

Chemical exchange

What happens if the ^1H spin changes its chemical environments during an NMR experiment?

Limiting cases

- Slow exchange
Spectra are the superposition of sub-spectra from each of the species present

$$\text{Condition:} \quad k < \Delta \quad \Delta = \Delta\delta \text{ or } J$$

k is the exchange rate

- Fast exchange
“Single” species NMR spectrum with averaged NMR parameters weighted by the relative populations

$$\text{Condition:} \quad k > 15\Delta \quad \Delta = \Delta\delta \text{ or } J$$

Between these limits

- Intermediate exchange
- Complex lineshape changes

Chemical exchange

- NMR timescale
 - rate of a process compared with an NMR parameter
- Simplifies NMR spectra
 - cyclohexane: axial/equatorial exchange

high temperature – single resonance

low temperature – complex AA'A"..BB'B"..

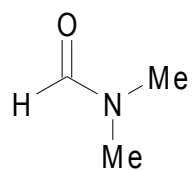
- Broadening as a consequence of uncertainty in the energy

If lifetime τ_A , energy uncertainty $\hbar \tau_A^{-1}$

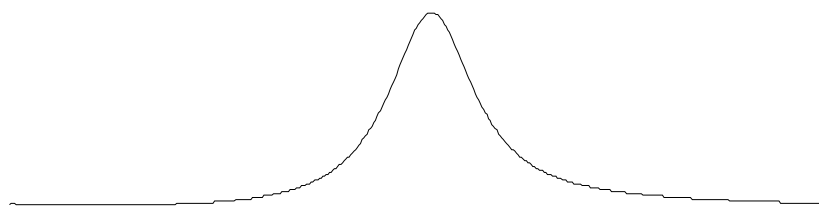
Since $E = h\nu$

Lines will be broadened by $(\pi\tau_A^{-1})$

Intermediate lineshapes



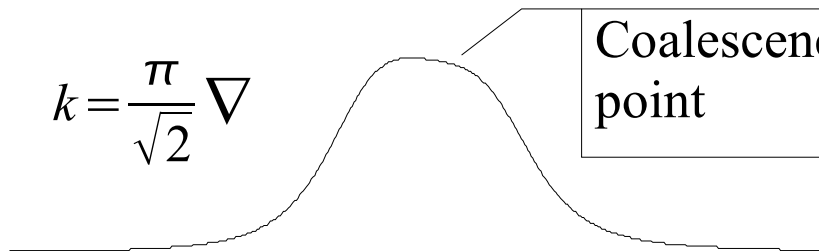
129°



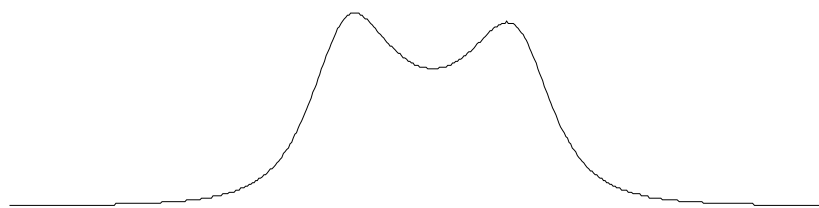
$$k = \frac{\pi}{\sqrt{2}} \nabla$$

Coalescence
point

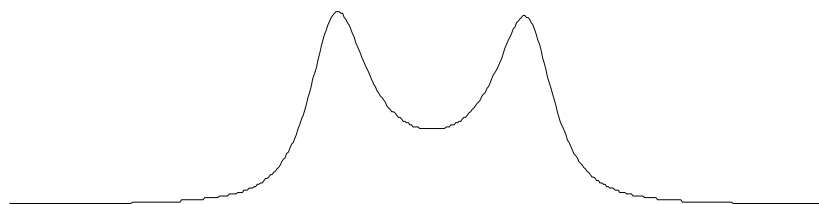
125°



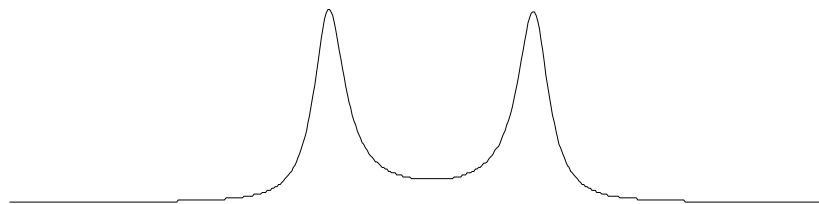
115°



106°



27°



0

100

200

300

400

500

Hz