

Spin-Lattice Relaxation Times

Reading Assignment: Silbey, Alberty, and Bawendi, Physical Chemistry, 15.1-5,7.; E. Breitmaier, W. Voelter, Carbon 13 NMR Spectroscopy, 3rd ed., 3.3.2.

Purpose Use the inversion recovery method to measure the T_1 relaxation times for the different chemical environments in a molecule. The T_1 values will be used to assess motion in different parts of the molecule.

Introduction

Spin-Lattice Relaxation When molecules absorb light they are transferred from lower energy states to higher energy states. This leaves the system out of equilibrium, and the system must undergo transitions from the upper states to lower states to get back to equilibrium. This process is illustrated in Figure 1. For nuclear magnetic resonance of protons, the energy level diagram has two energy levels, the lower state with protons "spin up", or aligned with the external field, and the higher state with protons "spin down", or aligned against the external field. Light in the radiofrequency region of the spectrum causes protons to "flip", or jump to higher energy levels. The process whereby the system returns to equilibrium involves spin flips to return to the lower energy state, and the excess energy is lost to the surroundings in the form of heat. The surroundings in magnetic resonance experiments is called the "lattice", therefore the name spin-lattice relaxation. The characteristic life-time of a spin in the upper state is called the spin-lattice relaxation time T_1 . T_1 is the average length of time that a proton remains in the same energy level. The spin-lattice relaxation time is also called the longitudinal relaxation time.

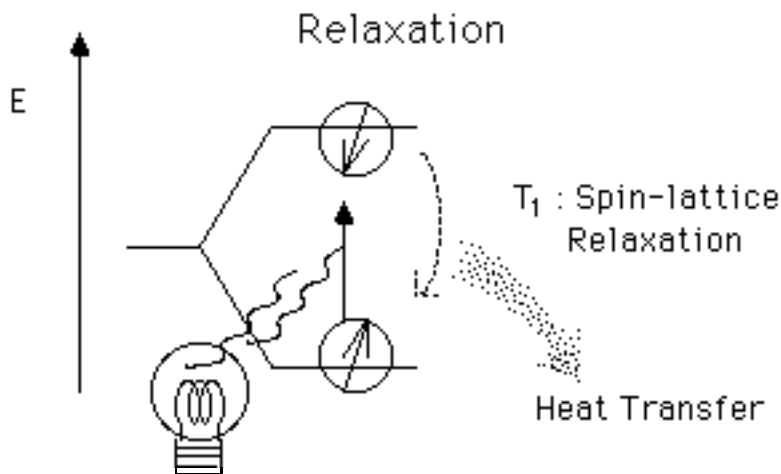


Figure 1. Absorption and spin-lattice relaxation

An easy way to visualize the process is shown in Figure 2, which illustrates an older method for measuring T_1 's called "saturation recovery." At left the molecules start at equilibrium. The radiofrequency source is then turned on, which causes transitions between the two levels. After the source has been on a short time the populations (number of spins in a given level) of the two levels are equalized. With equal populations, the two levels are said to be saturated and will no longer give a resonance signal. The source is then turned off, which allows the molecules to

return to equilibrium some time later. A good rule of thumb is that it takes about $5 \times T_1$ for the system to return to equilibrium.

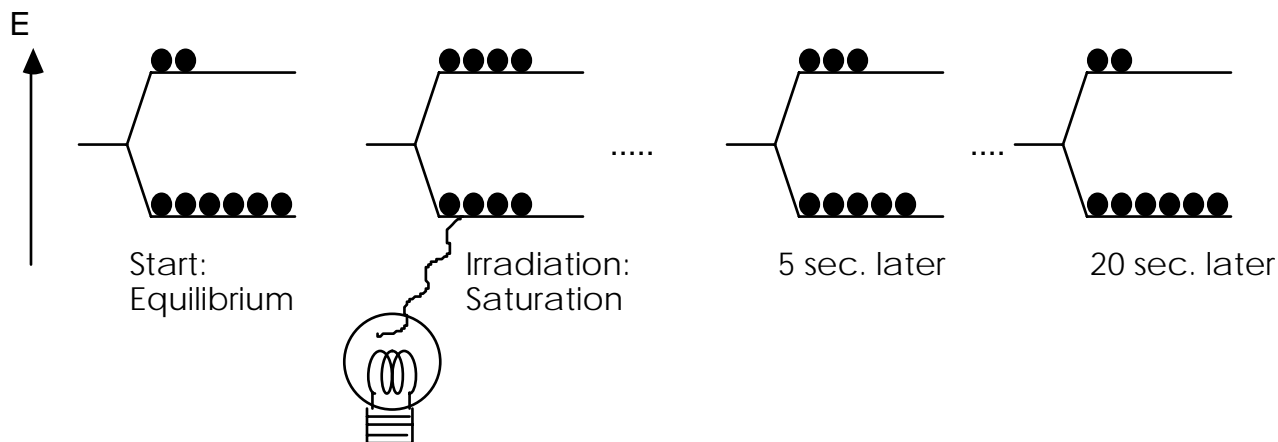


Figure 2. Saturation-recovery method for T_1 measurement

The NMR signal is caused by the net magnetization of the spins M_z , which is proportional to the difference in the populations of the two levels:

$$M_z \propto (\# \text{ spins in lower state}) - (\# \text{ spins in upper state}) \quad (1)$$

Spin-lattice relaxation is a first order kinetic process:

$$\frac{dM_z}{dt} = -\frac{1}{T_1} (M_z - M_0) \quad (2)$$

where M_z is the magnetization at time t and M_0 is the magnetization at equilibrium. Integrating equation 2 for the recovery from saturation gives:

$$M_z = M_0 e^{-t/T_1} \quad (3)$$

The Effect of Motion on T_1 Relaxation is caused by fluctuating magnetic fields in the sample. There are a number of sources of fluctuating magnetic fields. One example comes from paramagnetic substances in solution. Molecular oxygen is paramagnetic and greatly enhances spin-lattice relaxation; the effect of dissolved oxygen is so strong that oxygen must be removed by a process called "degassing" in order to study other sources of relaxation. Another source of fluctuating magnetic fields that is always present is the dipole-dipole coupling.

Nuclear spins interact through space. We often picture nuclear spins as small bar magnets; assume that we have two bar magnets situated as shown in Figure 3.

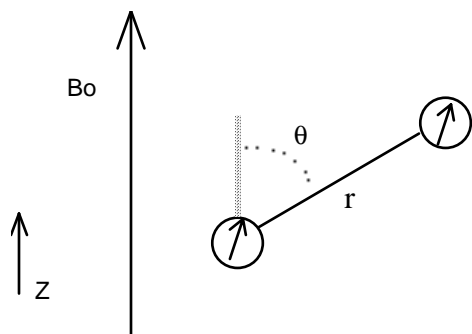


Figure 3. Dipole-dipole coupling of two nuclear spins

These bar magnets influence each other over a range of distances, this interaction is called the dipole-dipole coupling. The energy of the interaction is given by:

$$E = \frac{A}{r^3} (1 - 3 \cos^2\theta) \quad (4)$$

where r is the distance between the two spins and θ is the angle between the external field and the vector joining the two spins. The constant A depends on the magnetic moment of the two coupled spins and their spin orientations, up or down. When a molecule tumbles in solution the angle θ changes rapidly and at random causing a fluctuating magnetic field at each nucleus. This fluctuating magnetic field can bring about relaxation.

Not any fluctuating magnetic field will be efficient at bringing about relaxation. The fluctuations must have a large frequency component at the frequency of the transition in order to be efficient. In Figure 4, the transition frequency that corresponds to the magnetic resonance transition is shown at the top, the frequency is given as an angular frequency $\omega_0 = 2\pi\nu_0$. In our instrument, for protons, this frequency is 400MHz. In (a) we take as an example a large molecule. Large molecules reorient slowly in solution, therefore the angle θ also changes slowly. The fluctuating magnetic field caused by the slow tumbling of large molecules changes too slowly to be efficient at relaxation at the transition frequency, which causes a long T_1 . In (b) an intermediately sized molecule tumbles in solution at a rate that produces fluctuations that have frequency components that match the transition frequency. This motion will be efficient at causing relaxation and will give rise to a short T_1 . In (c) a small molecule is seen to tumble too rapidly causing fluctuating magnetic fields that have components at too high a frequency to cause efficient relaxation. Just as in (a) the T_1 will be long. Therefore, the motion of a molecule can be either too fast or too slow to cause efficient relaxation. Only when the motion of the molecule is matched to the transition frequency will relaxation be efficient and T_1 short.

The motion of a molecule can be characterized by a correlation time, τ_c . The correlation time is roughly the average time that a molecule spends in a given orientation. Large molecules tumble slowly and therefore have long τ_c . Small molecules tumble very rapidly and therefore have short τ_c . Only when the motion has τ_c about equal to $1/\omega_0$ will the relaxation be efficient.

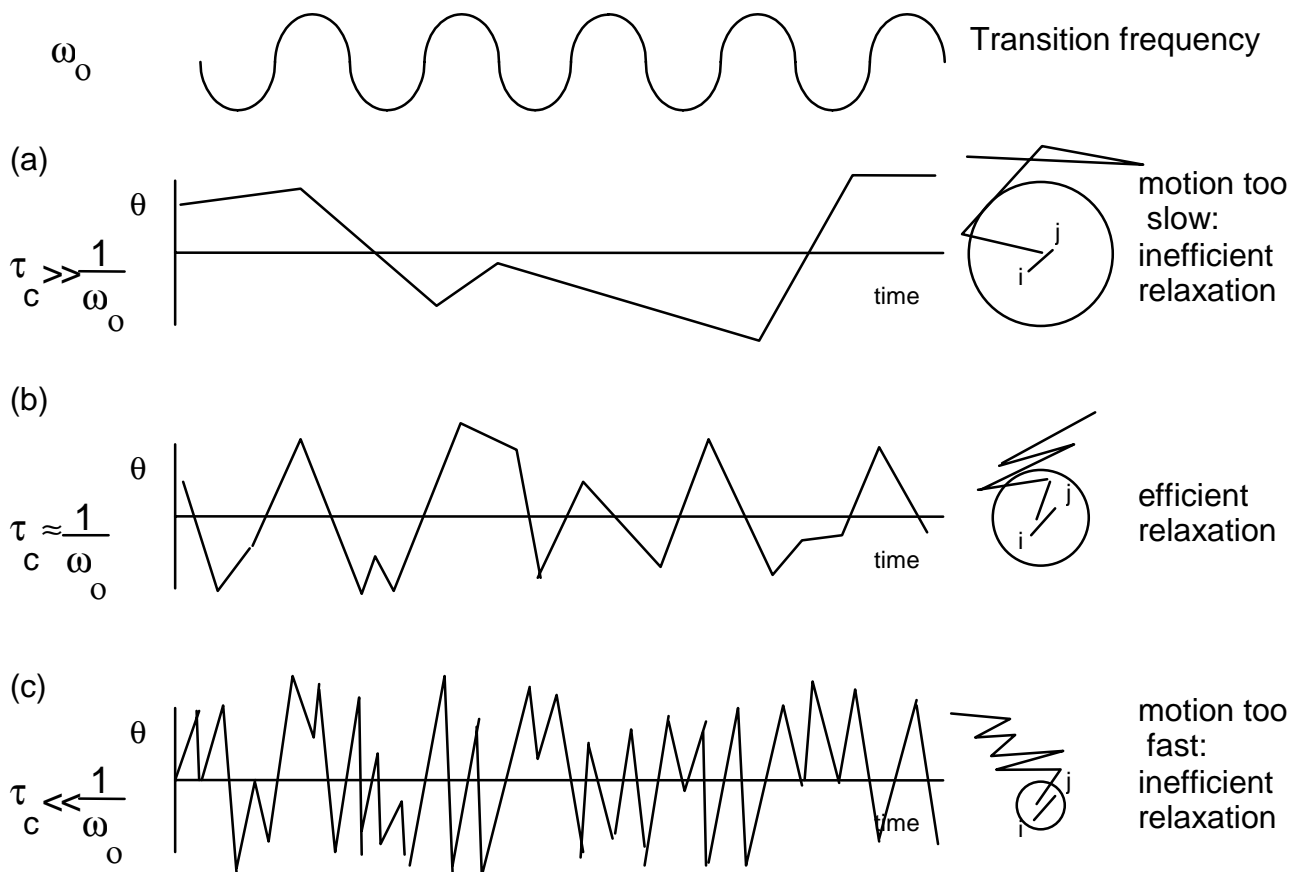
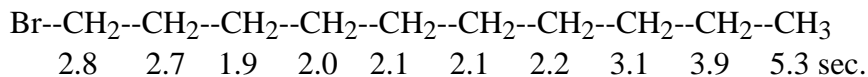


Figure 4. Effect of motion on relaxation. (a) When motions are slow relaxation is inefficient and T_1 is long. (b) When the frequency of the motions match the transition frequency relaxation is efficient and T_1 is short. (c) When motions are too fast, relaxation is once again inefficient. Small molecule reorientations are in this category. The fast motion regime is called “extreme narrowing.”

Molecular tumbling is not the only motion that can cause relaxation. Internal motion within a molecule can be very effective at causing relaxation. Most importantly, different parts of a molecule can have different frequencies of motion, because of rotation around single bonds. Decyl bromide is a good example of a molecule that has different motional regimes. The carbon-13 relaxation times for the carbons in decyl bromide are shown below.



At the methyl end of the chain the motions are too fast to provide an efficient mechanism for relaxation. Because the bromine is massive, the motions at the bromine end of the chain are slower and are therefore more efficient at relaxation. Notice that the minimum relaxation time occurs not next to the bromine, but three carbons away. This could mean that the motion at the methylenes adjacent to the bromine is too slow for the most efficient relaxation.

Diffusion, rotation, and molecular motions within the molecule all act essentially independently to change the relaxation time. For example, methyl group rotations (i.e. around the C-C bond leading to the methyl group) are always too fast to provide effective relaxation. However, the C-C bond may be wagging around because the methyl group is attached to a ring. This wagging motion may have the correct frequency components to provide efficient relaxation, leading to a short T_1 . Therefore, you need to consider all the motions that a particular nucleus may experience. Some may be too slow, some may be too fast, but if some are just at the right frequency the relaxation will be efficient leading to short T_1 's.

In summary, spin-lattice relaxation times are a sensitive probe of molecular motion within a molecule. Analysis of relaxation times can tell us whether a given chemical environment is in a rigid portion of the molecule or in a flexible part of the molecule. Assessing the motions within a molecule is the goal of this experiment.

However, caution must be exercised when interpreting relaxations times. For carbon-13, the biggest effect on relaxation is the number of attached protons for a given carbon-13. In decyl bromide for example, all motions being equal, the methyl carbon would be expected to relax more rapidly than the methylene carbons. A simple solution to this problem is to compare carbons with the same number of attached protons. For proton relaxation, between-molecule relaxation, as well as within molecule relaxation, is important. For this reason, carbon-13 relaxation is preferable for careful studies. In this lab experiment, however, we will use proton relaxation times in part to save time, but more importantly to provide information needed for next week's experiment on nuclear Overhauser effects (nOe).

Inversion Recovery Method The saturation-recovery method for T_1 determination was discussed above. A better method, available in pulsed spectrometers, is the inversion recovery pulse sequence. This sequence is discussed in detail in Atkins (see reading assignment). In essence, the inversion recovery sequence causes all the "up" spins to become down spins, and visa-versa. This creates a population inversion where there are more spins in the higher state than in the lower state. The spectrum of the system after inversion contains all negative going peaks. After inversion a period of time, τ , is chosen and then the spectrum is acquired. For short τ values, peaks in the spectrum are negative. For long τ values, the system is able to reach equilibrium and the spectrum appears normal. The spectra for various τ values are plotted on the same chart, giving the so-called partially relaxed spectra for the system, as shown in Figure 5. The T_1 value for each chemical environment can be obtained by fitting the peak intensity of each peak to the equation:

$$\ln(M_0 - M_z) = \ln(2M_0) - \frac{\tau}{T_1} \quad (5)$$

(Notice that taking the ln of both sides of Equation (3) would give $\ln(M_z) = \ln(M_0) - \tau/T_1$, the difference here is that the signal for small τ is negative.) The point where a peak changes from negative to positive is a rough measure of the T_1 , and is $\tau = T_1 \ln 2$.

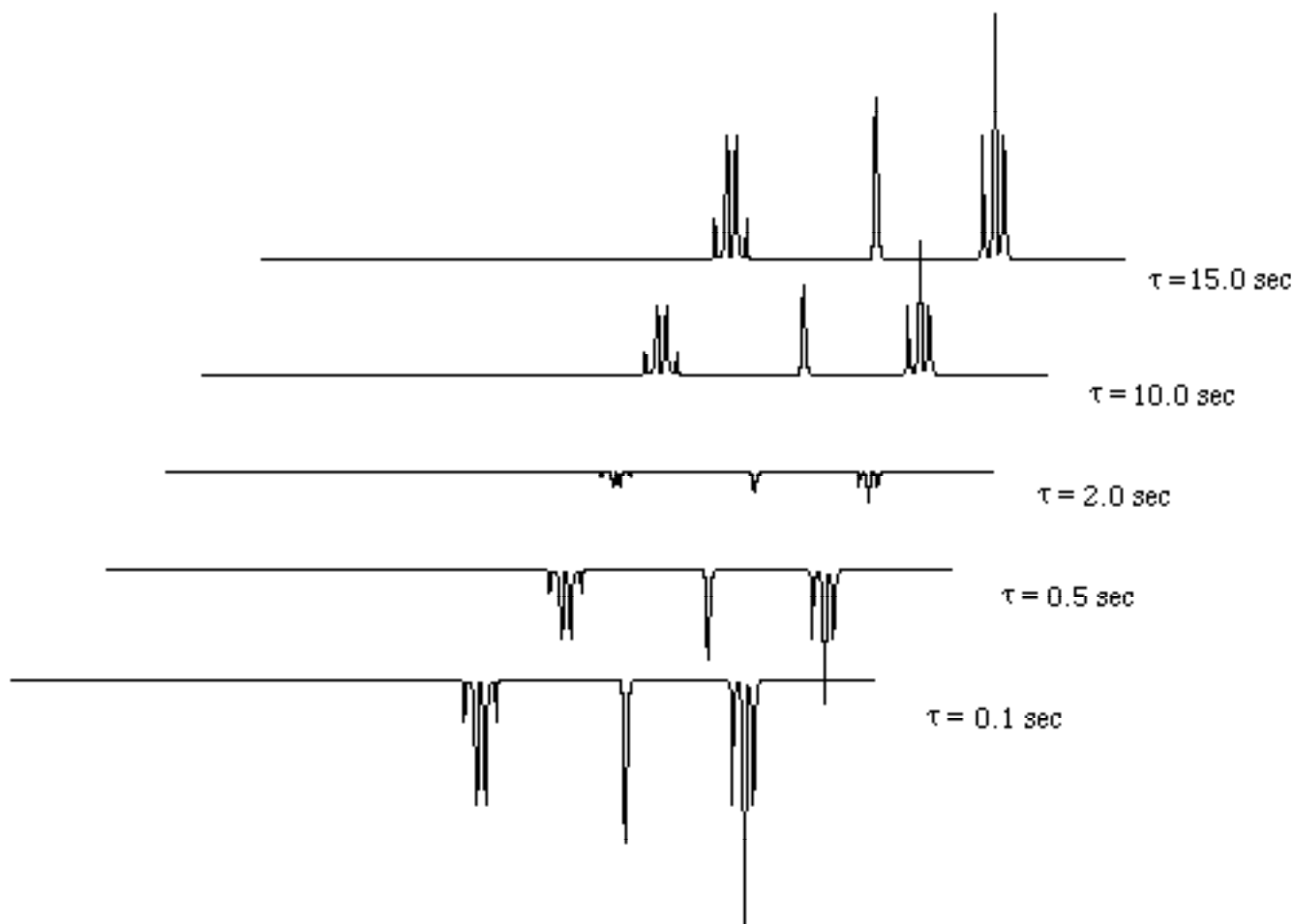


Figure 5. Partially relaxed spectra for different delay times (this is a simulated spectrum where all of the chemical environments have the same T_1 , which is not generally the case).

Procedure

You will be given a small organic compound to study. Beta-ionone is an example of such a compound. Dilute around 5mg in CDCl_3 . Filter the sample into a valved NMR sample tube and attach to the vacuum line. Degas the sample to remove oxygen using three freeze-pump-thaw cycles. A freeze-pump-thaw cycle is:

1. Freeze the sample with liquid nitrogen
2. Open the sample tube valve to the vacuum line and evacuate the tube for 20 sec.
3. Allow the sample to thaw. When the sample begins to liquify close the sample tube valve.
4. Thaw completely and return to step 1, above.

T₁ Determination by Inversion Recovery Bruker Avance 400 MHz NMR

The T₁ inversion recovery experiment can be run completely under automation from the Routine NMR mode of the spectrometer. You just run the experiment as you would any routine spectrum, you just choose the “T1 Proton” experiment rather than the regular PROTON experiment following the instructions below.

1. Take a normal automated 1-D spectrum using the PROTON experiment.
2. From XWin-NMR, expand the spectrum to focus on the region of interest. Click on the “sw-fo1” button at the lower left of the screen and write down the current SW and O1 settings.
6. Minimize the XWin-NMR window and set up another spectrum, however you need to enter the spectral width and oscillator offset parameters before clicking on Start. Choose the PROTONT1 experiment. Pull down the Parameters menu and choose Acquisition Parameter Editor. Change the D1 relaxation delay to 15 sec. Click on Save. Pull down the Parameters menu and choose Edit Acquisition Parameters. In the Acquisition parameters screen, enter the new SW and O1 settings. If the sample is very concentrated you can save time by setting NS to 4. Click on Save.
7. Now click on Start to take the T₁ data with the narrowed spectral width. The results will be printed out.
8. The chemical shift may be different than your previous PROTON experiment. Click on Spectrum to open the XWin-NMR window. Click on serial. In the Serial Window click on the rows button, and then click on the # button. Enter row number 10 and press enter. You should now see the spectrum for the longest delay. Click on the 1D-mode button. Click on plot to print out a new copy of the spectrum. In the lower left-hand side of the screen click on 2D to return to the Serial window. In the Serial window click on return to get back to the 2D-display.
9. You can click on oblique to see the relaxation data in a stacked-plot view. Click on the +/- button to alternatively see the positive and negative portions of the results.
10. Compare the chemical shifts and determine if the T₁ of at least one peak from every multiplet has been determined. If there are some peaks that were missed, use the “T₁ Manual Processing Instructions,” below, to get the results for the missing peaks.

T₁ Manual Processing Instructions

1. Click on Spectrum to open the XWin-NMR window if you haven't already.
2. Pull down the Analysis menu and choose Relaxation (T1/T2).

3. In the T1/T2 Relaxation window pull down the Process window and choose setup t1 parameters. In the Parameters window and check that NUMPTS = 10, FTTYPE = intensity, LISTTYP = vdlst, and change Start to 10. Click on SAVE.

4. Pull down the Process menu and choose Read SMX slice for peak selection [rpsc] to load the spectrum for the longest delay into the window. Expand the window to include only the peaks that you wish to analyze.

Automatic Peak Picking

5. Pull down the Analysis menu, slide right on Peak Picking, and choose Define Region. Press Enter to choose the currently selected parameters. Now pull down the Analysis menu, slide right Peak picking, and choose Define Output Device CURPRIN. In the Output device window, pull down the menu list for CURPRIN and choose screen. Click Save.

6. Pull down the Analysis menu, slide right on Peak Picking, and choose Adjust minimum intensity. Move the mouse up and down until the faint, blue horizontal line is near the bottom of the spectrum but above the noise in the baseline. Click left.

7. Pull down the Analysis menu, slide right on Peak Picking, and choose Generate 'intrng' and 'baslpnts' T1 [ppt1]. A list of the peaks that have been found will be listed on the screen. Check to see if your peaks are listed. If so, continue on. If not, return to step 6 and try a lower Minimum Intensity. Click OK.

8. Pull down the Analysis menu and choose Relaxation (T1/T2). Pull down the Process menu and choose Peak pick a series of spectra [PD].

9. Pull down the Process menu and choose Multi-component fit [simfit]. The T_1 results should be listed on the screen.

10. If you need to analyze more than one line, pull down the Process menu and choose Display the next peak [nxtp] repeatedly until the line you wish to analyze is shown, then pull down the Process menu and choose Multi-component fit [simfit] to do the analysis.

11. Click on return, to go back to the 2D display.

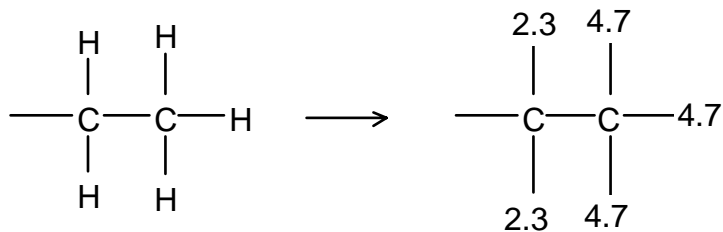
Note: Instead of pulling down menus, you can just type commands on the command line at the bottom of the screen. The commands you type are listed in [] in the pull down menus. For example, to go to the next line for curve fitting, you just type nxtp on the command line, and then type simfit to do the curve fit.

Report

A formal introduction and theory section are not necessary. Include the following information.

(1) Assign all of the peaks in the spectrum.

(2) Draw the structure, but replace each H with its relaxation time, as shown below.



(3) Decide which parts of the molecule have greater flexibility (faster motions) and which parts of the molecule have hindered motion (slower). Ring structures are good examples of hindered motion.

(4) Choose one of the following statements and explain your choice.

(a) The motion of the molecule, on the whole, is too fast, so that hindered motion provides more efficient relaxation.

(b) The motion of the molecule, on the whole, is too slow, so that freer motion provides more efficient relaxation.