

Dynamic Effects on NMR Spectra

“**NMR timescale**”: The ability of the NMR to distinguish between frequencies.

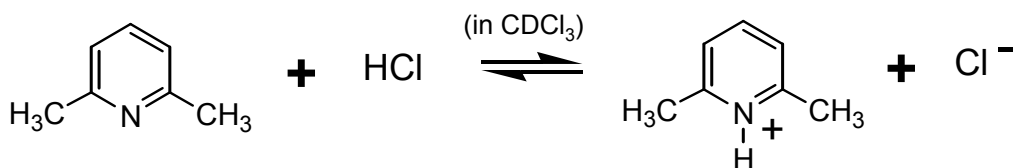
Depending on peakwidths & shift differences, this is nanoseconds-milliseconds.

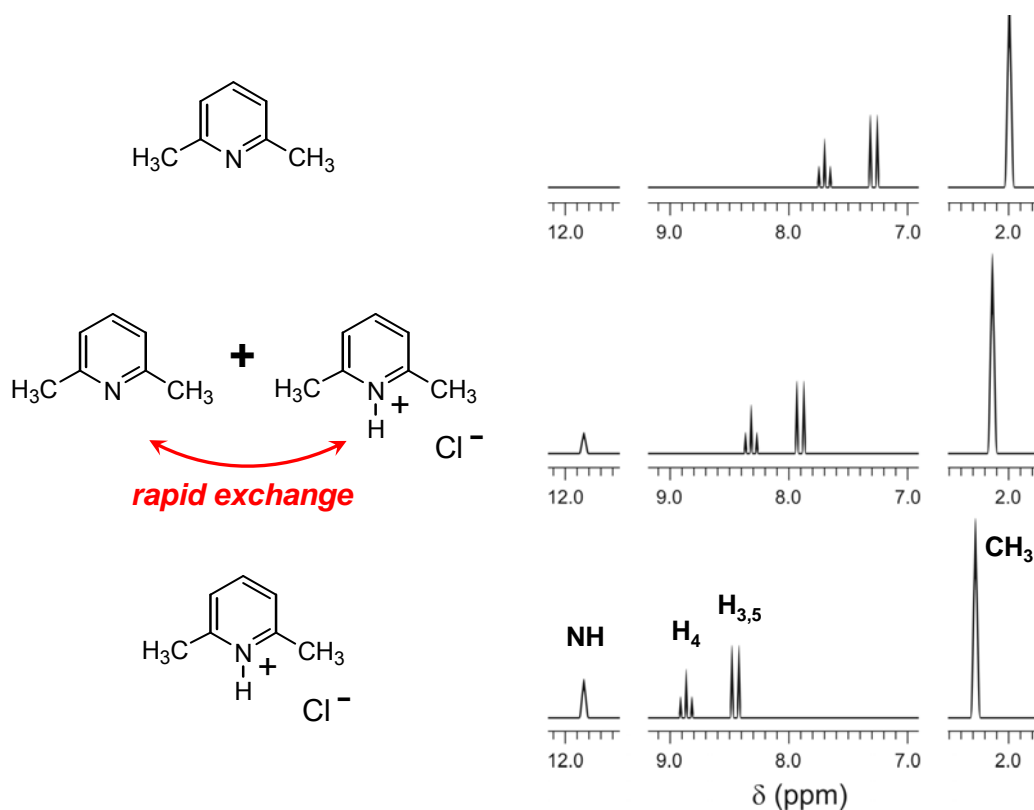
Dynamic Effects on NMR Spectra

For nuclei that undergo chemical exchange:

- If chemical exchange is **faster** than NMR timescale, then signals of components are **averaged**.

Example: Acid-base reactions.



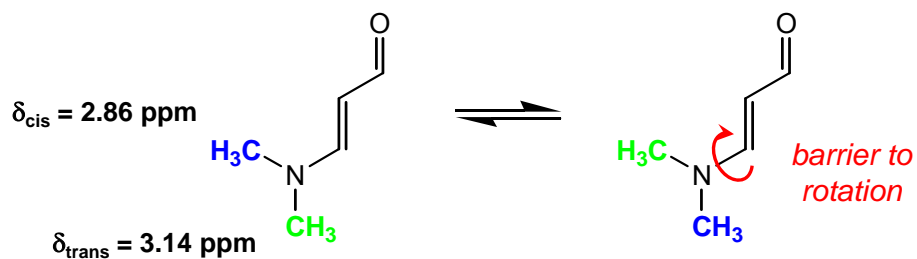


Measuring Dynamics with NMR

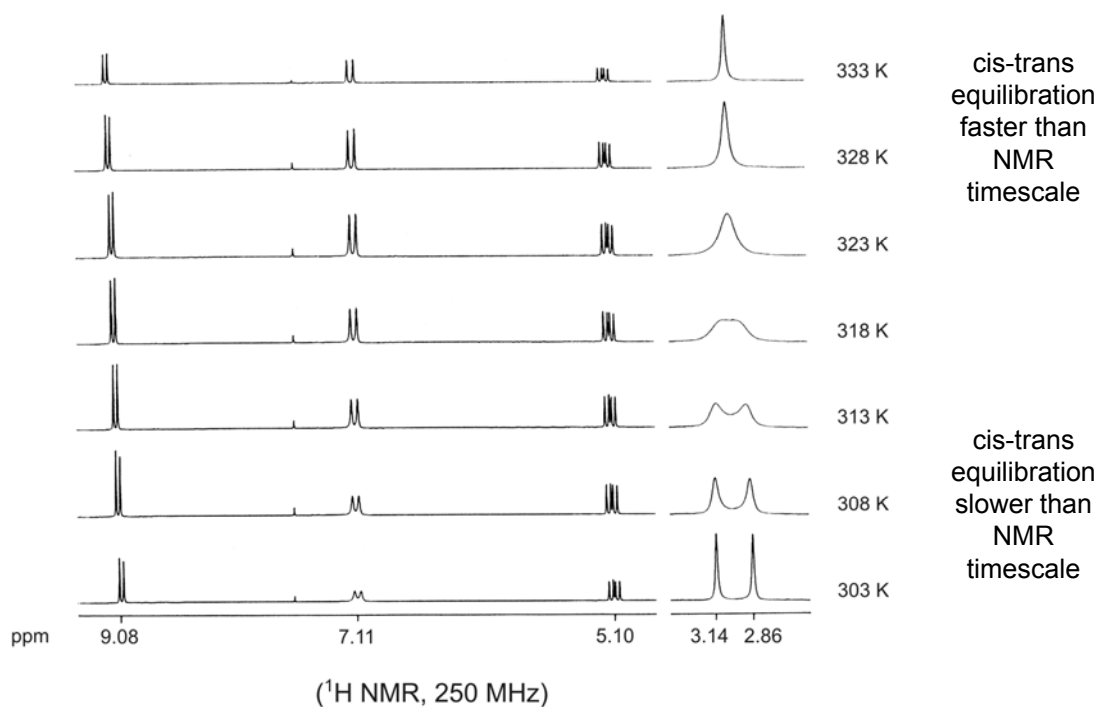
For nuclei that undergo chemical exchange:

- If chemical exchange is **slower** than NMR timescale, then all signals of components are observed.

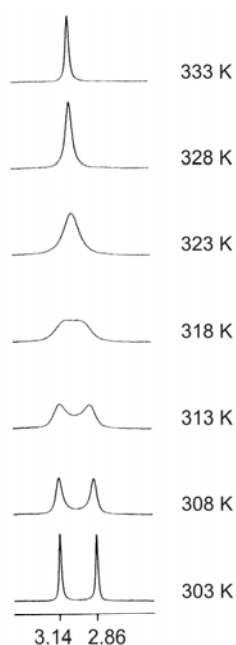
Example: Conformational equilibria.



Measuring Dynamics with NMR



Measuring Dynamics with NMR



Coalescence temperature:

Temperature where rate of exchange is identical to difference in peak frequency (where NMR is no longer able to distinguish frequencies).

← *coalescence temperature*
(T_c)

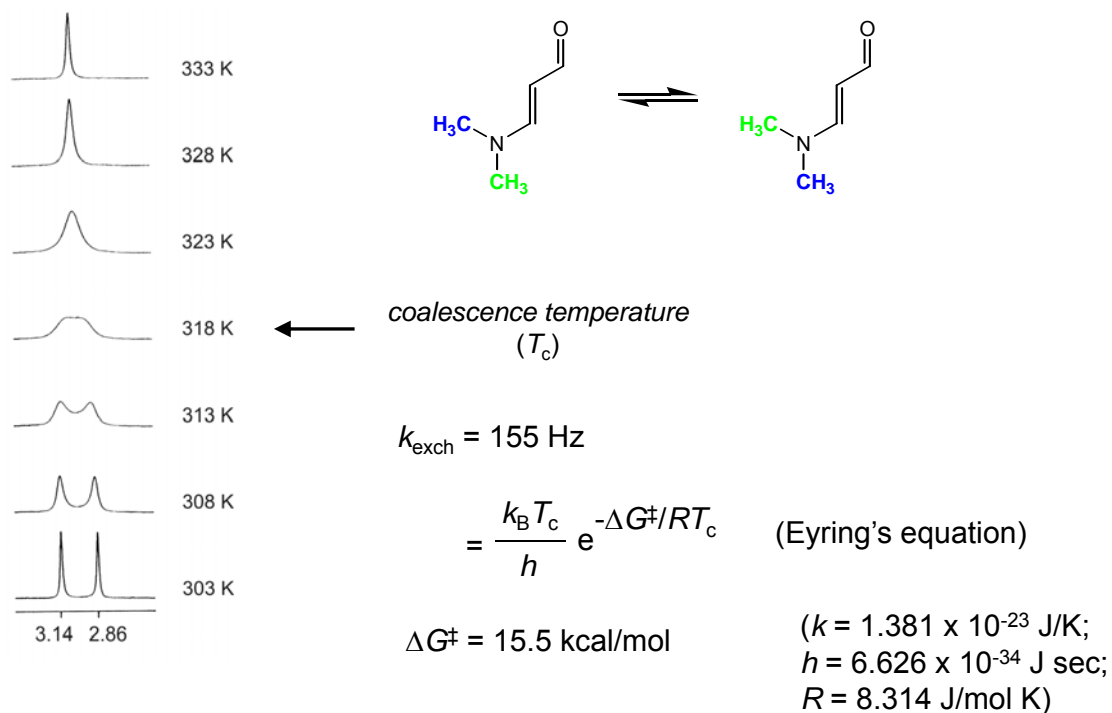
At the coalescence temperature,

$$k_{\text{exch}} = \pi(\Delta\nu)/\sqrt{2} = 2.22(\Delta\nu)$$

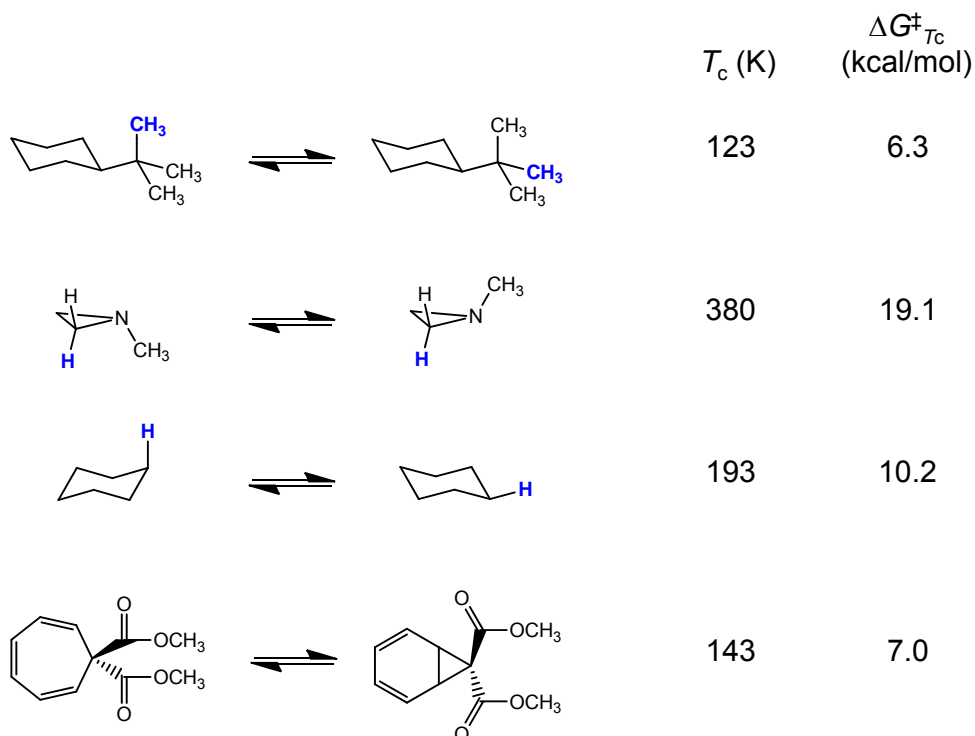
$$k_{\text{exch}} = 2.22(3.14 \text{ ppm} - 2.86 \text{ ppm})(250 \text{ Hz/ppm})$$

$$= 155 \text{ Hz}$$

Dynamic Effects on Chemical Shift



Dynamic Effects on Chemical Shift



Dynamic Effects on Chemical Shift

Very practical take-home lessons on dynamics:

1. Processes with intermediate exchange rates, or with many exchanging states, are sometimes broadened or poorly visible.

Example: Alcohol, amine, amide protons—anything that hydrogen bonds—sometimes smeared out.

2. Exchange in these protons also eliminates observed coupling.
3. Sometimes broadened resonances can be sharpened by heating or cooling sample (“VT” experiment).

Macromolecules and Tumbling

NMR requires rapid tumbling of bonded nuclei. (Can be due to molecular rotation or conformational freedom.)

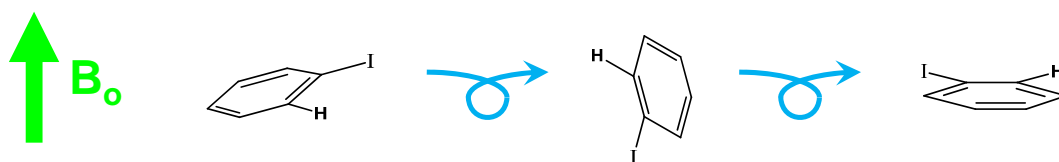
$$\text{rotational timescale } \Theta = \frac{\eta V}{kT} \propto \frac{\eta(\text{MW})}{RT}$$

So for small molecules (e.g., C₆H₅I), $\Theta = 1$ ps;
For macromolecules (polymers, proteins), $\Theta = 1$ -100 ns.

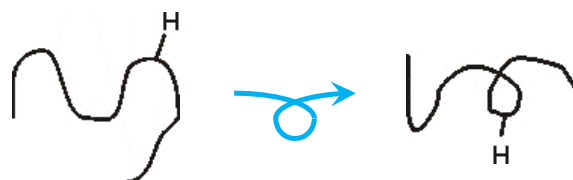
If $\nu_{\text{Larmor}} = 500$ MHz, $t_r = 2$ ns.
So t_r is of same magnitude as Θ .

Macromolecules and Tumbling

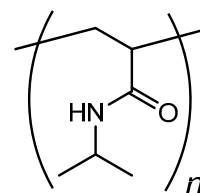
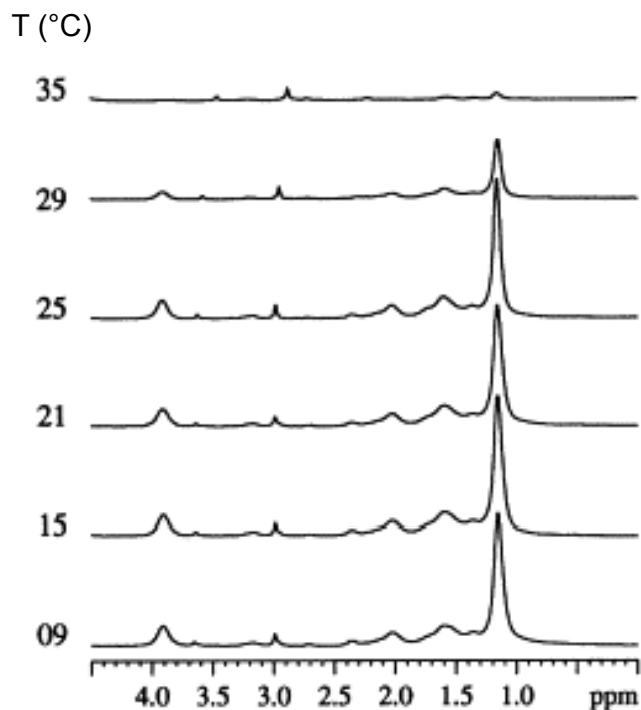
Small-molecule nuclei see an average of contributions from nearby bonds, electrons on NMR timescale.



Well-solvated macromolecules (polymers, peptides) substitute conformational motion for rotation; broadens peaks.



Macromolecules and Tumbling

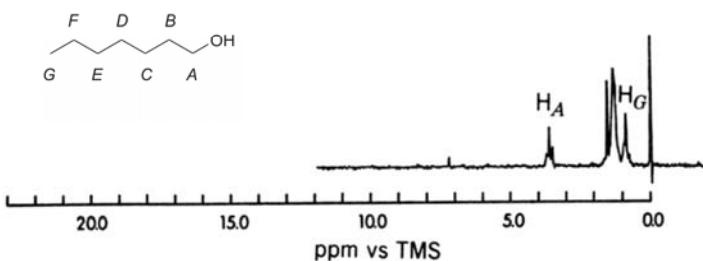


poly(N-isopropylacrylamide)

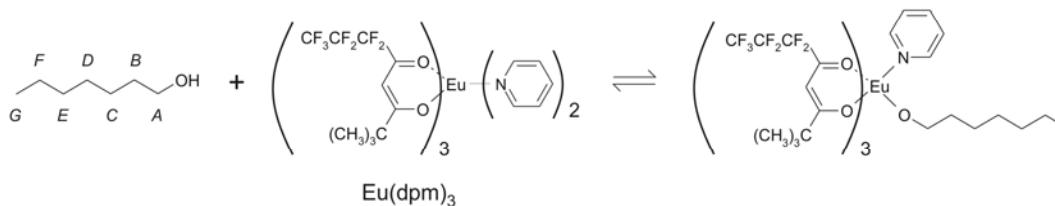
In D_2O , desolvates with increasing temperature

Chemical Shift Reagents

Molecules with badly overlapping resonances, but also Lewis basic or acidic sites, complex with shift reagent.

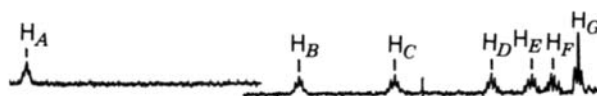


Chemical Shift Reagents



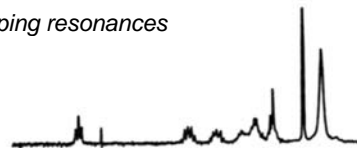
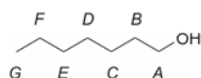
mole ratio
 $\text{Eu}(\text{dpm})_3/\text{heptanol}$

0.78



spreads out overlapping resonances

0.19



0

