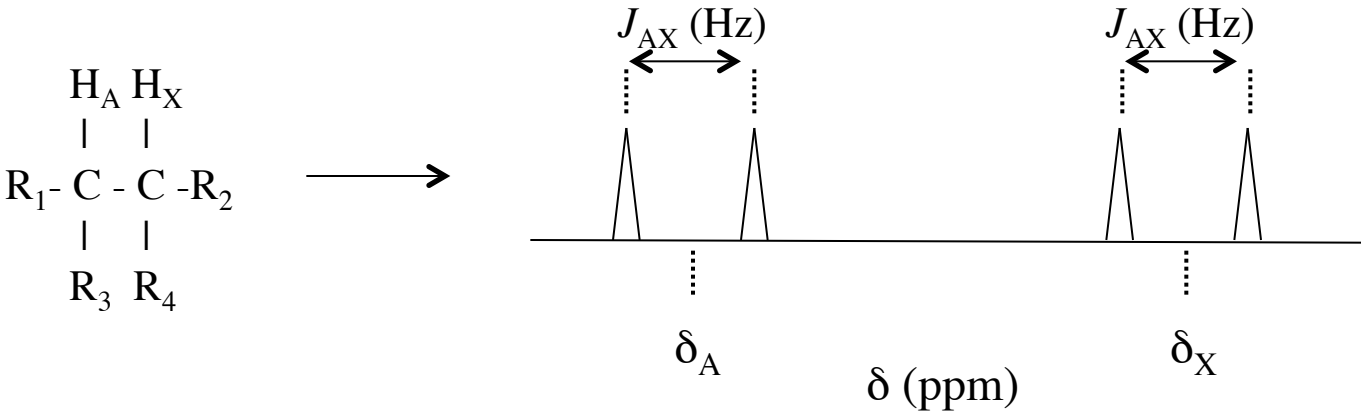
Coupling

THROUGH-BOND COUPLING

- Frequency-domain NMR ***signals*** are often split into two or more component ***peaks*** due to the effect of directly bonded nuclei or neighboring nuclei 2 or 3 bonds away



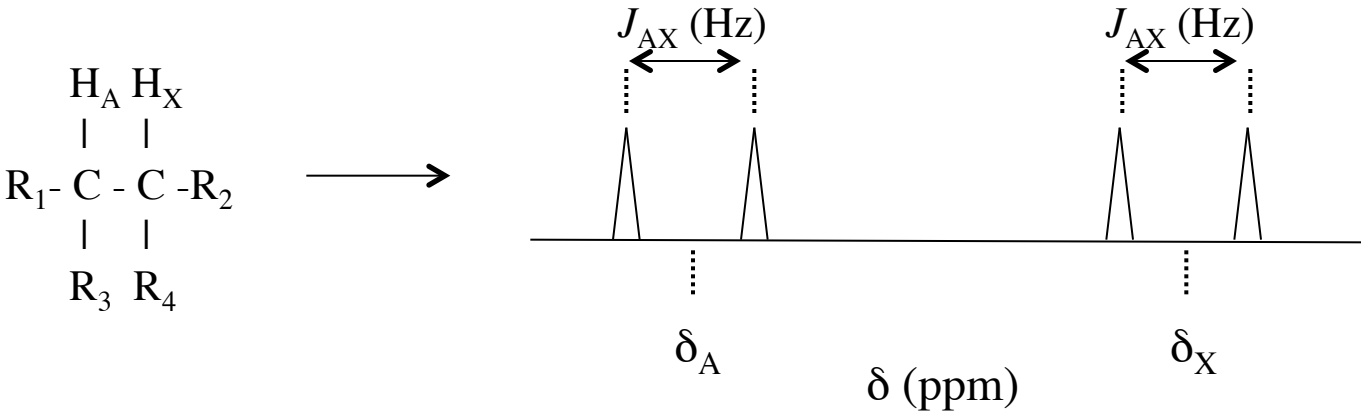
- This is due to ***through-bond coupling***, also known as ***scalar coupling***, ***indirect coupling***, ***spin-spin coupling***, or ***J coupling***……

- In the above example, the ***signal*** from H_A is split into two ***peaks*** (called a doublet), and the ***signal*** from H_X is, likewise, split into two ***peaks*** (a doublet)

- A signal split into two peaks is a ***doublet***, a signal split into three peaks is a ***triplet***, and so on (***quartet***, ***quintet***, ***sextet***, ***septet***)

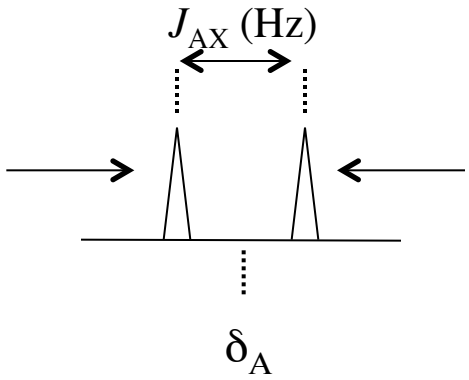
THROUGH-BOND COUPLING

- Coupling is mediated by bonding electrons and results in small resonance frequency changes depending on the spin state(s) of neighboring nuclei



- In the example above, if we consider spin A (for instance) in an ensemble of molecules, in some of the molecules spin X will be in the α (m = +1/2) state, and in others spin X will be in the β (m = -1/2) state
- The result is two slightly different resonance frequencies for those A nuclei with X in the α state compared to those A nuclei with X in the β state

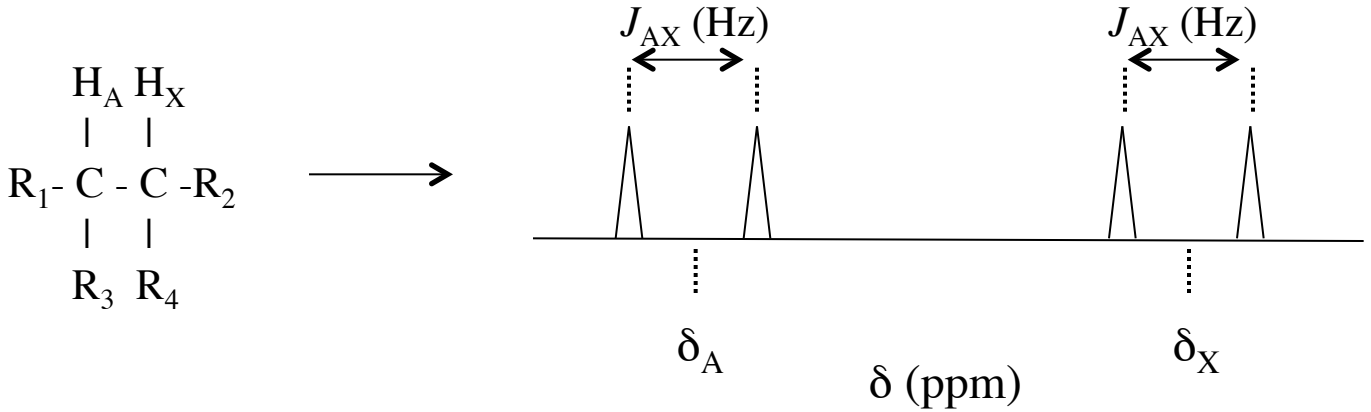
for spin X, m = +1/2, which effectively *deshields* spin A



for spin X, m = -1/2, which effectively *shields* spin A

THROUGH-BOND COUPLING

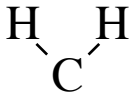
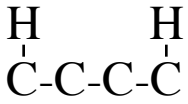
- The magnitude of the splitting between the component peaks of the signal is called the *coupling constant*, or *J*



- *J* is usually given a superscript and subscript, the former describing the number of bonds separating the coupled nuclei, the latter designating the two atoms involved
  -for the example above, $^3J_{AX}$ or $^3J_{HA,HX}$
- *J* is *always* measured in Hz
- *J* (in Hz) is *independent* of the magnitude of B_0
- The value of *J* measured from the splitting of the signal from one of the coupled nuclei is always the same as the value measured at the signal from the other coupled nucleus
- The chemical shift of the nucleus is the center of the multiplet (δ_A and δ_X)

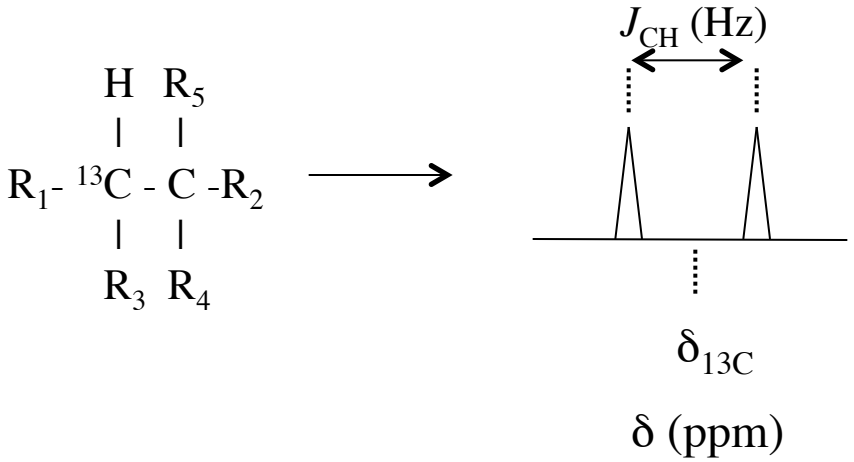
MAGNITUDES OF THROUGH-BOND COUPLING CONSTANTS

- The magnitude of the coupling constant, J, depends on the number of intervening bonds, as well as other structural factors
- The 1-bond H,H coupling constant is very large
- Typical 2-bond (***geminal***) H,H coupling constants are small (5-10 Hz), but occasionally can be much larger (for CH_2O, $^2J_{H,H} \approx 40$ Hz)
- Typical 3-bond (***vicinal***) H,H coupling tend to be somewhat larger than geminal coupling constants, and have a strong dependence on the torsional (dihedral) angle between the two C-H bonds (***Karplus relationship***)
- Typically, 4-bond couplings are too small to be observed, but, in special cases are large enough to be measured
- Normaly, 5-, 6-, etc.- bond couplings are too small to be observed

H-H	$^1J_{H,H} \approx 275$ Hz
	$^2J_{H,H} \approx$ 5-10 Hz typically
	$^3J_{H,H} \approx$ 5-20 Hz typically
	$^4J_{H,H} \approx$ usually small (unobservable), but can be as large as 7 Hz
	$^5J_{H,H} \approx$ usually too small to be observed

^{13}C-^{1}H Through-Bond Coupling

- In ^{13}C NMR spectra, through-bond coupling between ^{1}H and ^{13}C nuclei also results in splitting of ^{13}C NMR signals



- As with the H,H coupling constant, the magnitude of the ^{13}C,H coupling constant depends on the number of intervening bonds, and other factors as well
- The 1-bond ^{13}C,H coupling constant ($^{1}J_{CH}$) is very large
- Typical 2-bond ^{13}C,H coupling constants range up to ~20 Hz, and often are not observed
- Normally 3-, 4-, 5-, etc.-bond couplings are too small to be observed

^{13}C-H	$^{1}J_{C,H} \approx$ 100-250 Hz (typical values are 120-150 Hz)
^{13}C-C-H	$^{2}J_{C,H} \approx$ 1-20 Hz typically

Mechanism of Through-Bond Coupling: Dirac Model

- Coupling occurs through bonds, i.e. via interactions with bonding electron spins

- Consider the one-bond coupling ($^1J_{AX}$), for instance ^{1}H-^{13}C

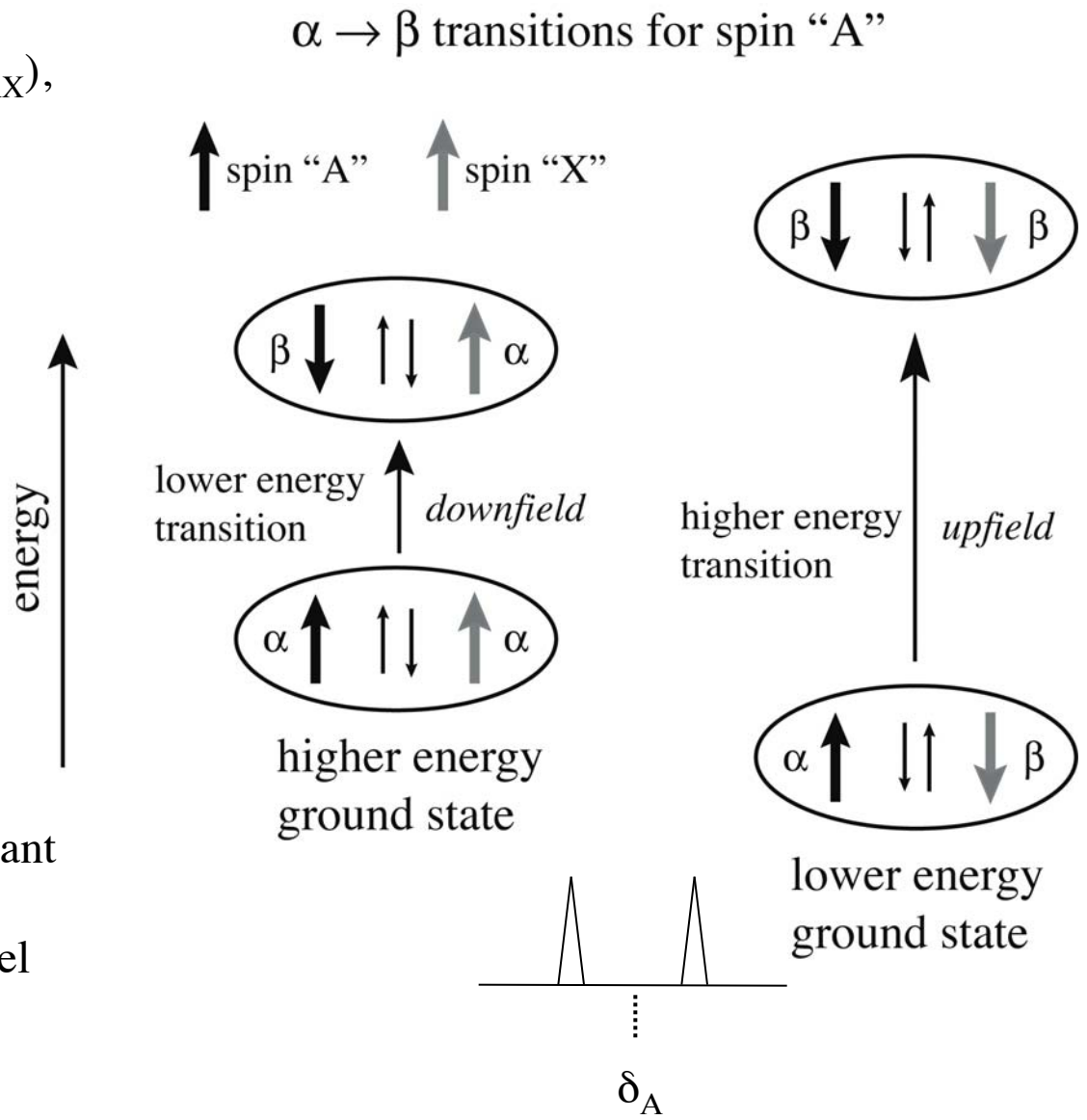
  -Energetically preferred states are normally those where nuclear and electron spins are *antiparallel*

  -Electron spins of bonding pair are antiparallel (*Pauli exclusion principle*)

  -Thus, for low energy states, if nuclear spins are *antiparallel*, then couplings are said to be ***positive***

  -In other words, the coupling constant is positive if it stabilizes the state where nuclear spins are antiparallel

  -Normally, for $\gamma > 0$, ^1J is positive

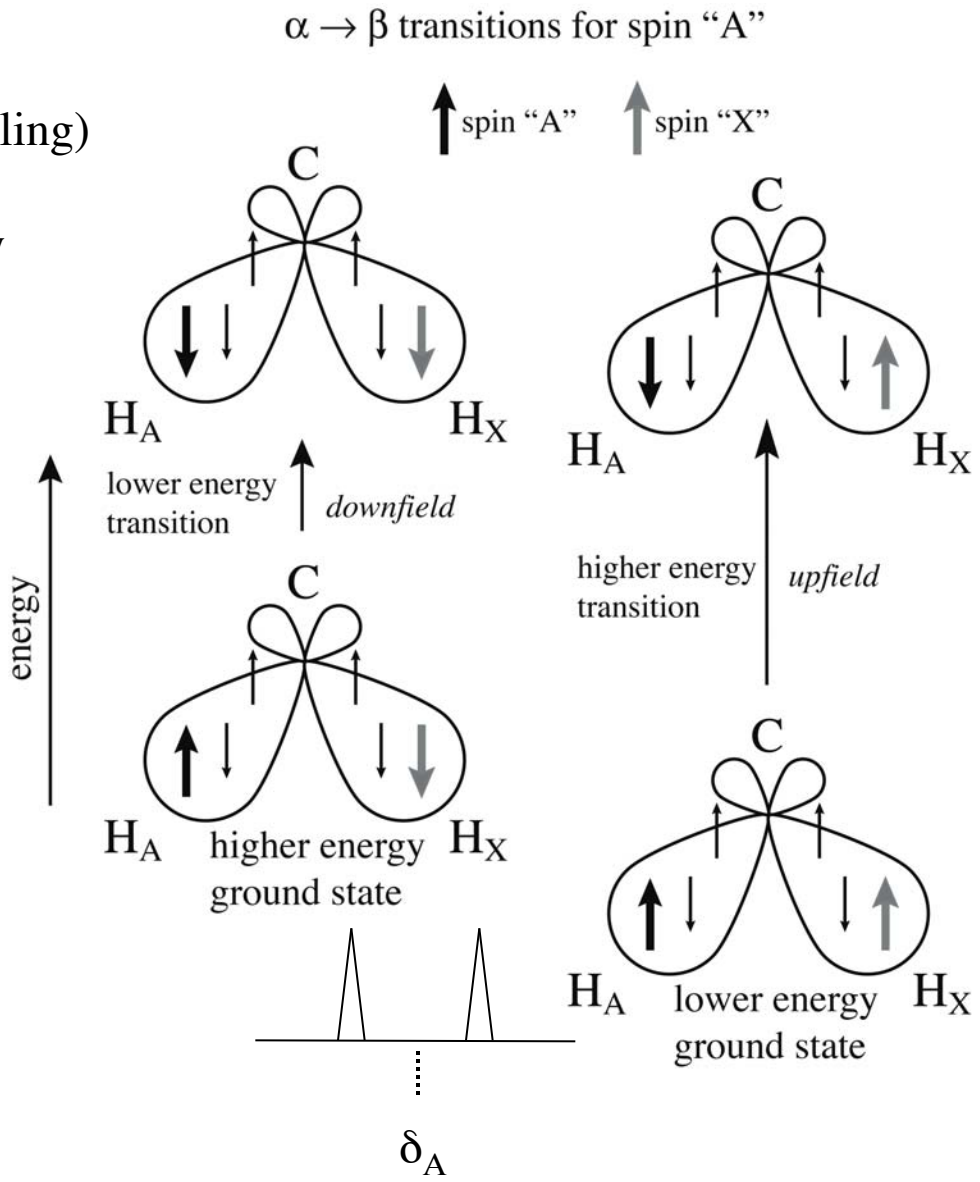


MECHANISM OF THROUGH-BOND COUPLING: DIRAC MODEL

- Coupling occurs through bonds, i.e. via interactions with bonding electron spins

- Consider the two-bond coupling ($^2J_{AX}$), for instance ^{1}H-^{12}C-^{1}H (geminal ^{1}H-^{1}H coupling)

  -Energetically preferred states are normally those where nuclear and electron spins are *antiparallel*
  -Electron spins of bonding pair are antiparallel (*Pauli exclusion principle)*
  -The energetically preferred state for the bonding electrons on the carbon atom is when these are parallel (*Hund's rule*)
  -Thus, for low energy states, if nuclear spins are *parallel*, then couplings are said to be ***negative***
  -In other words, the coupling constant is negative if coupling stabilizes the state where nuclear spins are parallel
  -Normally, for $\gamma > 0$, ^2J is negative



MECHANISM OF THROUGH-BOND COUPLING

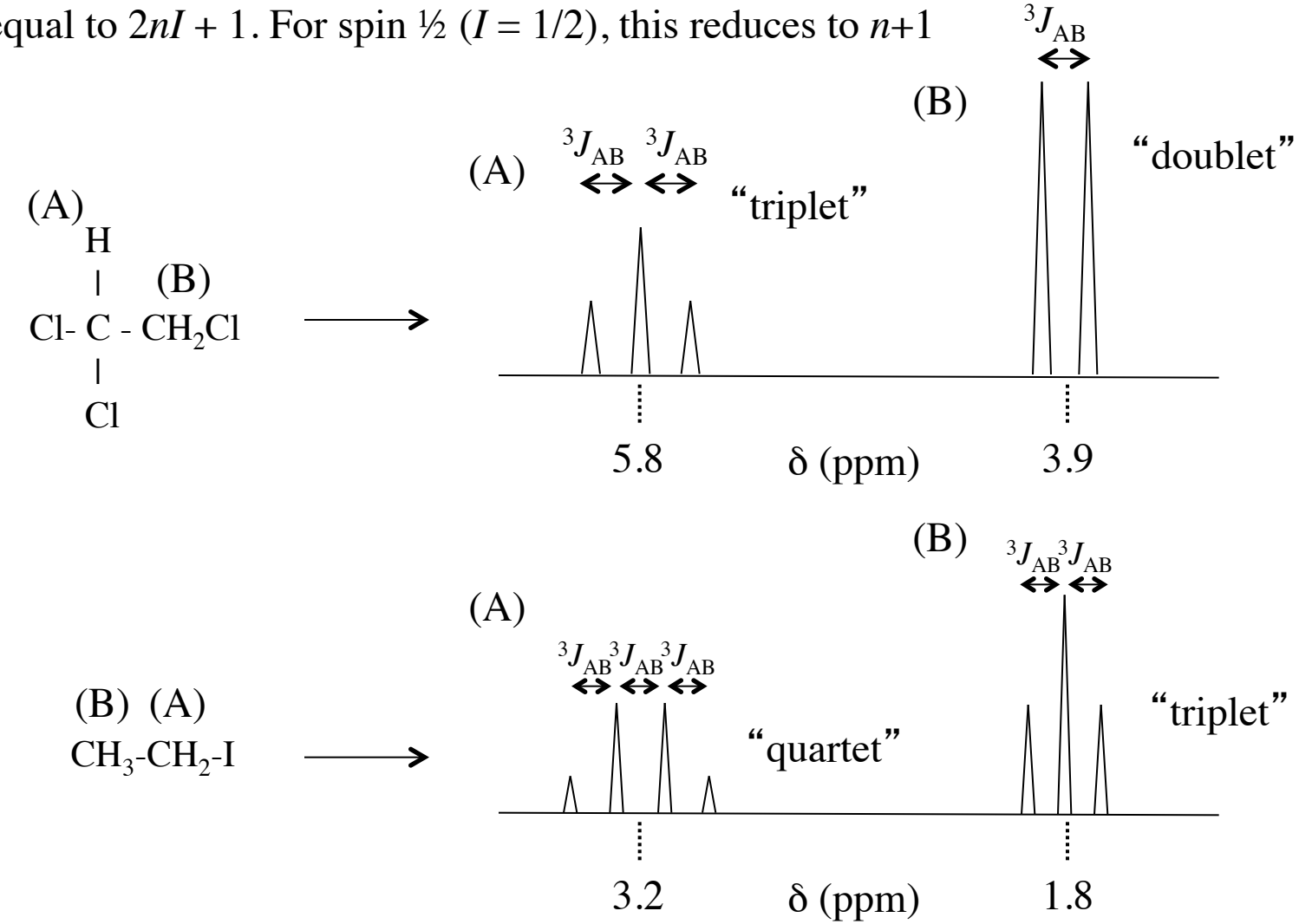
- Fermi contact: interaction of nuclear spins via bonding electrons
  - depends on electron density at the pair of nuclei
  - depends on the "*s*" electrons, or *s* character of the bond(s) between the nuclei
  - electron spins must be correlated, i.e. there must be a bond

- Dependence on "*s*" character
  -consider one bond ^{13}C-^{1}H couplings:

CH_3-CH_3	*s*, sp^3	1 × 1/4 = 1/4	125 Hz
CH_2=CH_2	*s*, sp^2	1 × 1/3 = 1/3	156 Hz
C_6H_6	*s*, sp^2	1 × 1/3 = 1/3	158 Hz
HC≡CH	*s*, *sp*	1 × 1/2 = 1/2	249 Hz

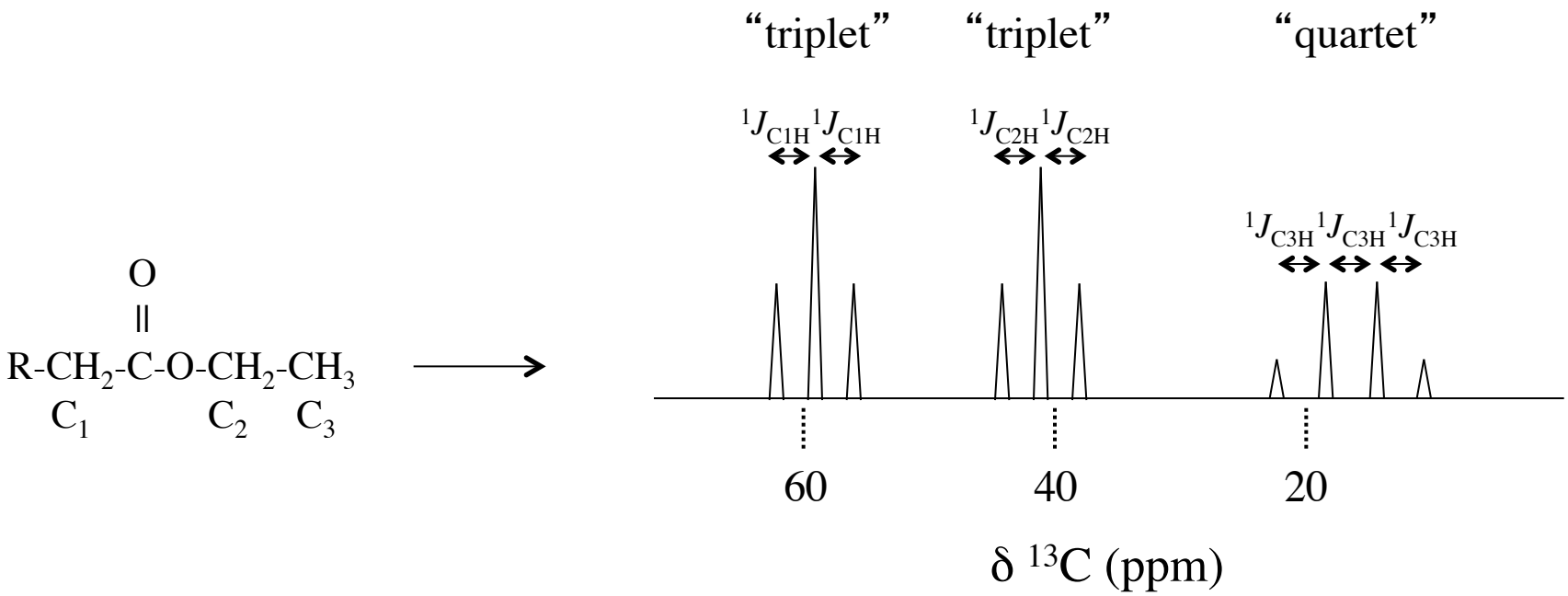
SPIN-SPIN SPLITTING: *N*+1 RULE

- Multiplet splitting patterns are determined by the number of nuclei (*n*) doing the splitting and the spin angular momentum quantum number (*I*)
- The general rule is *M* (the multiplicity, or number of peaks in the multiplet signal) is equal to $2nI + 1$. For spin ½ ($I = 1/2$), this reduces to $n+1$



SPIN-SPIN SPLITTING: *N*+1 RULE

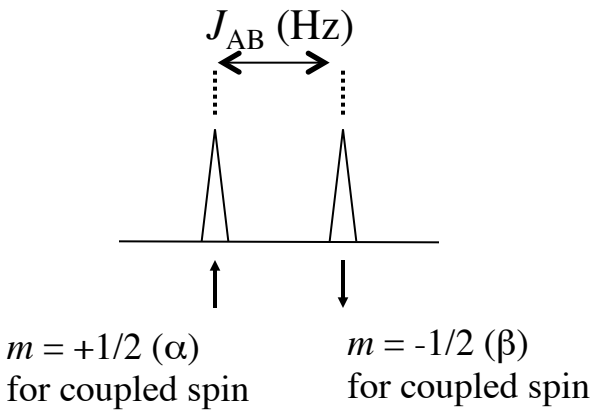
- In ^{13}C NMR spectra, normally only the 1-bond ^{13}C-H couplings are observed
- Both ^{1}H and ^{13}C are spin ½ (I = 1/2), so the n+1 rule applies

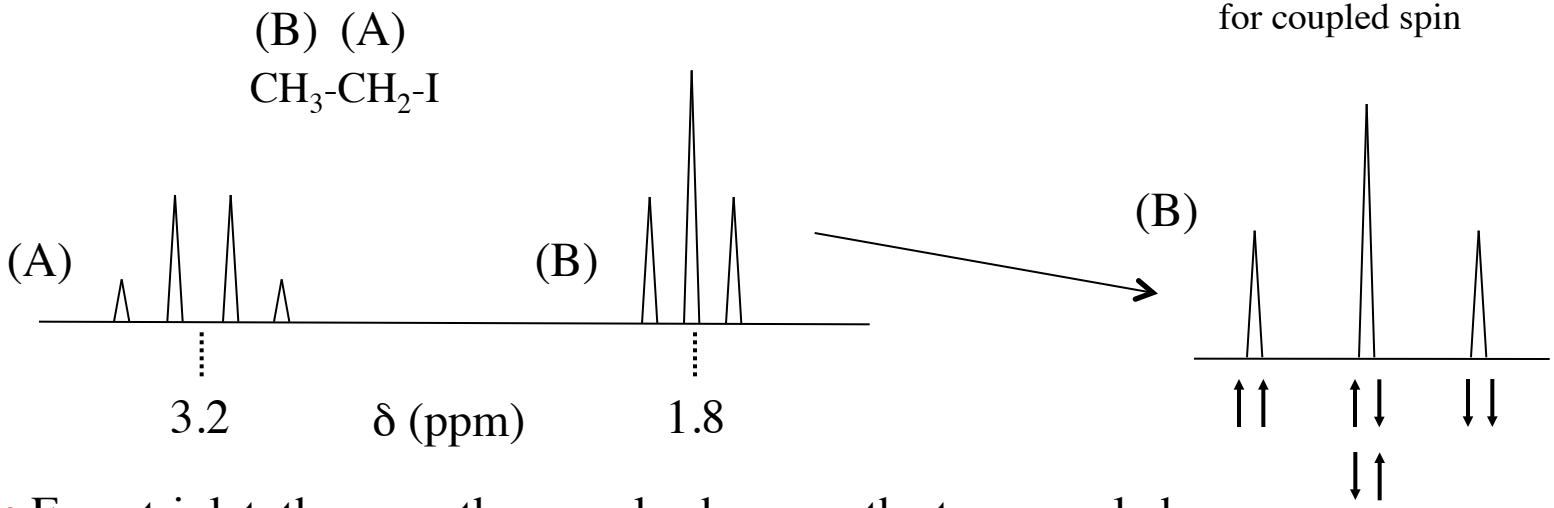


- ^{13}C nuclei are also coupled to directly bonded ^{13}C
- However, because ^{13}C comprises only about 1% of all C at natural abundance, the chance that a ^{13}C nucleus is next to another ^{13}C nucleus is very small, so no signal splitting normally results from ^{13}C-^{13}C coupling
- Signal splitting resulting from ^{13}C-^{13}C coupling will be observed in compounds synthesized with excess ^{13}C

Spin-Spin Splitting: Intensities and Pascal's Triangle

- For a doublet, we saw that there are two peaks, because the coupled spin can be in either the α or β state
- The *peak heights are equal* because, for the coupled spin, there are essentially equal numbers of spins in α and β states





- For a triplet, there are three peaks, because the two coupled spins can both be in the α state, they can both be in the β state, or one can be α and the other β
- The *relative peak heights are 1:2:1* because there are 2 ways that one spin can be α and the other β, and only one way both can be α and only one way both can be β

SPIN-SPIN SPLITTING: INTENSITIES AND PASCAL'S TRIANGLE

- The relative intensities of the multiplet components in a signal split by spin-spin coupling can be obtained from Pascal's triangle

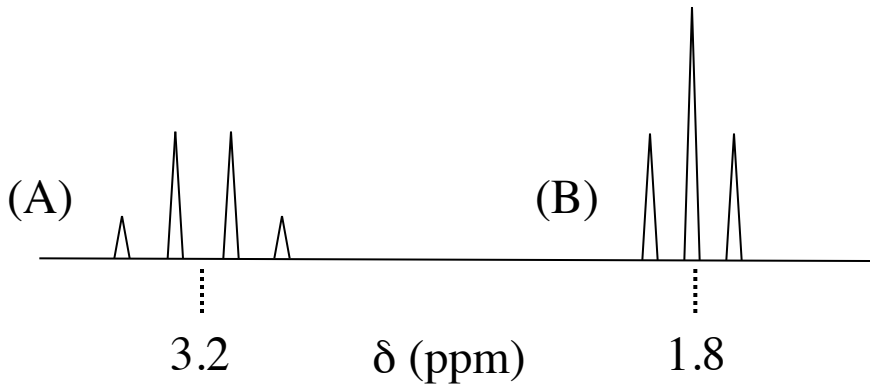
singlet					1						
doublet				1		1					
triplet				1		2		1			
quartet			1		3		3		1		
quintet		1		4		6		4		1	
sextet	1		5		10		10		5		1
septet	1	6		15		20		15		6	1

relative intensities (in the spectrum) 1 3 3 1 3 6 3

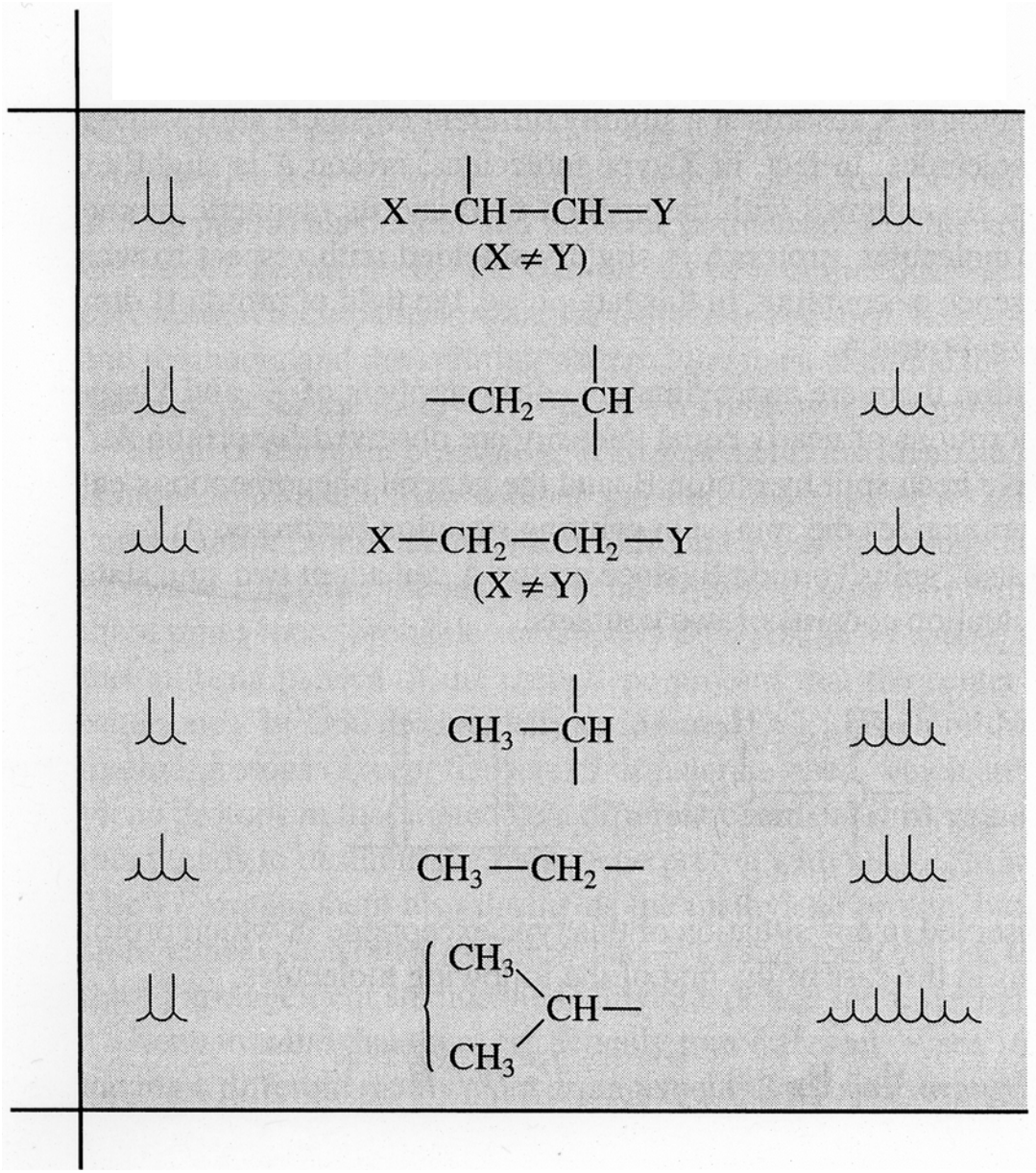
relative intensities (in the multiplet) 1 3 3 1 1 2 1

(B) (A)

CH_3-CH_2-I ⟶



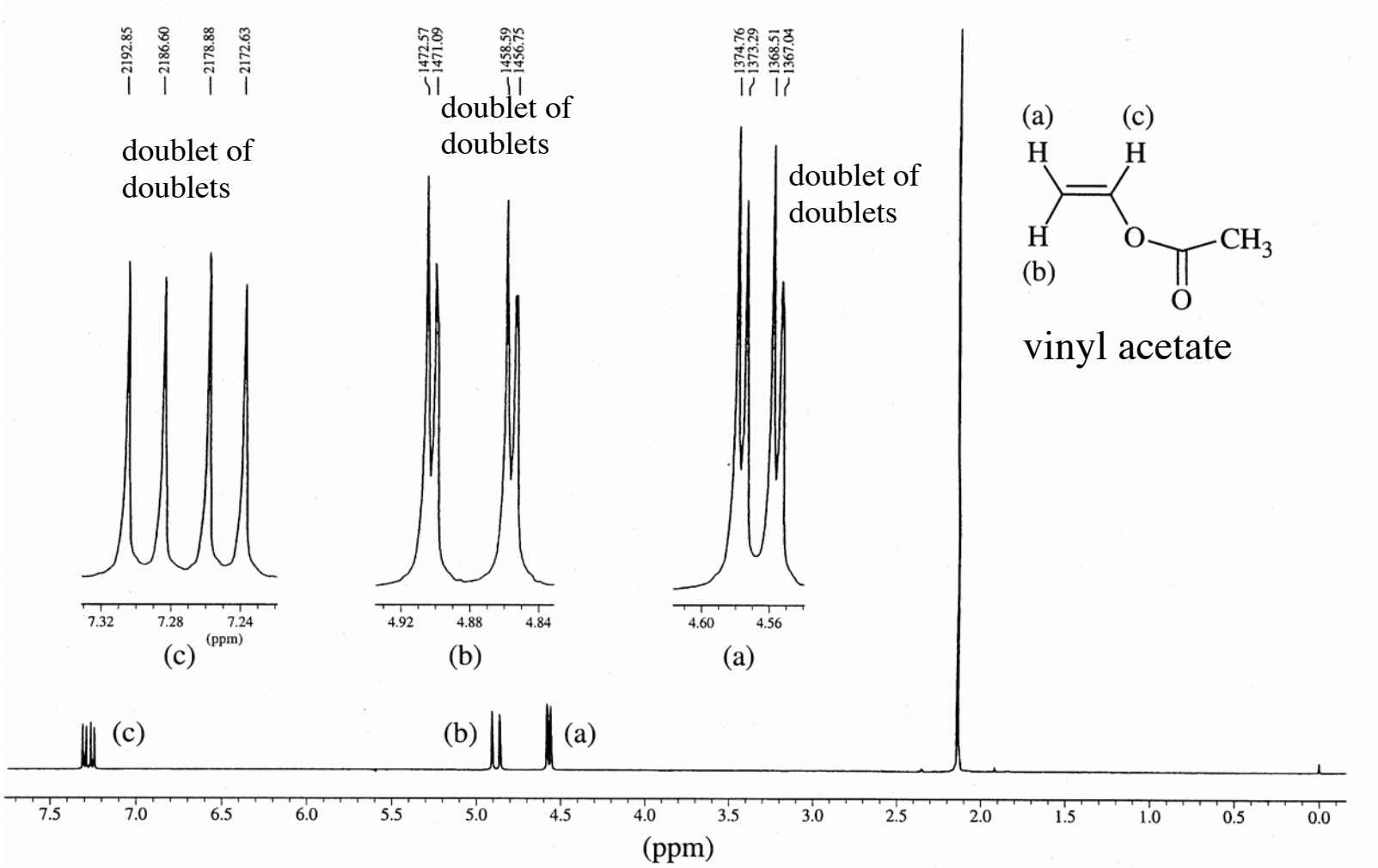
COMMON SPLITTING PATTERNS



- Some commonly observed splitting patterns

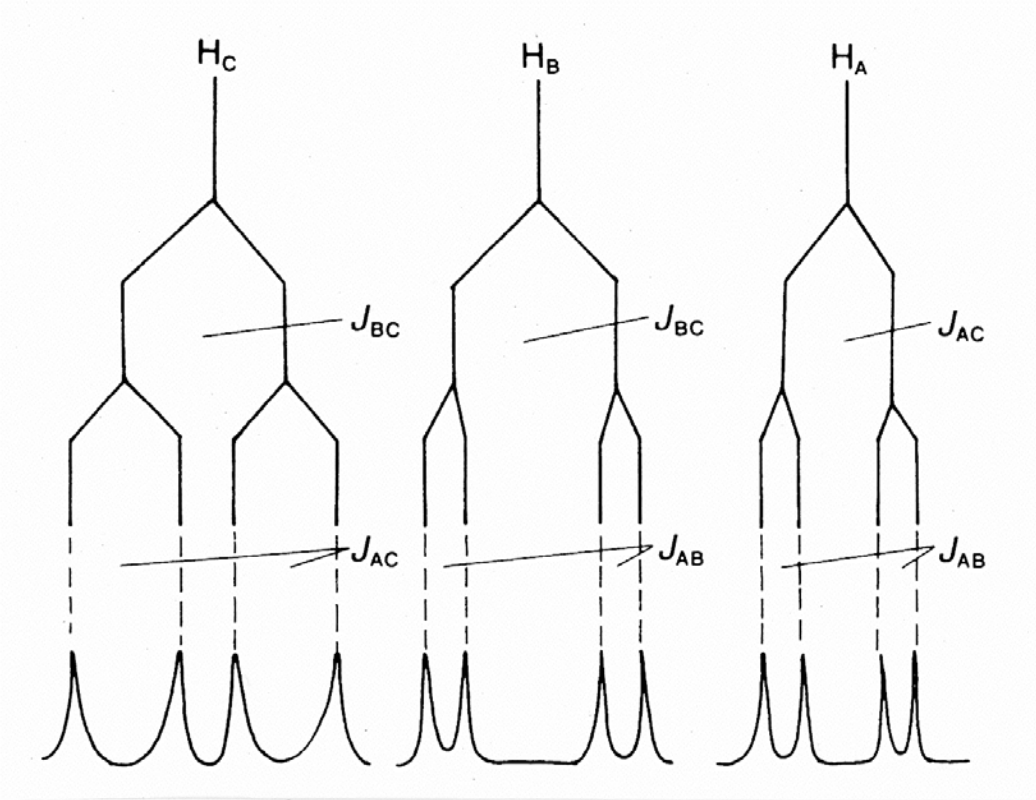
MULTIPLE/COMPLEX SPLITTING

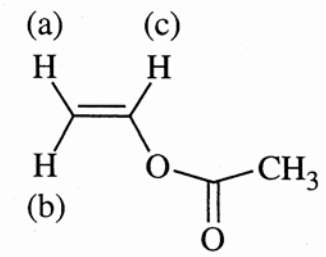
- Split signals can be split again by coupling to additional spins
  - in vinyl acetate, for instance, the signal from "c" is split into a doublet by "b", and this doublet is split into a doublet of doublets by "a"
  - likewise, "b" is split by "a" and "c", and "a" is split by "b" and "c"



MULTIPLE/COMPLEX SPLITTING

- The coupling constant between any two spins will be observed in the signal from each of the spins
- Observation of a coupling in more than one signal identifies coupled spins

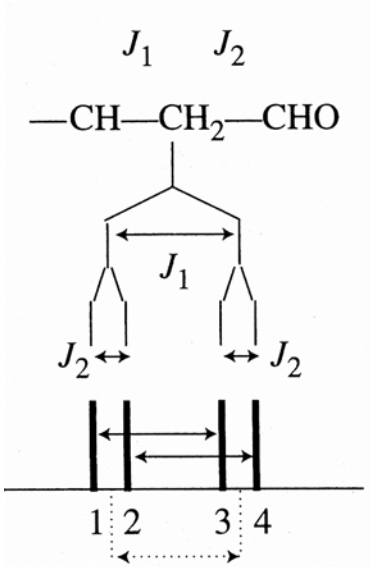




vinyl acetate

EXTRACTING THE COUPLING CONSTANTS

- Analysis and determination of coupling constants

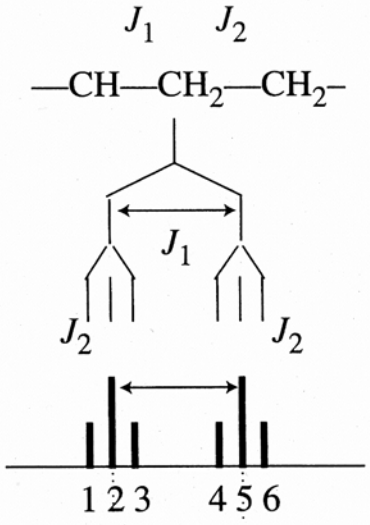


Doublet of Doublets (dd)

To obtain J_1 measure the difference between lines 1 and 3, or 2 and 4, in Hz.*

*Do not try to find the centers of the doublets!

J_2 is the spacing between lines 1 and 2, or 3 and 4



Doublet of Triplets (dt)

To obtain J_1 measure the difference between the most intense lines (2 and 5) in Hz

J_2 is the spacing between lines 1 and 2, or 2 and 3, or those in the other triplet.

Spin Decoupling

- It is often advantageous to reverse or remove the splitting caused by spin-spin coupling
- This is called *spin decoupling*
- Spin decoupling (or just "decoupling) can be used for several reasons
  - to simplify spectra
  - to assist in identification of coupling between nuclei
  - to improve signal-to-noise

- We'll discuss spin decoupling in the context of "double resonance" experiments