Modeling Xe chemical shifts on crystal surfaces

Cynthia J. Jameson
University of Illinois at Chicago
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 $R(\text{Xe-A})$ is: (for $A = \text{Xe or Kr or Ar or Ne}$)

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

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 $r_{\text{Xe-Xe}}$, $\sigma(\text{Xe atom})$

- **Limiting case**
  - One Xe on crystal
  - $\sigma(r_{\text{Xe-C}})$, short $r_{\text{Xe-C}}$

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

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

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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)

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 surface of the bulk Xe appear at 209 ppm
  \[ \sigma = \sum \sigma(r_{\text{Xe-Xe}}) \] nearest (short \( r_{\text{Xe-Xe}} \)) neighbors are below and in same plane.

• Xe in the middle of the bulk appear at 321 ppm
  \[ \sigma = \sum \sigma(r_{\text{Xe-Xe}}) \] nearest neighbors are below, above, and in same plane.
Xe on a chemically modified metal surface

H.J. Jänsch et al.

Xe can tell the difference between OC and H₃C-C surfaces. Xe can tell how many other Xe atoms are on the same surface.

Xe chemical shift

carbon monoxide

bulk

greater Xe coverage at lower T

ethyldiyne

Xe on OC-Ir(111)

Xe on H₃C-C-Ir(111)
QUALITATIVELY

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

Xe @OC-Ir(111):

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

• At lower T, larger \( \theta_{\text{Xe}} \),
  \[ \sigma = \sum \sigma(r_{\text{Xe-O}}) + \sum \sigma(r_{\text{XeXe}}) \]
  once in a while, Xe runs into other Xe
Xe can tell the difference between OC and H₃CC surfaces

- At low Xe coverage, \( \sigma = \sum \sigma(r_{\text{Xe-OC}}) \)
- or \( \sigma = \sum \sigma(r_{\text{Xe-H₃CC}}) \)
- intrinsic shielding response from Xe-OC is greater than the shielding response from Xe-H₃C at same distance
- however, potential functions permit Xe to stay closer to H₃C 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$_3$C

\[ \sigma(\text{Xe-OC}) \quad \text{and} \quad \sigma(\text{Xe-OC}) \]

\[ \sigma(\text{Xe-H}_3\text{C}), \; B_0 \perp \; \text{and} \; \| \]

![Graph 1: \( \sigma(\text{Xe-OC}) \) vs. \( R(\text{Xe-OC}_{\text{center of mass}}) \), Angstroms](image1)

![Graph 2: \( \sigma(\text{Xe-CH}_4) \) vs. \( R(\text{Xe-CH}_4_{\text{center of mass}}) \), Angstroms](image2)
Potential functions permit Xe to stay closer in the configuration Xe⋯H₃CH ($r_{\text{min}} = 4.05$ Å, $\varepsilon/k_B = 282$ K) compared to Xe⋯OC ($r_{\text{min}} = 4.25$ Å, $\varepsilon/k_B = 177$ K).

Xe-Xe pair distribution function determined by $r_{\text{min}} = 4.36$ Å $\varepsilon/k_B = 282$ 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 \textit{ab initio} $\sigma$(Xe-Xe) and $\sigma$(Xe-CO) tensor functions ]

• $^{129}$Xe in a xenon sheet
  [using \textit{ab initio} $\sigma$(Xe-Xe) tensor function]

Deduce Xe coverage ($\theta_{\text{Xe}}$) from observed chemical shift?
One-body distribution function for Xe@CO monolayer $\theta_r = 1.0$ on Ir(111) from grand canonical Monte Carlo simulations

Jameson, 2003

PROBABILITY of finding Xe at various locations
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.
Xe on OC-M
very small $\theta_r$

$\theta_r = 0.358$

GCMC SIMULATIONS

Jameson, 2003

$B_0 \perp$ to crystal surface

$B_0 \parallel$

$\sim 43.5$ ppm

$169.3$ ppm

span

$\sim 84.5$ ppm

$369.3$ ppm

span

$286.4$ ppm
GCMC SIMULATIONS

Low Xe coverage, $\theta_r$

<table>
<thead>
<tr>
<th>Xe chemical shift tensor component</th>
<th>Xe on OC-M very small $\theta_r$</th>
<th>(B_0) normal to surface</th>
<th>125.8 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_0) parallel to surface</td>
<td>169.3, 168.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>span \text{CALCD}</td>
<td>43.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

High Xe coverage

Results relative to free Xe atom

<table>
<thead>
<tr>
<th>Xe chemical shift tensor component</th>
<th>total chemical shift tensor Xe on OC-M (\theta_r = 0.358)</th>
<th>chemical shift tensor Xe sheet alone</th>
</tr>
</thead>
<tbody>
<tr>
<td>(B_0) normal to surface</td>
<td>369.3 ppm</td>
<td>243.5 ppm</td>
</tr>
<tr>
<td>(B_0) parallel to surface</td>
<td>286.4, 284.8</td>
<td>117.2, 116.2</td>
</tr>
<tr>
<td>span \text{CALCD}</td>
<td>84.5</td>
<td>127.3</td>
</tr>
</tbody>
</table>

C. J. Jameson, 2003
Comparison with Jänsch’s experiments

Xe on OC/ Ir(111)
very small $\theta_r$

GCMC SIMULATIONS

Xe on OC/ Ir(111)
small $\theta_r$

EXPERIMENTS

iso = 140.3 ppm
span = 43.5 ppm

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
  \textit{129Xe chemical shift measurements on a single crystal surface}

• H. J. Jänsch, P. Gerhard and M. Koch
  \textit{129Xe on Ir(111) --- NMR Study of Xe on a metal single crystal surface}

• M. Koch P. Gerhard and H. J. Jänsch,
  NMR of 129Xe on CO/Ir(111) and on multilayer Xe/Ir(111),
  Surface science \textbf{600}, 3586-3589 (2006)
CONCLUSIONS

• Difference between CO and ethylidyne is predictable from isolated Xe-OC, Xe-H$_3$CH 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$_3$C
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.