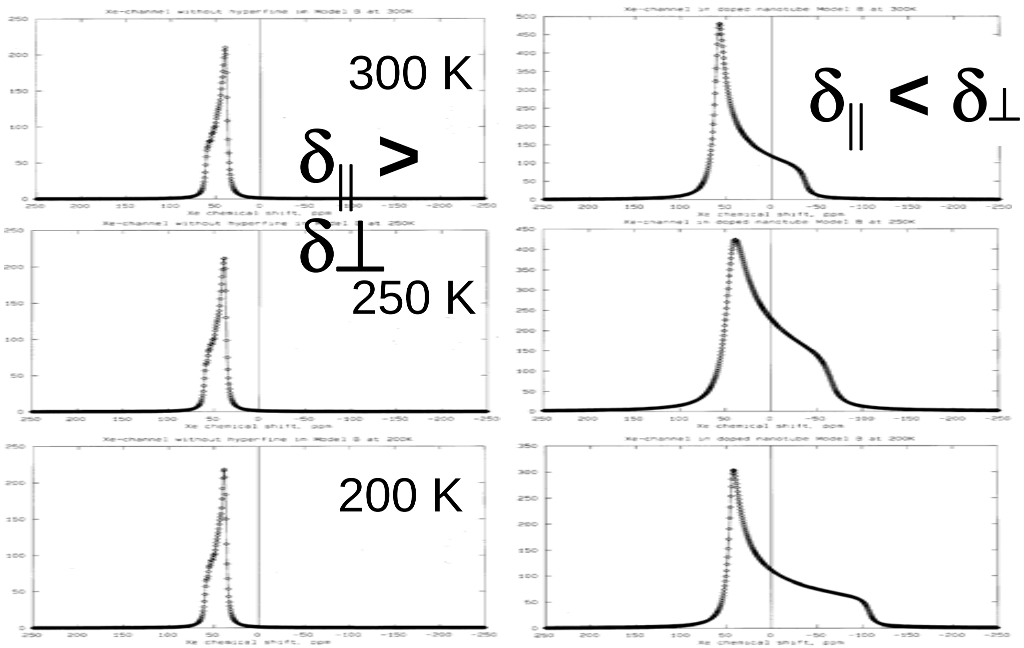
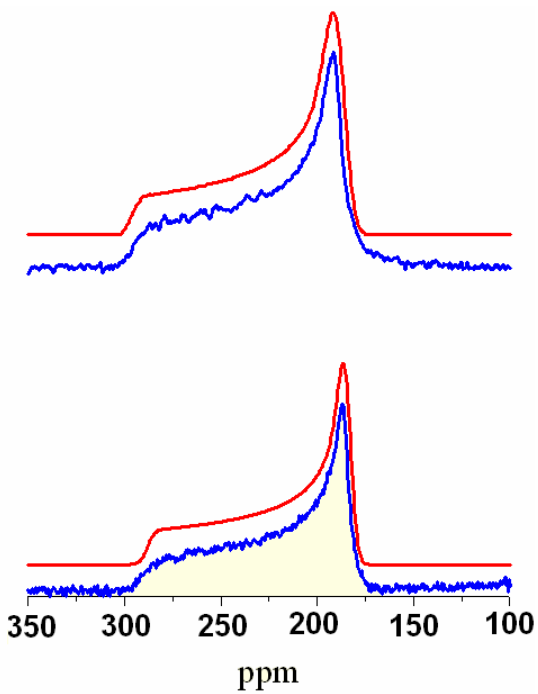
Xe NMR line shapes in channels decorated with paramagnetic centers

Devin N. Sears Lela Vukovic Cynthia J. Jameson



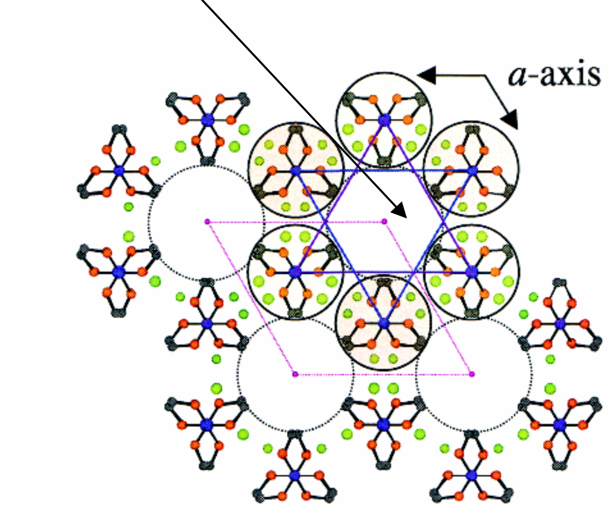
ENC 2006

Xe as a probe of porous materials with paramagnetic centers?



Wasylishen,XEMAT2003

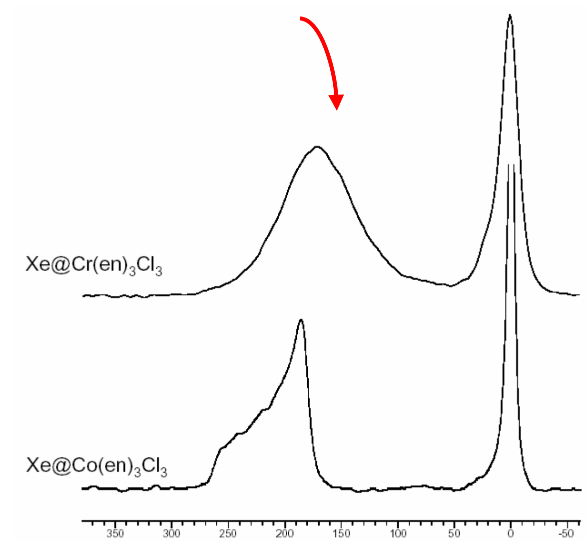
Xe inside these channels



same crystal structure

Ueda et al.
J.Phys. Chem. B 107, 180 (2003)

1000 scans using ~10% hyperpolarized xenon gas



Sears, Wasylishen,
Pacifichem 2005

[**Rh**](en)$_3$]Cl$_3$ crystal
[**Co**](en)$_3$]Cl$_3$ crystal
diamagnetic

[**Cr**(en)$_3$]Cl$_3$ crystal
paramagnetic

Xe can tell the difference!

METHODOLOGY:

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:
   Grand Canonical Monte Carlo

5. **Simulations produce:**
   Xe one-body distributions: where does Xe spend time?
   Average isotropic Xe chemical shift
   Xe line shapes characterizing Xe chemical shift tensor
   Xe distribution among cages or phases

THE MODEL

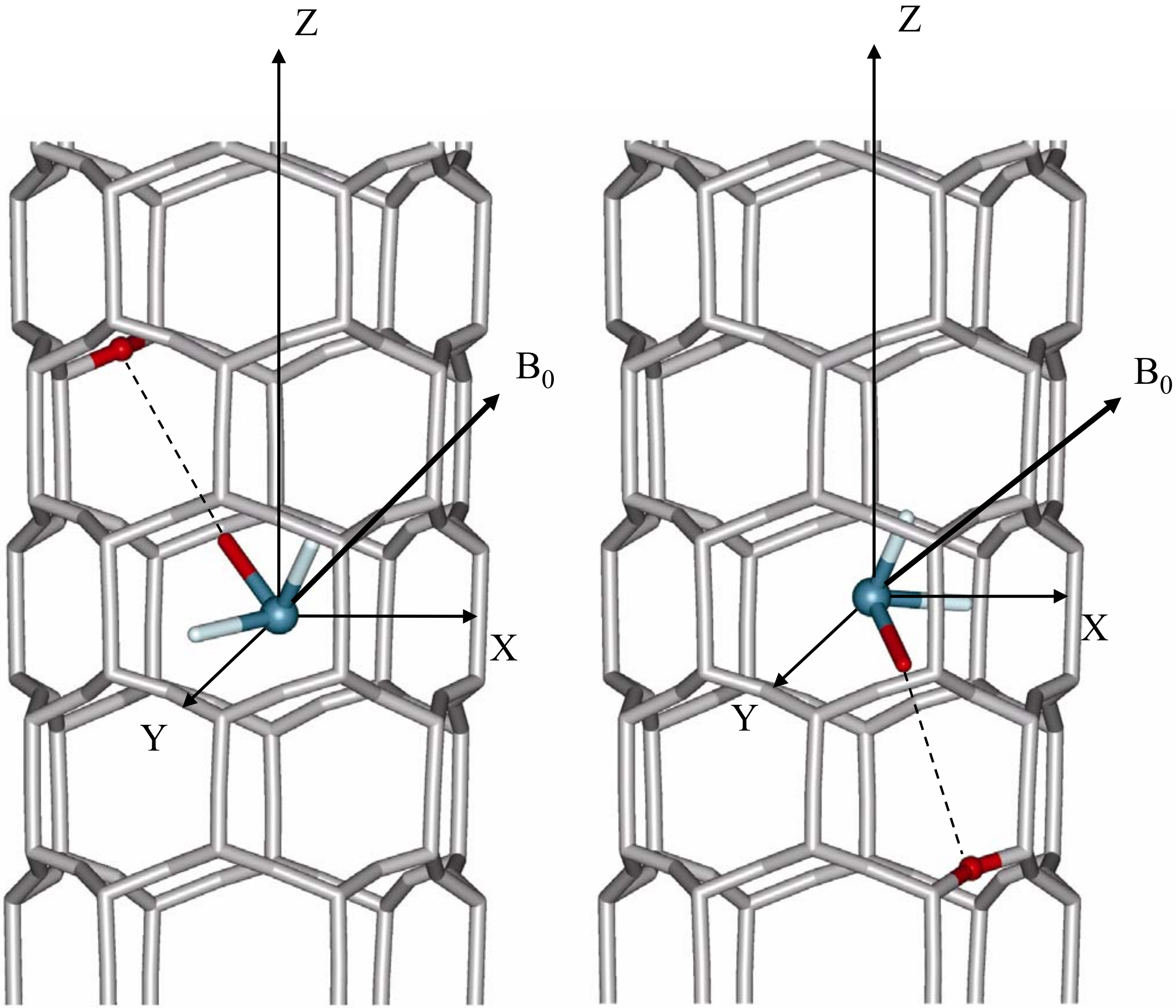
- **carbon nanotube as the channel**: constant surface density of channel atoms and constant structure (corrugation) of channel wall
- **O_2 molecule paramagnetic centers**: choose orientation either parallel or perpendicular to axis of channel
- vary concentration of paramagnetic centers
- vary distribution of paramagnetic centers
- vary diameter of channel (vary average Xe distance to paramagnetic center)

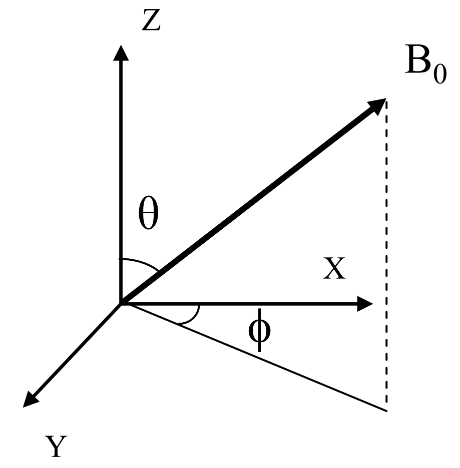
Xe shielding tensor in a channel in an external magnetic field (B_0) along direction (θ,ϕ):

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

one Xe tensor from interaction with ALL channel atoms

Lineshapes by grand canonical Monte Carlo



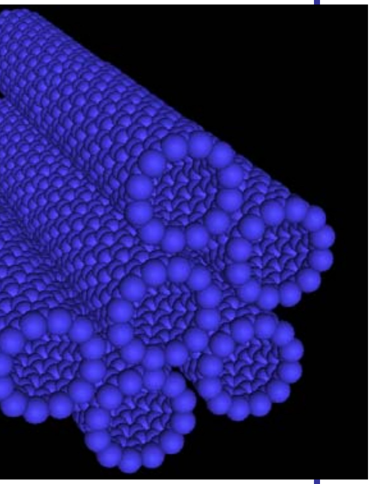


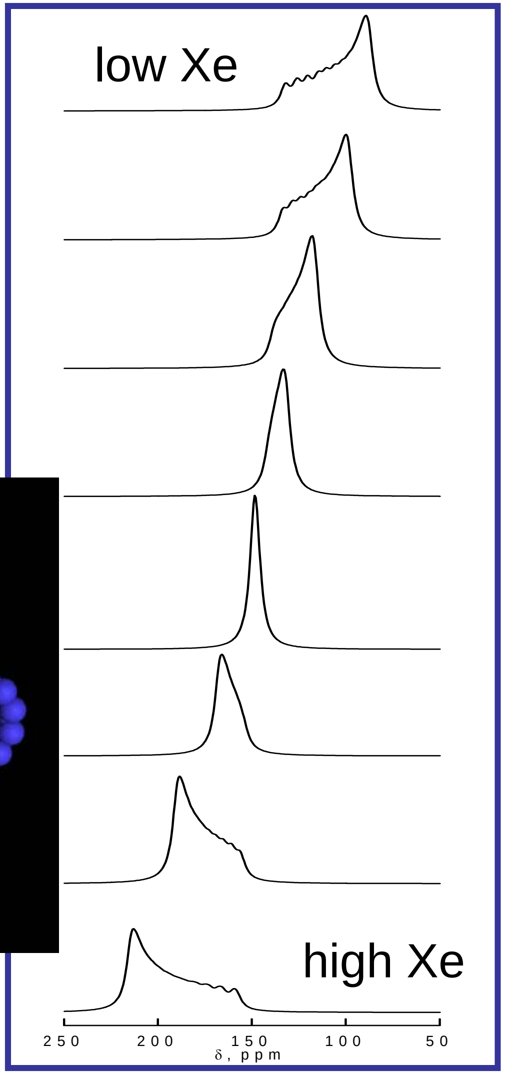
Random orientation of crystallites:
Probability that B_0 lies in any infinitesimal solid angle is
$d\zeta\ d\phi\ /\ 4\pi$, where
$\zeta = (-\cos\theta)$
Equal areas in $\zeta\phi$ plane correspond to equal probabilities

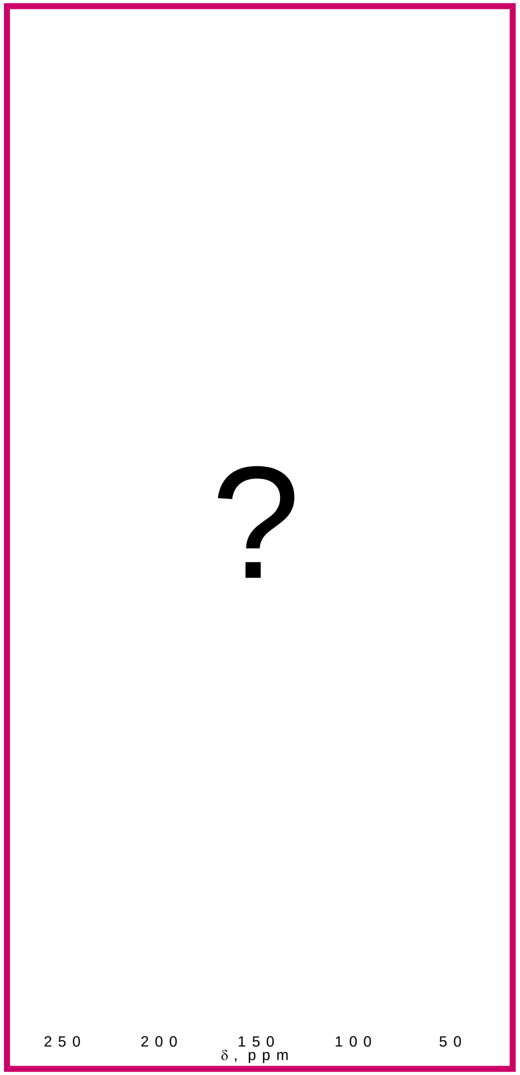
Consider one Xe-C at a time
(and one Xe-Xe at a time)

Xe in channels decorated with paramagnetic centers

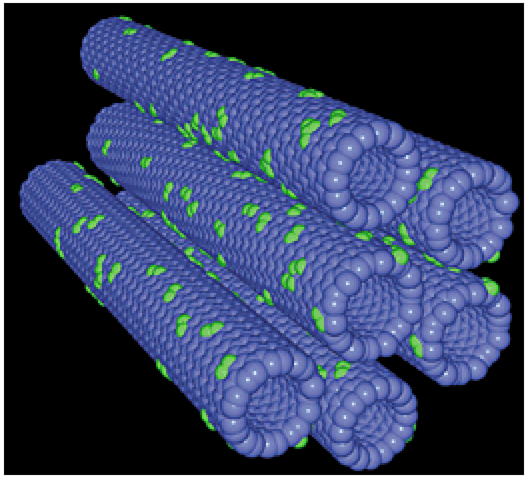
Xe in carbon nanotube channels







Xe in carbon nanotubes decorated with paramagnetic centers

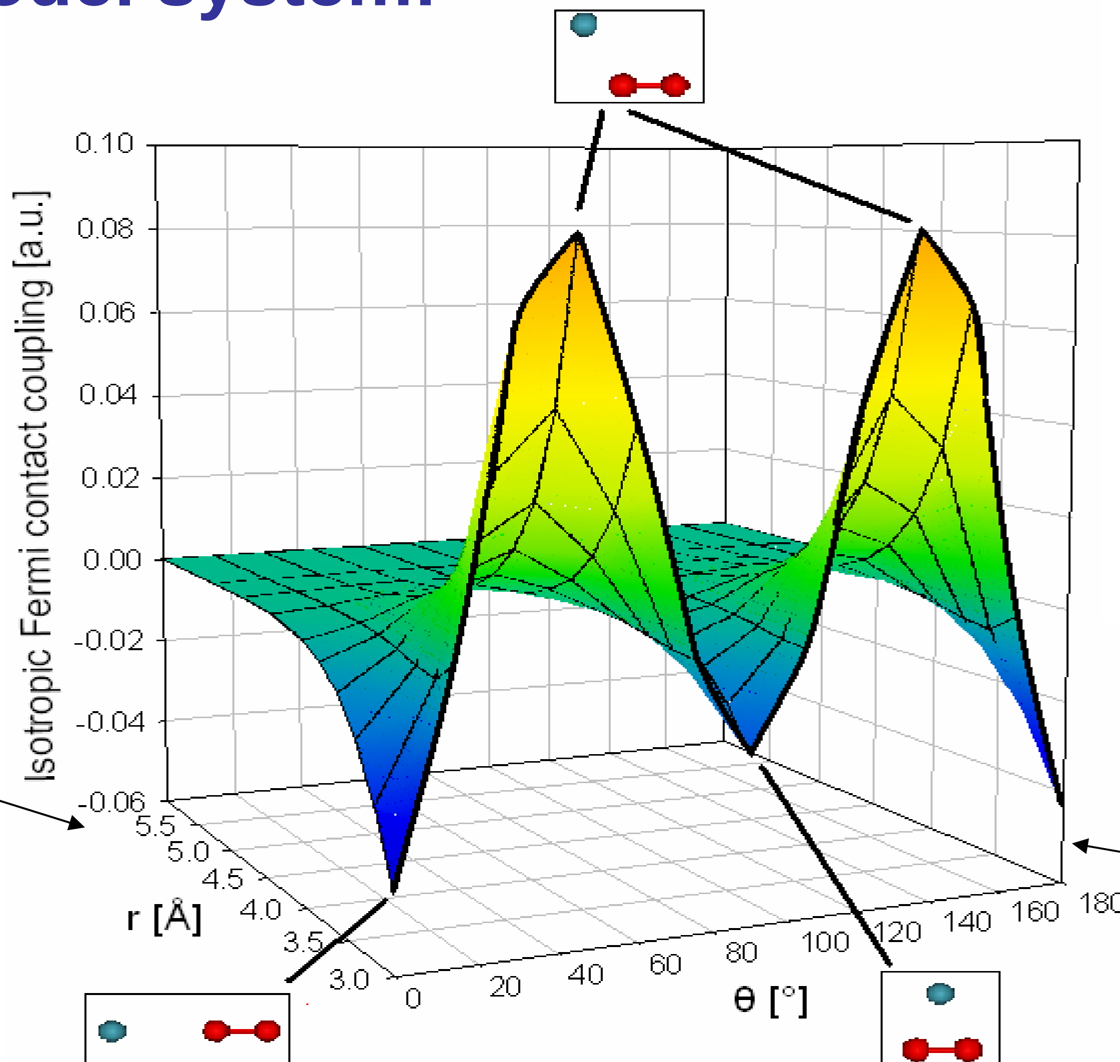


● O ● C

Study Xe in the presence of a paramagnetic center

Our model system:

$Xe@O_2$

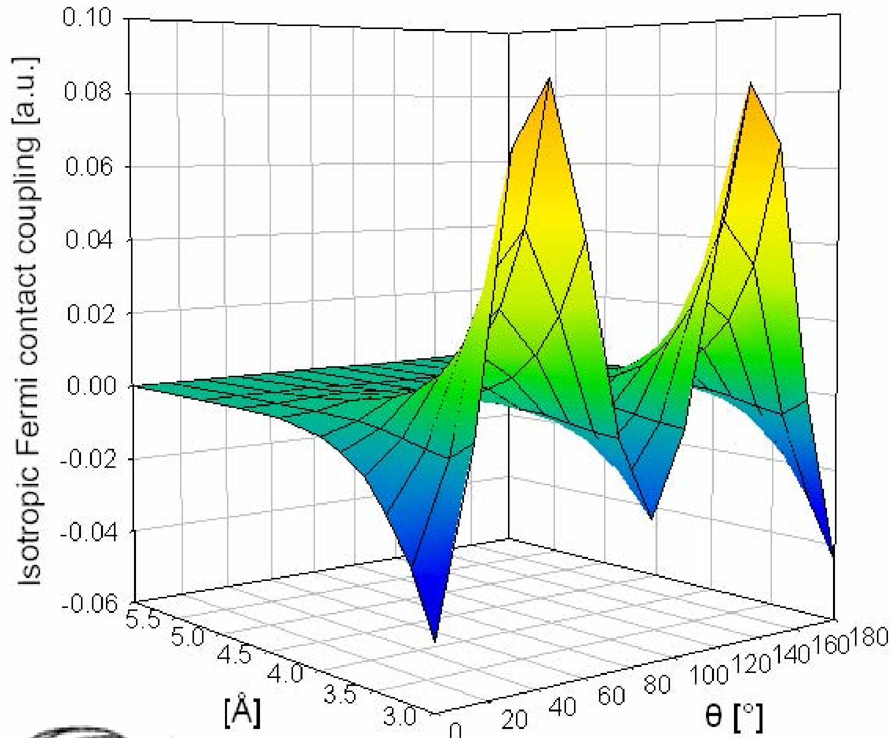


Isotropic part of the hyperfine tensor

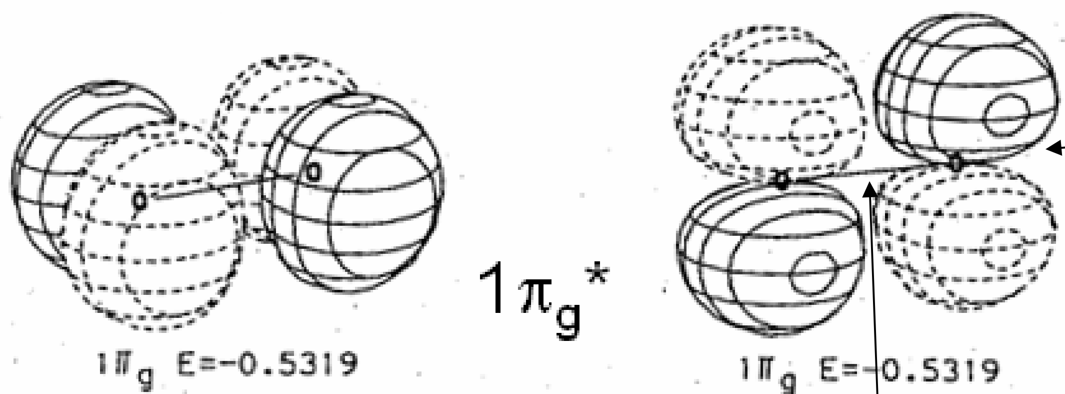
Xe can tell **how far away** **is the paramagnetic center and** **how it is oriented** **relative to the Xe position in the magnetic field!**

Lela Vukovic

Why the angle dependence?



Simple picture: Unpaired electron spins reside, one apiece, in the $1\pi_g{}^*$ molecular orbital of O_2:



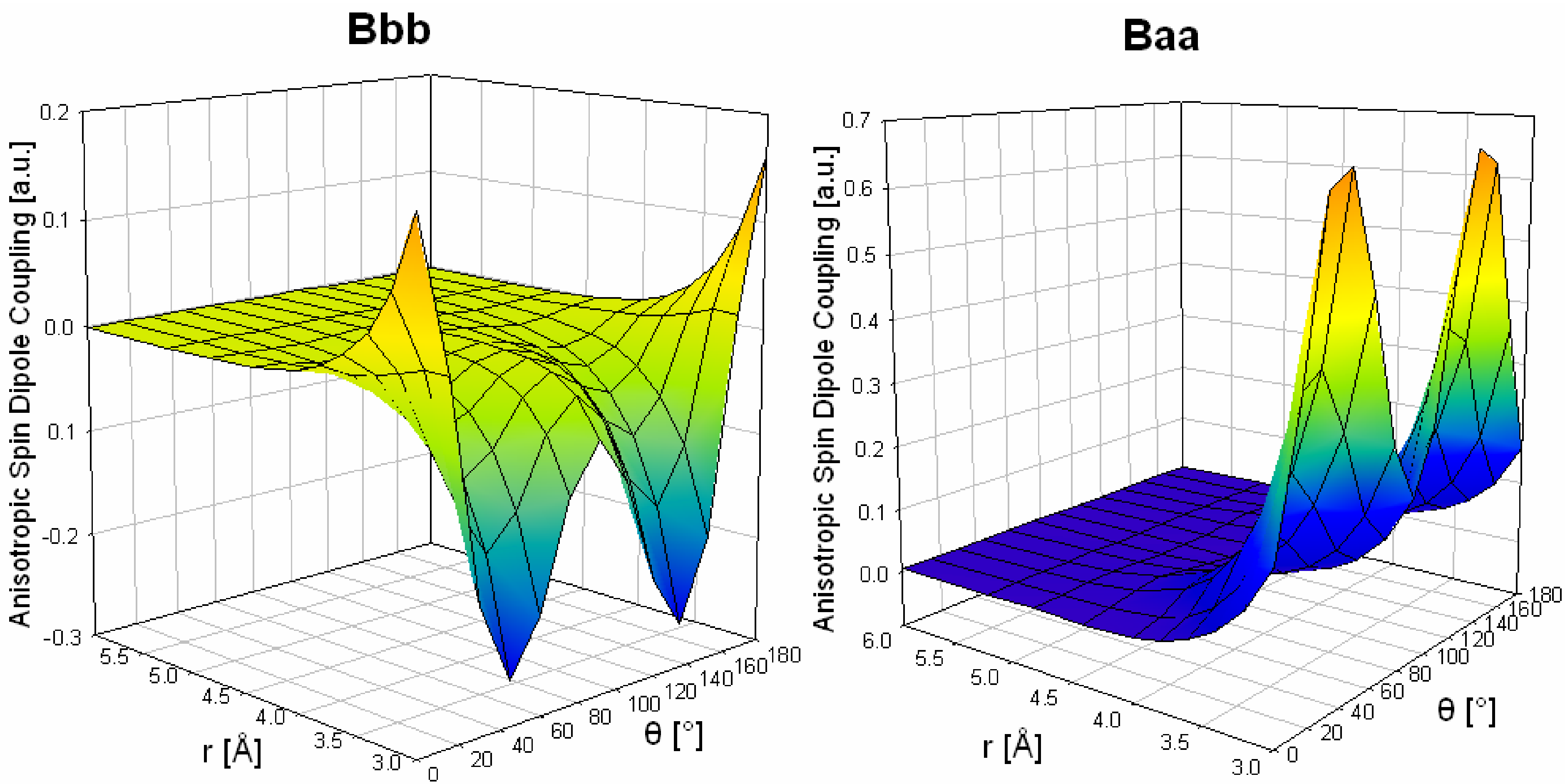
Xe (θ=0º)

At 0º and 90º the Xe encounters nodes of this O_2 molecular orbital where the spin density is nil

BEST at 45º !!

Xe (θ=90º)

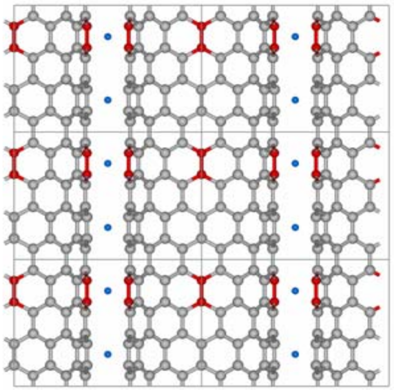
The dipolar part of the hyperfine tensor:



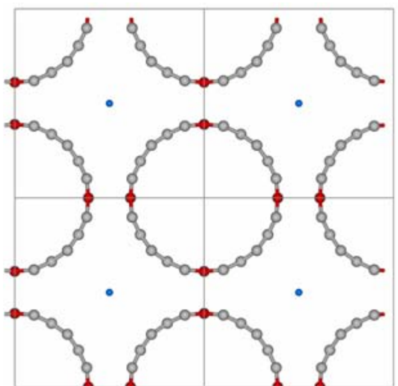
Two of the principal components of the traceless tensor. **The dipolar part is relevant to line shape of Xe in channels with paramagnetic centers.**

the models

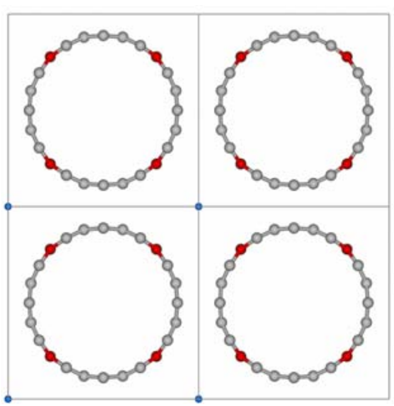
A



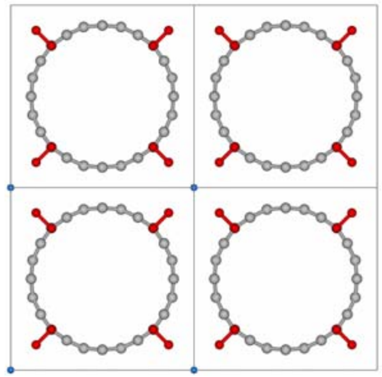
A



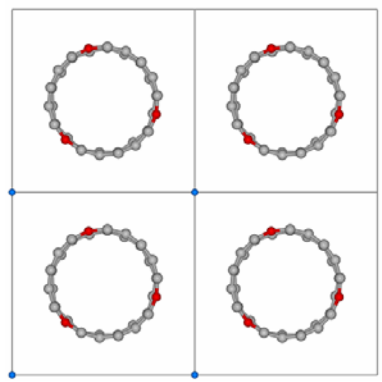
B



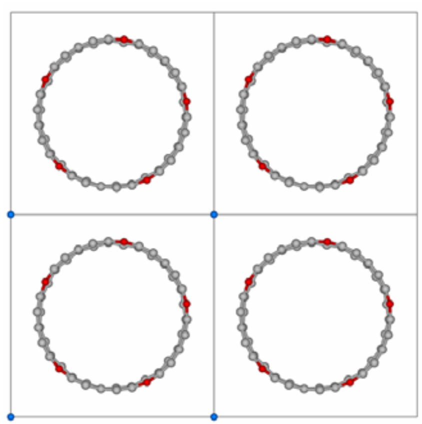
C



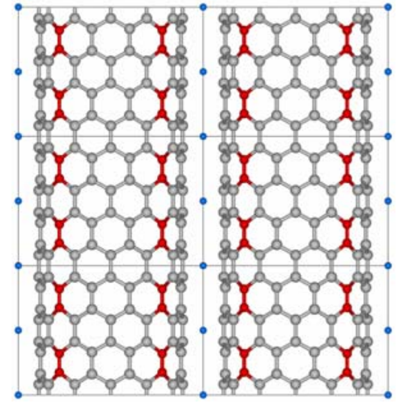
D



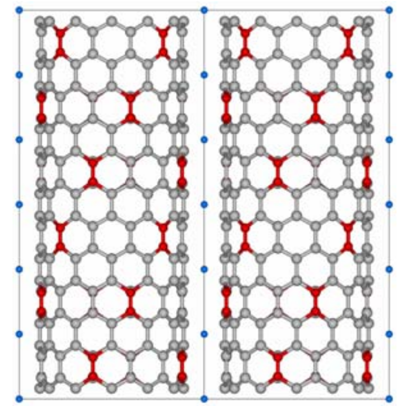
H



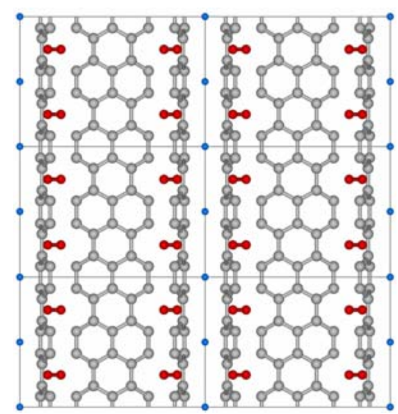
E



F

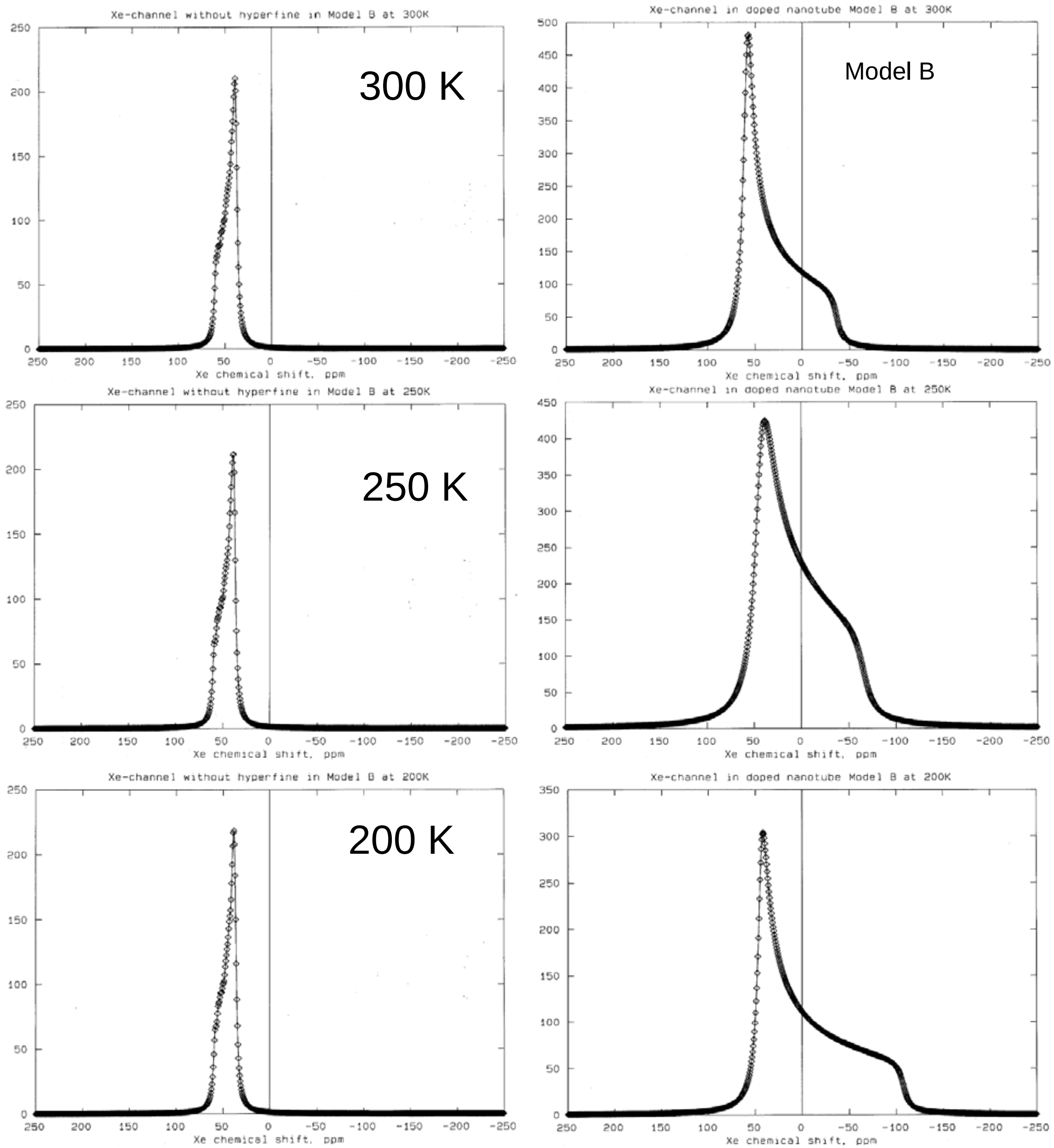


G



$\delta_{\parallel} > \delta_{\perp}$

Xe in Ne nano tube



$\delta_{\parallel} < \delta_{\perp}$

Xe in Ne nano tube **doped with O_2**

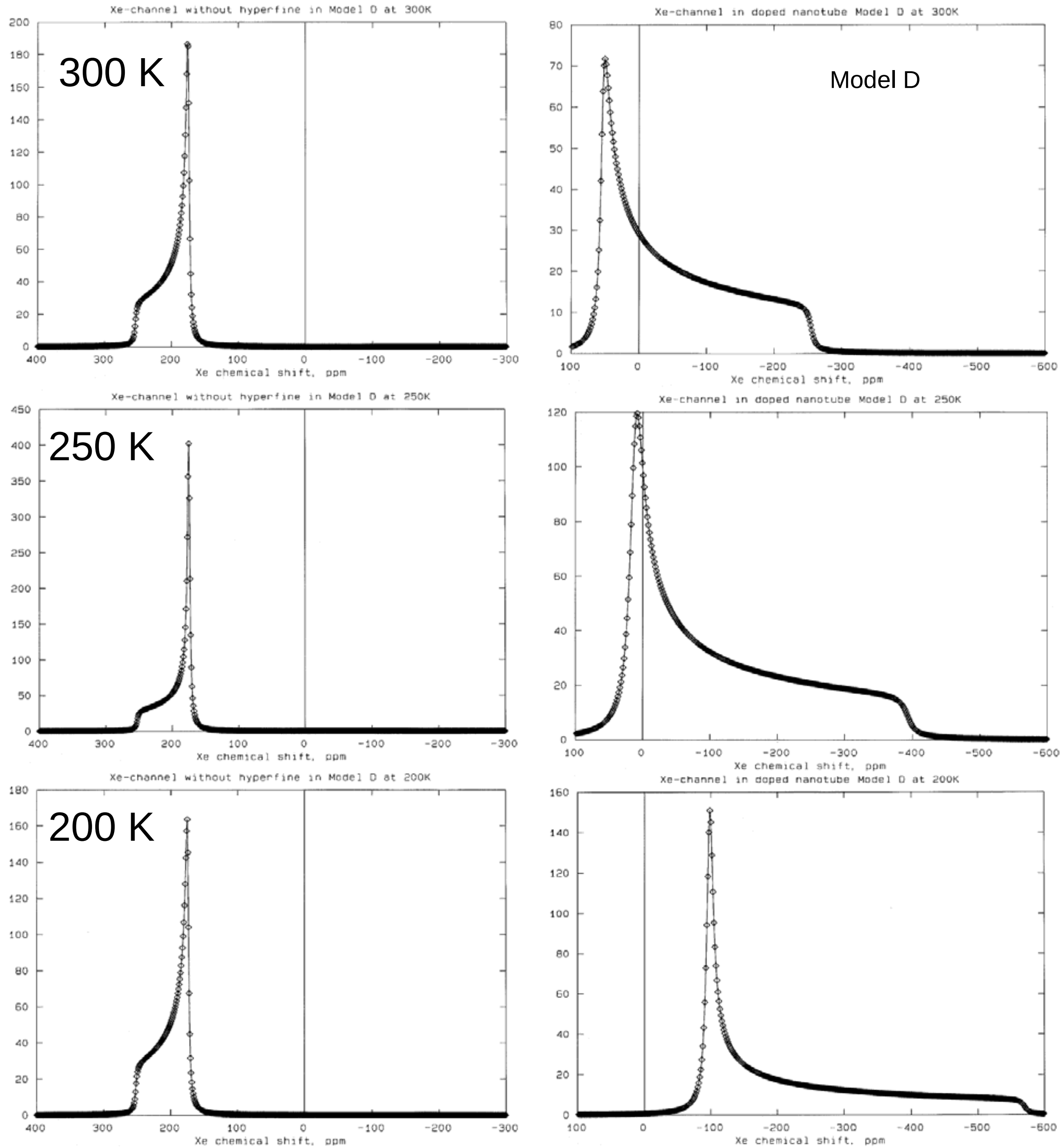
Model B

Note the change in sign of anisotropy of Xe chemical shift tensor!

Note the change with T !

Model D

Xe in
Ne
nano
tube

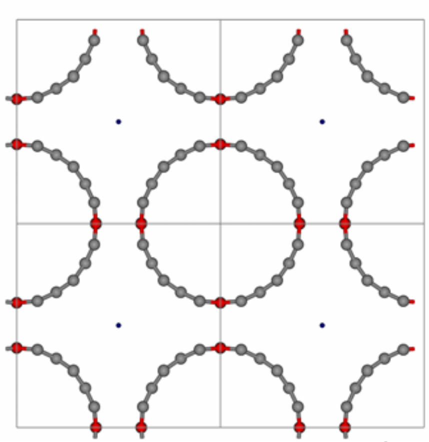


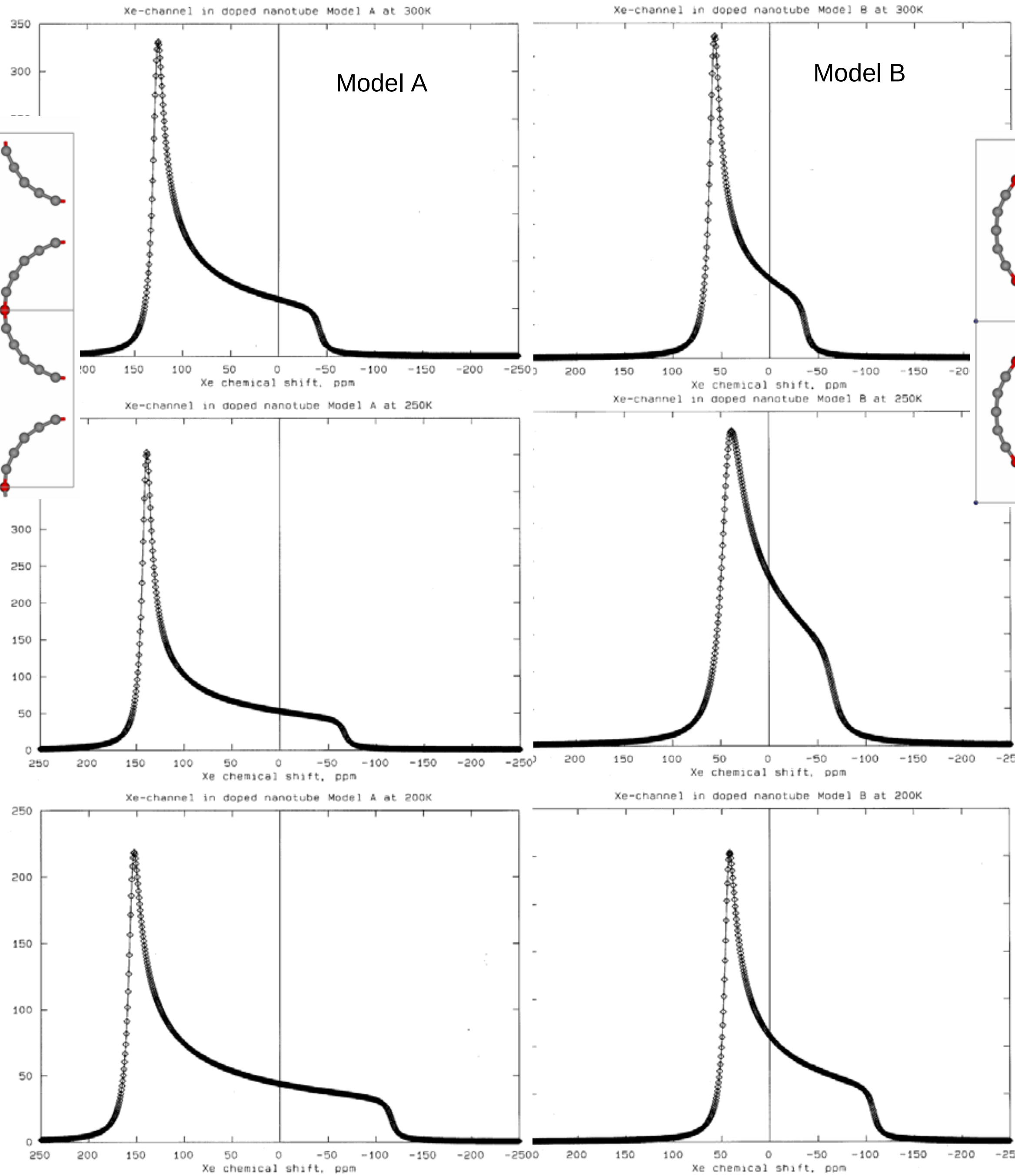
Xe
in Ne
nano
tube

**doped
with
O_2**

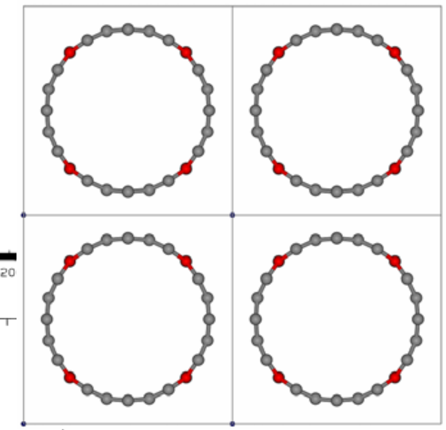
**NOTE the
change
in sign of
anisotropy
of Xe
chemical
shift
tensor**

Model A





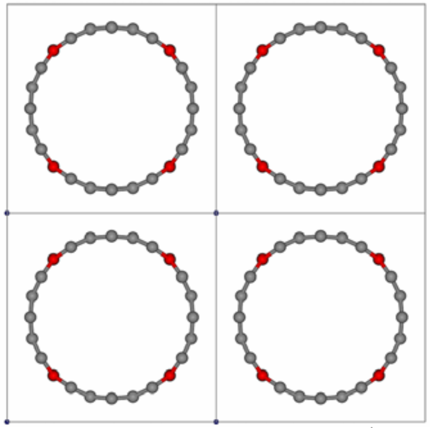
Model B



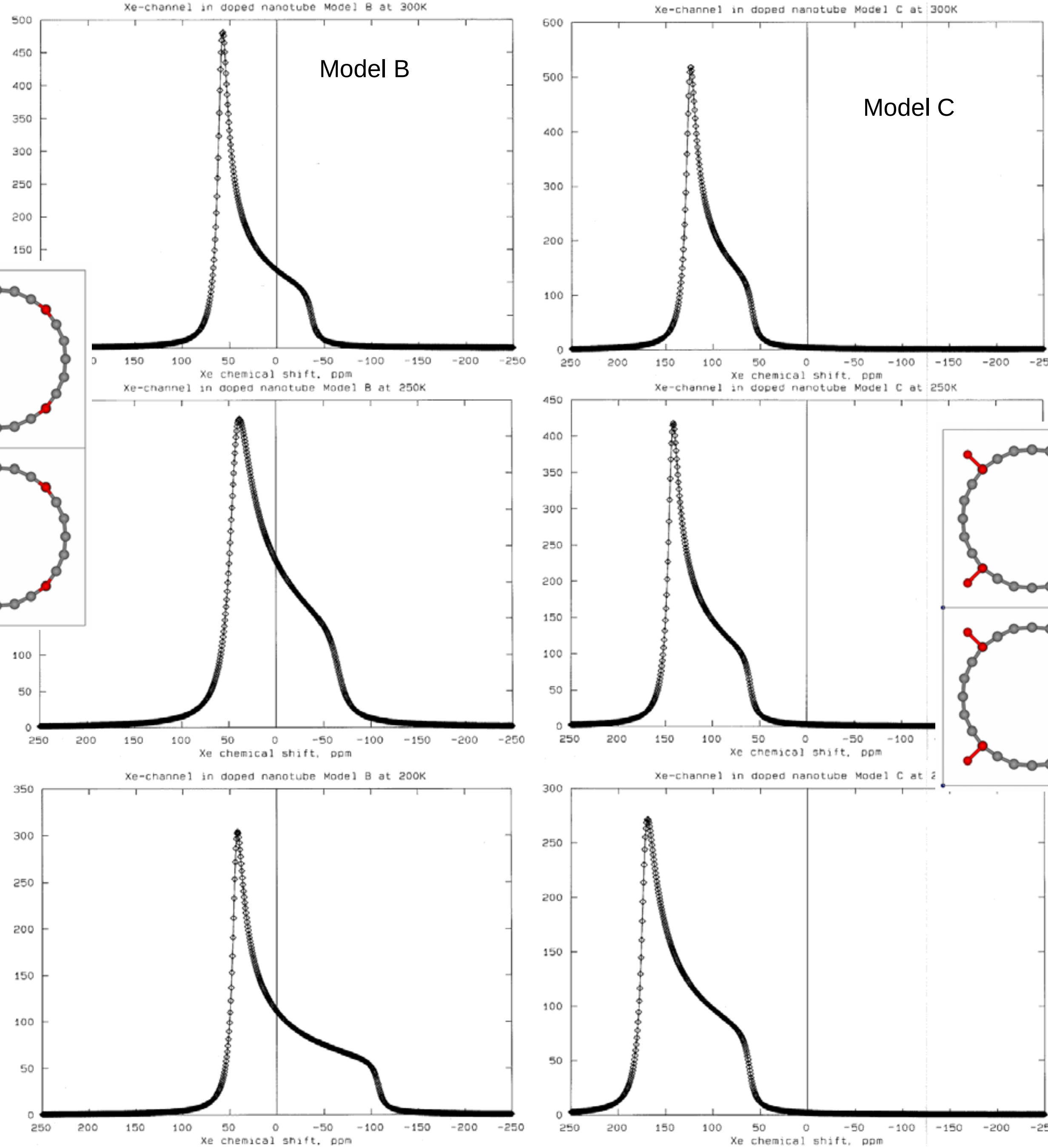
A and B have the same doping pattern in the nanotube; **different distribution of O_2 in the solid**

Model B

O-O axis **parallel** to channel axis

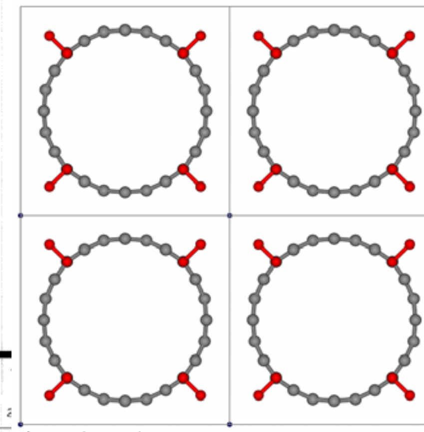


the same doping pattern in the nanotube; **but different orientation of O_2 axis**



Model C

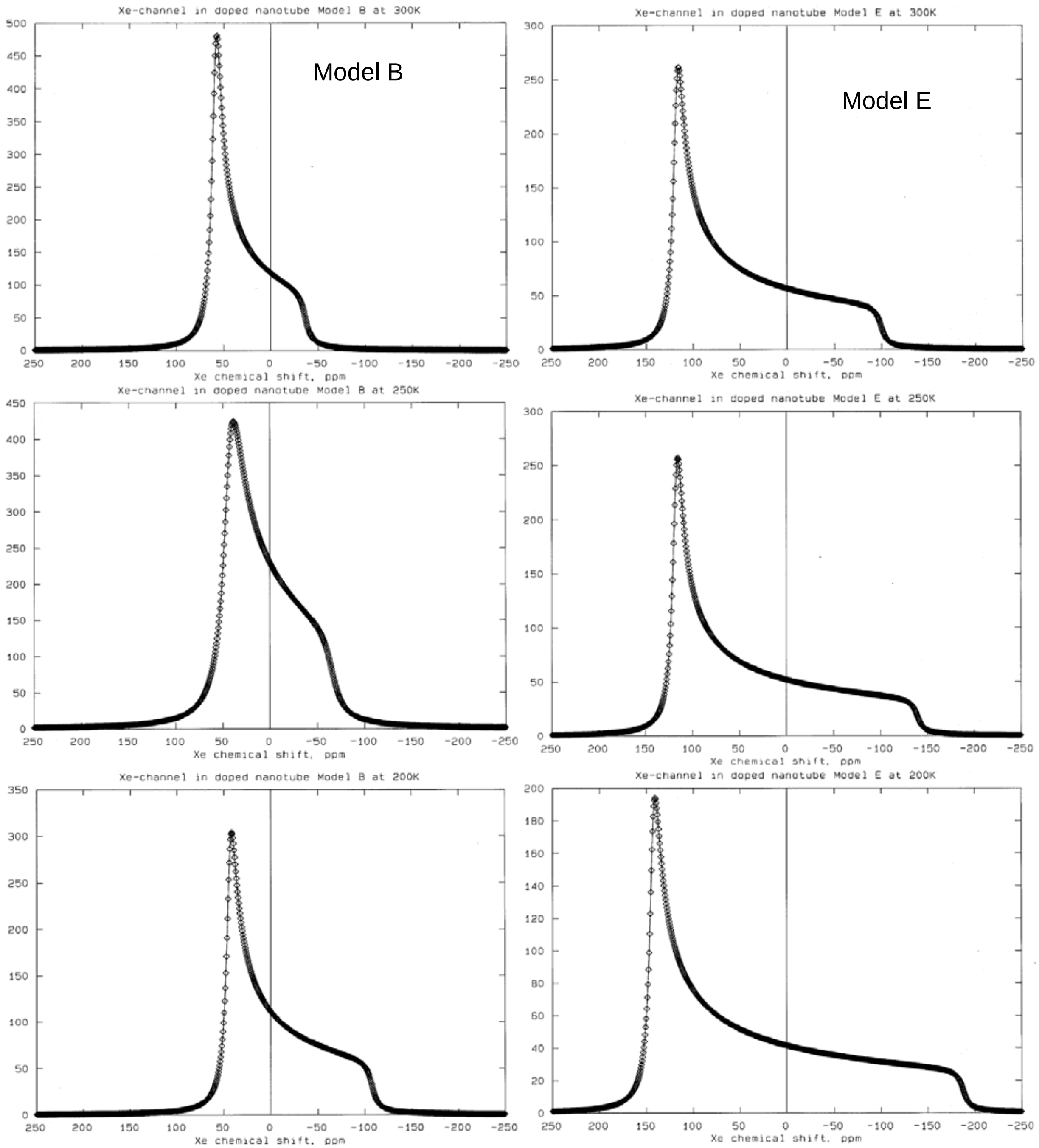
O-O axis perpendicular to channel axis



Model B

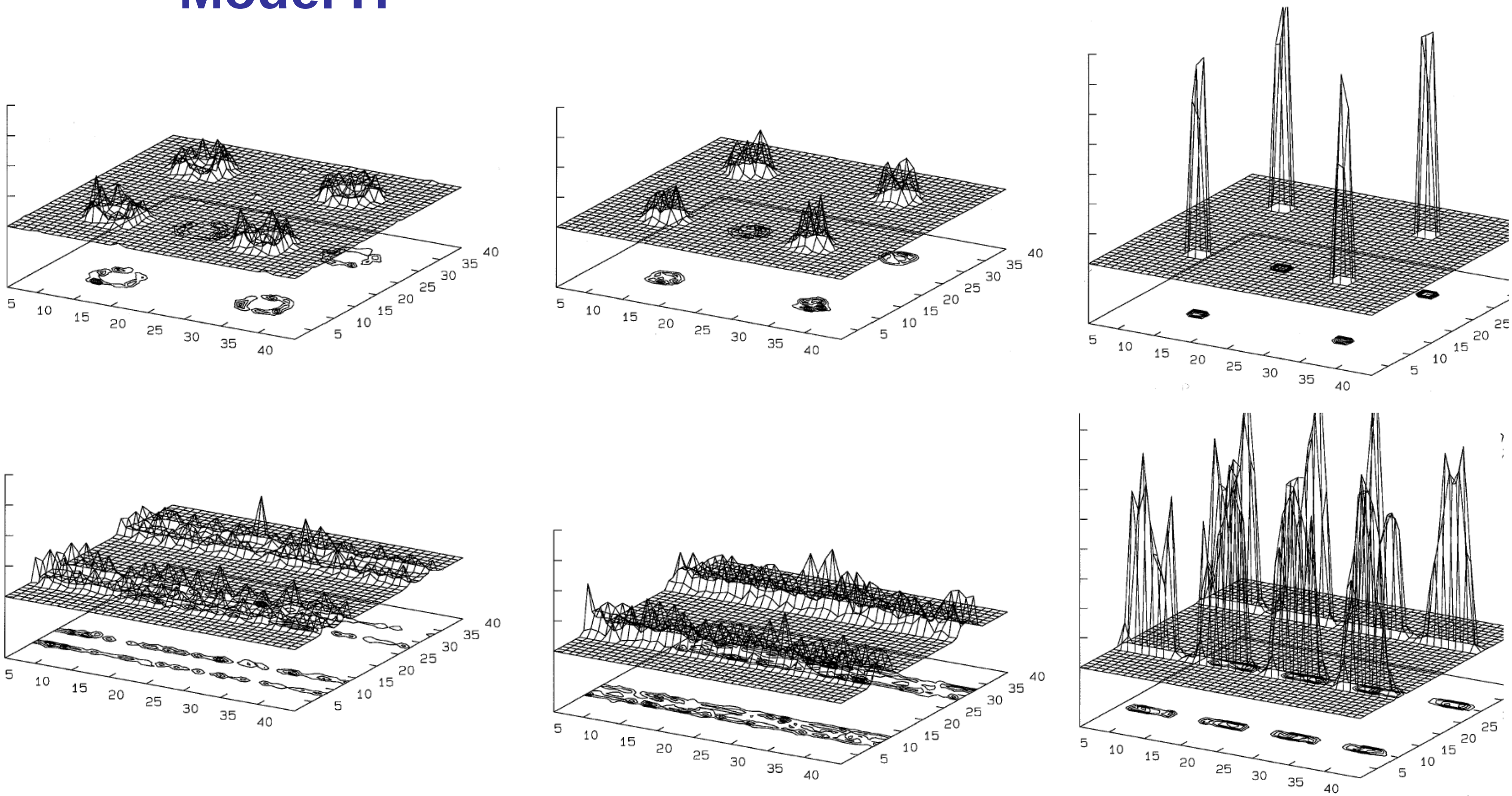
Model E

para-magnetic **axis at same orienta-tion** in the nanotubes



E has **<u>twice the concentration</u> of paramagnets** as **B** in the nanotube

Model H **Model B** **Model D**

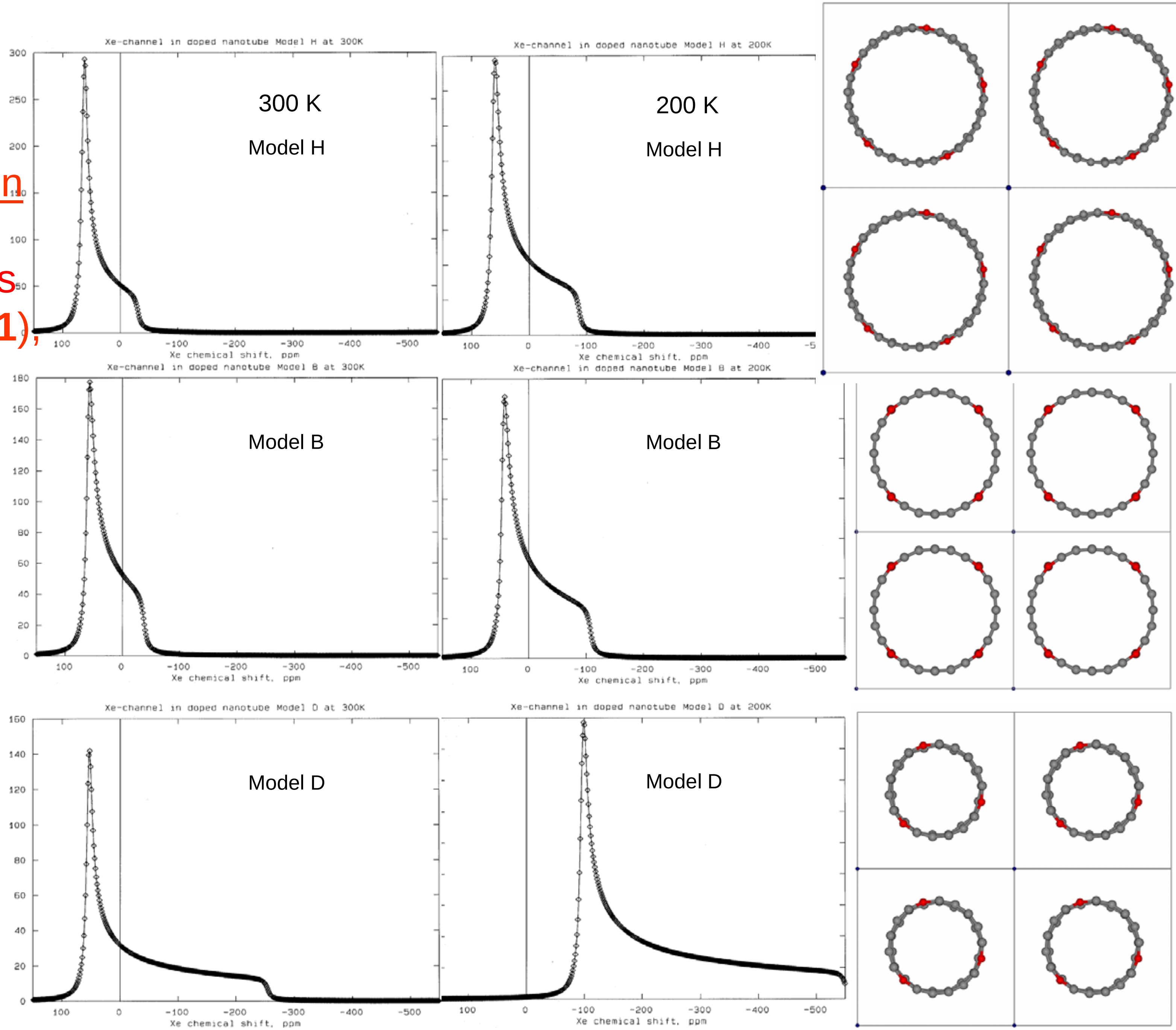


larger diameter **smaller diameter**

Xe one-body distribution functions in channels at 300 K

the same concentration of paramagnets **(O:Ne = 1:11)**, in the same orientation in the nanotube

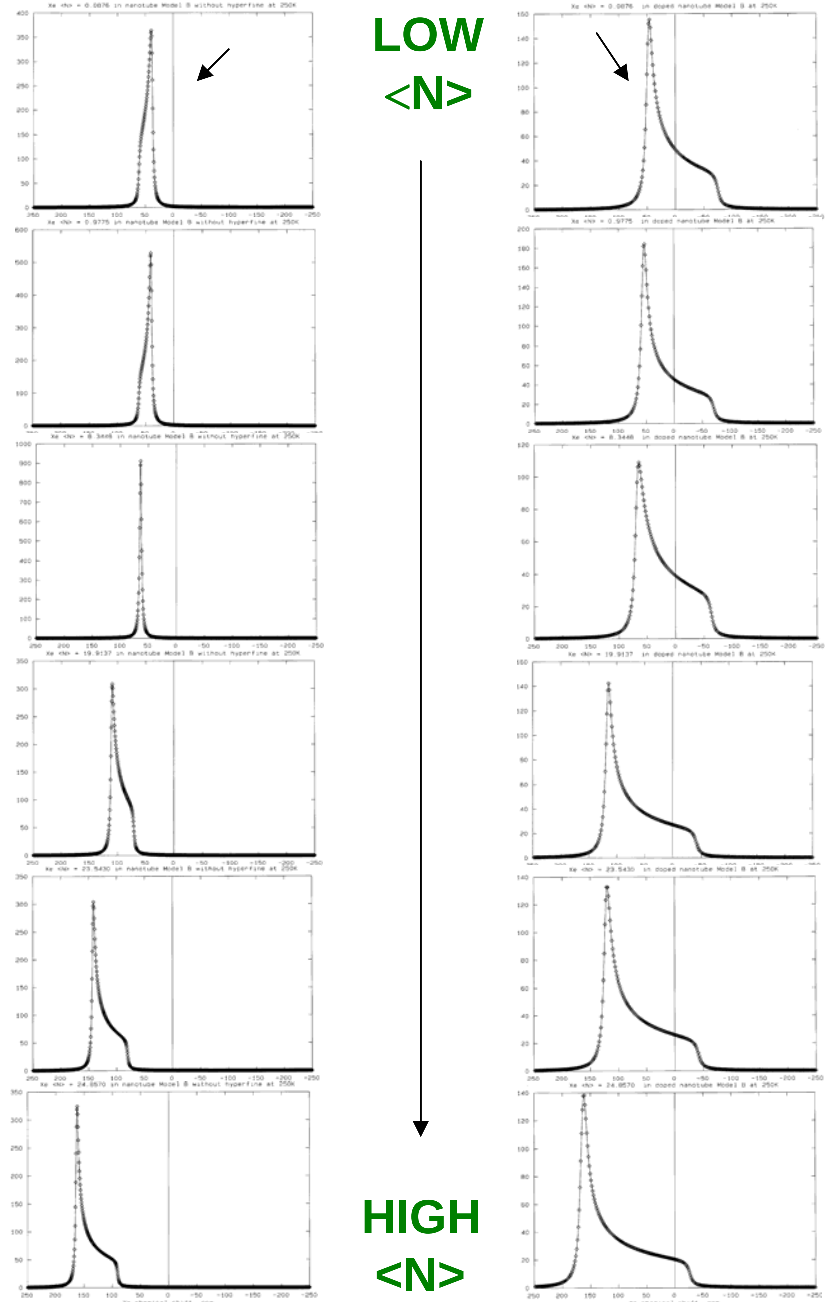
but different diameter channels



Line shape as a function of Xe occupancy

$\delta_{\parallel} > \delta_{\perp}$

$\delta_{\parallel} < \delta_{\perp}$

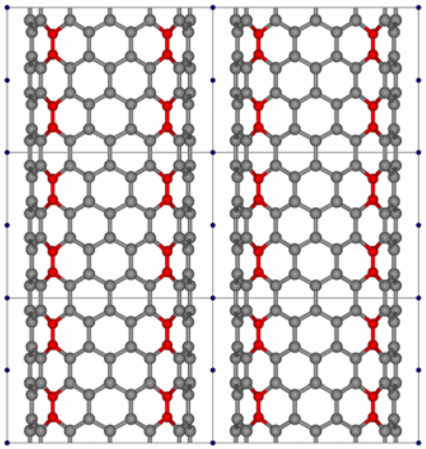


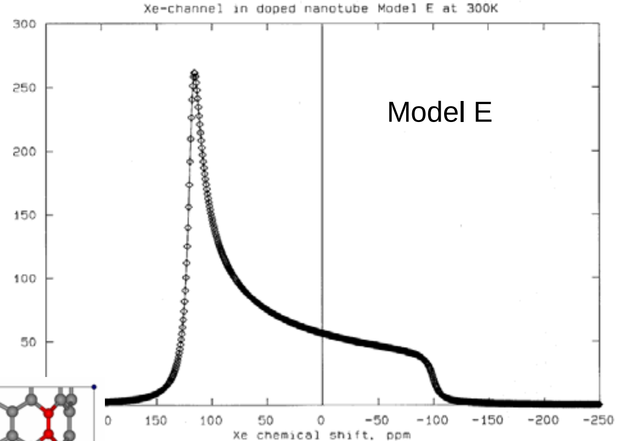
Typical diamagnetic channel

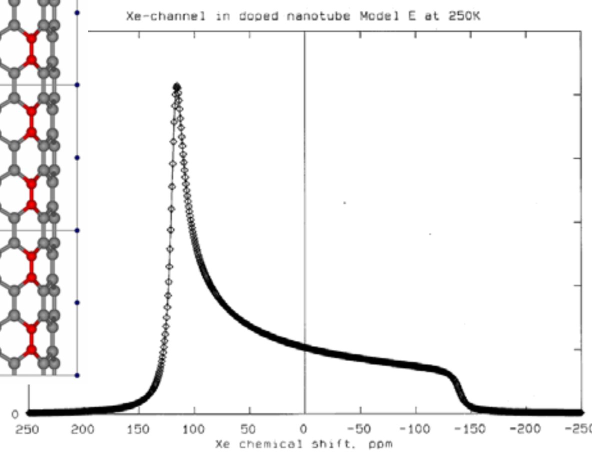
Channel with paramagnetic centers

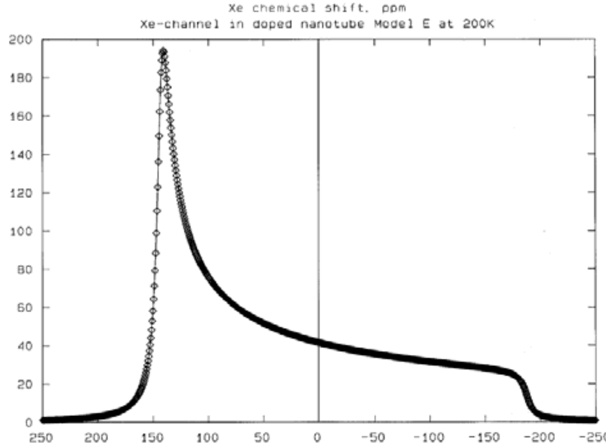
Model E

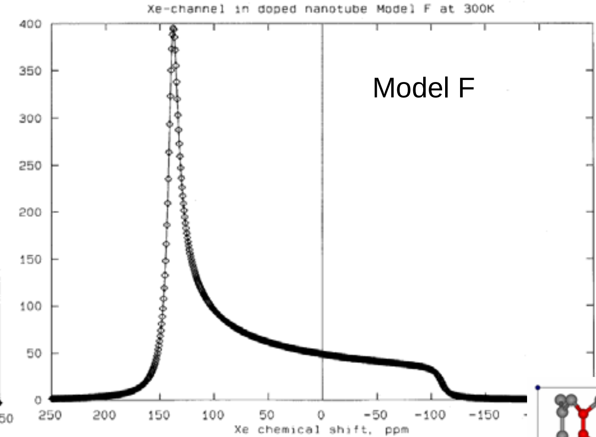
centers are stacked

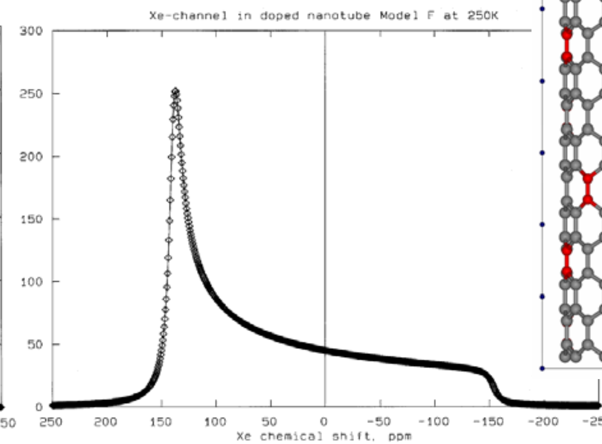


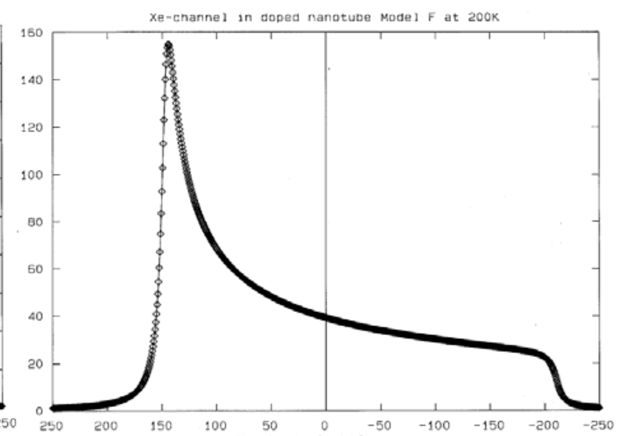






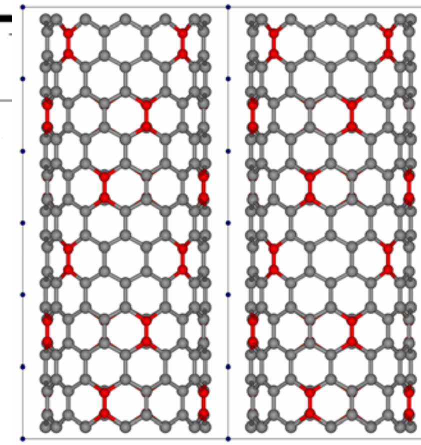






Model F

centers are in a spiral



Xe can detect small differences in distribution

Xe line shape signatures in diamagnetic channels

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

Xe line shape signatures in diamagnetic channels

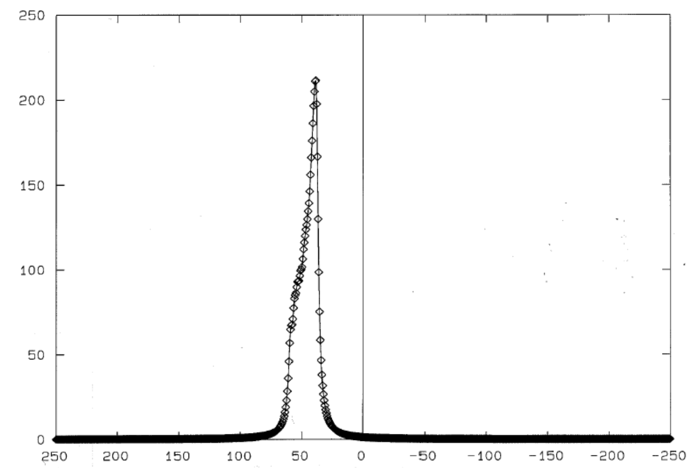
- *Linear behavior of each component with* ⟨N⟩ → orderly arrangement of Xe atoms in channel; Xe sits in register with sites along walls. Xe unable to do this when sites too close together
- *Non-linear behavior of tensor components with* ⟨N⟩ → non-uniform channel cross section.
- *crossing of tensor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

For polycrystalline material containing one-dimensional channels

are there signature Xe line shapes for channels with paramagnetic centers?

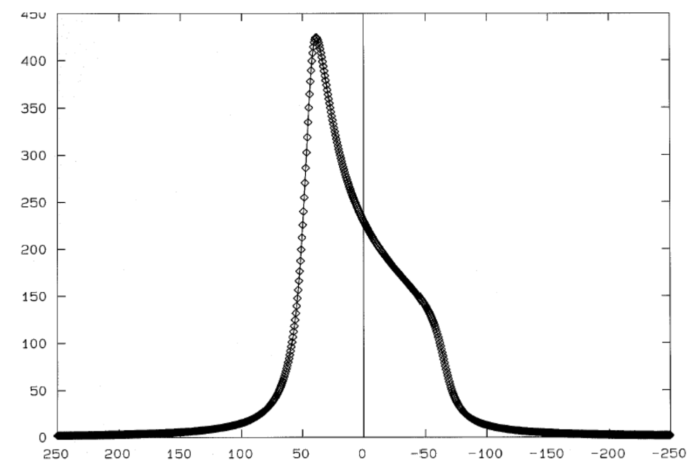
Xe line shape signatures in paramagnetic channels

axiality of the Xe chemical shift tensor at near zero occupancy:



- diamagnetic systems:
  $\delta\perp < \delta\parallel$

- ***presence of paramagnetic centers:*** $\delta\perp > \delta\parallel$



Xe line shape signatures in paramagnetic channels

with increasing Xe occupancy, ⟨N⟩:

- diamagnetic channels: crossing over of $\delta_{\|}$ with $\delta_{\perp}$; span decreasing with increasing ⟨N⟩, then increasing again, exhibiting isotropic-like shape at some intermediate ⟨N⟩.
- ***presence*** of paramagnetic centers: divergence of the individual components from each other as ⟨N⟩ increases; span increases monotonically with increasing ⟨N⟩.

Xe line shape signatures in paramagnetic channels

as T decreases, at low Xe occupancy

- diamagnetic channels: $\delta_{||}$ moves to more positive chemical shifts
- ***presence*** of paramagnetic centers: $\delta_{||}$ moves to more negative chemical shifts

Xe line shape signatures in paramagnetic channels

orientation of the paramagnets

- axis of the paramagnet **parallel** to channel axis: hyperfine contribution to Xe tensor is nearly all $\delta_{||}$ and ***negative***.
- axis of the paramagnet **perpendicular** to channel axis: hyperfine contribution to Xe tensor is nearly all $\delta_{\perp}$ and ***positive*** (relative to the free Xe atom), same sign as for diamagnetic channel.

Xe line shape signatures in paramagnetic channels

orientation of the paramagnets

as temperature decreases at low ⟨N⟩:

- axis of paramagnet ***parallel*** to axis of channel: $\delta_{||}$ and $\delta_{\perp}$ move to ***more negative*** chemical shifts.
- axis of paramagnet ***perpendicular*** to axis of channel: $\delta_{\perp}$ moves to ***larger positive*** chemical shifts (and $\delta_{||}$ somewhat does too).

Xe line shape signatures in paramagnetic channels

concentration of paramagnets

hyperfine contribution to span ($\delta_\perp - \delta_\parallel$) is proportional to the concentration of paramagnets within channel,

i.e., overall ***span increases with increasing concentration*** of paramagnetic centers

Xe line shape signatures in paramagnetic channels

decreasing average distance from channel center

- $\delta_{||}$ ***larger negative for shorter radial distances***
- ***span increases for shorter radial distances***

axis of paramagnet *parallel* to axis of channel

CONCLUSIONS

NMR line shapes of Xe in nanochannels can inform on various characteristics of paramagnetic centers in porous solids:

- the ***concentration*** of paramagnetic centers in the solid,
- the ***orientation*** of the axis of the paramag-netic center relative to the axis of the channel,
- the ***average distance*** of the paramagnetic centers from the channel axis, and
- the ***distribution*** of paramagnetic centers in the channel and throughout the solid.

Acknowledgments

Devin N. Sears thanks

The Alberta Ingenuity Fund

and the I. W. Killam Fund

for postdoctoral fellowships

Lela Vukovic is grateful for

Herbert Paaren Scholarship

Lubrizol Scholarship