

Density Matrix – Second Order Spectra

BCMB/CHEM 8190

Operators in Matrix Notation

If we stay with one basis set, properties vary only because of changes in the coefficients weighting each basis set function

$$\mu_x = \gamma(h/2\pi) \langle \psi | \mathbf{I}_x | \psi \rangle$$

$$\psi = c_1 \alpha\alpha + c_2 \alpha\beta + c_3 \beta\alpha + c_4 \beta\beta = \sum_j c_j \phi_j$$

$$\langle \psi | \mathbf{I}_x | \psi \rangle = \sum_{j,k} c_j^* c_k \langle \phi_j | \mathbf{I}_x | \phi_k \rangle$$

We need calculate $\langle \phi_j | \mathbf{I}_x | \phi_k \rangle$ only once if we stay with this basis set – these can be put in a $n \times n$ matrix.

$$\text{Matrix equivalent: } \langle \psi | \mathbf{I}_x | \psi \rangle = (c_1, c_2, \dots)^* \begin{bmatrix} & & & \\ & \mathbf{I}_x & & \\ & & & \\ & & & \end{bmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \end{pmatrix}$$

Special Case: Pauli Spin Matrices

$$|\mathbf{I}_x| = \begin{vmatrix} 0 & 1/2 \\ 1/2 & 0 \end{vmatrix}$$

Note: $\langle \alpha | \mathbf{I}_x | \alpha \rangle = 1/2 \langle \alpha | \beta \rangle = 0$

$\langle \alpha | \mathbf{I}_x | \beta \rangle = 1/2 \langle \alpha | \alpha \rangle = 1/2$

$$|\mathbf{I}_y| = \begin{vmatrix} 0 & -i/2 \\ i/2 & 0 \end{vmatrix}$$

$$|\mathbf{I}_z| = \begin{vmatrix} 1/2 & 0 \\ 0 & 1/2 \end{vmatrix}$$

How do they work? Try something we know: $\mathbf{I}_x | \alpha \rangle = 1/2 \beta$

$$\begin{vmatrix} 0 & 1/2 \\ 1/2 & 0 \end{vmatrix} \begin{vmatrix} 1 \\ 0 \end{vmatrix} = \begin{vmatrix} 0 \\ 1/2 \end{vmatrix} = 1/2 \begin{vmatrix} 0 \\ 1 \end{vmatrix} = 1/2 \beta$$

Operators are a matrix of numbers, Spin functions a vector of numbers

Larger Collections of Spin 1/2 Nuclei

$$\mathbf{I}_{Ax} = \begin{array}{c} \alpha\alpha \\ \beta\alpha \\ \alpha\beta \\ \beta\beta \end{array} \begin{array}{c} \left| \begin{array}{cccc} ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \\ ? & ? & ? & ? \end{array} \right| \end{array}$$

$\alpha\alpha \quad \beta\alpha \quad \alpha\beta \quad \beta\beta$

$\langle \alpha\alpha | \mathbf{I}_{Ax} | \beta\alpha \rangle =$
 $\langle \alpha\alpha | \frac{1}{2} | \alpha\alpha \rangle = \frac{1}{2}$

$$= \begin{array}{c} \left| \begin{array}{cccc} 0 & 1/2 & 0 & 0 \\ 1/2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1/2 \\ 0 & 0 & 1/2 & 0 \end{array} \right| \end{array} \quad \mathbf{I}_{Xx} = \begin{array}{c} \left| \begin{array}{cccc} 0 & 0 & 1/2 & 0 \\ 0 & 0 & 0 & 1/2 \\ 1/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \end{array} \right| \end{array}$$

Easier way: direct products: $\mathbf{E} \otimes \mathbf{I}_{Ax}$ with 2X2 matrices

Density Matrices and Observables for an Ensemble of Spins

Expectation values pertain to single spin properties; we observe net behavior of an ensemble of spins. For a particular system (two spin $\frac{1}{2}$ nuclei) operator representations are the same; all variations are in basis set coefficients. We need to average over these coefficients.

$$\overline{\langle \psi | \mathbf{I}_x | \psi \rangle} = (\overline{c_1, c_2, \dots})^* \begin{bmatrix} \\ \mathbf{I}_x \\ \end{bmatrix} \begin{pmatrix} \overline{c_1} \\ \overline{c_2} \\ \vdots \end{pmatrix} = \sum_{j,k} \overline{c_j^* c_k} \mathbf{I}_{x_{jk}}$$

Products of averaged coefficients can also be collected and used in matrix form. This is called a density matrix, ρ .

$$\overline{\langle \psi | \mathbf{I}_x | \psi \rangle} = \text{Tr} \overline{|c_j c_k^*|} | \mathbf{I}_x | = \text{Tr} | \rho | | \mathbf{I}_x |$$

Solving for the Time Dependence of

ρ

Our observables are time dependent (magnetization precesses).
All time dependence can also be put in basis set coefficients, or in coefficient products of the density matrix.

Schrodinger's time dependent equation ($\mathbf{H} \psi(t) = -i (\hbar/2\pi) d(\psi(t))/dt$)
Allows us to solve for dc_j/dt , $d/dt (c_j c_k^*) = c_j (dc_k^*/dt) + (dc_j^*/dt) c_k$

Result in terms of a density matrix is Liouville – von Neuman eq.

$$d/dt | \rho | = i / (\hbar/2\pi) \{ | \rho | | \mathbf{H} | - | \mathbf{H} | | \rho | \}$$

Implications: If we know ρ at any time (equilibrium at time 0) and know the Hamiltonian (\mathbf{H}), we can solve for ρ at any time, and calculate any observable as the $\text{Tr} | \rho | | \mathbf{O} |$ (\mathbf{O} is any operator).

Test: Does X Magnetization Precess in B_0 ?

- What elements of ρ dictate x magnetization?

$$\langle I_x \rangle = \text{Tr} [\rho] [I_x] - \text{examine spin } \frac{1}{2} \text{ case}$$

$$= \text{Tr} \begin{bmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{bmatrix} \begin{bmatrix} 0 & 1/2 \\ 1/2 & 0 \end{bmatrix} = 1/2\rho_{12} + 1/2\rho_{21}$$

- Therefore, consider $\rho(0) = \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix}$

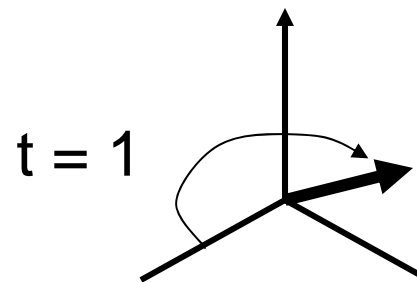
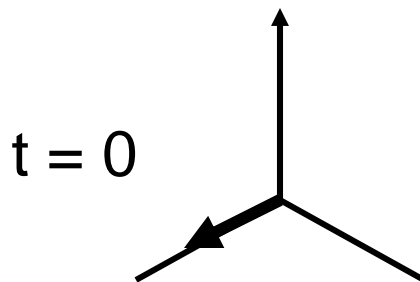
- What is H ?, $H = -(\gamma\hbar B_0/(2\pi))I_z = -(\gamma\hbar B_0/(2\pi)) \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix}$

- $\mathbf{d}/\mathbf{dt} \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix} =$

$$\mathbf{i}/\hbar(-\gamma\hbar\mathbf{B}_0) \left\{ \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix} \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} - \begin{bmatrix} 1/2 & 0 \\ 0 & -1/2 \end{bmatrix} \begin{bmatrix} 0 & \rho_{12} \\ \rho_{21} & 0 \end{bmatrix} \right\}$$

Consider evolution of one element

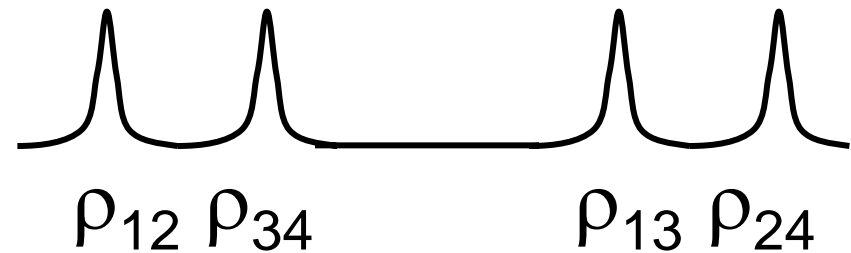
- $(d/dt)\rho_{12}(t) = i\gamma B_0(-\frac{1}{2} \rho_{12}(t) - \frac{1}{2} \rho_{12}(t)) = i\omega_0 \rho_{12}(t)$
- Solution: $\rho_{12}(t) = \rho_{12}(0) \exp(-i\omega_0 t)$ or:
 $= \rho_{12}(0) (\cos(\omega_0 t) - i \sin(\omega_0 t))$
- Same happens for $\rho_{21}(t)$
- hence elements corresponding to x magnetization precess



Density Matrix Simulation of 2nd Order Spectra

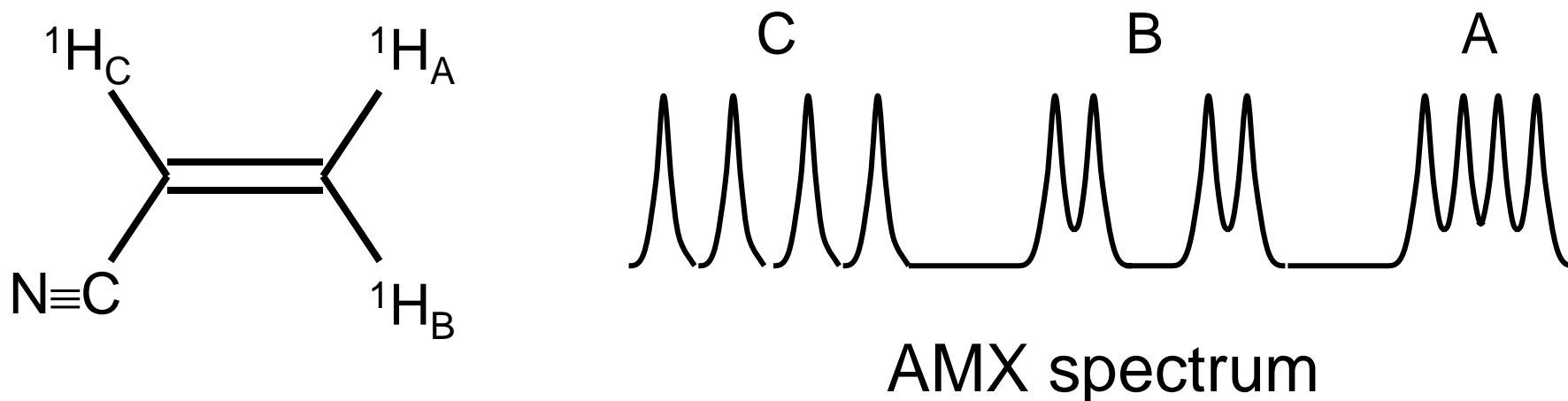
- For two spins basis set is: $\alpha\alpha, \alpha\beta, \beta\alpha, \beta\beta$

$$\rho = \begin{bmatrix} \rho_{11} & \rho_{12} & \rho_{13} & \cdot \\ \rho_{21} & \rho_{22} & \cdot & \cdot \\ \rho_{31} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{bmatrix}$$



- $\rho_{12}, \rho_{21}, \dots$ are associated with lines in an AX spectrum
- Don't have to have a 1:1 association if ψ is not an eigen function of \mathbf{H} .
- $c_i\phi_i + c_j\phi_j$ may evolve coherently as one line – ie ρ_{12}, ρ_{21} , are mixed
- Calculation of Mx still works!

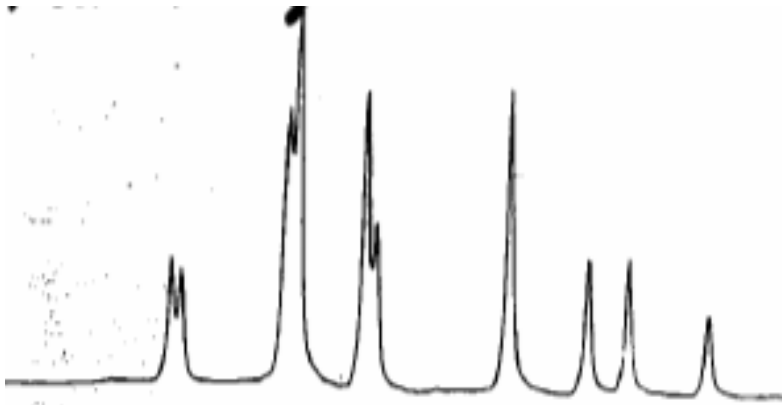
Second Order Spectrum Example: Acetonitrile



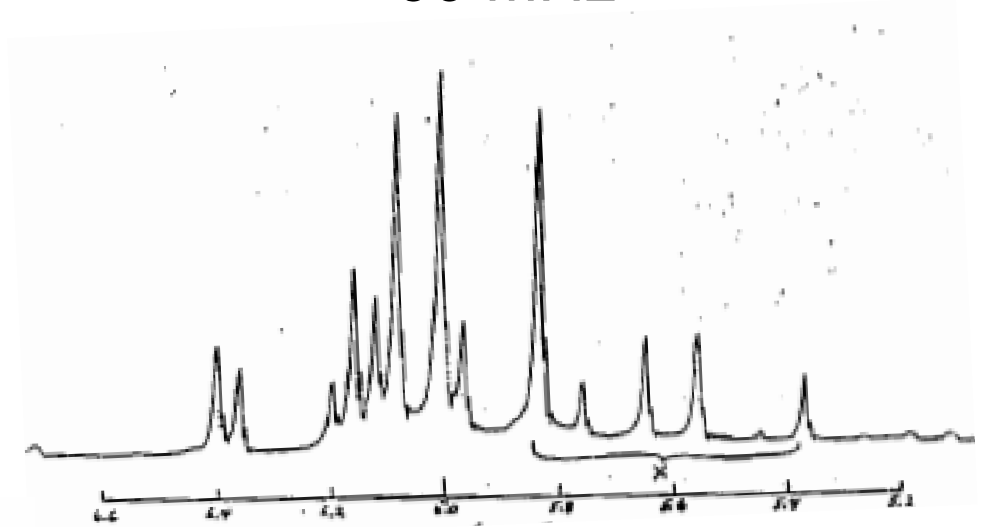
- Twelve lines, all equal intensities
- $J_{\text{AB}} = -2 \text{ Hz}$, $\delta_{\text{C}} = 5.6 \text{ ppm}$
- $J_{\text{AC}} = 11 \text{ Hz}$, $\delta_{\text{B}} = 6.1 \text{ ppm}$
- $J_{\text{BC}} = 16 \text{ Hz}$, $\delta_{\text{A}} = 6.3 \text{ ppm}$
- Actual spectrum is more complex, field dependent

Field dependence of second order spectra

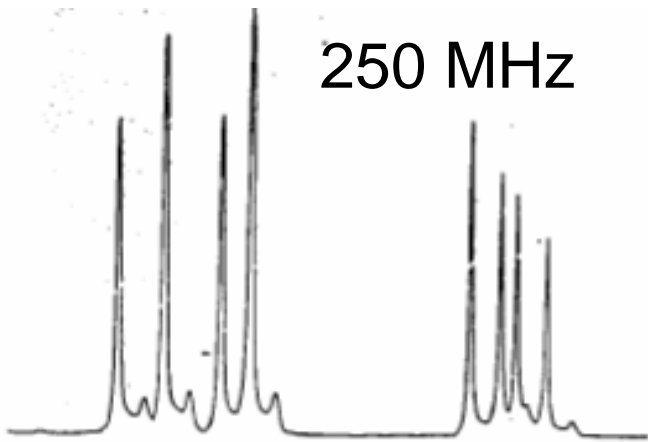
60 MHz



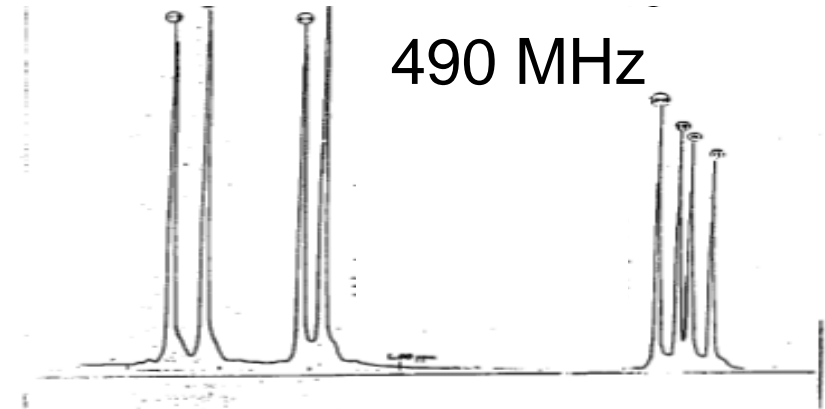
90 MHz



250 MHz



490 MHz



Line intensities: density matrix elements and transition probabilities

- $\rho_{kl} = c_k^* c_l$; $c_k^* c_l$ is the probability of being in state k
- $c_k^* c_k c_l^* c_l$ is the probability of starting in k and ending in l
- If we know we start in k, $c_k^* c_k = 1$, and just need c_l
- from Schrodinger equation: $dc_l/dt \propto \langle \phi_l | \mathbf{H}' | \phi_k \rangle$
- Integrating from $t = 0$ and combining with c_l^*
- $P_{k \rightarrow l} \propto |\langle \phi_l | \mathbf{H}' | \phi_k \rangle|^2$... gives line intensities

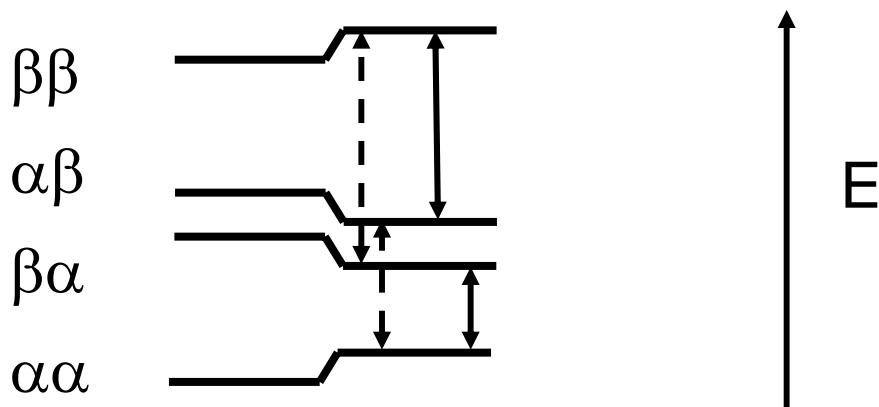
Understanding second order spectra

- A_2 vs AX or H_2O



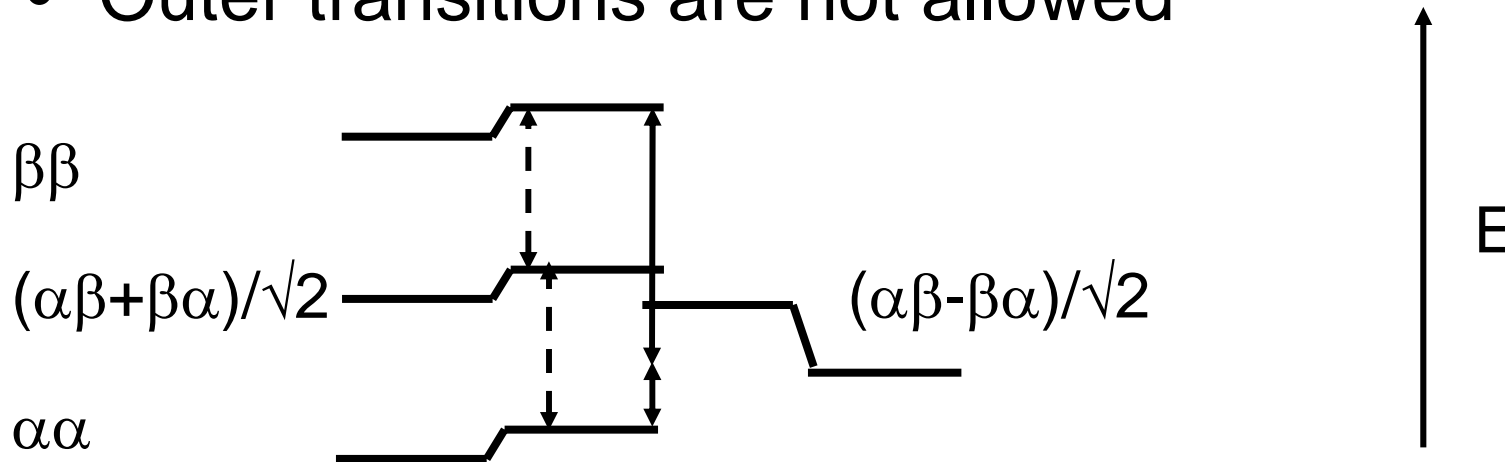
- For HF ..

- $P_{\beta\beta \rightarrow \alpha\beta} \propto |\langle \beta\beta | \gamma B_1 (I_{x1} + I_{x2}) | \alpha\beta \rangle|^2$; $I_x = (I_+ + I_-)/2$
- this is finite and same for all P_{ij}
- implies same line intensities



For an A_2 system:

- $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, $\beta\beta$ are not good wave functions
- Imply distinguishability
- Use: $\alpha\alpha$, $(\alpha\beta+\beta\alpha)/\sqrt{2}$, $(\alpha\beta-\beta\alpha)/\sqrt{2}$, $\beta\beta$
- $\langle \beta\beta | \gamma B_1 (I_{x1} + I_{x2}) | (\alpha\beta+\beta\alpha)/\sqrt{2} \rangle = (\frac{1}{2} + \frac{1}{2})/\sqrt{2}$
- $\langle \beta\beta | \gamma B_1 (I_{x1} + I_{x2}) | (\alpha\beta-\beta\alpha)/\sqrt{2} \rangle = (\frac{1}{2} - \frac{1}{2})/\sqrt{2} = 0$
- Outer transitions are not allowed

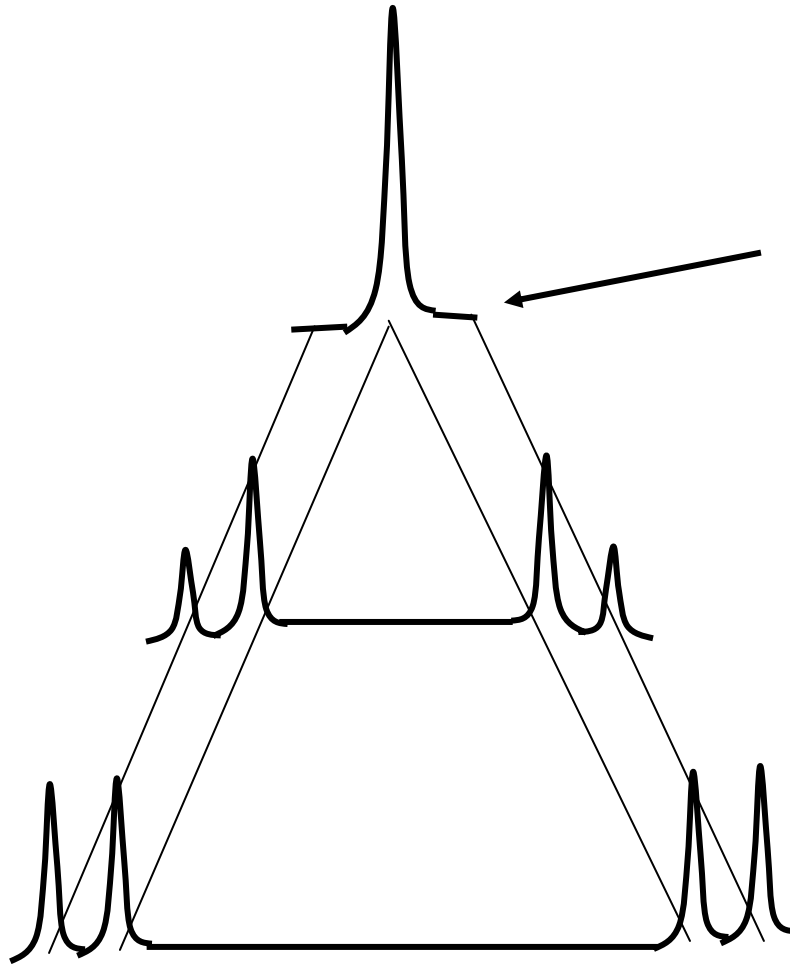


Intermediate behavior of 2nd order spectra

- H₂O

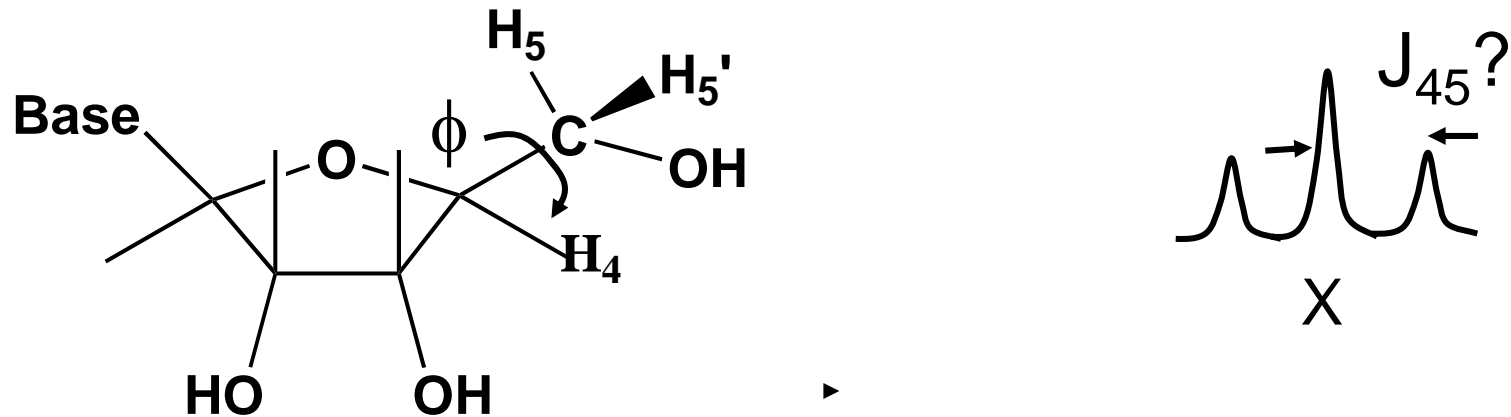
- AB

- HF



Outer lines are not
Observed
Couplings still exist

Second order effects can be important



- Coupling of H₄ and H₅, H₅' protons in ribose rings – an ABX system
- Karplus equation might be used to deduce torsion angle, but can couplings be measured from multiplet?
- For degenerate H₅, H₅', see a triplet, but splitting is $(J_{45} + J_{45'})/2$
- Cannot conclude that $J_{45} = J_{45}'$
- Answer: simulate spectra
- See: S.A Smith, J. Magn Res, **166**, 75 (1994); M.Veshtort, R.G.Griffin, J Magn. Res., **178**, 248-282 (2006)