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Molecular Spectroscopy: Polymer Analysis

Using FTIR, NIR and Raman

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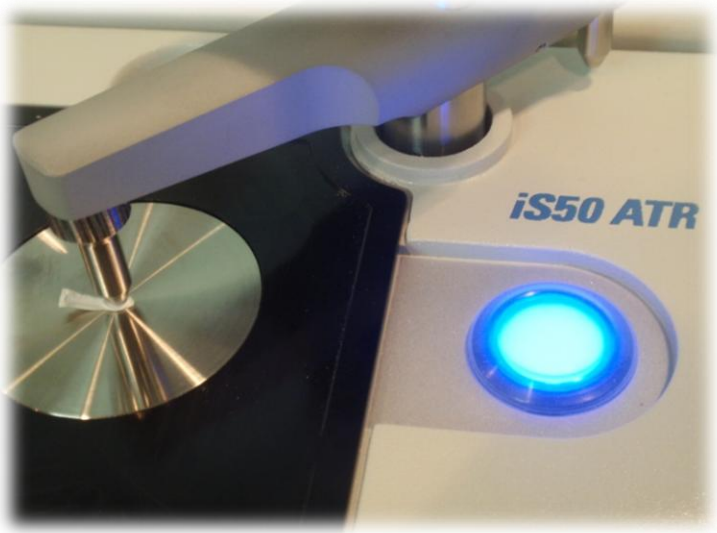
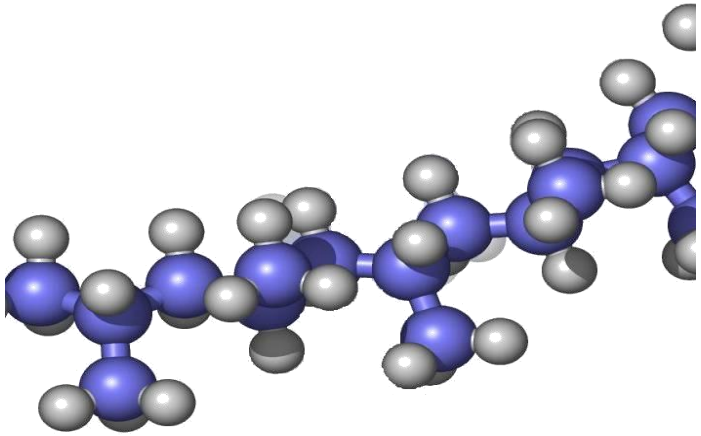
August 9, 2012

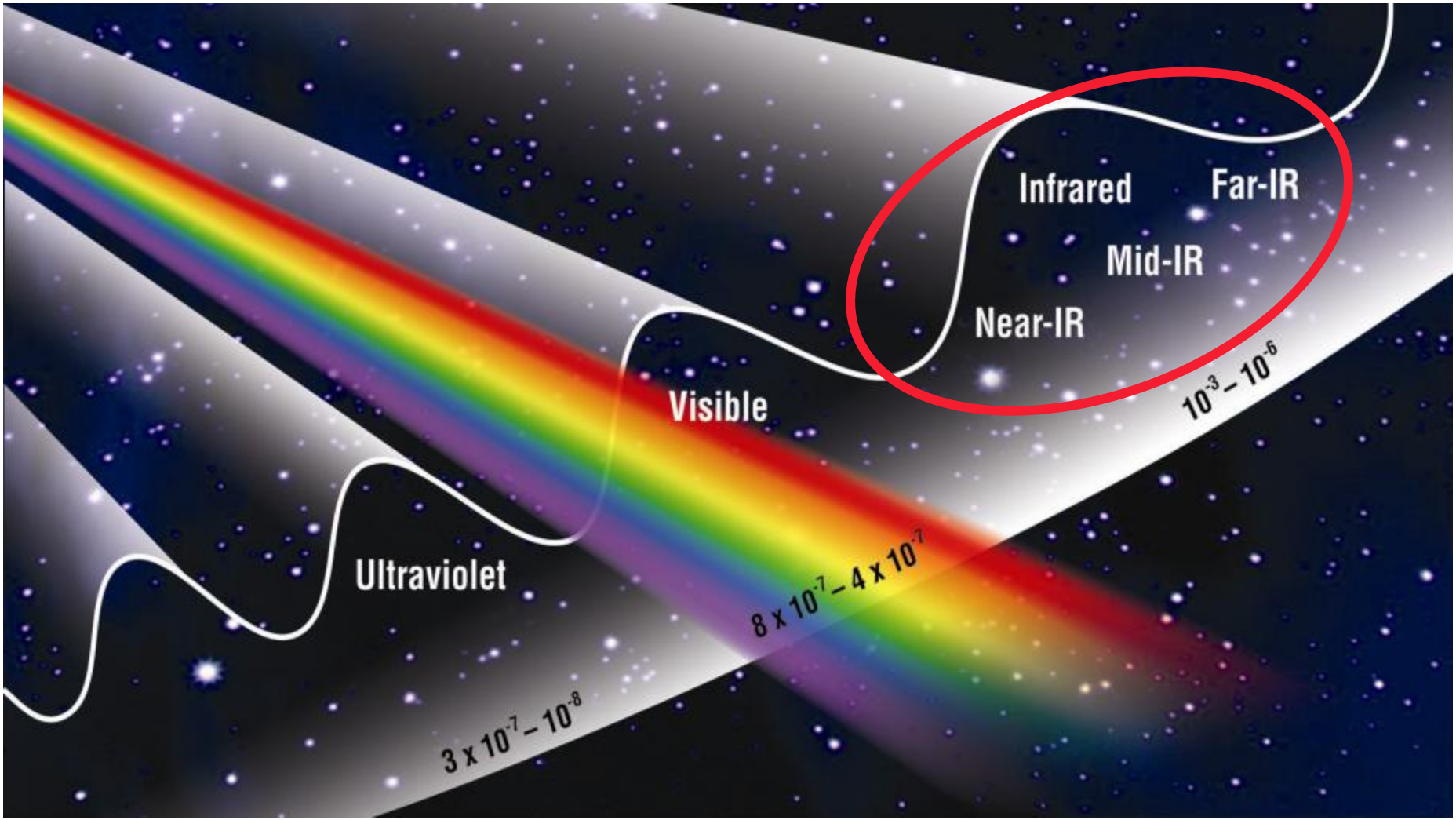
Outline of Polymer Analysis

- **Review of vibrational spectroscopy**
  - Infrared
  - Raman
- **Instrumentation**
  - Is50 with diamond ATR
  - Raman accessory
  - TGA and NIR modules
- **Polymer applications**
  - ATR into the Far IR
  - Raman for analysis and polymorphs
  - Near IR for Industrial Solutions
  - Formulation studies with TGA

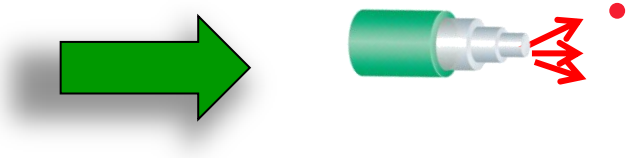




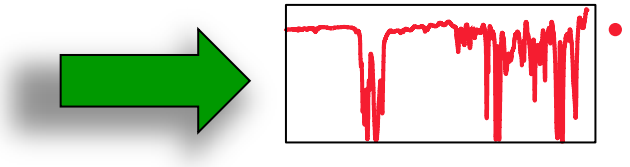
Transitions Guide to the EM Spectrum



Modes of Analysis with Molecular Spectroscopy



- **NIR**
  - Common in industrial applications
  - Deeply penetrating light



- **Mid-IR**
  - Most common type of molecular spectroscopy
  - Useful for most organic compounds

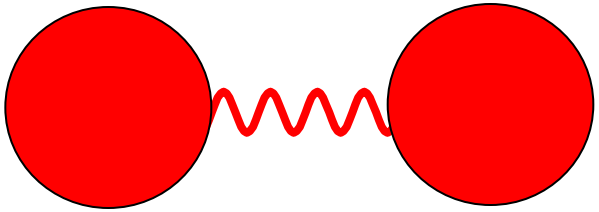
- **Far-IR**
  - Provides more information that mid-IR
  - Useful for inorganics and some organicc

- **Raman**
  - Complementary to infrared
  - Provides information when IR isn't suitable

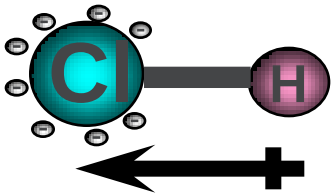
When Does a Material Absorb Infrared Light ?

- The frequency of the light must be identical to the frequency of the vibration (resonance)
  - Higher Frequency

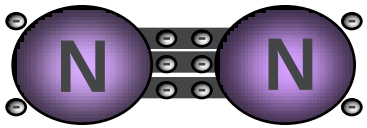
  - Lower Frequency



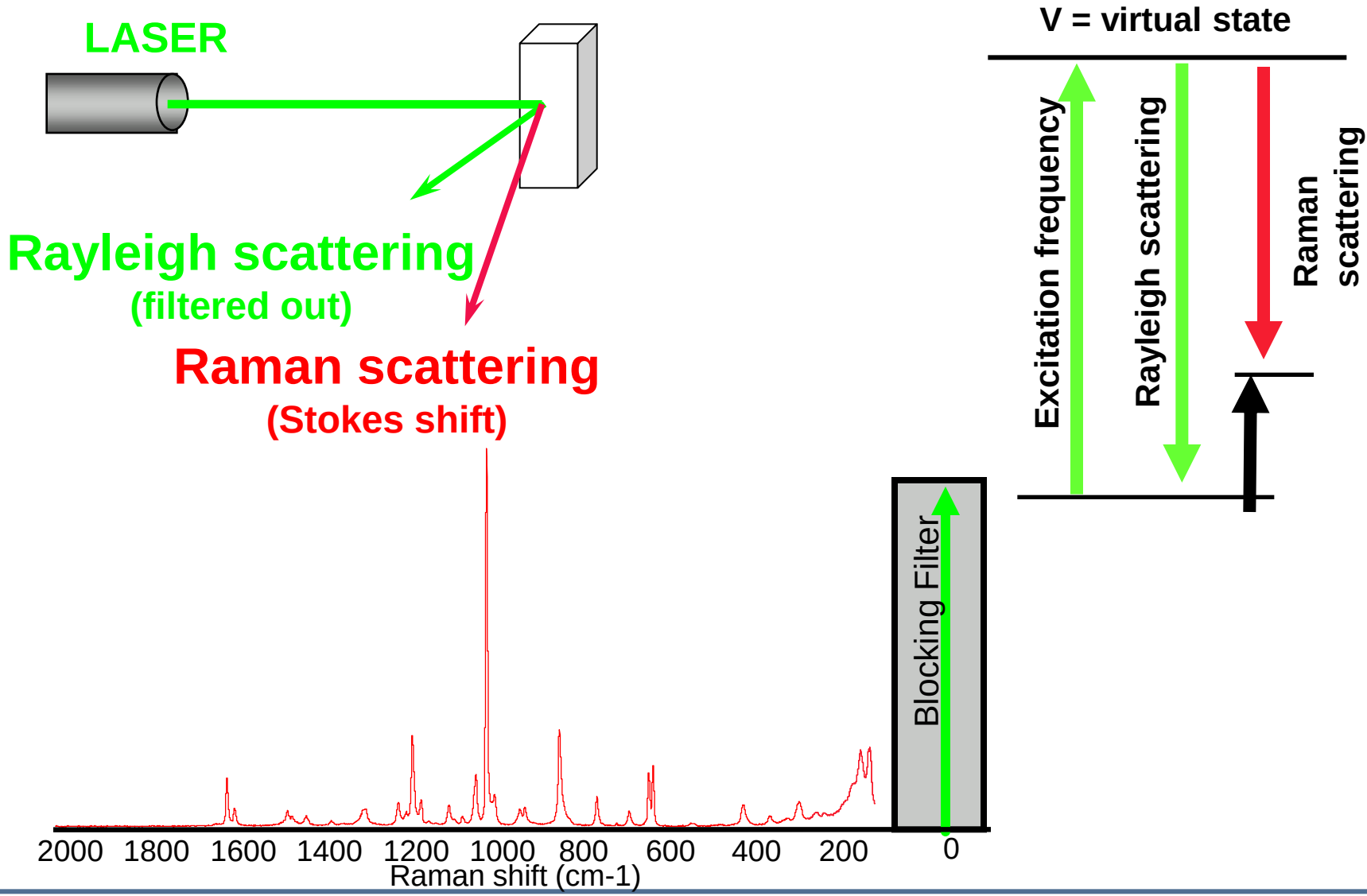
- The dipole of the molecule must change during the vibration
  - Strong Absorbance



  - No Absorbance



Raman Spectroscopy – The Raman Effect



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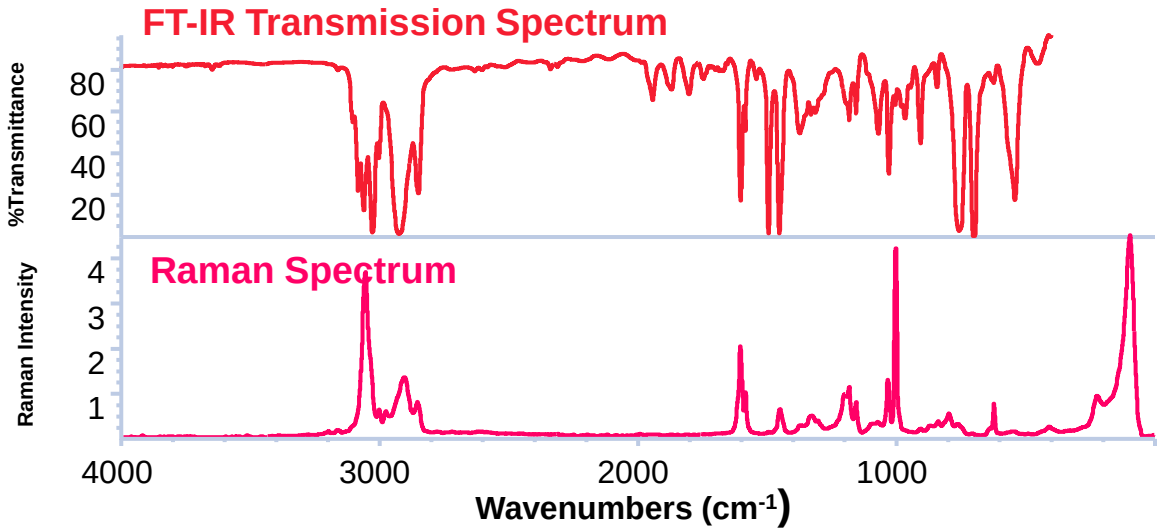
Raman Compared with Infrared

- Complementary information
  - Functional groups dominant in Infrared spectrum
  - Molecular backbone dominant in Raman spectrum
    - Raman often useful for characterizing morphology
  - Weak IR absorbers often strong Raman emitters and vice versa
    - Aqueous solutions pose fewer challenges with Raman



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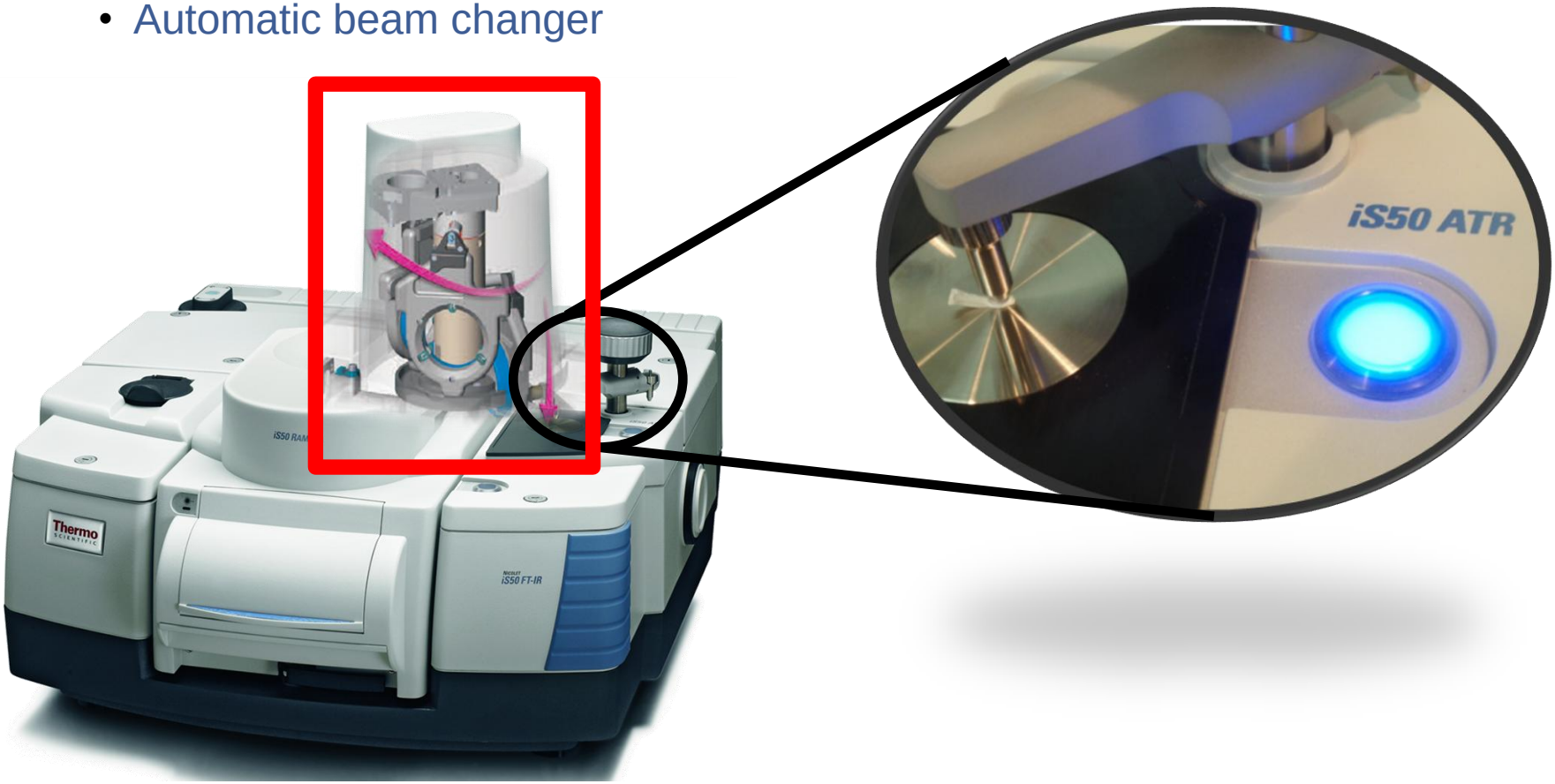
Instrumentation

Instrumentation

- Nicolet iS50
  - Diamond ATR
  - Raman in accessory compartment
  - Automatic beam changer



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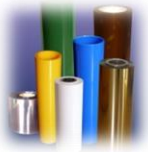
Instrumentation

- Nicolet iS50
  - NIR module
  - TGA module



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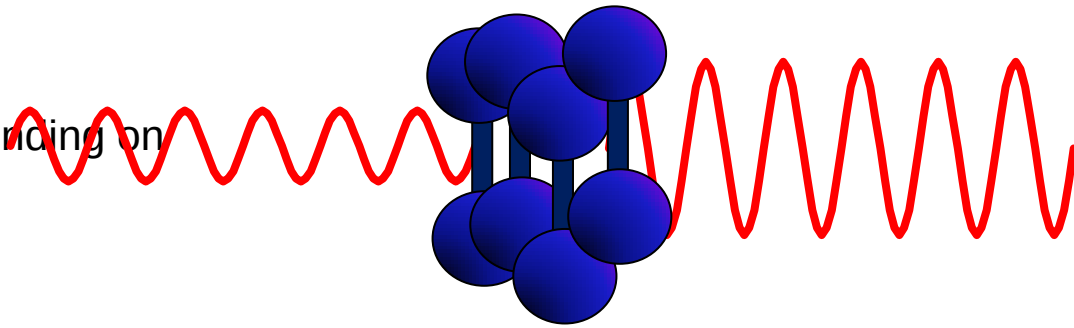
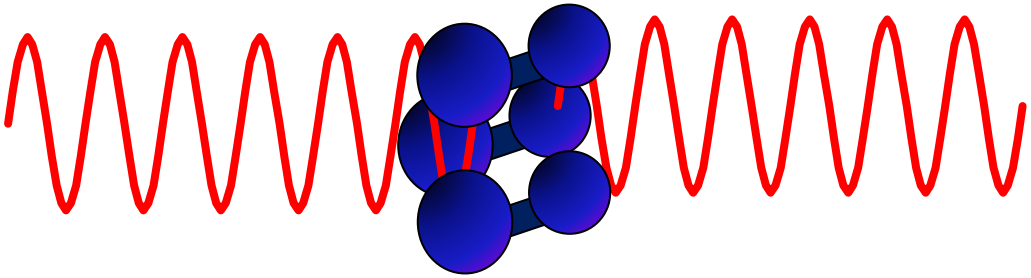
Polymer Orientation Studies

Polymer Orientation Studies

- Polymers are often stretched along an axis
  - IR absorption is sensitive to the orientation of the molecules
  - Different spectra are obtained depending on molecular bond orientation

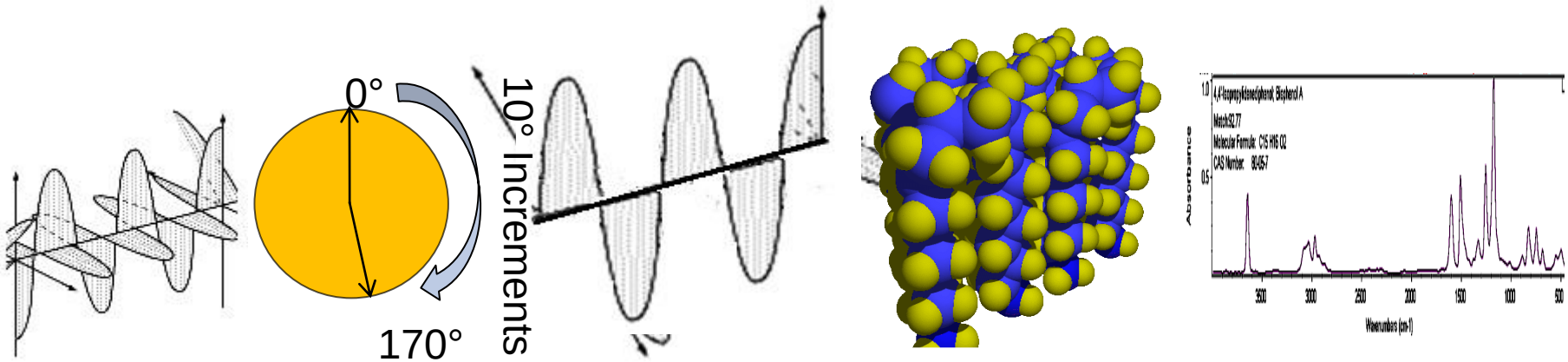


- FT-IR is used in the polymer industry
  - To do polarization studies
  - Determine crystallinity

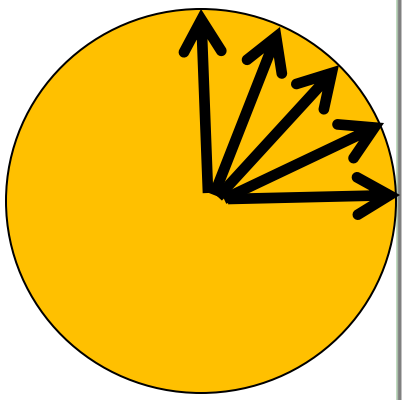


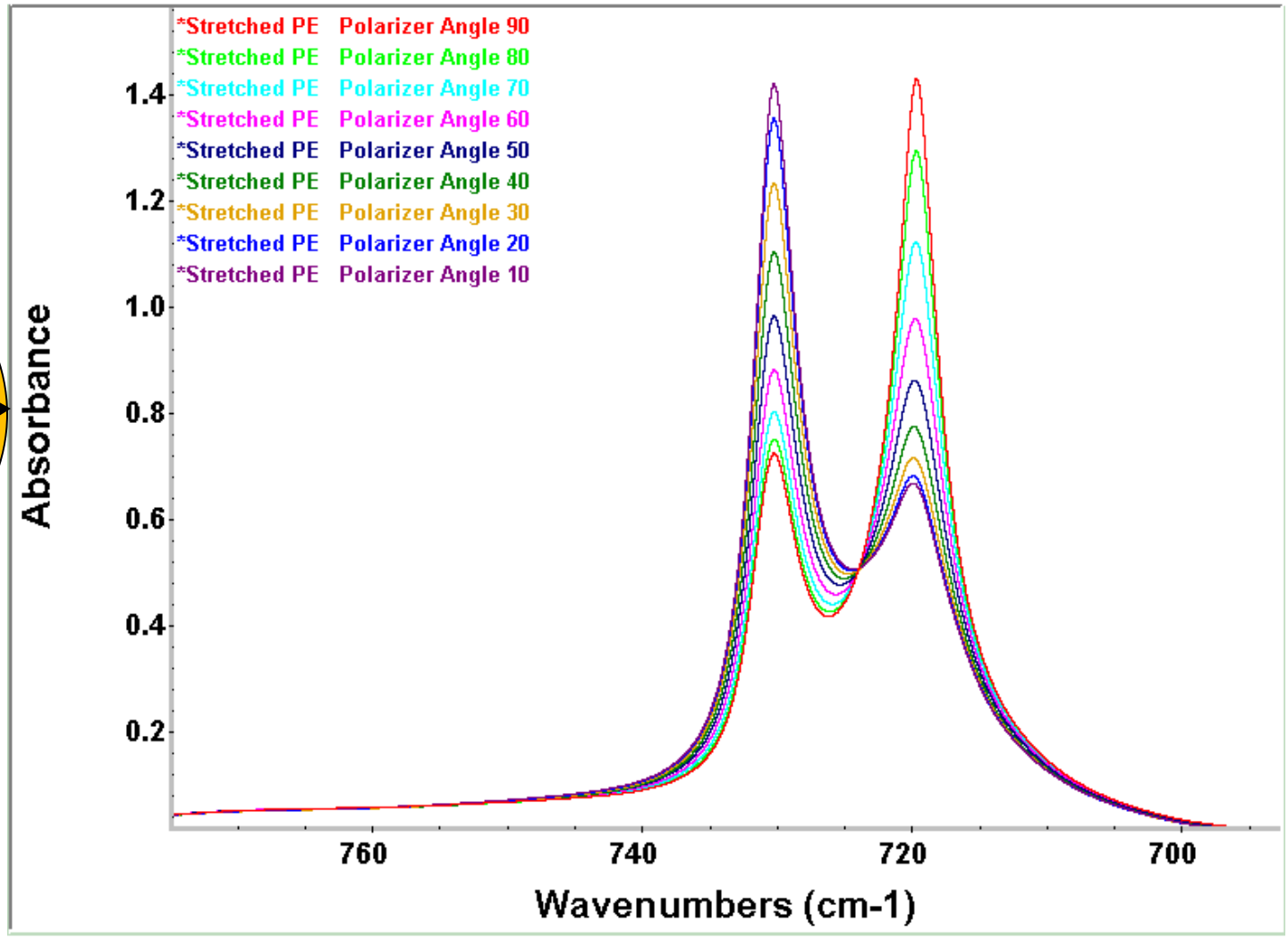
Polymer Orientation Studies

- Stretched Polyethylene film placed in instrument
- Polarizer automatically moved into beam path and rotated during data collection
- Series of spectra show changes in absorption as polarizer is rotated



Polymer Orientation Studies (FT-IR)





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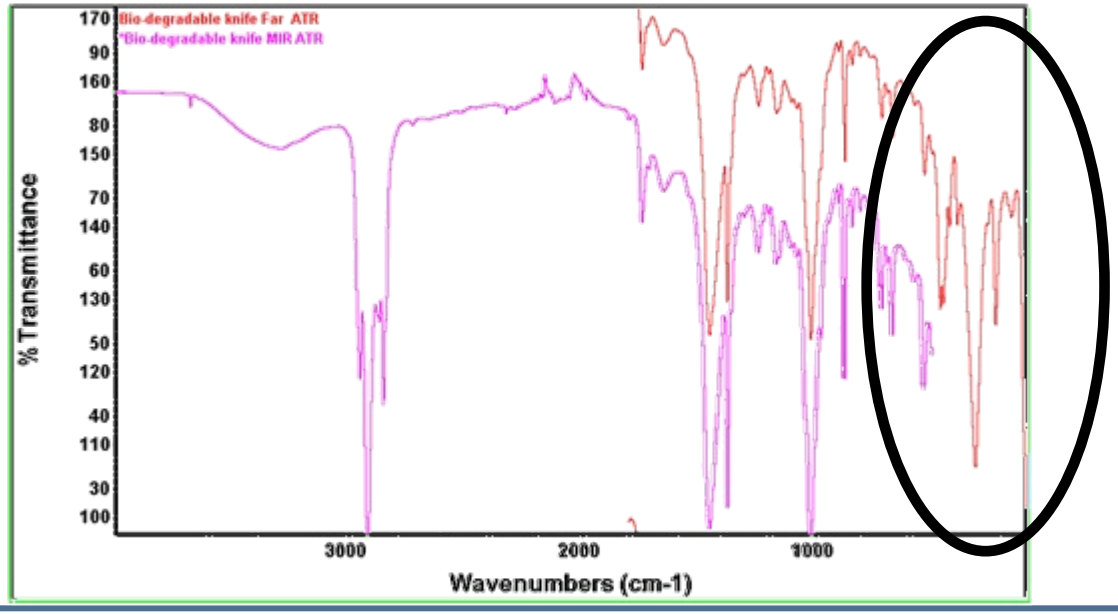
Far-IR: Extended Range

When Mid-IR isn't enough

Far-IR: Extended Range

- Infrared Spectroscopy
  - Generally encompasses 4000cm^{-1} to around 600cm^{-1}
    (wavelength 2.5 microns to 20 microns)
  - Limited by the detector, lens and window material

- Far Infrared
  - Diamond allows longer wavelengths to pass through
  - Down to ~200cm^{-1} (50 micron wavelength)
  - Diamond ATR crystals and windows allow Far IR



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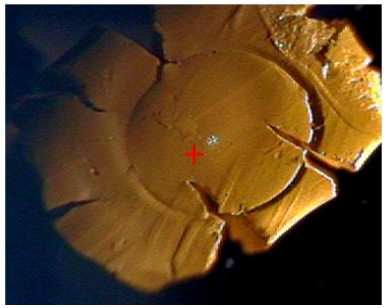
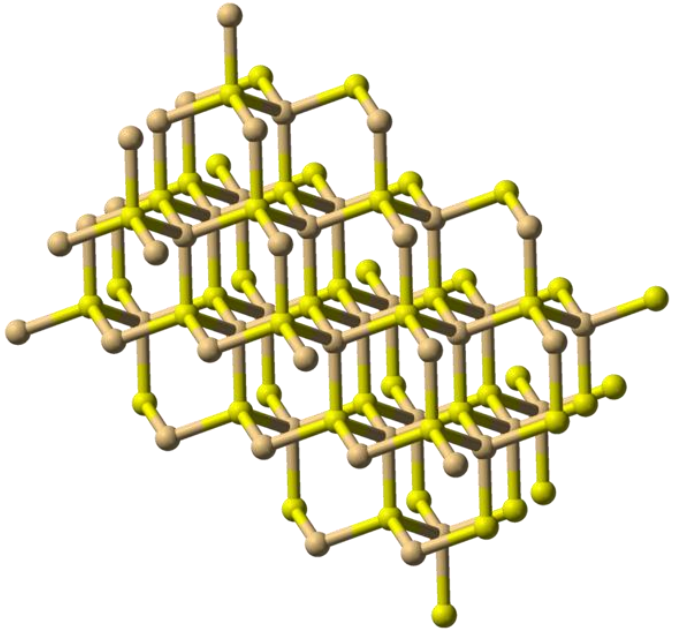
Far-IR: Extended Range

- Polymer additives and pigments are scrutinized for safety
  - Some pigments are banned because they are heavy metals (lead, cadmium)
  - Often these pigments have no mid-IR signature
  - Can be detected with Far-IR

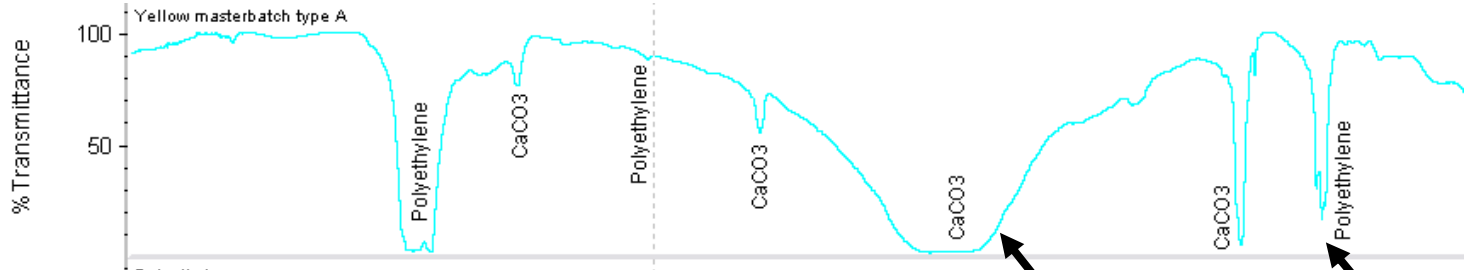
- Yellow pigmented polymer was obtained from a supplier
  - It was suspected to contain the banned pigment CdS
  - Mid-IR analysis using an ATR didn't show anything unusual





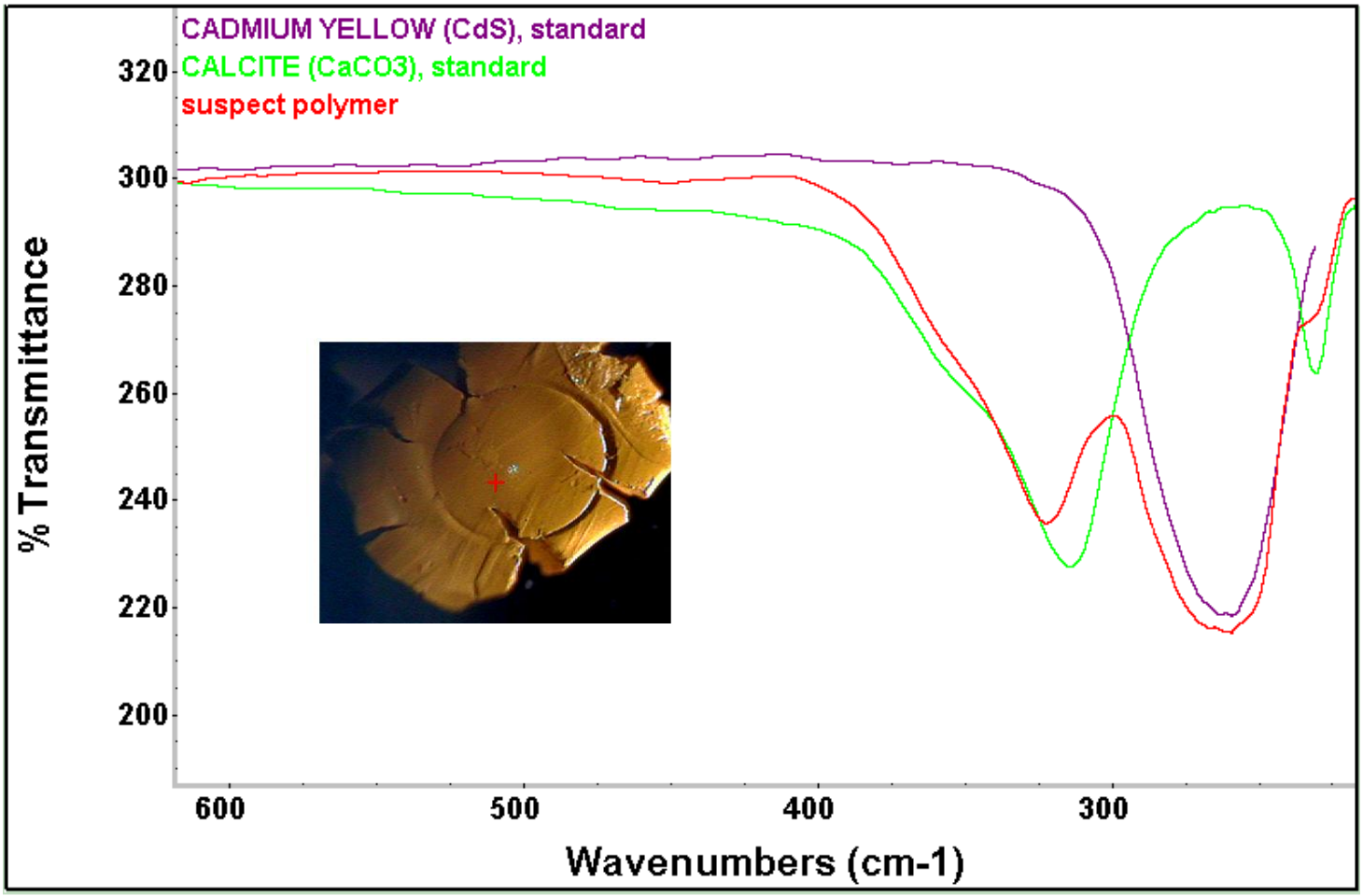
Far-IR: Extended Range

- Mid IR analysis
  - The spectrum shows spectral features of polyethylene and carbonated materials
  - There is <u>not enough information</u> to identify the yellow pigment composition



Far-IR: Extended Range

- Far IR using the diamond ATR
  - Shows that it contains cadmium pigment



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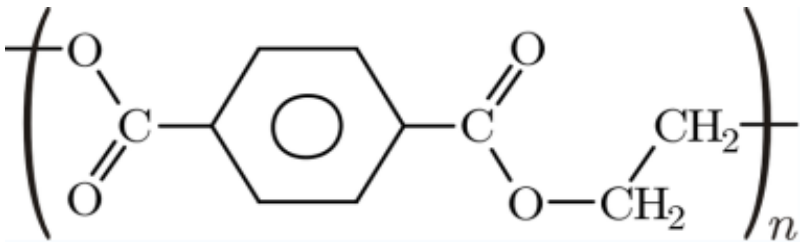
Raman in Conjunction with FT-IR

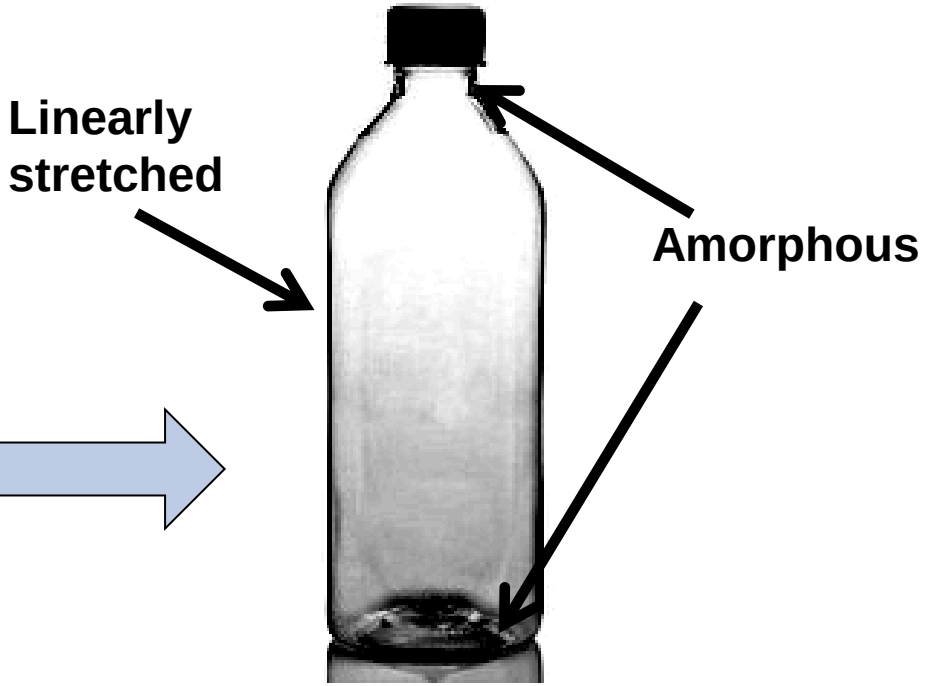
Raman complements infrared information with crystallinity, density and inorganics ID

Polymer Orientation Studies

- Polyethylene terephthalate (PET) used in making bottles

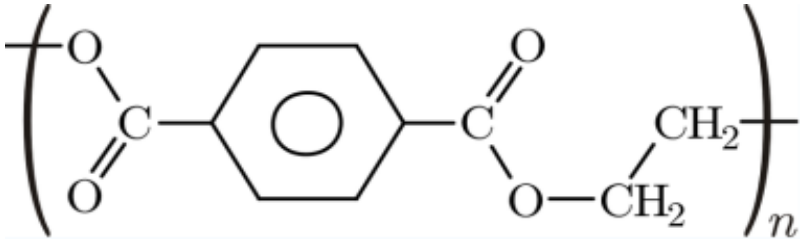


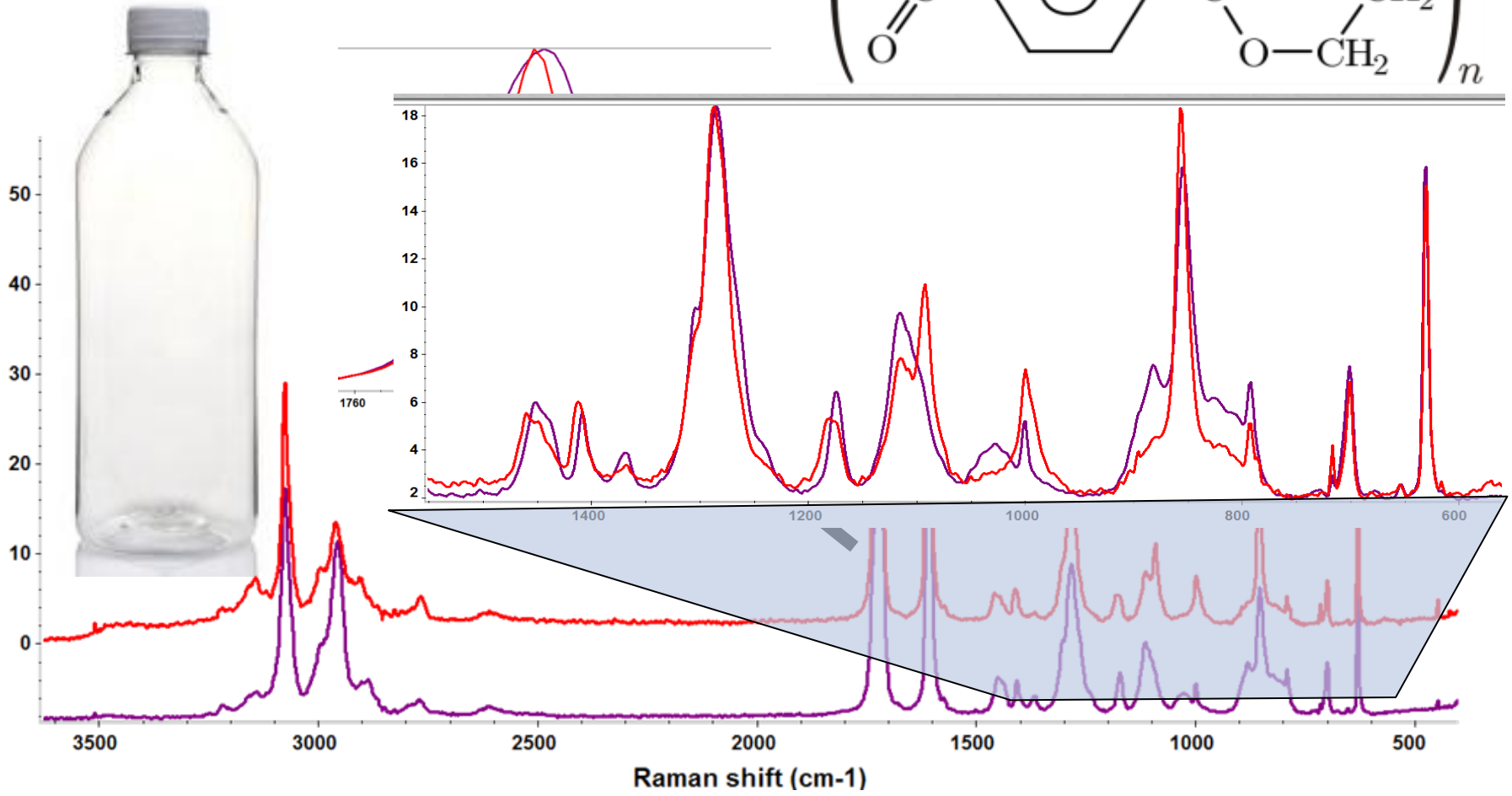
- Thick walled blanks are heated and blown into a mold
- The PET molecules in the sides of the bottle become stretched and linearly aligned



Polymer Orientation Studies (Raman)

Bottle side: Crystalline (PET)
Bottle Top: Amorphous (PET)





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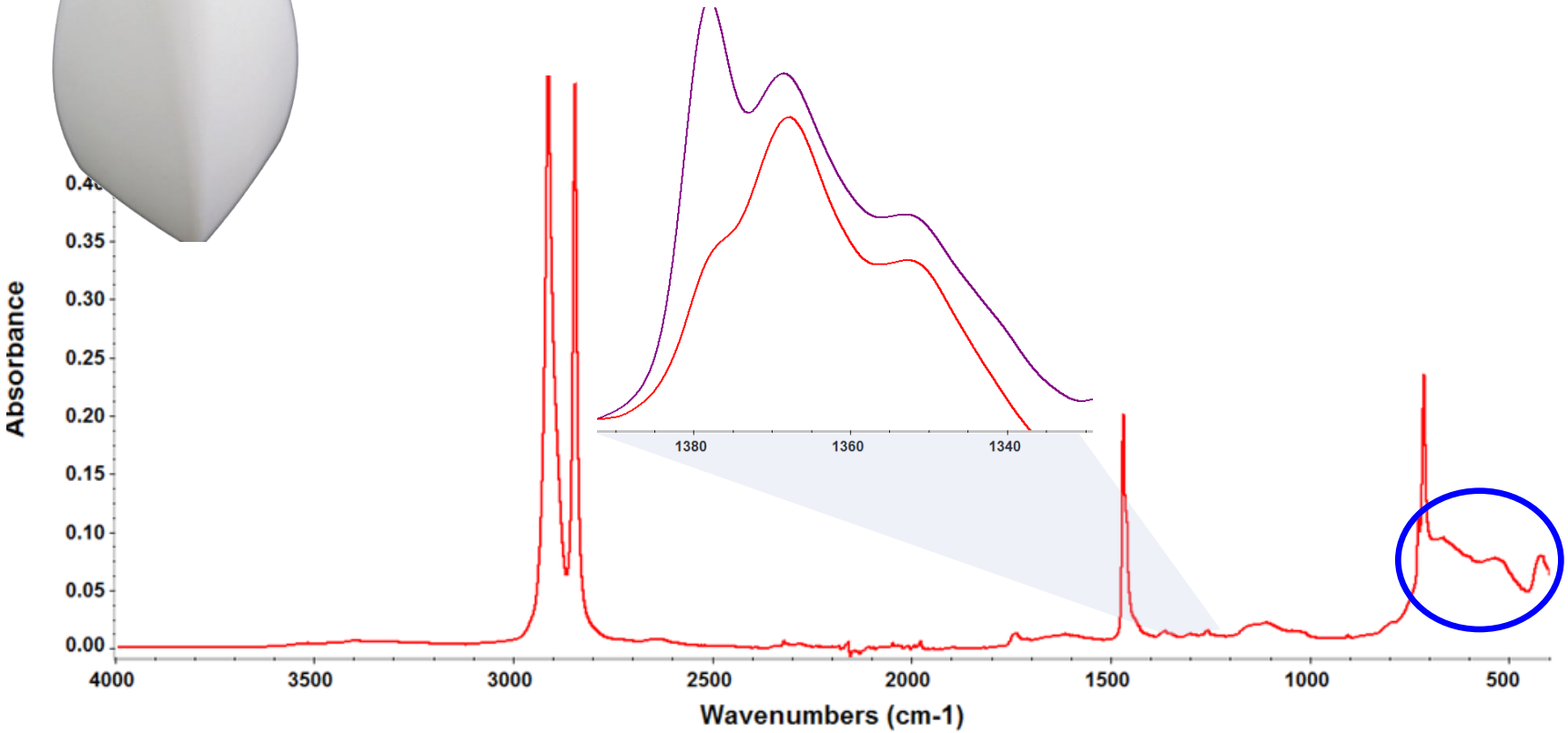
Raman complements FT-IR

- Mid infrared ATR
  - …Reveals the material being high density polyethylene, with “inorganic filler”



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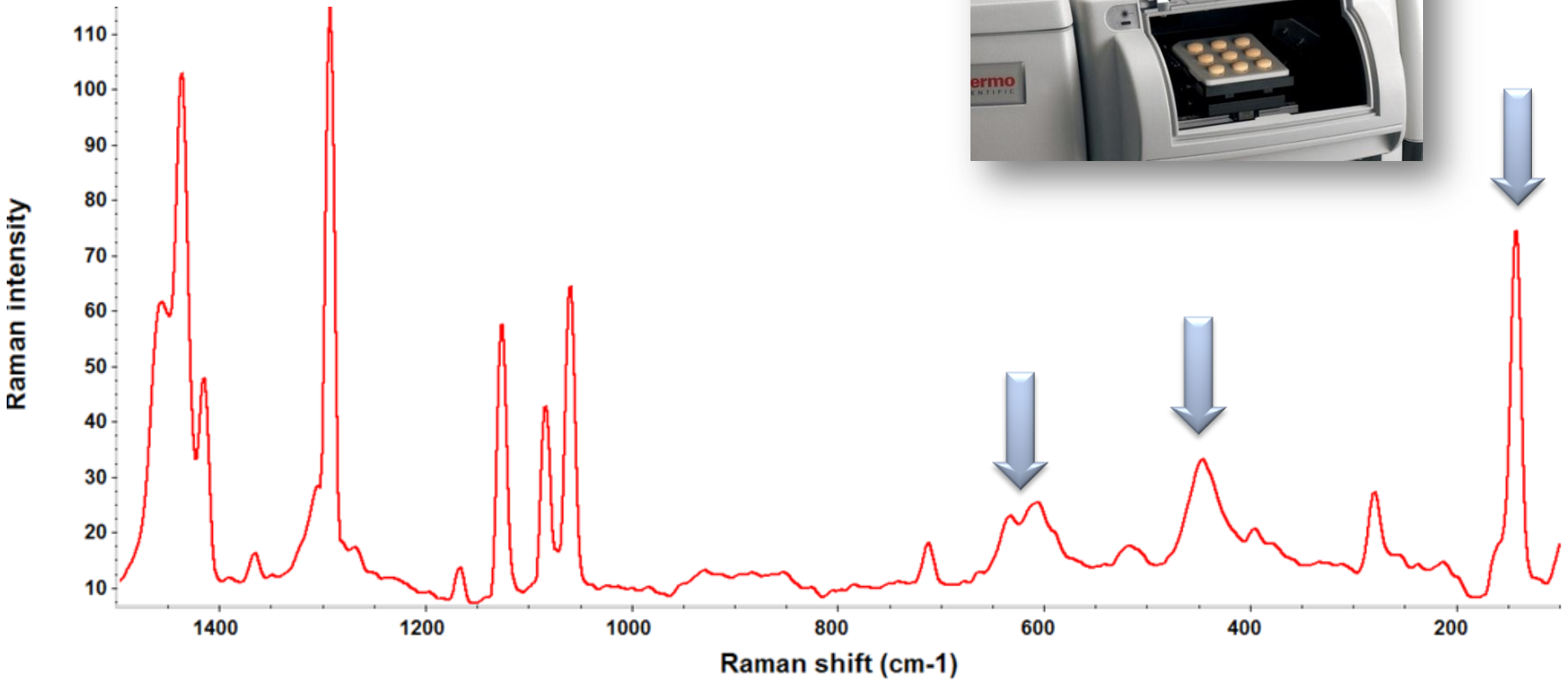
Raman complements FT-IR

- Same sample place in Raman module
  - Unique peaks show information on additives
  - Data combined with FT-IR gives a more complete picture of the material



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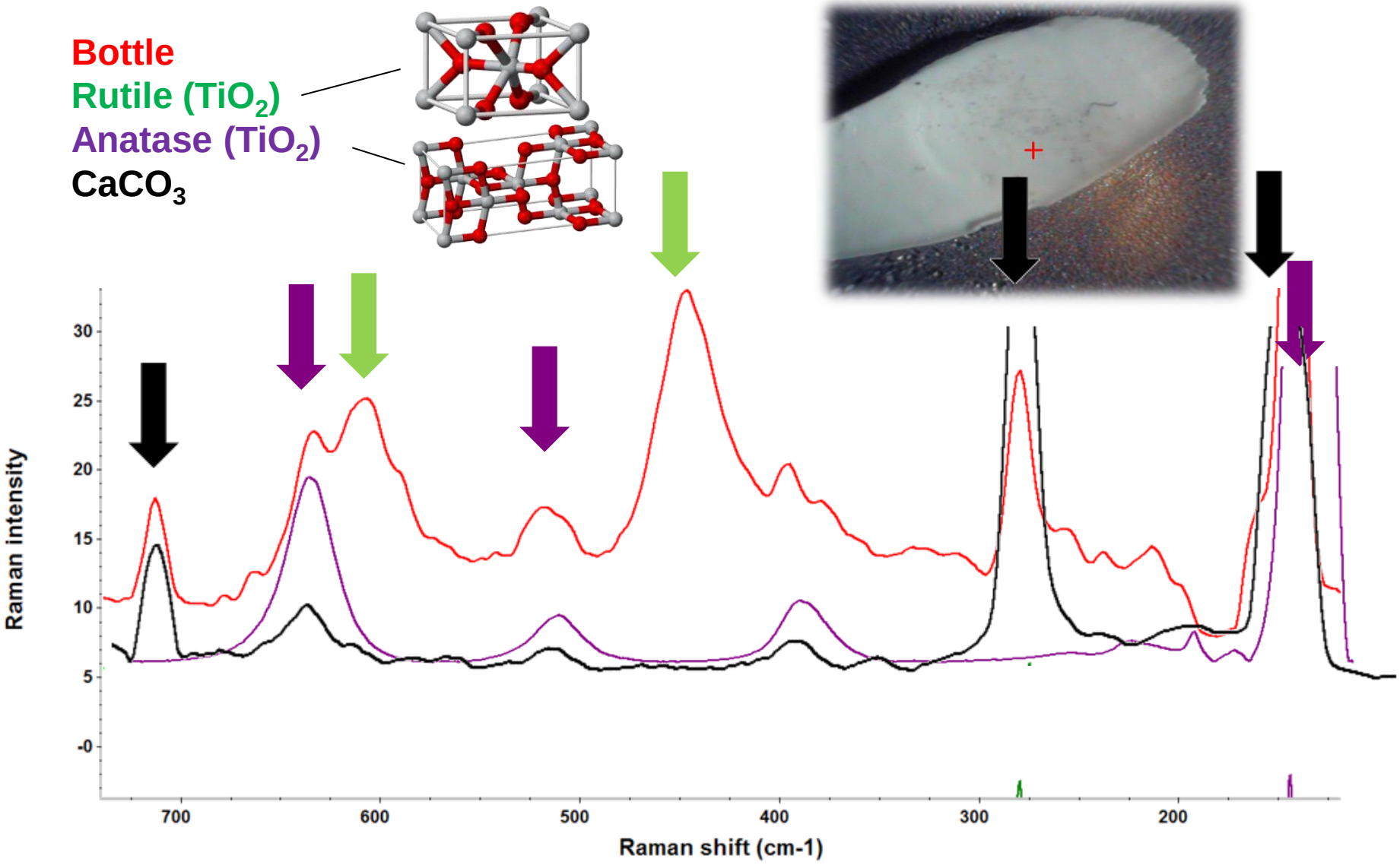
Raman complements FT-IR



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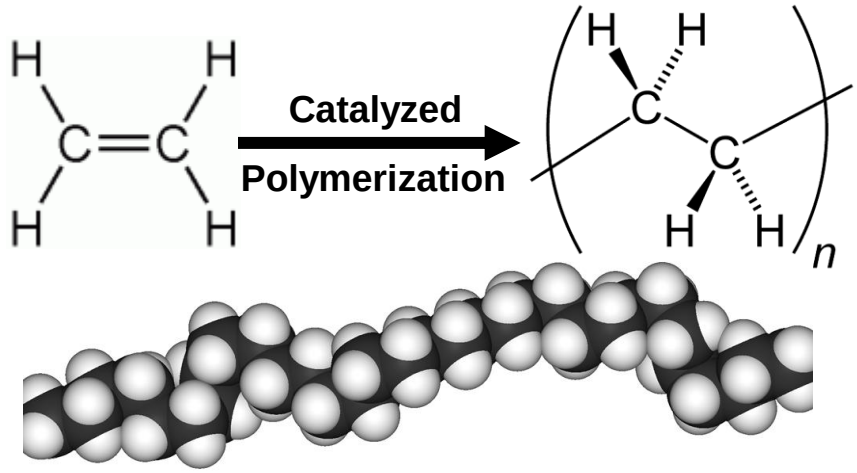
NIR Raw Material Identification

Method development in process environments

NIR for Raw Material Identification

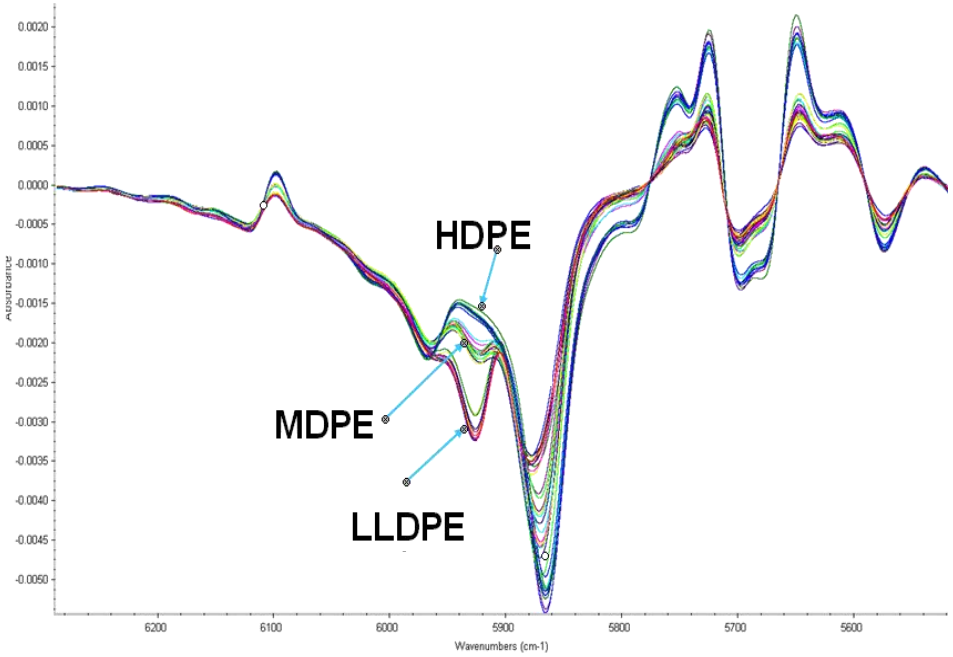
Polyethylene is often classified according to density, which in turn depends on numbers and size of side branches.

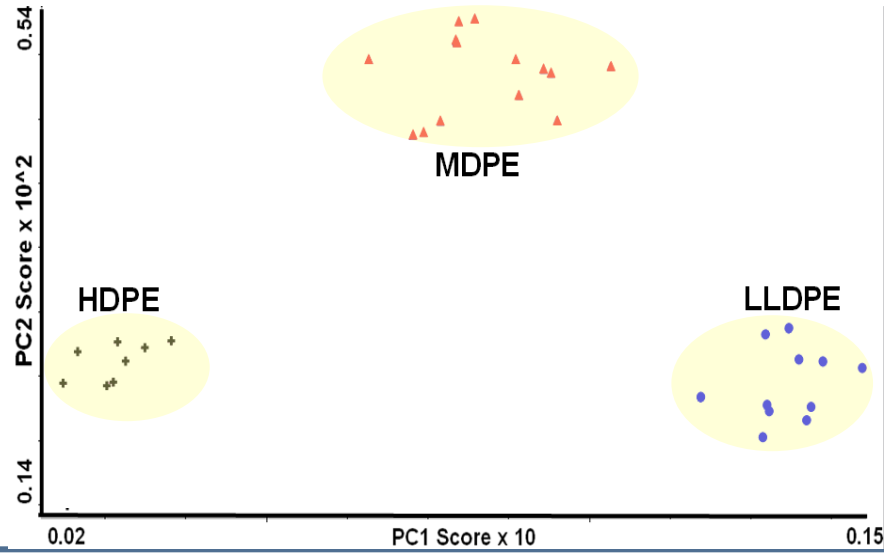
- Linear Low Density (LLDPE)
  - Large numbers of short branches
  - 0.915 – 0.925 g/cm^3
- Medium density (MDPE)
  - 0.926 – 0.940 g/cm^3
- High density (HDPE)
  - Very few branches
  - greater than 0.941 g/cm^3



NIR for Raw Material Identification

- NIR used for chemometric method development
- No sample preparation required
- Place sample on integrating sphere and get answer





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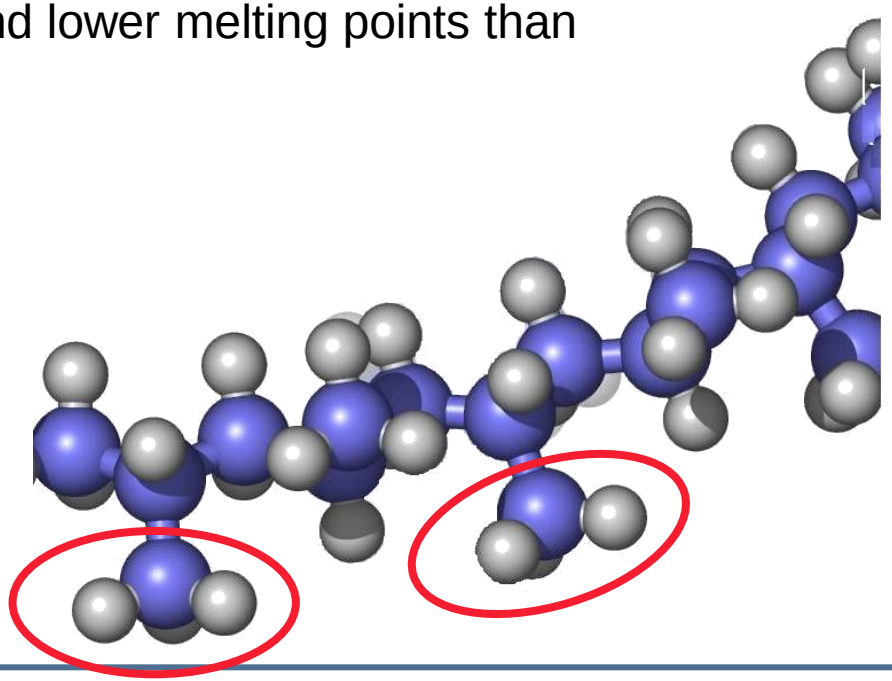
NIR for Raw Material Identification

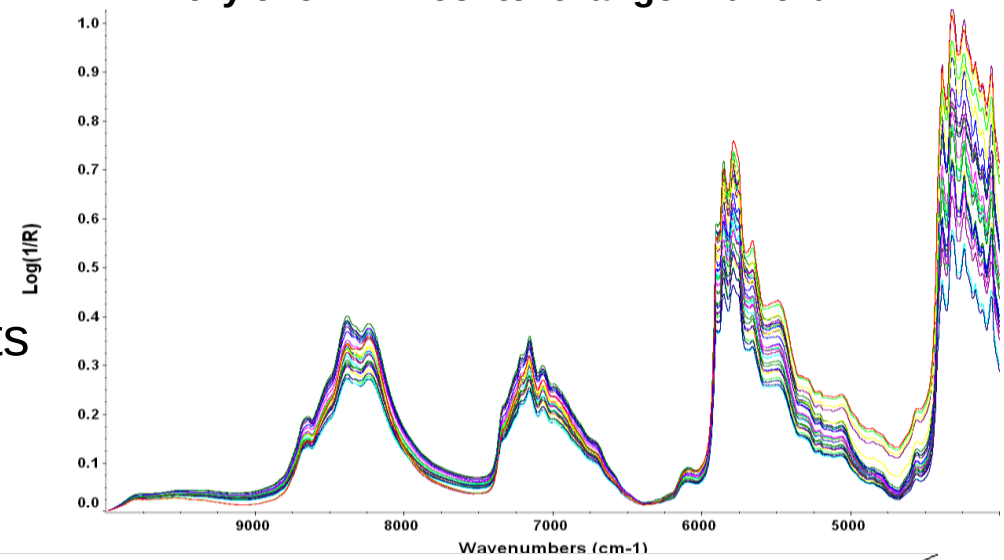
- Ethylene/Polypropylene Copolymers
  - Ethylene may be added in various amounts to propylene to form copolymer material
  - These copolymer materials exhibit high stiffness and impact strength
  - Additionally they have better clarity and lower melting points than polypropylene alone.

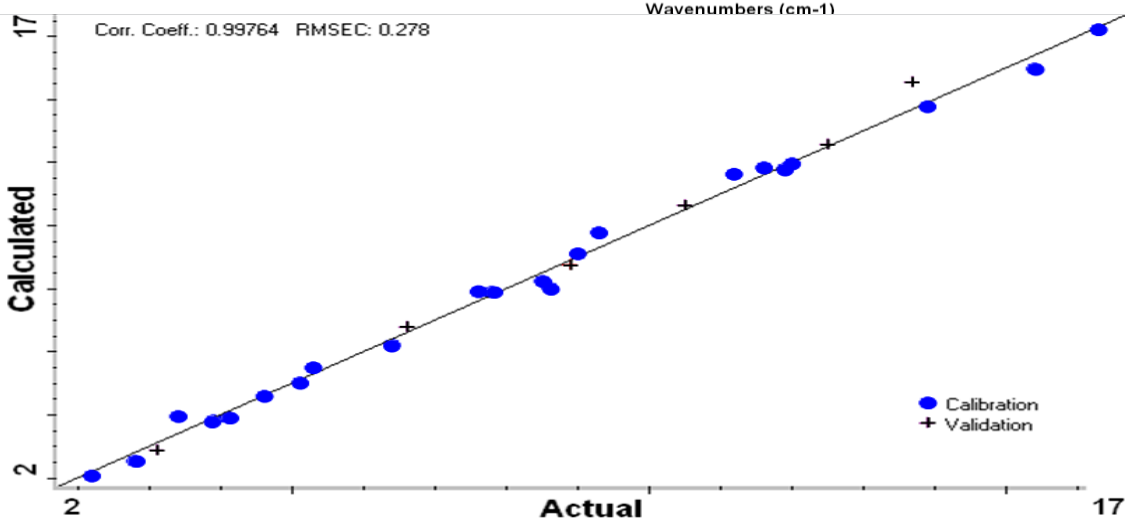


NIR for Raw Material Identification

- Quantitative results based on analyzing standard materials
- Method deployed into process plants using process instruments

Ethylene in PP content range 2%-16%





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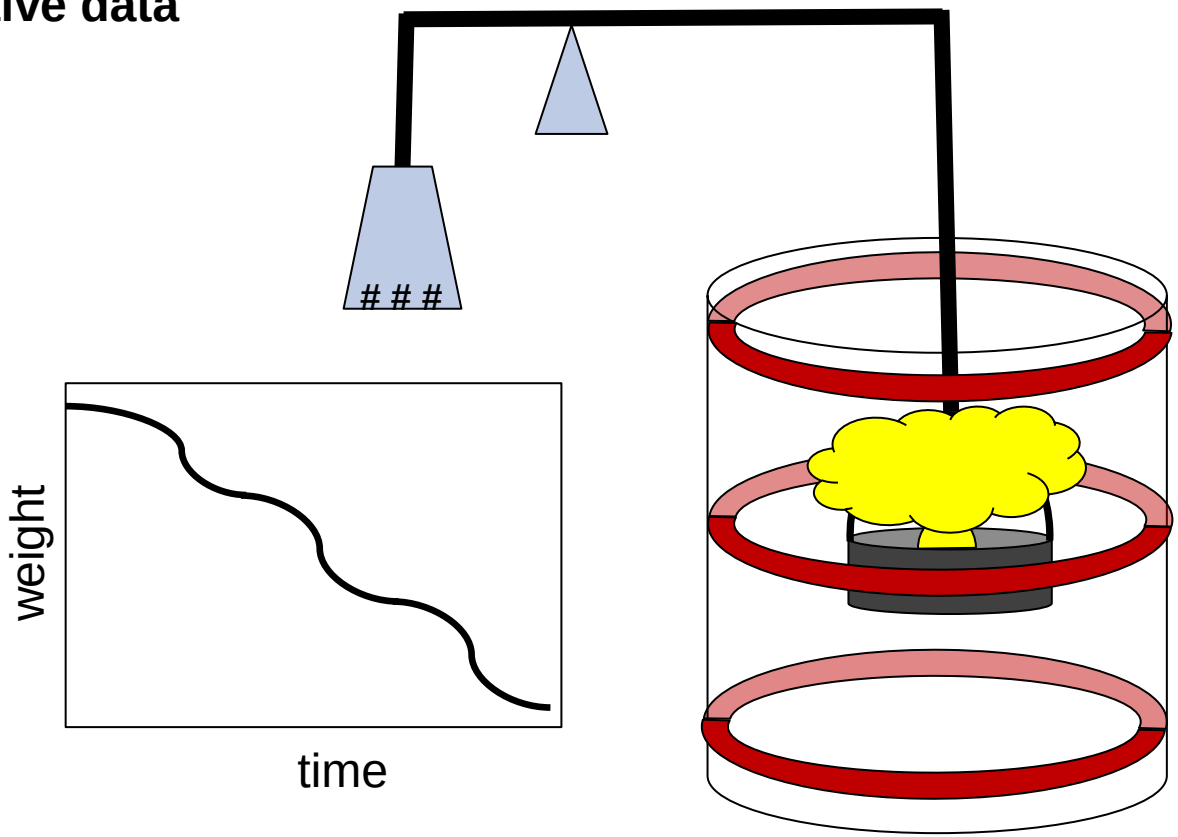
TGA-IR

The world leader in serving science

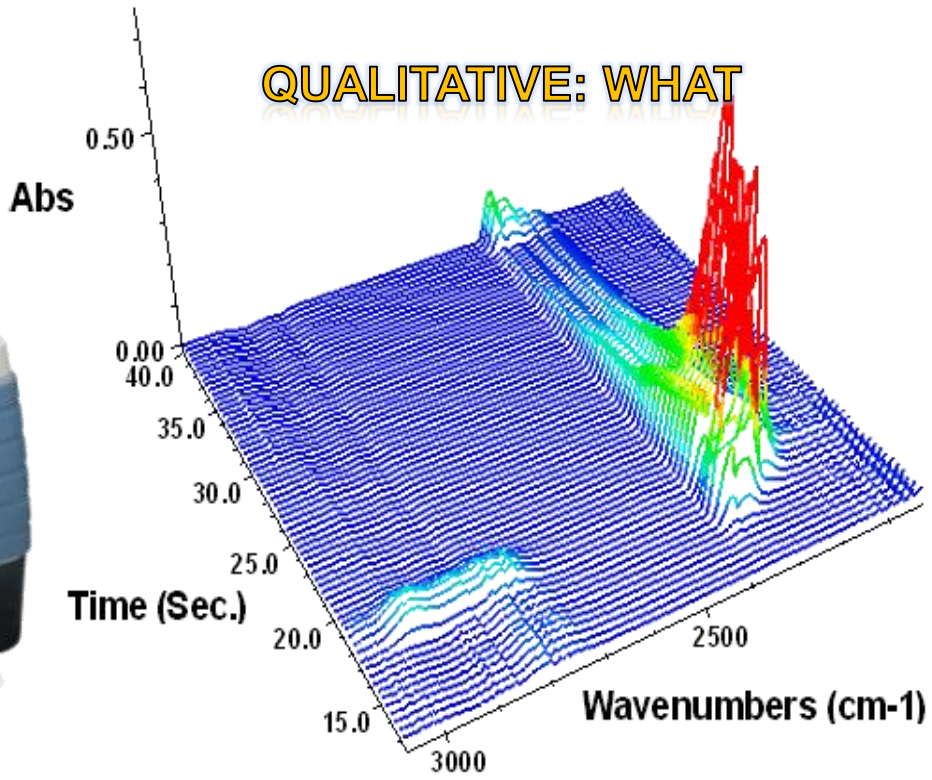
TGA IR

- TGA
  - Thermo Gravimetric Analysis (TGA)
  - The sample is precisely heated in a furnace
  - As the sample releases vapors, the weight loss is recorded
  - **Provides Quantitative data**



TGA IR

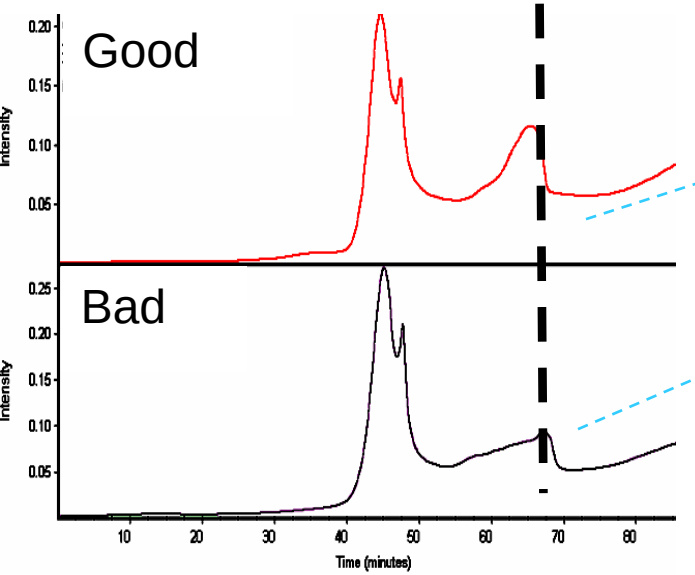
- TGA-IR
  - The vapor output of the TGA is coupled to an FT-IR gas cell
  - This allows the IR spectra of the vapors to be obtained
  - **Gives Qualitative Data**



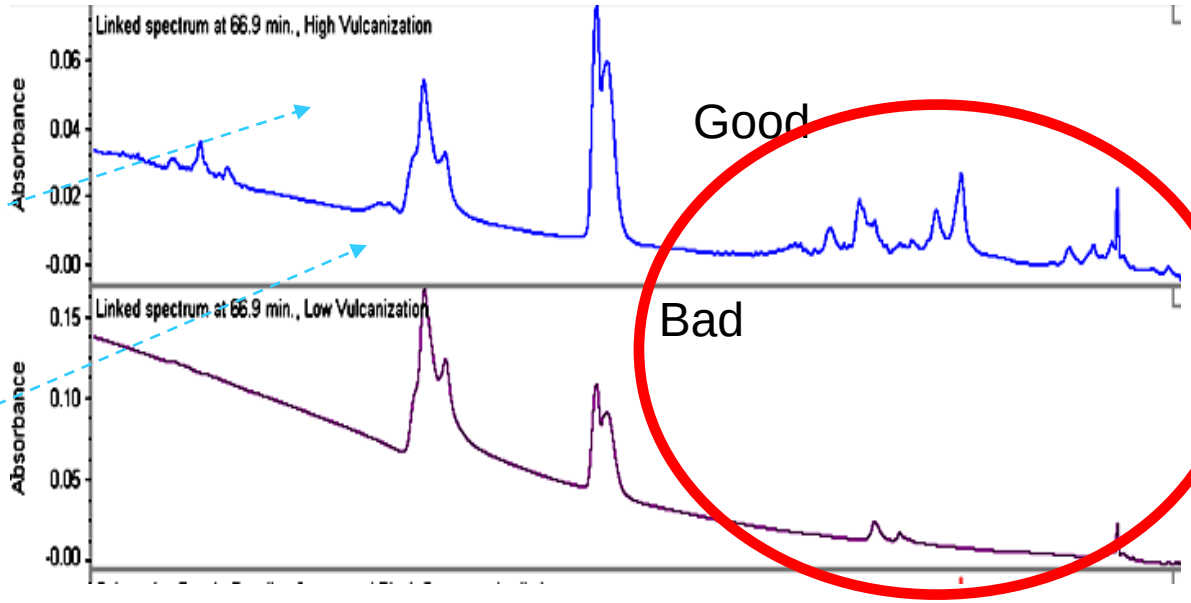
TGA IR

- Deformulation and Failure Analysis
  - Rubber gaskets were found to be failing in the field
  - TGA analysis of failing gaskets shows incorrect formulation

TGA



IR of vapor at 67 min



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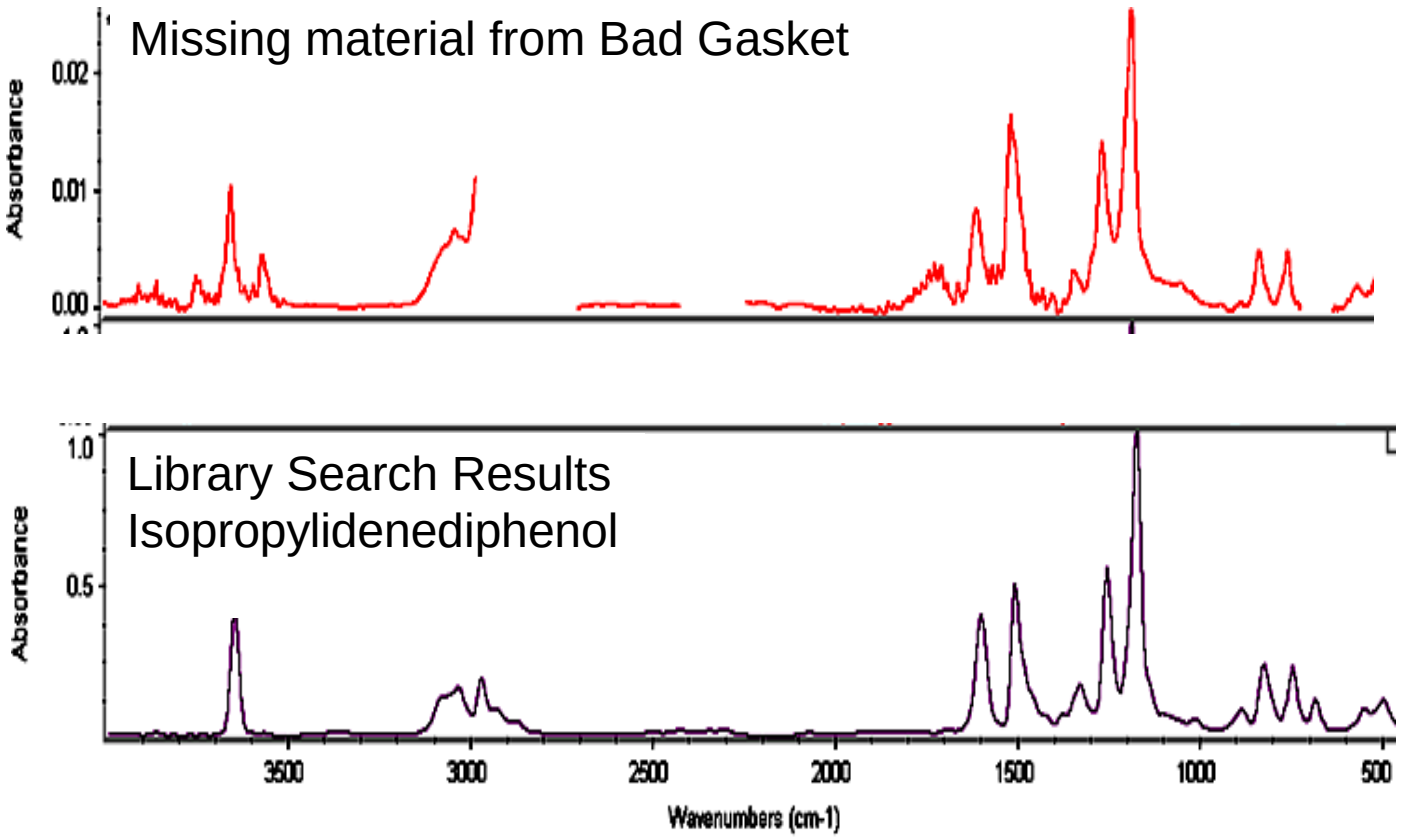
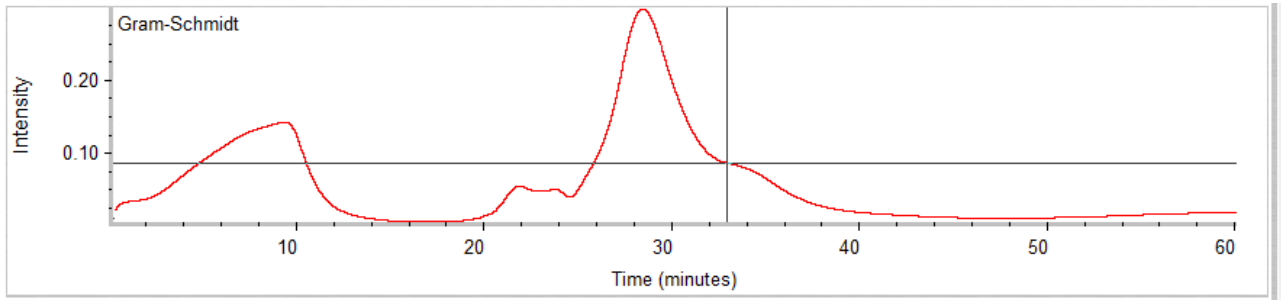
TGA IR

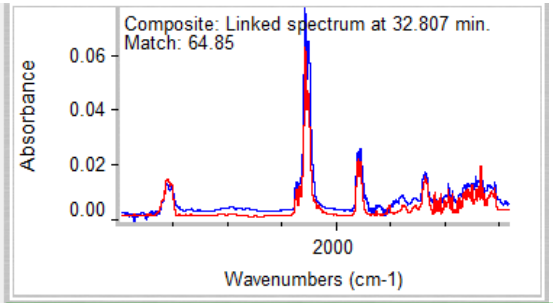
- Deformulation and Failure Analysis
  - Library search on the IR spectra
  - Shows incorrect formulation
  - Missing ingredient

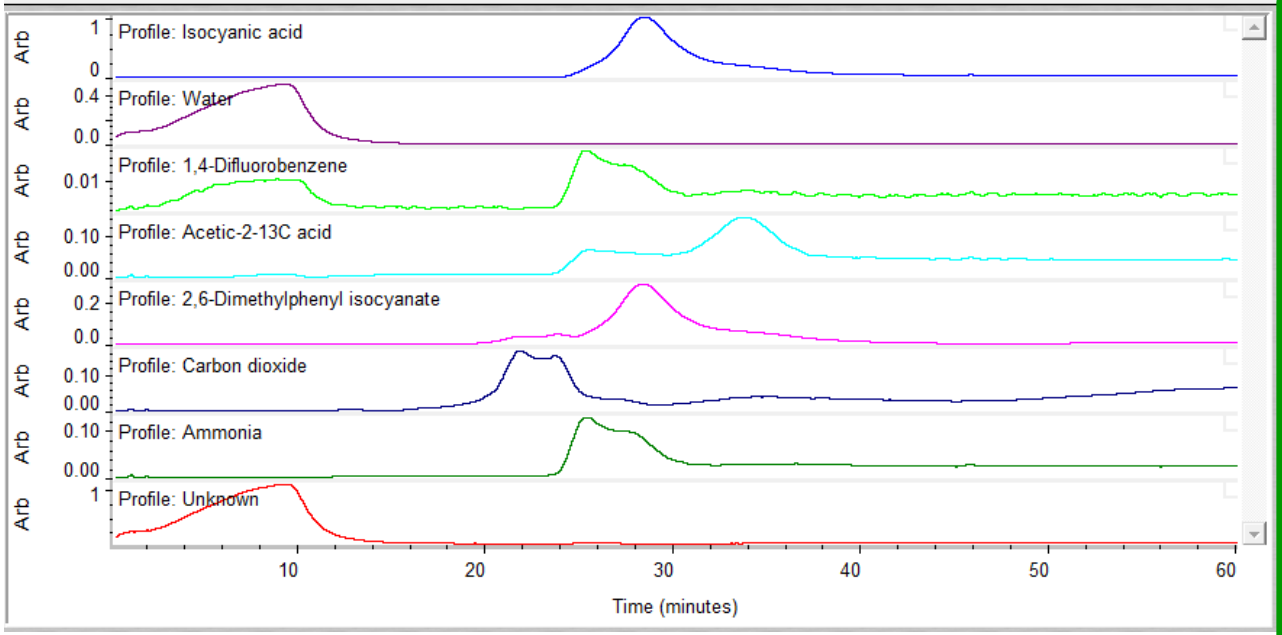


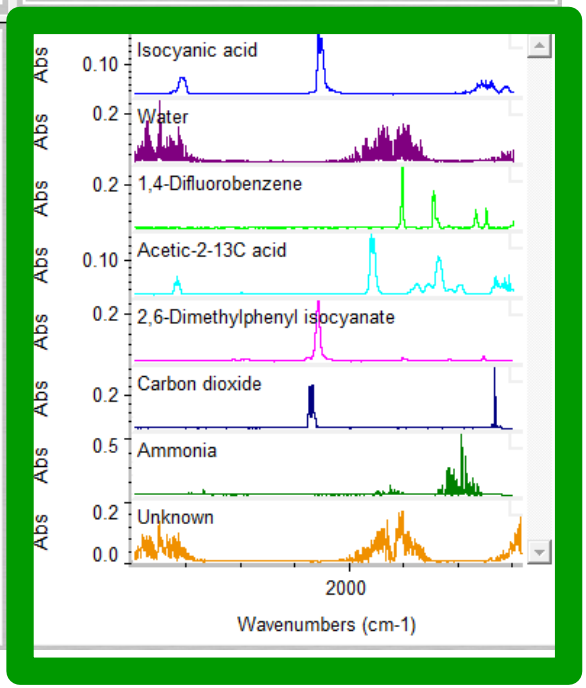
Troubleshooting in the Analytical Laboratory

- Deformulation of a polymer resin









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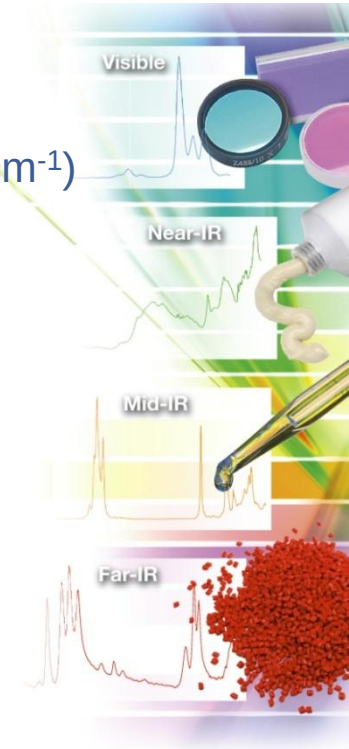
Conclusions

- Molecular vibrational spectroscopy is more than just mid-infrared
  - Molecular vibrations are useful from Near IR (10000 cm^{-1}) to Far IR (200cm^{-1})
  - Raman is a bit unique but is still based on vibrations

- Applications benefiting from vibrational spectroscopy
  - Orientation and crystallinity
  - Pigments and additives
  - Density and copolymers
  - Deformulation and failure analysis



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Learn more about the instruments used:

Thermo Scientific Nicolet iS50

Please feel free to email me

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