The Raman Fingerprint of Graphene

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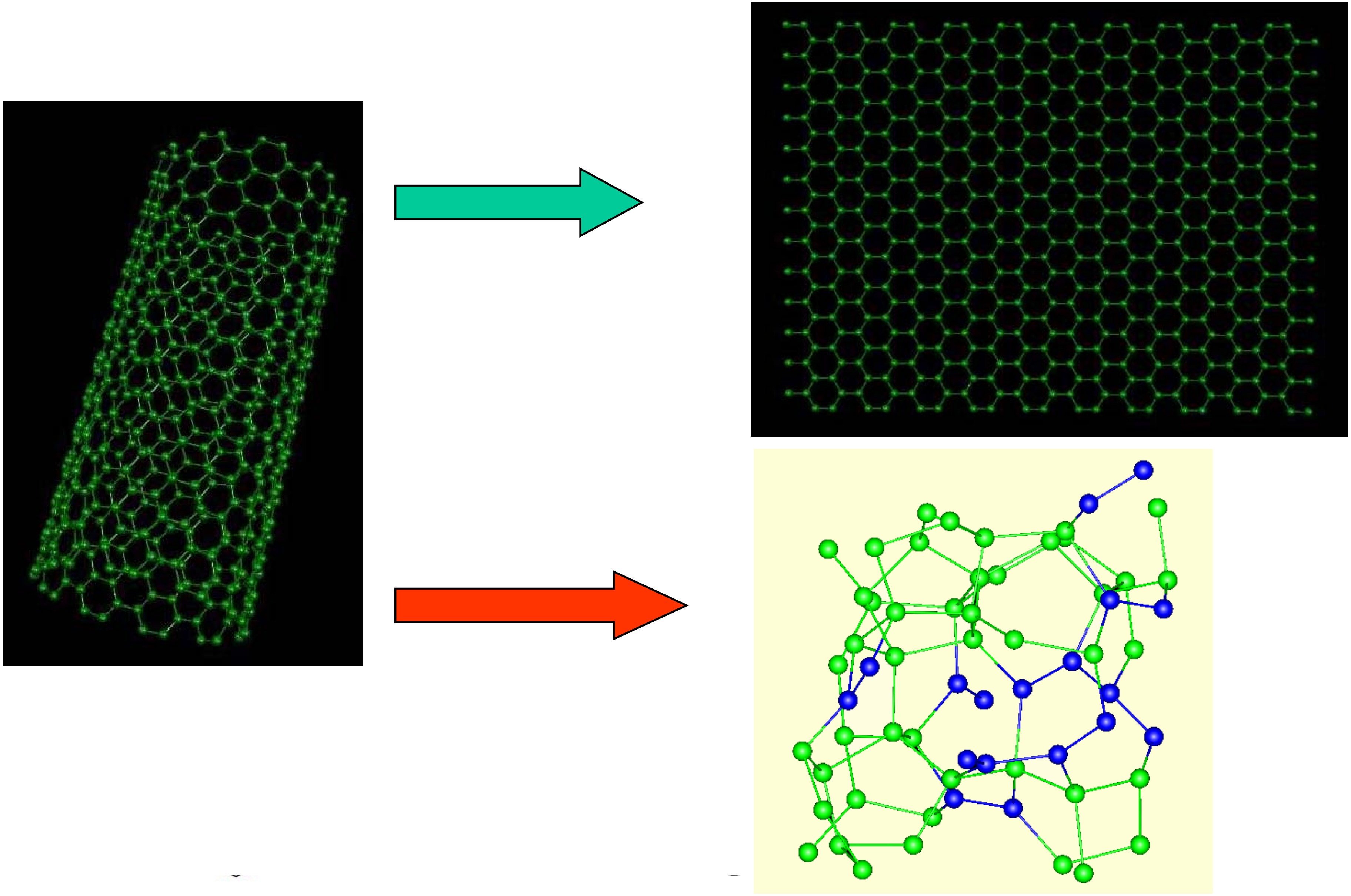
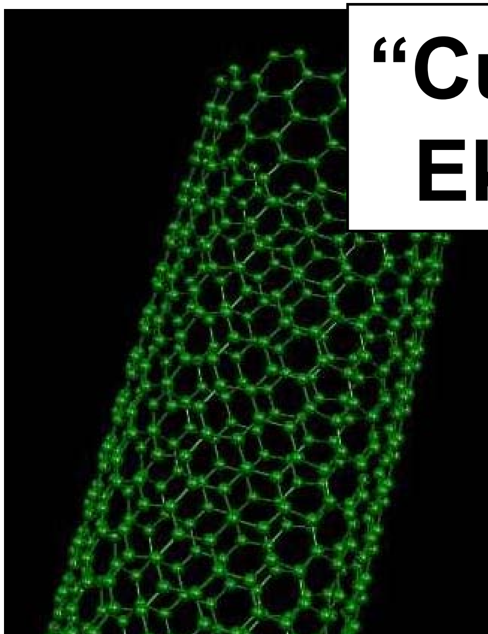
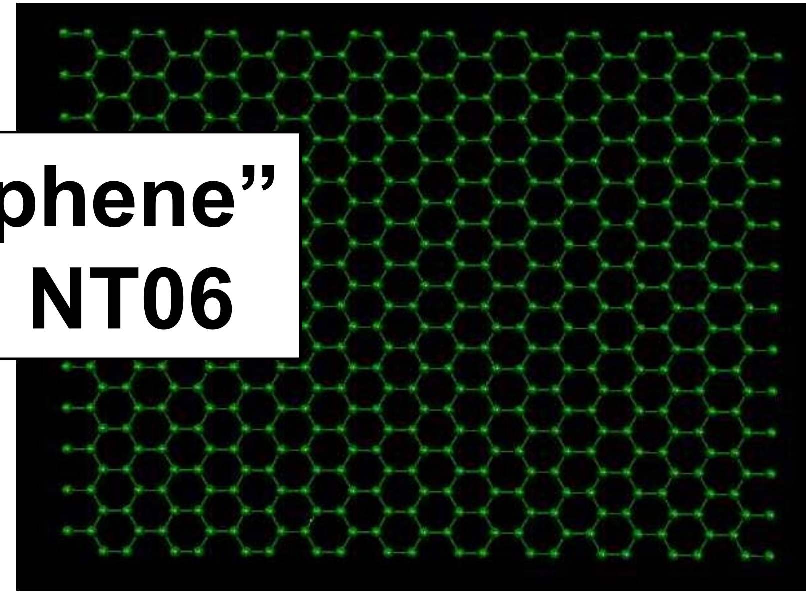
NanoTube-Evolution-Nagano 06

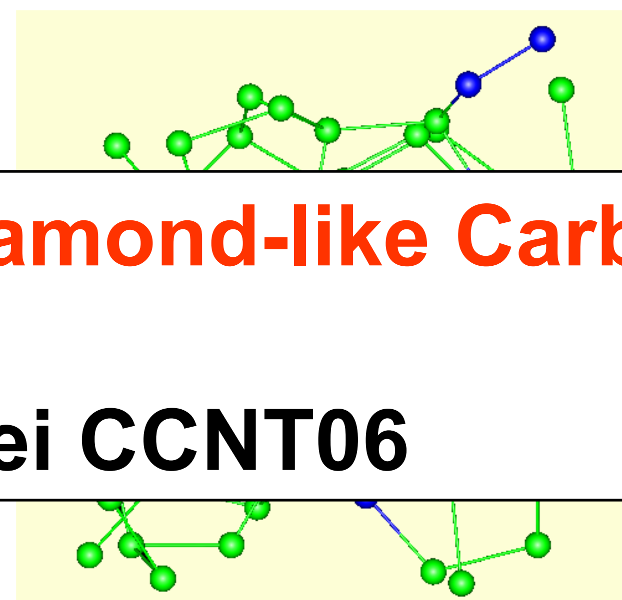


NanoTube-Evolution-Nagano 06





“Cut…. Get graphene”
Eklund-Sensei NT06



“Press (50GPa)…Get Diamond-like Carbon!”

S. Saito-Sensei CCNT06

Graphene

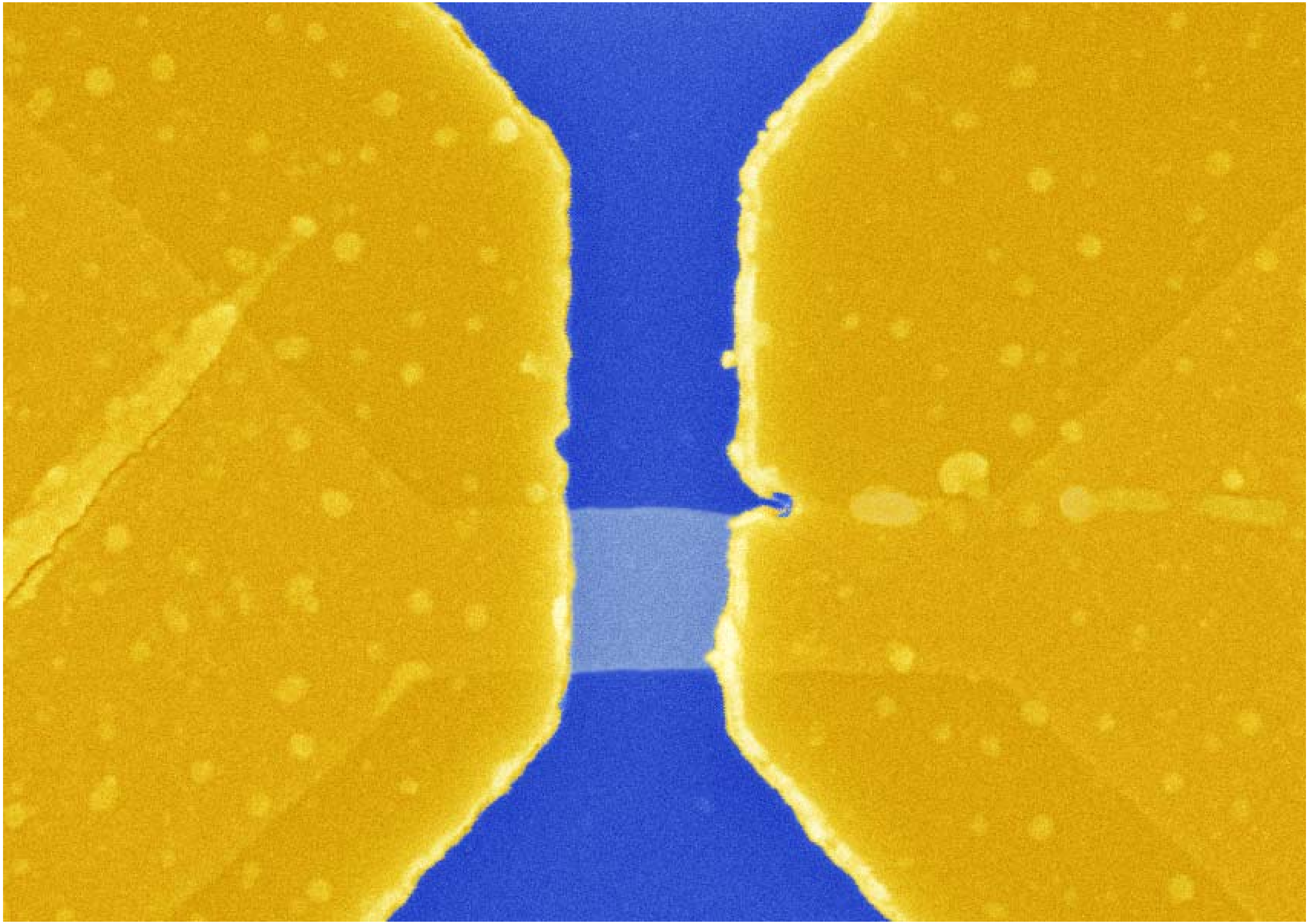
….big hype recently…

•Electron transport described by the (relativistic-like) Dirac equation Access to the rich and subtle physics of quantum electrodynamics in a relatively simple condensed matter experiment

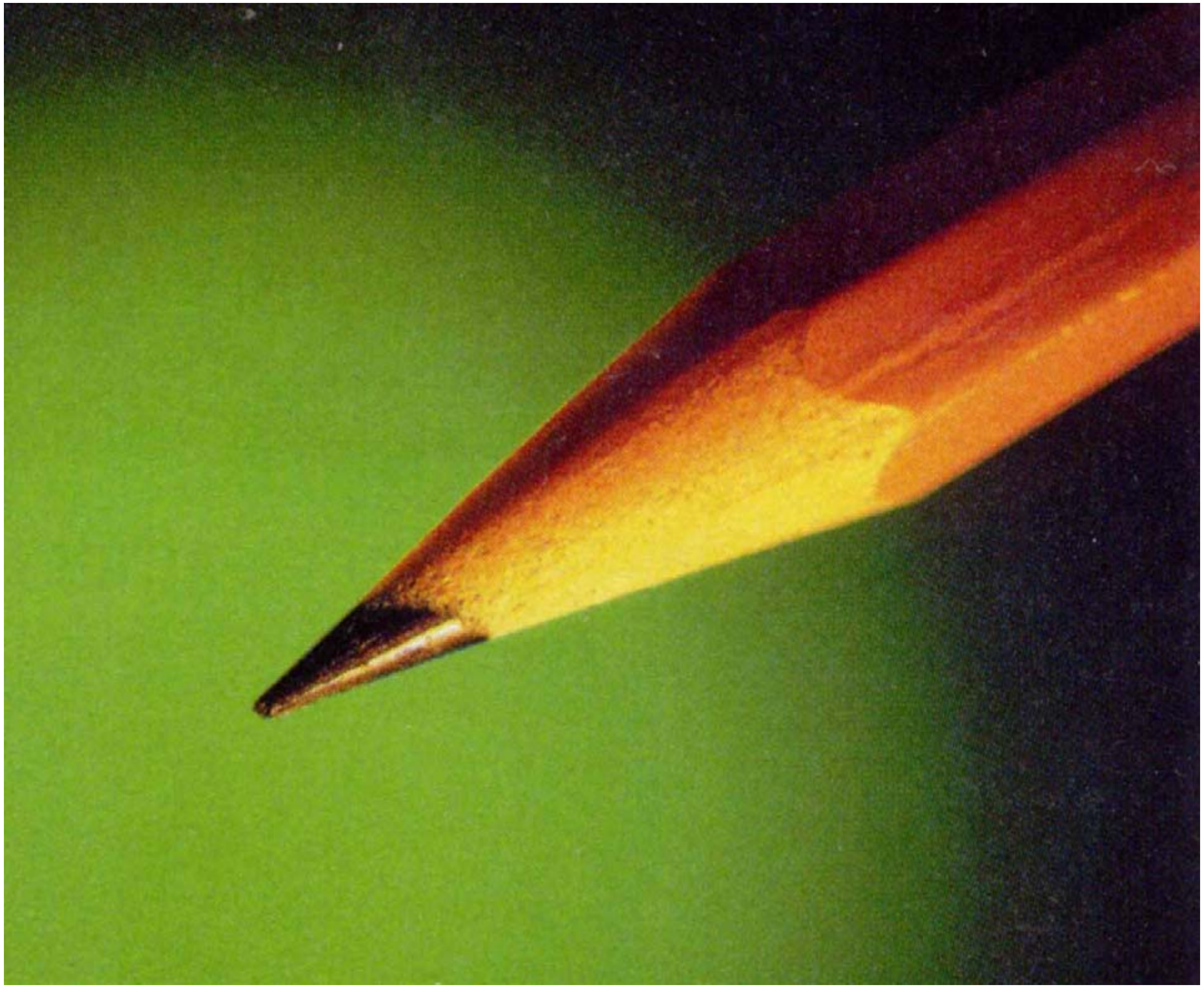
•Scalability of graphene devices to true nanometre dimensions makes it a promising candidate for future electronic applications, because of its ballistic transport at room temperature combined with chemical and mechanical stability.

•Graphene is the two-dimensional (2d) building block for carbon allotropes of every other dimensionality

Transistor: Graphene Ribbon

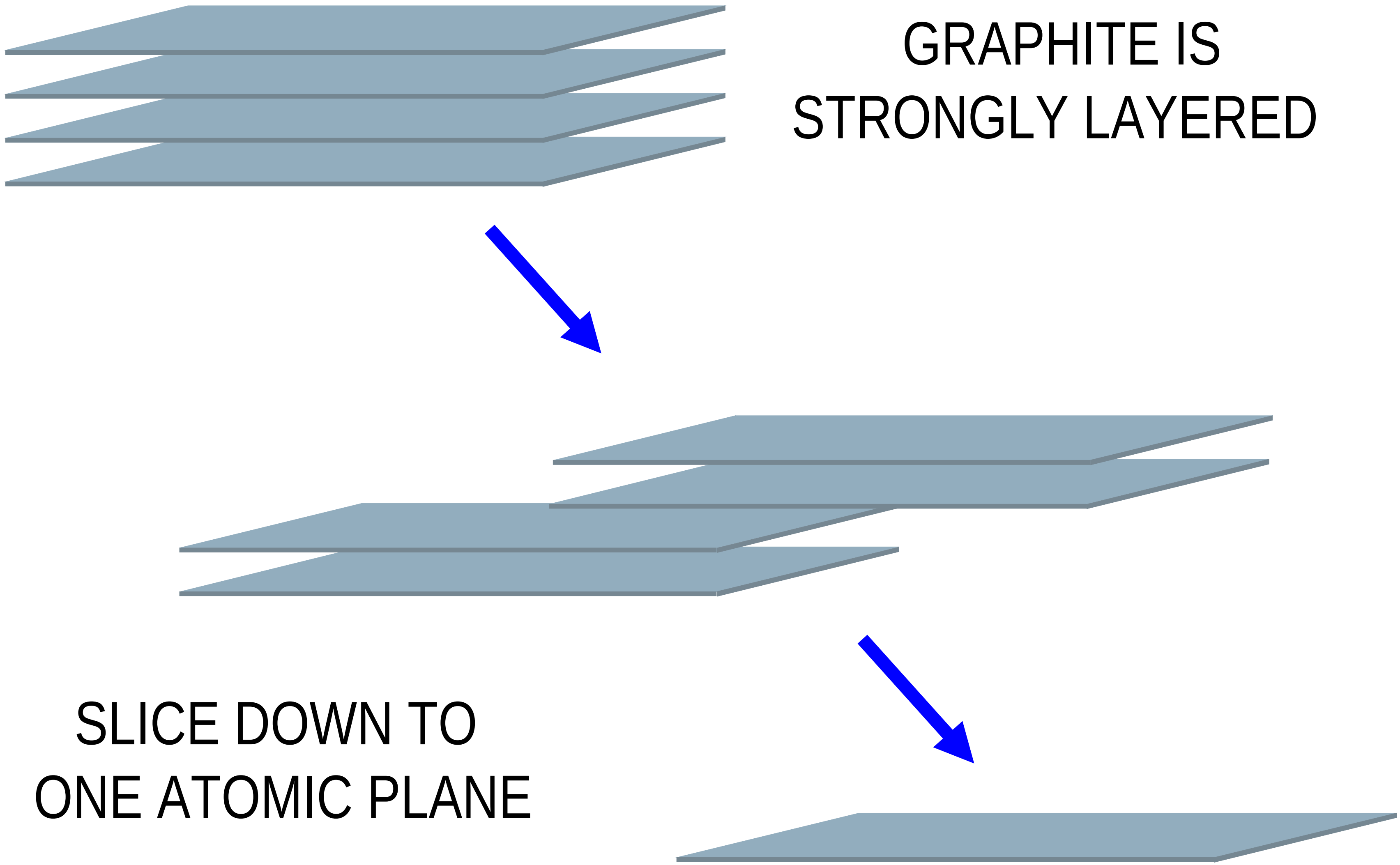


How to Make Graphene?



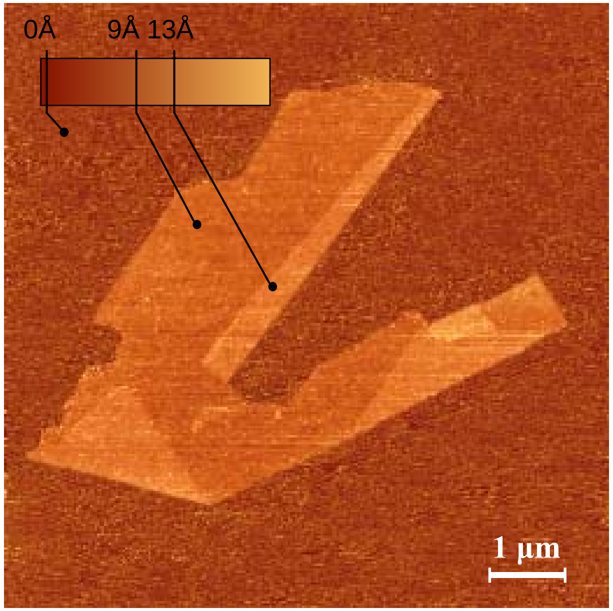
Drawing:
(micro) mechanical cleavage of graphite

How to Make Graphene?



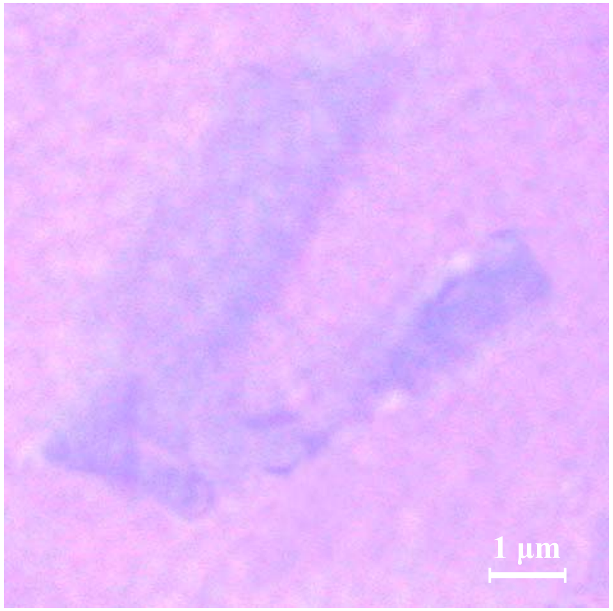
individual atomic sheets: do they exist?

Free-Standing Graphene

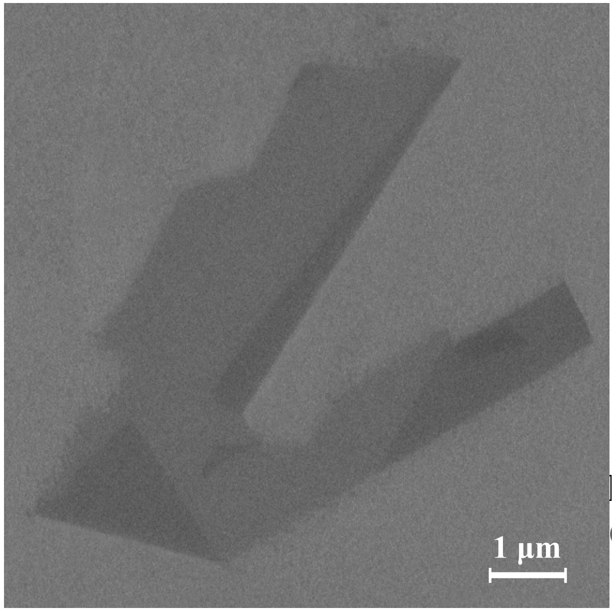


AFM

Key: Visual Identification



OPTICS

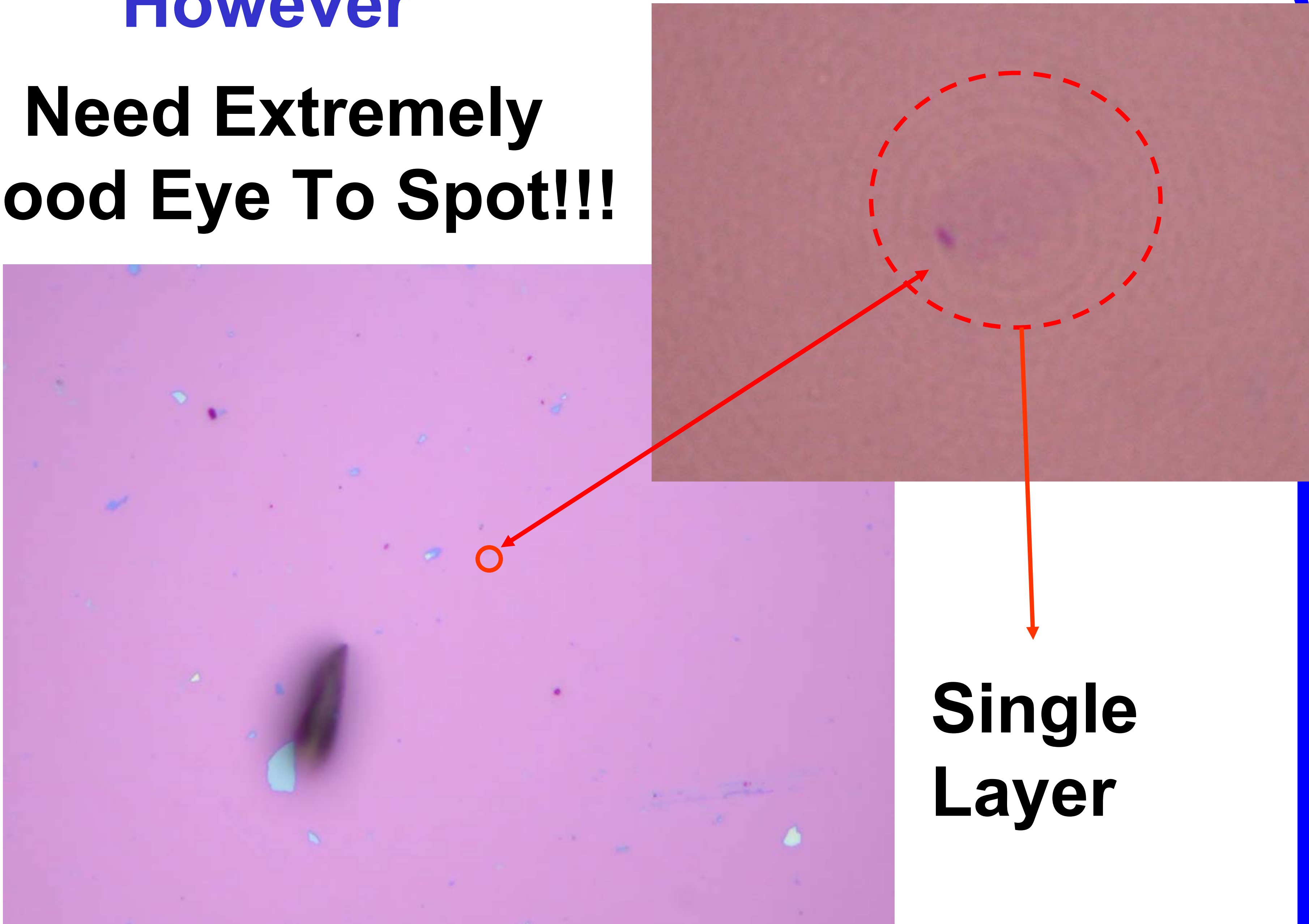


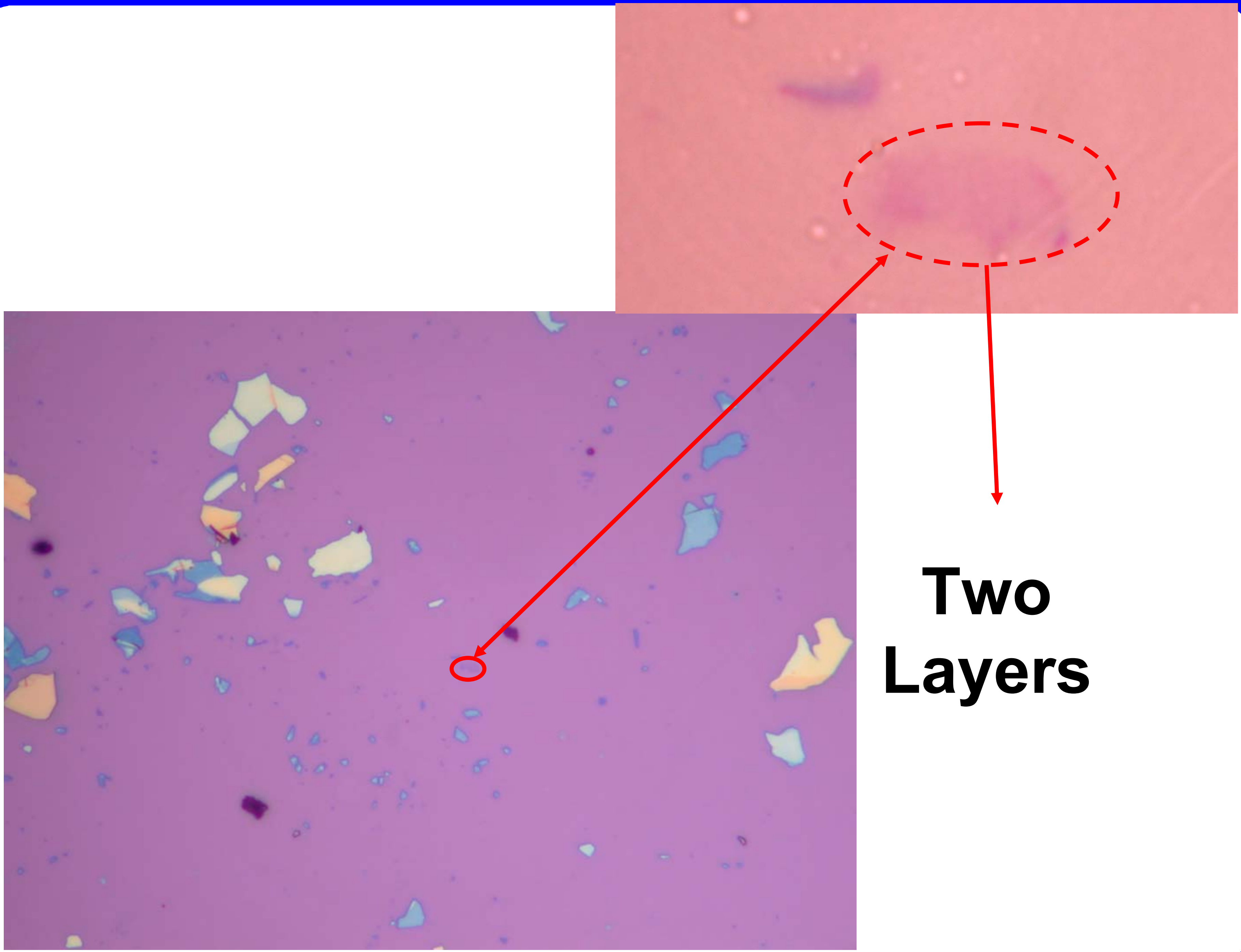
SEM

single layer of atoms visible by "naked" eye only on 300 nm SiO_2

However

Need Extremely Good Eye To Spot!!!





Two
Layers

One Comment…

Mechanical cleavage is nice and simple

However…
Low yield, messy, not scalable

Better to grow graphene directly on substrate

This can be done…

But…not the subject of this talk

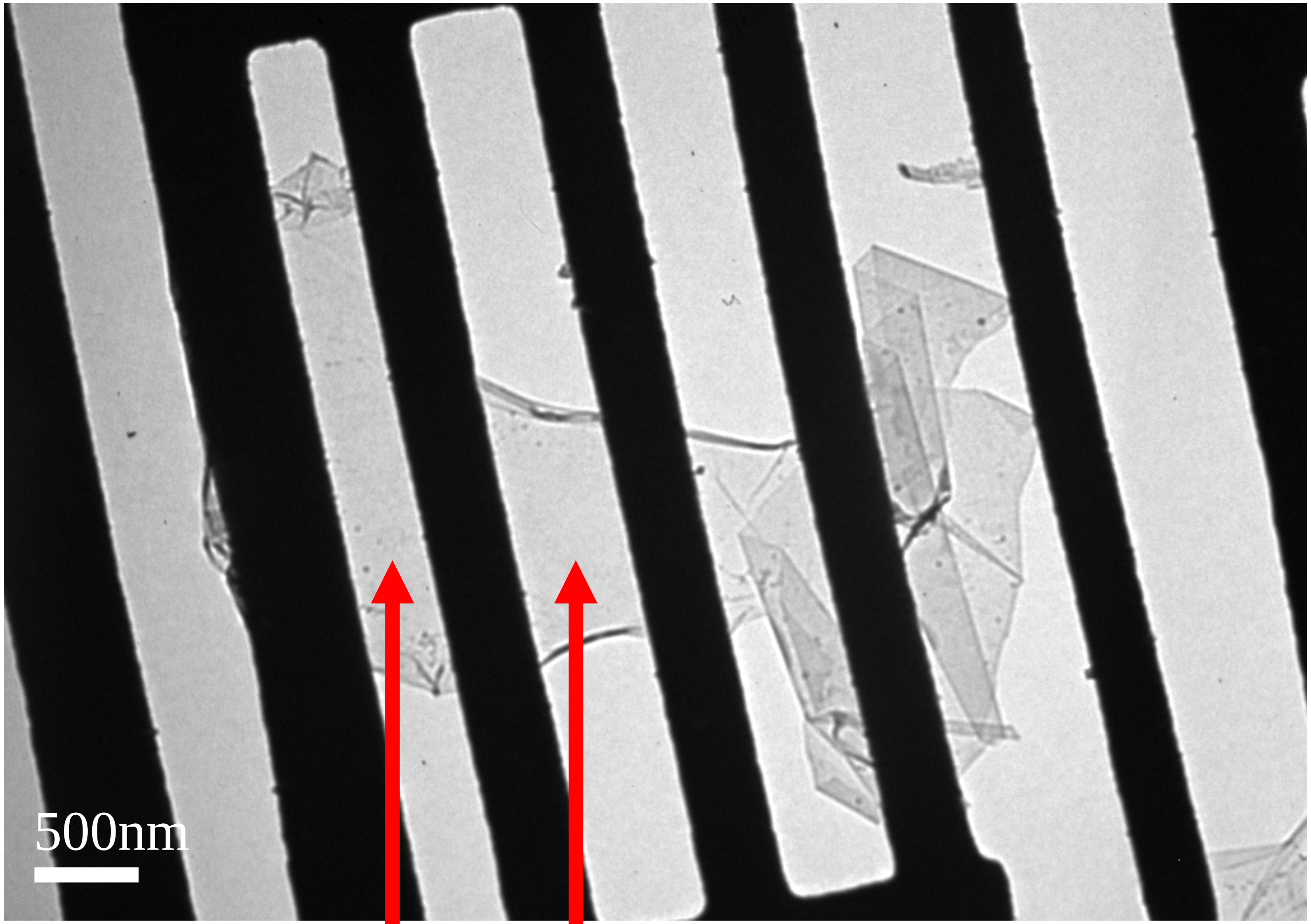
Another Comment

AFM thickness of single layer is 0.5-1.5 nm! Due to chemical contrast

We want to be 150% sure

TEM

Free-Hanging graphene sheets

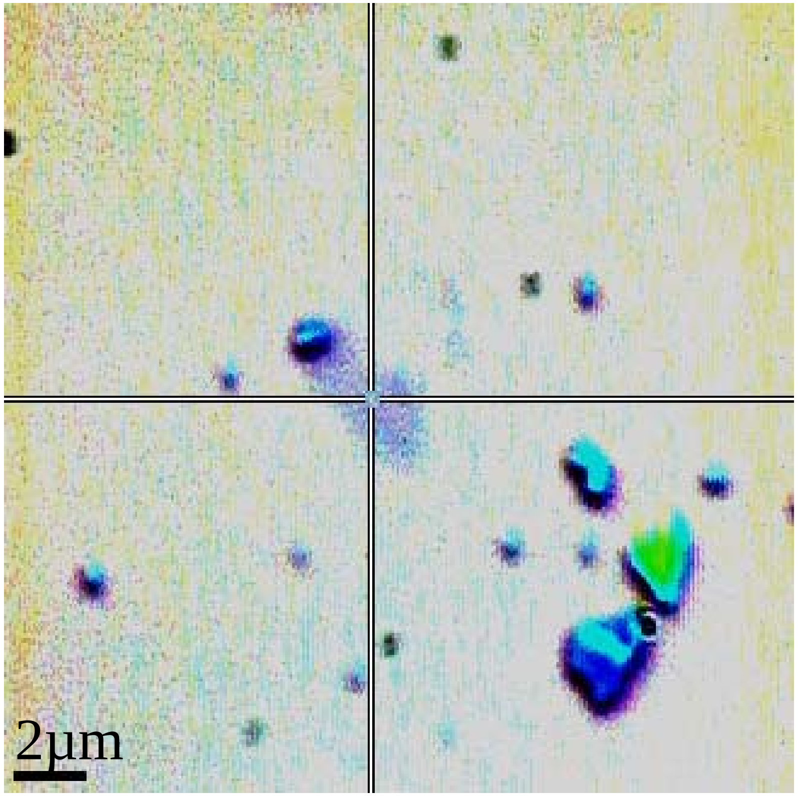


1 layer of graphene !

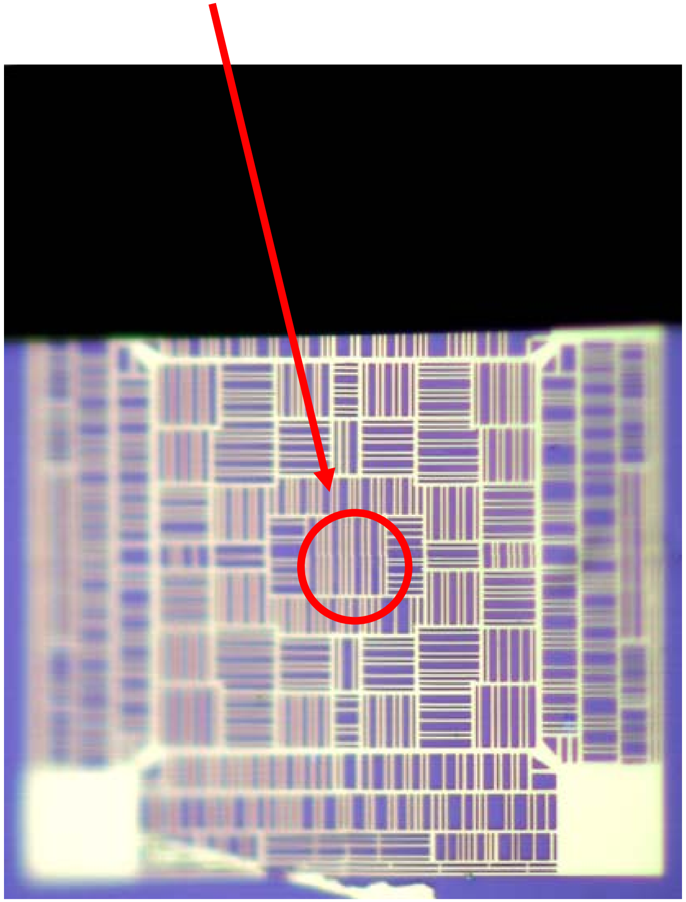
J. C. Meyer

Preparation

1. Graphene sheet on substrate

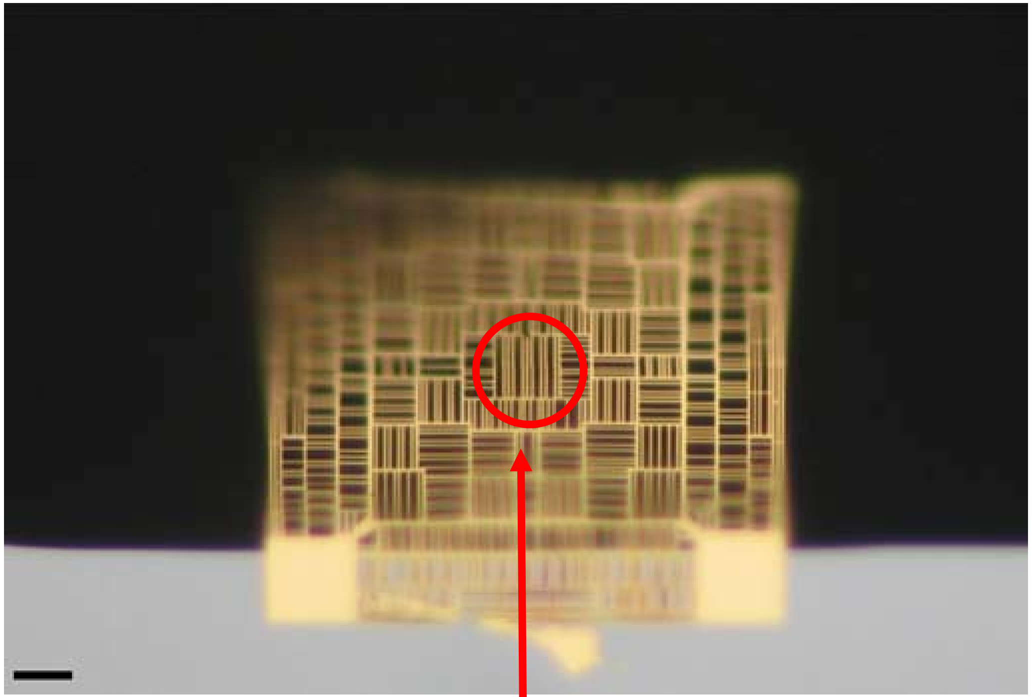


2. Metal grid patterned onto the flake



Preparation

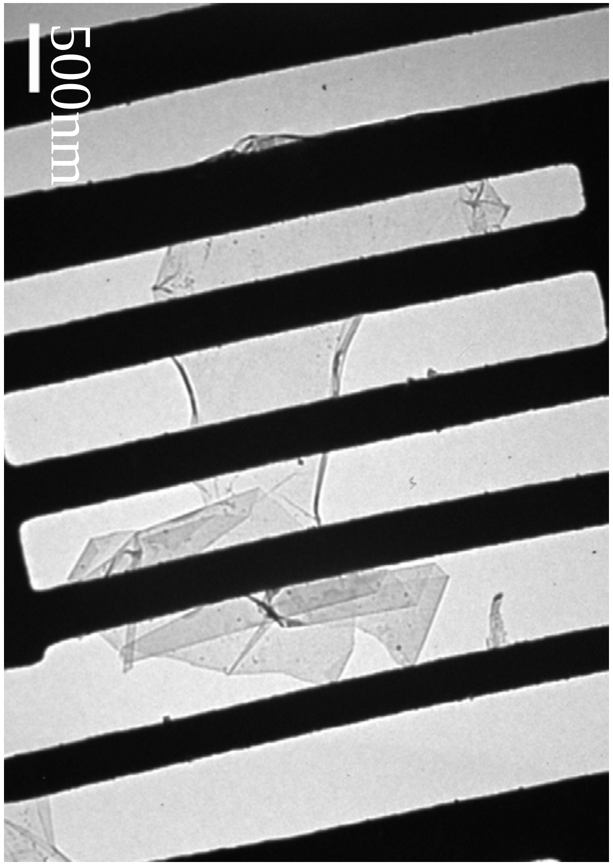
3. Etching of substrate



10µm

Flake remains
in metal grid

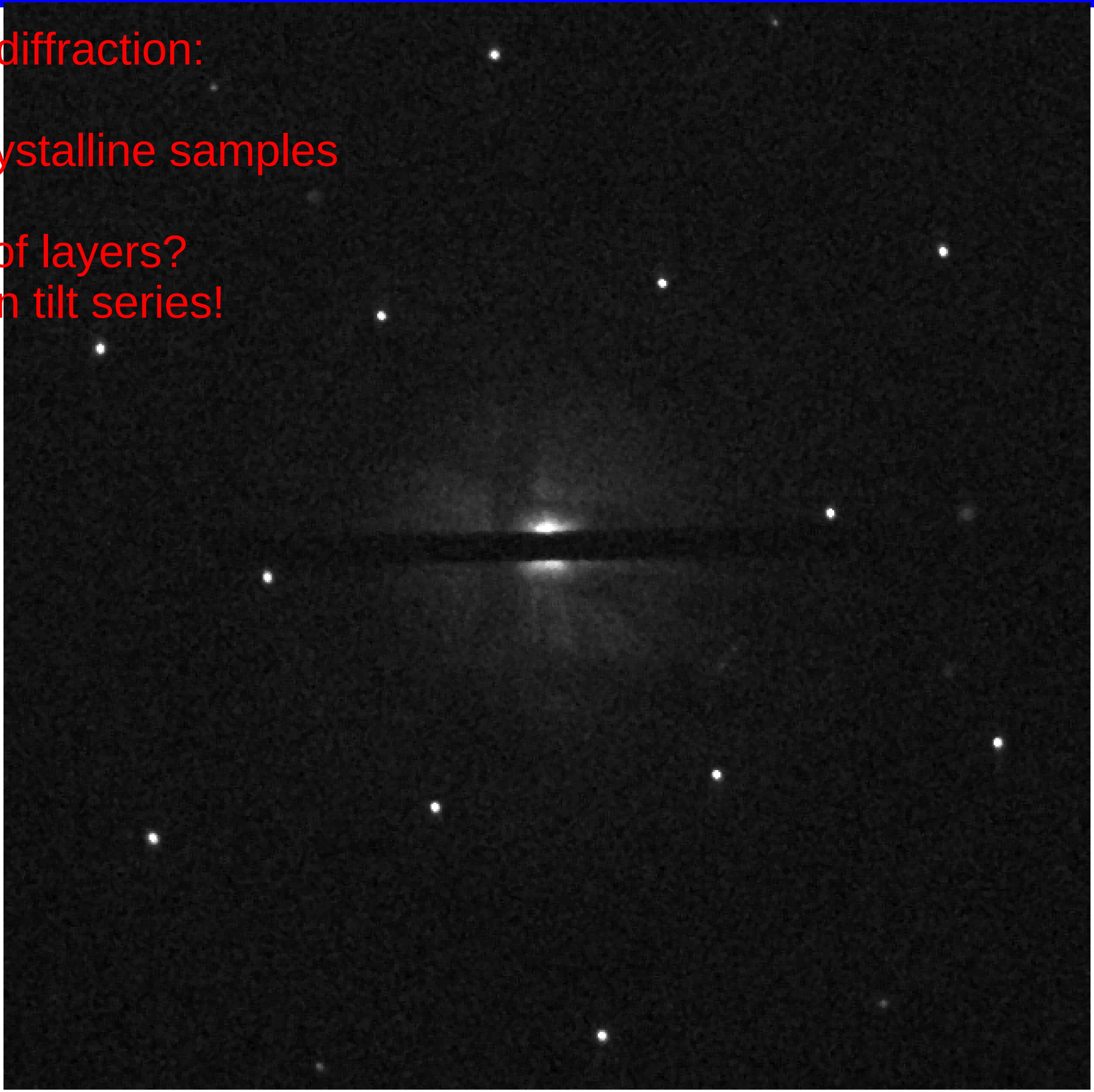
4. TEM and electron diffraction analysis



Electron diffraction:

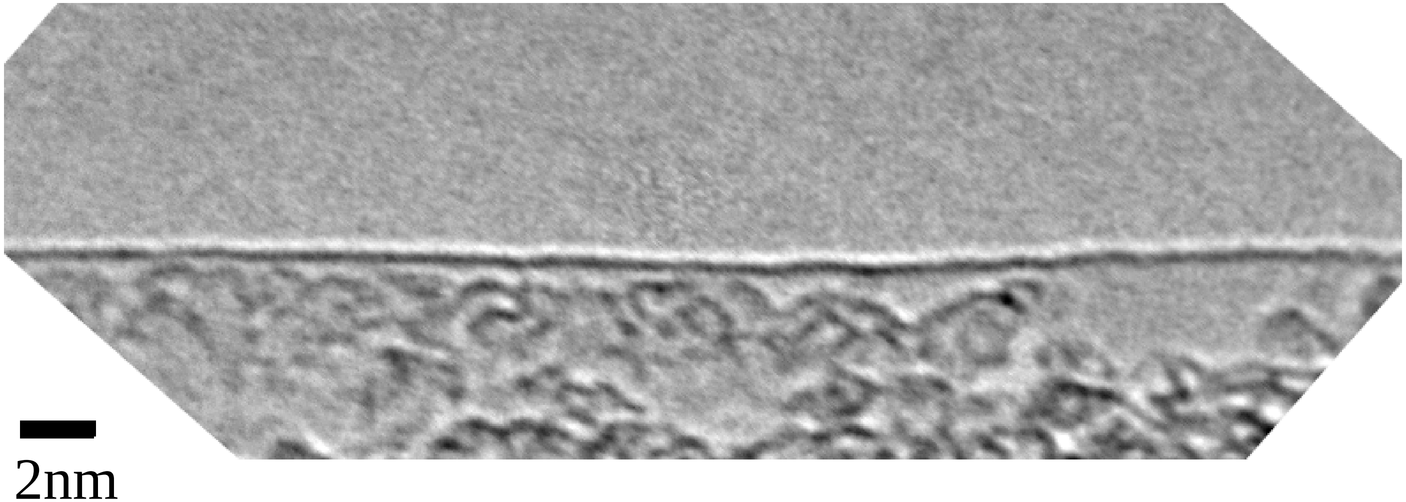
Highly crystalline samples

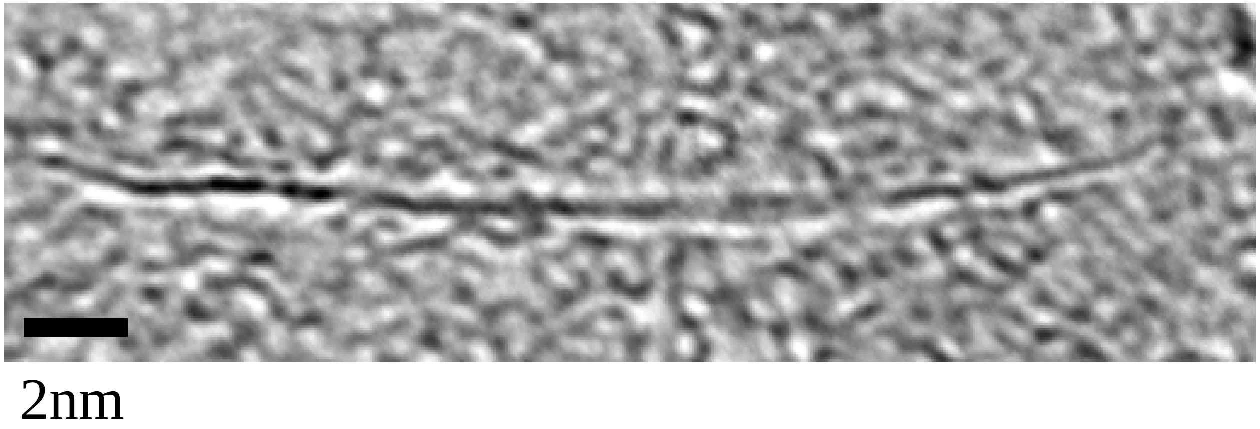
Number of layers?
Diffraction tilt series!



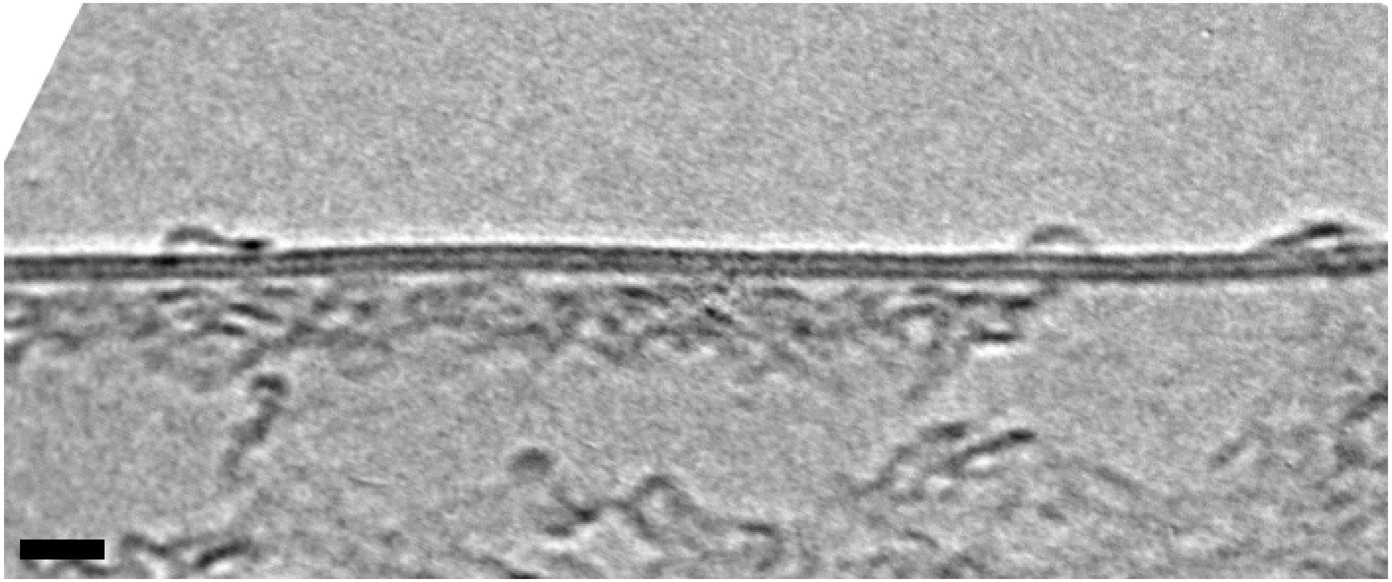
One-layer graphene

Sheets fold back at the edges, and sometimes show a wrinkle within the sheet. HRTEM analysis of the folding allows to verify the layer count.

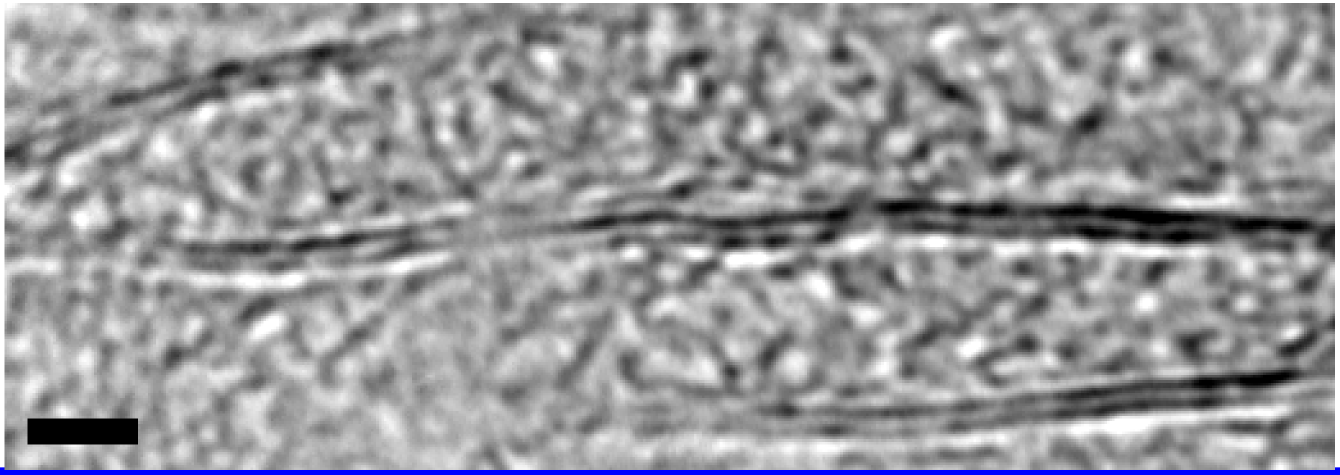




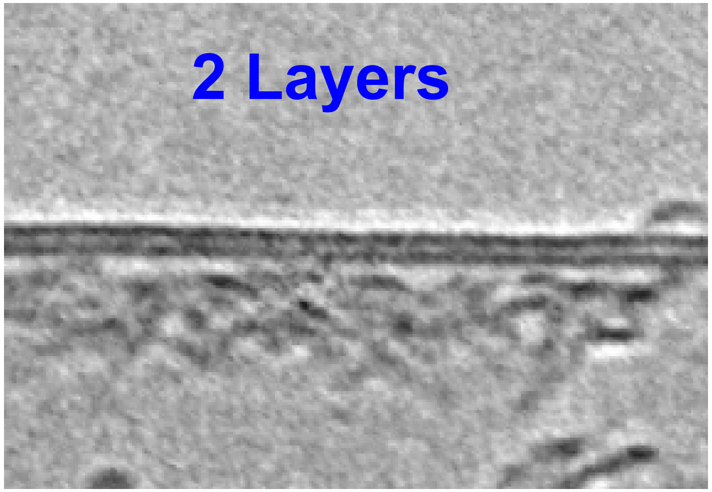
Two-layer graphene

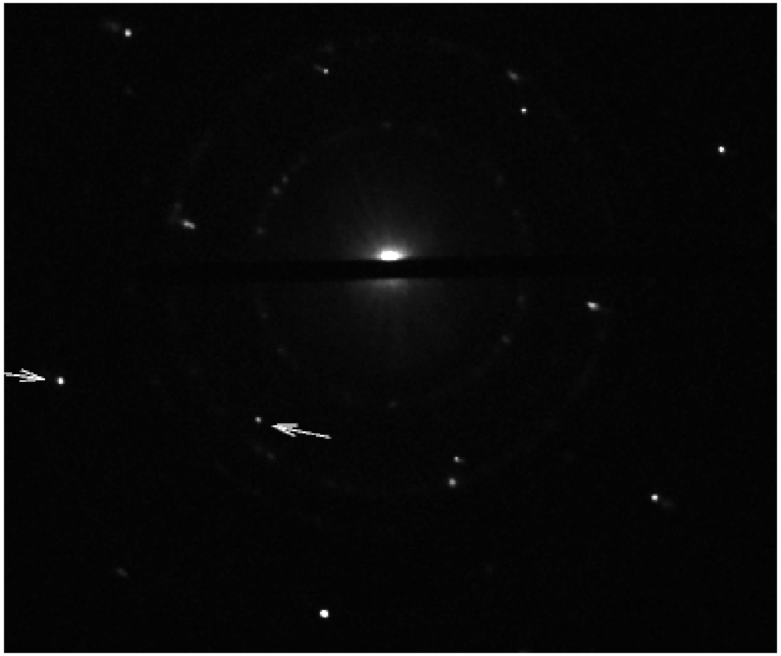


2nm

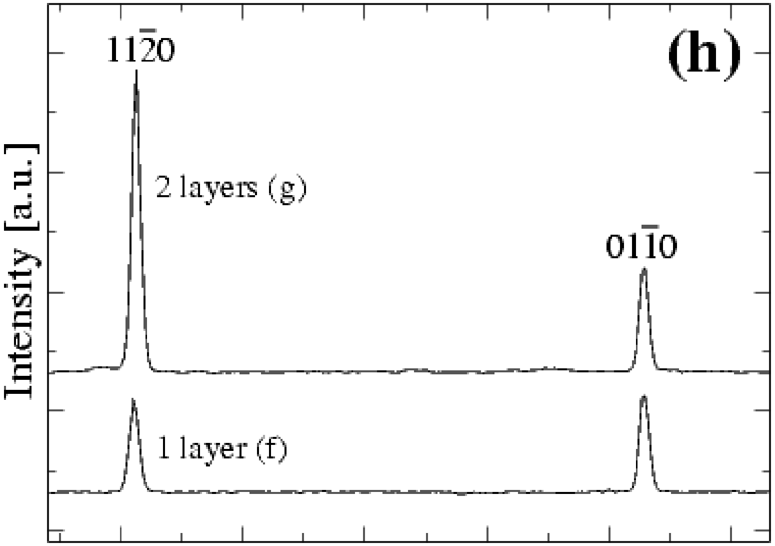


Two-Layer Graphene

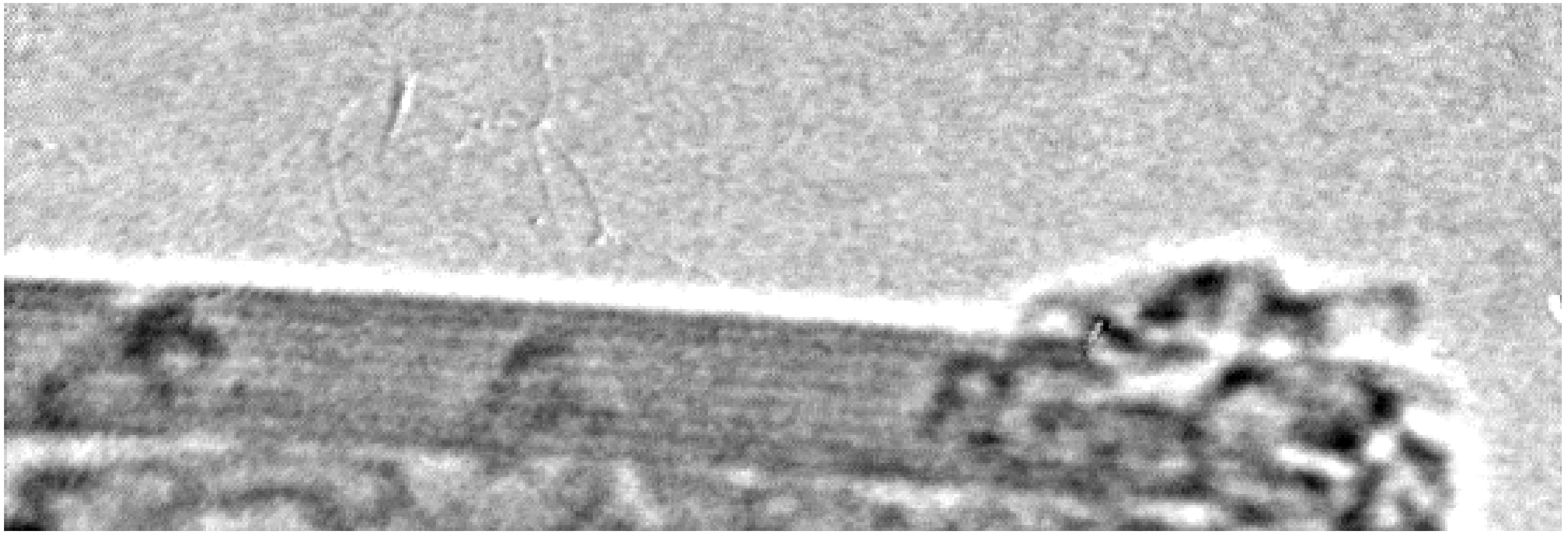




Stacking A/B

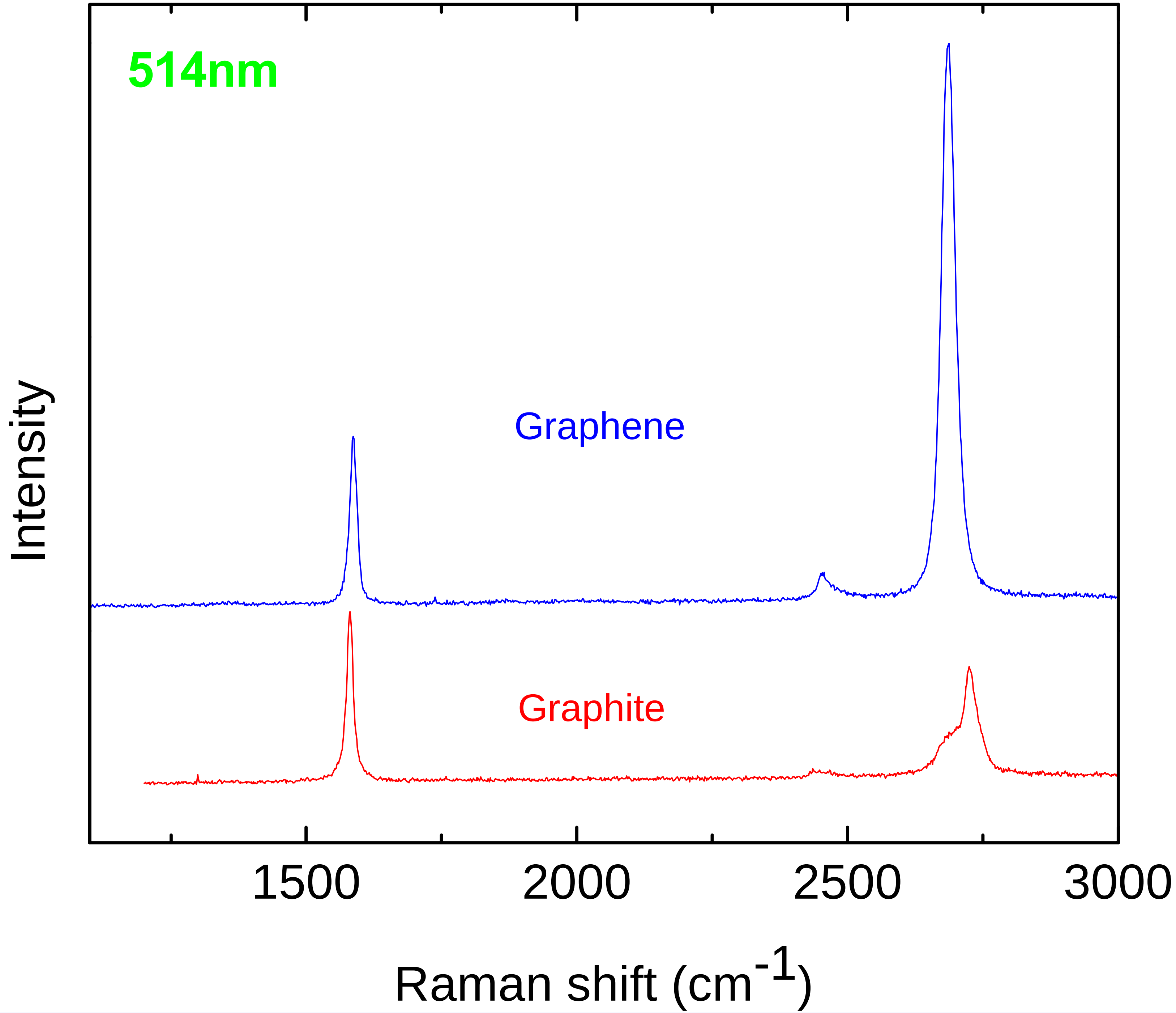


8 layers

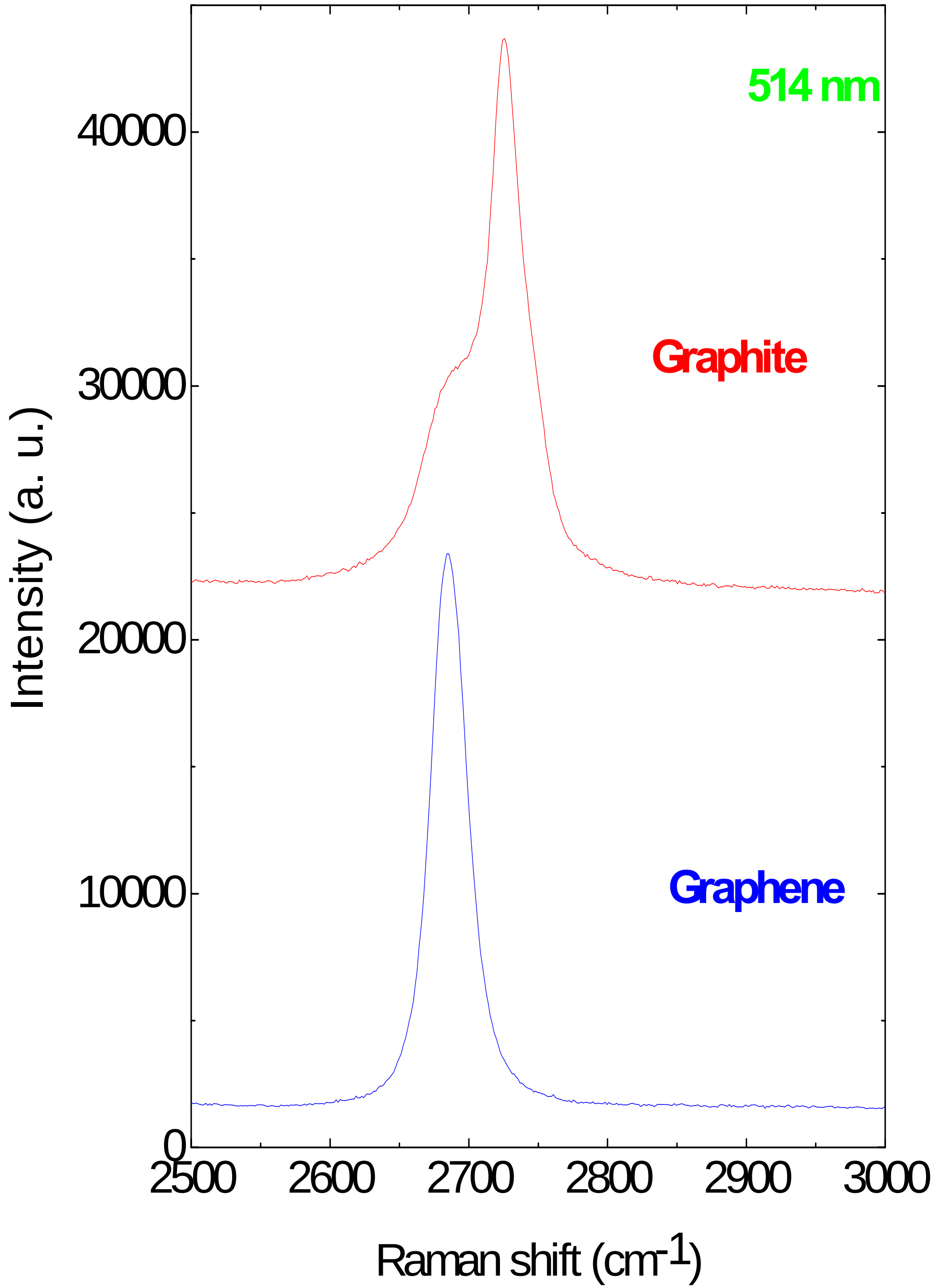


We Need
High Throughput
Non Destructive
Quick
Substrate Independent
Identification Technique

Raman Spectroscopy



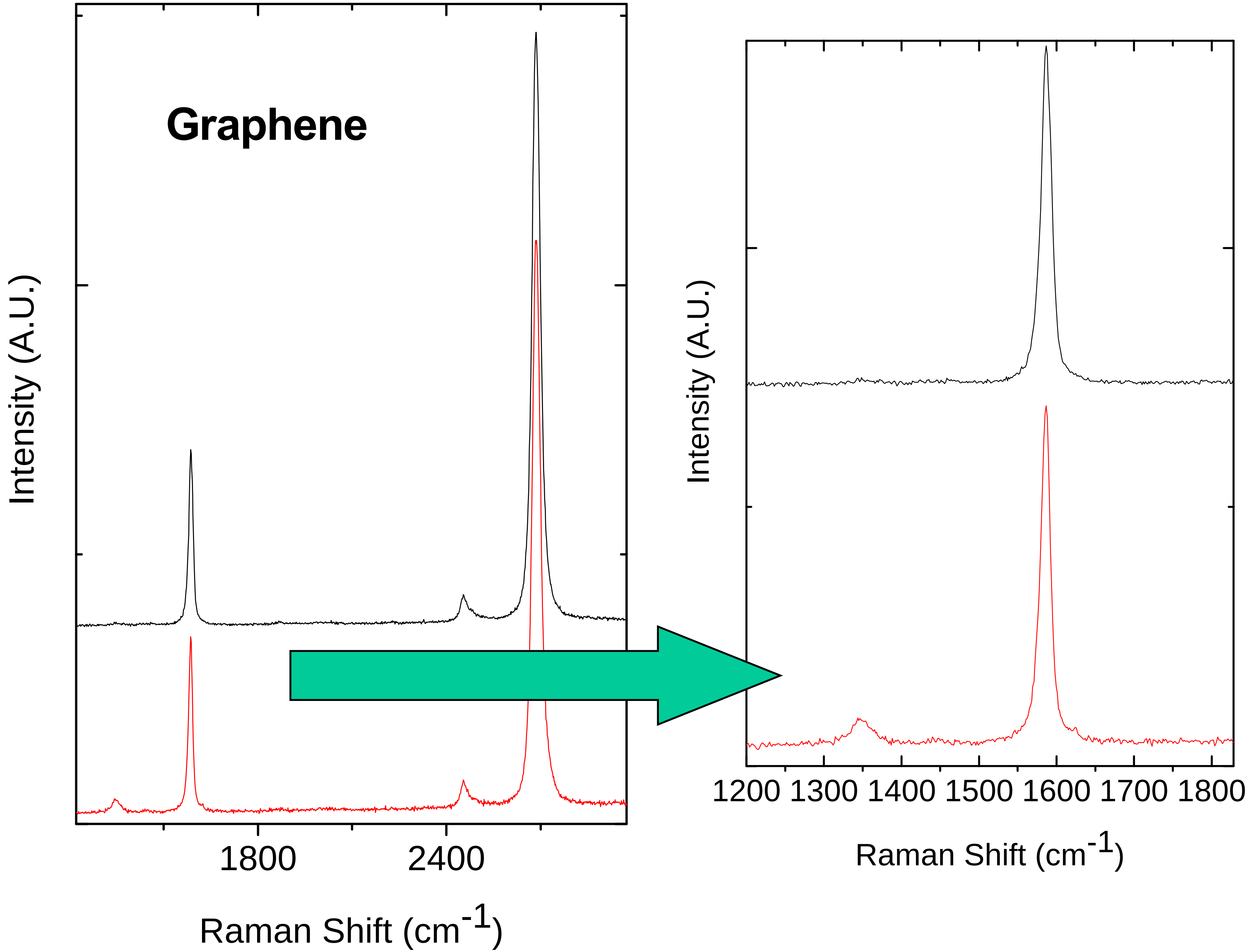
514nm
Graphene
Graphite
Intensity
1500
2000
2500
3000
Raman shift (cm^{-1})

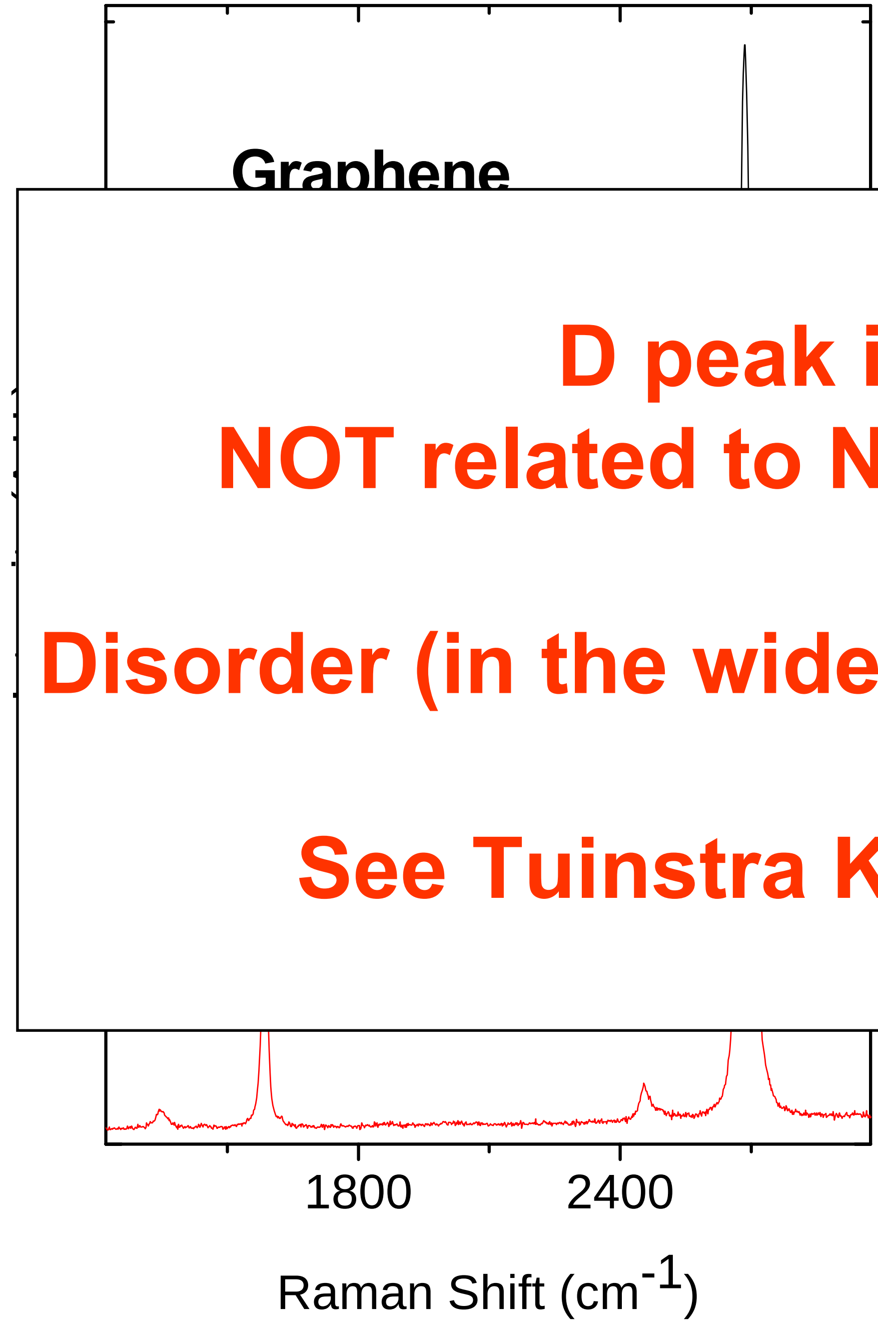


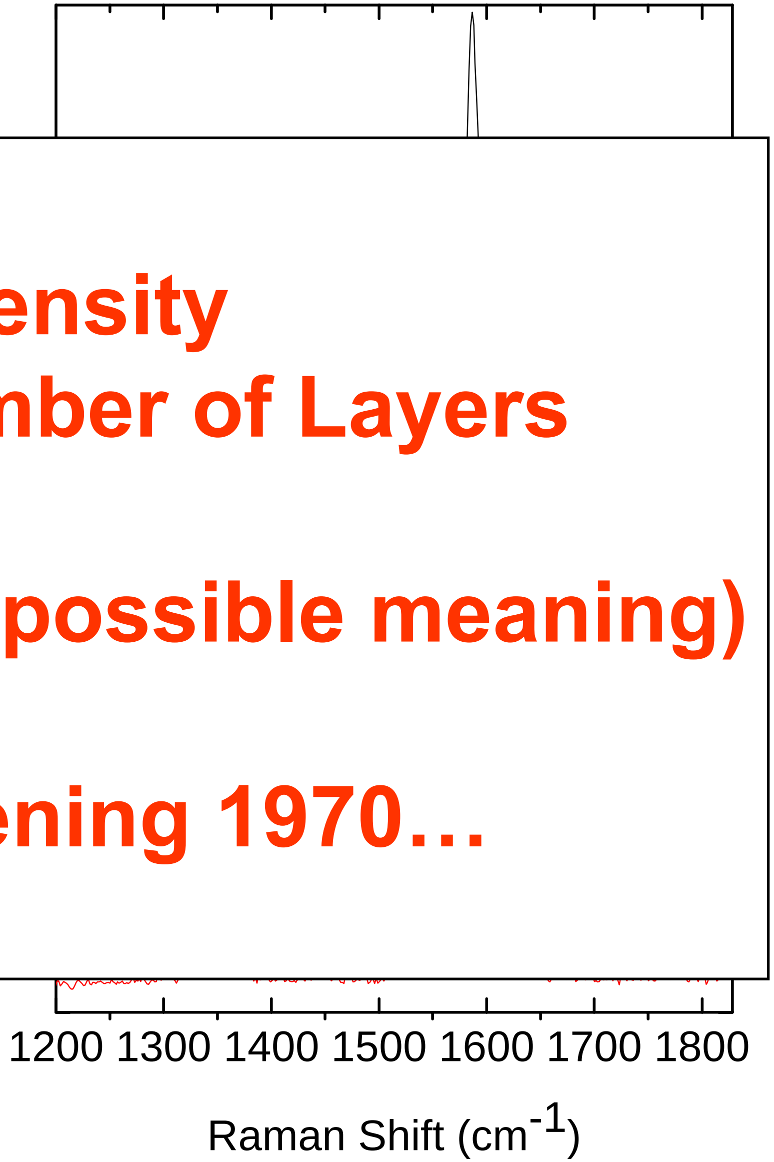
G' Peak

(2D peak)

Clear Fingerprint


Graphene
Intensity (A.U.)
1800
2400
Raman Shift (cm-1)
Intensity (A.U.)
1200 1300 1400 1500 1600 1700 1800
Raman Shift (cm-1)

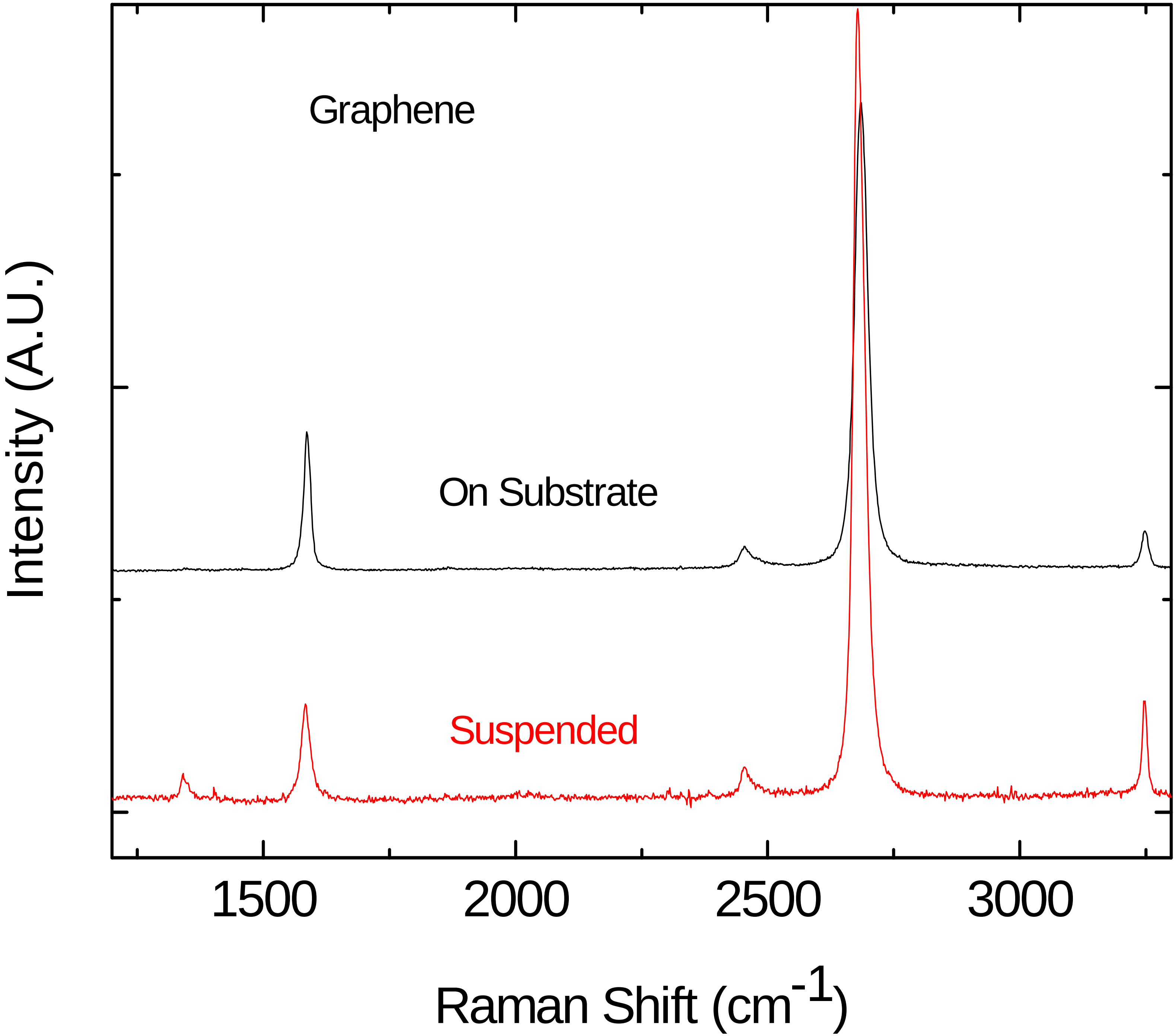


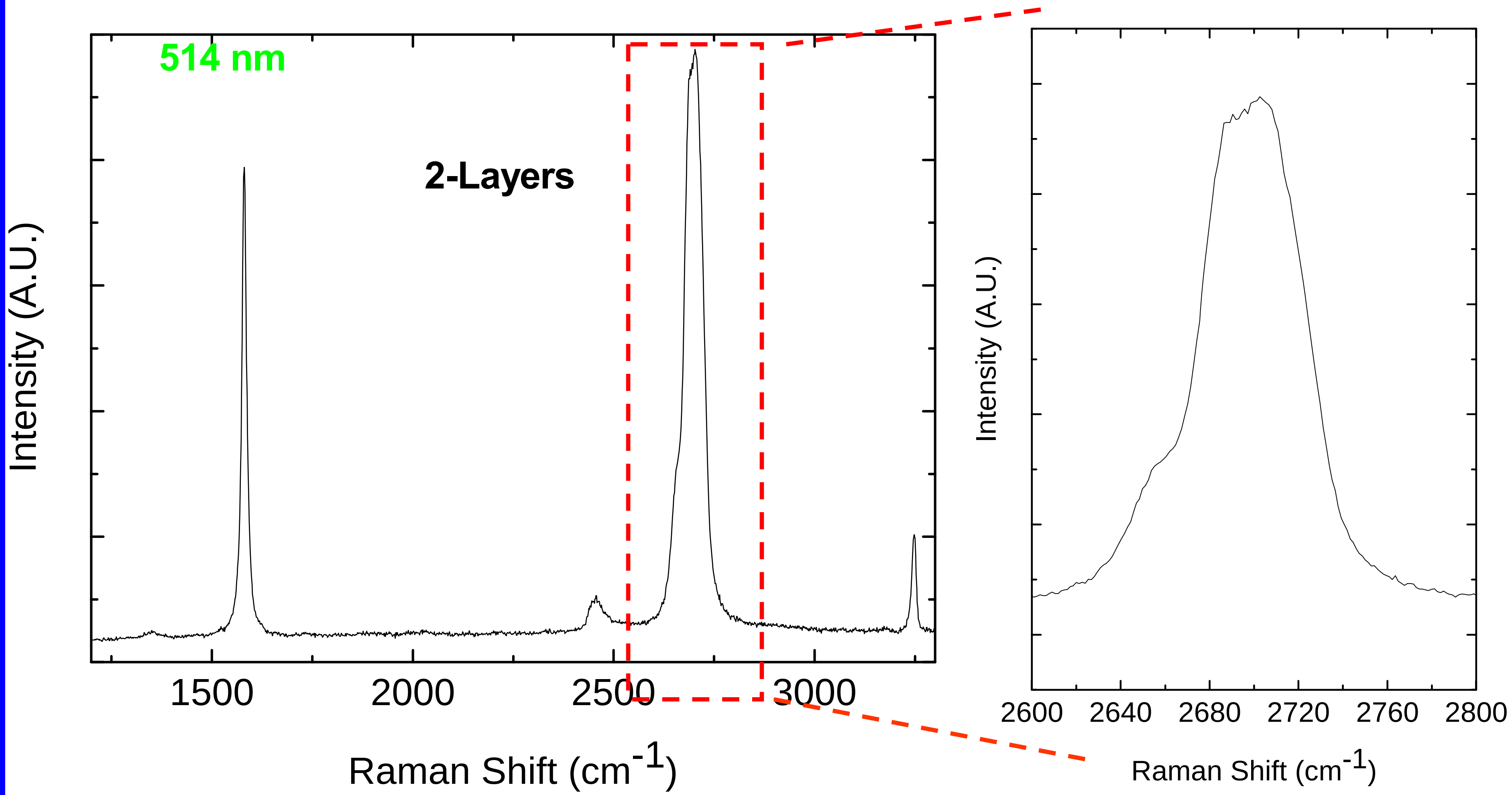


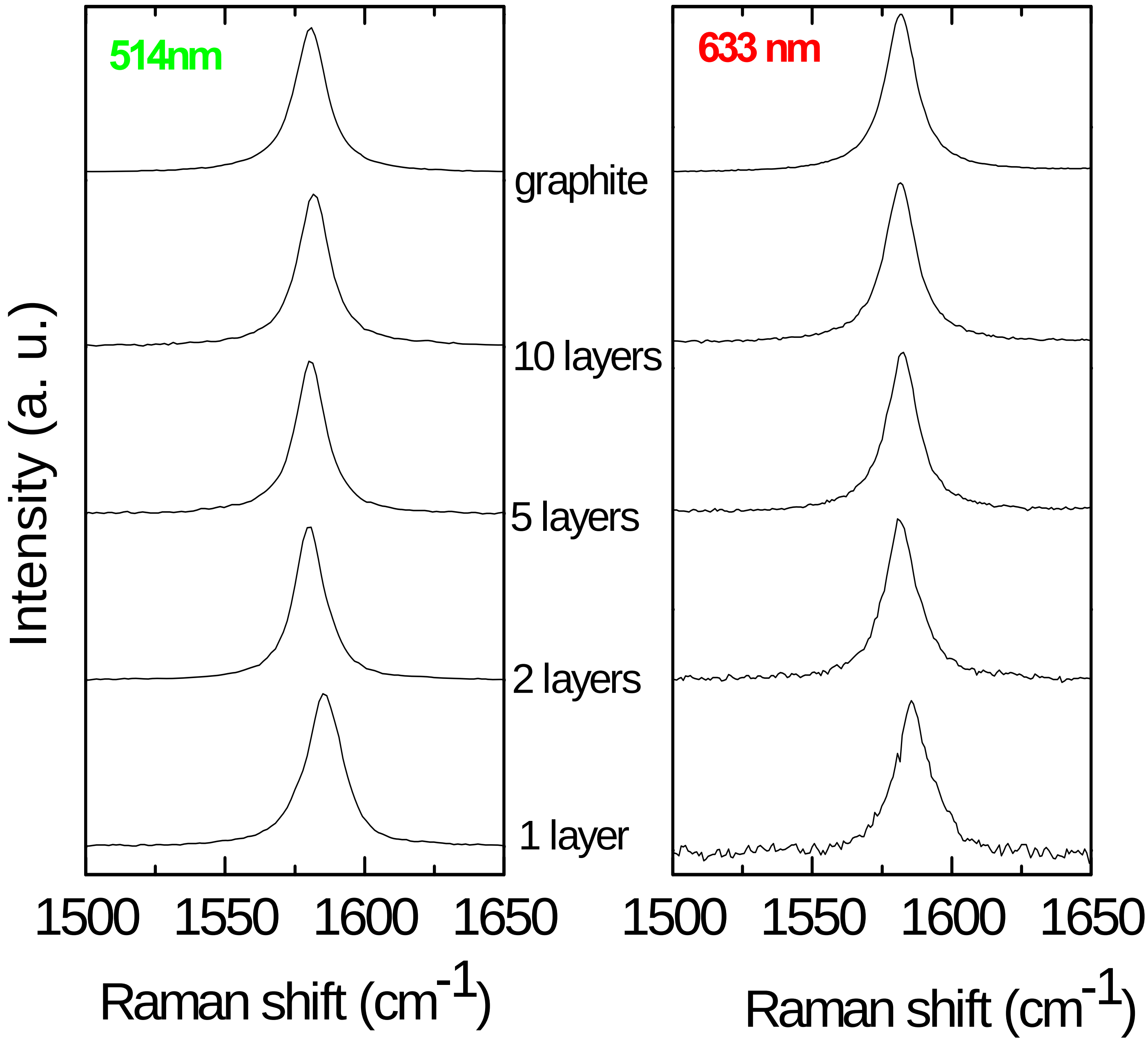
D peak intensity
NOT related to Number of Layers

Disorder (in the widest possible meaning)

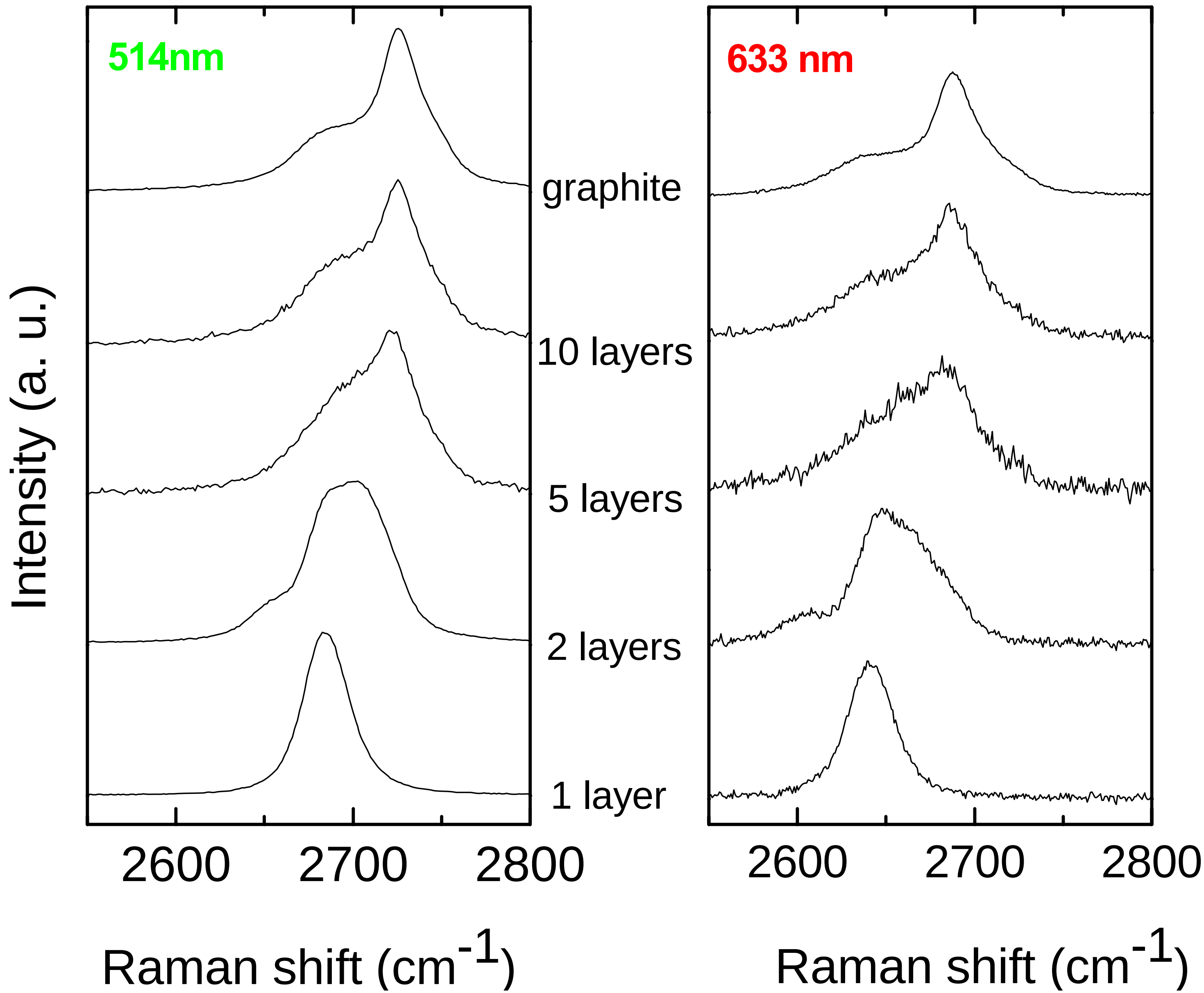
See Tuinstra Koening 1970…


Graphene
On Substrate
Suspended
Intensity (A.U.)
1500
2000
2500
3000
Raman Shift (cm-1)

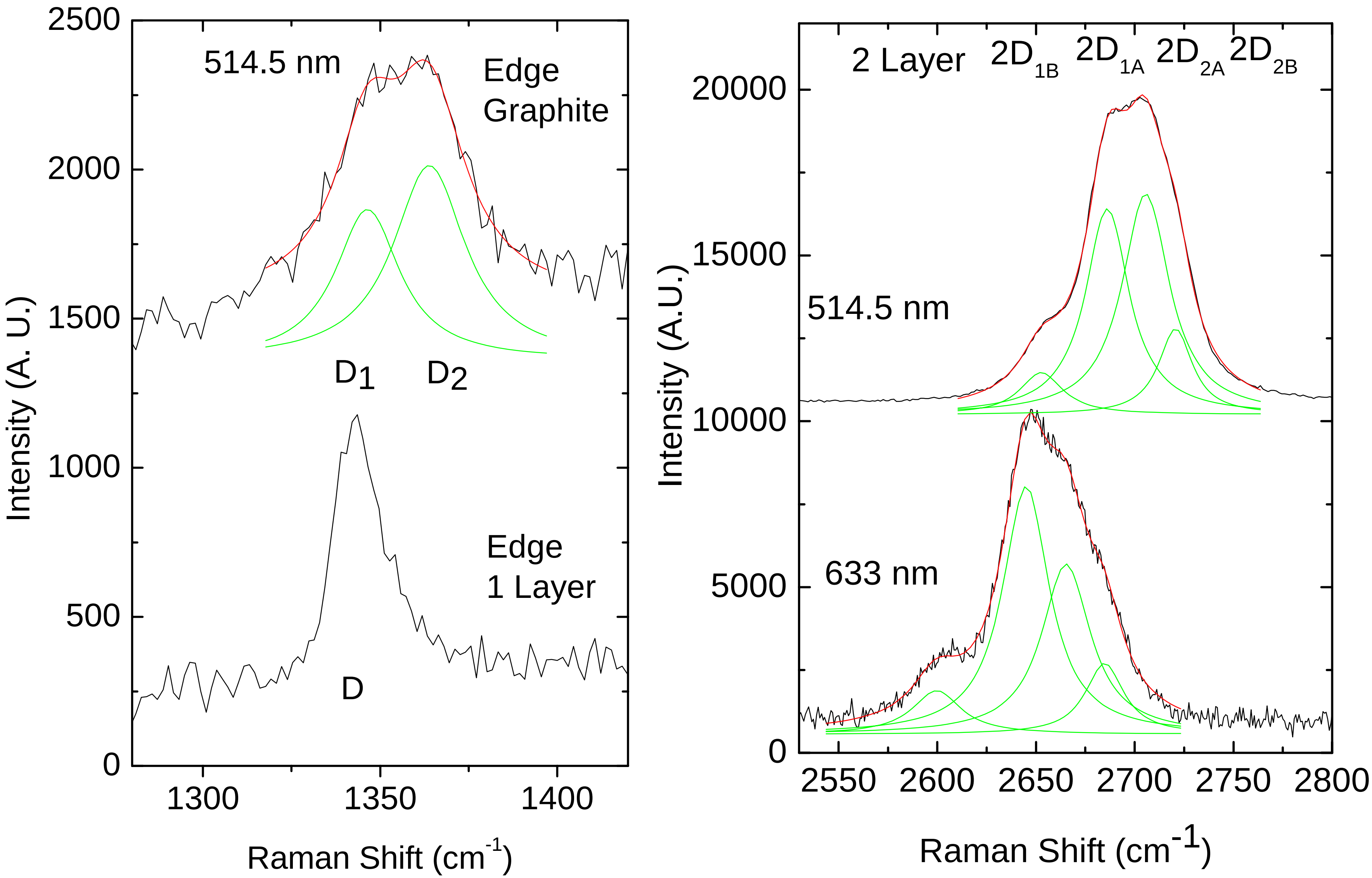

514 nm
2-Layers
Intensity (A.U.)
1500
2000
2500
3000
Raman Shift (cm-1)
Intensity (A.U.)
2600
2640
2680
2720
2760
2800
Raman Shift (cm-1)



Slight Upshift ~ 5cm^{-1}



514nm
633 nm
graphite
10 layers
5 layers
2 layers
1 layer
Intensity (a. u.)
2600
2700
2800
Raman shift (cm^{-1})



514.5 nm
Edge
Graphite
D1
D2
Edge
1 Layer
D
Intensity (A. U.)
Raman Shift (cm-1)
2500
2000
1500
1000
500
0
1300
1350
1400
2 Layer
2D1B
2D1A
2D2A
2D2B
514.5 nm
633 nm
Intensity (A.U.)
20000
15000
10000
5000
0
2550
2600
2650
2700
2750
2800
Raman Shift (cm-1)

The Origin of G' (2D) Peak

Named G' since is one of the 2 biggest peaks in graphite

BUT it is the second order of D peak

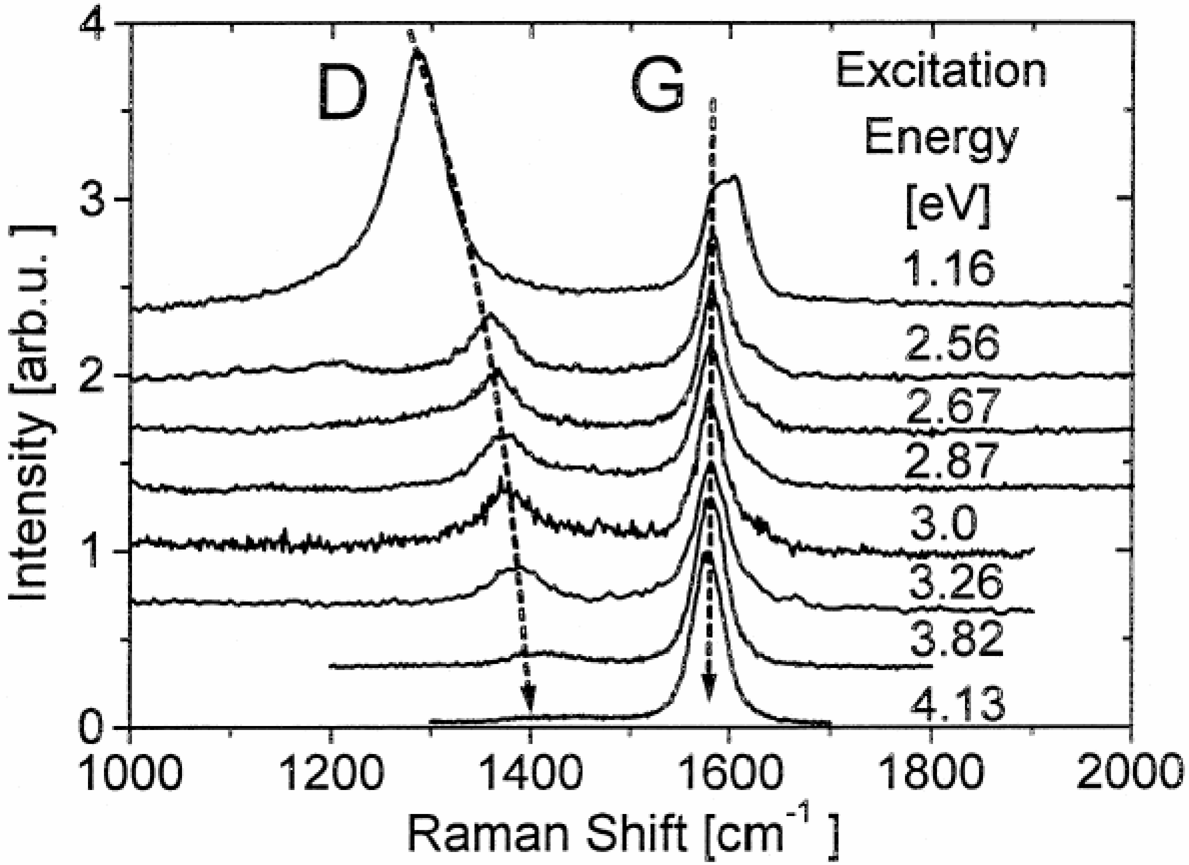
Nothing to do with G peak

D forbidden in perfect crystal By
Raman Fundamental Selection Rule **q~0**

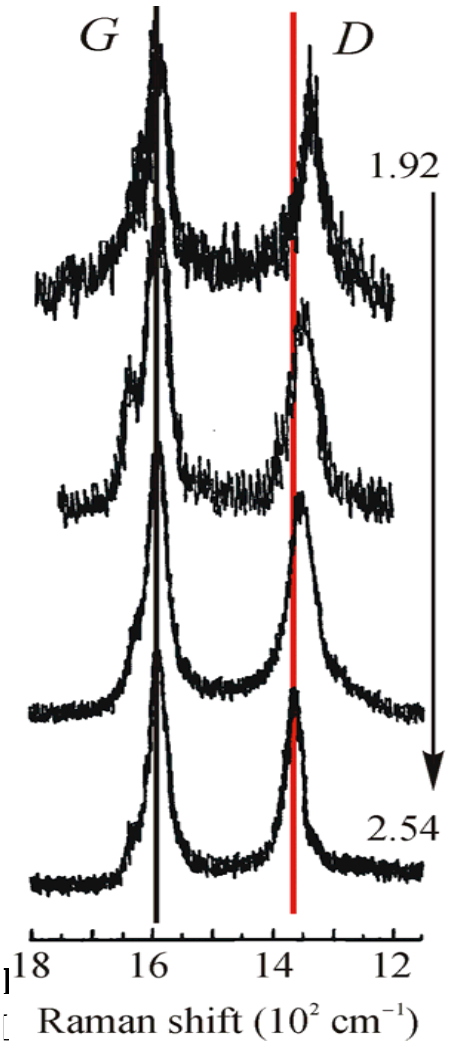
However 2nd order always allowed: q+(-q)=0

D Peak Dispersion

Pocsik *et al.* (1998)



Vidano *et al.* (1981)



D peak comes from LO phonons

(Ferrari Robertson 2000)

Active by double resonance

(Baranov 1988, Thomsen-Reich 2000)

Strongly dispersive due to Kohn Anomaly at K

(Piscanec et al. 2004)

However…

Second order no defect scattering necessary

In principle ALL phonons active

BUT

Double resonant phonons enhanced due to resonance and strong electron-phonon coupling

Previous double resonance models predict multiple D peaks for graphene

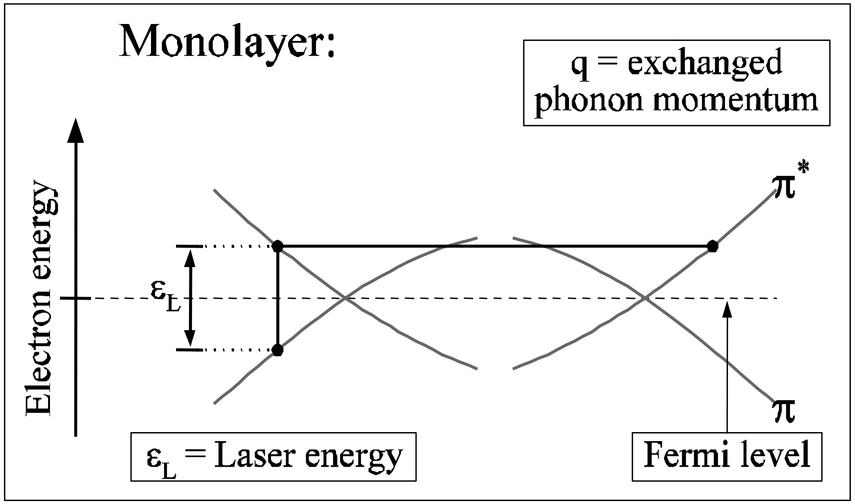
in contrast with experiments

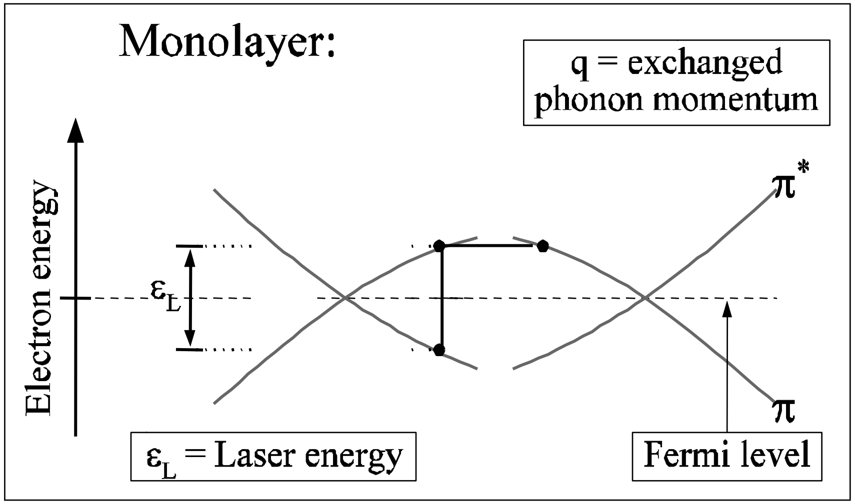
Double structure of 2D peak in graphite

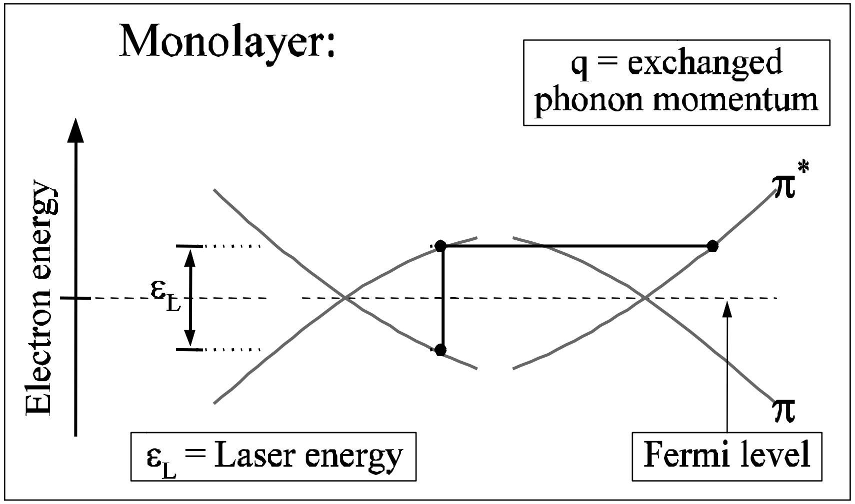
never explained

Traditional interpretation (1980)
2 Maxima in graphite
Phonon Density of States at K and M
WRONG since 2D disperses with excitation

KEY: Evolution of
Electron Bands with number of layers







Three Possible Processes

However: only 1 contributes

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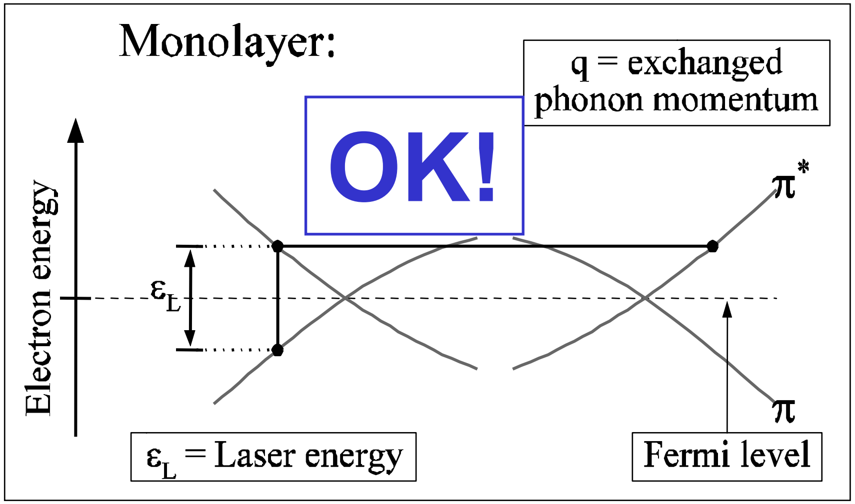
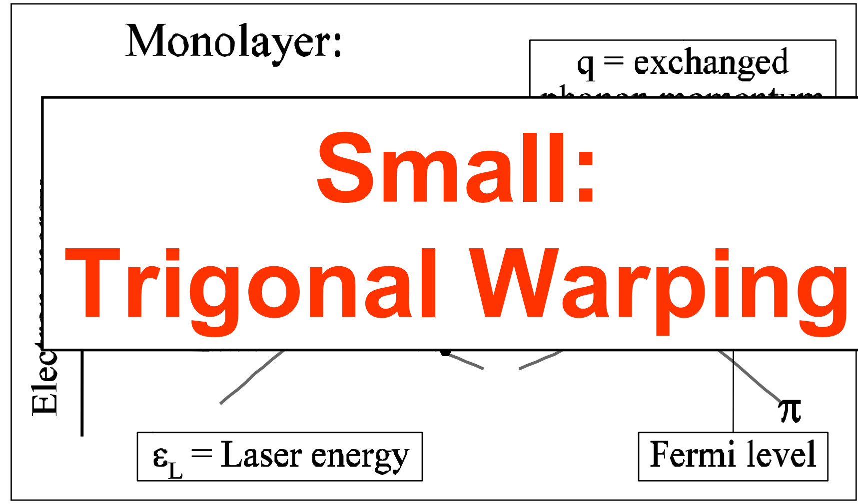
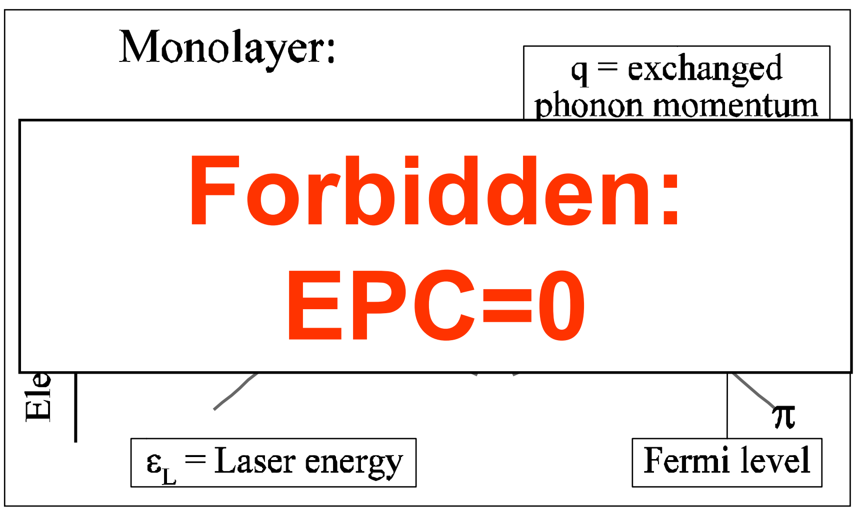




Three Possible Processes



However:
only 1 contributes

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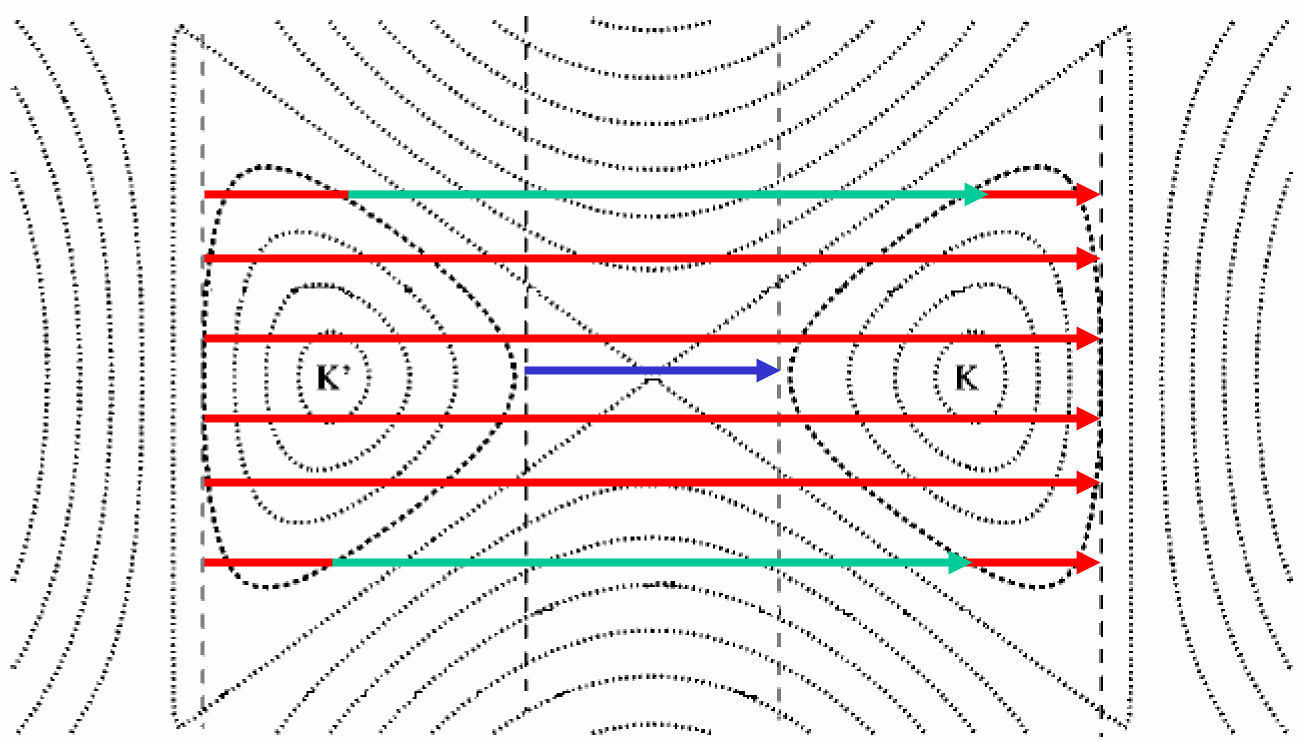
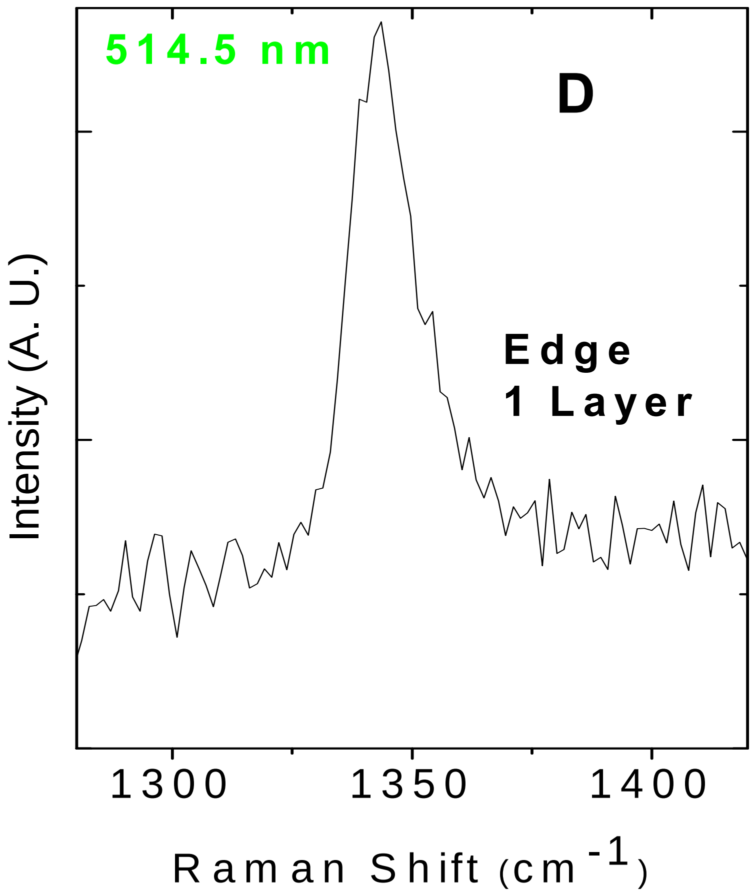
Trigonal Warping Effect

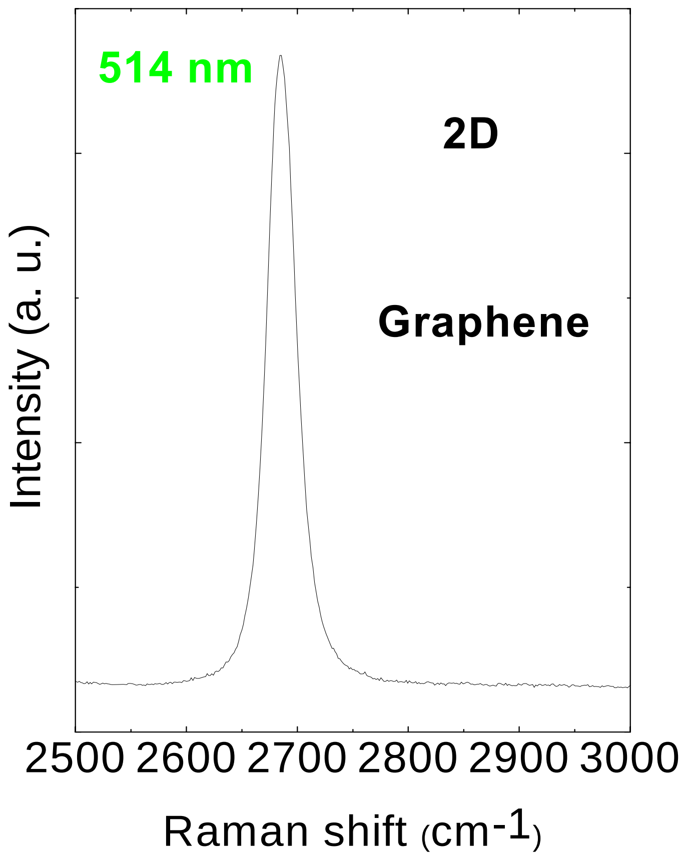


Adapted from: Kurti et al., Phys. Rev. B **65** 165433 (2002)

- q > K → Strong EPC and large portion of the phase-space
- q < K → Strong EPC but small portion of the phase-space
- q ~ K → EPC~0

1 Component D and 2D peaks





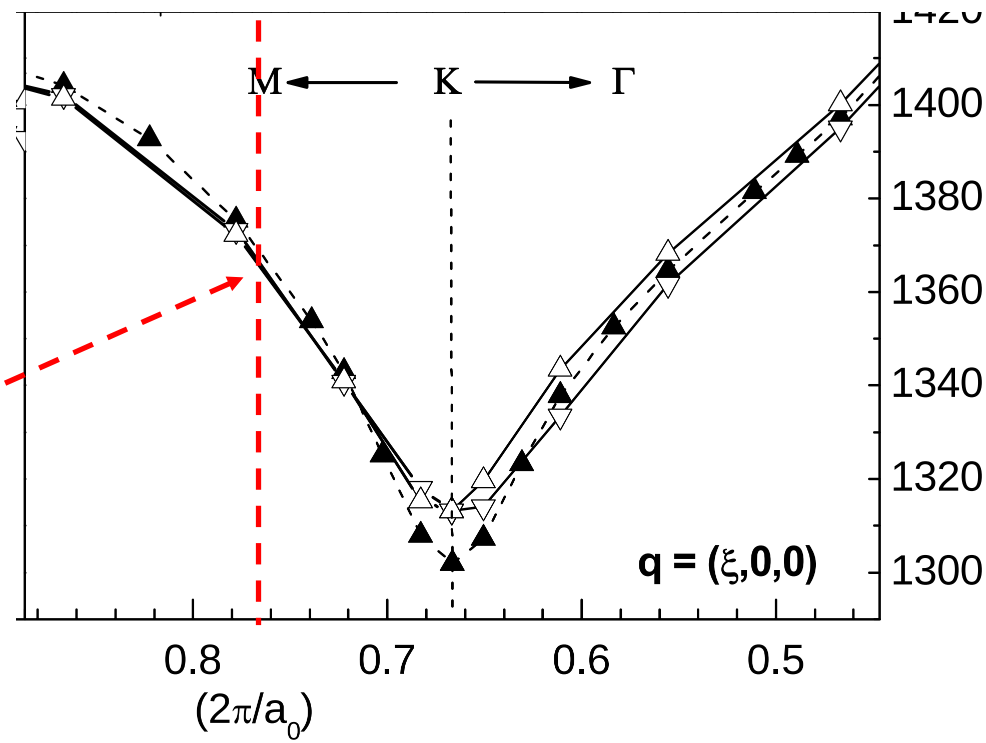
Two-layer Graphene

Two possibilities:

1) Phonon Splitting

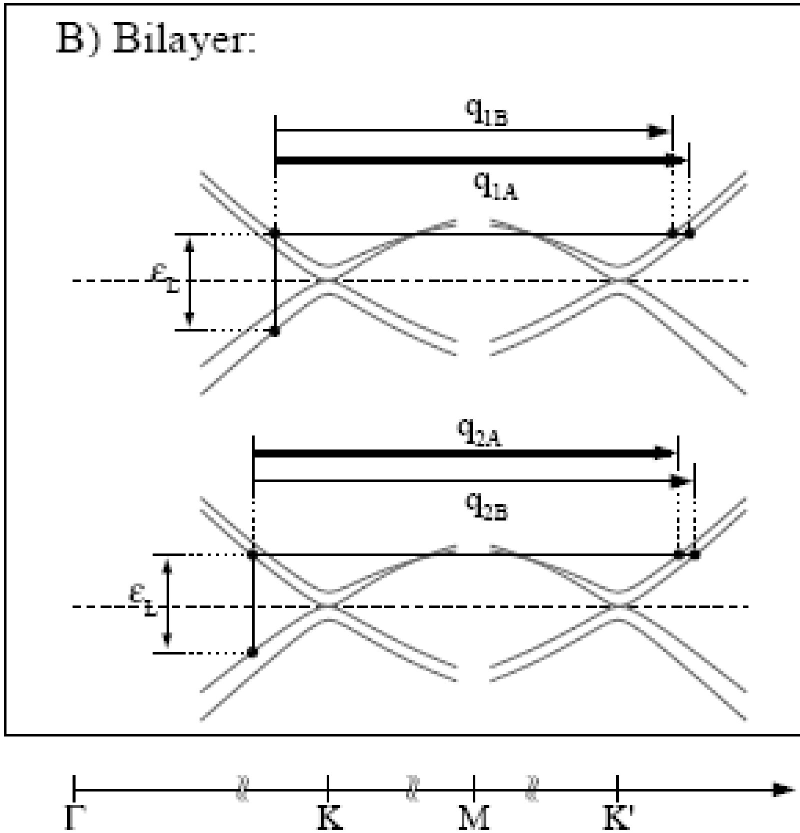
2) Band splitting

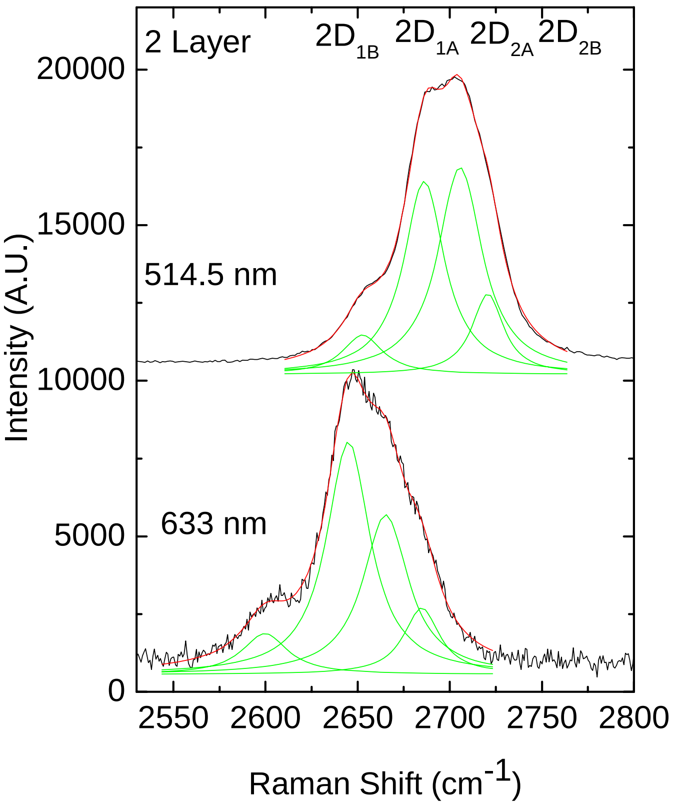
Phonon Splitting
K-M is Minor



PRL 93, 185503 (2004)

Band Splitting Main Effect





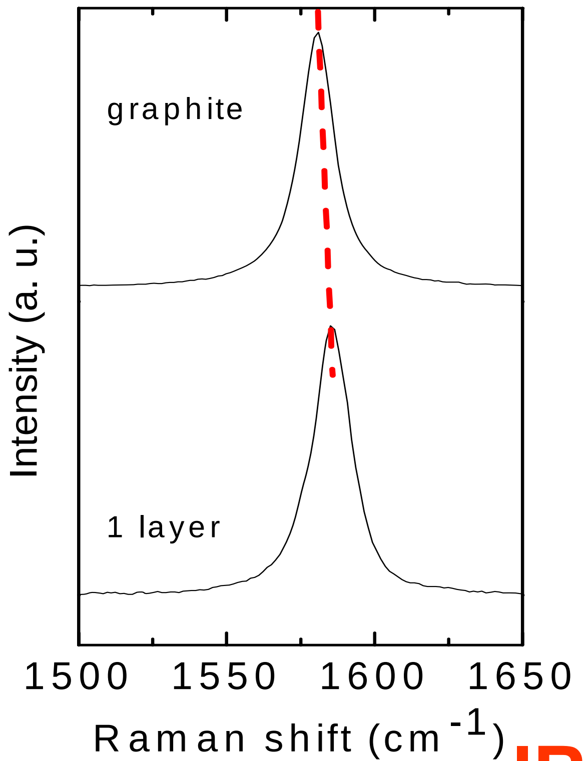
514.5	2 Layers			
Experimental	-44	-10	+10	+25
Theory	-44	-11	+11	+41
633				
Experimental	-55	-10	+10	+30
Theory	-44	-9	+9	+41

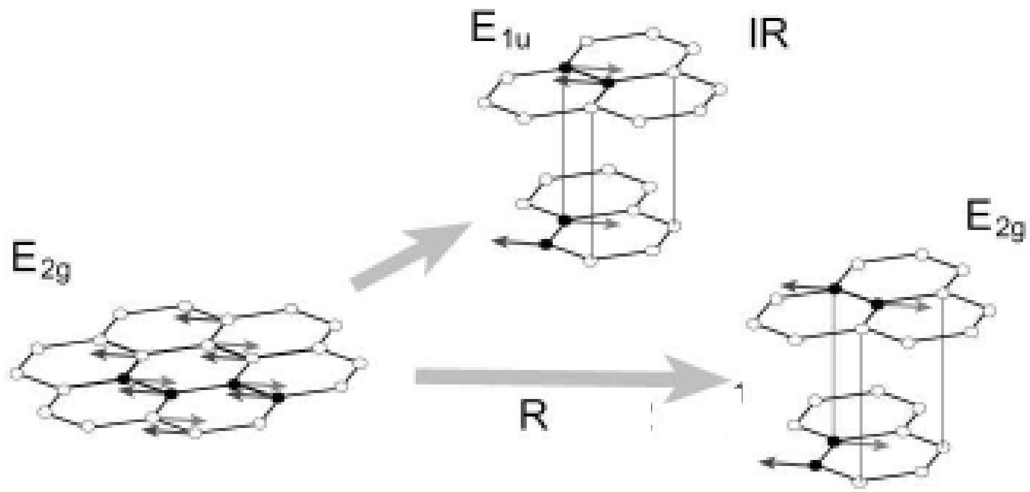
4 components

2 Most intense

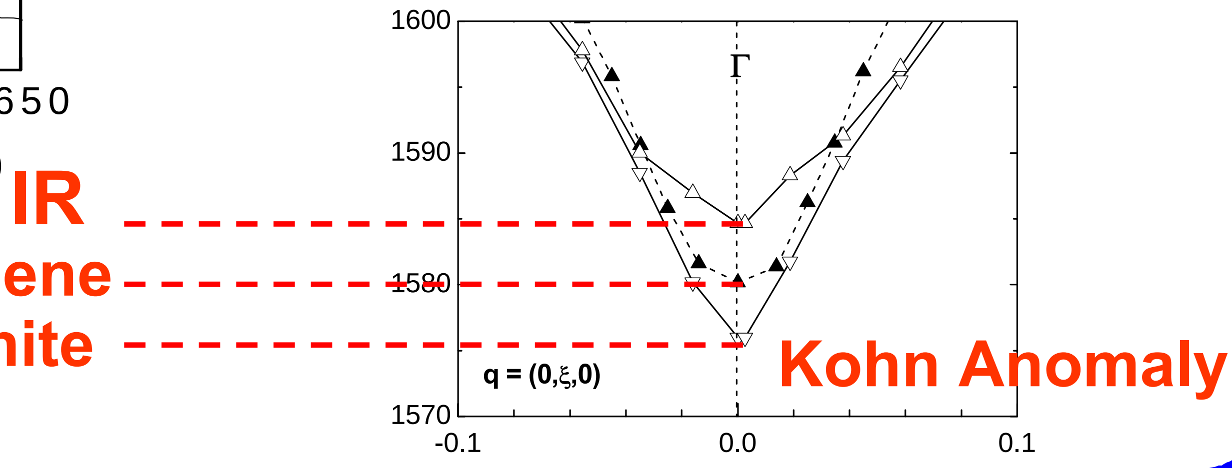
Origin of Small Upshift of G peak

~5 cm^{-1} Upshift





PRL 93, 185503 (2004)



Phonon-Linewidths and EPC

In a perfect crystal, phonon linewidths determined by Interaction with other elementary excitations:

$$\gamma = \gamma^{an} + \gamma^{EPC}$$

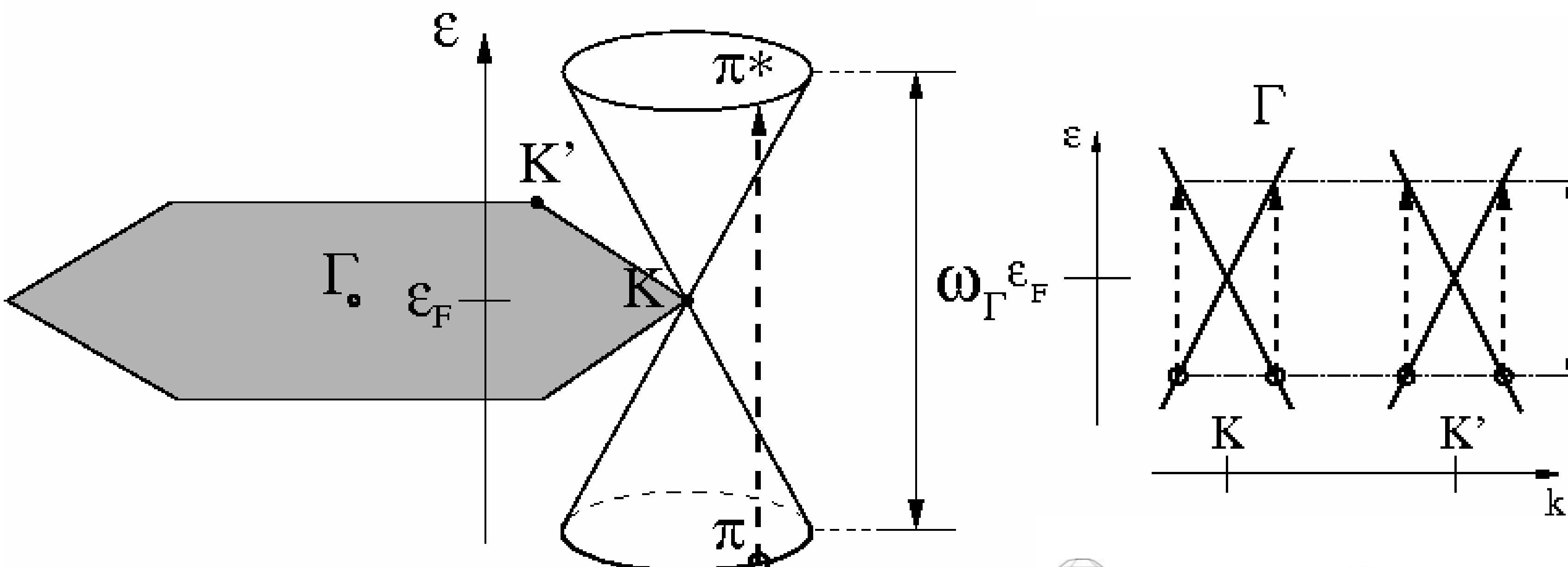
γ^{an} : anharmonic contribution, due to interaction With other phonons. Determined by anharmonic terms in interatomic potential.

γ^{EPC}: interaction with electron-hole pairs. Determined by EPC and present in systems with null electron gap

Γ-E_{2g}^{LO} Phonon Decay Processes

From the Fermi Golden Rule:

$$\gamma^{EPC}_{\Gamma - E_{2g}^{LO}} \propto \frac{EPC(\Gamma)^2}{\beta^2}$$



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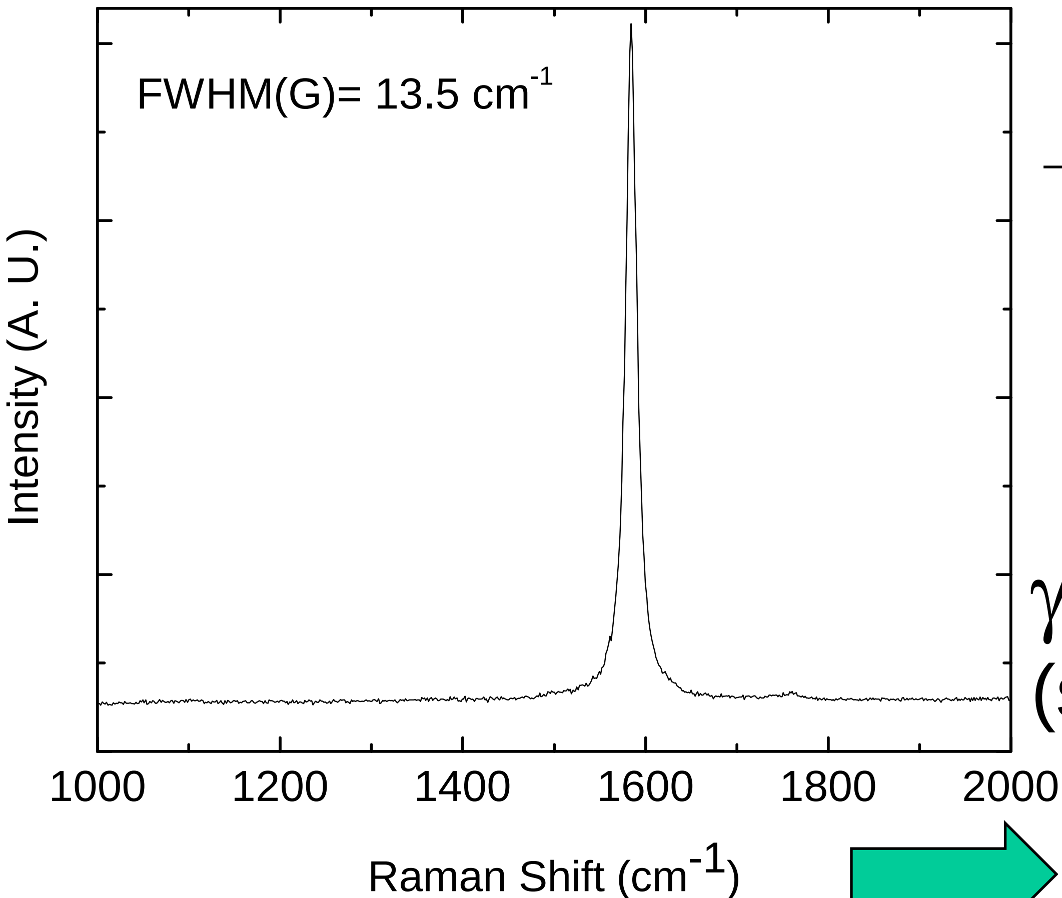
Γ-E_{2g}^{LO} : Graphite Raman G Peak

No D Peak

Single Crystal Graphite

No extra broadening due to disorder

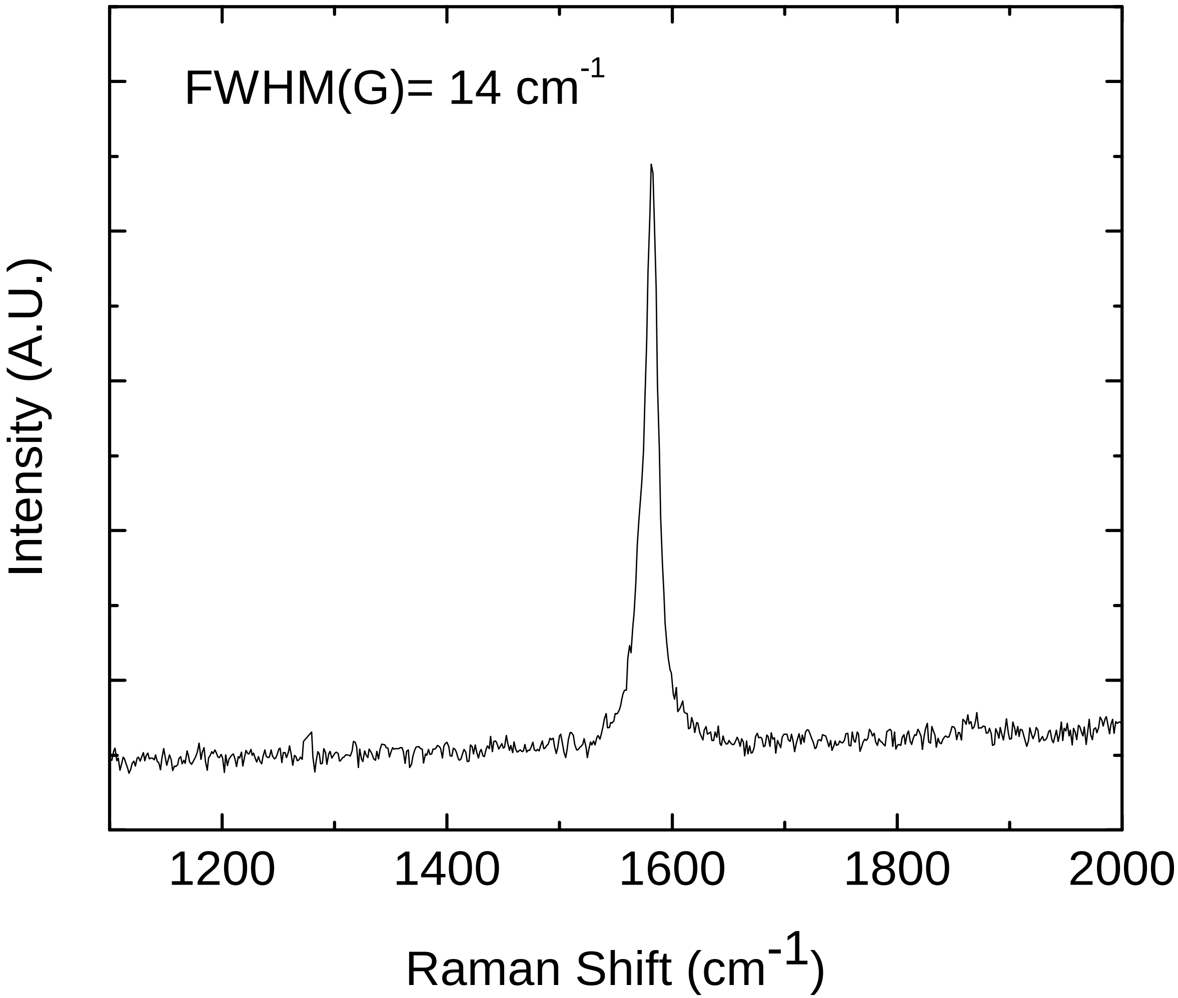


No FWHM(G) increase with temperature

$\gamma^{an} \leq 1.5$ cm^{-1} (spectrometer resolution)

EPC(Γ)=45.5 (eV/Å)^2

And… Single layer graphene…



Similar EPC

PRB 73, 155426 (2006)

Implications for Nanotubes

Single 2D peak graphene $\Rightarrow$
Single 2D peak in Single Wall CNT

Curvature and confinement
give diameter dependence

2D(SWNT)~2D (graphene)- A/d

2D position in Graphite
should not be used to scale

Distribution of SWNTs of different diameters,
distribution of 2D peaks

What about Multi-Wall?

First approximation each wall gives a 2D peak

DWNT two 2D peaks
(inner and outer wall)

HOWEVER, inter-wall interactions
Can change simple picture
Further splitting, Less peaks!

Details to follow…

Conclusions

Identified unique features of Raman spectrum, which fingerprints graphene amongst all other carbon allotropes.

The Raman spectrum evolution with increasing number of layers reflects the evolution of the electronic structure and electron-phonon interactions

Raman spectroscopy is a quick, high-throughput, non-destructive technique for the unambiguous identification of graphene layers.

Raman+Graphene is Good Fun!

CAMBRIDGE UNIVERSITY
DEPARTMENT OF ENGINEERING

ELECTRONIC DEVICES
AND MATERIALS GROUP

UNIVERSITY OF CAMBRIDGE

The Leverhulme Trust

EPSRC

THE ROYAL SOCIETY

CAPE Centre for Advanced Photonics and Electronics

www-cape.eng.cam.ac.uk

Funding:

- EU FAMOUS & CANAPE project
- Marie Curie Fellowship IHP-HPMT-CT-2000-00209
- The Royal Society
- EPSRC GR/S97620/01
- The Leverhulme Trust

MAX-PLANCK-GESELLSCHAFT

CPU:

- HPCF, Cambridge UK
- IDRIS, Orsay France

MANCHESTER 1824

Reference

arXiv:cond-mat/0606284

The Raman Fingerprint of Graphene

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Graphene is the two-dimensional (2d) building block for carbon allotropes of every other dimensionality. It can be stacked into 3d graphite, rolled into 1d nanotubes, or wrapped into 0d fullerenes. Its recent discovery in free state has finally provided the possibility to study experimentally its electronic and phonon properties. Here we show that graphene's electronic structure is uniquely captured in its Raman spectrum that clearly evolves with increasing number of layers. Raman fingerprints for single-, bi- and few-layer graphene reflect changes in the electronic structure and electron-phonon interactions and allow unambiguous, high-throughput, non-destructive identification of graphene layers, which is critically lacking in this emerging research area.