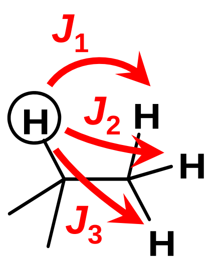
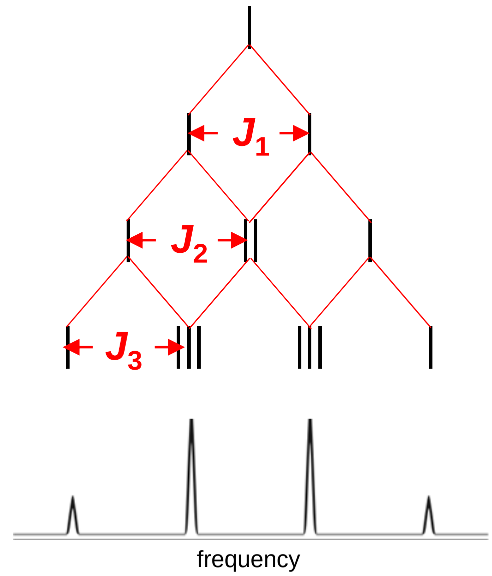
Spin-Spin Coupling: Simple Splitting and Pascal's Triangle

Can think of Pascal's triangle as a way of expressing splitting for multiple coupling constants J_1, J_2, J_3, etc., where $J_1 = J_2 = J_3$.

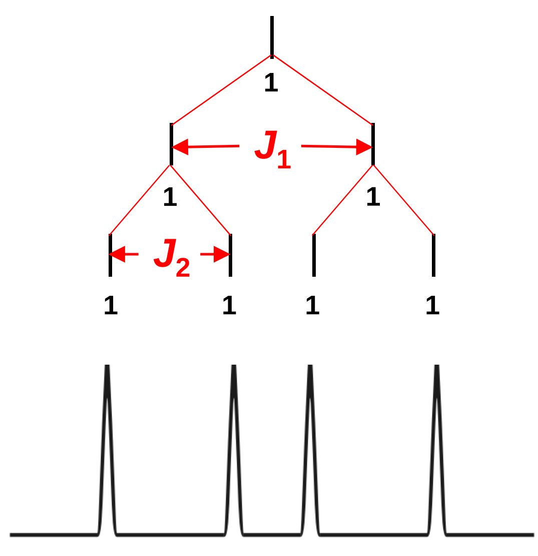




Spin-Spin Coupling: More Complex Splitting

What if coupling constants aren't equal?

Splitting pattern gets more complicated, doesn't follow Pascal's triangle.



doublet of doublets (dd)

Spin-Spin Coupling: More Complex Splitting

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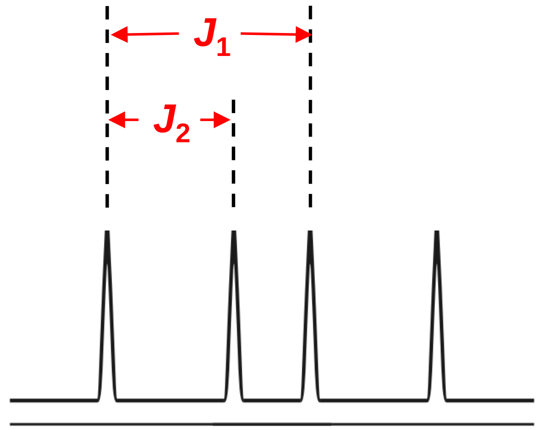
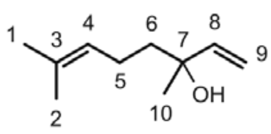
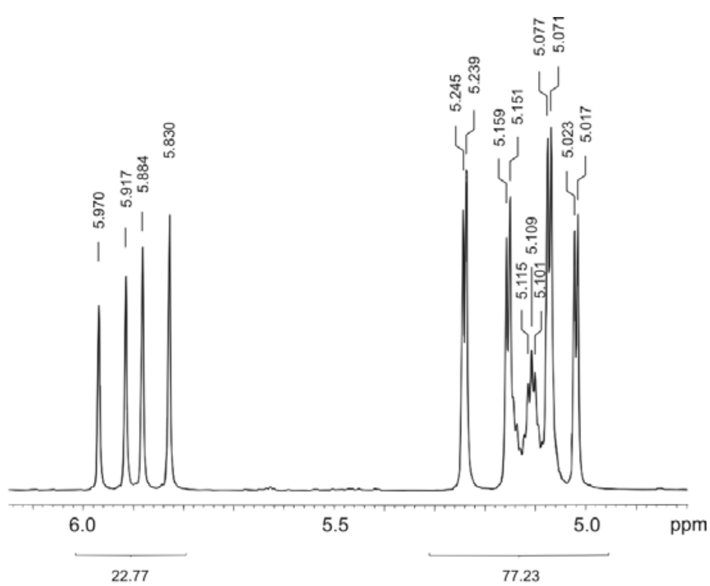
For case of doublet of doublets, can measure *J*'s directly from spectrum.



doublet of doublets (dd)

Spin-Spin Coupling: More Complex Splitting





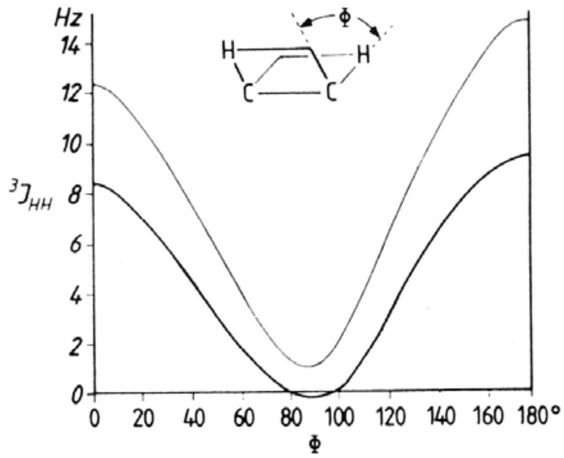
200 MHz [1]H NMR spectrum of linalool, 5-6 ppm region.

Nuclear Coupling and Geometry: The Karplus Equation

For vicinal coupling partners,

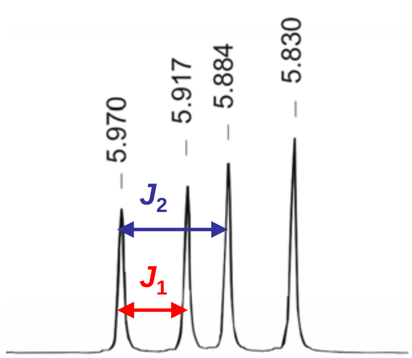
$$^{3}J_{H\text{-}H} = a(\cos^2\phi) + c$$

$$a(0\text{-}90°) < a(90\text{-}180°)$$



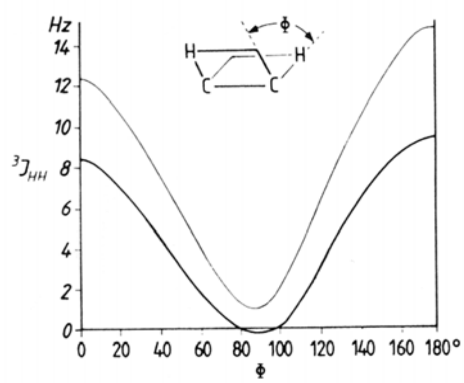
Nuclear Coupling and Geometry: The Karplus Equation

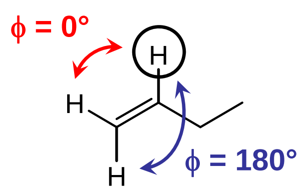
From spectrum of linalool…



J_1 = 10.6 Hz

J_2 = 17.2 Hz

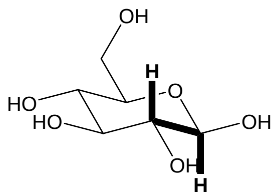




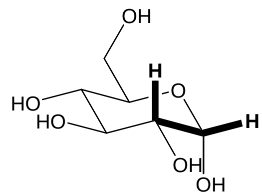
$J_{cis} < J_{trans}$

Applying the Karplus Equation

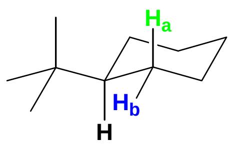
Other examples:



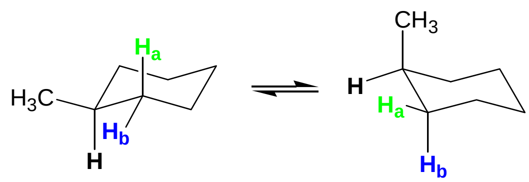
$J_{\alpha\text{-glucose}}$ = 7.8 Hz



$J_{\beta\text{-glucose}}$ = 3.6 Hz



$J_{H\text{-}Ha}$ = 12 Hz $J_{H\text{-}Hb}$ = 4 Hz



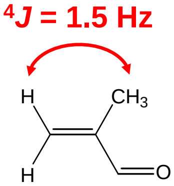
$J_{H\text{-}Ha}$ = 9 Hz $J_{H\text{-}Hb}$ = 4 Hz

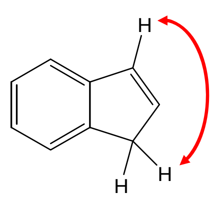
$$J_{TOT} = f_{ax\text{-}ax}(J_{ax\text{-}ax}) + f_{eq\text{-}eq}(J_{eq\text{-}eq})$$

Long-Range Coupling

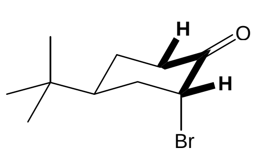
Occurs through multiple bonds or “W” conformation.

^4J = 1.5 Hz

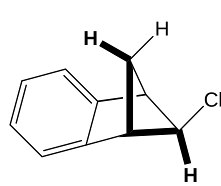




^4J = 2 Hz



^4J = 3 Hz



^4J = 7.4 Hz