CHE680
Advanced Analytical Chemistry
Lecture 3

Jamie Kim
Department of Chemistry
Buffalo State College

Outlines of Spectroscopy

1. Interactions of *electromagnetic radiation* (ER) with materials (electrons, nucleus, atoms, molecules, etc).

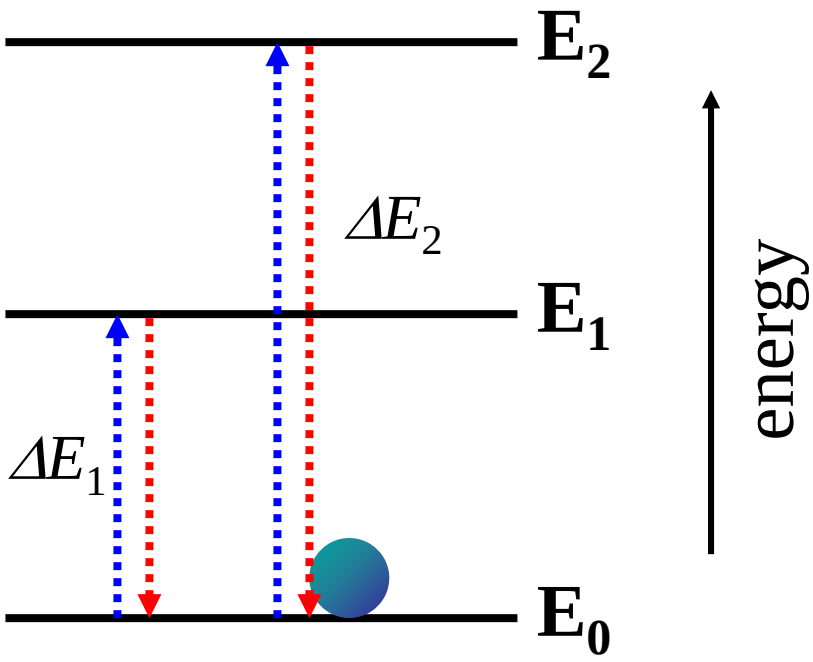
2. Absorption of ER under the limited conditions.

3. The energy (frequency or wavelength) of absorbed ER: molecular (or atomic) information under investigation (qualitative analysis)

4. The amount of absorbed ER: concentration (Beer's law, quantitative analysis)

Quantized Energy Level

radiation source

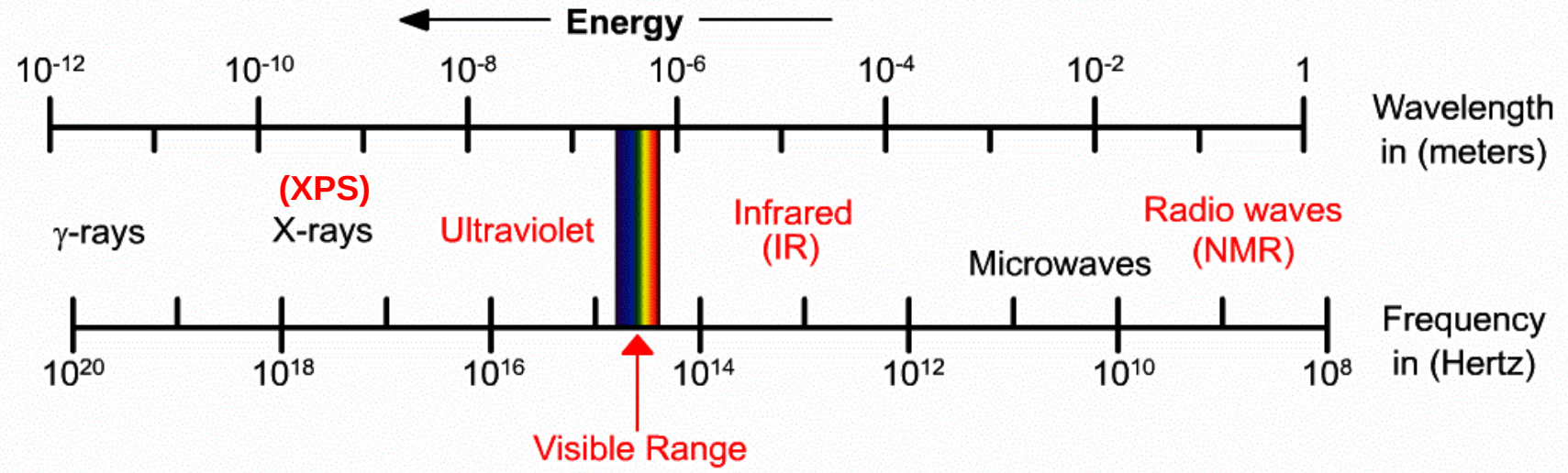


$$\Delta E_1 = E_1 - E_0 = h\nu = h(c/\lambda)$$

- Detection and identification of unknown compounds in a sample via *spectroscopy* is based on the specific energy difference (ΔE_1, ΔE_2, …) for individual compounds.
- This is why interference between analytes and resolution of spectra corresponding energy levels are important.

Electromagnetic Spectrum

Each type of spectroscopy focuses upon a specific region of the *electromagnetic spectrum*:



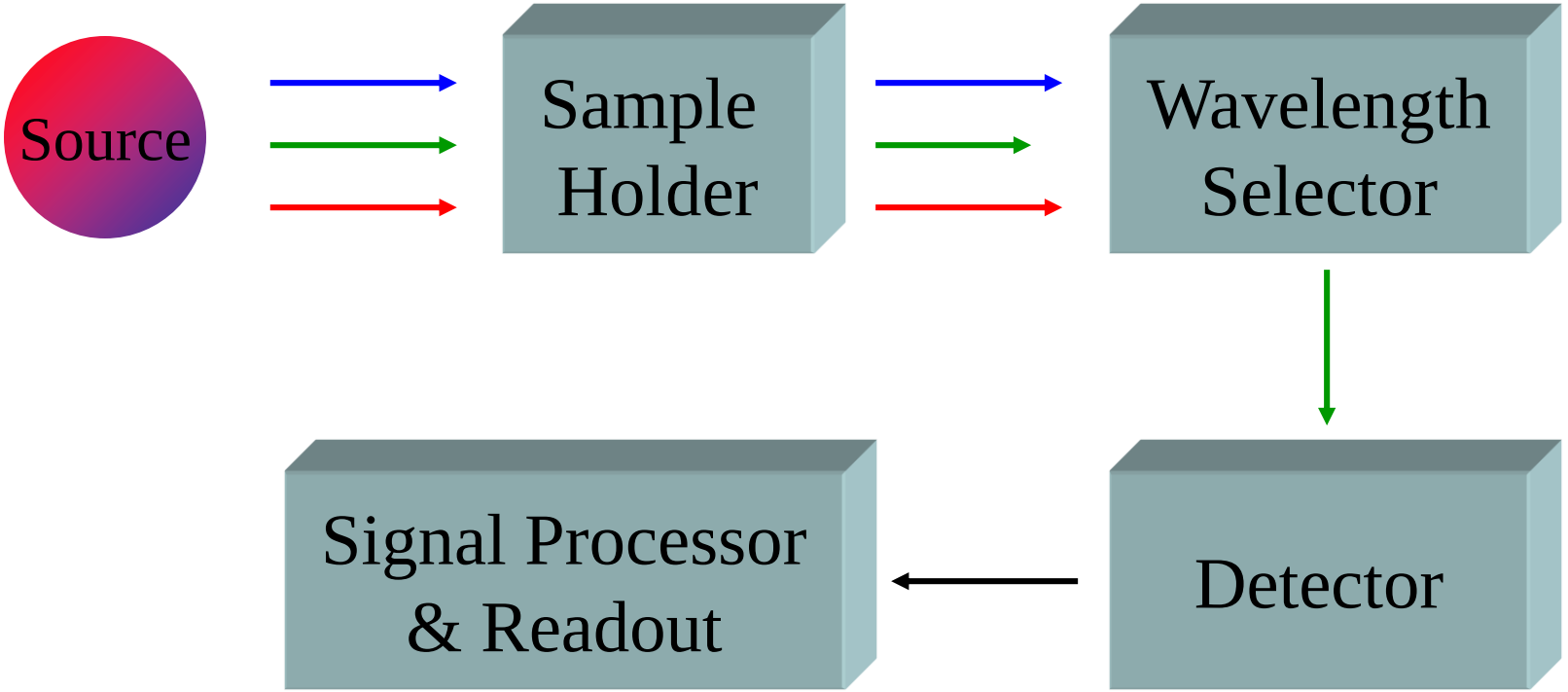
$c = \nu \cdot \lambda$, $\nu = c/\lambda$, or $\lambda = c/\nu$

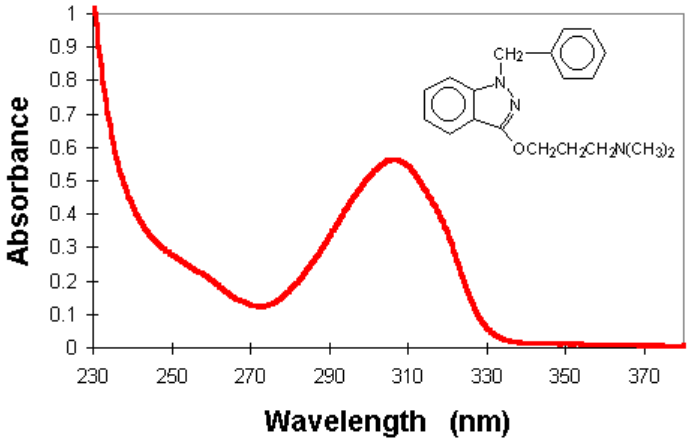
$$\bar{\nu} = \frac{1}{\lambda(m)} \cdot \frac{1m}{100cm}$$

XPS (*eV*)
UV/Vis (nm)
IR (cm^{-1})
NMR (MHz)

1.0 *eV* = 1240 nm = 1.24 μm = 8065.5 cm^{-1} = 2.43×10^9 MHz

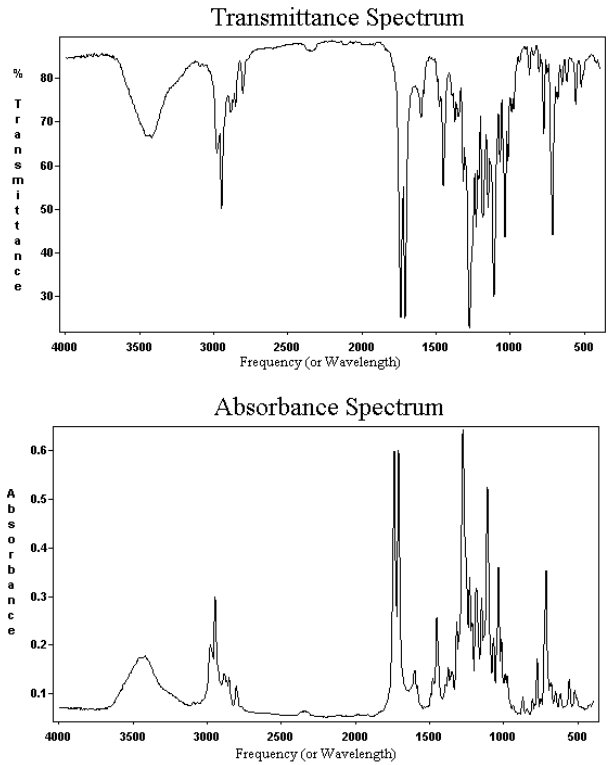
Schematics of Spectroscopy

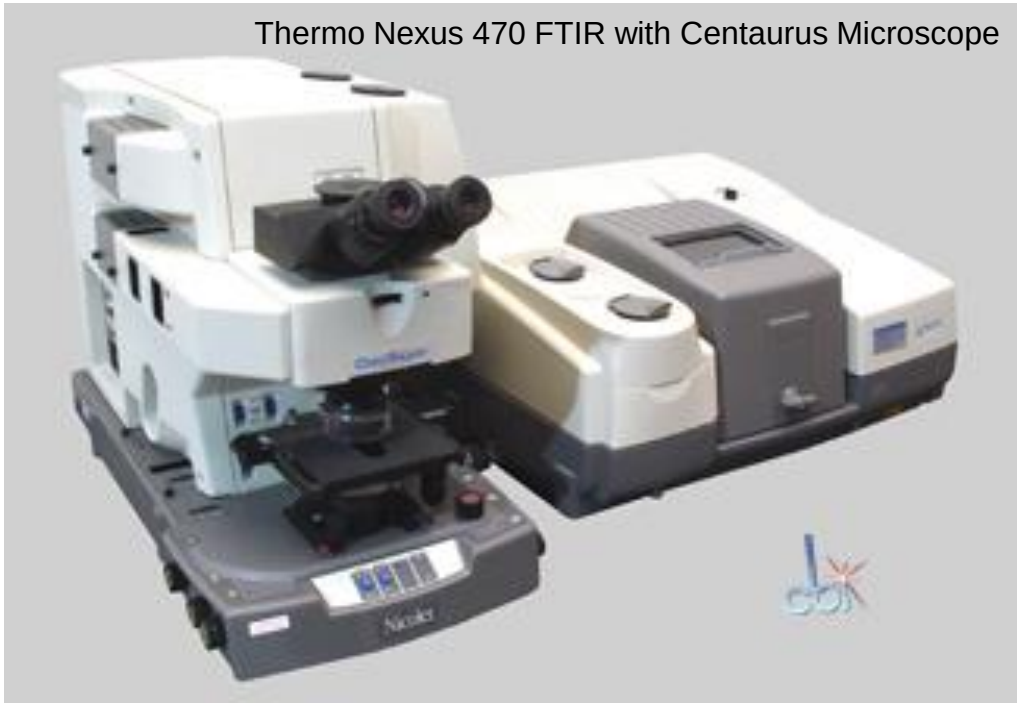




Infrared Spectroscopy

- Theory
- Chemical Information
- Instrumentation

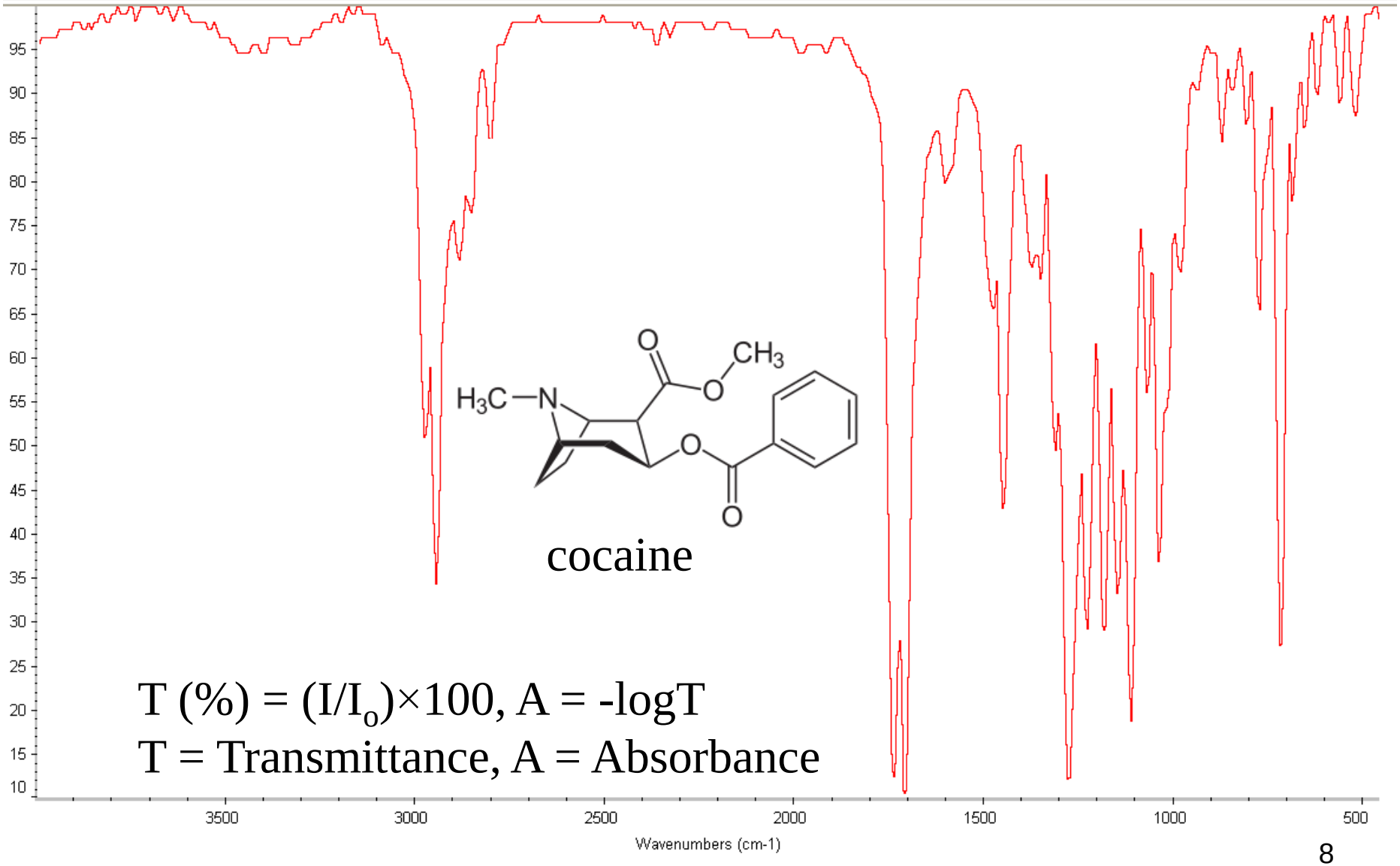




Brief Review

- Identification and confirmation of the existence of functional groups in the sample by the characteristic absorption peaks in the spectrum (typically 400 – 4000 cm^{-1})
- Absorption is based upon the vibrational motion of molecules
- Possible sample states: gas, liquid, solids, and thin films
- Data acquisition
  1. Transmission mode: gas, liquid, and solid
  2. Reflection mode (attenuated total reflection, specular reflection, and diffuse reflection): thin film
  3. microscopy
- Instrumentation:
  1. Dispersive spectrometer (scanning spectrometers): single beam and double beam
  2. Nondispersive spectrometer
  3. Fourier transform (FT) spectrometer: single beam

Infrared Spectrum (Transmittance)

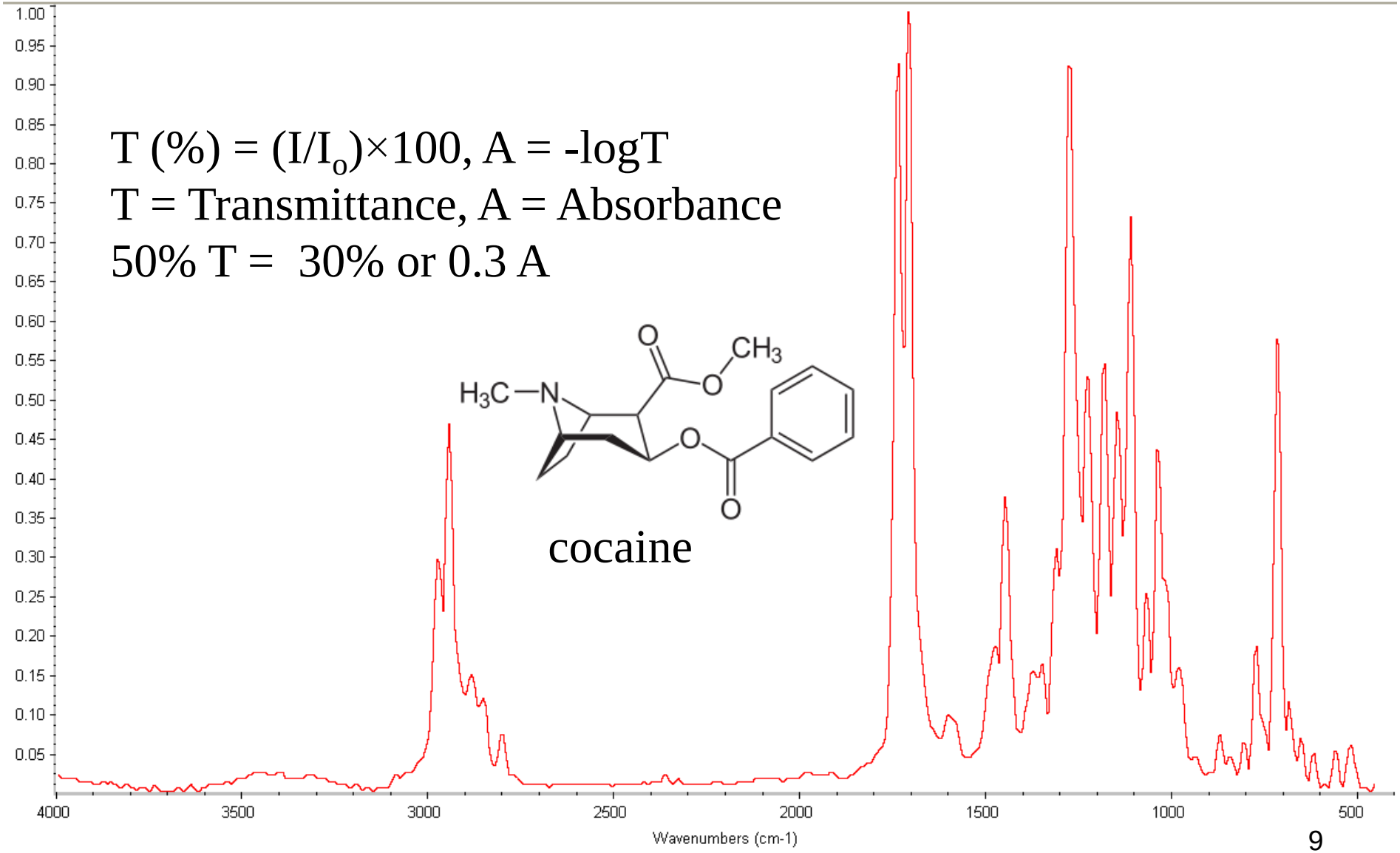


cocaine

$T\ (\%) = (I/I_o)\times 100,\ A = -\log T$

T = Transmittance, A = Absorbance

Infrared Spectrum (Absorbance)



$T\ (\%) = (I/I_o)\times 100,\ A = -\log T$

T = Transmittance, A = Absorbance

50% T = 30% or 0.3 A

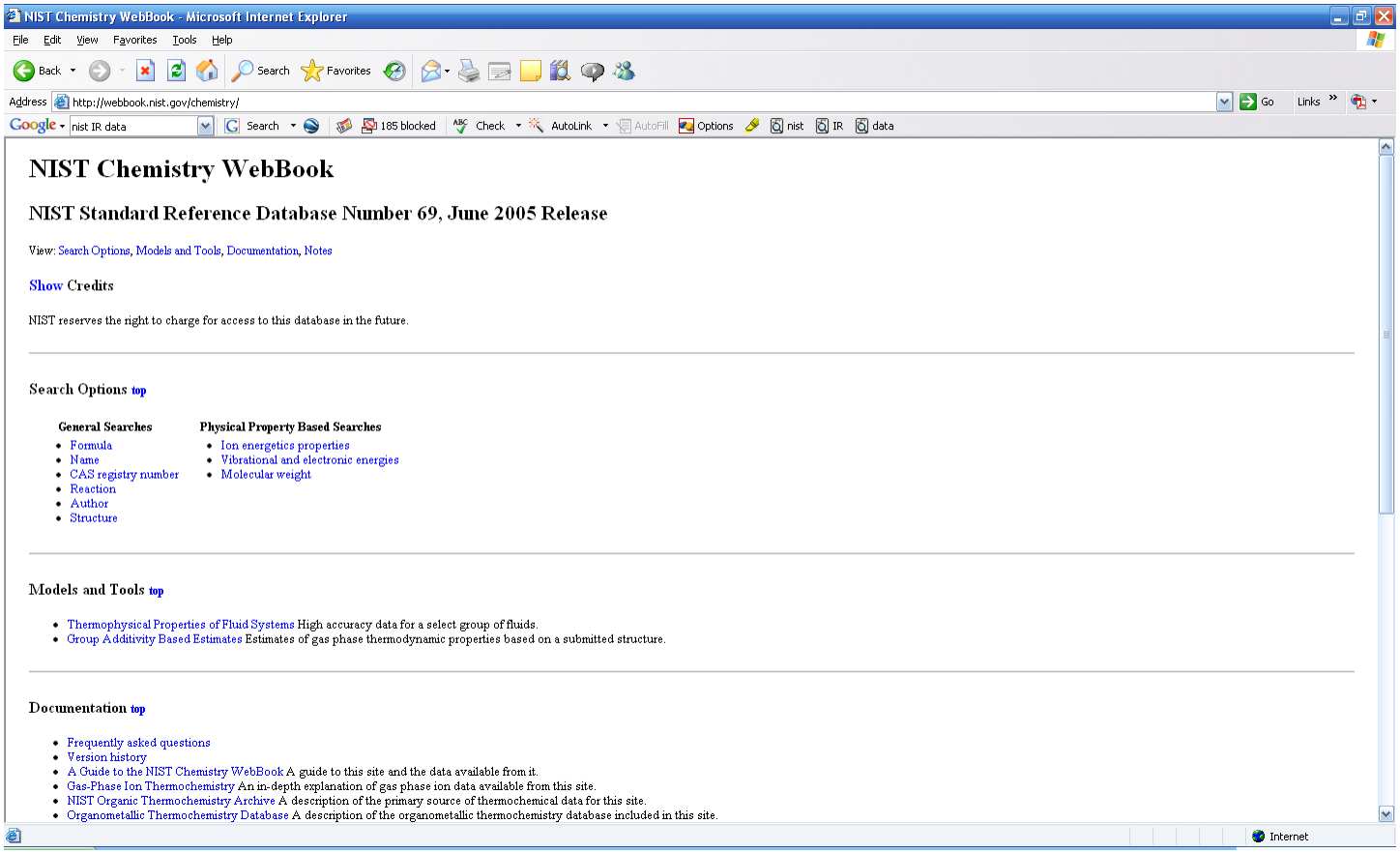
cocaine

Characteristic Vibrational Frequencies

Bond	Compound Type	Frequency range, cm^{-1}
C-H	Alkanes	2960-2850(s) stretch
		1470-1350(v) scissoring and bending
	CH_3 Umbrella Deformation	1380(m-w) - Doublet - isopropyl, *t*-butyl
C-H	Alkenes	3080-3020(m) stretch
		1000-675(s) bend
C-H	Aromatic Rings	3100-3000(m) stretch
	Phenyl Ring Substitution Bands	870-675(s) bend
	Phenyl Ring Substitution Overtones	2000-1600(w) - fingerprint region
C-H	Alkynes	3333-3267(s) stretch
		700-610(b) bend
C=C	Alkenes	1680-1640(m,w)) stretch
C≡C	Alkynes	2260-2100(w,sh) stretch
C=C	Aromatic Rings	1600, 1500(w) stretch
C-O	Alcohols, Ethers, Carboxylic acids, Esters	1260-1000(s) stretch
C=O	Aldehydes, Ketones, Carboxylic acids, Esters	1760-1670(s) stretch
O-H	Monomeric -- Alcohols, Phenols	3640-3160(s,br) stretch
	Hydrogen-bonded -- Alcohols, Phenols	3600-3200(b) stretch
	Carboxylic acids	3000-2500(b) stretch
N-H	Amines	3500-3300(m) stretch
		1650-1580 (m) bend
C-N	Amines	1340-1020(m) stretch
C≡N	Nitriles	2260-2220(v) stretch
NO_2	Nitro Compounds	1660-1500(s) asymmetrical stretch
		1390-1260(s) symmetrical stretch

Important IR Database

http://webbook.nist.gov/chemistry/

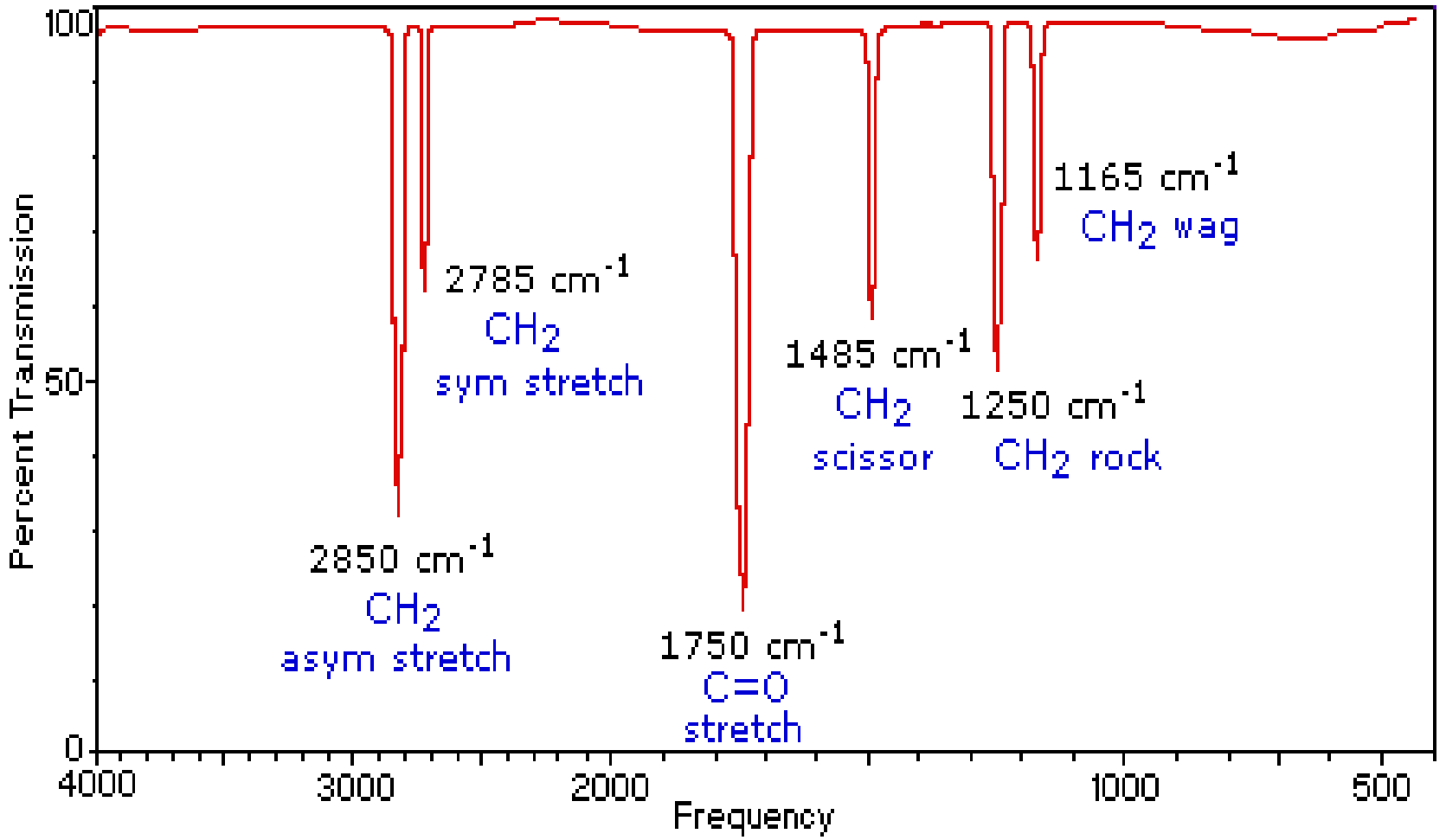


http://www.fdmspectra.com/fdm_ftir_organic.htm

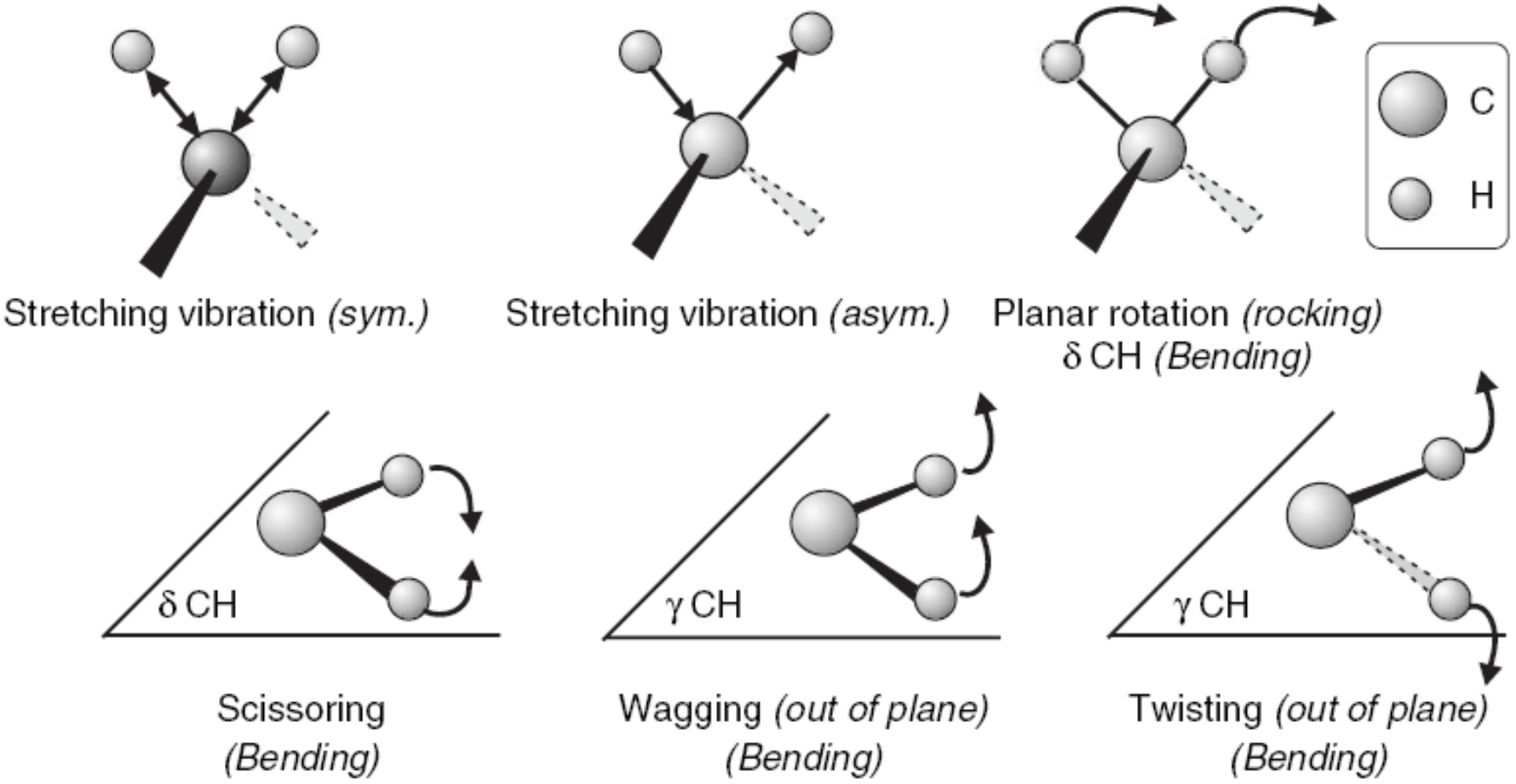
The Aldrich Library of FT-IR Spectra, Edition II

(18,454 infrared spectra of condensed-phase compounds Sigma-Aldrich Co., 1997)

Gas Phase Infrared Spectrum of Formaldehyde ($H_2C=O$)



http://www.cem.msu.edu/~reusch/VirtTxtJml/Spectrpy/InfraRed/infrared.htm



Stretching vibration *(sym.)*

Stretching vibration *(asym.)*

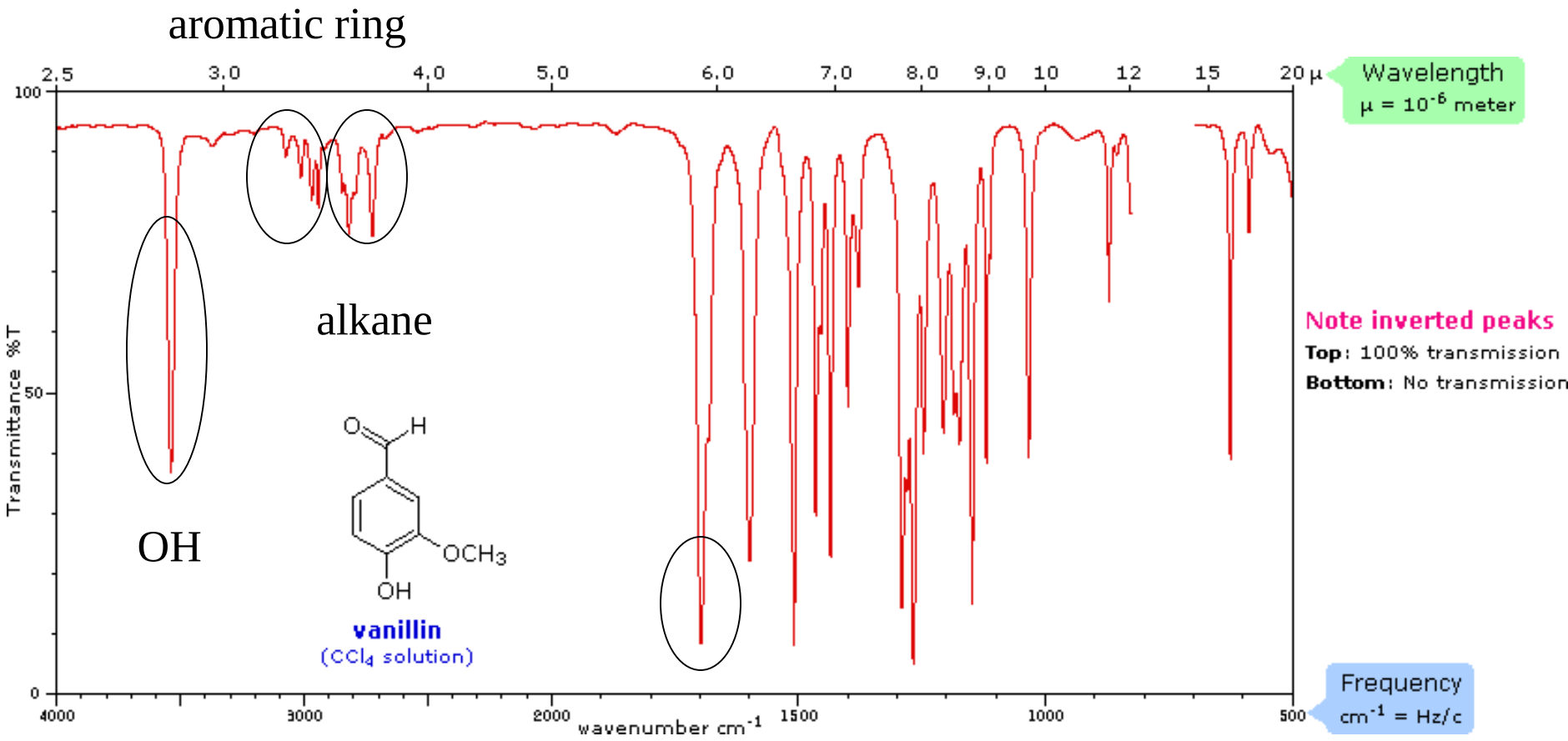
Planar rotation *(rocking)*
δ CH *(Bending)*

Scissoring
(Bending)

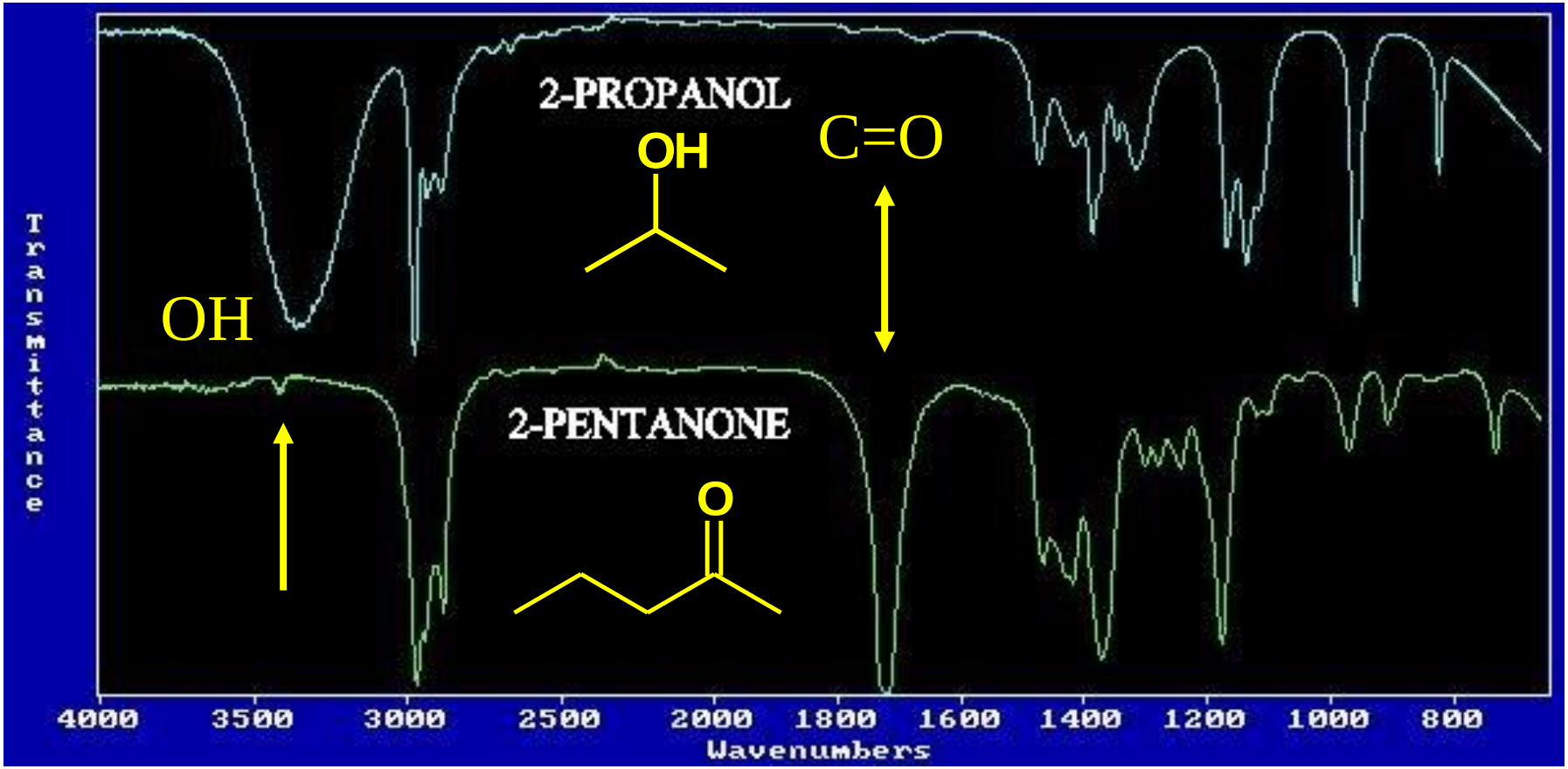
Wagging *(out of plane)*
(Bending)

Twisting *(out of plane)*
(Bending)

Interpretation IR Spectrum

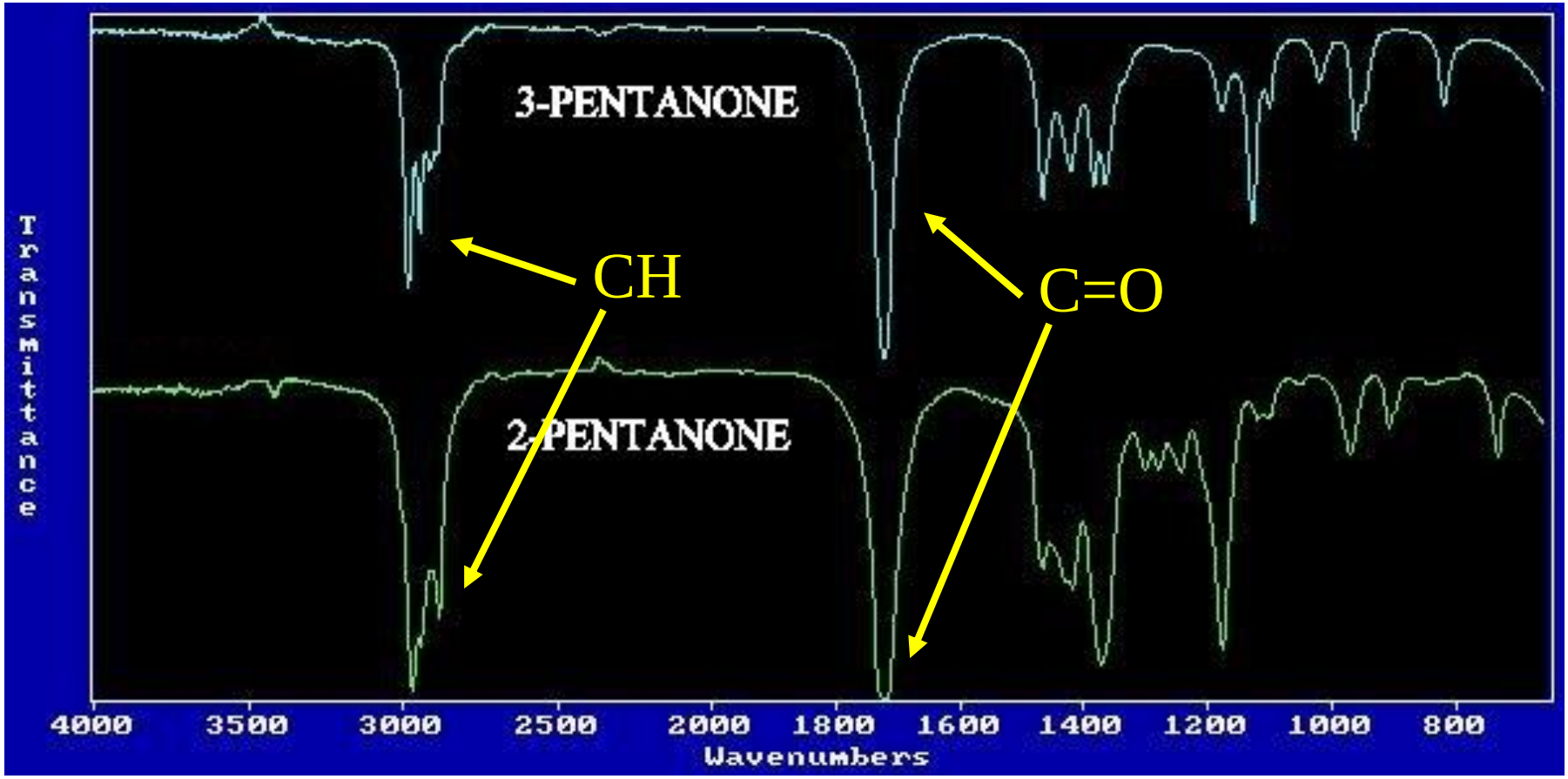


Good News



Infrared spectra provide characteristic vibrational signatures in terms of peak locations and intensities

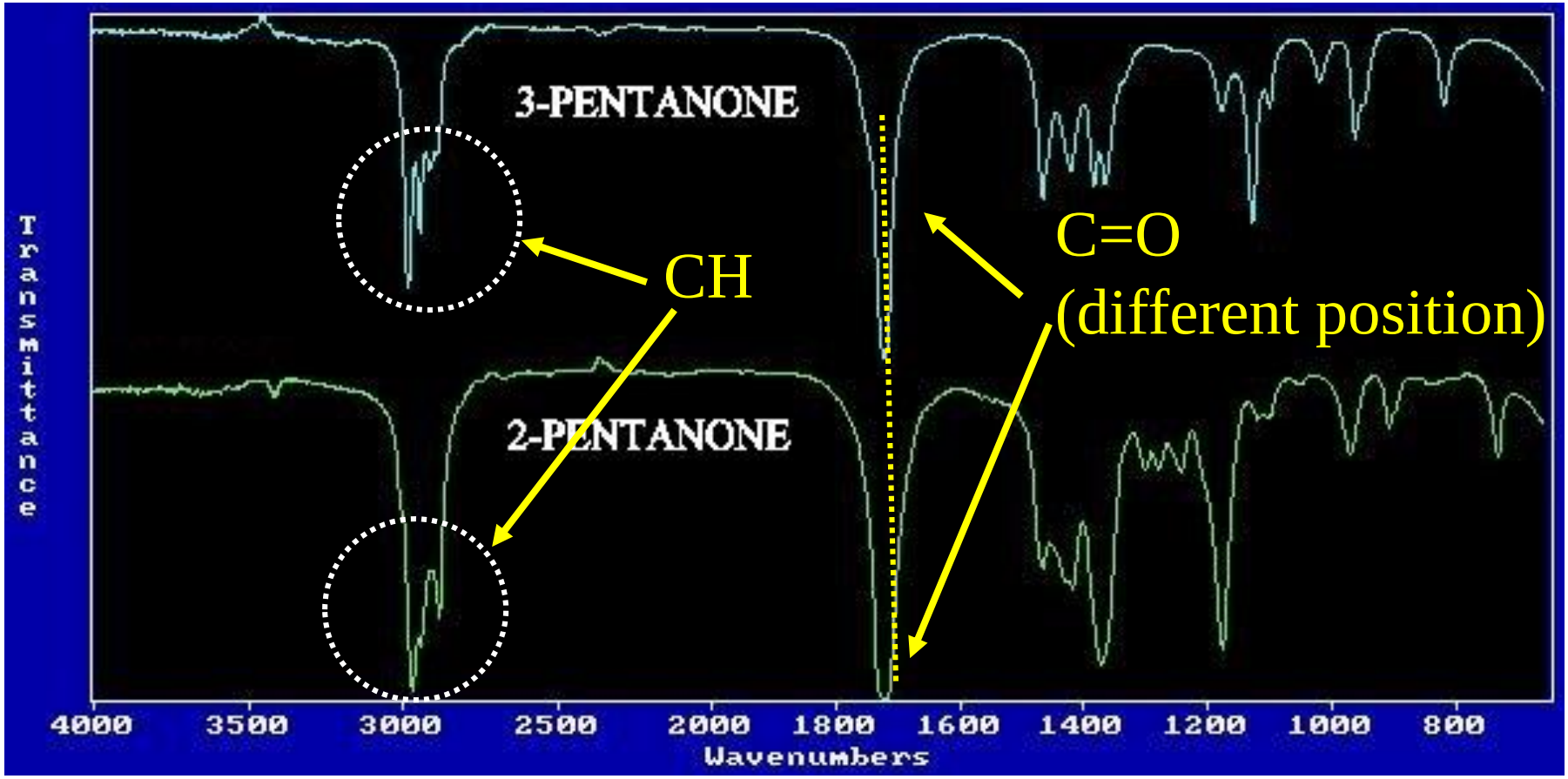
Bad News: Similar Features



2-pentanone vs. 3-pentanone

http://www.uwplatt.edu/~sundin/ir/irl.htm

Good News: Your Opportunity



2-pentanone vs. 3-pentanone

http://www.uwplatt.edu/~sundin/ir/irl.htm

Advantages

1. Easily accessible (available)
2. Relatively simple operation
3. Quick and fast data acquisition
4. Very stable instrument
5. Low operation cost
6. Nondestructive test
7. etc

Disadvantages

1. Low selectivity of functional groups & phase dependence (gas/liquid/solid)

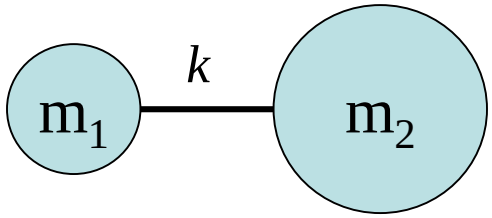
2. Difficult to deduce whole structures w/o complimentary experiments

3. Difficult to determine the concentrations of samples in a mixture

4. Purging the system is required due to the interference (H_2O and CO_2 in air)

5. Protection of optics (CsI, KBr beam splitter)

Origin of Vibrational Frequency



$$\nu_{vib} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \text{ and } \bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \quad (\mu = \frac{m_1 \cdot m_2}{m_1 + m_2})$$

- Vibration frequency depends on force constant (k) and reduced mass (μ)
- For a polyatomic molecule, each fundamental type of vibration is called a ***normal mode***. A normal mode is a collective motion of all the atoms in the molecule where each atom in the molecule moves in phase with each other at a particular frequency
- # of vibrational normal modes = $3N - 6$ for nonlinear, $3N - 5$ for linear), N = number of atoms in a polyatomic molecule (e.g., $H_2O = 3\times3 - 6 = 3$, $CO_2 = 3\times3 - 5 = 4$)
- 3 translational modes and 3 rotational modes (2 for linear)

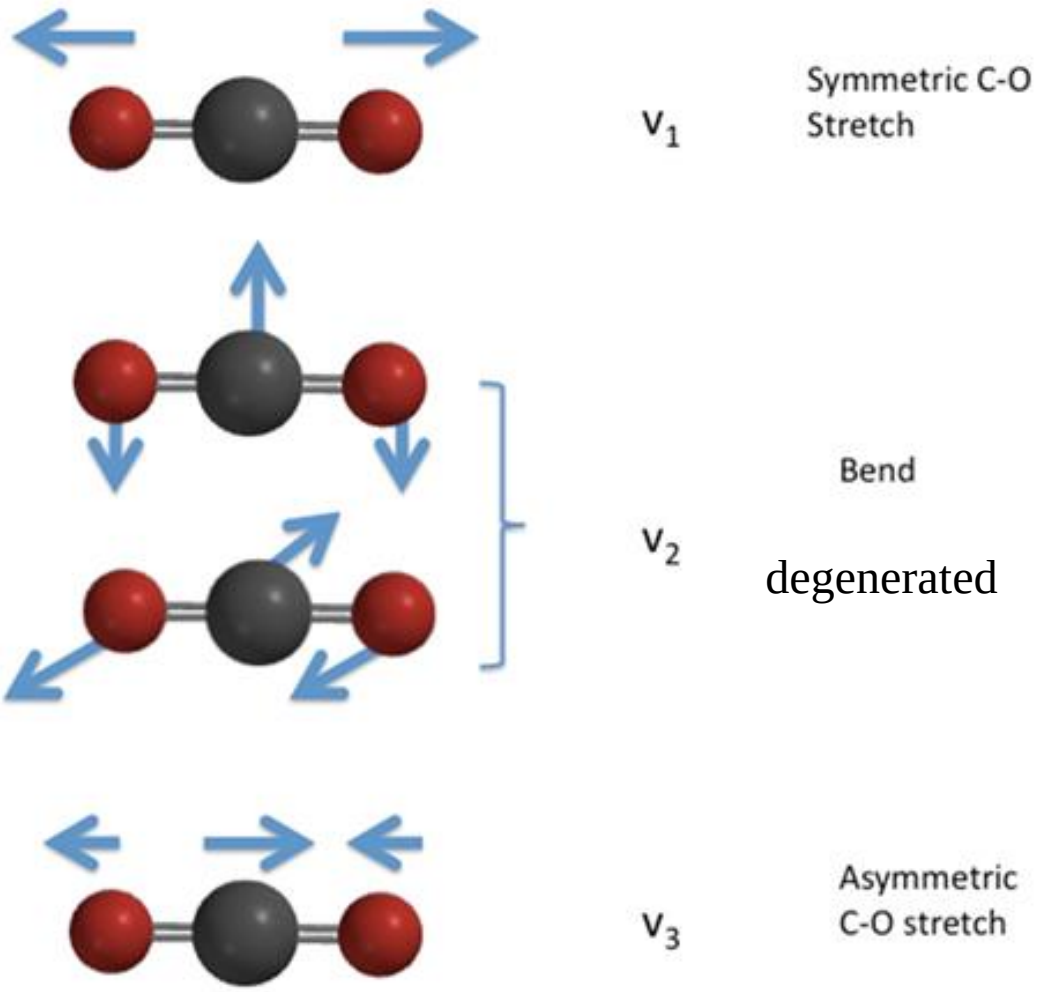
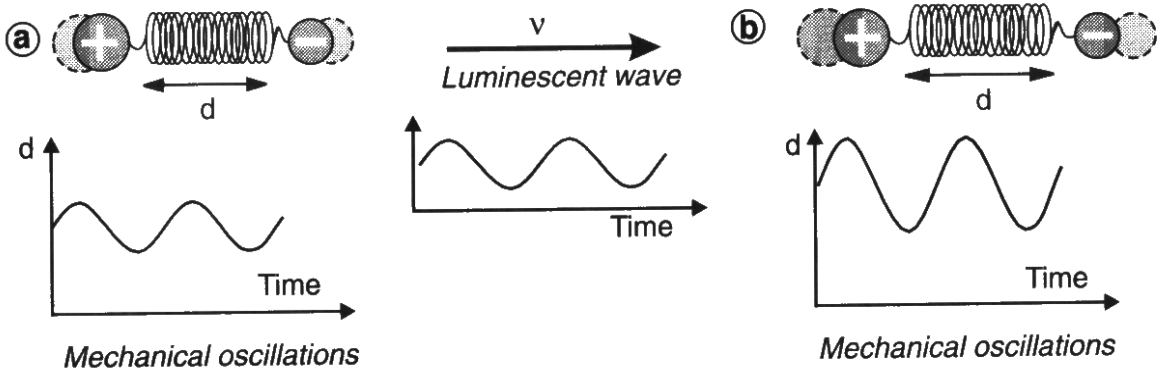


Fig. 1 Vibrational modes of CO_2

Origin of IR Absorption: Selection Rule

- There should be the interaction between an electromagnetic waves and a polar bond



- The dipole moment of the molecule should be changed via vibrational motion

$$\mu_{r,fi} = \langle f | \mu_r | i \rangle = -e \int \psi_f^* r \psi_i d\tau \neq 0 \; for \; absorption$$

ψ_f = final state wavefunction

ψ_i = initial state wavefunction

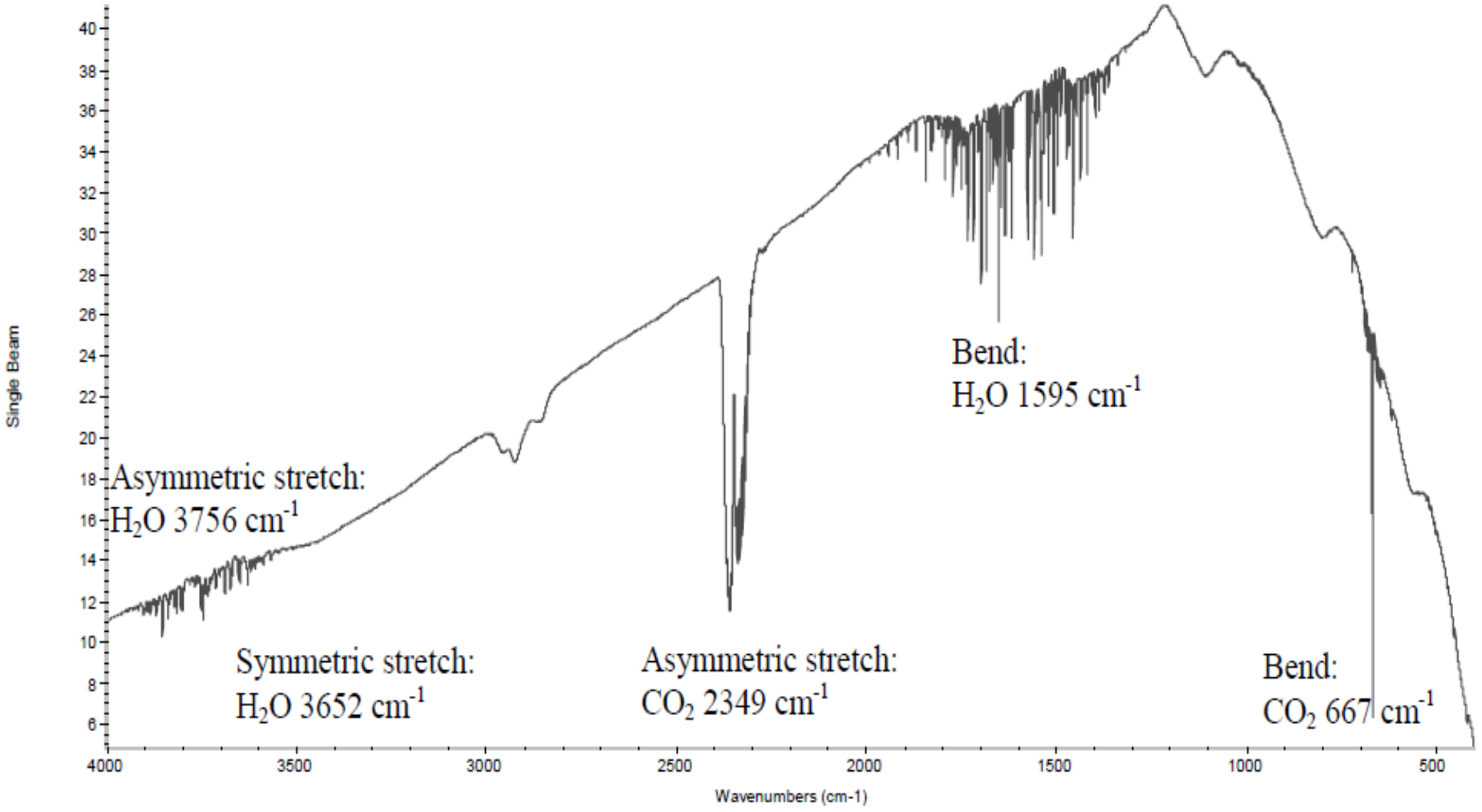
Complexity of Vibrational Frequency: Combination

- Anharmonicity produces *combination peaks* via coupling ($\nu_i + \nu_j$, $\nu_i - \nu_j$,……)

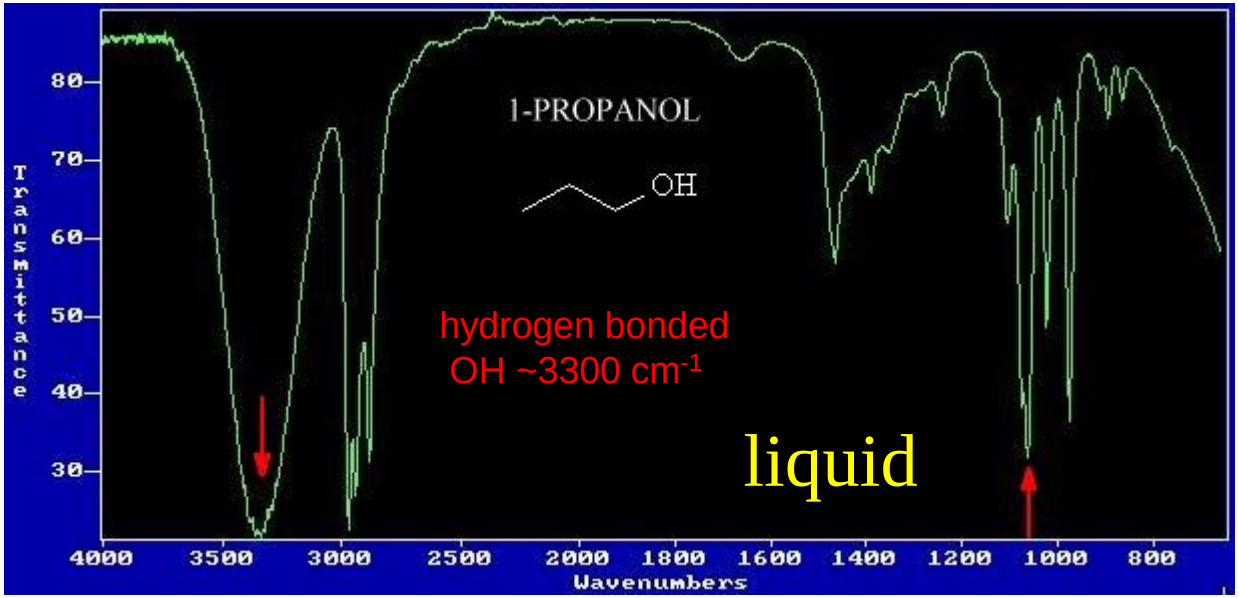
- There is a coupling between overtone peaks and one of the normal vibrational modes
- The conditions of coupling are;
  1. Energy levels of both peaks should be close
  2. They belong to the same symmetry species
- Coupling produces two peaks (one up, the other down)
- *Fermi resonance*

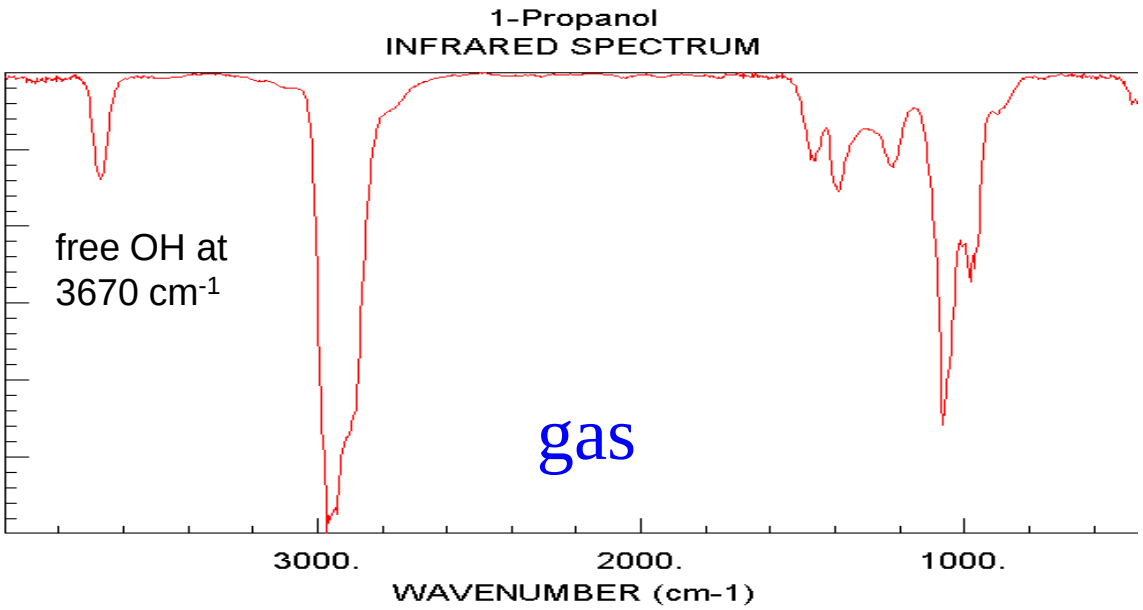
Complexity of Vibrational Frequency: Other Factors

- # of vibrational normal modes increases for polyatomic molecules
- CO_2 and H_2O in the instrument produce additional peaks (Vibrational-rotational spectrum)
- Chemical heterogeniety (chemical environments are different)
- Phase dependence
  1. Molecules are more homogenous for gas phase
  2. Molecules in condensed phases (liquid and solid) show heterogeneous line broadening


Single Beam
40
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)
Asymmetric stretch:
H2O 3756 cm-1
Symmetric stretch:
H2O 3652 cm-1
Asymmetric stretch:
CO2 2349 cm-1
Bend:
H2O 1595 cm-1
Bend:
CO2 667 cm-1

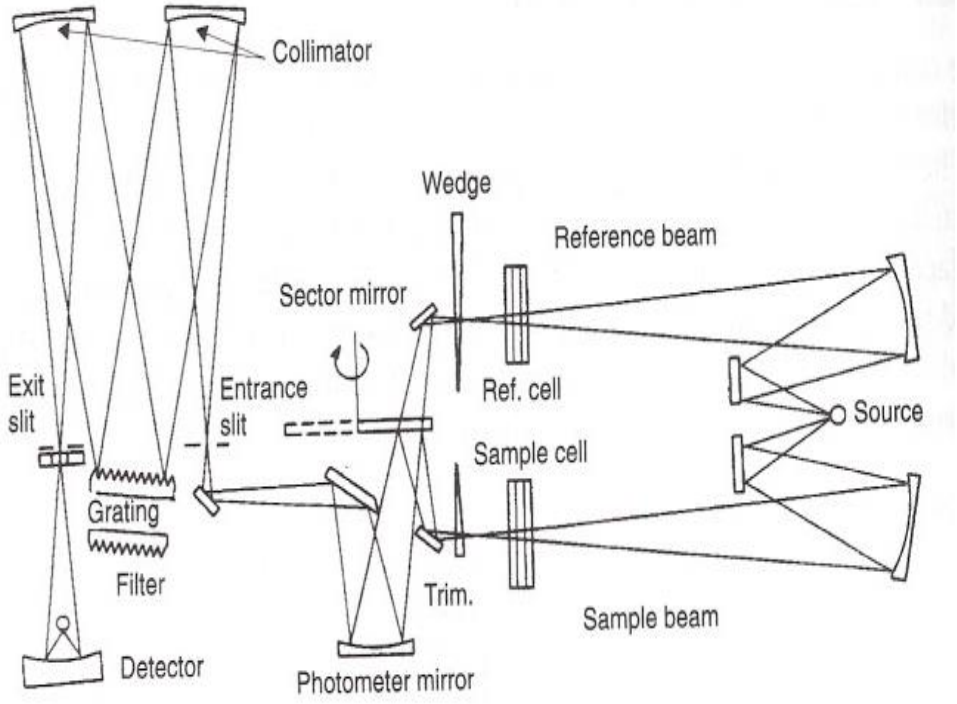
Phase Dependence for OH Group

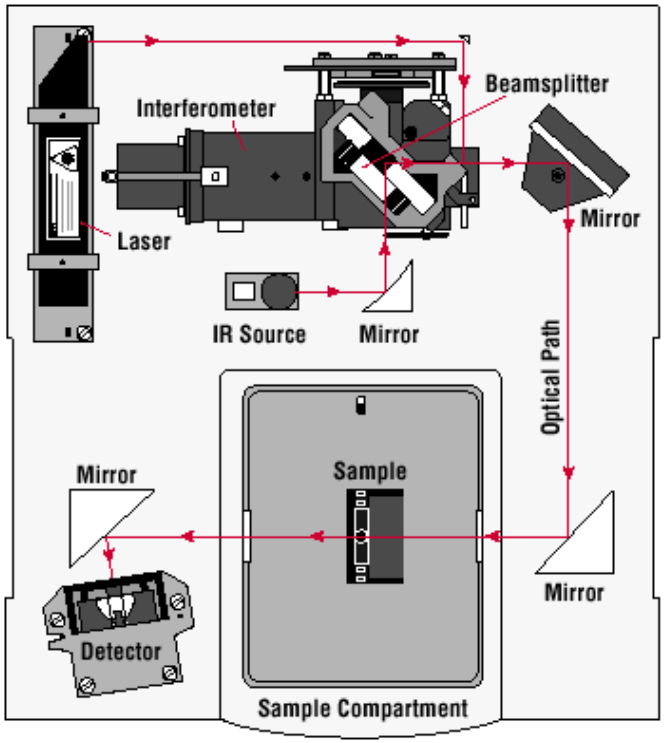




Instrumentation

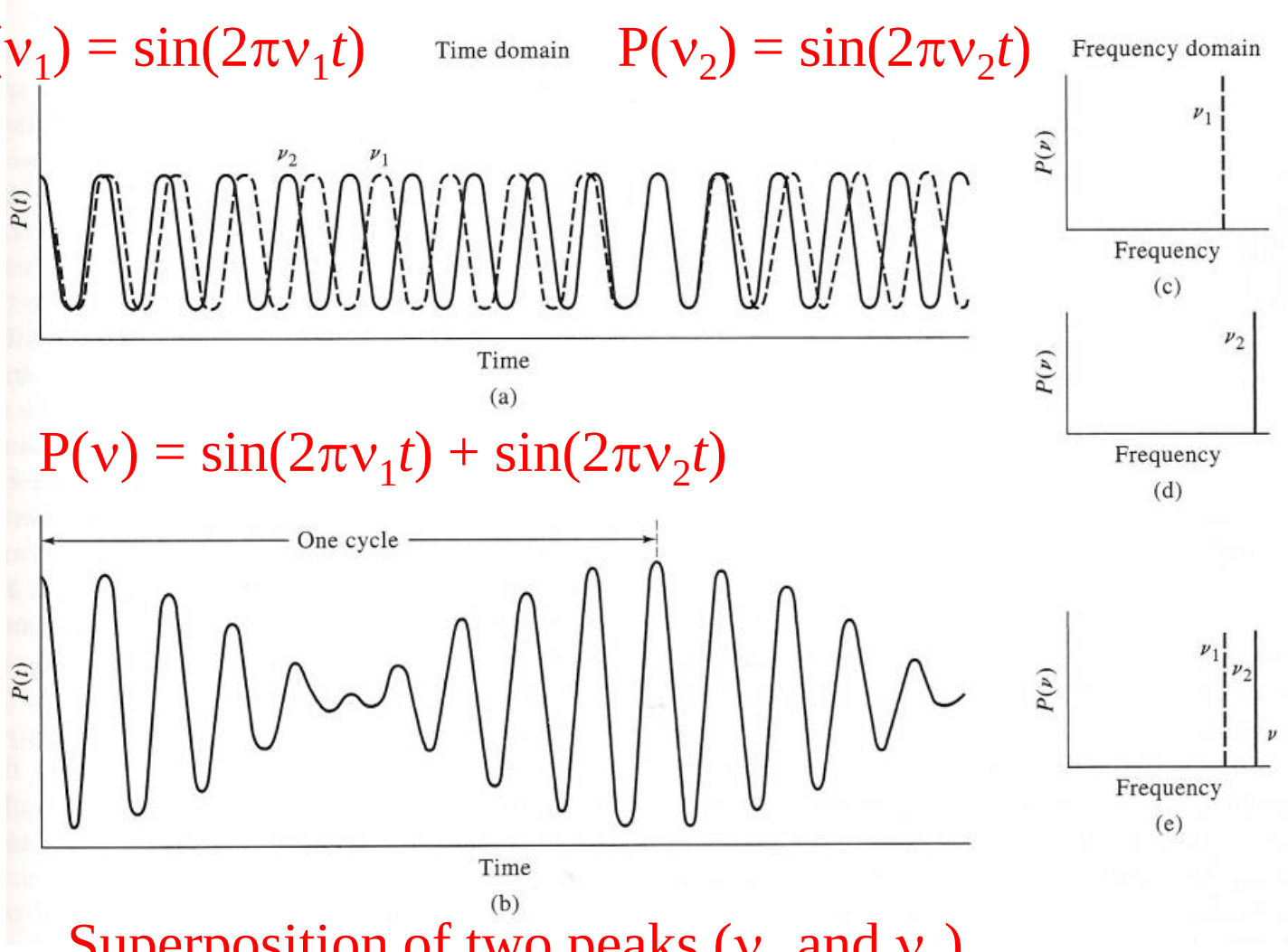
- Dispersive mode: sequential scanning data collection (double beam and single beam)
- Nondispersive mode: selected wavenumbers
- Fourier transform (FT): simultaneous collection





Fourier Transform Between Time and Wavenumber

$P(\nu_1) = \sin(2\pi\nu_1 t)$ Time domain $P(\nu_2) = \sin(2\pi\nu_2 t)$ Frequency domain

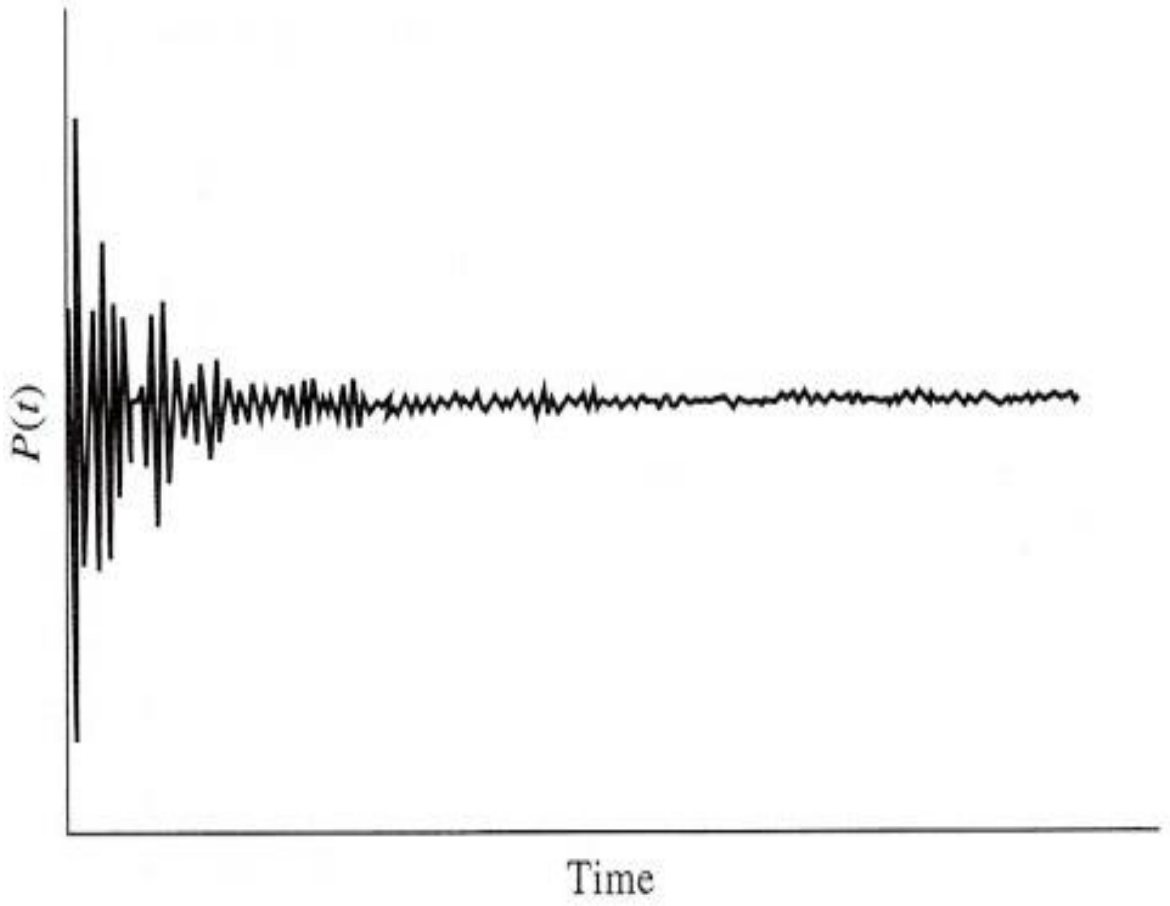


$P(\nu) = \sin(2\pi\nu_1 t) + \sin(2\pi\nu_2 t)$

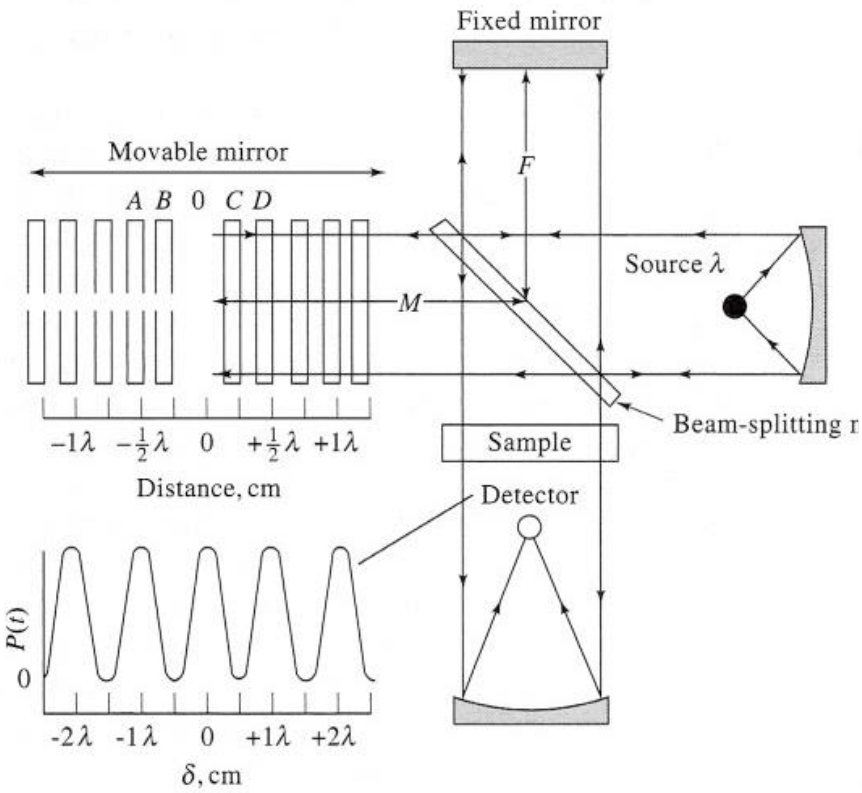
Superposition of two peaks (ν_1 and ν_2)

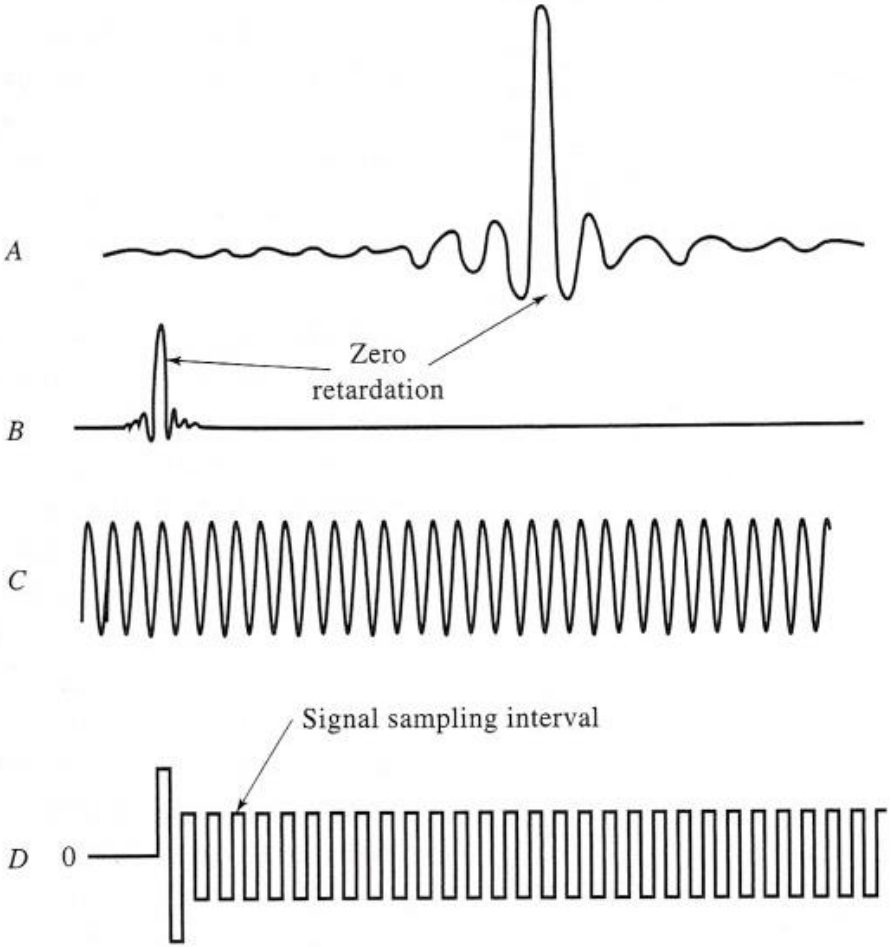
Superposition of All Wavenumbers (400 – 4000 cm^{-1})

$$P(\nu) = \sin(2\pi\nu_1 t) + \sin(2\pi\nu_2 t) + \sin(2\pi\nu_3 t) + \sin(2\pi\nu_4 t) + \ldots\ldots$$

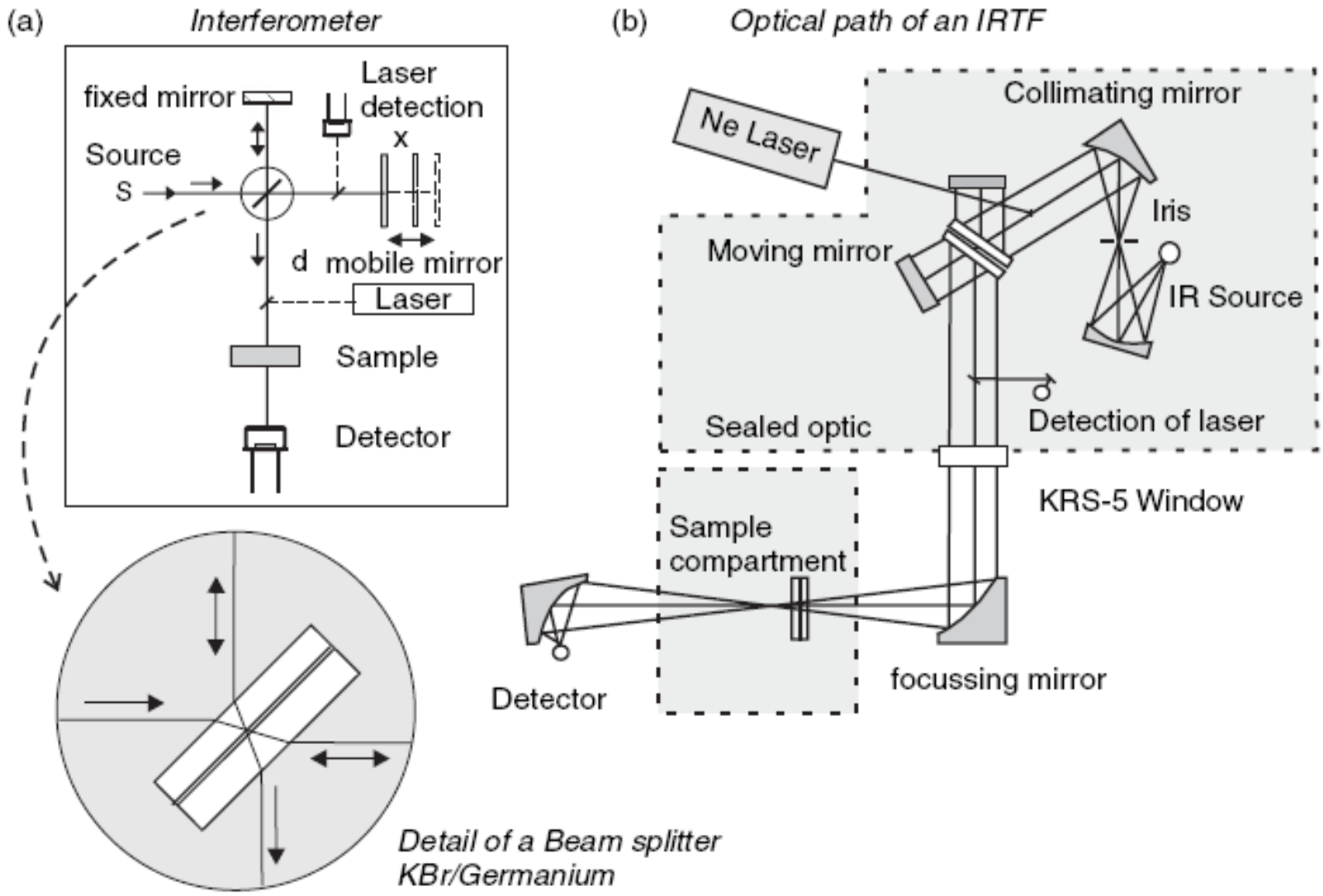


Interferogram: Conversion of Time to Location



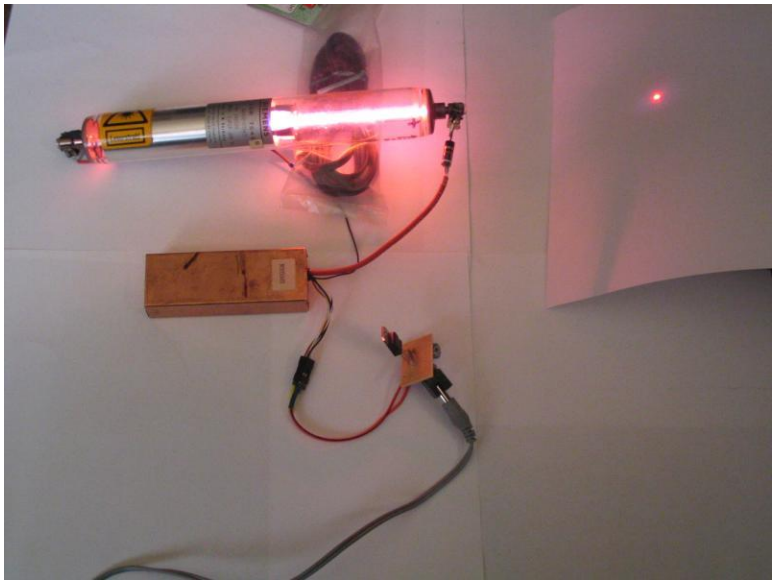


Interferogram and FTIR

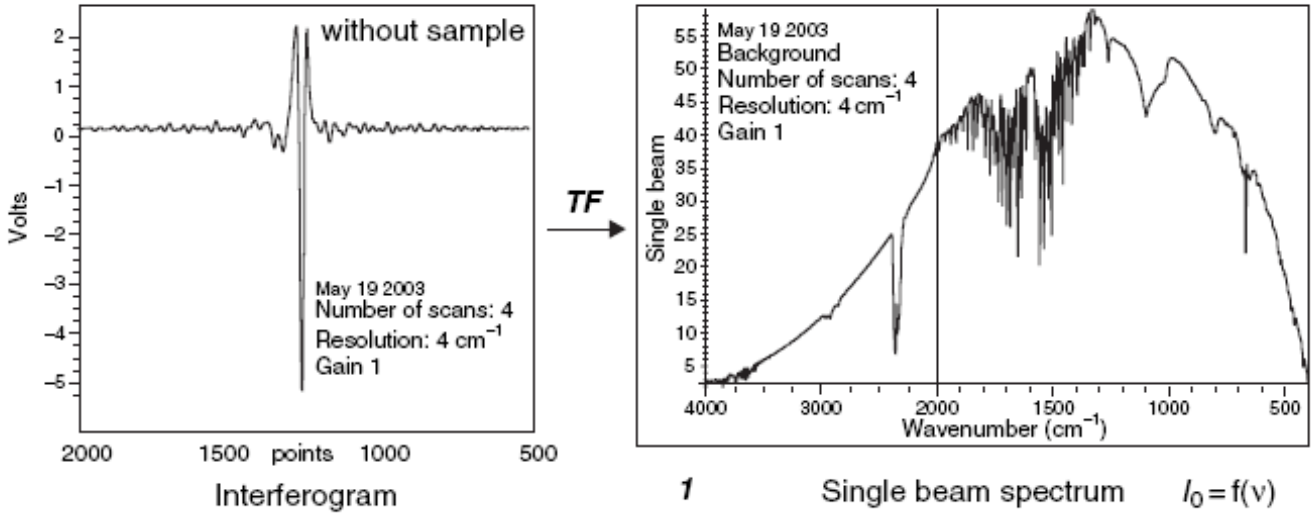


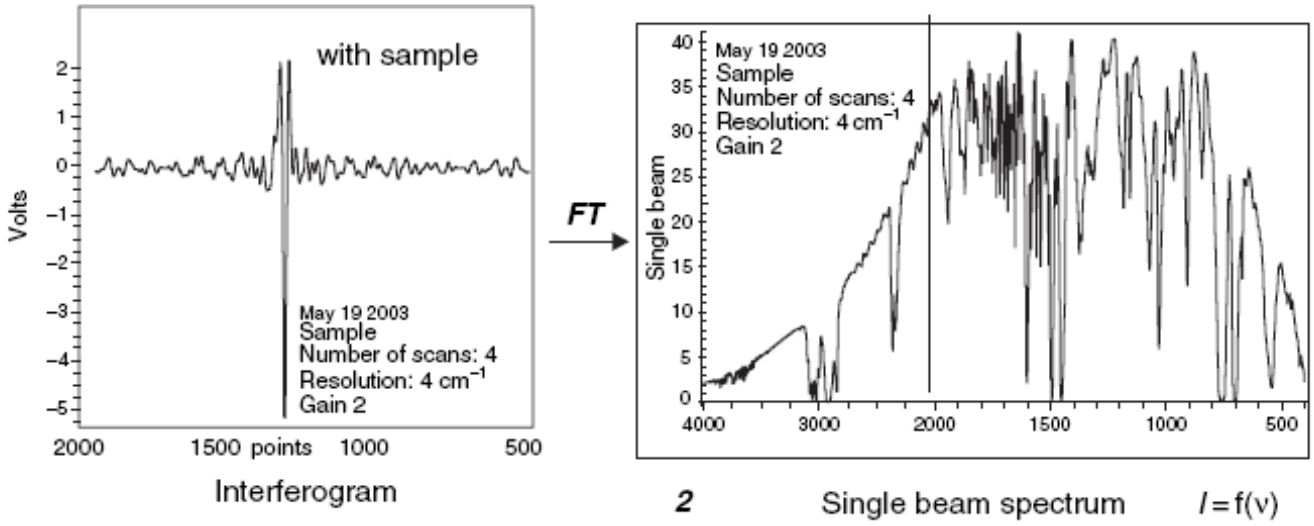
Why HeNe Laser in FTIR?

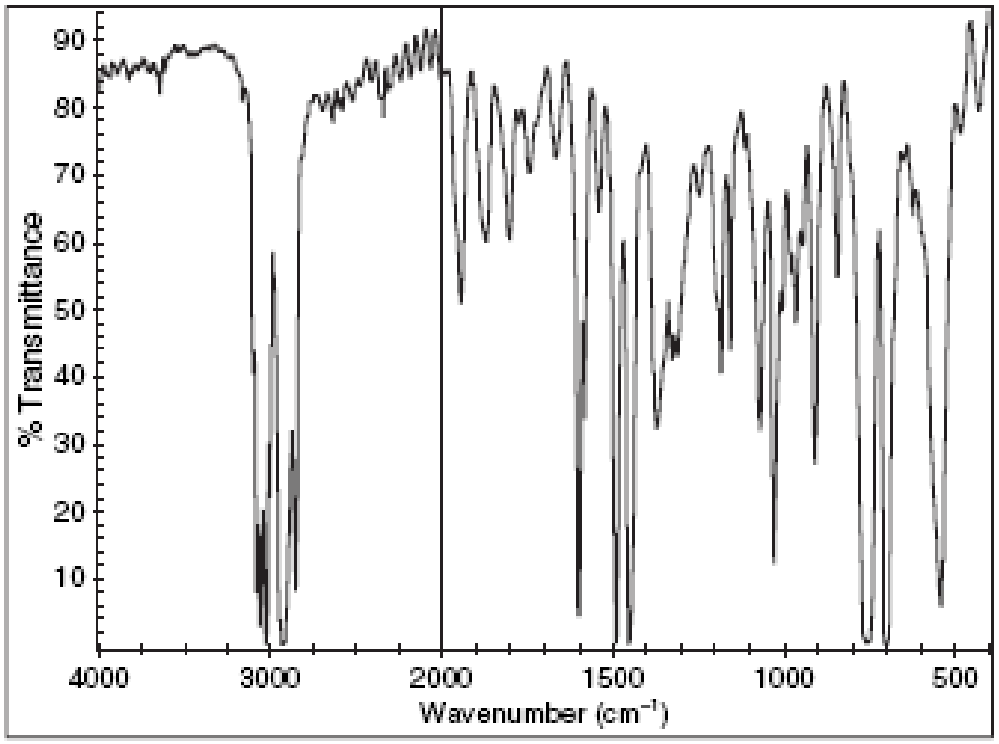
- The wavelength HeNe is very stable and reproducible (632.8 nm)
- Control of position (zero retardation) and speed of movable mirror for precise signal sampling & averaging



FTIR and Pseudo-Double Beam



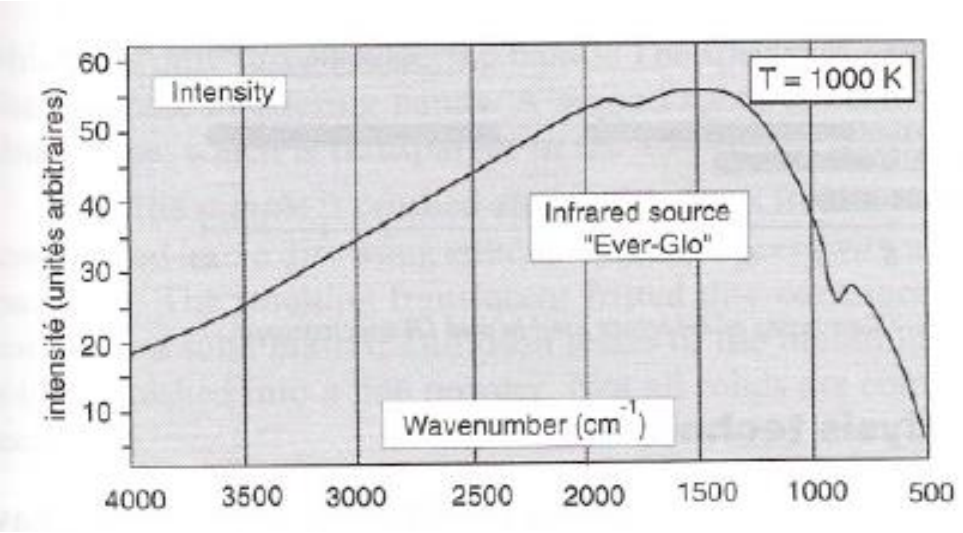




Spectrum after calculating ratio of emittances ***2/1***

IR Sources and Optics

- An inert solid (zirconium oxide) that is electrically heated to 1000 to 2000 K
- IR grade windows for instrumentation and sample holders: minimum absorption (fused silica, ZnSe, NaCl, CaF_2, sapphire (Al_2O_3), diamond, etc)



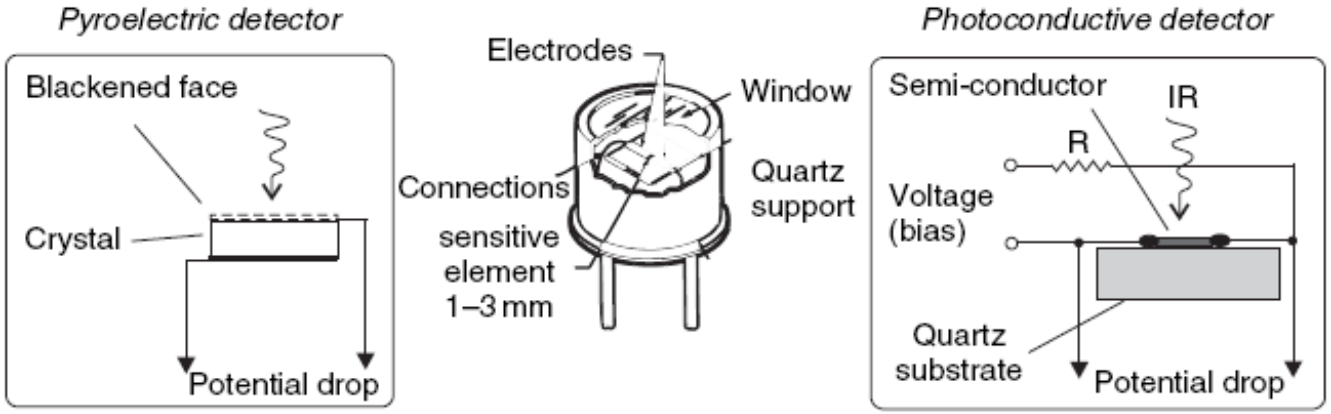
IR Detectors

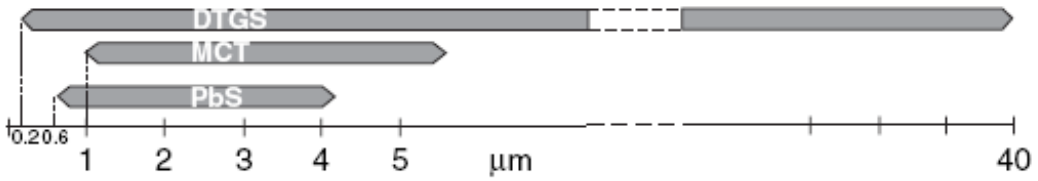
- Pyroelectric detectors
  a. IR is heat wave
  b. Thermoelectric materials produce electricity upon IR exposure
  c. Deuterated triglycine sulfate (DTGS) or lithium tantalate ($LiTaO_3$)

- Photodetectors
  a. Respond to IR (photon)
  b. Fast and more sensitive than pyroelectric detectors
  c. Cooling is required to reduce noise
  d. Photovotaic type: produces voltage (MCT)
  e. Photoconductive: changes conductivity (InSb)
  f. Photodiode: converts IR into current/voltage (InGaAs)

IR Detectors

- Pyroelectric detector: contain parts made of materials that exhibit electrical polarization as a response to the change in the material's temperature. Deuterated triglycine sulfate (DTGS) or lithium tantalate ($LiTaO_3$)
- Photodetector: Mercury cadmium telluride (MCT) or indium/antimony (In/Sb) at 77 K by liquid nitrogen





Various IR Detectors

	type	Spectral range(μm)
Indium gallium arsenide(InGaAs)	photodiode	0.7-2.6
Germanium	photodiode	0.8-1.7
Lead sulfide (PbS)	photoconductive	1-3.2
Lead selenide (PbSe)	photoconductive	1.5-5.2
Indium antimonide (InSb)	photoconductive	1-6.7
Indium arsenide (InAs)	photovoltaic	1-3.8
Platinum silicide (PtSi)	photovoltaic	1-5
Indium antimonide (InSb)	photodiode	1-5.5
Mercury cadmium telluride (MCT, HgCdTe)	photoconductive	0.8-25
Mercury zinc telluride (MZT, HgZnTe)	photoconductive	
Lithium tantalate ($LiTaO_3$)	pyroelectric	
triglycine sulfate (TGS and DTGS)	pyroelectric	

Beam Splitters and Detectors

IR range	*Beamsplitter*	*Detector*	*Spectral range (cm^{-1})*
Near-IR	Quartz	MCT-A**	11,700 - 2,800
		MCT-B**	11,700 - 2,800
		InSb*	10,000 - 2,800
		PbSe	11,000 - 2,800
		Si	15,800 - 8,600
	CaF_2	MCT-A**	11,700 - 2,100
		MCT-B**	11,700 - 2,100
		InSb*	10,000 - 2,100
		PbSe	11,000 - 2,100
		Si	15,000 - 8,600
Mid-IR	KBr	DTGS-KBr	7,400 - 350
		MCT-A**	7,400 - 600
		MCT-B**	7,400 - 400
	CsI†	DTGS-CsI	6,400 - 200
		MCT-A**	6,400 - 600
		MCT-B**	6,400 - 400
Far-IR	Solid substrate™	DTGS-PE	700 - 50

* Will not produce signal under intense light. During installation and alignment, start with smallest aperture setting. InSb detectors must be cooled with liquid nitrogen before use.

** These detectors must be cooled with liquid nitrogen before use.

† CsI beamsplitters are extremely hygroscopic (sensitive to moisture).

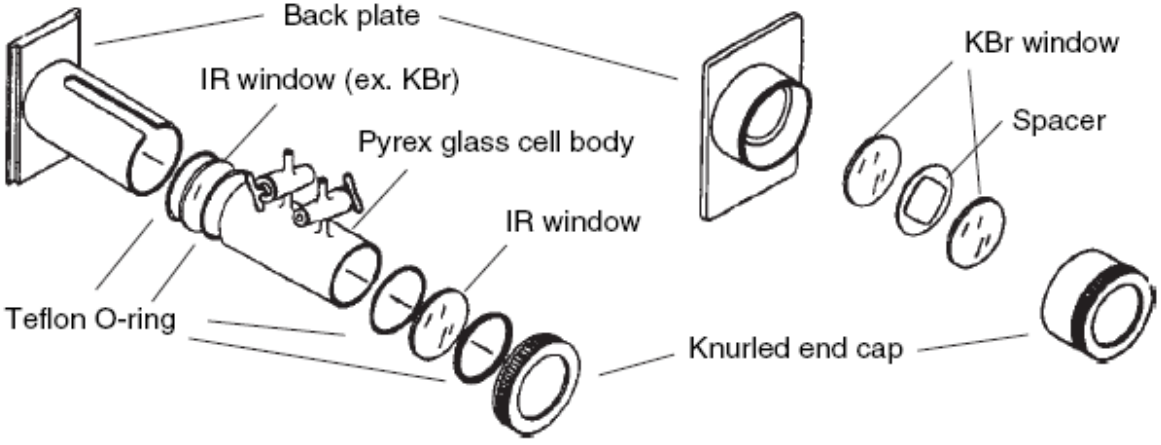
FTIR Anatomy

1. Parts inside the FTIR bench

2. Functions

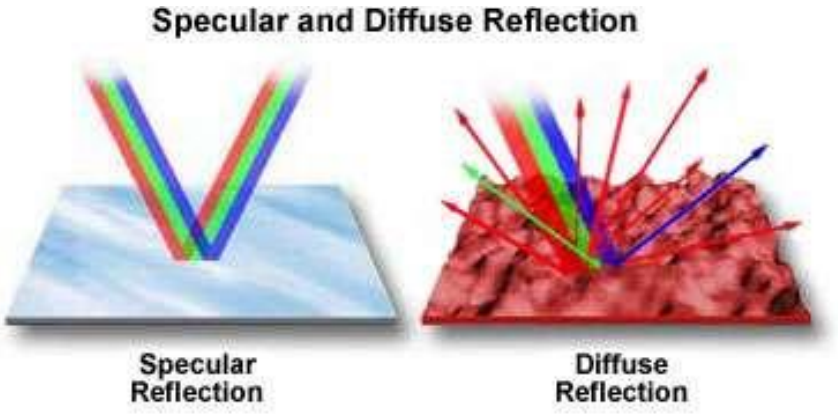
Transmission Mode

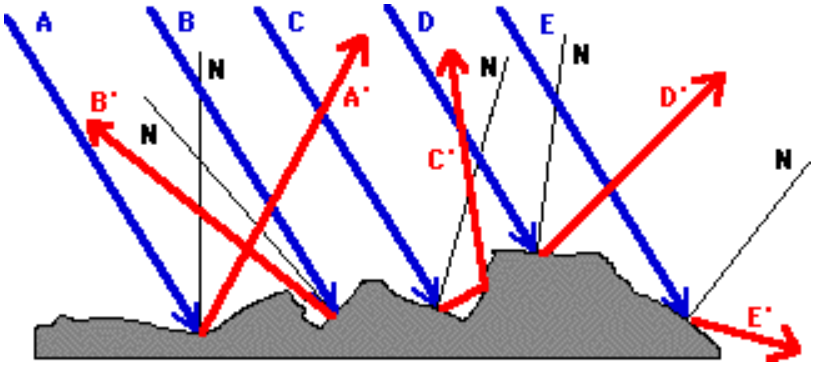
- Gas analyzer for gas
- NaCl, KBr or quartz cell for liquids
- KBr pallet or paraffin oil (NUJOL) for solids



commercial gas cell and
cell for liquid film

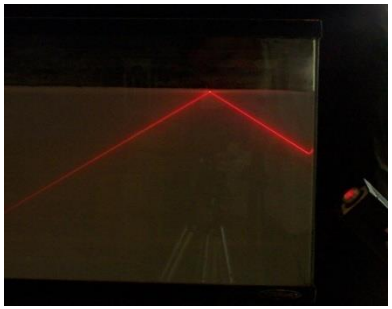
Diffuse vs. Specular Reflection



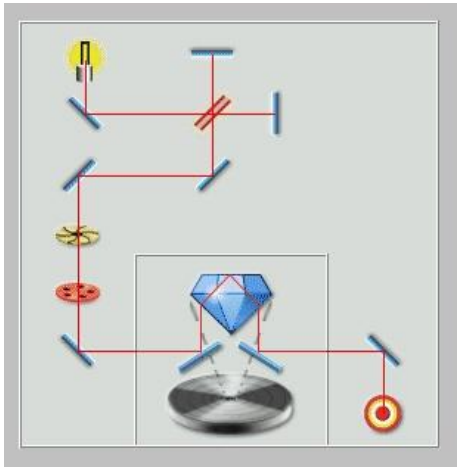


- The angular distribution of reflected light depends upon the nature of the surface
- When light the reflected light is at the opposite angle to the incident light, it is called specular reflectance (flat and mirror surface).
- Reflection from rough surfaces such as clothing, paper, and the asphalt roadway leads to a type of reflection known as **diffuse reflection**.
- Whether the surface is microscopically rough or smooth has a tremendous impact upon the subsequent reflection of a beam of light.

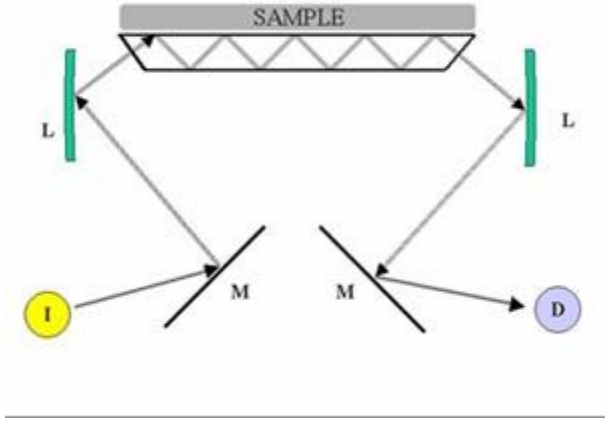
Reflection Mode: Attenuated Total Reflection



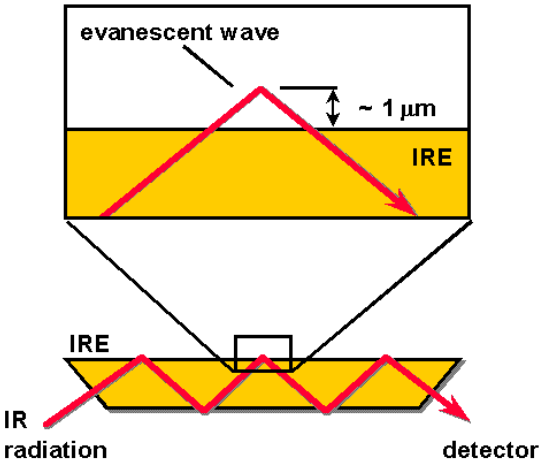
Total internal reflection (angle, refractive index)

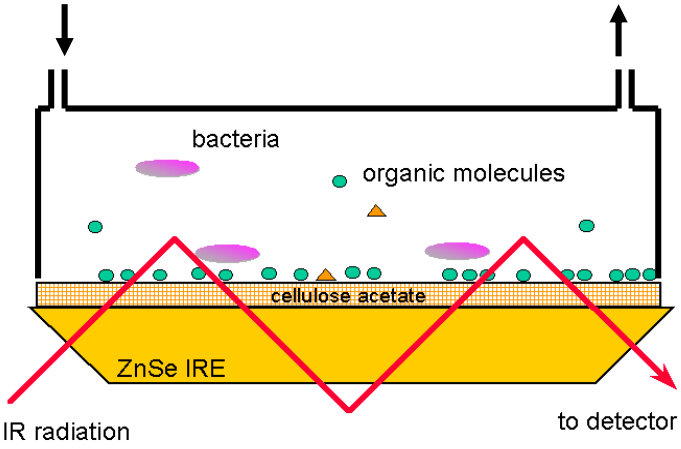


single reflection



multiple reflection





- Air/solid or liquid/solid interface
- In situ adsorption studies
- ZnSe, Si, Ge, etc

HW Problems

TBA