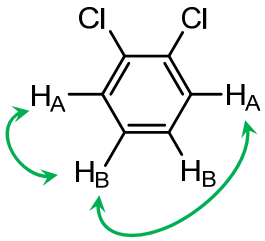
Chemical vs. Magnetic Inequivalence



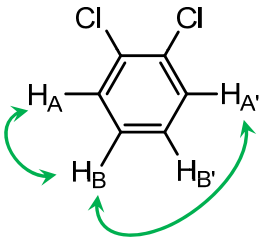
Issue:

Two H_A protons are chemically equivalent.

But they don't have the same geometric relationship with each coupling partner H_B.

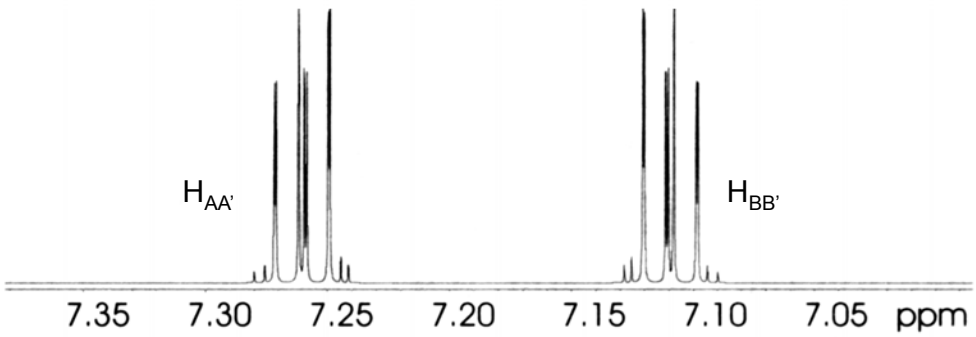
So what is coupling constant $J_{A,B}$? What does ^{1}H NMR look like?

Chemical vs. Magnetic Inequivalence



H_A $H_{A'}$ protons are chemically equivalent, magnetically inequivalent.

Result is multiple lines in NMR;
Coupling constants usually cannot be evaluated by inspection.



^{13}C NMR: Inherent Problems

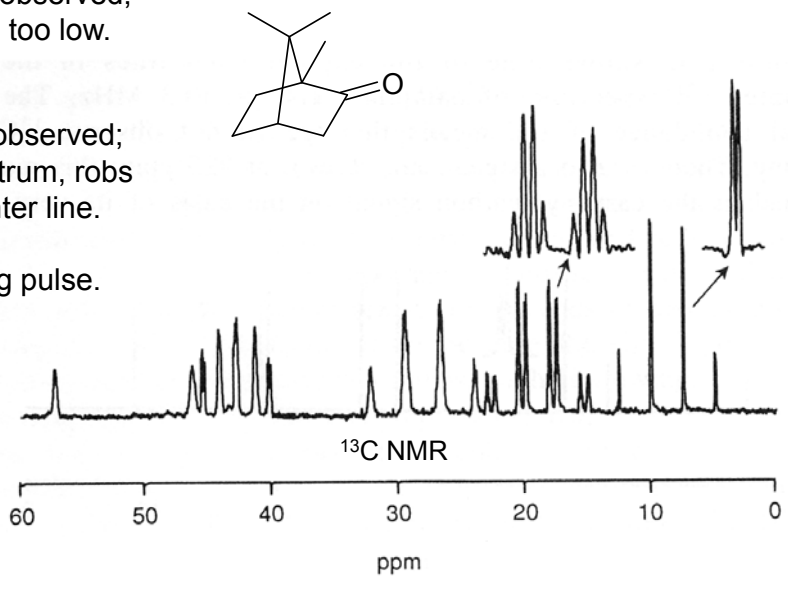
- Low abundance of ^{13}C (1.1%, vs. 99.9% for ^{1}H).
- Lower gyromagnetic ratio (1/4 that of ^{1}H).
- Slow T_1 relaxation times (10-100 sec, vs. 0.1-1 sec for ^{1}H).
- ^{13}C-^{1}H coupling complicates spectrum, robs center lines of intensity.

C-H Coupling and ^{13}C Broadband Decoupling

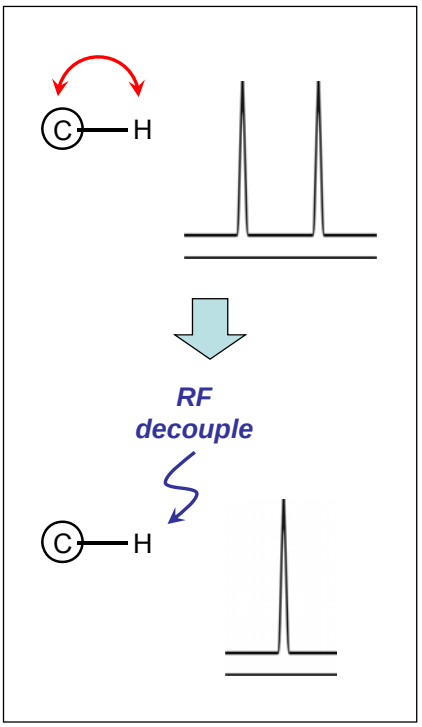
$^{1}H \leftarrow C$ coupling not observed; abundance of ^{13}C too low.

$^{13}C \leftarrow H$ coupling is observed; complicates spectrum, robs intensity from center line.

Solution: Decoupling pulse.



C-H Coupling and ^{13}C Broadband Decoupling



B_1 {^{13}C}

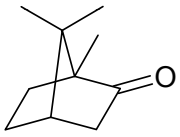
B_2 {^{1}H}

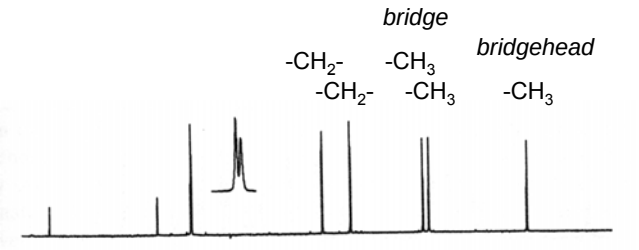
broadband decouple

oscillates (averages) spin states of all protons in sample (regardless of frequency);

"turns off" all C-H coupling.

^{13}C-^{1}H Coupling and ^{13}C Broadband Decoupling

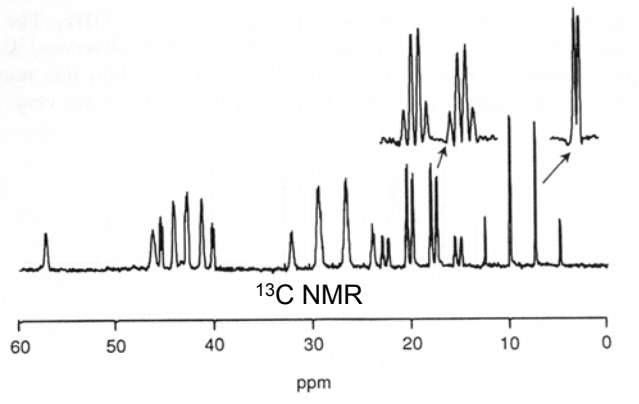




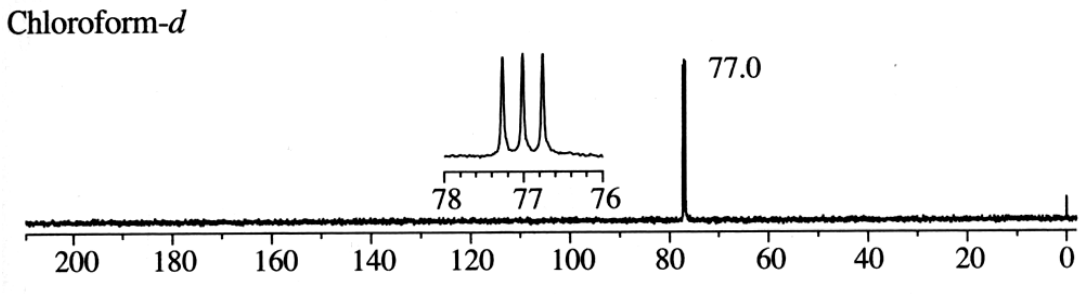
^{13}C NMR, ^{1}H (broadband) decoupled

Decoupling converts multiplets to stronger singlets.

BUT, longer T_1 means signals not integrable; C's without attached H's give small peaks.

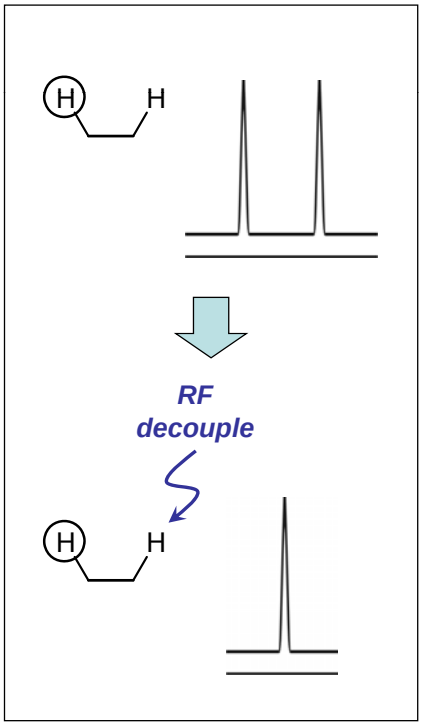


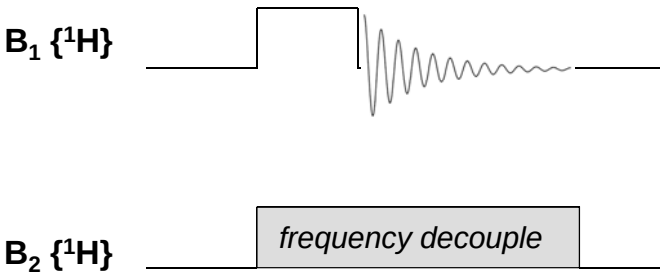
^{13}C NMR: Solvent Peaks



- 1:1:1 triplet is due to ^{13}C-^{2}H coupling; deuterium is spin I = 1, so has three spin states (+1, 0, -1).
- Peak intensity is low because $^{13}CDCl_3$ has no protons, so relaxation time T_1 is very long.

Selective Decoupling of ^{1}H-^{1}H

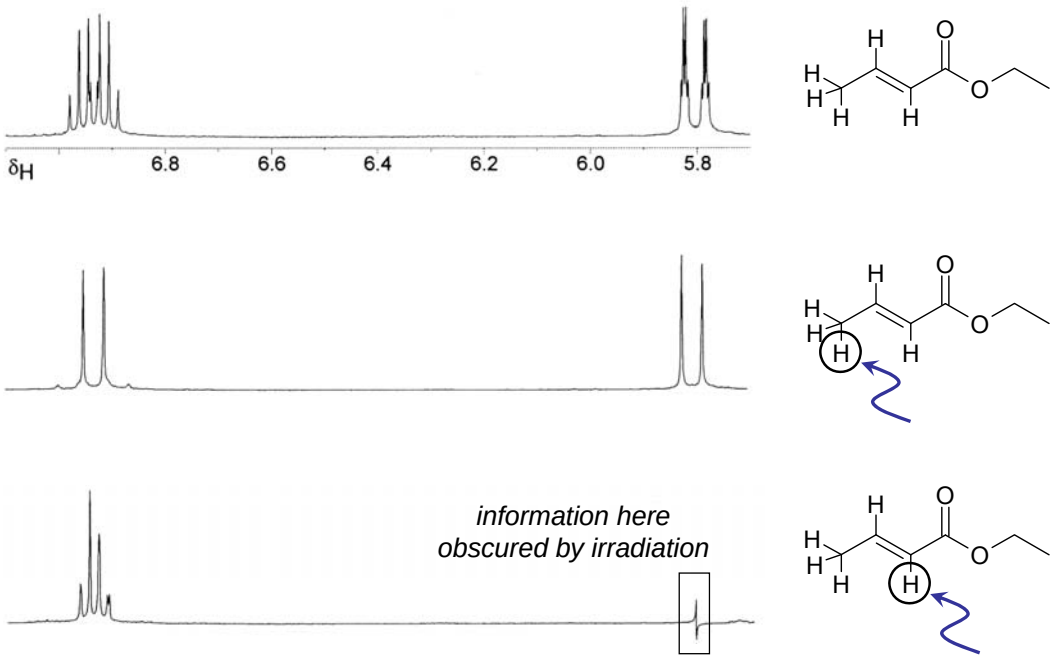




oscillates (averages) spin states of one set of protons in sample (at specified frequency);

"turns off" particular H-H coupling.

Selective Decoupling of ^{1}H-^{1}H



Selective Decoupling of ^{1}H-^{1}H