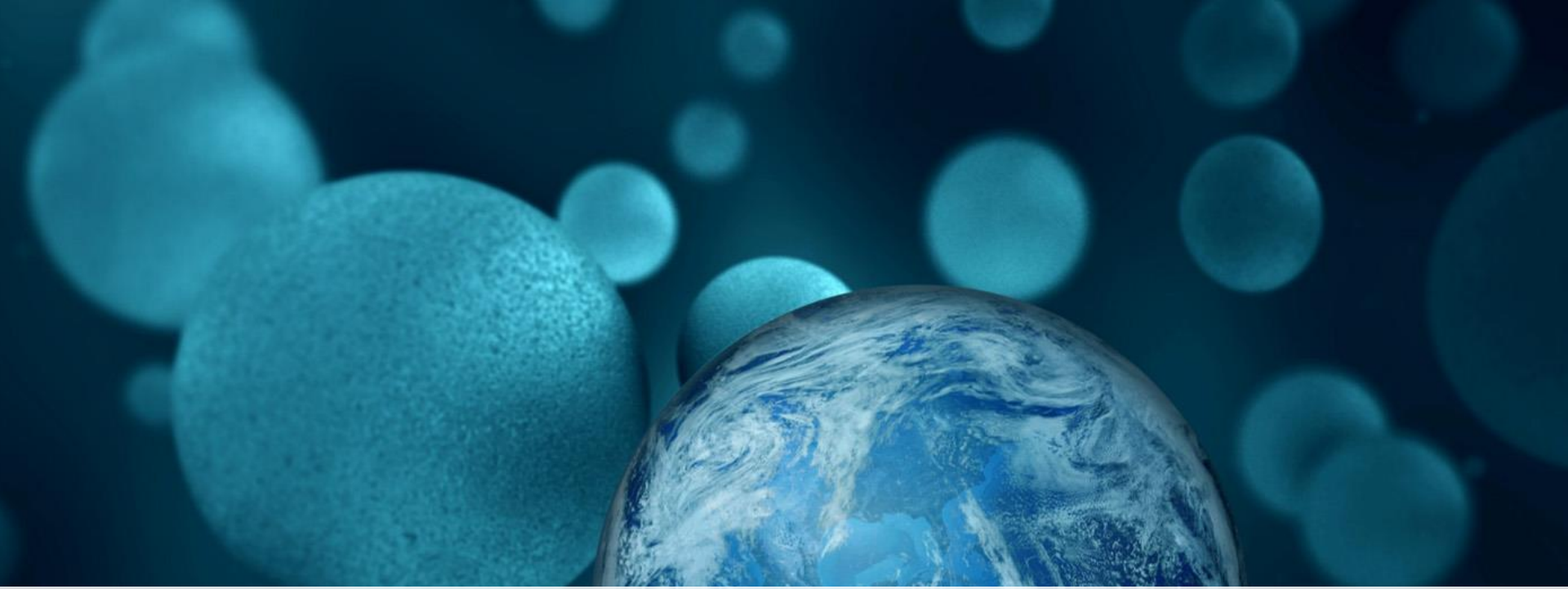


ThermoFisher SCIENTIFIC

Introduction to FTIR and Raman Spectroscopy

Theory and Practice

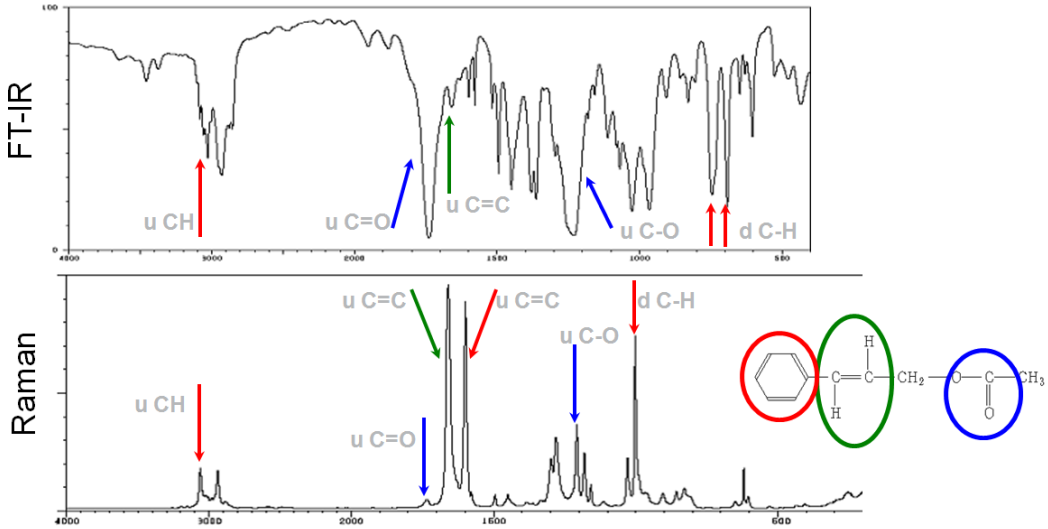
2017 Spectroscopic Solutions Seminar

The Power of Molecular Spectroscopy

- You can work fast…
  - Little or no sample prep, rapid screening
- …on a range of samples…
  - Organics, inorganics, films, coatings, paper, fibers, more
- …and answer basic questions…
  - What is this stuff? How much is in there? In what form?
- …or advanced questions.
  - What is the film thickness? What is the orientation? How do viscoelasticity and chemistry relate?

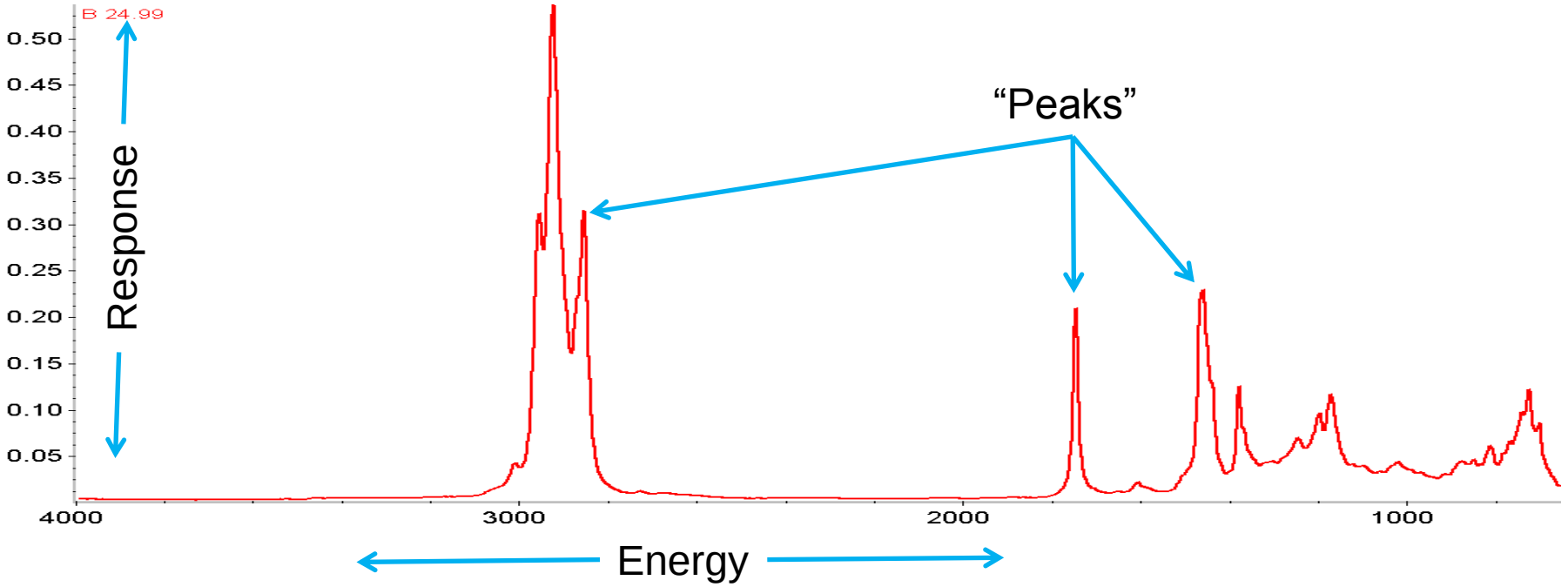
Vibrational Spectroscopy: FTIR and Raman

- Infrared Spectroscopy
  - Energy is absorbed directly…
  - …which results in peaks
- Raman Spectroscopy
  - High energy light strikes sample…
  - …the sample ‘takes’ some of the energy…
  - …which results in peaks
- Different methods but similar insights
  - The peaks provide information about the composition, concentration and more
  - Both are reporting upon vibrational motion of the molecules



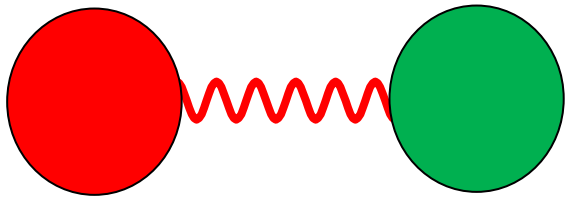
ThermoFisher SCIENTIFIC

Basics: Information in the Spectrum



- **Energy** varies along the x-axis
  - Expressed in wavelength (nanometers, microns) or **Wavenumber (cm^{-1})**
- **Response** (Intensity) is along the y-axis
  - Absorbance, transmittance, specular or diffuse reflectance, Raman scattering
- **Peaks** occur because different molecules interact with light differently
  - This is what enables spectroscopy to tell us something!

Basics: Spectroscopy and Composition



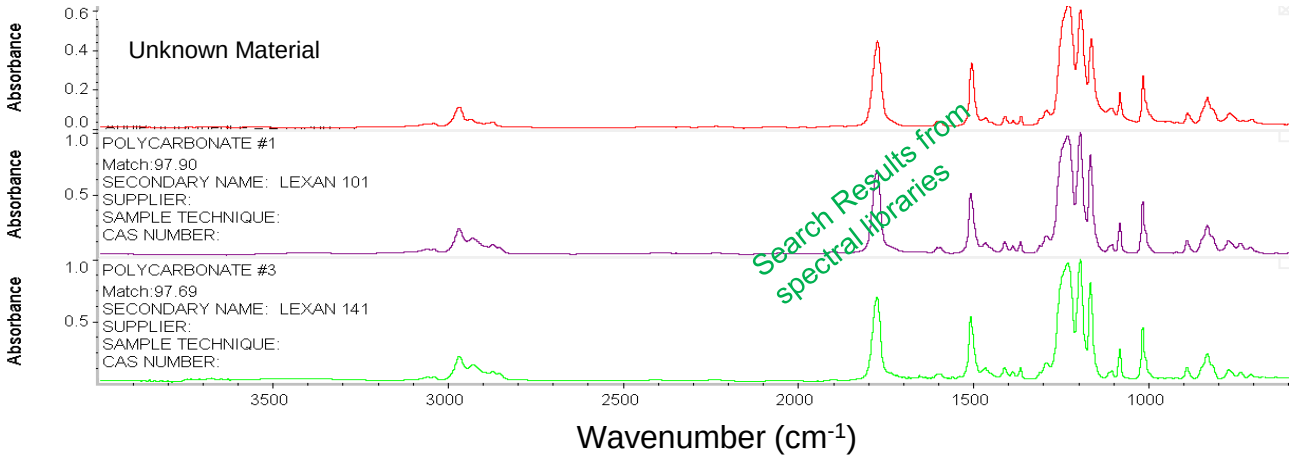
- Chemical bonds vibrate like springs
- Absorption occurs at the specific frequencies of those vibrations

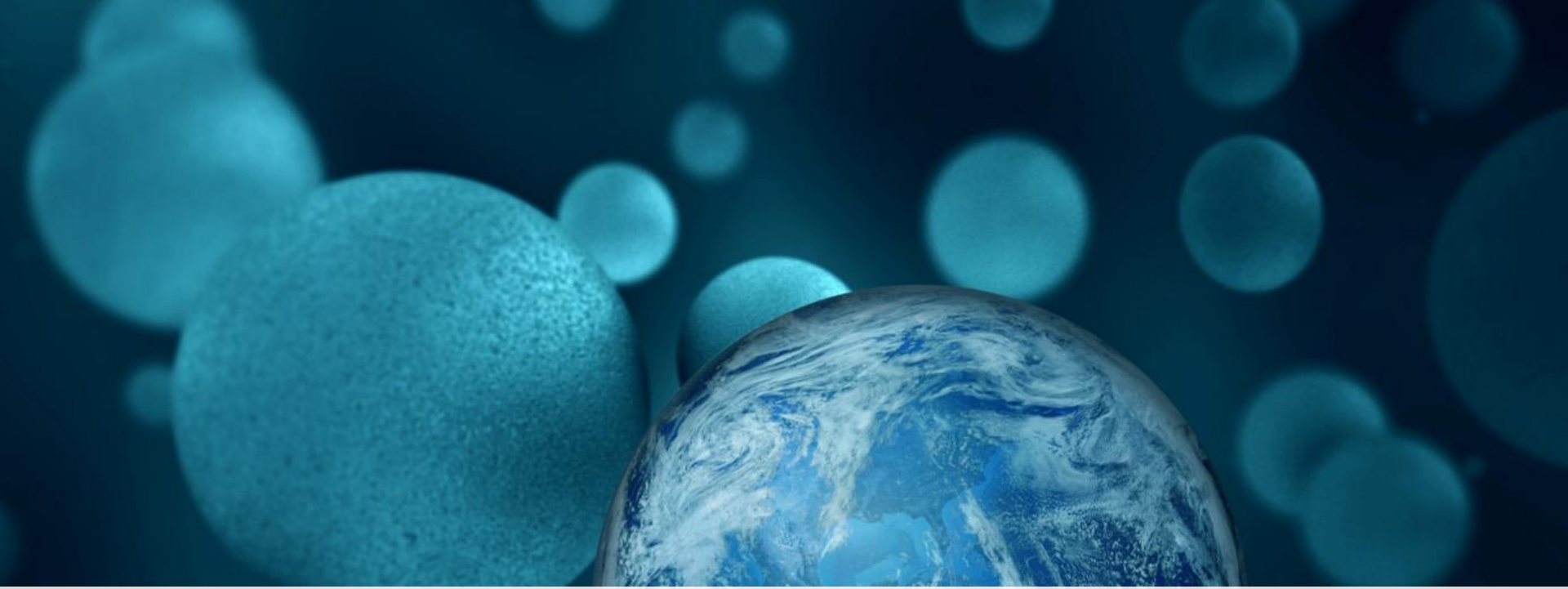
$$\text{Frequency of vibration} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

k ← Relates to bond strength

μ ← Relates to mass

  - As bond strength increases, frequency increases (C≡C > C=C > C-C)
  - As mass decreases, frequency increases (C-H > C-C > C-Cl > C-Fe)
- Which is why the peaks tell a story about the material!





ThermoFisher SCIENTIFIC

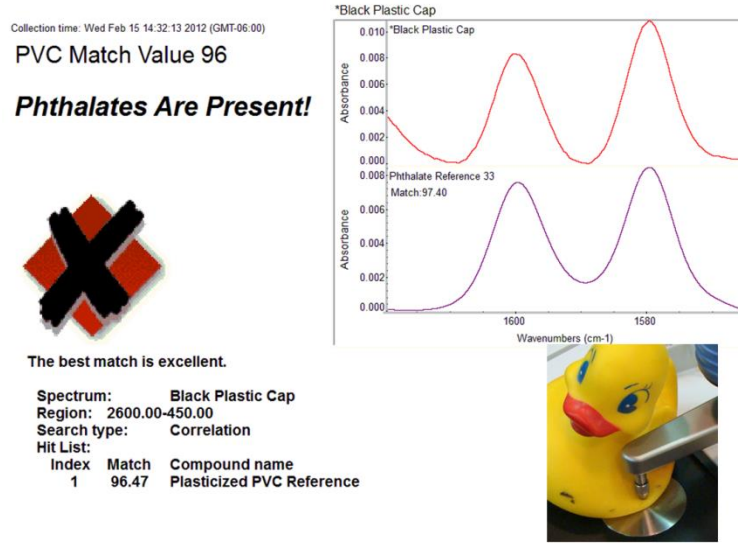
Fourier Transform Infrared Spectroscopy

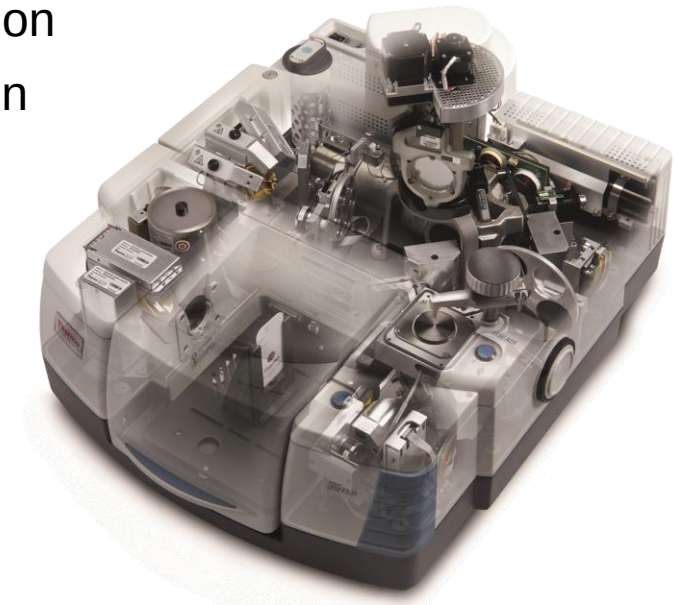
Basics: FTIR as a Laboratory Tool

- FTIR is used to solve problems
  - What is it? How much is in there?
- The ultimate Triage Technique
  - Get in…get an answer…act on it fast

- You generally need to accessorize
  - Add sampling tools, like ATR, Transmission
  - We will talk to that in the next presentation

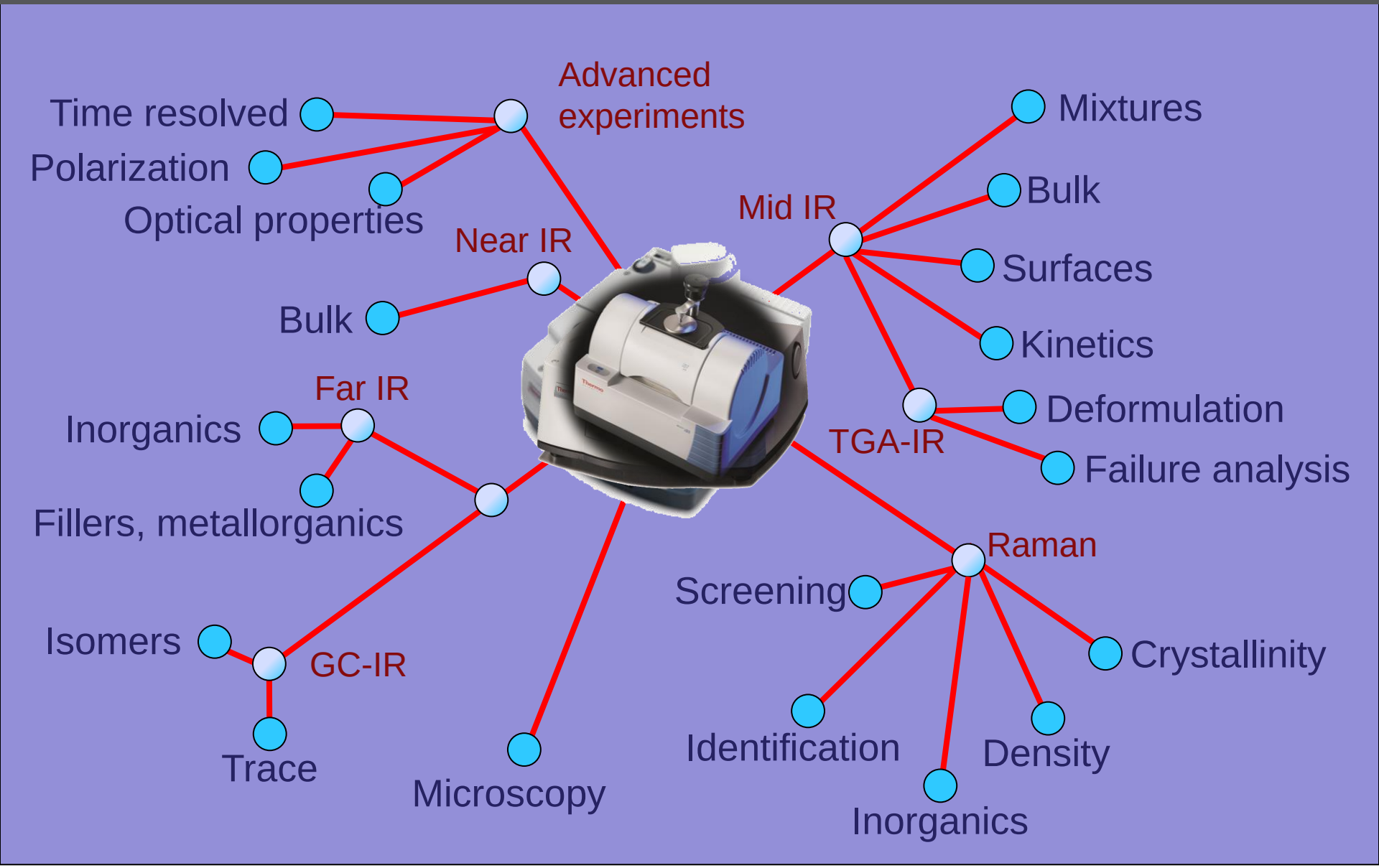
- What do you need?
  - Single action, repeated analyses?
  - Flexibility?
  - Microscopy?



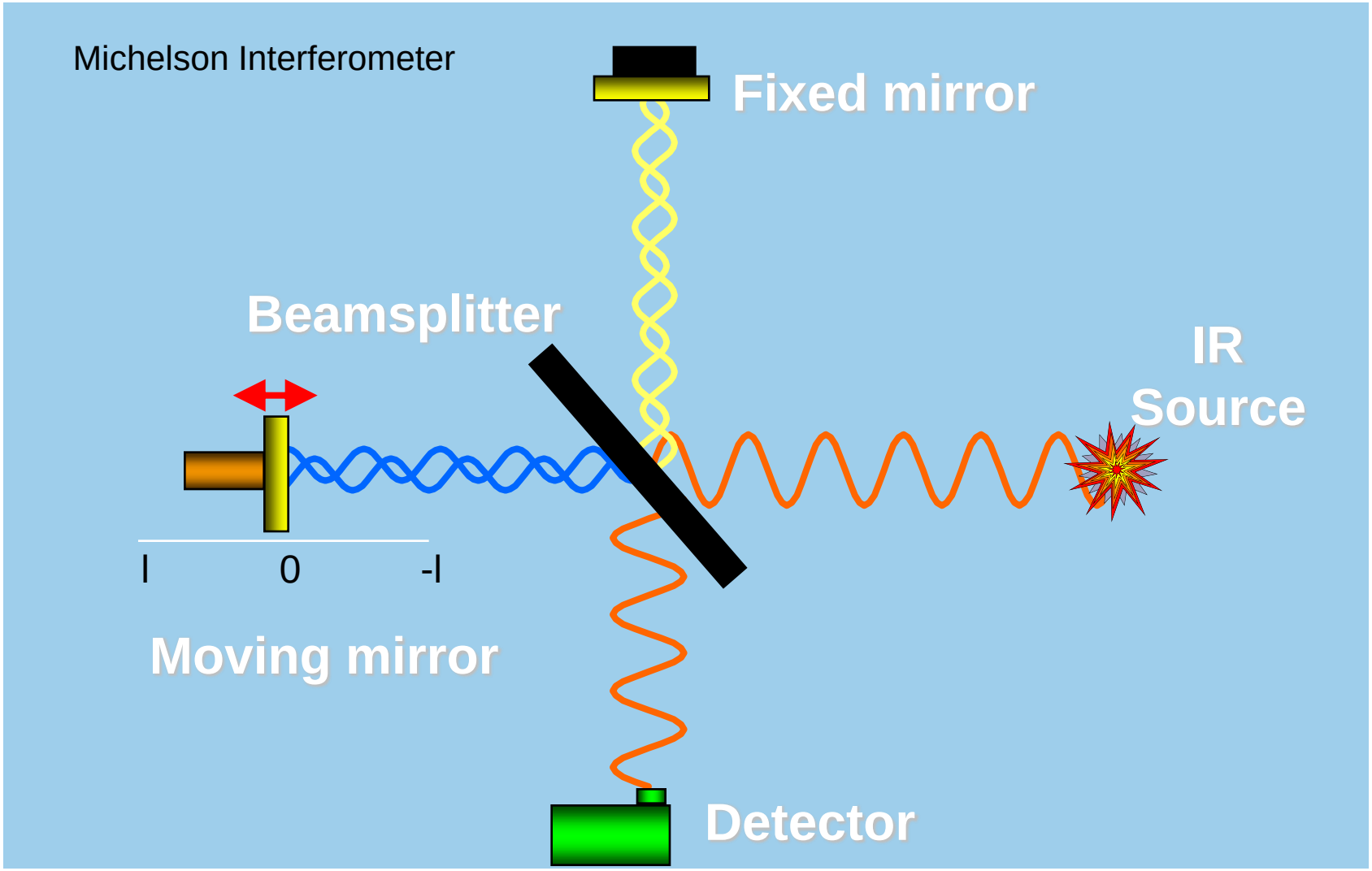


ThermoFisher SCIENTIFIC

Basics: Select the Right Tool for your Application



Basics: How FT-IR Works

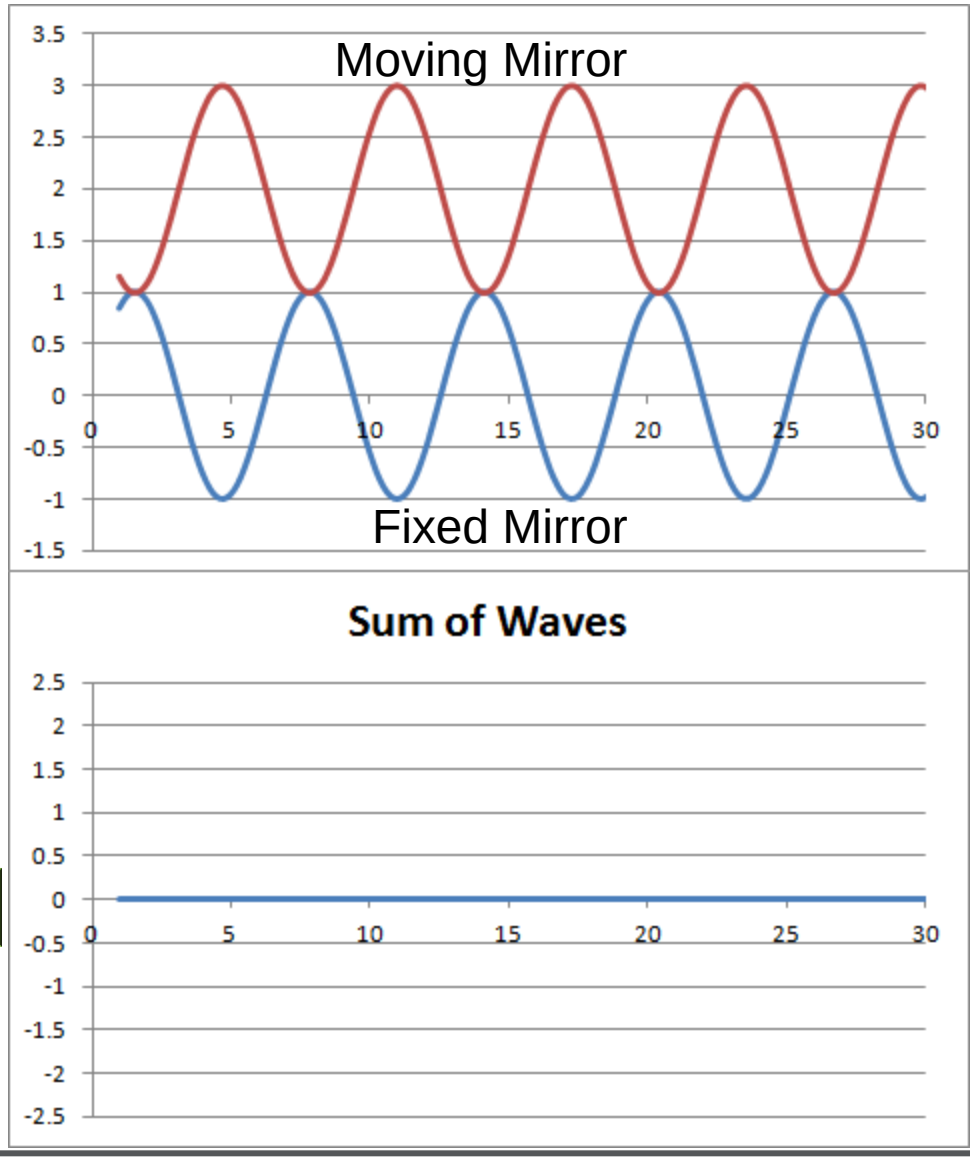


ThermoFisher SCIENTIFIC

Time Domain to Frequency Domain

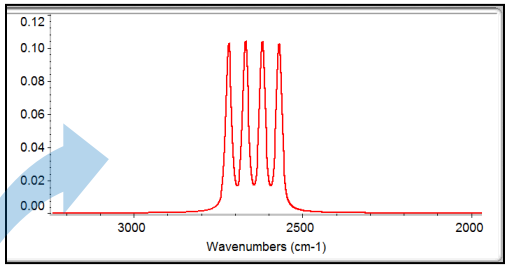
- One mirror moves…
- …one doesn't
  - This causes the two beams to 'interfere' when they recombine
  - Watch how the detector signal (bottom) varies with mirror movement (top)…
  - The result is a Time versus Detector Signal (Intensity) plot

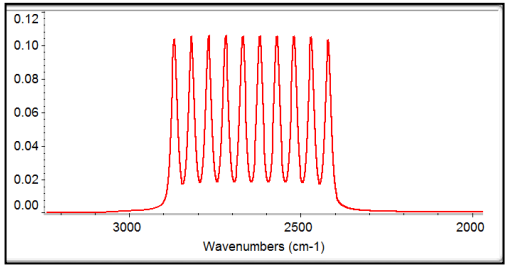
Detector Signal

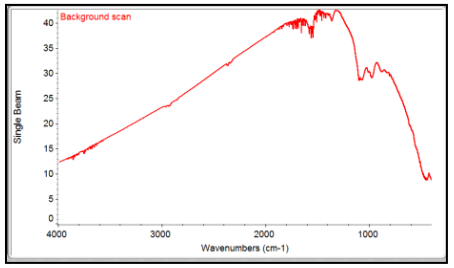


ThermoFisher SCIENTIFIC

The FTIR Interferogram





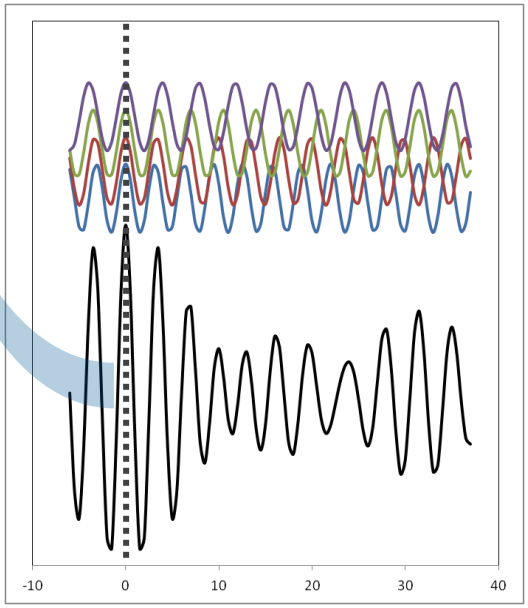


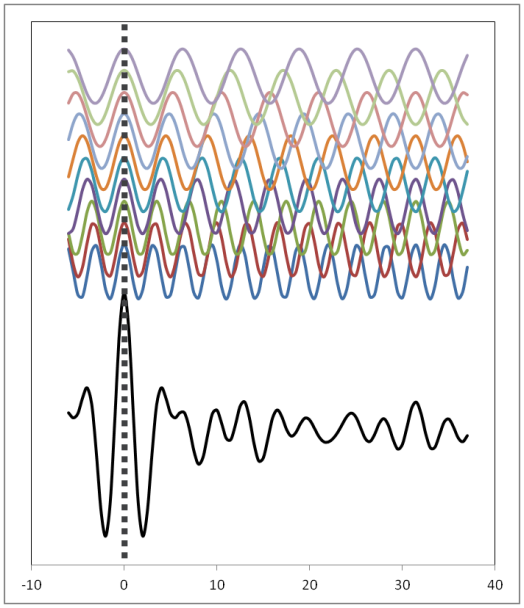
4 frequencies

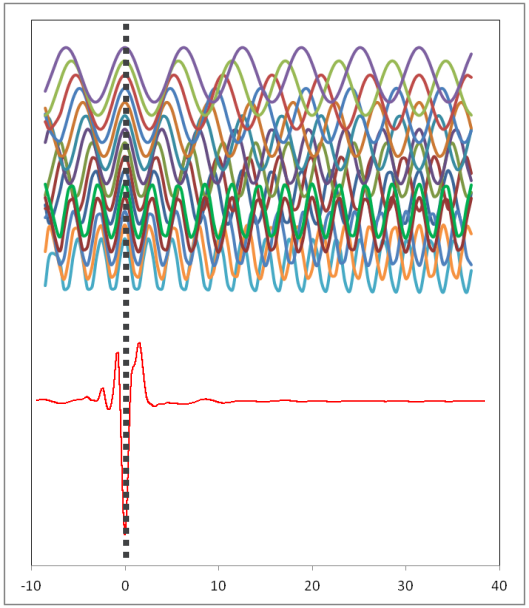
10 frequencies

Broadband source

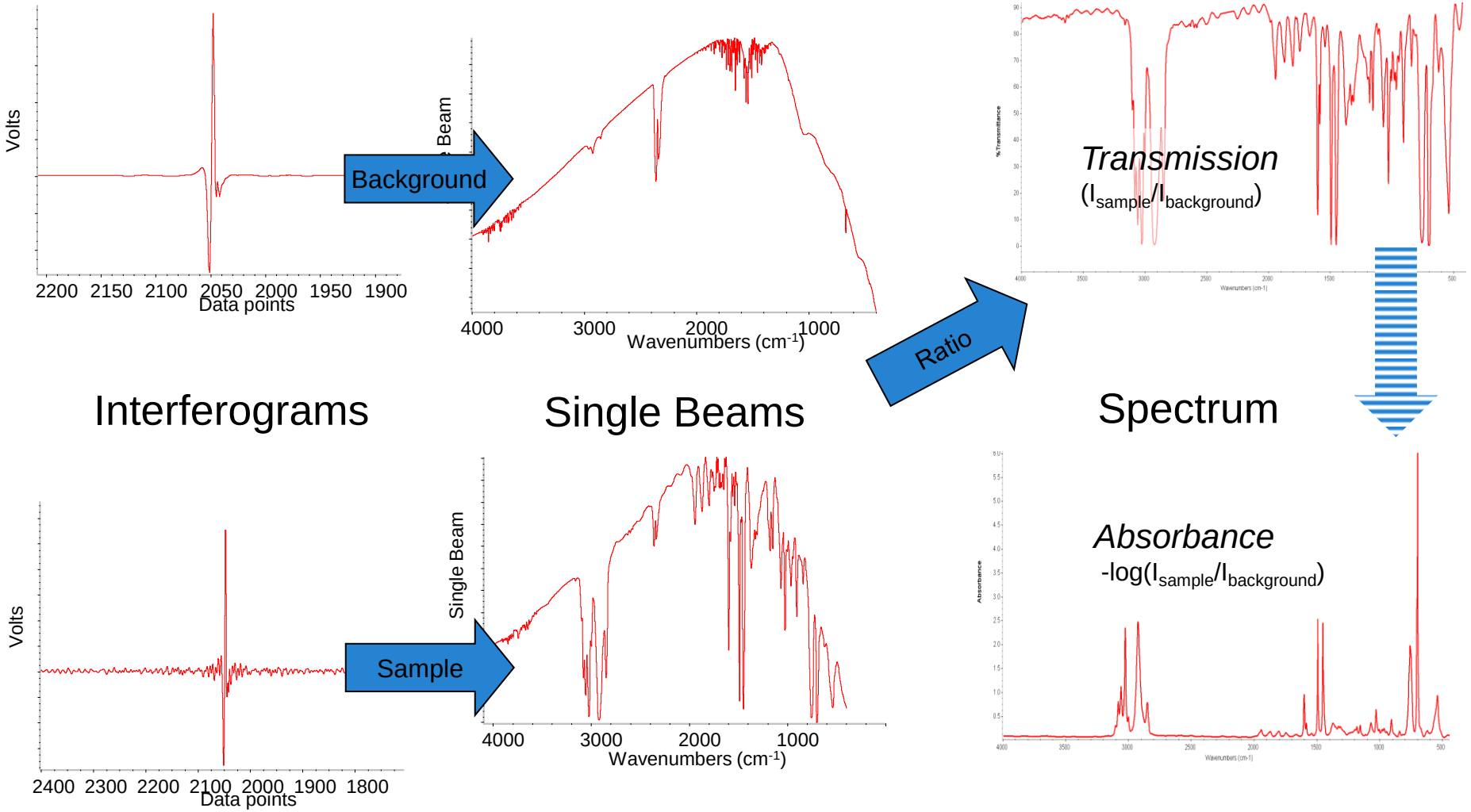
Fourier Transform





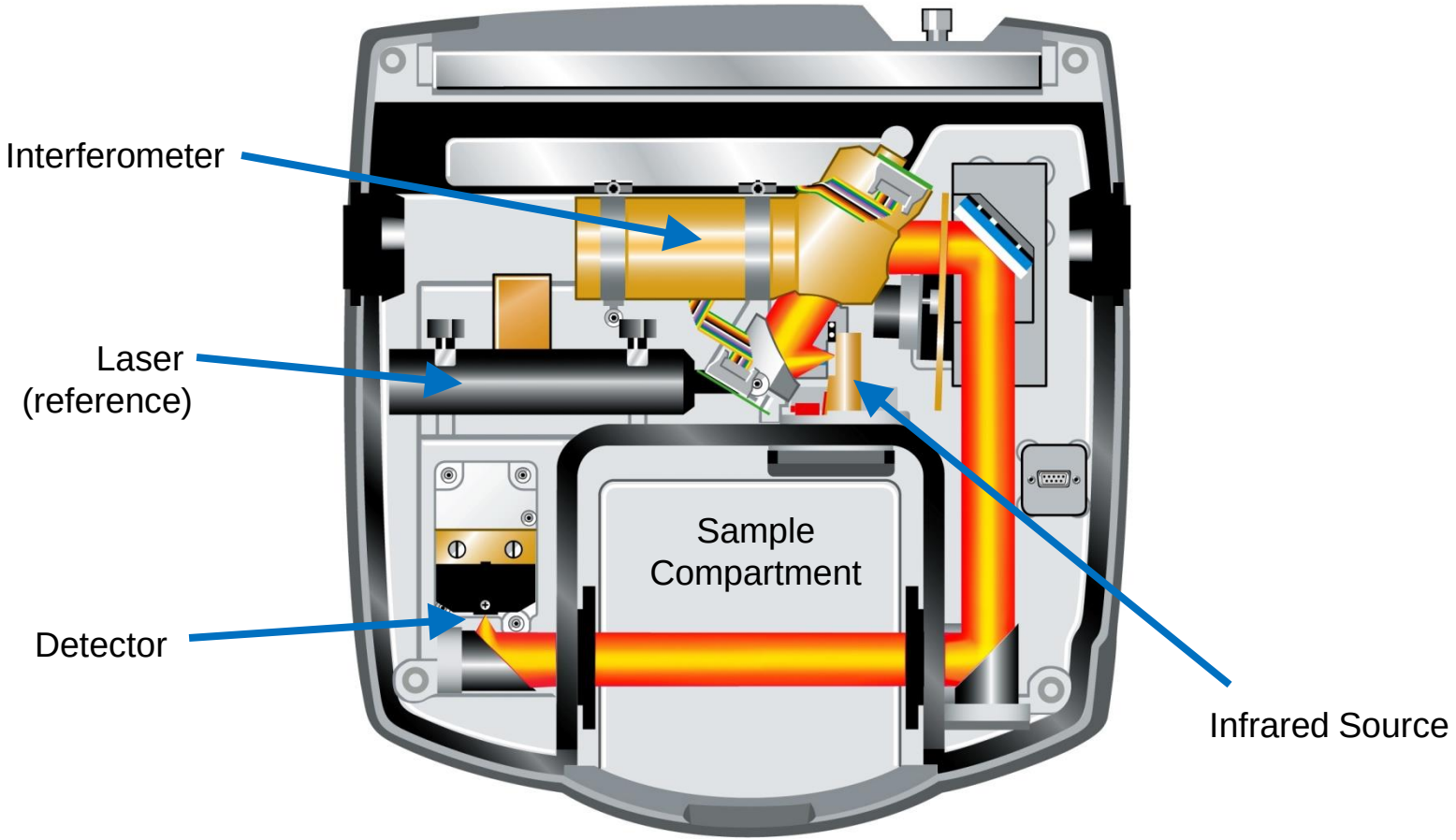


Raw Data to Final Spectrum



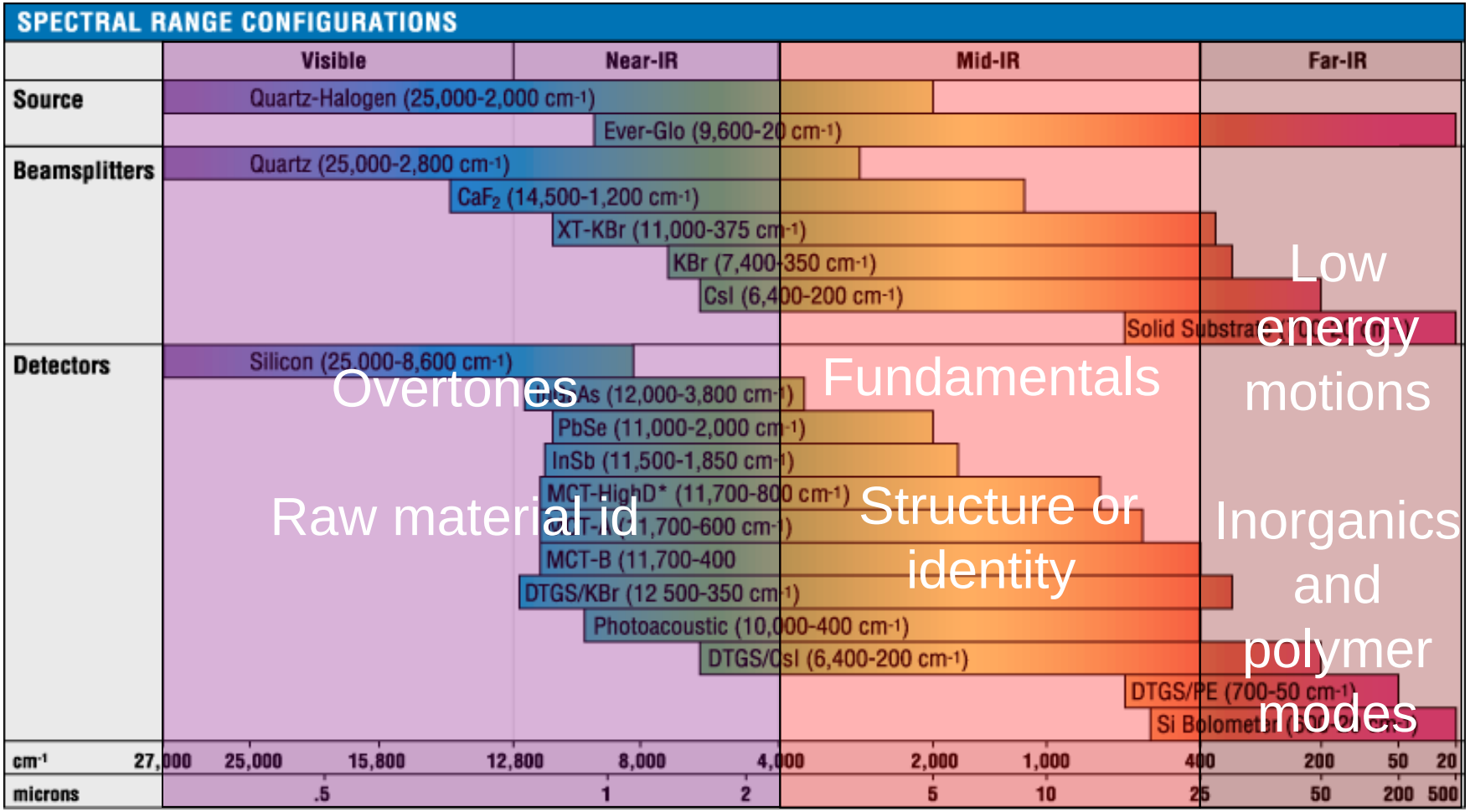
ThermoFisher SCIENTIFIC

Inside the FT-IR Spectrometer



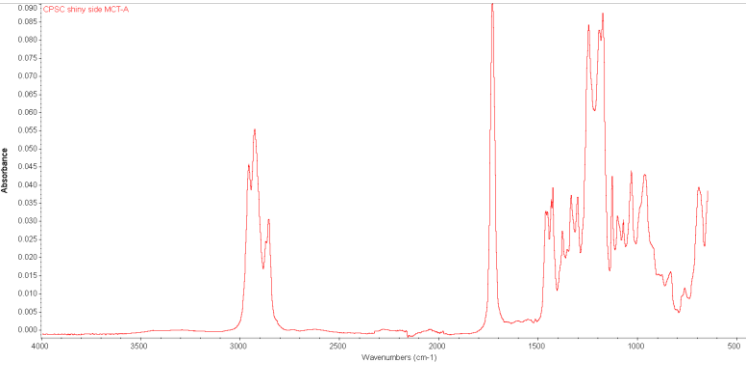
Thermo Scientific™ Nicolet™ iS™10 FT-IR Spectrometer
Simplicity of form, dependability of function

Choose Components to Set Spectral Range



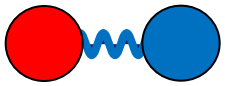
ThermoFisher SCIENTIFIC

The Rest is Up to Physics!

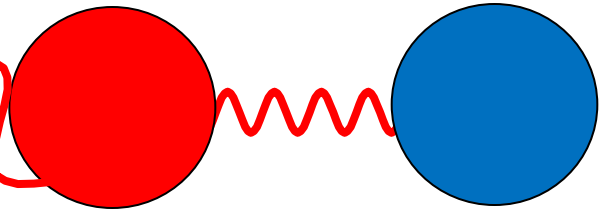


- ***The dipole moment must change***
- ***Molecules absorb specific frequencies***
  - Chemically similar materials absorb in the same range
    - Esters: around 1750 cm^{-1}
    - Hydrocarbons: around 3000 cm^{-1}
- Multiple uses
  - Identification
  - Quantitation
  - Kinetic studies

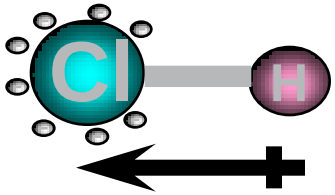
Basics: What Happens at the Sample?



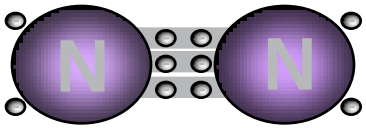
Light Mass, Dipole, High Frequency
Mid-IR



Heavy Mass, Dipole, Low Frequency
Far-IR



Only when there is a dipole change do you get IR peaks

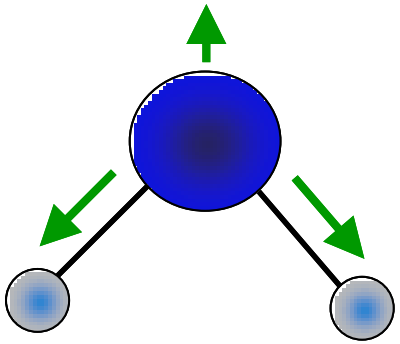


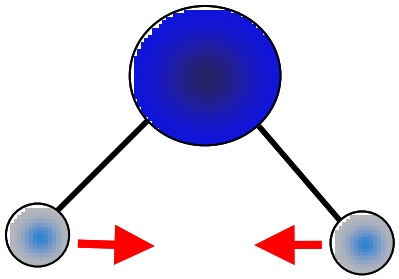
No Dipole, Nothing Happens

NIR: A powerful branch of the FT-IR Family

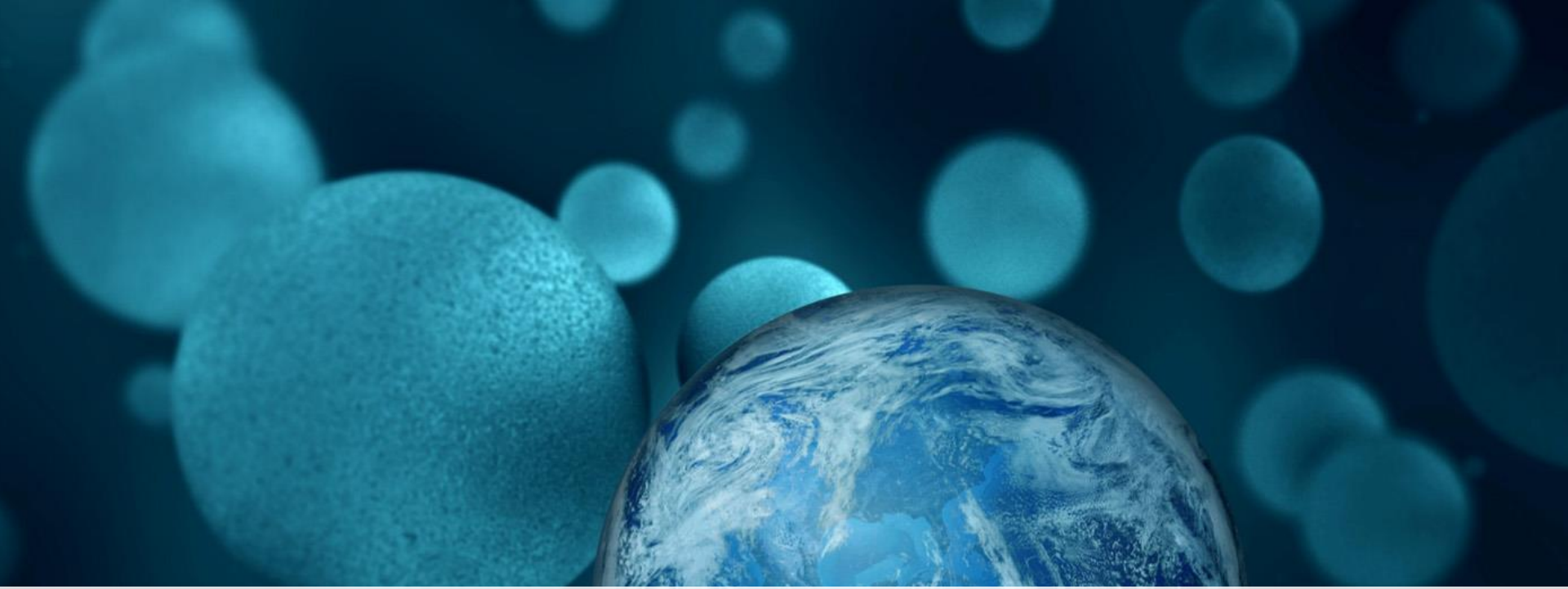
- NIR heavily used in industrial processes
  - Raw material identification (RMID)
  - “HOVal” for condensation analyses
  - Excellent for moisture detection
- Good Mid-IR generally means good NIR
  - NIR not covered today – ask for more information!

3600 cm^{-1} 5200 cm^{-1} 1600 cm^{-1}





Combination band in Water

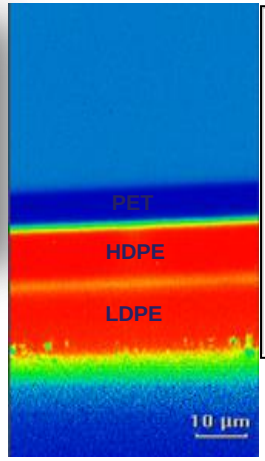


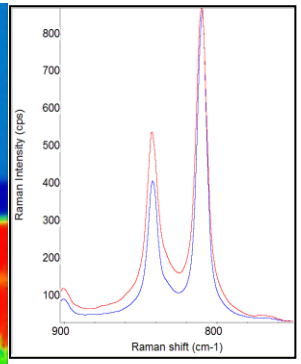
ThermoFisher SCIENTIFIC

Raman Spectroscopy

Basics: Raman as a Laboratory Tool

- Raman is used to solve problems
  - Non-destructively, non-invasively
  - Identify, map, image, depth profile
- Often coupled with a microscope
- Minimal or no Sample Preparation
- High Spatial Resolution
- What do you need?
  - Single action, repeated analyses?
  - Flexibility?
  - Imaging?





ThermoFisher SCIENTIFIC

Basics: Select the Right Tool for your Application

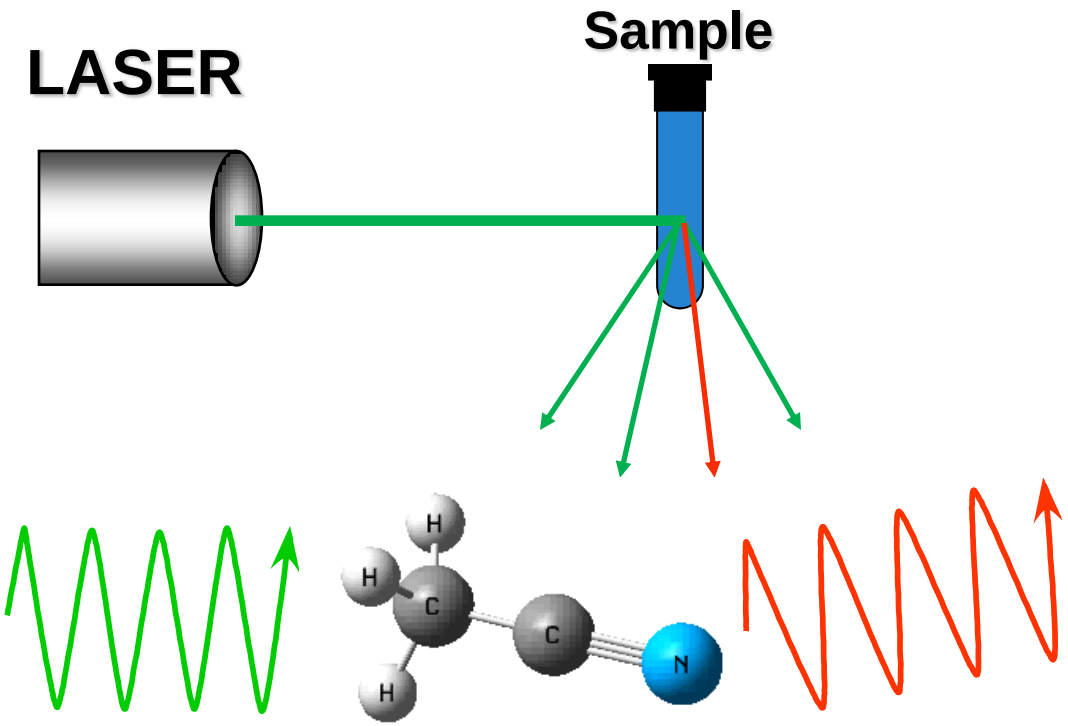
- **DXR2 Microscope**
  - Point and Shoot
  - Mapping

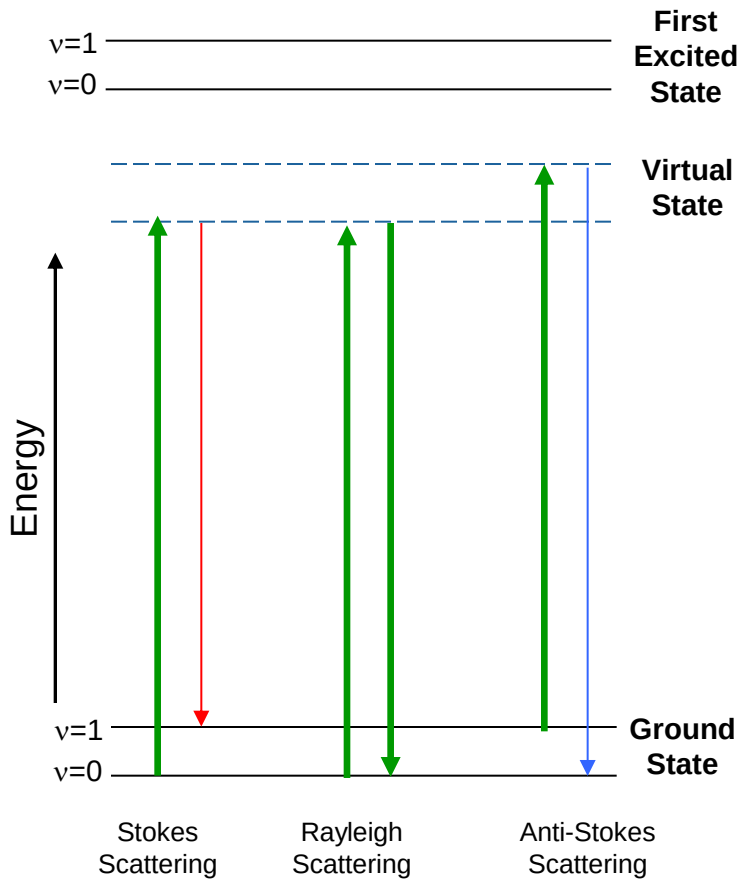
- **DXR2xi Imaging Microscope**
  - Fast Imaging
  - Image-driven collection

- **iS50 FT-Raman**
  - Sample compartment
  - Point and Shoot or Mapping

DXR2 Smart
- Bulk Sampling

Basics: Raman Spectroscopy

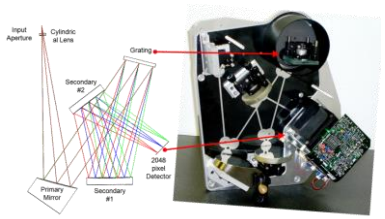


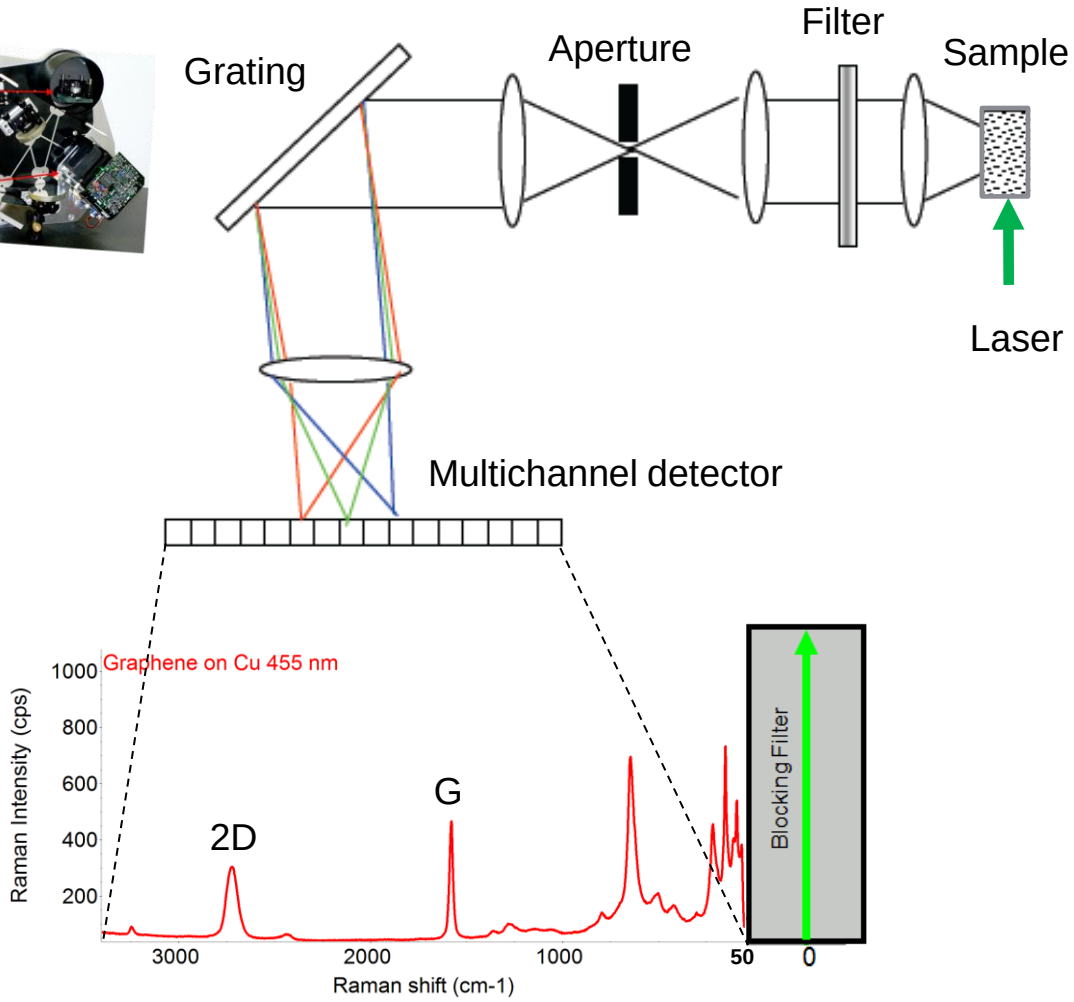


- Raman is a scattering technique
  - Sensitive to vibrational modes of covalent bonds in molecules
  - Most sensitive to highly symmetrical vibrations (i.e. C-C, Si-Si)
  - Sensitive to anything that changes bond energy (i.e. bond angle)

Basics: How Dispersive Raman Spectrometers Work

- DXR2 System Basics:
  - Lasers
    - 455 nm
    - 532 nm
    - 633 nm
    - 785 nm
  - Rayleigh rejection filter
    - 50 cm^{-1} cut-off
  - Apertures
    - Slit
    - Pinhole (confocal mode)
  - Gratings
    - Standard, 5 cm^{-1}
    - High Resolution, 2 cm^{-1}
  - Detectors
    - CCD, EMCCD



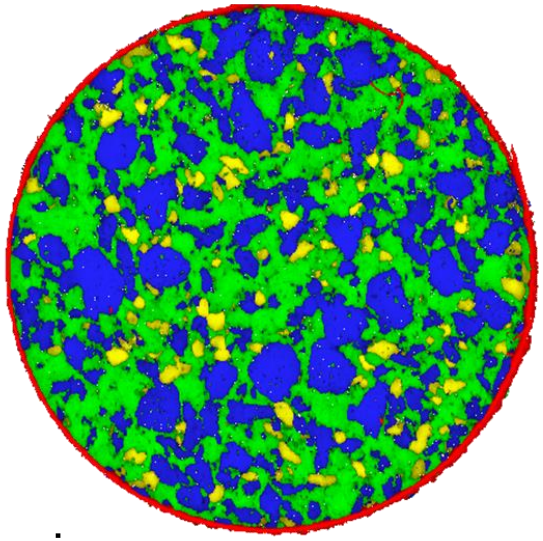


ThermoFisher SCIENTIFIC

Basics: Why so Many Options on the DXR2?

- Multiple Lasers (455, 532, 633 or 785 nm)?
  - Trade-off: Fluorescence versus Efficiency
    - Fluorescence can be very strong, >> Raman
    - Efficiency strongly depends upon excitation wavelength

$$\text{Efficiency} \propto 1/\lambda^4$$

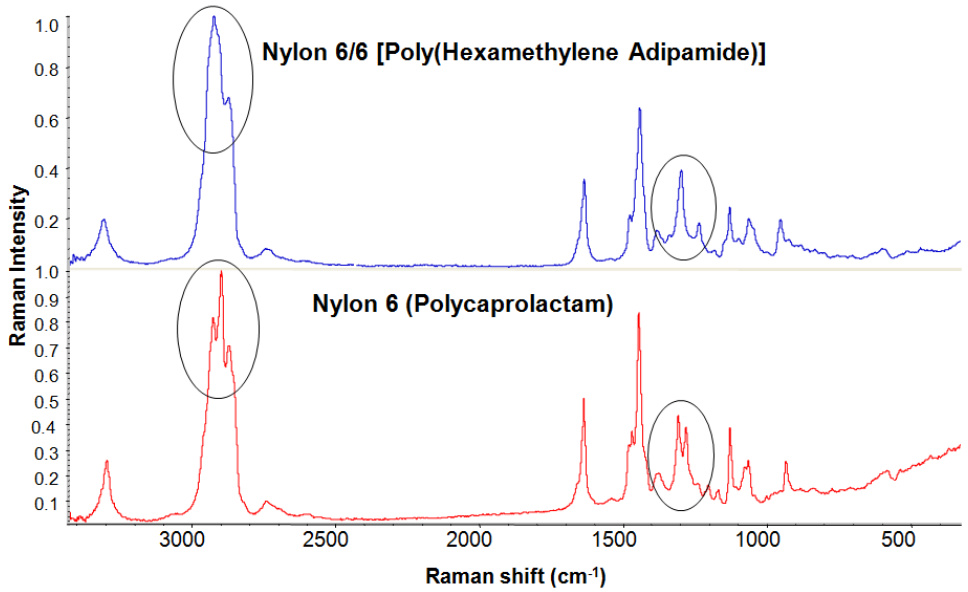


- High resolution versus standard resolution?
  - See closely spaced peaks, but…
  - Changes your available spectral range

- Detectors?
  - CCD: Standard detector, single point and mapping
  - EMCCD: Faster (not more sensitive), for fast imaging

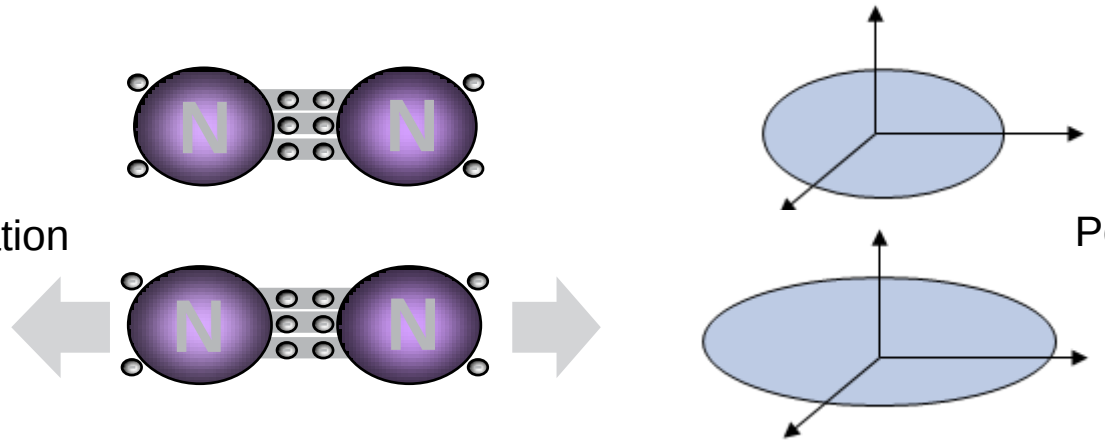
The Rest is Up to Physics (again)!

- ***There must be a polarizability change***
  - Basically, a change in the electron cloud
- Peaks occur at specific frequencies
- Peaks may display a polarization dependence
  - Orientation and molecular symmetry
- Multiple uses
  - Identification
  - Quantity
  - Kinetics



ThermoFisher SCIENTIFIC

Basics: What Happens at the Sample?

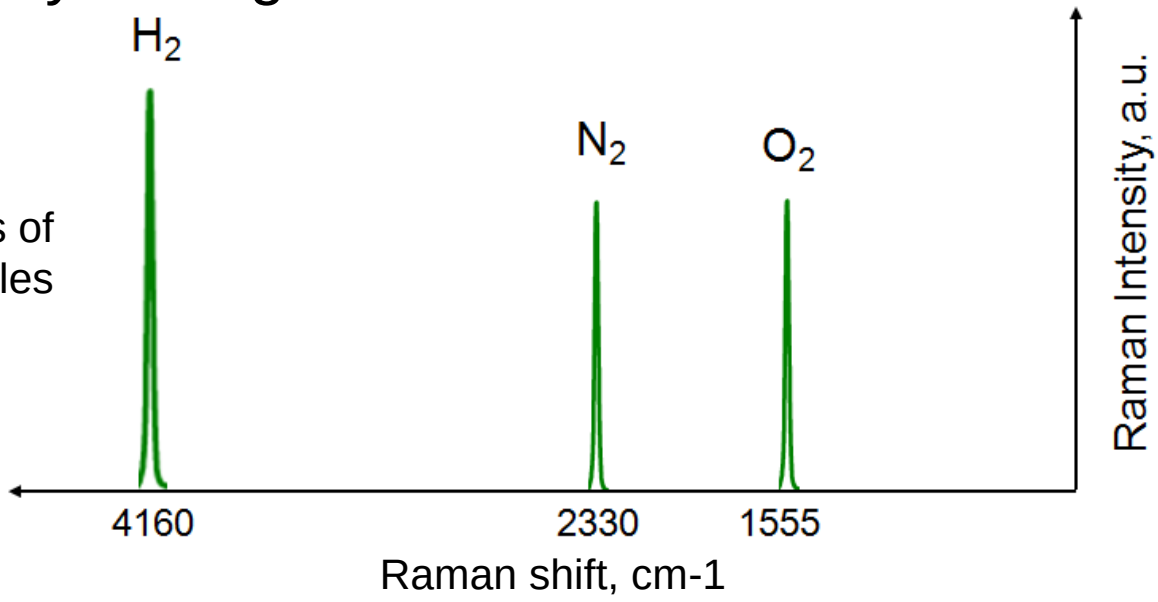


Molecular vibration

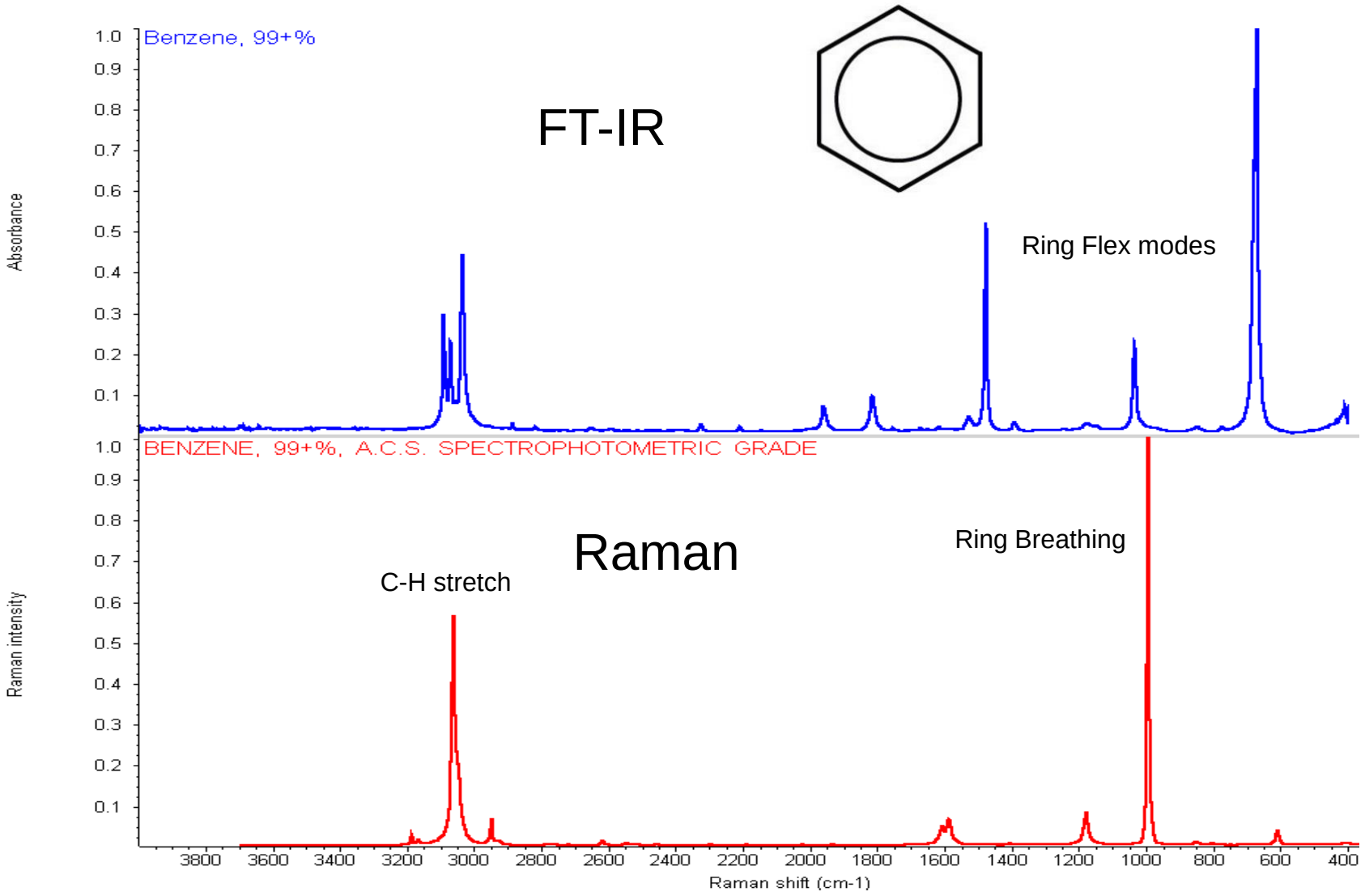
Polarizability Tensor

- IR → Dipole Change
- Raman → Polarizability Change

Fundamental vibrations of homonuclear diatomic molecules

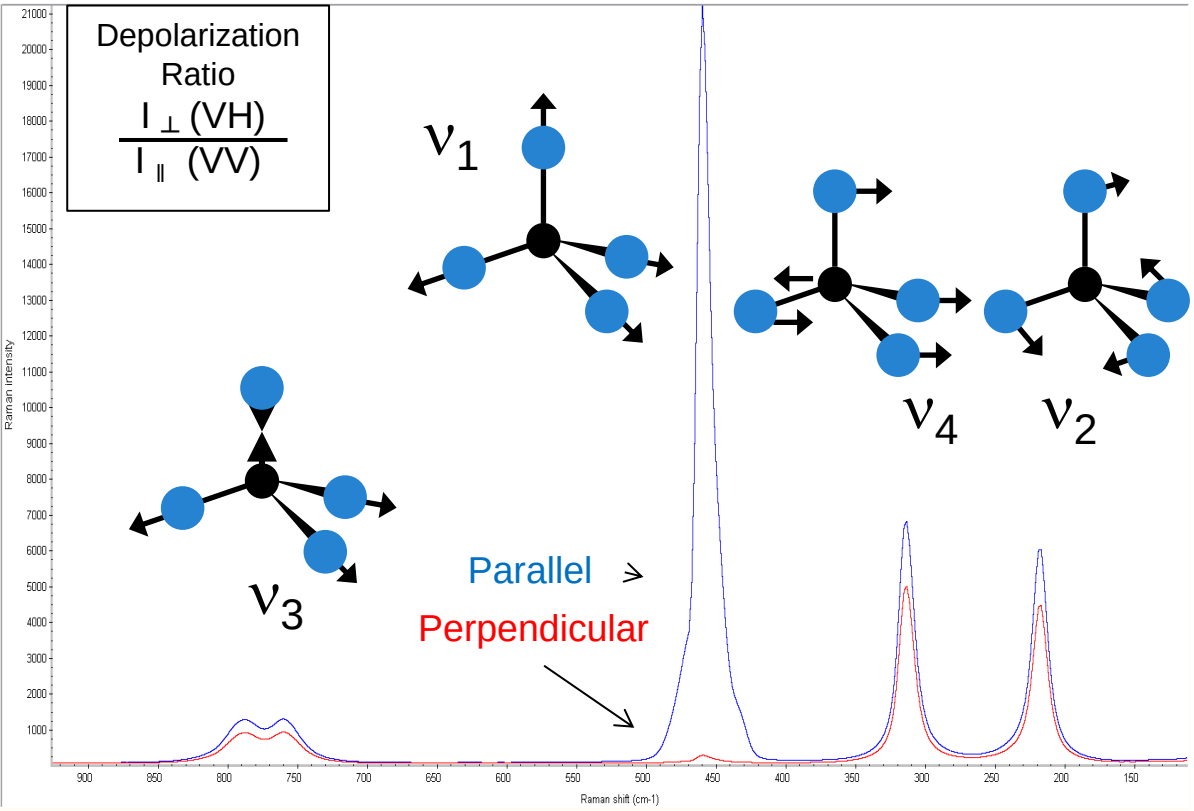


FT-IR and Raman Spectrum of Benzene



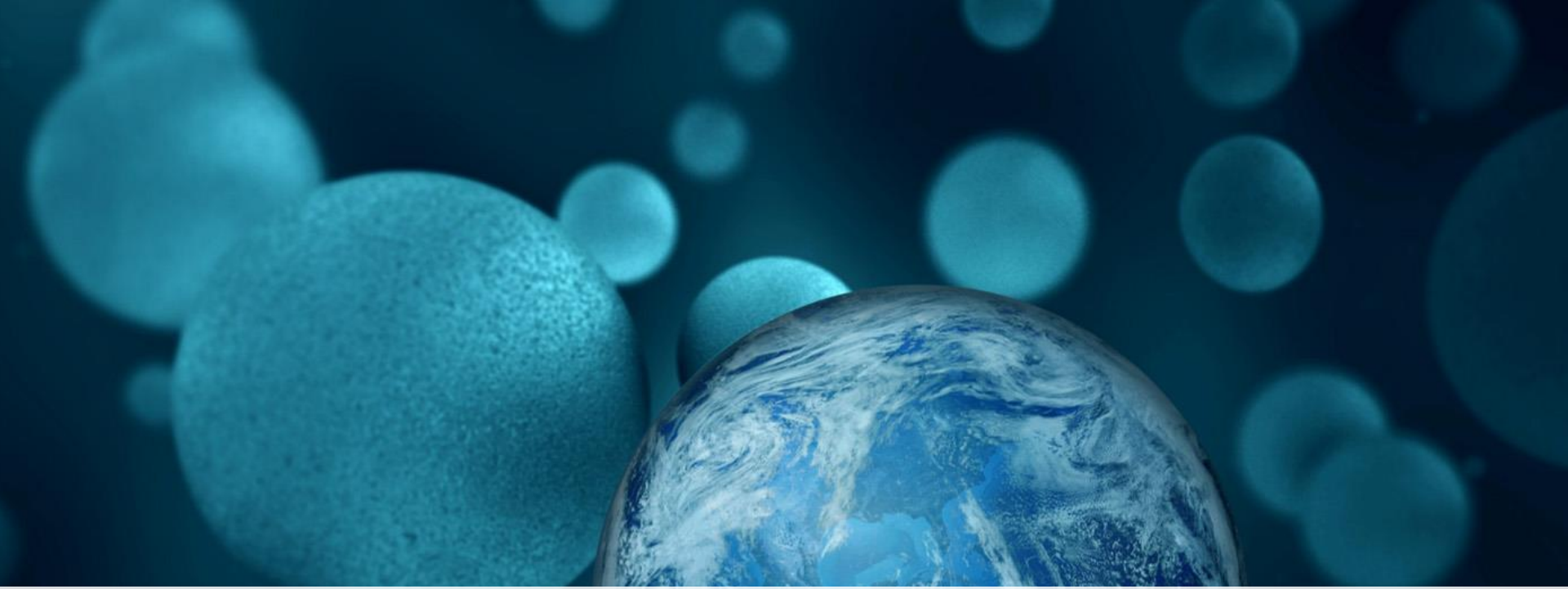
ThermoFisher SCIENTIFIC

Additional Information: Raman Polarization



- Used to characterize:
  - Molecular symmetry
  - Molecular orientation
  - Crystallinity
  - Morphological traits
- DXR2 Raman polarization
  - Automated laser polarization
  - Automated analyzer orientation

ThermoFisher SCIENTIFIC



ThermoFisher SCIENTIFIC

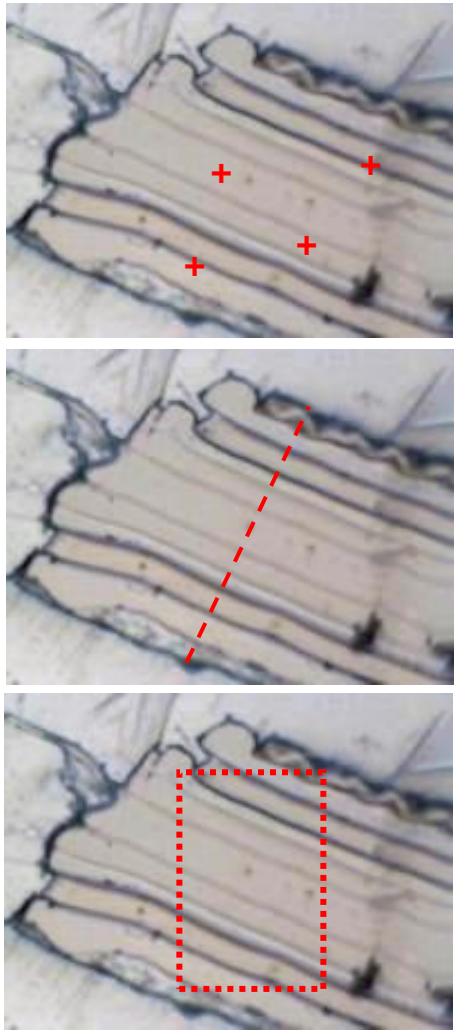
Extending Molecular Spectroscopy

Microspectroscopy and Multimodal Techniques

Basics: Microspectroscopy

- Combine FT-IR or Raman with microscope
- Probe content, homogeneity, contaminants
- FTIR or Raman
  - Today's last talk

- Point and shoot
- Line maps
  - Cross-Sections
- Area maps
- Chemical Images



Multimodal Techniques

- Relate Properties to Chemistry
  - Rheo-Raman or Rheo-IR
- Deformulate
  - TGA-IR
  - GC-IR
- Materials Analysis
  - XPS-Raman
  - AFM-Raman

Versatility: IR Microscopy, FT-Raman, Built-in ATR, automated Beamsplitter Exchanger, External experiment module

Versatility: The Thermo Scientific iXR Compact Raman Coupled with XPS

Molecular Spectroscopy: Research to Routine

- Discover.
  - Relate Viscosity to Chemistry
  - Biological imaging
- Solve.
  - Identify unknowns
  - Deformulate materials
- Assure
  - QA/QC on incoming, outgoing material
  - In-line process control