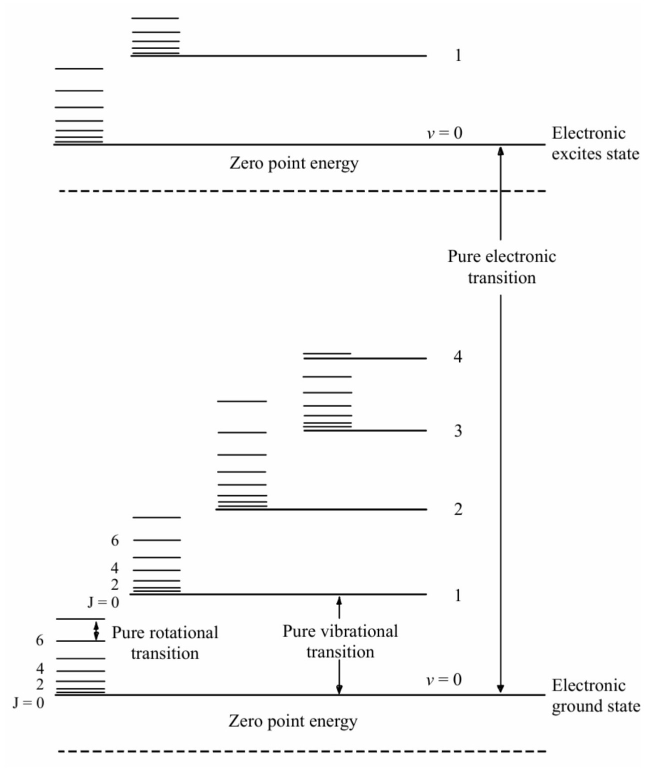
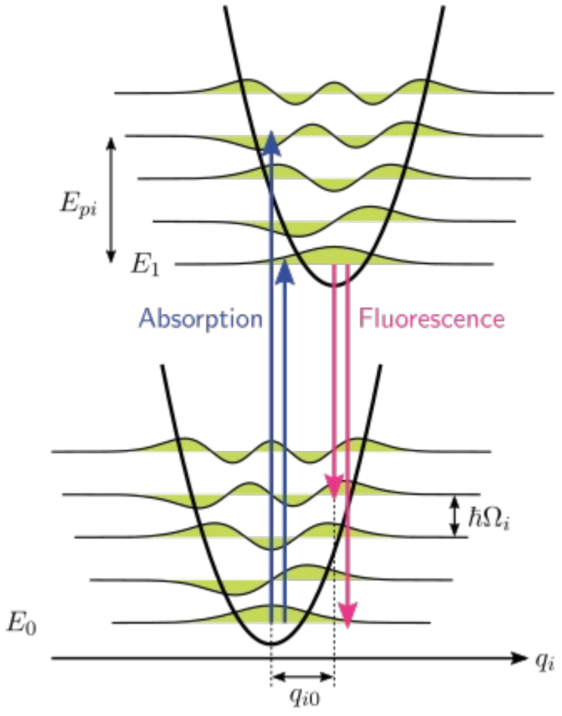
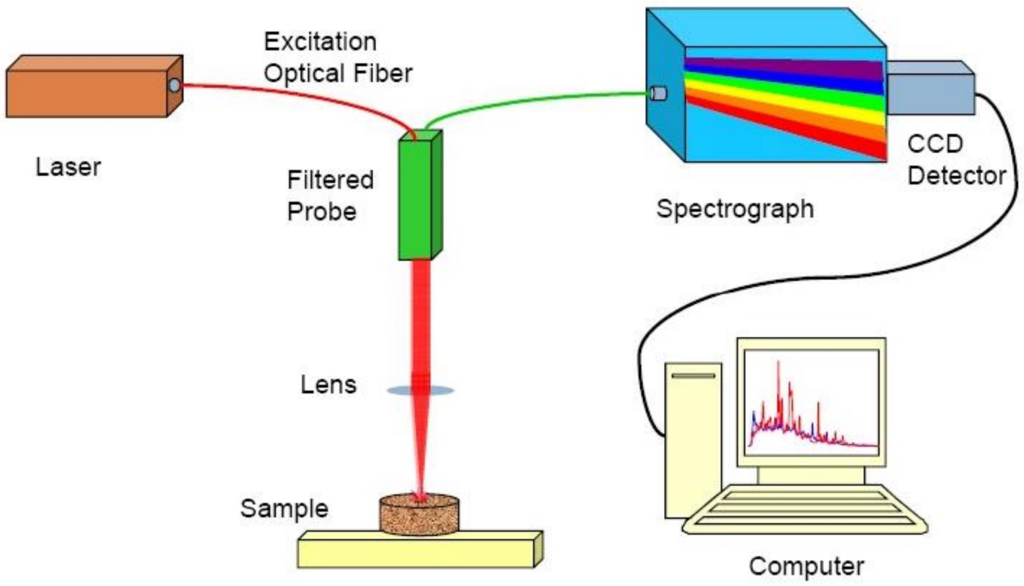
Raman Spectroscopy

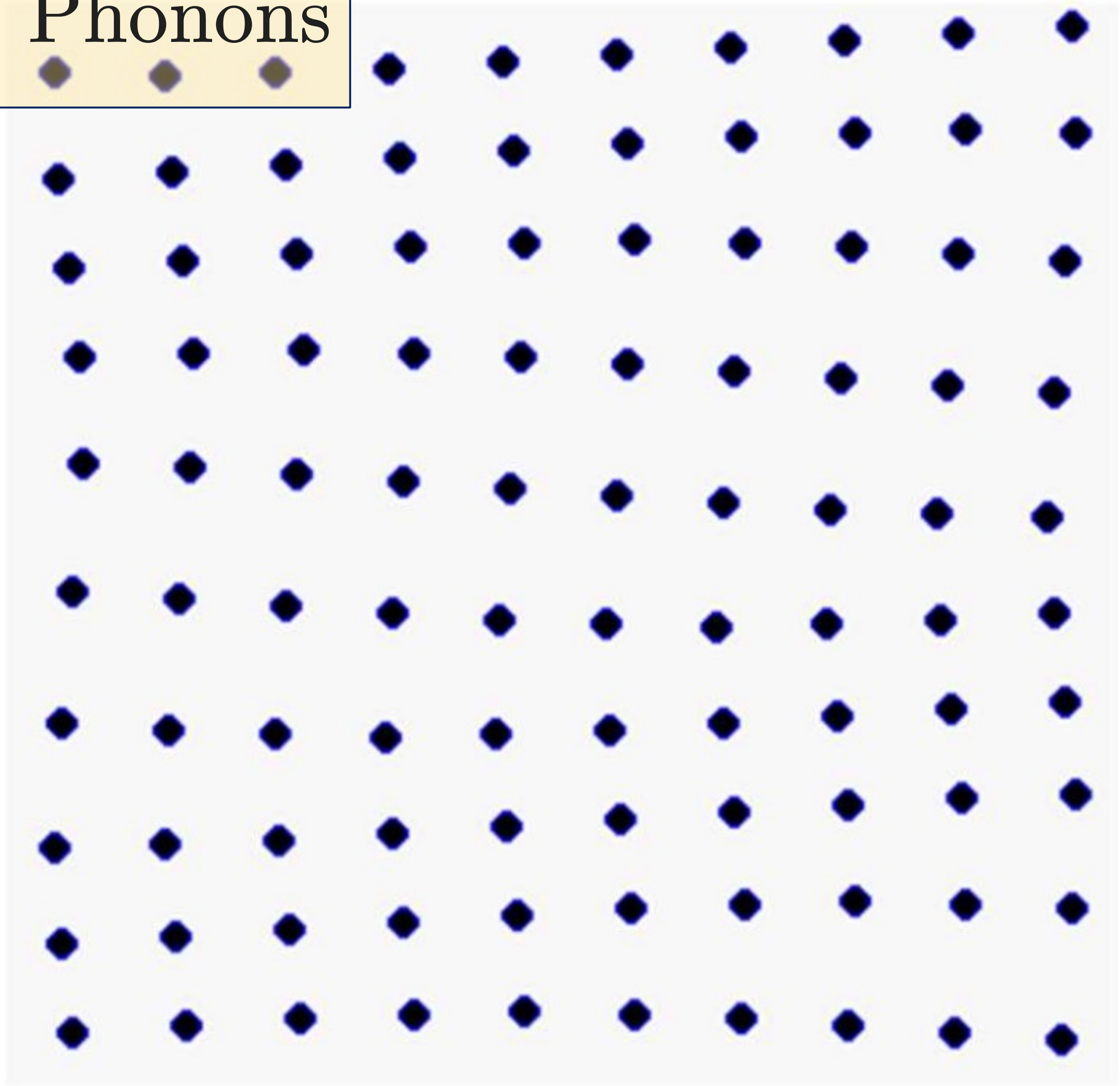
Parth Bhargava · A0310667E



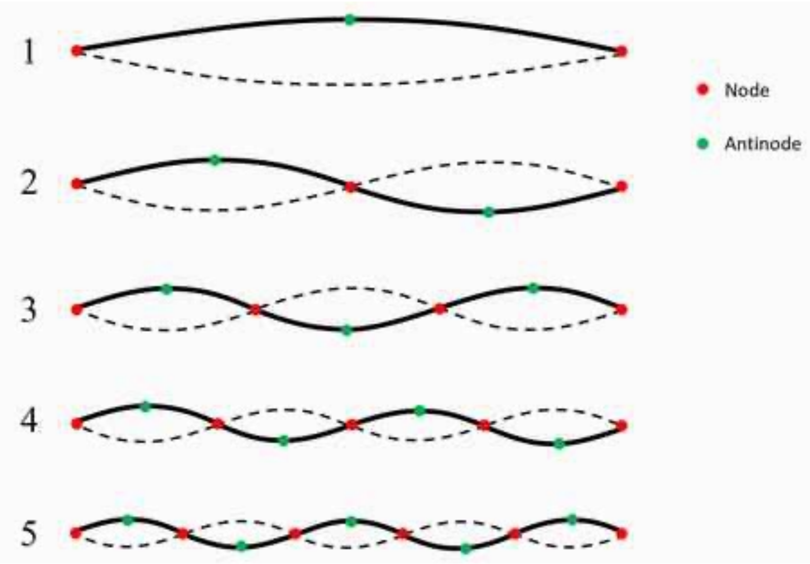




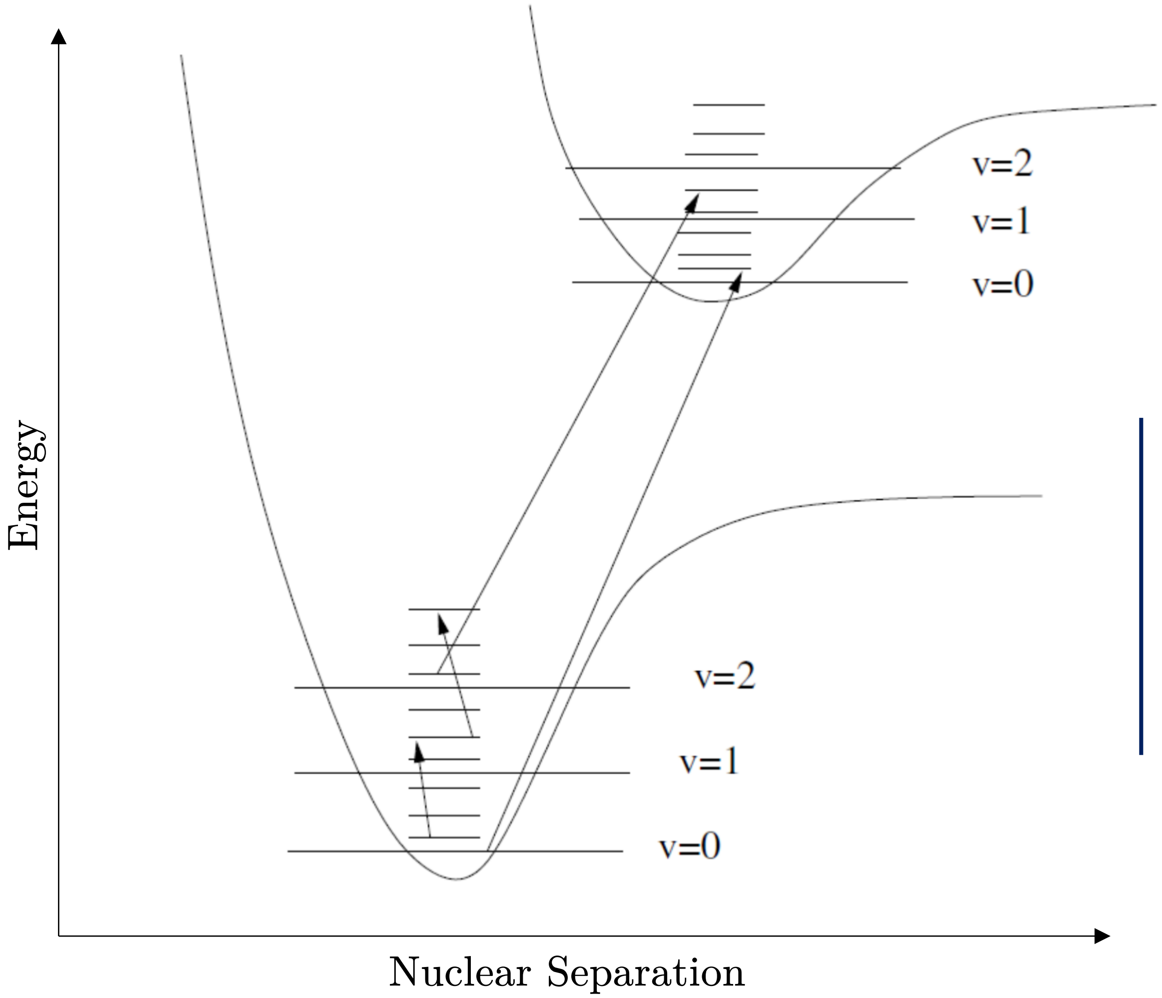
Phonons



A phonon is a quantized vibration of the crystal lattice. In a solid, atoms don't vibrate independently; they oscillate collectively. When a Raman photon interacts with the material, it creates or absorbs one phonon. The phonon's energy determines the Raman shift we measure.



Energy levels



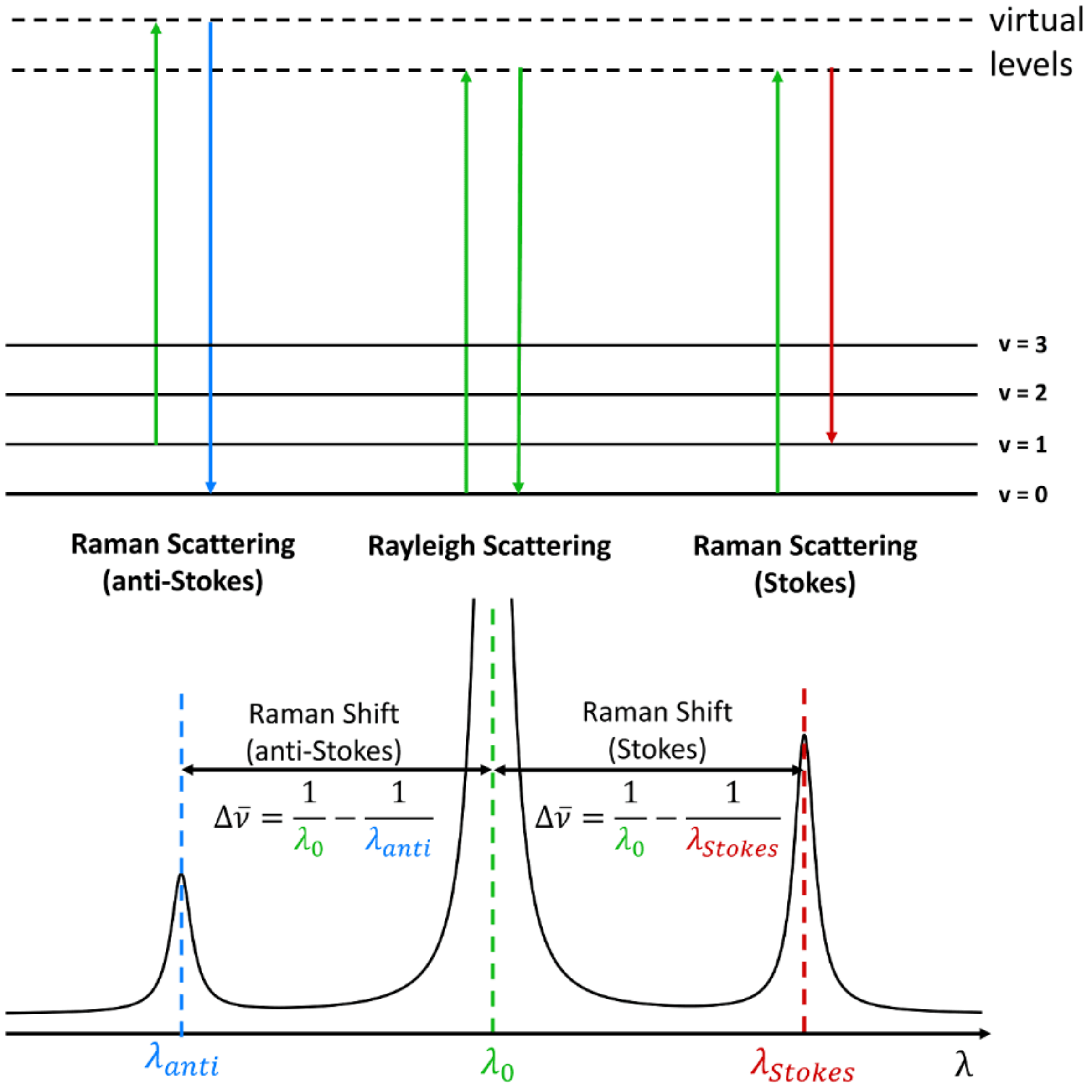
Molecules have quantized energy levels:

1. **Electronic** levels sit far apart (UV/visible light).
2. **Vibrational** levels are closely spaced within each electronic state (infrared range).
3. **Rotational** levels are even finer (microwave range).

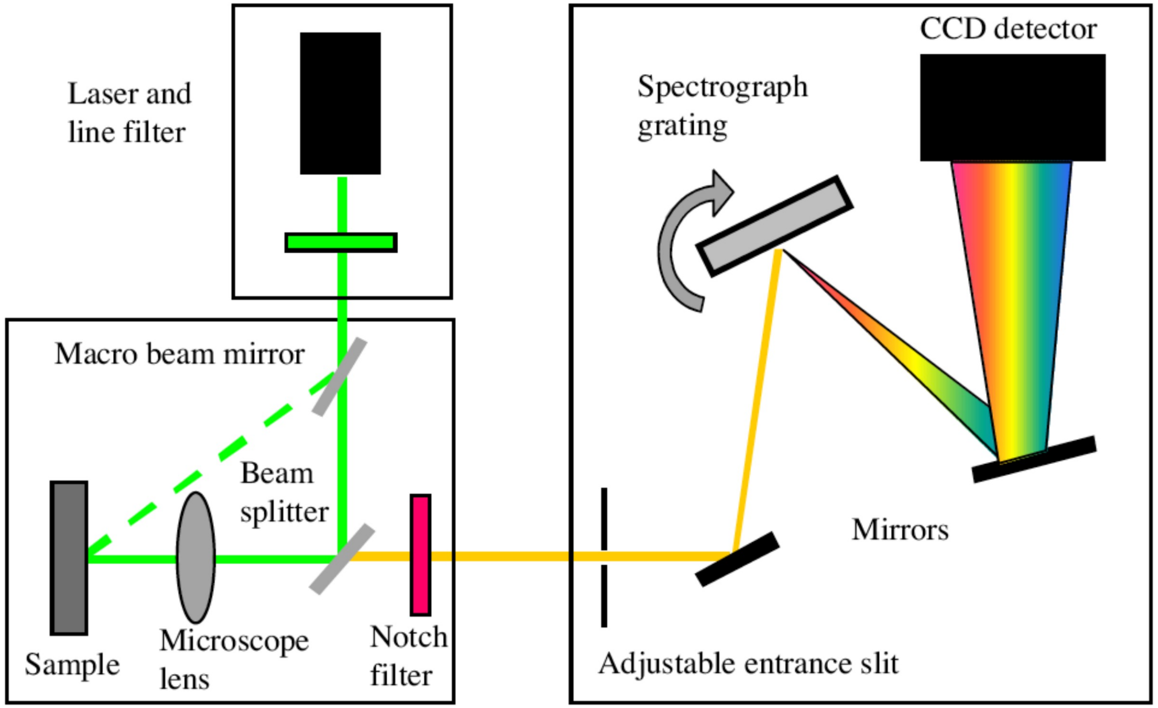
Raman spectroscopy probes the vibrational transitions. The photon does not need enough energy to reach an excited electronic state. Instead, it briefly excites the molecule to a **virtual state**, and the molecule drops back down to a different vibrational level. The energy difference between the incoming and scattered photon equals the **vibrational energy gap**.

Scattering

Stiffer bonds and lighter atoms vibrate at higher frequency, so the shift acts as a fingerprint of structure rather than composition.



The Experiment



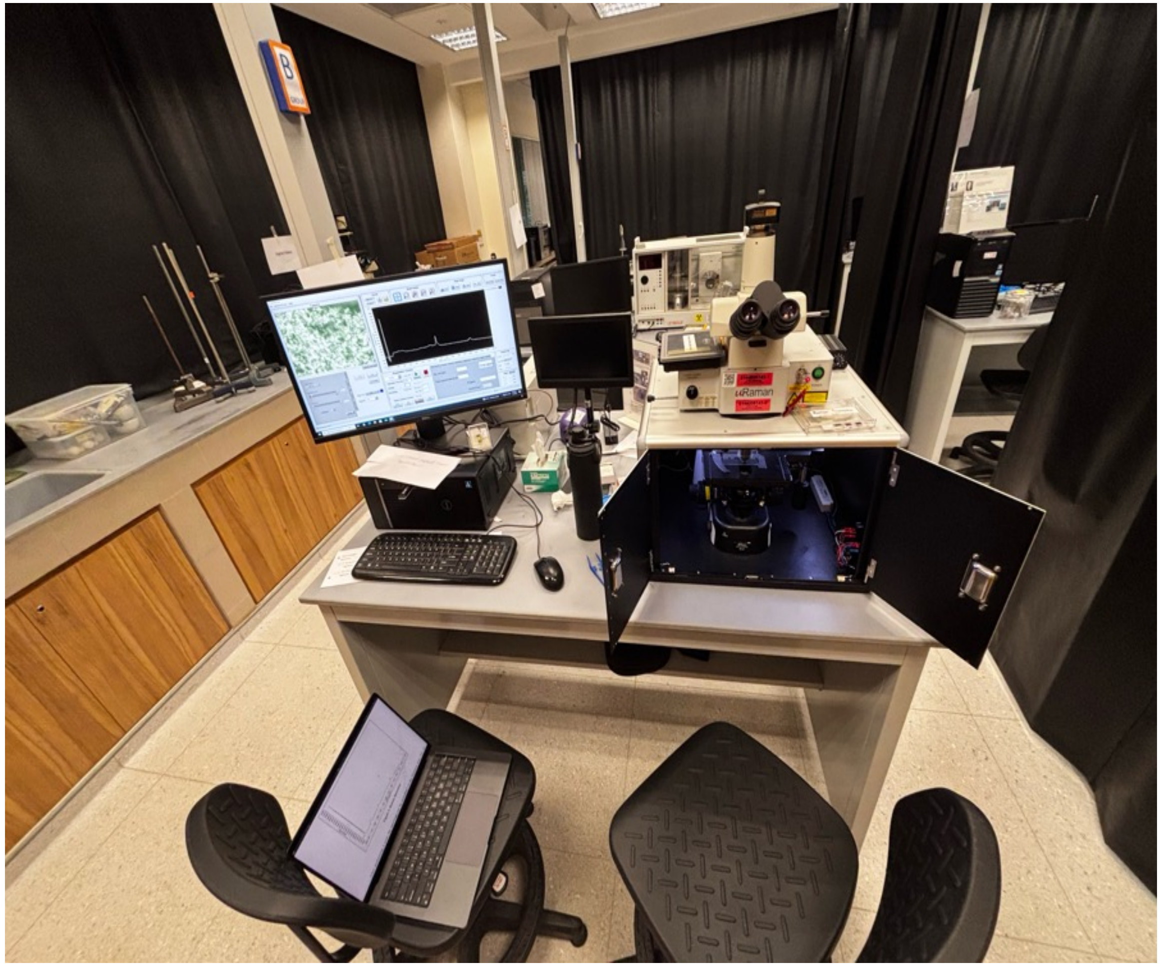
What is Raman spectroscopy?

When you shine a laser on a material, most photons bounce off unchanged. But a small fraction lose or gain energy by interacting with **lattice vibrations**. The **energy shift** tells you about the bonds in the sample. Different structures give different shifts, so a single spectrum can identify what you're looking at.

Objectives

- Identify the characteristic Raman bands of four carbon allotropes (graphite, HOPG, SWCNT, diamond)
- Determine if three unknown samples are genuine diamond
- Estimate the layer count of a graphene film
- Identify an unlabeled semiconductor wafer

Experimental Setup



uRaman-532TEC-Ci coupled to a Nikon Eclipse microscope

Instrument details

Laser	532 nm diode
Objective	Nikon 20× S Fluor (NA 0.75)
System	uRaman-532TEC-Ci
Spectral resolution	~26 cm^{-1} (from diamond FWHM)
Power control	5-position hardware attenuator + software
Protocol	Dark spectrum first, then sample acquisition

For each measurement, a dark spectrum was acquired first to establish the detector baseline. Multiple independent runs were taken per sample and averaged to check reproducibility. The run-to-run spread (shaded bands in plots) shows measurement consistency.

What to look for: Carbon Bands

Each vibrational mode in a carbon material shows up as a specific peak in the Raman spectrum. With 532 nm excitation, here are the bands we expect:

Diamond sp^3 (~1332 cm^{-1}): single sharp line from the tetrahedral carbon lattice. Completely different from the sp^2 bands.

D band (~1350 cm^{-1}): disorder-activated. Only shows up when defects or edges break the crystal symmetry. Stronger D relative to G means more disorder.

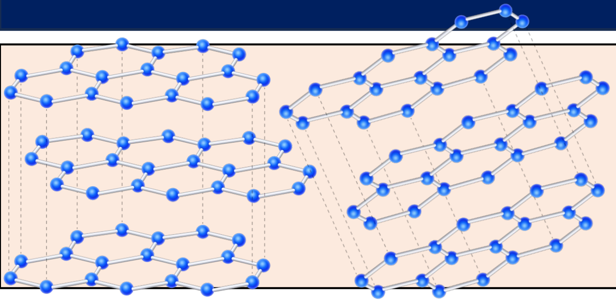
G band (~1580 cm^{-1}): in-plane C-C stretch. Present in all sp^2 carbon. Position is fairly stable.

D′ band (~1620 cm^{-1}): another disorder mode, appears as a shoulder on the G band. Hard to resolve without deconvolution.

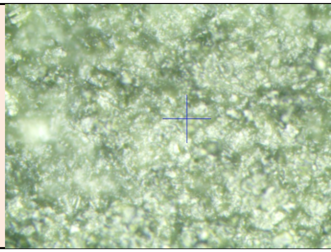
2D band (~2700 cm^{-1}): two-phonon overtone of D. Does not require disorder. Its shape and intensity relative to G tell you about layer stacking in graphene.

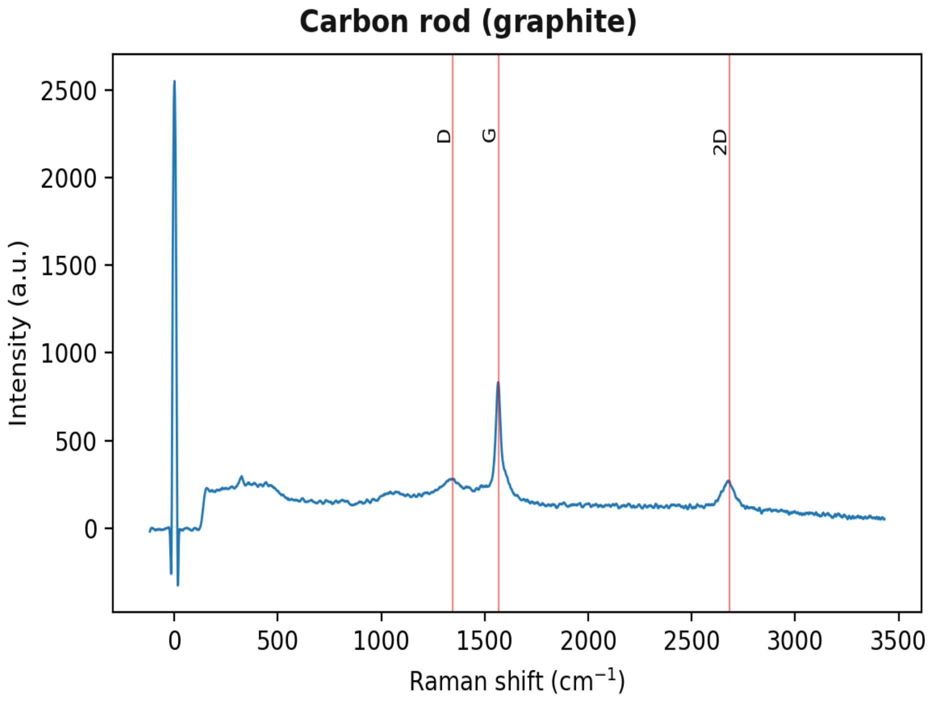
Quick diagnostic guide

G band present	sp^2 carbon confirmed
D/G intensity ratio	higher = more disorder
G-band FWHM	broader = less crystalline
2D/G ratio + 2D FWHM	graphene thickness indicator
Sharp line at 1332 cm^{-1}	diamond (sp^3)
D′ shoulder near G	additional disorder marker



Carbon Rod (Polycrystalline Graphite)





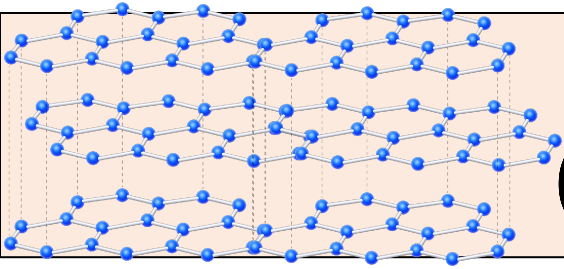
Averaged spectrum of 3 runs. Shaded band = run-to-run spread.

The spectrum shows all three expected sp^2 bands: D, G, and 2D.

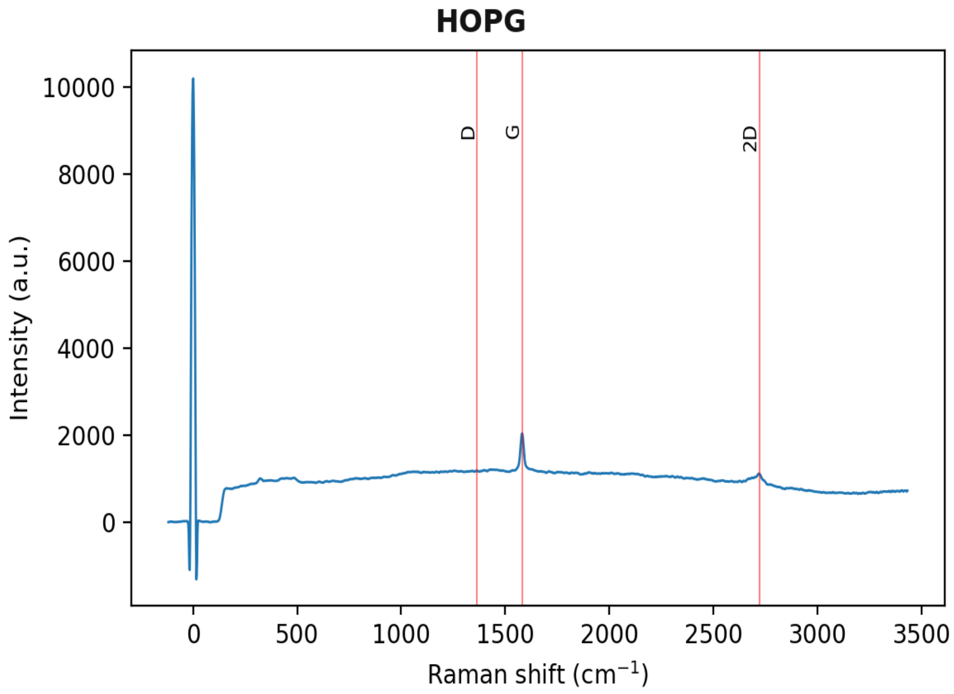
G band at 1566 ± 2 cm^{-1} is **14 cm^{-1}** below the ideal 1580. Since HOPG (measured next) sits right at 1581, this isn't a calibration problem.
The downshift comes from phonon confinement: in very small crystallites, the wavevector selection rule relaxes, letting phonons away from the zone centre contribute and pulling the observed G frequency down. This is characteristic of *nanocrystalline graphite*.

$D/G = 0.09 \pm 0.01$ confirms grain-boundary disorder. **FWHM(G) = 25 cm^{-1}** is broader than **HOPG's 18 cm^{-1}**.

2D band at 2681 ± 6 cm^{-1}.



HOPG
(Highly Oriented Pyrolytic Graphite)



Averaged spectrum of 3 runs. Shaded band = run-to-run spread.

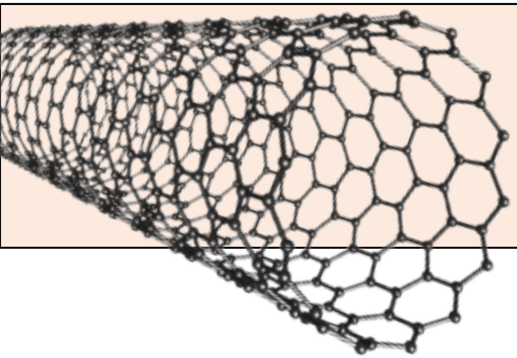
HOPG is our best-ordered sample, and the spectrum reflects that.

G band at 1581 ± 2 cm^{-1} matches the textbook value almost exactly. FWHM of just **18 cm^{-1}, the narrowest of all our samples**.

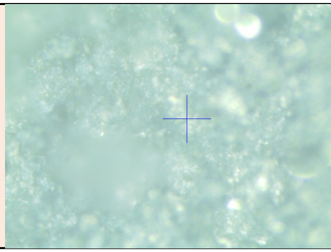
D/G = 0.04 ± 0.01 is less than half the carbon rod's, confirming *far fewer defects and better long-range crystalline order*. The D band is so weak it's hard to pin down its position (large uncertainty of ±15 cm^{-1}).

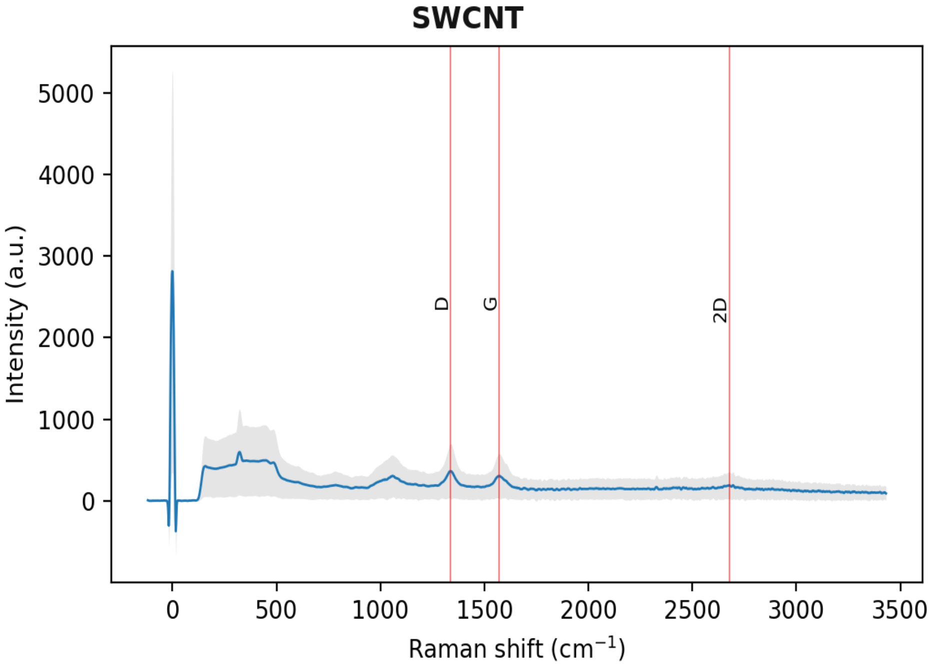
2D band at 2720 ± 2 cm^{-1} is shifted about 40 cm^{-1} higher than in the carbon rod. This reflects the strong AB stacking in HOPG, where interlayer coupling pushes the double-resonance condition to higher frequency.

HOPG serves as our reference for well-ordered graphite. Any other sp^2 sample can be compared against it.



SWCNT
(Single-Wall Carbon Nanotubes)





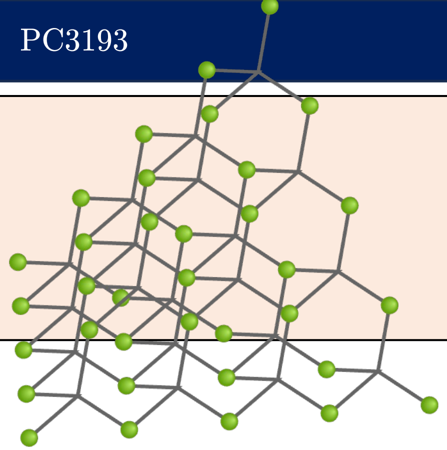
Averaged spectrum of 3 runs. Shaded band = run-to-run spread.

This is the most disordered sp^2 sample we measured.

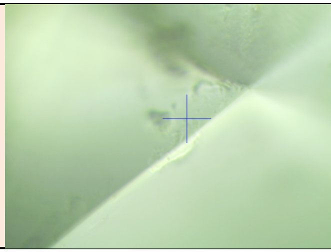
$D/G = 1.2 \pm 0.3$ means the D band is actually more intense than the G band. The nanotube bundle has a lot of structural discontinuities: tube ends, junctions, and defective sidewalls all activate the D mode.

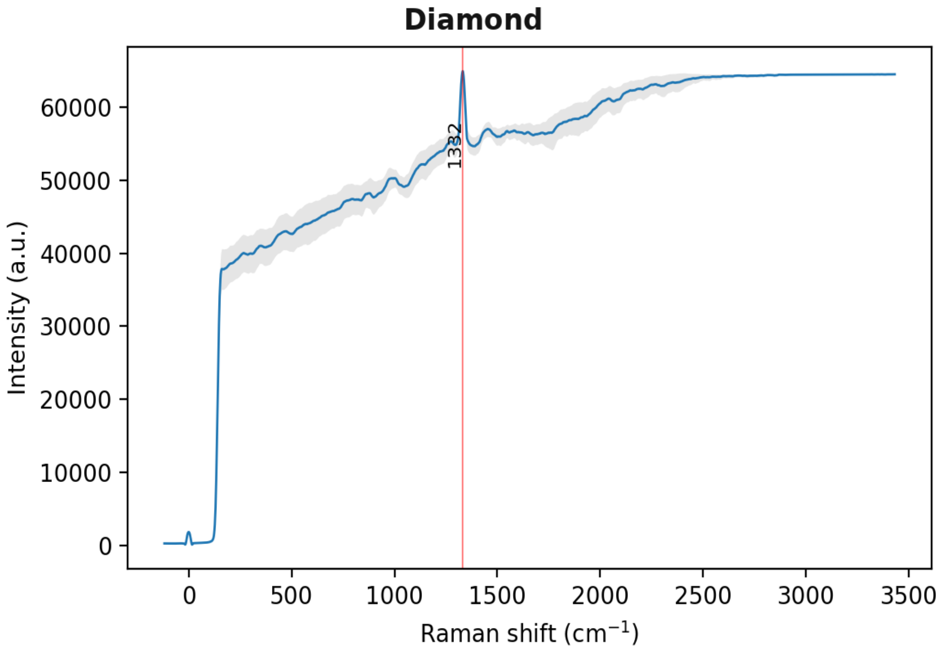
Both bands are broad (FWHM: D ~58 cm^{-1}, G ~65 cm^{-1}) and the run-to-run scatter in positions (±9 and ±13 cm^{-1}) is large. This reflects the *heterogeneity of the bundle*: each laser spot probes a different mixture of tube types and orientations.

G band at 1572 ± 13 cm^{-1}, slightly downshifted. **2D at 2677 ± 11 cm^{-1}.**



Diamond





Averaged spectrum of 3 runs. Shaded band = run-to-run spread.

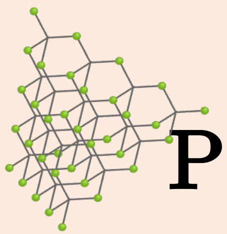
Diamond gives a completely different spectrum from sp^2 carbon.

A single sharp peak at 1333 ± 2 cm^{-1} from the zone-centre optical phonon of sp^3 carbon. Literature value is 1332 cm^{-1} ($\Delta = +1$ cm^{-1}).

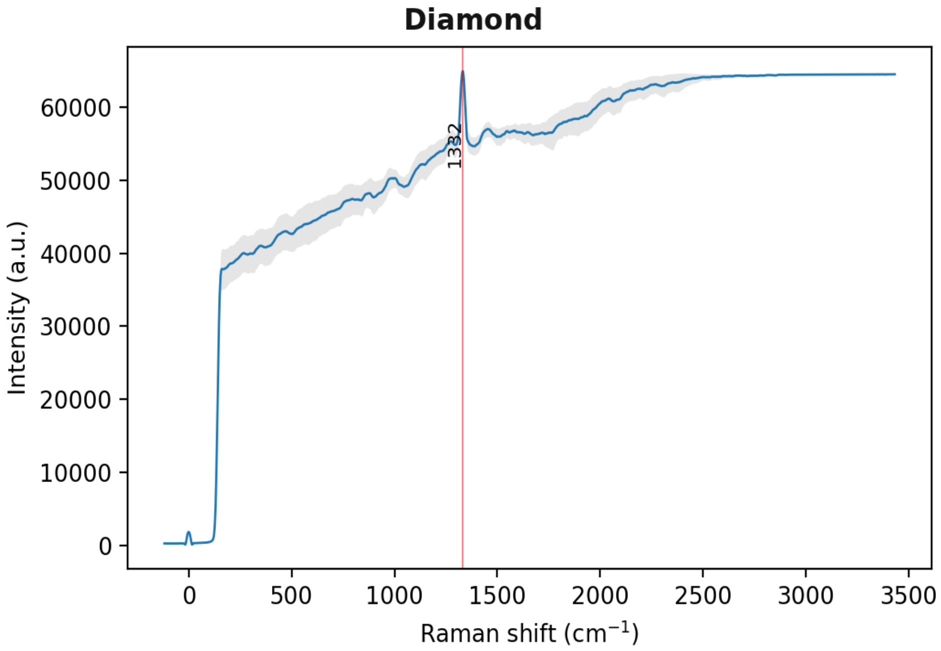
Measured FWHM ~26 cm^{-1} is instrument-limited: natural diamond linewidth is only 2-3 cm^{-1}. The width we see reflects the spectrometer's resolution, not the diamond.

No D or G bands confirms high-quality crystalline diamond with no sp^2 contamination.

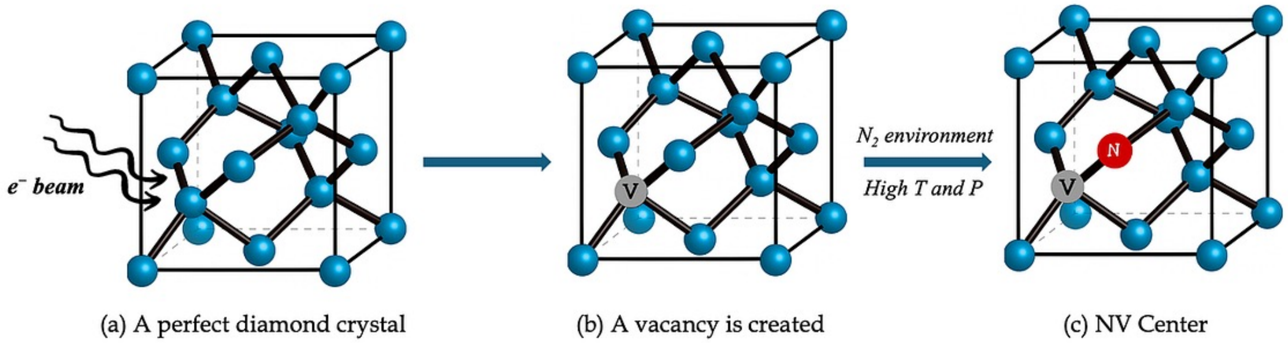
The baseline rises steadily toward higher Raman shifts. This is not noise. It is photoluminescence from nitrogen defect centres in the lattice, which we explain on the next slide.



Diamond Photoluminescence



Averaged spectrum of 3 runs. Shaded band = run-to-run spread.



(a) A perfect diamond crystal (b) A vacancy is created (c) NV Center

The rising slope in the diamond spectrum is **photoluminescence** from trace nitrogen or other **colour centres**. Under **532 nm** excitation, these defects fluoresce broadly at wavelengths longer than the laser line, which shows up as an **increasing background toward higher Raman shifts**. A small step-like discontinuity superimposed on this slope is an *acquisition artefact from detector segment stitching*, not a Raman feature.

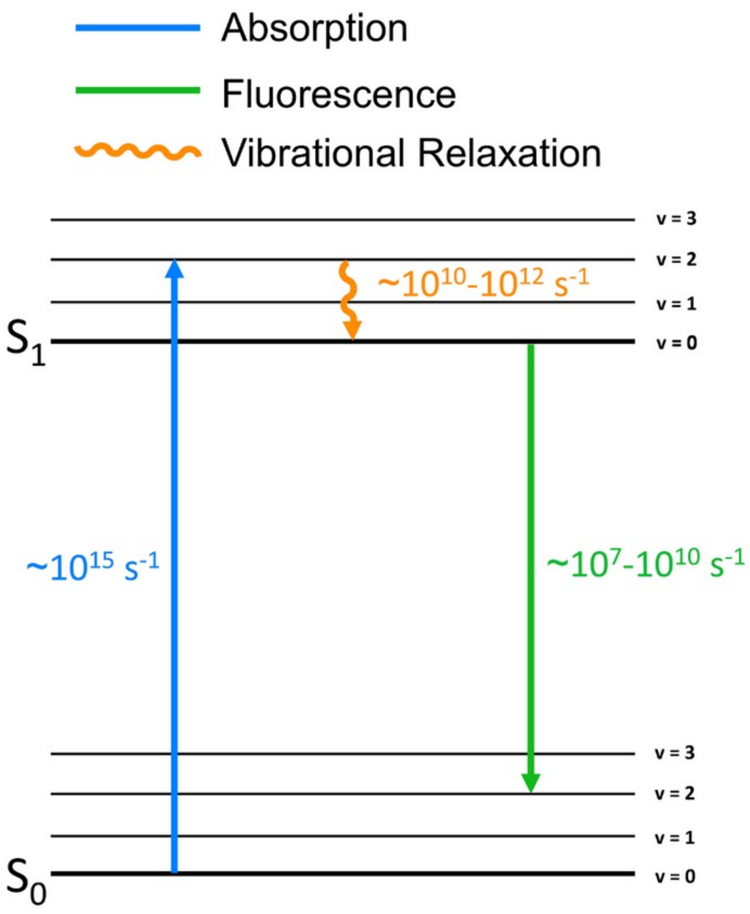
Why does diamond fluoresce?

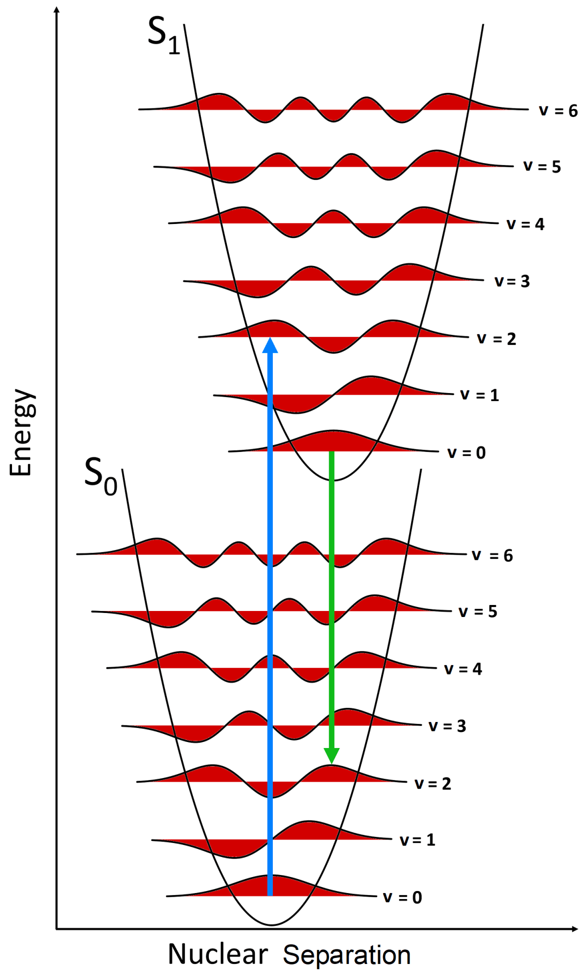
Natural diamond always contains trace impurities, most commonly **nitrogen atoms substituting for carbon** in the lattice.

Single nitrogen (**C centre**) and nitrogen-vacancy (**NV centre**) defects create *electronic states within the diamond bandgap*. When **532 nm** laser light excites these centres, they absorb and then re-emit photons at longer wavelengths (lower energy).

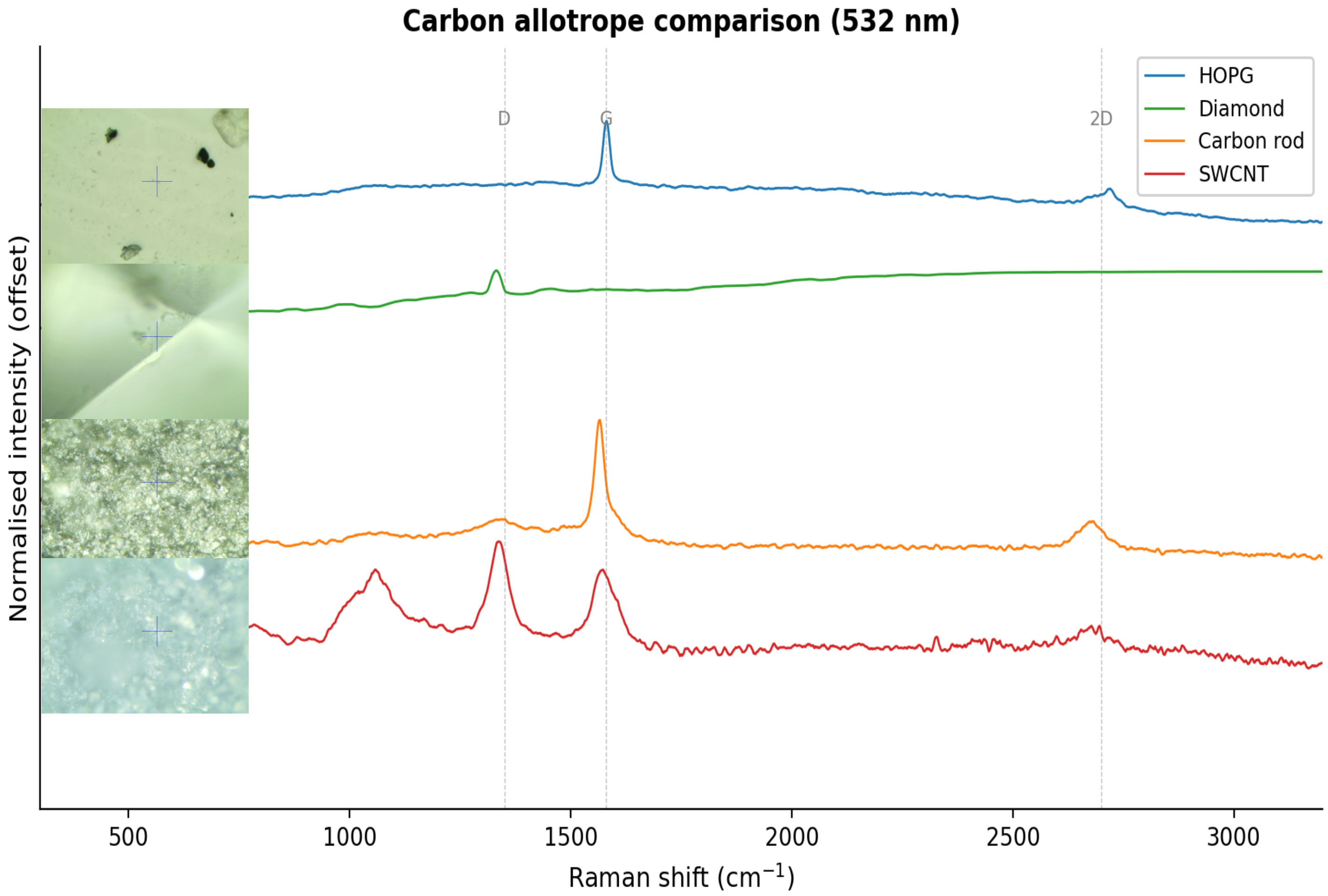
Since the fluorescence emission is broad and shifts to longer wavelengths, it appears as a **steadily rising background** when plotted against Raman shift (which increases with scattered wavelength).

This is a well-known feature of diamond Raman spectroscopy and is actually used in *gemology* to characterise diamond type and nitrogen content.





Allotrope Comparison



Spectra normalised to G-peak maximum; vertically offset for clarity.

HOPG

D/G = 0.04 · G = 1581 cm^{-1} · FWHM = 18 cm^{-1}

Best-ordered sp^2; minimal defects

Diamond

sp^3 at 1332 cm^{-1} · No D or G bands

sp^3 lattice; categorically different bonding

Carbon rod

D/G = 0.09 · G = 1566 cm^{-1} · FWHM = 25 cm^{-1}

G downshifted −14 cm^{-1}; phonon confinement

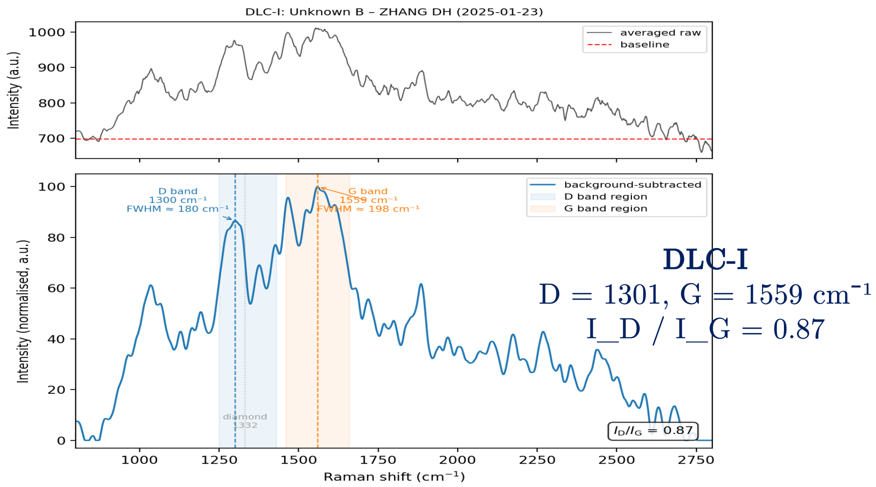
SWCNT

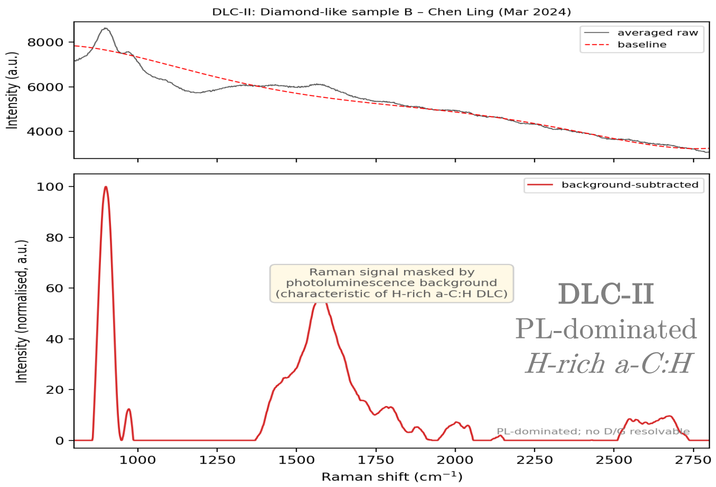
D/G = 1.2 · G = 1572 cm^{-1} · FWHM = 65 cm^{-1}

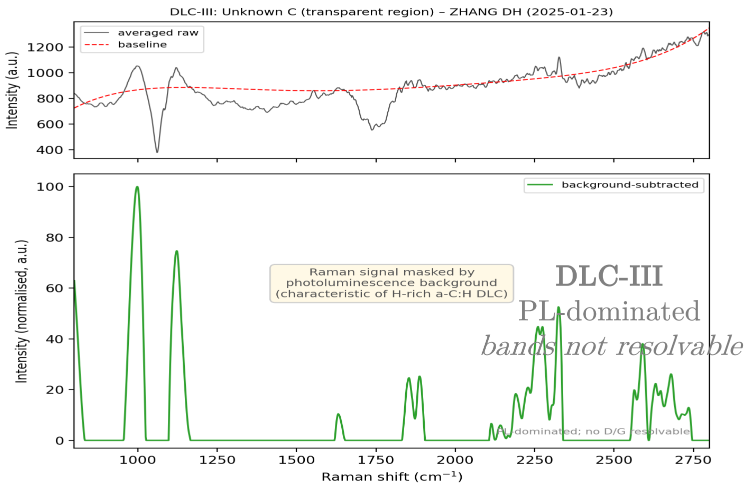
D > G; tube ends and defects dominate

D/G tracks disorder monotonically. Diamond stands apart — sp^3 bonding, no sp^2 modes.

Diamond-like Samples





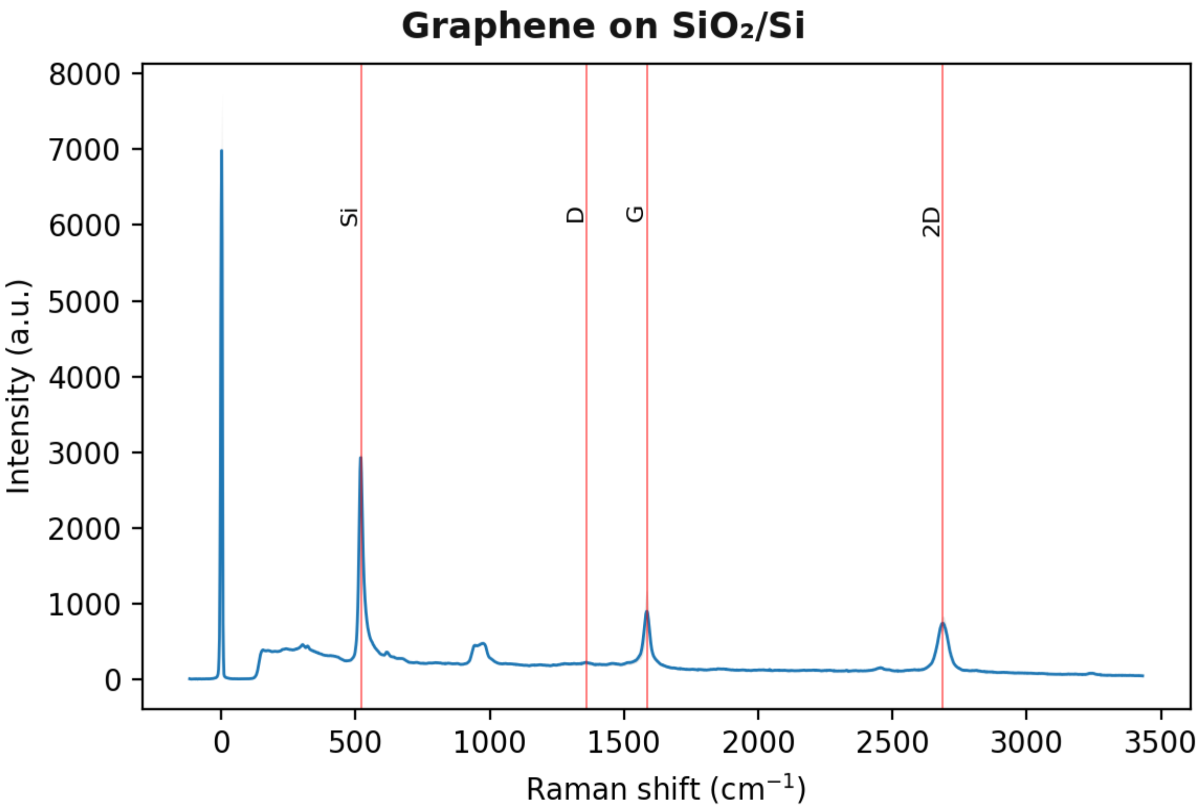


DLC-I shows two resolvable sp² bands: D at **1301 cm⁻¹** (FWHM ≈ 180 cm⁻¹) and G at **1559 cm⁻¹** (FWHM ≈ 198 cm⁻¹), with **I_D/I_G = 0.87**. Both bands are far broader than in graphite and the G band is redshifted — the fingerprint of *amorphous carbon (a-C)*. Not diamond.

DLC-II and **DLC-III** are both dominated by **broadband photoluminescence** — no Raman D or G peaks can be resolved above the background. The strong PL in DLC-II is characteristic of *hydrogen-rich amorphous carbon (a-C:H)*, where C–H bonds create fluorescent electronic states. DLC-III shows intermediate fluorescence with the same result: no identifiable Raman features.

None of the three samples are crystalline diamond. DLC-I has sp² amorphous character; DLC-II and III are masked by photoluminescence. Distinguishing diamond from ta-C in DLC-I would require XRD or electron diffraction.

Graphene Thickness



Averaged over 5 locations, 100 hardware averages each

2D/G thickness diagnostic

$$2D\ /\ G = 0.87$$

$\mathrm{FWHM_2D} = 54\ \mathrm{cm}^{-1}$

(averaged spectrum; per-location 1.0 ± 0.5)

Regime comparison

Monolayer: $2D/G > 2$, $\mathrm{FWHM} \approx 24\ \mathrm{cm}^{-1}$

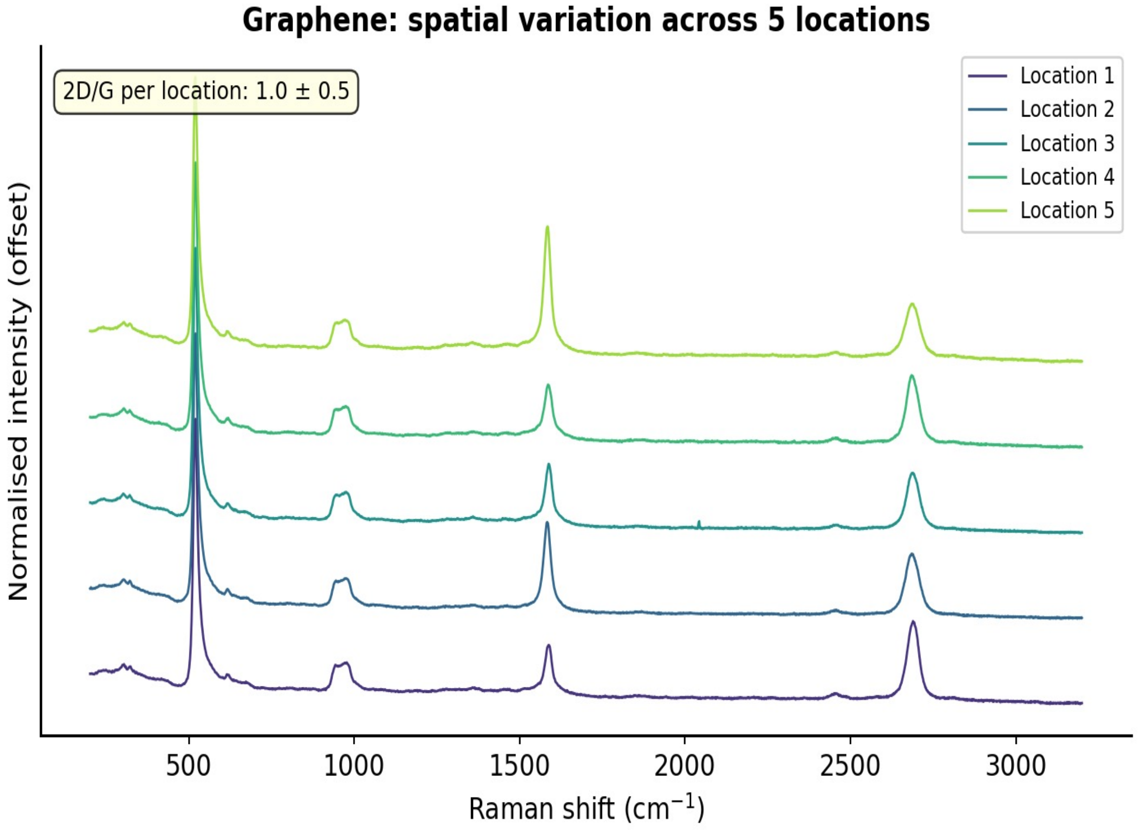
Few-layer: $2D/G \approx 0.8$–1, FWHM 40–55 cm^{-1}

Bulk graphite: $2D/G < 0.5$, asymmetric 2D

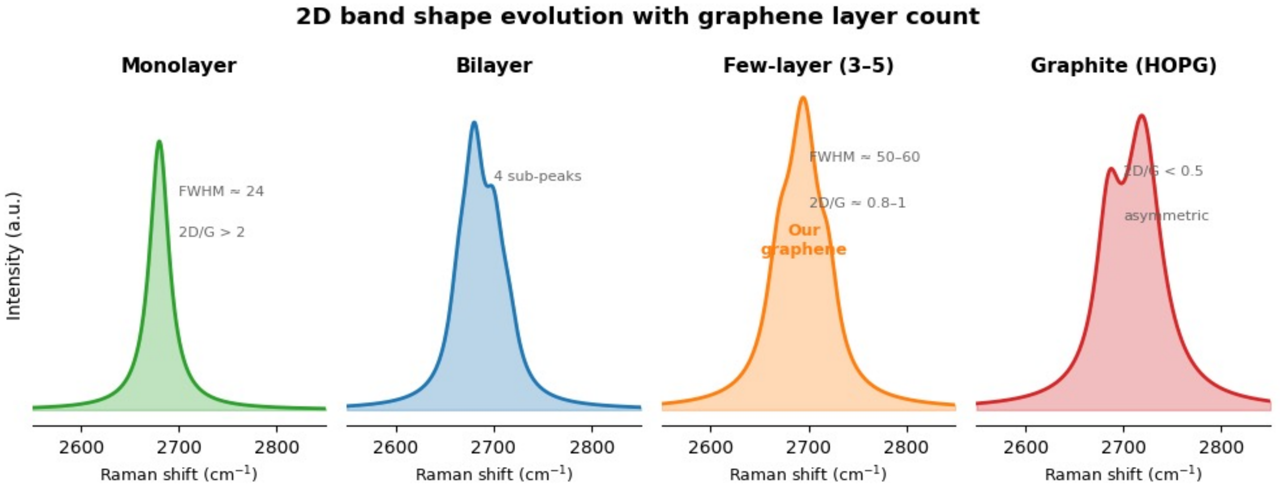
→ Few-layer (3–5 layers)

*The **521 cm⁻¹** Si peak confirms substrate penetration; SiO_2 thin-film interference enhances graphene Raman signal.*

Graphene: Spatial & Layer Evidence


Graphene: spatial variation across 5 locations

5 locations, 100 hardware averages each. Variation is thickness, not noise.


2D band shape evolution with graphene layer count

Layer-count assignment

$2D/G = 0.87 \quad\cdot\quad \mathrm{FWHM}(2D) = 54\ \mathrm{cm}^{-1}$

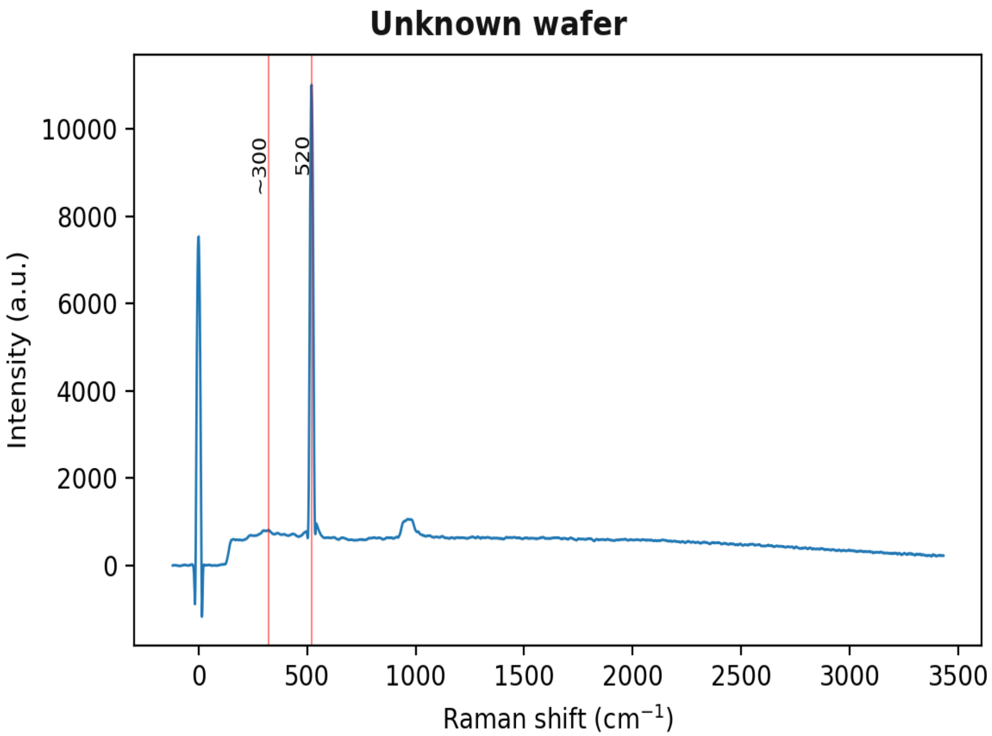
(averaged; per-location 1.0 ± 0.5)

$\mathrm{FWHM}(2D) = 54\ \mathrm{cm}^{-1}$, broadened beyond monolayer ($24\ \mathrm{cm}^{-1}$); multiple double-resonance pathways from layer stacking.

±50% scatter in 2D/G, genuine thickness inhomogeneity across the film. G position stable $\pm 2\ \mathrm{cm}^{-1}$.

→ Few-layer (3–5 layers)

Unknown Semiconductor



Unknown wafer: dominant 521 cm^{-1} line, weak 296 cm^{-1} combination

Identification

521 cm^{-1} ($\Delta = +0.3\ \text{cm}^{-1}$ vs 520.7 literature)

This is the *first-order transverse optical phonon* of crystalline silicon. **The match is nearly exact.**

A weaker feature near **296 cm^{-1}** is consistent with a known *two-phonon combination mode* in silicon.

No other peaks are present that would suggest a compound semiconductor like **GaAs** (peaks near **268 and 292 cm^{-1}**) or **GaN** (near **568 cm^{-1}**).

The wafer is crystalline silicon.

Error Analysis I

Instrument resolution

Diamond's natural linewidth is only **2-3 cm^{-1}**, but we measured **~26 cm^{-1}**. That means every FWHM in this experiment is the convolution of the true width with a **~26 cm^{-1}** instrument function.

For narrow peaks (**HOPG G: 18 cm^{-1}**), the instrument broadening dominates, so the true linewidth is even narrower.

For broad peaks (**SWCNT G: 65 cm^{-1}**), the instrument contribution is a smaller correction.

This same resolution limit is why **D′ at ~1620 cm^{-1}** (only **40 cm^{-1} from G**) can't be resolved as a separate peak.

Baseline subtraction & smoothing

The D/G ratios depend on how the background is subtracted. For HOPG where D is barely above the noise, the 10th-percentile baseline introduces **~10-20% systematic uncertainty**.

Repeating with a linear baseline shifts HOPG's D/G from **0.04 to about 0.03 (a 25% change)**. The qualitative ordering doesn't change, but the absolute values have *limited confidence for weak D bands*.

Savitzky-Golay smoothing (6 side points, 3rd order) was applied by the acquisition software for all samples except graphene (disabled to preserve the 2D band profile). This could *broaden measured FWHM by a few cm^{-1}*.

Error Analysis II

$\pm$ 50%

graphene 2D/G scatter across 5 locations

± 13 cm^{-1}

max run-to-run peak drift (SWCNT G band)

0 mW

software-reported laser power in all metadata

Spatial inhomogeneity: the graphene 2D/G ratio varies from about 0.5 to 1.5 across five locations. This is *real thickness variation* across the film, not measurement noise (the G band position stays stable at **1585 ± 2 cm^{-1}**). **It's the biggest single uncertainty in our thickness estimate.**

Run-to-run reproducibility: for well-defined peaks like HOPG G, the spread is less than **2 cm^{-1}** (instrument-limited). The SWCNT bundle has the worst reproducibility at **±13 cm^{-1}**, reflecting the *heterogeneous structure* of the sample rather than instrument drift.

Missing power data: the software reports **0 mW** for every measurement; actual power came from the hardware attenuator. This prevents comparing absolute intensities between samples, but all our ratios (**D/G, 2D/G**) are *self-normalising* and unaffected.

Conclusion

Carbon allotropes

All five Raman bands (**D, G, D′, 2D, sp^3**) identified across four allotropes. D/G ratios and G-band FWHM tracked disorder: **HOPG (D/G = 0.04, 18 cm^{-1})** to **SWCNT (D/G = 1.2, 65 cm^{-1})**. Carbon rod G downshift of **14 cm^{-1}** consistent with *phonon confinement in nanocrystalline graphite*.

Diamond-like samples

DLC-I shows two broad sp^2 bands (**D = 1301 cm^{-1}, G = 1559 cm^{-1}**, I_D/I_G = 0.87) , consistent with *amorphous carbon*, not diamond. **DLC-II and III** are dominated by photoluminescence; no Raman bands resolvable , consistent with *H-rich amorphous carbon (a-C:H)*. None of the three are crystalline diamond.

Graphene thickness

2D/G = **0.87**, FWHM(2D) = **54 cm^{-1}** → **few-layer graphene (3–5 layers)**. The **넘50%** scatter in 2D/G reflects *real thickness variation* across the film. Si peak at **521 cm^{-1}** confirms laser penetration through the film.

Unknown wafer

521 ± 2 cm^{-1} matches crystalline silicon (Δ = **+0.3 cm^{-1}**). No compound semiconductor signatures detected. **Identification is unambiguous.**

Thank You!

Parth Bhargava · A0310667E

Key references

[1] A. C. Ferrari, "Raman spectroscopy of graphene and graphite," Solid State Commun. 143, 47 (2007).

[2] Raman spectroscopy lab manual (provided).

[3] E. Smith and G. Dent, Modern Raman Spectroscopy: A Practical Approach (Wiley, 2005).

[4] K. Uchinokura et al., "Raman scattering by silicon," J. Phys. Chem. Solids 33, 811 (1972).

[5] S. E. Grillo et al., "Photoluminescence of Diamond," University of Bristol CVD Diamond Group.

[6] D. L. Andrews and R. H. Lipson, Molecular Photophysics and Spectroscopy, 2nd ed. (IOP Publishing, Bristol, 2021), Chap. 8.

[7] Edinburgh Instruments, "What is the Stokes Shift?" Edinburgh Instruments Resource Library. [Online]. Available: https://www.edinst.com/resource/what-is-the-stokes-shift/

[8] [Author unlisted], "Raman Spectroscopy — BSc Lecture Notes, Lec. 4," Dept. of Science, Tanta University. [Online]. Available: https://sci.tanta.edu.eg/files/Raman%20spectroscopy%20BSc-Lec4.pdf

[9] [Author unlisted], "Vibraciones moleculares y espectroscopia Raman," [in Spanish], idUS — Deposito de Investigacion, Universidad de Sevilla. [Online]. Available: https://idus.us.es/bitstreams/cfb4dfba-7630-4571-a771-38e35021e460/download

[10] J. S. Tse, "Lattice Dynamics," presented at the NRS 2018 Workshop, Advanced Photon Source, Argonne National Laboratory, 2018. [Online]. Available: https://www.aps.anl.gov/sites/www.aps.anl.gov/files/APS-Uploads/SECTOR3/Conferences/NRS2018/PDF/APS_IXS_JST.pdf