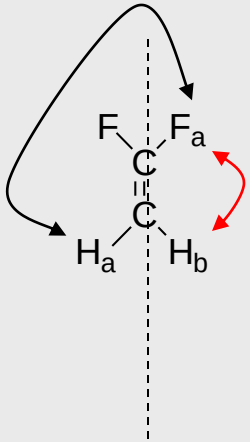
Magnetic Equivalence (Revisited)

Remember the following example:

1,1-difluroethene

- The two protons are chemically equivalent
- The two protons are not magnetically equivalent as they each have a different coupling constant to F (and respectively F_a)

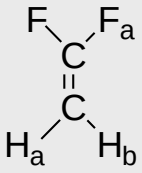
$J_{aF} \neq J_{bF}$



The confusion arises from the fact that although the two protons are not (by definition) magnetically equivalent, any difference in coupling constant to F and F_a respectively would be degenerate in energy

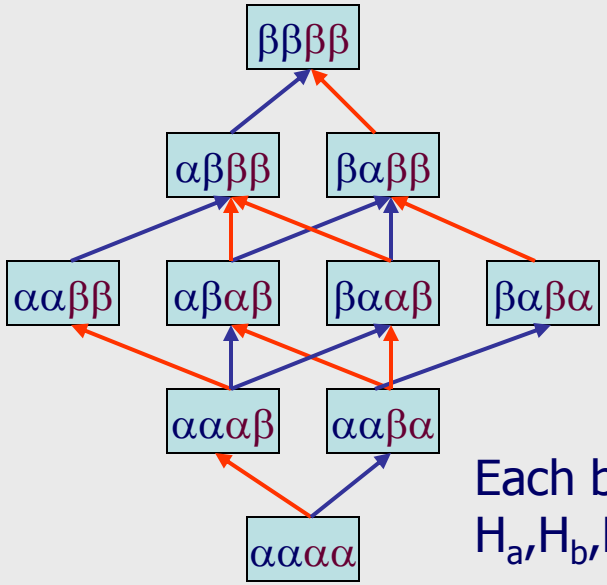
Magnetic Equivalence (Revisited)

Looking at the various spin states, you can see why there are spectral consequences for magnetic non-equivalence:



Let's use a to show α spin +½ and β to show spin −½

$J_{HF\text{-}trans}$ = 45 Hz, $J_{HF\text{-}cis}$ = 18 Hz
(and yes, $J_{Ha\text{-}F} = J_{Hb\text{-}F}$ and $J_{Ha\text{-}Fa} = J_{Hb\text{-}Fa}$!)



Each box:
H_a,H_b,F,F_a spin states

Second-Order Spectra

1. Spectra that can be analyzed and interpereted by the n+1 rule or the analysis we just covered are first-order spectra

2. Second order spectra are those that require advanced analysis due to the effects of:
   - Magnetic non-equivalence
   - The difference in chemical shift (ν, in Hz) between the two protons that are coupled is similar to the coupling constant (J)

3. We will consider $\Delta\nu/J$:
   - For $\Delta\nu/J > 10$, the pattern becomes first order and we say the two are weakly coupled
   - For $\Delta\nu/J < 10$, the pattern becomes second-order and we say the two protons are strongly coupled

Second-Order Spectra – Some nomenclature

1. There are general patterns for the finite number of possibilities for groups of coupled ^{1}Hs

2. Nuclei that are engaged in mutual coupling constitute a *spin system*

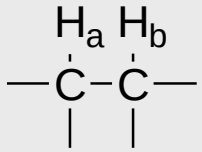
3. Each chemically distinct proton is assigned a letter, A,B,C…
   - If these protons are chemically and magnetically equivalent, they are subscripted like a chemical formula: A_2, B_2, etc.
   - If these protons are chemically equivalent, but not magnetically they are designated as AA’, BB’, etc.

4. If a pair protons are very different in chemical shift, they are assigned letters far apart in the alphabet – X, Y, Z

5. If three sets of protons are involved, with widely spaced chemical shift, an intermediate letter is used, M, N, etc.

Second-Order Spectra:

A2, AB and AX spin systems



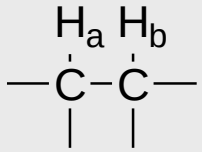
Starting with a very simple spin system – two vicinal protons, J = 7 Hz

If $\Delta\nu/J$ is large, a first order spectrum results – and we say the spin system is "AX" and weakly coupled (respective to chemical shift)

We see the expected first order spectrum – two doublets

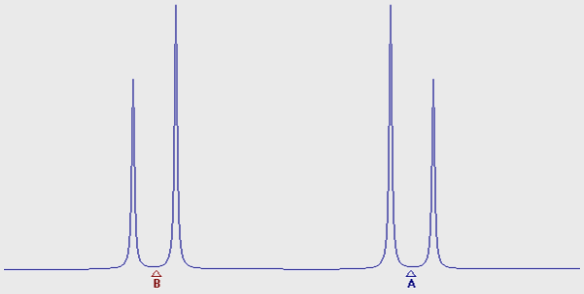
Second-Order Spectra:

A_2, AB and AX spin systems

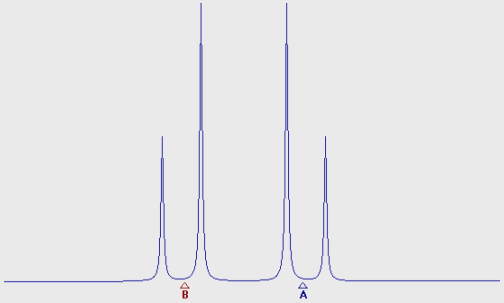


As $\Delta\nu/J$ becomes smaller, second order effects come into play, the energy levels of coupling overlap with those of chemical shift – and we say the spin system is "AB" and becoming strongly coupled

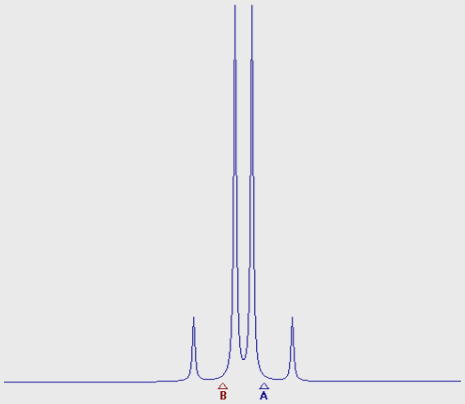
We see the progression, keeping J = 7 Hz



$\Delta\nu/J = 6$



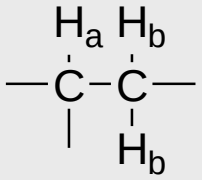
$\Delta\nu/J = 3$



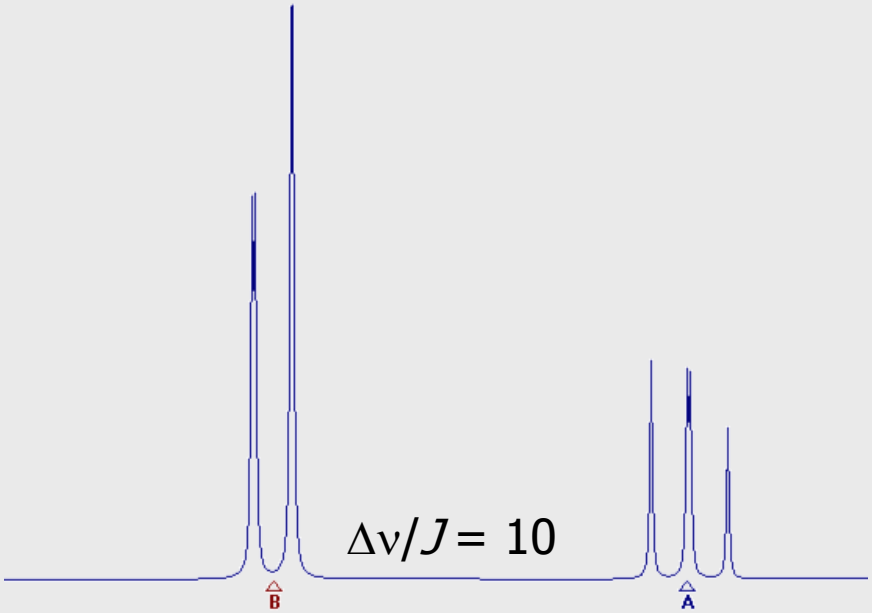
$\Delta\nu/J = 1$

Second-Order Spectra:

AX_2, AB_2 spin systems

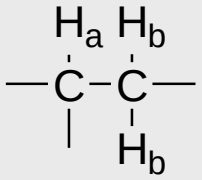


When $\Delta\nu/J$ is large, we see the first-order spectrum that we would expect – a doublet and triplet:

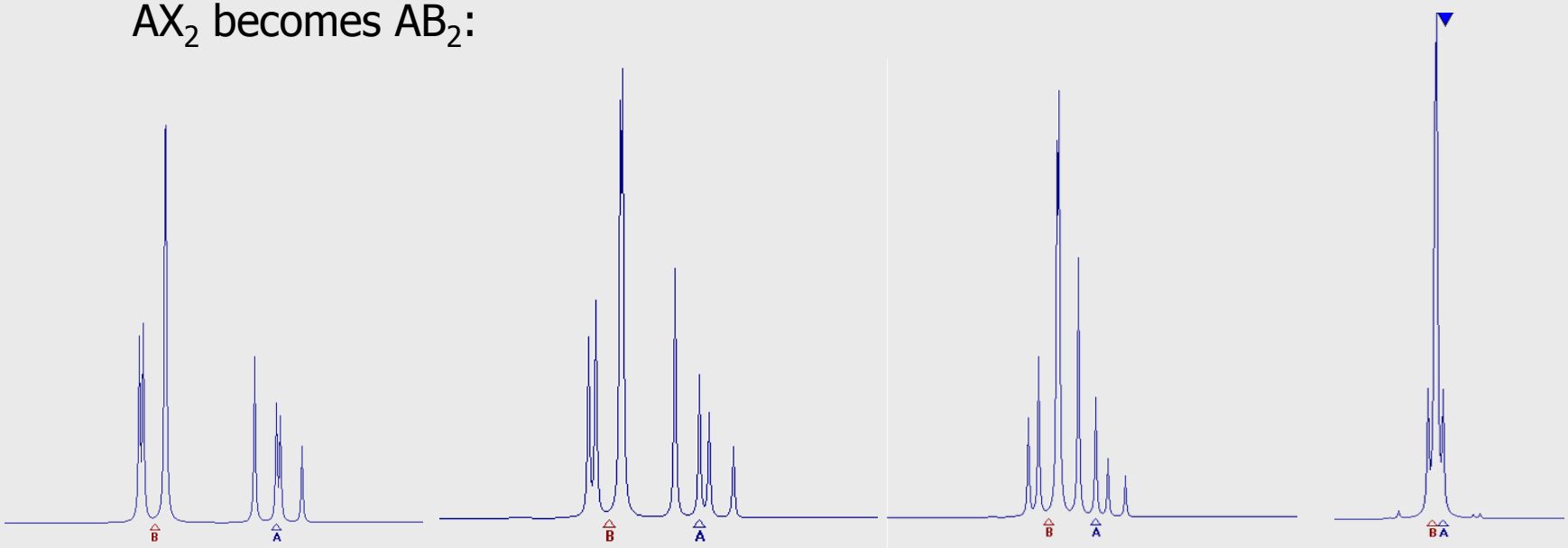


Second-Order Spectra:

AX_2, AB_2 spin systems



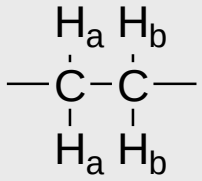
Again we see the progression into second-order behavior as $\Delta\nu/J$ is decreased;
AX_2 becomes AB_2:



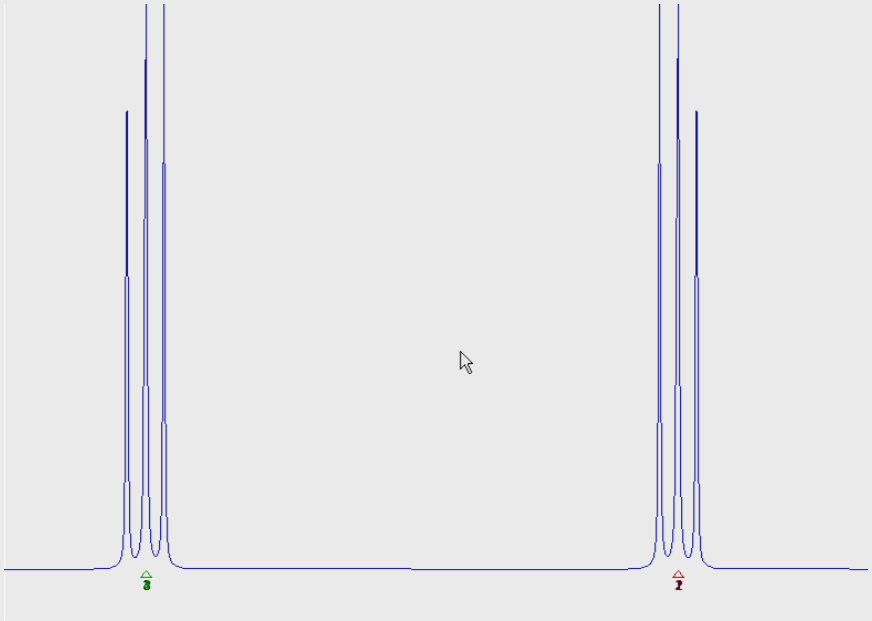
$\Delta\nu/J = 5$ $\Delta\nu/J = 3$ $\Delta\nu/J = 1.5$ $\Delta\nu/J = 0.3$

Second-Order Spectra:

A_2X_2, A_2B_2 spin systems



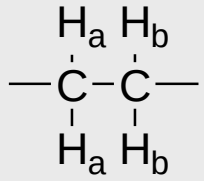
When $\Delta\nu/J$ is large, we see the first-order spectrum that we would expect – a pair of triplets:



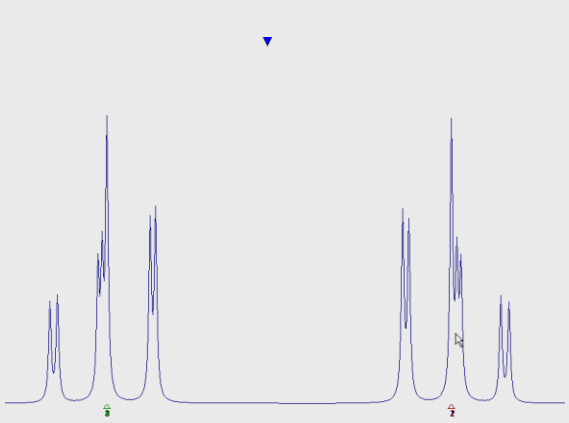
$\Delta\nu/J = 10$

Second-Order Spectra:

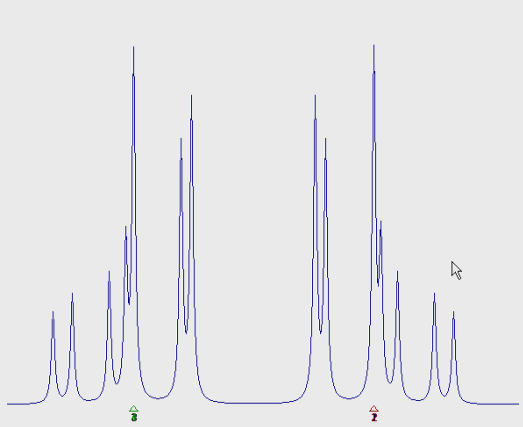
A_2X_2, A_2B_2 spin systems



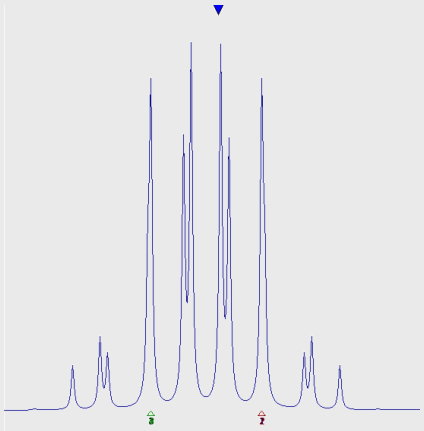
Now we will expect to see second order effects as becomes smaller; A_2X_2 becomes A_2B_2:



$\Delta\nu/J = 6$

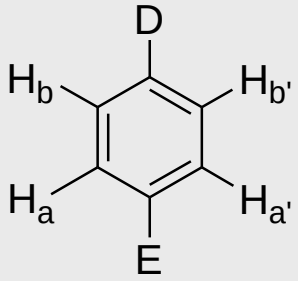


$\Delta\nu/J = 3$



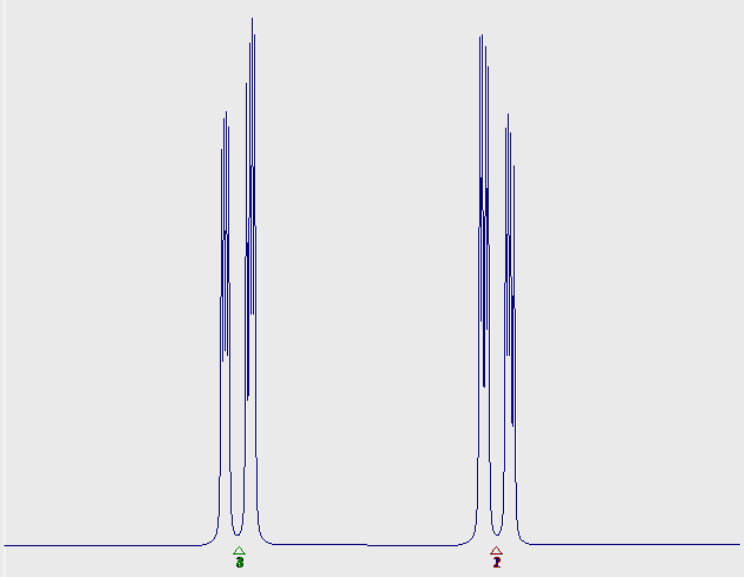
$\Delta\nu/J = 1$

Second-Order Spectra:



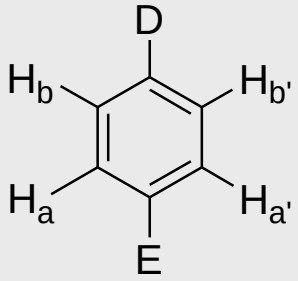
AA′XX′, AA′BB′ spin systems – here we see the consequence of magnetic non-equivalence

Starting out; J_{ortho} = 10 Hz, J_{meta} = 3 Hz, J_{para} = 0 Hz: the spectrum looks deceptively like two doublets



$\Delta\nu/J$ = 10, when D and E are very different electronegatively

Second-Order Spectra:



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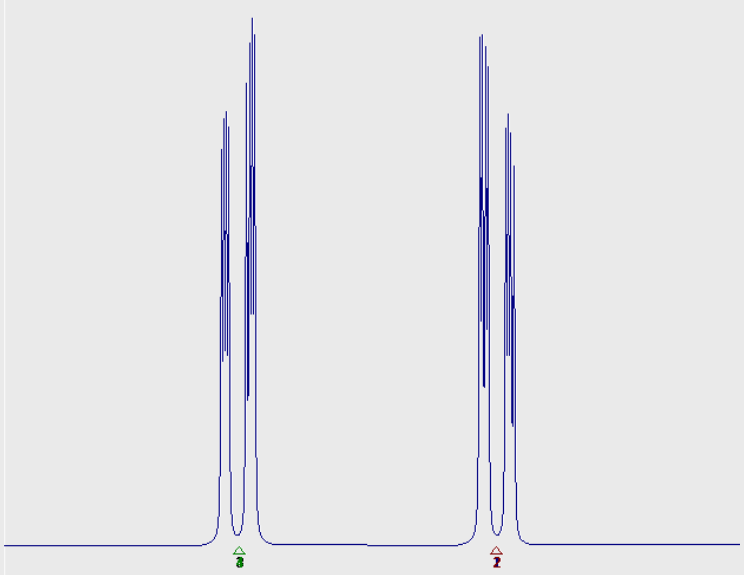
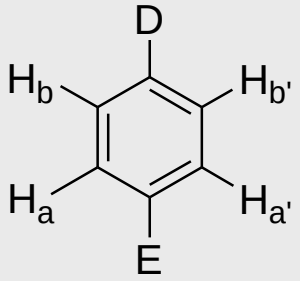


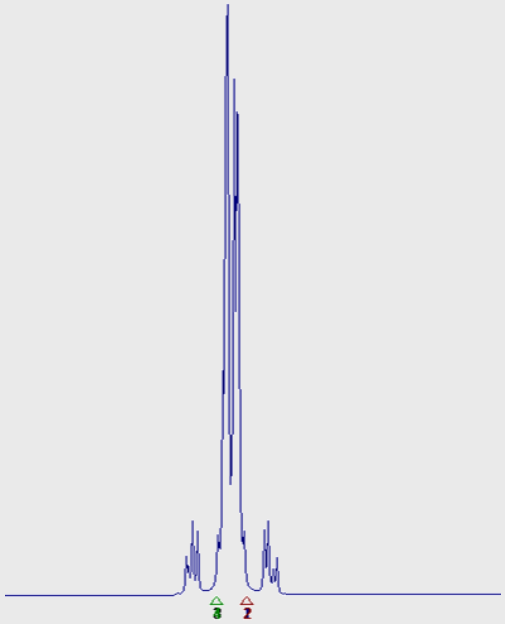
$\Delta\nu/J$ = 10, when D and E are very different electronegatively

Second-Order Spectra:



AA′XX′, AA′BB′ spin systems – here we see the consequence of magnetic non-equivalence

Starting out; J_{ortho} = 10 Hz, J_{meta} = 3 Hz, J_{para} = 0 Hz: as D and E approach one another as far as electronegativity, we clearly see the 2nd order effect:



$\Delta\nu/J$ = 1, when D and E are similar electronegativity

Second-Order Spectra – How are they analyzed?

1. Second order spectra can not be analyzed by traditional methods of comparison of *J*-values

2. Some of the simple patterns are recognizable to an experienced NMR analyst and can be used to interpret a spectrum

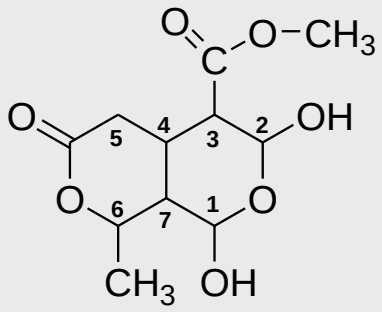
3. More complex spin systems are typically analyzed by spectral simulation software – the various expected *J*-values and differences in chemical shift can be entered and a theoretical spectrum produced

4. This software – WINDNMR, developed by Hans Reich at the University of Wisconsin, Madison, was used to produce the spectral patterns in this lecture – it is freeware available for download

5. More sophisticated software is available, and is usually part of any NMR processing package

Advanced Homework Assignment II:

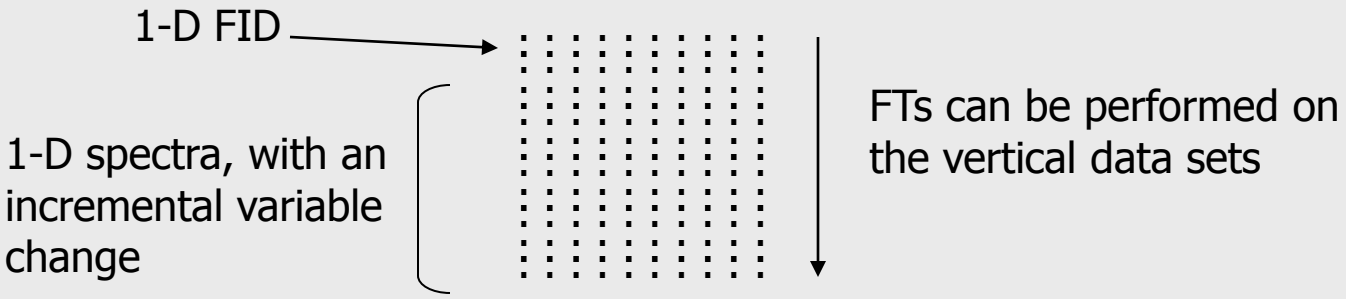
1. Based on your knowledge of first-order coupling patterns and the ability to use tables of *J*-values, make the stereochemical assignments for xylomollin, a secoiridoid-type monoterpene:



H	δ	mult	*J*s (Hz)
1	5.88	d	3
2	5.48	d	8
3	2.59	dd	10, 8
4	3.00	dddd	12, 10, 10, 5
5a	2.49	dd	17, 5
5b	2.54	dd	17, 12
6	4.52	dq	10, 7
7	1.75	ddd	10, 10, 3

A quick look at 2-D NMR techniques:

1. In actuality, the techniques we have already covered ^{1}H, ^{13}C, and DEPT are 2-D (frequency vs. intensity) however, by tradition the intensity component is dropped when discussing dimensionality

2. In the following techniques, many FIDs (proto-NMR spectra) are taken one after another, with some acquisition variable or pulse sequenced varied by small increments

3. Since each FID is a collection of digitized data points in the first dimension (say 10 points to make a spectrum) if 10 spectra are accumulated with an incremental change in variable, an FT can be performed in the other dimension