

Dynamics, below the coalescence temp, DMA in D2O.

When a nucleus spends time in two different environments, the signal it displays depends its life times in each of the two environments and the separation in Hz between the signals that would arise from each of the two species in the absence of exchange.

You are probably most familiar with the phenomenon of coalescence, which is when the resonances representing the inter-converting species merge. Spectra are collected at a range of temperatures. At the temperature at which coalescence occurs, $k_c = \pi\Delta\nu/\sqrt{2}$ where k_c is the rate of inter-conversion at the coalescence temperature T_c , $\Delta\nu$ is the separation between the lines a low temperature (in the absence of inter-conversion), assuming isolated two-site exchange (see 150+ experiments pg 144. . . and references therein).

At temperatures well above coalescence one observes a single signal whose resonant frequency and line width are averages of those of the two individual species' signals. One can measure the rate of inter-conversion between the two species nonetheless via accurate line width measurements (typically digital simulation of the line shape) or $T_{1\rho}$ measurement (see 150+ experiments pg 150 and references therein). The latter is especially useful because $T_{1\rho}$ depends on the strength of the spin lock field in which $T_{1\rho}$ is measured and is extremely sensitive to dynamics on the time scale of $k_c \approx 2\pi\nu_1$, where ν_1 is the strength of the spin lock field in Hz. Thus, one commonly measures $T_{1\rho}$ at a range of ν_1 values (called B_1 fields in practice, but still quoted in Hz). With knowledge of the T_1 in hand, k_c and $\Delta\nu$ can then be calculated from

$$1/T_{1\rho} - 1/T_1 = \pi^2\Delta\nu^2 \frac{(1/k_c)}{1 + (2\pi\nu_1/k_c)^2}$$
, which applies only in the absence of spin coupling and assumes that you are well above coalescence.

For the purposes of our course, in which we do not wish to bake any probes, and I want to use samples I can buy for cheap, we will have to work between room temperature and 70 °C. If you know of any samples for which this is well above coalescence or spans coalescence, I would love to know about them. In the mean time, we will learn how to measure k_c in cases where you are well below coalescence temperature.

Below coalescence one can nonetheless document and characterize chemical exchange via magnetization transfer. We will study bond rotation in N,N-dimethyl acetamide by saturation transfer. Thus, we will saturate one of the N methyl carbons and measure the extent to which this C hops into the other position by the extent to which the other N methyl gets saturated. This can also be done by saturating the methyl protons, but at the risk of complicating nOes, so we will use ^{13}C at natural abundance.

We will measure the ^{13}C pw90, measure the T_1 of one methyl, while saturating the other (and ^1H) and then measure the extent of magnetization transfer, all using the 'presat' pulse sequence. The combination of the T_1 of the ^{13}C in question, the intensity of the ^{13}C in question when the other is not being saturated (I_0) and the intensity of the ^{13}C in question when the other is being saturated (I) yield the rate constant k characterizing chemical exchange of the C in question from its position to the other position (i.e. in this instance the rate constant for amide group flips).

$$k_{\text{ex}} = \frac{(I_0 - I)}{T_1} \text{ *Error!}$$

where $T_{1,obs}$ is measured for the ^{13}C in question while the other ^{13}C resonance is being saturated (i.e. under magnetization transfer conditions).

For example for C A, $T_{1,obs}$ is measured using standard inversion-recovery using presat with satfrq set to C B's resonance frequency, **satmode='yyn'** and the *minimum satpower* sufficient satpower to saturate B. **p1=2*pw90, pw=pw90** for ^{13}C (calibrate these). **dm='yyy'** for continuous ^1H decoupling at previously calibrated dpwr, dof, dmm. Array d2, as for the determination of T_{1s} for ^1H . process and analyze as for ^1H , to determine C A's $T_{1,obs}$.

Now measure I and I_0 : revert to a standard presat experiment: **p1=0**. set a good long d1, 3 to 5* T_1 (as above). **ss=4**. **satmode='yyn','nnn'**. **nt=16**, or whatever is needed to get good signal:noise. integrate the resonance of A in both spectra. The first gives I and the second gives I_0 . I should be $< I_0$.

Use the above equations to calculate k_{ex} .

The above would normally be done at each of a series of temperatures. The Eyring plot of $\log(k/T)$ vs. T then yields the activation energy for the motion or chemical exchange process.

Measurement of k_{ex} for faster rates

Three dynamic regimes:

Slow exchange: $\Delta\omega \gg k$

the line width of each separated resonance gives the rate of exchange ; $1/T_2^* = 1/T_2 + k_{\text{exch}}$, where $1/T_2^*$ is determined by simulation of the resonances to obtain $\Delta\nu = 1/\pi T_2^*$ and T_2 is obtained, similarly, from a resonance observed at a low temperature at which exchange is negligible (k_{ex} is very small).

and, by magnetization transfer, $k_{\text{ex}} = \frac{(I_0 - I)}{I}$ *Error!

where $T_{1,\text{obs}}$ is measured for the ^{13}C in question while the other ^{13}C resonance is being saturated (i.e. under magnetization transfer conditions).

Approaching coalescence: $\Delta\omega > k$

Lines begin to broaden and approach one another

Individual lines' shapes now reflect both the separation $\Delta\omega_0$ of the original non-exchanging lines observed at low temperature and their line widths : $R_{2,0} = 1/T_{2,0}$.

$I(\nu) =$

Error!