Multiple spins systems

AX system

Calculate the coupling constant $^1J(^{31}P^{77}Se)$ to one decimal place, the chemical shift in Hz of phosphorus in molecules containing ^{77}Se, and this shift in ppm, to two decimal places.

1(a) $^1J(^{31}P^{77}Se)$ = 760.6 Hz
1(b) $\nu_P(^{77}Se)$ = 4415.6 Hz
1(c) $\nu_P(^{77}Se)$ = 36.34 ppm

AB system

Question: The four lines of the ^{31}P AB spectrum shown above are at

18906.223, 18679.424, 18280.477, 18053.680 Hz.

1. Calculate ν_A, ν_B and J_{AB} in Hz, all to one decimal place.

J_{AB} = 226.8 Hz; ν_M = 18479.95 Hz (152.1 ppm); δ_{AB} = 583.20 Hz (4.80 ppm)

$\nu_A = \nu_M - \delta_{AB}/2$ = 18188.35 Hz (149.70 ppm)

$\nu_B = \nu_M + \delta_{AB}/2$ = 18771.55 Hz (154.50 ppm)

ABX system

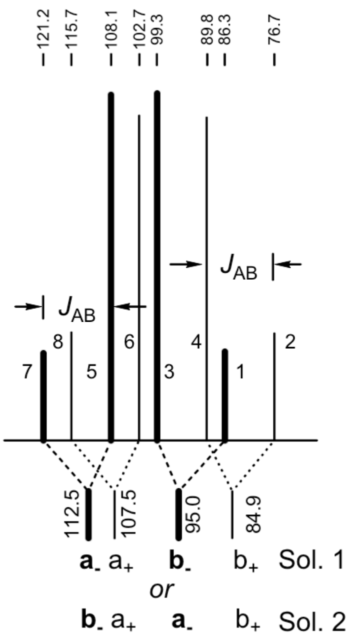
Chemical shift of the AB systems

121.2 ; 115.7 ; **108.1** ; 102.7 ; **99.3** ; 89.8 ; **86.3** ; 76.7

An ABX system will consists in two superimposed AB sub-spectra, with the same J_{AB}

All you need to do is to find the two AB sub-spectra + and –

1. Find the value of $^2J_{AB}$ = **13.1 Hz**
2. Solve the AB system for each quartet.



$c_- = (5+3)/2 = 103.7$

$\Delta\nu_{ab-} = \delta_- = \sqrt{(7-1)(5-3)} = 17.5$

$c_- \pm \delta_-/2 = 103.7 \pm 8.76 = 112.5, 94.9$

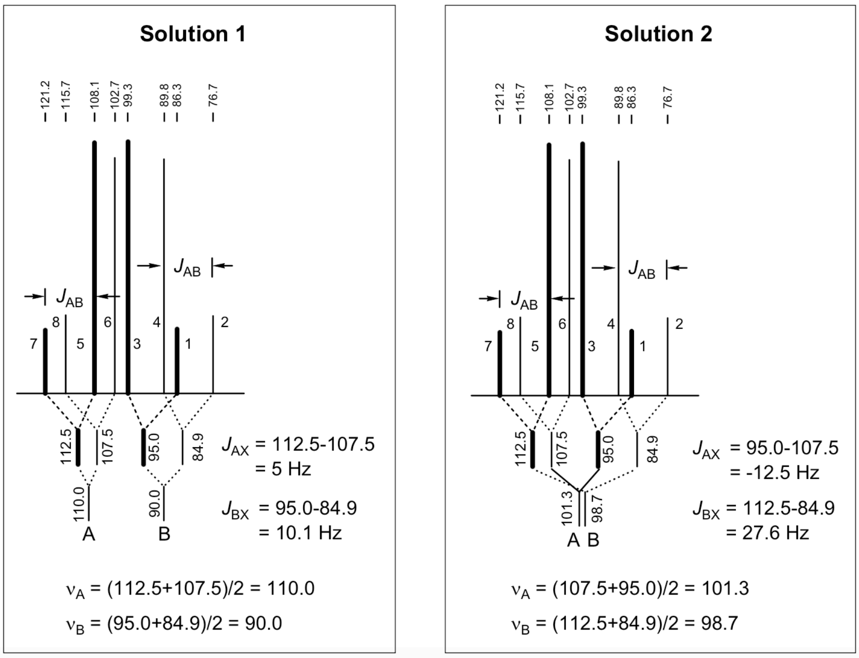
$c_+ = (6+4)/2 = 96.25$

$\Delta\nu_{ab+} = \delta_+ = \sqrt{(8-2)(6-4)} = 22.43$

$c_+ \pm \delta_+/2 = 96.25 \pm 11.21 = 107.5, 85.0$

At this stage, we know one of the bold lines is **a**, and the other **b**, but *we do not know which is which.* Similarly for the thin lines.

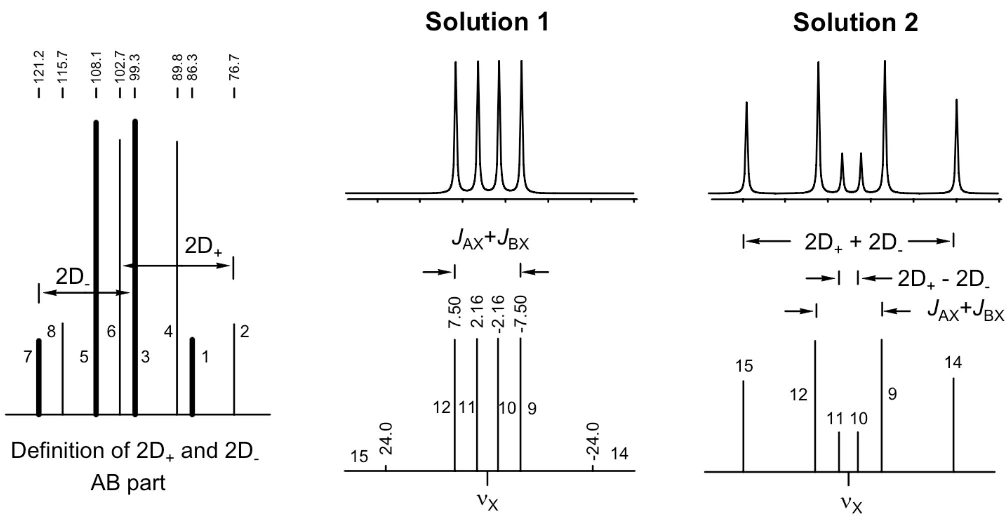
3. Compare the two solution you have found.



4. Cite some arguments to choose between both. **See Lecture slide 8-13**

5. The two lines having small intensity are combination lines and decrease in intensity as ν_A-ν_B increases. Their intensity is $\sin^2(\phi+-\phi-)$ for an intensity of 1 for the external lines of the X system.

   a. ϕ+ and ϕ- can be calculated from the formula $\sin^2\phi = J/2C$ (see slide #54) **In the solution below D = C**



   b. Give the calculated intensity of the two combinations lines considering the two solutions obtained before and conclude.

Solution 1

$\Phi_{1+} = 0.5\arcsin(J_{AB}/2D_+)$

$= 0.5\arcsin(13.0/26.0) = 15.0$

$\Phi_{1-} = 0.5\arcsin(J_{AB}/2D_-)$

$= 0.5\arcsin(13.0/21.9) = 18.2$

$i_{10} = i_{11} = \cos^2(\Phi_{1+} - \Phi_{1-})$

$= \cos^2(15.0 - 18.2) = 0.997$

$i_{14} = i_{15} = \sin^2(\Phi_{1+} - \Phi_{1-})$

$= \sin^2(15.0 - 18.2) = 0.003$

Solution 2

$\Phi_{2+} = \Phi_{1+}$

$= 15.0$

$\Phi_{2-} = 90 - \Phi_{1-}$

$= 90 - 18.2 = 71.8$

$i_{10} = i_{11} = \cos^2(\Phi_{2+} - \Phi_{2-})$

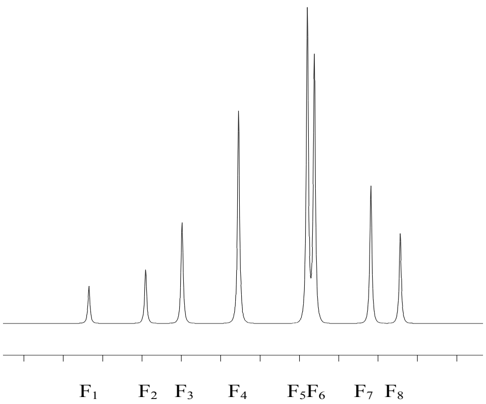
$= \cos^2(15.0 - 71.8) = 0.30$

$i_{14} = i_{15} = \sin^2(\Phi_{2+} - \Phi_{2-})$

$= \sin^2(15.0 - 71.8) = 0.70$

$\arcsin = \sin^{-1}$

AB_2 system



Frequency	*Intensity*
218.614	0.368
146.692	0.531
100.000	1.000
28.078	2.106
−59.464	3.101
−68.614	2.632
−140.536	1.363
−178.078	0.894

1. ν_A = 100.00 Hz
2. ν_B = 100 Hz and J_{AB} = 100 Hz

AA′XX′ system

In strict AA'XX' systems spectra are given by pairs of different species:

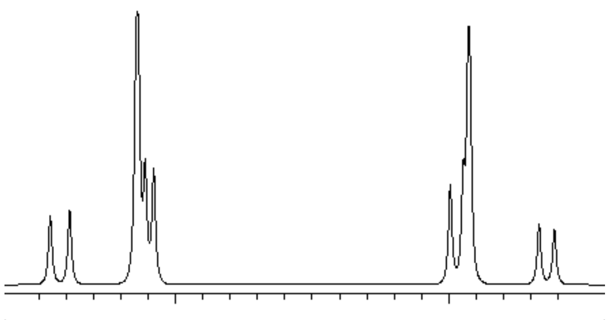
For these systems we define

$|K| = |J_{AA'} + J_{XX'}|$ "*J*" of one ab quartet

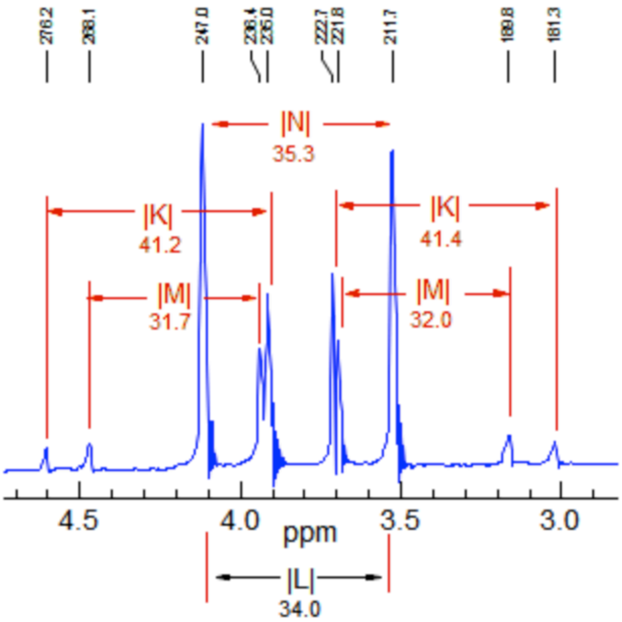
$|L| = |J_{AX} - J_{AX'}|$ "δ" of both ab quartet

$|M| = |J_{AA'} - J_{XX'}|$ "*J*" of other ab quartet

$|N| = |J_{AX} + J_{AX'}|$ "*J*" of doublet



For the molecule 7, the ^{19}F spectrum shows 10 lines with the following chemical shifts in Hz at:
276.2 ; 268.1 ; 247.0 ; 236.4 ; 235.0 ; 222.7 ; 221.8 ; 211.7 ; 189.8 ; 181.3.



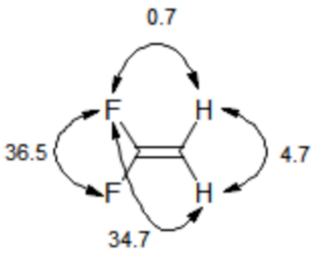
$|K| = |J_{AA'} + J_{XX'}|$ "J" of one ab quartet

$|L| = |J_{AX} - J_{AX'}|$ "δ" of both ab quartets

$|M| = |J_{AA'} - J_{XX'}|$ "J" of other ab quartet

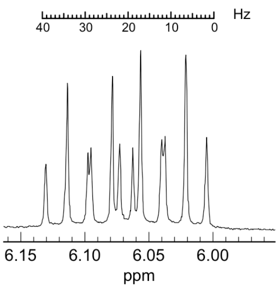
$|N| = |J_{AX} + J_{AX'}|$ "doublet"

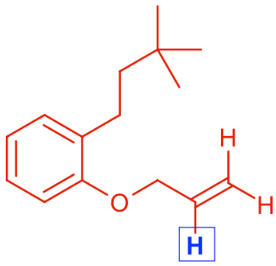
If we make the reasonable assumption that $J_{FF} > J_{HH}$ and J_{HF} (trans) > J_{HF} (cis) we get the following values:



1. Determine N = 35.3 Hz
2. Measure K (41.2 and 41.4 Hz) and M (31.7 Hz and 32.0 Hz).
3. Calculate L from the formulae given in equation 7 For K L = 33.8 Hz and for L = 34.2 Hz.
4. Calculate $J_{AA'}$ and $J_{XX'}$ by summing and subtracting K and M.
   $J_{AA'}$ = (K+M)/2 = 36.5 Hz; $J_{XX'}$ = (K-M)/2 = 4.7 Hz

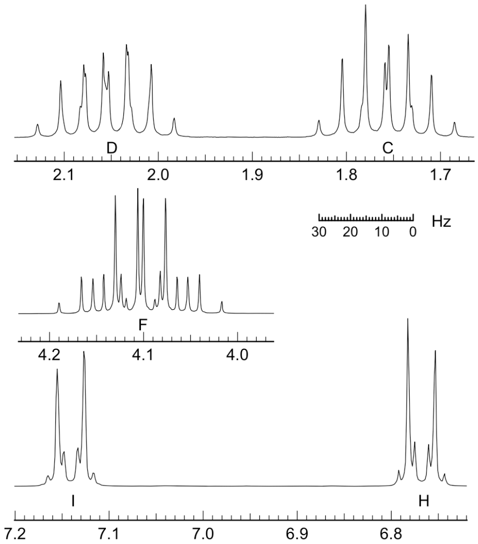
6. Calculate J_{AX} and $J_{AX'}$ by summing and subtracting L and N.
   J_{AX} = (N+L)/2 = 34.7 Hz; $J_{AX'}$ = (N-L)/2 = 0.7 Hz

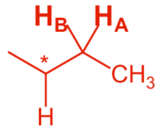




ddt, 17, 11, 5

Problem Set - NMR IV - corrections

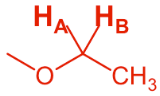




$\underline{AB}M_3Y$

δ 2.05, d quintets, J = 13.4, 7.5

δ 1.75, d quintets, J = 13.5, 7.5



$\underline{AB}X_3$

δ 4.13, dq, J = 11, 7

δ 4.08, dq, J = 11, 7

R_1, R_2 must be electron donating

AA'XX' (or AA'BB')