

- HRMS leads nicely into our application for today!
- Application of MS to real-world chemistry: Isotopic signatures.
  - Today, you learned that the  $^{12}\text{C} : ^{13}\text{C}$  ratio is 99 : 1.
    - In reality, this is an *average* value.
    - The actual ratio of isotopes is globally uneven, and we as humans have mapped it.
  - Indeed, isotope abundances vary by time and location due to air patterns, etc.
  - For example, Montana is home to 2% more  $^{13}\text{C}$  than Florida!
  - Implication: We can tell if a narcotic is made in the US (and where) or another country based on the isotopic abundance in it.
  - We can also track where a person, drug, or uranium sample is from.
    - Naturally, the government is very interested in this technology :)
  - You can also tell if a person eats corn or rice because this leads to different ratios of nitrogen isotopes in our bodies.

### 1.3 Infrared Spectroscopy

- 9/9:
- Lecture 2 recap.
    - In mass spectrometry, you ionize your sample  $[\text{M}]$  to the molecular ion  $[\text{M}]^+$ .
    - $[\text{M}]^+$  is detected as the parent peak.
      - The parent peak provides the molecular weight (MW) of the molecule.
      - The parent peak also reveals any isotopic signatures.
    - Many molecular ions — once formed — will fragment into cations  $[\text{M}-a]^+$ ,  $[\text{M}-b]^+$ ,  $[\text{M}-c]^+$ , etc.
      - More stable cations are formed more often, resulting in higher relative intensities.
      - The *most* stable fragment gives rise to the base peak.
    - Common fragments include those resulting from...
      - The loss of a methyl group;
      - The loss of a water molecule;
      - $\alpha$ -cleavage;
      - The McLafferty rearrangement (for ketones).
  - Today: Infrared Spectroscopy (IR).
    - Reading: Clayden et al. (2012), Chapter 3.
    - Prof. Elkin highly recommends the section on IR; be sure to read this!!
  - Lecture outline.
    - IR spectrometer schematic.
    - IR theory.
    - IR spectrum elements.
    - Key regions of an IR spectrum.
  - Principle: Irradiate a sample with infrared waves and detect where the sample absorbs these waves.
    - This technique is useful for identifying certain functional groups, namely those that absorb IR waves well.

- A schematic of an infrared spectrometer.

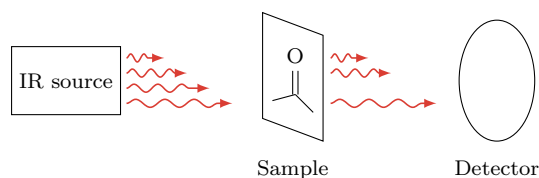


Figure 1.10: Infrared spectrometer schematic.

- We begin with a source of infrared radiation. This source shoots waves at our sample, which could be a molecule like acetone. The IR waves that the source emits have a range of frequencies.
- The sample will absorb certain frequencies, and the frequencies that are not absorbed are detected by a detector. In other words, the director detects the **transmittance** of the sample.
- **Transmittance**: How much of each frequency of radiation passes through the sample.
- IR theory.

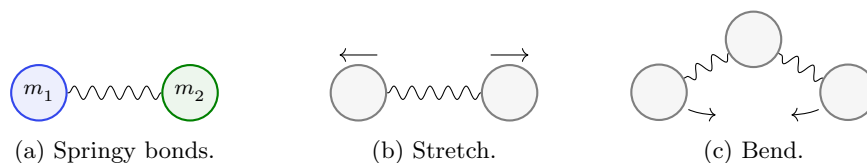


Figure 1.11: Infrared spectroscopy theory.

- Fundamental assumption: A chemical bond is like a spring between atoms.
  - Recall from Gen Chem that in science, we often call a spring a **harmonic oscillator**. If you don't quite remember this term, review your Gen Chem notes or Google it!!
- Let's dive a bit deeper into this analogy: Imagine we have two different atoms of masses  $m_1, m_2$  joined by a "spring," as in Figure 1.11a.
  - Just like a real spring, chemical bonds can vibrate in different ways: They can stretch and contract (as in Figure 1.11b), bend (as in Figure 1.11c), etc.
  - All of these different motions are called the **vibrational modes** of the chemical bonds.
- Bonds absorb energy from IR waves when the frequency ( $\nu$ ) of the IR wave matches the frequency of the stretching/bending motion.
  - In other words, when you hit the resonance frequency, you absorb energy.
  - This absorption of energy is detected as the loss of transmittance.
- The change in energy between vibrational modes is related to characteristics of the bond as follows.

$$\Delta E \approx \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

- $k$  is the force constant (proportional to the bond strength).
  - $m$  is the mass of atom 1 or 2.
  - Implication: Stronger bonds (i.e., those with larger values of  $k$ ) require more energy (i.e., higher  $\nu$  IR waves) to absorb.
  - Implication: Lighter atoms (i.e., those with lower values of  $m$ ) require more energy (i.e., higher  $\nu$  IR waves) to absorb.
- One additional requirement: The chemical bond must have a dipole in order to absorb IR waves.
  - Example:  $\text{C}\equiv\text{O}$  absorbs because O is more electronegative than C, but  $\text{N}\equiv\text{N}$  does not.

- Questions on IR theory.
  - Why do bonds absorb energy *only* when the frequency of the IR waves matches the frequency of the bond's vibration?
    - The answer to this question is beyond the scope of the class, but Prof. Elkin gives the quantum mechanical explanation.
    - Essentially, when a chemical bond absorbs energy, it gets excited to a higher-energy vibrational mode, which we may think of as a more intense vibration.
    - However, because vibrational modes are separated by a set amount of energy, lower energy photons won't have enough energy to make it to the next vibrational mode while higher energy photons will provide too much energy to reach anything stable.
  - Why don't bonds without dipoles absorb IR waves?
    - The explanation is also quantum mechanical, and hence also beyond the scope of this class.
    - Essentially, symmetric bonds and molecules lack something called a dipole moment, and zero dipole moment zeroes out the absorption in the math of quantum mechanics.
    - Note that there is some really cool math and physics underlying the answer to this question, and Prof. Elkin recommends you look it up if you're interested!!
    - In organic chemistry, however, we're more interested in what we can do with IR spectroscopy than in *exactly* how it works. Essentially, for this class, you should learn how it works well enough to make sense of the trends in spectrum interpretation presented in this lecture, but you don't need to go deeper than that for now.
  - Why do lighter atoms require more energy? It seems like it would take more energy to push around a heavier atom.
    - Check out the explanation in Clayden et al. (2012); it's pretty comprehensive and understandable.
- Example IR spectrum: Propionic acid (CCC(=O)O).

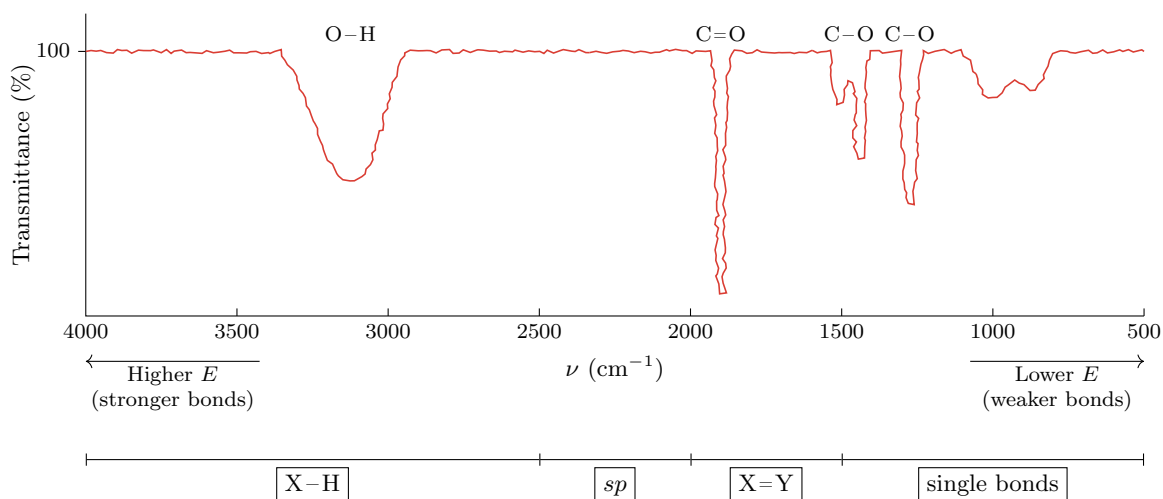


Figure 1.12: Infrared spectrum of propionic acid.

- The  $x$ -axis is the frequency of the IR waves, measured in wavenumbers ( $\text{cm}^{-1}$ ).
  - We typically are interested in the region from 4000–1500  $\text{cm}^{-1}$ .
- The  $y$ -axis is the percent transmittance.
- The **baseline** is 100%, which means pure transmittance (aka, no **absorption**).
  - Then we have **absorbance peaks**, each of which corresponds to a different chemical bond.

- We can further break the spectrum down into regions.
  - X–H bonds occur in the 4000–2500 cm<sup>−1</sup> region.
    - Peaks in this region are often broad. Specifically, a peak will be broad if the corresponding protons are **exchangeable**.
    - Hydrogen bonding can also lead to broadening.
    - We see this effect in both IR and NMR, so we'll talk about it more later this week!
    - For example, the O–H peak is broad because this acidic proton is exchangeable.
  - *sp*-hybridized atoms occur in the 2500–2000 cm<sup>−1</sup> region.
    - In other words, polar triple bonds show up here.
    - Examples: C≡N and C≡C'.
  - X=Y bonds occur in the 2000–1500 cm<sup>−1</sup> region.
    - This is for polar double bonds.
    - Examples: C=O, C=C',<sup>[5]</sup> and C=N.
  - Single bonds occur in the 1500–500 cm<sup>−1</sup> region.
    - Examples: C–C', C–O, and C–F.
  - Some of these regions are useful, and some less so.
- As you can infer from Figure 1.12, IR spectra look a bit like icicles.
- Note that C–O has two peaks because there are multiple bonding modes per bond.
- **Absorption:** The loss of transmittance.
  - We typically plot transmittance in a spectrum, but the two measures are inversely proportional.
- **Exchangeable** (proton): A hydrogen atom that is liable to break off of the rest of the molecule and be replaced by another hydrogen atom in solution.
  - This is very much related to acidic protons! Recall that a Brønsted acid will donate its proton and then the conjugate base will pick up a new (possibly new) proton all the time.
- **Diagnostic regions:** 4000–1500 cm<sup>−1</sup> (useful) and 1500–500 cm<sup>−1</sup> (useless).
- **Fingerprint region:** The region of an IR spectrum from 1500–500 cm<sup>−1</sup>.
  - Within the fingerprint region, we have so many overlapping peaks that the spectrum becomes difficult to interpret.
  - However, its shape is characteristic of a molecule, even if it doesn't tell you anything specifically. This is just like a real fingerprint! Your fingerprint doesn't tell anyone else your name, age, date of birth, etc. — but it does tell people that you're you!
- Key regions.

X–H		<i>sp</i>		X=Y	
FG	$\nu$ (cm <sup>−1</sup> )	FG	$\nu$ (cm <sup>−1</sup> )	FG	$\nu$ (cm <sup>−1</sup> )
O–H	3600–3200	C≡N	2200	C=O	1840–1630
N–H	3100–2700	C≡C'	2100	C=N	1700–1600
C–H	3000–2850	C=C=C'	1950	C=C'	1670–1600

Table 1.2: Key regions of an infrared spectrum.

<sup>5</sup>The prime on the second carbon indicates that the carbons have different substituents. This is necessary if we are to have a dipole (symmetric C=C bonds are nonpolar).

- Note that functional groups listed higher up in each column of Table 1.2 have stronger bonds, and thus absorb higher energy/higher  $\nu$  photons.
- Both O–H and N–H peaks are broad *if* the proton is exchangeable.
  - There is an example in Clayden et al. (2012) of an O–H that is so sterically encumbered that you don't get proton exchange!!
- Note also that C–H peaks are often weak, and may not show up at all in some spectra.
- Should this information be memorized, or will it be provided in a reference chart?
  - Memorize the general regions and trends (as presented in the discussion following Figure 1.12), but not the explicit data in Table 1.2.
- **Broad** (peak): An absorbance peak that stretches over a wide range of wavenumbers.
- **Sharp** (peak): An absorbance peak that is restricted to a narrow range of wavenumbers.
- What determines the *exact* absorption frequency of a chemical bond?

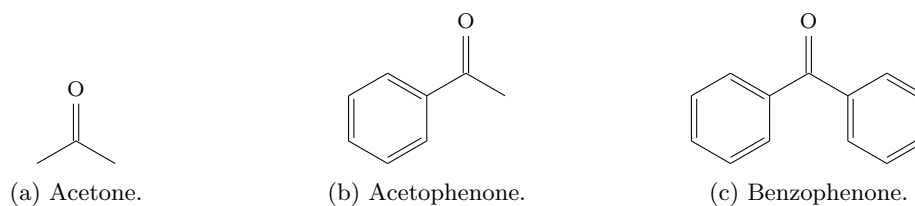


Figure 1.13: Related molecules with slightly different infrared absorption peaks.

- The exact frequency is determined by the atoms and functional groups surrounding the bond.
- For example, consider acetone, acetophenone, and benzophenone.
  - These three molecules all have C=O bonds, but their C=O bonds absorb IR waves at 1715, 1692, and 1664  $\text{cm}^{-1}$ , respectively.
  - This effect can be attributed to increasing conjugation with the  $\pi$ -systems of the aromatic rings.
- Indeed, the more conjugated the C=O bond, the weaker it is. Conjugation takes off 20–30  $\text{cm}^{-1}$  per conjugation!
- Conjugation is just one example, however; many other group of atoms can affect the absorption frequency.
- Guidelines for interpretation.
  - Look for the presence or absence of key functional groups.
    - This is really good for O–H, N–H,  $\text{C}\equiv\text{N}$ , C=O, C=N, C=C', etc.
  - We'll also rationalize trends.
    - Stronger bonds have higher frequencies, and hence get shifted to the left.
    - Weaker bonds have lower frequencies, and hence get shifted to the right.
    - Etc.
- Why do we use wavenumbers instead of per second for frequency?
  - Historical reasons; this is just the way chemists have always done it.

- Example spectrum: But-3-yn-2-one ( $\text{H}-\text{C}\equiv\text{C}-\text{C}(=\text{O})-\text{CH}_2\text{CH}_3$ ).

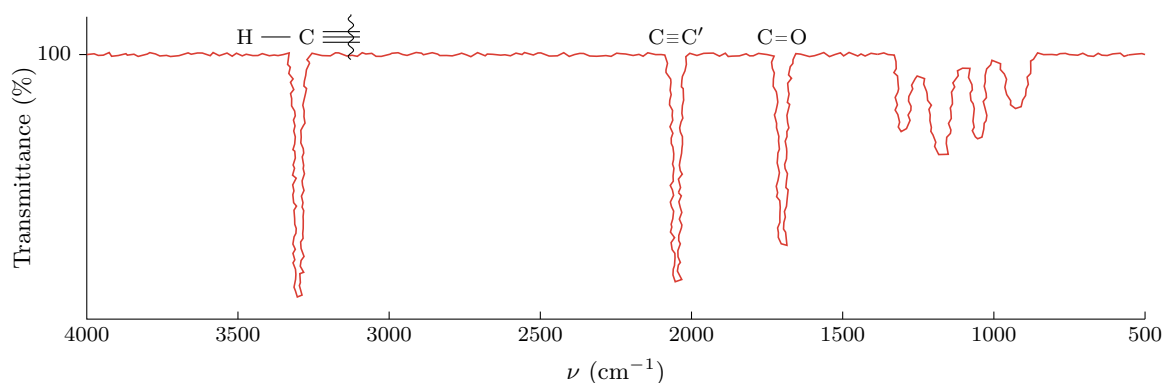


Figure 1.14: Infrared spectrum of but-3-yn-2-one.

- This spectrum is composed of four major elements: A sharp peak at  $3300\text{ cm}^{-1}$ , a sharp peak just to the left of  $2000\text{ cm}^{-1}$ , a sharp peak at  $1700\text{ cm}^{-1}$ , and the fingerprint region.
- The sharp peak at  $3300\text{ cm}^{-1}$  can be attributed to the propionic C–H bond.
- But wait: We said in Table 1.2 that C–H bonds lay between  $3000\text{--}2850\text{ cm}^{-1}$ . What gives?
  - The leftward shift is due to the unique chemical environment of this specific C–H.
  - In particular, the carbon in this bond is *sp*-hybridized. It follows that this C–H bond is more polarized. Thus, the bond is stronger than usual, and we need higher frequency IR waves.
- Evidence that propionic C–H bonds are stronger: Bond dissociation energies (BDEs).<sup>[6]</sup>
  - The BDE for a propionic C–H is about  $125\text{ kcal/mol}$ , while the BDE for an alkane C–H is about  $98\text{ kcal/mol}$ .
  - This difference is also reflected in the relative  $\text{p}K_{\text{a}}$ 's of the two hydrogens: Alkane C–H's have  $\text{p}K_{\text{a}}$ 's in the 50s, while propionic C–H's have  $\text{p}K_{\text{a}}$ 's in the 20s.
- Note that in this molecule, the *sp*<sup>3</sup> C–H stretch only absorbs weakly, hence why we don't see a peak around  $3000\text{ cm}^{-1}$ .
- There is some theory on how much a certain vibration will absorb, but for our purposes, we'll assume that all stretches absorb a good healthy amount of radiation.
- Application: IR is nondestructive.

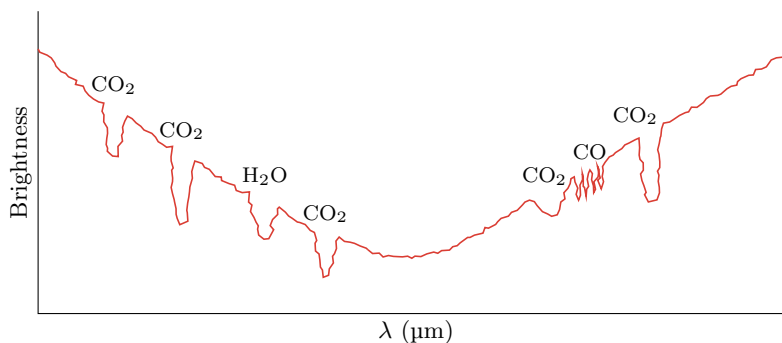


Figure 1.15: Infrared spectrum of the atmosphere of Mars.

<sup>6</sup>Look up BDEs in your Orgo I and Gen Chem notes if you don't remember them. These are important to know!!

- EA and MS are destructive analytical techniques, meaning that the sample gets destroyed (e.g., by burning or fragmentation) in the process. This requires sample in hand, some of which we can destroy.
- IR is nondestructive. This means that we can recover our sample after the experiment! In other words, IR spectroscopy can be run from afar.
- For example, consider the spectrum in Figure 1.15.
  - This is still an IR spectrum, even though the  $x$ -axis is in wavelength ( $\lambda$ ) — measured in  $\mu\text{m}$  — and  $y$ -axis is in brightness.
  - The spectrum has a bad baseline, but we'll just forgive this.
  - A number of vibrational modes of  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{CO}$  are recorded.
- What is this spectrum?
  - It is an IR spectrum of the atmosphere of Mars!
  - It was taken by the James Webb Telescope two years ago, in 2022.
  - We've had an IR spectrum of the moon since the 1940s, but this is new and cool!
- To generalize, here are some major applications of IR spectroscopy.
  - Space.
    - Just like the example in Figure 1.15, IR spectroscopy can be used to find new molecules in celestial bodies.
    - If you ever see a news story along the lines of “Amino acids found on an asteroid,” the amino acids in question were probably detected using IR spectroscopy.
  - Climate science.
    - Example: Measuring the concentrations of methane (a potent greenhouse gas) over the arctic.
  - Art.
    - Example: Authenticating old paintings.
    - Indeed, we can use IR to look for diagnostic pigments.
    - A nondestructive method like IR is better in this context than a destructive method like EA or MS because you obviously don't want to chip off a bit of the paint just for an analysis!
- Why is  $\text{CO}_2$  (a nonpolar molecule) IR active?
  - The stretching modes are IR silent.
  - However, some of the bending modes induce a dipole, and these are the IR active modes.
- Could we use IR to detect the presence of oxygen on Mars?
  - Oxygen is probably not IR active, so we could not use IR to detect its presence on Mars. There is probably another way, though!