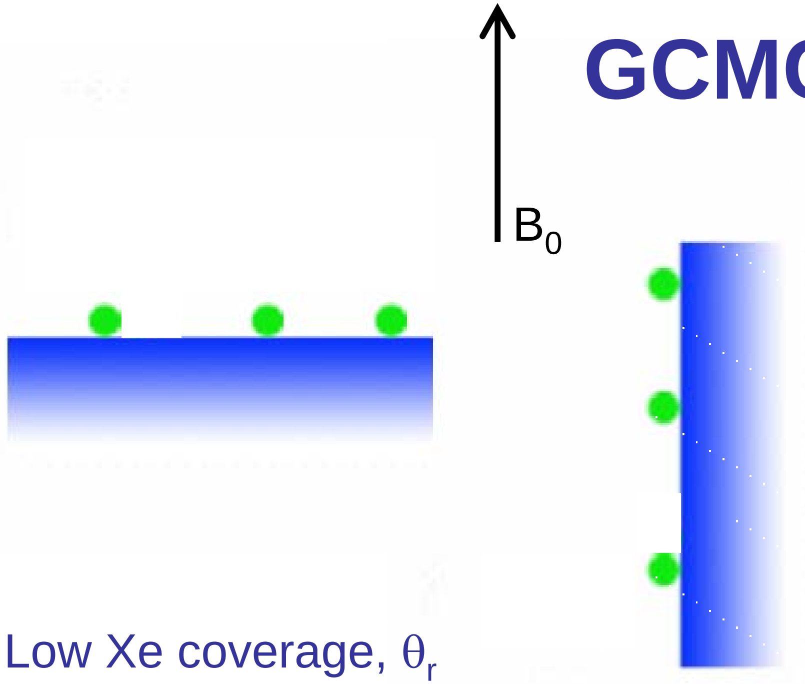


Xe on OC-M
θ_r = 0.358

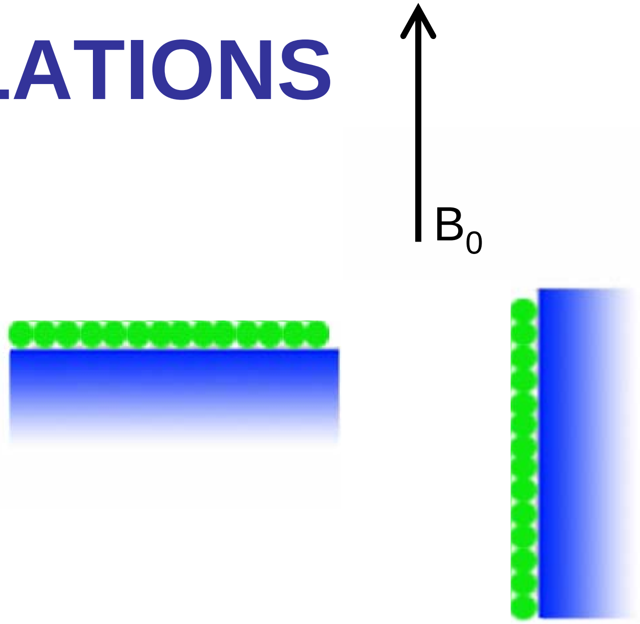




GCMC SIMULATIONS



Low Xe coverage, θ_r



High Xe coverage

Xe chemical shift tensor component	Xe on OC-M very small θ_r
B_0 normal to surface	125.8 ppm
B_0 parallel to surface	169.3, 168.6
span $_{\text{CALCD}}$	43.5

Results
relative to free Xe atom

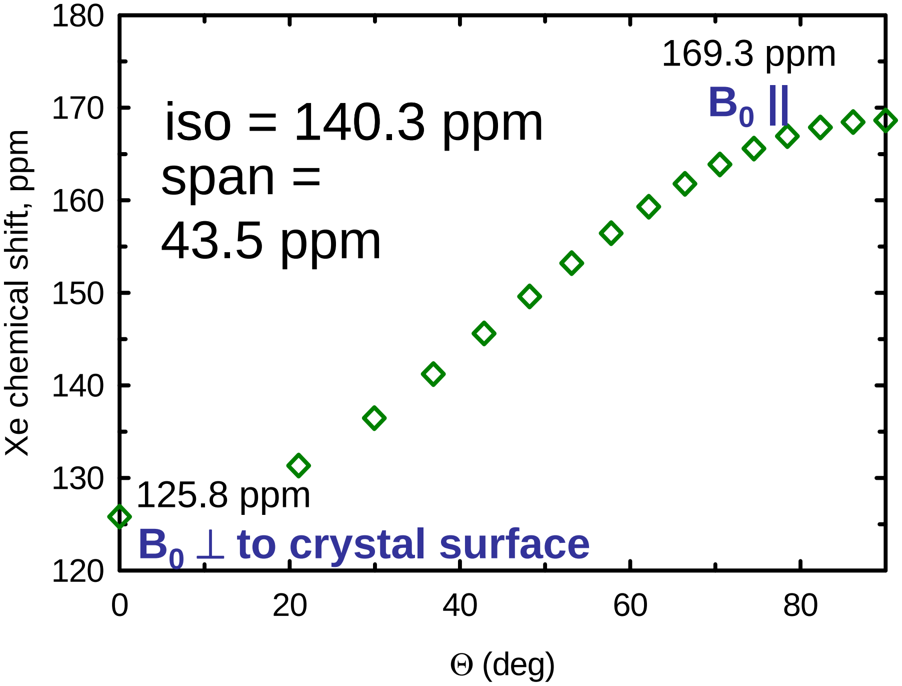
Xe chemical shift tensor component	total chemical shift tensor Xe on OC-M $\theta_r = 0.358$	chemical shift tensor Xe sheet alone
B_0 normal to surface	369.3 ppm	243.5 ppm
B_0 parallel to surface	286.4, 284.8	117.2, 116.2
span $_{\text{CALCD}}$	84.5	127.3

C. J. Jameson, 2003

Comparison with Jänsch's experiments

Xe on OCIr(111)
very small θ_r

GCMC SIMULATIONS



iso = 140.3 ppm
span = 43.5 ppm

169.3 ppm
B_0 ||

125.8 ppm
$B_0 \perp$ to crystal surface

Xe on OCIr(111)
small θ_r

EXPERIMENTS

iso = 165.2 ppm
span = 56.7 ppm

the same angle dependence

References for EXPERIMENTS

- H. J. Jänsch, P. Gerhard, M. Koch and D. Stahl *129Xe chemical shift measurements on a single crystal surface* Chem. Phys. Lett. **372**, 325-330 (2003).
- H. J. Jänsch, P. Gerhard and M. Koch *129Xe on Ir(111) --- NMR Study of Xe on a metal single crystal surface* Proc. Natl. Acad. Sci. PNAS **101**, 13715-13719 (2004).
- M. Koch P. Gerhard and H. J. Jänsch, NMR of 129Xe on CO/Ir(111) and on multilayer Xe/Ir(111), Surface science **600**, 3586-3589 (2006)

CONCLUSIONS

- **Difference between CO and ethylidyne is predictable from isolated Xe-OC, Xe-H_3CH shielding response**

- **Dependence on crystal orientation in the field is reproduced.** For sample geometry, the dominant Xe dimer is, respectively, perpendicular (Xe-O) or parallel (Xe-Xe) to the crystal surface

- **Can deduce Xe coverage from chemical shift**, very sensitive because each Xe-Xe contribution larger than Xe-OC or Xe-H_3C

GENERAL CONCLUSIONS

- The Xe NMR chemical shift is exquisitely sensitive 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.

ACKNOWLEDGMENT

This work was inspired by the elegant and exceedingly difficult series of experiments by Heinz J. Jaensch and his group in University of Marburg.