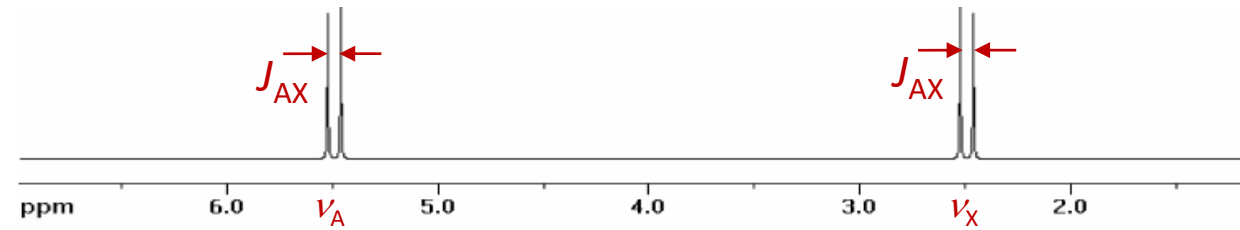


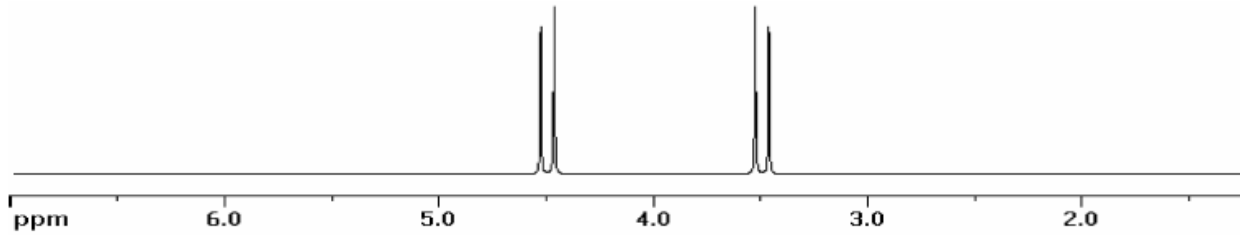
ANALISI DI SISTEMI DI SPIN

SISTEMI A DUE SPIN

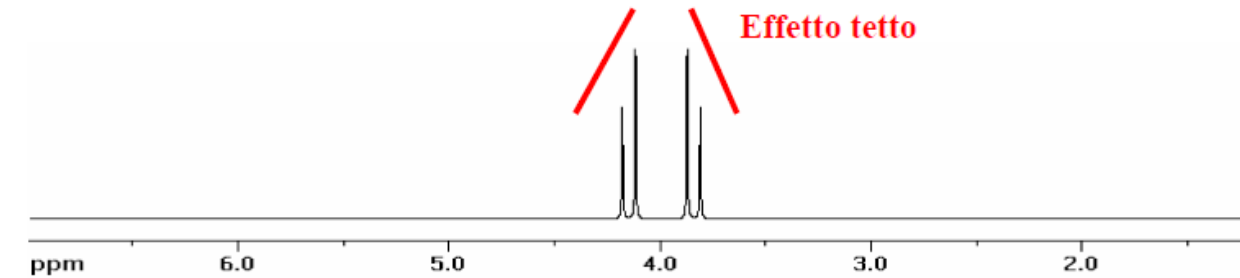
Sistema AX \rightarrow AB \rightarrow A₂



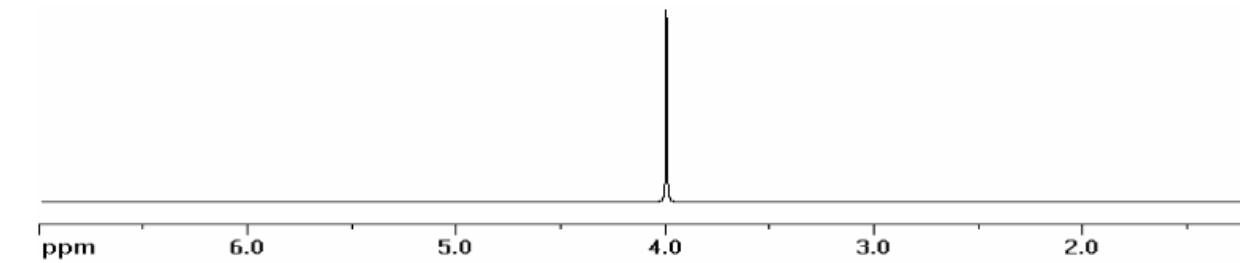
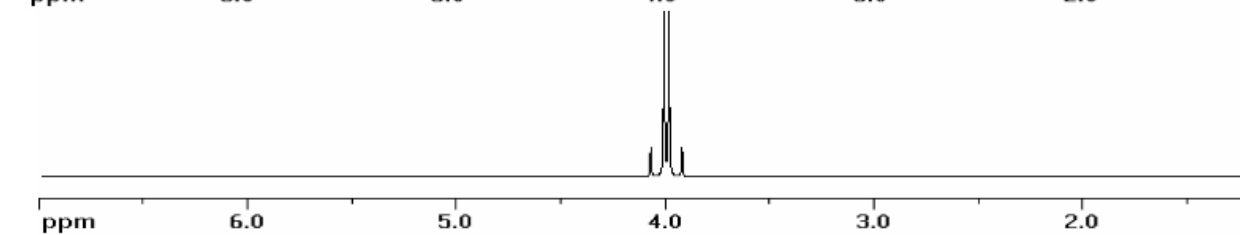
Accoppiamento debole:
sistema AX



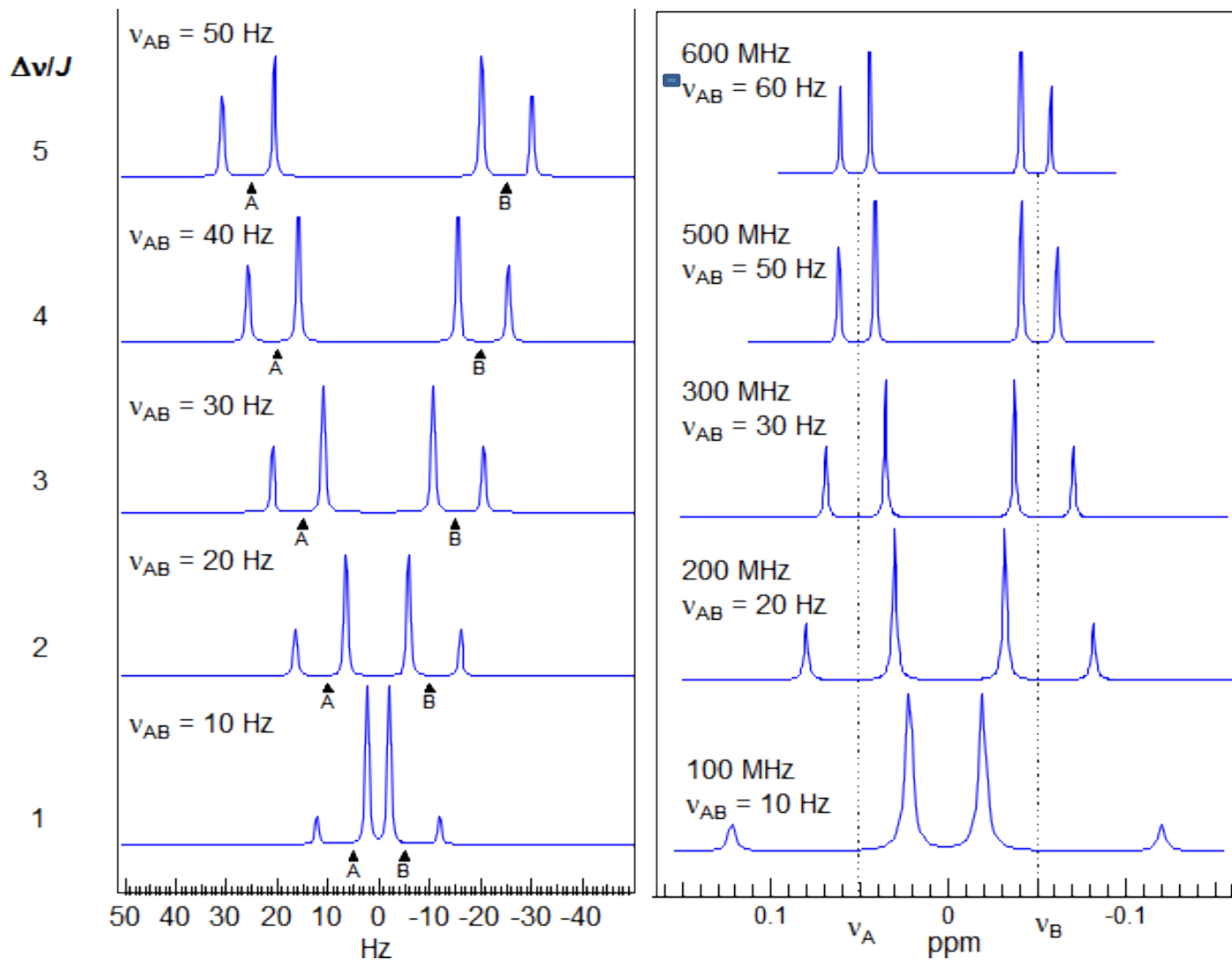
Accoppiamento forte:
sistema AB



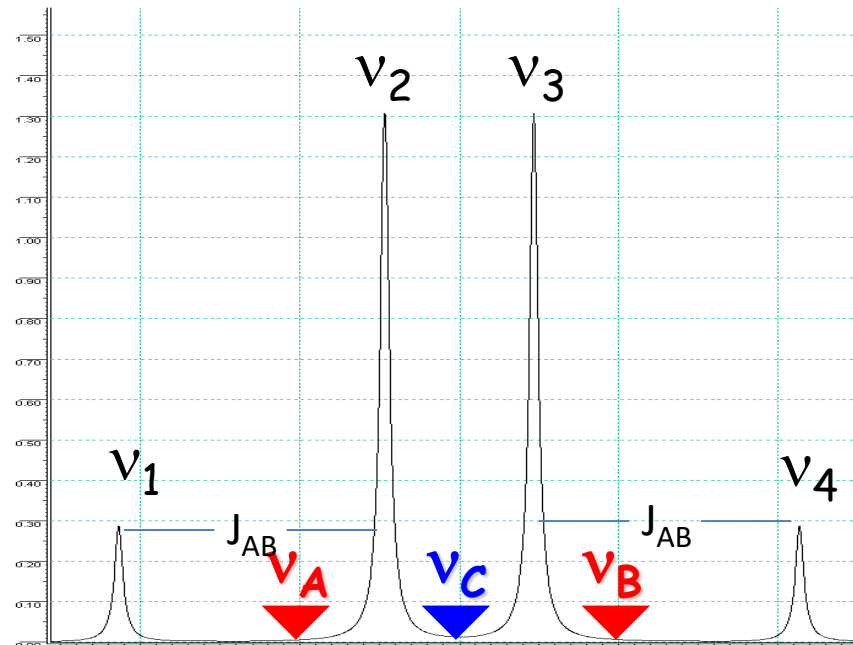
Coincidenza: sistema A₂



Sistema AX \rightarrow AB



Sistema AB



$$\Delta\nu_{AB} = (\nu_A - \nu_B) = \sqrt{(\nu_1 - \nu_4)(\nu_2 - \nu_3)} \text{ [Hz]}$$

$$J_{AB} = (\nu_1 - \nu_2) = (\nu_3 - \nu_4) \text{ [Hz]}$$

$$\nu_A = \nu_C + \frac{1}{2} \Delta\nu_{AB}$$

$$\nu_B = \nu_C - \frac{1}{2} \Delta\nu_{AB}$$

ANALISI DI UNO SPETTRO AB

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

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

2. Calculate the center position (in Hz):

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

3. Calculate ν_{AB} .

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

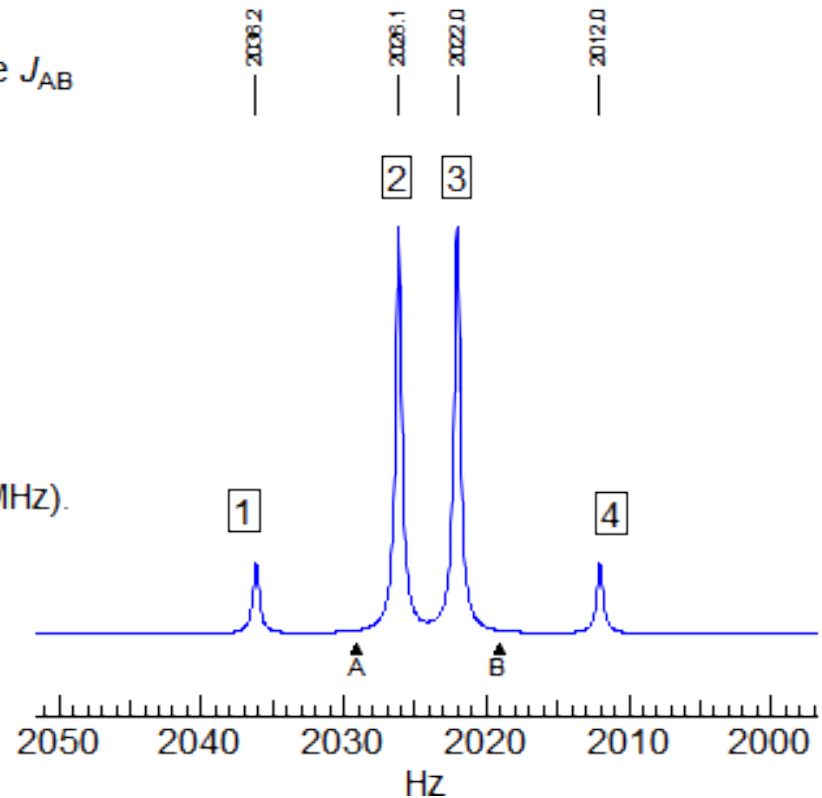
4. Calculate ν_A and ν_B (spectrometer frequency: 300 MHz).

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

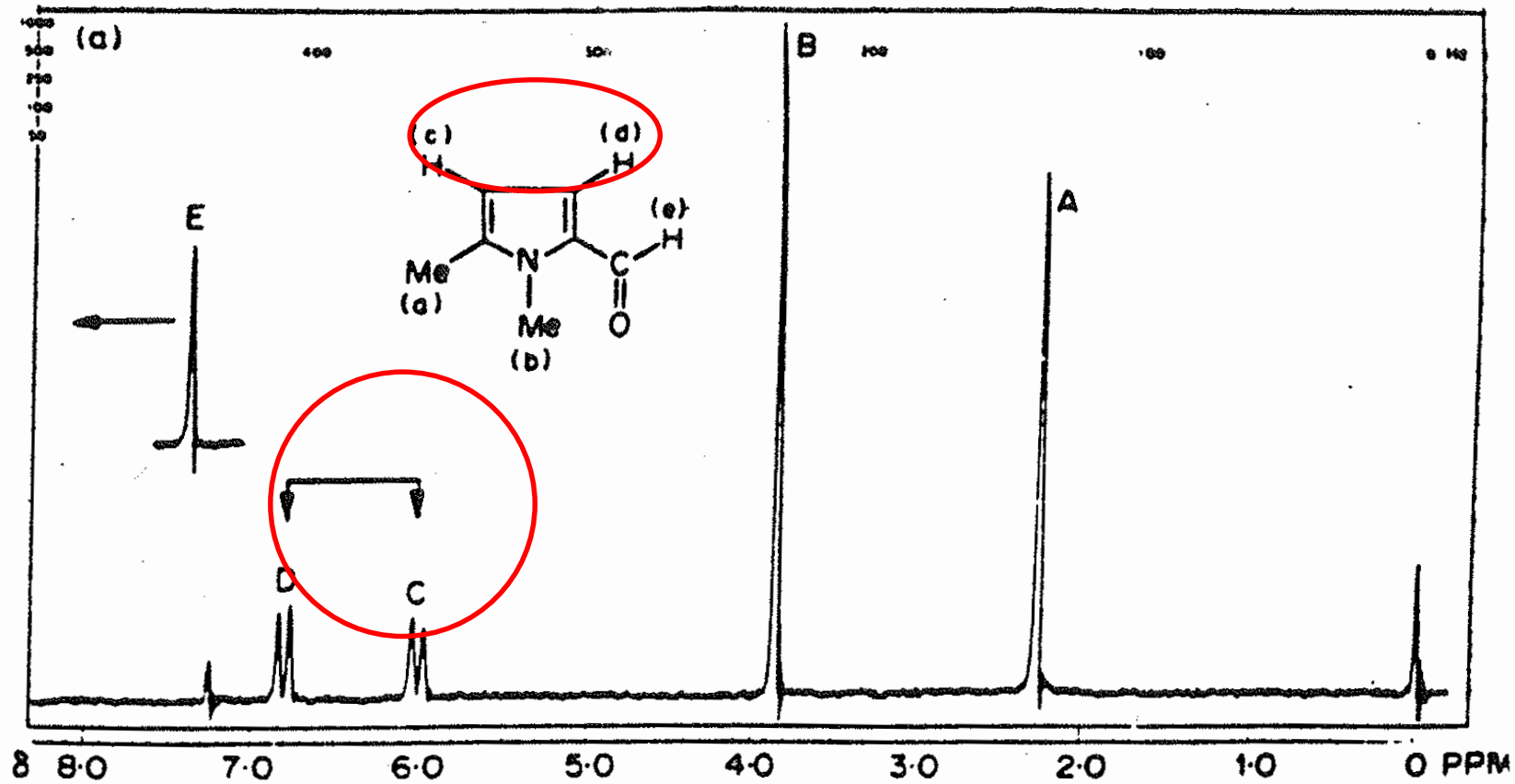
$$\nu_B = \nu_{\text{center}} - \frac{1}{2} \Delta\nu_{AB} = 2019.1 \text{ Hz}$$

$$\delta_A = \nu_A / \text{MHz} = 6.76$$

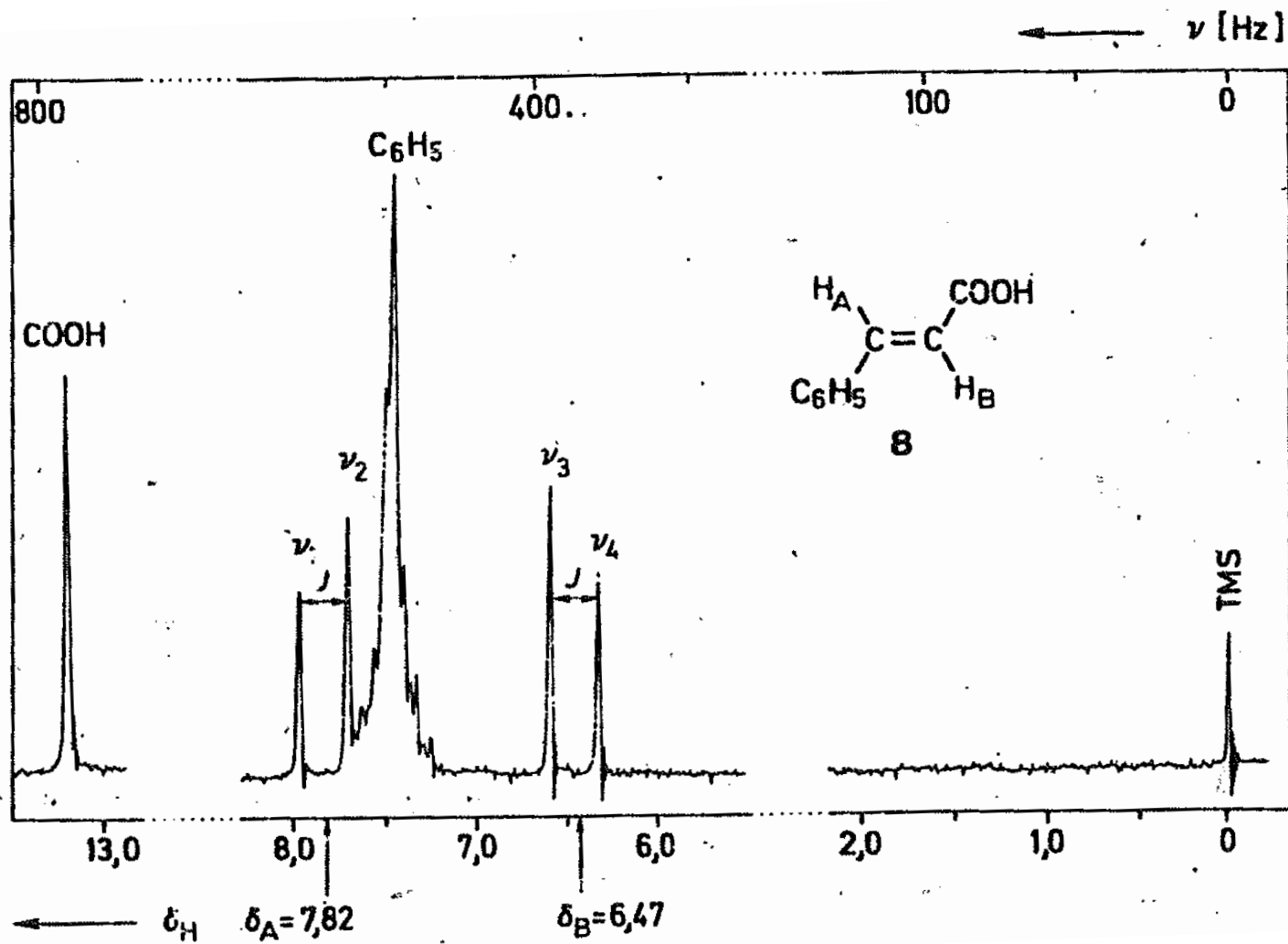
$$\delta_B = \nu_B / \text{MHz} = 6.73$$



SISTEMA AX

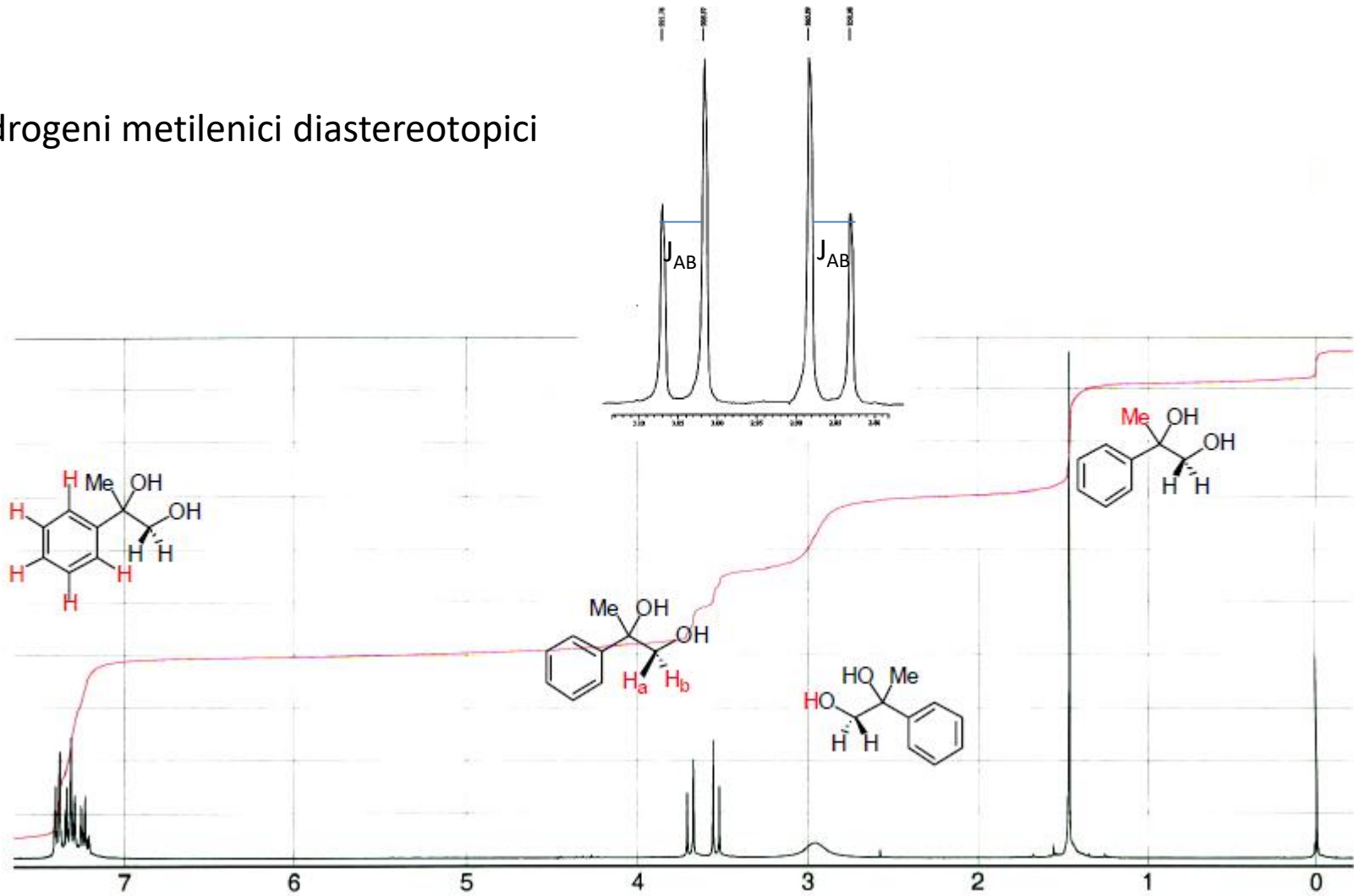


SISTEMA AB

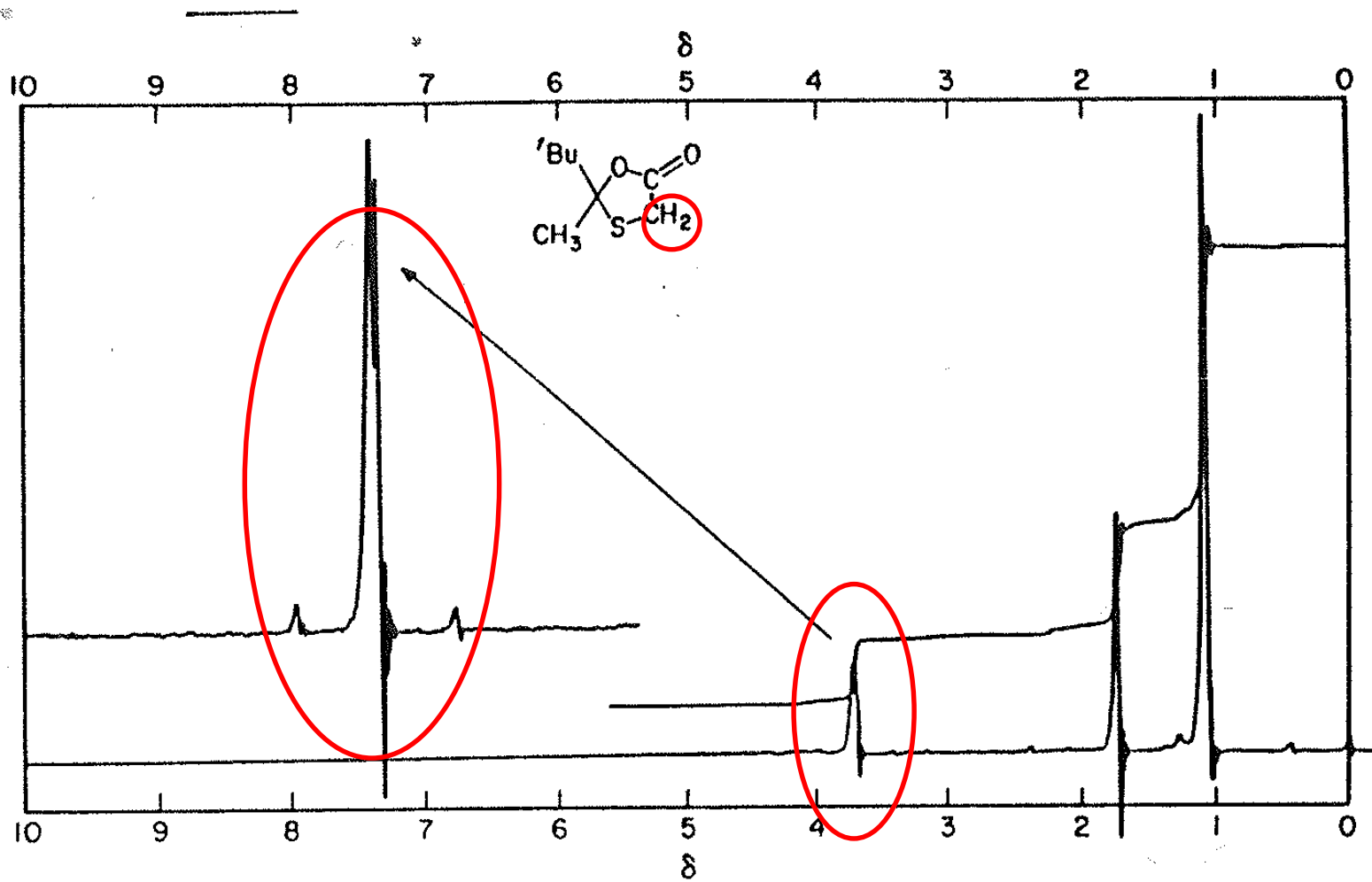


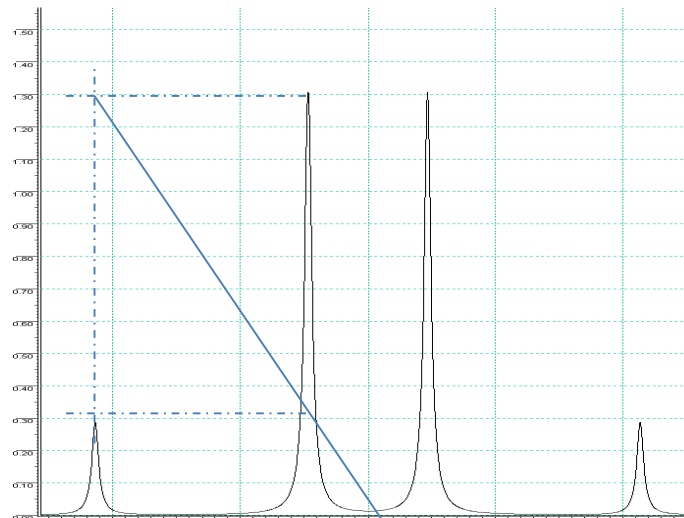
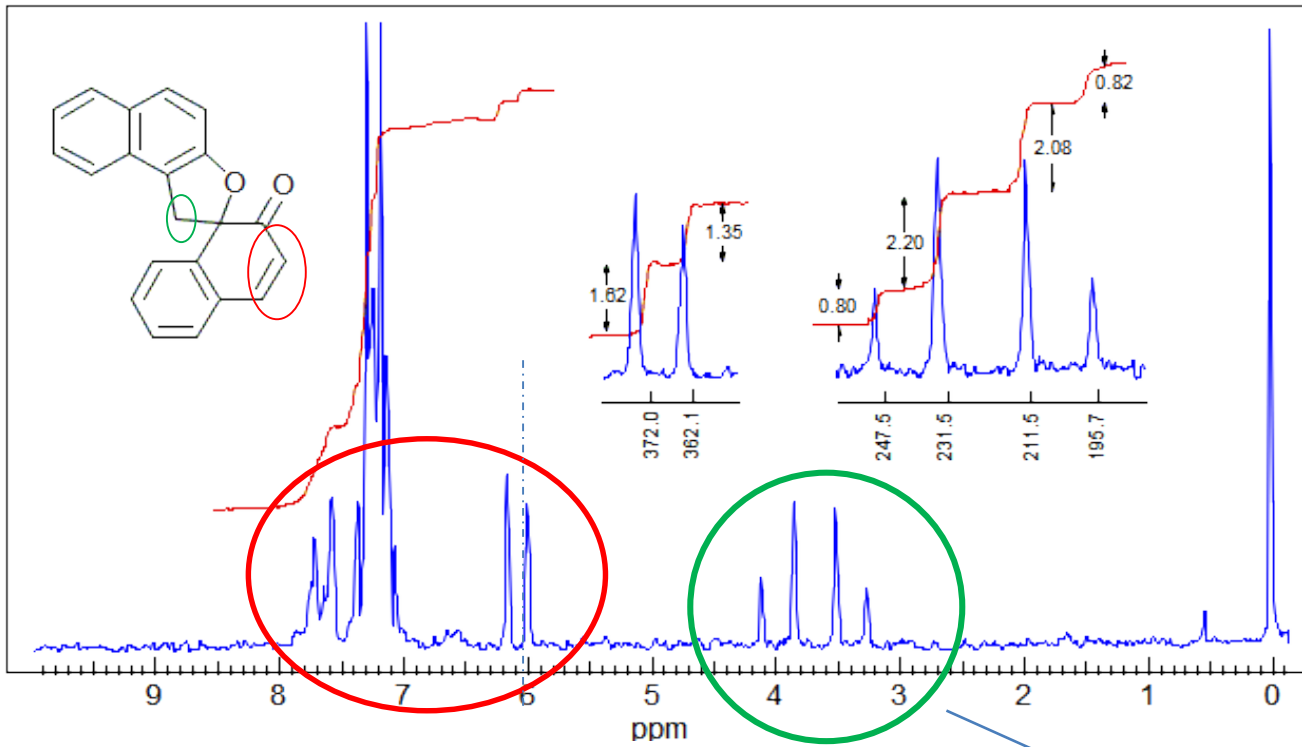
SISTEMA AB

Idrogeni metilenici diastereotopici



SISTEMA AB





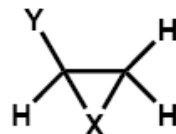
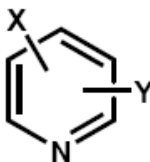
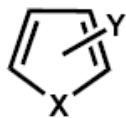
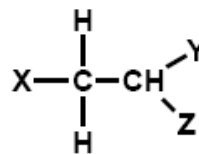
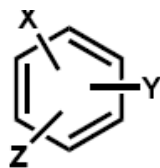
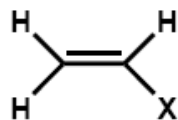
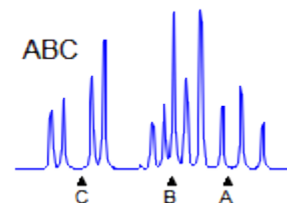
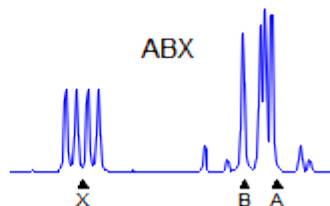
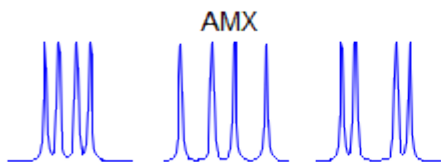
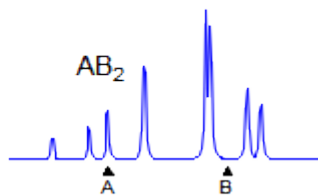
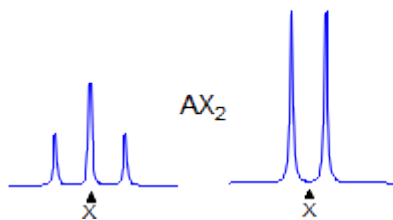
Non è un quartetto!

SISTEMI A TRE SPIN:

A₃

AX₂ → AB₂

AMX → ABX → ABC

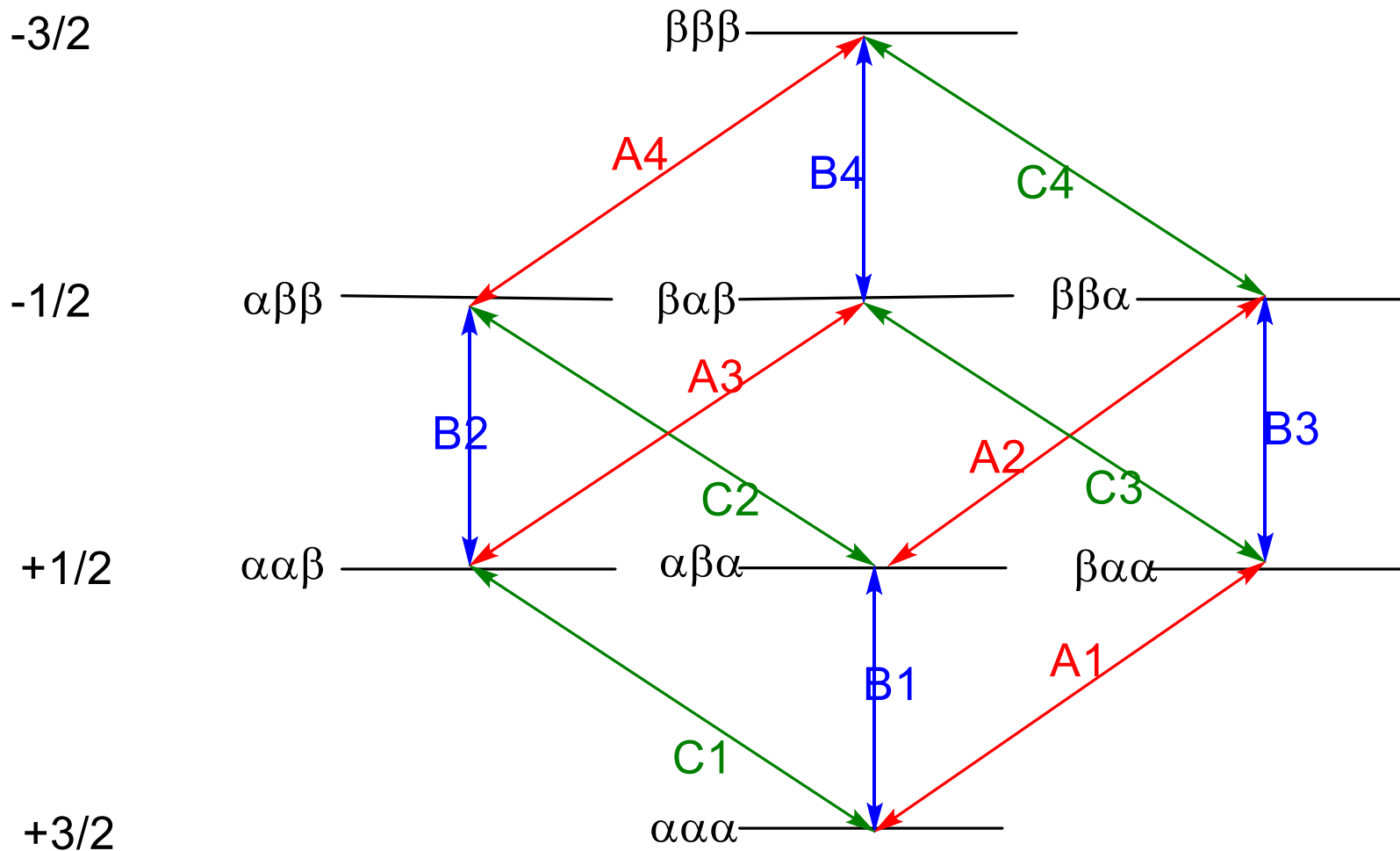


SISTEMI A TRE SPIN:

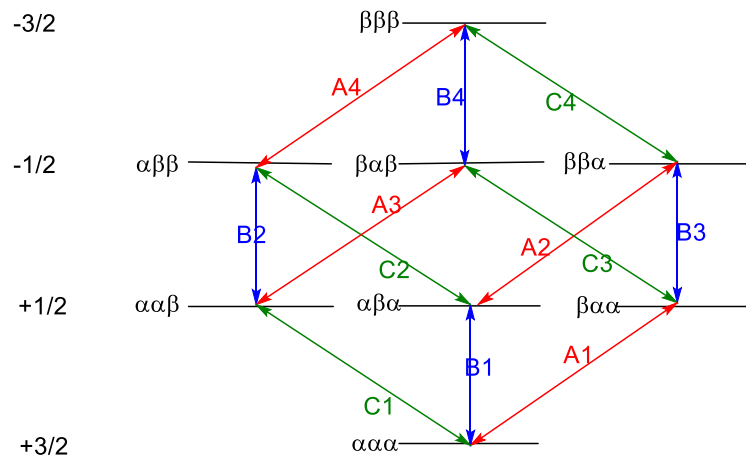
A₃

AX₂ → AB₂

AMX → ABX → ABC



AX₂



Transizioni di A

- A1 con X2 in αα
- A2 con X2 in βα
- A3 con X2 in αβ
- A4 con X2 in ββ

degeneri



Tripletto 1:2:1

Transizioni di X

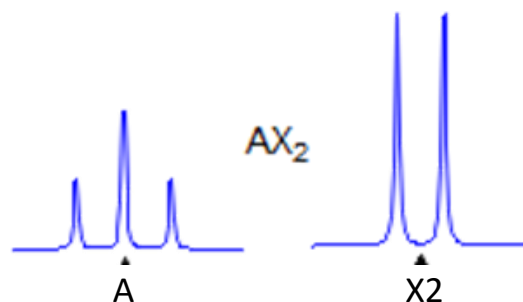
- B1C1 con A in α
- B2C2 con A in α
- B3C3 con A in β
- B4C4 con A in β

degeneri

degeneri



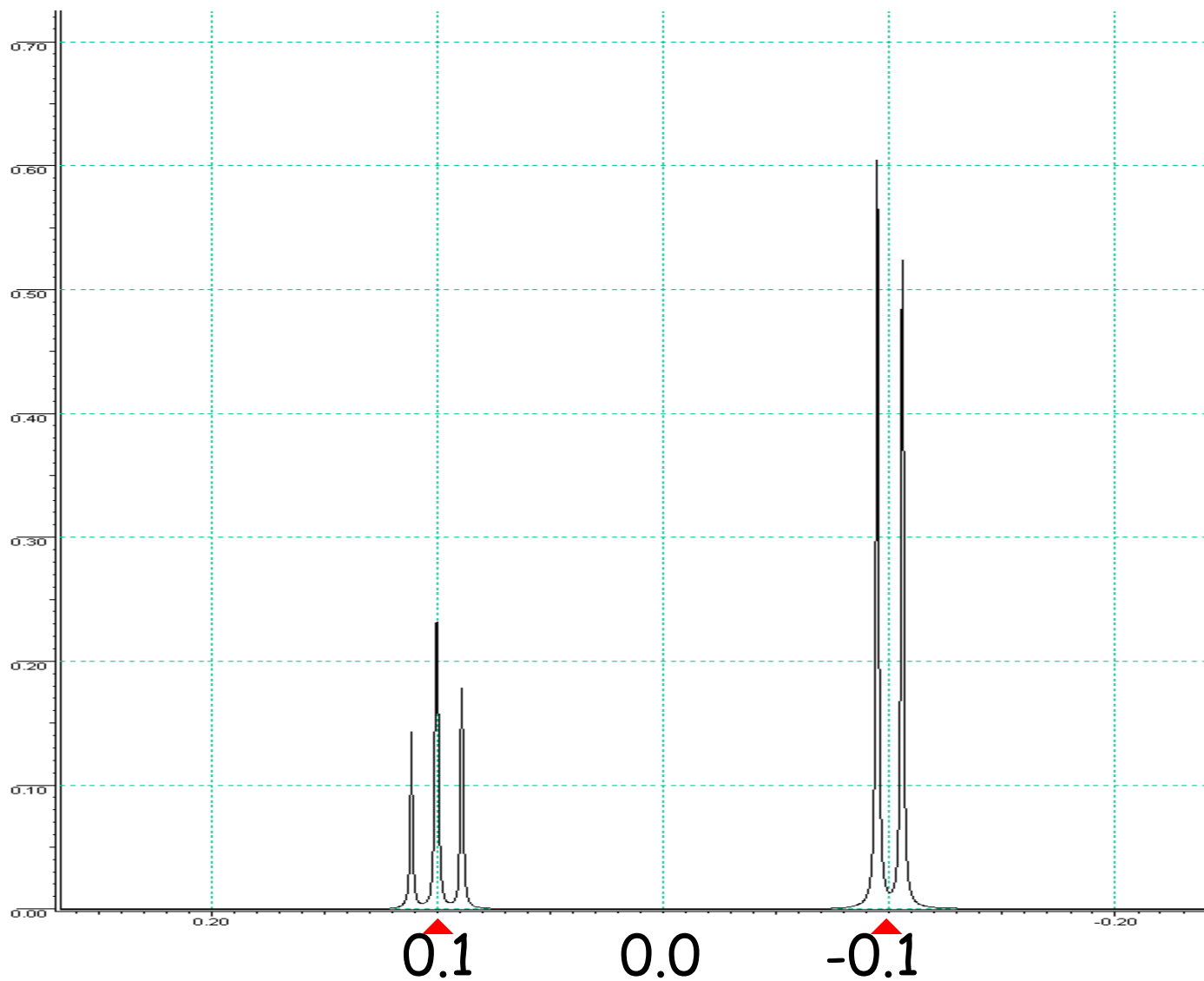
Doppietto 4:4

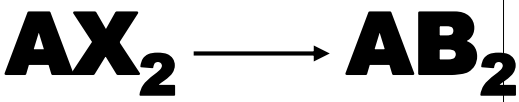


AX₂

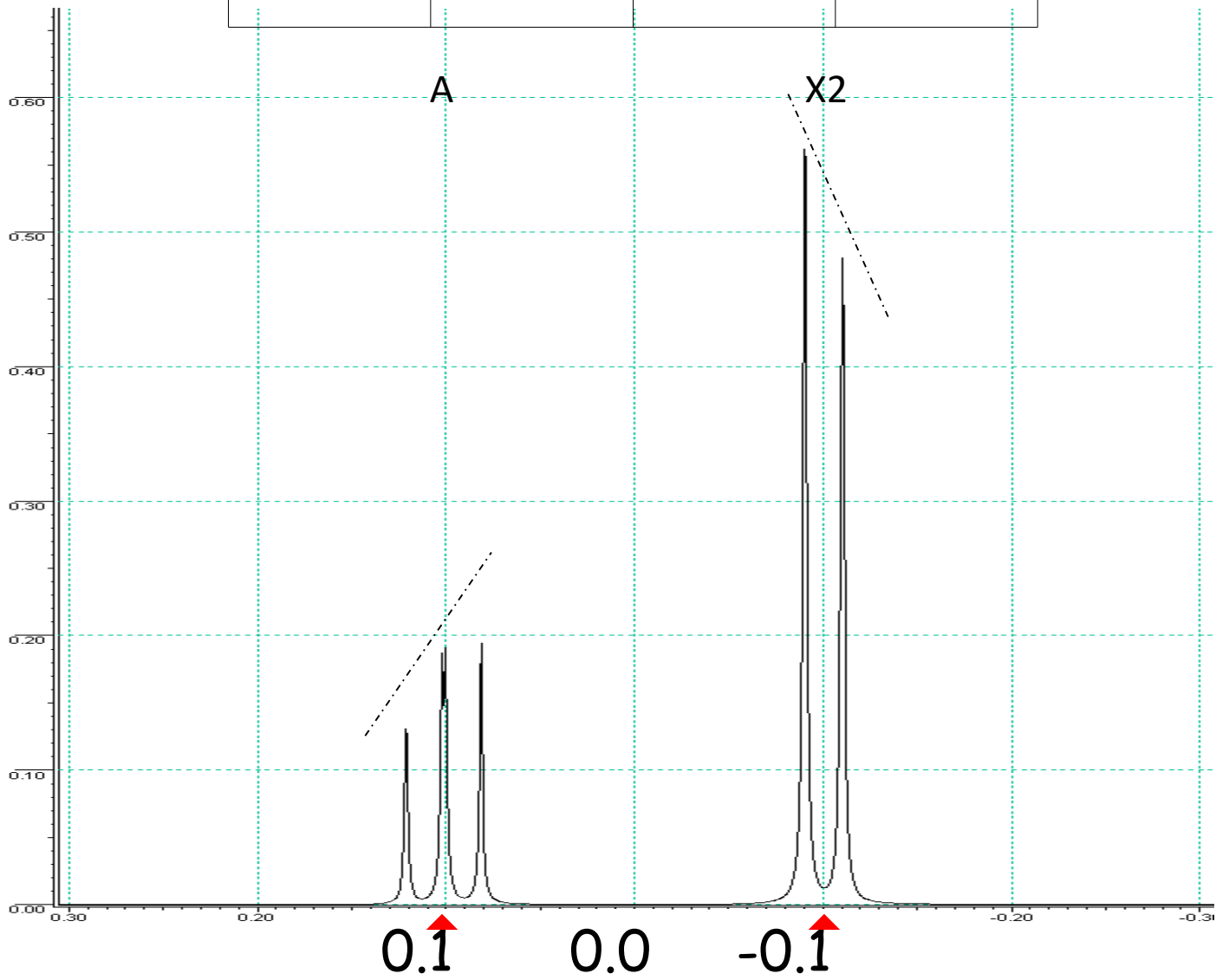
$\Delta\nu$ (ppm)	ν_{op} (MHz)	$\Delta\nu$ (Hz)	$\Delta\nu/J$
0.2	900	180	18

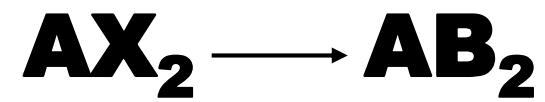
$J = 10 \text{ Hz}$



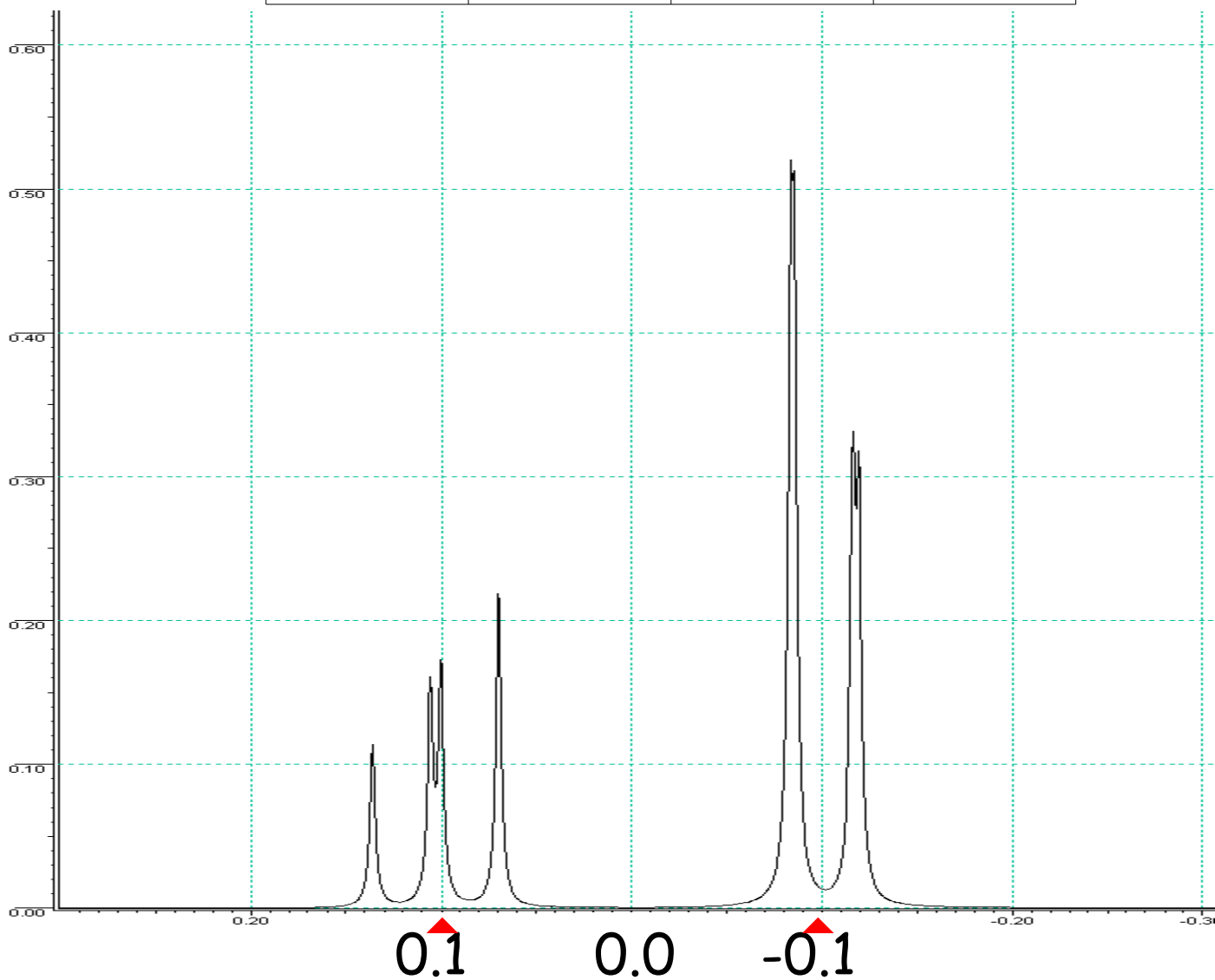


$\Delta\nu$ (ppm)	ν_{op} (MHz)	$\Delta\nu$ (Hz)	$\Delta\nu/J$
0.2	500	100	10



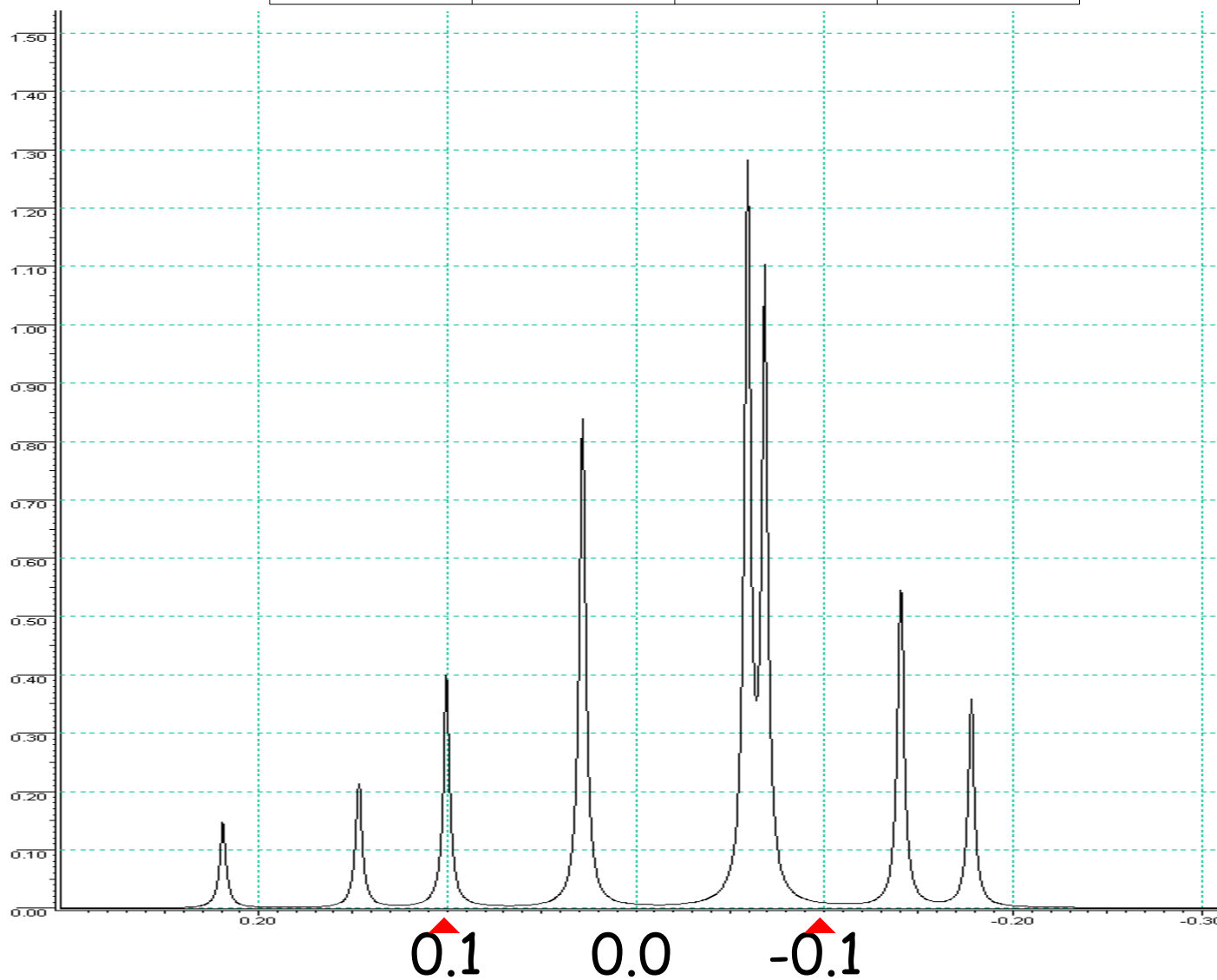


$\Delta\nu$ (ppm)	ν_{op} (MHz)	$\Delta\nu$ (Hz)	$\Delta\nu/J$
0.2	300	60	6



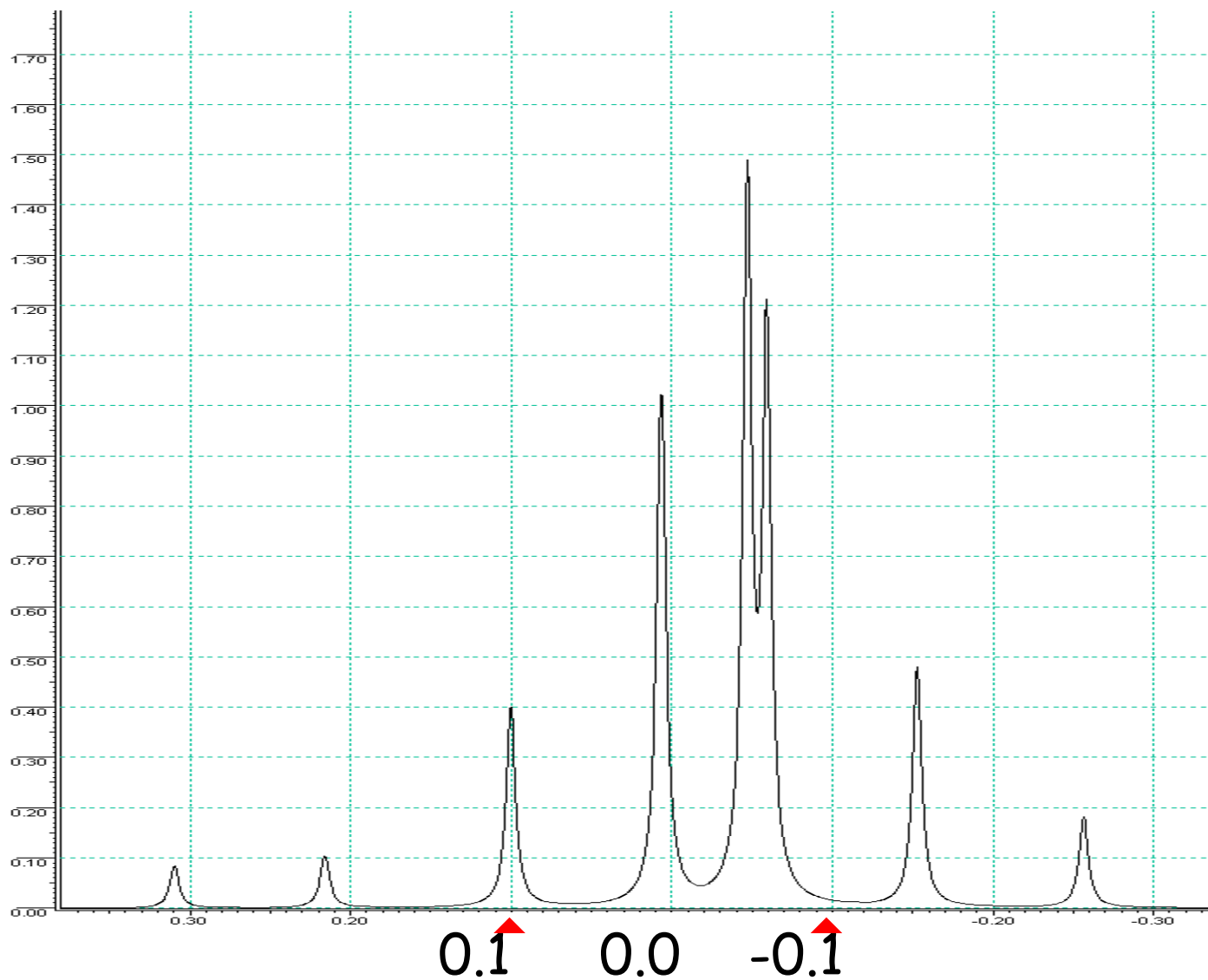
AB₂

$\Delta\nu$ (ppm)	ν_{op} (MHz)	$\Delta\nu$ (Hz)	$\Delta\nu/J$
0.2	100	20	2



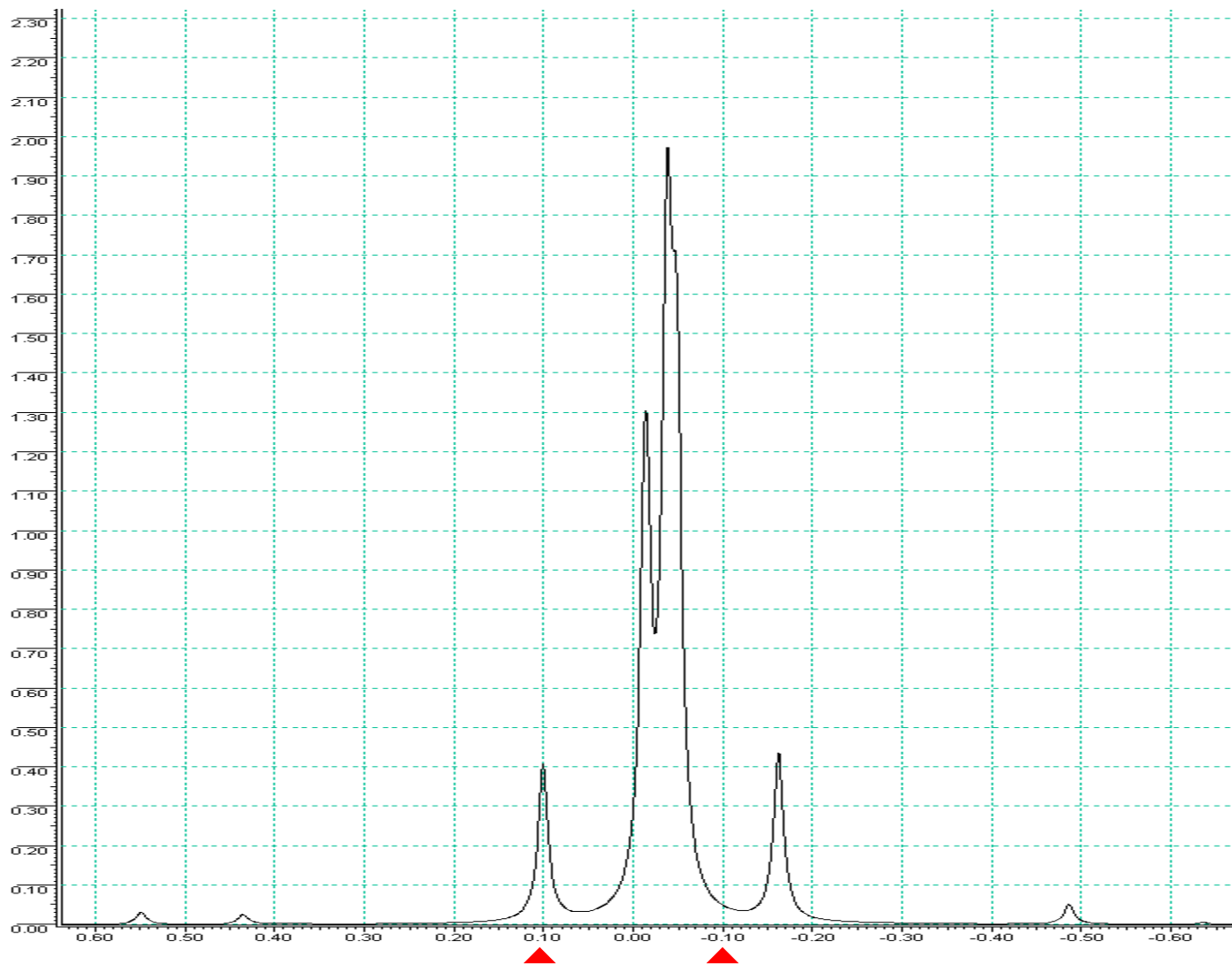
AB₂

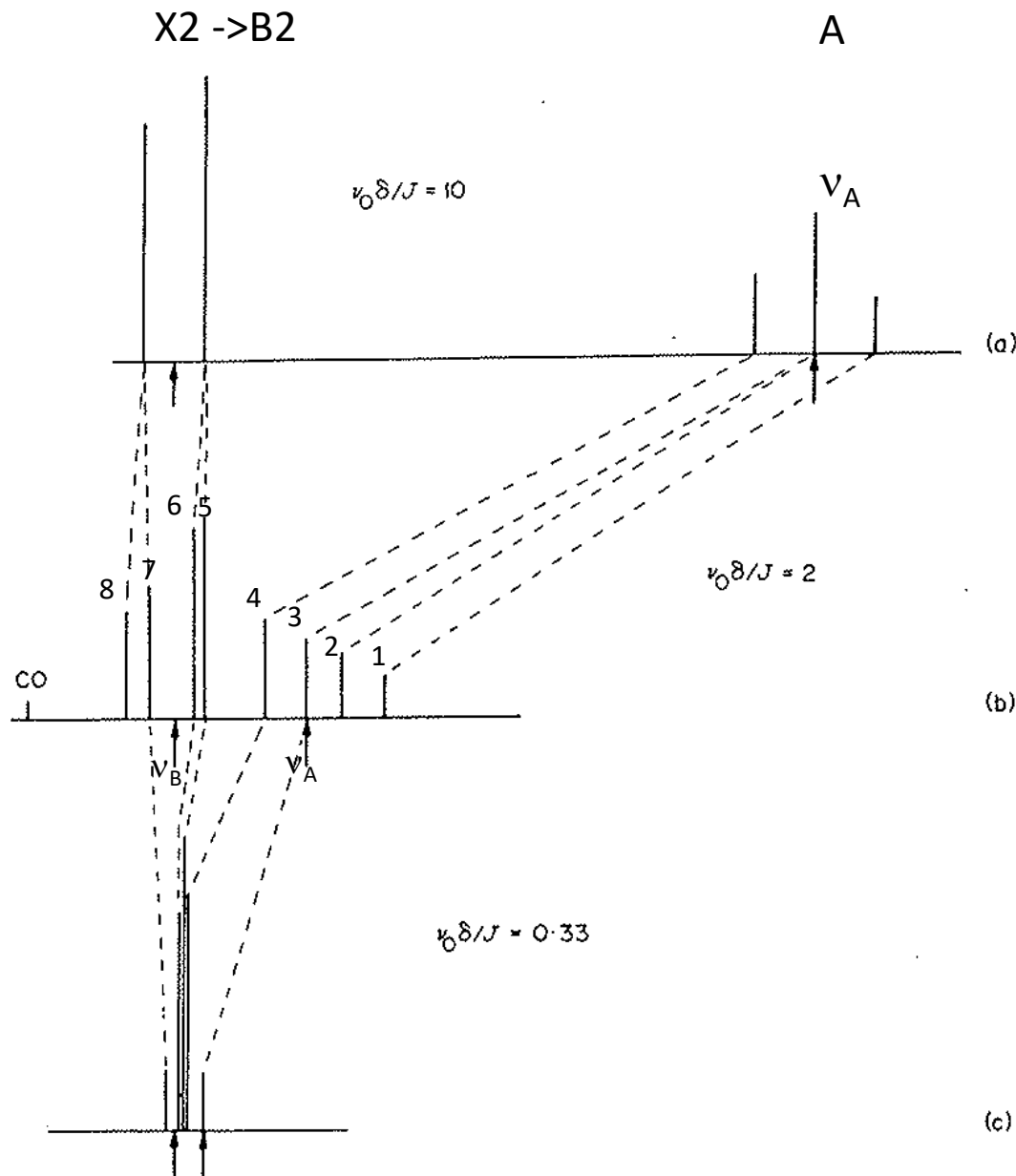
$\Delta\nu$ (ppm)	ν_{op} (MHz)	$\Delta\nu$ (Hz)	$\Delta\nu/J$
0.2	60	12	1.2



AB₂

$\Delta\nu$ (ppm)	ν_{op} (MHz)	$\Delta\nu$ (Hz)	$\Delta\nu/J$
0.2	30	6	0.6





1

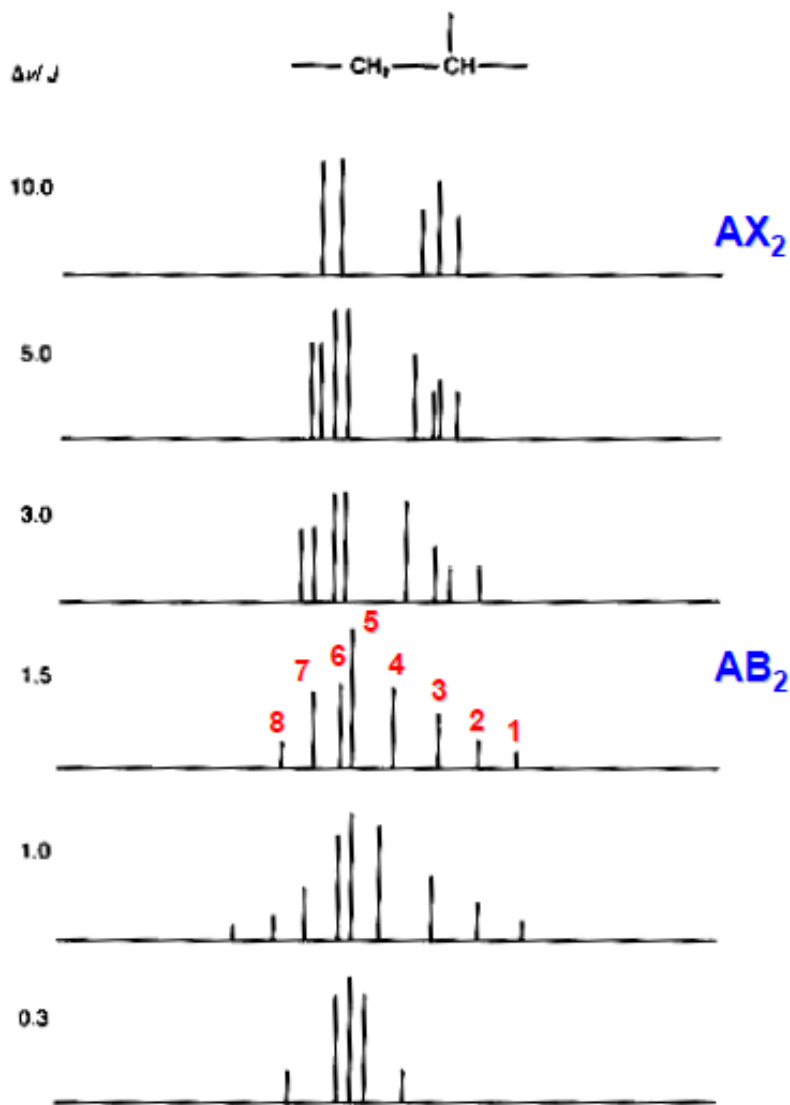
$$\nu_A = \nu_3$$

$$\nu_B = 1/2(\nu_5 + \nu_7)$$

$$J_{AB} = 1/3 (\nu_1 - \nu_4 + \nu_6 - \nu_8)$$

Figure 3.16 Diagram showing how the degenerate lines in an AB_2 spectrum separate as the chemical shift is reduced. In (c) the flanking lines are too weak to be observed. CO is a combination line.

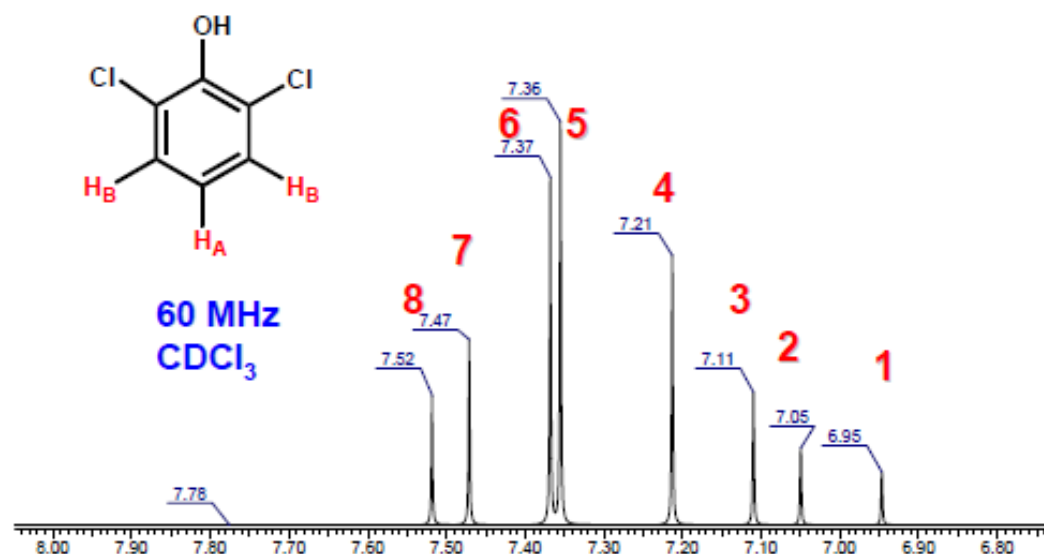
Accoppiamento di spin: sistema AX₂ e AB₂



I due nuclei B sono magneticamente equivalenti e accoppiano con la stessa J con A.

Il numero di linee sarà funzione del rapporto $\Delta\nu/J$

La costante di accoppiamento si ricava dal calcolo.

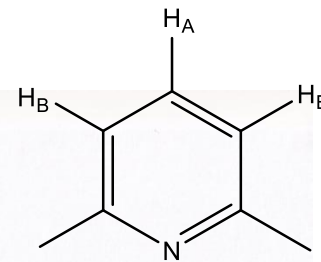


$$\nu_A = \nu_3 \text{ [Hz]}$$

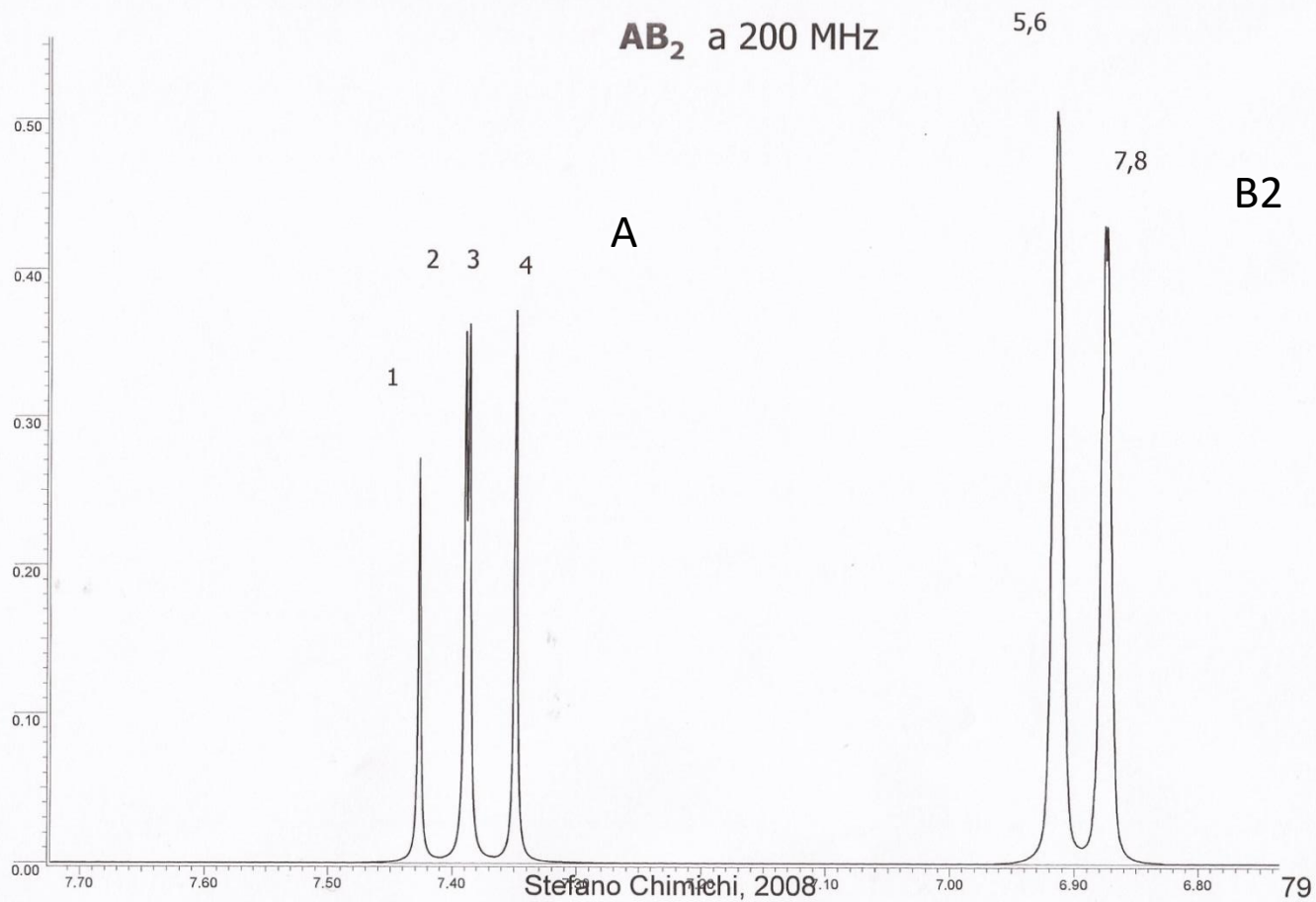
$$\nu_B = \frac{1}{2} (\nu_5 + \nu_7) \text{ [Hz]}$$

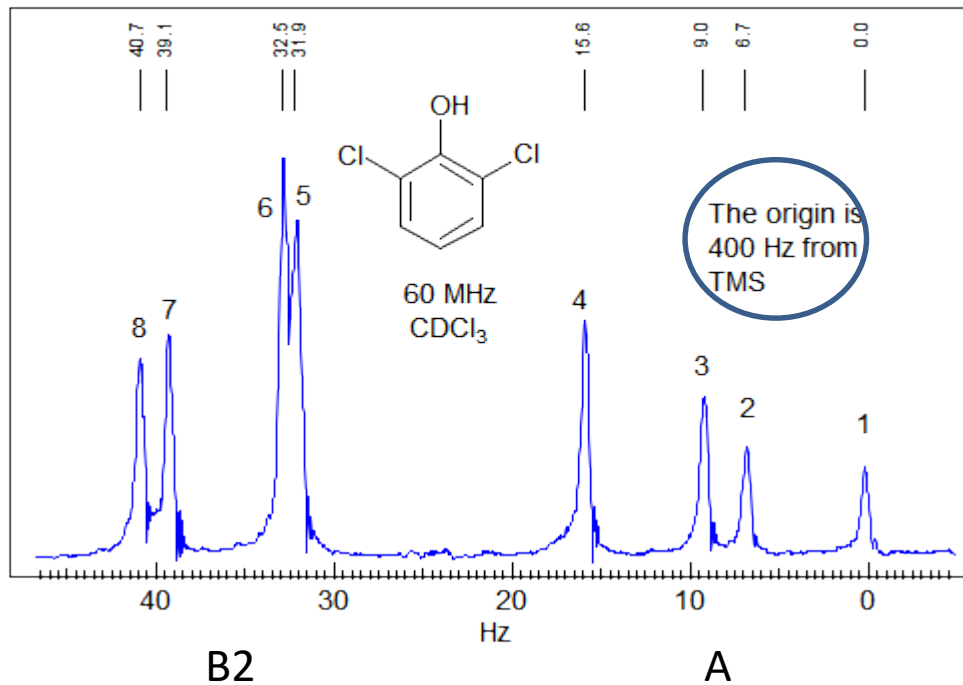
$$J_{AB} = \frac{1}{3} (\nu_1 - \nu_4 + \nu_6 - \nu_8) \text{ [Hz]}$$

2,6-dimetilpiridina



AB₂ a 200 MHz





In questo caso la parte a uno spin è a campo più alto e si numera da destra a sinistra

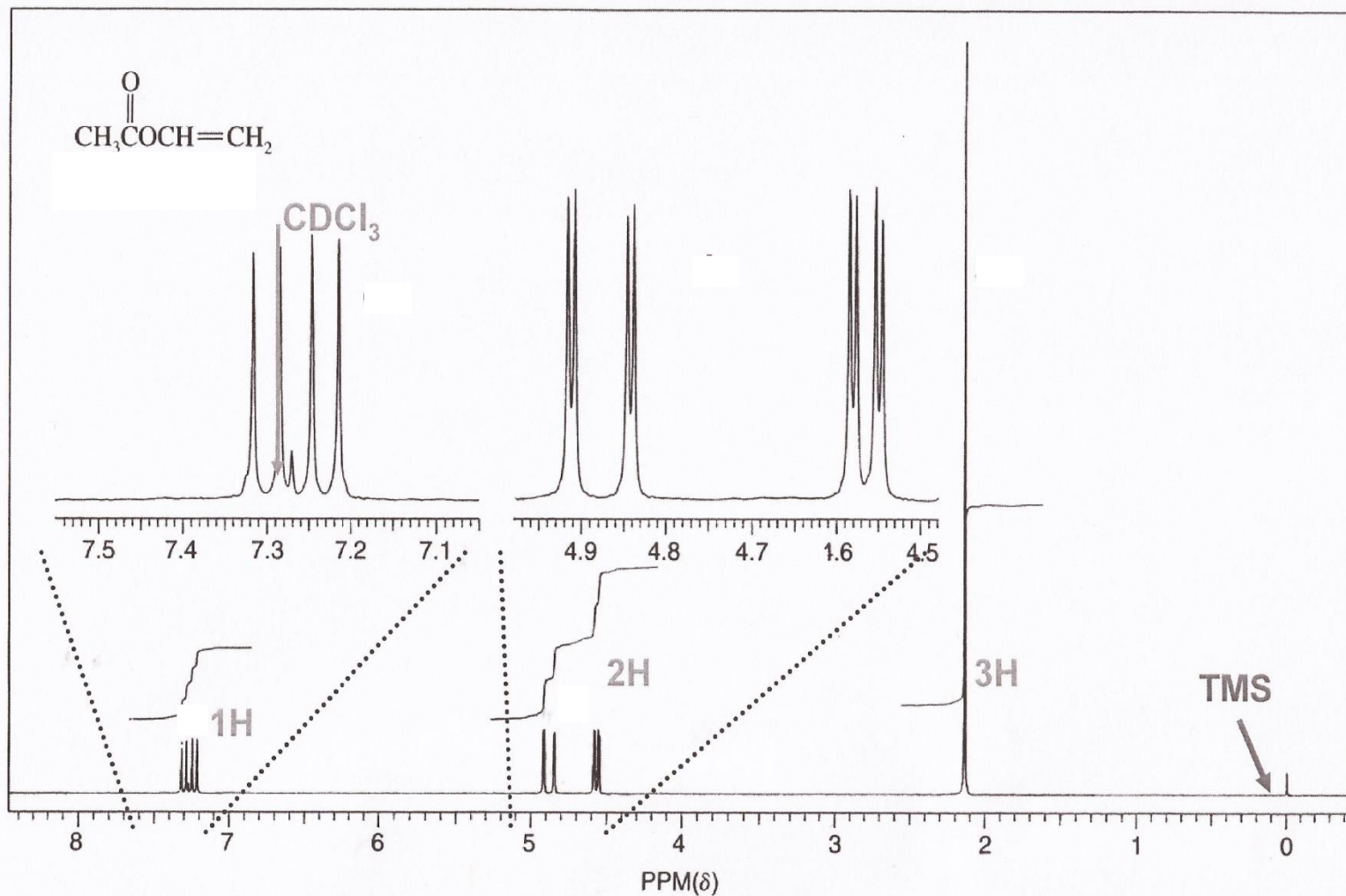
$$\nu_A = \nu_3 = 9.0 \text{ Hz} \quad (\delta_A = (9 + 400)/60 = 6.82 \text{ ppm})$$

$$\nu_B = (\nu_5 + \nu_7)/2 = (31.9 + 39.1)/2 = 35.5 \text{ Hz} \quad (\delta_B = (35.5 + 400)/60 = 7.26 \text{ ppm})$$

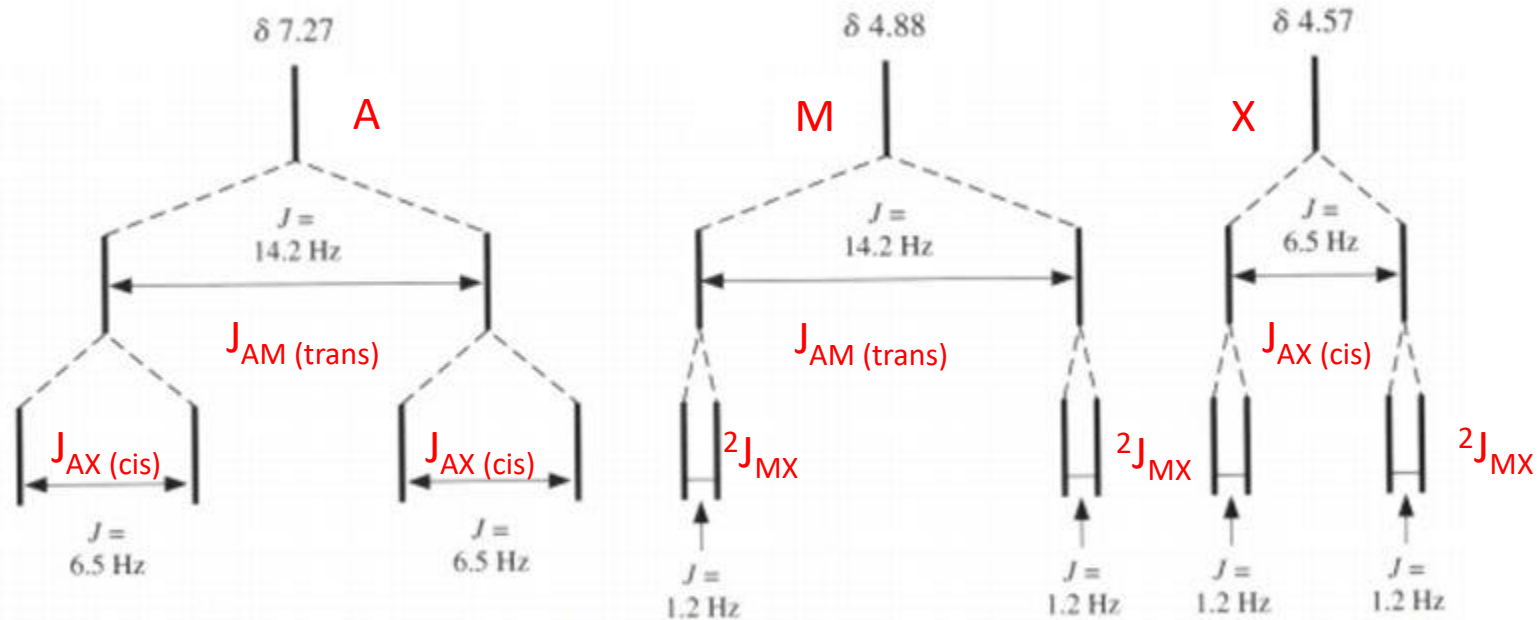
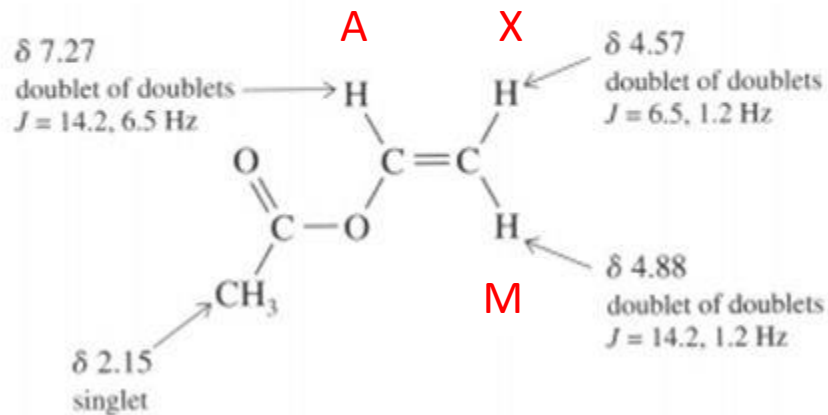
$$|J_{AB}| = |(\nu_1 - \nu_4 + \nu_6 - \nu_8)/3| = |(0 - 15.6 + 32.5 - 40.7)| / 3 = 7.9 \text{ Hz}$$

SISTEMA AMX

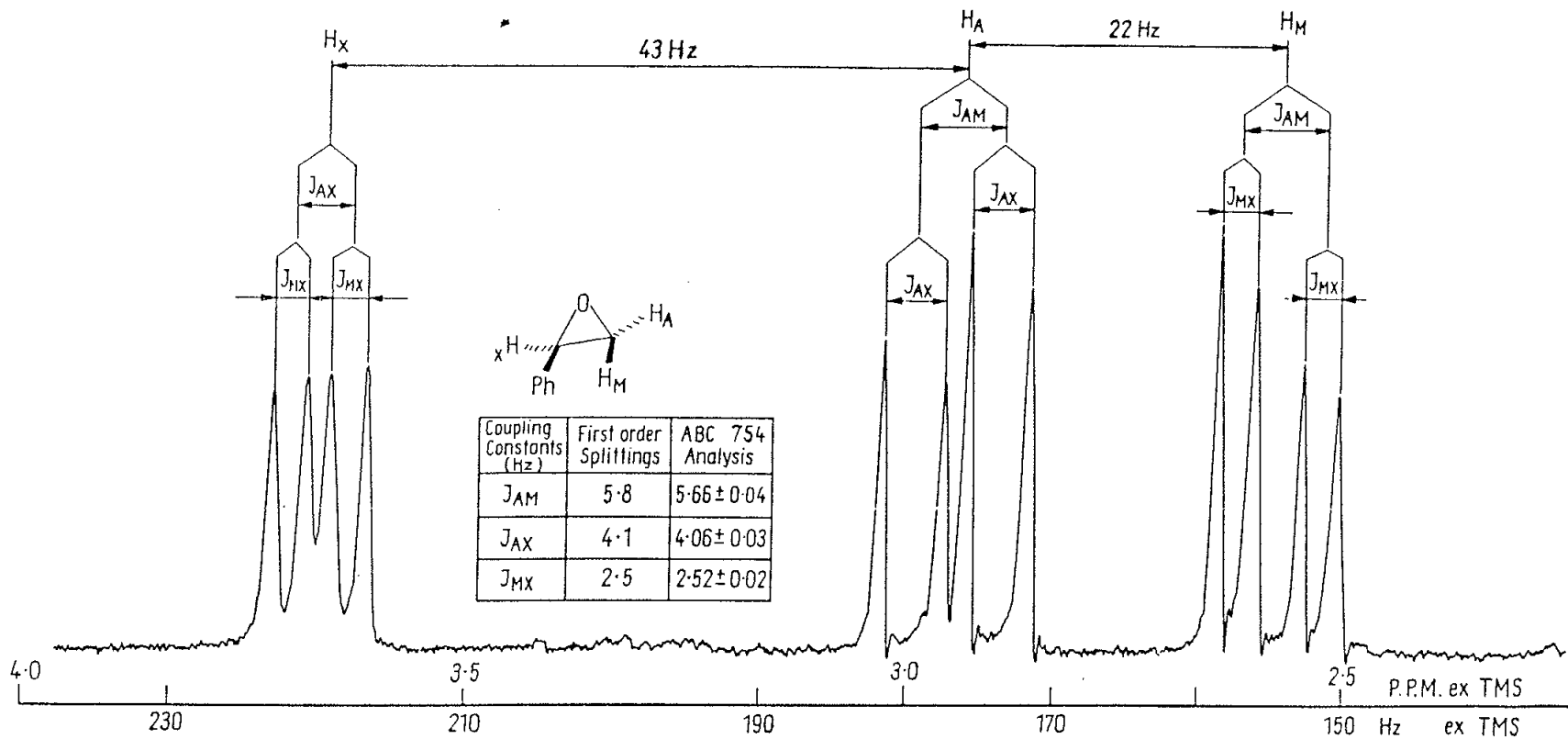
^1H NMR dell' Acetato di Vinile in CDCl_3 a 200MHz (4.7 T)



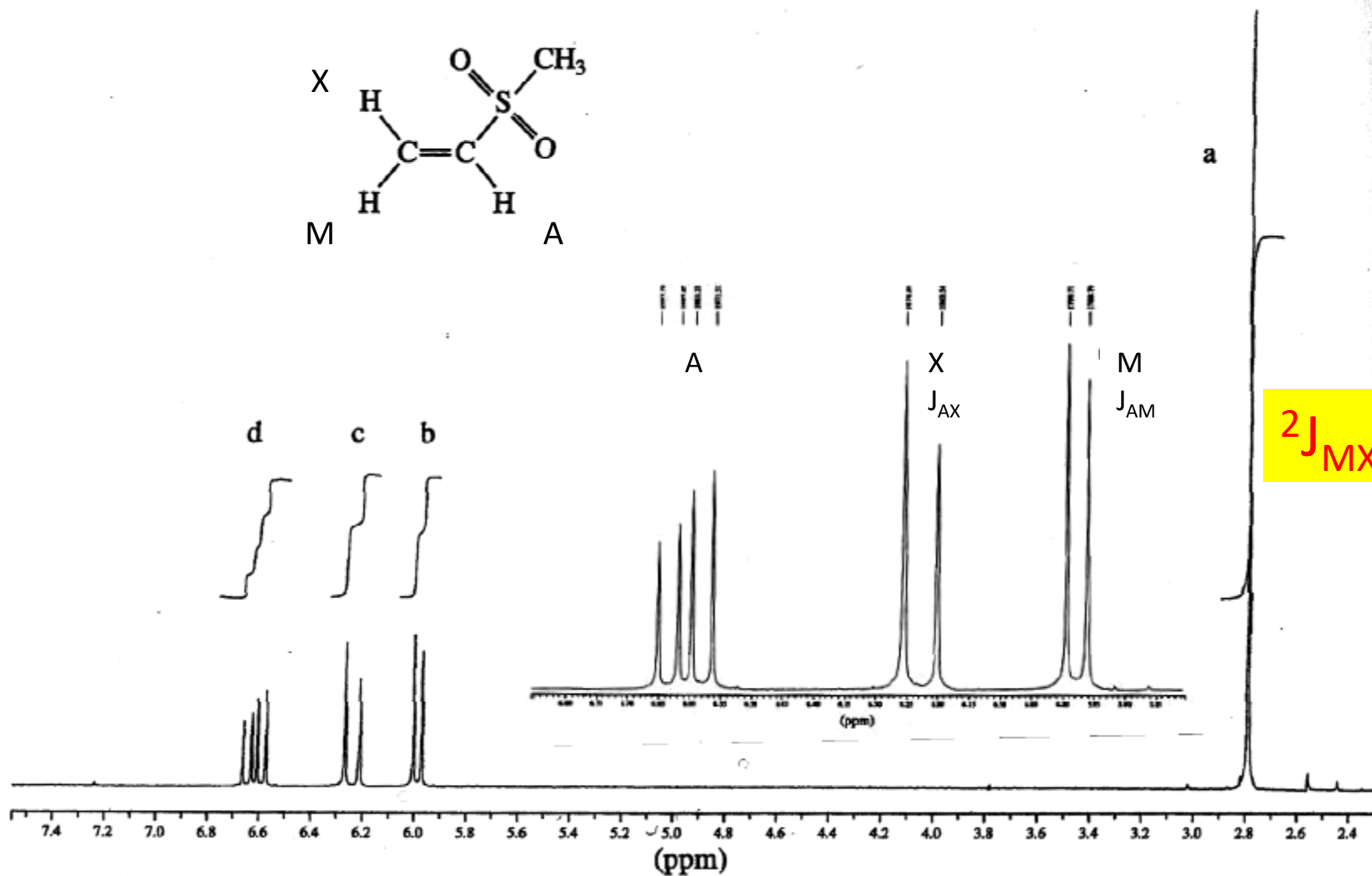
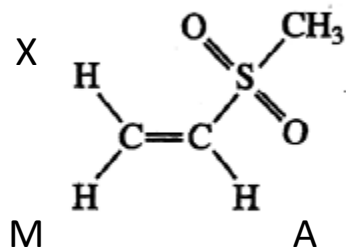
Sistema AMX



SISTEM AMX



Accoppiamento negli alcheni: spettro a 300 MHz



$2J_{MX} = 0!$

AMX \longrightarrow ABX

300 MHz ^1H NMR spectrum in DMSO-d_6

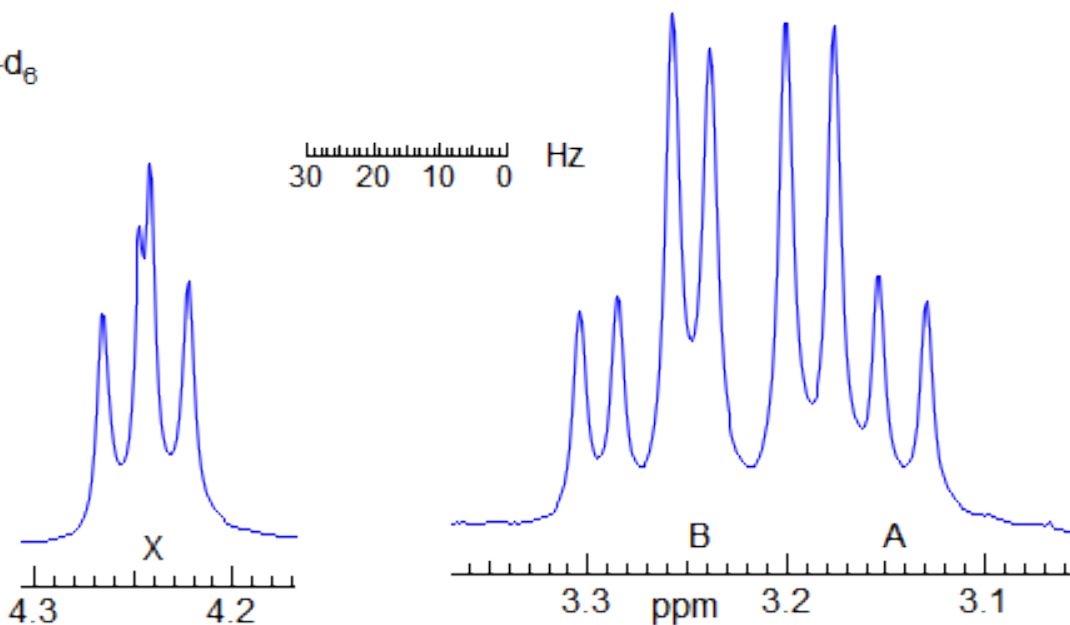
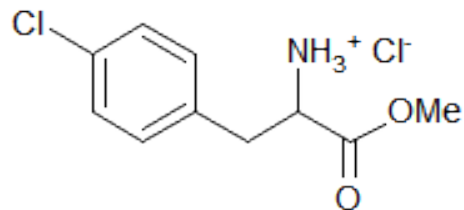


Figure 5-12.1. Sample ABX pattern

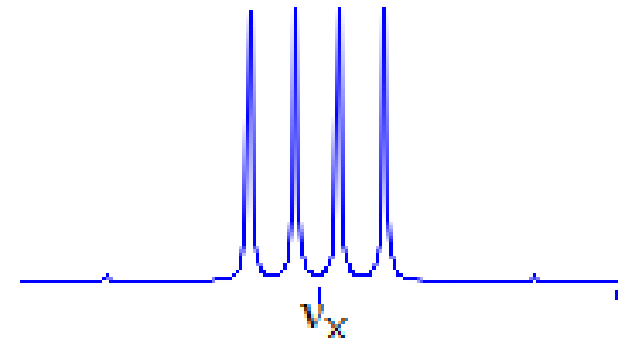
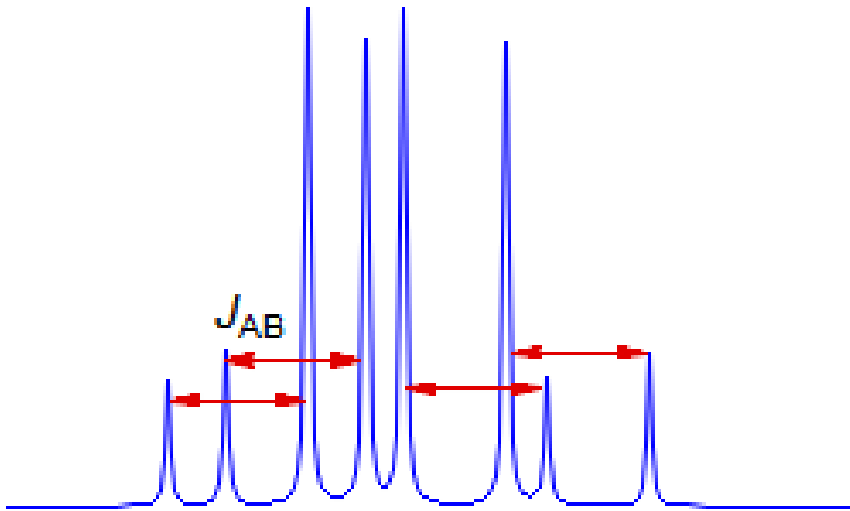
ABX

$\nu_{AB}/J = 2$ (secondo ordine ma AMX-type, ancora interpretabile come primo ordine senza fare grossi errori)

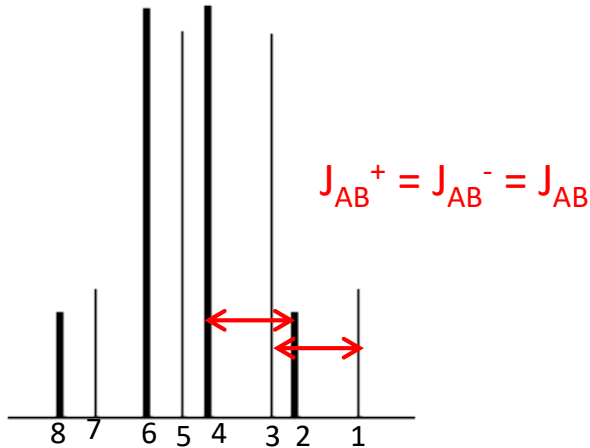
Riconoscere un pattern ABX

Parte AB: due pseudoquartetti AB (8 righe).

J_{AB} and ν_X si misurano direttamente gli altri (J_{AX} , J_{BX} , ν_A , ν_B) devono essere calcolati.

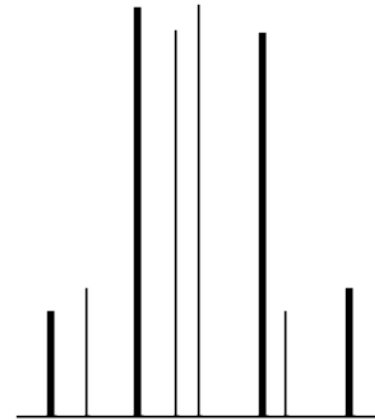


Riconoscere i «quartetti» AB



Correct choice of ab quartets

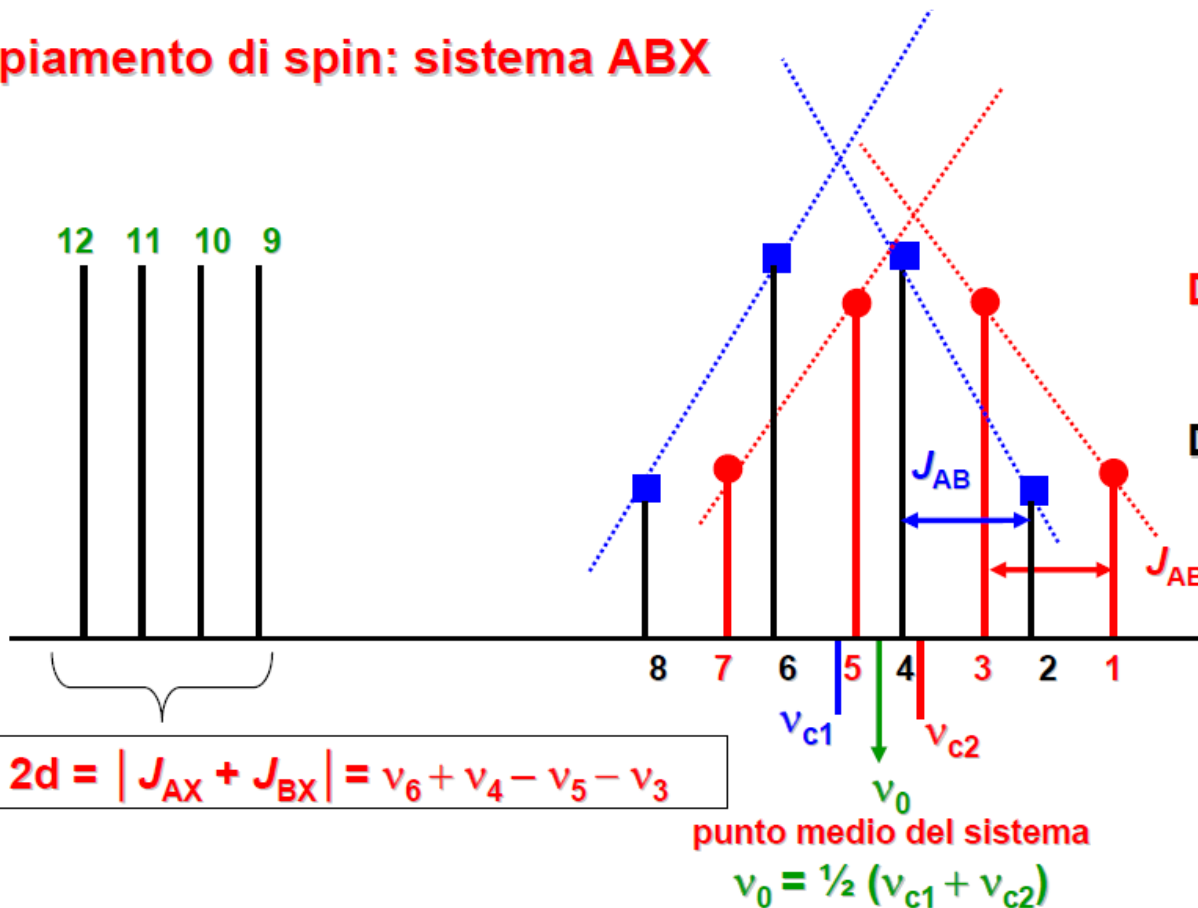
$J_{ab+} = J_{ab-}$, and intensities are OK
(i.e. the ab quartet with more closely spaced inner lines has the smaller outer lines.)



Incorrect ab quartets:

J_{ab} is OK, but intensities are wrong (i.e. the thin ab quartet should have much taller central lines)

Accoppiamento di spin: sistema ABX



$$\frac{1}{2}(v_A - v_B) = \frac{(\sqrt{4D_+^2 - J_{AB}^2} + \sqrt{4D_-^2 - J_{AB}^2})}{4}$$

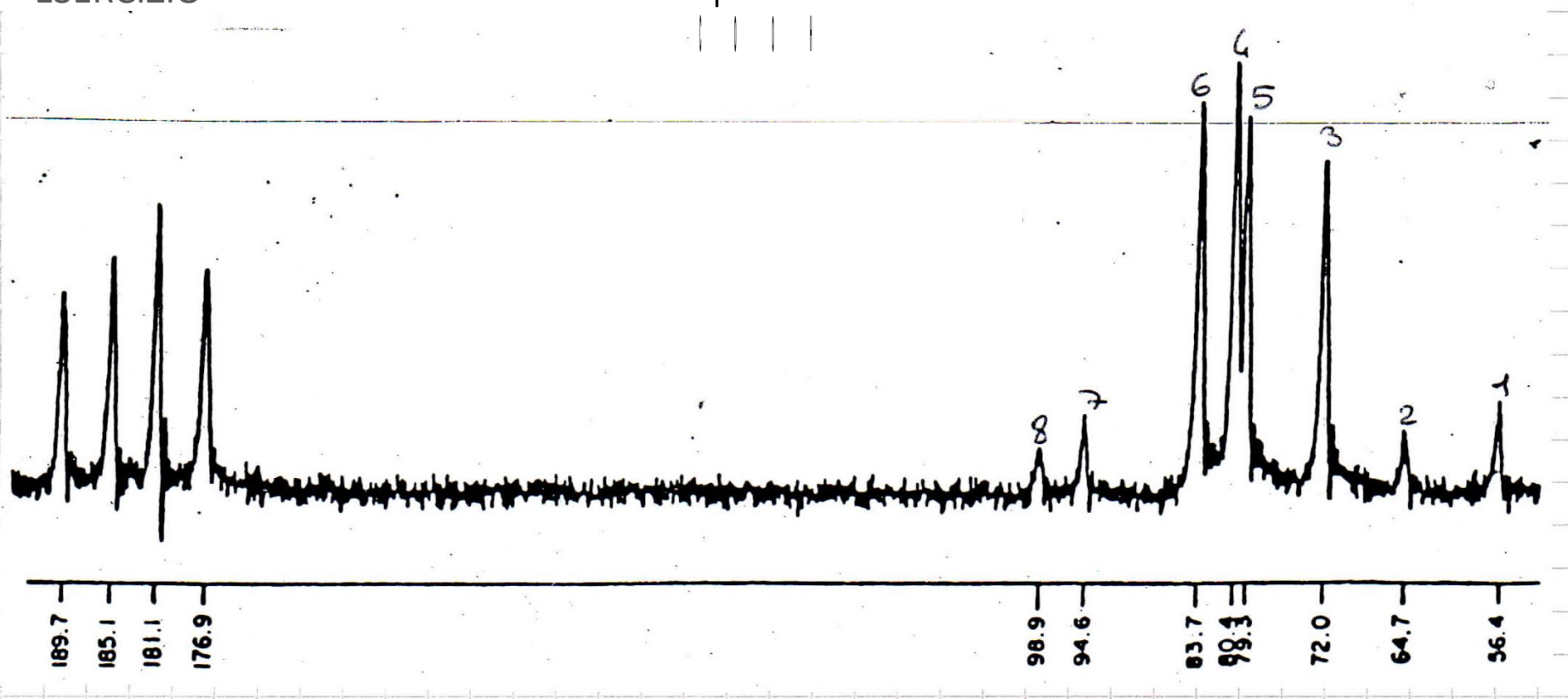
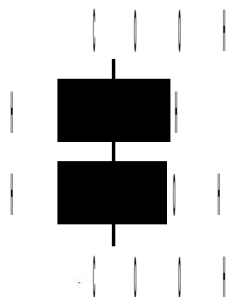
$$J_{AX} = \frac{\sqrt{4D_+^2 - J_{AB}^2} - \sqrt{4D_-^2 - J_{AB}^2} + (v_{12} - v_9)}{2}$$

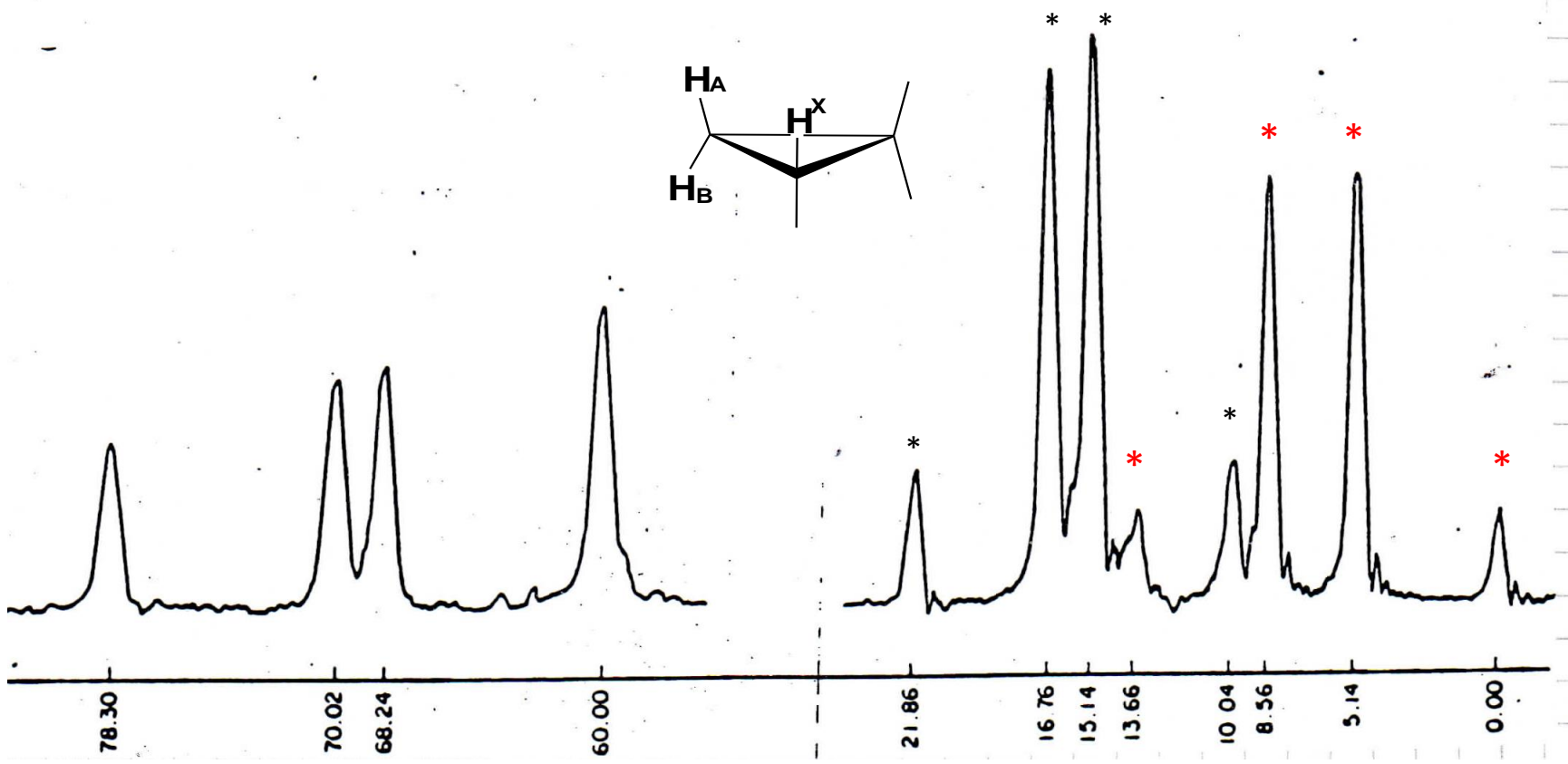
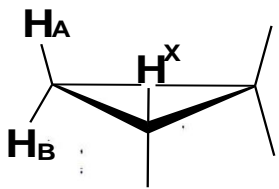
$$v_A = v_0 + \frac{1}{2}(v_A - v_B)$$

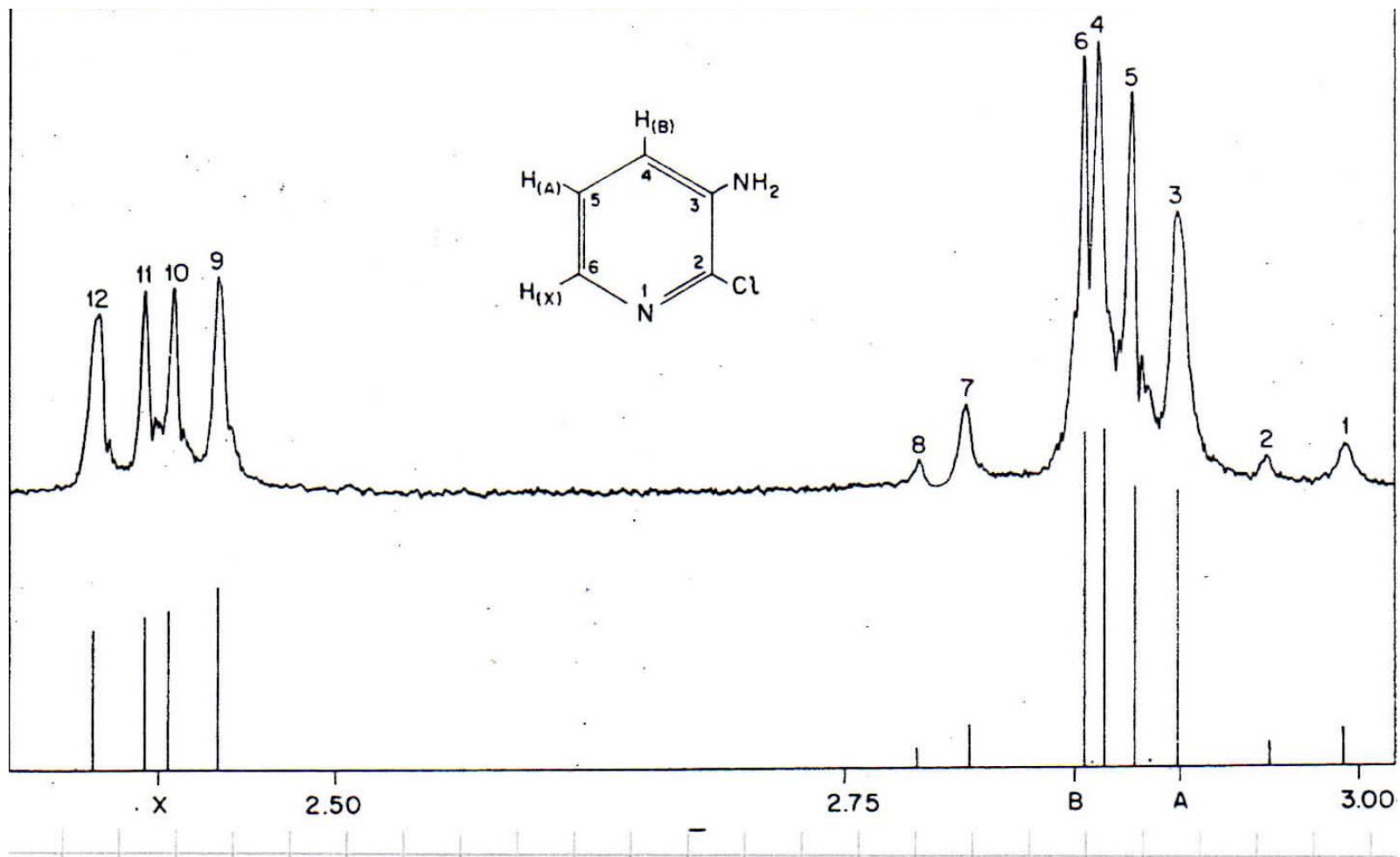
$$v_B = v_0 - \frac{1}{2}(v_A - v_B)$$

$$J_{BX} = (v_{12} - v_9) - J_{AX}$$

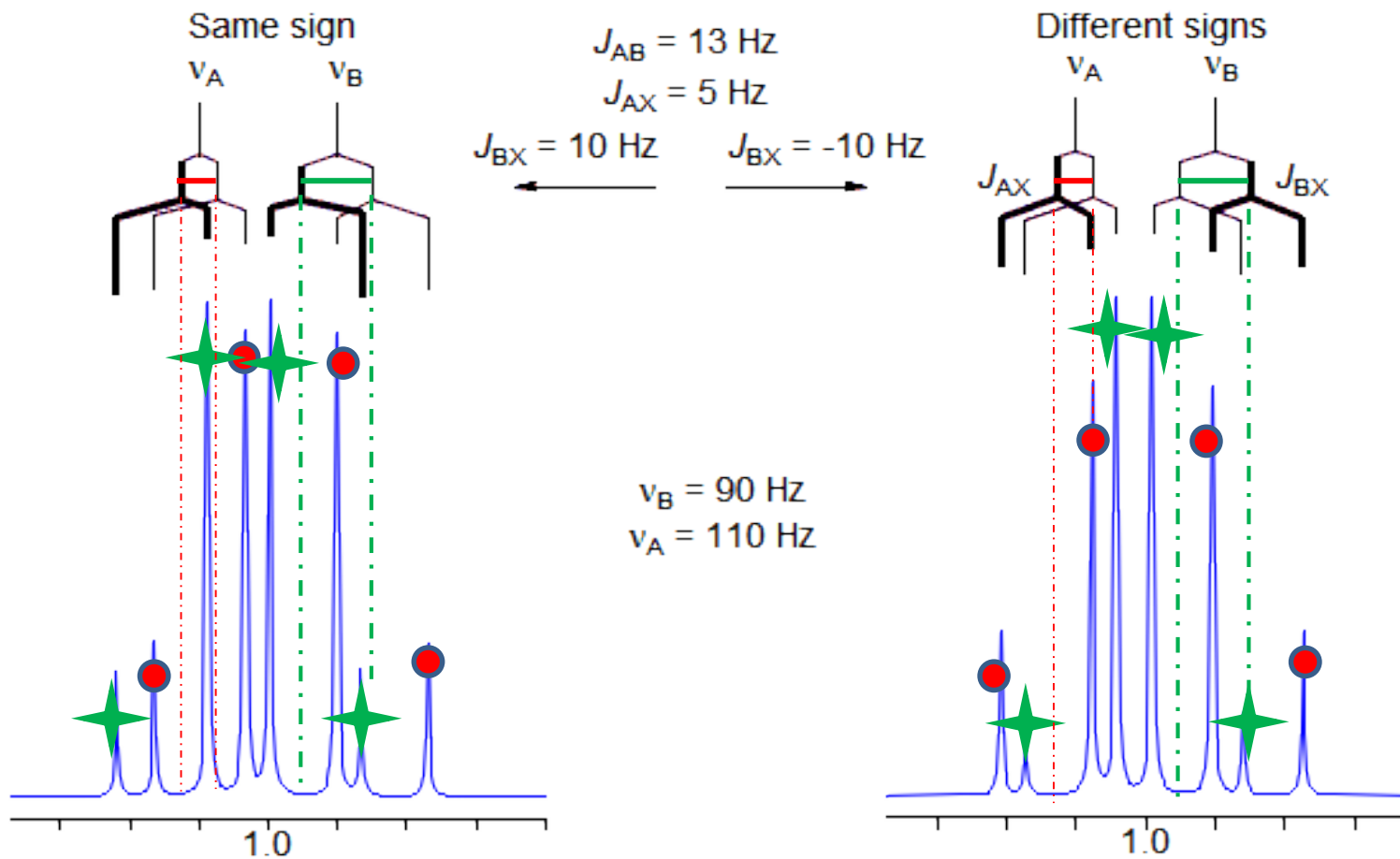
ESERCIZIO





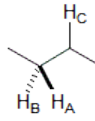


Effect of Relative Sign of J_{AX} and J_{BX} on an ABX pattern



$\nu_C = 270.00$

$J_{AB} = -13$ $\nu_A = 60$
 $J_{AC} = 9$ $\nu_B = 70$
 $J_{BC} = 2$ ν_C varies



$\nu_C = 210.00$

$\nu_C = 170.00$

$\nu_C = 120.00$

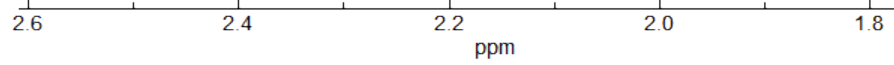
$\nu_C = 100.00$

$\nu_C = 90.00$

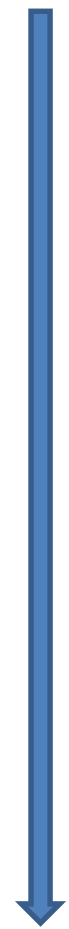
$\nu_C = 80.00$

How badly off are we, if we treat this as an AMX pattern. taking the peaks at face value?

$J_{AB} = 12.6, 11.3$ (actual: 13)
 $J_{AC} = 8.4, 7.1, 8.7$ (actual: 9)
 $J_{BC} = 1.8, 3.2, 3.2$ (actual 2)



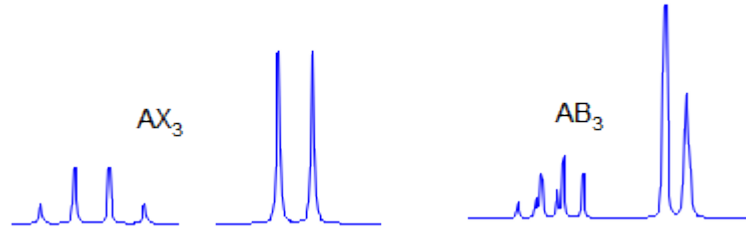
ABX



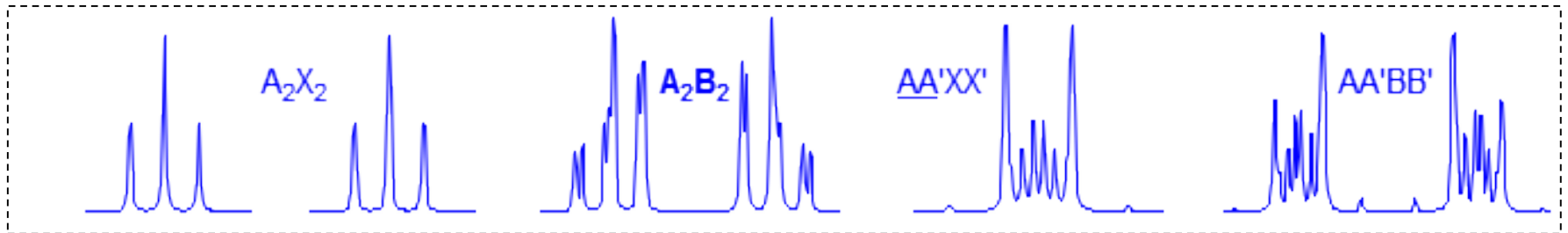
ABC

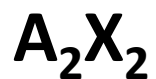
SISTEMI A QUATTRO SPIN

AX_3, AB_3



A_2X_2, A_2B_2
 $AA'XX' (AA'BB')$

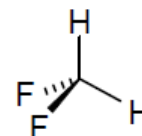
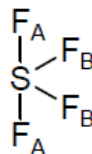
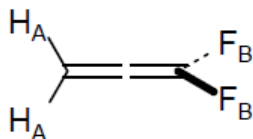
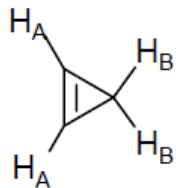




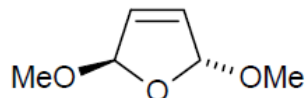
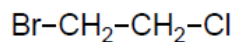
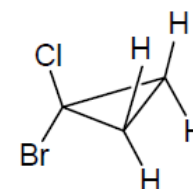
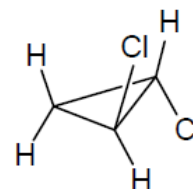
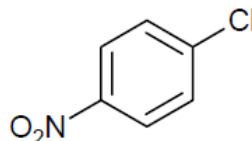
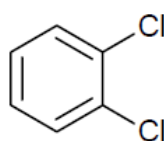
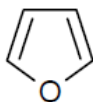
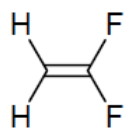
2 nuclei magneticamente equivalenti A accoppiano con 2 nuclei equivalenti X (B)

Veri A_2X_2 piuttosto rari

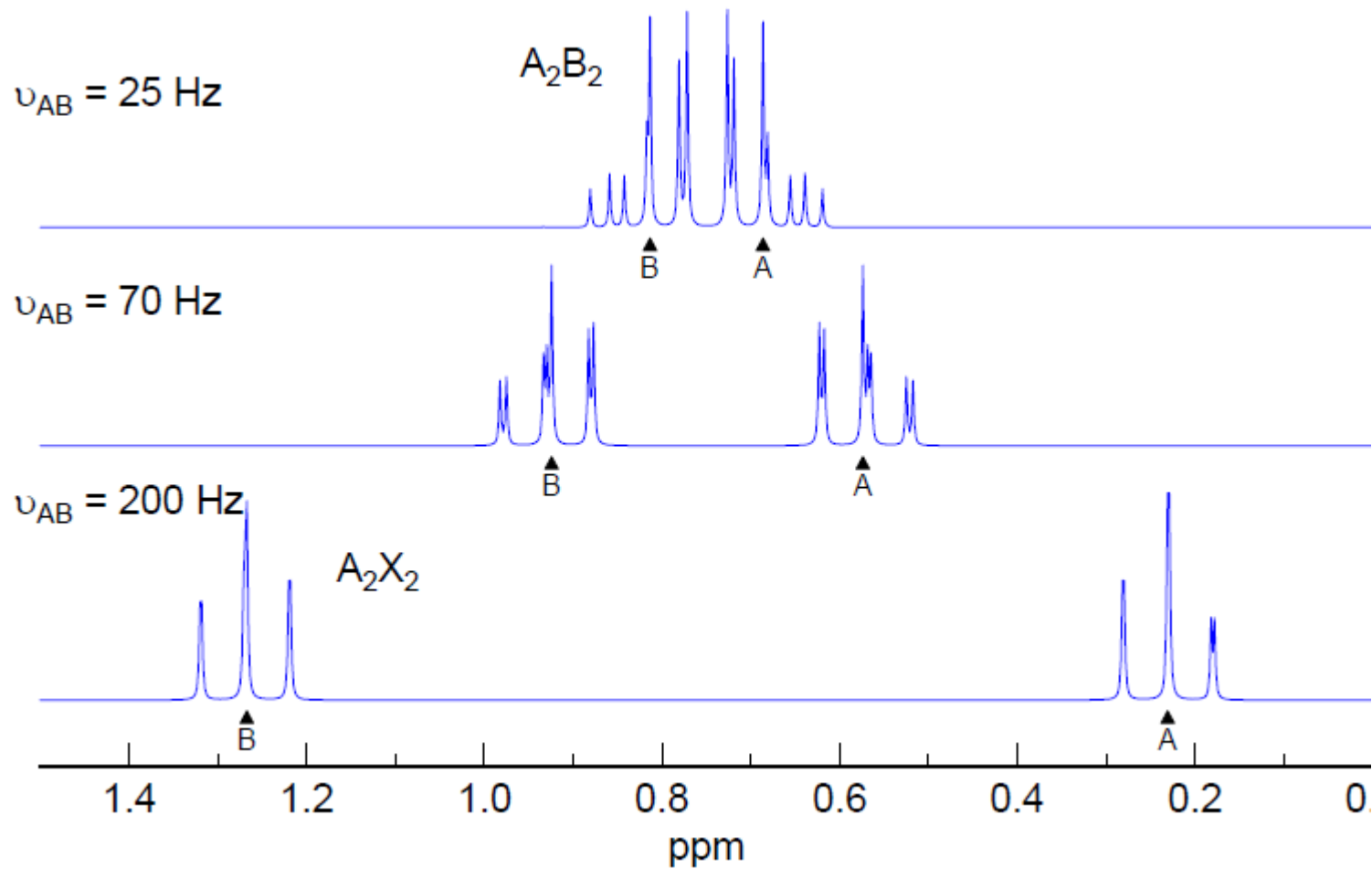
Esempi



Molto più comuni

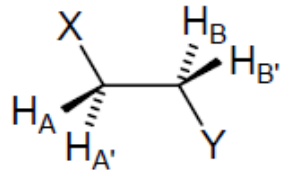


Se coincidentalmente $J_{AB} = J_{A'B'}$ allora il sistema diventa A_2B_2 o A_2X_2

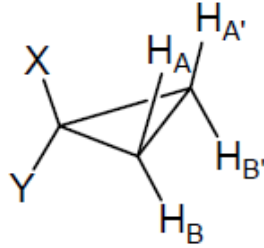


AA'XX'

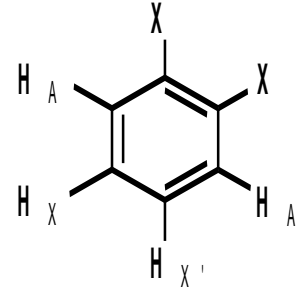
(AA'BB')



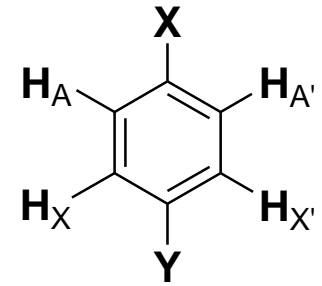
(a) AA'-Gem



(b) AA'-Vic



(c) ODCB



(c) p-DB

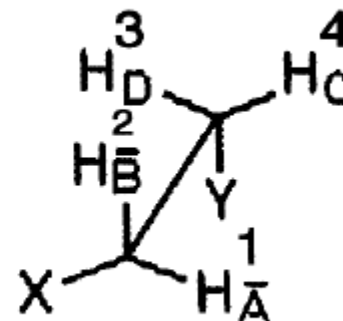
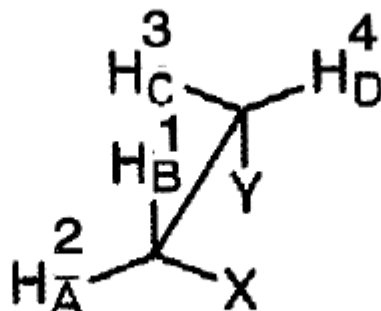
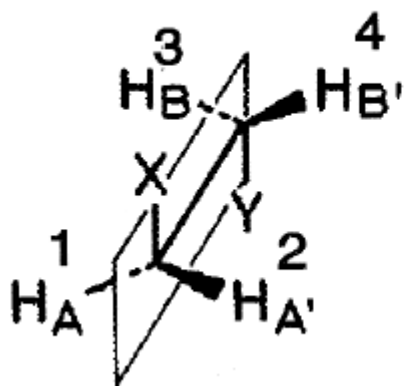
AA'XX': sistema a 4 spin in cui due nuclei chimicamente equivalenti (A) ma magneticamente non equivalenti accoppiano tra di loro e con due nuclei (X) chimicamente equivalenti ma magneticamente non equivalenti. Lo spettro è complesso e del secondo ordine con qualunque campo magnetico.

AA'XX' non è un sistema di spin del primo ordine indipendentemente dal campo applicato:

- i profili dei multipletti NON corrispondono a quelli previsti dal triangolo di Pascal
- le costanti di accoppiamento NON corrispondono alle distanze tra i picchi
- AA'XX' 20 righe, ogni parte AA' e XX' ha 10 righe con pattern centrosimmetrico
- AA'BB' 24 righe, la parte AA' e BB' non centrosimmetriche, il segnale nel suo complesso è centrosimmetrico

ACCOPPIAMENTO DI SPIN NEI SISTEMI IN ROTAZIONE

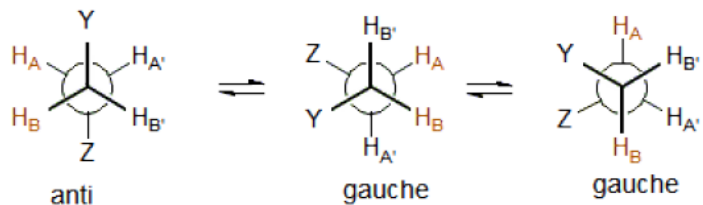
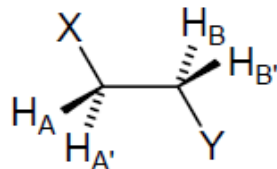
Caso di gruppi CH_2 in sistemi conformazionalmente liberi non chirali, quindi in cui gli H del CH_2 non sono diastereotopici.



In sistemi a catena aperta la libera rotazione può mediare il valore dei chemical shift nei vari conformeri rendendo i protoni H^1 e H^2 chimicamente equivalenti così come i protoni H^3 e H^4 . Lo stesso non può dirsi per il valore delle costanti di accoppiamento (ad es. $J_{\text{H}^1-\text{H}^3}$, $J_{\text{H}^1-\text{H}^4}$ sono diverse nei diversi conformeri) pertanto si può osservare un sistema semplice A_2X_2 (A_2B_2) oppure un sistema più complesso del tipo $\text{AA}'\text{XX}'$ ($\text{AA}'\text{BB}'$), a seconda della distribuzione dei conformeri

AA' gem

$$J_{AB} \neq J_{AB'}$$



$J_{AB} = 2.3$	$J_{AB} = 2.3$	$J_{AB} = 12$
$J_{AB'} = 12$	$J_{AB'} = 2.3$	$J_{AB'} = 2.3$

Per una distribuzione statistica dei 3 conformeri (33% l'uno, Y e Z piccoli)

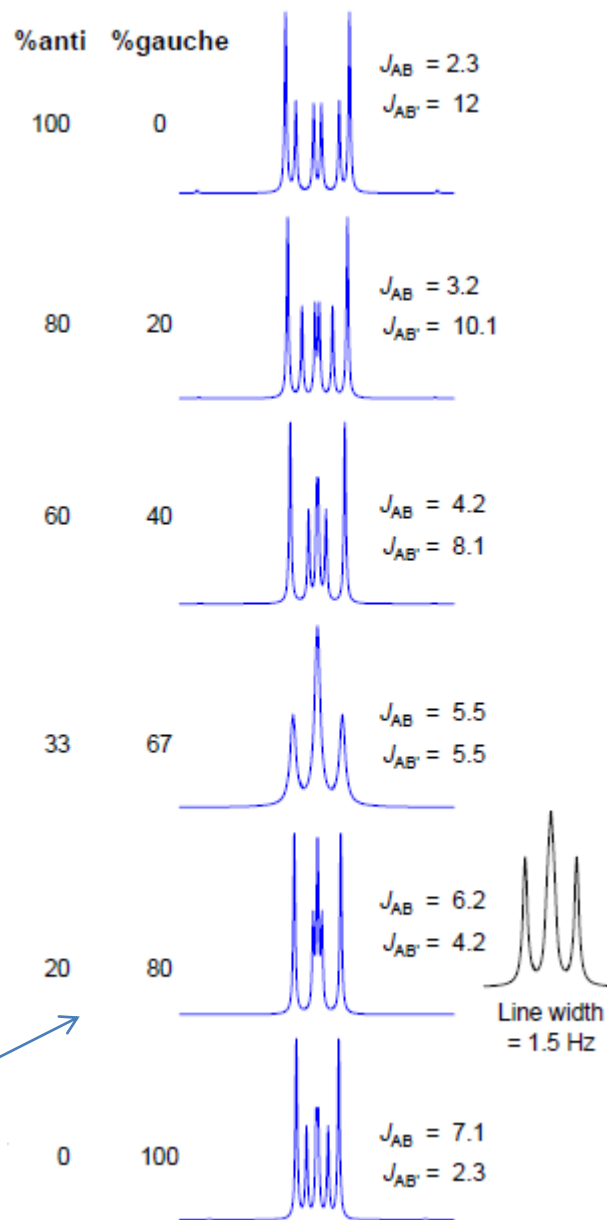
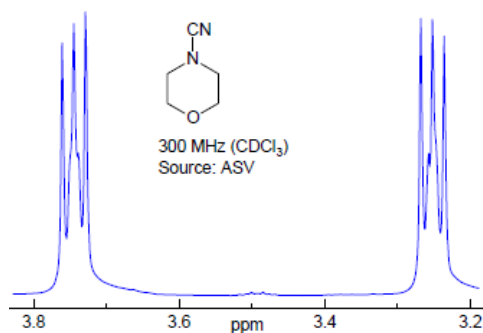
$$J_{AB} = (0.33)(2.3) + (0.33)(2.3) + (0.33)(12) = 5.46 \text{ Hz} \quad A_2X_2$$

$$J_{AB'} = (0.33)(12) + (0.33)(2.3) + (0.33)(2.3) = 5.46 \text{ Hz} \quad (A_2B_2)$$

Per una distribuzione dei 3 conformeri 0.6 (anti) / 0.4 (gauche)

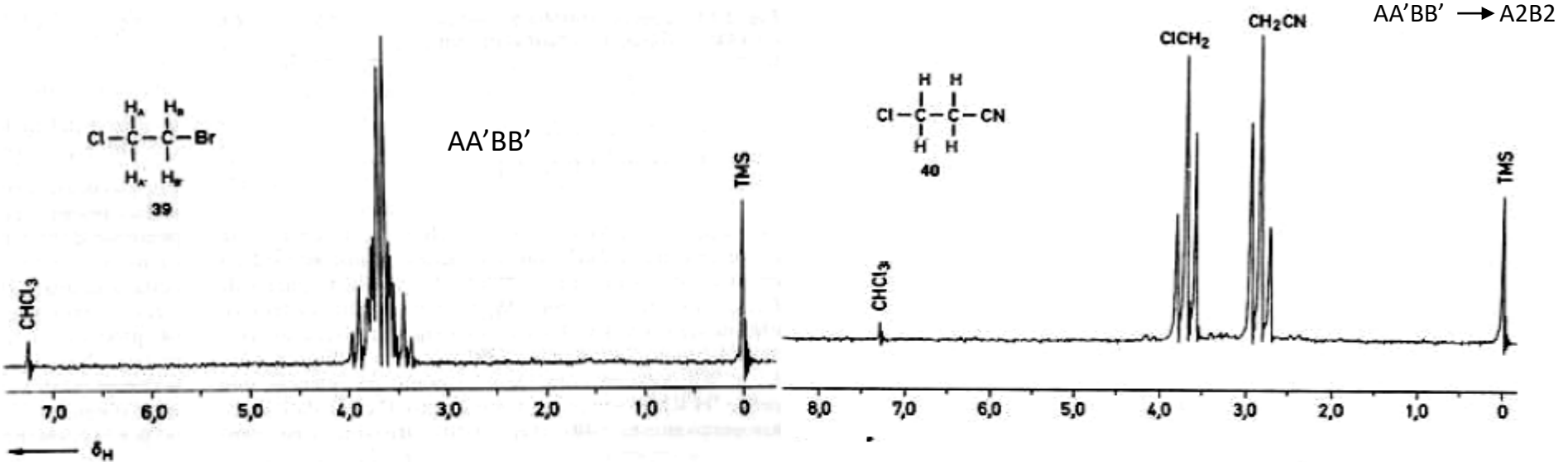
$$J_{AB} = (0.6)(2.3) + (0.2)(2.3) + (0.2)(12) = 4.24 \text{ Hz} \quad AA'XX'$$

$$J_{AB'} = (0.6)(12) + (0.2)(2.3) + (0.2)(2.3) = 8.12 \text{ Hz} \quad (AA'BB')$$

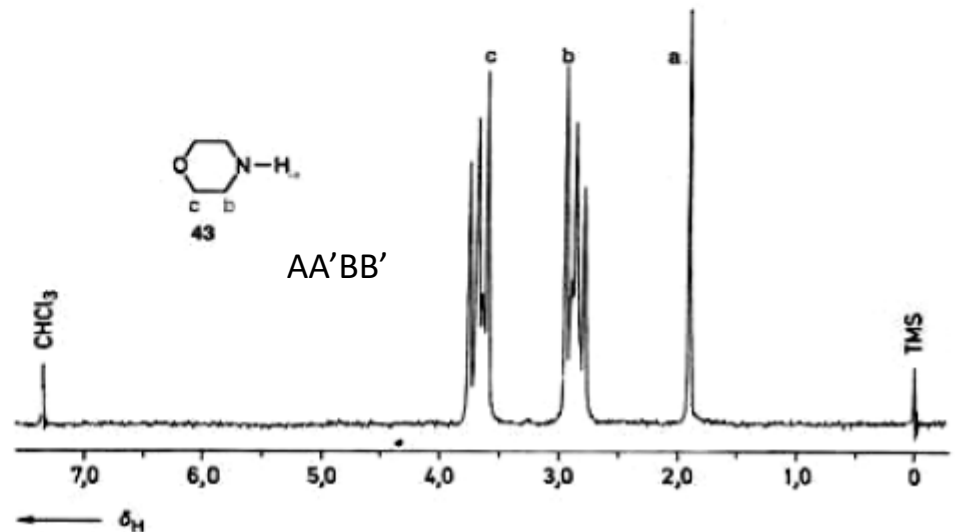
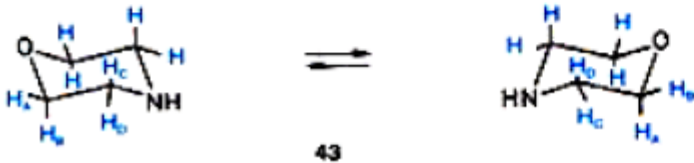


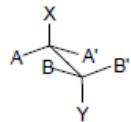
Accoppiamento di spin

Mobilità intramolecolare

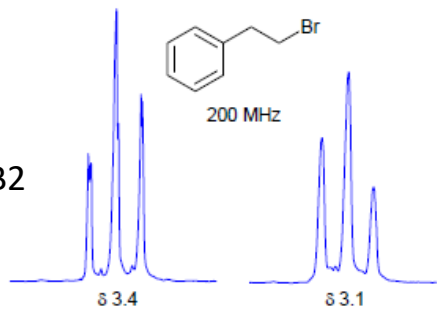


Il rapido equilibrio a Tamb. rende i protoni A e B chimicamente equivalenti ma non magneticamente equivalenti e pertanto un sistema AA'MM' verrà osservato.



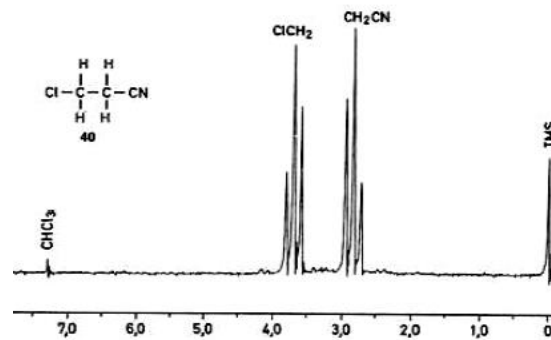
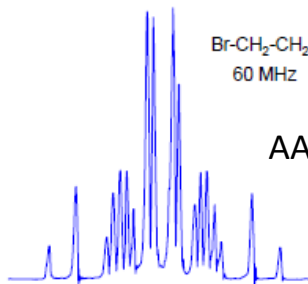


A2B2

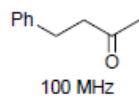


Br-CH₂-CH₂-Cl
60 MHz

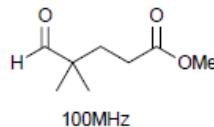
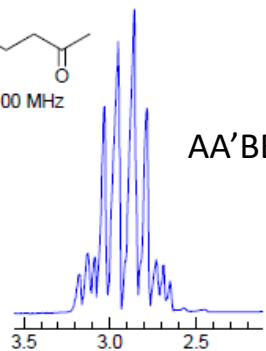
AA'BB'



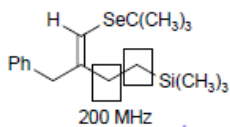
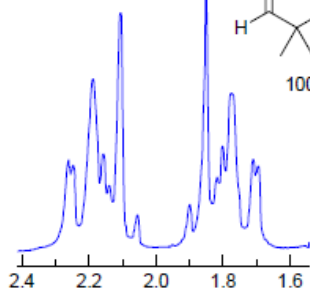
A2B2



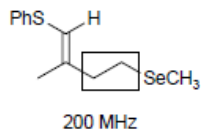
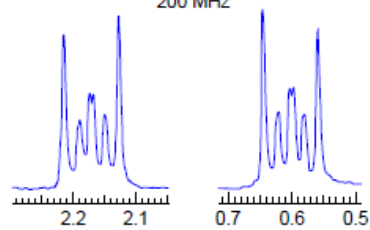
AA'BB'



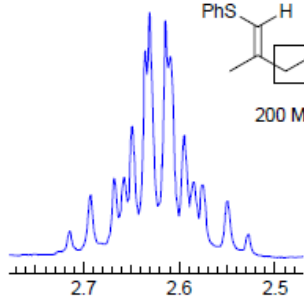
AA'BB'



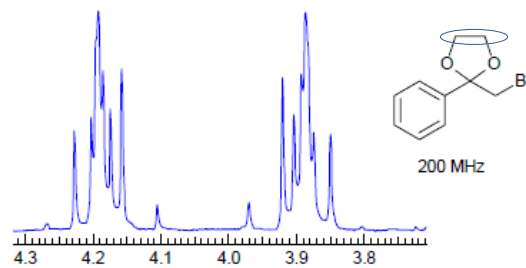
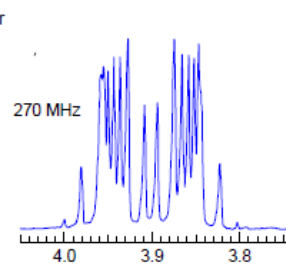
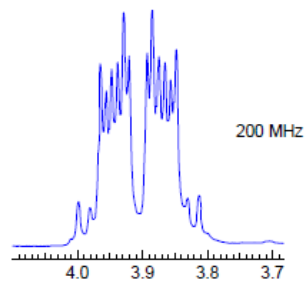
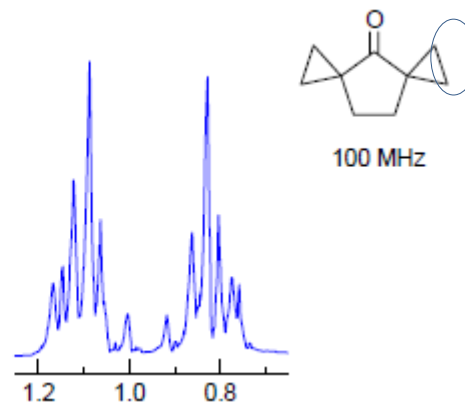
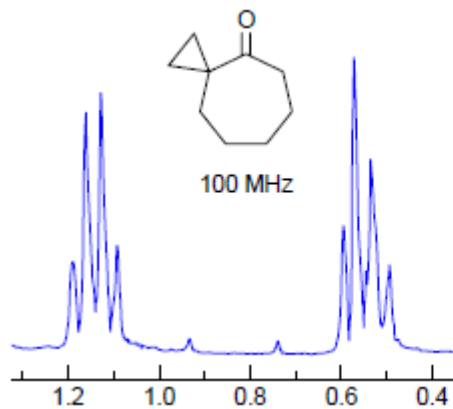
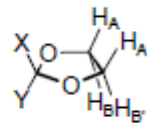
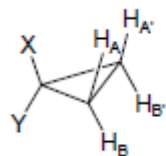
AA'XX'



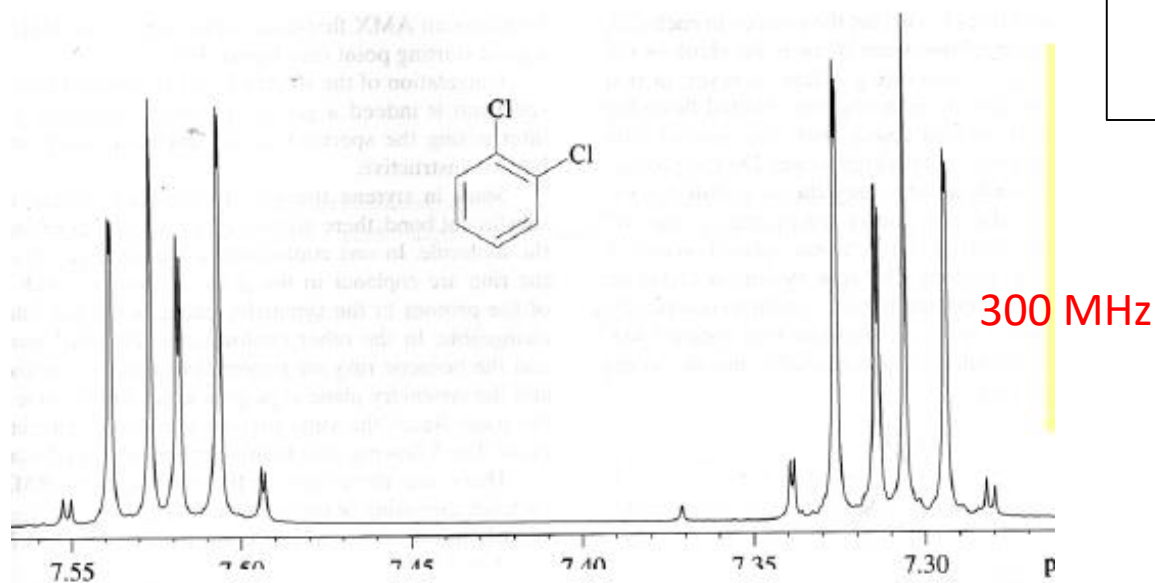
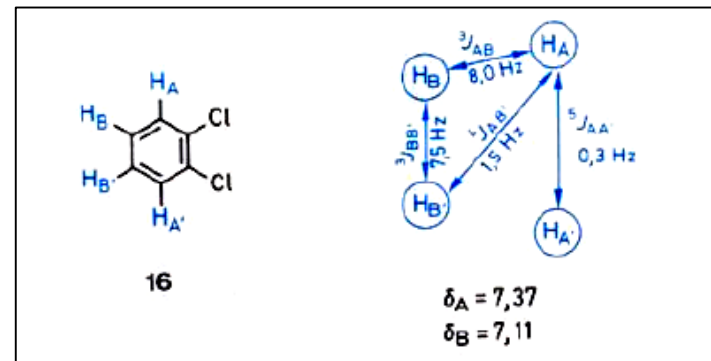
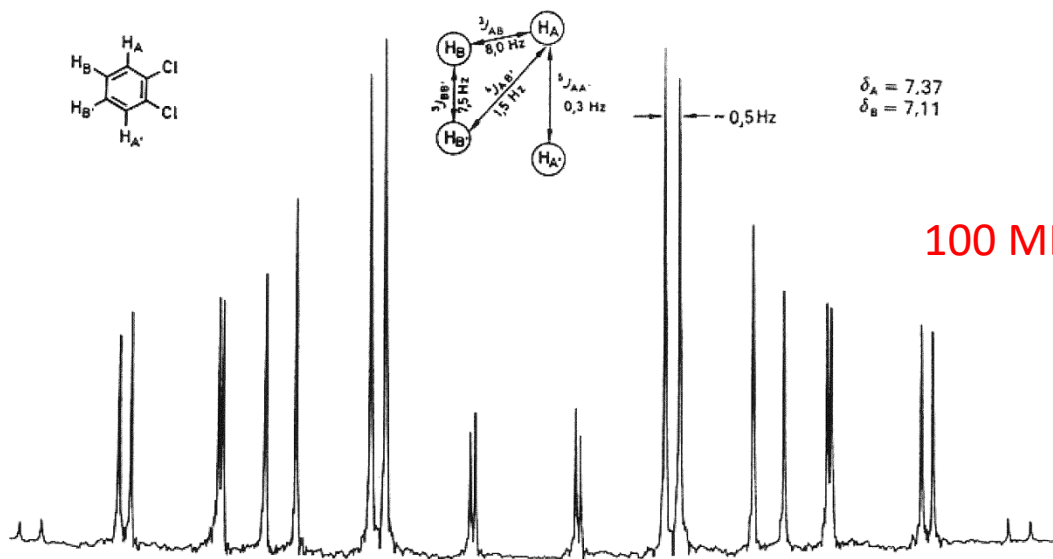
AA'BB'



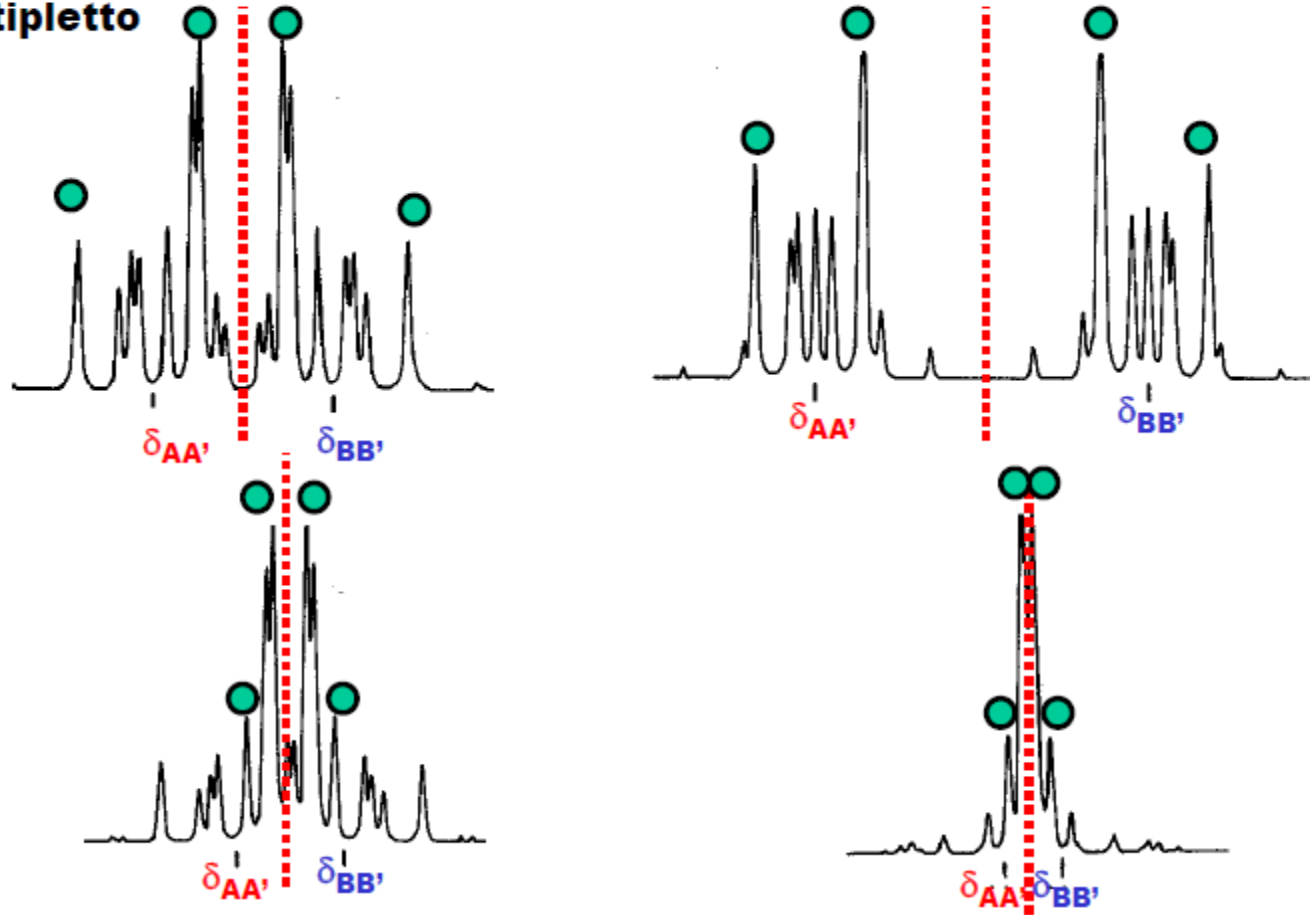
AA'-vic



AA'-ODCB

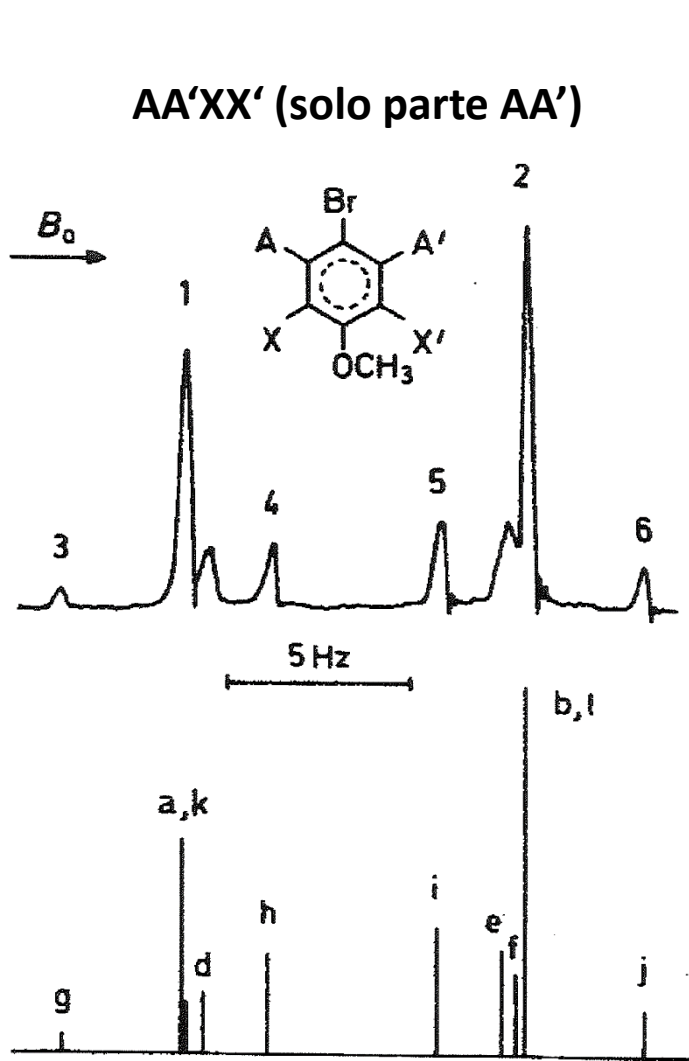


Un sistema del 2° ordine di tipo AA'BB' è molto complicato ma è caratterizzato da un elemento di simmetria costituito dal piano ortogonale che taglia a metà il multipletto

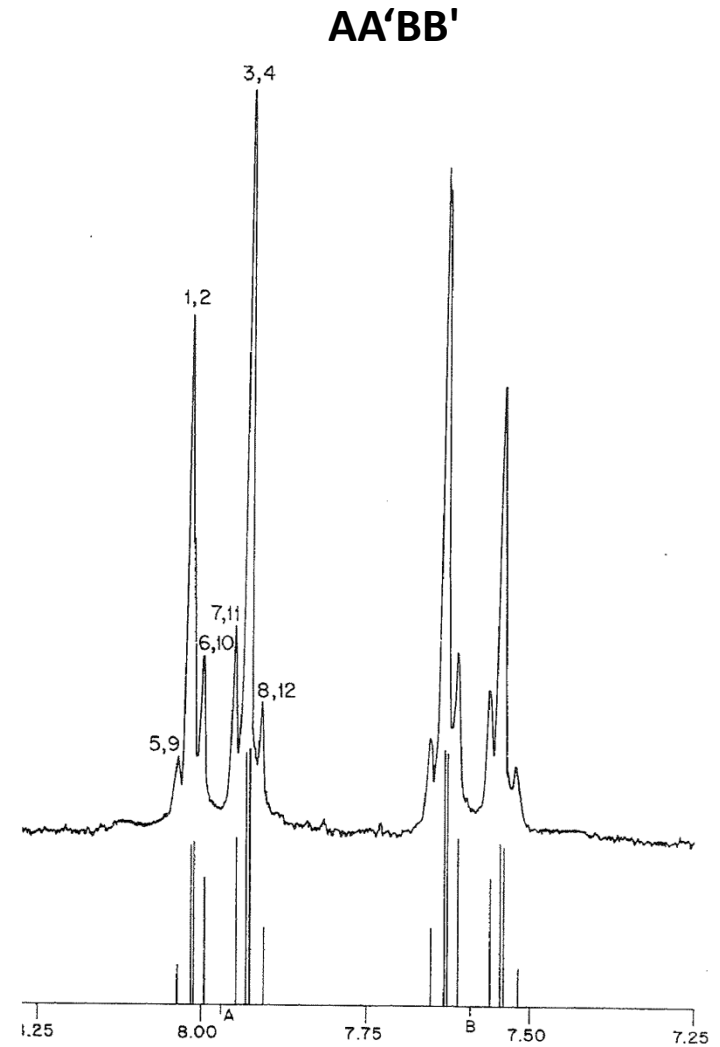


In molti casi il sistema è “apparentemente” semplice in quanto si vedono solo 4 segnali più intensi (qui marcati con un pallino) che lo rendono simile ad un sistema AB

AA'-p-disubstituted-benzene

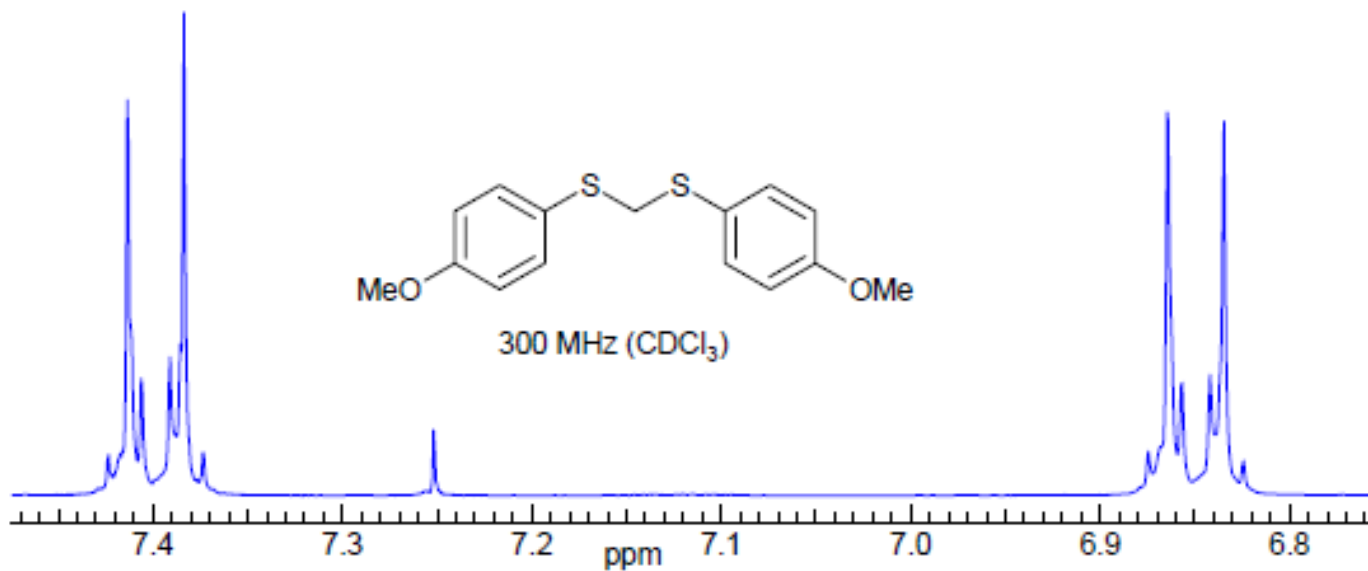


Solo la parte AA'!

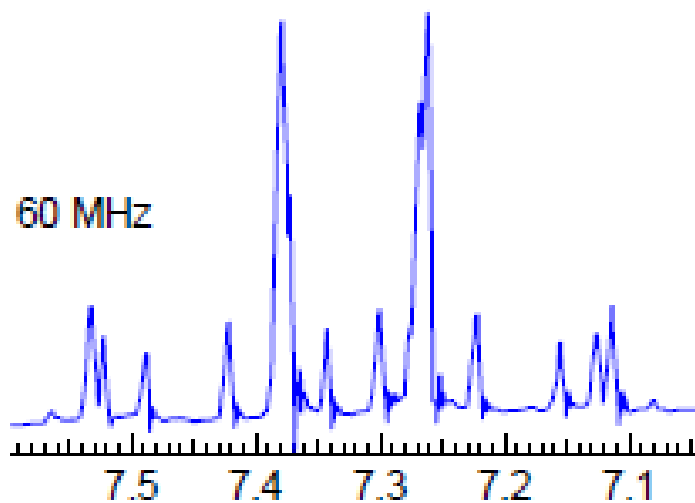


p-Clorobenzaldeide

AA'XX'

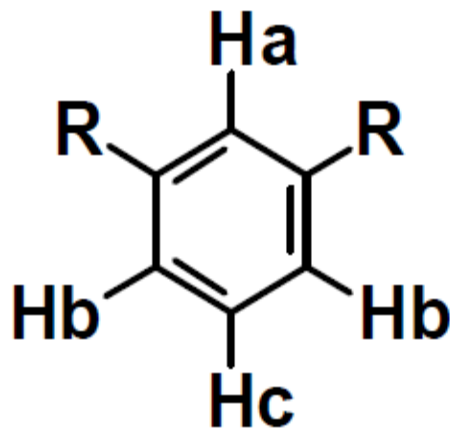


AA'BB'



AB₂C

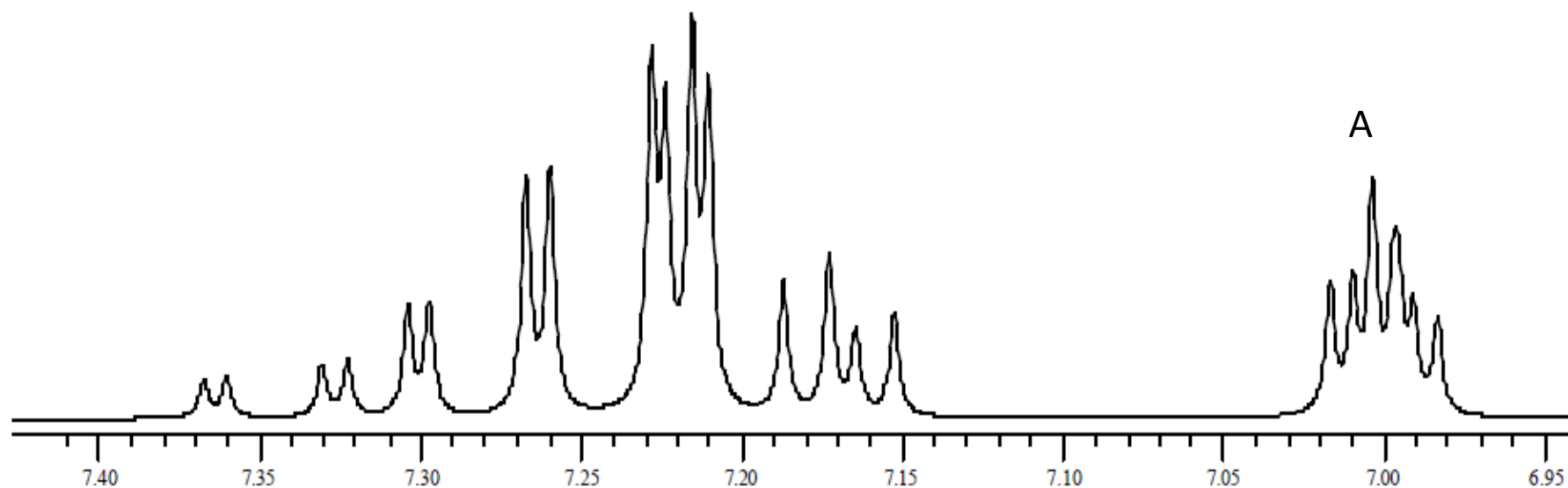
Benzene meta disostituito
con due sostituenti uguali



$${}^3J_{BC} = 7-8 \text{ Hz}$$

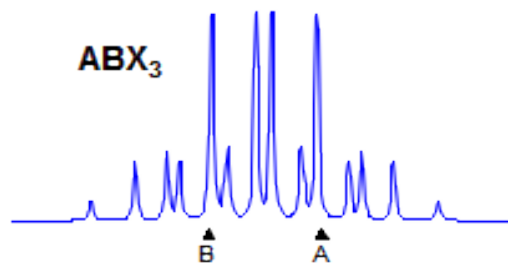
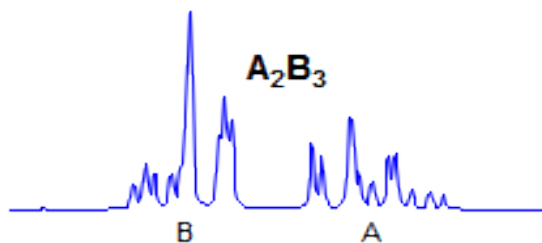
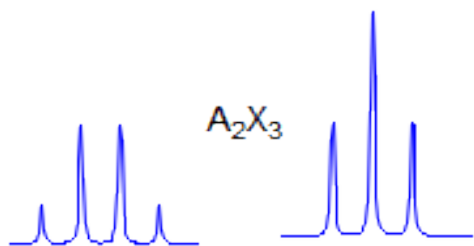
$${}^4J_{AB} = 1-2 \text{ Hz}$$

$${}^5J_{AC} = 0-0.5 \text{ Hz}$$



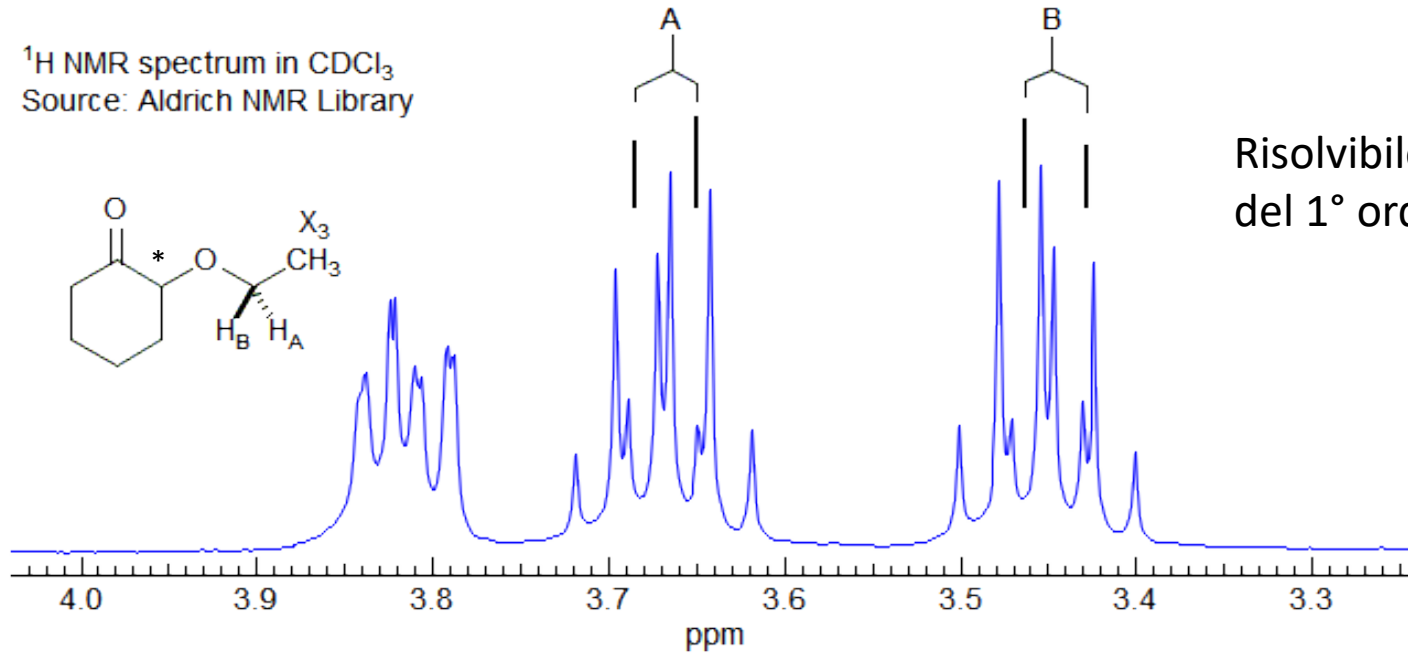
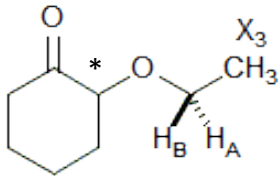
SISTEMI A CINQUE SPIN

A_2X_3 , A_2B_3
 ABX_3



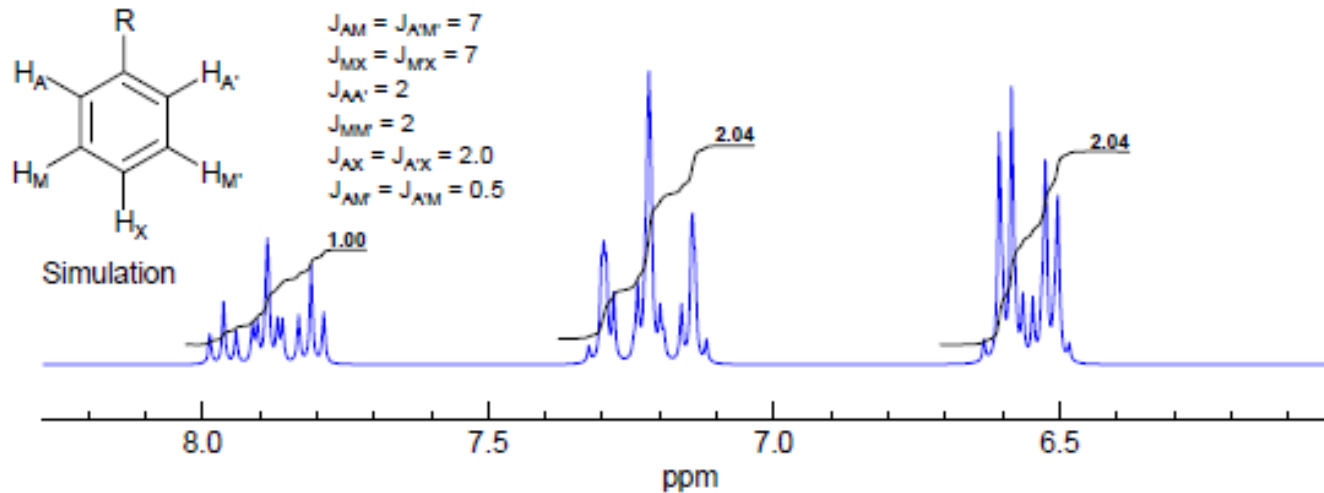
ABX₃

¹H NMR spectrum in CDCl₃
Source: Aldrich NMR Library

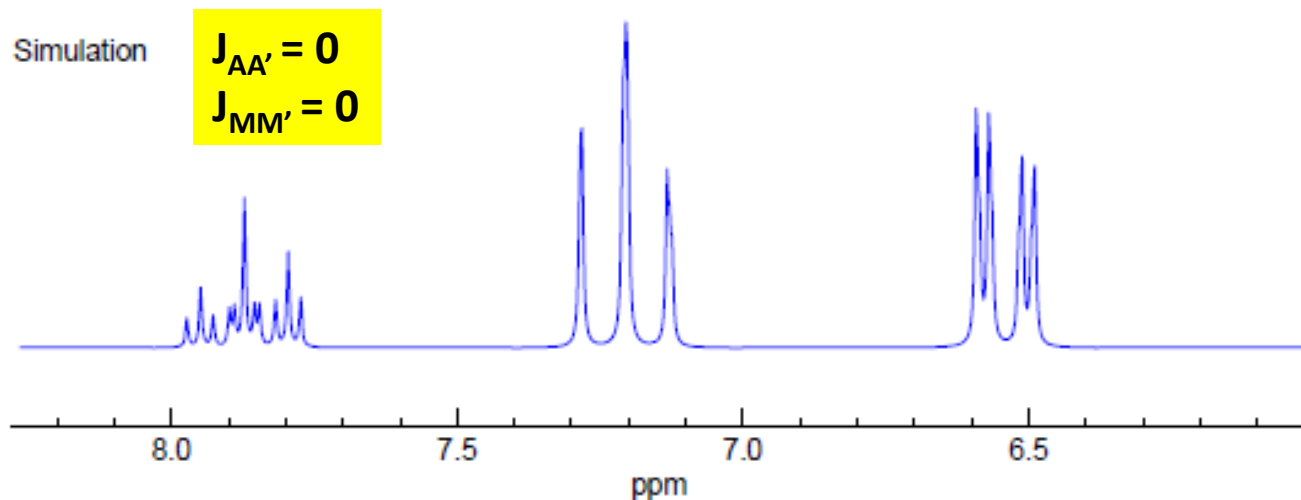


Risolubile come multipletto
del 1° ordine ddq

Benzene monosostituito: sistema AA'MM'X (AA'BB'X, AA'BB'C)



If we recalculate the spectrum after setting $J_{AA'} = 0$ and $J_{MM'} = 0$ then the spectrum becomes essentially first order (it would be completely first order if the chemical shifts between A, M and X were made larger).



MULTIPLIETTI DEL PRIMO ORDINE

MULTIPLIETTI DEL PRIMO ORDINE

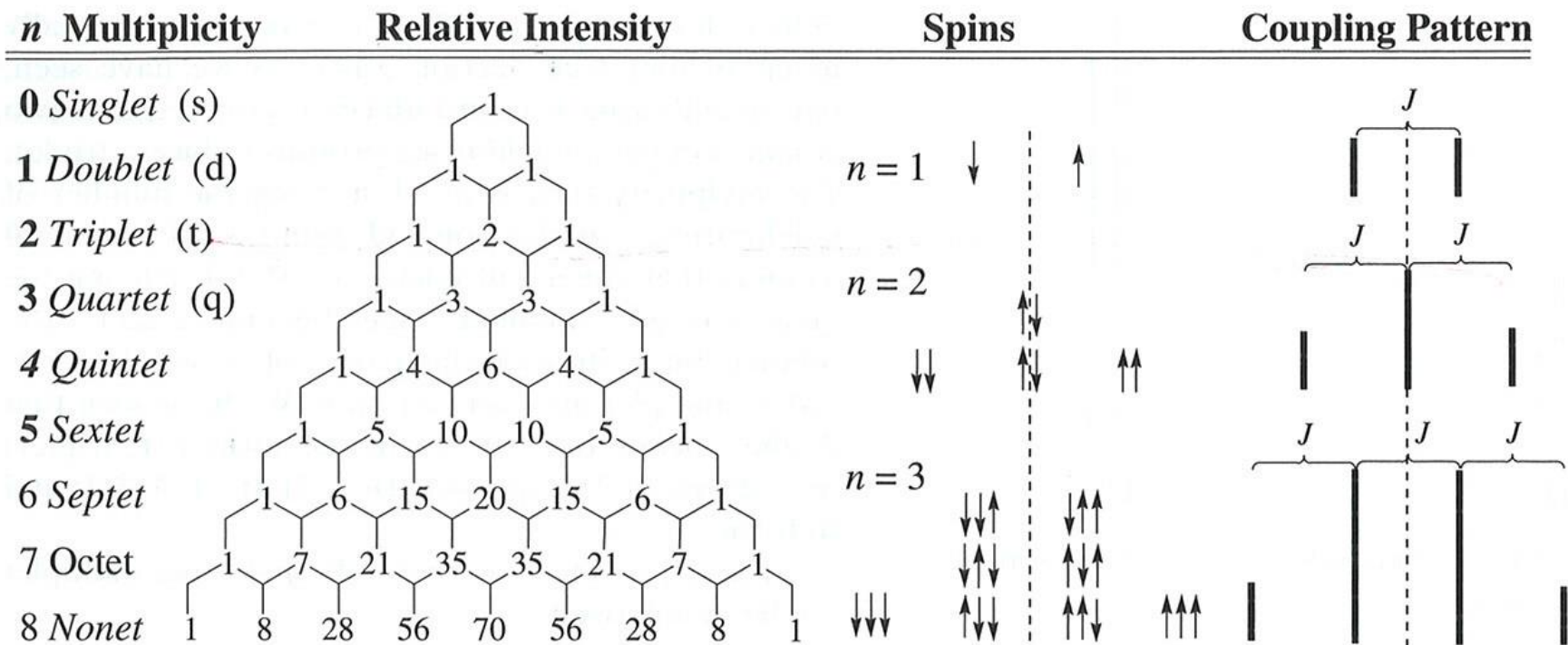


FIGURE 3.32 Pascal's triangle. Relative intensities of first-order multiplets; n = number of equivalent coupling nuclei of spin $1/2$ (e.g., protons).

MULTIPLIETTI DEL PRIMO ORDINE

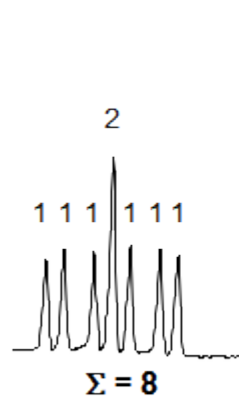
1. Tutti i multipletti del primo ordine sono centrosimmetrici. (a parte qualche distorsione possibile).

Ma ATTENZIONE: non tutti i multipletti centrosimmetrici sono del 1° ordine.

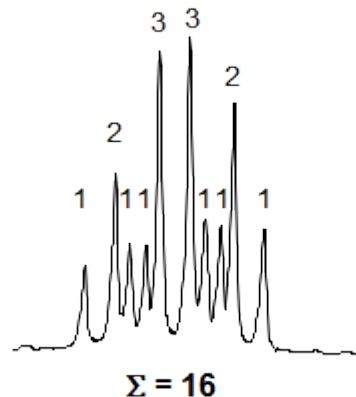
2. Assegnando intensità 1 al picco più esterno, gli altri devono avere intensità multipla secondo numeri interi (1x, 2x, 3x, 4x in altezza), e l'intensità totale deve essere una potenza di 2 (2, 4, 8, 16, 32, etc).

L'intensità di ciascuna riga esterna deve essere dunque $1/2^n$ dell'intensità totale dove n è il numero di protoni accoppiati con quello che si analizza.

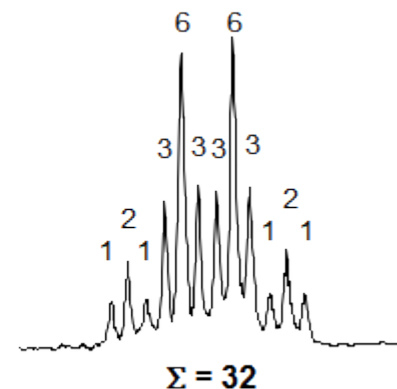
3. *Non ci possono essere linee più piccole di quelle esterne.* Per n grandi, queste possono essere confuse con il noise e in questo caso l'assegnazione delle intensità e quindi di n può essere difficile.



Accoppiato con altri 3 protoni
 $2^3 = 8$
3 valori di J
ddd



Accoppiato con altri 4 protoni
 $2^4 = 16$
4 valori di J
dddd

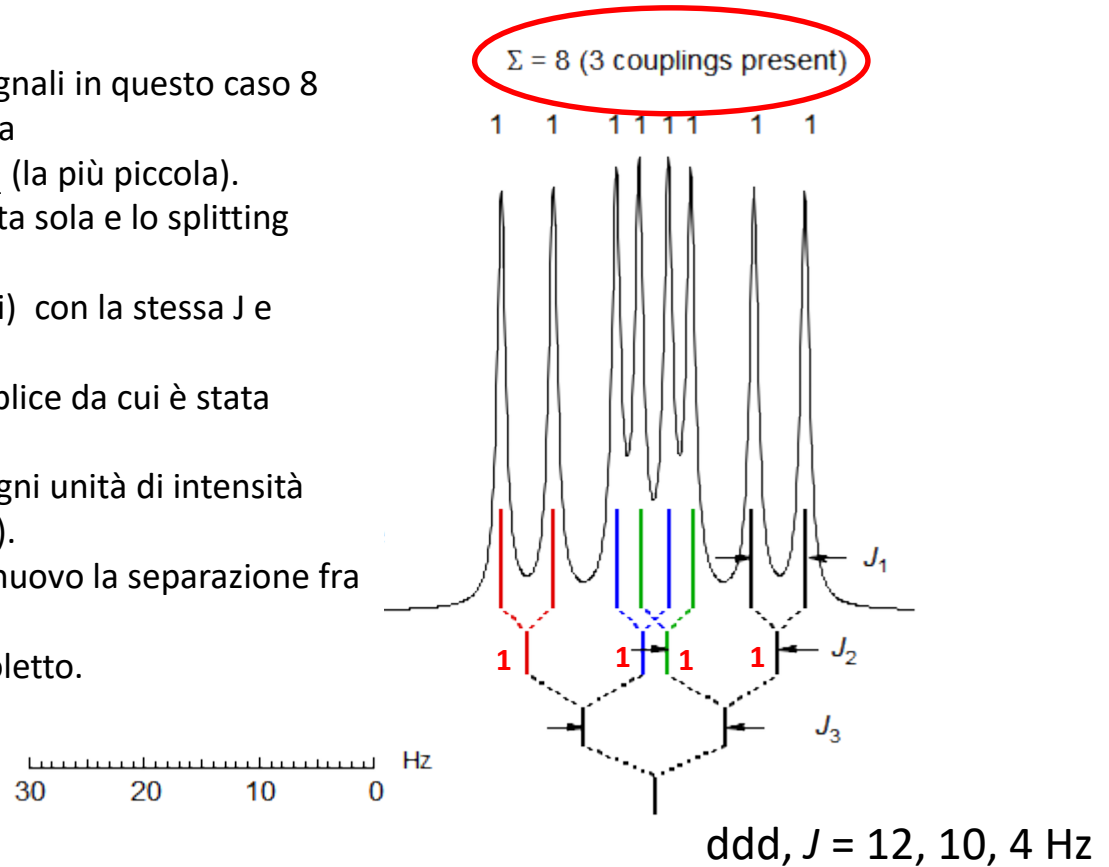


Accoppiato con altri 5 protoni
 $2^5 = 32$
5 valori di J
ddddd

Molteplicità: caso generale
(qualunque valore di J)

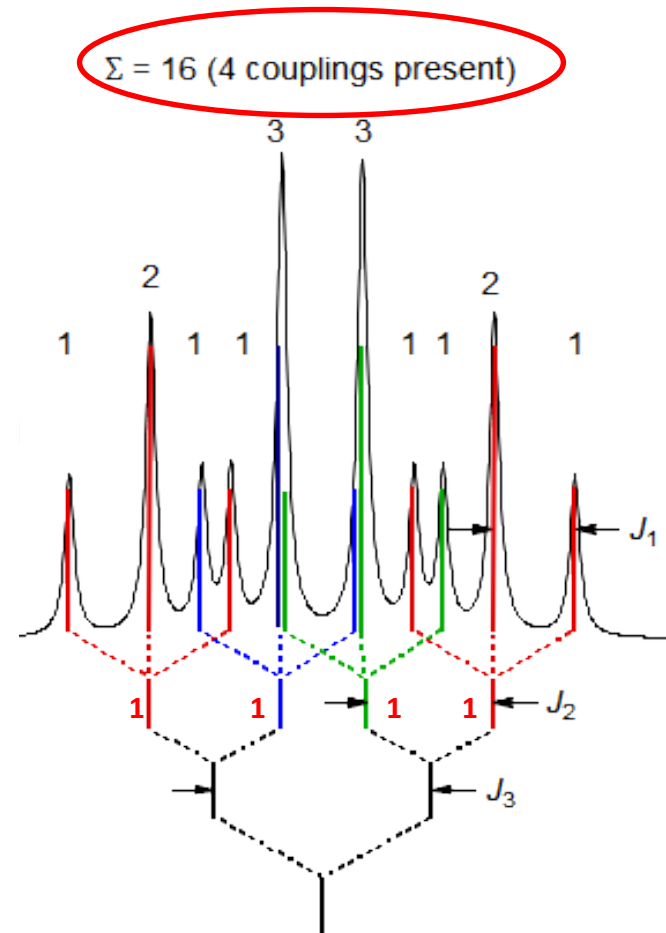
MULTIPLIETTI DEL PRIMO ORDINE

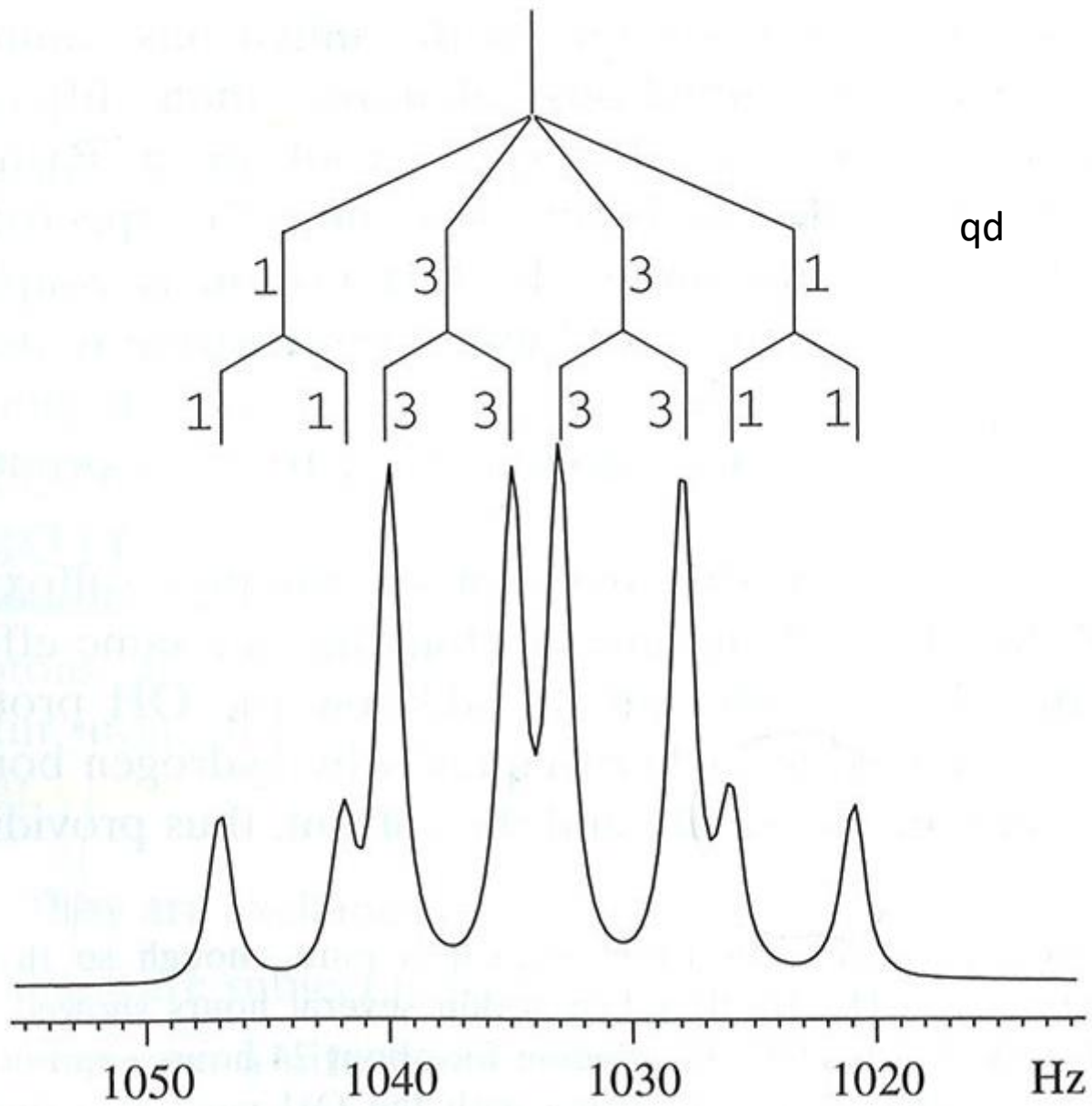
1. Si sommano le intensità relative dei segnali in questo caso 8
2. Si numerano le linee da sinistra a destra
3. Si guarda la separazione 1-2, che è la J_1 (la più piccola).
Siccome $I_1/I_2 = 1$, la J_1 compare una volta sola e lo splitting appartiene ad un doppietto
4. Cerco tutte le coppie di linee (doppietti) con la stessa J e considero il centro di queste.
5. Ne risulta un sottomultipletto più semplice da cui è stata rimossa la J_1
6. Tenere sempre conto delle intensità (ogni unità di intensità deve essere considerata una sola volta).
7. Nel primo sottomultipletto guardo di nuovo la separazione fra 1 e 2 che sarà la costante J_2
8. Ripeto il processo finché arrivo al singoletto.



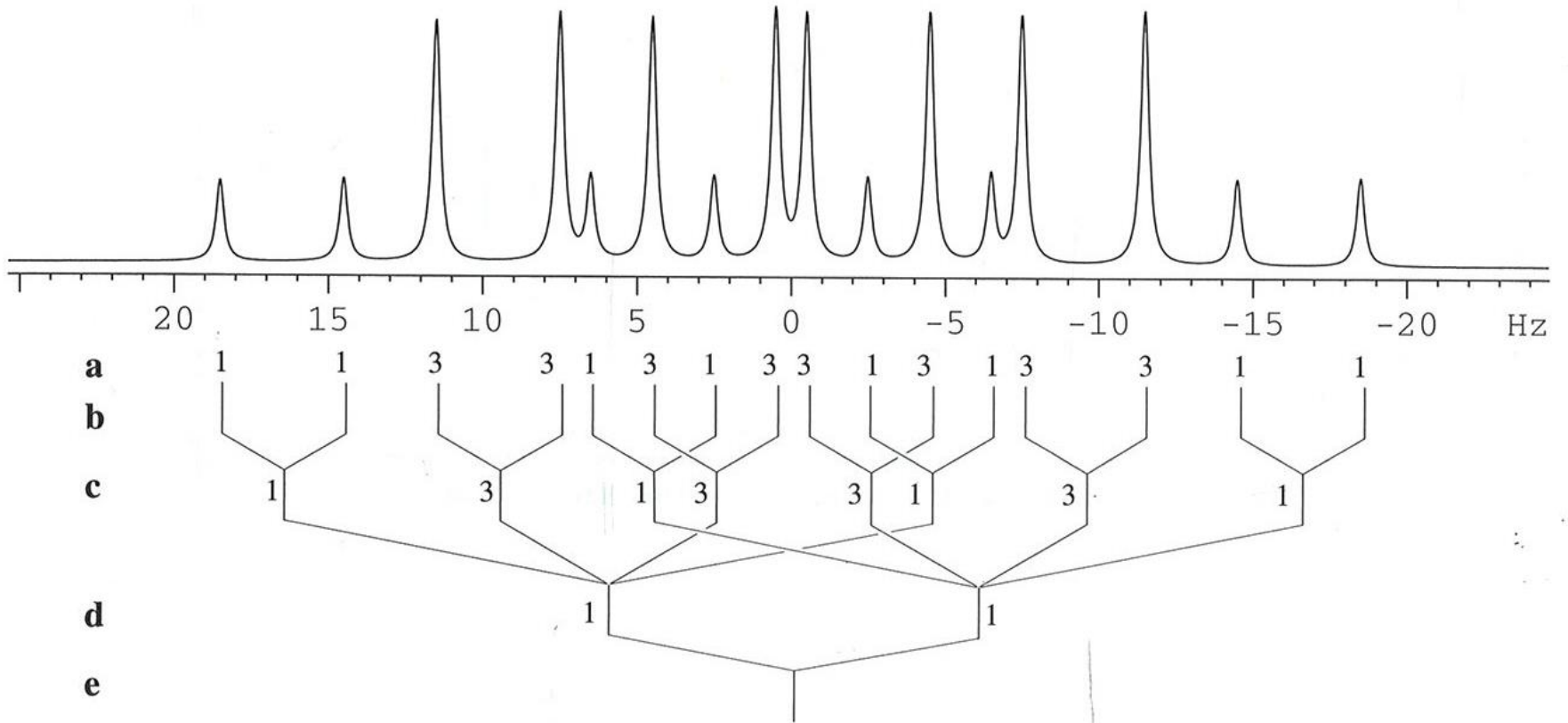
1. Come prima, la separazione fra 1 e 2 è J_1 , ma $I_1/I_2 = 1:2$ quindi è lo splitting di un tripletto e la stessa J appare due volte
2. Rimuovo J_1 del tripletto
3. Scrivo un sottomultipletto con i centri dei tripletti
4. Le due linee di intensità 3 sono la somma di due linee, una di intensità 1 e una di intensità 2.

ddt, $J = 16, 10, 6, 6$ Hz



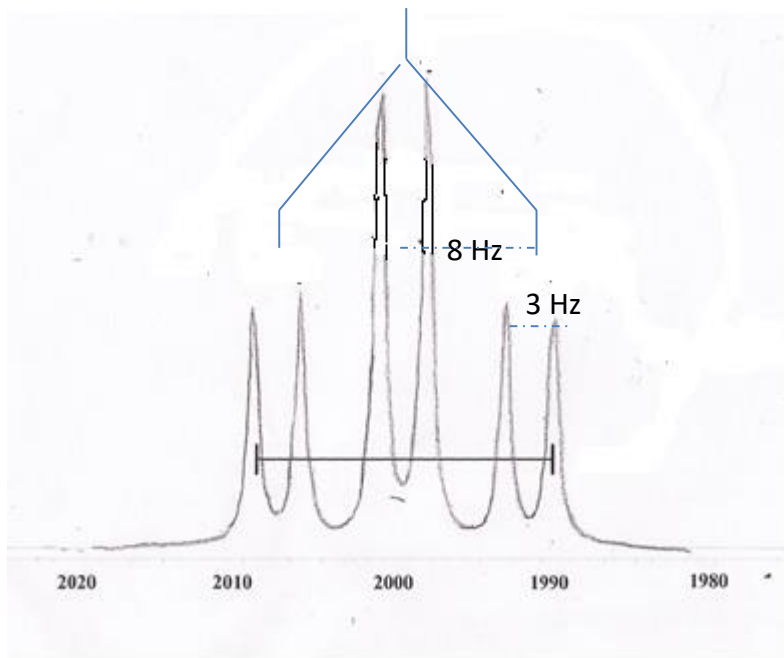


ddq



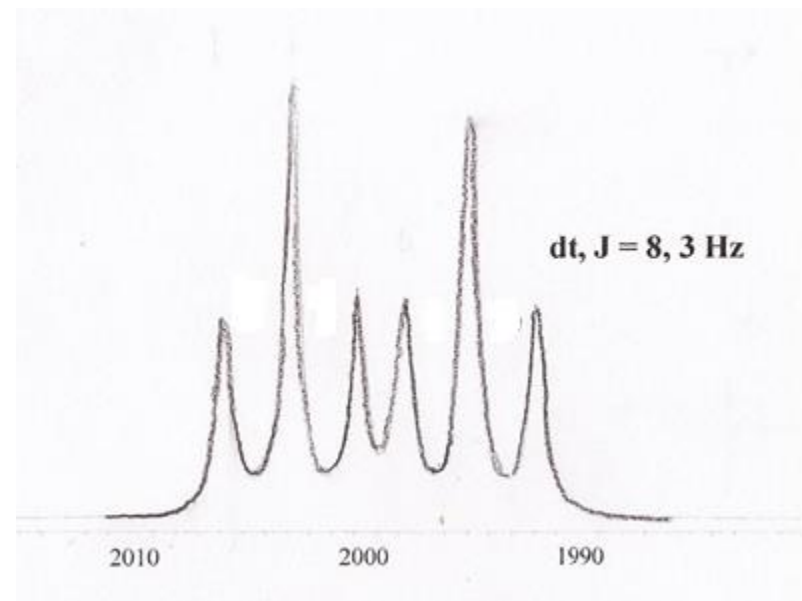
td, $J = 8$ e 3 Hz

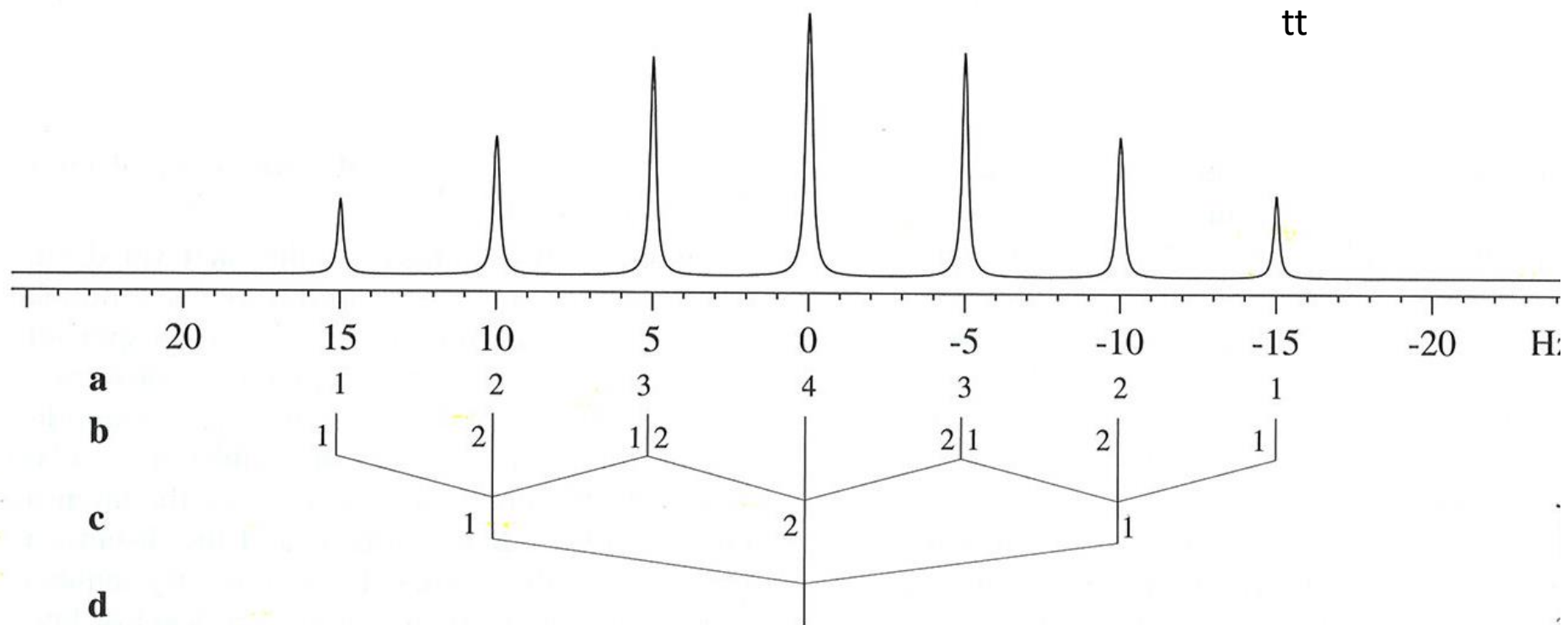
(tripletto di $J = 8$ Hz, splittato in un
doppietto di $J = 3$ Hz)



dt, $J = 8$ e 3 Hz

(doppietto di $J = 8$ Hz, splittato in un
tripletto di $J = 3$ Hz)





MULTIPLIETTI DEL PRIMO ORDINE

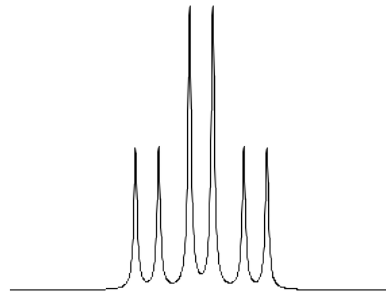
$I_{tot} = 8$

3 accoppiamenti

J1

J2 = J3

td



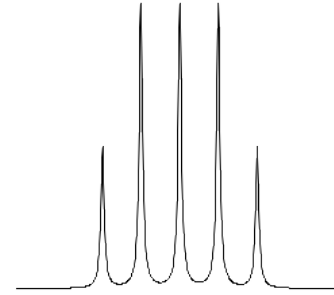
$I_{tot} = 8$

3 accoppiamenti

J1 = J2

J3

dt

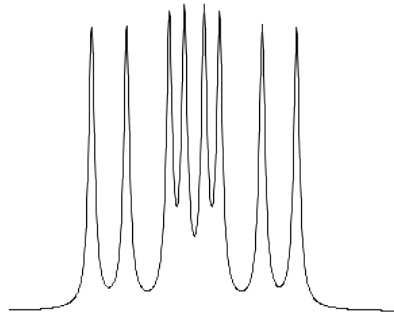


$I_{tot} = 8$

3 accoppiamenti

J1, J2, J3

ddd



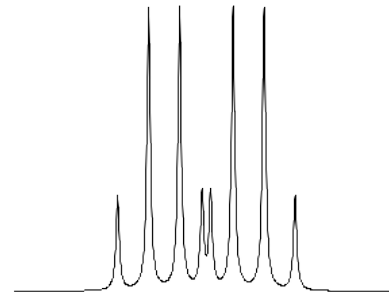
$I_{tot} = 16$

4 accoppiamenti

J1 = J2 = J3

J4

dq



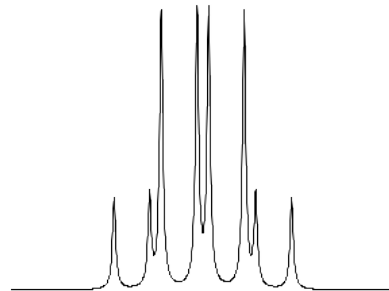
$I_{tot} = 16$

4 accoppiamenti

J1

J2 = J3 = J4

qd



1 1 1 1

$I_{tot} = 16$

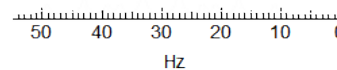
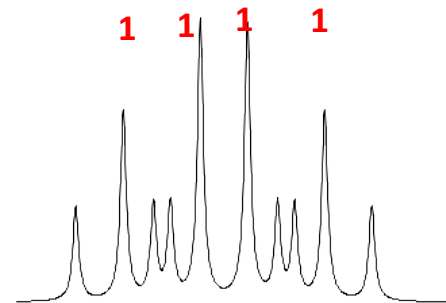
4 accoppiamenti

J1 = J2

J3

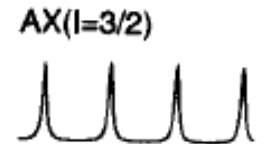
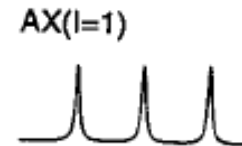
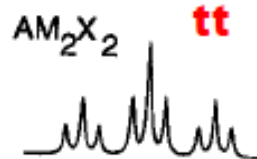
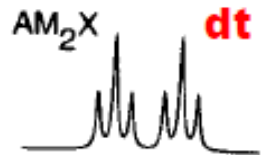
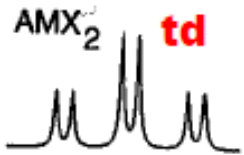
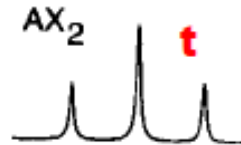
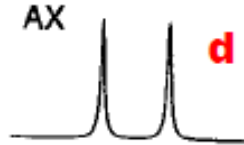
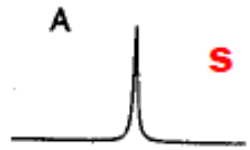
J4

ddt

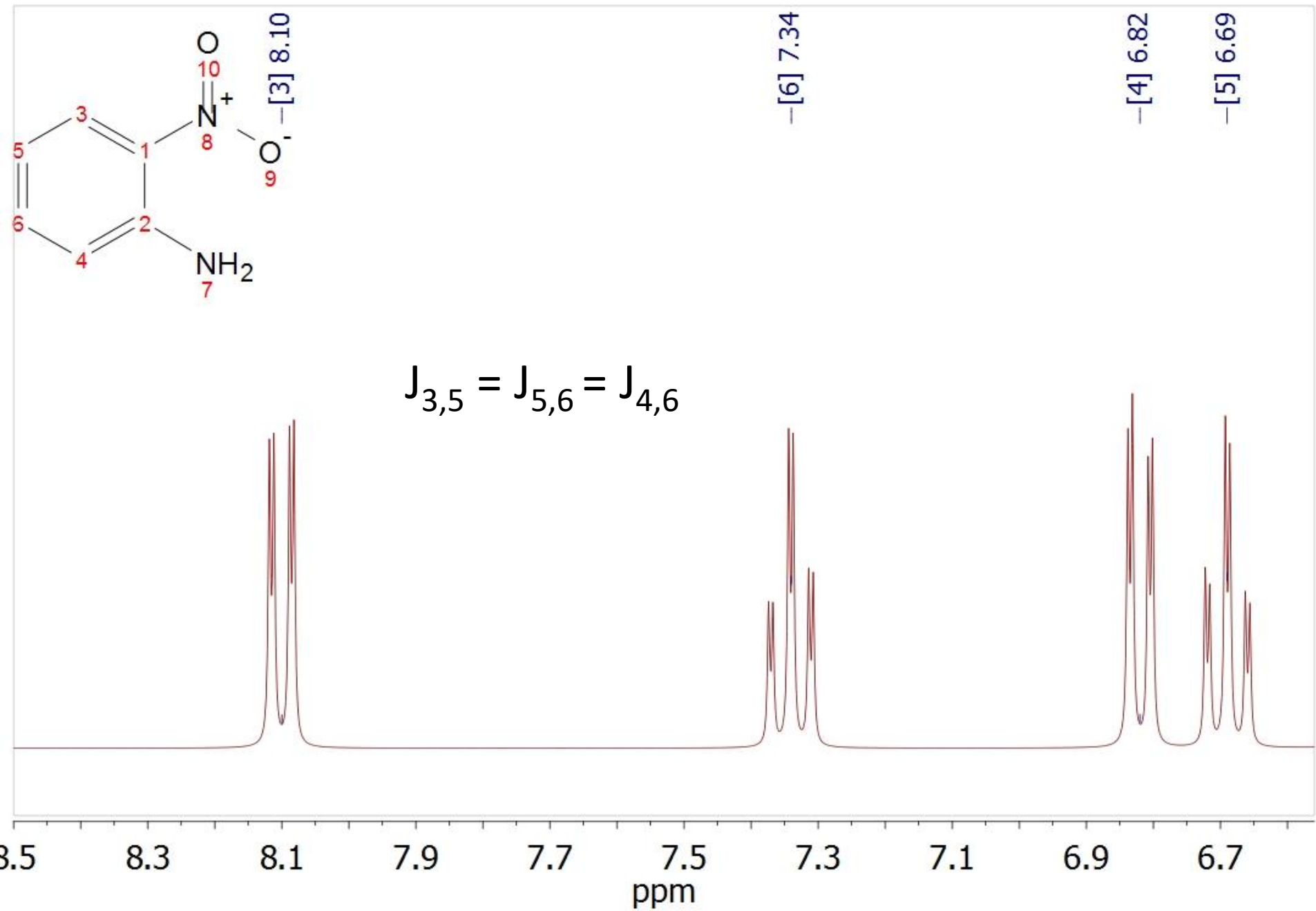


MULTIPLIETTI DEL PRIMO ORDINE

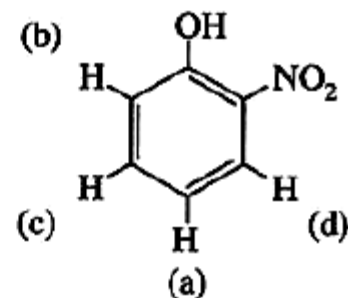
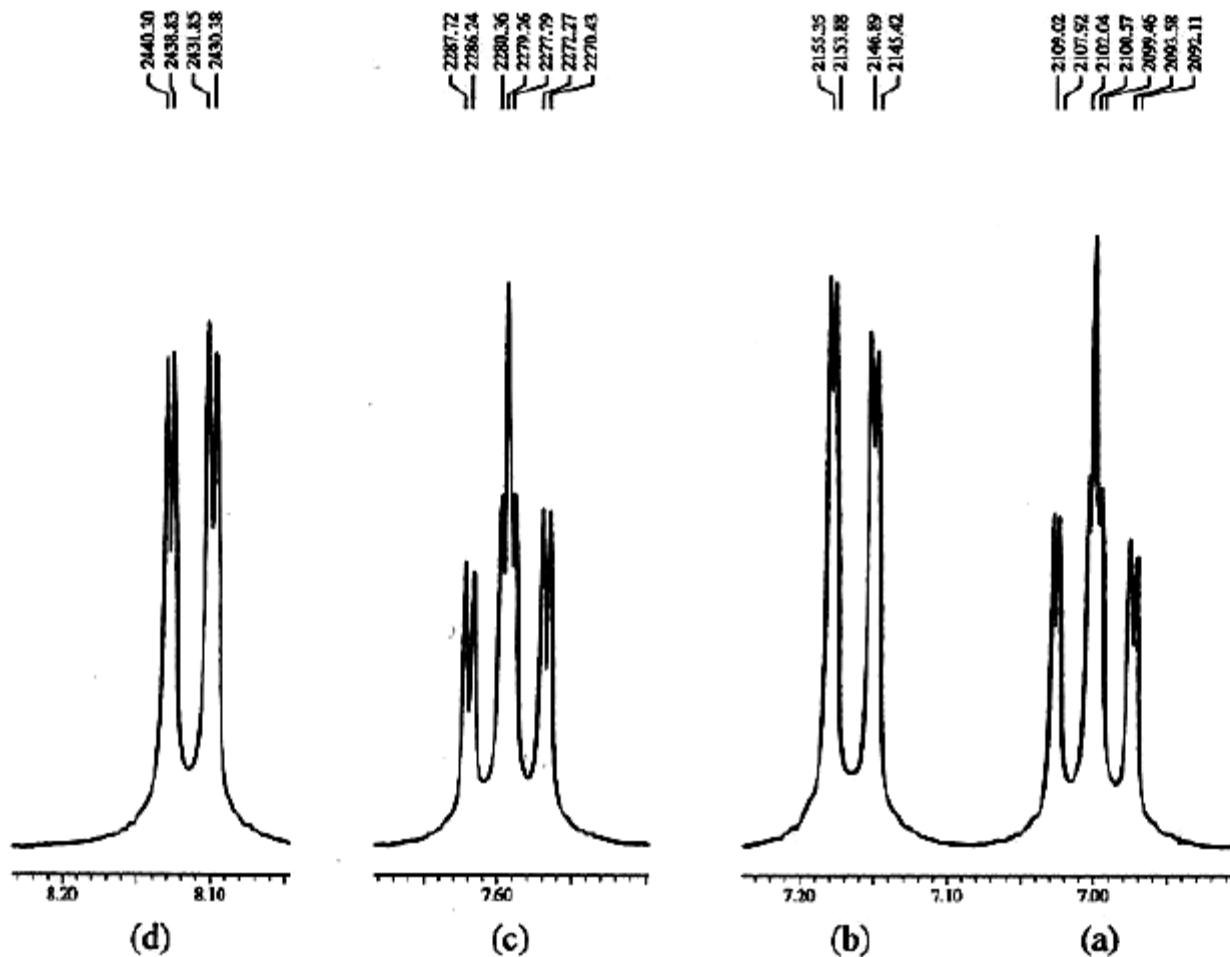
In generale la notazione che usa le lettere dell'alfabeto per indicare i protoni porta alla seguente classificazione dei sistemi del PRIMO ORDINE nei quali un protone (**A**) accoppia con uno o più protoni (o altri nuclei come negli ultimi due esempi) con una (sistemi **AX_n**) o due (sistemi **AX_nM_y**) costanti di accoppiamento



SISTEMI DEL PRIMO ORDINE IN BENZENI SOSTITUITI

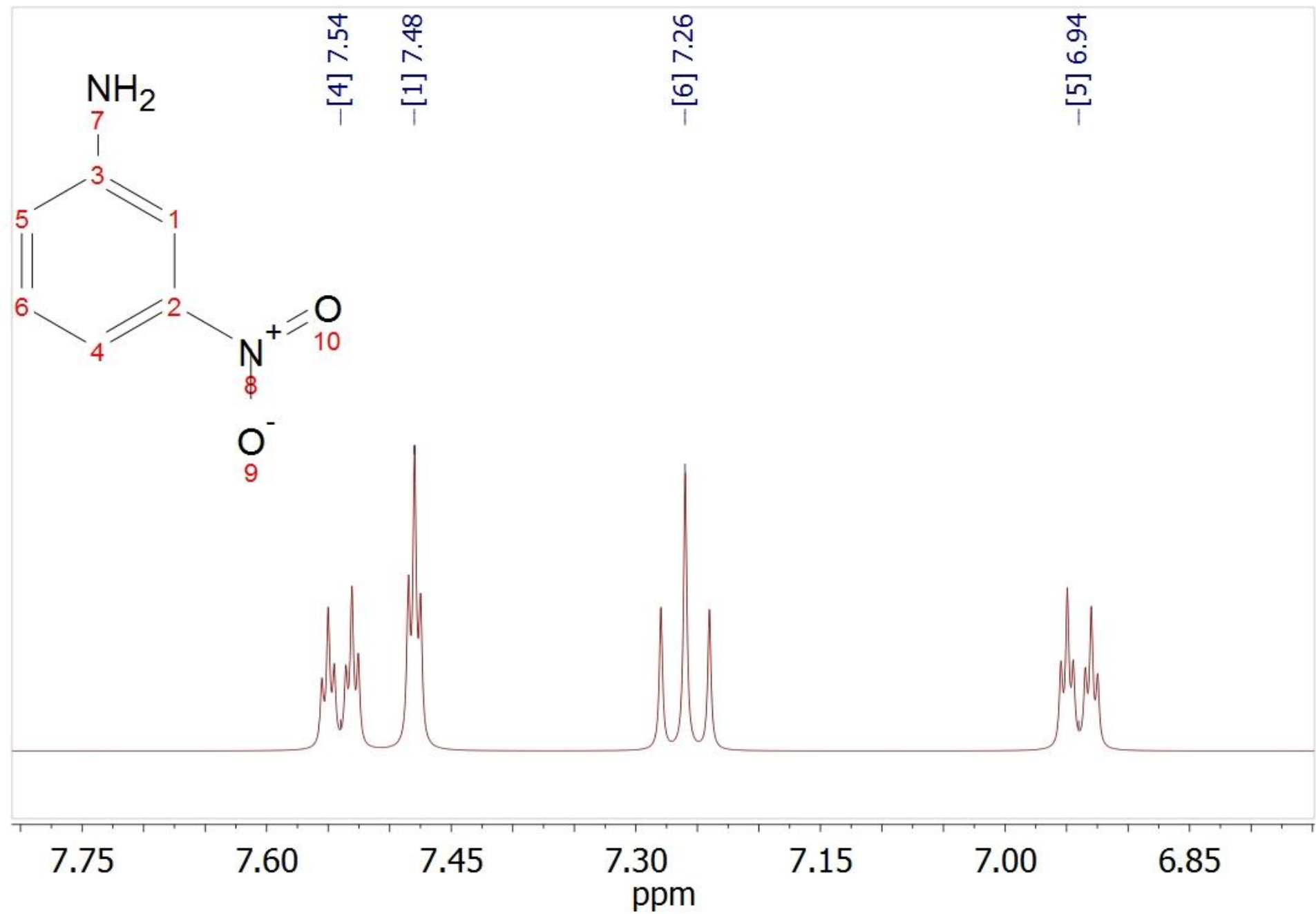


Accoppiamento in sistemi aromatici

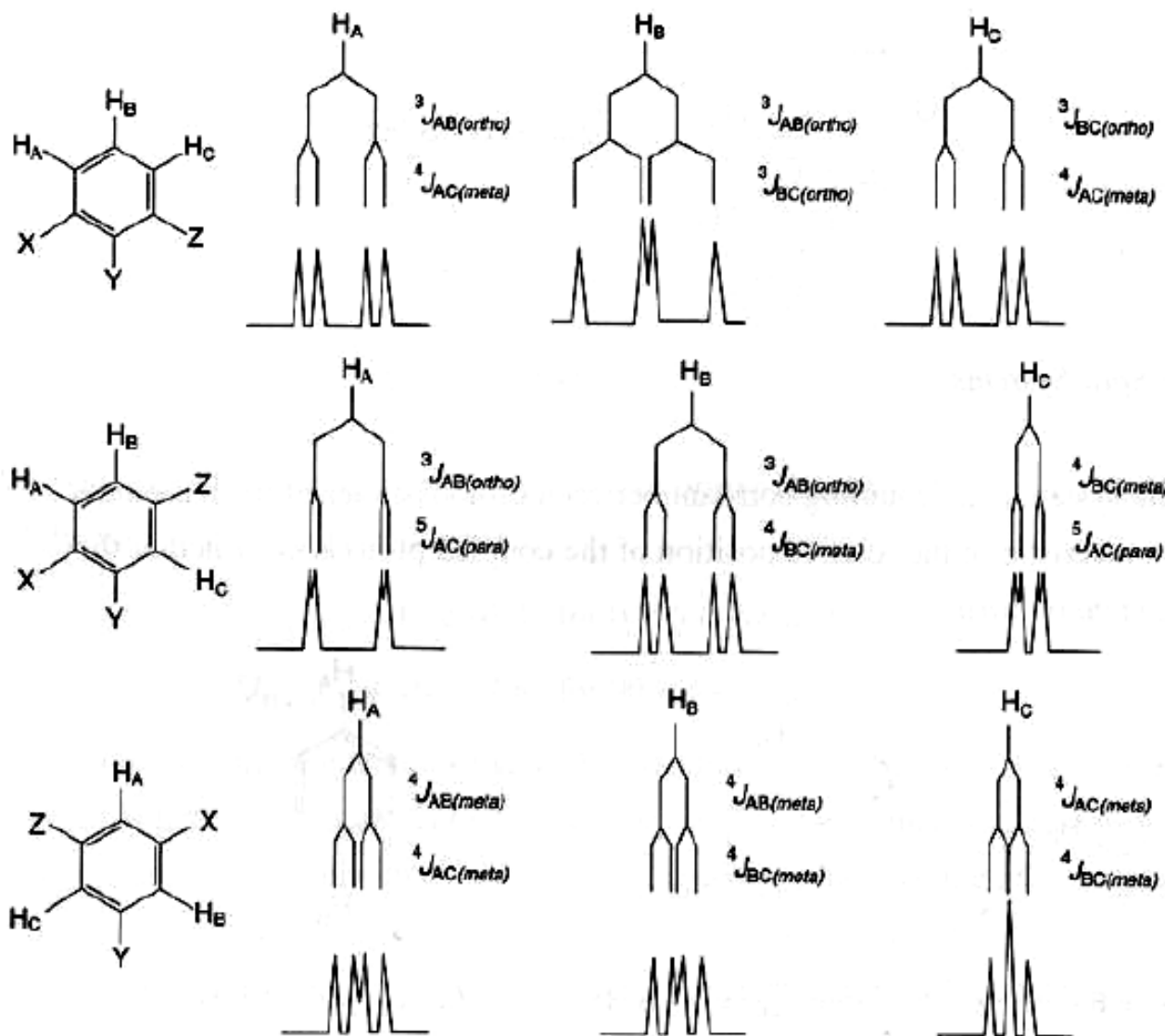


Spettro a 300 MHz
Calcolare le costanti
dai valori riportati.

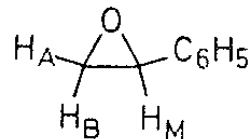
È possibile una analisi con l'approssimazione del primo ordine



Accoppiamento in sistemi aromatici

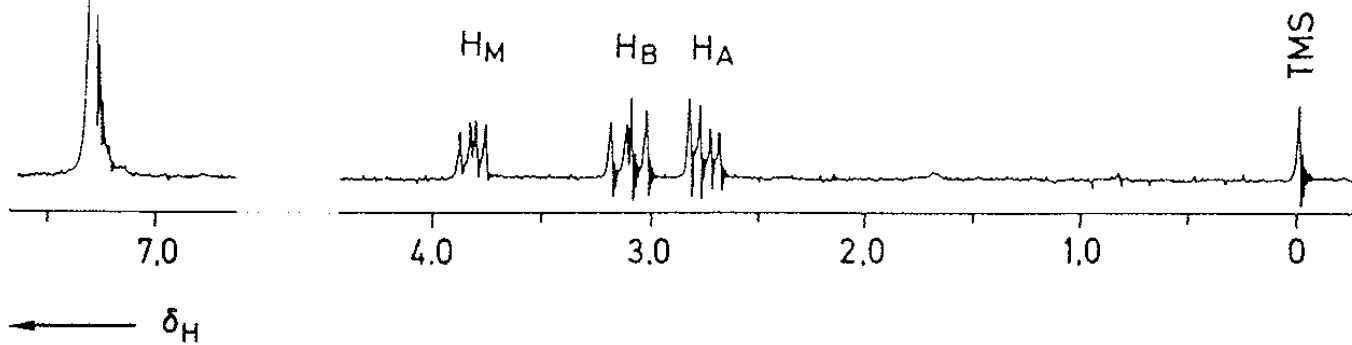


C₆H₅

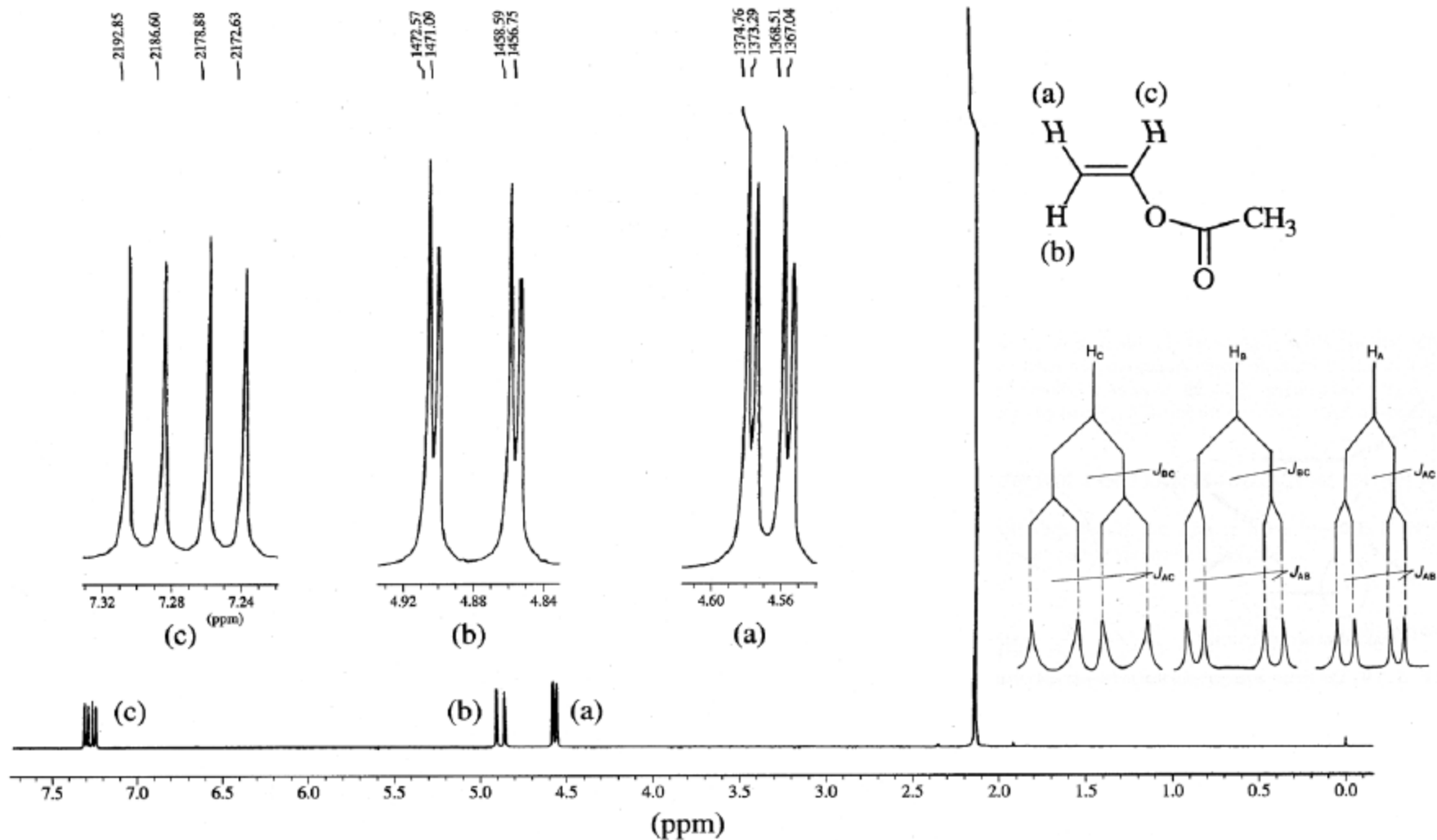


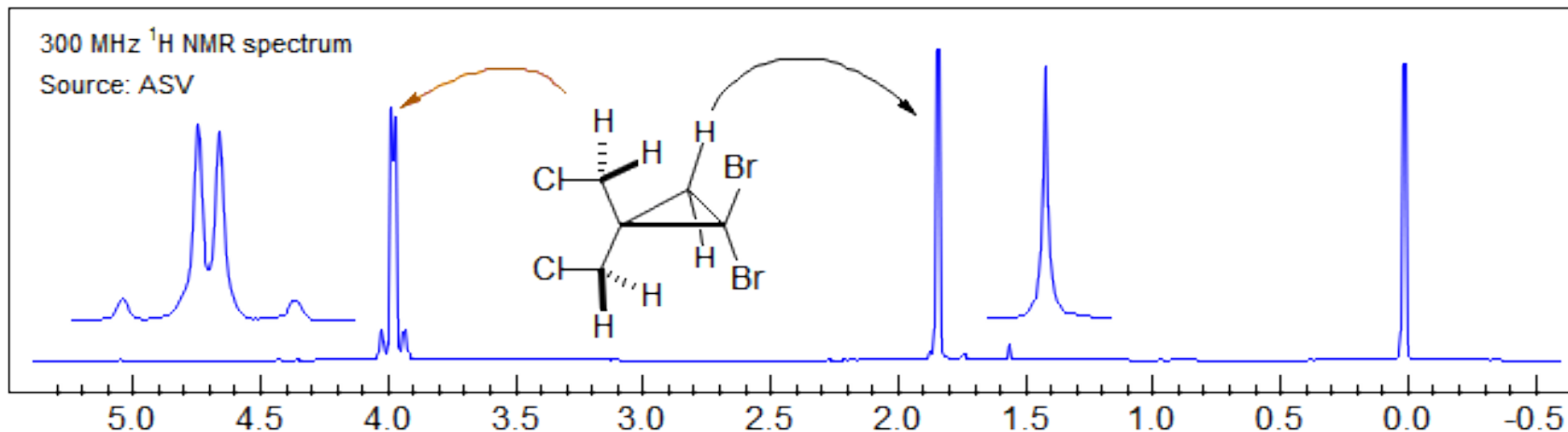
9

($J_{AB} = 5,7$; $J_{AM} = 2,4$; $J_{BM} = 4,1$ Hz)



Accoppiamento negli alcheni: spettro a 300 MHz





I PROTONI DEL GRUPPO CH_2Cl SONO
DIASSTEREOTOPICI MA NON QUELLI DEL CH_2
DEL CICLOPROPANO SIMMETRICI RISPETTO AL
PIANO

Passaggio del sistema di spin da AX ad AB

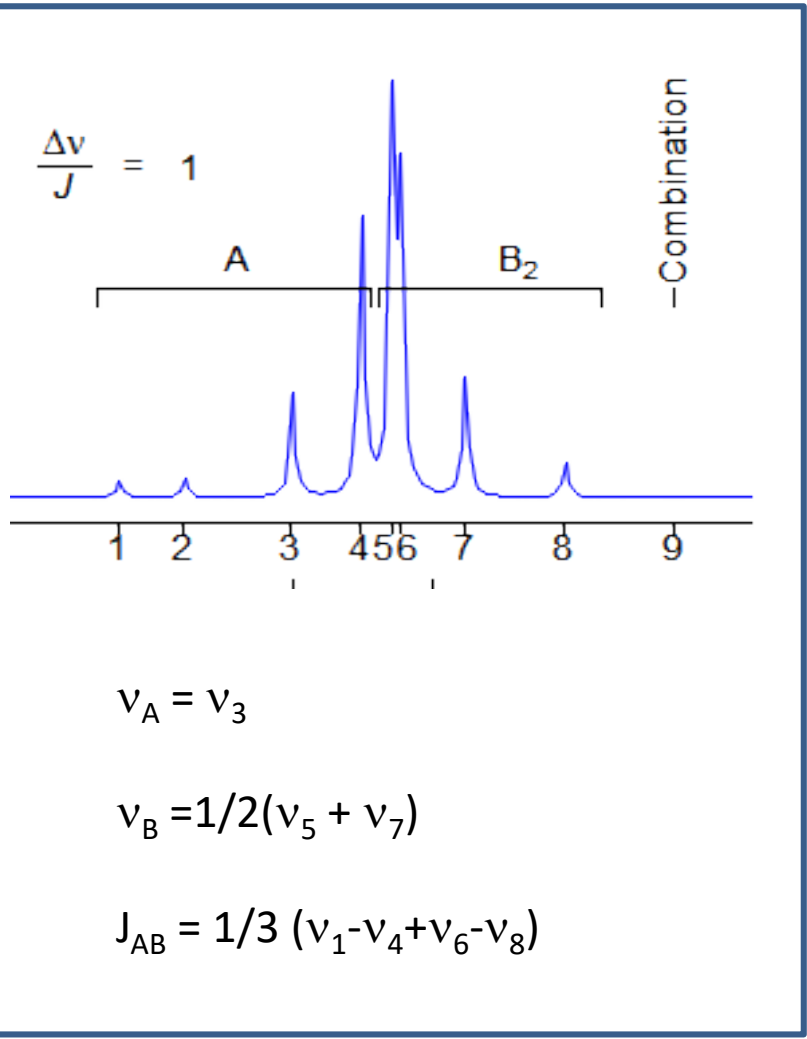
Δ (ppm)	J (Hz)	ν_p (MHz)	Δ (Hz)	ΔJ
02	10	900	180	18
02	10	500	100	10
02	10	300	60	6
02	10	100	20	2
02	10	60	12	12
02	10	30	6	06
02	10	10	2	02

AX_2



ANALISI DEL SISTEMA AB_2

AK_2



$\nu_A = \nu_3$

$\nu_B = 1/2(\nu_5 + \nu_7)$

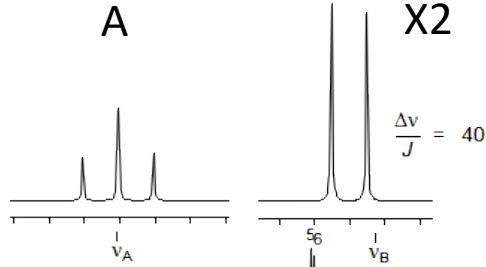
$J_{AB} = 1/3 (\nu_1 - \nu_4 + \nu_6 - \nu_8)$

AB_2

A

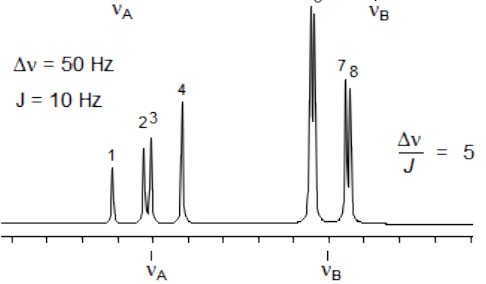
X2

$\frac{\Delta\nu}{J} = 40$

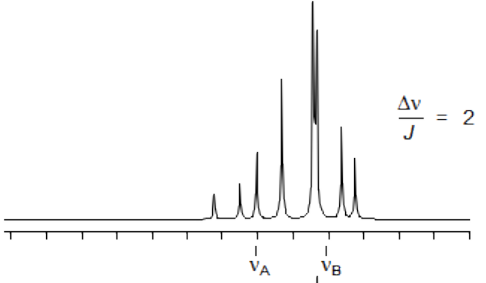


$\Delta\nu = 50 \text{ Hz}$
 $J = 10 \text{ Hz}$

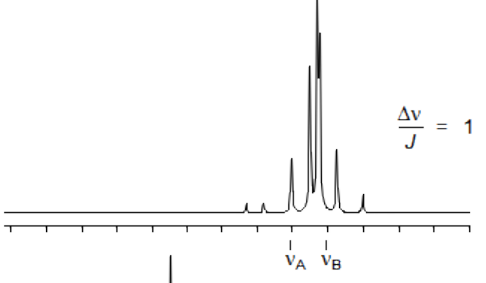
$\frac{\Delta\nu}{J} = 5$



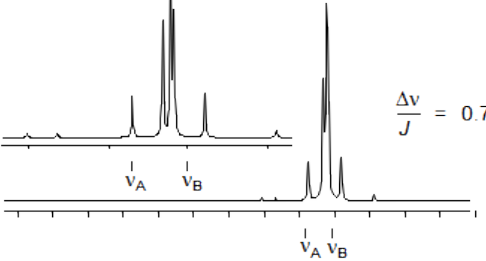
$\frac{\Delta\nu}{J} = 2$



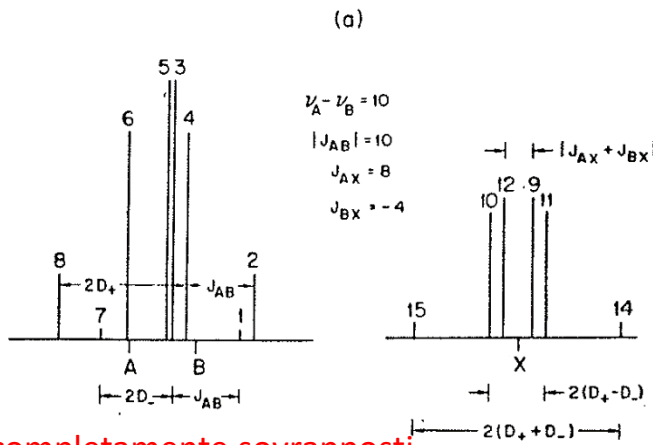
$\frac{\Delta\nu}{J} = 1$



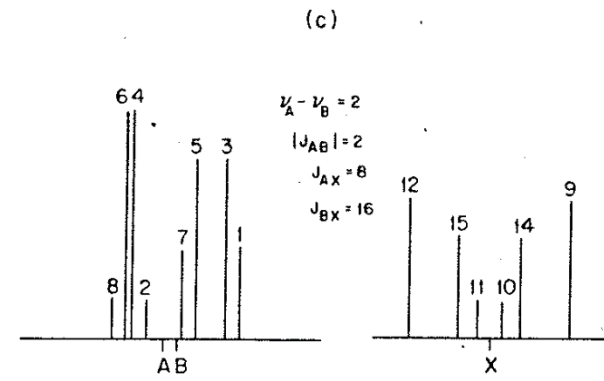
$\frac{\Delta\nu}{J} = 0.7$



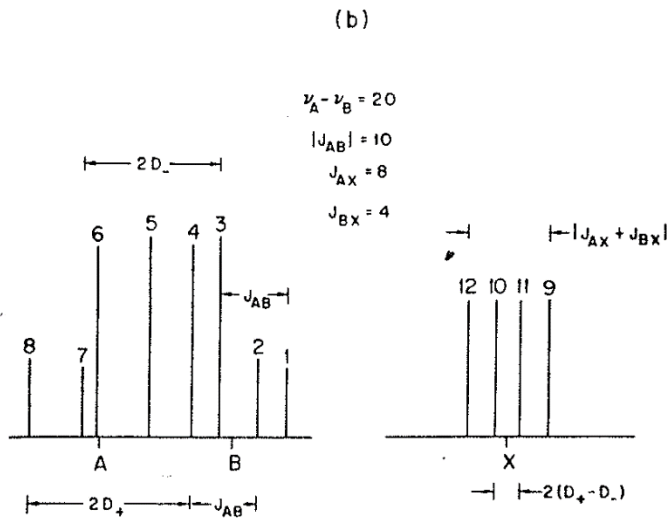
SPETTRI ABX CALCOLATI



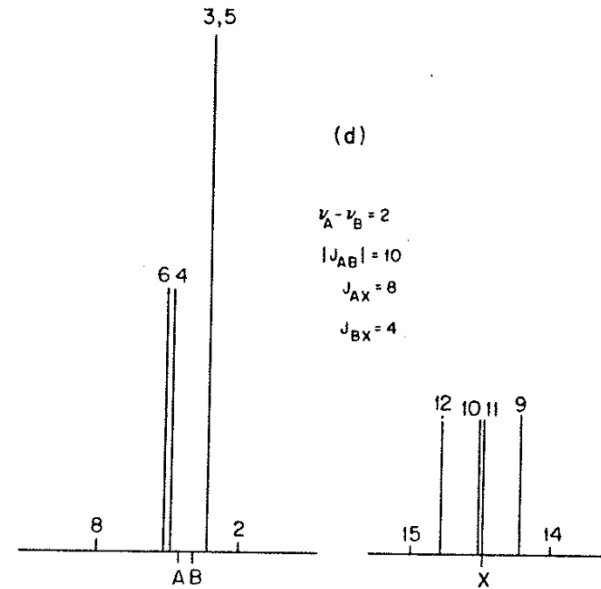
A e B completamente sovrapposti



A e B non sovrapposti

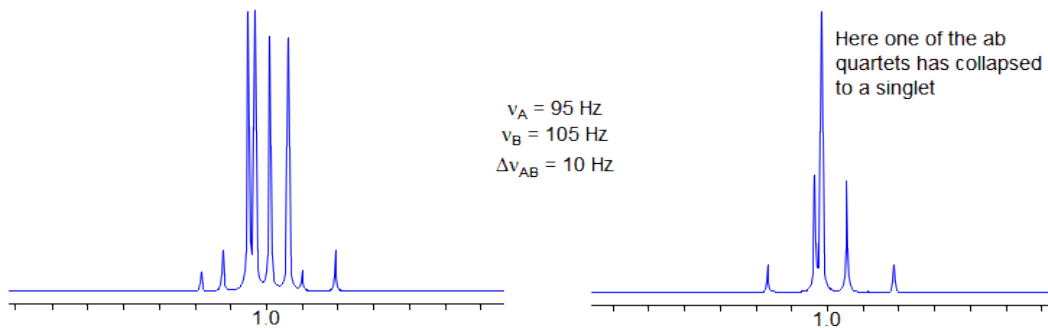
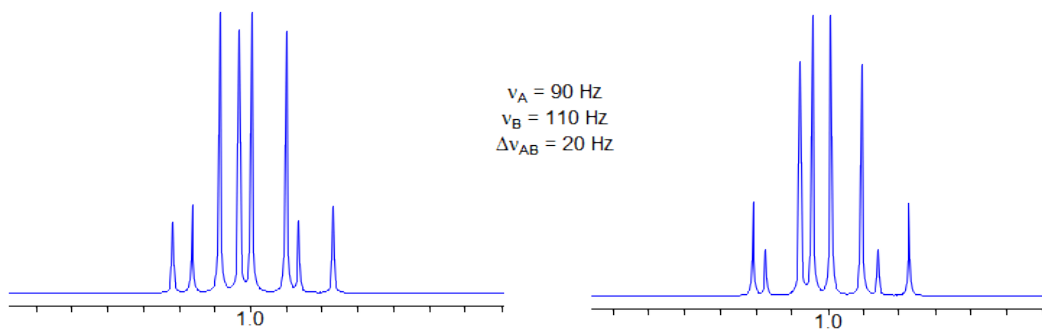
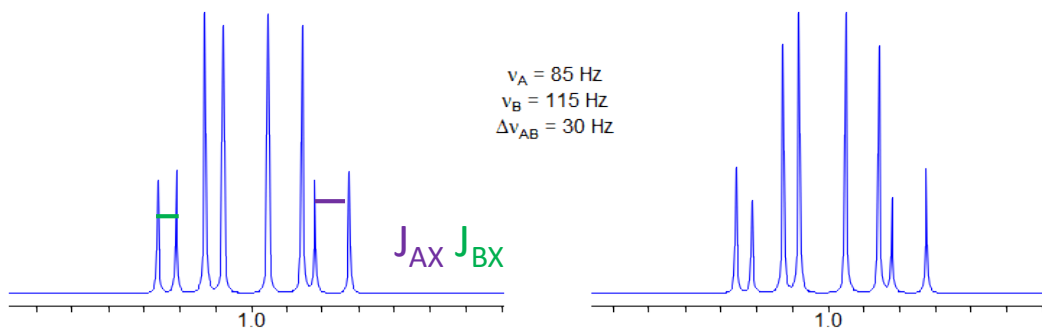
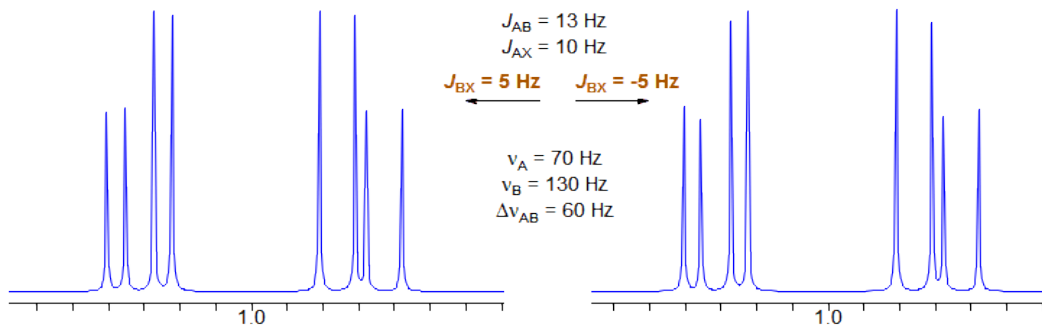


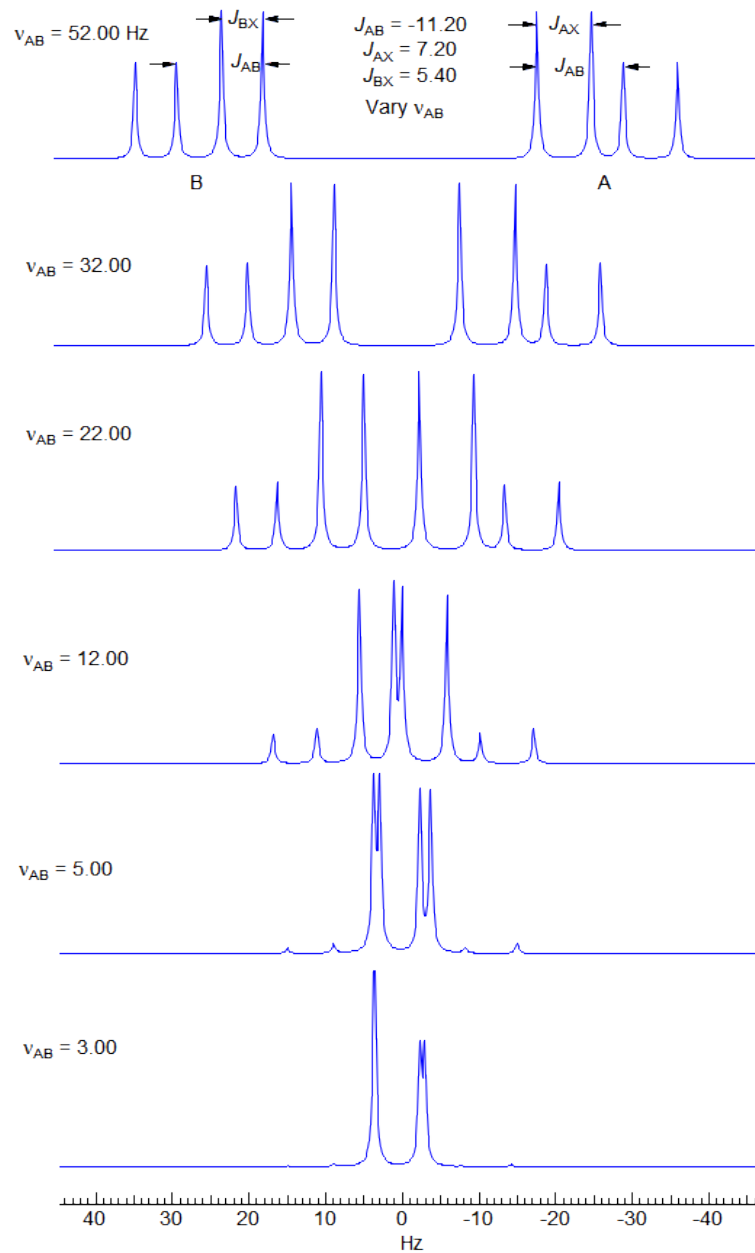
A e B parzialmente sovrapposti



5 linee (parte AB) invece di 8

Influenza della J

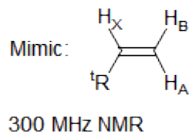




Influenza DEL CHEMICAL SHIFT

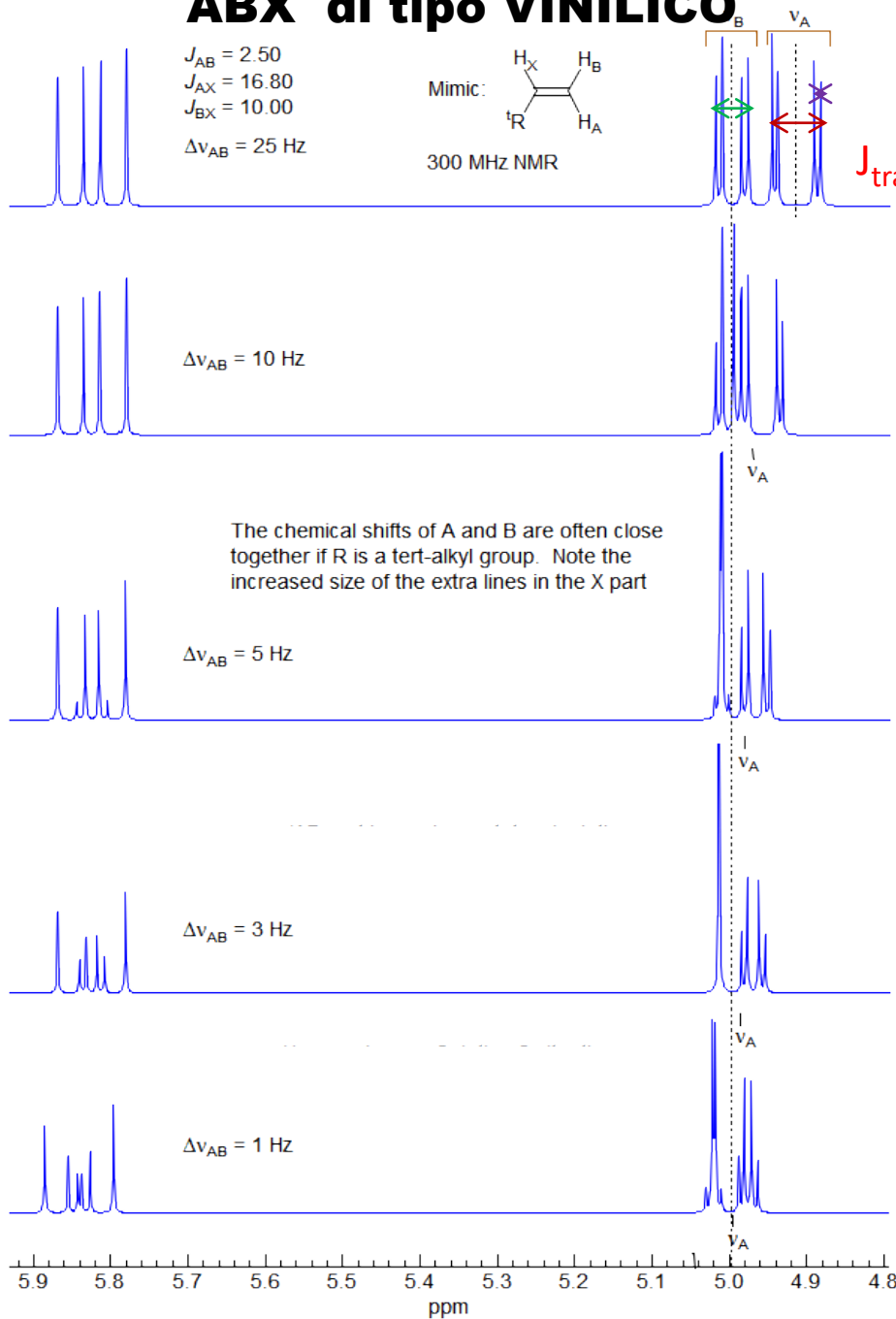
ABX di tipo VINILICO

$J_{AB} = 2.50$
 $J_{AX} = 16.80$
 $J_{BX} = 10.00$
 $\Delta\nu_{AB} = 25 \text{ Hz}$



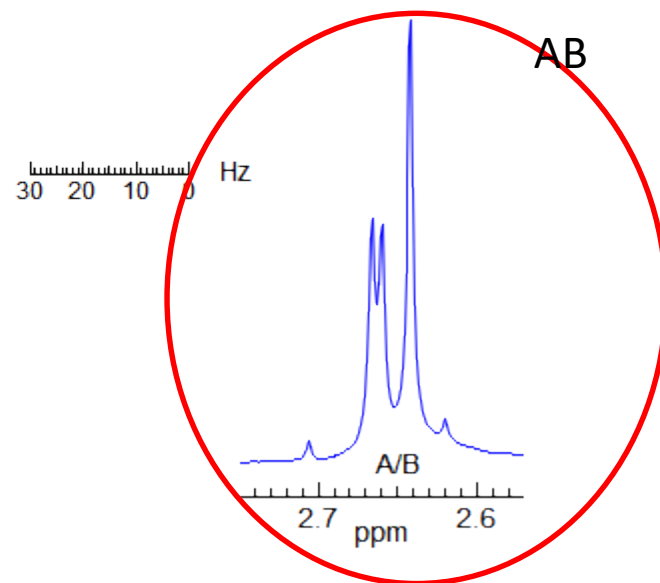
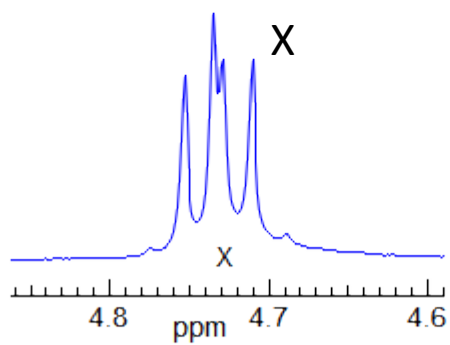
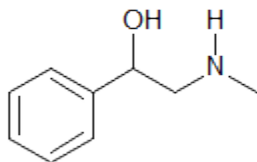
AMX

J_{trans} J_{cis} J_{gem}



ABX

(C₉H₁₃NO)
300 MHz ¹H NMR Spectrum in CDCl₃
Source: Aldrich Spectral Viewer/Reich

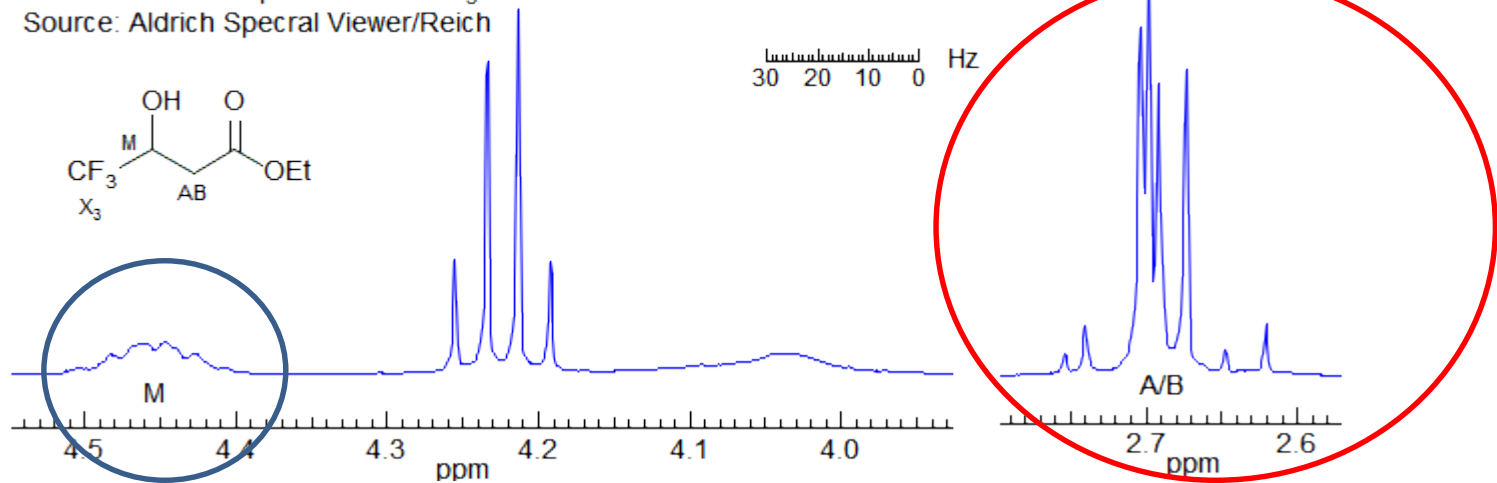


AMX \longrightarrow ABX

(C₆H₉F₃O₃)

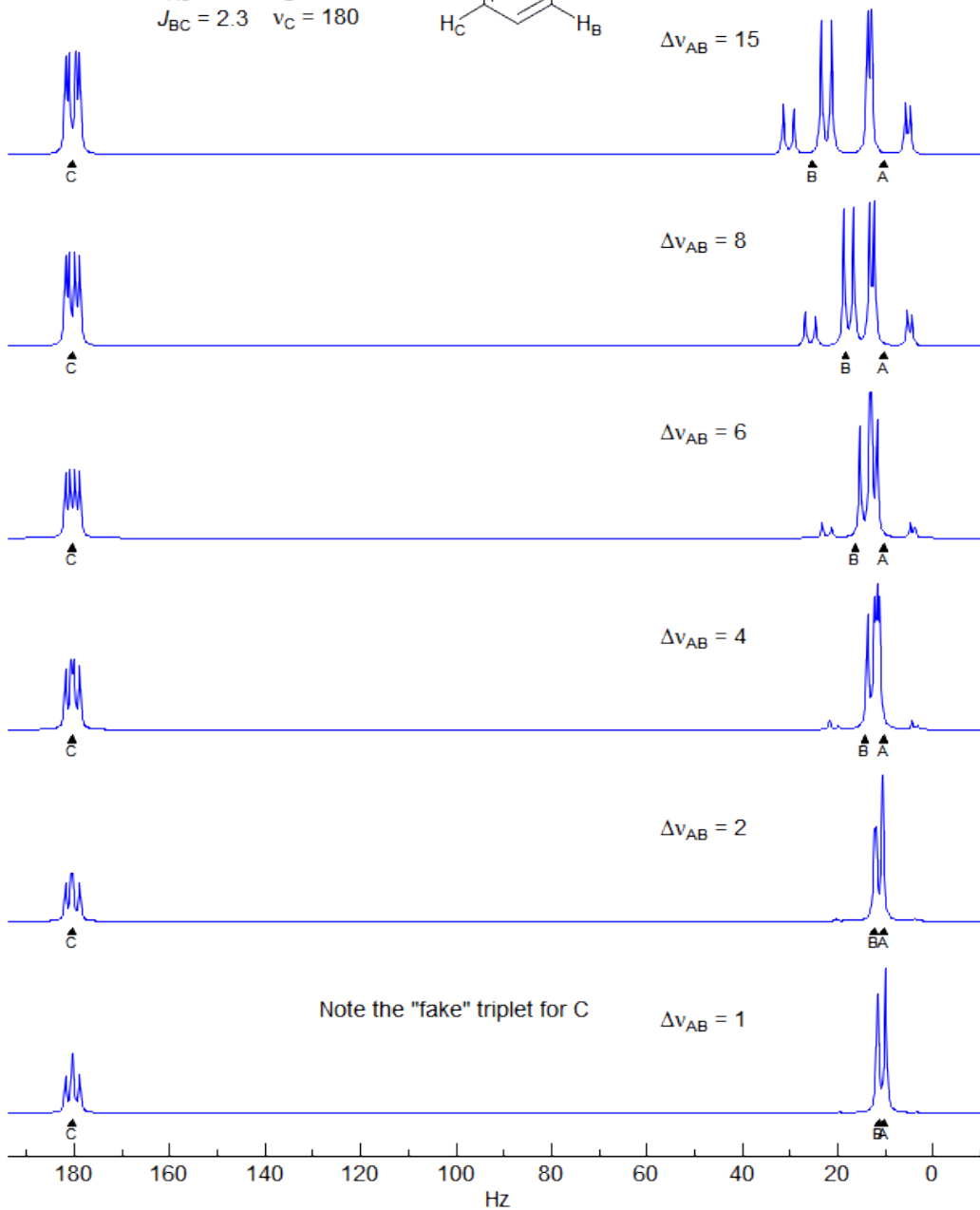
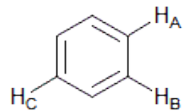
300 MHz ¹H NMR spectrum in CDCl₃

Source: Aldrich Spectral Viewer/Reich



Pattern ABX (in realtà un ABMX₃ siccome il nucleo M è accoppiato con I tre atomi di fluoro)
Non interpretabile come primo ordine.

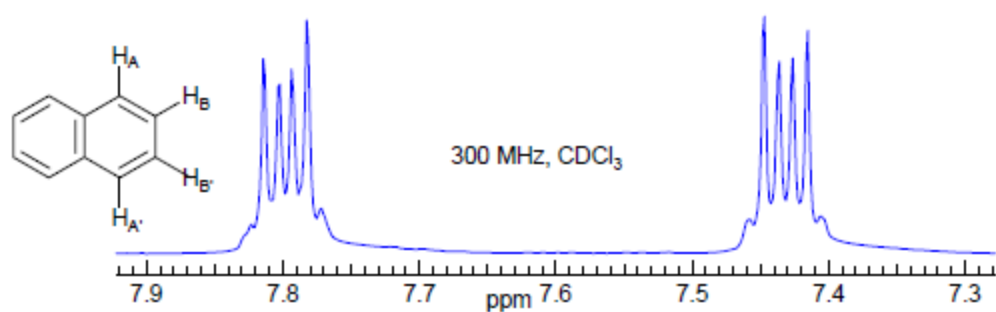
$J_{AB} = 8$ $\nu_A = 10$
 $J_{AC} = 0.8$ ν_B varies
 $J_{BC} = 2.3$ $\nu_C = 180$



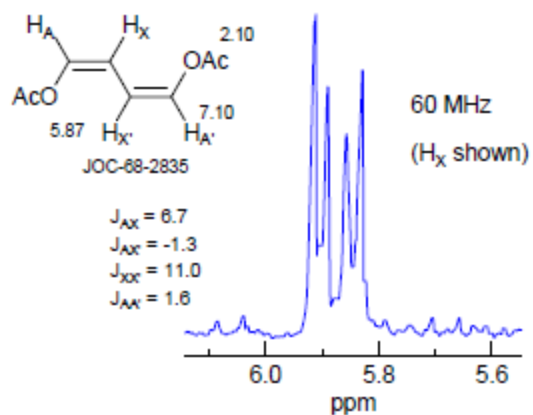
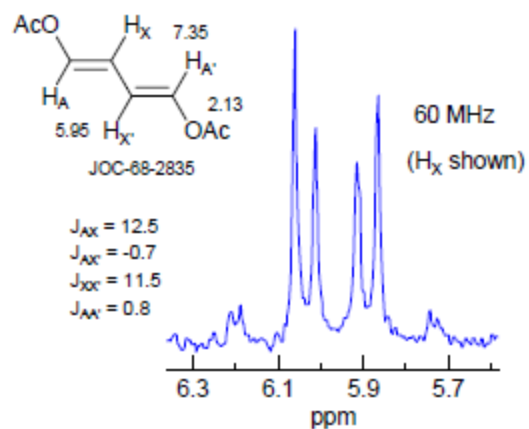
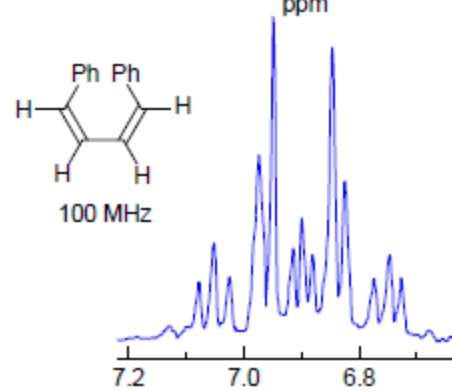
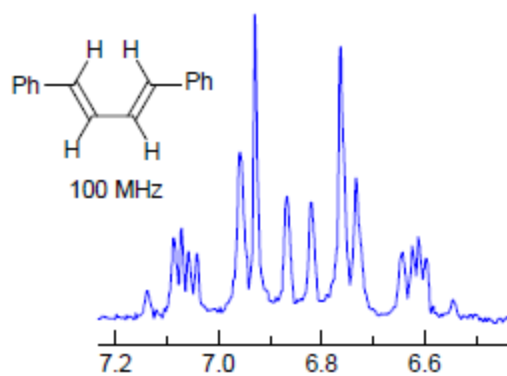
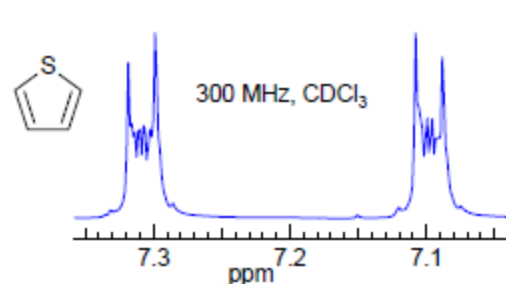
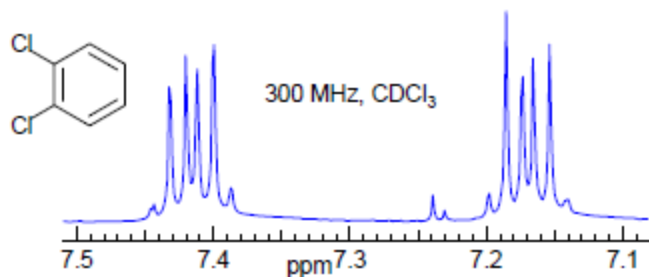
ABX



A₂X

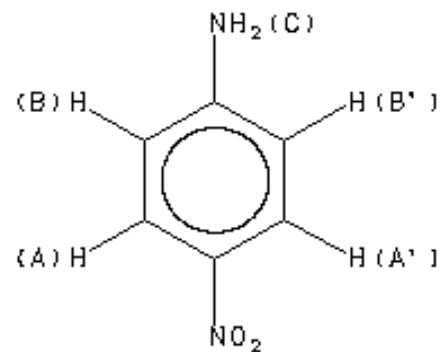


AA'XX' e AA'BB'



Parameter ppm Hz

D(A)	8.02
D(B)	6.76
D(C)	5.97
J(A,A')	3.0
J(A,B)	8.9
J(A,B')	0.3
J(A',B)	0.3
J(A',B')	8.9
J(B,B')	2.3



Accoppiamento in sistemi aromatici

È possibile una analisi con l'approssimazione del primo ordine

2690.33
2686.69
2686.65

2555.39
2554.28
2552.81
2551.71
2546.93
2545.83
2544.73
2543.62
2539.95
2538.47
2537.57
2532.22
2530.75
2529.28

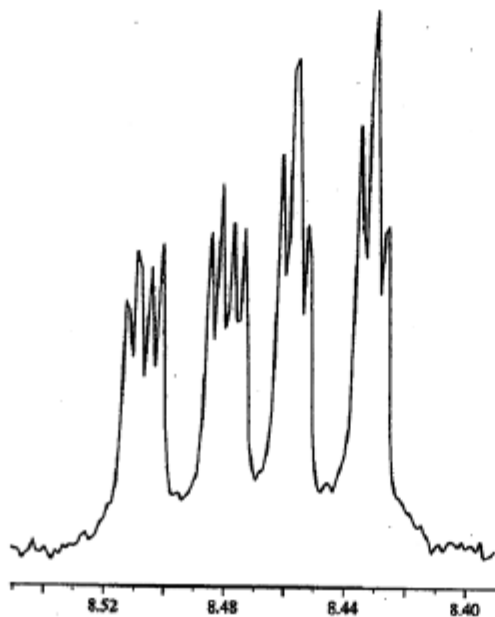
2325.22

2317.13

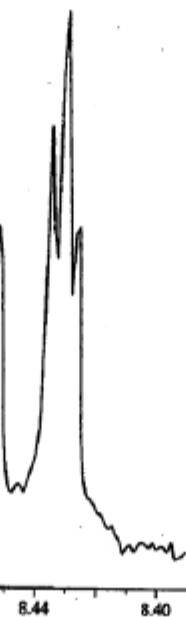
2309.41



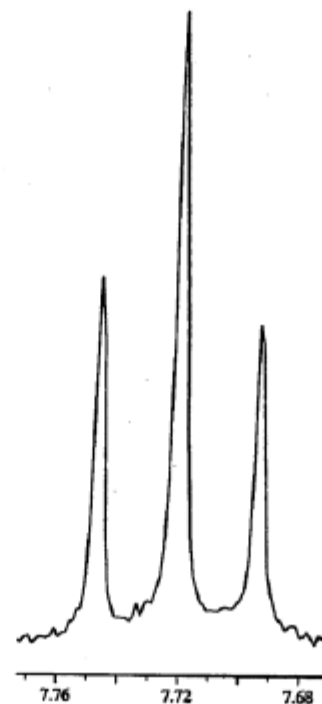
(d)



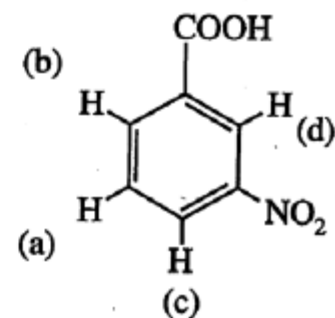
(c)



(b)



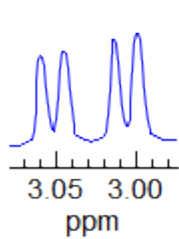
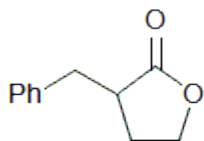
(a)



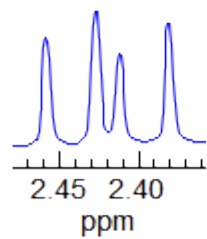
Spettro a 300 MHz
Calcolare le costanti
dai valori riportati.

ESERCIZI

Doublet of doublets (dd)

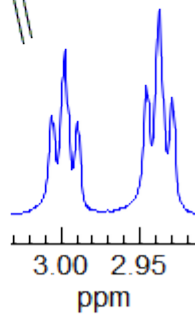
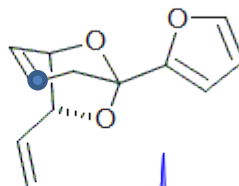


dd

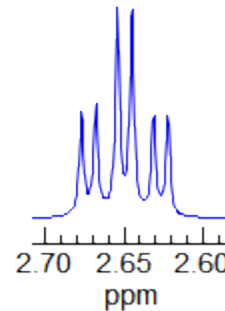
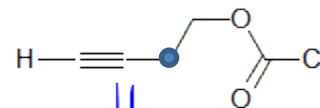


dd

Triplet of doublets or doublet of triplets (dt, td)

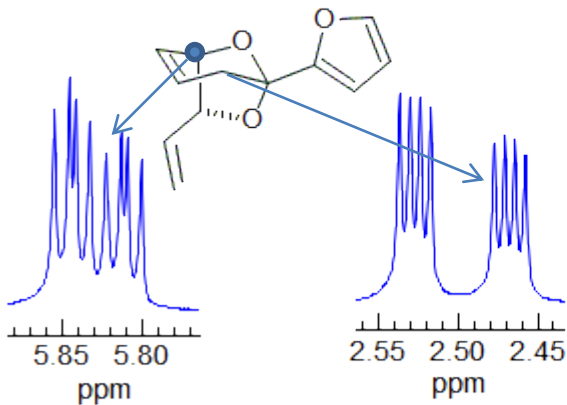


dt

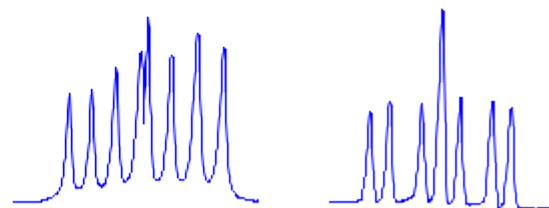


td

Doublet of doublet of doublets (ddd)

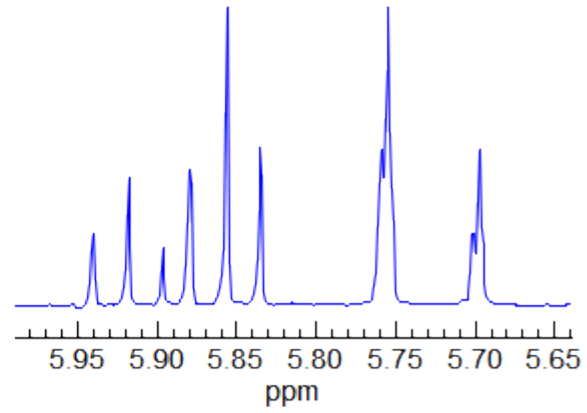
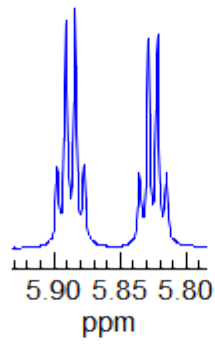
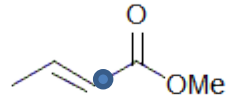
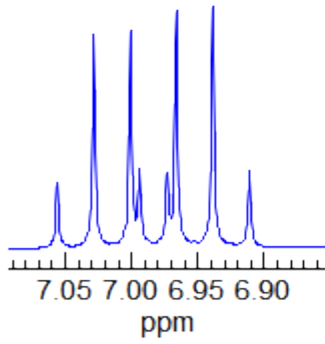
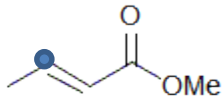


30 20 10 0 Hz



ESERCIZI

Doublet of quartets (dq)



Non 1° ordine