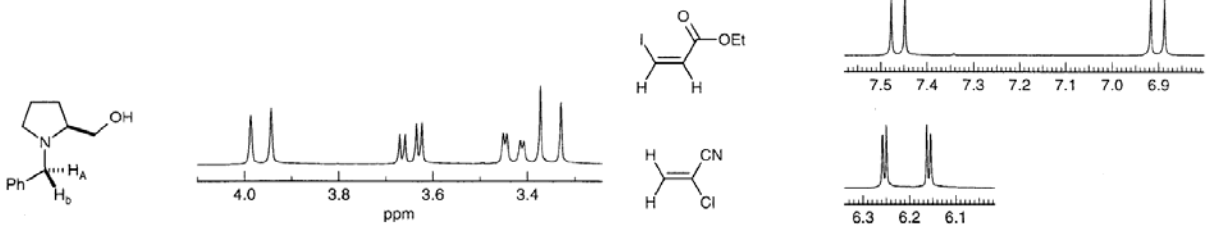
Common Multiplet Patterns and Their Analysis

AB and AX systems

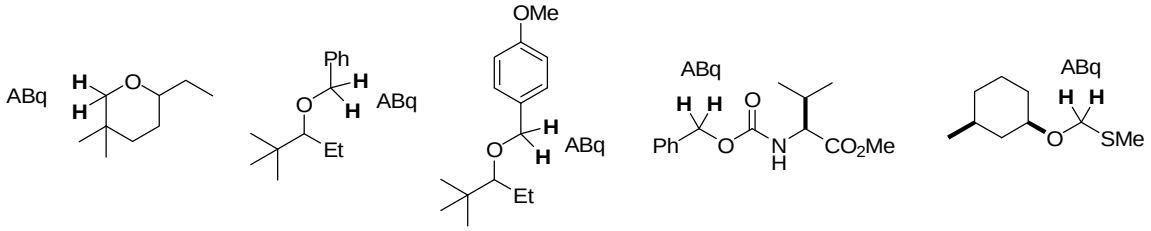
AX: Two protons, H_A and H_X, very different shifts. First order. J_{AX} can be directly obtained.
AB : Two protons, H_A and H_B, chemical shifts comparable to $J_{AB.}$ J_{AX} directly measurable, ν_A and ν_B must be calculated. See details below.
Some examples:



AB Quartet (ABq)

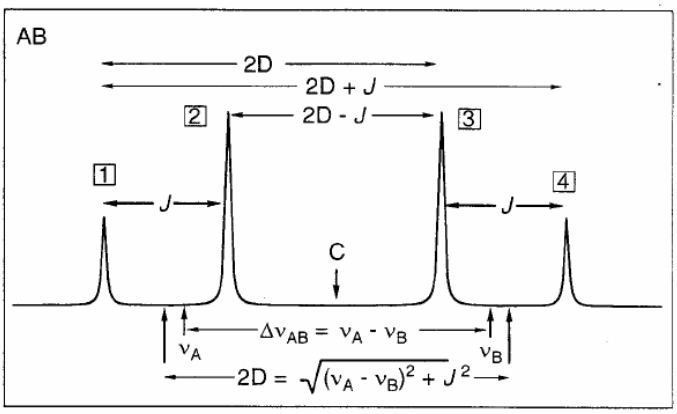
- AB quartets are common for molecules that contain two isolated protons coupled only to each other (ie $^2J_{CH}$).
- This sort of system is common with a number of protecting groups (eg Bn, BOM, PMB, Cbz, SEM, MOM, MTM etc) provided the protons of the CH_2 group are diasterotopic.
- The protons must be diastereotopic [otherwise they will be equivalent and the coupling will not be visible].

eg



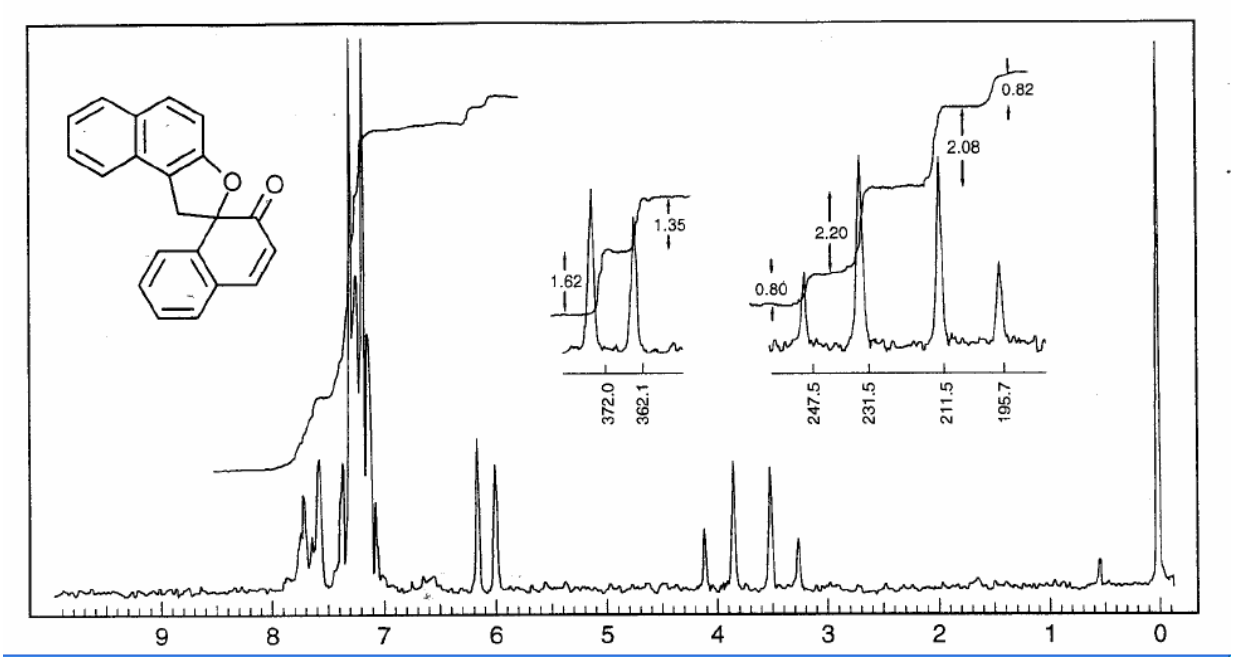
Four lines are present, with the inner two taller than the outer two. The correct method for calculating the chemical shifts of A and B is detailed below, however it is common to find the chemical shift reported as the center of the AB pattern eg δ 5.10 (2H, ABq, J = 12).

NB There is only one coupling constant! It can often be extracted by simple visual inspection, even down to $\Delta\nu/J$ = 0.5 even though this is not considered the 100% correct approach.



If $\nu_A - \nu_B$ were calculated believing the pattern were AX instead of AB, one would get 2D instead of the correct value.

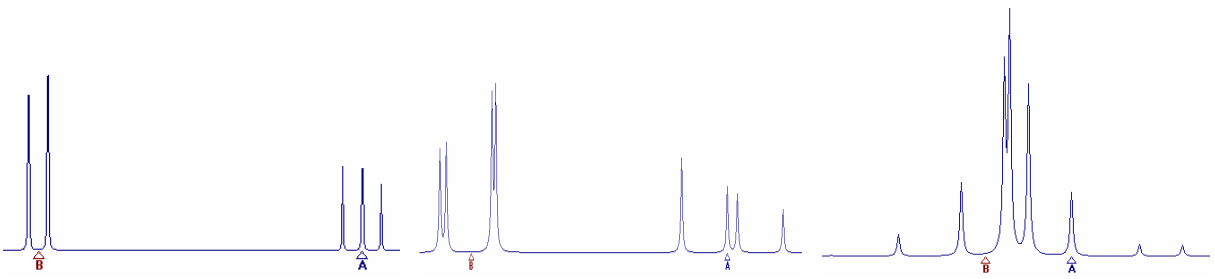
Example:


0.82
2.08
2.20
0.80
1.35
1.62
372.0
362.1
247.5
231.5
211.5
195.7
9
8
7
6
5
4
3
2
1
0

The Spectrum of AX_2 → AK_2 → AB_2

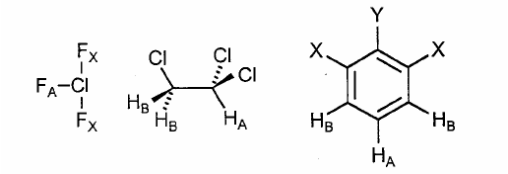
AX_2 First order. A is a triplet and X is a doublet (see below). J_{AX} can be directly obtained.

AB_2 Second order. Both JAB and VAB must be calculated - neither can be directly measured from the spectrum.



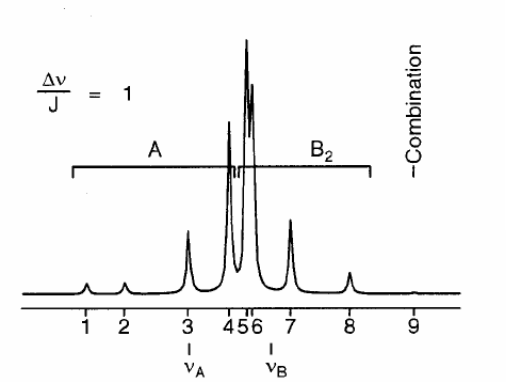
The AB_2 Pattern

- The AB_2 pattern can be observed for the following structural subunits (among others):



- An AB_2 multiplet contains 9 lines, although usually only 8 lines are visible (line 9 is usually too small to see):
    - There are 4 A lines and 4 B lines
    - Line numbering starts from the A side (the one-proton side)
    - The tallest line is always line 5. Line 9 is usually too small to see.

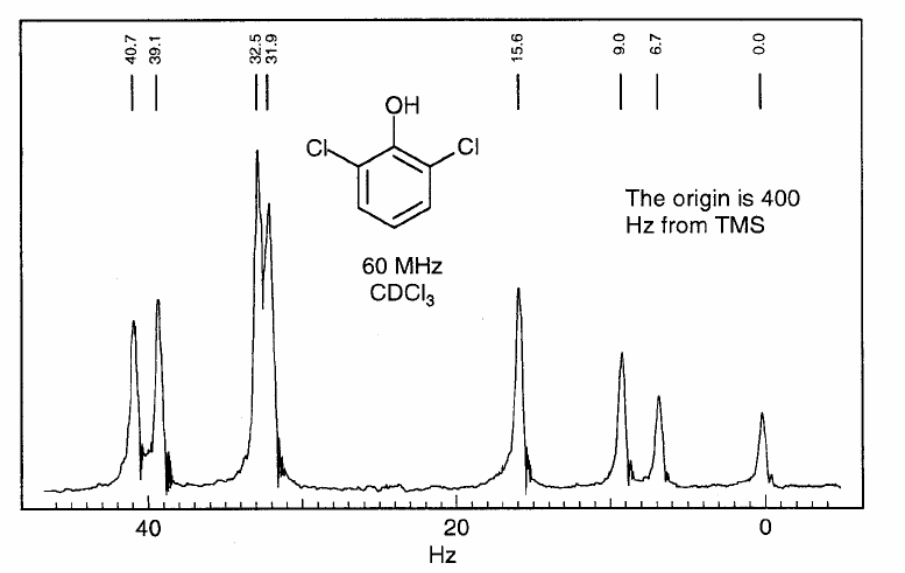
Although it is common to find this system reported as a multiplet (eg δ 4.70-4.82, 3H, m), the spectrum can be solved for ν_A, ν_B and J_{AB} using:



$$\nu_A = \nu_3$$

$$\nu_B = (\nu_5 + \nu_7)/2$$

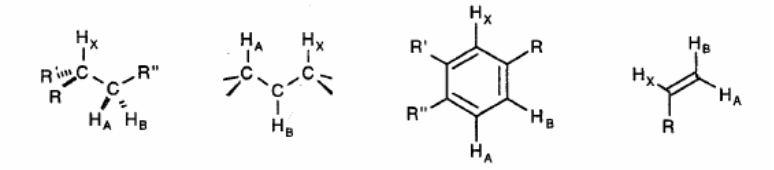
$$J_{AB} = (\nu_1 - \nu_4 + \nu_6 - \nu_8)/3$$



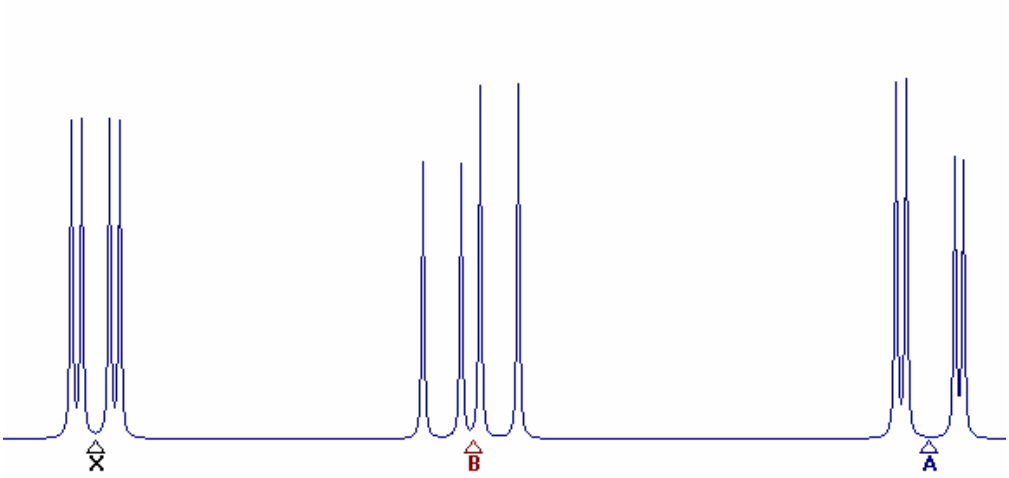
AMX and ABX Systems

AMX First order . Can be solved
ABX Second order . This is a very common pattern . J_{AB} is directly measurable, J_{AX}, J_{BX} and VAB can be calculated from the line positions of the spectrum (once it has been properly analyzed) .

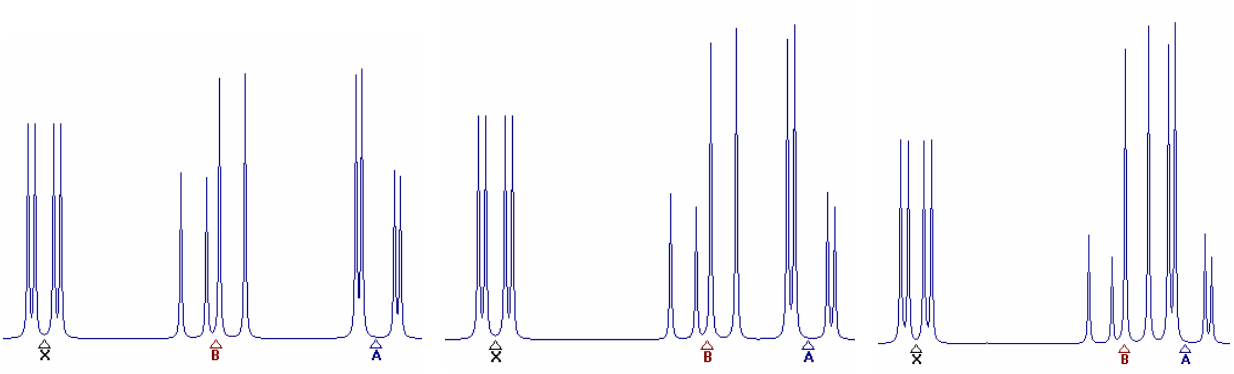
Very common in organic molecules:



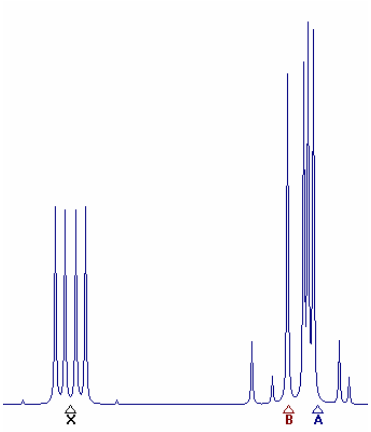
- The AMX end of the continuum is a pattern that is commonly analyzed in a direct fashion. Even with second-order effects the errors in chemical shifts and frequency are within what many consider to be 'acceptable' limits:



What happens as A and B get closer in chemical shift?



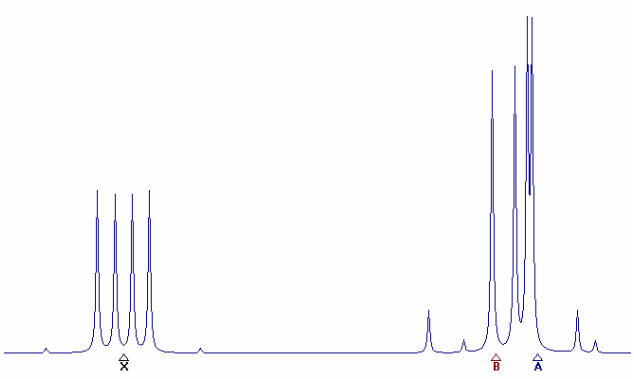
Left to right: $\Delta\nu_{AB}$ = 50, 30, and 20. For each spectrum J_{AB} = 12 Hz; J_{AX} = 2 Hz; J_{BX} = 8 Hz. All of these spectra can be/generally areanalyzed by an AMX approach (this is OK when $\Delta\nu_{AB} > J_{AB}$).



In this spectrum $\Delta\nu_{AB}$ = 10 and J_{AB} = 12 Hz; J_{AX} = 2 Hz; J_{BX} = 8 Hz.

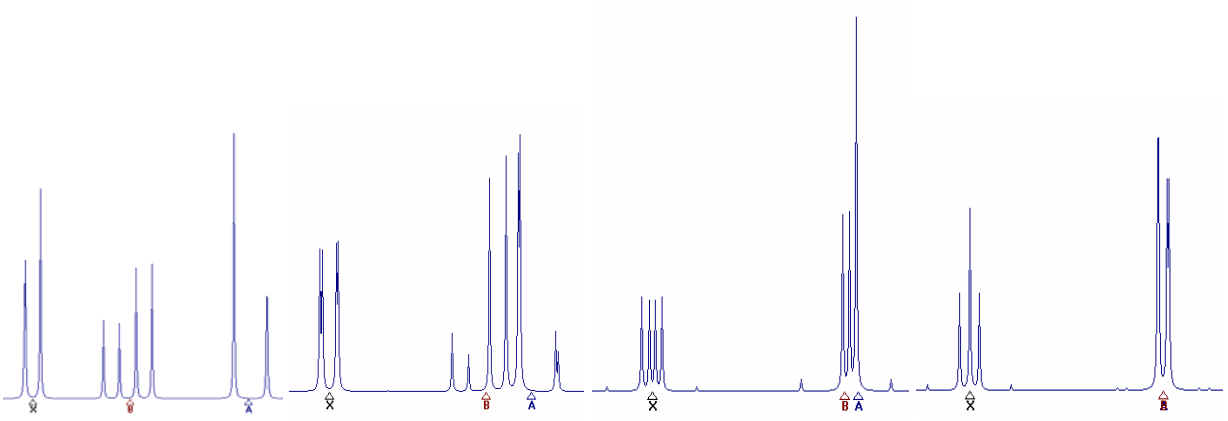
This is a classic ABX pattern, and although the coupling constants can be obtained by inspection, it is not possible to obtain the correct chemical shift for A and B or .

- Many ABX spectra are reported as multiplets, however there are solutions that allow the correct values for J_{AB}, J_{AX}, and J_{BX} to be obtained, as well as ν_A, ν_B, and ν_X.
- The ABX spectrum should show 14 lines, although how many are observed depends strongly on $\Delta\nu_{AB}$ (even in the spectrum below lines 9 and 14 are faint).



- The ABX pattern is the last point for where a complete analysis is still possible [although often it is painful!]
- ABX patterns are the simplest systems which show the phenomenon sometimes referred to as "virtual coupling" and they are the simplest systems in which both the magnitude and the sign of J coupling constants is significant

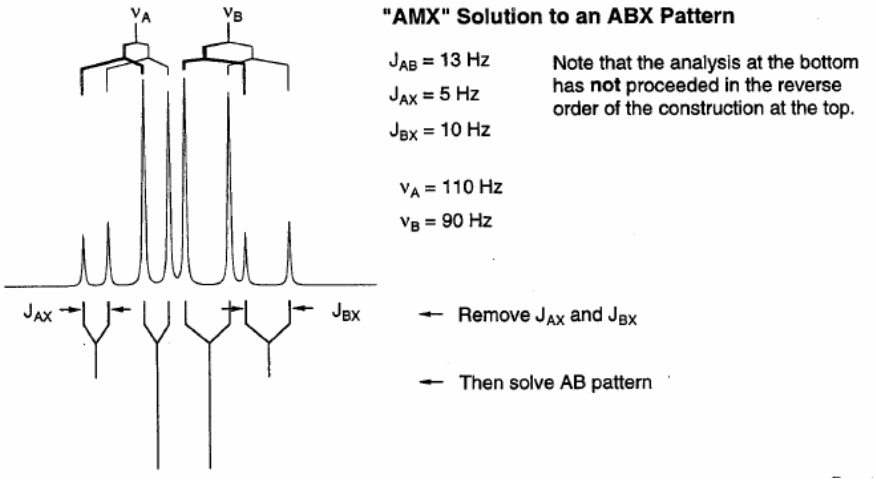
Caution should always be exercised when examining a system that contains very simple multiplicities in a complex molecule, or if your structure proof depends on the analysis of an ABX pattern. A closer look at the dependence of the ABX spectrum on $\Delta\nu_{AB}$ illustrates a potential problem with careless analysis:



$\Delta\nu_{AB}$ = 57, 18.7, 5, 0 (left to right) and J_{AB} = 15.7 Hz; J_{AX} = 0 Hz; J_{BX} = 7.7 Hz

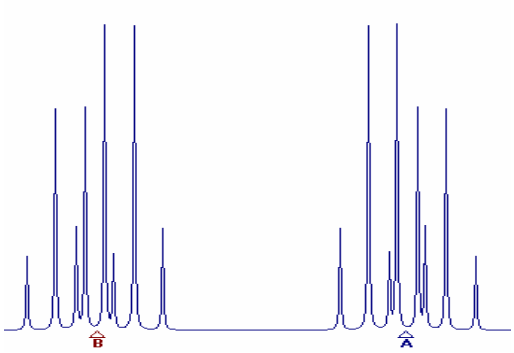
The First Order "AMX" Type Solution to ABX Patterns

Many ABX patterns are sufficiently close to AMX that a first-order solution has a good chance of being *essentially* correct. We identify the distorted doublet of doublets (J_{AB}, J_{AX}) which make up the A portion, as well as the dd (J_{AB}, J_{BX}) for B, and begin the analysis by first removing the J_{AX} and J_{BX} couplings, respectively. This leaves us with an AB pattern, which we can solve in the usual way.



The ABX_3 Pattern

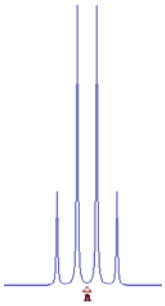
- The ABX_3 patterns is very common: most ethyl groups in a chiral molecule will have CH_2 protons diastereotopic, and thus form an ABX_3 system.

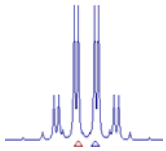


- Although there is an exact solution it is *very common* to find this system reported as a multiplet eg δ 4.02, 2H, m.

- For the exact solution, you first solve the four AB quartets, which are present in a 1:3:3:1 ratio (i.e., they represent the subspectra resulting from the four combinations of X spins: ↓↓↓; ↓↓↑/↓↑↓/↑↓↓; ↓↑↑/↑↓↑/↑↑↓; ↑↑↑). The solutions to these AB quartets give a 1:3:3:1 quartet for the A proton, and another for the B. These can then be solved as first order patterns.

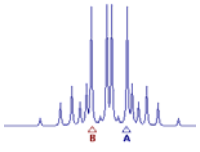
- It is not usually necessary to do an exact solution, however, since in almost all cases $J_{AX} = J_{BX}$ (or very nearly so). A first order "AMX" type of solution is sufficiently accurate:
    - Treat the pattern as an AB quartet of 1:3:3:1 quartets. ie view the pattern as an AB quartet, each line of which is split by the X_3 protons into a 1:3:3:1 quartet. The 1:3:3:1 quartets will have the normal intensity ratios of an AB quartet. To solve, identify the AB-quartet of q and then remove the X coupling. What remains is an AB quartet which can be solved in the usual way. Note that this corresponds exactly to the "AMX" solution for ABX patterns, in which we treat the pattern as an AB quartet, each half of which is split into a doublet by the X nucleus.
    - See simulated spectra on right where J_{AB}=-11 and J_{AX}=J_{BX}=6; $\Delta\nu$=0, 6, 12Hz top to bottom.





Now you can see why the system is often reported as a multiplet!

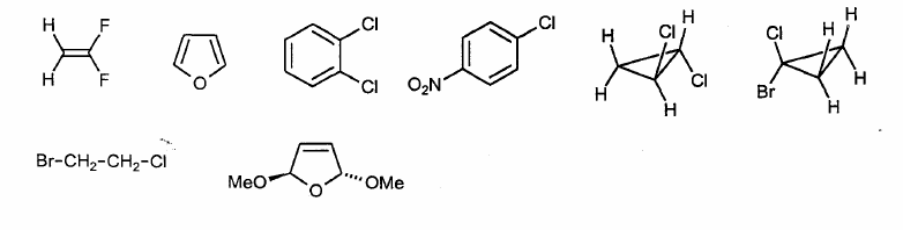
A simple empirical alternative is to do homonuclear decoupling. In less than a couple of minutes of instrument time you can:



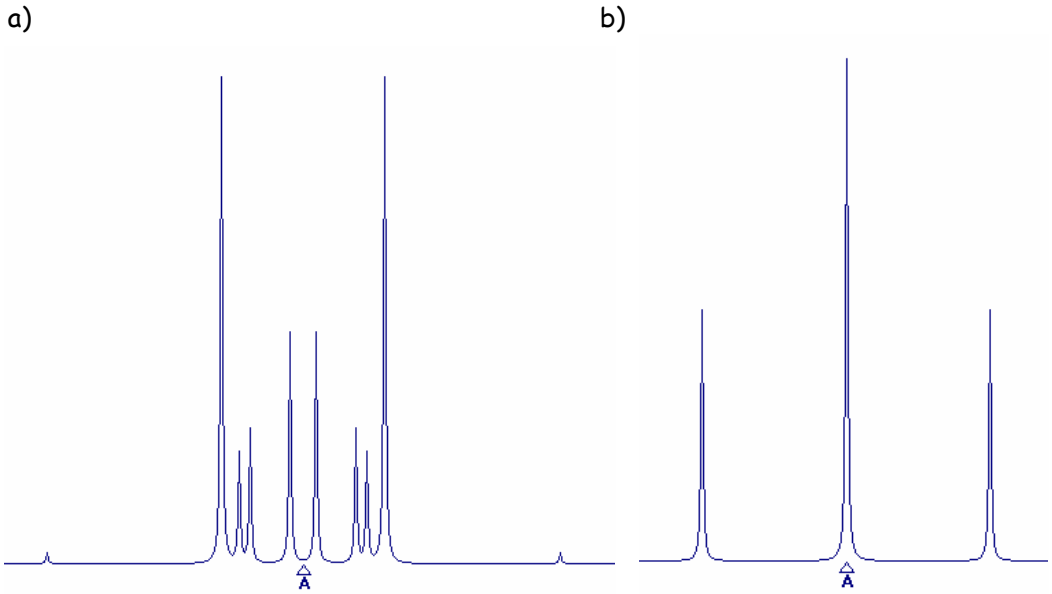
a) irradiate X_3 to give an ABq for A and B (this will give ν_A a nd ν_B as well as J_{AB})
b) irradiate A to give a quartet for B from which J_{BX} is readily obtained
c) given that $J_{AX} = J_{BX}$ in many cases it is not usually necessary to irradiate B to obtain J_{BX}, but it can be done, and may necessary if $J_{AX} \neq J_{BX}$

e) The AA'XX' Pattern

- AA'XX'and the closely related AA'BB'patterns appear in a number of commonly encountered symmetric 4-proton molecular fragments:



- AA'XX' Spectra consist of a maximum of two identical 10-line half spectra, each symmetrical about its midpoint, ν_A and ν_X, respectively.

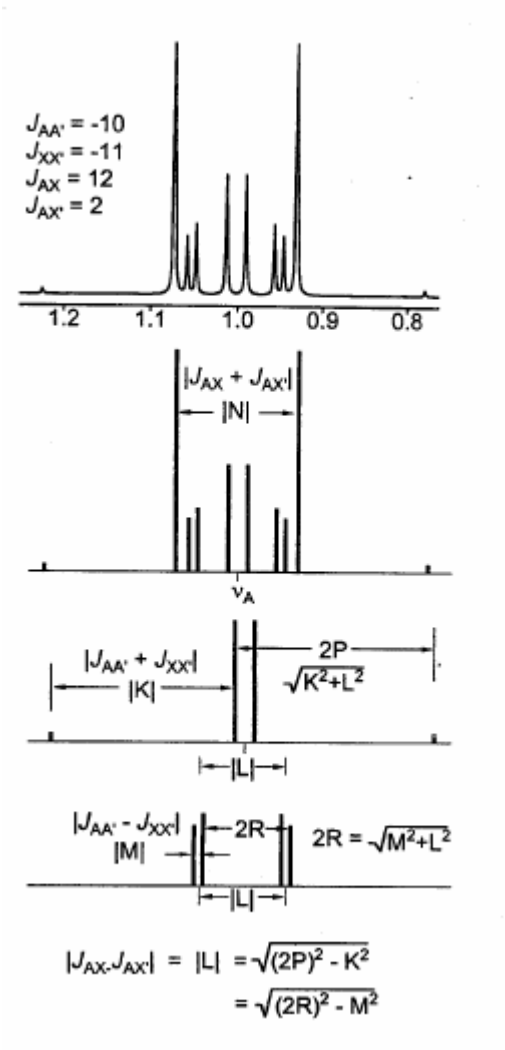


a) $J_{AA'}$ = 10, $J_{XX'}$ = 11; J_{AX} = 12; $J_{AX'}$ = 2 – the classic AA'XX' spectrum (signal shown for A only)

b) $J_{AA'}$ = 10, $J_{XX'}$ = 11; J_{AX} = 12; $J_{AX'}$ = 12 – when J_{AX} = $J_{AX'}$ the spectrum collapses to a triplet

Each half-spectrum consists of a 1:1 doublet (intensity 50% of the half spectrum) with separation [N], and two AB quartets, each with "normal" intensity ratios, and apparent couplings (J_{AB}) of [K] and [M] as indicated. Unfortunately, K and M cannot be distinguished, the relative signs of $J_{AA'}$and $J_{XX'}$are not known, nor is it known which number obtained is $J_{AA'}$and which is $J_{XX'}$. The same ambiguity occurs for J_{AX} and $J_{AX'}$.

To solve an AA'XX" pattern it is necessary to identify the three substructures: the "doublet" and the two AB quartets, then solve for K, L, M, and N, and then obtain the individual couplings.



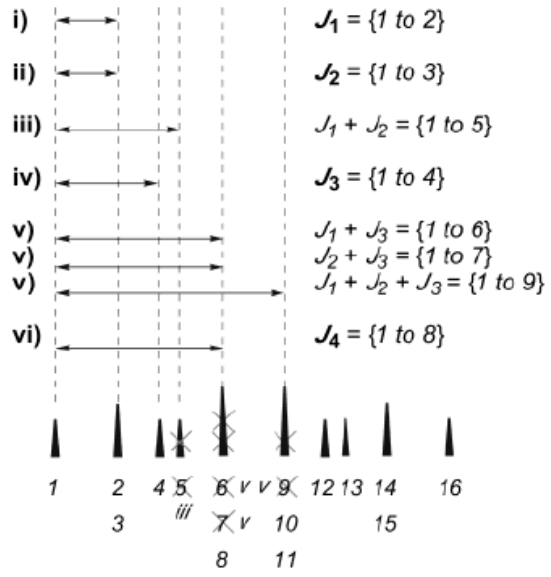
Chem 217 Section Handout: Hoye's Method

In this handout, thirteen multiplets are presented with their peak positions labeled in Hz. Try to use Hoye's Method to solve them. In the more complicated examples, you should consider using a computer program to assist you. The answers are given below. Except for problem 13, each example is taken from the Hoye papers; if you have trouble, you can consult the papers for assistance.

As a reminder, here is how the method works:

1. Consider every multiplet to be an *n*-th order doublet of doublets of… Assign each line a corresponding intensity.
2. The distance (in Hz) from 1-2 is J_1 and 1-3 is J_2.
3. Compute J_1+J_2. Add this value to the position of peak 1. Does this correspond to a line? If so, remove that component from consideration. Note: if that corresponds to a line, but the line is marked with more than one component, only remove one of the components from consideration. For example, if both 1-4 and 1-5 are J_1+J_2, only remove component 4.
4. 1 to the next highest component still being considered is J_3. Now compute J_1+J_3, J_2+J_3, and $J_1+J_2+J_3$ and remove those components from consideration as in step 3. Do not remove another instance of J_1+J_2. Continue this iterative process until all the coupling constants have been found.

Here is an example from the paper:



References:

(1) Hoye, T.R.; Zhao, H. *J. Org. Chem.* **2002**, *67*, 4014-4016.

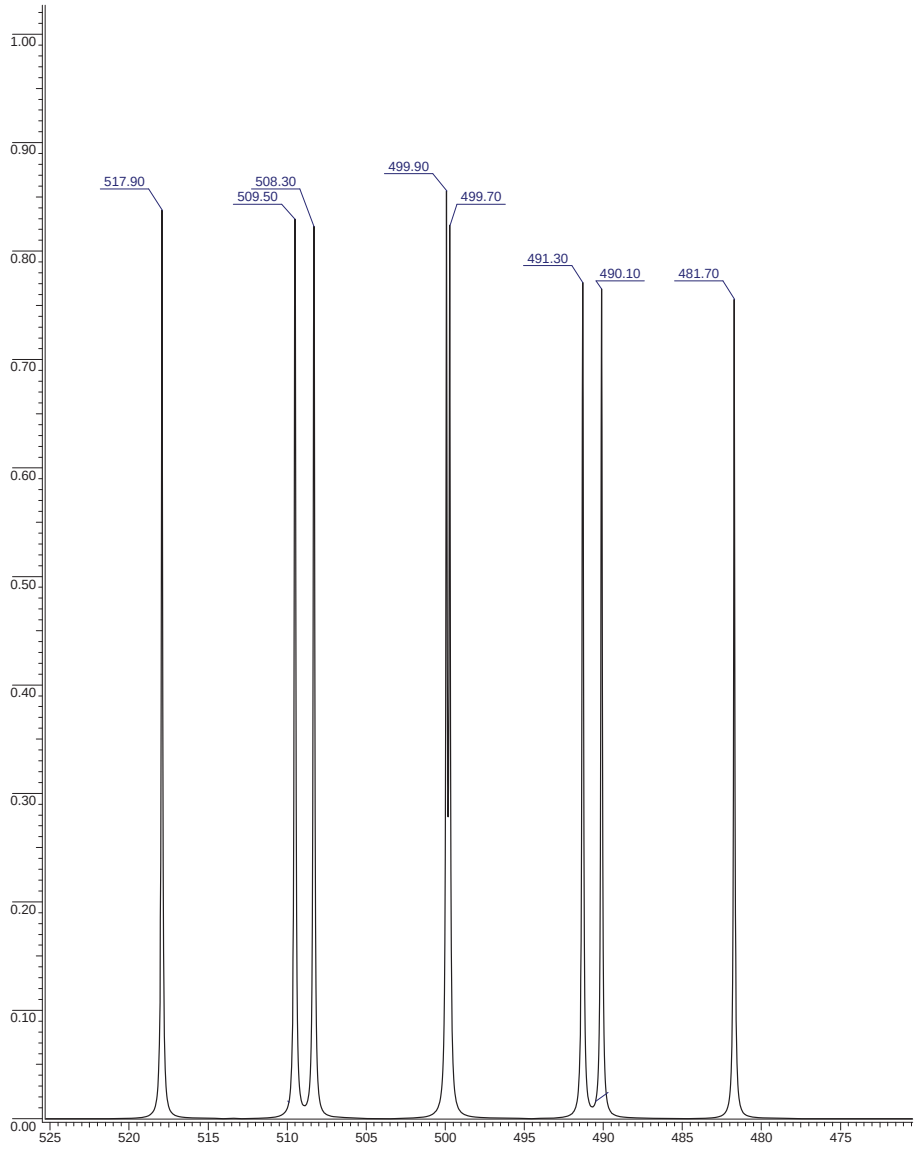
(2) Hoye, T.R.; Hanson, P.R.; Vyvyan, J.R. *J. Org. Chem.* **1994**, *59*, 4096-4103.

Answers:

1) 18.2, 9.6, 8.4
2) 16.6, 10.7, 5.9
3) 12.8, 11.0, 3.1
4) 8.7, 5.3, 1.4
5) 13.9, 4.3, 4.2, 4.0
6) 13, 6.5x3
7) 12, 3x2, 1
8) 6.2x2, 5.1x2
9) 14, 8.2, 7x2
10) 12.3, 9.4, 7.4, 3
11) 4, 7x3, 9.5x2
12) 2.5, 5.5, 7.5x3
13) 7x3, 10x2, 4x2

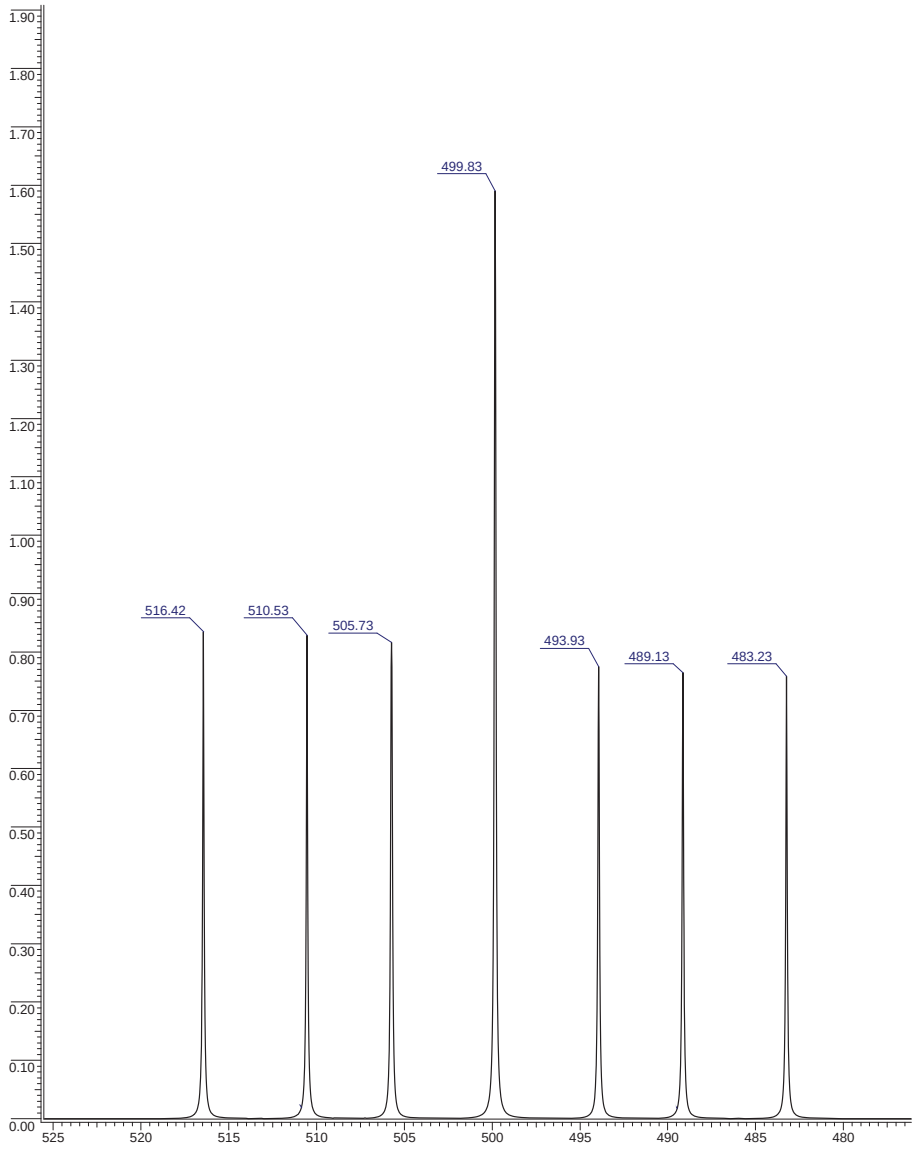
18/Feb/2009 04:36:13 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q01.HSP (modified on 18 FEB 2009)



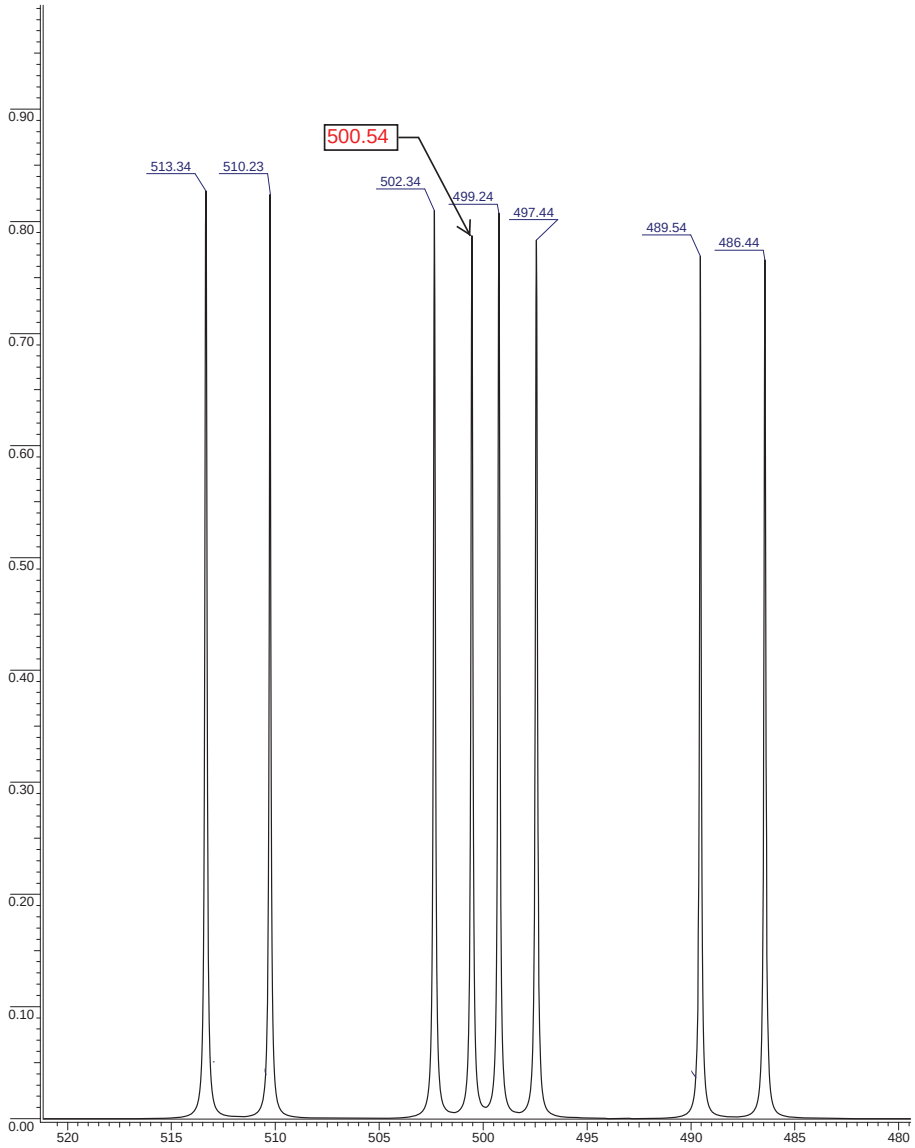
18/Feb/2009 04:35:09 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q02.HSP (modified on 18 FEB 2009)



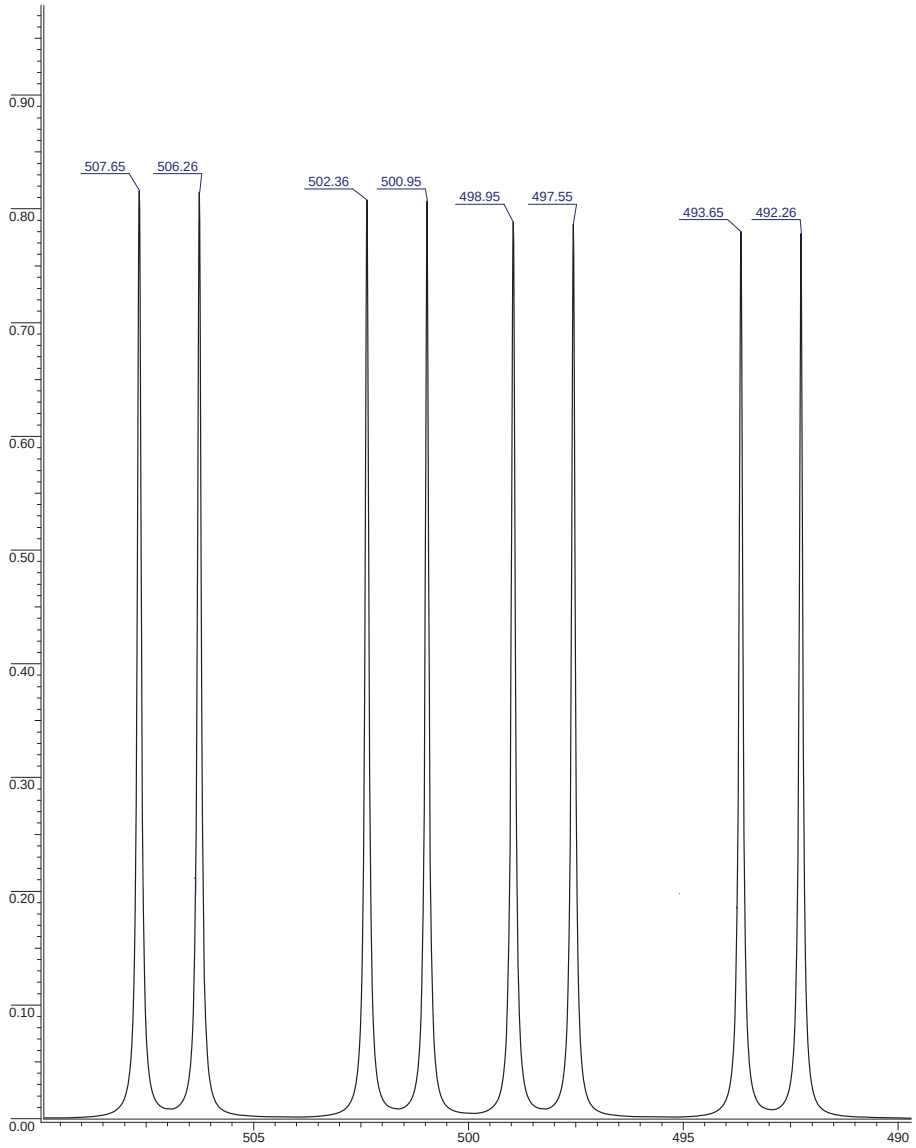
18/Feb/2009 04:37:04 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q03.HSP (modified on 18 FEB 2009)



18/Feb/2009 04:37:53 ACD/C+H NMR VIEWER (v.12.01)

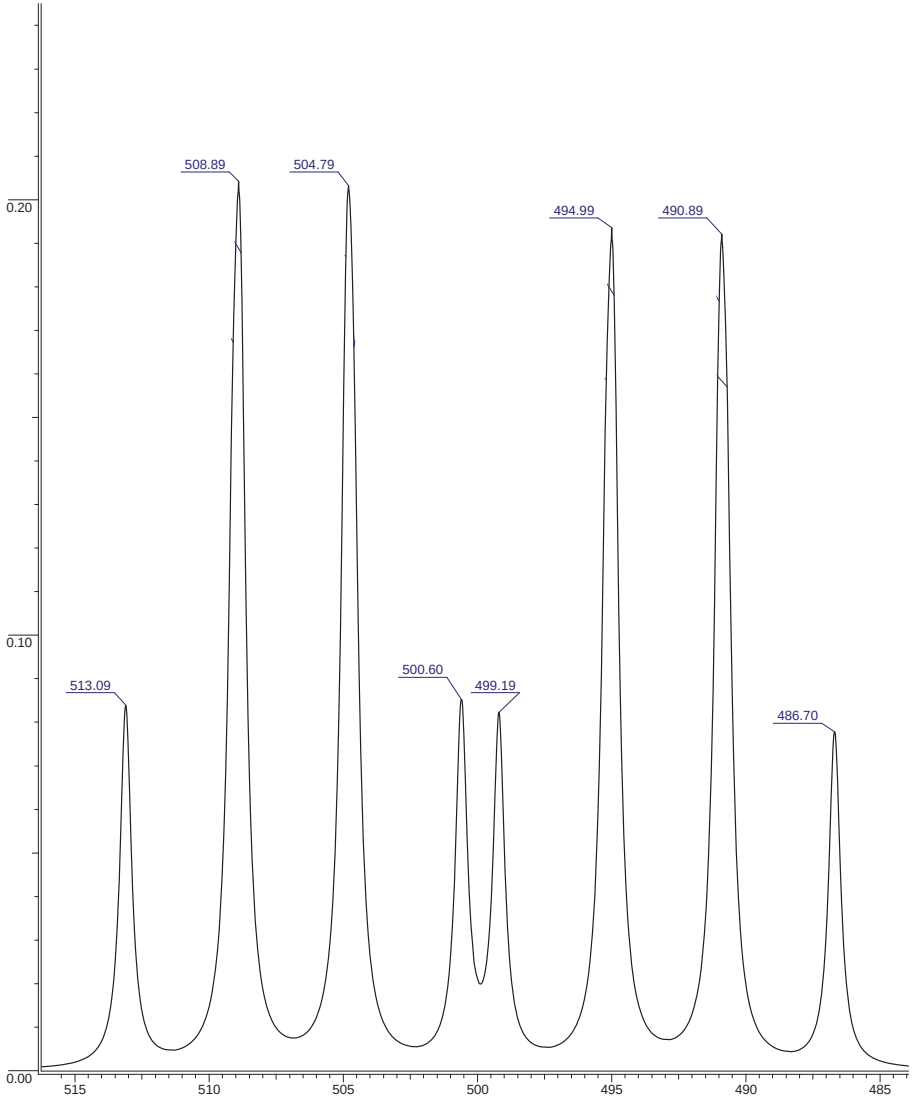
File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q04.HSP (modified on 18 FEB 2009)



18/Feb/2009 04:45:59 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q04.HSP (modified on 18 FEB 2009)

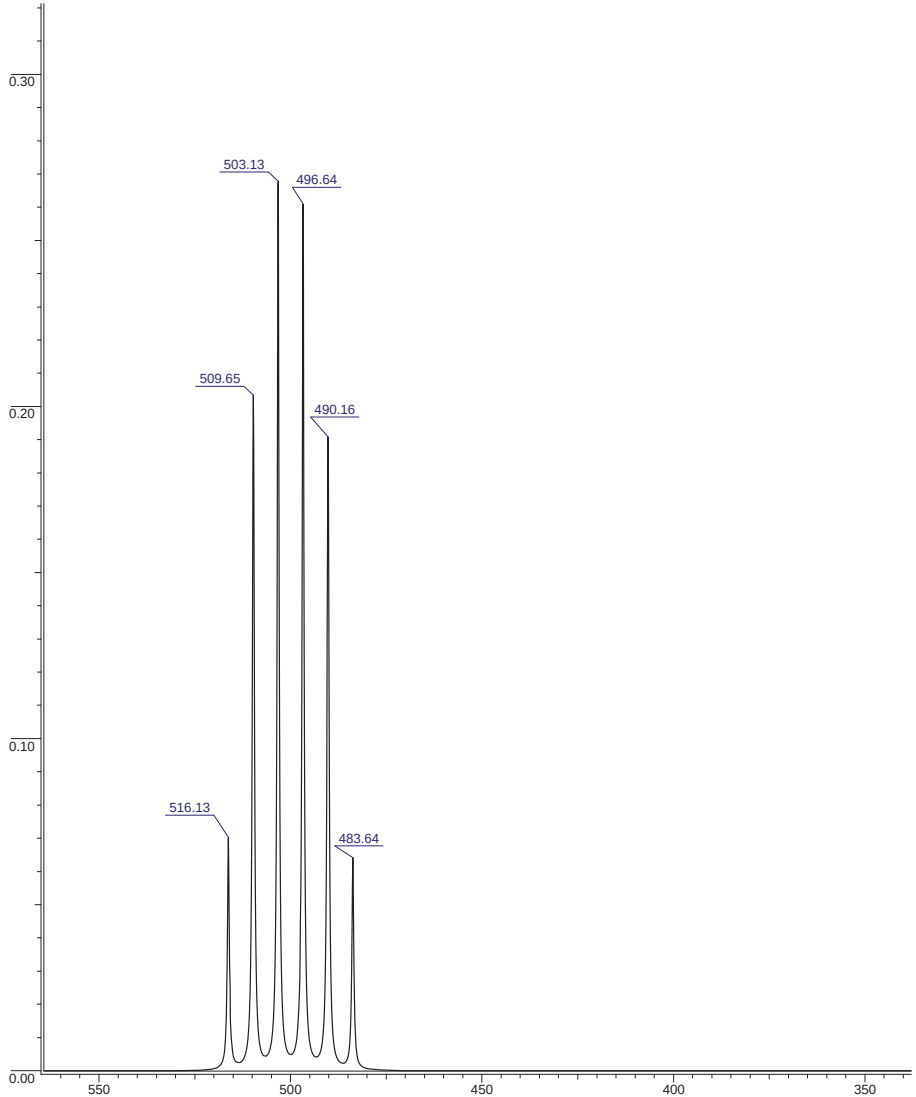
J	Grp.1	Grp.2	Value	Error



18/Feb/2009 04:50:11 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q06.HSP (modified on 18 FEB 2009)

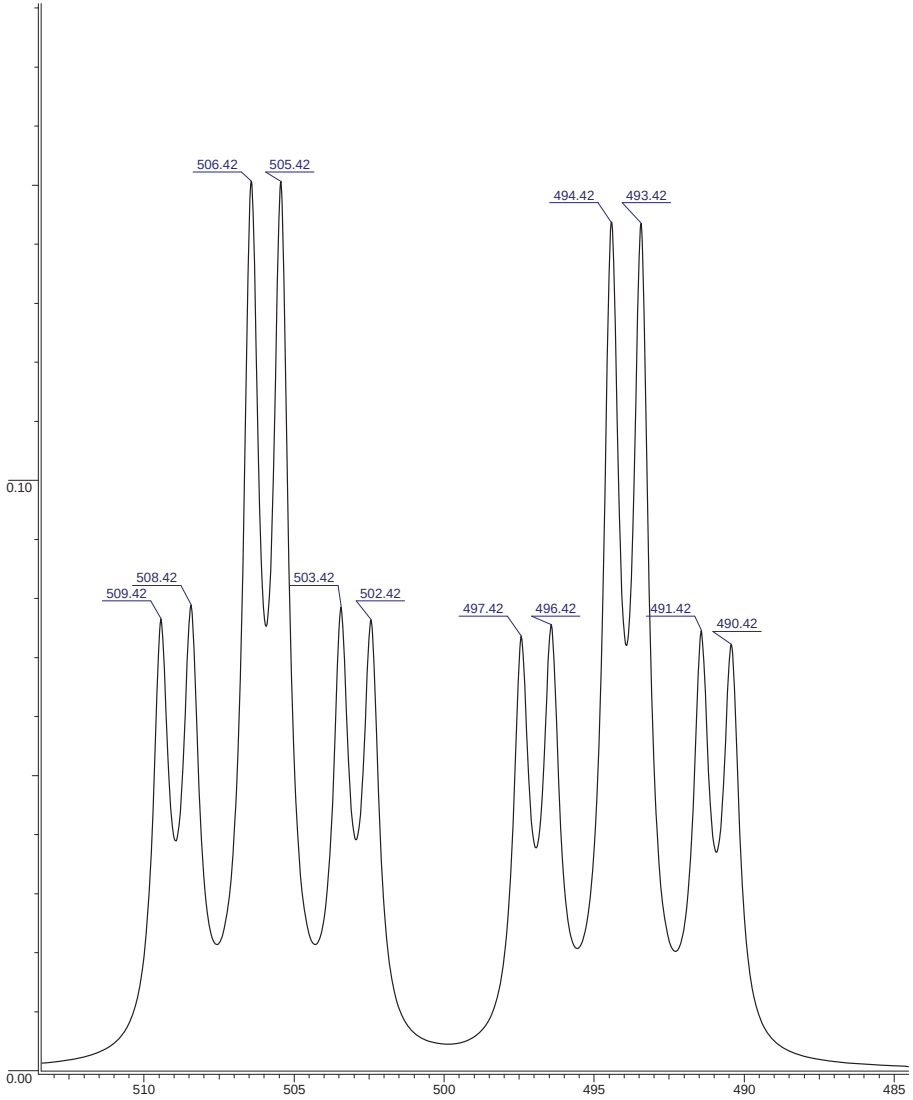
J	Grp.1	Grp.2	Value	Error



18/Feb/2009 04:48:23 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q07.HSP (modified on 18 FEB 2009)

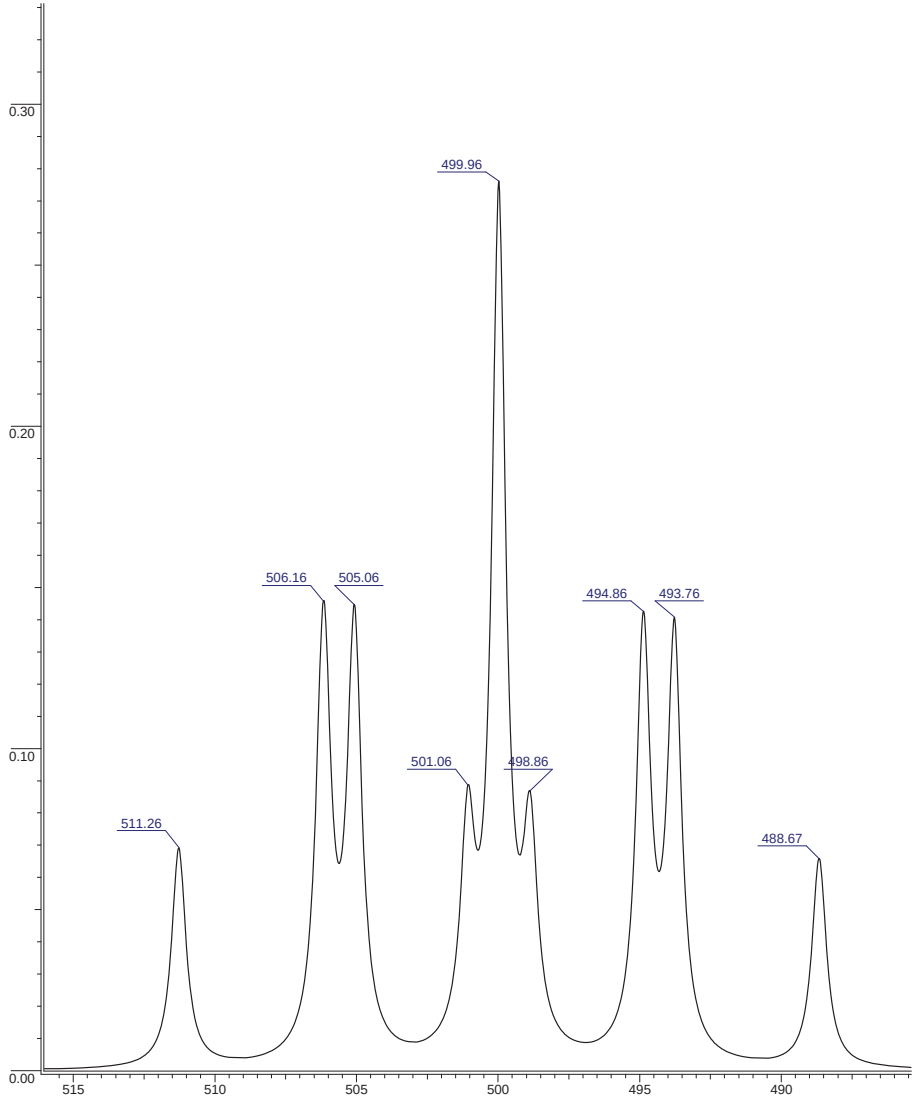
J	Grp.1	Grp.2	Value	Error



18/Feb/2009 04:51:34 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q08.HSP (modified on 18 FEB 2009)

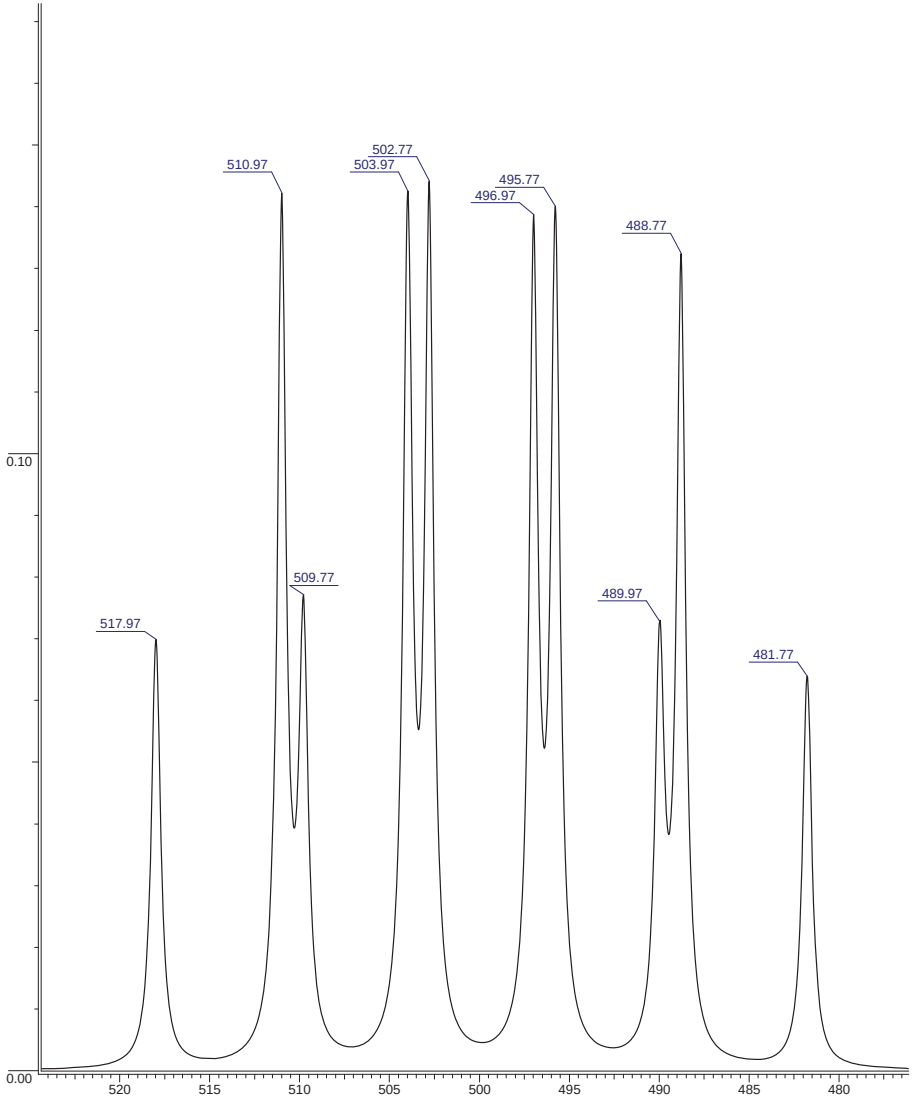
J	Grp.1	Grp.2	Value	Error



18/Feb/2009 04:52:09 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q08.HSP (modified on 18 FEB 2009)

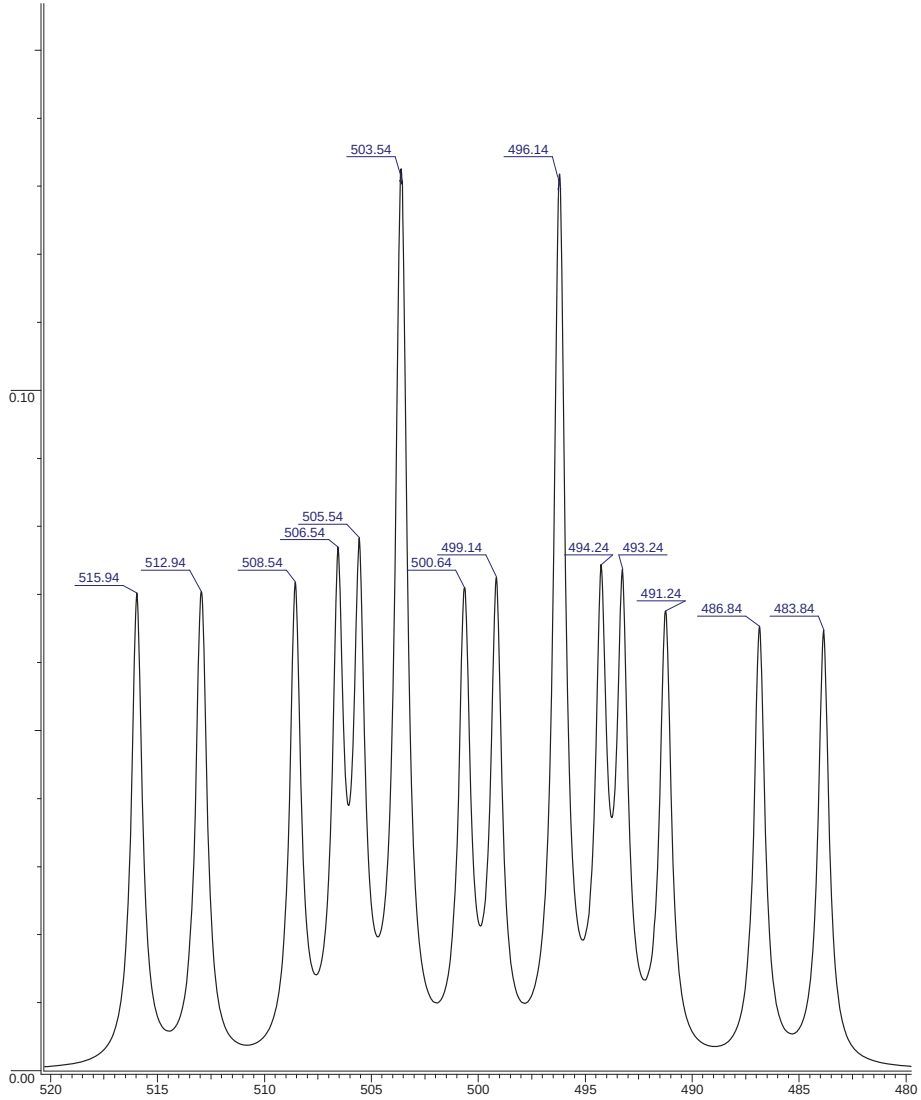
J	Grp.1	Grp.2	Value	Error



18/Feb/2009 04:53:12 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q10.HSP (modified on 18 FEB 2009)

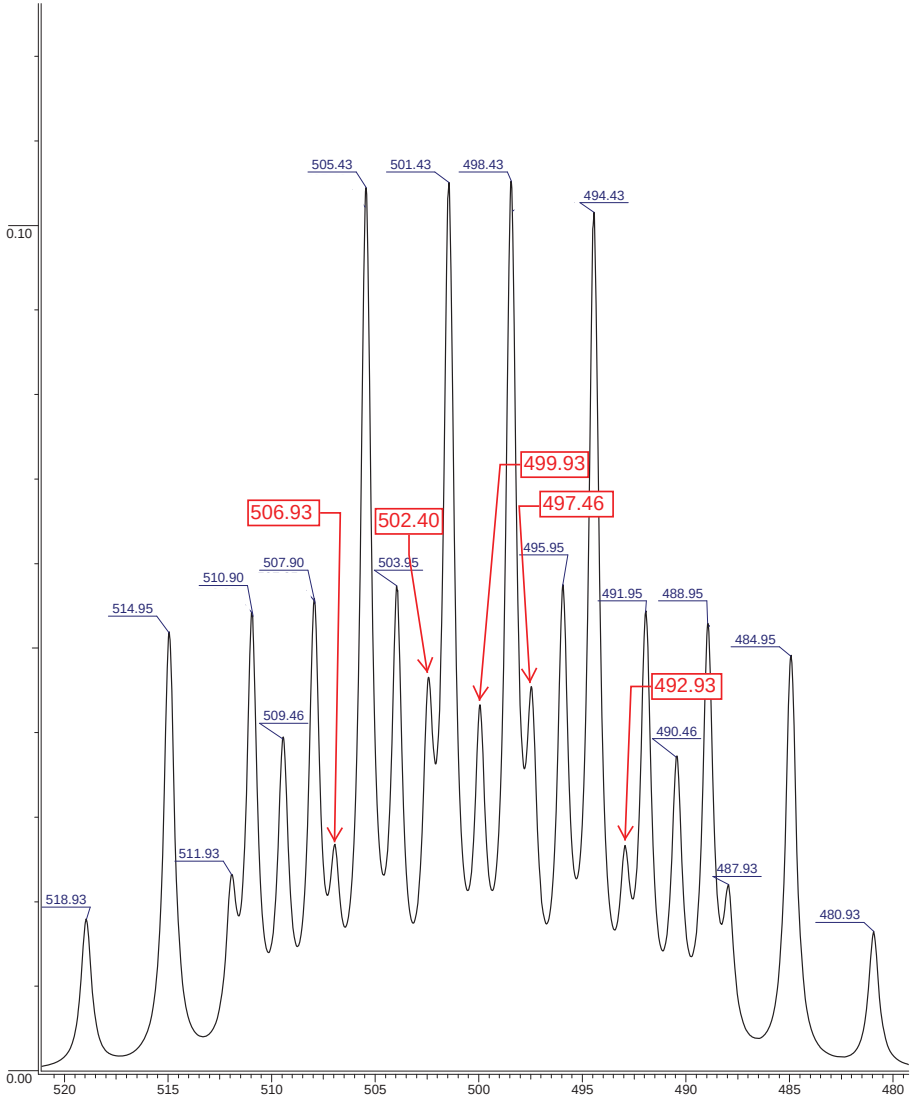
J	Grp.1	Grp.2	Value	Error



18/Feb/2009 04:55:27 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q11.HSP (modified on 18 FEB 2009)

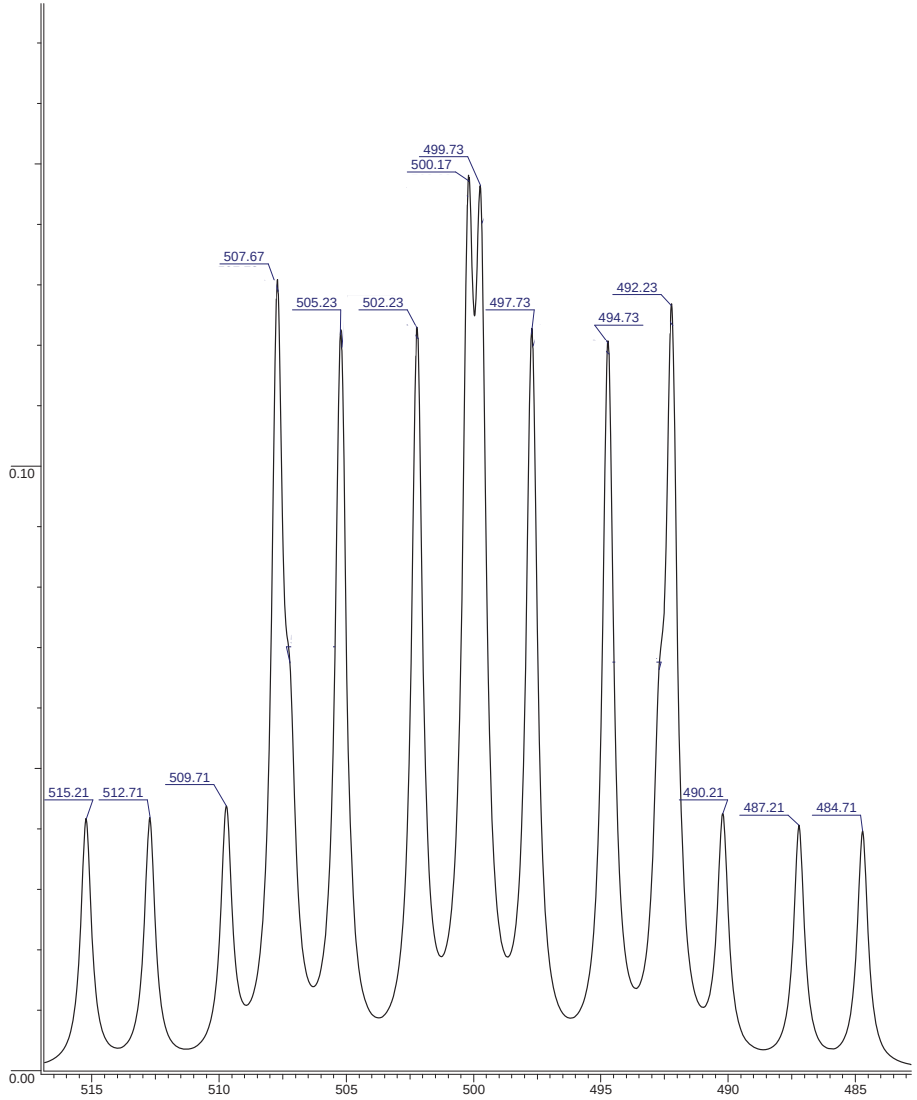
J	Grp.1	Grp.2	Value	Error



18/Feb/2009 04:57:21 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q12.HSP (modified on 18 FEB 2009)

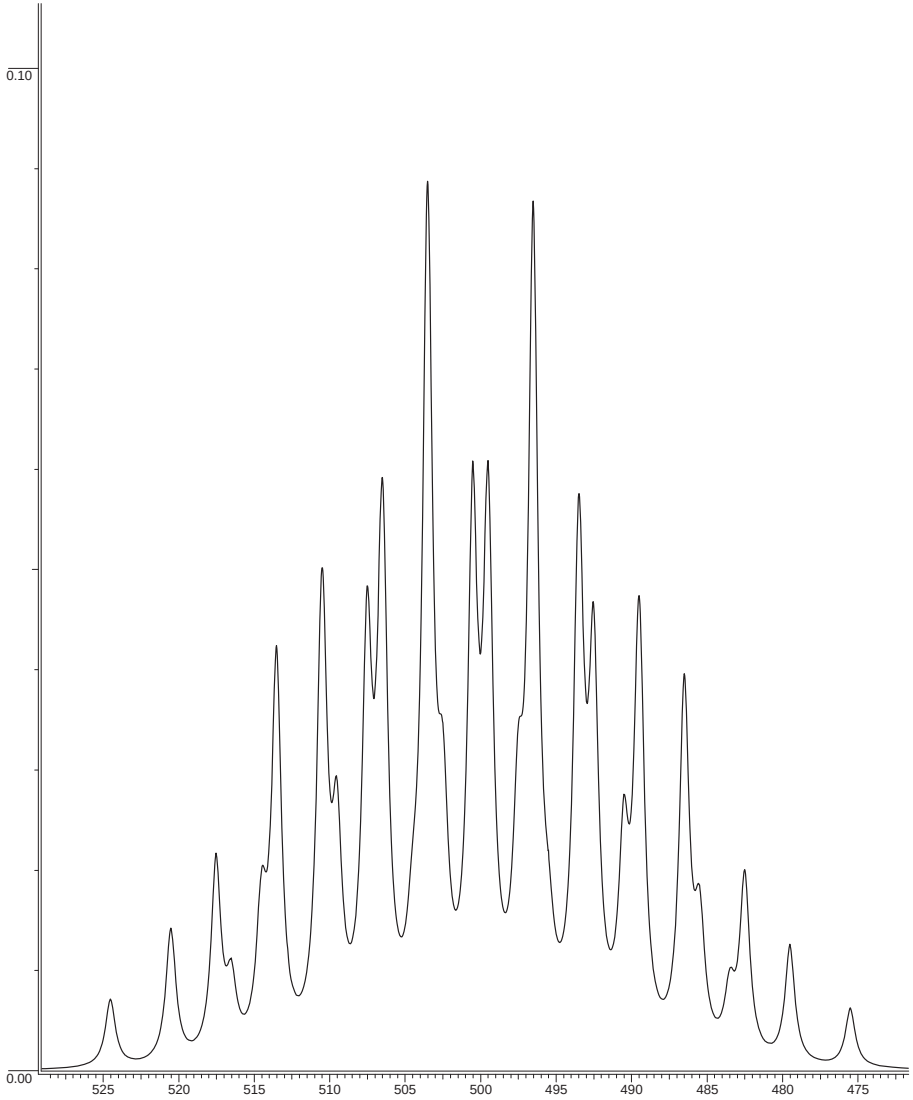
J	Grp.1	Grp.2	Value	Error



18/Feb/2009 05:28:39 ACD/C+H NMR VIEWER (v.12.01)

File Name C:\Users\Eugene Kwan\Desktop\Chem 217\coupling constants\q13.HSP (modified on 18 FEB 2009)

J	Grp.1	Grp.2	Value	Error



524.50
520.50
517.50
516.50
514.50
513.50
510.50
509.50
507.50
506.50
503.50
502.50
500.50
499.50
497.50
496.50
493.50
492.50
490.50
489.50
486.50
485.50
483.50
482.50
479.50
475.50