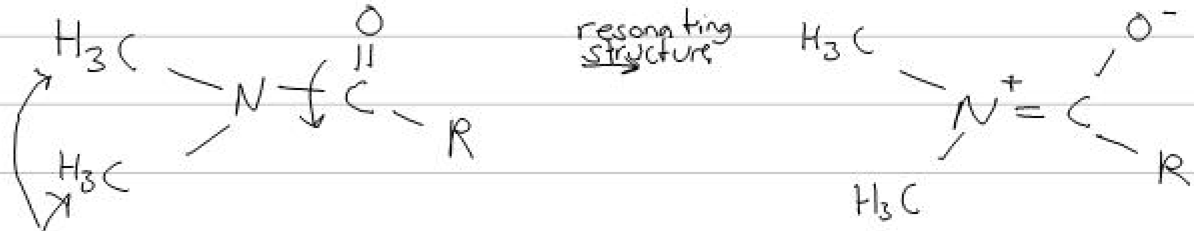
Slichter



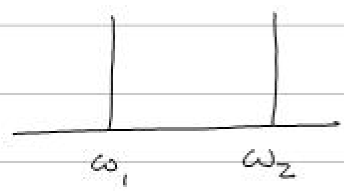
$R = H$ or CH_3

These protons will have slightly different chemical shifts.

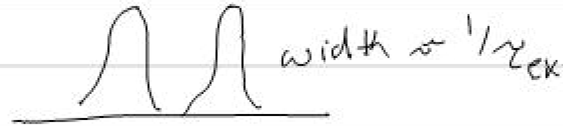
H_3C-CH_2-OH

$HO-CH_2-CH_3$

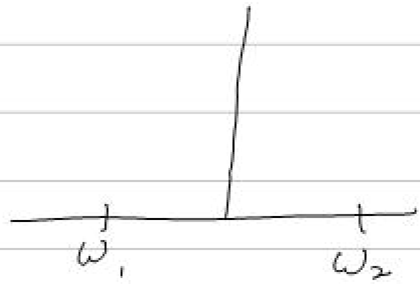
No exchange



FID will die more quickly if exchange occurs. The lines will broaden.



Motional Averaging would eventually give us,



The linewidth $\delta\omega = M_2 J(0) = M_2 \tau_{ex}$

second moment

$$M_2 = \int (\omega - \bar{\omega})^2 f(\omega)\, d\omega \text{ , so}$$

$$\delta\omega = \left(\frac{\omega_a - \omega_b}{2}\right)^2 \tau_{ex}$$

Modify Bloch equations for,

$$M_+ = M_x + i M_y$$

not second moment

$$\frac{\partial M_2}{\partial t} = i\omega_2 M_2 - R M_a$$

$$R \leftarrow \frac{1}{T_2}$$

$$\frac{\partial M_1}{\partial t} = i\omega_1 M_1 - R M_1$$

Let $k_{12} = \frac{\text{probability}}{\text{time}}$ that $1 \to 2$.

~~K_{21}~~ $K_{21} = \frac{\text{prob}}{\text{time}}$ $2 \to 1$.

So,

$$\frac{\partial M_1}{\partial t} = i\omega_1 M_1 - RM_1 - K_{12} M_1 + K_{21} M_2,$$

and for M_2.

At some time, N_1 N_2

$$\frac{dN_1}{dt} = -\frac{dN_2}{dt} = -K_{12} N_1 + K_{21} N_2$$

These are ≈ 0 in equilibrium.

So, $\frac{K_{21}}{K_{12}} = \frac{N_1^{eq}}{N_2^{eq}}$

~~For~~ For our system, $K_{21} = K_{12} = K$.

To decouple our different equations, look for eigensolutions.

Assume $M_1 = M_{1_0} e^{i\omega t}$, &c. for M_2.

Substituting,

$$i\omega M_1 = i\omega_1 M_1 - RM_1 - KM_1 + KM_2, \quad \&c.$$

Rearranging

$$0 = [-i(\omega - \omega_1) - (R+K)]M_1 + KM_2$$

$$0 = KM_1 + [-i(\omega - \omega_2) - (R+K)]M_2$$

This will only have solutions if the determinant of this matrix vanishes.

$$\omega = \frac{a+b}{2} + i(R) + ik \pm \frac{1}{(-2)}\sqrt{(a-b)^2 - 4k^2}$$

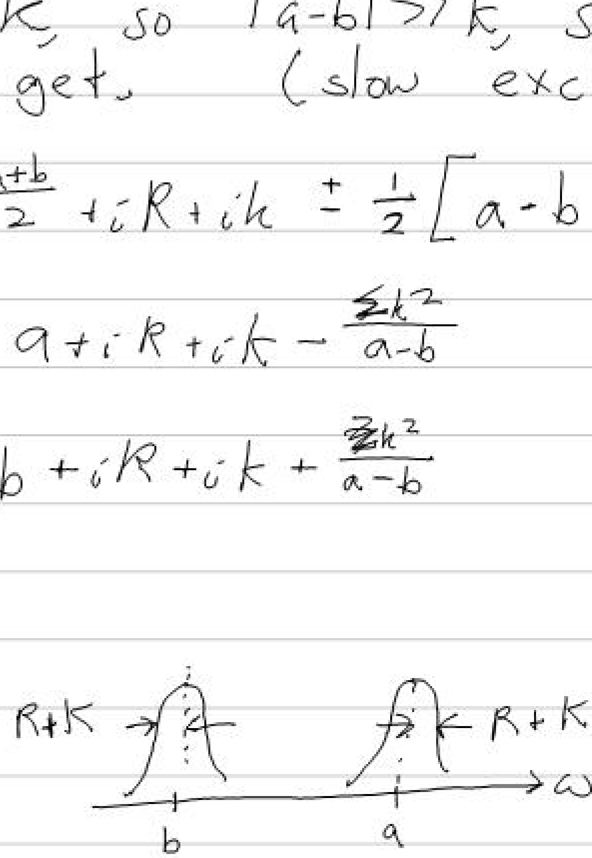
$a = \omega_1$, $b = \omega_2$, say $a > b$.

Suppose the chemical shift difference is $\gg k$, so $|a-b| \gg k$, so $(a-b)^2 \gg k^2$. We get. (slow exchange limit)

$$\omega = \frac{a+b}{2} + iR + ik \pm \frac{1}{2}\left[a-b - \frac{2k^2}{a-b}\right]$$

$$\omega_+ = a + iR + ik - \frac{\cancel{2}k^2}{a-b}$$

$$\omega_+ = b + iR + ik + \frac{\cancel{2}k^2}{a-b}$$



Collect Data

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Our peaks $\overbrace{\text{are not}}^{\text{Collect Data}}$ really centered at a & b, but the correction term is small in the slow exchange limit.

Fast exchange limit, $k \gg a-b$, $k^2 \gg (a-b)^2$

Small Spin Packet

Get

$$\omega_+ = \frac{a+b}{2} + iR + 2ik \quad \text{- small}$$

$$\omega_- = \frac{a+b}{2} + iR + \frac{(a-b)^2}{8k}$$

this would appear to be very broad, could only see if you could start the magnetizations out of phase