Chem 260 Laboratory 5

ELECTRON SPIN RESONANCE

1. Start the WINEPR SimFonia program. Make sure Solution is selected in the tool bar.
2. Click on H (Hamiltonian Parameters). Click OK and RUN to get the simulated spectrum for an unpaired electron with no hyperfine interaction. The default lineshape has a differential form, as this is the usual output of ESR spectrometers with field modulation. To view the integrated form use Processing/Integrate. Return by choosing Differentiate.
3. Now investigate what happens when nuclear spins are included in the simulation. Go back to H, Get Element and select Hydrogen. The appropriate data for nuclear spin, isotopic abundance and nuclear g-factor will appear. Enter 3.75 for the hyperfine constant A [G]. Click Insert to enter the parameters in the main Hamiltonian window. Click OK and then RUN.
4. You should see a pair of lines in the spectrum. You can check their separation with View/Distance. Left clicking sets the cursor positions; their separation is given at the bottom right of the window. Use right click to escape from this measurement mode.
5. Explore what happens when you have 2, 3, or 4 equivalent protons in the radical. To modify the simulation go back to the Hamiltonian and double click the H data in the main window. It should appear below, where you can edit it. Change the number of nuclei and click Insert. Use the Delete button (in this window) to remove unwanted data. Click OK and RUN the simulation. Notice the amplitude pattern as well as the line splittings.
6. Simulate the benzene anion spectrum and copy it to your report. (Paste Special/Picture.)
7. Now investigate the spectrum of an electron interacting with a single nitrogen nucleus. Why are there 3 lines? Try two equivalent nitrogens. Is the pattern of intensities the same as you had with equivalent H's?
8. Simulate and record the spectrum of the pyrazine anion: A_H = 2.66 G; A_N = 7.22 G.

NUCLEAR MAGNETIC RESONANCE – SPIN PRECESSION AND FOURIER TRANSFORMATION

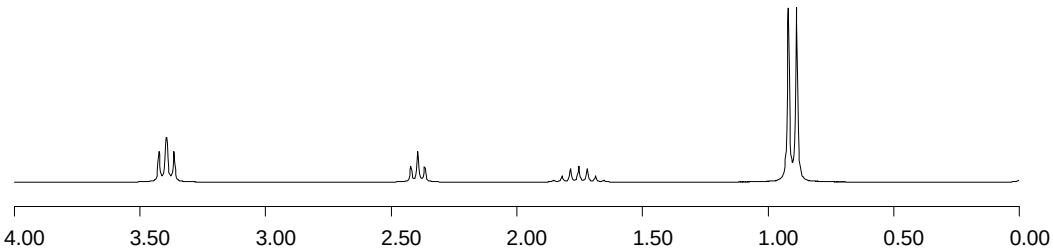
9. Start the FT-NMR program. On the opening screen, choose User-Defined Set of Frequencies, and on the next window 1-5 Single Frequencies
10. Start with a single nucleus. Enter the frequency (10 Hz), intensity (1) and leave T1 set at 0 (no spin-lattice relaxation, actually corresponds to infinite relaxation time, not zero!).
11. Continue to the next screen. Set the noise to zero, the flip angle to 90º, spectrum width to 1000 Hz, Quadrature Detection, and 1024 data points.
12. Continue. What you see is the free induction decay (FID) signal. Using ShowFID/all of it (or a time range) you can select the real or imaginary part of the precessing nuclear spin magnetization. Try ShowFID/Show Vectors. You may need to change the vector speed (in a pop-up window) to slow down movement in the vector diagram. Once it is adjusted, you should see the magnetization vector "flip" by 90º from the vertical *z*-axis into the *x*-*y* plane, where it precesses at the set frequency. This frequency (currently 10 Hz) is the

difference between the actual nuclear precession frequency and the spectrometer frequency (e.g. 400 MHz).

13. Try StartOver/Same frequencies… Set T2 to a smaller value, e.g. 0.2, and continue. You will see that the FID "relaxes" (decays) exponentially.
14. Select Cont/Zero fill and then Do FFT. The FID signal is Fourier transformed – the precession signal as a function of time is now displayed as amplitude against frequency.
15. Now explore what happens if there is more than one precession frequency. Go back to the beginning with Start Over/complete restart. Add a second frequency (e.g. 50 Hz) with the same intensity (1). The FID clearly shows two frequencies. Try the vector display, also. Fourier transformation gives the expected frequency spectrum.
16. Go back and try two higher frequencies, e.g. 100 and 110 Hz. Notice the pretty "beat" pattern. The frequency spectrum is similar to before. You might want to expand the scale with New View/New X-range.
17. You can try more complicated frequency patterns if you wish, but these will also be evident when you try the "real" spectra below.

PROTON MAGNETIC RESONANCE SPECTRA

1. Go back to the beginning and select Proton System from Menu. Choose 1,1,2,-Trichloropropane. Add TMS (check box at top left), use a 400 MHz spectrometer, no noise, 90º flip, 0.2 s T2, quadrature, 2048 data points.
2. Transform the FID. Shift the frequency so that TMS is at 0. Change to a delta scale, using New View/X-axis Label, and set the range from 0 to 8.
3. To view the J-J splitting you can expand regions of the spectrum using New View/Mouse X and Y. You can also use the integrate feature to tell the relative areas under the peaks. It shows that the doublet (right side of spectrum) has twice the protons as the triplet. Clearly, the doublet represents the CH_2 protons coupling to the CH, and the triplet comes from the CH proton resonance split by coupling to the CH_2 protons.
4. Now simulate the spectrum shown below. It has 6, 1, 2 and 1 protons at chemical shifts 0.91, 1.76, 3.4 and 2.4 respectively. The nuclear spin-spin couplings are J_{12} = 6.7, J_{23} = 6.5, J_{34} = 5.5 Hz, and all others zero. It is an alcohol with molecular formula $C_4H_{10}O$. Can you deduce its structure and explain the splitting patterns? Put your answers in your lab report.



OPTIONAL

^{13}C MAGNETIC RESONANCE SPECTRA

1. Go back to the beginning with Start Over/complete restart, and select Carbon System from Menu.
2. Choose Butyraldehyde. Add TMS. Select 100 MHz for the spectrometer operating frequency. Continue. Do FFT. Set noise to zero, flip angle to 90º, data points to 2048. Continue.
3. Zero fill and Do FT. Notice the ringing at each frequency. This is an artifact introduced by Fourier transforming a FID signal that has not decayed by the end of the acquisition time. Go back and change the relaxation time (T2) to a smaller value (e.g. 0.03 s).
4. Once you have a "clean" spectrum, adjust the frequency scale so that TMS is at zero (New View/New Freq. Zero). You need to decide which peak is due to TMS! You can try simulating the spectrum without TMS added, or you can deduce the answer by thinking about the intensities of the lines.
5. Now switch to a delta scale, using New View/X-axis Label. ^{13}C chemical shifts are very large! You may want to adjust the *x*-axis scale with New View/New X-range. 0–320 is a sensible range (the program puts tic-marks every 1/8 of the *x* axis.