Notation for Spin Systems

Capital letters A, B, C, M, A, X, Y, …….

- Same letter = same chemical shift (A_3, B_2, X_6, ….)
- Different letters = different chemical shifts

Letters close in the alphabet (A, B, C, …)

J [Hz] of the same magnitude as $\Delta\nu$ [Hz]

Letters separated in the alphabet (A, M, X,…)

large separation of chemical shifts

-different nuclei (^{1}H, ^{31}P, ^{195}Pt,…)

-same nuclei but $\Delta\nu$ [Hz] much larger than J

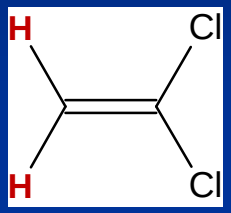
!! $\Delta\nu$ [Hz] depends on B_0 !!

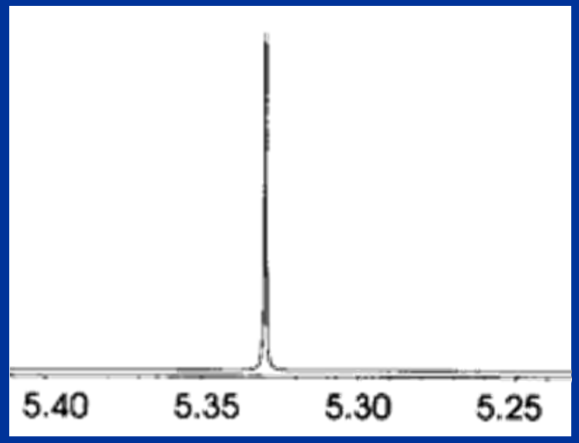
Notation for Spin Systems

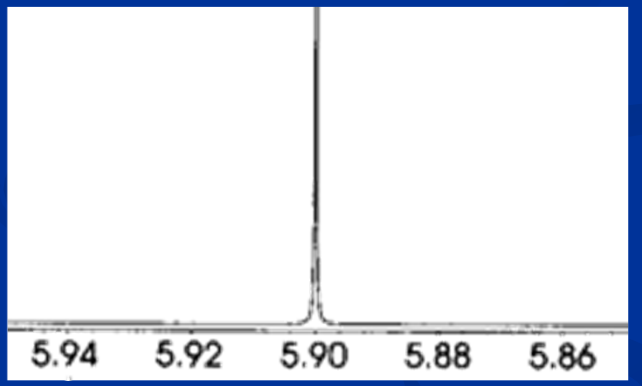
- Same letter = same chemical shift (A_3, B_2, X_6, ….)

CH_2Cl_2

A_2





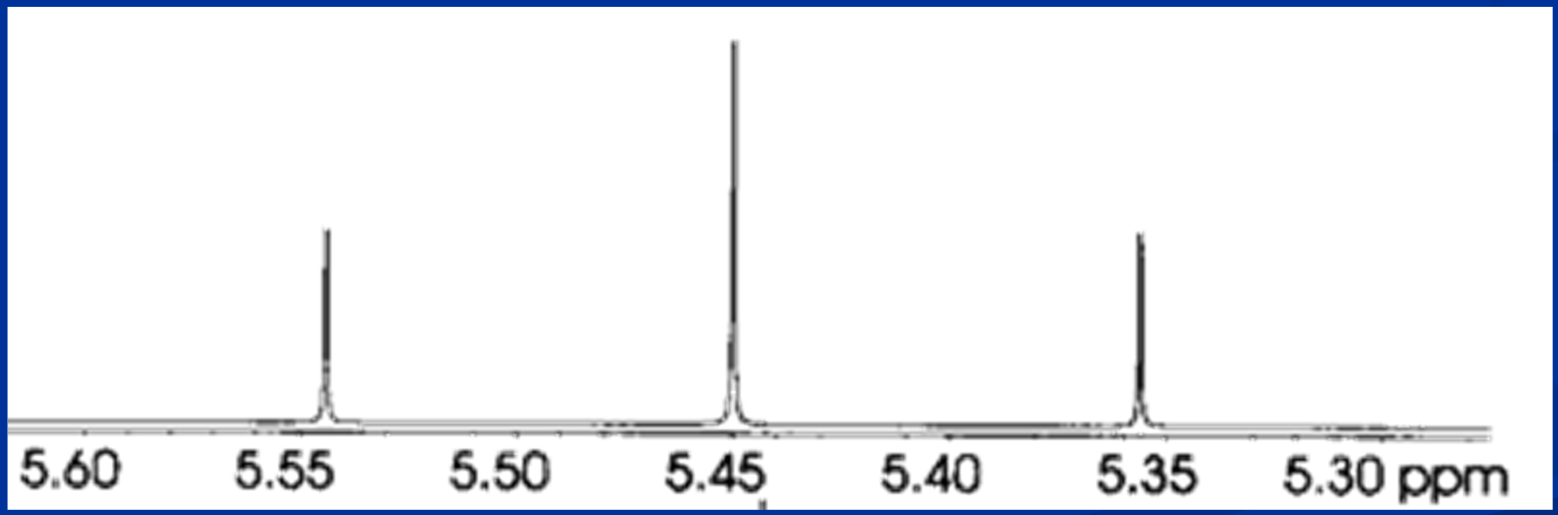


Notation for Spin Systems

- Different letters = different chemical shifts

CH_2F_2

A_2X_2



Notation for Spin Systems

Two situations:

a) Complete equivalence =

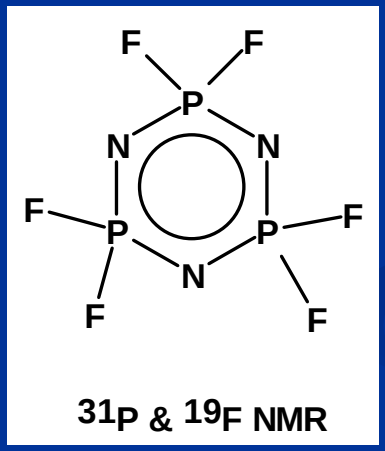
Chemical shift equivalence (isochronous nuclei)
+ magnetic (spin-coupling) equivalence (isotachous)

Magnetic equivalence = each member of one group of spins is coupled equally to all members of any other group

A_2B_2, A_2X_2,….

Notation for Spin Systems

b) Chemical shift equivalence, magnetic INequivalence
AA'BB', AA'XX', AA'A"XX'X", ….

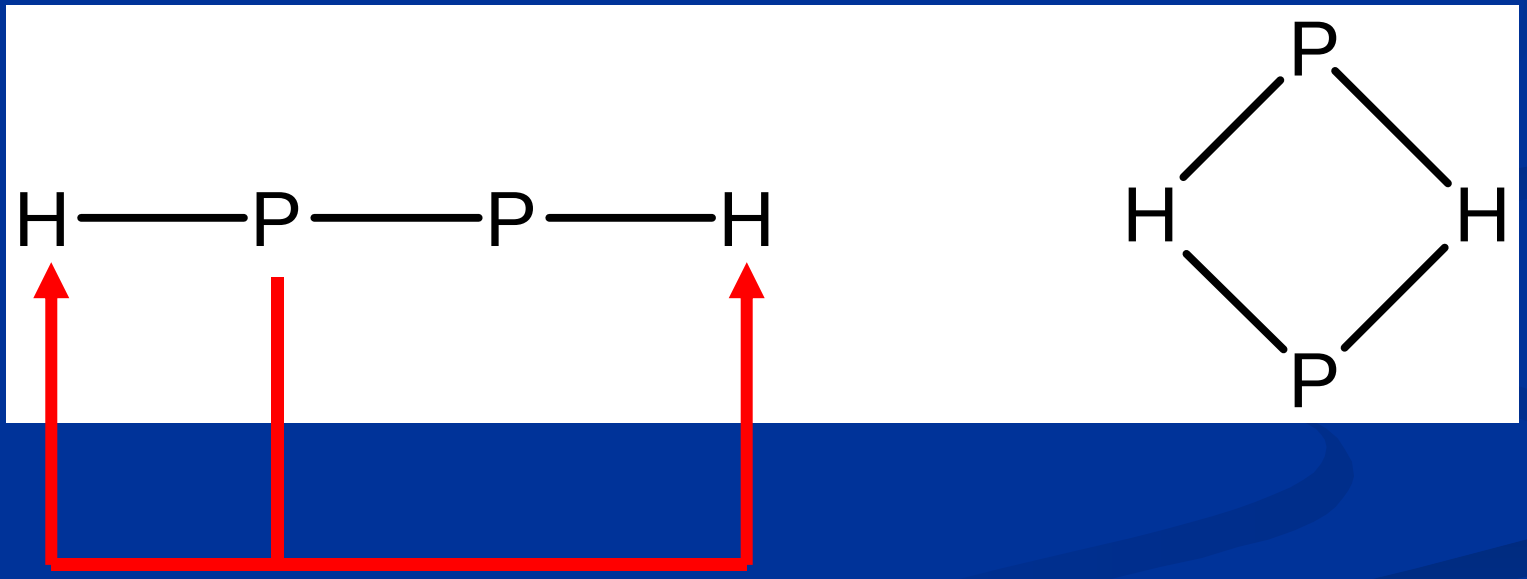


^{31}P & ^{19}F NMR

$AA'A''XX'X''X'''X^4X^5$ $[A[X]_2]_3$

Magnetic Inequivalence

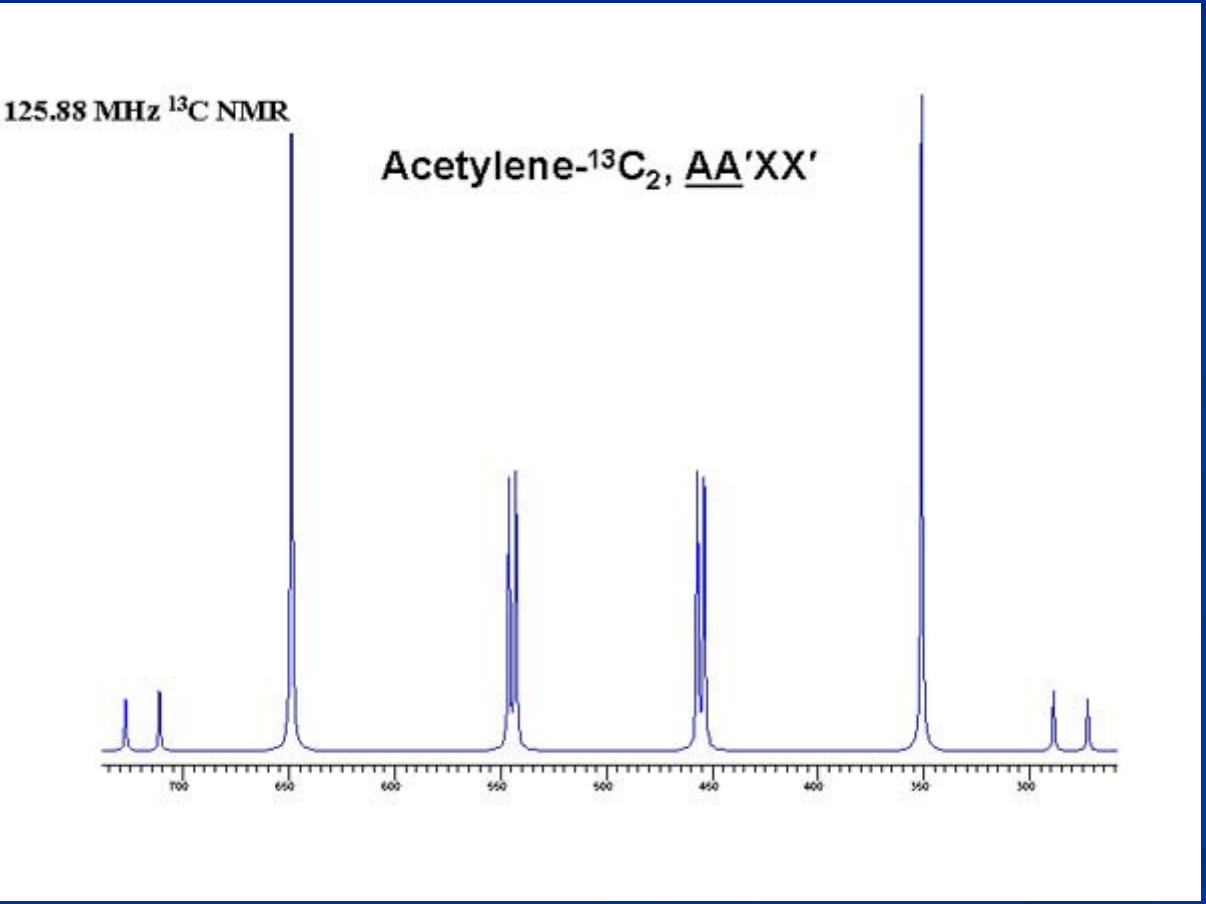
AA'XX' **A_2X_2**



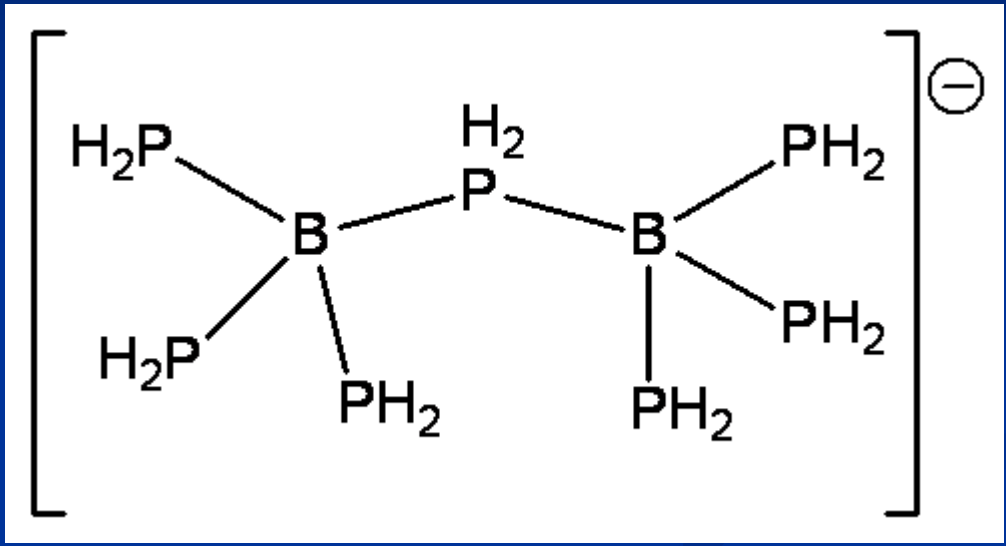
Prime vs. Bracket Notation

AA'BB'	$[AB]_2$
A_2B_2	$[A_2B_2]$
AA'BXX'	$[AX]_2B$
$AA'X_3X_3'$	$[AX_3]_2$

Magnetic Inequivalence



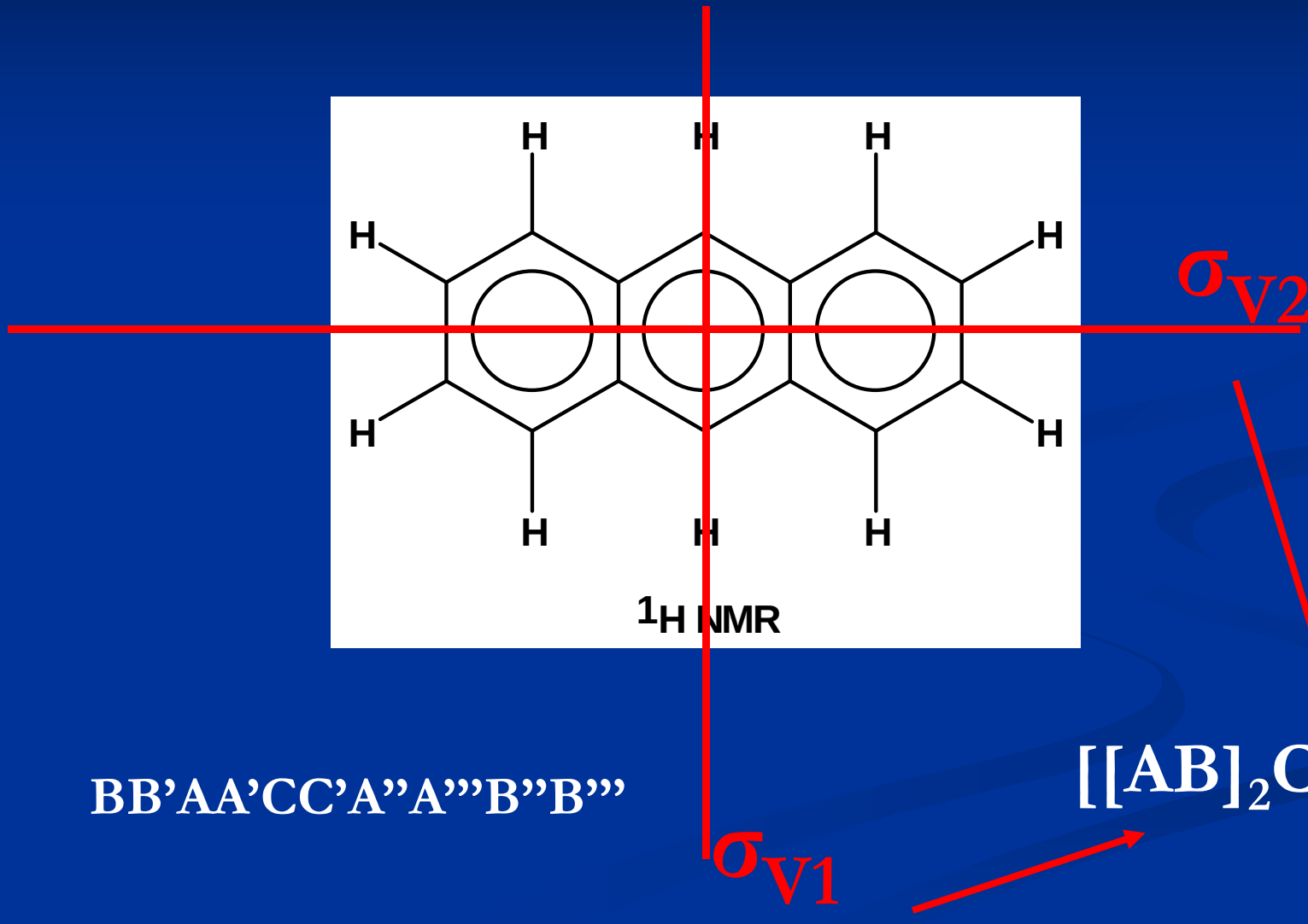
Magnetic Inequivalence



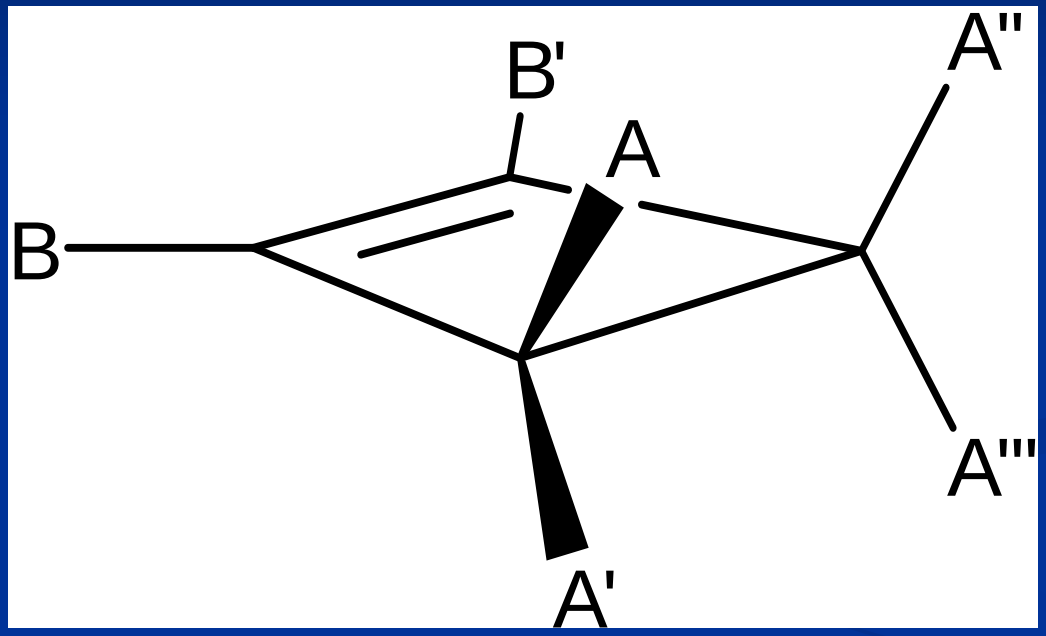
Bracket Notation

- Square brackets with subscript indicate repeated symmetry-related magnetically inequivalent groups of nuclei, e.g. $[AB]_2$
- Square bracket without subscript indicate magnetic equivalence of isochronous nuclei inside, e.g. $[A_6]$
- Each bracket represents a specific symmetry operation (see anthracene)
- Append a point group symbol to avoid ambiguity
- Free rotation – apply Mortimer rule = the most symmetrical conformer

Notation for Spin Systems



Notation for Spin Systems

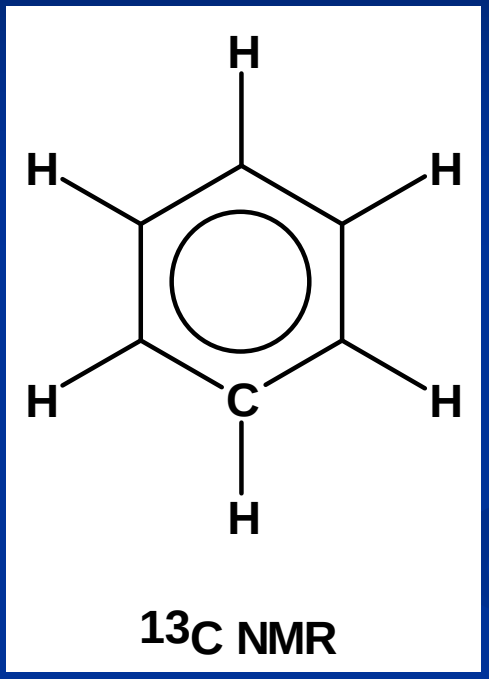


$[[A]_2B]_2$

Ring plane

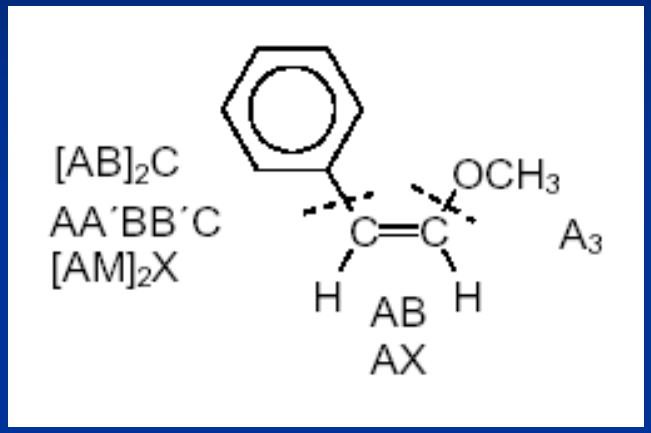
Plane perpendicular to ring

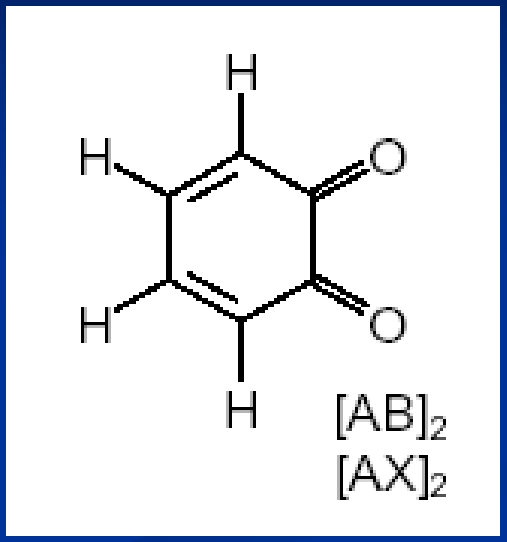
Notation for Spin Systems

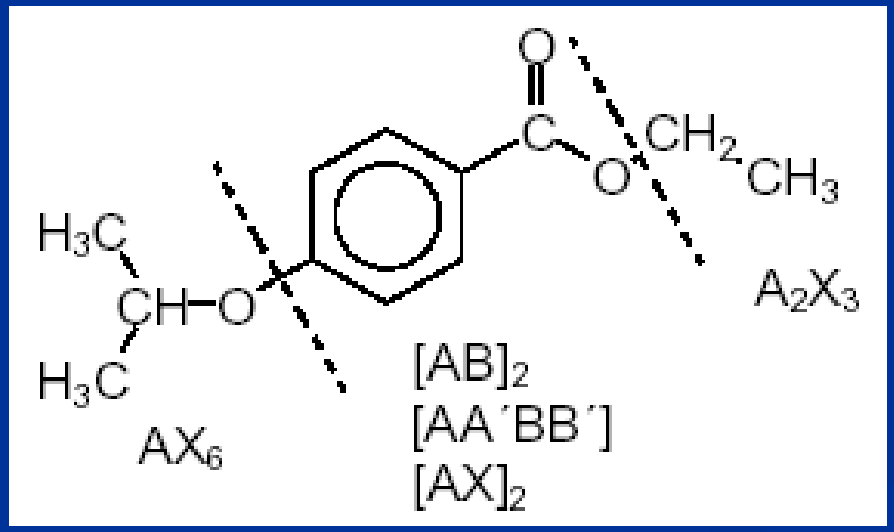


considering isotope shift: $A[BC]_2DX$

Spin Systems in ^{1}H NMR

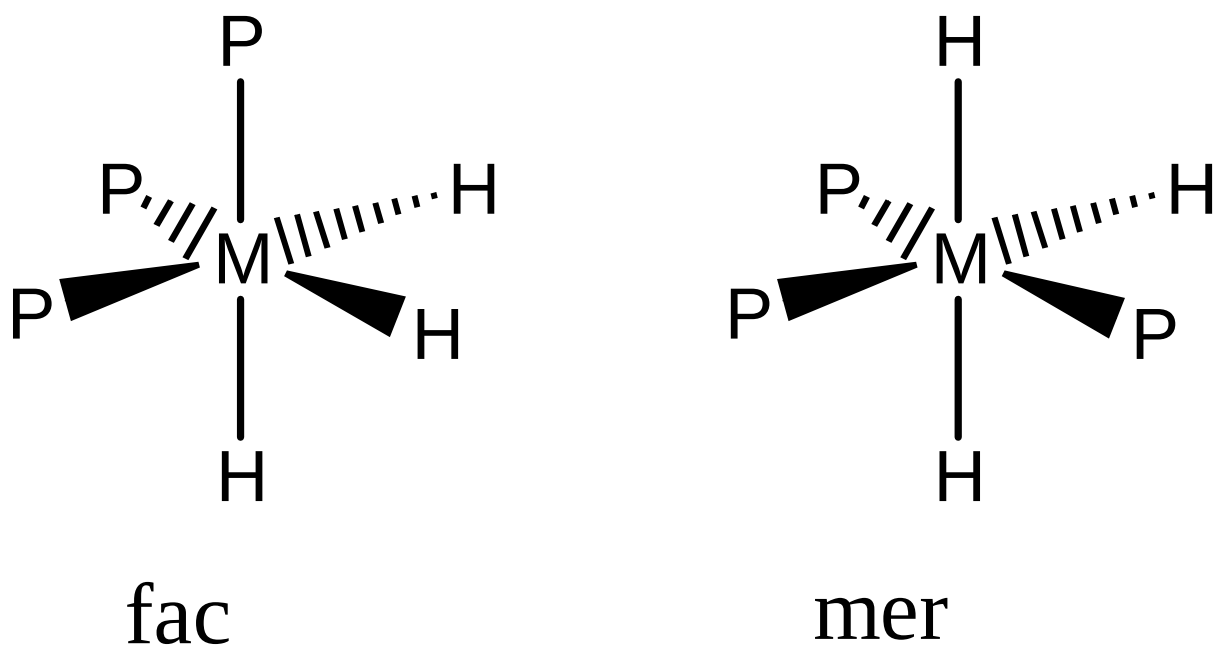






When separated by more than 3 bonds, the spin systems can be considered separately (with exceptions)

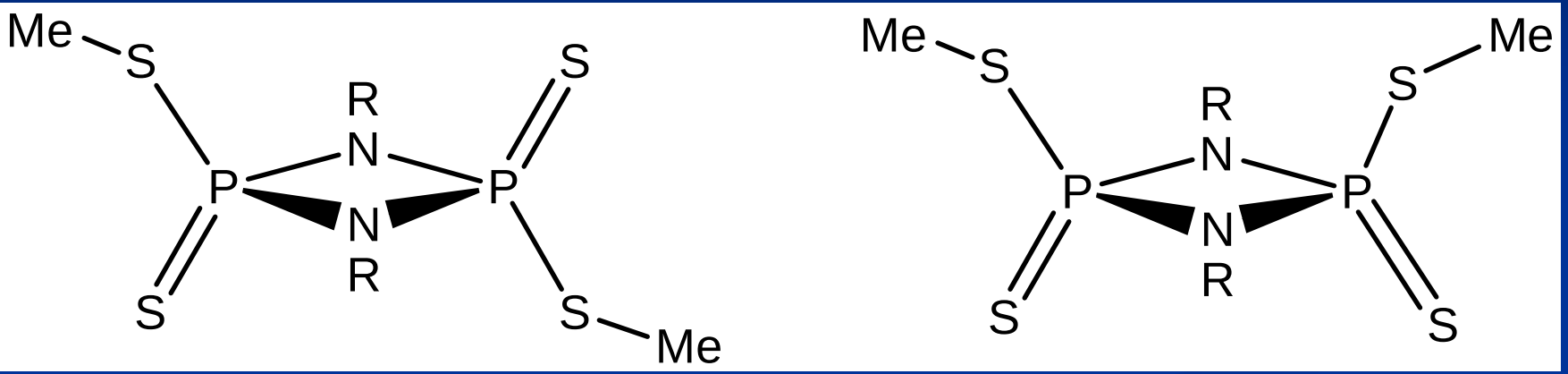
Spin Systems



AA'A"XX'X" **AB_2XY_2**

$^3J_{PH}$(cis) = 10 – 40 Hz
$^3J_{PH}$(trans) = 80 – 150 Hz

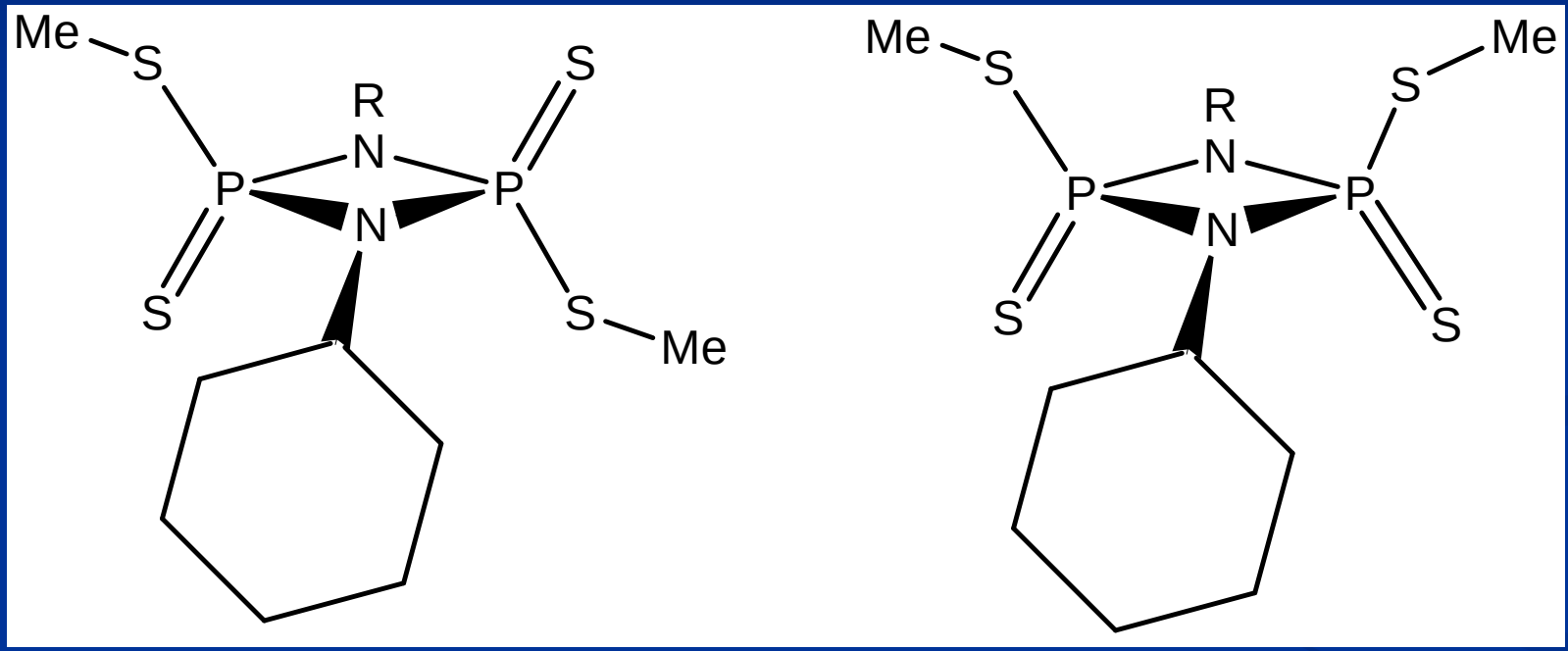
Spin Systems



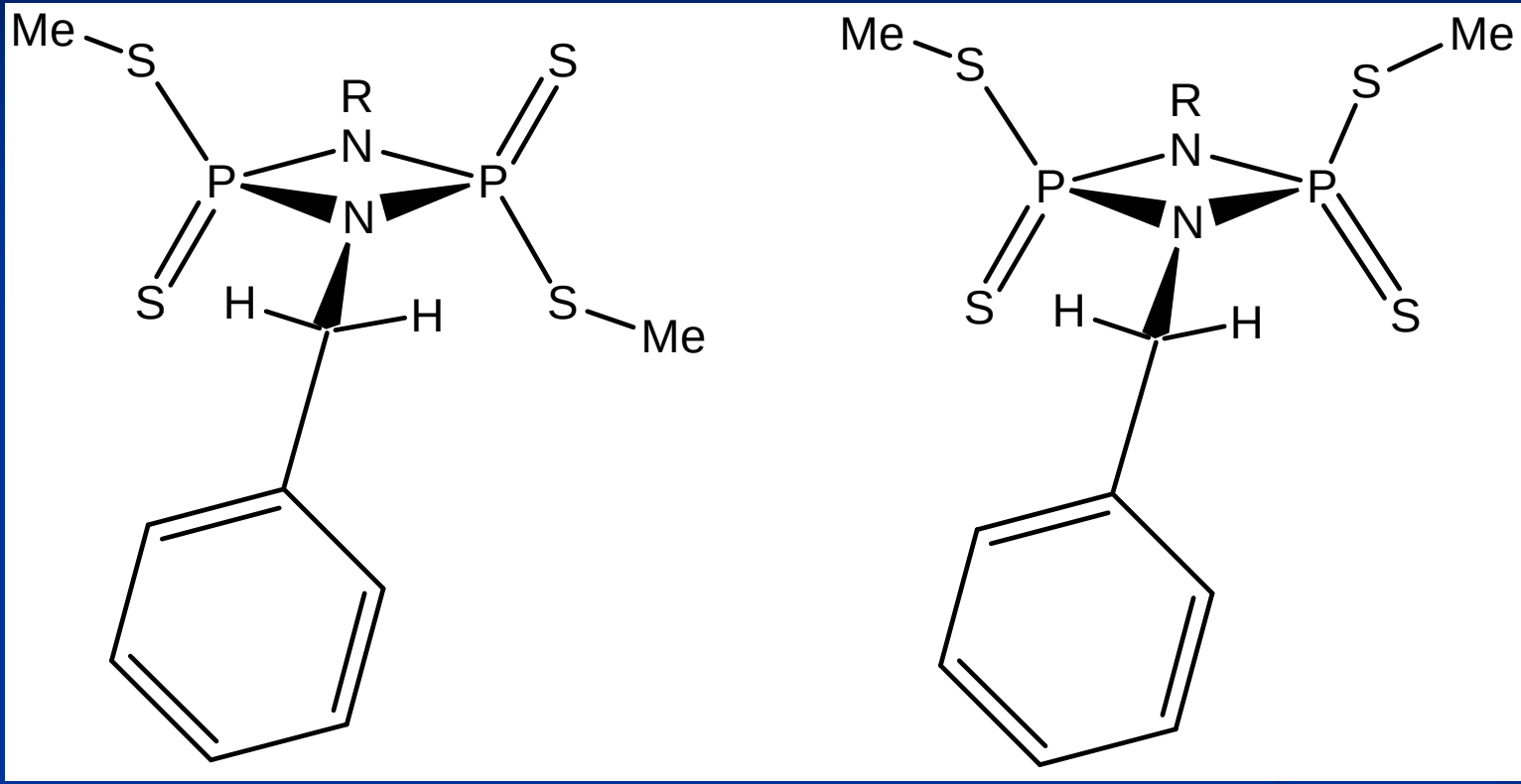
^{1}H, ^{31}P

^{13}C, ^{31}P

Spin Systems



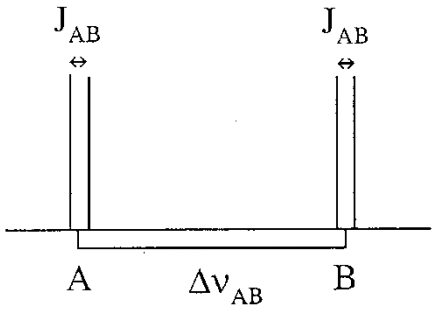
Spin Systems



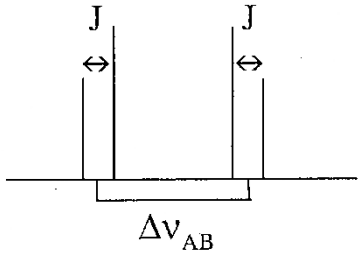
^{1}H, ^{31}P

AB System

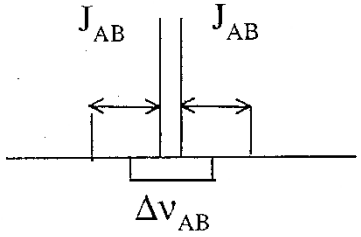
Spin-spin coupling



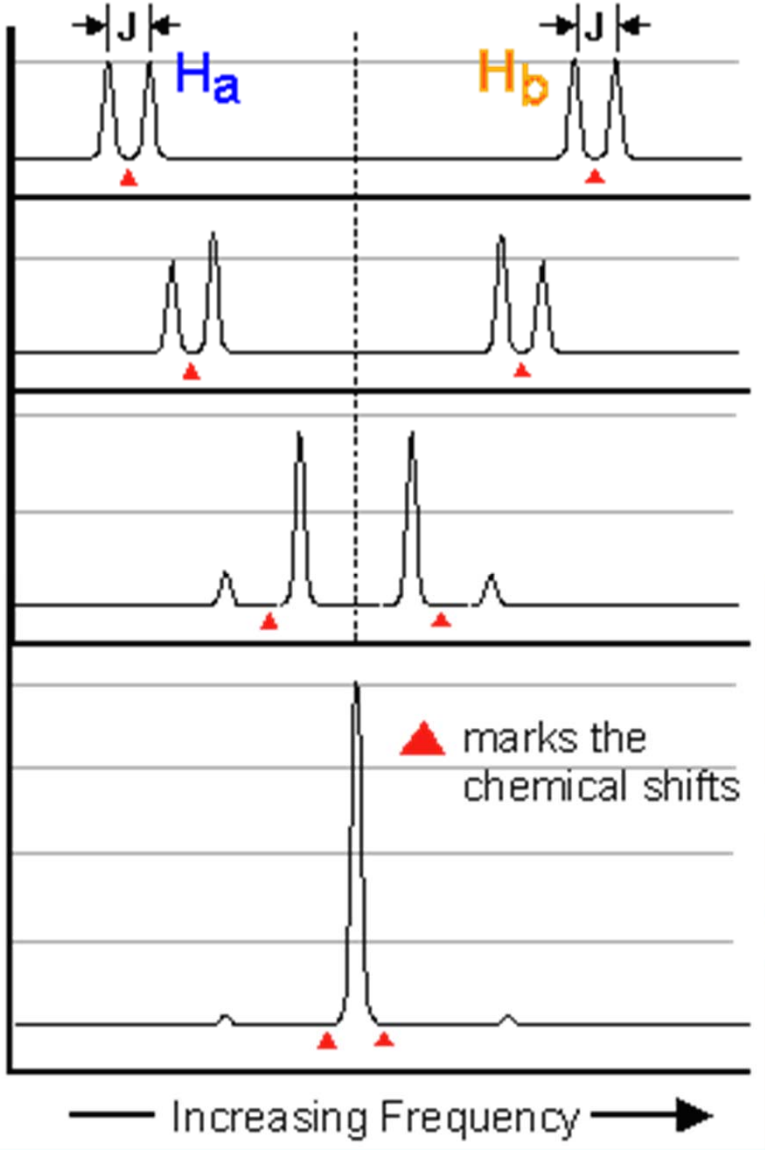
$\frac{\Delta\nu_{AB}}{J_{AB}} >> 1$



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



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



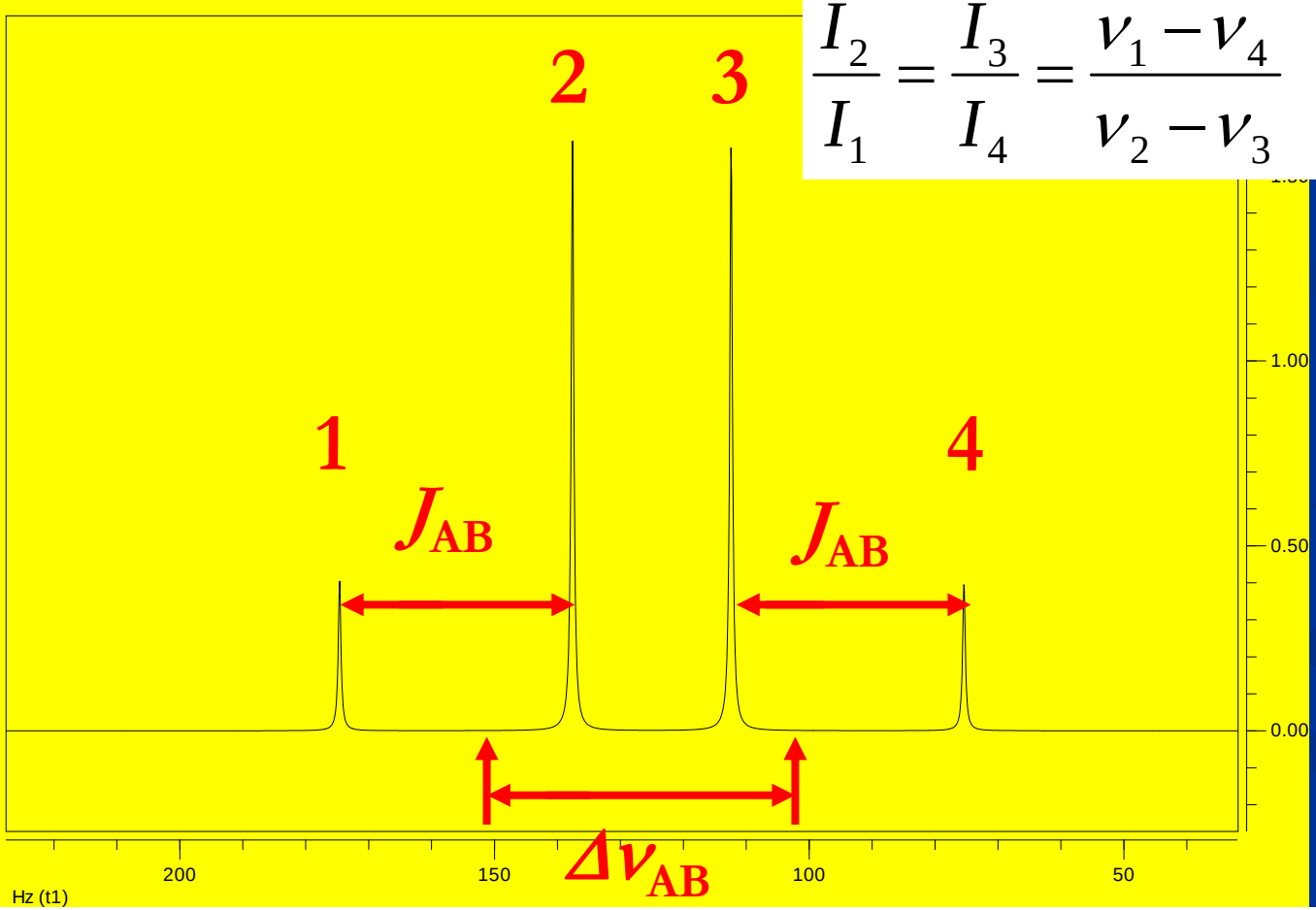
AB System

The simplest higher-order spin system

$$J_{AB} = \nu_1 - \nu_2 = \nu_3 - \nu_4$$

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

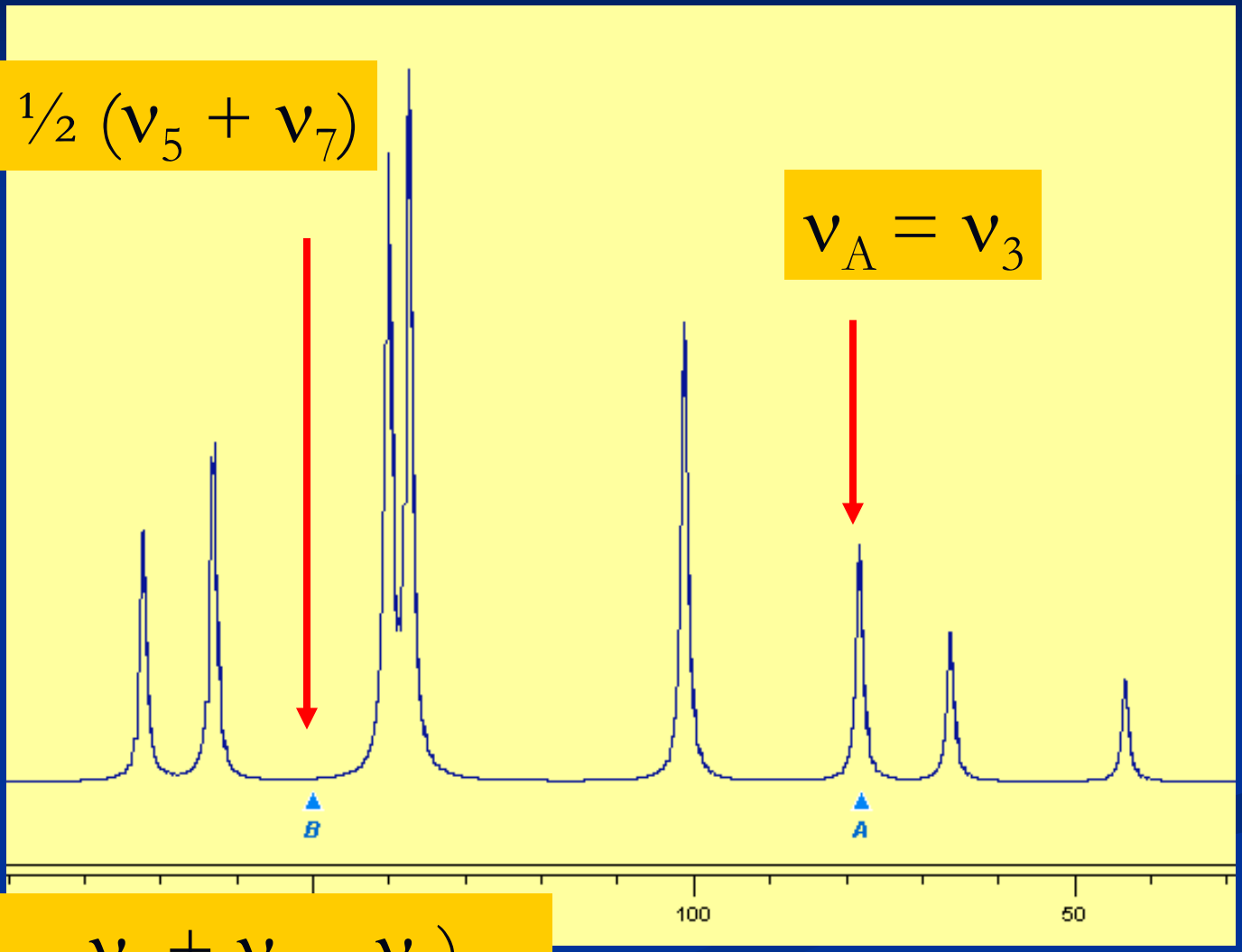
$$\frac{I_2}{I_1} = \frac{I_3}{I_4} = \frac{\nu_1 - \nu_4}{\nu_2 - \nu_3}$$



AB_2 Spin System

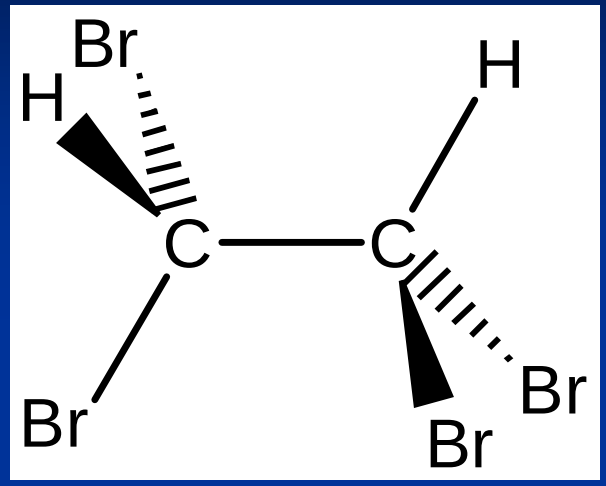
$\nu_B = \frac{1}{2} (\nu_5 + \nu_7)$

$\nu_A = \nu_3$

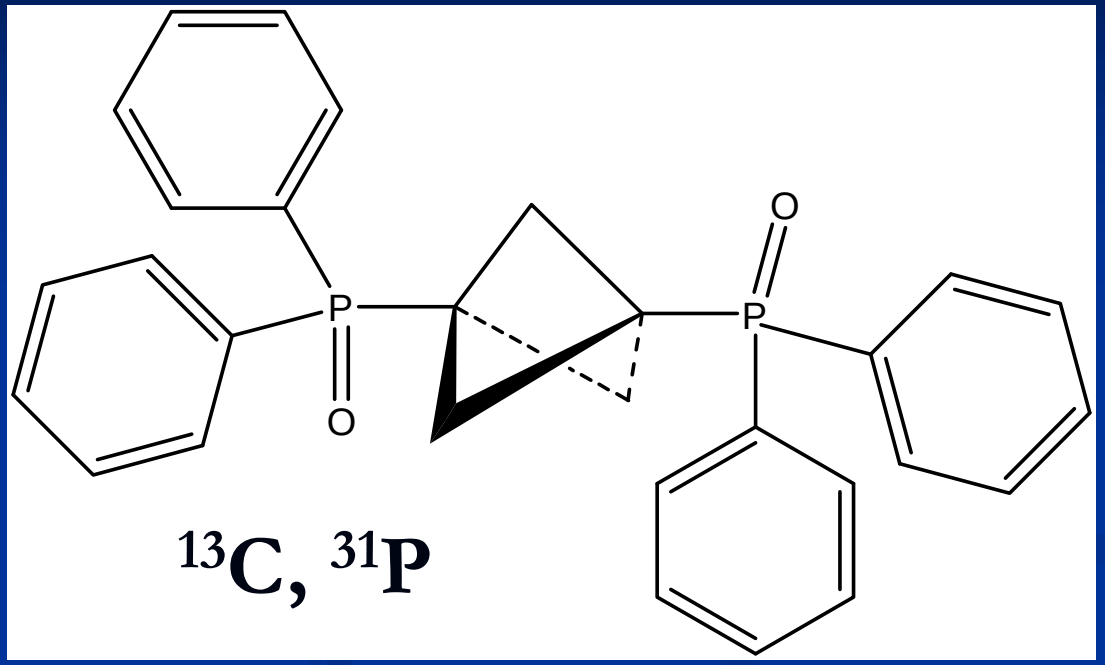


$J_{AB} = 1/3(\nu_1 - \nu_4 + \nu_6 - \nu_8)$

ABX Spin System



^{1}H, ^{13}C

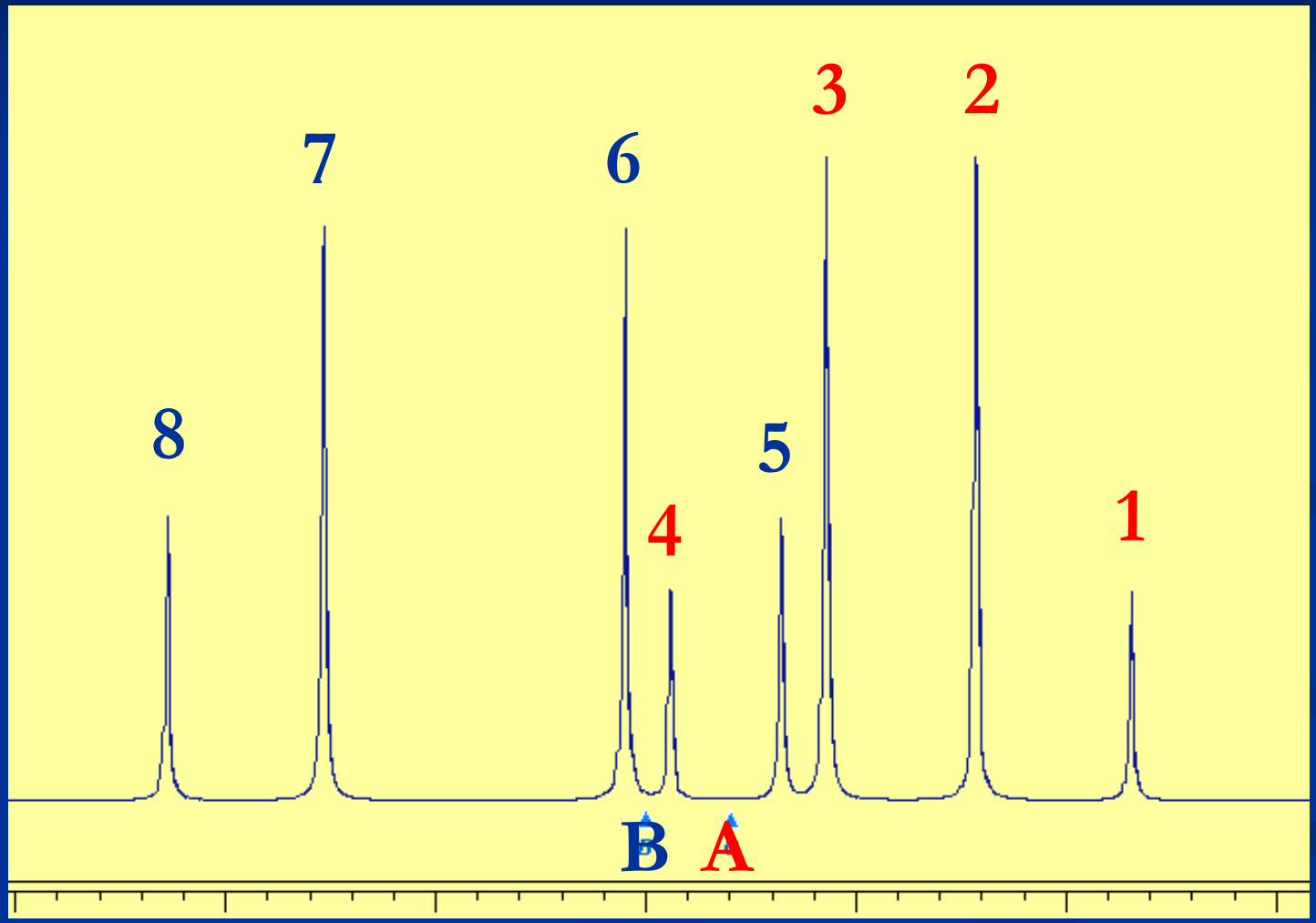


^{13}C, ^{31}P

AB part = 2 AB pseudoquartets = 8 lines

X part = 6 lines

AB Part of the ABX Spin System



ABX Spin System

$$J_{AB} = \nu_2 - \nu_1 = \nu_4 - \nu_3 = \nu_6 - \nu_5 = \nu_8 - \nu_7$$

$$J_{AX} + J_{BX} = \nu_{12} - \nu_9$$

$$\Delta\nu_{AB} = \nu_A - \nu_B$$

$$L = \tfrac{1}{2}(J_{AX} - J_{BX})$$

$$N = \tfrac{1}{2}(J_{AX} + J_{BX})$$

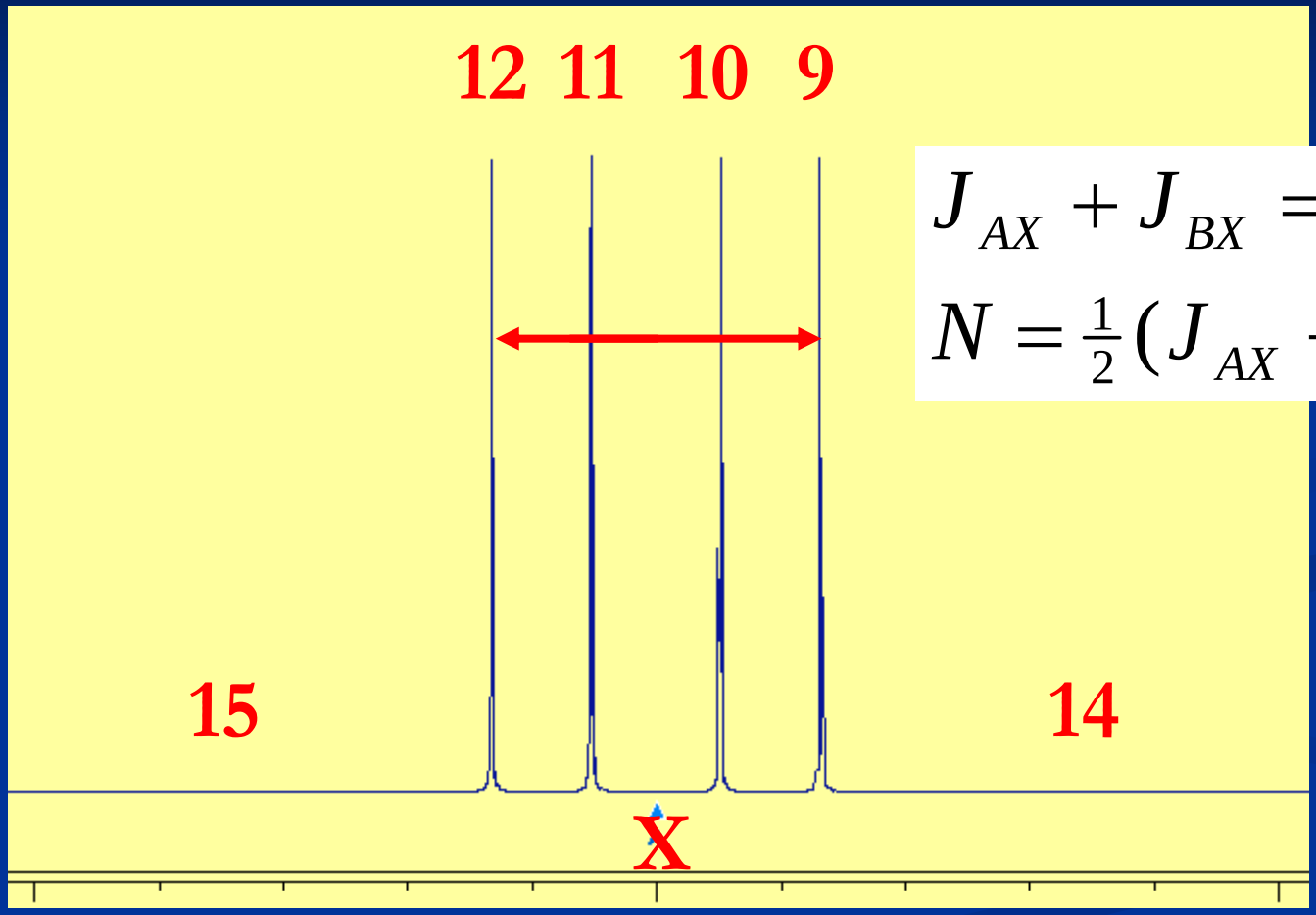
$$\Delta\nu_{AB}^{RED} = \Delta\nu_{AB} + L = \sqrt{(\nu_4 - \nu_1)(\nu_3 - \nu_2)}$$

$$Midp = \tfrac{1}{2}(\nu_A + \nu_B) + \tfrac{1}{2}N$$

$$\Delta\nu_{AB}^{BLUE} = \Delta\nu_{AB} - L = \sqrt{(\nu_8 - \nu_5)(\nu_7 - \nu_6)}$$

$$Midp = \tfrac{1}{2}(\nu_A + \nu_B) - \tfrac{1}{2}N$$

X Part of the ABX Spin System



$$J_{AX} + J_{BX} = \nu_{12} - \nu_{9}$$

$$N = \tfrac{1}{2}\left(J_{AX} + J_{BX}\right)$$

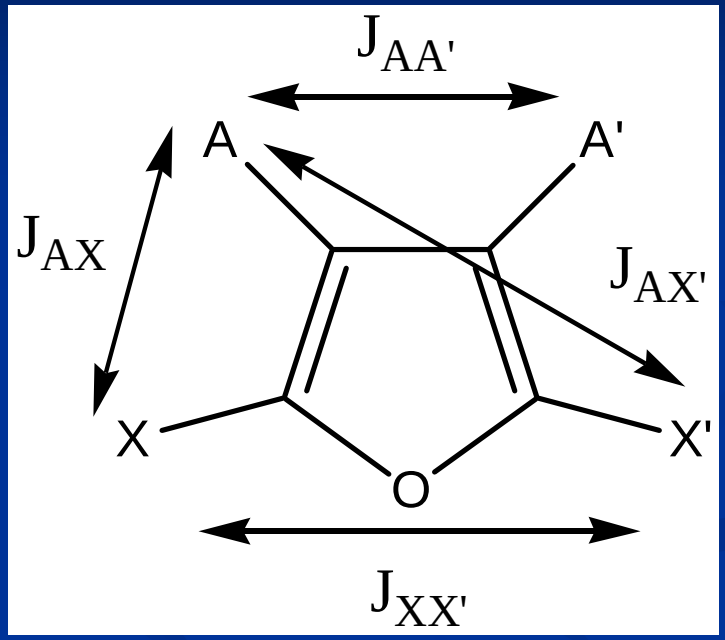
AA'XX' Spin System

4 coupling constants

Both part A and part X feature the same multiplet

symmetrical about ν_A or ν_X

Both parts have 12 lines with a center of symmetry at ν_A or ν_X



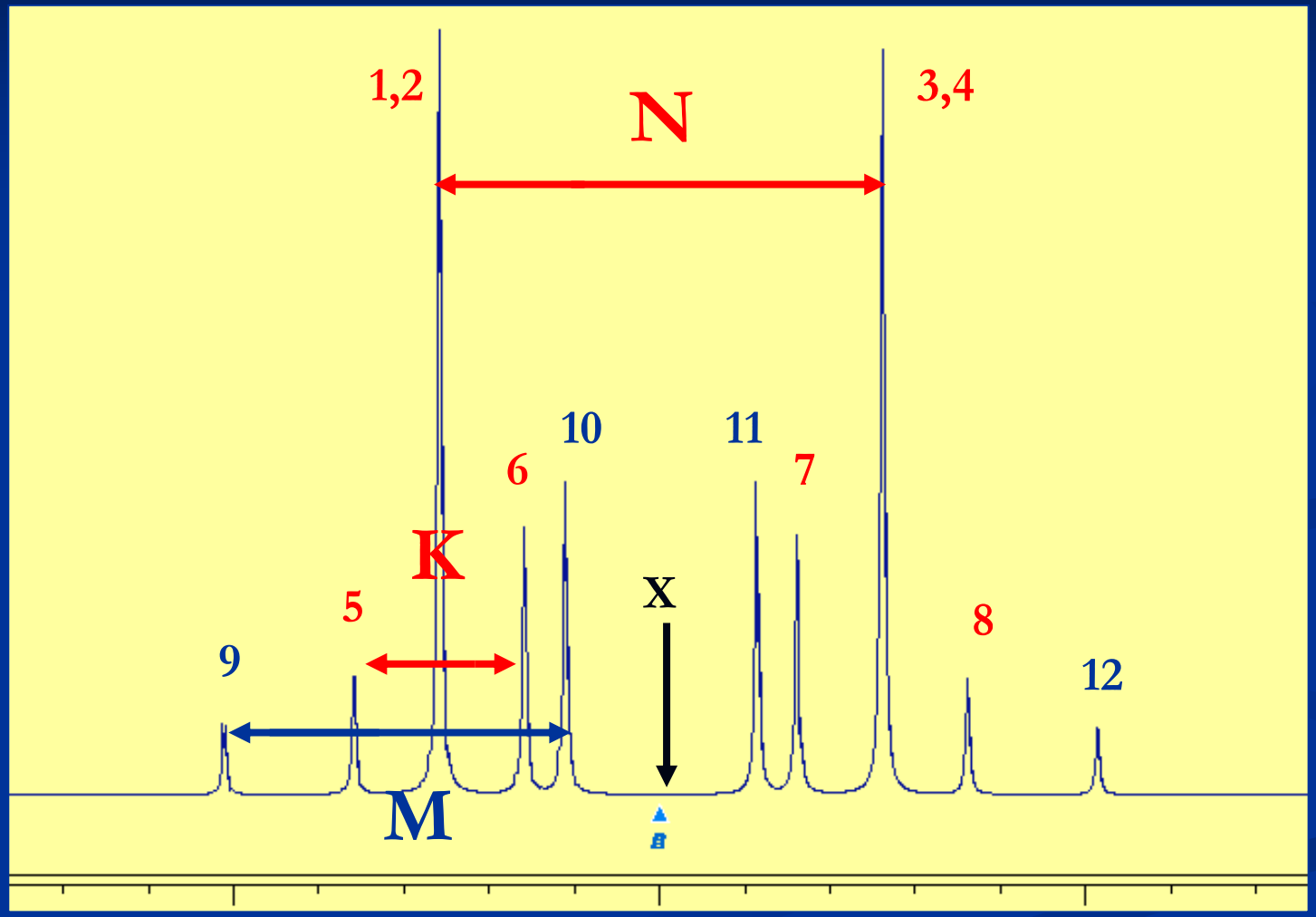
$$K = J_{AA'} + J_{XX'}$$

$$M = J_{AA'} - J_{XX'}$$

$$N = J_{AX} + J_{AX'}$$

$$L = J_{AX} - J_{AX'}$$

AA'XX' Spin System



AA'XX' Spin System

$$\left|N\right| = \nu_{1,2} - \nu_{3,4} = \left|J_{AX} + J_{AX'}\right|$$

$$\left|K\right| = \nu_5 - \nu_6 = \nu_7 - \nu_8 = \left|J_{AA'} + J_{XX'}\right|$$

$$\left|M\right| = \nu_9 - \nu_{10} = \nu_{11} - \nu_{12} = \left|J_{AA'} - J_{XX'}\right|$$

$$\left|L\right| = \sqrt{(\nu_6 - \nu_7)(\nu_5 - \nu_8)} = \sqrt{(\nu_9 - \nu_{12})(\nu_{10} - \nu_{11})} = \left|J_{AX} - J_{AX'}\right|$$

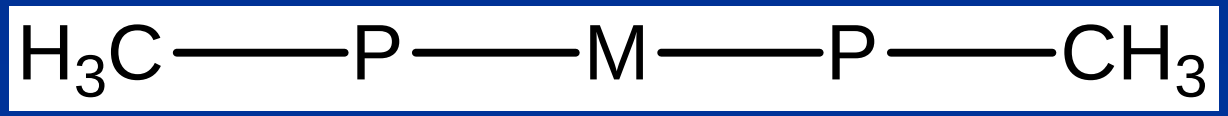
$$I_{1,2} = I_{3,4} = I_{5+6+7+8} = I_{9+10+11+12}$$

$$\frac{I_9}{I_{10}} = \frac{I_{12}}{I_{11}} = \frac{\nu_{10} - \nu_{11}}{\nu_9 - \nu_{12}}$$

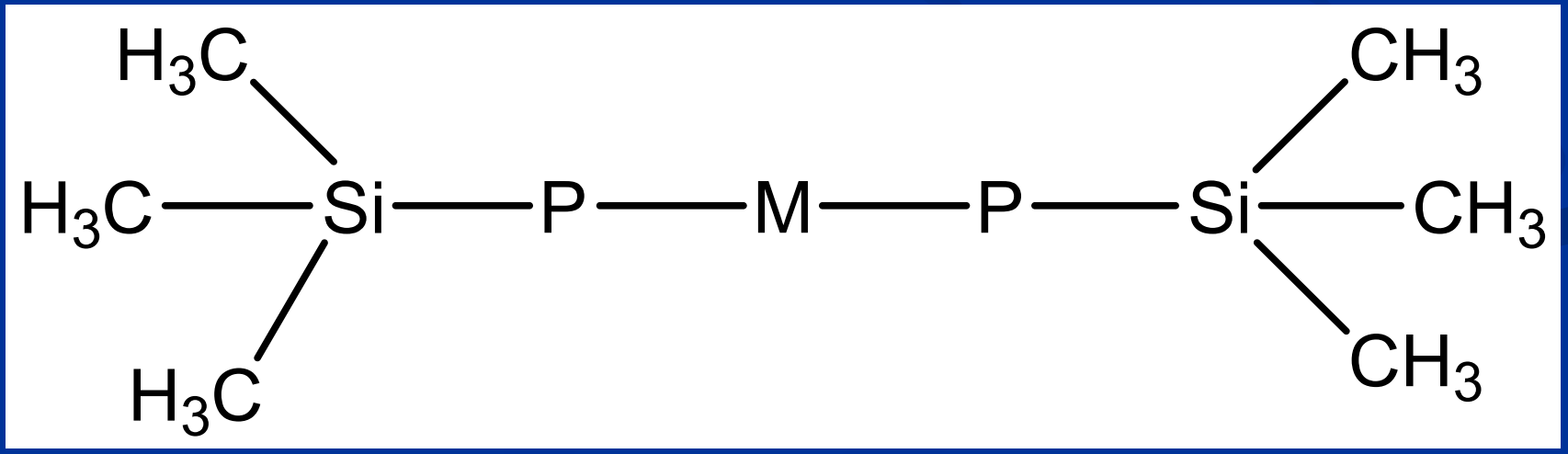
$$\frac{I_5}{I_6} = \frac{I_8}{I_7} = \frac{\nu_6 - \nu_7}{\nu_5 - \nu_8}$$

$AA'X_nX_n'$ Spin System

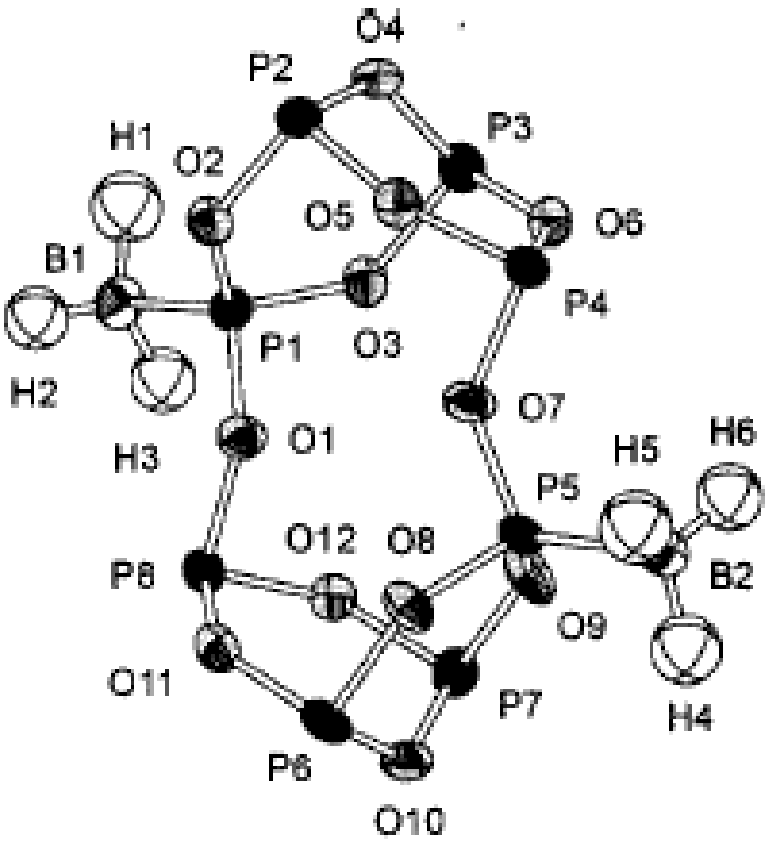
^{1}H and ^{31}P $AA'X_3X_3'$

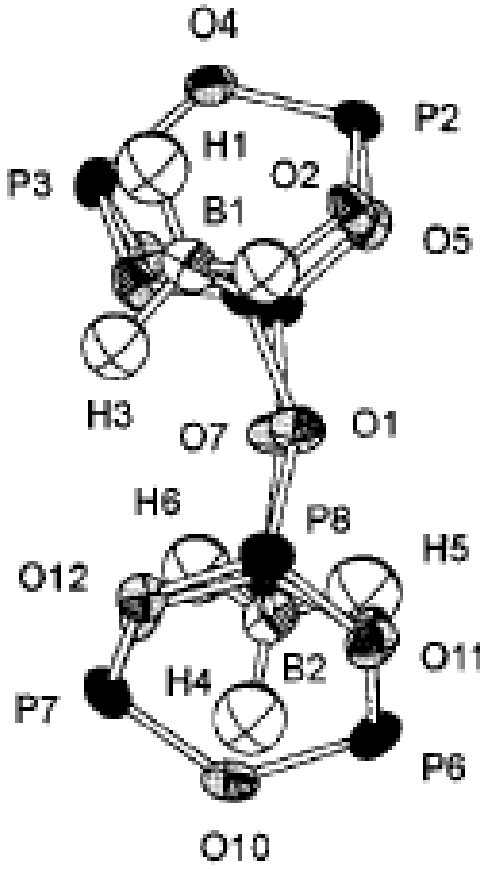


^{1}H and ^{31}P $AA'X_9X_9'$



$P_8O_{12} \cdot 2BH_3$





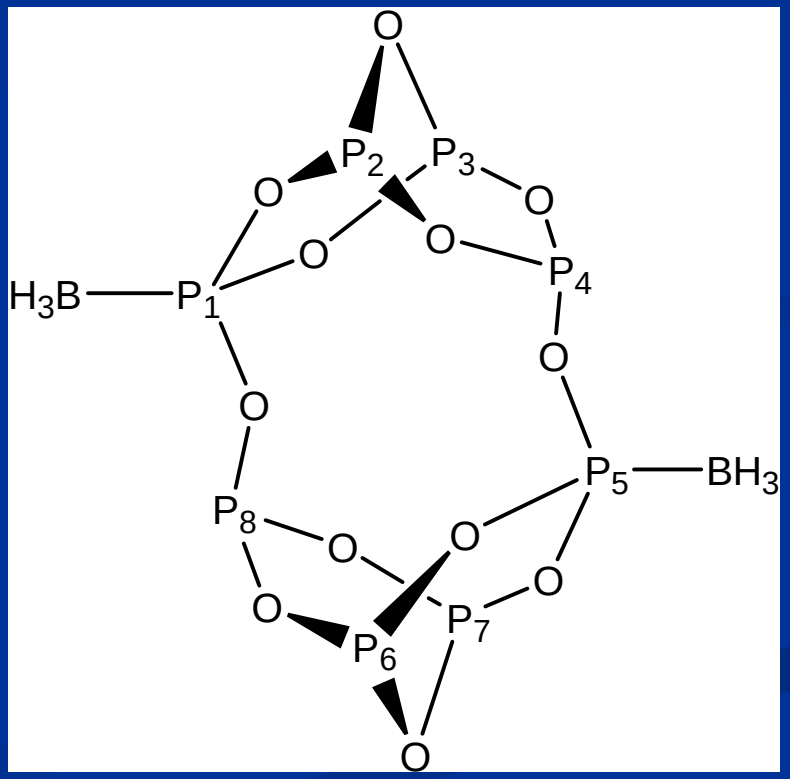
$P_8O_{12} \cdot 2BH_3$

C_{2h} Molecular symmetry

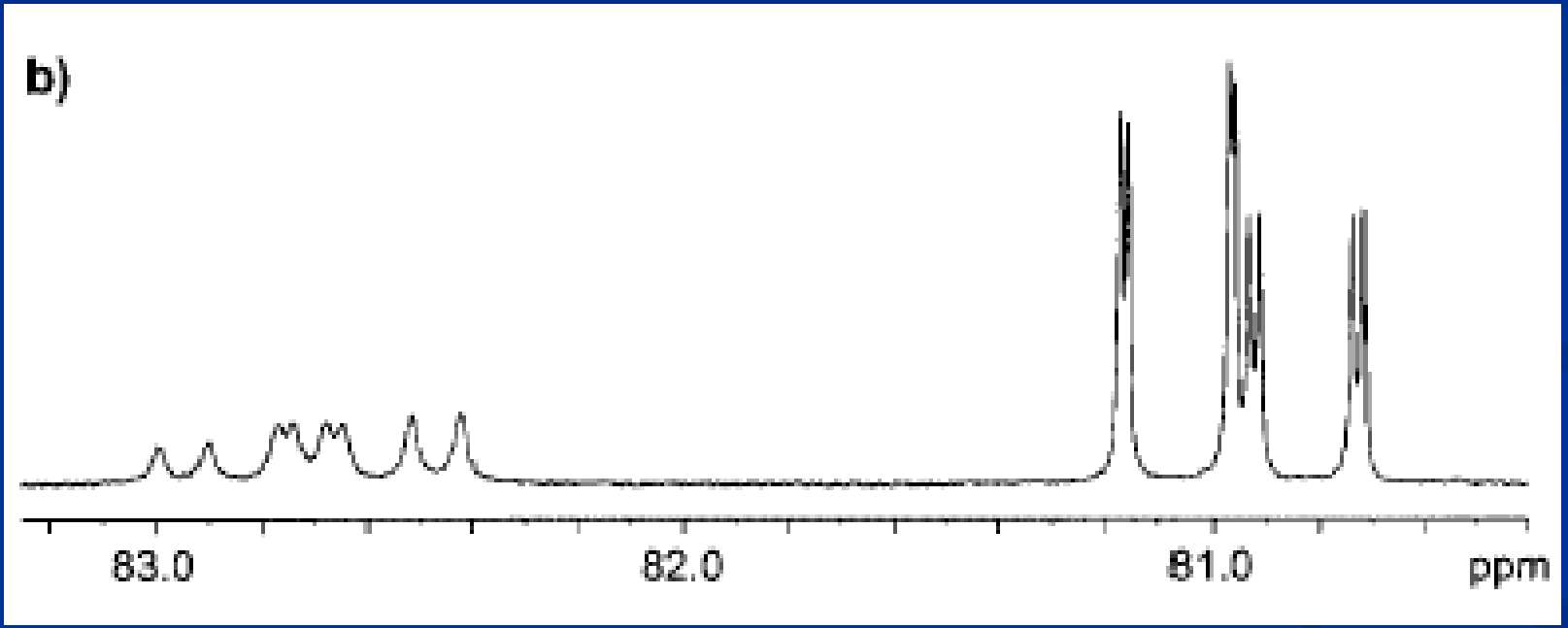
^{31}P Spin system AA'BB'B"B'"XX'

Nuclei		δ [ppm]
P_A:	P4, P8	82.65
P_B:	P2, P3, P6, P7	80.95
P_X:	P1, P5	70.5
H		0.8

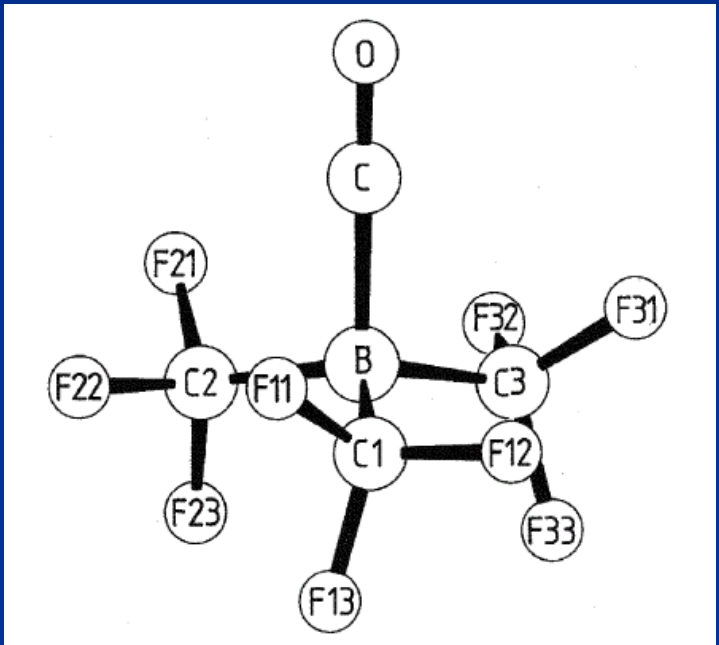
Coupling constants		[Hz]
$^2J_{AB}$:	J2-4, J3-4, J6-8, J7-8	29.2
$^2J_{BX}$:	J1-2, J 1-3, J5-6, J5-7	24.0
$^2J_{AX}$:	J1-8, J4-5	11.4
J_{AH}:	J4-H, J8-H	7.5

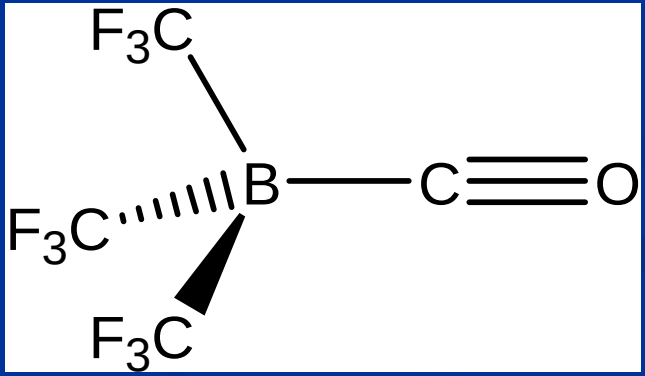


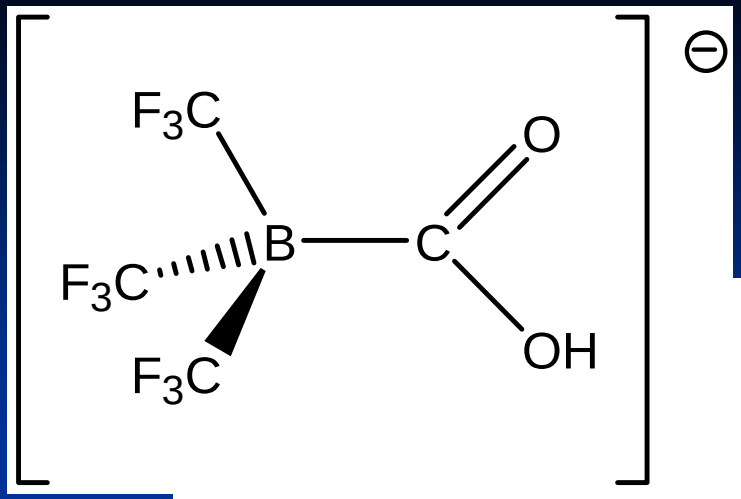
$P_8O_{12} \cdot 2BH_3$



Coupling Patterns







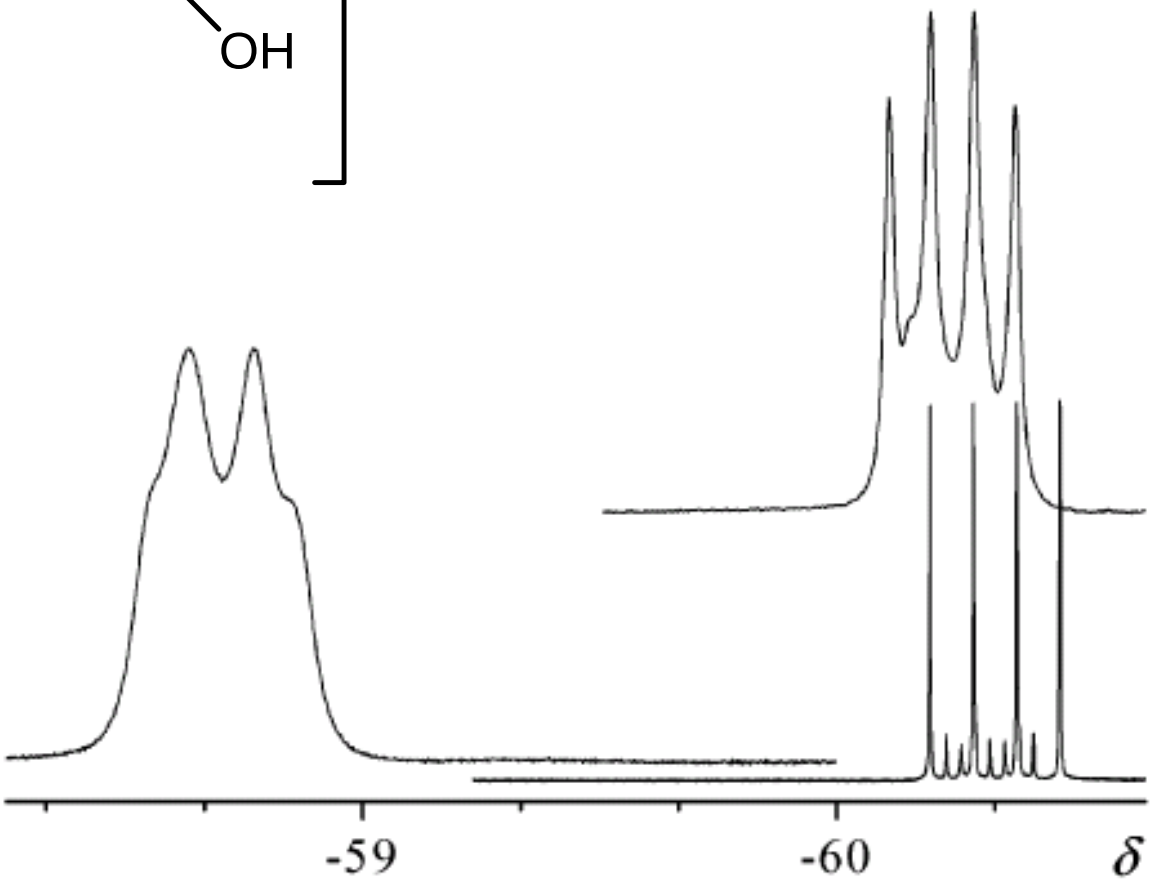


Figure 7. ^{19}F NMR spectra of $(CF_3)_3BCO$ (left), $[(CF_3)_3BC(O)OH]^-$ (right) and $[(CF_3)_3BCO_2]^{2-}$ (top).

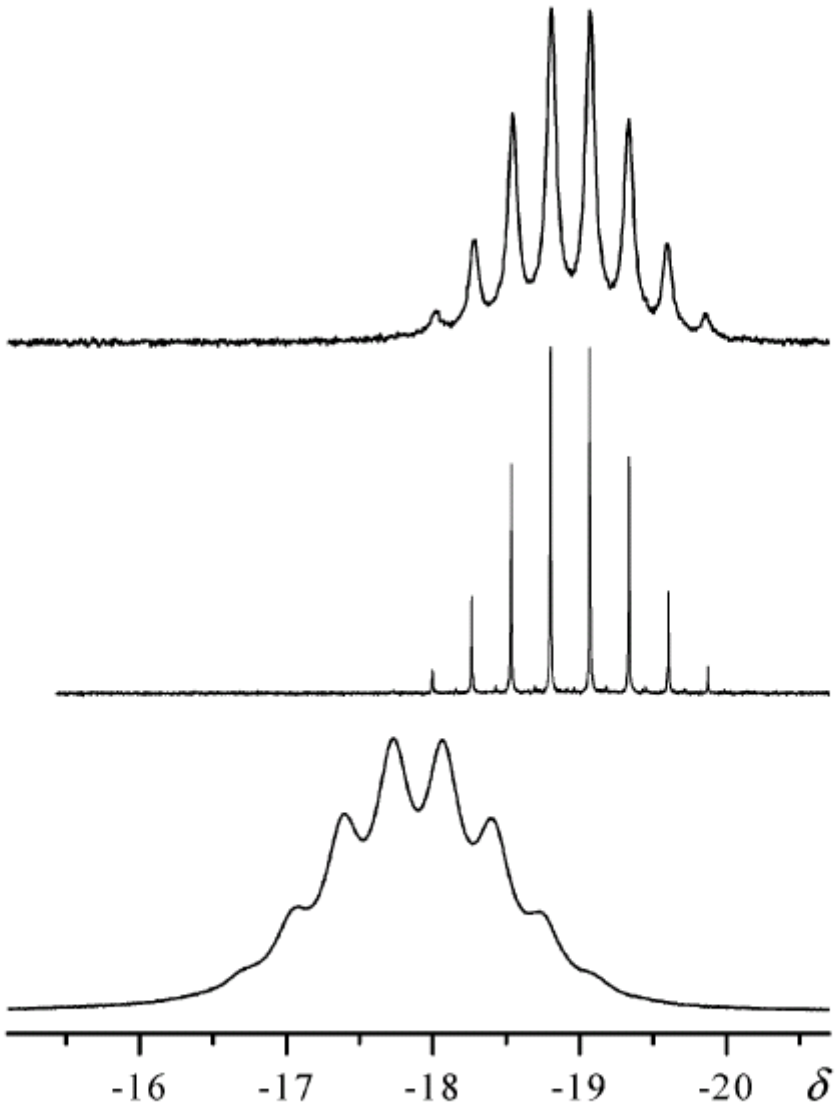


Figure 8. ^{11}B NMR spectra of $(CF_3)_3BCO$ (bottom), $[(CF_3)_3BC(O)OH]^-$ (middle) and $[(CF_3)_3BCO_2]^{2-}$ (top).

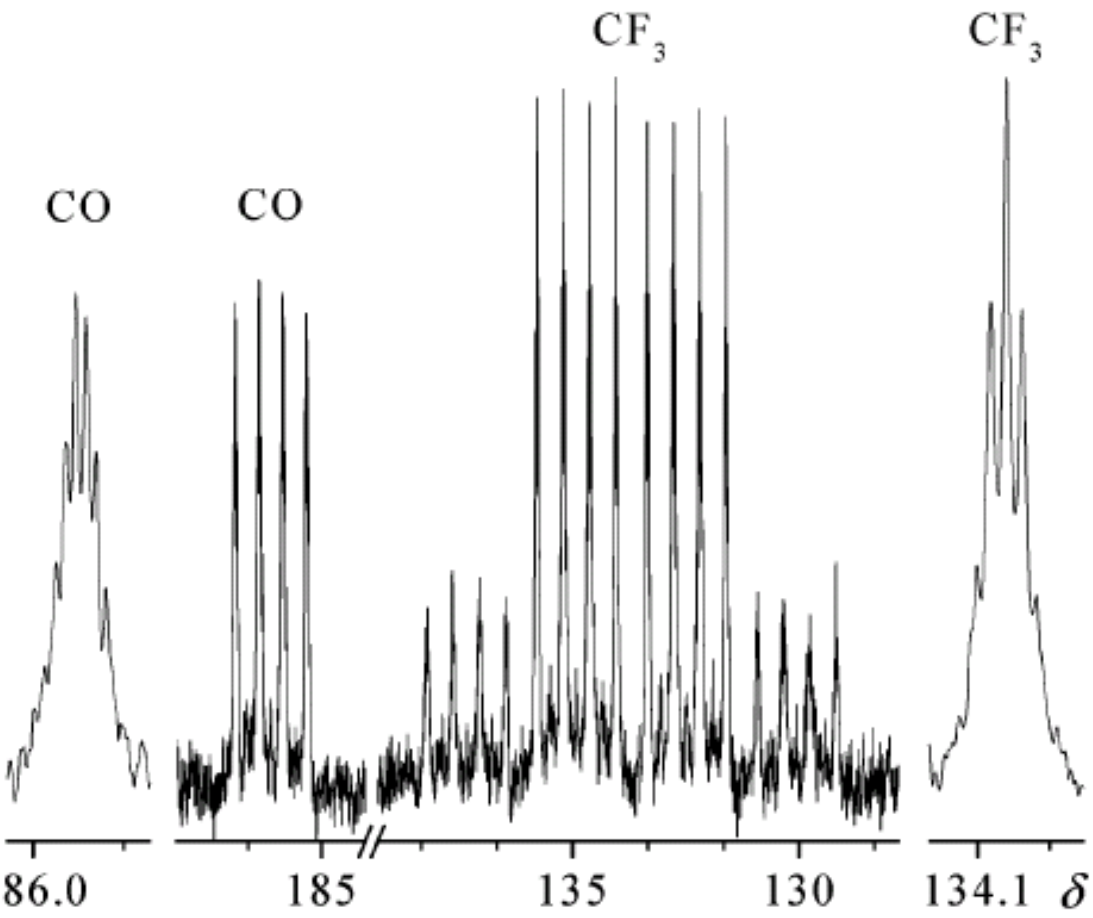
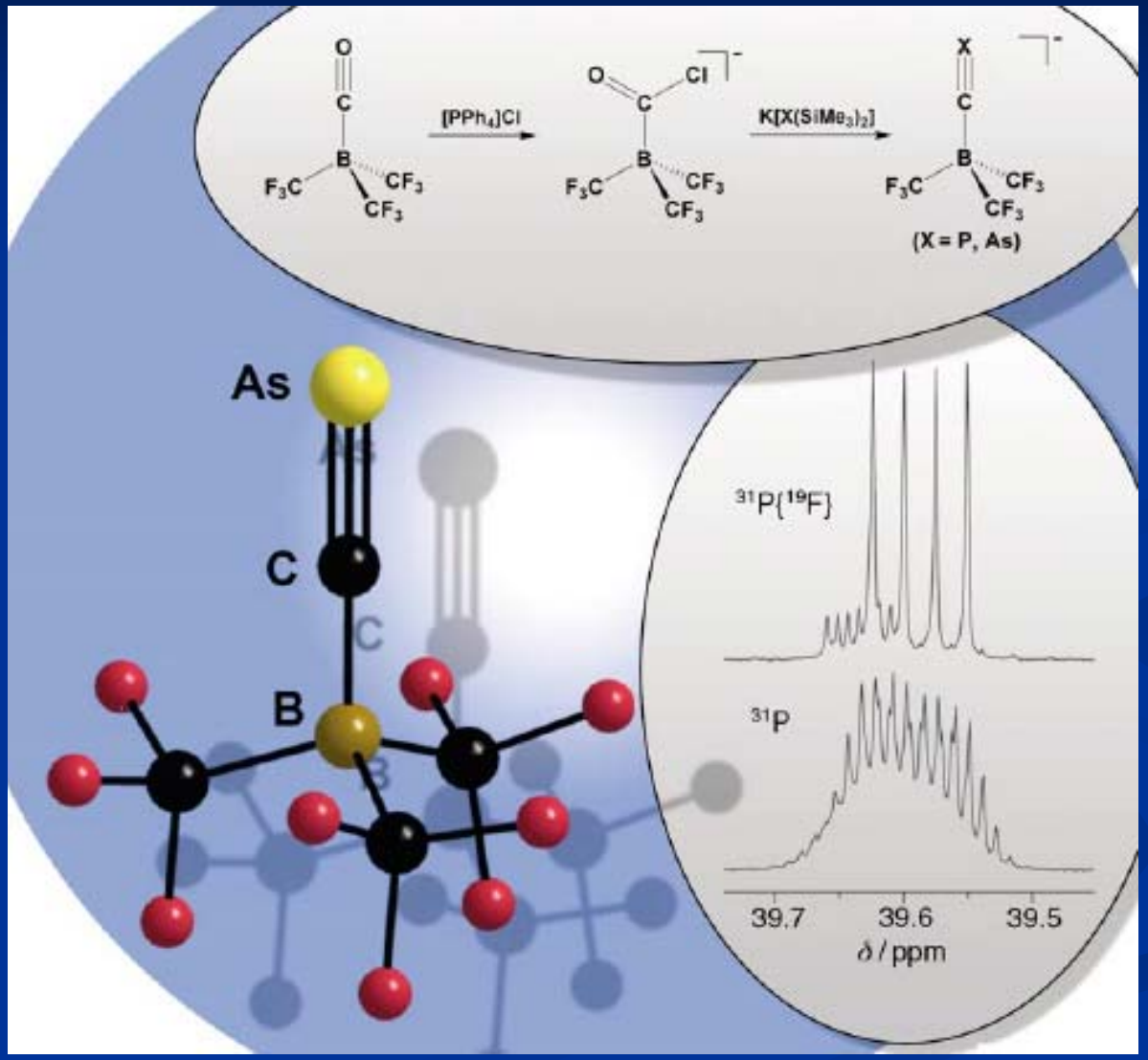


Figure 10. ^{13}C NMR spectrum of $[(CF_3)_3BC(O)OH]^-$. The expanded sections of the two signals show the $^3J(^{13}C,^{19}F)$ coupling patterns.


[PPh4]Cl
K[X(SiMe3)2]
(X = P, As)
As
C
C
B
31P{19F}
31P
39.7
39.6
39.5
δ / ppm

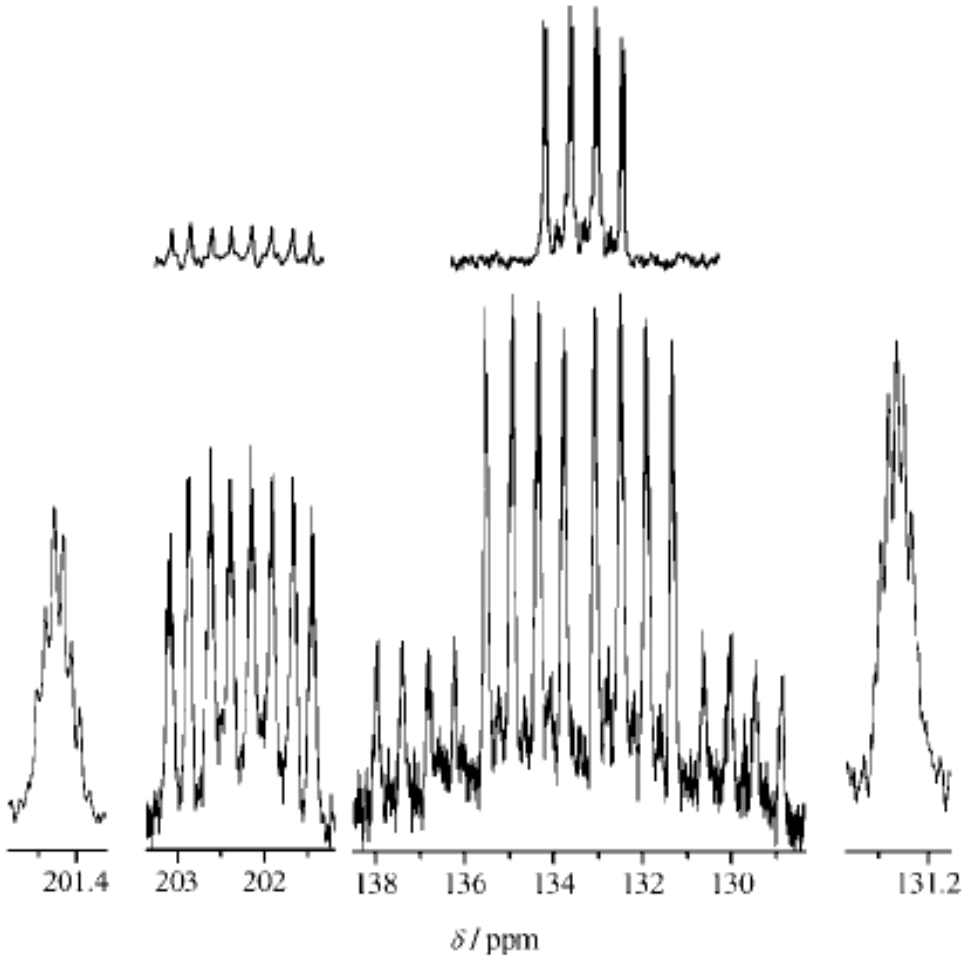


Figure 1. $^{13}C\{^{19}F\}$ NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of $[(CF_3)_3BCP]^-$ in CD_3CN solution.

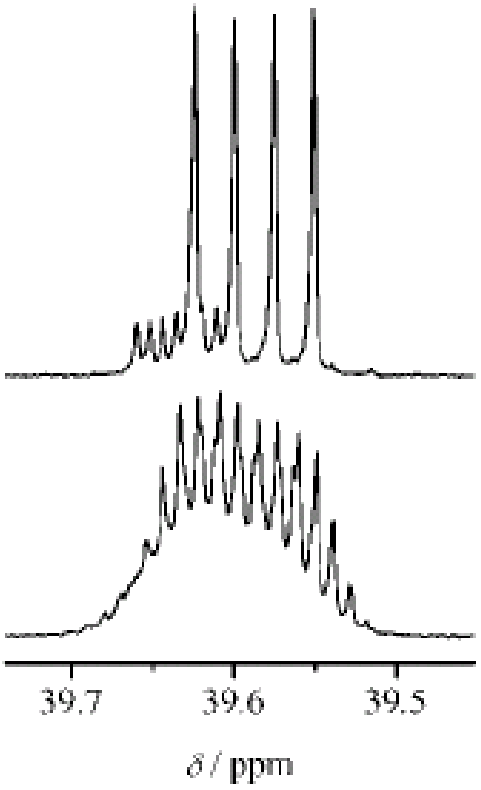
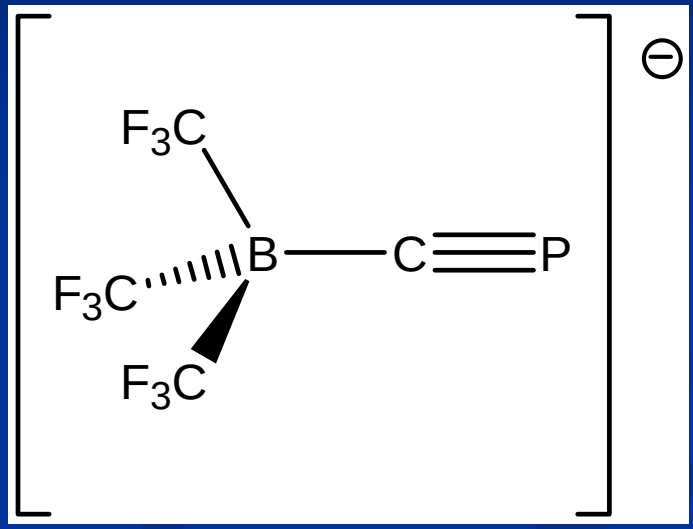


Figure 3. $^{31}P\{^{19}F\}$ NMR spectrum (top) and the ^{31}P NMR spectrum (bottom) of $[(CF_3)_3BCP]^-$ in CD_3CN solution.



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Simulations of NMR spectra