IR Spectroscopy

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Spectroscopy can be defined as the interaction between matter and light. Infrared spectroscopy is a very powerful technique which uses electromagnetic radiation in the infrared region for the determination and identification of molecular structure as well as having various quantitative applications within analytical chemistry (Figure 1).

We do not aim to provide a mechano-quantic description of light and its interaction with atoms, as this is out of the scope of this module. However, it is important to note that atoms can absorb energy from electromagnetic radiation; this absorbed energy alters the state of the atoms within the molecule. These changes are usually manifest in alterations to the frequency and **amplitude of molecular vibrations**, which may be measured and plotted to produce an infrared spectrum.

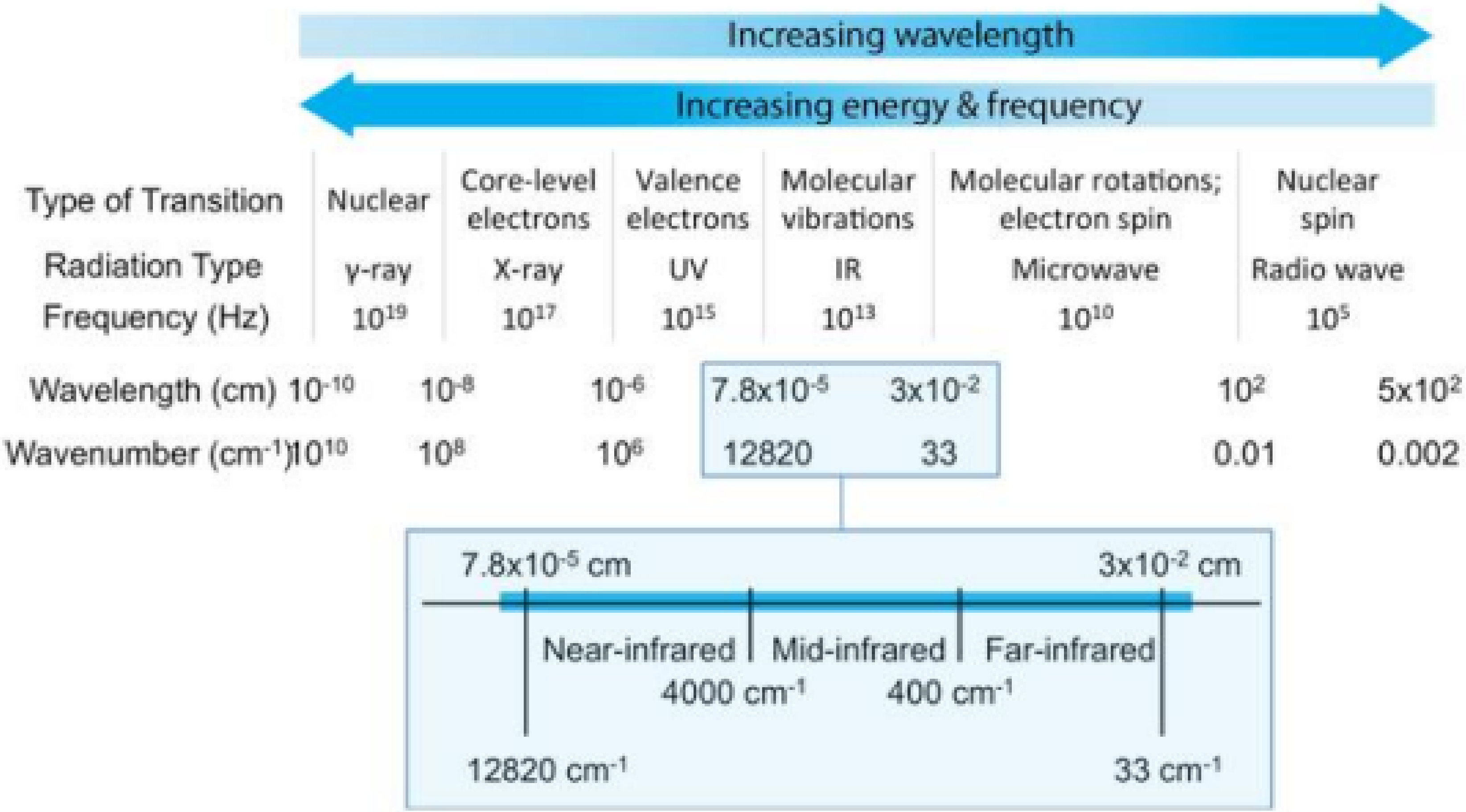


Figure 1: The electromagnetic spectrum and the infrared region.

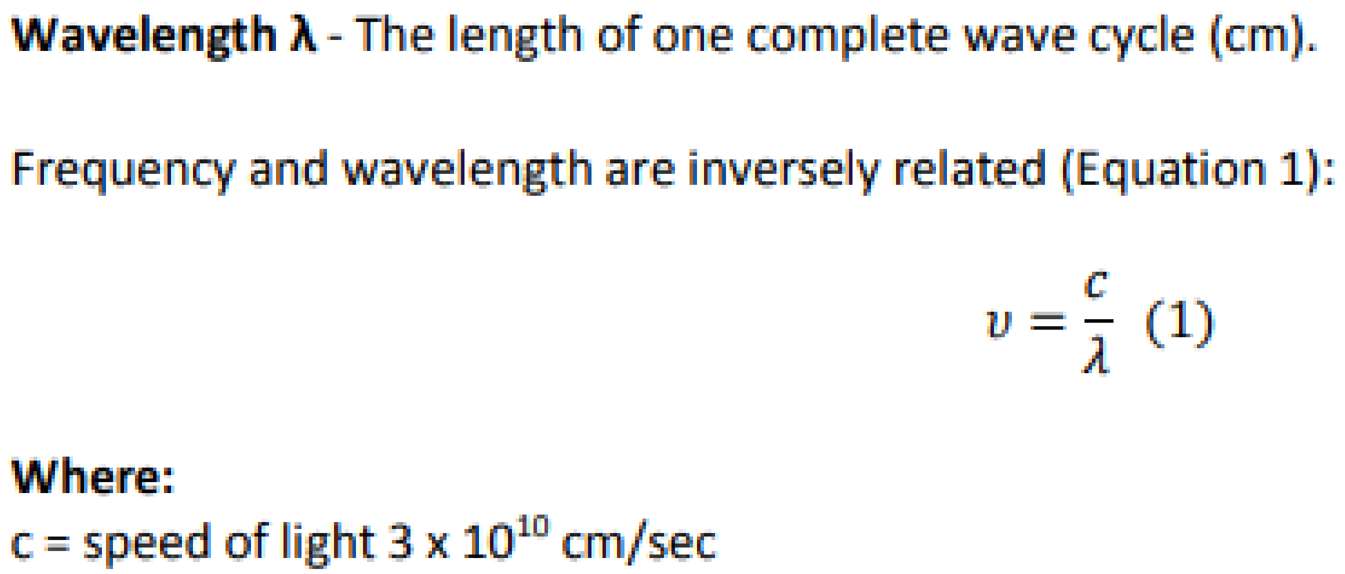
There are three well defined IR regions (near, mid and far). The boundaries between them are not clearly defined and debate still persists, but broadly they are defined as:

1. Near infrared (12820-4000 cm-1): poor in specific absorptions, consists of overtones and combination bands resulting from vibrations in the mid-infrared region of the spectrum.
2. **Mid-infrared (4000-400 cm-1): provides structural information for most organic molecules.**
3. Far Infrared (400-33 cm-1): has been less investigated than the other two regions; however, it has been used with inorganic molecules.

Electromagnetic Spectrum

The electromagnetic spectrum is the range of all possible frequencies of electromagnetic radiation, each of which can be considered as a wave or particle travelling at the speed of light, often referred to as a photon. These waves differ from each other in length and frequency.

Frequency (v) - the number of wave cycles that pass through a point in one second. Measured in Hertz (Hz).



Wavelength λ - The length of one complete wave cycle (cm).

Frequency and wavelength are inversely related (Equation 1):

$$\upsilon = \frac{c}{\lambda} \quad (1)$$

Where:
c = speed of light 3×10^{10} cm/sec

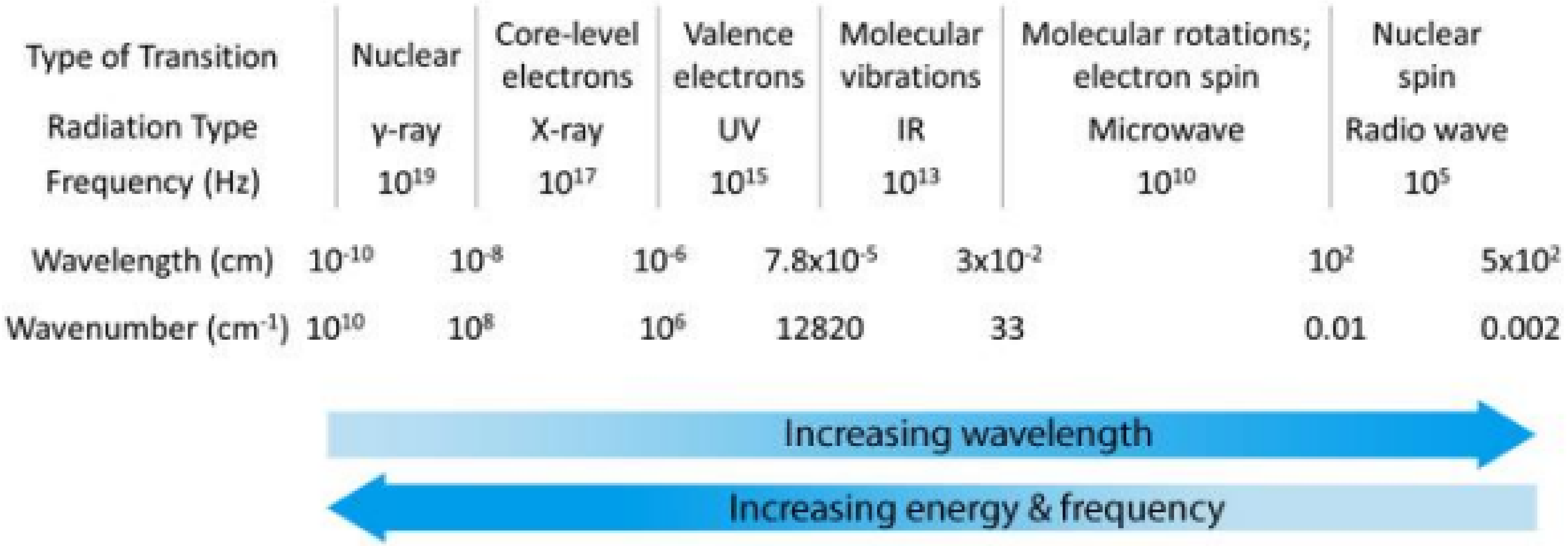
The energy of a photon (E in Joules) is related to wavelength and frequency as follows (Equation 2):

$$E = h\nu = \frac{hc}{\lambda} \quad (2)$$

Where:
h = Planck's constant 6.6 x 10^{-34} Joules-sec

Energy is directly proportional to frequency; therefore, high energy radiation will have a high frequency.

Energy is inversely proportional to wavelength, hence, short wavelengths are high energy and vice versa (Figure 2).

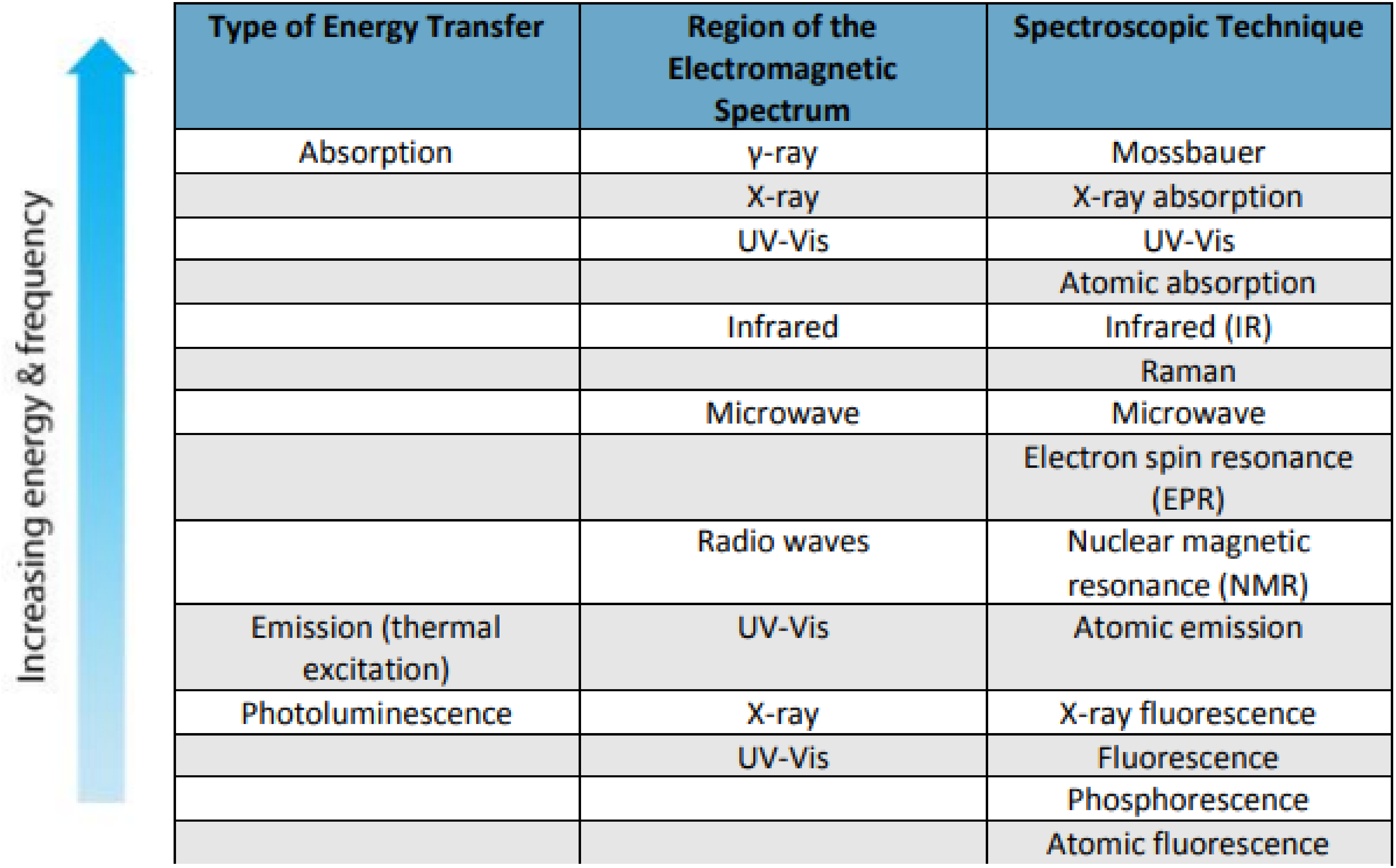


Type of Transition	Nuclear	Core-level electrons	Valence electrons	Molecular vibrations	Molecular rotations; electron spin	Nuclear spin
Radiation Type	γ-ray	X-ray	UV	IR	Microwave	Radio wave
Frequency (Hz)	10^{19}	10^{17}	10^{15}	10^{13}	10^{10}	10^{5}

Wavelength (cm) 10^{-10} 10^{-8} 10^{-6} 7.8×10^{-5} 3×10^{-2} 10^{2} 5×10^{2}

Wavenumber (cm^{-1}) 10^{10} 10^{8} 10^{6} 12820 33 0.01 0.002

Electromagnetic Radiation and Spectroscopy

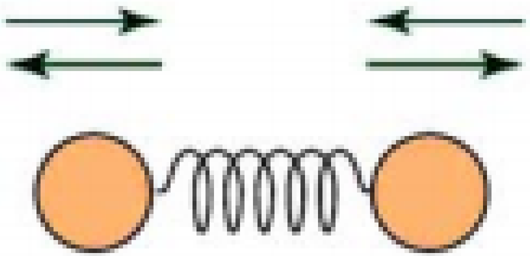


Type of Energy Transfer	Region of the Electromagnetic Spectrum	Spectroscopic Technique
Absorption	γ-ray	Mossbauer
	X-ray	X-ray absorption
	UV-Vis	UV-Vis
		Atomic absorption
	Infrared	Infrared (IR)
		Raman
	Microwave	Microwave
		Electron spin resonance (EPR)
	Radio waves	Nuclear magnetic resonance (NMR)
Emission (thermal excitation)	UV-Vis	Atomic emission
Photoluminescence	X-ray	X-ray fluorescence
	UV-Vis	Fluorescence
		Phosphorescence
		Atomic fluorescence

Table 1: Electromagnetic spectrum region, type of energy transfer, and the associated spectroscopic technique.

Infrared radiation is largely thermal energy.
It induces stronger **molecular vibrations** in covalent bonds, which can be viewed as springs holding together two masses, or atoms.

Specific bonds respond to (absorb) **specific** frequencies



The classical vibrational frequency for a diatomic molecule (with force constant k and masses m_1 and m_2) has been derived from Hooke's Law (Equation 3):

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}} \quad (3)$$

Where:

μ = reduced mass = $\frac{m_1 m_2}{m_1+m_2}$

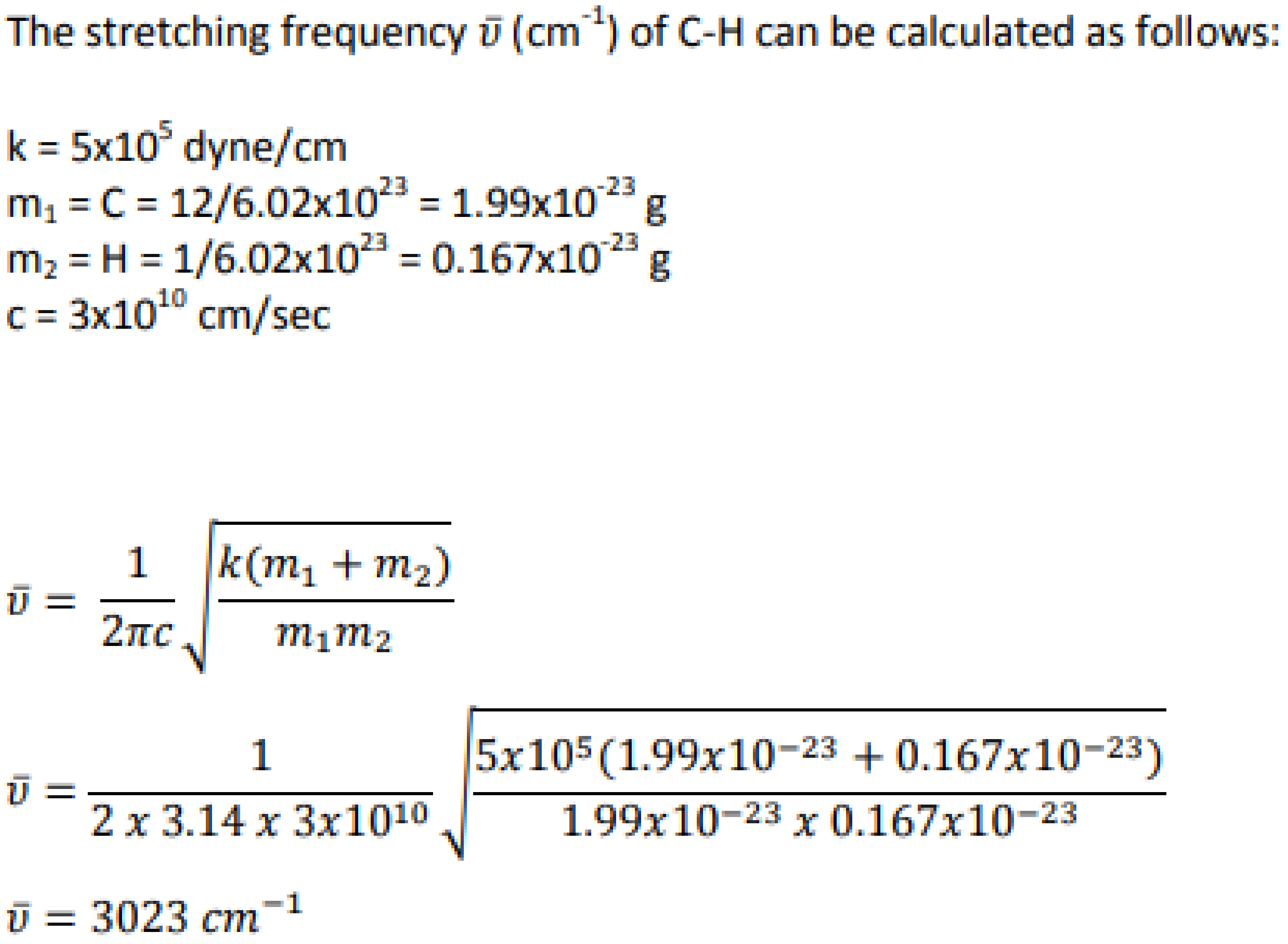
In terms of the wavenumber ($\bar{\upsilon}$) (Equation 4):

$$\bar{\upsilon} = \frac{\upsilon}{c} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1+m_2)}{m_1 m_2}} \quad (4)$$

Where:

c = speed of light = 3 x 10^{10} cm/sec

Calculation of Molecular Vibrations



The stretching frequency $\bar{\upsilon}$ (cm^{-1}) of C-H can be calculated as follows:

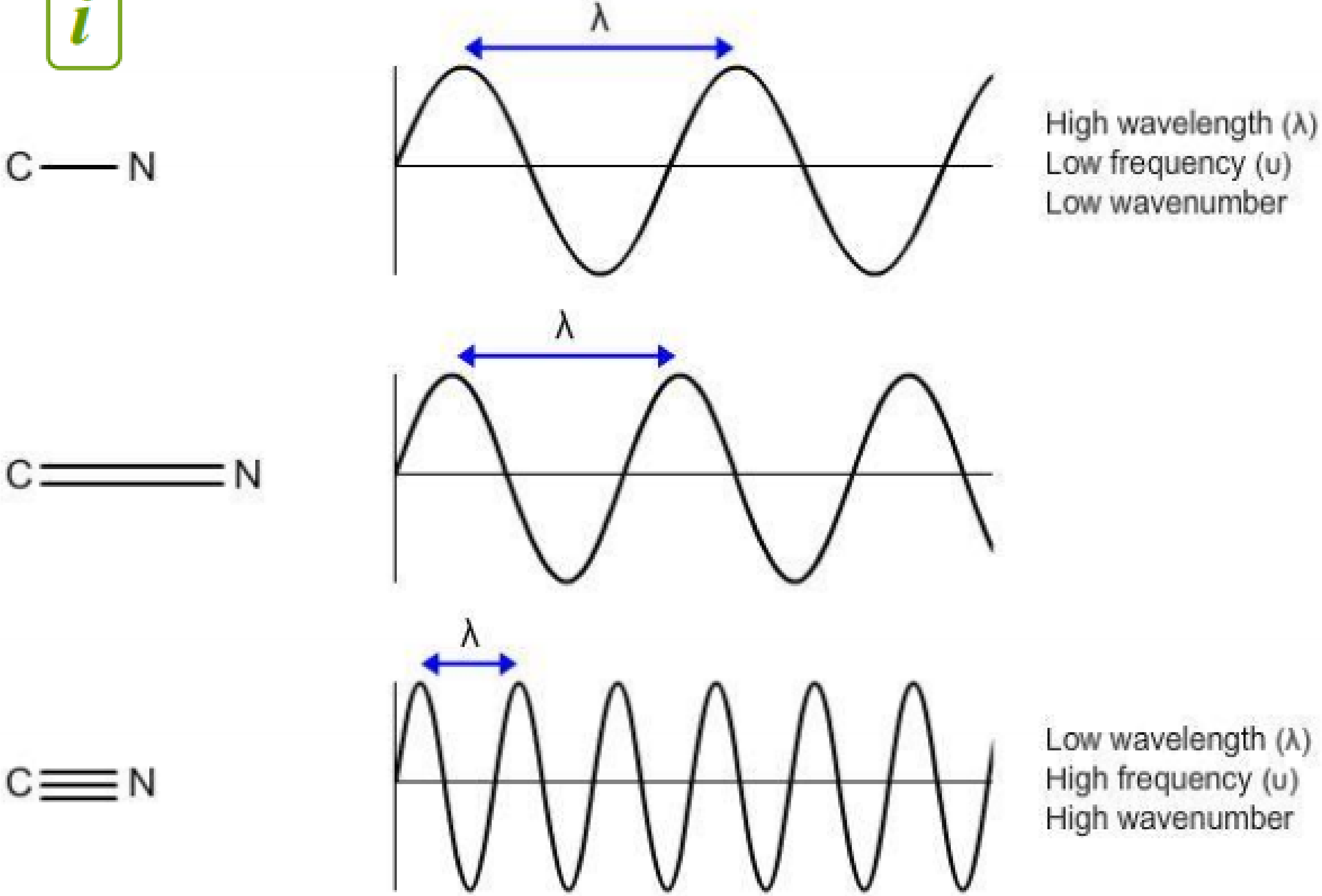
$k = 5x10^{5}$ dyne/cm
$m_1 = C = 12/6.02x10^{23} = 1.99x10^{-23}$ g
$m_2 = H = 1/6.02x10^{23} = 0.167x10^{-23}$ g
$c = 3x10^{10}$ cm/sec

$$\bar{\upsilon} = \frac{1}{2\pi c}\sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$

$$\bar{\upsilon} = \frac{1}{2\,x\,3.14\,x\,3x10^{10}}\sqrt{\frac{5x10^{5}(1.99x10^{-23} + 0.167x10^{-23})}{1.99x10^{-23}\,x\,0.167x10^{-23}}}$$

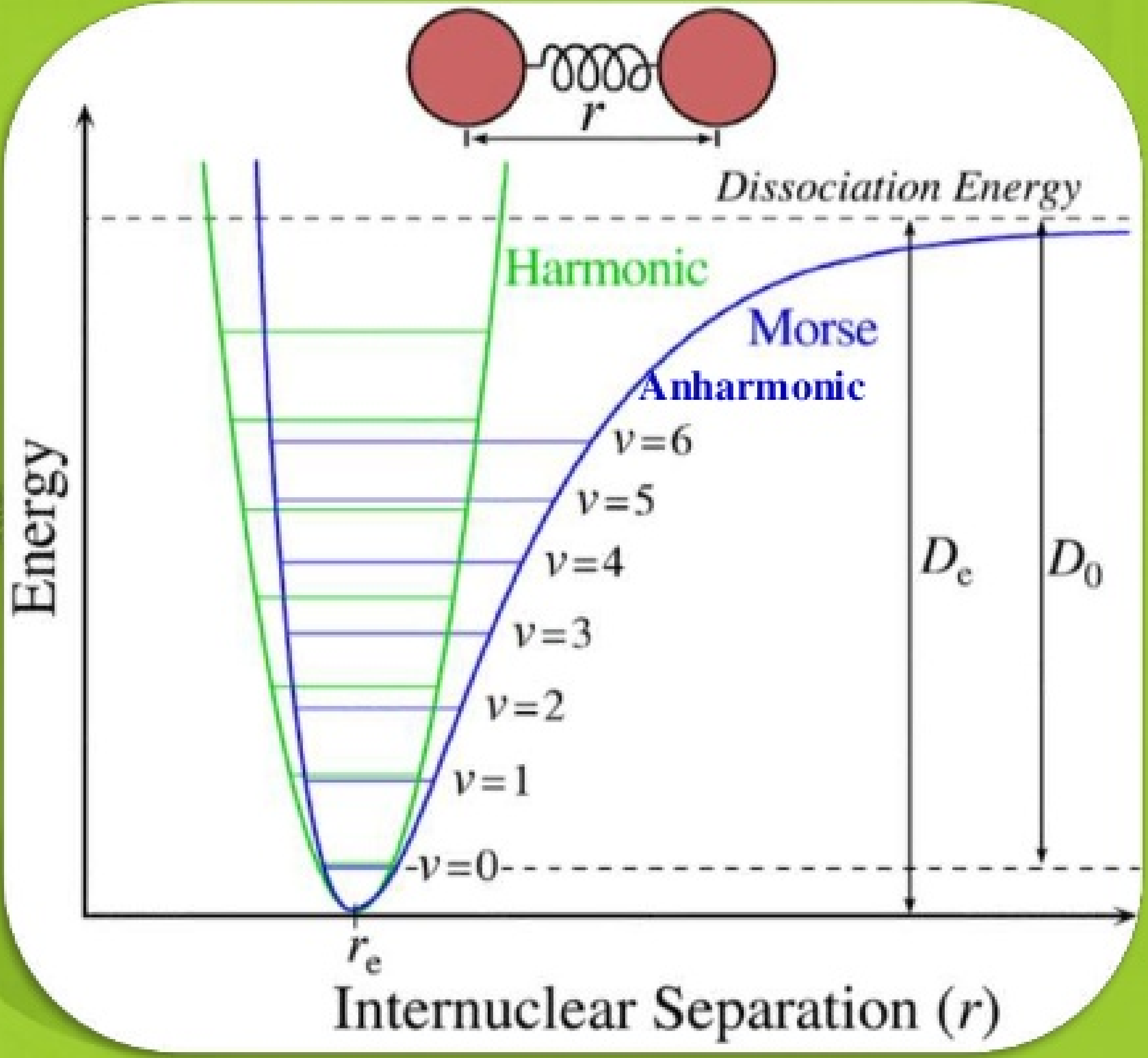
$$\bar{\upsilon} = 3023\ cm^{-1}$$

The observed values for C−H bonds are in the region 3320-2700 cm-1 , which differ from the calculated values as the calculation does not take into account the environment of the C−H group within the molecule.



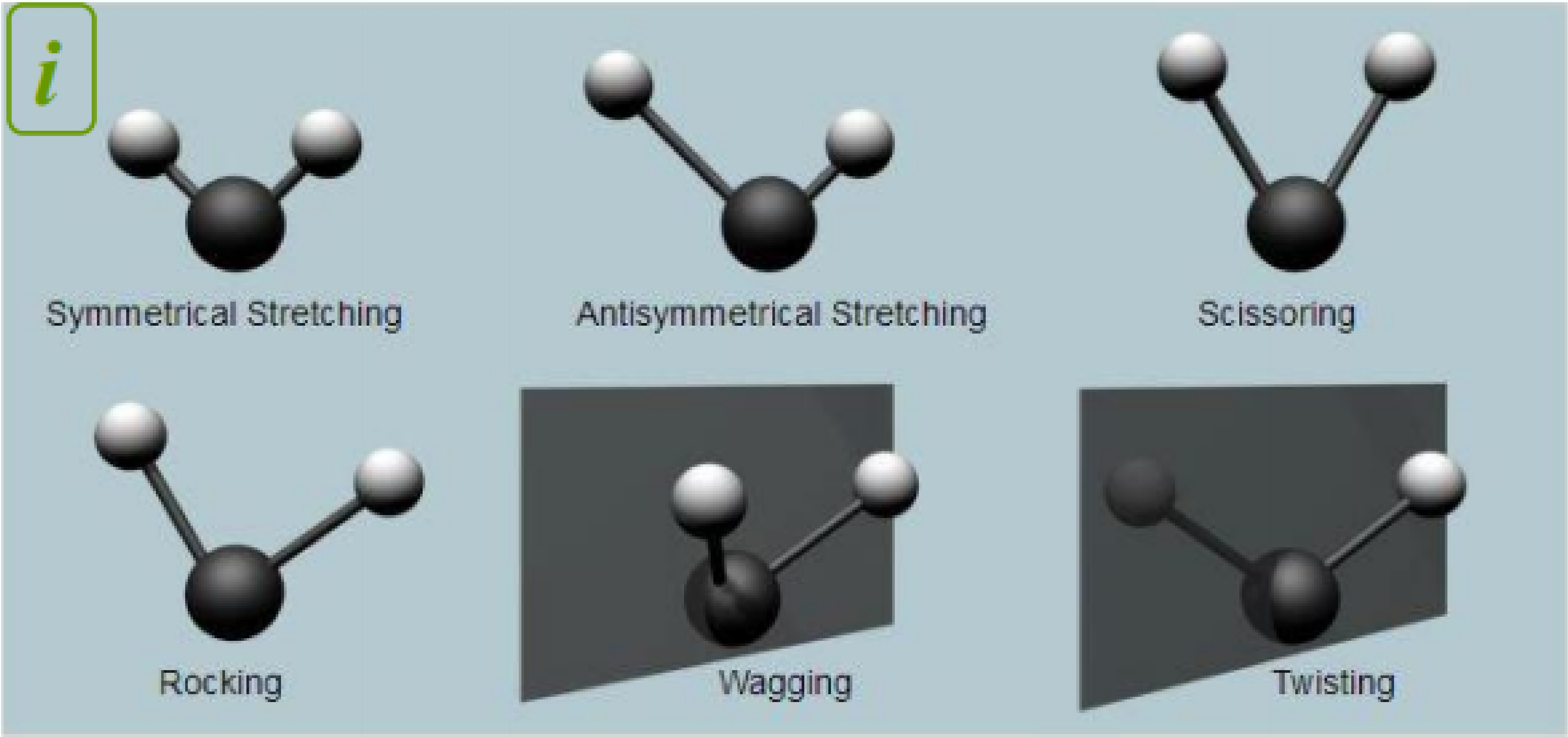
Comparison of wavelength, stretching frequency, and wavenumber of bonds with different strengths (i.e. single, double, and triple bonds).

Potential energy diagrams of oscillators



Infrared Active Modes

A molecule that is infrared active must undergo a **change in its dipole moment when vibrating**. The simplest modes of vibration that are infrared active are stretching and bending modes



For simplicity, we are going to illustrate the vibration modes in a linear molecule (acetylene in this case).

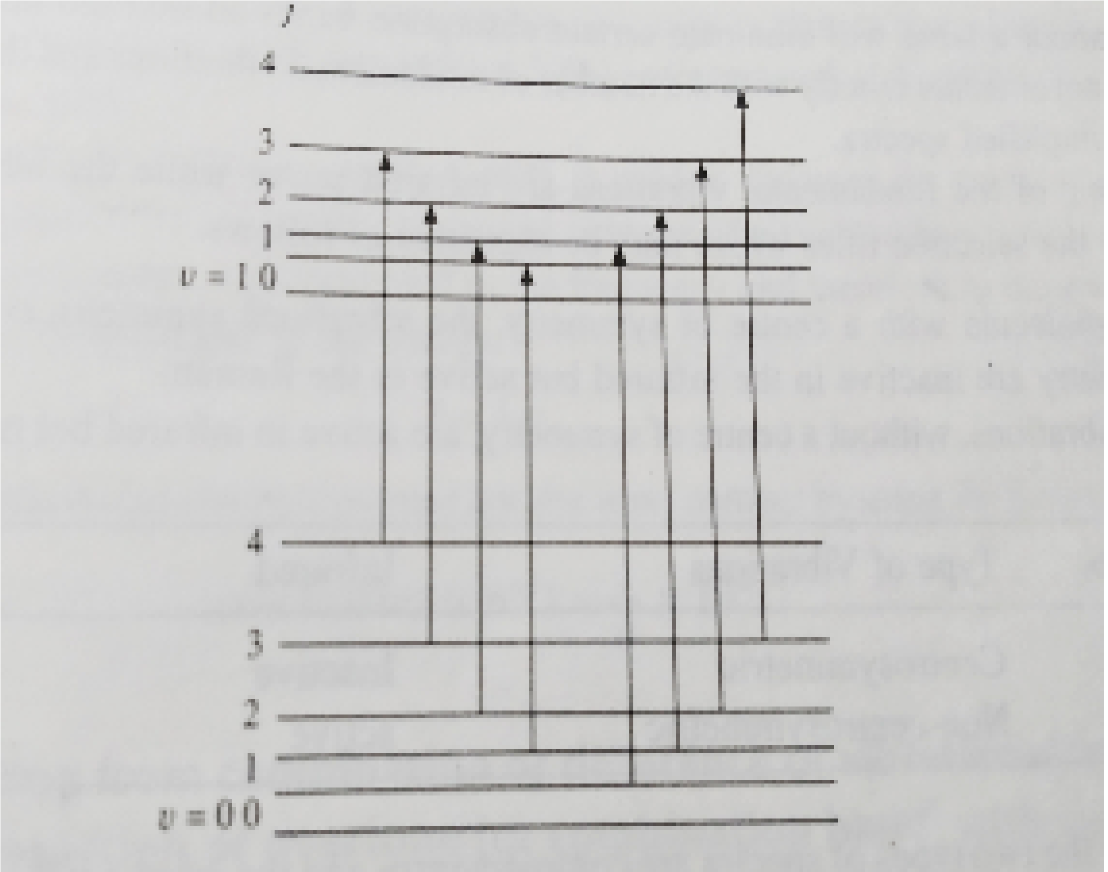
The symmetric C≡C stretching will not alter the acetylene’s dipole moment and it is **not infrared active**.

However, substitution of either of the H atoms in acetylene produces an asymmetric alkyne bond which will be IR active.

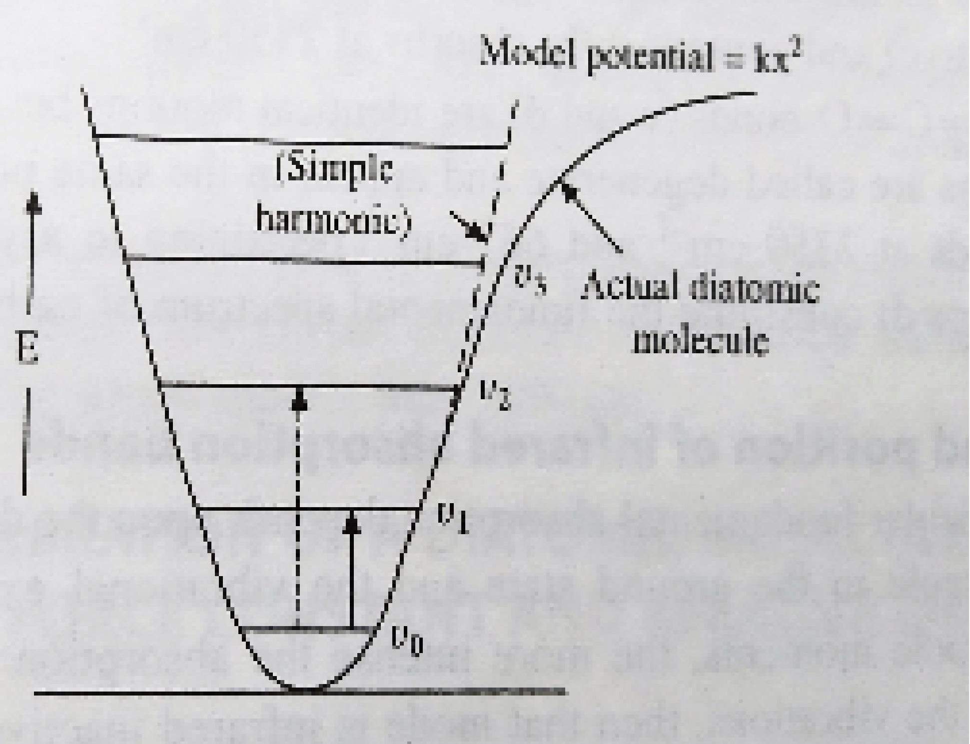
Homonuclear diatomic molecules such as Cl2, H2, N2, etc. will exhibit no infrared active modes as no change in their dipole moment is experienced during vibration.

Fundamental Vibration

It is clear that vibrational energy level are much more widely spaced than those of rotation. When a molecule absorb energy it either can change its j (rotational quantum number) value or it can change its vibrational and rotational levels. **When changes occur ΔJ or Δv is restricted to ±1.**



.3a Vibrational-rotational energy levels for a diatomic molecule.



b Potential energy curve for a diatomic molecule.

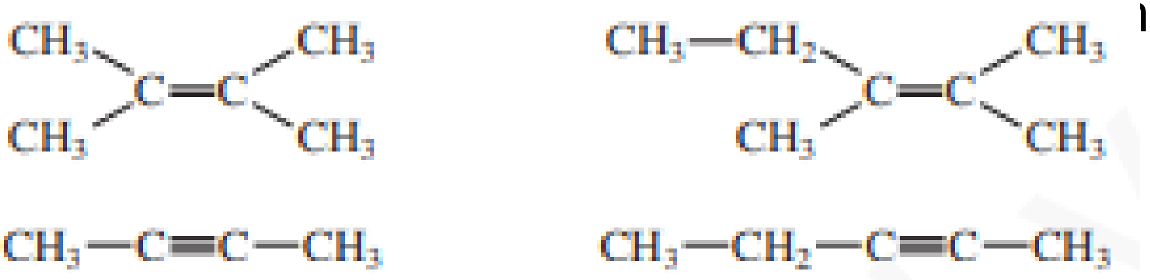
The vibrations we have been discussing are called **fundamental absorptions.** They arise from excitation from the ground state to the lowest-energy excited state. Usually, the spectrum is complicated because of the presence of weak overtone, combination, and difference bands. **Overtones** result from excitation from the ground state to higher energy states, which correspond to integral multiples of the frequency of the fundamental (ν). For example, you might observe weak overtone bands at $2\overline{\nu}$, $3\overline{\nu}$, ... Any kind of physical vibration generates overtones. If you pluck a string on a cello, the string vibrates with a fundamental frequency. However, less-intense vibrations are also set up at several overtone frequencies. An absorption in the infrared at 500 cm^{-1} may well have an accompanying peak of lower intensity at 1000 cm^{-1}—an overtone.

When two vibrational frequencies ($\overline{\nu}_1$ and $\overline{\nu}_2$) in a molecule couple to give rise to a vibration of a new frequency within the molecule, and when such a vibration is infrared active, it is called a **combination band.** This band is the sum of the two interacting bands ($\overline{\nu}_{comb} = \overline{\nu}_1 + \overline{\nu}_2$). Not all possible combinations occur. The rules that govern which combinations are allowed are beyond the scope of our discussion here.

One can calculate overtone, combination, and difference bands by directly manipulating frequencies in wavenumbers via multiplication, addition, and subtraction, respectively. When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called **Fermi resonance.** Again, only certain combinations are allowed. Fermi resonance is often observed in carbonyl compounds.

The IR Absorption Process

A molecule absorbs only selected frequencies (energies) of infrared radiation. The absorption of infrared radiation corresponds to energy changes on the order of 8 to 40 kJ/mole. Radiation in this energy range corresponds to the range encompassing the stretching and bending vibrational frequencies of the bonds in most covalent molecules. In the absorption process, those frequencies of infrared radiation that match the natural vibrational frequencies of the molecule in question are absorbed, and the energy absorbed serves to increase the amplitude of the vibrational motions of the bonds in the molecule. Note, however, that not all bonds in a molecule are capable of absorbing infrared energy, even if the frequency of the radiation exactly matches that of the bond motion. Only those bonds **that have a dipole moment** that changes as a function of time are capable of absorbing infrared radiation. Symmetric bonds, such as those of H_2 or Cl_2, do not absorb infrared radiation. A bond must present an electrical dipole that is changing at the same frequency as the incoming radiation for energy to be transferred. The changing electrical dipole of the bond can then couple with the sinusoidally changing electromagnetic field of the incoming radiation. Thus, a symmetric bond that has identical or nearly identical groups on each end will not absorb in the infrared. For the purposes of an organic chemist, the bonds most likely to be affected by etric alkenes (C=C) and alkynes (C



Symmetric

Pseudosymmetric

- Stronger the bond, higher the vibrational frequency
- Higher the masses of atoms, lower the vibrational frequency

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

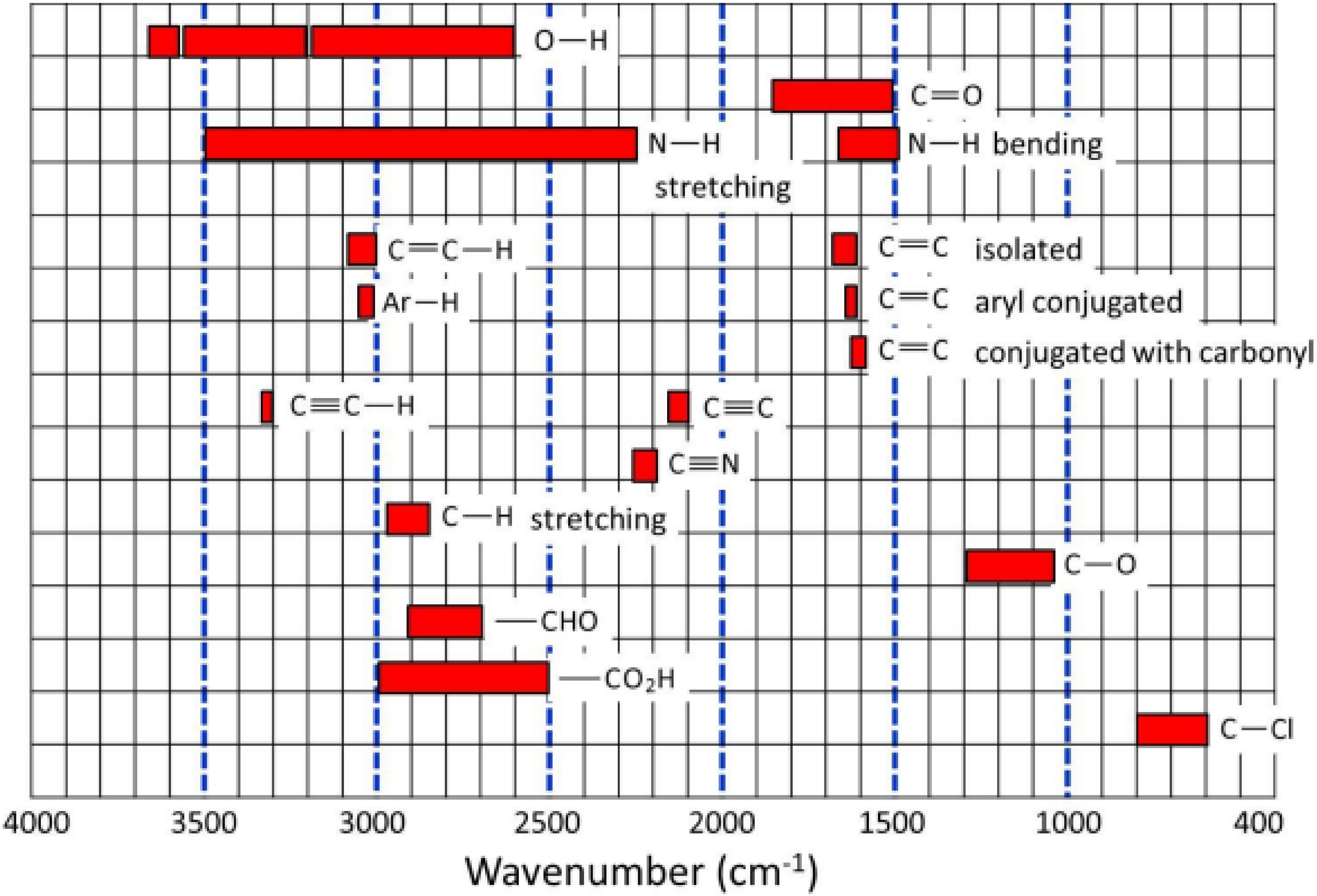
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

	C≡C	C=C	C−C
$\nu_{C\text{-}C}$	2150	1650	1200 cm^{-1}

	C≡C−H	C=C−H	C−C−H
$\nu_{C\text{-}H}$	3300	3100	2900 cm^{-1}

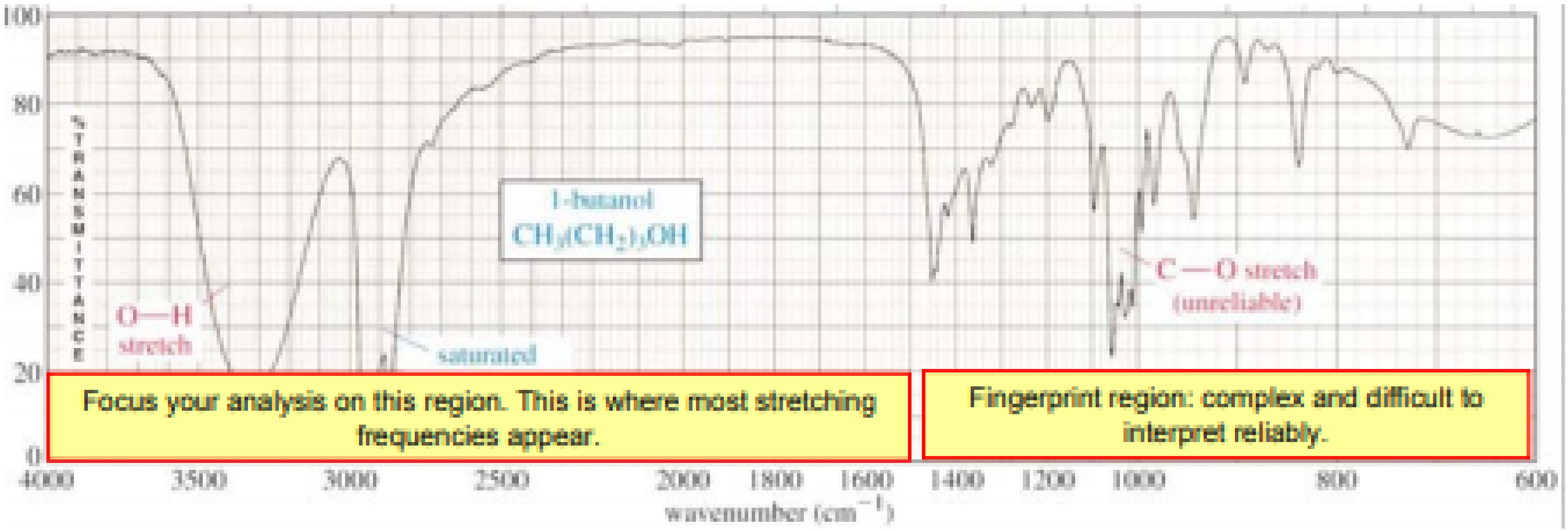
	C−H	C−C	C−O	C−Cl	C−Br	C−I
$\nu_{C\text{-}X}$	3000	1200	1100	750	600	500 cm^{-1}

Stretching frequency range of different functional Group



THE FINGERPRINT REGION

Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum. As a student, you should focus your analysis on the rest of the spectrum, that is the region to the left of 1400 cm^{-1}.

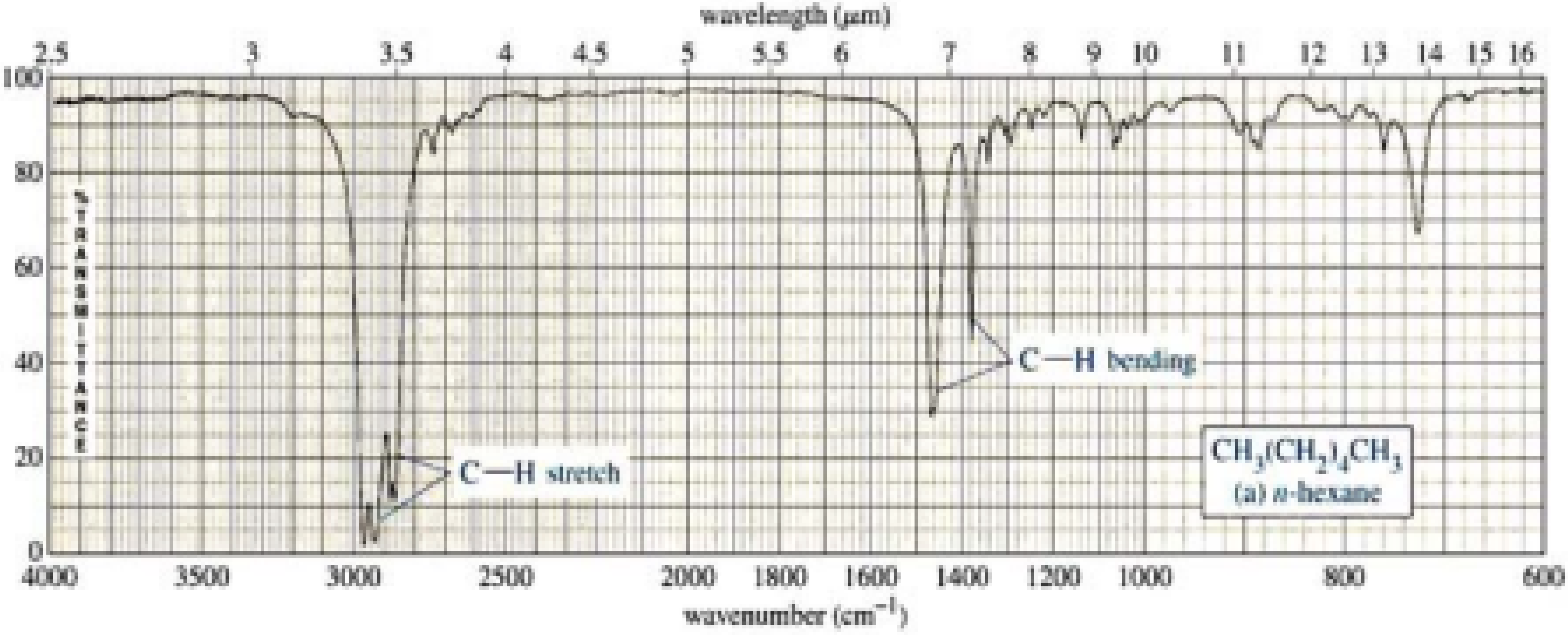


Focus your analysis on this region. This is where most stretching frequencies appear.

Fingerprint region: complex and difficult to interpret reliably.

IR SPECTRUM OF ALKANES

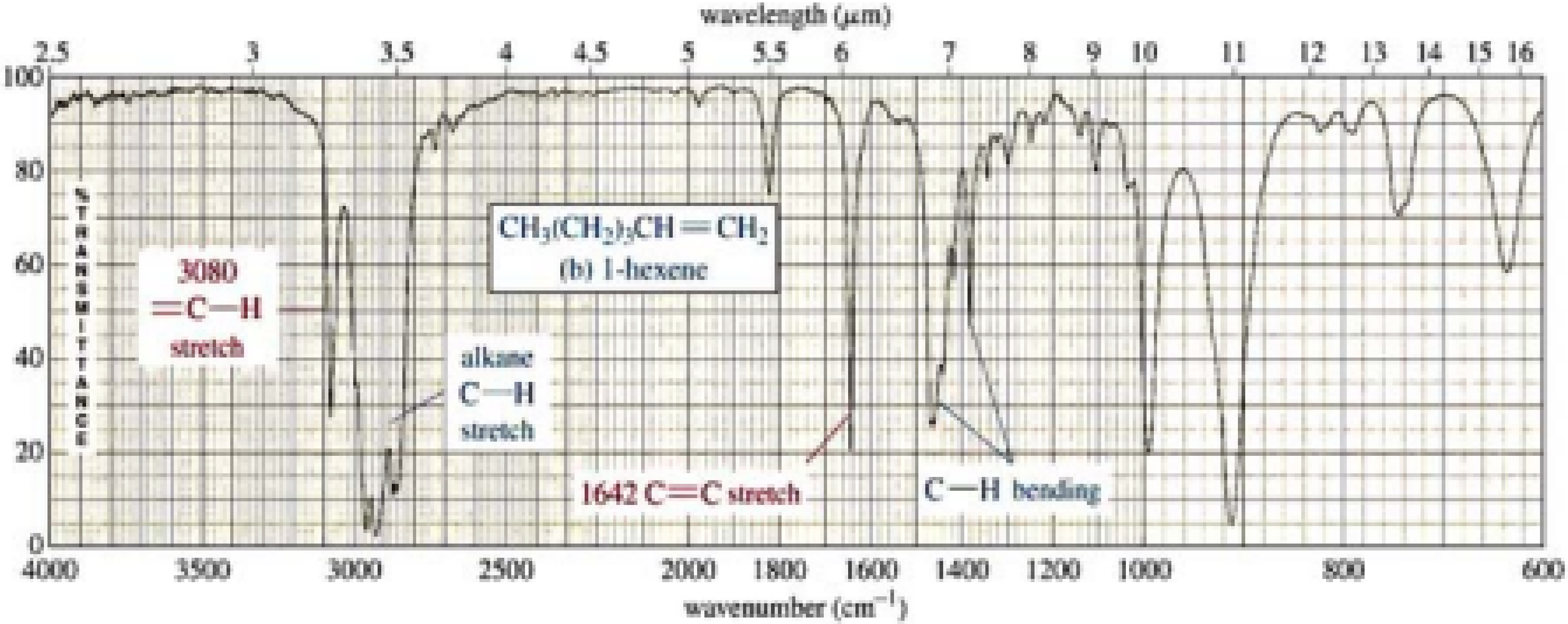
Alkanes have no functional groups. Their IR spectrum displays only C-C and C-H bond vibrations. Of these the most useful are the **C-H bands**, which appear around **3000 cm^{-1}**. Since most organic molecules have such bonds, most organic molecules will display those bands in their spectrum.



- **The spectra of simple alkanes are characterized by absorptions due to C–H stretching and bending**
- C–H stretch from 3000–2850 cm^{-1}

IR SPECTRUM OF ALKENES

Besides the presence of C-H bonds, alkenes also show sharp, medium bands corresponding to the **C=C bond stretching vibration** at about **1600-1700 cm^{-1}**. Some alkenes might also show a band for the =C-H bond stretch, appearing around **3080 cm^{-1}** as shown below. However, this band could be obscured by the broader bands appearing around 3000 cm^{-1} (see next slide)



✓ Alkenes are compounds that have a carbon-carbon double bond, –C=C–. The stretching vibration of the C=C bond usually gives rise to a moderate band in the region 1680-1640 cm-1 .

✓ Stretching vibrations of the –C=C–H bond are of higher frequency (higher wavenumber) than those of the –C–C–H bond in alkanes.

✓ This is a very useful tool for interpreting IR spectra: Only alkenes and aromatics show a C-H stretch slightly higher than 3000 cm-1 . Compounds that do not have a C=C bond show C-H stretches only below 3000 cm-1 .

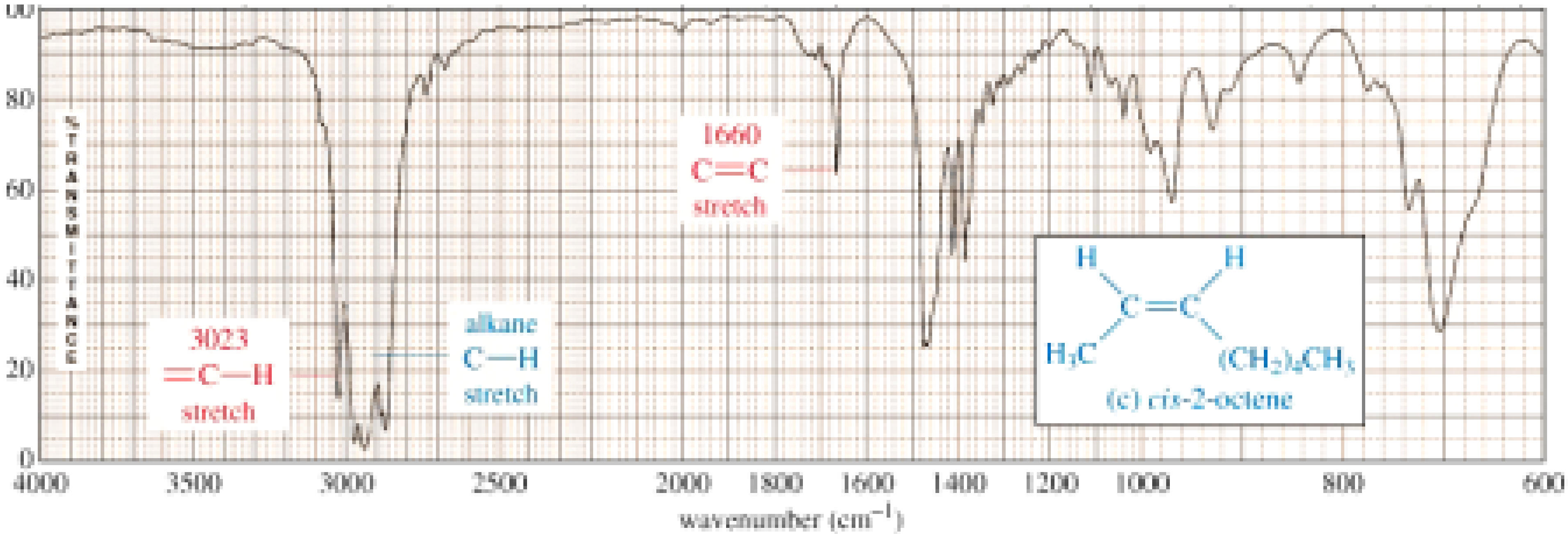
✓ The strongest bands in the spectra of alkenes are those attributed to the carbon-hydrogen bending vibrations of the =C–H group. These bands are in the region 1000-650 cm-1 (Note: this overlaps the fingerprint region).

✓ Summary:
✓C=C stretch from 1680-1640 cm-1

✓ =C–H stretch from 3100-3000 cm-1

IR SPECTRUM OF ALKENES

This spectrum shows that the band appearing around **3080 cm^{-1}** can be obscured by the broader bands appearing around 3000 cm^{-1}.



IR SPECTRUM OF ALKYNES

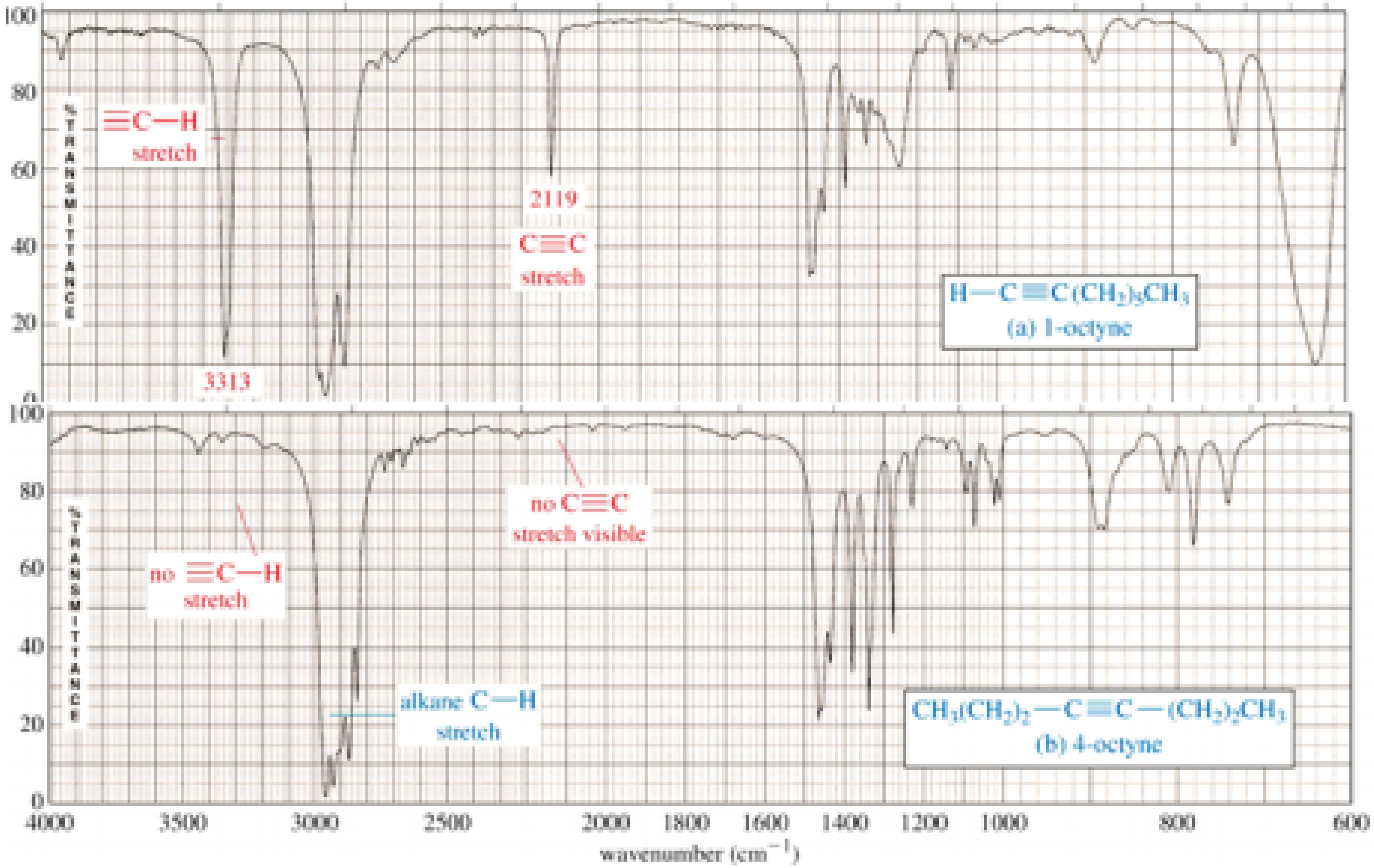
❖The most prominent band in alkynes corresponds to the **carbon-carbon triple bond**. It shows as a sharp, weak band at about **2100 cm^{-1}**. The reason it’s weak is because the triple bond is not very polar. In some cases, such as in highly symmetrical alkynes, it may not show at all due to the low polarity of the triple bond associated with those alkynes.

❖ Terminal alkynes, that is to say those where the triple bond is at the end of a carbon chain, have **C-H** bonds involving the sp carbon (the carbon that forms part of the triple bond). Therefore they may also show a sharp, weak band at about **3300 cm^{-1}** corresponding to the C-H stretch.

❖ Internal alkynes, that is those where the triple bond is in the middle of a carbon chain, do not have C-H bonds to the sp carbon and therefore lack the aforementioned band.

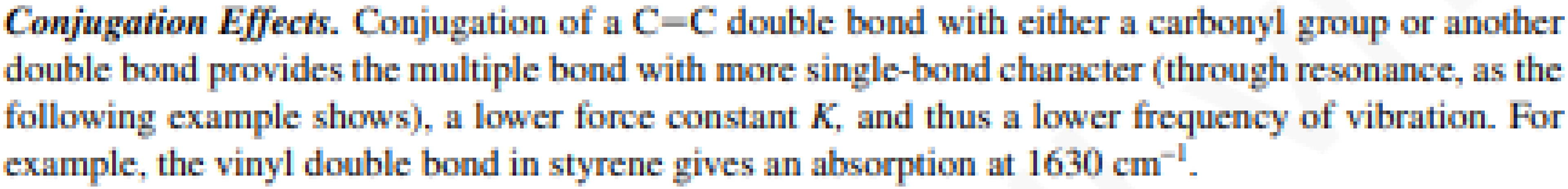
❖The following slide shows a comparison between an unsymmetrical terminal alkyne (1-octyne) and a symmetrical internal alkyne (4-

IR SPECTRUM OF ALKYNES

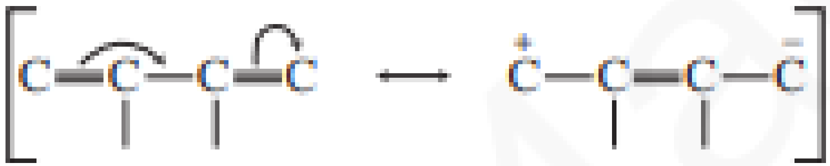


Discussion Section

- **Conjugation effect:**

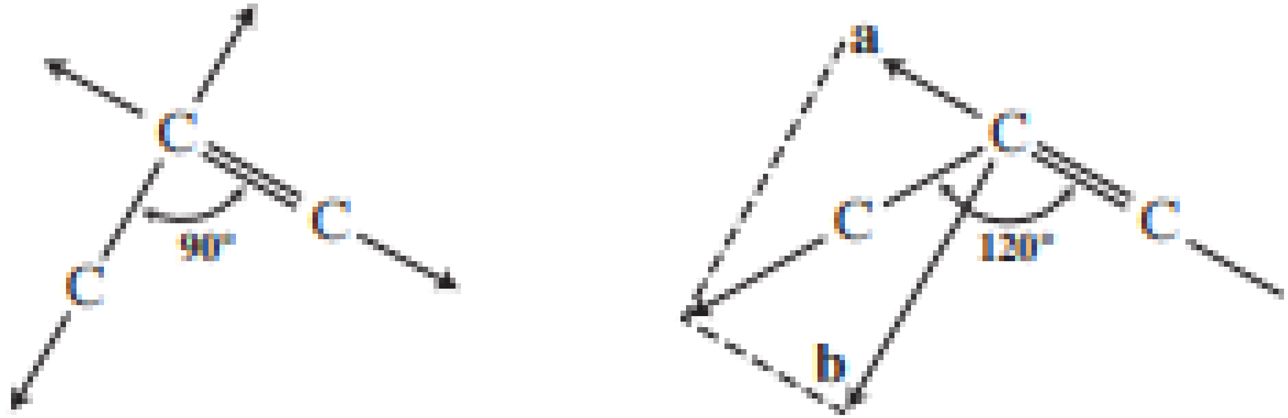


Conjugation Effects. Conjugation of a C=C double bond with either a carbonyl group or another double bond provides the multiple bond with more single-bond character (through resonance, as the following example shows), a lower force constant *K*, and thus a lower frequency of vibration. For example, the vinyl double bond in styrene gives an absorption at 1630 cm^{-1}.



- **Ring Size Effect with internal double Bond:** The absorption frequency of internal (endo) double bonds in cyclic compounds is very sensitive to ring size. As shown in Figure, the absorption frequency decreases as the internal angle decreases, until it reaches a minimum at 90° in cyclobutene. The frequency increases again for cyclopropene when the angle drops to 60°. This initially unexpected increase in frequency occurs because the C=C vibration in cyclopropene is strongly coupled to the attached C-C single-bond vibration.

When the attached C-C bonds are perpendicular to the C=C axis, as in cyclobutene, their vibrational mode is orthogonal to that of the C=C bond (i.e., on a different axis) and does not couple. When the angle is greater than 90° (120° in the following example), the C-C single-bond stretching vibration can be resolved into two components, one of which is coincident with the direction of the C=C stretch. In the diagram, components **a** and **b** of the C-C stretching vector are shown. Since component **a** is in line with the C-C stretching vector, the C-C and C=C bonds are coupled, leading to a higher frequency of absorption. A similar pattern exists for cyclopropene, which has an angle less than 90^0

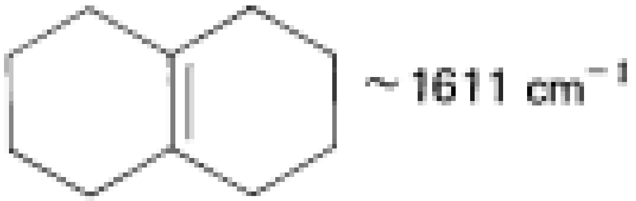


Endo double bonds

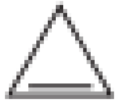
(a) Strain moves the peak to the right.
Anomaly: Cyclopropene

(b) If an endo double bond is at a ring fusion, the absorption moves to the right an amount equivalent to the change that would occur if one carbon were removed from the ring.

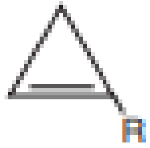
e.g.:



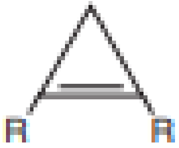
The effect of alkyl substitution on the frequency of a C=C bond in a ring.



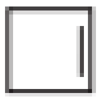
1656 cm^{-1}



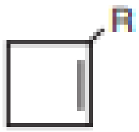
1788 cm^{-1}



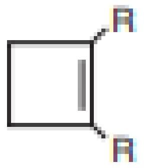
1883 cm^{-1}



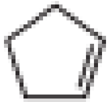
1566 cm^{-1}



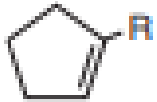
1641 cm^{-1}



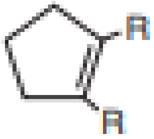
1675 cm^{-1}



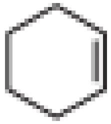
1611 cm^{-1}



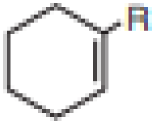
1650 cm^{-1}



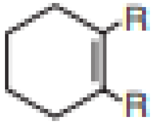
1679 cm^{-1}



1646 cm^{-1}



1675 cm^{-1}



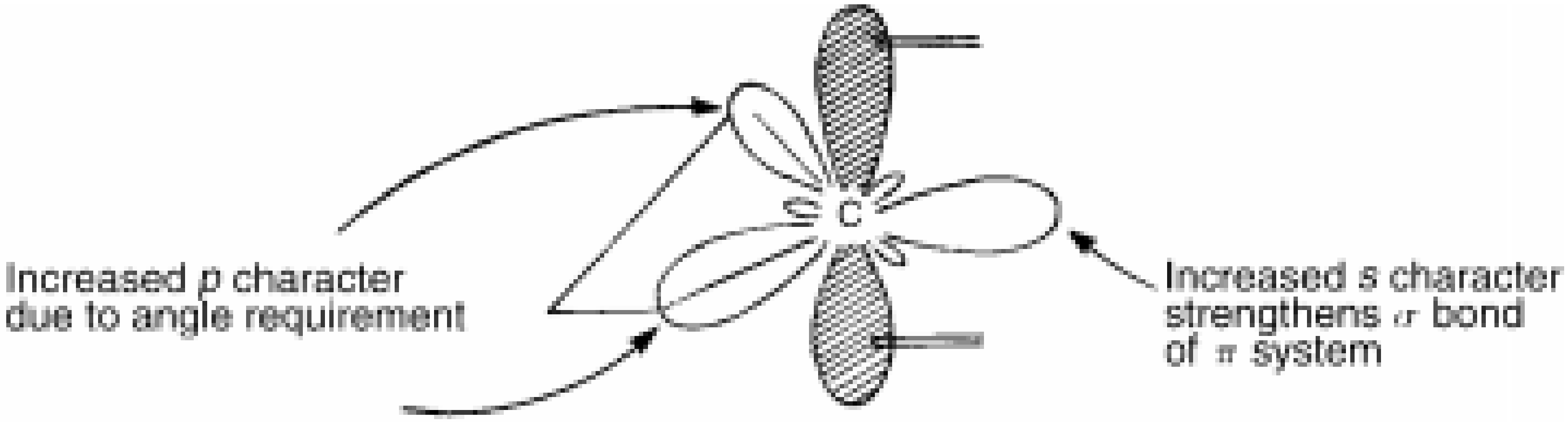
1681 cm^{-1}

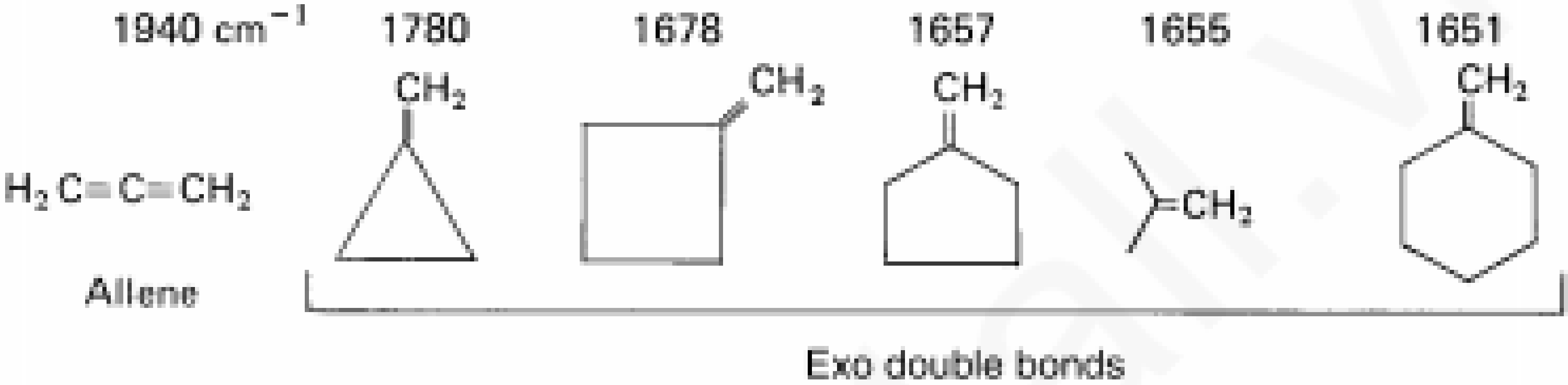
Significant increases in the frequency of the absorption of a double bond contained in a ring are absorved when one or two alkyl groups are attached directly to the double bond. The increases are most dramatic for small rings, especially cyclopropane. Base value of 1656 cm^{-1} for cyclopropane increase to 1788 cm^{-1} for mono-substituted to 1883 cm^{-1} for di-alkyl substitution

Ring Size Effect with external Double Bond

Ring size effect with External Double Bond: External (exo) double bonds give an increase in absorption frequency with decreasing ring size, as shown in Figure. Allene is included in the figure because it is an extreme example of an exo double-bond absorption. Smaller rings require the use of more p character to make the C-C bonds form the requisite small angles (recall the trend: sp = 180°, sp^2 = 120°, sp^3 = 109°, $sp^{>3}$ = $<109^0$). This removes p character from the sigma bond of the double bond but gives more s character, thus strengthening and stiffening the double bond. The force constant K is then increased, and the absorption frequency increases.

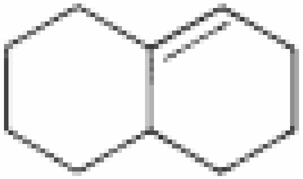
Ring Size Effect with external Double Bond





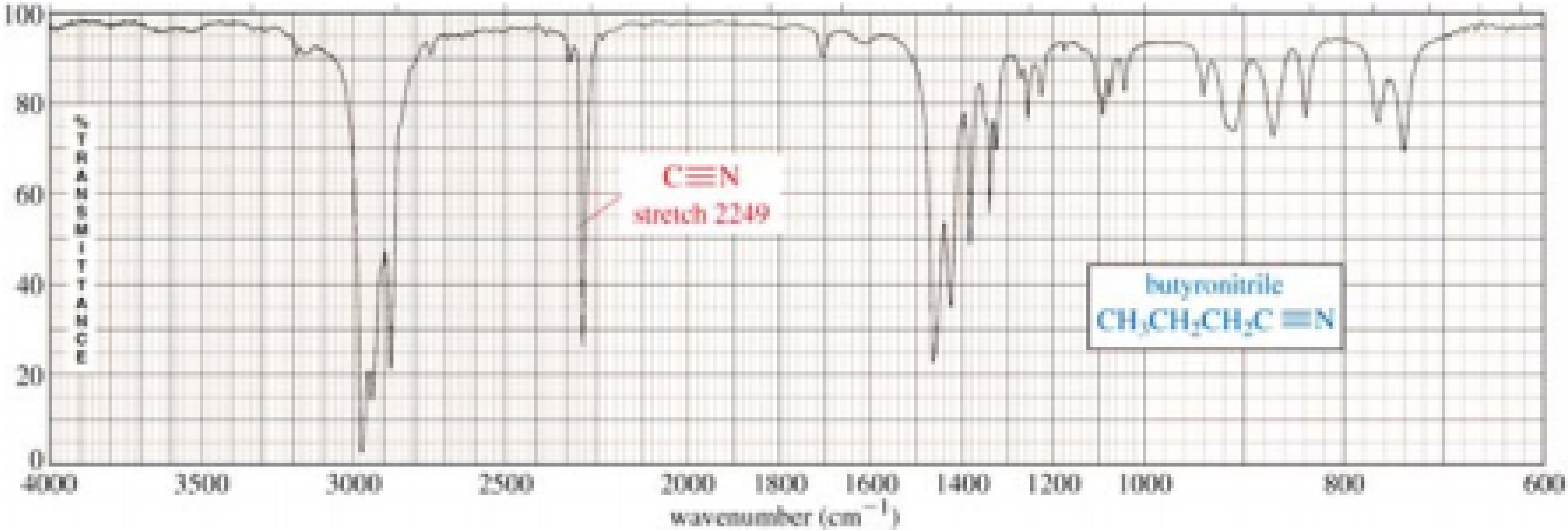
(a) Strain moves the peak to the left.

(b) Ring fusion moves the absorption to the left.



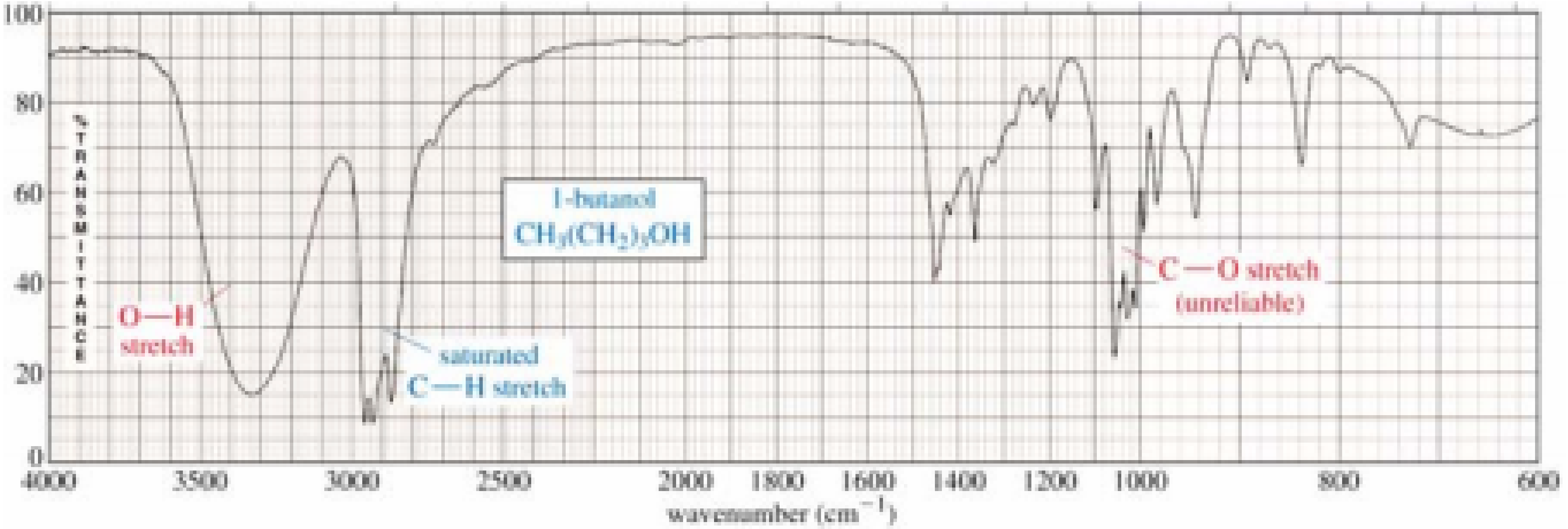
IR SPECTRUM OF A NITRILE

In a manner very similar to alkynes, nitriles show a prominent band around **2250 cm^{-1}** caused by the **CN triple bond**. This band has a sharp, pointed shape just like the alkyne C-C triple bond, but because the CN triple bond is more polar, this band is stronger than in alkynes.



IR SPECTRUM OF AN ALCOHOL

The most prominent band in alcohols is due to the **O-H bond**, and it appears as a strong, broad band covering the range of about **3000 - 3700 cm^{-1}**. The sheer size and broad shape of the band dominate the IR spectrum and make it hard to miss.



IR SPECTRUM OF ALDEHYDES AND KETONES

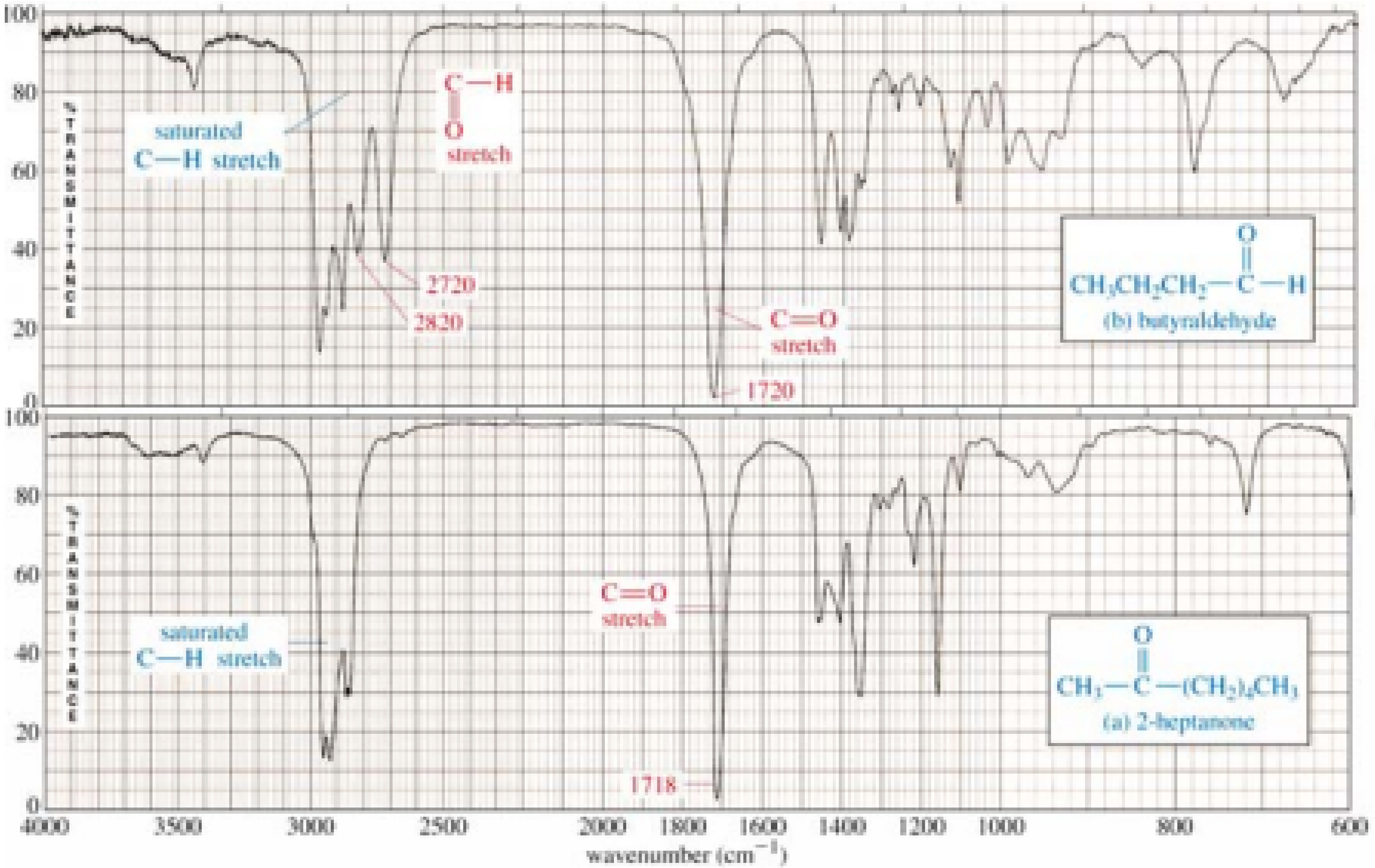
- Carbonyl compounds are those that contain the **C=O functional group**. In aldehydes, this group is at the end of a carbon chain, whereas in ketones it's in the middle of the chain. As a result, the carbon in the C=O bond of aldehydes is also bonded to another carbon and a hydrogen, whereas the same carbon in a ketone is bonded to two other carbons.

- Aldehydes and ketones show a strong, prominent, stake-shaped band around **1710 - 1720 cm^{-1}** (right in the middle of the spectrum). This band is due to the highly **polar C=O bond**. Because of its position, shape, and size, it is hard to miss.

- Because **aldehydes also contain a C-H bond** to the sp2 carbon of the C=O bond, they also show a pair of medium strength bands positioned about **2700 and 2800 cm^{-1}**. These bands are missing in the spectrum of a ketone because the sp2 carbon of the ketone lacks the C-H bond.

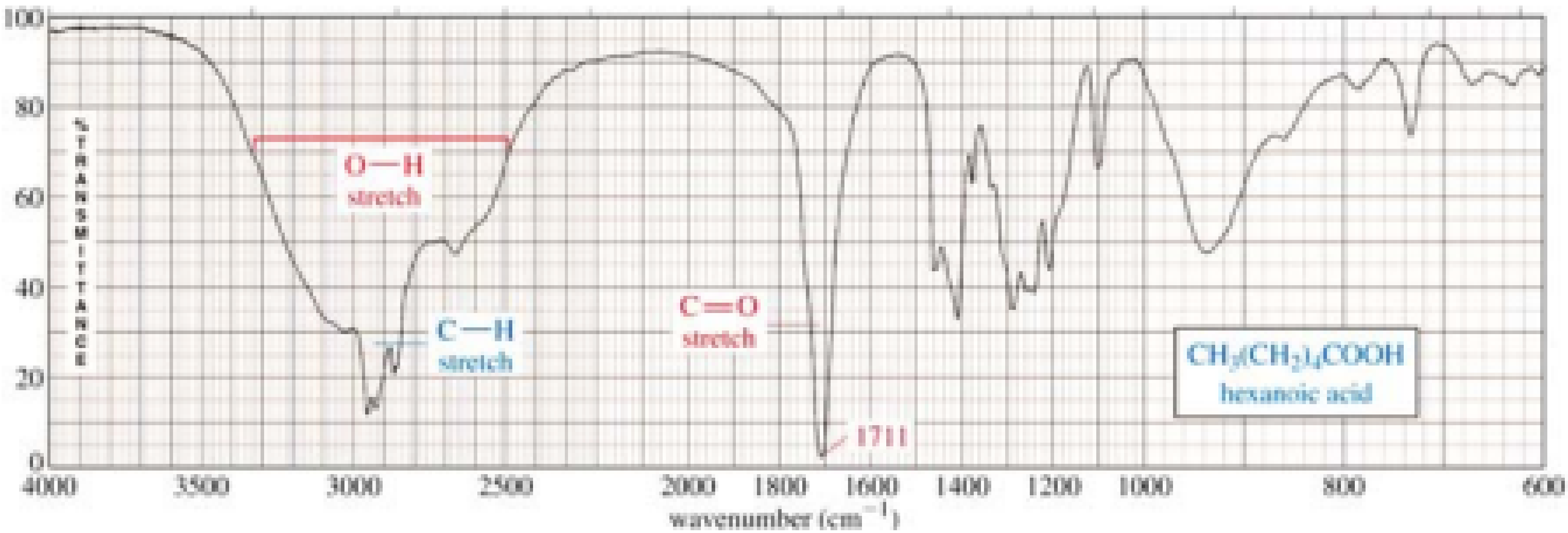
- The following slide shows a spectrum of an aldehyde and a ketone. Study the similarities and the differences so that you can distinguish between the two.

IR SPECTRUM OF ALDEHYDES AND KETONES



IR SPECTRUM OF A CARBOXYLIC ACID

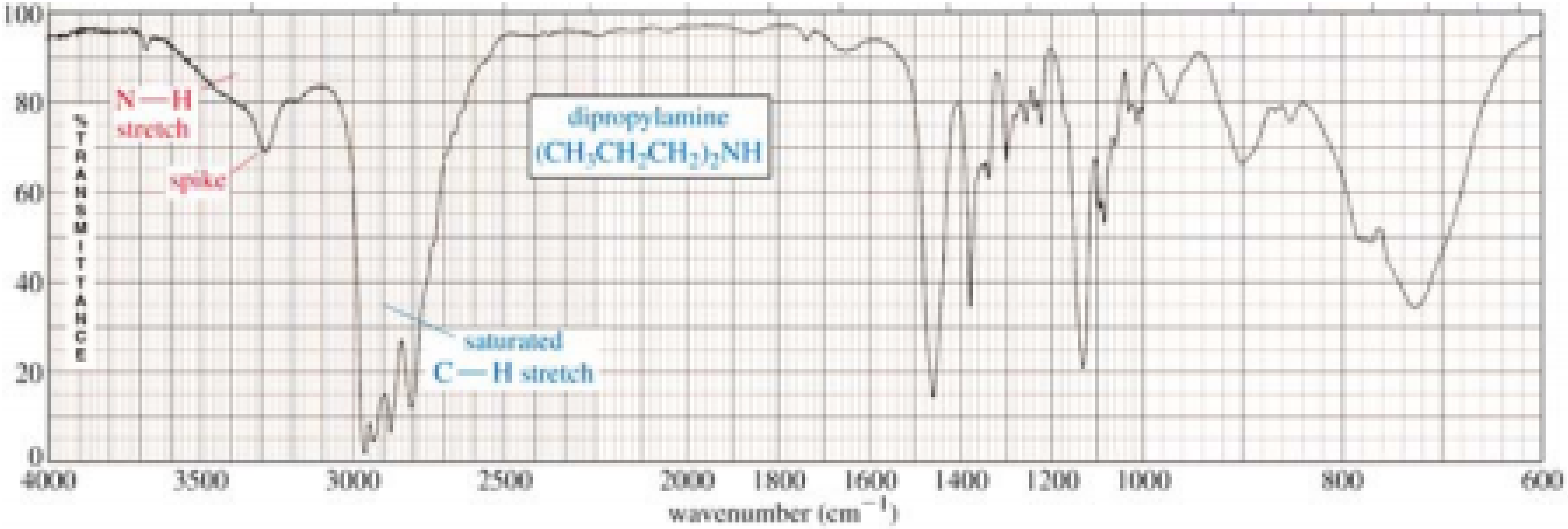
A carboxylic acid functional group combines the features of alcohols and ketones because it has both the **O-H bond** and the **C=O bond**. Therefore carboxylic acids show a very strong and broad band covering a wide range between **2800** and **3500 cm^{-1}** for the O-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** corresponding to the C=O stretch.



IR SPECTRA OF AMINES

The most characteristic band in amines is due to the **N-H bond stretch**, and it appears as a weak to medium, somewhat broad band (but not as broad as the O-H band of alcohols). This band is positioned at the left end of the spectrum, in the range of about **3200 - 3600 cm^{-1}**.

Primary amines have two N-H bonds, therefore they typically show two spikes that make this band resemble a molar tooth. Secondary amines have only one N-H bond, which makes them show only one spike, resembling a canine tooth. Finally, tertiary amines have no N-H bonds, and therefore this band is absent from the IR spectrum altogether. The spectrum below shows a secondary amine.



IR SPECTRUM OF AMIDES

The amide functional group combines the features of amines and ketones because it has both the **N-H bond** and the **C=O bond**. Therefore amides show a very strong, somewhat broad band at the left end of the spectrum, in the range between **3100** and **3500 cm^{-1}** for the N-H stretch. At the same time they also show the stake-shaped band in the middle of the spectrum around **1710 cm^{-1}** for the C=O stretch. As with amines, primary amides show two spikes, whereas secondary amides show only one spike.