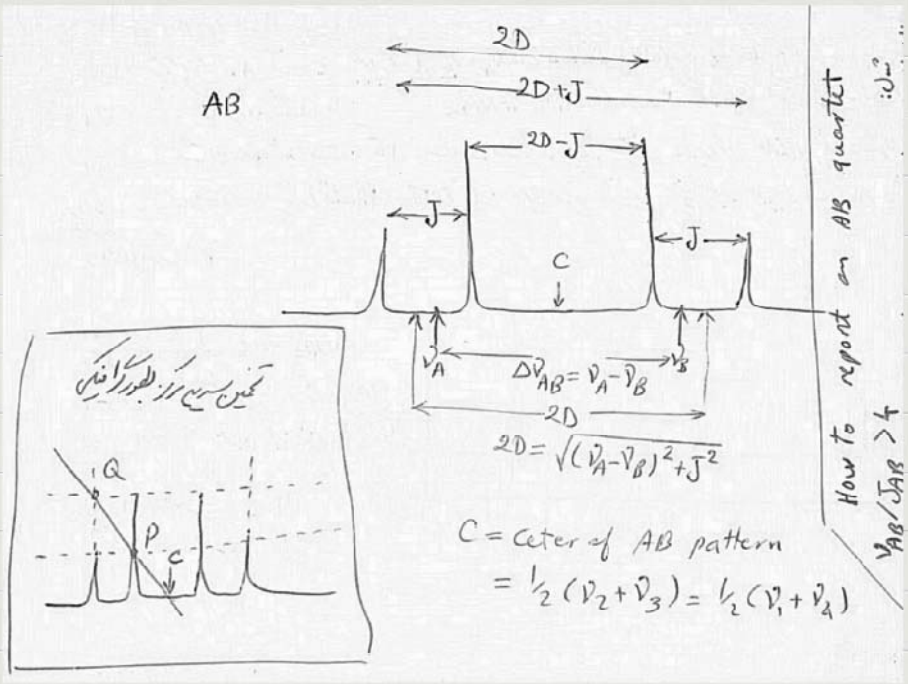


How to report an AB quartet

$\nu_{AB}/J_{AB} > 4$:مثال

3.68 (d, 1H, J = 10.3 Hz), 3.79 (d, 1H, J = 10.3 Hz)

$\nu_{AB}/J_{AB} < 4$

2.66 (ABq, 2H, $\Delta\delta_{AB}=0.05$, $J_{AB}=12.2$ Hz)

Center

2.63, 2.69 (ABq, 2H, $J_{AB}=12.2$ Hz) :روش

1 → Determine the four line positions in Hz and measure J_{AB}

$|J_{AB}| = (\nu_1 - \nu_2) = (\nu_3 - \nu_4) = 10\ Hz$

2 → calculate the center position (in Hz)

$\nu_{center} = \frac{1}{2}(\nu_2 + \nu_3) = 2024.1$

3 → calculate $\Delta\nu_{AB}$

$\Delta\nu_{AB} = \sqrt{(\nu_1 - \nu_4)(\nu_2 - \nu_3)} = 9.94\ Hz$

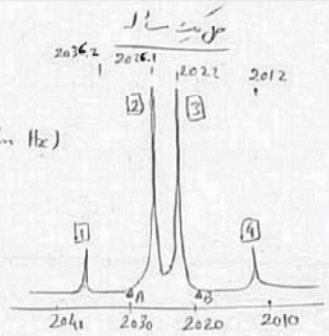
4 → calculate ν_A and ν_B (spectrometer frequency = 300 MHz)

$\nu_A = \nu_{center} + \frac{1}{2}\Delta\nu_{AB} = 2029.1\ Hz$

$\nu_B = \nu_{center} - \frac{1}{2}\Delta\nu_{AB} = 2019.1\ Hz$

$\delta_A = \nu_A / MHz = 6.76$

$\delta_B = \nu_B / MHz = 6.73$



Three-Spin Systems

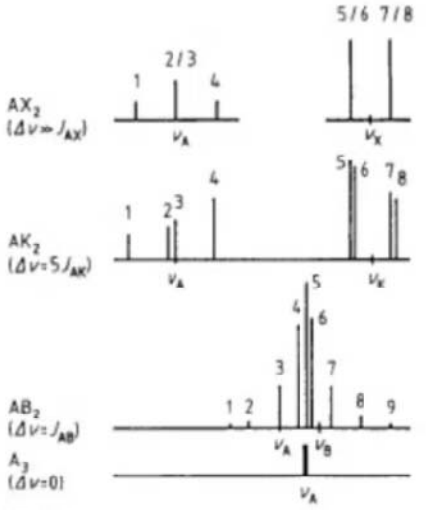
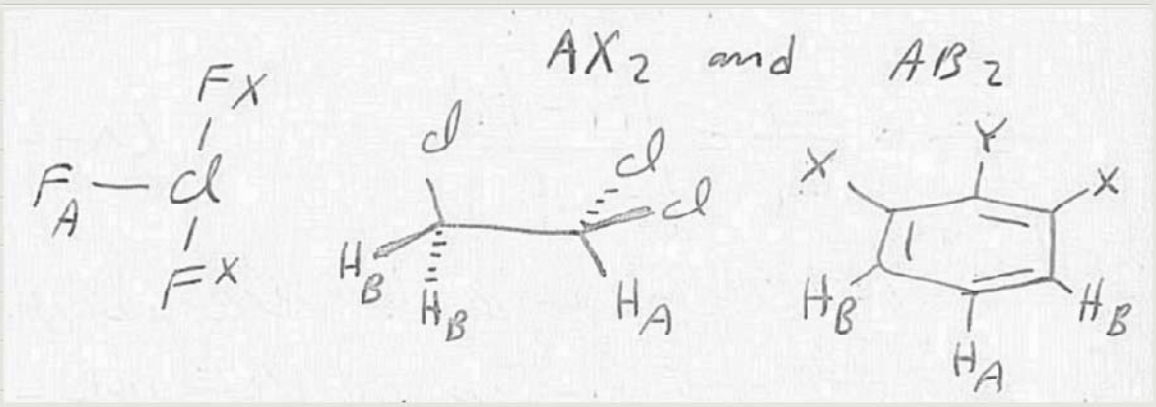


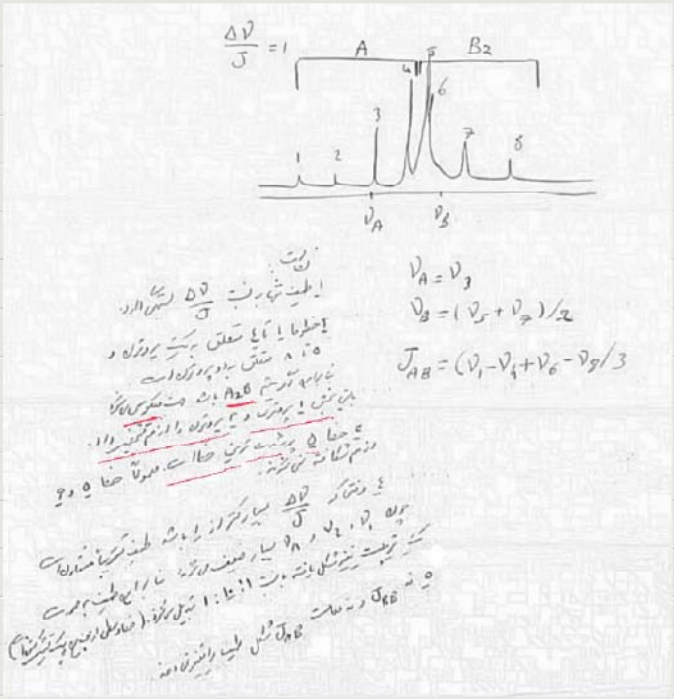
Figure 4-7.
Stick spectra for three-spin systems of the AX_2, AK_2, AB_2 and A_3 types; $J_{AX} = J_{AK} = J_{AB}$. The AK_2 spectrum was calculated with $\Delta\nu = 5\ J_{AK}$ and the AB_2 spectrum with $\Delta\nu = J_{AB}$.

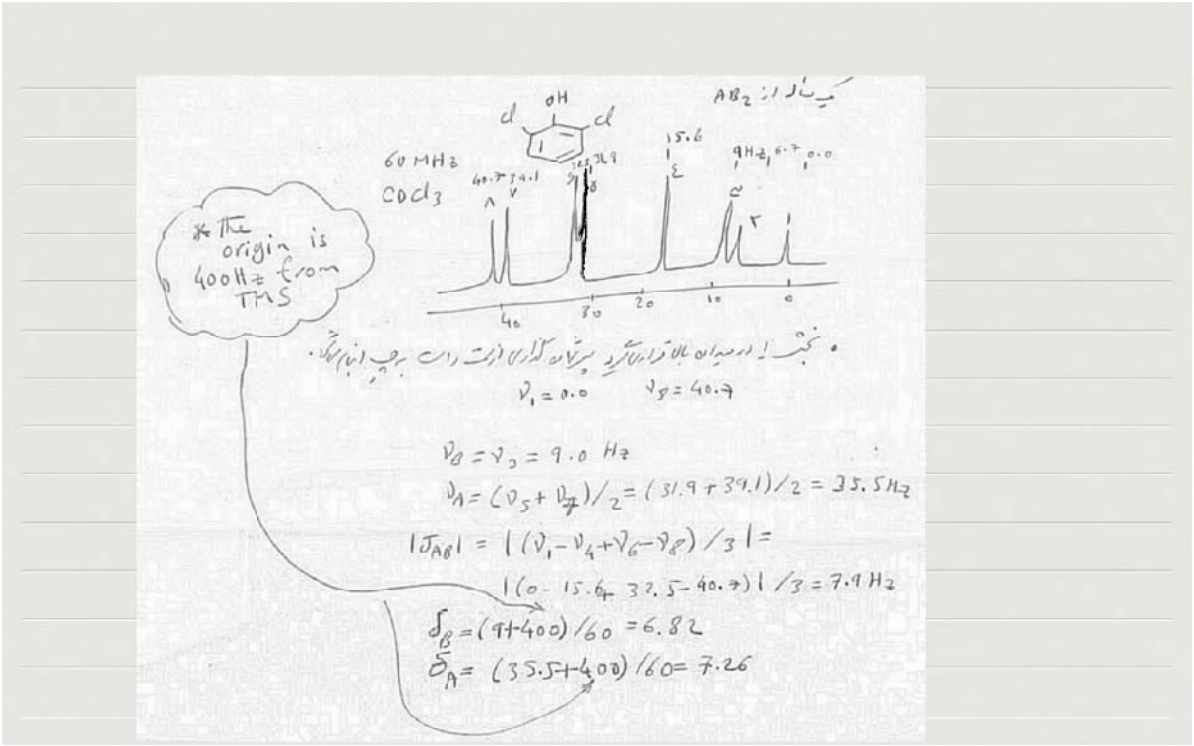
AB_2

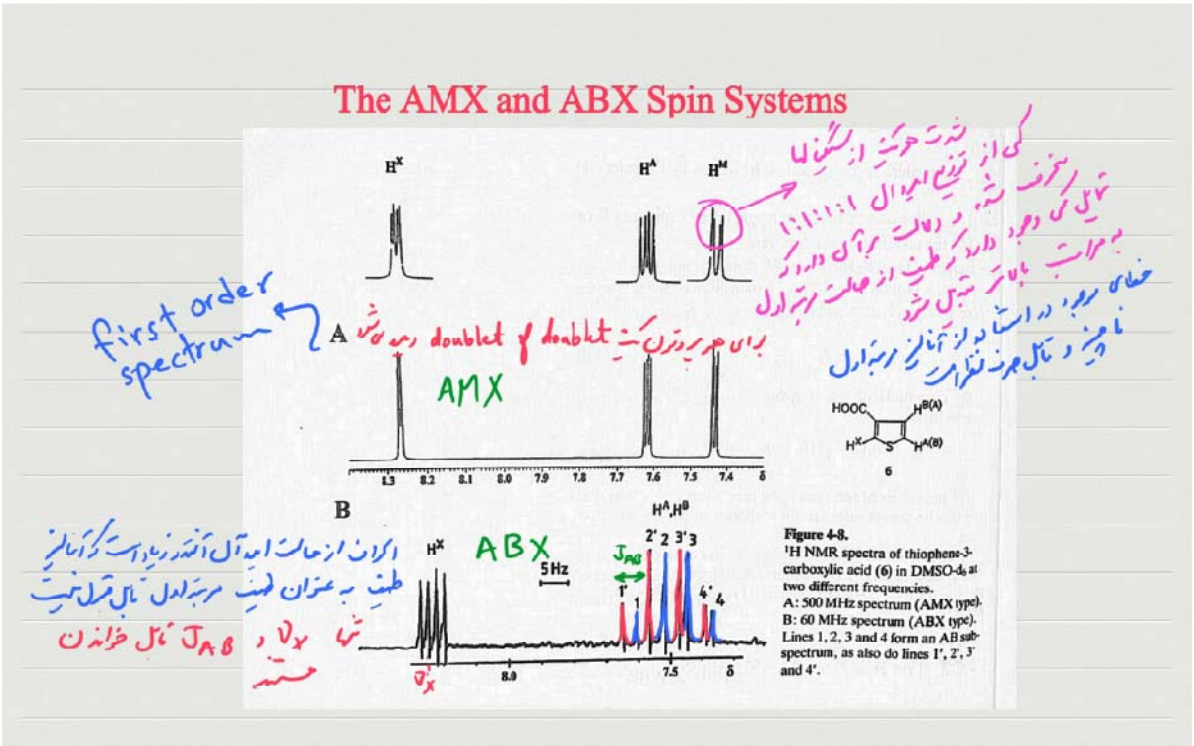
$\nu_A = f_3 \quad \nu_B = \frac{f_5 + f_7}{2}$

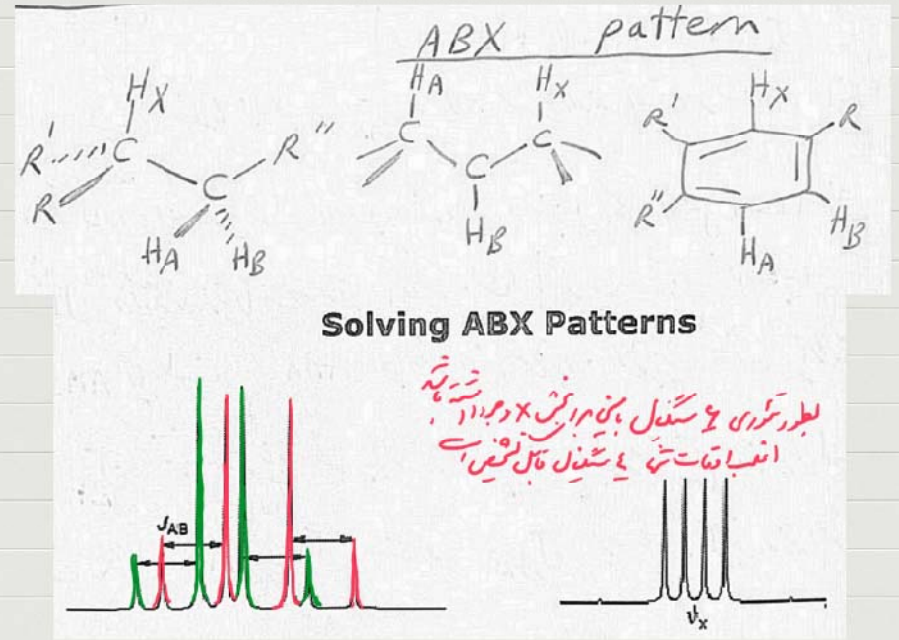
$|J_{AB}| = \frac{1}{3}\left|(f_1 - f_4 + f_6 - f_8)\right|$


AX2 and AB2
FX
F
A
Cl
FX
Cl
Cl
Cl
H
B
H
B
H
A
Y
X
X
H
B
H
B
H
A


Δν/J = 1
A
B2
1
2
3
4
5
6
7
8
νA
νB
νA = ν3
νB = (ν5 + ν7)/2
JAB = (ν1 − ν4 + ν6 − ν8)/3


60 MHz
$CDCl_3$
* The origin is 400Hz from TMS
$\nu_1 = 0.0$ $\nu_8 = 40.7$
$\nu_B = \nu_3 = 9.0$ Hz
$\nu_A = (\nu_5 + \nu_7)/2 = (31.9 + 39.1)/2 = 35.5$ Hz
$|J_{AB}| = |(\nu_1 - \nu_4 + \nu_6 - \nu_8)/3| =$
$|(0 - 15.6 + 32.5 - 40.7)|/3 = 7.9$ Hz
$\delta_B = (91 + 400)/60 = 6.82$
$\delta_A = (35.5 + 400)/60 = 7.26$


The AMX and ABX Spin Systems
first order spectrum
A
AMX
doublet of doublet
B
ABX
5Hz
HOOC
6
Figure 4-8.
^{1}H NMR spectra of thiophene-3-carboxylic acid (6) in DMSO-d_6 at two different frequencies.
A: 500 MHz spectrum (AMX type).
B: 60 MHz spectrum (ABX type).
Lines 1, 2, 3 and 4 form an AB subspectrum, as also do lines 1', 2', 3' and 4'.



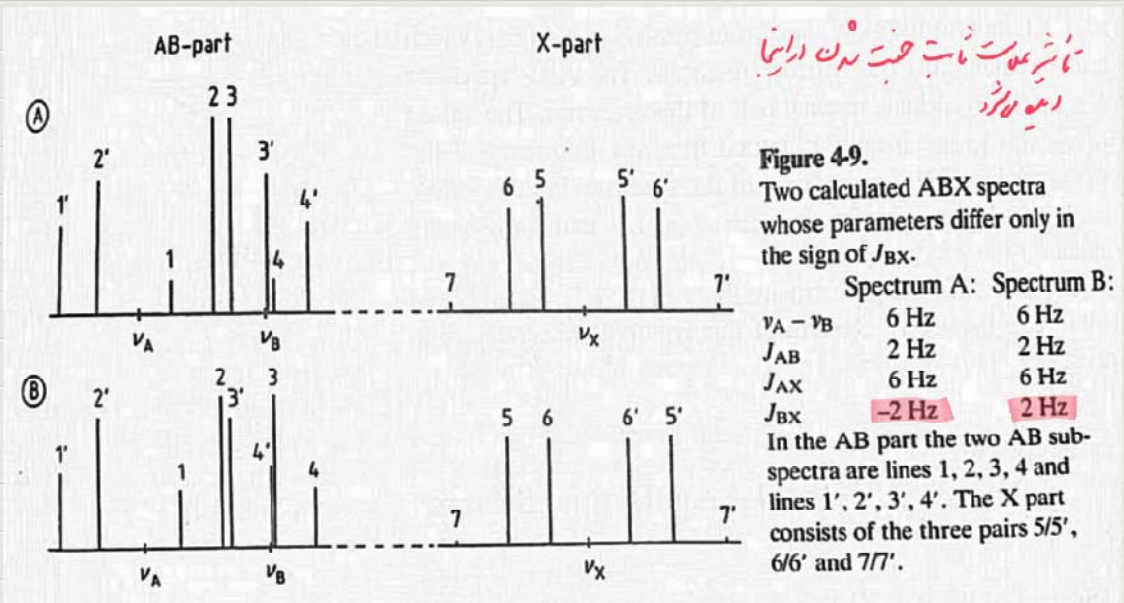
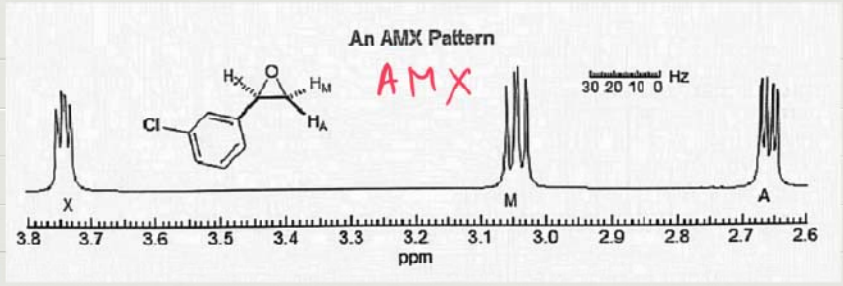


Figure 4-9.
Two calculated ABX spectra whose parameters differ only in the sign of J_{BX}.

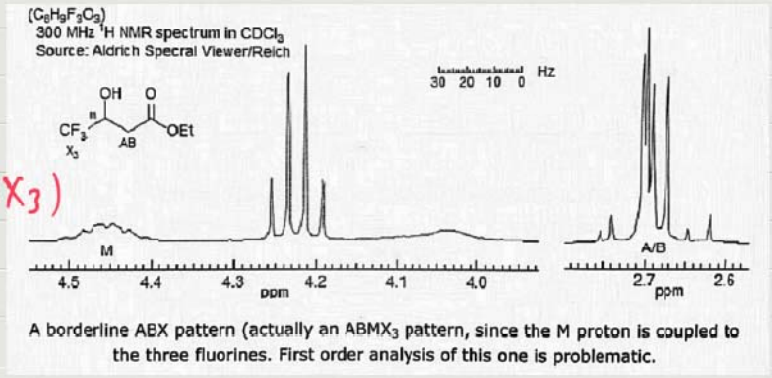
	Spectrum A:	Spectrum B:
$\nu_A - \nu_B$	6 Hz	6 Hz
J_{AB}	2 Hz	2 Hz
J_{AX}	6 Hz	6 Hz
J_{BX}	−2 Hz	2 Hz

In the AB part the two AB subspectra are lines 1, 2, 3, 4 and lines 1′, 2′, 3′, 4′. The X part consists of the three pairs 5/5′, 6/6′ and 7/7′.

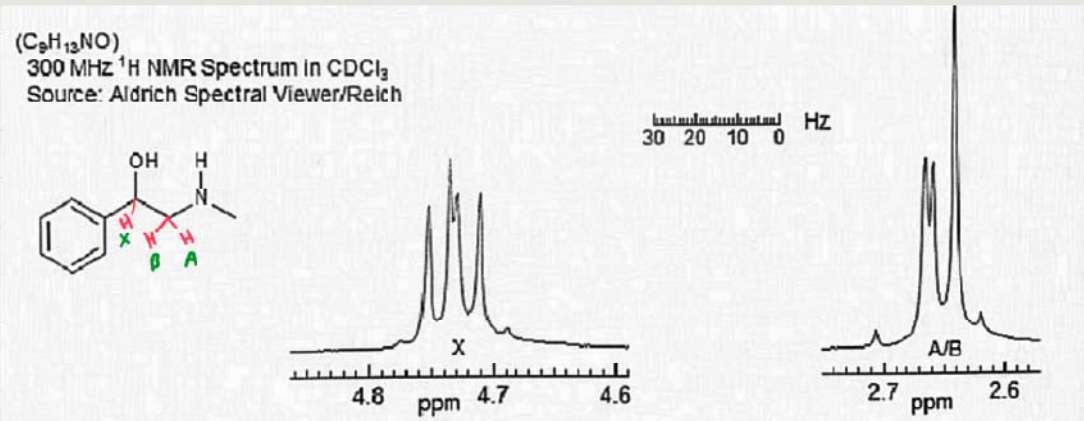


ABX

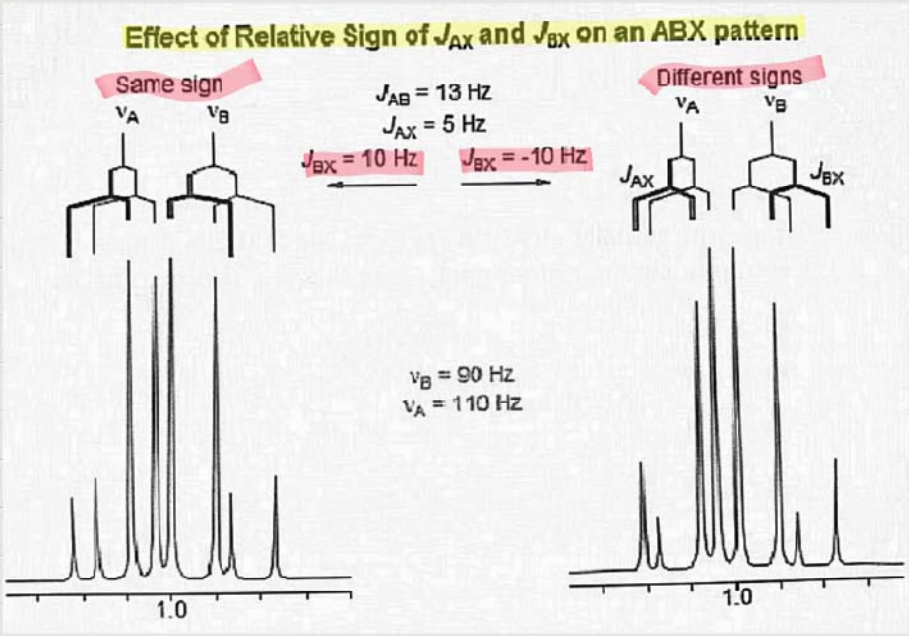
(ABMX$_3$)

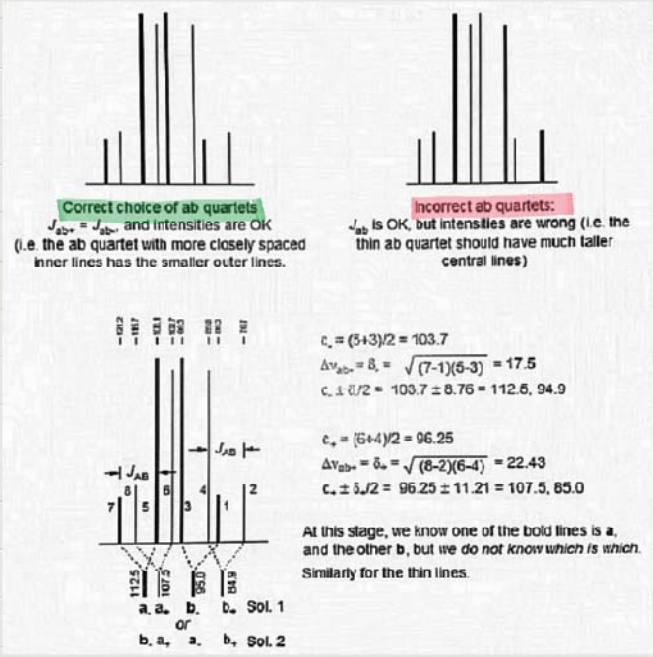


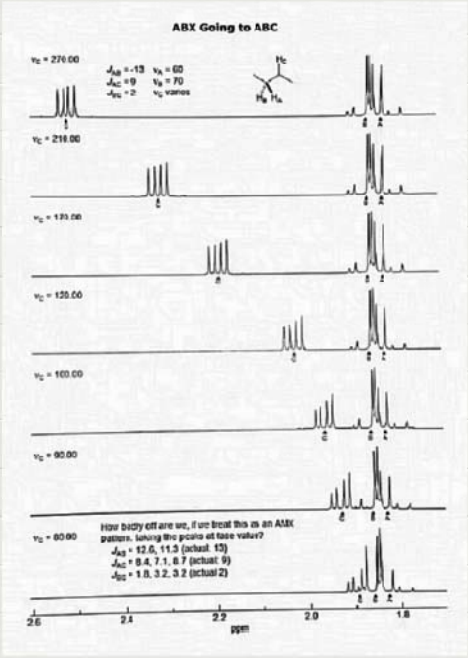
A borderline ABX pattern (actually an ABMX$_3$ pattern, since the M proton is coupled to the three fluorines. First order analysis of this one is problematic.

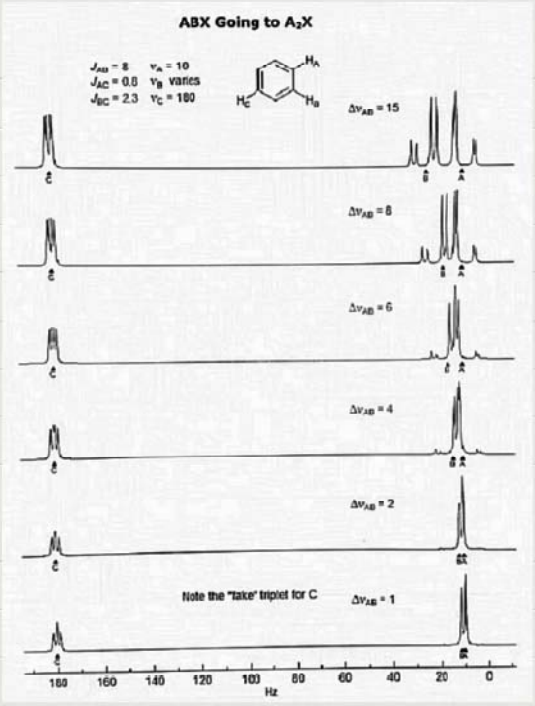


A deceptive ABX pattern, in which one of the ab sub-quartets has collapsed to a singlet.
No first-order analysis possible.


Effect of Relative Sign of J_{AX} and J_{BX} on an ABX pattern
Same sign
ν_A
ν_B
J_{AB} = 13 Hz
J_{AX} = 5 Hz
J_{BX} = 10 Hz
J_{BX} = -10 Hz
Different signs
ν_A
ν_B
J_{AX}
J_{BX}
ν_B = 90 Hz
ν_A = 110 Hz
1.0
1.0


Correct choice of ab quartets
$J_{ab+} = J_{ab-}$ and intensities are OK
(i.e. the ab quartet with more closely spaced inner lines has the smaller outer lines.
Incorrect ab quartets:
J_{ab} is OK, but intensities are wrong (i.e. the thin ab quartet should have much taller central lines)
$c_- = (5+3)/2 = 103.7$
$\Delta\nu_{ab-} = \delta_- = \sqrt{(7-1)(5-3)} = 17.5$
$c_- \pm \delta_-/2 = 103.7 \pm 8.76 = 112.5, 94.9$
$c_+ = (6+4)/2 = 96.25$
$\Delta\nu_{ab+} = \delta_+ = \sqrt{(8-2)(6-4)} = 22.43$
$c_+ \pm \delta_+/2 = 96.25 \pm 11.21 = 107.5, 85.0$
J_{AB}
J_{AB}
7 5 8 6 3 4 1 2
112.5 107.5 85.0 84.9
a, a+ b, b+ Sol. 1
or
b, a+ a, b+ Sol. 2
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.


ABX Going to ABC
How badly off are we, if we treat this as an AMX pattern, taking the peaks at face value?
ppm


ABX Going to A2X
Note the "fake" triplet for C
Hz

Four Spin Systems

A_2X_2 and A_2B_2 Spin Systems

دو جفت هسته معادل شیمیایی و مغناطیسی

طیف نسبت به مرکز (وسط) متقارن است

موارد دیگری که در آنها طیف متقارن هستند عبارتند از :

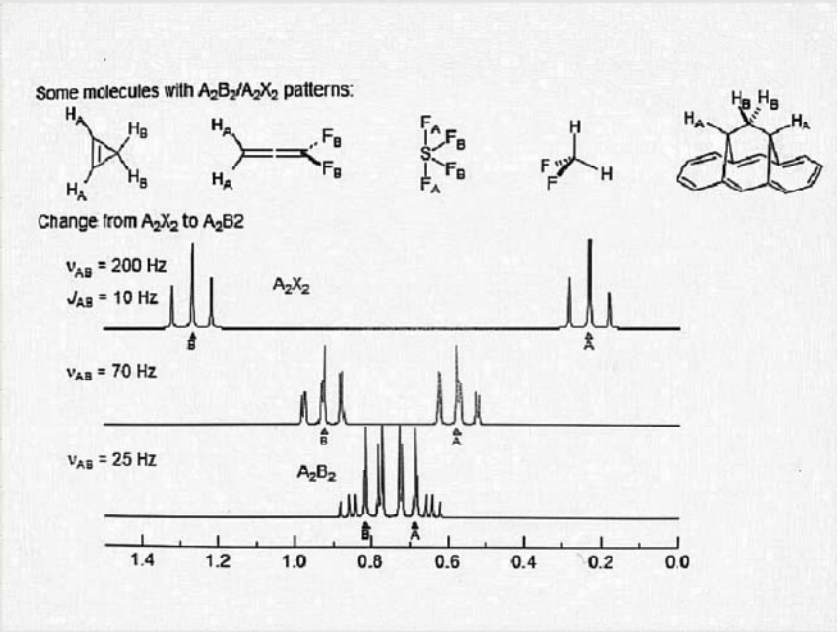
AA'BB' ، AA'XX' ، AB ، AX

هر نیمه از طیف A_2X_2 از یک تریپلت تشکیل می‌شود که آن را با روشهای مرتبه اول می‌توان آنالیز کرد.

طیف A_2B_2 تا هفت خط در هر نیمه از طیف دارد

مقادیر ν_A و ν_B معمولاً از فرکانس قوی‌ترین خط بدست می‌آید

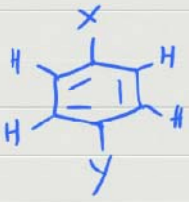
ظاهر طیف در هر مورد مجزا بستگی به $\frac{\Delta\nu}{J_{AB}}$ دارد

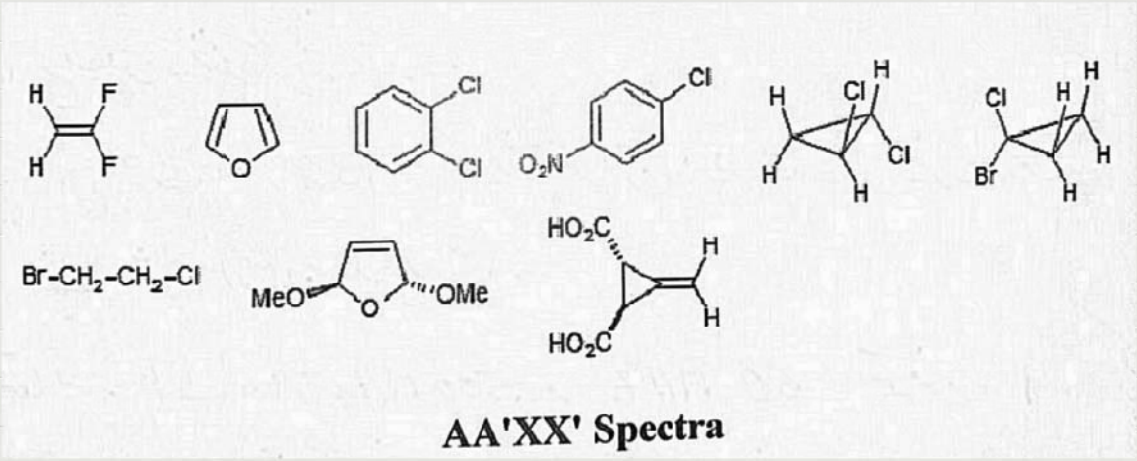


The AA'XX' and AA'BB' Spin Systems

$[AX]_2$ $[AB]_2$

وقتی که مولکول حاوی دو هسته پروتون باشد به نوری که هرهسته از طریق پوشش حول یک محور تکان یا انعکاس در یک صفحه تکان موقعیت خود را با هم عوض کنند





AA'XX' Spectra

Solving an AA'XX' Pattern

If all 10 lines are visible, and can be assigned to the large doublet and the two ab quartets, the process is straighforward, as shown for the solution of the ^{19}F NMR spectrum of 1,1-difluoroethylene below:

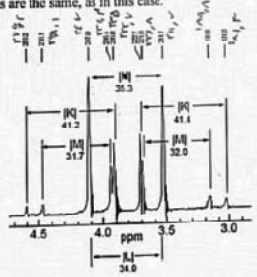
1. Determine N from the doublet separation (35.3 Hz).

2. Measure K (41.2 and 41.4 Hz) and M (31.7, 32.0 Hz) from the appropriate line separation ("J" of the two ab quartets).

3. Calculate L - it is the "δ_{ab}" of each of the ab quartets. For the K quartet we get: SQRT[(276.2-181.3)(235.0-222.7)] = 33.8 Hz, for the M quartet: SQRT[(268.1-189.8)(236.4-221.8)] = 34.2 Hz

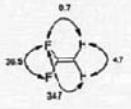
4. Calculate $J_{AA'}$ and $J_{XX'}$ by summing and subtracting K and M: $J_{AA'}$ = (K+M)/2 = (41.3+31.8)/2 = 36.5 Hz; $J_{XX'}$ = (K-M)/2 = (41.3-31.8)/2 = 4.7 Hz. Because we do not know which ab quartet is K, and which M, we do not know the relative signs of $J_{AA'}$ and $J_{XX'}$, nor do we know which coupling is which.

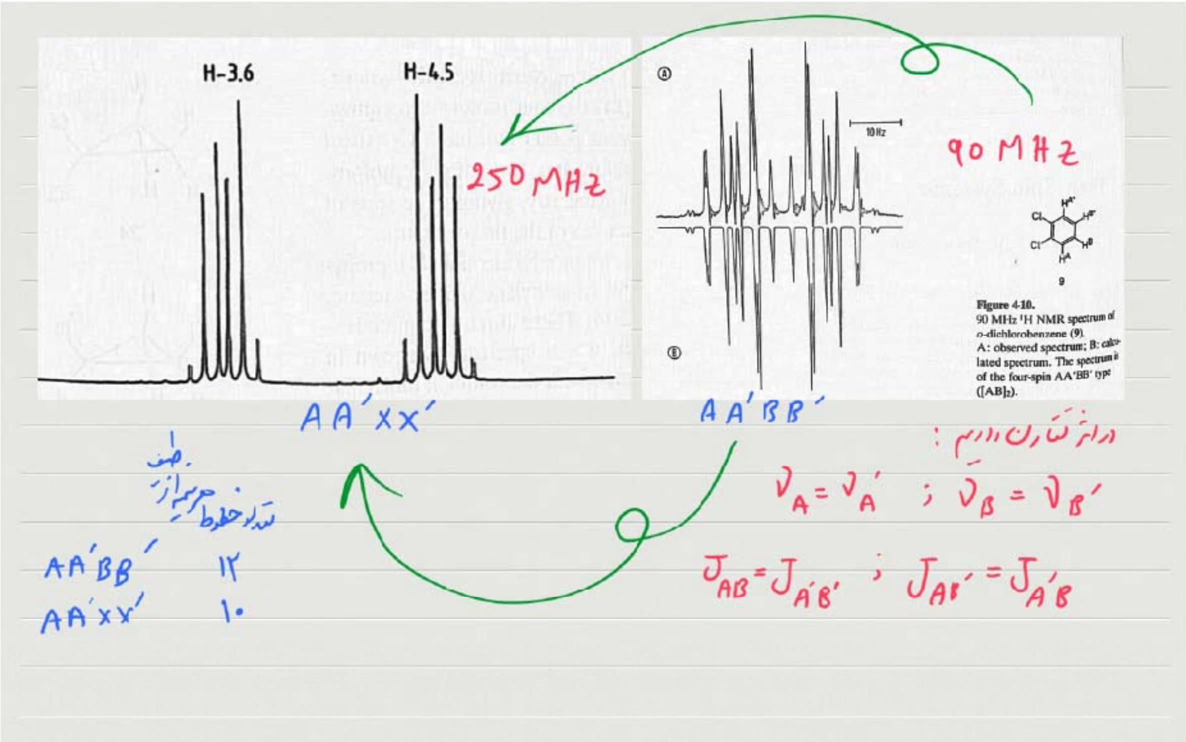
5. Calculate J_{AX} and $J_{AX'}$ by summing and subtracting L and N: J_{AX} = (N+L)/2 = (35.3+34.0)/2 = 34.7 Hz, $J_{AX'}$ = (N-L)/2 = (35.3-34.0)/2 = 0.7 Hz. Again, we do not know which coupling is which, but the relative signs can be determined: if |N| is larger than |L|, the signs are the same, as in this case.



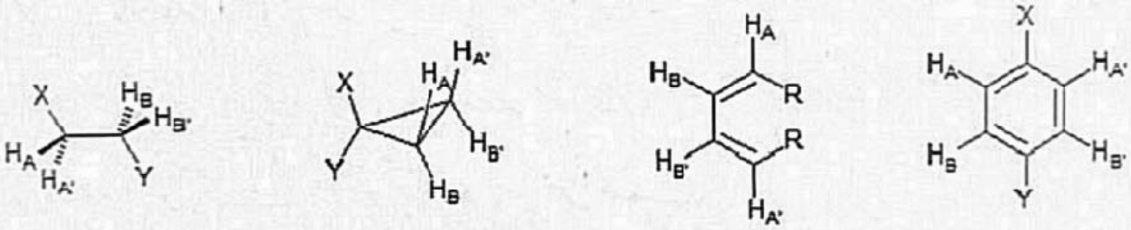
|K| = $|J_{AA'} + J_{XX'}|$ "J" of one ab quartet
|L| = $|J_{AX} - J_{AX'}|$ "δ" of both ab quartets
|M| = $|J_{AA'} - J_{XX'}|$ "J" of other ab quartet
|N| = $|J_{AX} + J_{AX'}|$ "doublet"

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

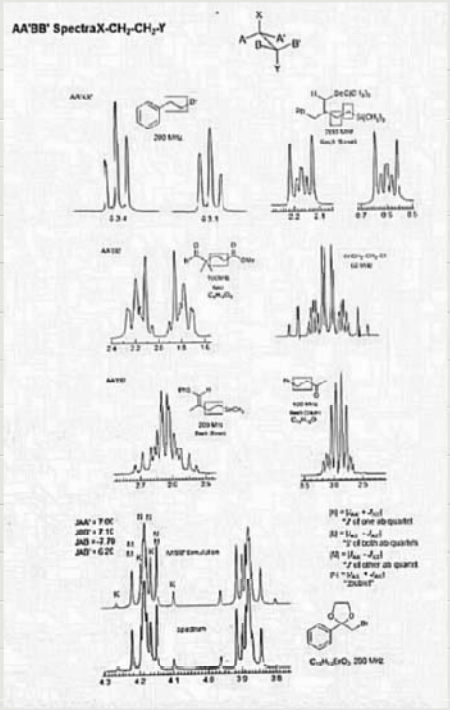




The AA'BB' Pattern



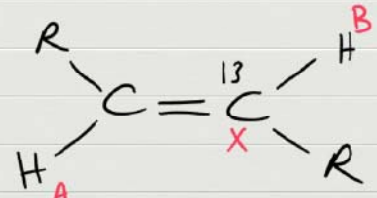
(a) AA'-Gem (b) AA'-Vic (c) ODCB o-Dichlorobenzene (d) p-Aromatic



Analysis of ^{13}C NMR Spectra

در بسیاری از موارد تنها آنالیز طیف ^{13}CNMR (بدون decoupling) کافی نیست

طیف ^{1}HNMR یعنی آمار ^{13}C در این طیف هم باید مورد آنالیز قرار گیرد

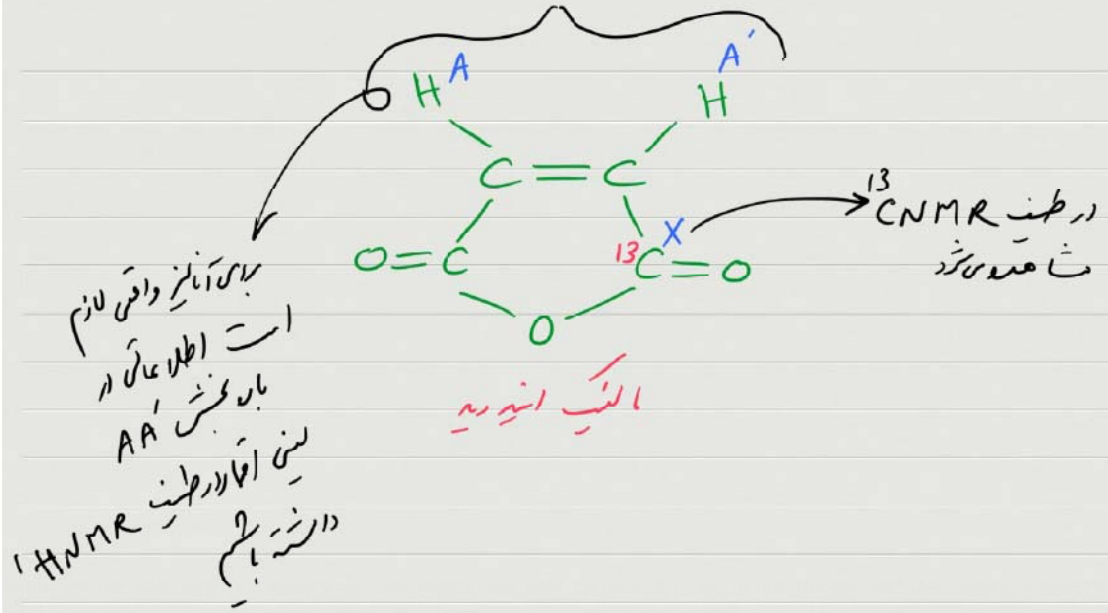


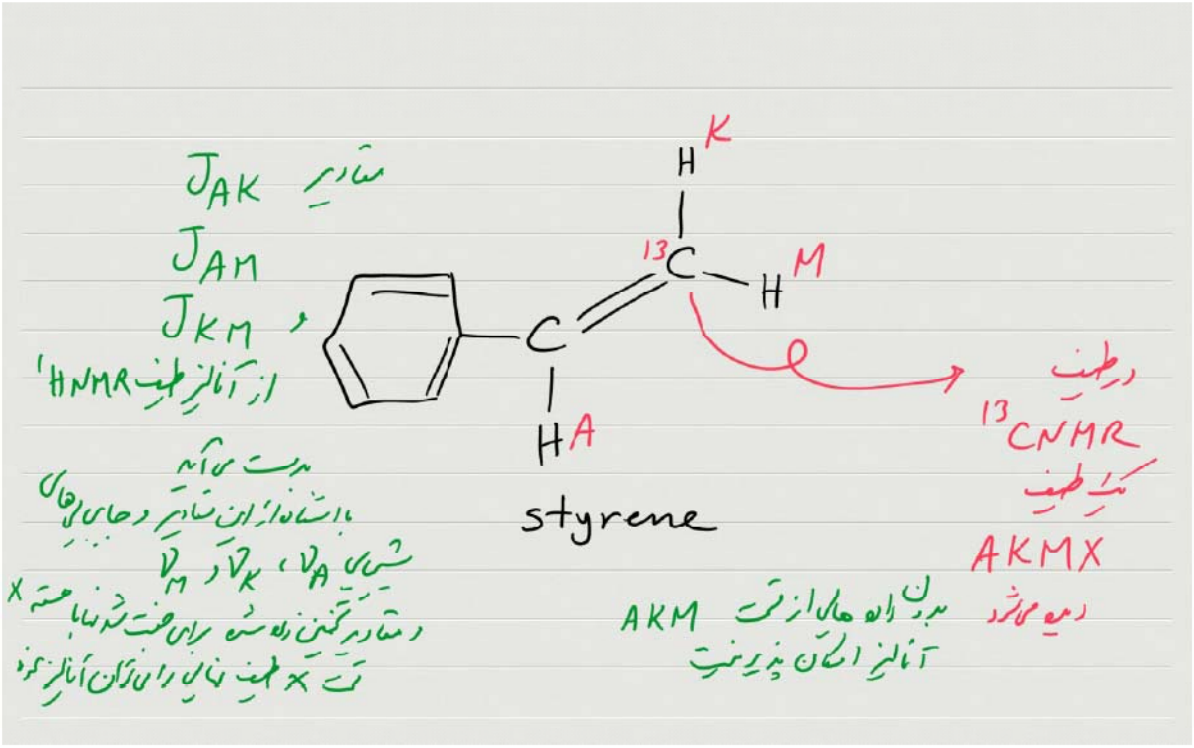
در طیف $^{13}CNMR$ تنها کشش X دیده میشود که از چهار (اتم اکسیژن) خط تشکیل شده است

در سیستم ABX ، ثابت J_{AX} و J_{BX} را نمیتوان از کشش X تعیین نمود

به همین دلیل بایستی کشش AB آنالیز شود. این کشش را با بررسی اتم ^{13}C

در طیف $^{1}HNMR$ میتوان آنالیز کرد.





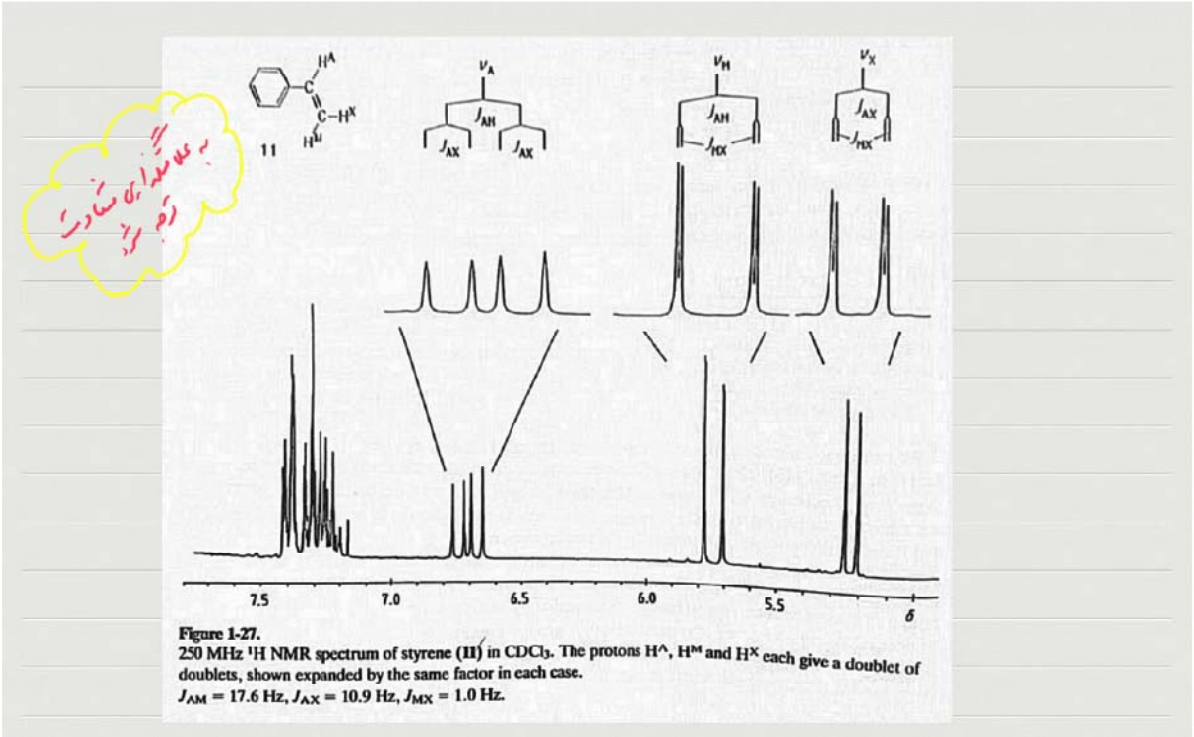


Figure 1-27.
250 MHz ^{1}H NMR spectrum of styrene (II) in $CDCl_3$. The protons H^A, H^M and H^X each give a doublet of doublets, shown expanded by the same factor in each case.
J_{AM} = 17.6 Hz, J_{AX} = 10.9 Hz, J_{MX} = 1.0 Hz.

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