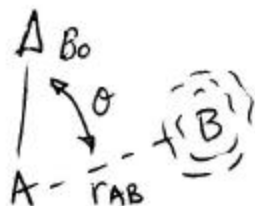


Relaxation

primary mech ($I = \frac{1}{2}$) dipole-dipole



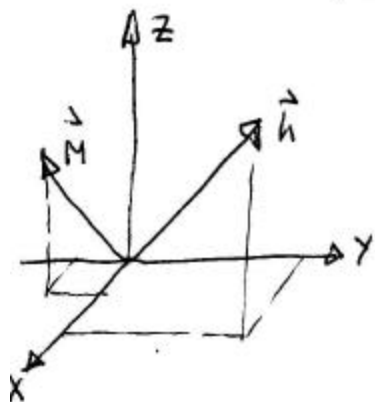
$$|\vec{B}_{loc}| = \mu_B (3\cos^2\theta - 1) / r_{AB}^3$$

Δ 's in θ cause \vec{B}_{loc} to fluctuate

define τ_c Molec. correlation time:
mean time required for θ to
change appreciably

Relaxation takes place iff \vec{B}_{loc} Δ 's
at freq $\sim \omega_0$ (the Larmor freq.)

$\vec{B}_{loc} = \vec{h}$; if \vec{h} has comp. at ω_0 these
components are also stationary
and will interact with \vec{M}



$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{h}$$

h_x, h_y, h_z all affect M_x, M_y ; T_2

h_x, h_y affect M_z ; T_1

h_z : has no effect on $M_z \sim T_1$

T_1 : how fast M_z reaches \rightleftharpoons

T_2 : " " M_x & M_y return to \rightleftharpoons

Recovery process:

$$M_z(t) = M_0 [1 - \exp(-t/T_1)]$$

$$M_x(t) = M_0 [\exp(-t/T_2)]$$

$$M_y(t) = M_0 [\exp(-t/T_2)]$$

k_z : Slow process

k_x, k_y : both slow/fast process

T_1 affected by fast dynamic processes at ω_0 (at

T_2 " " " $\hat{=}$ slow molec. processes.

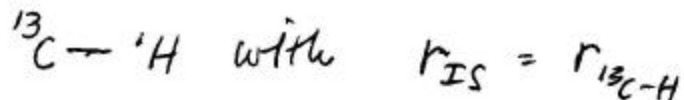
$$T_2 \leq T_1$$

Nuclear Relaxation: Spin Lattice Relaxation

Dipole - Dipole Relaxation (can't from class)

for ^{13}C

- 1.1% Nat. Abundance
- good chemical shift resolution
- due to low Natural Abund. ^{13}C are spatially isolated from each other
- mutual dipole-dipole effects are negligible between $^{13}\text{C} - ^{13}\text{C}$
- nearest effect from directly attached protons.



- carbons are internal to molecule: only intramolecular effects.

ex) $^{13}\text{C} - \text{H}$: decouple protons using BB irradiation \rightarrow Broad Band
used in T_1 measurements

decoupling results in simplifications: $M_S^z = 0$

let $I = ^{13}\text{C}$ & $S = ^1\text{H}$ and $\{^1\text{H}\} \sim$ decouple protons to remove scalar coupling

after Solomon, Phys. Rev., 99, 559 (1959).

$$\frac{dM_I^z}{dt} = -\rho (M_I^z - M_I^0) - \sigma (M_S^z - M_S^0)$$

$$\rho_{\text{IS}} = W_0 + 2W_1 + W_2$$

$$\sigma_{\text{IS}} = W_2 - W_0$$

- the transition prob. as discussed in class

$$\text{and } \frac{dM_I^z}{dt} = \frac{1}{T_1(I)} (M_I^z - M_I^0)$$

$$\text{obtain } \frac{1}{T_1(I)} = -\rho_{CH}$$

$J_n(\omega)$ are
spectral densities as
defined in class

$$= \frac{K^2}{20} [J_0(\omega_H - \omega_C) + 3J_1(\omega_C) + 6J_2(\omega_H + \omega_C)]$$

$$\text{where } K = \frac{\gamma_C \gamma_H \hbar}{r_{CH}^3}$$

Result: plot of T_1 (s) - vs - τ_C (Å) as function of field strength.

$$\text{use } r_{CH} = 1.09 \text{ \AA}$$

form of plot is same as for 'H - 'H
Relaxation

Extreme narrowing conditions: $\tau_C \ll \omega_C^{-1}$

then for N_H : # directly bound 'H

$$\frac{1}{T_1(I)} = \frac{N_H \gamma_H^2 \gamma_C^2 \hbar^2}{r_{CH}^6} \tau_C = 2.1 \times 10^{10} \cdot \tau_C \cdot N_H$$

$$\text{or obtain } \tau_C = \frac{4.7 \times 10^{-11}}{N_H \cdot T_1}$$

an estimate of correlation time

Relaxation Mechanisms: ^{of} Types and relative importance

Spin Rotation: a molecule in fluid medium is a rotating charge system.

Normally
more significant
for carbons
than
protons.

→ generates magnetic moment in addition to nuclear moments

- Molecular Collisions: Changes in rate of rotation & direction (axis, axes) causes this field to fluctuate
- if time scale is correct: may interact with nuclear magnetization.

Result (near centre of gravity of an isotropically tumbling molecule)

$$\frac{1}{T_1(SR)} = \frac{2 I k T}{3 \hbar^2} \cdot C^2 \cdot \tau_{SR}$$

where I is the moment of inertia

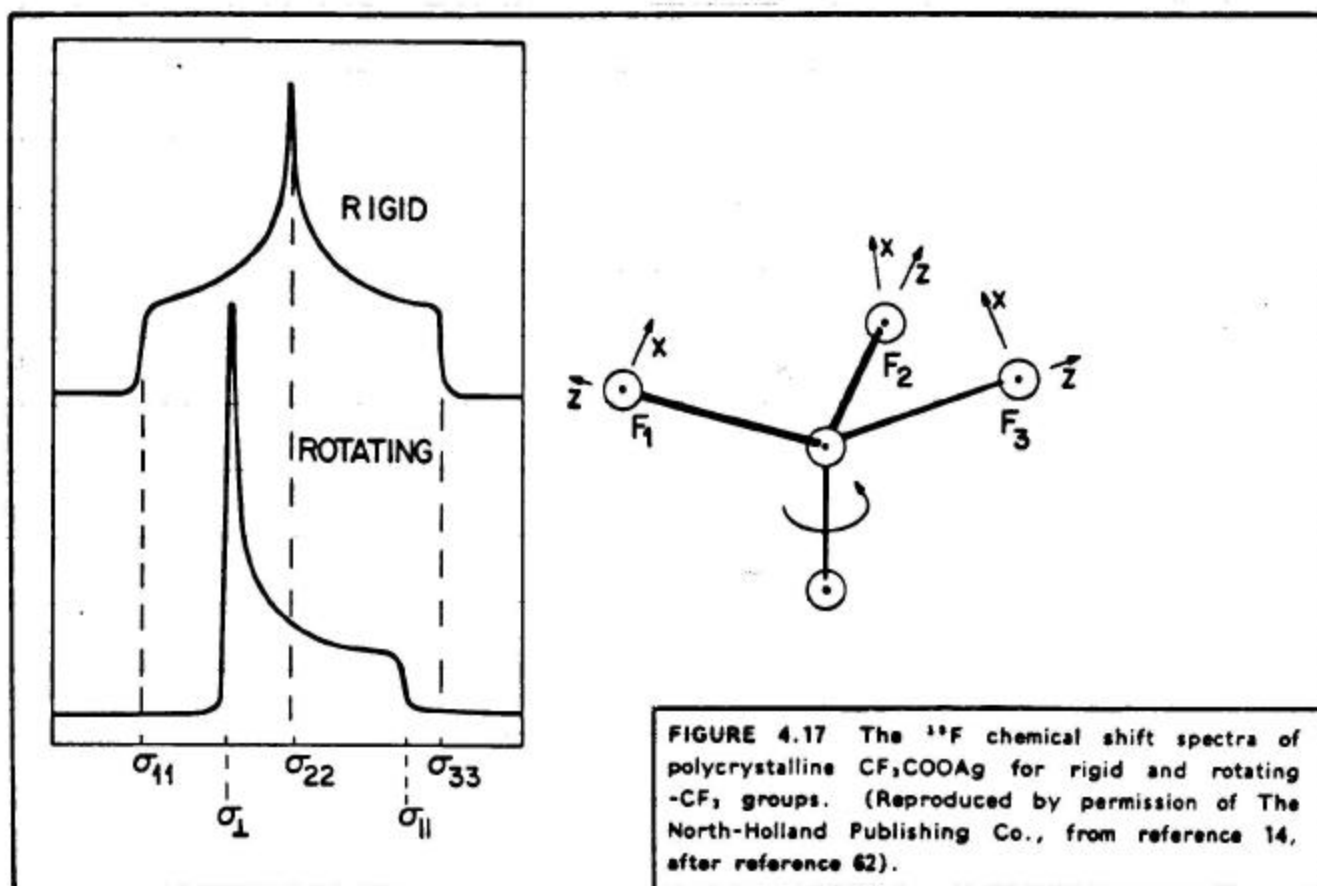
C averaged value of SR coupling tensor (normally weak)

and τ_{SR} the correlation time: different than τ_c

↑
expresses average time molecule remains in a given angular momentum state $\propto \tau_c^{-1}$

$T_1(SR)$ becomes shorter in liquids as Temperature is increased

- proton decoupling e.g. $\{^1\text{H}\}$ causes enhancement of ^{13}C magnetization \rightarrow NOE as discussed in class
- Know how to form NOE, measure it, quench it (see notes and text book)



Chemical shift anisotropy:

Chemical shift is a directional quantity
depends on orientation with respect to B_0

in liquids: Rapid motion averages this to isotropic values.

BUT: on the time scale of Molecular Motion:
the nucleus experiences fluctuations in
the local field from this source

fast motion limit:

$$\frac{1}{T_1(\text{CSA})} = \frac{2}{15} \gamma^2 B_0^2 (\sigma_{11} - \sigma_{\perp})^2 \tau_c$$

defined for anisotropic group
with axial symmetry.

B_0^2 : considerable effect for unsaturated/aromatic
carbons at high field.

$$\sigma_{11} = \sigma_{33} \quad \hat{z} \quad \sigma_{\perp} = \sigma_{11} = \sigma_{22}$$

Quadrupolar Relaxation:

What's a Quadrupole?

$I = \frac{1}{2}$ Spherical distribution of nuclear charge which is not affected by electric environment with molecule

$I > \frac{1}{2}$ charge distribution is spheroidal (nucleus spins about principle axis of spheroid)
• electric quadrupole moment exists!

two configurations: energies depend on orientation

Prolate (+)



oblate (-)



ex) Spherical / tetrahedral: NH_4^+ no electric field gradient (efg).
- tumbling won't have any effect.

In most Molec. ($I > \frac{1}{2}$) substantial (efg) are present and these interact with nuclear quadrupoles. The spin states are rapidly changed by tumbling of molecular framework

Result: additional pathways for energy exchange.

potent source of relaxation: is electric rather than magnetic in origin

quadrupoles don't interact with homogeneous electric field, BUT does interact with an electric field gradient.

electric quadrupole: eQ
unit atomic charge
dimension of (distance)² barn
 $\approx 10^{-28} \text{ m}^2$
negative or positive depending on shape (oblate, prolate)

Zeeeman energy levels are perturbed by etg especially important in solids

$$E = -\gamma \hbar B_0 m$$
$$m = I, I-1, \dots, -I$$

Assume molec. motion is rapid enough (liquids) to remove interaction

still appreciable contribution to T_1 & T_2

Extreme motional narrowing limit ($\omega_0 \tau_c \ll 1$)

$$\frac{1}{T_1(Q)} = \frac{1}{T_2(Q)} = \frac{3\pi^2}{10} \cdot \frac{(2I+3)}{I^2(2I-1)} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{e^2 q Q}{h}\right)^2 \tau_c$$

Some Quadrupole moments:

		Q
^2H	$I = 1$	$0.0028 (10^{-28} \text{m}^2)$
^6Li	1	-0.0008
^{10}B	3	.085
^{11}B	$3/2$.041
^{14}N	1	.01
^{17}O	$5/2$	-0.026
^{35}Cl	$3/2$	-0.10
^{37}Cl	$3/2$	-0.079

the term $\frac{3\pi^2}{10} \frac{(2I+3)}{I^2(2I-1)}$ -vs- I

14.8044	1
3.9478	$3/2$
.9475	$5/2$
.4028	$7/2$

the electric field gradient $\equiv "q"$

asymmetry parameter = η ; for cylindrical symmetry $\eta = 0$

$\frac{e^2 q Q}{h}$: quadrupole coupling const. (qcc)

- ^{14}N weak qcc \approx lines less than 1 Hz wide
 - \rightarrow for cases of high local symmetry
 - ex) NH_4^+ or $\text{N}^+(\text{CH}_3)_4$

- Most organic compds $g_{cc} \sim MHz$
very strong effects.
lines are 10A - 100 A Hz wide

\therefore ^{14}N is most abundant isotope
too difficult to observe so ^{15}N ($I = \frac{1}{2}$)
with 1.37% natural abundance is favored

^{17}O 0.037% Nat. Abund. No spin $\frac{1}{2}$
 $^{35}Cl, ^{37}Cl$ ~~99~~ $g_{cc} \sim 10^2 MHz$
Not practical to observe.
decouple themselves.
don't alter $^1H, ^{13}C$ spectra.
(in solids $^{13}C-Cl$ carbons often are
not observed)

2H ($I = 1$) quad. moment is small : observe in liq
(1 Hz linewidth)
- quad. effect dominate
- Simplified interpretation of molec. dynamics

deuterium labels often used to study in liquids
or solids in ordered / ~~disordered~~
disordered systems.

Scalar Relaxation:

- effect
- $I \geq 1$ a) broadens resonances
b) couples to $I = \frac{1}{2}$

ex) $^{14}\text{N} - \text{H}$ amines, amides, peptides

1:1:1 triplet with 50Hz spacing commonly observed collapsed in varying degrees by rapid transitions of ^{14}N between states.

ex) $^+\text{NH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ cation: 50Hz broadened triplet.

for amides, peptides: triplet not observed.

Similar to proton chemical exchange:

if due to chem. exchange: scalar relaxation of 1st kind.

qund. relaxation (No chem. exchange): scalar relaxation of 2nd kind

- collapse is more complete at lower temperatures where τ_c is longer and $\frac{1}{T_1(\nu)}$ is greater.

Paramagnetic Relaxation:

causes marked decreases in T_1 & T_2

why? large fluctuating fields generated by unpaired electron spins
 10^3 times largest nuclear moments!

$$\frac{1}{T_1(P)} = \frac{4\pi^2 \gamma^2 \eta N_p \mu_{\text{eff}}^2}{kT}$$

γ : for protons

η : solution viscosity

N_p : # paramagnetic ions per ml

μ_{eff} : effective magnetic moment of paramag. species

ex) use of paramagnetic complexes can eliminate NOE, hasten $T_1(\text{C})$ relaxation making ^{13}C spectra quantitative.

Relative Significance

for ^{13}C (diamagnetic solutions)

DD, SR in small symmetric molecules
 ↓
 dominates larger molecule & exclusive in macromolecules

CSA : ^{can} dominates at higher fields

P : dominate when solution contains paramagnetic ions / substances

Additivity:

$$\frac{1}{T_1(\text{obs})} = \frac{1}{T_1(\text{DD})} + \frac{1}{T_1(\text{SR})} + \frac{1}{T_1(\text{CSA})} + \frac{1}{T_1(\text{S})} + \frac{1}{T_1(\text{Q})} + \dots$$

Small to Moderately large molec.
 ↓
 decreases with increasing temp.

opposite effect to DD

increases with B_0^2
 ↓
 use strong field depend to sort out relative contribution of DD /

Special cases

For organic molecules: reveal assignments quantum or C= have long T_1 's are often suppressed

get information on rapid internal motions → methyl groups!

Nuclear Overhauser Effect

$I = {}^{13}\text{C}$, $S = {}^1\text{H}$ $\{^1\text{H}\}$ saturated $M_S^Z = 0$ as before

$$\text{then: } \frac{M_I(S \text{ irradiated})}{M_I^0} = 1 + \frac{\sigma}{\rho} \cdot \frac{M_S^0}{M_I^0}$$

\downarrow \leftarrow values of spin populations / mag.
 $\frac{\gamma_S}{\gamma_I}$ are $\propto \gamma$

${}^{13}\text{C}$

$$\frac{M_C\{^1\text{H}\}}{M_C^0} = 1 + \left[\frac{6J_2(\omega_H + \omega_C) - J_0(\omega_H - \omega_C)}{J_0(\omega_H - \omega_C) + 3J_1\omega_C + 6J_2(\omega_H + \omega_C)} \right] \cdot \frac{\gamma_H}{\gamma_C}$$

$$= 1 + \eta_{C-H}$$

\nwarrow
the ${}^{13}\text{C}\text{-}\{^1\text{H}\}$ NOE enhancement factor

$$\frac{\gamma_H}{\gamma_C} = 3.977 \quad \text{under extreme motional narrowing!}$$

$$\frac{M_C\{^1\text{H}\}}{M_C^0} = 1 + 0.5 \frac{\gamma_H}{\gamma_C} = 2.988$$

$$\eta = 1.988$$

NOE depends on dipole-dipole relaxation

other competing relaxation pathways detract from it. (common) esp in small molec.

C/H NOE is often less than maximal even under fast motion.

... can be used to back calculate other mech.

-H $r=1.099$
 section plot of
 NOE occurs at
 minima of
 T_1 plots.

$$\frac{1}{T_1(\text{other})} = \frac{1}{T_1(\text{obs})} \left(1 - \frac{\eta_{\text{obs}}}{\eta_0} \right)$$

maximal assuming fast motion,
 (does motional narrowing limit app)

field depend. proton/carbon take same form.

η varies between carbons: quench τ paramagnetic
 Cr acetyl acetonate.

Proton-Proton NOE:

$${}^1\text{H} - {}^1\text{H}: \frac{M_H(\text{irrad})}{M_H^0} = 1 + \left(\frac{6J_2(2\omega_H) - J_0(0)}{J_0(0) + 3J_1(\omega_H) + 6J_2(2\omega_H)} \right)$$

$$= 1 + \eta_{HH}$$

$$\frac{\delta_H}{\delta_H} = 1$$

• Chem shift must be suff. different

$$\eta_{\text{max}}^{HH} = 0.5$$

$\gamma = 0.0 \quad \tau_c \omega_0 \approx 1$
 = negative.

Note 0.0 on axis! near top

${}^1\text{H}$ obs
 ${}^{13}\text{C}$ obs.

- spin flipping
 - gated
 - inverse gated
- experiments

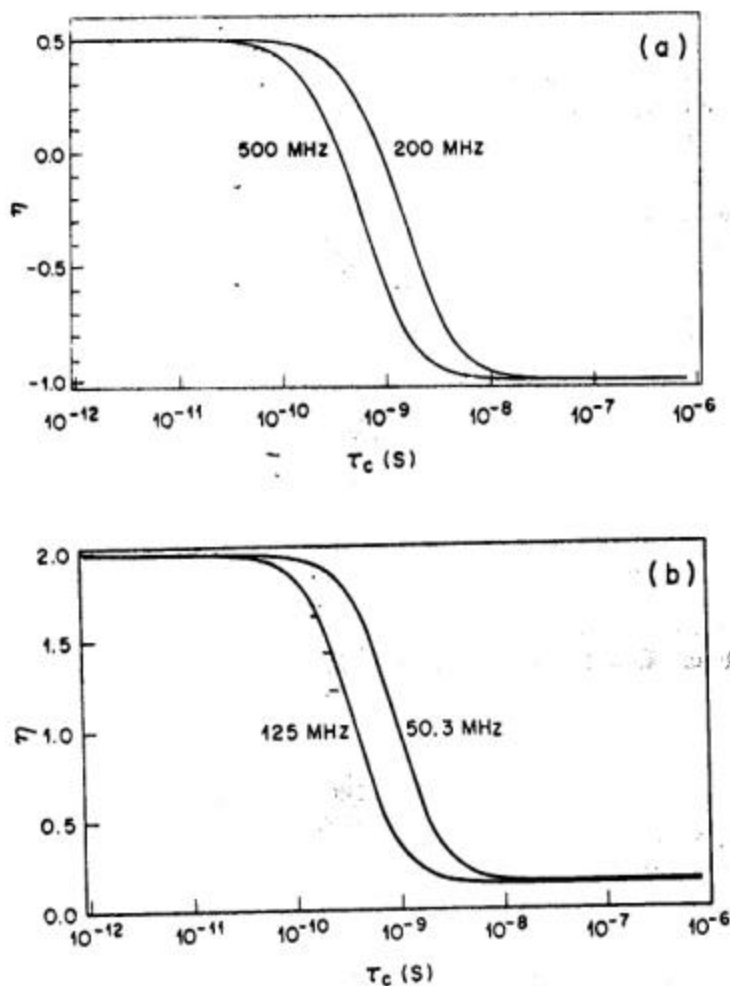


Fig. 5.8. (a) Nuclear Overhauser enhancement factor η for a proton, produced by irradiation of a neighboring proton(s), as a function of the correlation time τ_c , calculated for proton frequencies of 200 MHz and 500 MHz [Eq. (5.43)]. (b) Nuclear Overhauser enhancement factor η for a carbon-13 nucleus, produced by irradiation of neighboring proton(s), as a function of the correlation time τ_c , calculated for carbon-13 frequencies of 50.3 MHz and 125 MHz [Eq. (5.39)].

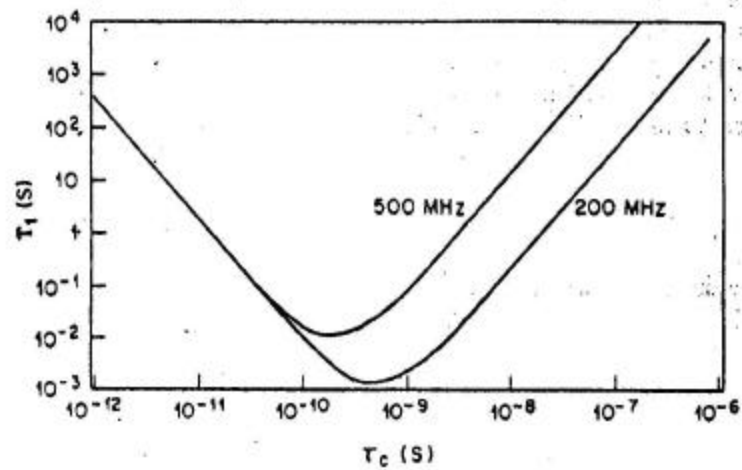


Fig. 1.9. Spin-lattice relaxation time T_1 (s) corresponding to mutual relaxation of water protons (intramolecular only) as a function of correlation time τ_c , as observed at 200 MHz and 500 MHz.

5.2 Spin Lattice Relaxation

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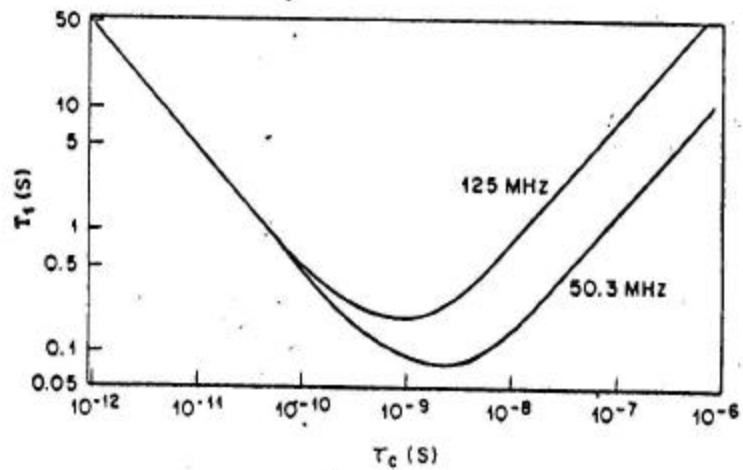


Fig. 5.3. Spin lattice relaxation time T_1 for a carbon-13 nucleus with one directly bonded proton as a function of the correlation time τ_c at 50.3 MHz and at 125 MHz. The proton is irradiated to remove scalar coupling [Eq. (5.25)].