Equivalence

- Chemical

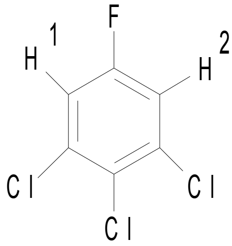
Nuclei equivalent by symmetry have the same chemical shift

  - static
  - time averaged

- Magnetic

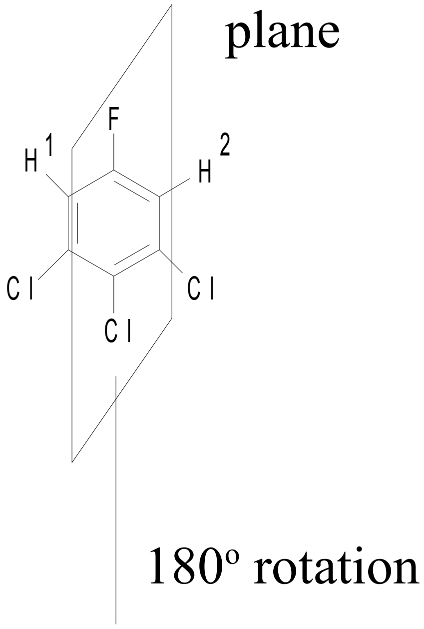
Symmetry equivalent nuclei must have same coupling to **all** other non-equivalent nuclei

Example



Look for NMR active nuclei: ^{1}H and ^{19}F

(can ignore Cl – no coupling)

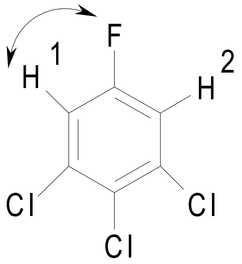


Chemically equivalent

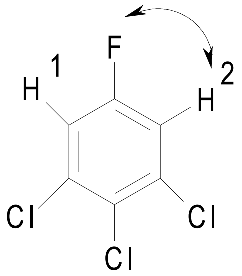
All other non-equivalent: only F

H^1 and H^2 chemically equivalent so do not look at coupling between these

H^1 to F: ortho



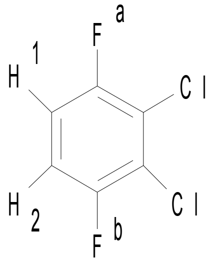
H^2 to F: ortho



H^1 and H^2 same coupling to F

- magnetically equivalent

Contrast with



By symmetry

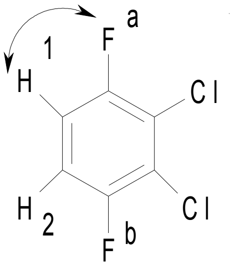
F^a and F^b chemically equivalent

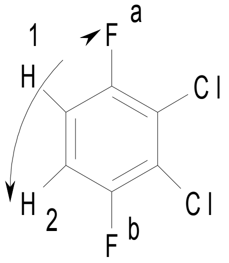
H^1 and H^2 chemically equivalent

Now for coupling must compare: H^1 and H^2 with F^a

H^1 and F^a : ortho

H^2 and F^a : meta





Not the same

Not magnetically equivalent

Notice

- do NOT compare the pairs {H^1, F^a}, {H^2, F^b}

Notation

Resonances at δ and coupled by J

- Assign each nucleus a capital letter from the English alphabet

1. $\Delta\delta > J$	Letters well apart **A M X** First order
2. $\Delta\delta \leq J$	Adjacent letters **A B C** Second order

- Magnetic equivalence is shown by a numerical subscript with the value showing the number of equivalent nuclei

A_3X A_3 e.g. a methyl group

- Chemical equivalence is shown by a ' superscript together with the same letter as the nucleu to which it is chemically equivalent

AA'XX' XX'X''X'''X''''

Spin-spin coupling

- Neighbouring nuclear spins aware of each other
    - alters their energy
    - additional linesplitting

- Analogy
  Two bar magnets N/S poles attract, N/N and S/S repel

- Two mechanisms
    - through space, dipolar, D
    - through bond, indirect, scalar coupling, J

- Pattern of splittings characteristic of the number of coupled spins and their spatial arrangement

Allows molecular connectivities to be determined

- Pairwise interaction

$$J\, I_1 . I_2$$

- J independent of the applied magnetic field B_0

- Can see spin-spin coupling over 4 to 5 bonds at most

Typical values for J
${}^2J_{HH}$ (geminal) = -12 Hz ${}^3J_{HH}$ (vicinal) = 5 Hz

Aromatic: ortho = 5-9 Hz, meta = 2-3 Hz, para = 0-1Hz

Effect on the NMR spectrum

Consider only first order spectra:

$$J \ll \Delta\delta \text{ (Hz)}$$

J independent of B_0 , $\Delta\delta$ increases with B_0
So all NMR spectra tend to first order as the magnetic field strength is increased

Method of successive splittings

- Take each pair of nuclei in turn

- Resonance split into $N+1$ lines where N is the number of magnetically equivalent nuclei

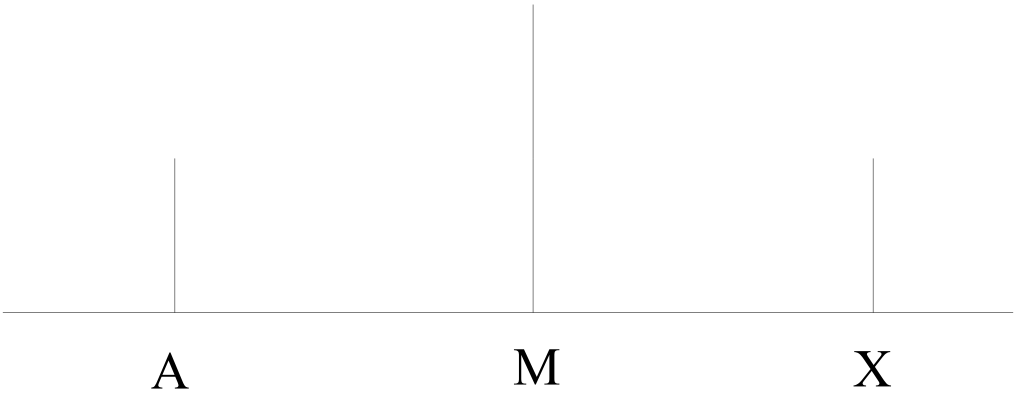
- Intensities given by the binomial coefficients of Pascals triangle

1	singlet
1 1	doublet
1 2 1	triplet
1 3 3 1	quartet
1 4 6 4 1	quintet

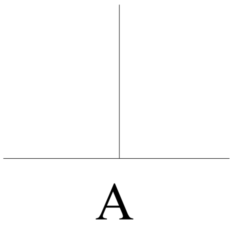
Example

A M_2 X spin system

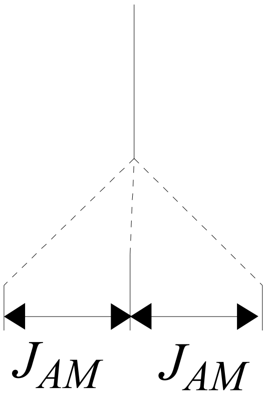
1. Draw arbitrary positions for the initial resonances



2. Start with the A spin



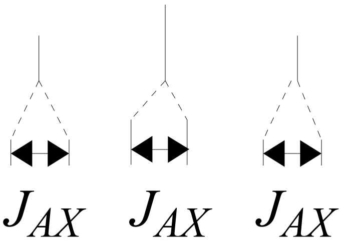
Now take each of the other spins in turn: a) M
M_2, two magnetically equivalent nuclei, $N = 2$
$N+1$ lines = 3 lines
Relative intensities 1: 2 :1



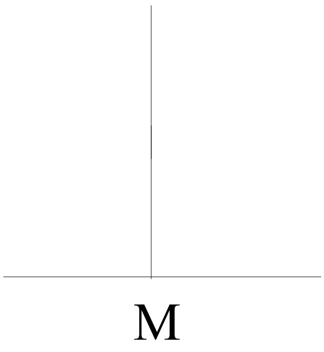
b) Using the splitting pattern from the M now take the X spin

X, one magnetically equivalent nucleus, $N = 1$
$N+1$ lines = 2 lines
Relative intensities 1:1

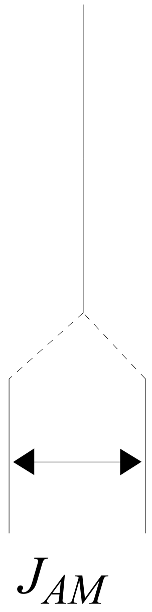
Each line in the pattern is split



3. Now take the M spin



Then take each of the other spins in turn:
a) A,
One magnetically equivalent nucleus, *N*= 1
N+*1* lines = 2 lines
Relative intensities 1: 1



Same splitting of M by A as for A by M

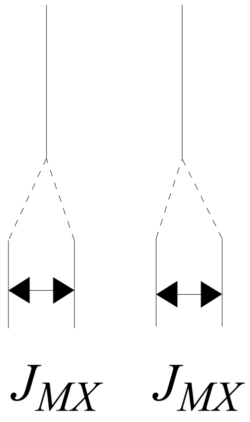
b) Using the splitting pattern from the A now take the X spin

X, one magnetically equivalent nucleus, $N = 1$

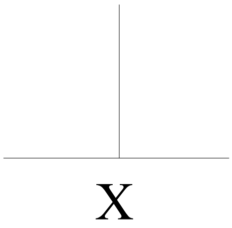
$N+1$ lines = 2 lines

Relative intensities 1:1

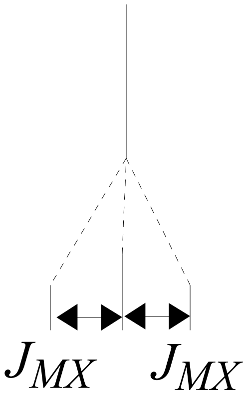
Each line in the pattern is split



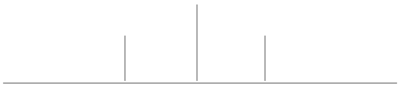
4. Now take X spin – just like the A
but with J_{MX}



Now take each of the other spins in turn: a) M
M_2, two magnetically equivalent nuclei, $N = 2$
$N+1$ lines = 3 lines
Relative intensities 1: 2 :1

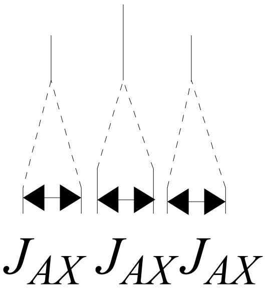


b) Using the splitting pattern from the M now take the A spin



X, one magnetically equivalent nucleus, *N*= 1
N+*1* lines = 2 lines
Relative intensities 1:1

Each line in the pattern is split



Special case

- when J equal :
  form a composite spin
  makes it easier to draw

Example

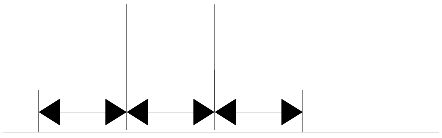
AM_2X $J_{AM} = J_{AX}$

A sees M and X as equivalent so $A[P]_3$

$$J_{A''P''} = J_{AM} = J_{AX}$$

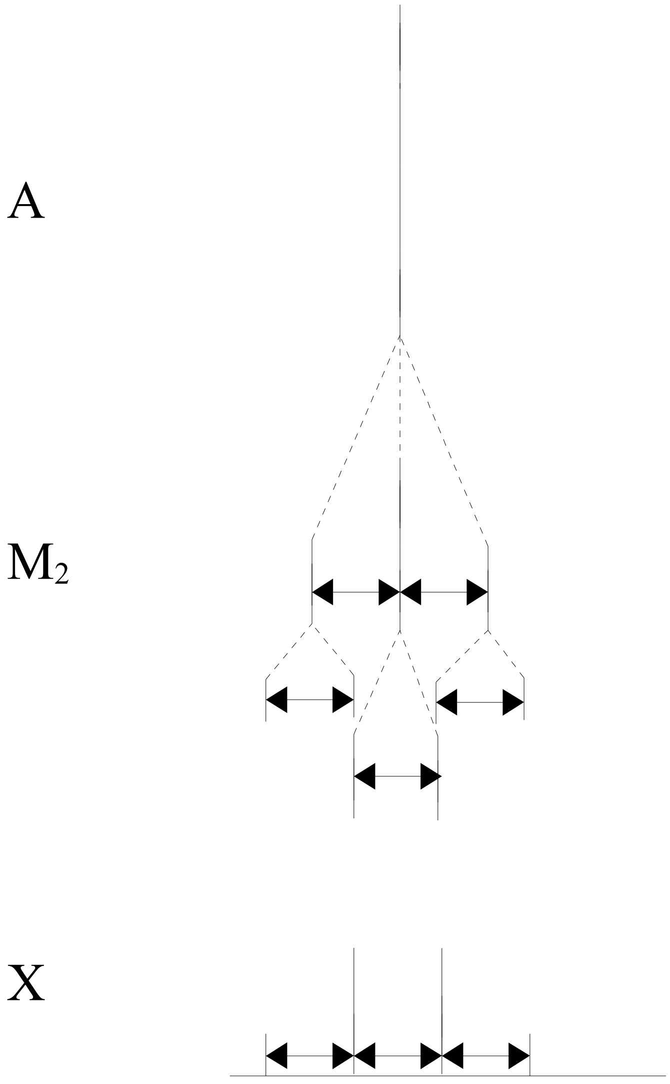
Three equivalent spins , $N+1 = 4$

Quartet



$J_{A''P''}$

Equivalent to



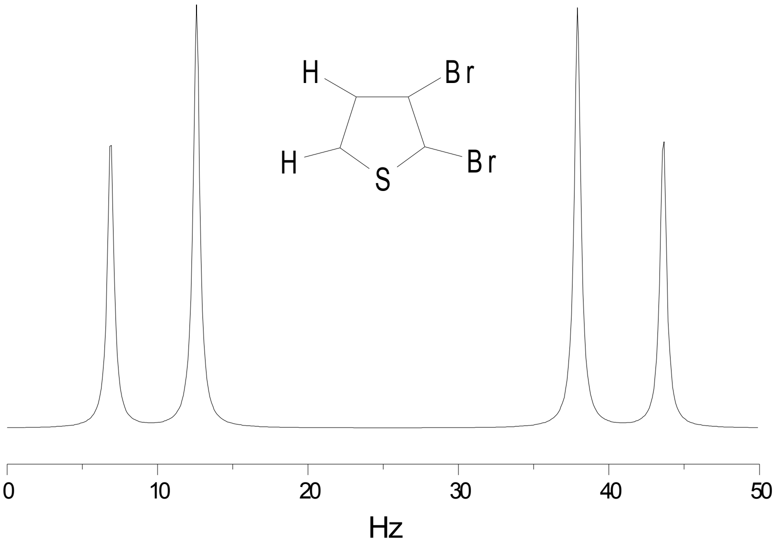
Second order coupling

Spectra more complex

- splitting pattern changes with B_0

AB example

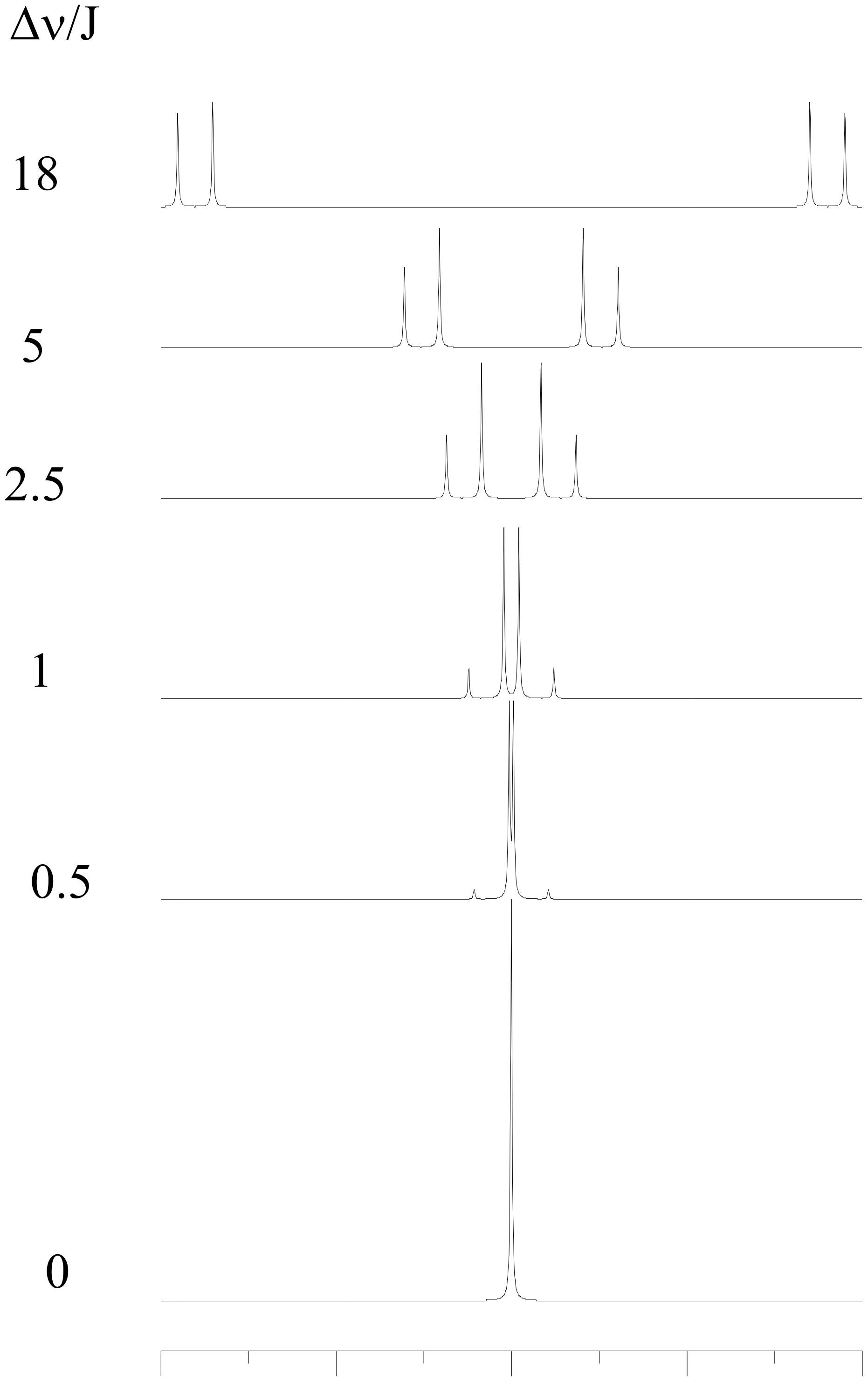
$\Delta\nu = 30.5$ Hz
$J = 5.7$ Hz



Doublets no longer equal intensity

- inner lines "steal" intensity from the outer

Overall changes



Connectivity

Spin-spin coupling shows connectivity between the NMR resonances

Powerful method for identifying a molecule

Need to know which resonance is coupled to which

Spin decoupling
- irradiation with a second radiofrequency
  - saturates the irradiated resonance
    - ignore its effect on the other nuclei

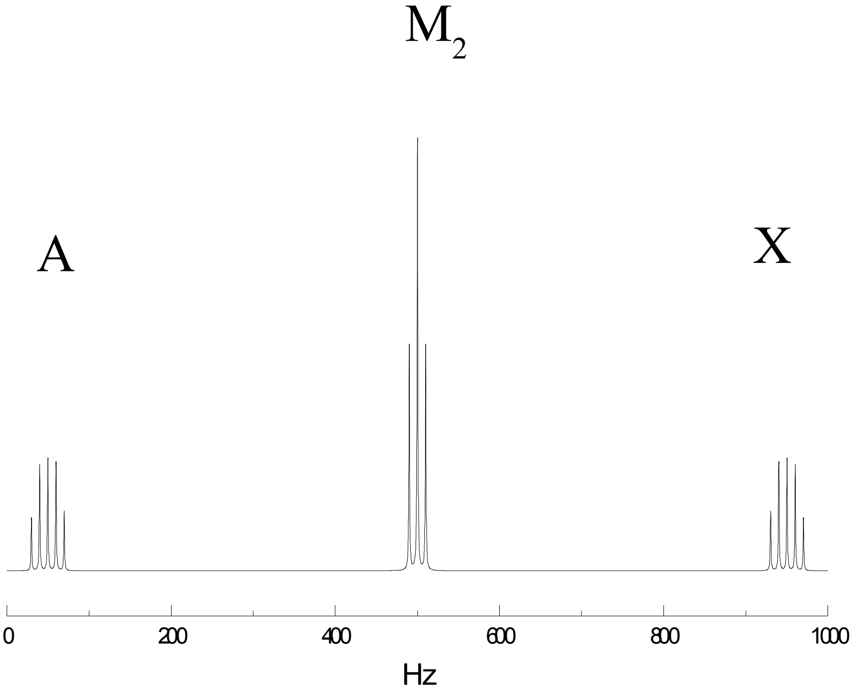
- older technique

COSY
- two dimensional NMR

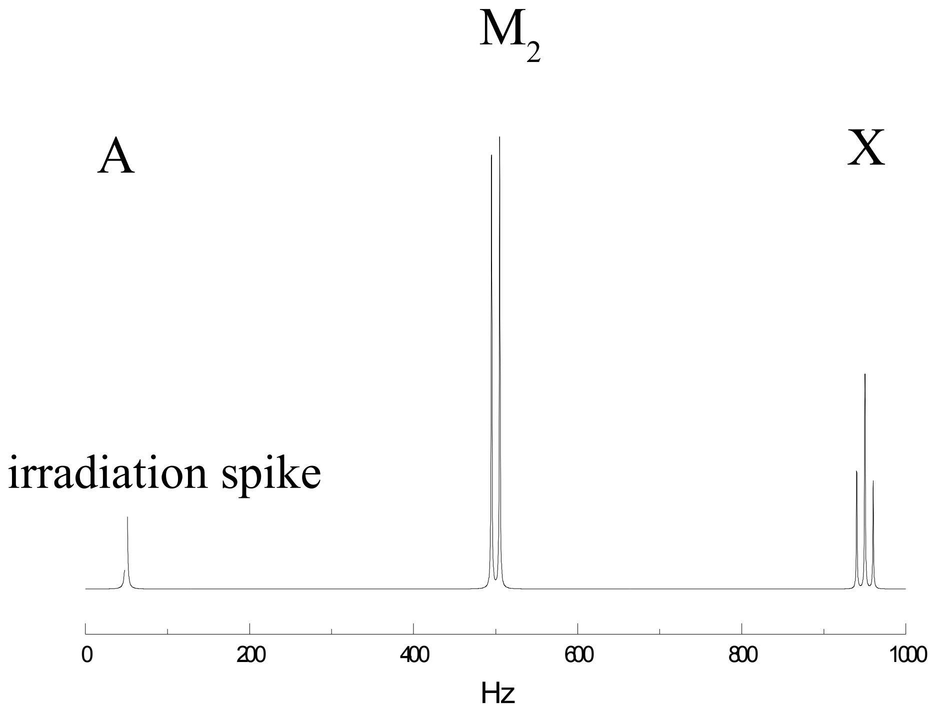
- coupled resonances show up as off-diagonal peaks

Spin decoupling

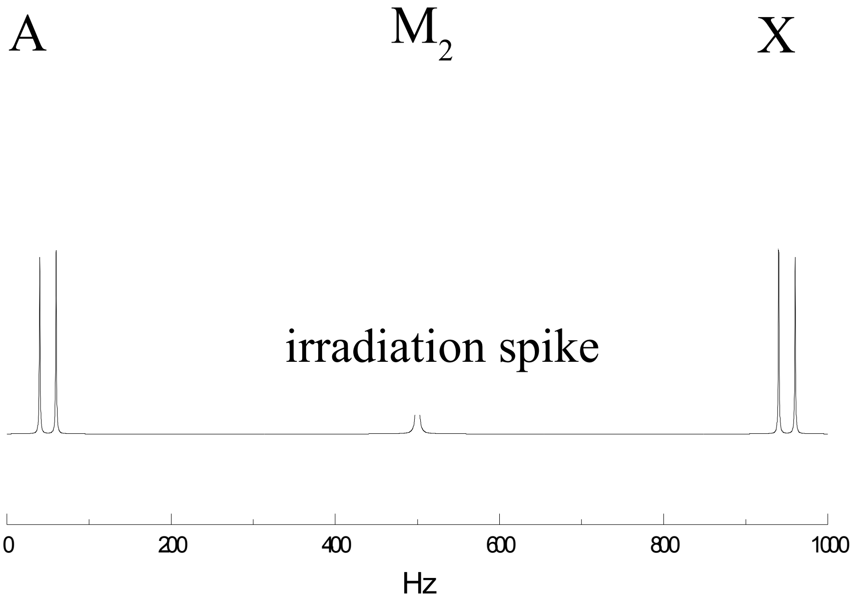
AM_2X $J_{AM} = J_{MX} = 10$ Hz $J_{AX} = 20$ Hz



Irradiate A



Irradiate M



Irradiate X