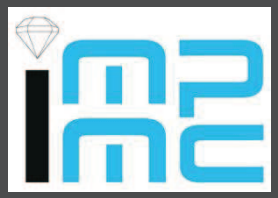
Applications of Raman spectroscopy to the study of graphitic carbons in the Earth sciences

The Raman spectrum of graphitic carbons: Theory

Characterizing graphitic carbons by Raman spectroscopy: Methodology



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Beyssac & Lazzeri EMU Notes in Mineralogy 2012

Graphitic carbons are

amorphous-like or turbostratic or microcrystalline or Monocrystalline…

opaque (high extinction coefficient for visible light)
=> Low penetration of laser, <200 nm (Lespade et al. 1984)

anisotropic (increasing anisotropy with graphitization)
=> Possible effect of sample orientation vs laser polarization

fragile (easily cleaved along the graphene layers)

heterogeneous (in terms of structure and chemistry)

Chemical and structural evolution of carbonaceous material during burial

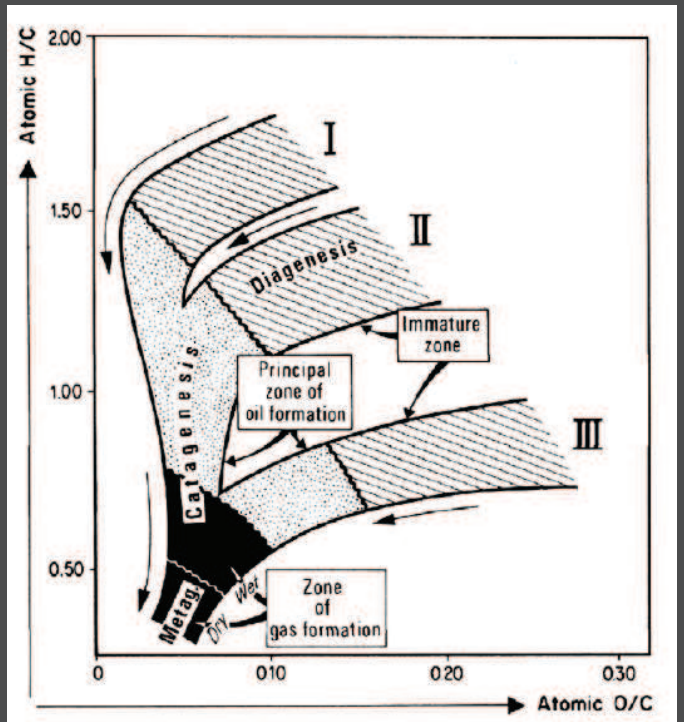


Fig. 32. General scheme of kerogen evolution from diagenesis to metagenesis in the van Krevelen diagram. Modified from Tissot and Welte (1978, p. 186).

Review by
Vandenbroucke & Largeau,
Organic Geochemistry (2007)

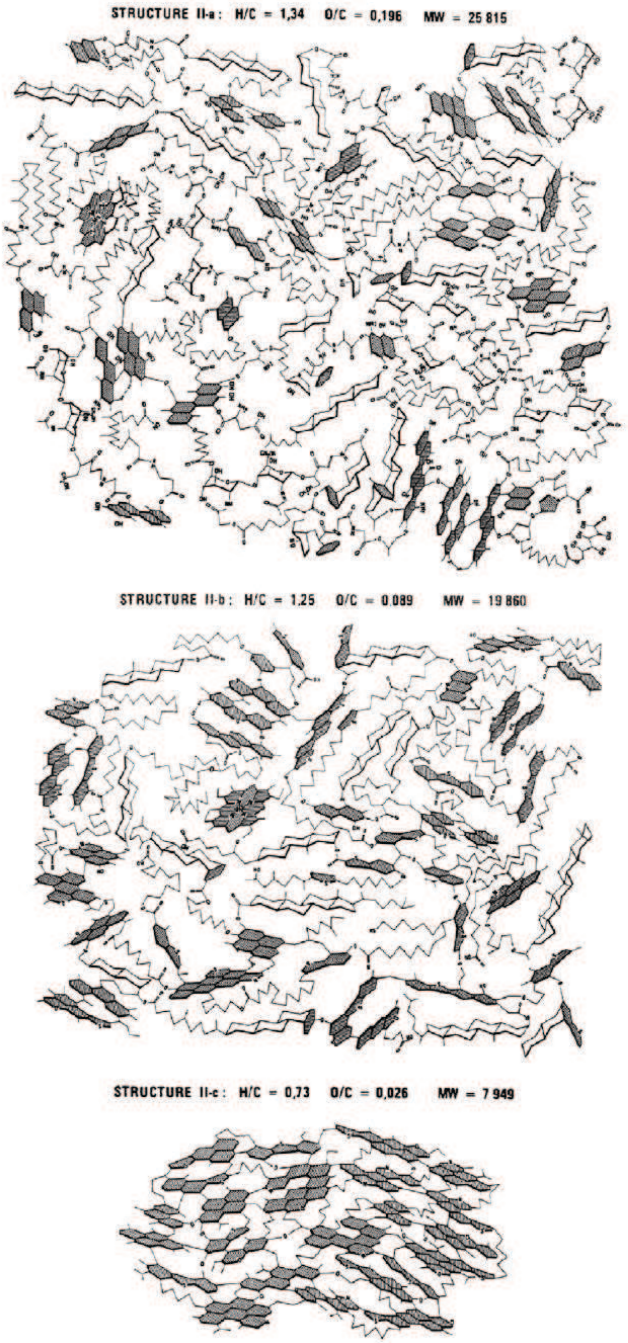


Fig. 57. Structural representation of Type II kerogen (analytical data from Paris Basin Toarcian series) at increasing maturity stages, corresponding to given atomic H/C and O/C ratios. Structure IIa: beginning of diagenesis; structure IIb: beginning of catagenesis; structure IIc: end of catagenesis. Adapted from Behar and Vandenbroucke (1987).

Quantifying the degree of graphitization

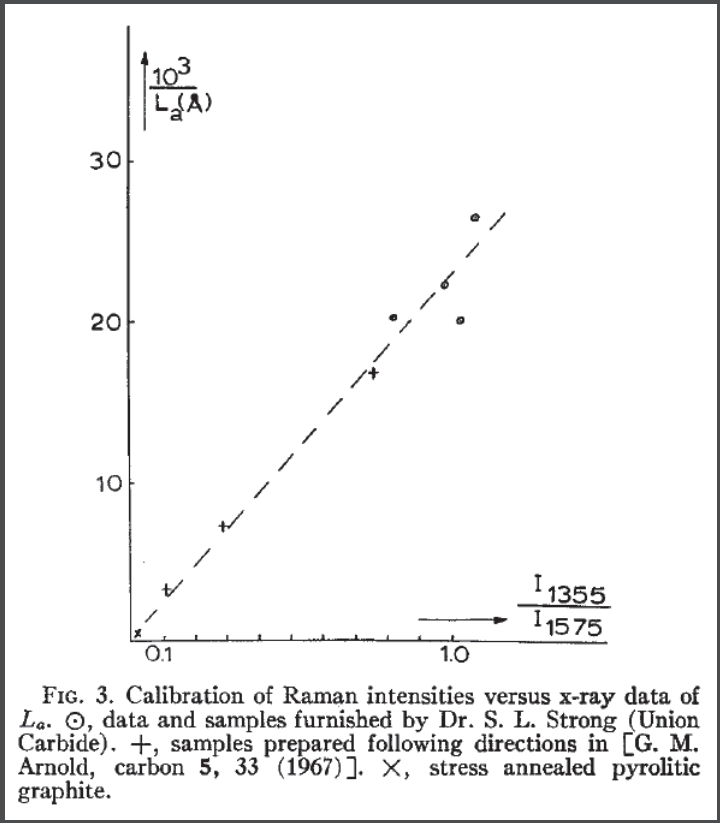
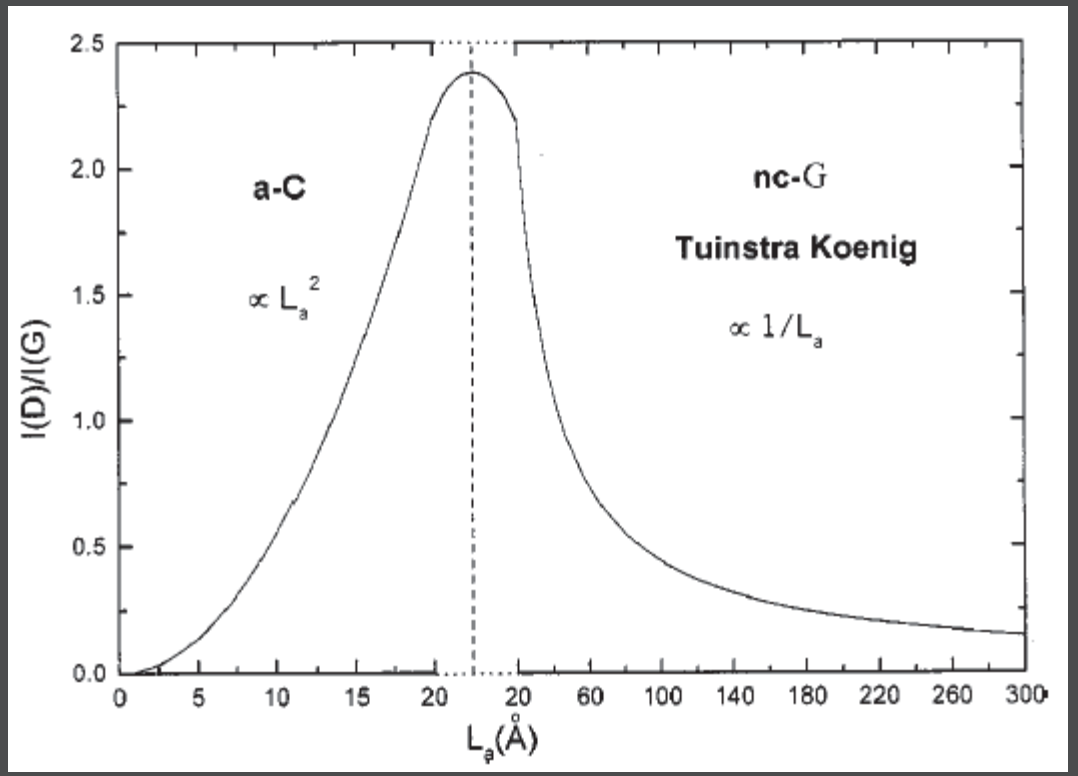
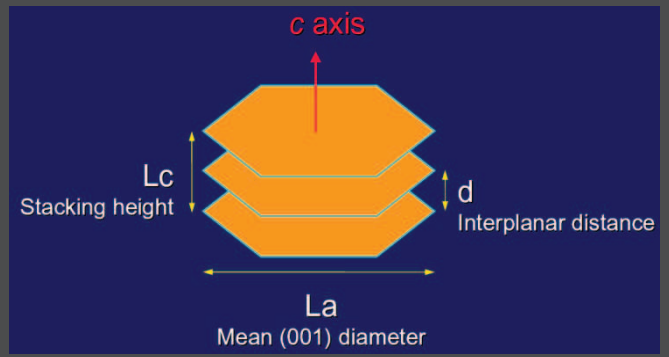


FIG. 3. Calibration of Raman intensities versus x-ray data of L_a. ⊙, data and samples furnished by Dr. S. L. Strong (Union Carbide). +, samples prepared following directions in [G. M. Arnold, carbon **5**, 33 (1967)]. ×, stress annealed pyrolitic graphite.

Tuinstra & Koenig, *J. Chem. Phys.*, 1970



Ferrari and Robertson, *Phys. Rev. B*, 2000



$$\frac{I(D)}{I(G)} = C'(\lambda) L_a^2.$$

$$\frac{I(D)}{I(G)} = \frac{C(\lambda)}{L_a},$$

For a review: Beyssac & Lazzeri EMU Notes in Mineralogy 2012

Protocol for Raman analysis of graphitic carbon materials

Raman spectroscopy is a surface analysis for graphitic carbons

Dispersivity of the defect bands => constant laser λ (514.5 nm)

Laser-induced heating => low-laser power (<0.5mW @ 514.5 nm)

Sample orientation versus laser polarization => not a problem except for graphite monocrystals

Structural defects induced by sample preparation (e.g. polishing) => analysis below a transparent mineral within the thin-section thickness

Intrinsic structural heterogeneity of natural graphitic carbons => to be documented

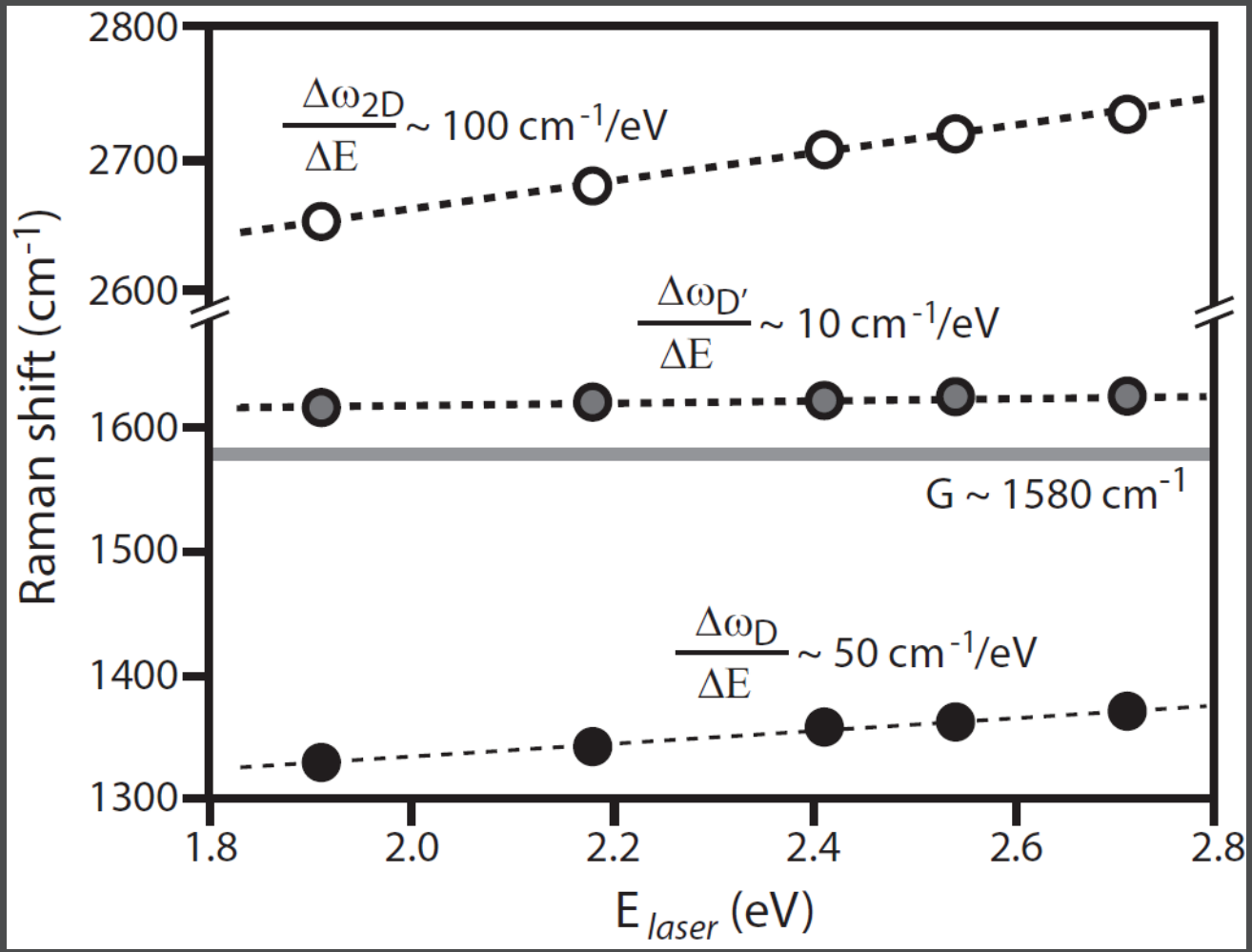
Extracting quantitative information from the Raman spectra => Peak fitting

…

See Beyssac & Lazzeri, EMU Notes in Mineralogy and references therein

Dispersivity of the defect bands: practical consequences

position and relative intensities=f(λ_{laser})



From Pimenta et al. (2007)

Dispersivity of the defect bands: practical consequences

position and relative intensities=f(λ_{laser})

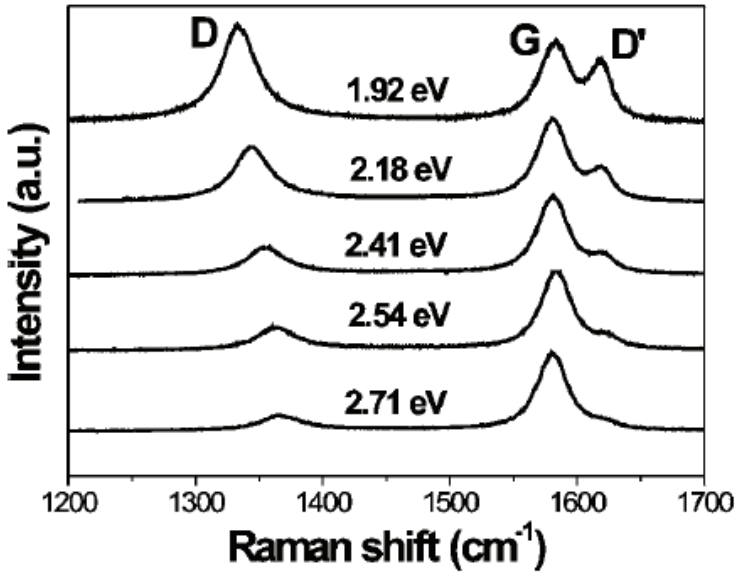


FIG. 2. (Color online) Raman spectra of the sample heat treated at 2000 °C, for five different laser energy values (1.92, 2.18, 2.41, 2.54, and 2.71 eV).

Spectra to be compared MUST be obtained at the very same laser wavelength

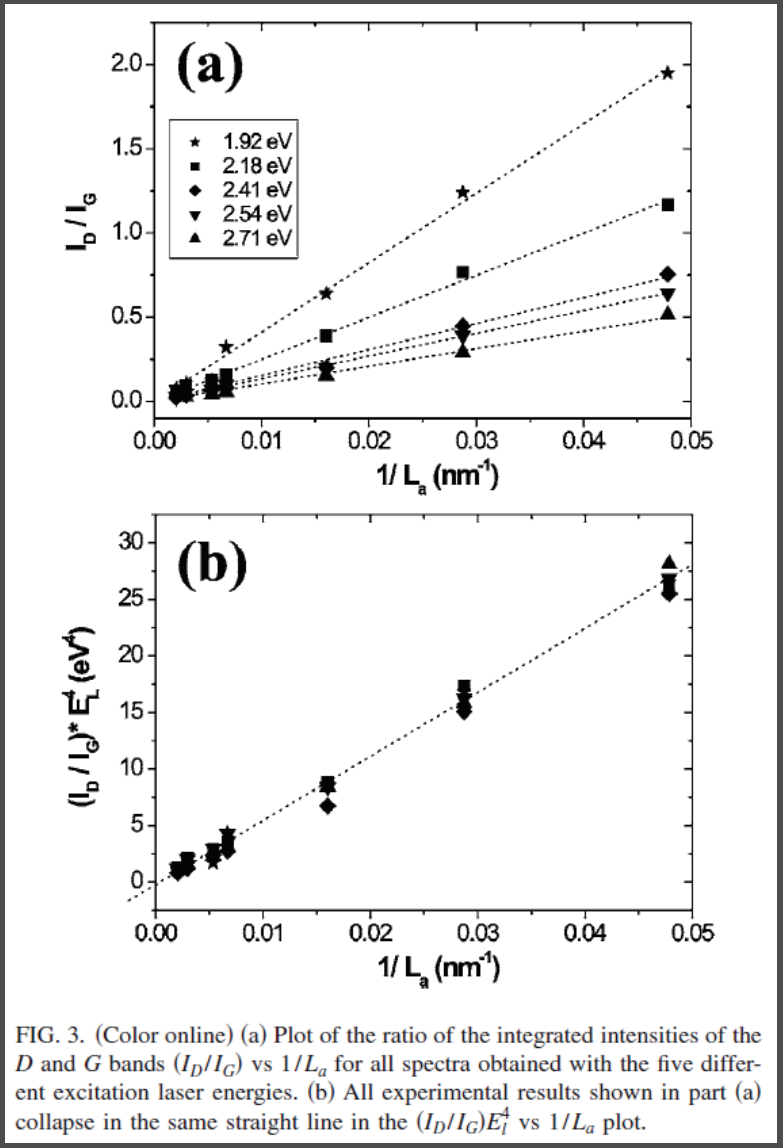
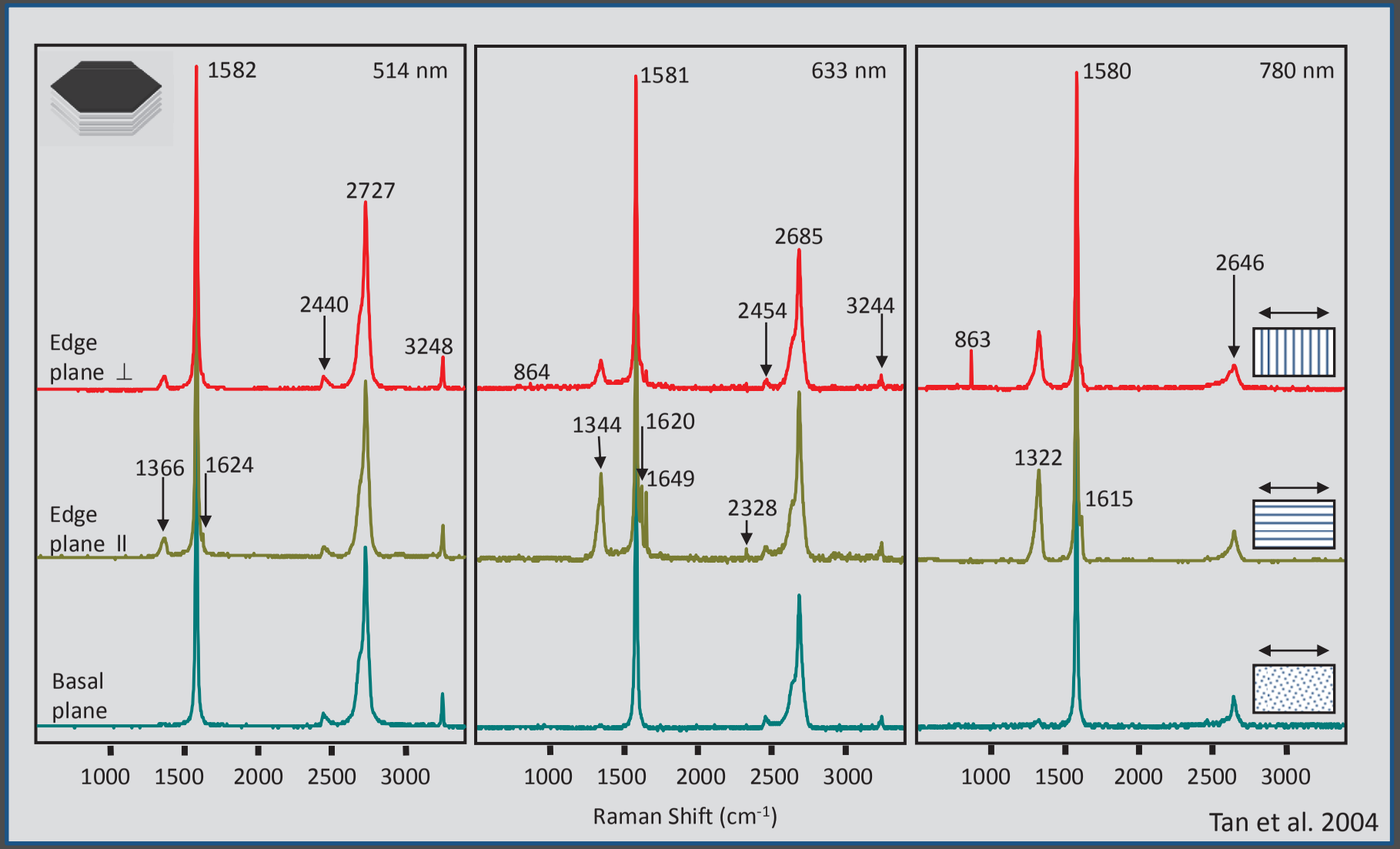


FIG. 3. (Color online) (a) Plot of the ratio of the integrated intensities of the D and G bands (I_D/I_G) vs $1/L_a$ for all spectra obtained with the five different excitation laser energies. (b) All experimental results shown in part (a) collapse in the same straight line in the $(I_D/I_G)E_l^4$ vs $1/L_a$ plot.

Cancado et al. (Applied Physics Letters 2006)

Sample orientation versus laser polarization

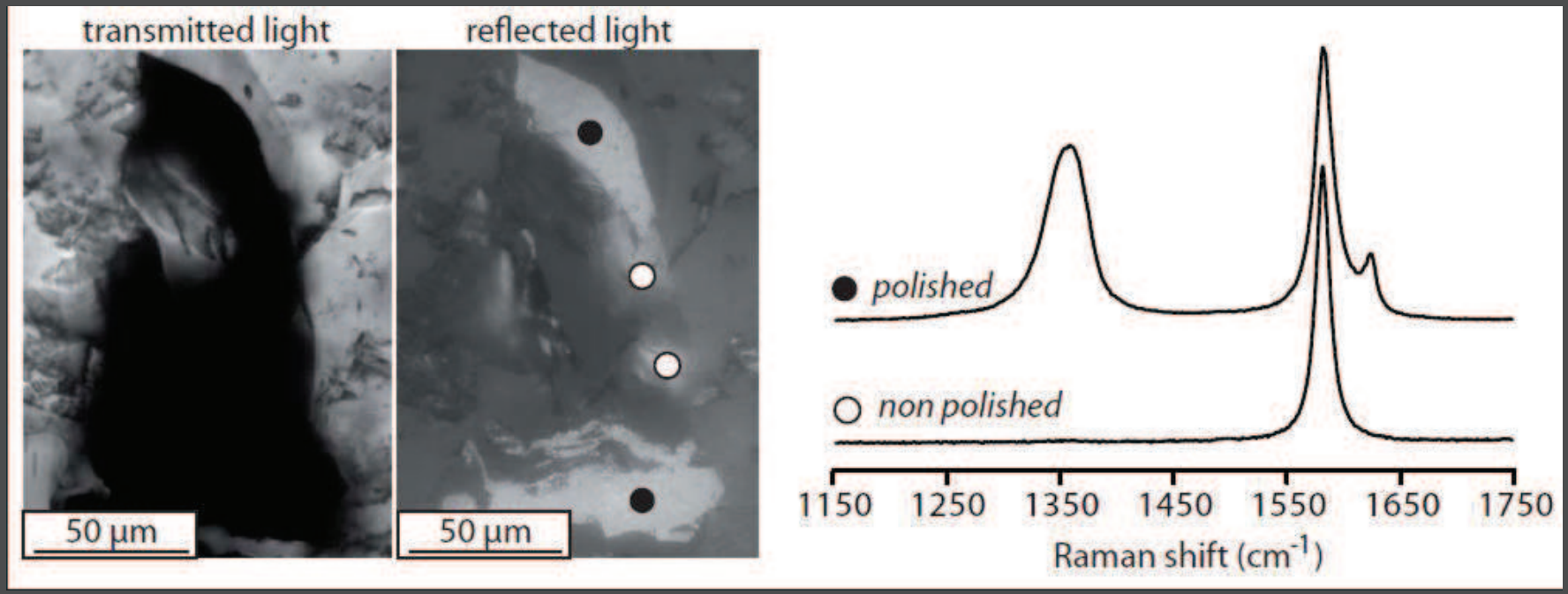


No significant effect @ 514 nm for graphitic C / microcrystalline graphite

For graphite monocrystal, use a circular polarization for the laser and measure same orientation

Structural defect induced by sample preparation (polishing, crushing, chemistry…)

Graphitic carbons are black, opaque materials, and as such have a high extinction coefficient for visible light. The direct consequence is that, in the visible range, the penetration of the laser in graphitic carbons is very low. Using C films with a well constrained thickness deposited by chemical vapor deposition on a corundum substrate, Lespade *et al.* (1984) estimated the argon laser (2.41eV, 514 nm) penetration depth at about 100-200 nm.



e.g. Pasteris (Applied Spectroscopy 1989), Beyssac et al. (2003)

Structural defect induced by sample preparation (polishing, crushing, chemistry…)

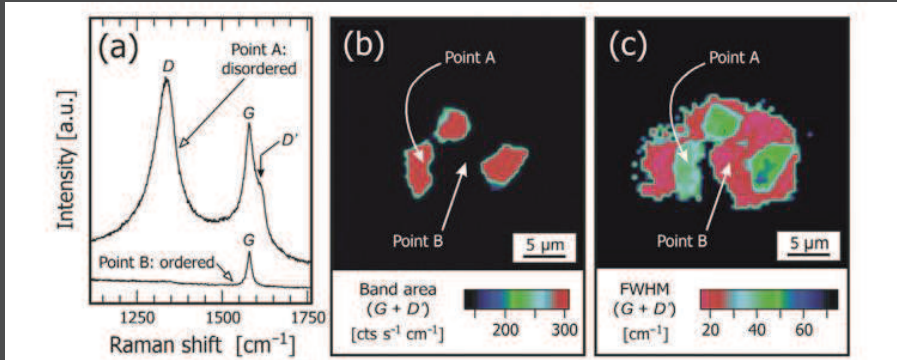
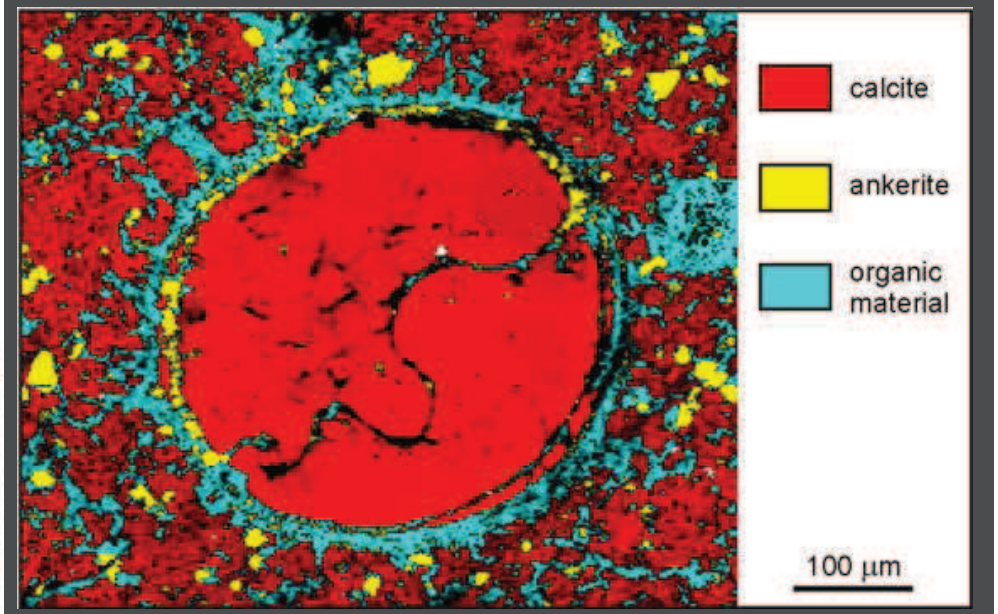
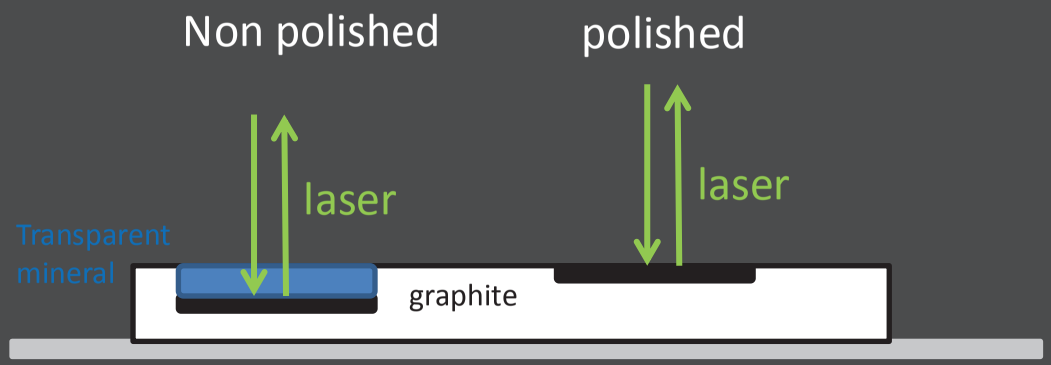


Fig. 19. Raman maps of a graphite flake in a metacarbonate (sample no. AL8-1; courtesy of A. Lepland) from the 3.8 Ga Isua Supracrustal Belt, Greenland, showing that graphite disorder can be induced by the polishing process. ***(a)*** The two Raman spectra show that graphite that has been exposed to the surface of the thin section is disordered (spectrum A) whereas the main graphite flake, analysed through a thin chlorite cover, appears well-ordered (spectrum B). ***(b)*** A Raman map of the surface, generated from the integral intensity of the band at ~ 1600 cm^{-1}, shows three micro-areas in which graphite is exposed at the surface. This map corresponds widely to an optical microphotograph taken in the reflected light mode (not shown). ***(c)*** A Raman map, recorded with the focus of the fully focused beam adjusted ~ 2 µm below the surface and generated from the broadening of the ~ 1600 cm^{-1} band, shows that only the three exposed areas have experienced structural disorder (large FWHMs) as a result of the mechanical polishing process. Surrounding micro-areas that are still covered by chlorite are well ordered (smaller FWHMs).

Nasdala et al. (EMU notes 2004)



Bernard et al. (EPSL 2007)



Analysis below a transparent mineral within the thin-section thickness

⇒ No structural mapping on polished sample.

Laser-induced heating

Photo-oxydation of graphitic C under the laser in air

Downshifting of G and D position

⇒ Must use low-laser energy (< 0.5mW @ 514.5 nm)

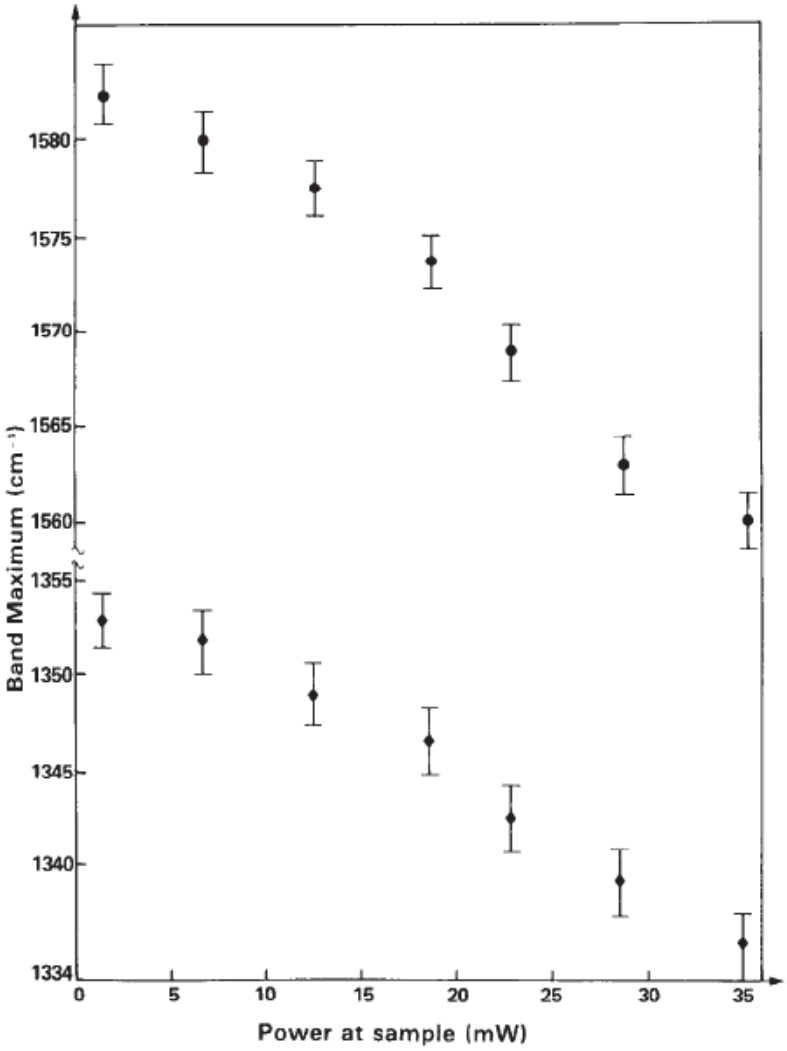
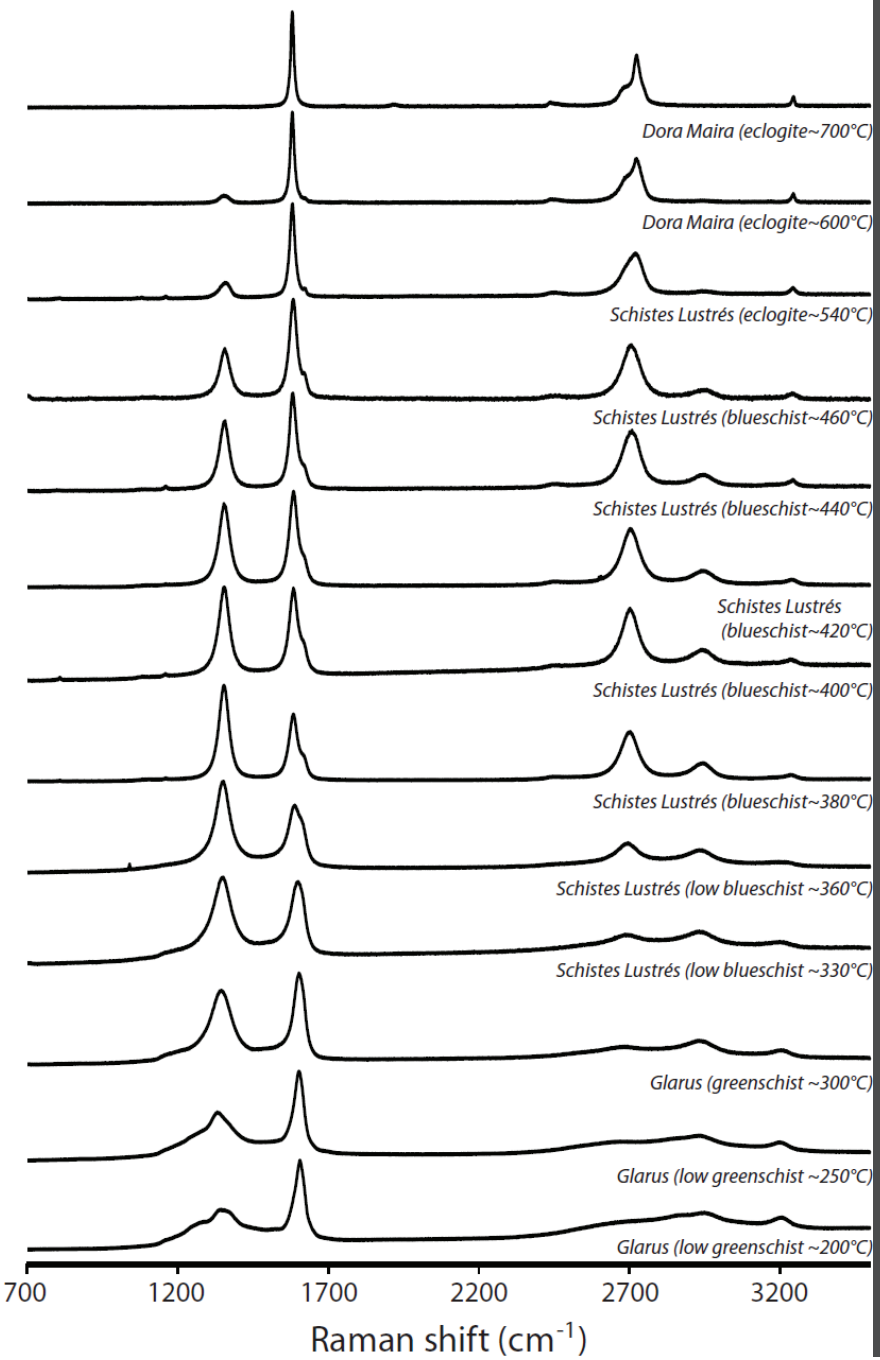


Fig. 3. E_{2g} (upper curve) and (lower curve) A_{1g} band positions for a single HMS4 carbon fibre as a function of incident laser beam power. A ×50 objective gave ~5 μm laser spot size at sample. Note the sensitivity of the band positions to the laser power.

Everall et al. (Carbon 1991)



Raman spectroscopy of graphitic carbons

1st and 2nd order

G band vs. Defect bands

Double-resonnance Raman theory for the defect Bands (Thomsen & Reich 2000; see Beyssac & Lazzeri EMU notes in Mineralogy for a review)

Frequency (cm^{-1})	Peak designation	Other peak designation	Raman process [1]	Remarks
1100	D''		D1P	Graphene – Martins Fereira *et al.* (2010)
1200		D4		Soots – Sadezky *et al.* (2005)
				Natural carbons – Lahfid *et al.* (2010)
1350	D	D1	D1P	
1500	(D''+D[4])	D3	(D2P)	Soots, amorphous carbons – Sadezky *et al.* (2005)
1580	G	G	1P E_{2g}	
1620	D'	D2	D1P	
2450	D+D''		2P	
2700	2D	S1	2P	
2950	D+D' / D+G	S2	D2P	
3240	2D'		2P	
3260	G+D'		D2P	Graphene – Martins Fereira *et al.* (2010)

[1] Raman process is one-phonon (1P), two-phonons (2P), defect-activated one-phonon (D1P), defect-activated two-phonons (D2P).

Beyssac & Lazzeri EMU Notes 2012

Raman versus XRD (tracking 3D ordering)

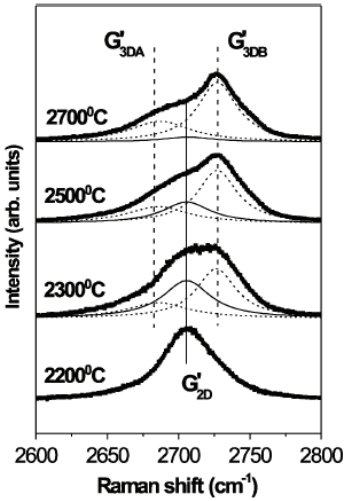


Fig. 16 G' band Raman spectra of samples heat treated to various temperatures T_{htt}, performed using E_{laser} = 2.41 eV (514.5 nm). The G' band changes from one peak to two peaks with increasing T_{htt}.[14]

Pimenta et al. (2007)

Spliting of the 2D band indicates
Local 3D ABAB stacking

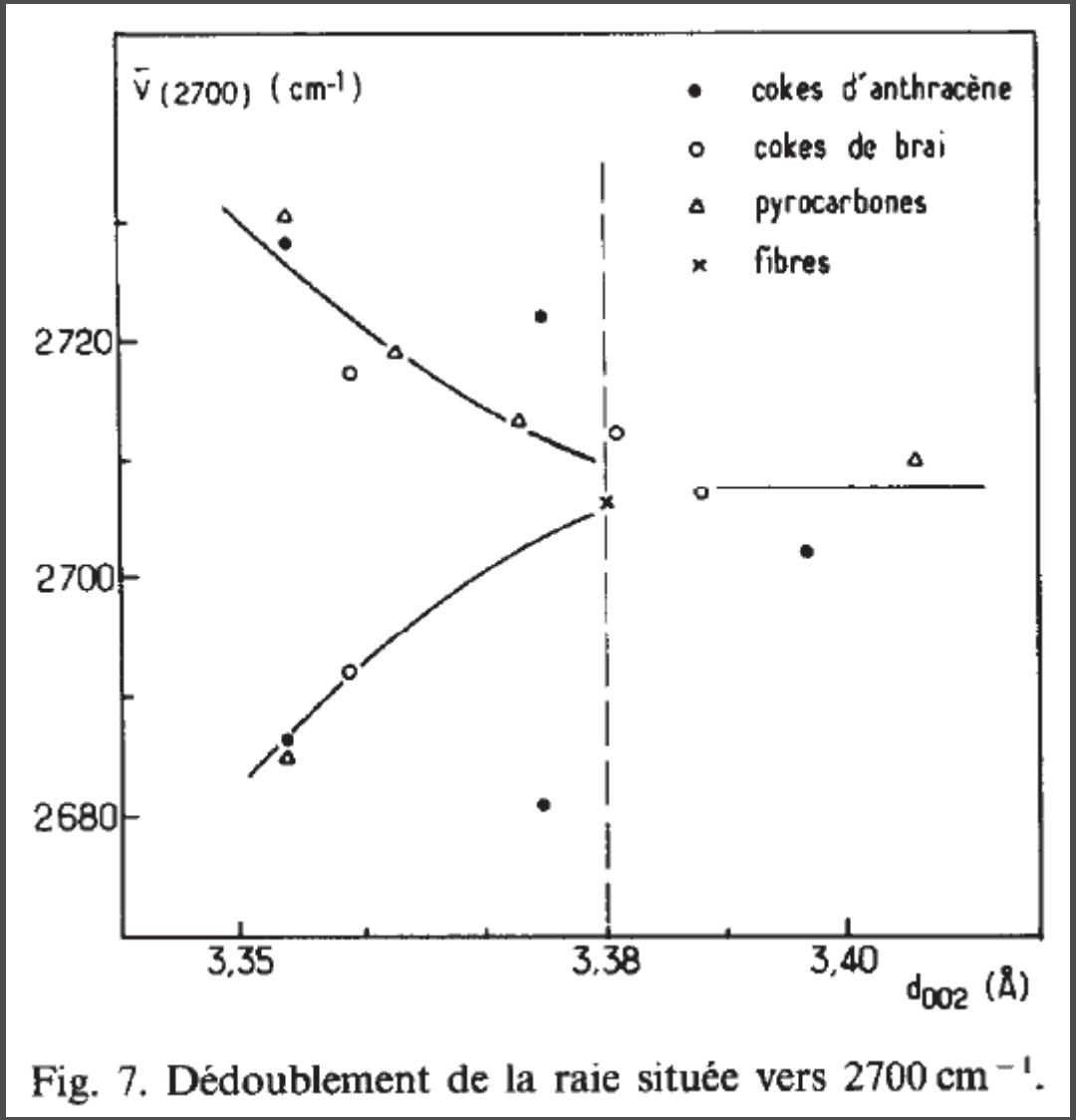
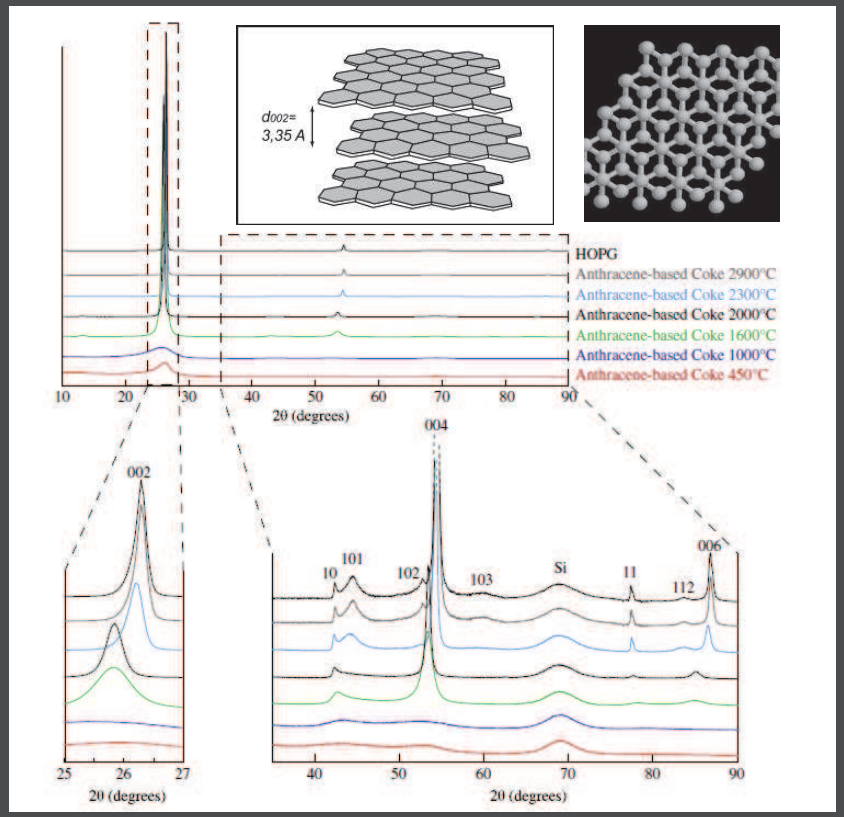
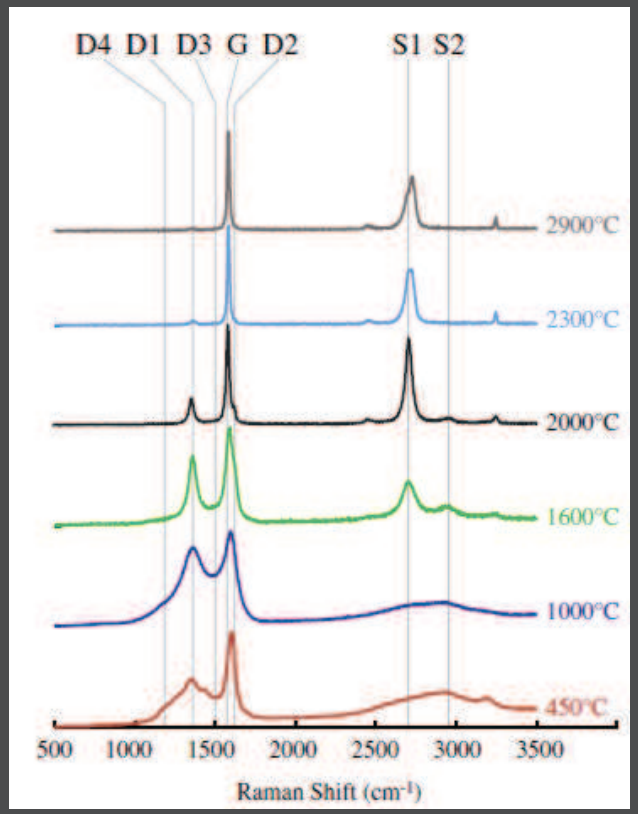


Fig. 7. Dédoublement de la raie située vers 2700 cm^{-1}.

Lespade et al. (Carbon 1984)

Raman versus XRD (tracking 3D ordering)





Bernard et al. (Carbon 2010)

	XRD	HRTEM	Raman
Sample preparation	destructive: bulk separates	destructive: bulk separates	nondestructive: in situ in thin sections or rock powders
Size of sample	bulk technique	hundreds of ångströms	μm^3
Scale	macro	micro	mini
Crystallite dimension measured	d (L_c, L_a)	d, L_c, L_a	L_a (L_c)
Information about crystallite size	indirect	direct	indirect
Analysis time	slow because of required sample preparation	very slow because of scale and complexity of analysis	relatively fast because of minimal sample preparation and scale of analysis

+ STXM-XANES
At the C k-edge

Wopenka & Pasteris (Am Min 1993)

Fitting spectra of graphitic carbons

Bonal et al. (GCA 2006)

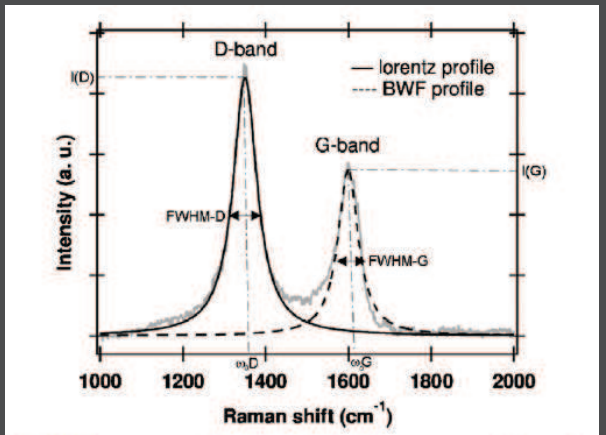


Fig. 1. Raman spectra of a polyaromatic carbonaceous material, intensity in arbitrary unit (a.u.). The D-band was fitted by a Lorenztian profile and the G-band by a Breit-Wigner-Fano profile to obtain the spectral parameters FWHM-D, FWHM-G, I_D, I_G, ω_0D, ω_0G.

Sadezky et al., *Carbon*, 2005

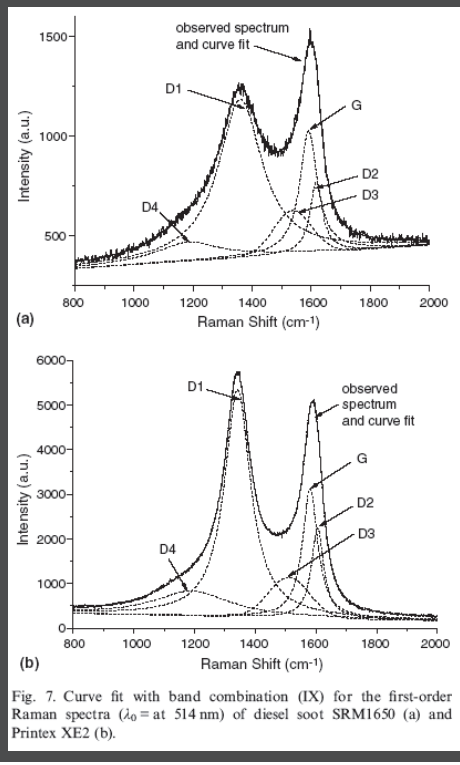


Fig. 7. Curve fit with band combination (IX) for the first-order Raman spectra (λ_0 = at 514 nm) of diesel soot SRM1650 (a) and Printex XE2 (b).

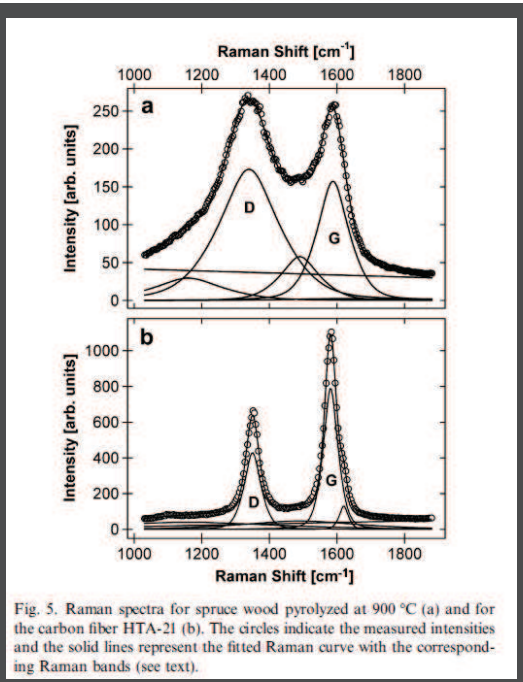
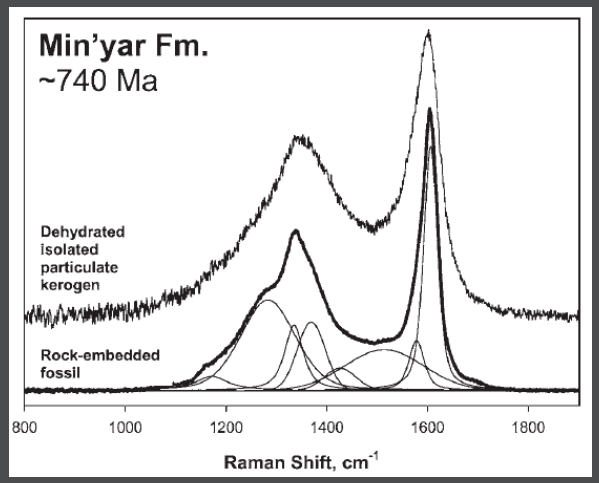


Fig. 5. Raman spectra for spruce wood pyrolyzed at 900 °C (a) and for the carbon fiber HTA-21 (b). The circles indicate the measured intensities and the solid lines represent the fitted Raman curve with the corresponding Raman bands (see text).



Zickler et al. (Carbon 2006)

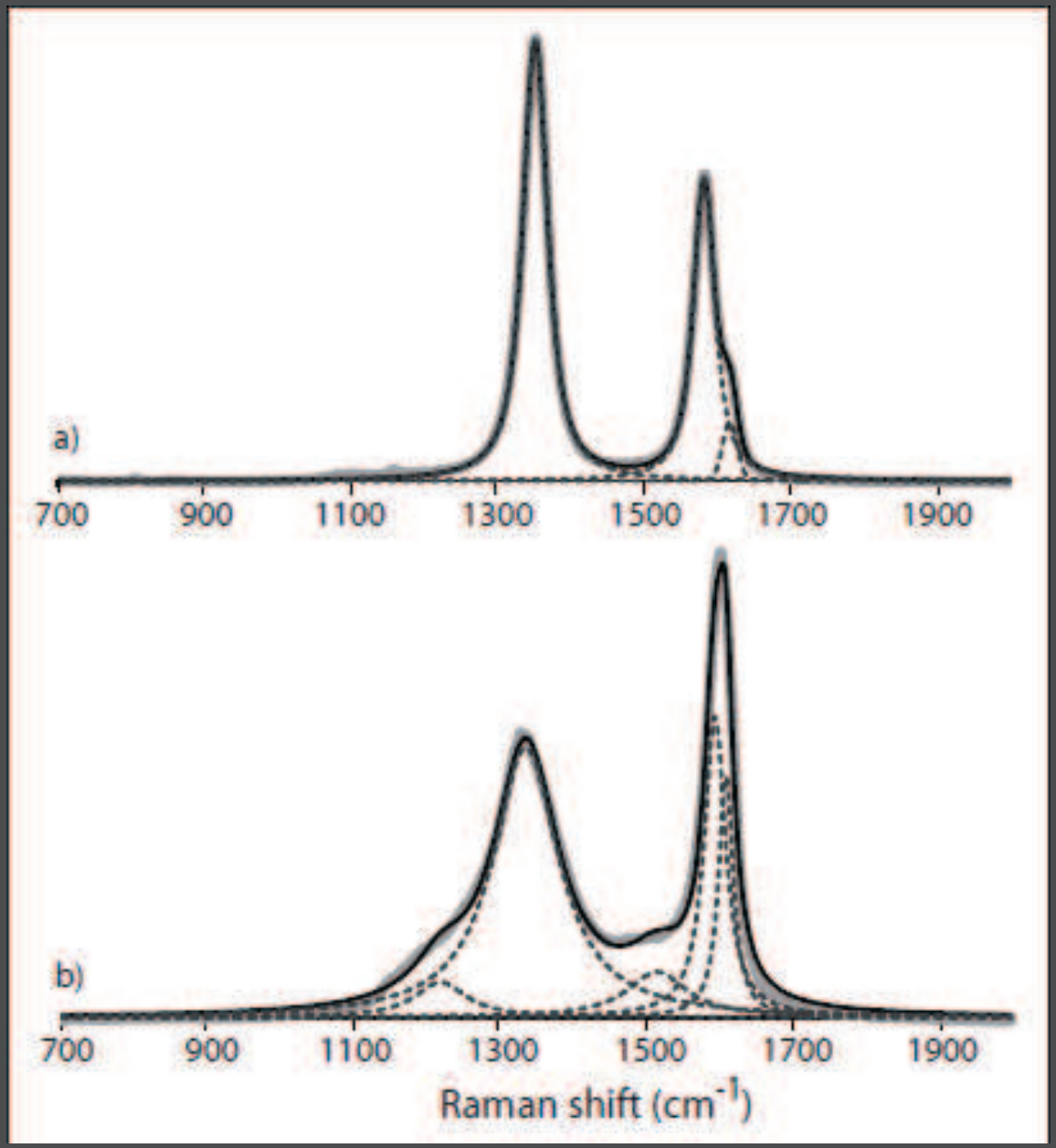
Schopf et al. (Astrobiology 2005)

Fiting spectra of graphitic carbons

Examples of peak-fitting procedures for Raman spectra of graphitic carbons. a) Peak-fitting in case of a very disordered graphitic carbon using 5 bands with pure Lorentzian shape. b) Peak-fitting in case of a graphitic carbon using 3 bands with Voigt profile (mix Gaussian-Lorentzian). Note that in all cases no *a priori restriction is* imposed on the band position, FWHM or intensity. Thick grey line is the measured spectrum, black line is the modeled spectrum, grey dashed lines are the peaks modeled.

Extraction of quantitative parameters (FWHM, position, aatios…)

Caution with I_D / I_G ratio



Beyssac et al. 2003; Beyssac & Lazzeri 2012

The Raman spectrum of graphite: theory

Michele Lazzeri

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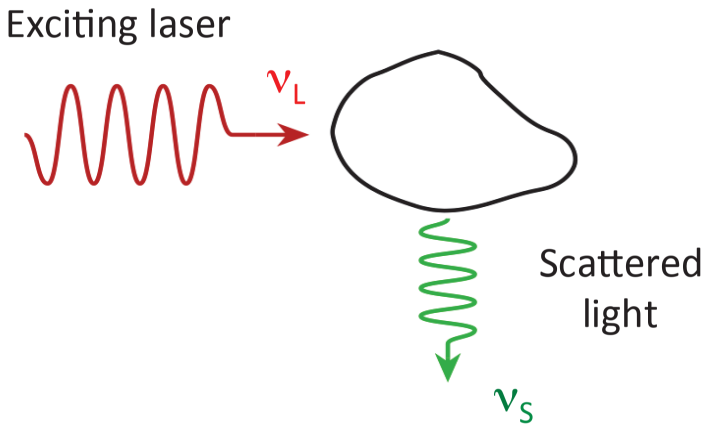
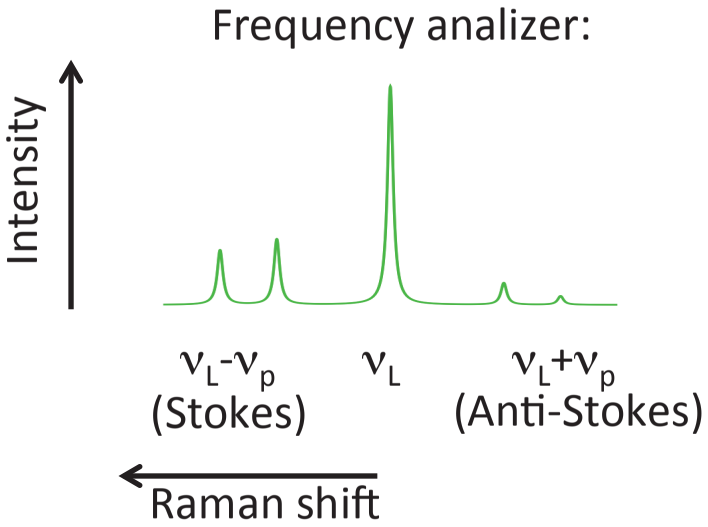
Graphite: model for sp2 carbons
Present unique features (theoretical understanding not easy)
Very well studied

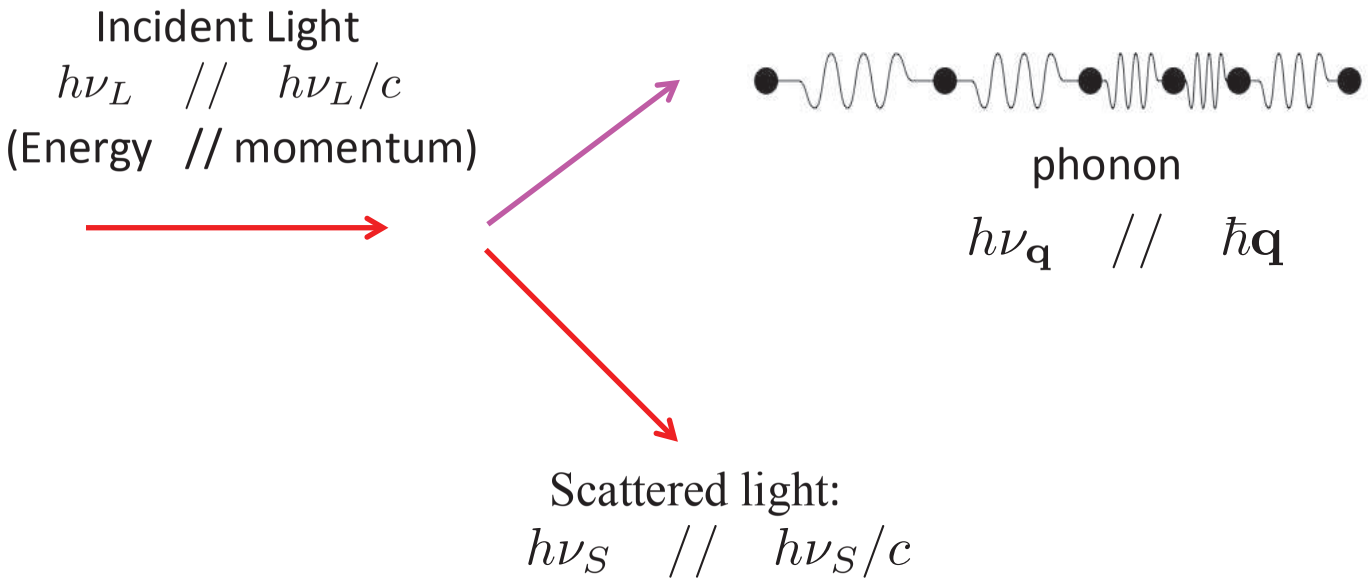
Here: introduction to the Double Resonance

Raman scattering





Vibrational Raman



c: Speed of light
h: Planck constant
$\hbar = h/(2\pi)$

Perfect crystal:
Energy + momentum conservation

$$\nu_L = \nu_S + \nu_{\mathbf{q}}$$
$$h\nu_L/c = h\nu_S/c + \hbar\mathbf{q}$$

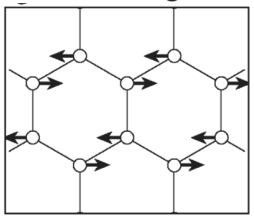
$$q = \nu_{\mathbf{q}}/c \simeq 0$$

Most intense processes: one-phonon excitation **q=0**

Other possible processes:
- Two-phonon excitation **–q, q** (**q≠0**)
- Defect-activated one-phonon (**q≠0**)

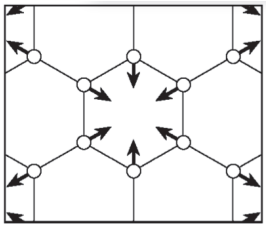
Graphite Raman spectra

Γ E_{2g}



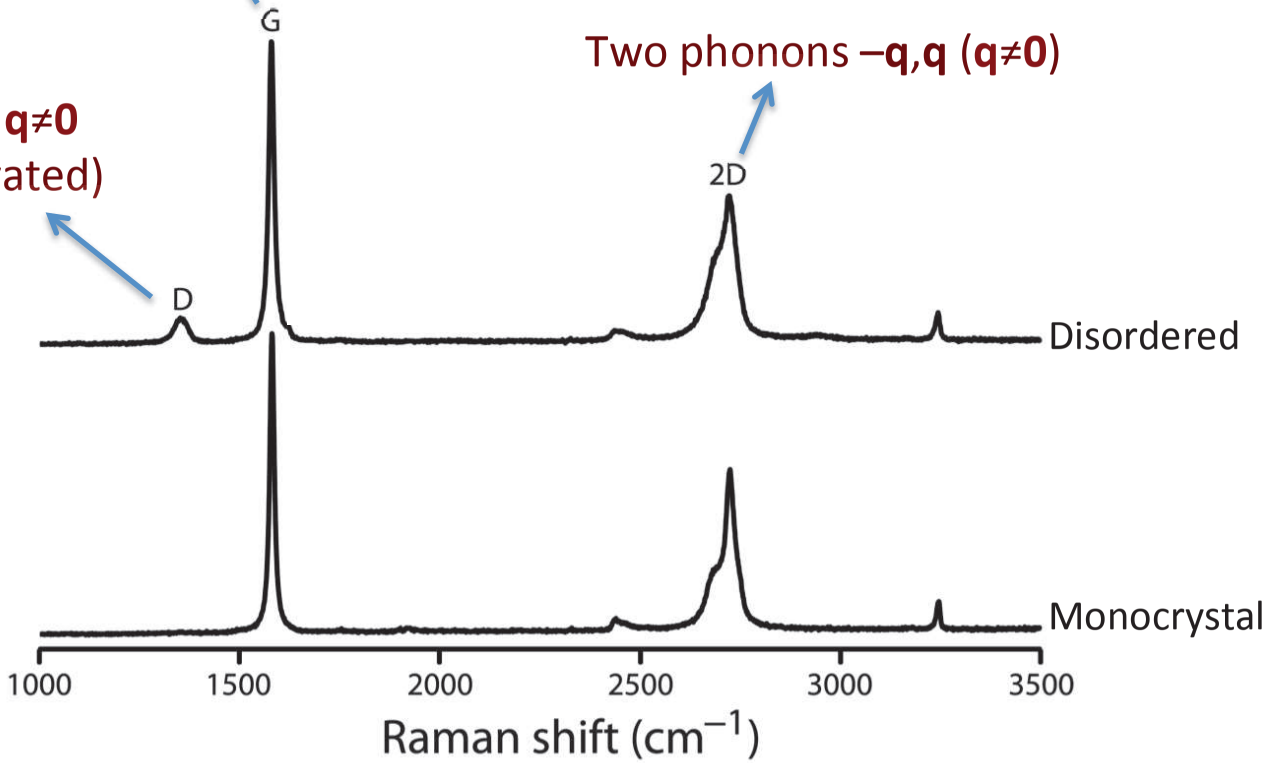
one phonon **q=0**

K A'_1



one phonon **q≠0**
(defect-activated)

Two phonons **–q,q** (**q≠0**)



G: « First-order » Raman

D/2D: Double resonance

Why are the D/2D peaks so unique?

Anomalously high intensity
Narrow peak, with well defined shape
Frequency depends on the laser energy

Double resonance
(Thomsen & Reich PRL 2000)

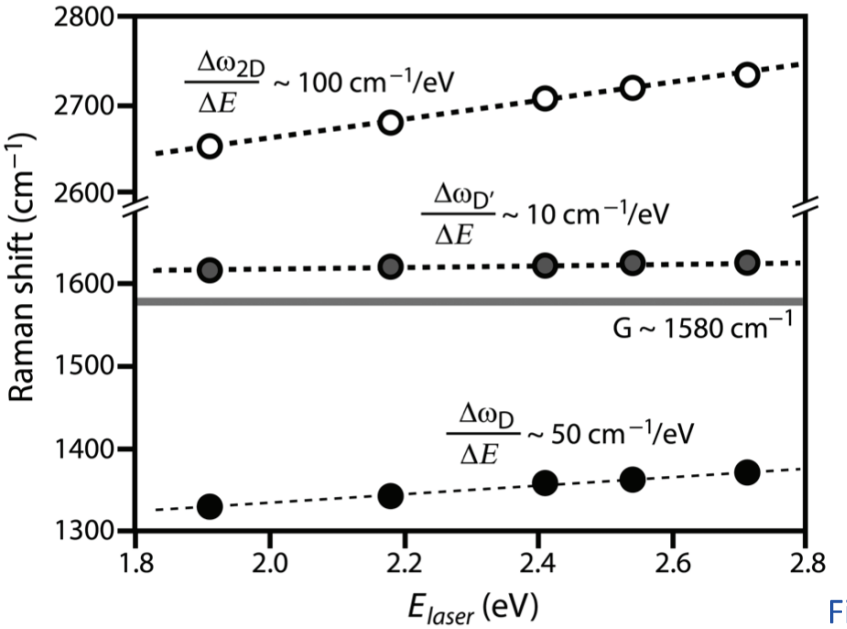


Fig. from Pimenta et al. PCCP (2007)

Quantum mechanics: basic concepts

$|a\rangle$: state of the system
ϵ_a : energy

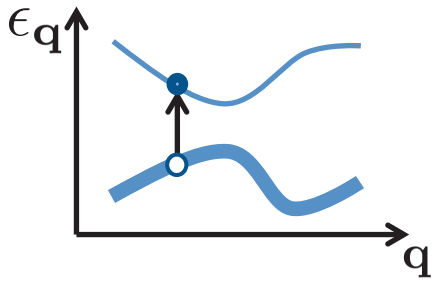
Ground state → excitations

Elementary excitations in a solid

- -light  $h\nu_L$ // $h\nu_L/c$
- -phononic  $h\nu_{\mathbf{q}}$ // $\hbar\mathbf{q}$
- -electronic

(Energy // momentum)

What is an electronic excitation?



$\varepsilon_{\mathbf{q}}$: Band structure (the energies an electron is allowed to have)
Ground state: lowest bands are occupied
highest bands are empty
Excitation: creation of an electron/hole pair
Vertical transition →zero momentum

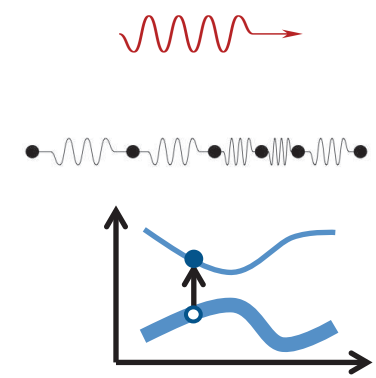
Quantum mechanics: basic concepts

$|a\rangle$: state of the system
ϵ_a : energy

Ground state → excitations

Elementary excitations in a solid

- -light
- -phononic
- -electronic



$h\nu_L \quad // \quad h\nu_L/c$

$h\nu_{\mathbf{q}} \quad // \quad \hbar\mathbf{q}$

$$|a\rangle = |\nu_L\rangle \bigotimes |ph\rangle \bigotimes |el\rangle$$

Raman: $|i\rangle = |\nu_L\rangle \bigotimes |G\rangle \bigotimes |G\rangle \quad \rightarrow \quad |f\rangle = |\nu_S\rangle \bigotimes |\nu_p\rangle \bigotimes |G\rangle$

Perturbation theory (1st order)

V Interaction potential → P_{if} (Transition probability)

(e.g.: electron/light; electron/phonon; electron/defects)

Fermi Golden rule
(Basic assumption: V is small)

$$P_{if} = \frac{2\pi}{\hbar} |\langle iVf \rangle|^2 \delta(\epsilon_i - \epsilon_f)$$

$\langle fVi \rangle$ Complex number which quantifies the interaction between i and f (linear in V → 1st order)

$$\delta(\epsilon) = 0 \quad \text{for} \quad \epsilon \neq 0 \qquad \Rightarrow \qquad \epsilon_i = \epsilon_f$$ (conservation of energy)

Perturbation theory (3rd order)

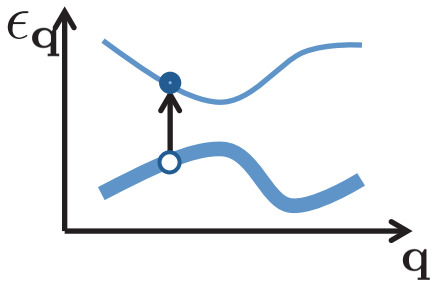
$$P_{if} = \frac{2\pi}{\hbar} \left| \sum_{a,b} \frac{\langle iVa\rangle\langle aVb\rangle\langle bVf\rangle}{(\epsilon_i - \epsilon_a - i\gamma)(\epsilon_i - \epsilon_b - i\gamma)} \right|^2 \delta(\epsilon_i - \epsilon_f)$$

$\sum_a$:Sum on all the possible excitations

γ :Small real number

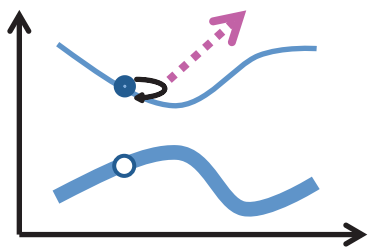
Raman scattering (one **q**=**0** phonon)
3 consecutive « virtual transitions »:

$i \rightarrow a$



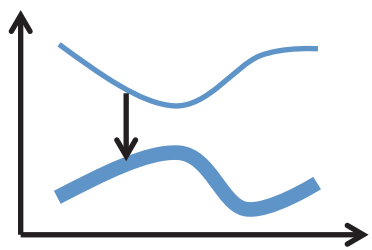
Light absorption
(electron/hole creation)

$a \rightarrow b$



Electron/phonon scattering
(phonon excitation)

$b \rightarrow f$



Light emission
(electron/hole recombination)

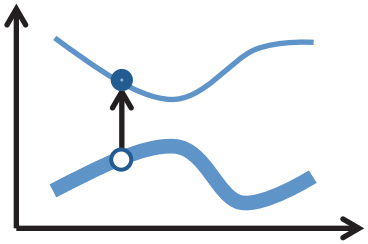
WARNING: In literature this is called « first-order » Raman

Perturbation theory (4th order)

$$P_{if} = \frac{2\pi}{\hbar} \left| \sum_{a,b,c} \frac{\langle iVa\rangle\langle aVb\rangle\langle bVc\rangle\langle cVf\rangle}{(\epsilon_i - \epsilon_a - i\gamma)(\epsilon_i - \epsilon_b - i\gamma)(\epsilon_i - \epsilon_c - i\gamma)} \right|^2 \delta(\epsilon_i - \epsilon_f)$$

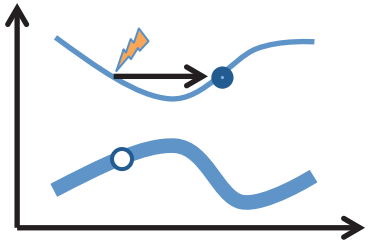
Raman scattering (one **q≠0** phonon, defect activated)
4 « virtual transitions »:

$i \rightarrow a$



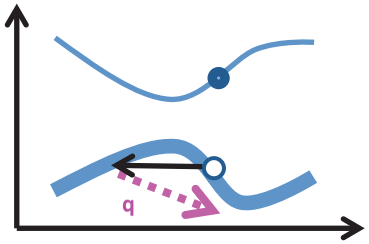
Light absorption

$a \rightarrow b$



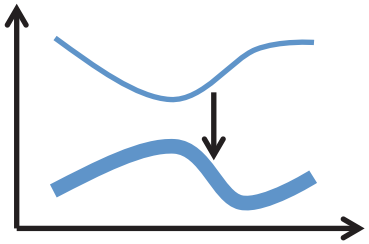
Defect scattering

$b \rightarrow c$



Electr/phon scattering

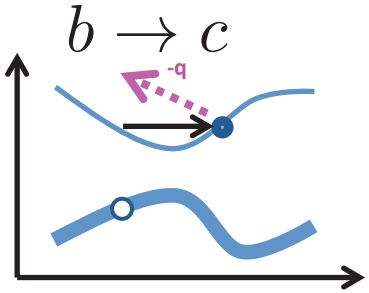
$c \rightarrow f$



Light emission

Two phonons -q,q:

$b \rightarrow c$



Electron/phonon scattering

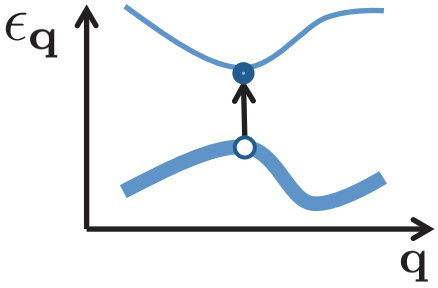
Partial summary:

Perturbation theory (standard textbook tool):
3rd order → excitation of one **q**=**0** phonon
4th order → excitation of two-phonons
excitation of one **q**≠**0** phonon (defect-activated)

Why are the D/2D peaks so intense?
Why are they small-width well defined peaks?
Why do they disperse with the Laser energy?

Double resonance (Thomsen & Reich, PRL 2000)

Resonant Raman



E_g (electronic gap): minimum energy for electronic excitation

$E_g \neq 0$ → insulators/semiconductors

$E_g = 0$ → metals/semi-metals

Raman: $$P_{if} = \frac{2\pi}{\hbar} \left| \sum_{a,b} \frac{\langle iVa \rangle \langle aVb \rangle \langle bVf \rangle}{(\epsilon_i - \epsilon_a - i\gamma)(\epsilon_i - \epsilon_b - i\gamma)} \right|^2 \delta(\epsilon_i - \epsilon_f)$$

In the virtual transitions the energy is not necessarily conserved (*e.g.* ε_i can be ≠ ε_a)

When $\varepsilon_i \approx \varepsilon_a$ → « resonance »

$E_g >> h\nu_L$: Non-Resonant Raman

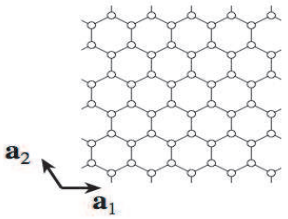
$E_g = 0$: Raman is always resonant

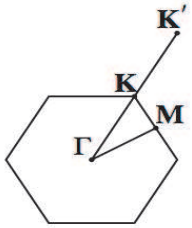
Graphite: $E_g = 0$ → Raman is always resonant (the physics is more complex)

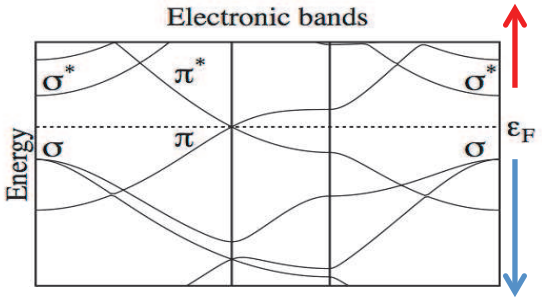
Graphite: band structure

Graphene/graphite: very similar band structure and very similar Raman spectra.

Grephene:



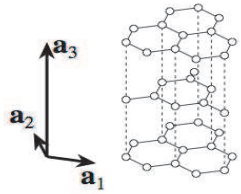


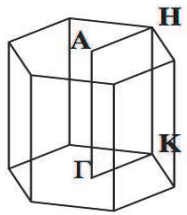


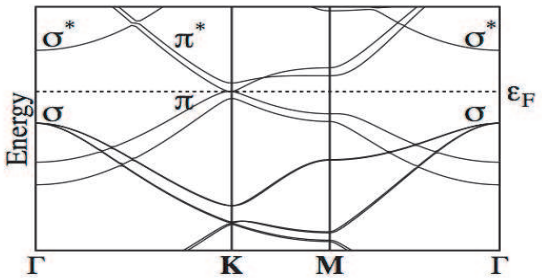
π* bands: lowest empty

π bands: highest occupied

Grephite:

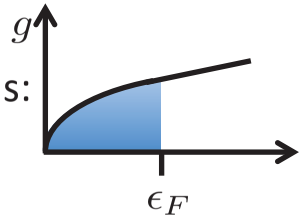




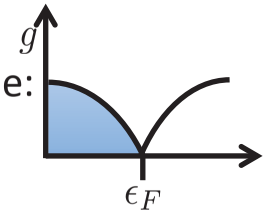


The « gap » is zero in only one point (**K**) of the Brillouin zone

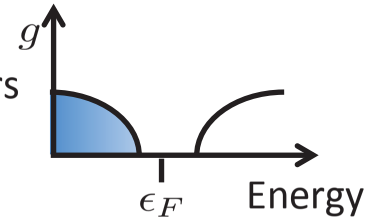
Metals:



Graphite/graphene: (semi-metals)



Semiconductors Insulators:



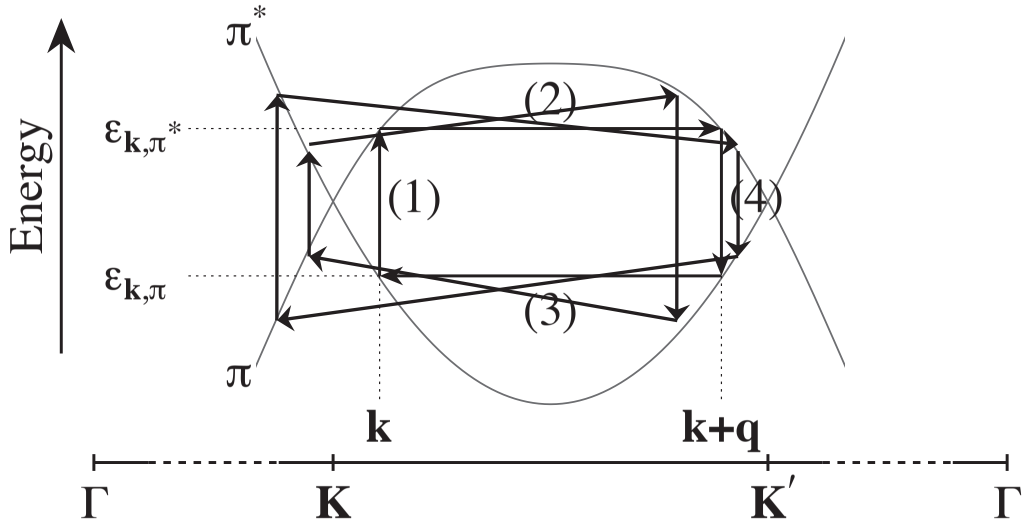
g = # of electronic states at a given energy

ε_F = Fermi level

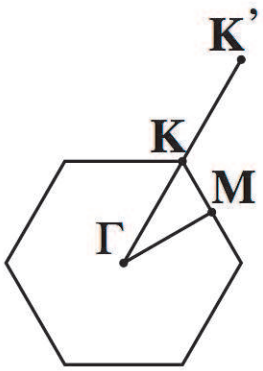
Double Resonance in graphite/graphene

D peak
(Defect-activated
4th order process)

(1) Light absorption
(2) Electron scattering with a defect
(3) Electron-phonon scattering
(4) Light emission



In principle: all the possible processes have to be considered



Double Resonance in graphite/graphene

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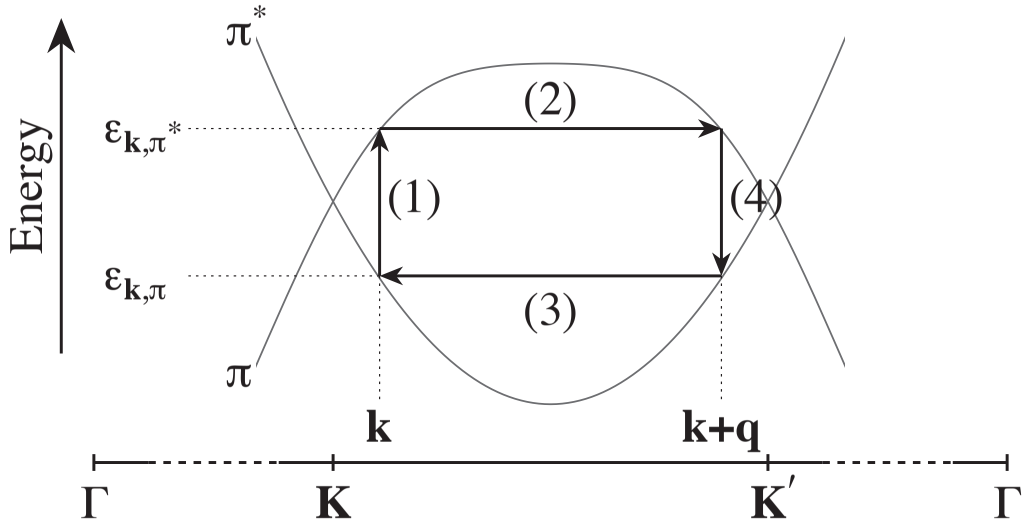
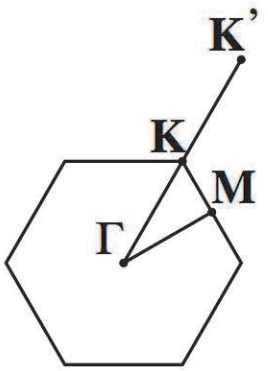


~~In general: all the possible processes have to be considered~~

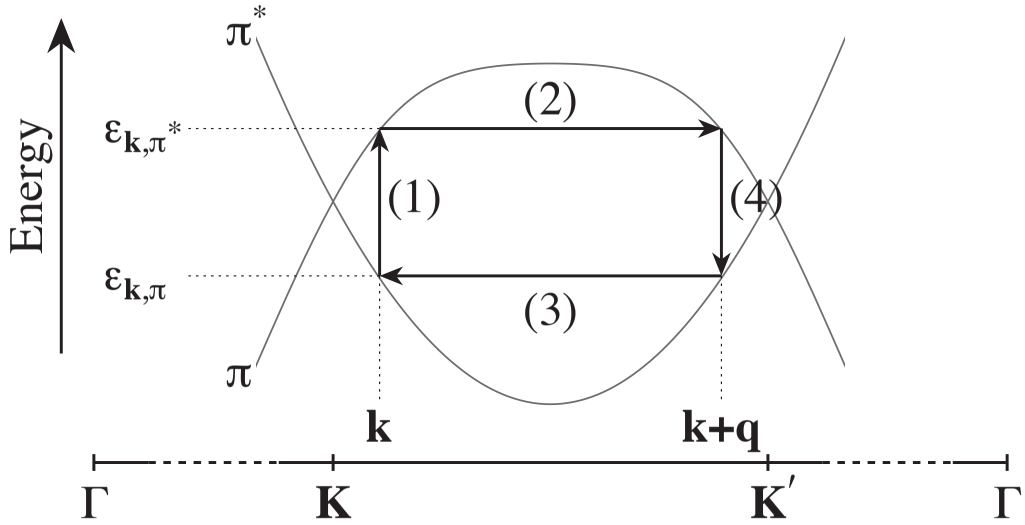
Thomsen & Reich (2000): The important processes take place only for certain values of k and q (selected by the conservation of energy in the virtual transitions)



Double Resonance in graphite/graphene

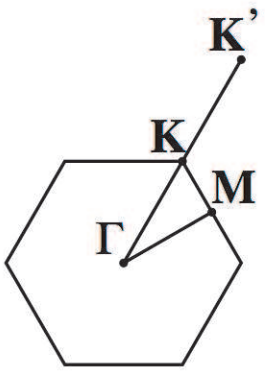
D peak
(Defect-activated
4th order process)

(1) Light absorption
(2) Electron scattering with a defect
(3) Electron-phonon scattering
(4) Light emission

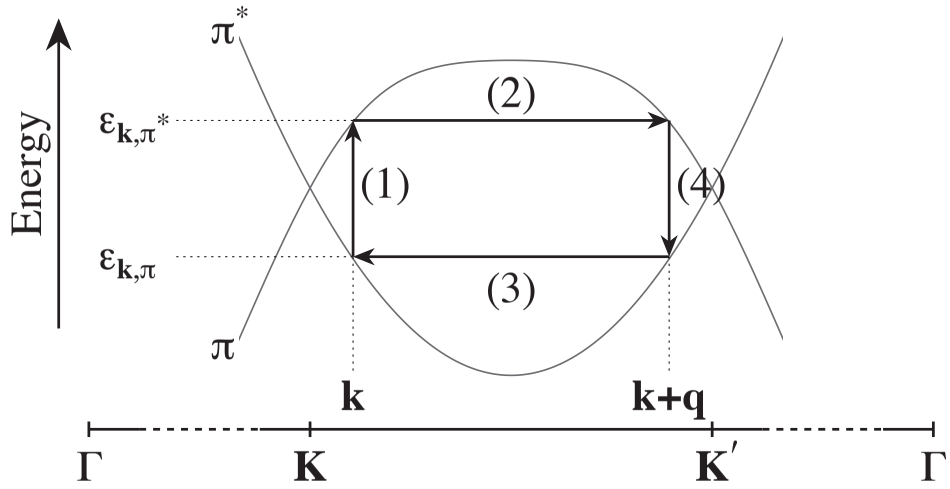


$$\epsilon_{\mathbf{k},\pi^*} - \epsilon_{\mathbf{k},\pi} = h\nu_L$$ → Selects **k**

$$\epsilon_{\mathbf{k}+\mathbf{q},\pi^*} = \epsilon_{\mathbf{k},\pi^*}$$ → Selects **q**



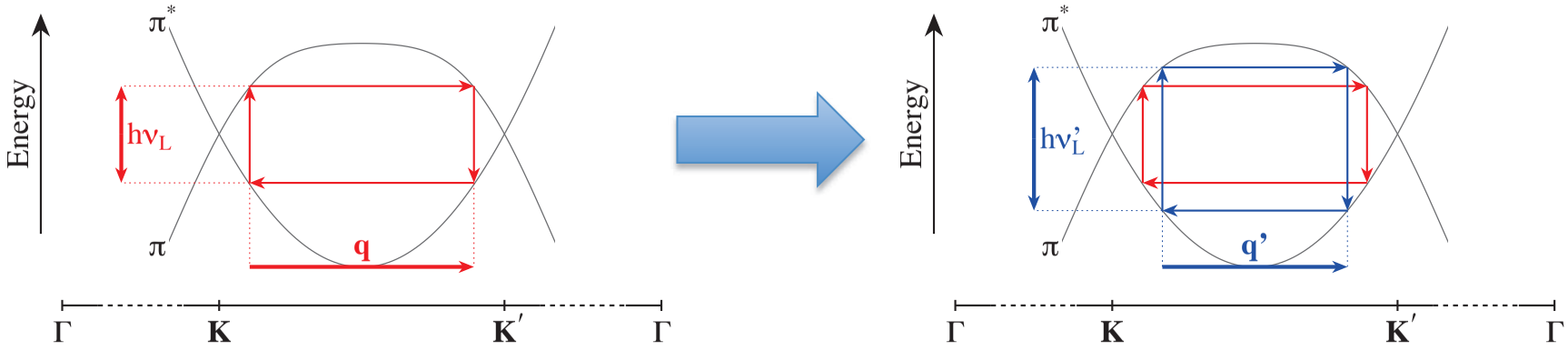
Double Resonance in graphite/graphene



Double resonance explains:

-Anomalously high intensity of D/2D peaks
-They are well-defined small-width peaks (not broad bands)
-The actual origin of the defect does not play a role

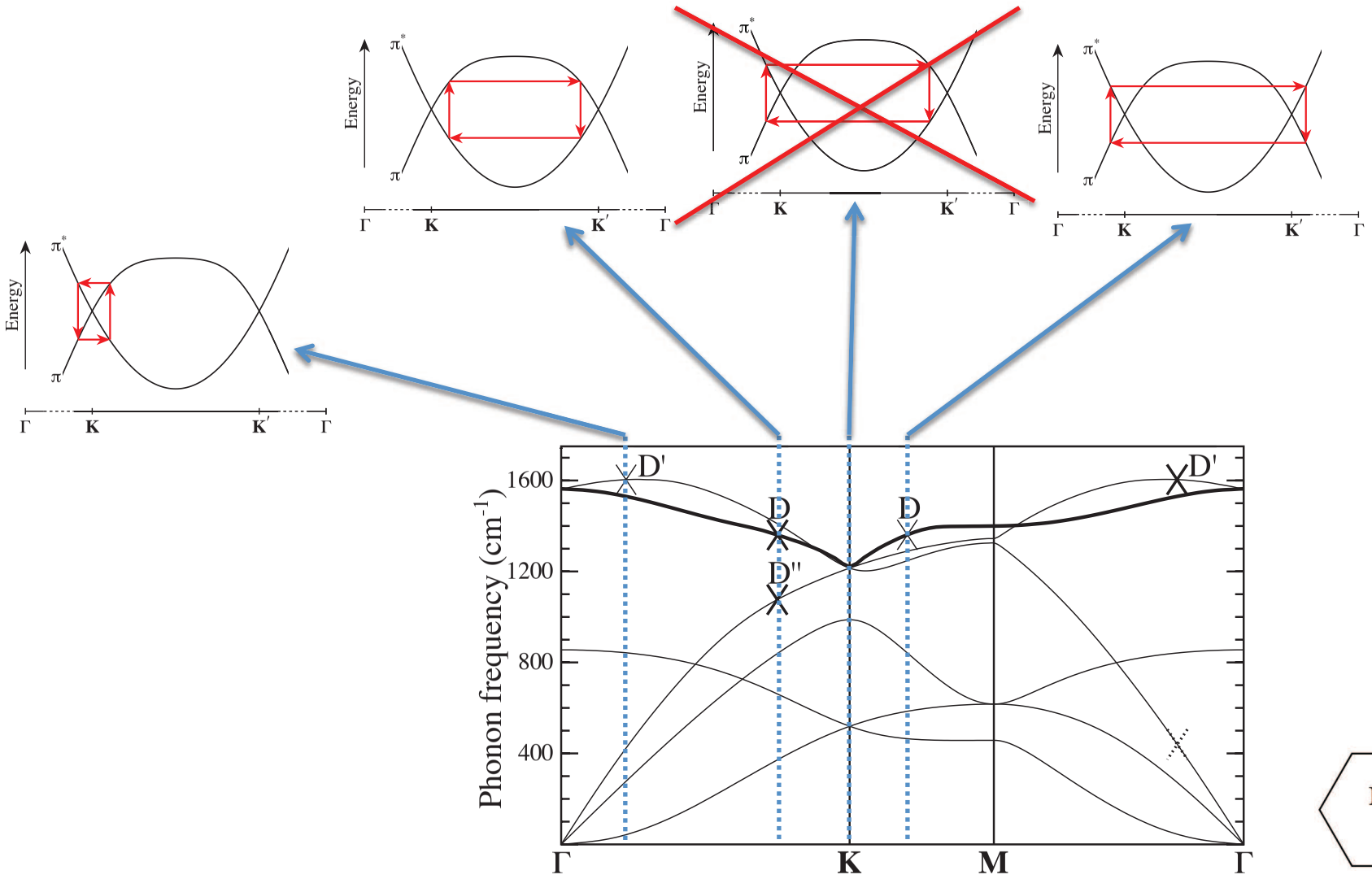
Double Resonance in graphite/graphene



Double resonance explains:

-Anomalously high intensity of D/2D peaks
-They are well-defined small-width peaks (not broad bands)
-The actual origin of the defect does not play a role
-The peaks shift by changing the laser energy

Attribution of the Raman peaks



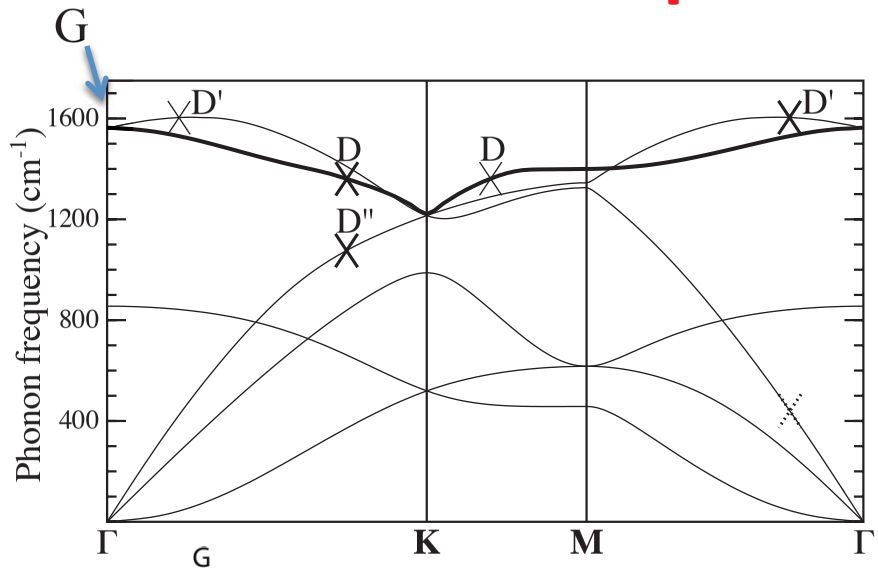
Attribution of the Raman peaks

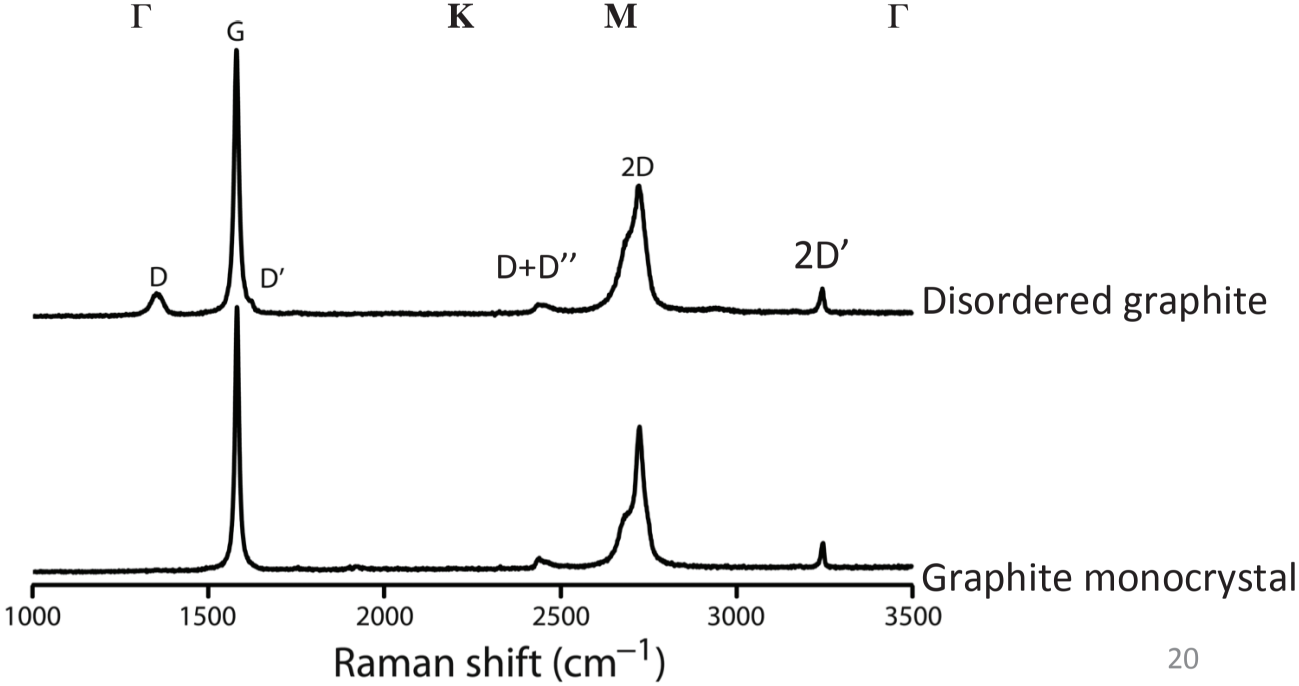
Lowest-order:
G → 1580 cm^{-1}

Double resonant:
1) Defect-activated:
D → 1350 cm^{-1}
D' → 1620

2) Two-phonon:
D+D'' → 2450 cm^{-1}
2D → 2700
2D' → 3240

λ_L = 514 nm





Raman as a tool to measure disorder

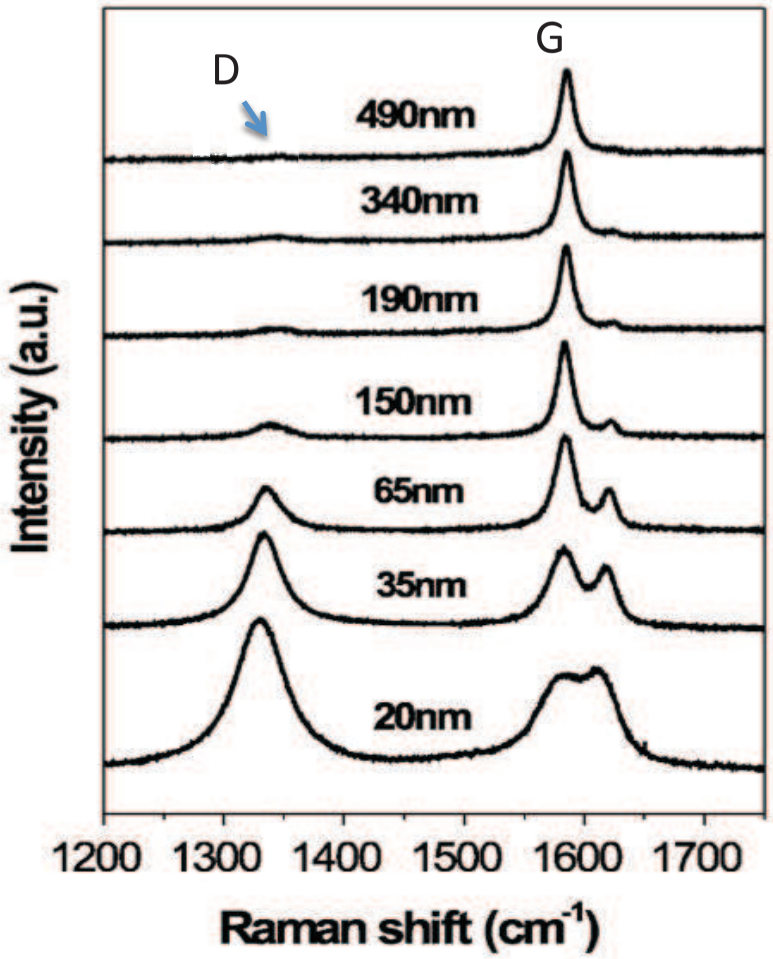


Fig. from Pimenta et al PCCP 2007

Can we quantify the disorder through the D peak?

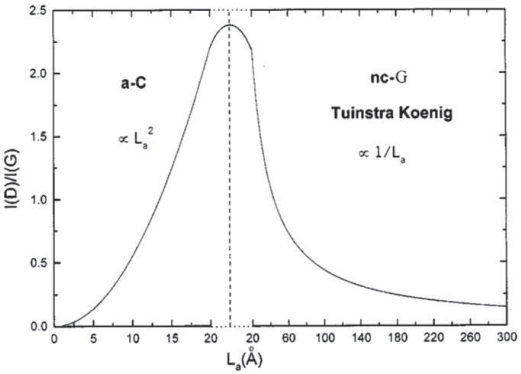
Tuinstra & Koenig relation (1970):

$$\frac{I_D}{I_G} \propto \frac{1}{L_a}$$

L_a = crystallite size

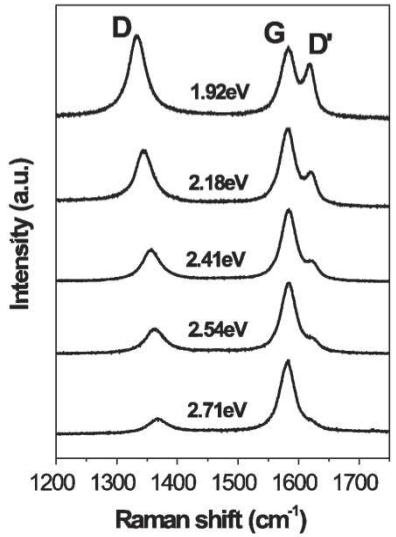
Validity limits of the TK relation

$I_D/I_G \propto 1/L_a$
only for
$L_a > 2$ nm



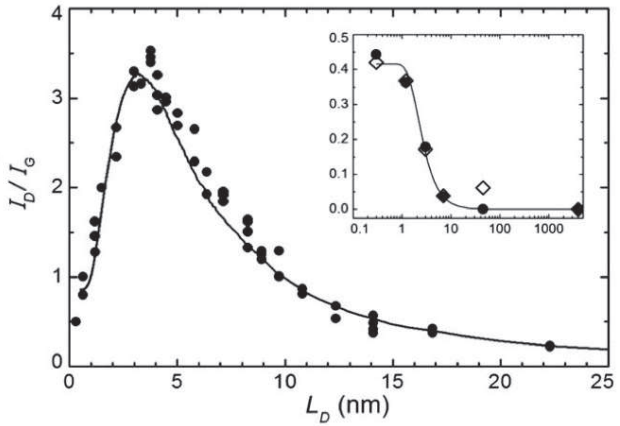
Ferrari & Robertson PRB 2000

I_D/I_G
depends also on ν_L



Cancado et al. 2006

The D peak can be activated by other sources of disorder!



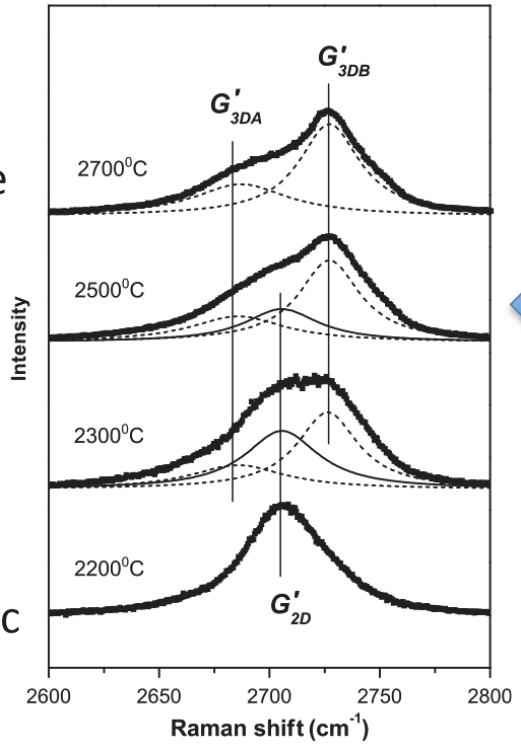
Point-defects induced by Ion-bombardment
Lucchese et al. Carbon 2010

2D shape and stacking order

Graphite:

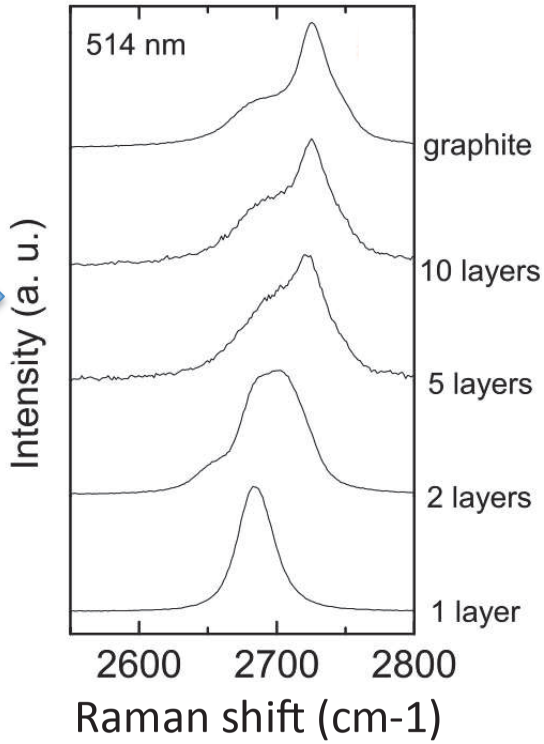
Crystalline

Turbostratic

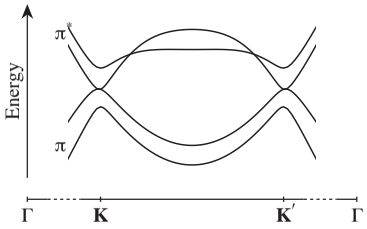


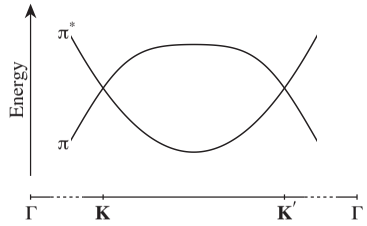
Laspade et al., Carbon 1984
Cancado et al., Carbon 2008

Graphene:



Ferrari et al., PRL 2006





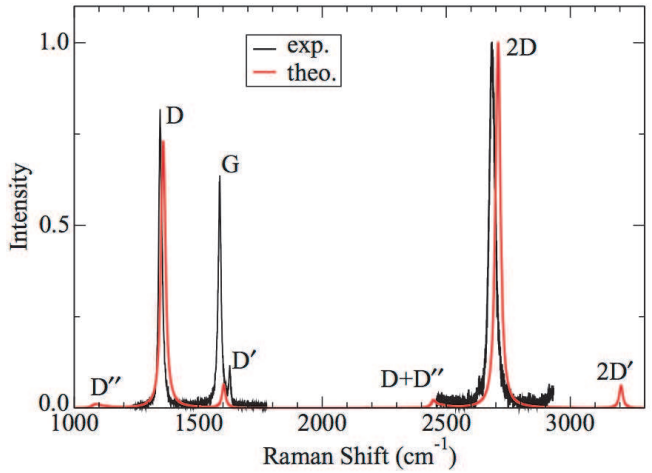
The 2D shape provides information on the stacking order

Conclusions

This talk: introduction to the Double Resonant Raman
in graphite (model sp2 carbon system)

2000: Thomsen & Reich → explanation of the general characteristics of the spectra

Nowadays: quantitative approach to describe Raman spectra in controlled experimental situations



Venezuela et al. PRB 2011

Characterization of natural samples is still heavily based on phenomenological model