

Infrared Spectroscopy

Functional Group Identification in Organic Compounds



■ Bonds as Springs

If you have taken a course in physics, you are likely familiar with Hooke's law, which describes the behavior of masses suspended by a spring. In a classical sense, chemical bonds behave much like springs—they stretch and compress at a certain frequencies. A useful formulation of Hooke's law is

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{f \frac{(m_1 + m_2)}{m_1 m_2}}$$

where $\tilde{\nu}$ is the vibrational frequency in units called **wavenumbers** (more on that later), f is a constant reflecting the strength of the spring (or bond), where a larger value corresponds to a stronger bond, c is the speed of light (3.0×10^{10} cm/s), and m_1 and m_2 are the masses of the atoms.

1. According to Hooke's law, do heavier atoms have higher or lower vibrational frequencies? Explain with reference to the equation.

Scan the QR code at right with your phone to open the interactive module.



2. Observe the C–H bond stretching animation. How many times does the bond stretch in ten seconds? You can touch the animation to pause it. One stretch is when the atom goes through a complete motion and returns to its starting position.
3. Change the bottom atom to carbon. How many times does the C–C bond stretch in ten seconds?
4. Which bond is stretching faster, the C–H or the C–C bond? Explain with reference to Hooke's law.

The number of times a bond stretches per second is its vibrational frequency in **hertz** (Hz).

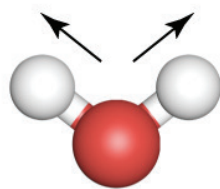
5. What is the approximate hertz frequency of the C–H bond in the animation? The C–C bond?
6. Arrange the following in order of increasing strength (from weakest to strongest): triple bonds, double bonds and single bonds.
7. According to Hooke's law, do stronger bonds have higher or lower vibrational frequencies? Explain, again with reference to the equation.
8. Change the bottom atom to oxygen and compare the frequency of a carbon-oxygen single bond to a carbon-oxygen double bond. Which has the higher vibrational frequency? Why?
9. Compare the frequency of a carbon-carbon single bond stretch to a carbon-oxygen single bond stretch. Which bond is stronger? How do you know?

■ Vibrational Modes

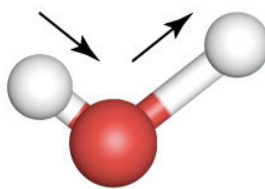
The stretching of covalent bonds that you have just observed is one type of **vibrational mode** that a molecule can undergo. Molecules vibrate by stretching, bending, rocking, wagging and twisting. For a molecule with N atoms, there are $3N - 6$ different vibrational modes. Let's consider a simple molecule, like water, H_2O .

10. How many vibrational modes does water have?

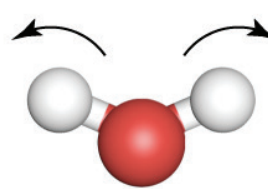
As pictured below, the vibrational modes are the symmetric stretch, the asymmetric stretch and the in-plane bend ("scissoring").



symmetric stretch



asymmetric stretch



in-plane bend (scissoring)

Scan the QR code to view animations of these vibrational modes.

11. Based on the animations of the vibrational modes of water, which modes have the highest frequency? Which has the lowest?

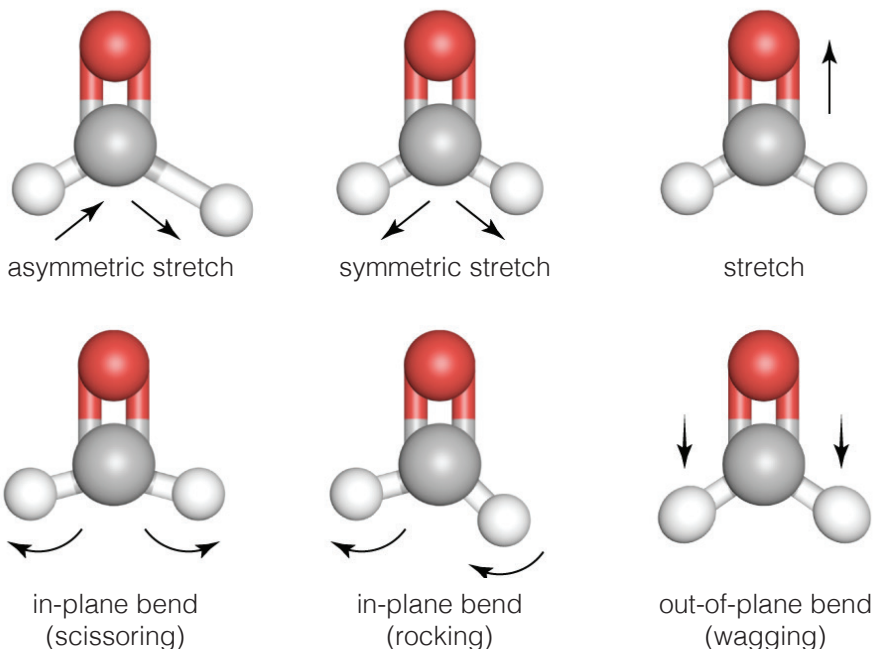


Consider formaldehyde, CH_2O .

12. How many vibrational modes does formaldehyde have?

13. Like water, formaldehyde has the asymmetric stretch, the symmetric stretch and the scissoring vibrational modes. What do you imagine the additional vibrational modes might be—that is, how else might formaldehyde be vibrating? Consider the descriptions at the top of the page.

The vibrational modes for formaldehyde are shown below. Scan the QR code to view the animations on your phone.



14. What are the two highest frequency vibrational modes for formaldehyde? What is the lowest frequency mode?

■ The Nature of Light

The speed of light, c , is a constant at 3.00×10^{10} cm/s. Like any wave, its speed is simply the **wavelength**, λ , times the **frequency**, ν .

$$c = \lambda \times \nu$$

The wavelength is the distance between any two consecutive peaks (or troughs) and the frequency is the number of peaks that pass a given point per second and is typically reported in hertz (Hz).

15. As the wavelength of light increases, the frequency *increases* / *decreases* (circle one).

16. The wavelength and frequency of light are *directly proportional* / *inversely proportional* (circle one).

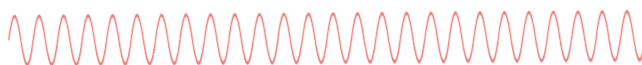
The energy of light, E , can be found as

$$E = h\nu = hc \frac{1}{\lambda}$$

where h is Planck's constant, 6.626×10^{-34} J·s.

17. As the frequency of light increases, the energy *increases* / *decreases* (circle one).

The energy of light is also directly proportional to the reciprocal of the wavelength, which is the number of oscillations per a given length of the wave.



18. Using a ruler, determine the centimeter wavelength of the wave shown above. What is the wavelength?

19. Count the number of oscillations that occur per centimeter in the above wave. This is the frequency in wavenumbers. What is the frequency in wavenumbers?

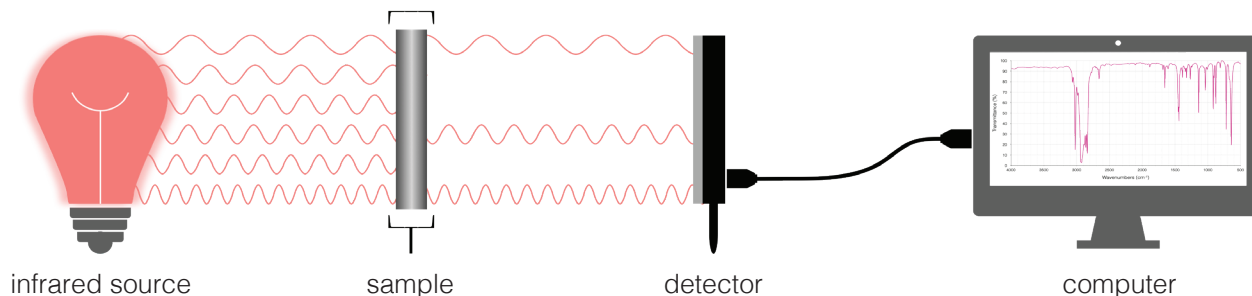
20. What is the mathematical relationship between your answers to the wavelength in centimeters and the frequency in wavenumbers?

The primary unit of frequency used in infrared spectroscopy is wavenumbers, which is the number of oscillations that occur per centimeter of the wave and has units of $1/\text{cm}$ or cm^{-1} ("reciprocal centimeters"). Like any unit of frequency, wavenumbers are directly proportional to the energy. To convert from a wavenumbers frequency to a hertz frequency, simply multiply by the speed of light in cm/s .

21. What is the hertz frequency of the above wave?

■ Infrared Spectroscopy

Quantum mechanics dictates that each type of vibrational mode is quantized—that is, only certain energies/frequencies are allowed. When infrared light is passed through a sample, if the frequency of light matches the frequency of a vibrational mode (a “resonant frequency”), then that frequency of light can be absorbed by the sample.



This is very much like pushing someone on a swing. If the frequency of pushing matches the frequency of the swinging, then the energy of pushing will be absorbed and transferred to the swing.

22. Why did some frequencies of light pass through the sample and make it to the detector?

23. What happened to the frequencies of light that did not make it to the detector?

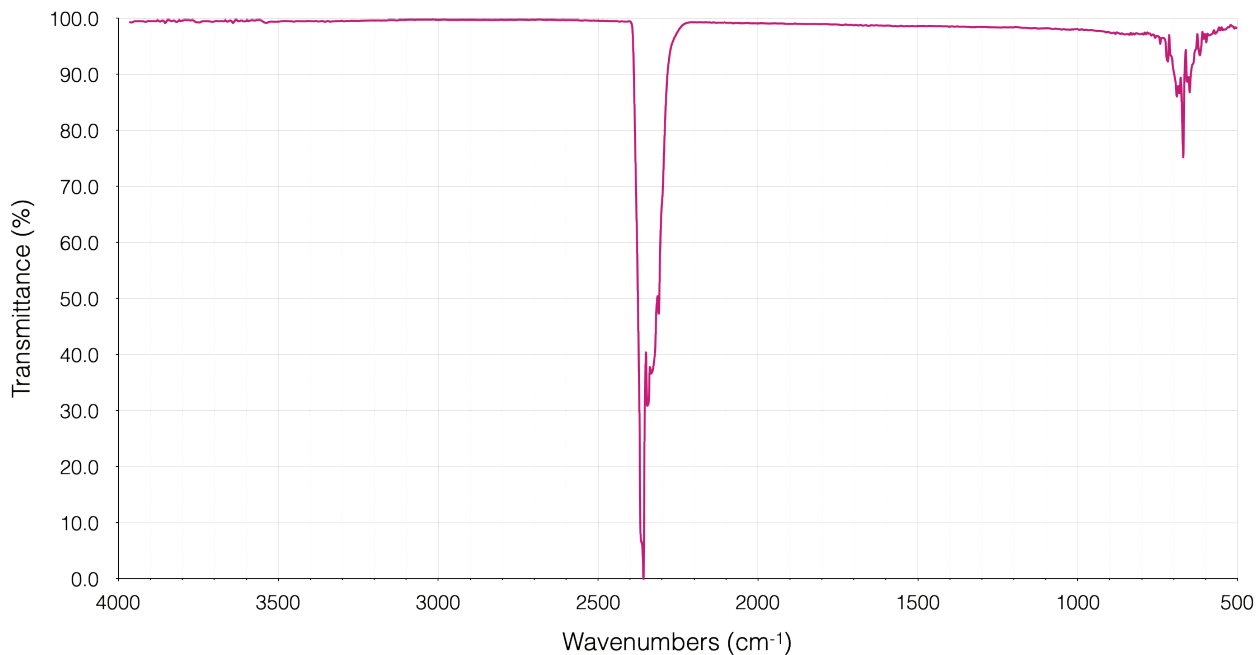
In order for a particular vibrational mode to absorb infrared light (commonly referred to as being “IR active”), the mode must result in a change in the **dipole moment** (μ) of the molecule. Recall that a dipole moment is found as

$$\mu = \delta \times d$$

where δ is the magnitude of the charge at either end of the dipole and d is the distance. Consider carbon dioxide, CO_2 .

24. How many vibrational modes do you expect CO_2 to have?

Infrared spectra are typically plotted as the **percent transmittance** versus the frequency in wavenumbers, ranging from about 500 cm^{-1} to 4000 cm^{-1} . The percent transmittance is simply the percentage of light of a particular frequency that was absorbed by the sample (0% transmittance equals 100% absorbance). This makes the peaks on infrared spectra appear upside down. Consider the infrared spectrum for CO_2 shown below.



Only two of the expected three peaks for CO_2 appears on the spectrum. This is because one of the vibrational modes *does not* result in a change in the dipole moment.

Scan the QR code at right with your phone to open the interactive module.



25. Label the peak for the CO_2 asymmetric stretch in the above spectrum. Why does it result in a change in the dipole moment?

26. Why does the symmetric stretching mode for CO_2 *not* result in a change in the dipole moment?

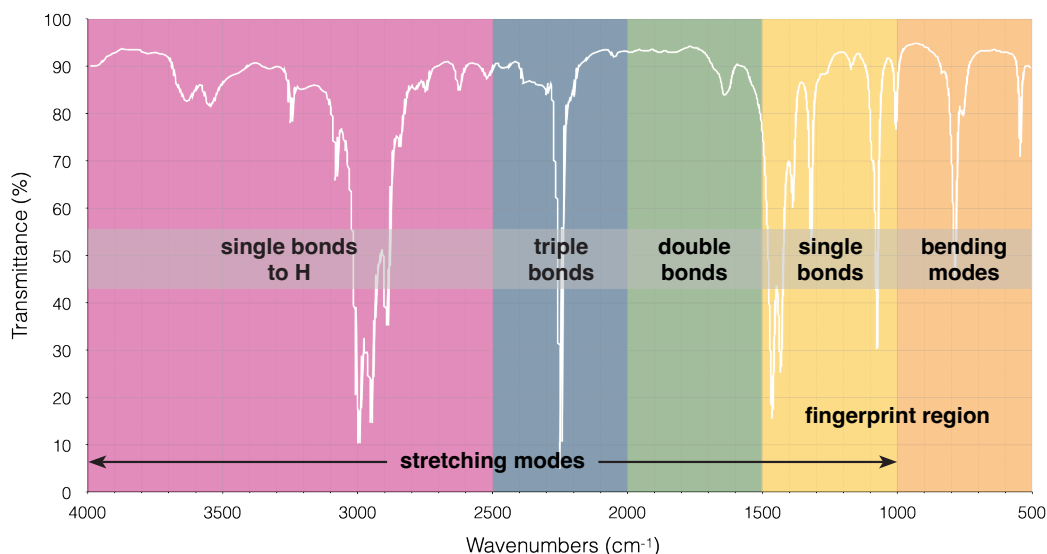
27. Label the peak for the in-plane bend for CO_2 . Why does it result in a change in the dipole moment?

Vibrational modes for bonds about which the molecule is symmetric tend to not experience a change in the dipole moment and do not give a peak on the infrared spectrum.

28. Draw the structure of a molecule (other than CO_2) with a bond whose stretching would likely not appear on the infrared spectrum.
29. With reference to the IR spectrum for CO_2 and the above interactive module, construct an explanation for why the peak for the asymmetric stretch is much more intense than the peak for the in-plane bend.
30. Which end of an infrared spectrum corresponds to higher energy vibrations?

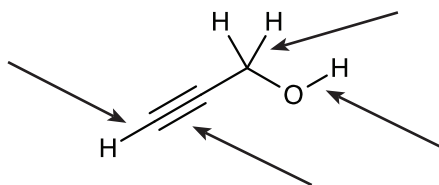
■ Analyzing Infrared Spectra

If we look at many infrared spectra, a pattern emerges. Stretching modes typically appear between 1000 and 4000 cm^{-1} , while bending modes are commonly below 1000 cm^{-1} . Bonds to hydrogen typically appear between 2500 and 4000 cm^{-1} , triple bonds between 2000 and 2500 cm^{-1} , double bonds between 1500 and 2000 cm^{-1} , and single bonds between 1000 and 1500 cm^{-1} . The entire region below 1500 cm^{-1} is referred to as the **fingerprint region**.

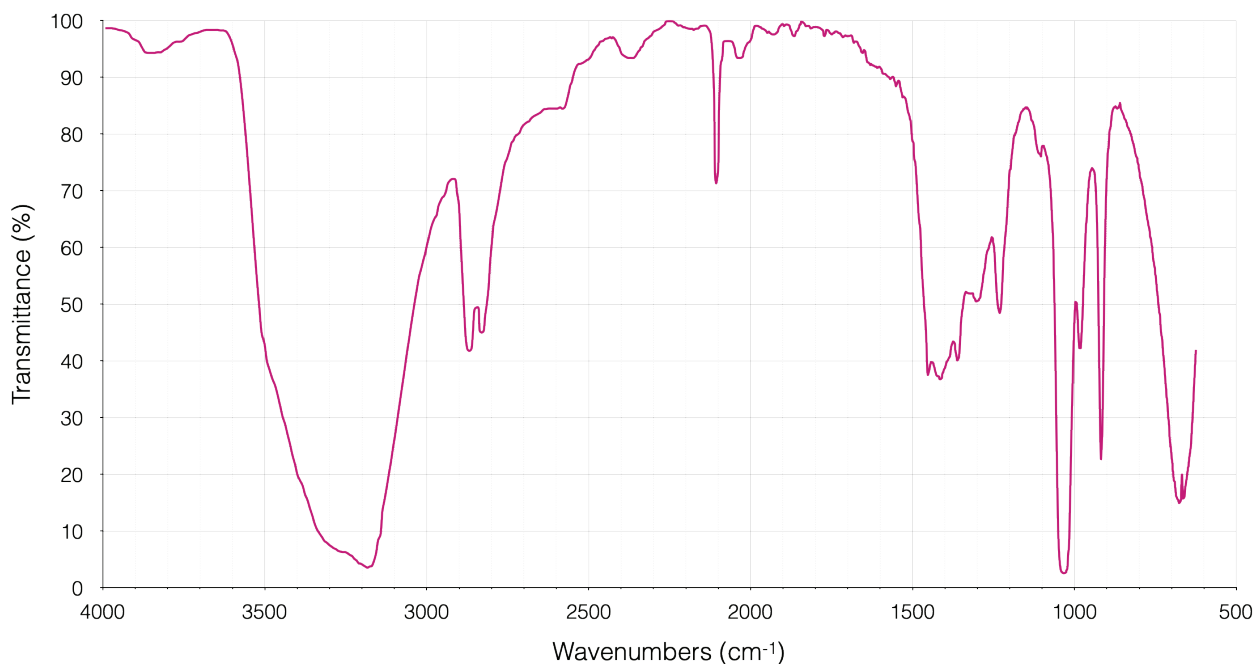


Although there is a lot of useful data in the fingerprint region, it is typically not analyzed. Infrared spectra are useful for determining the functional groups that are present or absent in a molecule—*rarely, if ever, will every peak outside of the fingerprint region be assigned.* A chart that correlates functional groups to their typical IR frequencies is provided on the last page.

31. Using the correlation table on the last page, label the expected frequency for each of the indicated bonds in propargyl alcohol.



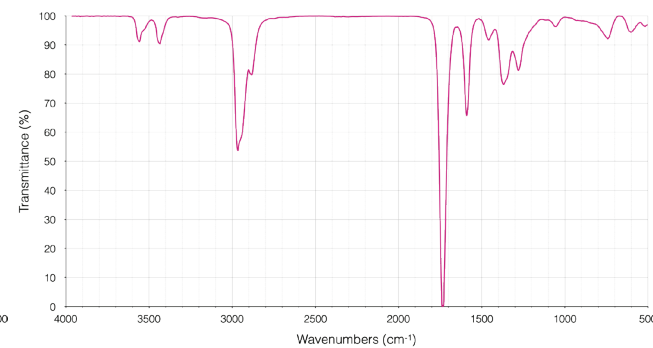
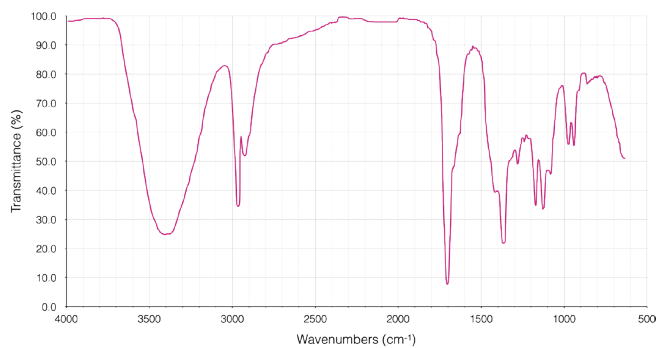
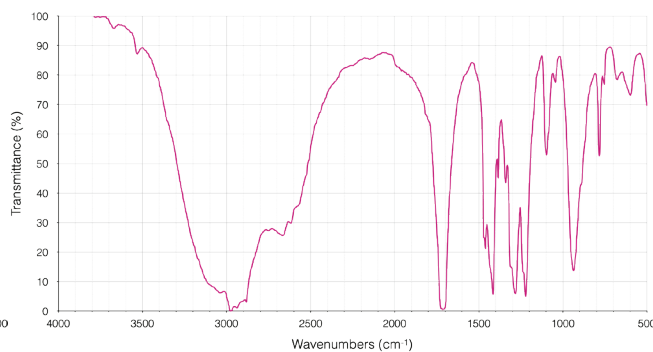
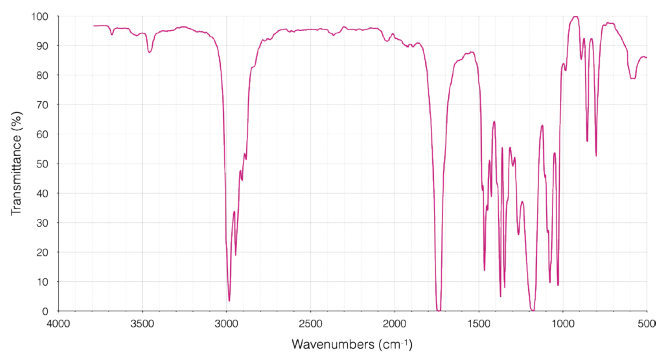
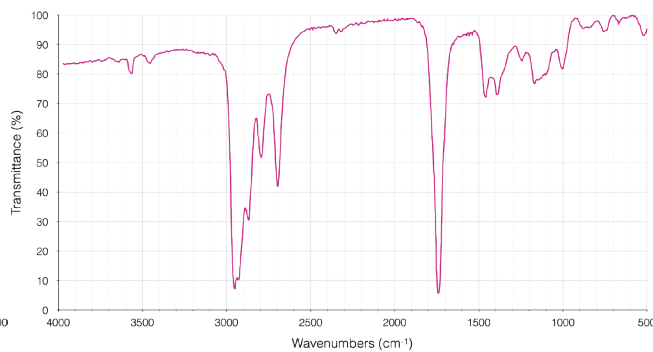
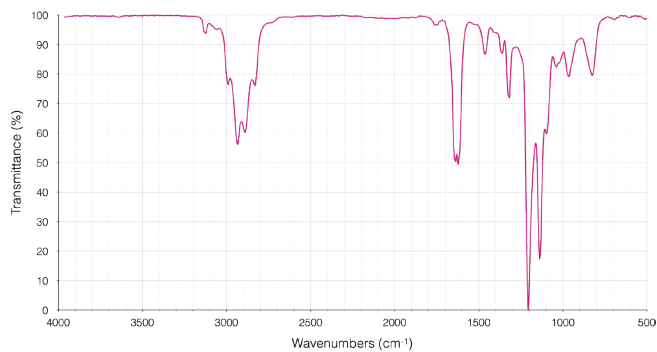
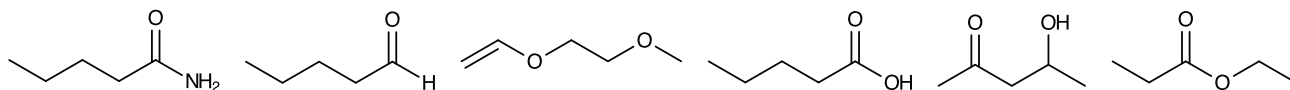
32. The spectrum for propargyl alcohol is shown below. Label each peak outside of the fingerprint region with the bond it represents.



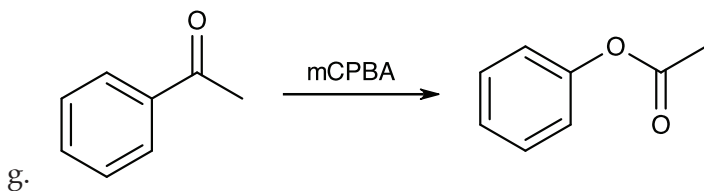
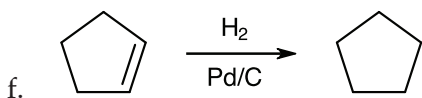
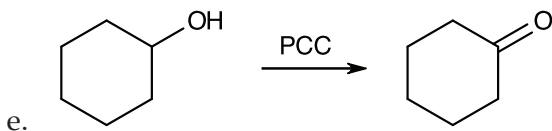
33. Which of the bonds that you labeled in question 31 is not readily observable on the spectrum? Why?
34. Can you identify any of the bonds in the fingerprint region? Label it on the spectrum.

Exercises

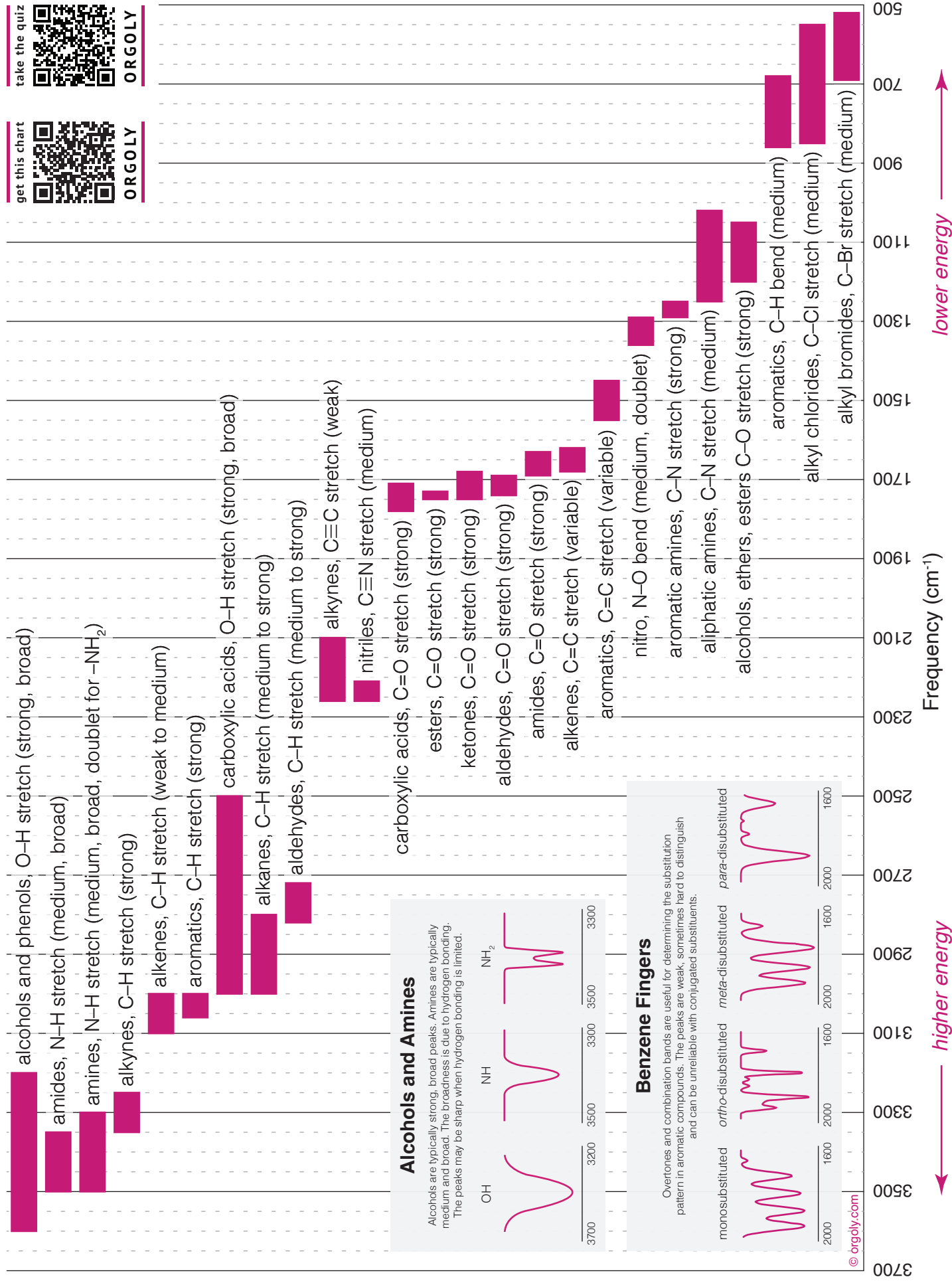
1. Match each of the following molecules to their corresponding IR spectrum. Label the peaks outside of the fingerprint region that correspond to each functional group. There is a functional group correlation chart on the last page for reference.



2. The observed frequency for the O–H bond stretch gets incrementally smaller in the following series of molecules: H_2O , CH_3OH , $\text{CH}_3\text{CH}_2\text{OH}$, $(\text{CH}_3)_2\text{CHOH}$. Explain this trend.
3. Draw the structure of a molecule with molecular formula C_4H_6 that:
- gives peaks at 2200 cm^{-1} and 3300 cm^{-1} .
 - gives a peak at 2200 cm^{-1} but not at 3300 cm^{-1} .
4. Explain how infrared spectroscopy could be used to monitor the progress of each of the following reactions.



Typical IR Frequencies by Functional Group



take the quiz



ORGOLY

get this chart



ORGOLY