

NUCLEAR MAGNETIC RESONANCE SPECTROPHOTOMETRY

Basis of the Experiment

A nuclear magnetic resonance (NMR) spectrometer is used to demonstrate the power of NMR to help determine the structure of organic molecules. Hydrogen and carbon-13 NMR spectra are recorded for a series of alcohols, hydrocarbons, and ketones. Chemical shifts, splitting patterns, and peak areas in the spectra are used to determine structure. An unknown is analyzed.

Apparatus

Bruker DRX-300 NMR spectrometer
5 mm NMR sample tubes

Reagents & Solutions

Alcohols

ethanol $\text{CH}_3\text{-CH}_2\text{-OH}$
tert Butyl Alcohol $(\text{CH}_3)_3\text{C-OH}$
2-butanol $\text{CH}_3\text{-CH}_2\text{-CH(OH)-CH}_3$
2-propanol $(\text{CH}_3)_2\text{CH-OH}$

Hydrocarbons

benzene C_6H_6
toluene $\text{C}_6\text{H}_5\text{-CH}_3$
cyclohexane C_6H_{12}

Ketones

acetone $\text{CH}_3\text{-CO-CH}_3$
methyl ethyl ketone $\text{CH}_3\text{-CO-CH}_2\text{-CH}_3$

Lock Solvent

Deuterated Chloroform CDCl_3

Background

Nuclear magnetic resonance (NMR) spectroscopy provides the chemist with information about molecular structure. NMR can only be performed on molecules containing nuclei with the property spin. When nuclei with spin are placed in a magnetic field distinct magnetic energy levels are formed. An NMR spectrum is a plot of absorbed energy by a molecule with magnetic energy levels as a function of the photon frequency, ν . The frequency axis has units of PPM relative to the operating frequency, ν_0 , of the NMR spectrometer. This quantity is referred to as the chemical shift, δ , and is calculated by the following equation.

$$\delta = (\nu_0 - \nu) \times 10^6 \nu_0$$

The environment around a nucleus determines the its absorption frequency or chemical shift. Hydrogen nuclei in a $-\text{CH}_3$ group adjacent to a Cl will have a different chemical shift than those next to a $-\text{CH}_2-$ group. Your text has table of hydrogen and carbon-13 (C-13) chemical shifts.

The multiplicity of a peak is related to the number of adjacent nuclei with spin. A CH_3 group adjacent to a Cl will have one peak in its spectrum. A CH_3 group adjacent to a $-\text{CH}-$ group will have two equal peaks in its spectrum at the chemical shift for $-\text{CH}_3$. A CH_3 group adjacent to a $-\text{CH}_2-$ group will have three peaks in its spectrum at the chemical shift for $-\text{CH}_3$, with a ratio of 1:2:1. Only nuclei non-equivalent to the one in question and less than three bonds away will split a peak. This process is called spin-spin splitting. Please see your text and/or class notes for more information.

In hydrogen NMR, the area of a spectral peak is proportional to the number of nuclei of that given type. Therefore, comparing the ratio of peaks at a given chemical shift will provide the ratio of the number of hydrogens of a given type in the molecule.

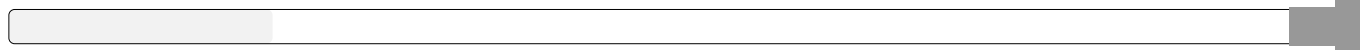
The peak area in C-13 NMR is not proportional to the number of C-13s in the molecule. Additionally, in C-13 spectroscopy you do not see splittings from hydrogen nuclei because the spectrometer is set up to eliminate this interaction. See the NMR chapter of Skoog, or the hypertext book *The Basics of NMR* (<http://www.cis.rit.edu/htbooks/nmr/>) for details of the theory of NMR.

Procedure

1. Obtain a hydrogen NMR spectrum of each of the alcohols, hydrocarbons, and ketones listed under reagents and solutions. Use the pulse sequence or experiment on the spectrometer called *PROTONEXP*. Rationalize the observed chemical shifts, splitting patterns, and peak areas.
2. Obtain a ^{13}C NMR spectrum for one alcohol, one hydrocarbon, and one ketone (three total) listed under reagents and solutions. Use the pulse sequence or experiment on the spectrometer called *C13CPD32*. Explain the observed chemical shifts, peak areas, and the splitting patterns.
3. Obtain an unknown from your instructor and prepare an NMR sample in the lock solvent CDCl_3 . Obtain hydrogen and ^{13}C NMR spectra of your unknown as above.

Sample Preparation

1. All of the above compounds should be soluble in chloroform. Therefore, CDCl_3 will be used as the deuterated lock solvent. If your sample did not dissolve in Cl_3CD , acetone- D_6 ($\text{CD}_3\text{-CO-CD}_3$) or deuterium oxide (D_2O) may be used.
2. Fill an NMR sample tube with 3.5 cm of the deuterated lock solvent. (Please note that the deuterated lock solvents acetone- D_6 and deuterium oxide absorb water (H_2O) from the atmosphere and become contaminated.) Minimize the time the bottles are open.



3.5 cm deuterated lock solvent in NMR sample tube, final sample concentration $\approx 1\%$

3. Add one drop of the sample to the NMR tube.
4. Place the cap on the tube and mix by shaking the tube.
5. Position the tube in the blue sample tube holder using the depth gauge.

Operation of the Spectrometer

1. Log on to the spectrometer as `scha311`. (See lab instructor for system password.)
2. Type `iconnmr` in the unix window, and press return.
3. Click on Routine Spectroscopy.
4. Log in again as `scha311`.
5. Click on Inject/Eject and follow instructions.
6. Click on Filename and follow instructions.
7. Click on Set Solvent and select your solvent (CDCl_3 will appear as `CDCl3`) from the list.
8. Click on Set Experiment and choose your experiment. (*e.g.* `protonexp`)
9. Click on Start and wait for spectrum to come out of printer. (This takes about 8 minutes.) In this time the spectrometer is performing several operations.
 - a) Spinning the sample so the magnetic field is more homogenous over the sample.
 - b) Locking the magnetic field to the deuterium signal so that the field does not drift when a truck passes outside.
 - c) Shimming or homogenizing the magnetic field so the peaks in the spectrum are well resolved.
 - d) Adjusting the receiver gain so the signal has the appropriate amplitude.
 - e) Recording the time domain spectrum.
 - f) Fourier transforming the time domain spectrum.
 - g) Integrating the peaks in the spectrum.
 - h) Plotting the spectrum.
10. If any one of these steps fails to be completed successfully, a spectrum will not be produced.
11. Click on exit when the spectrum has been printed.
12. You may choose to eject your sample and quit, eject your sample and insert a new one, or use the same sample and take a different spectrum.
13. When you are finished, eject your sample and log out.