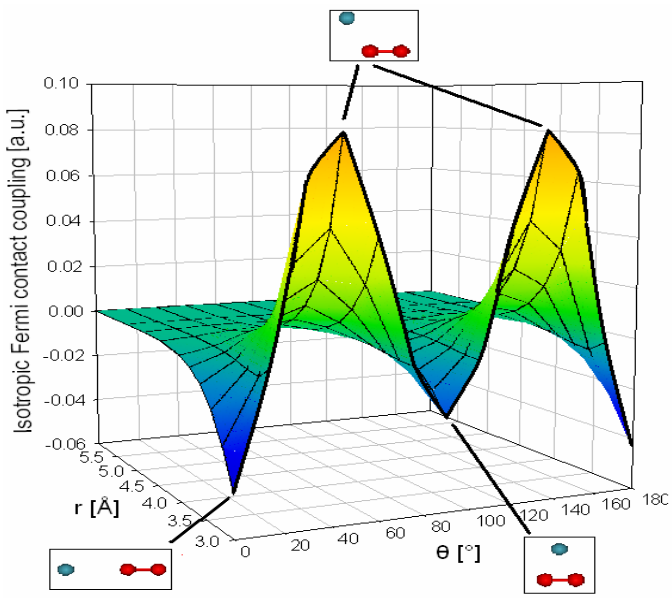


Intermolecular hyperfine tensor for Xe-O_2 and density and temperature dependence of Xe chemical shifts in oxygen gas

Lela Vukovic and Cynthia J. Jameson

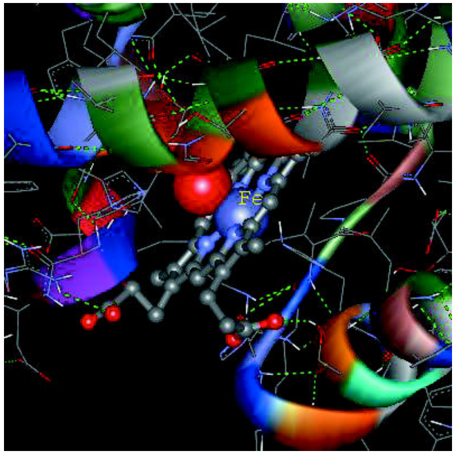
ENC 2005

UIC
University of Illinois at Chicago

Paramagnetic centers play important roles

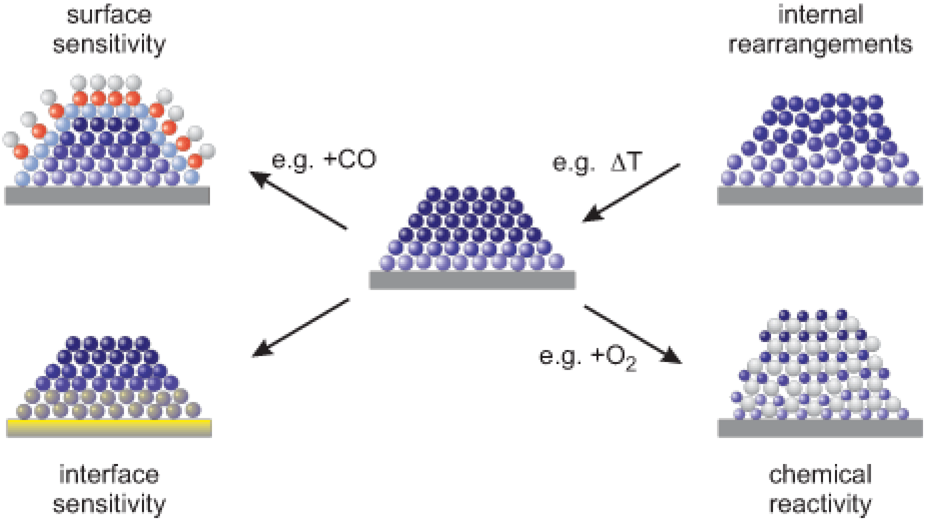
haem proteins:

- catalysis – peroxidases, catalases
- electron transfer – cytochromes
- oxygen transport and storage – globins
- nitric oxide transport – nitrophorin



www.linux-magazin.de

Structure and particularly the interfacial characteristics of the particles are strongly correlated with their magnetic properties.



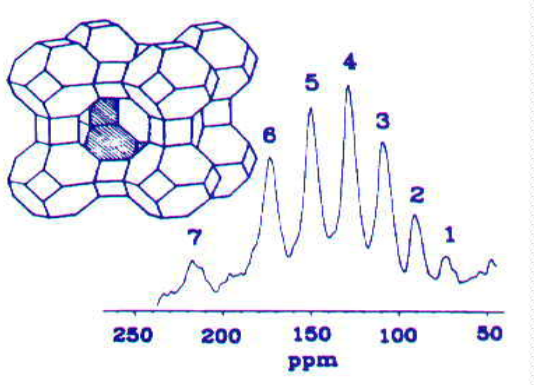
Paramagnetic centers at solid surfaces

(from Chemical Physics Magnetic Resonance Group, Fritz-Haber Institute)

Xe is a good probe of porous materials

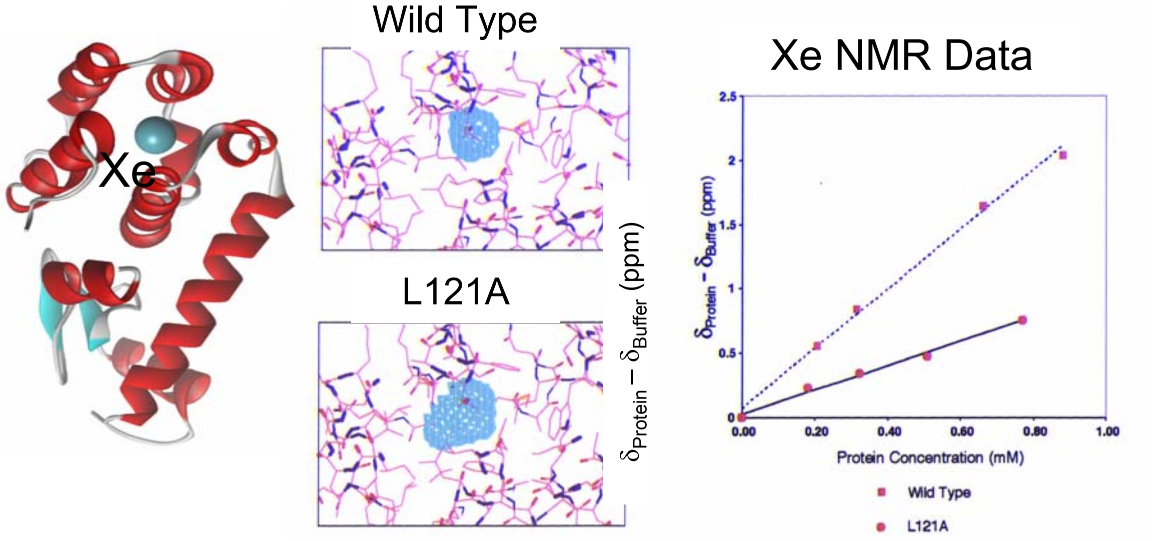
distributions of adsorbed atoms among cages

small differences in amino acids near the pocket



C. J. Jameson, A. K. Jameson, R. Gerald, A. C. de Dios, J. Chem. Phys. 97, 417 (1992).

Xe in zeolite NaA



S.M. Rubin, M.M. Spence, B.M. Goodson, D.E. Wemmer, A. Pines.
Proc. Natl. Acad. Sci. **97** (17) 9472-9475 (2000)

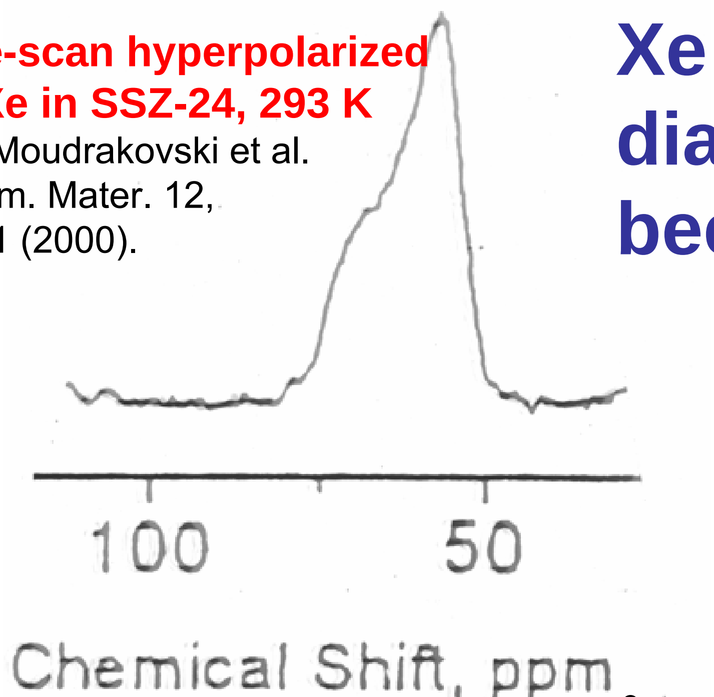
Xe in protein pocket

Quantitative understanding of Xe chemical shifts in porous diamagnetic materials has been demonstrated

EXPERIMENT

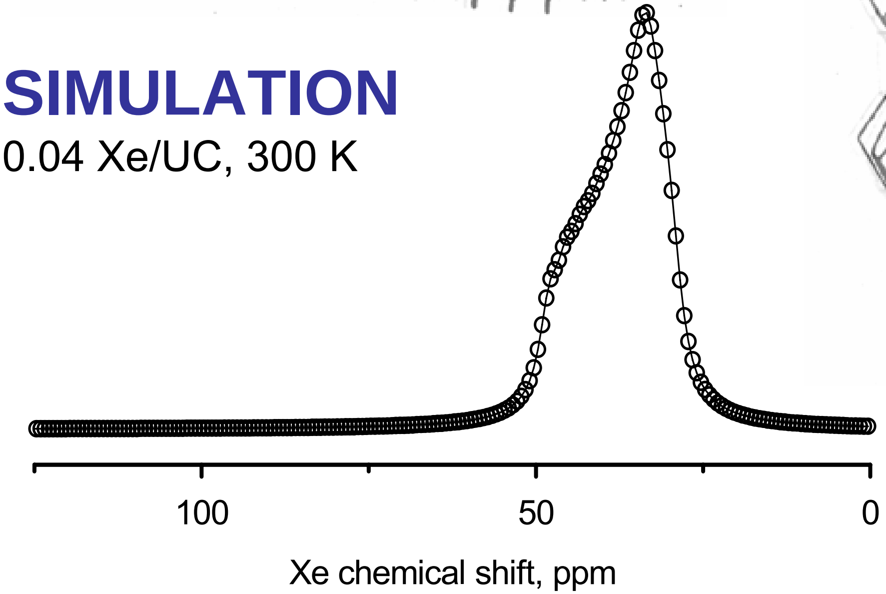
one-scan hyperpolarized ^{129}Xe in SSZ-24, 293 K

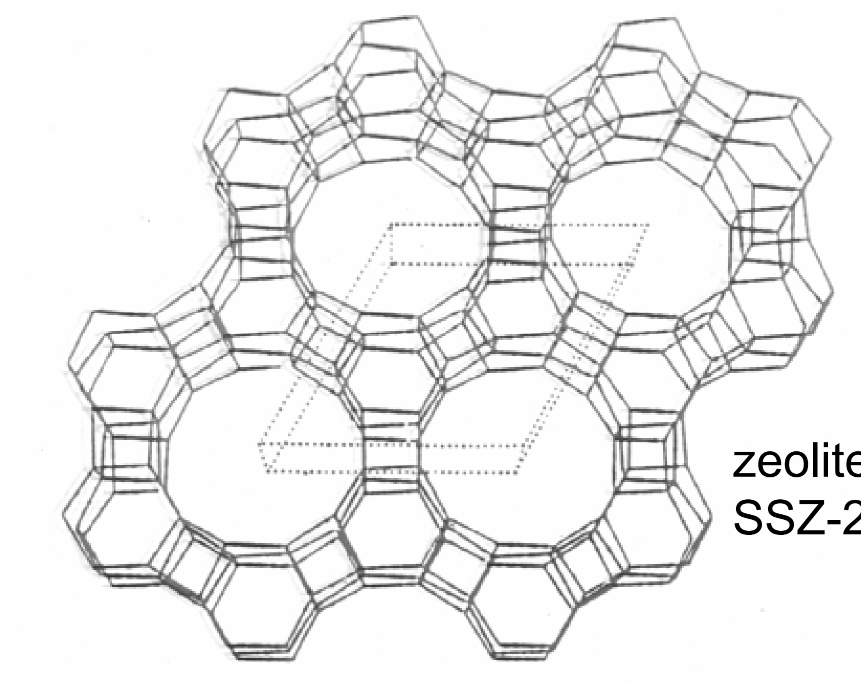
I.L. Moudrakovski et al.
Chem. Mater. 12,
1181 (2000).



SIMULATION

0.04 Xe/UC, 300 K



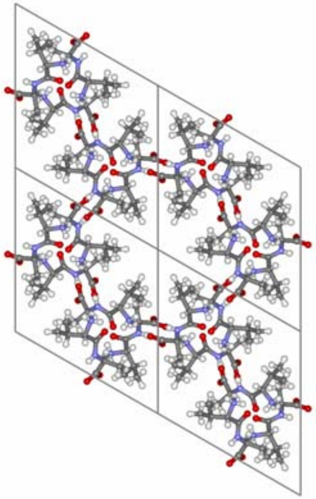


zeolite
SSZ-24

GCMC simulation uses the same shielding and potential functions as for Xe in silicalite.

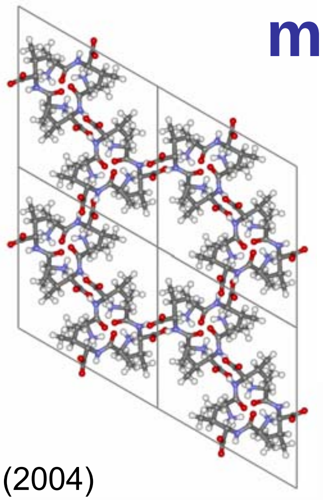
C.J. Jameson, JACS, 126, 10450 (2004)

in channels of molecular crystals



L-Val-L-Ala

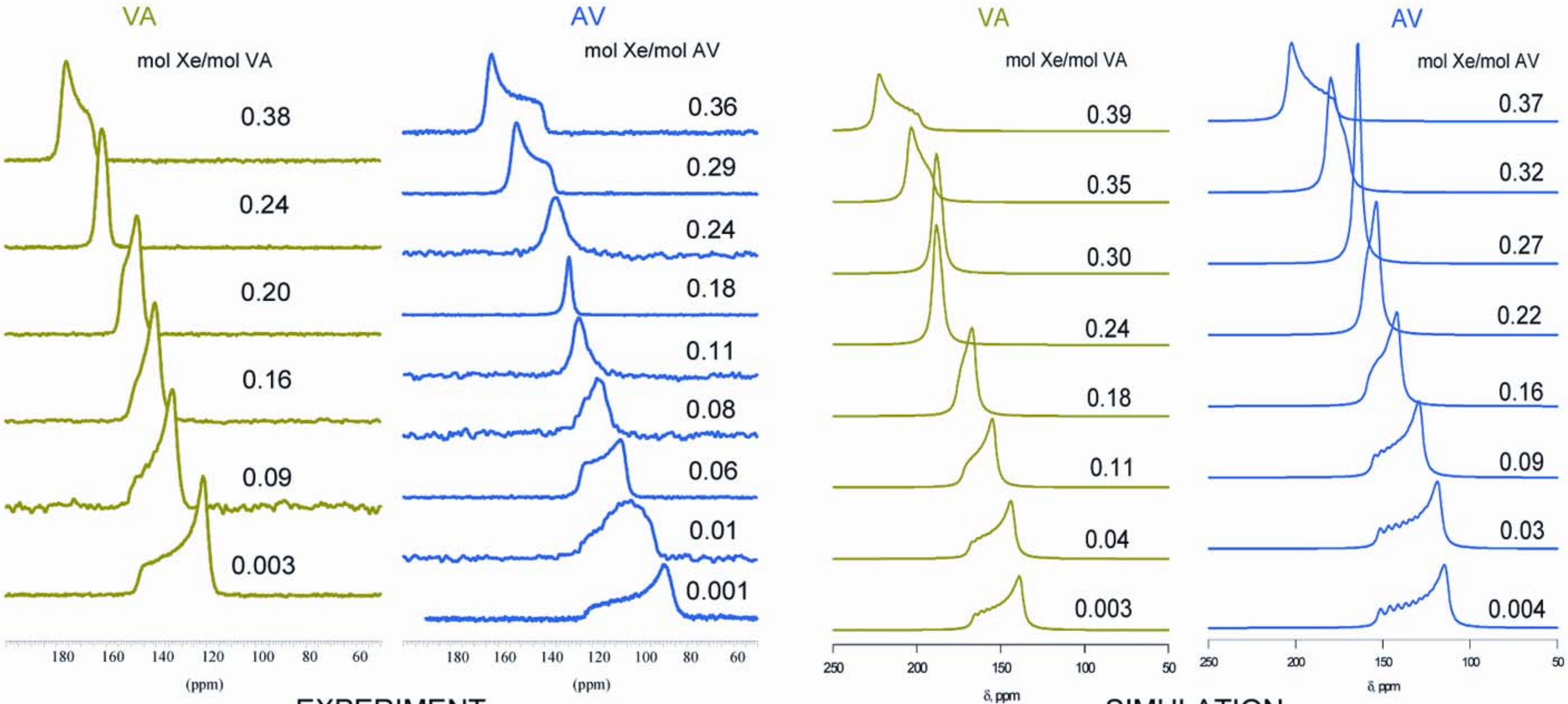
VA



L-Ala-L-Val

AV

PNAS 101, 17924 (2004)

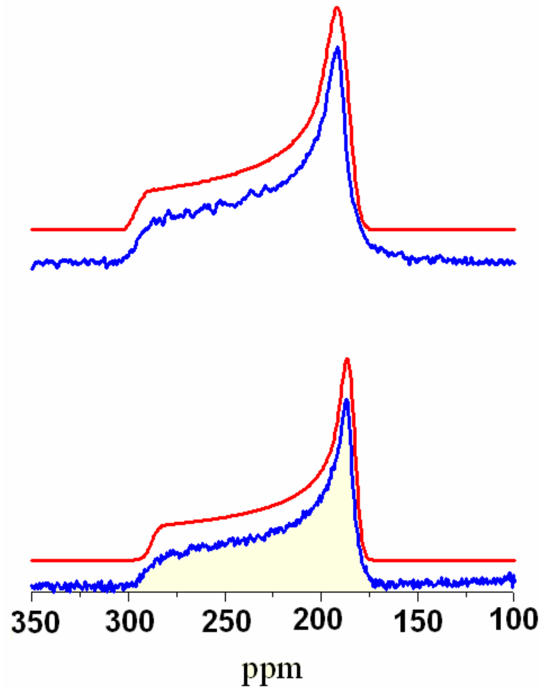


EXPERIMENT

SIMULATION

Xe NMR spectra

Xe as a probe of porous materials with paramagnetic centers?



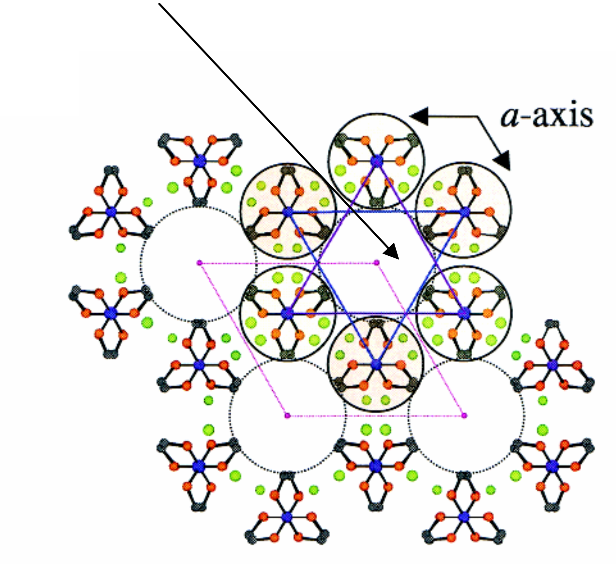
Wasylishen et al., 2004

[Rh(en)3]Cl3 crystal

[Co(en)$_3$]Cl$_3$ crystal

diamagnetic

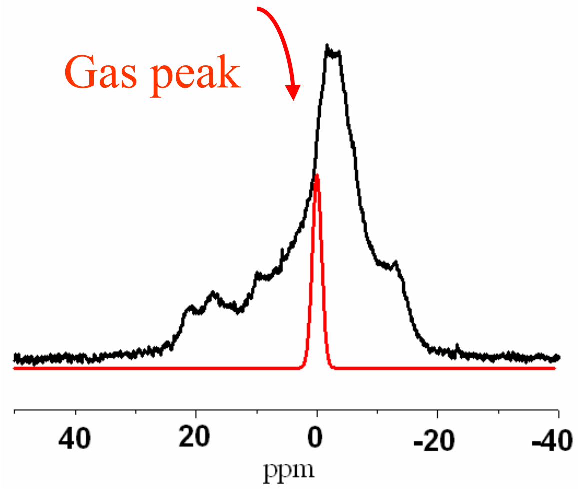
Xe inside these channels



same crystal structure

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

1000 scans using ~10% hyperpolarized xenon gas



Wasylishen et al., 2004

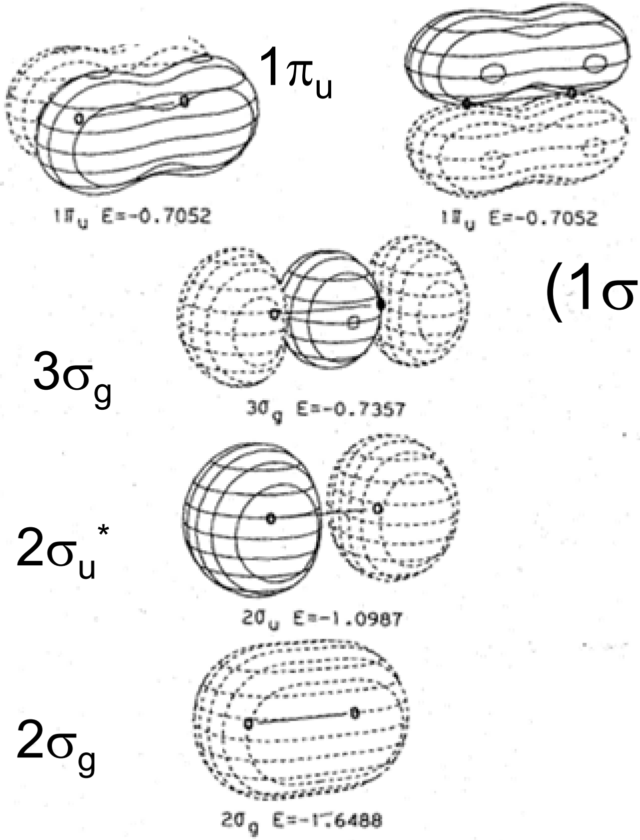
[**Cr**(en)$_3$]Cl$_3$ crystal

paramagnetic

Xe can tell the difference!

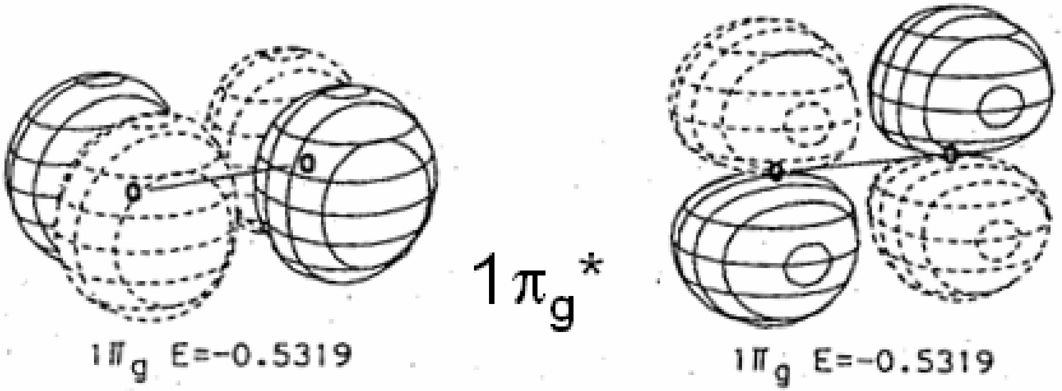
Study Xe in the presence of a paramagnetic center

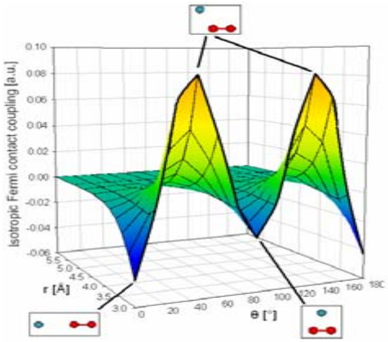
Our model system:



O_2 molecule has two unpaired electrons

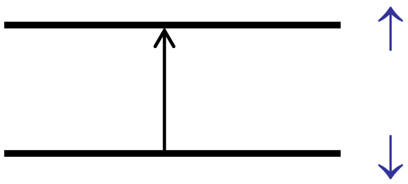
$(1\sigma_g)^2(1\sigma_u^*)^2(2\sigma_g)^2(2\sigma_u^*)^2(3\sigma_g)^2(1\pi_u)^4\mathbf{(1\pi_g^*)^2}$

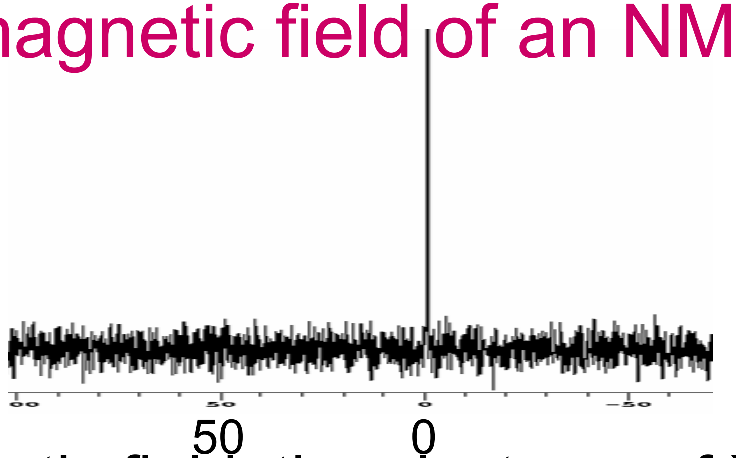




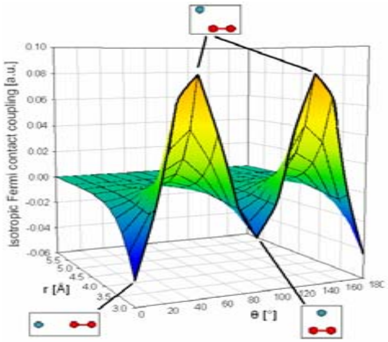
The Xe atom in an NMR experiment

The Xe nucleus is a magnetic dipole that has two states in the presence of the magnetic field of an NMR spectrometer.



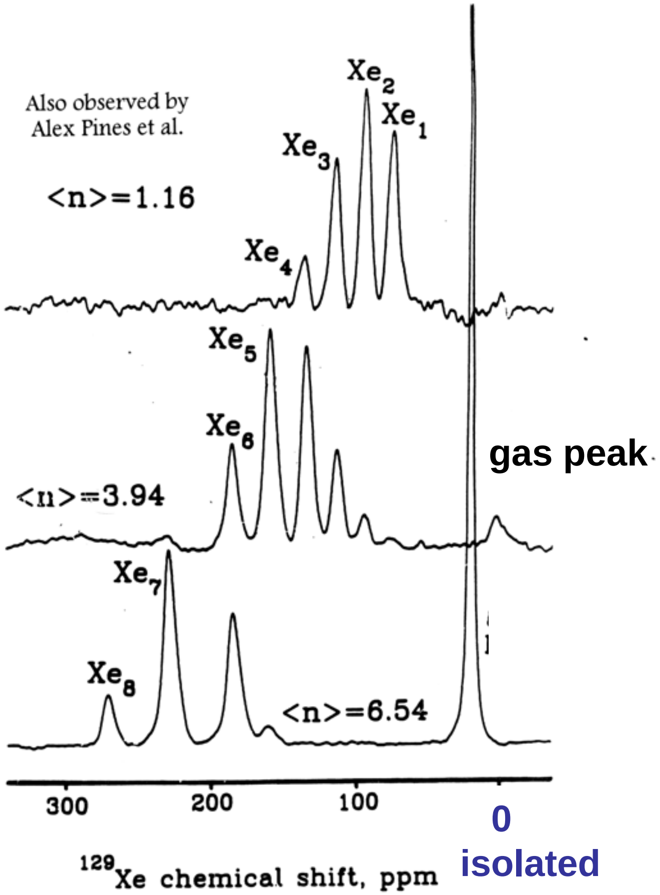


In the presence of a magnetic field, the electrons of Xe atom provide a diamagnetic response, that is, a shielding effect, the characteristic "**NMR chemical shift**" of the free Xe atom. A sample of very very low density Xe gas serves as an NMR sample of individual non-interacting Xe atoms, a reference which we can call 0 ppm on the Xe chemical shift scale.



The Xe atom in an NMR experiment

The Xe chemical shift is very sensitive to the presence of neighbors.



0

isolated Xe atom

Xe atom in a magnetic field in the presence of a diamagnetic molecule,N_2

A Xe atom in the presence of a diamagnetic molecule such as N_2 experiences an intermolecular deshielding effect that can be calculated quantum mechanically.

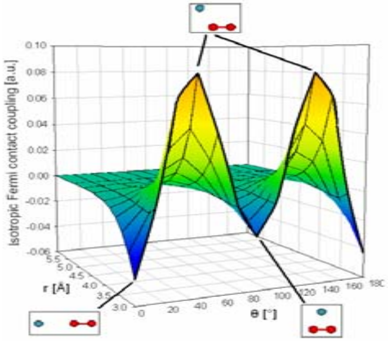
This intermolecular response leads to a positive Xe chemical shift compared to the reference Xe atom. The chemical shift increases with density, with increasing probability of encounters between Xe and N_2 in the gas.

$$\sigma(T,\rho_{N2}) = \sigma(\text{Xe atom}) + \boldsymbol{\sigma_1(T)\,\rho_{N2}} + \ldots$$

The **density coefficient $\sigma_1(T)$** is the ‘per molecule average’ over such probabilities, if ρ_{N2} is a number density:

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

Xe in the presence of a paramagnetic molecule O_2

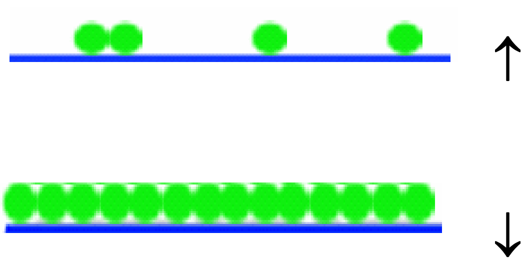


There is an <u>additional interaction</u> for Xe in O_2 because of the unpaired electrons:

the hyperfine shift

The mechanism of the hyperfine shift

The average electron spin magnetic moment (along the B_0 direction) of unpaired spins depends on B_0 and the temperature



The **relative populations** of electron spin states at a given temperature determine the **average** electron spin magnetic moment along B_0

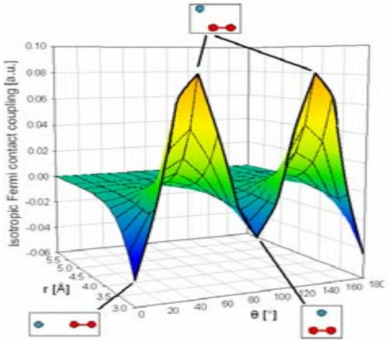
The interaction between the Xe nucleus and the unpaired electrons of O_2 molecule is:

Interaction Energy = $\mathcal{A}\mathbf{S}\bullet\mathbf{I}$

providing a fractional correction to the local magnetic field at the nucleus:

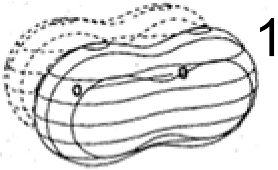
$$\Delta B/B_0 = -(g_e\,\mu_B/3kT)\bullet(\mathcal{A}/g_{Xe}\mu_N)$$

O_2, a paramagnetic molecule

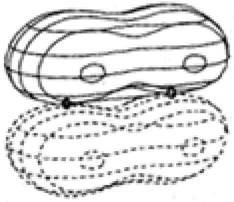


O_2 molecule has two unpaired electrons

$1\pi_u$



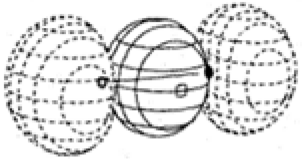
1π u E=-0.7052



1π u E=-0.7052

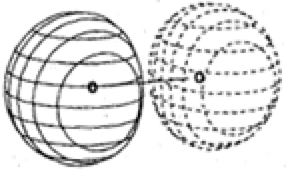
$$(1\sigma_g)^2(1\sigma_u{}^*)^2(2\sigma_g)^2(2\sigma_u{}^*)^2(3\sigma_g)^2(1\pi_u)^4\mathbf{(1\pi_g{}^*)^2}$$

$3\sigma_g$



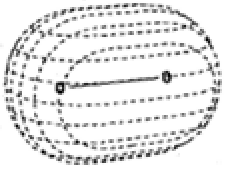
3σ g E=-0.7357

$2\sigma_u{}^*$

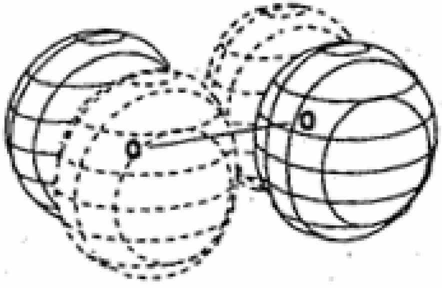


2σ u E=-1.0987

$2\sigma_g$

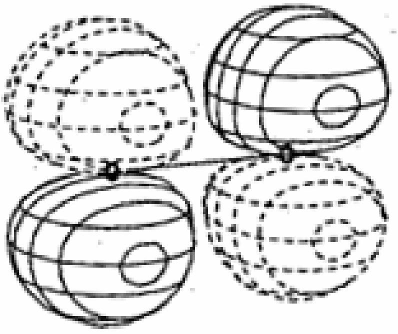


2σ g E=-1.6488



1π g E=-0.5319

$1\pi_g{}^*$



1π g E=-0.5319

Quantum Mechanical Calculations

For the system Xe@O_2 , we calculate quantum mechanically

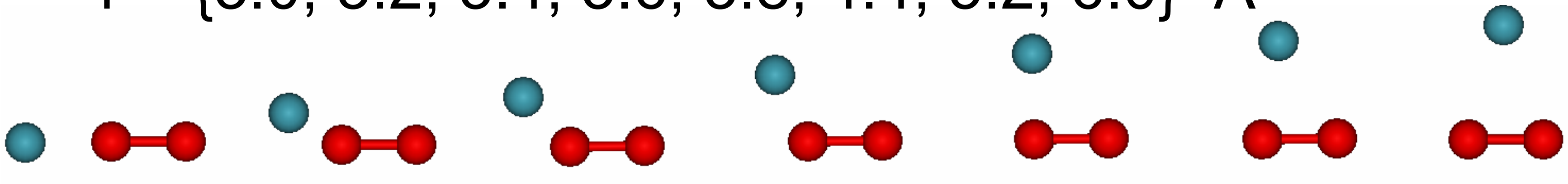
the net electron spin density at the position of the Xe nucleus, or the $\mathcal{A}$ tensor itself .

We do this at various distances R and angles θ.

Configurations:

$\theta = \{0, 15, 30, 45, 60, 75, 90\}$ º

$r = \{3.0, 3.2, 3.4, 3.6, 3.8, 4.4, 5.2, 6.0\}$ Å



θ=0º

θ=90º

Using 240 basis functions on Xe and 80 on O_2.

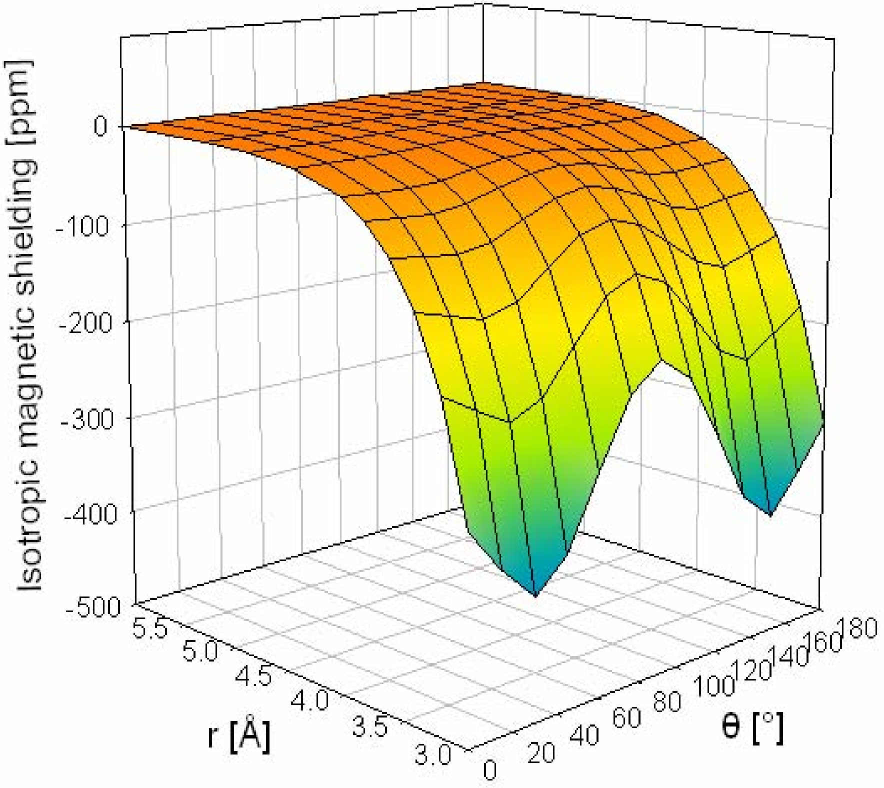
Quantum mechanical calculations of **intermolecular shielding**

Xe atom in the presence of O_2 experiences

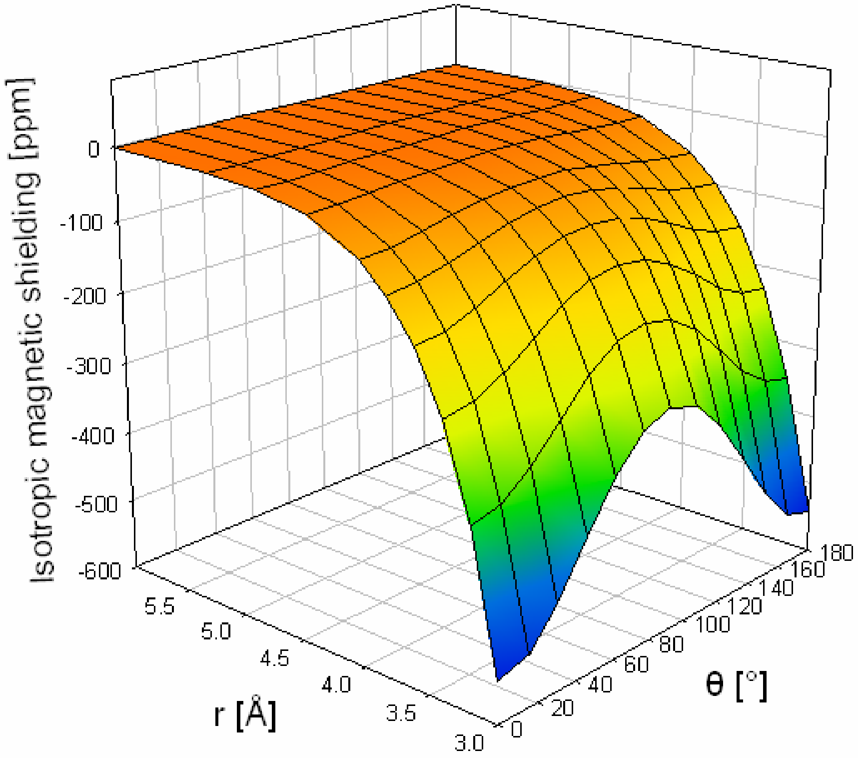
a very similar intermolecular deshielding effect

as for Xe in diamagnetic N_2

- Distance and angle dependence
- Magnitudes

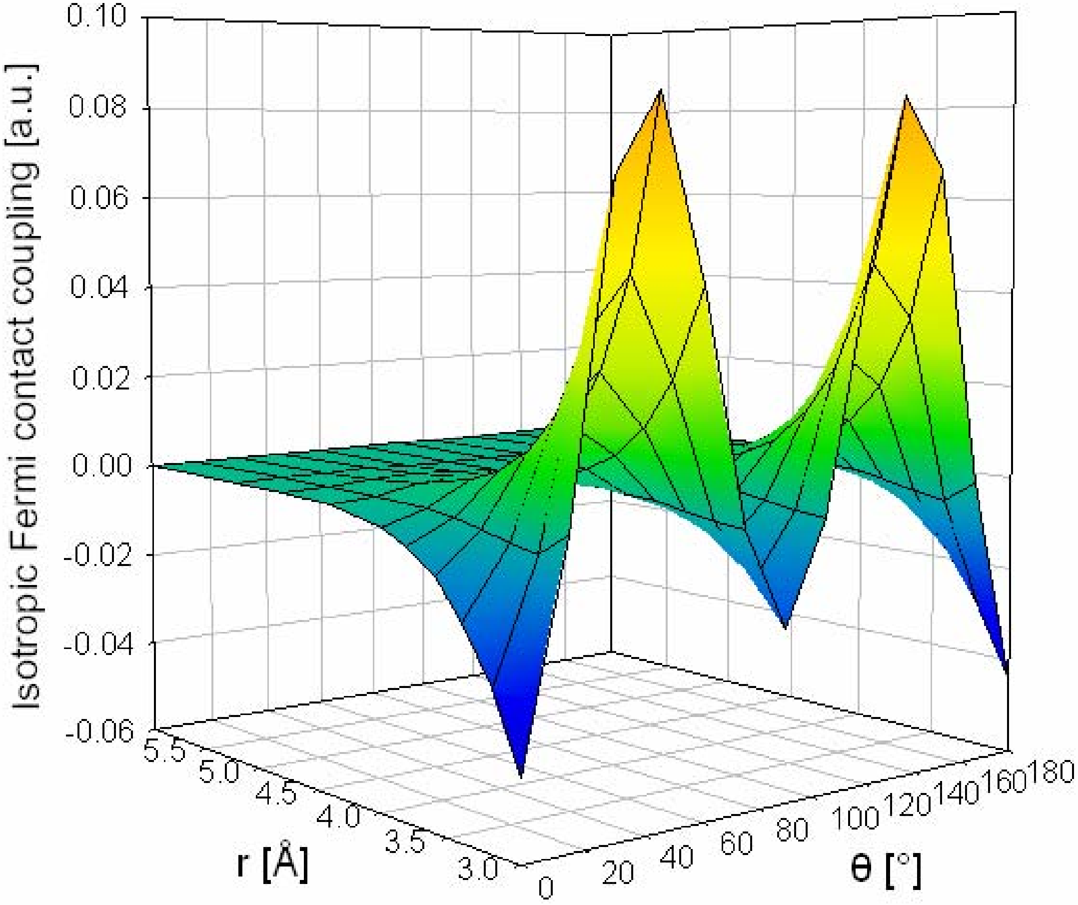


$Xe@O_2$



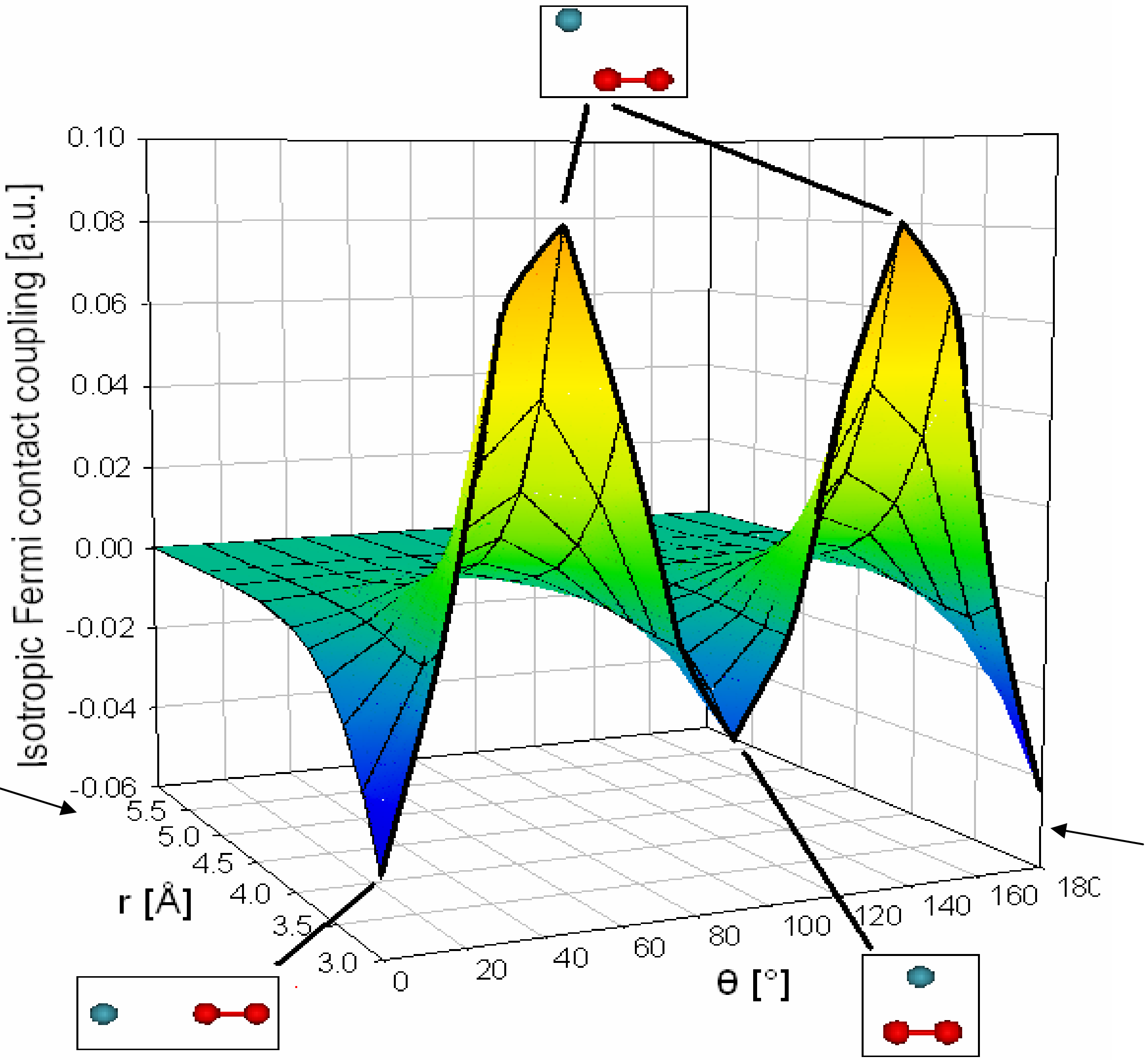
$Xe@N_2$

Quantum mechanical calculations of the **hyperfine interaction** for Xe@O_2



Isotropic Fermi contact coupling surface

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

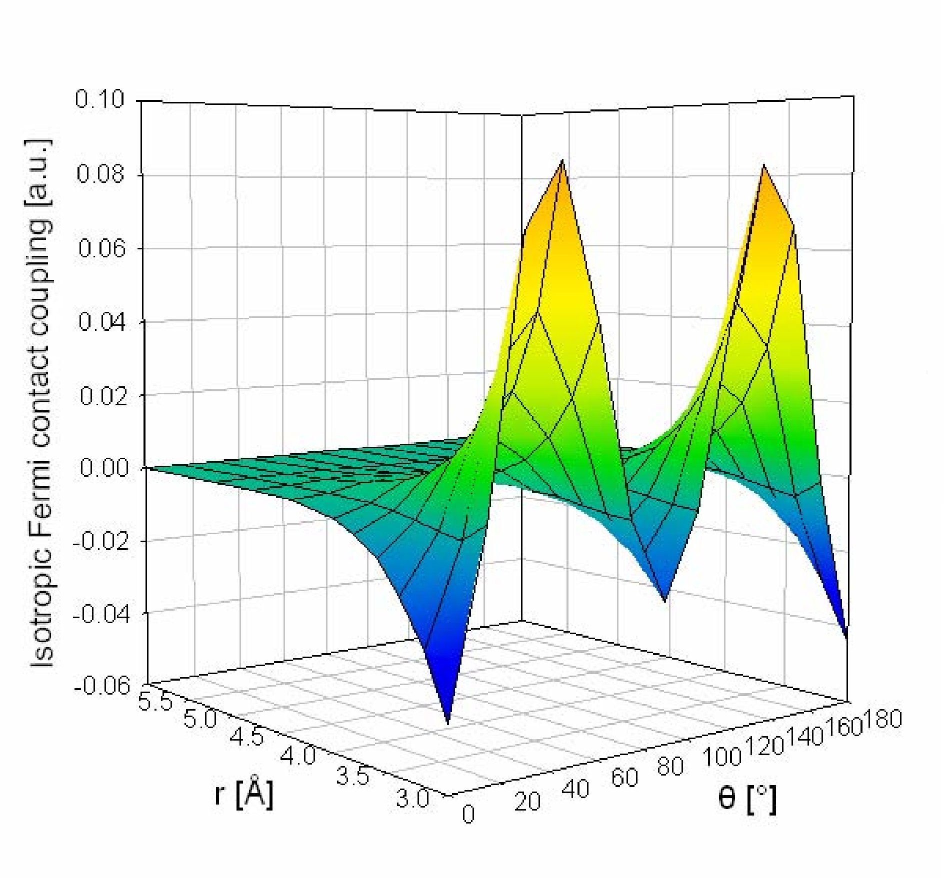


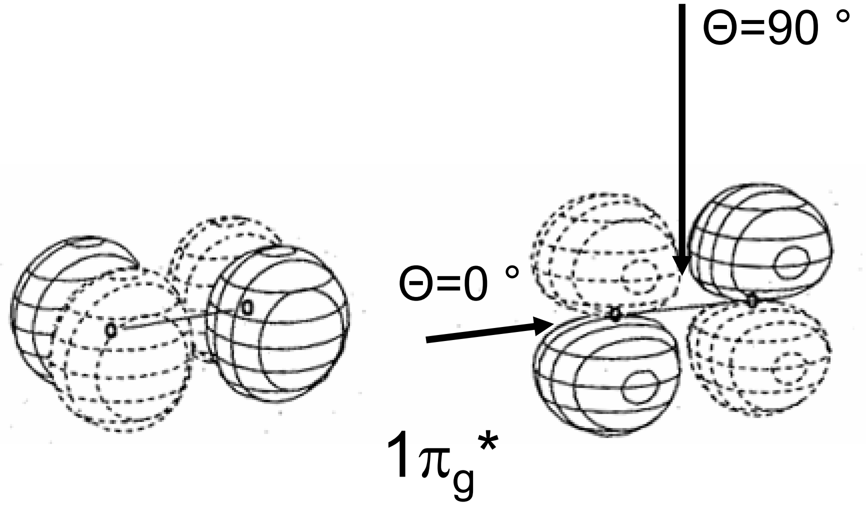
distance

angle

Isotropic part of the hyperfine tensor

Isotropic part of the hyperfine tensor for Xe@O_2





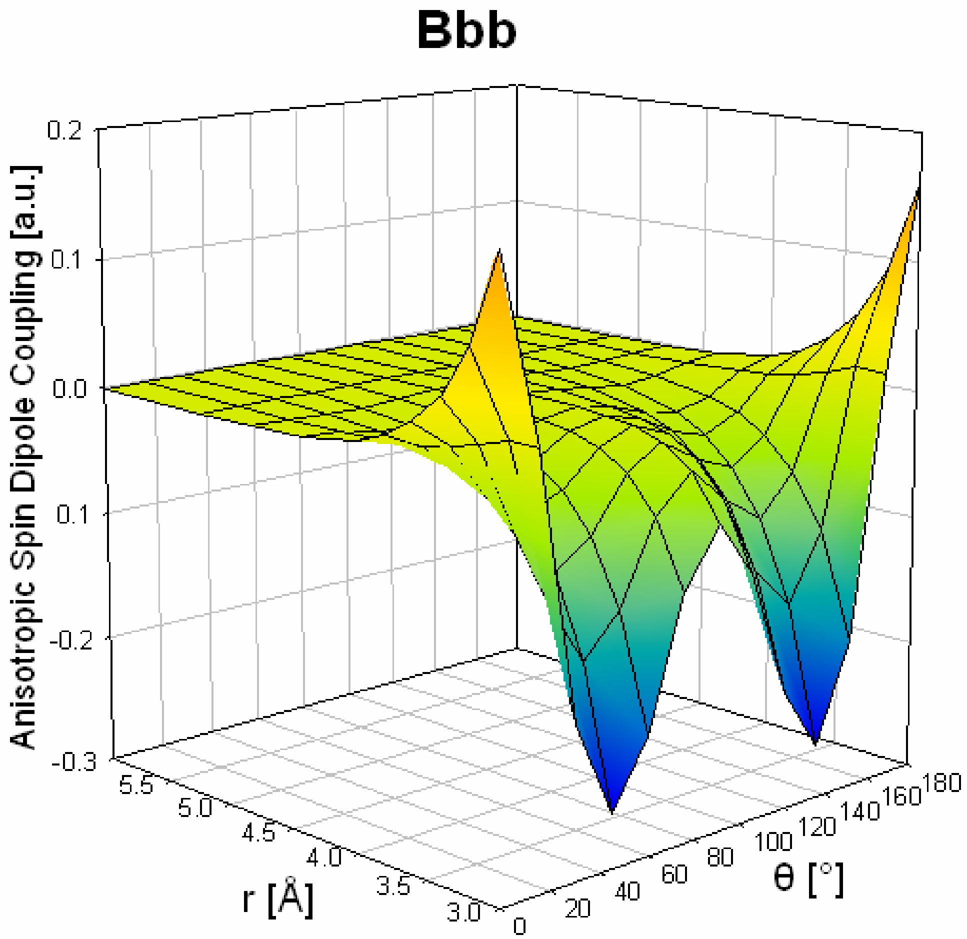
Minima occur at the angles which coincide with the nodal planes of the O_2 molecule.

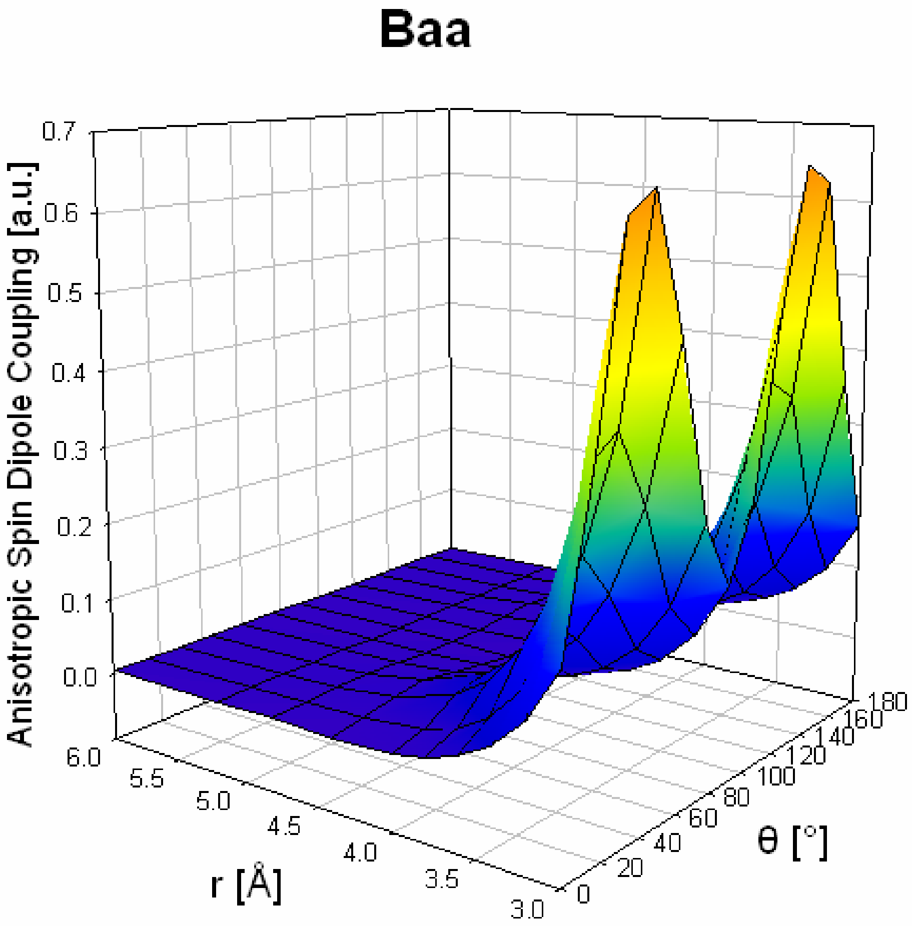
Angle dependence:

maximum at **θ = 45°**

minimum at **θ = 0°, 90 °**

The dipolar part of the hyperfine tensor:

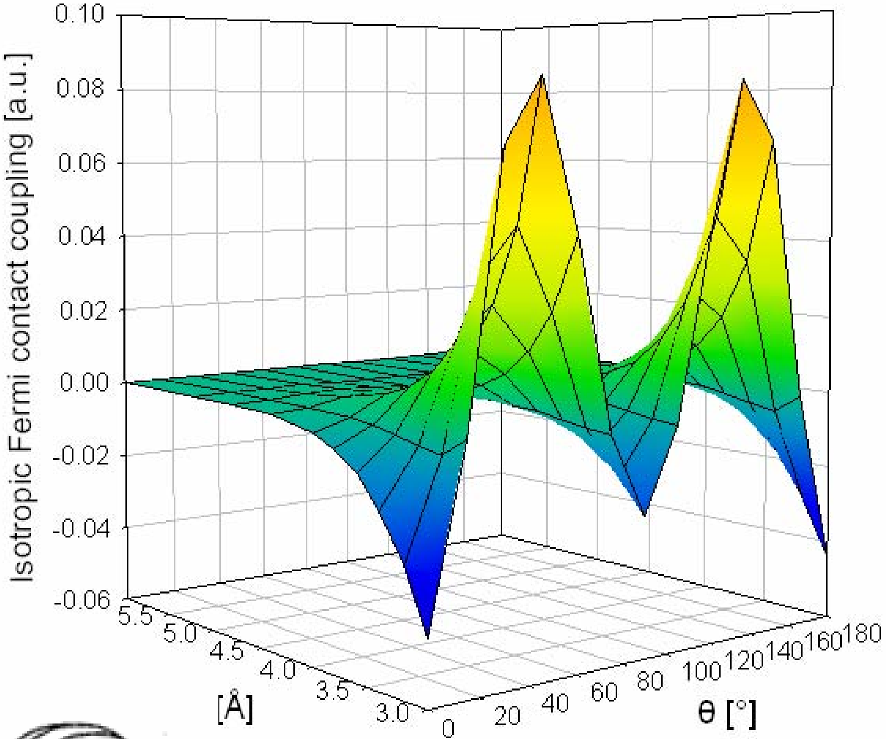


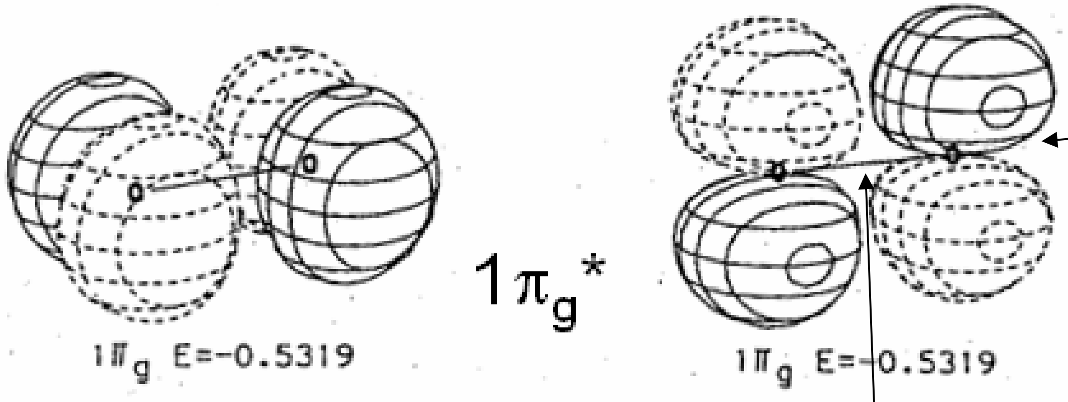


Two of the principal components of the traceless tensor. **The dipolar part is relevant to line shape of Xe in channels with paramagnetic centers.**

Why the angle dependence?

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





$1\pi_g^*$

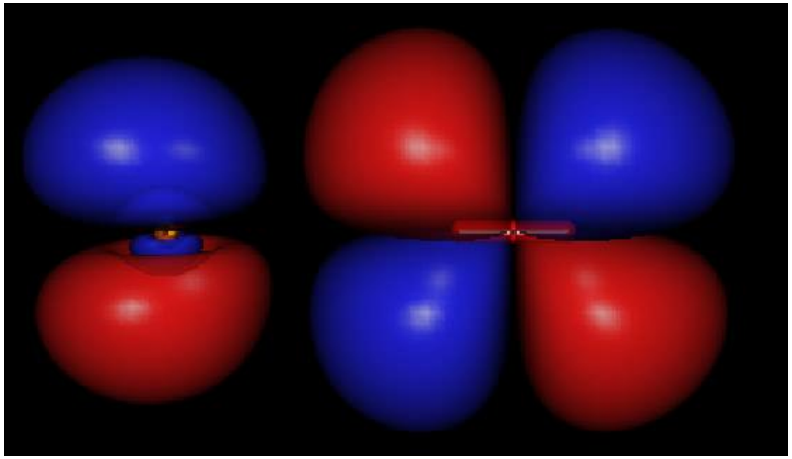
Xe (θ=0º)

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

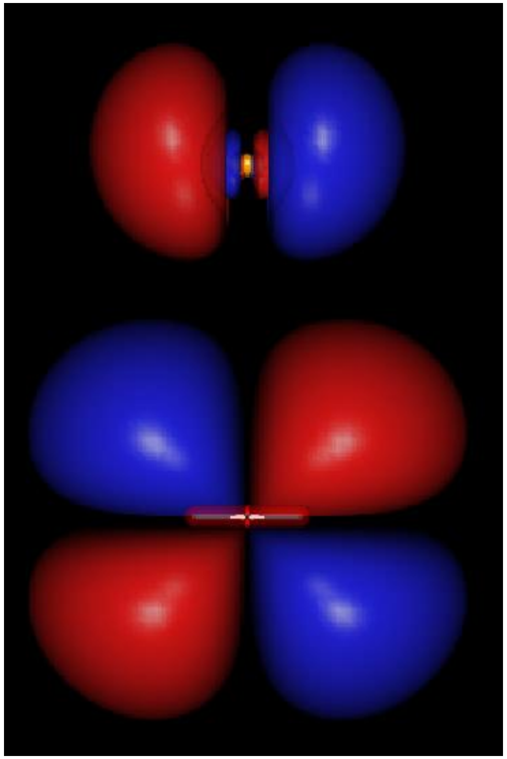
BEST at 45º !!

Xe (θ=90º)

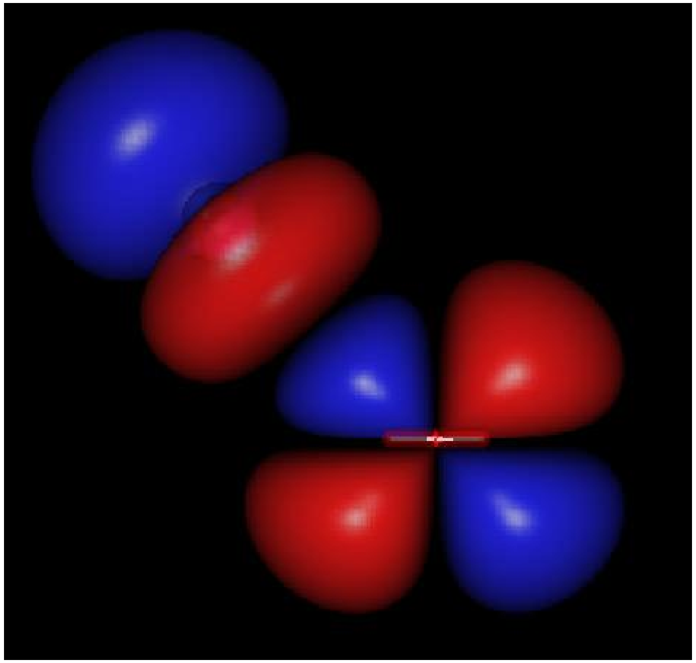
Largest contribution to spin density comes from this MO in the XeO$_2$ complex.



Xe-O$_2$, 180^{o} orientation, $r_{Xe\text{-}O2}$ = 4.0 Å

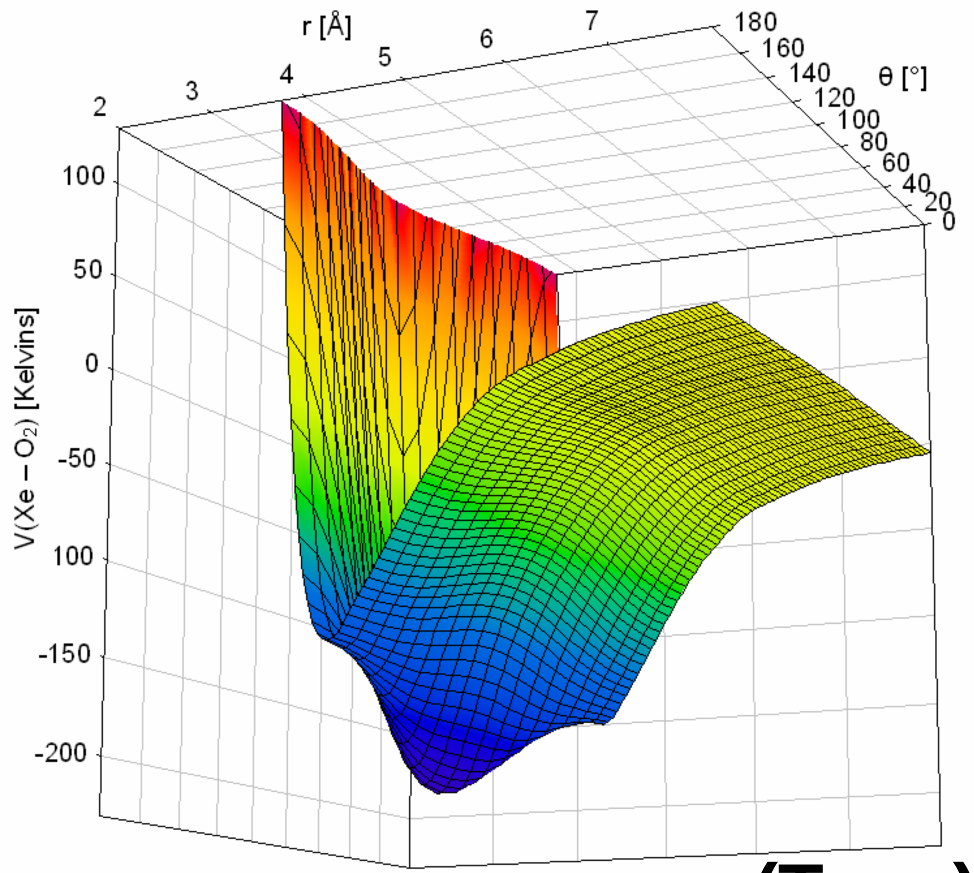


Xe-O$_2$, 90^{o} orientation, $r_{Xe\text{-}O2}$ = 4.0 Å



Xe-O$_2$, 45^{o} orientation, $r_{Xe\text{-}O2}$ = 4.0 Å

Testing the calculations



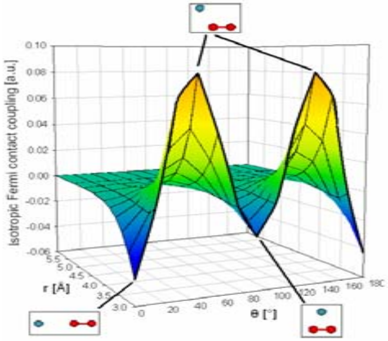
High quality potential function from:
V. Aquilanti, D. Ascenzi, D. Cappelletti, M. de Castro, and F. Pirani, J. Chem. Phys. 109, 3898 (1998)

Using this potential energy function, **$V(R,\theta)$**, the hyperfine tensor and shielding values are averaged over all configurations. The average is expressed as the density coefficient of the chemical shift.

$$\sigma(T,\rho_{O2}) - \sigma(\text{Xe atom}) = \sigma_1(T)\rho_{O2} + \ldots$$

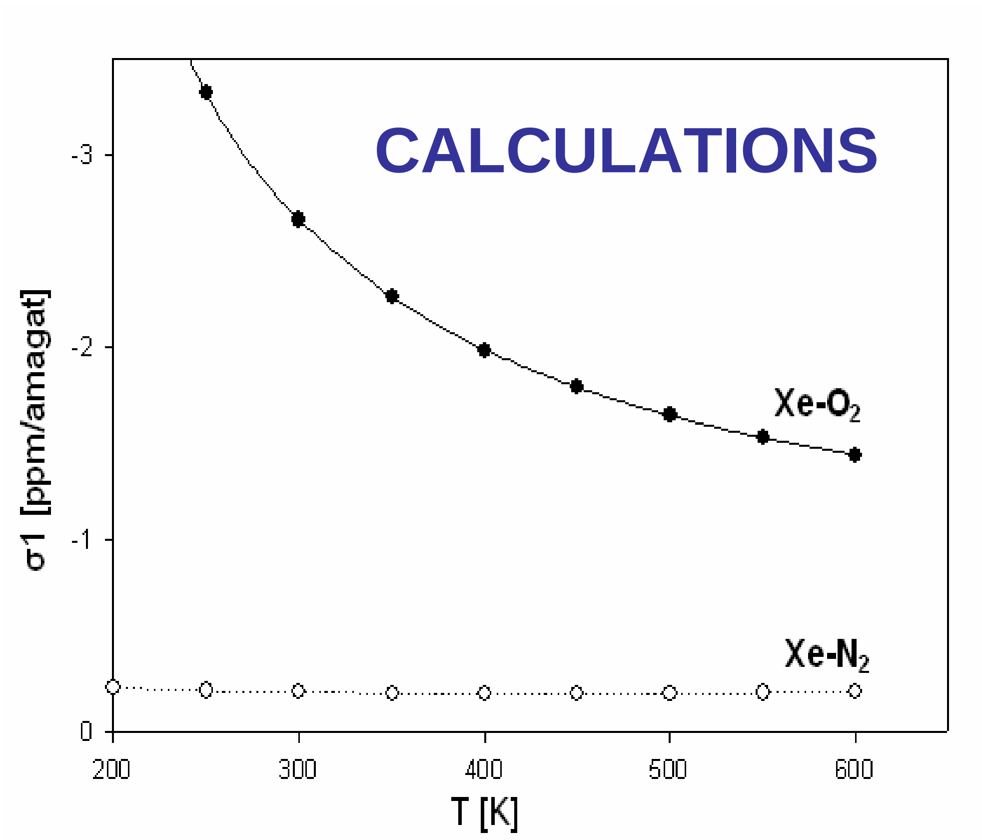
$$\sigma_1(T)_{diam} = 2\pi\int\{\sigma(R,\theta) - \sigma(\infty)\}\, e^{-V(R,\theta)/kT} R^2 dR$$

$$\Delta B/B_0 = -\text{ constant}^* \int\{\rho_{spin}(R,\theta) - \rho_{spin}(\infty)\} e^{-V(R,\theta)/kT} R^2 dR$$

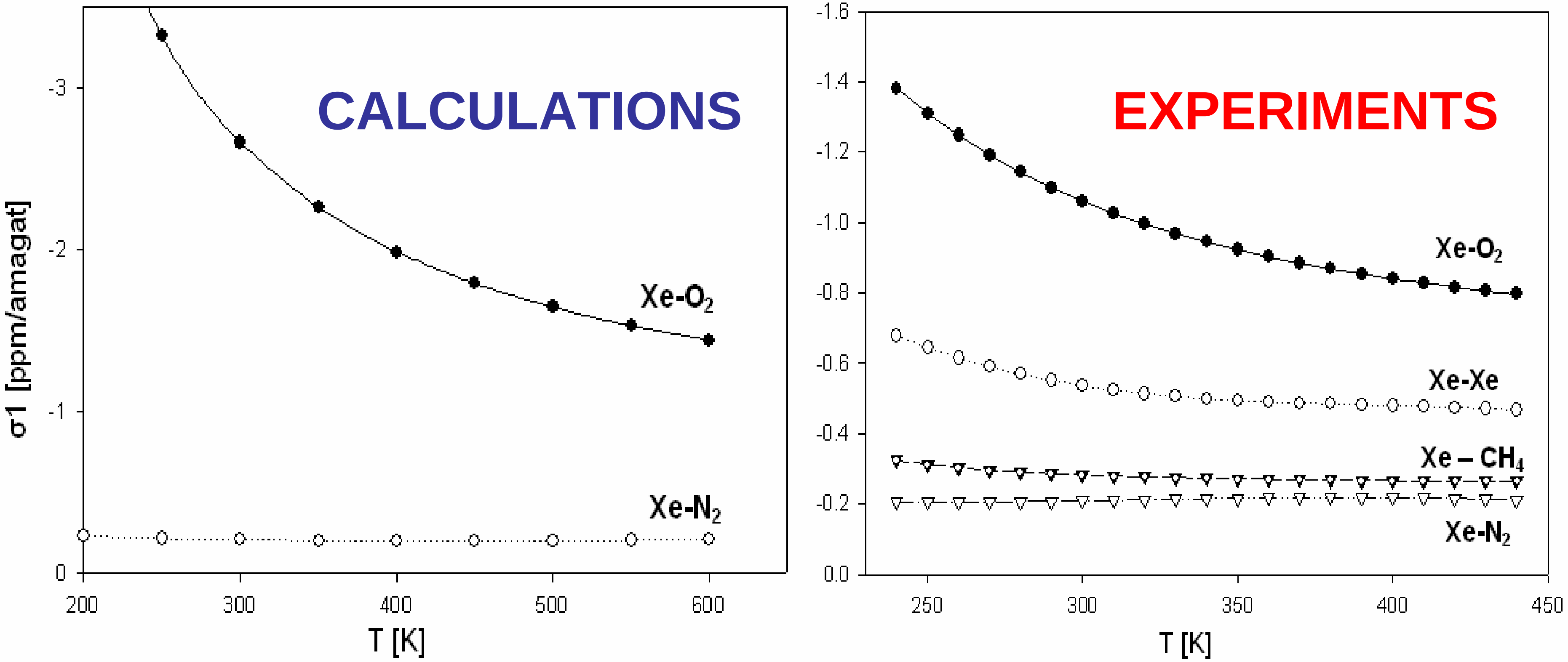


Averaging over all $Xe@O_2$ configurations

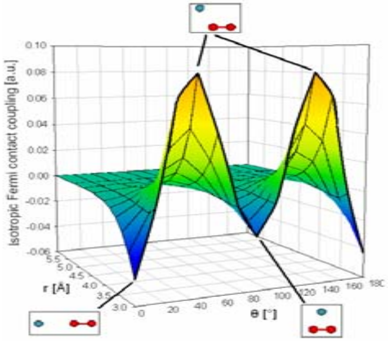
Averaging over all $Xe@O_2$ configurations, we obtain both (a) the usual chemical shift response to a diamagnetic molecule, and (b) also the Fermi contact contribution that only a paramagnetic molecule can provide.



An experimental test:



Data from Jameson et al. Mol. Phys. 29, 1919 (1975), J. Chem. Phys. (1975-1978)



CONCLUSIONS

This analysis is a fundamental step towards a quantitative understanding of hyperfine shifts of Xe in the presence of paramagnetic centers in solids.

- **magnitude of Xe chemical shift much larger than for diamagnetic counterpart**
- **obtained the correct sign**
- **correct temperature dependence**
- **our results suggest applications of Xe NMR as probe of paramagnetic centers in materials.**

THANKS to

and
Herbert Paaren Scholarship
Lubrizol Scholarship

and to Devin N. Sears
for help with Gaussian98