Pre-lab preparation. (1) In Ch 5 and 12 of the text you will find examples of the most common functional groups in organic molecules. In your notebook, provide generic examples of the following compound classes: (a) alkane, (b) alkene, (c) alkyne, (d) alkyl halide, (e) alcohol, (f) amine, (g) ether, (h) aldehyde, (i) ketone, (j) carboxylic acid, (k) ester, (l) anhydride, (m) amide, (n) acyl halide, (o) nitrile, (p) arene (this term usually implies a benzenoid aromatic compound; draw benzene as an example), (q) there are lots more, but did we miss any common ones?

Now for a little refresher on structures and properties... (2) Compounds in these classes can contain rings, of course, but for which classes can the functional group itself be part of a ring? For example, the –O– of an ether can be within a ring, but the –OH of an alcohol cannot (why?!)

(3) Note that there are several different types of amines and amides — classified as 1°, 2°, and 3°. Draw a generic example of each. (4) Which compound classes contain a carbonyl group?

(5) This lab is designed so that you do NOT need to read the IR chapter in the text first! (you're welcome) In fact, after you complete this experiment, you will be able to breeze right through that chapter. Whoosh.

You were introduced to IR spectroscopy last semester during the cyclohexene lab. You may remember that we heated cyclohexene in the presence of a black Pd/C catalyst and found that alkenes had gotten together and decided to swap Hs to make cyclohexane and benzene, as indicated by GC and IR of the final hydrocarbon mixture. IR was able to provide some indications of key structural changes that took place, though the changes were rather subtle in that case. For most common classes of organic compounds, IR will provide clear indications of functional groups and other structural features that may be present.
Infrared spectroscopy measures the frequencies of IR light absorbed by a sample and the intensities of the absorptions. The vibrational frequencies depend on the nature of the vibration (bending vs stretching), bond strengths, and the masses of the atoms involved in the vibration. The intensities depend on the change in dipole moment that accompanies the vibration as well as the number of bonds involved. While an appreciation of these factors is helpful in understanding an IR spectrum, it is often sufficient simply to recognize the general frequency range and appearance of an absorption peak to determine what functional group is present.

In Part 1 of this experiment, you will compare and contrast actual IR spectra of a variety of different compounds and determine what key absorptions are characteristic of each functional group or can be attributed reliably to other specific structural features. This part is going to be done at your lab bench with a series of IR spectra cards. In Part 2, you'll be running your very own IR spectra on the new, ultra-high-tech ATR FT-IR (Attenuated Total Reflectance Fourier Transform IR) This instrument is especially good for obtaining spectra of solids, such as the ones you saved from last semester — fluorenone, benzoic acid, benzocaine, and acetanilide. You can do this part before, during, or after Part 1 — whenever the instrument is free.

Part 1 — Each group will find two decks of cards containing IR spectra and the structures of the compounds to which they belong. These decks will be used for all the lab sections, so please don't write on them. Your goal in this lab is to identify the important IR absorptions that are characteristic of certain compound classes and functional groups. You will also be looking at the variations within groups of similar compounds, the effect of having two or more functional groups in proximity, and effect of isotopic substitution. Write the answers to the questions in your notebook as you go.

Start by separating the spectra in the orange card set according to functional groups. Most of the important vibrations will be above 1500 cm\(^{-1}\). Notice that the fingerprint region (below 1500 cm\(^{-1}\)) of is quite complex in most of the spectra. If you happen to notice some features in that region that are common to certain structural features, fine, but if you try to make sense out of every peak you'll never get finished.

1 Notice that in each spectrum there is an absorption for the C–H stretches (these may be partly obscured by other stretches) around 3000 cm\(^{-1}\). Compare the C–H stretches that you see
in the various hydrocarbons (alkanes, alkenes, alkynes, aromatic compounds). Note that most of these have a cluster of peaks in the same place; in some cases additional peaks are present. How do you account for the presence of these extra peaks? That is, what's different about some of the C–H stretches? Are these C–H bonds stronger or weaker than the main group? Why?

2 Now, focusing just on the informative region of each spectrum (i.e. not the fingerprint region and not the C–H stretches), what are the characteristic absorptions of each of the following compound classes? In some cases, the answer may be "none". What structural feature do you think is responsible for each key absorption?

- a Alkane
- b Alkene
- c Alkyne
- d Alcohol
- e Ether
- f Amine
- g Nitrile
- h Aldehyde
- i Ketone
- j Carboxylic acid
- k Anhydride
- l Ester
- m Amide

3 Within several of these categories are both cyclic and acyclic compounds. Is there any discernable difference in the spectra of cyclic and acyclic compounds? Are the key absorptions shifted, perhaps? Is the a peak somewhere that can be attributed to the presence (or absence) of a ring?

4 Look at the spectra of the carbonyl-containing compounds (ignore the anhydrides for now). Is there a noticeable difference in the carbonyl group stretching frequency among these? If so, what is the structural explanation? (hint: You may want to think about resonance.)

5 Bonds that are similar in frequency and near each other in the structure often stretch in combination. Look at the N–H stretches of primary amines and primary amides. The two peaks do not correspond to vibrations of the individual bonds, but rather to symmetric and asymmetric combinations of those stretches. Pretend that your body is the N and your hands are the Hs. Stand up and demonstrate these stretches for your partner. Next, tuck your hands under your armpits, flap your elbows, and cluck like a chicken. Now stop that — people are staring.
Notice the same feature in the carbonyl stretching region of anhydrides. Have your partner demonstrate the symmetric and asymmetric carbonyl stretches this time.

6 Now let's think a little about absorption intensities. Absorption of IR radiation requires a change in dipole moment accompanying the vibration that gets excited. We don't need to calculate dipole moments to understand this, only to appreciate the following: (1) the more polar the bond, the larger its dipole moment, and the larger the change in its dipole moment during a stretch (since dipole moment depends on the magnitude of the charges and their separation). (2) If there is zero dipole moment by symmetry and it remains zero during the vibration, no IR stretch is observed. In this case there's no oscillating charge to interact with the oscillating electric vector of the light, so the vibration is invisible.

(a) Compare the intensities of the double bond stretches of the alkenes and carbonyl compounds, and explain the dramatic difference. Why is one type so much more intense than the other? (b) Look at the alkyne spectra again. Why does one compound of the three not display the peak around 2100 cm$^{-1}$?

7 The blue set of cards contains spectra of compounds with more than one functional group, as well as some aromatic compounds. (a) First, compare the spectra of compounds with their functional groups isolated from each other. How do these stretching frequencies compare with the compounds in the first set of cards? (b) Now look at the spectra of compounds with conjugated $\pi$-bonds. How does conjugation affect the stretching frequencies of the double and triple bonds? Is the stretching frequency of a C=O affected more by conjugation with a C=C or with an aromatic ring? (c) Explain the effect of conjugation on the C=O stretching frequency. (Draw resonance structures.) (d) Can the same explanation be applied to the conjugated nitriles?

8 Now look at the compounds that have an O or an N lone pair conjugated with a C=C. How do the frequency and intensity of the C=C stretch compare with that of a simple alkene? Explain. (Draw resonance structures.)

9 Look at the pages of IR spectra of simple aromatic compounds. Are there any features that appear characteristic of aromatic rings? Are there any discernable differences among the ortho-, meta-, and para-ethyltoluene isomers?
Finally, compare the spectra of compounds with isotopic substitution on the separate pages. Bond stretching frequencies depend on the bond strength, as we've already seen, and on the masses of the bonded atoms. This dependence is described by Hooke's law

\[ \frac{\sqrt{N}}{\alpha} \propto \sqrt{\frac{k}{m}} \]

where \( k \) is the force constant for the bond and \( m \) is the reduced mass,

\[ m = \frac{m_1 m_2}{m_1 + m_2} \]

\( m_1 \) and \( m_2 \) being the masses of the bonded atoms.

In the three sets of compounds, HCBr\(_3\) and its deuterated analog, acetone and its \(^{13}\)C and \(d_6\) analogs, and ethanol and ethanol–OD, explain the differences in some of the vibrational frequencies. Are the frequency differences *roughly* in accord with what you would expect from Hooke's law? (The correlation will probably not be perfect because the stretches are not strictly confined to a single pair of atoms — nearby atoms get into the act a bit as well.)

Your final task in Part 1 will be to apply what you learned to solving the two attached problems. Each of these asks you to select the compound from the set given that is responsible for each of the four IR spectra shown. Turn in the duplicate pages of your notebook *at the end of the lab period*, and you're done. (but don't forget about part 2)

**Part 2 — IR spectra of solid samples.** Your next task will be to measure IR spectra of the fluorenone, benzoic acid, benzocaine, and acetanilide samples that you saved from last semester. Coordinate with one other group. Your group should run two of the solids; the other group should run the other two. The instructor and/or TA will show you how to use the ATR FT-IR spectrometer. This instrument will only require a tiny amount of solid, which is pressed by an anvil against a ZnSe crystal. Please be very careful not to scratch the crystal.

Hang on to the spectra until the next lab period. If you're lucky you will get NMR spectra of some of these compounds to analyze along with your IRs during the next lab period.
1. Each IR spectrum below belongs to one of the compounds shown. Write the letter of the spectrum below the compound to which it belongs. Draw an X through the four compounds whose spectra are not shown.

- CH₃CH₂CH₂—C≡N
- Cyclic compound
- CH₃CH₂—OH
- CH₃CH₂—Cl
- CH₃CH₂—CO₂H

A

B

C

D
2. The IR spectra below belong to four of the compounds shown. Write the letter of the spectrum below the appropriate compound. Draw an X through the five compounds whose spectra are not shown.

![Chemical structures and IR spectra](image)

A

B

C

D