

## EXPERIMENT 9

# SPECTROSCOPY. NUCLEAR MAGNETIC RESONANCE (NMR) AND INFRARED (IR)

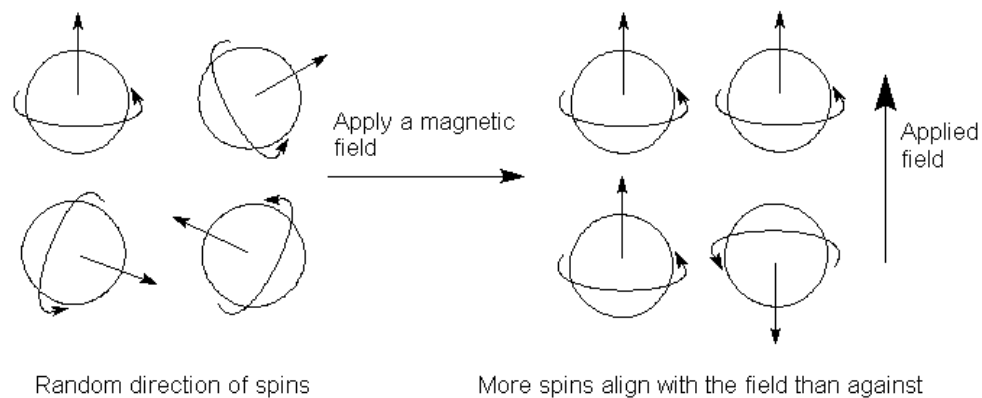
### Materials Needed

- approx 100 mg of an ester synthesized in Expt #7 - (octyl acetate, benzyl acetate, or isopentyl acetate)
- approx 1 mL NMR solvent  $\text{CDCl}_3$
- 1 NMR tube with cap, Pasteur pipet
- Salt plates, acetone wash solvent

### BACKGROUND

**NMR Spectroscopy.** The nuclei of some atoms behave as if they were spinning similar to the way a top spins about its axis. The number of neutrons in the nucleus is critical to its ability to exhibit such behavior. Hence, only the nuclei of certain isotopes of an atom can spin. Important examples of spinning nuclei are  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$ , whereas  $^{12}\text{C}$  and  $^{16}\text{O}$  are two nuclei that do not spin. It is important to realize that, much like a top, nuclei that spin have at least two possible *spin states*, i.e., they can spin either in a clockwise or a counterclockwise direction.

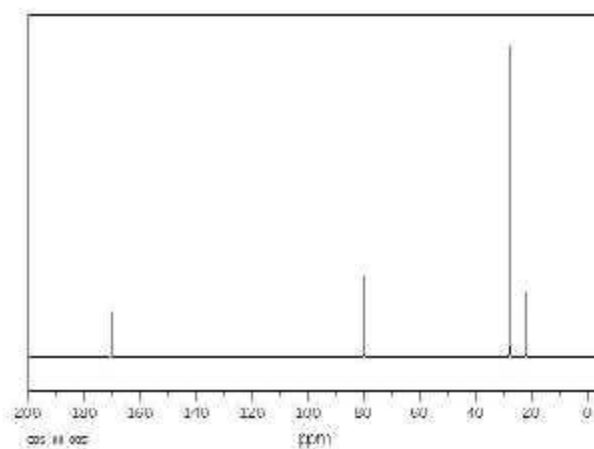
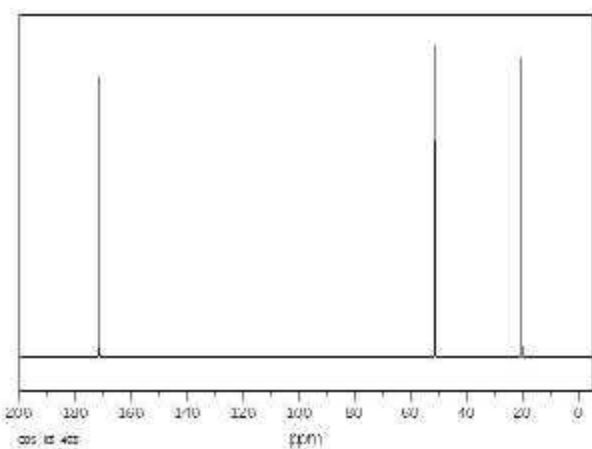
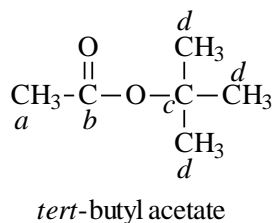
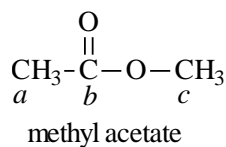
Because a nucleus is positively charged, its spinning generates a small magnetic field. One can thus view a spinning nucleus as a small magnet with north and south poles. When such a nucleus is placed inside a magnetic field the different spin states available to it will correspond to different energy levels for the nucleus. Nuclear magnetic resonance (NMR) describes the fact that such a nucleus will absorb radio waves that have a frequency that is equal to the energy difference between the spin states. This absorption of energy causes the nucleus to be excited to the



higher energy spin state. In simpler terms, the nucleus reverses the direction in which it is spinning. (The spinning nuclei at right in the diagram above become like the one at bottom right.) A nucleus inside a magnetic field that is flipping its spin due to its absorption of radio waves is said to be *resonating*.

**The exact resonance frequency of a nucleus depends on its chemical environment.** In other words, the presence of other nearby atoms in the same molecule affects it. One way this happens is through an electronegativity difference that causes the atom to become more electron rich or electron poor. A greater electron density around a nucleus tends to shield it from the magnetic field of the NMR instrument (it doesn't feel the full impact of the magnetic field) and, hence, it resonates at a lower frequency. Conversely, an electron-poor nucleus (an atom with a partial positive charge) resonates at a relatively higher frequency.

In this experiment we will obtain carbon NMR spectra of the esters from experiment #7. A carbon NMR spectrum shows all of the different frequencies absorbed by the carbon atoms in a molecule. These frequencies show up as *peaks* on a graph of intensity vs frequency. (Frequency is given in units of parts per million or ppm for reasons we won't go into here.) The number of peaks in a carbon NMR spectrum tells you how many distinct carbon atoms there are in the molecule. Often two or more carbon atoms in a molecule have the same chemical environment and, thus, give only one peak and are considered equivalent. Two illustrative examples are given below.



Methyl acetate gives 3 peaks in its carbon NMR spectrum. (None of the carbons are equivalent, thus we see one peak for each carbon in the molecule). The *b* carbon is the most electron poor (partially positive) so it resonates (gives a peak) at the highest frequency of the three. Similar reasoning leads to the conclusion that the *a* carbon will resonate at the lowest frequency. *tert*-Butyl acetate, on the other hand, has only four peaks in its NMR spectrum even though there are six total carbons in the molecule. This is because the three methyl group carbons are all equivalent to each other. Also note that carbon *a* in *tert*-butyl acetate will have a very similar resonance frequency to that of carbon *a* in methyl acetate and ditto for the *b* carbons in the two molecules.

**IR Spectroscopy.** Covalent bonds in organic molecules behave much like springs with two weights (the bonded atoms) attached. The specific vibration frequency of such a spring is given by the mathematical equation known as Hooke's law. Applying Hooke's law to the bonds in a molecule results in three predictions:

1. The frequencies of vibration correspond to frequencies of radiation in the infrared region of the electromagnetic spectrum.
2. Bonds to lighter atoms (e.g. hydrogen) have the highest vibrational frequencies. So, C-H, N-H, and O-H bonds have the highest frequency vibrations (higher than C-C, C-N, C-O etc).
3. Stronger bonds have higher frequencies of vibration and therefore, multiple bonds have higher frequencies than single bonds. So C≡C is higher than C=C, which is higher than C-C. Also C=O is higher than C-O.

Thus, the bond vibrations in a molecule can be stimulated by specific frequencies of IR radiation. When this happens the energy of the IR radiation is absorbed as the molecule becomes vibrationally excited. An IR spectrometer measures the frequencies of IR that are absorbed by a molecule. Because each type of bond in the molecule absorbs its own specific frequency, the IR spectrum graph shows the types of bonds that are present in the molecule. In our case, the ester product we are testing contains the following bonds; C=O, C-O, C-H, C-C all of which should show characteristic peaks on the IR spectrum.

## **PROCEDURE**

**General** - Come together in groups of four to six for this experiment. (Team up with the other groups in the lab that synthesized the same ester as you.) Each group will be assigned a fume hood to work in. Each group will prepare samples for both NMR and IR analysis. Then the instructor will demonstrate the operation of the NMR spectrometer and print out a spectrum for each ester analyzed. The TA will assist with obtaining the IR spectra.

### **NMR Procedures**

**Safety Precautions** -  $\text{CDCl}_3$  has harmful fumes avoid breathing it and dispense it in a fume hood.

**Preparing the Sample.** NMR tubes and solvents are very costly so please be very careful with the tubes and do not waste the solvent. Also, be very careful when capping and uncapping your NMR tube. The tubes are fragile and the caps are tight so it is easy to break a tube in the process of capping it. Use a Pasteur pipet to add the ester to the NMR tube to a height of approximately 2-3 mm. Now add the  $\text{CDCl}_3$  solvent carefully to a height in the tube of approximately 5 cm. Cap the tube with the plastic cap provided and label your tube by writing on the side of the cap with a permanent felt tip marker

### **IR Procedures**

**Preparing the Sample.** Place a few drops of ester on a salt plate and then place another salt plate on top to make an "ester sandwich". The TA will assist in operating the IR instrument. After, you get a satisfactory printout of your spectrum, clean the salt plates off with acetone, rinsing into a waste beaker in the fume hood in the IR lab.

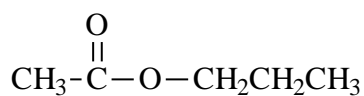
## PRELABORATORY QUESTIONS

### EXPERIMENT 9

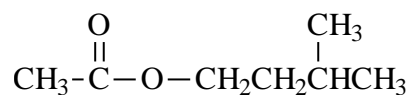
### SPECTROSCOPY. NUCLEAR MAGNETIC RESONANCE (NMR) AND INFRARED (IR)

Name \_\_\_\_\_ Section \_\_\_\_\_ Date \_\_\_\_\_

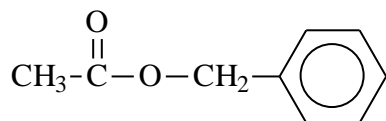
Predict the number of peaks in the carbon NMR of the compounds to be examined in today's lab.



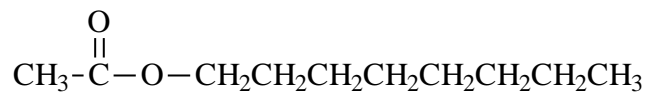
propyl acetate



isopentyl acetate



benzyl acetate



octyl acetate

## IN-LAB OBSERVATIONS/DATA

### EXPT 9 - SPECTROSCOPY. NMR AND IR SPECTRA OF AN ESTER.

Names \_\_\_\_\_ Section \_\_\_\_\_ Date \_\_\_\_\_

Ester analyzed \_\_\_\_\_

#### Observations

ester \_\_\_\_\_  $\text{CDCl}_3$  \_\_\_\_\_

NMR sample solution \_\_\_\_\_

#### Mass Data

NMR tube and cap (g) \_\_\_\_\_ NMR tube, cap, and ester (g) \_\_\_\_\_ ester (g) \_\_\_\_\_

#### Results

Structure of the ester with carbons labeled as in the examples on page 2 of this lab handout. (Label equivalent carbons, if there are any, with the same letter.)

C-13 resonance frequencies (ppm)	carbon(s) (a,b,c,.. from labeled structure above)	IR absorption frequencies ( $\text{cm}^{-1}$ )	Type of Bond

## QUESTIONS

1. Explain how the carbon NMR and IR spectra provide evidence for the structure of the ester you prepared.
  
2. Why does the C=O carbon resonate at nearly the same frequency in all of the esters analyzed as well as in the example esters discussed on page 2? Also explain why its resonance frequency is so high compared to the other carbons in the molecules.
  
3. Carbon is not the best nucleus to use for NMR experiments partly because  $^{12}\text{C}$ , a nucleus with no net spin and therefore unable to do NMR, is the main isotope of carbon that occurs on earth. The experiment we did only looked at the  $^{13}\text{C}$  atoms in the sample. Look up the natural abundances of C-12 and C-13 isotopes. What percent of the carbons in your sample were you actually seeing in your spectrum?