Principle and Application of FT-IR

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Safety:

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

Acknowledgment:

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

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Outline

- Chemical bond and molecular vibration
- Instrumentation
- Data interpretation
- Methods
Why FT-IR?
Molecular Vibration-1

Covalent bond is not static.
Molecular Vibration-2

Stretching
(The bond length changes)

Bending
(The bond angle changes)
Spring Model of Chemical Bond

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

- Spring between two spheres
- Heteronuclear diatomic molecules: HCl, CO Infrared active
- Homonuclear diatomic molecules: O₂, H₂, N₂, and Cl₂ Infrared inactive
Bond Vibration Frequency

1. for a stronger bond (larger $k$ value), wave number increases.
   
   As examples of this, in order of increasing bond strength compare:
   
   **CC bonds**: C-C (1000 cm$^{-1}$), C=C (1600 cm$^{-1}$) and C≡C (2200 cm$^{-1}$),
   
   **CH bonds**: C-H (2900 cm$^{-1}$), C=C-H (3100 cm$^{-1}$) and C≡C-H (3300 cm$^{-1}$),

2. for heavier atoms attached (larger $m$ value), wave number decreases.
   
   As examples of this, in order of increasing reduced mass compare:
   
   C-H (3000 cm$^{-1}$)
   
   C-C (1000 cm$^{-1}$)
   
   C-Cl (800 cm$^{-1}$)
   
   C-Br (550 cm$^{-1}$)
   
   C-I (about 500 cm$^{-1}$)
Beer–Lambert Law

\[ A_T = \varepsilon_1 b c_1 \]

- \( I_0 \) = Incident beam intensity
- \( I \) = Transmitted beam intensity
- \( A \) = Absorbance = \(- \log_{10} \frac{I}{I_0} \)
- \( b \) = Optical path length
- \( c \) = Solution Concentration (M/L)
- \( \varepsilon \) = Molar Absorptivity (L/M cm)

\[ A = \log_{10} \frac{100}{\%T} \]

\[ \%T = 100 \cdot \frac{I}{I_0} \]
Exploring the inner space…

Dispersive IR spectrometer

Data collection is very time consuming.
The Michelson interferometer produces interference fringes by splitting a beam of monochromatic light so that one beam strikes a fixed mirror and the other a movable mirror. When the reflected beams are brought back together, an interference pattern results.
Interference of Two Beams of Light
Interference Is a Superpositioning of Waves
Data Collection

S/B for transmittance
S-B for absorption
Location of Peaks in an IR Spectrum

Two General Regions in an IR Spectrum:

> 1400 cm⁻¹
Functional Group Region

< 1400 cm⁻¹
Fingerprint Region
Regions of FT-IR Spectrum

- Single bond stretch
- Triple bonds
- Double bonds
- Fingerprint region skeletal vibrations
- Bend
- Rock
Sample IR Spectrum

- 2785 cm⁻¹ CH₂ sym stretch
- 2850 cm⁻¹ CH₂ asym stretch
- 1485 cm⁻¹ CH₂ scissor
- 1250 cm⁻¹ CH₂ rock
- 1165 cm⁻¹ CH₂ wag
- 1750 cm⁻¹ C=O stretch
Sample IR Spectrum
Guide to Analyzing an IR Spectrum

2-methyl-1-pentene

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2-propyn-1-ol

Wavenumber (cm$^{-1}$)

4000 3000 2000 1500 1000 500

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acrylamide
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ethyl benzyl ketone

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How could you use IR to differentiate $\text{C}_4\text{H}_8\text{O}_2$ isomers?
Signal Intensity in an IR Spectrum

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

- most polar: $\text{O-H}$
- most intense
- $\text{O-C}$

- least polar: $\text{C-H}$
- least intense

$\text{N-H}$
Signal Intensity in an IR Spectrum

An alkene C=C stretch generally appears $\sim 1650$ cm$^{-1}$. 

Asymmetric

1-heptene

Symmetric

3-heptene
Transmission Mode

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

<table>
<thead>
<tr>
<th>Crystal/Material</th>
<th>$n_0$</th>
<th>LWL, cm$^{-1}$</th>
<th>$d_p$ (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond/ZnSe</td>
<td>2.4</td>
<td>525</td>
<td>2.00</td>
</tr>
<tr>
<td>Germanium</td>
<td>4.0</td>
<td>780</td>
<td>0.66</td>
</tr>
</tbody>
</table>

$n_0 =$ refractive index of ATR crystal
LWL = long wave length cut-off
$d_p =$ depth of penetration in microns @ 1000 cm$^{-1}$ assuming sample refractive index of 1.5 and 45 degree angle of incidence.
ATR-2

Advantages:

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

Sample: Powder, Film, liquid
Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

What are the advantages of diffuse reflectance?

- **Little to no sample preparation** – just place in the sample cup
- **Fast and easy cleanup** – dump the cup and blow or rinse clean
- **No need for pressed KBr pellets or messy mulls** – samples can be run neat or diluted with KBr powder
Spectra of Trehalose with DRIFT mode
Polarization-Modulation Infrared Reflection-Absorption Spectroscopy (PM-IRRAS)
Micro FT-IR – Bruker LUMOS
Identify Unknown Substance

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Mapping
Library Search

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Summary

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

Questions?