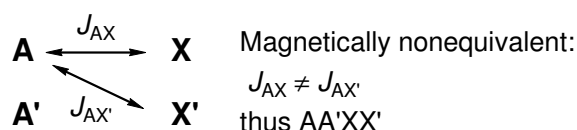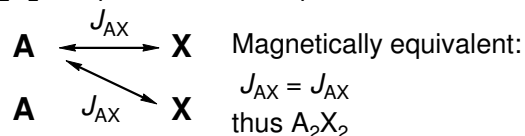# 5.7  Pople Nomenclature for Coupled Spin Systems

The analysis of complex NMR patterns is assisted by a general labelling method for spin systems introduced by Pople. Each set of chemically equivalent protons (or other nuclei) is designated by a letter of the alphabet. Nuclei are labeled **AX** or **AMX** if their chemical shift differences are large compared to the coupling between them ($\Delta\delta > 5J$). Nuclei are labeled with adjacent letters of the alphabet (**AB**, **ABC**, **MN** or **XYZ**) if they are close in chemical shift compared to the coupling between them (i.e. if they are *strongly coupled*).

If groups of nuclei are magnetically equivalent, they are labeled $A_nB_n$, etc. Thus $CH_3$ groups are $A_3$, or $X_3$. A group of magnetically equivalent nuclei must have identical chemical shifts, and all members of the group must be coupled equally to nuclei outside the group.  If nuclei are chemical shift equivalent but not magnetically equivalent, then they are labeled **AA'**, **BB'B''** or **XX'**.  Thus in an $A_2X_2$ system the **A** nucleus must have identical couplings to the two **X** nuclei.  In an **AA'XX'** system, on the other hand, $J_{AX} \neq J_{AX'}$. There are usually profound differences in the appearance of $A_2X_2$ compared to **AA'XX'** patterns.

$$A \xleftrightarrow{\;J_{AX}\;} X$$
$$A \xrightarrow{\;J_{AX}\;} X$$

Magnetically equivalent:
$J_{AX} = J_{AX}$
thus $A_2X_2$

$$A \xleftrightarrow{\;J_{AX}\;} X$$
$$A' \xrightarrow{\;J_{AX'}\;} X'$$

Magnetically nonequivalent:
$J_{AX} \neq J_{AX'}$
thus AA'XX'

## Two-Spin Systems

**AX**  First order.  Significant parameters: $J_{AX}$. **A** and **X** are each doublets.

**AB**  $J$ is directly measurable,  $\nu_A$ and $\nu_B$ must be calculated.  Intensities are distorted: the doublets are not 1:1; the inner lines are larger, the outer lines smaller.

## Three-Spin Systems

**AX$_2$**  First order.  Significant parameters: $J_{AX}$. **A** is a triplet, **X** is a doublet.

**AB$_2$**  Second order.  Both $J_{AB}$ and $\nu_{AB}$ must be calculated - neither can be directly measured from the spectrum. Significant parameters: $J_{AB}$, $\nu_{AB}$.
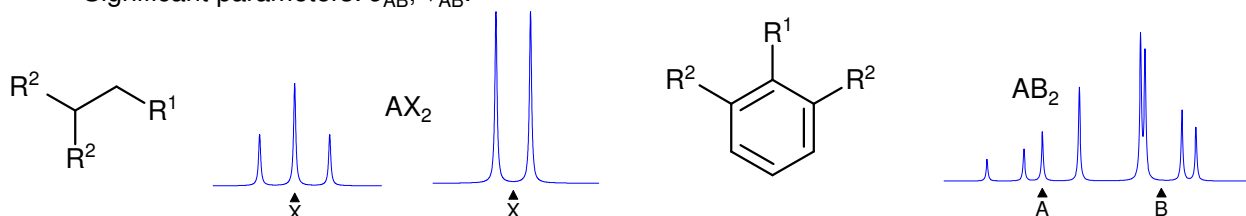
**AMX**  First order. Significant parameters: $J_{AM}$, $J_{AX}$, $J_{MX}$. **A**, **M** and **X** are each doublet of doublets (assuming all three couplings are large enough to detect). Typical systems are trisubstituted benzenes, vinyl groups, and monosubstituted furans and thiophenes.

**ABX**  Second order.  This is a very common pattern. $J_{AB}$ is directly measurable. The parameters $J_{AX}$, $J_{BX}$, $\nu_A$ and $\nu_B$ can be calculated from the line positions of the spectrum once it has been properly analyzed.

**ABC**  Second order.  This pattern can only be accurately solved using computer simulation methods. Manual analysis as a distorted ABX or even AMX pattern will lead to approximate values of coupling constants, which in severe cases can be drastically wrong.
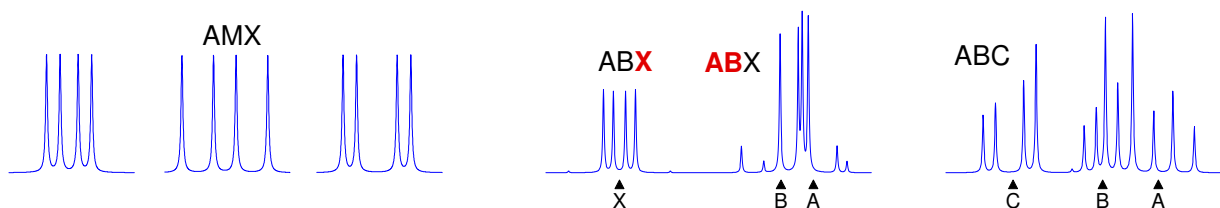
## Four-Spin Systems

**AX₃**         First order.  Significant parameters: $J_{AX}$.  Commonly seen in $CH_3CHXY$ groups.

**AB₃**         Second order.  Computer simulation required to solve.
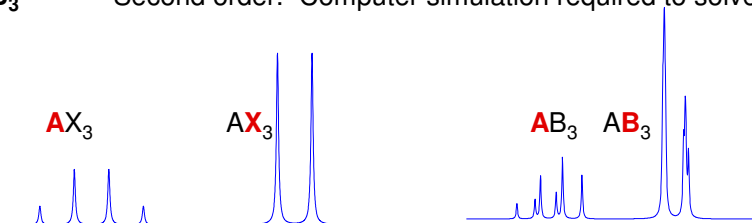


**A₂X₂**        First order.  This is a very rare pattern. **A** and **X** are each triplets.

**A₂B₂**        Second Order. Rare.

**AA'XX'**      Second order.  Common pattern. Can be solved by hand, but there are several ambiguities.  For example, one cannot distinguish $J_{AA'}$ from $J_{XX'}$.  Significant parameters: $J_{AA'}$, $J_{XX'}$, $J_{AX}$, $J_{AX'}$.  The **AA'** and **XX'** patterns are each centrosymmetric, and they are identical to each other, hence the inability to distinguish A from X parameters. A common type is $X\text{-}CH_2\text{-}CH_2\text{-}Y$, which is often just two triplets.   Also common are p-disubstituted benzenes:  and dioxolanes:

**AA'BB'**      Second order.  This is a common pattern.  Requires computer simulation to solve.  Seen in $X\text{-}CH_2CH_2\text{-}Y$ groups where X and Y have similar shift effects.  The entire multiplet is centrosymmetric (i.e., the **AA'** part is a mirror image of the **BB'** part).
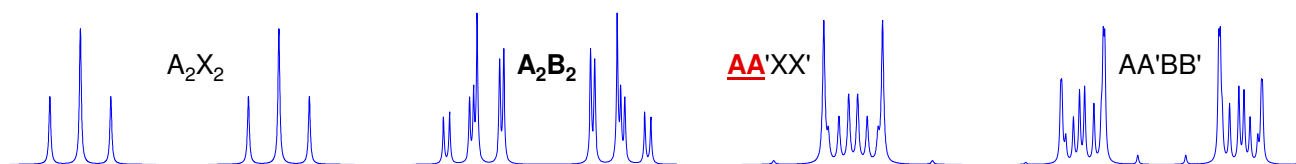


 **AMPX**       First order. Commonly seen in ortho and meta disubstituted benzenes, 2- or 3-substituted pyridines and related aromatics.
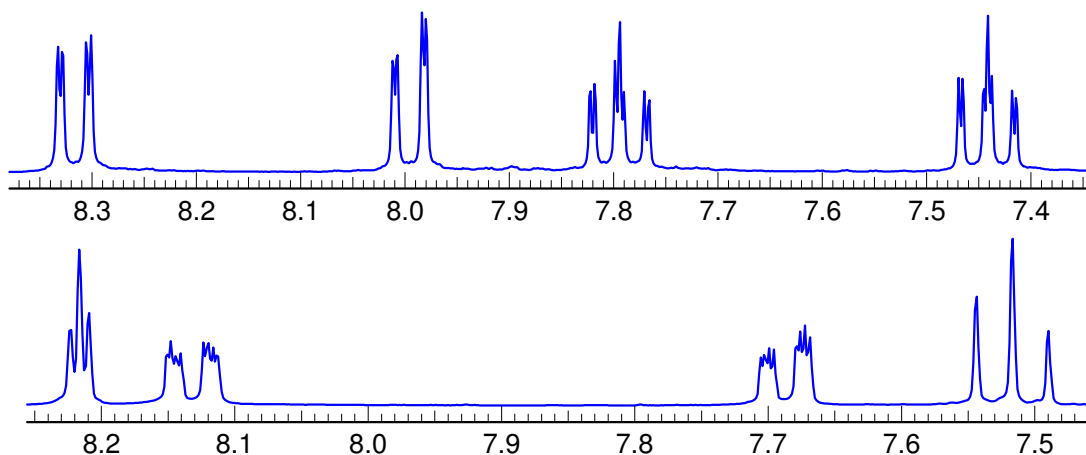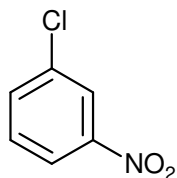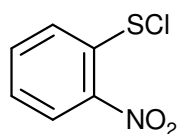
## Five-Spin Systems

**A₂X₃**      First order.  Very common pattern: ethyl groups: $CH_3CH_2$-R where R is an achiral electron withdrawing group (if R is chiral then we get an $ABX_3$ pattern)

**A₂B₃**      Second order. Seen in ethyl groups $CH_3CH_2$-R where R is a metal: e.g. $CH_3CH_2$-$SiR_3$.
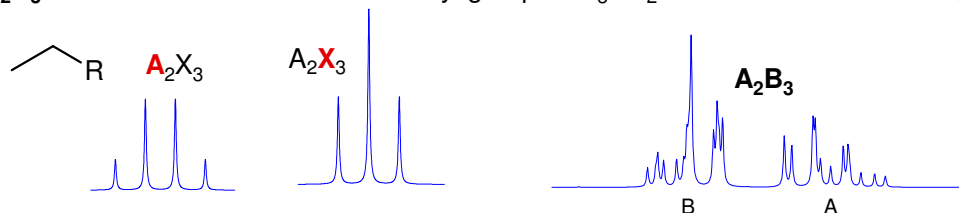
**ABX₃**      Second order, but some types are soluble by hand.  Commonly seen in ethyl groups in chiral molecules where the $CH_2$ protons are diastereotopic. For these the X part is always a triplet. Methyl-substituted alkenes can also give this pattern.   Shown below are the $A_2$ / AB parts.
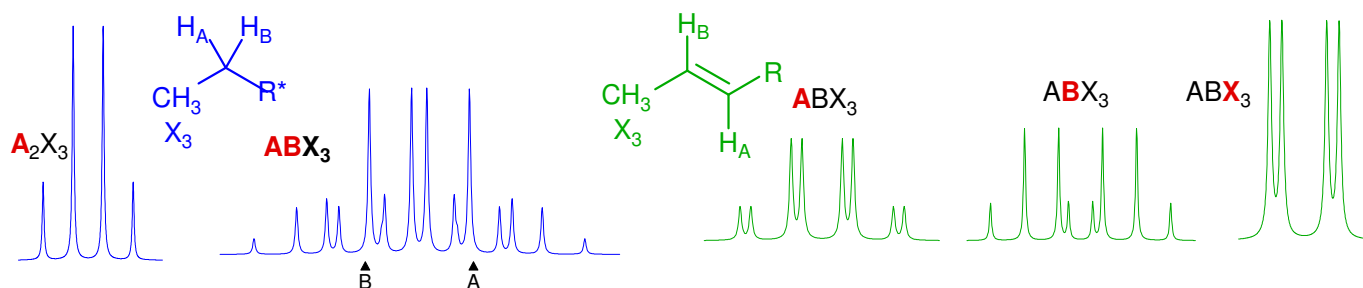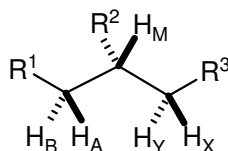
**AAMM'X**    Second order.  Part structures like -$CH_2$-$CH_2$-CH- can appear to be first order (t, q, t).

**AA'BB'C**    Always second order.  Commonly seen in monosubstituted phenyl groups.

R = electron withdrawing          R = electron donating
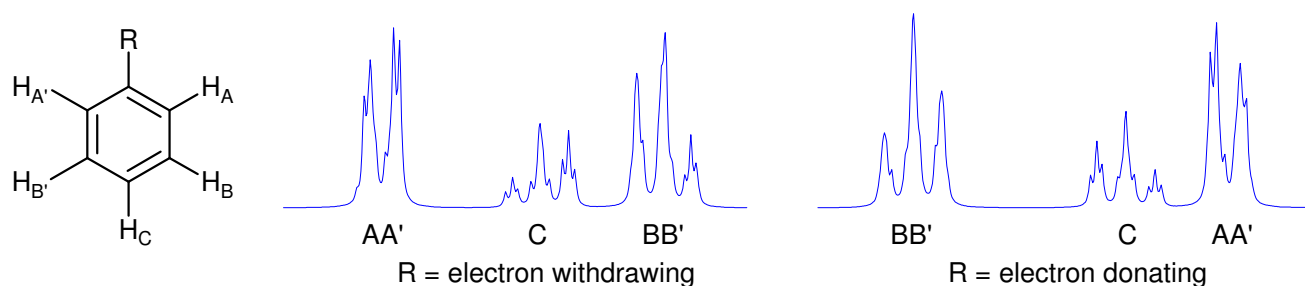
**ABMXY**    Second order.  Part structures like -$CH_2$-CH-$CH_2$- are actually two **ABX** patterns which share a common X.

# Six-Spin Systems

**AA'MM'XX'**   Not actually first order, but a common type, $R^1$-$CH_2$-$CH_2$-$CH_2$-$R^2$ often looks nearly first-order, especially if $R^1$ and $R^2$ are relatively small groups. Usually two triplets and a pentet, (or a pentet (2H) and a triplet (4H) if $R^1$ and $R^2$ are identical).
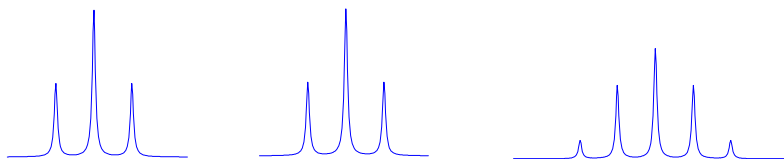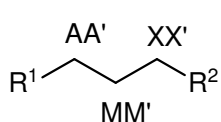


**ABMX$_3$**   Second order. There are two types here (at least): those with $R^1$ and $R^2$ on the same carbon, and those with the R groups vicinal. For the former, if $R^1$ and $R^2$ are different, the **AB** part is an **AB** quartet, each half of which is split by three protons, thus an **AB** quartet of pentets, or an **AB** quartet of doublets of doublets. If $R^1$ and $R^2$ are the same, or the chemical shift between A and B is very small, then the AB part might be a pentet or a doublet of quartets.
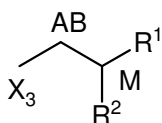


If $R^1$ and $R^2$ are vicinal then the **AB** part always has the appearance of the **AB** part of an **ABX** system (an ab quartet of doublets), the M part is ddq, and the X$_3$ part a doublet.
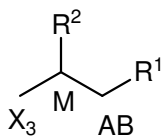
## Seven-Spin Systems

**AX$_6$**    First order.  Common pattern: isopropyl groups: $(CH_3)_2CH$-R where R is a heteroatom or a carbon bearing no protons. Usually a septet and a doublet.   When R is a metal like Si or Sn the $CH_3$ and CH protons can be close in chemical shift, and give a complex pattern $(AB_6)$ or even a singlet.



$^iPr_3Si$-Cl

$(AB_6)_3$
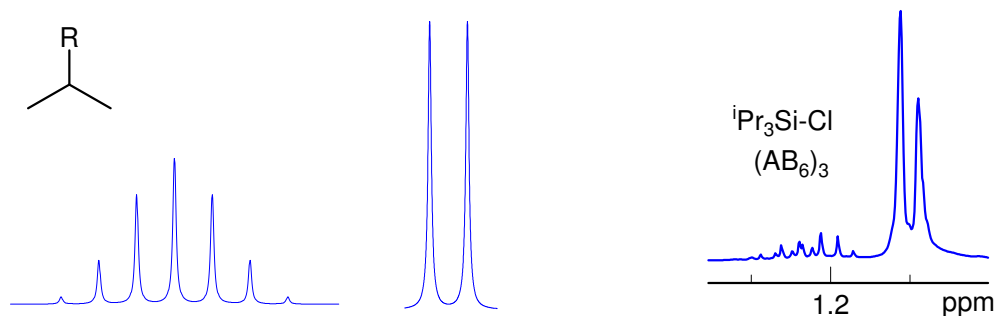
**A$_3$MM'XX'**  Not actually first order. However, a common type, n-propyl groups $CH_3$-$CH_2$-$CH_2$-R, are usually nearly first oder if chemical shifts are large enough.  Usually approximately two triplets and a sextet.
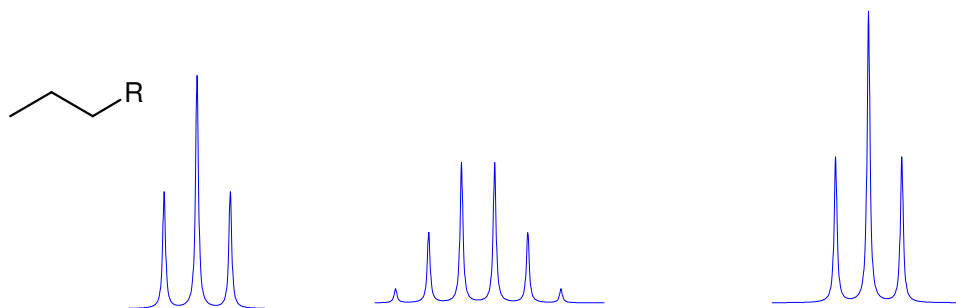
# 5.8 Symmetry in NMR Spectra

Protons and other nuclei in NMR spectra can be classified as heterotopic, diastereotopic, enantiotopic and homotopic. Heterotopic and diastereotopic protons will have different chemical shifts and couplings to neighboring magnetic nuclei, enantiotopic and homotopic protons will have identical chemical shifts. They may or may not have identical couplings to other nuclei. Distinction can be made by the substitution test.

## The Substitution Test for Equivalance of Protons

For a pair of protons to be tested, replace one and then the other with another group (one not present in the molecule). Compare the two structures formed. If they are identical, the protons are homotopic, if they are enantiomers, the protons are enantiotopic, if they are diastereomers then the protons are diastereotopic, if they are structural isomers, the protons are constitutionally heterotopic.
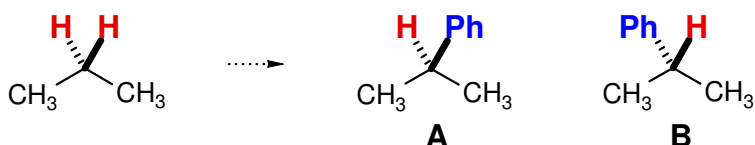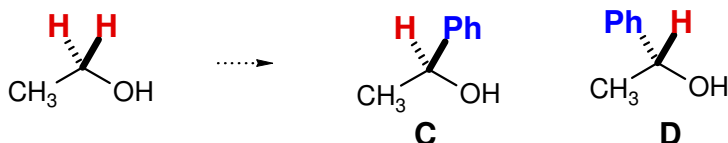
### Homotopic Protons:



The structures **A** and **B** are **identical**, the two protons are **homotopic**.

### Enantiotopic Protons:

Enantiotopic protons normally have identical chemical shifts. However, when the molecule is placed in a chiral environment (say with an optically active solvent, cosolvent or Lewis acid) then the protons can become diastereotopic. This is in contrast to homotopic protons, which are always identical.



The structures **C** and **D** are **enantiomers**, the two protons are **enantiotopic**.

### Diastereotopic Protons:

The concept of diastereotopicity was first introduced during the early days of NMR spectroscopy, when certain kinds of molecules gave unexpectedly complex NMR spectra, leading to some confusion about the orgins of this hitherto undetected phenomenon (Nair, P. M.; Roberts, J. D. *J. Am. Chem. Soc.*, **1957**, *79*, 4565). A typical situation where diastereotopic protons are seen is a $CH_2$ group in a chiral molecule (one with an asymmetric center, or other types of asymmetry).
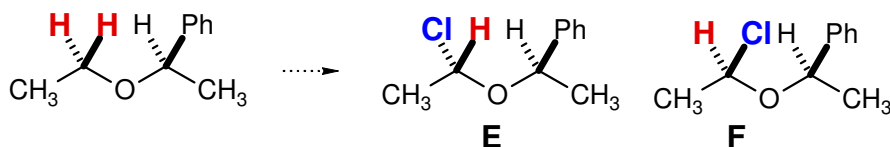


The structures **E** and **F** are **diastereomers**, the two protons are **diastereotopic**.

A more subtle form of diastereotopism is demonstrated in the classical example of diethyl acetal below. Even though diethyl acetal has no asymmetric centers, the $CH_2$ group is diastereotopic. This can be shown by applying the substitution test, which creates a pair of diastereomers **G** and **H**. Thus the ethyl group forms an $ABX_3$ pattern (see Section 5-HMR-13). The key to understanding this type of diastereotopicity is that the molecule has a plane of symmetry (hence is achiral). However, there is no plane of symmetry that bisects the $CH_2$ protons, so they are nonequivalent.
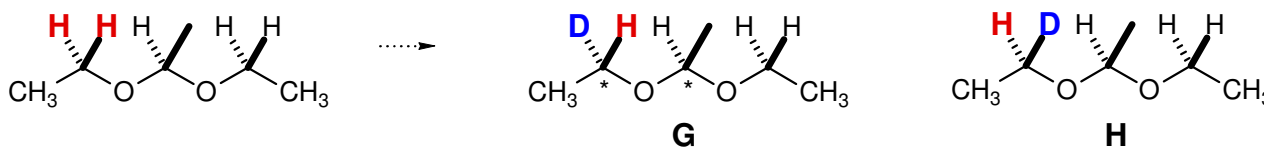
The dibromocyclopropane spectrum illustrates this effect in a different context - the protons of the $CH_2Cl$ group are diastereotopic. However, the protons of the cyclopropane $CH_2$ group are not, since they are related by a plane of symmetry.



300 MHz $^1H$ NMR spectrum
Source: Aldrich Spectra Viewer

$C_5H_6Br_2Cl_2$
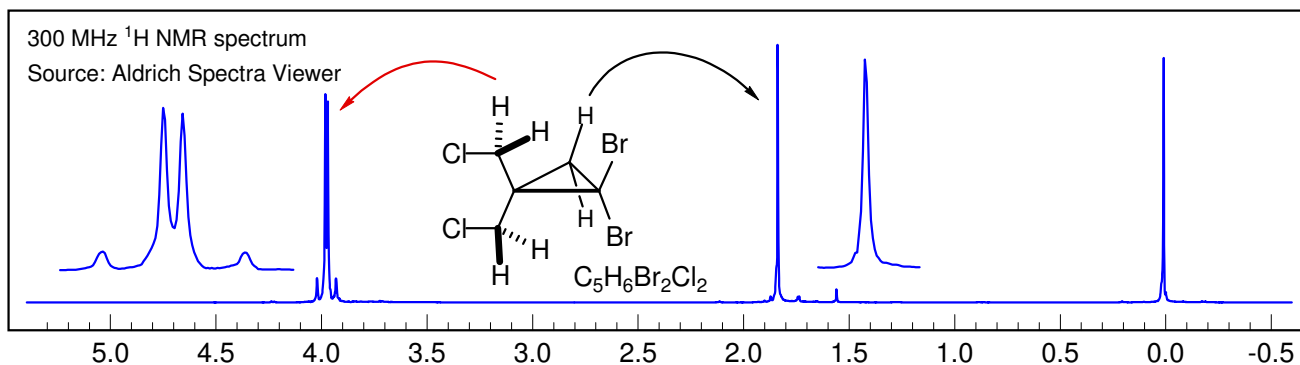
Not all $CH_2$ groups in chiral molecules are diastereotopic - in the chiral molecules below the $CH_2$ is on a $C_2$ axis of symmetry, and the protons are homotopic. In general, $CH_2$ groups (or other similar groups like $CHMe_2$, $CHF_2$, etc) will be diastereotopic when part of a chiral molecules unless the $CH_2$ group is on a $C_2$ rotation axis.
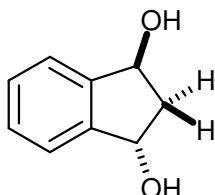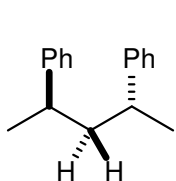


**Exercise**: Why are three of the aromatic carbon $^{13}C$ NMR signals in this compound doubled?



75 MHz $^{13}C$ NMR spectrum in $CDCl_3$
Source: Bill Sikorski/Reich

Click for full Spectrum
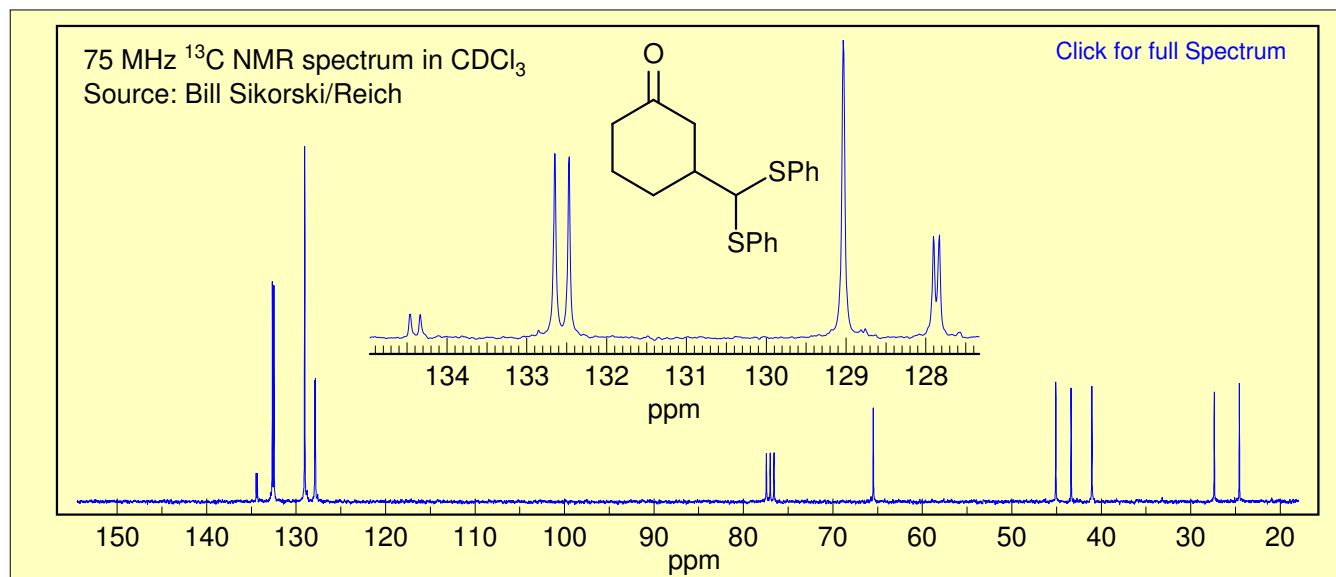
*Constitutionally Heterotopic Protons:*
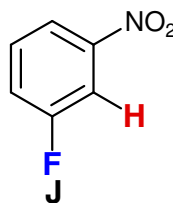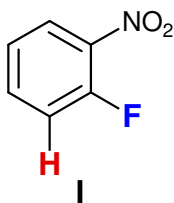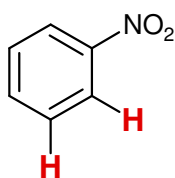


The structures **I** and **J** are **structural isomers**, the two protons are **heterotopic**.

## Magnetic Equivalence

There is an additional element of symmetry which is important for NMR spectroscopy, the magnetic equivalence or inequivalence of nuclei. Protons that are enantiotopic or homotopic will have the same chemical shift, but they will not necessarily be magnetically equivalent. For two protons to be magnetically equivalent they not only have to have the same chemical shift, but *they must also each have the same J coupling* to other magnetic nuclei in the molecule. This is easiest to see from some specific examples.

The two vinyl and two allylic protons in cyclopropene are each magnetically equivalent because each of the A protons is equally coupled to the two X protons. The spectrum consists of two identical triplets ($A_2X_2$ system).



Magnetically equivalent
A and X protons ($A_2X_2$)

Magnetically inequivalent
A and X protons (AA'XX')

$J_{AX} \neq J_{AX'}$

2.20   2.15   2.10

1.45   1.40

On the other hand, the two pairs of equivalent protons in trans-bis(carbomethoxy)cyclopropane are NOT magnetically equivalent, because each of the A protons is coupled differently to the two X protons (one is a *trans* coupling, the other a *cis*). In the Pople nomenclature, such magnetically inequivalent nuclei are given an AA' designation. Thus the bis(carbomethoxy)cyclopropane is referred to as an AA'XX' system, where A and A' refer to protons that are symmetry equivalent but not magnetically equivalent. The spectrum will be much more complicated than two triplets, and *both sets of protons will be identical*.

Two more examples are 1,1-difluoroallene, which is an $A_2X_2$ system, and 1,1-difluoroethylene, which is an AA'XX' system (see 5-HMR-14.2 for a spectrum).



$A_2X_2$

AA'XX'

$J_{AX} \neq J_{AX'}$

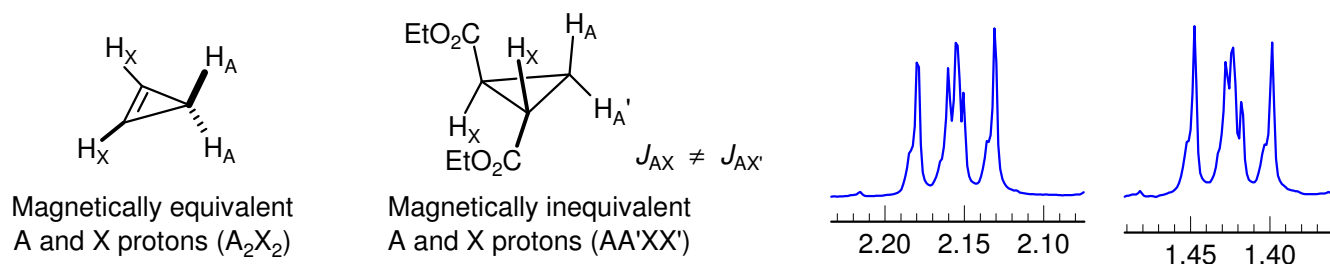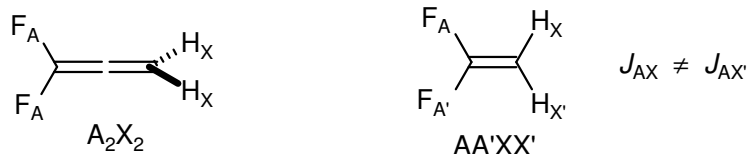In general any system which contains chemical shift equivalent but magnetically inequivalent nuclei of the AA' type will not give first order splitting patterns, although sometimes the spectra may appear to be first order ("deceptively simple" spectra). For example, X-CH$_2$-CH$_2$-Y systems are of the AA'XX' type, but the coupling constants $J_{AX}$ and $J_{AX'}$ are often close enough in size that apparent triplets are seen for each CH$_2$ group. See Section 5-HMR-14 for examples.

Two important generalizations:

- **Coupling between symmetry equivalent but magnetically inequivalent nuclei typically will affect the appearance of the NMR spectrum.** In fact, it is the coupling between the equivalent nuclei that is responsible for the complexity of spectra of the AA'BB'.. type.

- **Coupling between magnetically equivalent nuclei does not affect NMR spectra**, cannot be detected, and thus can be ignored.

## The NMR Time Scale

It is important to recognize that diastereotopic and magnetic equivalence effects are subject to the time scale of the NMR experiment, which is on the order of tenths of a second (see Sect 8-TECH-3). Flexible molecules will often have several conformations, some of which may have lower symmetry than others. However, since these conformations are typically interconverting rapidly *on the NMR time scale*, the observed symmetry in the NMR spectrum will be that of the most symmetric conformation reachable. Thus cyclohexane is a sharp singlet at room temperature, whereas at -100 °C the ring inversion is slow on the NMR time scale, and a much more complex spectrum results (see Sect 5-HMR-5.3).

# 5.9 Second Order Effects in Coupled Systems

For first order systems $J$ and $\delta$ values are directly measurable from line positions. However protons or groups of protons form first order multiplets only if the chemical shift differences between the protons ($\Delta v$) are large compared to the coupling constants between them ($J$), i.e. if $\Delta v / J$ (all in **Hz**) is < 5 then **second order** effects appear. When $\Delta v / J$ < 1 then second order effects become very pronounced, often preventing detailed manual interpretation of multiplets, or giving incorrect coupling constants if first order behavior is assumed.

There are a number of changes that occur in NMR spectra which are the result of degenerate or near-degenerate energy levels in strongly coupled systems i.e. when $\Delta / J$ becomes small (in English: whenever the coupling constant between two nuclei is similar in magnitude to the chemical shift between them, the spectra get complicated). If the spectrum is measured at higher spectrometer frequency the chemical shifts (in Hz) become larger, whereas the coupling constants stay the same, so the spectrum usually gets simpler. Exceptions are the AA'XX' type of systems, which are field independent, and usually cannot be completely solved from line positions and intensities alone.

The effects of spectrometer field strength on the ability to resolve NMR coupling information is illustrated in this set of spectra of ethylbenzene, plotted at a constant Hz scale. The aromatic signals go from nearly a singlet at 60 MHz to a reasonably resolved set of peaks at 600 MHz (spectra courtesy of Kris Kolonko). This increase in information content and greater ease of interpretation of NMR spectra at higher magentic field strength is the main justification for the additional expense of more powerful magnets.
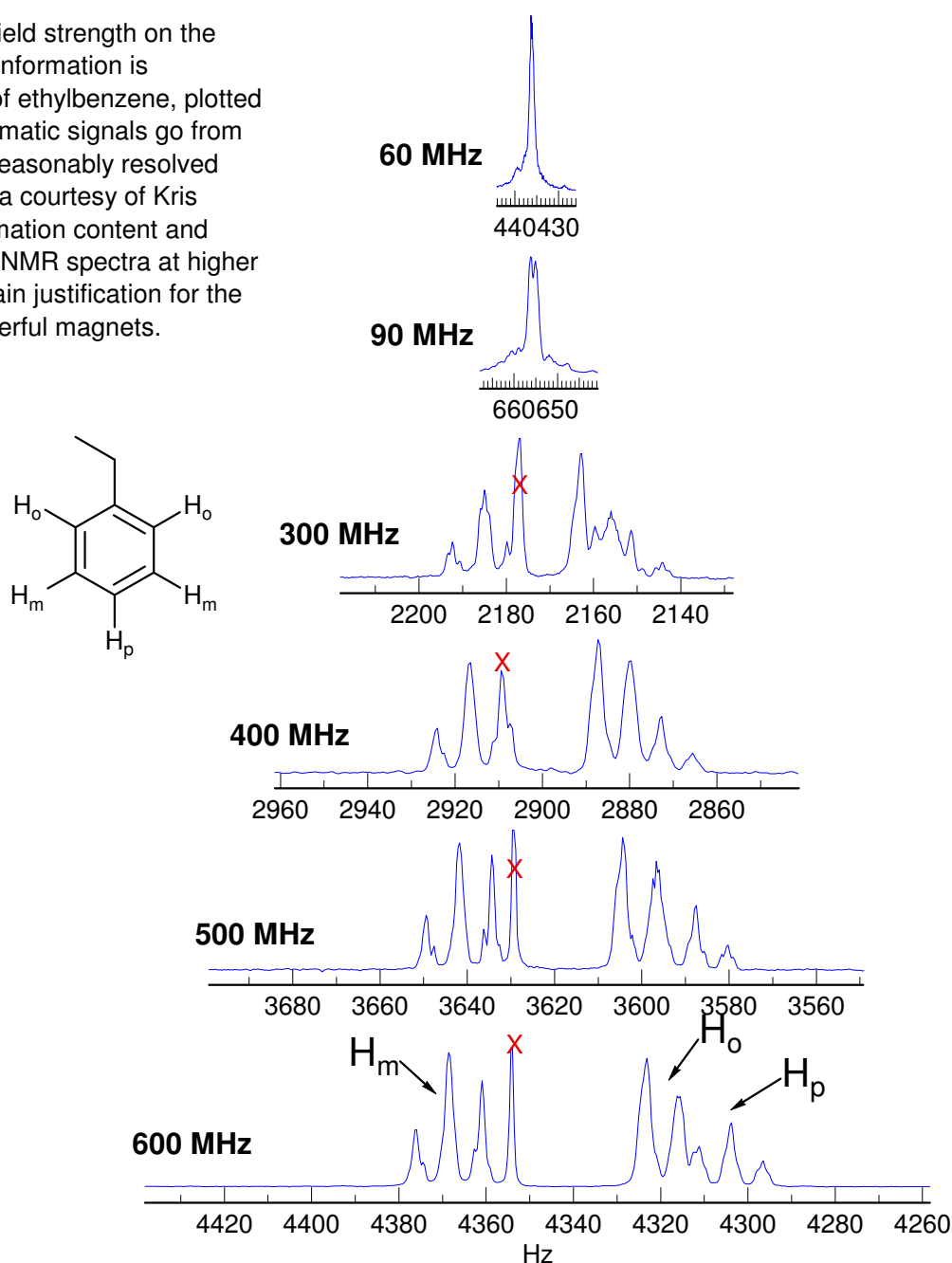
We can define a hierarchy of coupling patterns which show increasingly larger number of second-order effects:

AX and all other first order systems ($AX_2$, AMX, $A_3X_2$, etc.)
AB (line intensities start to lean, $J$ can be measured, $\delta$ has to be calculated)
$AB_2$ (extra lines, both $J$ and $\delta$ have to be calculated)
ABX, $ABX_2$, $ABX_3$, $J_{AB}$ can be measured, others require a simple calculation
ABC (both $J$ and $\delta$ can only be obtained by computer simulation)
AA'XX' (these do not become first order even at higher fields)
AA'BB'
AA'BB'X (etc)

1.  A universally observed effect is that as chemical shifts become comparable to couplings, line intensities are no longer integral ratios (AB and higher).  The lines away from the chemical shift of the other proton (outer lines) become smaller and lines closer (inner lines) become larger (see the triplets below)  -  the multiplets "lean" towards each other (some call this a "roof" effect).  The leaning becomes more pronounced as the chemical shift difference between the coupled multiplets becomes smaller.



$C_3H_7BrO$
300 MHz $^1$H NMR spectrum in $CDCl_3$
Source: Aldrich Spectra Viewer/Reich
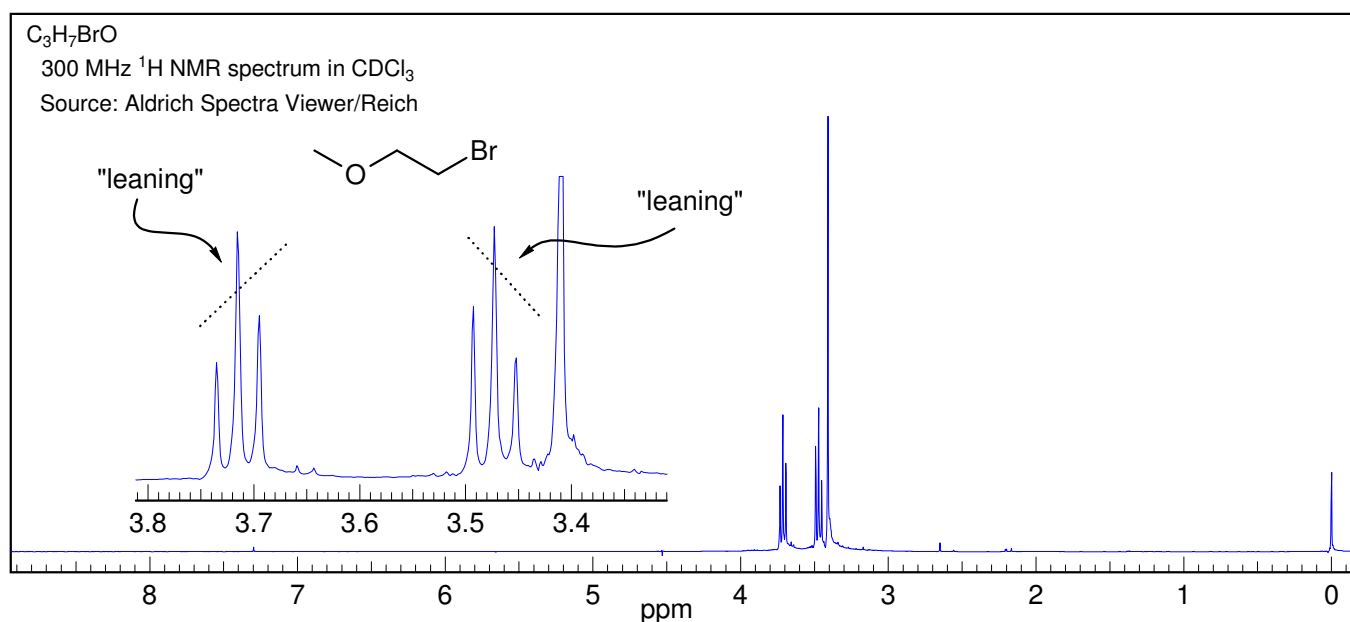
2. Line positions are no longer symmetrically related to chemical shift positions (AB), eventually calculations may have to be carried out to obtain $\delta$ and $J$ (ABX and higher).

3. Some or all of the coupling constants can no longer be obtained from line separations ($AB_2$ and higher).

4. The signs of coupling constants affect line positions and intensities (ABX and higher).

5. Additional lines over that predicted by simple coupling rules appear. First, lines which formally have intensities of 2 or more split into the component lines. Eventually combination lines, which no longer can be assigned to any one nucleus appear ($AB_2$ and higher). A nice example is provided by the compound below. For the $BrCH_2CH_2O$ group the two methylenes at $\delta$ 3.48 and $\delta$ 3.81 have a relatively large chemical shift separation, and they form recognizable triplets, although with a little leaning. For the $MeOCH_2CH_2O$ group the chemical shift between the $CH_2$ groups is small, and the signals are a complicated multiplet with only a vague resemblance to a triplet. There is likely an additional complication from variability in the size of the two different vicinal couplings in the two patterns (see Section 5-HMR-15 for more on this). The additional lines can lead to "Virtual coupling" effects: apparent coupling to protons that are actually not coupled. See Section 5-HMR-16)



C_5H_{11}BrO_2
300 MHz ^1H NMR spectrum in CDCl_3
Source: Aldrich Spectra Viewer/Reich
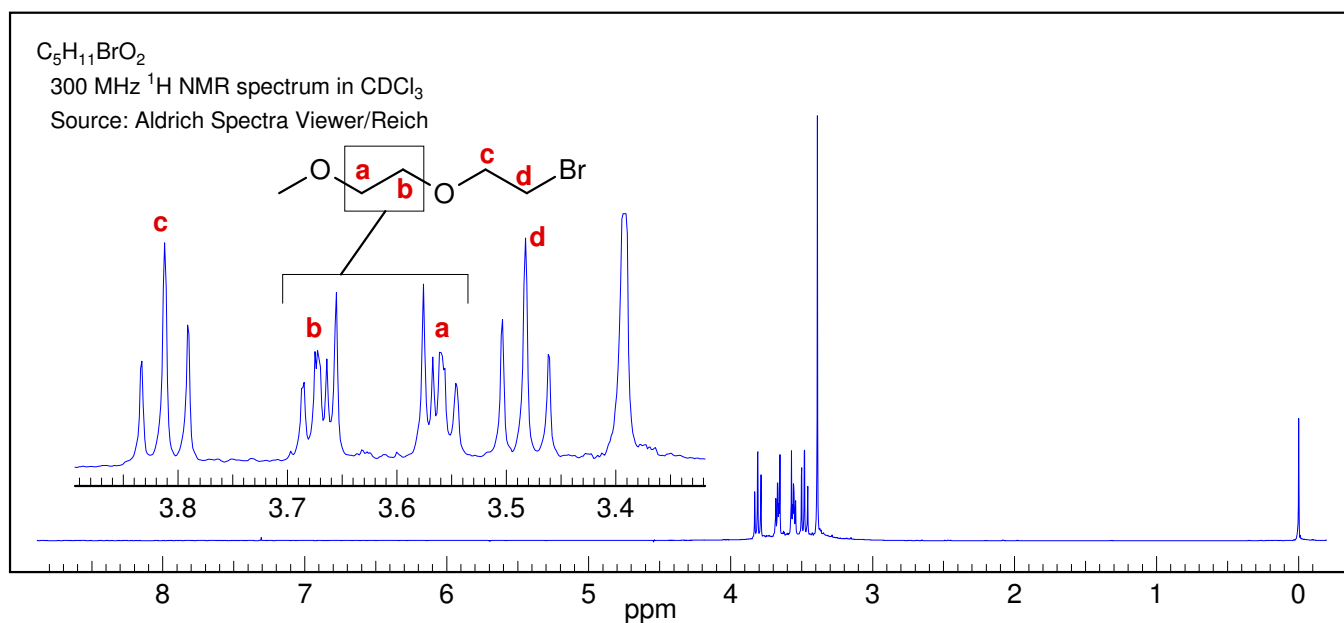
6. Coupling between equivalent nuclei (e.g., $J_{AA'}$ or $J_{XX'}$) affects line count and positions. Second order effects will appear even if $\Delta v / J$ is large when groups of **magnetically non-equivalent** protons with identical chemical shifts are coupled to each other (see Section 5.8). Thus $Me_3Si\text{-}CH_2\text{-}CH_2\text{-}OH$ is not just two triplets, since the $CH_2CH_2$ is an AA'XX' system (see Section 5-HMR-14) These patterns do not get simpler at higher field strengths.



C_5H_{14}OSi
300 MHz ^1H NMR spectrum in CDCl_3
Source: Aldrich Spectra Viewer/Reich
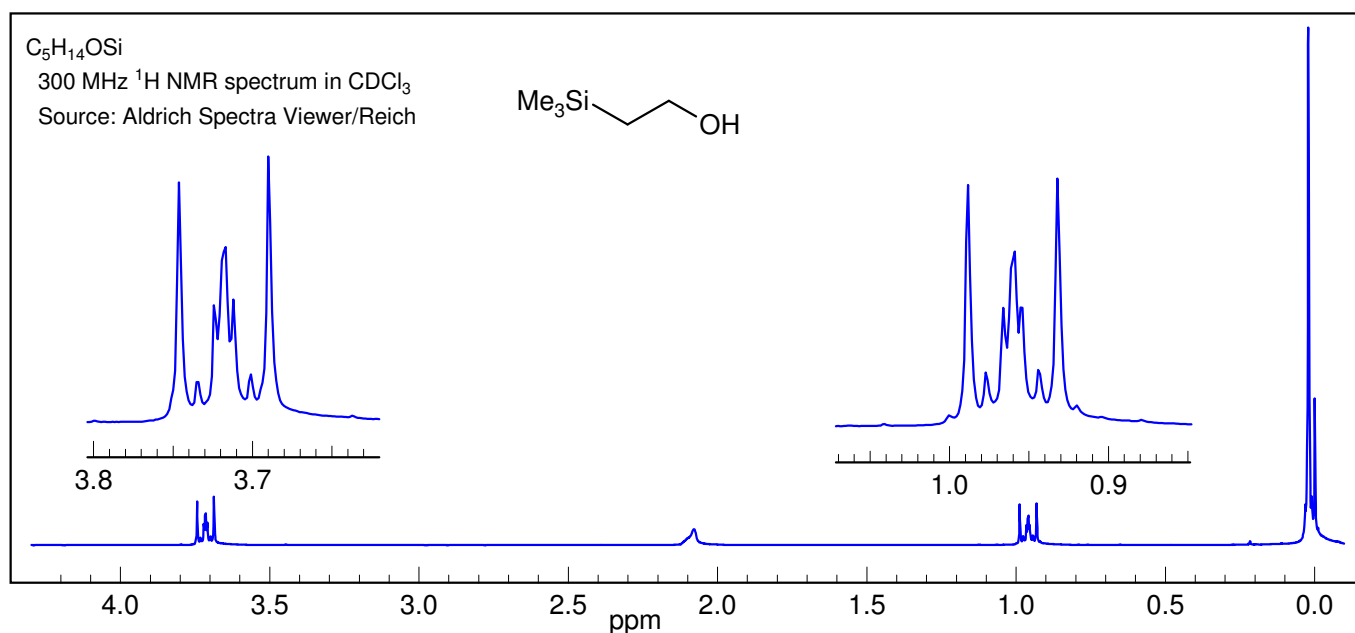
7. Computer analysis becomes mandatory to extract accurate $J$ and $\delta$ values (ABC and higher). A typical example is the spectrum below, where a near coincidence of $H^2$ and $H^3$ leads to a complex spectrum. Even here one can make some sense of the multiplets - the one at $\delta$ 5.55 is $H^3$, essentially a doublet of multiplets ($J \approx 10$), at $\delta$ 5.72 another dm, with $J \approx 17$ corresponding to $H^4$. The peaks between 5.8 and 6.0 are $H^1$ and $H^2$, one can guess at some of the couplings from the downfield half of the $H^3$ ddd, but this becomes quite risky.



$C_6H_7NO_2$
300 MHz $^1$H NMR spectrum in CDCl$_3$
Source: Aldrich Spectra Viewer/Reich

$J_{12} = 5.4$
$J_{13} = -1.0$
$J_{14} = -1.5$
$J_{23} = 10.1$
$J_{24} = 16.9$

Simulation
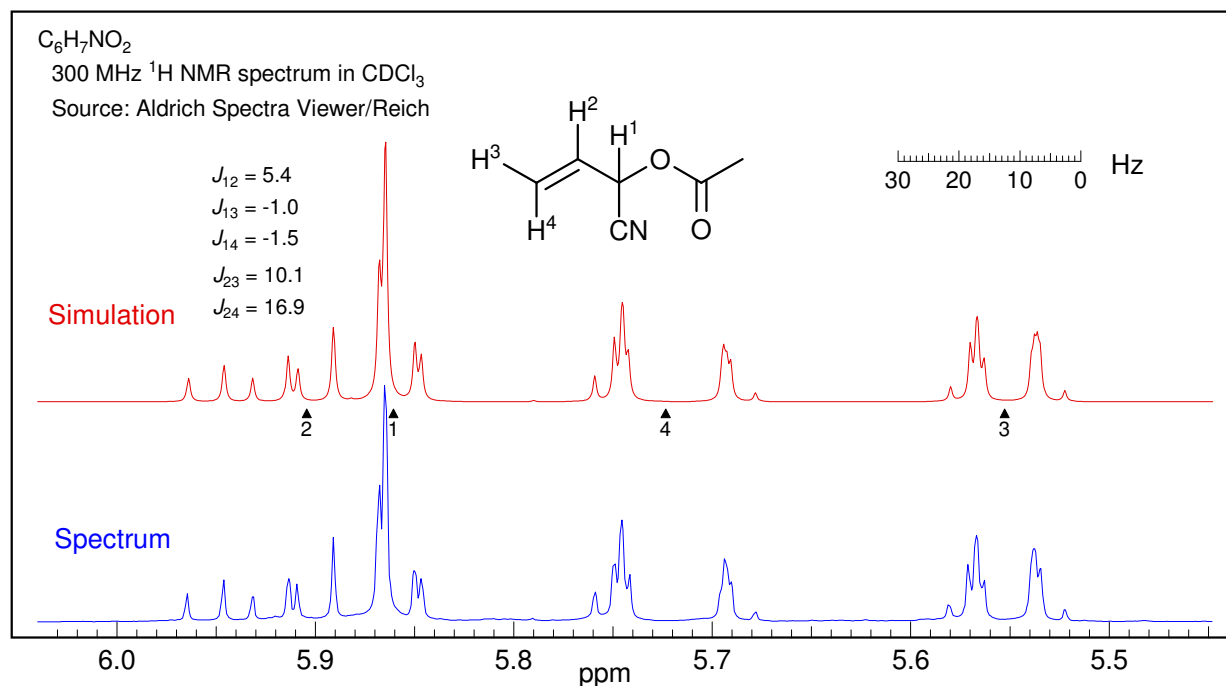
Spectrum

A computer simulation of this spectrum was performed with WINDNMR, and gave the simulated spectrum shown, using the $J$ values indicated. To give some idea of what this involves, it took about 60 minutes of manual fiddling with $J$ and $\delta$ values in WINDNMR to arrive at this simulation (which is not completly optimized). Second order spectra like this are extremely sensitive to the paramater values - even a 0.1 Hz offset in several of the parameters significantly reduced the quality of the fit. Note that the chemical shift difference between $H^1$ and $H^2$ is 13.2 Hz, more that twice the value of the coupling between the two protons. The complexity is the result of the overlap between the upfield part of the $H^2$ multiplet (which is over 30 Hz wide) and the downfield part of the $H^1$ multiplet, which makes several of the energy levels degenerate, or nearly so.

8. Ultimately spectra become so complex that the only useful information is integration, chemical shift and general appearance, as in the spectrum of cyclohexyl chloride, where only the proton $\alpha$ to the chlorine gives an interpretable multiplet (a tt), and even here the coupling constants obtained could be in error because of second order effects (possible virtual coupling).



$C_6H_{11}Cl$
300 MHz $^1$H NMR spectrum in CDCl$_3$
Source: Aldrich Spectra Viewer/Reich
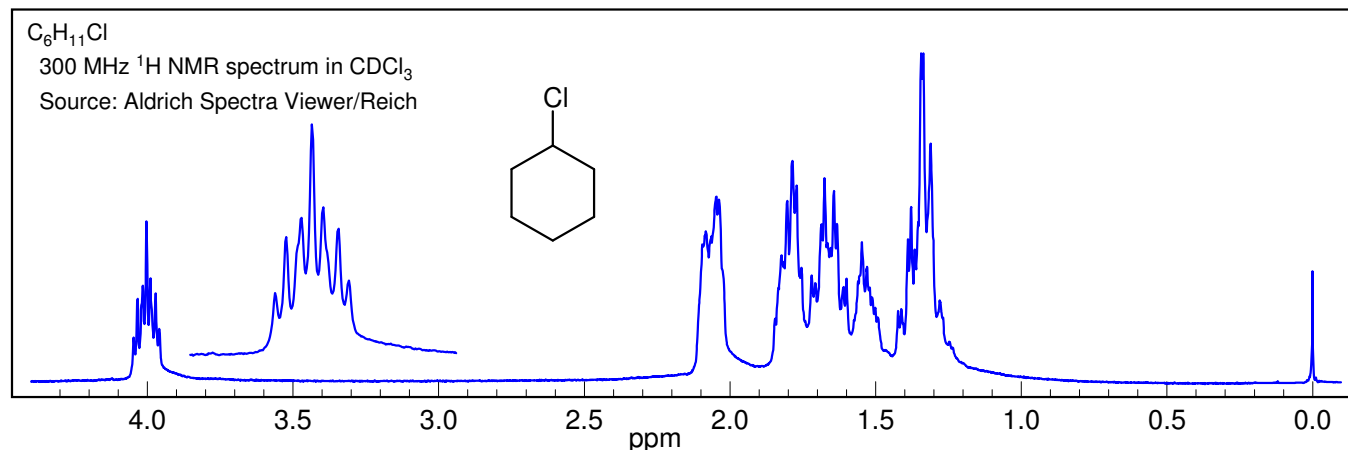
# 5.10  AX and AB Spectra

The simplest molecules that show *J* coupling contain two spin 1/2 nuclei separated by 1, 2, 3 (occasionally 4 and 5) bonds from each other. If the chemical shift between the protons is large compared to the coupling between them ($\nu_{AX} \gg J_{AX}$), we label them as $H_A$ and $H_X$.  If the chemical shift is comparable to the coupling between the protons ($\nu_{AB} < 5\, J_{AX}$), we have an **AB** system.  Some molecules that give AB/AX patterns are shown below (spectra are all at 300 MHz):

· Disubstituted alkenes

$C_5H_7IO_2$
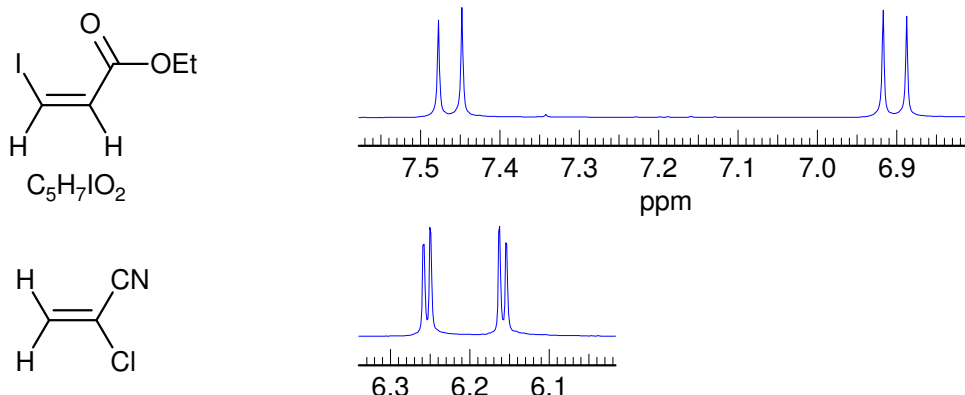
· 1,2,3,4- and 1,2,3,5-tetrasubstituted benzenes; polysubstituted furans, pyridines, and other aromatic systems
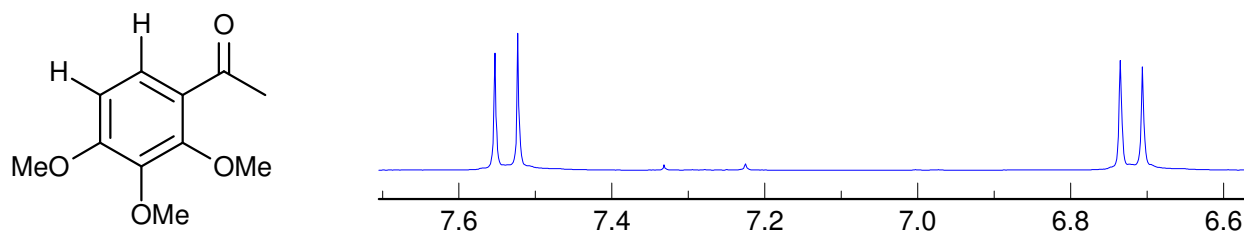
· Benzyl, methoxymethyl and related protecting groups in chiral molecules, and other isolated diastereotopic $CH_2$ groups.

300 MHz $^1$H NMR Spectrum CDCl$_3$

$C_{16}H_{16}O_3$

$C_{15}H_{17}N$
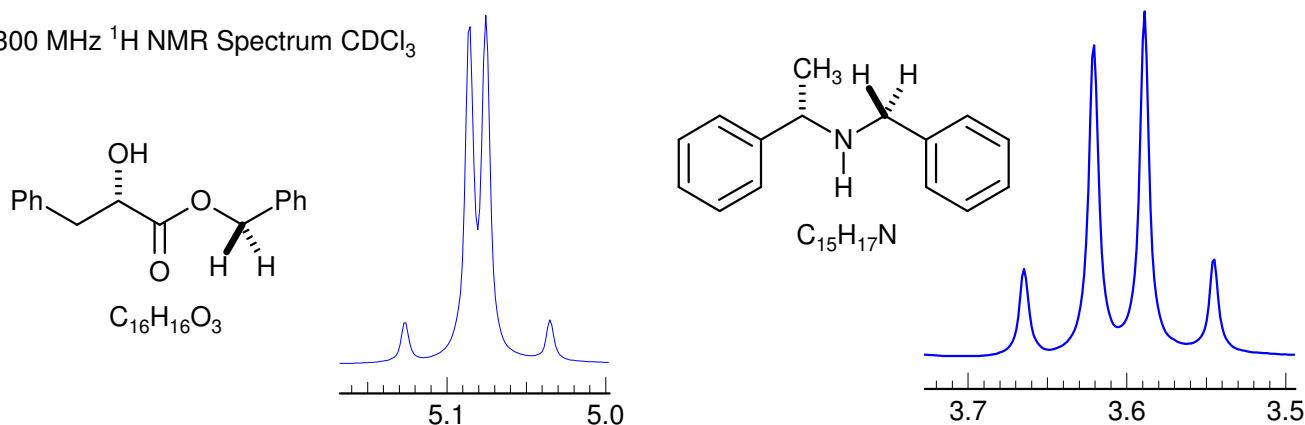
**Exercise**: Assign the protons in this partial $^1$H NMR spectrum.



$C_{12}H_{17}NO$
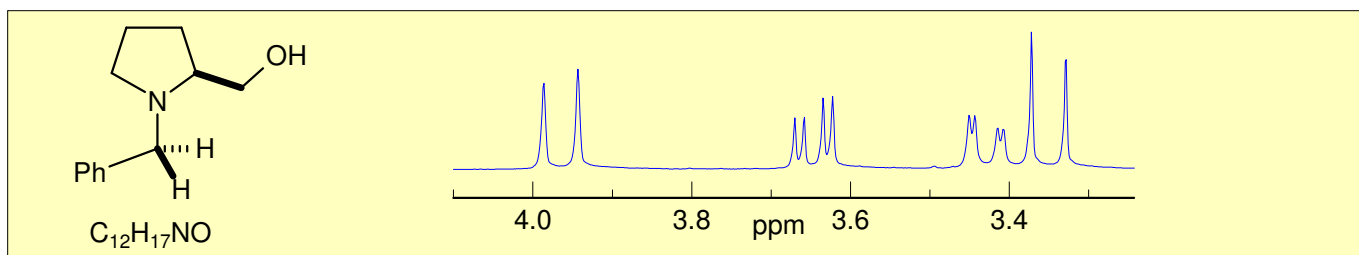
**Exercise**: Assign the protons in this spectrum.



$C_{12}H_{18}O_6$
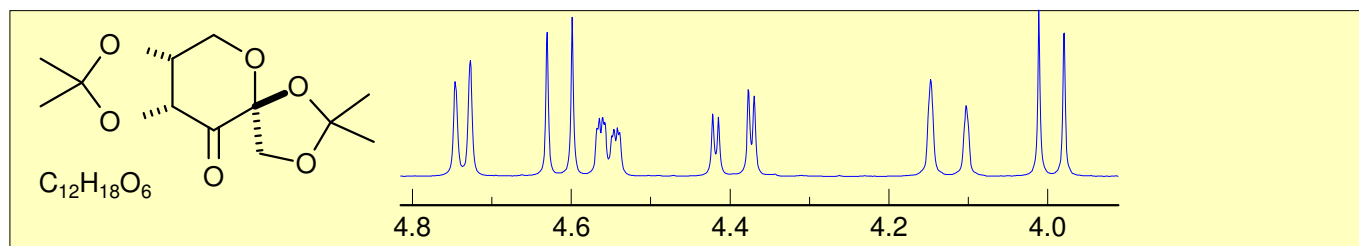
# Energy Levels of AX and AB Spectra

The four energy levels for an AX system are given in a very straightforward way by the equation below, by substituting the four possible spin combinations of $m_A$ and $m_X$ (++, +-, -+, --):

$$E = -(m_A\nu_A + m_X\nu_X) + m_A m_X J_{AX}$$

There are four states: $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, $\beta\beta$. We will use the convention: $\alpha\alpha$ is the lowest energy state ($\alpha$ is aligned with the field, $m = +\frac{1}{2}$) and $\beta\beta$ is the highest energy state ($\beta$ is aligned against the field, $m = -\frac{1}{2}$). The first term in the equation is the chemical shift part, the second term the coupling part. If the coupling is a small perturbation, then the energy is simply the sum of the two parts. In energy level terms, this means that the energy separation of the $\alpha\beta$ and $\beta\alpha$ states is large compared to $J$.

| State | $m_A$ | $m_B$ | $m_T$ | Energy |
|-------|-------|-------|-------|--------|
| $\beta\beta$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-1$ | $-[(-\frac{1}{2})\nu_A + (-\frac{1}{2})\nu_X] + (-\frac{1}{2})(-\frac{1}{2})J = \frac{1}{2}(\nu_A + \nu_X) + J/4$ |
| $\beta\alpha$ | $-\frac{1}{2}$ | $+\frac{1}{2}$ | $0$ | $-[(-\frac{1}{2})\nu_A + (+\frac{1}{2})\nu_X] + (-\frac{1}{2})(+\frac{1}{2})J = \frac{1}{2}(\nu_A - \nu_X) - J/4$ |
| $\alpha\beta$ | $+\frac{1}{2}$ | $-\frac{1}{2}$ | $0$ | $-[(+\frac{1}{2})\nu_A + (-\frac{1}{2})\nu_X] + (+\frac{1}{2})(-\frac{1}{2})J = -\frac{1}{2}(\nu_A - \nu_X) - J/4$ |
| $\alpha\alpha$ | $+\frac{1}{2}$ | $+\frac{1}{2}$ | $+1$ | $-[(+\frac{1}{2})\nu_A + (+\frac{1}{2})\nu_X] + (+\frac{1}{2})(+\frac{1}{2})J = -\frac{1}{2}(\nu_A + \nu_X) + J/4$ |

Only transitions with $\Delta m_T = \pm 1$ are allowed. The $\alpha\alpha$ to $\beta\beta$ (double quantum) and $\alpha\beta$ to $\beta\alpha$ (zero quantum) transitions are forbidden, since they involve simultaneous changes in both spins.

## AX → AB → A₂



$\Delta\nu = \nu_A - \nu_B$

$$2D = \sqrt{\Delta\nu^2 + J^2}$$

$$Q = \frac{J}{\Delta\nu + 2D}$$

$Q \to 0$  $\Delta\nu \gg J$
$Q \to 1$  $\Delta\nu \to 0$
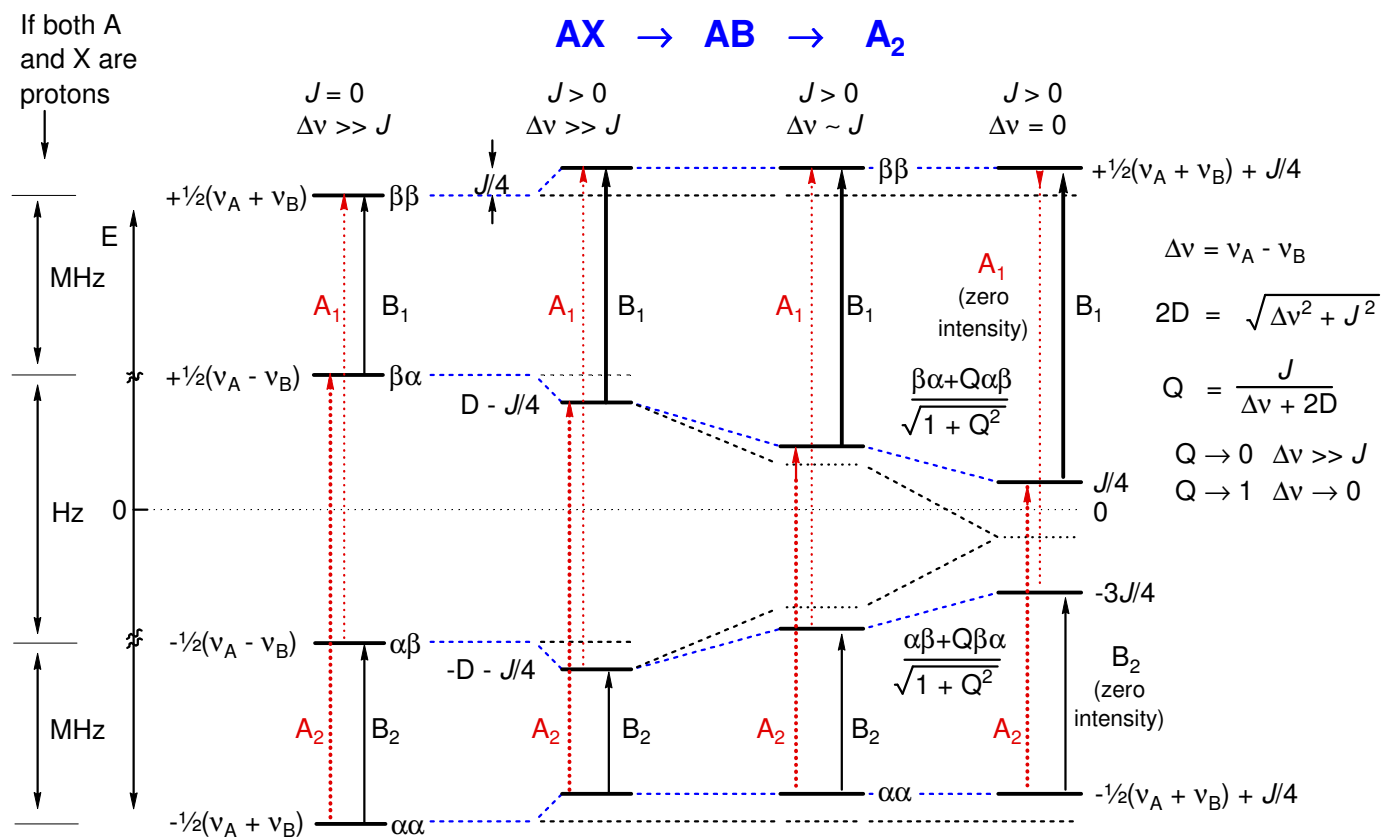
# AB Spectra

When the energies of the $\alpha\beta$ and $\beta\alpha$ states approach each other, they begin to mix, the $\alpha\beta$ state develops some $\beta\alpha$ character and vice versa (the mixing parameter Q specifies the degree of mixing). The energy of the $\beta\alpha$ state, instead of $\frac{1}{2}(v_A - v_B)$, then becomes $\frac{1}{2}[(v_A - v_B)^2 + J^2]^{\frac{1}{2}}$ (here defined as D)

| State | $m_A$ | $m_B$ | $m_T$ | Energy |
|-------|-------|-------|-------|--------|
| $\beta\beta$ | $-\frac{1}{2}$ | $-\frac{1}{2}$ | $-1$ | $+\frac{1}{2}(v_A + v_X) + J/4$ |
| $\beta\alpha$ | $-\frac{1}{2}$ | $+\frac{1}{2}$ | $0$ | $+D - J/4$ |
| $\alpha\beta$ | $+\frac{1}{2}$ | $-\frac{1}{2}$ | $0$ | $-D - J/4$ |
| $\alpha\alpha$ | $+\frac{1}{2}$ | $+\frac{1}{2}$ | $+1$ | $-\frac{1}{2}(v_A + v_X) + J/4$ |

$$D = \frac{1}{2}[(v_A - v_B)^2 + J^2]^{\frac{1}{2}}$$

$$Q = \frac{J}{\Delta v + 2D}$$

$$Q \to 0 \quad \Delta v \gg J$$
$$Q \to 1 \quad \Delta v \to 0$$

In addition to these perturbations in energy levels, the probability of the transitions (i.e. line intensities) also varies - the $A_1$ and $B_2$ transitions become weaker and eventually disappear (i.e. they become forbidden), leaving only the $A_2$ and $B_1$ lines, which appear exactly at the chemical shifts of A and B when $\Delta v$ becomes 0.
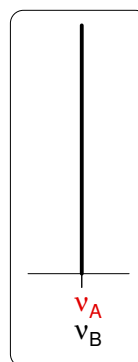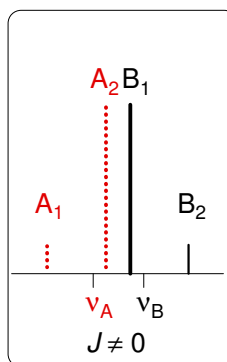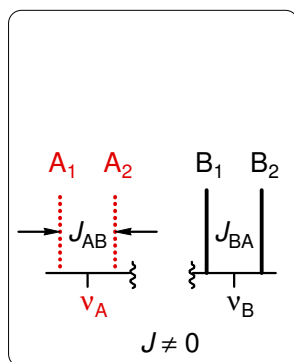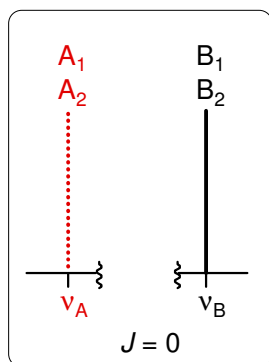


**Intensities:**

$$i_{A2} = i_{B1} = \frac{(1 + Q)^2}{(1 + Q^2)}$$

$$i_{A1} = i_{B2} = \frac{(1 - Q)^2}{(1 + Q^2)}$$

$$\frac{i_{A2}}{i_{A1}} = \frac{i_{B1}}{i_{B2}} = \frac{(v_{A1} - v_{B2})}{(v_{A2} - v_{B1})}$$

Four lines are present, as for an AX spectrum, and J is the same:

$$|J_{AB}| = (v_1 - v_2) = (v_3 - v_4)$$

The line intensities, i, are no longer 1 : 1 : 1 : 1, but given by the ratios:

$$\frac{i_2}{i_1} = \frac{i_3}{i_4} = \frac{(v_1 - v_4)}{(v_2 - v_3)}$$

$v_A$ and $v_B$ are *not* exactly halfway between line 1 and line 2, or between line 3 and line 4.

$C$ = center of AB pattern
$$= \frac{1}{2}(v_2 + v_3) = \frac{1}{2}(v_1 + v_4)$$

$$\Delta v_{AB} = \sqrt{(2D)^2 - J^2}$$

$$= \sqrt{(v_1 - v_3)^2 - J^2}$$

$$= \sqrt{(v_1 - v_4)(v_2 - v_3)}$$
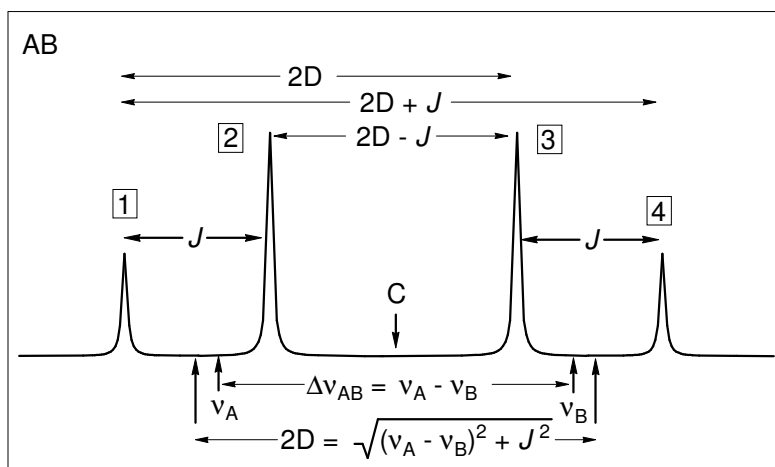


If $v_A - v_B$ were calculated as if the pattern were AX instead of AB, one would get 2D instead of the correct value.

2D/Δν is the error in the measured chemical shift $\nu_{AB}$.

**AB Quartet with increasing $\nu_{AB}$**
**Constant $J_{AB} = 10$ Hz**
all printed at **same Hz scale**

**AB Quartet with $J_{AB} = 10$ Hz and $\nu_{AB} = 0.1$ ppm**
at various spectrometer frequencies
all printed at **same ppm scale**

| Δν/J | 2D/Δν |
|------|-------|
| 5 | 1.02 |
| 4 | 1.03 |
| 3 | 1.05 |
| 2 | 1.12 |
| 1 | 1.41 |

$\nu_{AB} = 50$ Hz
A   B

$\nu_{AB} = 40$ Hz
A   B

$\nu_{AB} = 30$ Hz
A   B

$\nu_{AB} = 20$ Hz
A   B

$\nu_{AB} = 10$ Hz
A   B

50 40 30 20 10 0 -10 -20 -30 -40
Hz

600 MHz
$\nu_{AB} = 60$ Hz

500 MHz
$\nu_{AB} = 50$ Hz

300 MHz
$\nu_{AB} = 30$ Hz

200 MHz
$\nu_{AB} = 20$ Hz

100 MHz
$\nu_{AB} = 10$ Hz

0.1   $\nu_A$   0   $\nu_B$   -0.1
ppm
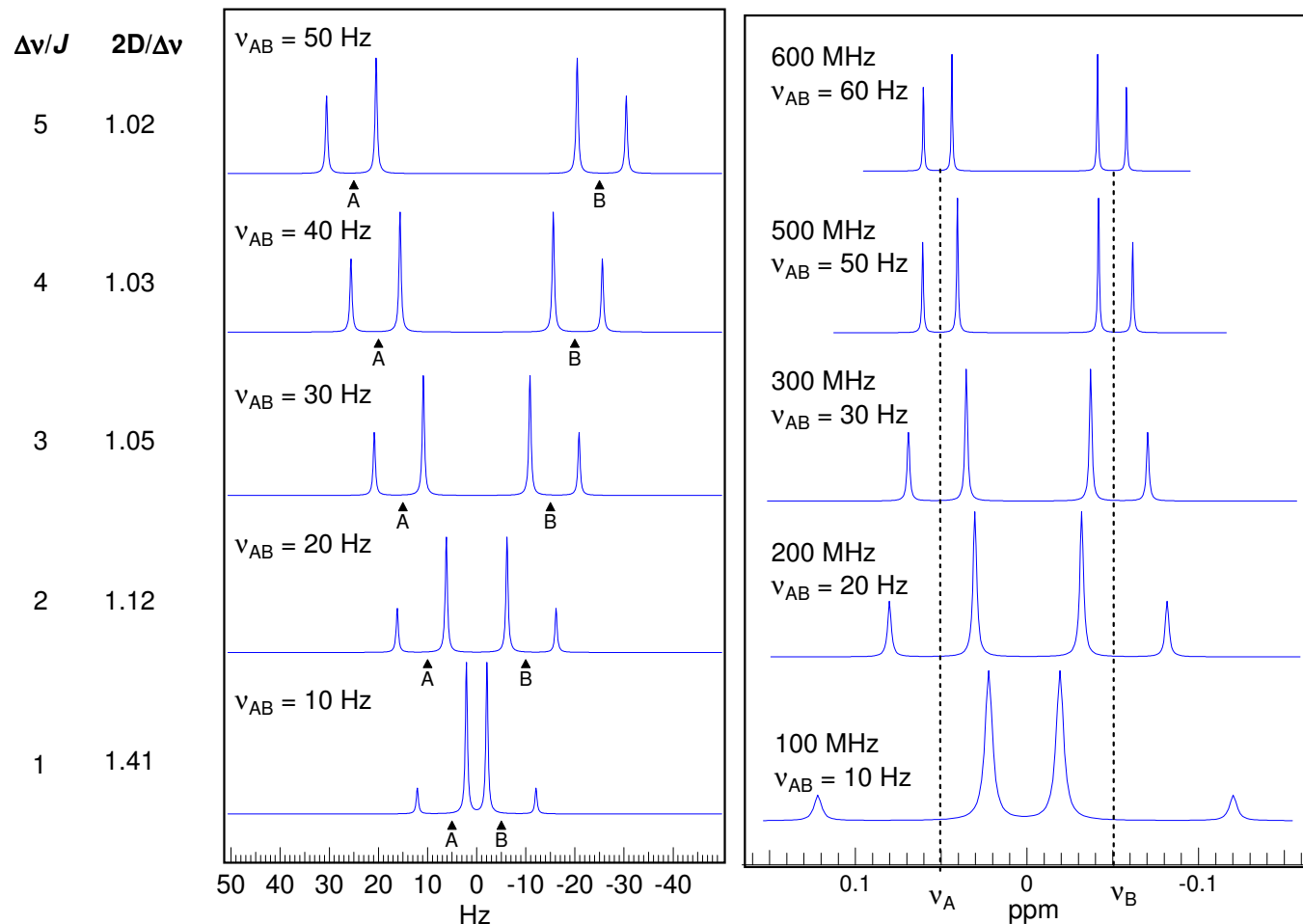
The distinction between an AB q and a regular q is not always trivial. In fact, if an AB quartet has the same Hz separation between the center two lines as the coupling constant $J$, then the intensities of the four lines are 1:3:3:1, exactly the same as for a regular q. Of course, an ABq must always integrate to at least 2 protons, and that may help with a distinction in this peculiar case.

Consider the muliplet below, which at first glance might be identified as a ddq. However, a proper analysis, which first removes the two smaller couplings, the dd, gives a child multiplet that does NOT have the correct line positions for a q (separation **A** is NOT the same as J, as required for a ddq). Rather, the intensities are those of an AB q, each line of which is split into a dd.



30   20   10   0   Hz

J

A

$J \neq A$
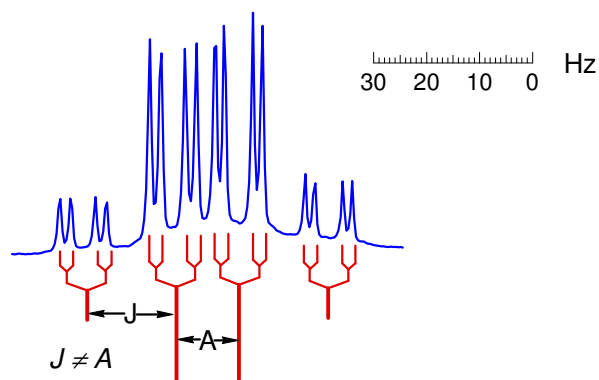
This multiplet is centered at δ 2.64 and appears in the spectrum of 3-(methylthio)butyraldehyde. Which protons are these?
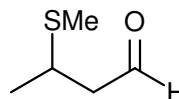
## Solving an AB pattern:

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

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

2.  Calculate the center position (in Hz):

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

3.  Calculate $\nu_{AB}$.

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

4.  Calculate $\nu_A$ and $\nu_B$ (spectrometer frequency: 300 MHz).

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

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

    $\delta_A = \nu_A / MHz = 6.76$

    $\delta_B = \nu_B / MHz = 6.73$

**Graphical method for determining the position of a leaning coupled partner**. The point **Q** is the horizontal projecti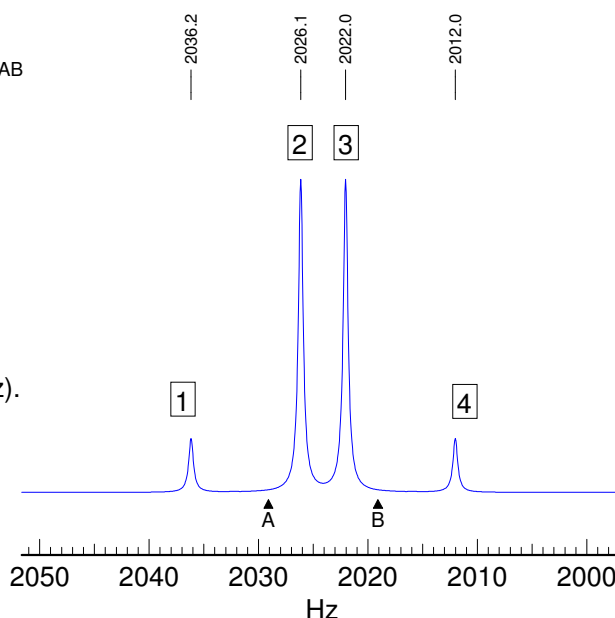on of the tip of line 2 on the position of line 1, and point **P** is the projection of the line 1 on the position of line 2. The line through **P** and **Q** intersects the baseline at the midpoint between the chemical shifts of A and B (point **C**) (http://www.ebyte.it/library/docs/kts/KTS_isoAB_Geometry.html). You can use this method to quickly estimate where a leaning doublet's coupling partner should be, if other peaks obscure the region of interest, or to determine whether you are looking at a leaning doublet, or two unrelated peaks.
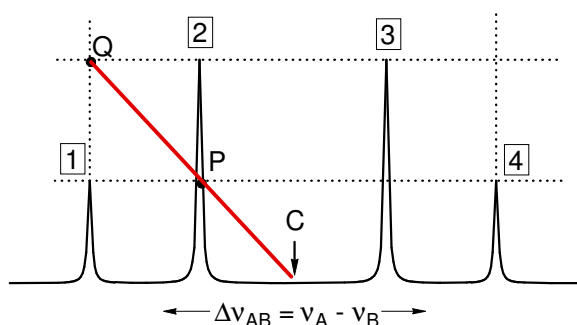
## How to report an AB quartet.

Journals require that NMR spectra be reported in text format.  There are several ways an AB quartet could be reported:

1.  Treat the pattern as first order (i.e., as two doublets).  This is OK for AB quartets with a large $\nu_{AB} / J_{AB}$ ratio, say > 4, where the error in chemical shifts caused by simply taking the middle of each doublet is small:

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

2.  For closely spaced AB quartets ($\nu_{AB} / J_{AB} < 4$) the AB character should be explicitly shown, to indicate that the pattern was recognized, and the shifts were calculated correctly.  One way is to report the chemical shift of the center of the AB quartet, and $\Delta\delta_{AB}$ and $J_{AB}$.

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

3. A third way is to report the two chemical shifts, and the coupling.

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

Note that the latter two formats not only use less journal space but also contain more information than the "first order" format (1).  There is nothing in the first description that specifies that the two doublets are coupled to each other, yet that would be obvious from observing the spectrum.

Shown above is the 60 MHz spectrum of Abel's ketone in $CDCl_3$ solution. There are three sets of protons that one would expect to form AB quartets. **Exercise**: Identify them on the structure.
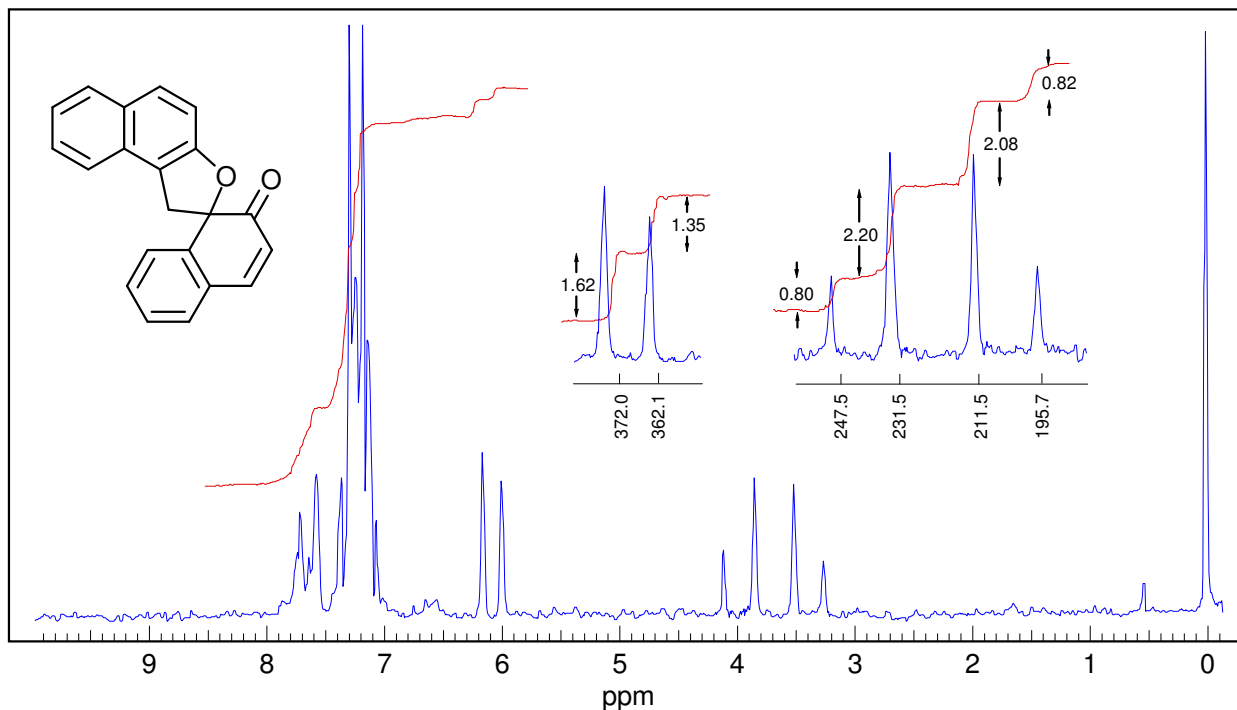


The AB quartet at 3.7 δ can be analyzed as follows:

$J_{AB}$ = 247.5 - 231.5 = 16.0          i. e. $J_{AB}$ = 15.9 Hz
$J_{AB}$ = 211.5 - 195.7 = 15.8

$\Delta\nu$ = $[(247.5 - 195.7)(231.5 - 211.5)]^{\frac{1}{2}}$ = 32.19          i. e. $\Delta\nu$ = 32.25 Hz
$\Delta\nu$ = $[(247.5 - 211.5)^2 - (15.9)^2]^{\frac{1}{2}}$ = 32.30

Center = 221.60 Hz or 221.50 Hz so:
   $\nu_A$ = 237.6 Hz, 3.96 δ
   $\nu_B$ = 205.4 Hz, 3.42 δ

Intensity Ratios:
   Observed: $i_2/i_1$ = 2.75; $i_3/i_4$ = 2.54
   Calculated: $(\nu_1 - \nu_4)/(\nu_2 - \nu_3)$ = 2.59

The doublet at 6.1 δ is the B part of an AB quartet. **Where is A?**

$J_{AB}$ = 372.0 - 362.1 = 9.9
$i_3/i_4$ = 1.2 = $[(\nu_2 + 9.9) - 362.1] / (\nu_2 - 372.0)$

Solve for $\nu_2$: 471.0
$\nu_1 = \nu_2 + J_{AB}$ = 480.9
Solve the AB quartet: $\nu_A$ = 475.9 Hz or 7.93 δ
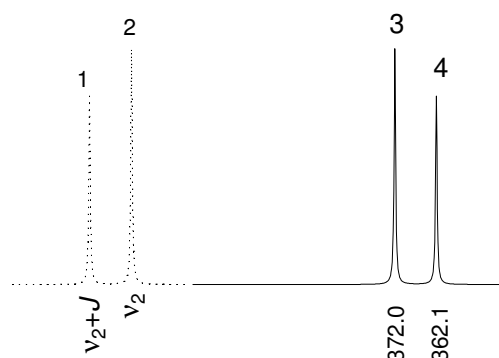


This is a little off because the intensity ratio is not very accurate, but allows proper assignment. You could also use the graphical method illustrated on the previous page.

**Exercise**: Why are the peak heights of the downfield doublet (ca δ 7.7) lower than those of the upfield one at δ 6.1? Hint: Section 5-HMR-06

**Exercise**: The dibenzyl ester of aspartic acid salt has two different diastereotopic Ph-CH$_2$ groups. Identify the peaks and calculate $\delta_{AB}$ and $\nu_{AB}$ for each.



300 MHz $^1$H NMR spectrum
Source: Aldrich Spectra Viewer

Peak labels: 1512.4, 1500.2, 1494.0, 1481.9, 1480.4, 1467.5, 1466.4, 1453.6

$C_{18}H_{19}NO_4 \cdot TsOH$

ppm axis: 5.0, 4.9
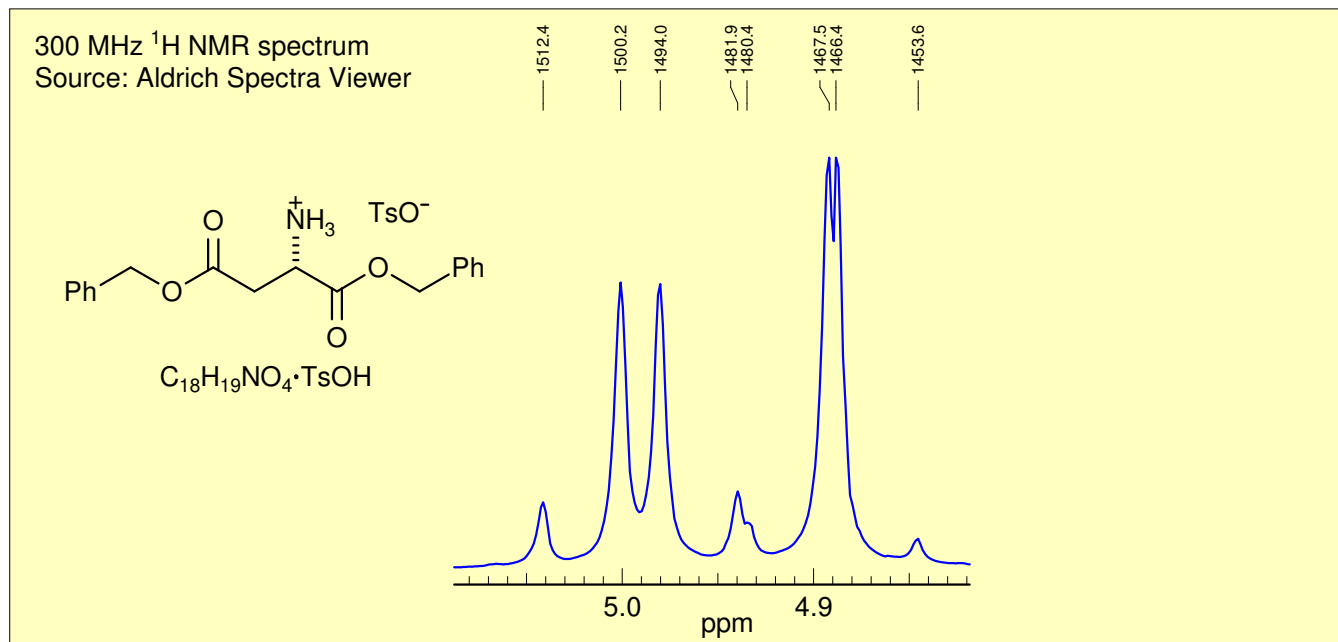
# 5.11  The AX$_2$ and AB$_2$ Patterns

Some examples of molecules containing three spin systems in which two of the nuclei are magnetically equivalent are shown below.  Perhaps the most common type is 1,2,3-trisubstituted benzenes in which the 1 and 3 substituents are identical.
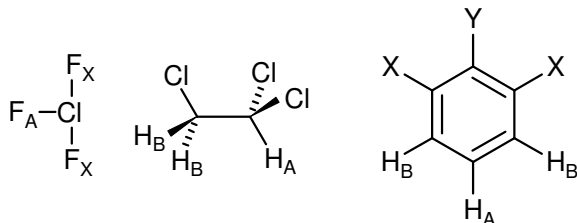
AX$_2$ and AB$_2$ patterns are not as common as AMX, ABX and ABC, but there is an important reason for examining them in some detail.  The transition of an AX$_2$ to an AB$_2$ spin system provides additional insight into the appearance of second order effects.  In the AB pattern there are two effects of this type:

• The line intensities no longer follow simple rules

• The arithmetic average of line positions no longer gives true chemical shifts, although the coupling constant $J_{AB}$ can still be directly measured from the spectrum.

In AB$_2$ spectra a third and fourth effects appear: none of the line separations correspond to $J_{AB}$, and additional lines appear which are not predicted by simple multiplet rules.  The additional lines arise from splitting of double-intensity lines, as well as from the appearance of new transitions.

The AB$_2$ spectra illustrate this process.   In the top spectrum we have $\Delta v/J \gg 5$, and the system is effectively AX$_2$, it consists of an A triplet and a B doublet.  As $\Delta v/J$ becomes smaller, the double-intensity middle line of A and both B lines split into two lines.  An additional line which is not a direct descendant of any of the AX$_2$ lines appears (a combination line: $\alpha\beta\alpha \rightarrow \beta\alpha\beta$).  Since it is essentially a forbidden transition it is usually quite weak, but can sometimes be observed.  In the bottom spectrum ($\Delta v/J = 0.7$) the intensity of line 9 is 0.4% of the most intense line (line 5).

When $\Delta v/J < 1$ the spectrum takes on the appearance of a triplet, with a very intense and broadened central line.  Finally, as $\Delta v/J$ approached 0 ($v_A = v_B$) the outer lines disappear completely, and we are left with a singlet.

$\Delta v = 50$ Hz

$J = 10$ Hz
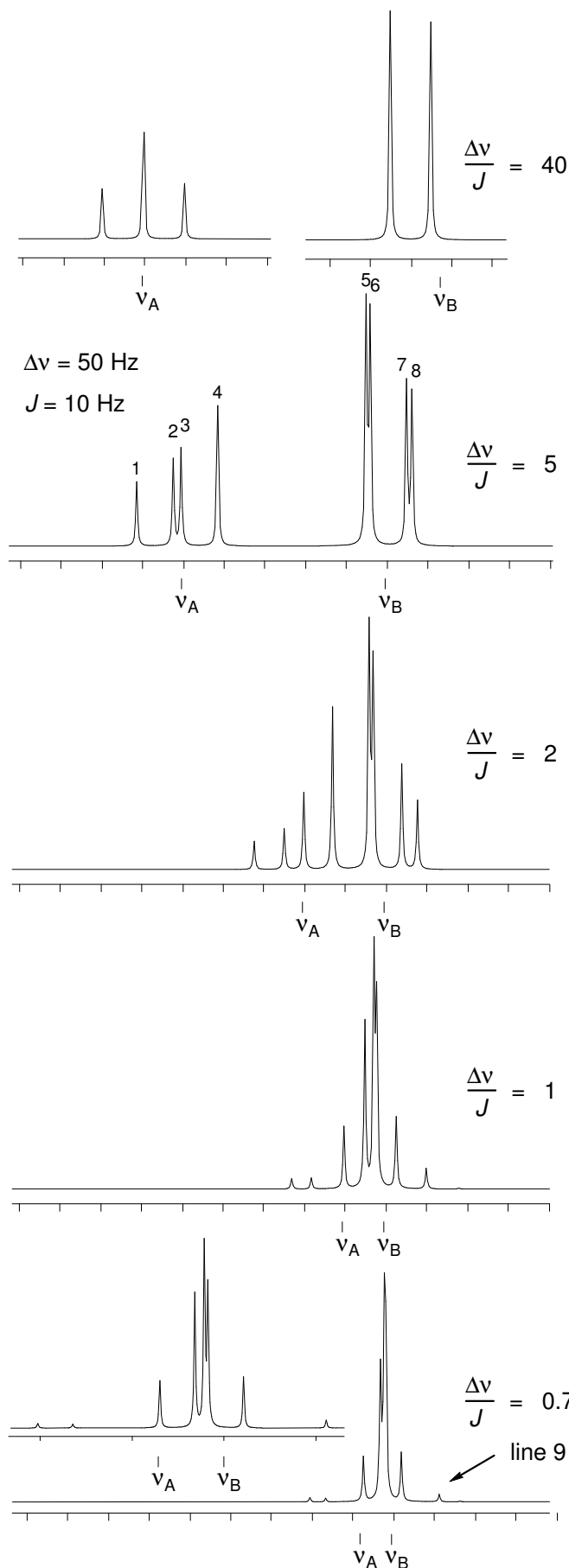
## Solving an AB₂ Pattern

To analyze an $AB_2$ pattern, we number the lines as shown, the four A lines $\nu_1$- $\nu_4$, the four B lines $\nu_5$- $\nu_8$, and the very weak combination line $\nu_9$.  The arithmetic is simple:

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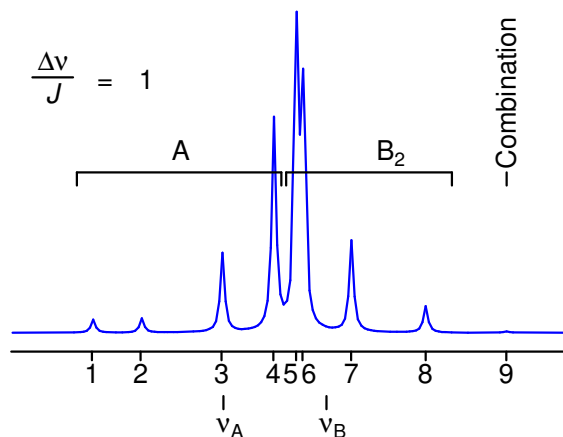


$$\nu_A = \nu_3$$
$$\nu_B = (\nu_5 + \nu_7)/2$$
$$J_{AB} = (\nu_1 - \nu_4 + \nu_6 - \nu_8)/3$$

Some points to remember about $AB_2$ patterns:

1.  The spectrum depends **only** on the ratio $\Delta\nu/J$.

2.  Note that lines 1-4 must correspond to the one-proton part, lines 5-8 to the two-proton part.  Thus, if the pattern is $A_2B$ then the numbering proceeds in the reverse direction.  Distinguish the one and two proton parts by integration.

3.  Line $\nu_5$ is the most intense line.  The lines $\nu_5$ and $\nu_6$ often do not split up.

4.  When $\Delta\nu/J$ is much less than 1 the spectra appear nearly symmetrical since $\nu_1$, $\nu_2$ and $\nu_8$ become very weak. The spectrum then has the appearance of a distorted triplet with a 1:10:1 area ratio (the peak heights will not be in this ratio since the center line consists of several closely spaced ones.

5. Neither $J_{BB}$ nor the sign of $J_{AB}$ affect the appearance of the spectrum.
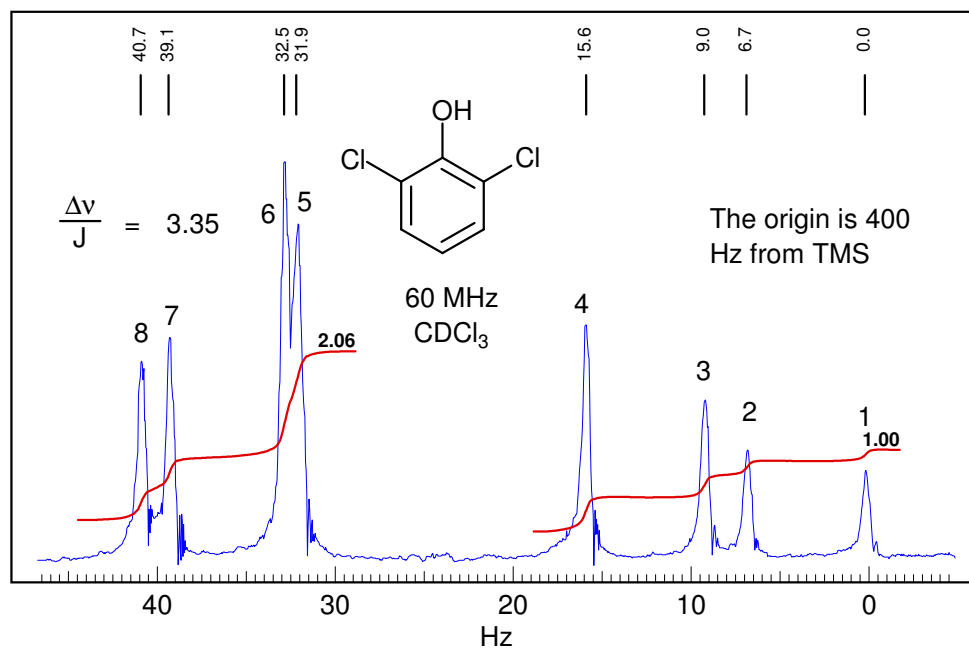


The "1H" part is upfield of the "2H" part here so numbers run from right to left:  $\nu_1 = 0.0$ . . . $\nu_8 = 40.7$

$\nu_B = \nu_3 = 9.0$ Hz ($\delta_B = (9 + 400)/60 = 6.82$)

$\nu_A = (\nu_5 + \nu_7)/2 = (31.9 + 39.1)/2 = 35.5$ Hz ($\delta_A = (35.5 + 400)/60 = 7.26$)

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

# 5.12 ABX Pattern

**AMX**, **ABX** and **ABC** patterns, and various related spin systems are very common in organic molecules. Below some of the structural types which give **ABX** patterns.

**AMX Patterns**. Three nuclei coupled to each other and separated by a large chemical shifts compared to the coupling between them can be analyzed in first order fashion (Sect. 5-HMR-3): the **A**, **M** and **X** signals are each a doublet of doublets, and the couplings can be extracted by inspection.

**Exercise**: How can the assignments for the **A** and **M** protons be done in the example below (see Sect. 5.5)?

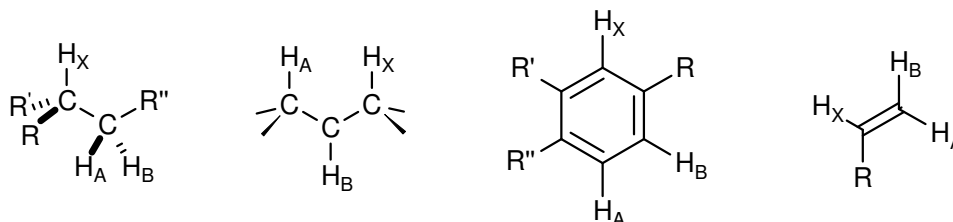**An AMX Pattern**

$C_8H_7ClO$
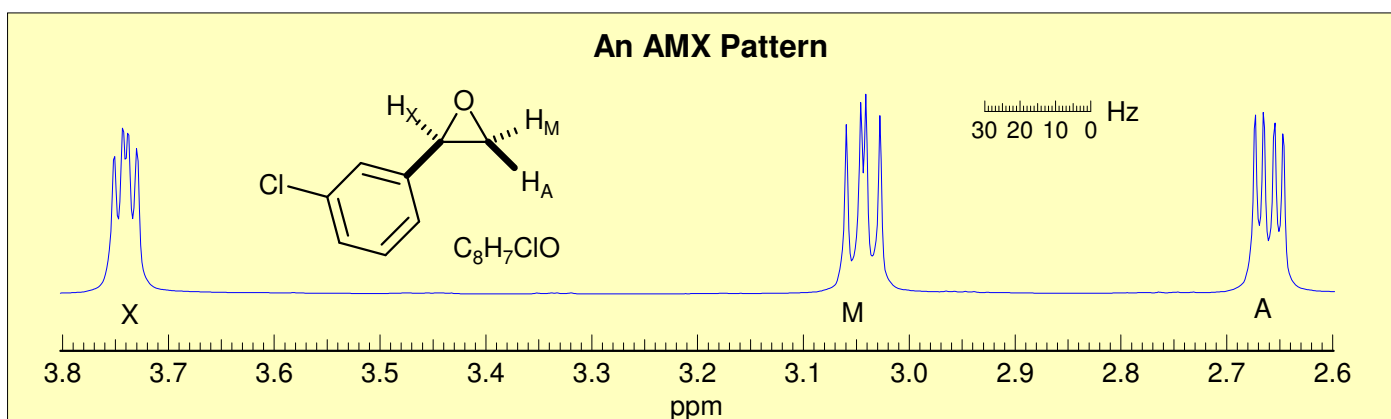
**ABX Patterns**. When two of the protons of an **AMX** pattern approach each other to form an **ABX** pattern, the characteristic changes in intensities of a strongly coupled system (leaning) are seen, and, as the size of $J$ approaches the value of $\nu_{AB}$ more complicated changes arise, so that the pattern can no longer be analyzed correctly by first order methods. A typical **ABX** spectrum is shown below:

300 MHz $^1H$ NMR spectrum in DMSO-$d_6$
Source: Aldrich Specral Viewer/Reich

**Figure 5-12.1**. Sample ABX pattern

For this spectrum $\nu_{AB}$ is less than twice $J$, and a first order (**AMX**-type) interpretation starts to become imprecise, although, in this particular case, it is unlikely to lead to a substantial misinterpretation. On the other hand, for the spectrum below (which is actually an **ABMX$_3$**, where X = $^{19}F$), the second order effects are so large than a first order interpretation may lead to grossly inaccurate couplings, both in magnitude and sign, and a possible misassignment of the structure.

$(C_6H_9F_3O_3)$
300 MHz $^1$H NMR spectrum in CDCl$_3$
Source: Aldrich Specral Viewer/Reich

**Figure 5-12.2**. A borderline **ABX** pattern (actually an **ABM$_3$X** pattern, since the **X** proton is coupled to the three fluorines. First order analysis of this one is problematic.

Even more likely to mislead is the **ABX** pattern below, for which any form of first order analysis could lead to wildly incorrect structure interpretations, or even a "false negative" during synthesis of a molecule (i.e., your reaction was actually successful, but you conclude that if failed because the NMR spectrum does not appear to fit the expected structure).



300 MHz $^1$H NMR Spectrum in CDCl$_3$
Source: Aldrich Spectral Viewer/Reich

$C_9H_{13}NO$
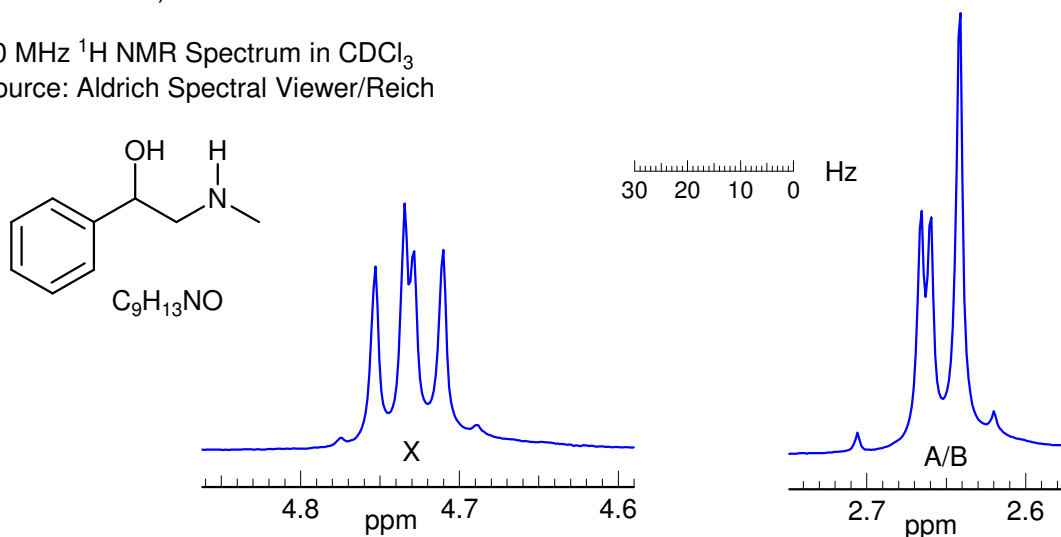
**Figure 5-12.3**. A deceptive **ABX** pattern, in which one of the **ab** sub-quartets has collapsed to a singlet. No first-order analysis possible.

For these reasons, we will examine **ABX** patterns in some detail. In the progression from first-order NMR patterns to incomprehensible jungles of peaks, they represent the last stopping point where a complete analysis (by hand or hand calculator)  is still possible, and where insights into the problems that arise in the analysis of more complex systems can be achieved.  Specifically, **ABX** patterns are the simplest systems which show the phenomenon sometimes referred to as "virtual coupling" (see Sect. 5-HMR-16) and they are the simplest systems in which both the *magnitude* and the *sign* of *J* coupling constants is significant.  Furthermore, as illustrated above, there are several pathological forms of **ABX** patterns which are sufficiently nonintuitive that the unwary spectroscopist can mis-assign coupling constants and even structures.

**Development of an ABX Pattern**.  Consider the stick diagram below which represents an **ABX** pattern in which we sequentially turn on first the A-X and then the B-X coupling:
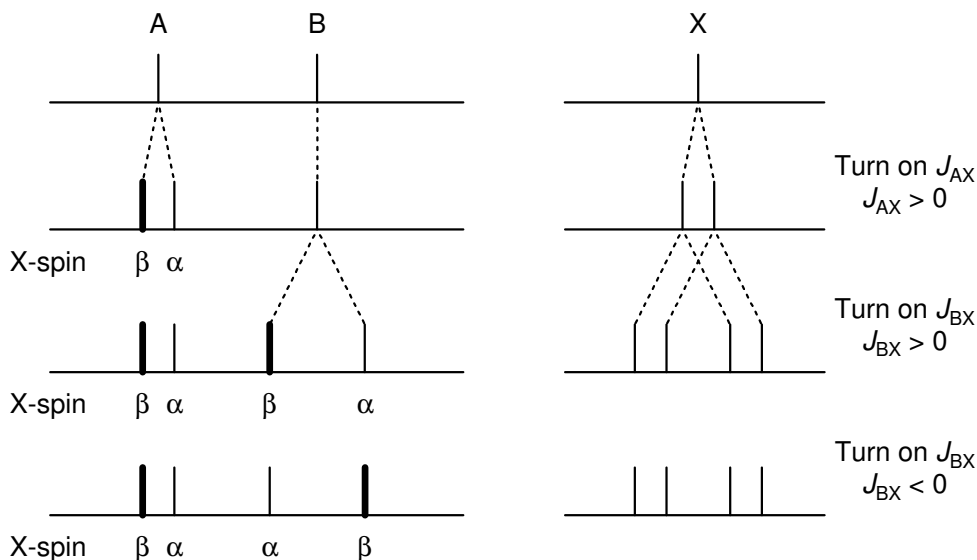


One of the two lines in the **A**-pattern arises from those molecules with the spin of the **X**-nucleus aligned against the field (β) and the other from those which have the X-spin aligned with the field (α).  Similarly for the **B**-pattern. Note, however, that the line assignments of the pattern with both $J_{AX}$ and $J_{BX}$ nonzero will be different depending on the relative sign of $J_{AX}$ and $J_{BX}$, as illustrated in the Figure.  Up to this point the line positions are identical.

The key to understanding **ABX** patterns is to realize that *the **A** and **B** nuclei with spin of X = α and those with spin of X = β are actually on different molecules, and cannot interact with each other.*  Thus, when we finally turn on $J_{AB}$, it will be the X = α line of **A** and the X = α line of **B** that will couple to form an **AB**-quartet.  Similarly, the two X = β lines will form a second AB-quartet.  Since the line intensities and line positions of an **AB** quartet depend on the "chemical shift" between the nuclei, it is clear that the different relative signs of $J_{AX}$ and $J_{BX}$ will result in different spectra.  The **ABX** pattern is thus the simplest spin system for which the discerning spectroscopist can identify the relative signs of coupling constants by analysis of the pattern.  The figure below shows the final **AB** part of the **ABX** pattern for the two cases.

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



$J_{AB}$ = 13 Hz
$J_{AX}$ = 5 Hz
$J_{BX}$ = 10 Hz    $J_{BX}$ = -10 Hz

$\nu_B$ = 90 Hz
$\nu_A$ = 110 Hz
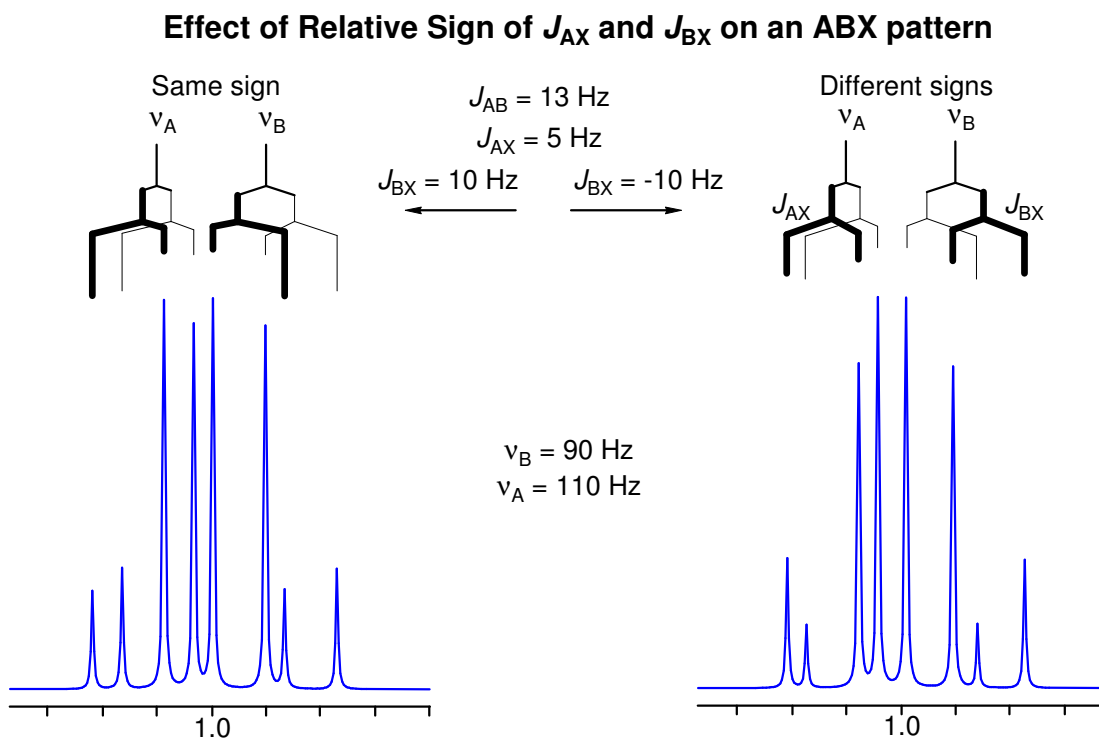
# Solving ABX Patterns

**Recognizing an ABX Pattern**. A typical **ABX** spectrum consists of an unsymmetrical 8-line pattern integrating to two protons which has 4 doublets with the same separation $J_{AB}$ (each doublet shows strong "leaning"). This is the **AB** part. The **X** part is a symmetric 6-line pattern, integrating to one proton, with four lines dominant (often looking like a dd). The 5th and 6th lines (marked with red arrows) are usually small, and not often seen. $J_{AB}$ and $\nu_X$ are directly measureable, the other parameters ($J_{AX}$, $J_{BX}$, $\nu_A$, $\nu_B$) must be calculated.
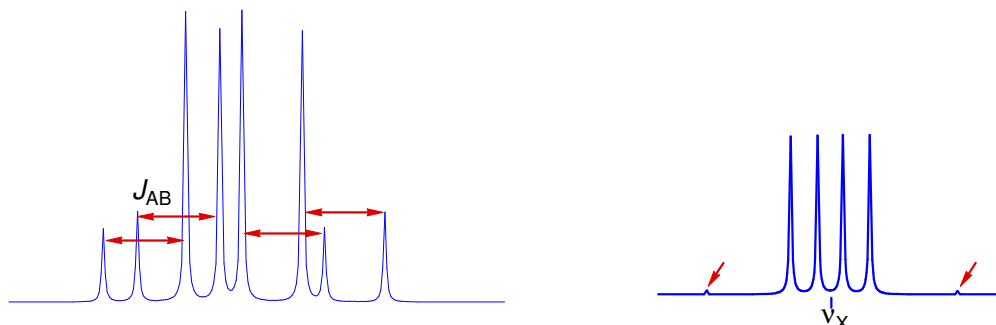


The **AB** part consists of two superimposed **ab** quartets (8 lines) which have normal intensities and line separations, both of which have identical $J_{AB}$ values, but can have very different $\nu_{ab}$ values. We will use "a" and "b" for the **AB**-subquartets of the **AB** part of an **ABX** pattern. Occasionally one of the **ab** quartets has $\nu_{ab} = 0$, and appears as a singlet. Such systems appear as a five line pattern, with one **ab** quartet and a singlet (see Fig. 5-12.3 for an example). There are also several other deceptive forms with one or more lines superimposed.

The **X** part usually consists of an *apparent* doublet of doublets, although *apparent* triplets are not uncommon. There are two other lines which are often too weak to be detected (total of 6 lines). They become large when $J_{AB} > \nu_{AB}$.

**First Order "AMX" Type Solution.** Many **ABX** patterns are sufficiently close to **AMX** (i.e., $\nu_{AB} \gg J_{AB}$) that a first-order solution has an excellent chance of being correct. We identify the distorted doublet of doublets ($J_{AB}$, $J_{AX}$) which make up the **A** portion, as well as the dd ($J_{AB}$, $J_{BX}$) for **B**, and begin the analysis by first removing the $J_{AX}$ and $J_{BX}$ couplings, respectively. This leaves us with an **AB** pattern, which we can solve in the usual way. Since this is a first-order analysis there is no information about the relative signs of $J_{AB}$ and $J_{BX}$.

$J_{AB} = 13$ Hz

$J_{AX} = 5$ Hz

$J_{BX} = 10$ Hz

$\nu_A = 110$ Hz

$\nu_B = 90$ Hz
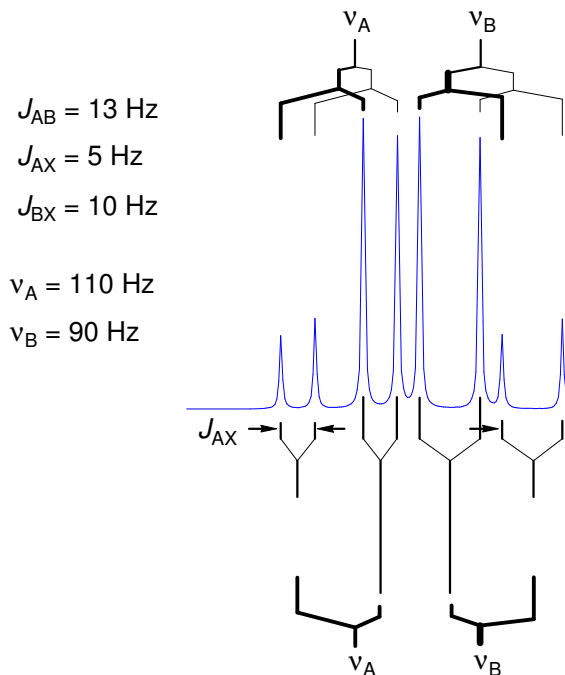


## Exact solution to an ABX Pattern

← 2. Then remove $J_{AX}$ and $J_{BX}$ (solve two d)

← 1. Solve the two AB patterns

Note that the approximate analysis at the bottom proceeds in the reverse order as the exact one at the top.

## Approximate "AMX" Solution

← 1. Remove $J_{AX}$ and $J_{BX}$ (solve two dd)

← 2. Then solve AB pattern

For **ABX** patterns which are of the "Solution 1" type (see below) this analysis will lead to $J$ and $\delta$ values that are quite close to correct. The errors become larger when $J_{AX}$ and $J_{BX}$ are very different in size (especially if they are different in sign) and, of course, when $\nu_{AB}$ is small compared to $J_{AB}$. However, such an analysis, carelessly applied, can be completely wrong if the system is of the "Solution 2" type.

**Correct Analysis of ABX Patterns**. In order to correctly analyze an **ABX** pattern of arbitrary complexity we have to reverse the order of extraction of coupling constants compared to the **AMX** solution above. We have to first solve for $J_{AB}$, and then for $J_{AX}$ and $J_{BX}$. Proceed in the following order:

1. *Identify the two **ab** quartets*. These can usually be recognized by the characteristic line separations and "leaning." We will use the notation **ab$_+$** and **ab$_-$** for the two quartets (+ identifies the one with the larger $\nu_{ab}$). Number the lines of one **ab** quartet 2,4,6,8 and the other 1,3,5,7 (NOTE: these line numbers will not typically be in sequence in the spectrum). Check to make sure that $J_{ab+} = J_{ab-}$, and that the **ab** quartet with the taller middle lines has the shorter outer lines. Note that **ABX** patterns are not affected by the sign of $J_{AB}$.

If the **ABX** pattern verges on **AMX** ($\nu_{AB}/J_{AB} \gg 2$), then line intensity patterns will not allow unambiguous choice of **ab** subquartets. Such systems can normally be analyzed as an **AMX** pattern, but with the limitation that the relative sign of $J_{AX}$ and $J_{BX}$ is indeterminate. If you complete the full **ABX** treatment with the wrong assignment of quartets, the signs of $J_{AX}$ and $J_{BX}$ will be wrong, and there will be small errors in their magnitude. This could ultimately lead to a wrong Solution 1/2 assignment (see below) if you use the signs of couplings to make the distinction.

Another situation in which the choice of **ab** subquartets can be difficult is in systems verging on **ABC**, where all of the line intensities are distorted. This is where computer simulations might become necessary.
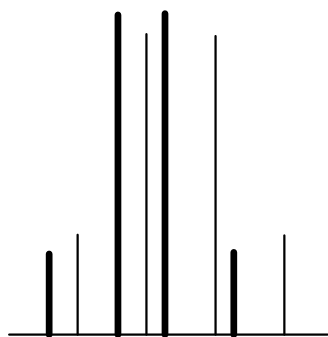


Correct choice of **ab** quartets
$J_{ab+} = J_{ab-}$, and intensities are OK
(i.e. the **ab** quartet with more closely spaced inner lines has the smaller outer lines.
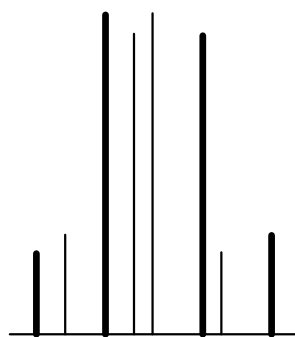
Incorrect **ab** quartets:
$J_{ab}$ is OK, but intensities are wrong (i.e. the thin **ab** quartet should have much taller central lines)

2. *Solve the two **ab** quartets.* Treat the **ab** subquartets as normal **AB** patterns, and obtain the four "chemical shifts," $\nu_{a+}$, $\nu_{b+}$ and $\nu_{a-}$, $\nu_{b-}$.
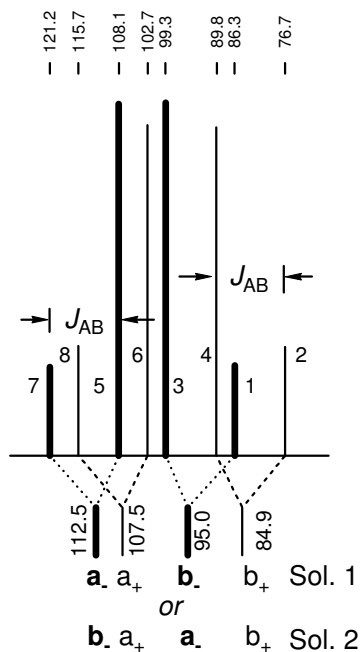


$c_- = (5+3)/2 = 103.7$

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

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

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

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

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

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

Similarly for the thin lines.

3. *Identify the correct solution.*   At this point in the analysis we encounter an ambiguity.  We know that each of the **ab** quartets consists of two **a** and two **b** lines, but we do not know which half is **a** and which is **b**.  There are thus two solutions to all **ABX** patterns which have two **ab** quartets. (The only exceptions are those **ABX** patterns in which one of the **ab** quartets has collapsed to a singlet.  For these there is only one solution.)  The two solutions are obtained by pairing up one each of a $\delta_+$ and a $\delta_-$ line (i.e. in the stick spectra shown, pair up one bold and one light line - solution 1 corresponds to pairing up the nearest neighbors, solution 2 to the remote ones, where we have swapped the $a_-/b_-$ assignments of the bold lines).  The analysis is completed as below:

**Solution 1**

121.2  115.7  108.1  102.7  99.3   89.8  86.3   76.7

$J_{AB}$

$J_{AB}$

8  6  4  2
7  5  3  1

112.5   107.5   95.0   84.9

$J_{AX}$ = 112.5-107.5 = 5.0 Hz

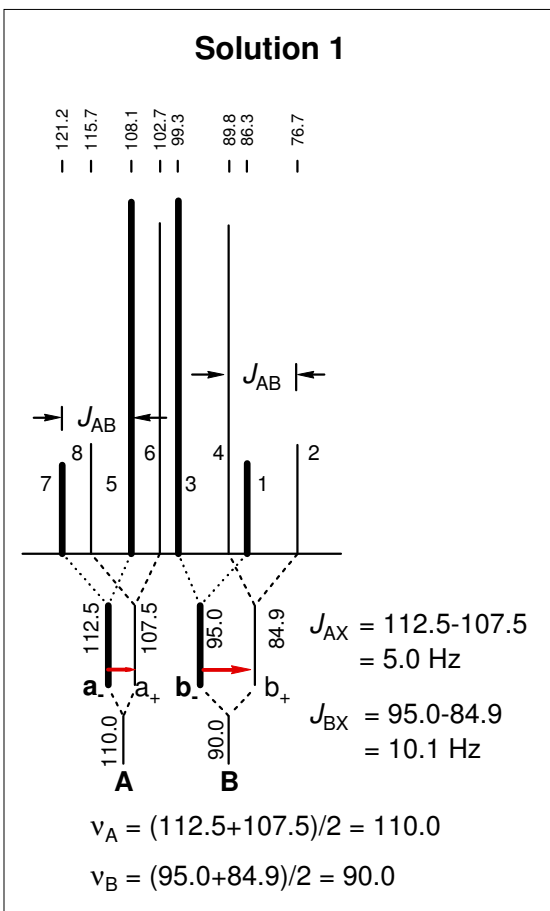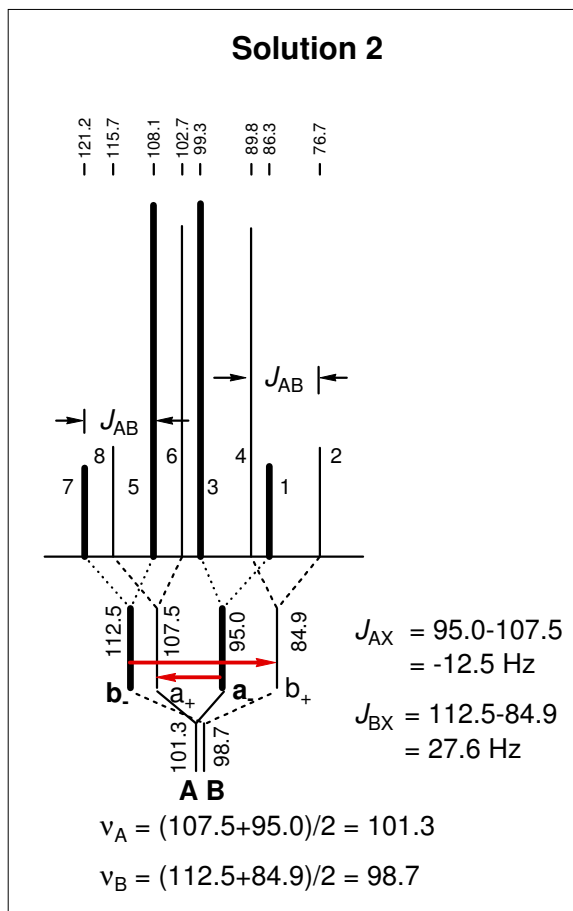**a**$_-$  a$_+$  **b**$_-$  b$_+$

$J_{BX}$ = 95.0-84.9 = 10.1 Hz

110.0   90.0

**A**     **B**

$\nu_A$ = (112.5+107.5)/2 = 110.0

$\nu_B$ = (95.0+84.9)/2 = 90.0

*or*

**Solution 2**

121.2  115.7  108.1  102.7  99.3   89.8  86.3   76.7

$J_{AB}$

$J_{AB}$

8  6  4  2
7  5  3  1

112.5   107.5   95.0   84.9

$J_{AX}$ = 95.0-107.5 = -12.5 Hz

**b**$_-$  a$_+$  **a**$_-$  b$_+$

$J_{BX}$ = 112.5-84.9 = 27.6 Hz

101.3   98.7

**A B**

$\nu_A$ = (107.5+95.0)/2 = 101.3

$\nu_B$ = (112.5+84.9)/2 = 98.7

The **relative** sign of $J_{AX}$ and $J_{BX}$ is given by the direction of vectors from bold to thin lines (i.e., whether the X = $\alpha$ lines are upfield or downfield of the X = $\beta$ lines).  Note that in this specific case, for Sol. 1 the two red arrows (each going from a "-" to a "+" line) are in the same direction, meaning that $J_{AX}$ and $J_{BX}$ have the same sign, whereas for Sol. 2 they are in opposing directions, and thus $J_{AX}$ and $J_{BX}$ have different signs.

   As part of the solution we obtain the relative signs of $J_{AX}$ and $J_{BX}$.  In the example above, this means that for Solution 1 the couplings are either both positive or both negative, and for Solution 2 one is positive and one negative. Note that there are also **ABX** patterns where the signs of $J_{AX}$ and $J_{BX}$ are the same in both solutions, and where they are different in both solutions.

The relative signs of $J_{AX}$ and $J_{BX}$ are determined by the way in which the **ab** quartets overlap. For the statements below, "lines" refers to the $v_a$ and $v_b$ line positions obtained by solving the **ab₋** and **ab₊** quartets. Solution 1 is defined as the one with the larger difference between $v_A$ and $v_B$. Thus Solution 1 always has the least distorted **X**-part. The vectors are drawn from **a₋** to **a₊** and from **b₋** to **b₊** (bold to thin) in each case.

(1) If the lines of **ab₋** and **ab₊** alternate, then $J_{AX}$ and $J_{BX}$ have the same signs in one solution, and opposite signs in the other. This is the case for the current example.

(2) If the lines of **ab₊** do not overlap those of **ab₋**, then $J_{AX}$ and $J_{BX}$ have the same sign in Solutions 1 and 2.

(3) If the lines of **ab₋** are inside those of **ab₊**, then $J_{AX}$ and $J_{BX}$ have opposite signs in both Solutions 1 and 2.
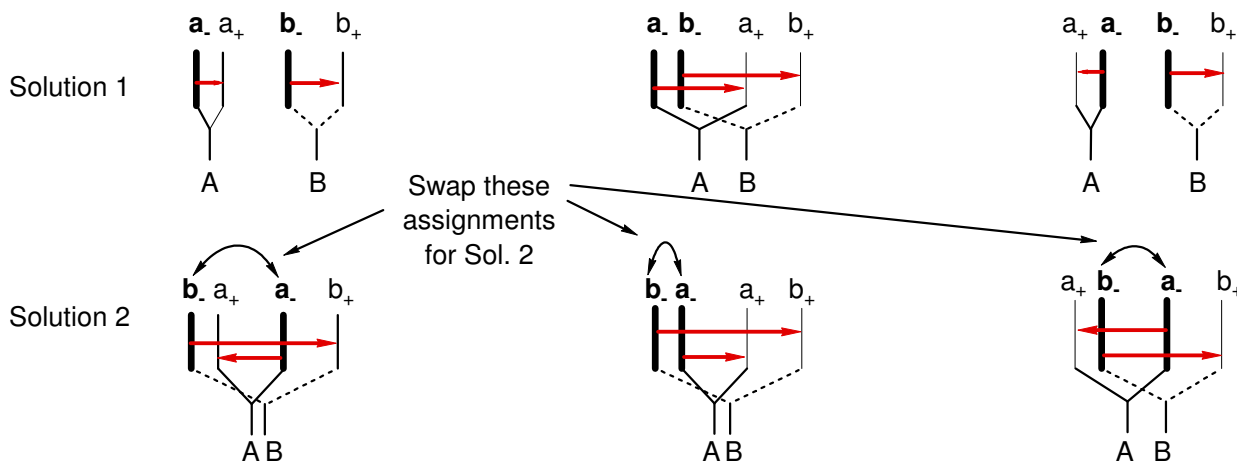


**Distinguishing Between Solutions 1 and 2**. Which solution is the correct one? Several criteria can be used to make the assignment:

1. *Magnitude of the couplings*. Sometimes one of the solutions gives unreasonable couplings. In the example above, if we are dealing with proton-proton couplings, Solution 2 looks dubious because one of the couplings, $J_{BX}$ at 27.6 Hz, is larger than usually observed for $J_{HH}$. A coupling this large is not impossible for a proton spectrum, but rather unlikely.

2. *Signs of coupling constants*. Sometimes the sign of the coupling constants is definitive. If the structure fragment is known, the signs can sometimes be predicted, and may rule out one solution. For example, **all vicinal couplings ($^3J_{HCCH}$) are positive**, geminal couplings ($^2J_{HCH}$) at sp³ carbons are usually negative. A common structure fragment which gives **ABX** patterns is $CH_X$-$CH_AH_B$. Here both $J_{AX}$ and $J_{BX}$ must have the same sign. On the other hand, if the pattern is $CH_A$-$CH_BH_X$ (a much less common situation) then the signs must be different. Note, however, that if you misidentified the **ab** subquartets, then the signs of the coupling constants you calculated may be wrong.

3. *Analysis of the X-Part*. It is important to note that *all* lines have identical positions in both Solutions 1 and 2. The intensities of the **AB** part are also identical for both solutions. However, the *intensities* of the lines in the **X**-part are always different, and this is the most reliable and general way to identify the correct solution.

For the vast majority of **ABX** patterns encountered in organic molecules, Solution 1 is correct. Solution 2 spectra are found when **A** and **B** are close in chemical shift and the size of $J_{AX}$ and $J_{BX}$ are very different, and especially when they have different signs.

**Checking your solution arithmetic.** There are a couple of checks you can run to make sure that there has not been a calculation error:

1. The difference in the centers of the two **ab** quartets should be half the average of $J_{AX}$ and $J_{BX}$:

$$| c_+ - c_- | = 1/2[J_{AX} + J_{BX}]$$

2. The average of the two centers should be equal to the average of the two chemical shifts:

$$1/2 | c_+ + c_- | = 1/2 | v_A + v_B |$$

**Analysis of the X-Part of ABX Patterns**.  The **X** part of an **ABX** pattern is maximally a centrosymmetric 6-line pattern. However, in many cases it closely resembles a doublet of doublets, and it is often treated as such. However, the couplings obtained are only approximate. The errors become larger when $J_{AX}$ and $J_{BX}$ differ greatly in size, and especially if they have different signs. The sum of $J_{AX} + J_{BX}$ will be correct, but the individual values will be incorrect, with the errors increasingl as $v_{AB}$ becomes smaller.  The values of $J_{AX}$ and $J_{BX}$ will be completely wrong if we are dealing with a Solution 2 pattern.

The **X**-part consists of 6 lines, of which only four are usually visible.  The two additional lines are often weak, but can be seen in Solution 2 patterns for which $v_A$ and $v_B$ are close together, and the X-part is consequently significantly distorted.  The lines are numbered as follows: the two most intense are 9 and 12, they are separated by $J_{AX} + J_{BX}$.  The inner pair of the remaining lines are 10 and 11, their separation is $2D_+ - 2D_-$.  The outer lines (often invisible) are 14 and 15, separated by $2D_+ + 2D_-$.  Line 13 has intensity of zero.  These line assignments are not always straightforward: sometimes lines 10 and 11 are on top of each other, resulting in a triplet-like pattern, sometimes 10 and 11 are very close to 9 and 12, leaving just a doublet.

| Solution 1 | Solution 2 |
| --- | --- |



Definition of $2D_+$ and $2D_-$
AB part
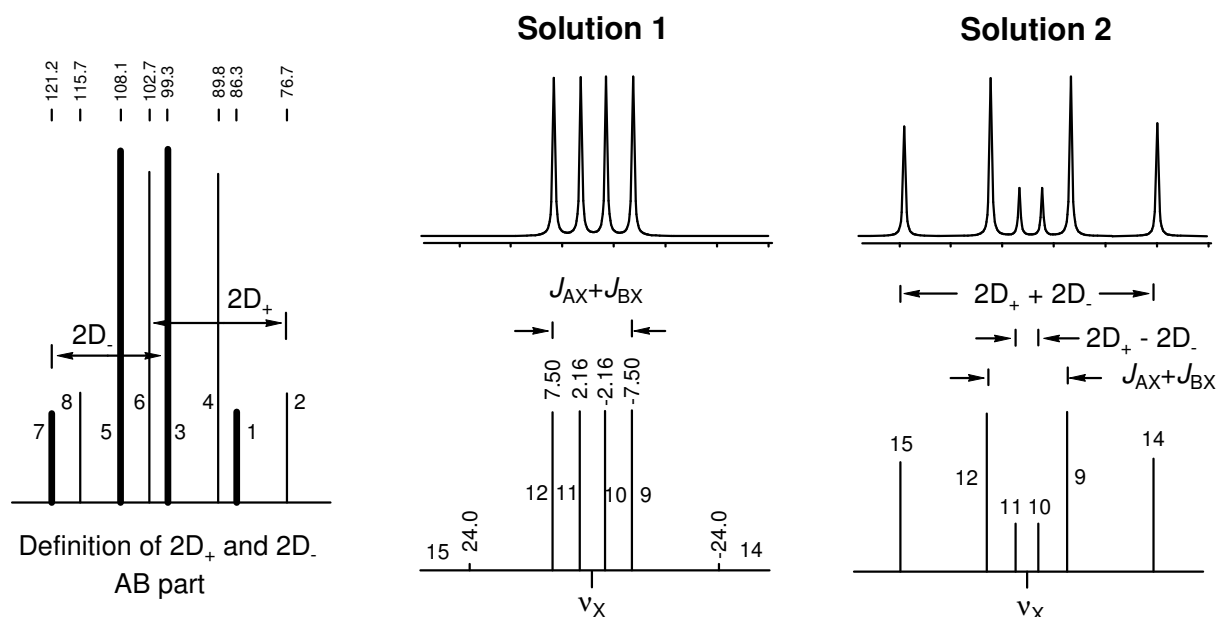
To carry out an intensity calculation we define lines 9 and 12 to have intensity 1 ($i_9 = i_{12} = 1.0$), and proceed as outlined below:

### Solution 1

$$\Phi_{1+} = 0.5 \arcsin(J_{AB}/2D_+)$$
$$= 0.5 \arcsin(13.0/26.0) = 15.0$$
$$\Phi_{1-} = 0.5 \arcsin(J_{AB}/2D_-)$$
$$= 0.5 \arcsin(13.0/21.9) = 18.2$$
$$i_{10} = i_{11} = \cos^2(\Phi_{1+} - \Phi_{1-})$$
$$= \cos^2(15.0 - 18.2) = 0.997$$
$$i_{14} = i_{15} = \sin^2(\Phi_{1+} - \Phi_{1-})$$
$$= \sin^2(15.0 - 18.2) = 0.003$$

### Solution 2

$$\Phi_{2+} = \Phi_{1+}$$
$$= 15.0$$
$$\Phi_{2-} = 90 - \Phi_{1-}$$
$$= 90 - 18.2 = 71.8$$
$$i_{10} = i_{11} = \cos^2(\Phi_{2+} - \Phi_{2-})$$
$$= \cos^2(15.0 - 71.8) = 0.30$$
$$i_{14} = i_{15} = \sin^2(\Phi_{2+} - \Phi_{2-})$$
$$= \sin^2(15.0 - 71.8) = 0.70$$

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

Below is another complete worked example of an **ABX** pattern solution.  The "eyeball method" is the one described in the previous pages, the "formula method" is the one commonly presented in NMR books.  We recommend the "eyeball" method" because it follows the actual coupling tree in a systematic manner, whereas the "formula method" extracts the information in a mathematically correct but non-intuitive fashion.  Both will give identical answers.

# Solving an ABX pattern - Summary

1. Pick two quartets in the **AB** part. The quartet with the largest effective chemical shift is the + quartet, the other the - quartet, i.e. $\delta_+ > \delta_-$; $D_+ > D_-$; $ab_+$: [2], [4], [6], [8]; $ab_-$: [1], [3], [5], [7].

2. Solve the AB quartets: $J_{AB} = [8] - [6] = [4] - [2] = [7] - [5] = [3] - [1] = 11.2$ Hz

$\Delta\nu_{ab+} = \delta_+ = \sqrt{([8]-[2])([6]-[4])} = 12.2$ Hz;     $\Delta\nu_{ab-} = \delta_+ = \sqrt{[7]-[1])([5]-[3])} = 10.4$ Hz

$c_+ = ([6]+[4])/2 = 221.5$                $c_- = ([5]+[3])/2 = 215.2$

$2D_+ = [8]-[4] = 16.6$                $2D_- = [5]-[1] = 15.2$

Choose one method of doing the calculations. The "eyeball" method on the left, which was described on the previous pages, or the "formula" method on the right, in which no attempt is made to follow the development of the pattern but the equations governing the line positions are solved directly.

3e. Calculate the line positions (solve $ab_+$, $ab_-$)

Solve $ab_+$

$c_+ \pm \delta_+/2 = 221.5 \pm 12.2/2$

$\nu_{a+}, \nu_{b+} = 227.5, 215.4$
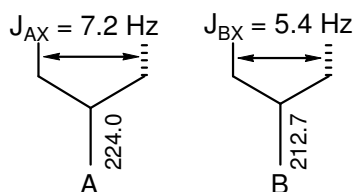
Solve $ab_-$

$c_- \pm \delta_-/2 = 215.2 \pm 10.4/2$

$\nu_{a-}, \nu_{b-} = 220.4, 210.0$

We don't know at this point which line is **a** and which line is **b**

4e. The two solutions for the **AB** part are obtained by pairing up one each of a $\delta_+$ and a $\delta_-$ line, i.e. each $ab_+$, $ab_-$ is half **A** and half **B**, but don't know which. Thus:

Solution 1

$\nu_A = \dfrac{227.6 + 220.4}{2}$     $\nu_B = \dfrac{215.4 + 210.0}{2}$

$= 224.0$ Hz          $= 212.7$ Hz

$J_{AX} = 7.2$ Hz   $J_{BX} = 5.4$ Hz



A    B

Solution 2

$\nu_A = \dfrac{227.6 + 210.0}{2}$     $\nu_B = \dfrac{220.4 + 215.4}{2}$

$= 218.8$ Hz          $= 217.9$ Hz

$J_{AX} = 17.6$ Hz   $J_{BX} = -5.0$ Hz



A    B

*Reich, U.Wisc. Chem. 605*                5-HMR-12.10                ABX
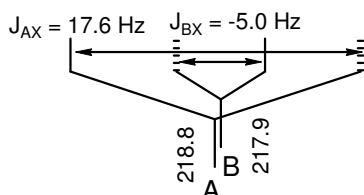
3f. Calculate

$\delta_+ + \delta_- = 12.2 + 10.4 = 22.6$

$\delta_+ - \delta_- = 12.2 - 10.4 = 1.8$

$c_+ + c_- = 436.7$

$c_+ - c_- = 6.3$

4f. Solution 1

★ $\nu_A + \nu_B = c_+ + c_- = 436.7$

$\nu_A - \nu_B = 1/2(\delta_+ + \delta_-) = 11.3$

★ $|J_{AX} + J_{BX}| = 2(c_+ - c_-) = 12.6$

$|J_{AX} - J_{BX}| = \delta_+ - \delta_- = 1.8$

Add and subtract each pair of equations:

$\nu_A = \dfrac{436.7 + 11.3}{2}$     $\nu_B = \dfrac{436.7 - 11.3}{2}$

$= 224.0$ Hz          $= 212.7$ Hz

$J_{AX} = \dfrac{12.6 + 1.8}{2}$     $J_{BX} = \dfrac{12.6-1.8}{2}$

$= 7.2$ Hz          $= 5.4$ Hz

Solution 2

★ $\nu_A + \nu_B = c_+ + c_- = 436.7$

$\nu_A - \nu_B = 1/2(\delta_+ - \delta_-) = 0.9$

★ $|J_{AX} + J_{BX}| = 2(c_+ - c_-) = 12.6$

$|J_{AX} - J_{BX}| = \delta_+ + \delta_- = 22.6$

Add and subtract each pair of equations:

$\nu_A = \dfrac{436.7 + 0.9}{2}$     $\nu_B = \dfrac{436.7 - 0.9}{2}$

$= 218.8$ Hz          $= 217.9$ Hz

$J_{AX} = \dfrac{12.6 + 22.6}{2}$     $J_{BX} = \dfrac{12.6-22.6}{2}$

$= 17.6$ Hz          $= -5.0$ Hz

★ Same for both solutions

## 5. Analyzing the **X** Part

Solution 1 and Solution 2 are defined such that Solution 1 has the larger $v_A - v_B$ value (i.e. the larger chemical shift difference between the **A** and **B** nuclei). Hence Solution 1 always corresponds to the one with the least distorted **X** part. To properly identify the correct solution in ambiguous cases it is necessary to do an intensity calculation. The six **X** lines are numbered as follows: the two most intense are 9 and 12, they are separated by $J_{AX} + J_{BX}$. The inner pair of lines are 10 and 11, their separation is $2D_+ - 2D_-$. The outer pair of lines (often invisible) are 14 and 15, separated by $2D_+ + 2D_-$. Line 13 has intensity 0.

Define the intensity of lines 9 and 12 = 1.0, and calculate the relative intensity of lines 10 and 14. For this example Solution 1 has a fairly normal appearance close to a dd, whereas Solution 2 has all 6 lines clearly visible.

Solution 1

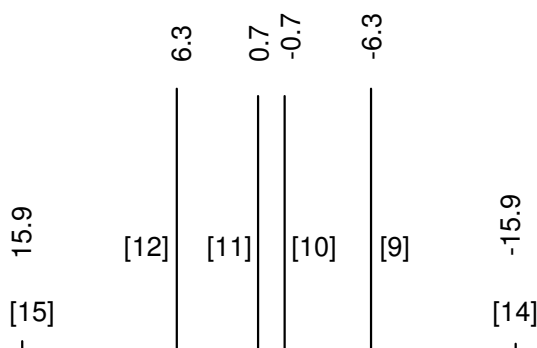$$\Phi_{1+} = \frac{1}{2}\arcsin\left(\frac{J_{AB}}{2D_+}\right)$$

$$= \frac{1}{2}\arcsin\left(\frac{11.2}{16.6}\right) = 21.2\,°$$

$$\Phi_{1-} = \frac{1}{2}\arcsin\left(\frac{J_{AB}}{2D_-}\right)$$

$$= \frac{1}{2}\arcsin\left(\frac{11.2}{15.2}\right) = 23.7\,°$$

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

$$= \cos^2(21.2 - 23.7) = 0.995$$

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

$$= \sin^2(21.2 - 23.7) = 0.0019$$

Solution 2

$$\Phi_{2+} = \Phi_{1+} = 21.2\,°$$

$$\Phi_{2-} = 90 - \Phi_{1-} = 90 - 23.7 = 66.3\,°$$

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

$$= \cos^2(21.2 - 66.3) = 0.498$$

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

$$= \sin^2(21.2 - 66.3) = 0.502$$

# A Simple ABX Pattern as $\nu_{AB}$ is Changed



$\nu_{AB}$ = 52.00 Hz

$J_{BX}$

$J_{AB}$

$J_{AB}$ = -11.20
$J_{AX}$ = 7.20
$J_{BX}$ = 5.40

Vary $\nu_{AB}$

$J_{AX}$

$J_{AB}$

B

A

$\nu_{AB}$ = 32.00

$\nu_{AB}$ = 22.00

$\nu_{AB}$ = 12.00

$\nu_{AB}$ = 5.00

$\nu_{AB}$ = 3.00

40    30    20    10    0    -10    -20    -30    -40

Hz

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

$J_{AB}$ = 13 Hz
$J_{AX}$ = 10 Hz

$J_{BX}$ = 5 Hz  ←        →  $J_{BX}$ = -5 Hz

$\nu_A$ = 70 Hz
$\nu_B$ = 130 Hz
$\Delta\nu_{AB}$ = 60 Hz

1.0            1.0

$\nu_A$ = 85 Hz
$\nu_B$ = 115 Hz
$\Delta\nu_{AB}$ = 30 Hz

1.0            1.0

$\nu_A$ = 90 Hz
$\nu_B$ = 110 Hz
$\Delta\nu_{AB}$ = 20 Hz

1.0            1.0

Here one of the ab
quartets has collapsed
to a singlet

$\nu_A$ = 95 Hz
$\nu_B$ = 105 Hz
$\Delta\nu_{AB}$ = 10 Hz

1.0            1.0

# ABX with Accidental Coincidences



ν_AB = 18
J_AB = 11.20
J_AX = 7.20
J_BX = 5.40

Normal

**AB**

**X**

X

A

B

ν_AB = 13.2
J_AB = 11.20
J_AX = 7.20
J_BX = 5.40

Middle two **AB** lines accidentally
superimposed

X

A

B

ν_AB = 12
J_AB = 11.20
J_AX = 7.20
J_BX = 5.40

Here the middle two lines have
moved past each other

X

A

B

ν_AB = 3
J_AB = 11.20
J_AX = 7.20
J_BX = 5.40

Both **ab** quartets are collapsing
to singlets, one a little ahead of
the other

X

A B

# ABX with Accidental Coincidences

$\nu_{AB} = 3$
$J_{AB} = 10.2$
$J_{AX} = 5.0$
$J_{BX} = -2.0$    **X**

One of the **ab** quartets has
collapsed to a singlet

**AB**

**Solution 1 = Solution 2**

$\nu_{AB} = 0.5 \cdot (J_{AX} - J_{BX})$

(**ab** quartet + singlet)

X     A B

120   100   80   60   40   20   0
Hz

---

$\nu_{AB} = 4$
$J_{AB} = 2.0$
$J_{AX} = 17.0$
$J_{BX} = 10.0$

**Solution 1 = Solution 2**

$\nu_{AB} = 0.5 \cdot (J_{AX} - J_{BX})$

(**ab** quartet + singlet)

**X**

X     A B

120   100   80   60   40   20   0
Hz

---

$\nu_{AB} = 14$
$J_{AB} = 8.0$
$J_{AX} = 8.0$   **X**
$J_{BX} = 8.0$

Here is an interesting "pathological" **ABX**
pattern. If $J_{AB} = J_{AX} = J_{BX}$ and $\nu_{AB}$ is just
right, the **AB** part **completely** mimics a
pentet

$J_{AB} = J_{AX} = J_{BX}$

(**AB** part is fake pentet)

6.08

4.11     4.03

1.00       1.01

X      A      B

120   100   80   60   40   20   0
Hz

---

$\nu_{AB} = 0$
$J_{AB} = 12.0$
$J_{AX} = 2.0$   **X**
$J_{BX} = 12.0$

**$\nu_{AB} = 0$**

(**X** part is more or less a triplet, even
though $J_{AX}$ and $J_{BX}$ are very different)

X         A B

120   100   80   60   40   20   0
Hz

# ABX of the Vinyl Type

$\nu_B$   $\nu_A$

$J_{AB}$ = 2.50
$J_{AX}$ = 16.80
$J_{BX}$ = 10.00

$\Delta\nu_{AB}$ = 25 Hz

Mimic:

$H_X$   $H_B$

$^tR$   $H_A$

300 MHz NMR

$\Delta\nu_{AB}$ = 10 Hz

$\backslash$
$\nu_A$

The chemical shifts of A and B are often close together if R is a tert-alkyl group. Note the increased size of the extra lines in the X part

$\Delta\nu_{AB}$ = 5 Hz

$|$
$\nu_A$

(AB part is an ab quartet + singlet)

Solution 1 = Solution 2

$\Delta\nu_{AB}$ = 3 Hz

$|$
$\nu_A$

Here we have a Solution 2 situation

$\Delta\nu_{AB}$ = 1 Hz

$|$
$\nu_A$

5.9   5.8   5.7   5.6   5.5   5.4   5.3   5.2   5.1   5.0   4.9   4.8

ppm

# ABX Going to ABC

$\nu_C = 270.00$

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



C

B  A

$\nu_C = 210.00$

C

B  A

$\nu_C = 170.00$

C

B  A

$\nu_C = 120.00$

C

B  A

$\nu_C = 100.00$

C

B  A

$\nu_C = 90.00$

C

B  A

$\nu_C = 80.00$

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)

C  B  A

2.6          2.4          2.2          2.0          1.8
ppm

# ABX Going to A₂X

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



$\Delta\nu_{AB} = 15$

C     B     A

$\Delta\nu_{AB} = 8$

C     B   A

$\Delta\nu_{AB} = 6$

C     B A

$\Delta\nu_{AB} = 4$

C     B A

$\Delta\nu_{AB} = 2$

C     BA

Note the "fake" triplet for C     $\Delta\nu_{AB} = 1$

C     BA

180   160   140   120   100   80   60   40   20   0

Hz

# Sample ABX Spectra

300 MHz $^1$H NMR Spectrum CDCl$_3$
Source: Aldrich Spectra/Reich

OH

Ph $\cdots$ O $\quad$ Ph

H H O

C$_{16}$H$_{16}$O$_3$

Hz
30 20 10 0

10.39

4.45 4.40 4.35

1.97

1.00

3.12

3.2 3.1 3.0 2.9 2.8

7.3 7.2 7.1

5.15 5.10 5.05

10 9 8 7 ppm 5 4 3 2 1 0

---

300 MHz $^1$H NMR spectrum in CDCl$_3$
Source: Aldrich Specral Viewer/Reich

OH $\quad$ O

CF$_3$ $\quad$ OEt

C$_6$H$_9$F$_3$O$_3$

Hz
30 20 10 0

2.7 2.6
ppm

4.5 4.4 4.3 4.2 4.1 4.0
ppm

10 9 8 7 6 5 4 3 2 1 0
ppm

*Reich, U.Wisc. Chem. 605* $\qquad$ 5-HMR-12.19 $\qquad$ ABX

# Sample ABX Spectra

300 MHz $^1$H NMR spectrum in CDCl$_3$
Source: Aldrich Specral Viewer/Reich

C$_4$H$_8$O$_2$

30  20  10  0  Hz

3.0   2.9   2.8   2.7   2.6

3.8   3.7   3.6   3.5

2.14   2.11   1.00   3.00

9   8   7   6   5   4   3   2   1   0   ppm

300 MHz $^1$H NMR spectrum in methanol-d$_4$
Source: Aldrich Specral Viewer/Reich

Me$_3$N$^+$   (CH$_2$)$_{14}$CH$_3$

Cl$^-$

C$_{23}$H$_{48}$ClNO$_2$

30  20  10  0  Hz

5.7   5.6

2.8   2.7   2.4

3.9   3.8   3.7

10   9   8   7   6   5   4   3   2   1   0   ppm

# ABX$_m$Y$_n$Z$_o$ Patterns

In real molecules **AB** patterns that are coupled to more than just one **X** proton appear frequently. There may be several **X** protons (**ABX$_2$**, **ABX$_3$**) or there may be two or more different protons coupled to the **AB** part (**ABXY**, **ABXYZ**). Some part structures illustrate these common types:

| H$_B$ H$_A$ | H$_B$ H$_A$ | H$_B$ H$_A$ | H$_B$ H$_A$ | H$_B$ H$_A$ | H$_B$ H$_A$ |
| AB | ABX | ABXY | ABXY | ABXYZ | ABX$_3$ |
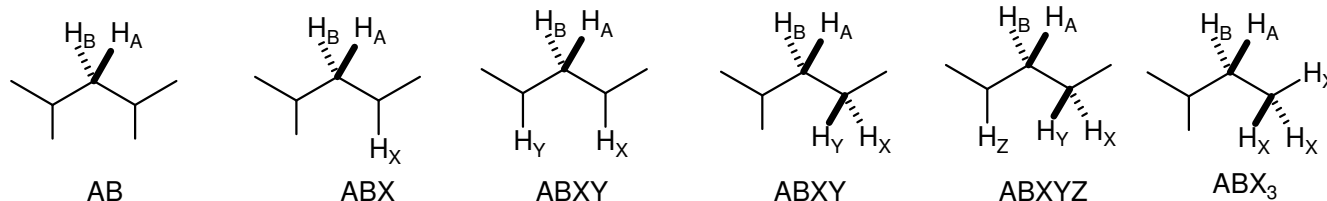
Most such spectra can be at least approximately analyzed in a straightforward fashion using an **AMX**-type approach, by treating the two **A** lines of the parent **AB** quartet as each being split into a dd, ddd, dddd, dt, etc by the **X**, **Y** and **Z** protons. Similarly for the two lines of the **B** part. Fortunately, except in very unusual cases, there is no Solution 1/Solution 2 ambiguity, since the **A** lines and **B** lines can be distinguished because each shares common couplings.

1. Here is an **AB** pattern, and a simple **ABX** pattern derived from it

$J_{AB} = -12.00$

$J_{AX} = 14.0$
$J_{BX} = 6.0$
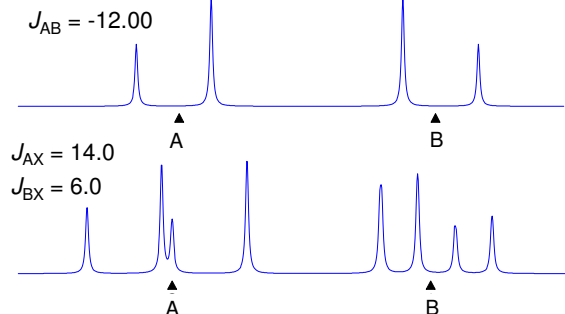
2. Here one additional coupling has been added to both **A** and **B**. Note how the original **A** and **B** lines are now each dd (**ABXY**)

$J_{AX} = 14.0$
$J_{AY} = 4.0$

$J_{BX} = 6.0$
$J_{BY} = 2.0$
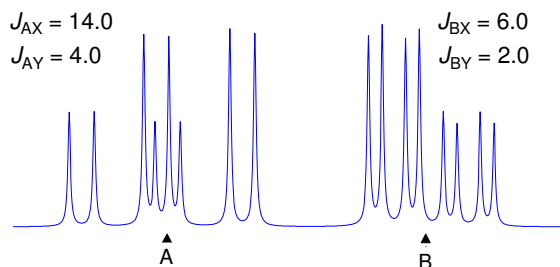
3. Here $J_{AX} \approx J_{AB}$, giving a triplet of doublets on the downfield side

$J_{AX} = 12.0$
$J_{AB} = 12.0$

$J_{BX} = 6.0$
$J_{BY} = 2.0$
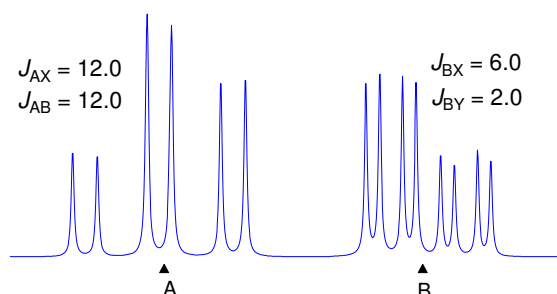
4. Here an aditional coupling has been added to H$_B$, note that each of the original B lines is now a ddd (**ABXYZ**)

$\nu_{AB} = 41$
$J_{AX} = 14.0$
$J_{AY} = 4.0$

$J_{BX} = 6.0$
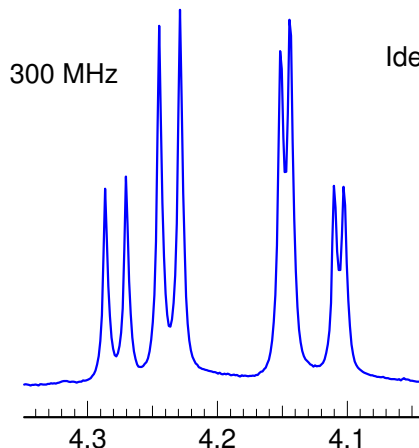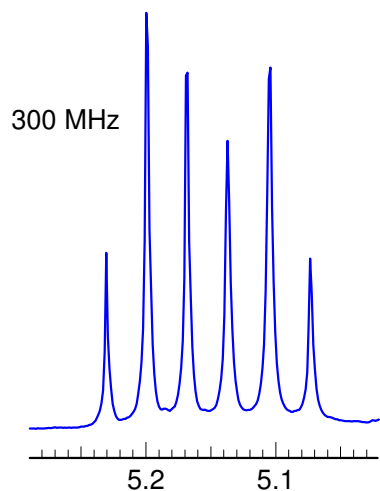$J_{BY} = 2.0$
$J_{BZ} = 1.0$
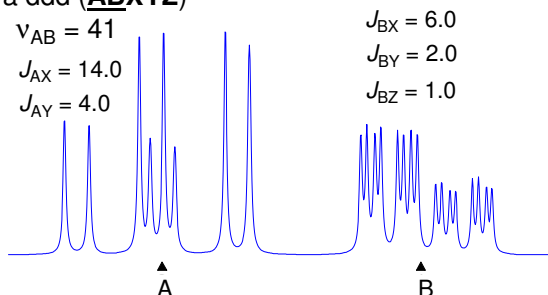
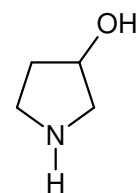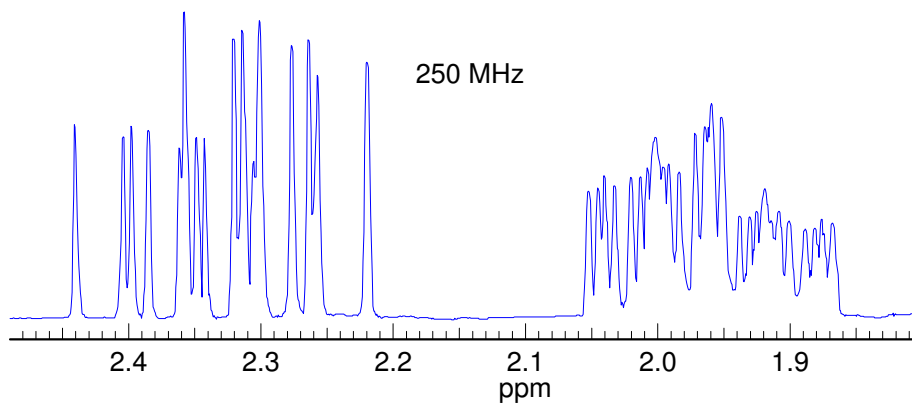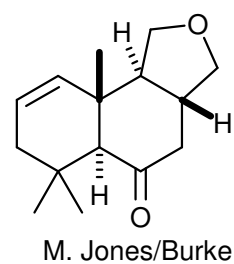5. As we move **A** and **B** closer together, the leaning increases, and some small second order effect are seen
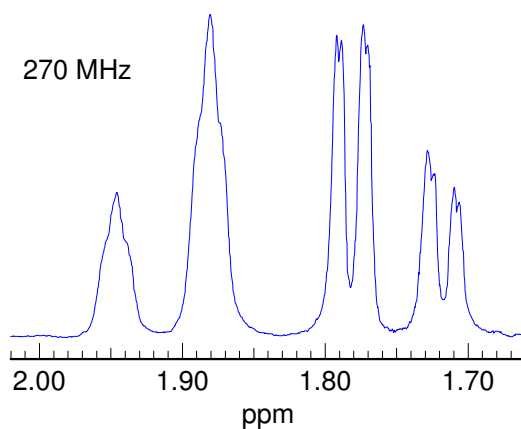
$\nu_{AB} = 30$
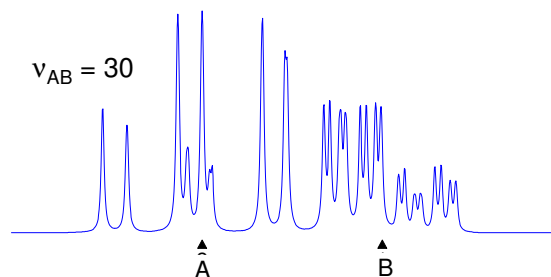
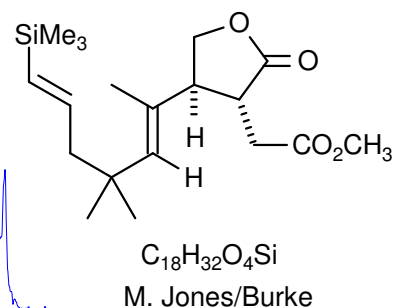6. When $\nu_A$ approaches $J_{AB}$ the spectrum becomes complicated, no meaningful analysis possible by hand

$\nu_{AB} = 11$
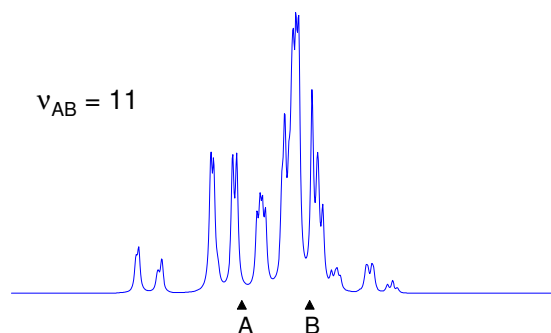
# Examples of <u>AB</u>X$_m$Y$_n$Z$_o$ Patterns

300 MHz

300 MHz

Identify the protons that are shown



5.2    5.1

4.3    4.2    4.1

C- Fry

Ph$_2$P

OMe

O. Daugulis/Vedejs
C$_{19}$H$_{25}$OP

2.3    ppm    2.2    2.1

SiMe$_3$

C$_{18}$H$_{32}$O$_4$Si
M. Jones/Burke

2.70    ppm    2.60    2.50

270 MHz

270 MHz

5.6    5.5    ppm    5.4

2.00    1.90    1.80    1.70
ppm

M. Jones/Burke

250 MHz

2.4    2.3    2.2    2.1    2.0    1.9
ppm

OH
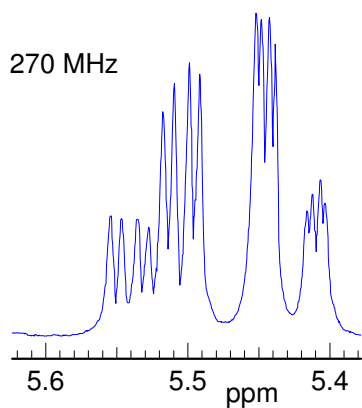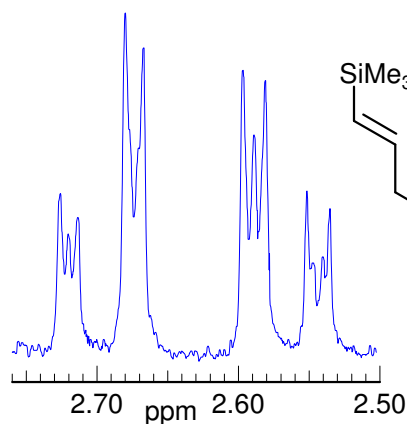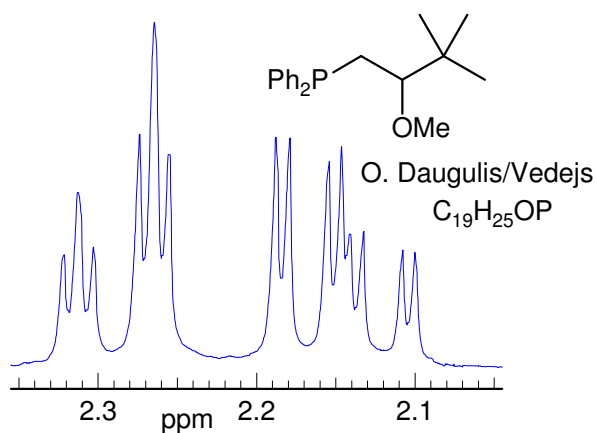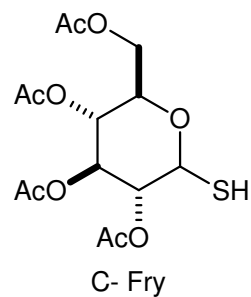
# 5.13 ABX₃ Spectra

**ABX₃** patterns are very common in organic molecules. 1-Substituted-1-alkenes show this pattern. As can be seen in the example of trans-1-propene below, the **AB** part of the pattern is essentially an **AB** quartet, each line of which is split into a quartet by the $^2J$ and $^3J$ coupling to the methyl groups. As is common for most 4-spin systems, when the chemical shift between the two of the protons becomes small (as in cis-1-bromo-1-propene) the spectrum becomes very complicated, and can no longer be analyzed so simply.
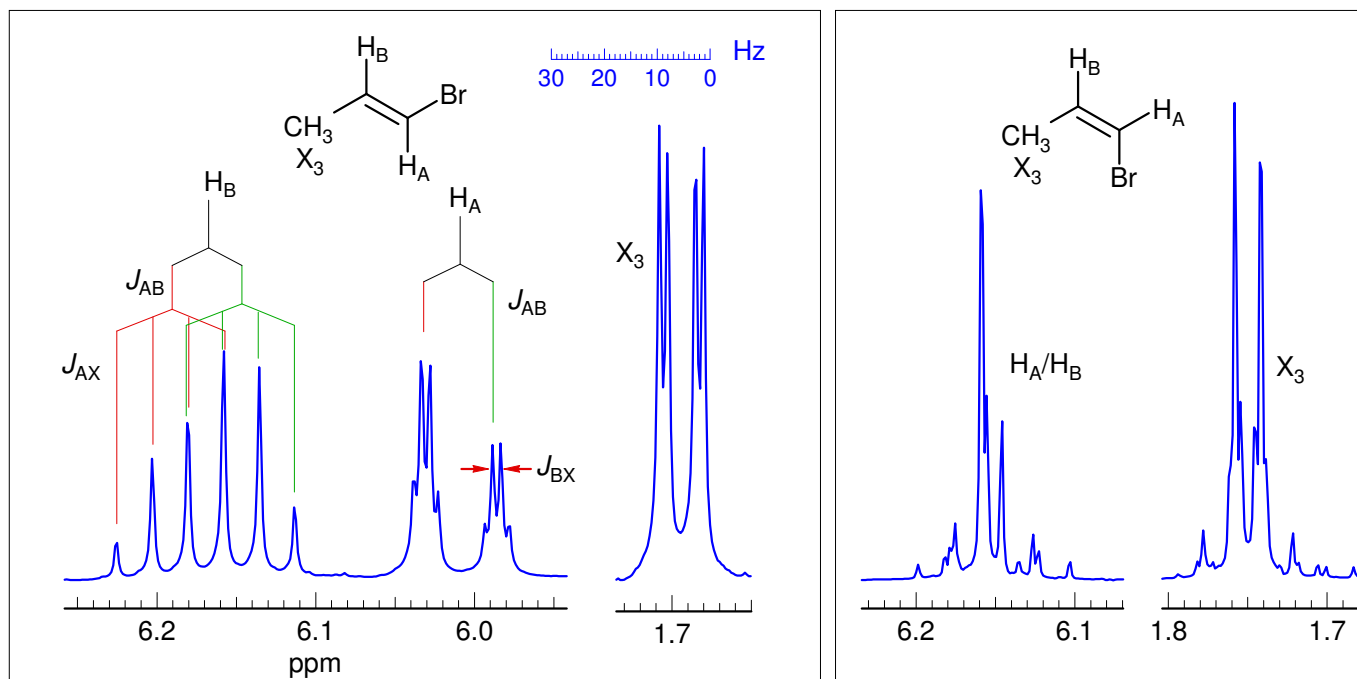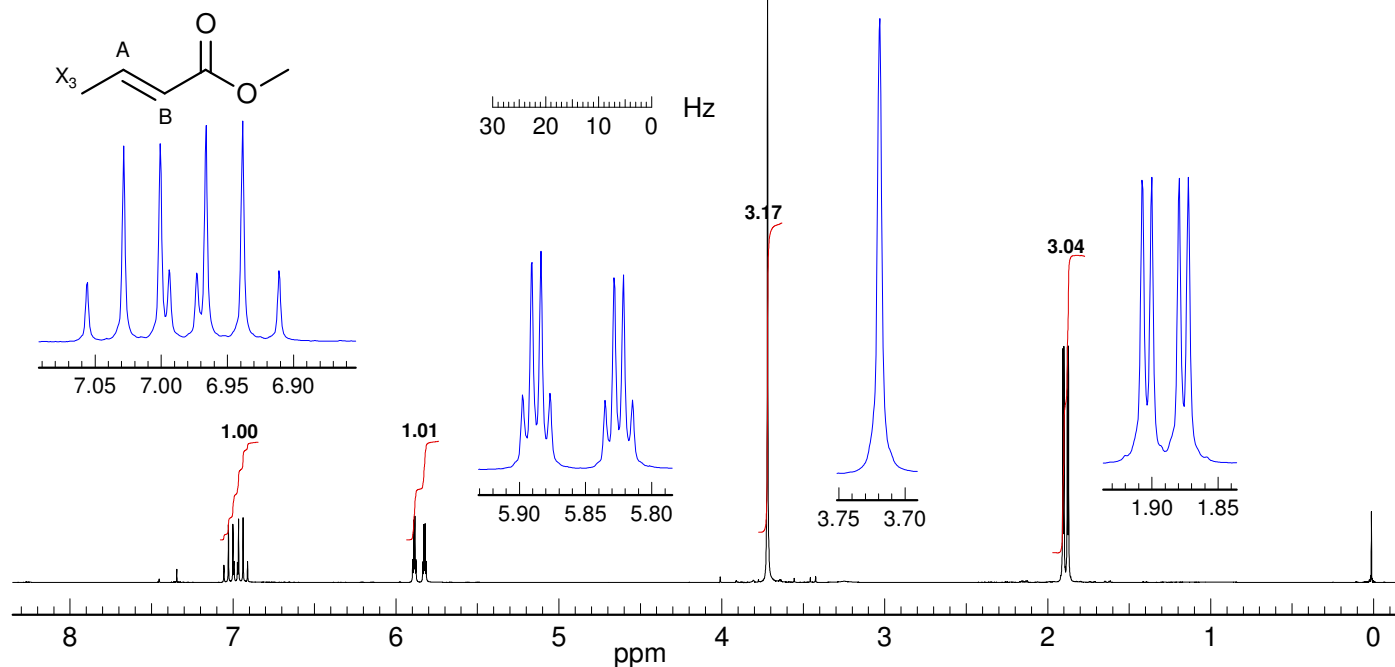


Another sample **ABX₃** spectrum of methyl crotonate is shown below (this one is really AMX₃).

**Problem R-27L** C₅H₈O₂
250 MHz ¹H NMR spectrum in CDCl₃
Source: Adam Fiedler/Reich

Most ethyl groups in chiral molecule will have diastereotopic $CH_2$ protons, and thus form an **ABX$_3$** system. The partial $^1H$ NMR spectrum of 2-ethoxycyclohexanone below illustrates a typical pattern. The **A** and **B** signals are well separated, and can be readily understood and solved as a first order "**AMX$_3$**" pattern.



$^1H$ NMR spectrum in CDCl$_3$
Source: Aldrich NMR Library

C$_8$H$_{14}$O$_2$
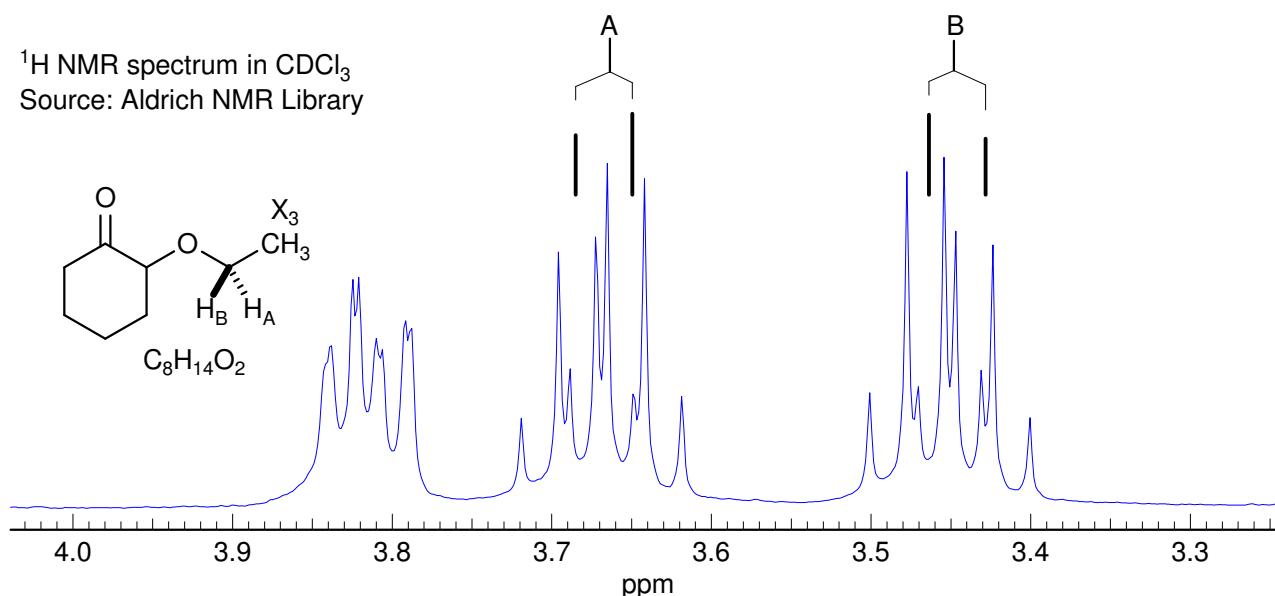
Just as for **ABX** systems, there is an exact solution, in which one first solves the four **AB** quartets, which are present in a 1:3:3:1 ratio (i.e., they represent the subspectra resulting from the four combinations of **X** spins: ααα; ααβ/αβα/βαα; αββ/βαβ/ββα; βββ). The solutions to these **AB** quartets give a 1:3:3:1 quartet for the **A** proton, and another for the **B**. These can then be solved as first order patterns.

Exact Solution of **ABX$_3$**

Approximate Solution: **AMX$_3$**
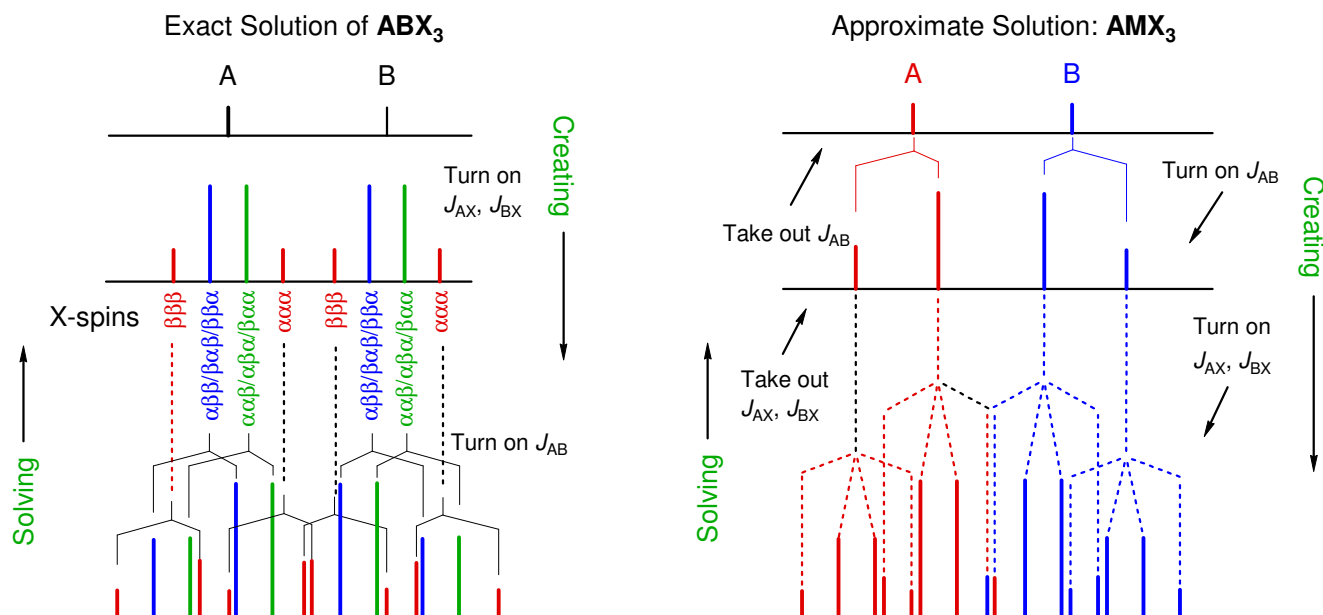


Fortunately, it is rarely necessary to do an exact solution. If $J_{AX} = J_{BX}$ (or very nearly so), which is usually the case, then a first order treatment of the pattern as an "**AMX$_3$**" type is quite accurate. What is done here is to treat the pattern as an **AB** quartet of 1:3:3:1 quartets. In other words, we view the pattern as an **AB** quartet, each line of which is split by the **X$_3$** protons into a 1:3:3:1 quartet. The four 1:3:3:1 quartets will have the normal intensity ratios of an **A**B quartet. To solve, identify the **AB**-quartet of q and then remove the **X** coupling. What remains is an **AB** quartet which can be solved in the usual way. Note that this corresponds exactly to the "**AMX**" solution for **ABX** patterns (see 5-HMR-12.3), in which we treat the pattern as an **AB** quartet, each half of which is split into a doublet by the X nucleus.

The simulated spectra shown mimic **ABX$_3$** patterns (**AB** part) of OCH$_2$CH$_3$ groups in chiral molecules. In these spectra all 16 of the lines are resolved, and recognition of the pattern is relatively easy. In real molecules it is common for several of the lines to be superimposed (especially since $J_{AB}$ is often nearly twice as large as $J_{AX}$), making recognition of this pattern more difficult. In situations where the distereotopic shift is small, the pattern can be mistaken for a quartets of doublets (see the $\nu_{AB}$ = 6 Hz spectrum).

It is not necessary for a molecule to have a center of chirality to show diastereoptopic CH$_2$ groups. Molecules with two ethyl groups attached to a prochiral center can also have **ABX$_3$** patterns, as illustrated in the spectra of the diethoxysilanes below. The left structure has enantiotopic CH$_2$ protons, the right has diastereotopic ones (see Section 5-HMR-8 for the substitution test).



200 MHz
$J_{AB}$ = -11 Hz
$J_{AX} = J_{BX}$ = 7 Hz

$\nu_{AB}$ = 20 Hz

$\nu_{AB}$ = 12 Hz

$\nu_{AB}$ = 6 Hz

$\nu_{AB}$ = 0 Hz
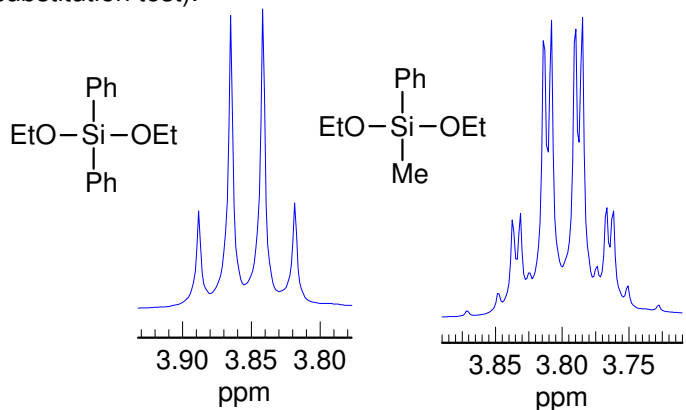
The spectrum of diethyl sulfite below is of historical interest - this type of diastereotopicity was first recognized for this molecule (Finegold, H. *Proc. Chem. Soc.*, **1960**, 283), with the correct explanation and analysis described in a classic paper (Kaplan, F.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 4666), which also reported the first recognition that $^2J$ and $^3J$ at sp$^3$ carbons have different signs. Diethyl acetals of aldehydes or diethyl ketals of unsymmetrical ketones also form **ABX$_3$** patterns.
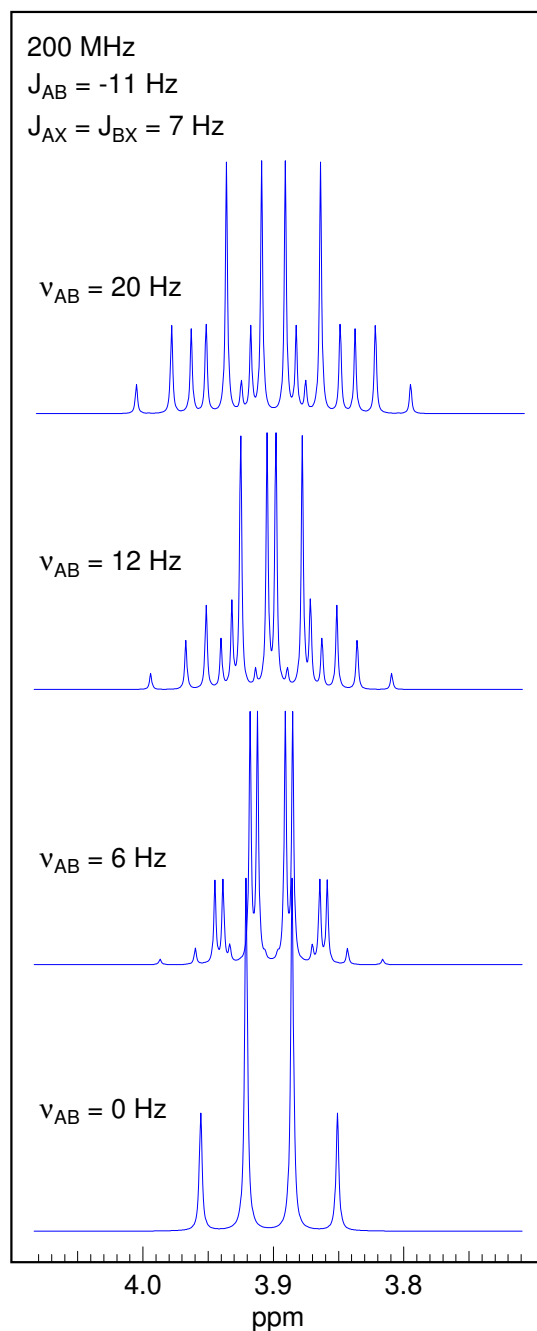
The spectra of dichloroacetaldehyde diethyl acetal illustrate that a molecule which contains diastereotopic protons can give decidedly simpler NMR spectra at low field than at high field. The $CH_2$ group appears as a simple quartet at 90 MHz: the outer lines of the **ABX₃** pattern are too small to see, and the splitting of the inner lines is too small to resolve. At 300 MHz, on the other hand, the $CH_2$ group is much more complex since $H_A$ and $H_B$ of the ethoxy are now far enough apart to give a well-developed **ABX₃** pattern,
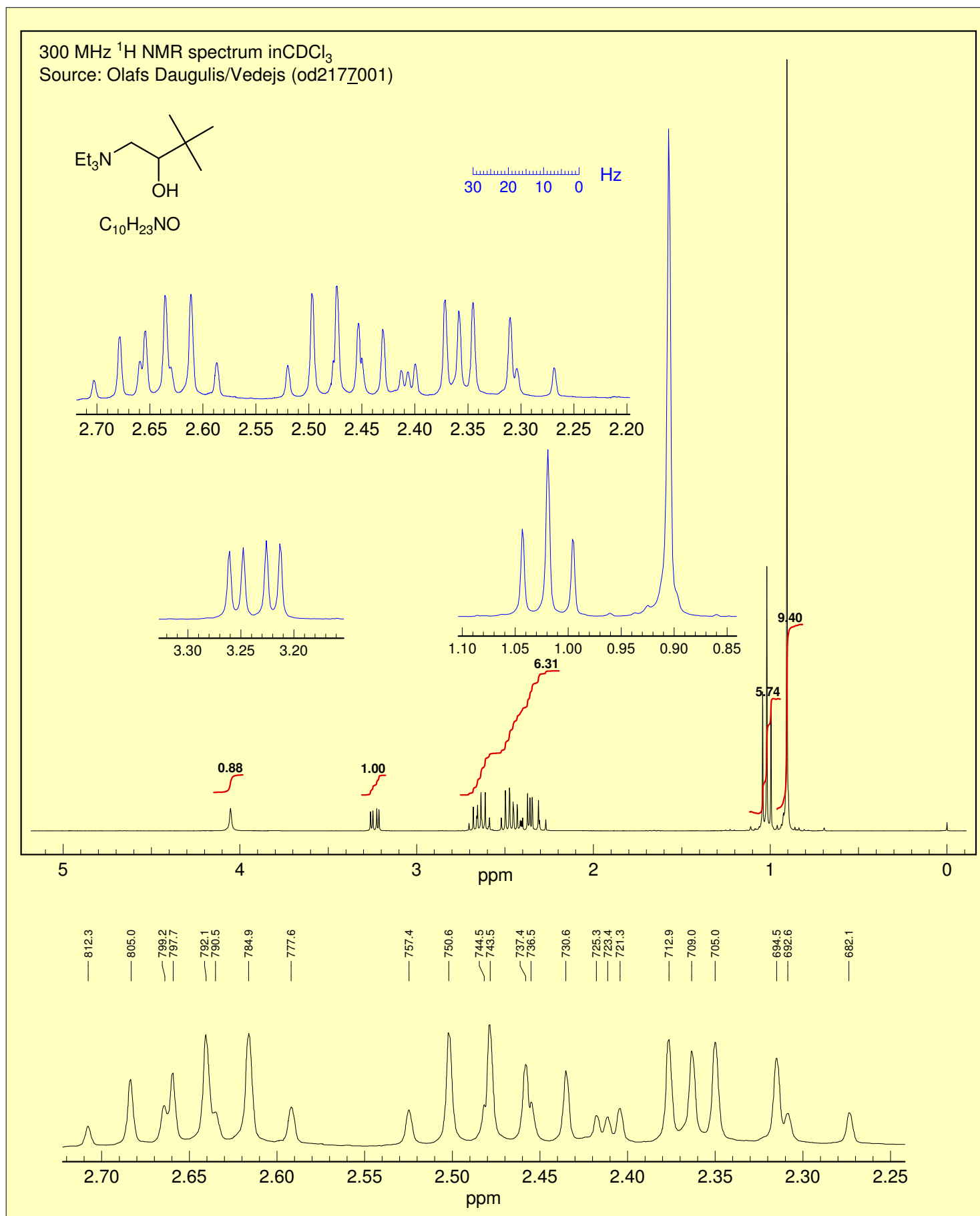
**R-18AG - <span style="color:red">90 MHz</span>**



$C_6H_{12}Cl_2O_2$
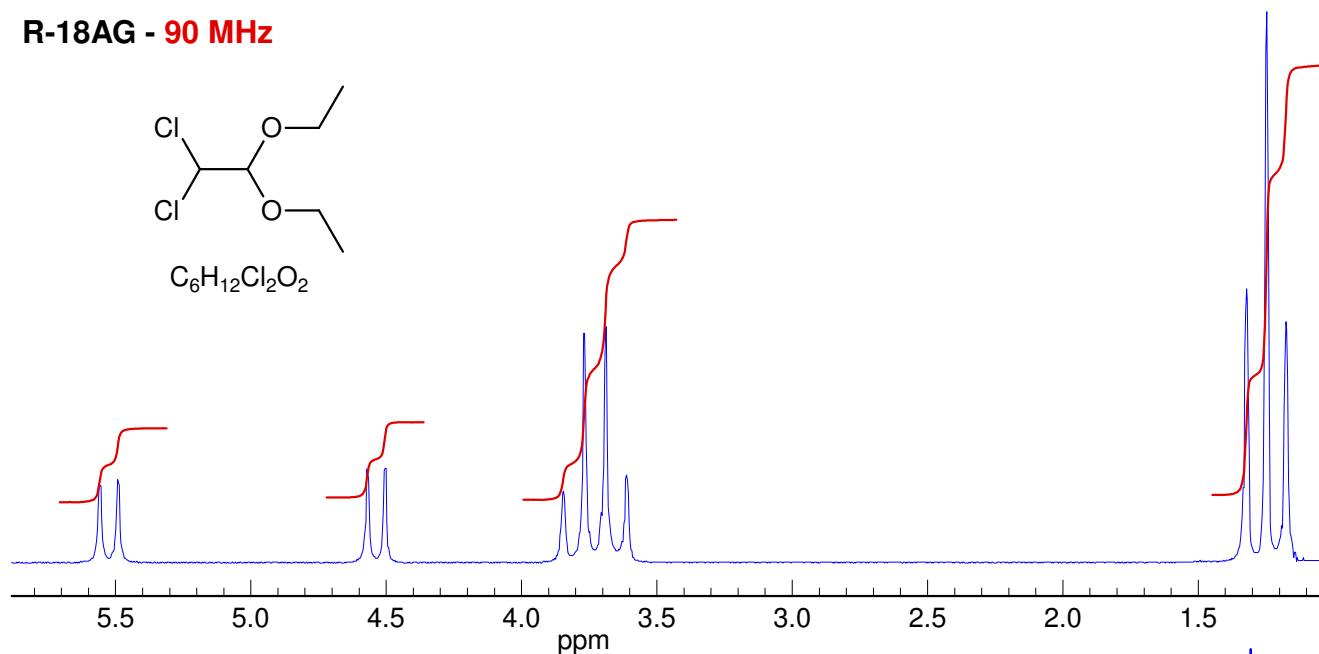
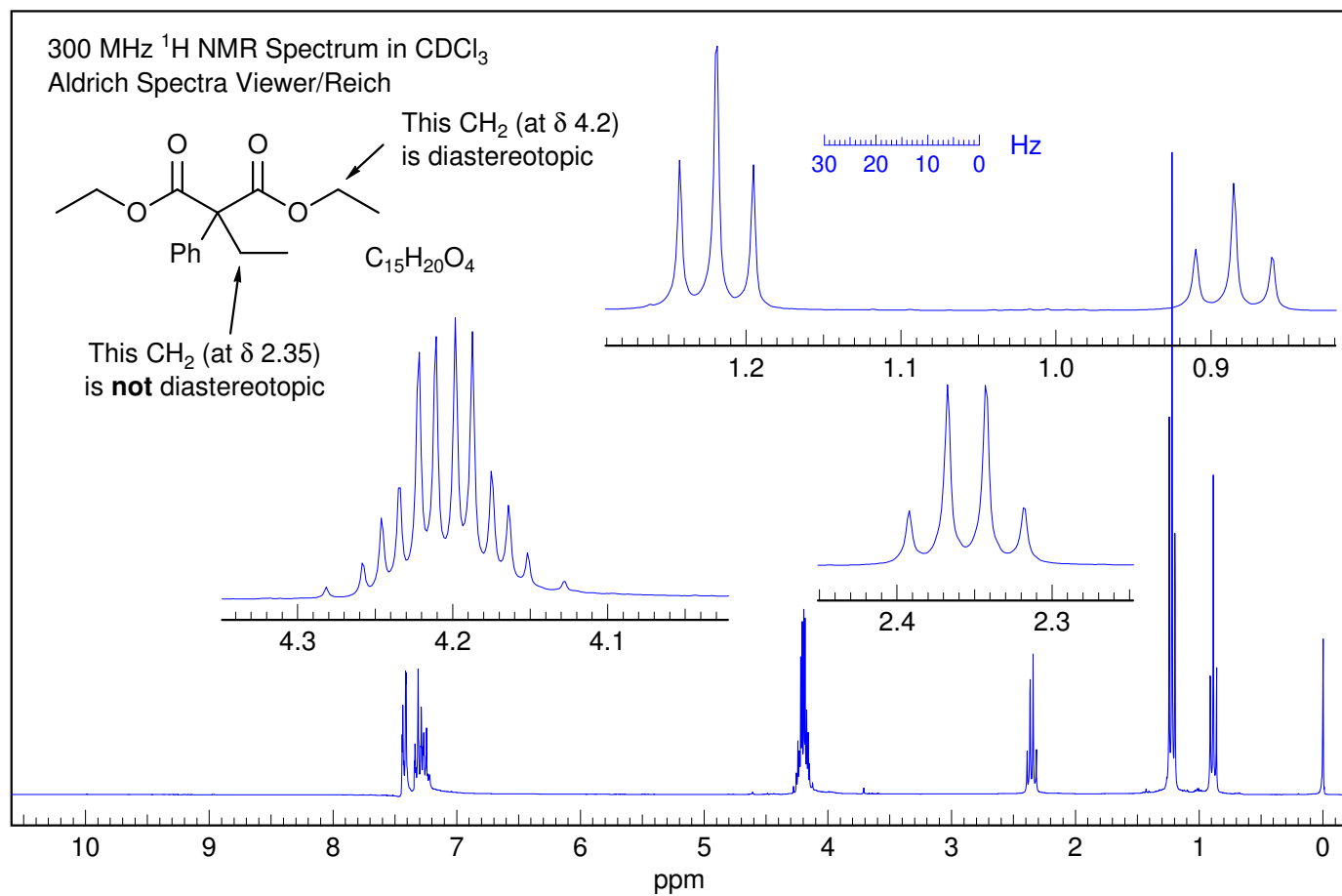**<span style="color:red">300 MHz</span>**

Aldrich Spectra Viewer
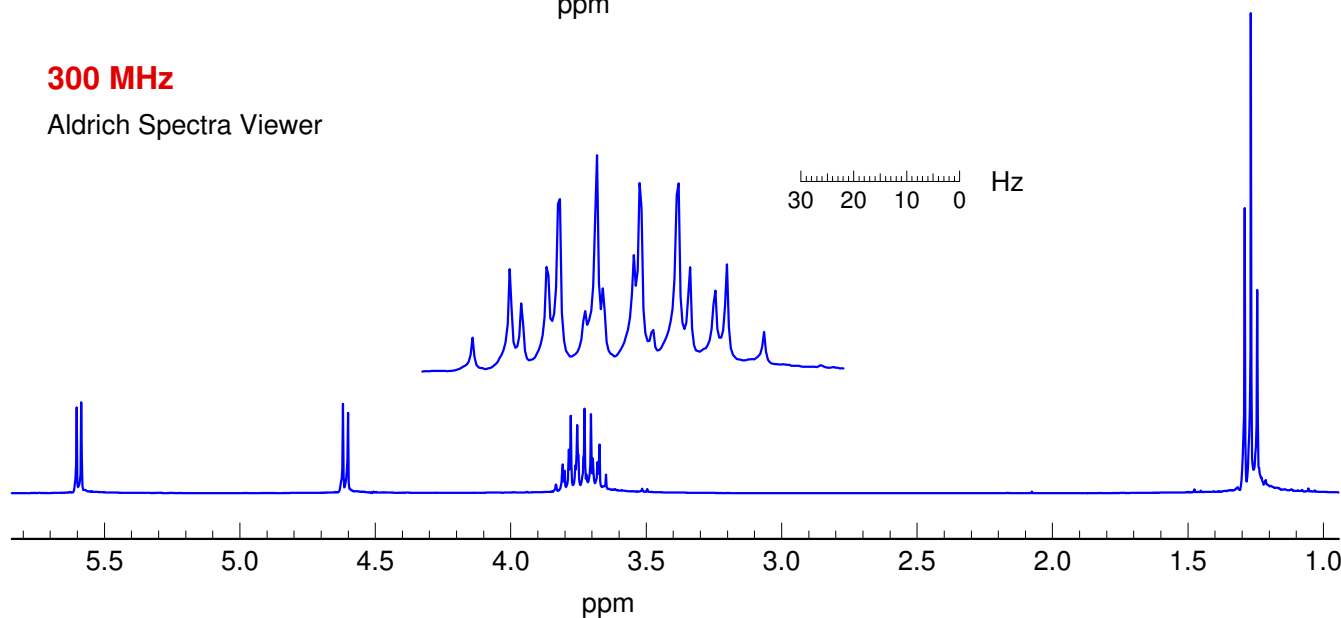


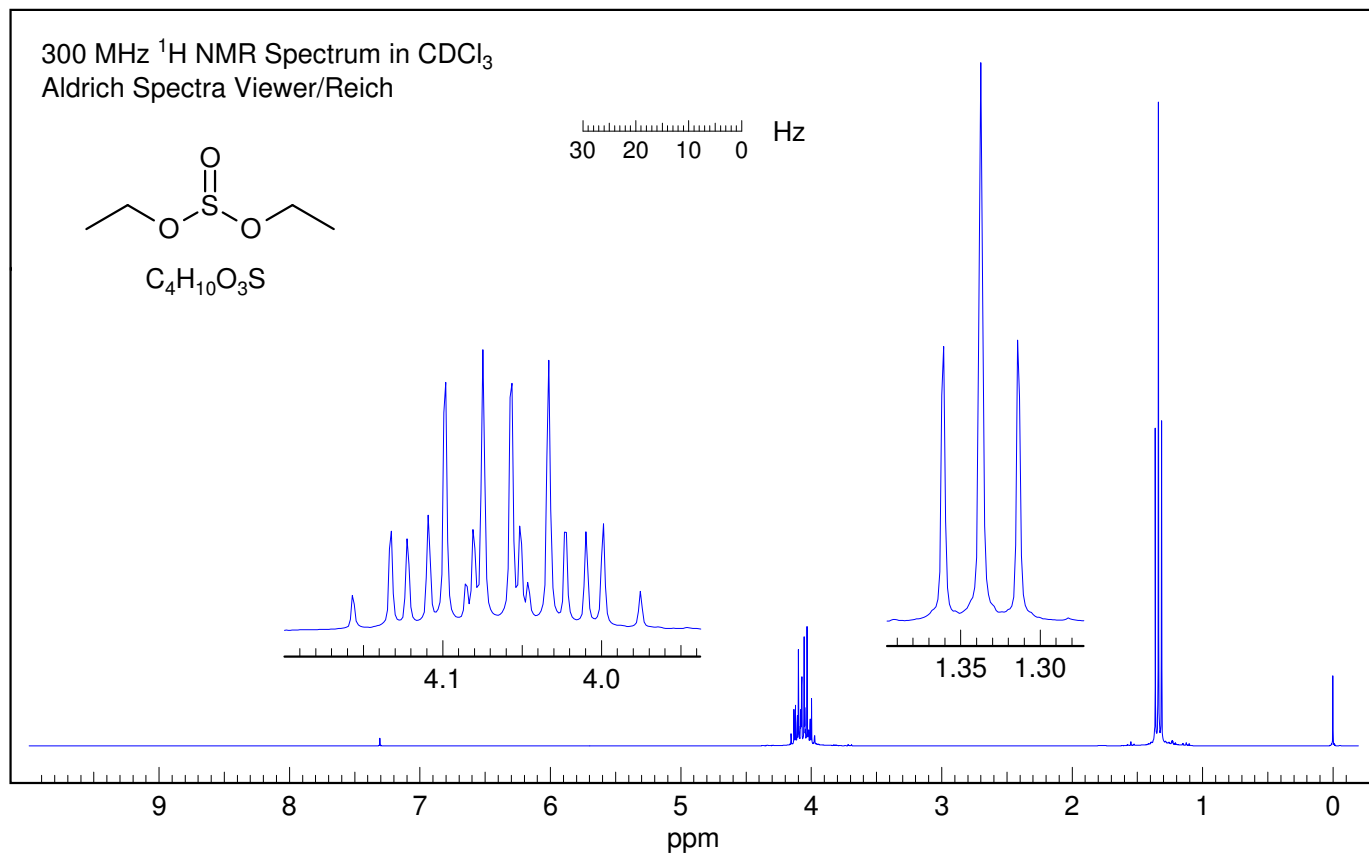**Exercize**: Identify the peaks in the $CH_2$ pattern at 300 MHz.

Exercize: Analyze the spectrum below, determine δ and *J* values

300 MHz $^1$H NMR spectrum inCDCl$_3$
Source: Olafs Daugulis/Vedejs (od2177001)

Et$_3$N

OH

C$_{10}$H$_{23}$NO

Hz
30  20  10  0

2.70  2.65  2.60  2.55  2.50  2.45  2.40  2.35  2.30  2.25  2.20

3.30  3.25  3.20

1.10  1.05  1.00  0.95  0.90  0.85

9.40

5.74

6.31

0.88

1.00

5  4  3  ppm  2  1  0

812.3
805.0
799.2
797.7
792.1
790.5
784.9
777.6
757.4
750.6
744.5
743.5
737.4
736.5
730.6
725.3
723.4
721.3
712.9
709.0
705.0
694.5
692.6
682.1

2.70  2.65  2.60  2.55  2.50  2.45  2.40  2.35  2.30  2.25
ppm

# Sample ABX₃ Spectra

300 MHz ¹H NMR Spectrum in CDCl₃
Aldrich Spectra Viewer/Reich

$C_4H_{10}O_3S$



300 MHz ¹H NMR Spectrum in CDCl₃
Aldrich Spectra Viewer/Reich

This CH₂ (at δ 4.2) is diastereotopic

This CH₂ (at δ 2.35) is **not** diastereotopic

$C_{15}H_{20}O_4$

More ABX₃ patterns:



300 MHz ¹H NMR Spectrum
Aldrich Spectra Viewer

$C_7H_{12}O_4$



300 MHz ¹H NMR Spectrum
Aldrich Spectra Viewer

$C_6H_{12}O_3$
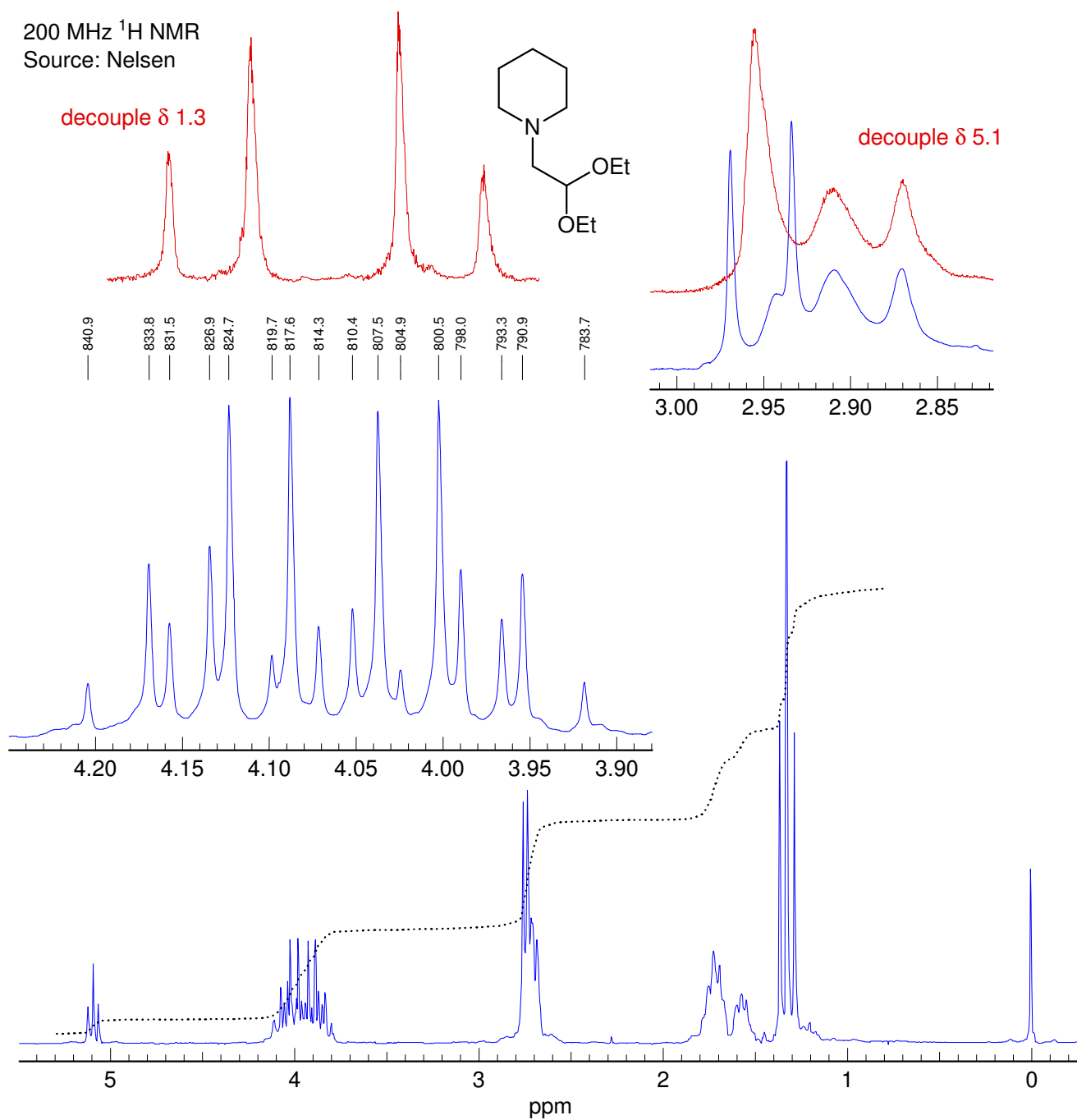
The spectra below provide some details of a typical fully developed **ABX₃** system. If the CH₃ group is decoupled, then we are left with a simple **AB** quartet, exactly analogous to **AMX₃** solution described above.

## Sample ABX₃ Pattern

200 MHz ¹H NMR
Source: Nelsen

decouple δ 1.3

decouple δ 5.1



840.9 | 833.8 | 831.5 | 826.9 | 824.7 | 819.7 | 817.6 | 814.3 | 810.4 | 807.5 | 804.9 | 800.5 | 798.0 | 793.3 | 790.9 | 783.7

# ABMX$_3$ Patterns

Spin system where the CH$_2$ protons of a diastereotopic ethyl group are coupled to another proton (**ABMX$_3$**) can also be readily understood and analyzed by a simple extension of the **ABX$_3$** analysis. The CH$_2$ of the ethyl group is an **AB** quartet, each line of which is split into quartets from coupling to the CH$_3$ protons. The quartets are then split again by coupling to **M**, giving a ddq for each of the CH$_2$ protons. Some structure fragments which give such patterns are shown below. For **2** the **M** nucleus is the spin 1/2 phosphorus. In each case R$^1$ and R$^2$ must be different to make the CH$_2$ group diastereotopic.
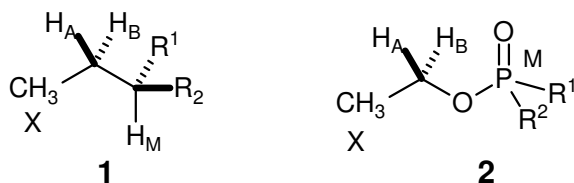


The spectrum of **3** below is of this type. One of the two dq of each proton is shown schematically above the simulation, which is plotted with a narrow line width so all of the lines can be resolved. Note that in this case the coupling of **A** and **B** to the **X$_3$** protons are identical, but **A** and **B** are coupled differently to the **M** proton. The **M** proton in addition also coupled to two others labeled **P** and **Q**.

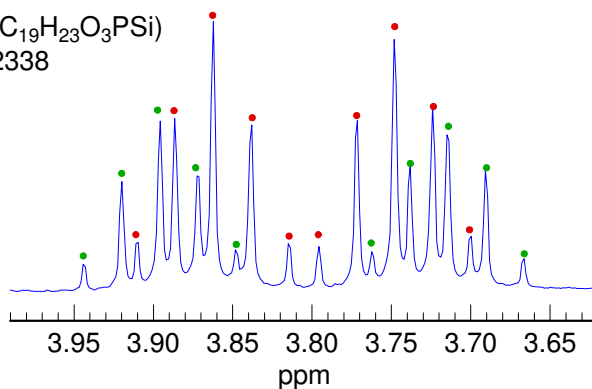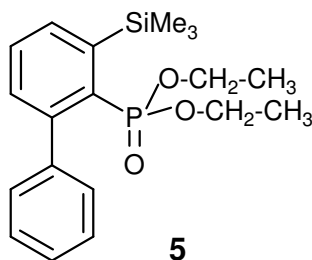300 MHz $^1$H NMR Spectrum in CDCl$_3$
Aldrich Spectra Viewer

$\nu_{AB}$ = 86.0 Hz
$J_{AX}$ = $J_{BX}$ = 7.3
$J_{AB}$ = -13.7
$J_{AM}$ = 9.9
$J_{BM}$ = 4.6
$W_{1/2}$ = 0.30

Simulation
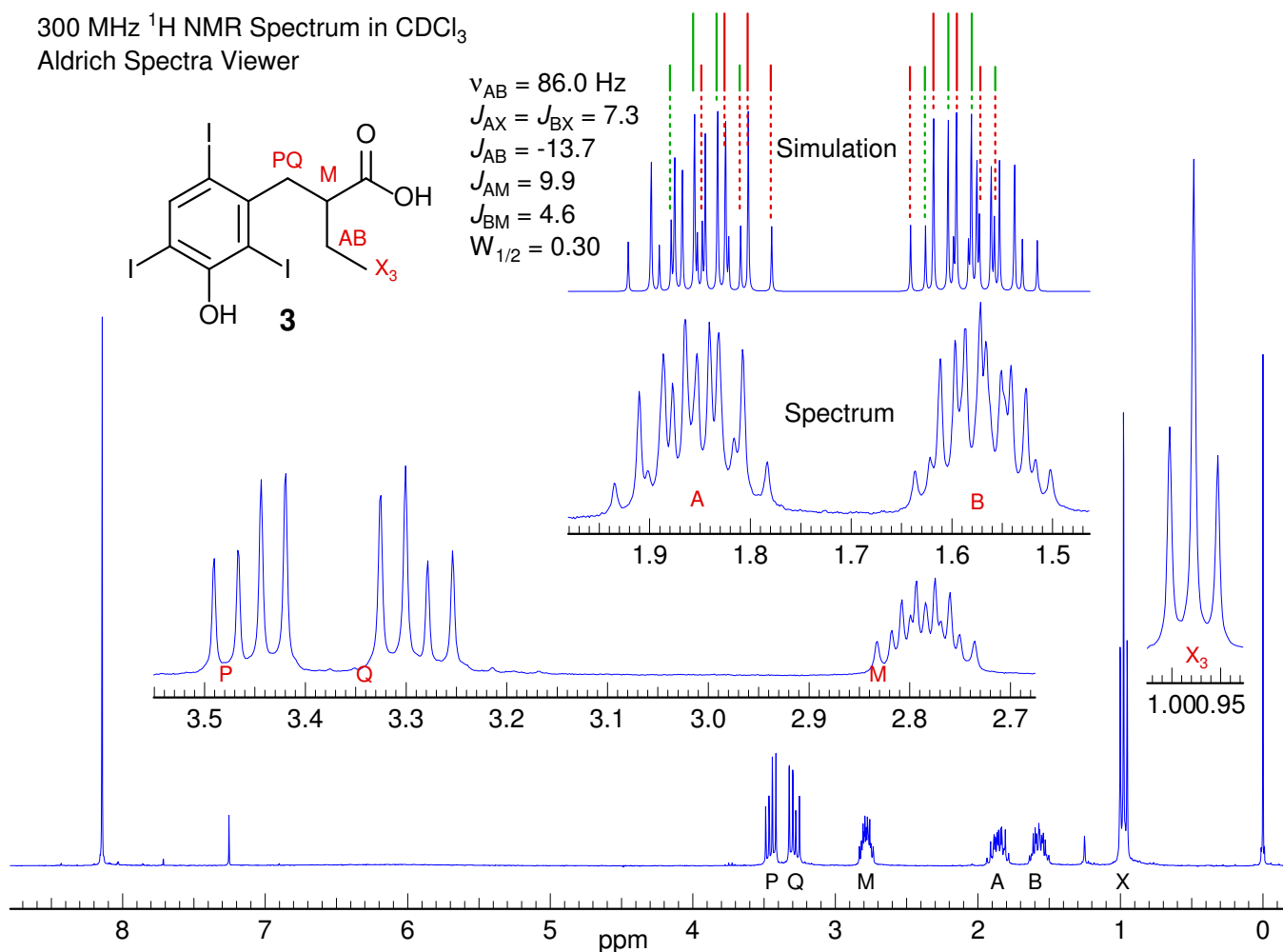
Spectrum

It is fairly common for **ABMX₃** patterns of the CH-CH$_A$H$_B$-CH$_3$ type (**1**) to show nearly equal $J_{AX}$, $J_{BX}$, $J_{AM}$ and $J_{BM}$. In this case the CH$_A$H$_B$ group appears as an **AB** quartet of pentets. The partial NMR spectrum below shows the β CH$_2$ signal of isopropyl 2-methylbutyrate (**4**). The downfield signal is a clean doublet of pentets, the upfield one closer to a ddq.

300 MHz $^1$H NMR Spectrum in CDCl$_3$ (C$_8$H$_{16}$O$_2$)
Aldrich Spectra Viewer
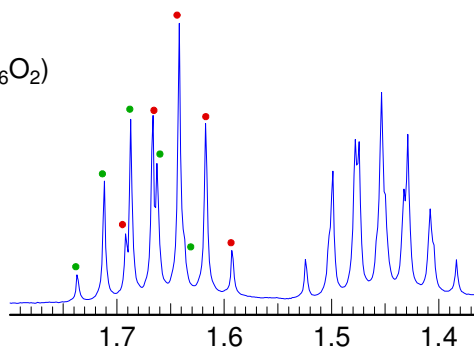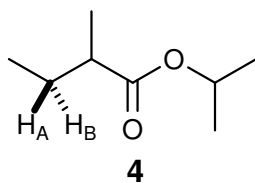


The phosphonate **5** has the diastereotopic OCH$_2$ protons coupled equally to the CH$_3$ group and the phosphorus, so here also a dp is seen for each proton (**AB** quartet of pentets).

300 MHz $^1$H NMR Spectrum in CDCl$_3$ (C$_{19}$H$_{23}$O$_3$PSi)
Olafs Daugulis/Vedejs *JOC* **1998**, *63*, 2338



**Exercise:** Assign the protons and completely solve the pattern below,

300 MHz $^1$H NMR Spectrum in CDCl$_3$
Olafs Daugulis/Vedejs (OD.070) *JOC* **1998**, *63*, 2338
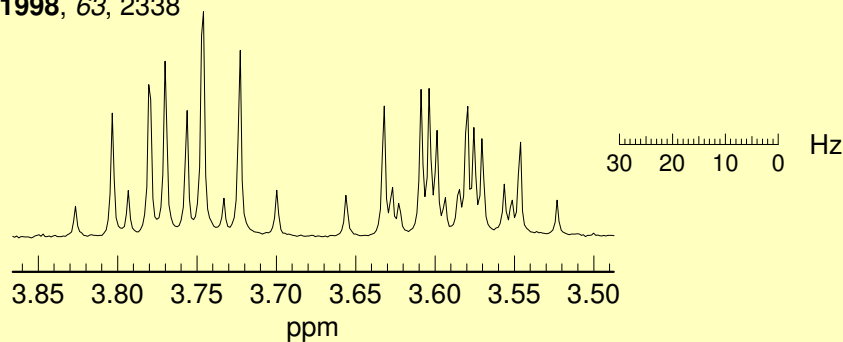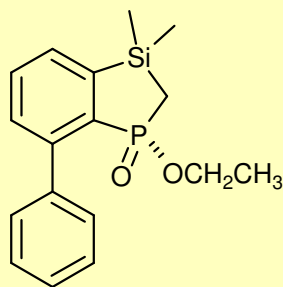
# 5.14   A₂X₂ and AA'XX'  Spectra

In **A₂X₂** and **A₂B₂** patterns the two **A** nuclei and the two **X** (B) nuclei are magnetically equivalent: they have t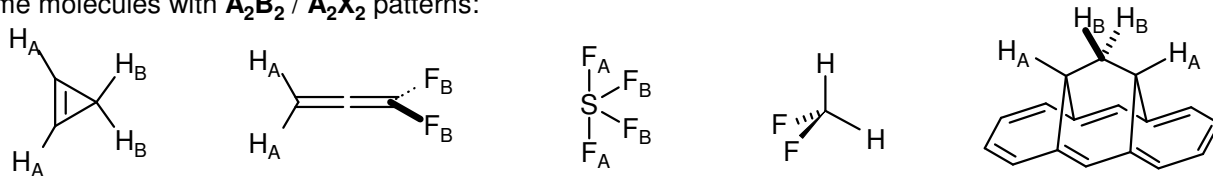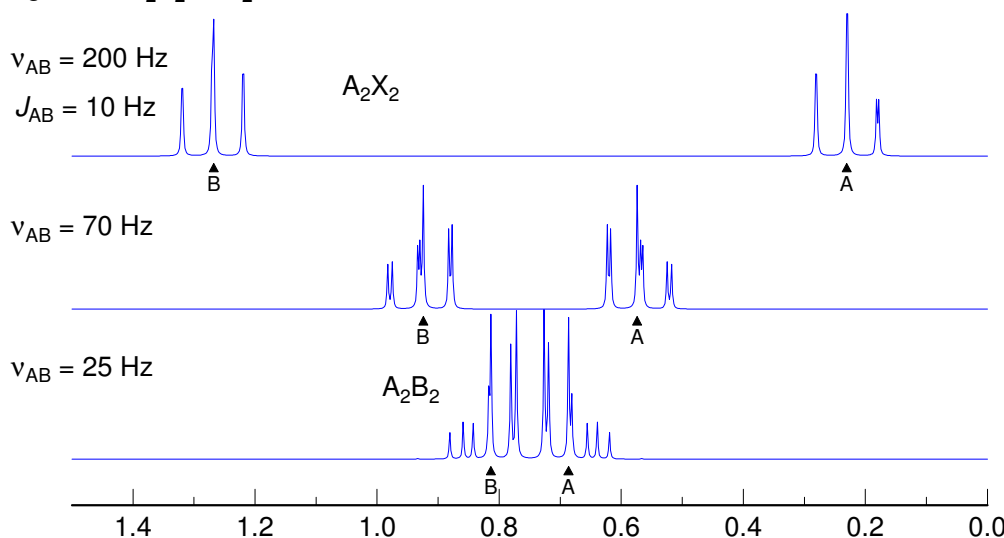he same chemical shift by symmetry, and each **A** proton is coupled equally to the two **X** (or **B**) protons.  True **A₂X₂** patterns are quite rare.   Both the **A** and **X** protons are identical triplets.  More complicated patterns are seen when the chemical shift difference approaches or is smaller than the $J_{AB}$ coupling.  However, both **A₂B₂** and **AA'BB'** always give centrosymmetric patters (**A₂** part mirror image of the **B₂** part).

Some molecules with **A₂B₂** / **A₂X₂** patterns:

Change from **A₂X₂** to **A₂B2**

$\nu_{AB}$ = 200 Hz

$J_{AB}$ = 10 Hz

A₂X₂

B          A

$\nu_{AB}$ = 70 Hz

B          A

$\nu_{AB}$ = 25 Hz

A₂B₂

B   A

| 1.4 | 1.2 | 1.0 | 0.8 | 0.6 | 0.4 | 0.2 | 0.0 |

AA'XX' and **AA'BB'** spectra are much more common.  Here each **A** proton is coupled differently to the **B** and **B'** protons (or **X**, **X'** nuclei).  Some molecules with such patterns are:

Br–CH₂–CH₂–Cl
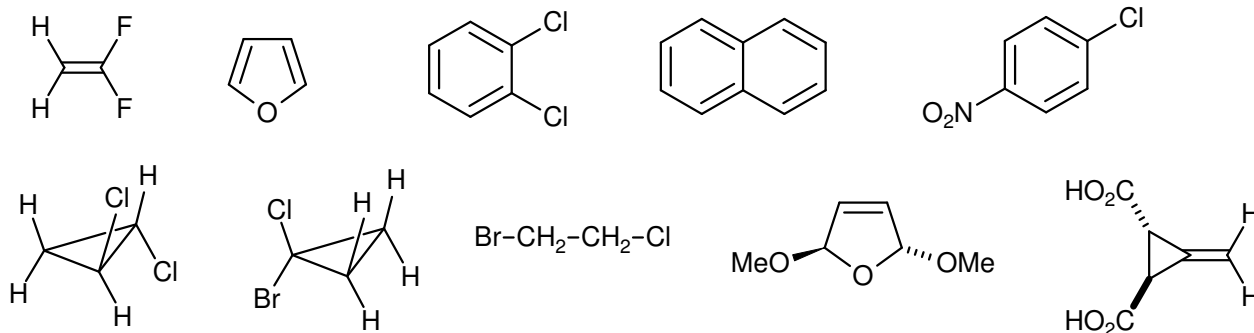
Such molecules give inherently second-order multiplets. Only if the $J_{AB}$ coupling is identical to the $J_{AB'}$ coupling by accident does the system become **A₂B₂** or **A₂X₂**, and a first order pattern is seen (if $\nu_{AB}$ is large enough).

# AA'XX' Spectra

**AA'XX'** spectra consist of two identical half spectra, one for **AA'** and one for **XX'**, each a maximum of 10 lines, each symmetrical about its midpoint, $\nu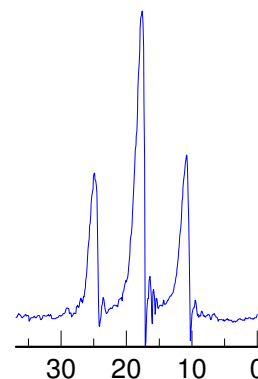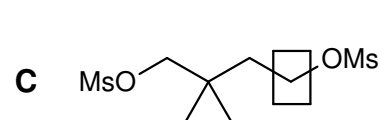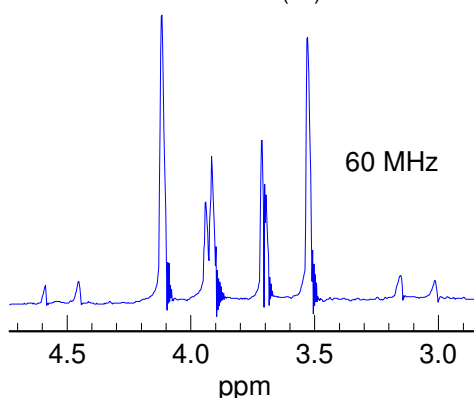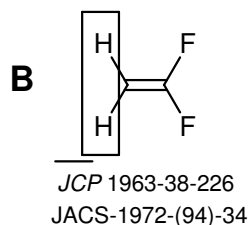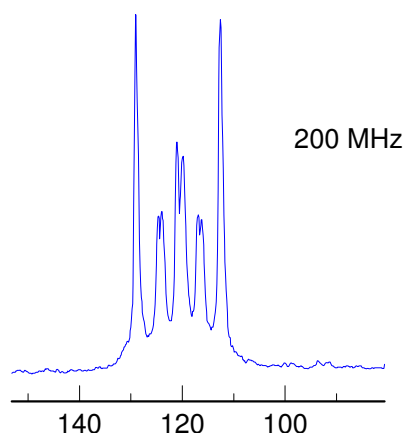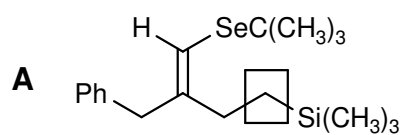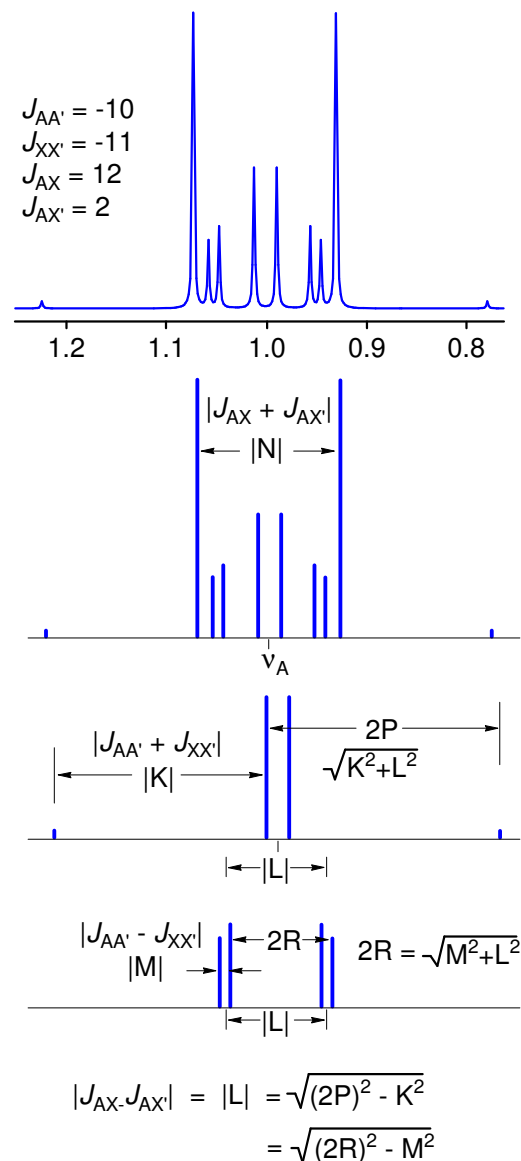_A$ and $\nu_X$, respectively. See example B below. The appearance of the spectrum is defined by four coupling constants: $J_{AA'}$, $J_{XX'}$, $J_{AX}$ and $J_{AX'}$. The spectrum is sensitive to the relative signs of $J_{AX}$ and $J_{AX'}$, but not to the relative signs of $J_{AA'}$ and $J_{XX'}$. The relationship between these, and the directly measurable values K, L, M, and N are given below and in the graphic.
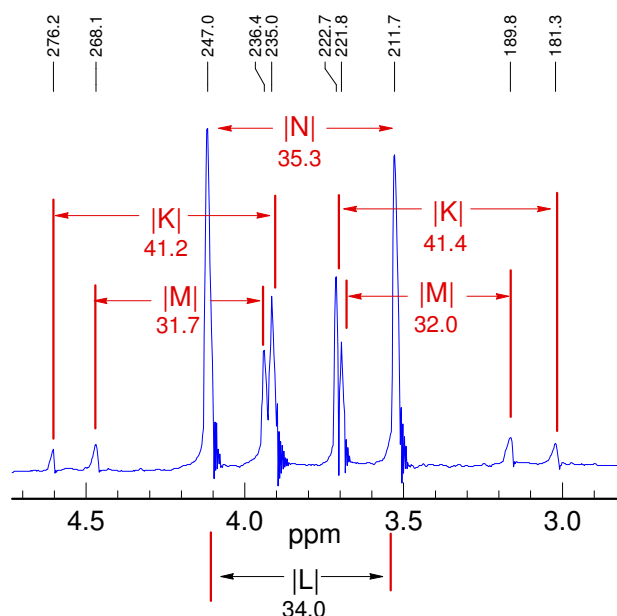
$$|K| = |J_{AA'} + J_{XX'}| \qquad \text{"}J\text{" of one } \textbf{ab} \text{ quartet}$$

$$|L| = |J_{AX} - J_{AX'}| \qquad \text{"}\delta\text{" of both } \textbf{ab} \text{ quartets}$$

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

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

Each half-spectrum consists of a 1:1 doublet with a separation of N (intensity 50% of the half spectrum), and two **ab** quartets, each with "normal" intensity ratios and $\nu_{ab} = |L|$. One has apparent couplings ($J_{ab}$) of $|K|$ and the other of $|M|$, as indicated. Unfortunately, K and M cannot be distinguished, the relative signs of $J_{AA'}$ and $J_{XX'}$ are not known, nor is it known which number obtained is $J_{AA'}$ and which is $J_{XX'}$. It is also not known which coupling is $J_{AX}$ and which is $J_{AX'}$, but the relative signs of $J_{AX}$ and $J_{AX'}$ can be determined: if $|N|$ is larger than $|L|$, signs are the same. Thus the ^{19}F and ^{1}H spectra of 1,1-difluoroethylene (B) are identical, so it is not possible to distinguish which coupling is $^2J_{FF}$ and which is $^2J_{HH}$, nor can one tell which is the *cis* $J_{HF}$ and which is *trans* $J_{HF}$. This would have to be done using information about such couplings obtained from compounds where the assignments are not ambiguous.

$J_{AA'}$ = -10
$J_{XX'}$ = -11
$J_{AX}$ = 12
$J_{AX'}$ = 2



$|J_{AX} + J_{AX'}|$
← $|N|$ →
$\nu_A$

$|J_{AA'} + J_{XX'}|$
$|K|$
2P
$\sqrt{K^2+L^2}$
$|\leftarrow|L|\rightarrow|$

$|J_{AA'} - J_{XX'}|$
$|M|$
←2R→
$2R = \sqrt{M^2+L^2}$
$|\leftarrow|L|\rightarrow|$

$$|J_{AX}\text{-}J_{AX'}| = |L| = \sqrt{(2P)^2 - K^2}$$
$$= \sqrt{(2R)^2 - M^2}$$



**A**

Ph—CH₂ ... with H, SeC(CH₃)₃ and Si(CH₃)₃

200 MHz

**B**

H / F, H / F (1,1-difluoroethylene)

*JCP* 1963-38-226
JACS-1972-(94)-34

60 MHz

**C**

MsO ... OMs

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

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

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

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

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

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



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

If we make the reasonable assumption that $J_{FF} > J_{HH}$ and $J_{HF}$ (trans) > $J_{HF}$ (cis) we get the following values:
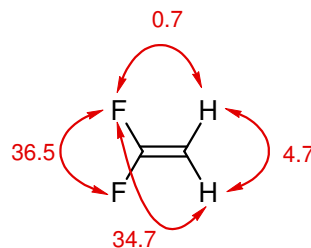
**Special Cases of AA'XX' patterns:** Unfortunately a large fraction of **AA'XX'** patterns are missing lines, which means that some or all of the coupling constants may be indeterminate. Below are summarized several common (and some less common) situations where a reduced number of lines is seen.

In the situation where $J_{AX} = J_{AX'}$ (i.e. L = 0, **A₂X₂**) the spectrum collapses to a triplet. In other words, the effective "chemical shift" of each of the **ab** quartets is zero, and thus each gives a single line at $\nu_A$. This is more or less the situation with many acyclic compounds of the X-CH₂-CH₂-Y type, provided that X and Y are not too large, but cause very different chemical shifts. See example C.

In the situation where $J_{AA'} \approx J_{XX'}$ (which is often approximately the case with X-CH₂-CH₂-Y and p-disubstituted benzenes) the M **ab** quartet collapses to two lines since M = 0. See example A.

In cases where $J_{XX'}$ is zero, both **ab** quartets will have the same $J_{ab}$ (M = K) and will be identical, leaving only 6 lines. This is nearly the case for situations like symmetrical o-disubstituted benzenes or 1,4-disubstituted butadienes, where $J_{AA'}$ is a 3-bond coupling, and $J_{XX'}$ a 5-bond coupling. In these situations L is small (i.e.$J_{AX}$ is close to $J_{AX'}$) and the central lines of the K and M quartets will likely be superimposed, whereas the small outer lines may be distinct -- the outer lines are separated by just under twice the value of $J_{XX'}$, the inner lines by just a fraction of $J_{XX'}$.

If the signs of $J_{AX}$ and $J_{AX'}$ are different the N lines will be relatively close together. This is the case for AA'XX' patterns of the AA' vicinal type, where $J_{AB}$ is a geminal coupling, hence negative, and $J_{AB'}$ is vicinal, and hence positive. In the limit, if $J_{AX} = -J_{AX'}$ then the N lines can collapse to a singlet.

# 5.15  The AA'BB' Pattern

As **A** and **X** of the **AA'XX'** spectrum move closer together, the lines of the 1:1 doublet (N) each split into two lines, for a total of twelve in each half-spectrum.  The **AA'** 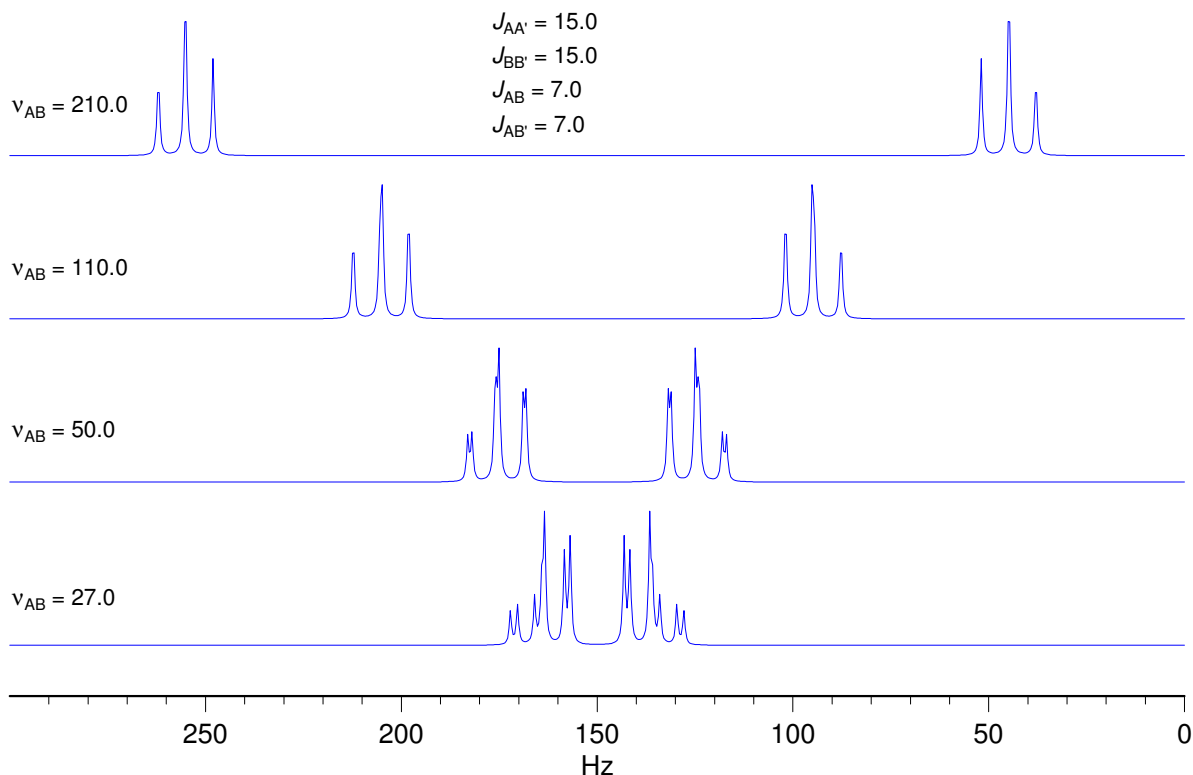and **BB'** parts are no longer centrosymmetric, but develop a mirror image relationship, so that the entire pattern is centrosymmetric.  As is found for all **AX** to **AB** transformations, "leaning" occurs, the inner lines increase and the outer lines decrease in intensity, culminating in just a single line when $\nu_{AB}$ = 0.  **AA'BB'** patterns can be solved manually, but the process is difficult, and is better done with computer simulations.

Typical molecular fragments which give **AA'BB'** patterns are:



(a) AA'-Gem          (b) AA'-Vic          (c) ODCB          (d) p-Aromatic
                                           o-Dichlorobenzene
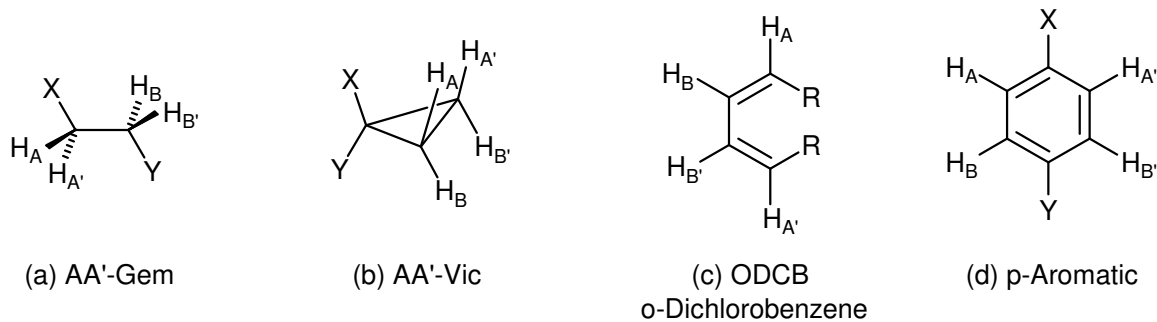
(a) **AA' Geminal (X-CH$_2$CH$_2$-Y)**.  This is the most common type of **AA'BB'** pattern.  The appearance can range from essentially perfect triplets, to rather complicated patterns which cannot be easily analyzed.  The two spectral parameters which control appearance of the spectrum are chemical shift difference $\nu_{AB}$, and the difference between the two vicinal coupling constants $J_{AB}$ and $J_{AB'}$.  If $\nu_{AB}$ is small (**AA'BB'**), then the pattern will always be complicated, no matter what the coupling constants are.  If $J_{AB} \approx J_{AB'}$ then the pattern will mimic **A$_2$X$_2$/A$_2$B$_2$** and triplets will be seen if the chemical shift is large enough.

Changing chemical shifts while keeping coupling constants static for an **AA'BB'** system with $J_{AB} = J_{AB'}$



$J_{AA'}$ = 15.0
$J_{BB'}$ = 15.0
$J_{AB}$ = 7.0
$J_{AB'}$ = 7.0

$\nu_{AB}$ = 210.0

$\nu_{AB}$ = 110.0

$\nu_{AB}$ = 50.0

$\nu_{AB}$ = 27.0

The key feature that determines the complexity of **AA'BB'** patterns of $CH_2$-$CH_2$ groups is the relative size of $J_{AB}$ and $J_{AB'}$, which is determined largely by the conformational properties of the X-$CH_2CH_2$-Y fragment. For acyclic systems, if the X and/or Y groups are small, then the populations of the *anti* and *gauche* conformations will be close to statistical (1:2). As can be seen from the table and the simulated spectra below, the two averaged couplings become approximately equal when there is 67% of *gauche* isomer, and the spectrum will mimic an **A$_2$B$_2$** pattern -- triplets if $\nu_{AB}$ is large enough ($\nu_{AB} \gg J_{AB}$). If X and Y are large, then the anti isomer will be favored and the pattern will be more complex. In practice, adjacent $CH_2$ groups often look like triplets, and thus the *gauche* conformation must usually be favored. For cyclic systems (e.g., N-cyanomorpholine) the ring constrains the -$CH_2CH_2$- fragment to mostly the gauche conformation, and clean triplets are not usually seen.
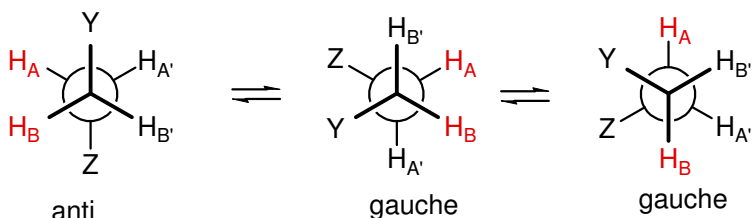
The coupling constants were calculated using the simple Karplus equations below. The spectra shown were calculated using **AA'XX'** formulas (i.e. the chemical shift between **A** and **B** is large compared to $J_{AB}$).

$$J_\Theta = J_o \cdot \cos^2 \Theta$$

$J_o$ = 12 Hz for $\Theta > 90°$
$J_o$ = 9 Hz for $\Theta < 90°$

$$J_{AA'} = J_{BB'} = -13 \text{ Hz}$$

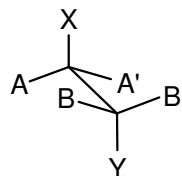| anti | gauche | gauche |
|---|---|---|
| $J_{AB}$ = 2.3 | $J_{AB}$ = 2.3 | $J_{AB}$ = 12 |
| $J_{AB'}$ = 12 | $J_{AB'}$ = 2.3 | $J_{AB'}$ = 2.3 |
| $J_{A'B'}$ = 2.3 | $J_{A'B'}$ = 12 | $J_{A'B'}$ = 2.3 |
| $J_{A'B}$ = 12 | $J_{A'B}$ = 2.3 | $J_{A'B}$ = 2.3 |

Thus for **60/40** anti/syn we have:

$J_{AB}$ = (0.6)(2.3) + (0.2)(2.3) + (0.2)(12) = **4.24**
$J_{AB'}$ = (0.6)(12) + (0.2)(2.3) + (0.2)(2.3) = **8.12**

300 MHz (CDCl$_3$)
Source: Aldrich Spectra Viewer

### %anti/gauche

| 100 / 0 | $J_{AB}$ = 2.3 |
| | $J_{AB'}$ = 12 |

| 80 / 20 | $J_{AB}$ = 3.2 |
| | $J_{AB'}$ = 10.1 |

| **60 / 40** | $J_{AB}$ = **4.2** |
| | $J_{AB'}$ = **8.1** |

| 33 / 67 | $J_{AB}$ = 5.5 |
| | $J_{AB'}$ = 5.5 |

| 20 / 80 | $J_{AB}$ = 6.2 |
| | $J_{AB'}$ = 4.2 |

Line width = 1.5 Hz

| 0 / 100 | $J_{AB}$ = 7.1 |
| | $J_{AB'}$ = 2.3 |
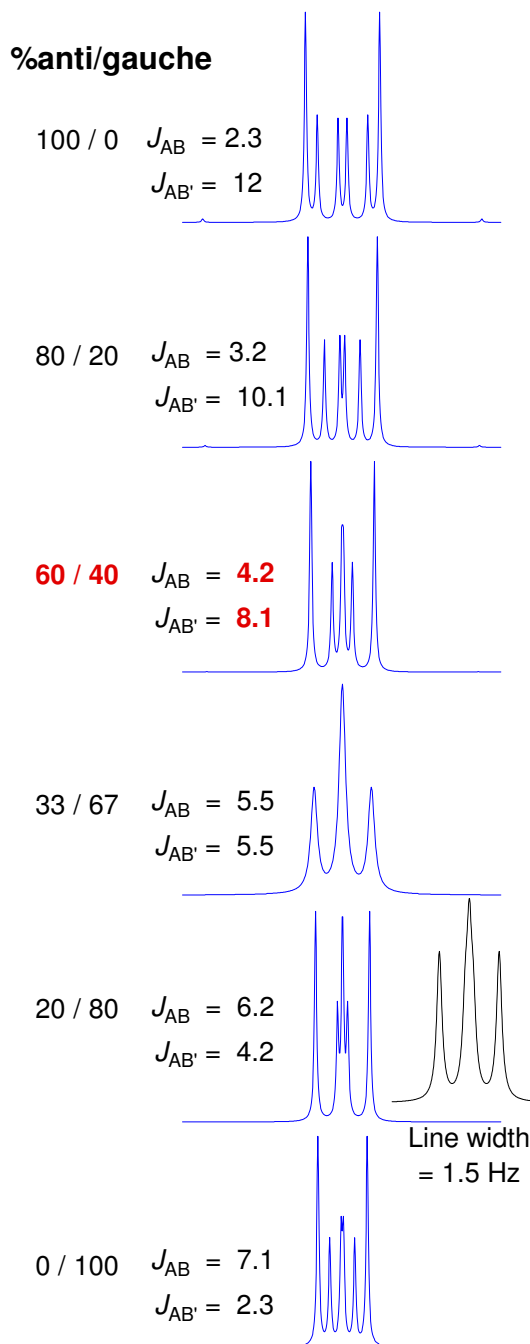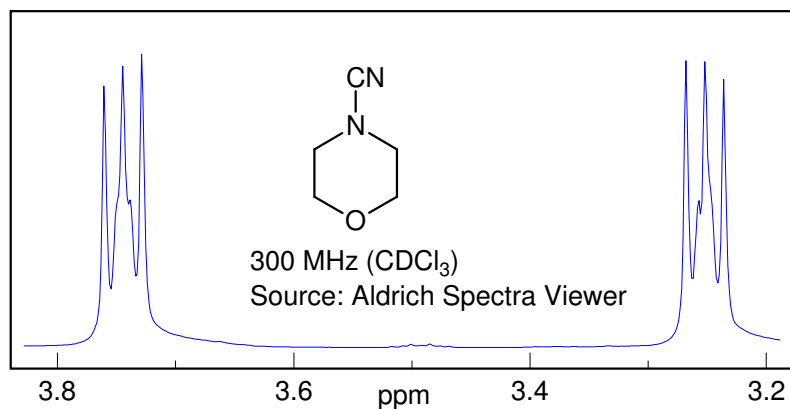
It is a common misconception that the equalization of coupling constants (and hence the appearance of triplets) is a consequence of free rotation around the $CH_2$-$CH_2$ bond. In fact, there is free rotation around almost all such bonds in acyclic molecules at accessible temperatures. The appearance of more complicated patterns is the result of a preference for the anti conformation over the gauche (or vice versa), and has nothing to do with the rate of rotation. See section 5-HMR-09 for some additional examples.

New 35-01 Rev 42-11

# AA'BB' Spectra X-CH$_2$-CH$_2$-Y

X
A—⟨ ⟩—A'
B      B'
Y

## AA'XX'



Br

C$_8$H$_9$Br

Why is the triplet at 3.55 much taller than the one at 3.15?

3.6   3.5   3.4   3.3   3.2   3.1

H      SeC(CH$_3$)$_3$

Ph

Si(CH$_3$)$_3$

200 MHz
Reich (Bowe)

2.2   2.1        0.7   0.6   0.5

## AA'BB'



O              O
H              OMe

100MHz
Reich
C$_8$H$_{14}$O$_3$

2.4   2.2   2.0   1.8   1.6

Br-CH$_2$-CH$_2$-Cl
60 MHz

## AA'BB'

PhS      H

SeCH$_3$

200 MHz
Reich (Bowe)

2.7   2.6   2.5

Ph

O
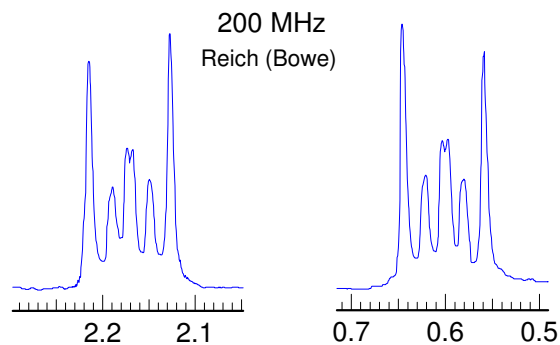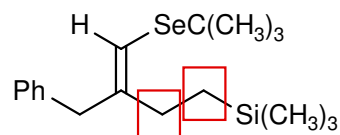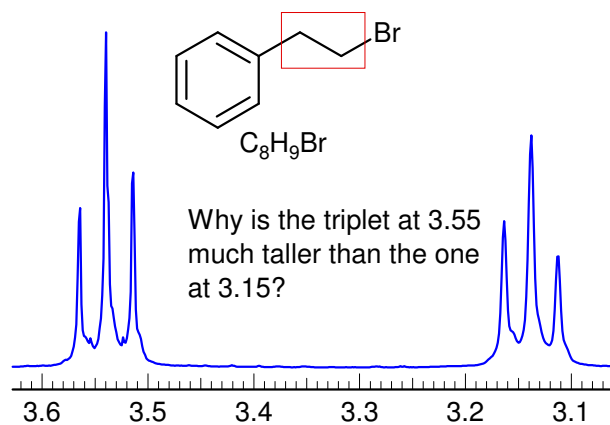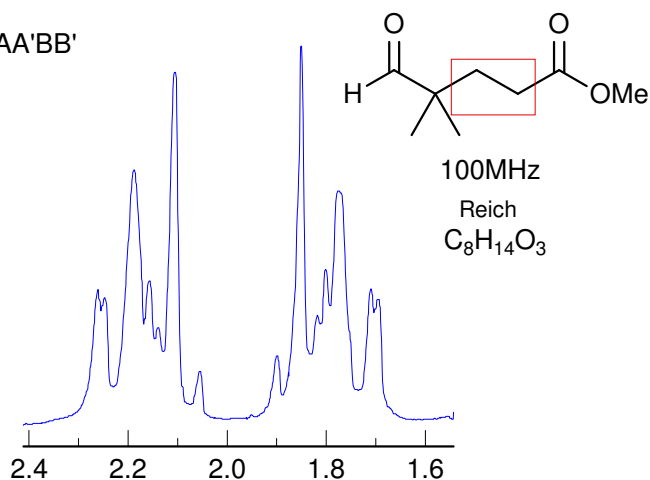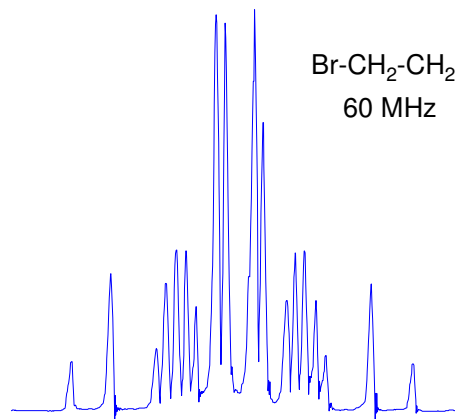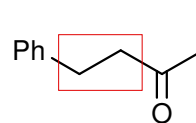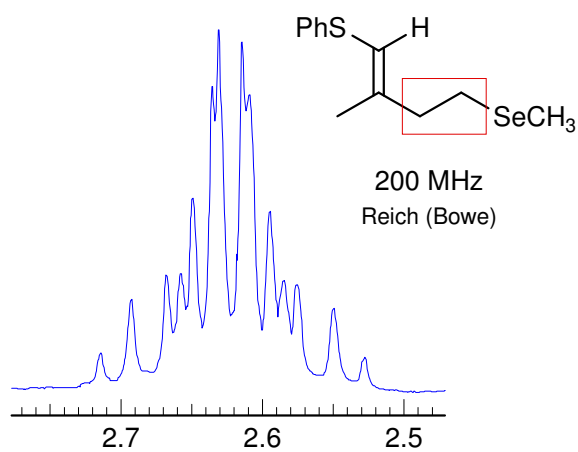
100 MHz
Reich (Olson)
C$_{10}$H$_{12}$O

3.5   3.0   2.5
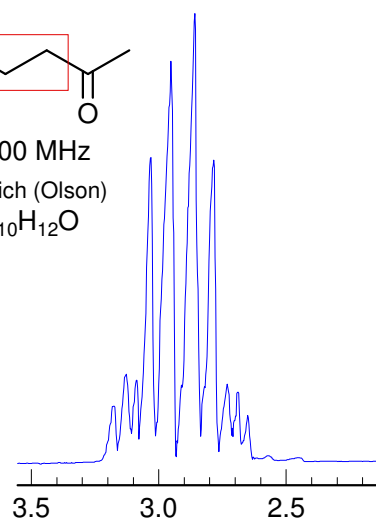
(b) **AA' Vicinal**.  This type of **AA'BB'** pattern is much less common than type (a).  It appears principally in 1,1-disubstituted cyclopropanes, 2,2-disubstituted 1,3-dioxanes and other similar structures.  The patterns are never triplets because $J_{AB}$ is invariably quite different from $J_{AB'}$.

The N doublet peaks are close together in these patterns, often inside the K and M **ab** quartets, because $J_{AX}$ is negative, and $J_{AX'}$ is positive (N = $J_{AX}$ + $J_{AX'}$). Since $J_{AA'} \approx J_{XX'}$ the K **ab** quartet has very small outer peaks, and the inner peaks will then be close to the N doublet peaks. Similarly the "**ab**" M quartet will have a near zero "coupling" (M = $J_{AX}$ + $J_{AX'}$) and so will be essentially be two singlets, or two very closely spaced doublets, not resolved the spectrum below.  These features can be seen in the dioxolane spectrum below, which has been simulated using the parameters shown (red trace). Peak labels are for the **AA'XX'** assignments.  Since this is actually an **AA'BB'** pattern, the N lines each split into two clos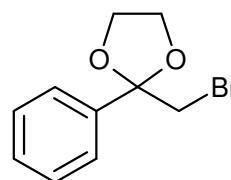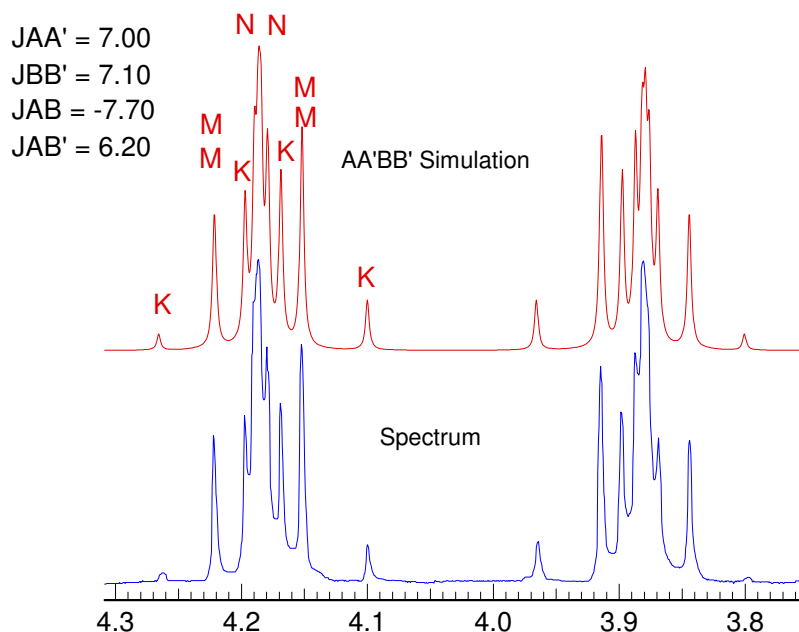ely spaced ones. Because the A/X shift difference is diastereotopic in nature, most of these patterns tend toward **AA'BB'** except at very high field strength.

JAA' = 7.00
JBB' = 7.10
JAB = -7.70
JAB' = 6.20

AA'BB' Simulation

Spectrum

$C_{10}H_{10}BrO_2$, 200 MHz

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

Here some **AA'BB'** spectra of dioxolanes.

200 MHz
Reich (Bowe)

$C_5H_9BrO_2$
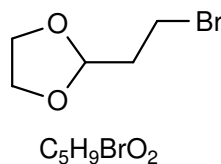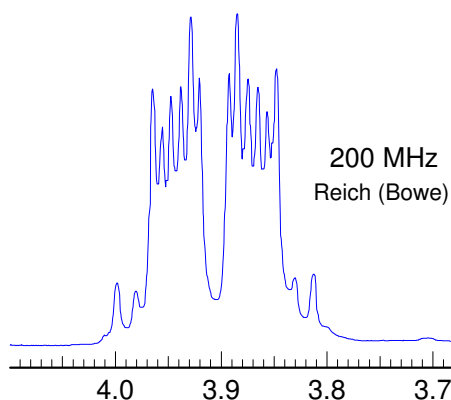
270 MHz
Reich (Bowe)
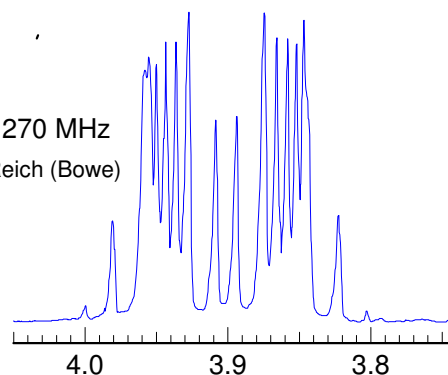
Unsymmetrical 1,1-disubstituted cyclopropanes often have **AA'XX'** patterns that have a quartet-like appearance. Because $J_{AA'}$ is close to $J_{AX'}$, the M quartet is essentially a doublet, and the L quartet is very strongly leaning (see the spectra and simulation below). This means that the central two line clusters have essentially 3/4 of the intensity (N+K), and the M lines 1/4, just as for a regular quartet

JAA' = 10.00
JBB' = 10.30
JAB = -4.20
JAB' = 7.70
VAB = 59.45

AA'BB' Simulation

$HO_2C$

$H_A$  $H_{A'}$

HO

$H_B$  $H_{B'}$

300 MHz
CDCl₃/DMSO-d₆

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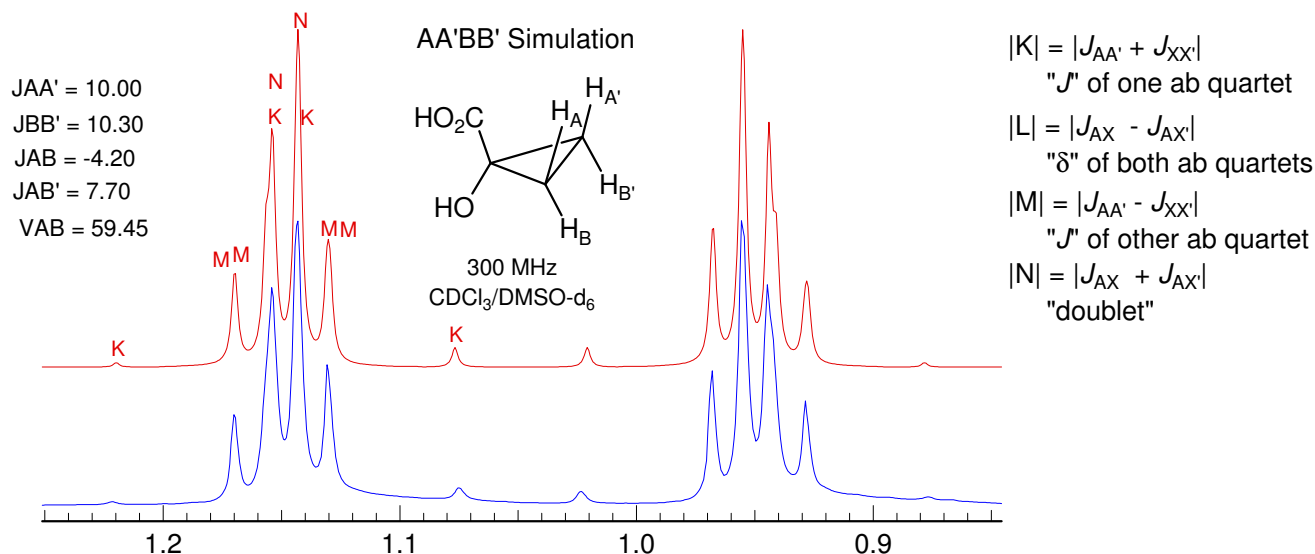


The half-spectrum of 1-phenyl-1-cyanocyclopropane illustrates this effect. Here $J_{AA'}$ and $J_{XX'}$ are a little more different than in the above example so the M quartet is visible as four lines. This 2-proton multiplet could be mistaken for a doublet of quartets by the unwary spectroscopist.

JAA' = 9.40
JBB' = 10.20
JAB = -5.30
JAB' = 7.60

VAB = 93.52

300 MHz

**AA'BB'** Simulation

NC

$H_A$  $H_{A'}$

Ph

$H_B$  $H_{B'}$





100 MHz

Reich (Renga)



100 MHz

Reich (Renga)
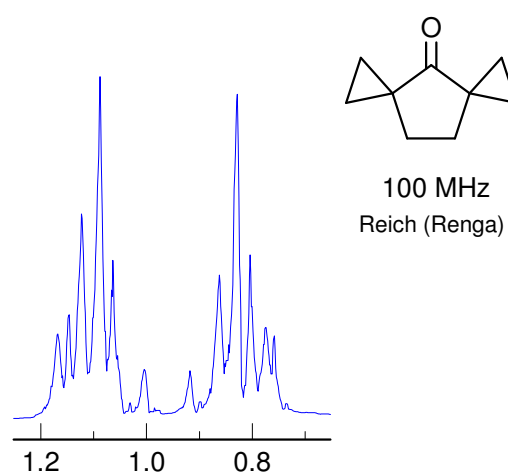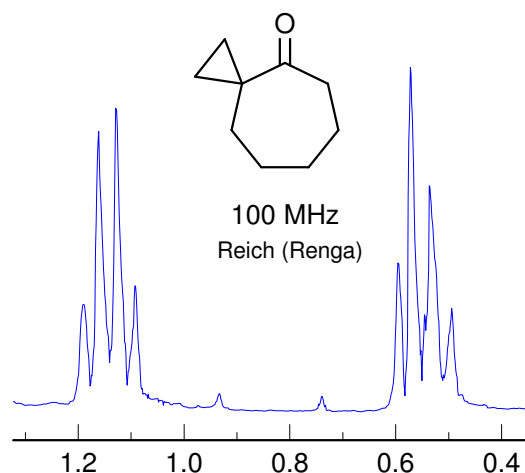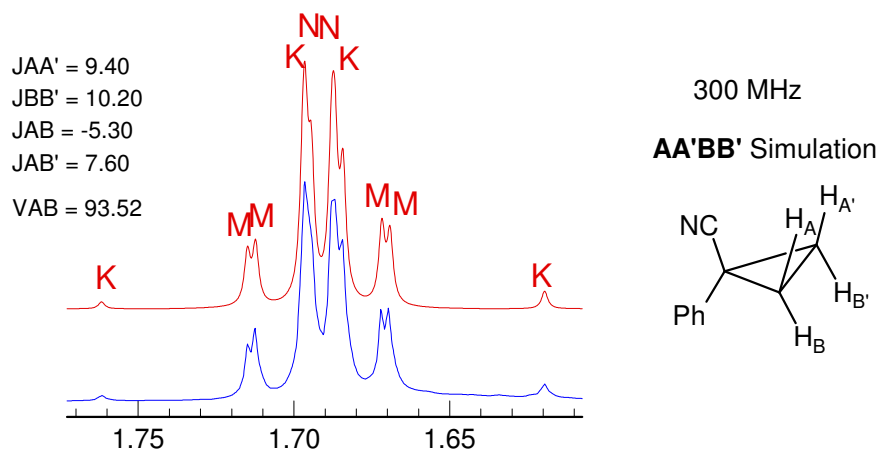
(c) **o-Dichlorobenzene (ODCB) Type**. This kind of **AA'BB'** pattern never approaches **A₂X₂** because $J_{AB}$ (*ortho* coupling) is always much larger than $J_{AB'}$ (*meta* coupling). It is seen in symmetrically 1,4-disubstituted dienes and ortho disubstituted benzenes. Note that for all **AA'XX'** / **AA'BB'** systems the **A** and **X** / **B** patterns are identical (although they have a mirror-image relationship). This is in spite of the fact that the coupling relationships of **A** and **X** / **B** are often quite different in molecules of this type. The spectra often have the appearance of a dd.

For most **AA'XX'** patterns of this type $J_{XX'}$ is a 3-bond coupling, and $J_{AA'}$ a 5-bond coupling, Thus the K and M **ab** quartets will be nearly superimposed (the $J_{ab}$ values differ by $2J_{AA'}$), often leaving only 6 resolvable lines (Simulation A, naphthalene, o-dichlorobenzene). Even with the small $J_{AA'}$ values that are usually seen, the central lines of the K and M quartets will likely be superimposed, whereas the small outer lines may be distinct -- they will be separated by just under twice the value of $J_{AA'}$, the inner lines by just a fraction of $J_{XX'}$ (Simulation B, spectrum of biphenylene and the 1,4-diacetoxybutadienes).

**Simulated Spectra (AA' part only):**



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

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

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

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

**A**
JAA' = 0.00
JXX' = 7.00
JAX = 7.00
JAX' = 2.50

**B**
JAA' = 0.40
JXX' = 7.00
JAX = 7.00
JAX' = 2.50

**Spectra:**



300 MHz, CDCl₃



300 MHz, CDCl₃

300 MHz, CDCl₃

Only **X** part shown

AcO—C(Hx 7.35)=CH(HA')... *JOC* **1968**, 2835

$J_{AX} = 12.5$
$J_{AX'} = -0.7$
$J_{XX'} = 11.5$
$J_{AA'} = 0.8$

60 MHz

($H_X$ shown)

HA=CHx ... OAc 2.10 ... 7.10 HA' ... 5.87 Hx' ... *JOC* **1968**, 2835

$J_{AX} = 6.7$
$J_{AX'} = -1.3$
$J_{XX'} = 11.0$
$J_{AA'} = 1.6$

60 MHz

($H_X$ shown)

300 MHz, CDCl$_3$
Reich (Whipple)

As with all such NMR spectra, the patterns get more complex when the chemical shift between the protons becomes smaller (**AA'BB'**). Some examples (both **A** and **B** shown):

100 MHz

I. L. Reich

100 MHz

I. L. Reich
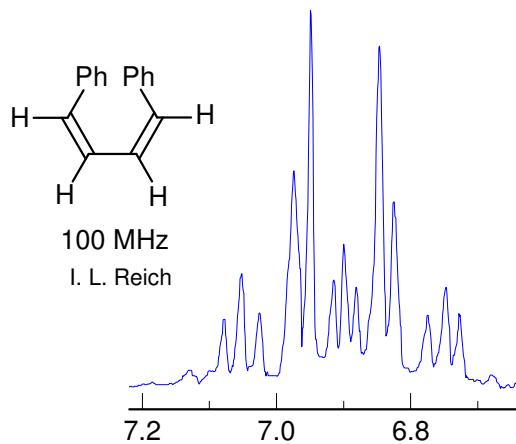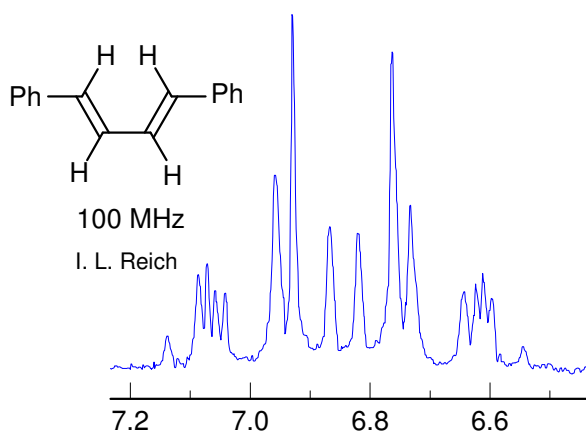
Rev 41-06

(d) **p-Disubstituted Benzene Type**. These usually resemble a two **AX** doublets or an **AB** quartet, with some small extra lines.

For **AA'XX'** patterns of this type, the two $^3J$ meta couplings ($J_{AA'} = J_{XX'}$) are likely to be very close in size so that the M ab quartet collapses to two lines since M = 0 or very small (Simulation B). In addition, the para-coupling ($J_{AX'}$) is nearly zero, which makes L ≈ N. Thus the two lines of the M quartet will appear at or close to the chemical shift of the N doublet, leaving only a doublet and one **ab** quartet, whose doublets will be on both sides of the N+M lines (simulation A). This is why p-substituted benzenes are often incorrectly described as doublets, since the extra lines corresponding to the K quartet amount to only 1/4 of the total intensity, and appear fairly close to the dominant M+N doublet.

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

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

**Simulated Spectra (AA' part only):**



**A**

Equal $J_{meta}$
$J_{para} = 0$

JAA' = 2.00
JXX' = 2.00
JAX = 8.00
JAX' = 0.00

M "ab quartet" collapsed (J = 0)

N+M

$J_o + J_p$

**B**

Equal $J_{meta}$
$J_{para} = 0.8$ Hz

JAA' = 2.00
JXX' = 2.00
JAX = 8.00
JAX' = 0.60

**C**

Different $J_{meta}$
$J_{para} = 0.8$ Hz

JAA' = 1.80
JXX' = 2.20
JAX = 8.00
JAX' = 0.60

**Spectra:**



300 MHz (CDCl$_3$)

Reich (Sikorski)
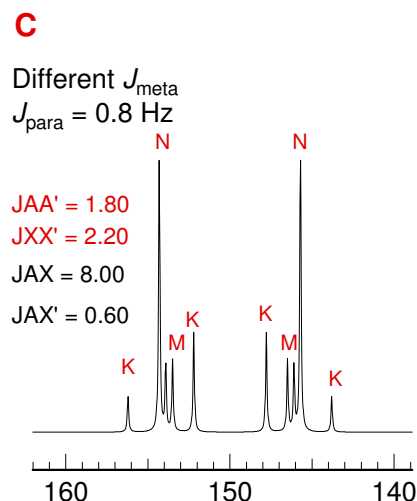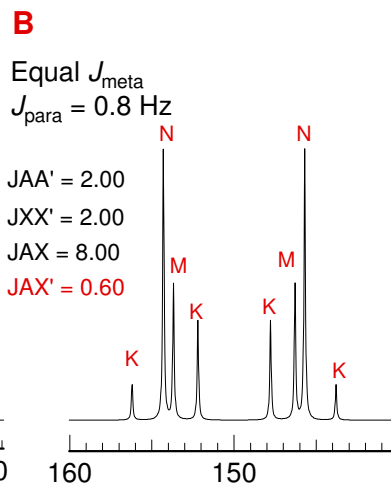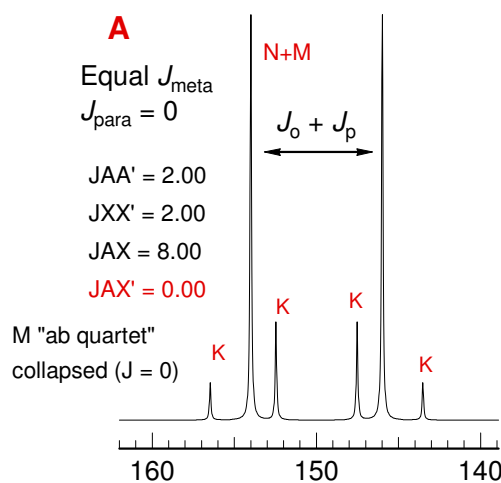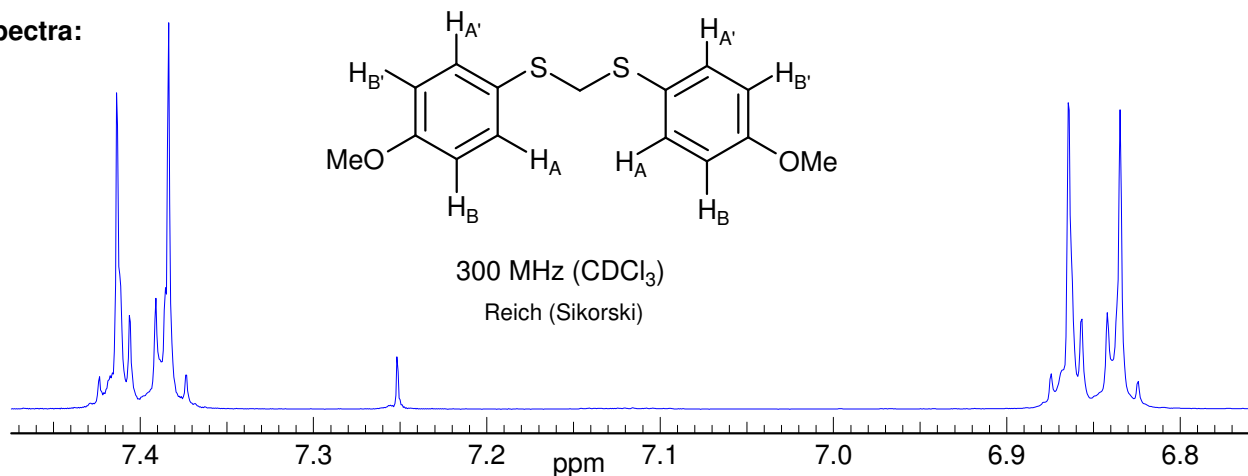
When the chemical shift between **A** and **B** is small (as in p-bromochlorobenzene below), the usual leaning effects are seen, additional lines appear, and the extra lines become more pronounced. As 300 MHz a more "normal" **AA'BB'** pattern is seen
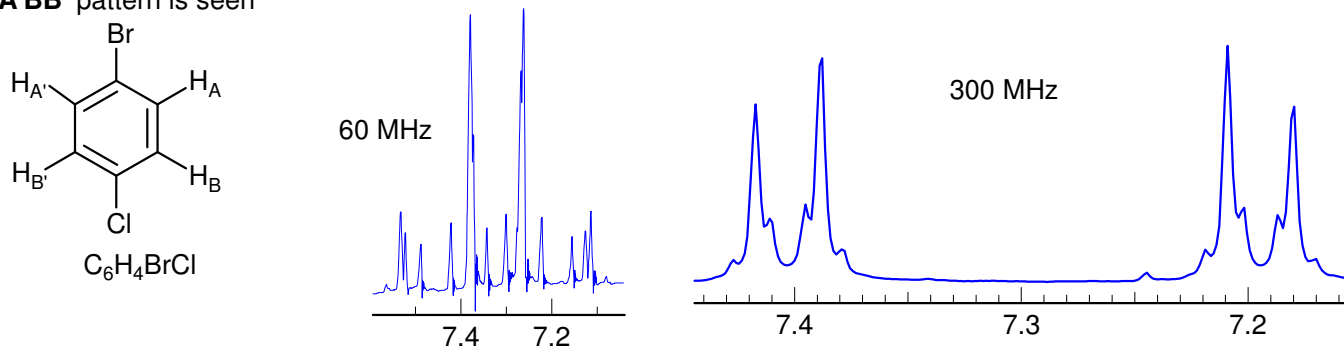


(e) **Miscellaneous**. In the 1,3-substituted cyclobutane below the $^4J_{HH}$ ($J_{AA'}$, $J_{BB'}$ and $J_{AB'}$) are large enough that the expected first-order **AB** quartet is not seen, but a much more complicated pattern. In this case, as in the p-disubstituted benzene case above the "AB" character dominates the appearance of the multiplet, largely because the coupling interactions between either of the **AB** protons and the **A'B'** protons are much weaker than the **A** to **B** and the **A'** to **B'** couplings (i.e. the **AB** pair is nearly isolated from the **A'B'** pair).



Reich (Wesley)
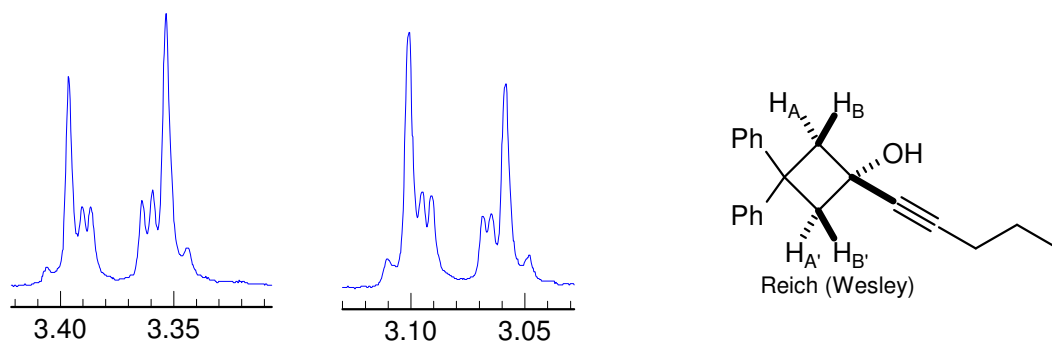
Trans-1,2-disubstituted cyclopropanes can form **AA'BB'** patterns. Some examples
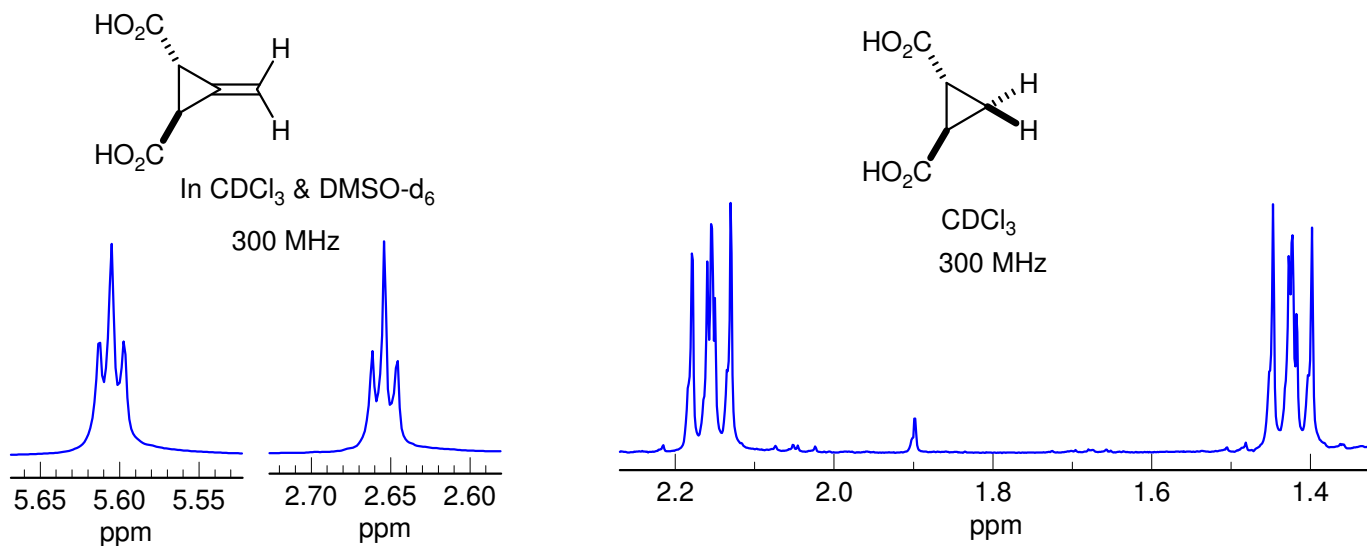
# Origin of Complexity in Patterns of the AA'XX'... Type

There are two situations where spin systems containing **AA'XX'** type do not show unusual complexity.  One is where $J_{AX} = J_{AX'}$, in which case the pattern becomes first order **A$_2$X$_2$**.

The second is systems in which there is no coupling between both of the chemical shift equivalent protons, i.e., $J_{AA'} = J_{XX'} = 0$.  In such cases the degeneracy between spin states is no longer present, and first order systems result.  Consider two examples.  A monosubstituted benzene is an **AA'BB'C** or **AA'MM'X** system.  A simulated spectrum is shown below



Simulation data:
$J_{AM} = J_{A'M'} = 8$
$J_{MX} = J_{M'X} = 8$
**J$_{AA'}$ = 2**
**J$_{MM'}$ = 2**
$J_{AX} = J_{A'X} = 2.0$
$J_{AM'} = J_{A'M} = 0.5$

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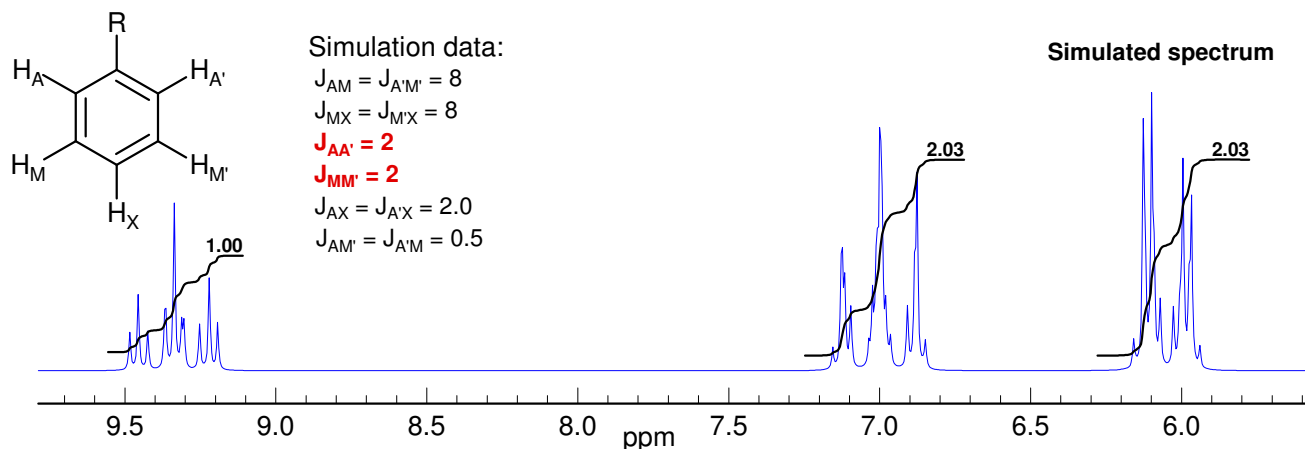
If we recalculate the spectrum after setting $J_{AA'} = 0$ and $J_{MM'} = 0$ then the spectrum becomes essentially first order (it would be completely first order if the chemical shifts between **A**, **M** and **X** were made larger).

Simulation     **J$_{AA'}$ = 0**
               **J$_{MM'}$ = 0**

**Simulated spectrum**
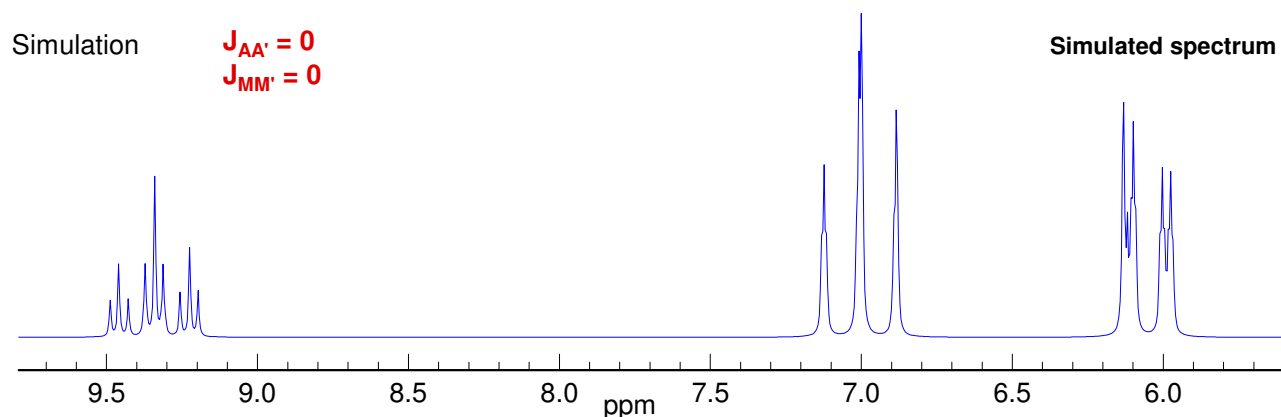


For this reason, some spin systems which are formally of the **AA'XX'** type, but in which there is no significant spin-spin coupling between the equivalent protons show first order spectra.  For example, the fairly common spin system below of the **AA'BB'X** type shows no unusual complexity (beyond that of normal ABX patterns) because there is no coupling between the **A** and **A'** protons, nor between the **B** and **B'** protons. Such systems are sometimes defined as **(AB)$_2$X** to indicate that magnetic inequivalence is not a factor. The spectrum of 1,2,3-trichloropropane is an example.

300 MHz $^1$H NMR in CDCl$_3$
  Source: Aldrich Spectra Viewer/Reich



C$_3$H$_5$Cl$_3$
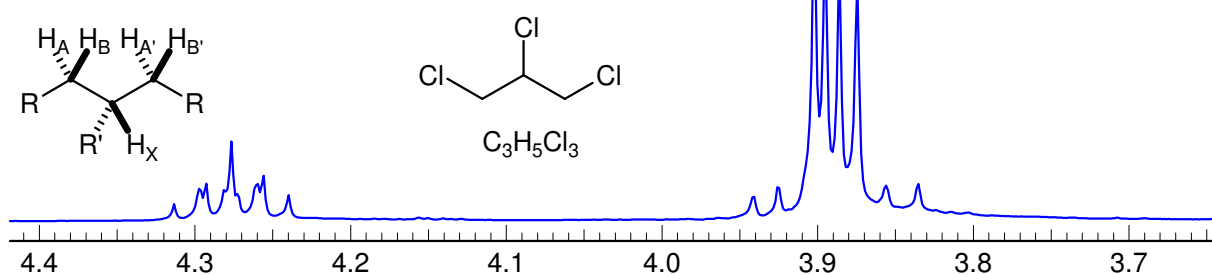
Contrast this with the NMR spectrum of dibromosulfolane below.

**Actual Spectrum 250 MHz, CDCl₃**



4.85   4.80   4.75
Hz

4.10   4.05   4.00   3.95
Hz

3.60   3.55   3.50
Hz
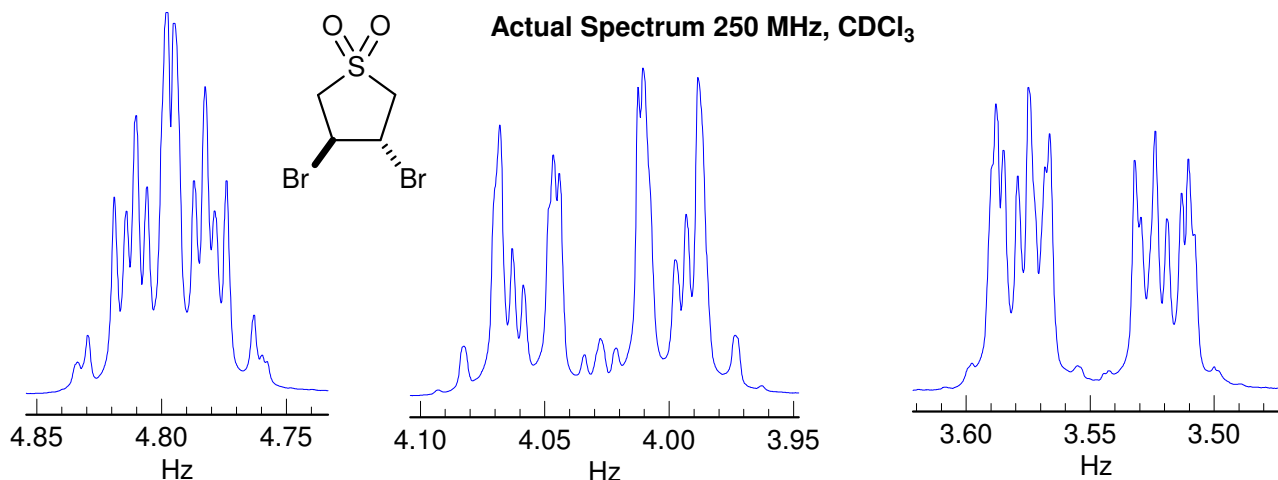
Why is this spectrum so complex? In this **AA'MM'XX'** system, although there is no significant coupling between **A** and **A'** or **M** and **M'**, there is coupling between **X** and **X'**, making the whole system a highly second order one (remember: anything coupled to a strongly coupled pair like the **XX'** protons becomes second order).



$\delta_A = 3.7$    $J_{AM} = J_{A'M'} = -13$
$\delta_B = 4.03$   $J_{MX} = J_{M'X'} = 5$
$\delta_X = 4.40$   $J_{AA'} = 0$
                     $J_{MM'} = 0$
                     $J_{AX} = J_{A'X'} = 8.0$
                     $J_{AM'} = J_{A'M} = 0$
                     **$J_{XX'} = 6$**

**Simulated spectrum**

$H_X$        $H_M$        $H_A$

$J_{XX'}$ = 6 Hz

4.5   4.4   4.3   4.2   4.1   4.0   3.9   3.8   3.7   3.6
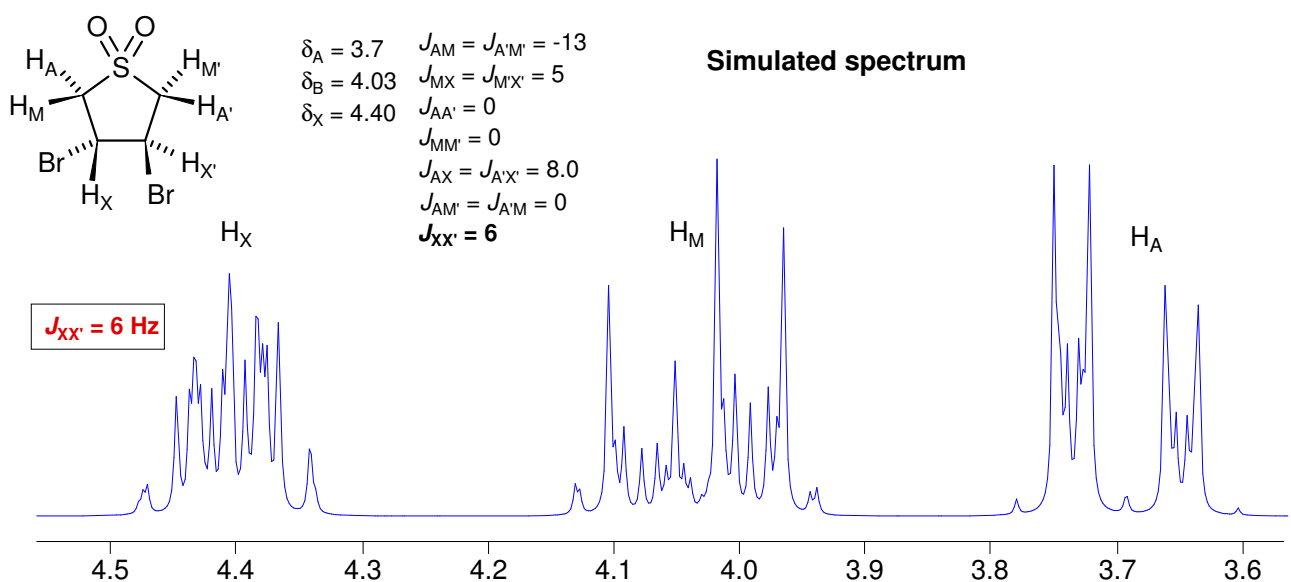
If we remove the **XX'** coupling, the system becomes essentially first order (two isolated **AMX** patterns).  We could better describe it as an **(AMX)₂** rather than an **AA'MM'XX'** spin system.

**Simulated spectrum**

$J_{XX'}$ = 0



4.5   4.4   4.3   4.2   4.1   4.0   3.9   3.8   3.7   3.6
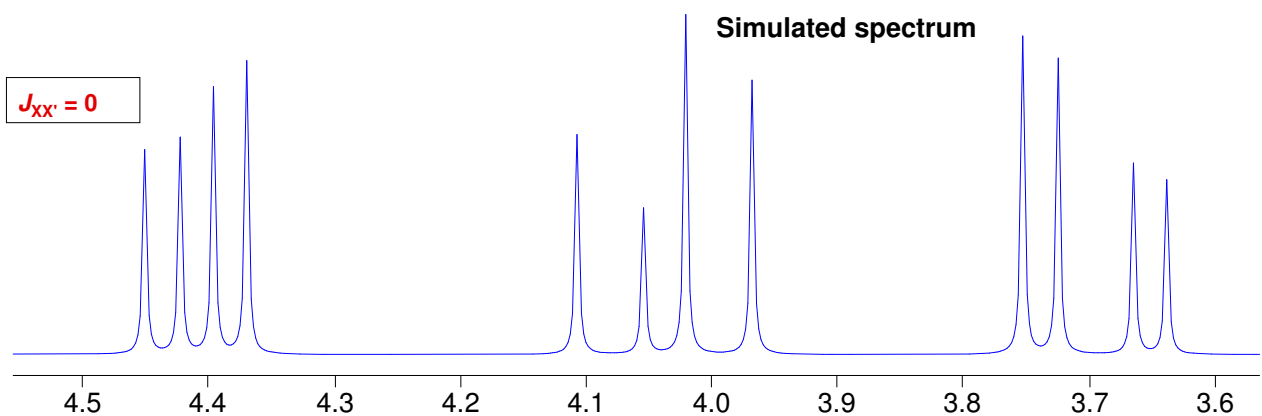
Another example of the same spin system is shown below.

300 MHz $^1$H NMR spectrum in CDCl$_3$.
Source:Charlie Fry/Reich

Note the extra peaks - these are not impurities or bad tuning.  The additional complexity arises because we have an **AA'BB'XX'** system here.  Even though $J_{AA'}$ and $J_{BB'}$ are essentially 0, the fact that **X** and **X'** are significantly coupled causes the **AB** signals to become complicated



AA'BB'XX'

The aromatic protons are also an **AA'BB'** system



AA'BB'XX'

6.8    6.7
ppm

8.00

6.17  5.80

2.11

3.90

7    6    5    4    3    2    1    0
ppm

# 5.16 Virtual Coupling

The term "virtual coupling" refers to an NMR phenomenon in which apparently first-order multiplets contain false coupling information. In extreme cases, protons that are not actually coupled will show splitting. More commonly, the magnitude of coupling constants obtained by first-order analysis is incorrect. All virtual coupling effects arise when protons, well isolated from other protons in chemical shift, are coupled to a group of other protons *which are strongly coupled to each other*. By strongly coupled we mean that these protons are *both* close in chemical shift and coupled to each other with $J > \Delta\nu$.

On the following pages are examples which illustrate the virtual coupling phenomenon in several different systems. One simple way to summarize these effects is as follows: when two or more protons are strongly coupled, then *any protons coupled to them will give multiplets with false coupling information and/or unexpectedly complex multiplet structure*. Furthermore, the *strongly coupled protons themselves will contain misleading multiplet structure*. Virtual coupling effects are also frequently encountered in heteronuclear magnetic equivalence NMR situations, e.g. in transition metal phosphine complexes (see Sect. 7-MULTI-2)

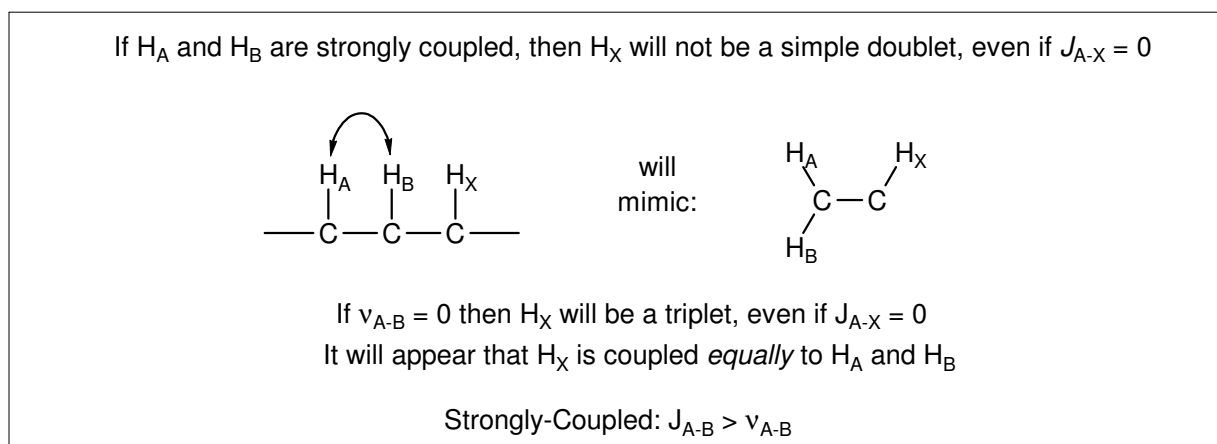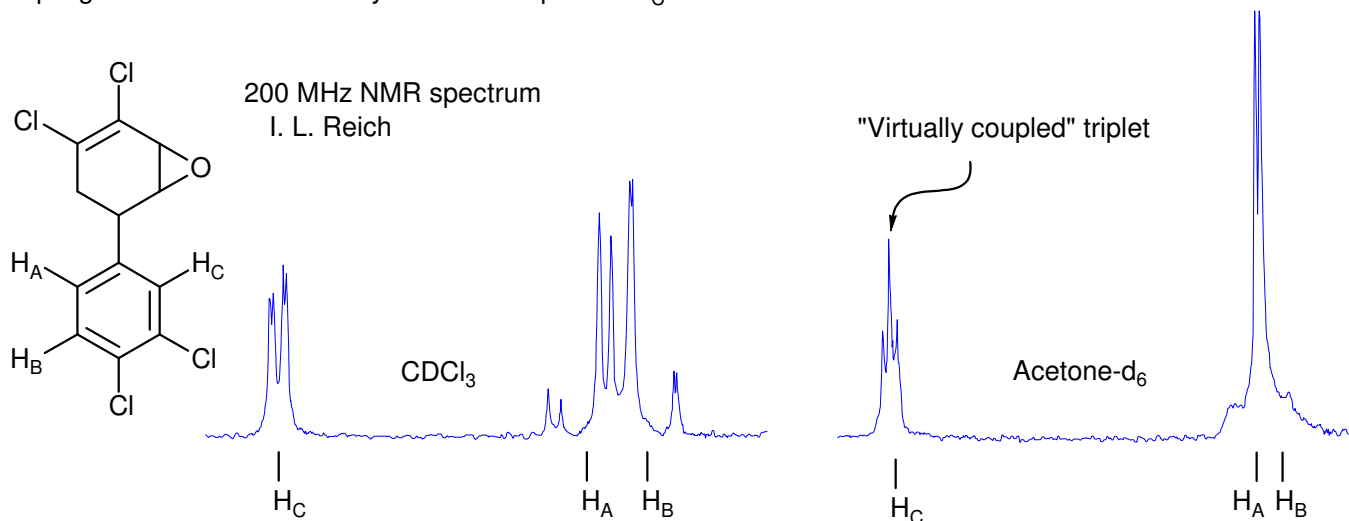The simplest systems to show virtual coupling effects are **ABX** patterns, where the **X**-multiplet will give incorrect values for $J_{AX}$ and $J_{BX}$ when it is analyzed as a doublet of doublets if $\nu_{AB}$ is similar to or smaller than $J_{AB}$. What is particularly insidious about this effect is that analysis of the **AB** part by a first-order method (treatment of each part as a distorted doublet of doublets) will give the same incorrect values for $J_{AX}$ and $J_{BX}$.



If $H_A$ and $H_B$ are strongly coupled, then $H_X$ will not be a simple doublet, even if $J_{A-X} = 0$

will mimic:

If $\nu_{A-B} = 0$ then $H_X$ will be a triplet, even if $J_{A-X} = 0$

It will appear that $H_X$ is coupled *equally* to $H_A$ and $H_B$

Strongly-Coupled: $J_{A-B} > \nu_{A-B}$

A typical example of virtual coupling is provided by the epoxide below. $H_A$ and $H_B$ are more or less first order when the spectrum is taken in CDCl$_3$ because $H_A$ and $H_B$ have a significant chemical shift (although typical second order effects are starting to appear). However, in acetone-d$_6$, $H_A$ and $H_B$ are essentially superimposed, and $H_C$ appears as a *triplet*, as if $H_A$ and $H_B$ were equally coupled to $H_C$, leading to a very different structure assignment. The small coupling visible for $H_B$ and $H_C$ in CDCl$_3$ is probably not entirely real - it is the beginning of the "virtual coupling" effect which eventually leads to a triplet for $H_C$



200 MHz NMR spectrum
I. L. Reich

"Virtually coupled" triplet

CDCl$_3$

$H_C$

$H_A$  $H_B$

Acetone-d$_6$

$H_C$

$H_A$  $H_B$

These effects can be understood by examining the behavior of the **X** part of an **ABX** system as $\Delta\nu_{AB}$ becomes small. In this simulation, $J_{AX}$ is set to 0; nevertheless when $\Delta\nu_{AB} < 15$ Hz the **X** part shows clear indications of coupling to $H_A$, as does the **AB** part, i.e. virtual coupling.

$H_X$

$J_{AB} = 10$ Hz
$J_{BX} = 7$ Hz

$J_{AX} = 0$

Mimic:

$H_A$ $H_B$ $H_X$
$-C-C-C-$

As soon as $\nu_{AB}$ approaches $J_{AB}$, It looks as if **X** is coupled to **both A** and **B** (i.e. **X** is a dd)

$\Delta\nu_{AB} = 40$ Hz

$\Delta\nu_{AB} = 20$ Hz

$\Delta\nu_{AB} = 10$ Hz

$\Delta\nu_{AB} = 5$ Hz

$\Delta\nu_{AB} = 1$ Hz

**A, B Part**    $\Delta\nu_{AB} = 10$ Hz

The AB part also shows the "fake" coupling.

|    |    |    |    |    |
|----|----|----|----|----|
| 40 | 30 | 20 | 10 | 0 |

Hz

**A, B Part**    $\Delta\nu_{AB} = 0$ Hz

$\Delta\nu_{AB} = 0$ Hz

Looks like:

$H_A$ $H_X$
$-C-C-$
$H_B$

|    |    |    |     |     |
|----|----|----|-----|-----|
| 20 | 10 | 0  | -10 | -20 |

Hz

The only hint that the **X** part is not a simple triplet is the appearance of the small outer peaks (lines 15 and 16 of the **X** part) and the extra lines in the **AB** part.

|    |    |    |    |   |
|----|----|----|----|---|
| 40 | 30 | 20 | 10 | 0 |

Hz

# Virtual Coupling in X of an ABX system

**AMX**

**ABX**

Q = "Mixing coefficient"

$$Q = \frac{J}{\Delta\nu + 2D}$$

M          AM

A
α          α ......... αα
           β ......... αβ
X = β       β    α ......... βα
                β ......... ββ

B          AB

A
α          α ......... αα
           β ......... αβ $\rightarrow$ $(\alpha\beta + Q\beta\alpha)/\sqrt{1+Q^2}$
X = β       β    α ......... βα $\rightarrow$ $(Q\alpha\beta + \beta\alpha)/\sqrt{1+Q^2}$
                β ......... ββ

These are transitions
of the X nucleus

           β          β ......... ββ
X = α       β    α ......... βα
           α    β ......... αβ
                α ......... αα

$J_{AX}$   $J_{MX}$

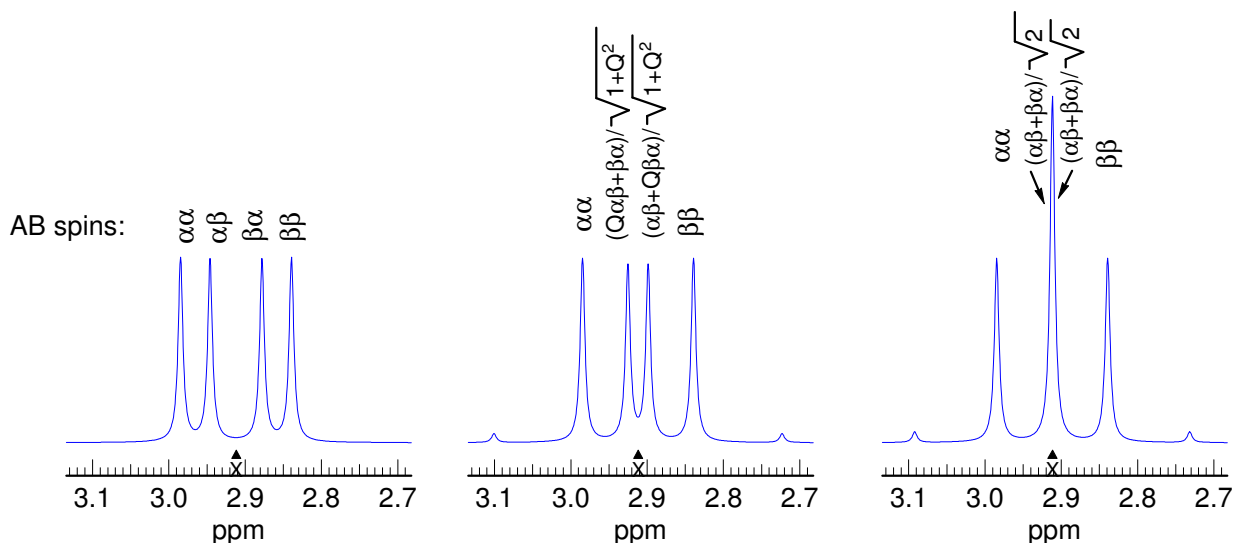           β          β ......... ββ
X = α       β    α ......... βα $\rightarrow$ $(Q\alpha\beta + \beta\alpha)/\sqrt{1+Q^2}$
           α    β ......... αβ $\rightarrow$ $(\alpha\beta + Q\beta\alpha)/\sqrt{1+Q^2}$
                α ......... αα

$J_{AX}$   $J_{BX}$

As $\nu_{AB} \rightarrow 0$, Q $\rightarrow$ 1
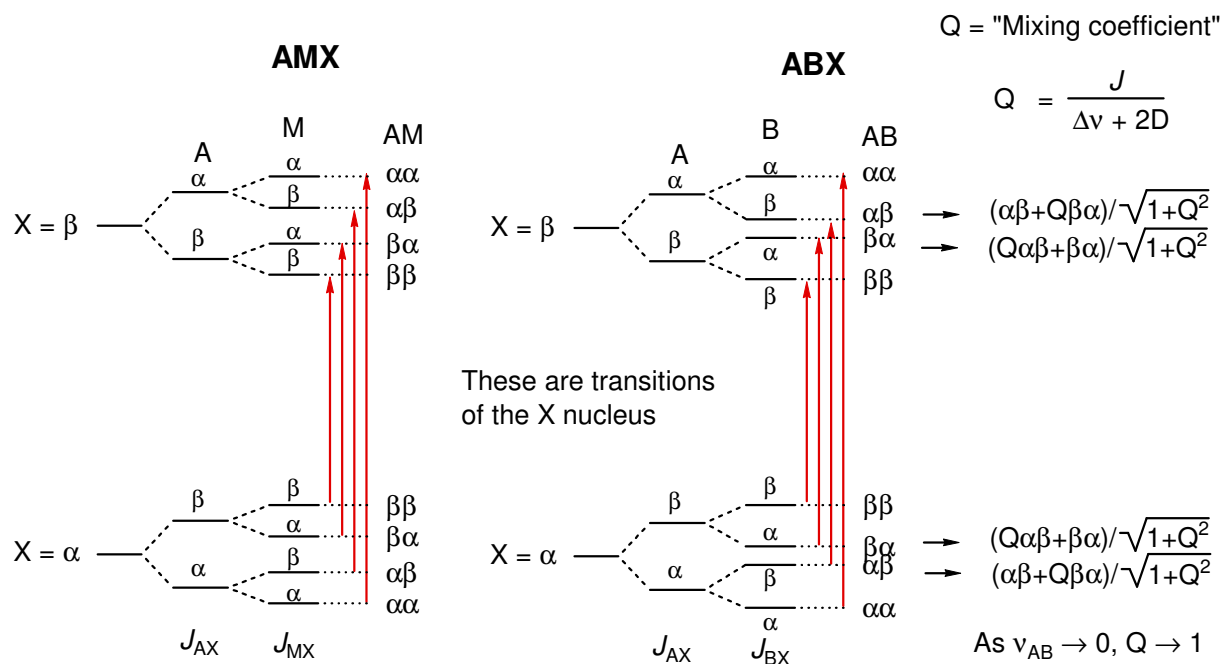
As the chemical shift between H$_A$ and H$_B$ becomes smaller, the αβ state begins to mix with the βα state, and the βα state mixes with the αβ (the mixing coefficient is Q). This results in their energies becoming closer together, and eventually, when $\nu_{AB}$ = 0, Q becomes 1, and the two energy levels consist of equal parts αβ and βα, and their energies are identical (the **X** part becomes a triplet).

The Illustration is for both $J_{AX}$ and $J_{BX}$ > 0

AB spins:

αα αβ βα ββ

3.1   3.0   2.9   2.8   2.7
ppm

αα  $(Q\alpha\beta+\beta\alpha)/\sqrt{1+Q^2}$  $(\alpha\beta+Q\beta\alpha)/\sqrt{1+Q^2}$  ββ

3.1   3.0   2.9   2.8   2.7
ppm

αα  $(\alpha\beta+\beta\alpha)/\sqrt{2}$  $(\alpha\beta+\beta\alpha)/\sqrt{2}$  ββ

3.1   3.0   2.9   2.8   2.7
ppm

# "Virtual Coupling" Effects

An important generalization in this area is that the severity of the "virtual coupling" effects is very strongly dependent on $J_{AB}$ - if $J_{AB}$ is larger than $J_{AX}$ and $J_{BX}$ then the **X** part is profoundly changed (i.e. doublet to triplet). On the other hand, when $J_{AB}$ is smaller than $J_{AX}$ or $J_{BX}$ then the perturbations are much less dramatic, leading to small additional lines and minor errors in apparent coupling constants. A case of this type is provided by the three compounds below. The aromatic protons are well separated in **1** and **3** and thus are pretty much first order, but in **2** $H_A$ appears nearly on top of $H_B$. As a result, $H_X$ shows non-first order structure.
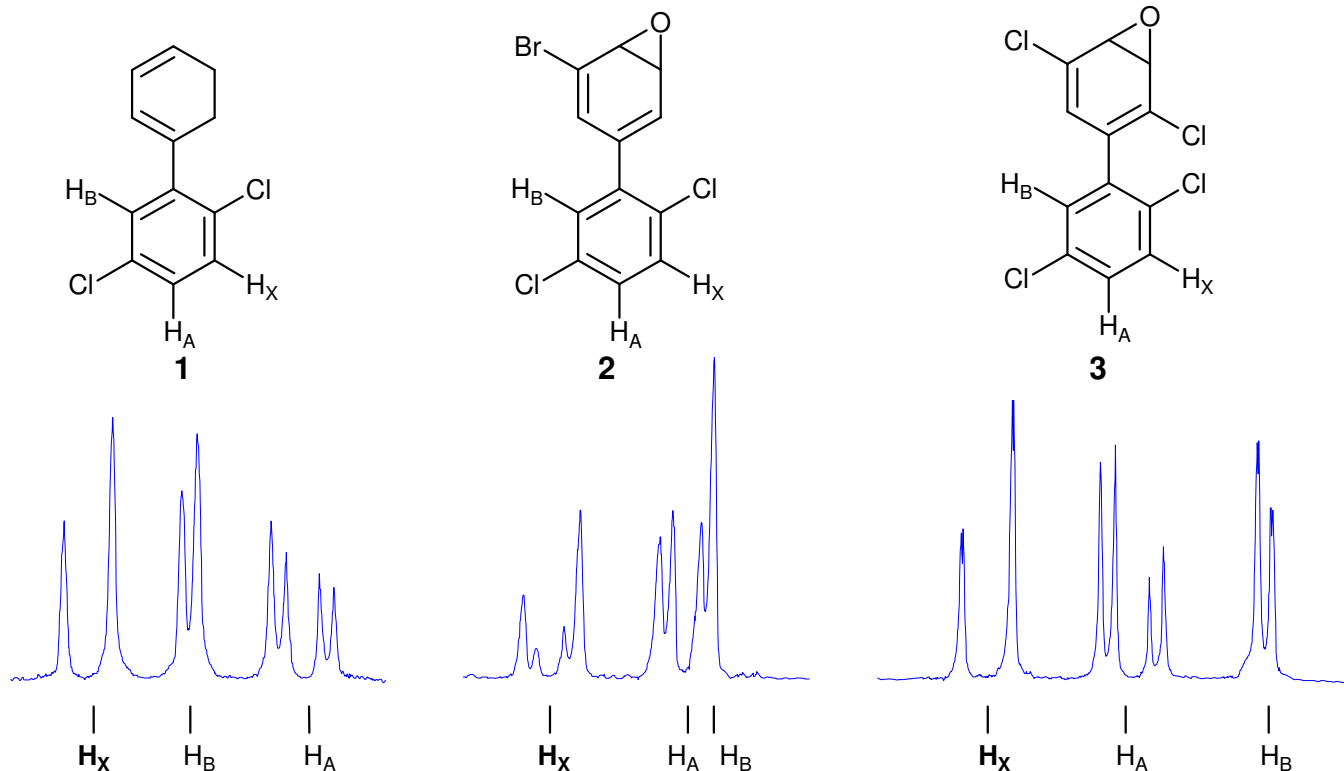


One of the main reasons that complex NMR spectra are simpler to interpret at higher field strengths is that many virtual coupling effects are ameliorated or disappear altogether as chemical shift differences (in Hz) become larger. Exceptions are AA'BB', AA'XX' patterns and more complicated analogs (such as **AA'BB'X**). These are always non-first order (if there is coupling between **A** and **A'** or **B** and **B'**) because they always satisfy the criteria for virtual coupling: **A** and **A'** have zero chemical shift at any field strength. If **A** and **A'** are also coupled to each other ($J_{AA'} > 0$) then the **A** and **B** protons, or any other protons coupled to **A** or **B** can give complex or misleading multiplets.

**What are those Impurities?** A student in the course brought me the NMR spectrum of acrolein shown below, with the question: why can't I get rid of the impurities, I've distilled the compound twice?

Acrolein: $C_3H_4O$
200 MHz $^1H$ NMR spectrum in $CDCl_3$
Source: R. R. Dykstra RRDI-257/Reich
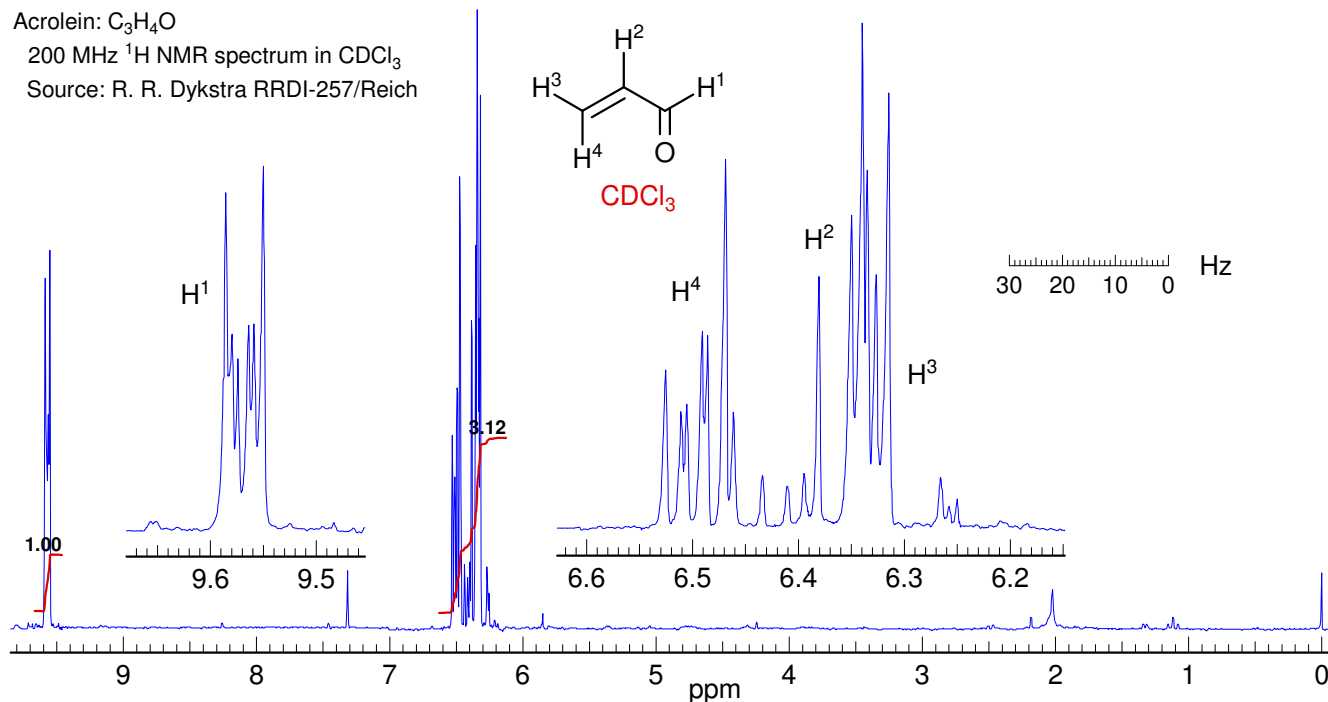


The answer? The compound is perfectly pure, as shown by its NMR spectrum in benzene-$d_6$, which is essentially first order. The problem with the spectrum in $CDCl_3$ is that two of the protons ($H^2$ and $H^3$) are nearly superimposed and are strongly coupled, so that all the others which are coupled to them become very complicated. Benzene, like other aromatic solvents, causes significant upfield shifts (especially in molecules with a high dipole moment, like this one) which removes the degeneracy and leads to an essentially first-order spectrum.

Acrolein: $C_3H_4O$
200 MHz $^1H$ NMR spectrum in benzene-$d_6$
Source: R. R. Dykstra/Reich
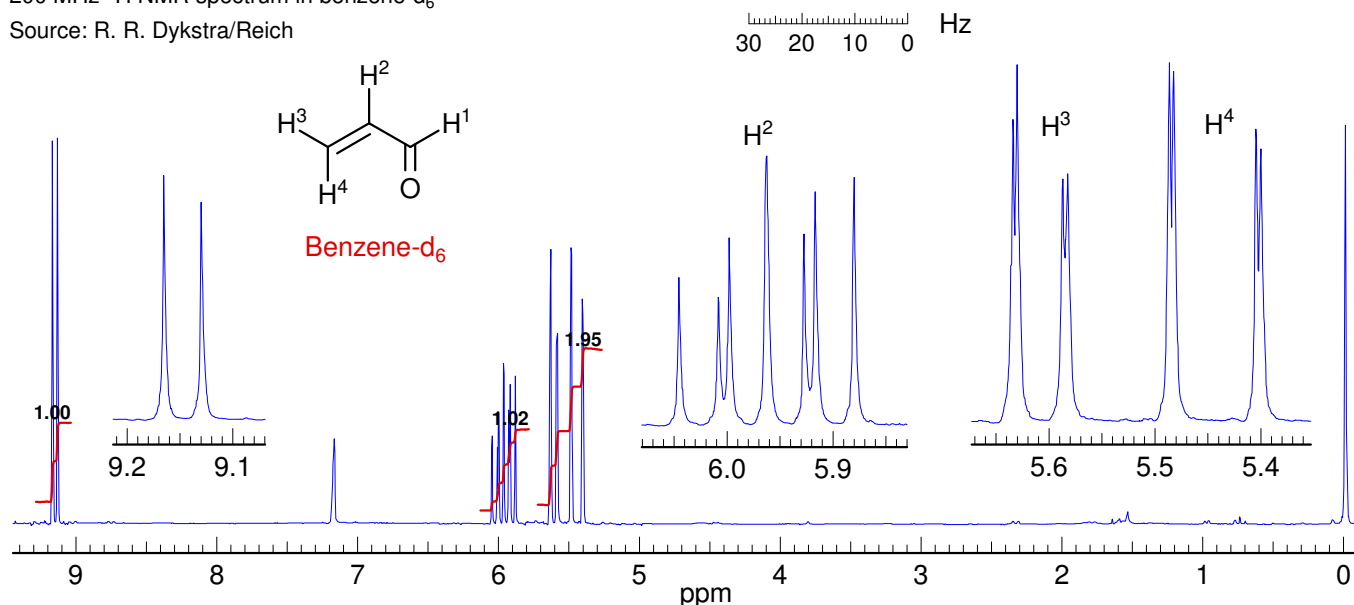


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**Exercise**: Use WINDNMR to simulate first the benzene-$d_6$ spectrum, and then the $CDCl_3$ spectrum (all you should need to do is adjust the chemical shifts). Which two protons are superimposed in the $CDCl_3$ spectrum?

**Is it the Right Stuff?** Accidental coincidences of chemical shifts and the resulting virtual coupling effects can lead to surprisingly deceptive NMR spectra, sufficiently so that the unwary researcher could conclude that a synthesis had failed. An interesting case is the phenyl region of the NMR spectrum below:



$C_{13}H_{17}NO$
300 MHz $^1$H NMR spectrum in CDCl$_3$.
Source: Alison Wendlandt/Stahl
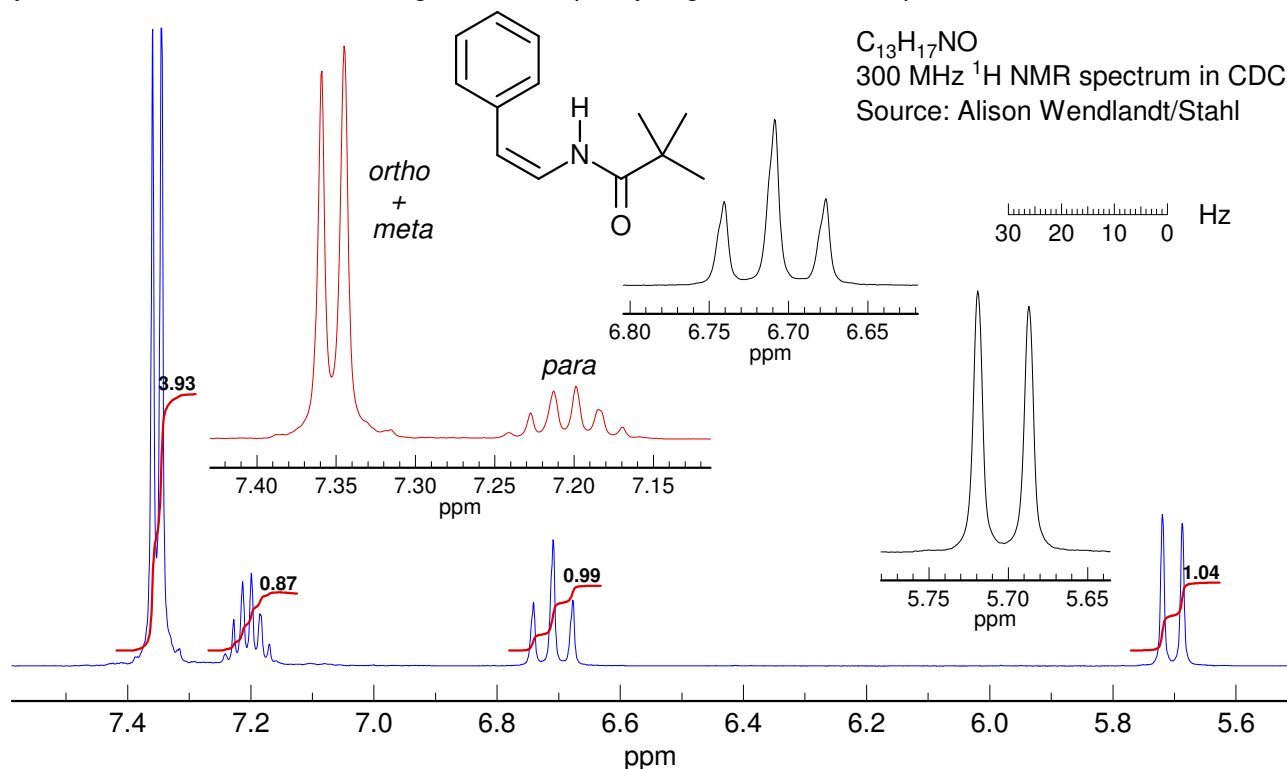
Taken at face value the aromatic region of the *cis* isomer looks like a 4H doublet and a 1H multiplet (pentet or sextet) with *J* of 4.3 Hz, hardly compatible with a monosubstituted phenyl group. Yet this is simply a phenyl group in which the *ortho* and *meta* protons accidentally have identical chemical shifts (or nearly so). Since they are strongly coupled to each other, the four protons behave as a unit, and the *para* proton appears to be equally coupled to all four, leading to the apparent doublet and pentet - a classical case of virtual coupling. The apparent coupling constant of 4.3 Hz is the average of the *ortho* and *meta* couplings.

In the trans isomer below the *meta* and *para* protons are a little further apart, and easily recognized for what they are (although still not even close to a first order pattern).
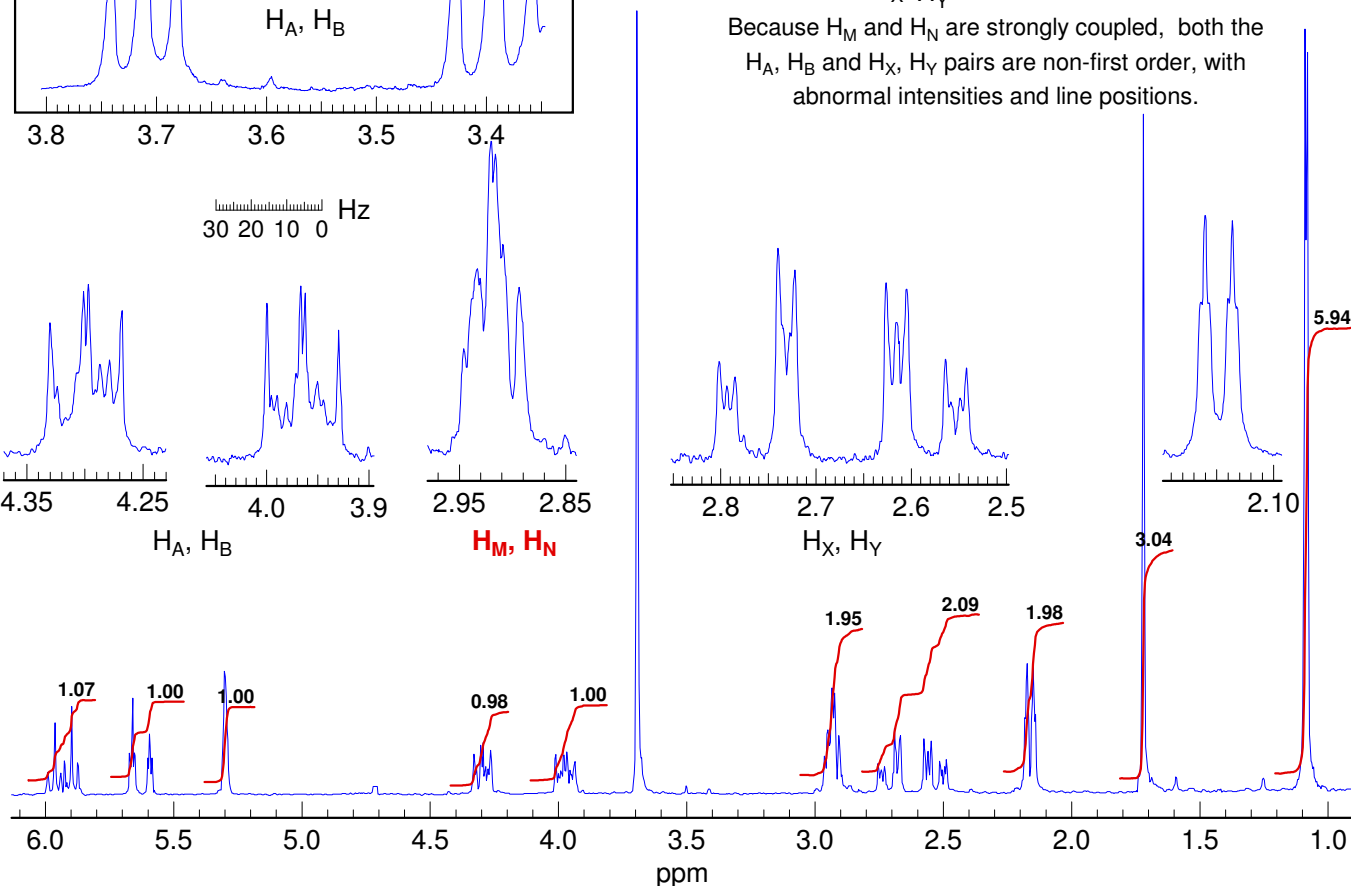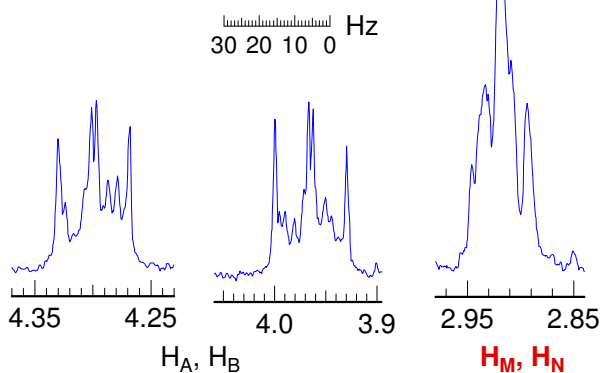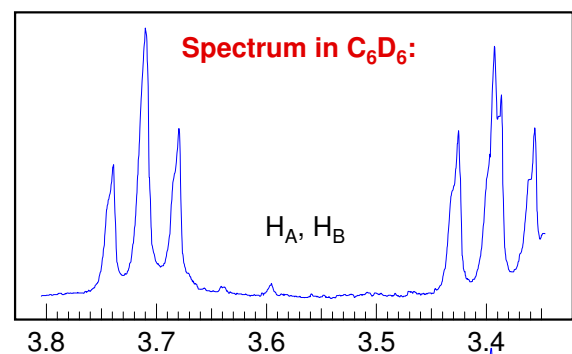


$C_{13}H_{17}NO$
300 MHz $^1$H NMR spectrum in CDCl$_3$.
Source: Alison Wendlandt/Stahl
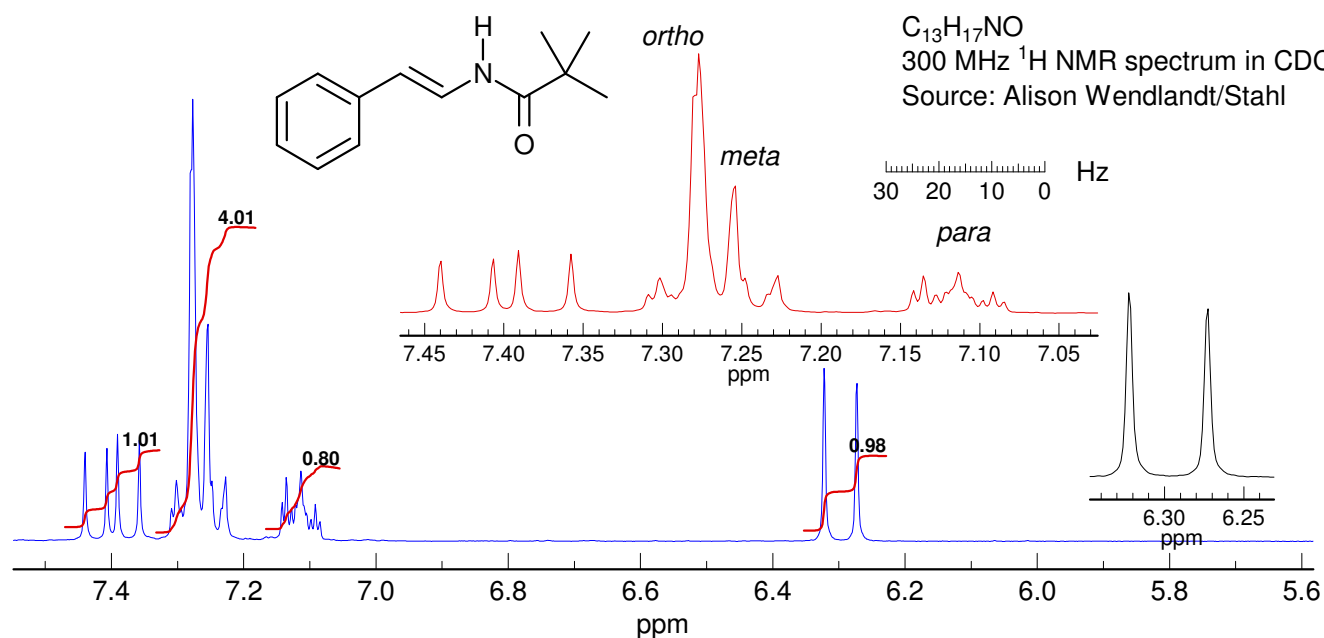
**Why is my Spectrum so Ugly?** In this spectrum there is an accidental superposition of two protons, **H_M** and **H_N**, which are coupled to each other. All of the protons coupled to these two, **H_A**, **H_B**, **H_X**, and **H_Y**, show strongly second order distorted multiplets, with extra lines and non-centrosymmetric structure. A simple method to address this kind of problem is to take the spectrum in an aromatic solvent (or even just add a few drops of benzene-d$_6$ or pyridine to the sample), which in many cases moves the protons around enough that the second-order effects are reduced or eliminated. When the spectrum is taken in benzene, **H_M** and **H_N** are shifted away from each other, and **H_A** and **H_B** now show more or less first order multiplets.

C

270 MHz $^1$H NMR spectrum in CDCl$_3$
(Source: Margaret K. Jones/S. D. Burke)



**Spectrum in C$_6$D$_6$:**

H$_A$, H$_B$

3.8   3.7   3.6   3.5   3.4
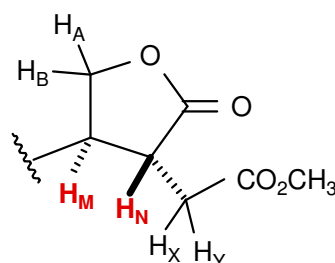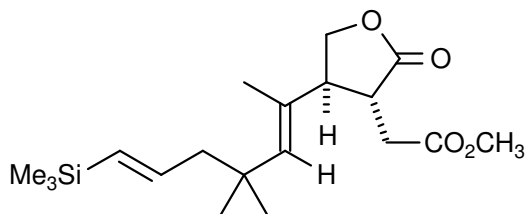
Because H$_M$ and H$_N$ are strongly coupled, both the H$_A$, H$_B$ and H$_X$, H$_Y$ pairs are non-first order, with abnormal intensities and line positions.

30 20 10 0   Hz

4.35   4.25    4.0   3.9    2.95   2.85    2.8   2.7   2.6   2.5    2.10

H$_A$, H$_B$    **H$_M$, H$_N$**    H$_X$, H$_Y$

5.94

3.04

1.95    2.09    1.98

1.07   1.00   1.00    0.98    1.00

6.0      5.5      5.0      4.5      4.0      3.5      3.0      2.5      2.0      1.5      1.0

ppm

# Methyl Region  AMX$_3$ --->  ABX$_3$  --->  AA'X$_3$

Methyl groups usually give reliably simple multiplets in NMR spectra. However, if a methyl group is coupled to a proton which is part of a strongly-coupled system, then its NMR signal can give complex and misleading information

In these simulated spectra, the methyl group is coupled to H$_A$, which is in turn coupled to H$_B$.  When the chemical shift of H$_A$ and H$_B$ become close, then all signals become second order.

C—C—CH$_3$
H$_B$ H$_A$

$J_{AB}$ = 7.5
$J_{A-CH3}$ = 7.5
$J_{B-CH3}$ = 0

Vary δ

$\nu_{AB}$ = 0 Hz

$\nu_{AB}$ = 1 Hz

$\nu_{AB}$ = 2 Hz

$\nu_{AB}$ = 4 Hz

$\nu_{AB}$ = 6 Hz

$\nu_{AB}$ = 10 Hz

$\nu_{AB}$ = 14 Hz

$\nu_{AB}$ = 20 Hz

$\nu_{AB}$ = 30 Hz

B    A                                    CH$_3$
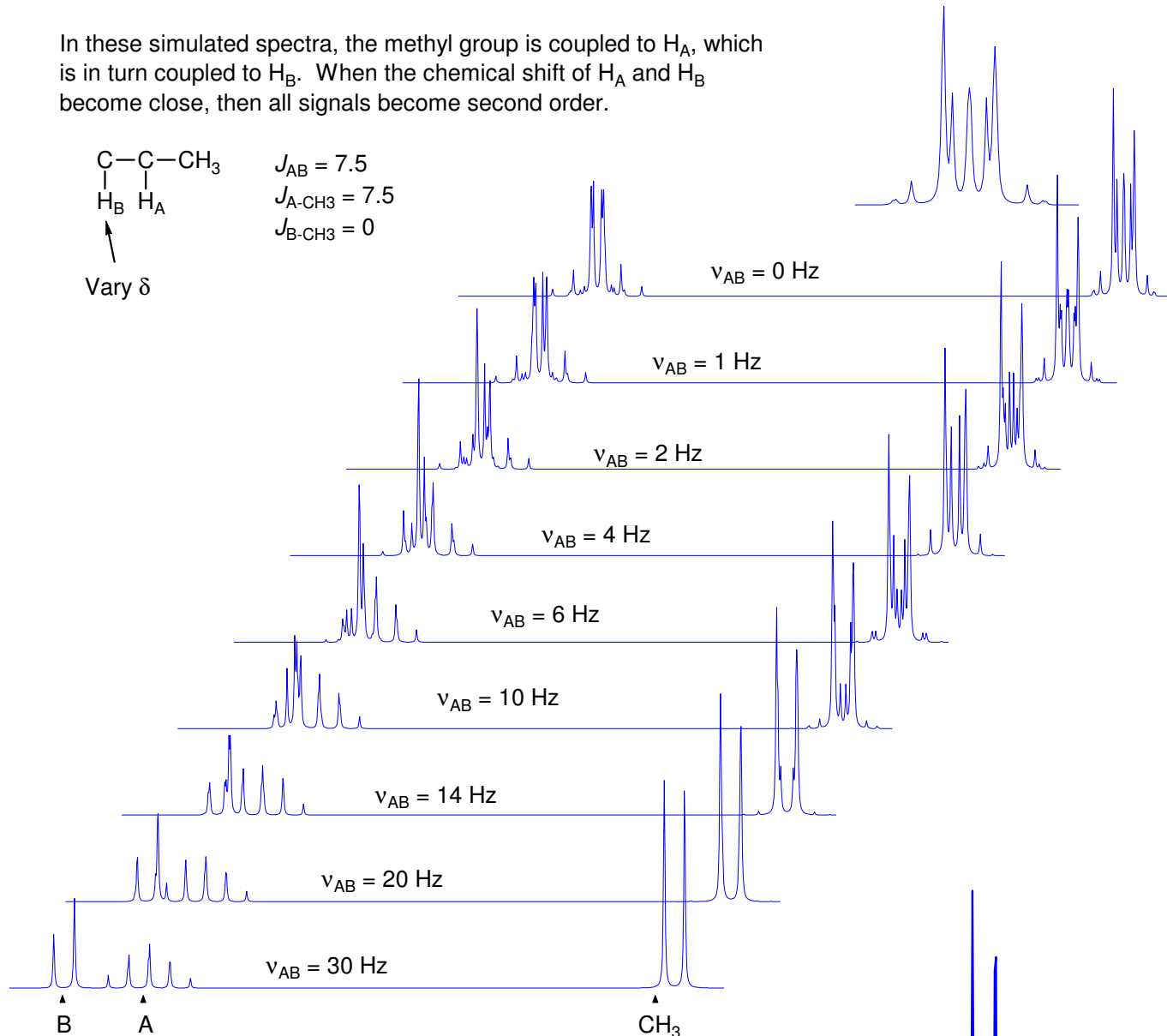
300 MHz $^1$H NMR spectrum
Source: Aldrich NMR Library

In this compound there is a small chemical shift difference between H$^2$ and H$^{3t}$ (Δν close to $J$) which leads to complicated multiplets for H$^{3c}$ and the methyl group (as well as for H$^2$ and H$^{3t}$).

H$^2$        H$^{3t}$

H$^{3c}$

H$^{3c}$    H$^{3t}$  H$^2$  CH$_3$

3.3    3.2    3.1    3.0    2.9    2.8    2.7    2.6
ppm

1.55        1.40
ppm