FT-IR vs. Raman Spectroscopy: Principles, Applications, and Comparisons

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Interaction between matter and light beam

- What are molecular vibration and vibrational spectroscopy
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Interaction Between Matter and Electromagnetic (EM) Radiation

Interaction Type	Description	Spectroscopy Examples	
Absorption	Energy is taken up by matter, causing transitions (electronic, vibrational, rotational).	UV-Vis, IR, X-ray Absorption	
Emission	Excited matter releases energy as EM radiation.	Fluorescence, Phosphorescence, AES	
Scattering	EM radiation is redirected by matter.	Raman (Inelastic), Rayleigh (Elastic)	
Reflection/Refraction	Light changes direction at boundaries.	Optical Microscopy, FT-IR (ATR mode)	
Transmission	Radiation passes through matter, may be attenuated.	UV-Vis, IR	
Photoelectric Effect	Photons eject electrons from material surfaces.	XPS, UPS	
Photochemical Reactions	Radiation induces chemical changes.	Photopolymerization, Photolysis	





What is Molecular Vibration?

•Definition:

Periodic motion of atoms within a molecule, where atoms move relative to each other but the overall molecule stays intact.

•Why "vibration"?

- Chemical bonds act like **springs** between atoms.
- Atoms naturally oscillate due to thermal energy and quantum effects.
- These oscillations occur in distinct vibrational modes.

•Types of Vibrations:

- Stretching bond lengths change
- Bending bond angles change
- **Twisting/Wagging** complex out-of-plane motions

•Why it matters:

Molecular vibrations absorb light at specific energies → **Basis of IR & Raman spectroscopy** for identifying molecular structures.

Northwestern University Atomic and Nanoscale Characterization Experimental Center

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Ball-and-Spring Model of Molecular Vibration



Stretching

- The bond length changes 0
- No angle change 0



Symmetric stretching

Asymmetric strecthing



In-plane scissoring

In-planer rocking

Out-of-plane wagging Out-of-plane twisting











Infrared Spectroscopy







Infrared (IR) Spectroscopy --- Dipole Moment

•Process: Absorption of IR radiation by a molecule.

•Transition: Molecule absorbs energy → jumps from a lower to a higher vibrational energy level.

•Requirement: Vibration must cause a change in the dipole moment of the molecule.

•Result: Absorption spectrum showing which energies (frequencies) are absorbed.

Change in Dipole Moment (IR-active)

•Dipole moment is the separation of charge in a molecule (think positive and negative ends).

•A vibration is **IR active** if it causes a **change in the dipole moment** of the molecule.

Examples of IR-active:

•Stretching in **polar bonds** like O–H, C=O, or N–H

•Bending in molecules like H₂O (which has a permanent dipole)

Nonpolar symmetric stretches (like O=O) won't show up in IR.







Functional Group -- Vibration Frequencies -- IR Peaks

What Happens?

•Chemical bonds in molecules can vibrate (like stretching or bending).

•These vibrations create specific IR peaks that we can measure.

What Affects the IR Peak Position?

1. Bond Strength: Stronger bonds = higher frequency (bigger wavenumber).

for a stronger bond (larger k value), the vibration frequency increases, the wave number increases.

C-C	C=C	C≡C
1000 cm ⁻¹	1600 cm ⁻¹	2200 cm ⁻¹
C-C-H	C=C-H	C≡C-H
2900 cm ⁻¹	3100 cm ⁻¹	3300 cm ⁻¹

Hookes' Law



2. Atom Mass: Lighter atoms = faster vibration (higher frequency).

for heavier atoms attached (larger m value), the vibration frequency decreases, the wave number

decreases.

C-H	C-C	C-Cl	C-Br	C-I
3000 cm ⁻¹	1000 cm ⁻¹	800 cm ⁻¹	550 cm ⁻¹	500 cm ⁻¹

Chemical Environment Matters!

•Nearby groups can change the vibration and shift the peak.

Example: C=O in a ketone (R-C(=O)-R') vs. an ester (R-C(=O)-O-R') vs. a carboxylic acid (-C(=O)-OH) will have slightly different peaks.



Wave number $\propto \frac{\sqrt{Bond Strength}}{Atomic Mass}$





IR Applications

Identification of Functional Groups

Detect –OH, –C=O, –NH₂, –CH₃, etc. via characteristic absorption bands

• Surface and Coating Analysis

Study thin films, corrosion products, and surface treatments

Polymer Characterization

Monitor polymerization, crosslinking, and degradation

Qualitative & Quantitative Analysis

Identify unknown compounds Measure concentration of components in mixtures

• Etc.







Regions of FT-IR Spectrum







Signal Intensity in IR spectrum

a less polar bond. 9000 most polar least polar N-HΗ O -> >

least intense

A more polar bond will have a stronger absorption than

An alkene C=C stretch generally appears ~1650 cm⁻¹.

Asymmetric > Symmetric



most intense









Fingerprint region of an FT-IR spectrum

1. Energy of Vibrational Modes:

•Stretching modes (e.g., C-H, C=C, C=O) involve the direct elongation or compression of bonds, which requires more energy. As a result, they typically appear at higher wavenumbers, above 1500 cm⁻¹ (e.g., C-H stretching at 3000 cm⁻¹, C=C stretching at 1600 cm⁻¹).

•Bending, wagging, twisting, and rocking modes involve changes in bond angles or the orientation of groups of atoms, which require less energy. These lower-energy vibrations naturally fall in the fingerprint region (1500–600 cm⁻¹).

2. Types of Vibrations in the Fingerprint Region:

•**Bending:** Includes in-plane and out-of-plane bending of bonds, like C-H bending in aromatic rings (e.g., 1200–1000 cm⁻¹ for in-plane, 900–700 cm⁻¹ for out-of-plane in polystyrene).

•Wagging and Twisting: These are out-of-plane deformations, often seen in -CH₂- groups or aromatic

•**Rocking:** Involves a rocking motion of a group, such as $-CH_2$ - rocking modes (typically around 800–700 cm⁻¹).

3. Stretching Modes in the Fingerprint Region:

•some **stretching modes** can appear, but they are less common and typically involve **heavier atoms or weaker bonds**:

•C-C stretching in the polymer backbone or aromatic rings can appear around 1000–1200 cm⁻¹, but these often couple with bending modes, making the spectrum complex.
•M-O in the wavenumber range of 400-600 cm⁻¹

4. Why Bending Modes Dominate:

•Bending-type vibrations are more numerous and varied because they depend on the molecule's overall geometry and involve multiple atoms. For example, a single C-H bond can **stretch in one way**, but it can **bend in-plane, out-of-plane, wag, or rock**, each producing a different vibrational frequency.

Regions in IR Spectrum			
4000 to 400 cm⁻¹			
Functional group	Finger print		
Above 1500 cm ⁻¹	Below 1500 cm ⁻¹		
Stretching vibrations	Mostly bending vibrations		
Simple	Complicated		
Same for different compounds	Different for each compound		











Case Study: Hydrogen-terminated Silicon Wafer

Hydrogen-terminated silicon wafer (often called H-Si) has a very clean surface with Si–H bonds but very little else, assuming the surface is well-prepared and oxide-free.

Vibration Mode	Wavenumber (cm ⁻¹)
Si–H stretching	~2080–2100 cm ⁻¹

What You Shouldn't See If Surface is Clean:

•No Si–O–Si peaks (~1000–1100 cm⁻¹) \rightarrow would indicate oxidation •No –OH or C–H bands \rightarrow would mean contamination



Why You Usually Don't See Si–Si Peaks in FT-IR:

•IR absorption requires a change in dipole moment during vibration.

•Si–Si bonds are non-polar and symmetric, so their vibrational modes cause almost no dipole change → they are IR inactive (or extremely weak).

•Instead, Si–Si stretching vibrations are more often detected by: **Raman spectroscopy** (they're **Raman-active**). A **strong peak at ~520 cm⁻¹** is characteristic of **Si–Si optical phonon** (the classic crystalline silicon peak).

Ohtake, T. and Iijima, K. (2019) Journal of Surface Engineered Materials and Advanced Technology, 9, 29-37.





Nano IR and IR Mapping



Height image (a) and resulting Photothermal AFM-IR spectra (b) from a contaminant on a bare silicon wafer. The resulting match from the FTIR library identifies the contaminant as Polyethylene terephthalate.



Optical Mapping





Macro- Micro- Nano- IR Analysis







Thermo Nicolet iS50 for bulk samples such as powder, film, liquid

Bruker Lumos IR Microscope for micrometer spot analysis

Bruker nanoIR for nanoscale analysis





Raman Spectroscopy







Raman Spectroscopy

- **Polarizability** is how easily the electron cloud around a molecule can be distorted by an electric field (like from a laser). How **stretchy the electron cloud** is.
- Raman Requirement: Vibration must cause a change in polarizability.
- A vibration is **Raman active** if it causes a **change in polarizability**.



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EXPLORING INNER SPACE



Polarizability Change (Electron Cloud Distortion)



- Polarizability change during vibration
- Raman active
- Infrared inactive
- Polarizability unchanged during vibration
- Raman inactive
- Infrared inactive
- Polarizability unchanged during vibration
- Raman inactive
- Infrared active

Comparison Example:

•Helium: Low polarizability – small, tightly held electrons.

•lodine (I₂): High polarizability – large molecule with lots of loosely held electrons.





Raman Peak Shift

Understand Peak Shifts

• Shifts in Raman peak position (compared to standard/reference) tell you about **changes in bonding** or **chemical environment**.

Red Shift (to lower wavenumbers):

- Weaker bond (lower force constant)
- o Bond lengthening
- Hydrogen bonding
- Increased mass (e.g., isotope substitution)
- o Increased temperature

Blue Shift (to higher wavenumbers):

- Stronger bond (higher force constant)
- o Bond shortening
- Electron withdrawal (electronegative atoms nearby)
- o Decreased mass



Hookes' Law



Theoretical vibrational frequency can be calculated with quantum chemistry software like Gaussian, ORCA, etc.





Lattice Vibration – Raman Peak

Material Type	Raman Feature Type	Peak Behavior
Crystalline solid	Lattice vibrations (- phonons – collective excitation)	Sharp, well-defined peaks (e.g., 520 cm ⁻¹ for c-Si)
Amorphous	Local/disordered vibrations	Broad bands, shifted from crystal values
Nanocrystal	Confined phonons	Shifted and broadened phonon-like peaks
Molecular/non-crystal	Bond-specific vibrations	Peaks for individual bonds (e.g., Si–Si)



Collective Excitation





Case study: Silicon



The two peaks can be used to estimate crystalline-to-amorphous ratio.

 A_c/A_a

Si-Si Bond in Raman

• The Si–Si bond is **non-polar**, but it's highly polarizable, especially in crystalline or amorphous silicon. That makes it very Raman active, particularly for stretching modes.

Raman Features:

- The dominant Raman mode for crystalline Si is the first-order Si–Si stretching mode at ~520 cm⁻¹.
- For amorphous Si, this peak is broader and red-shifted (typically ~480 cm⁻¹).
- Higher-order modes (overtones, combinations) can appear at higher wavenumbers (e.g., ~960 cm⁻¹, ~1500 cm⁻¹), but are much weaker.

Bending Modes:

- The bending, wagging, or rocking modes of Si–Si bonds are generally Raman inactive or very weak because they don't involve a significant change in polarizability.
- However, these might show up in IR, depending on the local environment (like in **Si–O–Si** frameworks in silicates).





Number of Layers of MoS₂ Determined Using Raman Spectrocopy





Figure 2b: Raman spectra of MoS₂ in the fingerprint region.

Number of Layers	$\Delta \omega = A_1 g - E_2 g^1 (cm^{-1})$
Bulk	~25
Bilayer	~21–22
Monolayer	~19–20



1µm



Residual Stress vs Raman Spectroscopy

а

С

Micro-Raman scattering measurements were performed on the GaN in a backscattering geometry with the 488 nm line of an Ar-ion laser.

The relation between Raman shift and stress is given by

 $\Delta \omega$ (cm⁻¹) = 6.2 σ (GPa)

Table 1Biaxial stress at each point on the free-standing GaN held under stress.

Position	А	В	С
$\frac{\overline{\Delta\omega \ (\text{cm}^{-1})}}{\sigma \ (\text{MPa} \)}$	0.45	0.02	-0.25
	73 (tensile)	3.2	-40 (compressive)



J. Kim, K. Baik, C. Park, S. Cho, S. J. Pearton, F. Ren, Phys. Status Solidi A 2006, 203, 2393.





Depth Profiling using Confocal Raman



Ying Song et al. Depth Profiling of Ion-Implanted 4H–SiC Using Confocal Raman Spectroscopy, Crystals, 10(2), 10.3390/cryst10020131.





Raman Spectroscopy at Variable Temperature



a wide temperature range, -196°C to 600°C

Ilaria Costantini et al. Use of Temperature Controlled Stage Confocal Raman Microscopy to Study Phase Transition of Lead Dioxide (Plattnerite), Minerals 2020, 10(5), 468







Raman Spectroscopy-Summary-1







Raman Spectroscopy-Summary-2

Advantages of Raman Spectroscopy

- Provides chemical/bonding information at sub-micron scale
- Analyzes materials in all states: solid, liquid, gas, ambient, vacuum, inert, dynamic
- Enables depth profiling in transparent or semi-transparent materials (micron resolution)
- Offers wide in-situ capabilities: temperature, environment, strain, and reaction monitoring
- Aqueous solution works well

Disadvantages of Raman Spectroscopy

- Fluorescence can obscure Raman signal (laser choice may help)
- Laser-induced material degradation possible
- Does not provide elemental information
- Low Raman scattering efficiency \rightarrow detection limit ~1% for most materials





Horiba LabRAM Raman System with Integrated TERS Capabilities





-196 C to 600 C

- Multi-Laser Capability: 473 nm, 532 nm, 633 nm, and 785 nm
- Ultra-Low-Frequency Filters enabling Raman spectroscopy down to 5 cm⁻¹
- Integration with TERS (Tip-Enhanced Raman Spectroscopy)
- Heating/cooling stage





Quantitative Analysis of IR and Raman

Key Conditions for Reliable Quantitative Use



- FT-IR: Absorbance (A) ∝ concentration × pathlength × molar absorptivity
- **Raman**: Intensity ∝ concentration × laser power × cross-section

🔽 2. Use a Calibration Curve

- Prepare known standards at different concentrations
- Measure their peak areas
- Fit a curve (usually linear or polynomial)
- o Use this to determine unknowns

🔽 3. Ensure Consistent Conditions

- Same pathlength, sample preparation, instrument settings
- Correct for **baseline**, **scattering**, and **noise**
- Use **internal standards** if matrix effects are significant
- 4. Choose the Right Peak
- Select well-resolved, non-overlapping peaks
- Ideally, choose a peak that doesn't shift with concentration or environment



Beer-Lambert Law

 $A = \varepsilon * l * c$

A: absorption
ε: molar absorptivity
l: path length
C: concentration





I_R is the Raman intensity
I₀ is the incident laser intensity
c is the concentration of the molecule
σ is the Raman scattering cross-section





Quantitative Analysis of IR and Raman



Figure 1: Raman spectra from 0.25, 0.50, 1.0, 2.0, 4.0, 6.0, and 8.0 M guanidine hydrochloride. Inset shows a zoomed-in area of the 1010 cm⁻¹ peak that was used for peak fitting.

Choose strong and sharp peak



Figure 2: Average Raman peak area of 1010 cm⁻¹ peak from 3 sets of measurements plotted as a function of guanidine hydrochloride concentration. Error bars represent standard deviation over 3 measurements per data point.

By courtesy of Horiba application note





Comparison

	IR Spectroscopy	Raman Spectroscopy
Light source	Broadband mid IR light beam (25 um to 2.5 um)	Laser (473 nm, 532 nm, 633 nm, and 785 nm)
Spectral range	$400 - 4000 \text{ cm}^{-1}$ for transmission 600 to 4000 cm ⁻¹ for ATR	$50 - 4000 \text{ cm}^{-1}$
Light interaction	Absorption at certain frequencies	Inelastic scattering from laser
Requires	Change in dipole moment in chemical bond during vibration	Change in polarizability in chemical bond during vibration
Good for	Polar bonds and asymmetric vibration such as C-H, O-H, C=O	Symmetric, non-polar vibrations such as Si-Si, O ₂ , N ₂ , CO ₂ , C=C
Examples	Organics, polymer	Inorganics, carbon materials
Aqueous sample	Poor (Water is a strong adsorber and has huge IR peaks.)	Excellent (Water is Raman inactive.)
Result information	Functional group identification	Crystallinity and phase, Stress/strain effects, Defects and disorder





Data Interpretation & Identification with Free AI

- Analyze Spectrum: Read and describe the raw spectrum
- **Peak Assignment**: Help identify functional groups or molecular vibrations corresponding to peaks in the spectrum.
- **Fingerprint Region Matching**: Compare experimental spectra with known spectra for material identification.
- Material Comparison: Determine differences between two samples (e.g., before and after treatment).

However, careful review is critical due to a lot of mistakes.













Al-driven Data Analysis



Key Peaks & Likely Functional Groups:

- ~3300 cm⁻¹ (Broad, strong): Likely indicates O–H stretch (alcohols or phenols) or N–H stretch (amines/amides), especially if broad.
- 2) ~2950–2850 cm⁻¹ (Sharp peaks):
 C–H stretching in alkanes (sp³ C–H).
- ~1700 cm⁻¹ (Strong peak): Classic C=O stretch — could be from ketones, aldehydes, carboxylic acids, esters, etc.
- 4) ~1600 cm⁻¹ and ~1500 cm⁻¹: Could correspond to C=C stretches (aromatic rings or alkenes), or N–H bending (if amides).
- 5) \sim 1250–1000 cm⁻¹:

C–O stretching — possibly ethers, esters, or alcohols.

6) \sim 700–900 cm⁻¹:

Could be **aromatic C–H out-of-plane bending**, useful in identifying substituted benzene rings.





Thank You for Your Attendtion!

QUESTIONS?

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