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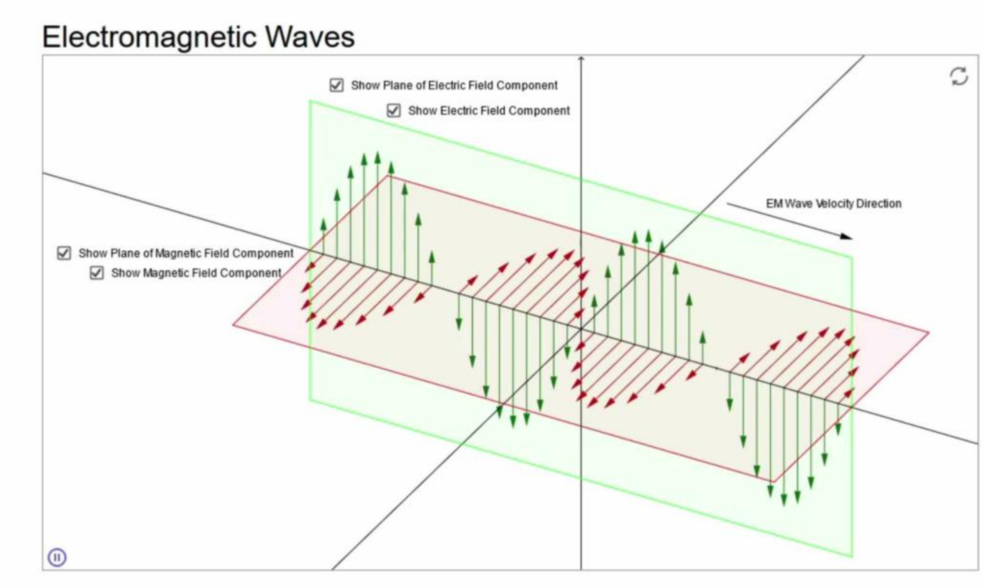
Fourier Transform Infrared Spectroscopy

Summer 2021 High School Outreach Program

RPI Department of Chemistry and Chemical Biology | August 10, 2021

Infrared Light Characteristics – Light Waves

- Light is called **electromagnetic radiation** and is composed of an electric field and a magnetic field, both oscillating orthogonal to each other.
- The direction of propagation of light is also orthogonal to both the electric field and the magnetic field’s direction(s) of oscillation.



Electromagnetic Waves

☑ Show Plane of Electric Field Component

☑ Show Electric Field Component

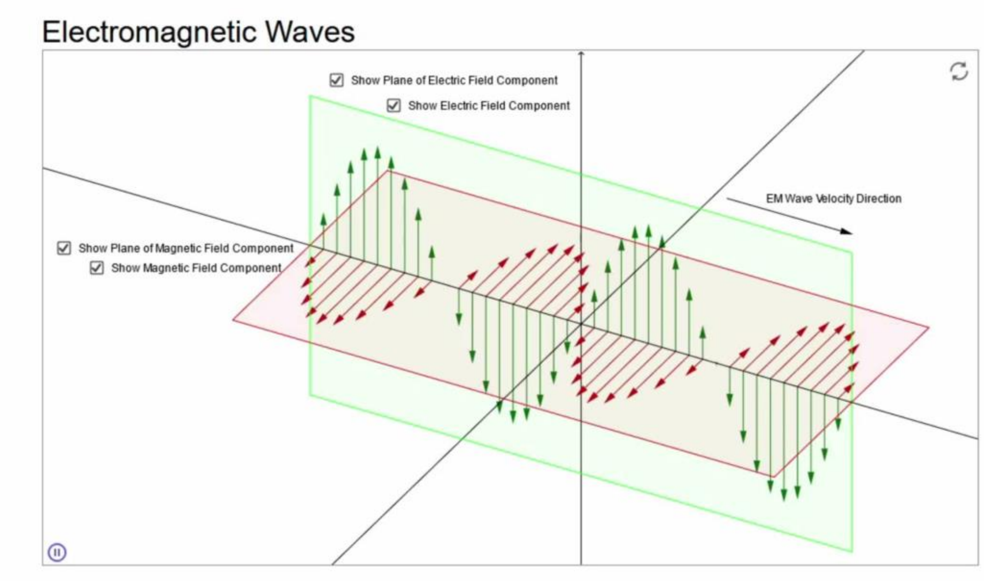
☑ Show Plane of Magnetic Field Component

☑ Show Magnetic Field Component

Walsh, Tom *oPhysics: Interactive Physics Simulations*, https://ophysics.com/em3.html

Infrared Light Characteristics – Light Waves

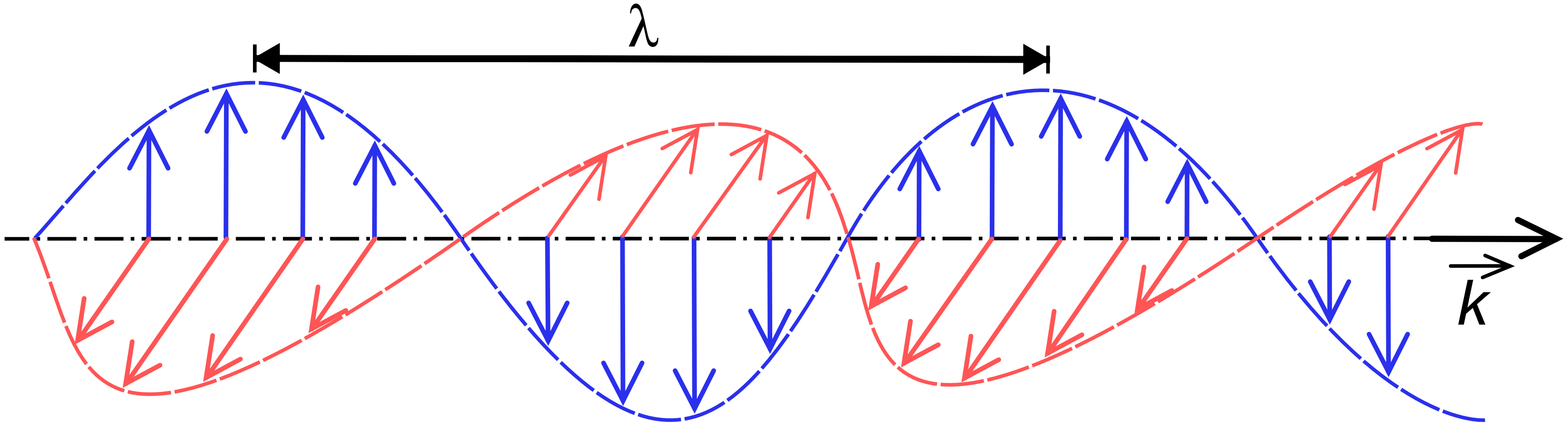
- These two fields take the form of sine waves, causing the overall light wave (sometimes called a “ray”), to take the form of a 3-dimensional wave.
- The oscillations of both of these waves, in sync take place in cycles or periods. A period is going from one point of 0 amplitude, through a maximum, to a minimum, and back to a point of 0 amplitude. The **period** (T) is the time this cycle takes in seconds.
- During propagation, the amplitude of the electric and magnetic fields also oscillates with respect to time.



Walsh, Tom *oPhysics: Interactive Physics Simulations*, https://ophysics.com/em3.html

Infrared Light Characteristics - Wavelength

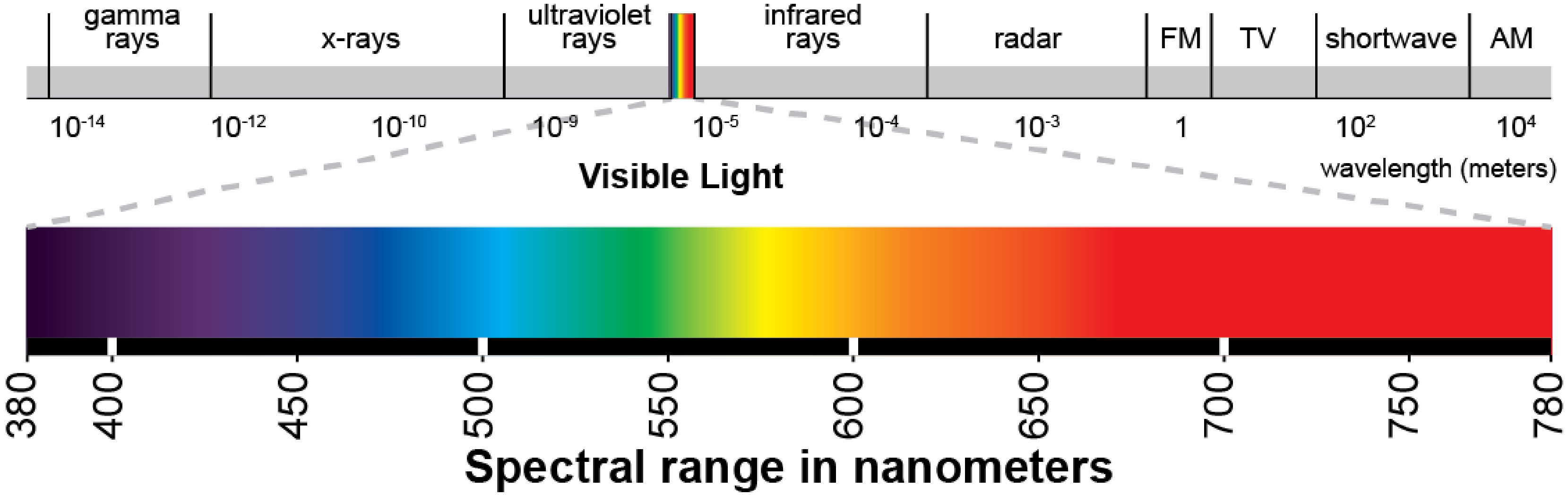
- The distance a wave travels in a period is called the **wavelength** (λ) of the light.
- We usually define this as the distance between one maximum to the next maximum, or between one minimum to the next minimum.



LumenLearning, *Electromagnetic Waves and their Properties*, https://courses.lumenlearning.com/boundless-physics/chapter/electromagnetic-waves-and-their-properties/

Infrared Light Characteristics - Wavelength

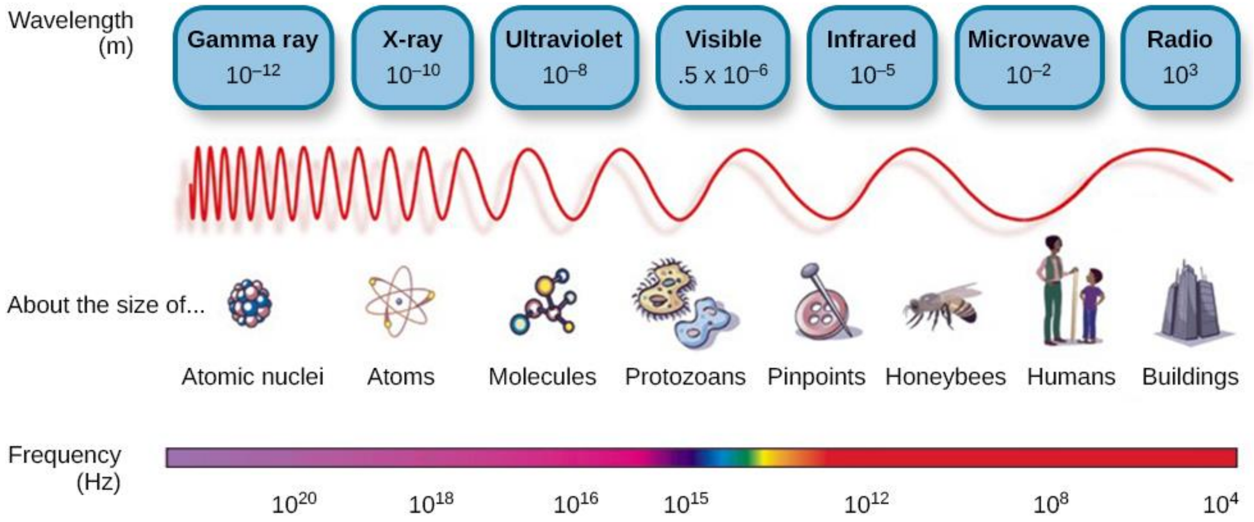
- The wavelength defines several properties, most notably color.
- Wavelengths are expressed in units of distance/period. However, the period portion is generally omitted, rather being simply expressed in distance (usually in a variant of meters, in optical spectrometry generally nanometers).
- Wavelength is inversely proportional to the energy of light.



Evaluating the Quality of a Grow Light Using Spectrum, Eye Hortilux, https://eyehortilux.com/grow-lighting-guide/measuring-light-for-plant-growth/evaluating-quality-grow-light-using-spectrum/

Infrared Light Characteristics – Frequency

- **Frequency** (f) is the inverse of the number of seconds a cycle takes (the period, T).
  - $f = \frac{1}{T}$ Units: 1/seconds = s^{-1} = Hertz (Hz)
- Using this definition of frequency along with the speed of light in meters/second (c), we can define the relationship between wavelength and frequency.
  - $c = \lambda f = \frac{2.998x10^8 m}{s}$ λ must be in meters!



LumenLearning, *Waves and Wavelengths*, https://courses.lumenlearning.com/wsu-sandbox/chapter/waves-and-wavelengths/

Infrared Light Characteristics – Wavenumber

- In infrared spectroscopy we often find it useful to represent light parameters in **wavenumbers** (ṽ).
- Wavenumbers can be thought of as the number of waves per unit of distance.
- Wavenumbers are the inverse of wavelength, meaning that they are proportional to frequency, and thereby energy.
  - $\tilde{\nu} = \frac{1}{\lambda} \propto f \propto E$ Units: cm^{-1}

Infrared Light Characteristics - Energy

- We care about the proportionality of the various characteristics of light to the energy of the light because the energy is what gives information about bonds etc.
- Frequency is the characteristic that's easiest to convert to energy.
  - $E = hf$ h is Planck's constant = 6.626×10^{-34} j·s
- From this relation others can be constructed.
  - $E = \frac{hc}{\lambda} = hc\tilde{\nu}$ Units: joules (j)

Infrared Light Characteristics – Particle/Wave Duality

- **Blackbody radiation** – When a body is heated, IR light is given off.
  - Planck showed that this light is given off in specific energetic amounts. This is called quantization.
- Due to this quantization, light can be treated as particles, each having a specific energy.
  - Remember, the energy of light: $E = hf$
  - Planck energy levels: $0, hf, 2hf$ ...
  - Therefore, the energy levels are due to certain amounts of quantized energy, i.e., light particles or **photons**.

Infrared Light Characteristics – Particle/Wave Duality

- However, we already know that light can also be treated as a wave.
- *Heisenberg uncertainty principle*: $\Delta p \Delta x > h$ (approximation)
    - In more simple terms, as we know more about the momentum (Δp, wave nature), we know less about the position (Δx, particle nature). This is because h is constant.

Infrared Light and Bonds – Absorbing Light

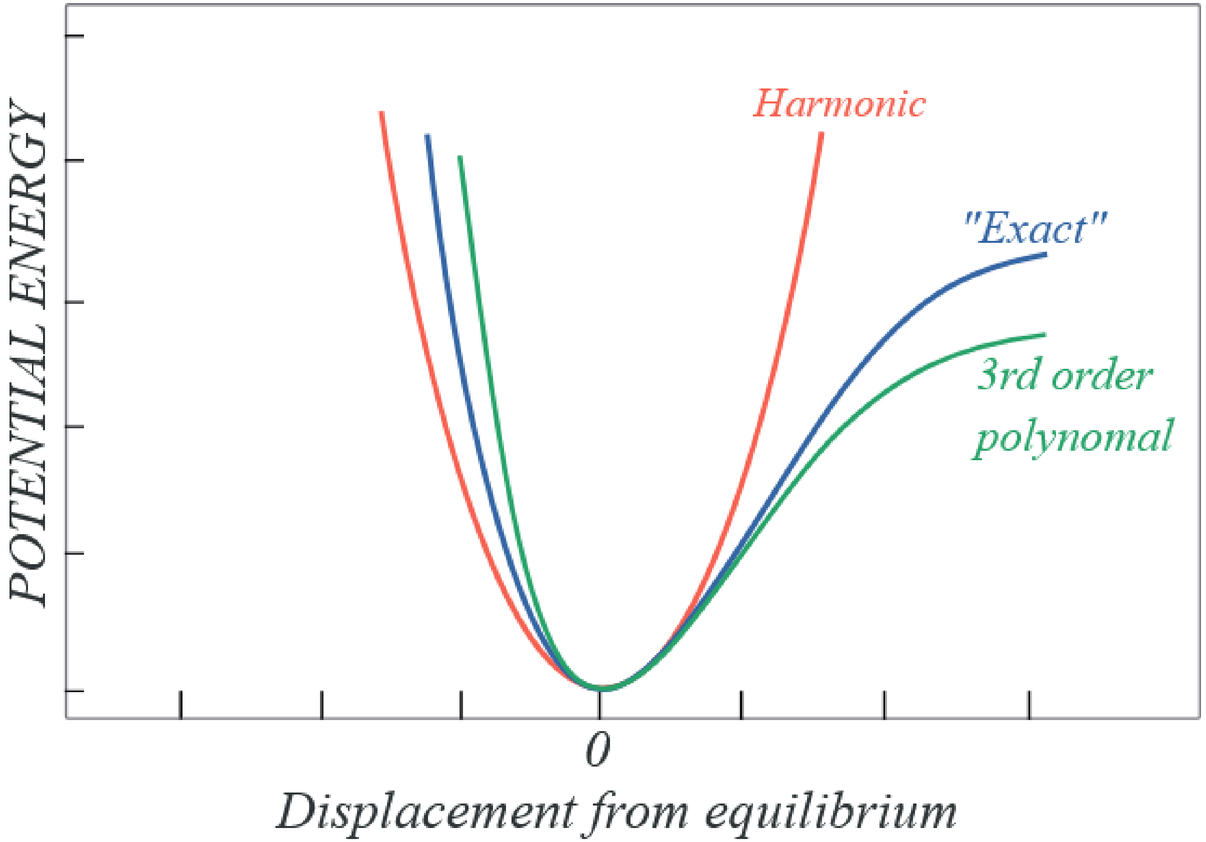
- Bonds, being made of areas of electron density, react to light.
- In the case of infrared light, the bonds respond to an incident photon by vibrating.
- This can be thought of in two ways:
  - Photon absorbance
  - Wave interference
- In the case of photon absorbance, we are regarding the particle nature of light. A photon will collide with a bond and donate the energy present to excite the electrons to a higher vibrational state.
- In the case of wave interference, we are regarding the wave nature of light. As a light wave collides with electrons, it can constructively add to the wave nature of the electrons, thus donating the energy present and exciting the electrons to a higher vibrational state.

Infrared Light and Bonds – Hooke's Law

- When infrared light causes a bond to vibrate, this is done by electron promotion.
- Since energy is quantized, bonds have vibrational sublevels within the potential well.
- This can be simulated via Hooke's Law for an oscillator, which yields a parabola, in which vibrational levels exist.
  - *Hooke's Law*: $E = -k\Delta x$ where k is the stiffness of the spring and Δx is the distance traveled by the spring.
- We can modify Hooke's Law to yield wavenumber, which is useful for predicting IR vibrations.
  - $\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$ k is the force constant in dynes/cm, μ is the reduced mass in g.

Infrared Light and Bonds – Hooke’s Law Vs Reality

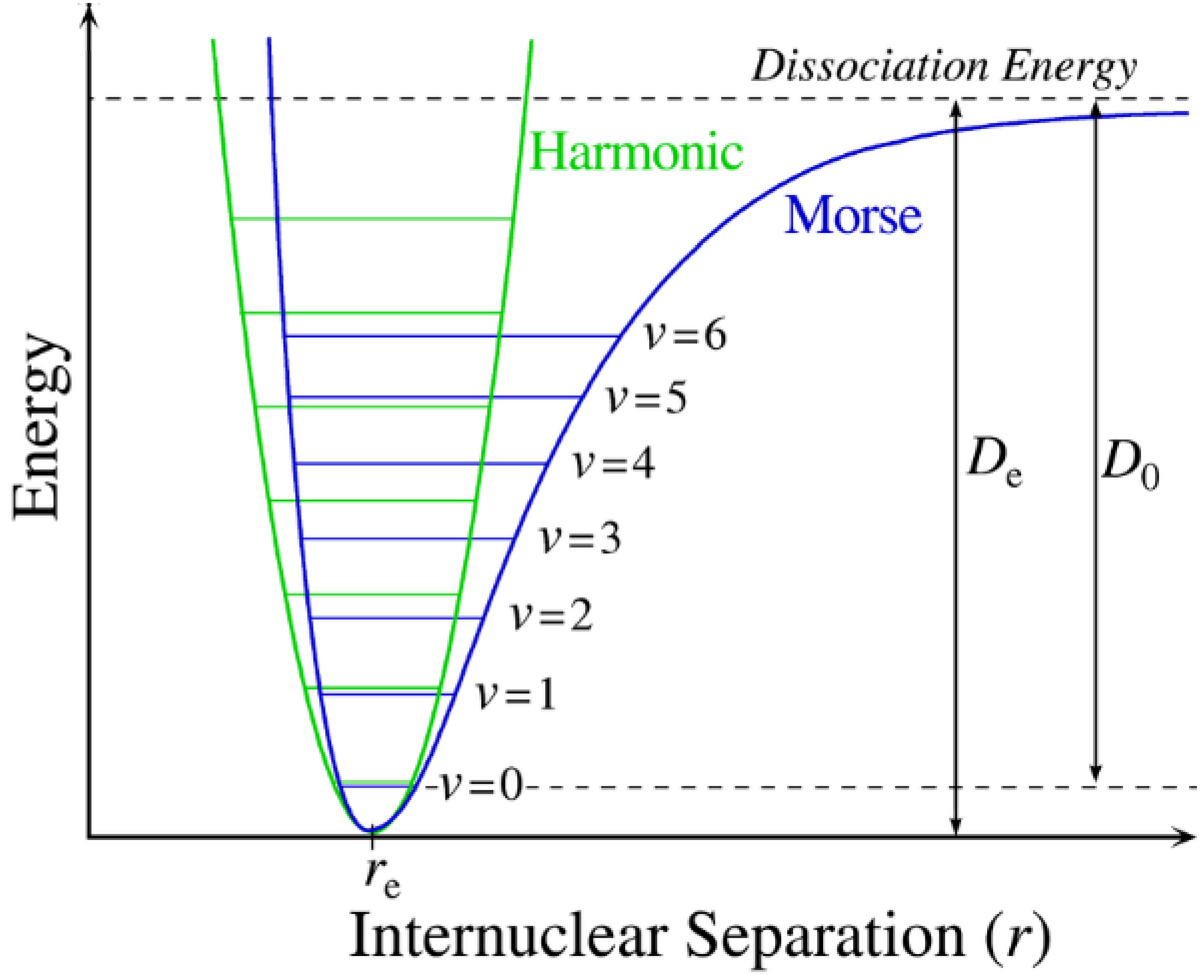
- While Hooke’s Law is a useful way of simulating the potential well of a bond, it does not contain the dissociation limit, which is the point at which the atoms get far enough away from each other that they no longer interact, causing the bond to dissociate.



Kelly, Peter; *The Harmonic Oscillator Approximates Vibrations*; UC Davis; May 11, 2021; Accessed via https://chem.libretexts.org/@go/page/13415 on July 5, 2021)

Infrared Light and Bonds – Morse Potential

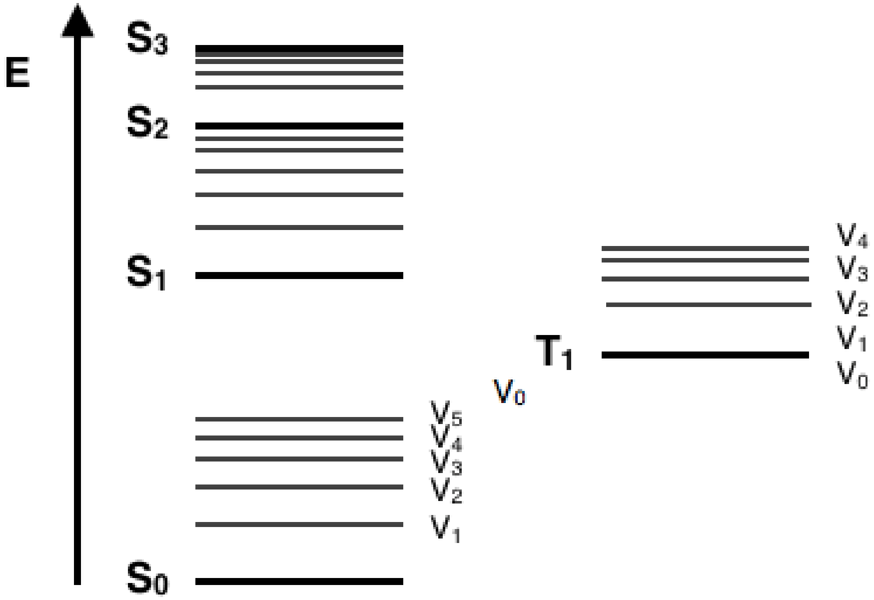
- An even better approximation is the Morse potential.



Kelly, Peter; *The Harmonic Oscillator Approximates Vibrations*; UC Davis; May 11, 2021; Accessed via https://chem.libretexts.org/@go/page/13415 on July 5, 2021)

Infrared Light and Bonds – Jablonski Diagram

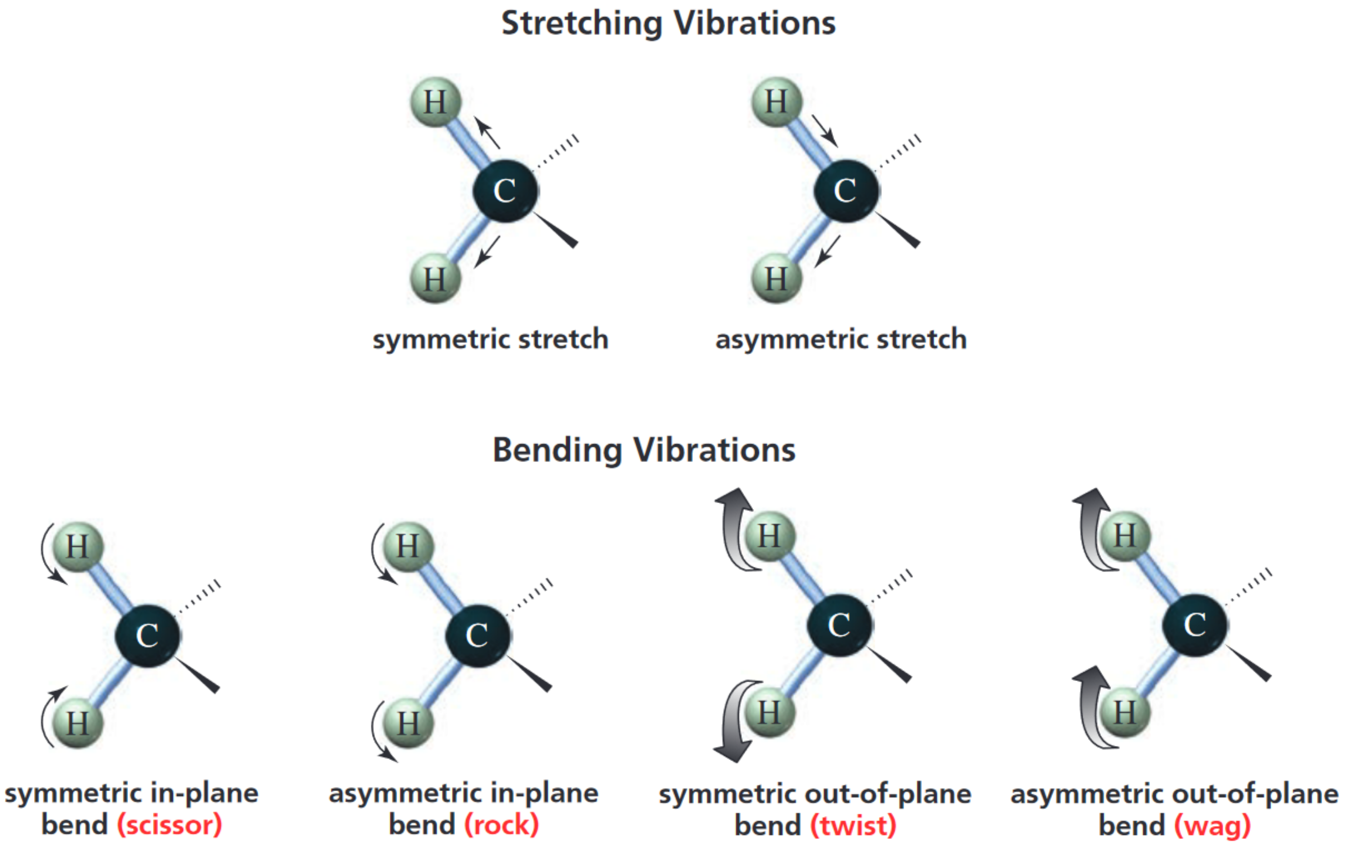
- The Jablonski diagram was proposed by Aleksander Jablonski and is used to illustrate the molecular transitions that lead to absorptions and emissions.
- S_0 is called the ground state and is the state that a given moiety exists in most commonly.
- $V_1, V_2 \ldots V_n$ are the vibrational sublevels of a given state.
  - These are called sublevels, or the manifold, as they do not require a change in molecular orbitals, merely in vibrational speed.



McEwen, Jordan; *Jablonski diagram*; UC Davis; August 15, 2020; (Accessed via https://chem.libretexts.org/@go/page/1769 on July 5, 2021)

Infrared Light and Bonds – Types of Vibrations

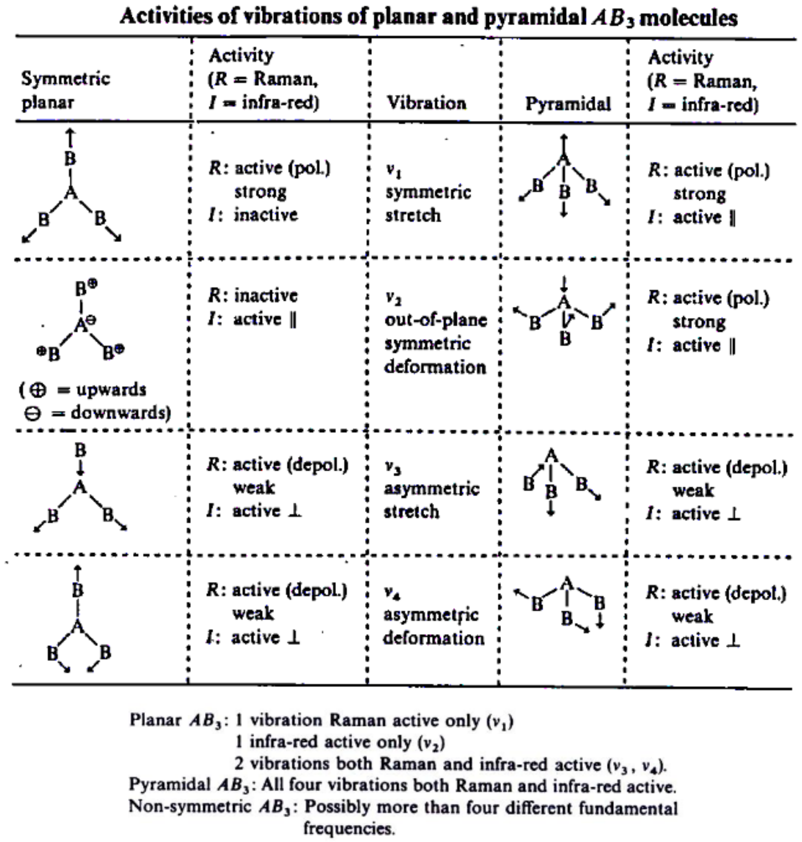
- **Stretching Vibration** – A vibration taking place parallel to the bond vector.
- **Bending Vibration** – A vibration taking place out of parallel with the bond vector.



Bruice, *Organic Chemistry*, pp. 586

Infrared Light and Bonds – IR Active Vibrational Constraints

- For a molecular vibration to be visible on an IR spectrum the vibration must result in a change in overall dipole moment.



Activities of vibrations of planar and pyramidal AB_3 molecules

Symmetric planar	Activity (R = Raman, I = infra-red)	Vibration	Pyramidal	Activity (R = Raman, I = infra-red)
	R: active (pol.) strong I: inactive	ν_1 symmetric stretch		R: active (pol.) strong I: active ∥
(⊕ = upwards ⊖ = downwards)	R: inactive I: active ∥	ν_2 out-of-plane symmetric deformation		R: active (pol.) strong I: active ∥
	R: active (depol.) weak I: active ⊥	ν_3 asymmetric stretch		R: active (depol.) weak I: active ⊥
	R: active (depol.) weak I: active ⊥	ν_4 asymmetric deformation		R: active (depol.) weak I: active ⊥

Planar AB_3: 1 vibration Raman active only (ν_1)
1 infra-red active only (ν_2)
2 vibrations both Raman and infra-red active (ν_3, ν_4).
Pyramidal AB_3: All four vibrations both Raman and infra-red active.
Non-symmetric AB_3: Possibly more than four different fundamental frequencies.

Ramalingam, M.; *Physical Methods in Chemistry II, Unit II: Infrared and Raman Spectroscopy*; Bharathidasan University, Tiruchirappalli; http://oms.bdu.ac.in/ec/admin/contents/160_P16CH41_2020052904251921.pdf Pp. 12

Infrared Light and Bonds – Number of Vibrations

- There are several modes of vibrations that can occur per molecule. To calculate the number of degrees of freedom that can manifest vibrationally, the number of rotational degrees of freedom must be subtracted from the degrees of freedom for the total molecule (3n where n is the number of atoms)
  - For a linear molecule this is N = 3n-5
  - For a nonlinear molecule this is N = 3n-6

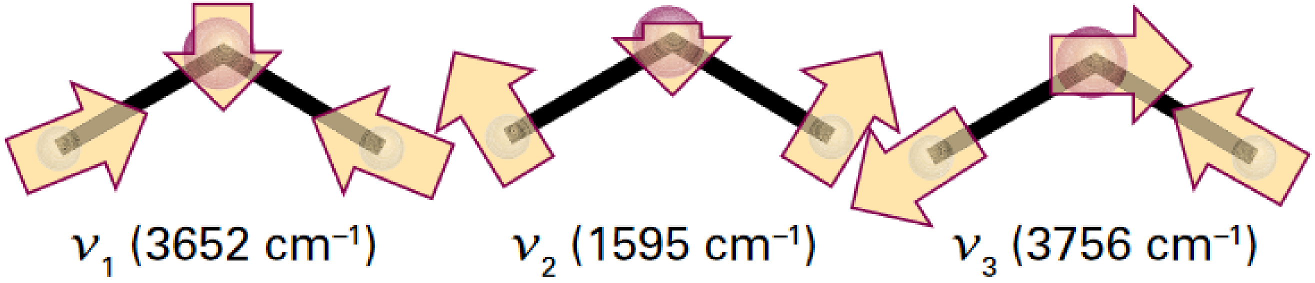


Figure 11D.3 The three normal modes of H_2O. The mode ν_2 is predominantly bending, and occurs at lower wavenumber than the other two.

Atkins et al, *Atkins' Physical Chemistry*, pp. 452

Infrared Light and Bonds – Experimental Numbers of Vibrations

- At times in experimental data, the number of vibrations seen in an infrared spectrum may be less than the expected amount arising from a given species.
- This can be due to a few things.
    - Instrument broadband capability
    - Instrument resolving capability
    - Molecular symmetry
    - Low absorption
- It is also possible to see more absorbing bands than expected
    - Overtones
    - Combination bands

Infrared Light and Bonds – Vibrational Coupling

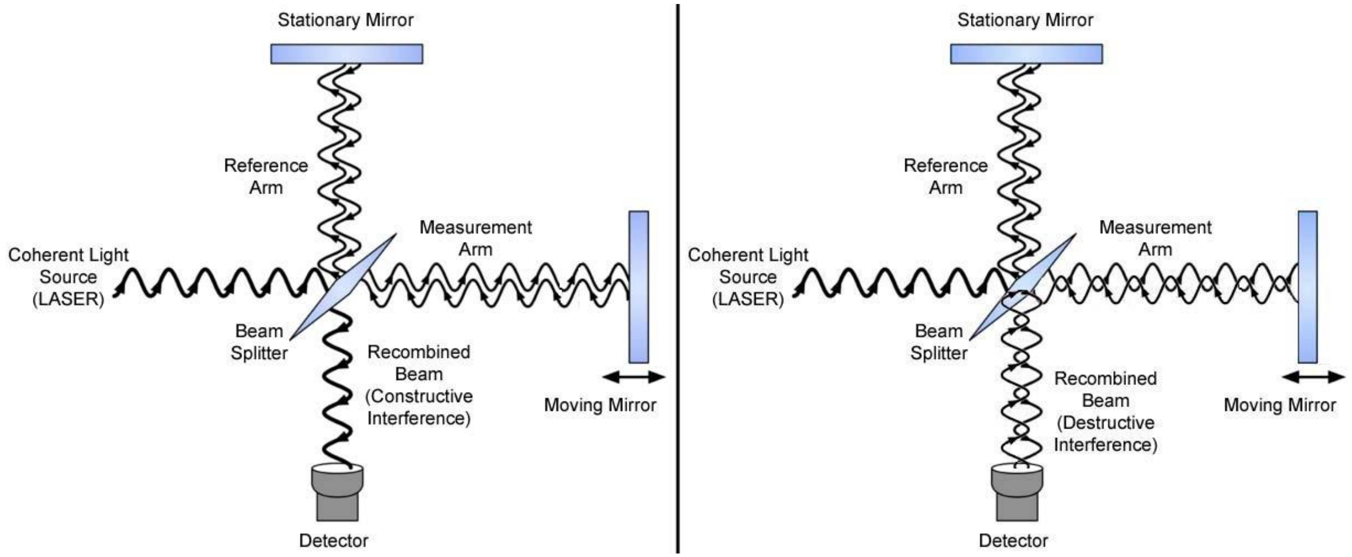
- Vibrational coupling is when 2 vibrations occur at the same time and influence the overall energy of the resultant absorptions.
- Coupling can occur if:
  - Two bending vibrational groups share a bond.
  - Two stretching vibrations share an atom.
  - A bending vibrational bond is shared with a stretching vibration.
- Ex. Carbon dioxide coupling of scissoring (bending) with symmetric and asymmetric stretches.

Instrumentation From Vibration to Spectrum – IR Sources & Detectors

- For infrared spectroscopy, we use what is called a **broadband source**. A broadband source means that it emits across a large band of wavelengths.
- If you remember in our discussion of photons we mentioned how when a sold is heated, it gives off blackbody radiation. This radiation is in the form of IR light and is what most IR sources are based off of.
  - Nernst Glower
  - Globar
  - Incandescent nichrome wire
- IR detectors are generally based on the incident light causing a change in the temperature of a material and in turn the resistance.

Instrumentation From Vibration to Spectrum – Interferometry

- An interferometer relies on the wave nature of light, and allows light to be separated by wavenumber, and thus by wavelength or frequency.
- This is achieved via passing the light through a beam splitter, which is a semi-silvered mirror. What this does is separate the light into two beams, or paths.
- One of these paths contains a mirror at a set distance, and the other contains a movable mirror. The beams are reflected after travelling a certain distance and are recombined by the beam splitter.



Muelaner, Jody; *Laser Interferometers*, https://www.muelaner.com/laser-interferometers/

Instrumentation From Vibration to Spectrum – Interferometry

- Upon detection, the interference minima ar maxima can be observed, in relation to the difference in path length (dx or δ). This is called an interferogram.
  - More specifically, in the context of FTIR, an interferogram is a plot of ligh intensity in either absorbance or transmittance vs δ in cm.
- This interferogram is where all our spectral information arises from. However, we are unable to use the information contained in the central maxima, as the intensity is generally too high.
- We instead use the 'edges' of the interferogram.

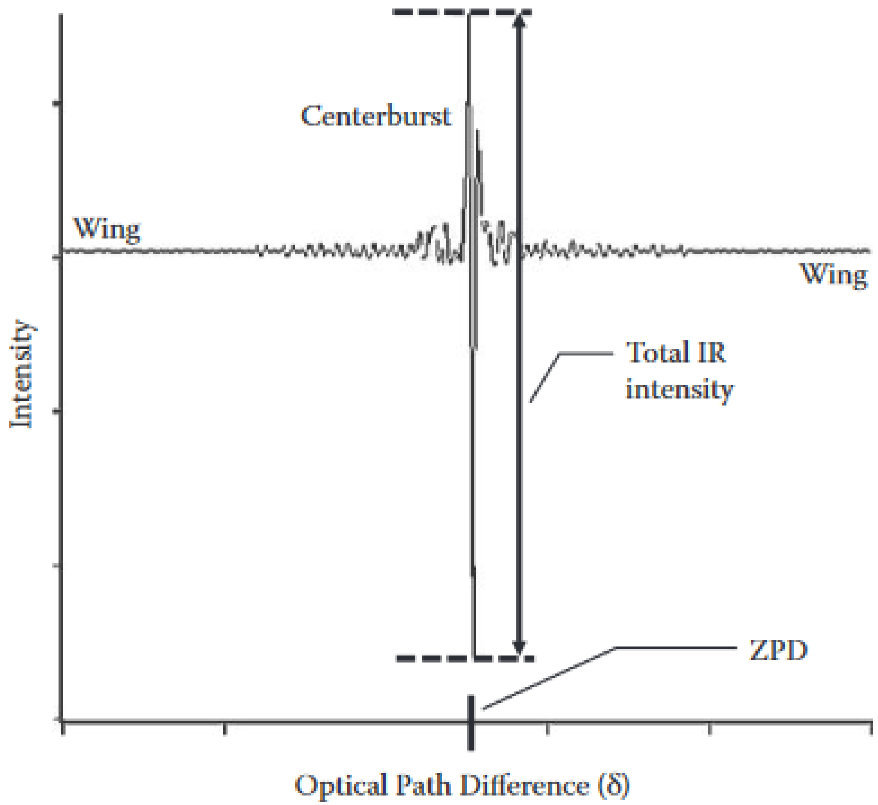


FIGURE 2.9 A real-world interferogram obtained when many wavenumbers of light pass through the interferometer together.

Smith, Brian C.; *Fundamentals of Fourier Transform Infrared Spectroscopy*; 27

Instrumentation From Vibration to Spectrum – Fourier Transforms

- Once we have an interferogram, we must convert it into a spectrum.
- To do this, a Fourier transform is applied to the interferogram.
  - The Fourier transform is in essence, a method of converting a domain into it's inverse. For example, if a spectrum was taken in time (s), a F.T. could be used to convert it to frequency (s^{-1}).
  - The function used to perform a Fourier transform is $\mathcal{F}(\xi) = \int_{-\infty}^{\infty} f(x) e^{-2\pi i x \xi} dx$.
- By using this F.T. on the interferogram, δ(cm) is converted to wavenumber(cm^{-1}).

Instrumentation From Vibration to Spectrum – Transmittance

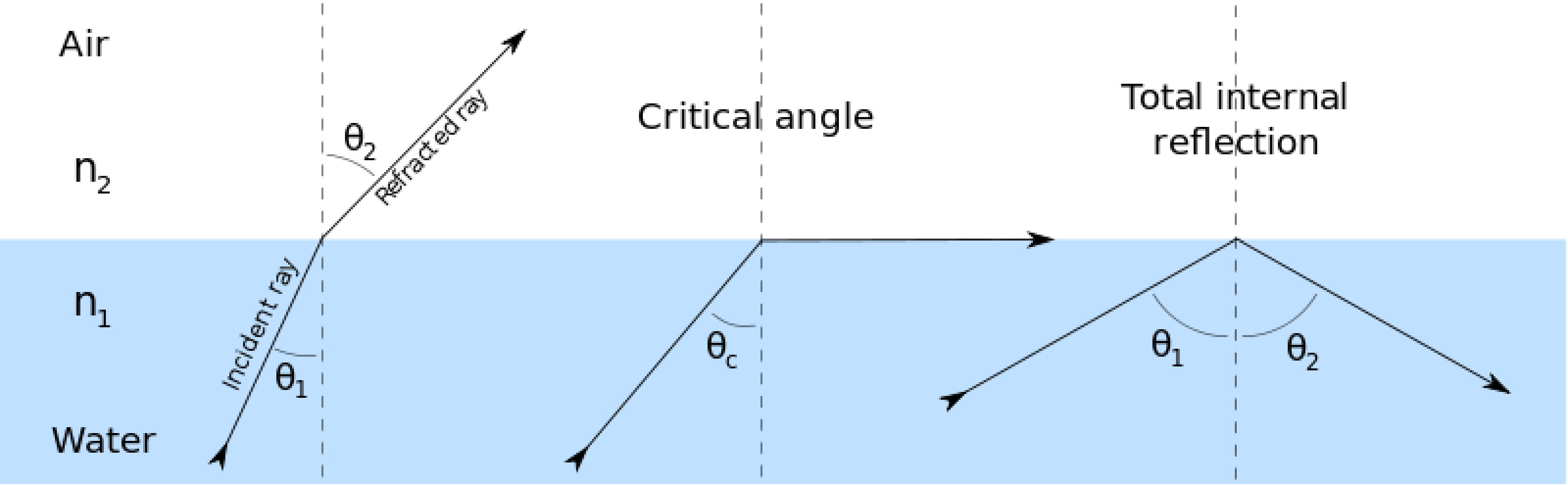
- When measuring the amount of light absorbed by an analyte, one method of expressing this quantitatively is transmittance.
- Transmittance is a ratio of the intensity of the light produced by the source (generally called a blank or a 0 measurement), compared to the intensity of the light after being passed through an analyte. This is generally expressed as a percentage.
  - $\%T = \frac{I}{I_0} * 100\%$ Units: percentage
- A drawback to transmittance measurements, however, is that the response of transmittance to a change in concentration is not linear. For transmittance, Beer’s law becomes:
  - $-\log_{10}(T) = -\log_{10}\left(\frac{I}{I_0}\right) = \varepsilon bC$ where ε is the molar absorptivity coefficient in (Lmol^{-1}cm^{-1}), b is path length in cm, and C is molar concentration (molL^{-1})

Instrumentation From Vibration to Spectrum – Absorbance

- To have a linear response to concentration, absorbance must be used. Since transmittance is an exponential response to concentration, taking the log of transmittance yields a linear response to concentration.
- However, this linear response is inversely proportional to concentration. Thus, in defining absorbance, a negative is included, to make it proportional to concentration. Hence, a more concentrated species absorbs more.
- The expression for absorbance from transmittance is:
  - $A = -\log_{10}(T) = \log_{10}\left(\frac{I_0}{I}\right)$
- Thus, Beer's law can be defined as:
  - $A = b\varepsilon C$
- Absorbance being a log scale does not have units, however for plotting, generally AU's or absorbance units are used, since conventionally units are needed for axes.

Instrumentation From Vibration to Spectrum - ATR

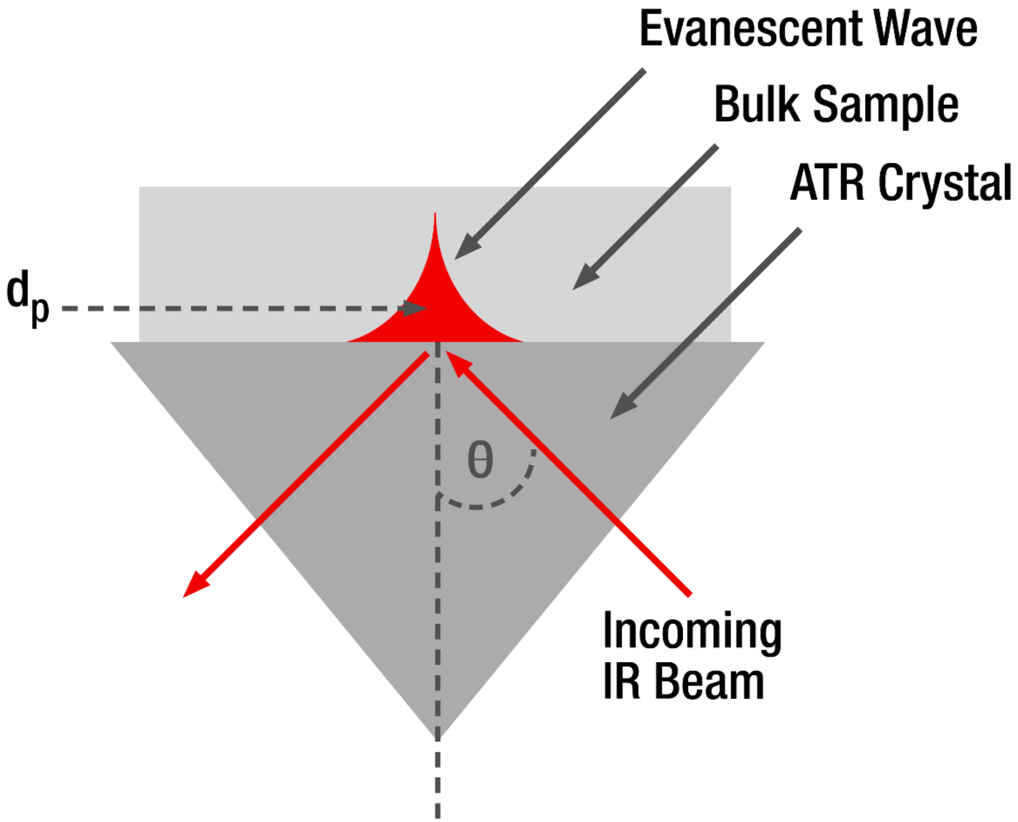
- Attenuated total reflectance is a technique generally used to investigate solids via FTIR.
- To understand ATR, one must first understand total internal reflection (TIR).
  - TIR occurs due to Snell's Law, which describes how light at the junction of two refractive indexes is 'bent' based on the angle of initial incidence.
  - *Snell's Law*: $n_1 \sin(\theta_1) = n_2 \sin(\theta_2)\ where\ n_1 > n_2$
- At a specific angle of incidence called the critical angle ($\theta_{critical}$), the incident light cannot escape the medium with a higher refractive index and is rather fully reflected inside this medium.



Rebecca H., *Ask the Van*, University of Illinois Department of Physics, January 30, 2016, https://van.physics.illinois.edu/qa/listing.php?id=42038&t=why-does-total-internal-reflection-happen

Instrumentation From Vibration to Spectrum - ATR

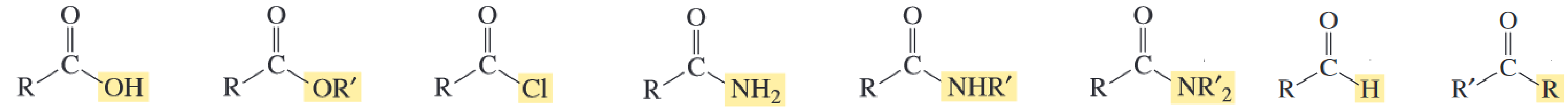
- So how does total internal reflection allow IR light to hit the sample if it’s reflecting before it hits the sample?
  - The story is a bit more complex. When TIR occurs, a small amount of light passes into the medium with the lower refractive index in what’s referred to as an evanescent wave, due to quantum tunnelling.
- The evanescent wave is also reflected, and travels back into the other medium, generally a diamond. This can then be passed into a detector and provide the IR information following the Fourier transform.



Attenuated Total Reflectance, Anton Paar GmbH, https://wiki.anton-paar.com/en/attenuated-total-reflectance-atr/

Useful Vibrations – Carbonyls

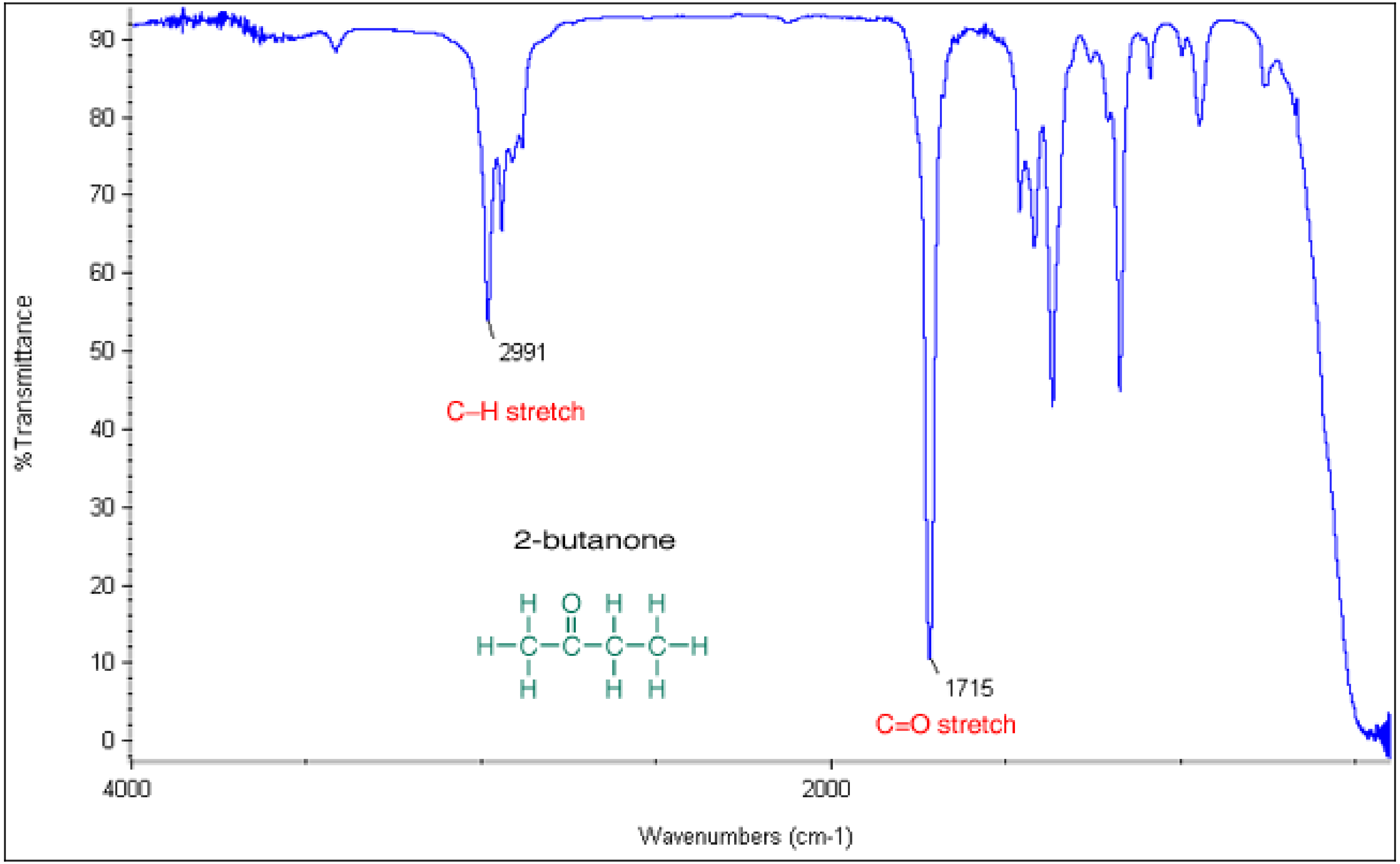
- Carbonyls are a functional group that consists of a carbon-oxygen double bond and are often found in both monomers and polymers.
- Due to the high electronegativity of oxygen, carbonyls are electron withdrawing groups (EWG), meaning that they draw electron density away from the rest of the molecule. This results in an intense absorbance peak as the C=O bond has a large dipole moment, and thus a larger capability for a change in dipole moment.
- A carbonyl group is also found in other functional groups, like carboxylic acids, and the derivatives of these groups, like acyl chlorides, esters, and amides.



carboxylic acid ester acyl chloride amides aldehyde ketone

Bruice, *Organic Chemistry*, pp. 686-687

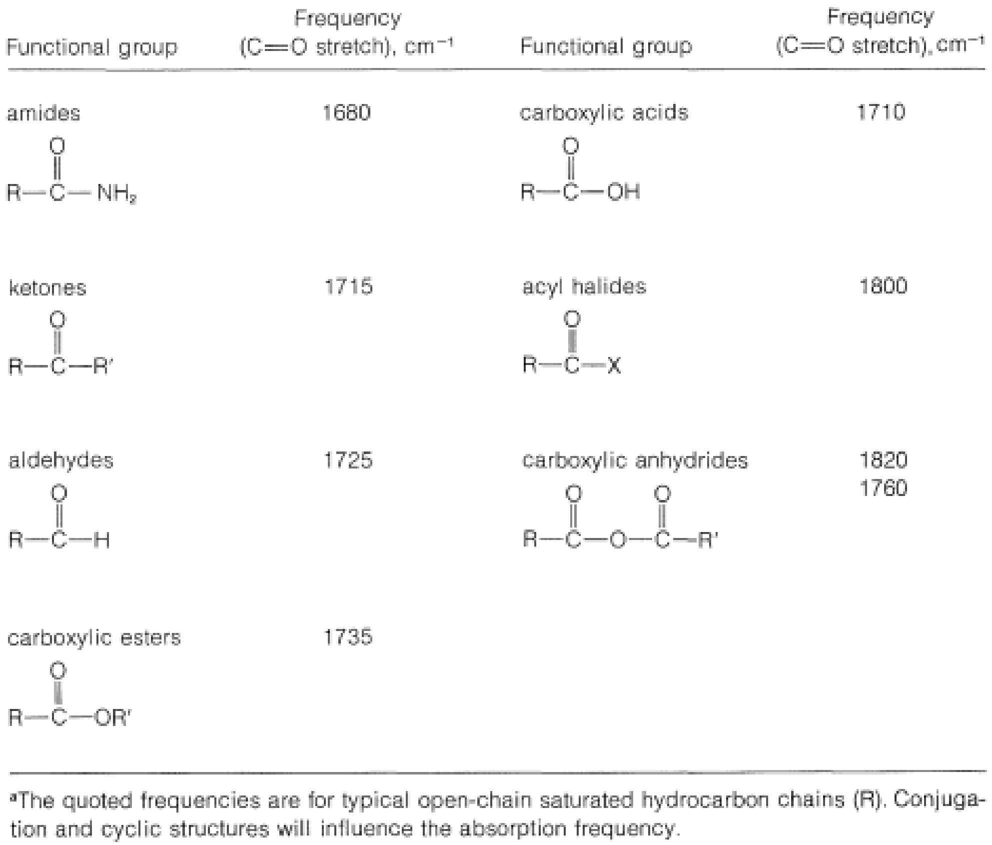
Useful Vibrations – Carbonyls



IR Spectroscopy Tutorial: Ketones; University of Colorado, Boulder; 2011; https://orgchemboulder.com/Spectroscopy/irtutor/ketonesir.shtml

Useful Vibrations – Carbonyls

- Carbonyl vibrations can be found between $1780 cm^{-1}$ and $1650 cm^{-1}$.
- The position of these vibrations are influenced by the groups around it.



Functional group	Frequency (C=O stretch), cm^{-1}	Functional group	Frequency (C=O stretch), cm^{-1}
amides $R-\overset{O}{\overset{\|}{C}}-NH_2$	1680	carboxylic acids $R-\overset{O}{\overset{\|}{C}}-OH$	1710
ketones $R-\overset{O}{\overset{\|}{C}}-R'$	1715	acyl halides $R-\overset{O}{\overset{\|}{C}}-X$	1800
aldehydes $R-\overset{O}{\overset{\|}{C}}-H$	1725	carboxylic anhydrides $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R'$	1820 1760
carboxylic esters $R-\overset{O}{\overset{\|}{C}}-OR'$	1735		

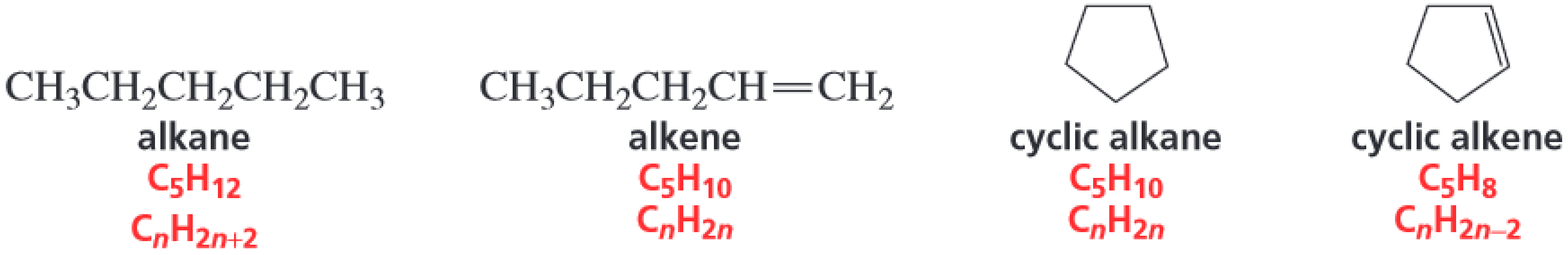
[a] The quoted frequencies are for typical open-chain saturated hydrocarbon chains (R). Conjugation and cyclic structures will influence the absorption frequency.

- By using an instrument with good enough resolution, and carefully finding the maxima of the absorbance due to a carbonyl, useful clues to the surroundings of the carbonyl group can be obtained.

Robert, John D.; Caserio, Marjorie C.; *Basic Principles of Organic Chemistry*; 2nd edition; W. A. Benjamin, Inc.; Menlo Park, CA; 1977; (accessed via https://chem.libretexts.org/@go/page/22269 on July 7 2021)

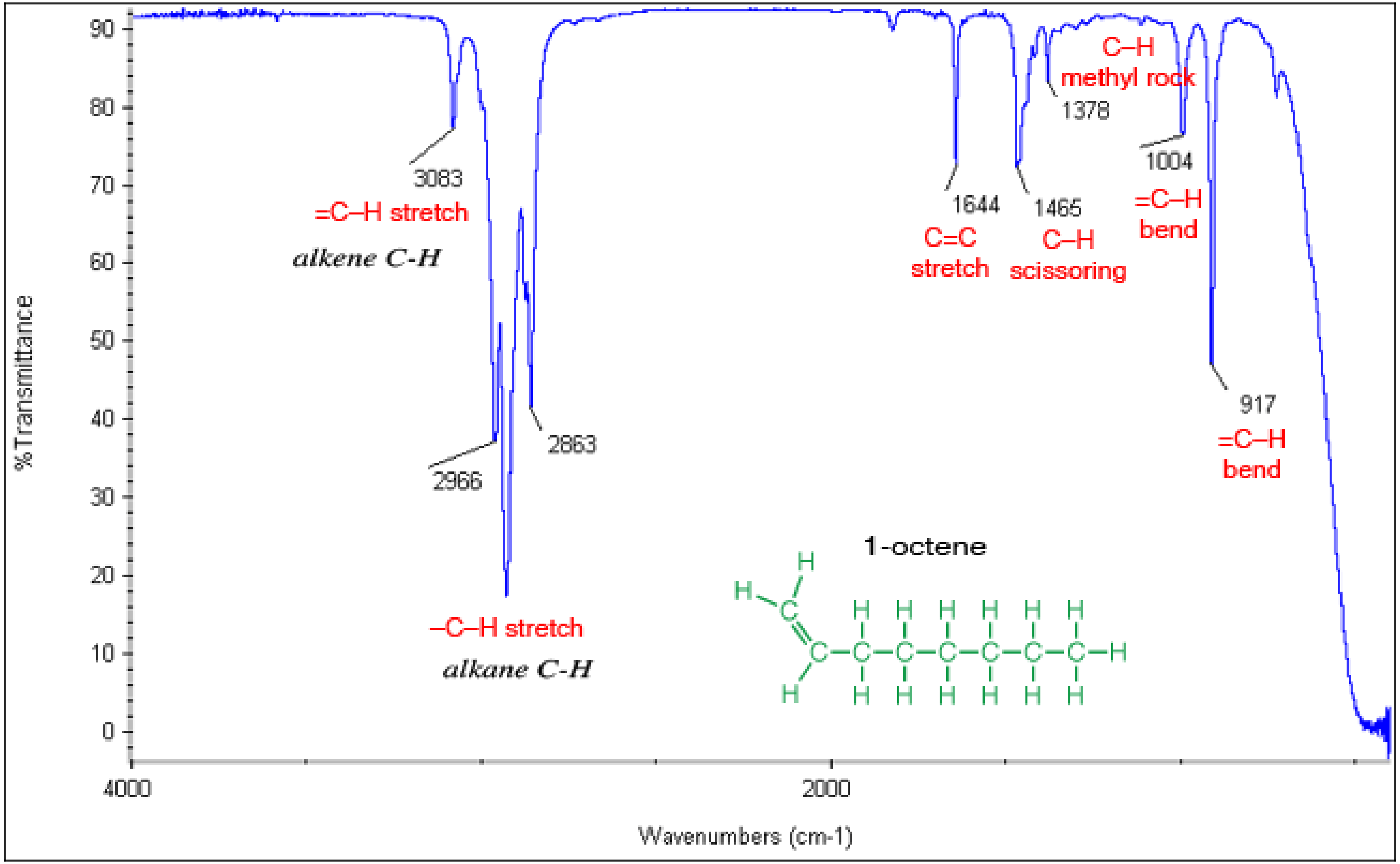
Useful Vibrations – Alkenes

- Alkenes are also commonly found functional groups in monomers and polymers. These consist of a carbon-carbon double bond.
- Due to the lack of a dipole moment in the C=C bond, the absorbance peak due to this group tends to be less intense. This bond vibration is dependent on an overall molecular dipole, or an induced dipole moment due to Van Der Waals forces.
- The C=C stretch vibration occurs most prominently at approximately 1650cm^{-1}, being visible between 1680cm^{-1} and 1600cm^{-1}, and a terminal alkene having a smaller peak at approximately 3080cm^{-1}, appearing between 3020cm^{-1} and 3100cm^{-1}.



Bruice, *Organic Chemistry*, pp. 191

Useful Vibrations – Alkenes



IR Spectroscopy Tutorial: Alkenes; University of Colorado, Boulder; 2011; https://orgchemboulder.com/Spectroscopy/irtutor/alkenesir.shtml

Useful Vibrations – Hydroxyls

- Hydroxyl groups are one of the most distinctive FTIR vibrations, with the O-H stretch causing a wide peak centered around 3250cm^{-1}. These groups can be found in both alcohols and carboxylic acids.
- The largest issue with using hydroxyl peaks as identificatory peaks is that if water contamination is present in the sample, it will yield an O-H stretching vibration, with very high intensity, as water contains 2 O-H bonds that the stretching vibration can take place via.
- Additionally, O-H bonds can be found in carboxylic acids. In a carboxylic acid, the hydrogen is not very strongly bonded to the oxygen, which leads to a large amount of band broadening.

Useful Vibrations – Nitrogen Containing Groups

- There are several nitrogen-containing functional groups found in polymers, such as nitrile groups, heterocyclic rings, imines, and amines. Amines and aliphatic heterocycles contain a C-N single bond, imines and aromatic heterocycles contain a C-N double bond, and nitriles contain and C-N triple bond.
- Nitrogen containing groups vibrate via the N-H stretch mode, which visually looks similar to the O-H stretching vibration. This band centers around 3400cm^{-1} and spans from 3300 to 3500.
- CH_3-N vibrations take place at approx. 2815cm^{-1} and are often lost among the CH_3 alkane vibrations.
- Nitrile vibrations occur as a weak peak between 2260cm^{-1} and 2222cm^{-1}.
- Nitrogenic double bonds generally occur between 2120cm^{-1} and 2160cm^{-1}. However, in the case of an imine a medium intensity band occurs between 1640 cm^{-1} and 1690cm^{-1}.

Useful Vibrations – C-H Bonds

- Another useful technique for characterizing molecules is examining the C-H bond vibration region. The frequency and thus wavenumber of these vibrations is dependent on the hybridization (bonding) of the carbon the proton is bound to.
- If any bonding other than single bonding is present in the molecule, absorption bands will occur t the left of 3000cm^{-1}, given that C-H vibrations of a sp^3 carbon occur lower than 3000cm^{-1}.
- C=C-H stretches occur around 3020cm^{-1} to 3100cm^{-1}, and CΞC-H stretches occur around 3300cm^{-1}.

Useful Vibrations – Aromatics & Delocalization

- When several double bonds are 1 single bond apart, the electrons are delocalized across the whole network of bonds. This is called electron delocalization, as the electrons are not tethered to any one atom, but rather belong to the entire molecular orbital. This is also referred to as a molecule being aromatic or having aromaticity.
- Electronic delocalization results in a changing of bond energy, and thus vibrational frequency and wavenumber.

Useful Vibrations – Hydrogen Bonding

- Like delocalization, hydrogen bonding can influence the wavenumber of a bond that can experience hydrogen bonding.
  - Bonds that can have hydrogen bonding occur are N-H, O-H, and F-H.
  - These bonds are very polar, resulting in the hydrogen being largely electron deficient. What can then take place is this electron deficient proton can interact with the lone pairs on a nitrogen, oxygen, or fluorine.
- When hydrogen bonding occurs, the peak is broadened significantly, as the number of vibrational states that one of these bonds can occupy is increased drastically.

Useful Vibrations – Summary Tables

Table 13.4 Frequencies of Important IR Stretching Vibrations

Type of bond	Wavenumber (cm^{-1})	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

Table 13.5 Carbon–Hydrogen Stretching Vibrations

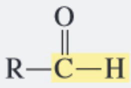
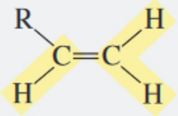
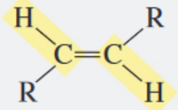
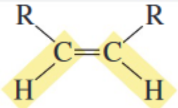
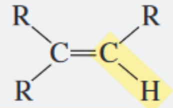
	Wavenumber (cm^{-1})
C≡C—H	~3300
C=C—H	3100–3020
C—C—H	2960–2850
 $R-\overset{\overset{\displaystyle O}{\|}}{C}-H$	~2820 and ~2720

Table 13.6 Carbon–Hydrogen Bending Vibrations

		Wavenumber (cm^{-1})
CH_3- $-CH_2-$ $-\underset{\vert}{CH}-$		1450–1420
CH_3-		1385–1365
	terminal alkene (monosubstituted)	990 and 910
	terminal alkene (disubstituted)	890
	trans	980–960
	cis	730–675
	trisubstituted	840–800

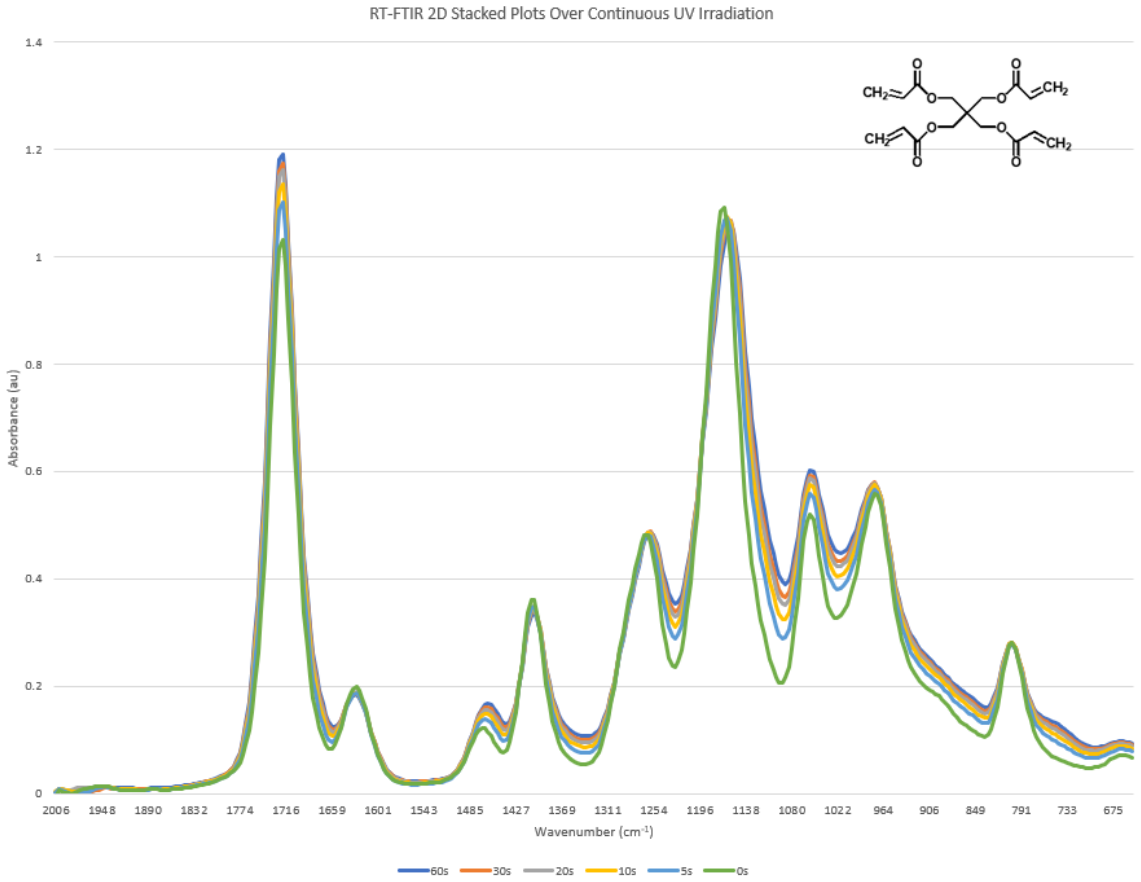
Bruice, *Organic Chemistry*, Pp. 589, 595, 597

Polymer Kinetics – Real Time Studies

- Real time ATR-FTIR is a technique in which a fast Fourier transform (FFT) is used to rapidly process interferograms. This allows several (>90) interferograms to be taken per second. By doing this, the formation and degradation of functional groups can be observed over the course of a reaction.
  - Before the FFT, the speed at which interferograms could be processed was the main detractor to FTIR.
- The FFT is a pared-down form of the FT, allowing a computer to rapidly perform numerical approximations of a Fourier transform, similar to the computational methods used in a molecular dynamics simulation.

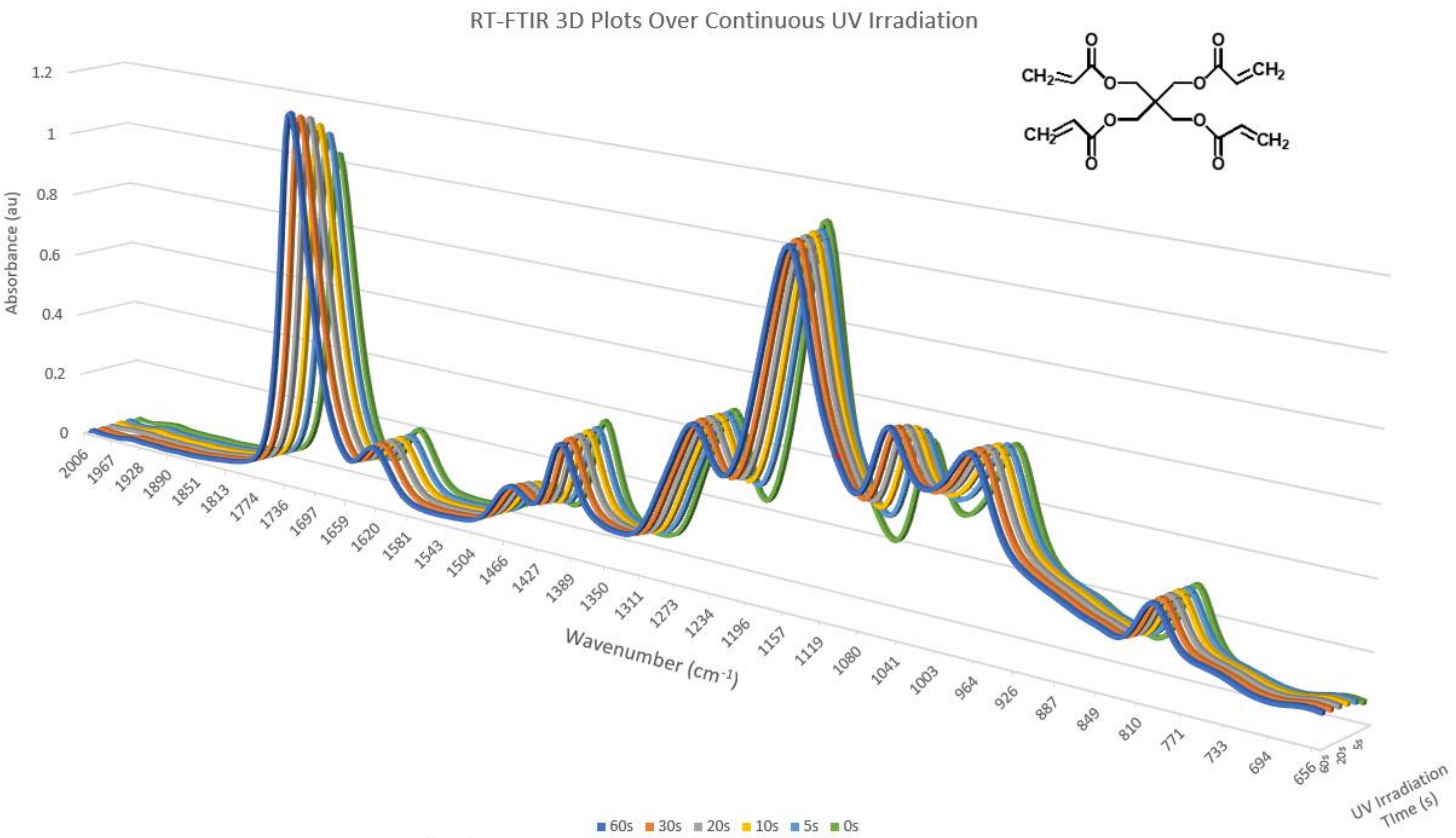
Polymer Kinetics – RT-FTIR Stacked Plots in 2-D & 3-D

- In polymer kinetic studies, it is at times useful to generate what are called stacked plots. Stacked plots are useful qualitatively, as they allow one to see the growth and decay of certain bond peaks.
- By observing the growth and decay of these bond-resultant peaks, as time progresses, the real time FTIR plot allows us to effectively “see” the change in bond amounts quantitatively.
- At times it is also useful to plot these in 3-D, for easier viewing of the peaks’ growth and decay relative to each other.



Data courtesy Dr. Yeongsik Kim

Polymer Kinetics – RT-FTIR Stacked Plots in 3-D

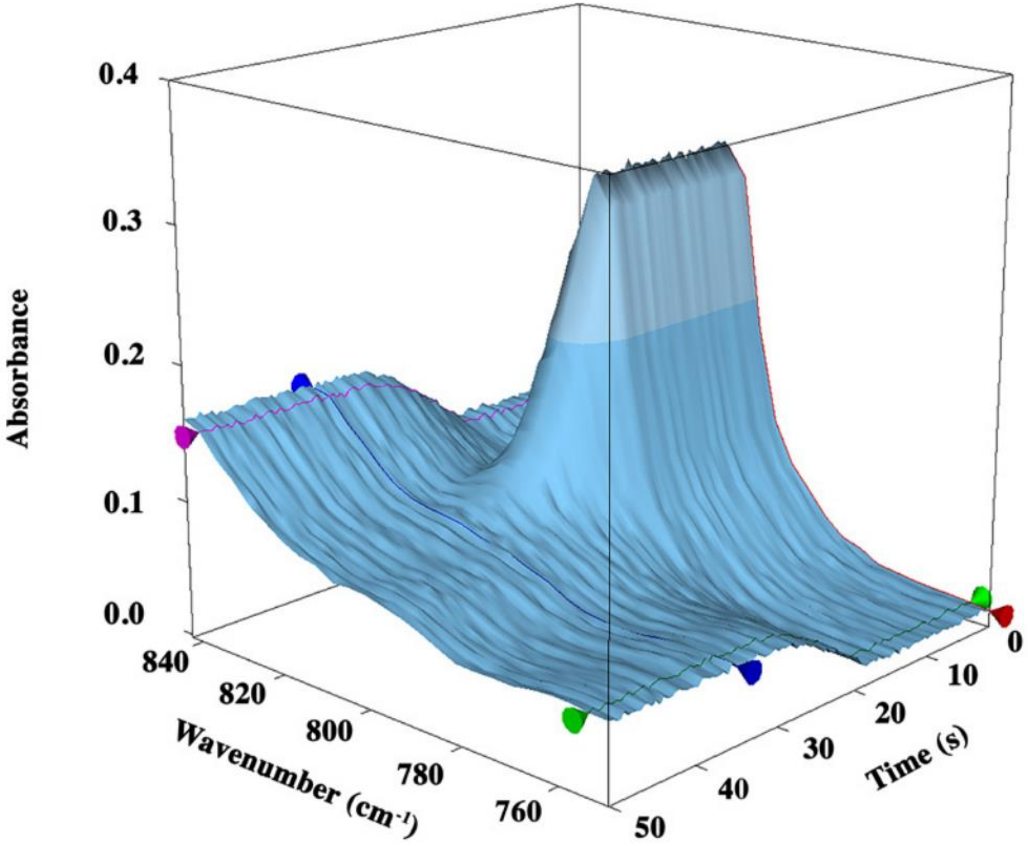


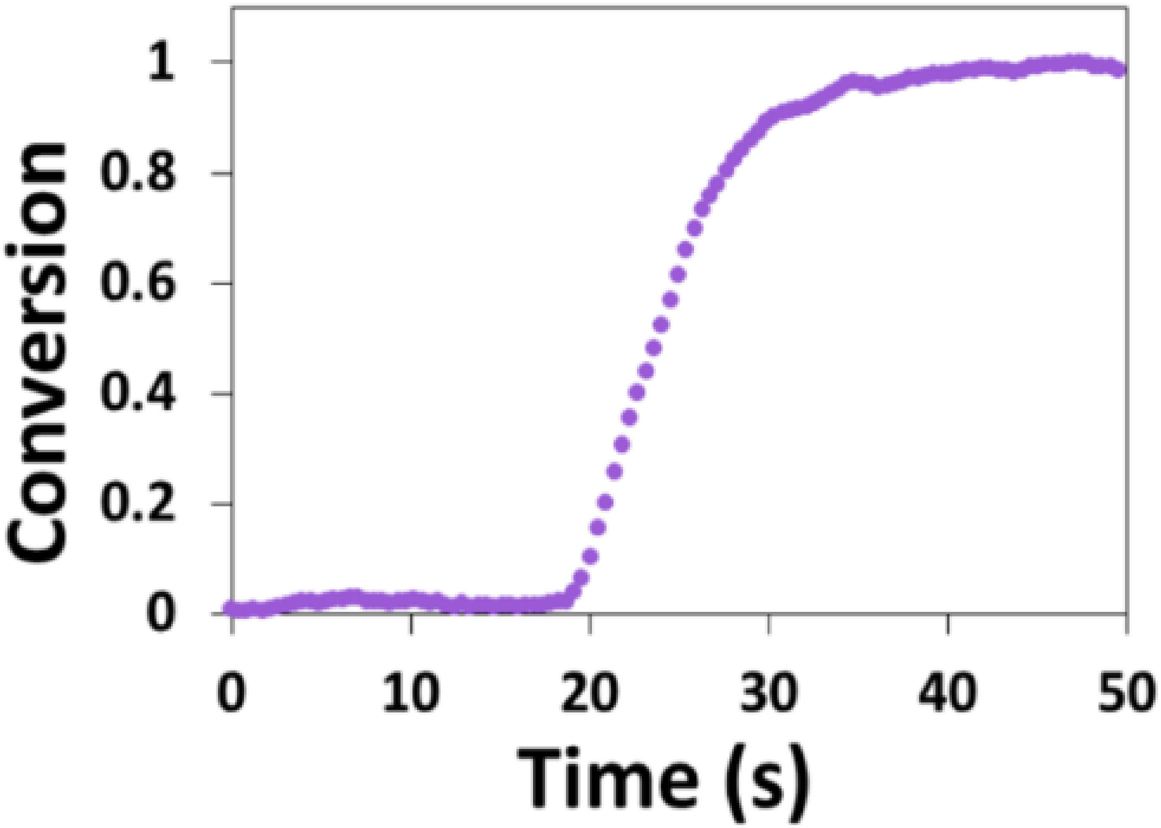
Data courtesy Dr. Yeongsik Kim

Polymer Kinetics – RT-FTIR %Conversion

- Percent conversion plots are used in the study of polymerization reactions, to monitor how far a reaction has progressed. This is drawn from a correlation of concentration of monomer decreasing, to the amount of polymer formed.
- Thus, by monitoring the decay of the monomeric concentration, we are simultaneously monitoring the formation of polymer.
- A percent conversion plot is useful as it allows us to find the onset of the reaction, and to visually ‘see’ how the reaction behaves as it progresses.
- By mapping the absorbance of a monomer bond that is not present in the polymer such as an alkene to a scale of 0 to 1 or 0% to 100% conversion, a plot can be generated.
- To do this mapping, the initial absorbance of the alkene (A_0) is taken as 0% conversion, or a value of 0. The final absorbance (A_f) is taken as 100% or a value of 1. Following this, an expression can be generated to find the percent conversion of each absorbance value (A_I).

Polymer Kinetics – RT-FTIR %Conversion





Kaplan Scientific, *Monitor Photocuring in real-time via ATR-FTIR Now uniquely with illumination through the ATR crystal!*, March 10, 2020, https://kaplanscientific.nl/monitor-photocuring-in-real-time-via-atr-ftir-now-uniquely-with-illumination-through-the-atr-crystal/

Polymer Kinetics – Reference Peaks

- In developing percent conversion charts, we must have a reference to compensate for variances in the baseline(s) of the spectra.
- Generally, this reference is via a peak with significant intensity, that does not change over the course of the reaction.
  - Oftentimes, this is a carbonyl peak, as they tend to be found in monomers but are not consumed in the reaction.
- By monitoring the fluctuations in these supposedly static peaks, we can effectively monitor the fluctuations in the baseline quantitatively, rather than qualitatively.
- However, as some bonds vibrate more intensely as a response to IR light, using these peaks as corrections is not as simple as simply subtracting the difference between the peaks from the baseline, a certain proportionality constant must be found. Thus, the use of these peaks to correct the baseline is generally a built in function of most FTIR processing software.

Practice Problem 1

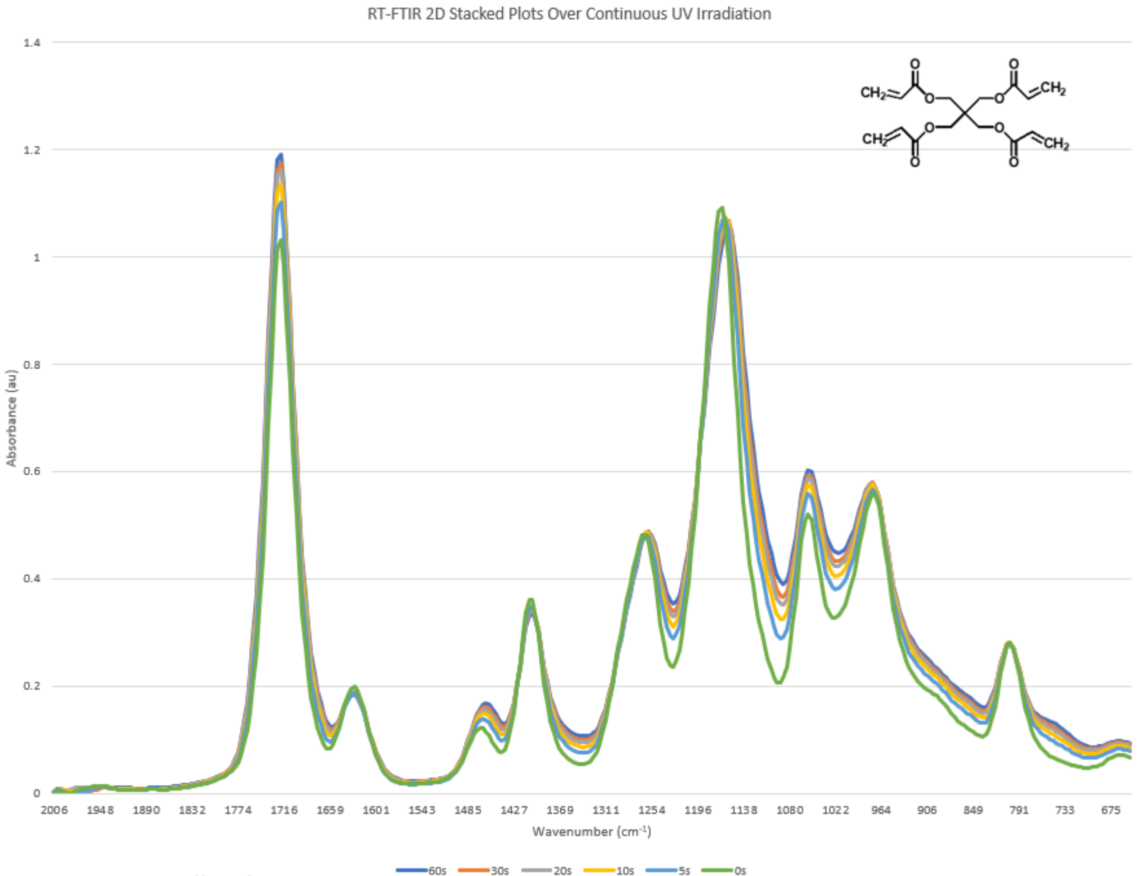
The beam of an infrared CO_2 LASER has a wavelength of 10.6 microns (μm). Find 1. the wavenumber in cm^{-1}, 2. frequency in THz, and 3. the energy in j.

Practice Problem 2

Match the given FTIR spectrum to the species that produced it.

Practice Problem 3

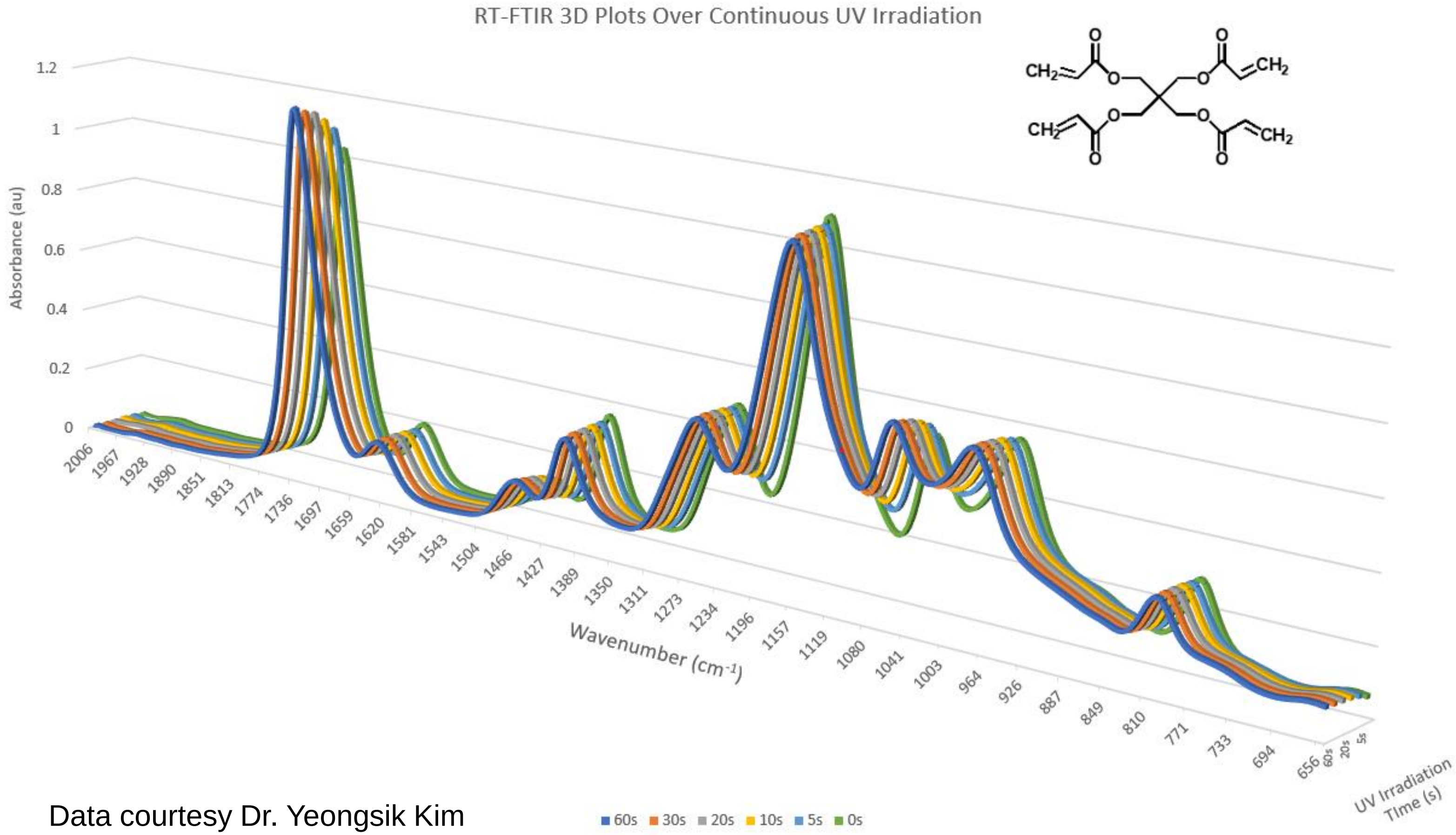
The stacked plots below were generated in an ATR-RT-FTIR study of a polymerization reaction. What bonds are being consumed in the reaction? What bonds are being formed?



Data courtesy Dr. Yeongsik Kim

Practice Problem 3

The stacked plots below were generated in an ATR-RT-FTIR study of a polymerization reaction. What bonds are being consumed in the reaction? What bonds are being formed?



Data courtesy Dr. Yeongsik Kim

Practice Problem 3

- Peak centering around 1724cm^{-1}:

- Peak centering around 806cm^{-1}:

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