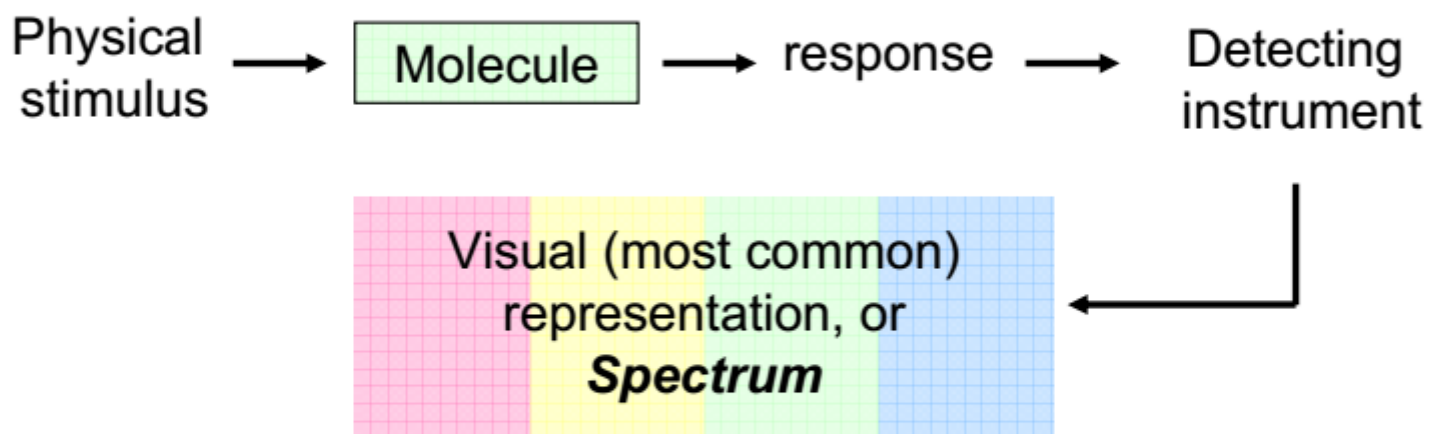# INFRARED SPECTROSCOPY
(IR)

Theory and Interpretation of
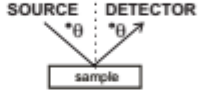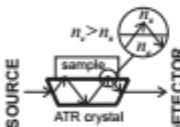IR spectra
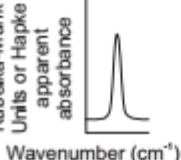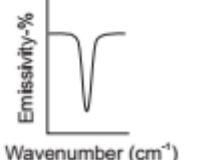
INSTRUMENTAL METHODS OF STRUCTURE DETERMINATION

1. **Nuclear Magnetic Resonance (NMR)** – Excitation of the nucleus of atoms through radiofrequency irradiation. Provides extensive information about molecular structure and atom connectivity.

2. **Infrared Spectroscopy (IR)** – Triggering molecular vibrations through irradiation with infrared light. Provides mostly information about the presence or absence of certain functional groups.

3. **Mass spectrometry** – Bombardment of the sample with electrons and detection of resulting molecular fragments. Provides information about molecular mass and atom connectivity.
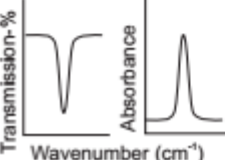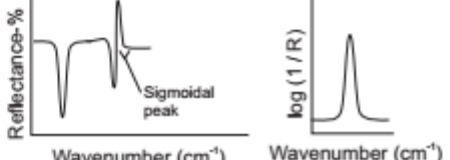
4. **Ultraviolet spectroscopy (UV)** – Promotion of electrons to higher energy levels through irradiation of the molecule with ultraviolet light. Provides mostly information about the presence of conjugated π systems and the presence of double and triple bonds.

SPECTROSCOPY - Study of spectral information

Physical stimulus → Molecule → response → Detecting instrument

Visual (most common) representation, or *Spectrum*

Upon irradiation with infrared light, certain bonds respond by vibrating faster. This response can be detected and translated into a visual representation called a spectrum.
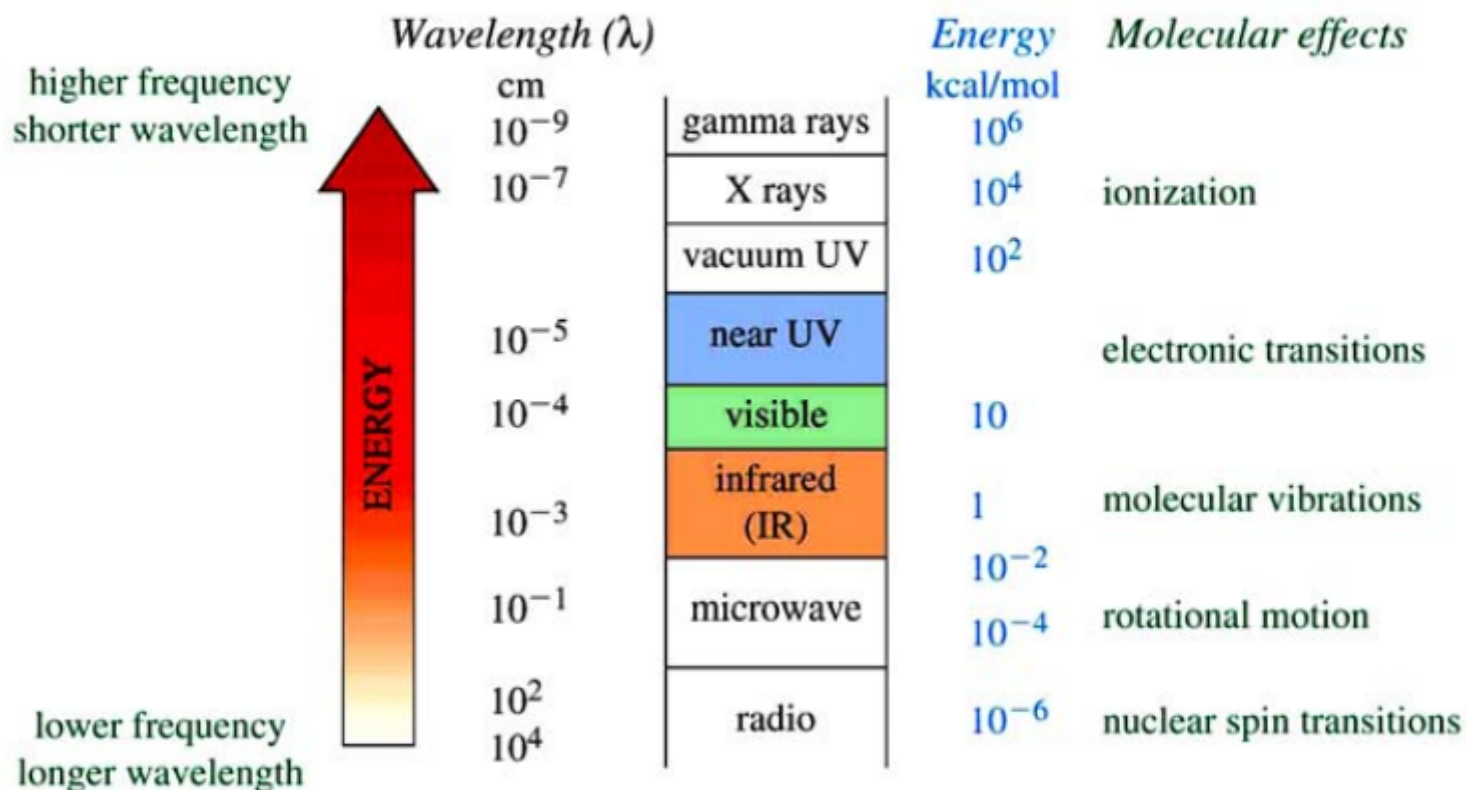
Transmission	Reflection			Emission

| | Laboratory techniques (10^{-9} - 10^{-1} g sample) | | | |

| Remote sensing atmospheres/ hydrospheres | Laboratory microscope, mapping & polarization possible | | | Handheld devices (10^{-2}-10^1 g sample) |
| | | | | Remote sensing planetary surfaces |

Typical sample geometry

| SOURCE sample DETECTOR Transmission | SOURCE DETECTOR *θ *θ sample Specular reflectance or bidirectional reflectance | $n_s>n_a$ sample ATR crystal Attenuated total reflection | sample Diffuse reflectance or biconical reflectance | DETECTOR sample SOURCE=sample > 0 °K Emission |

Sample preparation & possible experiments

| • powder, powder-carrier, low n polished wafer, films, liquids & gases • high T & P, kinetic & strain experiments | • high n polished solid, films • depth profiles possible if incident angle is varied • high T & P, kinetic & strain experiments possible | • powder, powder-carrier, films, solids, liquids • sample must not scratch/react with crystal & $n_s>n_a$ • depth profiles & strain experiments | • powder, powder-salt mix • high T & kinetic experiments | • powder, powder-salt mix |

Quantification/Analysis procedure

| Beer-Lambert law & characterize grainsize, density & thickness | Kramers-Kronig | Kramers-Kronig & characterize grainsize & density | Kubelka-Munk or Hapke & characterize grainsize, density & sample depth | Beer-Lambert law & characterize grainsize & density |

Typical spectra

| Transmission-% / Absorbance Wavenumber (cm^{-1}) | Reflectance-% Sigmoidal peak Wavenumber (cm^{-1}) | log (1 / R) Wavenumber (cm^{-1}) | Kubelka-Munk Units or Hapke apparent absorbance Wavenumber (cm^{-1}) | Emissivity-% Wavenumber (cm^{-1}) |

SPECTRUM INTERPRETATION PROCESS

1. Recognize a *pattern.*

2. Associate patterns with *physical parameters.*

3. Identify possible meanings, i.e. *propose explanations.*

Once a spectrum is obtained, the main challenge is to extract the information it contains in abstract, or hidden form. This requires the recognition of certain patterns, the association of these patterns with physical parameters, and the interpretation of these patterns in terms of meaningful and logical explanations.

EFFECT OF ELECTROMAGNETIC RADIATION ON MOLECULES

| Wavelength (λ)		Energy	Molecular effects
higher frequency shorter wavelength	**cm**	**kcal/mol**	
	10^{-9} gamma rays	10^6	
	10^{-7} X rays	10^4	ionization
	vacuum UV	10^2	
	10^{-5} near UV		electronic transitions
	10^{-4} visible	10	
	10^{-3} infrared (IR)	1	molecular vibrations
		10^{-2}	
	10^{-1} microwave	10^{-4}	rotational motion
	10^2 10^4 radio	10^{-6}	nuclear spin transitions
lower frequency longer wavelength			

ENERGY

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

equilibrium
bond length

stretched

compressed
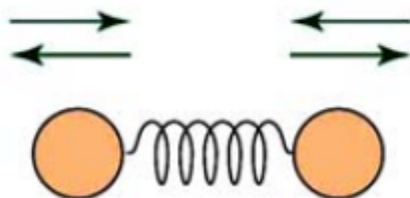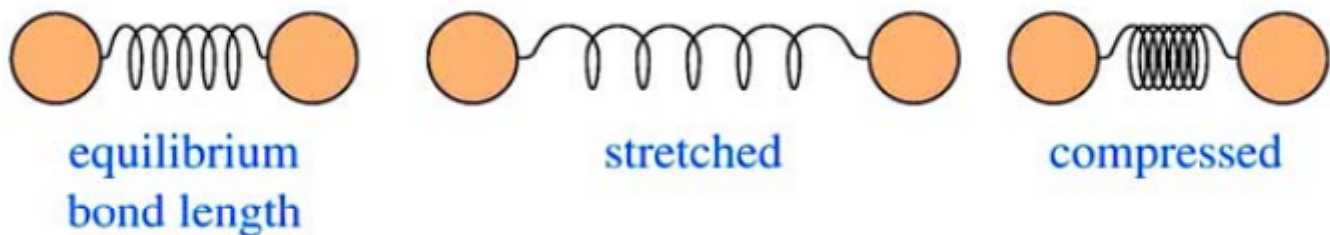
VIBRATIONAL MODES

- Covalent bonds can vibrate in several modes, including **stretching, rocking, and scissoring**.
- The most useful bands in an infrared spectrum correspond to stretching frequencies, and those will be the ones we'll focus on.

symmetric stretching   antisymmetric stretching   bending (scissoring)
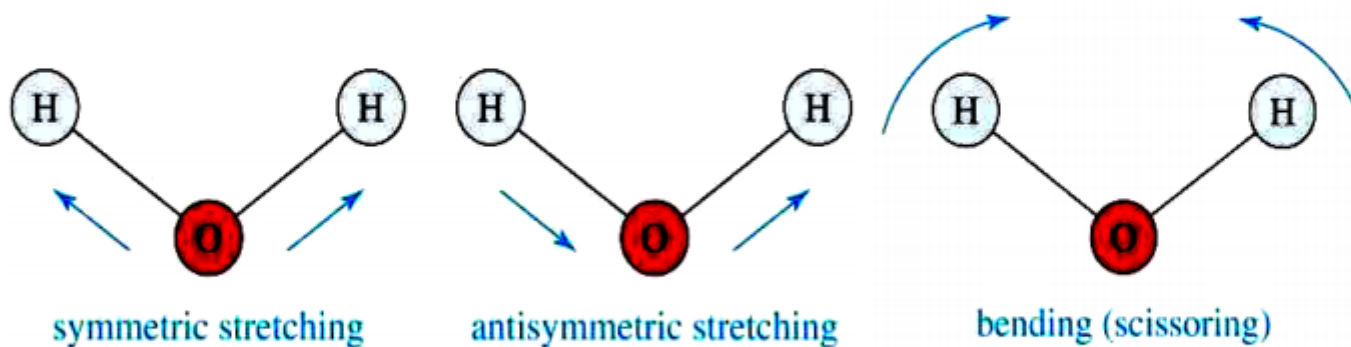
TRANSMISSION vs. ABSORPTION

When a chemical sample is exposed to the action of **IR LIGHT**, it can **absorb** some frequencies and **transmit** the rest. Some of the light can also be reflected back to the source.
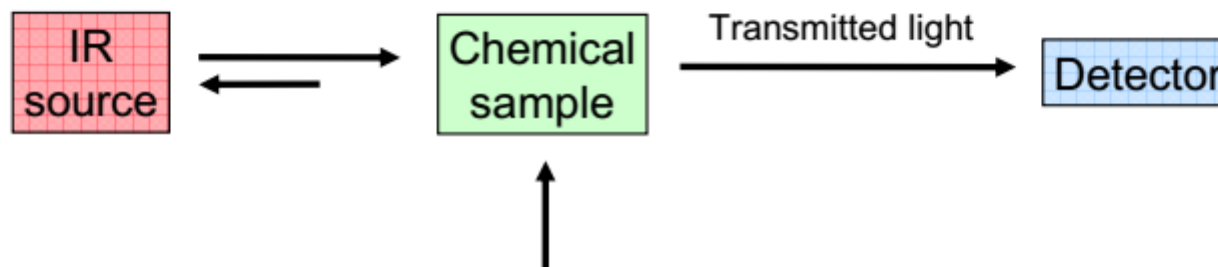

From all the frequencies it receives, the chemical sample can **absorb** (retain) **specific frequencies** and allow the rest to pass through it (transmitted light).

The detector detects the transmitted frequencies, and by doing so also reveals the values of the absorbed frequencies.

AN IR SPECTRUM IN ABSORPTION MODE

The IR spectrum is basically a plot of transmitted (or absorbed) frequencies vs. intensity of the transmission (or absorption). Frequencies appear in the *x*-axis in units of inverse centimeters (wavenumbers), and intensities are plotted on the *y*-axis in percentage units.
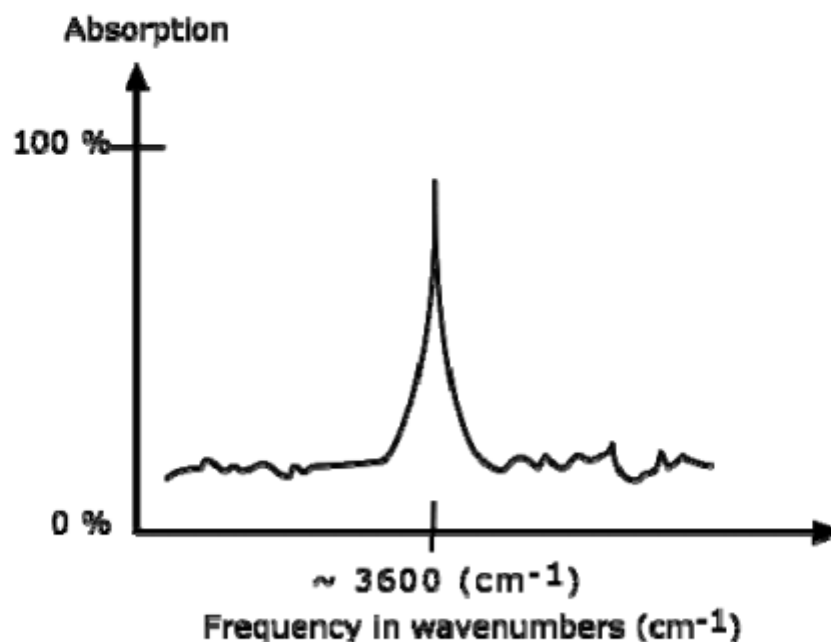
The graph above shows a spectrum in **absorption** mode.

AN IR SPECTRUM IN TRANSMISSION MODE
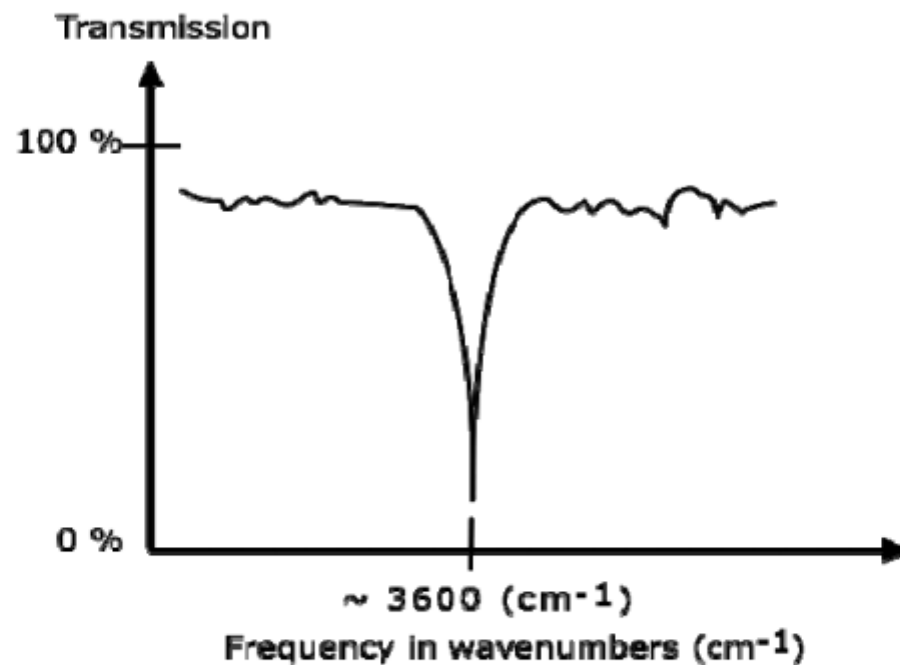
The graph above shows a spectrum in **transmission** mode.
This is the most commonly used representation and the one found in most chemistry and spectroscopy books. Therefore we will use this representation.

CLASSIFICATION OF IR BANDS

IR bands can be classified as **strong** (s), **medium** (m), or **weak** (w), depending on their relative intensities in the infrared spectrum. A strong band covers most of the *y*-axis. A medium band falls to about half of the *y*-axis, and a weak band falls to about one third or less of the *y*-axis.
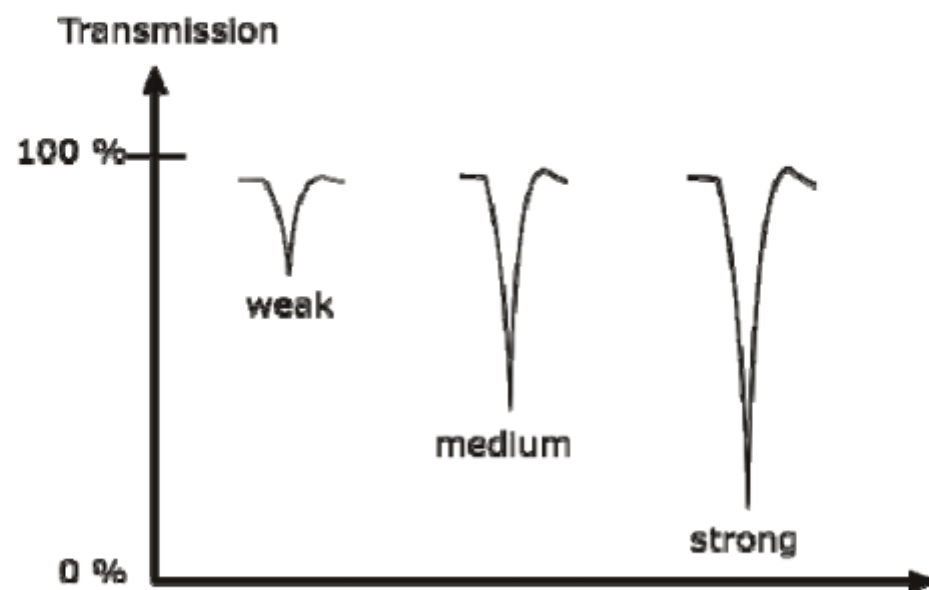
INFRARED ACTIVE BONDS

Not all covalent bonds display bands in the IR spectrum. **Only polar bonds do so. These are referred to as IR active**.

The intensity of the bands depends on the magnitude of the **dipole moment** associated with the bond in question:

- Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
- Medium polarity bonds and asymmetric bonds produce medium bands.
- Weakly polar bond and symmetric bonds produce weak or non observable bands.
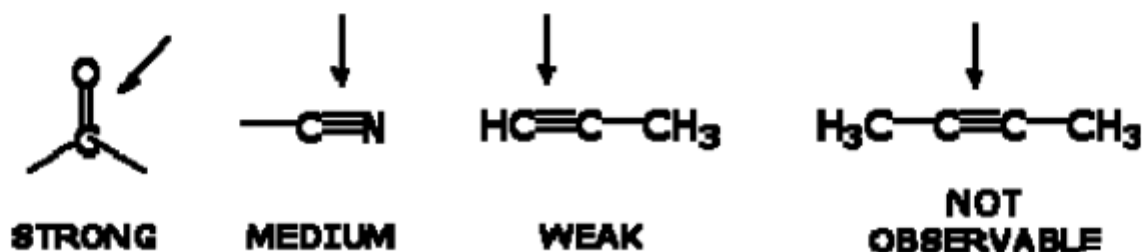
INFRARED BAND SHAPES

Infrared band shapes come in various forms. Two of the most common are **narrow** and **broad**. Narrow bands are thin and pointed, like a dagger. Broad bands are wide and smoother.

A typical example of a broad band is that displayed by O-H bonds, such as those found in alcohols and carboxylic acids, as shown below.
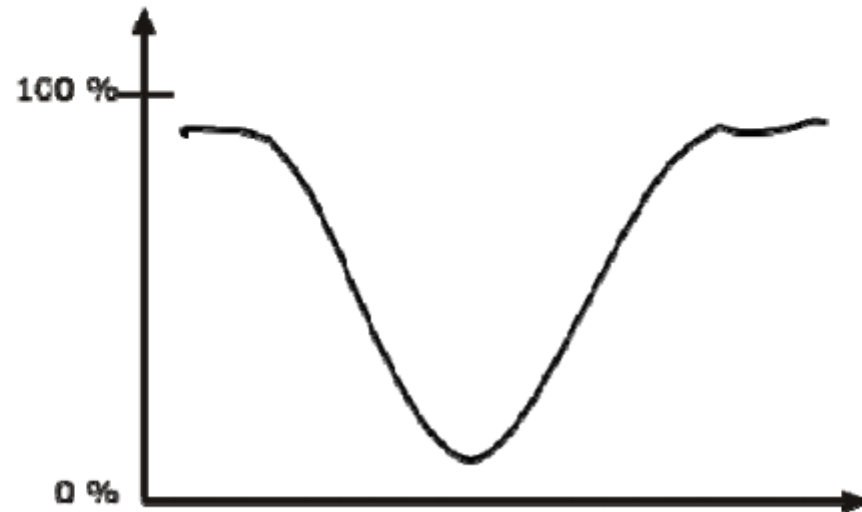
INFORMATION OBTAINED FROM IR SPECTRA

- IR is most useful in providing information about the presence or absence of specific **functional groups**.

- IR can provide a **molecular fingerprint** that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.

- IR **does not** provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.

- Therefore it is very limited in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.
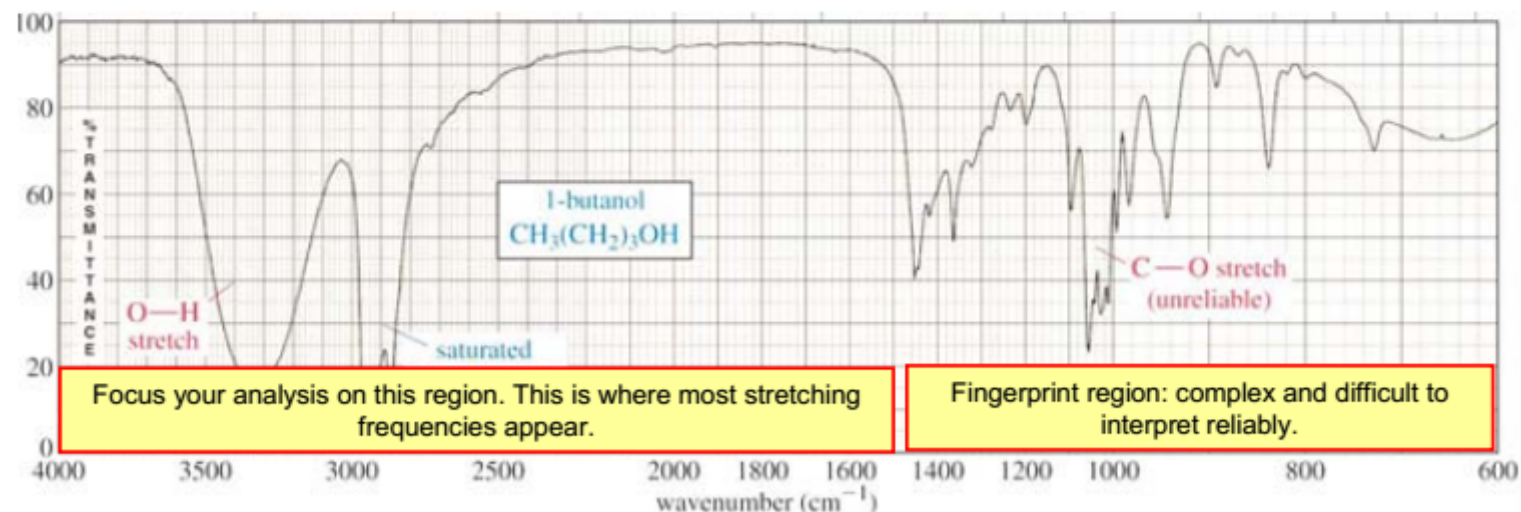
IR ABSORPTION RANGE

The typical IR absorption range for covalent bonds is **600 - 4000 cm^{-1}**. The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a sharp band around 2200-2400 cm^{-1} would indicate the possible presence of a C-N or a C-C triple bond.
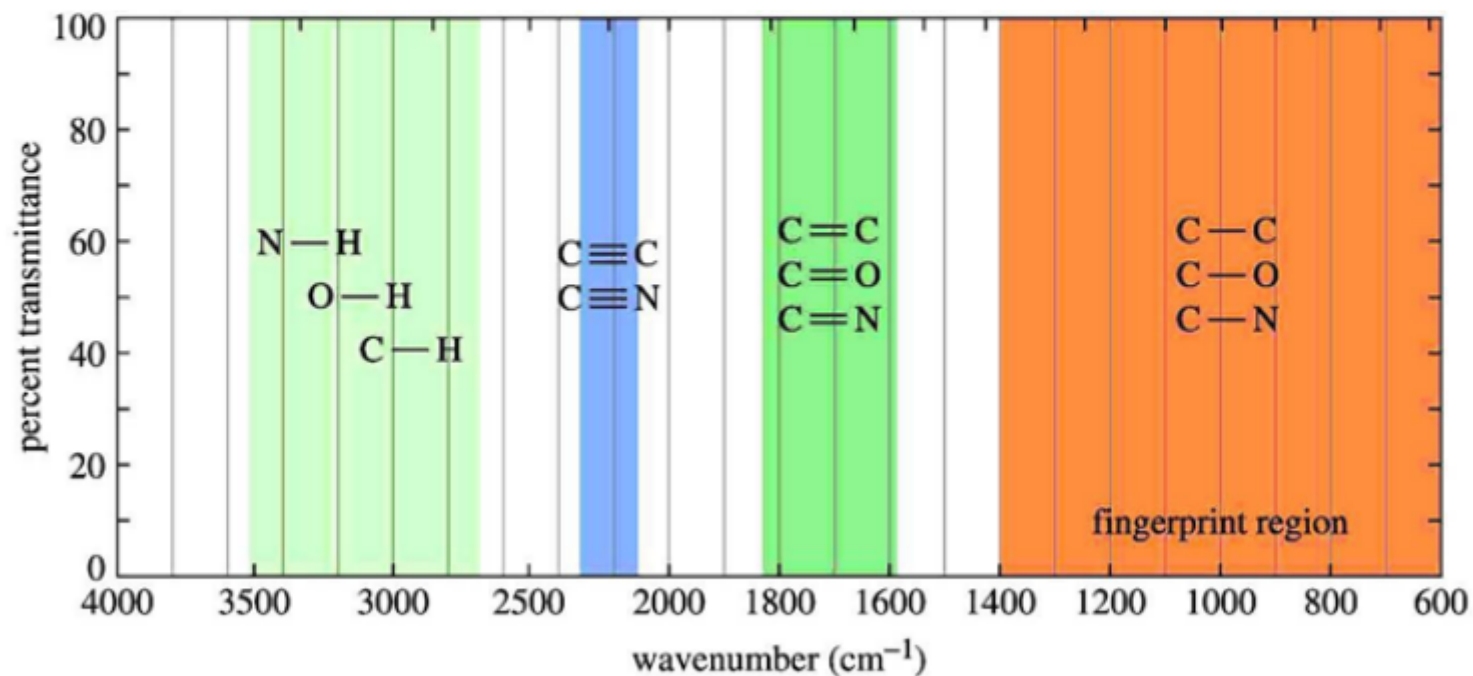
THE FINGERPRINT REGION

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}.

1-butanol
$CH_3(CH_2)_3OH$

O—H stretch

saturated

C—O stretch (unreliable)

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

Fingerprint region: complex and difficult to interpret reliably.
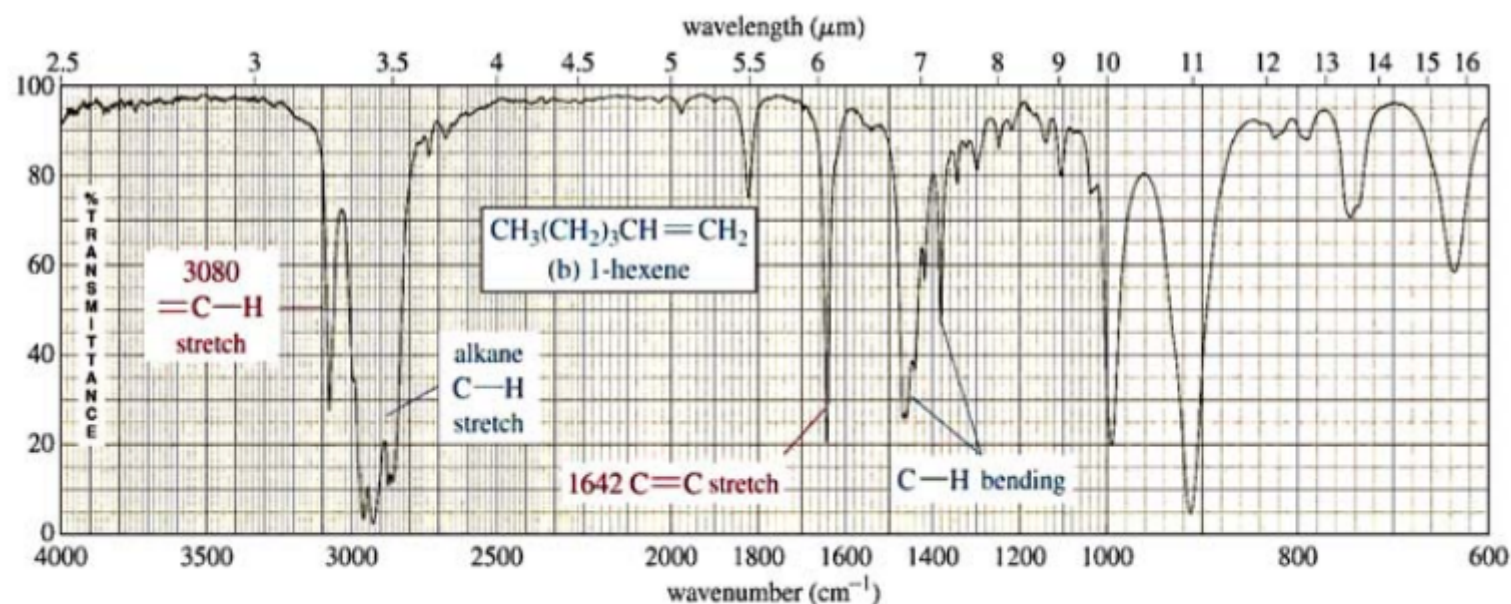
IR SPECTRUM OF ALKANES

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.
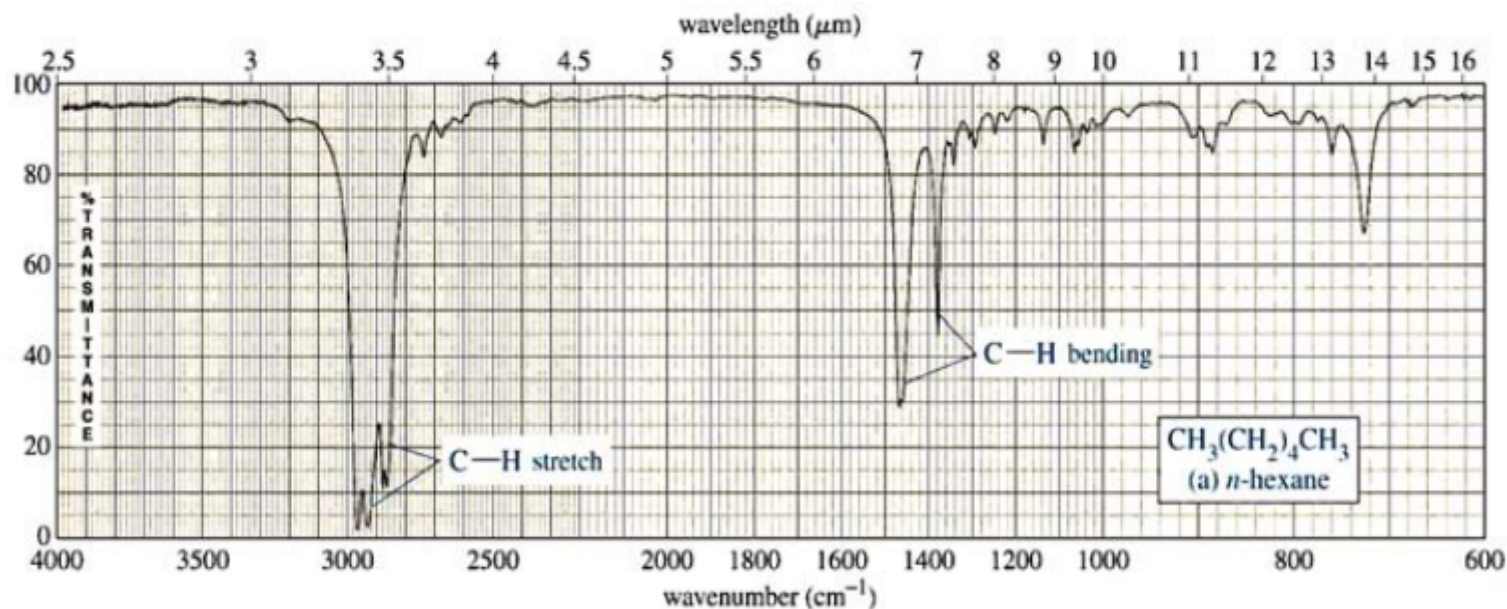
wavelength (μm)

C—H bending

C—H stretch

$CH_3(CH_2)_4CH_3$
(a) *n*-hexane

wavenumber (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)

wavelength (μm)

3080
=C—H
stretch

$CH_3(CH_2)_3CH=CH_2$
(b) 1-hexene

alkane
C—H
stretch

1642 C=C stretch

C—H bending

wavenumber (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.
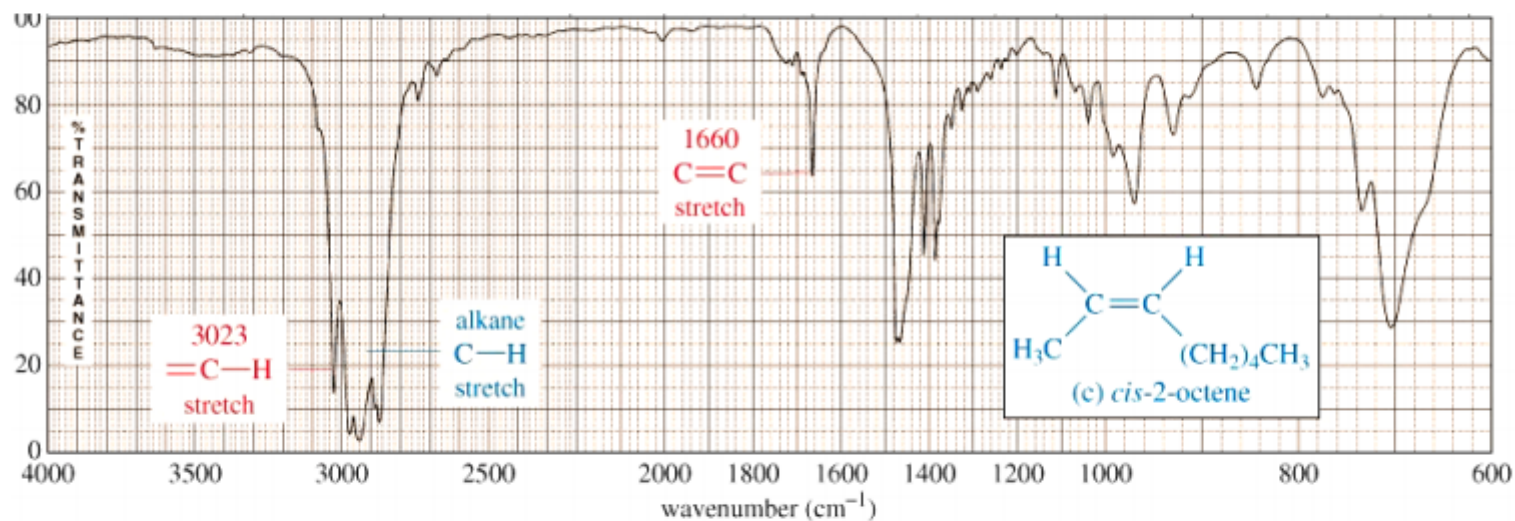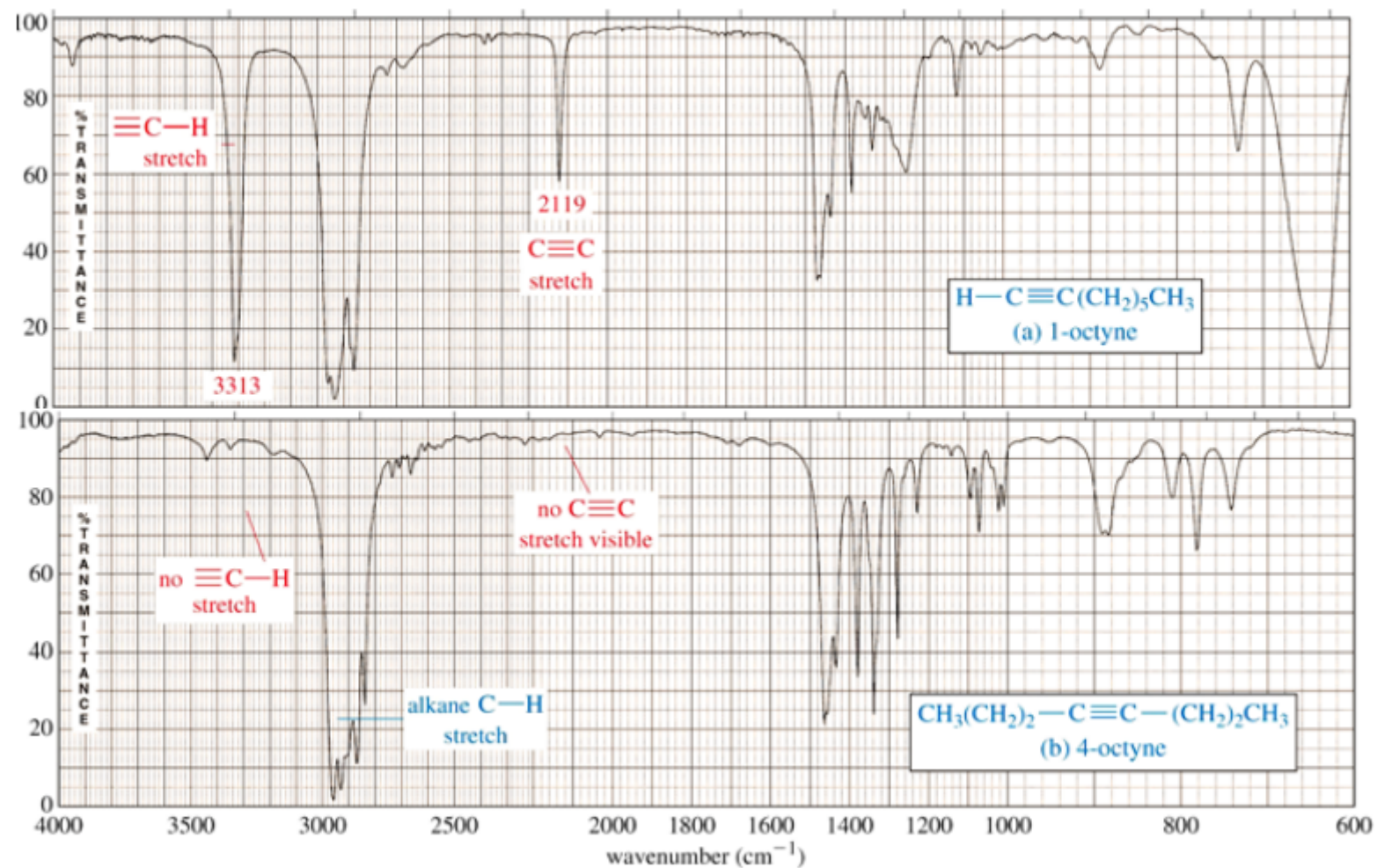
IR SPECTRUM OF ALKYNES

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-octyne).
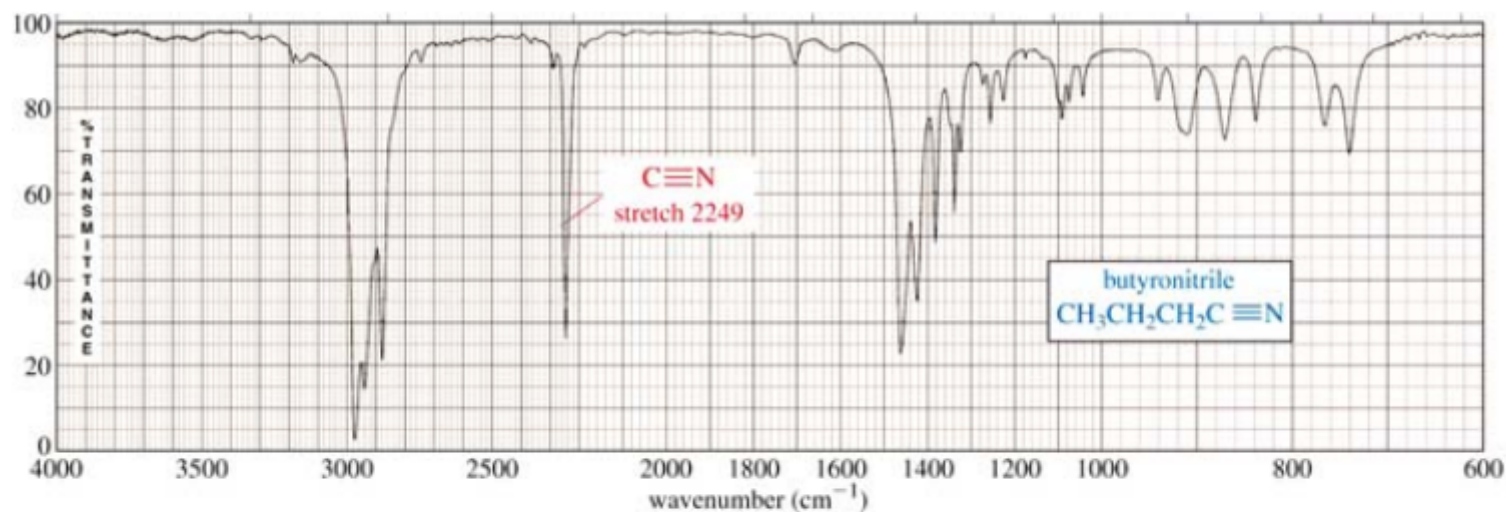
IR SPECTRUM OF ALKYNES

Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

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.
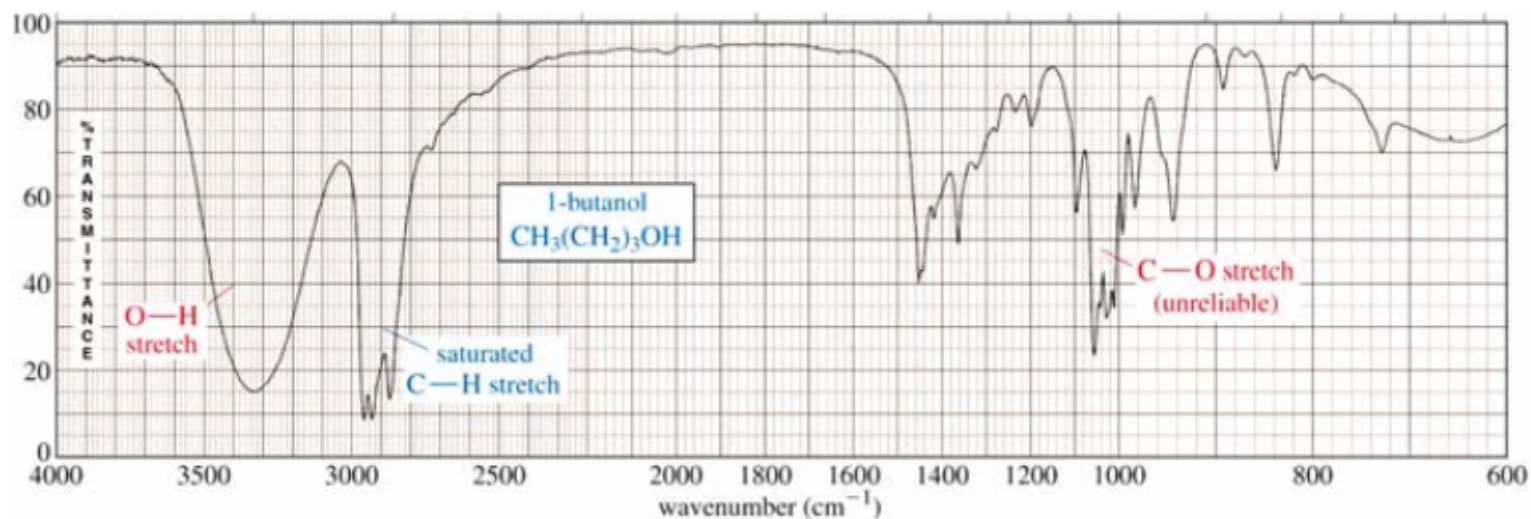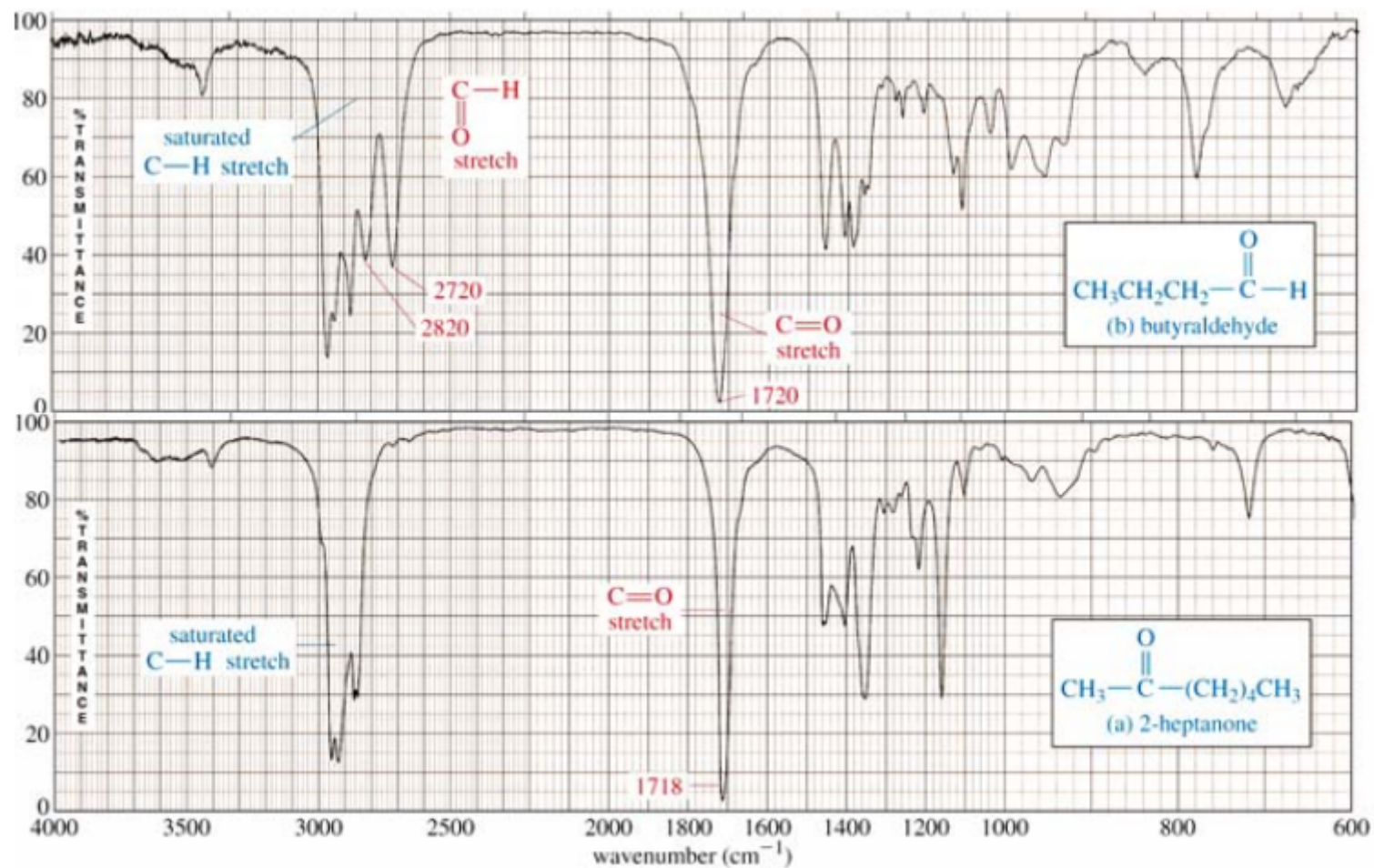
IR SPECTRUM OF ALDEHYDES AND KETONES

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 sp^2 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 sp^2 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

Graphics source: Wade, Jr., L.G. *Organic Chemistry*, 6th ed. Pearson Prentice Hall Inc., 2006

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.
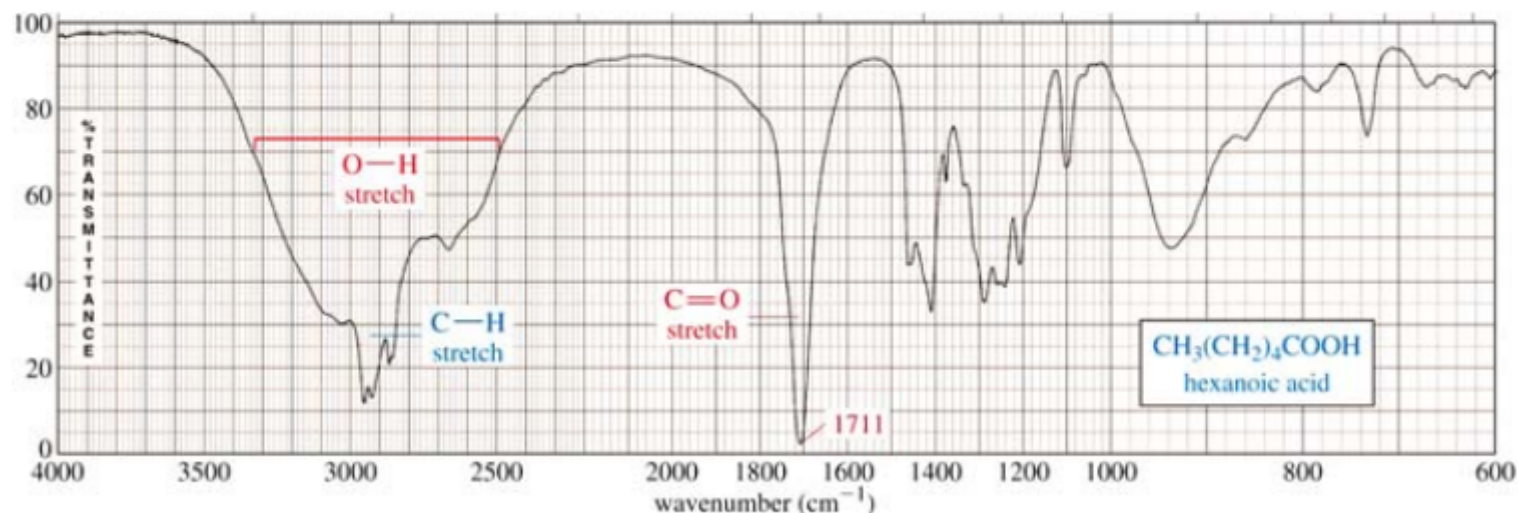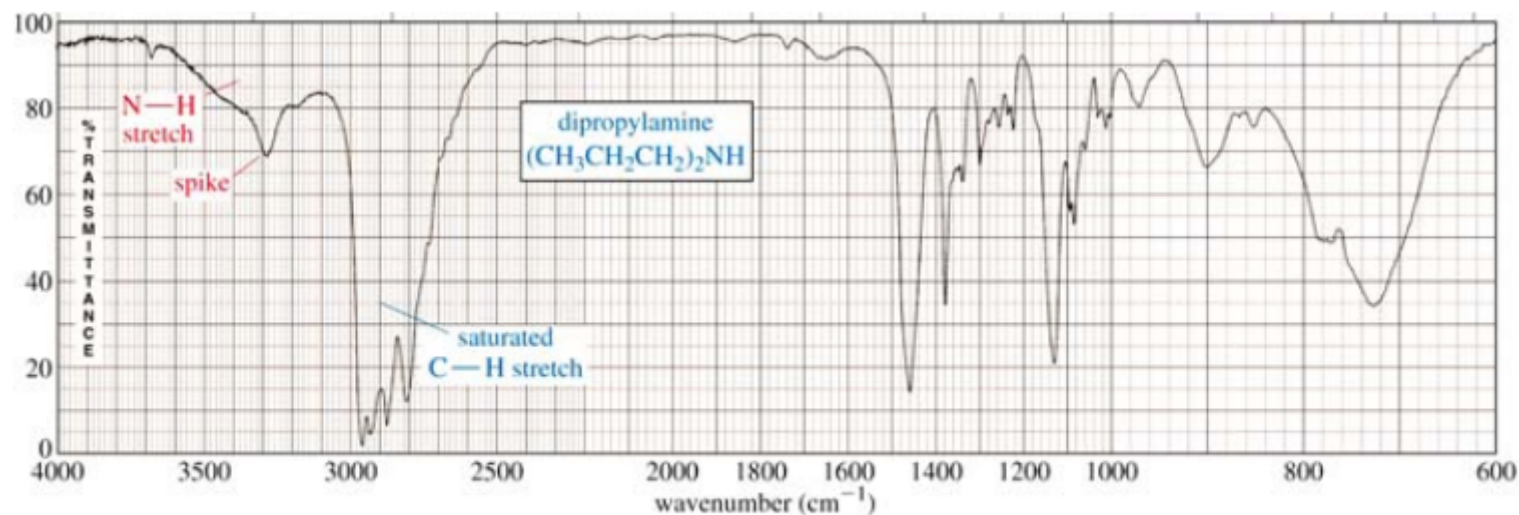
IR SPECTRA OF AMINES

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.

dipropylamine
$(CH_3CH_2CH_2)_2NH$

N—H stretch
spike
saturated C—H stretch

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.
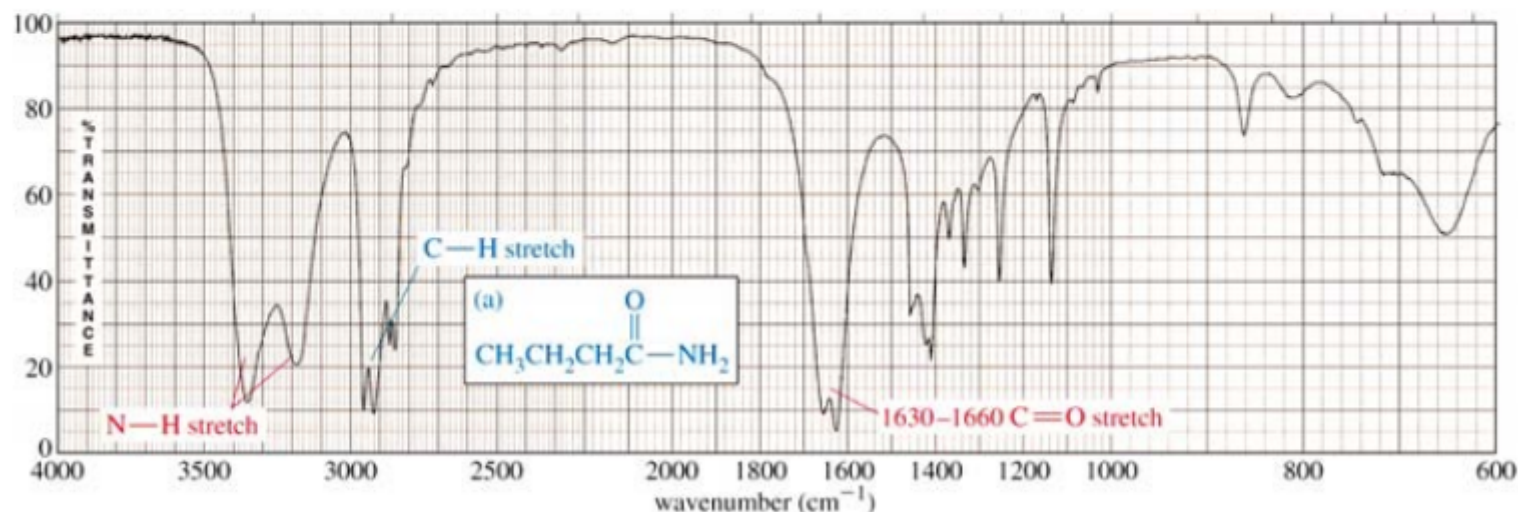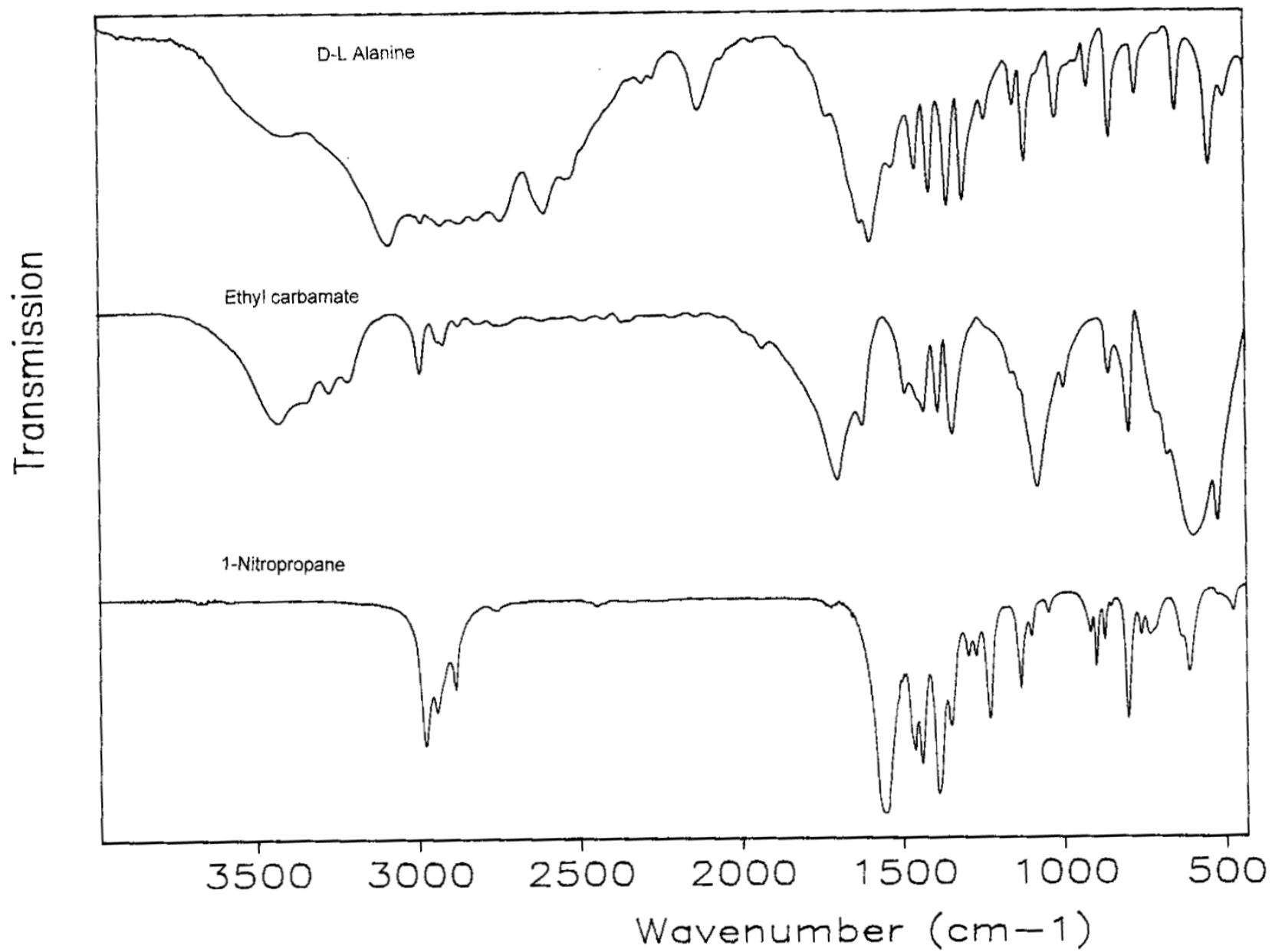
FIGURE 8-8 The infrared spectra of three compounds of formula $C_3H_7O_2N$.
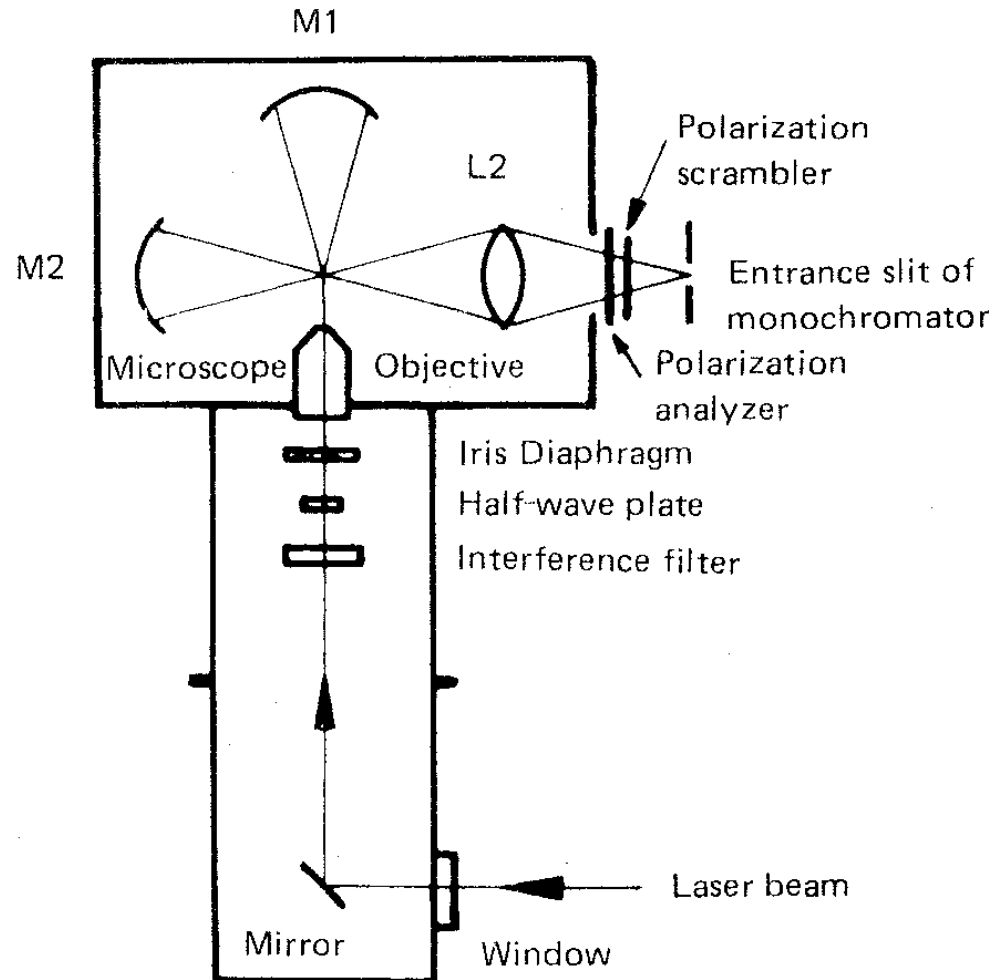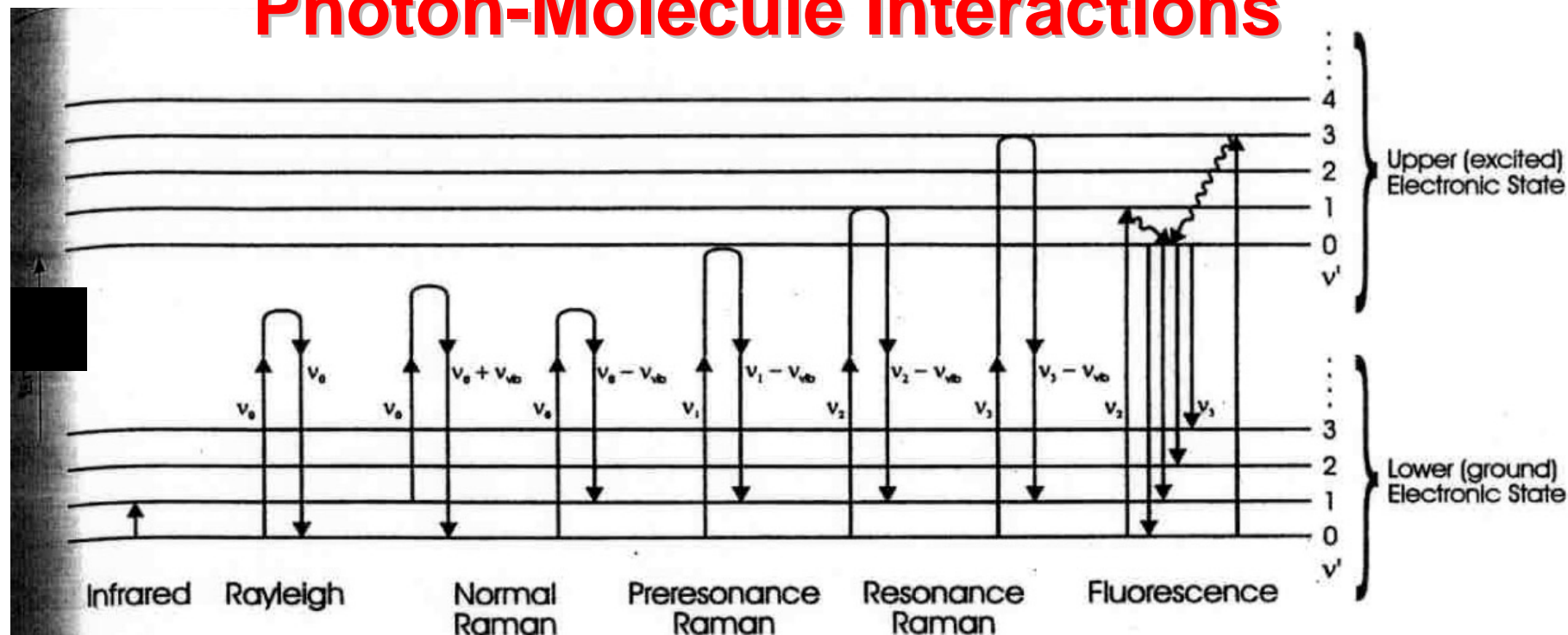
RAMAN SPECTROSCOPY

Figure 7-9   The arrangement of the optical components in a typical dispersive Raman spectrometer sample compartment.

Photon-Molecule Interactions

When light interacts with a vibrating diatomic molecule, the induced dipole moment has 3 components:

$$\mu_z(t) = \alpha_{zz}^{equil} \vec{E}_{max} \cos 2\pi \nu_0 t +$$ Rayleigh scatter

$$\frac{1}{2}\frac{d\alpha_{zz}}{dr}\Delta r_{max}\vec{E}_{max}\cos 2\pi(\nu_0 + \nu_{vib})t +$$ Anti-Stokes Raman scatter

$$\frac{1}{2}\frac{d\alpha_{zz}}{dr}\Delta r_{max}\vec{E}_{max}\cos 2\pi(\nu_0 - \nu_{vib})t$$ Stokes Raman scatter
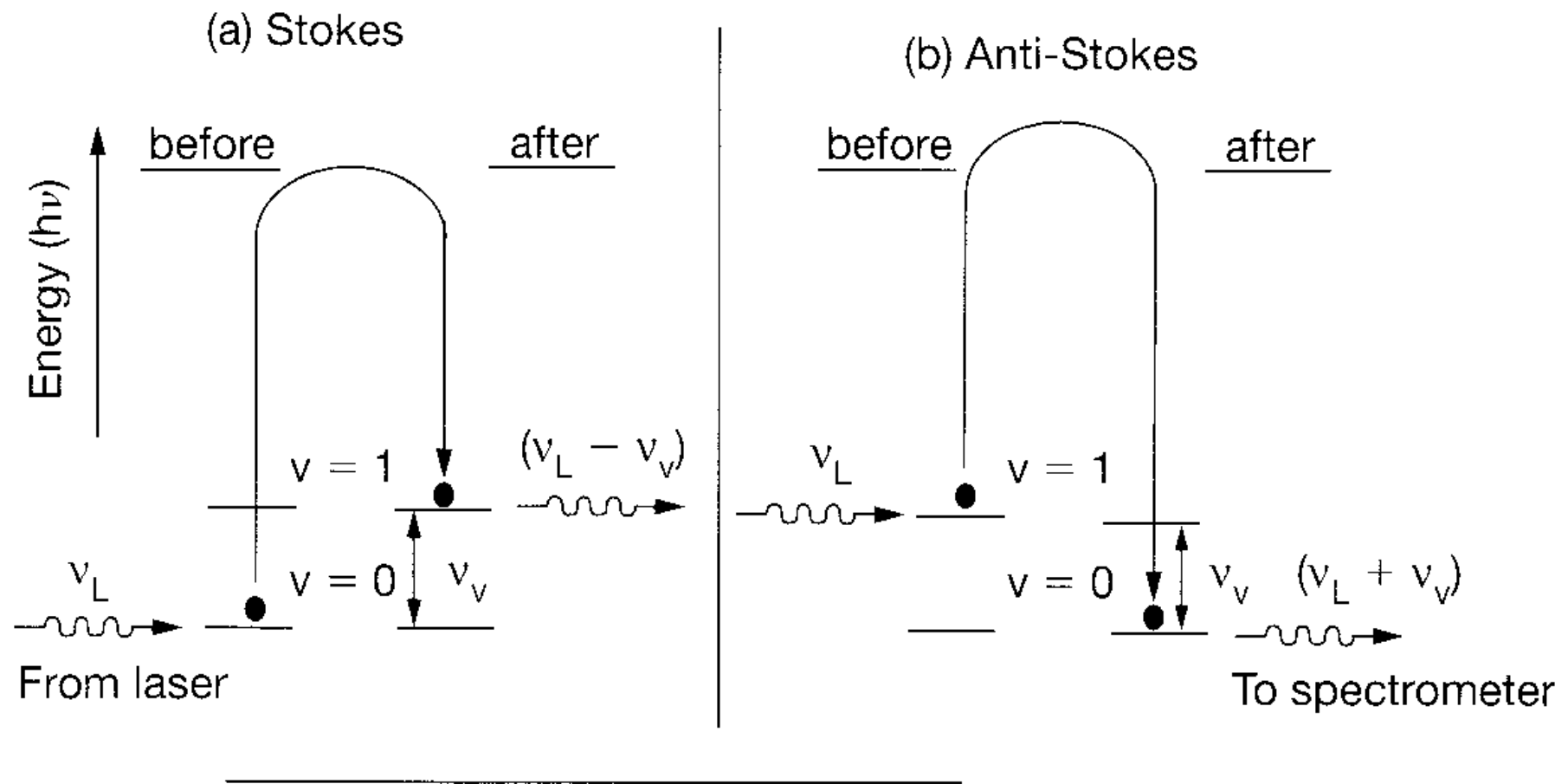
Kellner et al., *Analytical Chemistry*

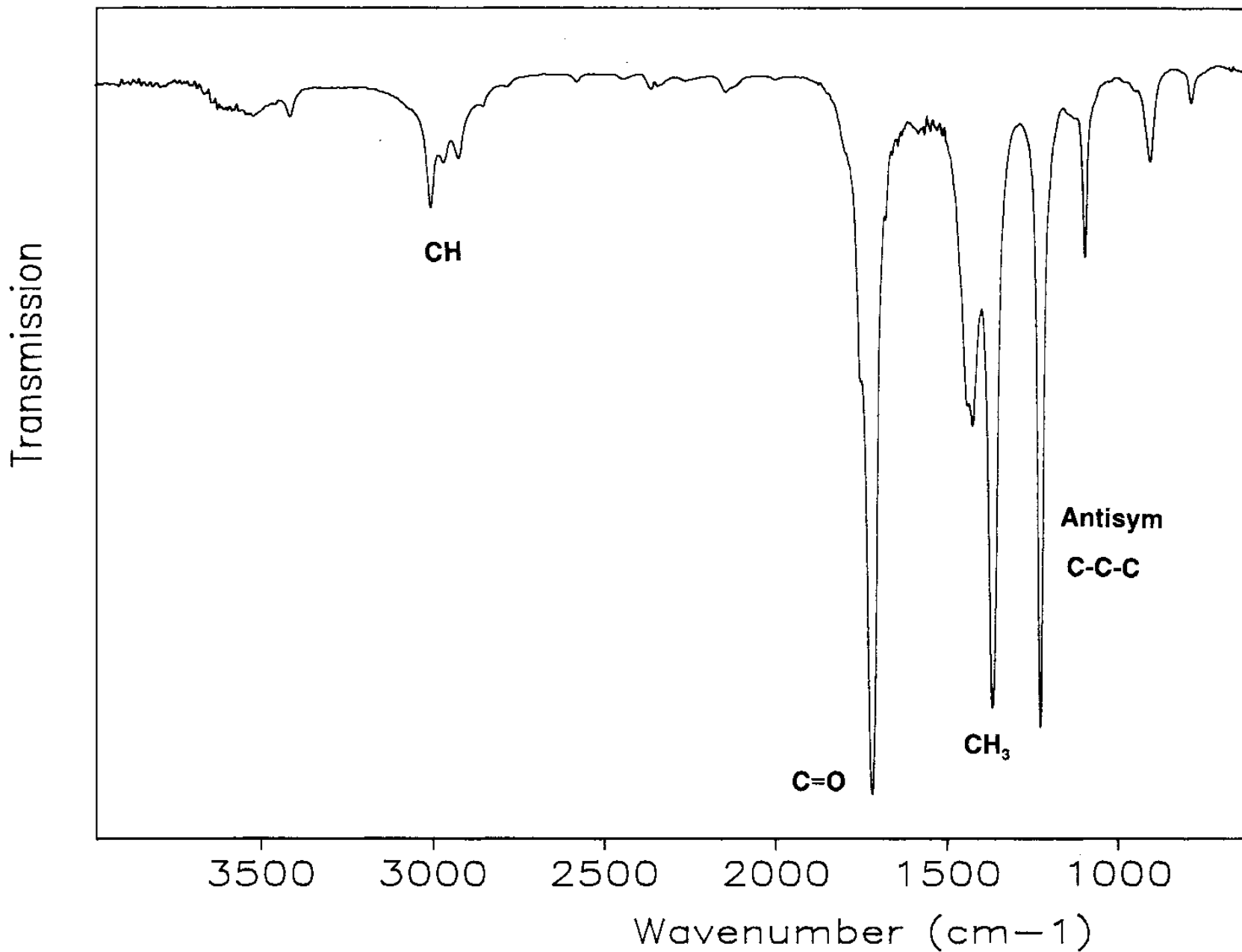**Figure 7-2** The mechanism of Raman scattering.

Figure 7-1 The infrared spectrum of a thin film of acetone $(CH_3)_2CO$ between two KBr plates.
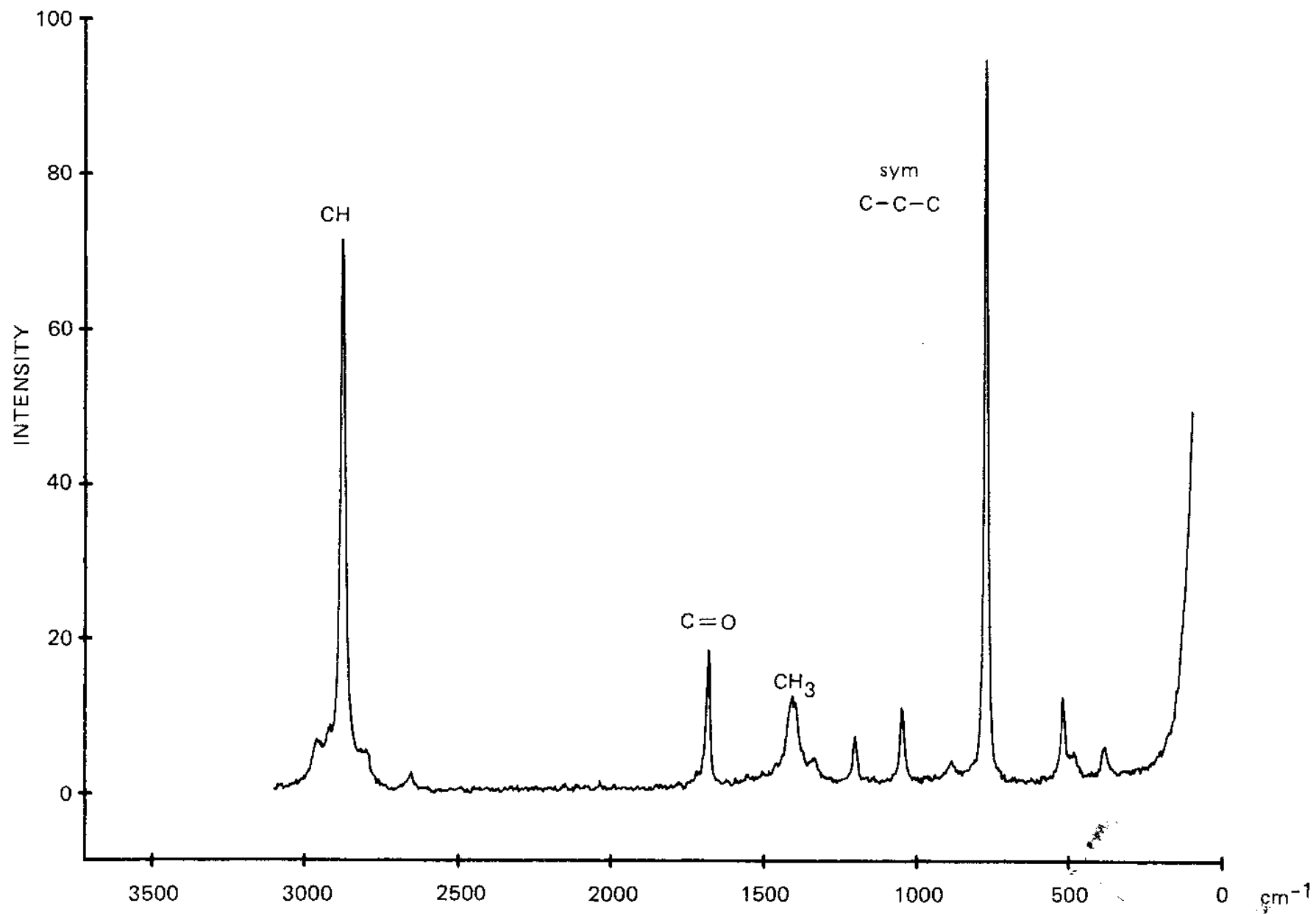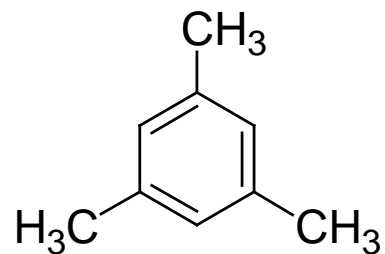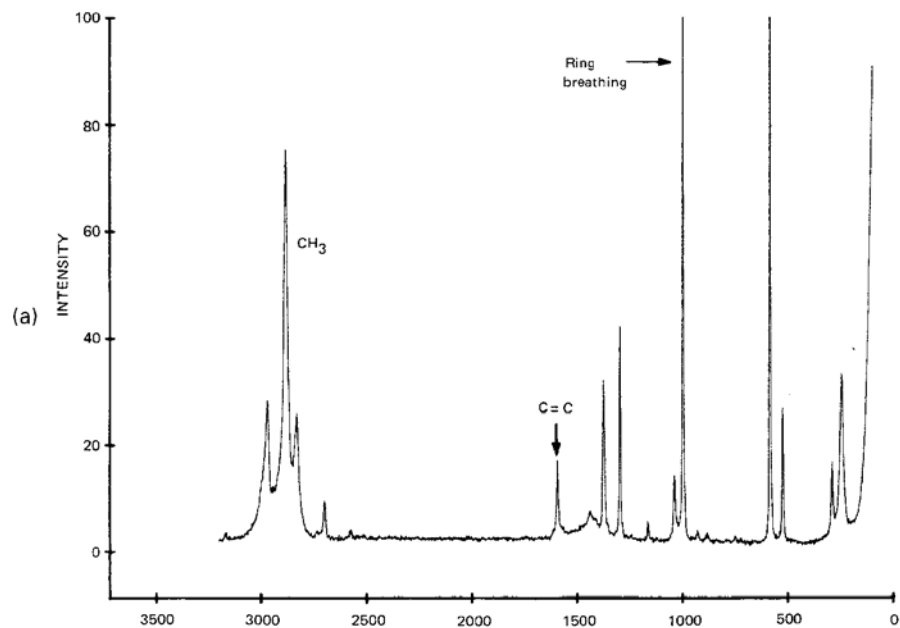
Figure 7-3 The Raman spectrum of acetone.

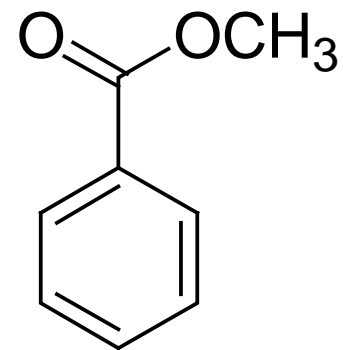1000 cm^{-1} a symmetrical in-plane ring deformation also known as a ring-breathing vibration
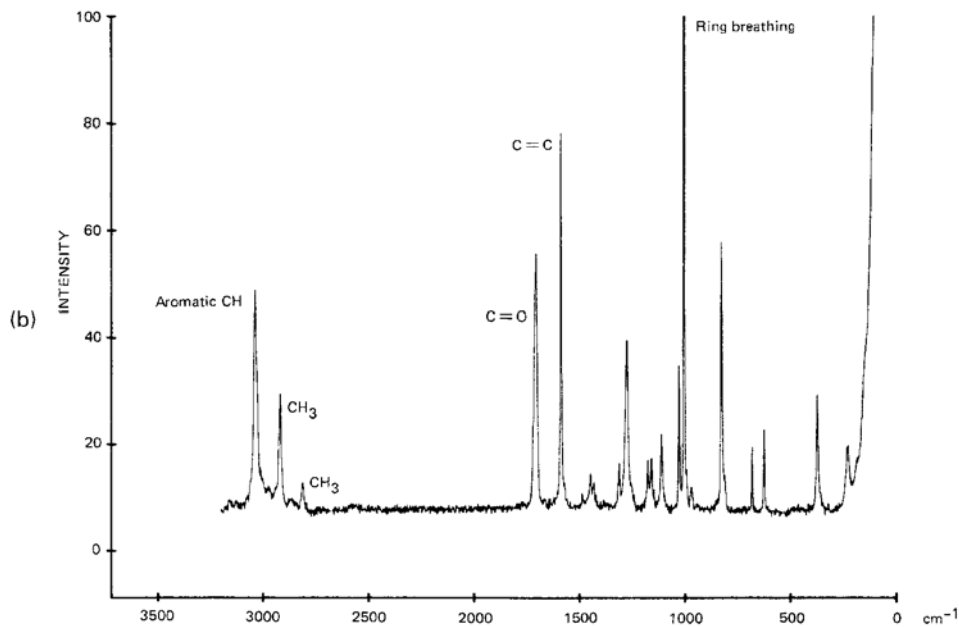
Figure 9-12 Raman spectra of (a) 1,3,5-trimethylbenzene (mesitylene) and (b) methyl benzoate.
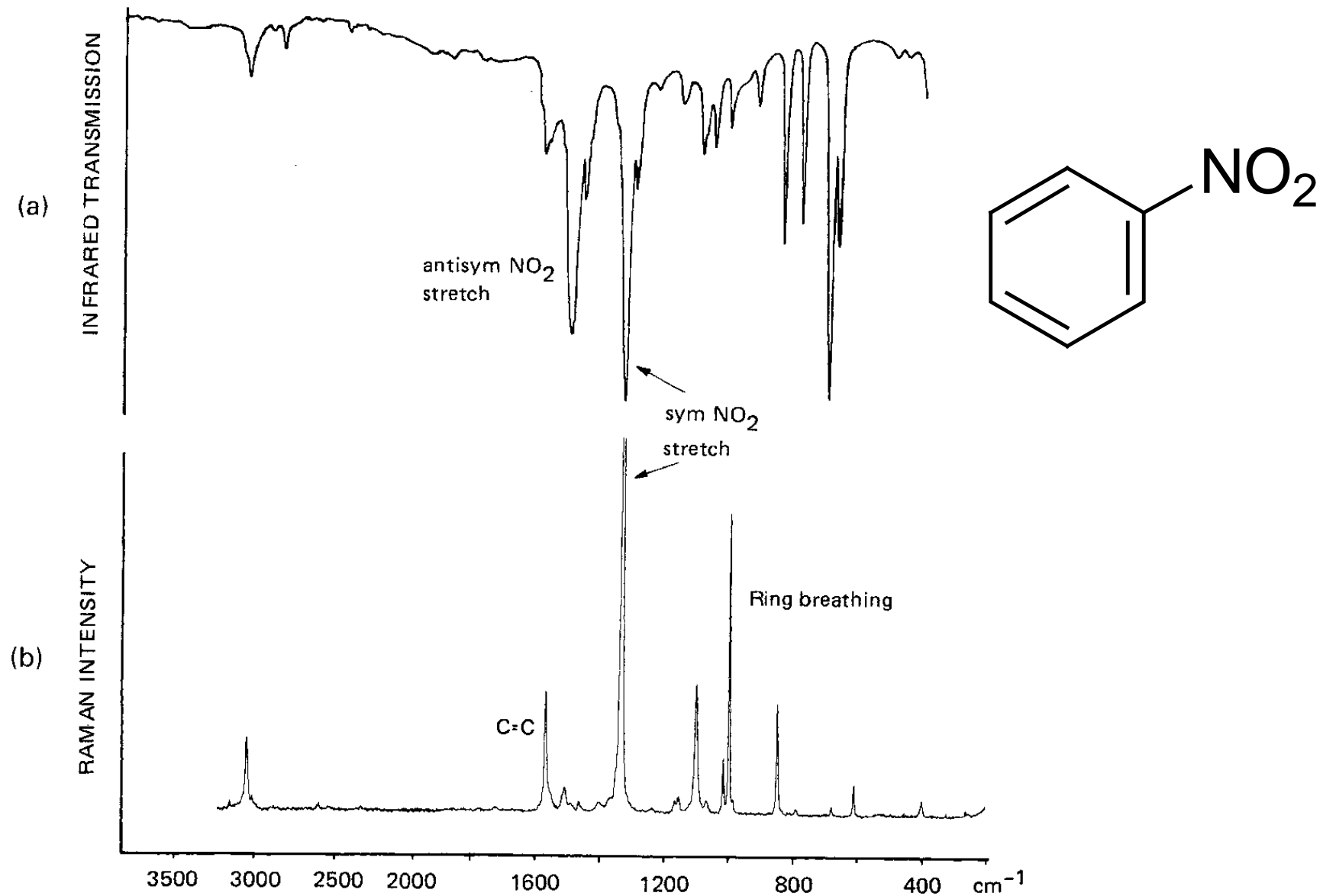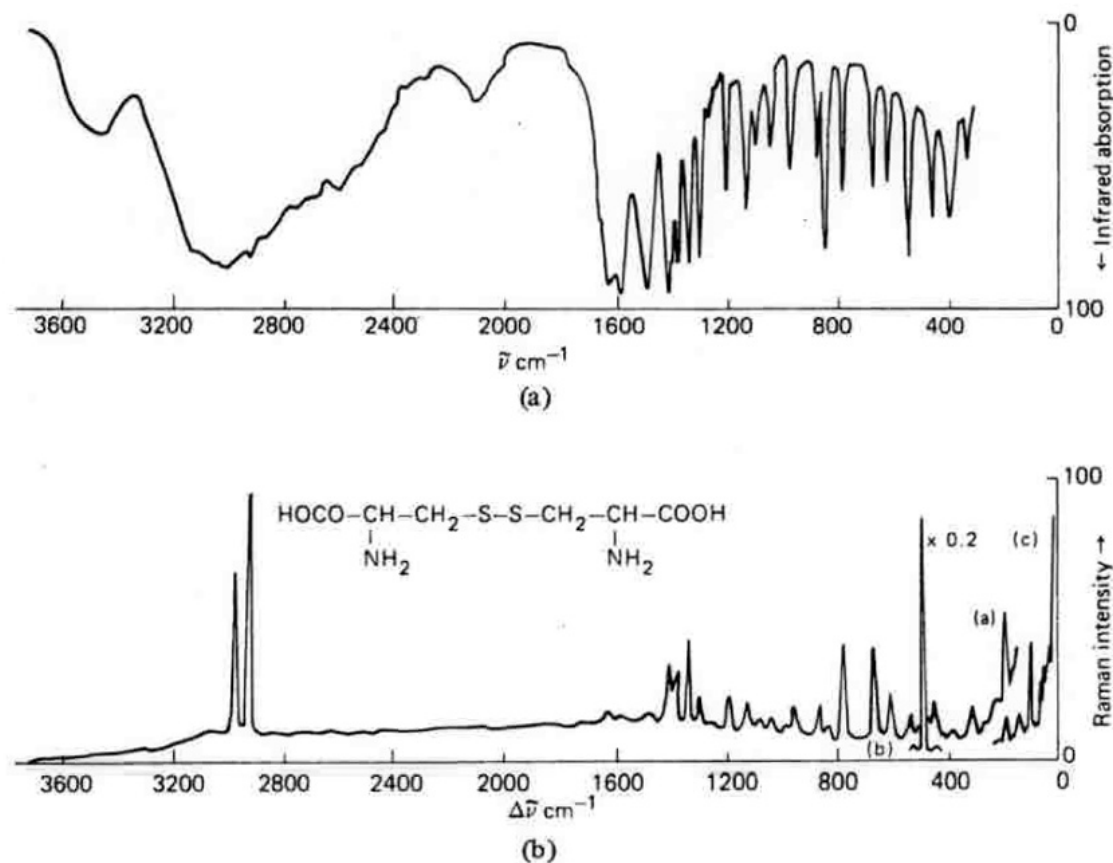
Raman vs IR Spectra

Figure 9-13 (a) Infrared and (b) Raman spectra of nitrobenzene.

Raman vs IR Spectra

FIGURE 16-13 Infrared (a) and Raman (b) spectra of crystalline cystine. Note that the NH_3^+ stretching vibration dominates the 3000-cm^{-1} region in the IR spectrum, whereas the Raman spectrum shows sharp bands due to CH and CH_2 stretching modes. The NH_3^+ deformation and the carboxylate antisymmetric vibrations near 1600 cm^{-1} are much stronger in the IR spectrum. The strong Raman band at 410 cm^{-1} is due to the —S—S— stretch; this band is somewhat obscured and weak in the IR spectrum. [With permission of VCH Verlagsgesselschaft from B. Schrader, *Angew. Chem. Int. Ed. Engl.*, *12*, 884 (1973).]

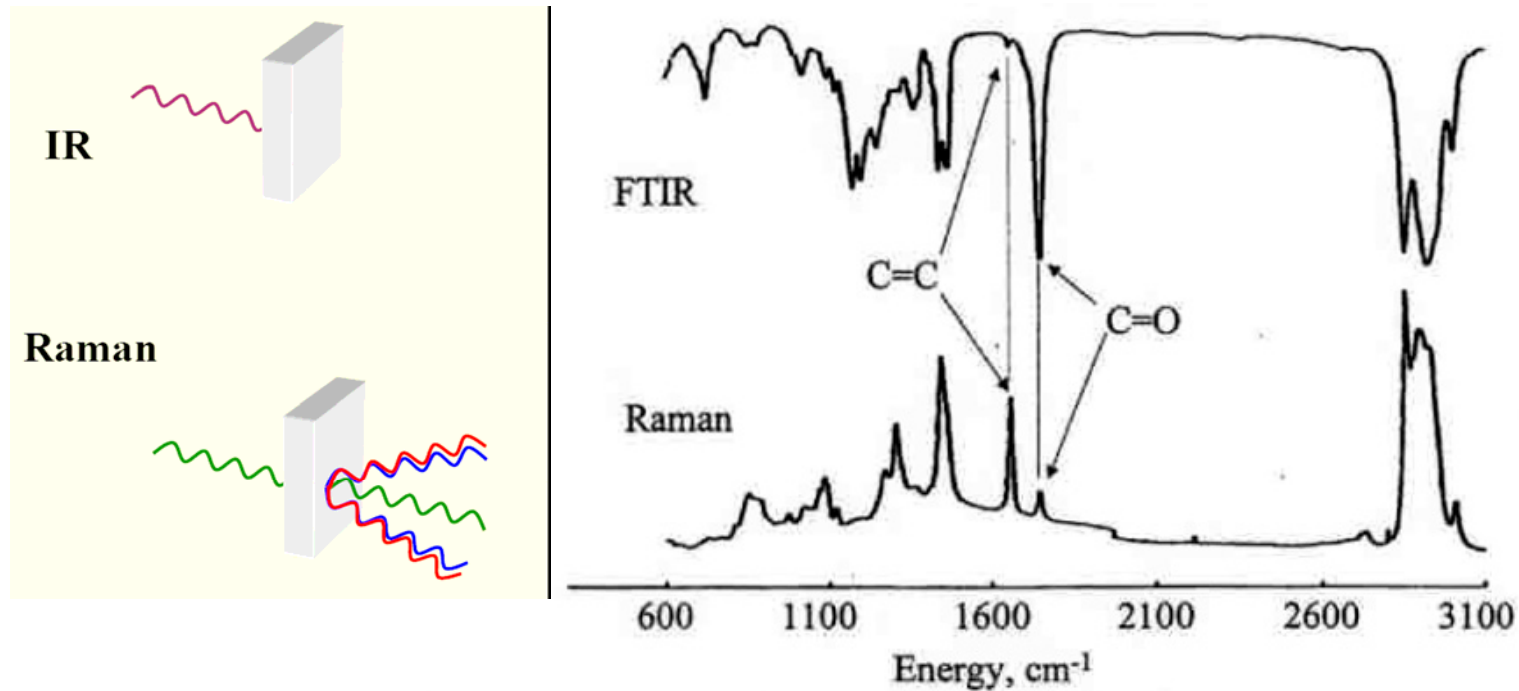Ingle and Crouch, *Spectrochemical Analysis*

Raman vs IR Spectra
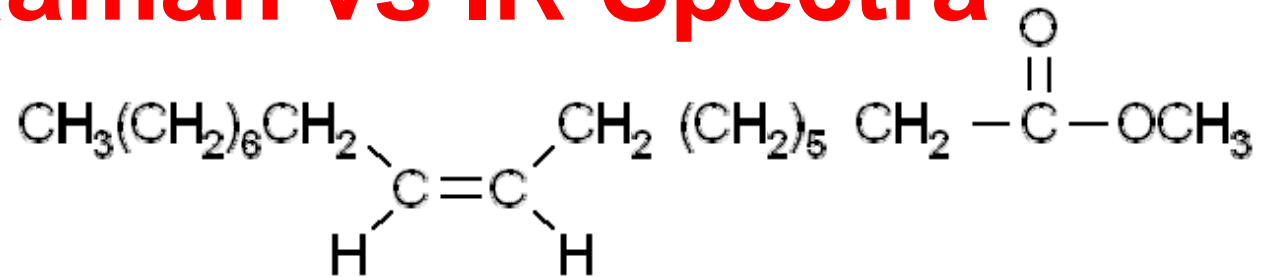
Figure 2.2. FTIR (upper) transmission and Raman scattering (lower) of oleic acid methyl ester.

McCreery, R. L., *Raman Spectroscopy for Chemical Analysis, 3rd ed.*, Wiley, New York: 2000

Raman and pearl
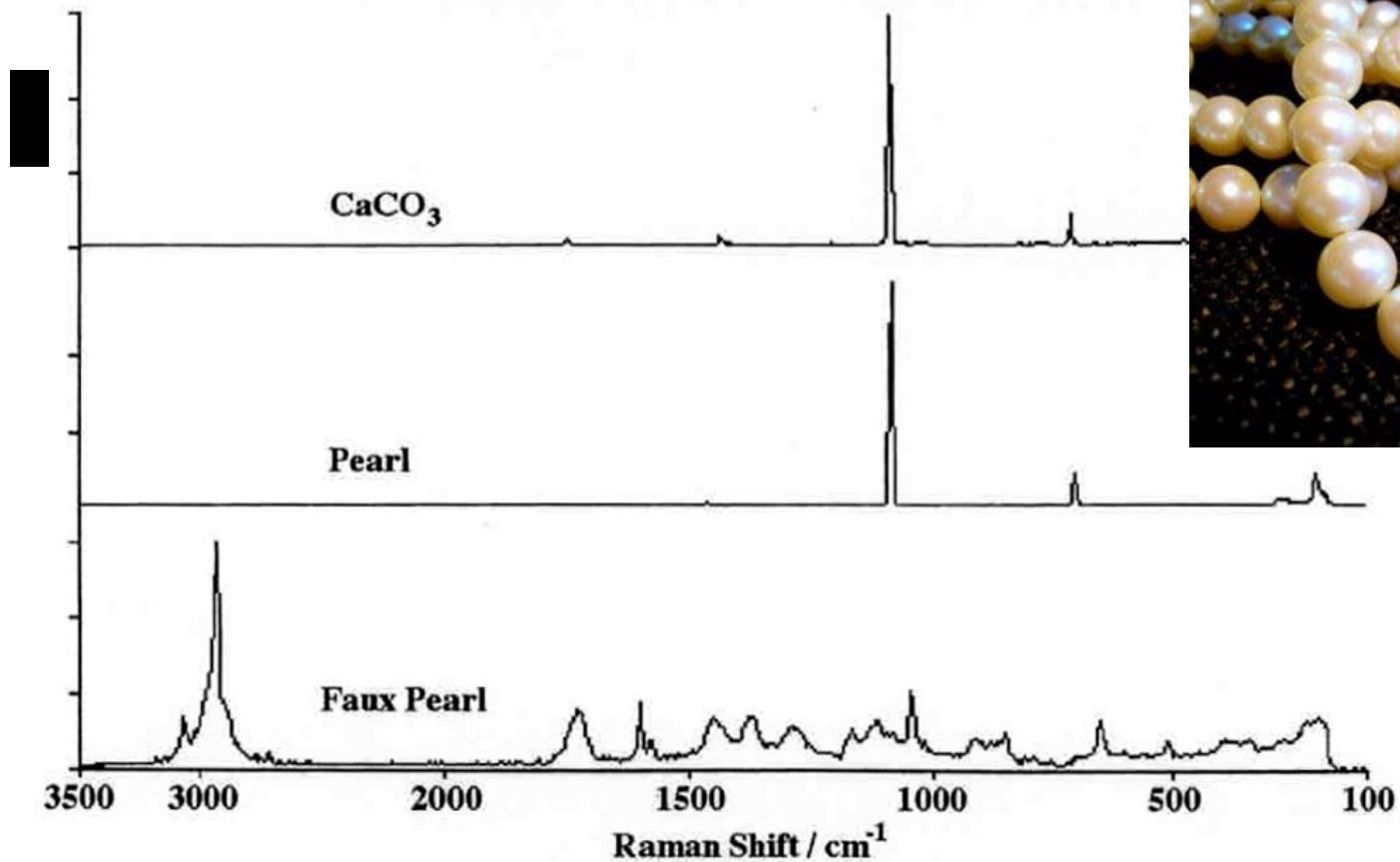
Figure 3 The Raman spectra of calcium carbonate (top), natural pearl (middle), and faux pearl (bottom). (Adapted with permission from Ref. 9.)

Lewis, I. R.; Edwards, H. G. M., *Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line,* Marcel Dekker, New York: 2001.0

Ivory or Plastic?

Figure 14 Specimen of (a) carved cat and (b) bangles, believed to be of ivory; 16th to 19th centuries.

Lewis, I. R.; Edwards, H. G. M., *Handbook of Raman Spectroscopy: From the Research Laboratory to the Process Line,* Marcel Dekker, New York: 2001.

Ivory or Plastic?
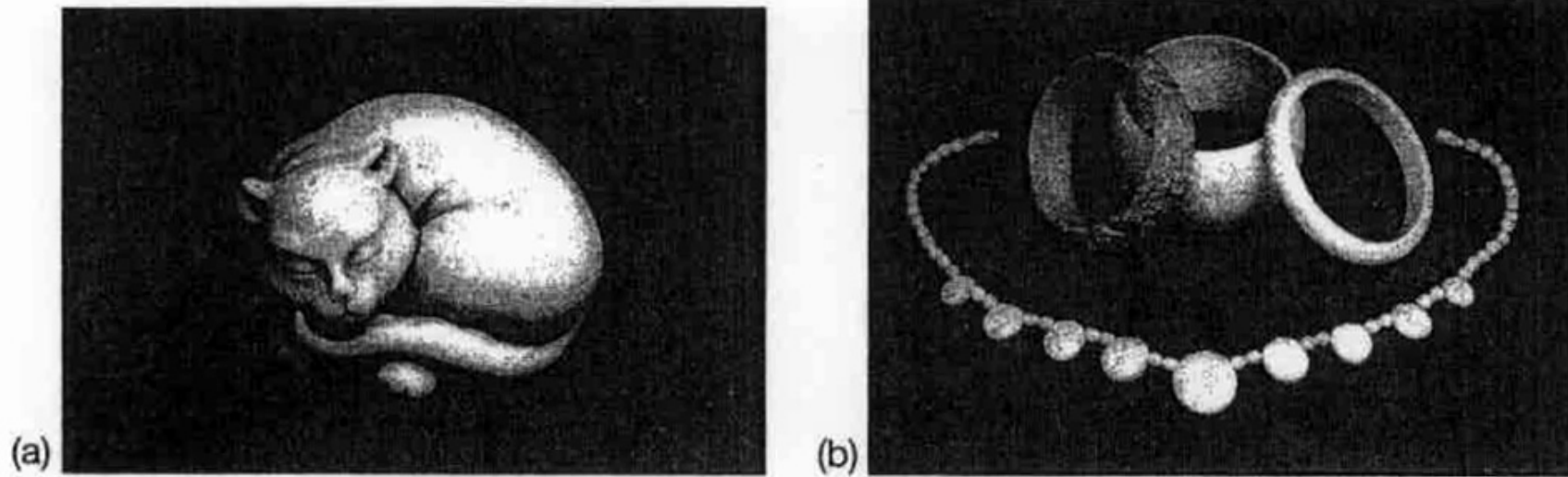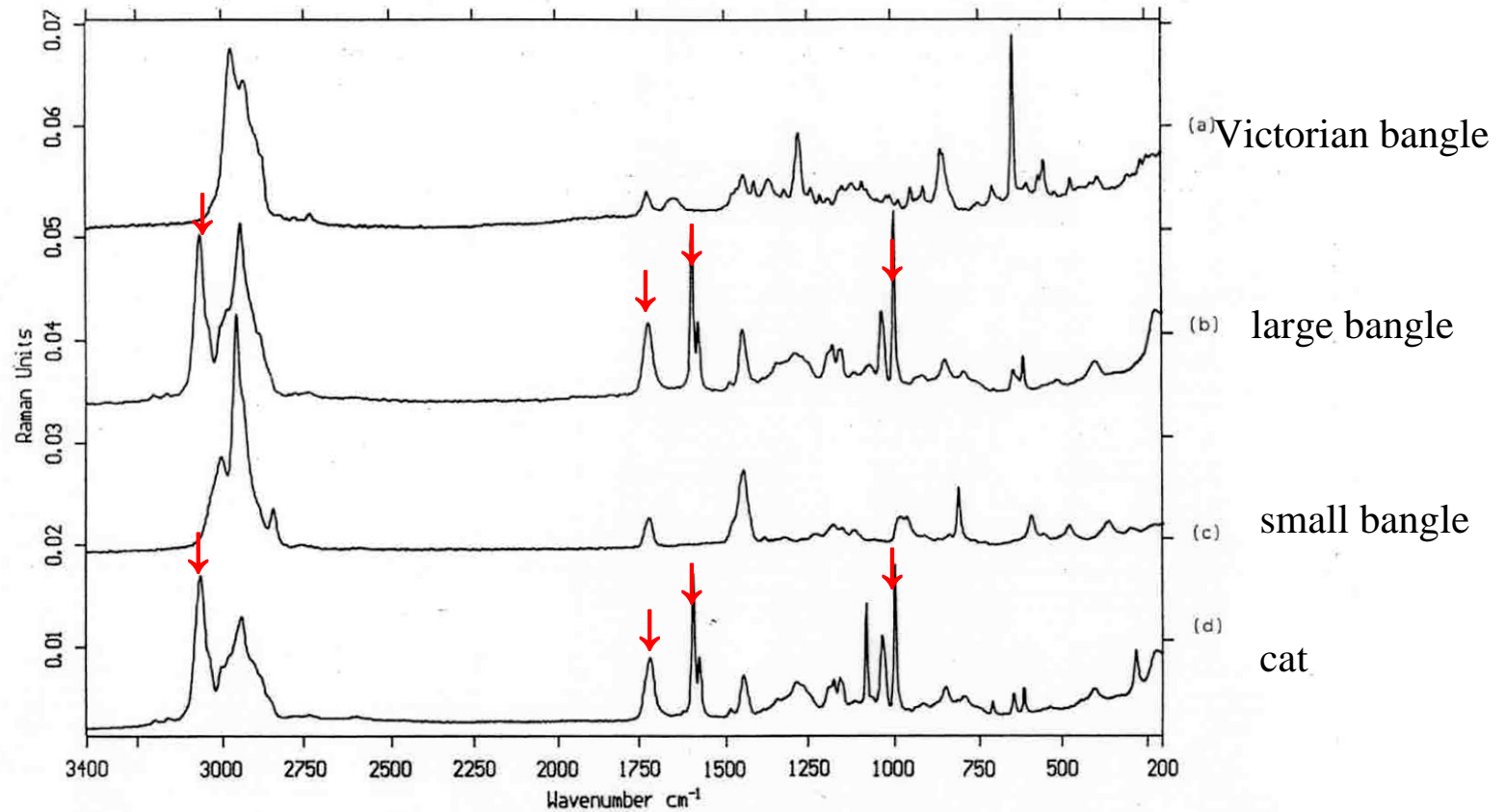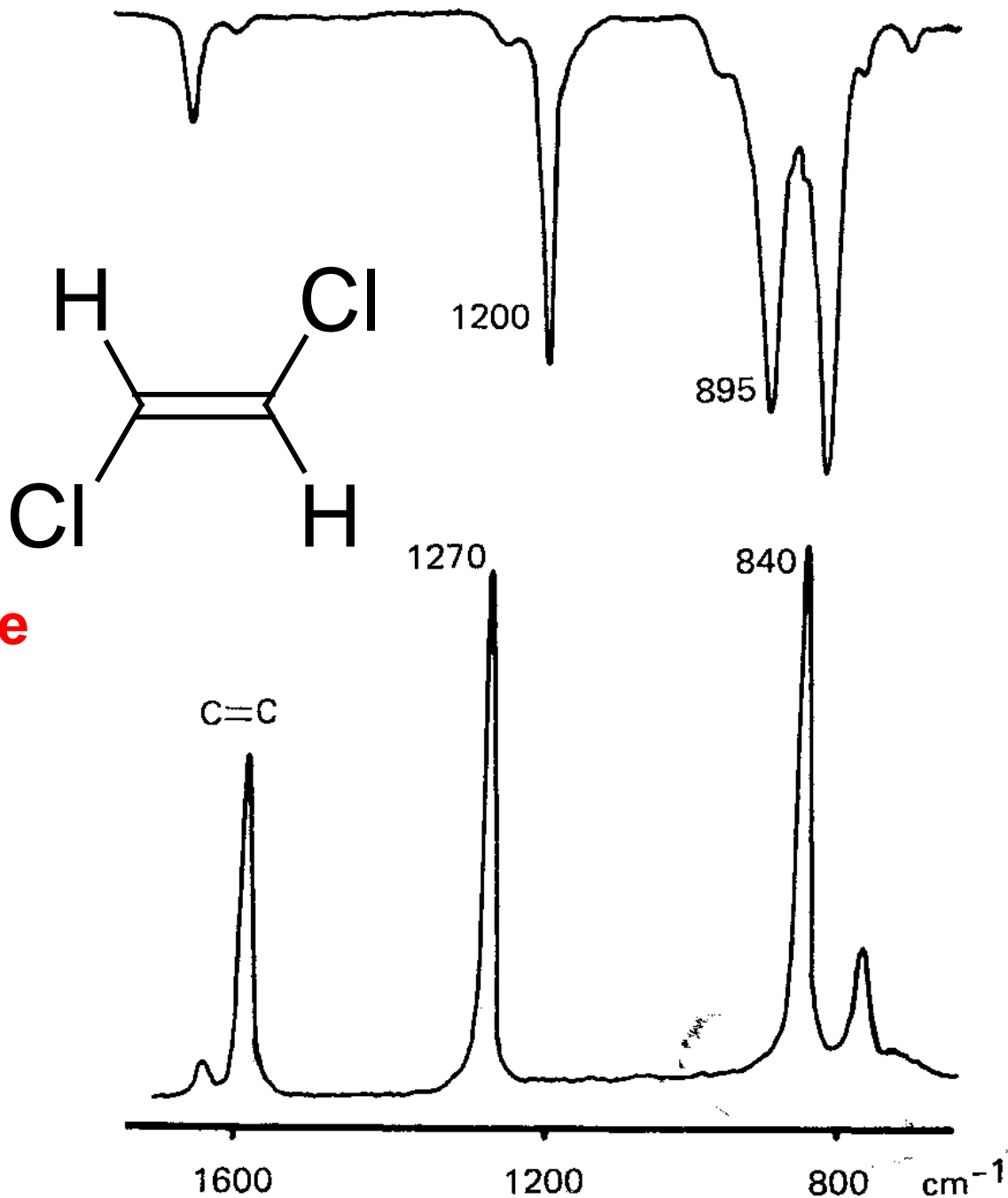

Figure 15 FT-Raman spectra of fake ivory specimens: (a) carved Victorian bangle, (b) large bangle, (c) small bangle, (d) cat. The absence of the characteristic proteinaceous features in true ivory near 1650 and 1450 cm^{-1} and the strong phosphate mode near 960 cm^{-1} should be noted. Also, the presence of the aromatic ring bands at 3060, 1600, and 1000 cm^{-1} in (b) and (d) indicate a polystyrene resin content, whereas the carbonyl stretching band at 1725 cm^{-1} in all fake specimens indicates the presence of poly(methyl methacrylate). In the cat specimen, the band at 1086 cm^{-1} uniquely identifies a calcite additive in the specimens of imitation ivory studied. (Reproduced with permission from HGM Edwards, DW Farwell. Ivory and simulated ivory artifacts: Fourier-transform Raman diagnostic study. Spectrochimica Acta, Part A, 51:2073–2081. © 1995, Elsevier Science B.V.)

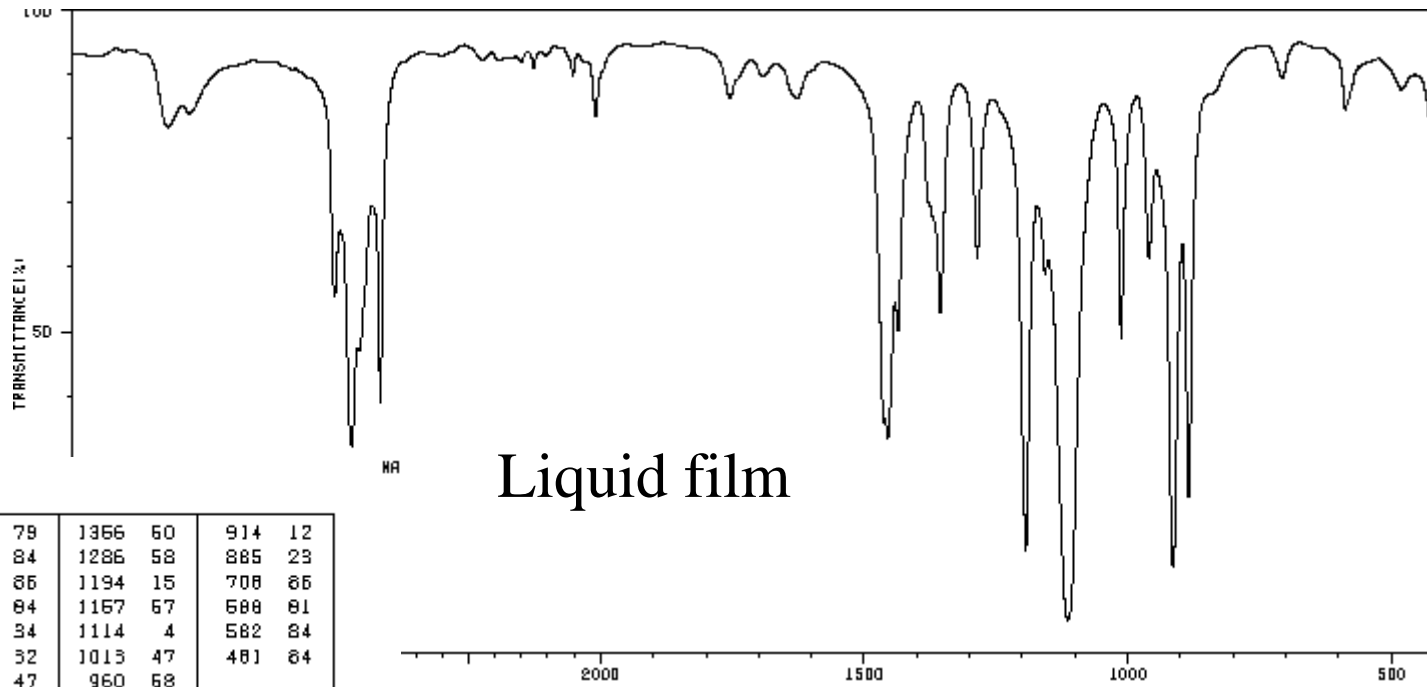No signal C=C
895 C–Cl (antisym) **(a)**
1200 C–H (antisym)

**Portions of the
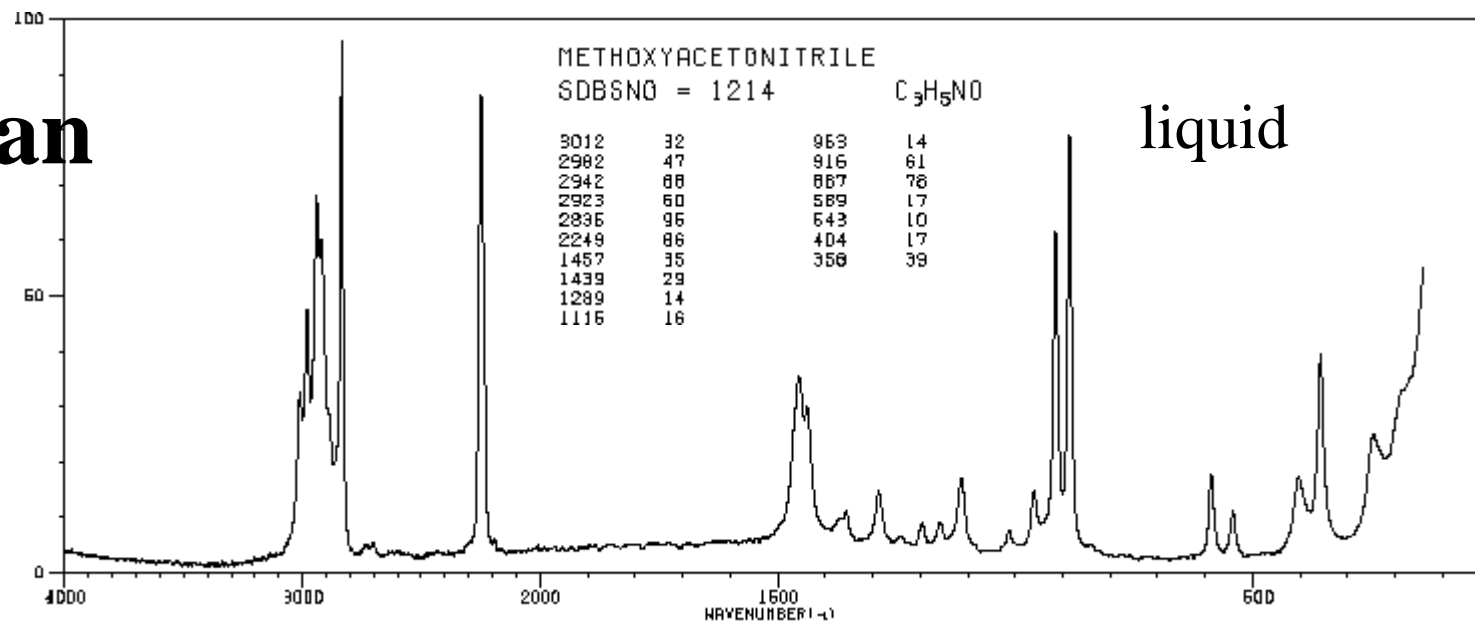(a) IR and (b) Raman
(b) Spectra of
(E)-1,2-dichloroethene**

1580 C=C
1270 C–Cl (sym)
840 C–Cl(sym) **(b)**

1200

895

1270

840

C=C

1600   1200   800   cm⁻¹

IR

TRANSMITTANCE (%)

NA

3638	79	2019	79	1366	60	914	12
3556	81	1755	84	1286	58	885	23
3007	53	1691	86	1194	15	708	86
2942	31	1628	84	1157	57	588	81
2914	44	1463	34	1114	4	582	84
2834	37	1458	32	1013	47	481	84
2106	86	1437	47	960	68		

Raman

METHOXYACETONITRILE

SDBSNO = 1214 C_3H_5NO

liquid

3012	32	963	14
2982	47	916	61
2942	88	867	78
2923	60	589	17
2835	95	543	10
2249	86	404	17
1457	35	358	39
1439	29		
1289	14		
1116	16		

WAVENUMBER (cm^{-1})
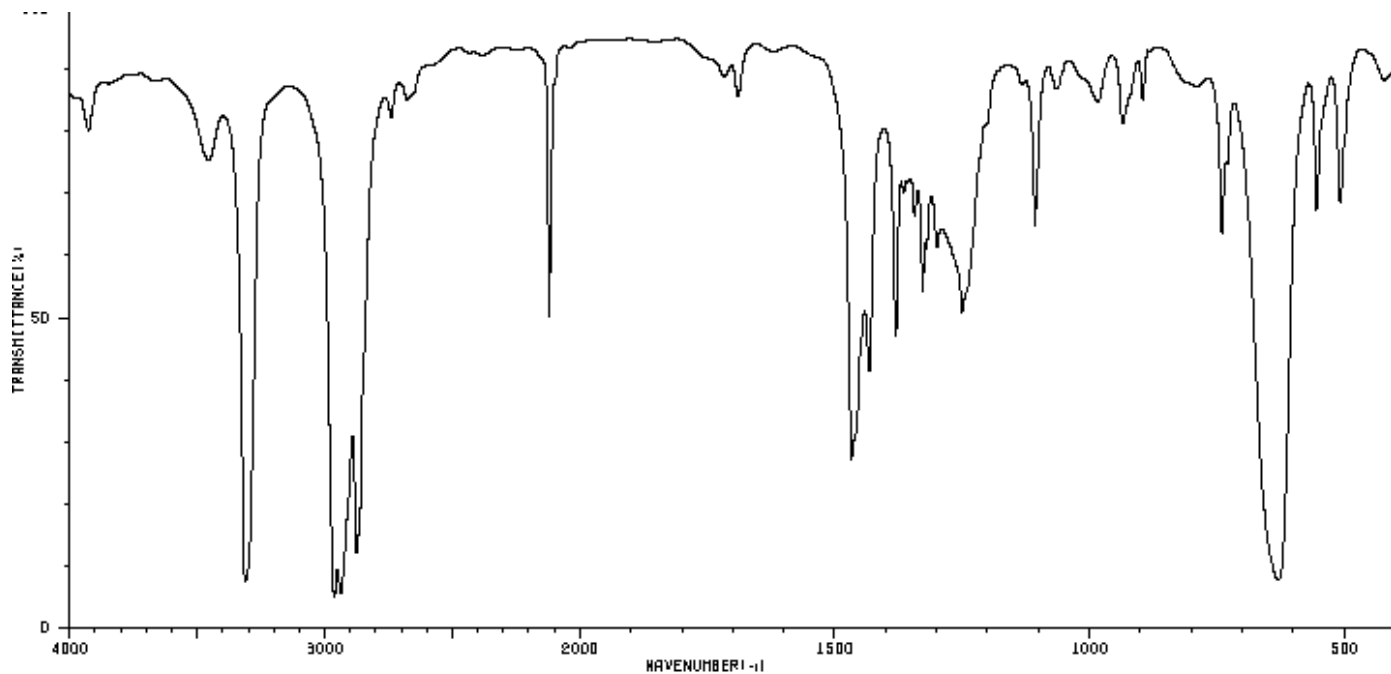
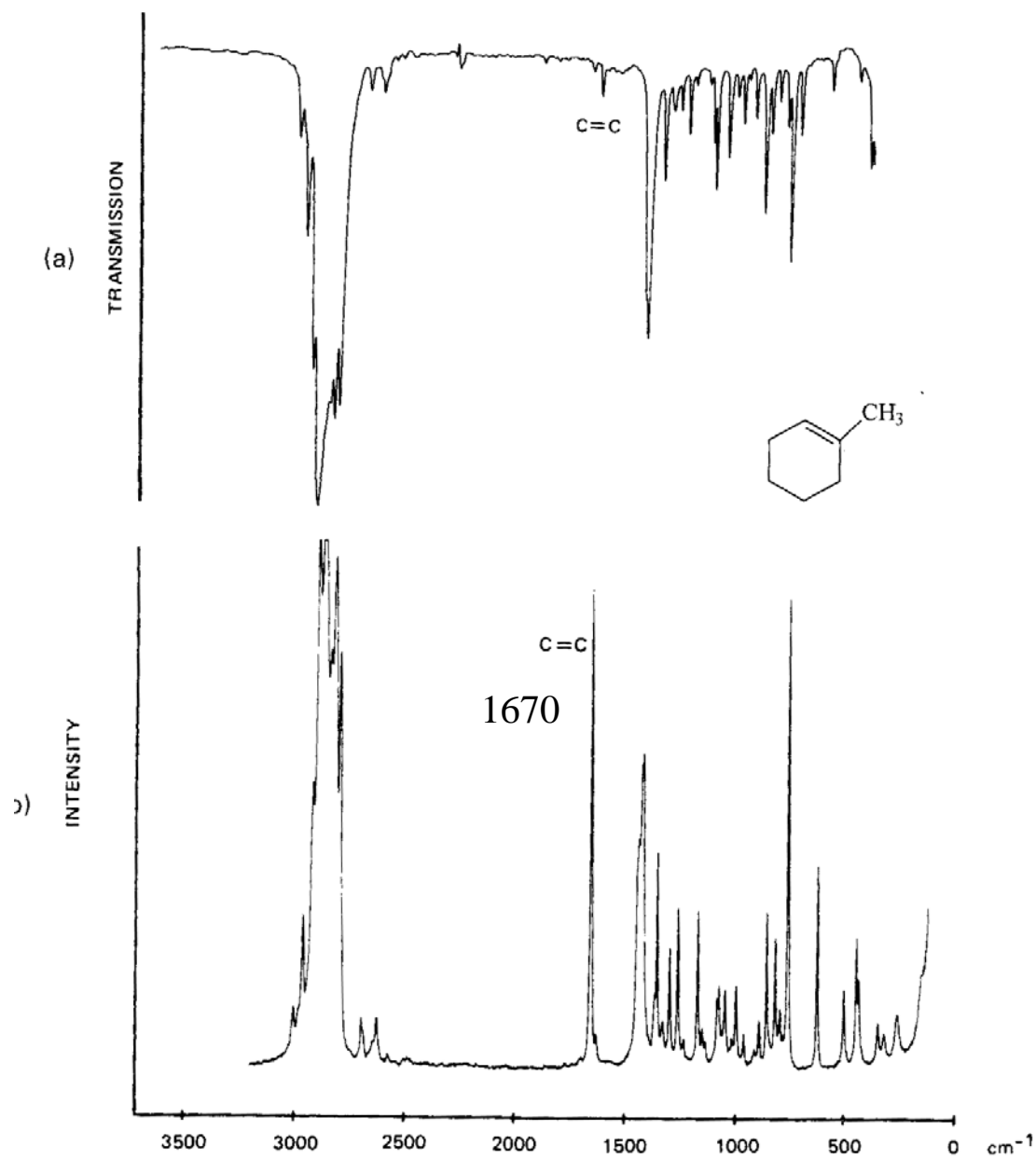|									
3926	77	2679	81	1432	39	1260	49	740	60
3455	72	2120	49	1380	46	1107	62	730	72
3311	7	2097	84	1366	86	1063	84	630	7
2962	4	1717	86	1344	64	983	81	666	64
2937	5	1690	81	1328	52	934	79	609	66
2876	11	1467	26	1320	56	895	61		
2738	29	1461	29	1300	58	793	84		

$$HC \equiv C - (CH_2)_3 - CH_3$$
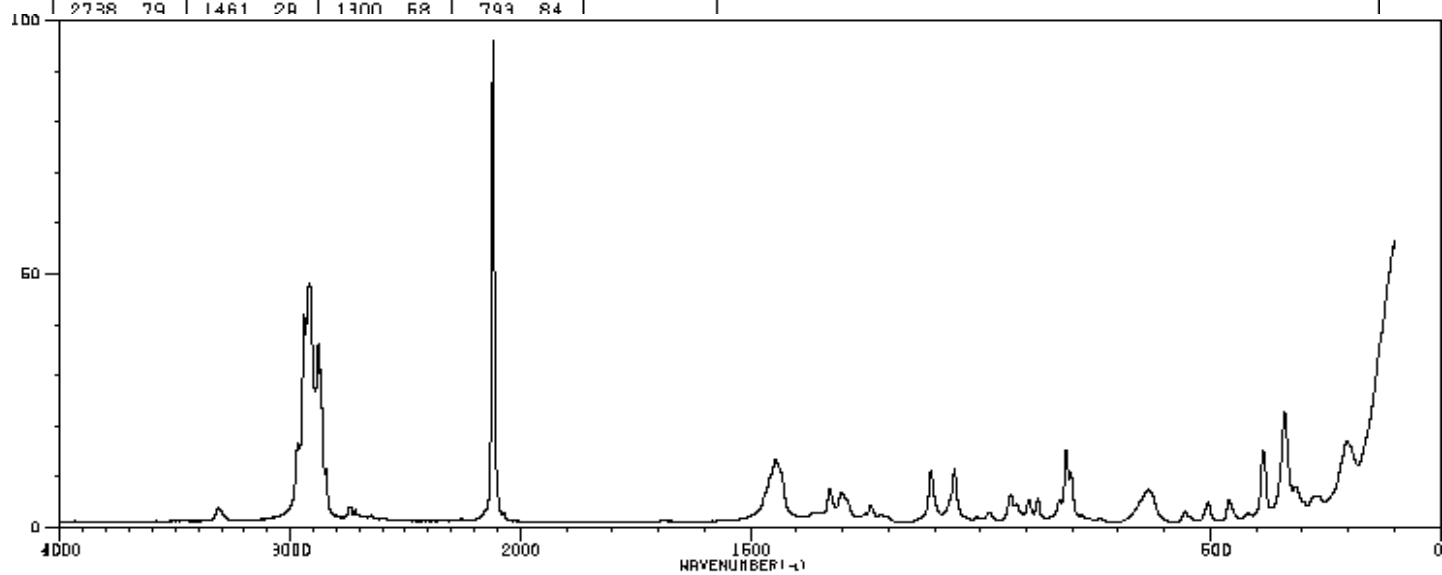
Figure 9-15 (a) Infrared and (b) Raman spectra of 1-methylcyclo-hexene.

Advantages of Raman over IR

• Water can be used as solvent.

○ Very suitable for biological samples in native state (because water can be used as solvent).

• Although Raman spectra result from molecular vibrations at IR frequencies, spectrum is obtained using visible light or NIR radiation.

=>Glass and quartz lenses, cells, and optical fibers can be used. Standard detectors can be used.

○ Few intense overtones and combination bands => few spectral overlaps.

• Totally symmetric vibrations are observable.

○ Raman intensities α to concentration and laser power.

Advantages of IR over Raman

- Simpler and cheaper instrumentation.

- Less instrument dependent than Raman spectra because IR spectra are based on measurement of intensity *ratio*.

- Lower detection limit than (normal) Raman.

- Background fluorescence can overwhelm Raman.

- More suitable for vibrations of bonds with very low polarizability (e.g. C–F).