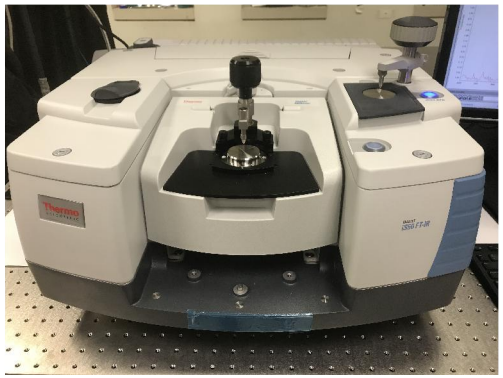
Principle and Application of FT-IR



Xinqi Chen, PhD

Research Associate Professor

Department of Mechanical Engineering

NUANCE-Keck-II Manager

Northwestern University

Safety:

- Never leave your samples in the facility after your session
- Report abnormal issues immediately
- Safety training on chemicals, compressed gas, LN, etc.

Acknowledgment:

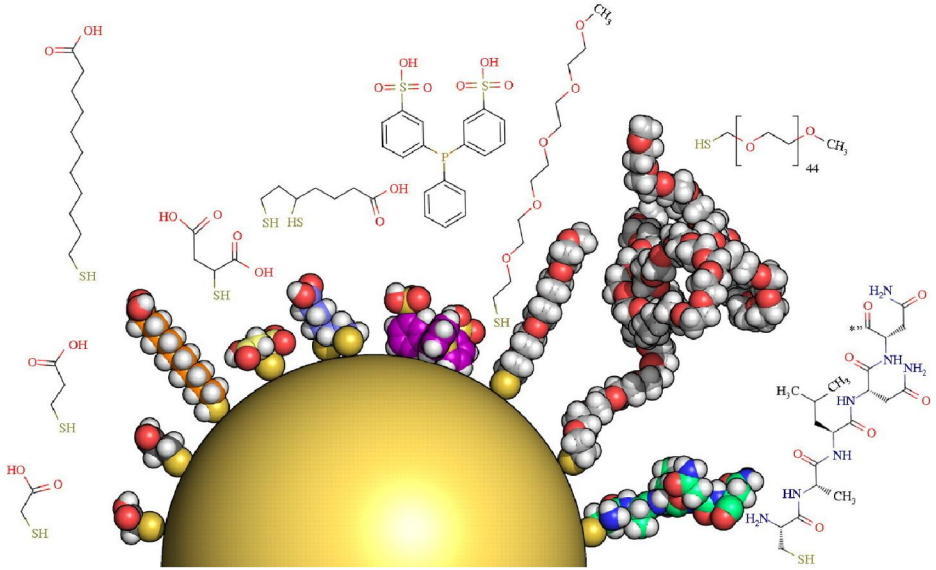
Publications which result from research that made use of the Keck-II facility's instruments should include the following acknowledgments:

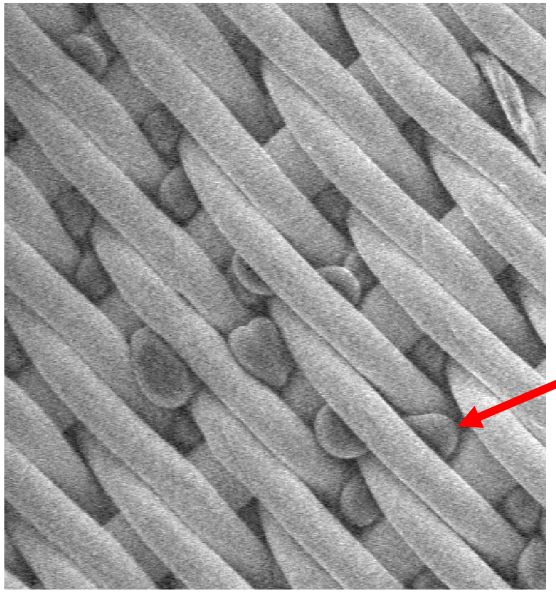
"This work made use of the Keck-II facility of Northwestern University's NUANCE Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the MRSEC program (NSF DMR-1720139) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN."

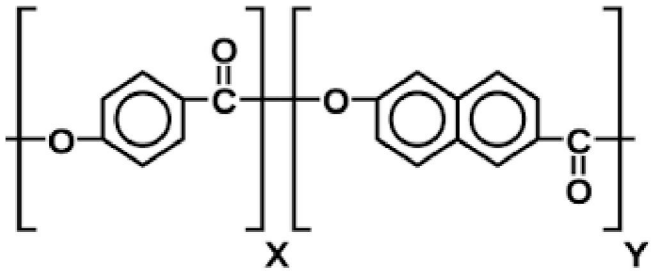
Outline

- Chemical bond and molecular vibration
- Instrumentation
- Data interpretation
- Methods

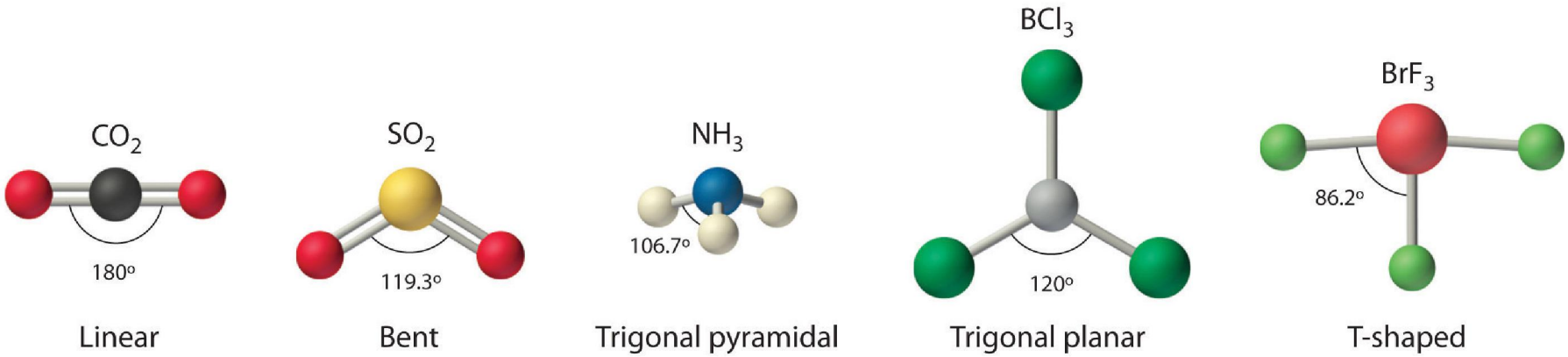
Why FT-IR?







Molecular Vibration-1

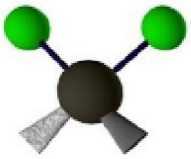


Covalent bond is not static.

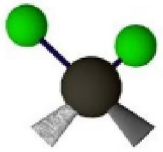
Molecular Vibration-2

Stretching

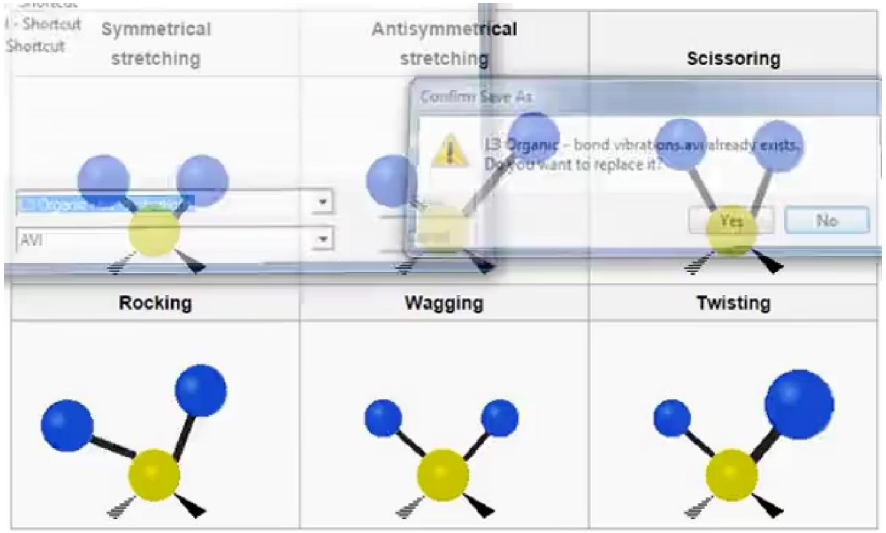
(The bond length changes)



SYMMETRIC STRECHING

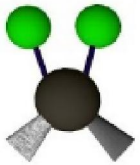


ANTISYMMETRIC STRECHING

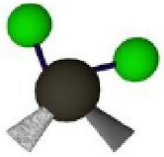


Bending

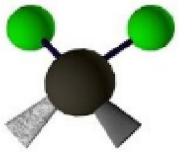
(The bond angle changes)



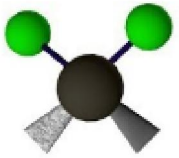
SCISSORING



ROCKING



WAGGING

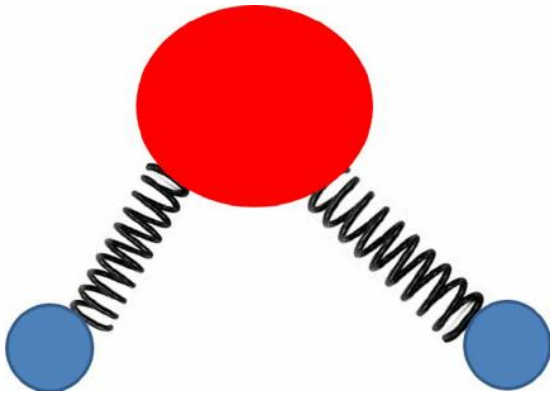


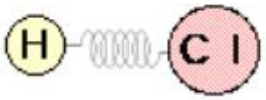
TWISTING

Spring Model of Chemical Bond

Infrared light and a molecule only interact when the dipole moment of the molecule changes due to vibration.

Spring between two spheres



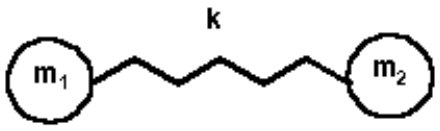


Heteronuclear diatomic molecules : HCl, CO Infrared active

Homonuclear diatomic molecules : O_2, H_2, N_2, and CL_2 Infrared inactive

Bond Vibration Frequency

Hookes' Law



$$\bar{\upsilon} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \mu = \frac{m_1 . m_2}{m_1 + m_2}$$

$\bar{\upsilon}$ = frequency

μ = reduced mass

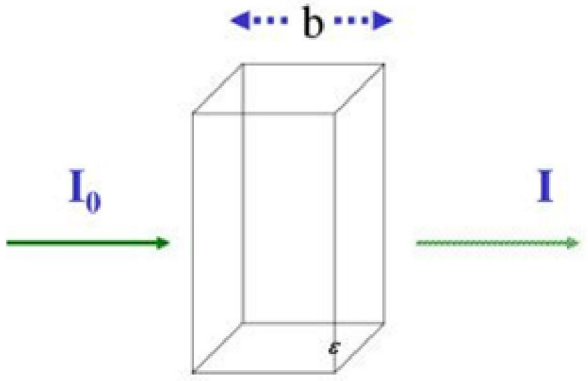
1. for a stronger bond (larger k value), wave number increases.

As examples of this, in order of *increasing bond strength* compare:
CC bonds: C-C (1000 cm^{-1}), C=C (1600 cm^{-1}) and C≡C (2200 cm^{-1}),
CH bonds: C-C-H (2900 cm^{-1}), C=C-H (3100 cm^{-1}) and C≡C-H (3300 cm^{-1}),

2. for heavier atoms attached (larger m value), wave number decreases.

As examples of this, in order of *increasing reduced mass* compare:
C-H (3000 cm^{-1})
C-C (1000 cm^{-1})
C-Cl (800 cm^{-1})
C-Br (550 cm^{-1})
C-I (about 500 cm^{-1})

Beer–Lambert Law



$$A_T = \varepsilon_1 b c_1$$

I_0 = Incident beam intensity

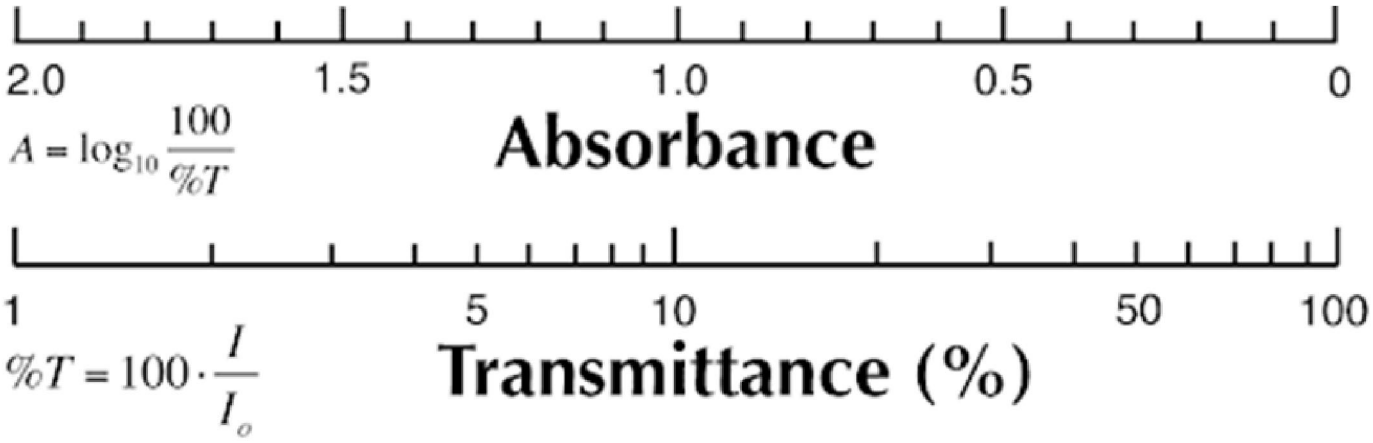
I = Transmitted beam intensity

A = Absorbance = $- \log_{10} I / I_0$

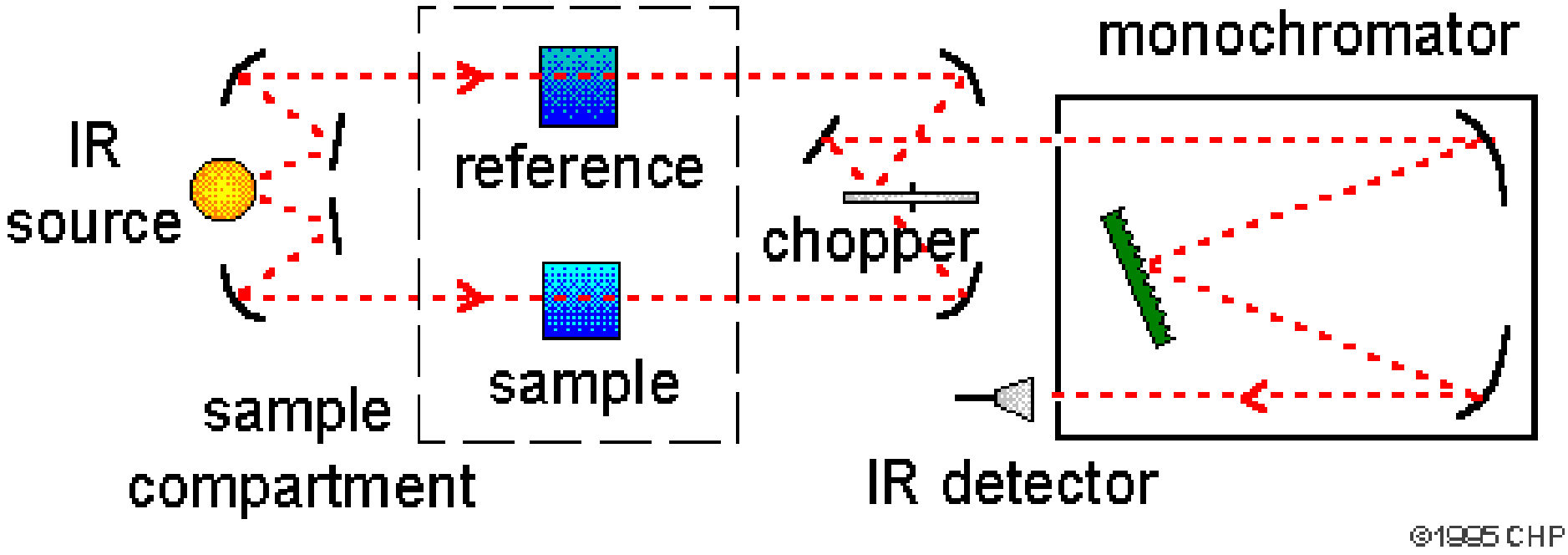
b = Optical path length

c = Solution Concentration (M/L)

ε = Molar Absorptivity (L/M cm)

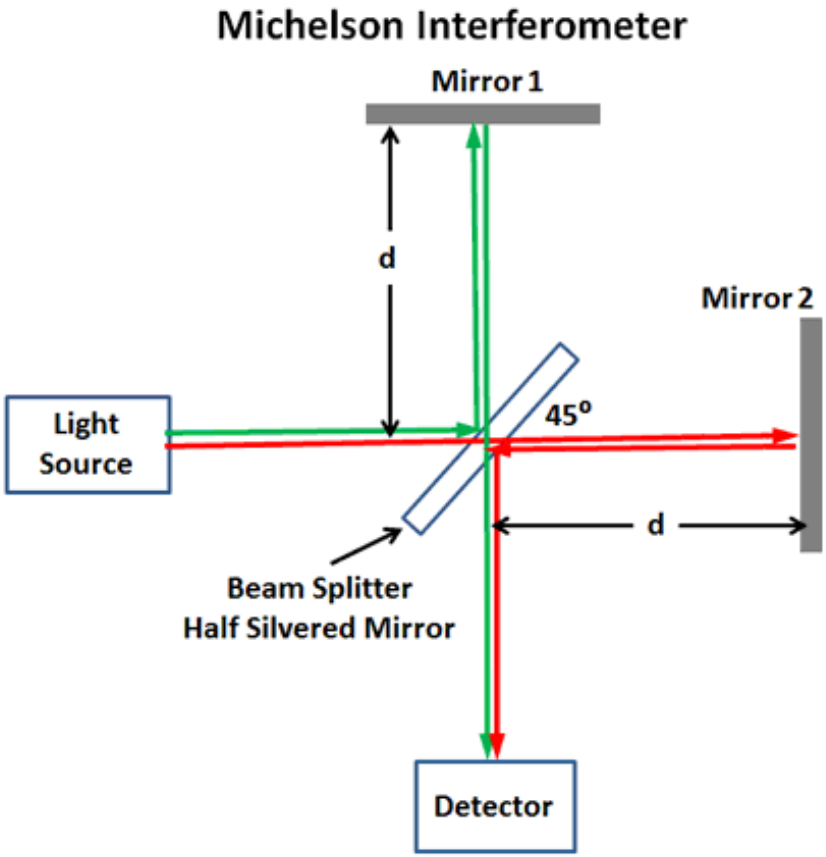


Dispersive IR spectrometer

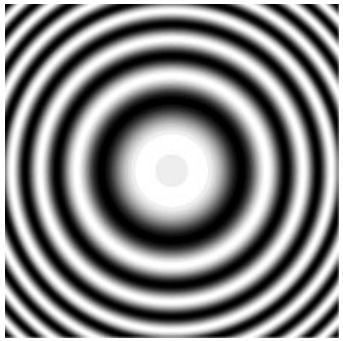


Data collection is very time consuming.

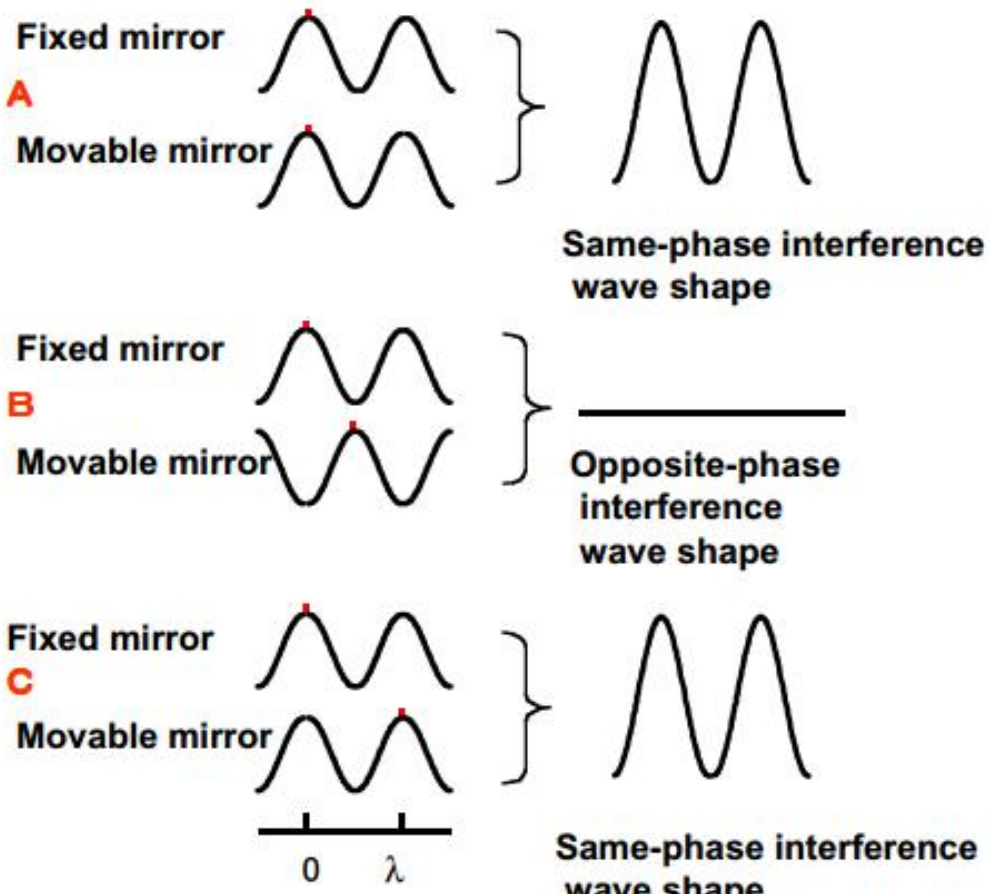
Michelson Interferometer

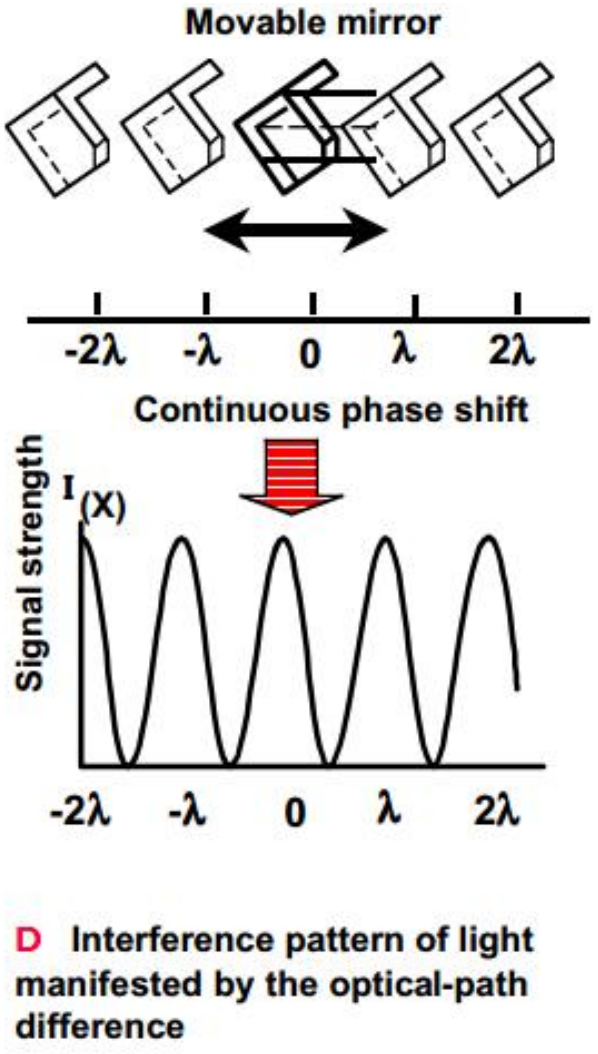


The Michelson interferometer produces interference fringes by splitting a beam of monochromatic light so that one beam strikes a fixed mirror and the other a movable mirror. When the reflected beams are brought back together, an interference pattern results.



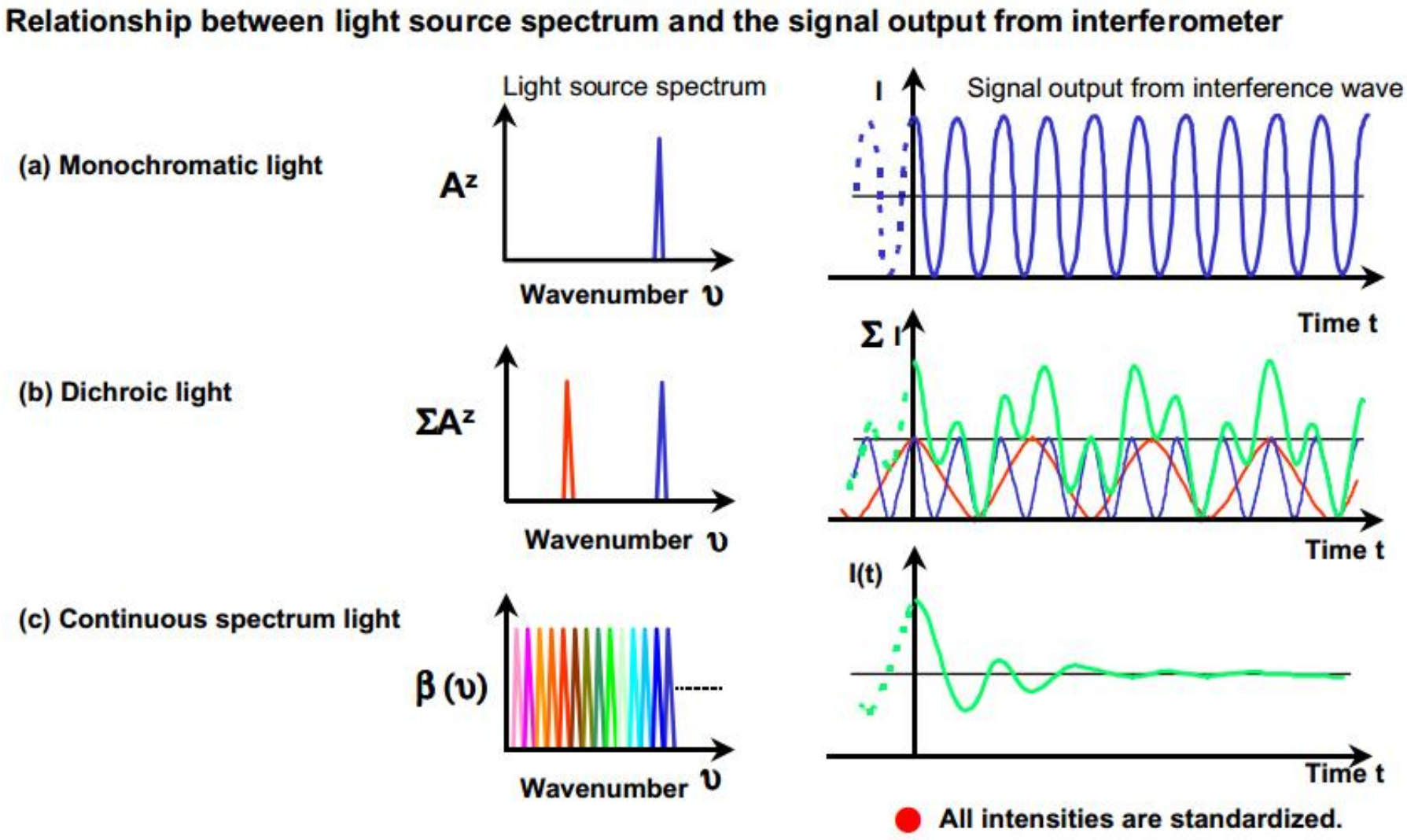
Interference of Two Beams of Light



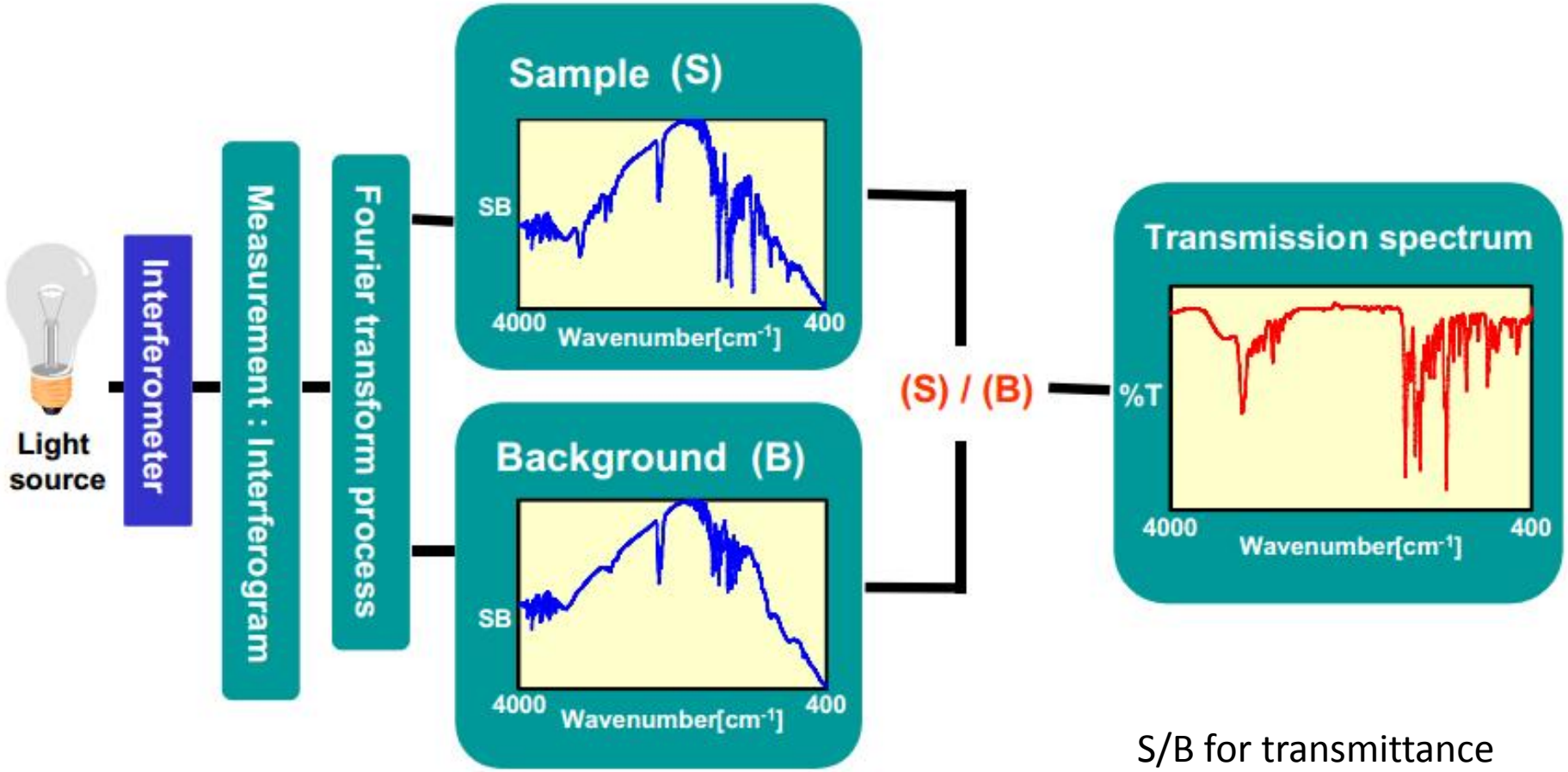


D Interference pattern of light manifested by the optical-path difference

Interference Is a Superpositioning of Waves



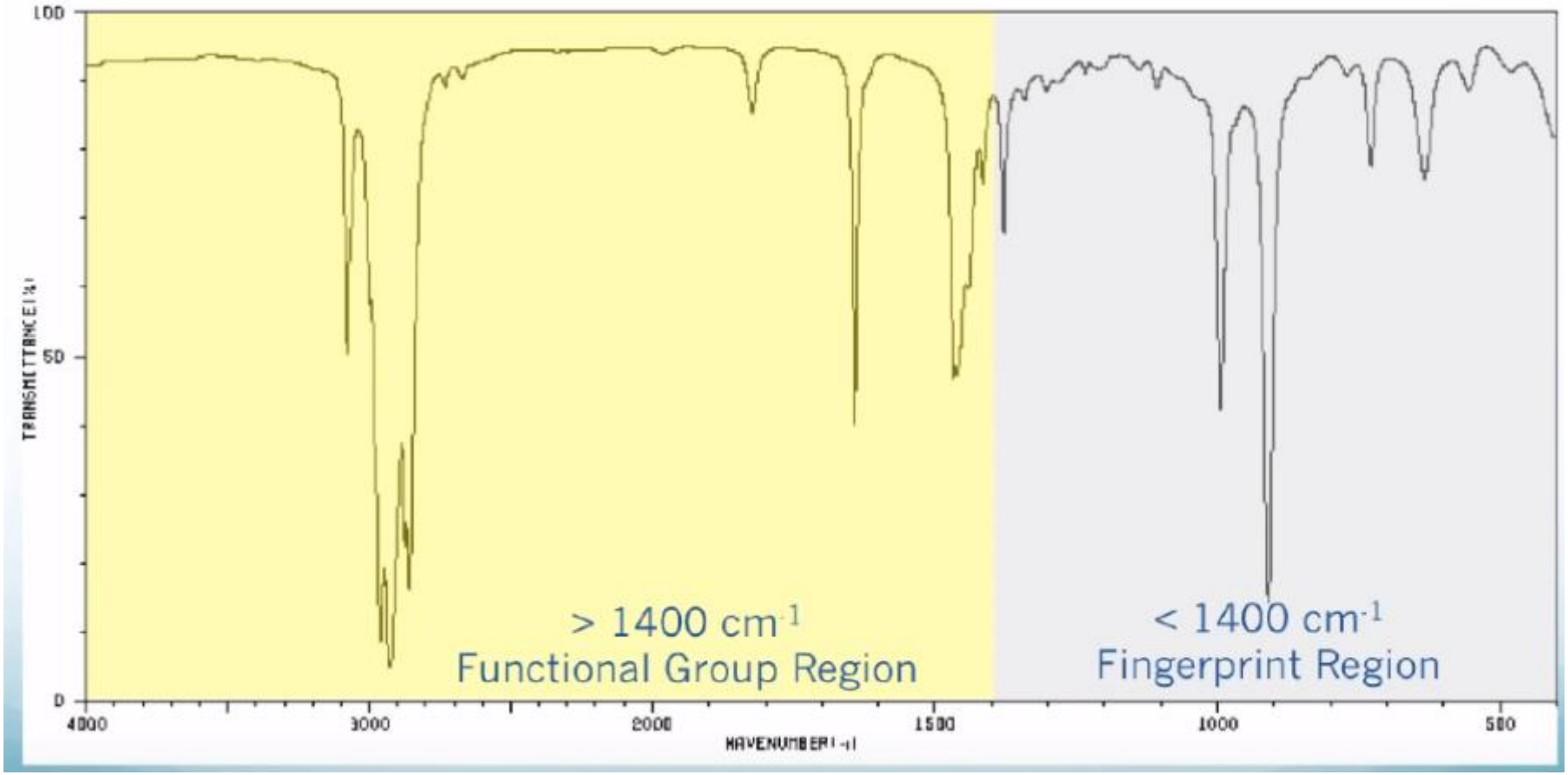
Data Collection



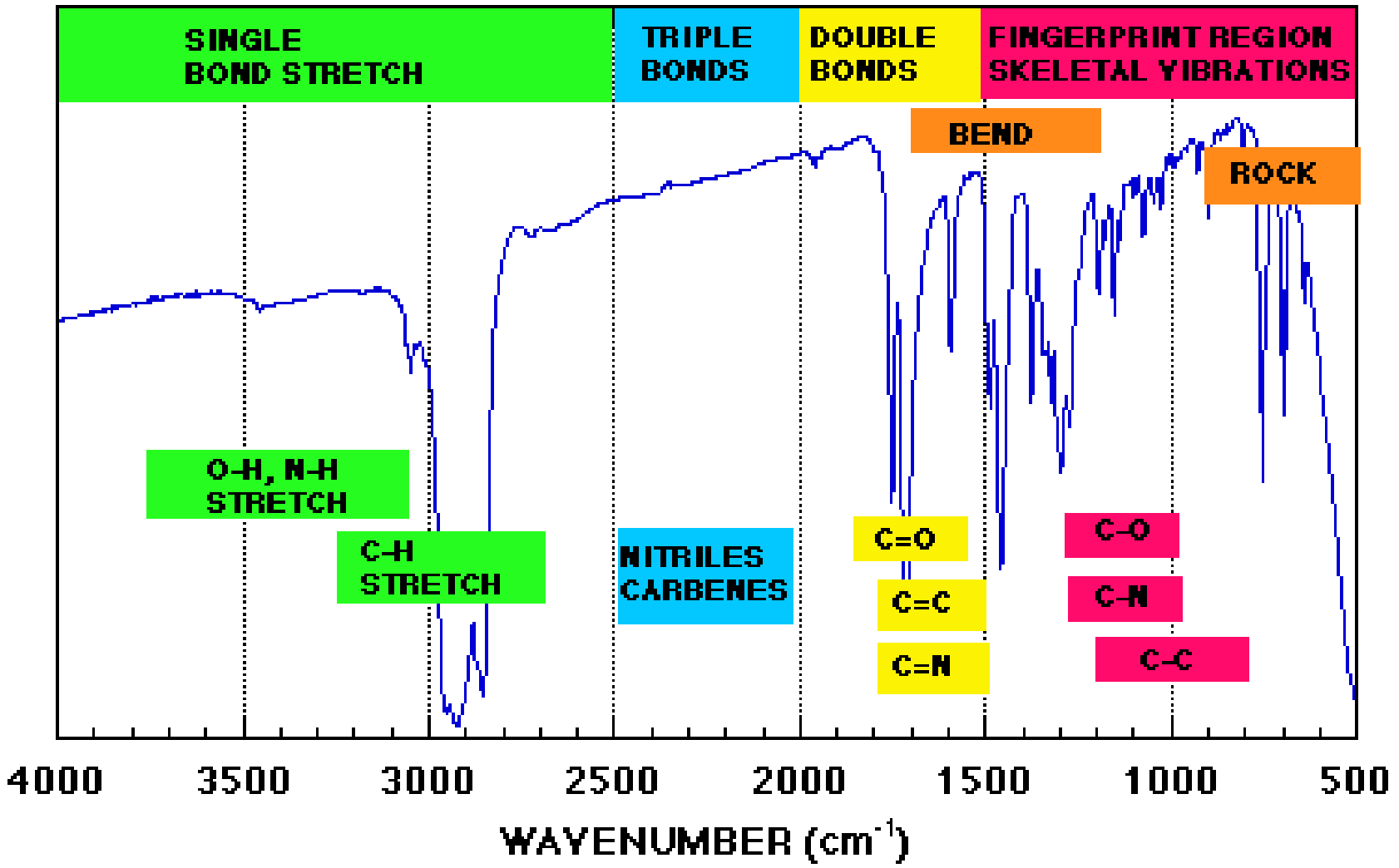
S/B for transmittance
S-B for absorption

Location of Peaks in an IR Spectrum

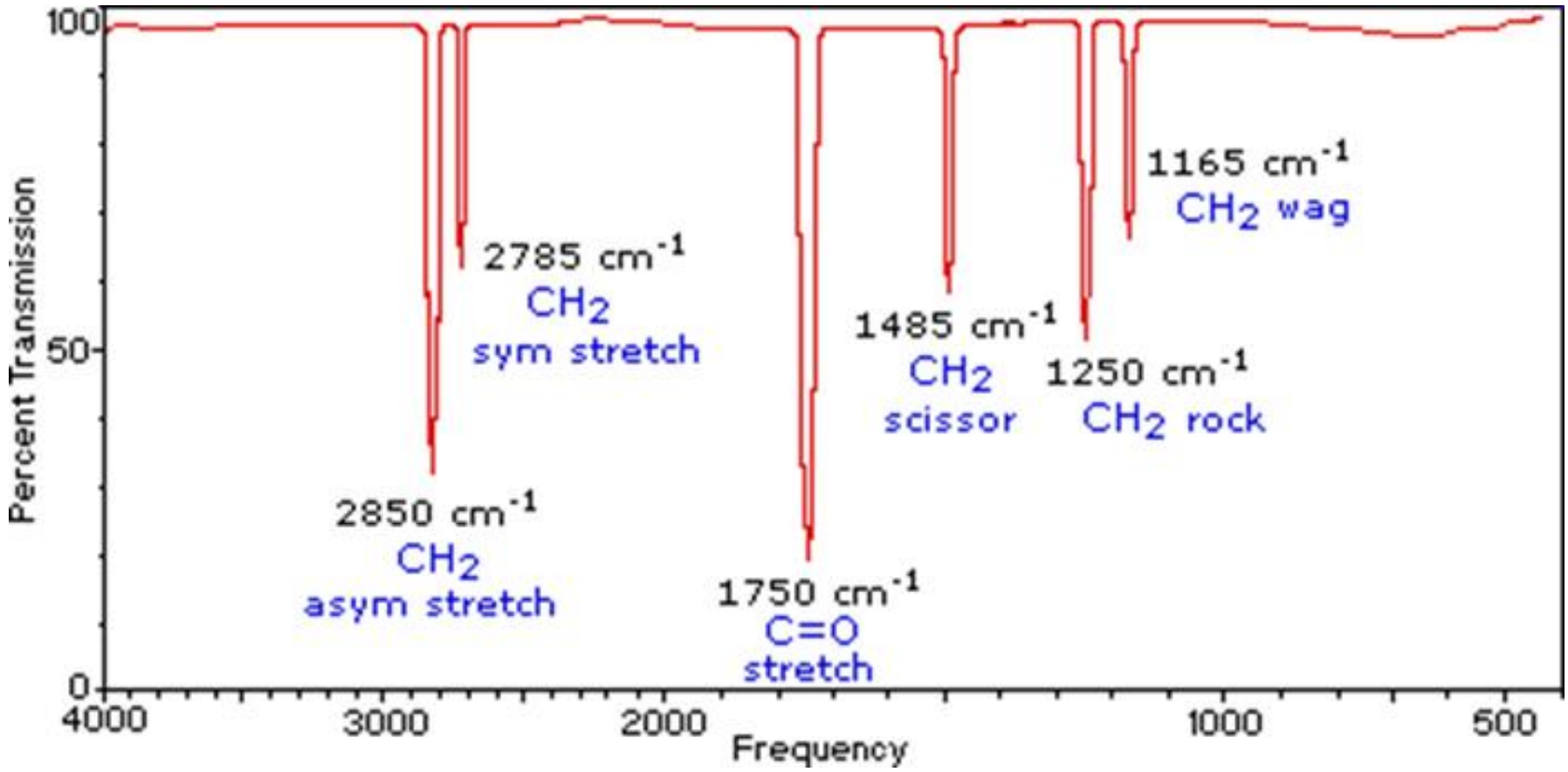
Two General Regions in an IR Spectrum:



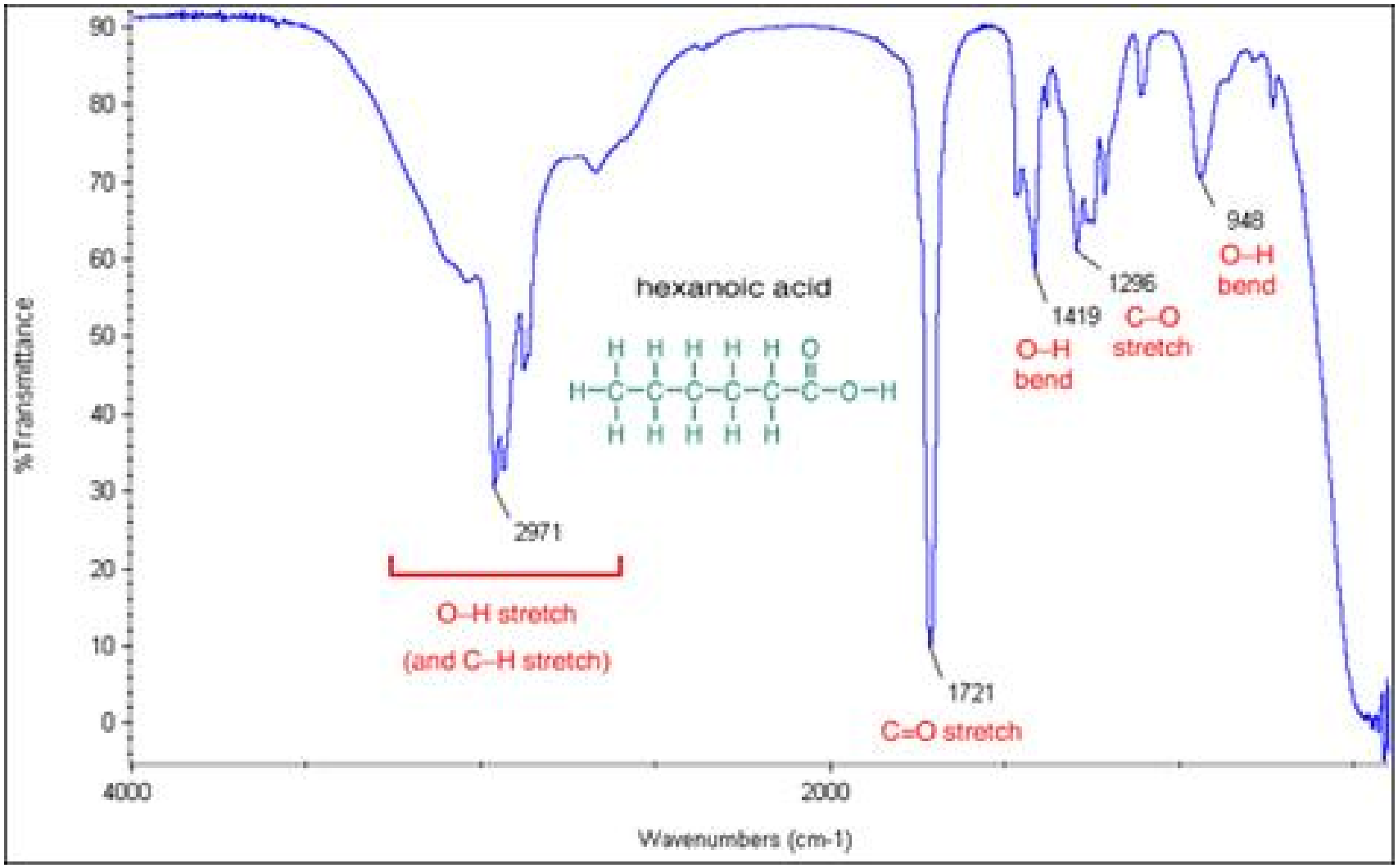
Regions of FT-IR Spectrum



Sample IR Spectrum

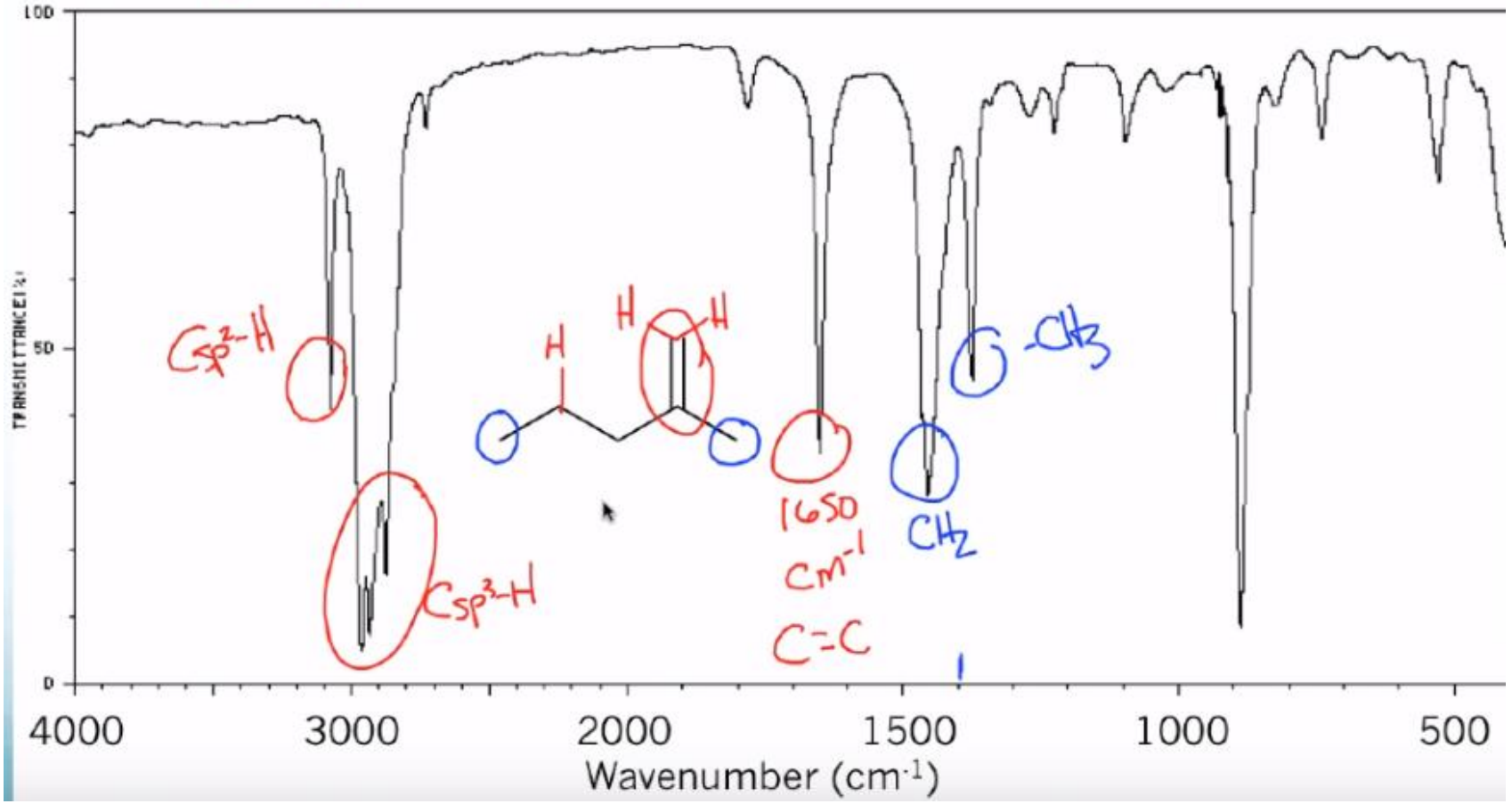


Sample IR Spectrum



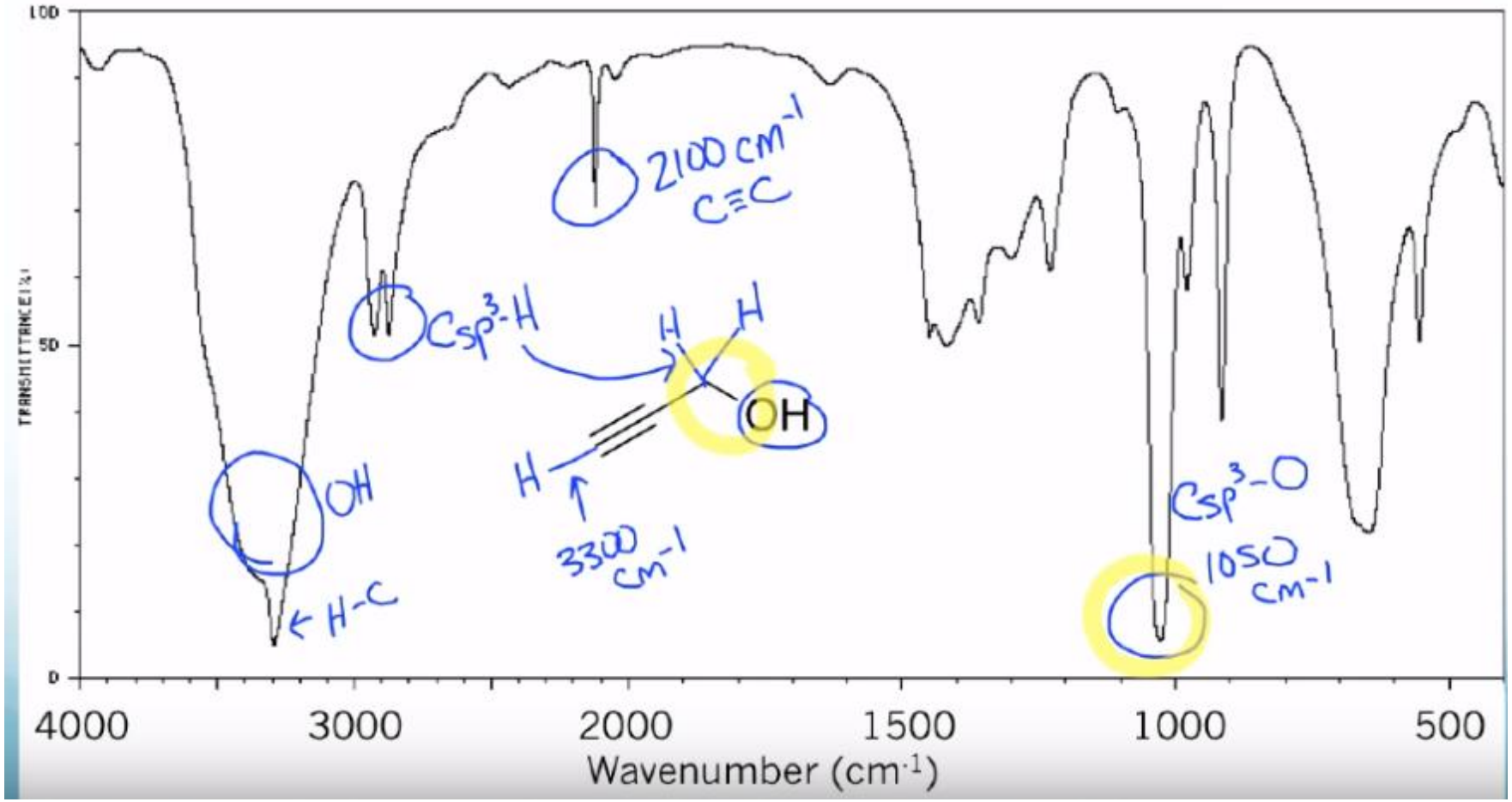
Guide to Analyzing an IR Spectrum

2-methyl-1-pentene



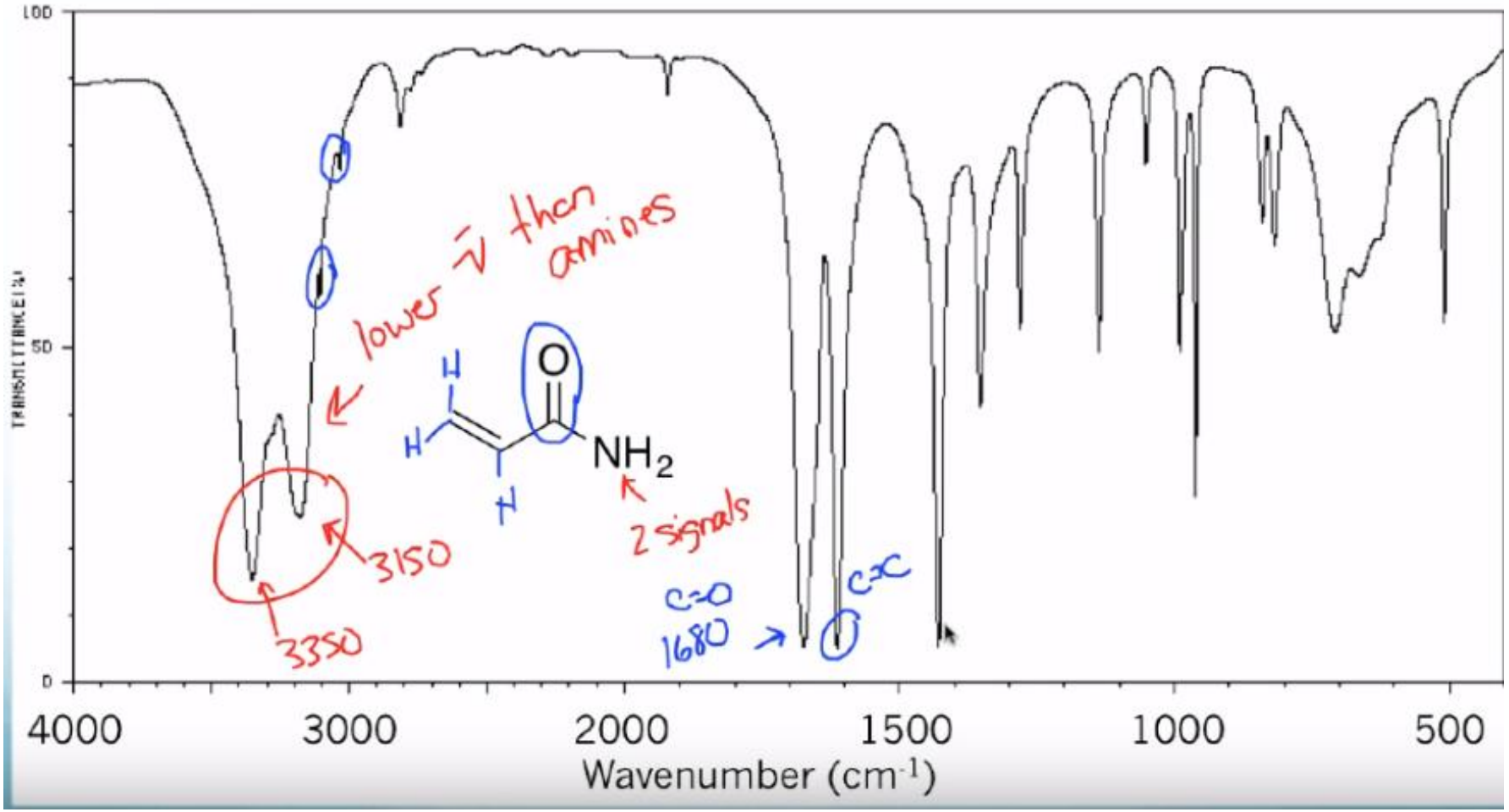
Guide to Analyzing an IR Spectrum

2-propyn-1-ol



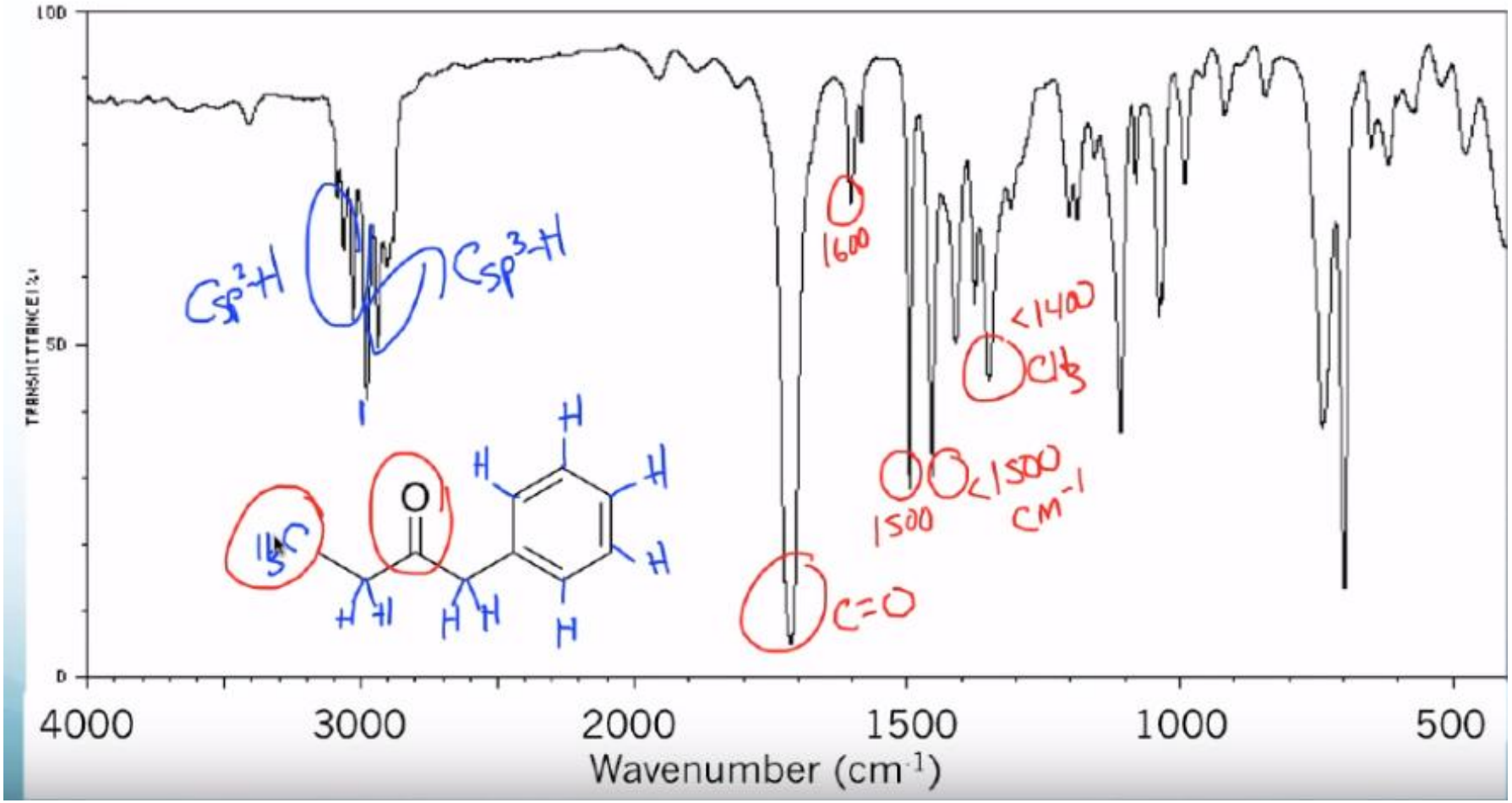
Guide to Analyzing an IR Spectrum

acrylamide



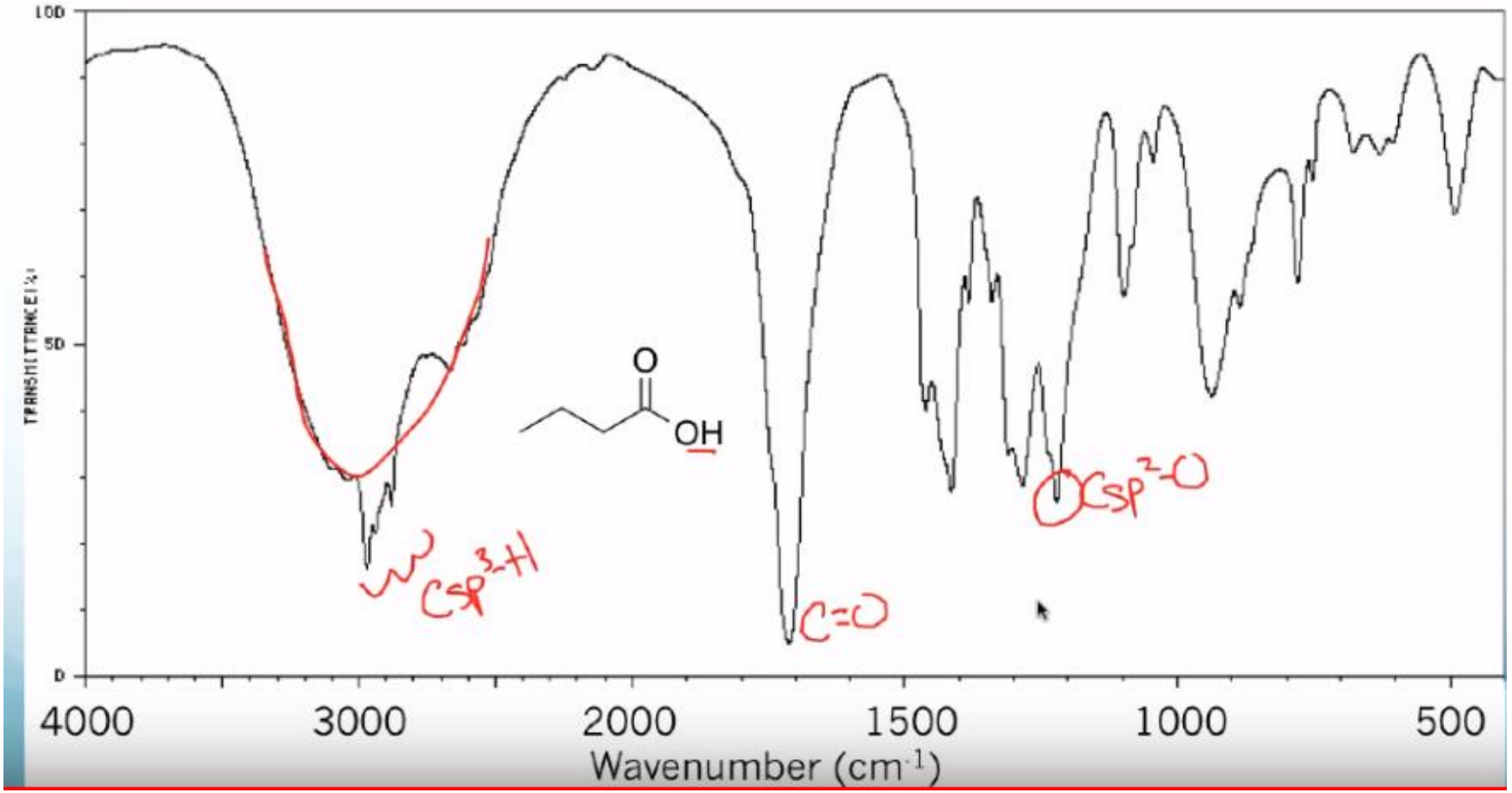
Guide to Analyzing an IR Spectrum

ethyl benzyl ketone



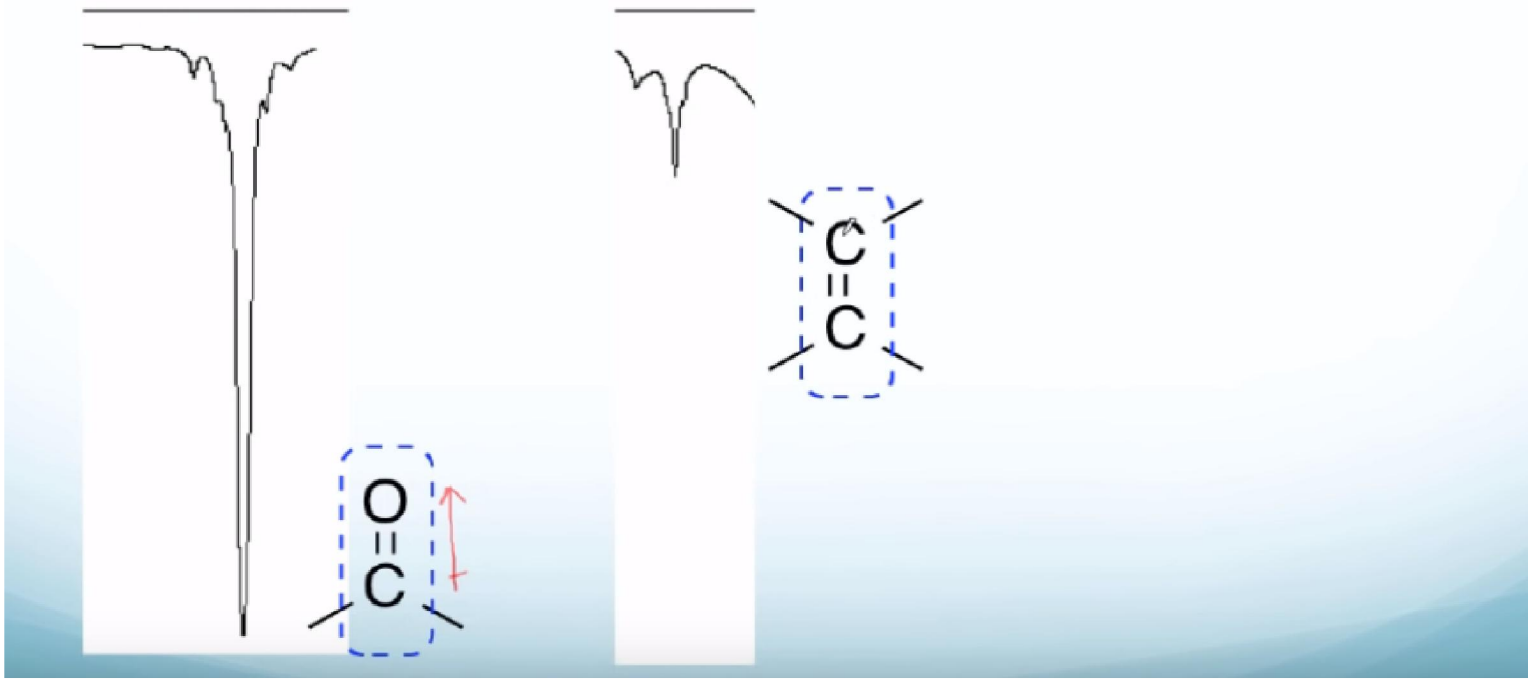
Guide to Analyzing an IR Spectrum

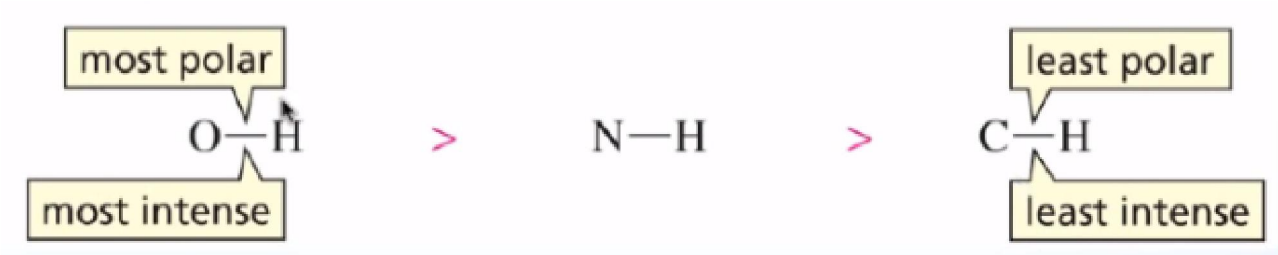
How could you use IR to differentiate $C_4H_8O_2$ isomers?



Signal Intensity in an IR Spectrum

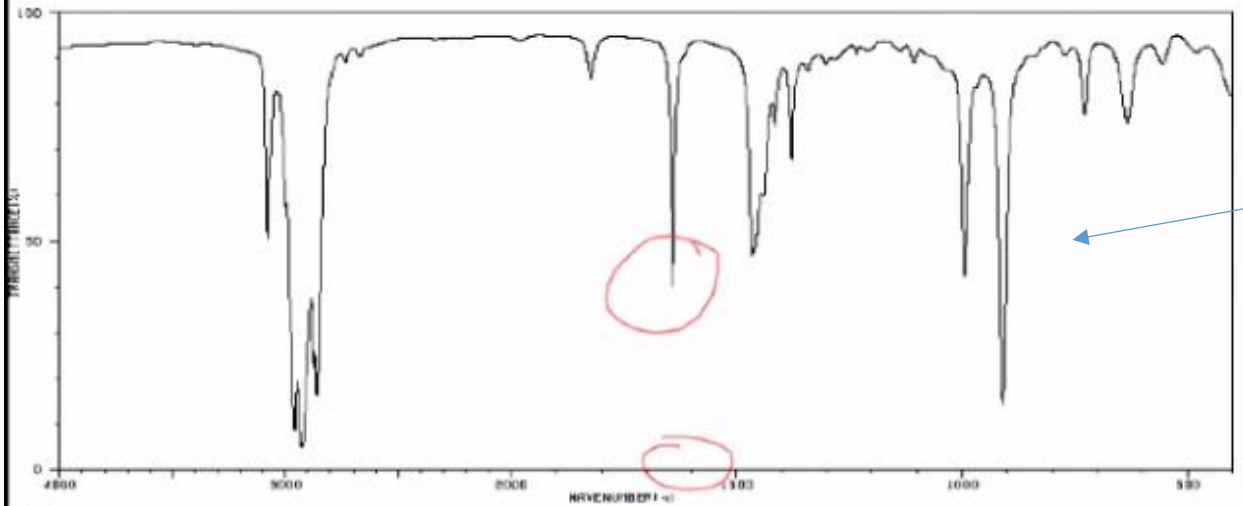
A more polar bond will have a stronger absorption than a less polar bond.





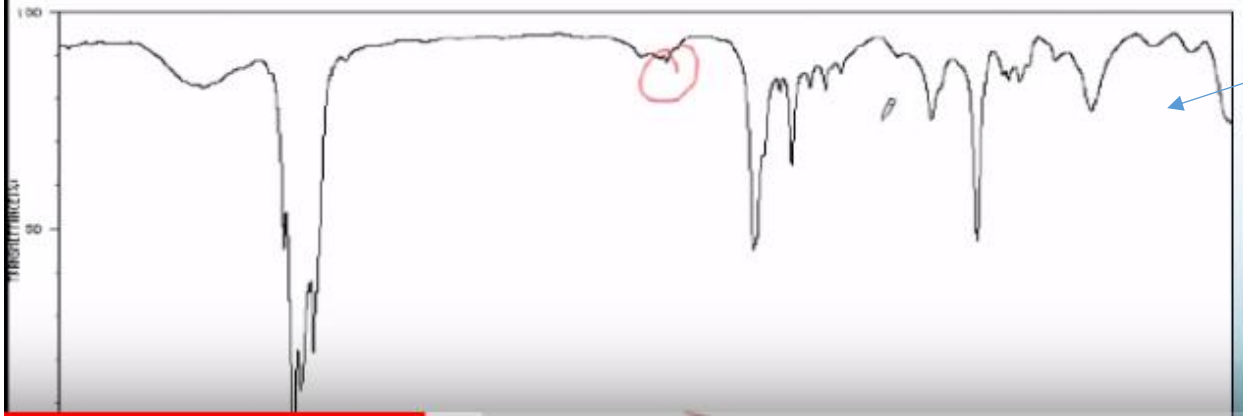
Signal Intensity in an IR Spectrum

An alkene C=C stretch generally appears ~1650 cm^{-1}.



Asymmetric

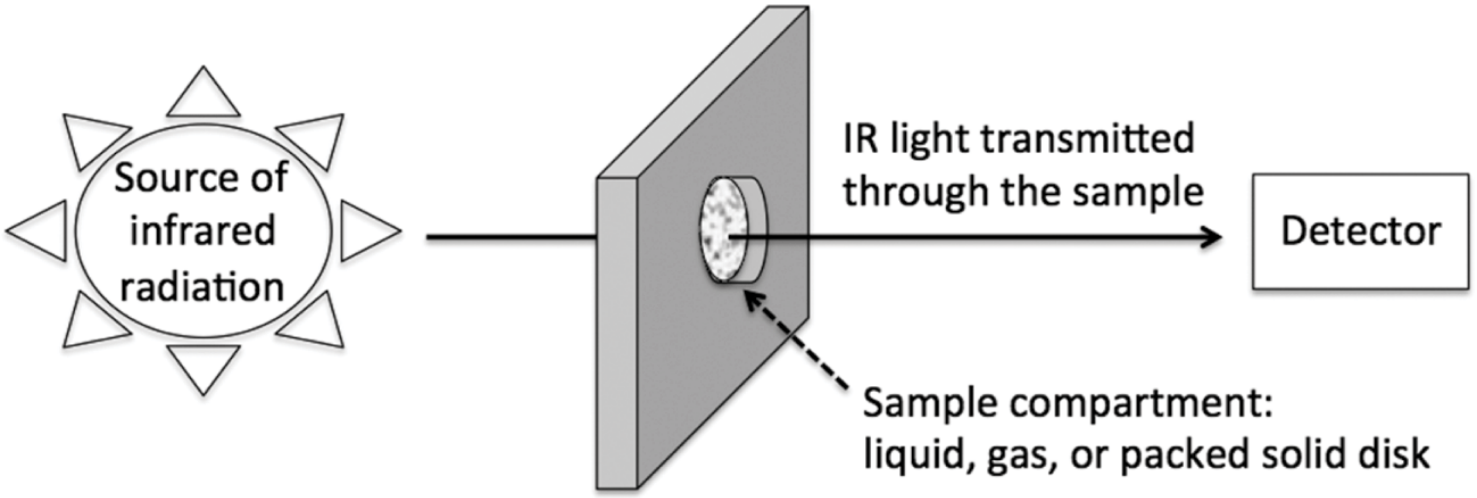
1-heptene



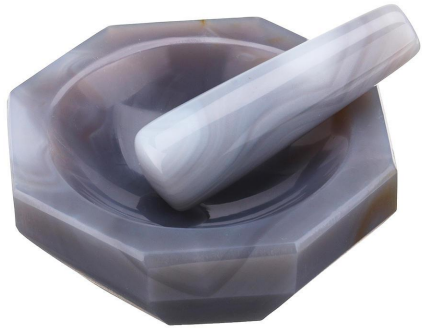
Symmetric

3-heptene

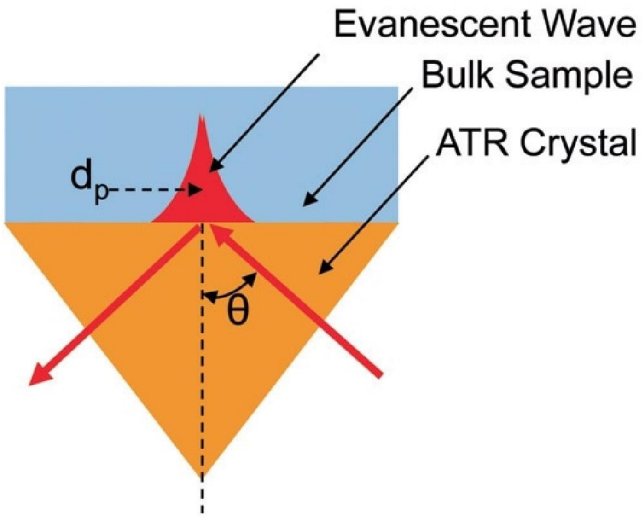
Transmission Mode



- **Economical** – cells and mounts are generally inexpensive
- **Well established** – most traditional form of sample measurement
- **Excellent spectral information** – ideal for qualitative measurements
- **Great for quantitative work** – many standard operating procedures are based on transmission



Attenuated Total Reflection (ATR) Mode



	n_0	LWL, cm^{-1}	d_p (um)
Diamond/ZnSe	2.4	525	2.00
Germanium	4.0	780	0.66

$$d_p = \frac{\lambda}{2\pi\sqrt{n_o^{\,2}\sin^2\theta - n_s^{\,2}}}$$

n_0 = refractive index of ATR crystal
LWL = long wave length cut-off
d_p = depth of penetration in microns @ 1000 cm^{-1} assuming sample refractive index of 1.5 and 45 degree angle of incidence.

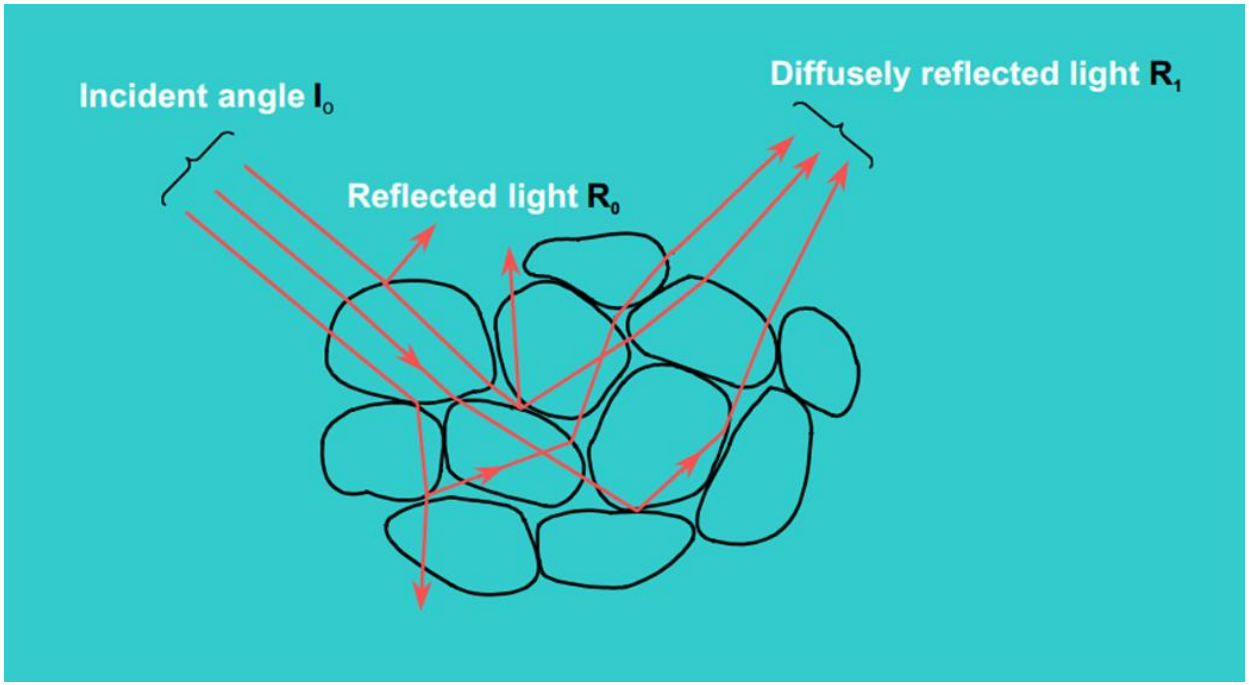
ATR-2

Advantages:

- **Minimal sample preparation**—place the sample on the crystal and collect data
- **Fast and easy cleanup—**simply remove the sample and clean the surface of the crystal
- **Analysis of samples in their natural states—**no need to heat, press into pellets, or grind in order to collect spectra
- **Excellent for thick or strongly absorbing samples—** ideal for difficult samples like black rubber

Sample: Powder, Film, liquid

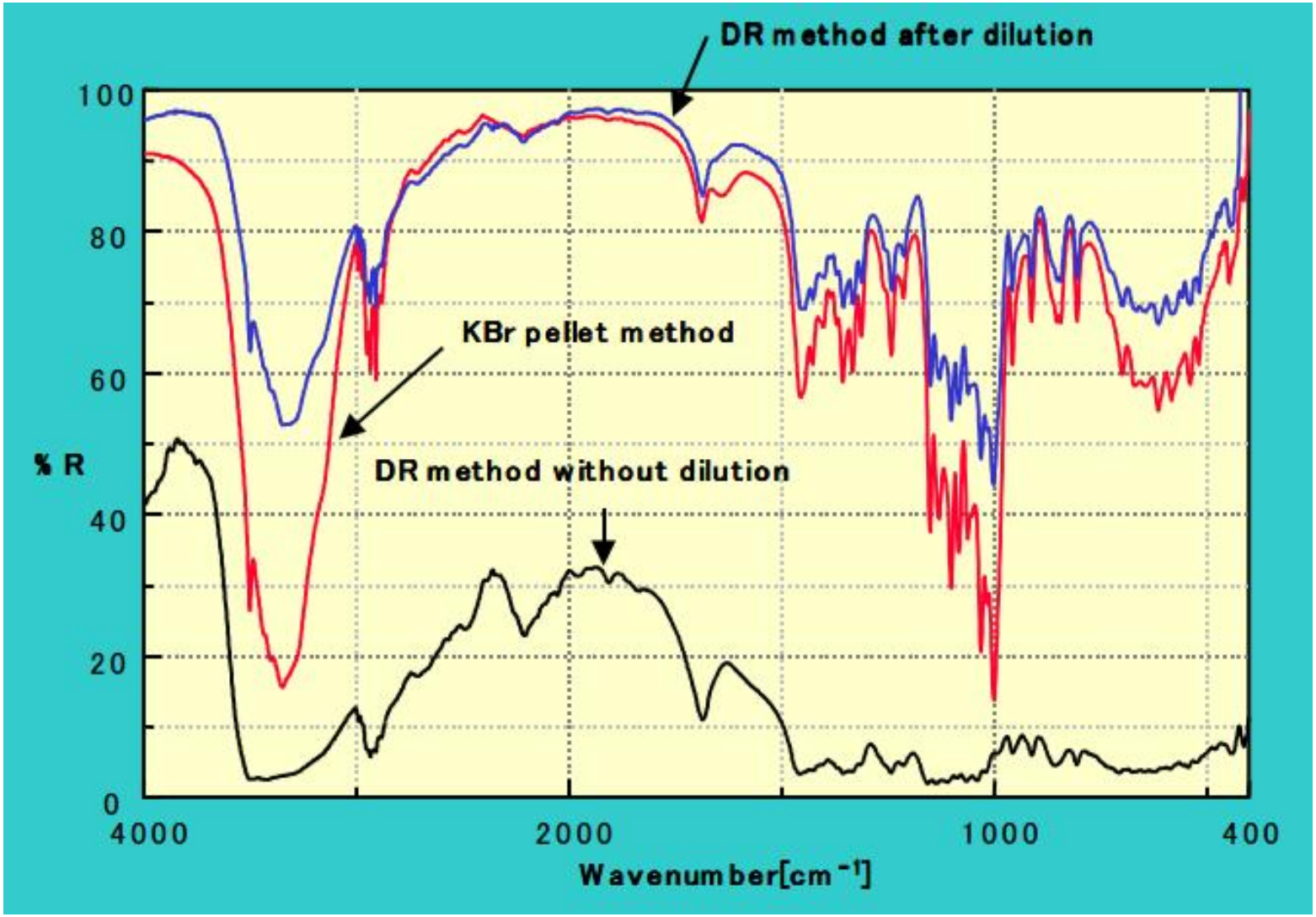
Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)



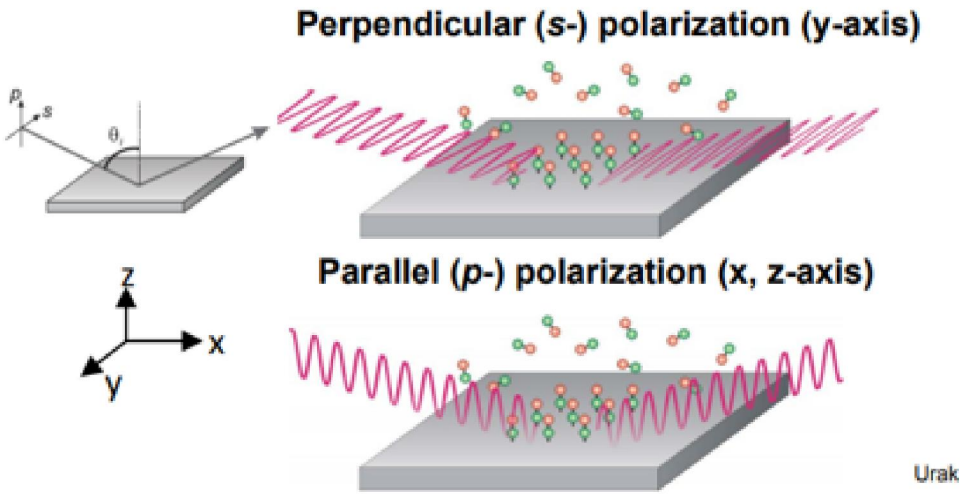
What are the advantages of diffuse reflectance?

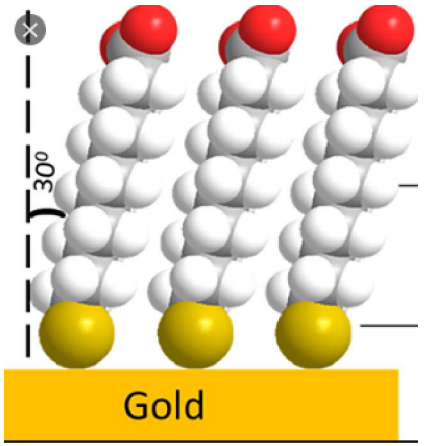
- **Little to no sample preparation** – just place in the sample cup
- **Fast and easy cleanup** – dump the cup and blow or rinse clean
- **No need for pressed KBr pellets or messy mulls** – samples can be run neat or diluted with KBr powder

Spectra of Trehalose with DRIFT mode



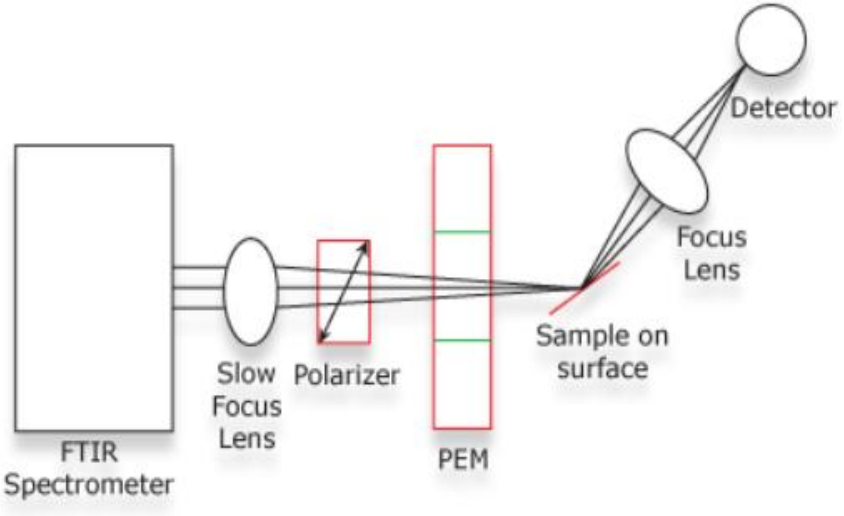
Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS)



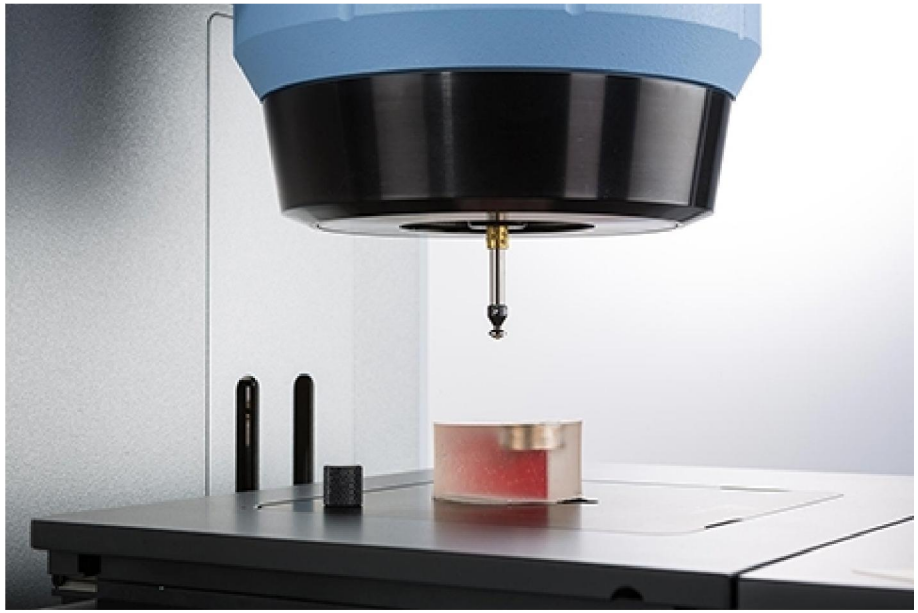


R_p - R_s = ΔR

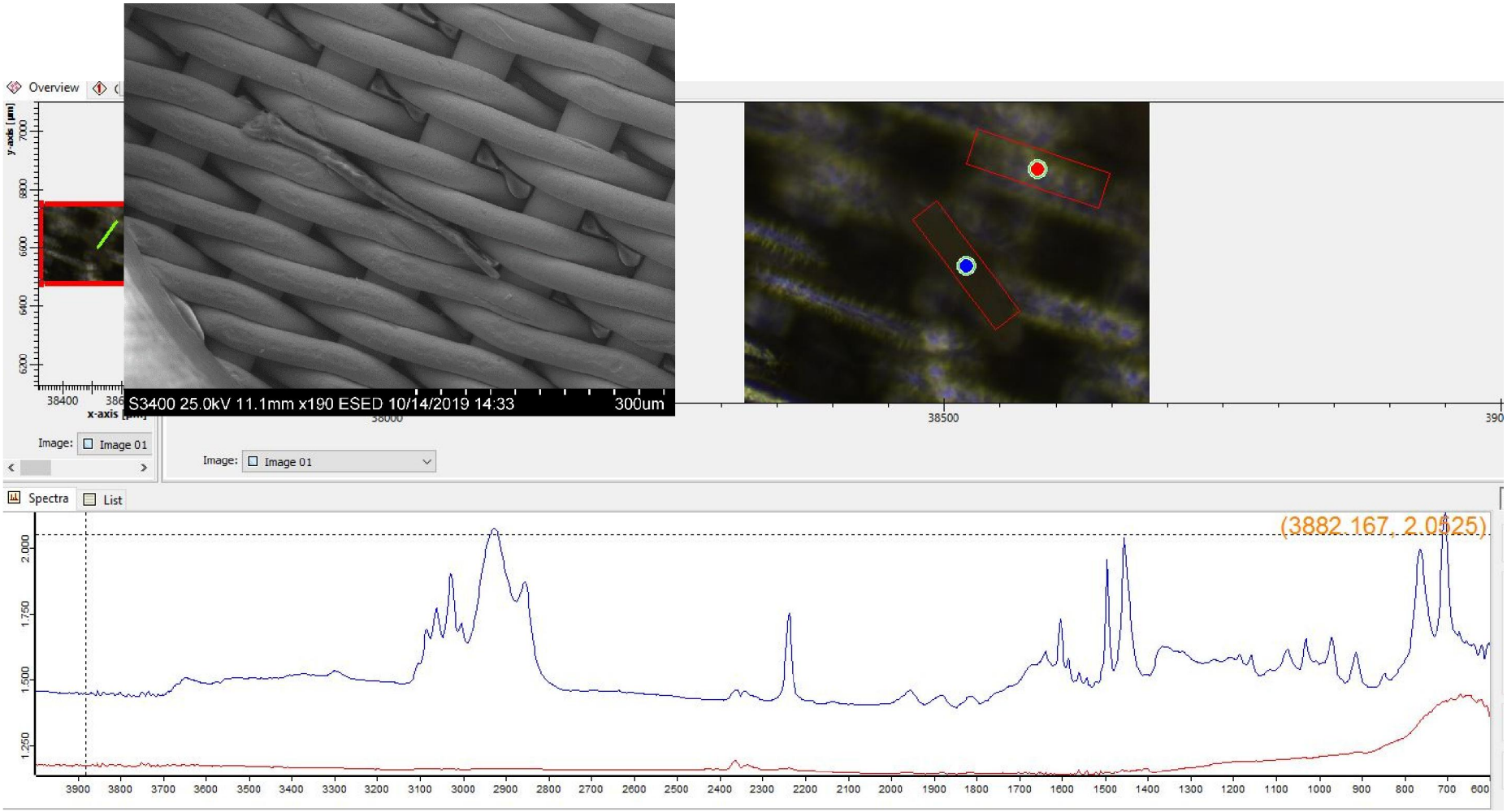
Parallel polarization	Perpendicular polarization	Difference
surface + gas	gas	surface



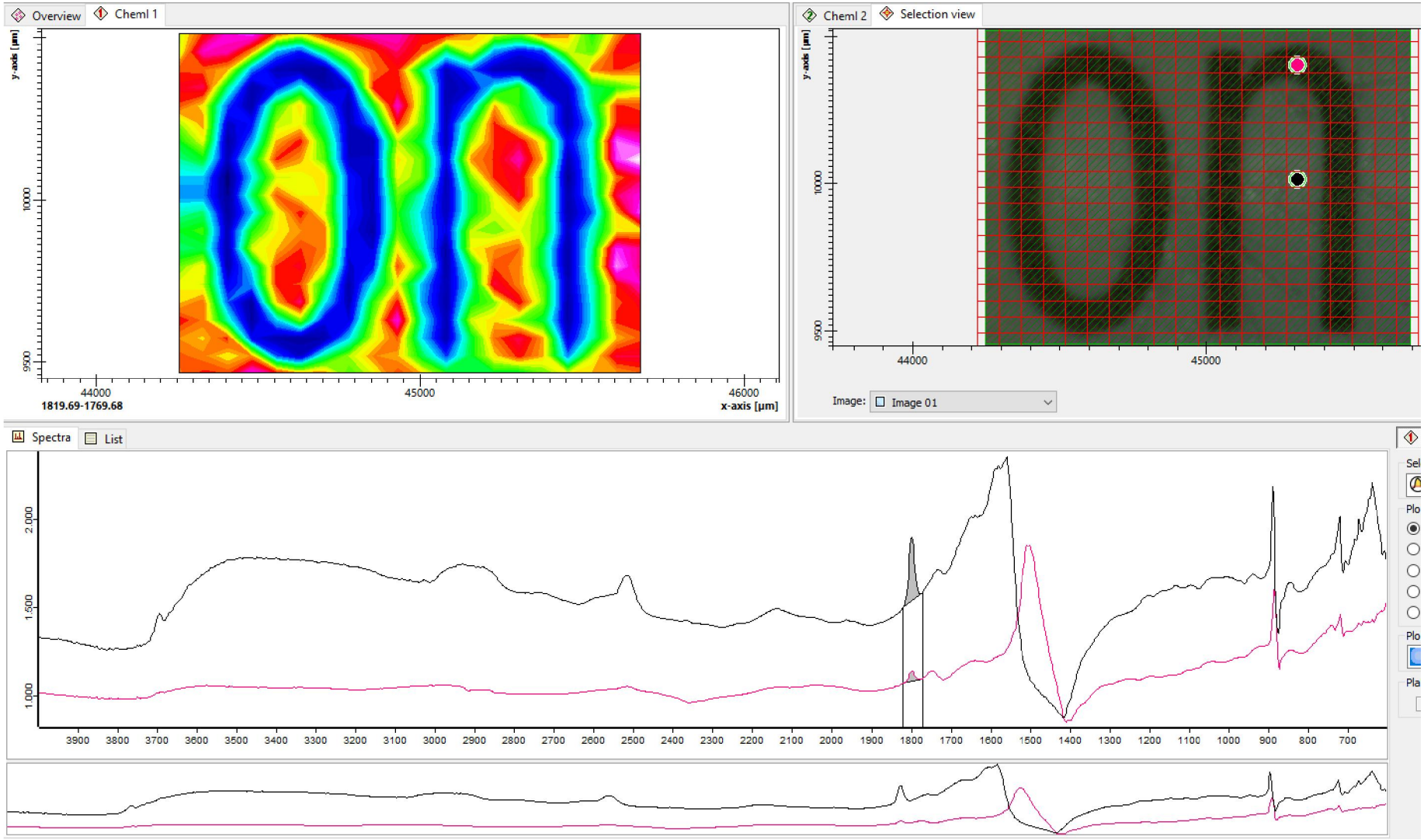
Micro FT-IR – Bruker LUMOS



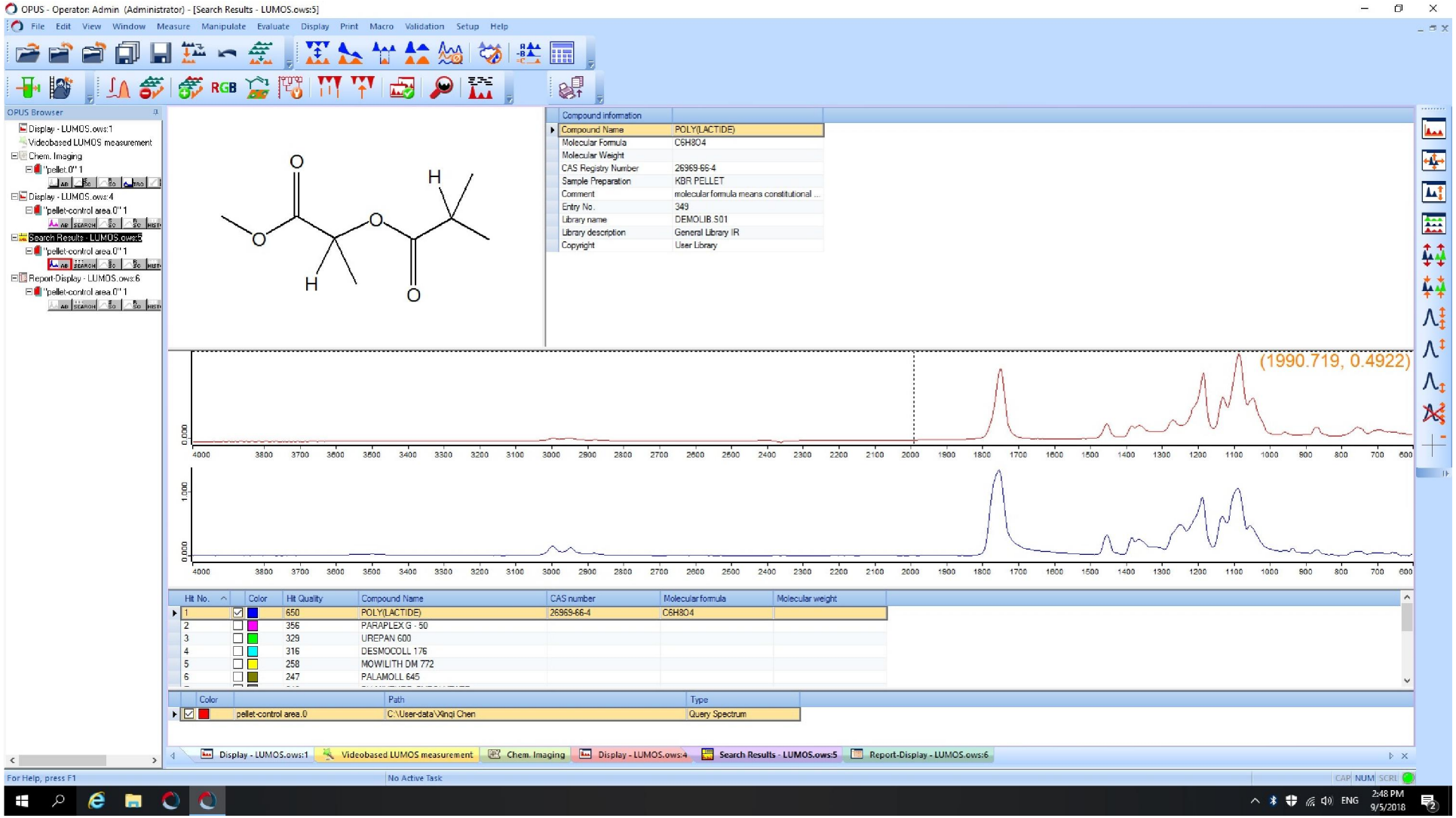
Identify Unknown Substance



Mapping


Overview
ChemI 1
y-axis [µm]
10000
9500
44000
45000
46000
1819.69-1769.68
x-axis [µm]
ChemI 2
Selection view
y-axis [µm]
10000
9500
44000
45000
Image:
Image 01
Spectra
List
2.000
1.500
1.000
3900 3800 3700 3600 3500 3400 3300 3200 3100 3000 2900 2800 2700 2600 2500 2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700

Library Search



Summary

- FT-IR can identify chemical group, but not molecular structure.
- It is sensitive to chemical bond with big dipole moment.
- It is qualitative method, but quantitative with standard samples
- There are ATR, transmission, DRIFT, and IRRAS mode.
- It is suitable for powder, film, liquid, gel, paint etc.

Thanks for your attention

Questions?