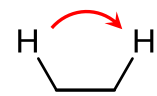
The Nuclear Overhauser Effect (NOE): Probing Molecular Geometry Through Space

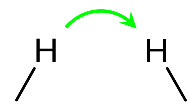
Scalar coupling:

- **Through bonds.**
- Exhibited in splitting, *J*.
- **Used to determine connectivity.**

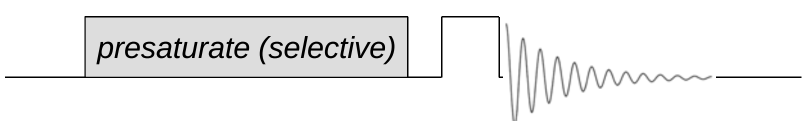


Dipolar coupling:

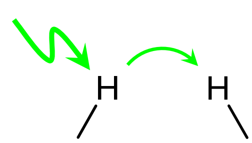
- **Through space.**
- Exhibited in magnetization transfer.
- Fundamentally different from scalar coupling.
- Changes peak *intensities*.
- Partly responsible for T_1 relaxation of nuclei.
- **Used to determine spatial relationships.**
- Falls off w/ $1/r^6$; nuclei should be within 5 Å.



The Nuclear Overhauser Effect (NOE): Probing Molecular Geometry Through Space



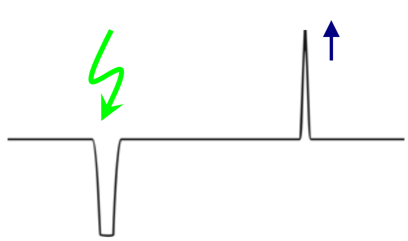
Not the same as decoupling!



magnetization transfer

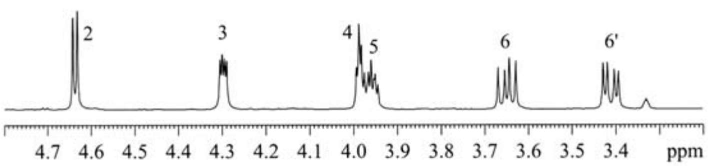
before presaturation

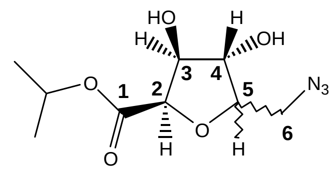
after presaturation



Usually, NOE spectra are displayed as the *difference* between on-resonance saturation and off-resonance saturation.

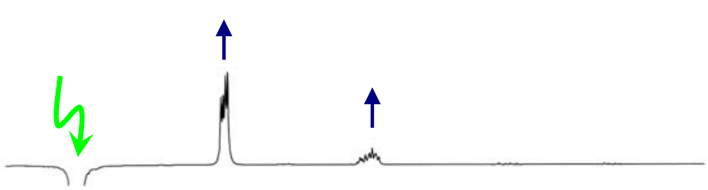
Nuclear Overhauser Effect (NOE)

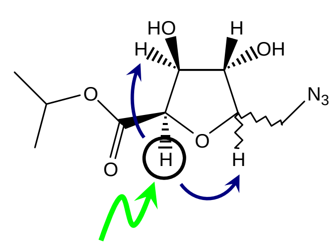


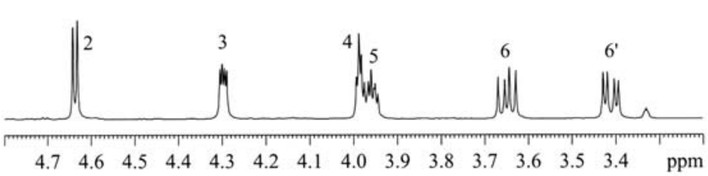


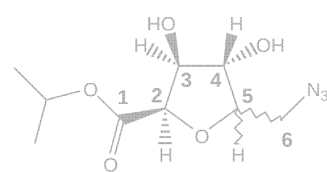
stereochemistry @ C_5*?*

Nuclear Overhauser Effect (NOE)



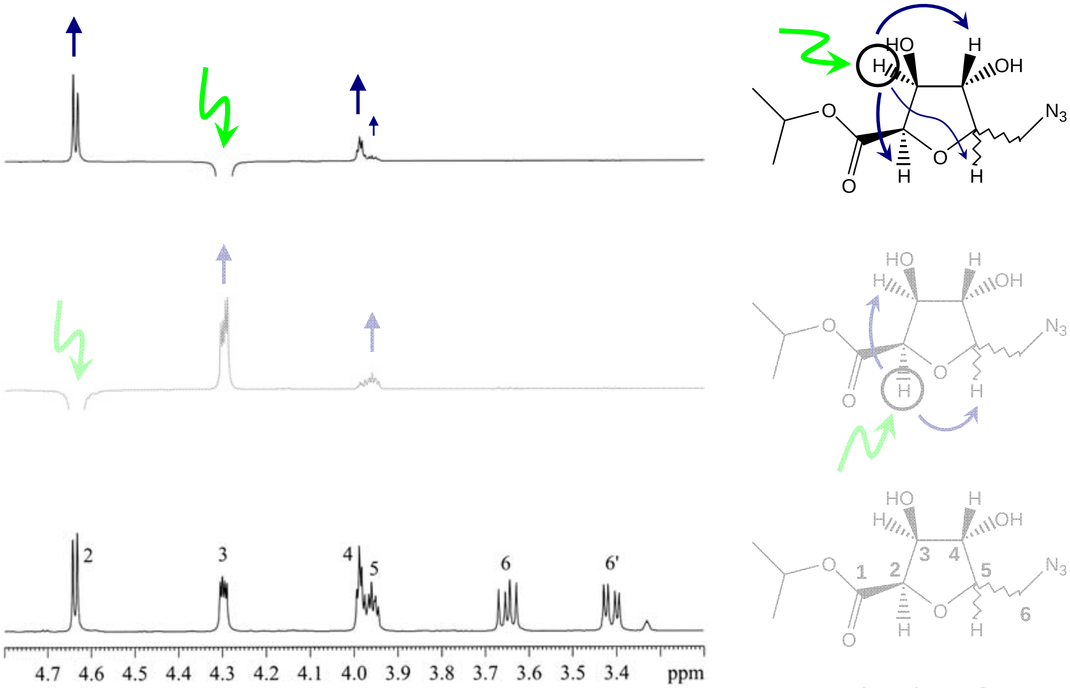






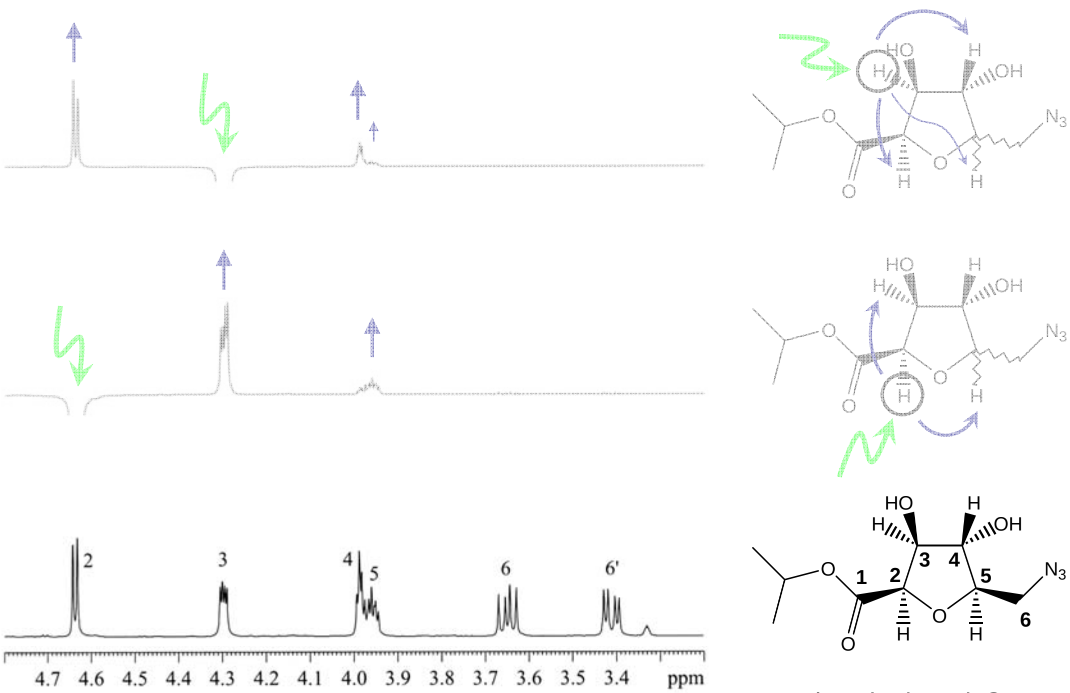
stereochemistry @ C_5*?*

Nuclear Overhauser Effect (NOE)



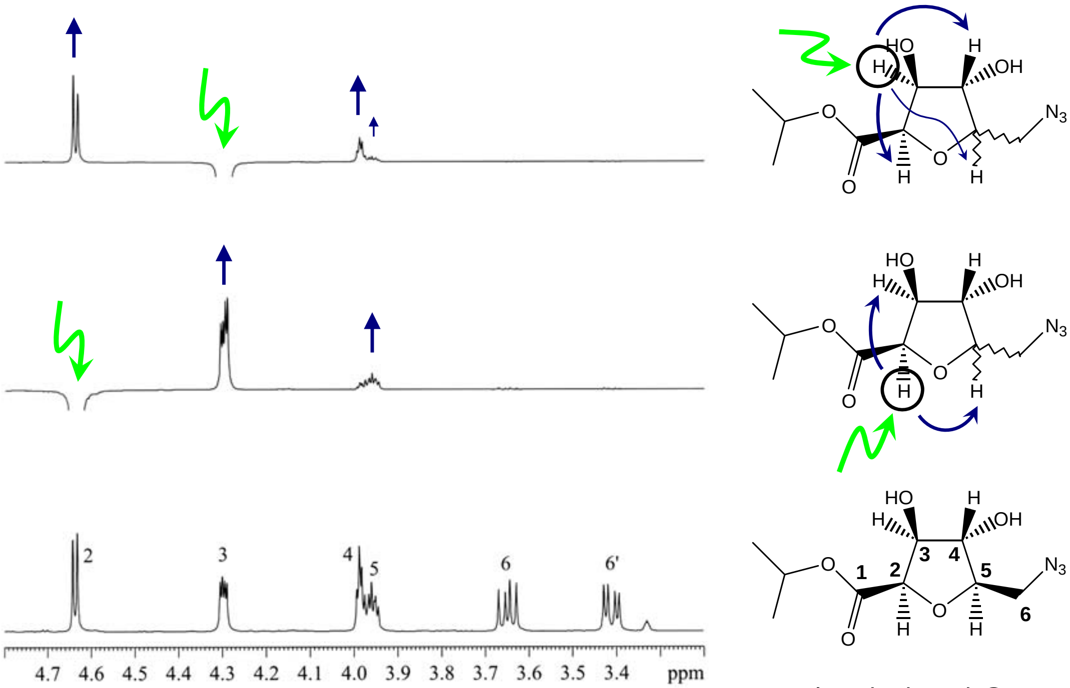
stereochemistry @ C_5?

Nuclear Overhauser Effect (NOE)



cis-substituted @ C_5.

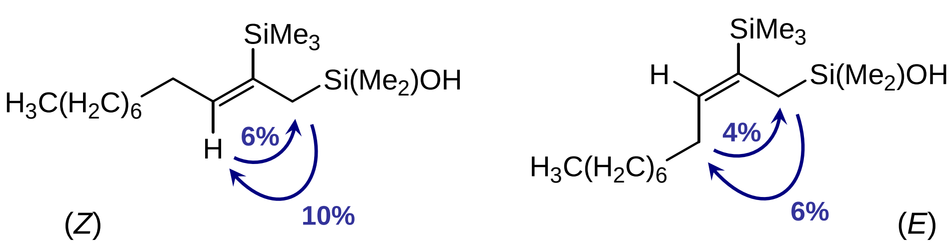
Nuclear Overhauser Effect (NOE)



cis-substituted @ C_5.

Nuclear Overhauser Effect (NOE)

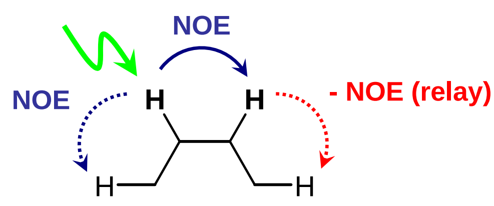
- Intensity of magnetization transfer, and thus difference NOE peaks, is somewhat related to internuclear distance ($1/r^6$). Often expressed as % intensity change.



- However, NOE intensities also depend on other NOE relaxation partners, local environment, so % values cannot be trusted completely.

Nuclear Overhauser Effect (NOE)

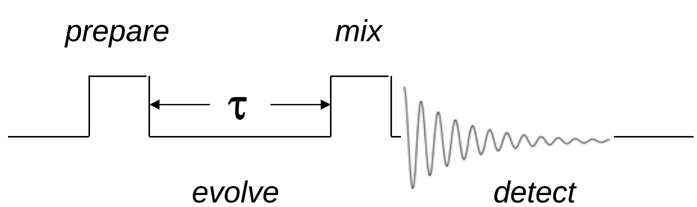
• Other NOE's, relay pathways will affect intensities.



odd # NOE steps give **positive** NOEs intensities,
even # NOE steps give **negative** NOE intensities,

Example: camphor

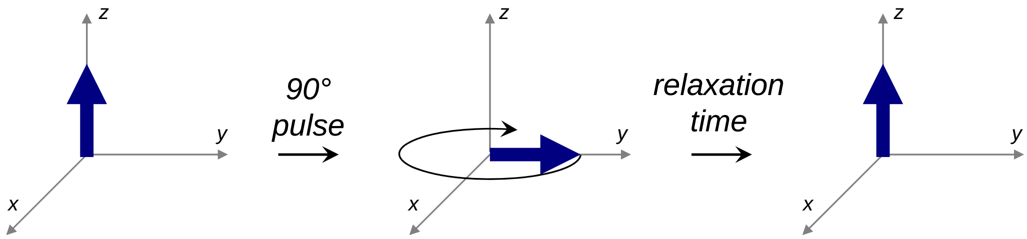
Multiple Pulse Experiments



- τ is less than full relaxation time of FID, so second pulse interrupts relaxation.
- Varying τ (time between pulses) and observing change in FID (or spectrum) gives additional information about system.
- All of NMR techniques from here on will be multi-pulse experiments.

Inversion-Recovery: Measuring T_1

In a typical, single-pulse experiment,

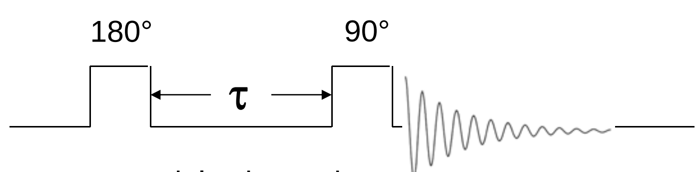


Actual, on *z* axis: T_1

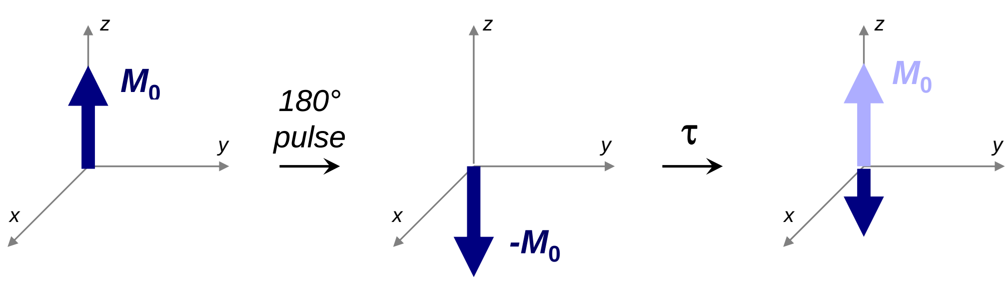
Measured, on *x* axis: $(T_1 + T_2)/T_1T_2$

How do we measure T_1 without confounding influence of T_2?

Inversion-Recovery: Measuring T_1

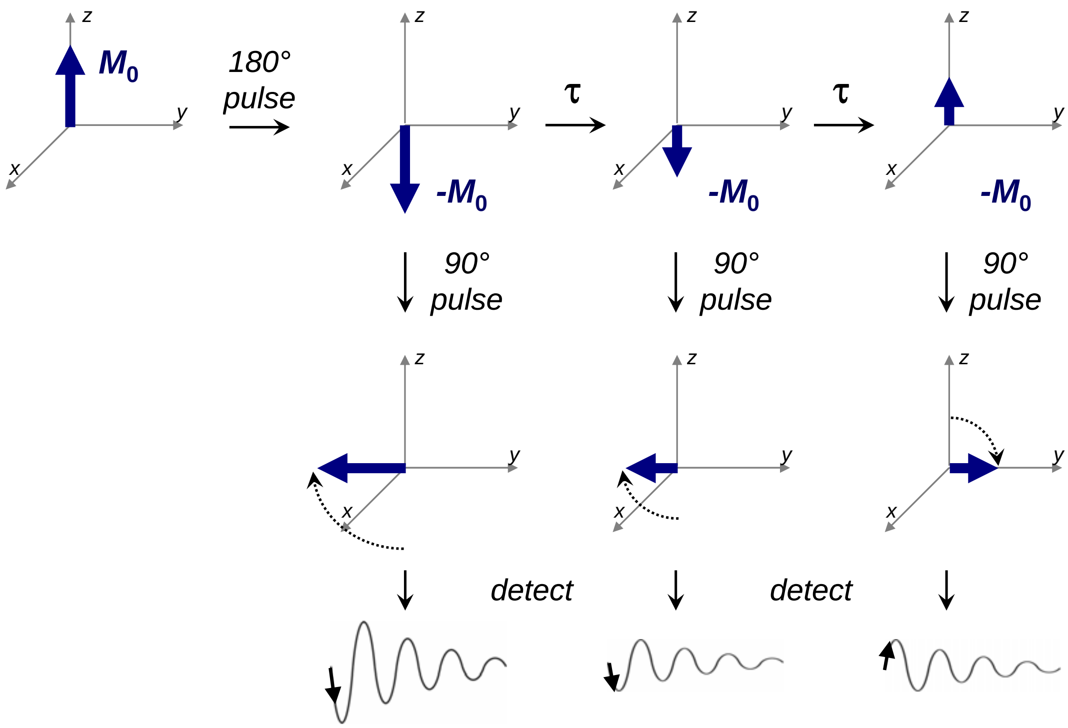


τ delay is used to determine T_1

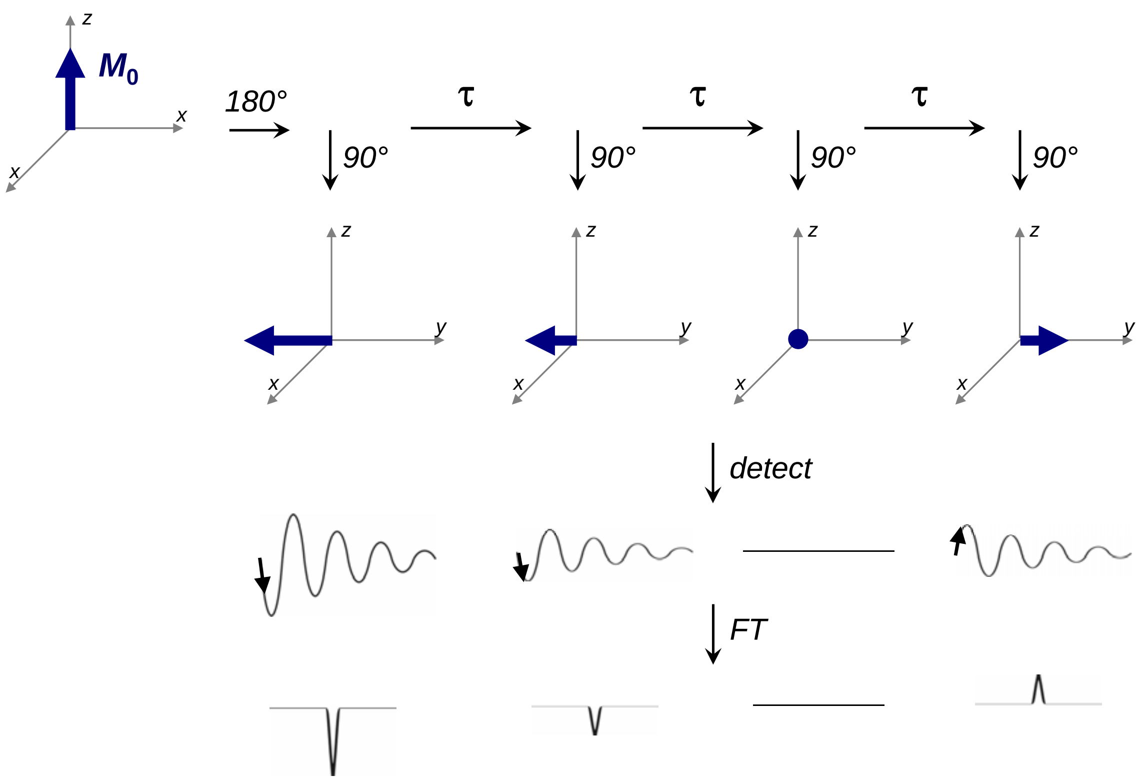


- Relaxation from $-M_0$ back to M_0 determined solely by T_1; no (x,y) component to experience T_2 decoherence
- No (x,y) component to detect either

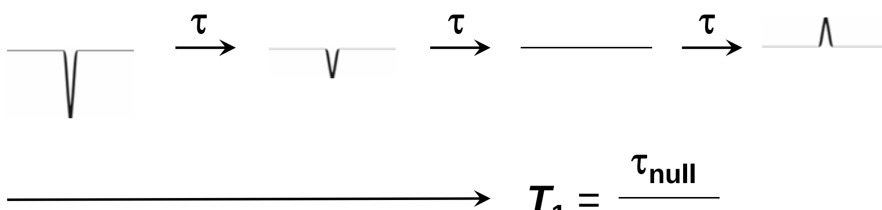
Inversion-Recovery: Measuring T_1



Inversion-Recovery: Measuring T_1



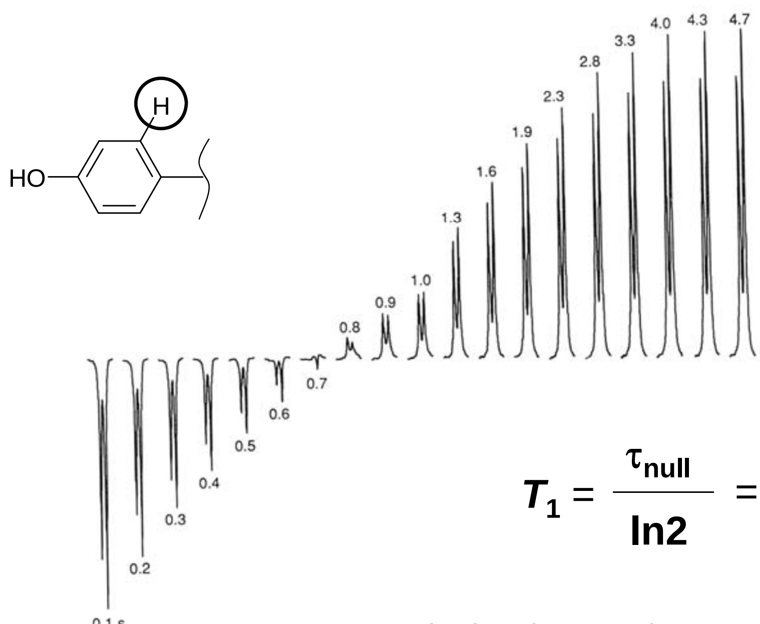
Inversion-Recovery: Measuring T_1



$$T_1 = \frac{\tau_{null}}{\ln 2}$$

Delay time at which no FID is observed (τ_{null}) corresponds to T_1 (half-life of magnetization decay).

Inversion-Recovery: Measuring T_1



$$T_1 = \frac{\tau_{null}}{\ln 2} = 1 \text{ sec}$$

Method and calculation are now automated in spectrometers.

Inversion-Recovery: Measuring T_1