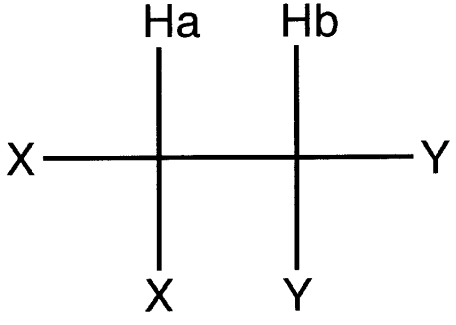
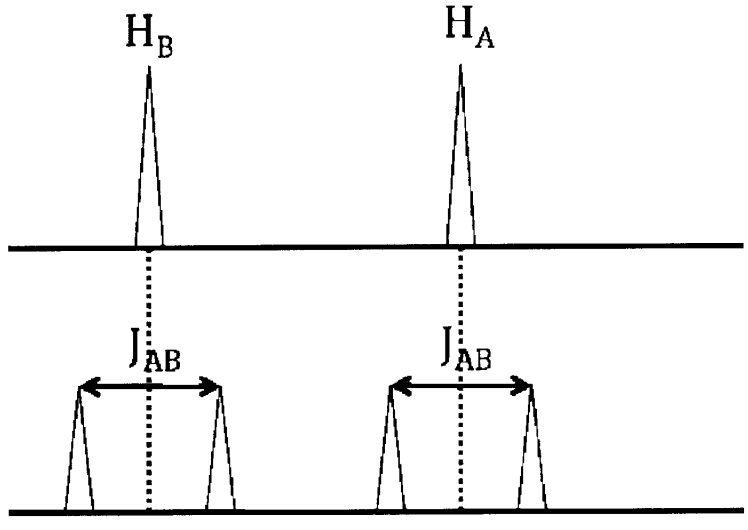
Spin-Spin Splitting (Coupling) : J is coupling constant in Hertz



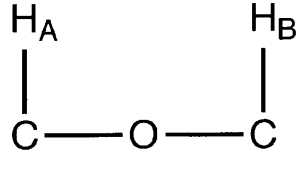
$X \neq Y$



Limitations of Coupling

2 to 3 bonds separating nuclei (typically not seen further than 3 bonds

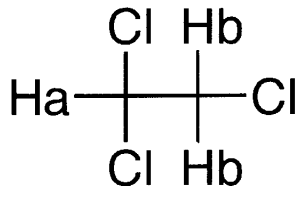
usually no coupling across O, N, S, C=O



H_A and H_B would not couple due to the oxygen

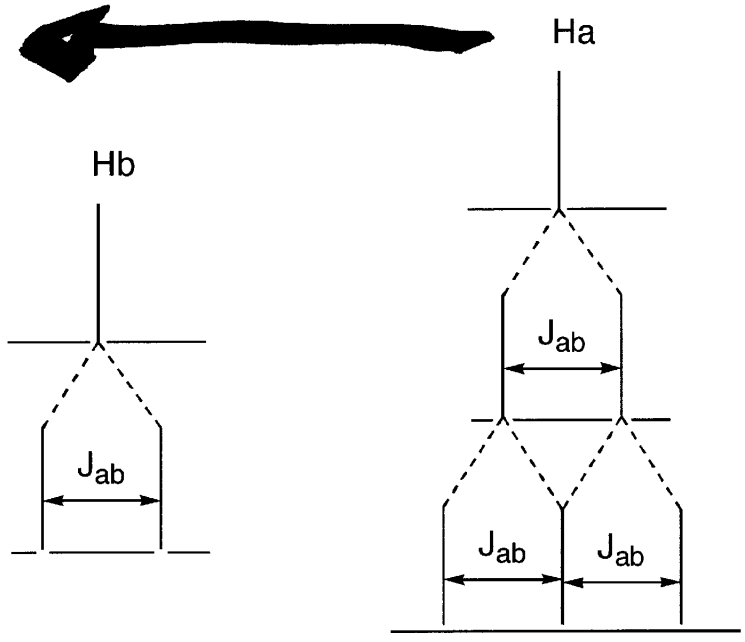
there are exceptions to these rules

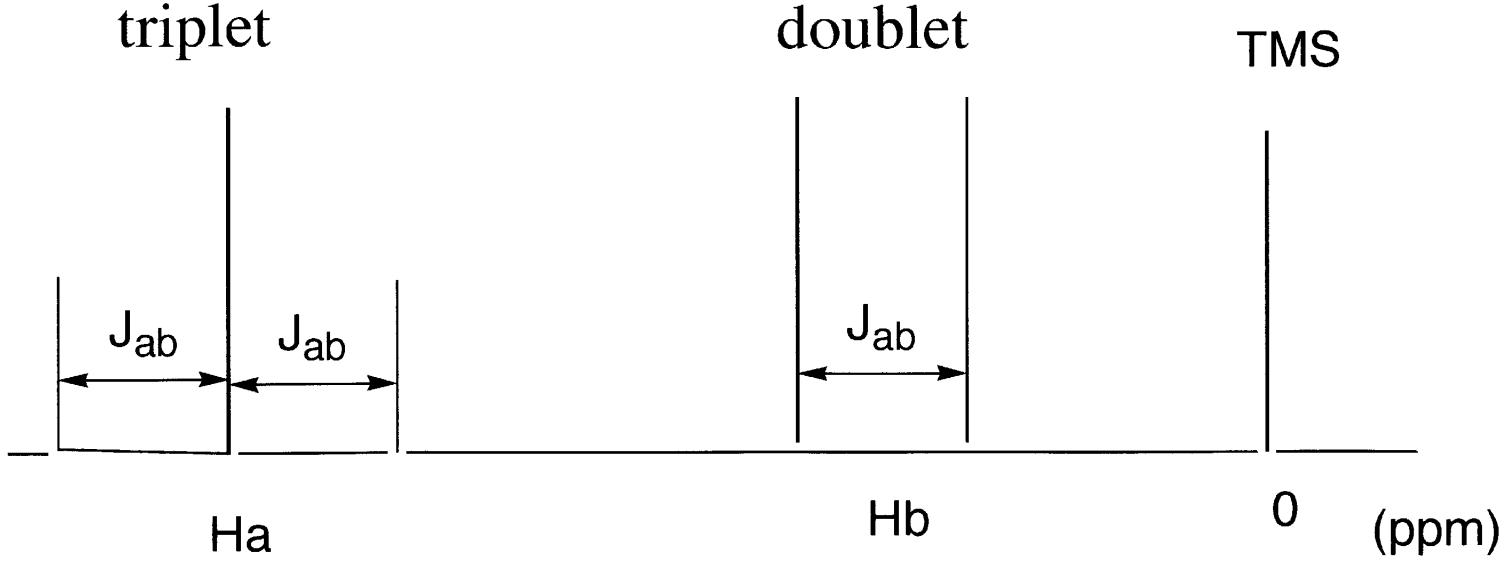
Spin-Spin Splitting (Coupling) : more complex example



1,1,2-trichloroethane

achiral (not chiral)





Multiplicity via Pascal's Triangle

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1

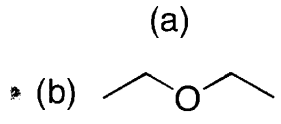
represents intensities of singlet, doublet (1 to 1),
triplet (1 to 2 to 1), quartet (1 to 3 to 3 to 1), quintet (1 to 4 to 6 to 4 to 1)

multiplicity) can be described by the rule: $2nI + 1$

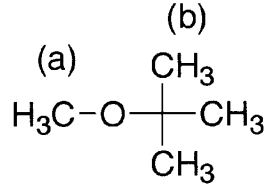
where I = spin and n = the number of equivalent hydrogens that are nearby (2 or 3 bonds away) from the hydrogen that is being examined

Since $I = \frac{1}{2}$ for ^{1}H, this rule can be simplified to the n+1 rule

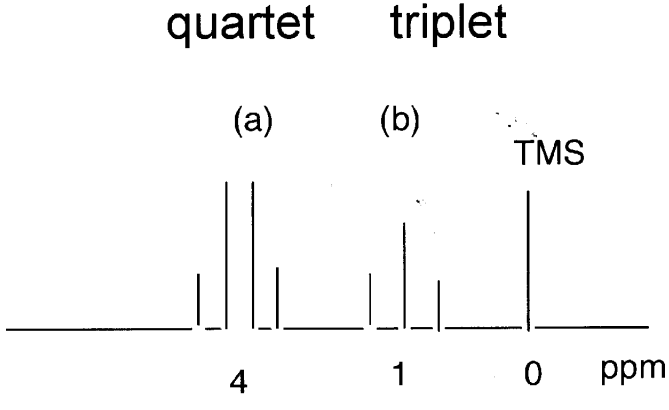
Consider examples below and the types hydrogens (a and b)



diethyl ether

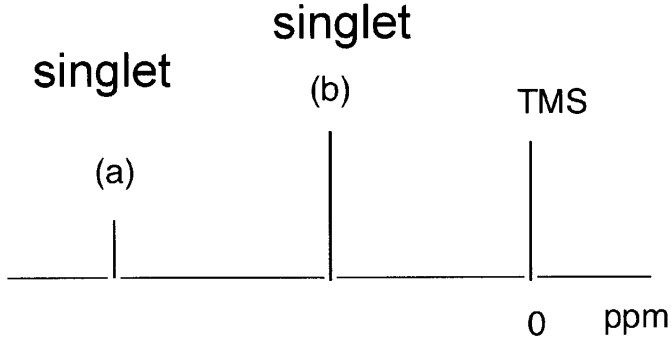


methyl tert-butyl ether
or
methyl 1,1-dimethylethyl ether



2 CH_2's 2 CH_3's

Area ratio would be 4:6 or 2:3



1 CH_3 3 CH_3's

Area ratio would be 3:9 or 1:3

No stereogenic centers present. No coupling across oxygen

Both molecules should have 2 signals. Both have ether functional groups.

"Intensity"determined by the number of hydrogens that make the particular signal

Carbon NMR

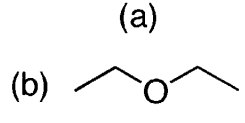
^{12}C has 6 protons and 6 neutrons no nuclear spin, invisible in NMR

^{13}C has 6 protons and 7 neutrons stable isotope, occurs in 1.1% abundance

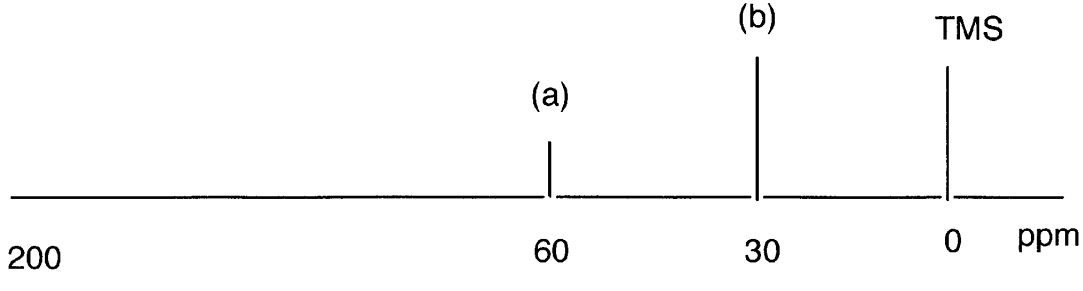
NMR active

^{14}C has 6 protons and 8 neutrons radioactive, half life is $t_{1/2}$ = 5730 years

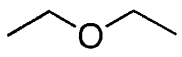
^{13}C NMR spectrum is usually run broad band ^{1}H decoupled
(this means to irradiate all protons so there is no ^{1}H spin-spin coupling to ^{13}C)
so that all the ^{13}C signals are singlets.



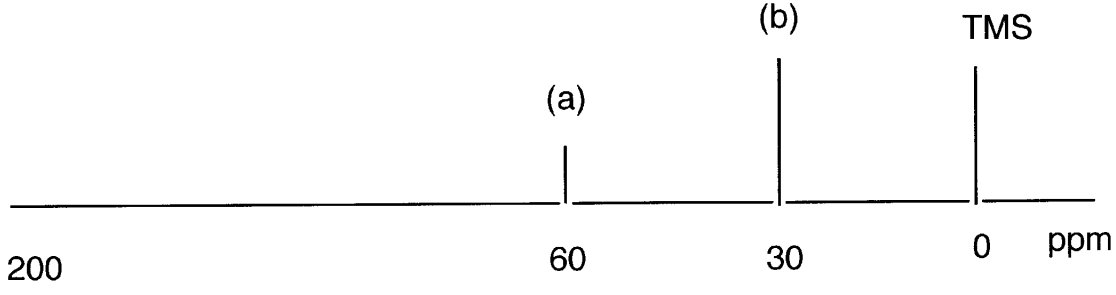
diethyl ether



(a)

(b) 

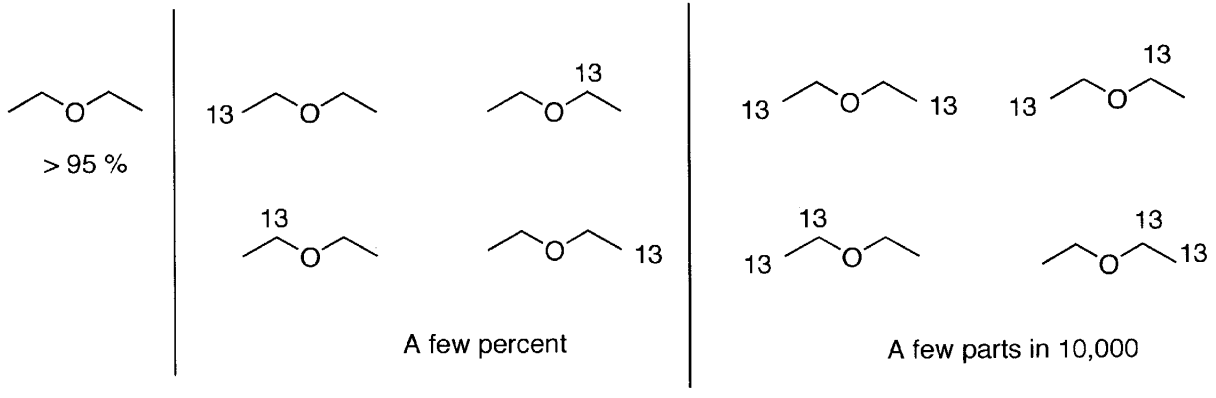
diethyl ether



There are two different carbons in diethyl ether - hence 2 signals

no ^{13}C-^{13}C spin-spin coupling -

chance of two being next to each other is 0.01 x 0.01 = 0.0001



Integration of ^{13}C NMR Spectra not common

In ^{1}H NMR spectra, the area of the peak gives relative number of H's

In ^{13}C NMR spectra, the intensity or area of the peak cannot easily be used

Irradiation (decoupling) of ^{1}H transfers energy to ^{13}C - alters signal intensity

^{13}C can be slow to relax back to starting state - alters signal intensity

Methyls with 3 H's often intense
Quaternary carbons with no H's often weak signals

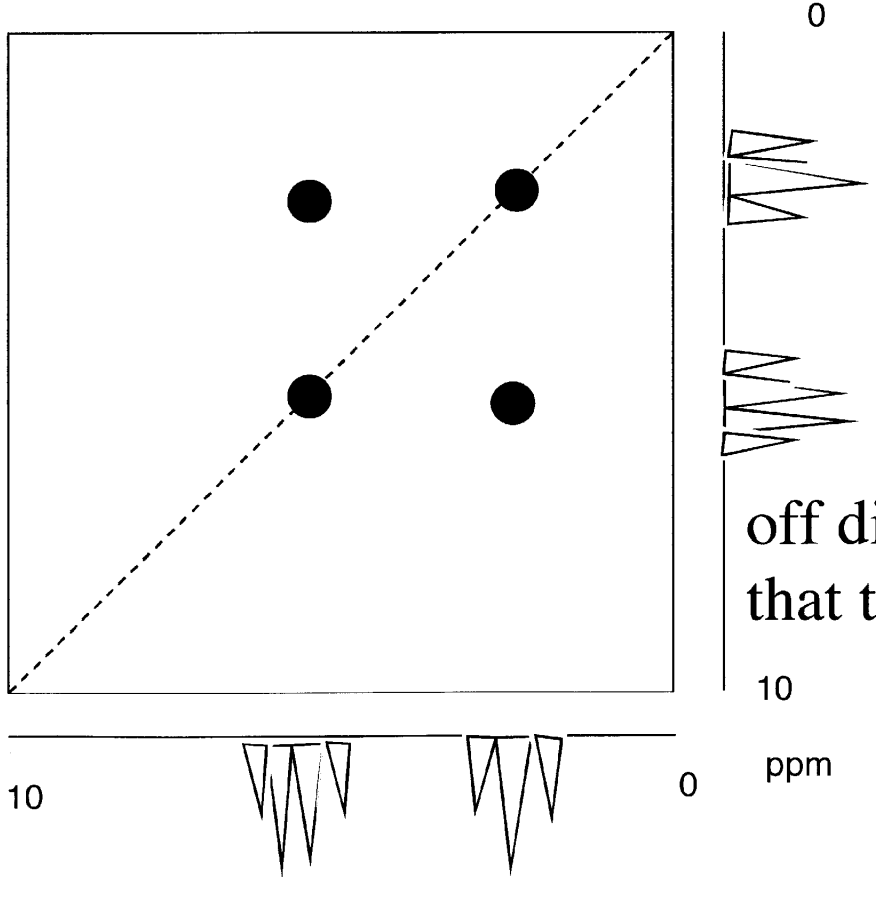
2 Dimensional (2D) NMR Spectrometry

Two major types of experiments:

1. Through bond energy transfer (dependent on coupling constants, J)

2. Through space energy transfer (NOE = Nuclear Overhauser effect)

Correlation Spectroscopy (COSY) - through bonds - e.g. ethyl ether

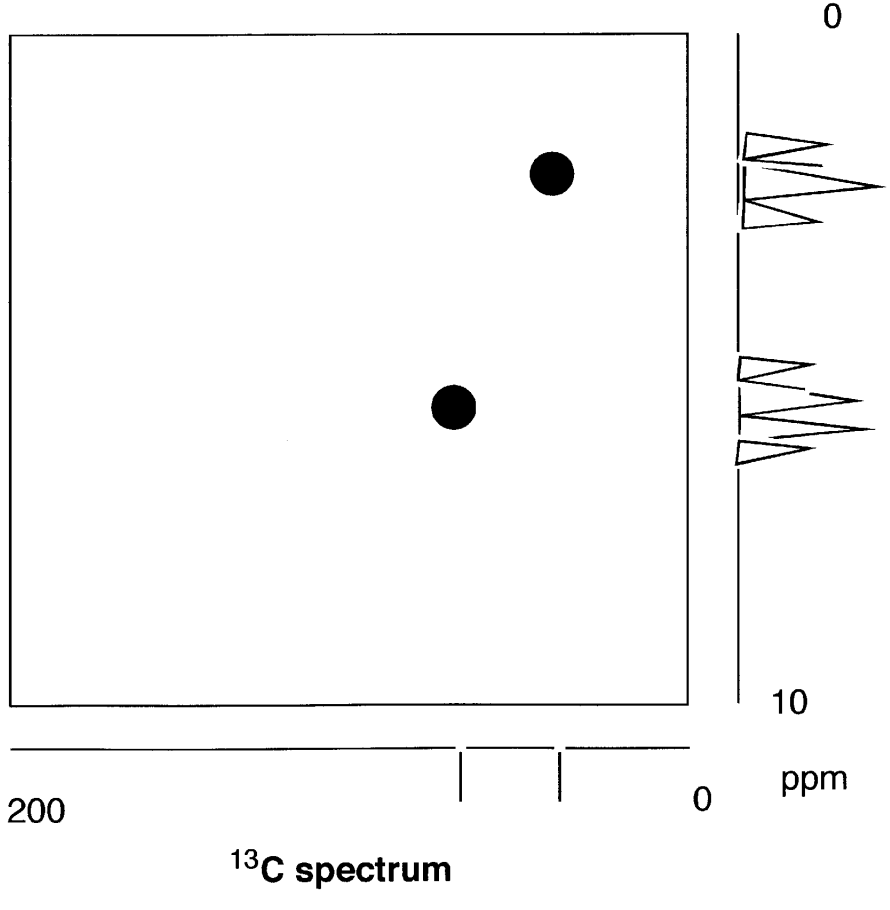


off diagonal cross peaks show
that the triplet and the quartet correlate

Heteronuclear Correlation Spectroscopy (HETCOR)

Heteronuclear Multiple Quantum Coherence (HMQC)

correlates the ^{1}H NMR spectrum with the ^{13}C NMR spectrum
gives connectivity of carbons and hydrogens

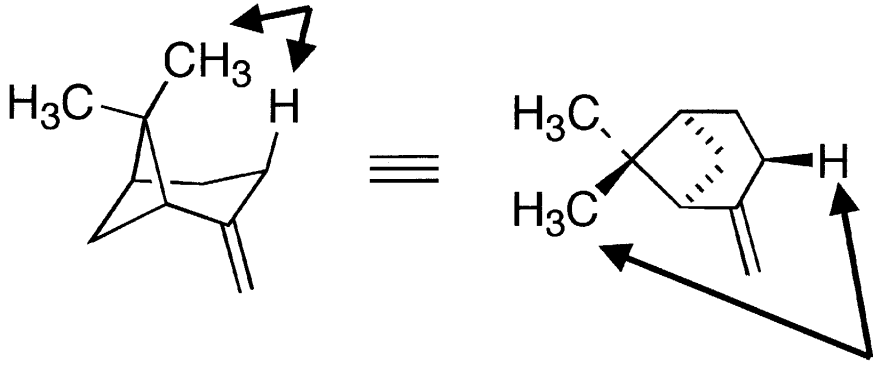


for ethyl ether

Nuclear Overhauser Effect (NOE) - through space energy transfer

The effect drops off proportionally to $1/r^6$ where r = internuclear distance

β-pinene: two drawings of the same molecule



see additional graphics page on our web site and build with models

This technique allows you to distinguish between the two methyl groups in β-pinene (major constituent of turpentine)

If the single diastereotopic H shown on the methylene is irradiated, it will transfer energy via the NOE effect to the closest methyl group and will produce an enhanced signal -
irradiation of that methyl will enhance that diastereotopic hydrogen

3D structures of proteins with 100,000 molecular weight and thousands of atoms done