

Product Characterisation 2023

Prof. Sergei G. Kazarian

s.kazarian@imperial.ac.uk

Office:440 Bone building

www.imperial.ac.uk/vsci

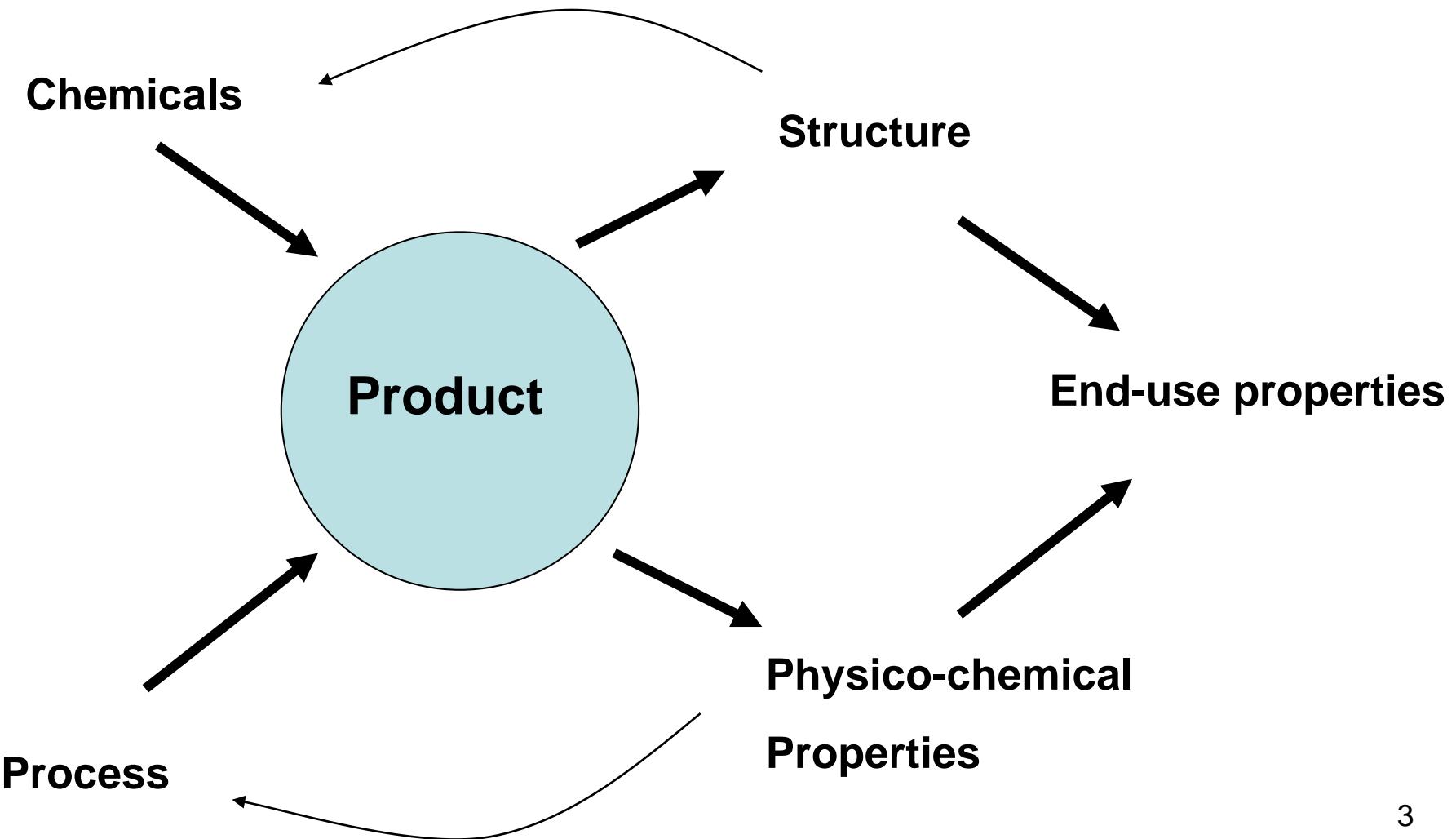
<http://www.imperial.ac.uk/people/s.kazarian>

- Initiated **Product Characterisation** course in 2003

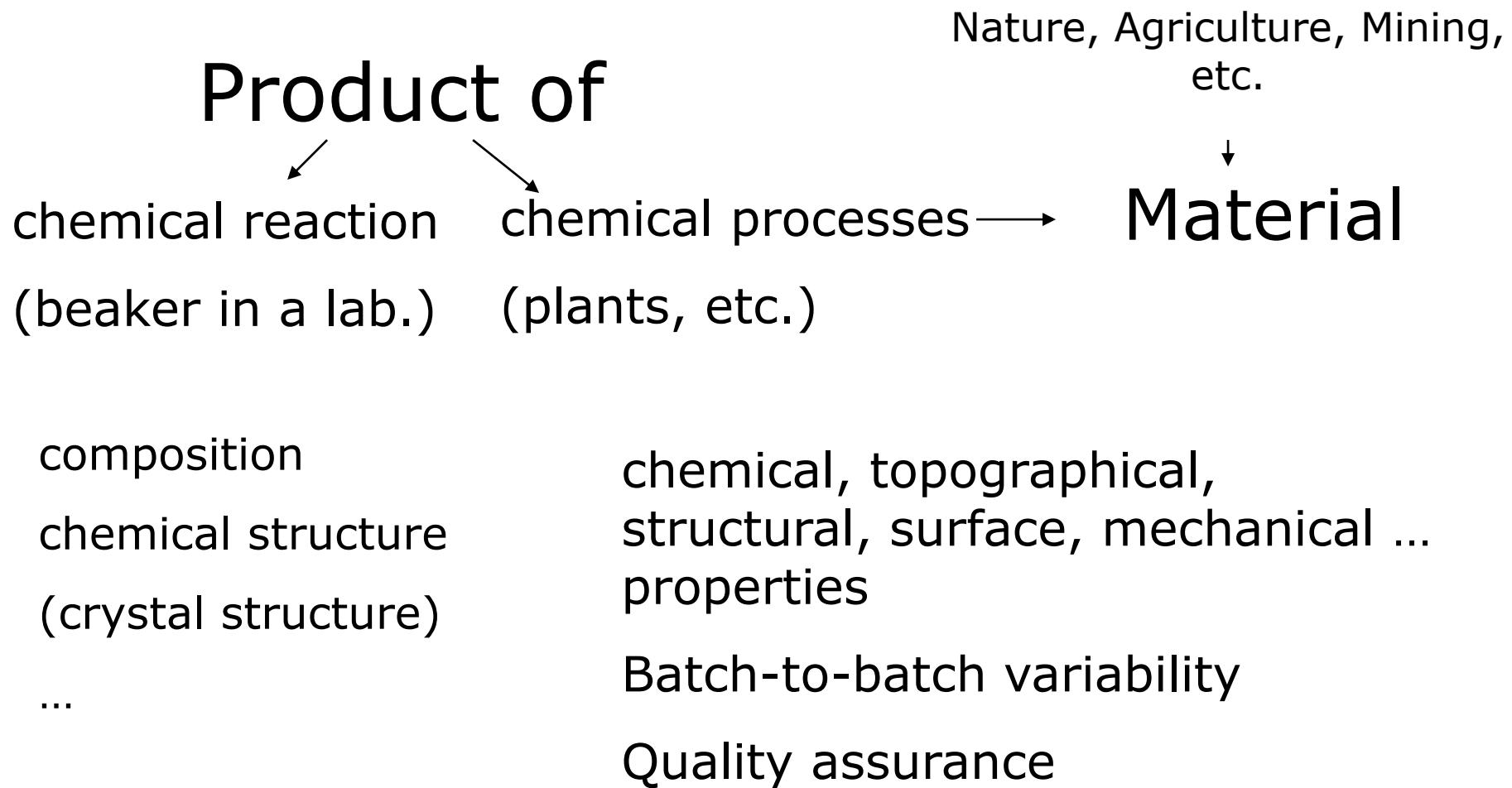
Product Characterisation

- Product and Materials Characterisation
- Introduction to vibrational spectroscopy (IR, Raman)
- Infrared spectroscopy
- Raman spectroscopy
- “Demonstration” of spectroscopic measurements
- Fundamentals
- Applications

Product Characterisation



Product – vs. Materials Characterisation



or a Product in a store, supermarket or ...

EXAMPLE: PRODUCTS FROM POLY(VINYL CHLORIDE) - PVC

annual production (2020): ~ 40 million tons

55 kg PVC products per U.S. citizen



Life

Product Characterisation

Vibrational Spectroscopy: Infrared and Raman

- Basic principles and fundamentals,
- Broad range of applications
- Potential and limitations of
- these tools for product characterisation
- Advanced methods (chemical imaging)

Product design goal:

minimum cost and/or maximum profit

Vibrational Spectroscopy

- Fundamentals of vibrational spectroscopy and Infrared spectroscopy
- Application of ATR-FTIR spectroscopy
- Raman spectroscopy
- Applications to polymeric materials, pharmaceuticals and nanomaterials
- FTIR spectroscopic imaging and applications

Recommended books for my lectures

- Atkins P. W. “Physical Chemistry” (7th, 8th, 9th and 10th Editions).
- Smith A. L. “Applied Infrared Spectroscopy”
- Hollas J. M. “Basic Atomic and Molecular Spectroscopy” (RSC)
- Ball D. W. “Physical Chemistry” (Thomson Brooks/Cole
- Stuart B. “Infrared Spectroscopy: fundamentals and applications”
- Applied Spectroscopy published by SAGE
- www.imperial.ac.uk/vsci (Resources – Teaching Materials)

Coming up....

- Fundamental of vibrational spectroscopy
- “Demonstration”
- Selection rules
- Quantitative law
- Modes of measurements: Transmission and ATR
- What the best way to analyse product?

Spectroscopy

- Light and matter
- What is spectroscopy?
- Applications of spectroscopy
- Electromagnetic spectrum
- Units in spectroscopy
- Origin of molecular spectra
- Harmonic oscillator
- Infrared Spectroscopy
- Beer-Lambert Law

Spectroscopy

Spectroscopy is the study of matter using electromagnetic radiation

Spectroscopy is the study of matter and its properties by investigating light, sound, or particles that are emitted, absorbed or scattered by the matter under investigation

- Atomic spectra (X-ray)
- Electronic spectra (UV/Vis)
- Vibrational spectra (Infrared and Raman)
- Rotational spectra (Microwave)

Interaction of light with matter

- Light and matter are not fundamentally different from one another.
- Both forms can exhibit the properties of either particles or electromagnetic waves, depending on the type of the experiments performed.
- $E = h\nu$
- In spectroscopy we quantitatively measure the consequences of the interaction of light with matter

Spectroscopy

- The principle of frequency-matching resonance
- Spectroscopy is the study of matter using electromagnetic radiation
- **Spectroscopy for determination of molecular structure and physical characteristics of materials**
- Vibrational spectroscopy: method of observing molecular vibrations
- Applications: products and processes

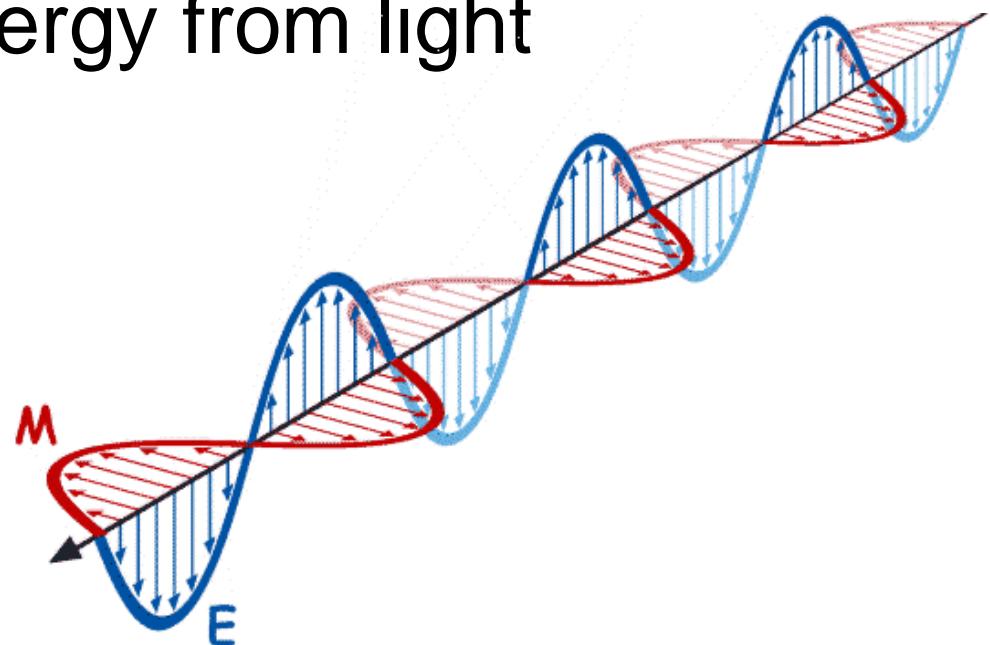
Interaction of light with matter

Light, with its oscillating electric and magnetic fields, interacts most strongly with charged particles of matter

- Matter yielding energy in the form of light
 - **Emission**
- Matter receiving energy from light
 - **Absorption**

Necessary conditions for such exchanges to occur?

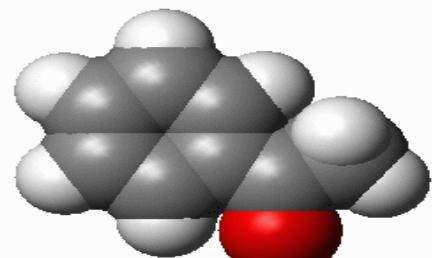
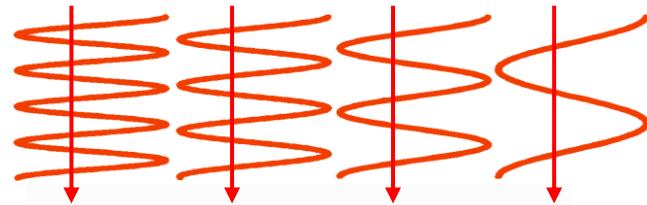
The energy of absorbed radiation must exactly match that of a transition in atom or molecule



Vibrational Infrared Spectroscopy: method of observing molecular vibrations

$\lambda = 2 - 20 \text{ micrometers}$

$1/\lambda = (5000 \text{ cm}^{-1} - 500 \text{ cm}^{-1})$

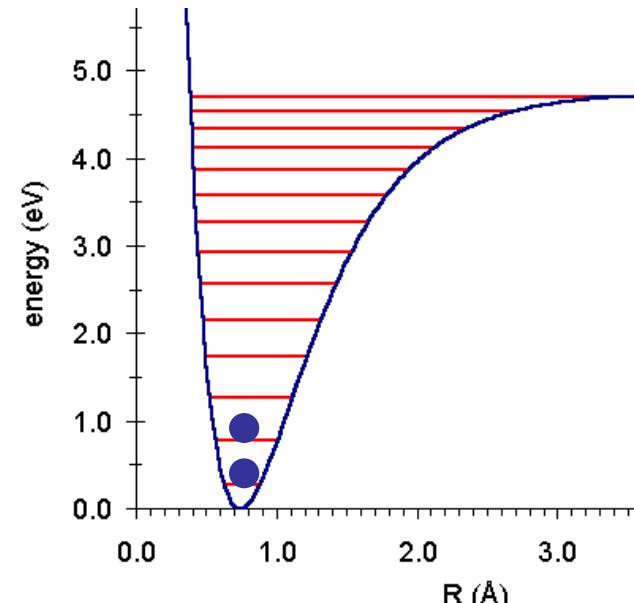


IR - Absorption

Schematics

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}}$$

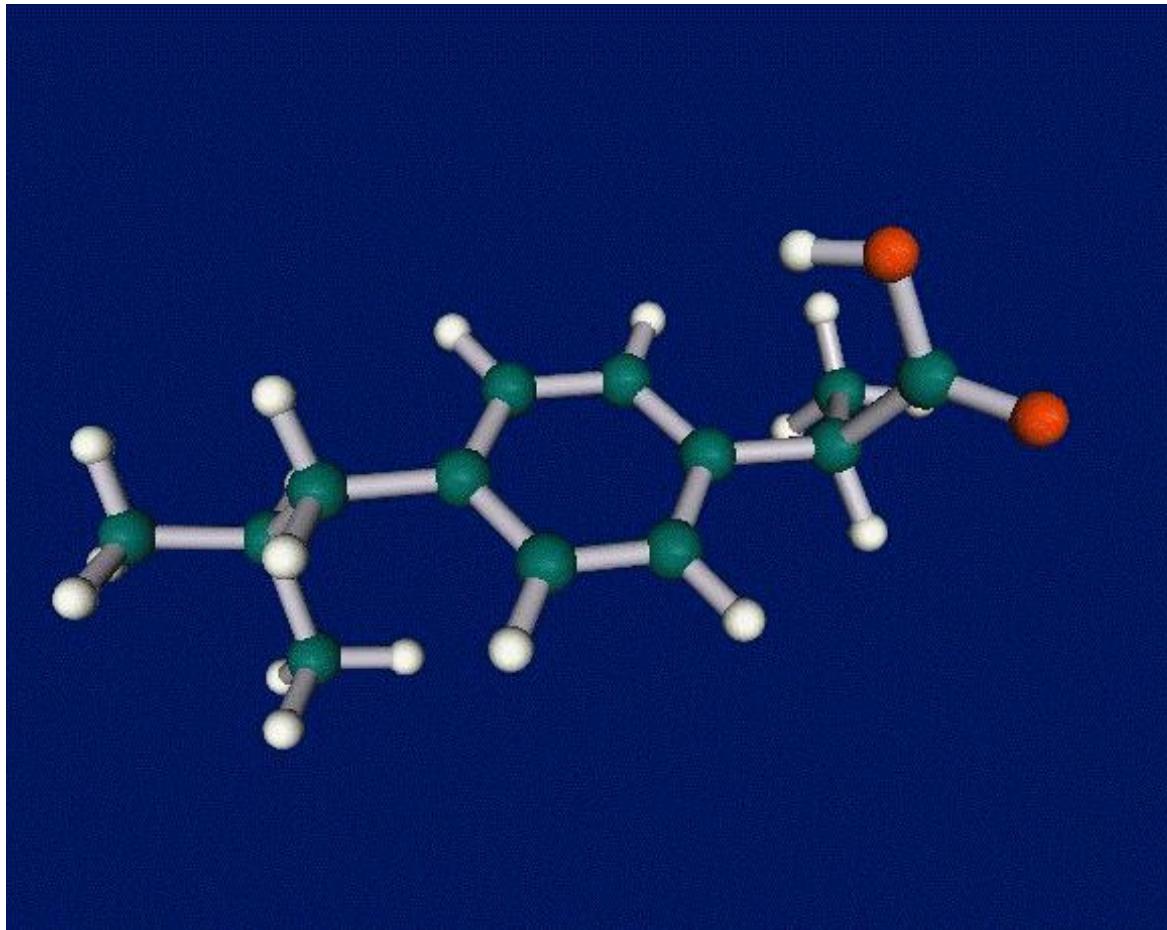
The frequency of absorbed radiation exactly matches the frequency of vibration of a functional group in a molecule



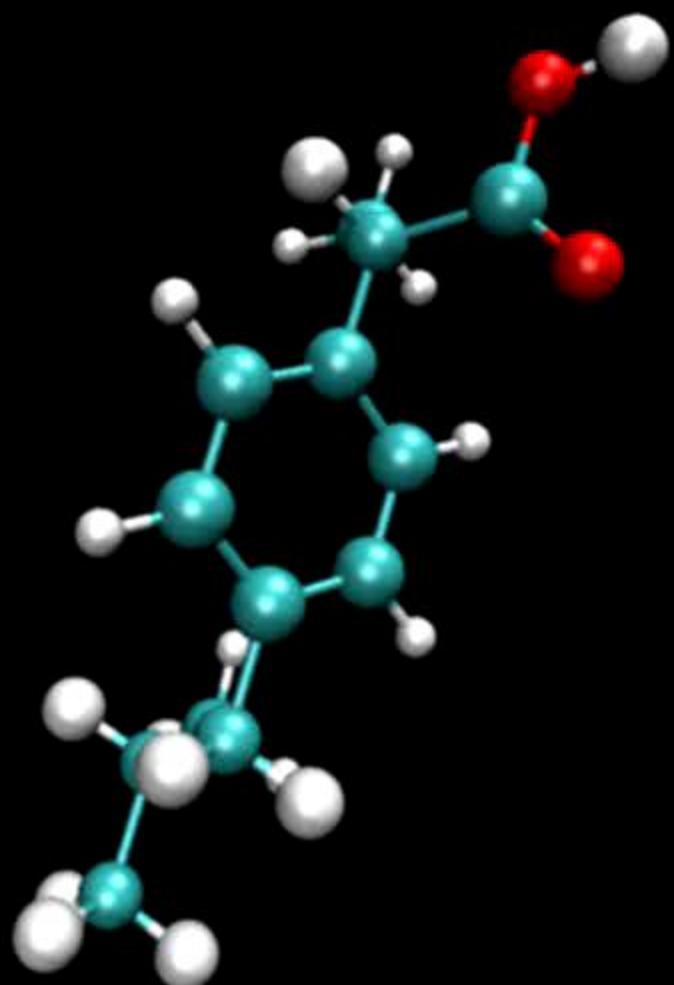
Quantum mechanics description

Example: spectrum of ibuprofen

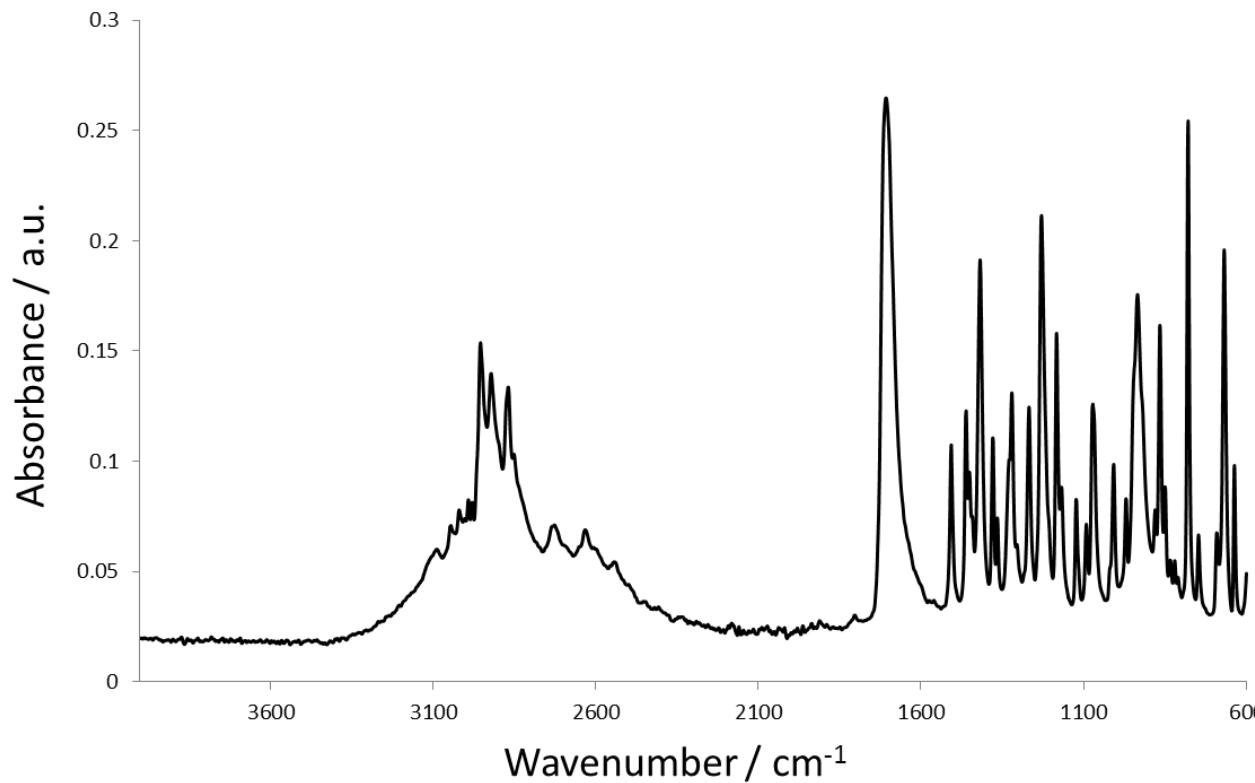
(see structure of ibuprofen molecule below, we “will obtain” infrared spectrum of ibuprofen tablet.



In animation, which we will see in the lecture, vibrations of O-H and C-H groups functional groups will be demonstrated

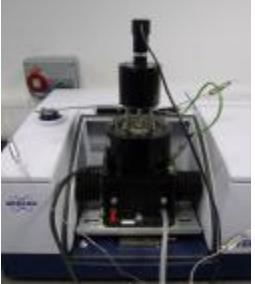
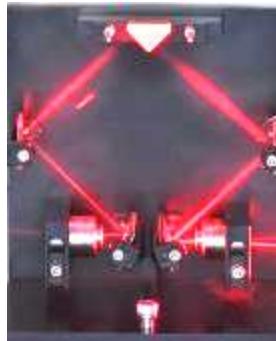


Definition of Spectrum (infrared)



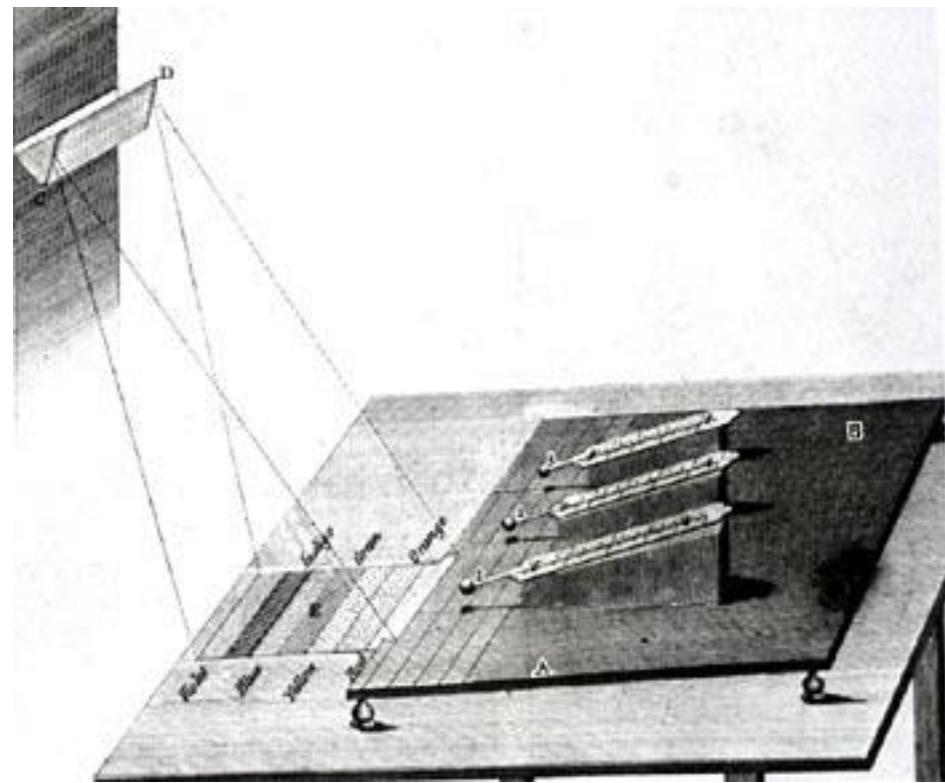
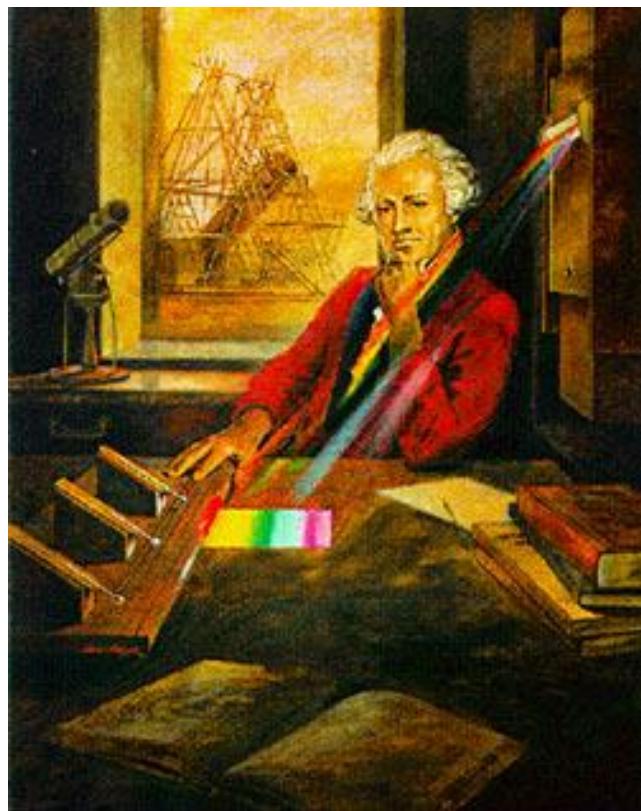
Spectrum is a representation of what electromagnetic radiation is absorbed or emitted by the sample
(this spectrum of ibuprofen tablet will be discussed later)

Examples of advanced infrared spectrometers and accessories



Infrared and William Herschel

a British Astronomer who measured temperature of different colours and discovered existence of infrared:



1738-1822

Invisible Radiation Photography 20

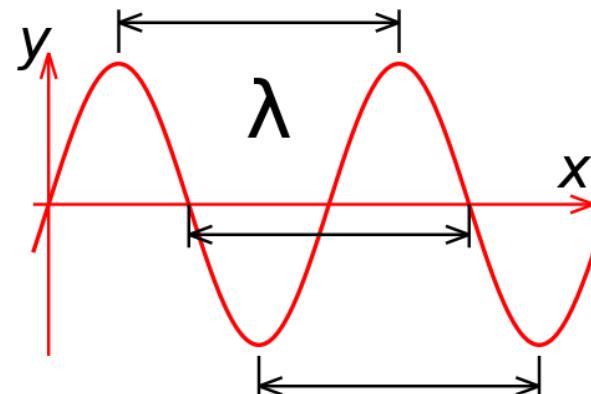
Units in Spectroscopy

λ	Wavelength	length of one wave (m) <i>in UV/Vis, the most common unit is nm</i>
ν	Frequency	waves / s (Hz)
$\tilde{\nu}$	Wavenumber	- waves / cm <i>in IR/Raman, the most common unit is cm⁻¹</i>

$$\lambda = \frac{c}{\nu}$$

$$\tilde{\nu} = \frac{1}{\lambda} \quad \tilde{\nu} = \frac{\nu}{c}$$

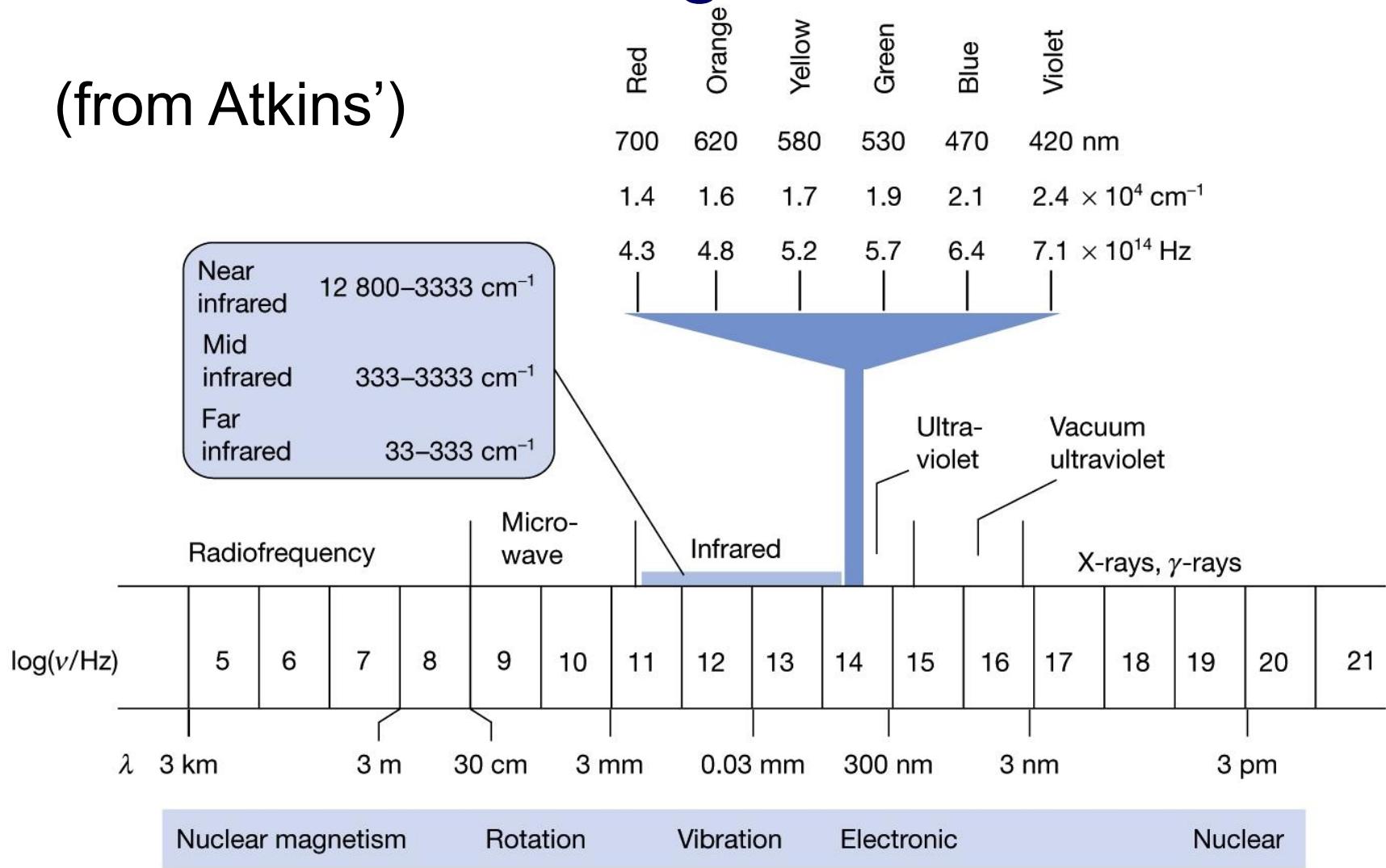
$$E = h\nu = hc/\lambda = hc\tilde{\nu}$$



where c = speed of light and h = Planck's constant

Electromagnetic Waves

(from Atkins')



Note that frequencies of molecular vibrations are in infrared region of the spectra

Decreasing wavelength

Regions of infrared spectrum

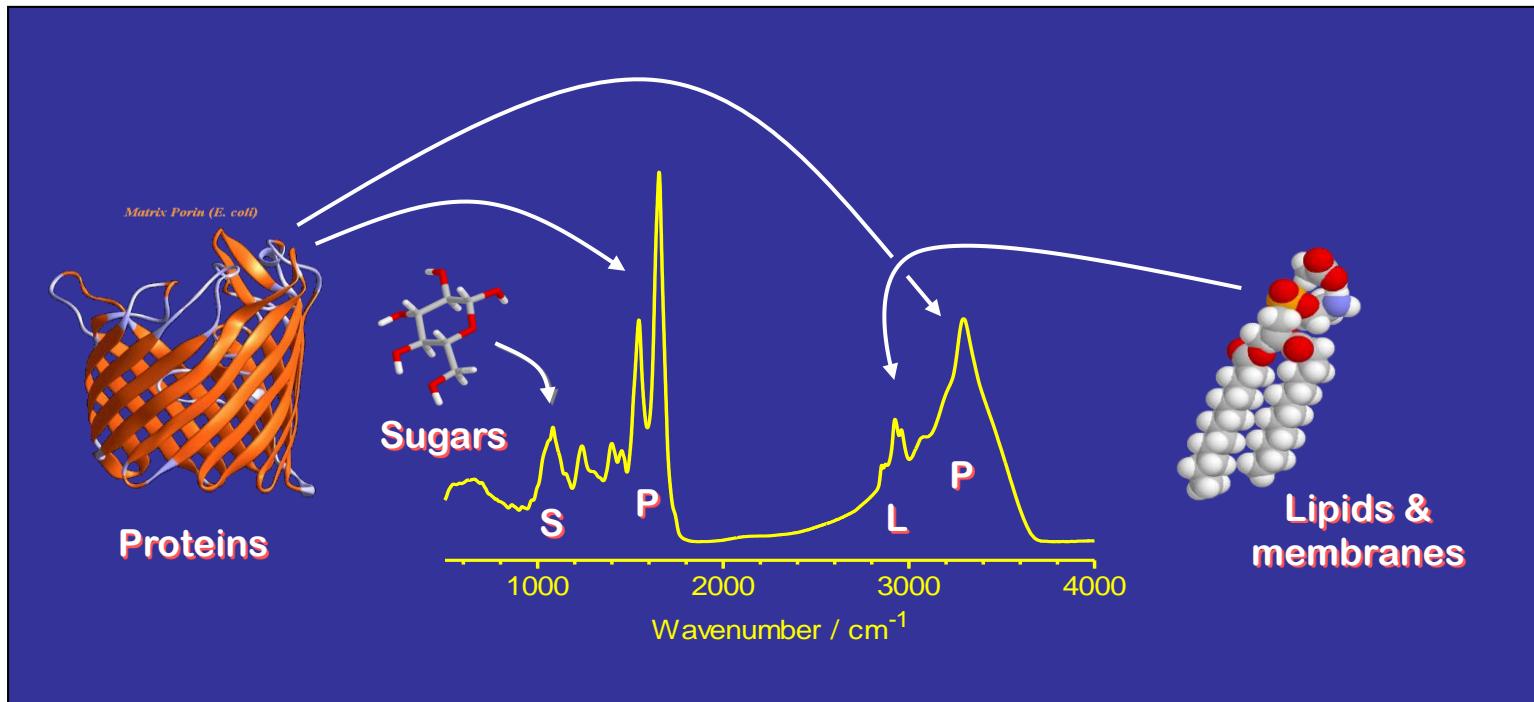
Near-IR $14000\text{-}4000\text{ cm}^{-1}$ Overtones/harmonics

Mid-IR **$4000\text{-} 400\text{ cm}^{-1}$** **Molecular vibrations**

Far-IR $400\text{-}10\text{ cm}^{-1}$ Rotations / low energy vibrations

Infrared Spectroscopy

Understanding the spectroscopic features of complex molecular systems by **Infrared Spectroscopy**



Note that in infrared spectrum of a biological sample (skin, cells, tissue, etc.) spectral bands of proteins, sugars and lipids are clearly seen

The Harmonic Oscillator

$$V(x) = - \int_0^x F(x) dx \\ = \frac{1}{2} k x^2.$$

Schrödinger equation:

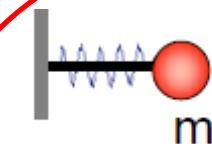
$$d^2\psi/dx^2 + (2m/\eta^2)(E - \frac{1}{2}kx^2)\psi = 0$$

$$\psi = H_v(\xi) \exp(-\xi^2/2) \quad \text{Wave-function}$$

$$E = (v + \frac{1}{2})h\nu \quad v = 0, 1, 2, \dots (\text{quantum number})$$

v = frequency

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

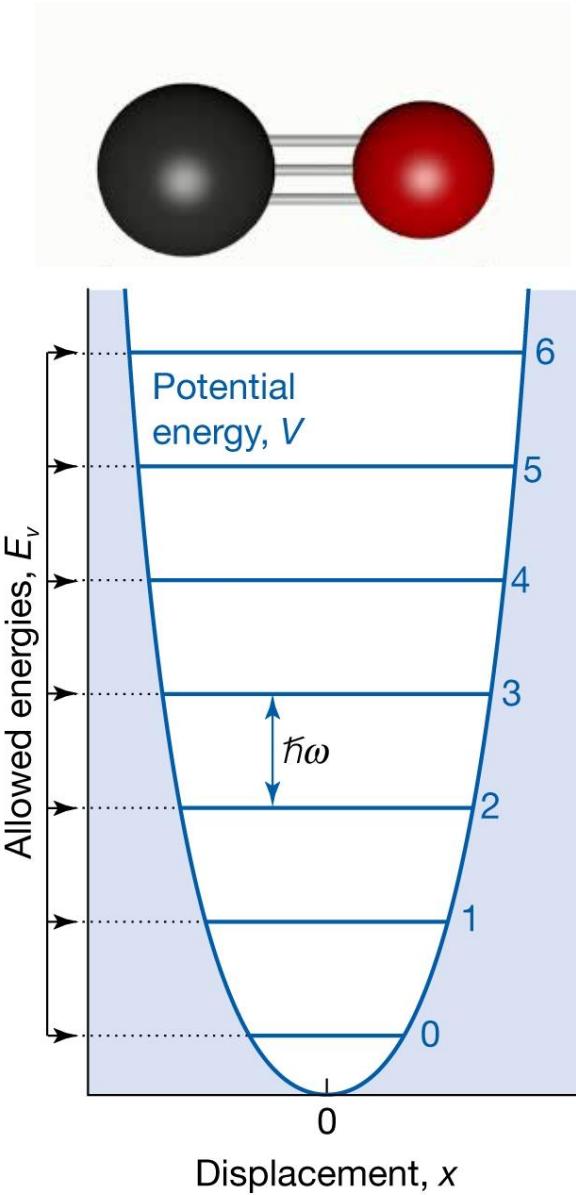

$$F = -kx$$

F = force

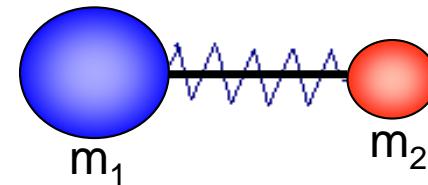
x = displacement

k = force constant
(spring constant)

Vibrations of a diatomic molecule



Vibrations



$$E = (v + \frac{1}{2})h\nu$$

$$v = 0, 1, 2, 3, \dots$$

$$\tilde{\nu} = \frac{\nu}{c}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}} \quad \tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\Delta v = \pm 1 \quad (\text{for harmonic oscillator})$$

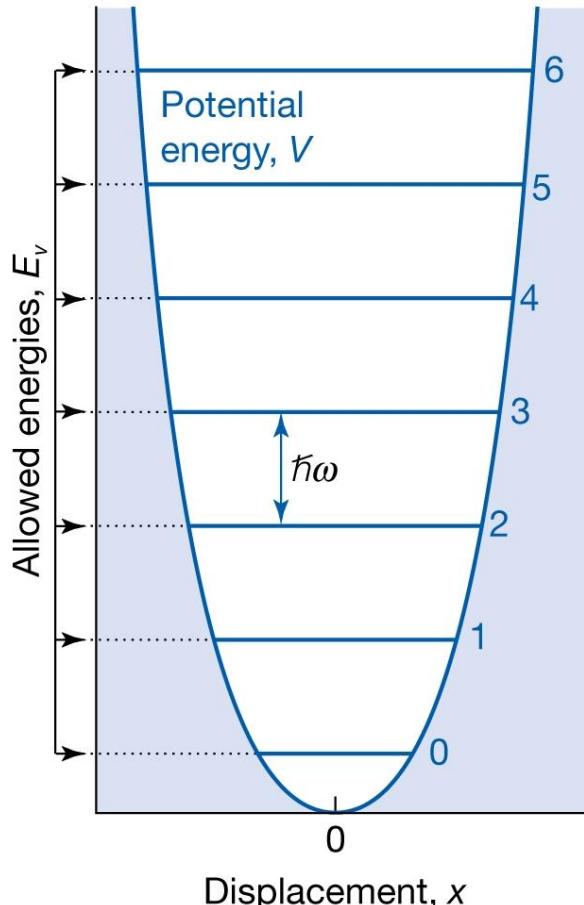
Selection rule

Separation of energy levels: $\Delta E = h\nu$

Allowed transitions? See selection rule above

Vibration of diatomic molecule

The energy levels of harmonic oscillator



$$E = (v + \frac{1}{2})h\nu$$

$v = 0, 1, 2, 3\dots$

h is Planck's constant =
 $6.626 \times 10^{-34} \text{ J s}$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}}$$

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

$\Delta v = \pm 1$ (for harmonic oscillator)

Separation of energy levels:

$$\Delta E = h\nu$$

$$\nu = \omega/2\pi$$

$$\eta = h/2\pi$$

Calculation of the force constant

$$E = (v+1/2)hv$$

$$v = 1/2\pi (k/m)^{1/2}$$

k = force constant

**m = reduced mass if both of the ends move (μ),
for example A-----B (diatomic molecule)**

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

**ΔE = the number obtained from the spectrum,
thus it is possible to find the force constant for
the bond**

$$\Delta E = hv = hc\tilde{v}$$

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \tilde{v} = \frac{v}{c}$$

Vibration of diatomic molecule

When a bond vibrates, they behave like springs, and can be described as harmonic oscillators.

Can be described by Hooke's Law:

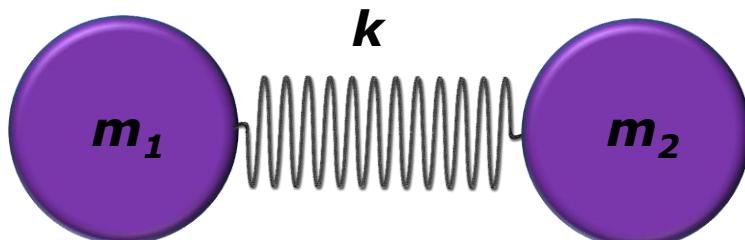
$$\text{Frequency} \quad \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

Force constant
(bond strength)

Reduced mass

Where:

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

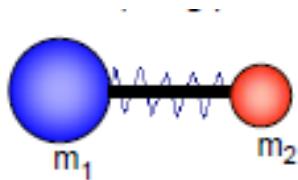


Frequency/wavenumber therefore depend on **strength of bond and mass of atoms** either end of the bond.

Force constant of a chemical bond: Exercise

The wavenumber of the fundamental vibrational transition of $^{79}\text{Br}^{81}\text{Br}$ is 323.2 cm^{-1} .

Calculate the force constant of the bond [$m_1(^{79}\text{Br})=78.9183 \text{ u}$, $m_2(^{81}\text{Br})=80.9163 \text{ u}$; $u = 1.66 \cdot 10^{-27} \text{ kg}$]



$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

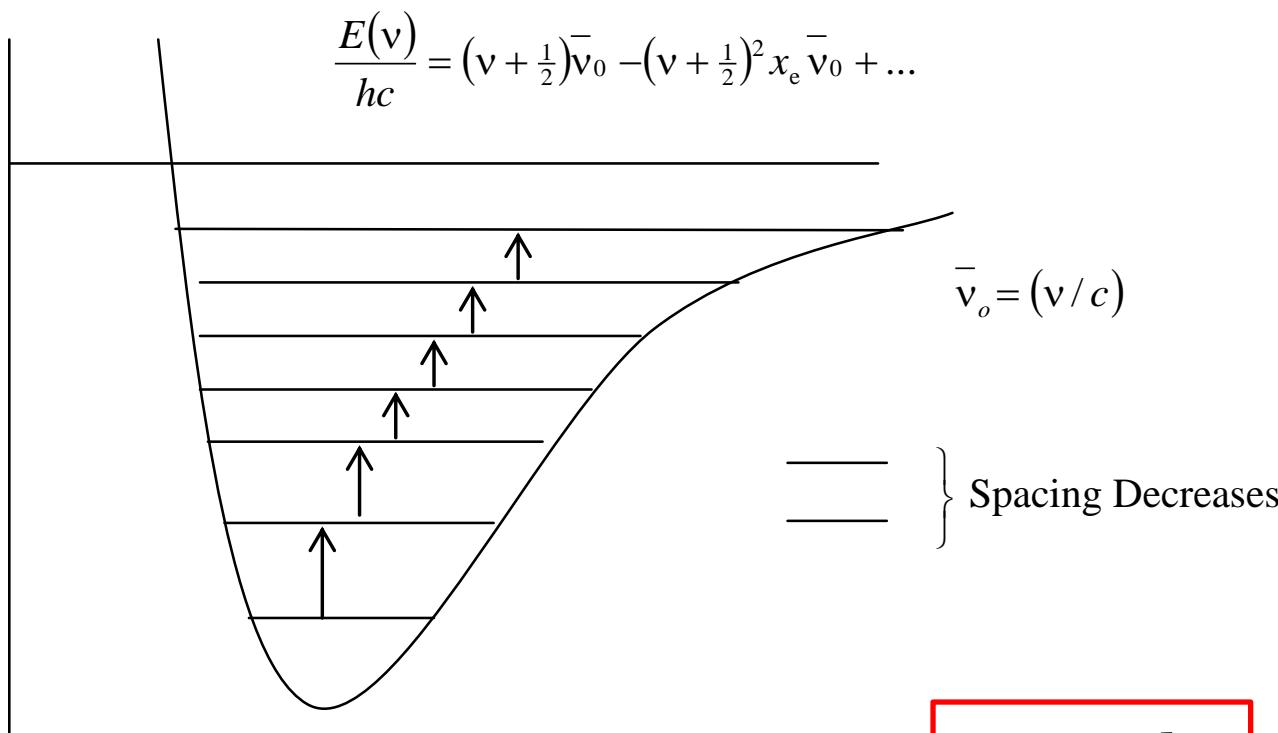
$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$$

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

$$k=245.9 \text{ N/m}$$

(using $\mu=6.63 \cdot 10^{-26} \text{ kg}$ reduced mass and $c=\lambda\nu$)

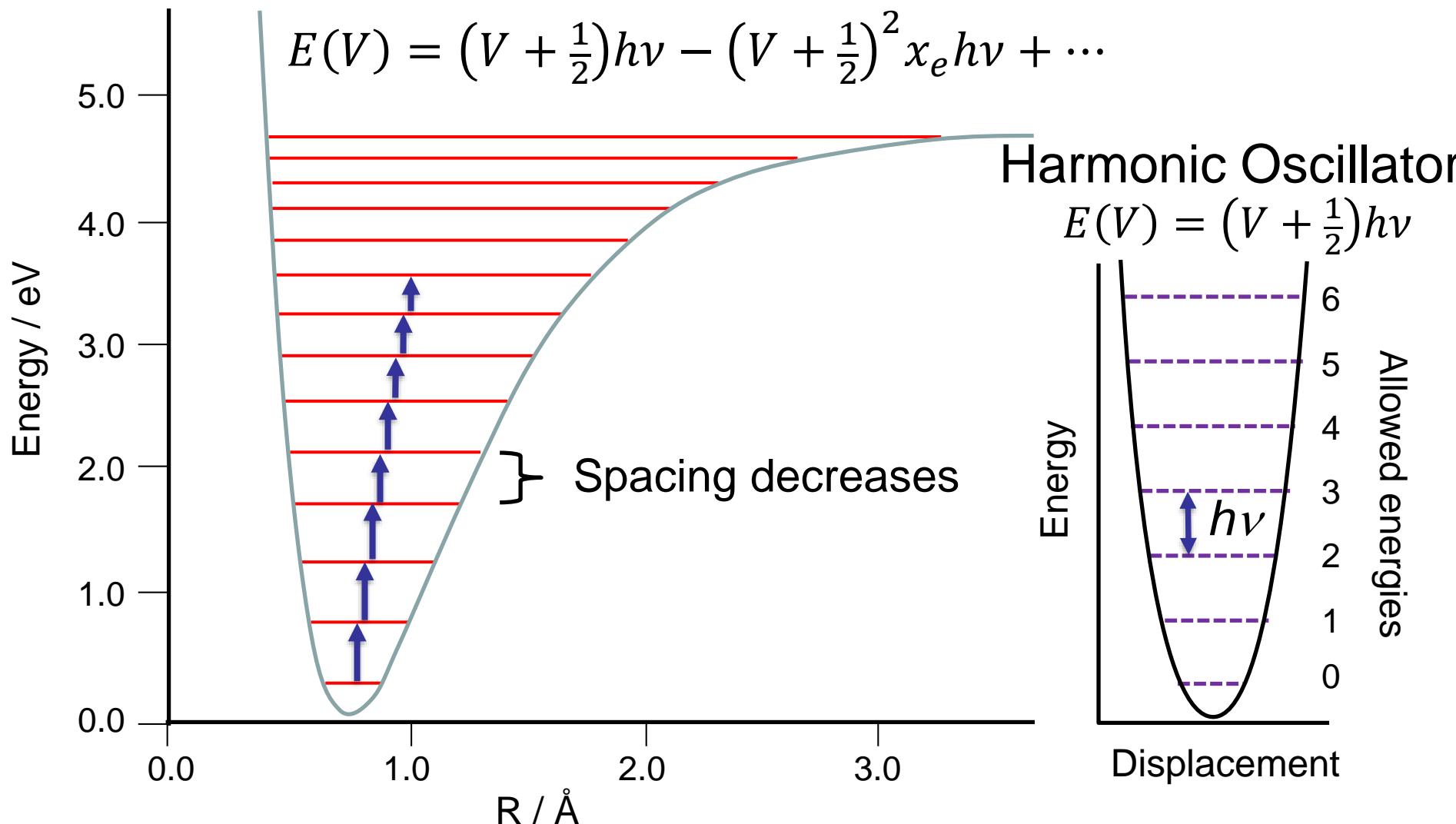
Anharmonic Vibrations of Real Molecules



$$F = -kx$$

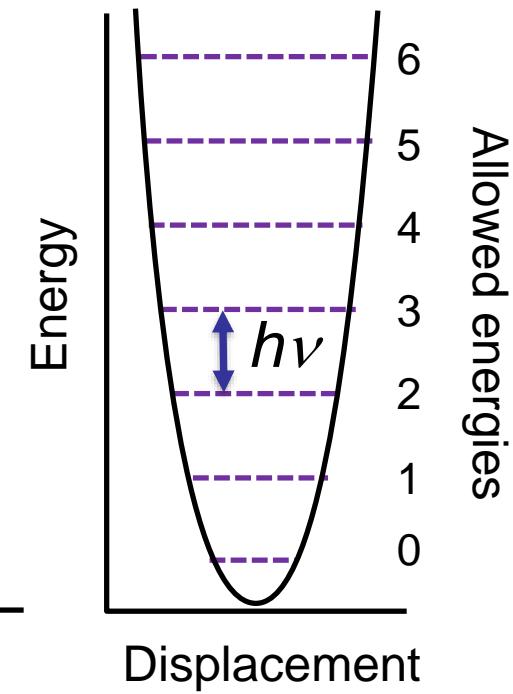
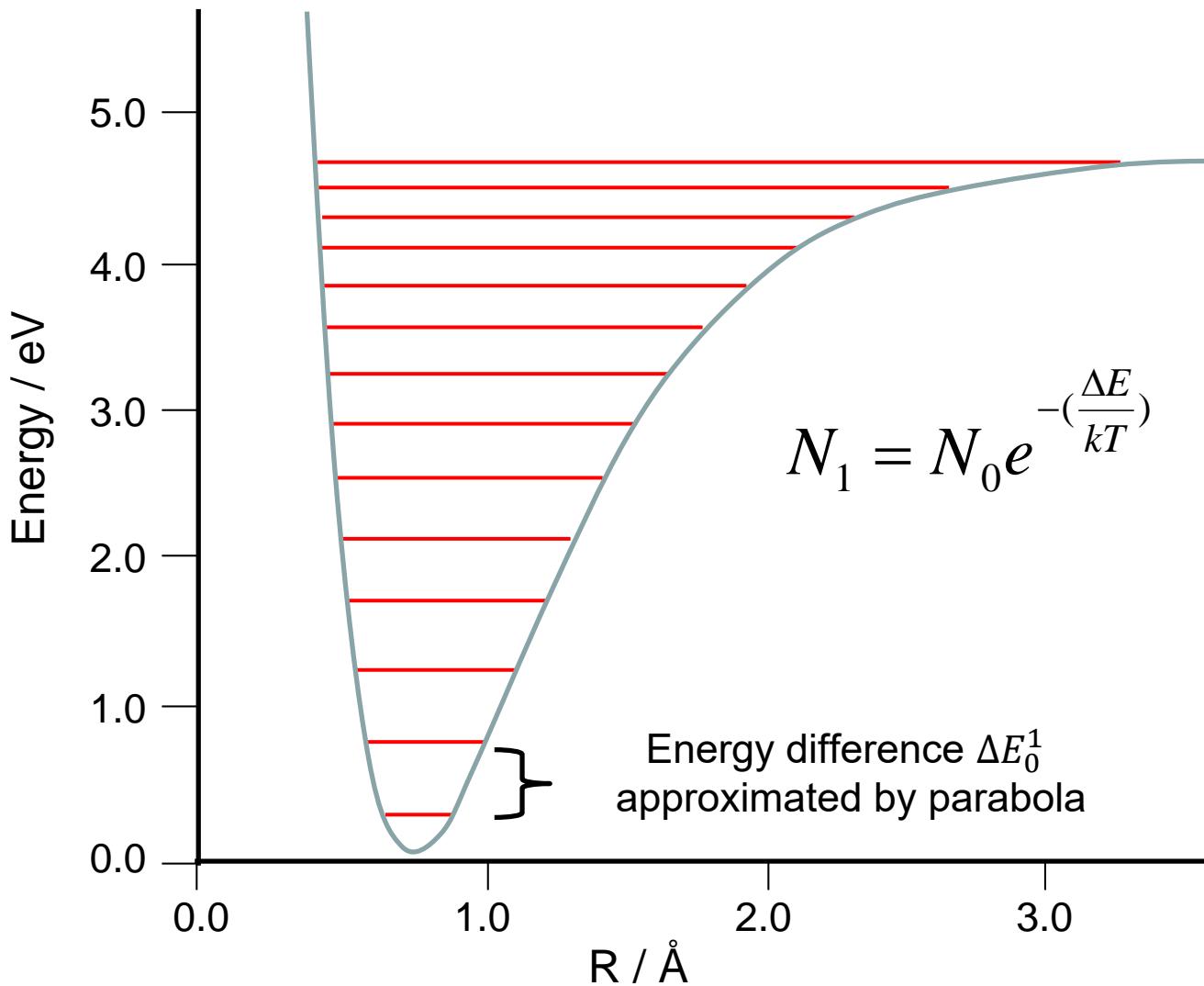
The bonds in actual molecules are not obeying Hook's law exactly. The force needed to compress a bond by a definite distance is larger than the force required to stretch this bond, thus potential is anharmonic

Anharmonic Vibrations of Real Molecules



Anharmonic Vibrations of Real Molecules

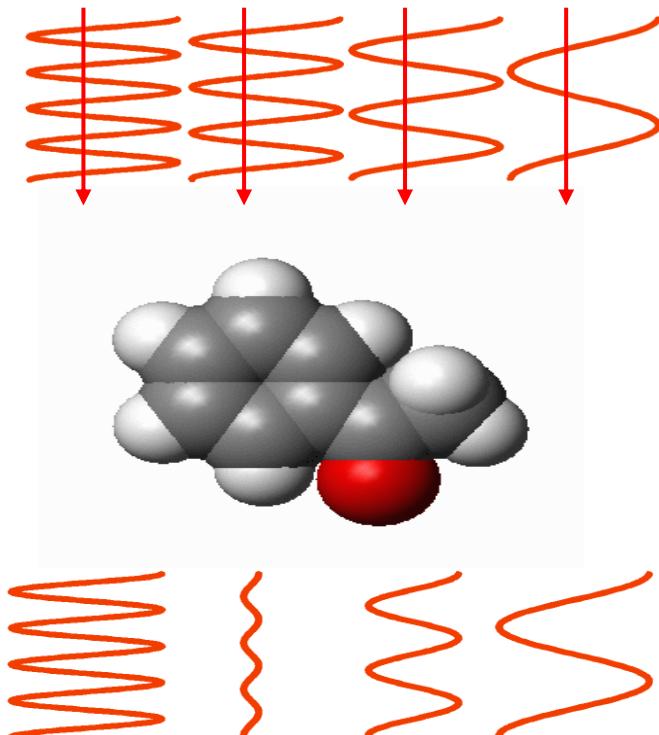
Below is an animation, shown in the lecture, that explains why the harmonic model is suitable for real molecules



Infrared Spectroscopy

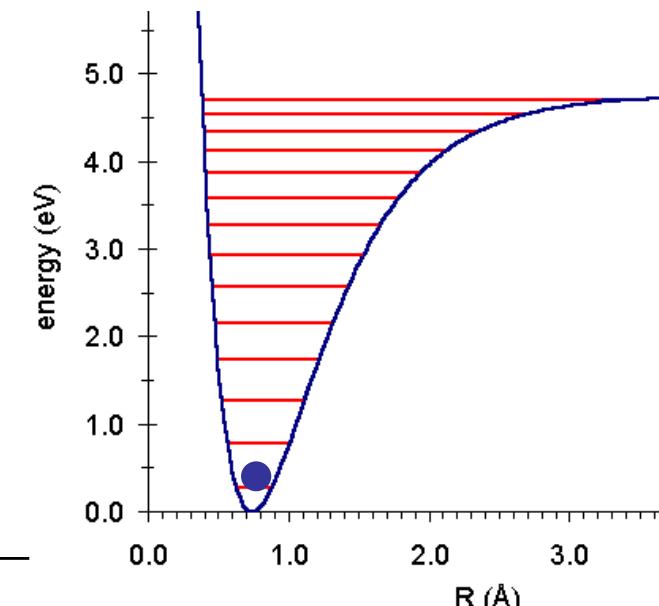
$\lambda = 2 - 20 \text{ microns}$

$1/\lambda = (5000 \text{ cm}^{-1} - 500 \text{ cm}^{-1})$



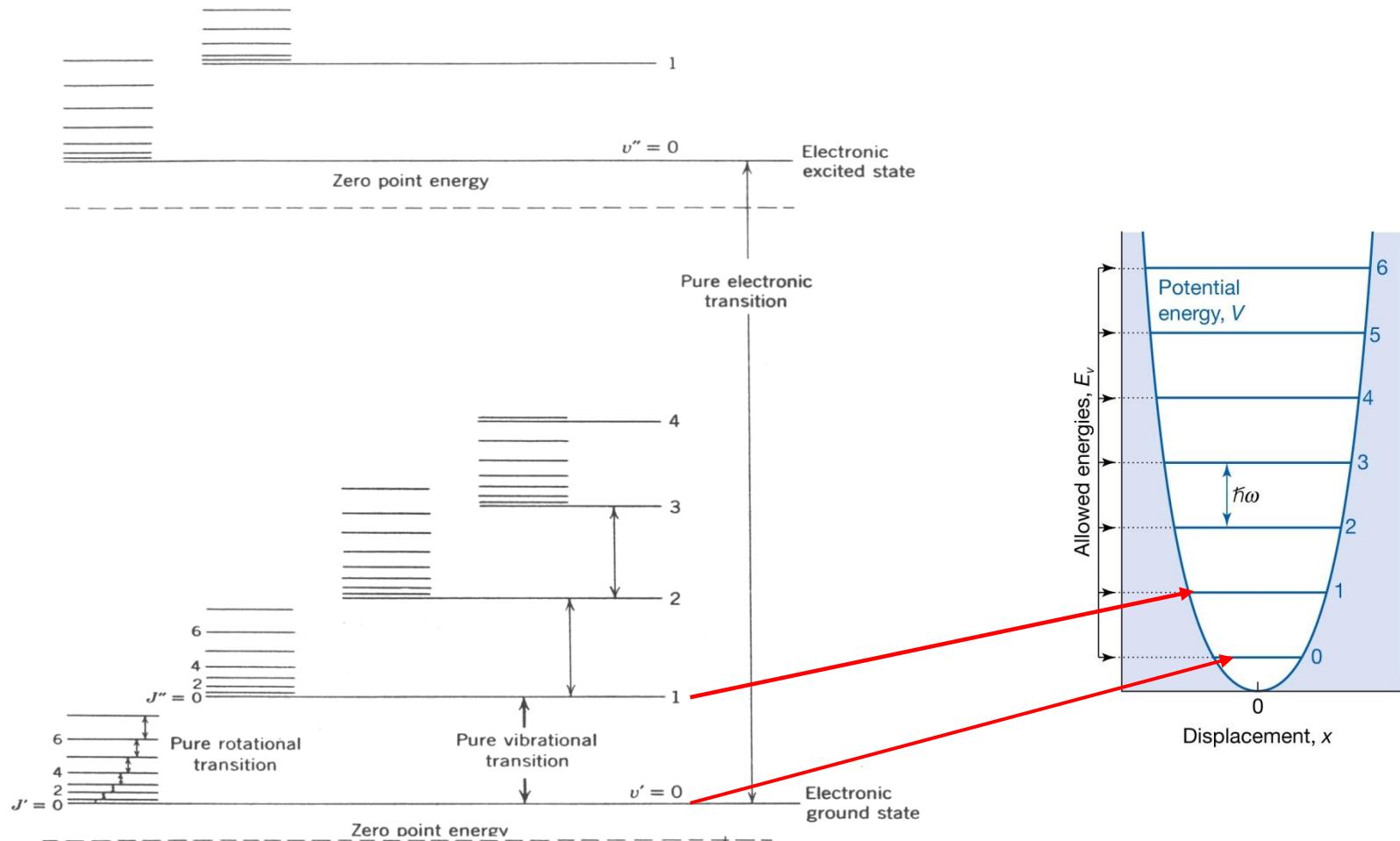
IR - Absorption

$$\nu = \frac{1}{2\pi} \sqrt{\frac{\kappa}{\mu}}$$



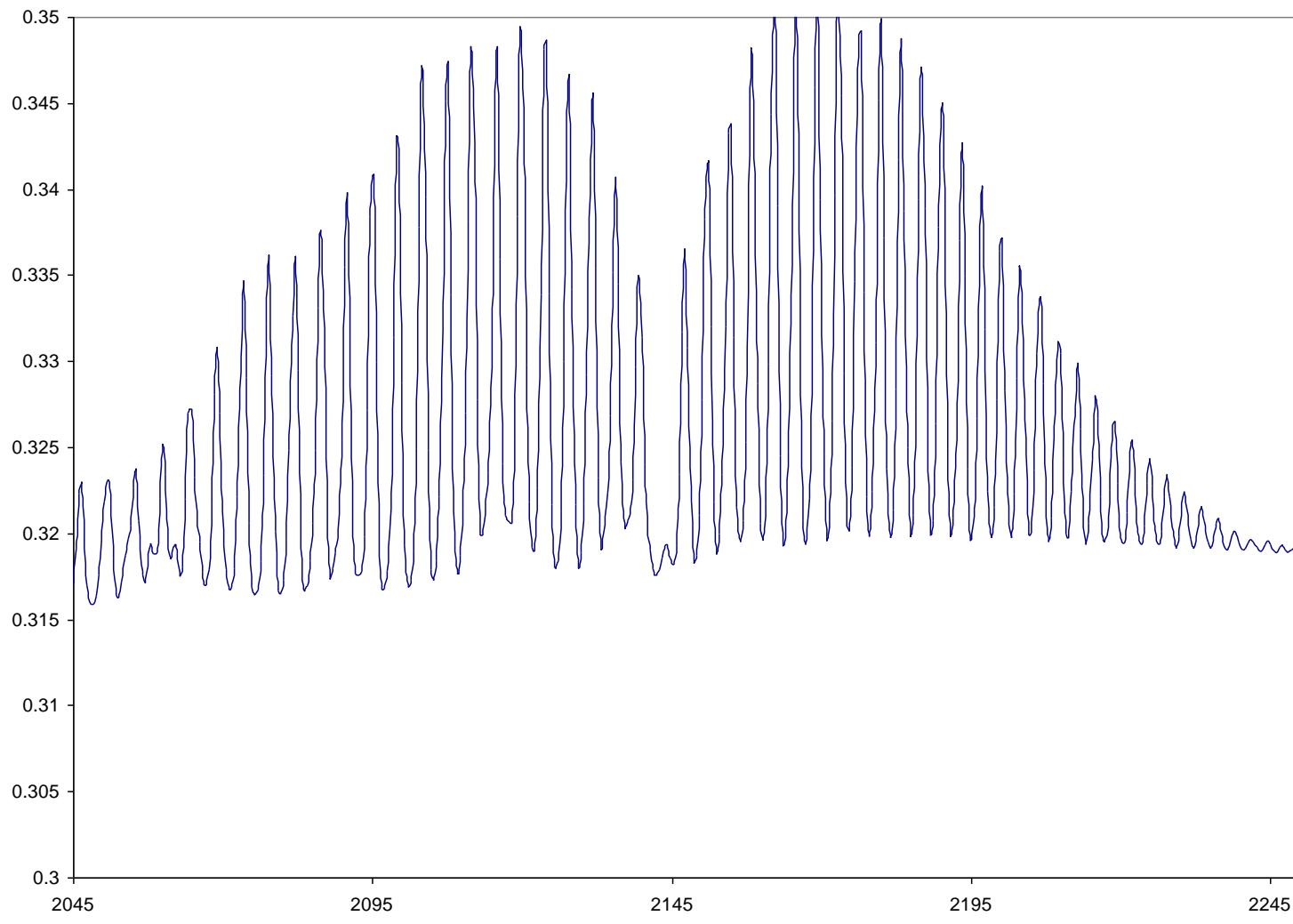
Energy levels of a diatomic molecule

This schematic shows energy levels for electronic, vibrational and rotational transitions



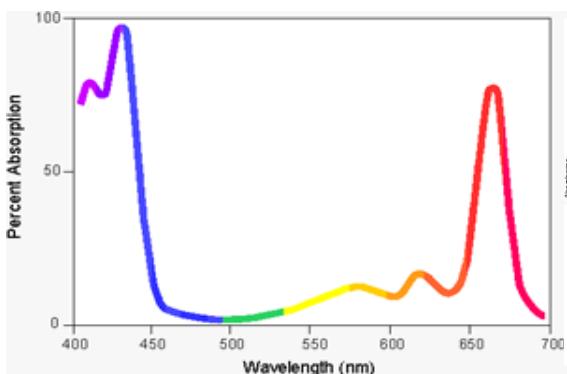
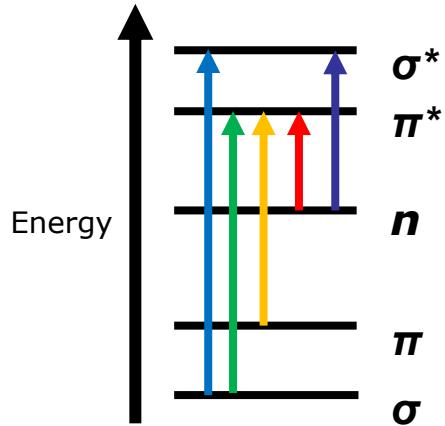
(the actual spacings of electronic levels are much larger, and those of rotational levels are much smaller than those shown in the figure)

Infrared spectra of gaseous molecules (rotations and vibrations): CO

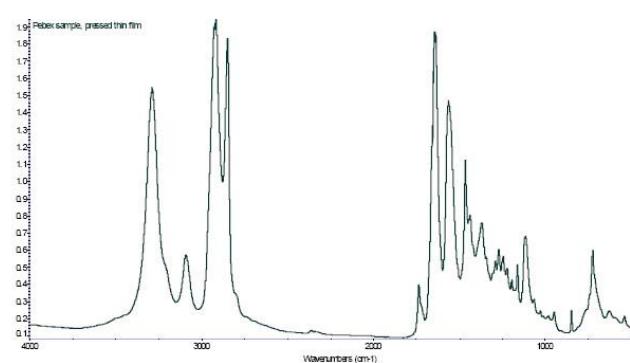
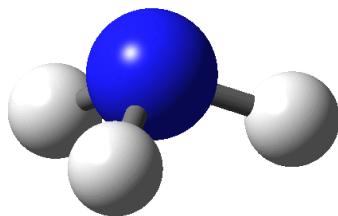


Energy Levels and Molecular Spectroscopy

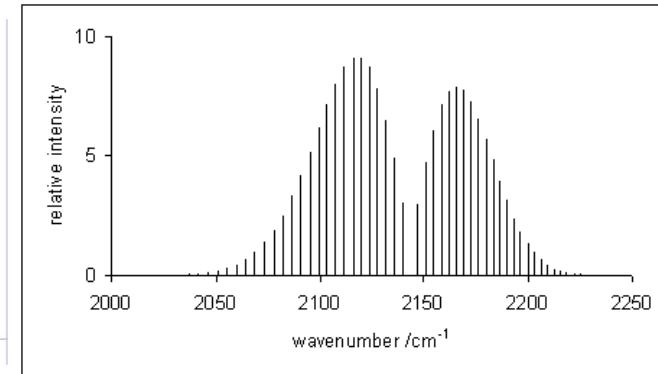
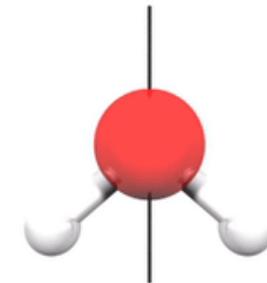
UV/Vis



Infrared



Microwave



Electronic transitions

Molecular vibrations

Molecular rotations

(The spectrum on the right shows rotational-vibrational spectrum of gaseous CO)

Some definitions

Infrared (IR) active	able to absorb infrared radiation
Vibrational selection rule	transitions can only occur between two adjacent energy levels: $\Delta\nu = \pm 1$
Fundamental transition	transition from ground state to first excited state: $0 \rightarrow 1$
Anharmonic motion	oscillatory motion in which the restoring force is not proportional to the displacement
Selection rule for IR activity	the motion corresponding to a normal mode should be accompanied by a change of dipole moment: $\frac{\partial \mu}{\partial r} \neq 0$
Normal mode	an independent, synchronous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode

Vibrations of polyatomic molecules

The normal modes of large molecules correspond to characteristic motions of functional groups and the spectrum can be used as an analytic tool.

e.g. Hydrocarbons have absorption bands as follows:

2850 – 2960 cm⁻¹ C – H stretching

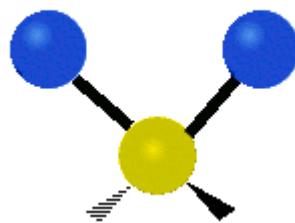
1340 – 1665 cm⁻¹ C – H bending

700 – 1250 cm⁻¹ C – C stretching

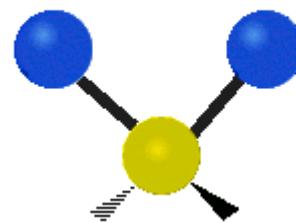
1620 – 1680 cm⁻¹ C = C stretching

Molecular vibrations

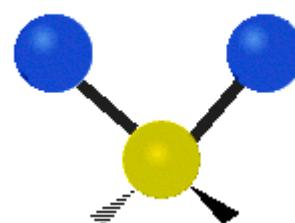
There are a number of motions available for bonds in a molecule. Most of which, to some extent, will be present in an IR spectrum.



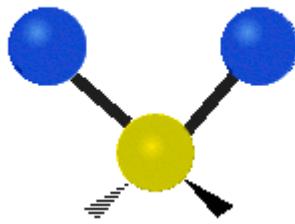
Symmetric stretching



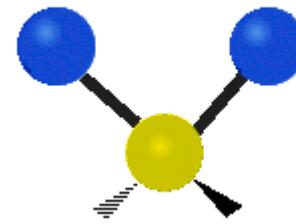
Asymmetric stretching



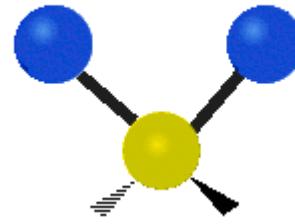
Twisting



Wagging



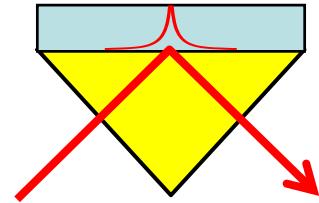
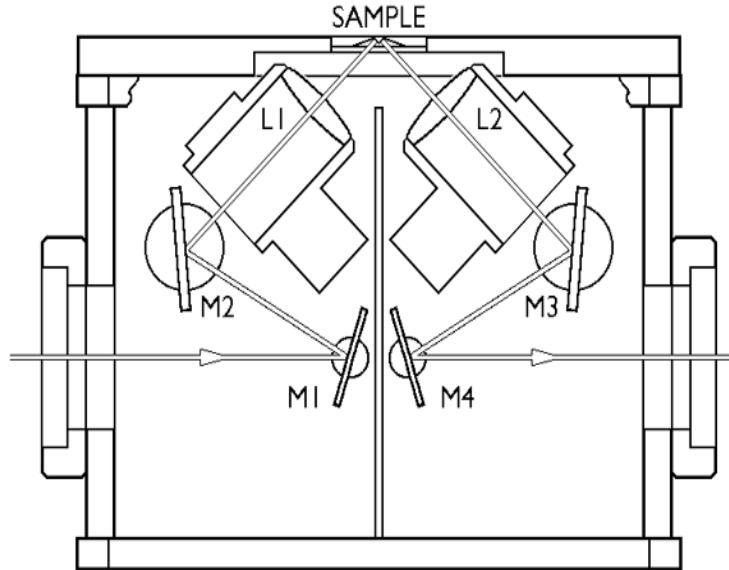
Scissoring



Rocking

“Demonstration”: measurements of IR spectra

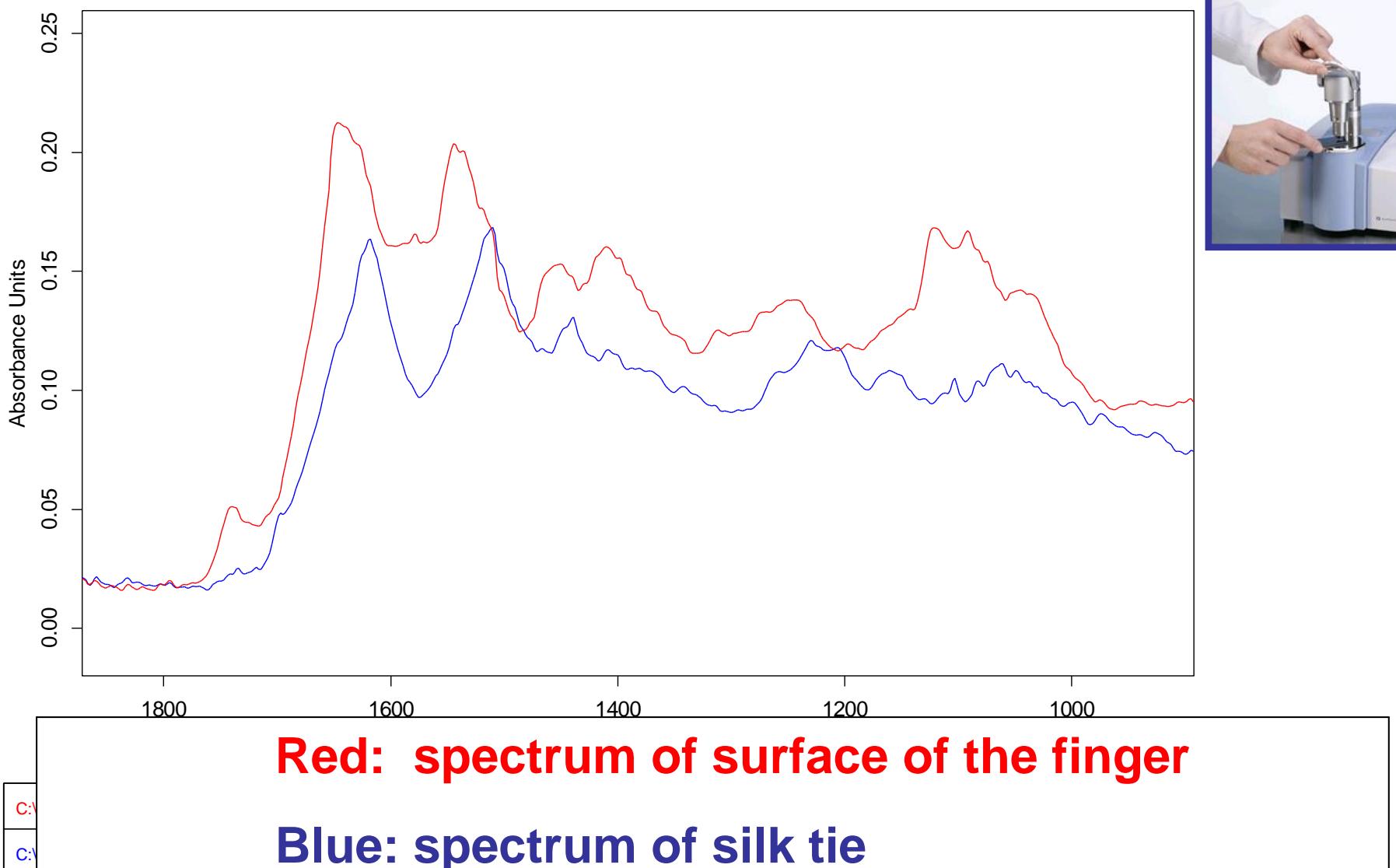
Diamond ATR FTIR spectroscopy



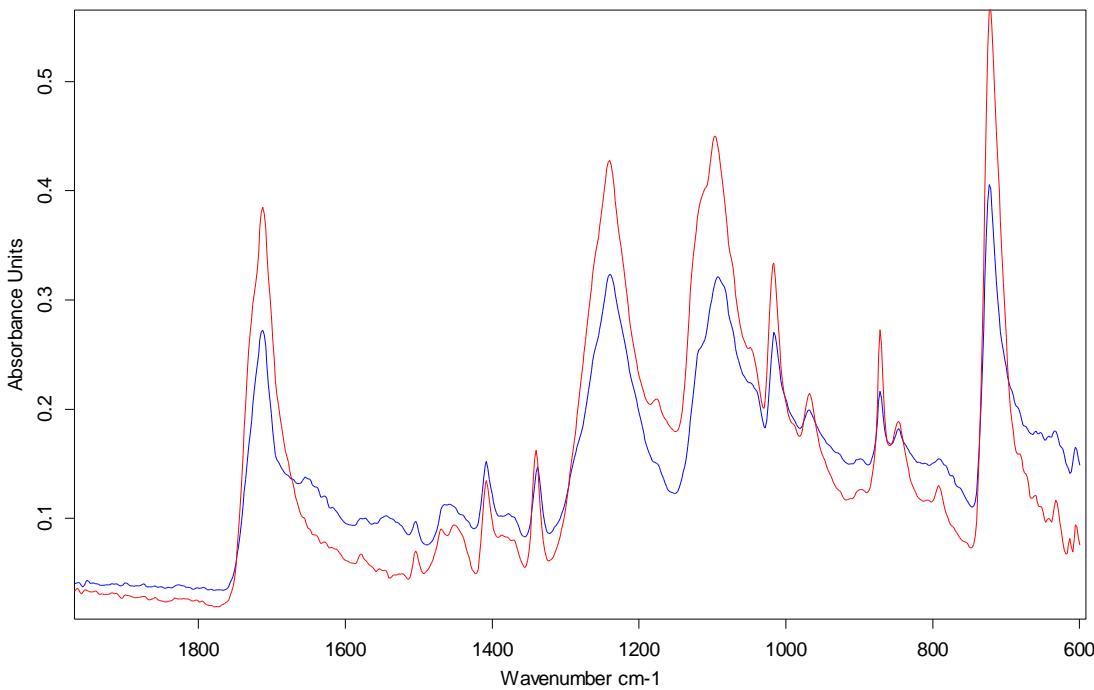
These ATR accessories are based on single reflection inverted prism

Golden gate accessory
(Specac, Ltd.)

From live demonstration of studying spectra of a tie: Infrared spectra of silk tie and surface of the finger



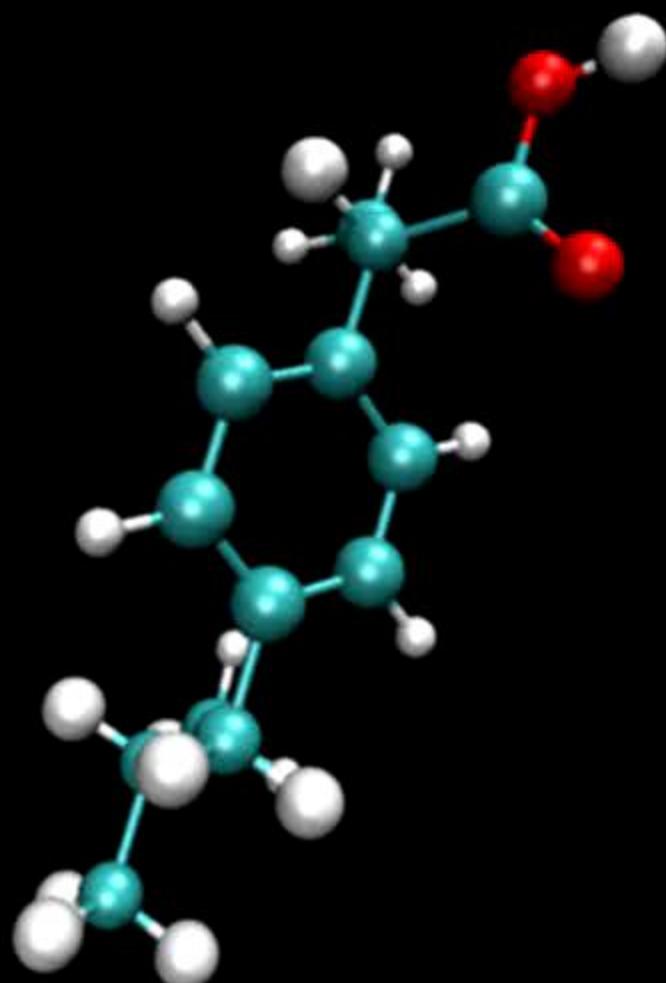
Infrared spectra of polyester tie and water/coca-cola bottle



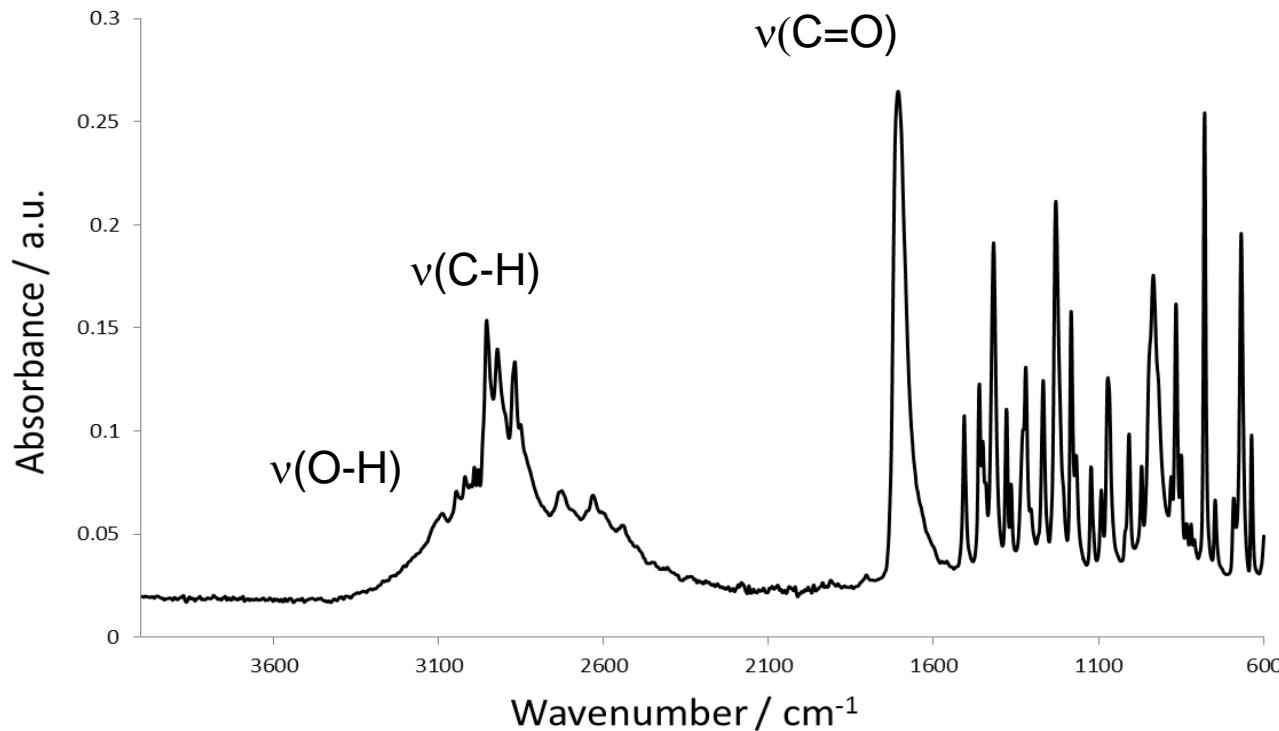
C:\andrew\film.0	film	sample form	2005/12/09
C:\andrew\Tie.0	Tie	sample form	2005/12/09

Red: spectrum of coca-cola PET bottle

Blue: spectrum of polyester tie



Number of vibrations and infrared spectrum of ibuprofen



Spectrum is a representation of what electromagnetic radiation is absorbed or emitted by the sample

Infrared spectrum of ibuprofen tablet

Vibrations of Polyatomic Molecules

- The vibrational motion may be a complicated combination of stretching and bending but in the approximation of harmonic distortion (restoring force proportional to deformation) all the motion may be expressed as a superposition of independent harmonic modes – **the normal modes**.

Normal mode – an independent, synchronous motion of atoms or group of atoms that may be excited without leading to the excitation of any other normal mode.

- Each normal mode has a discreet vibrational frequency. In some cases, two or more modes may be **degenerate**.

Polyatomic molecules
(N>2 atoms) have

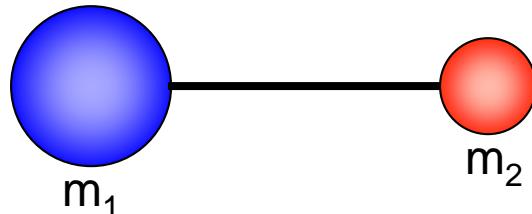
$$\left\{ \begin{array}{l} 3N-5 \text{ (linear)} \\ 3N-6 \text{ (non-linear)} \end{array} \right.$$

normal modes

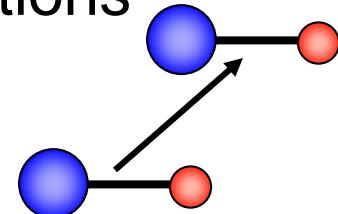
Detailed explanation of the above equations will be during the lecture

Molecular spectroscopy

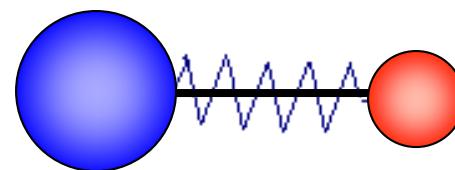
Diatomc molecule



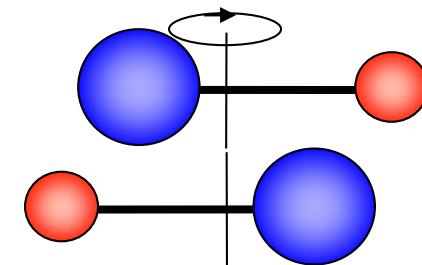
Translations



Vibrations

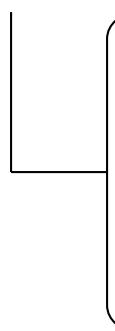


Rotations



Energy levels for molecules

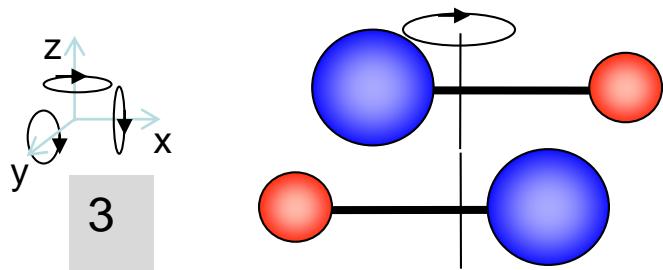
- Electronic transitions
- Molecular motion
 - Translations
 - Vibrations
 - Rotations



Degrees of freedom and vibrations of molecules

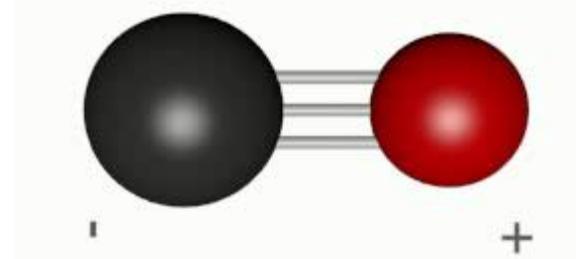
Molecule with N atoms has
3N 'degree of freedom'

Rotations

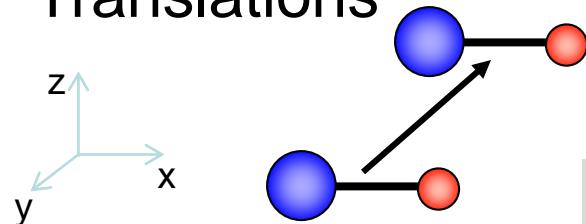


3 'orthogonal' rotations

(or 2 if molecule is linear)



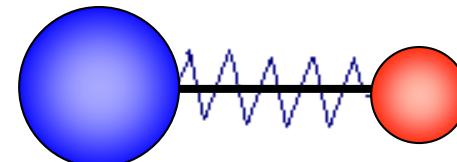
Translations



3 'orthogonal' translations

3

Vibrations



remaining vibrations

3N-6 (for non-linear)

(or 3N-5 if molecule is linear)

Question

- Which of the following molecules may show
 - a) infrared absorption spectra
 - b) Raman spectra (we will discuss later)



To answer these questions we need to consider selection rules, first for infrared spectra

How does light interact with vibrating molecule?

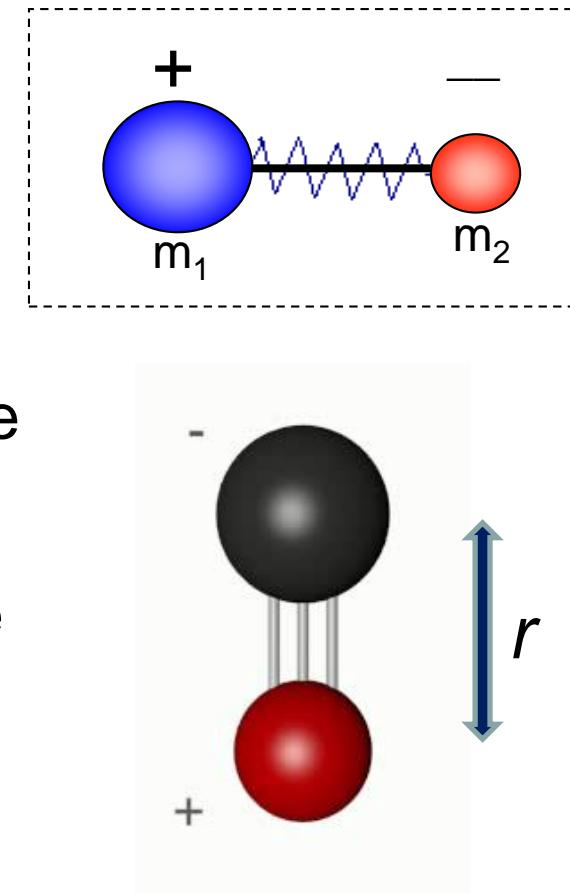
Selection Rule

$$\frac{\partial \mu}{\partial r} \neq 0$$

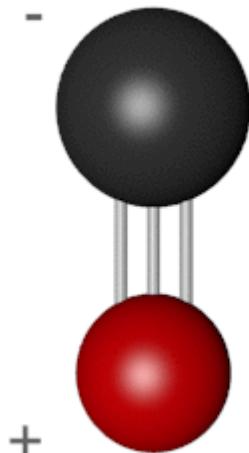
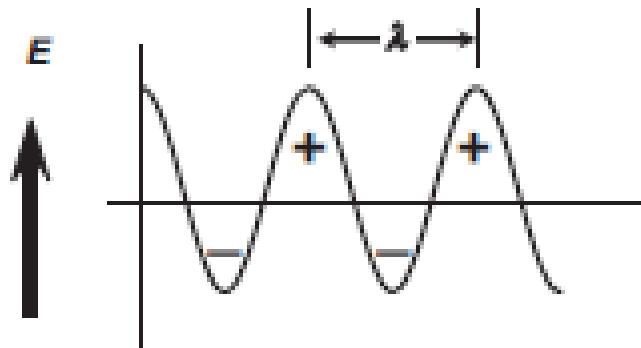
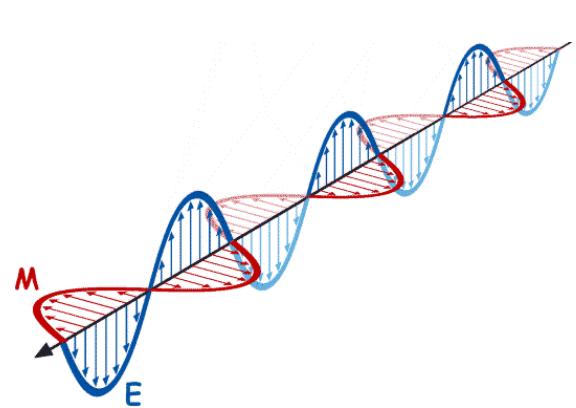
Infrared active

μ is a dipole moment, $\mu = q \times r$, q is charge and r is distance (e.g. bond length).

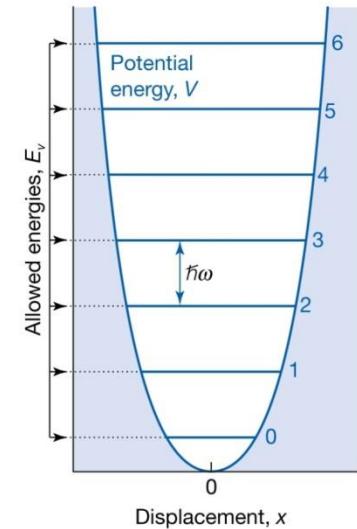
The dipole moment is a measure of the asymmetry of the charge distribution on the two atoms (for diatomic molecules)



Change of dipole moment during molecular vibration



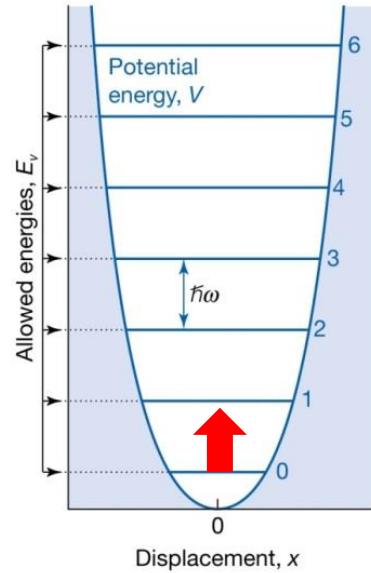
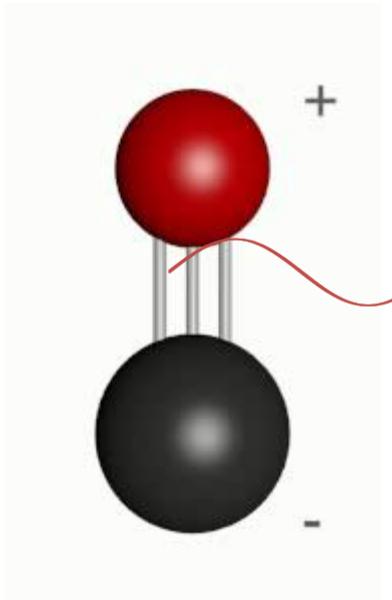
$$\frac{\partial \mu}{\partial r} \neq 0$$



$$E = (v + \frac{1}{2})h\nu$$

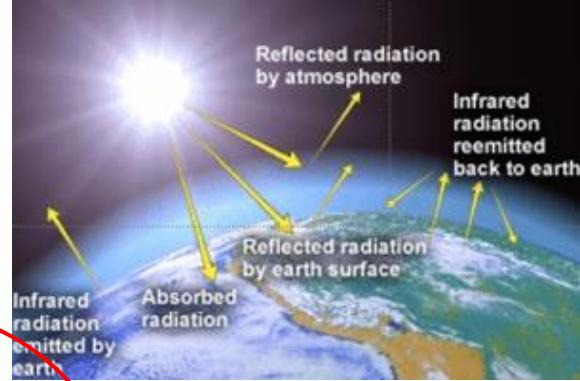
For example, $v = 0$

Change of dipole moment during molecular vibration

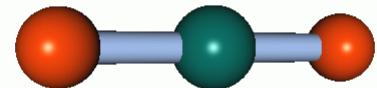


- Photon of correct frequency interacts with changing electric field of vibrating molecule
- Amplitude of vibration changes but vibrational frequency does not
- Vibrational amplitude is quantised

Vibrations of CO₂ and global warming



stretching CO₂

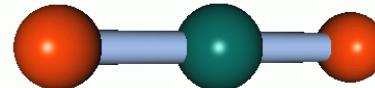
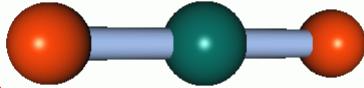


not “asymmetric”

v_1

v_3

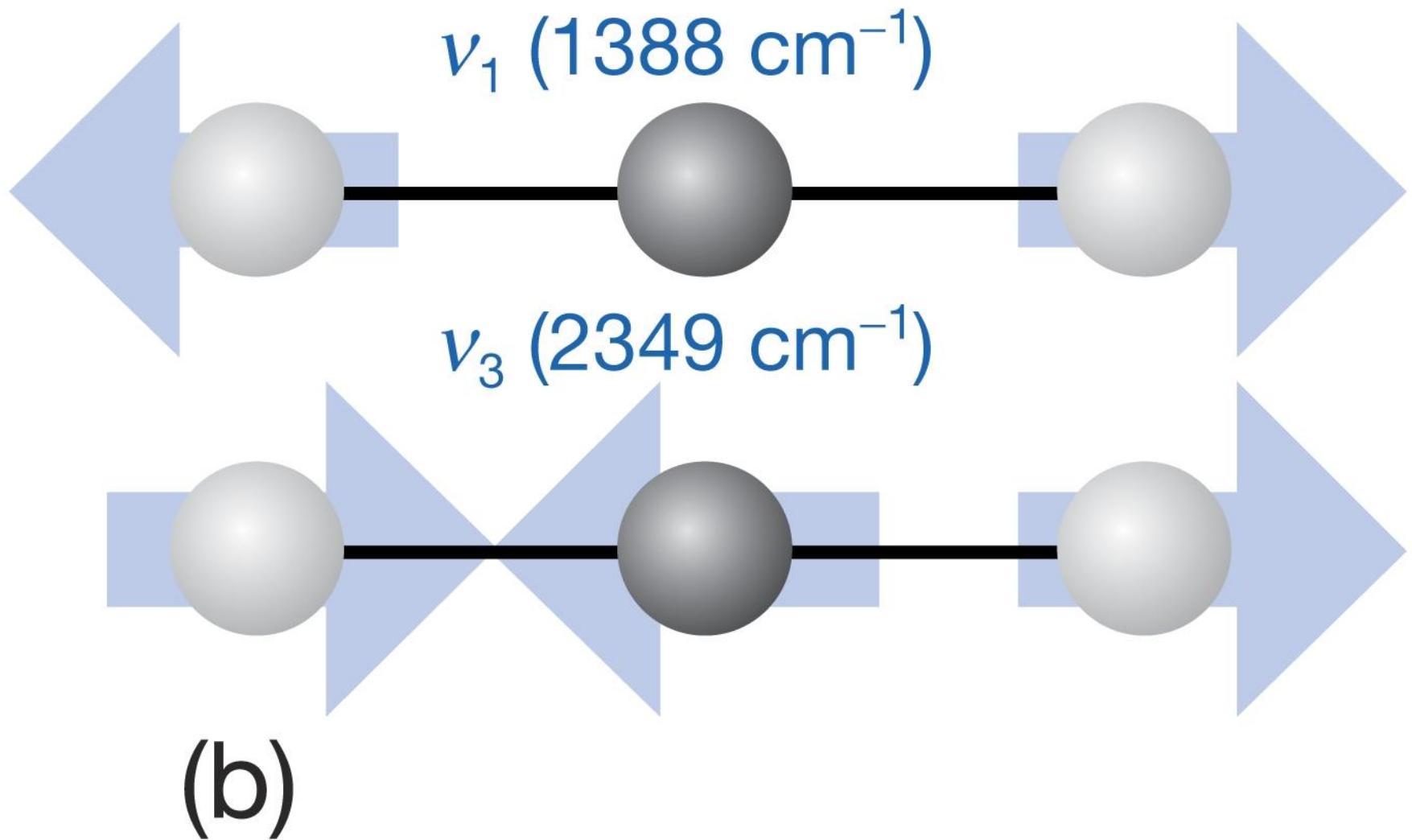
bending CO₂



v_2

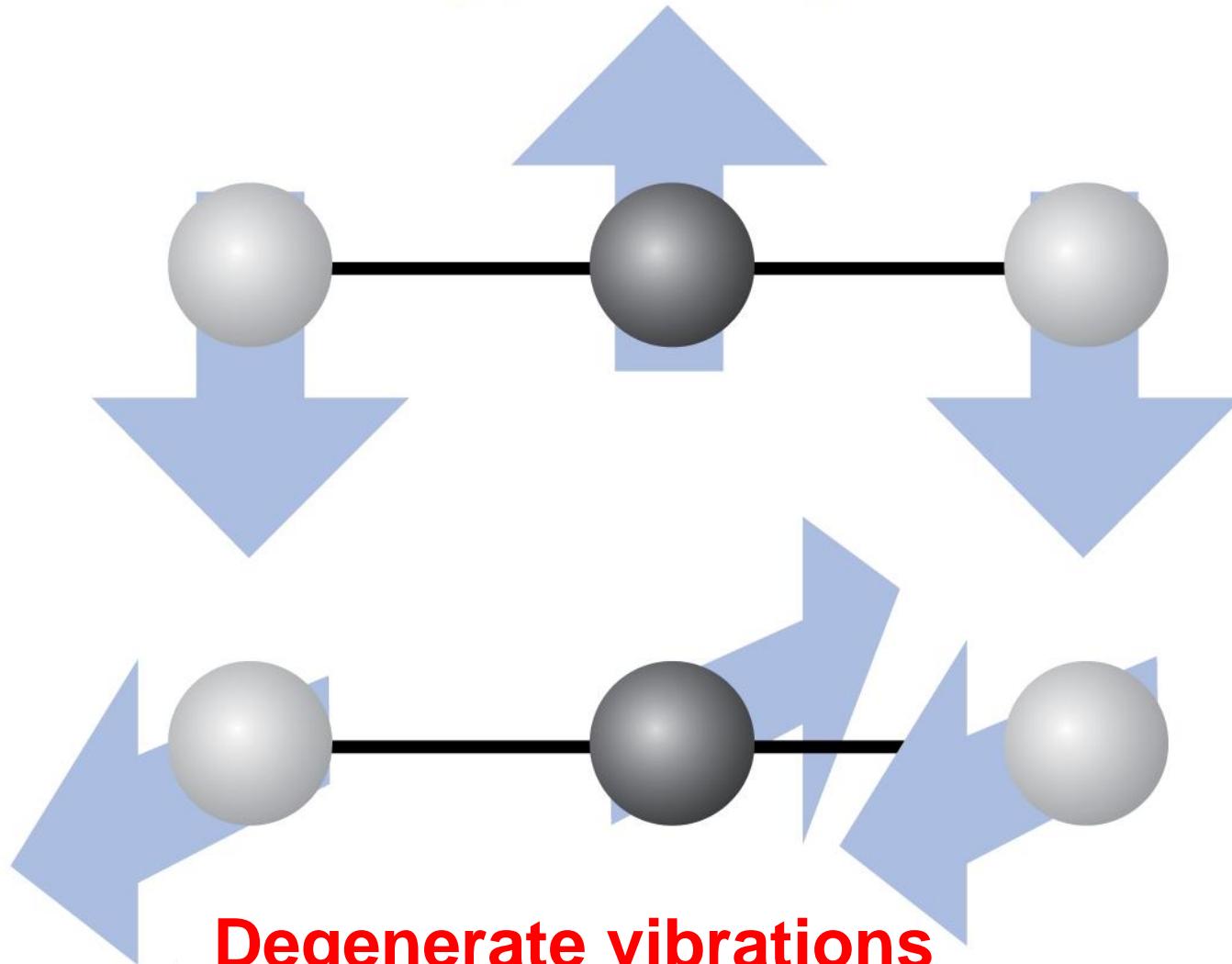
Vibrations of CO₂ molecules is an excellent example to understand why some vibrations of CO₂ absorb infrared radiation

Stretching modes of carbon dioxide molecule



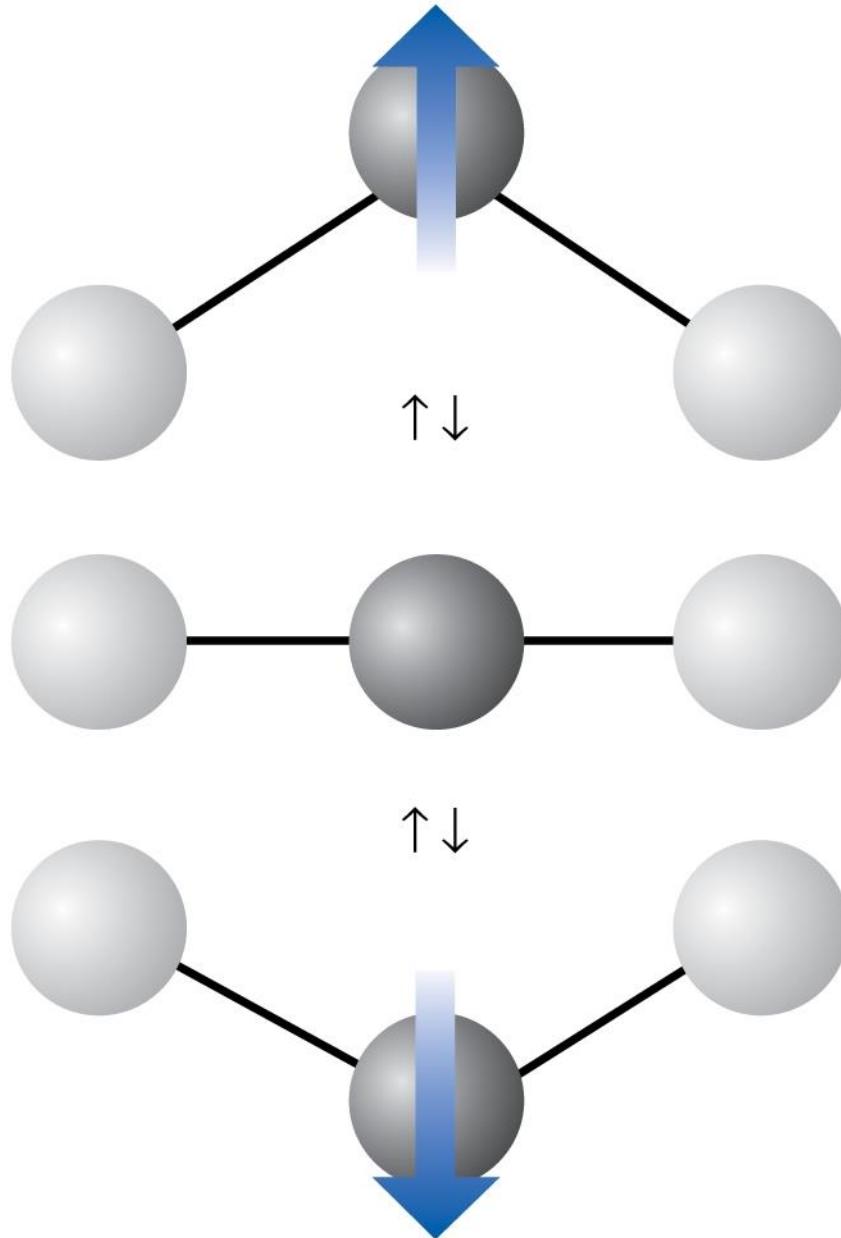
Bending modes of carbon dioxide molecule

ν_2 (667 cm⁻¹)



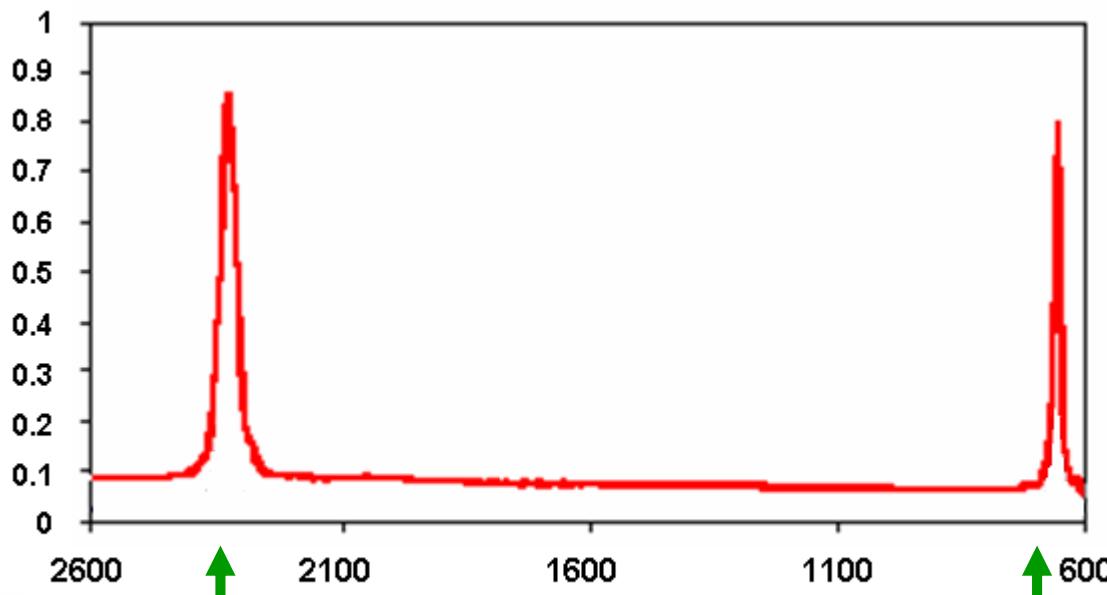
Degenerate vibrations

The oscillating dipole as a result of vibration of a molecule



Infrared, CO₂ and Global Warming

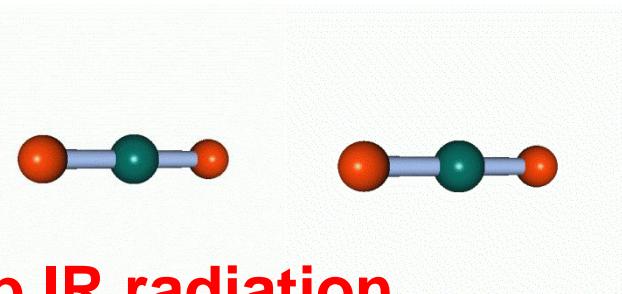
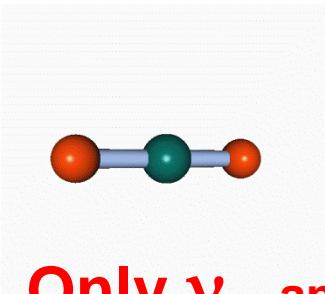
Infrared spectrum of liquid CO₂



100 bar,
25 °C

ν_3

ν_2



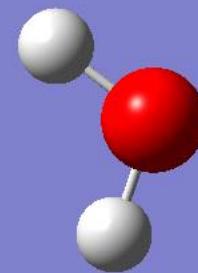
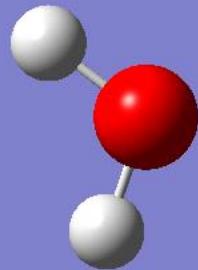
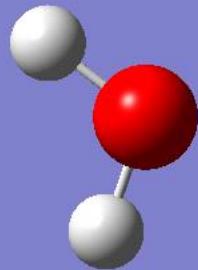
Only ν_3 and ν_2 absorb IR radiation

Vibrational modes of water molecule

Symmetric stretch 3652 cm^{-1}

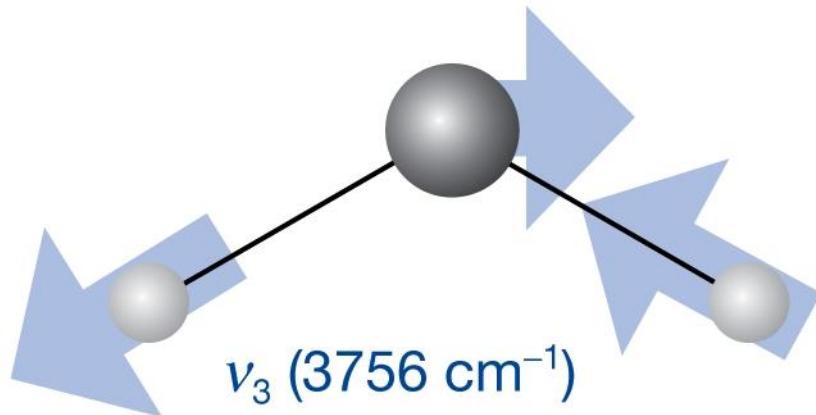
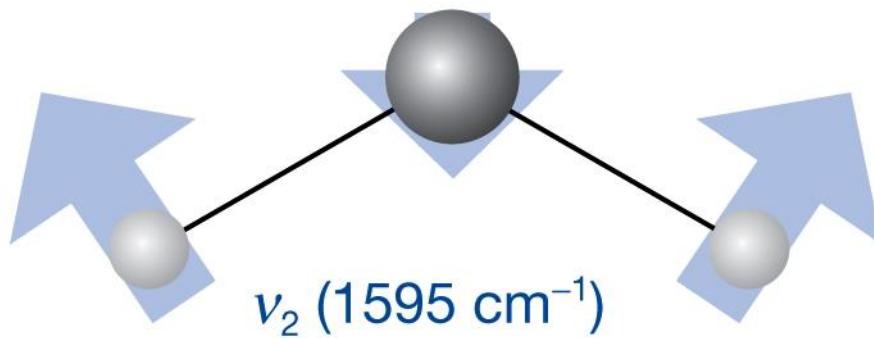
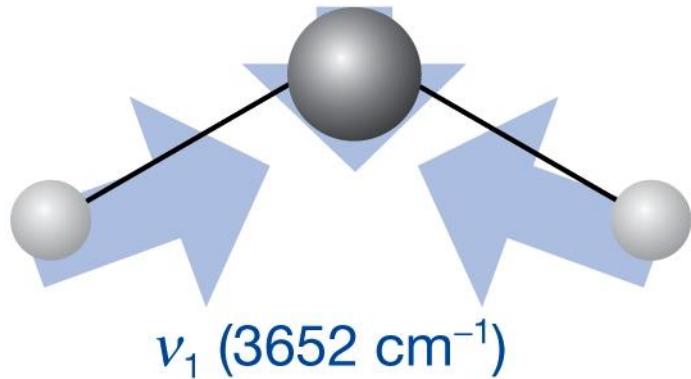
Asymmetric stretch 3756 cm^{-1}

HOH bend 1595 cm^{-1}



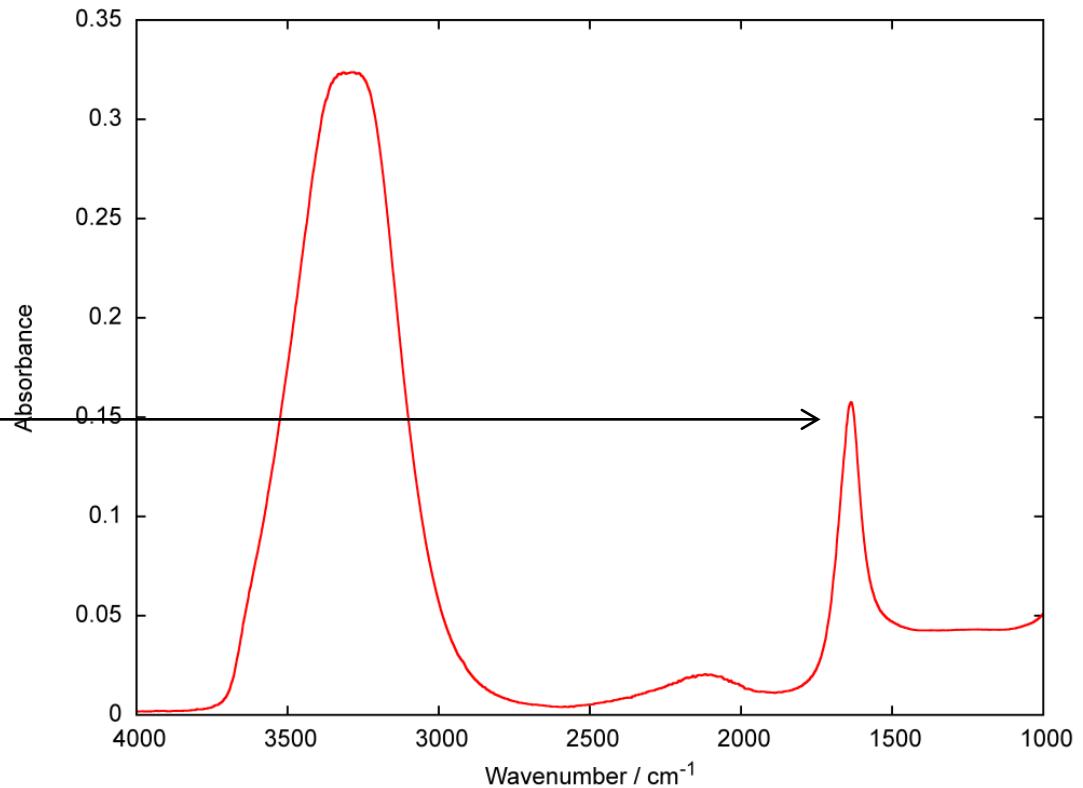
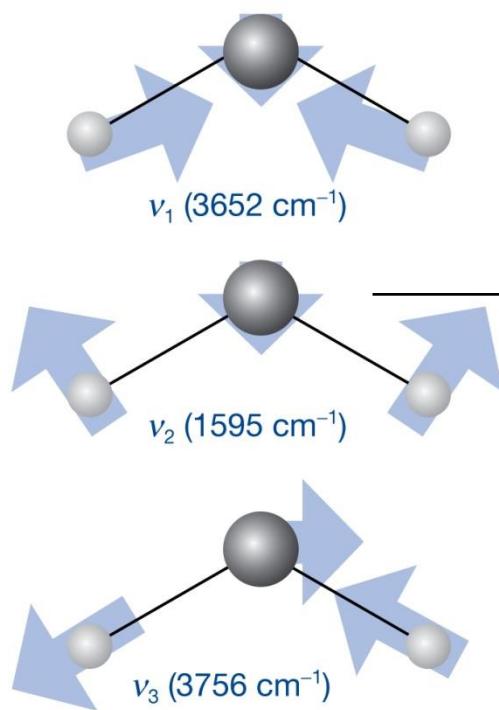
All 3 vibrations are infrared active

Vibrational modes of water molecule



Infrared spectrum of liquid water

Spectrum is a representation of what electromagnetic radiation is absorbed or emitted by the sample



How does light interact with vibrating molecule?

Selection Rule

$$\frac{\partial \mu}{\partial r} \neq 0 \quad \text{Infrared active}$$

μ is a dipole moment, $\mu = q \times r$, q is charge and r is distance (e.g. bond length).

The dipole moment is a measure of the asymmetry of the charge distribution on the two atoms (for diatomic molecules)

Which of the following molecules may show Infrared spectrum?

- H_2
- CH_3Cl
- SF_6
- N_2
- HCl
- CO_2
- $^{79}\text{Br}^{81}\text{Br}$

Vibrations of SF₆ (UF₆)

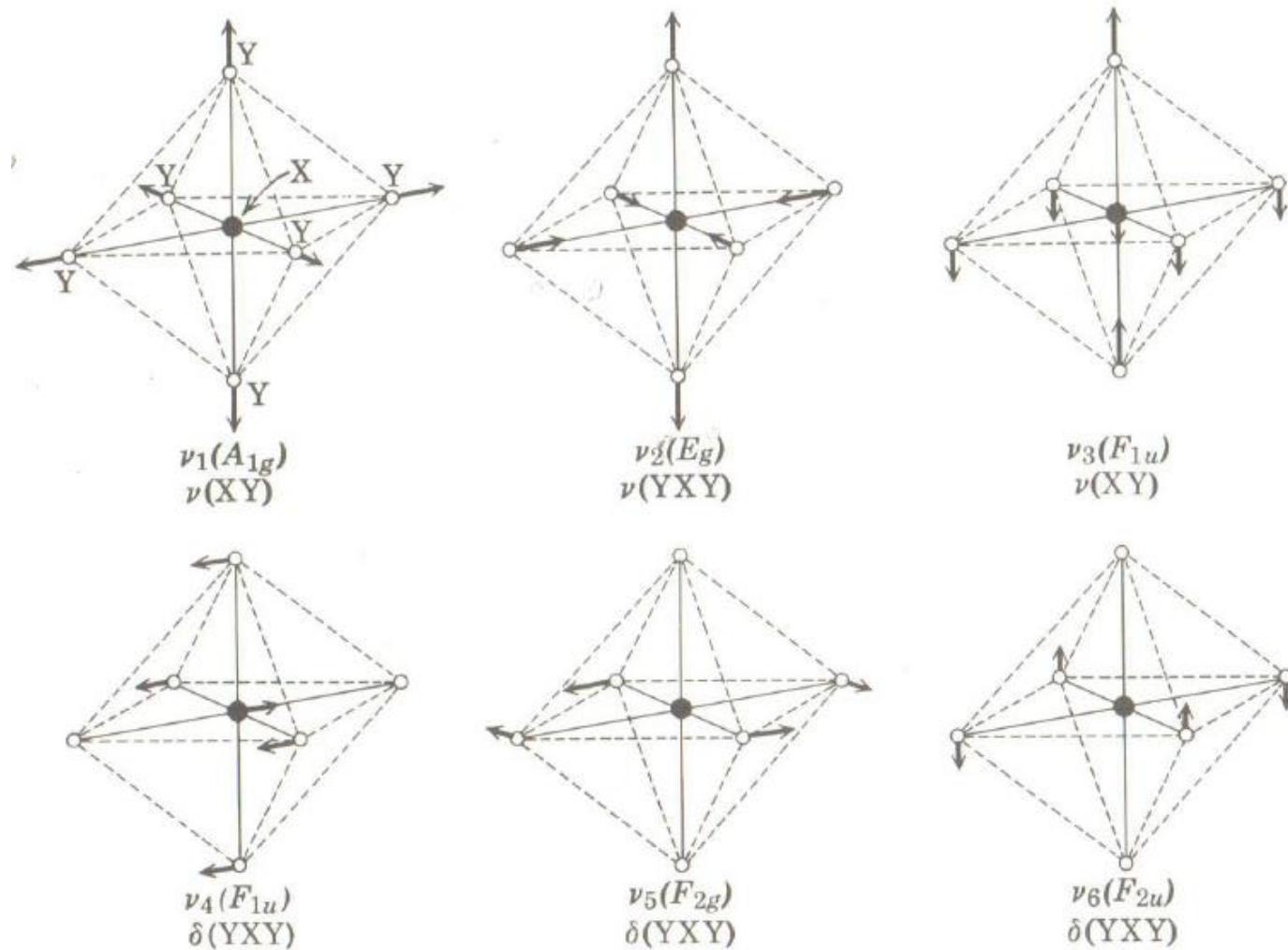


Fig. II-15. Normal modes of vibration of octahedral XY₆ molecules.

Beer-Lambert Law

One of the powers of spectroscopy is the ability to deduce the quantity of an absorbing materials in a sample – **Beer Lambert Law**

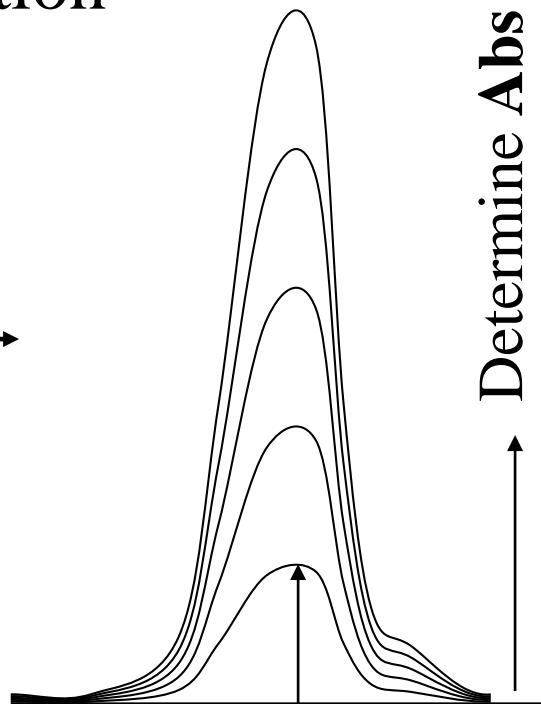
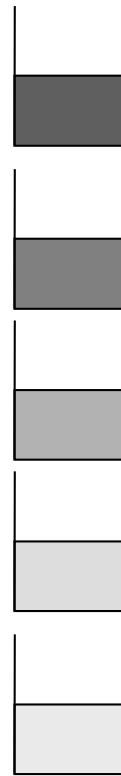
Beer-Lambert Law

Make solutions

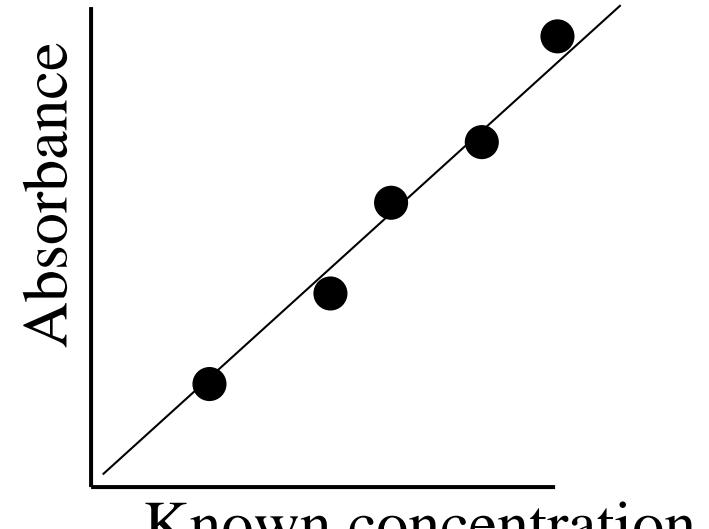
with

Measure (Absorbance = A)

known concentration



Determine Abs



a = coefficient

b = path length (thickness)

c = concentration

$$A = abc$$

$$c = A/ab$$

Beer-Lambert Law

Make solutions with known concentration
Measure Absorbance (A)
Determine **Molar Absorptivity (ϵ)**

$$A = \epsilon cl$$

$$c = A/\epsilon l$$

A = Absorbance

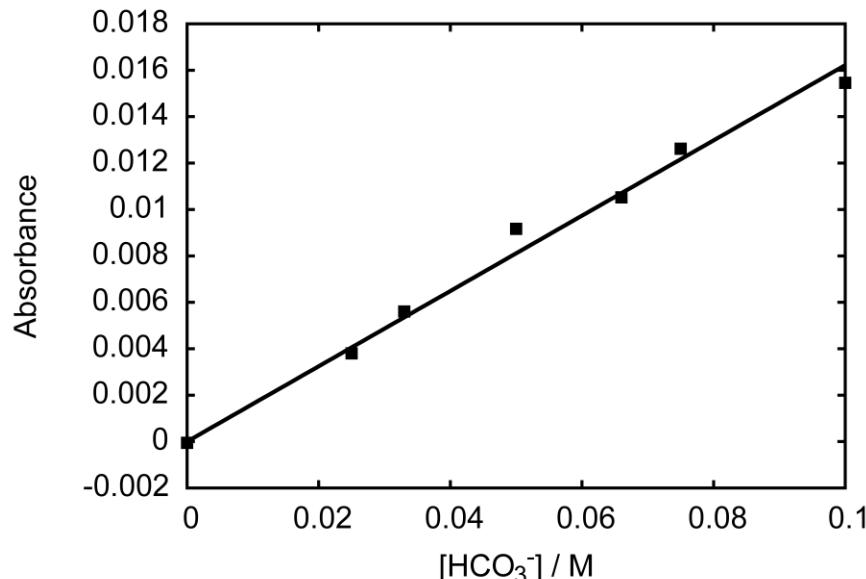
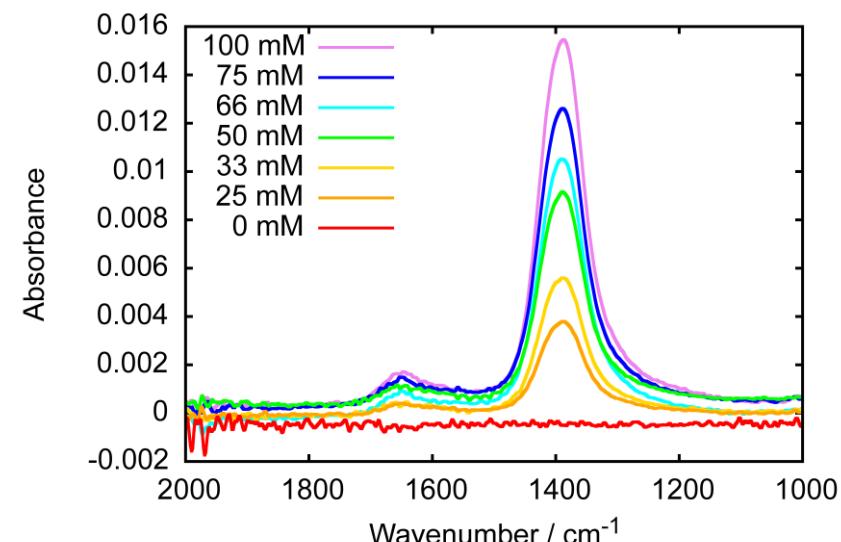
c = concentration

l = length = thickness (pathlength)

ϵ = Molar Absorptivity

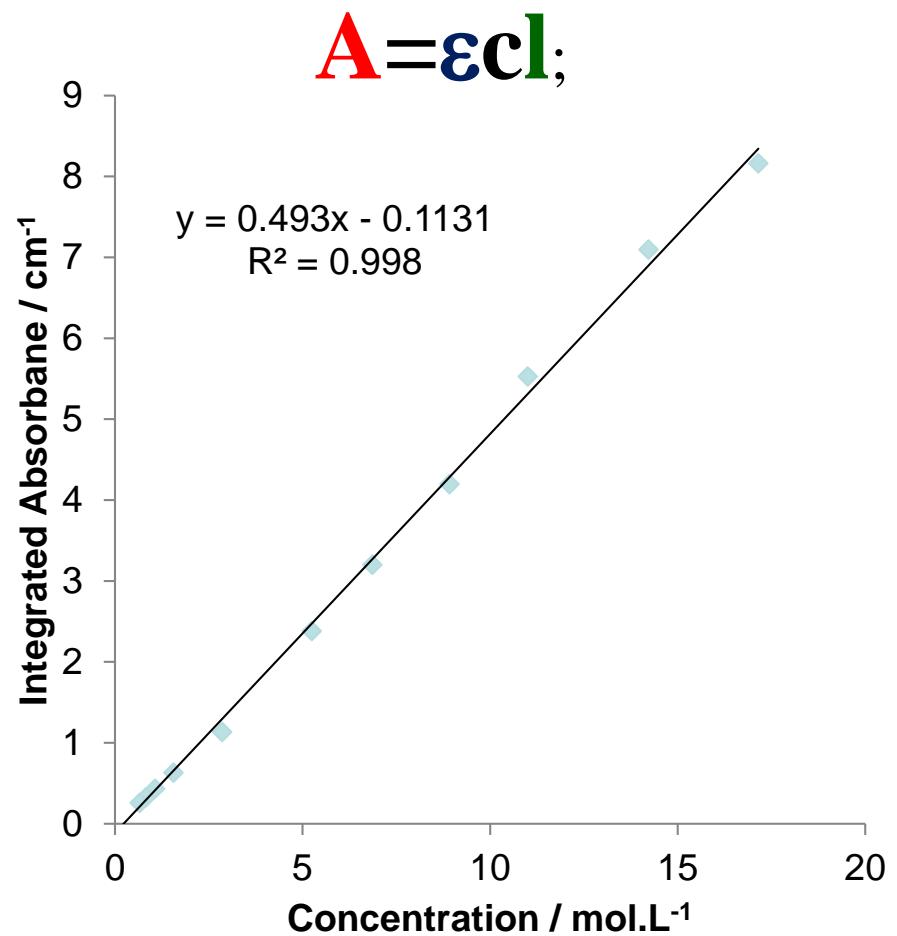
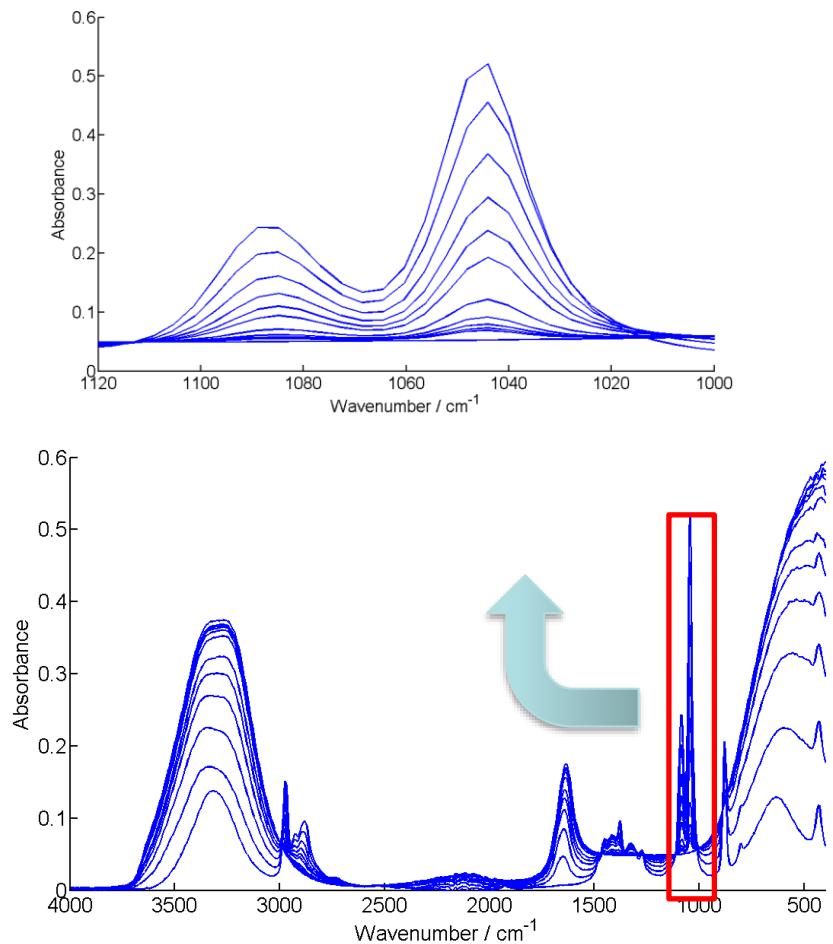
or Absorption coefficient

or Extinction coefficient



Beer-Lambert Law

Ethanol – water solutions

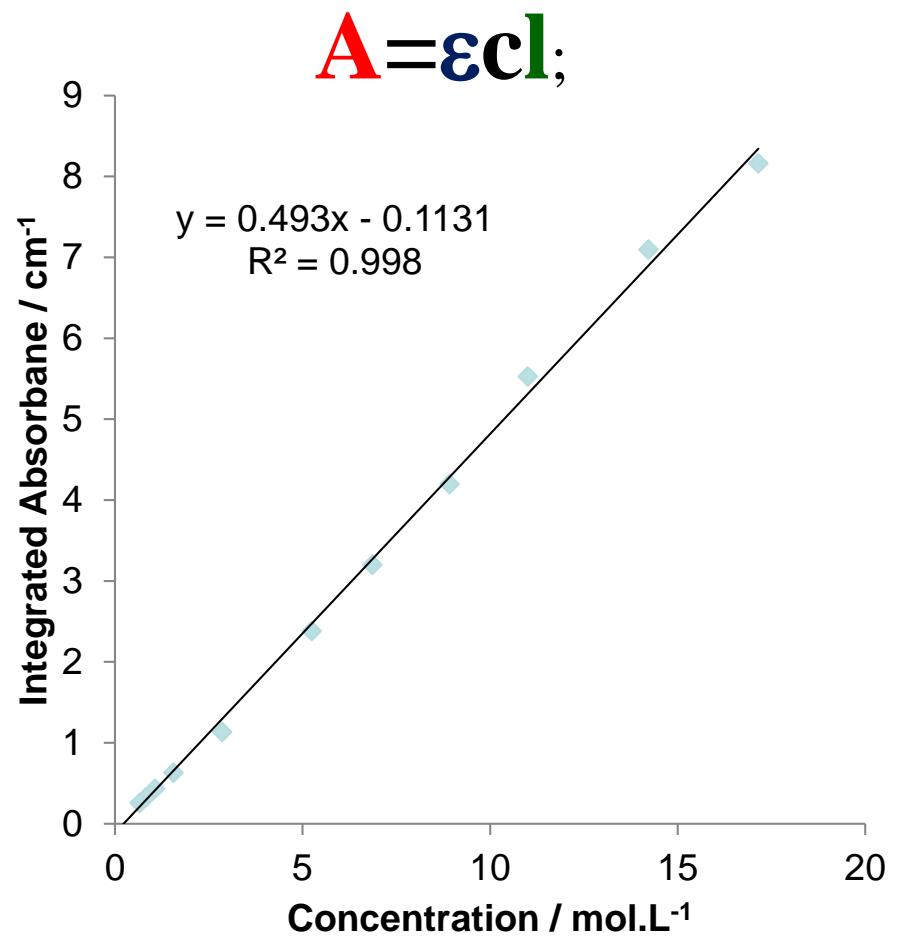
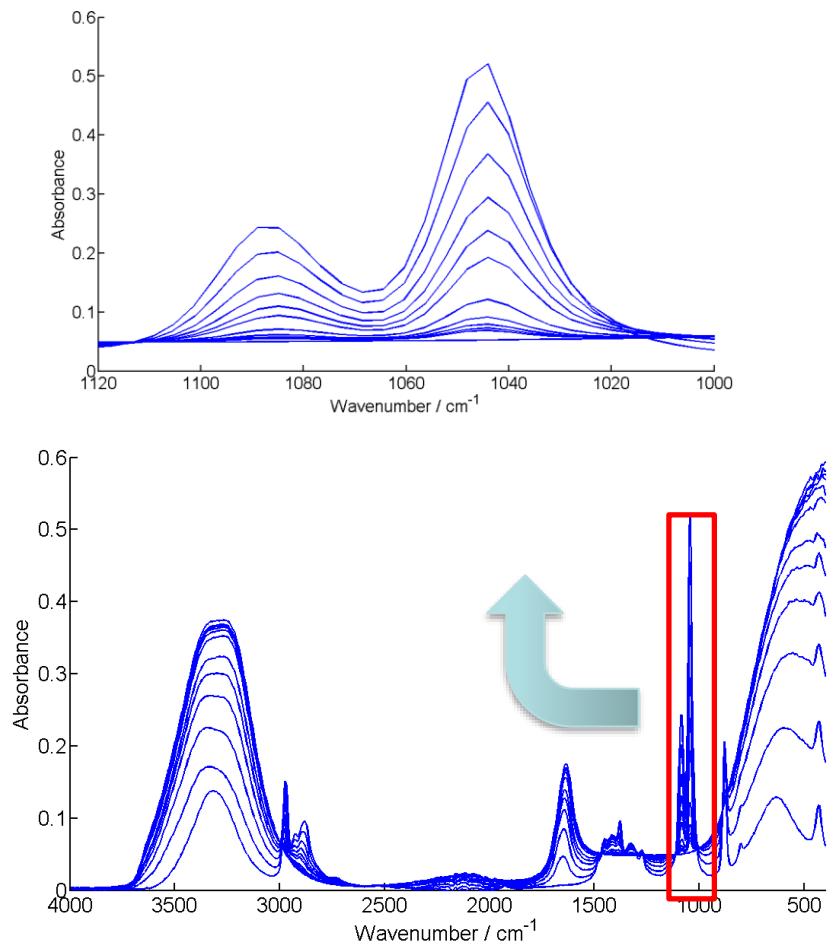


Hand sanitiser products

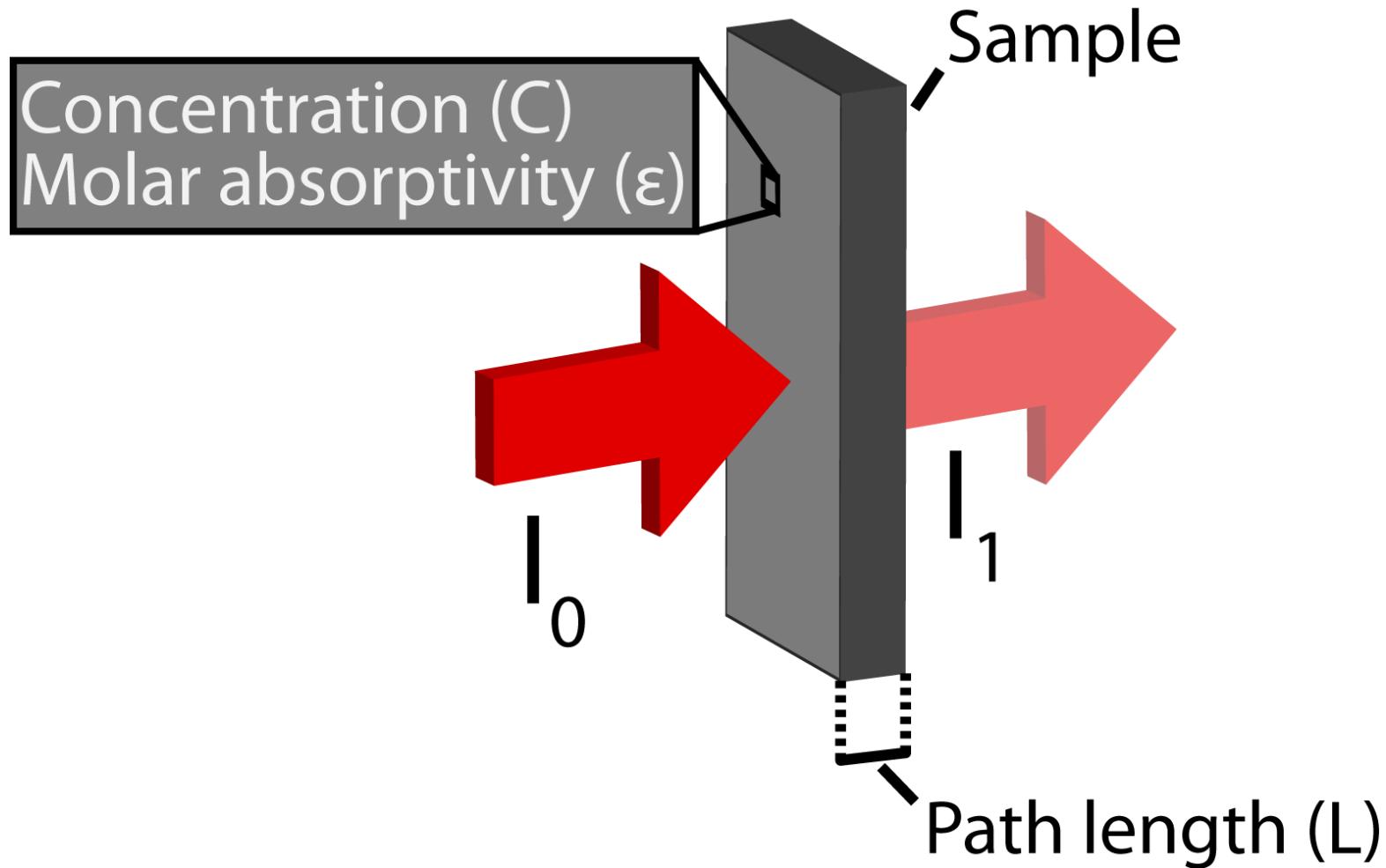


Beer-Lambert Law

Ethanol – water solutions



Beer-Lambert Law



Beer-Lambert Law

Each layer of equal thickness absorbs a constant fraction of the radiant passing through it (for homogenous systems):

$$-\frac{dI}{db} = a_b I \quad \ln I_0 / I = a_b b$$

The absorption of a species is proportional to its concentration, c:

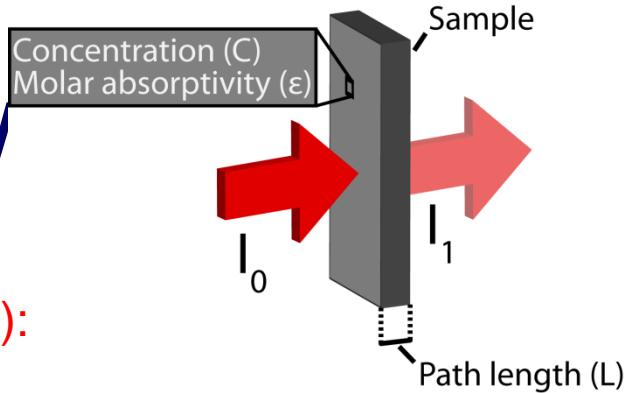
$$-\frac{dI}{dc} = a_c I \quad \ln I_0 / I = a_c c$$

The combined relationship is written:

$$\ln I_0 / I = a_c c a_b b = A$$

$$A = \epsilon c b = \epsilon c l$$

C = concentration,
b = path length,
 ϵ = molar absorptivity



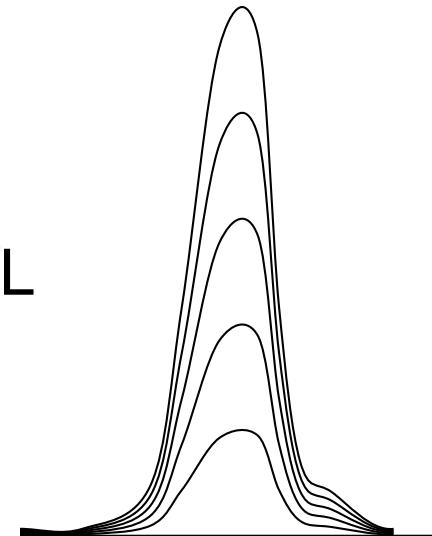
Beer-Lambert Law

Exercise

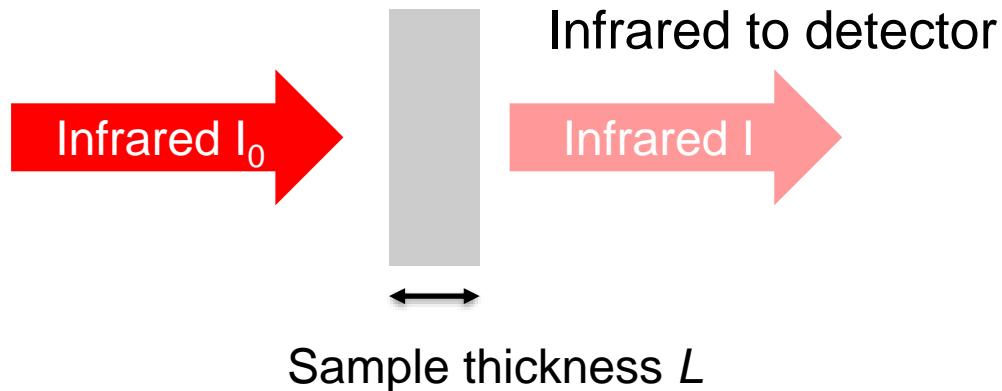
The molar absorption coefficient (molar absorptivity) for infrared band of a dye dissolved in 1 mm thick polymer film is known to be $0.5 \times 10^6 \text{ cm}^2/\text{mol}$. The measured absorbance of this band was 0.5. Calculate concentration of a dye in the polymer film.

$$A = \epsilon cl;$$

$$0.5 = 0.5 \times 10^6 \times c \times 0.1 \text{ cm}; \quad c = 0.01 \text{ mol/L}$$

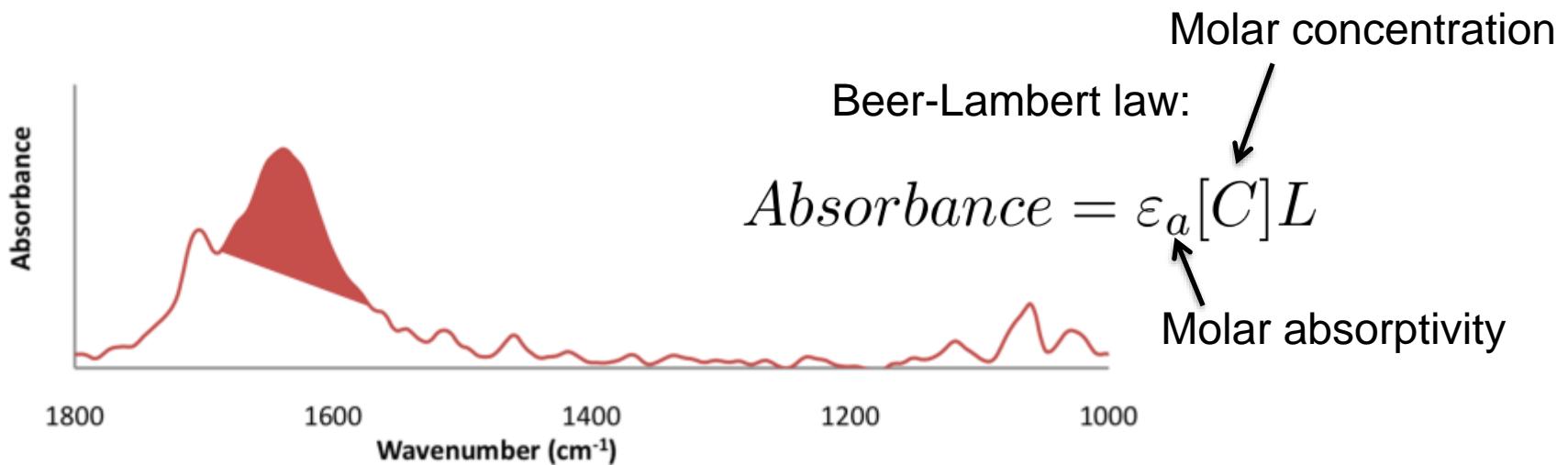


Beer-Lambert Law

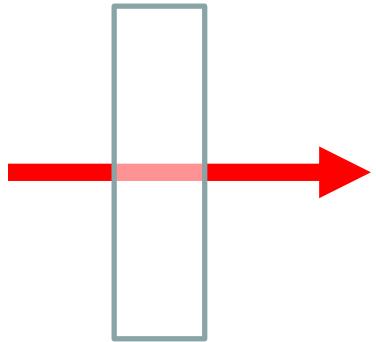


$$\text{Transmittance} = I/I_0$$

$$\text{Absorbance} = -\log_{10} (\text{Transmittance})$$



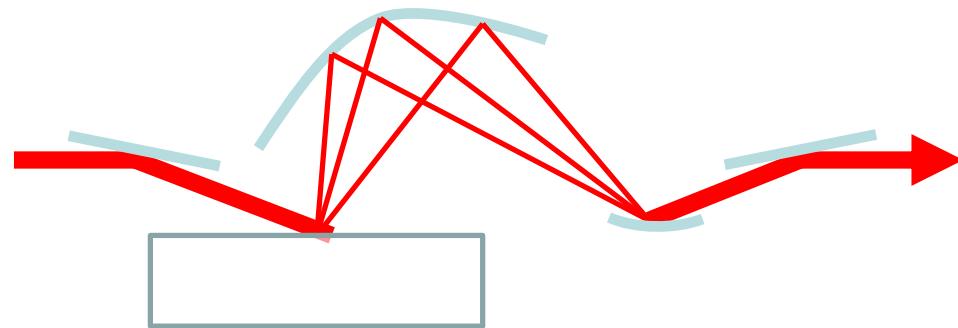
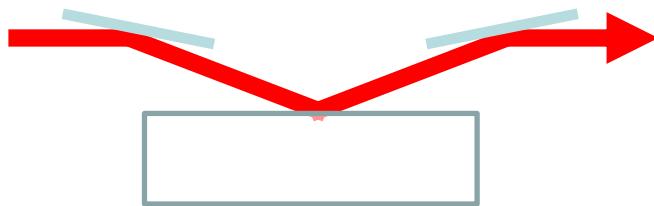
Sampling methods in infrared spectroscopy: transmission



Common methods:

- Liquid films between (transparent) salt plates
- Thin solid films
- Diluted in KBr + pressed into disc
- Bulk measurement

Sampling methods: External Reflection



Specular

- Thin films on reflective substrates
- Surface coatings

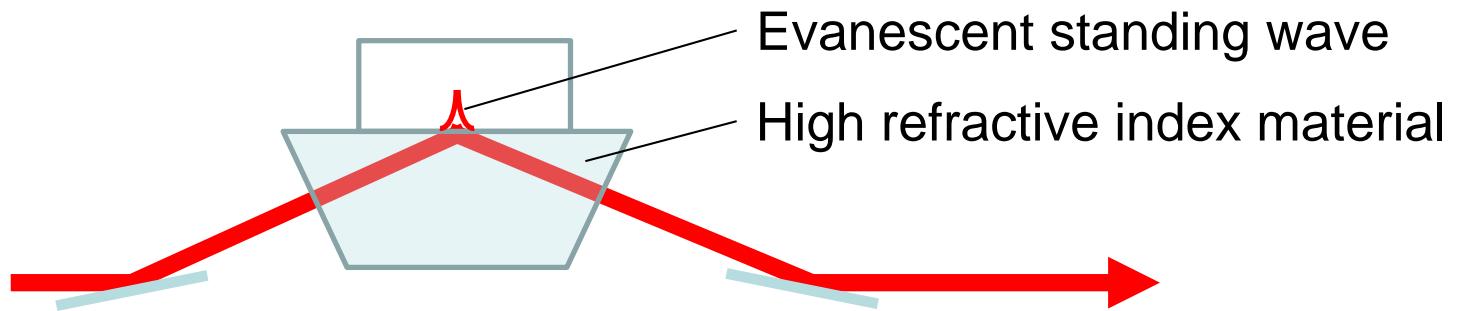
Surface sensitive

Diffuse (DRS, DRIFTS)

- Powdered samples
- Textured surfaces
 - Fibres, papers etc.

Sampling methods: Internal reflection

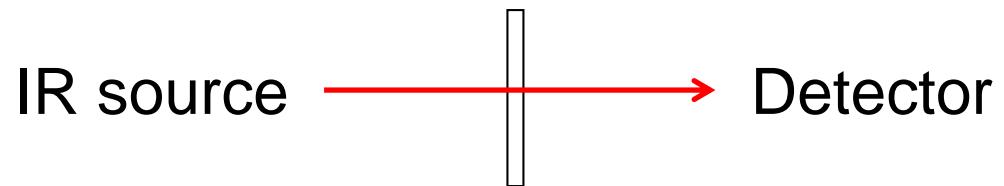
Attenuated Total Reflection: ATR



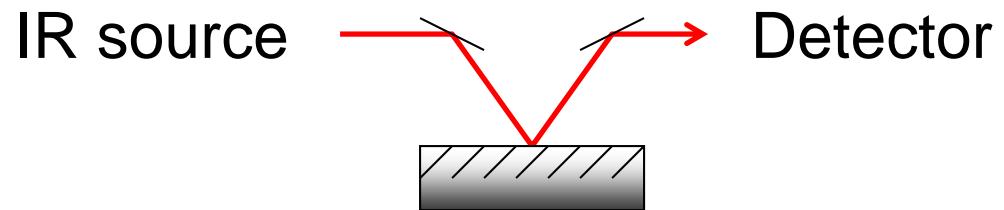
- Small ($0.2\text{-}3 \mu\text{m}$) penetration depth
- Ideal for strongly absorbing samples
- Surface sensitive – no bulk properties
 - (without sample preparation)

Infrared sampling methods

Transmission

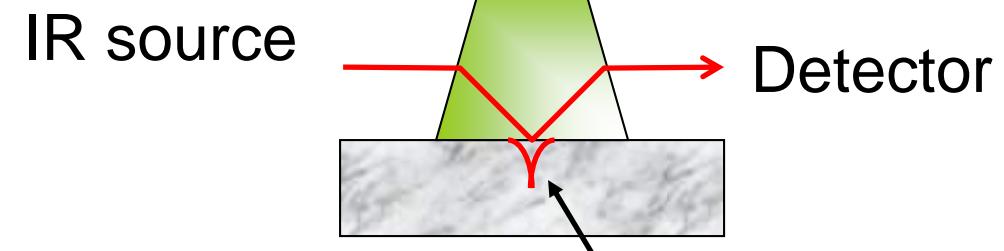


Reflection



Attenuated Total Reflection (ATR)

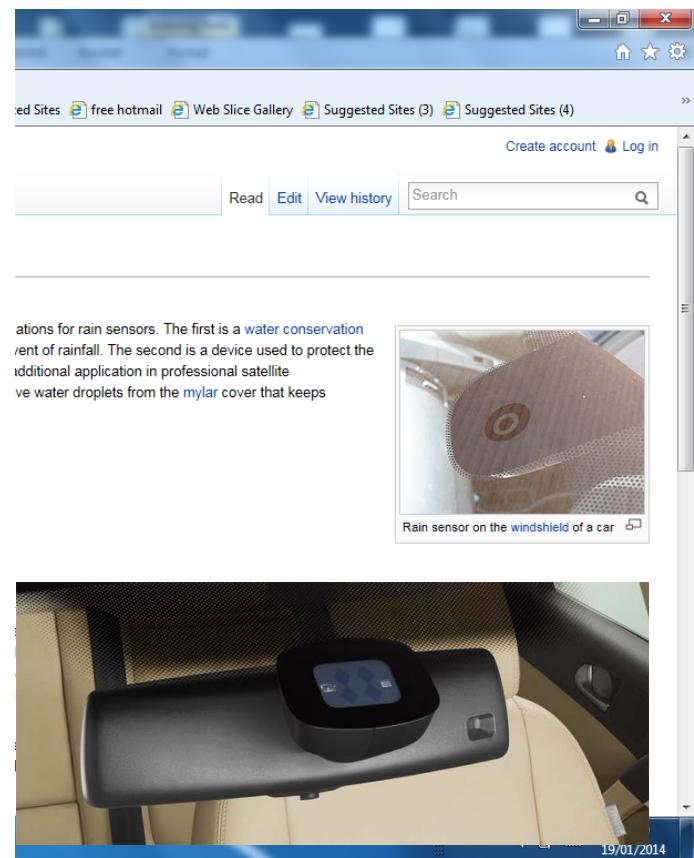
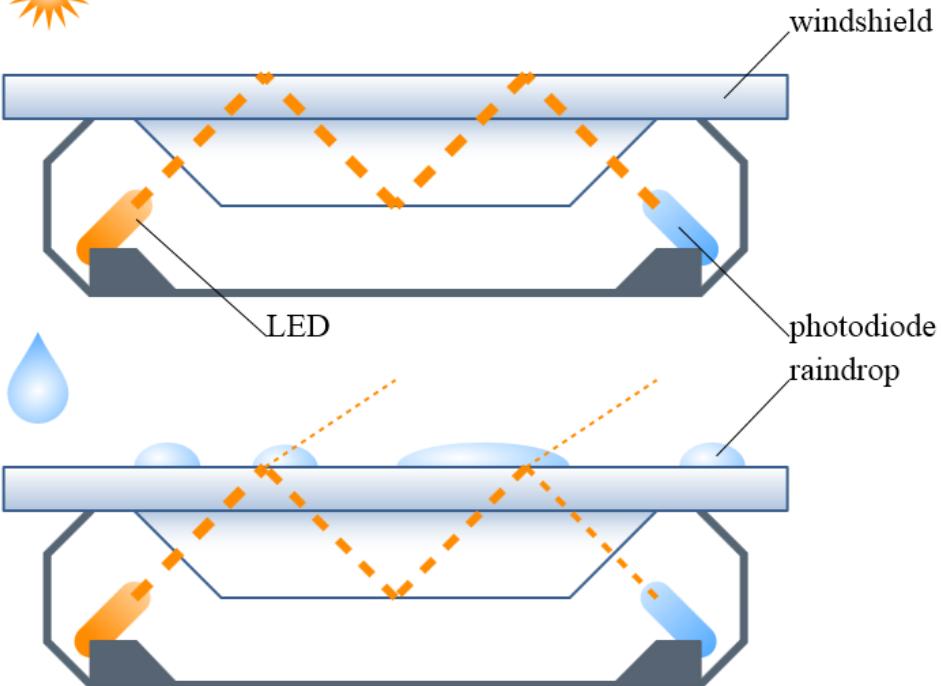
(schematic)



Evanescence wave

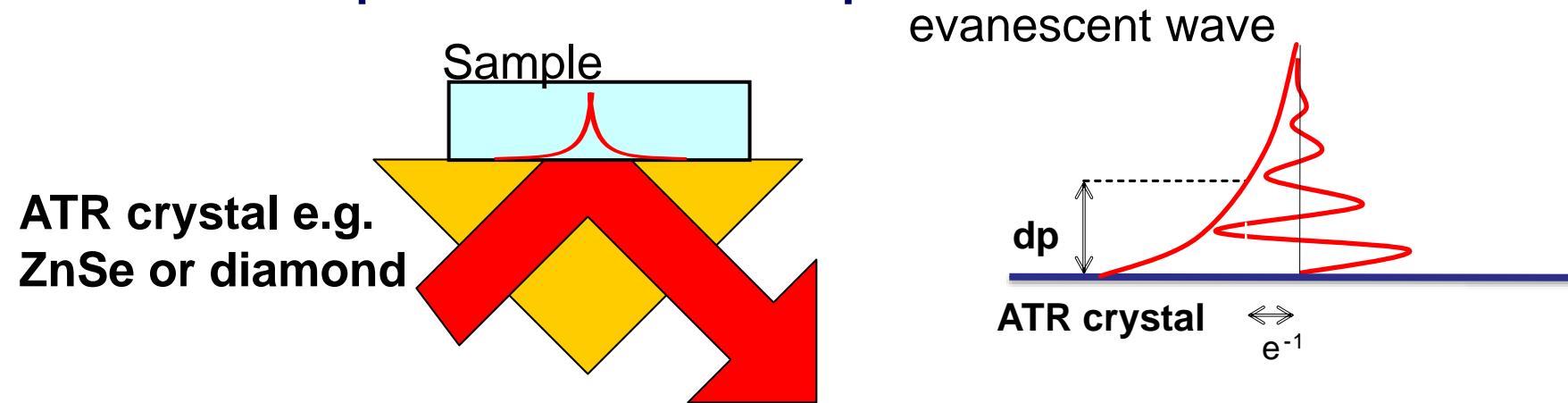
Total Internal Reflection

Rain sensor on car windshield



Automotive sensors. The most common modern rain sensors are based on the principle of total internal reflection: an infrared light is beamed at a 45-degree angle into the windshield from the interior — if the glass is wet, less light makes it back to the sensor, and the wipers turn on.

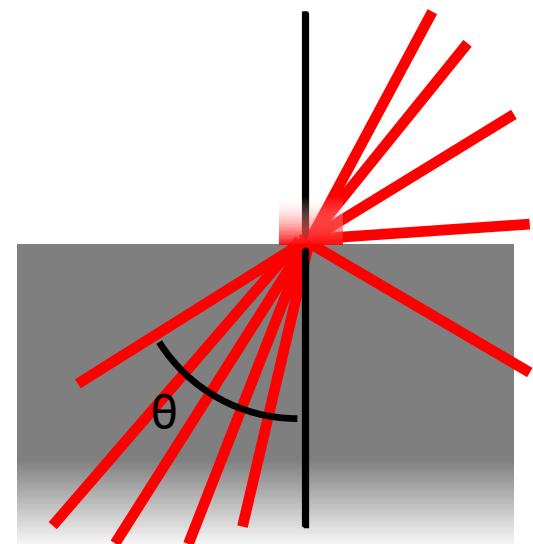
ATR (Attenuated Total Reflection) and penetration depth of IR beam



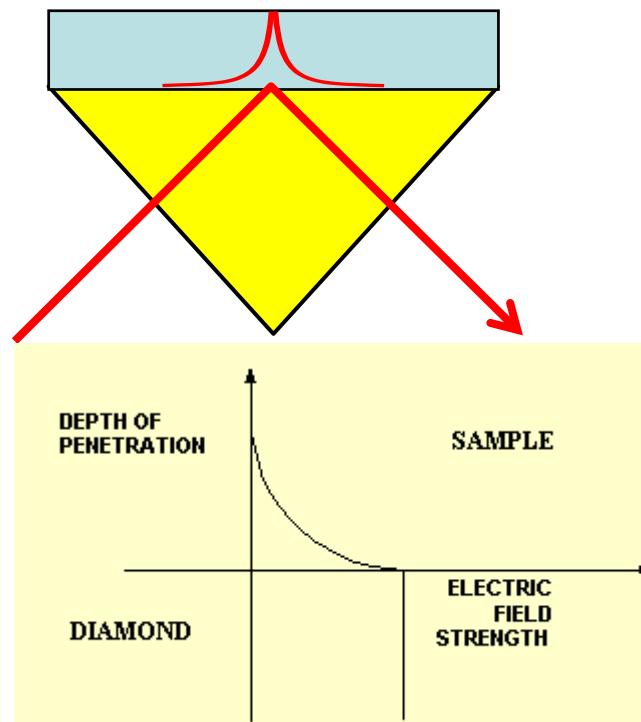
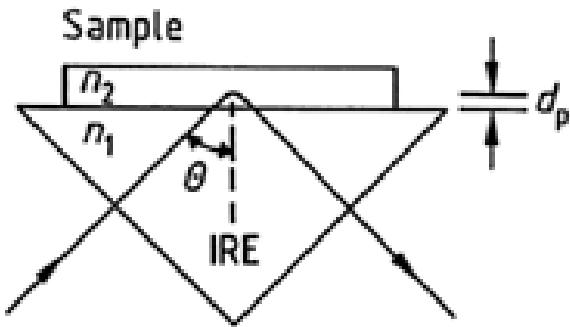
$$d_p = \frac{\lambda}{2\pi \cdot (n_1^2 \sin^2 \theta - n_2^2)^{1/2}}$$

$$d_p \sim 0.2 - 3 \mu\text{m} \text{ (in mid-IR)}$$

Total internal reflection occurs when
Incident angle of beam is greater than
Its critical value



Attenuated Total Reflection (ATR) infrared spectroscopy



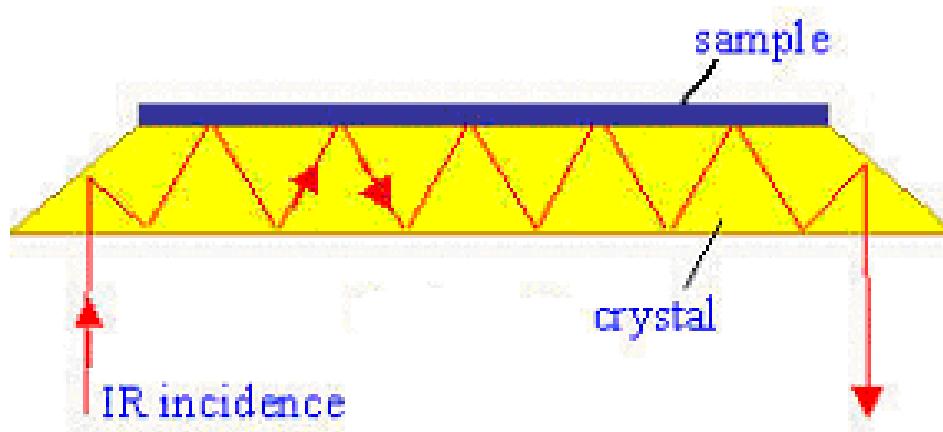
$$d_p = \frac{\lambda}{2\pi \cdot n_1 \cdot \left[\sin^2(\theta) - \left(\frac{n_2}{n_1} \right)^2 \right]^{0.5}}$$

$$E(z) = E_0 \exp(-z/d_p)$$

**ATR-IR: penetration depth d_p ranges from 0.2 μm to 3 μm
In mid-infrared region**

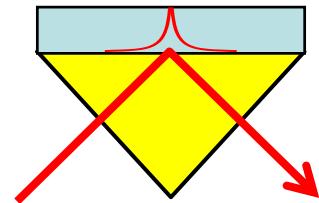
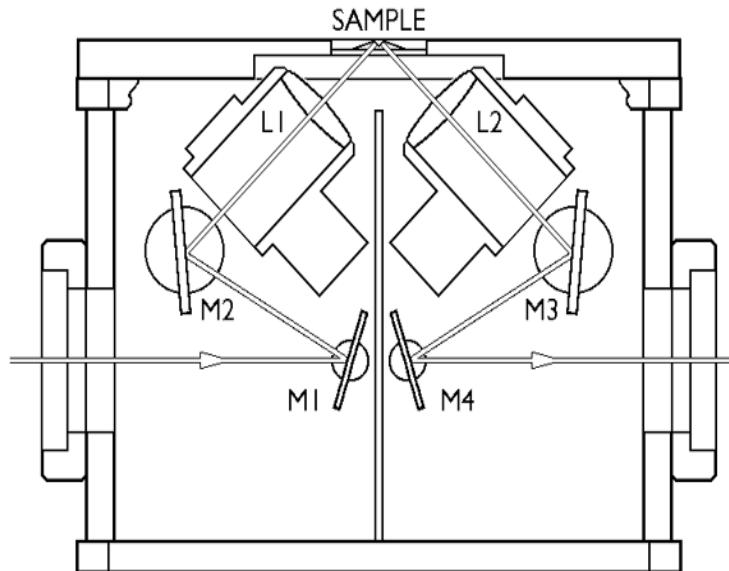
Relative ease of sample preparation
Aqueous samples can be studied

Multiple-reflection ATR infrared spectroscopy



This is used to enhance the absorbance spectral bands by increasing the pathlength of light in sample measured via multiple reflections

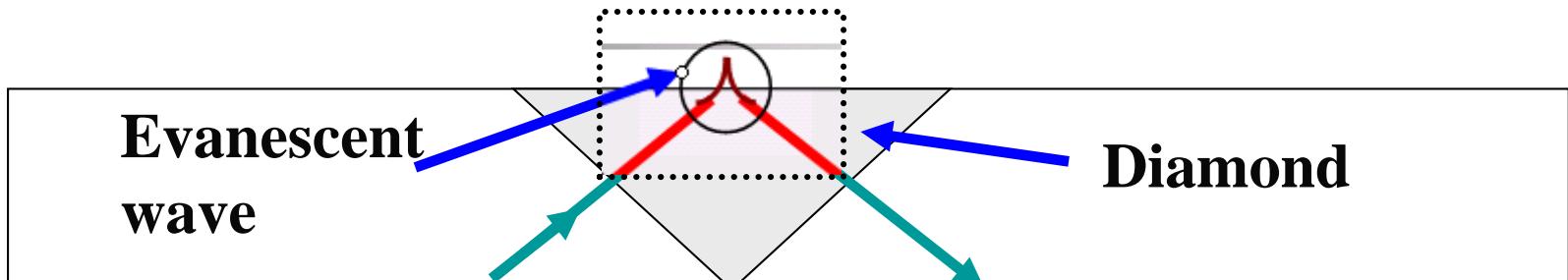
Diamond ATR FTIR spectroscopy



These ATR accessories are based on single reflection inverted prism

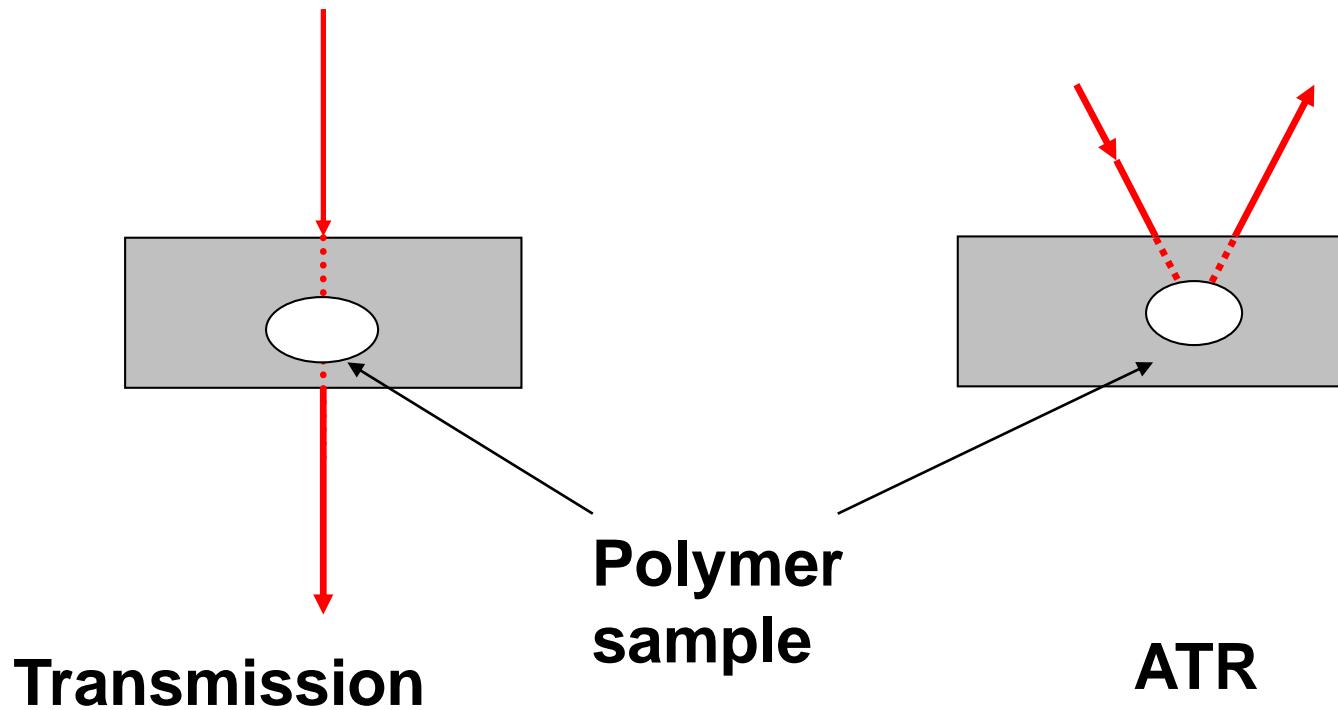
Golden gate accessory
(Specac, Ltd.)

Attenuated Total Reflection (ATR) - Diamond Accessory

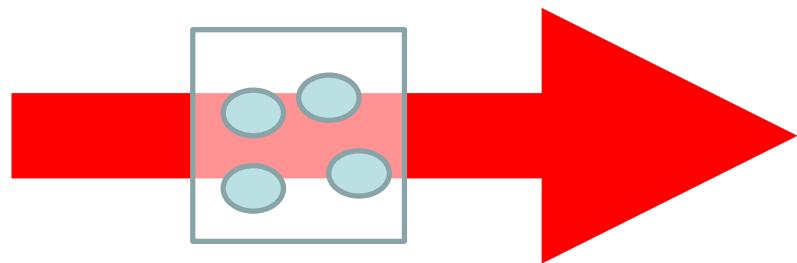
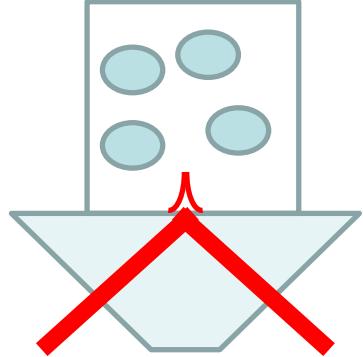


- Small amount of sample
- Study aqueous samples, corrosive materials
- Mechanical strength allows compression
- Reproducible results
- Ease of cleaning

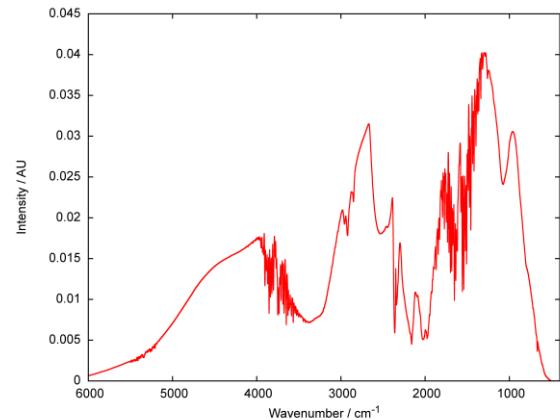
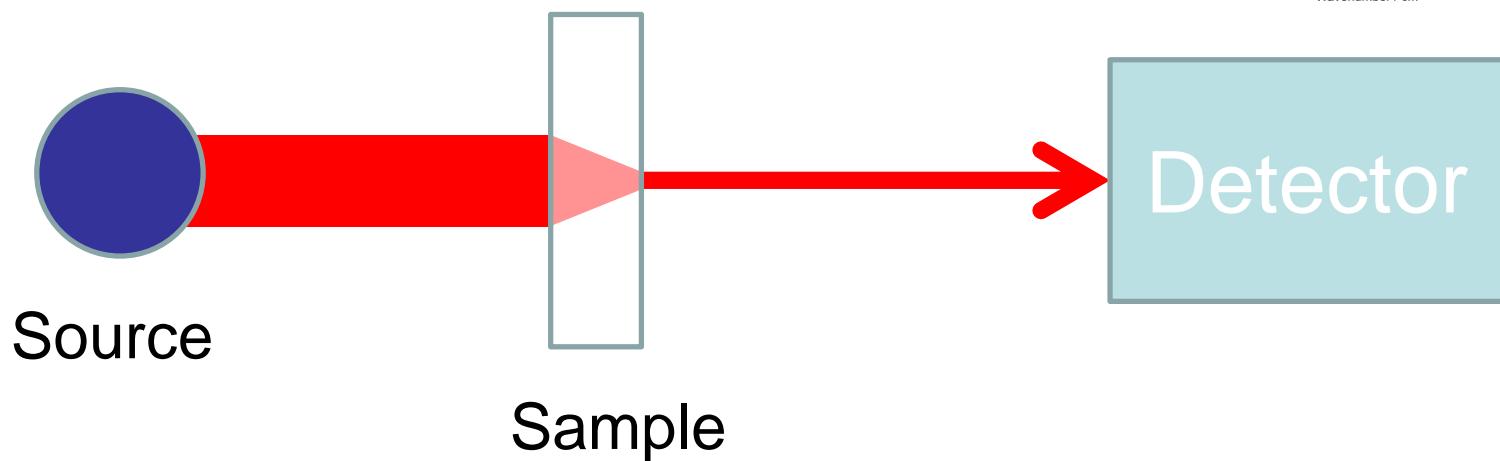
Effect of the pathlength in transmission and ATR mode



Effect of the pathlength in transmission and ATR mode

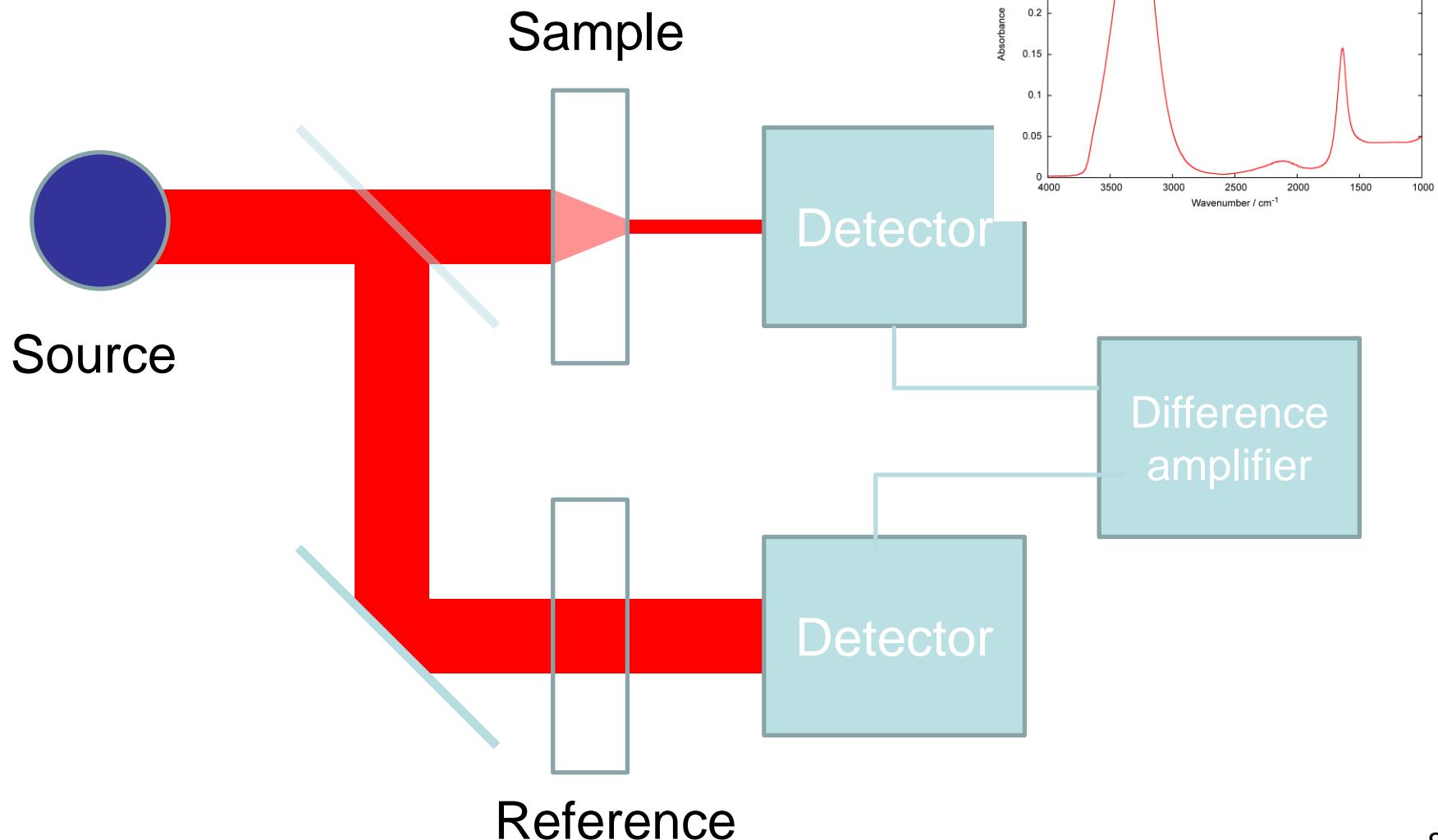


Simple IR Spectrometer

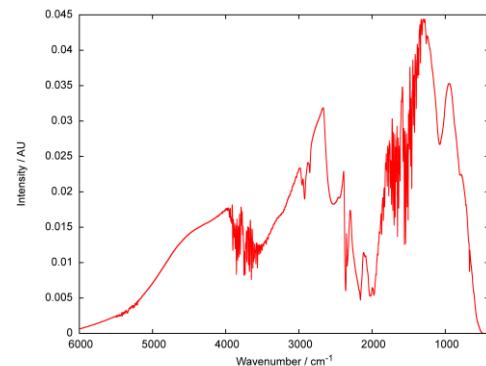
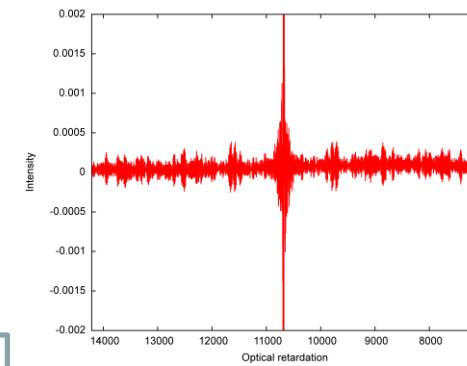
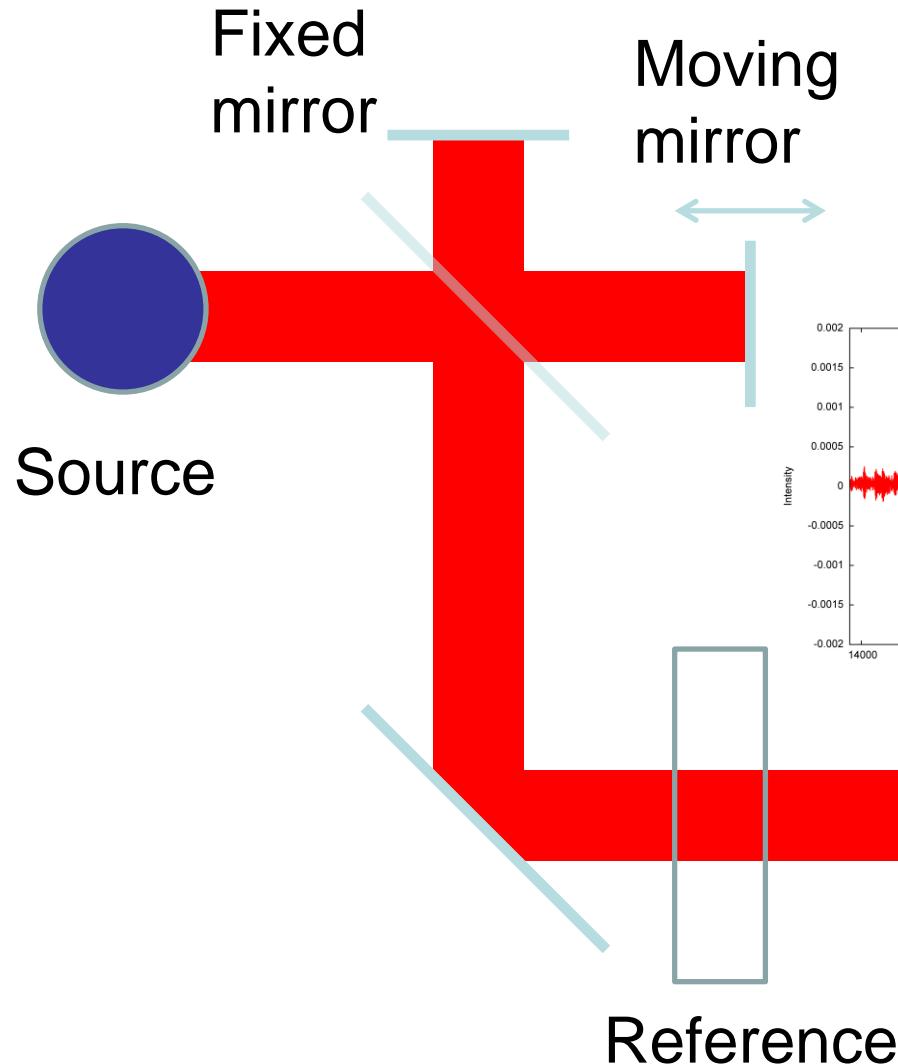


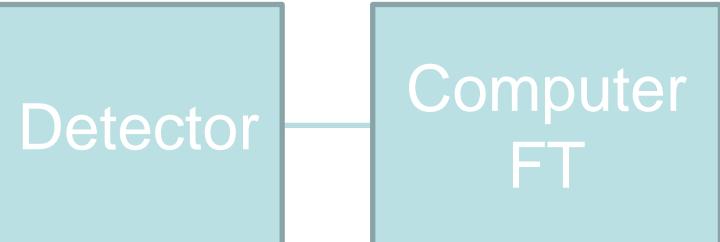
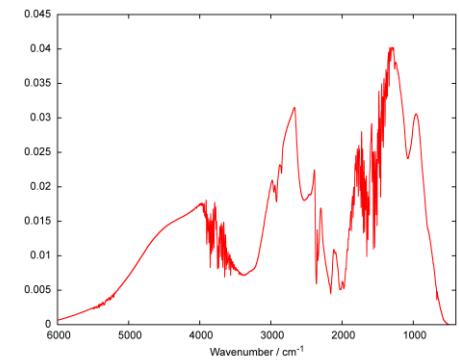
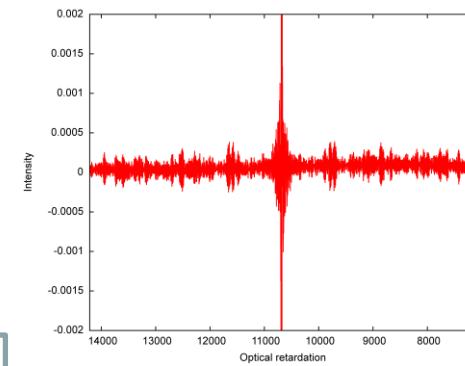
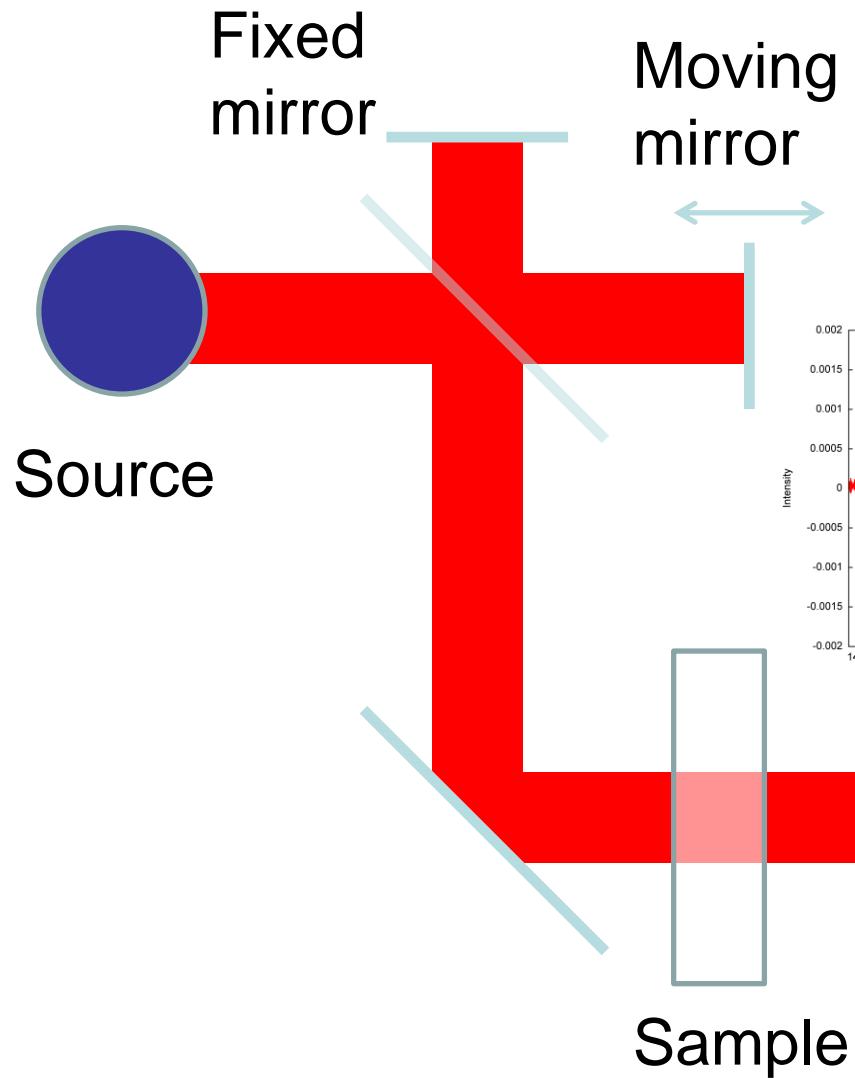
Does not take properties of source
or optics into account

Dual Beam IR Spectrometer

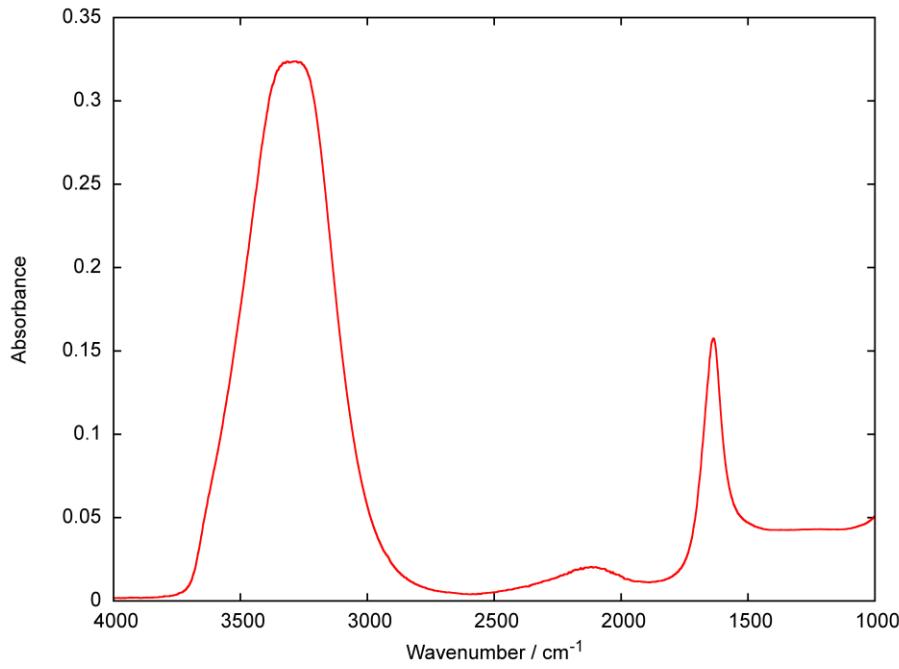
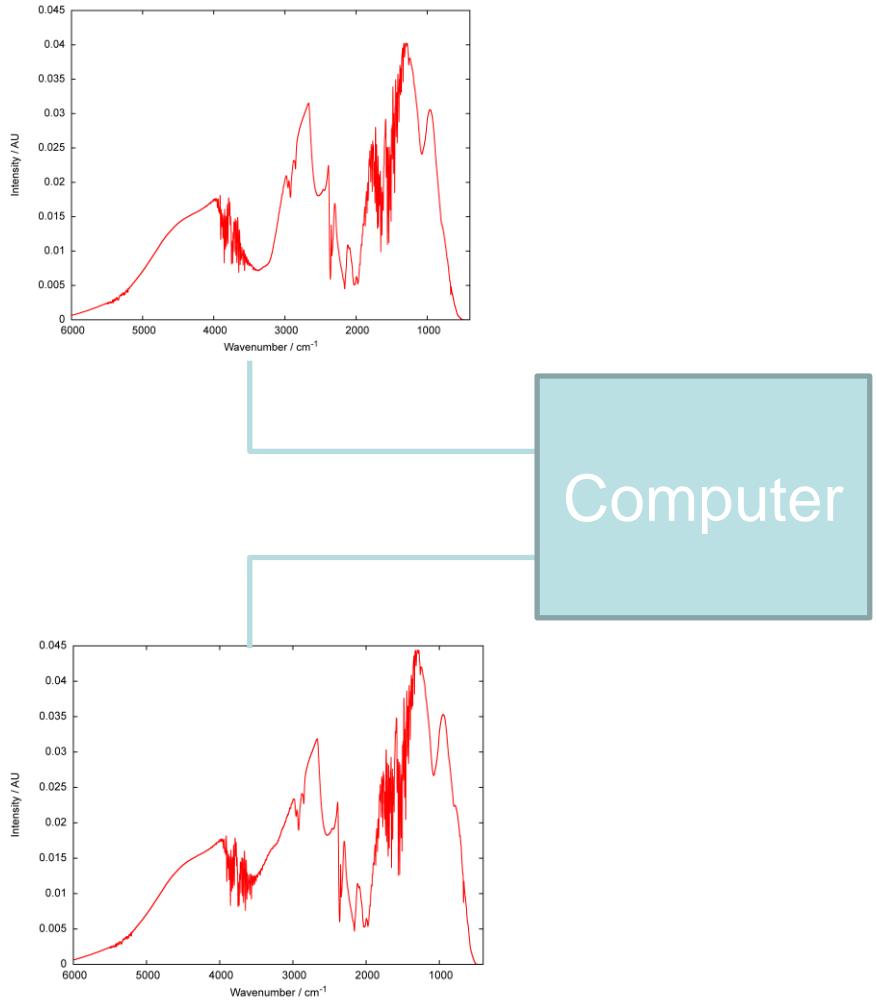


Fourier Transform (FTIR) Spectrometer

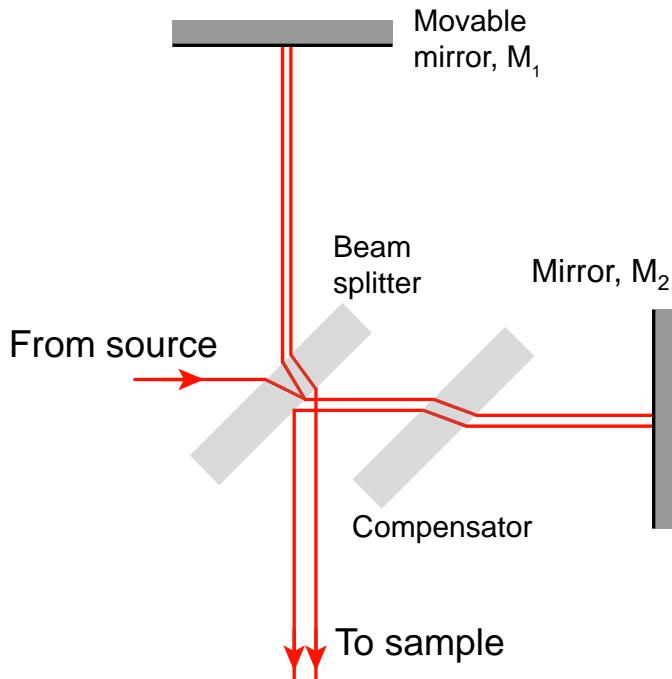




Fourier Transform (FTIR) Spectrometer



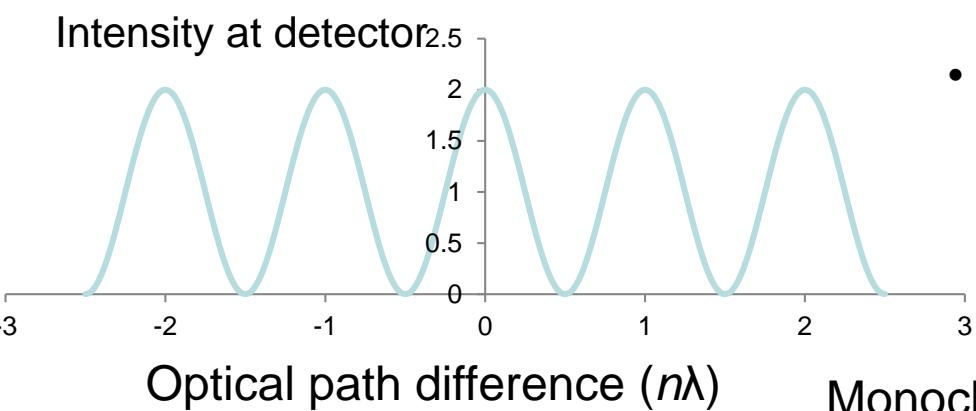
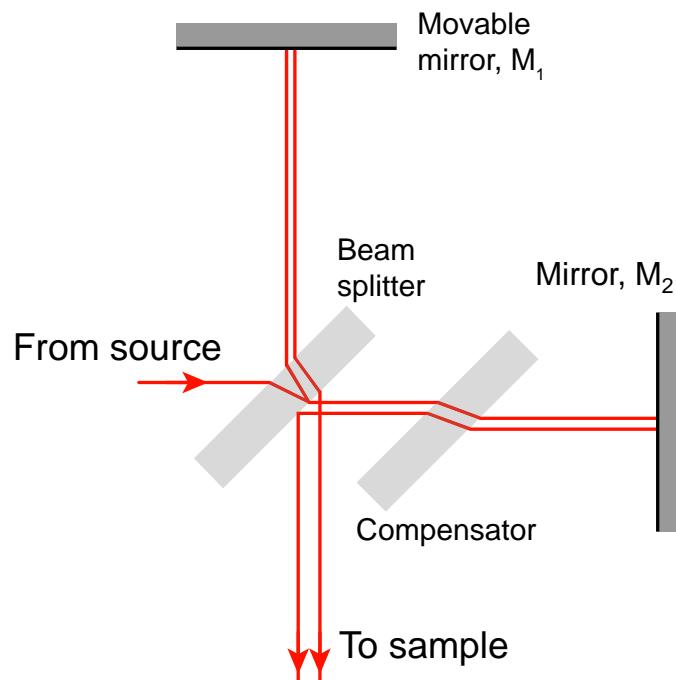
Fourier Transform Infrared (FT-IR) Spectroscopy



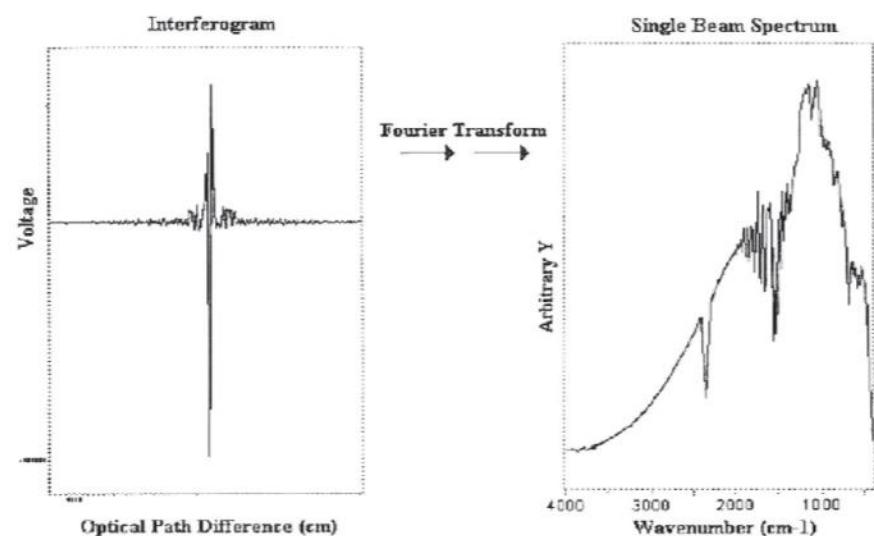
Michelson interferometer

- Using a Michelson interferometer (in FT-IR spectroscopy) instead of a diffraction grating enables spectra to be obtained quickly and signal to noise is improved.
- Infrared light from source passes through the beam splitter where half is sent to M_1 , half to M_2
- Optical path difference 'x' is the difference between the distances travelled by the beams from the beam splitter to M_1 and M_2 and back
- Beams are recombined and interfere with each other
 - Constructive interference of wavelength λ at $x=n\lambda$ where $n = 0, 1, 2, \dots$
 - Destructive interference of wavelength λ at $x/2=n\lambda$ where $n = 1, 2, 3, \dots$

Fourier Transform Infrared (FT-IR) Spectroscopy

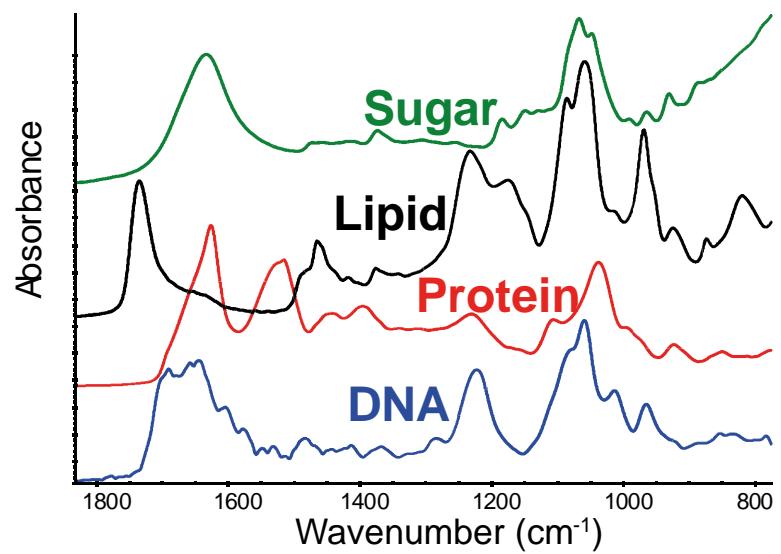
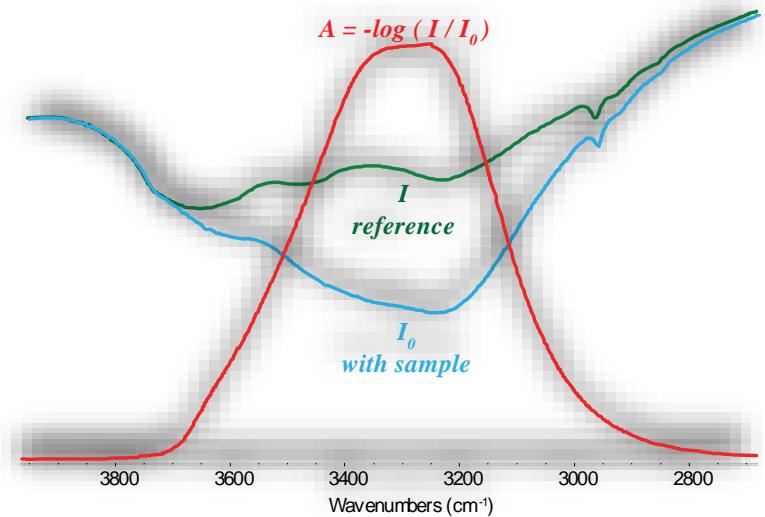
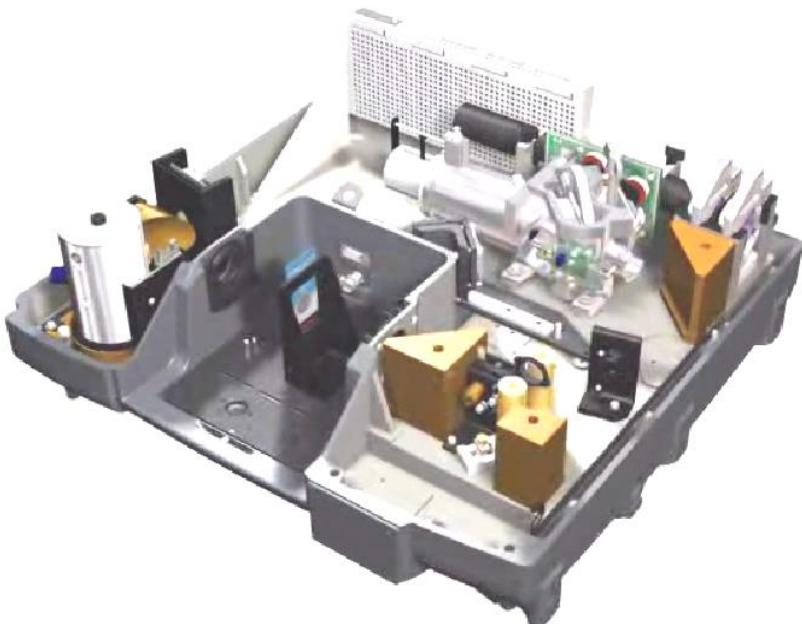


Monochromatic light



- Interference of polychromatic light results in an interferogram
- Fourier Transform of an interferogram results in an infrared spectrum (FT-IR):

FTIR spectroscopy



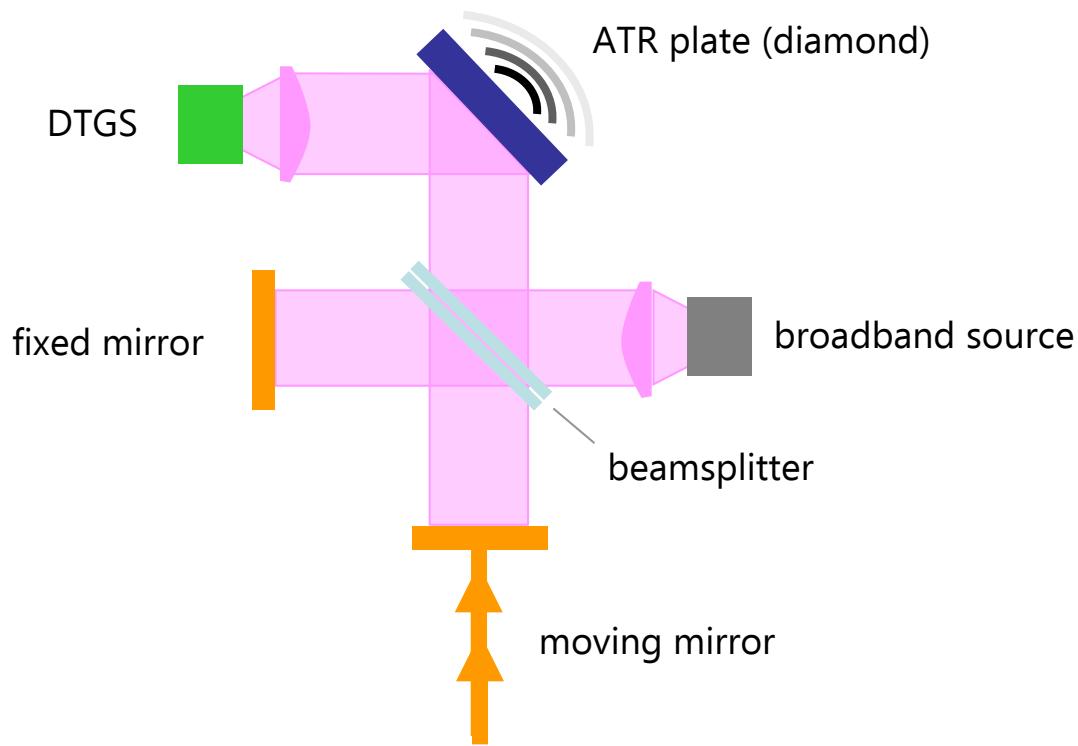
Handheld FTIR (Ahura)

650 to 4000 cm^{-1} @ 4 cm^{-1} resolution

Single-bounce diamond ATR – ‘press-and-shoot’

Temperature/shock/drop rugged

MIL-STD 810F









Infrared selection rules

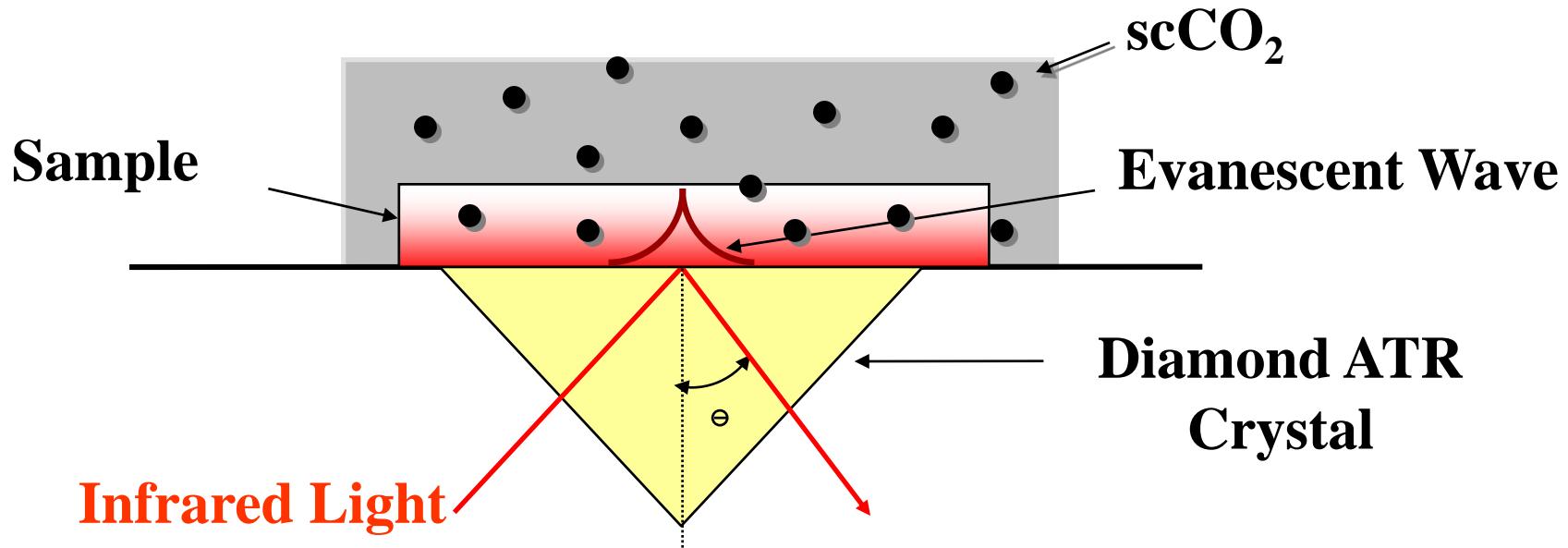
$$\Delta V = \pm 1 \text{ (for harmonic oscillator)}$$

$$\frac{\partial \mu}{\partial r} \neq 0 \quad \text{Infrared active}$$

μ is a dipole moment, $\mu = q \times r$, q is charge and r is distance (e.g. bond length).

$3N - 5$ vibrational modes for linear molecules
 $3N - 6$ for non-linear molecules

In situ high-pressure ATR (Attenuated Total Reflection)- IR

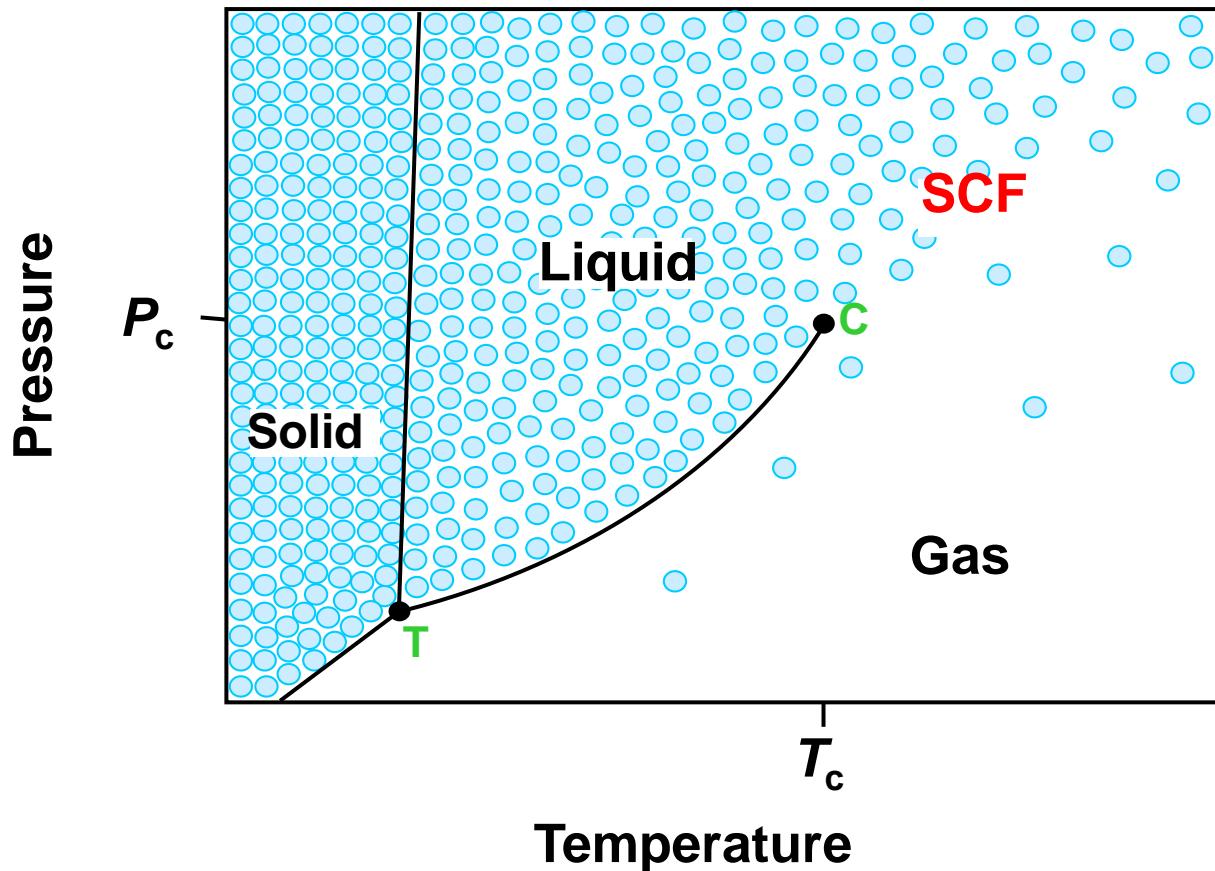


$$d_p = \frac{\lambda}{2\pi \cdot (n_1^2 \sin^2 \theta - n_2^2)^{1/2}}$$

INTEGRATING MATERIALS PROCESS ENGINEERING AND MOLECULAR SPECTROSCOPY:

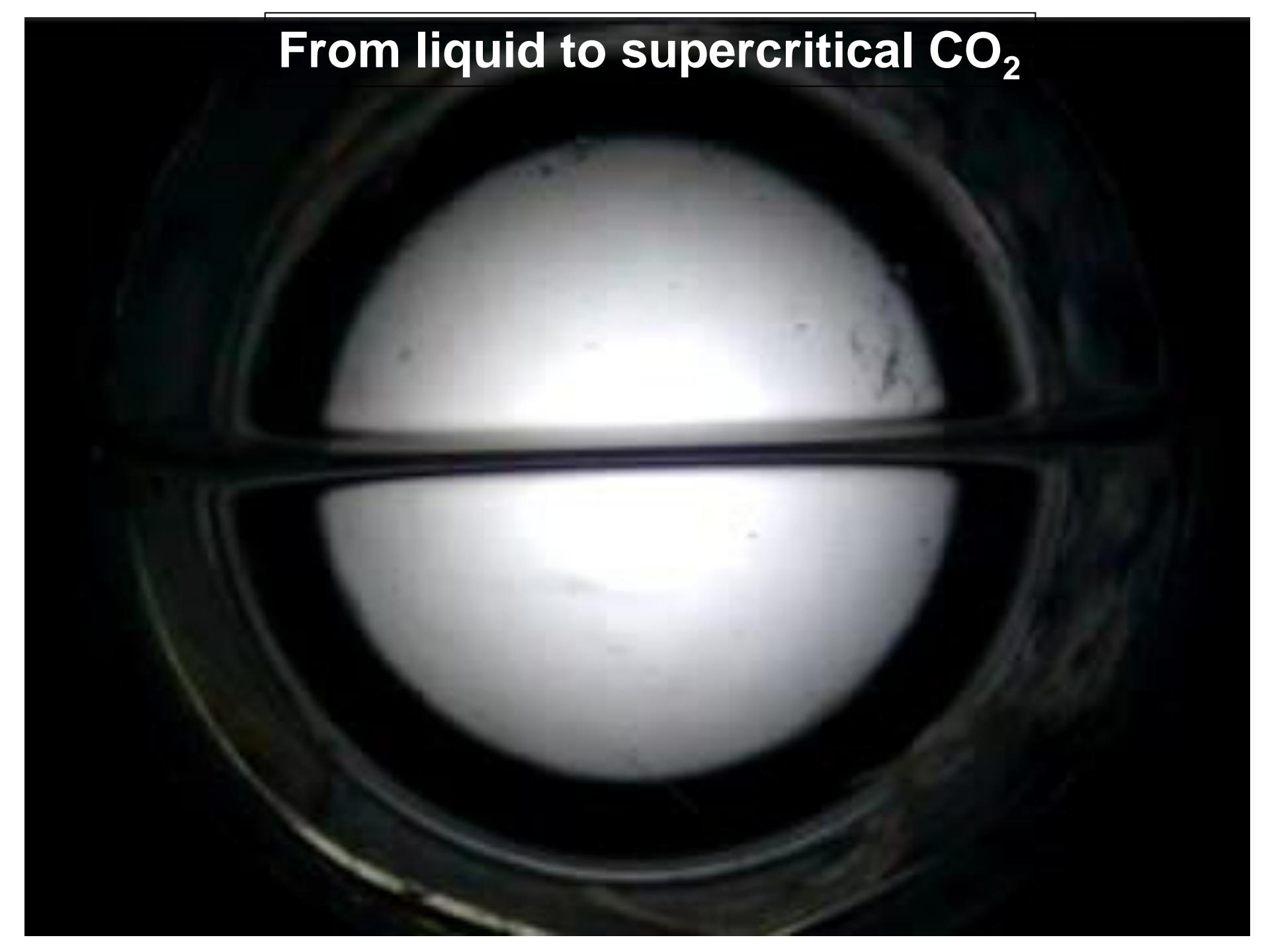
**Infrared spectroscopy for supercritical fluid
processing of polymeric materials**

PHASE DIAGRAM of CO₂



$$P_c = 73 \text{ bar}; \quad T_c = 31^\circ\text{C}.$$

From liquid to supercritical CO₂



Supercritical CO₂ and Polymers

- **Significant solubility**
- **Swelling (20%)**
- **Plasticisation - Tg reduction**

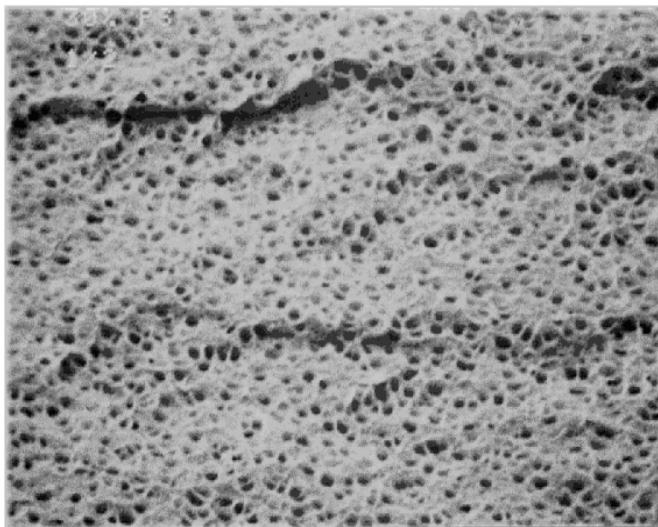
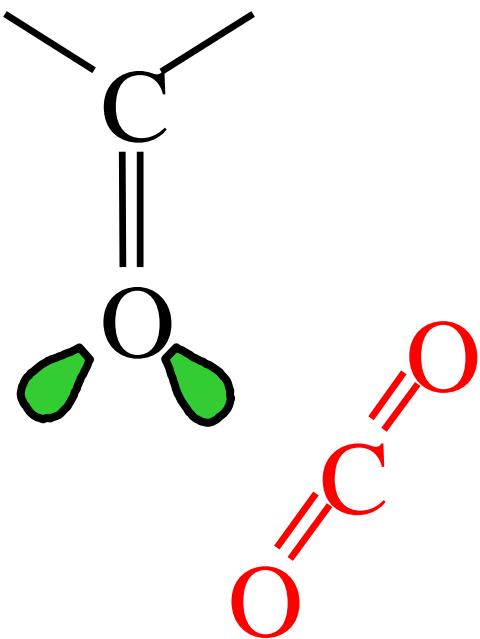
Tg of PMMA 105 °C (ambient conditions)

Tg of PMMA 40 °C (800 psi of CO₂)

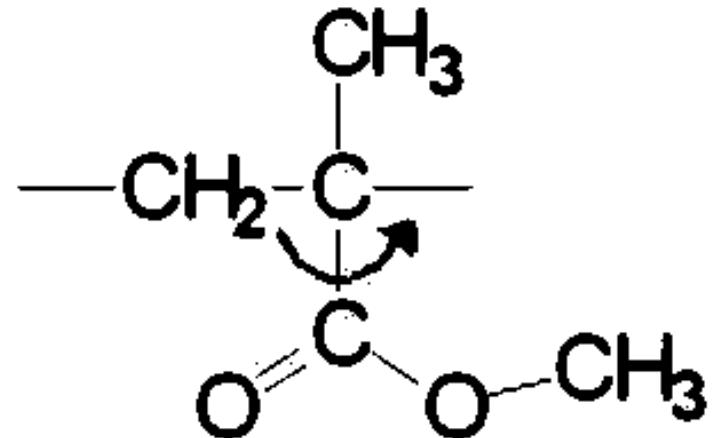
SUPERCRITICAL FLUIDS FOR SUSTAINABLE TECHNOLOGY

- **WATER AND CARBON DIOXIDE**
 - Environmentally acceptable, non-toxic, non-flammable, inexpensive
 - Adjustable solvent strength
 - High diffusion coefficients
 - Low viscosity
 - Easy to remove from product

Supercritical Fluids: from molecular interactions to processing

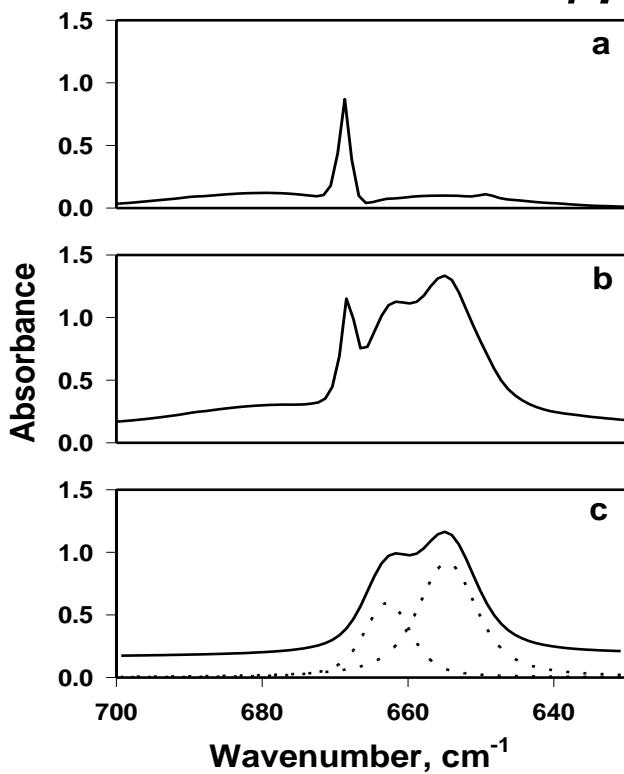


www.imperial.ac.uk/vsci



IR Evidence of Interaction between CO₂ and polymer

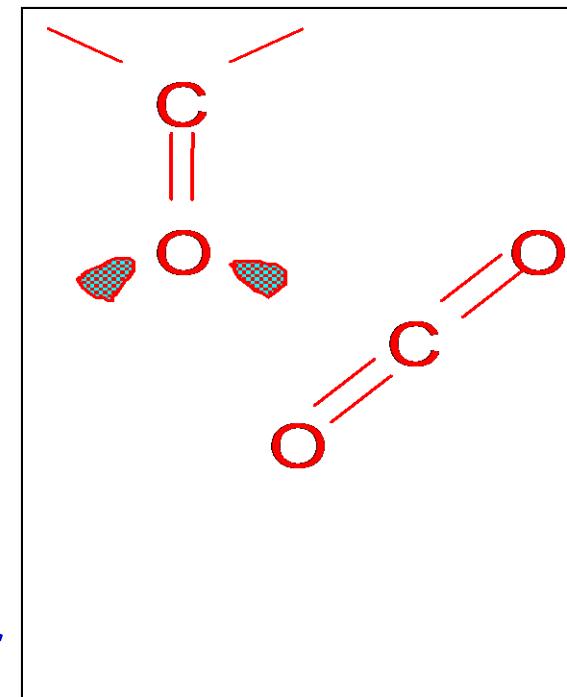
J. Am. Chem. Soc.,
1729, 118, 1996



CO₂

CO₂/polymer

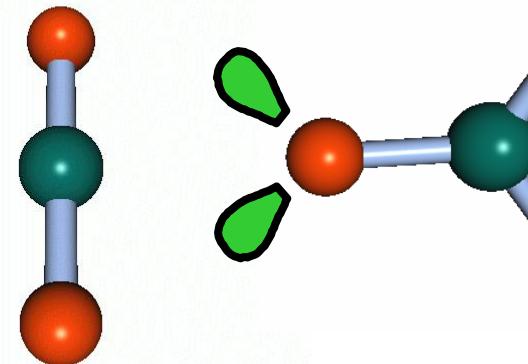
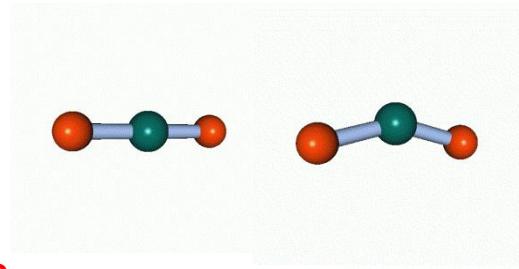
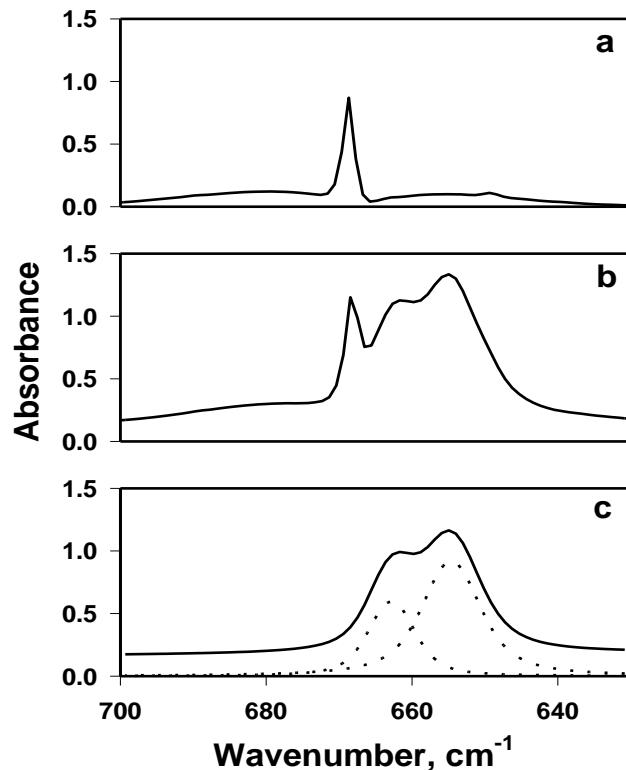
CO₂ in the polymer



ca. 4 kJ/mol

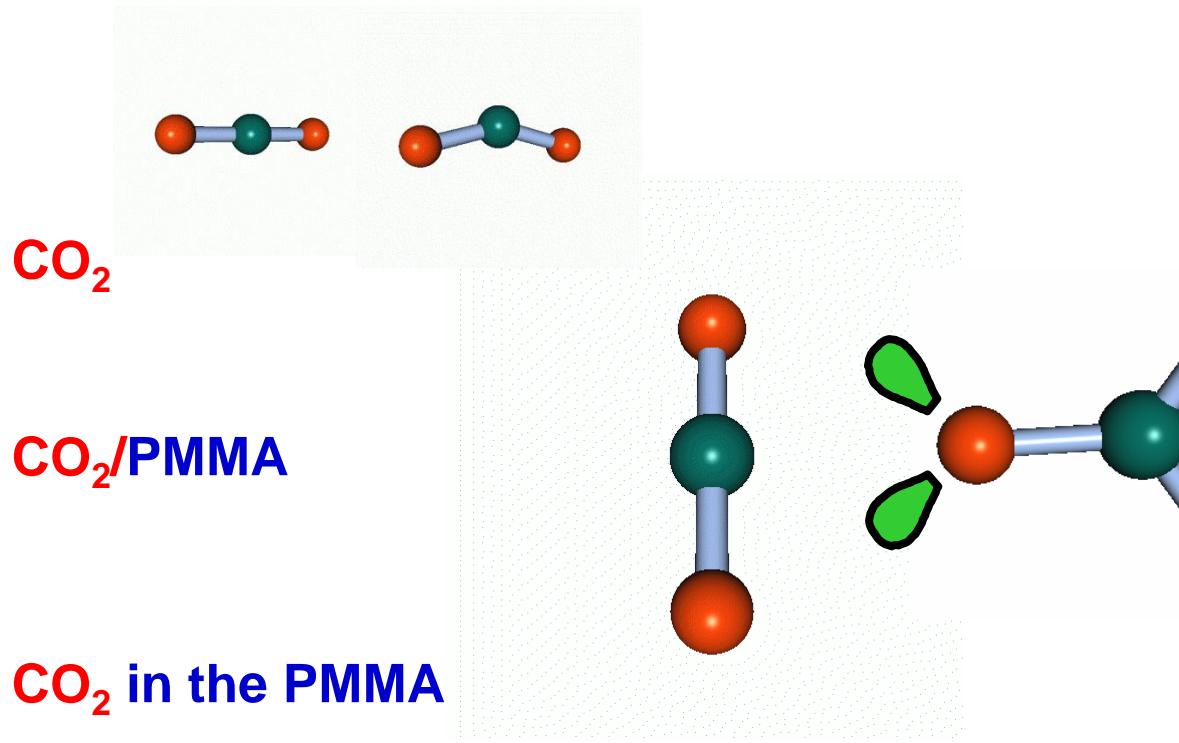
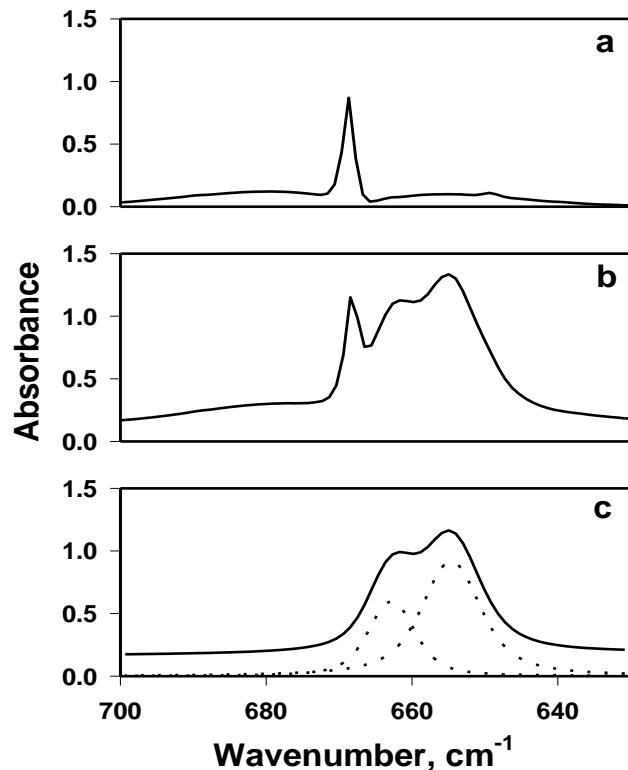
Removal of the degeneracy of the bending mode

Spectroscopic evidence of Interaction between CO₂ and polymer (PMMA)



- **Proposed weak Lewis Acid-Base Interaction**
ca. 4 kJ/mol

Spectroscopic evidence of Interaction between CO₂ and polymer (PMMA)



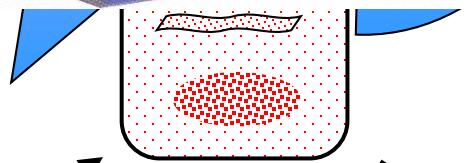
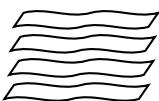
- **Proposed weak Lewis Acid-Base Interaction**
ca. 4 kJ/mol

Dyeing to be clean

Pure C
Recyc

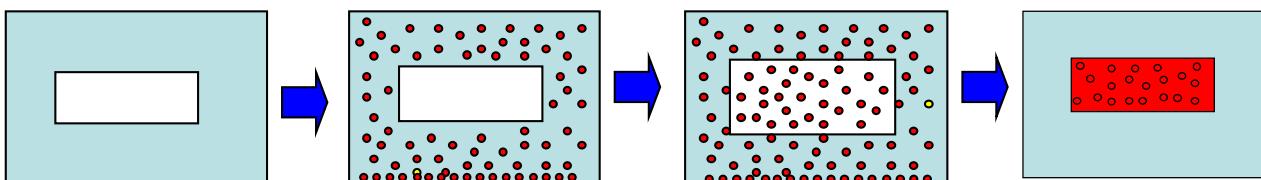


Un-Treated
Fabric

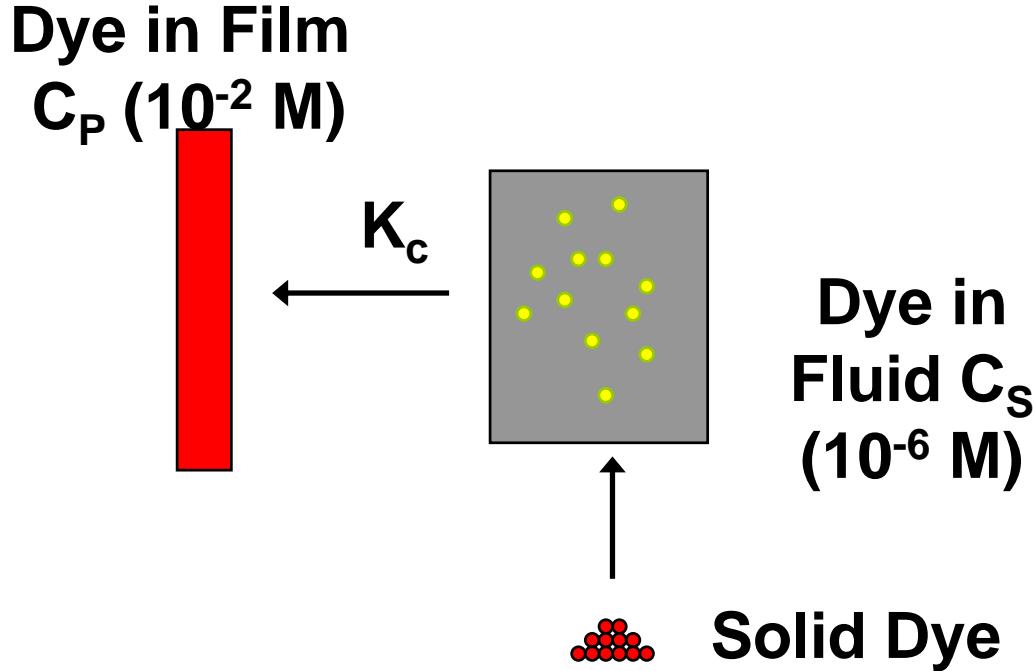


**Dyeing
Chamber**

Dyed
Fabric

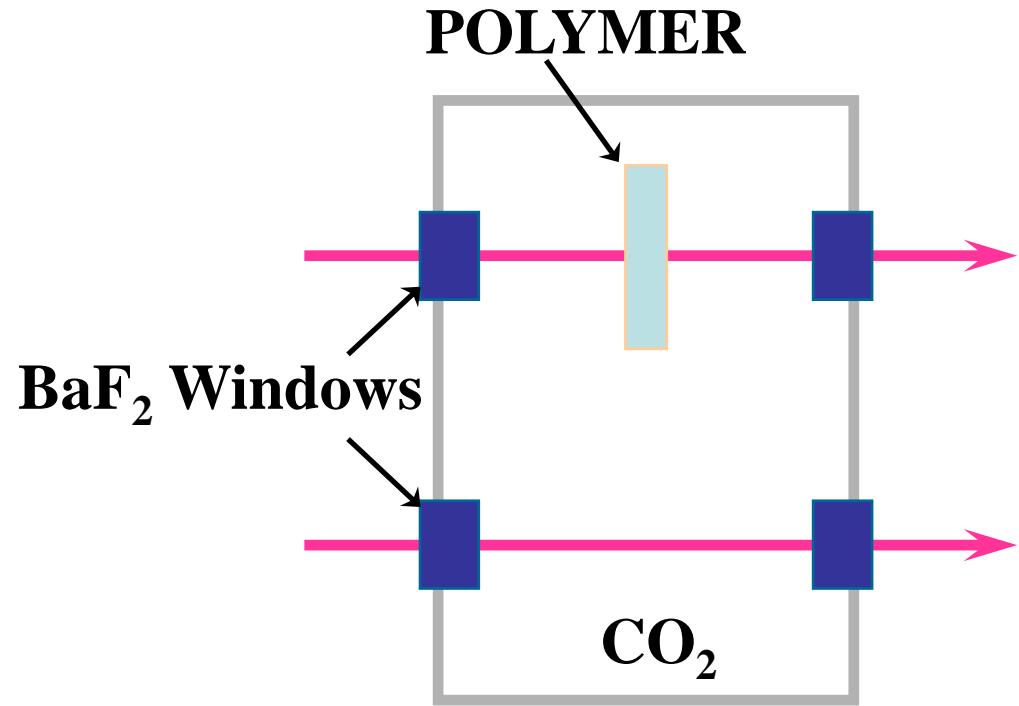
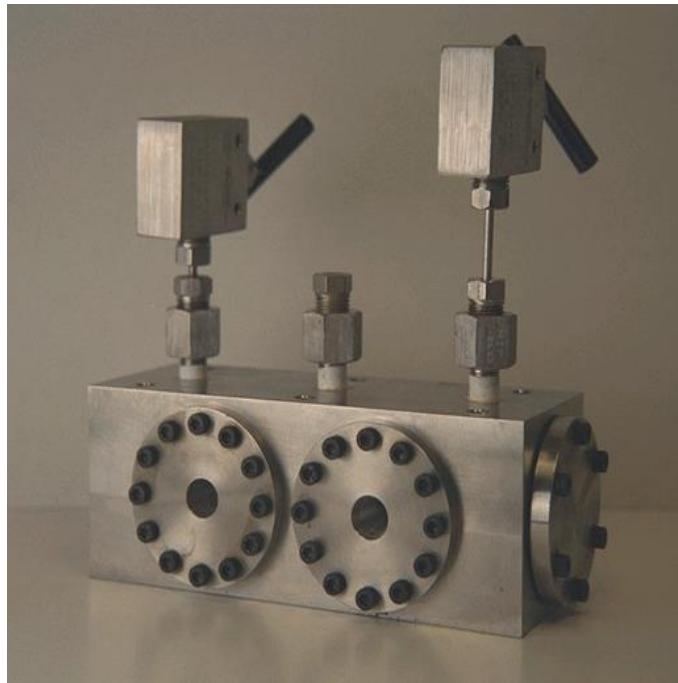


Dye Partitioning



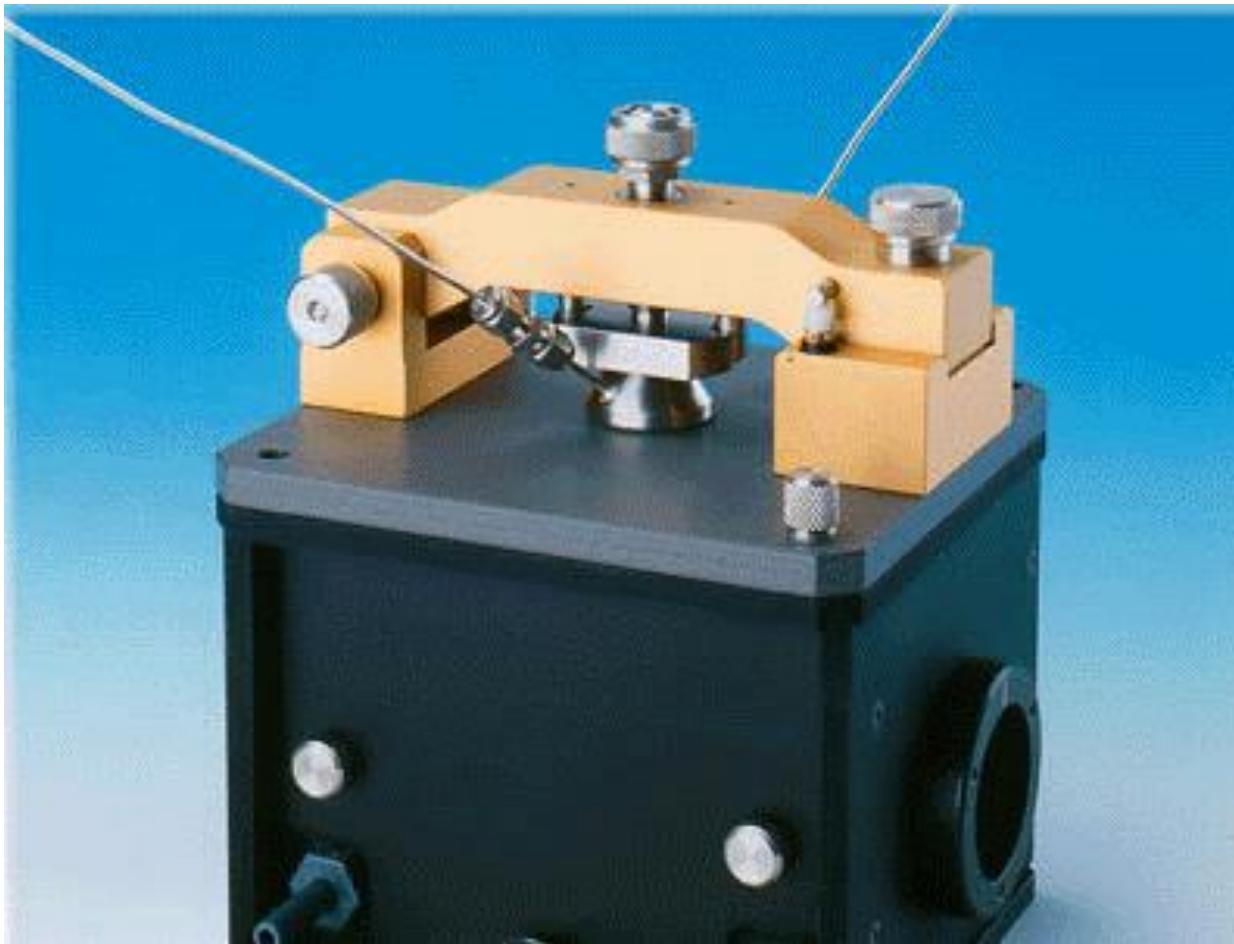
- Large K_c in favor of polymer drives scCO_2 dyeing process.
- Partition coefficient is a key property for design

In situ FTIR and UV/Vis Spectroscopy of Polymer-Supercritical Fluids System

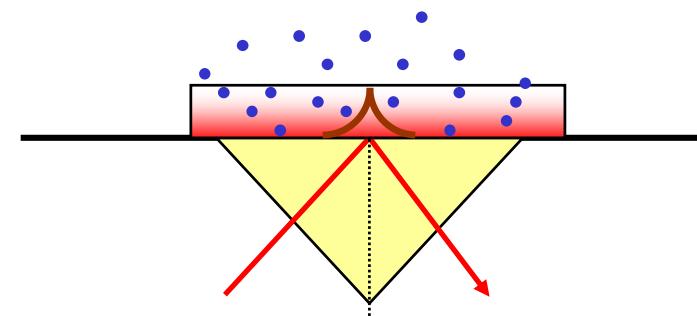
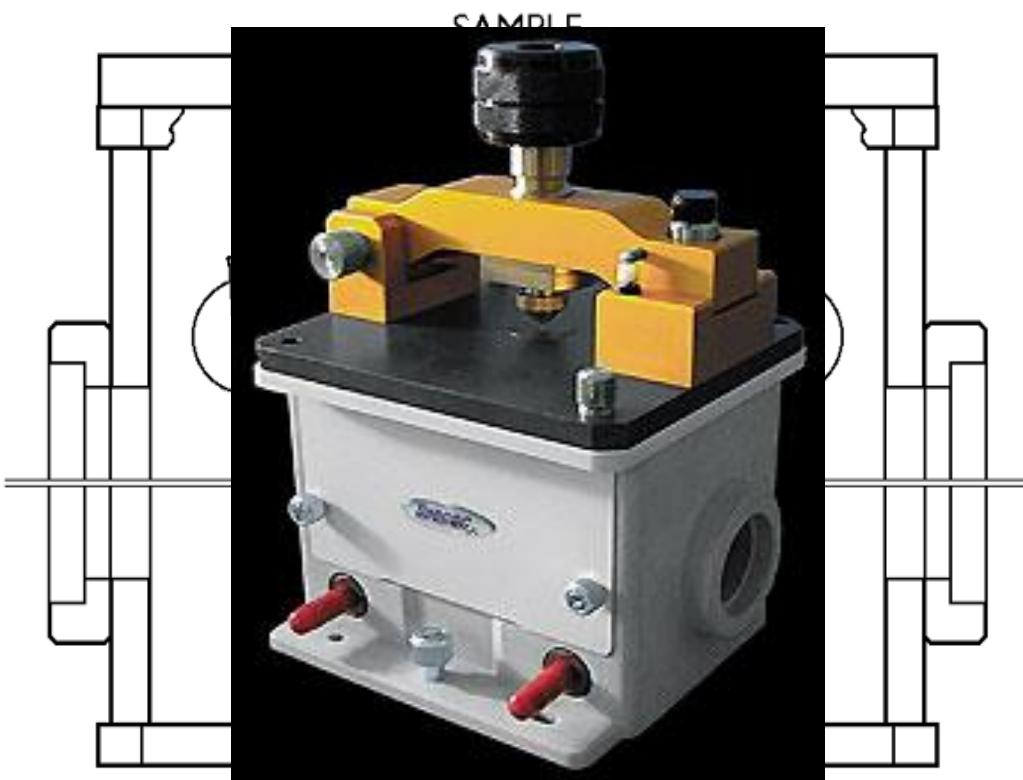


**Partitioning of solutes with relevance to separation;
Extraction and impregnation; drying and dyeing.**

High-Pressure ATR-IR Cell for Supercritical Fluids Studies



Golden opportunity in infrared to study polymers under pressure



ATR- IR spectroscopy

$$d_p = \frac{\lambda}{2\pi \cdot n_1 \cdot \left[\sin^2(\theta) - \left(\frac{n_2}{n_1} \right)^2 \right]^{0.5}}$$

$$d_p = 0.2 - 3 \mu\text{m}$$

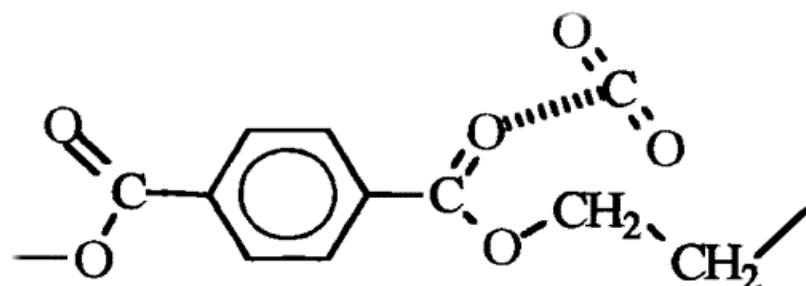
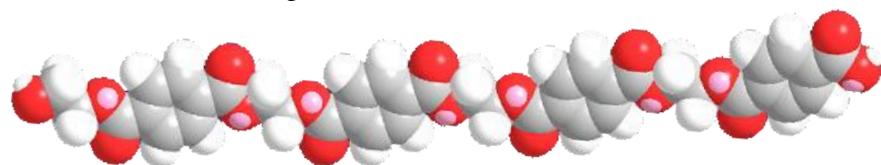
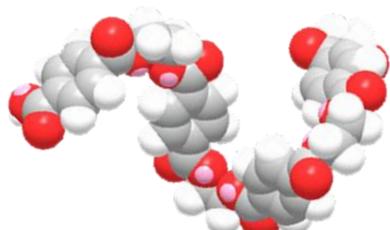
Golden Gate accessory (Specac, Ltd.)

Poly(ethylene terephthalate) (PET)

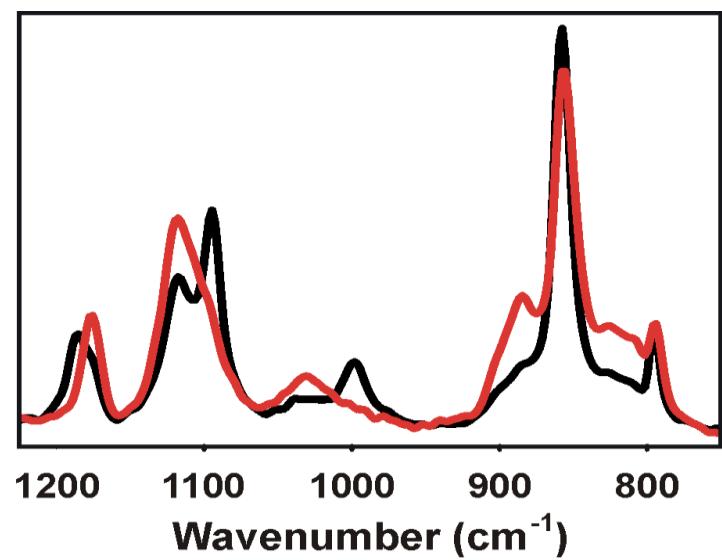
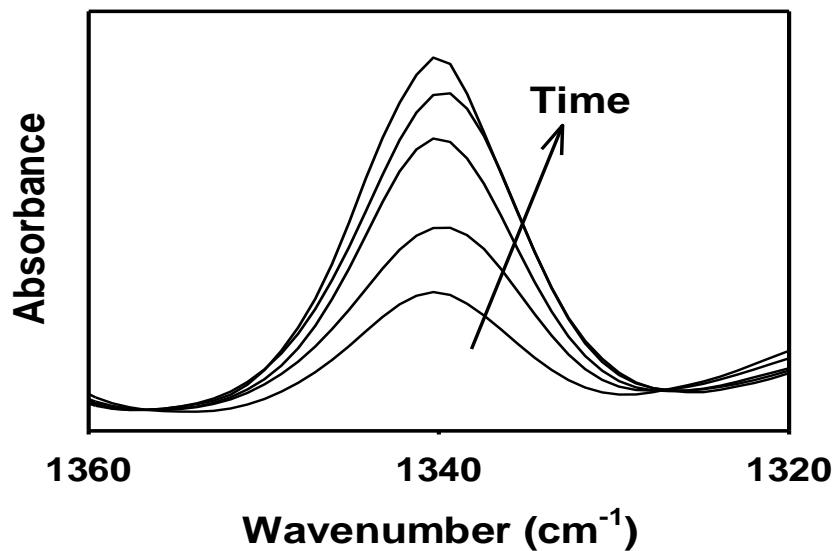
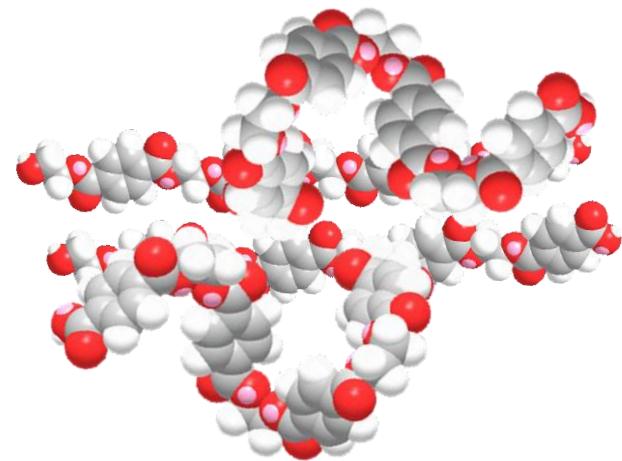
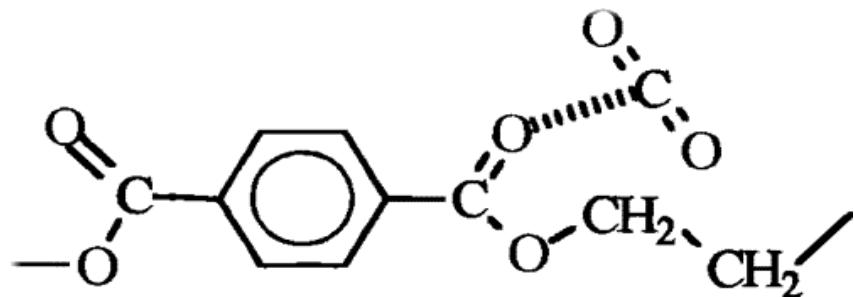
- Significant commercial importance: films, fibres, and bottles.



- 3 possible morphologies: amorphous, ordered amorphous, and crystalline

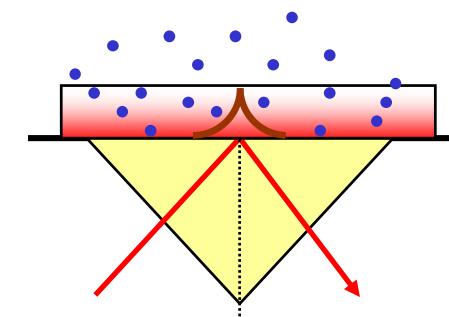
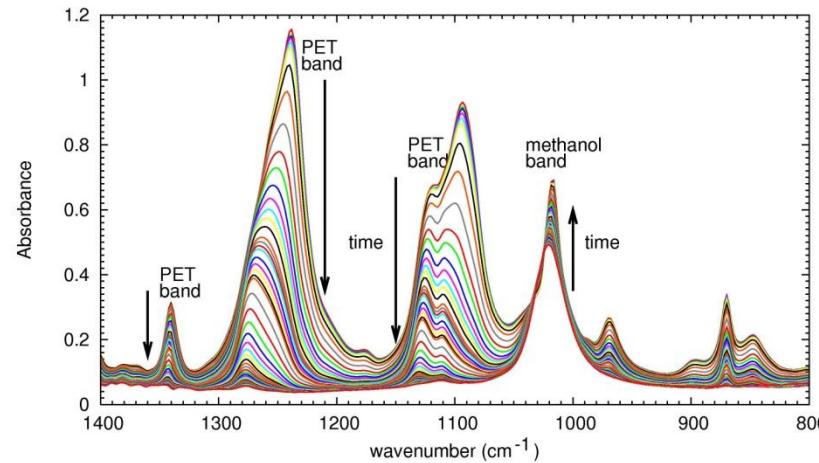


CO_2 -induced crystallisation of PET



Infrared spectra of PET under high-pressure CO_2

Decomposition of PET under near-critical water or high-temperature methanol

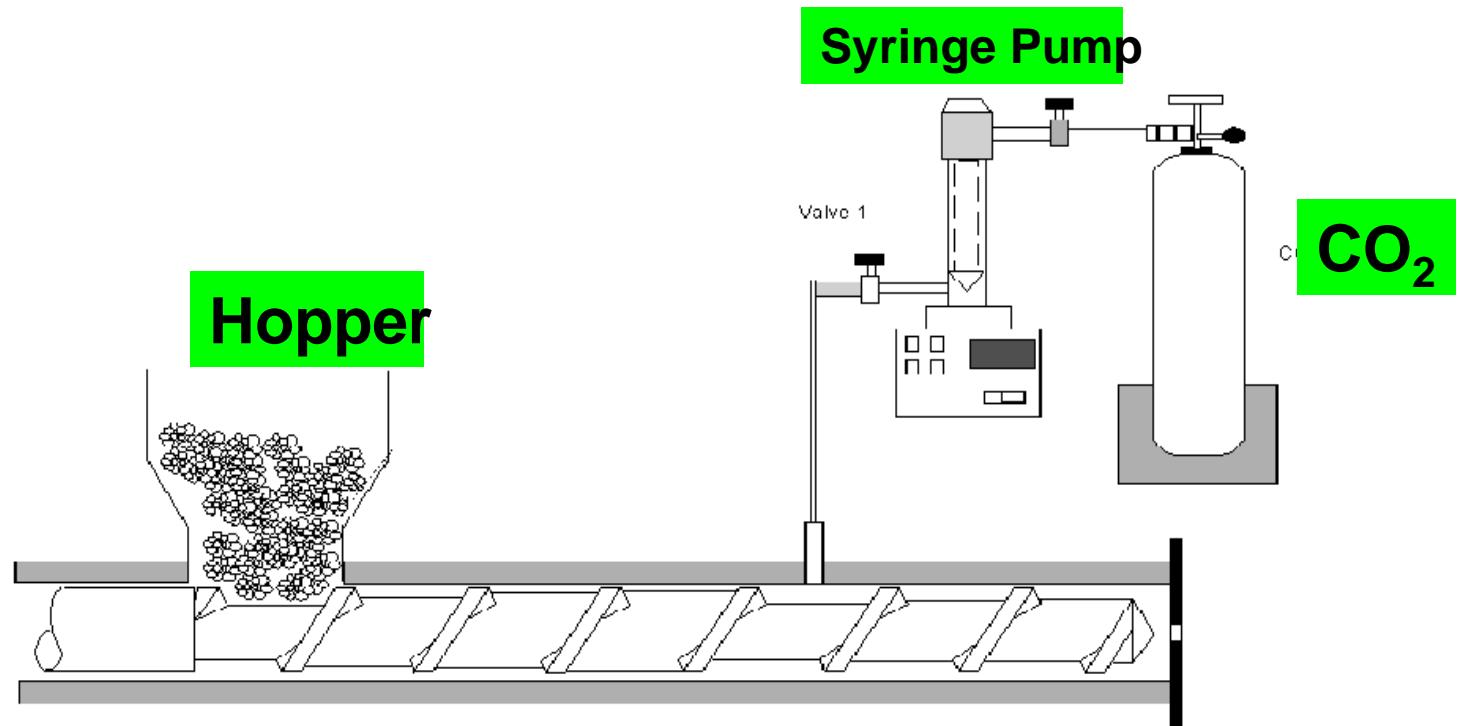


Macromol. Symp. 265, (2008) 195-204.

POLYMER PROCESSING

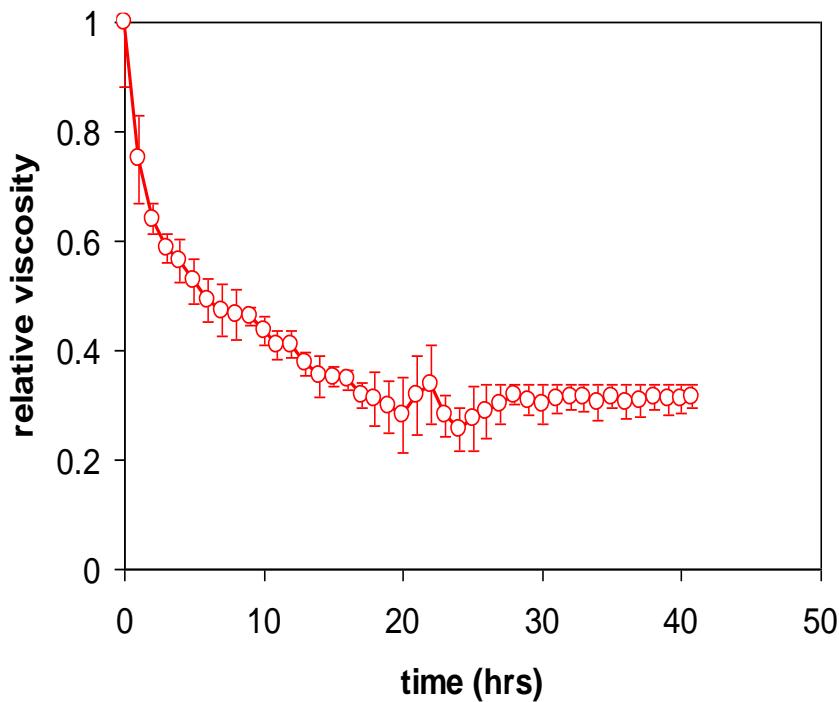
- Melt extrusion and high shear forces are necessary for thermoplastics processing
- These conditions limit the choice of the processing systems
- Conventional processing of thermolabile polymers produces significant waste
- Polymer processing with scCO₂ at lower temperatures can be advantageous

SUPERCritical CO₂- INDUCED POLYMER VISCOSITY REDUCTION

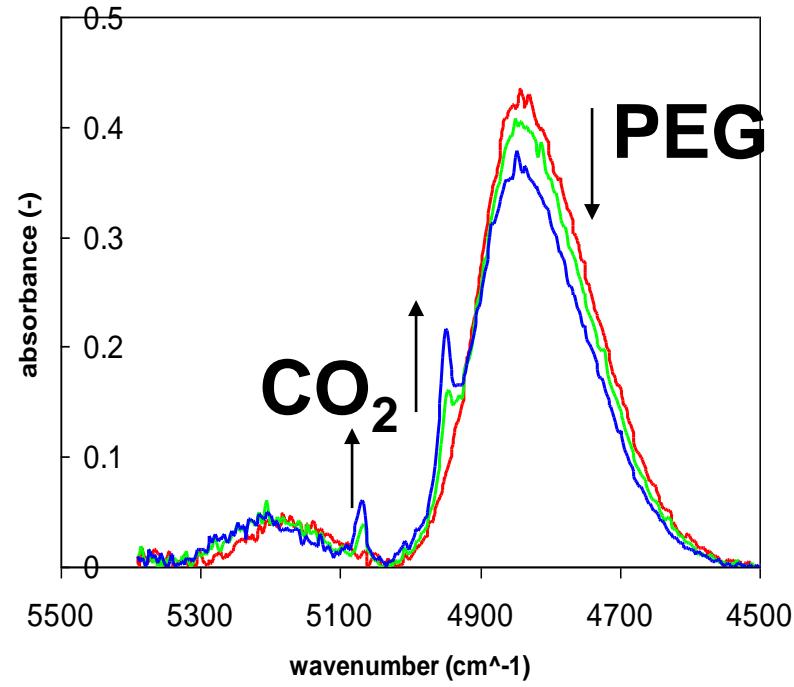


Extruder and scCO₂ Injection System

Combining Rheology and Spectroscopy: Supercritical CO₂ and Poly(ethylene glycol)



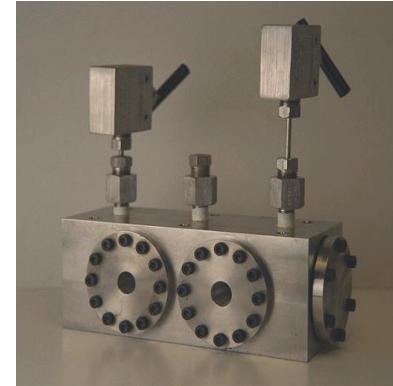
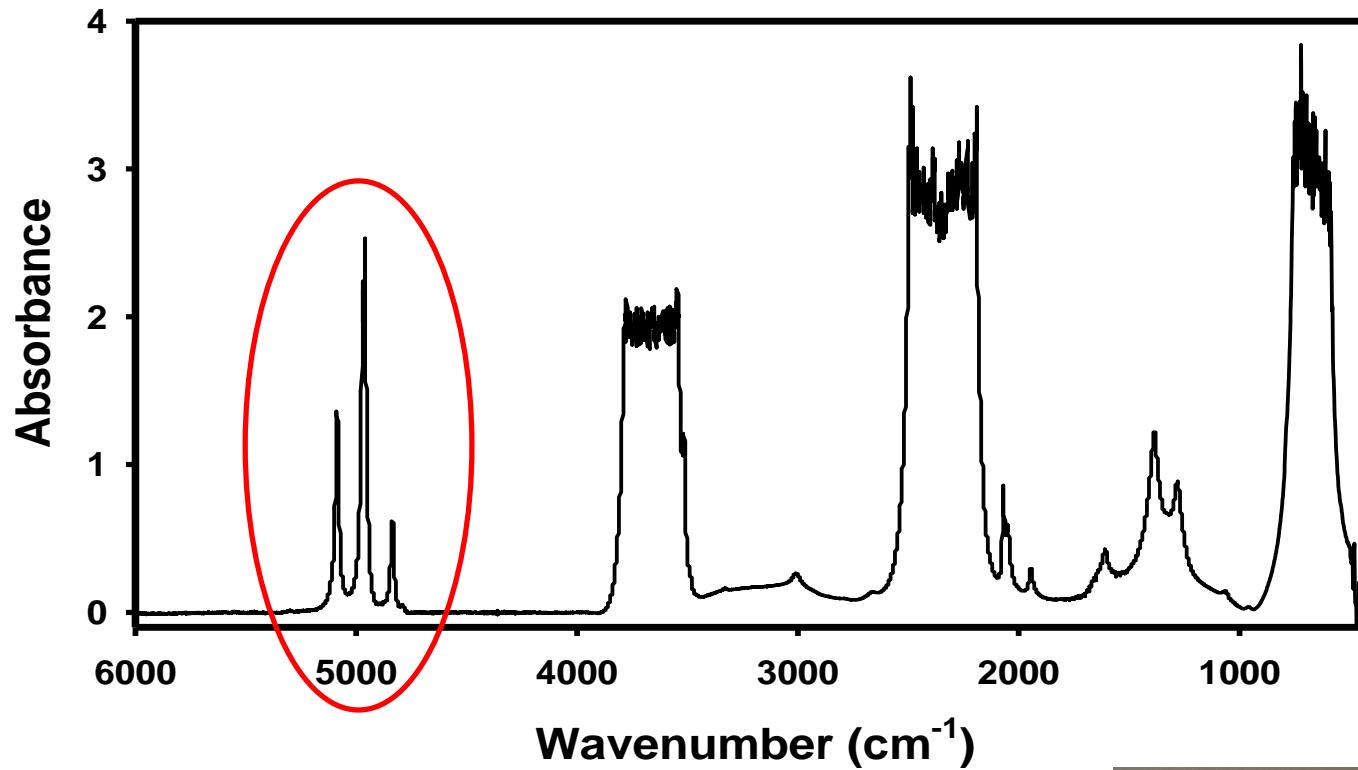
Viscosity reduction



IR spectra of PEG and CO₂

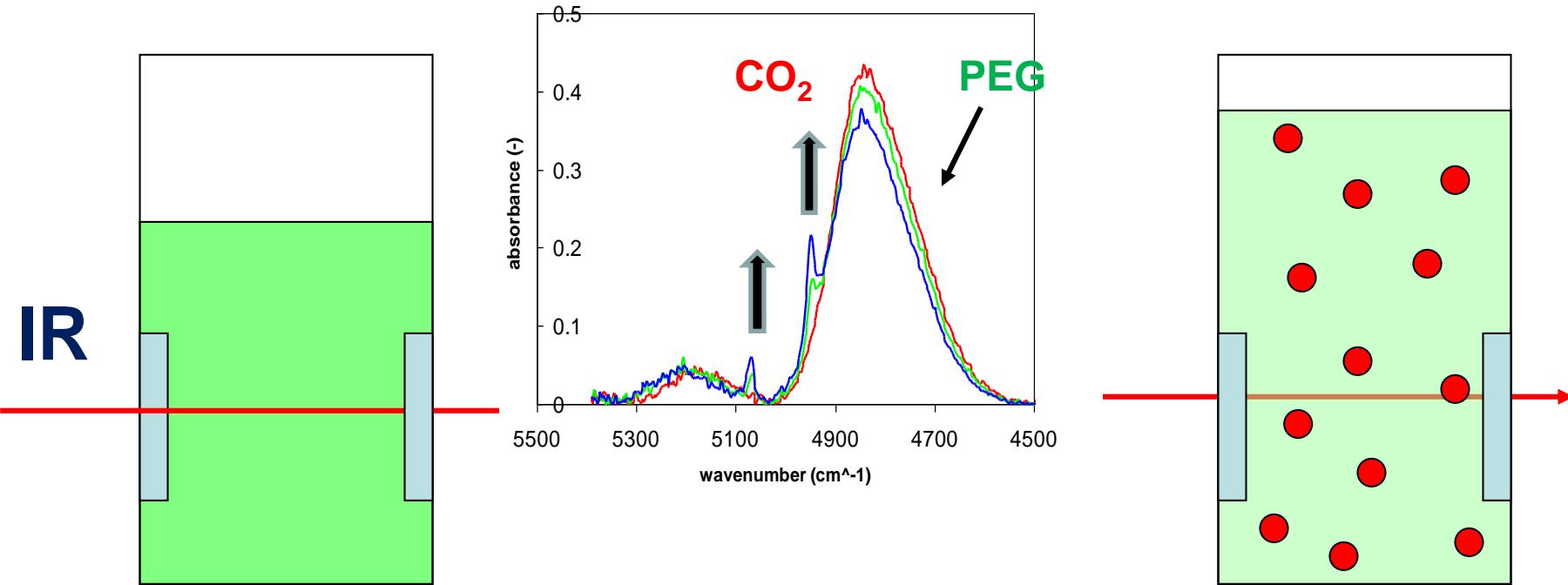
IR Spectrum of scCO₂

174 bar and 50 °C



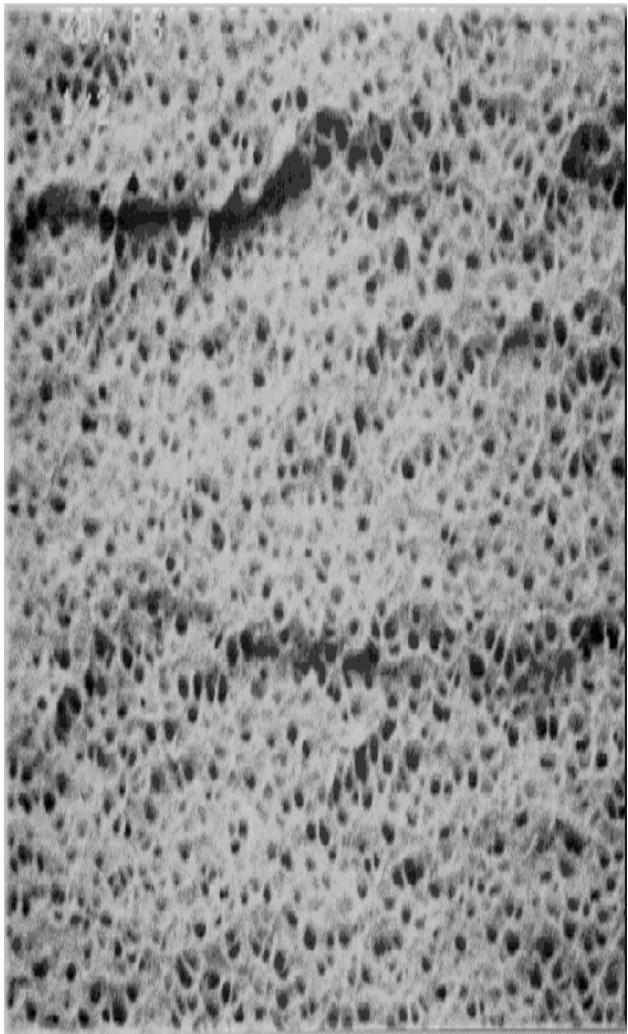
In Situ Spectroscopic Measurement of CO_2 Sorption and liquid PEG Swelling

Guadagno T., Kazarian S. G. *J. Phys. Chem. B* 108 (2004) 13995



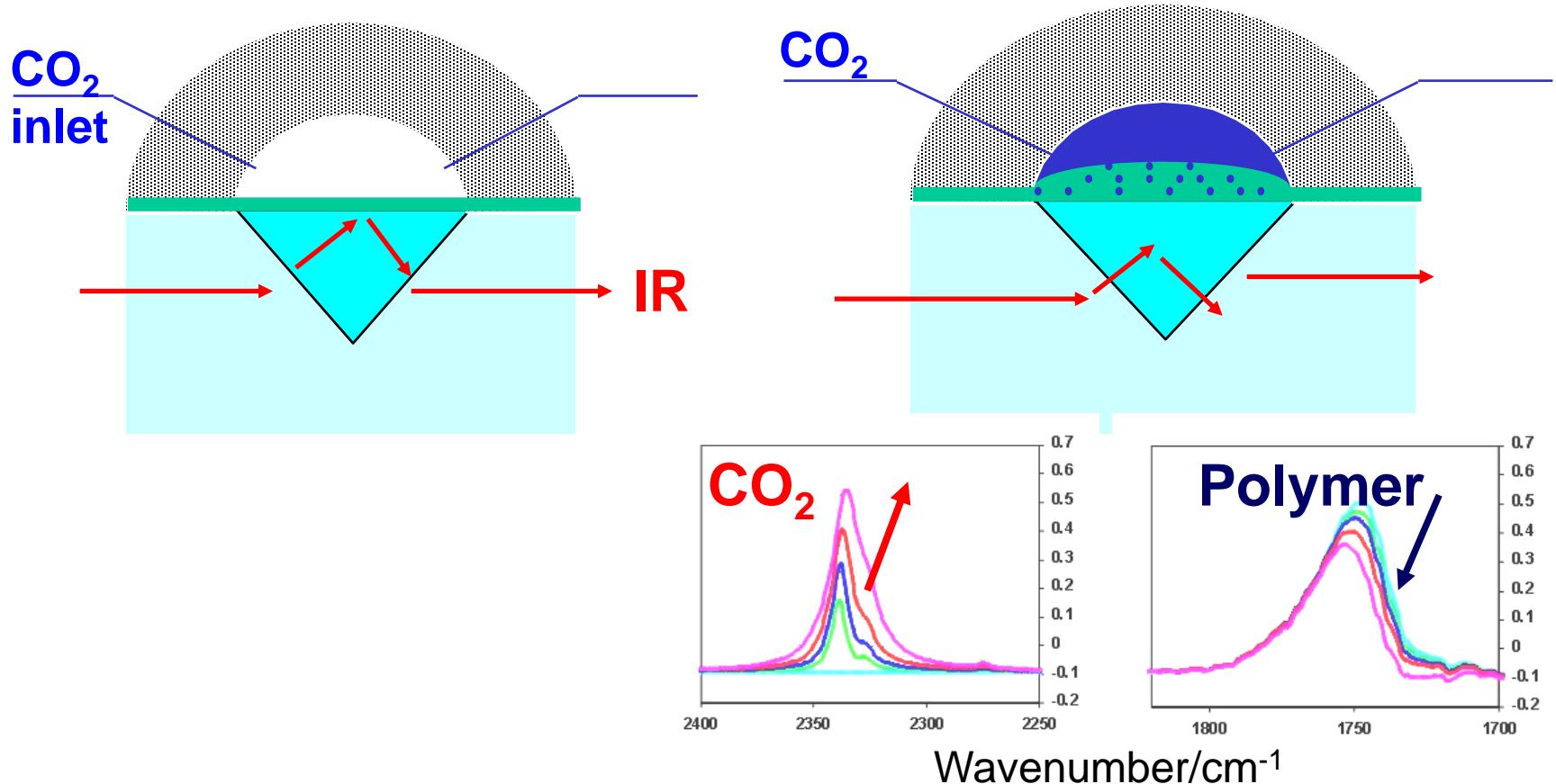
- IR bands of PEG provide changes in PEG density
- IR bands of CO_2 provide CO_2 concentration

Supercritical CO₂-assisted Tissue Engineering



- foams of biodegradable polymer
- poly(lactide-co-glycolide)
- scaffolds for liver, cartilage, bone
- drug/polymer formulations
- scCO₂ offers advantages
 - tuning porosity or pore size
 - CO₂ solubility and polymer swelling needs to be measured

How do polymers behave under pressure?



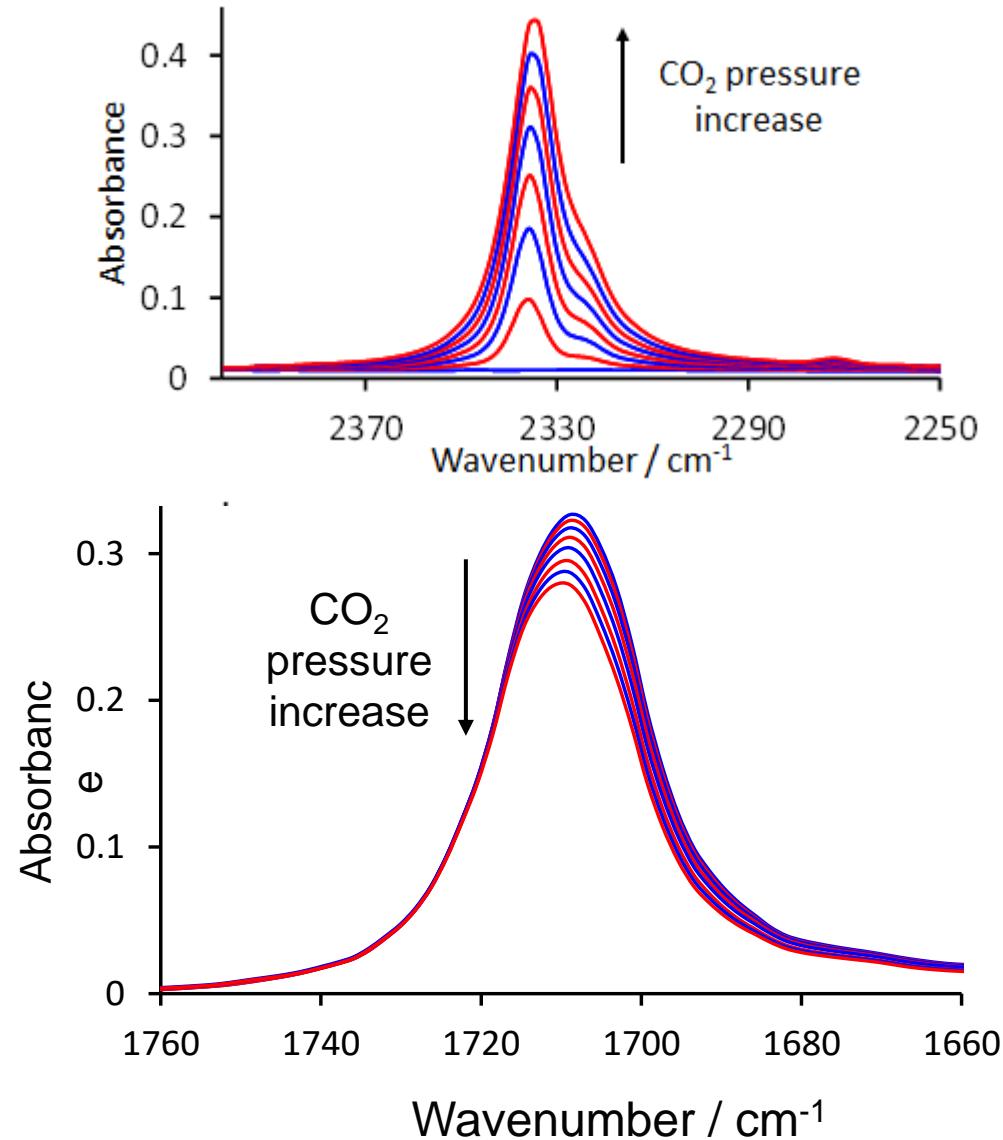
The absorbance of IR bands of CO_2 polymer → sorption
polymer → swelling

Effect of Pressure on CO₂ Sorption and Polymer Swelling

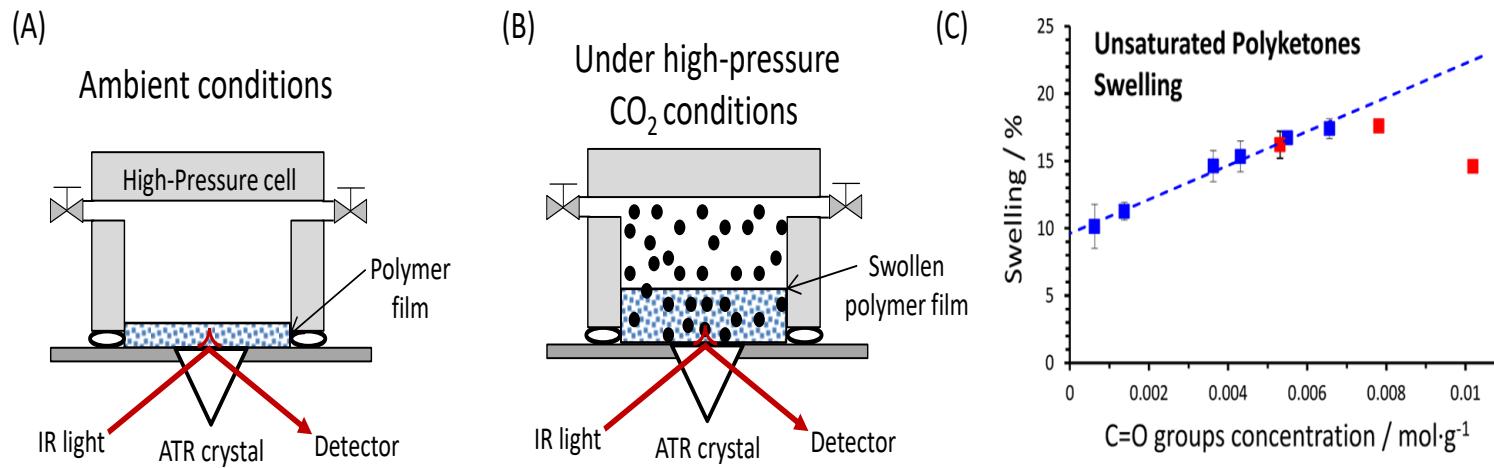
- As pressure is increased the absorbance of the CO₂ bands increases. Height of the band is used to quantify CO₂ sorption into the polymers
- As pressure is increased the absorbance of the polymer bands decreases
- Absorbance of the band is used to determine polymer swelling

$$\text{Swelling} = \frac{A^0}{A} - 1$$

- $\nu(\text{C=O})$ polymer band at 1710 cm⁻¹ was used to calculate swelling



In situ ATR-FTIR of polymer swelling under high-pressure CO₂



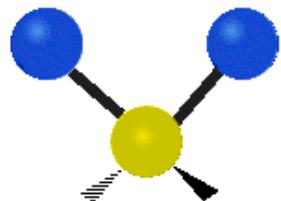
- Current trends and opportunities for the applications of in situ vibrational spectroscopy to investigate the supercritical fluid processing of polymers
A.V.Ewing and S. G.Kazarian Journal of Supercritical fluids (2018) 134, 89-96.
<https://doi.org/10.1016/j.supflu.2017.12.011>

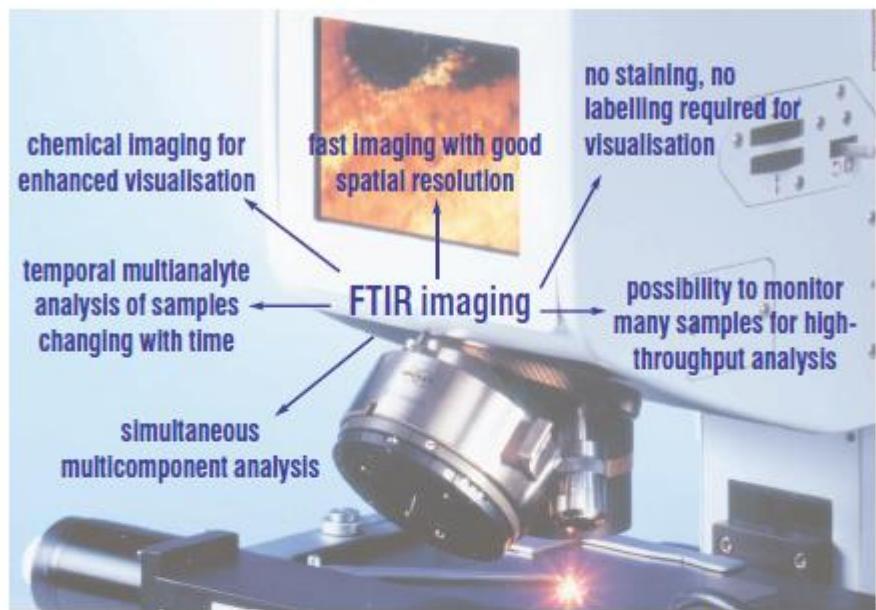
Vibrational Spectroscopy for Product Characterisation

- Infrared (FTIR) spectroscopy
- Applications of ATR FTIR spectroscopy
- Raman spectroscopy
- Applications to polymeric materials and pharmaceutical samples
- FTIR spectroscopic imaging

Thank you!

Questions?





A closer look at polymers

FTIR imaging is emerging as a powerful technique for analysing polymer mixtures. By providing simultaneous chemical and spatial information, heterogeneous polymeric materials can be characterised easily. *Sergei Kazarian & Julia Higgins explain.*

In Brief

- Optimum blends achieved through process visualisation with FTIR microscopy
- Produces a spatial distribution map and no staining is needed
- Applications include medicine, engineering, pharmaceuticals and materials science
- Exhibits generality, specificity and sensitivity

Blends of different polymers are often explored in the search for polymeric materials with desirable properties. A recently emerged technology, Fourier-transform infrared (FTIR) imaging, provides a new and powerful method to characterise these blends.

FTIR imaging can be used to analyse multilayer polymer films, polymer-drug formulations, composite materials and polymeric fibres. In many cases, these materials are mixtures.

By mixing a relatively expensive polymer with an inexpensive one, the

overall cost of the product can be significantly reduced. Mixing might also result in a material with new mechanical properties, when, for example, a glassy and a rubbery polymer are mixed. The properties of polymer blends can be tuned by changing the ratio of the components. However, properties largely depend on mixing efficiency. Adding a compatibiliser can improve mixing by reducing interfacial tension between the polymer phases. Compatibilisers can also help to achieve better dispersion and im-

This article is available on the BB

Please also look at the web-site of my research group for further information on FTIR imaging:
www.imperial.ac.uk/vsci

“FTIR imaging is set to find broad applications in forensic, materials colloid science, engineering and pharmaceuticals” S. Kazarian

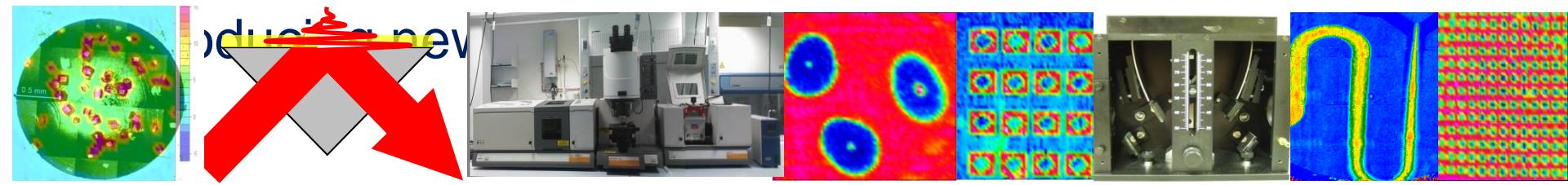
IR spectroscopy is “most nearly universal chemical spectroscopy. As a structural tool, its generality, sensitivity and specificity are hard to match” Richard Palmer

New Opportunities with FT-IR Imaging

- What is FT-IR Imaging?
- Micro and macro ATR-FTIR imaging
- Spatial resolution we can achieved
- Imaging of polymer blends
- Imaging of hair and biomedical samples
- Drug release and tablet compaction
- In situ imaging with a diamond ATR
- FTIR imaging in transmission and refraction
- ATR imaging with variable angle of incidence
- Solving problems for industry

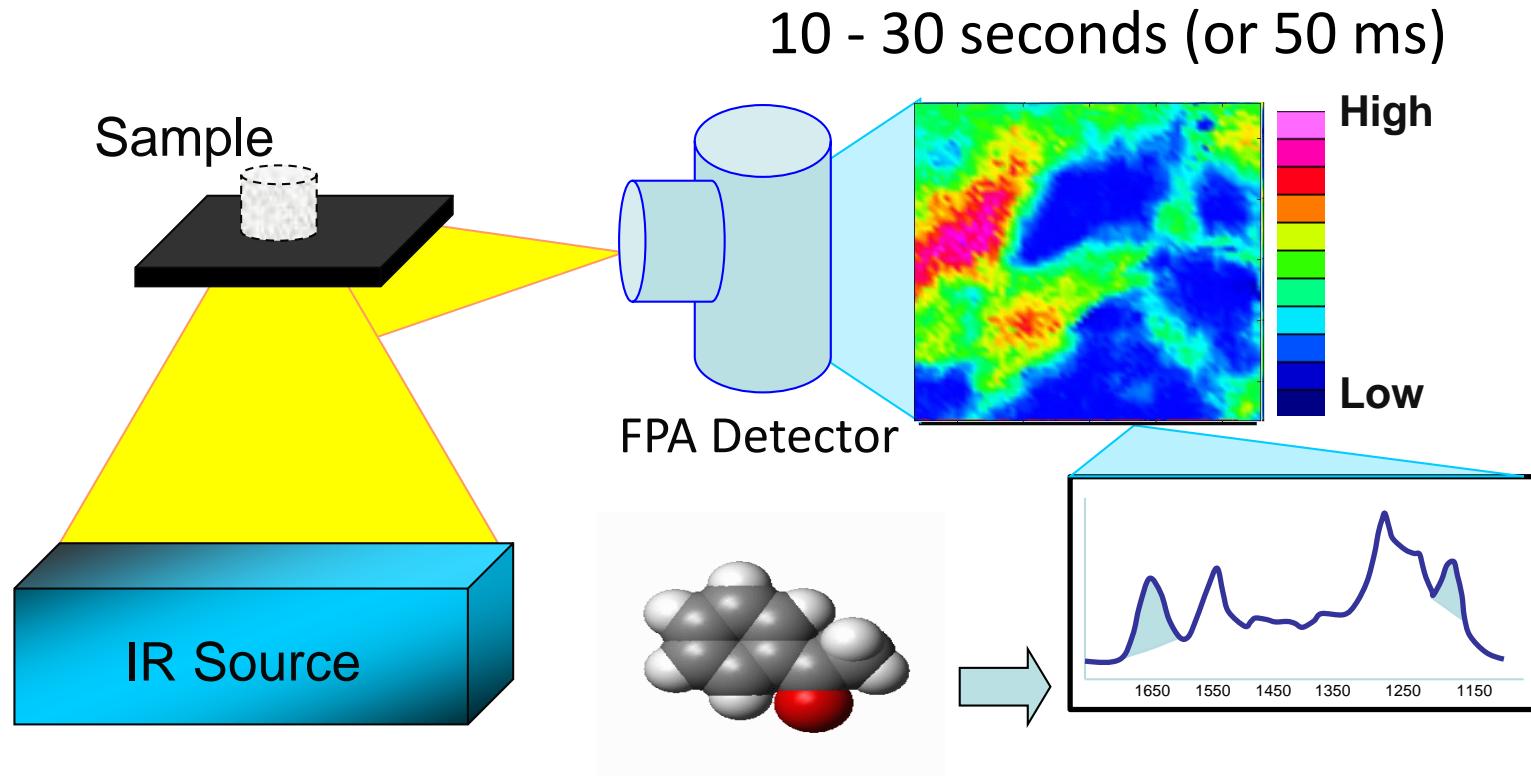
Solving problems for products in industry using FTIR spectroscopic imaging

- Release of drugs from tablets and formulations: (AbbVie, BMS, Pfizer, GSK, Daiichi Sankyo) (problems in tablet dissolution)
- Studies interactions of formulations with hair (Unilever)
- Understanding crude oil fouling (BP)
- Studies of latex film drying (BASF) (optimisation paint drying)
- Purification of antibodies (BMS and GSK)
- Imaging of micro-formulations in microfluidic flows



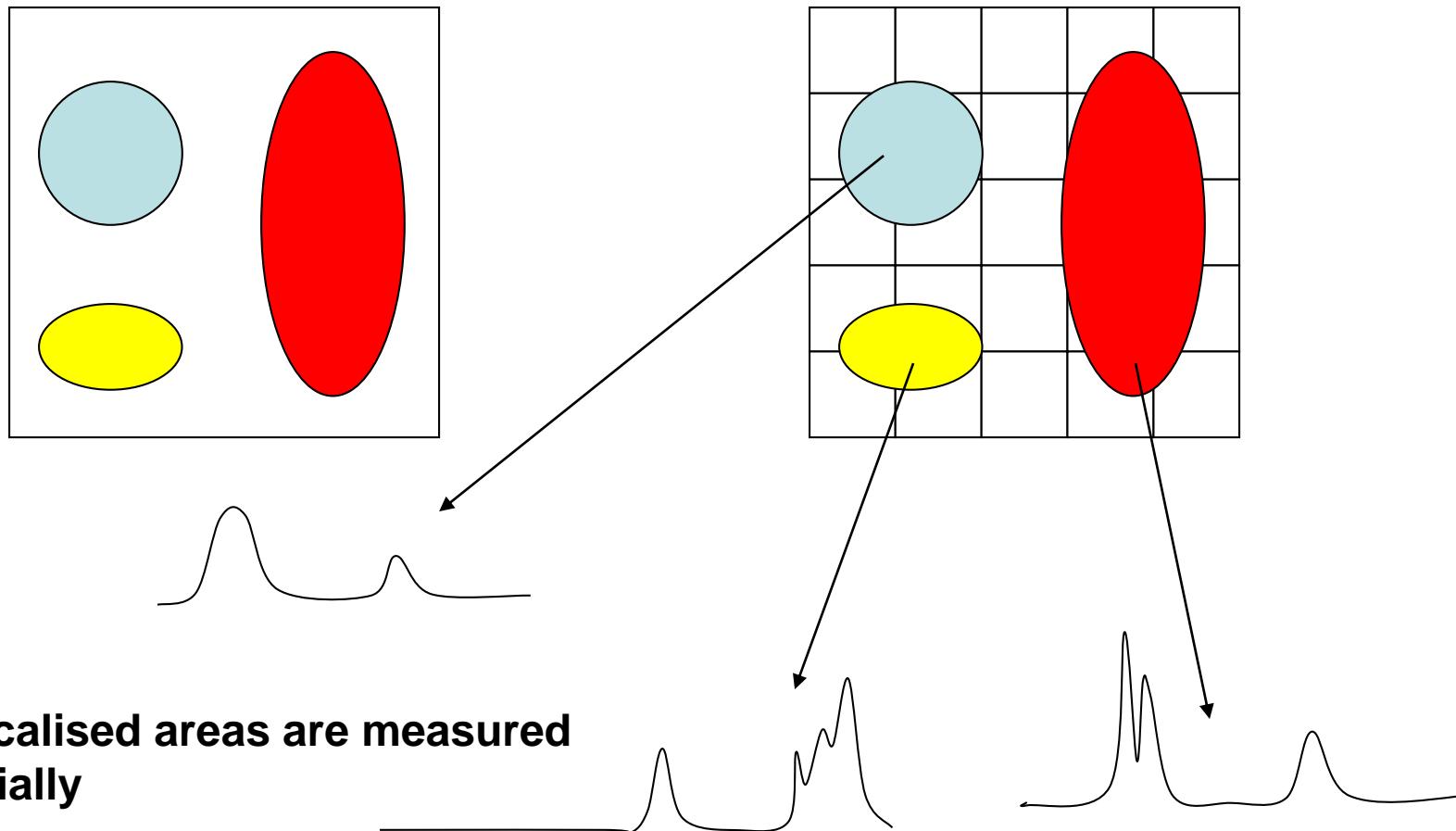
Chemical imaging with IR spectroscopy

Chemical photography: one image is worth a thousand spectra

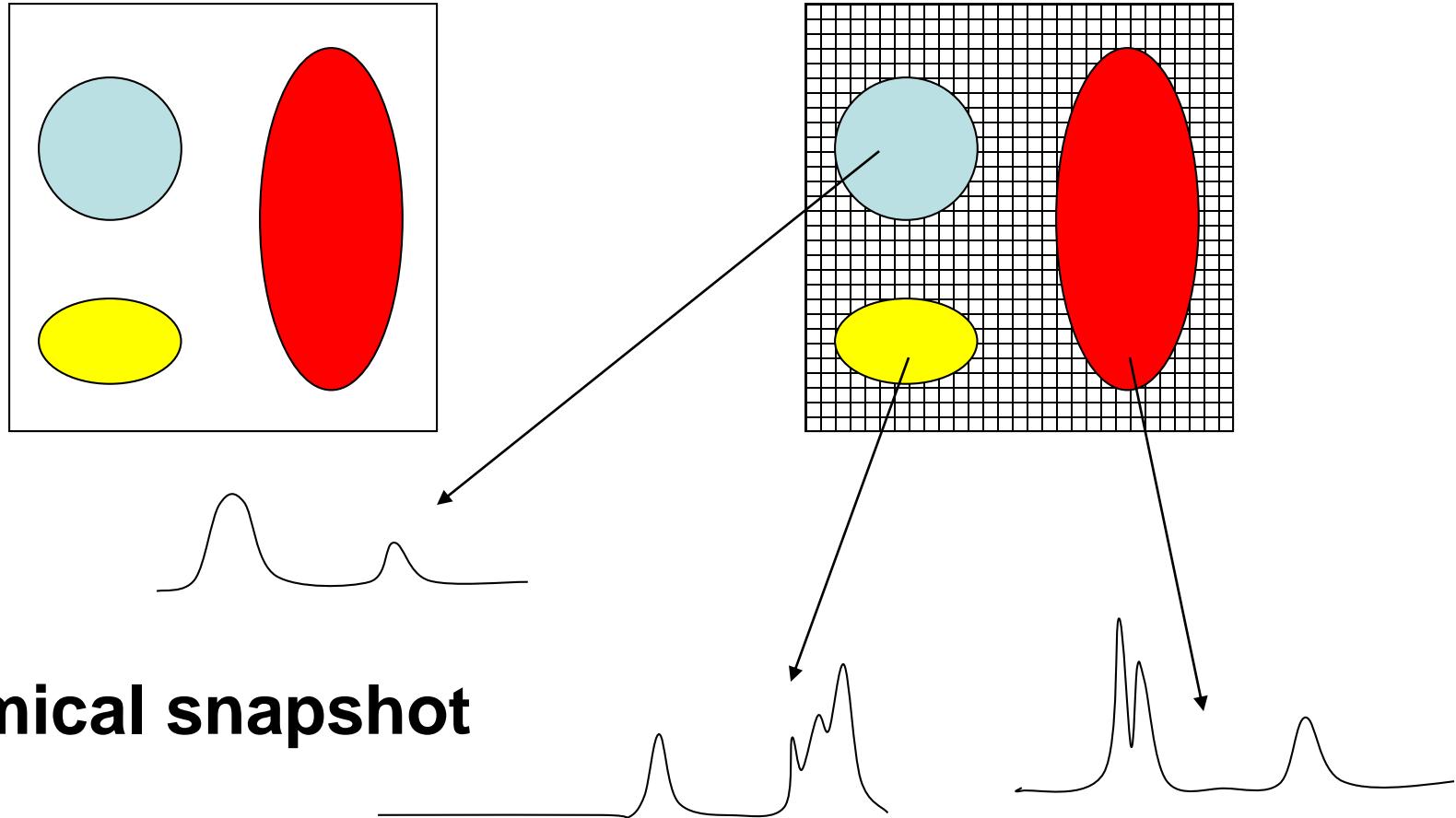


Combining FTIR spectrometer with an infrared array detector
(64 x 64 or 128 x 128 pixels)

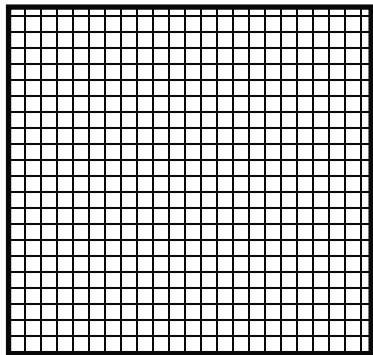
FT-IR microscopy via mapping-conventional approach (with a single element detector)



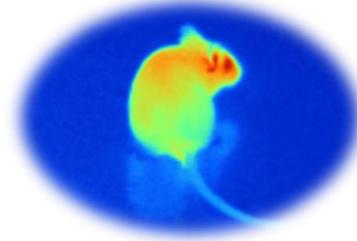
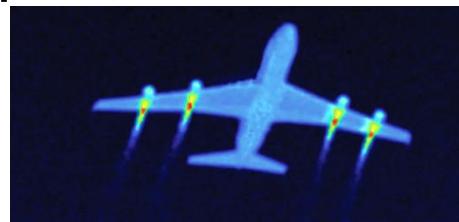
FT-IR Imaging with FPA (Focal Plane Array) Detector



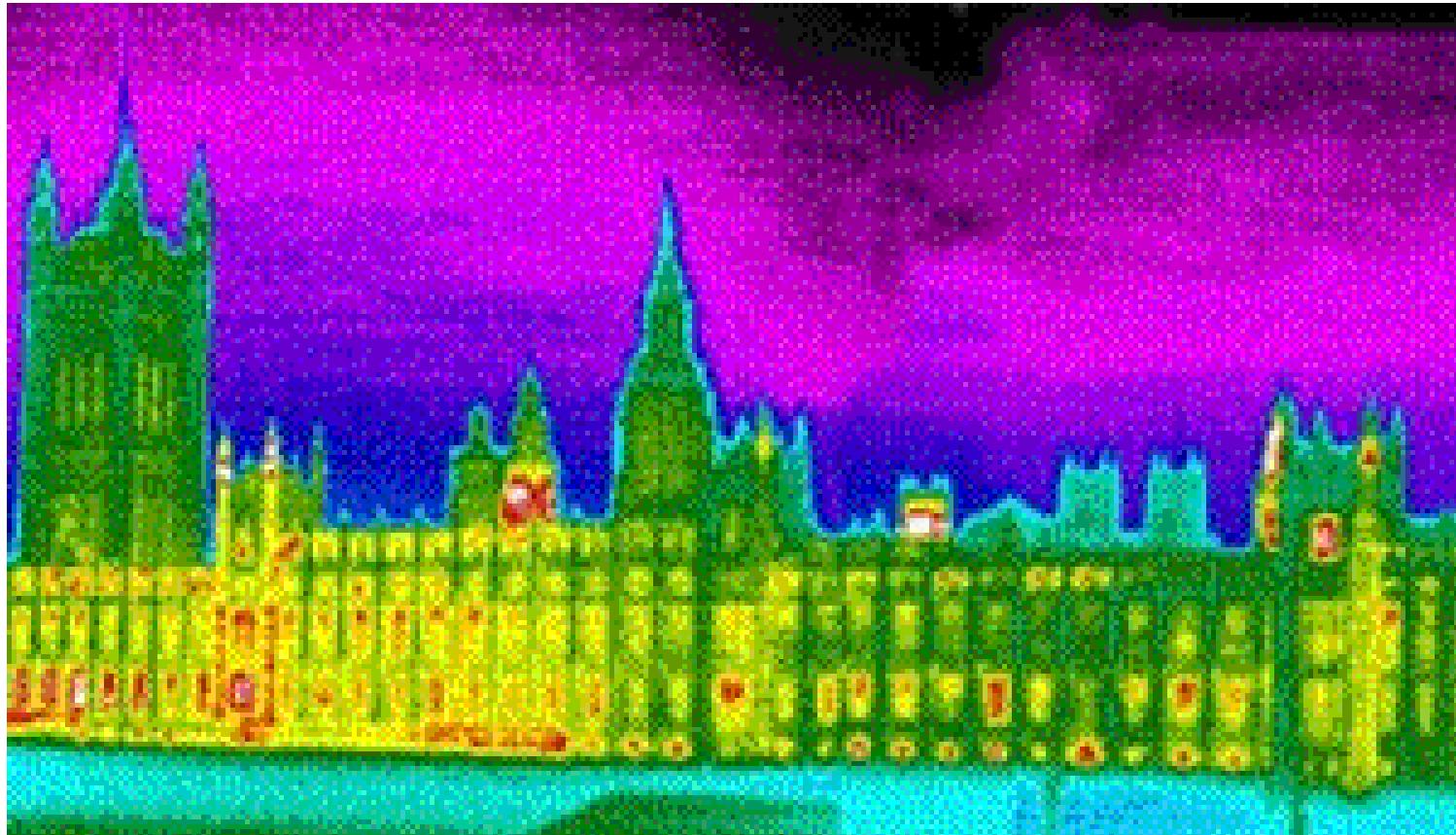
Seeing it in infrared light



IR array detector

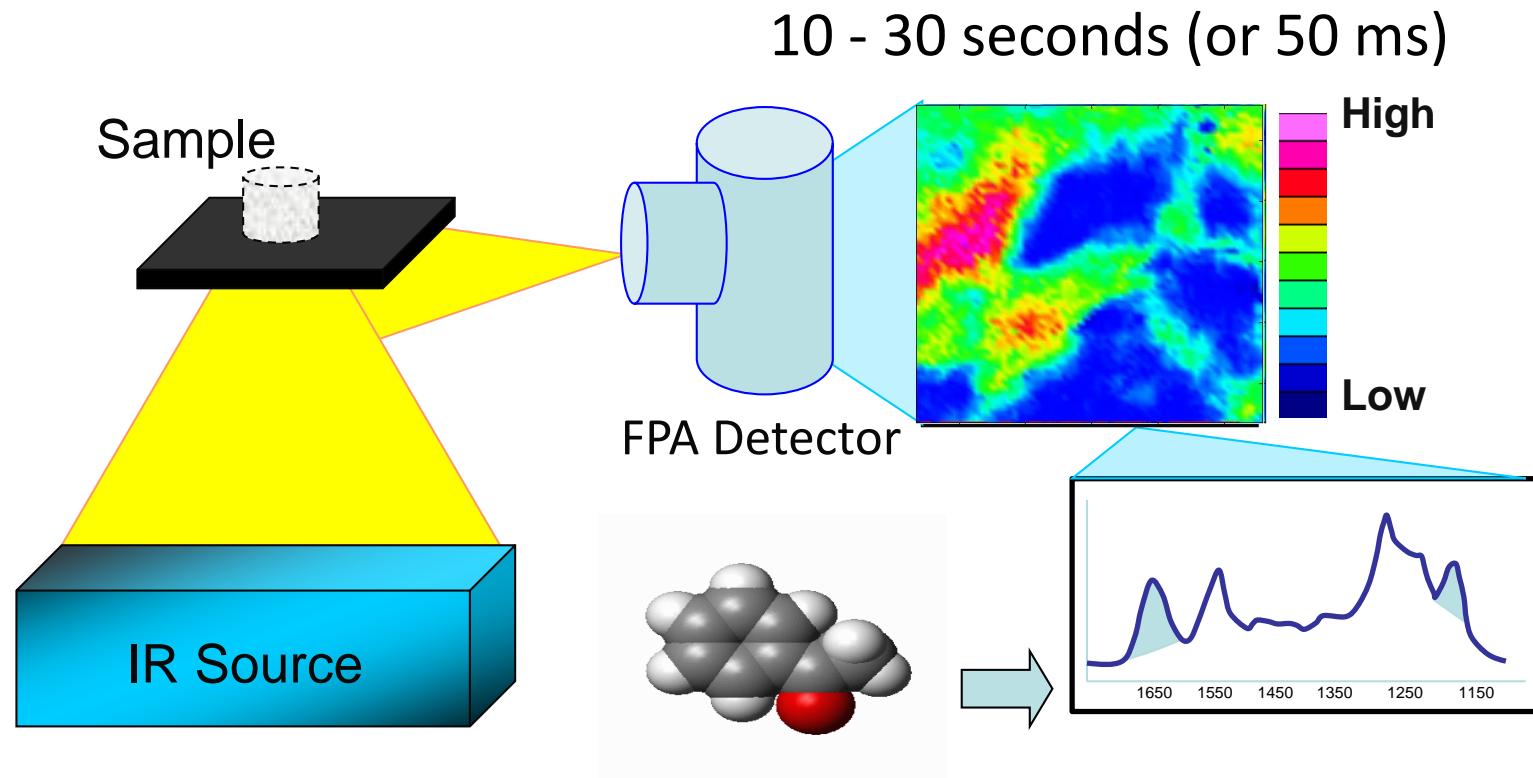


Infrared image of the Houses of Parliament



Chemical imaging with IR spectroscopy

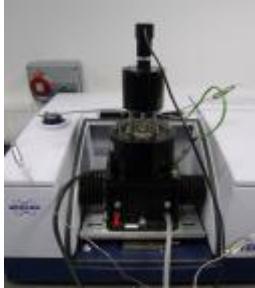
Chemical photography: one image is worth a thousand spectra



Combining FTIR spectrometer with an infrared array detector
(64 x 64 or 128 x 128 pixels)

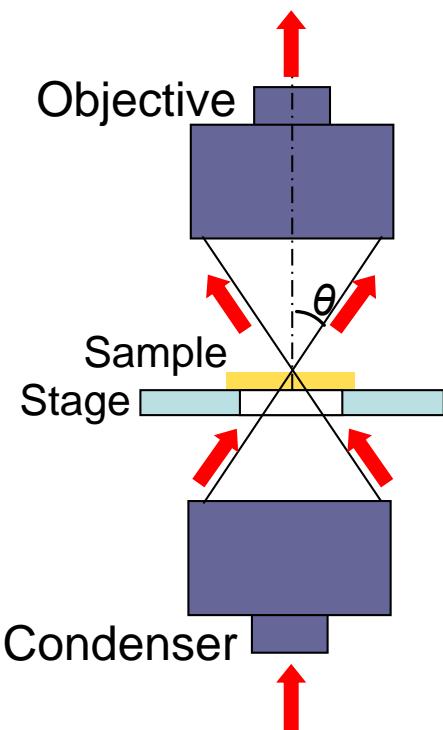
The FPA has a pixel size of 40 μm , spectral range 5000 - 950 cm⁻¹ and can be used also in the near IR by substituting the Ge window with a BaF₂ window

Advanced chemical imaging systems

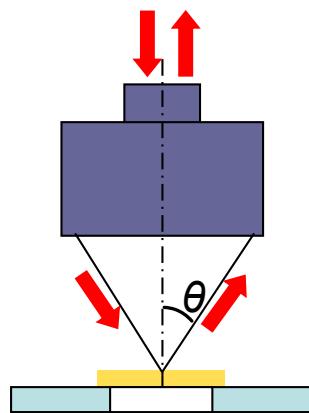


Common infrared microscopy sampling techniques

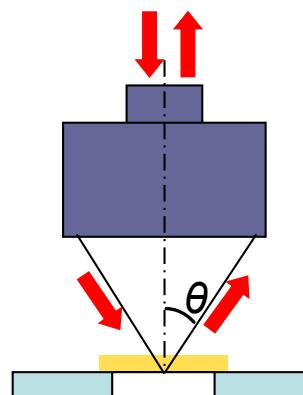
Transmission



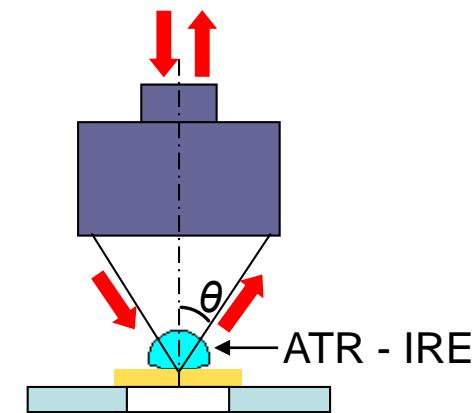
Reflectance



Absorption/
Reflectance



Micro - ATR



Sample thickness:
10 – 20 μm

Sample thickness:
NA

Sample thickness:
5 - 10 μm

Sample thickness:
NA

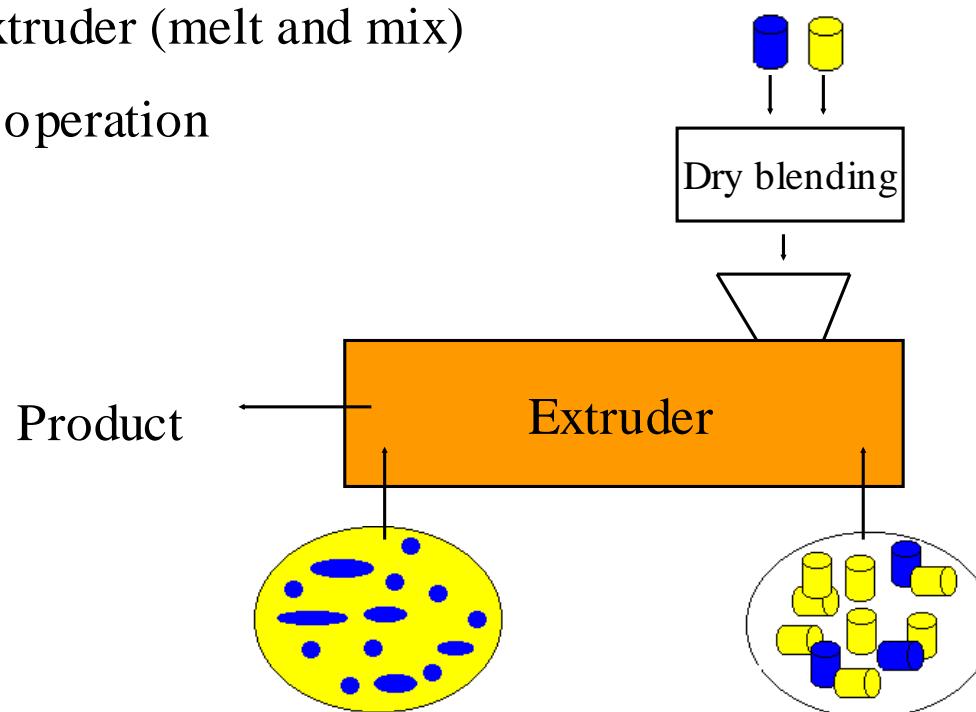
FTIR Imaging of Heterogeneous Materials and Products

- It is possible to engineer new materials by blending or mixing.
- The quality of the product in almost all polymer processes depends in part on how well the material was mixed.
- Better understanding of mixing process helps to optimise its conditions and increase the quality of the final product

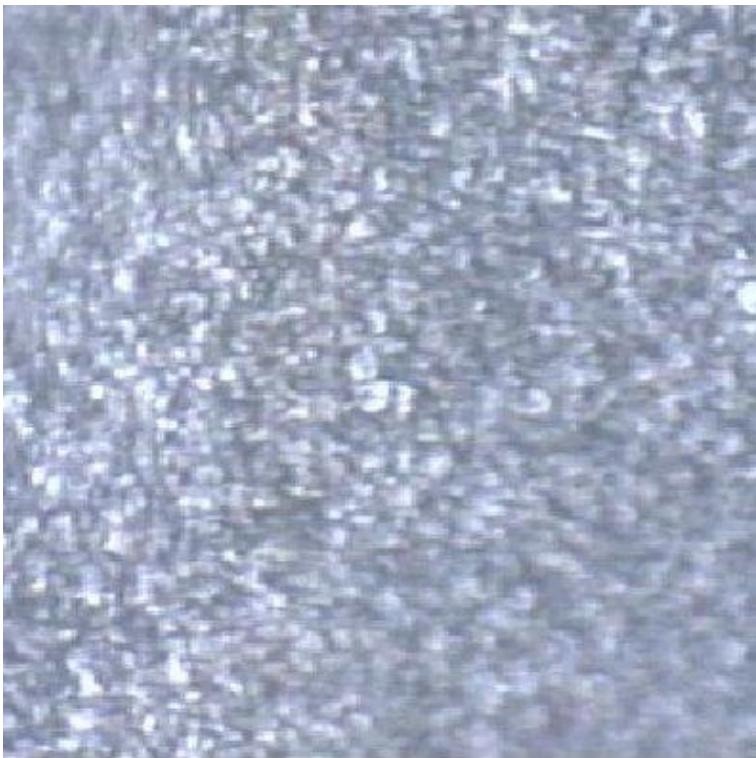
Mixing Polystyrene and Polyethylene: an example of first applications of FTIR imaging

What is the blender or mixer?

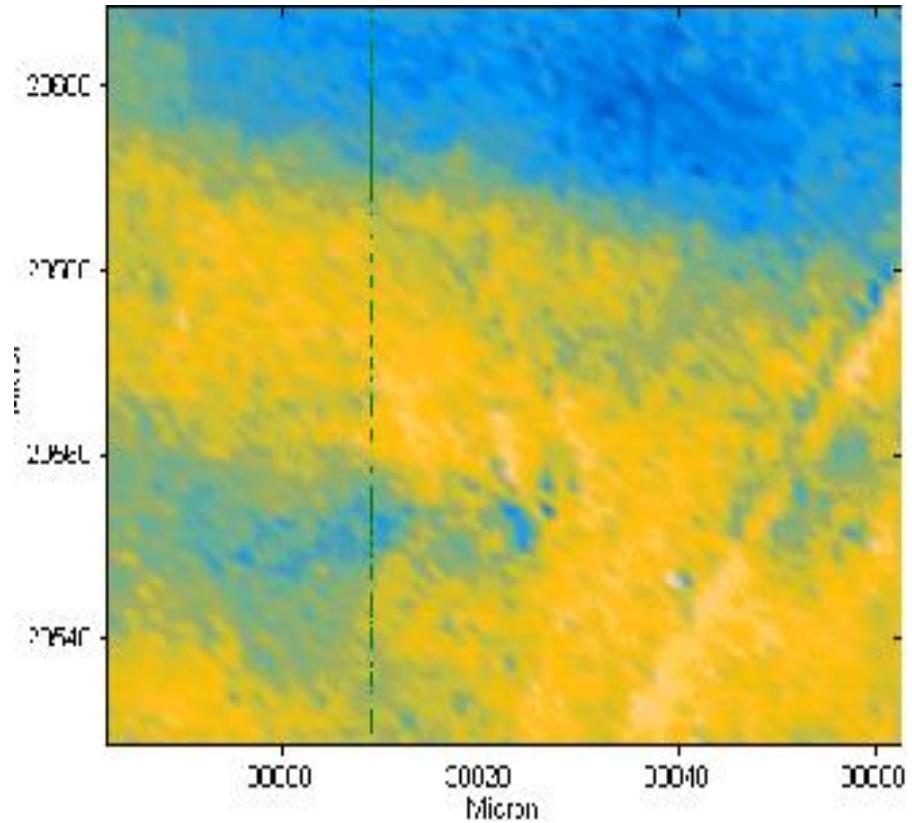
- Twin-screw Extruder (melt and mix)
- Continuous operation



FT-IR Imaging of PS/LDPE blend - no compatibilizer



Optical image



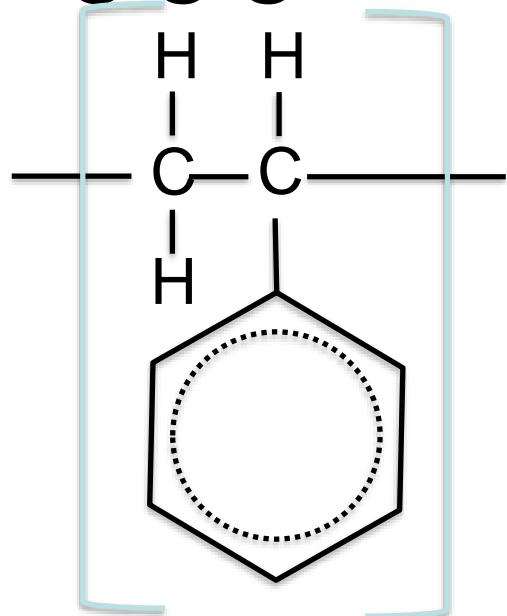
FTIR image

FTIR image was obtained by plotting absorbance of a spectral band of polystyrene as a function of all 4096 pixels in FPA array detector (area is $50 \times 50 \mu\text{m}^2$)

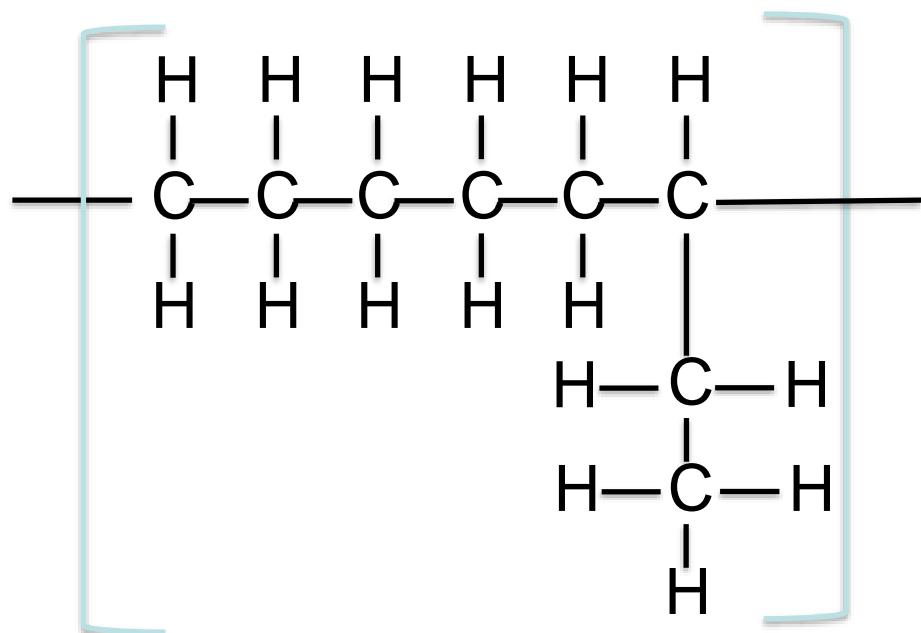
Tri-block copolymer (SEBS) compatibilizer for PS/LDPE polymer blends

-S-S-S-S-S-EB-EB-EB-EB-EB-S-S-S-

S-S-S-



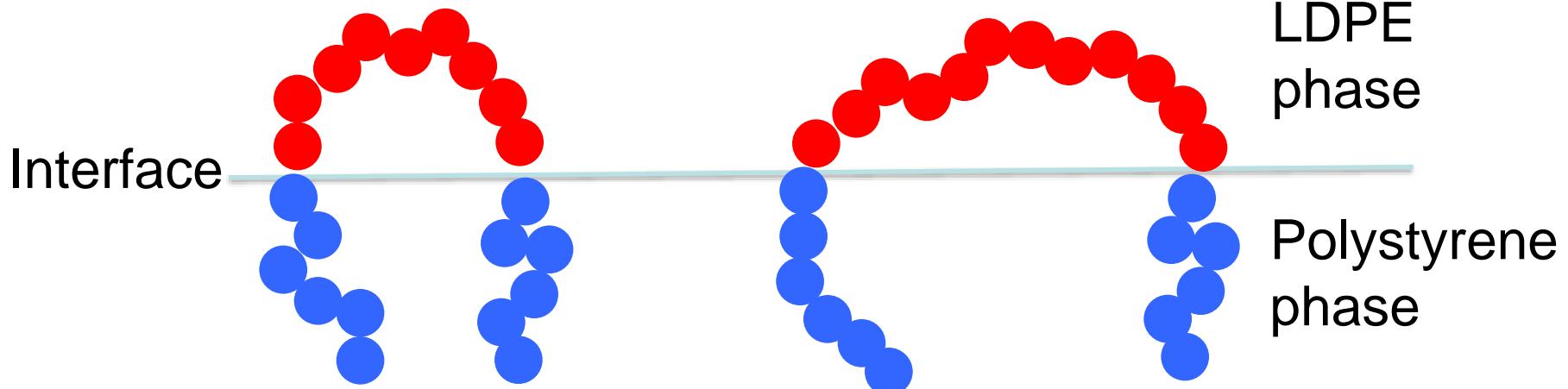
Polystyrene
(PS)



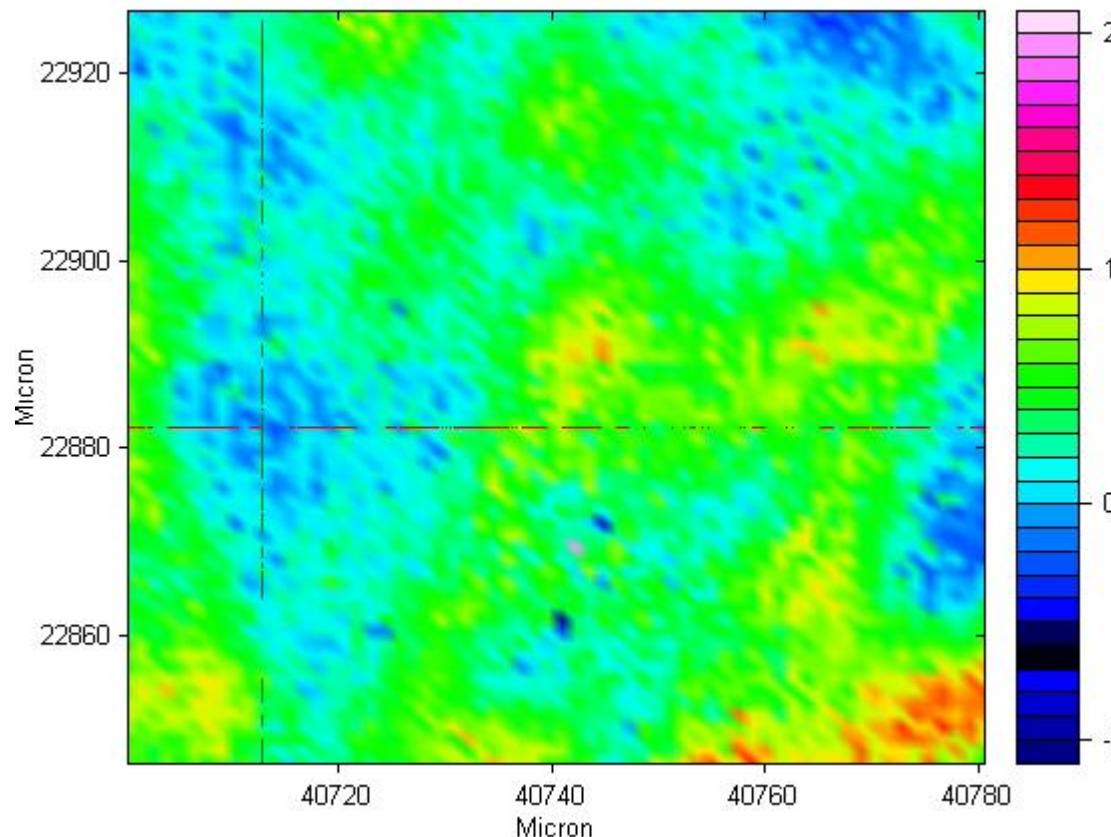
Poly(ethylene-butylene)
(PEB)

How does it work?

- Works as a surfactant (emulsifying effect)
 - Reduces interfacial tension (enhancing interfacial adhesion)
 - Stabilises morphology
- S-S-S-S-S-S-EB-EB-EB-EB-EB-EB-S-S-S-S-S-



FTIR Imaging of PS/LDPE blend - 5% of compatibilizer



FTIR image was obtained by plotting absorbance of a spectral band of polystyrene as a function of all 4096 pixels in FPA array detector

Polymer blends used in friction bearing PA/PTFE



Interesting Properties:

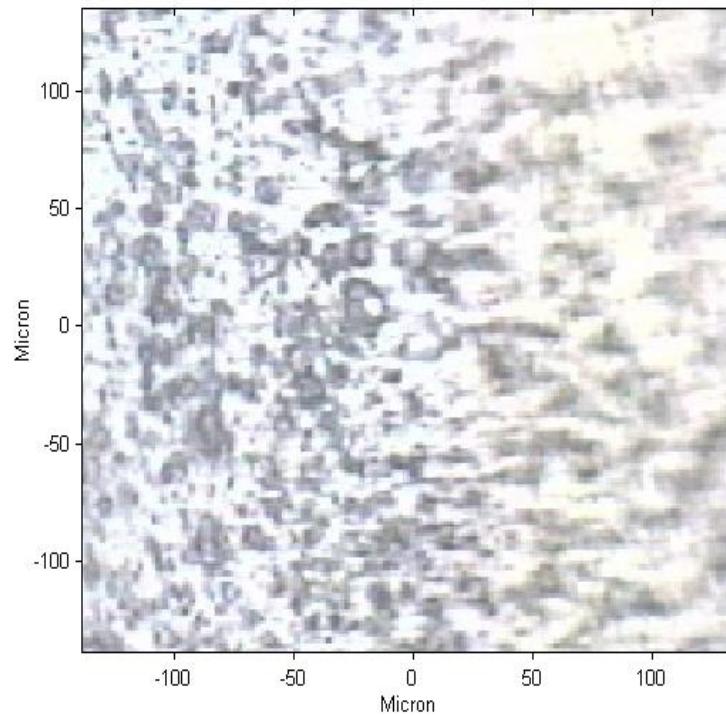
- low frictional resistance, lubricant-, wear- and maintenance-free bearings and hinges;
- combination of **PTFE** (excellent gliding properties, but expensive and hard to process) and **PA** (easy to process, strong, tough, resilient, resistant to oils, solvents, alkali).
- Compounding both materials means trying to combine fire and water!

Easy to analyze:

- Strong IR and Raman spectra (easy to distinguish)

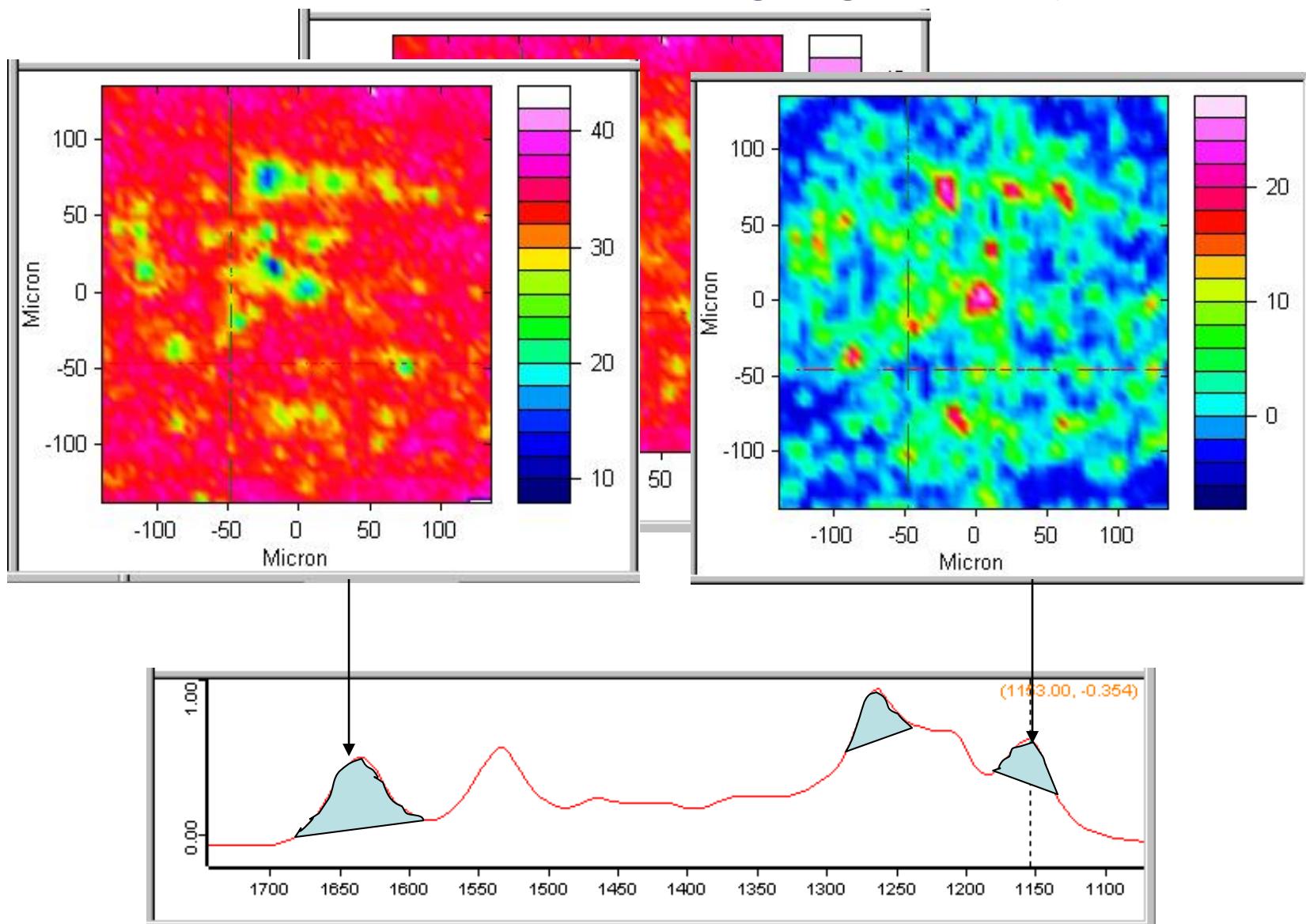
Polymer blend used in friction bearing

80% PA, 18% PTFE, 2% Silicon Oil



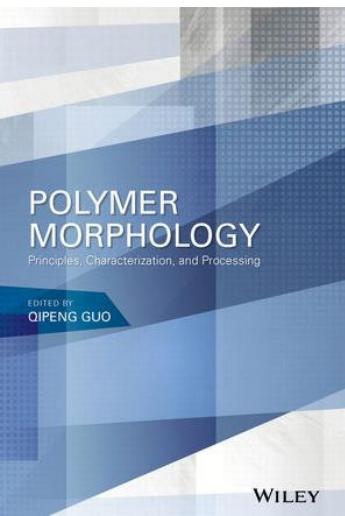
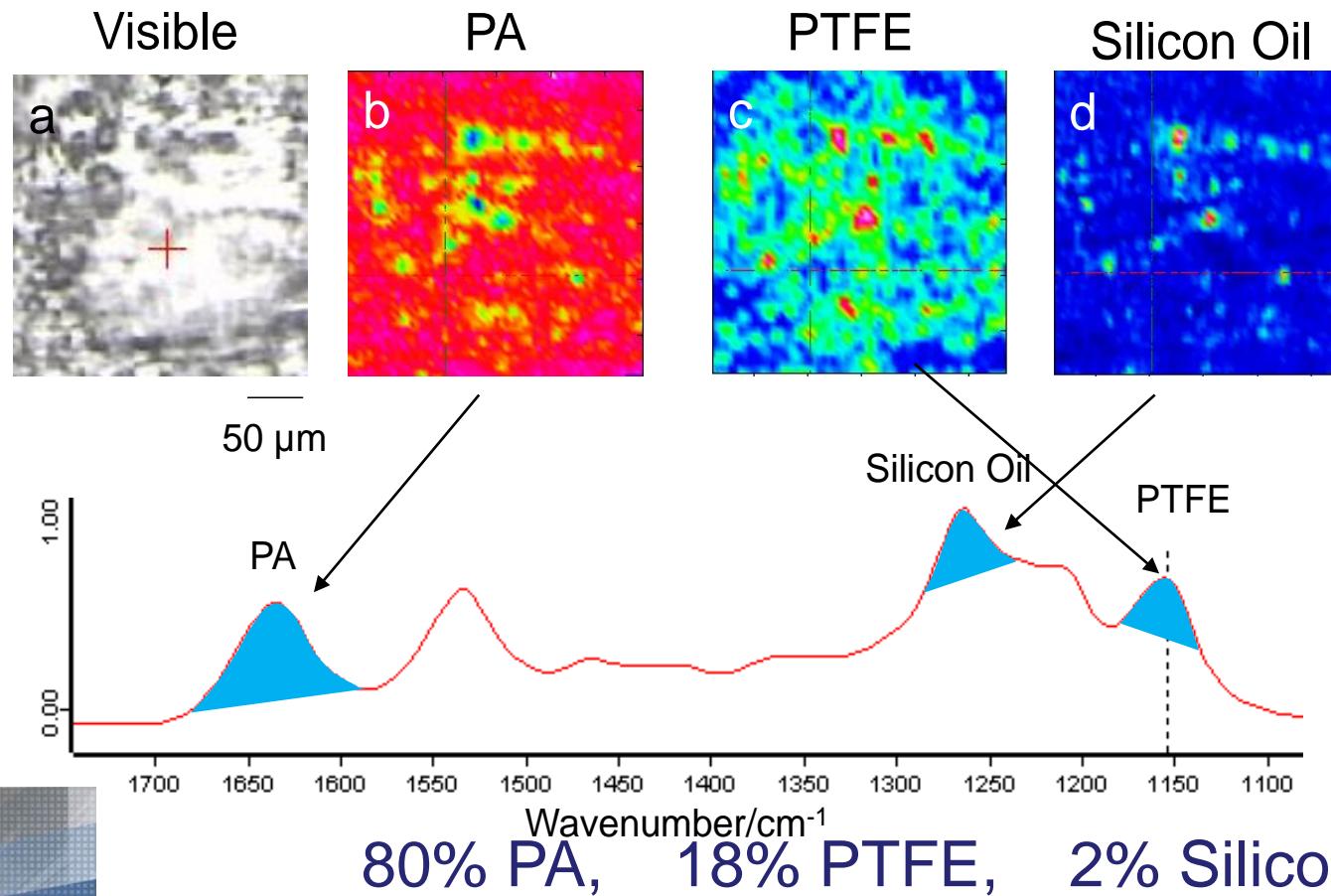
Optical image

Transmission FT-IR imaging of polymer blend



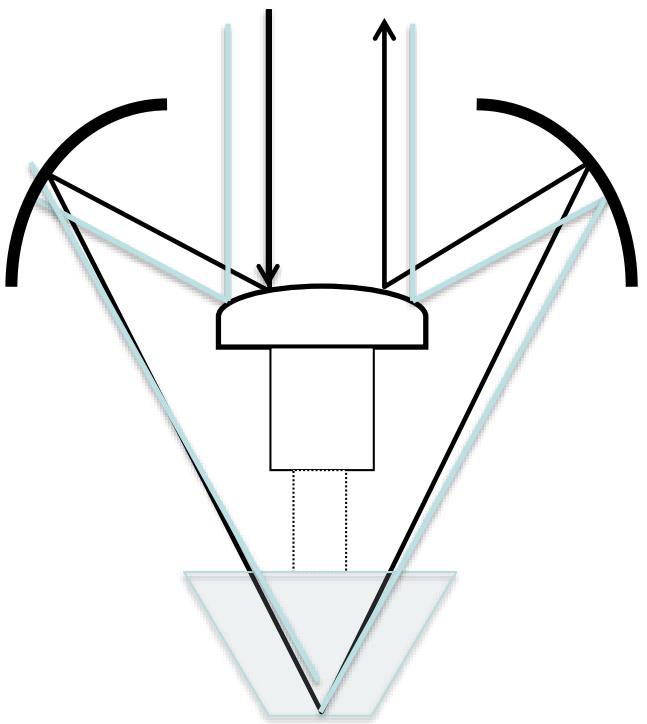
FTIR image was obtained in transmission by plotting absorbance of a spectral band of PTFE (right) and polyamide (left) as a function of all 4096 pixels in FPA array detector

Transmission FT-IR imaging of polymer blend



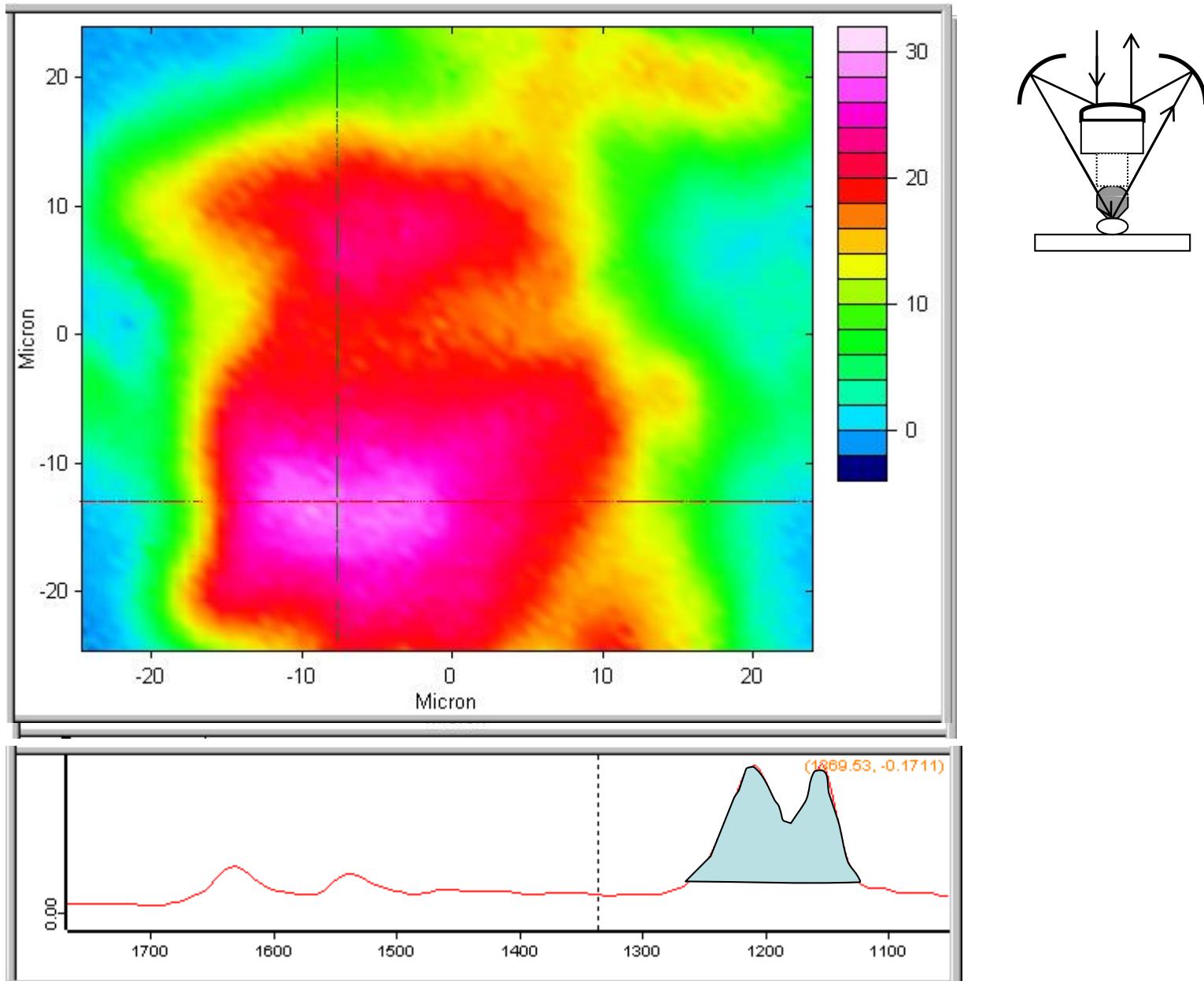
Polymer Morphology:
Principles, Characterization, and Processing
Ed. Qipeng Guo (2016)

A Closer Look with micro ATR-IR Imaging

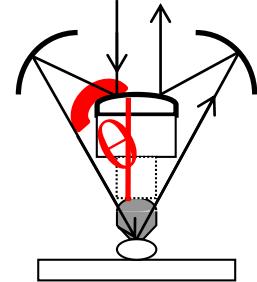


As IR is form of light,
microscope optics can be
made

Closer look with micro-ATR imaging



Rayleigh Criterion

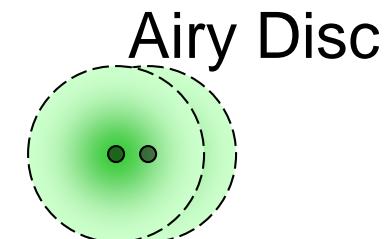


An **Airy disk** is the central bright circular region of the pattern produced by light diffracted when passing through a small circular aperture.

$$r = \frac{1.22\lambda}{2NA}$$

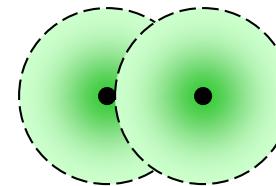
λ is wavelength of light

Not resolved



$$NA = n \sin \theta$$

Just resolved

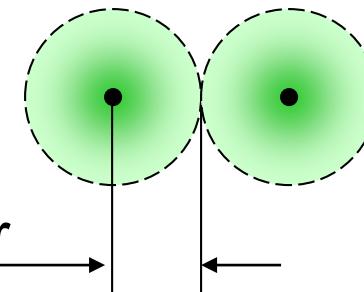


NA: Numerical Aperture

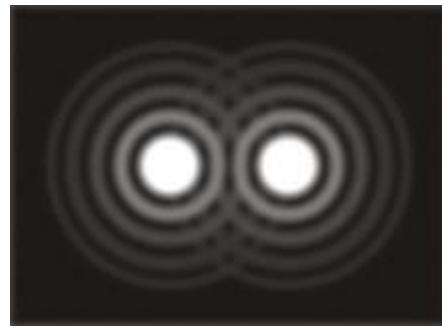
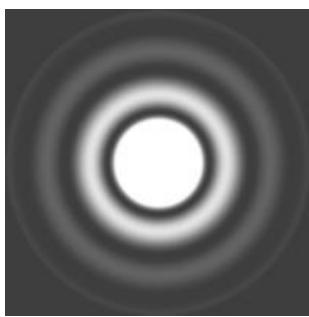
n is refractive index of the medium between objective and the sample.

Higher NA leads to high spatial resolution

Resolved

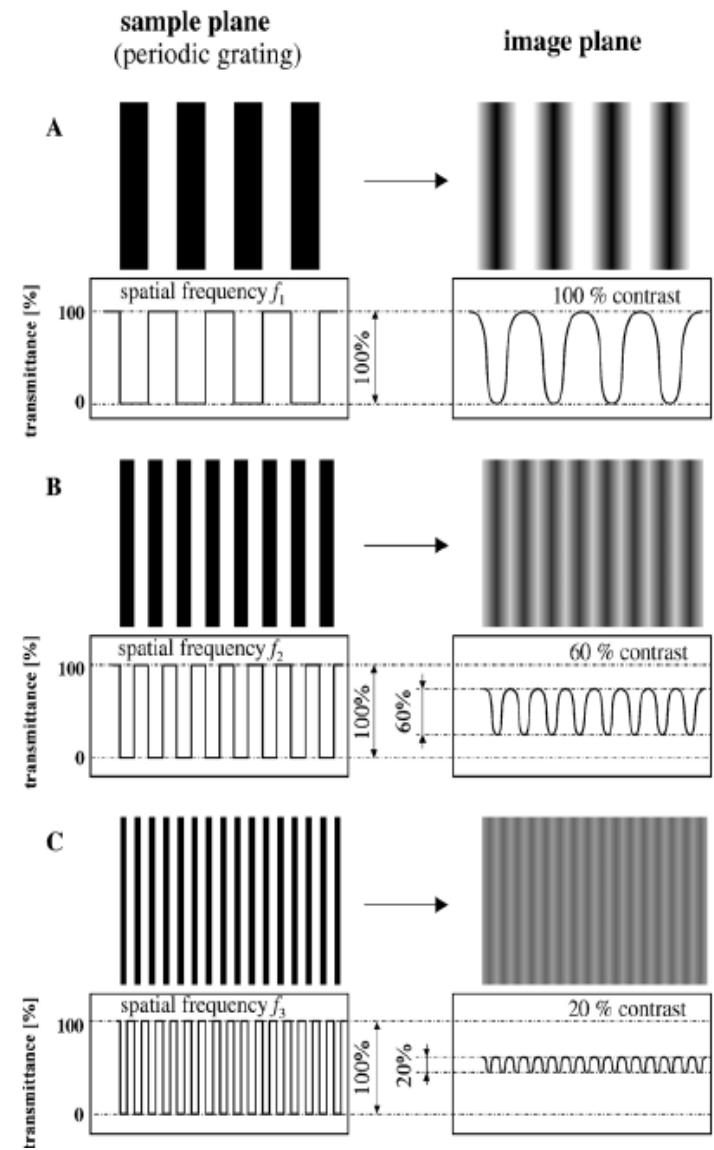
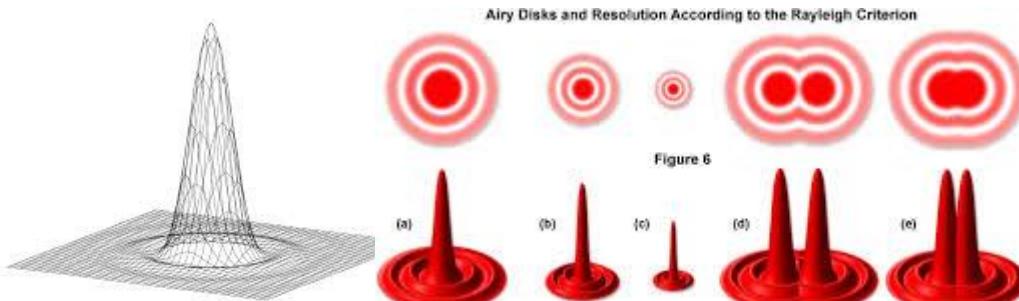


Airy disk and Rayleigh criterion

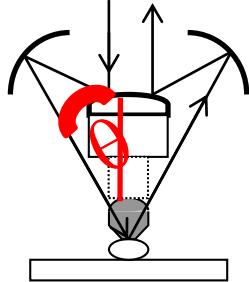


Airy disk is a diffraction pattern

$$r = \frac{1.22\lambda}{2NA}$$



Micro-ATR FTIR imaging



Germanium ATR objective can be used with an IR microscope.

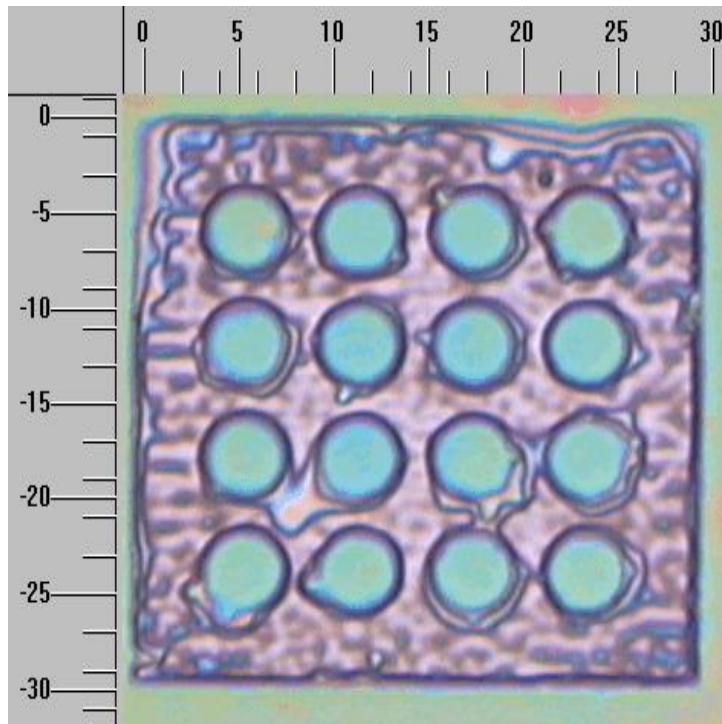


Provides small field of view ($50 \times 50 \mu\text{m}^2$) with very high spatial resolution because of increased NA of objective due to high refractive index of Ge (n=4)

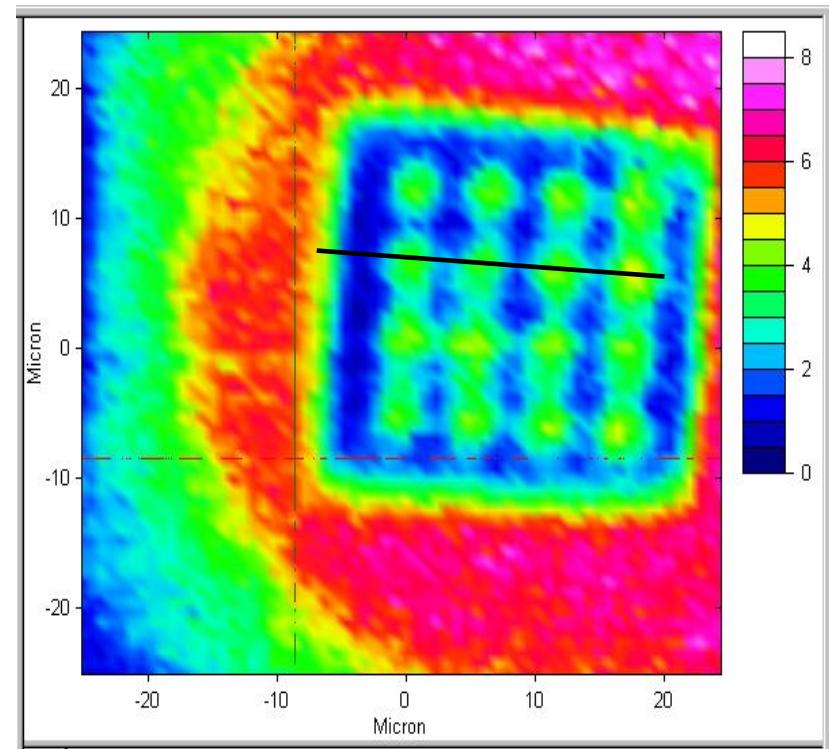
$$r = \frac{1.22\lambda}{2NA}$$

$$NA = n \sin \theta$$

Enhanced spatial resolution can be achieved with ATR crystal

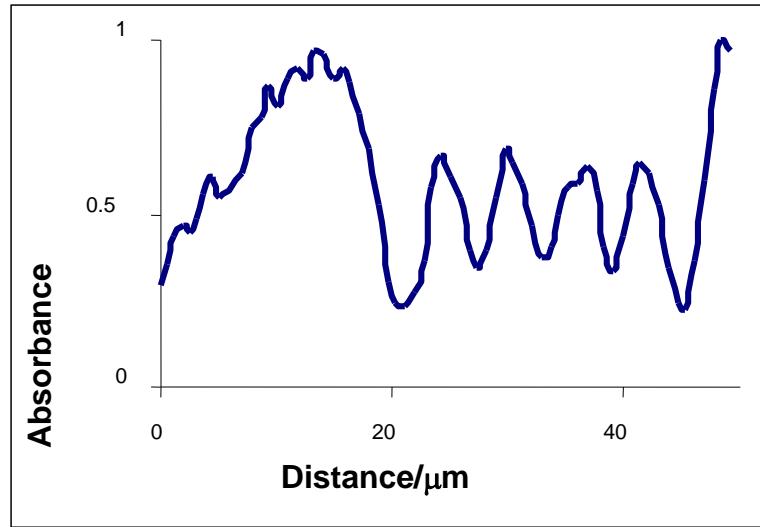


Visible image of a silicon wafer
coated with pattern of PMMA film



FTIR image of the same grid,
based on absorbance of the $\nu(\text{C}=\text{O})$
band at 1723 cm^{-1}

Spatial Resolution



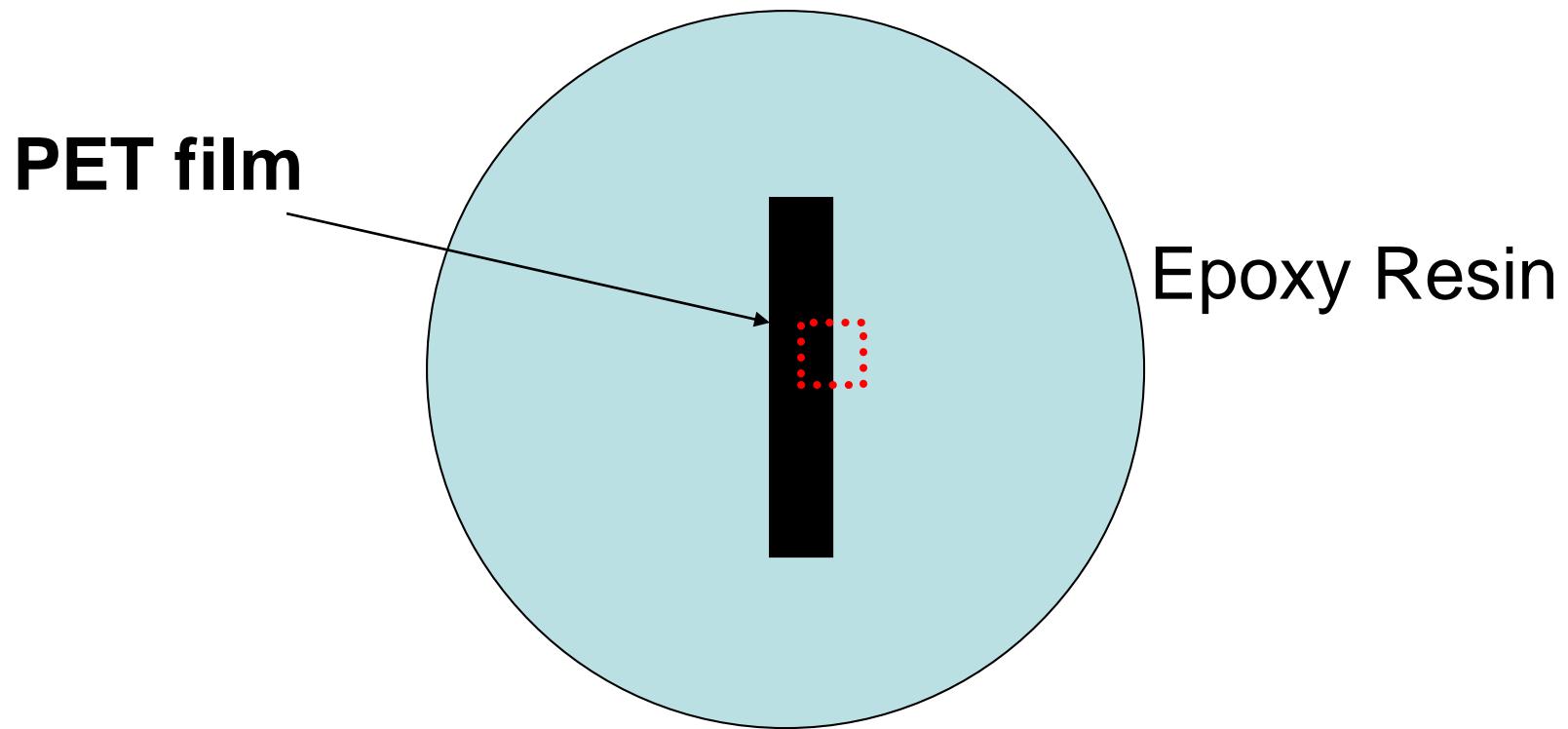
$$r = \frac{1.22\lambda}{2NA}$$

$$NA = n \sin \theta$$

We use $\nu(\text{C=O})$ band at 1723 cm^{-1} , thus $\lambda = 5.9 \mu\text{m}$.
NA in air = 0.6. Thus, spatial resolution = $11.8 \mu\text{m}$.

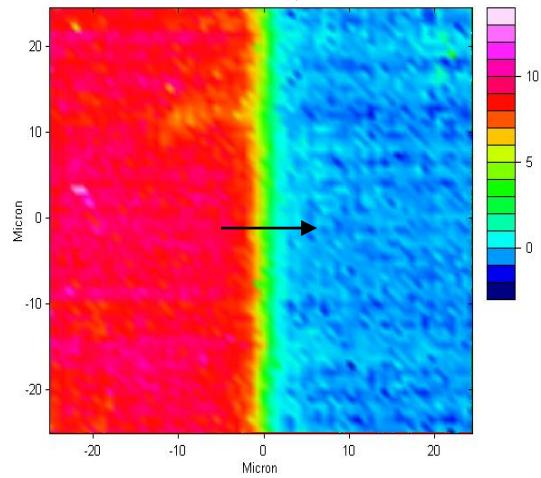
However, for Ge $n= 4$, thus spatial resolution = ca.
 $3 \mu\text{m}$.

Sample of PET/epoxy laminate:
a representative of real samples where
refractive indices are not too different

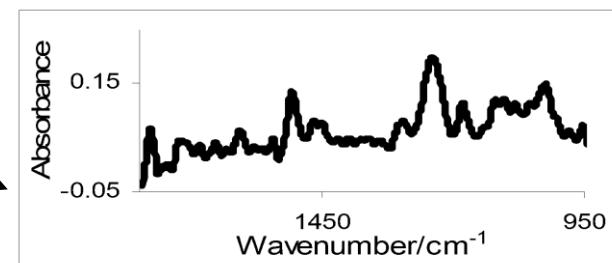
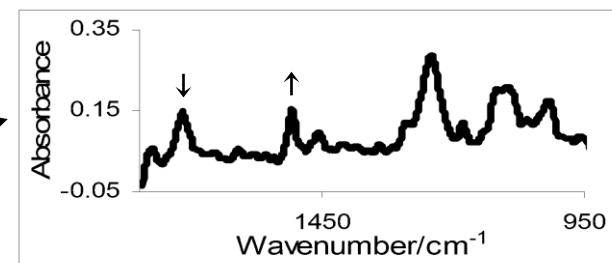
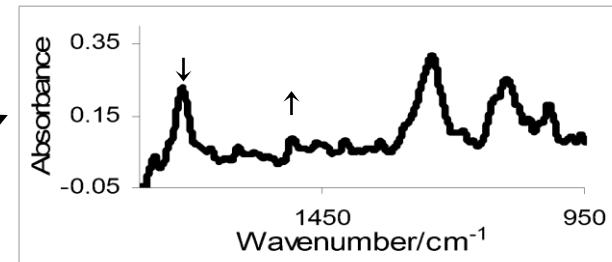
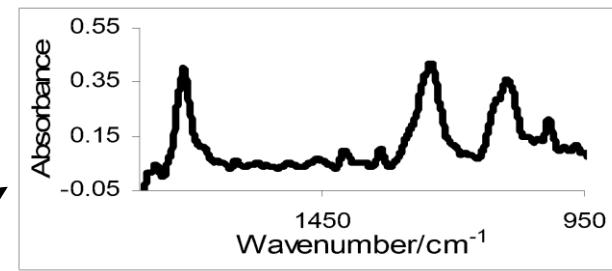
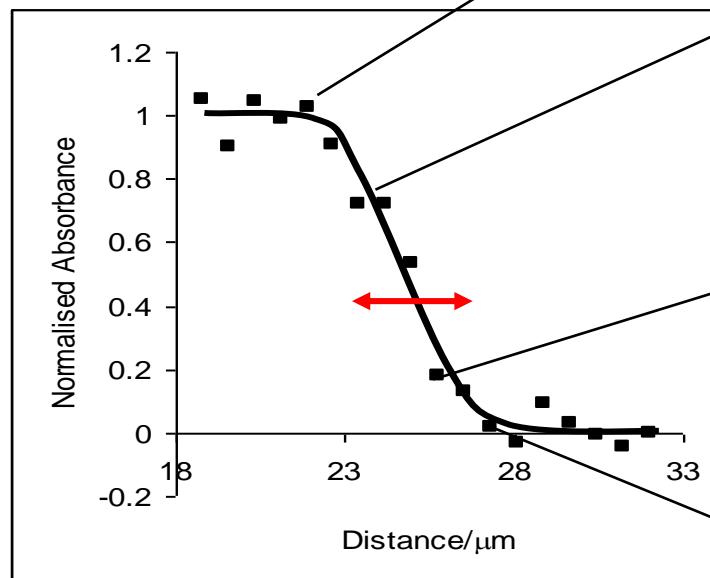


FTIR image of the interface of PET/epoxy laminate

50 x 50 μm^2



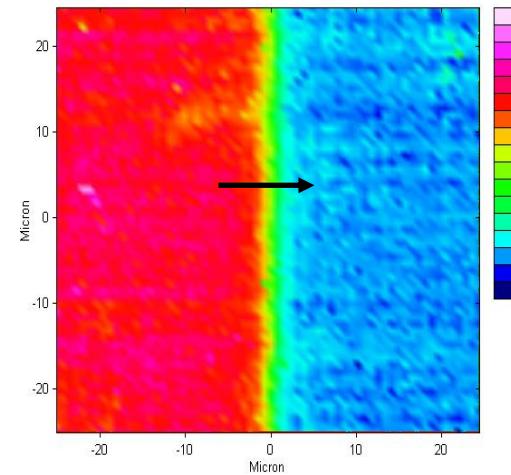
4 μm



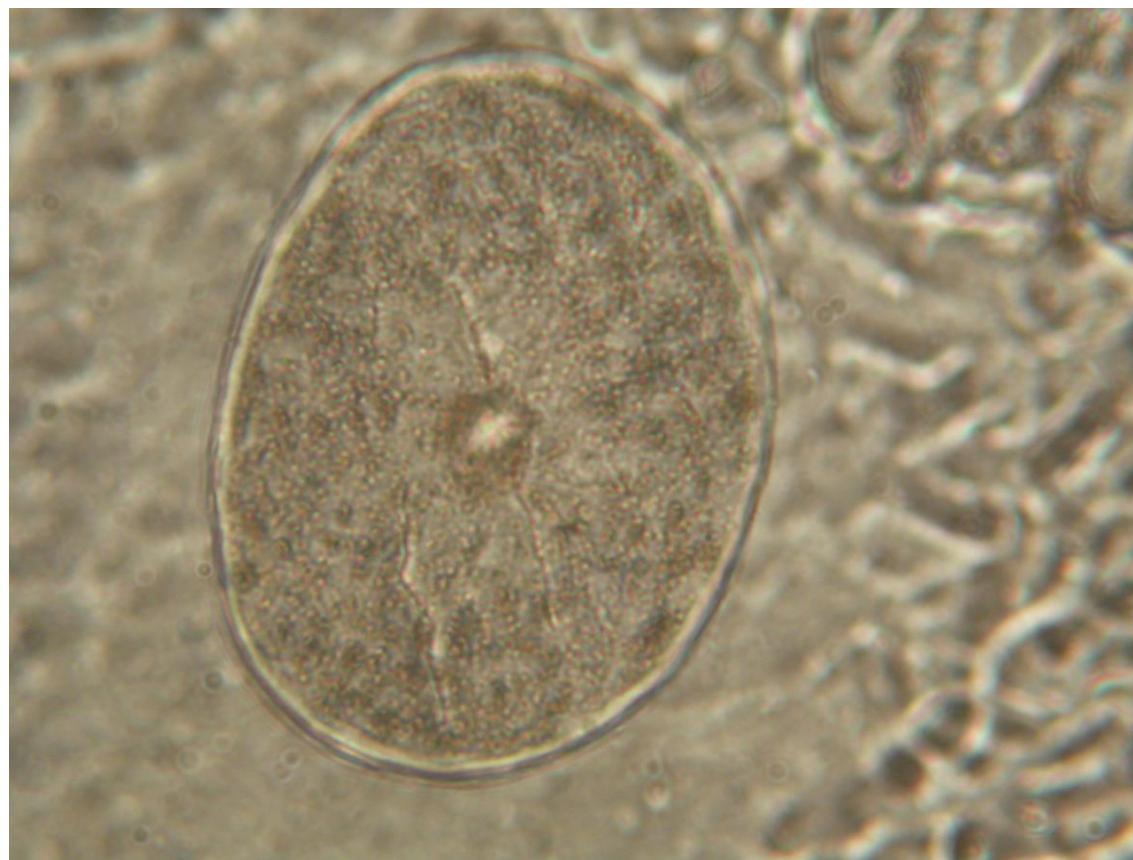
Enhanced spatial resolution with micro ATR Imaging

- the test in previous slide provided the value of achieved spatial resolution
- the value ca. $4 \text{ } \mu\text{m}$ at ca. 1600 cm^{-1} ($\lambda = 6 \text{ } \mu\text{m}$)
- spatial resolution is assessed by measurement of real sample
- via 5-95% absorbance profile

$$r = \frac{1.22\lambda}{2NA}$$



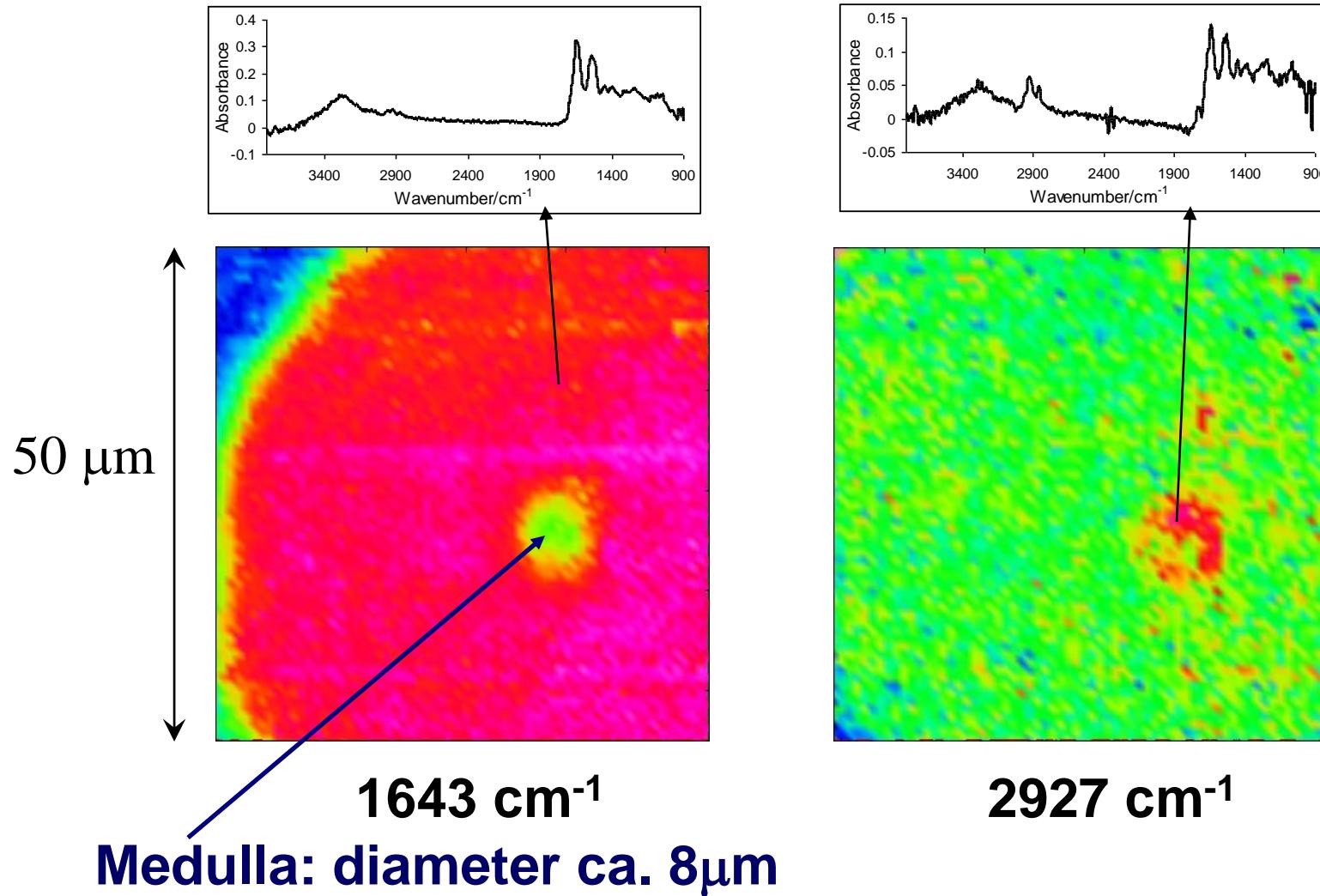
Visible image of the cross-session of hair



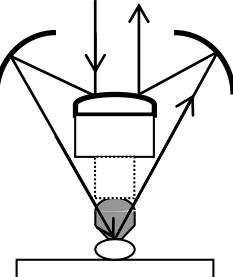
← →

140 µm

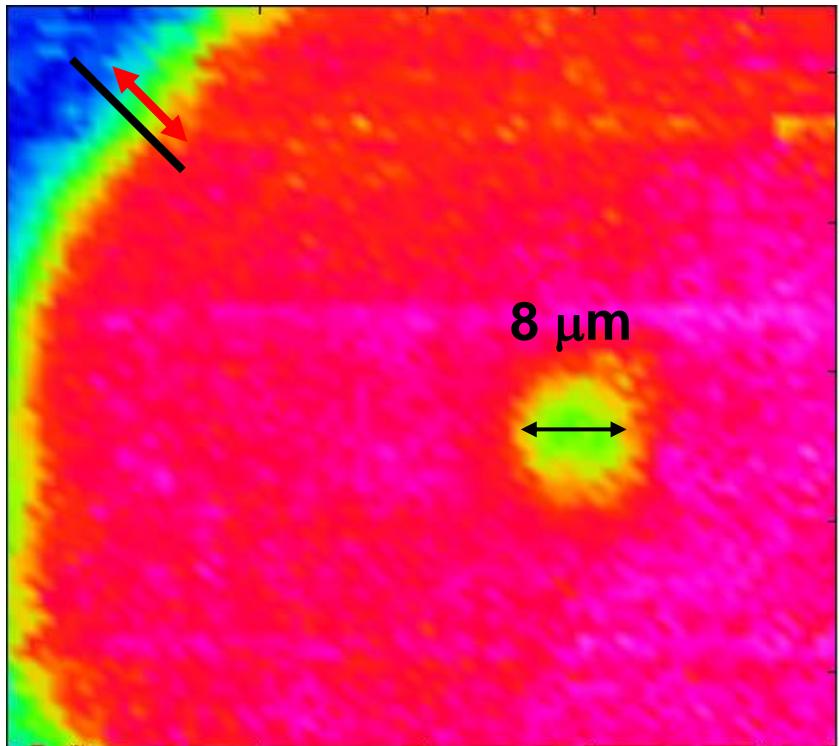
Imaging of Human Hair Without Synchrotron



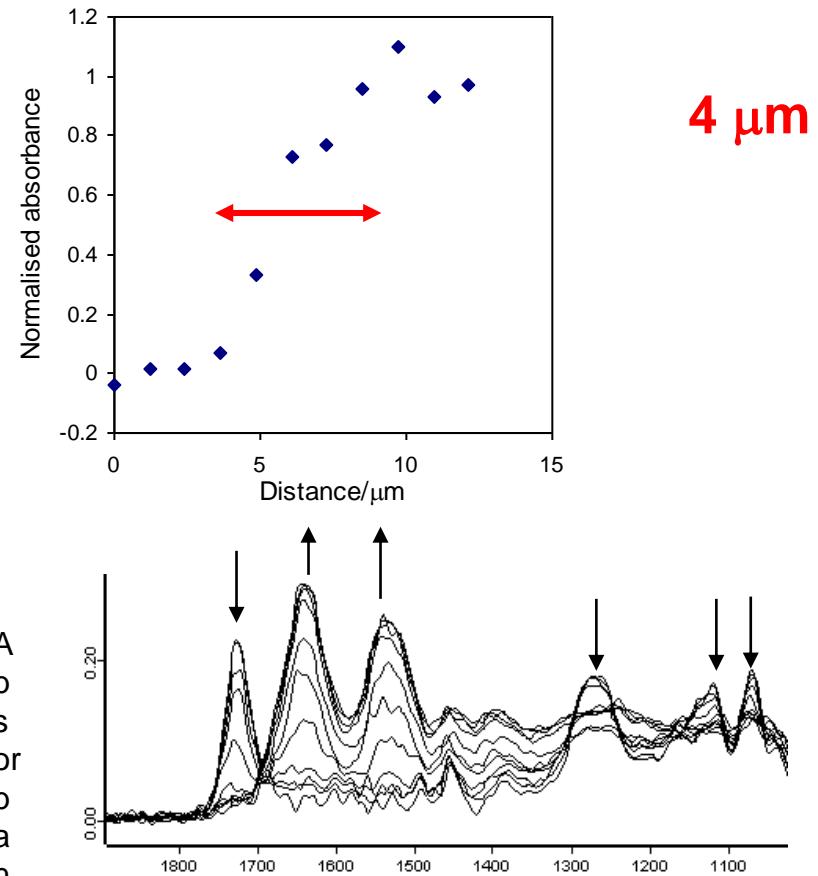
Micro ATR-FTIR imaging of hair: imaging without a synchrotron



10 μm

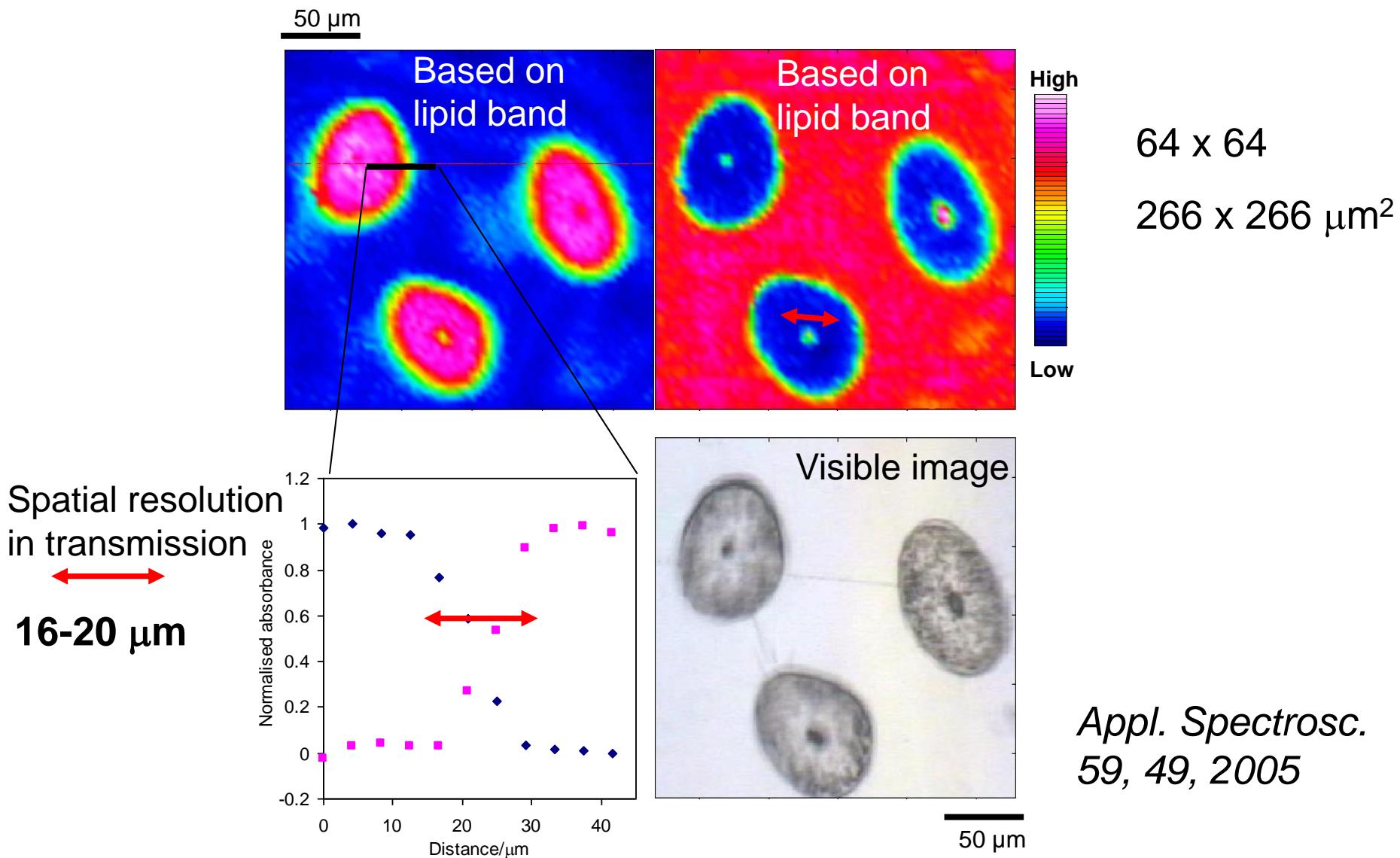


Chemical information (via spectra) from
the very central part of human hair can be
obtained with Micro ATR imaging

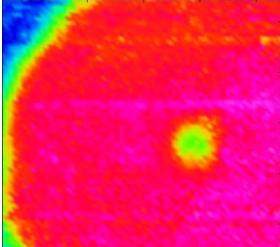


Transmission FTIR imaging of hair

Although medulla is clearly visible in transmission, spectra from medulla will contain information from the surrounding areas because the spatial resolution ca. 20 μm



Breaking the diffraction limit



$$r = \frac{1.22\lambda}{2NA}$$

50 μm

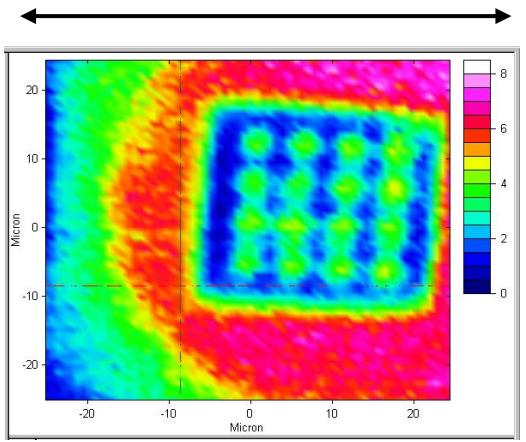


Image obtained with the band at $\lambda = 6 \mu\text{m}$

$$NA = n \sin \theta$$

n is the refractive index
(for Ge $n = 4$)

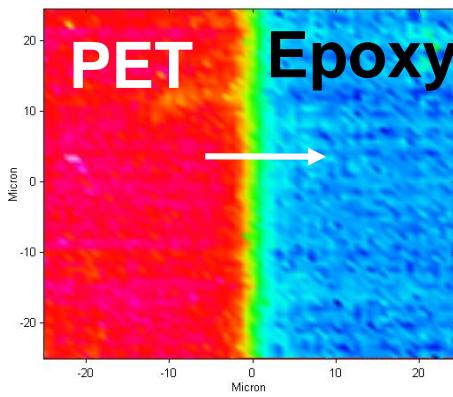
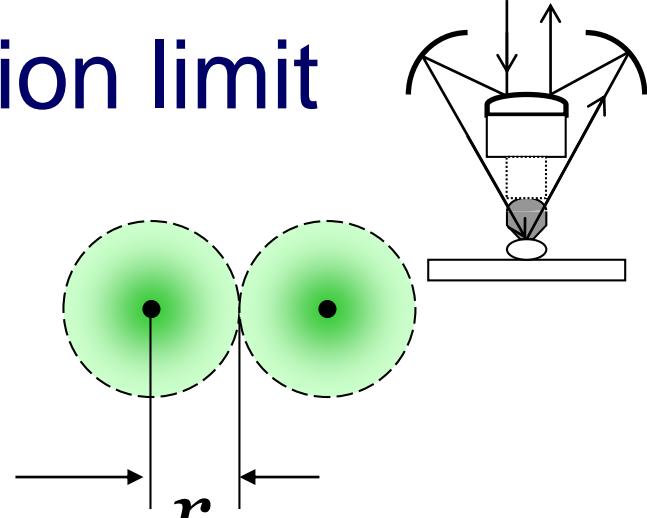
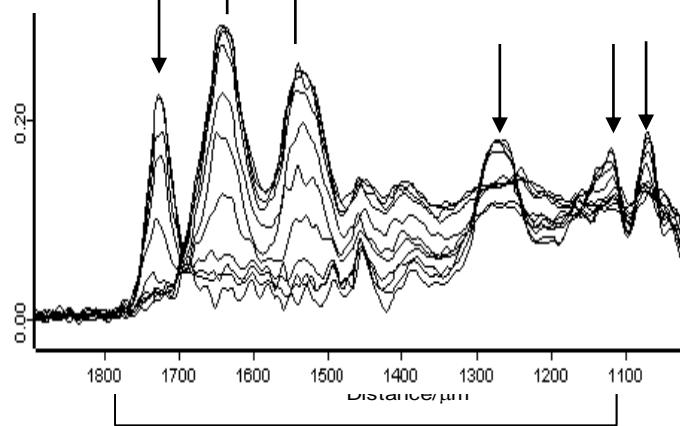


Image of the interface

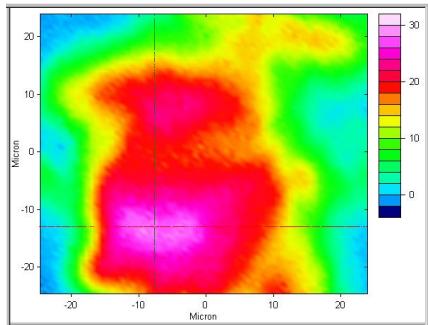


Absorbance profile for the band at $\lambda = 6 \mu\text{m}$

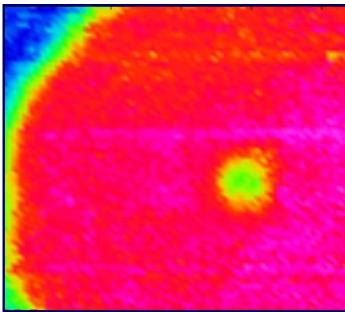
Spatial resolution $2-4 \mu\text{m}$ has been achieved which is beyond the diffraction limit of IR light in air
Spectra are different within a distance of less than 1 μm

ATR imaging with enhanced resolution

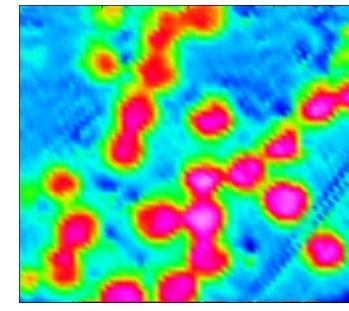
Broad range of applications



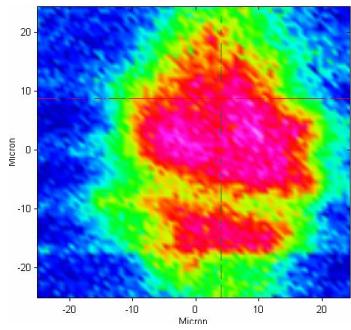
Polymer blends



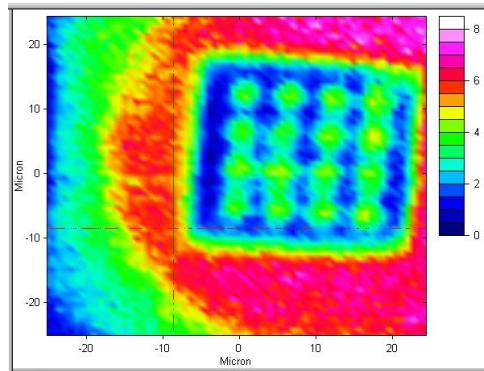
Imaging of hair
without synchrotron



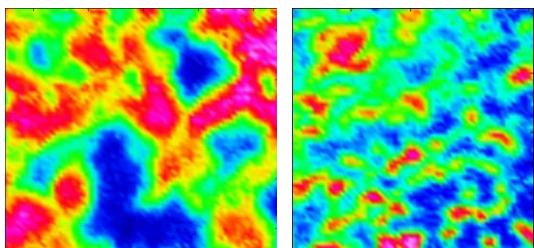
Fibres in
polymer matrix



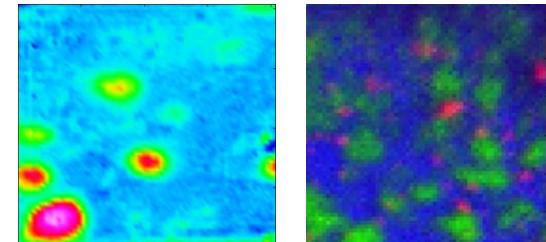
Skin surface



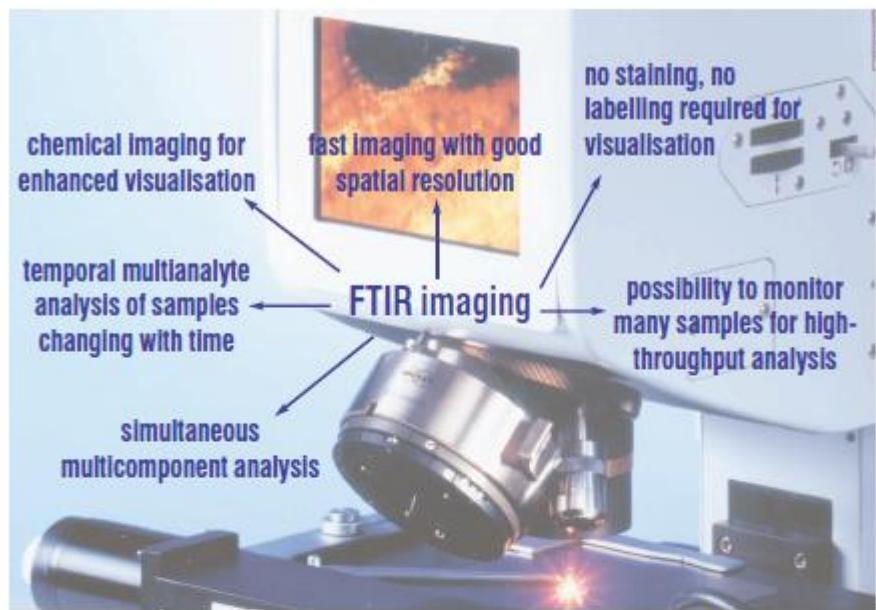
Spatial resolution
beyond diffraction limit
with micro-ATR



Biomaterials for tissue engineering



Emulsions Tablets



A closer look at polymers

FTIR imaging is emerging as a powerful technique for analysing polymer mixtures. By providing simultaneous chemical and spatial information, heterogeneous polymeric materials can be characterised easily. *Sergei Kazarian & Julia Higgins explain.*

In Brief

- Optimum blends achieved through process visualisation with FTIR microscopy
- Produces a spatial distribution map and no staining is needed
- Applications include medicine, engineering, pharmaceuticals and materials science
- Exhibits generality, specificity and sensitivity

Blends of different polymers are often explored in the search for polymeric materials with desirable properties. A recently emerged technology, Fourier-transform infrared (FTIR) imaging, provides a new and powerful method to characterise these blends.

FTIR imaging can be used to analyse multilayer polymer films, polymer-drug formulations, composite materials and polymeric fibres. In many cases, these materials are mixtures.

By mixing a relatively expensive polymer with an inexpensive one, the

overall cost of the product can be significantly reduced. Mixing might also result in a material with new mechanical properties, when, for example, a glassy and a rubbery polymer are mixed. The properties of polymer blends can be tuned by changing the ratio of the components. However, properties largely depend on mixing efficiency. Adding a compatibiliser can improve mixing by reducing interfacial tension between the polymer phases. Compatibilisers can also help to achieve better dispersion and im-

This article is available on the BB

Please also look at the web-site of my research group for further information on FTIR imaging:
www.imperial.ac.uk/vsci

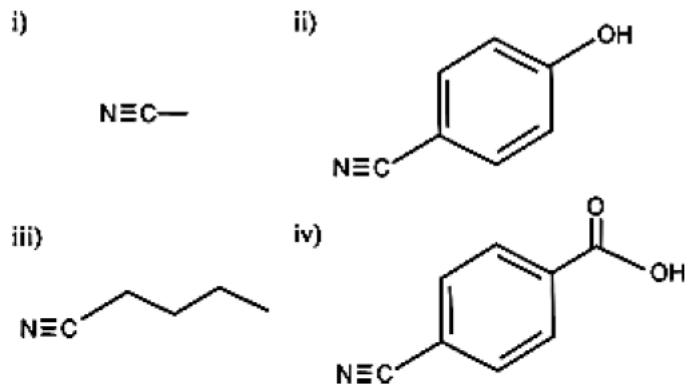
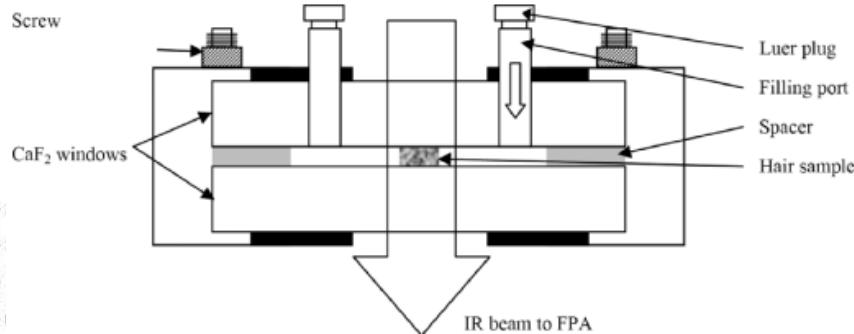
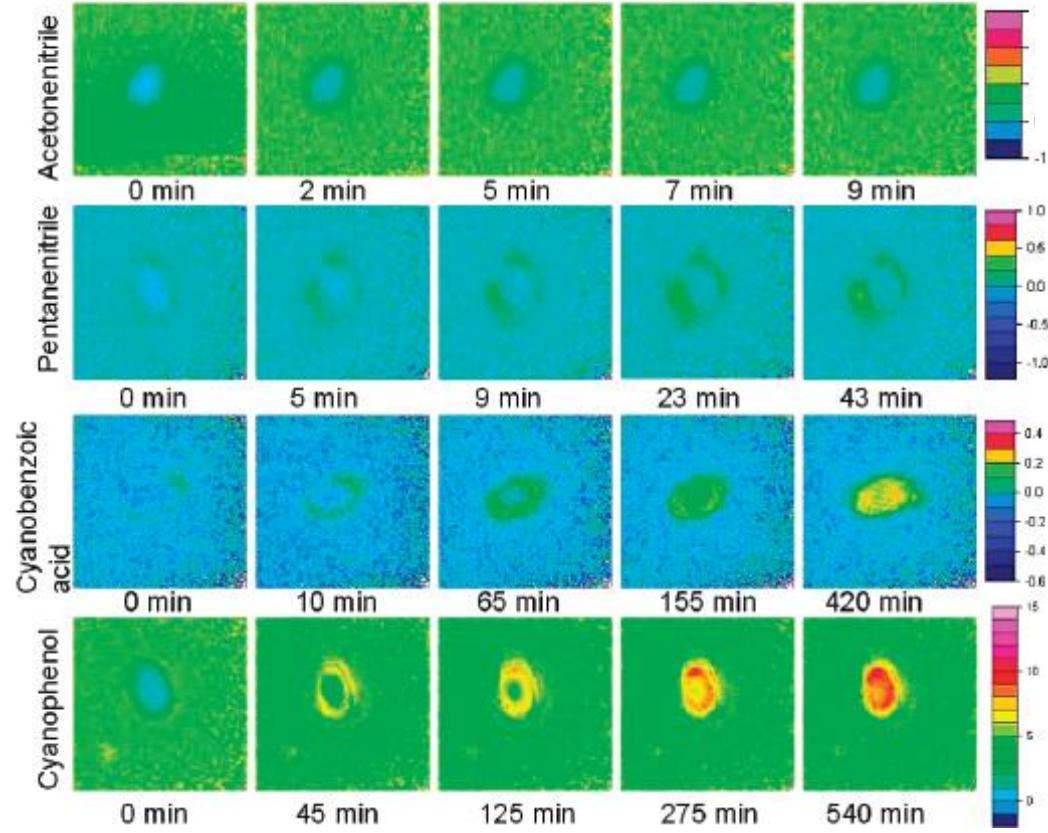
“FTIR imaging is set to find broad applications in forensic, materials colloid science, engineering and pharmaceuticals” S. Kazarian

IR spectroscopy is “most nearly universal chemical spectroscopy. As a structural tool, its generality, sensitivity and specificity are hard to match” Richard Palmer

In situ diffusion in human hair with transmission FTIR imaging

Collaboration with Unilever:

Demonstration of the potential of in situ FT-IR imaging to study the diffusion of model chemicals across the hair cross-section.

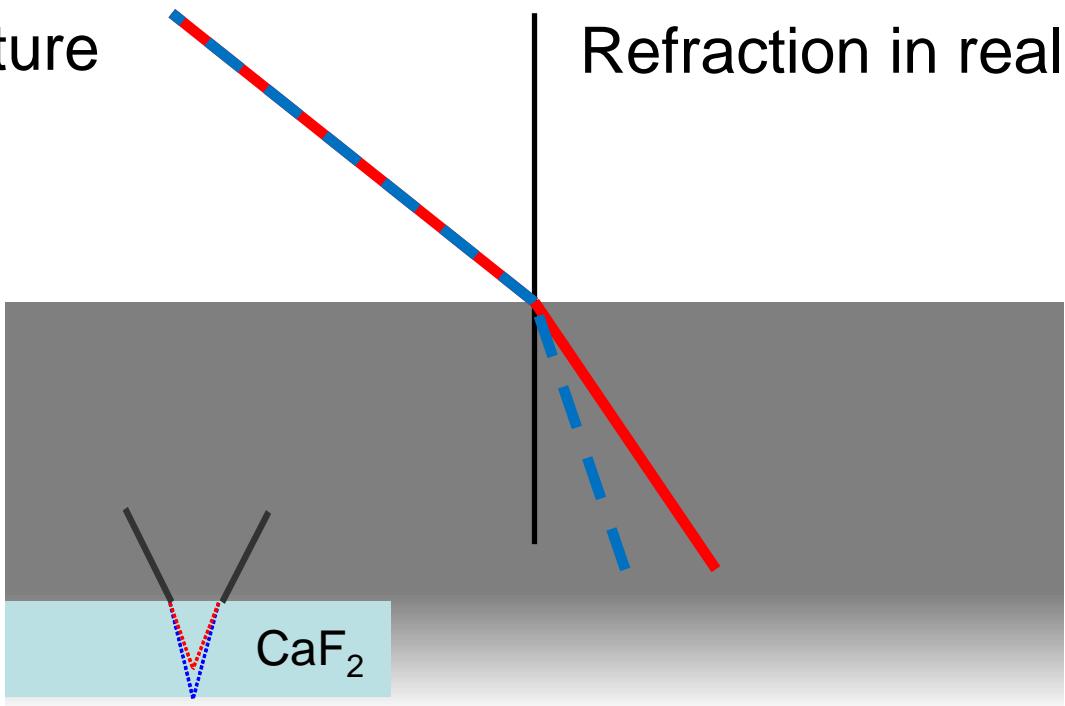


Refraction and Chromatic Aberration

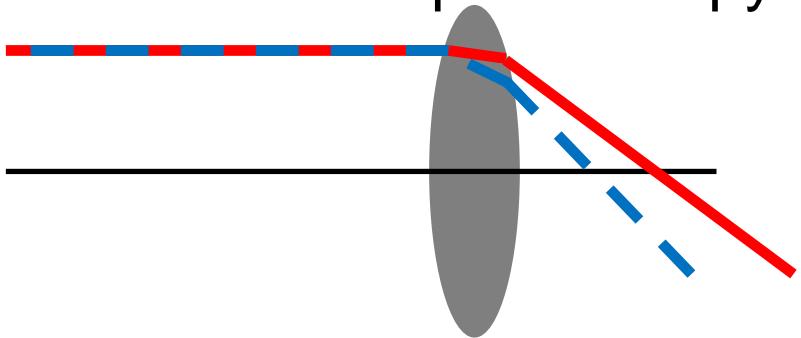
Refraction in popular culture



Refraction in reality



Refraction in spectroscopy



- Light of shorter wavelengths bent more than longer wavelengths, giving chromatic aberration.
- In transmission, effects of refraction are unavoidable

?

Effect of refraction

CaF₂

REVIEW OF SCIENTIFIC INSTRUMENTS

VOLUME 72, NUMBER 3

MARCH 2001

Resolution limits for infrared microspectroscopy explored with synchrotron radiation

G. L. Carr^{a)}

National Synchrotron Light Source, Brookhaven National Laboratory, U.S.A.

IR microspectroscopy 1617

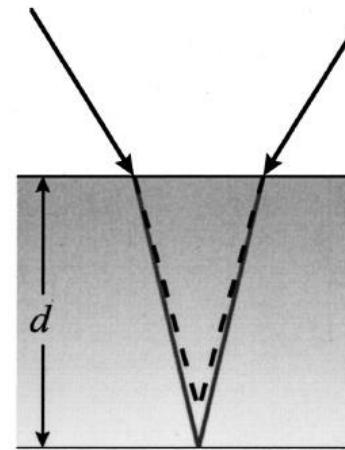
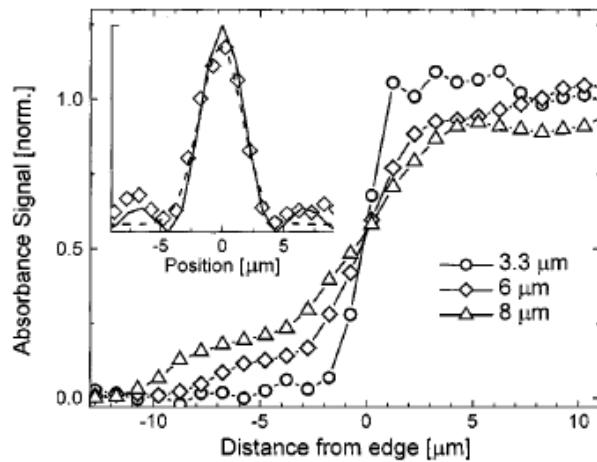
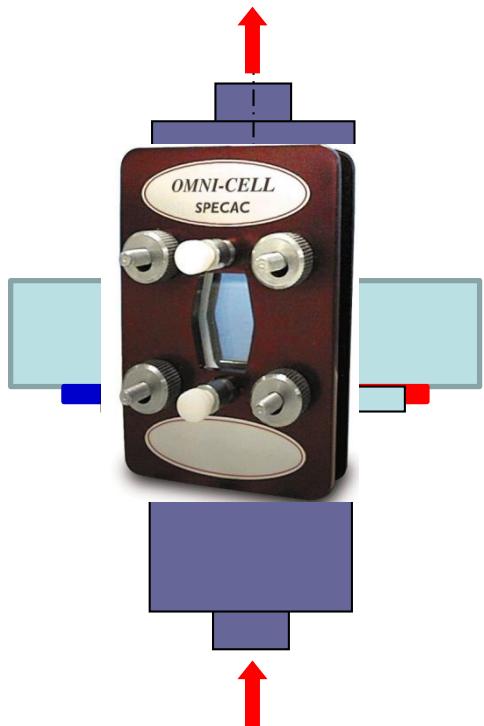


Illustration of the focus shift that occurs for dispersive substrates.

“There are cases where this problem cannot be avoided, for example, samples sandwiched between two substrates as in a liquid or compression cell. In order to achieve optimal spatial resolution, the measurement must be repeated for each wavelength range of interest, adjusting the instrument’s focus to match the spectral range.” (Carr G. L. Review Sci. Instrum. 72, 1613, 2001.)



Effect of refraction on FTIR images measured in transmission

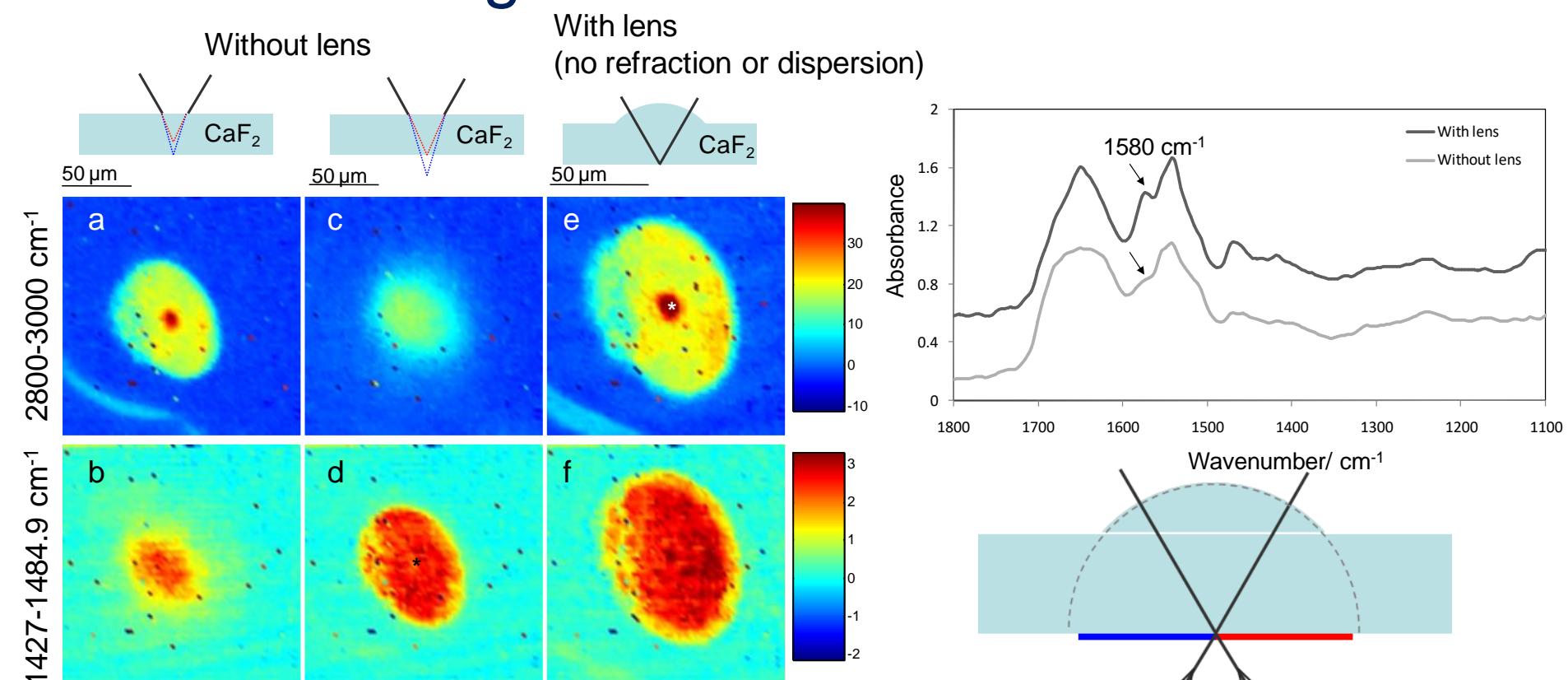


through a flat infrared transparent window; refraction makes the focal length depending on wavelength (chromatic aberration)

through a hemisphere light does not refract

through a pseudo hemisphere by placing a lens on top of window; no refraction

Removal of refraction of light in FTIR images measured in transmission



Size of images a-d is 170 $\mu\text{m} \times 170 \mu\text{m}$

Size of images e and f is 120 $\mu\text{m} \times 120 \mu\text{m}$

(refractive index of CaF₂ is 1.4)