Nuclear Overhauser Enhancement (NOE)

NOEs arise from nuclear spin dipole-dipole interactions. All NMR-active nuclei (spin≠0) have a magnetic dipole, having a field similar to a bar magnet:
Nuclear Overhauser Enhancement (cont.)

A 13C nucleus will “feel” the presence of a 1H nucleus via the proton’s dipolar field.

In the case shown below, the dipolar field is \( \sim 30 \) degrees from being opposite of the applied static magnetic field.

\[
\Delta E_{dd} \propto \gamma_i^2 \gamma_j^2 \left\langle \sum_j \frac{\tau_c}{r_{ij}^6} \right\rangle_t
\]
Population Description for Protons

\[ \Delta E = \gamma_H B_o \]

\[ \frac{N_\beta}{N_\alpha} = e^{-\Delta E/RT} \sim 1 - \frac{\Delta E}{RT} \]

\[ v_o = 500 \text{MHz} \]
Population Description for Protons

Since $\Delta E/RT \ll 1$

$N_\beta \sim N_\alpha (1 - \Delta E/RT)$

so Claridge’s (Chap. 8)

$\Delta = \Delta E/2RT$

Easiest to use simple numbers, since populations are $\sim$ linear.

[following Sanders&Hunter]
Population Description for Protons

Since $\Delta E/RT \ll 1$

Easiest to use simple numbers, since populations are $\sim$ linear.

The figure is qualitatively correct, or precisely for 80,000 protons.

What’s shown is the excess population.

[following Sanders&Hunter]
Population Description for $^{13}C$

Since

$\gamma_C \sim \gamma_H / 4$

population excess is 1/4th for $^{13}C$ than for $^1H$. 

$\nu_0 = 125$MHz
Population Description for Two-Spin Heteronuclear System

\[
\begin{align*}
\beta \beta & \quad \longrightarrow \quad \beta \alpha \\
\alpha \beta & \quad \longrightarrow \quad \alpha \alpha
\end{align*}
\]

\[13^C\text{ } J_{CH} \text{ } 125\text{MHz}\]
Population Description for Two-Spin Heteronuclear System

\[ \beta\beta \quad \beta\alpha \quad \alpha\alpha \]

\[ \text{\textsuperscript{1}H} \quad J_{CH} \quad 500\text{MHz} \]
Population Description for Two-Spin Heteronuclear System

Equilibrium Zeeman populations

\[ ^1H \quad 500\text{MHz} \]

\[ ^{13}C \quad 125\text{MHz} \]

\[ J_{CH} \]
Population Description of Decoupling

Decoupling ~ equalizes populations along 1H transitions
Relaxation will always work to re-establish Zeeman populations. The theory goes beyond this discussion, but hand-waving, we get to something similar to that shown above.
ZQ does not happen in the heteronuclear case with no (ZQ) degenerate energy levels.
Population Description of NOE

DQ does occur, giving populations something like this.
Population Description of NOE

\[ \eta \propto 1 + \frac{\gamma_H}{2\gamma_C} \]

signal is enhanced by ~3 for 13C

\[ \frac{5}{(2)} \]

\[ \frac{3}{(8)} \]
Summary of NOE in Heteronuclear NMR

- By far the most common use of NOE in heteronuclear NMR is for signal enhancement. Distance determinations using $(1/r^6)$ typically are used only in homonuclear ($^1\text{H}-^1\text{H}$) NMR (but see Claridge section 8.9.2).

- Decoupling is not sufficient to affect X-nucleus intensities alone (requires relaxation, typically a few seconds).

- Energy-dependent relaxation creates NOEs:
  - double quantum relaxation creates positive NOEs (positive $\gamma$)
    - dominant in heteronuclear systems
    - low MW (small $\tau_c$) in homonuclear systems
  - zero-quantum relaxation creates negative NOEs
    - high MW (large $\tau_c$) in homonuclear systems

- The enhancement maximizes at $1 + \gamma_H/2\gamma_X$. Note lack of r dependence!!

  $1\text{H} \rightarrow 1.5 \quad 13\text{C} \rightarrow 3 \quad 15\text{N} \rightarrow 4$

The X-nucleus enhancements are significantly larger for polarization transfer, but a J-coupling must then be present.

Note: enhancement can go to zero for negative $\gamma_X$ Use INEPTRD for 29Si!
NOE Growth for Positive $\gamma$ Nuclei

$\eta$

$e.g. \quad ^{13}C$

Int.

$t$

$M(H)_{eq}$

$M(C)_{eq}$

with NOE

w/o NOE

larger $r$
Heteronuclear NOEs: Positive $\gamma$ Nuclei
NOE Growth for Negative $\gamma$ Nuclei

e.g. $^{29}\text{Si}$ Int.

$\eta$

$t$

$M(H)_{eq}$

$M(Si)_{eq}$

with NOE: $-\gamma$

with NOE larger $r$
Heteronuclear NOEs: Negative $\gamma$ Nuclei

$^{29}\text{Si}, ^{15}\text{N}, ^{119}\text{Sn}$

Diagram showing the relationship between $t$ and $\eta$ with $M(H)_{eq}$ and $M(Si)_{eq}$.