

CHEM202

Organic Chemistry

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Module 1: Spectroscopy and Characterisation

Lecture 5: ^1H NMR Coupling

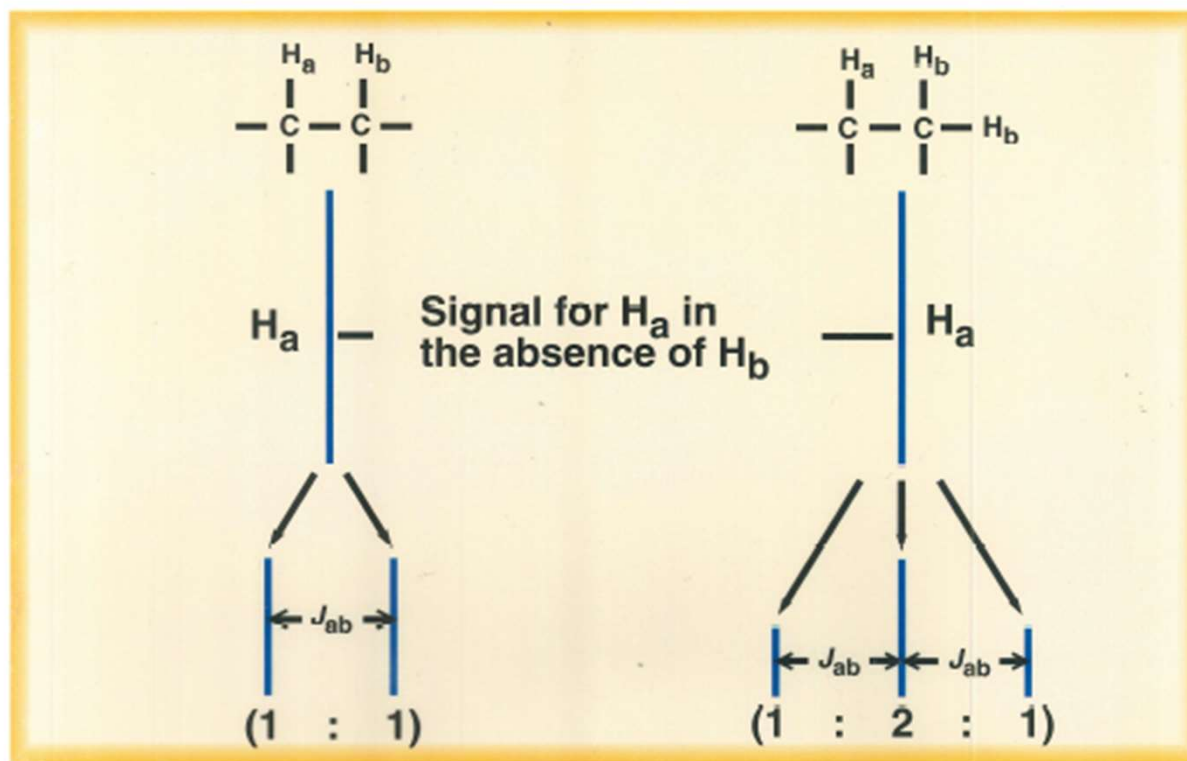
Why do chemists make use of deuterated solvents (e.g. CDCl_3 , CD_3OD) for proton NMR?

Principles of ^1H NMR Spectroscopy *cont.*

- Coupling; geminal, vicinal, long range.
- First order data
- Spin systems
- Magnitude of coupling constants

Coupling

- used to establish connectivity and determine molecular geometry
- The $(2/n + 1)$ rule:** If a hydrogen has a set of n non-equivalent hydrogens on the same or adjacent atoms then the signal is split into $(n + 1)$ peaks.



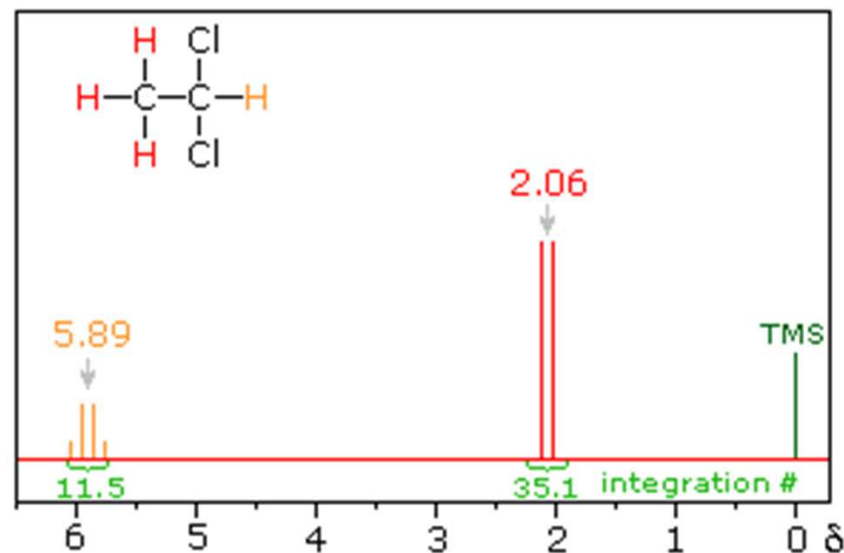
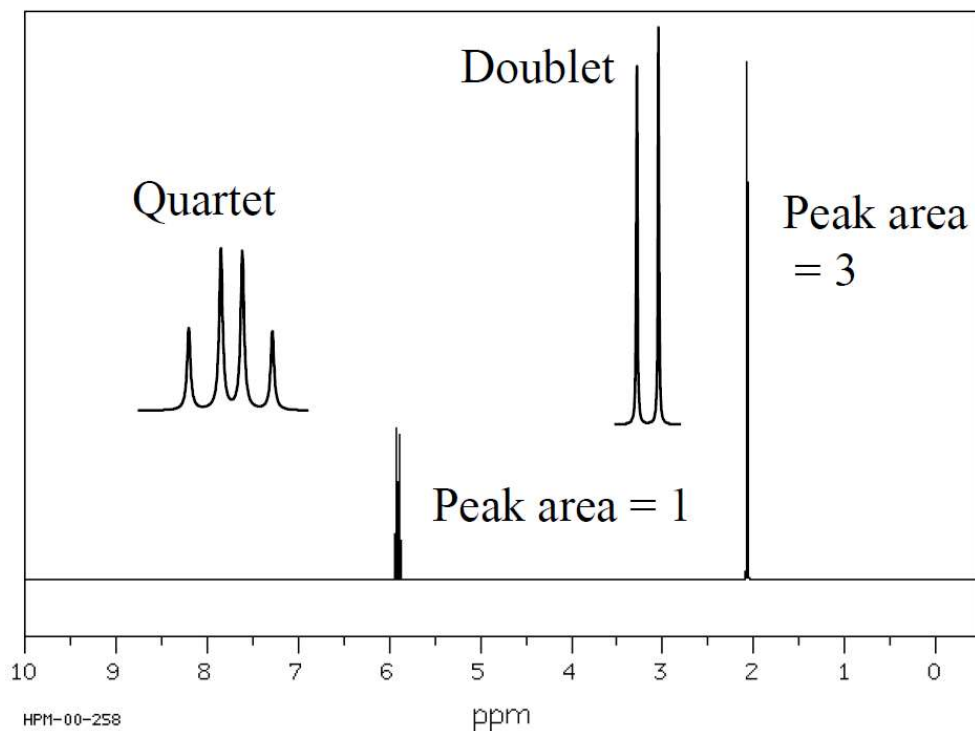
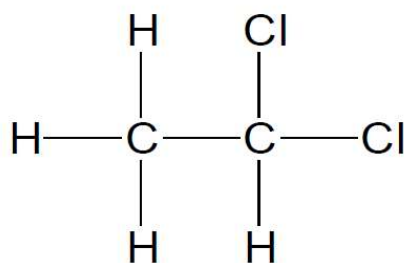
Coupling cont.

- Hence by observing the multiplicity n can be determined. Remember coupling is reciprocal: if A splits B by x Hz, then B also splits A by x Hz.
- The relative intensities of the multiplets, which are symmetrical about their midpoints, are given by Pascal's triangle.

n	=	0				1				s	
		1			1		1			d	
		2		1		2		1		t	
		3		1		3		3		q	
		4	1		4		6		4	1	qt

Features of the ^1H NMR Spectrum

\Rightarrow a typical 1-D ^1H -nmr spectrum is a plot of intensity vs chemical shift (δ)



For clearly resolved split signals, chemical shift is measured at the midpoint of the split structure (gray arrows)

Coupling in a nutshell

Coupling arises because neighbouring nuclides are in varying spin states

Remember the $2I+1$ rule stating the number of spin states a nucleus has

Nuclei 'see' neighbouring nuclei in these varying spin states

Remember the populations of these spin states, even in the presence of a strong magnetic field, is roughly equal (ppm differences)

'Seeing' these nuclei in one or the other spin state results in slightly different resonant frequencies. The difference in frequency is the **coupling constant (J)**.

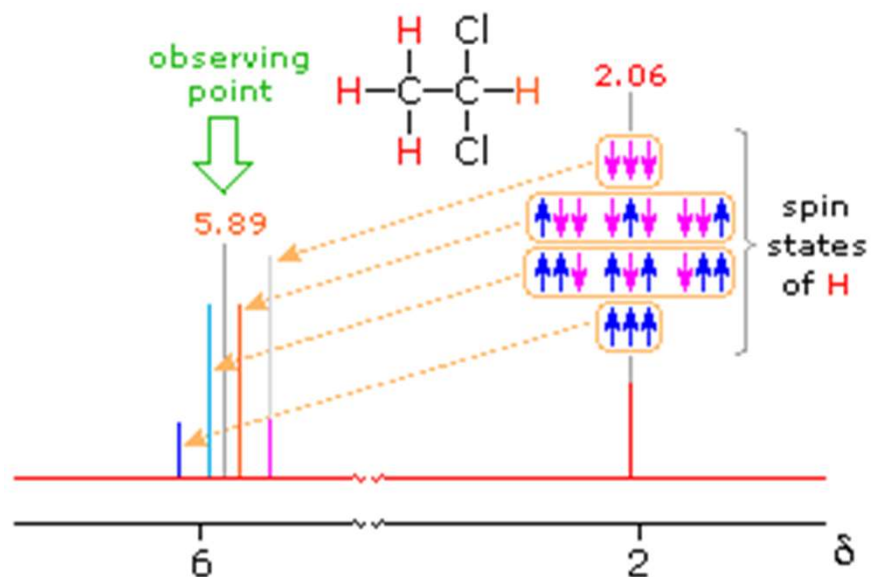
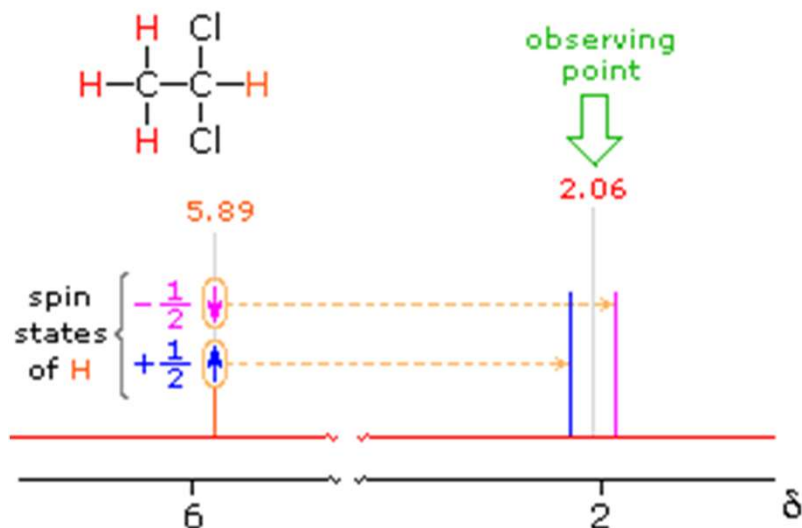
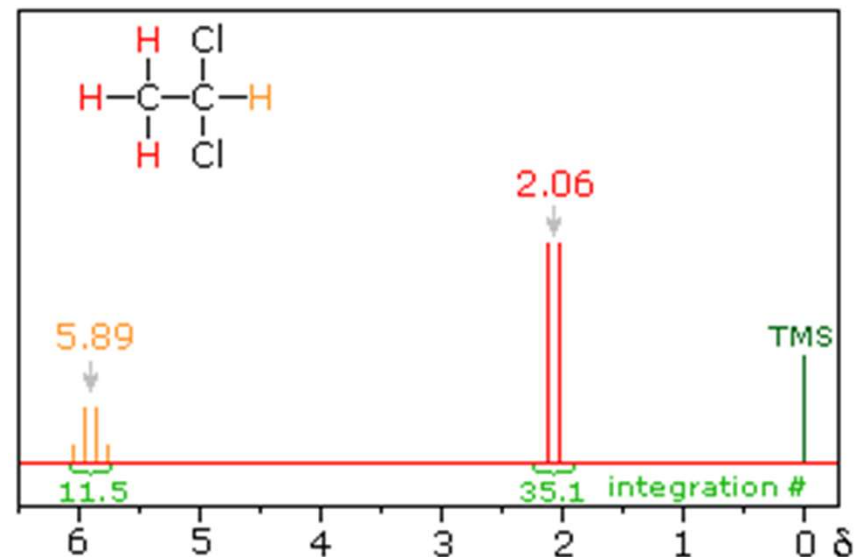
Coupling is not observed between magnetically equivalent nuclei.

This 'seeing' or communication is a **through-bond-interaction** and typically only observed to nuclei 3 or fewer bonds away.

Splitting thus provides information on the connectivity of the nuclei causing the signals in the NMR

Simple examples

- If there is one neighbour, with two possible spin states, two signals (a 1:1 doublet) will be observed. (shown)
- If there is one neighbour with 3 possible spin states, a 1:1:1 triplet will be observed. (not shown!)
- If there are **three** neighbours, each with two possible spin states, **four** different configurations of the neighbours are possible, and four signals will be observed in a 1:3:3:1 ratio (shown)



Coupling cont.

- Hence by observing the multiplicity n can be determined. Remember coupling is reciprocal: if A splits B by x Hz, then B also splits A by x Hz.
- The relative intensities of the multiplets, which are symmetrical about their midpoints, are given by Pascal's triangle.

n	=	0				1				s
		1			1		1			d
		2		1		2		1		t
		3		1		3		3		1
		4	1		4		6		4	1
										q
										qt

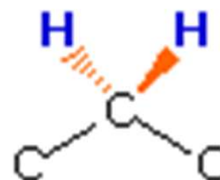
Coupling cont.

For very simple compounds we do see these “text book” multiplets.

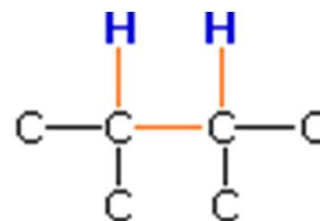
However, for most compounds this is an over simplification as the magnitude of coupling is influenced by **geometry** and the **range** of the interaction. This leads to more complex splitting patterns.

Coupling range

- *geminal* through **two** bonds (H's attached to same atom)
- *vicinal* through **three** bonds (H's attached to adjacent atoms)
- *long-range* through greater than three bonds



Geminal Hydrogens



Vicinal Hydrogens

Spin Systems

The analysis of connectivity in complex molecules can be simplified by identifying spin systems, that is substructures within a molecule through which coupling extends.

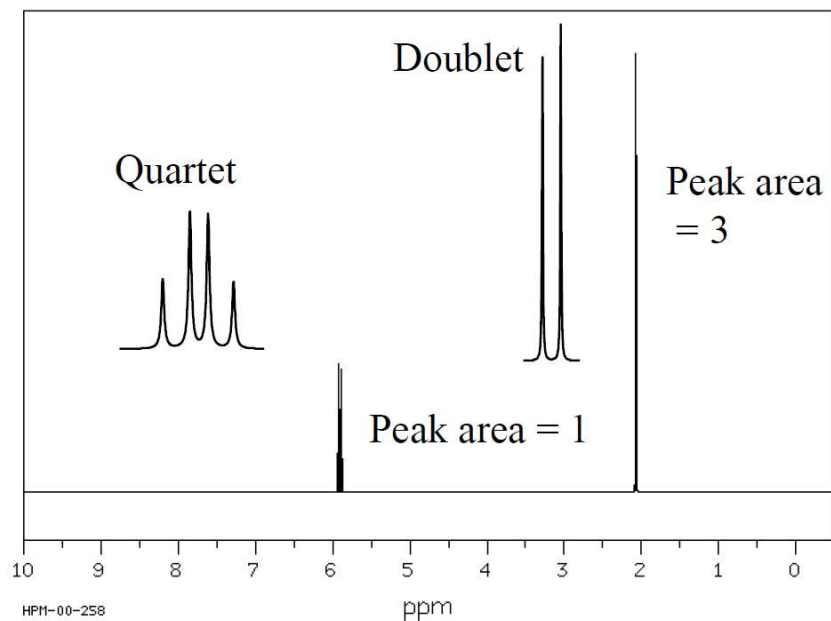
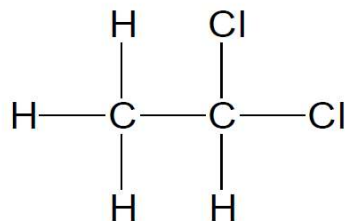
Nomenclature of spin systems

A different letter is used to describe each different proton environments (ie different chemical shift) within a spin system. Each letter represents a set.

- i) Protons separated by a **small chemical shift** difference (of the same order as the coupling between the relevant nuclei ie J in Hz $\sim \Delta\nu$ in Hz) are designated by the letters A, B, C
- ii) Protons separated by a **large chemical shift** difference ($\Delta\nu / J > 7$) are designated by the letters A..., X... Eg for three well-separated chemical shifts the letters A... M..., X are used
- iii) The number of protons in each set is designated by a subscript number

Features of the ^1H NMR Spectrum

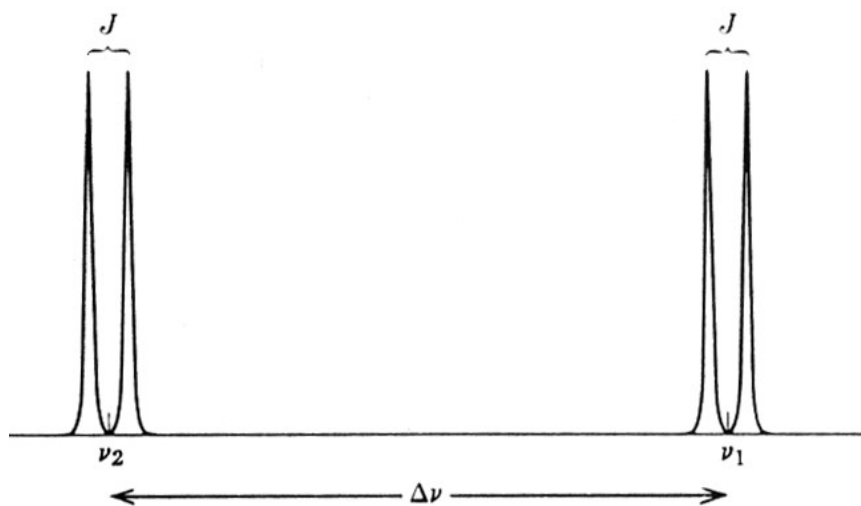
\Rightarrow a typical 1-D ^1H -nmr spectrum is a plot of intensity vs chemical shift (δ)



1st Order Analysis

If $\Delta\nu / J > 7$ then δ and J can values can be directly read from the spectrum

- $\Delta\nu > J$ nuclei are said to be weakly coupled eg AX
- $\Delta\nu \sim J$ nuclei are said to be strongly coupled eg AB
- all first order spectra, nuclei are weakly coupled



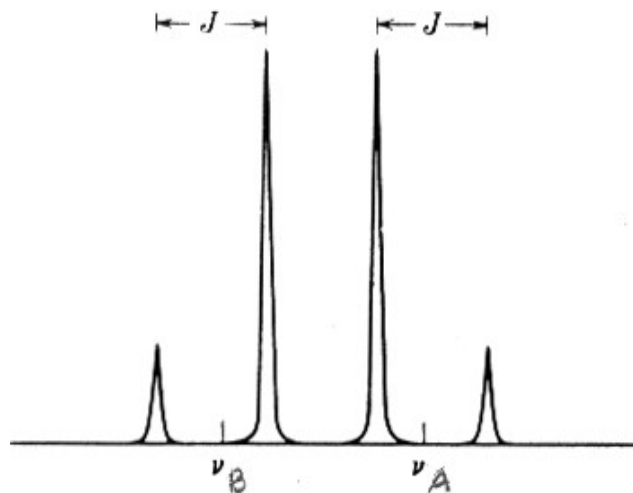
Spin-spin coupling between two protons with very different chemical shifts.

Strongly coupled systems

In this case the mid-points of multiplets no longer reflect the true δ and the line intensities may be distorted

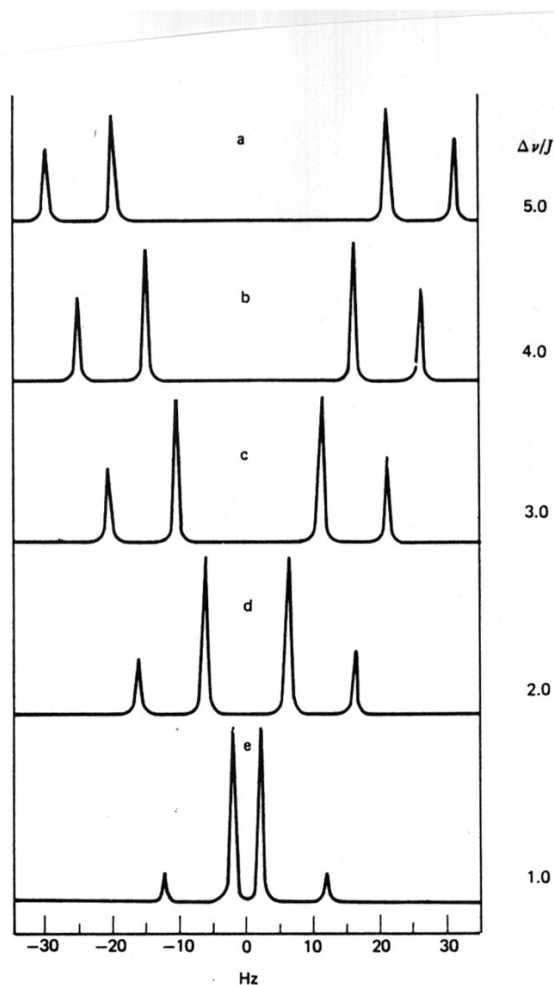
Analysis is usually more complicated, but some systems are easily recognised eg the AB system

- *Two strongly coupled nuclei, AB system ($\nu_A - \nu_B = J_{AB}$)*
- Observe a 4-line pattern
- symmetrical about the midpoint
- No longer 1:1 doublets!



"Center of gravity," instead of linear mid-points, for shift position location (due to "low" $\Delta\nu/J$ ratio).

Non 1st Order Analysis cont.



Change in an AX system spin coupling with a decreasing difference in chemical shifts and a large J value (10 Hz); the AX notation is explained in the text.

•Chemical shifts, δ_A and δ_B , are ‘the centre of gravity’ of each doublet. To calculate the true δ of each we need to know the absorption frequencies (ν , in Hz)

$$J_{AB} = \nu_2 - \nu_1 = \nu_4 - \nu_3$$

$$\text{midpoint} = (\nu_A + \nu_B) / 2$$

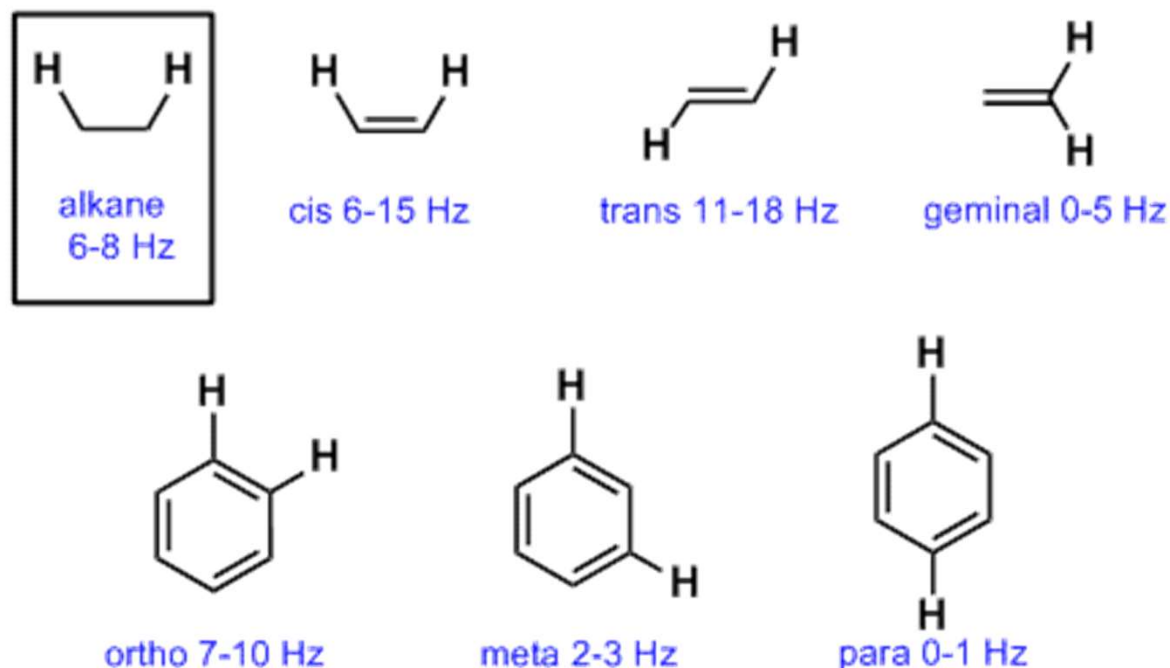
$$[= (\nu_2 + \nu_3) / 2 \text{ or } (\nu_1 + \nu_4) / 2]$$

$$\nu_B - \nu_A = [(\nu_4 - \nu_1)(\nu_3 - \nu_2)]^{1/2}$$

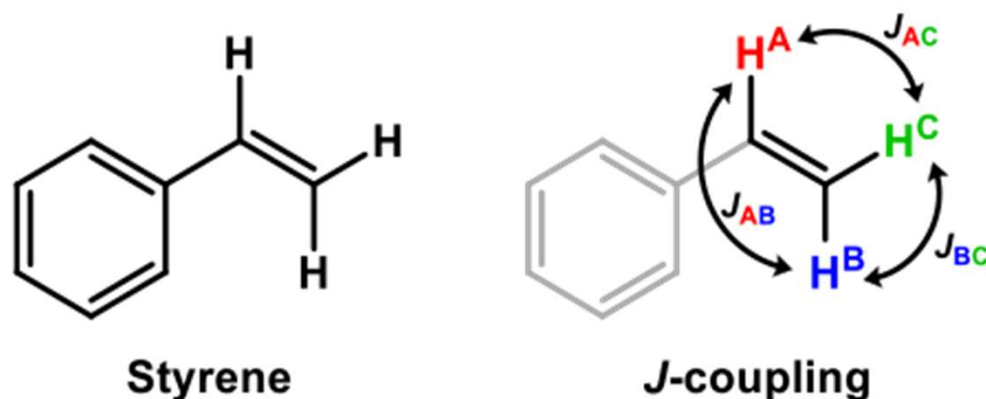
Intensity ratio

$$I_2/I_1 = I_3/I_4 = (\nu_4 - \nu_1)/(\nu_3 - \nu_2)$$

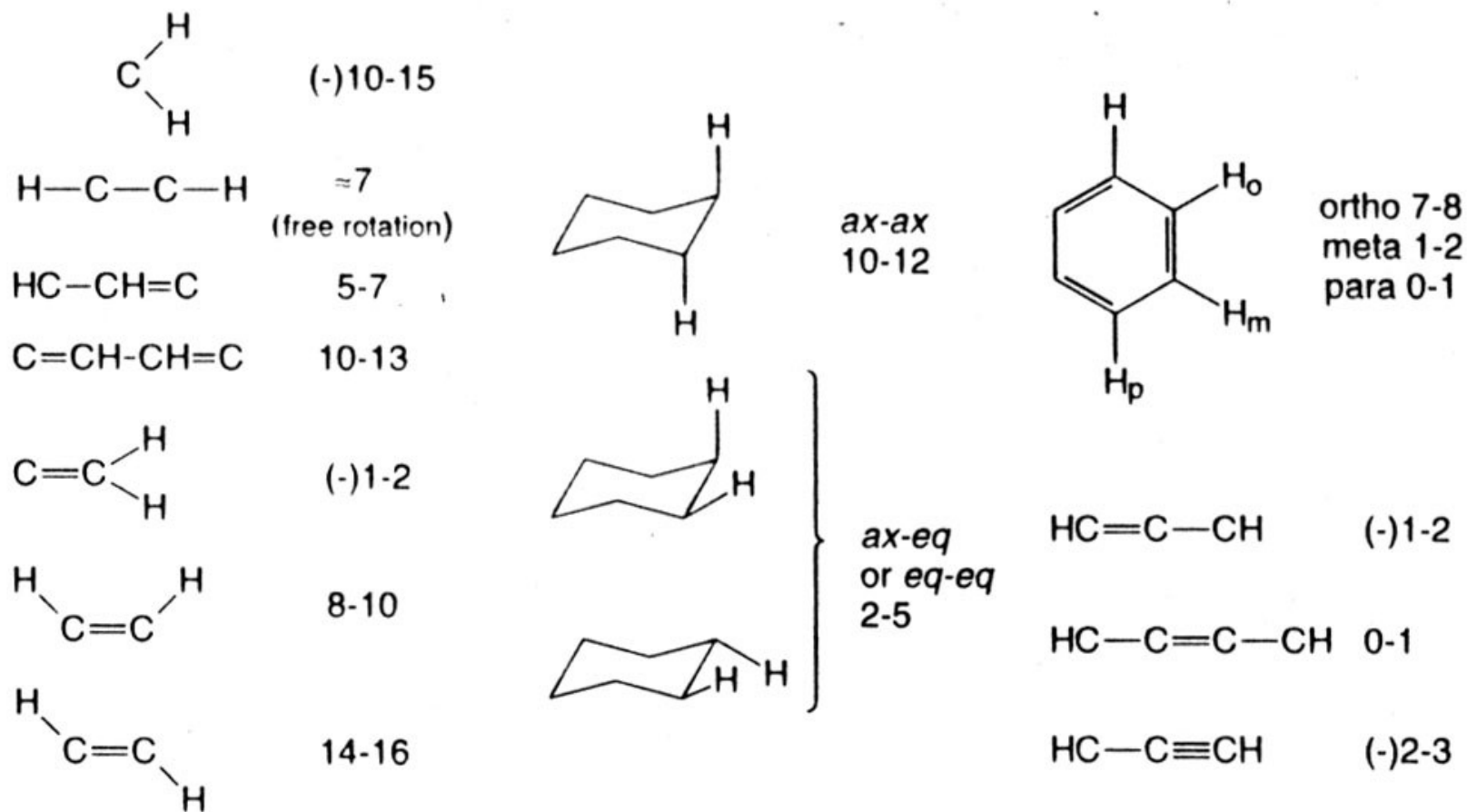
Magnitude of Coupling Constants



Coupling notation



Magnitude of Coupling Constants

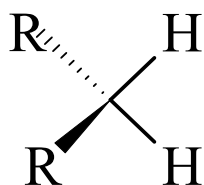


Examples of some typical $^1\text{H}-^1\text{H}$ coupling constants (Hz).

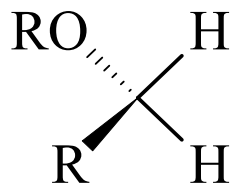
What determines the magnitude of J?

a) Geminal

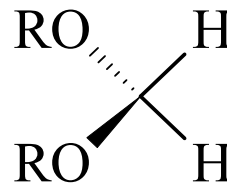
- hybridisation (see table of J values)
- the presence of EWGs
- addition of EWGs to the carbon causes a decrease in the observed J



12.5



10.5



6.0

Observed J value (Hz)

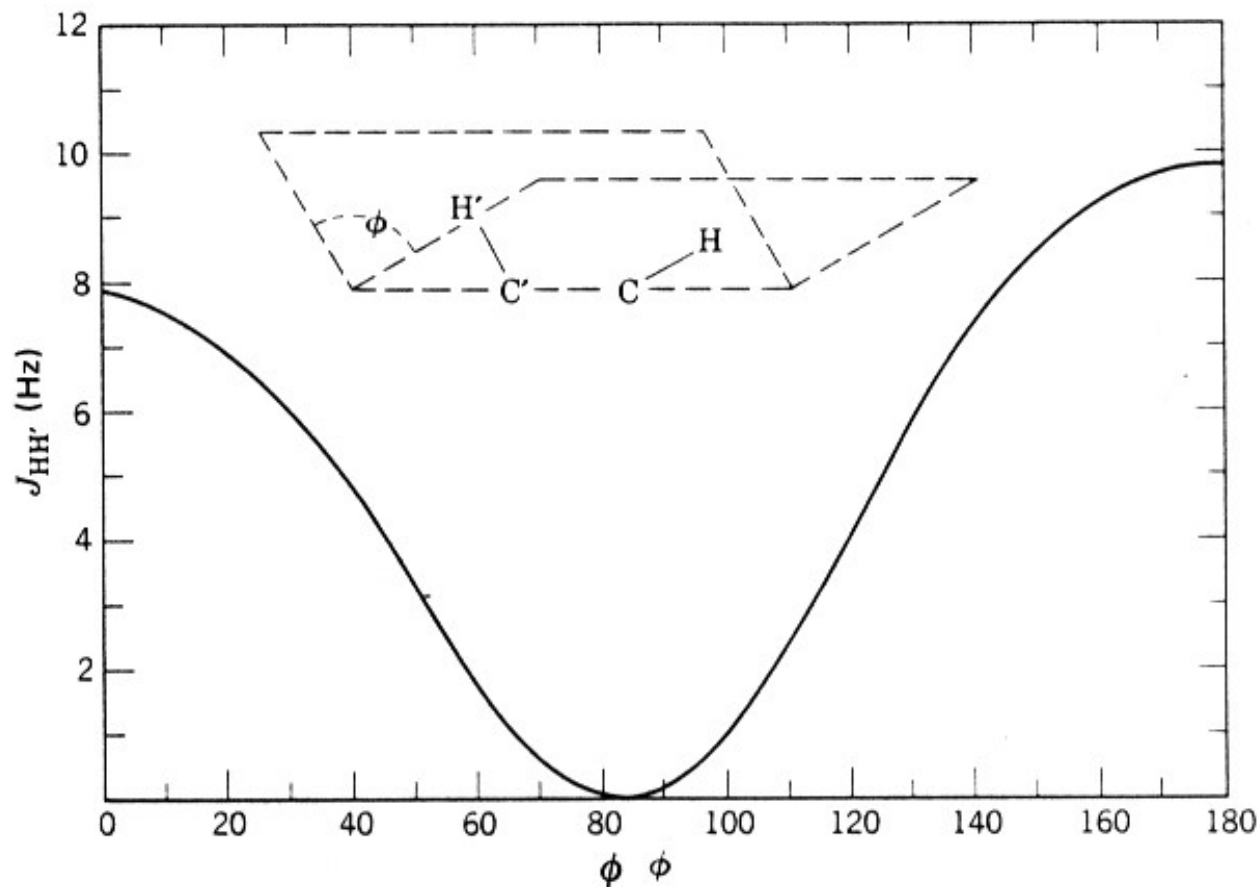
b) Vicinal Coupling

Three major influences in saturated systems

- substituent effects
 - electronegative groups $\Rightarrow J \downarrow$
- bond lengths
 - an increase in C-C bond length $\Rightarrow J \downarrow$
- dihedral angle (ϕ)
 - huge impact on J, yields useful conformational information

Karplus Relationship (vicinal, 3J)

- describes relationship between ϕ and J



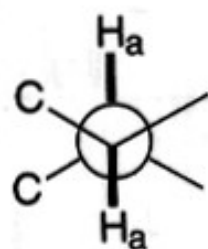
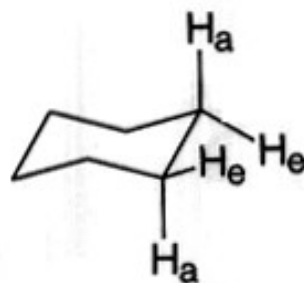
The vicinal Karplus correlation. Relationship between dihedral angle and coupling constant for vicinal protons.

Magnitude of Coupling Constants

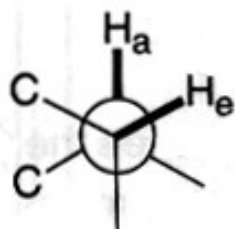


	(-)10-15				
$\text{H}-\text{C}-\text{C}-\text{H}$	≈ 7 (free rotation)		<i>ax-ax</i> 10-12		ortho 7-8 meta 1-2 para 0-1
$\text{HC}-\text{CH}=\text{C}$	5-7				
$\text{C}=\text{CH}-\text{CH}=\text{C}$	10-13				
	(-)1-2		<i>ax-eq</i> or <i>eq-eq</i> 2-5	$\text{HC}=\text{C}-\text{CH}$	(-)1-2
$\text{H}-\text{C}=\text{C}-\text{H}$	8-10			$\text{HC}-\text{C}=\text{C}-\text{CH}$	0-1
	14-16			$\text{HC}-\text{C}\equiv\text{CH}$	(-)2-3

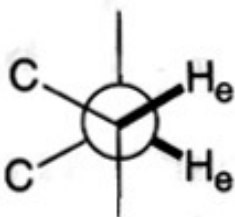
Examples of some typical $^1\text{H}-^1\text{H}$ coupling constants (Hz).



$\phi = 180^\circ$
 $J \approx 10-12 \text{ Hz}$

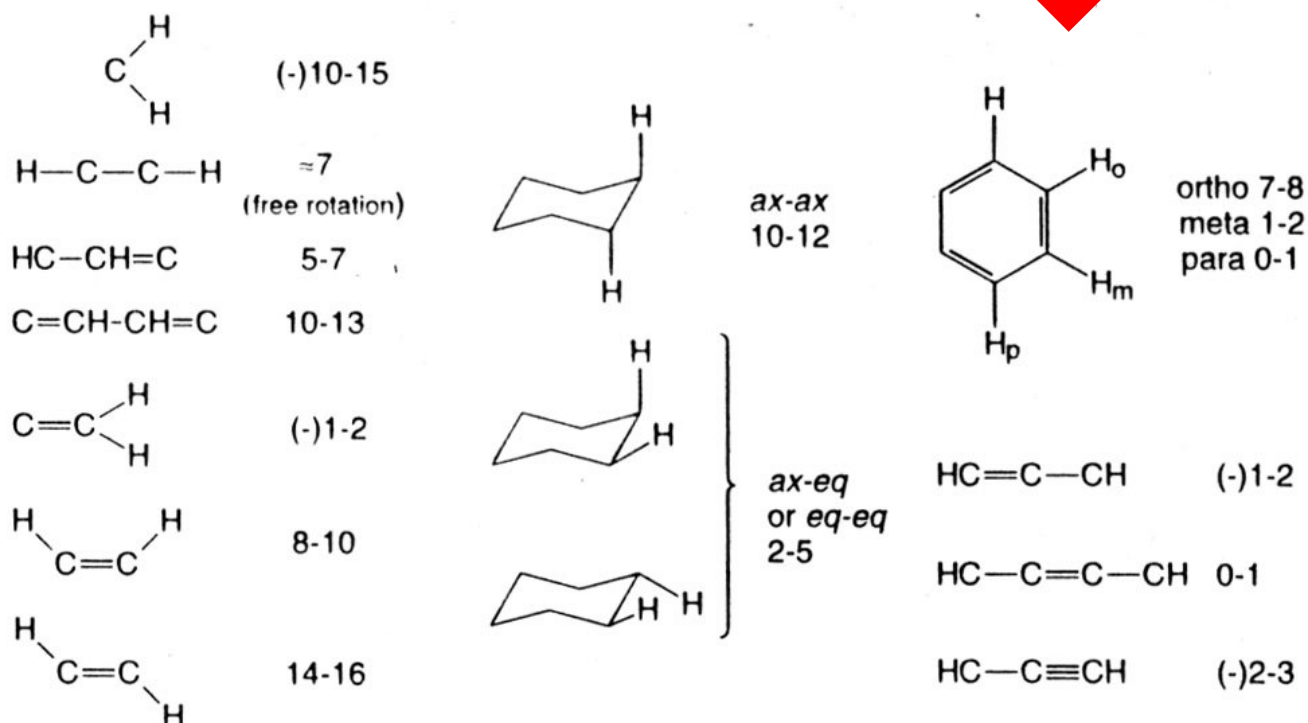


$\phi = 60^\circ$
 $J \approx 2-5 \text{ Hz}$



c) Long range spin-spin coupling

- commonly observed over 4 or 5 bonds eg aromatic systems, see Table of J values
- J values are typically small (0-3 Hz). Small J-values may be manifested as line broadening.



Examples of some typical $^1\text{H}-^1\text{H}$ coupling constants (Hz).