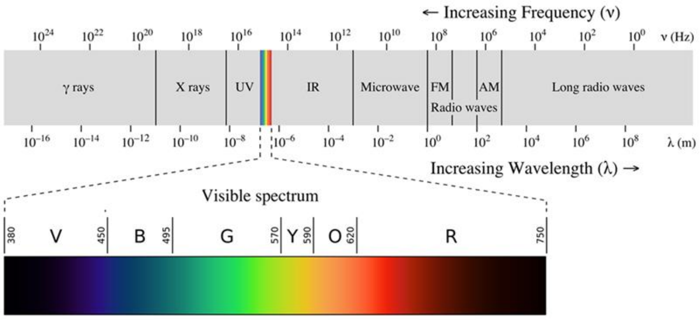
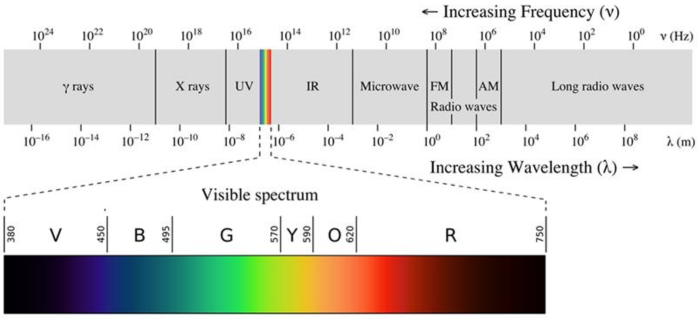
Infrared Spectroscopy



Introduction to Infrared Spectroscopy

- What is infrared spectroscopy?
- Theory of IR
- Instrumentation
- Applications & Exercises

What is Infrared?



- The Infrared region is divided into: near, mid and far-infrared.
- The primary source of infrared radiation is thermal radiation. (heat)
- It is the radiation produced by the motion of atoms and molecules in an object. The higher the temperature, the more the atoms and molecules move and the more infrared radiation they produce.

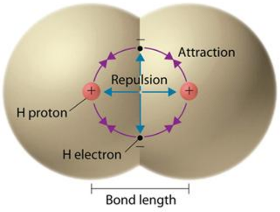
Infrared region

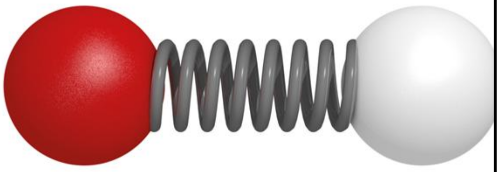
Frequency $\omega = \frac{c}{\lambda}$ Wavenumber $\varpi = \frac{1}{\lambda}$

NEAR INFRARED:	0.8 -2.5 μm,	12500 - 4000 cm^{-1}
MID INFRARED:	2.5 - 25 μm,	4000 - 400 cm^{-1}
FAR INFRARED:	25 - 1000 μm,	400 - 10 cm^{-1}

Divisions arise because of different optical materials and instrumentation.

Vibrating diatomic molecule





$$F = -k\,(R - R_e)$$

$$\omega = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

$$\varpi = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2}$$

F – restoring force
k – force constant
R – internuclear distance
R_e – equilibrium distance
μ – effective mass

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

Simple harmonic oscillator

Energy $V = \frac{1}{2} k x^2$ $\quad \mathrm{x} = \mathrm{R} - \mathrm{R_e}$

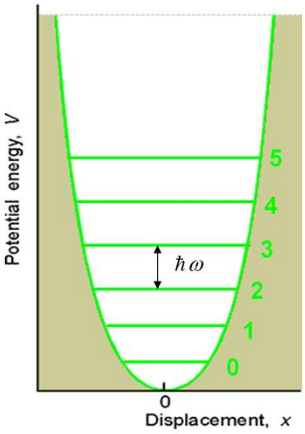
$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 = E\psi$$

Permitted energy levels of the harmonic oscillator $E_\nu = \left(\nu + \frac{1}{2}\right)\hbar\,\omega$

ν - Vibrational quantum number

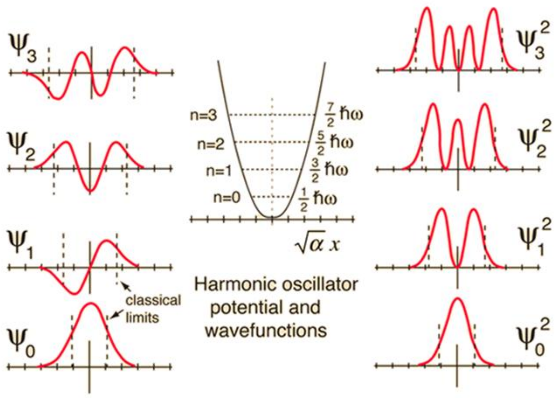
$$G_\nu = \left(\nu + \frac{1}{2}\right)\varpi$$

Zero-point energy $E_0 = \frac{1}{2}\hbar\,\omega$



Simple harmonic oscillator

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2}+\frac{1}{2}k\,x^2=E\psi$$



Harmonic oscillator potential and wavefunctions

Simple harmonic oscillator

Selection rule for the harmonic oscillator undergoing vibrational changes

$$\Delta \nu = \pm 1$$

Applying the selection rule:

$$\Delta G_{\nu} = G_{\nu+1} - G_{\nu} = \left(\nu + 1 + \frac{1}{2}\right)\varpi - \left(\nu + \frac{1}{2}\right)\varpi = \varpi$$

The vibrating molecule will absorb energy only from radiation which it can coherently interact and this must be radiation of its own oscillation frequency

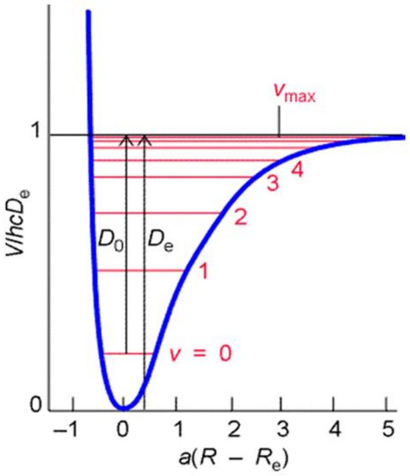
Anharmonic oscillator

- Bond – not a perfect Elastic nature
- Does not obey exactly simple harmonic motion
- Dissociates
- Not a ideal parabola

$$V = hcD_e\{1 - e^{-ax}\}^2$$

$$a = \left(\frac{\mu\omega^2}{2hcD_e}\right)^{1/2}$$

D_e – Dissociation energy

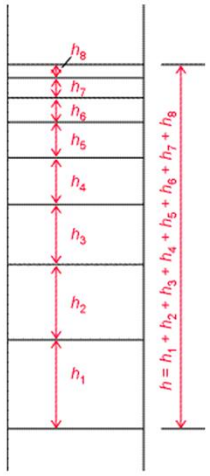


Anharmonic oscillator

Allowed vibrational energy levels:

$$G_\nu = \left(\nu + \frac{1}{2}\right) \varpi - \left(\nu + \frac{1}{2}\right)^2 x_e \varpi$$

$$x_e = \frac{a^2 \hbar}{2\mu\omega} = \frac{\varpi}{4D_e}$$ Anharmonicity constant

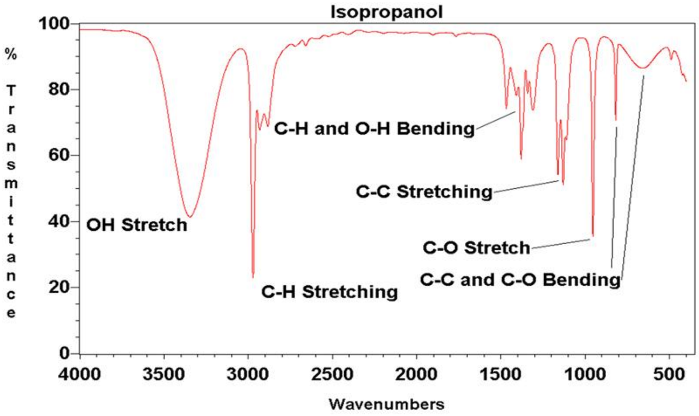


Selection rule: $\Delta\nu = \pm1, \pm2, \pm3\ldots$

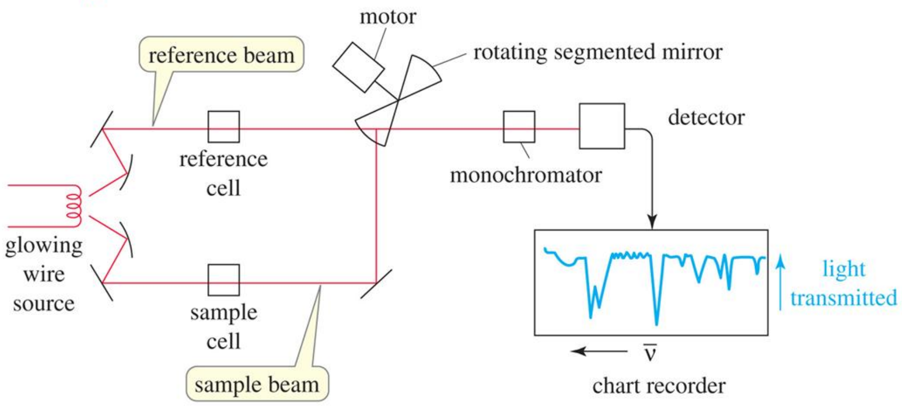
Overtone

Lower intensities
Around double ϖ

IR spectra


Isopropanol
% Transmittance
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
OH Stretch
C-H Stretching
C-H and O-H Bending
C-C Stretching
C-O Stretch
C-C and C-O Bending

IR spectrometer



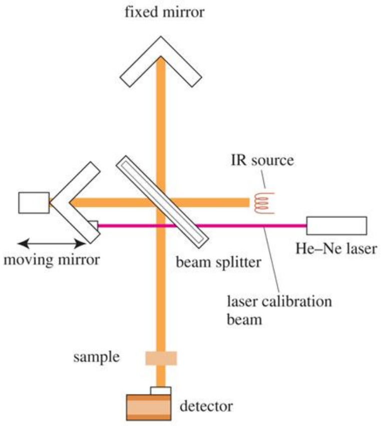
<u>Detectors</u>:

- Pyroelectric detectors (DTGS)
- Semiconductor detectors (MCT)

FT-IR spectrometer

- Has better sensitivity.
- Less energy is needed from source.
- Completes a scan in 1 to 2 seconds.
- Takes several scans and averages them.
- Has a laser beam that keeps the instrument accurately calibrated.

Michelson interferometer



Beam splitter: KBr crystal covered by Ge

FT-IR spectrometer

When the 2 beams recombine:

Optical Path Difference $\delta = 2x$

Constructive interference $\delta = n\lambda$

Destructive interference $\delta = (n + 1/2)\lambda$

Interferogram

For a monochromatic radiation:

$$I(\delta) = B(\omega_0)\cos(2\pi\delta\omega_0)$$

For a polychromatic radiation:

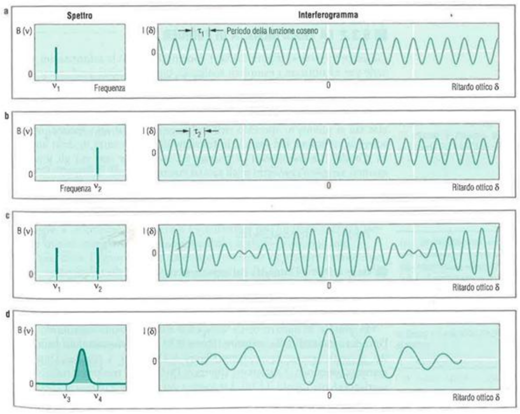
$$I(\delta) = \int_0^\infty B(\omega_i)\cos(2\pi\delta\omega_i)d\omega$$

FT-IR spectrometer

Spectrum

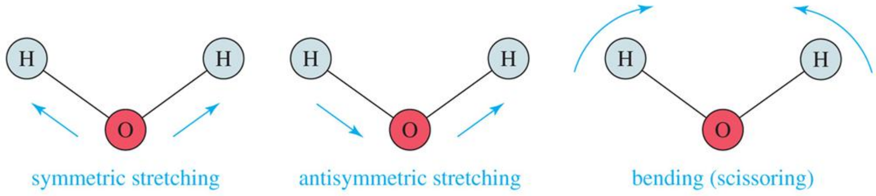
Applying a Fourier Transform (FT):

$$B(\omega) = \int_{-\infty}^{\infty} I(\delta)\cos(2\pi\delta\omega)d\delta$$



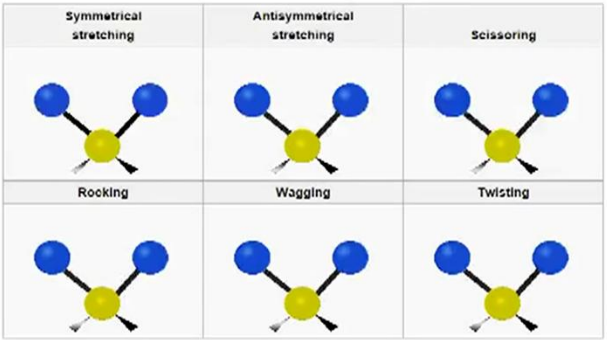
Infrared Spectroscopy

The bonds between atoms in the molecule stretch and bend, absorbing infrared energy and creating the infrared spectrum.

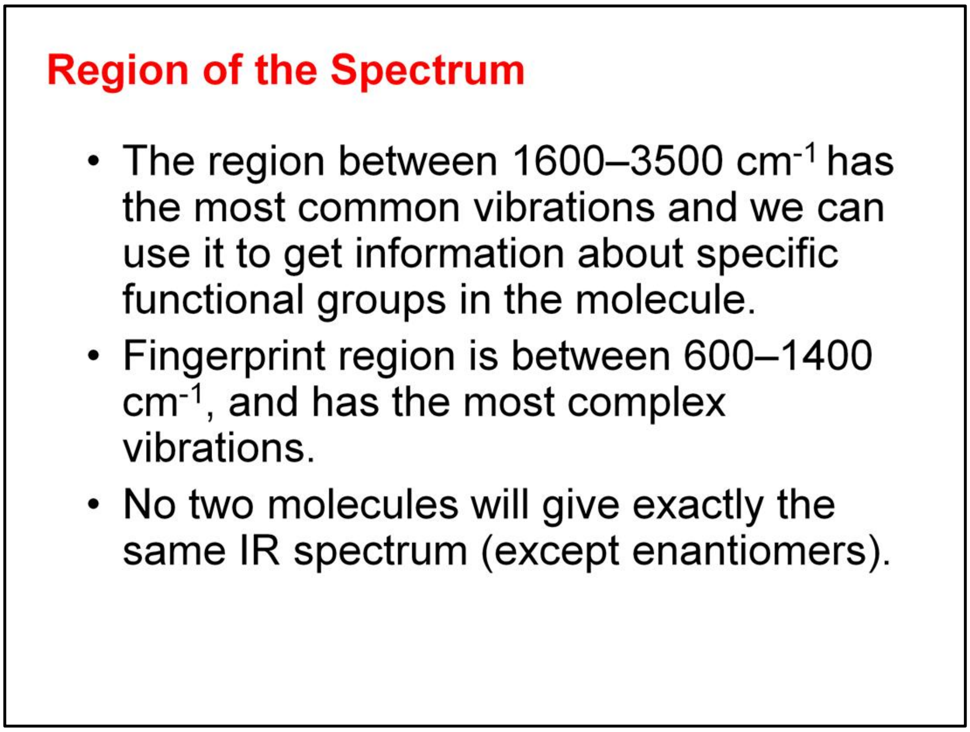


- A nonlinear molecule with *n* atoms has 3*n* - 6 fundamental vibrational modes.
- Water has 3(3) - 6 = 3 modes. Two of these are stretching modes, and one is a bending mode (scissoring).

Molecular vibrations



Intensities of absorption bands are proportional to the change of dipole magnitudo.



Region of the Spectrum

- The region between 1600–3500 cm^{-1} has the most common vibrations and we can use it to get information about specific functional groups in the molecule.
- Fingerprint region is between 600–1400 cm^{-1}, and has the most complex vibrations.
- No two molecules will give exactly the same IR spectrum (except enantiomers).

Stretching Frequencies

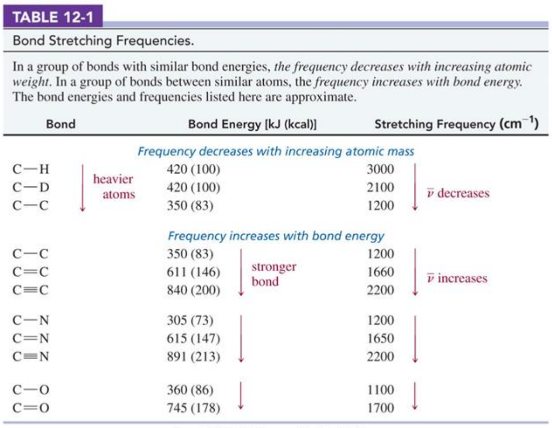


TABLE 12-1

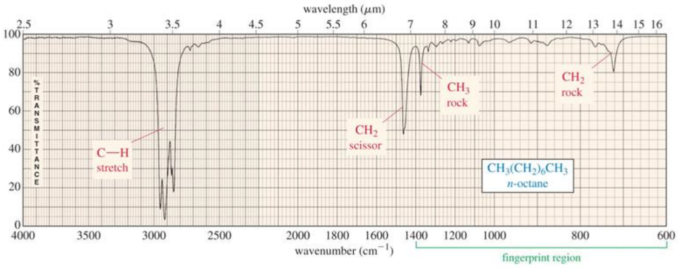
Bond Stretching Frequencies.

In a group of bonds with similar bond energies, *the frequency decreases with increasing atomic weight*. In a group of bonds between similar atoms, the *frequency increases with bond energy*. The bond energies and frequencies listed here are approximate.

Bond		Bond Energy [kJ (kcal)]		Stretching Frequency (cm^{-1})	
Frequency decreases with increasing atomic mass					
C—H	heavier atoms ↓	420 (100)		3000	↓ $\bar{\nu}$ decreases
C—D		420 (100)		2100	
C—C		350 (83)		1200	
Frequency increases with bond energy					
C—C		350 (83)	stronger bond ↓	1200	↓ $\bar{\nu}$ increases
C=C		611 (146)		1660	
C≡C		840 (200)		2200	
C—N		305 (73)	↓	1200	↓
C=N		615 (147)		1650	
C≡N		891 (213)		2200	
C—O		360 (86)	↓	1100	↓
C=O		745 (178)		1700	

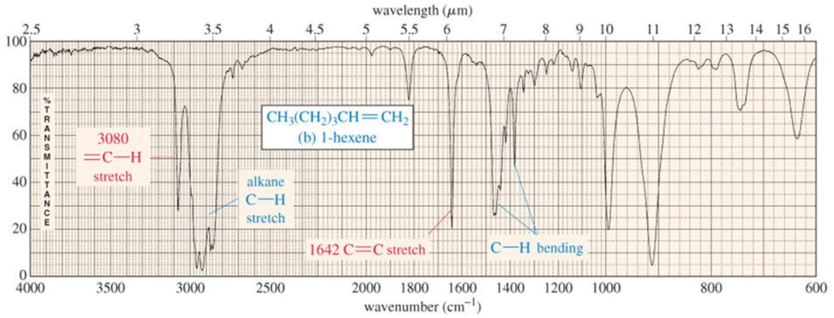
- Frequency decreases with increasing atomic mass.
- Frequency increases with increasing bond energy.

IR Spectrum of Alkanes



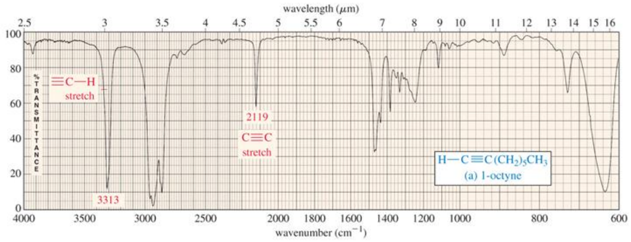
- An alkane will show stretching and bending frequencies for C—H and C—C only.
- The C—H stretching is a broad band between 2800–3000 cm^{-1}, a band present in virtually all organic compounds.
- In this example, the importance lies in what is not seen, i.e., the lack of bands indicates the presence of no other functional group.

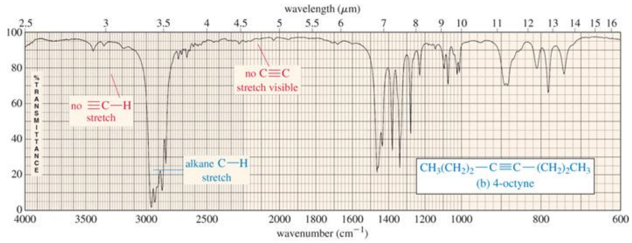
IR Spectrum of Alkenes



- The most important absorptions in the 1-hexene are the C═C stretch at 1642 cm^{-1}, and the unsaturated stretch at 3080 cm^{-1}.
- Notice that the bands of the alkane are present in the alkene.

IR Spectrum of Alkynes

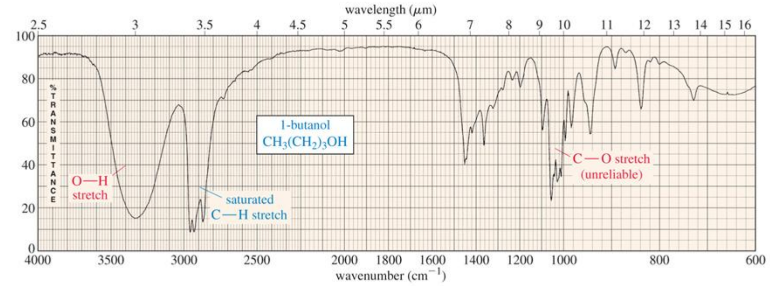




O-H and N-H Stretching

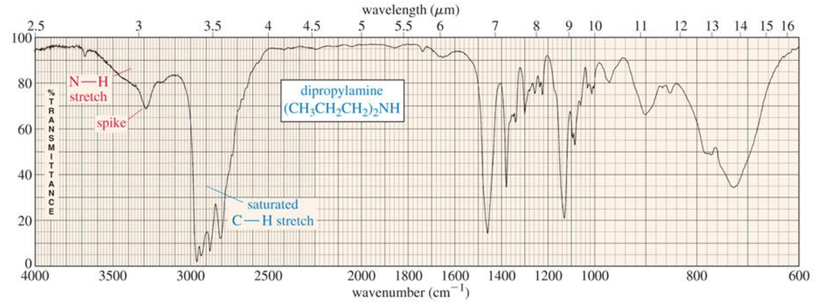
- Both of these occur around 3300 cm^{-1}, but they look different:
  - Alcohol O—H is broad with rounded tip.
  - Secondary amine (R_2NH) is broad with one sharp spike.
  - Primary amine (RNH_2) is broad with two sharp spikes.
  - No signal for a tertiary amine (R_3N) because there is no hydrogen.

IR Spectrum of Alcohols



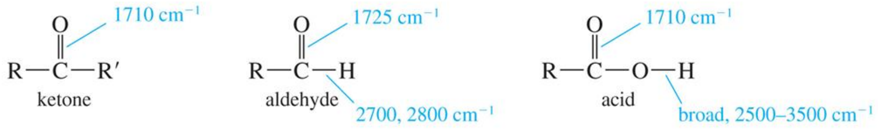
- The IR spectrum of alcohols will show a broad, intense O—H stretching absorption centered around 3300 cm^{-1}.
- The broad shape is due to the diverse nature of the hydrogen bonding interactions of alcohol molecules.

IR Spectrum of Amines



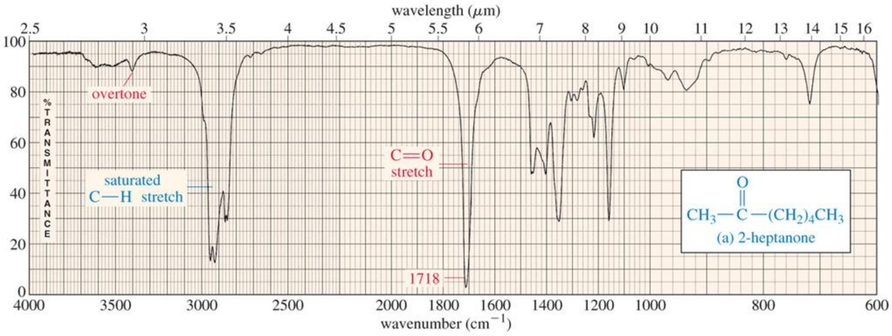
- The IR spectrum of amines show a broad N—H stretching absorption centered around 3300 cm^{-1}.
- Dipropylamine has only one hydrogen so it will have only one spike in its spectrum.

Carbonyl Stretching



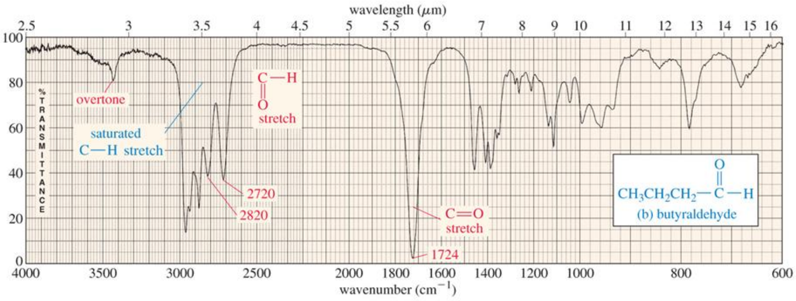
- The C═O bond of simple ketones, aldehydes, and carboxylic acids absorb around 1710 cm^{-1}.
- Usually the carbonyl is the strongest IR signal.
- Carboxylic acids will have O—H also.
- Aldehydes have two C—H signals around 2700 and 2800 cm^{-1}.

IR Spectrum of Ketones



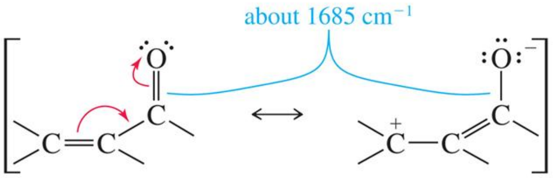
- The spectrum of 2-heptanone shows a strong, sharp absorption at 1718 cm^{-1} due to the C═O stretch.

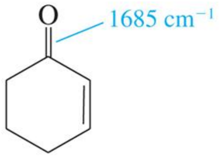
IR Spectrum of Aldehydes



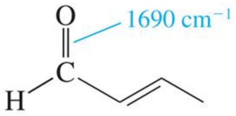
- Aldehydes have the C═O stretch at around 1710 cm^{-1}.
- They also have two different stretch bands for the aldehyde C—H bond at 2720 and 2820 cm^{-1}.

Variation in C=O Absoprtion

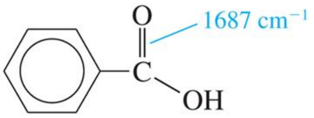




2-cyclohexenone

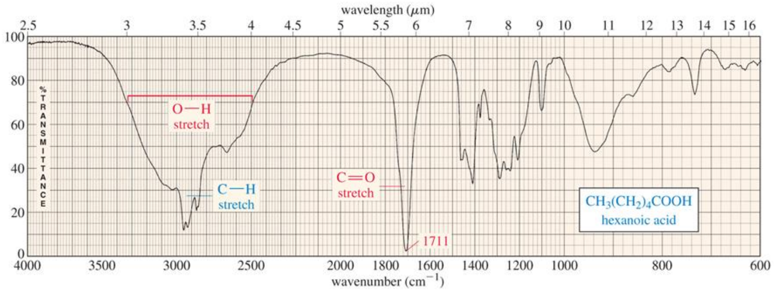


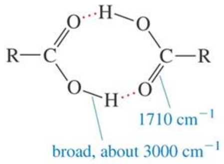
2-butenal



benzoic acid

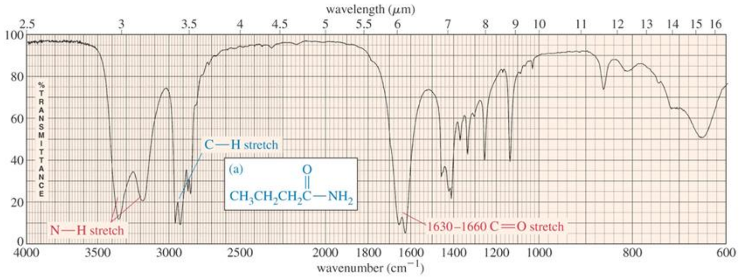
O-H Stretching in Carboxylic Acids





- This O—H absorbs broadly, 2500–3500 cm^{-1}, due to strong hydrogen bonding.
- Both peaks need to be present to identify the compound as a carboxylic acid.

IR Spectrum of Amides



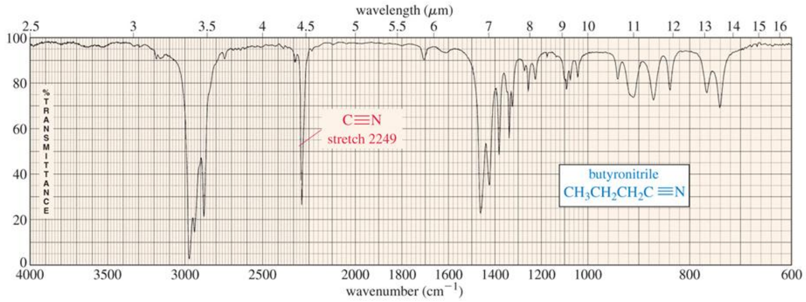
- Amides will show a strong absorption for the C═O at 1630–1660 cm^{-1}.
- If there are hydrogens attached to the nitrogen of the amide, there will N—H absorptions at around 3300 cm^{-1}.

C-N Stretching

$C-N$	1200 cm^{-1}	
$C=N$	1660 cm^{-1}	*usually strong*
$C\equiv N$	> 2200 cm^{-1}	

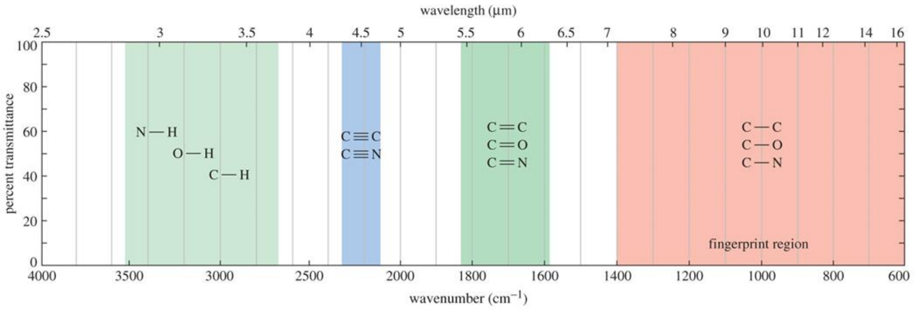
For comparison, $C\equiv C$ < 2200 cm^{-1}

IR Spectrum of Nitriles



- A carbon nitrogen triple bond has an intense and sharp absorption, centered at around 2200 to 2300 cm^{-1}.
- Nitrile bonds are more polar than carbon–carbon triple bonds, so nitriles produce stronger absorptions than alkynes.

Summary of IR Absorptions



Summary of IR Absorptions

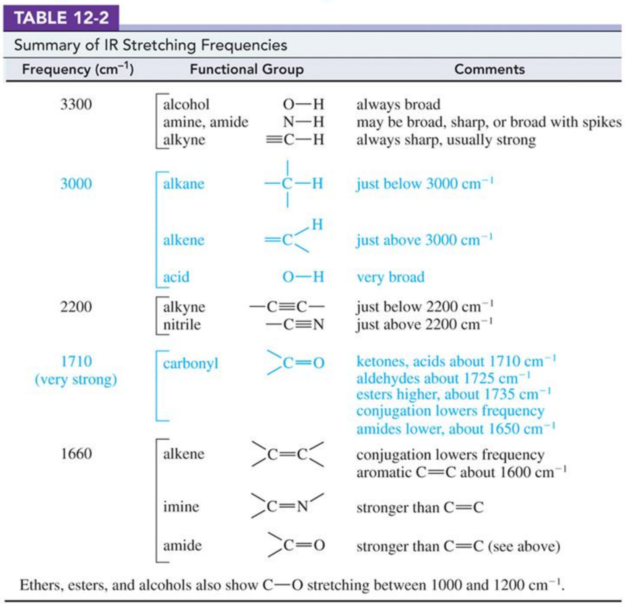


TABLE 12-2

Summary of IR Stretching Frequencies

Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	≡C—H	always sharp, usually strong
3000	alkane	—C—H	just below 3000 cm^{-1}
	alkene	=C—H	just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C≡C—	just below 2200 cm^{-1}
	nitrile	—C≡N	just above 2200 cm^{-1}
1710 (very strong)	carbonyl	C=O	ketones, acids about 1710 cm^{-1} aldehydes about 1725 cm^{-1} esters higher, about 1735 cm^{-1} conjugation lowers frequency amides lower, about 1650 cm^{-1}
1660	alkene	C=C	conjugation lowers frequency aromatic C=C about 1600 cm^{-1}
	imine	C=N	stronger than C=C
	amide	C=O	stronger than C=C (see above)

Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm^{-1}.

How to determine molecular structure

Number of insaturations:

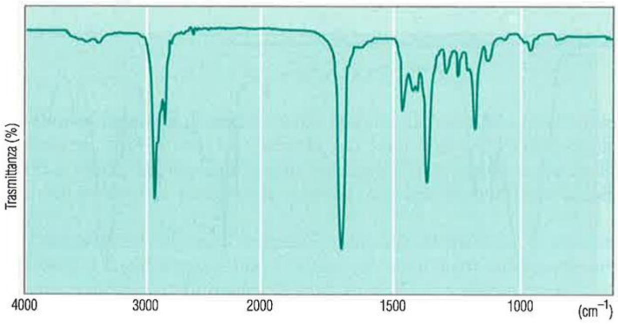
$$n_{ins}=C+\frac{N}{2}-\frac{H}{2}-\frac{X}{2}+1 \ (X=Cl, Br, I)$$

- Multiple bonds
- Cyclic structures

Example 1

$C_6H_{12}O$

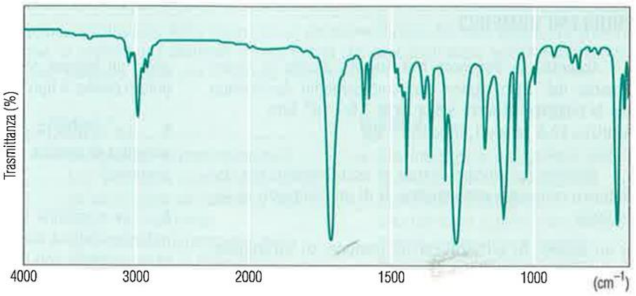
$$n_{ins} = 6 - \frac{12}{2} + 1 = 1$$



Example 2

$C_9H_{10}O_2$

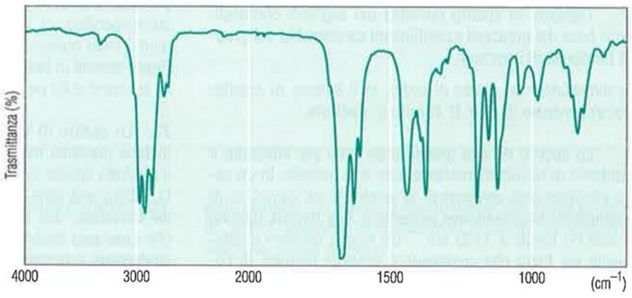
$$n_{ins} = 9 - \frac{10}{2} + 1 = 5$$



Example 3

$C_{10}H_{16}O$

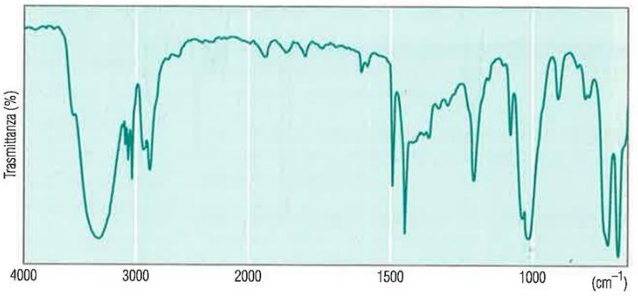
$$n_{ins} = 10 - \frac{16}{2} + 1 = 3$$



Example 4

C_7H_8O

$$n_{ins} = 7 - \frac{8}{2} + 1 = 4$$



Example 5

$C_6H_{10}O$

$$n_{ins} = 6 - \frac{10}{2} + 1 = 2$$