Chapter 5- Fourier Transform Infrared Spectroscopy (FTIR)

Contents:
- light - electromagnetic wave
- molecular effects of infrared adsorption
  -- molecular vibration
  -- dipole change
- interpretation of IR spectra
- Instrumentation and sampling techniques
  -- transmission spectroscopy
  -- attenuated total reflection (ATR)
  -- diffuse reflection
  -- Polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS)
- Raman spectroscopy

What is light? -- Electromagnetic Radiation

Dual nature of light:
- Photons as particle:
  Photons have energy but no mass
- Photons as wave:
  Electric and magnetic fields oscillating in space and time

Electromagnetic Radiation

- Radiation is absorbed & emitted in photons. The defining characteristic of a photon is that its energy cannot be split into smaller pieces.
- Each photon's energy is defined by its frequency (ν) or wave length (λ) or wave number (\(\bar{\nu}\))
- \(E_{\text{photon}} = h\nu = hc/\lambda = hc\bar{\nu}\)
  - \(h = \text{Planck's constant}, 6.63 \times 10^{-34} \text{ J s}\)
  - \(c = \text{speed of light}, 3.00 \times 10^8 \text{ m s}^{-1} (\text{or } 3.00 \times 10^{10} \text{ cm s}^{-1})\)
  - Wavenumber, \(\bar{\nu} = 1/\lambda\)
- Energy unit:
  - Wavelength (\(\lambda\)): meter or micron
  - Frequency (\(\nu\)): Hz (cycle/s)
  - Wavenumber: \(\text{cm}^{-1}\)

1 eV = 8065.54 cm\(^{-1}\) = 96.4853 kJ/mol = 23.0605 kcal/mol
Atoms and molecules can absorb electromagnetic radiation, but only at certain energies (wavelengths).

Infrared (IR) absorbed by organic molecules:
- Just below red in the visible region
- IR range: 400-4000 cm$^{-1}$ (wavelengths 25-2.5 μm)
- Photon energy = 0.8-8.0 x 10$^{-20}$ J
- Molar photon energy = 4.9-49 kJ/mol = 1.2-12 kcal/mol

IR photon energy << covalent bond energy. Absorbing IR radiation should not trigger substantial chemical changes. But IR radiation contains more energy than random thermal motion at room temperature (~ 0.6 kcal/mol)
Infrared Regime

It is useful to divide the infrared region into three sections: near, mid and far infrared.

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength range (μm)</th>
<th>Wavenumber range (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Near</td>
<td>0.78 - 2.5</td>
<td>12800 - 4000</td>
</tr>
<tr>
<td>Middle</td>
<td>2.5 - 25</td>
<td>4000 - 500</td>
</tr>
<tr>
<td>Far</td>
<td>25 - 1000</td>
<td>400 - 10</td>
</tr>
</tbody>
</table>

Molecular effects of infrared adsorption

1) IR radiation does not have enough energy to induce electronic transitions as seen with UV. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational states.

2) For a molecule to absorb IR, the vibrations within a molecule must cause a net change in the dipole moment of the molecule.

3) The alternating electrical field of the radiation interacts with fluctuations in the dipole moment of the molecule.

4) If the frequency of the radiation matches the vibrational frequency of the molecule (resonance), radiation will be absorbed, causing a change in the amplitude of molecular vibration.

Molecular vibration induced by IR adsorption

Molecular vibrations
The positions of atoms in a molecule are not fixed; they are subject to a number of different vibrations. Vibrations fall into the two main categories of stretching and bending.

Stretching: Change in inter-atomic distance along bond axis

Asymmetric stretching

Symmetric stretching

Molecular vibration induced by IR adsorption

**Bending:** Change in angle between two bonds. There are four types of bend:
- Rocking
- Scissoring
- Wagging
- Twisting

![Molecular vibration induced by IR adsorption](http://en.wikipedia.org/wiki/Infrared_spectroscopy)

Molecular vibration induced by IR adsorption

The stretching frequency of a bond can be approximated by Hooke’s Law. Two atoms and the connecting bond are treated as a simple harmonic oscillator composed of 2 masses (atoms) joined by a spring: According to Hooke’s law, the vibration frequency of the spring is is expressed by:

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

where \(k\) is the force constant, \(m\) is the mass, \(\nu\) is the vibration frequency.

In the classical harmonic oscillator, \(E = \frac{1}{2} kx^2 = \hbar\nu\), where \(x\) is the displacement of the spring. Thus, the energy or frequency is dependent on how far one stretches or compresses the spring, which can be any value. If this simple model were true, a molecule could absorb energy of any wavelength.

Molecular vibration induced by IR adsorption

How much movement occurs in the vibration of a C-C bond?

For a C-C bond with a bond length of 154 pm, the variation is about 10 pm.

For C-C-C bond angle a change of 4° is typical. This moves a carbon atom about 10 pm.

Energy curve for a vibrating spring (left) and energy constrained to quantum mechanical model (right).

Molecular vibration induced by IR adsorption

However, vibrational motion is quantized during IR adsorption. It must follow the rules of quantum mechanics to fit the following formula:

\[E = (n + 1/2)\hbar\nu\]

where \(\nu\) is the vibration frequency, \(n\) is the quantum number (0, 1, 2, 3, . . . ). The lowest energy level is \(E_0 = 1/2\hbar\nu\), the next highest is \(E_1 = 3/2\hbar\nu\). According to the selection rule, only transitions to the next energy level are allowed. These correspond to bands called overtones in an IR spectrum.
A molecule is not just two atoms joined on a spring, of course. A bond can come apart, and it cannot be compressed beyond a certain point. A molecule is actually an anharmonic oscillator. As the interatomic distance increases, the energy reaches a maximum, as seen in Figure. Note how the energy levels become more closely spaced with increasing interatomic distance in the anharmonic oscillator. The allowed transitions, $h\nu$, become smaller in energy. Therefore, overtones can be lower in energy than predicted by the harmonic oscillator theory.

The following formula has been derived from Hooke's law. For the case of a diatomic molecule,

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{f(m_1 + m_2)}{m_1 m_2}}$$

where $\tilde{\nu}$ is the wavenumber (cm$^{-1}$), $m_1$ and $m_2$ are the mass of atoms 1 and 2, respectively, $c$ is the velocity of light (cm/s), $f$ is the force constant of the bond (dyne/cm)

Equation shows the relationship of bond strength and atomic mass to the wavenumber (vibration frequency) at which a molecule will absorb IR radiation. As the force constant increases, the wavenumber increases.
Correlation of Quantized Absorptions

<table>
<thead>
<tr>
<th>Group</th>
<th>Bond</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol</td>
<td>O-H</td>
<td>3200 - 3640</td>
</tr>
<tr>
<td>Amine</td>
<td>N-H</td>
<td>3300 - 3500</td>
</tr>
<tr>
<td>Alkyne</td>
<td>sp C-H</td>
<td>3300</td>
</tr>
<tr>
<td>Aromatic</td>
<td>aryl C-H</td>
<td>3000 - 3100</td>
</tr>
<tr>
<td>Alkenes</td>
<td>sp² C-H</td>
<td>3020 - 3080</td>
</tr>
<tr>
<td>Alkanes</td>
<td>sp³ C-H</td>
<td>2850 - 2960</td>
</tr>
<tr>
<td>Aldehydic</td>
<td></td>
<td>2750</td>
</tr>
<tr>
<td>Nitriles</td>
<td>C=O</td>
<td>2250</td>
</tr>
<tr>
<td>Alkyne</td>
<td>C=C</td>
<td>2200</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>C=O</td>
<td>1650 - 1800</td>
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<tr>
<td>Amino</td>
<td>C-N</td>
<td>1200</td>
</tr>
<tr>
<td>Ether</td>
<td>C-O</td>
<td>1100</td>
</tr>
<tr>
<td>Chloro</td>
<td>C-Cl</td>
<td>550 - 780</td>
</tr>
<tr>
<td>Bromo</td>
<td>C-Br</td>
<td>510 - 650</td>
</tr>
<tr>
<td>Iodo</td>
<td>C-I</td>
<td>485 - 600</td>
</tr>
</tbody>
</table>

Molecular vibration induced by IR adsorption

- IR Absorption is quantized
  Different bonds absorb different units of energy
  Absorption reported in wavenumbers (cm⁻¹)

- Uses infrared light to excite bonds
  Light is absorbed by functional group and group vibrates

Dipole movement induced by IR adsorption

- Before the IR beam and molecule interact, the H-Cl molecule is at rest. After the interaction, the photon has been absorbed, and its energy deposited into the H-Cl molecule as bond stretching motion. Energy is conserved in the reaction since all the photon’s energy has been transferred to the molecule as vibrational energy.

- We detect the absorbance of the photon by a decrease in infrared intensity at the wavenumber of the light absorbed, giving an absorption feature in the IR spectrum of the molecule due to the dipole moment.

Molecular effects of infrared adsorption

- IR active
  HCl
  Variation of μ during vibration
  IR active

- IR inactive
  O₂
  No Variation of μ during vibration
  IR inactive

Only vibrations which occur with variation of μ are active in IR spectroscopy.

From O. Chiantore
**Molecular effect of IR adsorption**

**Dipole change**

- Only vibrational modes that change the dipole moment can interact with light and lead to absorption.
- $\nu_1$
  - Infrared Inactive
  
- $\nu_2$
  - Infrared Active
  
- $\nu_3$
  - Infrared Active

- CO$_2$ is infrared active, but not all of its modes are.

**Selection rule for infrared spectroscopy**

**prerequisites for Infrared active**

That is, the molecules can interact with light and lead to infrared absorption only when all the following requirements are met:

1) The frequency of the infrared light must be identical to the frequency of the vibration (resonance).
   
   *Absorption is quantized, Different bonds absorb different units of $E$*

2) The dipole of the molecule must change during vibration.

3) The direction of the dipole change must be the same as the direction of the electric filed vector.

**Quantification of Infrared Adsorption**

- Trasmittance ($T$)
  - 100 - 0 %
  - full transparent
  - full absorber

- Absorbance ($A$)
  - 0 - $\infty$

\[ T = \frac{I}{I_0} \]
\[ A = \log \frac{I_0}{I} = \log \frac{I_0}{I} \]

**Acquisition of infrared spectra**

**Format of IR spectra**

- Transmission spectrum
  
- Adsorption spectrum
Infrared Spectra of materials

Interpretation of infrared spectra

Interpretation of infrared spectra

Adsorption bands in IR spectra

Where to Begin Interpretation

- Find C-H stretches as your starting point
- C-H absorb ≈ 2850-3000 cm⁻¹

<table>
<thead>
<tr>
<th>Hybridization</th>
<th>Bond Type</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp³ hybridized</td>
<td>C-H</td>
<td>2850-3000</td>
</tr>
<tr>
<td>sp² hybridized</td>
<td>C-H</td>
<td>2850-3000</td>
</tr>
<tr>
<td>sp hybridized</td>
<td>C-H</td>
<td>3300</td>
</tr>
</tbody>
</table>

- Heavy atom stretches.

Many bands & many overlaps

4) use IR database


8/15/2015
Interpretation of infrared spectra

**Aromatics**
- C–H stretch from 3100-3000 cm\(^{-1}\)
- Overtones, weak, from 2000-1665 cm\(^{-1}\)
- C–C stretch (in-ring) from 1600-1585 cm\(^{-1}\)
- C–C stretch (in-ring) from 1500-1400 cm\(^{-1}\)
- C–H "oop" from 900-675 cm\(^{-1}\)

[Image: http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html]

**Alcohols (-OH)**
- O–H stretch, hydrogen bonded 3500-3200 cm\(^{-1}\) -- broad lump peak
- C–O stretch 1260-1050 cm\(^{-1}\) (s)

[Image: http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html]

**Ether**
- C–O absorb ≈ 1100 cm\(^{-1}\)
- C–O absorption weak to medium intensity

[Image: http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html]

**Ketone**: carbonyl band C=O
- Aliphatic ketones: 1715 cm\(^{-1}\)
- \(\alpha, \beta\)-unsaturated ketones: 1685-1666 cm\(^{-1}\)

[Image: http://orgchem.colorado.edu/hndbksupport/irtutor/tutorial.html]
Interpretation of infrared spectra

**Ketone:** carbonyl band C=O
- aliphatic ketones 1715 cm\(^{-1}\)
- \(\alpha, \beta\)-unsaturated ketones 1685-1666 cm\(^{-1}\)

Interpretation of infrared spectra

**Nitro compounds:** N-O
- N–O asymmetric stretch from 1550-1475 cm\(^{-1}\)
- N–O symmetric stretch from 1360-1290 cm\(^{-1}\)

Interpretation of infrared spectra

**Primary amine:** R-NH\(_2\)
- N–H: two bands from 3400-3300 and 3330-3250 cm\(^{-1}\)
- N–H bend from 1650-1580 cm\(^{-1}\)
- C–N stretch (aromatic amines) from 1335-1250 cm\(^{-1}\)
- C–N stretch (aliphatic amines) from 1250–1020 cm\(^{-1}\)
- N–H wag (primary and secondary amines only) from 910-665 cm\(^{-1}\)

Interpretation of infrared spectra

**Halogens:**
- C–Cl absorption weak to medium intensity
  - C–Cl absorb ≈ 550-780 cm\(^{-1}\)
Database of infrared spectra

Books
• Hummel D.O., Scholl, F. Atlas of polymer and plastic additives, vol 1-3 VCH Publisher, Weinheim, 1991
• Merck E, Merk FTIR Atlas, VCH verlagges, Weinheim, 1988

Electronic database
Bio-Rad IR Databases, Bio-Rad's Informatics Division

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

FTIR quantitative analysis

Limitations to Beer’s law

Is the absorbance really linear with respect to the variables?

Path Length: Essentially this is always found to be linear.

Concentration: Intermolecular interactions
Shifting chemical equilibrium

Molar absorptivity: Solution’s index of refraction
Also, there are a number of ways that an instrument can itself skew the behavior away from linearity

Beer-Lambert or Beer’s Law:
A straightforward study of the absorption process of photons passing through an absorbing medium
The intensities of the peaks are directly related to the amount of sample present

\[ A = \log_{10} \left( \frac{I_0}{I} \right) = \epsilon bc \]

This is a spectroscopic experiment because \( \epsilon \) depends upon the wavelength of light employed. Hence, the absorbance is wavelength dependent.
Absorbance adds in a multicomponent system – assuming the various components do not interact.
Transmittance is the directly measured property but absorbance is directly related to concentration.
Summary of FTIR

**Advantages of FTIR:**
- FTIR is an ambient technique. The instrument is relatively inexpensive.
- A universal technique, *i.e.*, solids, liquids, gases, and powders can be routinely analyzed.
- IR spectra are information rich; peak positions, intensities, widths, and shapes in a spectrum all give useful information about the analyte.
- IR is relatively fast and easy technique. Most samples can be prepared and scanned in less than five minutes.
- IR is very sensitive. Micro to nano gram quantities can routinely be detected.

**Disadvantages of FTIR:**
- Homonuclear compounds don’t absorb.
- Aqueous solutions difficult to analyze because the strong absorbance of water.
- Some compounds give broad bands that interfere with other compounds.
- Complex mixtures difficult.
- Dark (black) compounds often absorb the IR beam completely, *i.e.*, 0% transmittance.

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Project timeline

- Every student will independently accomplish the report of the project at first.
- Every student will turn in the project report on **November 16, 11:00am** (firm deadline!).
- From November 16 to November 27, the students in the same group will work together to make the slides for a common presentation for each group.
- On **November 28, 11:00am**, every group will turn in the electronic file of the presentation. After you turn in the presentation file, you will not be allowed to make any change of your slides.
- On **November 28 and 30**, the groups will make presentation (the duration time for presentation is 18 minutes. Your talk can not be less than 17 minutes, but can not exceed 18 minutes). One student will be selected by each group to make the presentation on behalf of the group.

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How to analyze the sample from a car accident
Chapter 5- Fourier Transform Infrared Spectroscopy

Contents:
- light - electromagnetic wave
- molecular effects of infrared adsorption
  -- molecular vibration
  -- dipole change
- interpretation of IR spectra
- Instrumentation and sampling techniques
  -- attenuated total reflection (ATR)
  -- diffuse reflection
  -- Polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS)
- Raman spectroscopy

FTIR instrumentation

http://www.forumsci.co.il/HPLC/FTIR_page.html
FTIR instrumentation

An interferogram is generated because of the unique optics of an FT-IR instrument. The key components are a moveable mirror and beam splitter. The moveable mirror is responsible for the quality of the interferogram, and it is very important to move the mirror at constant speed. The moveable mirror is often the most expensive component of an FT-IR spectrometer.

A Fourier transform is a mathematical operation used to translate a complex curve into its component curves. The complex curve is an interferogram generated by overlapping light waves. The standard infrared spectrum is calculated from the Fourier-transformed interferogram, giving a spectrum in percent transmittance (%T) vs. light frequency (cm⁻¹).

FTIR sampling techniques

1) transmission
2) attenuated total reflection (ATR)
3) Specular reflectance
4) Diffuse reflectance
5) DRIFTS (diffuse reflectance Fourier transform spectroscopy)
6) PM-IRRAS (polarization modulation infrared reflection adsorption spectroscopy)
7) portable FTIR (optical fiber)
FTIR sampling technique - transmission

A choice on sampling technique exists for the following types of samples:
- solid powder (mixed with KBr)
- thin solid films (black samples excluded)
- liquid (no water involved)
- gas

Powder preparation procedure:
(a) The powder sample and KBr must be ground to reduce the particle size to less than 5 mm in diameter. Otherwise, large particles scatter the infrared beam and cause a slope baseline of spectrum.
(b) Add a spatula full of KBr into an agate mortar and grind it to fine powder until crystallites can no longer be seen and it becomes somewhat “pasty” and sticks to the mortar.
(c), (d) (e) shown in Figure

Kit for pressing powder samples

FTIR transmission measurement

FTIR sampling technique - ATR

Attenuated total reflection (ATR) infrared spectroscopy:
At each reflection, the light beam penetrates the sample to a depth of a few microns and is absorbed at the characteristic absorption frequencies. Zinc Selenide (ZnSe) crystal is most commonly used for ATR accessory.

Evanescent wave:
• The defining feature of ATR spectroscopy is the presence of an evanescent wave. The evanescent wave is a special type of electromagnetic radiation
• It is present only in the regime of supercritical internal reflection
• It propagates parallel to the interface
• Its intensity decreases exponentially with the distance from the sampling surface of IRE

Penetration depth
• Its penetration depth is on the order of wavelength
• Intensity of Evanescent wave decreases exponentially with the distance
• The penetration depth is a function of experimental parameters, for example, it is dependent upon the sample material
FTIR sampling technique - ATR

The penetration depth $d_p$ is defined as the distance form the crystal-sample interface where the intensity of the evanescent decays to $1/e$ (37%) of its original value. It can be given by:

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

Where $\lambda$ is the wavelength of the IR radiation, $n_1$ and $n_2$ are the refractive indices of the ATR crystal and the sample respectively, $\theta$ is the angle of incidence.

- If the ZnSe crystal ($n_1=2.4$) is used, the penetration depth for a sample with the refractive index of 1.5 at 1000cm$^{-1}$ is estimated to be 2.0 µm when the angle of incidence is 45°.
- If the Ge crystal ($n_1=4.0$) is used, the penetration depth is about 0.664 µm.
- The depth of penetration can be controlled either by varying the angle of incidence or by selection of crystals.

Properties of ATR crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>$n_1$</th>
<th>LWL, cm$^{-1}$</th>
<th>dp</th>
<th>Water Solubility, g/100g</th>
<th>pH Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond/KRS-5</td>
<td>2.4</td>
<td>250</td>
<td>1.66</td>
<td>Insoluble</td>
<td>1-14</td>
</tr>
<tr>
<td>Germanium</td>
<td>4</td>
<td>780</td>
<td>0.65</td>
<td>Insoluble</td>
<td>1-14</td>
</tr>
<tr>
<td>Silicon</td>
<td>3.4</td>
<td>1500</td>
<td>0.84</td>
<td>Insoluble</td>
<td>1-12</td>
</tr>
<tr>
<td>ZnS</td>
<td>2.2</td>
<td>850</td>
<td>2.35</td>
<td>Insoluble</td>
<td>5-9</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.4</td>
<td>525</td>
<td>1.66</td>
<td>Insoluble</td>
<td>5-9</td>
</tr>
</tbody>
</table>

$p_1$ = refractive index of ATR crystal

LWL = long wave length cut-off

dp = depth of penetration in microns @ 1000 cm$^{-1}$

FTIR sampling technique - ATR

Attenuated total reflection infrared (ATR-IR) spectroscopy:
- for thick films or bulk lump material with smooth surface
- for materials which are either too thick or too strong absorbing to be analyzed by transmission spectroscopy.
- liquid samples
- no sample preparation is required for ATR analysis.

ATR/spectroscopic flow cell
- It provide real-time chemical information of molecular absorption at the aqueous-solid interface.
- It can monitor bacterial attachment and biofilm growth on the surface of ZnSe, Ge, Si or the surface of cellulose acetate.
- Studies with model compounds, e.g., proteins, polysaccharides, humic and fulvic acids can provide valuable information on the adsorption to polymer surfaces.

ATR characterization of a membrane’s sulfonic acid groups and for the determination of the sulfonation degree of the polymer, sample provided by Hongying Zhou
FTIR sampling technique – diffuse reflectance

1) When the IR beam enters the sample, it can either be reflected off the surface of a particle or be transmitted through a particle.
2) The IR energy reflecting off the surface is typically lost.
3) The IR beam that passes through a particle can either reflect off the next particle or be transmitted through the next particle. This transmission-reflectance event can occur many times in the sample, which increases the pathlength.
4) Finally, such scattered IR energy is collected by a spherical mirror that is focused onto the detector.
5) The detected IR light is partially absorbed by particles of the sample, bringing the sample information.

FTIR sampling technique – diffuse reflectance

Specular reflection versus diffuse reflection

• Specular reflection: When an infrared beam is focused on the surface of a particulate sample, it can interact with the sample two ways. First it may simply reflect off the sample surface in the same way visible light reflects off a mirror. This phenomenon, called “specular reflection”, is a function of the refractive index of the sample.
• Specular reflection is suitable for smooth surface that can strongly reflect IR beam.

• Diffuse reflection collects infrared radiation from the IR beam that passes through a particle can either reflect off the next particle or be transmitted through the next particle. This transmission-reflectance event can occur many times in the sample, which increases the pathlength.
• Diffuse reflection collects scattered IR energy,
• Diffuse reflection is used for rough sample and particle assembly.

FTIR sampling technique: PM-IRRAS

PM-IRRAS:
Polharization modulation infrared reflection adsorption spectroscopy

S-polarized:
Electric field lies in the plane formed by incident and reflected waves.
For p-polarized light, the electric field has a component perpendicular to the surface and a component parallel to the surface

P-polarized:
Electric field lies perpendicular to the plane formed by incident and reflected waves.
For s-polarized light, the electric field is parallel to the surface plane
FTIR sampling technique: PM-IRRAS

1) The IRRAS is dependent upon the optical constants of the thin film and substrate, the angle of incidence, as well as the polarization of the incident IR radiation.
2) The phase shift of the perpendicular component, $s$, exhibits no significant dependence upon the variation of the angle of incidence.
3) Because the phase shift of the perpendicular component, $s$, is nearly 180° for all the angles of incidence, the net amplitude of the IR radiation parallel to the substrate surface is zero.
4) The phase shift of the parallel component, $p$, strongly depends upon the angle of incidence. The $p$-polarized component goes through a maximum at 88°. At such grazing incidence, the $p$-polarized radiation sums up of $E_p$ and $E_p'$, leading to a net combined amplitude that is almost twice that of the incident radiation.

PM-IRRAS

- PM-IRRAS has a surface-enhanced effect; and it is used for characterization of very thin films or monolayer.
- It can determine molecular orientation and conformation in organic/biological polymer films.
- It can be used to analyze films (e.g., Lipid film) on water-solid interface.

PM-IRRAS analysis organic monolayer on inorganic substrate

PM-IRRAS spectrum of poly-L-lysine on gold substrate

PM-IRRAS spectrum of arachidic acid monolayer at the air/water interface

PM-IRRAS spectrum of organic monolayer on the ITO glass substrate, sample provided by HyungEui Lee

PM-IRRAS spectrum obtained from virus on Au substrate, by courtesy Rafael Vega and C. Mirkin

Application of PM-IRRAS in biology
The monolayer is a double C18 tailed lipid, with a dual-purpose headgroup. The headgroup can chelate metals, dimerizing given a metal with high enough coordination number. The headgroup also has a portion designed to bind 2,4,6-Trimaminopyrimidine (TAP). This lipid was studied by transferring a monolayer onto a gold substrate and using the Polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) mode of FTIR.

FTIR sampling techniques

This table is meant to serve as a general guide for method selection based on the physical form of a sample. Upon assessment of a specific sample it is possible that none of the listed techniques will be suitable.

<table>
<thead>
<tr>
<th>Sample Form</th>
<th>ATR</th>
<th>Specular reflectance</th>
<th>PM-IRRAS</th>
<th>DRIFTS</th>
<th>Transmission</th>
</tr>
</thead>
<tbody>
<tr>
<td>monolithic solid</td>
<td></td>
<td></td>
<td>x</td>
<td></td>
<td></td>
</tr>
<tr>
<td>particle</td>
<td>x</td>
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</tr>
<tr>
<td>fiber</td>
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<tr>
<td>microtome cut</td>
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<td>thin films (micron)</td>
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<td>x</td>
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</tbody>
</table>

FTIR Imaging

- FTIR microscope
  - Provide FT-IR spectra for samples down to about 10 μm in size
  - Two primary modes of FT-IR microscopy: reflectance and transmission
  - More advanced mode: ATR
FTIR Imaging

Closer examination in right figure reveals that the spectrum at one of the spots has CH$_3$, CH$_2$, NH and OH absorptions typical of proteins, while neighbouring spectra just show finger grease.
Chapter 5
Raman Spectroscopy

Contents:
- light - electromagnetic wave
- molecular effects of infrared adsorption
  -- molecular vibration
  -- dipole change
- interpretation of IR spectra
- Instrumentation and sampling techniques
  -- attenuated total reflection (ATR)
  -- diffuse reflection
  -- Polarization modulation infrared reflection adsorption spectroscopy (PM-IRRAS)
- Raman spectroscopy

Principle of Raman spectroscopy
interaction between light (electromagnetic radiation) and molecules

1) Electromagnetic radiation consists of oscillating electric and magnetic fields.

2) Both of these fields have the potential to interact with molecules, however the magnetic interaction is much less likely to cause transitions to occur, and so the electric effect dominates.

3) Usually in rotational and vibrational spectroscopy, the transitions of interest are those involving the interaction between the electric dipole moment of the molecule (µ) and the electric field of the radiation (E).

Energy of interaction = µE

µ can be considered as:
µ = Σ qr
where q is a charge and r is its distance from the centre of the molecule.

In absorption spectroscopy, the photon transfers its energy to the molecule, resulting in its transition to a higher energy state. In emission spectroscopy, the molecule drops from a higher energy state to a lower one, and the energy lost in this process is emitted as a photon.

When a beam of radiation with a frequency which will lead to a transition is passed through a sample, the chances of absorption or emission being induced are equal. Whether net absorption or emission is seen depends on the population of the energy levels.
Principle of Raman spectroscopy

Interaction between light (electromagnetic radiation) and molecules

1) Usually in rotational and vibrational spectroscopy, the transitions of interest are those involving the interaction between the electric dipole moment of the molecule (\( \mu \)) and the electric field of the radiation (\( E \)).

\[
\text{Energy of interaction} = \mu E
\]

\( \mu \) can be considered as:

\[
\mu = \sum q_ir_i
\]

where \( q_i \) is a charge and \( r_i \) is its distance from the centre of the molecule.

Selection rule for Raman active - polarizability

For IR spectroscopy, it is necessary for the molecule to have a permanent electric dipole. This is not the case for Raman spectroscopy, rather it is the polarizability (\( \alpha \)) of the molecule which is important.

The oscillating electric field of a photon causes charged particles (electrons and, to a lesser extent, nuclei) in the molecule to oscillate. This leads to an induced electric dipole moment, \( \mu_{\text{ind}} \), where

\[
\mu_{\text{ind}} = \alpha E
\]

This induced dipole moment then emits a photon, leading to either Raman or Raleigh scattering.

The energy of this interaction is also dependent on the polarizability:

\[
\text{Energy of interaction} = \frac{-1}{2}\alpha E^2
\]

The energies of Raman transitions are relatively weak. To counter this, a higher intensity of the exciting radiation is used.

For Raman scattering to occur, the polarizability of the molecule must vary with its orientation. One of the strengths of Raman spectroscopy is that this will be true for both heteronuclear and homonuclear diatomic molecules.

Comparison between Raman and IR Spectroscopy

They are complementary, both measure the vibrational energies of molecules

- **Raman**
  - The photon causes a momentary distortion of the e-distribution around a bond, followed by re-emission of radiation as the bond returns to its normal state. (The dipole then disappears)
  - To be active, the polarizability of the molecule must change

- **IR**
  - To be active, the dipole moment of the molecule must change
  - (Dipole = a molecule with a charge difference)
### Principle of Raman spectroscopy

**Selection rule for Raman active-- polarizability**

**Must be change in polarizability**

- Non-Polar groups such as C-S, S-S, C=C, C≡C (triple bond), N=N and heavy atoms (I, Br, Hg) strong scatterers

- Symmetric stretching vibrations are much stronger scatterers than asymmetric stretching vibrations

### Principle of Raman spectroscopy

**The basic set-up of a Raman spectrometer is shown below. Note that the detector is orthogonal to the direction of the incident radiation, so as to observe only the scattered light. The source needs to provide intense monochromatic radiation, and so is usually a laser.**

1) Raman spectroscopy collect scattered radiation.

2) The criteria for a molecule to be Raman active are also different to other types of spectroscopy. Raman active does NOT require a permanent dipole moment.

### Principle of Raman spectroscopy

**Types of scattering**

Consider a light wave as a stream of photons each with energy $hv$. When each photon collides with a molecule, two type of photon emission of which are considered below:

- **Elastic, or Raleigh scattering:**
  
  This is when the photon simply 'bounces' off the molecule, with no exchange in energy.

- **Inelastic, or Raman scattering:**
  
  This is when there is an exchange of energy between the photon and the molecule, leading to the emission of another photon with a different frequency to the incident photon.

### Principle of Raman spectroscopy

**Selection rule for Raman active-- polarizability**

**IR spectroscopy:**

- Adsorption:
  
  (radiation at a certain frequency is adsorbed due to the resonance of molecular vibration)

- observed peak is due to molecular vibration

**Raman spectroscopy:**

- scattered emission:
  
  (radiation at a certain frequency is scattered by the molecule with shifts in the wavelength of the incident beam)

- observed frequency shifts are related to vibrational changes in the molecule

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*From Kiera Jones*
Principle of Raman spectroscopy

Selection rule for Raman active - energy quantitized

Rotational
To find allowed rotational transitions, the total angular momentum quantum number for rotational energy states, $J$, must be considered. Raman spectroscopy involves a 2 photon process, each of which obeys: 

$$\Delta J = \pm 1$$

Therefore, for the overall transition, 

$$\Delta J = 0, \pm 2$$

where $\Delta J = 0$ corresponds to Raleigh scattering, $\Delta J = +2$ corresponds to a Stokes transition, and $\Delta J = -2$ corresponds to an anti-Stokes transition.

Vibrational
To find allowed transitions the vibrational quantum number, $\nu$, must be considered. For the overall transition, 

$$\Delta \nu = \pm 1$$

Transitions where $\Delta \nu = \pm 2$ are also possible, but these are of weaker intensity.

Principle of Raman spectroscopy

Selection rule for Raman active
The molecule is originally at the $E_2$ energy state. The photon interacts with the molecule, exciting it with an energy $h \nu$. However, there is no stationary state of the molecule corresponding to this energy, and so the molecule relaxes down to the energy levels $E_1$ or $E_3$. This process emits a photon in two ways:

**Anti-Stokes transition:**
If the molecule relaxes to energy state $E_1$, it will have lost energy, and so the photon emitted will have energy $h \nu_{r1}$, where $h \nu_{r1} > h \nu_i$.

**Stokes transitions:**
If the molecule relaxes to energy state $E_3$, it will have gained energy, and so the photon emitted will have energy $h \nu_{r2}$, where $h \nu_{r2} < h \nu_i$.

For rotational spectroscopy, both Stokes and anti-Stokes transitions are seen.

For vibrational spectroscopy, Stokes transitions are far more common, and so anti-Stokes transitions can effectively be ignored.

Principle of Raman spectroscopy

Summary of the selection rules for Raman active

1) For Raman scattering to occur, the polarizability of the molecule must vary with its orientation. (However, Raman active does NOT require a permanent dipole moment).

2) For vibrational or rotational transitions, the total angular momentum quantum number for rotational energy states must be met.

3) For rotational spectroscopy, both Stokes and anti-Stokes transitions are seen. For vibrational spectroscopy, Stokes transitions are far more common, and so anti-Stokes transitions can effectively be ignored.

Application of Raman spectroscopy

How does it work?

Material Identification through Raman spectroscopy.

Brand Security

Anti-counterfeiting

Comparing Infrared with Raman spectroscopy

3.) Active Raman Vibrations:
- need change in polarizability of molecule during vibration
- polarizability related to electron cloud distribution

example:

O = C = O  IR inactive

O = C = O  IR active

IR & Raman are complimentary. Can be cases where vibration is both IR & Raman active (e.g. SO2 – non-linear molecule)

In general:
IR tends to emphasize polar functional groups (R-OH, etc.)
Raman emphasizes aromatic & carbon backbone (C=C, -CH2-, etc.)
- Raman does not “see” many common polar solvents can use with aqueous samples – advantage over IR

Raman frequency range: 4000 -60 cm⁻¹(Stokes and anti-stokes)

Infrared and Raman Spectra of Benzene
Application of Raman spectroscopy

Initial Phase of CdS Deposition on InP(100) at 200°C

![Graph showing Raman shift vs. Scattering intensity. A broad shoulder on the low frequency side of the CdS phonon peak indicates an interfacial reaction leading to an In-S rich layer.]

Application of Raman spectroscopy

Confocal Raman microscopy for three-dimensional imaging

![Confocal Raman microscopy diagram with images of a sample and corresponding Raman spectra.](http://www.kos0.com/brnls/resource/techno/1350.pdf)

Application of Raman spectroscopy

Confocal Raman microscopy for imaging of food

(a) Raman image of instant gravy thickener particles. (Scan range: 50 x 50 m, 150 x 150 pixels, 22,500 spectra, 70 ms/spectrum, excitation: 532 nm Nd:Yag.) (b) Corresponding Raman spectra.

Application of Raman spectroscopy

Raman peak is sensitive to stress in materials

![Diagram showing the shift of the diamond 1332 cm⁻¹ band with compressive stress.](http://www.renishaw.com/UserFiles/acrobat/UKEnglish/SPD-PO-080.pdf)

If a compressive stress is applied to a sample, the binding distance of the atoms is reduced resulting in a higher vibrational frequency. The Raman line of this vibration is shifted to higher frequencies. Accordingly, a tensile strain shifts the Raman lines to lower wavenumbers.

The Raman shift of diamond 1332 cm⁻¹ band increases with compressive stress. Calibration of this shift to stress is very complicated for non-hydrostatic stress fields; but we expect it to be of similar magnitude to the hydrostatic value, a shift of 2.4 cm⁻¹ GPa⁻¹.
Advantages of Raman spectroscopy

- Raman spectroscopy is useful for analyzing molecules without a permanent dipole moment which would not show up on an IR spectrum.
- It can be used to determine bond lengths in non-polar molecules.
- Water compatible—water is a weak Raman scatter.
- It is useful for determining the identity of organic and inorganic species in solution, as the Raman transitions for these species are more characteristic than for IR, where the transitions are much more affected by the other species present in the solution.
- Raman spectroscopy is sensitive the stress in materials, and it is also used for detection of crystal orientation.
- No sample preparation

<table>
<thead>
<tr>
<th>Analytical Capabilities of IR and Raman</th>
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</thead>
<tbody>
<tr>
<td><strong>Analytical Capabilities</strong></td>
</tr>
<tr>
<td>Primary beam</td>
</tr>
<tr>
<td>Secondary beam</td>
</tr>
<tr>
<td>Spatial resolution</td>
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<tr>
<td>Sampling depth</td>
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<tr>
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</tr>
<tr>
<td>Detection Limit</td>
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<td>Organic/inorganic</td>
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*No one analytical technique provides all the answers.*