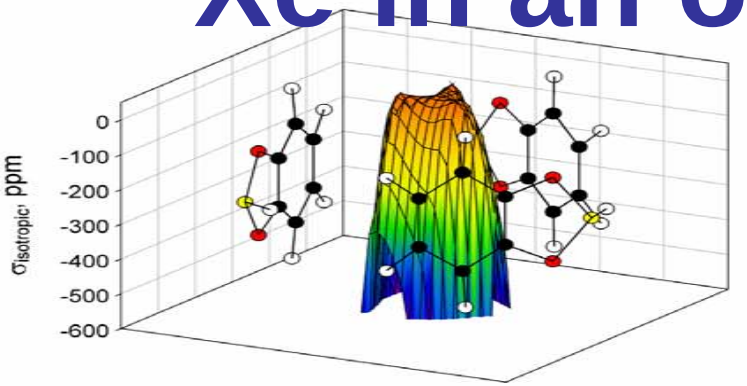
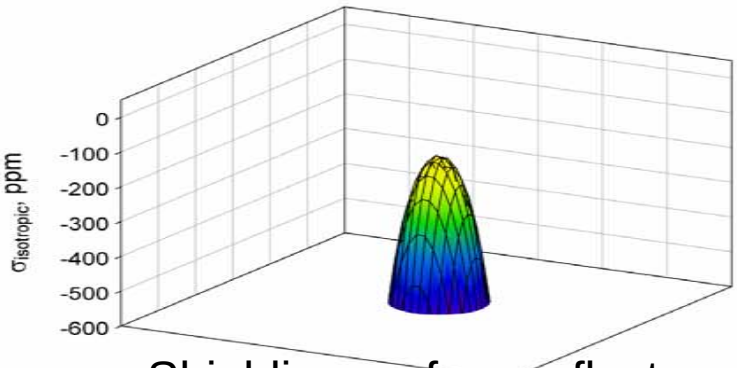
Xe in an organic nanochannel

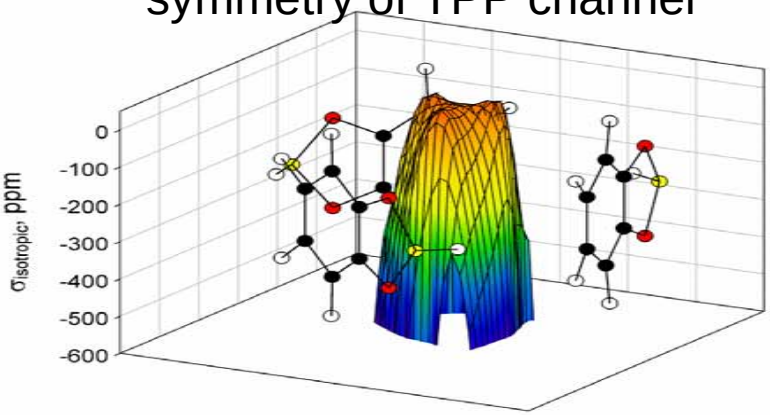
Devin N. Sears

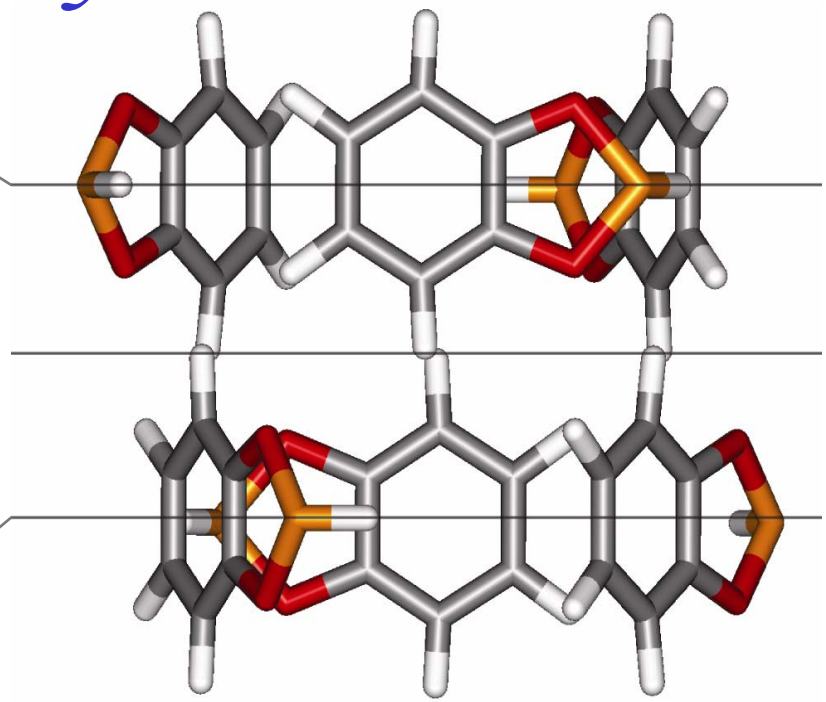
Cynthia J. Jameson





Shielding surface reflects symmetry of TPP channel

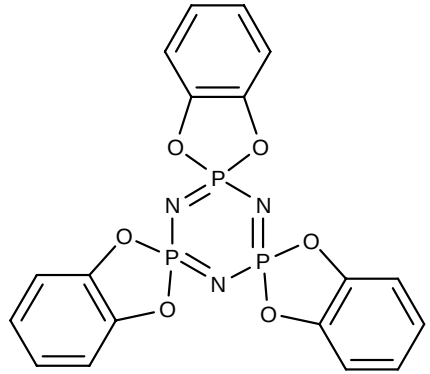




University of Illinois at Chicago

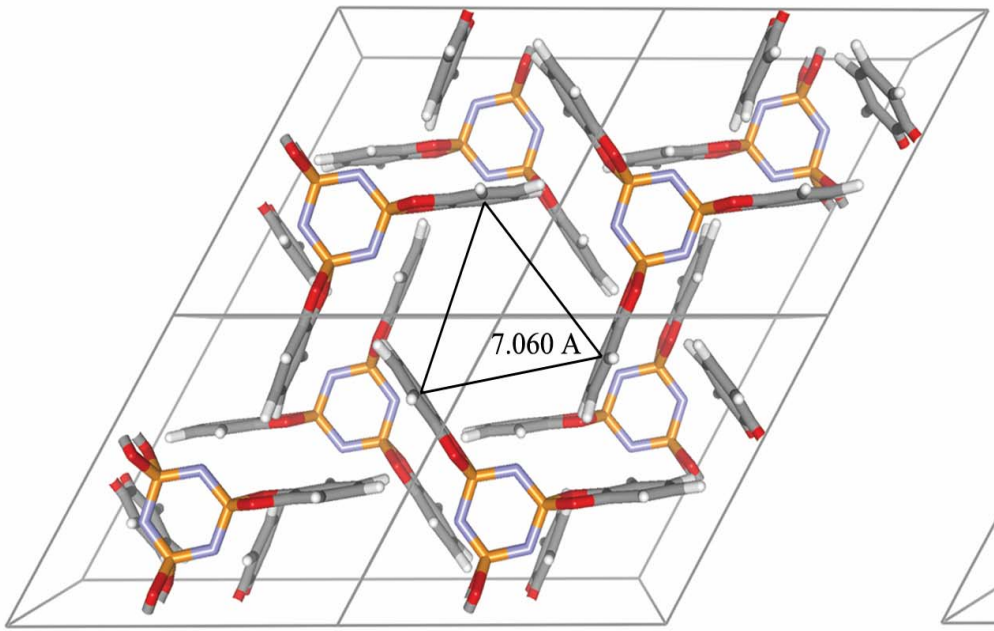
Organic molecular crystal forms nanochannels

- With or without inclusion compounds
  - Polyethylene oxide (peo)
  - Benzene (bz)

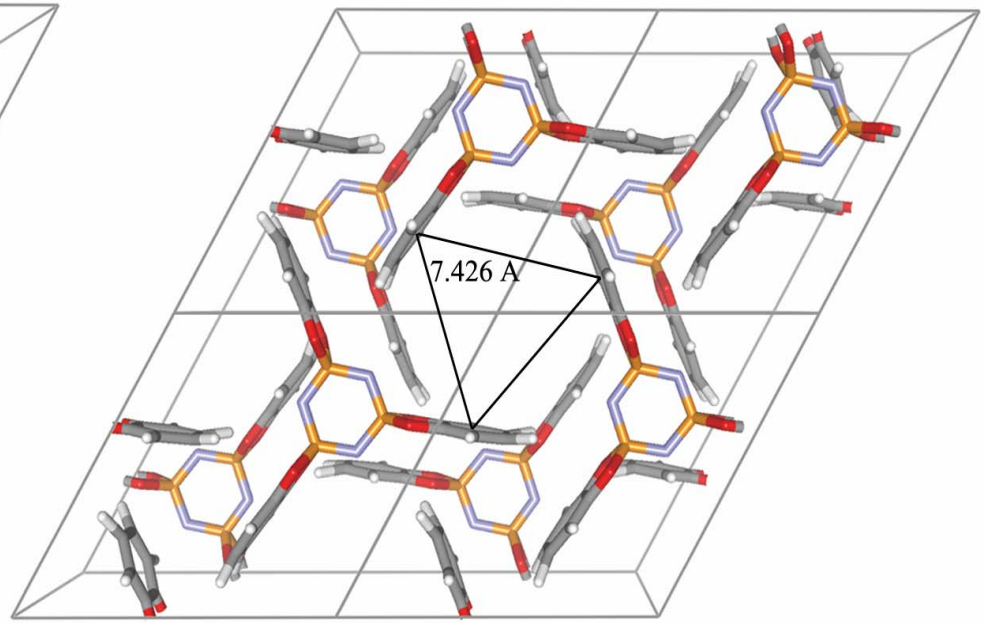


Tris(o-phenylenedioxy)cyclotriphosphazene (TPP)

TPP/peo channel[1]

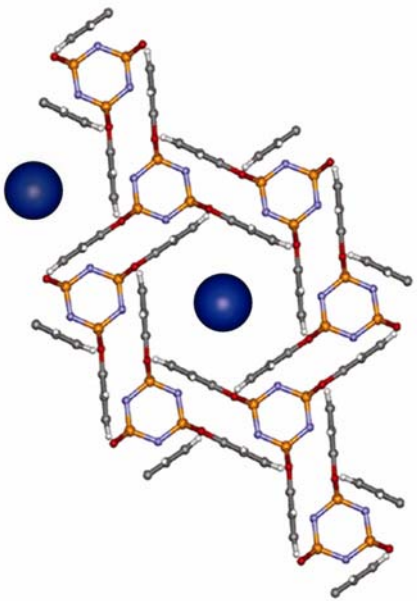


TPP/bz channel[2]

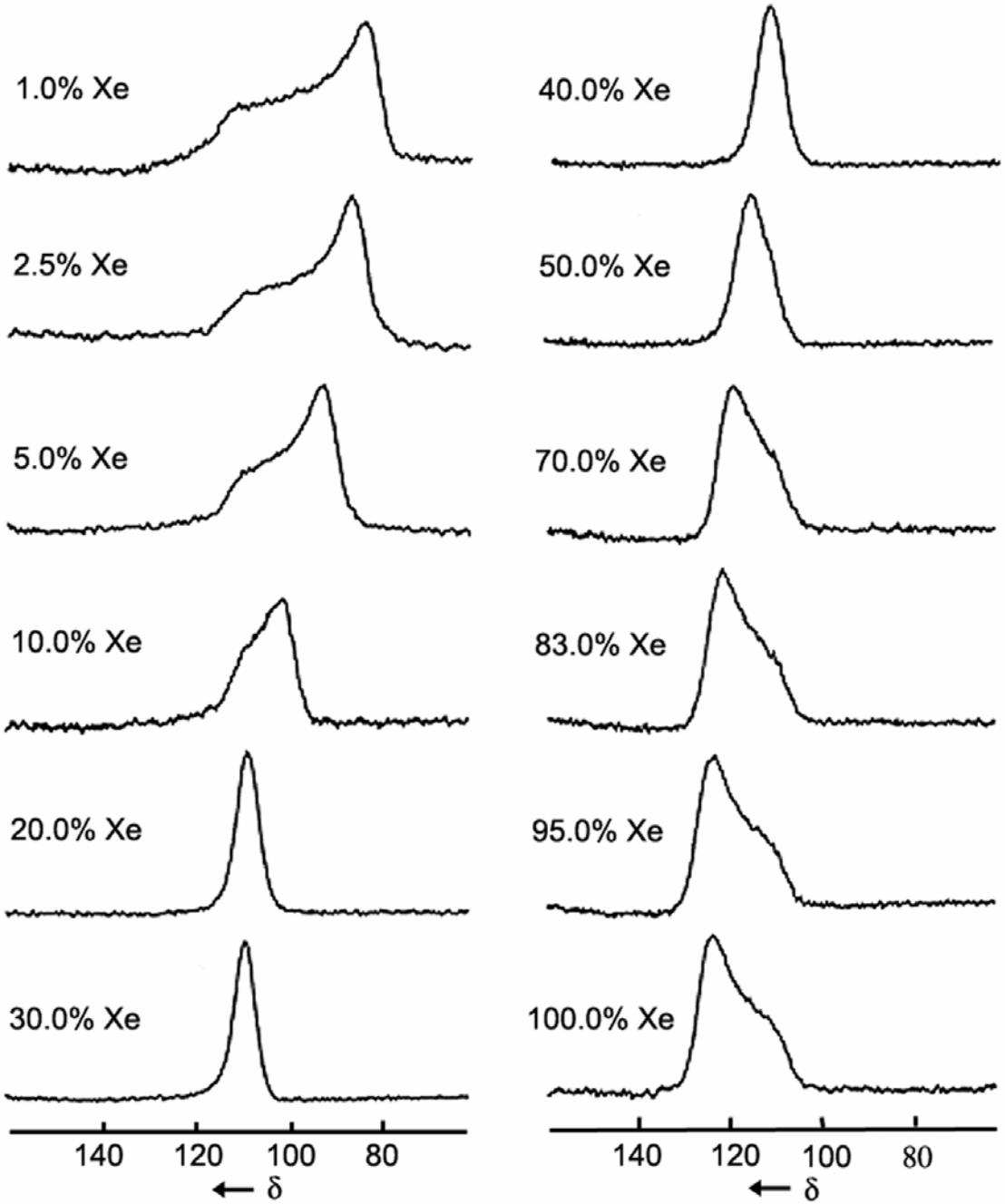


Motivation:

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

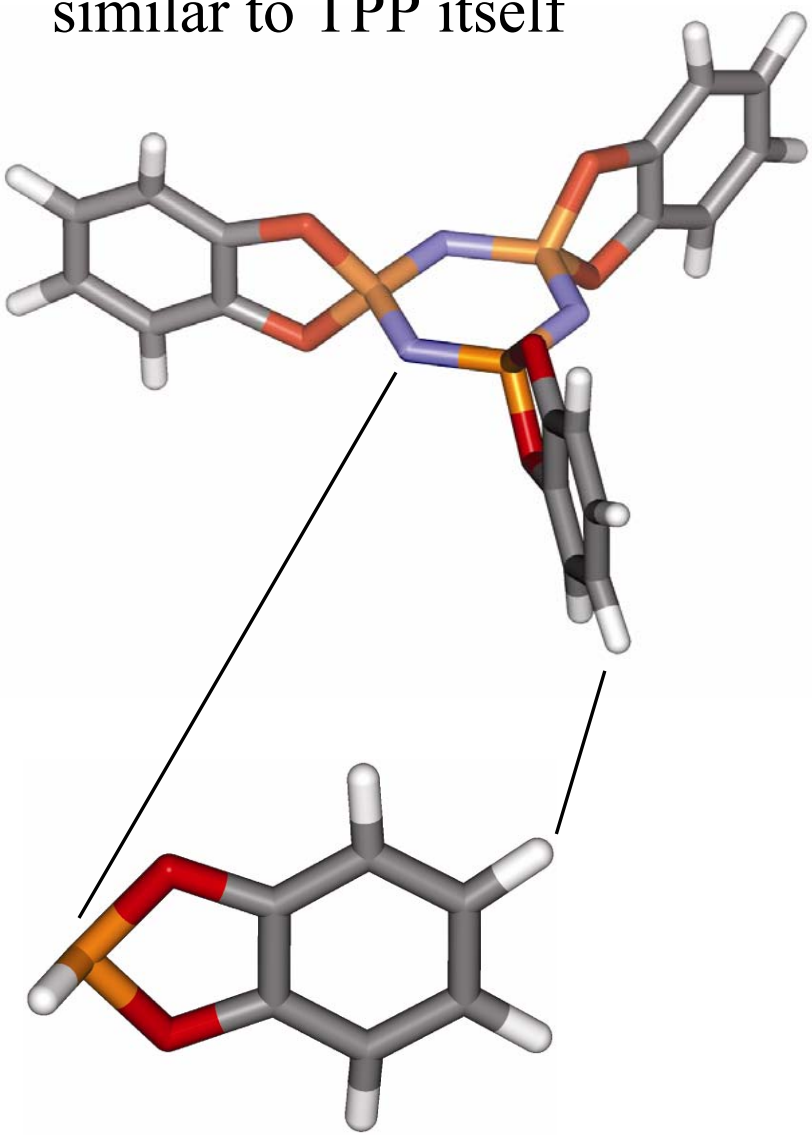


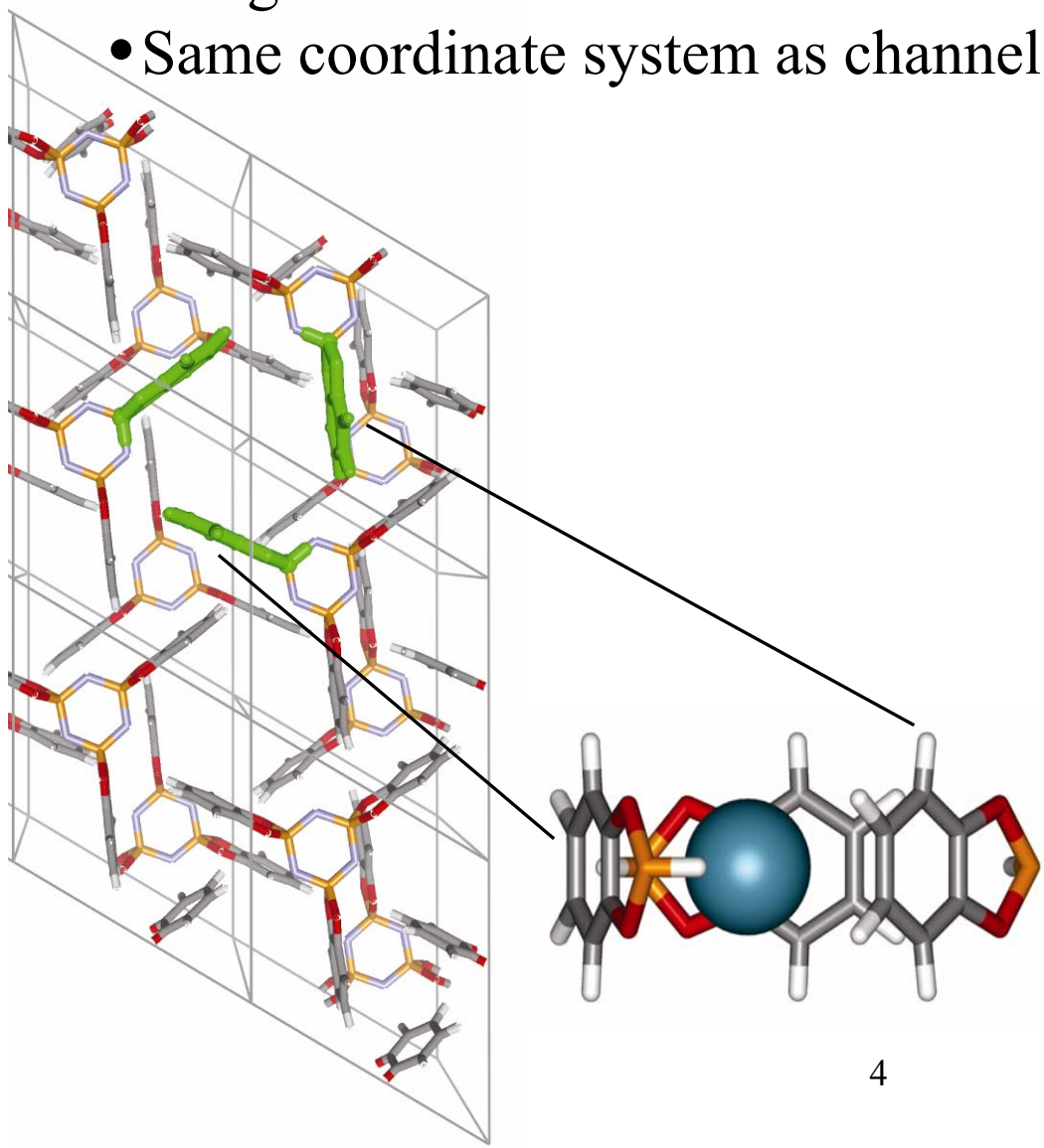
P. Sozzani, A. Comotti, R. Simonutti, T. Meersmann, J.W. Logan, A. Pines
Angew. Chem. Int. Ed. 39, 2695-2699 (2000)



Model for TPP channel

- Suitable molecular fragment has electron density distribution similar to TPP itself
- Channel comprised of a trimer of fragments
- Same coordinate system as channel



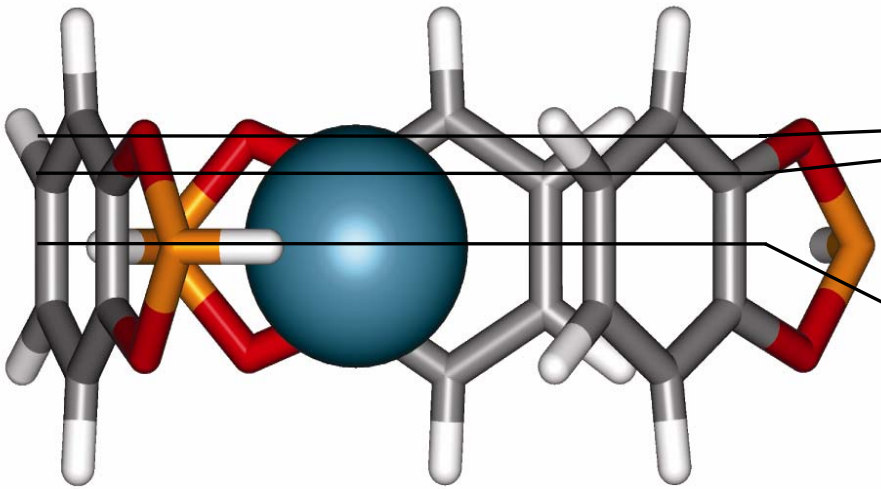


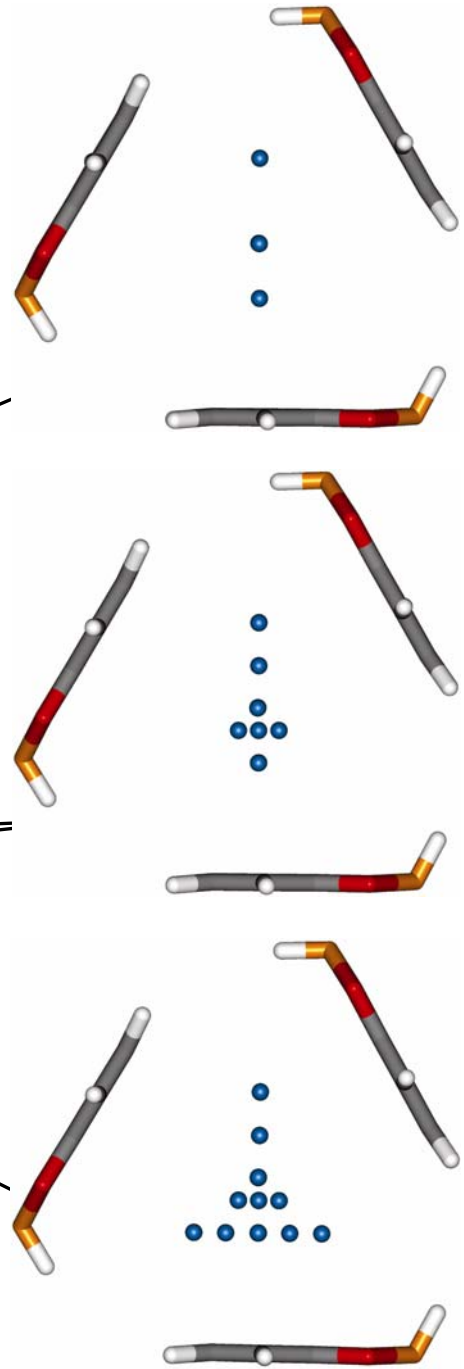
Ab initio calculations

- Use trimer in calculations
- 6311-G** basis set on C,O, and H atoms
- 240 basis functions on Xe atom

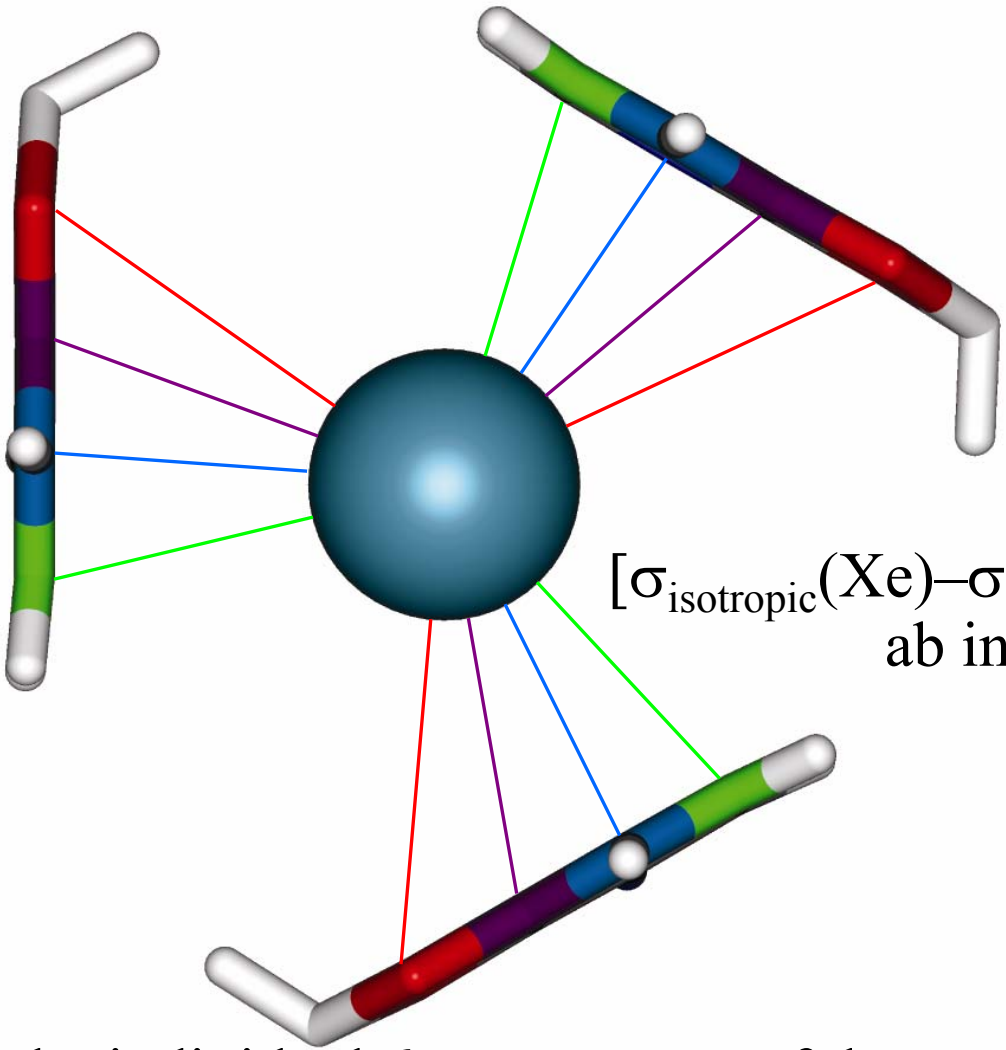
  (26s19p13d)+3s2p4d9f

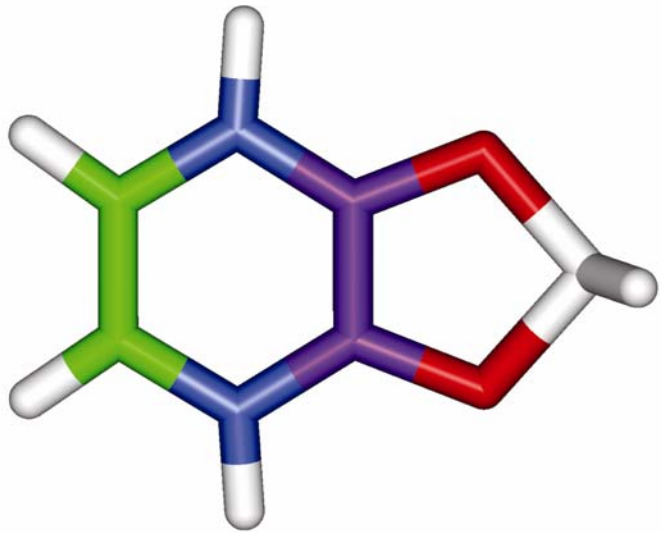
  Uncontracted





Representation of ab initio values by site-site functions

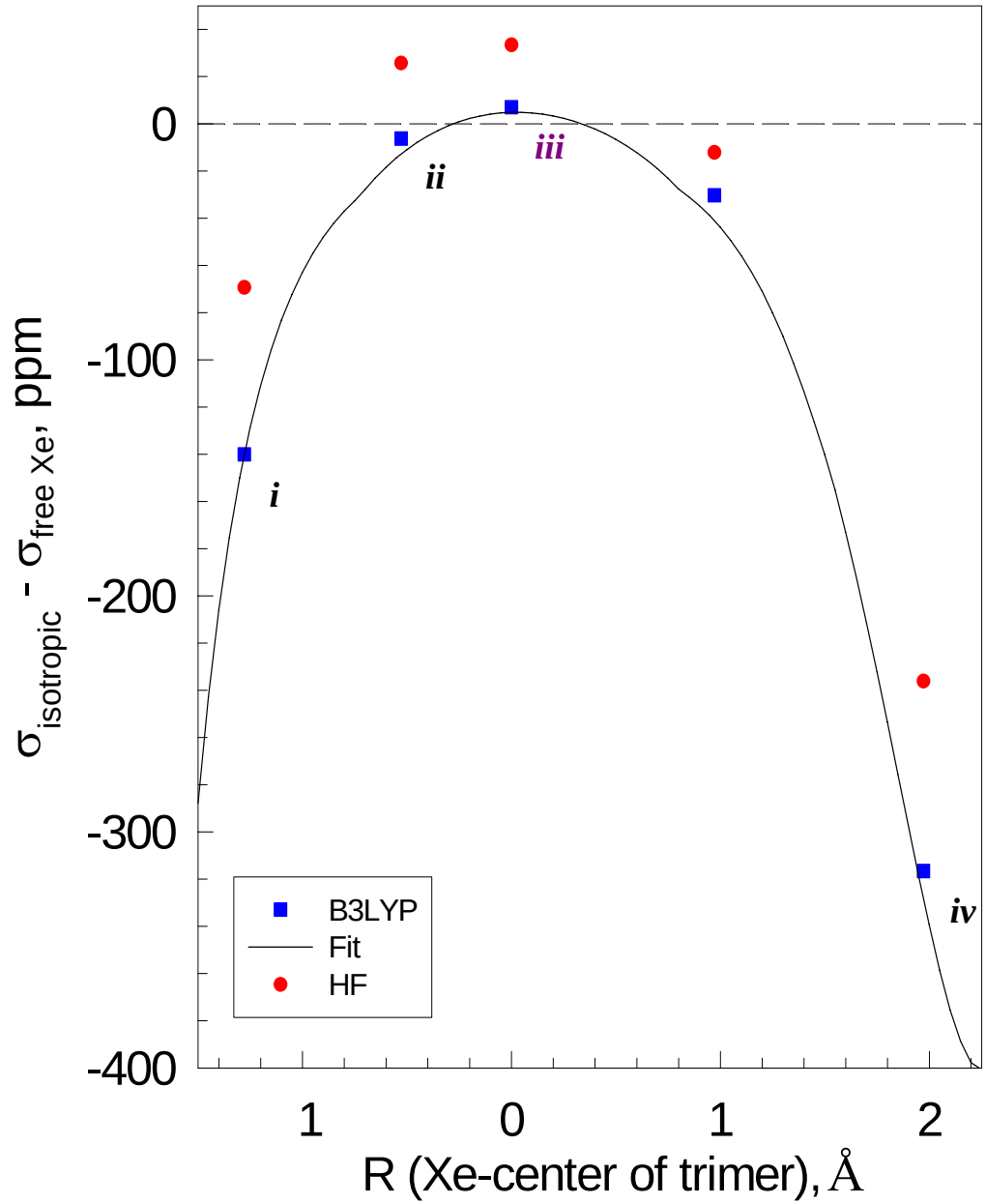


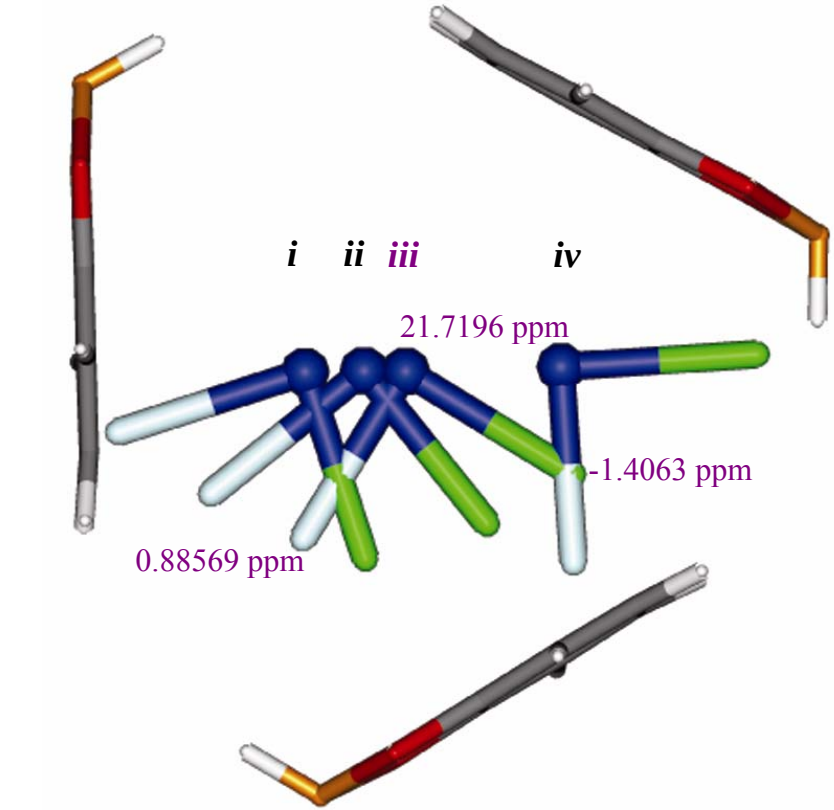


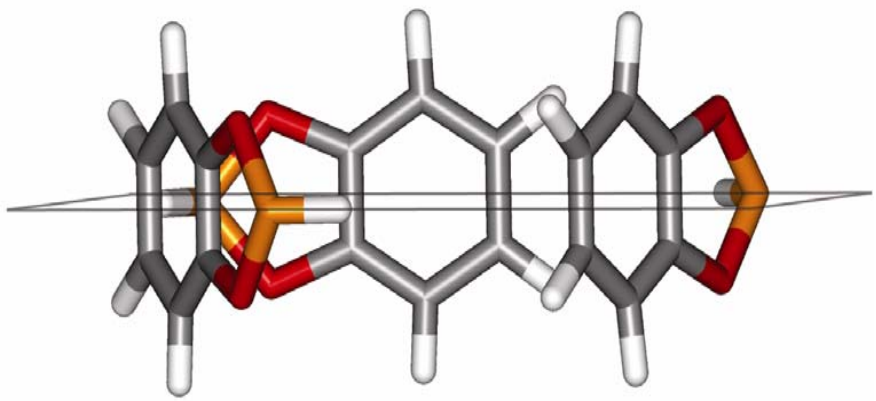
$$[\sigma_{isotropic}(Xe)-\sigma(free)]_{ab\ initio} = \sum_i O_6 r_{Xe_i}^{-6} + O_8 r_{Xe_i}^{-8} + O_{10} r_{Xe_i}^{-10}$$
$$+\sum_j B_6 r_{Xe_j}^{-6} + B_8 r_{Xe_j}^{-8} + B_{10} r_{Xe_j}^{-10}$$
$$+\sum_k C_6 r_{Xe_k}^{-6} + C_8 r_{Xe_k}^{-8} + C_{10} r_{Xe_k}^{-10}$$
$$+\sum_l A_6 r_{Xe_l}^{-6} + A_8 r_{Xe_l}^{-8} + A_{10} r_{Xe_l}^{-10}$$

The individual 6 components of the symmetric σ tensors are likewise fitted to site-site $\sigma_{||}$ and σ_{γ}

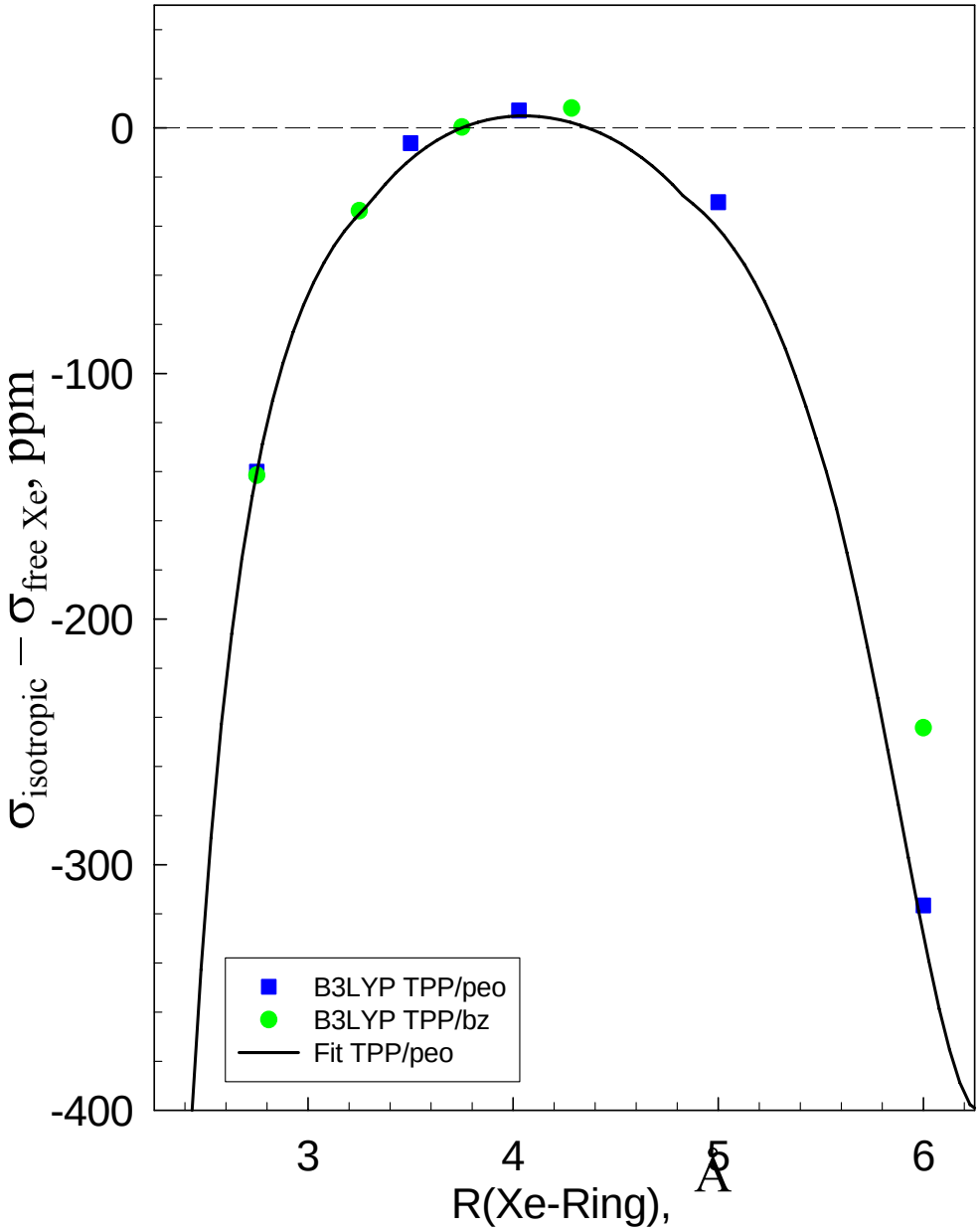
Xe shielding tensor in the trimer



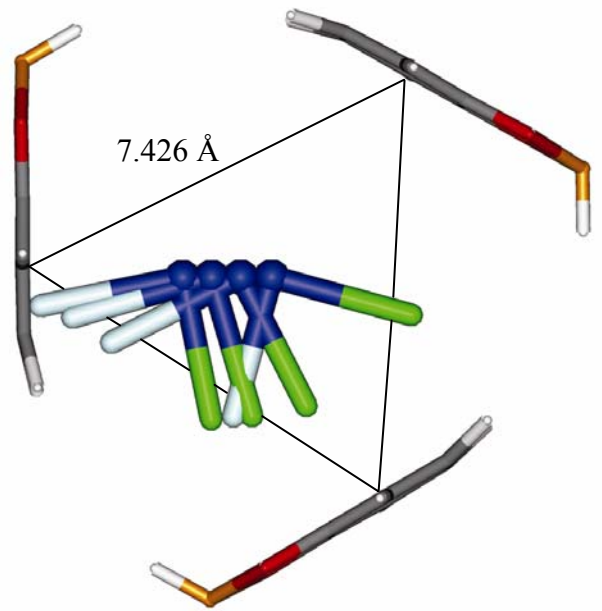




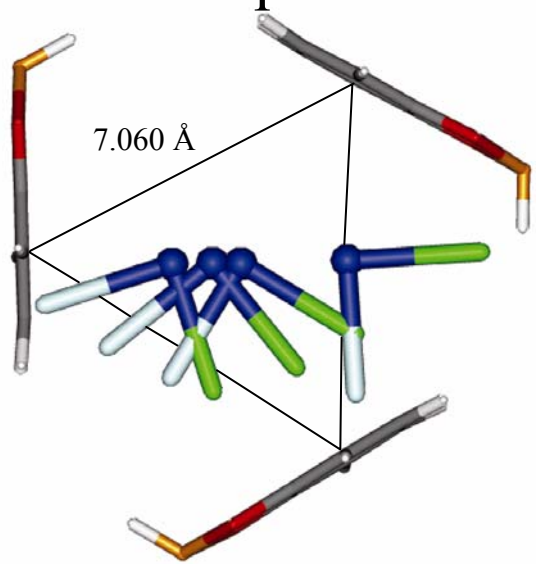
Effects of channel dimension on Xe shielding



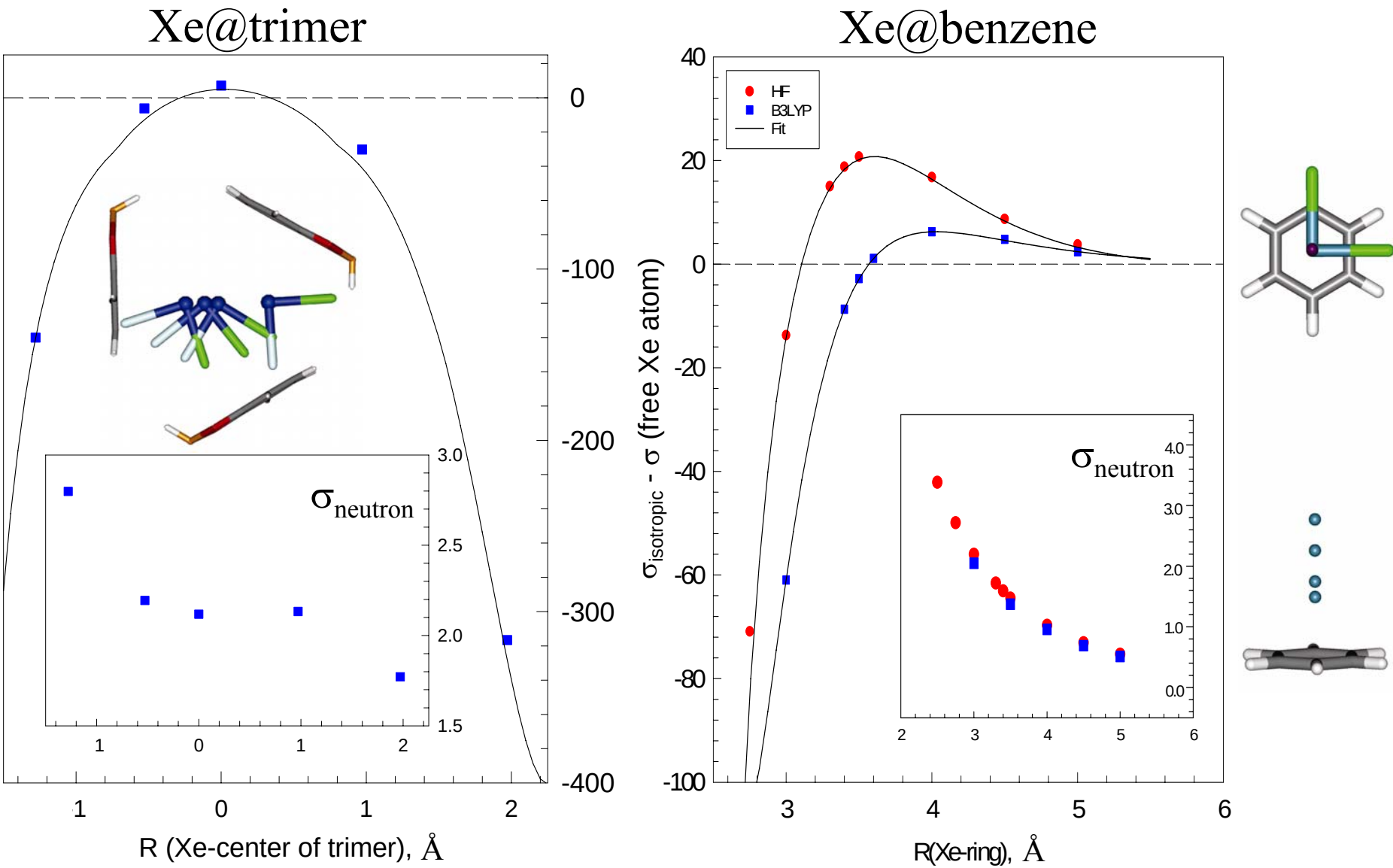
TPP/bz



TPP/peo

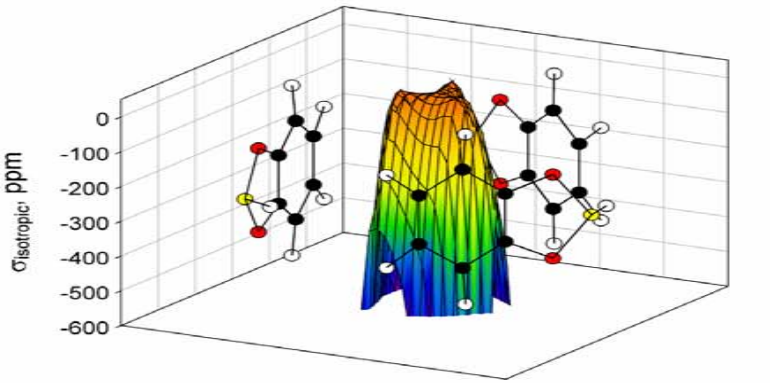


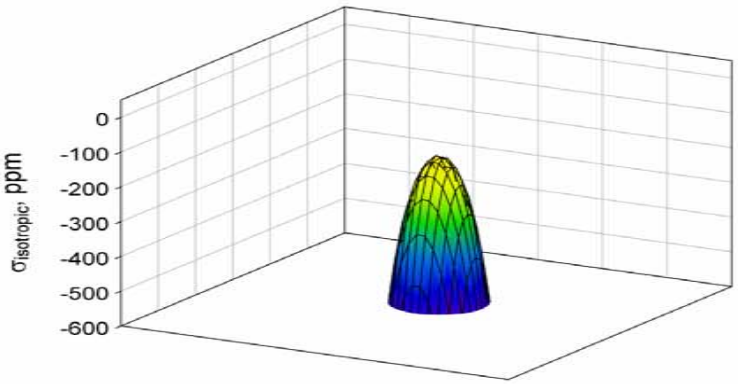
What is the role of ring currents?

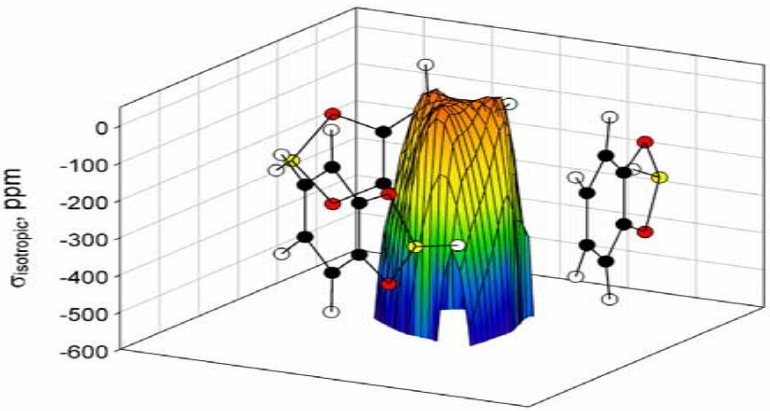


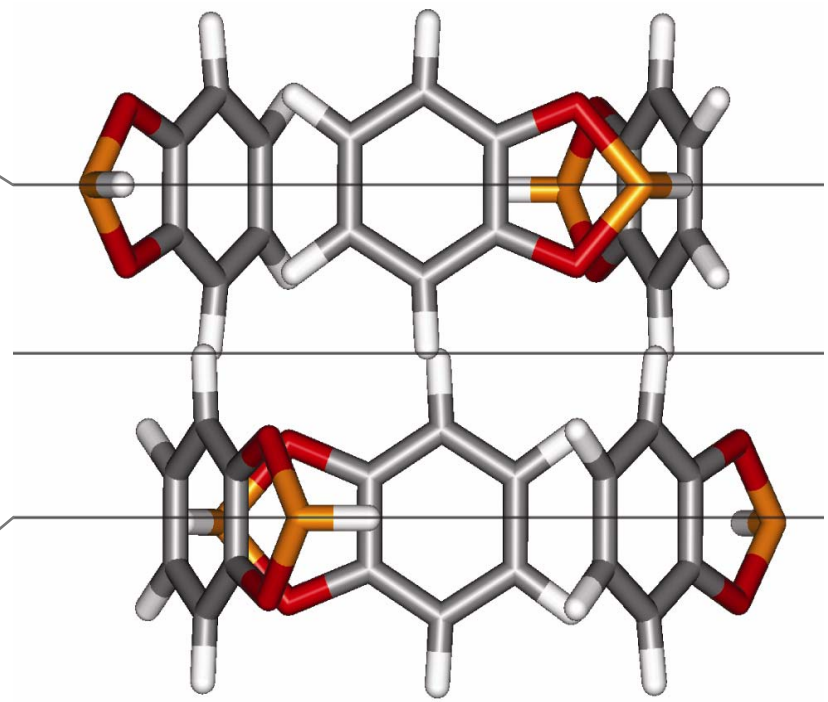
Ring currents are not significant for σ_{Xe} in Xe@aromatics

The Xe isotropic shielding surface in model channel of 2 trimers



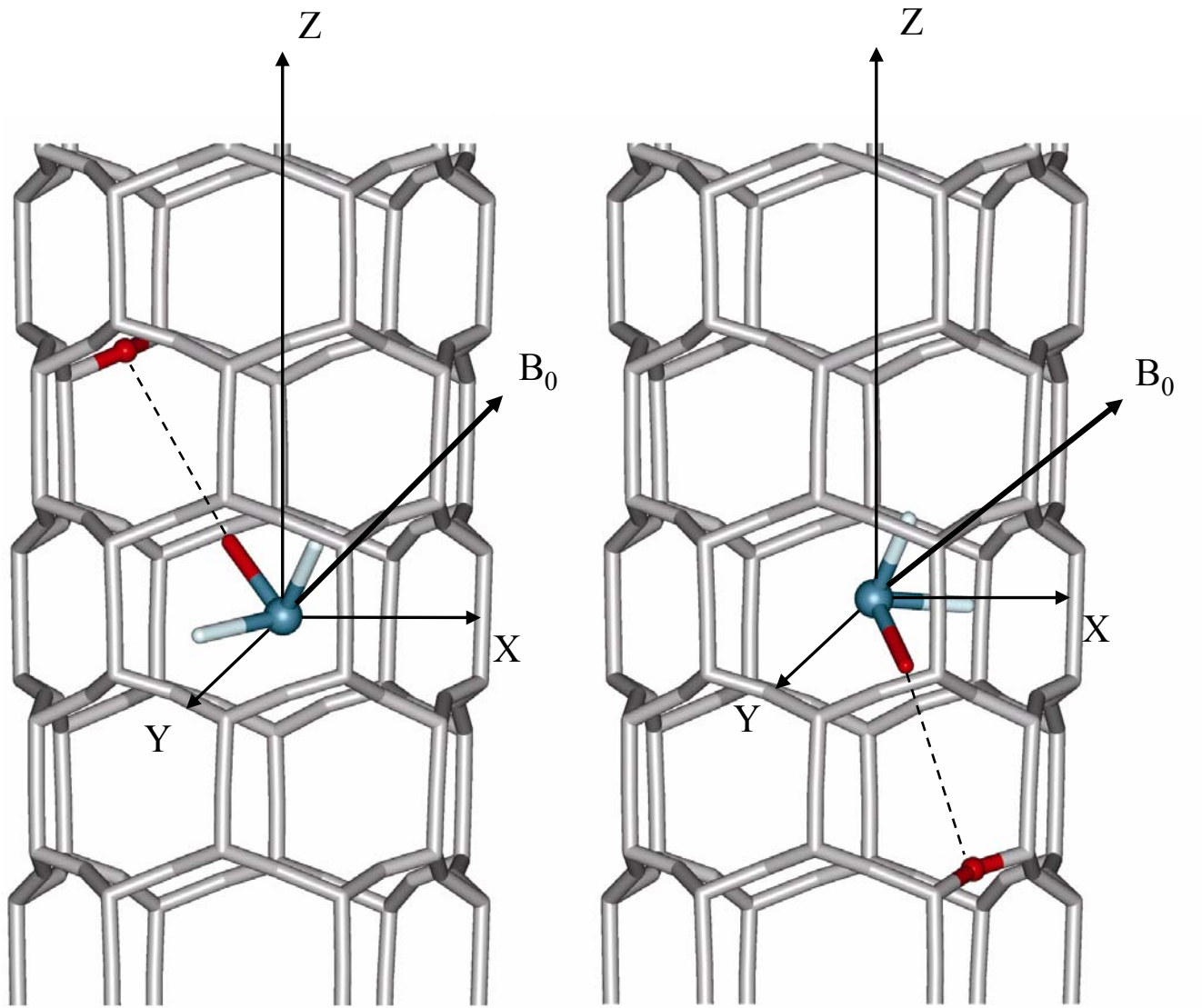


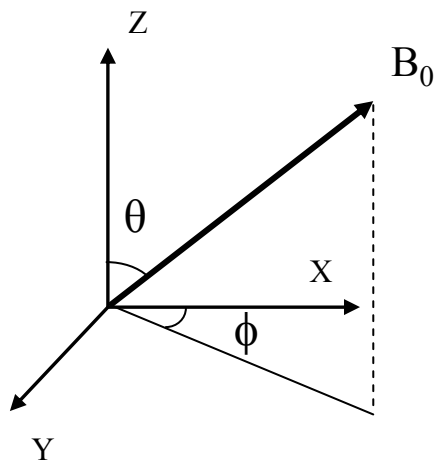




Shielding surface reflects symmetry of TPP channel

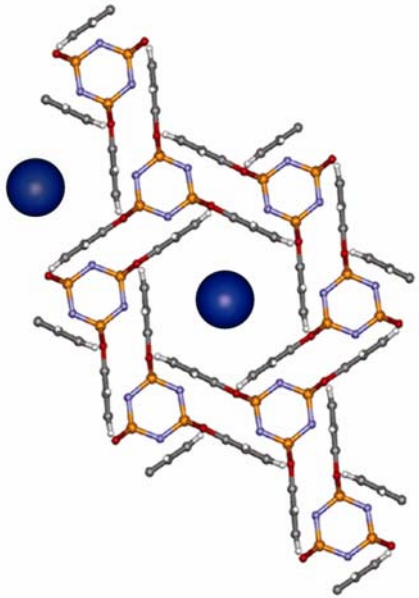
Lineshapes by grand canonical Monte Carlo



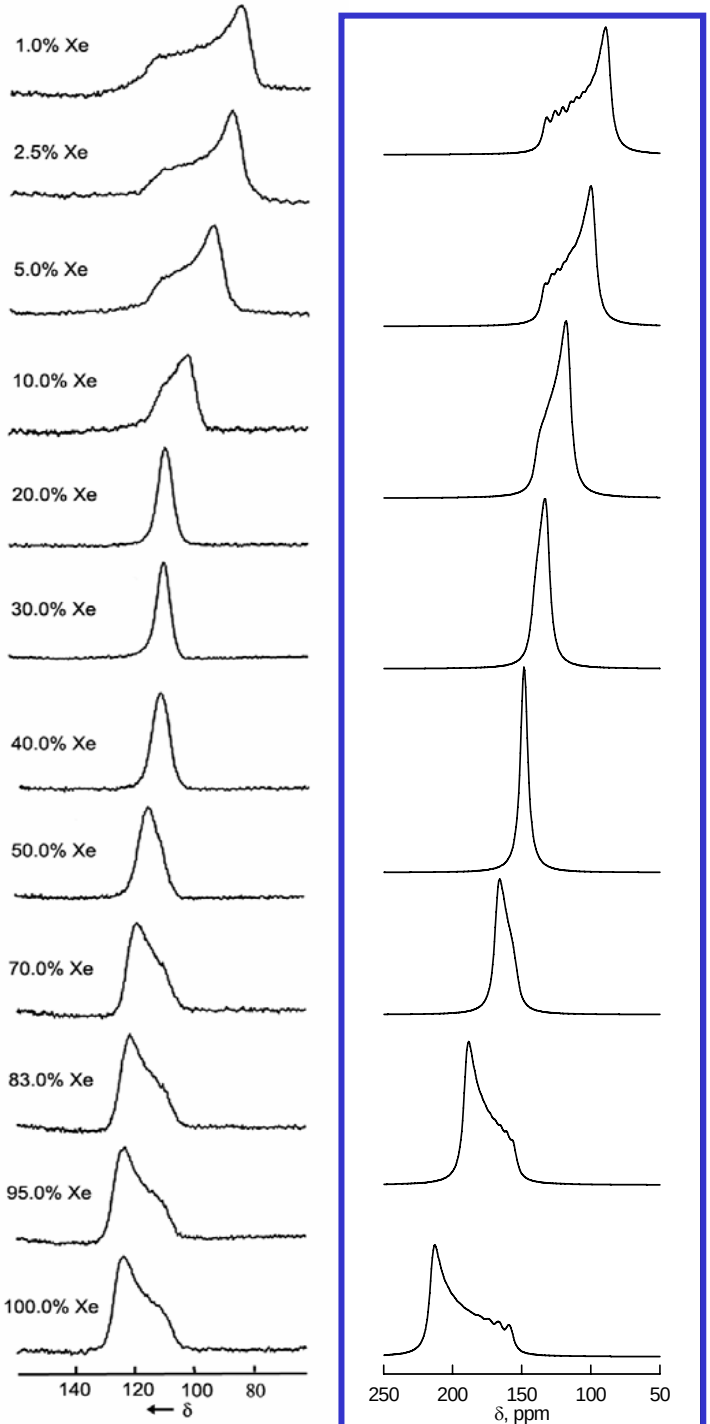


Random orientation of crystallites:
Probability that B_0 lies in any infinitesimal solid angle is
$d\zeta\, d\phi / 4\pi$, where
$\zeta = (-\cos\theta)$
Equal areas in $\zeta\phi$ plane correspond to equal probabilities

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



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



⟨n⟩ = 0.063 Xe/UC

0.406

0.737

0.961

1.368

1.666

1.931

2.088

GCMC SIMULATIONS using trial functions fitted to ab initio shielidng calculations Jameson 2003

NMR lineshapes in nanochannels provide the average Xe shielding tensor in confined geometries just as we have seen for Xe in AlPO4-11

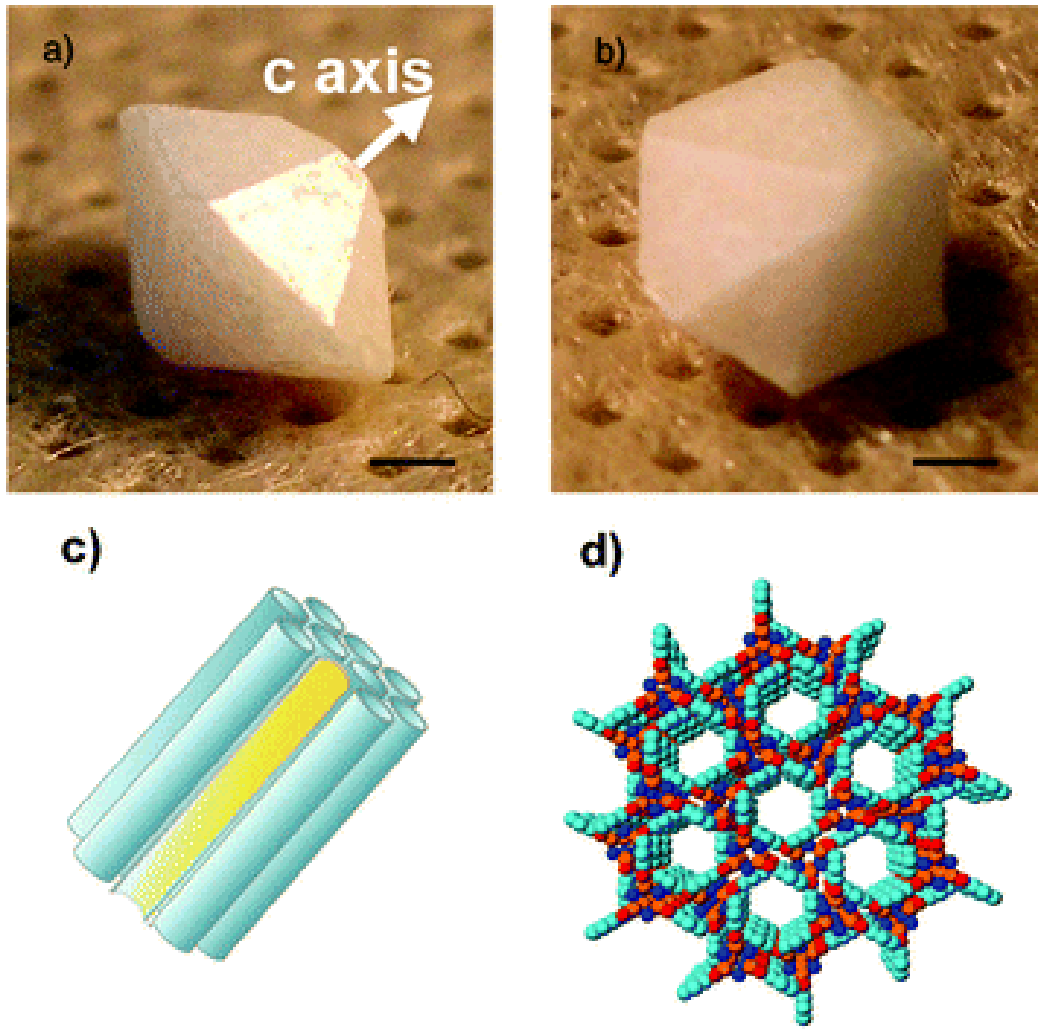
- Simulations demonstrate separately which part of the observed NMR lineshape characteristics provides the **signature of the channel architecture**, and which part provides information on the **electronic structure of the atoms constituting the channel**.
- The variation in lineshape as a function of loading in real systems can be reproduced.
- The additive dimer tensor model can work well in channels and cavities of arbitrary size and shape.

Conclusions

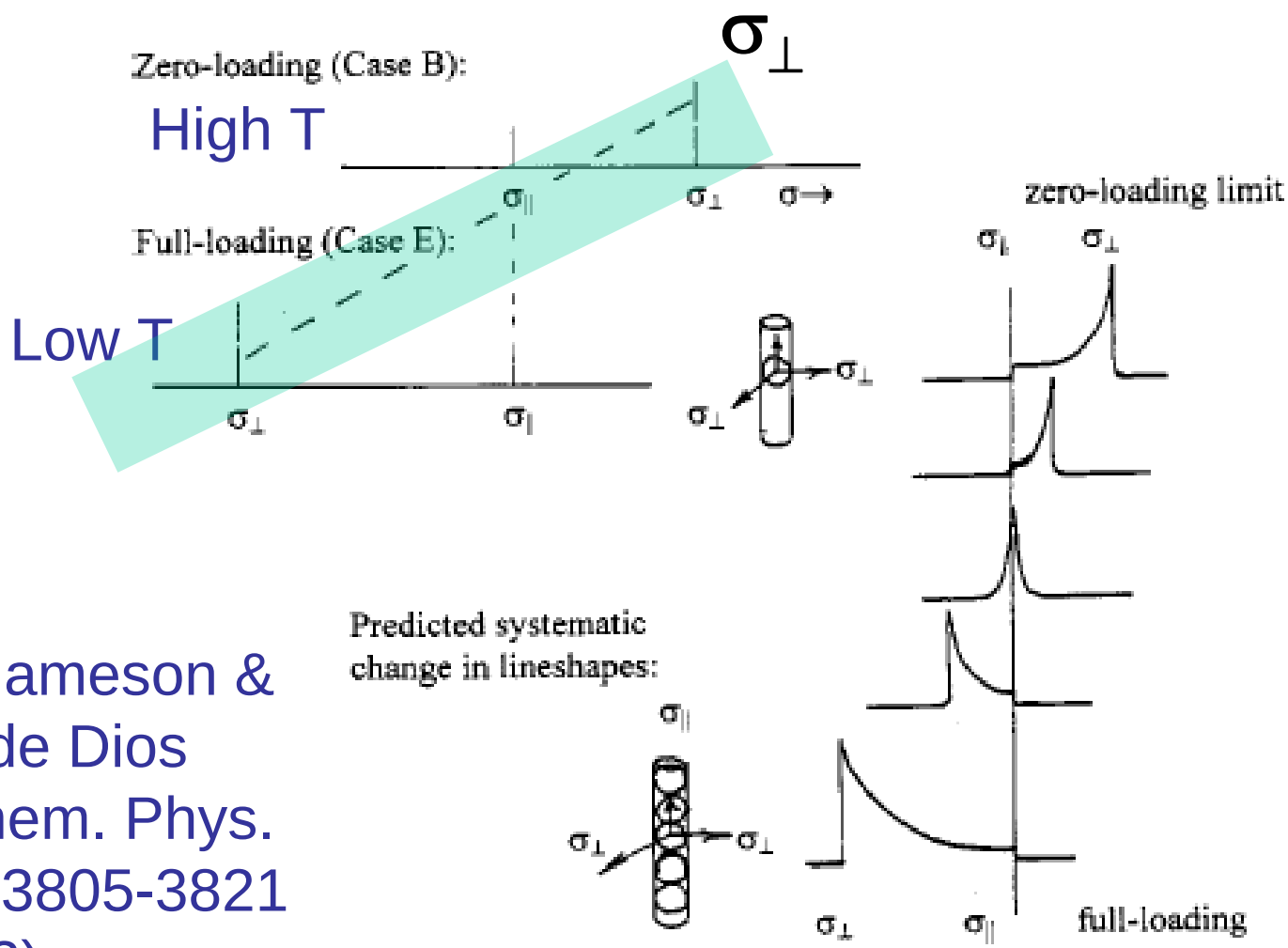
- Ab initio calculation of Xe in an organic nanochannel
- For Xe shieldings in aromatic nanochannels:
  - Electron correlation is important
  - Ring currents do not dominate
- Grand canonical Monte Carlo simulations
  - qualitatively reproduces observed changes in Xe lineshapes
- No qualitative differences in Xe lineshapes in
  - aromatic channels vs silicate or phosphate channels

Single crystal experiments

A. Comotti, S. Bracco,L. Ferretti, M. Mauri, R. Simonutti and P. Sozzani Chem Commun 2007, 350-352



Expected change with temperature for Xe in smooth narrow-bore channel

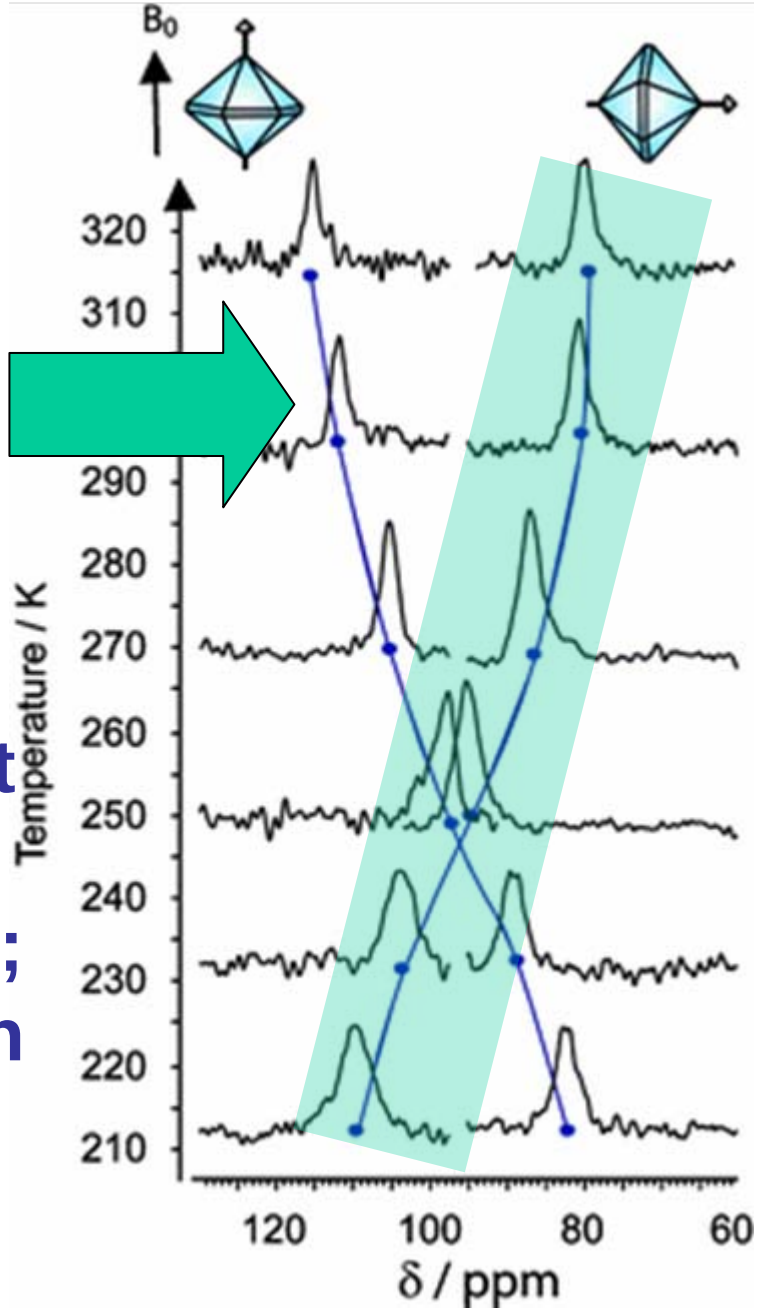


C.J.Jameson & A.C.de Dios
J. Chem. Phys. 116, 3805-3821 (2002)

HP ^{129}Xe NMR

θ

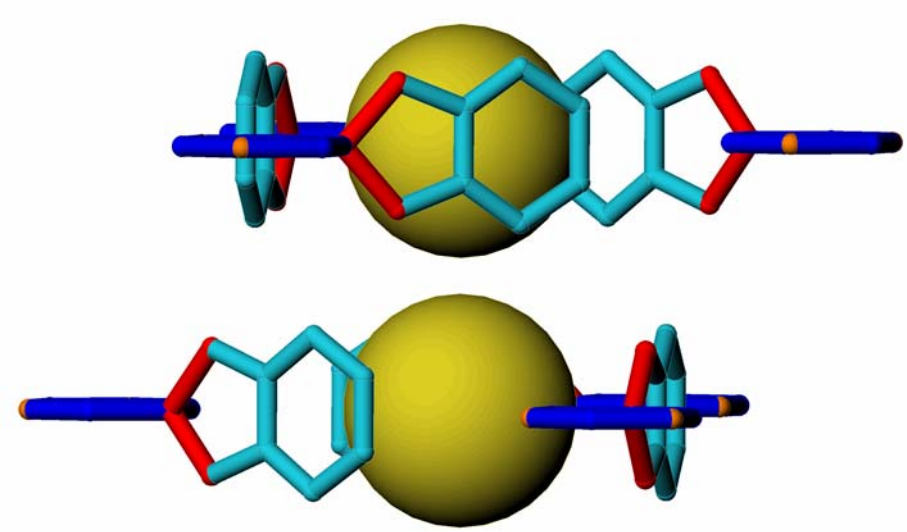
|| is puzzling! expected almost no change with T since σ || not dependent on Xe loading; increases with increasing T WHY?

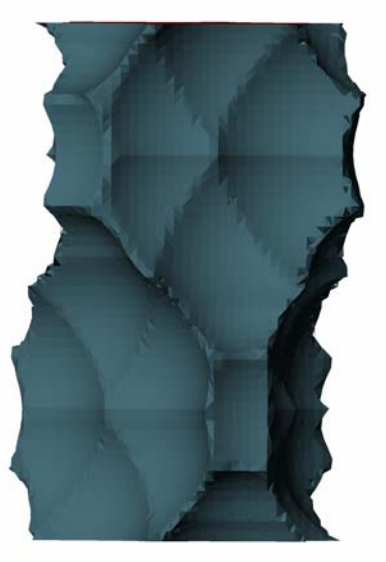


⊥ goes as expected from increasing Xe loading with decrease in T

A. Comotti, S. Bracco, L. Ferretti, M. Mauri, R. Simonutti and P. Sozzani Chem. Commun. 2007, 350-352

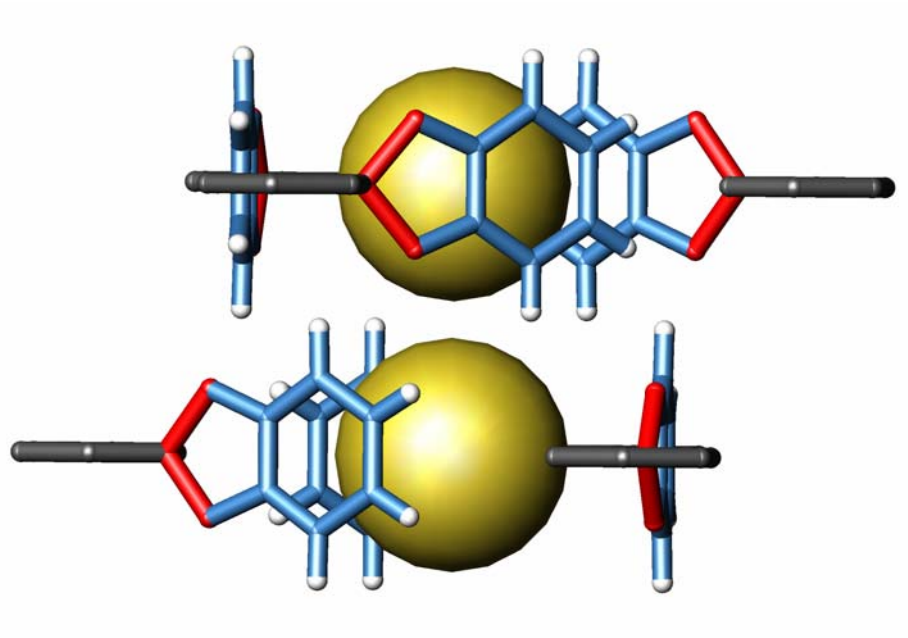
the channel is not a smooth pipe





Graphics courtesy of A. Comotti

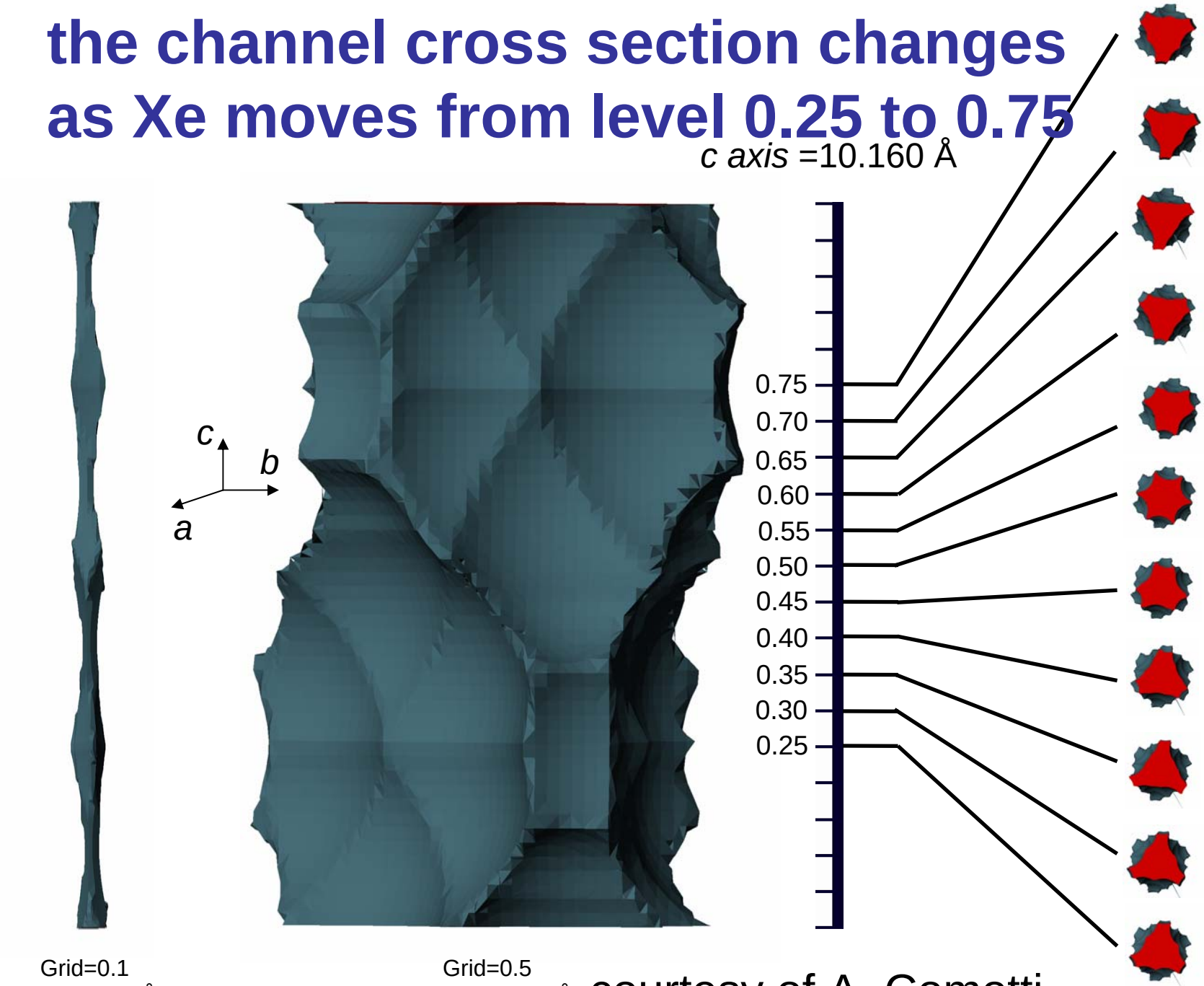
Xe at the “sweet spot” in the center of the triangle,
on the plane at level 0.25 and level 0.75 in the unit cell



level 0.5 is between these two Xe positions

Graphics courtesy of A. Comotti

the channel cross section changes as Xe moves from level 0.25 to 0.75

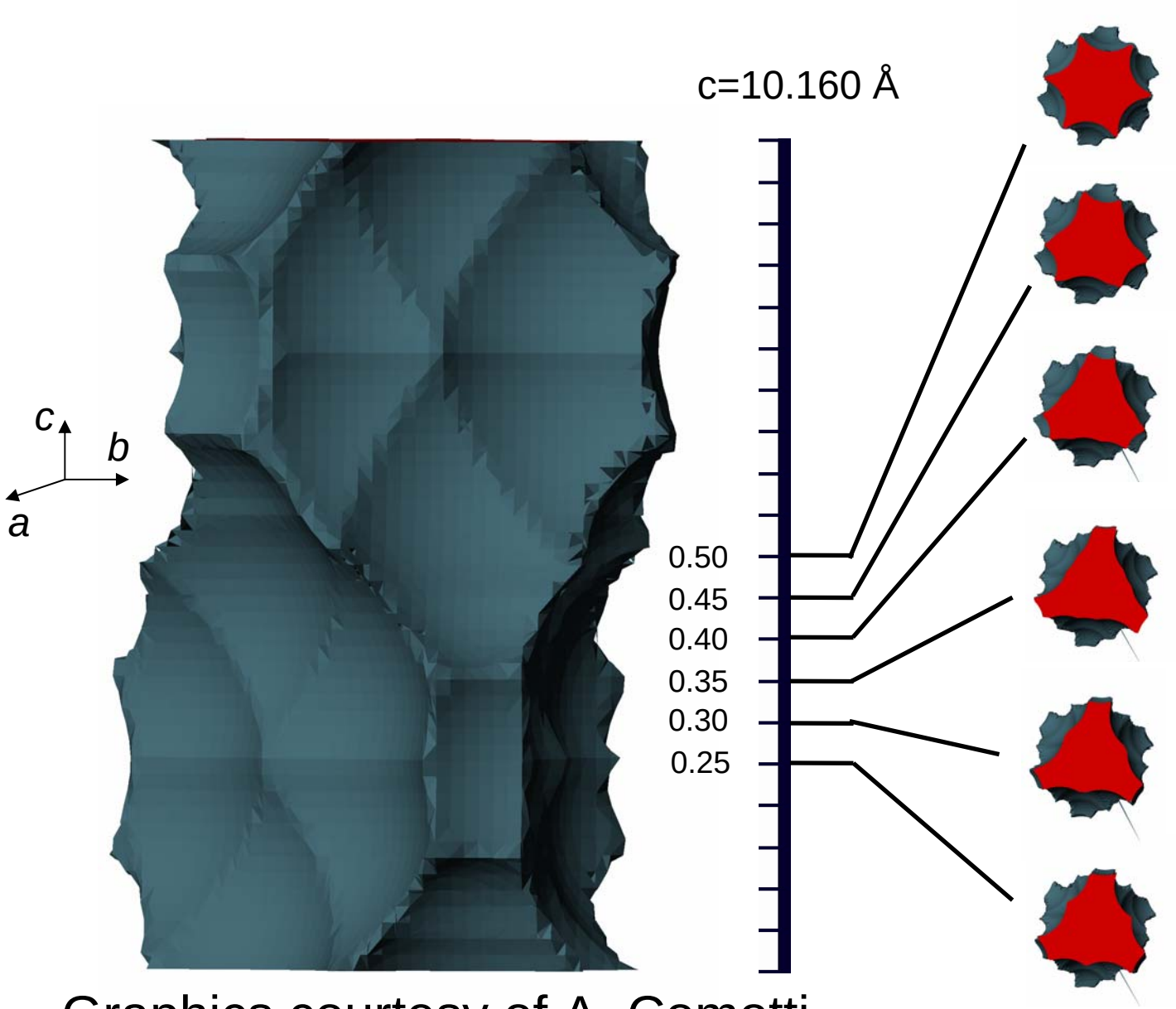


Grid=0.1
radius=2.2 Å

Grid=0.5
radius=0.2 Å

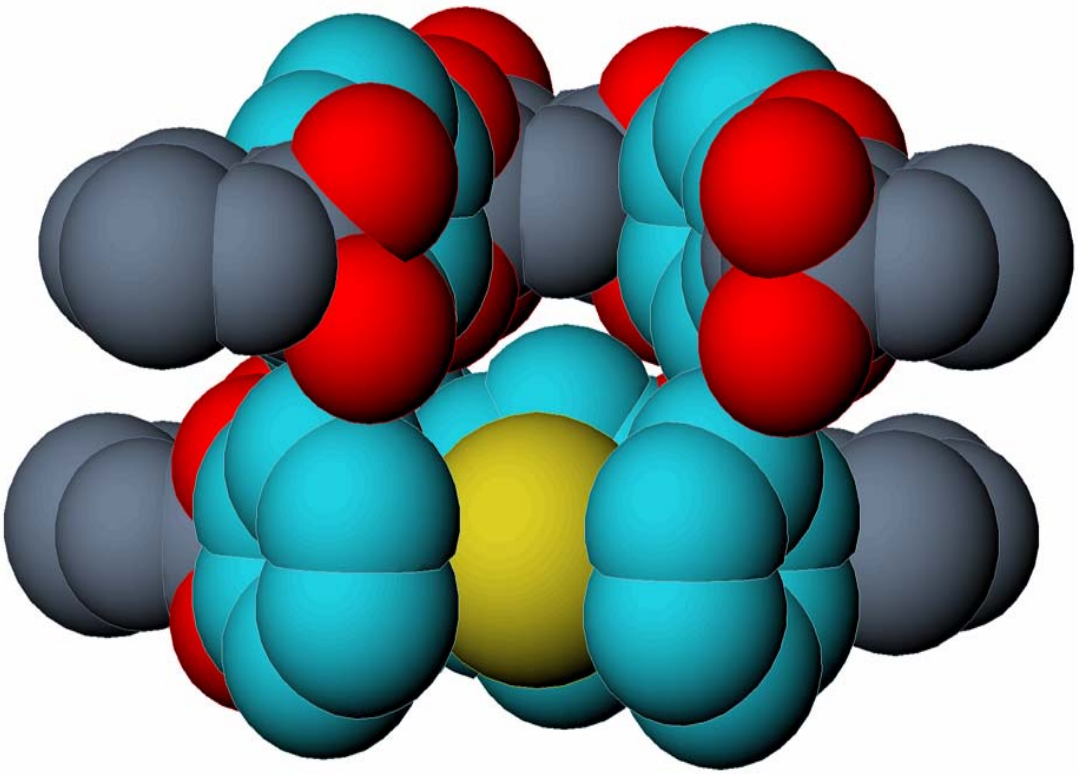
courtesy of A. Comotti

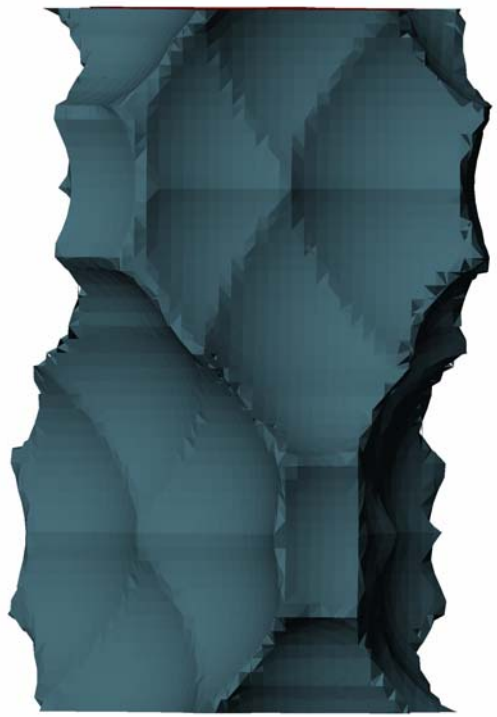
take a closer look



Graphics courtesy of A. Comotti

Our *ab initio* calculations revealed highly deshielded Xe positions at the level of the O atoms

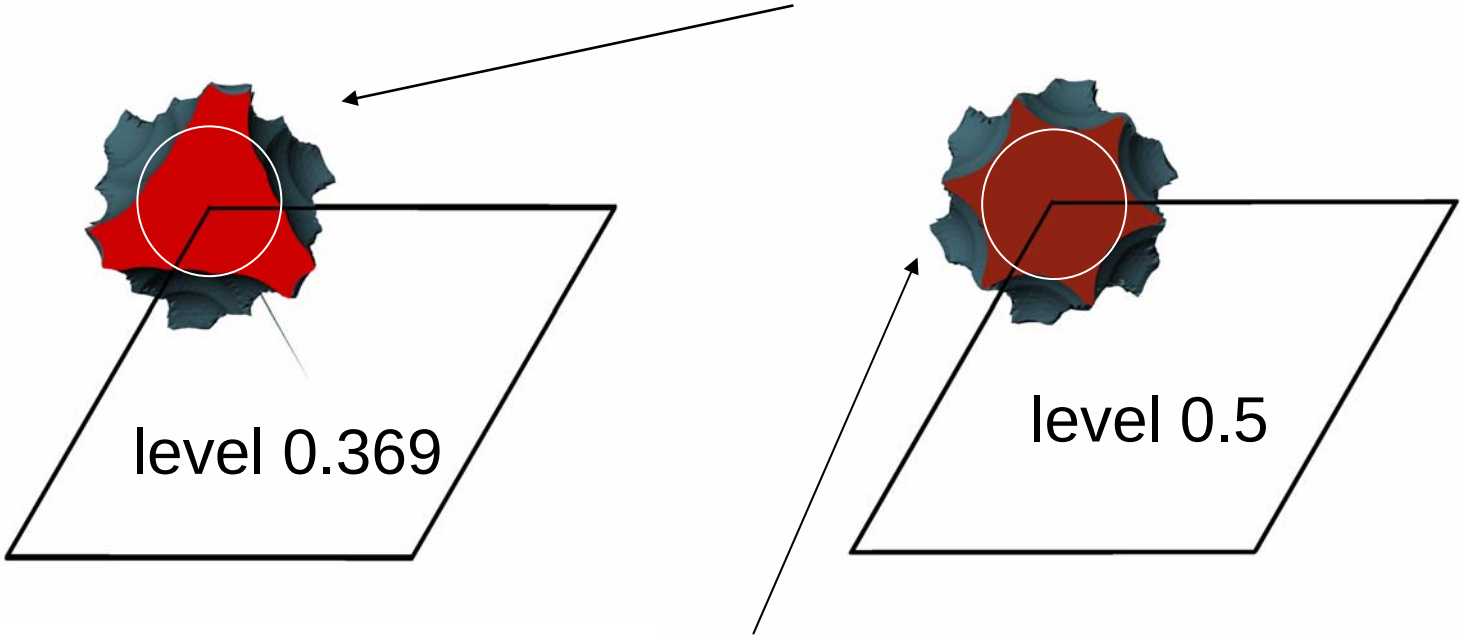




oxygen atoms are at level 0.131 and 0.369

Graphics courtesy of A. Comotti

on the plane of the oxygen atoms we find smaller cross-section of the channel



on the plane at level 0.5 between two layers We find larger cross-section of the channel

radius of the shown circle is 2.1 Å

Graphics courtesy of A. Comotti

Why parallel component of Xe chemical shift tensor increases with increasing temperature

- Highly crowded Xe positions (at levels 0.131 and 0.369)
- Xe atom has to pass through highly crowded (but also highly deshielded) Xe positions at level 0.369 to get from sweet spot at level 0.25 through the less crowded between-layers region at level 0.5 so as to get to the other sweet spot at level 0.75
- At higher temperatures Xe can have higher probability of being found at these highly crowded (and highly deshielded) positions.

Acknowledgments

and thanks to Angiolina Comotti for hosting CJJ at the Department of Materials Science

and P. Sozzani research group