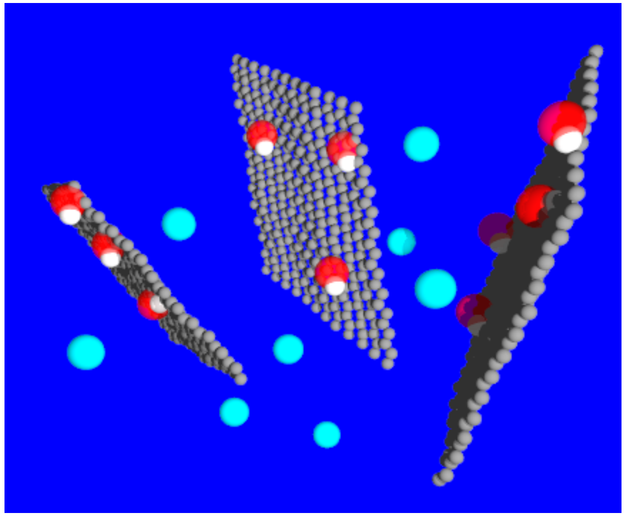
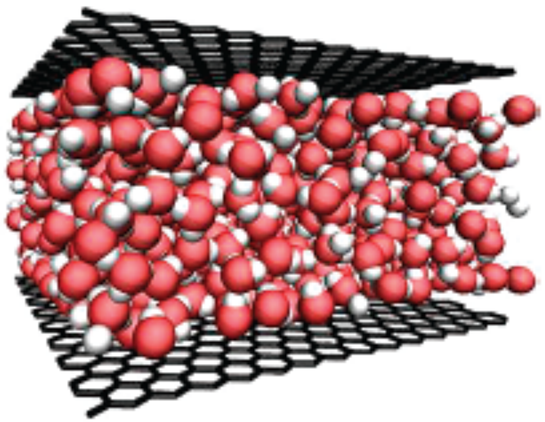
Raman signatures of SLG dispersed in *degassed* water
("*eau de graphene*")



George Bepete[1], Carlos Drummond[1], Alain Pénicaud[1], Eric Anglaret[2]
Centre de Recherche Paul Pascal, CNRS Bordeaux, France
Laboratoire Charles Coulomb, Université de Montpellier, France

Why studying SLG in water ?

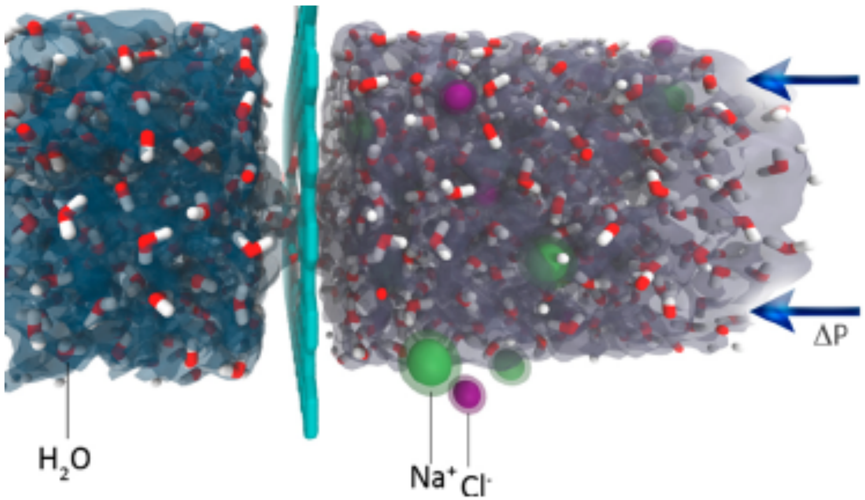


Flow/friction of water between GR flakes

Falk et al, Nanolett. 2010

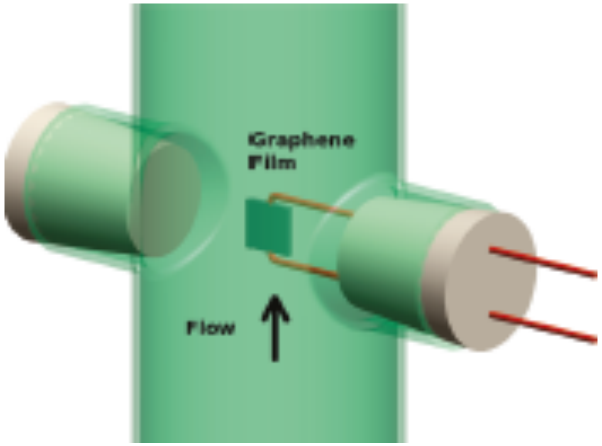
Aqueous precursors for
GR-based films/materials

@extremetech.com



Water dessalination

Cohen-Tannoudji et al, Nanolett. 2012



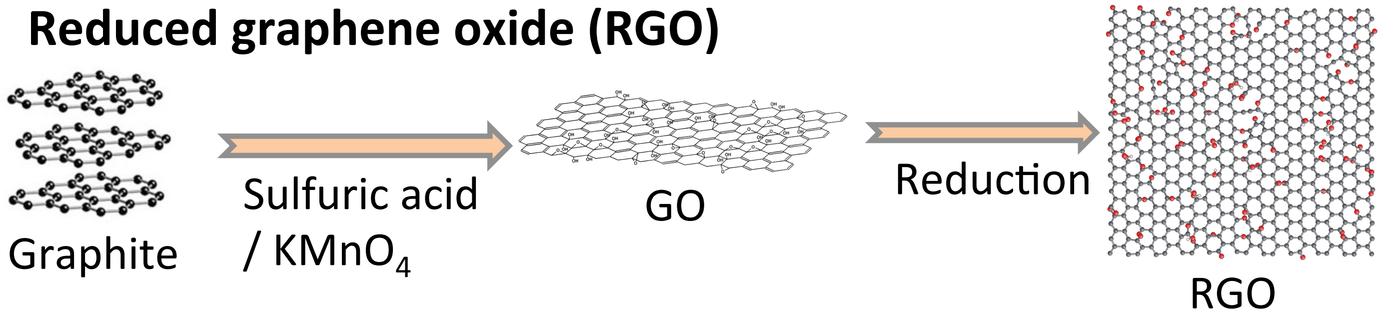
Harvesting energy
from waterflow over GR

Dhiman et al, Nanolett. 2011

E. Anglaret et al, Graphene 2017

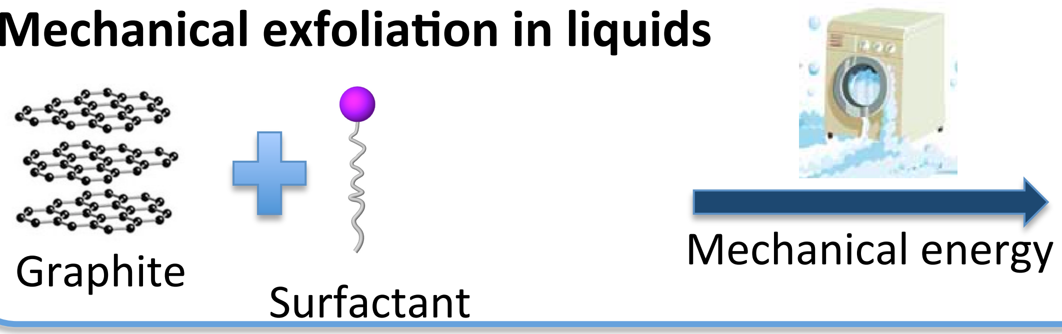
How to disperse/stabilize SLG in water ?

Reduced graphene oxide (RGO)



Many defects
Or
Surfactants

Mechanical exfoliation in liquids



Few layers graphene
Concentration < 0.07 g/L
Surfactants

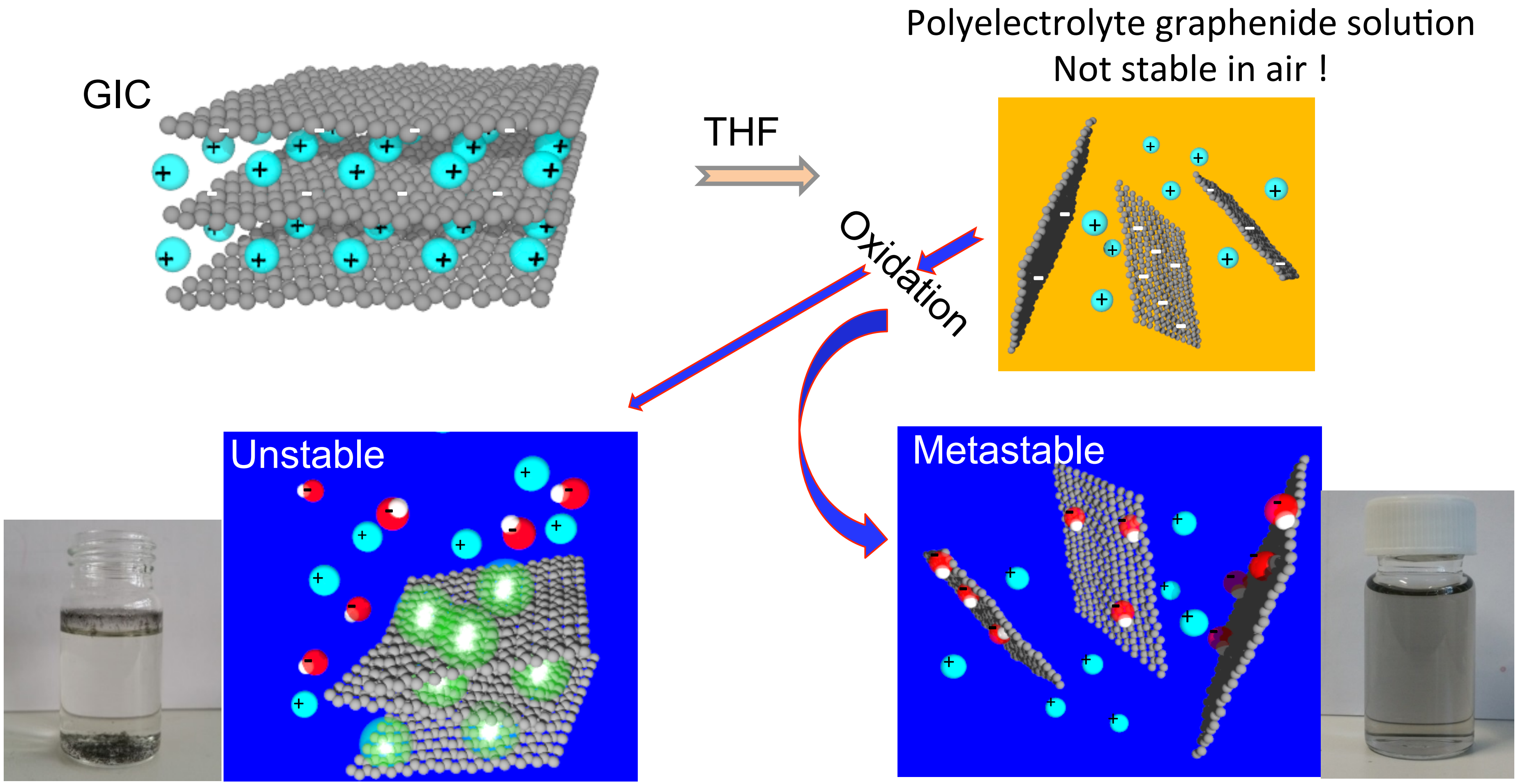
→ **Dissolution of graphite intercalation compounds (GIC) in polar aprotic solvent**

Drummond & Penicaud., Acc. Chem. Res. 2013

→ **+Transfer and stabilization of graphenide ("SLG anions") in *degassed* water**

Bepete et al., Nature Chemistry, 28 Nov. 2016

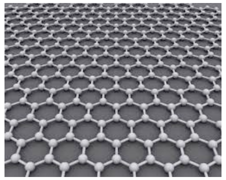
Stabilizing SLG in water



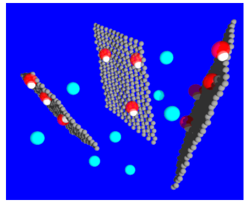
Unstable in water
(pH=11)

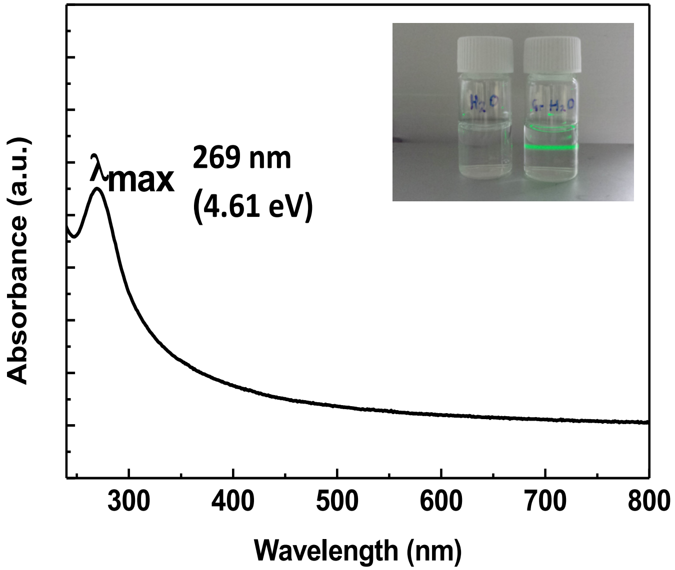
Metastable (for months)
in *degassed* water
(c=0.16 g/L≈400 m^2/L , pH=8)
No surfactant/organic additives

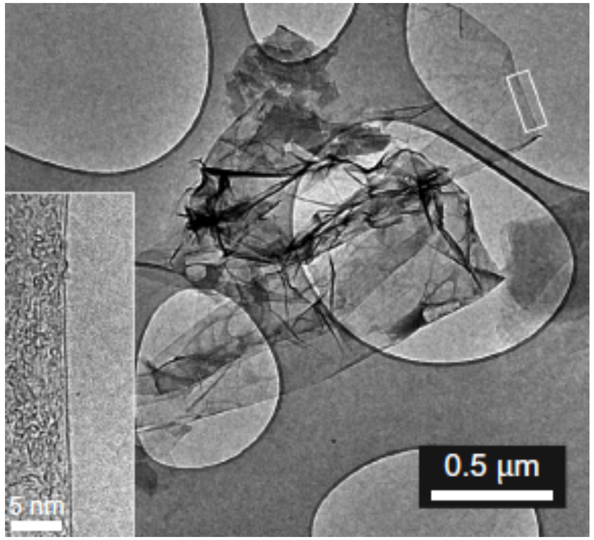
Bepete et al., Nature Chemistry, 28 Nov. 2016

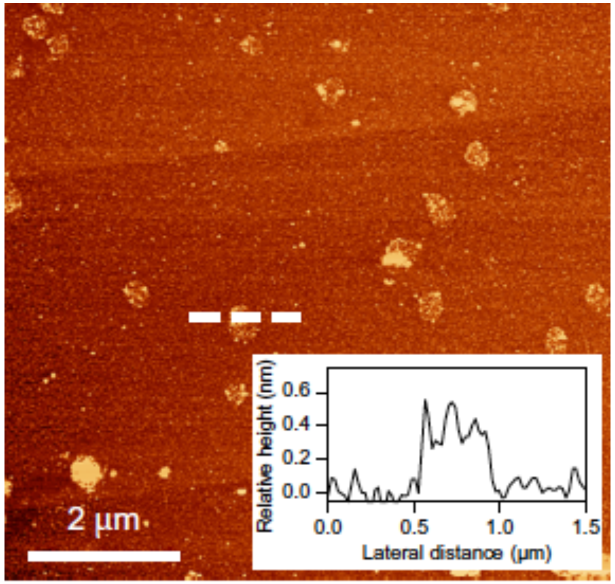


Evidences of SLG in “eau de graphene”







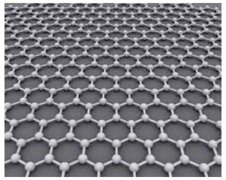


SLG in *degassed* water
(no surfactant/organic additives)

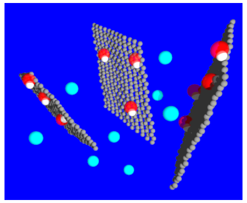
c=0.16 g/L≈400 m^2/L , pH=8

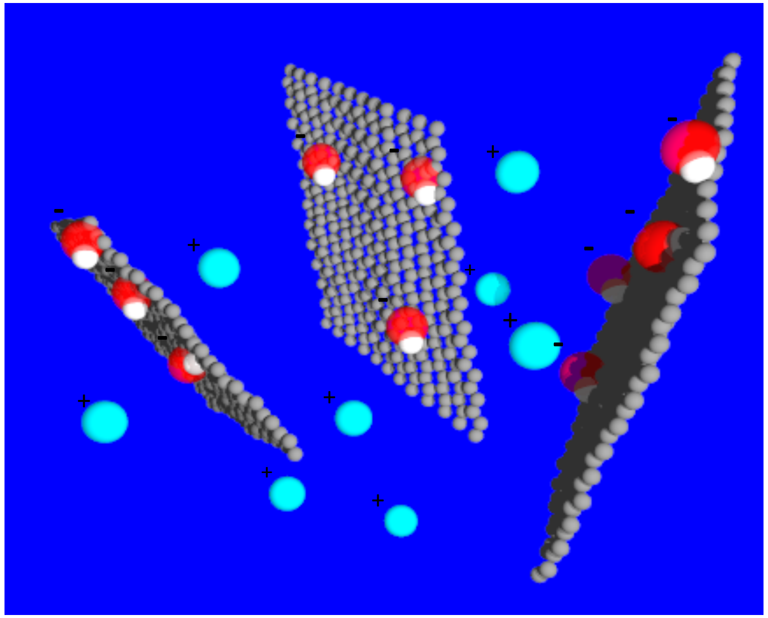
Typical flake size 100 nm-1 µm

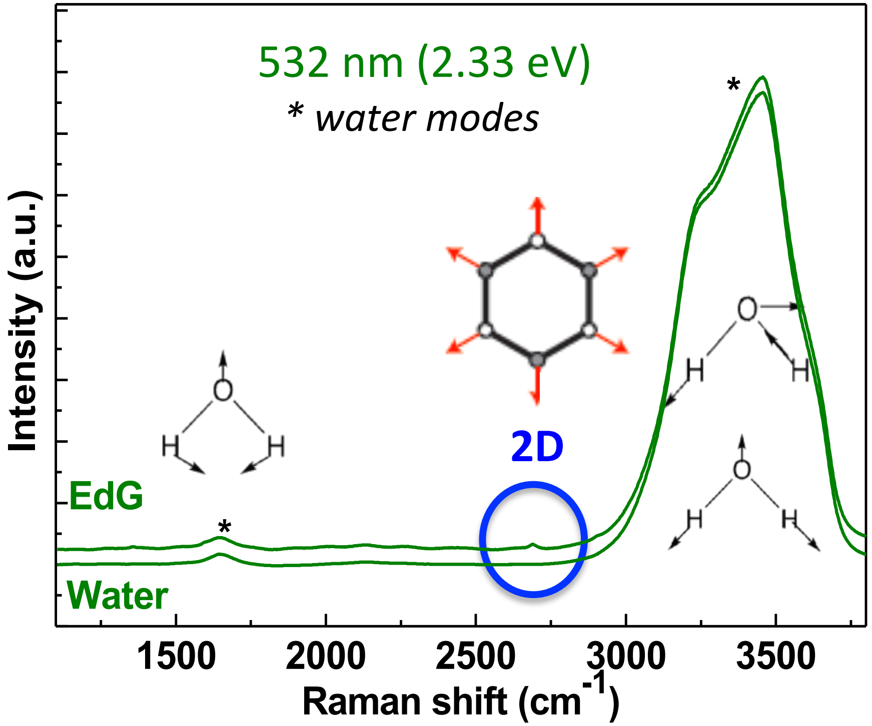
Bepete et al., Nature Chemistry, 28 Nov. 2016



Raman signatures of "eau de graphene"

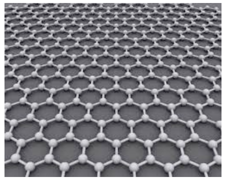




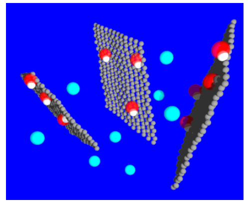


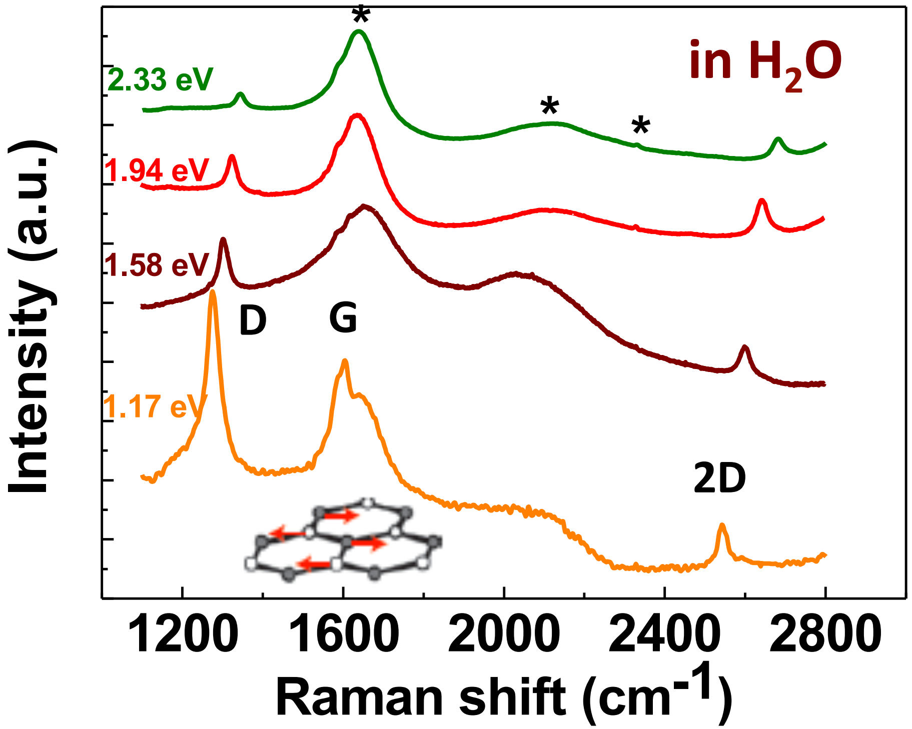
Metastable in *degassed* water
(c=0.16 mg/mL, pH=8)
No surfactant/organic additives

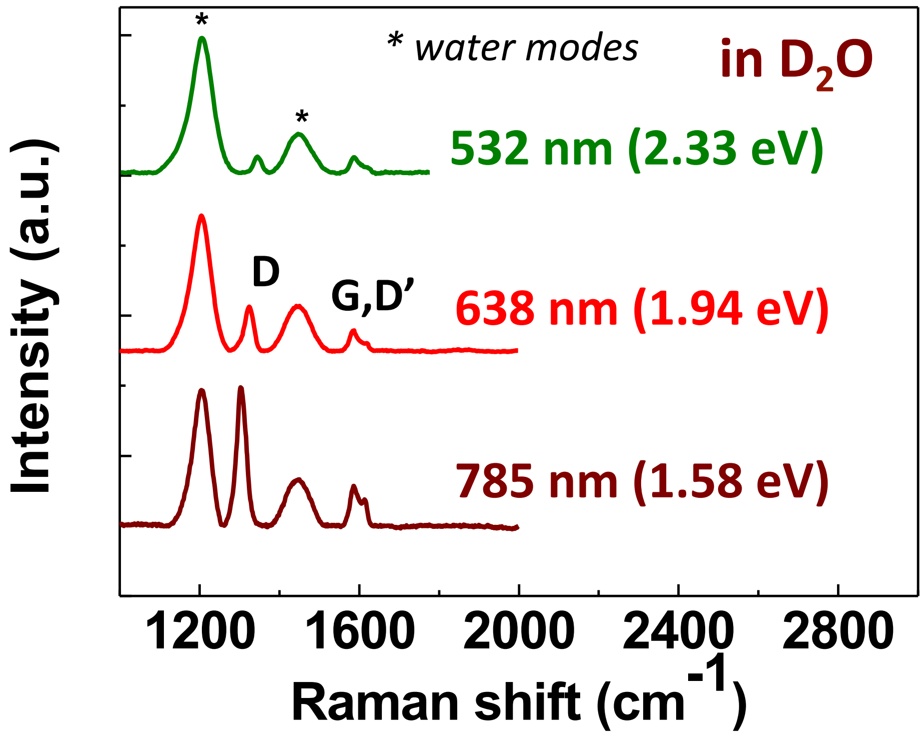
E. Anglaret et al, Graphene 2017



Raman signatures of "eau de graphene"

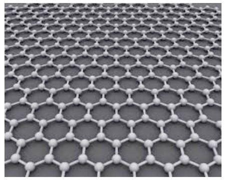




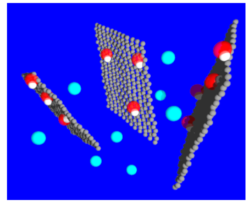


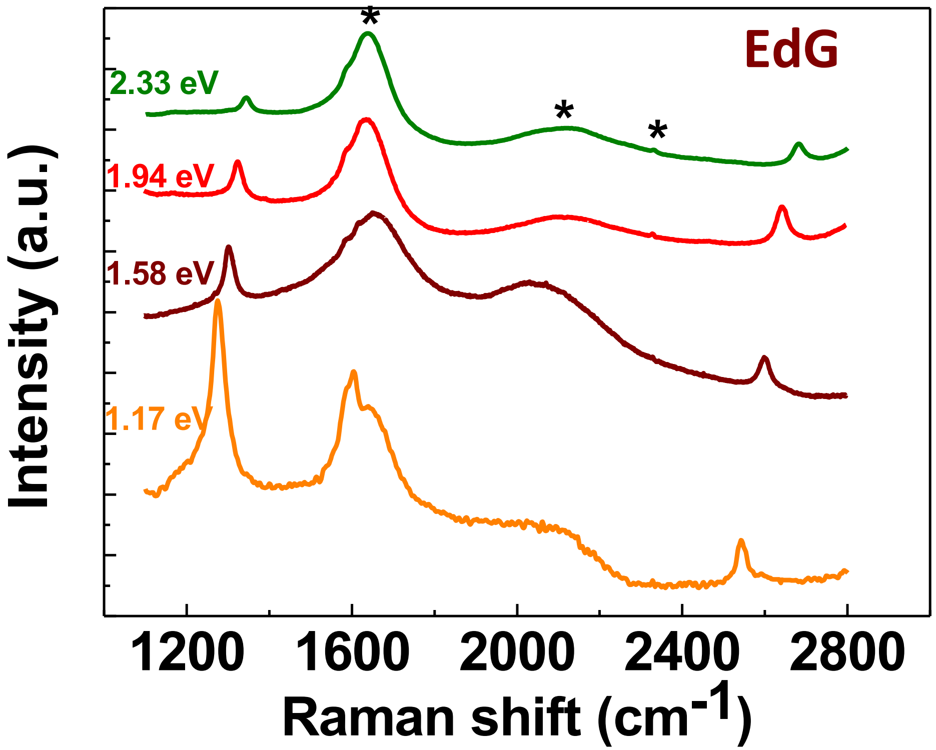
Intensity of SLG bands comparable to that of OH bending
Relative intensities of SLG increase at low laser energies

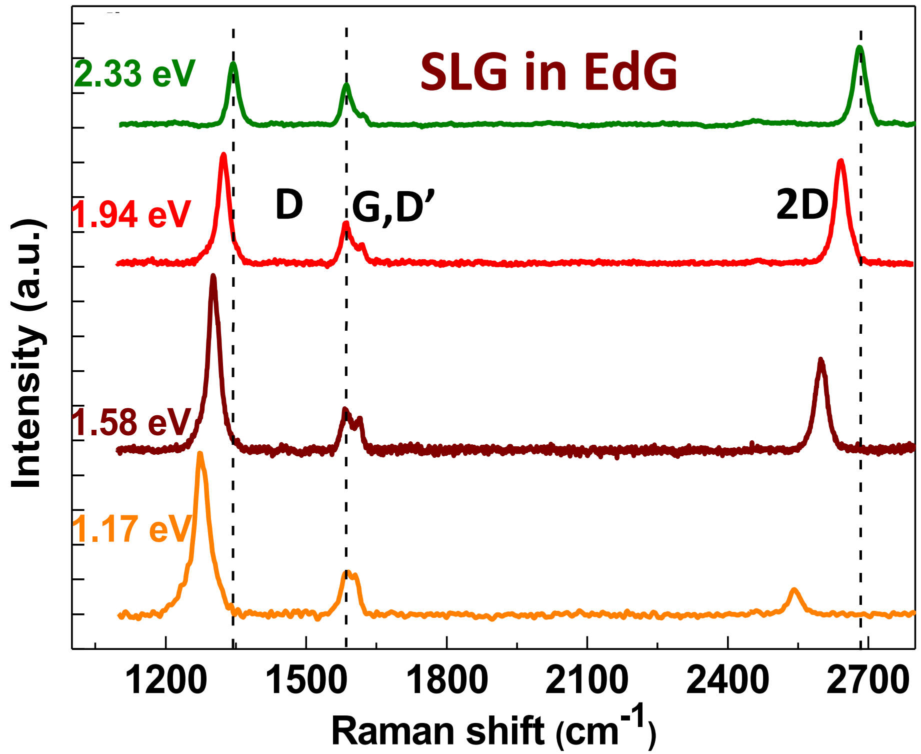
E. Anglaret et al, Graphene 2017



Raman signatures of SLG in "eau de graphene"

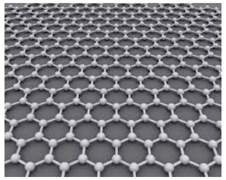




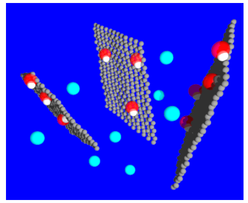


Water substraction

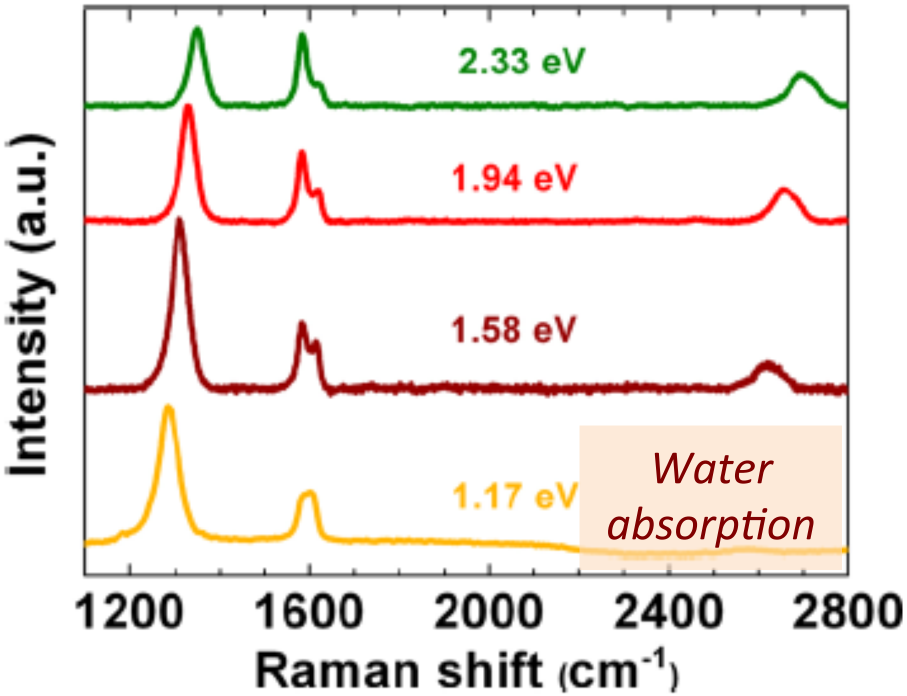
Bepete et al, J. Phys. Chem. C 2016



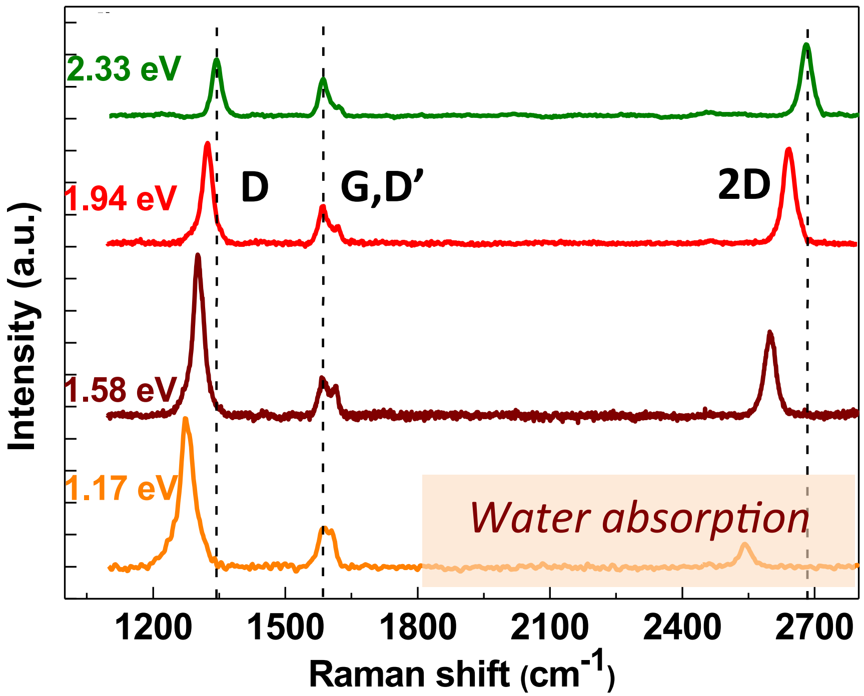
Raman signatures of SLG in "eau de graphene"



FLG in sodium cholate stabilized aqueous suspensions

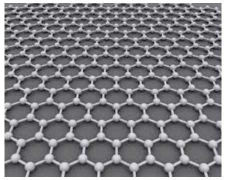


SLG in EdG



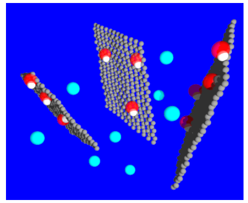
Intrinsic signature of (an ensemble of) SLG in water :
a narrow and intense 2D band

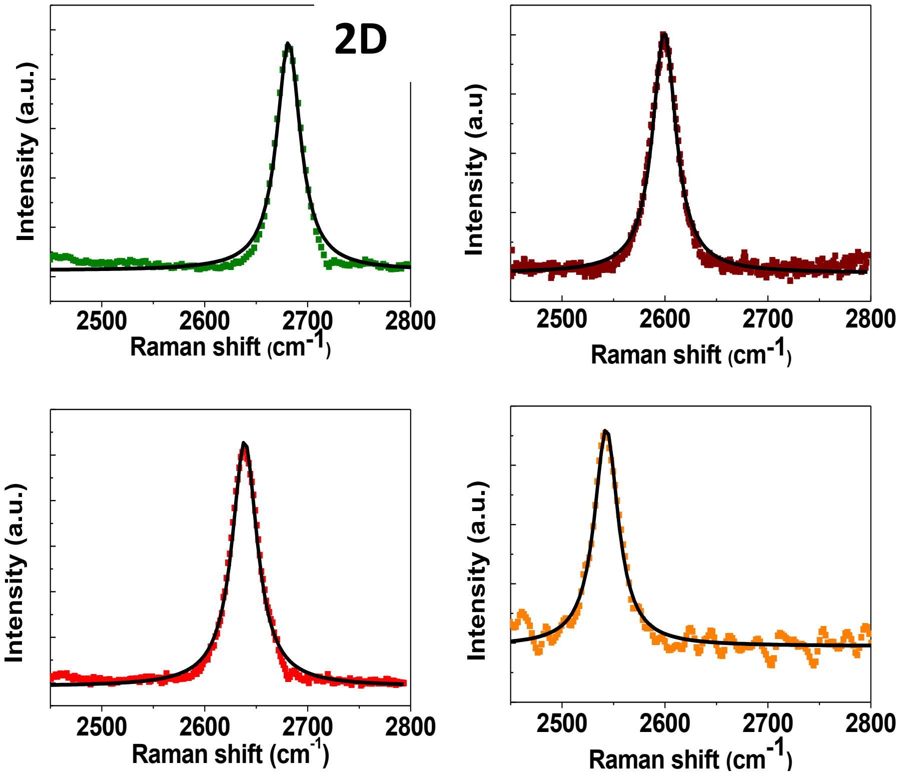
Bepete et al, J. Phys. Chem. C 2016



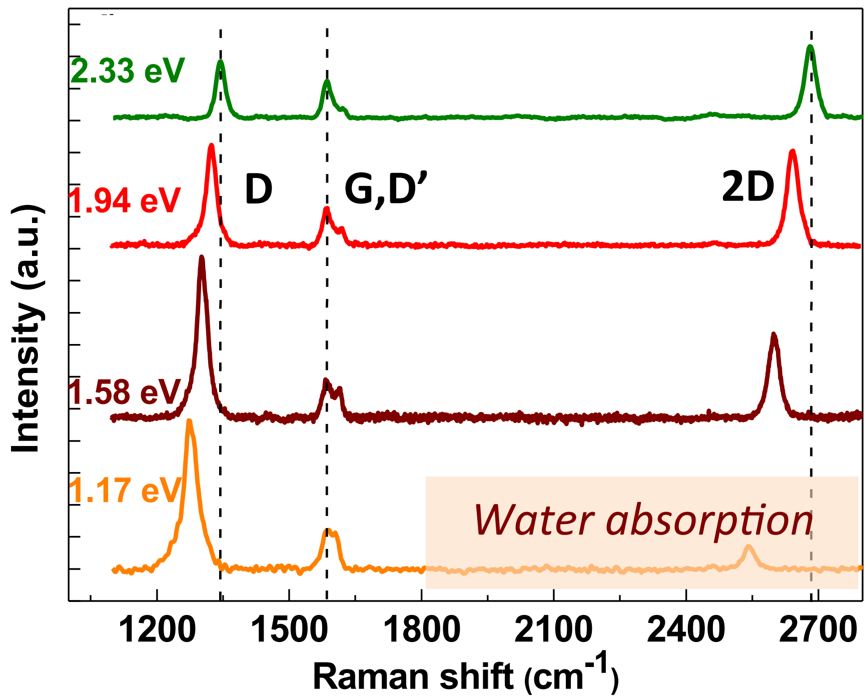
Raman signatures of SLG in "eau de graphene"

Single layerness





SLG in EdG

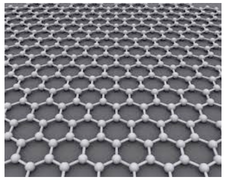


Intrinsic signature of (an ensemble of) SLG in water :
a symmetric, narrow and intense 2D band

27 cm^{-1} < **FWHM$_{2D}$** <30 cm^{-1}

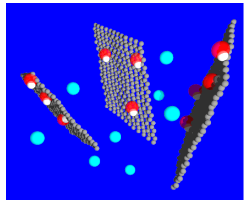
2.7< **A$_{2D}$/A$_G$** <3.5

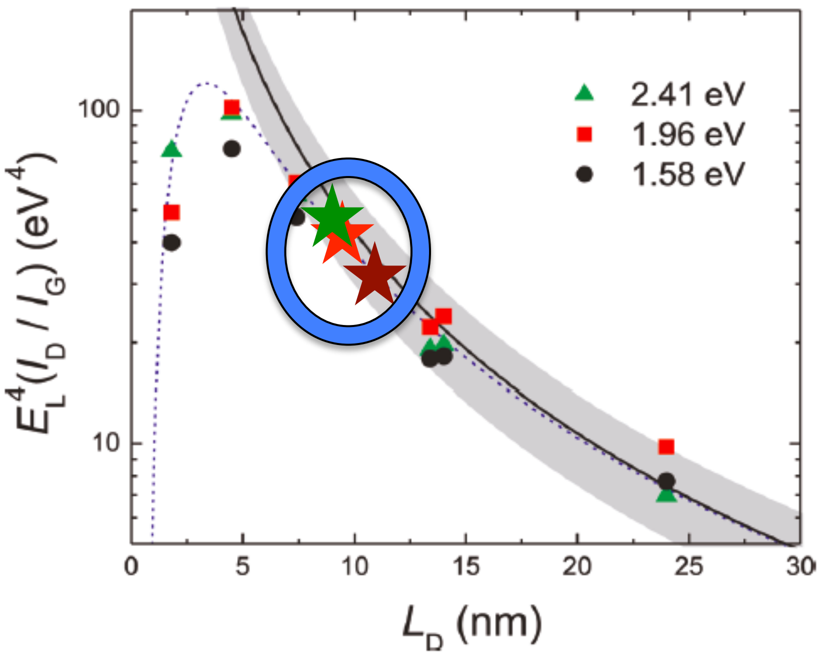
E. Anglaret et al, Graphene 2017



SLG in "eau de graphene"

Defects

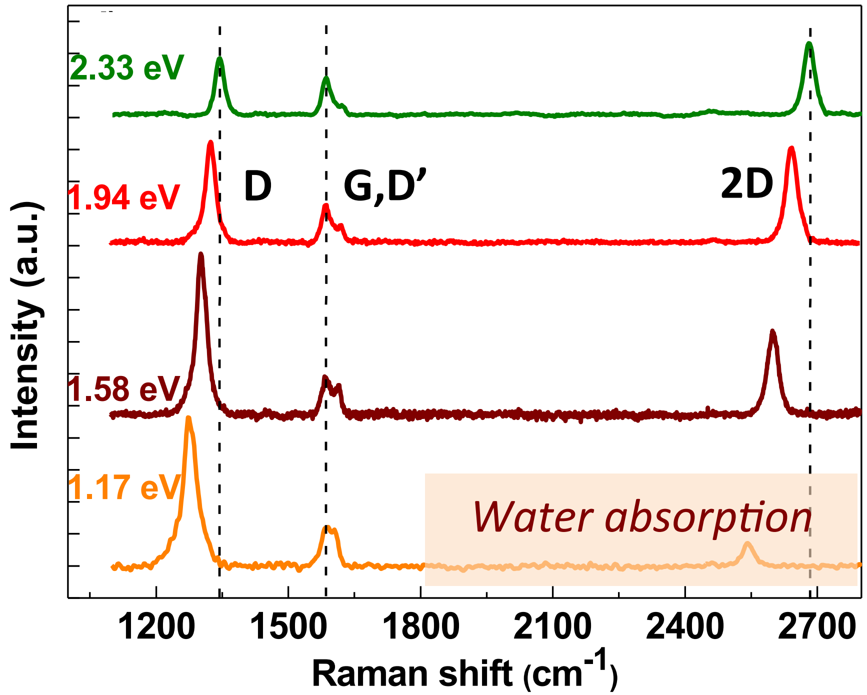




Large SLG on silicon wafer, with vacancies

Cançado et al, Nanolett. 2011

SLG in EdG



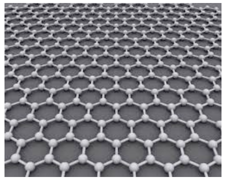
Bepete et al, J. Phys. Chem. C 2017

Exposition of graphenide to moisture→functionnalisation by –H or –OH groups

→ I_D is dominated by the contribution of point defects

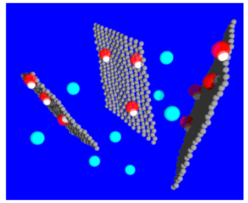
L_D=8-10 nm (300-400 ppm)

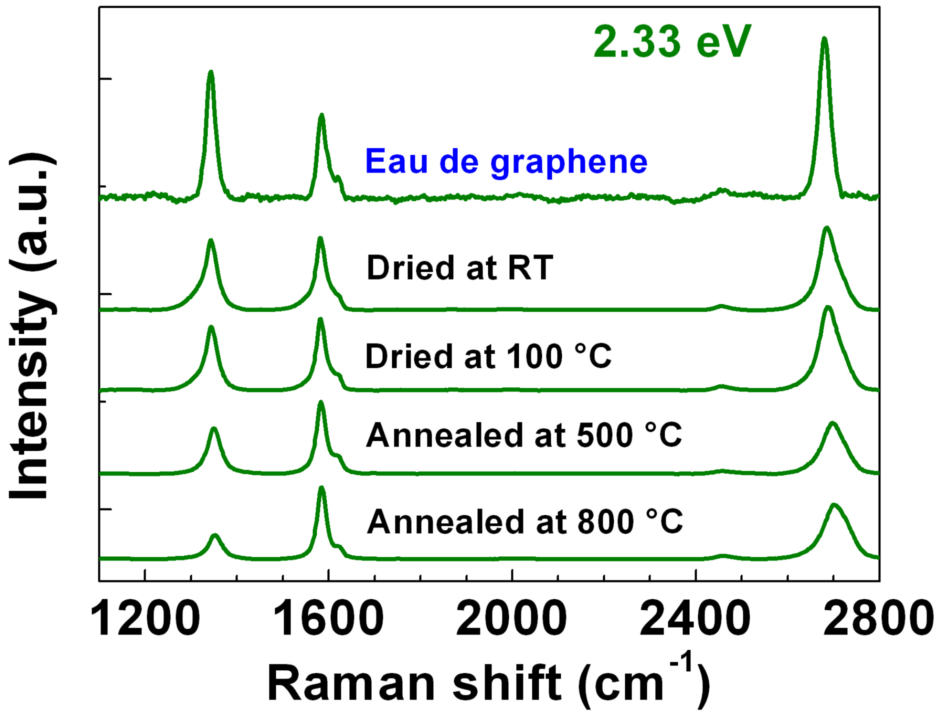
E. Anglaret et al, Graphene 2017

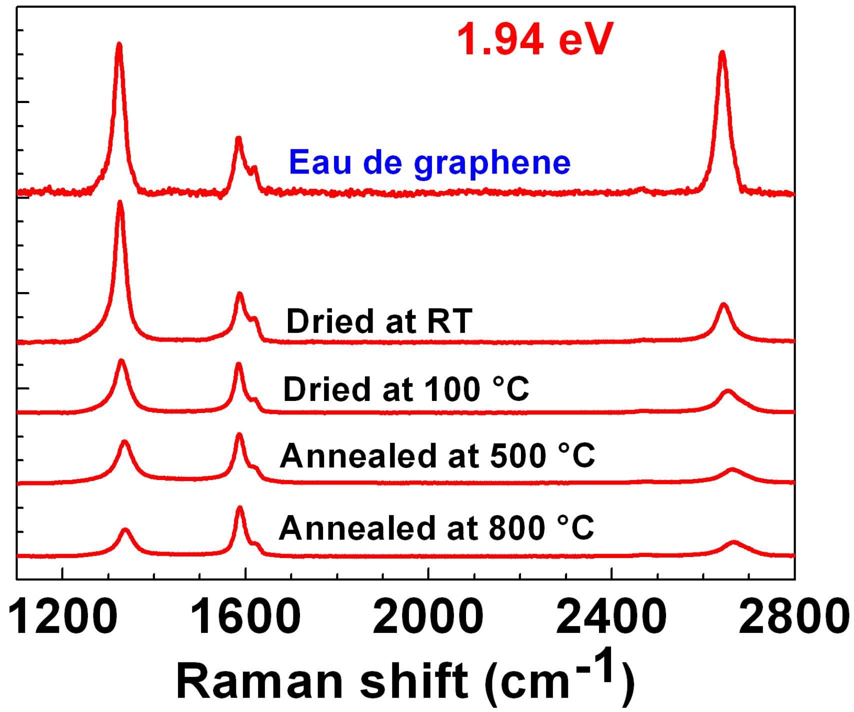


SLG in "eau de graphene"

Defects in annealed films



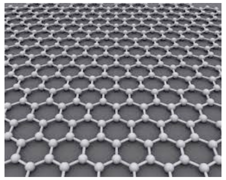




Upshift, broadening and decrease of 2D → **interlayer interactions**

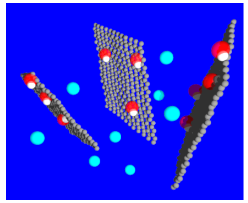
I_D/I_G decreases ($I_D/I_{D'}$ as well) → **curing of point defects**

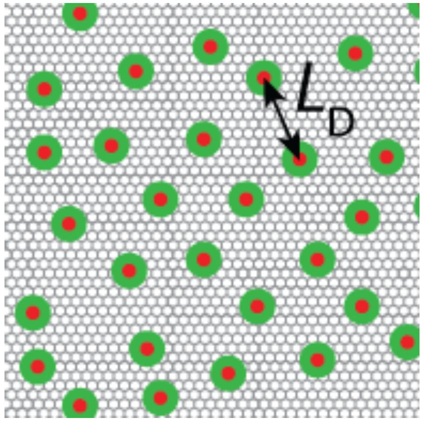
Bepete et al, J. Phys. Chem. C 2016

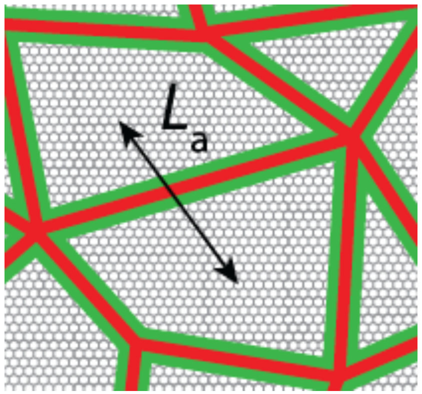


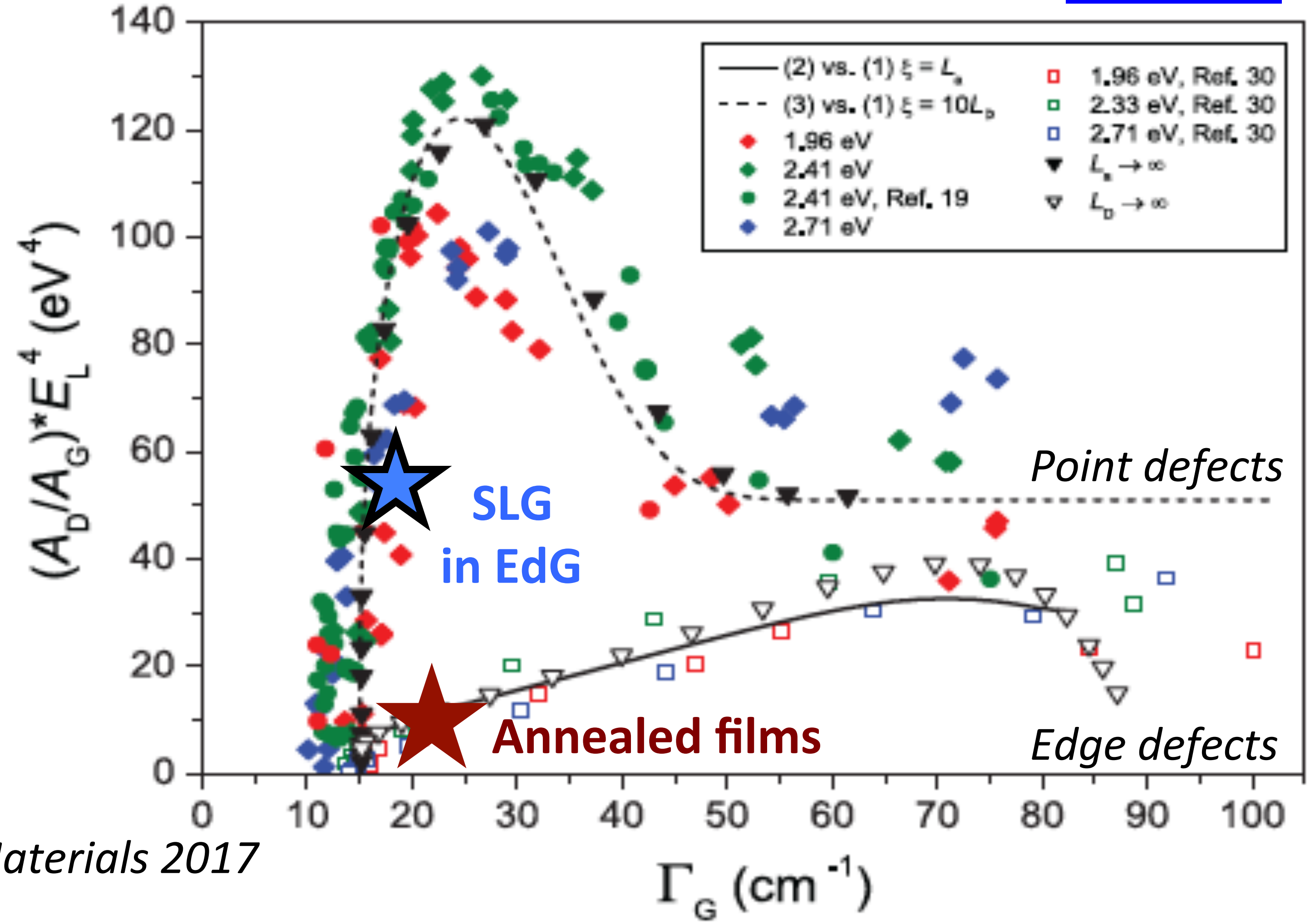
SLG in "eau de graphene"

Defects in annealed films







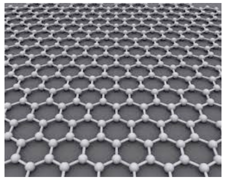


Cançado et al, 2D Materials 2017

D band in "eau de graphene" is dominated by point defects

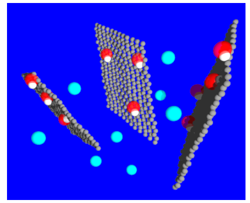
D band in annealed films is dominated by edge defects

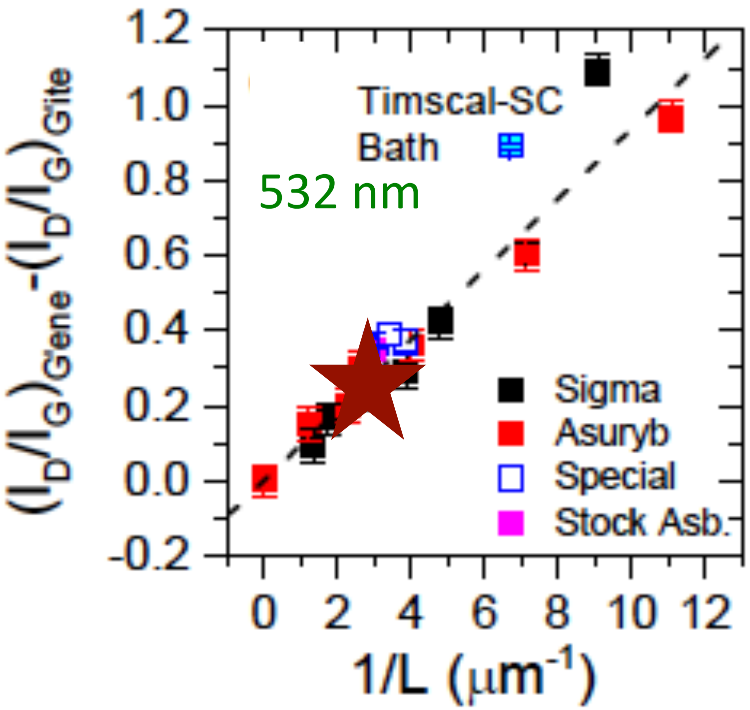
E. Anglaret et al, Graphene 2017



SLG in "eau de graphene"

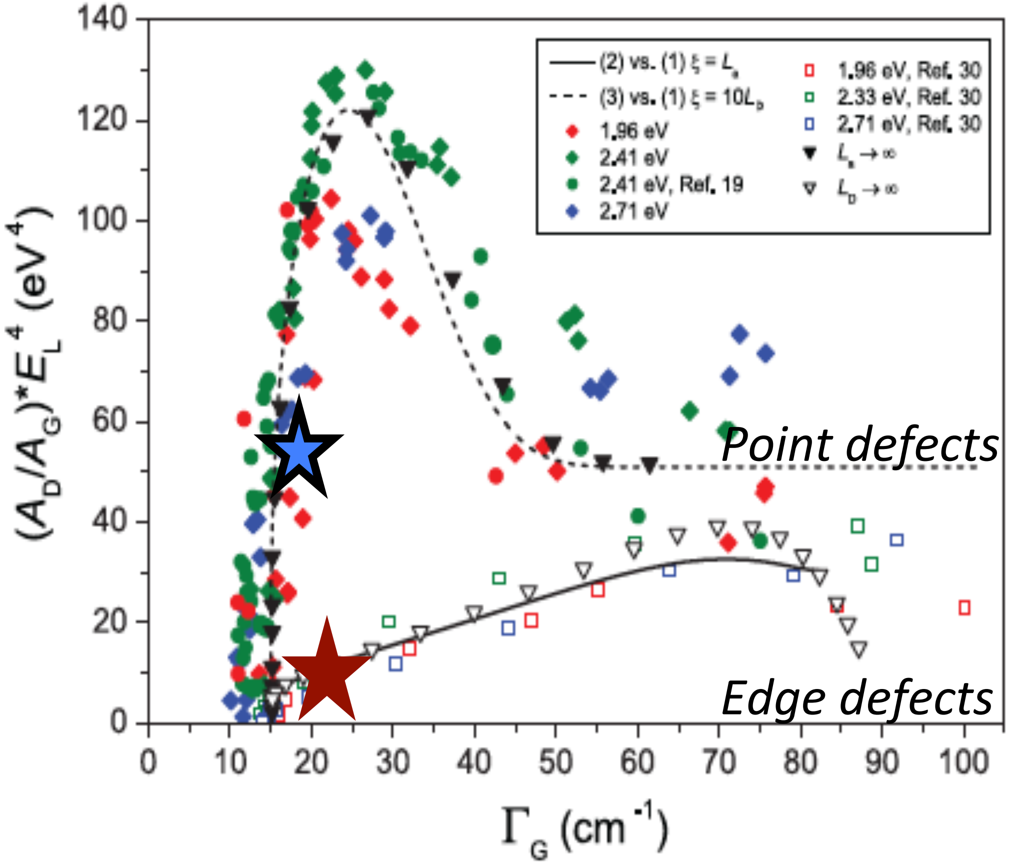
Defects in annealed films





FLG films (from water/surf. dispersions)

Backes et al, Nanoscale 2016

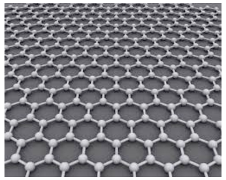


Cançado et al, 2D Materials 2017

I_D in annealed films is dominated by edge defects

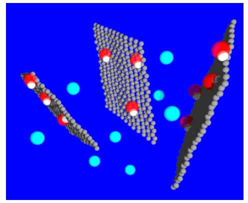
$\langle L_{flake}\rangle_{measured} \approx$ 300 nm $\approx \langle L_{flake}\rangle_{actual}$

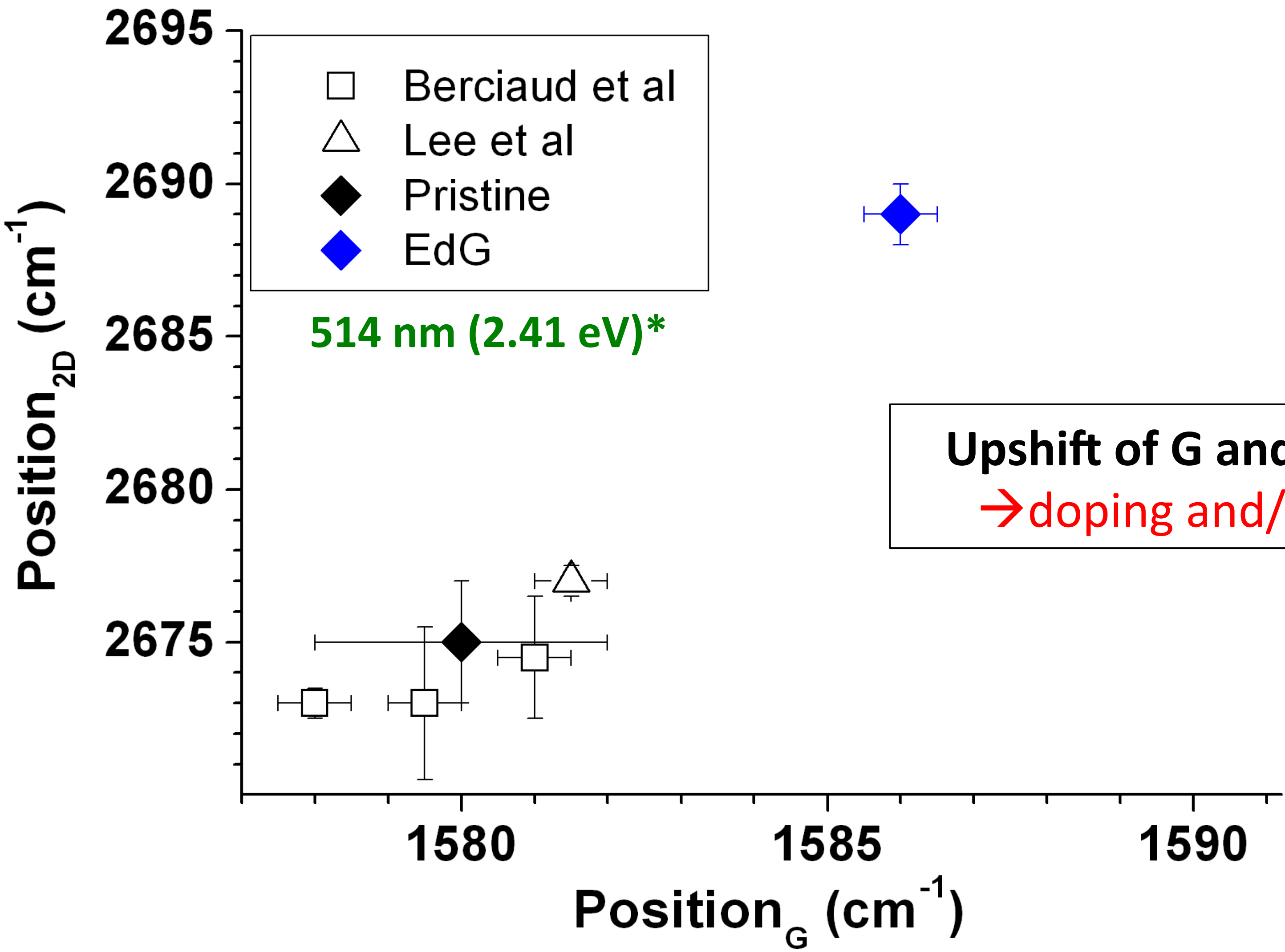
E. Anglaret et al, Graphene 2017



SLG in "eau de graphene"

Doping and strain ?

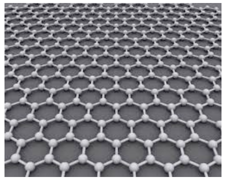




Upshift of G and 2D in EdG
→doping and/or strain?

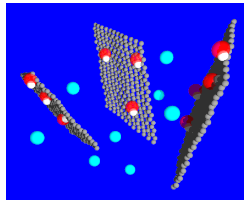
Bepete et al, J. Phys. Chem. C 2016

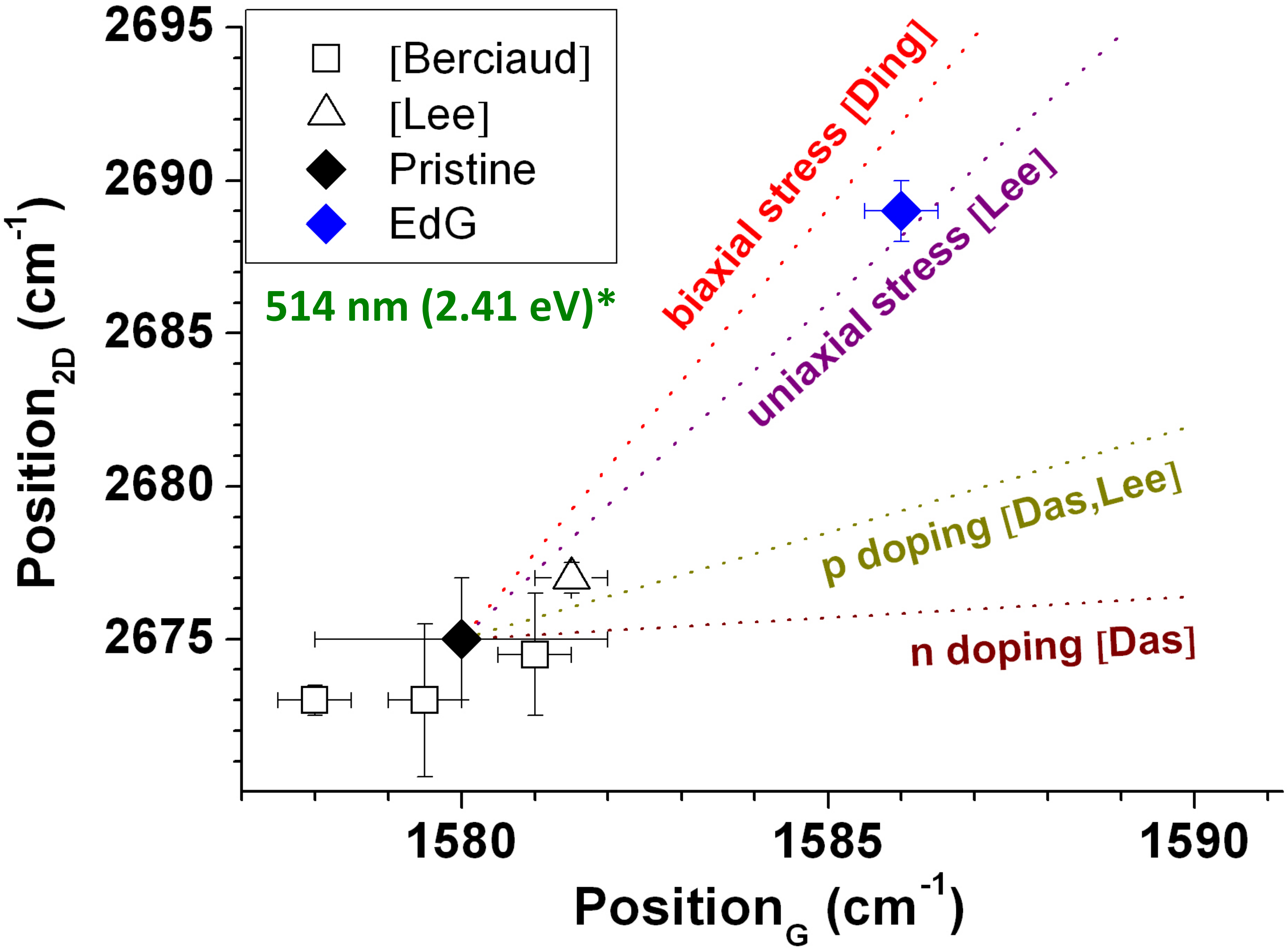
** Considering a dispersion of 97 cm^{-1}.eV^{-1} for 2D*



SLG in "eau de graphene"

Doping and strain





Lee et al, Nat. Comm. 2012

Bepete et al, J. Phys. Chem. C 2016

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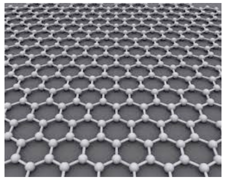
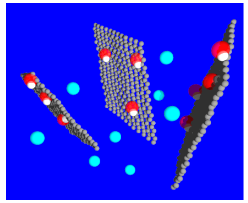
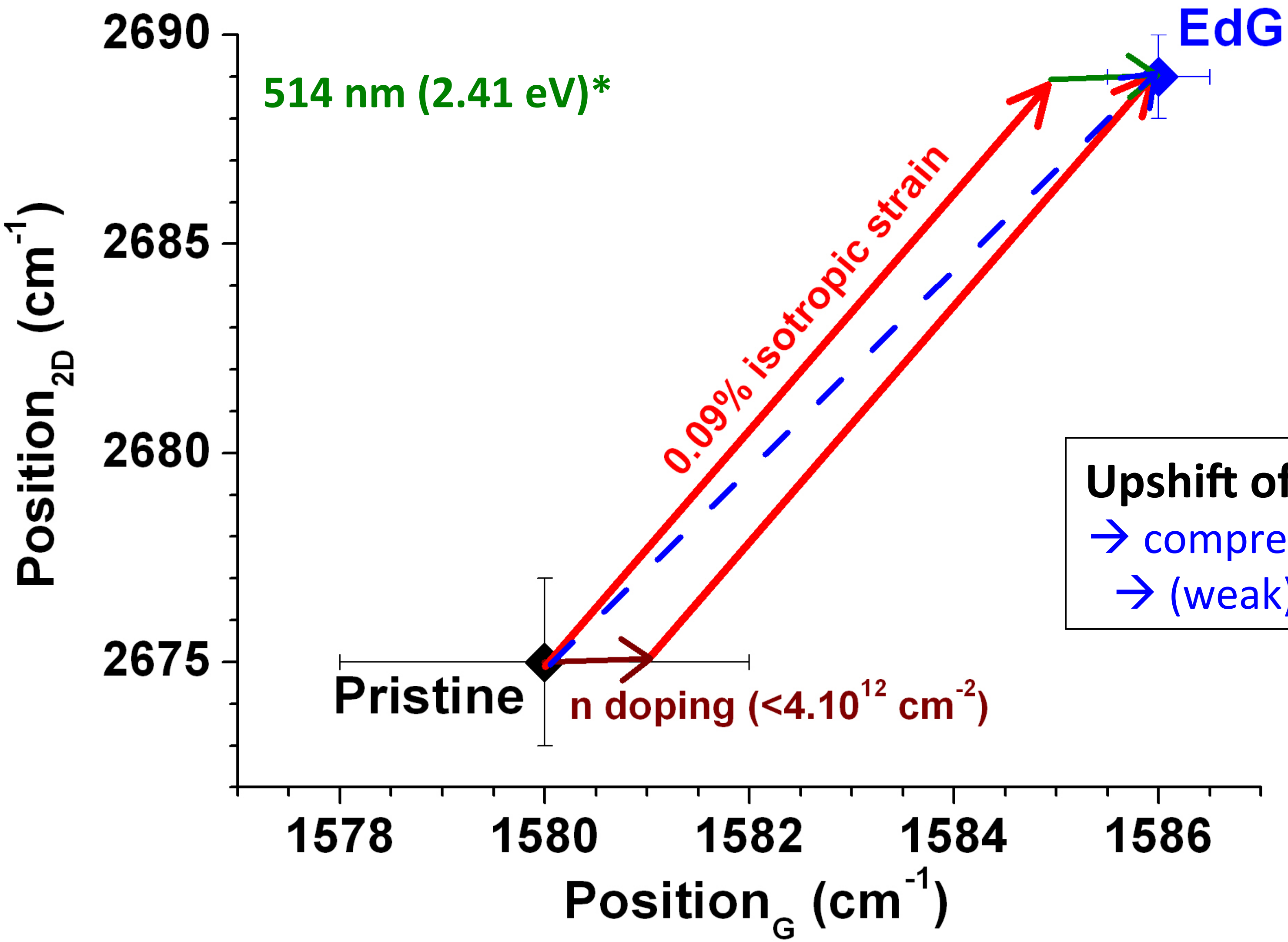


SLG in "eau de graphene"

Doping and strain





Lee et al, Nat. Comm. 2012

Bepete et al, J. Phys. Chem. C 2016

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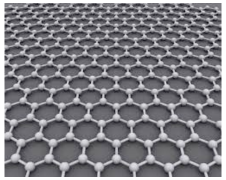
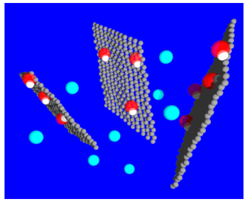


Raman study of SLG dispersed in water
"*eau de graphene*"



Single layerness

Narrow, intense 2D band → $FWHM_{2D}=28\pm2\ cm^{-1}$

Defects

D band dominated by sp^3 defects in EdG → $L_D\approx$8-10 nm (300-400 ppm)

D band dominated by edge defects in annealed films → $\langle L_a\rangle \approx$ 300 nm

Electronic and mechanical interactions

(Heterogeneous ?) compressive strain (≈-0.1%)

Weak doping ($<4.10^{12}\ cm^2$)

Coming soon…

Microscopic origin of strain ?

Influence of charge density and pH ?

Extend results to larger flakes

E. Anglaret et al, Graphene 2017