Istituto Nazionale di Fisica Nucleare

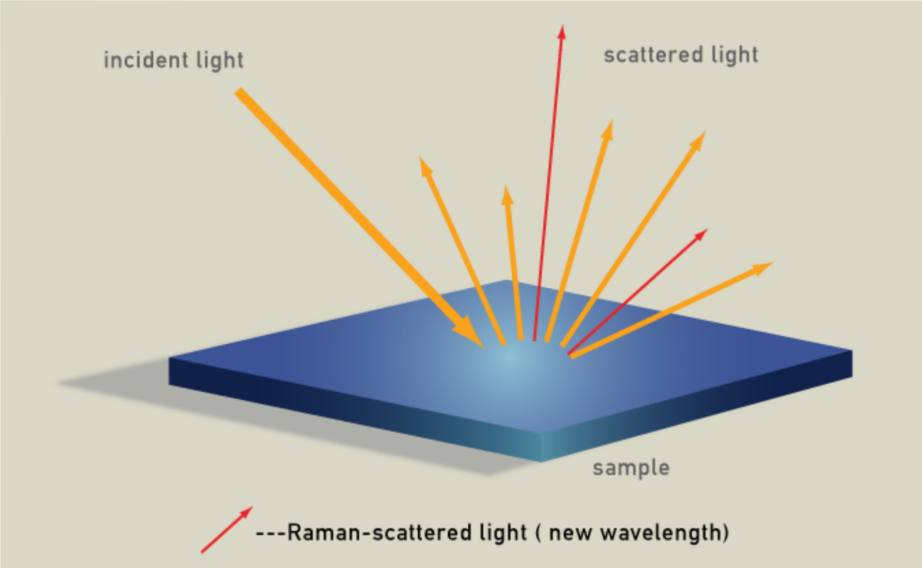
Laboratori Nazionali di Frascati

Raman Spectroscopy of Graphene

Alessandra Di Gaspare

Laboratori Nazionali di Frascati

Raman Spectroscopy: basics



Optical Spectroscopy for Material Science

Photons: probe and output

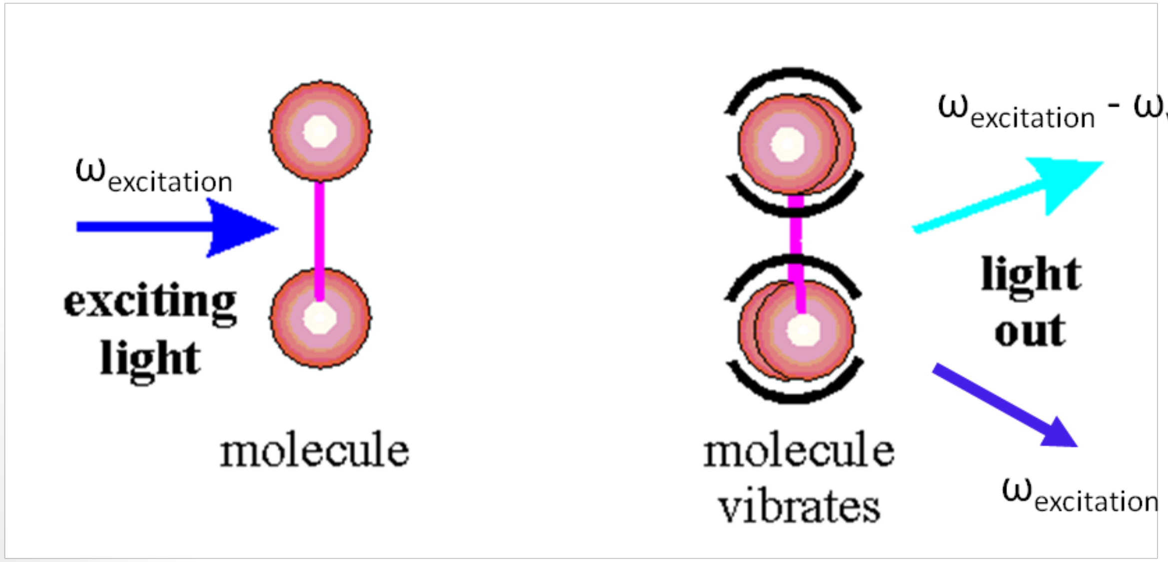
measure of scattered light at $\nu' = \nu_{ex} + \Delta\nu$

non-linear process

by considering VIS light and typical $\Delta\nu$

—> Vibrational levels in material systems

(molecules, solids,…)

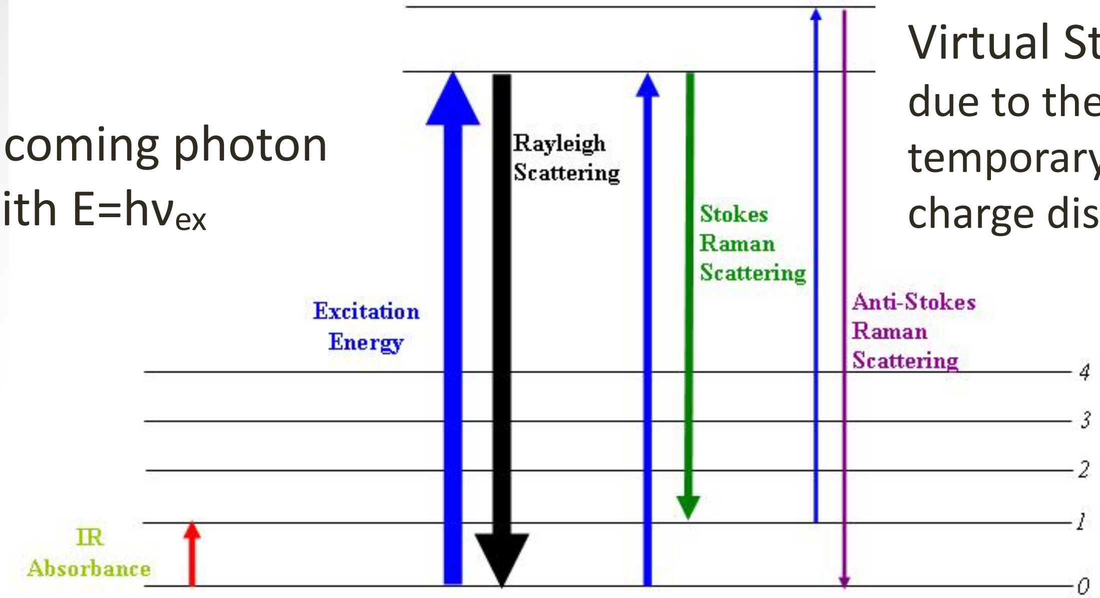


Raman Scattering

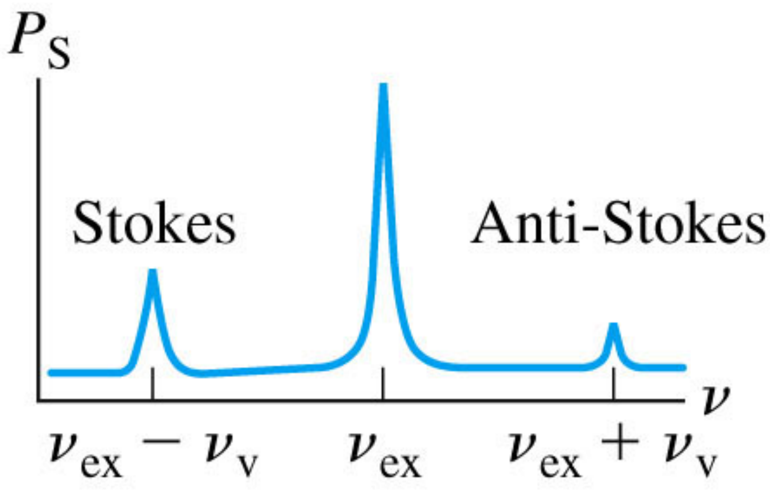
Rayleigh scattering, photon energy unchanged

Raman Mechanism

incoming photon with $E=h\nu_{ex}$



Virtual State due to the temporary charge distr.



Vibrational State

(b)

Spatial charge separation under electric field $\boldsymbol{E}$ induced dipole moment $\boldsymbol{\mu}$; ***emission of photons with*** $I \propto \mu''$

$\boldsymbol{\mu}=\alpha \boldsymbol{E}$, α: polarizability; $\boldsymbol{E}=\boldsymbol{E}_0 \cos 2\pi\nu_0 t$ —> $\boldsymbol{\mu}=\alpha \boldsymbol{E}_0 \cos 2\pi\nu_0$

Internal vibrational motion with Eigenfrequency ν_M —> $q=q_0 \cos 2\pi\nu_M t$

Polarizability $\alpha = \alpha_{q=0} + (\partial\alpha/\partial q)_{q=0}\, q$ + higher order terms

$\boldsymbol{\mu} = \alpha\, \boldsymbol{E} = (\alpha_{q=0} + (\partial\alpha/\partial q)_{q=0}\, q_0 \cos 2\pi\, \nu_M t)\, \boldsymbol{E}_0 \cos 2\pi\, \nu_0 t$

$=\alpha_{q=0}\, \boldsymbol{E}_0 \cos 2\pi\nu_0 t + 1/2 (\partial\alpha/\partial q)_{q=0}\, q_0\, \boldsymbol{E}_0\, [\cos 2\pi(\nu_0 - \nu_M)t + \cos 2\pi\, (\nu_0 + \nu_M)t]$

Why Raman?

Information on rotational and vibrational levels

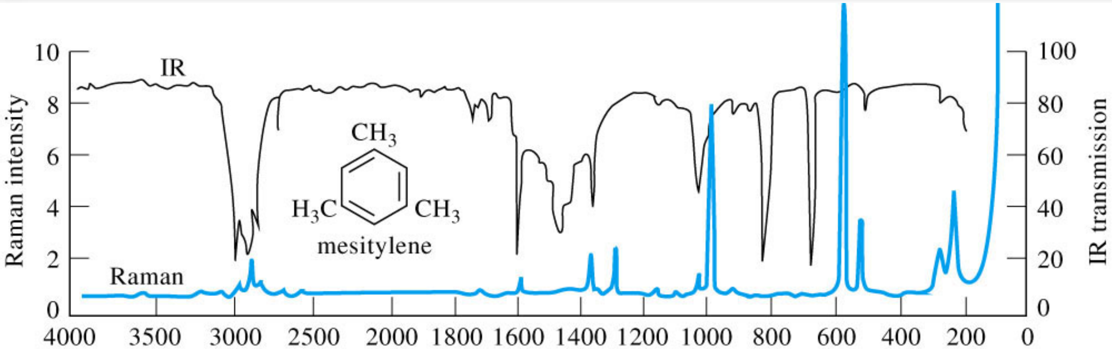
- Raman effect small but accessible by use of lasers

Raman Intensities are 0.001% of Source Intensity and $\propto \nu^4$

VIS and UV sources, Lasers; $\Delta\nu <\approx 4000\ cm^{-1}$

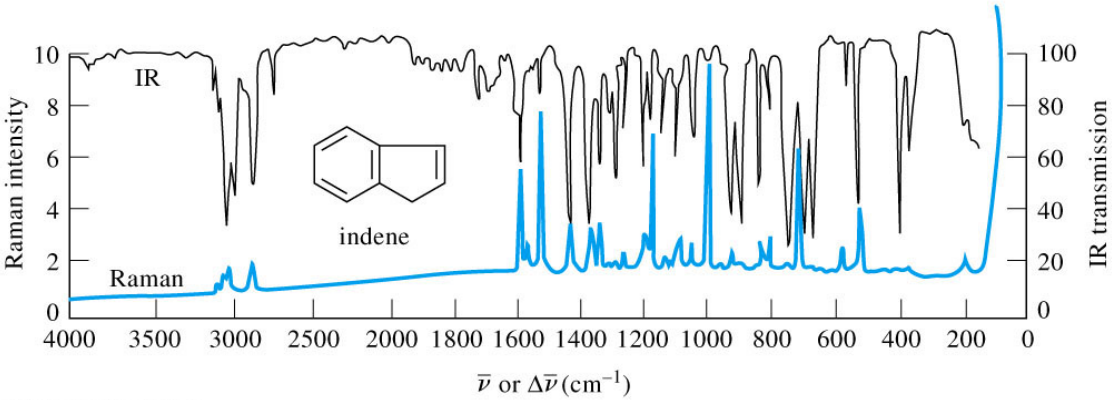
(vibrational transitions in molecules, phonons in solids, el. transitions)

- In situ analysis of organic and inorganic compounds
- Analysis of aqueous solutions and solids (water does not interfere)

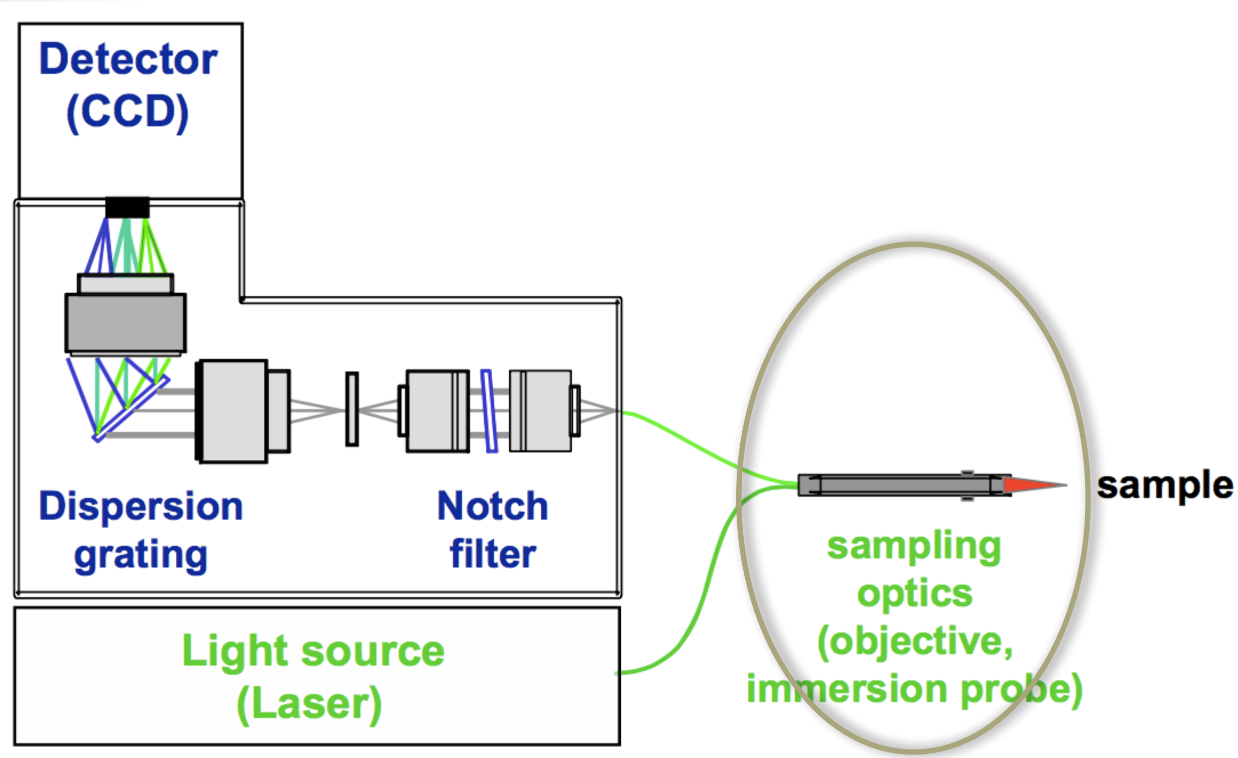


Raman Shift
$\Delta\lambda$=10 um
ΔE= 124 meV
$\Delta\nu$=1000 cm^{-1}

- Complementary information to IR spectroscopy



Raman Spectroscopy Systems

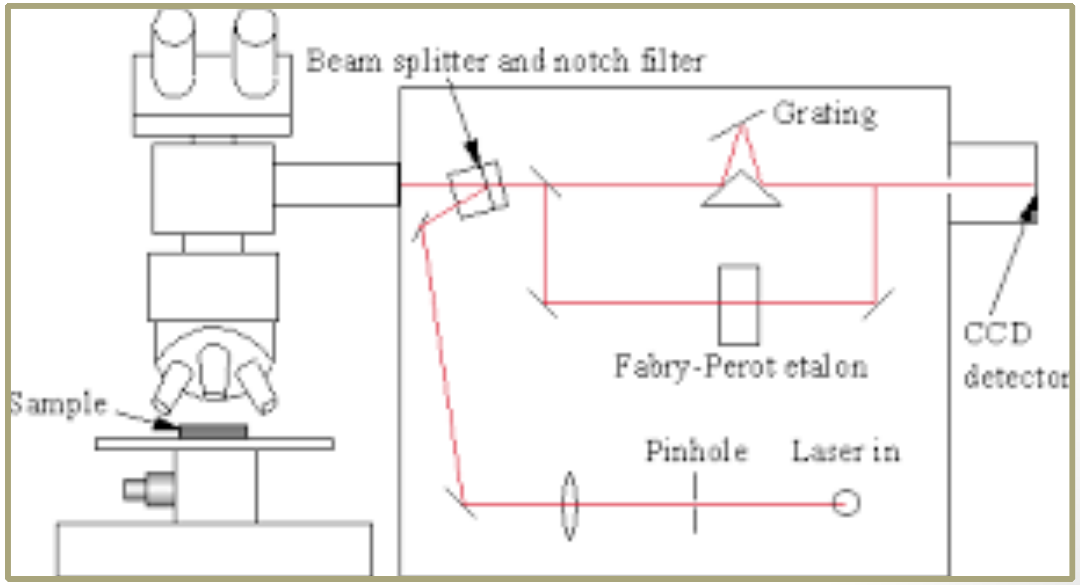


- holographic notch filters 80% T of Raman light
- 324 - 1339 nm available
- single transmission grating 0 - 4400 cm^{-1} (multiplex)
- high light throughput cooled CCD (~ 40% QE)

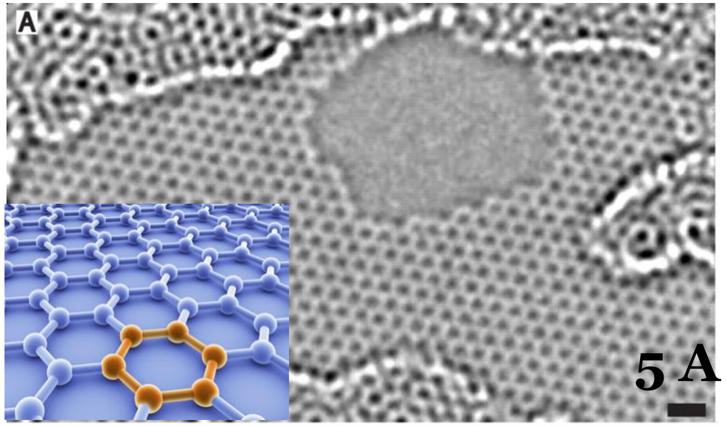
Such Elements can be included in a Raman Microscope:

-diffraction limit lateral resolution

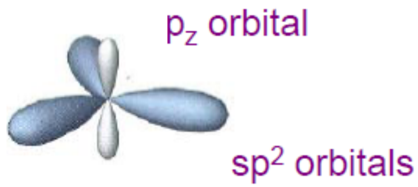
-optical and Raman images (2D mapping)

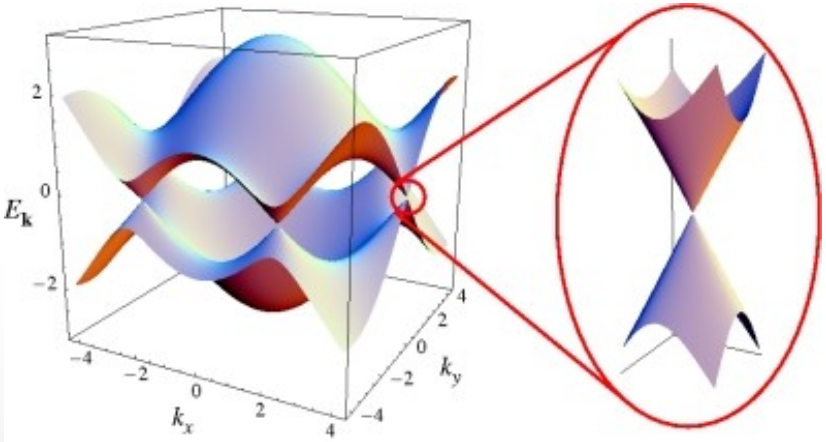


Graphene as emerging platform material



Graphene
(Nobel prize in 2010)
2D-honeycomb array of C-atoms
linear dispersion at the Dirac Point
electrons and holes are massless relativistic particles with v_F 10^6 m/s



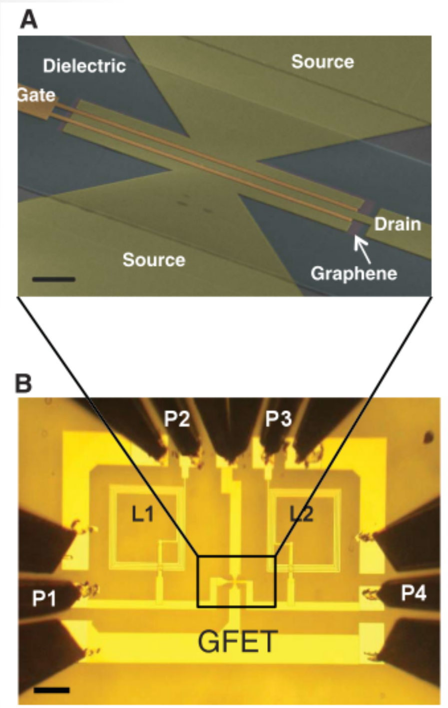


Gapless material
High chemical stability, carrier mobility $\mu \sim 2*10^5\ cm^2/Vs$

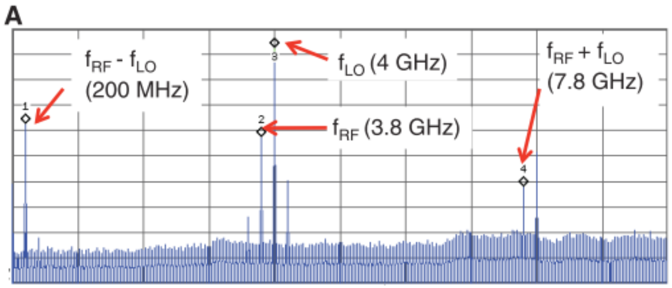
Broad range of applications…

Graphene Device Technology

1.Microwave Mixers for ICs

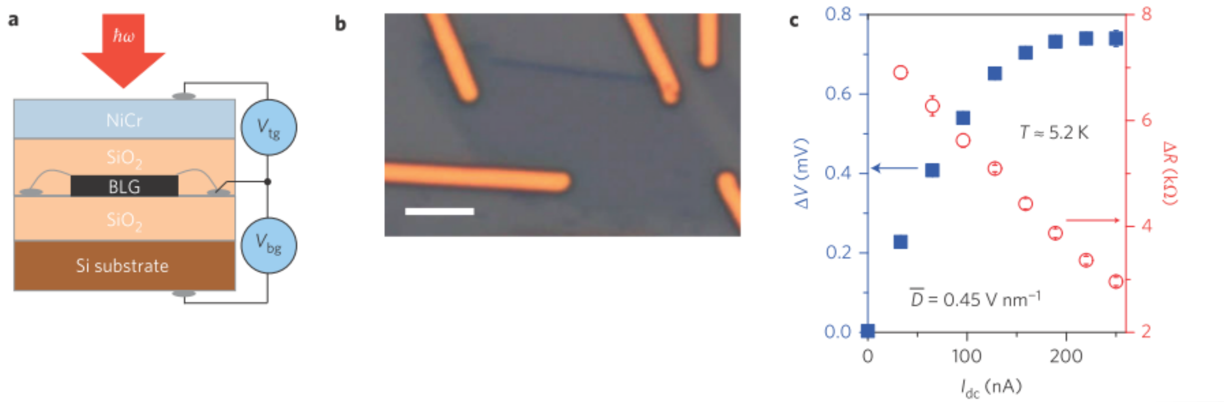


Y. – M. Lin et al, Science 2011
IBM group
Graphene from CVD on SiC
Mixer operation up to 10GHz



2.Hot-Electron Bolometers in the IR range

J. Yan, Nat. Nano 2012
Univ. Maryland
HEB response at the charge neutrality point
Exfoliated graphene



Graphene @LNF The GARFIELD Project

GARFIELD
Graphene Active FIlms for ELectronic devices and radiation Detection

INFN
Istituto Nazionale di Fisica Nucleare
Laboratori Nazionali di Frascati

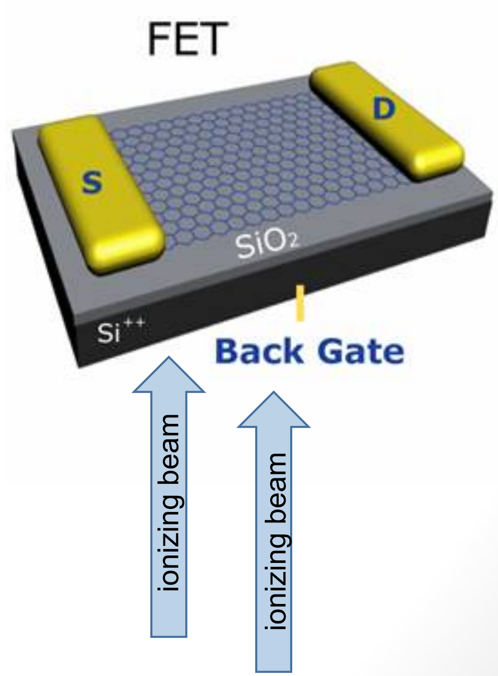
Funded by CSN5-INFN, 2-years project started in 2014

GARFIELD Key concept:
G-based devices for novel schemes of radiation detection

Objectives of the Project:

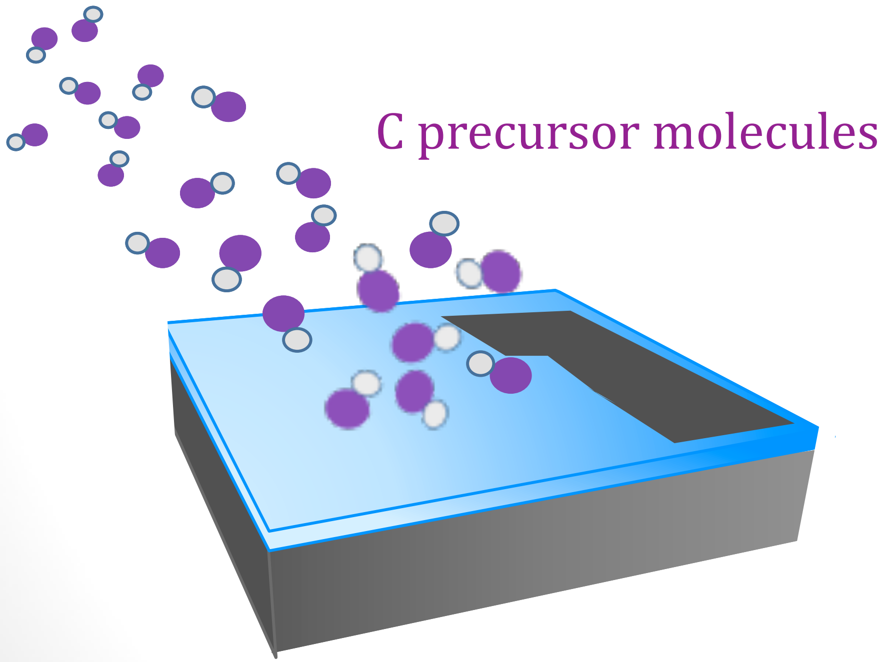
•Implementation of a full-capability graphene-platform within the LNF-INFN (Material Science Lab - DAFNE-L)

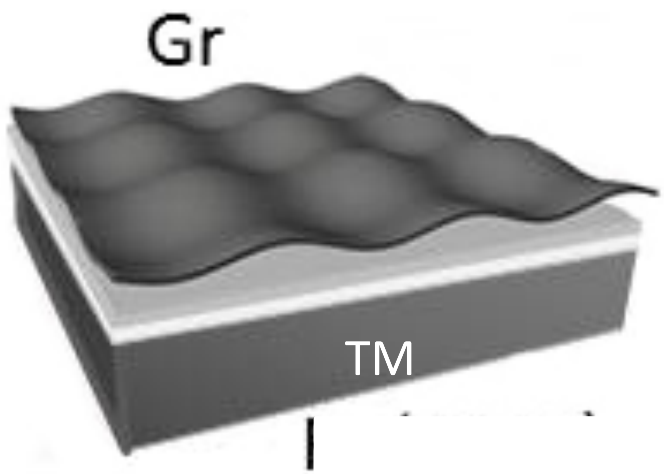
•Development of graphene-based detectors for application of recognized interest to the INFN (prototypes/proof-of-concepts devices)



Epitaxial Graphene on Transition Metals

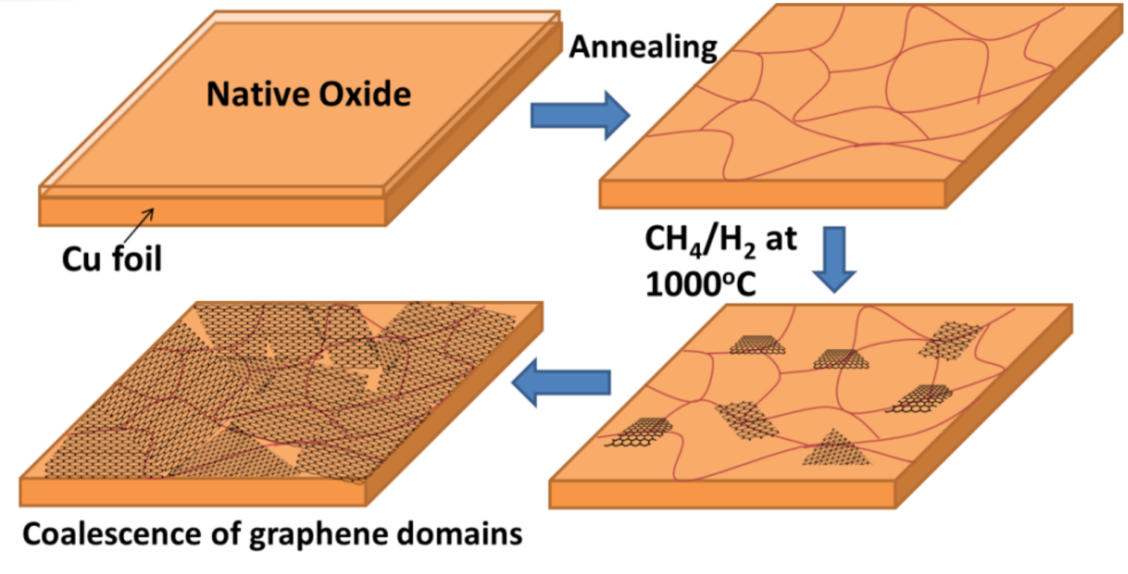
- Chemical Vapor Deposition (CVD) on transition metal substrates: the most promising and readily accessible method to obtain high-quality graphene on large area
- Self-limiting growth; Low defect density





TM: Ir, Ru, Pt, Re, Rh, Ni, Fe, Cu, alloys (PtRh, NiAl, ...)

Graphene CVD on Cu

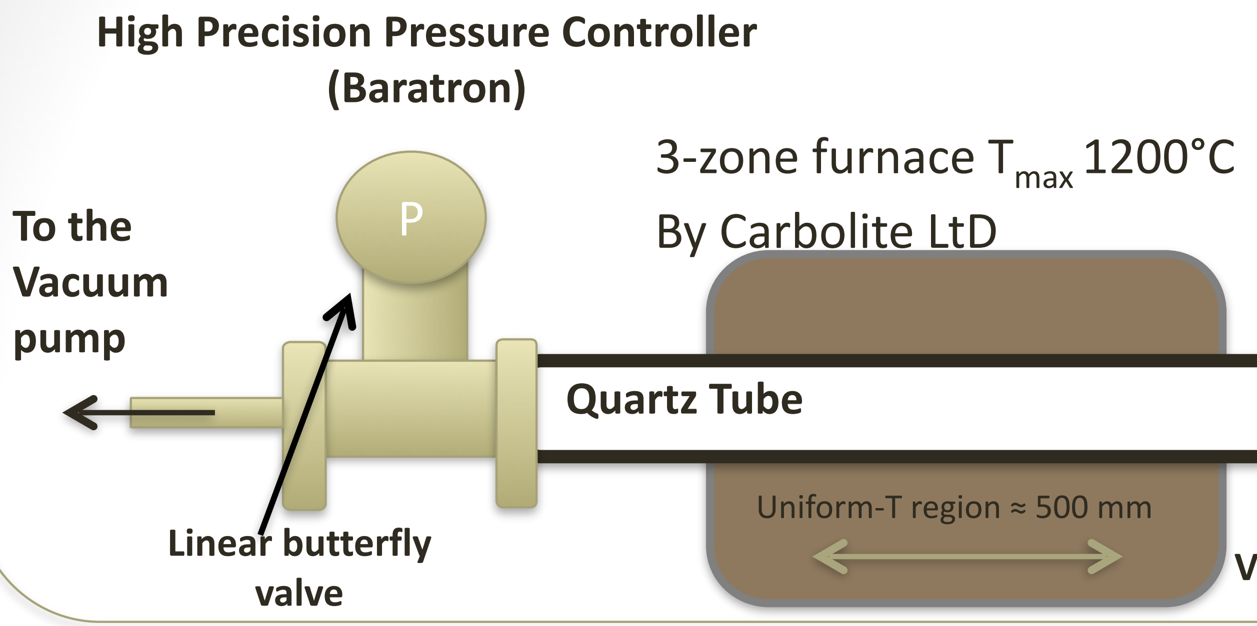


Substrate easy to remove, inexpensive,…
T 1000°C, pressure not usable in UHV systems

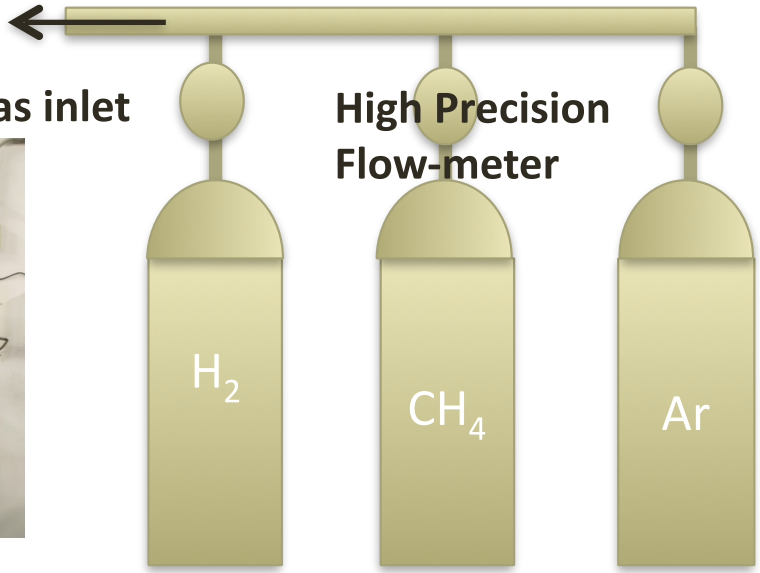
Atmospheric pressure CVD System
Quartz Tube Chamber (High-T, controlled atmosphere)

The Graphene CVD Facility @LNF

TUBE FURNACE WITH CONTROLLED ATMOSPHERE

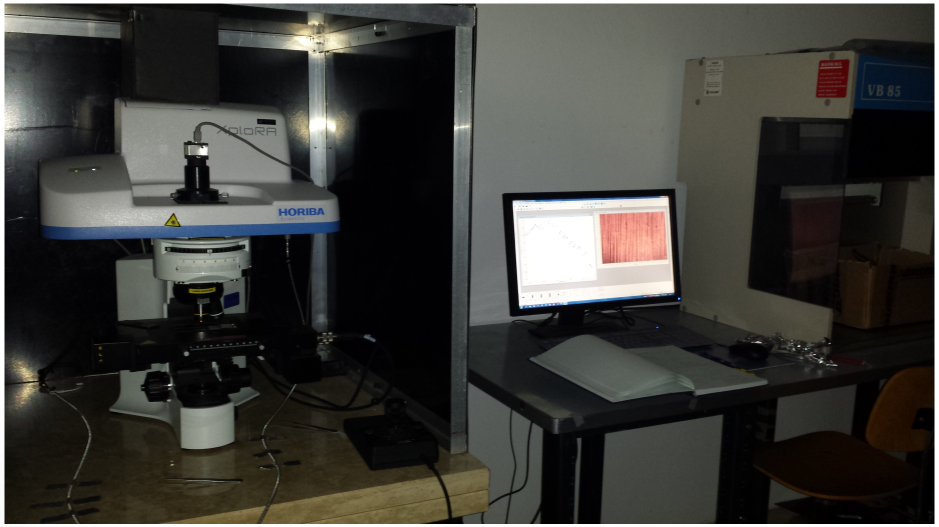


GAS DISTRIBUTION CIRCUIT

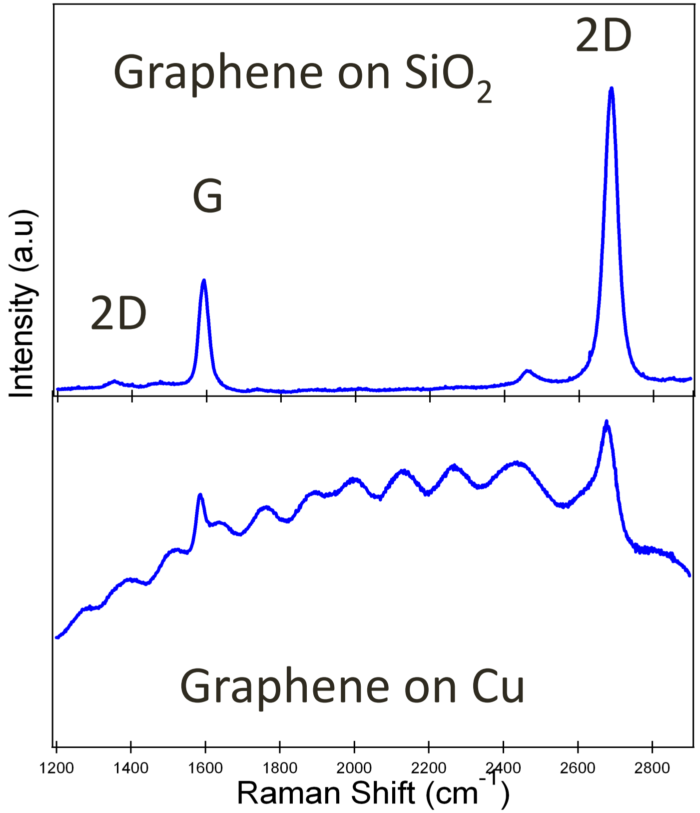


Spectroscopic Analysis of Graphene

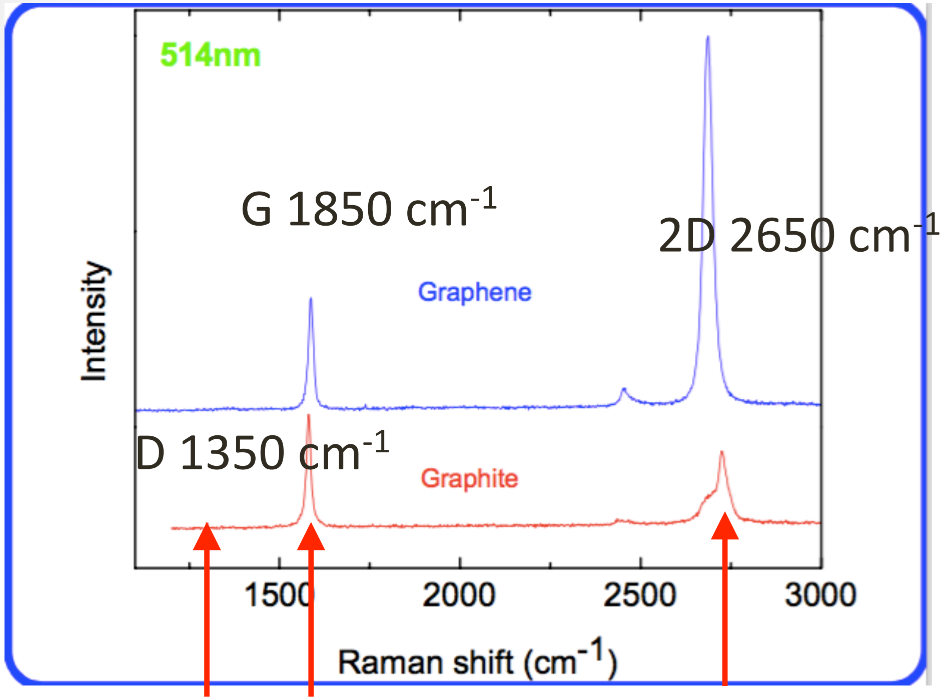
- Raman Spectroscopy:
- strongest spectral fingerprint, 2D-mapping, multilayer, defects,… (*non-metallic substrate*)
- High Throughput, Non Destructive, Quick, Substrate Independent Identification



MicroRaman @LNF



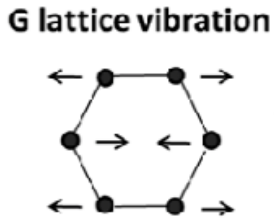
Spectroscopic Analysis of Graphene

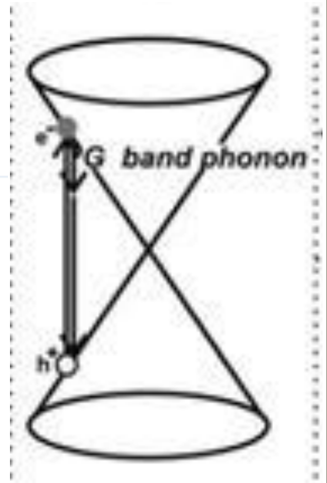


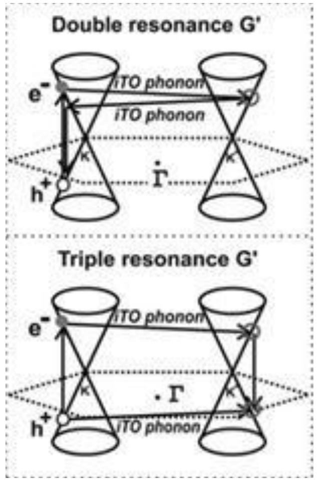
Raman Data from Ferrari group
A. Ferrari et al, presentation @NT2006

3 spectral fingerprints

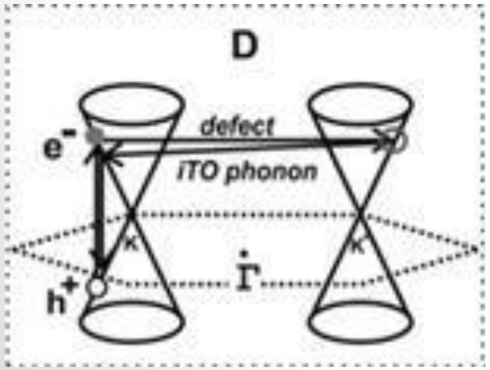
1- G peak: in plane phonon vibration (sp2 carbon)







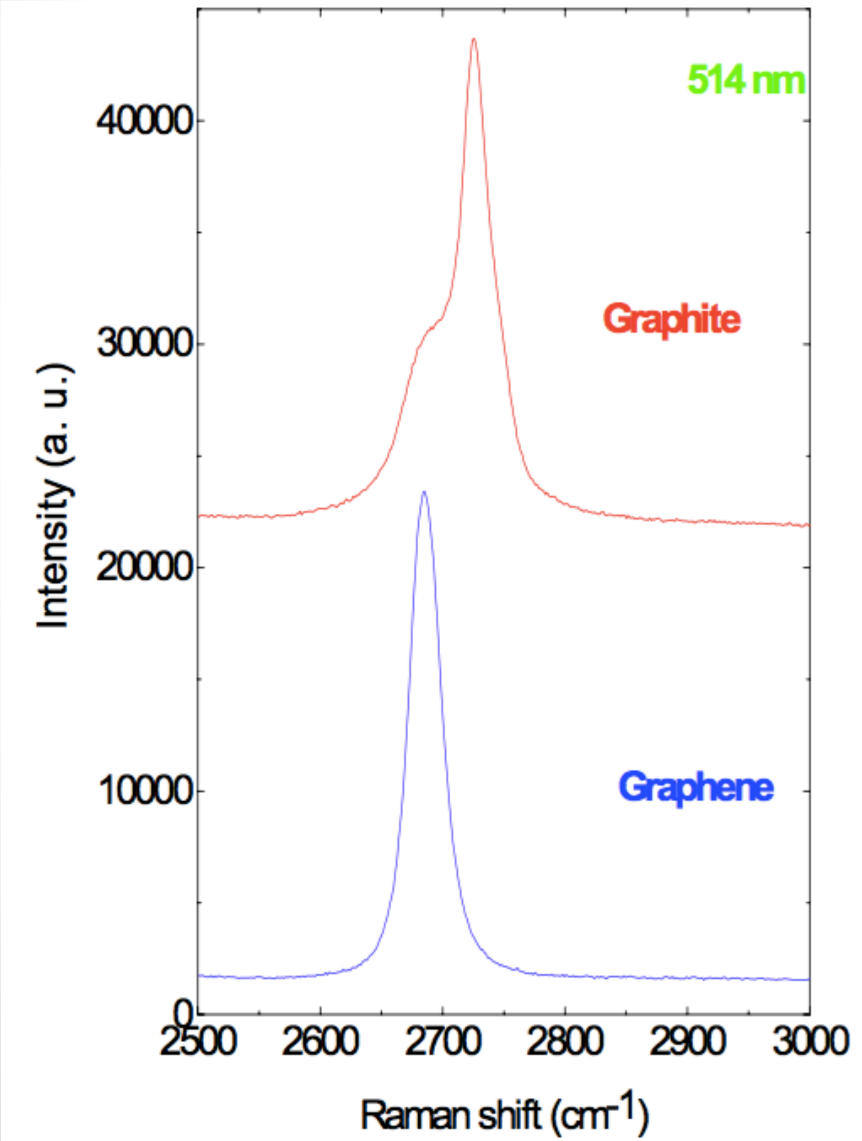
2- 2D peak: II-order overtone of a different in- plane vibration



3- D peak: intervalley phonon and defect scattering
not visible in **pristine graphene** because of crystal symmetries.
A charge carrier must be excited and inelastically scattered by a phonon, then a second elastic scattering by a defect or zone boundary must occur to result in recombination
The presence and the weight of the D peak i related to order and defects!!!

2D peak

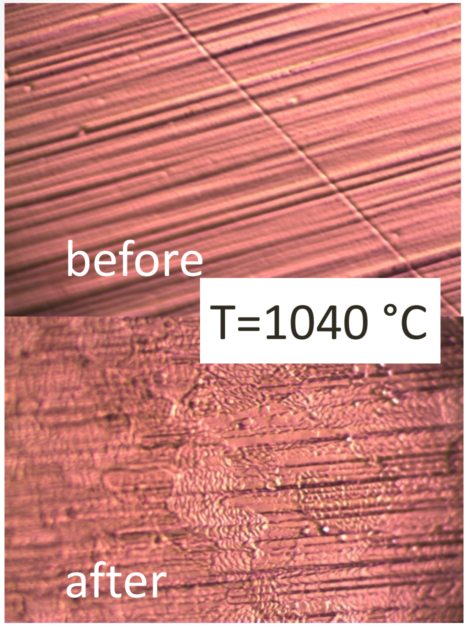
2D peak in sp2 carbon is always allowed because the second scattering (either on the initially scattered electron/hole or its complementary hole/electron) in the process is also an inelastic scattering from a second phonon

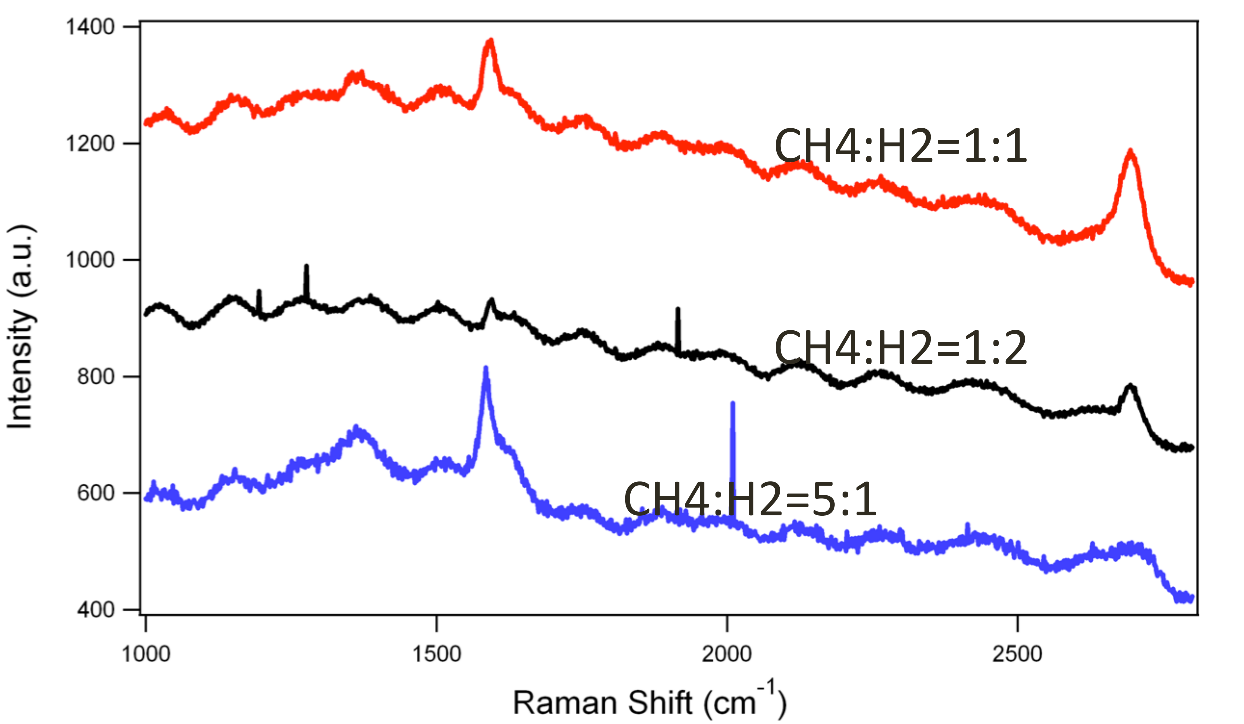


Raman Data from Ferrari groupA. Ferrari et al, presentation @NT2006

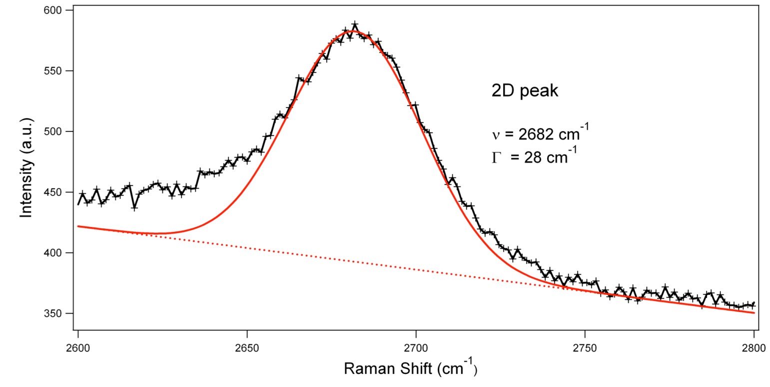
Because of added forces from the inter-layer interactions, as the number of graphene layers increases, the spectrum will change from that of single-layer graphene, namely a splitting of the 2D peak into an increasing number of modes that can combine to give a wider, shorter, higher frequency peak…
the number of layers can be derived from the ratio of peak intensities, I_{2D}/I_G !!!

Raman Spectra of Graphene-on-Cu

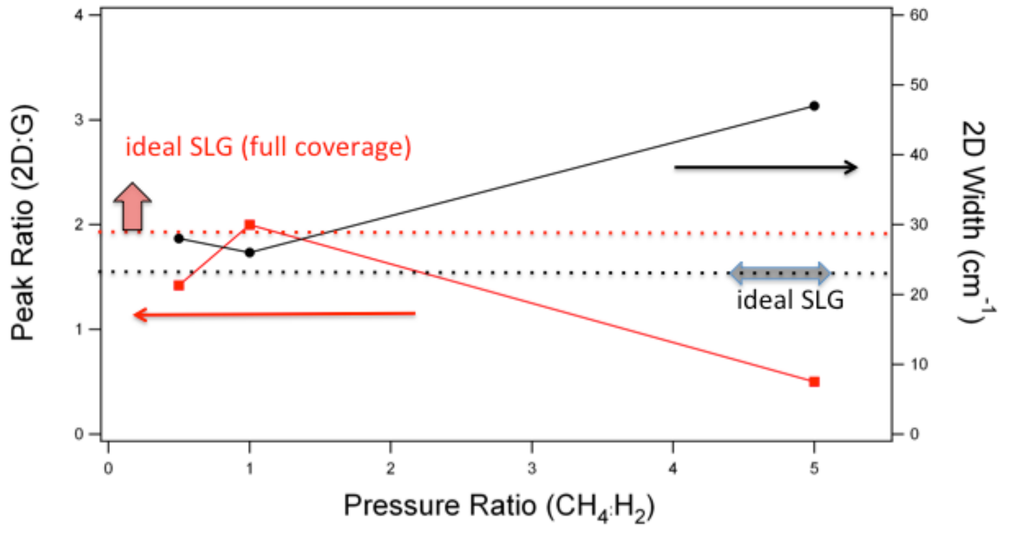




Peak Analysis

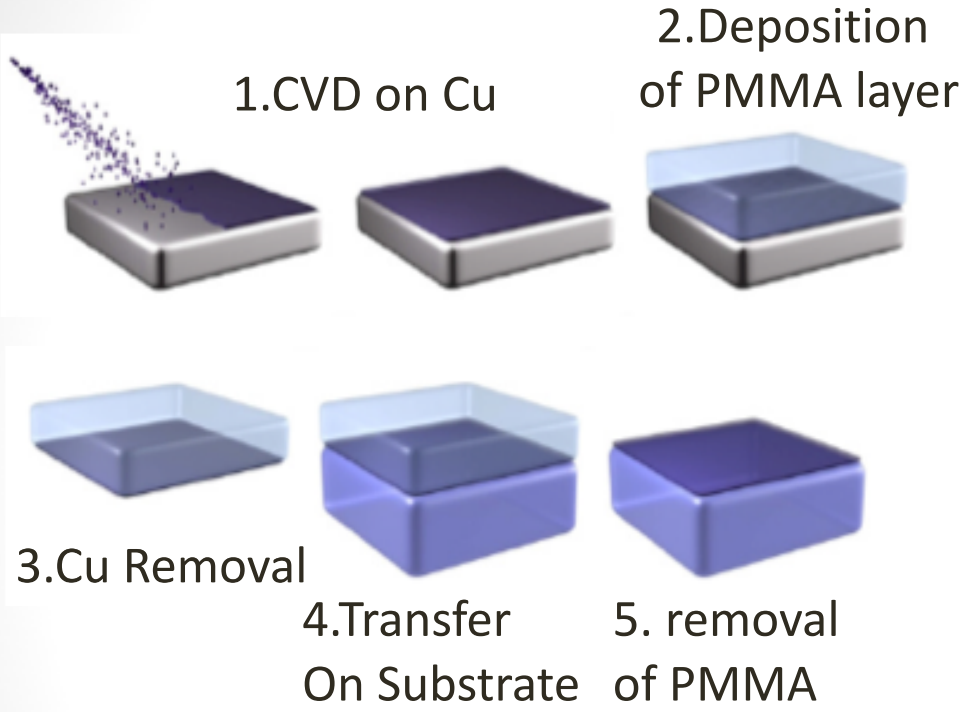


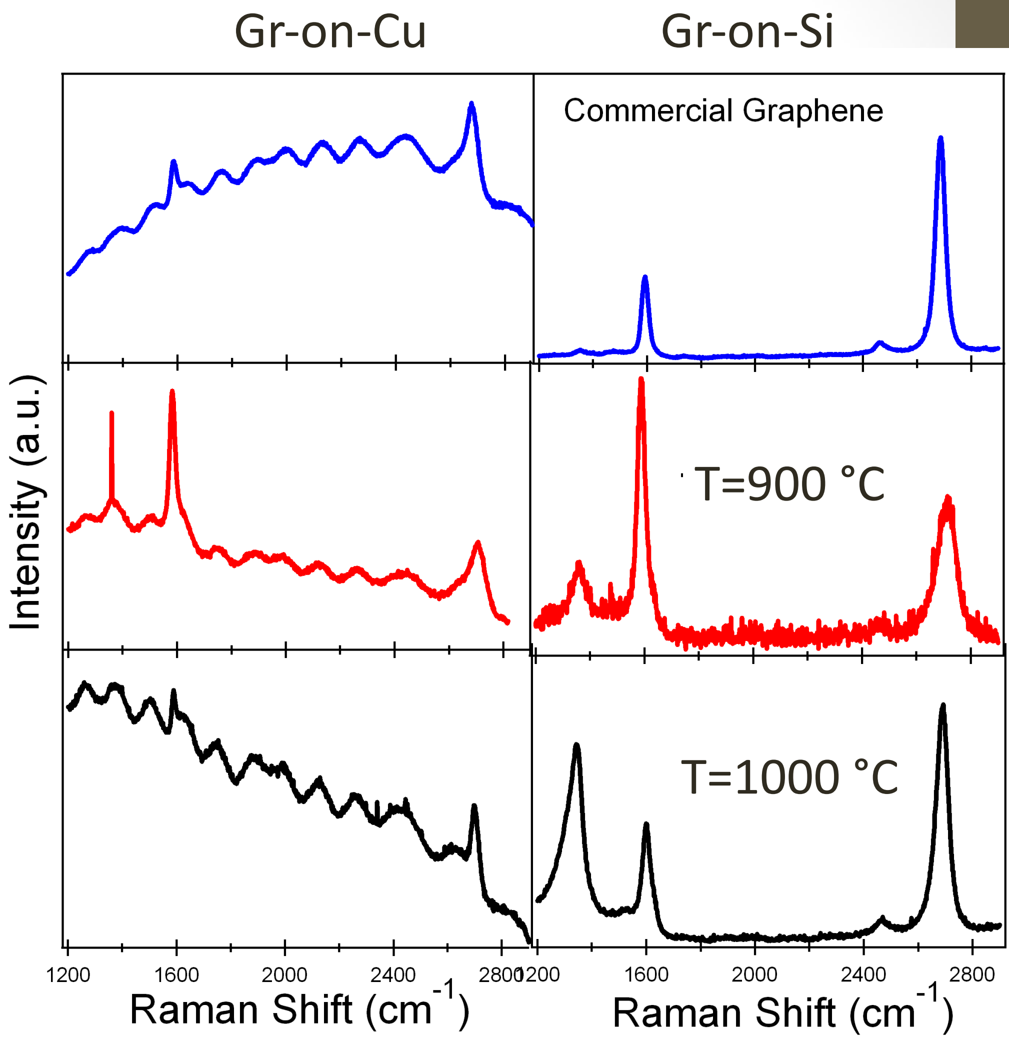
linear baseline + gaussian fit

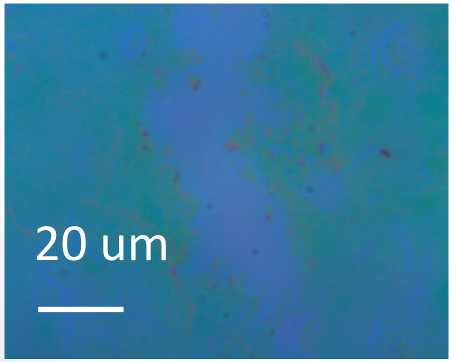


Graphene on Silicon

Graphene Transfer







optical and Raman images

Today

1-Graphene Monolayer grown @LNF and transfered on SiO2/Si

2-Graphene Monolyayer on Cu Substrate

3-Raman on Highly Oriented Pyrolytic Graphite
highly-pure -laminar and ordered graphite artificially synthesized
Standard substrate for different Scanning Probe Microscopes (STM, etc…)