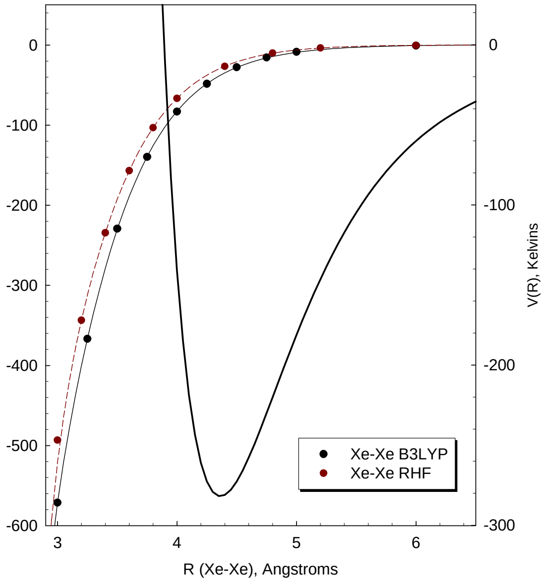


Xe chemical shifts in mixtures of gases

Cynthia J. Jameson and Devin N. Sears

University of Illinois at Chicago

Xe in mixtures of gases

ADVANTAGES:

The model system is the same as the physical system.

Direct comparison with experiment is possible when the potential function is well known from

molecular beam scattering,
van der Waals spectroscopy,
and thermophysical properties.

EXAMPLES:

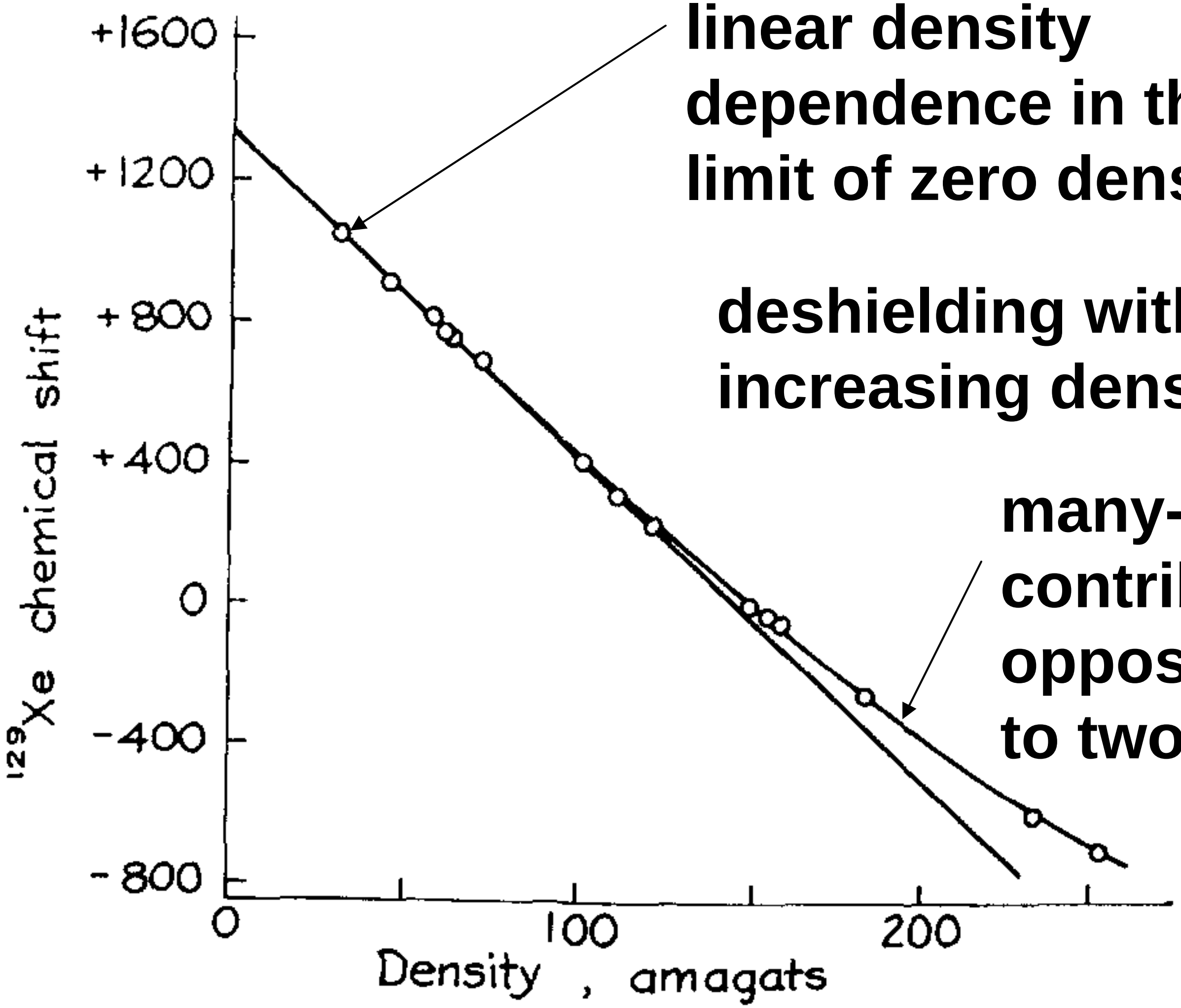
- Xe-Xe, Kr, Ar
- Xe-CO_2, Xe-CH_4, Xe-CF_4

Motivation

- The rare gas pairs provide a means by which the electron correlation part of the intermolecular shielding response can be probed since the PES are accurately known, and the experiments are straightforward and simple (gas phase in the binary collision limit).
- The nature of the intermolecular shielding tensor can be examined, i.e. $\sigma_{||}$ vs. $\sigma_{\perp}$, signs, magnitudes, dependence on collision partner.

EXPERIMENTS

^{129}Xe chemical shift in Xe gas



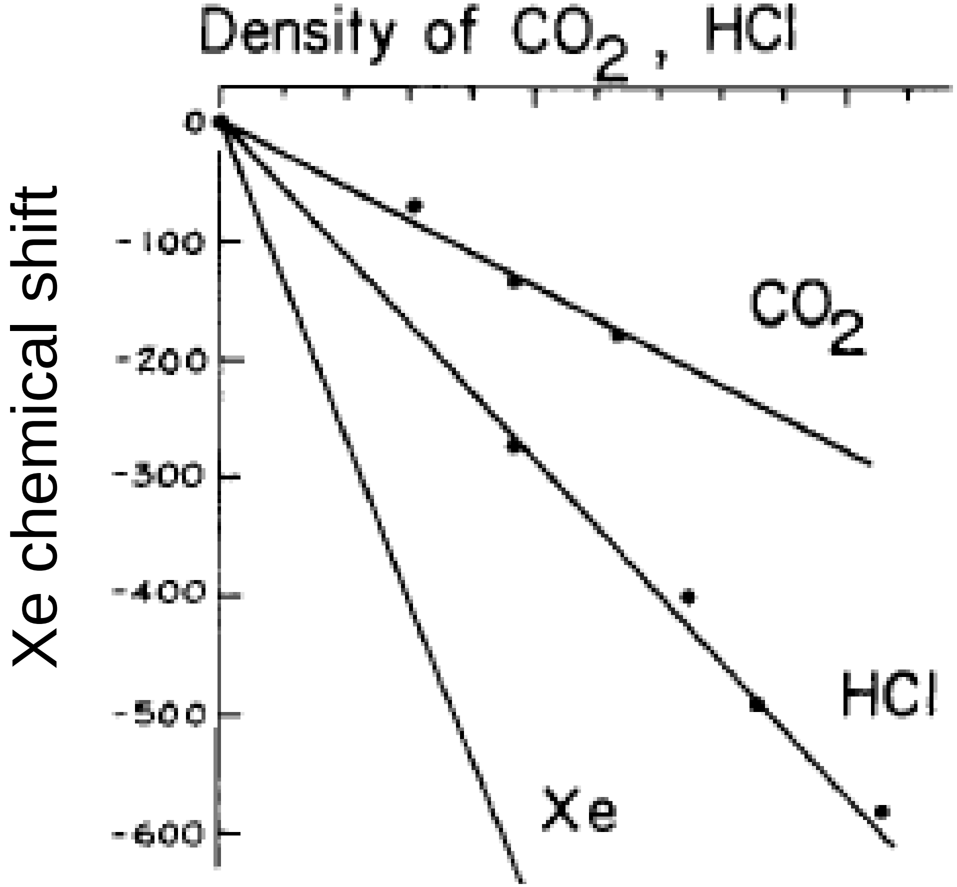
linear density dependence in the limit of zero density

deshielding with increasing density

many-body contributions opposite sign to two-body

Jameson et al. J. Chem. Phys. 53, 2310-2321 (1970).

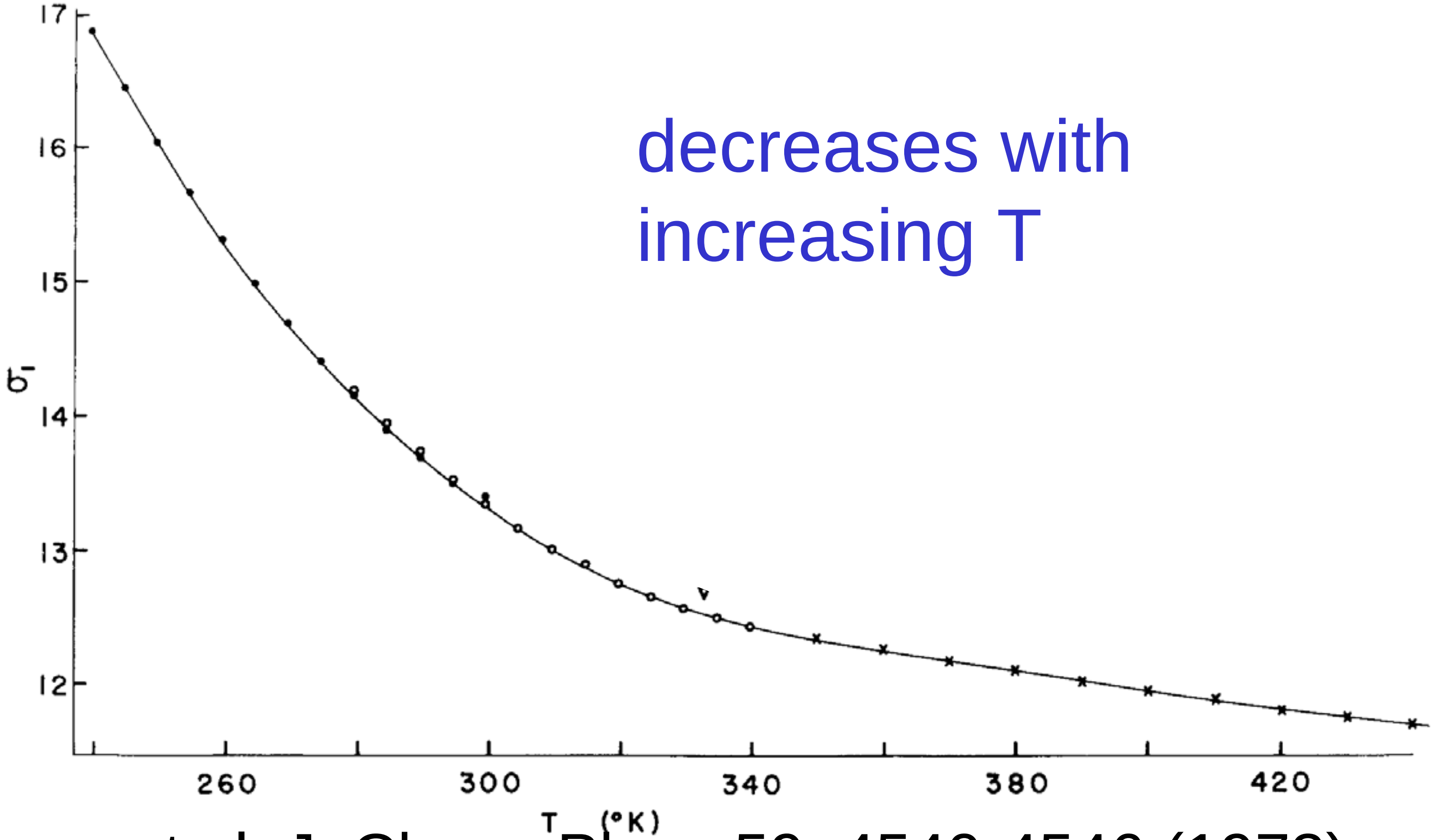
^{129}Xe chemical shift in gas mixtures



$$\sigma = \sigma_0 + \sigma_1(\text{Xe}\text{–}\text{Xe})\rho_{\text{Xe}} + \sigma_1(\text{Xe}\text{–}\text{A})\rho_{\text{A}}$$

Jameson et al. J. Chem. Phys. **53**, 2310-2321 (1970).

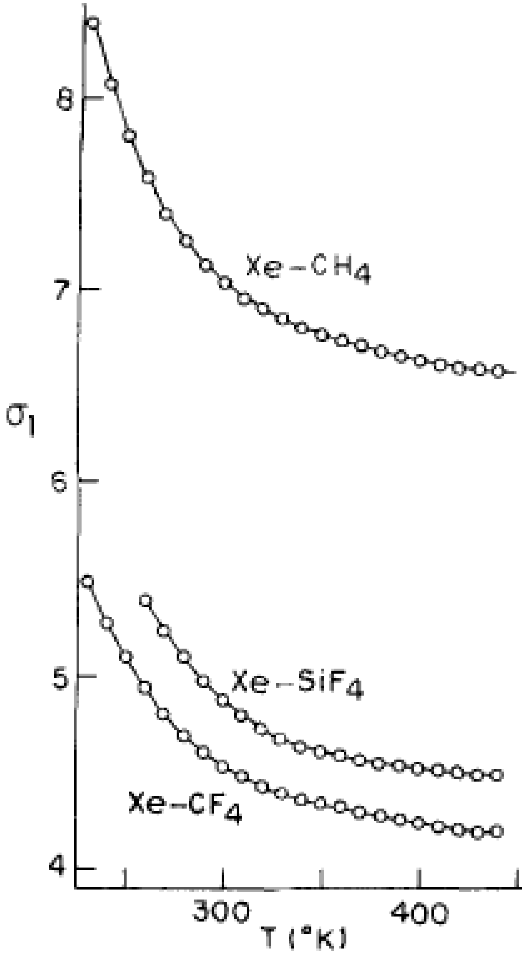
density coefficient of the ^{129}Xe chemical shift, the second virial coefficient of shielding, $\sigma_1(T)$

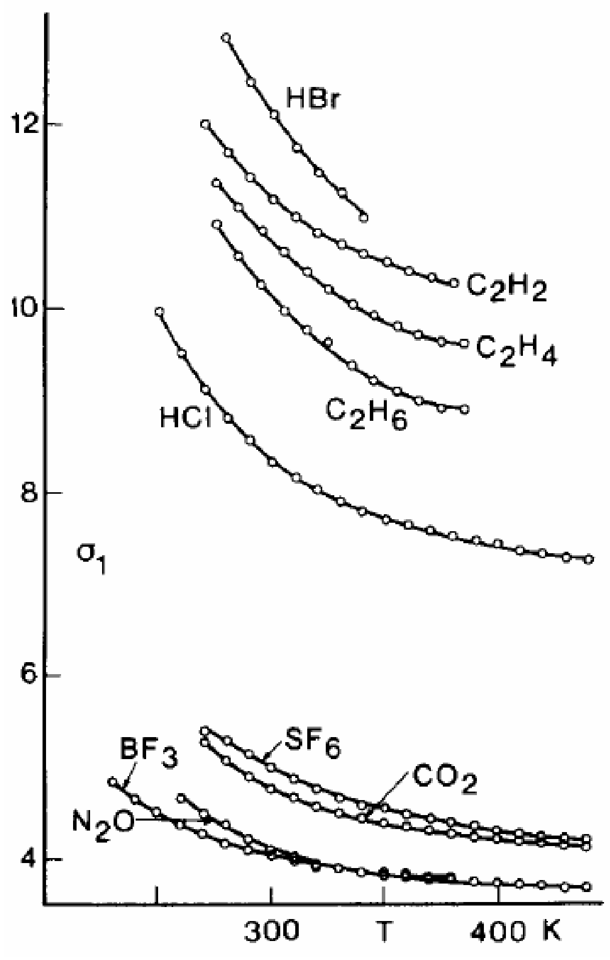


decreases with
increasing T

Jameson et al. J. Chem. Phys. **59**, 4540-4546 (1973).

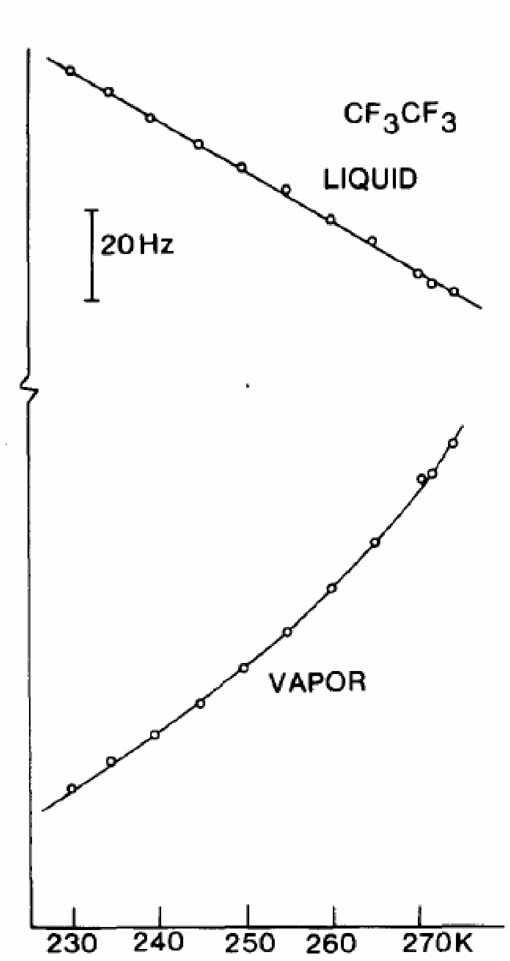
density coefficient of the ^{129}Xe chemical shift





Jameson et al. J. Chem. Phys. 65, 3401-3406 (1976);
J. Chem. Phys. 66, 5226-5230 (1977).

Gas-to-liquid shift



Vapor in equilibrium with liquid

Jameson et al. J. Chem. Phys**.** 70, 5916-7 (1979).

THEORETICAL APPROACH

- Consider two-body contribution only
- Second-virial coefficient of shielding
- Hartree-Fock calculations of shielding tensor components
- Include electron correlation
- Compare with experiments using best intermolecular potential functions

BASIS SET for Xe

40 basis functions
(uncontracted 29s 21p 17d 9f).
The core (25s 18p 13d) was taken
from Partridge and Faegri;
this was augmented by
3s 2p 4d and 9f orbitals
with exponents taken from D. Bishop.

References:
- H. Partridge and K. Faegri, NASA Technical Memo 103918 (1992).
- D.A. Bishop and S.M. Cybulski, Chem. Phys. Lett. **211**, 255 (1993)

Large enough so that the counterpoise correction to the ^{129}Xe shielding function is negligible in every case,
~ +0.03 ppm where the
intermolecular shielding is -63.35 ppm (0.05%)
and less (<0.01%) at longer distances.

Basis sets for rare gas atoms

- 240 basis functions for the **Xe** atom

  uncontracted (26s19p13d) + 3s2p4d9f
- 128 basis functions for the **Kr** atom

  uncontracted (21s16p10d) + spd
- 85 basis functions for the **Ar** atom

  uncontracted (20s15p0d) + 4d
- 77 basis functions for the **Ne** atom

  uncontracted (18s13p0d) + 4d

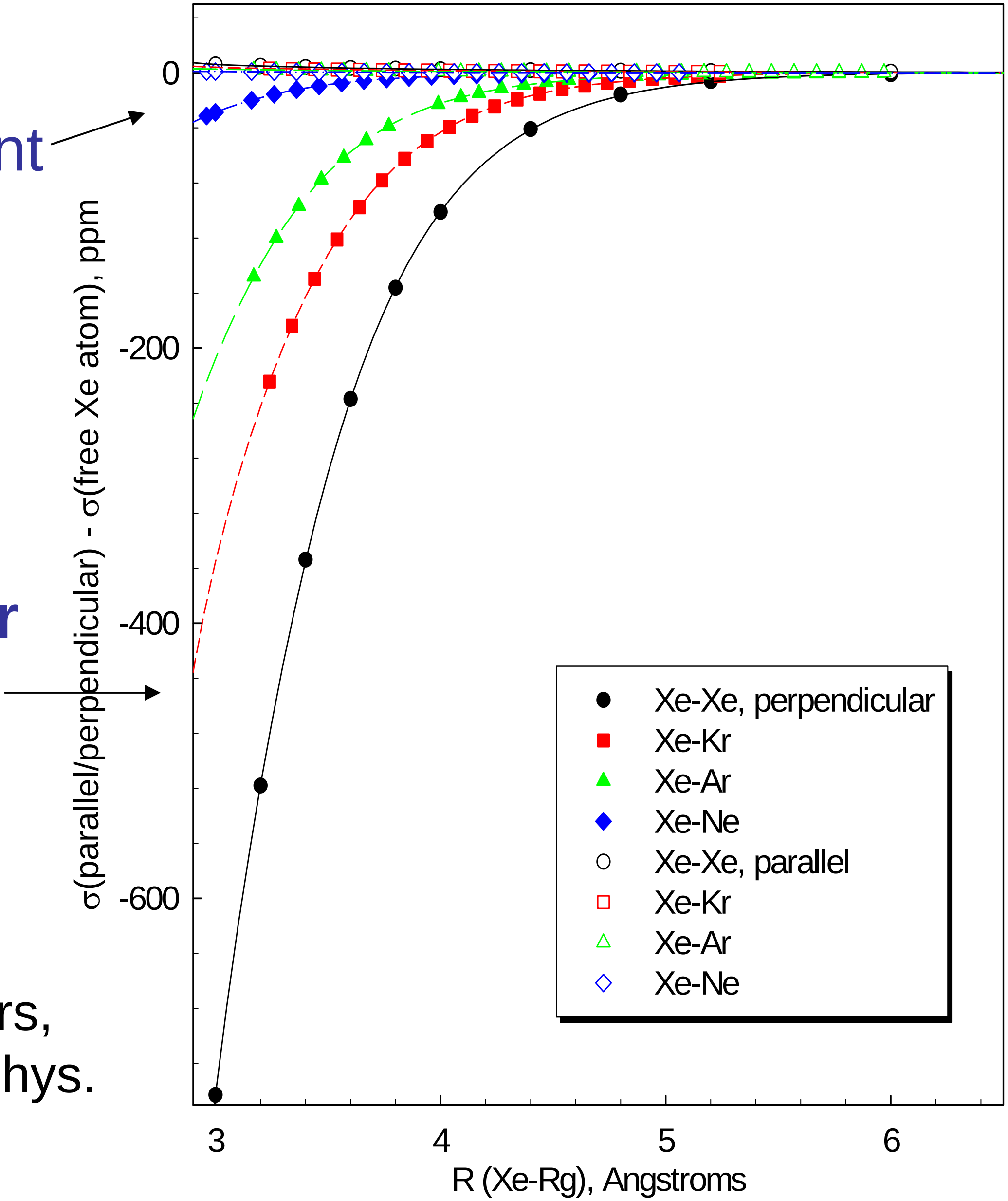
References:

- H. Partridge and K. Faegri, NASA Technical Memo 103918 (1992).
- D.A. Bishop and S.M. Cybulski, Chem. Phys. Lett. **211**, 255 (1993)

Hartree-Fock Results – Tensor Components

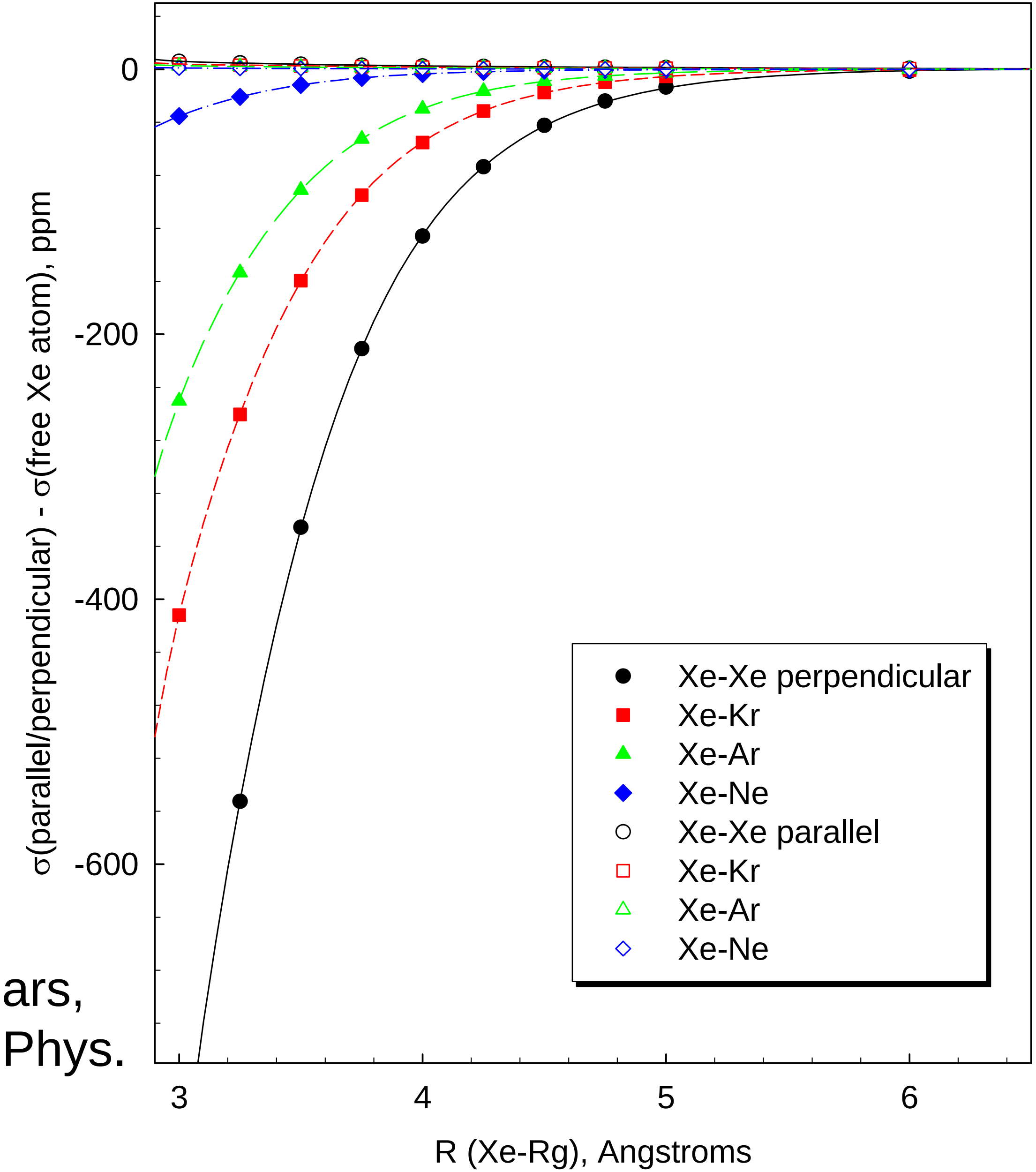
Parallel component is small!

Perpendicular component is large.



C. J. Jameson, D. N. Sears, A. C. de Dios, J. Chem. Phys. 118, 2575-2580 (2003).

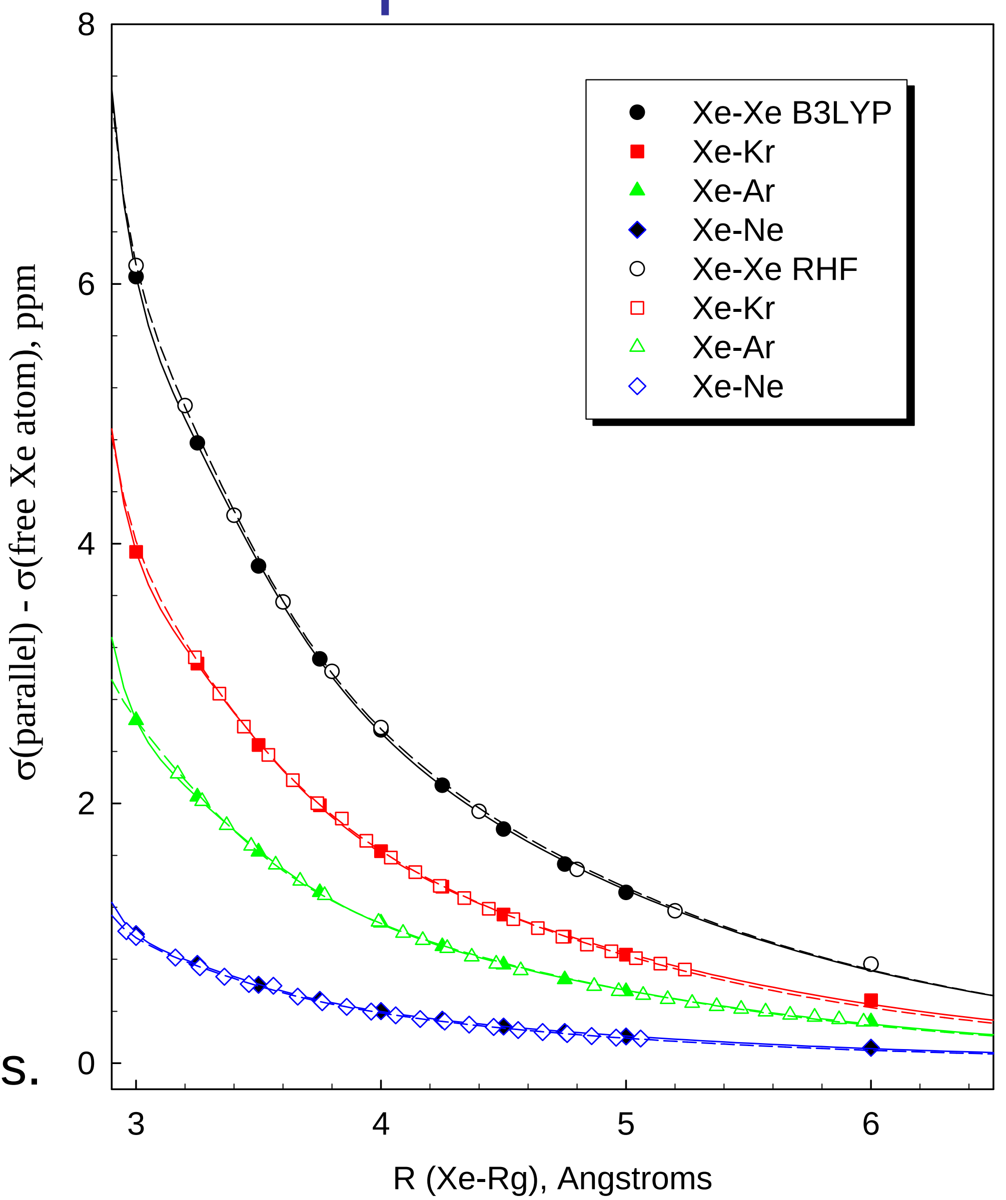
DFT Results – Tensor Components



C. J. Jameson, D. N. Sears,
A. C. de Dios, J. Chem. Phys.
118, 2575-2580 (2003).

Xe-Rg Shielding Tensors: Parallel Components

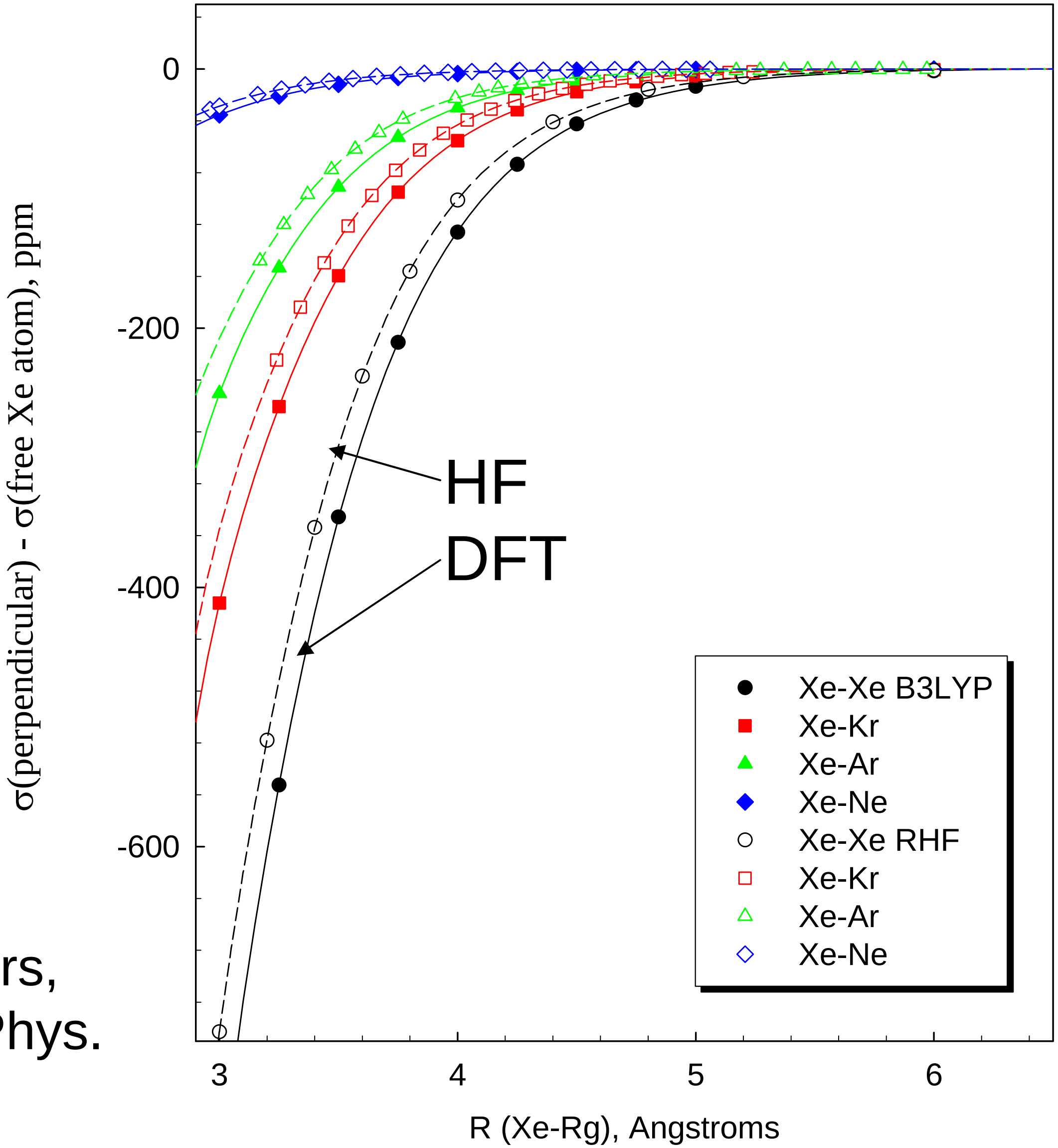
These components have nil electron correlation



C. J. Jameson, D. N. Sears, A. C. de Dios, J. Chem. Phys. 118, 2575-2580 (2003).

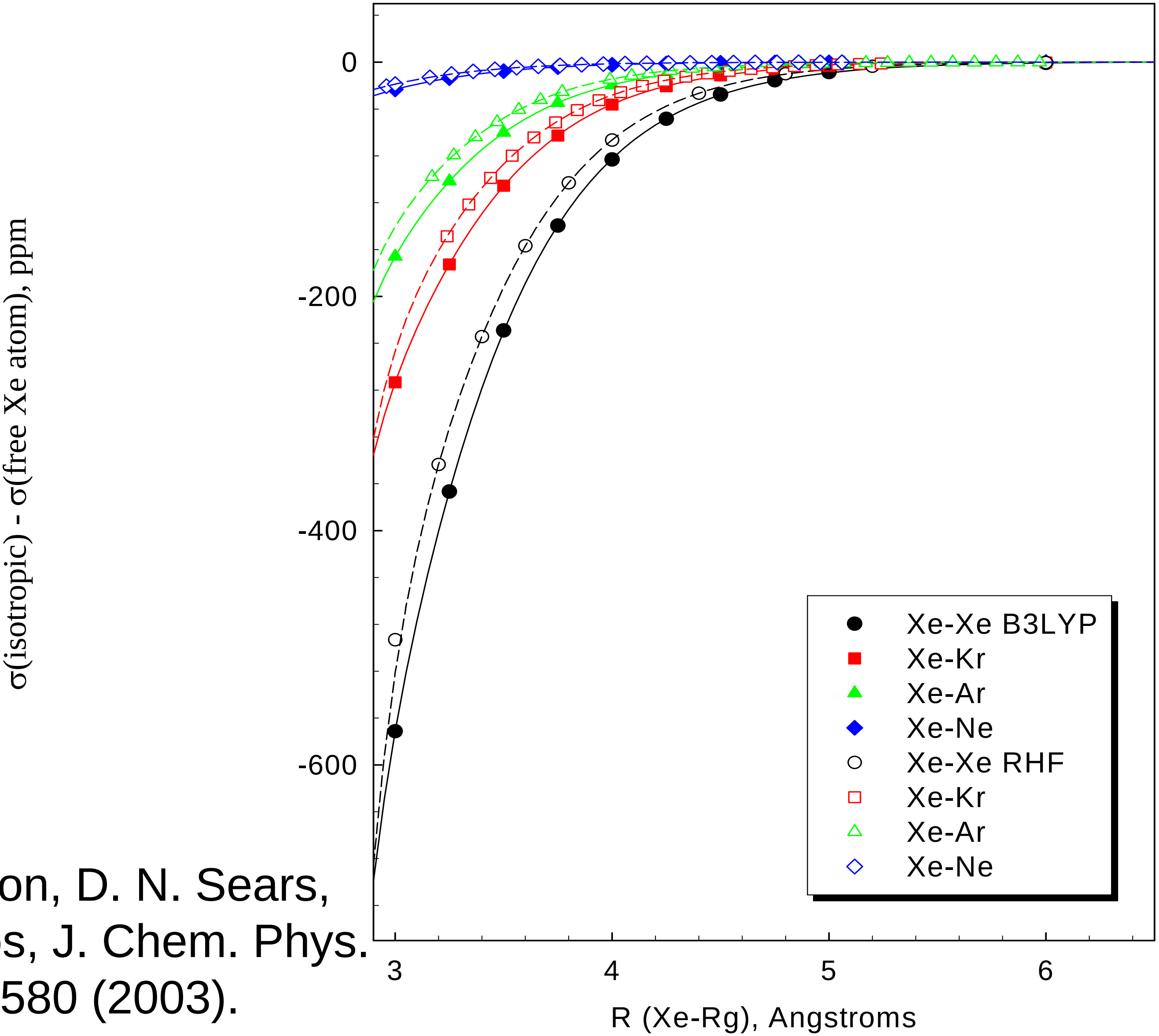
Xe-Rg Shielding Tensors: Perpendicular Components

Electron correlation gives additional deshielding



C. J. Jameson, D. N. Sears, A. C. de Dios, J. Chem. Phys. 118, 2575-2580 (2003).

Xe Isotropic Shieldings



C. J. Jameson, D. N. Sears,
A. C. de Dios, J. Chem. Phys.
118, 2575-2580 (2003).

Intermolecular Chemical Shifts

in GAS phase:

$\sigma(T, \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \ldots$

$\sigma_1(T) =$ **second virial coefficient of shielding =**

$$\int\int[\sigma(r, \theta, \phi) - \sigma(\infty)] \times$$

$$\exp[-V(r,\theta,\phi)/kT]r^2 dr \sin\theta d\theta d\phi$$

Need 2 functions:

$[\sigma(r, \theta, \phi) - \sigma(\infty)]$ & $V(r,\theta,\phi)$

for Xe in gas phase mixtures

Using samples which have small amounts of Xe with varying amounts of other gas

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)_{XeXe}\,\rho_{Xe} + \sigma_1(T)_{XeRg}\,\rho_{Rg} + \sigma_2(T)_{XeXe}\,\rho_{Xe}^2 + \ldots$$

Subtract out the Xe-Xe contributions

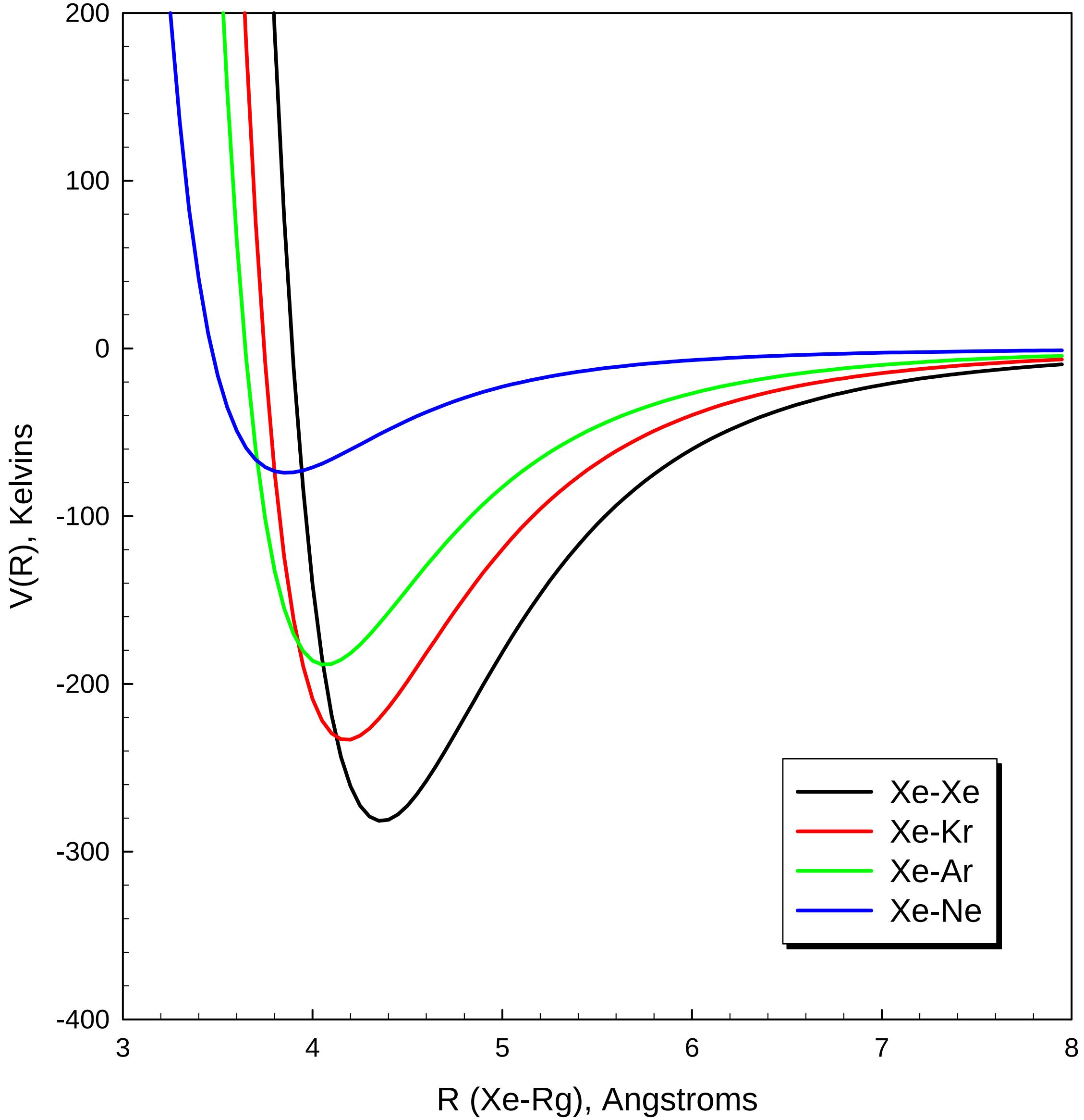
$$\sigma_1(T)_{XeRg} = 4\pi \int_0^\infty \{\sigma(R) - \sigma(\infty)\}\, e^{-V(R)/kT}\, R^2\, dR$$

EXPERIMENT **SHIELDING SURFACE** **PROBABILITY**

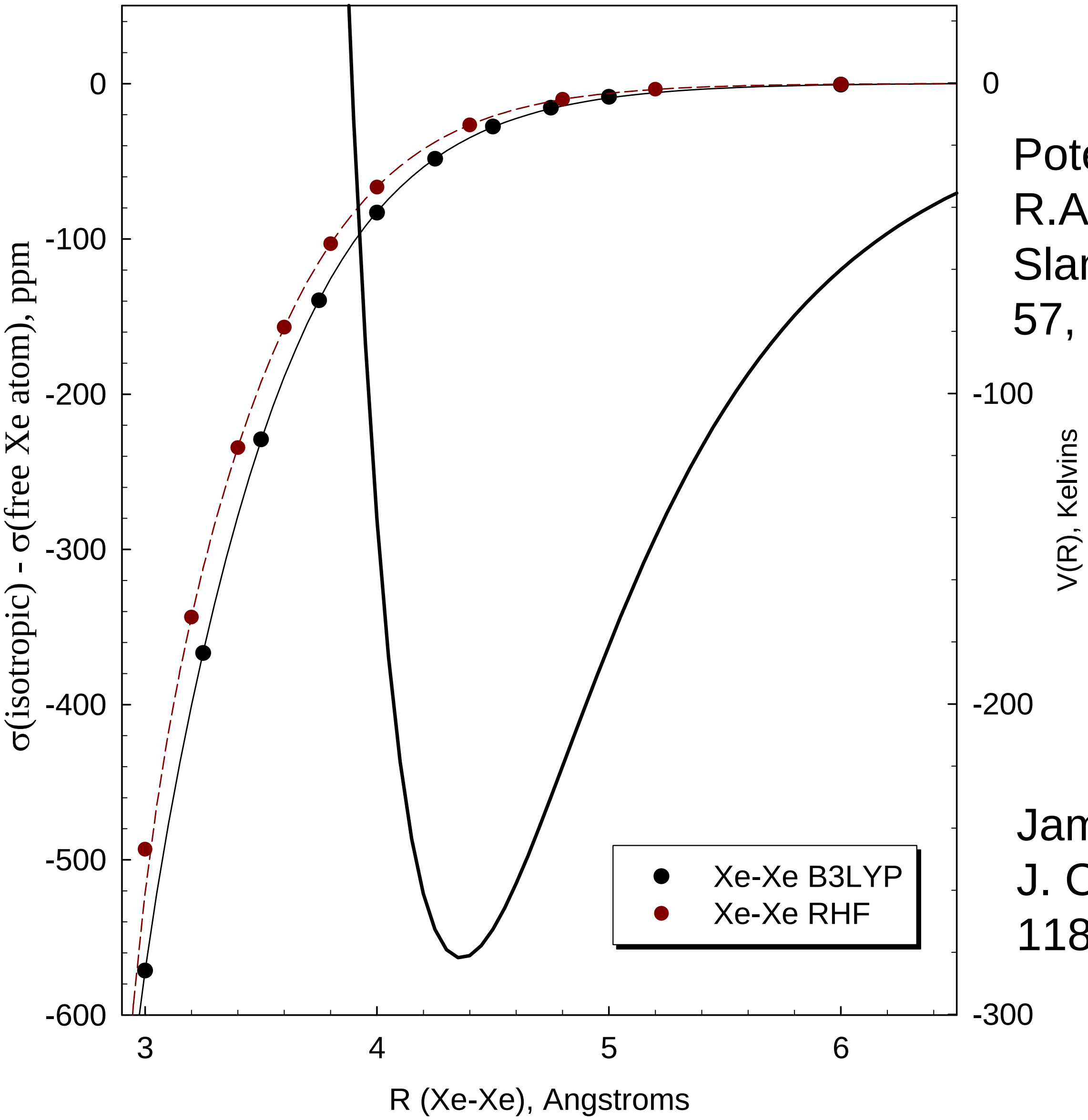
V(R) = Xe–rare gas potential function

Jameson et al. 1970

Xe - Rg Intermolecular Potentials (Aziz et al.)



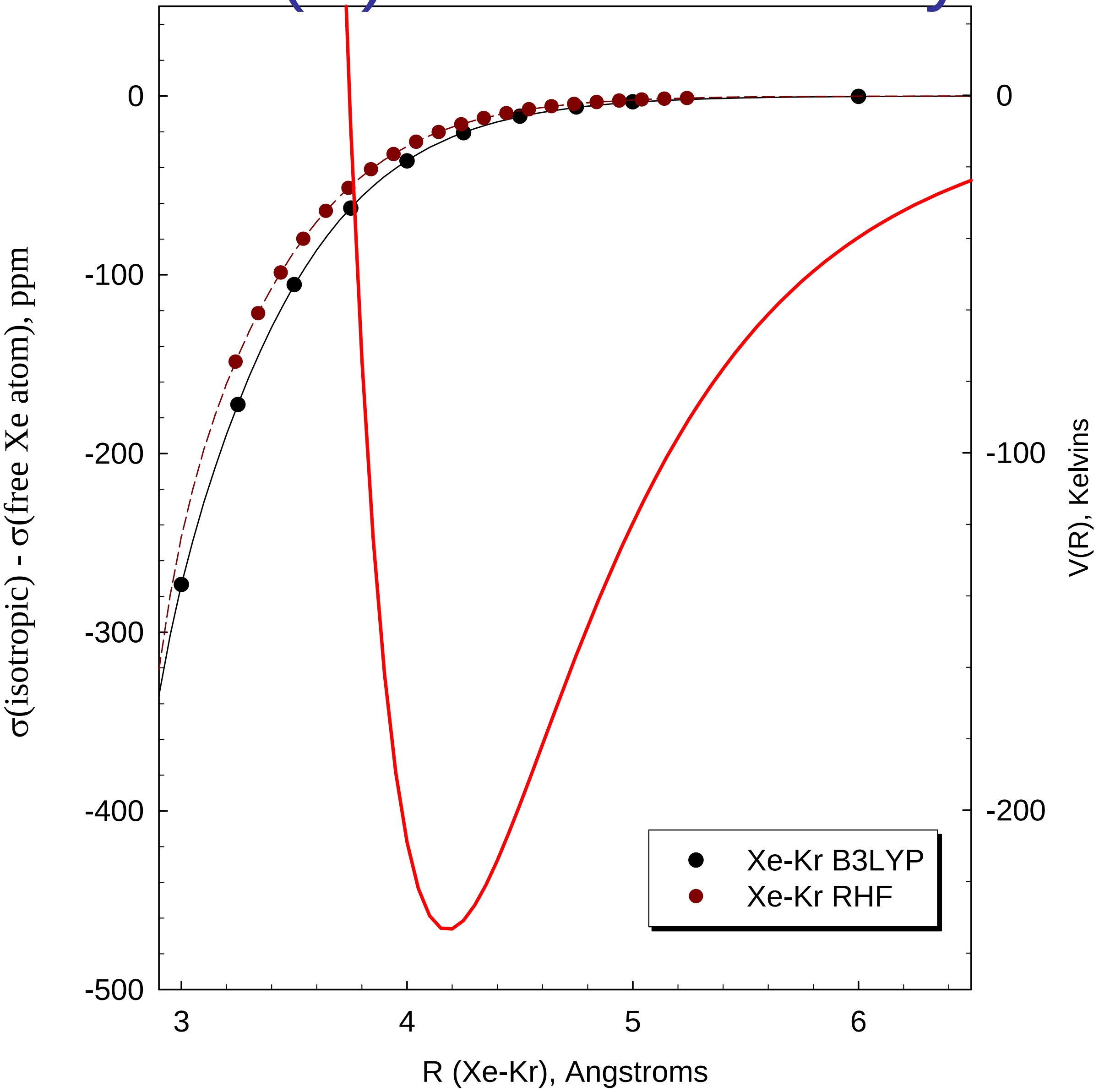
Xe shielding function σ(R) and potential function V(R) for the Xe-Xe system



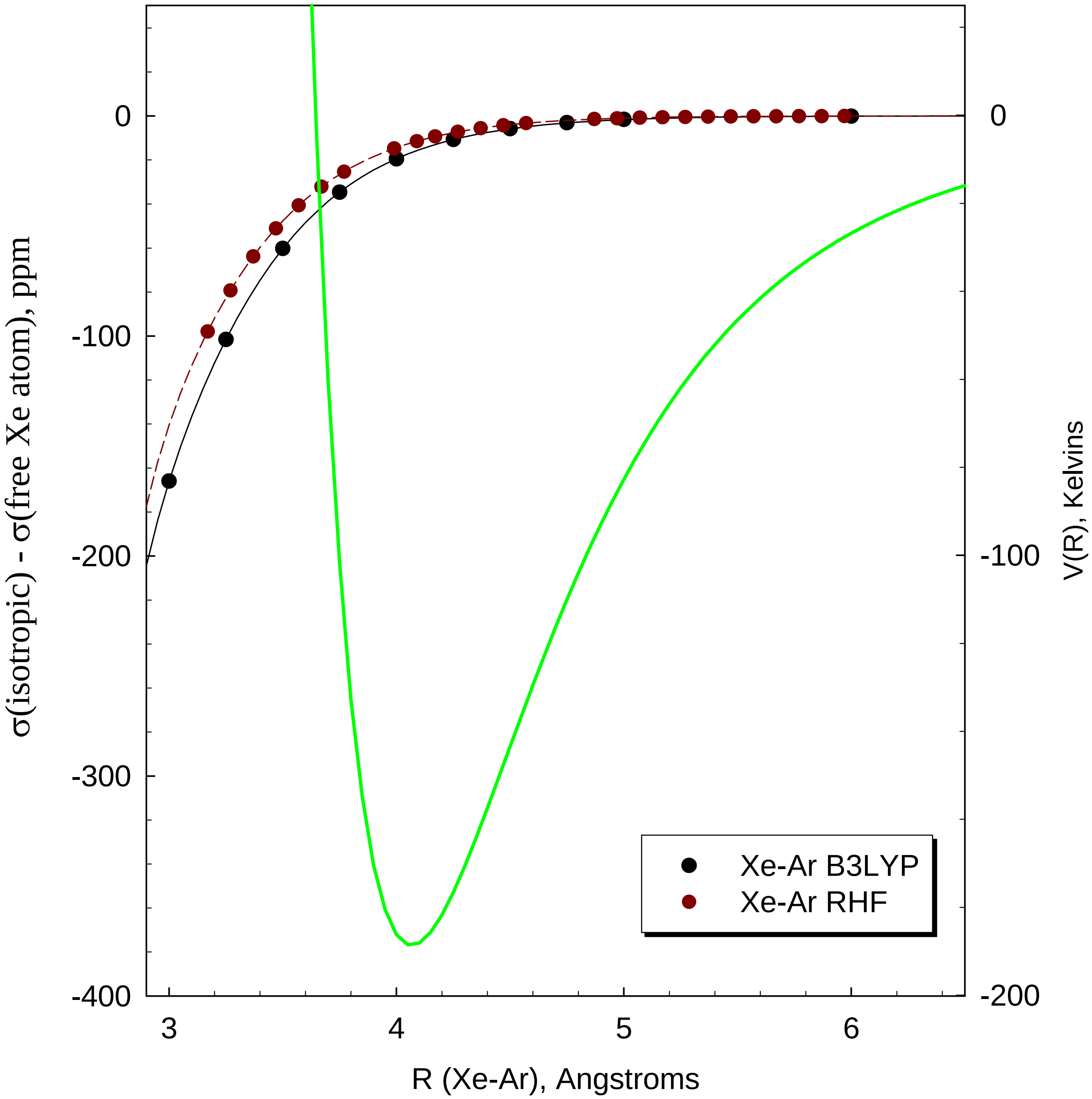
Potential function:
R.A. Aziz and M.J. Slaman, Mol. Phys. 57, 825 (1986)

Jameson et al.
J. Chem. Phys.
118, 2575 (2003)

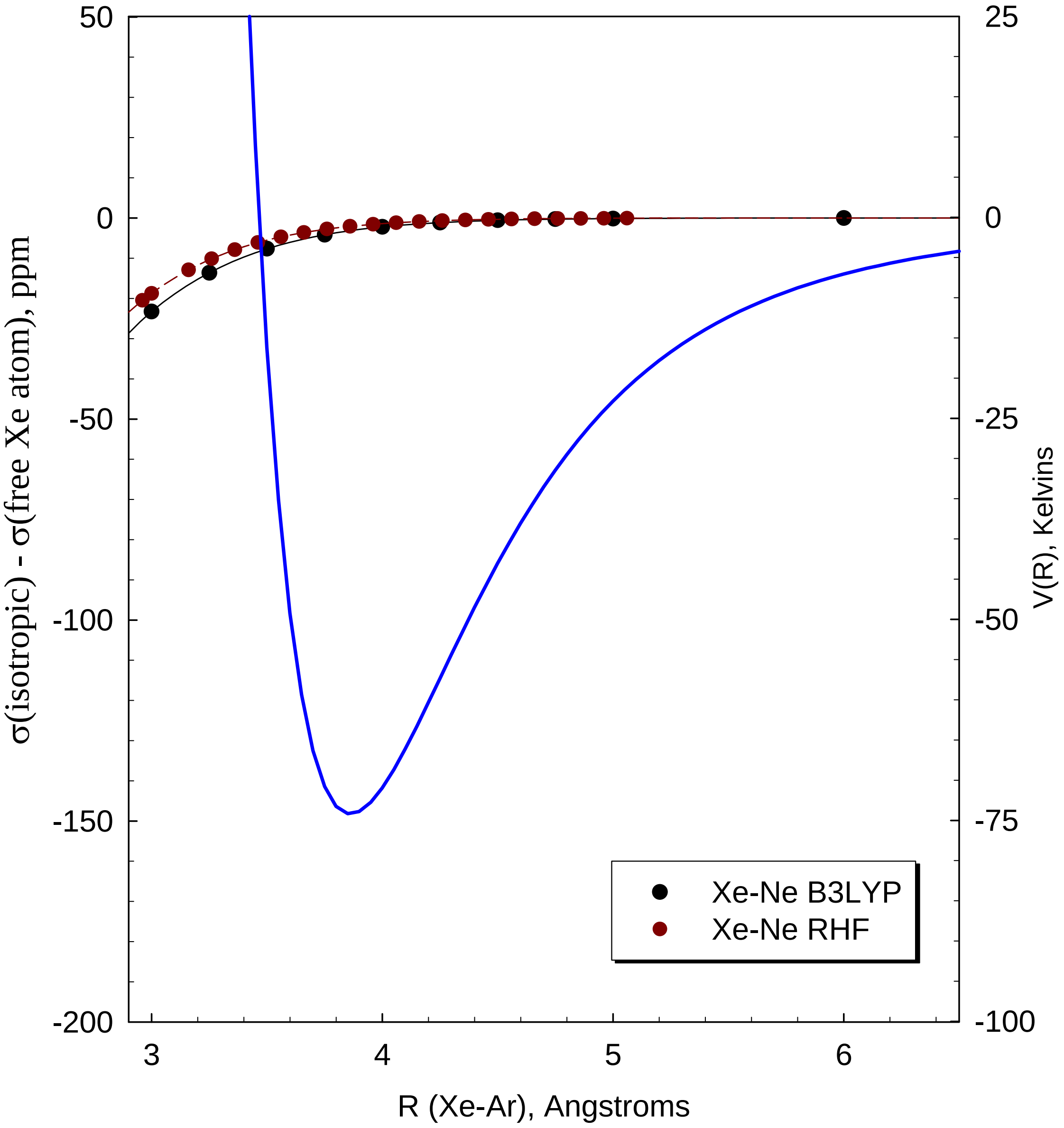
Xe Shielding Function σ(R) and Potential Function V(R) for the Xe-Kr System



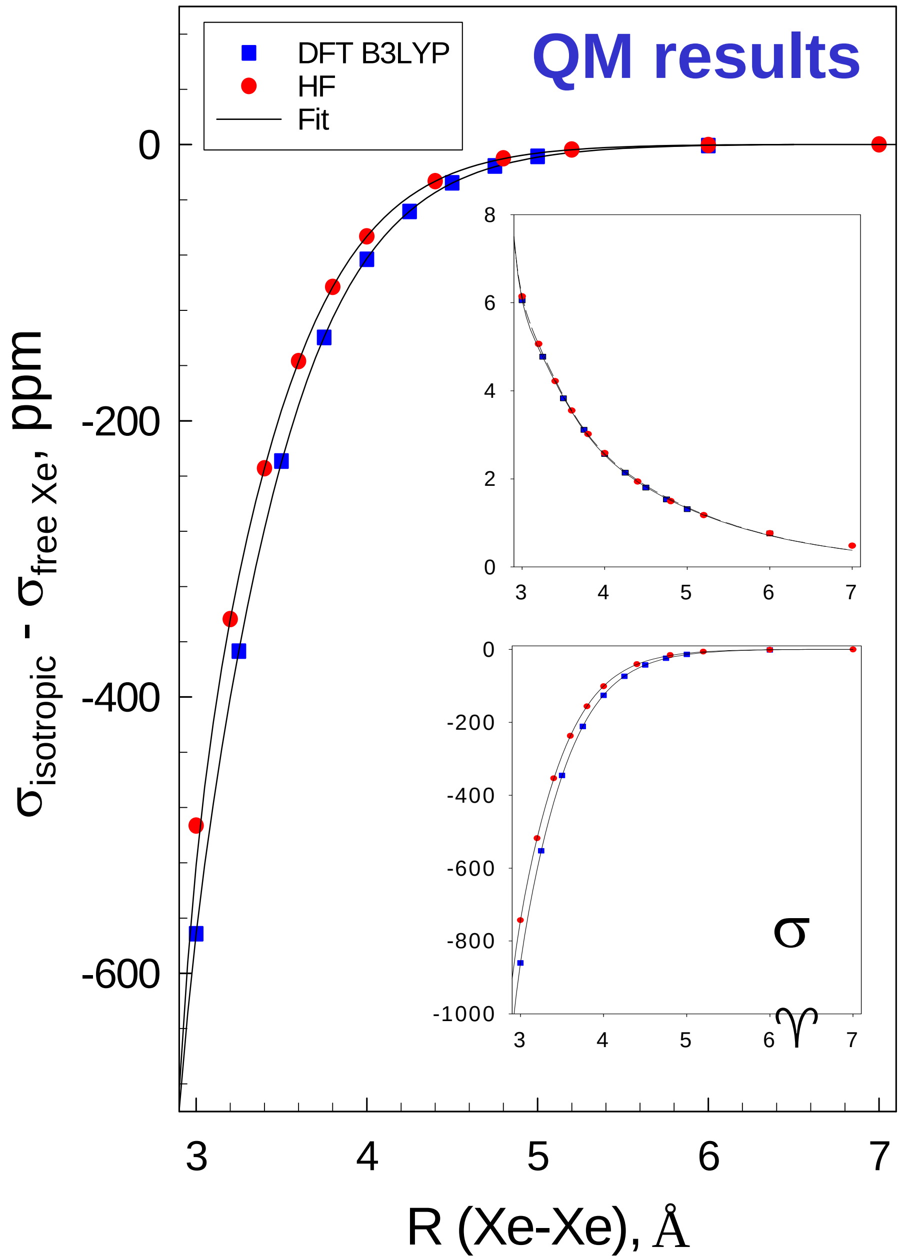
Xe Shielding Function σ(R) and Potential Function V(R) for the Xe-Ar System



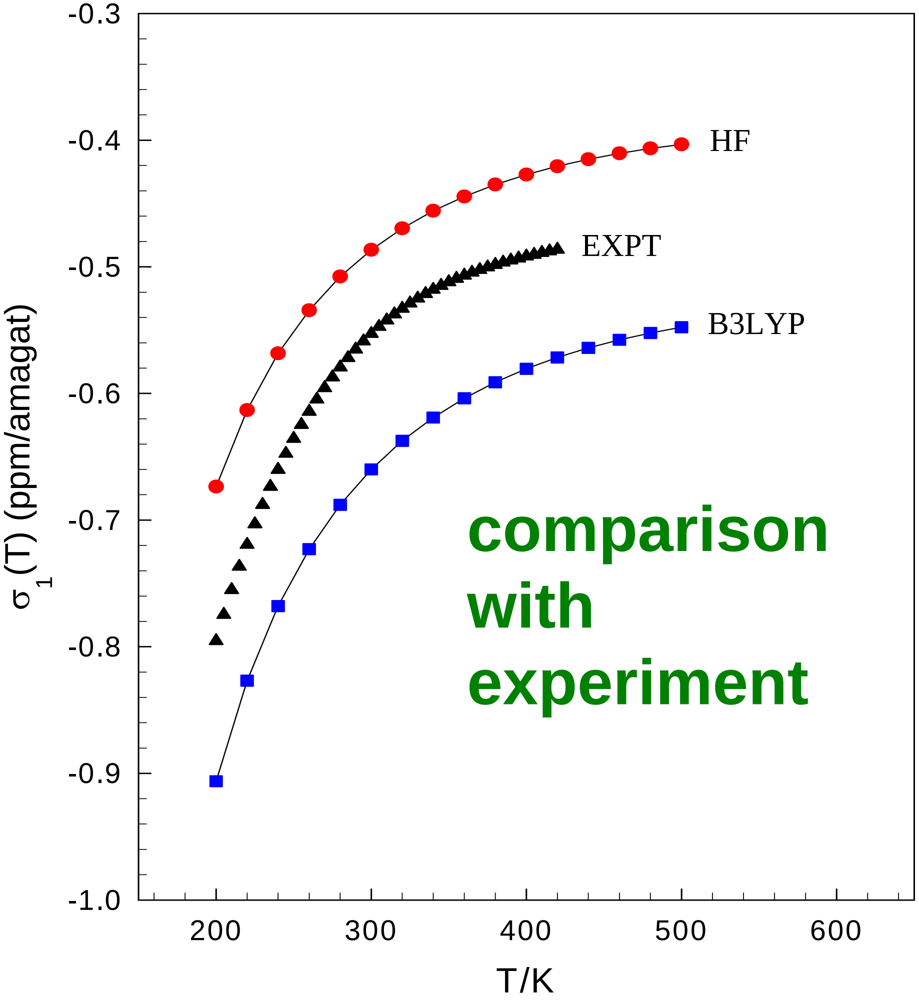
Xe Shielding Function σ(R) and Potential Function V(R) for the Xe-Ne System



Xe-Xe diatomic molecule shielding



QM results



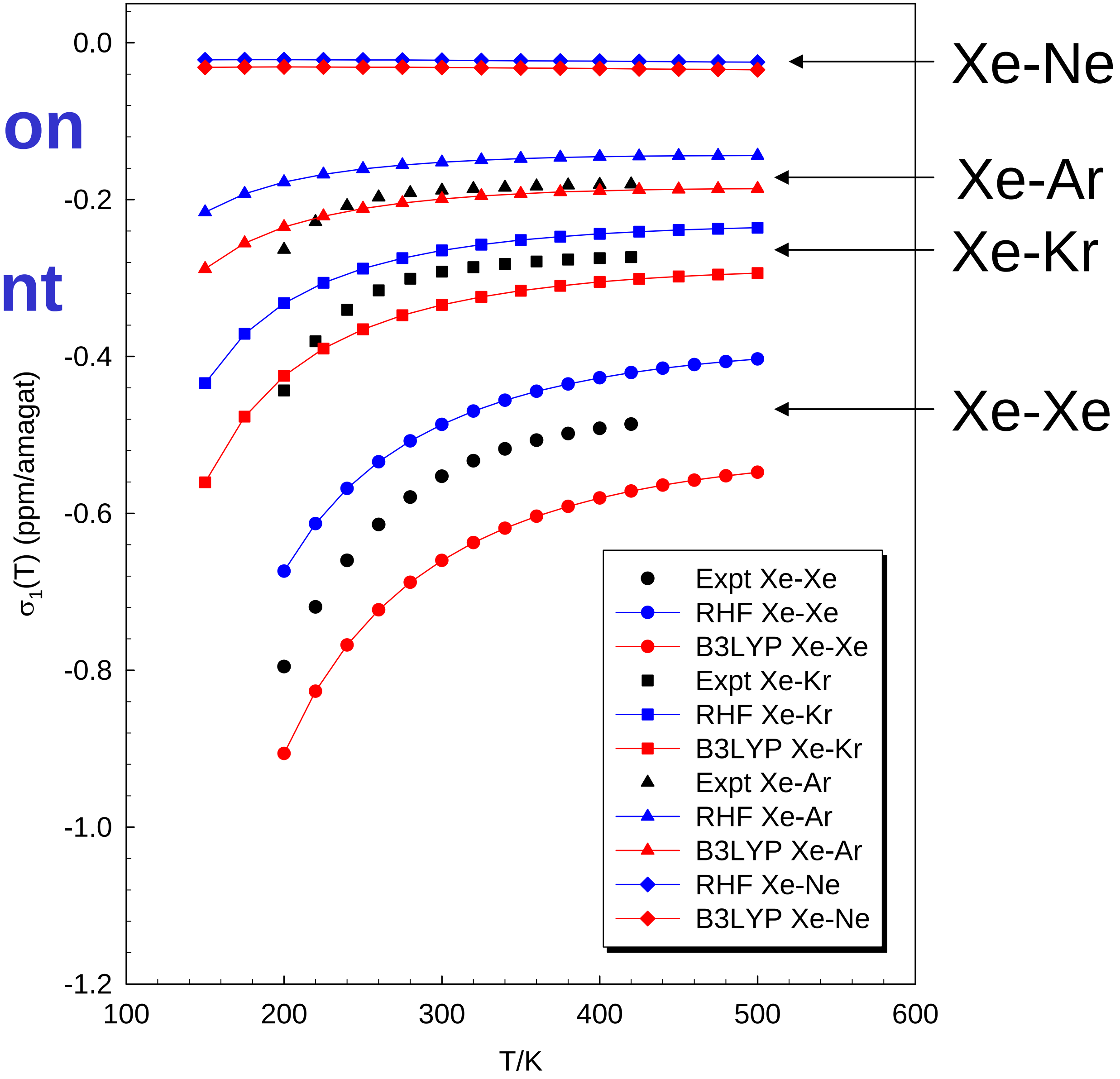
comparison with experiment

$$\sigma_1(T) = \int_0^\infty [\sigma_{Xe-Xe} - \sigma_{freeXe}] e^{\frac{-V(R)_{Xe-Xe}}{kT}} R^2 dR$$

$V(R)_{Xe-Xe}$ Aziz-Slaman Potential

$\sigma_1(T)_{EXPT}$ vs. $\sigma_1(T)_{CALC}$ calculated using $\sigma(R)_{RHF}$ and $\sigma(R)_{DFT}$

comparison with experiment



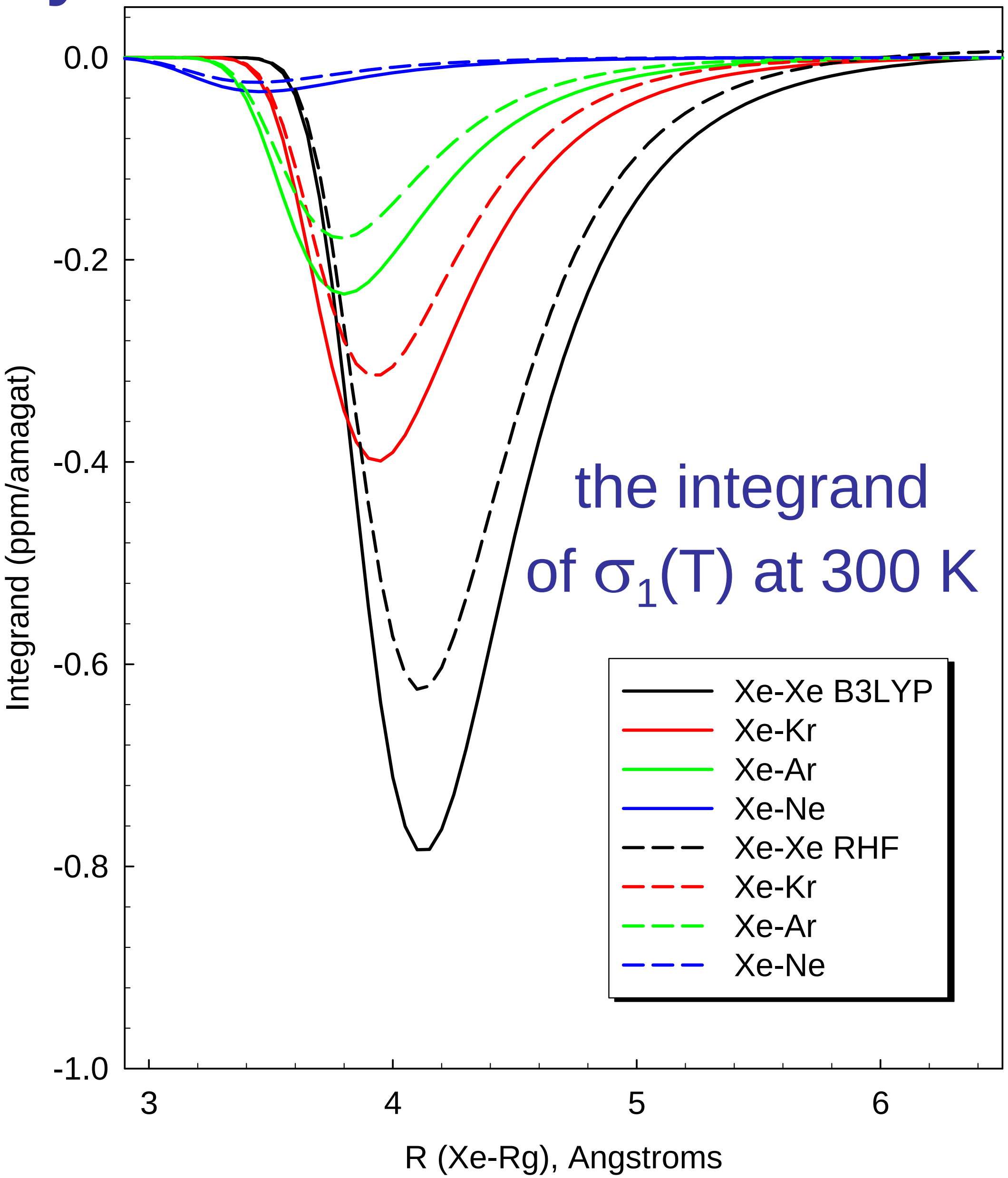
The range of interaction measured by the intermolecular chemical shift

i.e., which distances contribute most to the observed density coefficient?

$$\sigma_1(T) = \int 4\pi \{\sigma(r) - \sigma(\infty)\}\ e\text{-}V(r)/kT\ r^2\ dr$$

Take a look at the integrand as a function of r

The range of interaction measured by the intermolecular chemical shift



the integrand of $\sigma_1(T)$ at 300 K

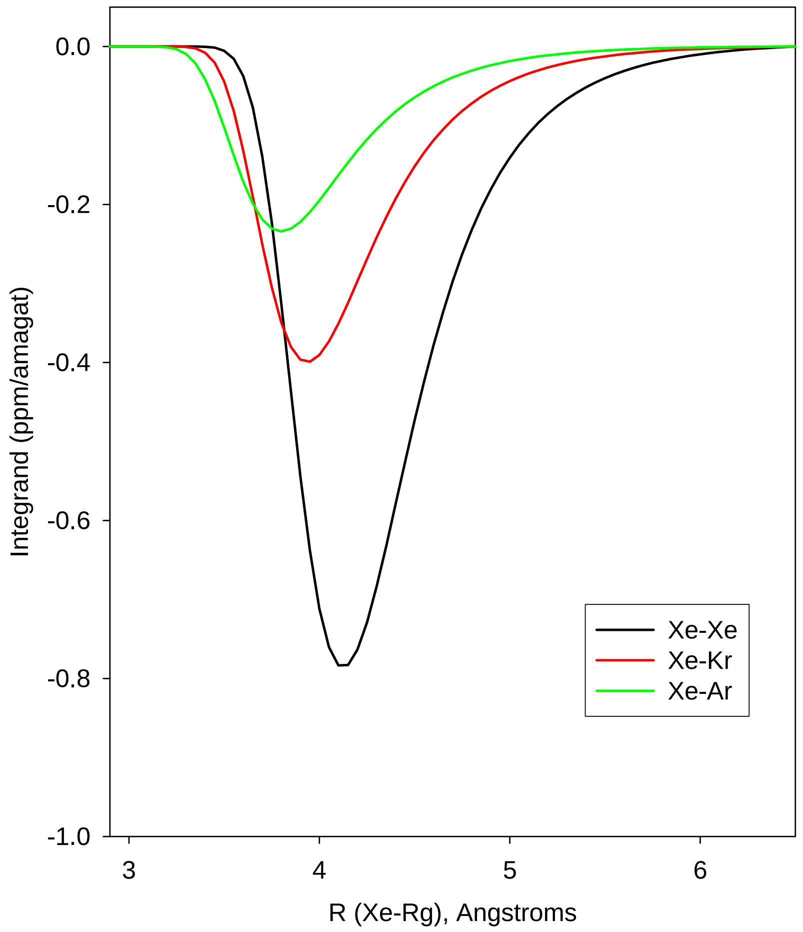
or **which distances contribute to the observed density coefficient of the chemical shift?**

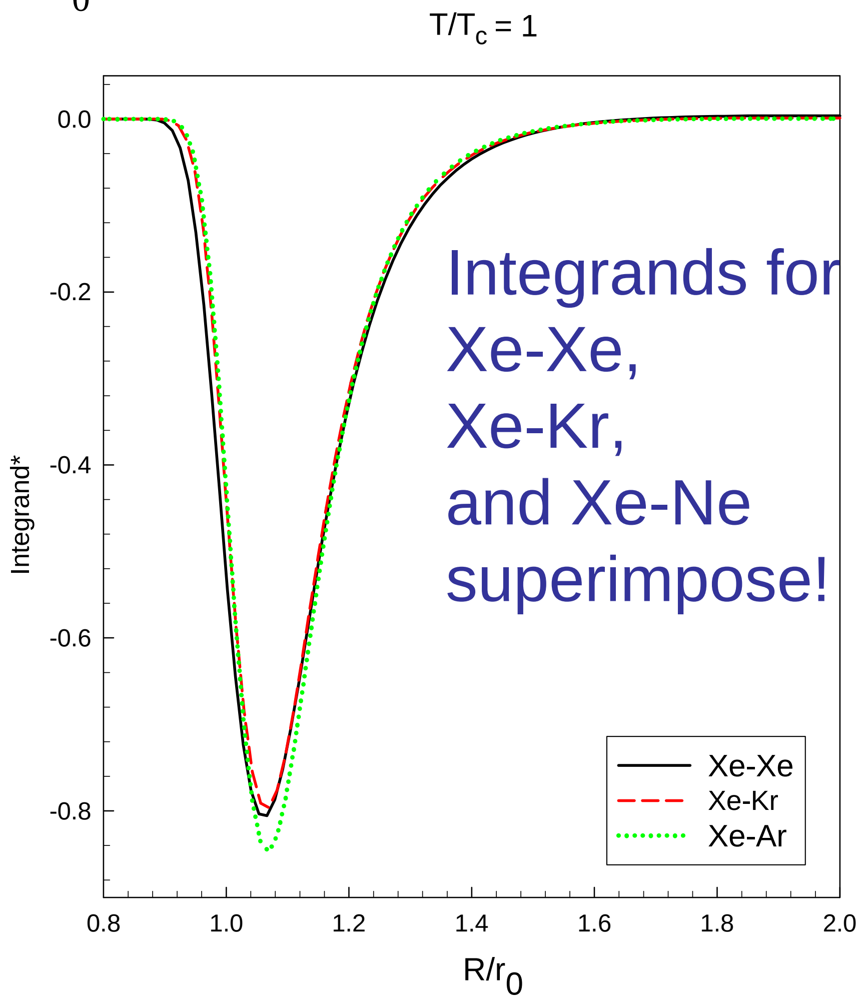
C. J. Jameson, D. N. Sears, A. C. de Dios, J. Chem. Phys. 118, 2575-2580 (2003).

SCALING:
corresponding states

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\,\rho + \sigma_2(T)\,\rho^2 + \ldots$$

$$\sigma_1(T) = 4\pi \int_0^\infty \{\sigma(r) - \sigma(\infty)\}\, e^{-V(r)/kT}\, r^2\, dr$$





Integrands for Xe-Xe, Xe-Kr, and Xe-Ne superimpose!

Integrand* stands for scaled values using the scaling factor $\{[\alpha_{Xe}(0)/\alpha_{Rg}(0)]\bullet[IP_{Xe}/IP_{Rg}]\bullet[(IP_{Xe}+IP_{Rg})/2IP_{Xe}]\}*\sigma(r)$

Why do we find a corresponding states type of scaling in the intermolecular chemical shift?

Both the **intermolecular potentials** and the **shielding functions** scale!

The distance parameter in the potential scales with r_0 and temperature scales with T_c

The distance parameter in the Xe shielding function scales with r_0 and the response at the Xe nucleus for various Rg partners scales as

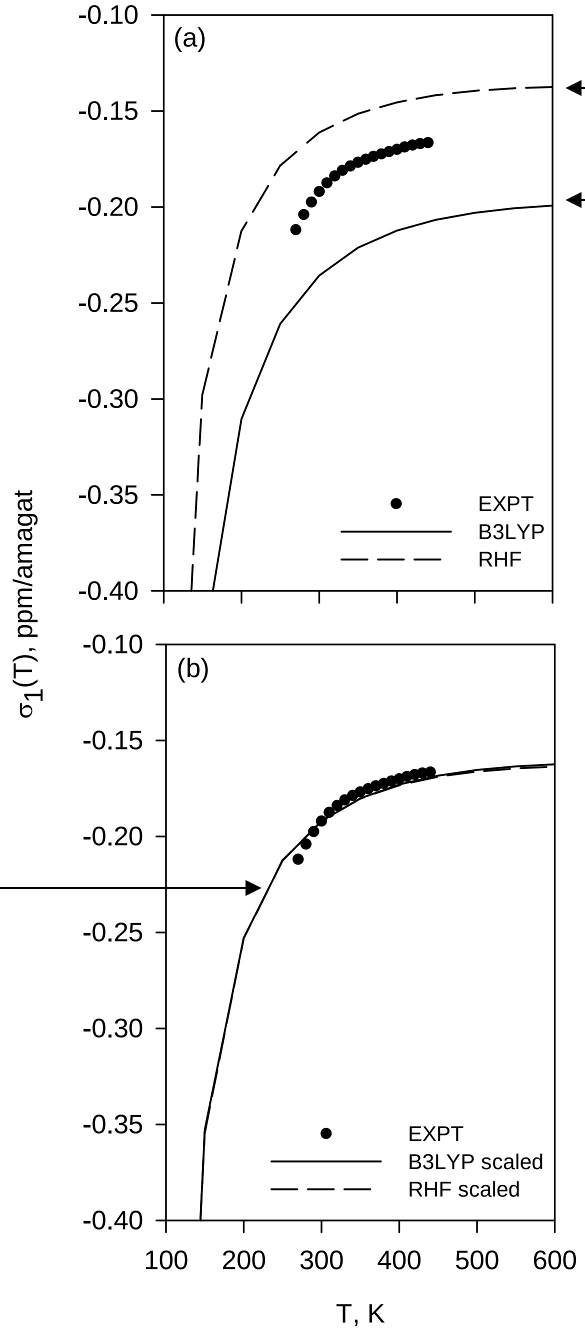
$$\{[\alpha_{Xe}(0)/\alpha_{Rg}(0)]\bullet[IP_{Xe}/IP_{Rg}]\bullet[(IP_{Xe}+IP_{Rg})/2IP_{Xe}]\}*\bullet\sigma(r)_{Xe\text{-}Xe}$$

Xe interacting with linear molecules

- Xe-CO_2
- Xe-N_2
- Xe-CO

There are, as yet, no accurate PES for these pairs

Density coefficient of the Xe-CO$_2$ intermolecular chemical shift:



Hartree-Fock

DFT/B3LYP

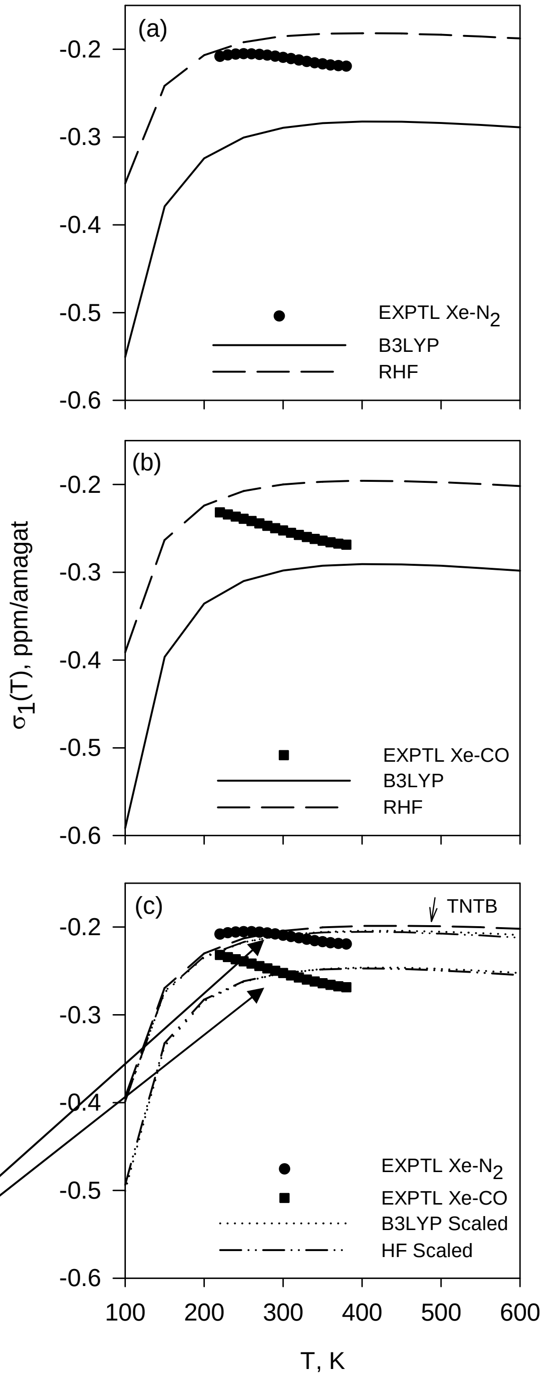
Calculations:
D. N. Sears,
C. J. Jameson,
J. Chem. Phys.
121, 2151-2157
(2004)

Experiment:
C. J. Jameson,
A..K. Jameson,
S.M.Cohen,
J. Chem. Phys.
66, 5226-30
(1977)

1.16 x $\sigma(R)_{RHF}$ gives excellent agreement with experiment

Intermolecular potential functions for Xe-N_2 and Xe-CO **fail to reproduce temperature dependence** of the density coefficient of the intermolecular chemical shift, although **the magnitude at 300 K agrees with experiment**

for 1.15 x $\sigma(R)_{RHF}$



Xe-N_2

Experiment:
C. J. Jameson,
A..K. Jameson,
H. Parker,
J. Chem. Phys.
68, 3943-4
(1978)

Xe-CO

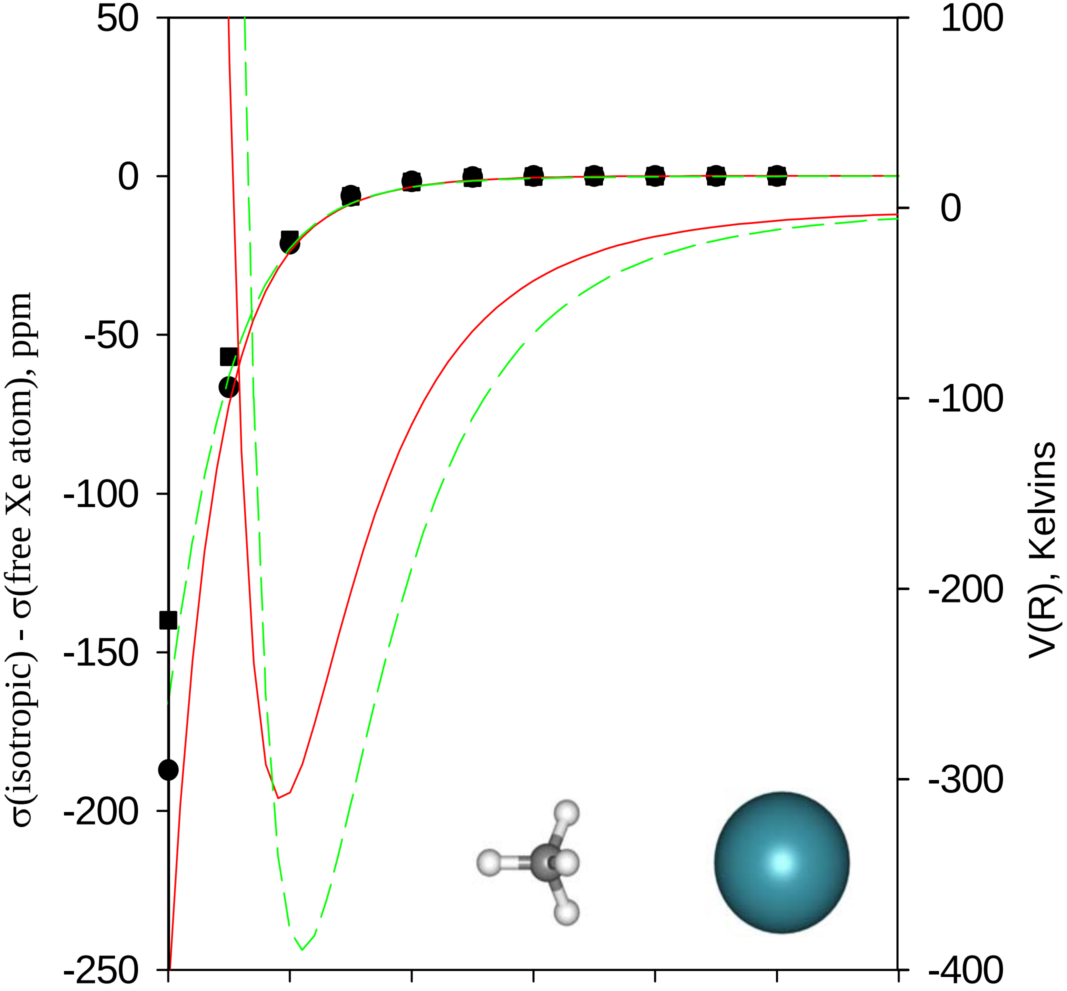
Xe-N_2

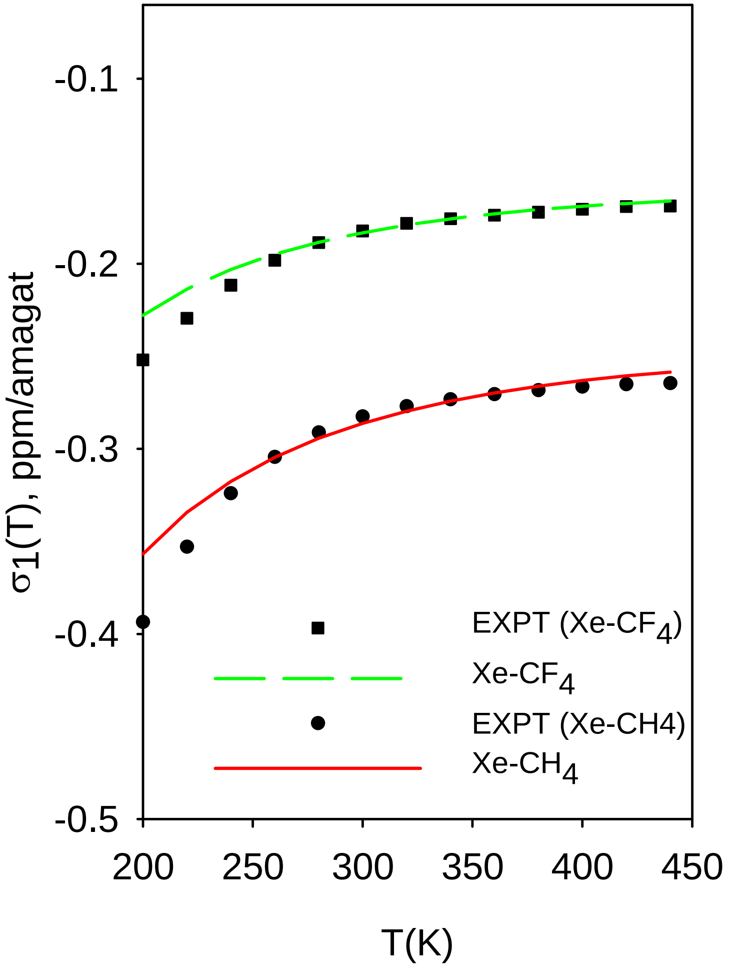
Xe-CO

Xe interacting with spherical top molecules

- Xe-CH_4
- Xe-CF_4

Xe-CH_4/CF_4 shielding functions





Calculations: Jameson et al, JCP 121, (2004)
Potential (Xe-CH_4): Liuti et al, Chem. Phys. 126, 1 (1988)
Experiments: Jameson et al, 65, 3401 (1976)

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\,\rho + \sigma_2(T)\,\rho^2 + \ldots$$

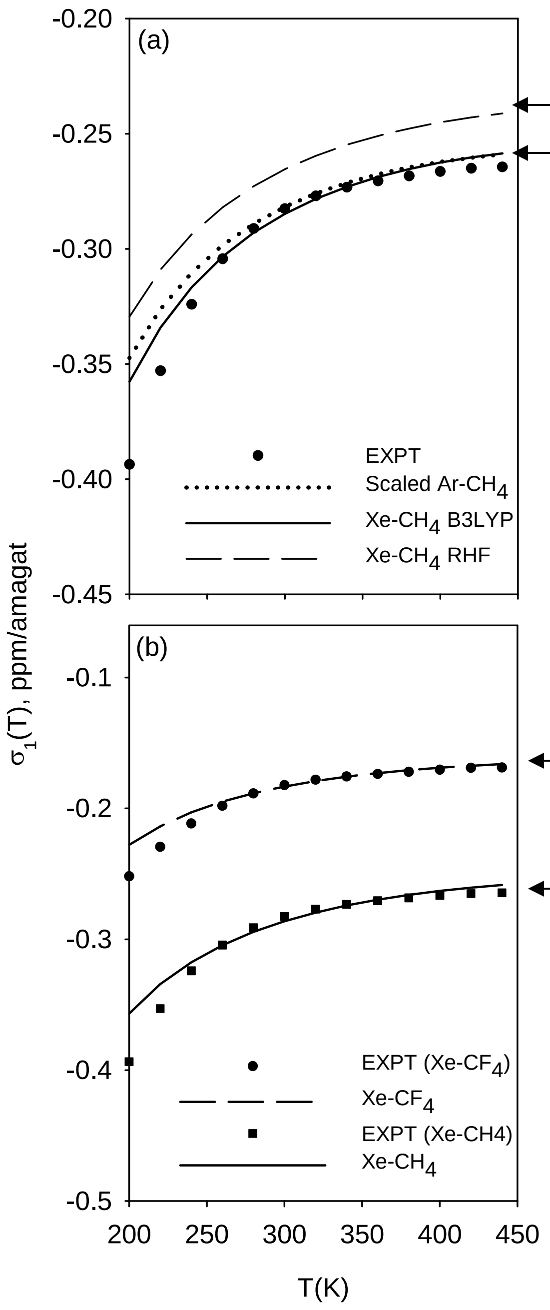
$$\sigma_1(T) = 4\pi\int_0^\infty\int_0^\pi\int_0^{2\pi}\{\sigma(R,\theta,\phi) - \sigma(\infty)\}\,e^{-V(R)/kT}\,R^2dR\sin\theta d\theta d\phi$$

Density coefficients of intermolecular $Xe\text{-}CH_4$ and $Xe\text{-}CF_4$ chemical shifts

agree with EXPERIMENT

if calculated with $\sigma(R)_{DFT/B3LYP}$
[Hartree-Fock underestimates]

Puzzle:
Why does CF_4 give much smaller Xe chemical shifts?



$Xe\text{-}CH_4$

Hartree-Fock

DFT/B3LYP

$Xe\text{-}CF_4$

$Xe\text{-}CH_4$

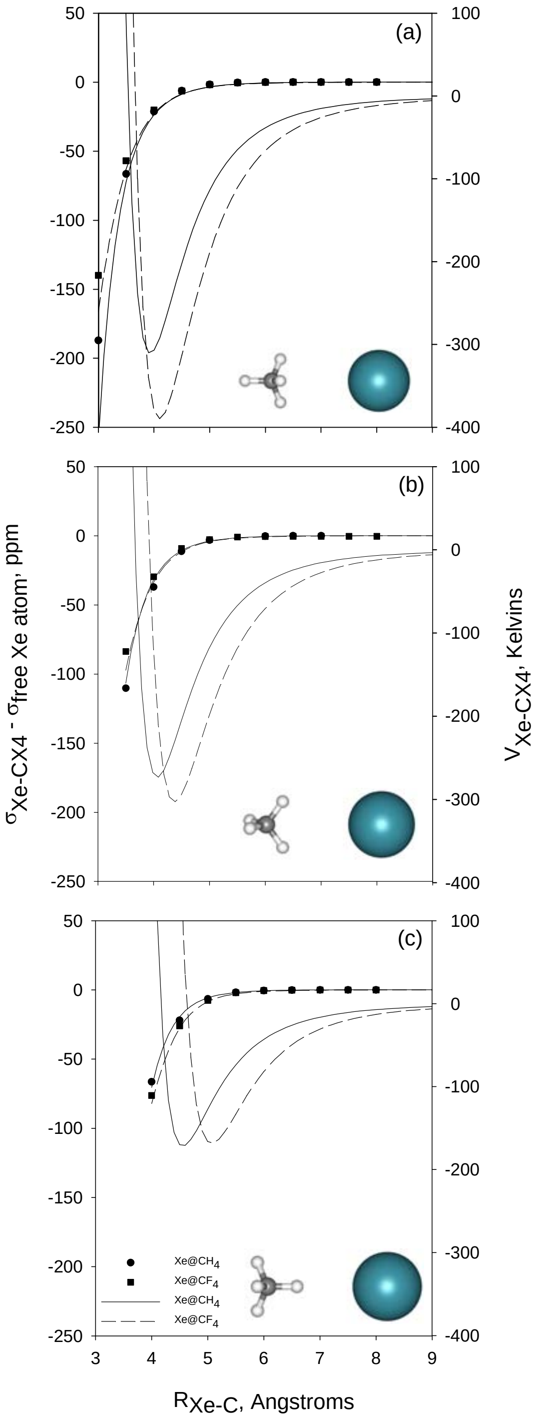
Experiment:
C. J. Jameson,
A..K. Jameson,
S.M. Cohen,
J. Chem. Phys.
65, 3401-6
(1976)

Comparison of
σ(Xe-CH$_4$)
vs. σ(Xe-CF$_4$)

and V(Xe-CH$_4$)
vs. V(Xe-CF$_4$)

along 3
trajectories.

V(Xe-CF$_4$)
keeps Xe from
sampling
highly deshielded
σ values at
shorter distances



CONCLUSIONS

- Calculations provide the **correct sign of the shift** and the **correct sign of the temperature coefficient** in all cases.
- **Electron correlation contributes** to Xe shielding functions. **1.16 x $\sigma(R)_{RHF}$ reproduces experimental data in the gas phase in most cases.**
- DFT-B3LYP overestimates the electron correlation contribution.
- Relativistic contributions to the Xe intermolecular shielding function have been neglected in this study. They may be opposite in sign to electron correlation contributions.
- The density coefficient of the intermolecular chemical shift does scale according to the law of corresponding states.
- Similarly good results are obtained where good potential functions are available, e.g., for Xe with CO_2, CH_4 and CF_4

Acknowledgments

NSF

Experiments:

A. Keith Jameson
Sheila M. Cohen
Harriet Parker

Calculations:

Angel C. de Dios