Experiment 4 – IR Exercise

Learning Objectives

- Understand principles behind IR Spectroscopy as it relates to the stretching & bending of bonds
- Observe the inverse relationship between vibrational frequency and bond length
- Analyze spectra to predict functional groups and bonds in an organic molecule
- Understand the role resonance plays in vibrational frequencies
- Observe effects on sample preparation on quality of spectra

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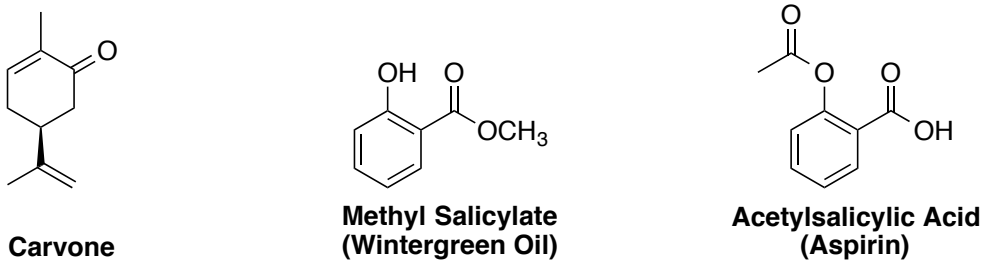
* Please find “How to Prepare & Assignments” after the procedure

In this experiment, students will study the infrared (IR) spectra of aspirin, carvone, and methyl salicylate (wintergreen oil). The purpose of the experiment is to become familiar with IR spectroscopy, including sample preparation and the interpretation of IR spectra for bond and functional group identification. Carvone is a monoterpenoid that is the oxidation product of limonene, the main component in citrus oil. Methyl salicylate is used in chewing gum for flavor and in muscle rubs for its cooling, pain-relieving (analgesic) properties. Carvone and methyl salicylate are liquids and their IRs are obtained directly from a very small drop of pure (aka “neat”) material. Methyl salicylate is the hydrolysis product of aspirin, a commonly known analgesic used for headaches. Aspirin is a solid and is diluted with the hydrocarbon mixture nujol to prepare the sample for IR analysis.



Carvone | **Methyl Salicylate (Wintergreen Oil)** | **Acetylsalicylic Acid (Aspirin)**

Figure 1. Structures of compounds to be analyzed by IR.

IR spectroscopy is similar to spectrophotometry, a common technique in the general chemistry labs used to determine the concentration of colorful samples based on absorbance of visible light. In spectrophotometry, a sample (ex. solution of red dye) *absorbs a specific wavelength of light* in the visible range of the electromagnetic spectrum (**Figure 2**). The spectrophotometer displays an absorbance value that is correlated to the concentration of the solution. **IR spectroscopy explores a different range of radiation in order to determine the types of bonds and functional groups present within a molecule**. Every molecule has a unique IR spectrum with multiple absorbances at specific frequencies, known as **wavenumbers (cm^{-1})**.

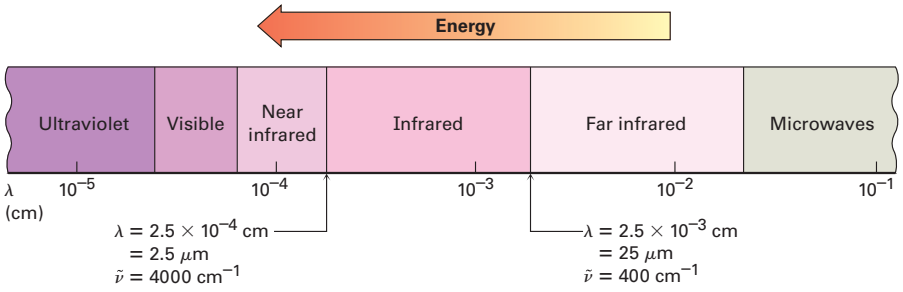


Figure 2. Electromagnetic spectrum, highlighting infrared (IR) region

Molecules are always in motion at rapid rates that are difficult to fathom! *Translational* motion is when a whole molecule moves to a different space. The rate of translational vibrations is highest for gases and lowest for solids. Bonds within molecules are constantly *rotating*, particularly sigma or single bonds. *Translational and rotational vibrations are not detected by IR spectroscopy.*

IR active bonds are those that exhibit **antisymmetric stretching** and **out-of-plane bending** (**Figure 3**). Stretching and bending of bonds in organic molecules occur at frequencies (wavenumbers) within the IR range, between 400 – 4000 cm^{-1}. Absorption of IR radiation in the spectrometer results in the *amplified* stretching and bending of bonds characteristic of its functional group.

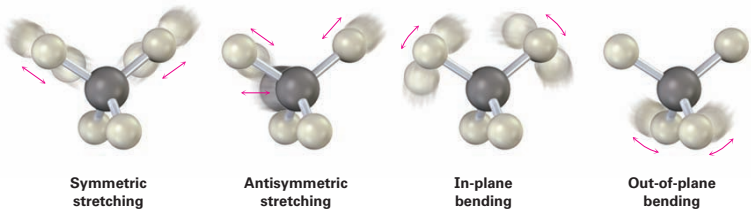


Figure 3. Stretching and bending vibrations.

$\bar{\nu}$ **Wavenumber** is the preferred unit for IR spectroscopy, simply because the values are easier to work with than wavelength (compare 400 cm^{-1} and 2.5 x 10^{-3} cm). Wavenumber is the inverse of wavelength **(eq. 1)**. Though it's not a typical frequency unit (cycles per second or s^{-1}), *wavenumber is proportional to frequency* so the terms are used interchangeably in IR discussions.

$$\bar{\nu} = \frac{1}{\lambda} \qquad \textbf{(eq. 1)}$$

The general rule in understanding IR spectra is that longer bonds go through a vibrational cycle less frequently and **shorter bonds vibrate more frequently.**

Longer Bond = Slower (↓) Stretching Frequency

	O-H	C-H	C=O
Bond Length (pm)	100	110	120
Stretching Frequency (cm^{-1})	3300	2900	1700

During IR analysis, energy is absorbed by each IR active bond and the remaining transmitted (not absorbed) IR frequencies are detected by the instrument and plotted on the spectrum – wavenumber vs. % transmittance (%T).

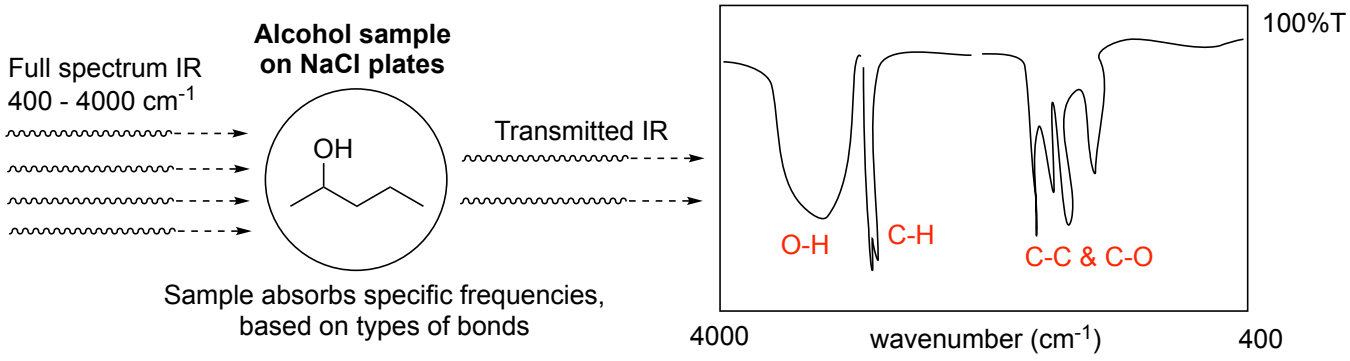


Figure 4. Crude diagram of IR spectroscopy and amateur sketch of alcohol spectrum.

Bonds **expand & contract (stretch)** at relatively higher frequencies (1000 – 4000 cm^{-1}) and **C-H out-of-plane bending** occurs at lower frequencies between 500 – 1000 cm^{-1}. Note that out-of-plane bending occurs within the **fingerprint region**, which displays characteristic signals for specific compounds, like its unique fingerprint. The region between *1000 – 1500 cm^{-1} is often ignored* due to complex overlap of the numerous C-C, C-N, and C-O bonds often present in organic molecules. A complete table of functional groups, bonds, and expected wavenumber ranges is at the end of this document and posted separately on Canvas. Typical examples and trends are discussed below.

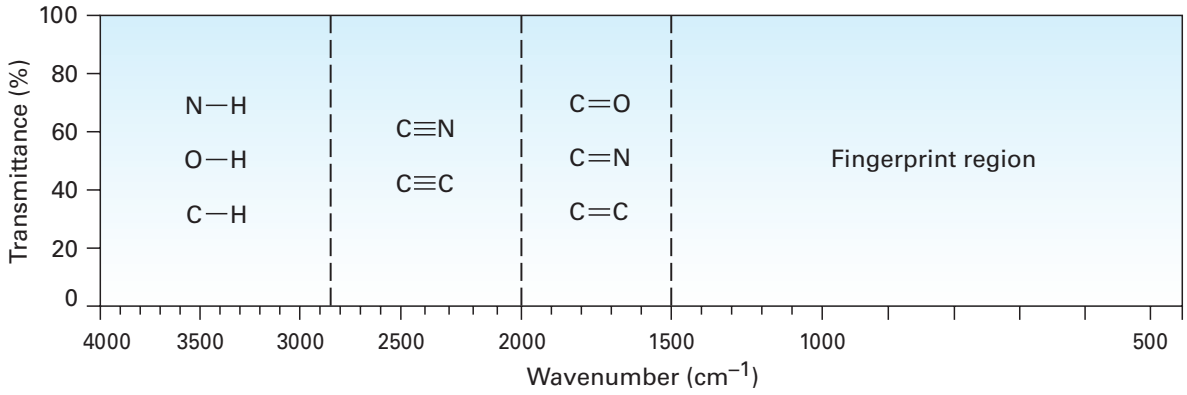


Figure 5. Four main regions of the IR spectrum.

The main *factors affecting bond length* and vibrational frequency are **atomic radius**, **hybridization** or type of bond, and **conjugation** (resonance). Single bonds to hydrogen are the shortest bonds because hydrogen is the smallest atom and thus have the highest stretching frequencies (2800 – 4000 cm^{-1}). Single bonds between sp^3 hybridized C-C, C-N, and C-O are the longest bonds and have the lowest stretching frequencies (1000 – 1500 cm^{-1}), though these signals are typically ignored in IR spectra as mentioned above.

Atoms that are sp^2 hybridized, typically double bonds, are held closer together and stretch more frequently (1500 – 2000 cm^{-1}) than corresponding single bonds. A sharp signal around 1700 cm^{-1} is characteristic of a carbonyl (C=O). The identity of the carbonyl functional group determines a more specific range of stretching frequency. This allows the observer to predict whether the carbonyl is within an aldehyde or carboxylic acid, for example. This trend continues with sp hybridized atoms, often triple bonds, which stretch between 2000 – 2800 cm^{-1}.

The ranges presented above are general guidelines. When the functional group is **conjugated**, or participates in resonance, the overall *bond length is increased* and the ***stretching frequency decreases***. This is exemplified in **Figure 6** below. The quickest way to spot a conjugated functional group is to look for alternating double-single-double- bonds.

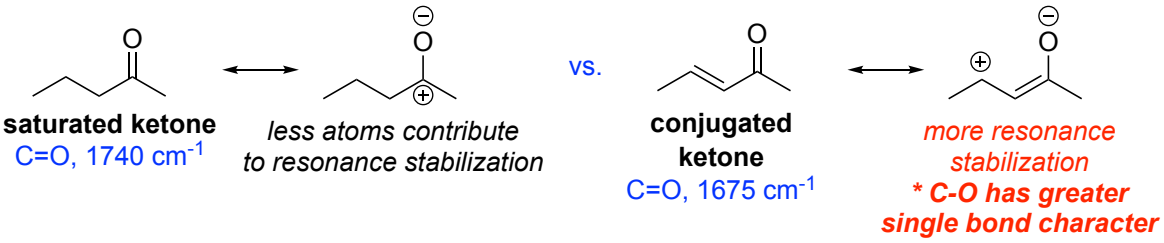
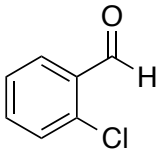


Figure 6. Comparison of stretching frequencies in a saturated vs. conjugated ketone.

This lab exercise will focus on using IR spectra to confirm the presence of functional groups in known compounds. Before running the IR sample, signals are predicted by making a **list of all functional groups** in the molecule. The IR table of values (end of this document) provides the expected range of frequencies for each type of bond within each type of functional group. A worked example of the predicted IR signals and assignment of a literature spectrum is presented below.

Steps for predicting IR spectra

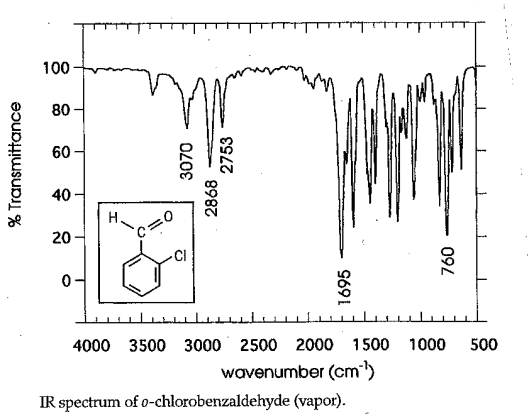
- Determine each **functional group** in the molecule (ex. *ortho*-chlorobenzaldehyde).
- Use the **IR Table** (end of this document) to find the IR active **bonds** within each functional group (FG) and its expected wavenumber range.
    - Be sure to list **all bonds and vibrations**.
        - FG's may have *multiple IR active bonds*.
        - Some bonds have two different vibrations (ex. C-H bonds in arenes stretch and bend).
    - Don't forget to determine whether any **double bonds** are **saturated** or **conjugated** (participate in resonance with a neighboring pi bond).
- **If alkenes or an aromatic ring is present:** Use **IR Table 2** to determine the more specific range of C-H bending frequencies. The **substitution patterns** of an alkene or arene ring affect the C-H bending vibrations.



***o*-Chlorobenzaldehyde**

Functional Groups:

- Aromatic Ring
- Aldehyde
- Aryl Chloride



IR spectrum of *o*-chlorobenzaldehyde (vapor).

Table 1. IR Analysis of *o*-chlorobenzaldehyde

* This column would be filled in after your actual IR sample is run. This is example will not be obtained in this lab.

ø Specific out-of-plane bending vibrations (Table 2 in IR reference sheet)

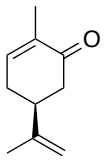
† Values approximated from the x-axis of the IR spectrum.

Functional Group	Bond Assignment (C=O, N-H, etc.)	Expected Wavenumber, cm^{-1}	Literature Wavenumber (cm^{-1})	Observed* Wavenumber (cm^{-1})
Aromatic ring *o*-disub	C-H stretch	3100 – 3000	3070	
	C=C	1625 – 1440	~1600†	
	C-H bend	900 – 680 (770 – 735)ø	760	
Aldehyde (conj.)	C-H stretch	2900 – 2800 & 2800 – 2700, doublet	2868 & 2753	
	C=O	1715 – 1680	1695	
Aryl Chloride	C-Cl	< 600 – 840	~800†	

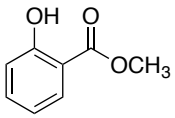
Properly identifying functional groups is half the battle! The IR tables give typical ranges, but remember that factors like conjugation could cause certain bonds to be outside of that range. An acceptable limit outside of the range is 40 cm^{-1} above or below, as long as the structure supports the outlier (ex. highly conjugated bonds may be outside the range). Otherwise, if no signal is observed within that range, it should be reported as "not observed." There are often multiple bonds in the same range, causing signal overlap. One signal may be assigned to two or more bonds along with a note to the reader. A final factor is the **variation in C-H out-of-plane bending frequencies**. Large ranges are listed for a C-H bend in an aromatic ring (900 – 680 cm^{-1}). Incorporating the substitution pattern of the ring narrows this range (770 – 735 cm^{-1}). More relationships are given in the tables at the end of this PDF.

PROCEDURE

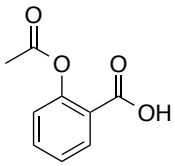
Overview: Predict the IR signals for carvone, wintergreen oil, and aspirin. Watch the demonstrations on preparing and running IR samples, then obtain the IR spectra of carvone, methyl salicylate, and aspirin. Use salt plates (pure NaCl) to support the sample. NaCl does not absorb IR radiation making it an ideal material to hold samples. The NaCl plates are very fragile and break easily. Handle them with care and never wash them with water (they will dissolve!). Instead, use small amounts of the acetone saturated with NaCl provided in the IR kit. Students will also complete an IR worksheet after interpreting IR spectra.



Carvone



Methyl Salicylate (Wintergreen Oil)



Acetylsalicylic Acid (Aspirin)

Predict spectra: Make three tables (one for each compound) with **functional groups**, **bonds**, and **expected wavenumber ranges**. Use the IR table and steps on the previous page for predicting IR bond vibrations and corresponding wavenumber ranges. Note that one functional group may have several IR active bonds (ex. carboxylic acid contains C=O and O-H) and that C-H bonds in alkenes and arenes have two vibrations (stretch and be nd).

Students will interpret two IR spectra per compound: one from the **literature** and one obtained by TAs (**observed**). Interpret the spectra by looking for a signal within each expected range and listing the corresponding wavenumber in the table. It is important to note that **not every signal in the IR spectrum will be assigned to a bond**! As discussed on the previous page, some signals may not be observed and some may be slightly outside the expected range.

IR of liquid samples - carvone and methyl salicylate: Touch the liquid with the tip of a pipet to pick up a small drop of liquid then touch the center of the salt plate with the tip of the pipet, using your thumb to apply pressure. This small amount of liquid should be enough to obtain a good IR. Cover the plate with the other half and spread the liquid by rotating the plates. Place the plates inside the plate holder, being careful not to break the plates, as demonstrated by your TA and obtain the IR spectrum. A "nice looking" IR will contain bands ending in sharp peaks rather than being flat at the bottom. Flat signals or a diagonal baseline are a result of too much sample being used.

IR of a solid sample: Place a microspatula-full of the solid in a mortar and add just one drop of Nujol. Grind the mixture with a pestle for about a minute to get a dense paste (aka "Nujol mull"). Grinding the solid very well is necessary since big solid particles will scatter IR light and lead to curved baselines and distorted spectra. Scoop some of the mull with the rubber policeman provided in the IR kit and spread it on one of the salt plates. Cover with the other plate and rotate them to further spread the mull. Obtain the IR the same way you did for the liquid sample. Keep in mind that Nujol absorbs IR radiation as well. Take a look at the IR of Nujol for reference and to avoid confusing Nujol peaks for sample peaks. It is fairly common for a student's first mull to contain too much Nujol, in which case the procedure is repeated (but you'll be better at it next time!).

Safety First!	**Clean- up**
- Wear gloves when preparing the sample using mortar & pestle. Gloves should be changed often and removed immediately after completion of the chemical operation.	- Clean the salt plates, the mortar and pestle, and the rubber policeman with a little acetone (sat. w NaCl) and tissue paper. Wear gloves when cleaning and remove when you're done.
- Methyl salicylate is toxic.	- Dispose of tissue paper in the trash and **pipets in solid-waste**.
- Carvone is an irritant.	

References

- Mohrig, J. R.; Hammond, C. N.; Schatz, P. F. "Infrared Spectroscopy" in *Techniques in Organic Chemistry*. Freeman: New York, **2006**.
- Palleros, D. R. "Infrared Spectroscopy" in *Experimental Organic Chemistry*. Wiley: New York, **2000**.

How to Prepare & Assignments - Follow Exp 4 Canvas Module…

Before Lab

- Read this PDF and/or listen to podcast
- Attend and/or watch **lab lecture,** taking notes on **lecture templates,** and the **pre-lab videos**
- Practice the lab online, including common mistakes, on the **Slugs@home platform**
- **Pre-lab questions** incorporated into **Pre-lab Quiz** – check Canvas for due date

Lab Notebook Preparation – *Required before lab;* Use the **worksheet** to prepare your **lab notebook** …

- **Purpose:** brief summary of the main lab goals and structures of carvone, wintergreen oil, & aspirin
- **Reagent Table** – add chemical properties; Wikipedia is a reliable source for chemical info
- **Procedure with Diagrams** – hand-drawn using procedure in this PDF, Slugs@home, & class notes
  - Instructions, sketches, & labels for all **equipment, chemical names** with **amounts**, & **transfers**
  - Format: Break it up with flow charts, bullet-points, comic strip, and/or whatever works for you!

During Lab

- Check the **safety rules** to dress for lab and arrive a few minutes early to **Thimann Labs**
- **Pre-lab talk:** tips for success and open Q&A; Show your **lab notebook pages** to your TA
- Perform the experiment with a partner, fill out data & observations in **lab notebook**

After Lab – each partner submits separate, individual assignments

- Upload **Notebook Pages** to Canvas by midnight on lab day – graded on completeness / participation
- Complete & upload the **Lab Report** on GradeScope (GS) – due date on Canvas

Pre-lab Questions – incorporated into Exp 4 Pre-Lab Quiz taken individually on Canvas before lab

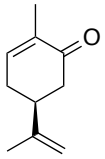
1. What happens when IR radiation is absorbed by an organic sample? How is the frequency of the radiation used to determine the functional groups in the molecule?

2. In IR spectroscopy, we normally talk about "frequencies" when in reality we are referring to wavenumbers. What is the mathematical relationship between frequency and wavenumber? Between wavenumber and wavelength? What are the units most commonly used for frequency, wavelength, and wavenumber?

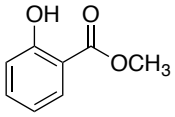
3. What is the range for the IR fingerprint region? Why are the bands in this region of limited use in structure elucidation?

4. What is Nujol? Where (what wavenumbers) does it absorb IR radiation?

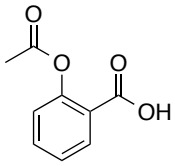
Examine these structures to answer #5-9…



Carvone



Methyl Salicylate (Wintergreen Oil)



Acetylsalicylic Acid (Aspirin)

5. Is the ketone in carvone classified as saturated or conjugated?

6. Is the ester in wintergreen oil classified as saturated or conjugated?

7. Is the carboxylic acid in aspirin saturated or conjugated? The ester?

8. What is the substitution pattern of each alkene in carvone (mono-, di-, tri-, or tetrasubstituted)?

9. What is the substitution pattern of the aromatic ring in wintergreen and aspirin (monosubstituted, ortho-, meta-, or para-disubstituted)?

Lab Report

- **IR Tables**
  - Revise and type three separate tables with predictions & interpretation of the IR spectra…
    - carvone,
    - methyl salicylate,
    - aspirin.

- **In-Lab Question: What is the relationship between bond length and wavenumber?**
  - Provide at least one example per compound's spectrum that supports this trend (ex. longer vs. shorter bond in carvone correlating to higher vs. lower wavenumber).

- **IR Problem Set** – next page

- There is no Abstract section for the Exp 4 report.

IR Problem Set

1. Briefly explain how one could use IR spectroscopy to distinguish between the following pairs of isomers: list the IR active bonds and expected wavenumber range to determine which signals are pertinent.
Hint: start by drawing the structures of each.

a) CH_3CH_2OH & CH_3OCH_3	**b)** cyclohexane & 1-hexene	**c)** $CH_3CH_2CO_2H$ (carb. acid) & $HOCH_2CH_2CHO$ (alcohol & aldehyde)

2. What **functional group(s)** might the following molecules contain?

a) A compound with a strong absorption at 1710 cm^{-1} _____

b) A compound with a strong absorption at 1540 cm^{-1} _____

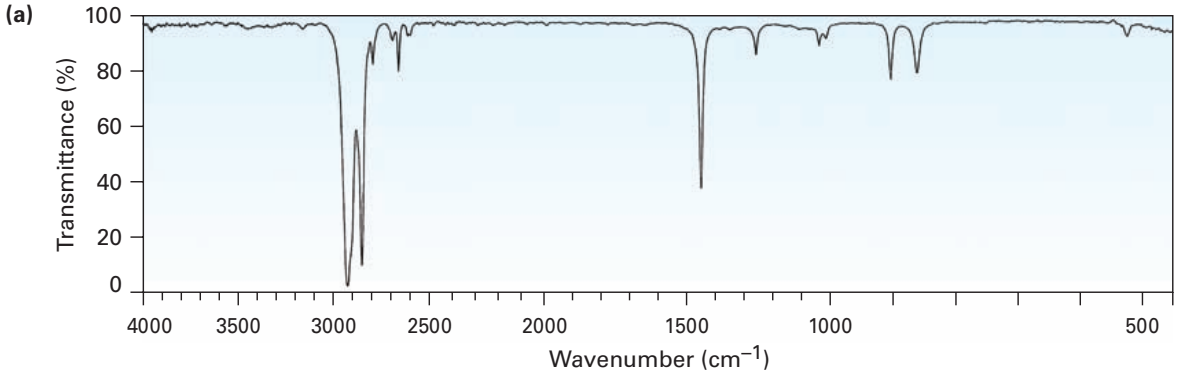
c) A compound with strong absorptions at 1720 cm^{-1} *and* 2500-3100 cm^{-1} _____

3. Acetone (CH_3COCH_3) and 2-propen-1-ol ($H_2C{=}CHCH_2OH$) are isomers. Draw the structures below. How could you **distinguish them by IR spectroscopy**? Reference expected wavenumber ranges from the IR table of values (last pages).

4. Propose at least two structures each for compounds that meet the following descriptions:

a)	**b)**
C_5H_8, with IR absorptions at 3300 *and* 2150 cm^{-1}	C_4H_8O, with a strong IR absorption at 3400 cm^{-1}

5. Consider the two IR spectra below. One is for cyclohexane and the other for cyclohexene. **Draw both structures and correlate to the spectra below.** Briefly explain your answer, referencing expected **wavenumber ranges** from the IR table of values (next page).



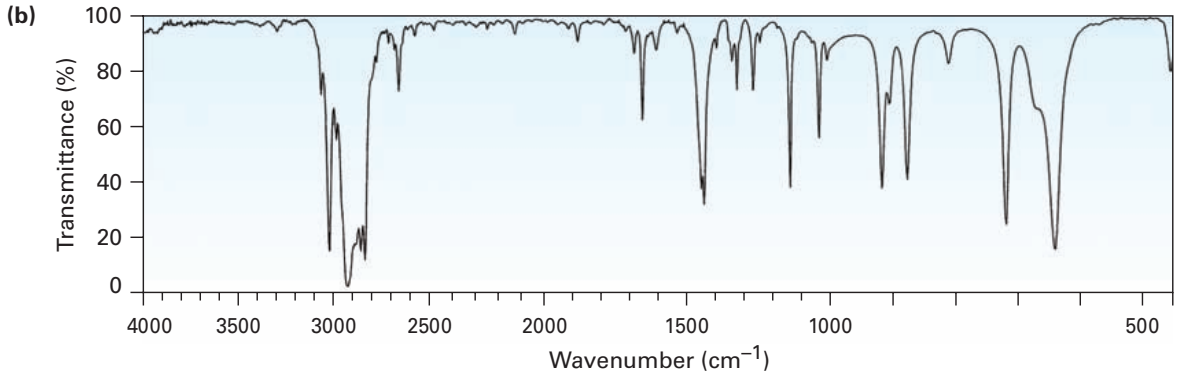


Table 1. Characteristic IR Absorption Peaks of Functional Groups[i]

Functional Group & Bond Vibration	Position (cm^{-1})	Intensity*	Notes
Alkanes			
C-H stretch	2990 – 2850	m to s	
Alkenes			
=C-H stretch	3100 – 3000	m	
C=C stretch	1680 – 1620 (sat.) 1650 – 1600 (conj.)	w to m	
=C-H bend	995 – 685	s	See Table 2 for detail
Alkynes			
≡C-H stretch	3310 – 3200	s	
C≡C stretch	2250 – 2100	m to w	
Aromatic Compounds			
C-H stretch	3100 – 3000	m to w	
C=C stretch	1625 – 1440	m to w	Often hidden in fingerprint region
C-H bend	900 – 680	s	See Table 2 for detail
Alcohols**			
O-H stretch	3550 – 3200	br, s	Hydrogen bonded (typical)
Amines			
N-H stretch	3550 – 3250	br, m	Primary (two bands) Secondary (one band)
Nitriles			
C≡N stretch	2280 – 2200	s	
Aldehydes			
C-H stretch	2900 – 2800 & 2800 – 2700	s	H-C=O Fermi doublet
C=O stretch	1740 – 1720 (sat.) 1715 – 1680 (conj.)	s	
Ketones			
C=O stretch	1750 – 1705 (sat.) 1700 – 1665 (conj.)	s	
Esters**			
C=O stretch	1765 – 1735 (sat.) 1730 – 1715 (conj.)	s	
Carboxylic Acids**			
O-H stretch	3200 – 2500	br, m to w	
C=O stretch	1725 – 1700 (sat.) 1715 – 1680 (conj.)	s	
Amides			
N-H stretch	3500 – 3150	m	Primary (two bands) Secondary (one band)
C=O stretch	1700 – 1630	s	

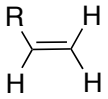
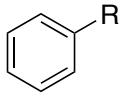
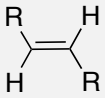
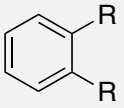
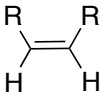
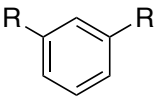
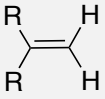
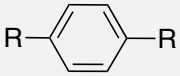
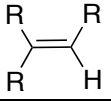
Table 1 cont'd

Vibration	Position (cm^{-1})	Intensity	Notes
Anhydrides**			
C=O stretch	1850 – 1800 & 1790 – 1740	s	
Acid Chlorides			
C=O stretch	1815 – 1770	s	
Nitro Compounds			
NO_2 stretch	1570 – 1490 & 1390 – 1300	s	
Thiols[ii]			
R-S-H stretch	2550 – 2600		
Alkyl & Aryl Halides†			
C-F stretch	1000 – 1400		Hidden in fingerprint region
C-Cl stretch	< 600 – 840		
C-Br stretch	< 700		
C-I stretch	< 600		

* Abbreviations: s = strong; m = medium; w = weak; br = broad; sat. = saturated; conj. = conjugated

** Alcohols, Esters, Carboxylic Acids, and Anhydrides also absorb in the fingerprint region due to the C-O stretch (1300 – 1000, s).

Table 2. Out-of-Plane C-H Bending Vibrations in Alkenes and Aromatics

Alkene Structure	Position (cm^{-1})	Phenyl Structure	Position (cm^{-1})
Mono-substituted 	997 – 985 & 915 – 905	Mono-substituted 	770 – 730 & 720 – 680
Disubstituted, *trans* 	980 – 960	Disubstituted, *ortho* 	770 – 735
Disubstituted, *cis* 	730 – 665	Disubstituted, *meta* 	810 – 750 & 725 – 680
Disubstituted, symm. 	895 – 885	Disubstituted, *para* 	860 – 800
Trisubstituted 	840 – 790		

[i] Adapted from…Mohrig, J. R.; Hammond, C. N.; Schatz, P. F. "Infrared Spectroscopy" in *Techniques in Organic Chemistry*. Freeman: New York, 2006.