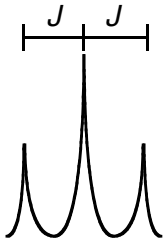
Dr. Laurie S. Starkey, Cal Poly Pomona - NMR Spectroscopy: Spin-Spin Coupling

The magnitude of the coupling between two neighboring protons is determined by their spatial relationship. When considering the dihedral angle between hydrogens (as observed via a Newman projection), the maximum coupling constant (*J*) occurs at 0˚ and 180˚ (eclipsed and anti protons, respectively), and is at a minimum when they are at 90˚ (orthogonal protons). Spin-spin coupling can occur through 2, 3 or even 4 bonds and can be generally classified as small (<3 Hz), medium (~7 Hz) or large (>10 Hz). Not all protons are split by neighboring protons. Protons on N or O are acidic and are exchangeable. As a result, these signals usually do not couple with neighboring protons (**OH and NH are typically broad singlets**). Also, since protons on carbonyls have very small coupling constants, **aldehyde H's typically appear as singlets**.

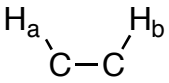
a doublet with a small *J*



a triplet with a large *J*

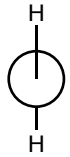
General coupling constants (called "*J* values")

vicinal (3-bond)

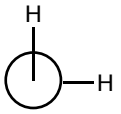


J_{ab} ~7 Hz
(freely rotating, so no fixed dihedral angle)

0˚ dihedral angle
large coupling
J_{ab} ~ 2-14 Hz



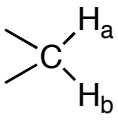
180˚ dihedral
large coupling
J_{ab} ~ 4-16 Hz



90˚ dihedral
small coupling
J_{ab} ~0-2 Hz

(for fixed dihedral angles - no free rotation)

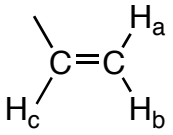
geminal (2-bond)



J_{ab} ~10–15 Hz

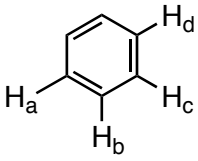
note: only nonequivalent hydrogens will experience splitting, so this geminal coupling is for diastereotopic H's only (i.e., those near a chiral center).

geminal (alkene)	J_{ab} ~1–2 Hz
trans (alkene)	J_{ac} ~11–18 Hz
cis (alkene)	J_{bc} ~6–15 Hz



note: *gem* coupling in an alkene (sp^2 CH_2) is **much** smaller than for an alkane (sp^3 CH_2): ~1 vs. ~12 Hz!

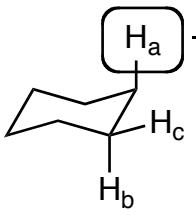
longer-range coupling is also possible (very small)



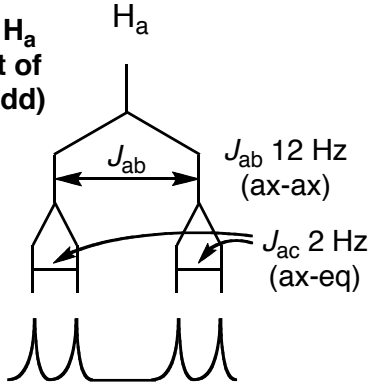
ortho J_{ab} ~7-10 Hz
meta J_{ac} ~2-3 Hz
para J_{ad} ~0-1 Hz

---

cyclohexane (ax-ax)	J_{ab} ~10–13 Hz (180˚ dihedral)
cyclohexane (ax-eq) or (eq-eq)	J_{ac} ~2–5 Hz (60˚ dihedral)



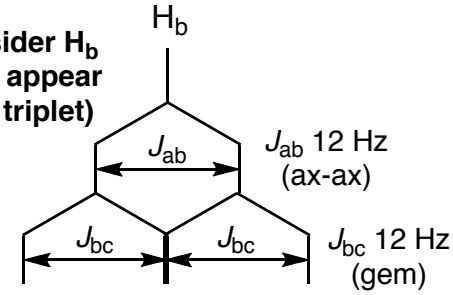
consider H_a (a doublet of doublets, dd)

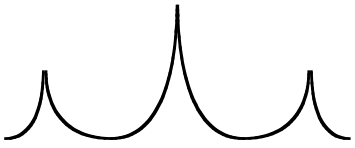


a doublet of doublets, dd
(four peaks but not a quartet - all equal heights/integration, and not even spacing between peaks)

*note: H_b (a doublet of doublets, dd) may appear as an apparent **triplet** if the large gem coupling (J_{bc}) is about the same as the large ax-ax coupling (J_{ab}). i.e., if J values are equal, then two neighbors result in a triplet (n+1 rule).*

consider H_b (may appear as a triplet)





this dd appears as an apparent triplet, t (three peaks with even spacing and 1:2:1 peak height ratio)