Experiment 13 —

Dynamic NMR Dry Lab

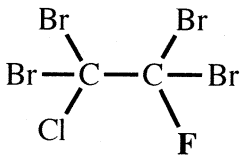
Pre-lab preparation. (1) You have an exam coming up this Friday, so no pre-lab write-up. (2) However, if necessary, please review conformations of cyclic and acyclic molecules before coming to lab. (3) Bring enough of your model set that you can make the molecules whose NMR spectra you will be analyzing.

Part 1 — On the following pages you will find 6 molecules and a set of NMR spectra for each. The first four are ^{19}F NMR spectra, the next two are ^{13}C and ^{1}H. The ^{19}F nucleus has two spin states, just like the proton, so the principles are basically the same. *In each case, explain the dynamic process that leads to the observed variation in the spectra with temperature.* Focus on the two extremes — the low-T spectrum, where the change is slow on the NMR timescale and the high-T spectrum, where the change is fast on the NMR timescale.

You will also use the program WinDNMR to simulate a few of the spectra and obtain rate constants and timescales for the process of interest. In one case you will extract activation parameters from the temperature and rate data provided.

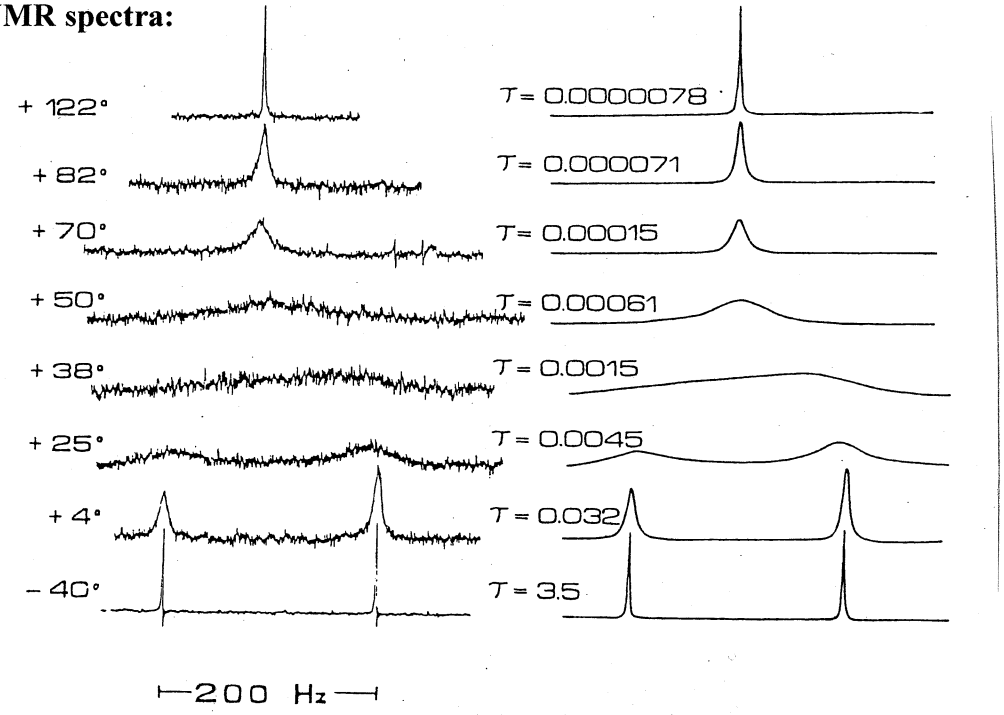
Explain the dynamic process and answer the other questions in your notebook as you go. Turn in the duplicate copies of your notebook pages and you're done.

1 1-chloro-2-fluoro-1,1,2,2-bunchabromoethane.



Draw Newman projections of the three stable conformations of the compound. Models may be helpful. Actual and simulated ^{19}F spectra are shown below. Explain why there are two peaks in the –40°C spectrum, even though there are three staggered conformers. Explain why there is one peak in the +122°C spectrum.

56.4 MHz ^{19}F-NMR spectra:



The lifetimes (τ values, in seconds) above are the ones that gave the best simulations of the experimental spectra. (You will be doing this for the next molecule.) Let's use the values given to determine the activation parameters for this process.

The Arrhenius equation,

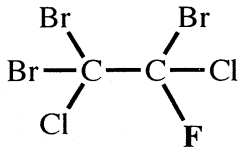
$$k = Ae^{-Ea/RT}$$

can be rewritten as

$$\ln(k) = \ln(A) - E_a/RT$$

By plotting ln(k) vs 1/T, you can find the activation energy and the Arrhenius "A-value". The rate constant, k, is just $1/\tau$. The temps need to be in Kelvin. A typical conformational change has $A \approx 10^{13.3}\text{sec}^{-1}$. E_a for rotation around the C–C bond of ethane is 3 kcal/mol. How do the A and E_a you found compare with these values? Explain any significant differences.

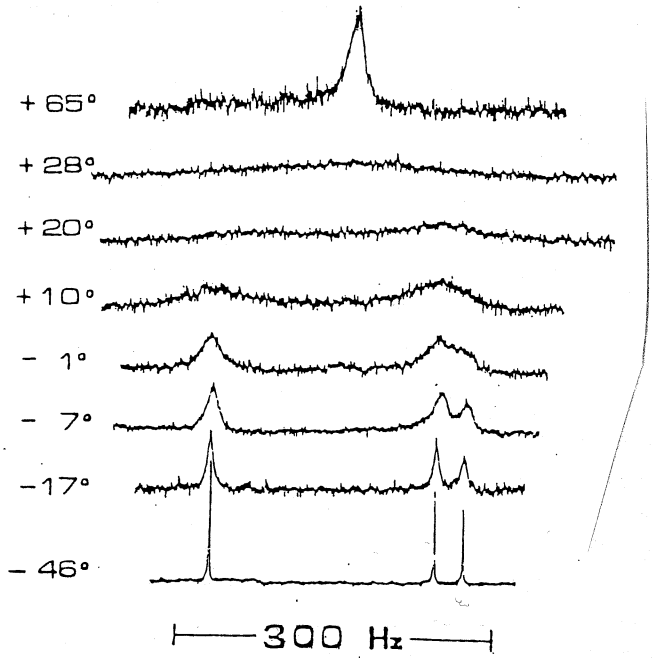
2 1,1,2-tribromo-1,2-dichloro-2-fluoroethane



This one is more interesting. Notice first that it has a stereocenter. Choose either configuration — it doesn't matter. Draw Newman projections of the three staggered conformations. Explain why there are three separate ^{19}F signals in the low-temperature spectrum this time. Feel free to speculate as to which two are likely responsible for the two signals that are close together, but keep in mind that this is just speculation. Why is there just one signal at the high-temperature extreme?

The concept of "fast" and "slow" on the NMR timescale were not quantified properly in lecture. Observation of distinct signals for different conformers of a molecule depends on the rate of their interconversion but also on the frequency difference ($\Delta\nu$) between their NMR signals. Note that as the temperature increases the two upfield signals coalesce first, since these are close in frequency, then as the temperature continues to increase the signals that are farther apart begin to coalesce.

56.4 MHz ^{19}F-NMR spectra:



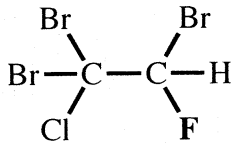
Let's do some simulations to determine the timescales of the conformational changes in this molecule. Find the program WinDNMR under the "course related" programs, and fire it up. Click on "DNMR" in the upper left-hand corner; then select "3-spin" in the menu directly below it. You can access the relevant parameter set via the "Parameters" menu or via the settings displayed across at the top of the screen.

We need to give the program the starting frequencies, rate constants for interconversions of pairs of conformers, and percentage of each conformer at equilibrium. Note the "300 Hz" bar below the spectra on the previous page. The frequency range in the program should also be set at 300Hz (you may need to go into the "Parameter settings" pannel to find this. We need to get the three peaks positioned with the proper separation in Hz. 0 Hz is the extreme right edge of the screen, and 300 Hz is the left edge. V_a, V_b, and V_c are the relative frequencies of the peaks on this scale. Set the first frequency, V_a, to 30 Hz. Now set V_b to place the second peak 30 Hz from the first, and V_c to put the third peak 210 Hz from the second. Although it might not be entirely correct, we're going to assume that all three rate constants, k_{ab}, k_{ac}, and k_{bc}, are all the same. Set them all to an artificially slow 0.01 sec^{-1} to start. Set the %s of a, b, and c to 25, 30, and 45 — these are just approximations based on that low-T spectrum, but they should be close enough. Click on "OK". You should see a spectrum that looks something like the -46 °C one on the previous page. Use the blue ↑ and ↓ arrows just above the spectrum on the left to vertically scale the spectrum so that the three signals aren't off scale.

Now let's see if we can simulate the spectra at +20°C and at –1°C. Your mission is to determine the rate constant k (again, we're assuming the values for k_{ab}, k_{ac}, and k_{bc} are all equal), that produces a spectrum as close as possible in appearance to the ones at +20 °C and at –1°C. Try entering different values for k and see what happens. You may need to adjust the vertical scale again. Also estimate the uncertainty in each of these values. That is, how accurate do you think your numbers are? For example, if the simulations with k between, say 550 and 650 sec^{-1} all provide a good match to the spectrum of interest, then you'd report 600 ±50. And be reasonable about sig figs — "613.4 ± 50" makes no sense, does it?

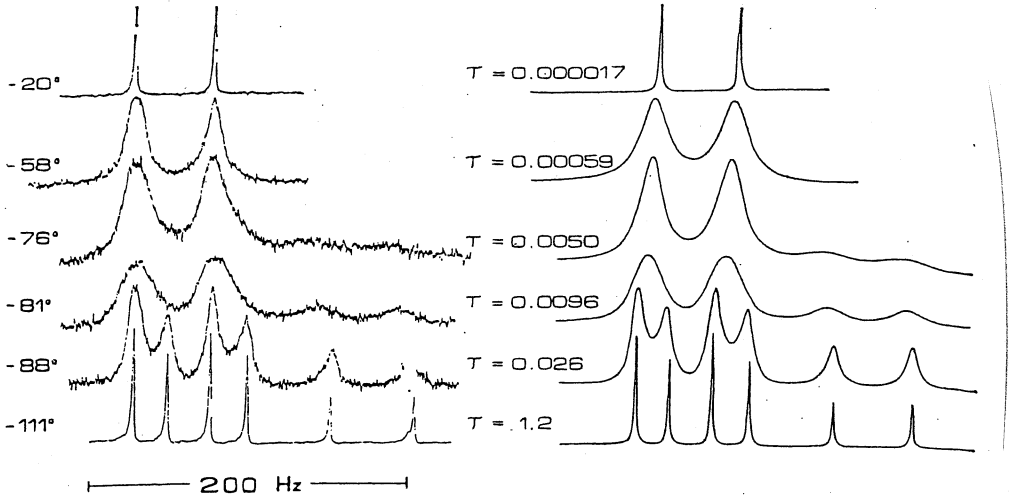
For each temperature, report your k value and the corresponding timescale, τ. Report τ in seconds and in ms, μs, or ns, whichever is most reasonable in each case.

3 1,1,2-tribromo-1-chloro-2-fluoroethane



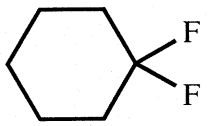
Note that we now see geminal coupling between ^{19}F and ^{1}H with J ≈ 40-50 Hz! How cool is that?

56.4 MHz ^{19}F-NMR spectra:



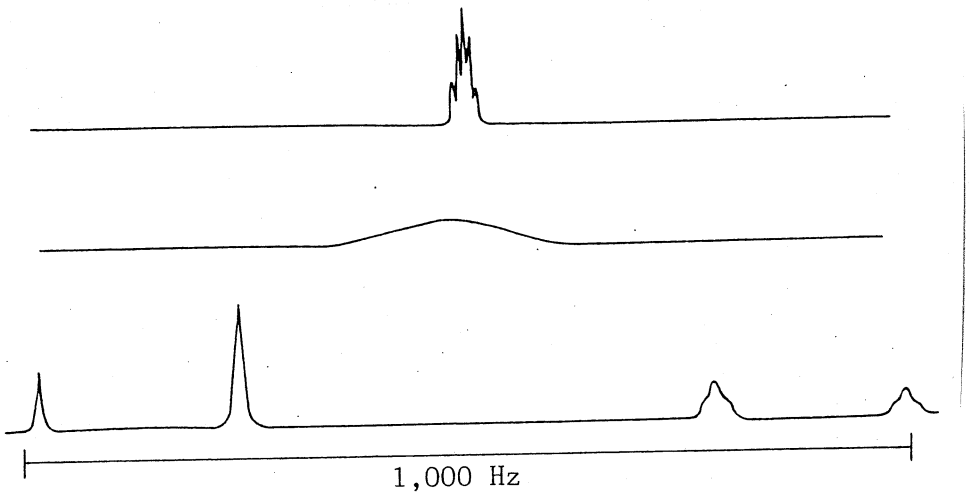
Take a look at the high-T spectrum first. That may help you explain what's going on at the low-T extreme.

4 1,1-difluorocyclohexane

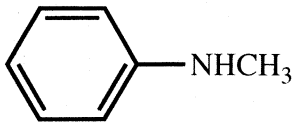


This compound displays ^{19}F-^{19}F geminal coupling with J ≈ 250 Hz! Yowza. And to make things even more interesting, each fluorine can also couple to the neighboring protons, with J_{vic} that depends on dihedral angle, although these ^{19}F-^{1}H couplings aren't completely resolved in the lowest-T spectrum below.

^{19}F spectra:

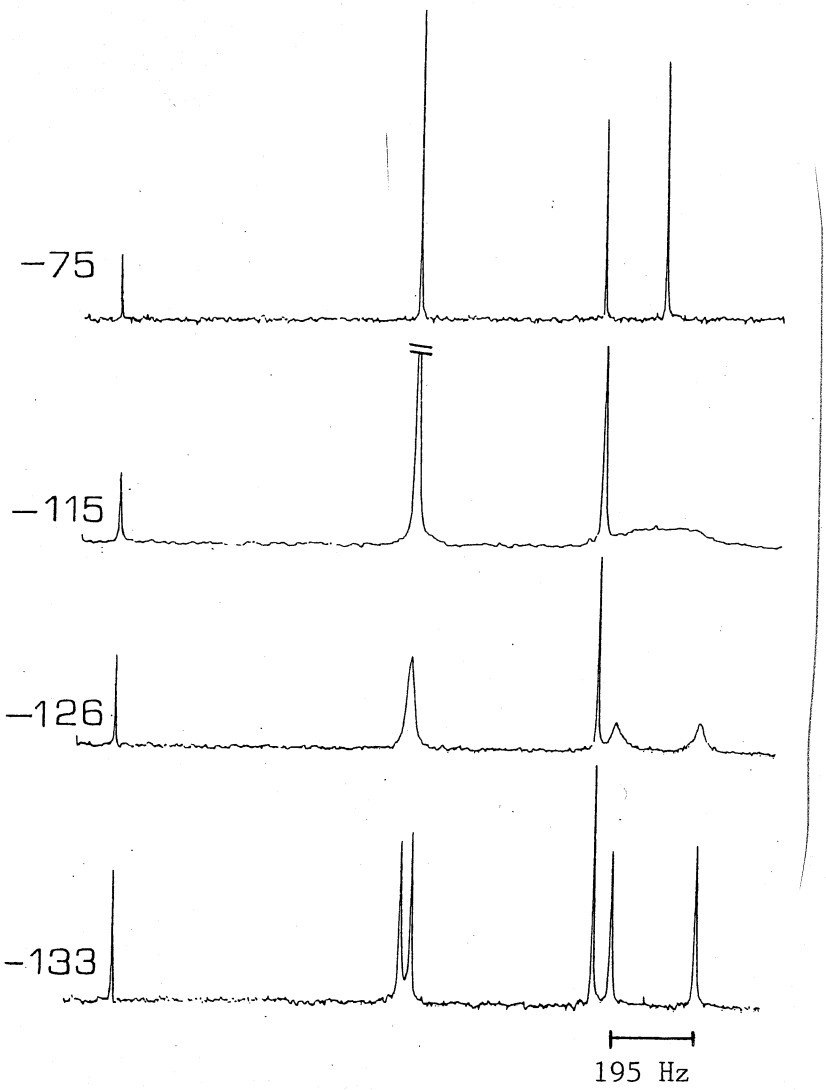


5 N-methylaniline



Broadband ^{1}H-decoupled ^{13}C spectra of the aromatic region are shown below. (i.e., the signal for the methyl C is not shown)

25.2 MHz ^{13}C spectra (Me_2O solvent)**:**



Use WinDNMR to determine the rate constant and corresponding lifetime for the interconversion of the conformers of methyl aniline at -115 °C by simulating the coalescence of the two upfield signals. These are 195 Hz apart and can be assumed to have a ratio of 1:1.

Select DNMR and "2-spin", then enter appropriate values for V_a and V_b and the %s. Adjust "$k_{ab} + k_{ba}$" until you have a reasonable match. Don't forget that you can use the blue ↑ and ↓ arrows to vertically scale the spectrum as necessary. Report the rate constant (with error limits) and the lifetime.

6 Ethanol

Here are two ^{1}H NMR spectra. The first is of very pure ethanol. The sample is sufficiently pure and dilute that the –OH signal shows splitting. You don't see that every day, eh? The second spectrum is ethanol with 1% formic acid (whose signals are off scale to the left).

(a) Explain the difference between the two spectra. (b) Draw a tree diagram to account for the beautiful splitting pattern of the δ3.6 signal in the upper spectrum. (c) Why do you think the signals for alcohol –OH protons often appear as broad singlets under ordinary conditions?

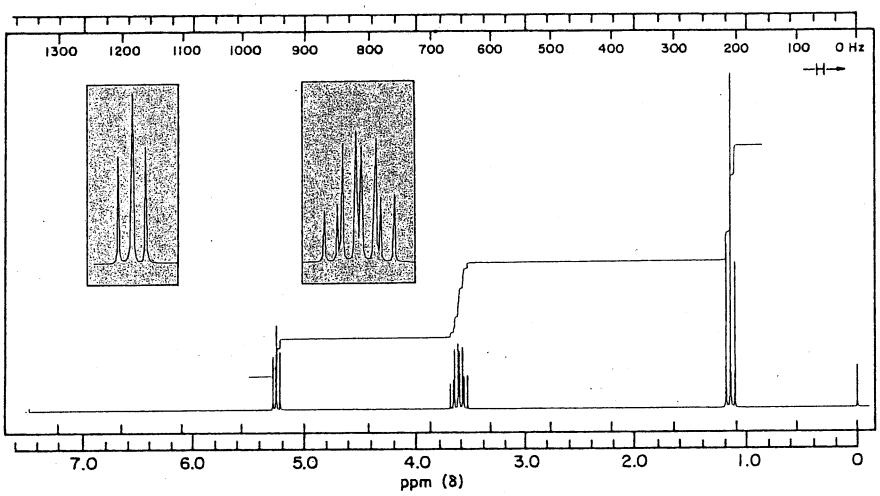


FIGURE 13.38 NMR spectrum of pure ethyl alcohol.

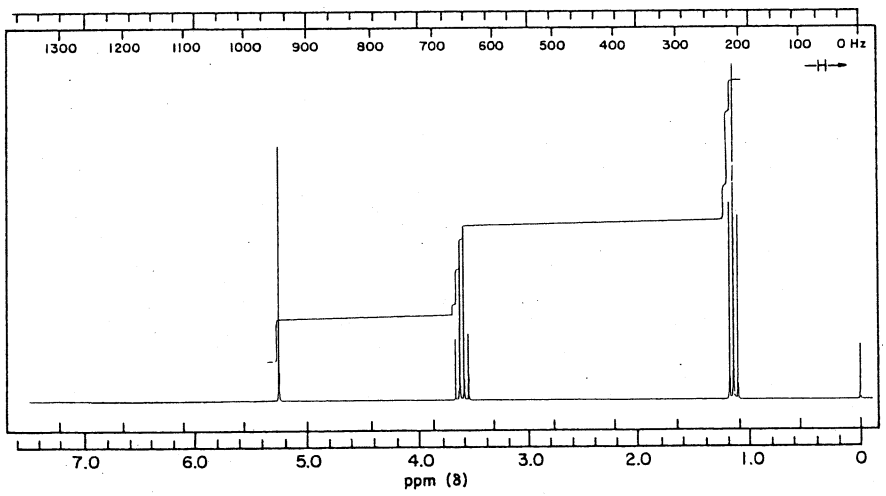


FIGURE 13.39 NMR spectrum of ethyl alcohol containing 1% formic acid.