

M.Sc., Physics, II Semester
Atomic & Molecular Physics
Unit-4 IR & Raman Spectroscopy

Dr. ANUJ KUMAR,

What is Spectroscopy?

- ▣ “seeing the unseeable”
- ▣ The study of how 'species' (i.e., atoms, molecules, solutions) react to electromagnetic radiation. Some studies depend on how much light an atom absorbs. The electromagnetic radiation absorbed, emitted or scattered by the molecule is analyzed.
- ▣ Spectroscopy is an analytical technique which helps determine structure.
- ▣ It destroys little or no sample.
- ▣ The amount of light absorbed by the sample is measured as wavelength is varied.

Types of Spectroscopy

- ▣ Infrared (IR) & Raman spectroscopy measures the bond vibration frequencies in a molecule and is used to determine the functional group.
- ▣ Mass spectrometry (MS) fragments the molecule and measures the masses.
- ▣ Nuclear magnetic resonance (NMR) spectroscopy detects signals from hydrogen atoms and can be used to distinguish isomers.
- ▣ Ultraviolet (UV) spectroscopy uses electron transitions to determine bonding patterns, Conjugation.

Useful spectroscopic regions

Wavelength (cm ⁻¹)	Regions	Cause
10 ⁸	γ (gamma)-ray	Change of nuclear configuration
10 ⁶	X-ray	Change of electron distribution
10 ⁴	Visible & ultraviolet	-do-
100	IR	Change of configuration
1	Microwave	Change of Orientation
10 ⁻²	Radiowave	E.S.R.
10 ⁻³	Radio	N.M.R.

Vibrational Spectroscopy

- ▣ It is an important method for the elucidation of polymer conformation.
- ▣ Widely used to identify polymers, their conformation, end groups, branching, cross linking, crystallinity, hydrogen bonding, fold structures, composition and sequence distribution in copolymers.
- ▣ Raman, IR and INS spectroscopic techniques are used for study.

Applications of Vibrational Spectroscopy

- Recognition of constituent **functional** groups
- Identification of the spectra of individual molecules
- Determination of the **molecular structure** of molecules
- Ascertain the **nature of interactions** between molecules
- Make **quantitative measurements** of structural components
- Measure orientation of molecules in a confined system

Vibrational Spectroscopy Basics

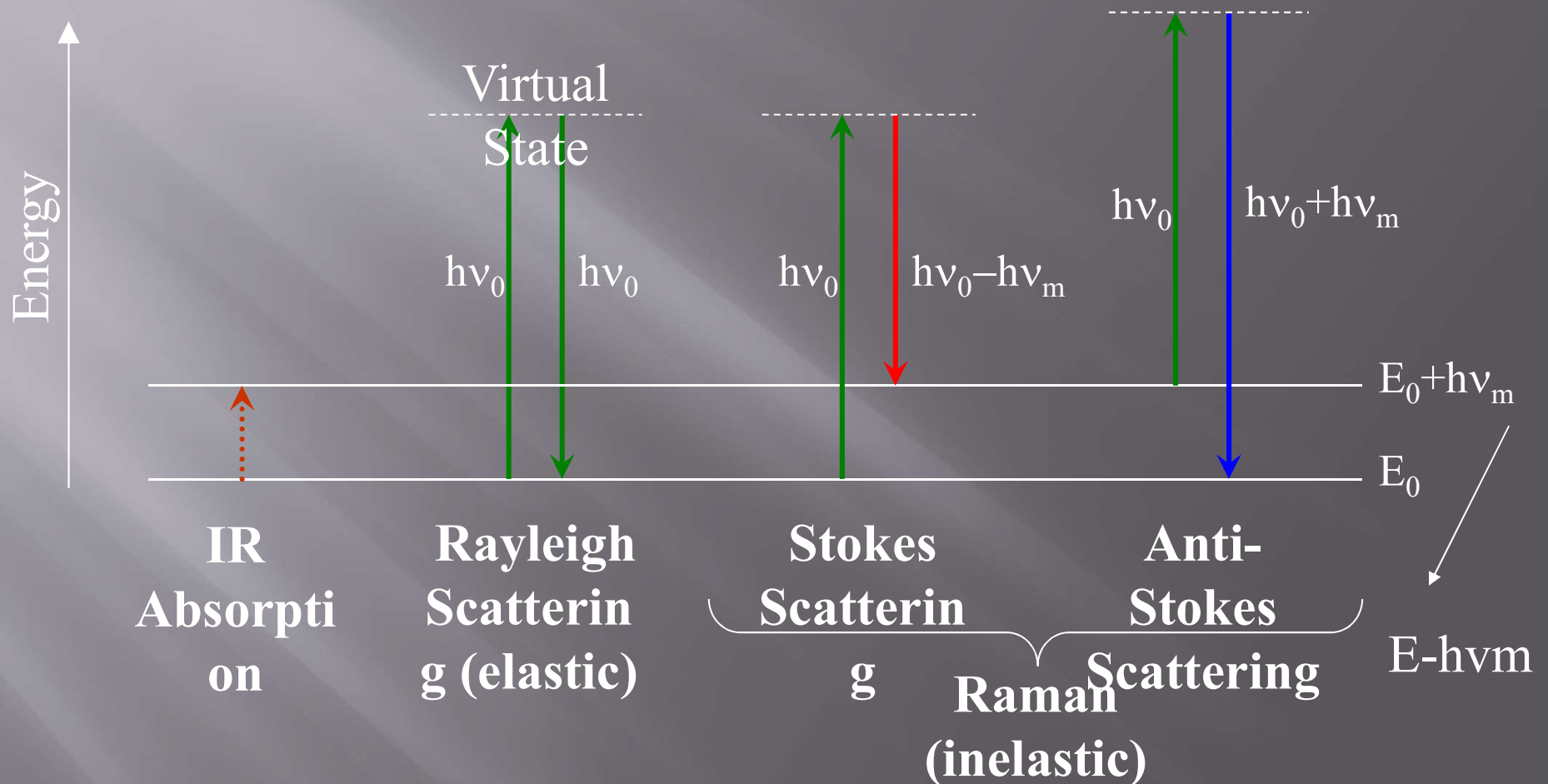
Infrared

- Absorption (1 photon)
- Change in dipole moment (O-H, N-H, C=O)
- Sample preparation necessary
- Non-aqueous samples

Raman

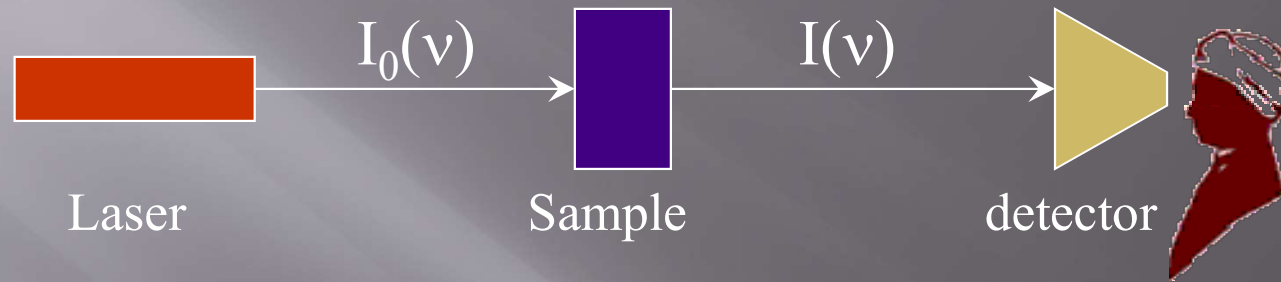
- Absorption & Emission (2 photon)
- Change in polarisability (C=C, S-S, aromatics)
- Little to no sample preparation necessary
- Aqueous and non-aqueous samples

Photon Absorption and Scattering

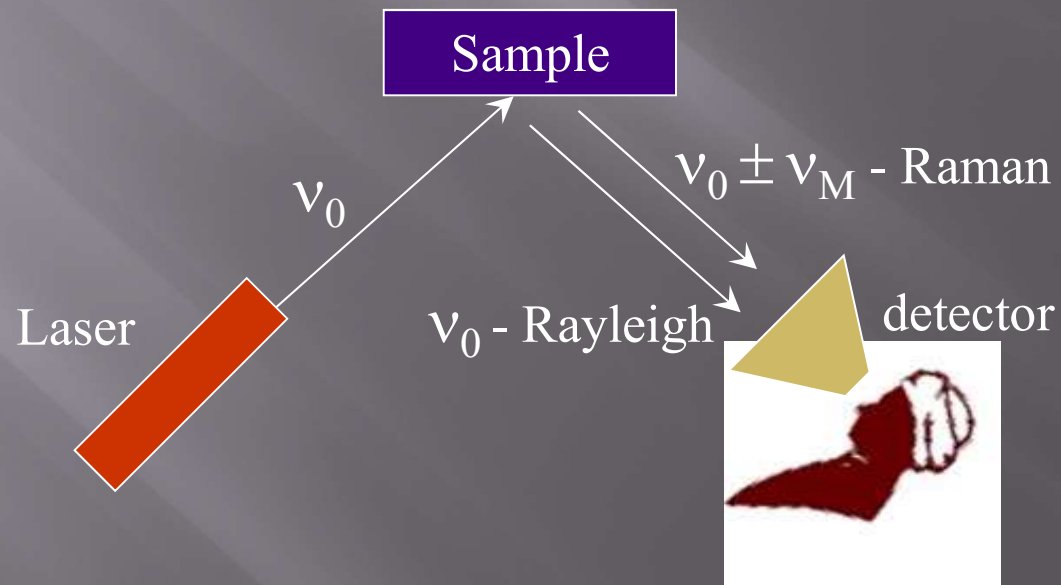


The Raman effect comprises a very small fraction, about 1 in 10^7 of the incident photons.

IR & Raman spectrography



IR Spectrography - Absorption



Raman Spectrography - Scattering

Selection Rules for IR

- ▣ The energy of IR radiation is insufficient to excite electronic transition, but does cause vibrational or rotational excitation.
- ▣ The electric field, E , of the IR radiation interacts with the electric field of the molecule (dipole moment, μ).
- ▣ Magnitude of dipole moment, μ , is determined by
 - Charge, δ^-
 - Separation of charge, s_e

$$\mu = \delta^- \times s_e$$

Selection Rules for IR

- ▣ The dipole moment of the molecule must change due to a vibration or rotation to absorb IR radiation:

$$\delta\mu/\delta q \neq 0$$

$$I_{ir}^{1/2} = \delta\mu/\delta q$$

- ▣ The direction of the dipole change must be the same as the direction of the electric field vector: The vectors E and μ are coupled.
- ▣ The frequency of the light must be identical to the frequency of the vibration: $E = h\nu$
- ▣ Molecules with permanent dipole moments are IR active (e.g. H-Cl, H₂O).

Selection Rules for Raman

- ▣ The process of inducing a dipole is called polarisation P , and the degree to which the electron cloud is distorted is referred to as an atom's (or molecule's) polarisability, α .

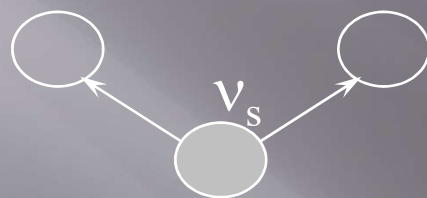
$$P = \alpha E$$

- ▣ The induced dipole moment must change the polarisability of the molecule during the vibration.

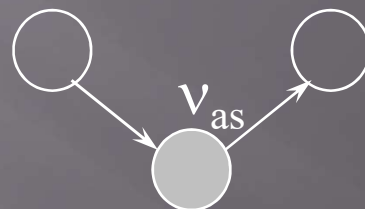
$$\frac{\delta\alpha}{\delta q} \neq 0$$

- ▣ Band intensity depends upon the extent of polarisability change.

Types of Molecular Vibrations

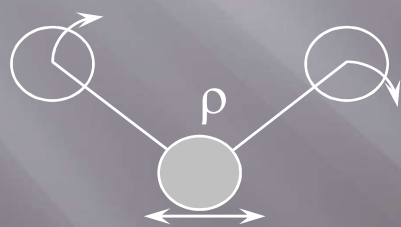


Symmetric



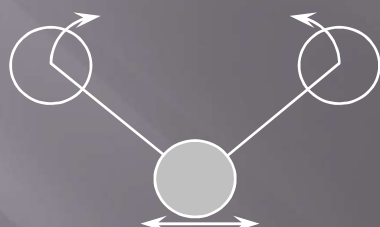
Antisymmetric

Stretch: Change in Bond Length.

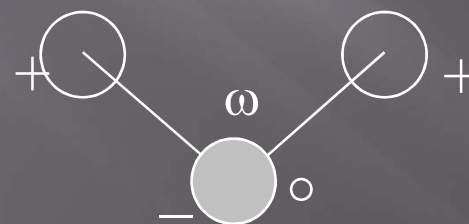


Rockin

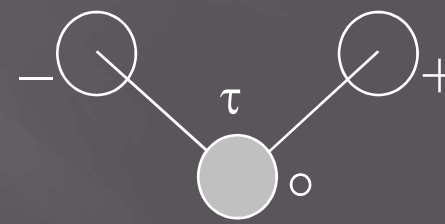
ρ



Scissoring



Wagging



Twisting

Bend: Change in Bond Angle.

Vibrational Modes

- ▣ **Fundamental:**
 - At R.T. most molecules are in the ground state ($n=0$).
 - A transition from the lowest vibrational state to a vibrationally excited state produces a fundamental band ($n=0 \Rightarrow 1$).
- ▣ **Overtone:**
 - Transitions to higher excited states produce overtone bands ($n=0 \Rightarrow 2$).
 - These overtone bands are weaker than fundamental bands.
- ▣ **Combination:**
 - A transition in which more than one vibration changes its degree of excitation.
- ▣ **Hot Band:**
 - A transition that originates in an excited vibrational state.

Vibrational Regions

- ▣ Far-IR Region
 - Molecular rotations
 - 200-10 cm^{-1}
 - 50-1000 μm
- ▣ Mid-IR Region
 - Fundamental molecular vibrations
 - 4000-200 cm^{-1}
 - 2.5-50 μm
- ▣ Near-IR Region
 - Overtones and combinations of IR
 - 12800-4000 cm^{-1}
 - 0.78-2.5 μm

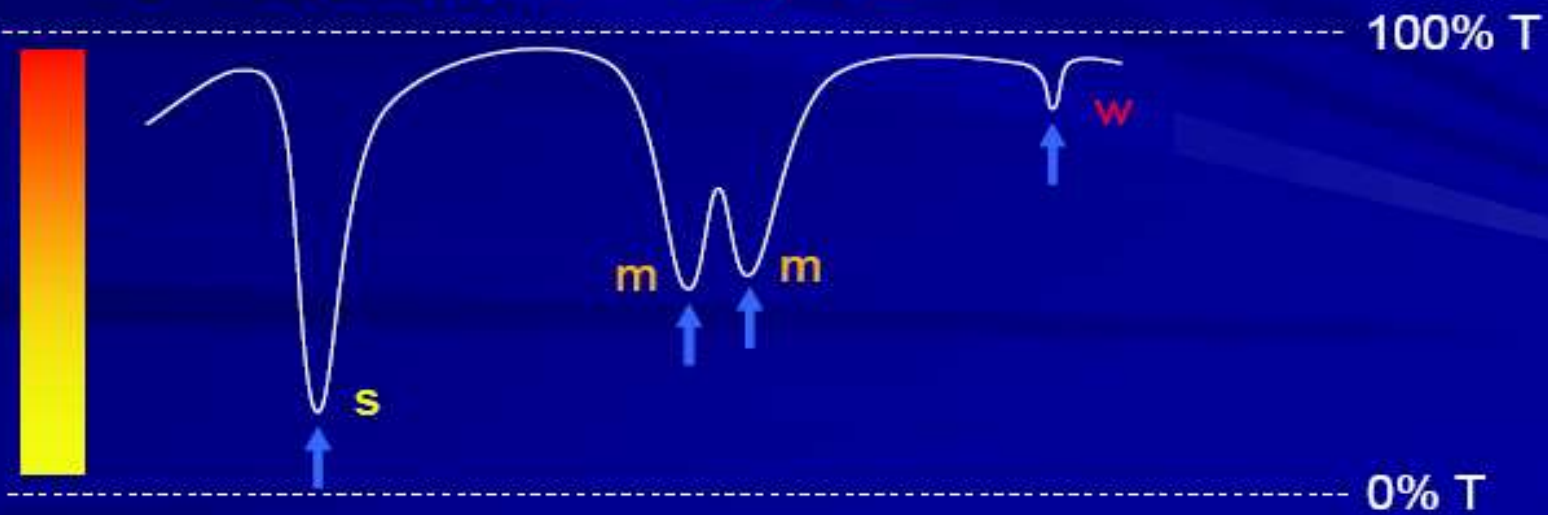
Factors Influencing Vibrational Frequency

- ▣ Mass of attached atom
 - As the mass increases the wavenumber decreases.
e.g. C-H, C-C, C-O, C-I
3000, 1200, 1100, 500 cm^{-1}
- ▣ Strength of chemical bond
 - As bond strength increases so does the wavenumber.
e.g. C-C, C=C, C≡C
1200, 1650, 2150 cm^{-1}
- ▣ Hybridization
 - Bonds are stronger in the order $sp > sp^2 > sp^3$.
- ▣ Resonance
 - Conjugation lowers the energy required for the bond to vibrate.
e.g. Isolated α,β -unsaturated, and $\alpha,\beta,\gamma,\delta$ -unsaturated ketones,
1715, 1690, 1675 cm^{-1}

Infrared Spectrum

Record

- Wave number location of IR “band” (position of max %T)
- Intensity of IR “band”
 - s = strong (low %T), m = medium, w = weak (high %T)
 - vs = very strong, vw = very weak



Energy Trends

- Energy follows vibration frequency of atoms

- Light atoms vibrate more rapidly

- CH, NH, OH vibrations $> 2800 \text{ cm}^{-1}$

- Multiple bonds vibrate more rapidly

- Triple bonds

- C \equiv C (2100-2200) C \equiv N (2240-2280)

- Double bonds

- C=O (1680-1750) C=C (1620-1680)

- Single bonds

- C–O (1025-1200)

- Stretching $>$ Bending $>$ Wagging/Twisting

Fingerprint Region ($< 1500 \text{ cm}^{-1}$)

- Many bands & *many overlaps*

- Heavy atom stretches
- All bends, etc.

Should have simple molecule (or *other* evidence for structure) before *interpreting* bands in this region

- Overall pattern reflects molecular structure

Pattern from 1400-600 = “molecular fingerprint”

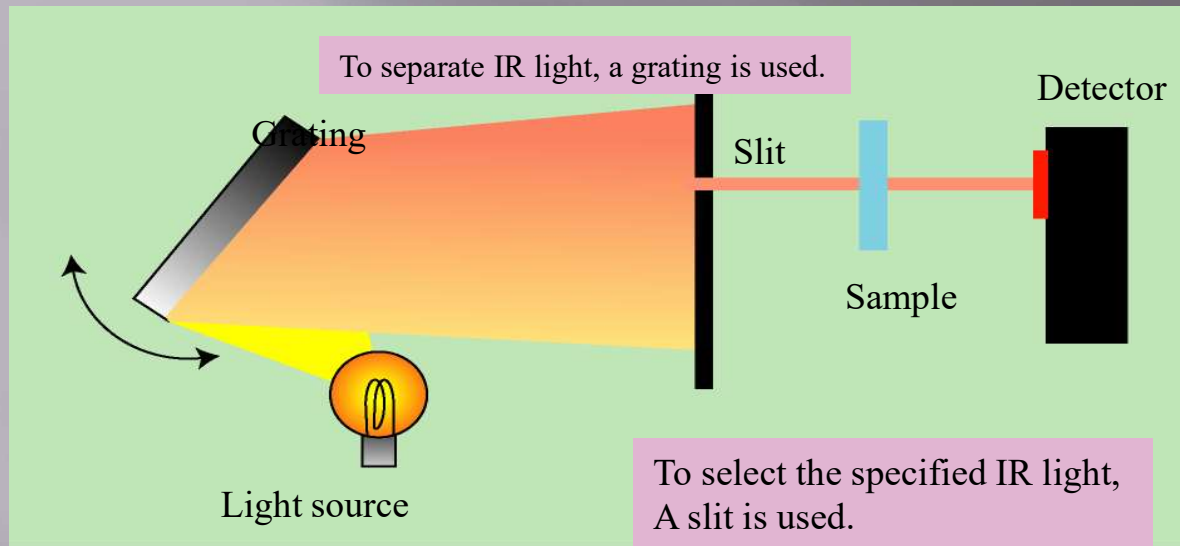
Intensity Trends

- Follows change in dipole caused by vibrating atoms
 - Polar bonds (strong bond dipoles) absorb strongly
 - O–H
 - C=O, C≡N
 - C–O
 - Nonpolar bonds absorb weakly
 - C≡C, C=C
- Follows # overlapping bands
 - CH bands tend to overlap
 - Molecules contain many CH
 - CH absorptions tend to be strong

FT-IR Spectrometer

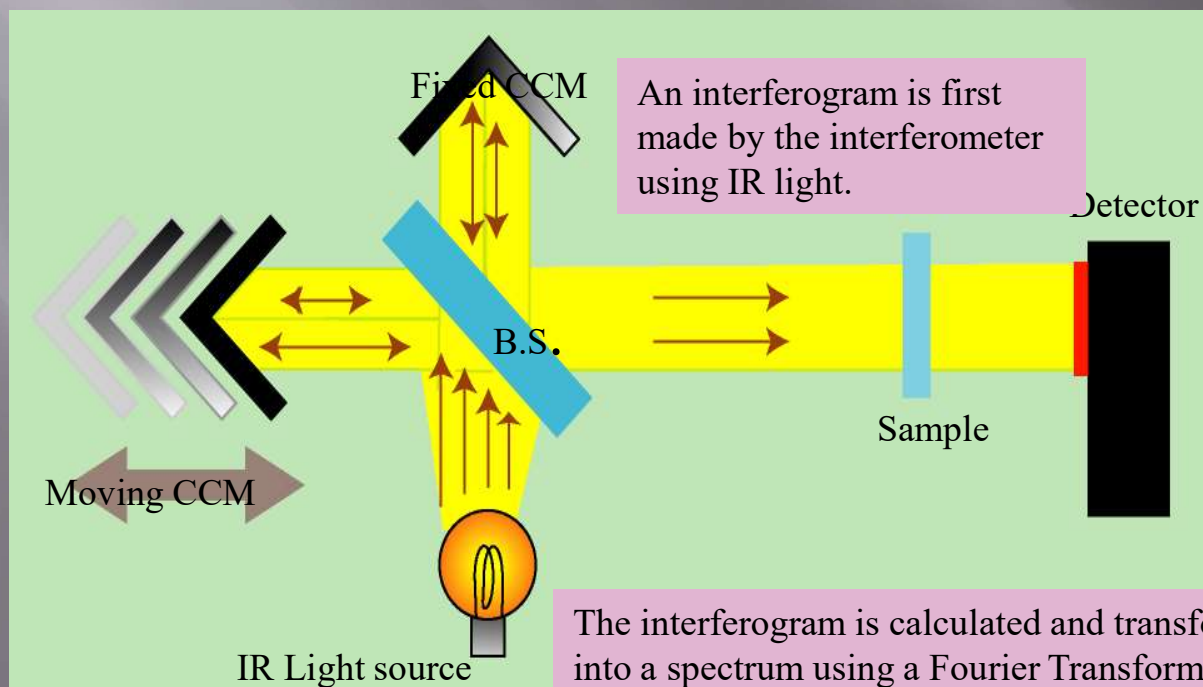
- ▣ Uses an interferometer.
- ▣ Has better sensitivity.
- ▣ Less energy is needed from source.
- ▣ Completes a scan in 1-2 seconds.
- ▣ Takes several scans and averages them.
- ▣ Has a laser beam that keeps the instrument accurately calibrated.

Comparison Between Dispersion Spectrometer and FTIR



Dispersion Spectrometer

In order to measure an IR spectrum, the dispersion Spectrometer takes several minutes. Also the detector receives only a few % of the energy of original light source.



FTIR

In order to measure an IR spectrum, FTIR takes only a few seconds. Moreover, the detector receives up to 50% of the energy of original light source. (much larger than the dispersion spectrometer.)

Principal

For monochromatic illumination

$$I(x) = \frac{1}{2}I_0(u)T(u)(1 + \cos 2\pi x u)$$

For polychromatic

$$I(x) = \frac{1}{2}\int I_0(u)T(u) du + \frac{1}{2}\int I_0(u)T(u) \cos 2\pi x u du$$

Fourier transform of $I_0(u)T(u)$

Advantage: Multiplex or Fellgett advantage

2. Throughput or Jacquinot advantage

Carbon-Carbon Bond Stretching

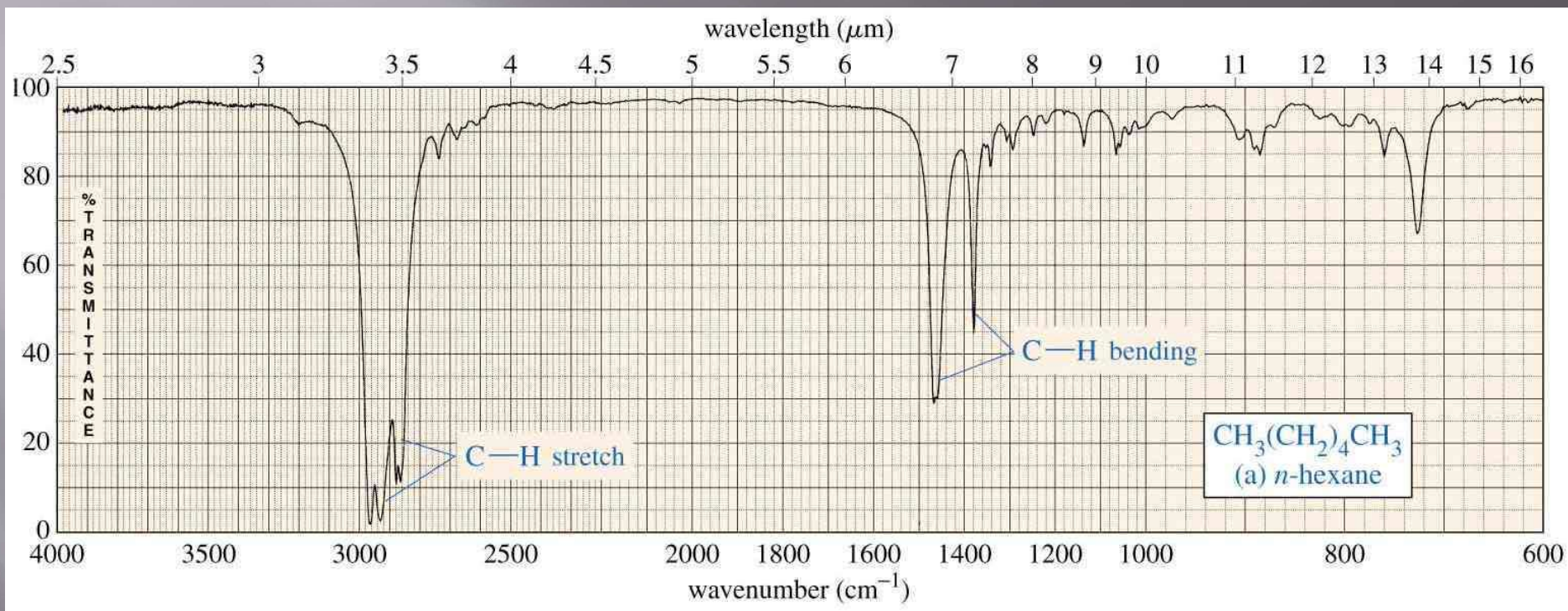
- ▣ Stronger bonds absorb at higher frequencies:
 - C-C 1200 cm^{-1}
 - C=C 1660 cm^{-1}
 - C \equiv C 2200 cm^{-1} (weak or absent if internal)
- ▣ Conjugation lowers the frequency:
 - isolated C=C 1640-1680 cm^{-1}
 - conjugated C=C 1620-1640 cm^{-1}
 - aromatic C=C approx. 1600 cm^{-1}

Carbon-Hydrogen Stretching

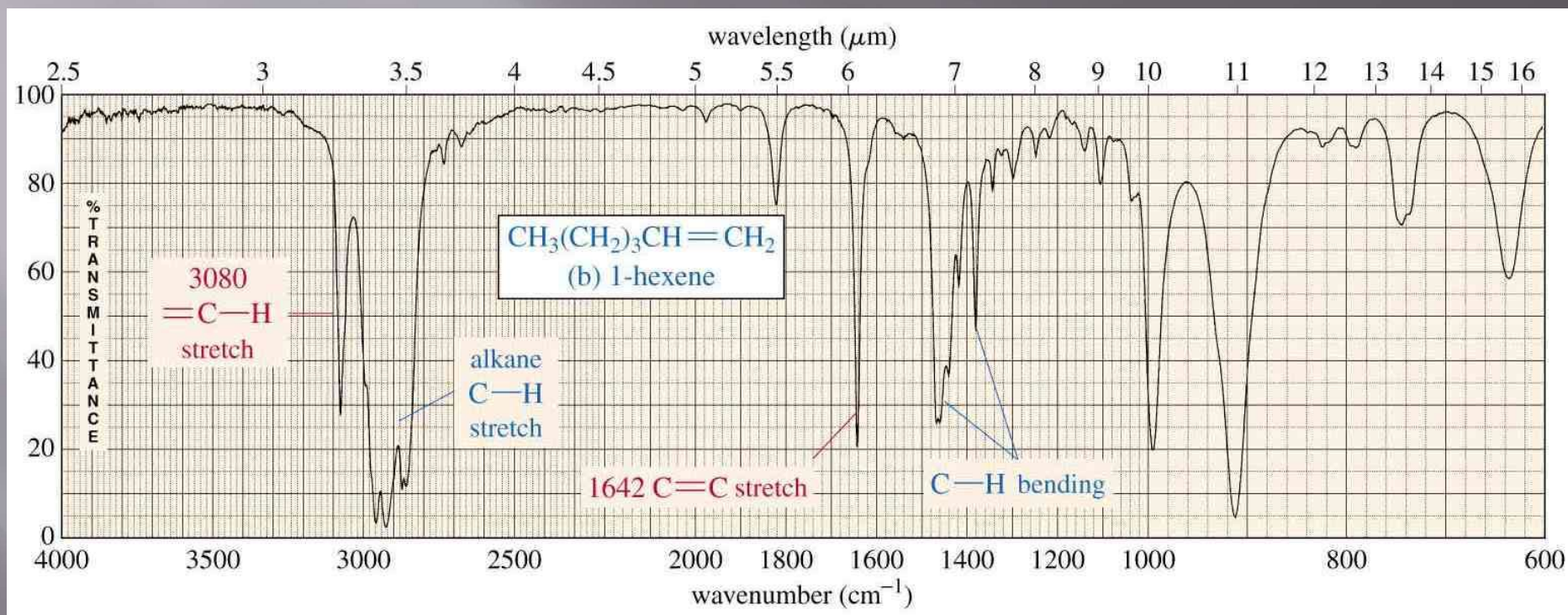
Bonds with more *s* character absorb at a higher frequency.

- sp^3 C-H, just below 3000 cm^{-1} (to the right)
- sp^2 C-H, just above 3000 cm^{-1} (to the left)
- sp C-H, at 3300 cm^{-1}

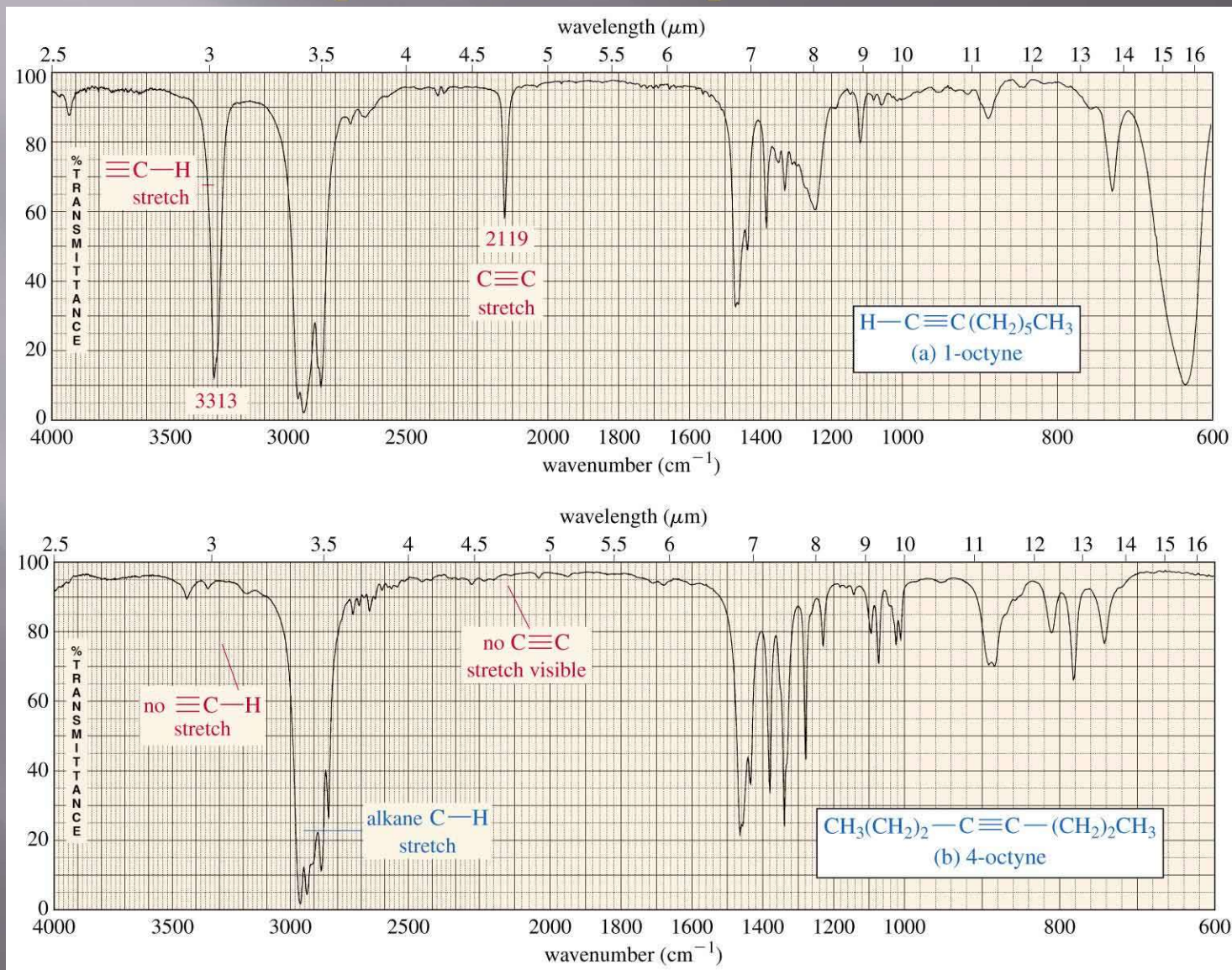
An Alkane IR Spectrum



An Alkene IR Spectrum



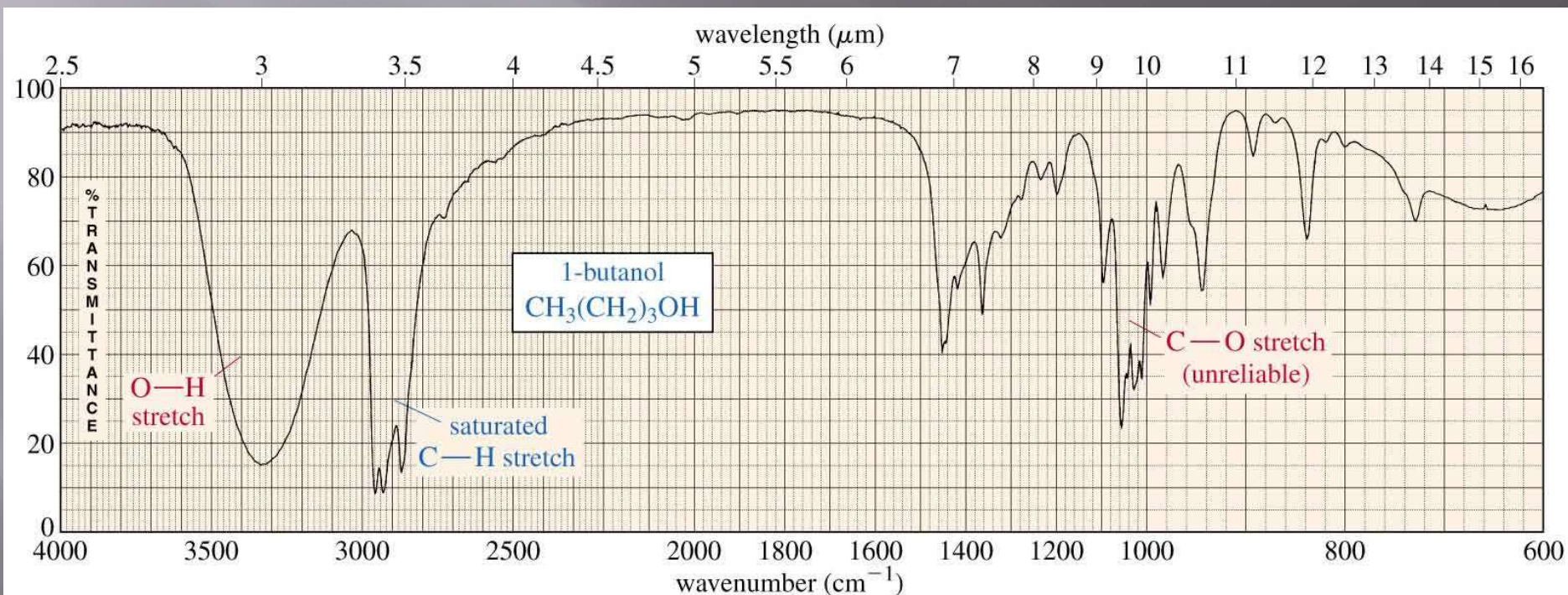
An Alkyne IR Spectrum



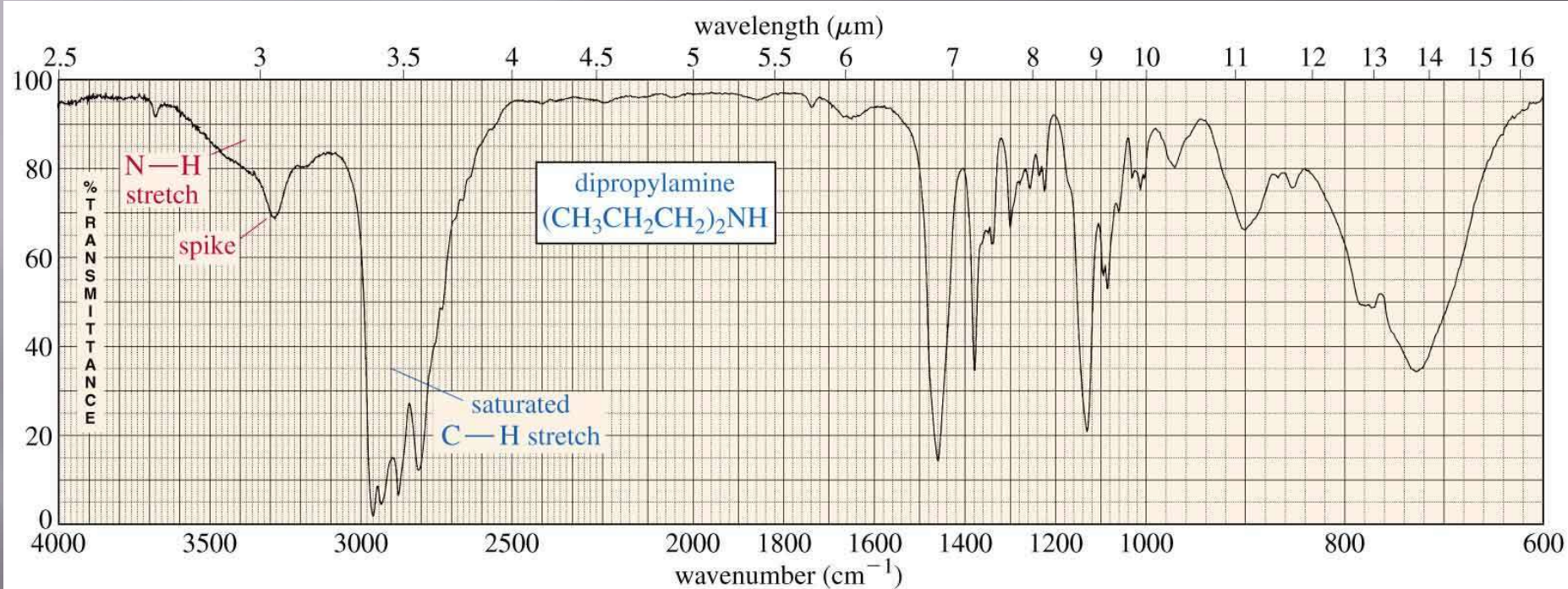
O-H and N-H Stretching

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

An Alcohol IR Spectrum



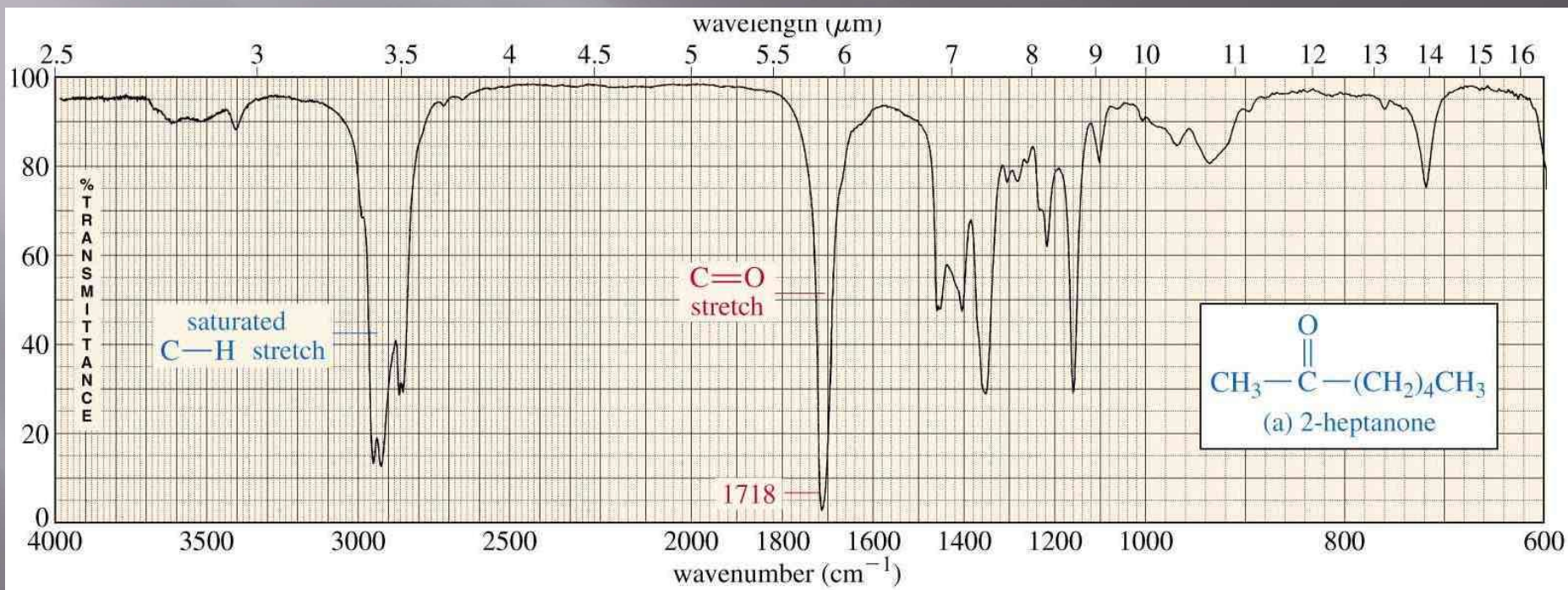
An Amine IR Spectrum



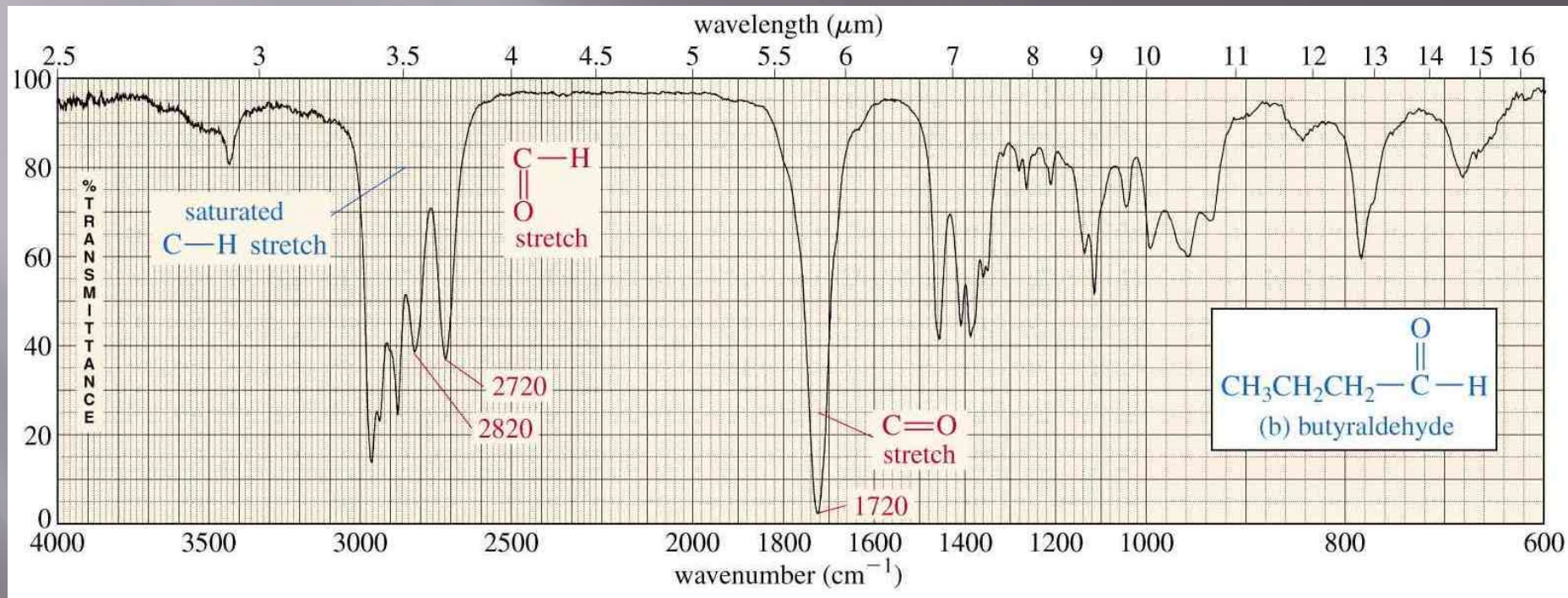
Carbonyl Stretching

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

A Ketone IR Spectrum

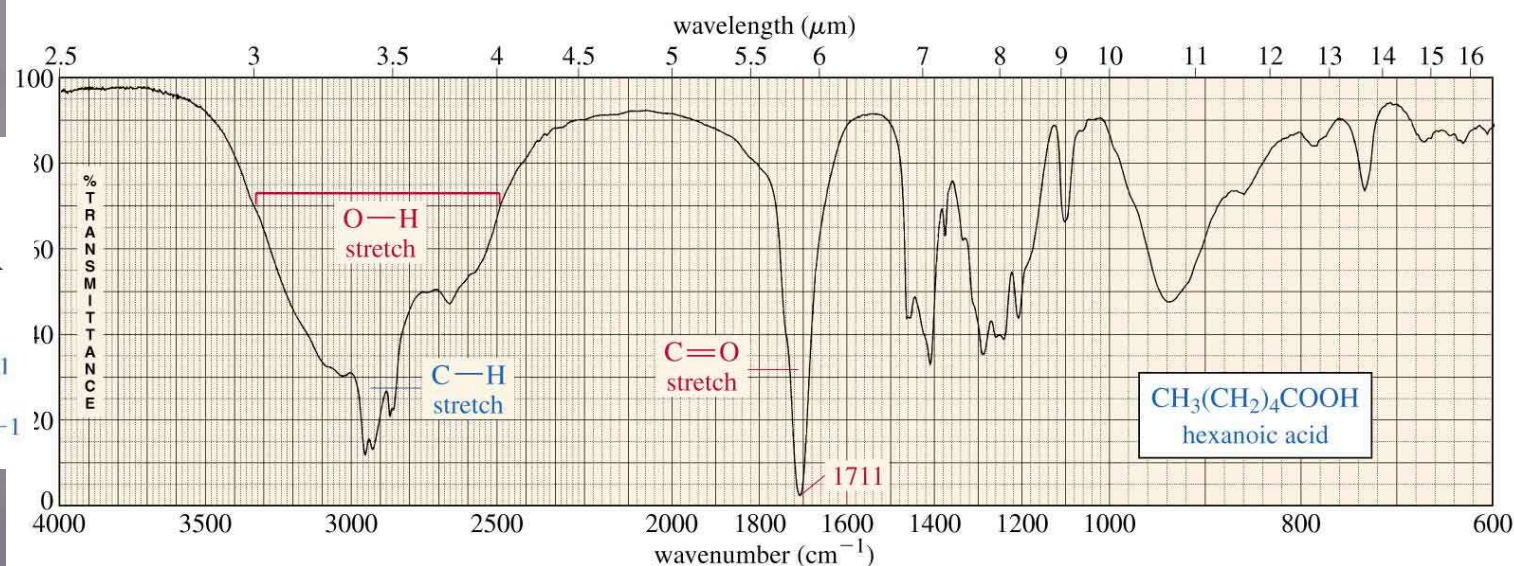
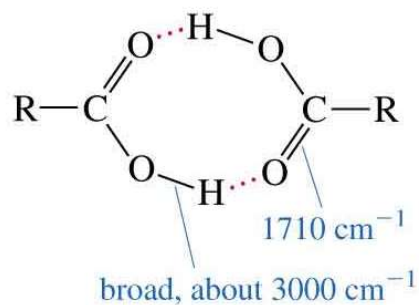


An Aldehyde IR Spectrum



O-H Stretch of a Carboxylic Acid

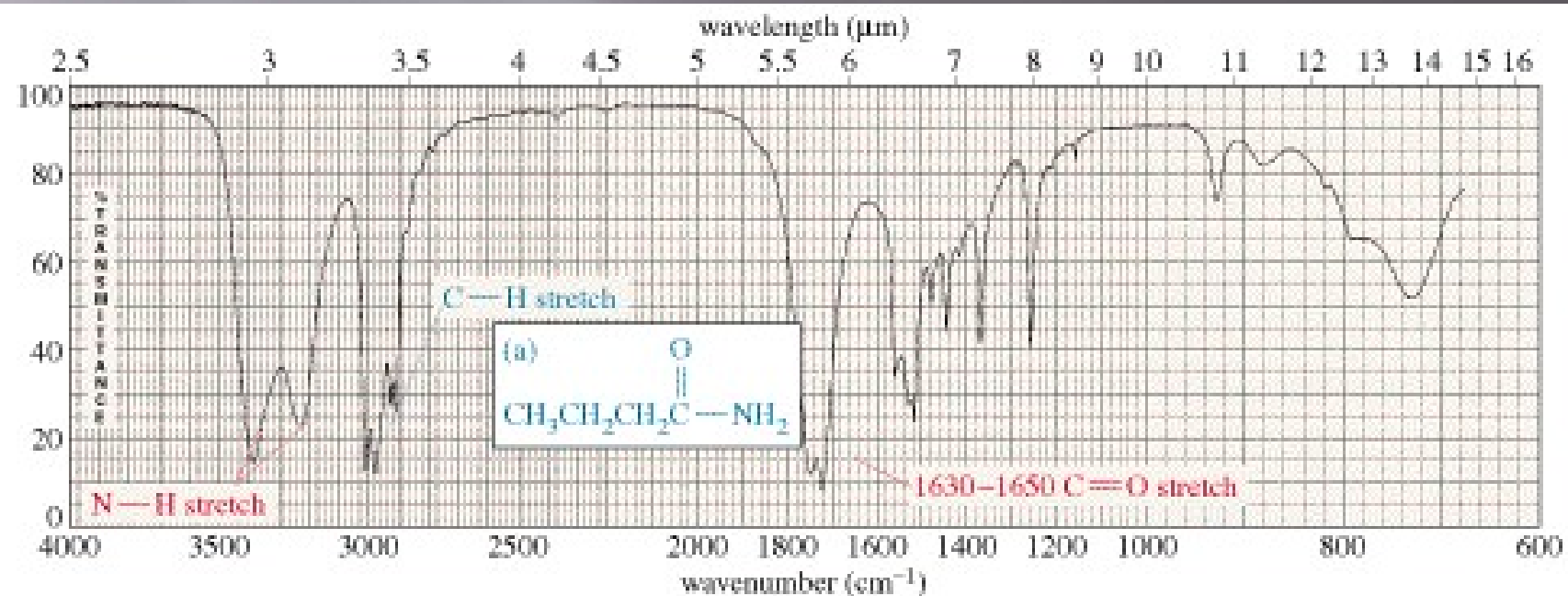
This O-H absorbs broadly, 2500-3500 cm^{-1} , due to strong hydrogen bonding.



Variations in C=O Absorption

- ▣ Conjugation of C=O with C=C lowers the stretching frequency to $\sim 1680\text{ cm}^{-1}$.
- ▣ The C=O group of an amide absorbs at an even lower frequency, $1640\text{-}1680\text{ cm}^{-1}$.
- ▣ The C=O of an ester absorbs at a higher frequency, $\sim 1730\text{-}1740\text{ cm}^{-1}$.
- ▣ Carbonyl groups in small rings (5 C's or less) absorb at an even higher frequency. =>

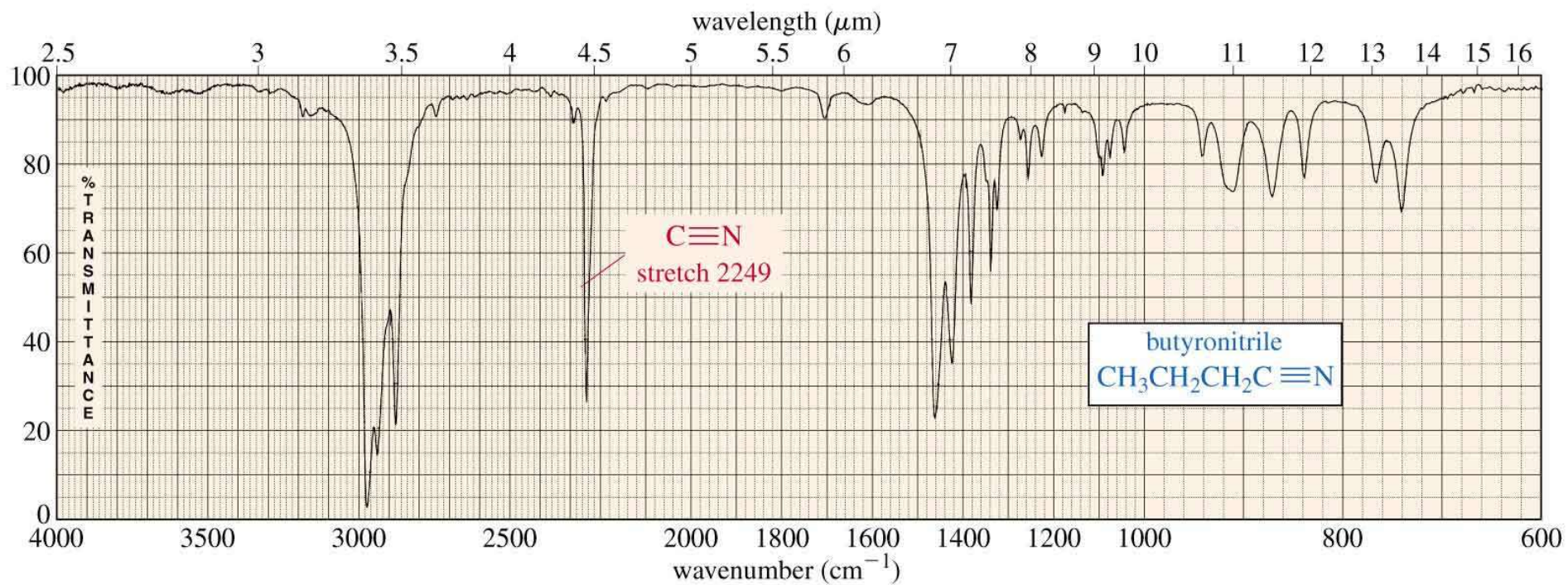
An Amide IR Spectrum



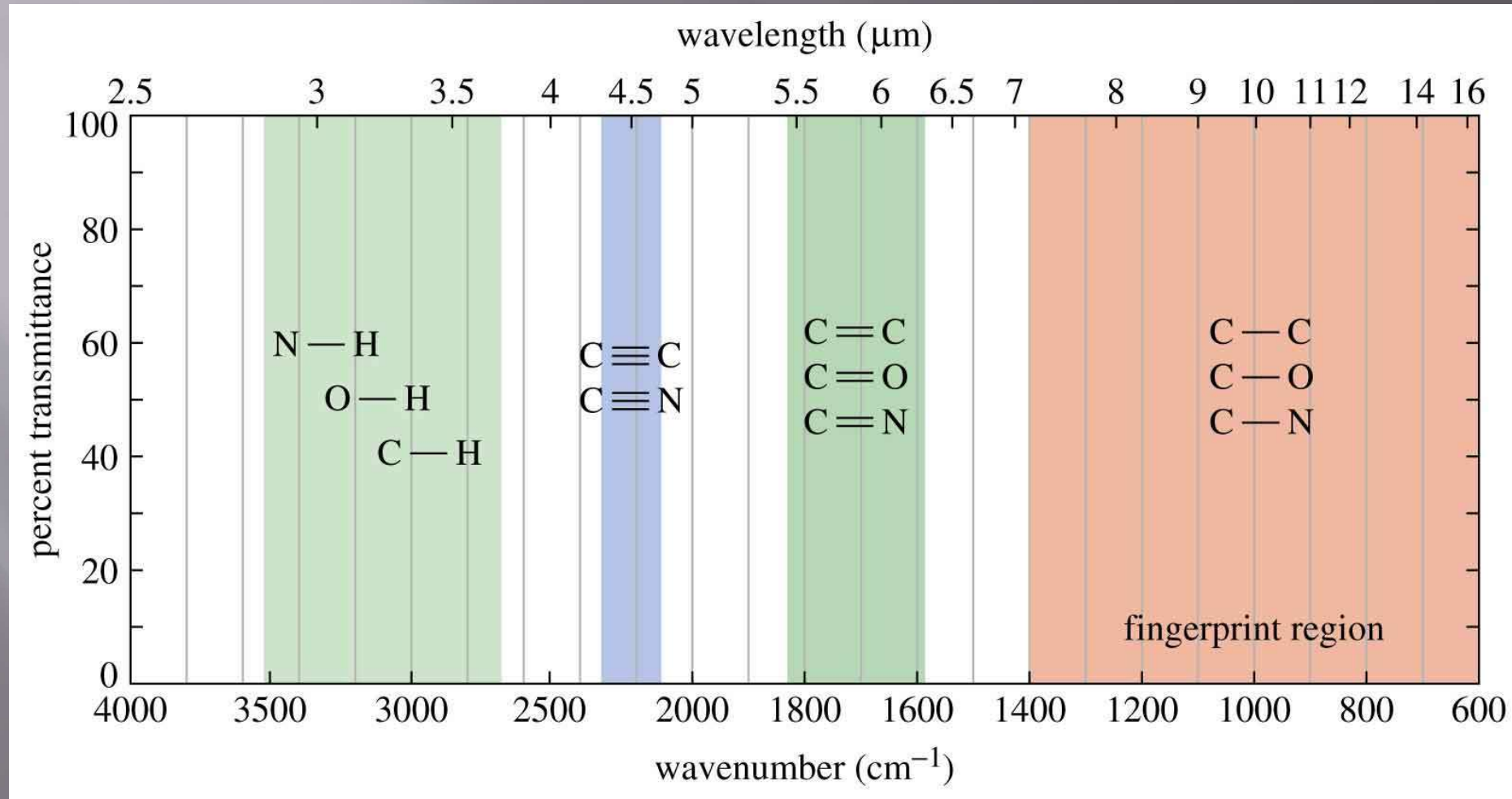
Carbon - Nitrogen Stretching

- ▣ C - N absorbs around 1200 cm^{-1} .
- ▣ C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region.
- ▣ C \equiv N absorbs strongly just *above* 2200 cm^{-1} . The alkyne C \equiv C signal is much weaker and is just *below* 2200 cm^{-1} .

A Nitrile IR Spectrum



Summary of IR Absorptions



Characteristic IR absorptions of some functional Groups

Functional Group	Absorption (cm^{-1})	Intensity	Functional Group	Absorption (cm^{-1})	Intensity
Alkane			Amine		
C-H	2850-2960	Medium	N-H	3300-3500	Medium
Alkene			C-N	1030-1230	Medium
=C-H	3020-3100	Medium	Carbonyl compound		
C=C	1640-1680	Medium	C=O	1670-1780	Strong
Alkyne			Carboxylic acid		
≡C-H	3300	Strong	O-H	2500-3100	Strong, broad
C≡C	2100-2260	Medium	Nitrile		
Alkyl halide			C=N	2210-2260	Medium
C-Cl	600-800	Strong	Nitro		
C-Br	500-600	Strong	NO ₂	1540	Strong
Alcohol					
O-H	3400-3650	Strong, broad			
C-O	1050-1150	Strong			
Arene					
C-H	3030	Weak			
Aromatic ring	1660-2000	Weak			
	1450-1600	Medium			

Sir Chandrashekhara Venkata Raman



- ❑ November 7, 1888-November 21, 1970
- ❑ Won the Noble Prize in 1930 for Physics
- ❑ Discovered the "Raman Effect"
- ❑ Besides Discovering the Raman Effect, He studied extensively in X-Ray Diffractions, Acoustics, Optics, Dielectrics, Ultrasonics, Photo electricity, and colloidal particles.

Raman Spectroscopy

Raman effect is a 2-photon scattering process

These processes are inelastic scattering:

Stokes scattering: energy lost by photon:



Photon in

Photon out

No vibration

Vibration

Anti-Stokes scattering: energy gained by photon:



Photon in

Photon out

Vibration

No vibration

But dominant process is elastic scattering:

Rayleigh scattering



Photon in

No vibration



Photon out

No vibration

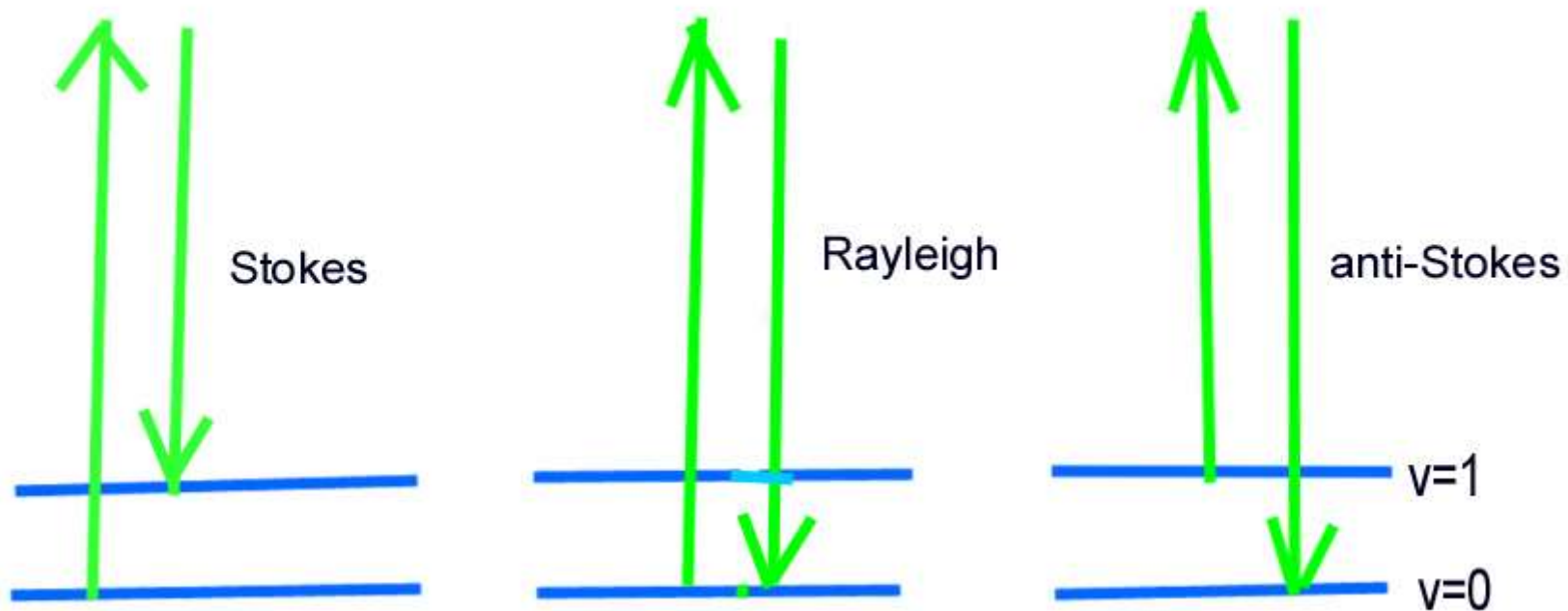
If incident photon energy E ; vibration energy ν , then
in terms of energy, photon out has energy:

$E - \nu$ Stokes scattering

$E + \nu$ anti-Stokes scattering

E Rayleigh scattering

Representation in terms of energy levels:



Arrow up = laser photon in; Arrow down = Raman scattering out

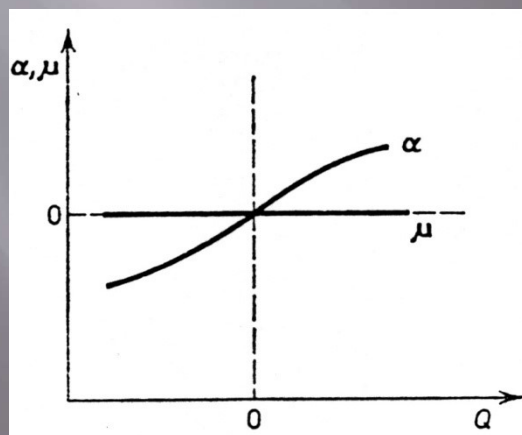
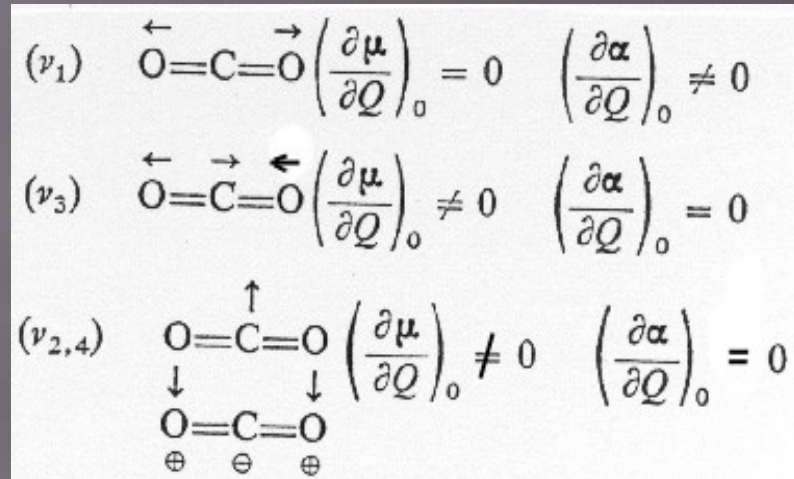
Example: There are 4 normal modes of CO₂. Only ν_1 is Raman active

μ is dipole moment;

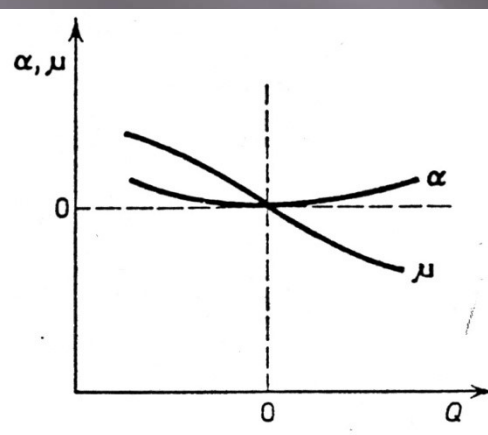
α is polarizability;

Q is vibration coordinate, The slopes

are measured at $Q = 0$ (I.e. at the equilibrium position).



ν_1



ν_3

Change in dipole moment, μ , and polarizability, α , during CO₂ vibrations

Uses of Raman Spectroscopy

Raman spectroscopy has become more widely used since the advent of FT-Raman systems and remote optical fibre sampling. Previous difficulties with laser safety, stability and precision have largely been overcome.

Basically, Raman spectroscopy is complementary to IR spectroscopy, but the sampling is more convenient, since glass containers may be used and solids do not have to be milled or pressed into discs.

Instrumentation

Dispersive Raman instruments

Laser → Sample → Double or triple monochromator



signal processing and output ← Photomultiplier tube

The monochromators are required to separate the weak Raman signal from the intense, nearby Rayleigh scattering. Typical lasers are Ar⁺ (e.g. green line, 514.5 nm) or Kr⁺ (e.g. yellow line, 530.9 nm).

Fourier transform Raman spectrometer

The Raman instrument can be on the same bench as the FTIR. Often, a YAG:Nd³⁺ laser (1064 nm) is used to excite the sample, so that the excitation energy is lower than the absorption band energies of organic systems. Fluorescence is then minimized.

Instruments may be combined with a microscope, or optical fibre, so that scanning over a few (microns)² of surface area, and Raman mapping is easily performed.

Special types of Raman spectroscopy

(see Hollas, Modern Spectroscopy, Wiley)

Resonance Raman (RR) scattering

When the laser excitation frequency is near (or coincident) with an electronic absorption band, intensity enhancement can occur by a factor of 10^2 - 10^6 , compared with normal Raman scattering. Electronic transitions are often localized in one part of a molecule, so that RR provides information about vibrations of the chromophore, especially those exhibiting a large change in geometry between the two electronic states.

RR is used in analytical chemistry to achieve detection limits 10^{-6} - 10^{-8} M.

Surface enhanced Raman spectroscopy (SERS):

Raman scattering is enhanced (typically by 10^3 - 10^6 times) when the analyte is adsorbed on colloidal metallic surfaces,

e.g. on colloidal Ag prepared by reduction of Ag^+ with citrate, in particle size range 25-500 nm.

Stimulated Raman scattering (SRS)

The Raman scattering from a laser is observed in the forward direction from the sample (i.e. in the same direction, or at a small angle to the incident laser radiation).

Vibrational progressions are observed for certain modes.

Coherent anti-Stokes Raman spectroscopy (CARS)

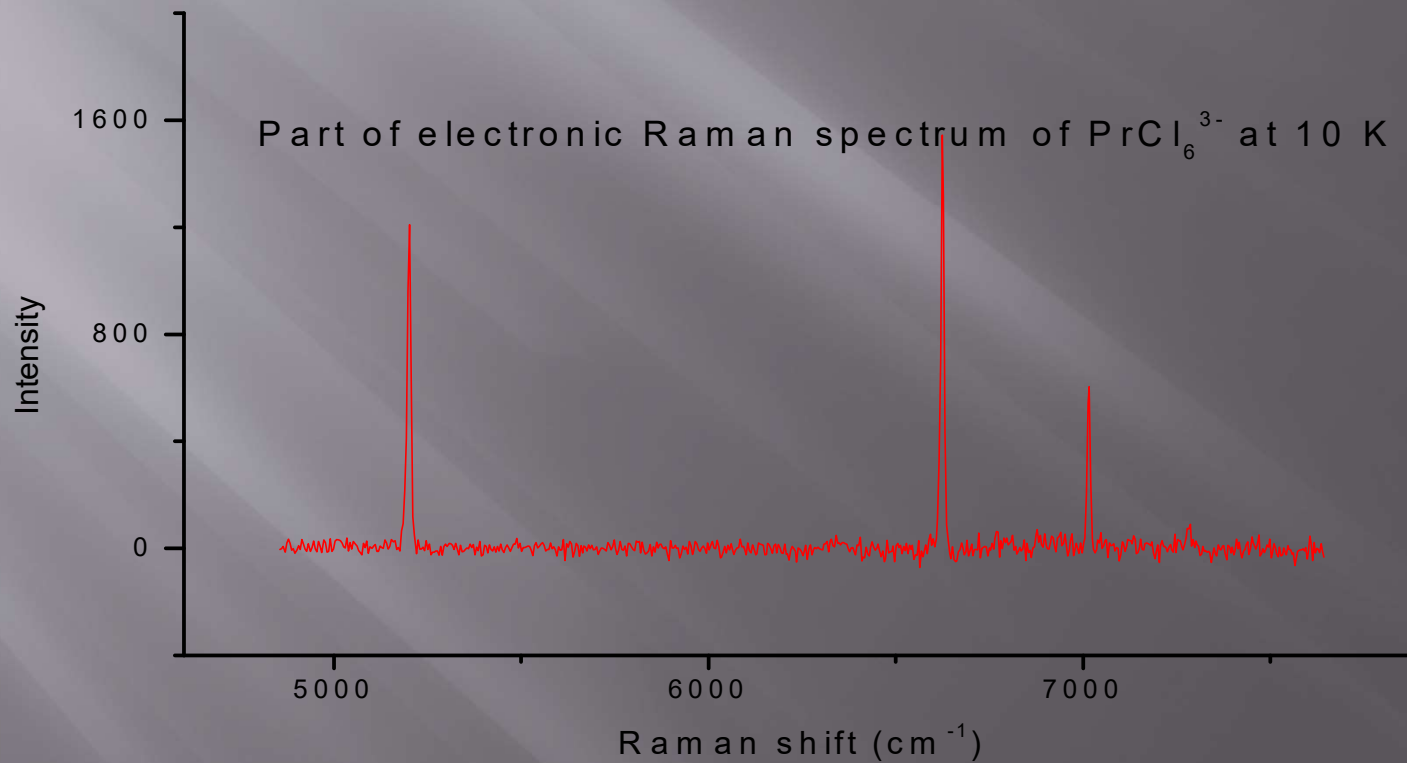
Radiation from two lasers is incident on the sample, and the intensity of the outgoing wave energy gives information about the vibrational modes of the sample.

Hyper-Raman spectroscopy

Very weak scattering at twice the laser frequency, $2\nu_0$, is called Hyper-Rayleigh scattering. Similarly, Stokes and anti-Stokes hyper-Raman scattering occur at $2\nu_0 \pm \nu_{\text{vib}}$, where ν_{vib} is a vibration frequency. The selection rules differ from those of Raman scattering.

Electronic Raman scattering

Raman scattering can occur from electronic states, as well as from vibrations. At room temperature the bands are very broad, and merge into the background. At low temperatures (<80 K), the bands sharpen, and give information about the energies of electronic states of the molecule.



Thank You !