

Many Body Effects on Optical Properties of Graphene

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Students

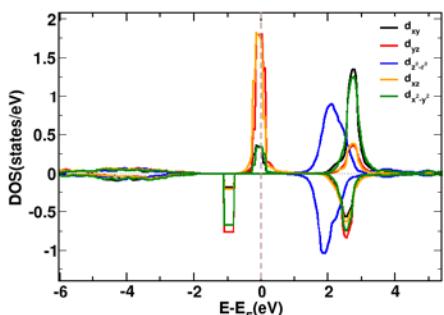
Pawan, Premlata, Jitender



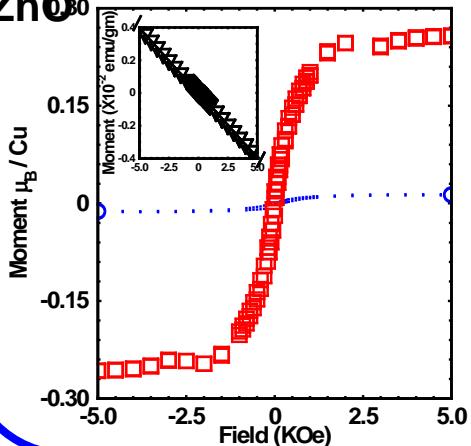
Research Activities

ZnO

1. Ferroelectricity and half metallic state in doped ZnO

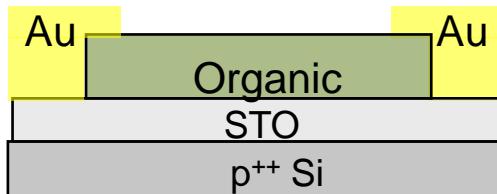


2. Ferromagnetism in non magnetic ion doped ZnO



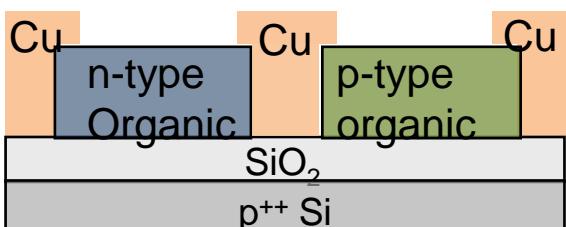
Organic Electronics

1. Low voltage Field Effect Transistor



2. Microscopic Mechanism of charge transport

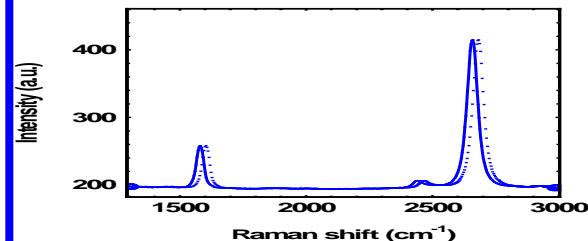
3. Organic Inverter



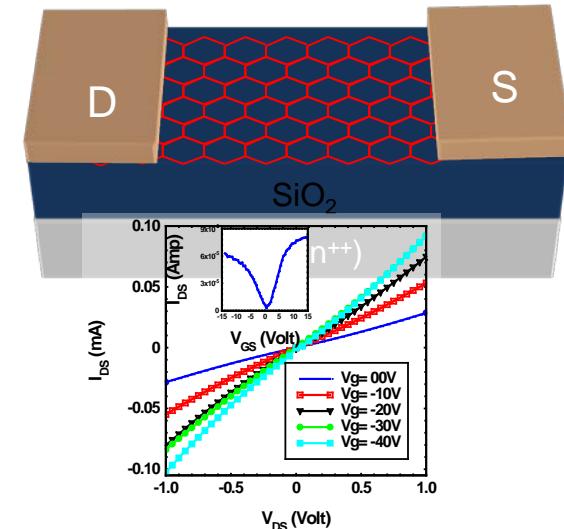
4. Transparent-Flexible OTFT

Dirac Materials (Graphene & MoS₂)

1. Growth of Graphene & MoS₂



2. High Mobility Transistor



3. Many Body Effects

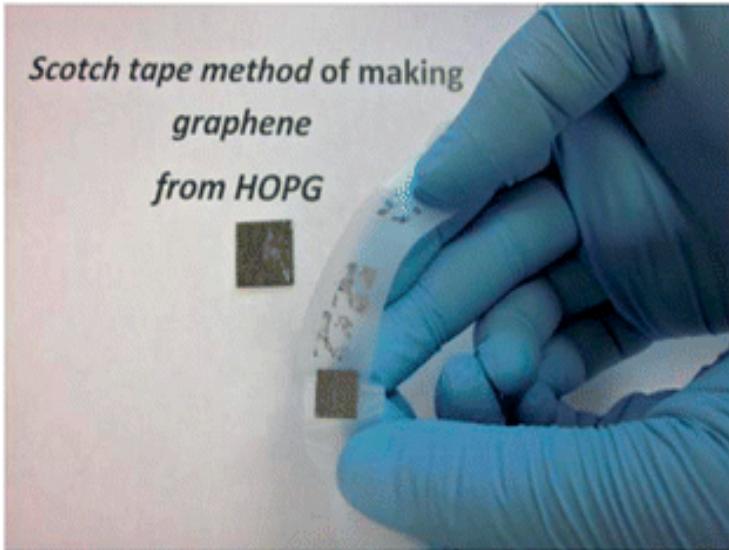
Plan of this talk

- Introduction to graphene bandstructure and “chirality”.
- Growth and characterization of graphene.
- Robustness of universality under interlayer coupling and many body interactions.
- Doping of graphene to modulate the e-e interaction on universality
- How to break this universality ?



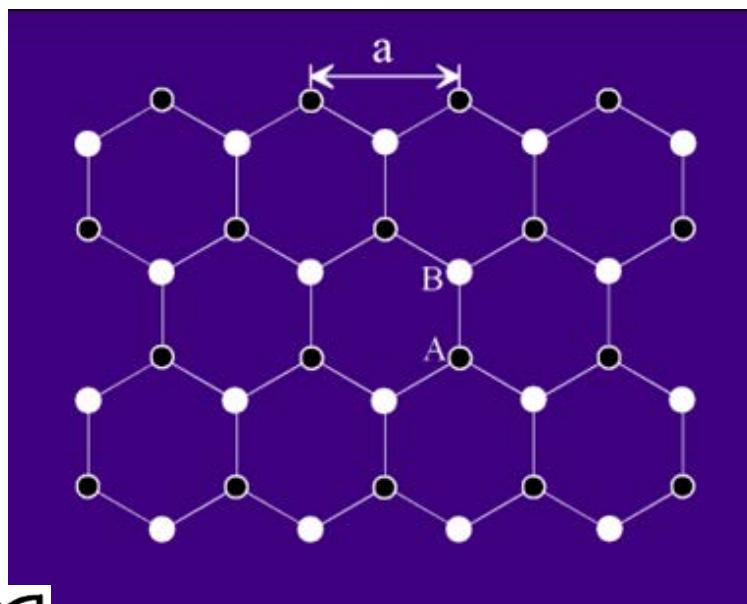
What is graphene?

In 2004, graphene was discovered by Andre Geim and Kostya Novoselov (Univ. of Manchester).



Science 306, 666 (2004)

2010 Nobel Prize in Physics



Q1. How thick is it? million times thinner than paper
(The interlayer spacing : 0.33~0.36 nm)

Q2. How strong is it? stronger than diamond
(Maximum Young's modulus : ~1.3 TPa)

Q3. How conductive is it? better than copper
(The resistivity : $10^{-6} \Omega \cdot \text{cm}$)
(Mobility: 200,000 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)

Novel Phenomena in Graphene

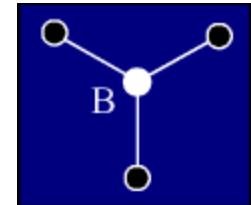
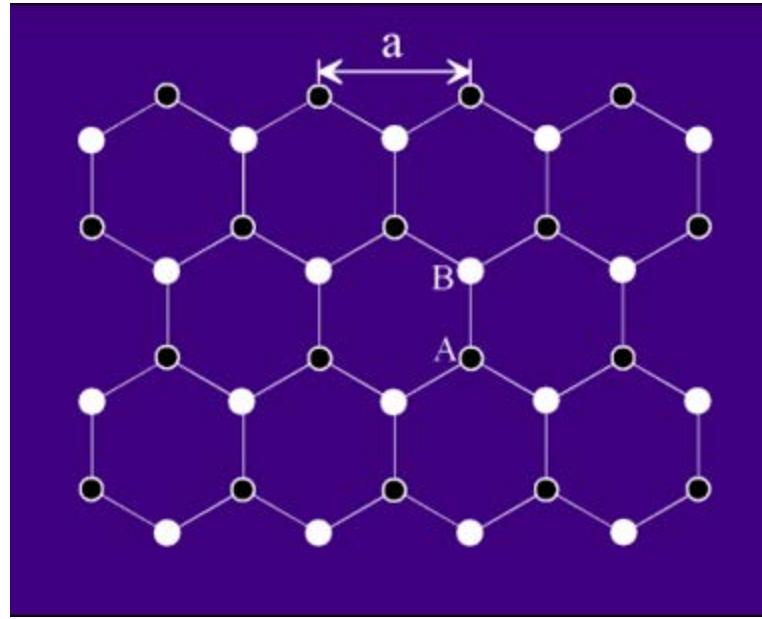
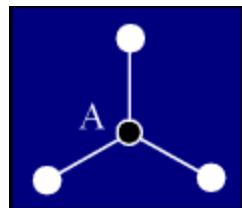
- Quantun Hall effect
- Fractional QHE
- Berry's phase
- Klein tunneling
- Kondo Effect
- Majorana Fermion

Potential Applications of Graphene

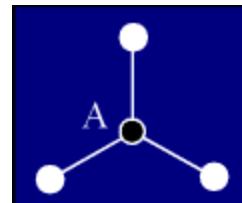
- Membranes for ultra filtration
- Composites and coating
- Energy storage
- Biomedical
- Sensors
- Fast Electronic devices



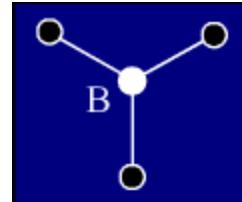
2 different ways of orienting bonds means there are 2 different types of atomic sites



Sublattice \equiv Pseudospin



$\equiv |A\rangle$ or spin up (\uparrow)



$\equiv |B\rangle$ or spin down (\downarrow)

Bandstructure of Monolayer Graphene

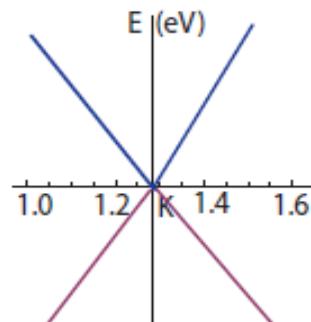
Define Unit Cell



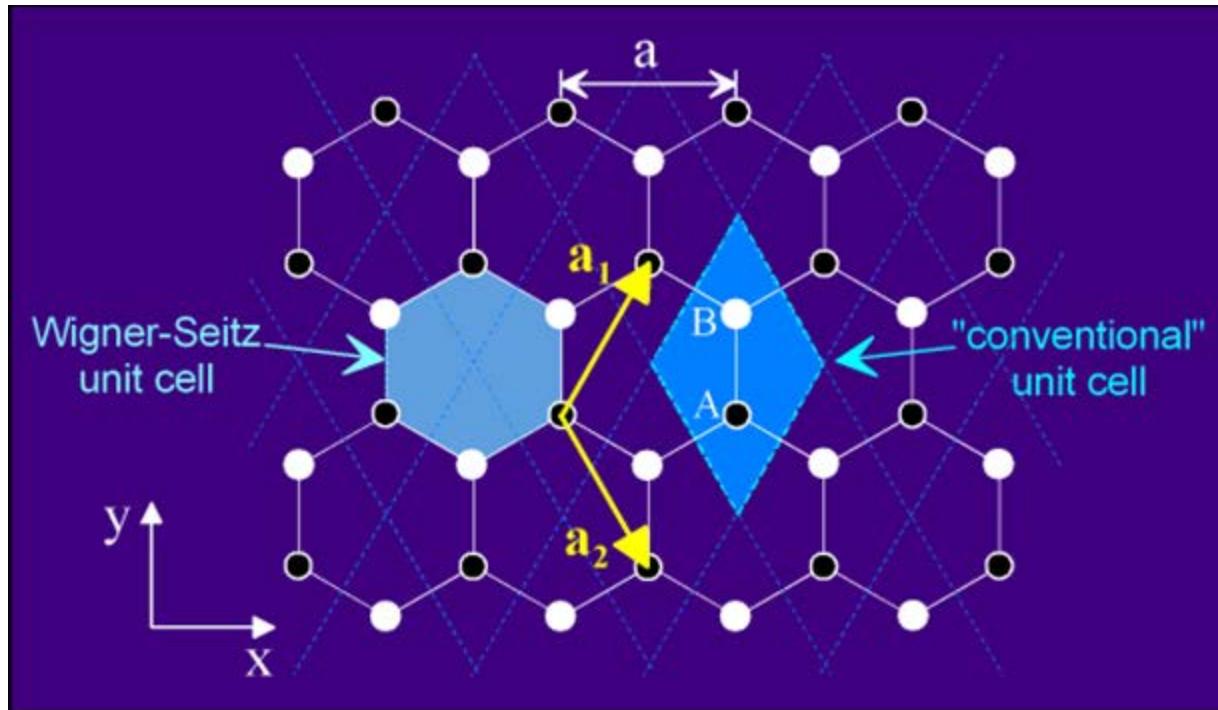
Tight Binding Model



Energy Dispersion Relation (E vs k plot)



Unit Cell



Two atoms per unit cell

Triangular/rhombic/hexagonal unit cell – hexagonal Brillouin zone

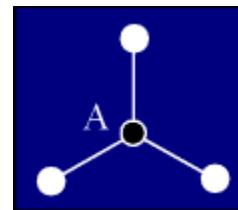
Tight binding model of monolayer graphene

Bloch functions

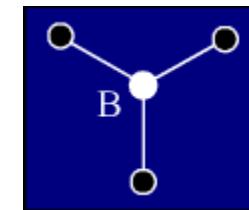
$$\Phi_j(\vec{k}, \vec{r}) = \frac{1}{\sqrt{N}} \sum_{\vec{R}_j}^N e^{i\vec{k} \cdot \vec{R}_j} \varphi_j(\vec{r} - \vec{R}_j)$$

sum over all type
j(i) atomic sites
in N unit cells

atomic
wavefunction



$j=1$ (A sites)



$j=2$ (B sites)

$$H_{ij} = \langle \Phi_i | H | \Phi_j \rangle; \quad S_{ij} = \langle \Phi_i | \Phi_j \rangle$$

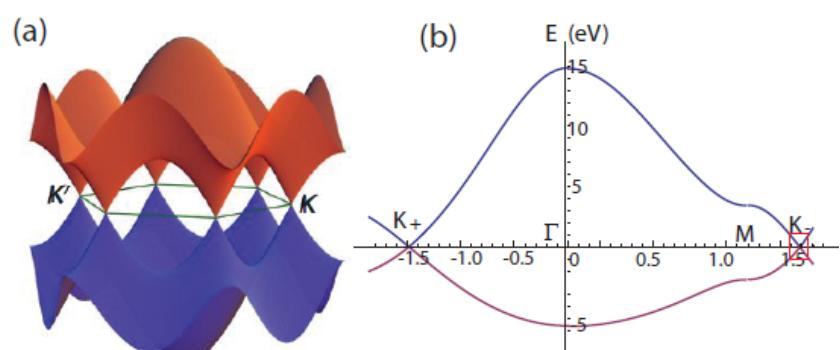
$$H = \begin{pmatrix} \varepsilon_0 & -\gamma_0 f(\vec{k}) \\ -\gamma_0 f^*(\vec{k}) & \varepsilon_0 \end{pmatrix}; \quad S = \begin{pmatrix} 1 & sf(\vec{k}) \\ sf^*(\vec{k}) & 1 \end{pmatrix}$$

$$f(\vec{k}) = \sum_{\delta_j=1}^3 e^{i\vec{k} \cdot \vec{\delta}_j} = e^{ik_y a / \sqrt{3}} + 2e^{-ik_y a / 2\sqrt{3}} \cos\left(\frac{k_x a}{2}\right)$$

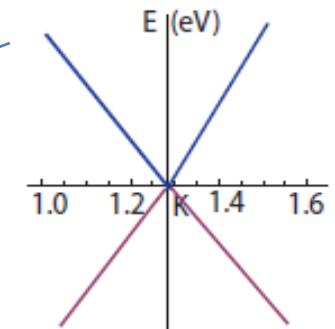
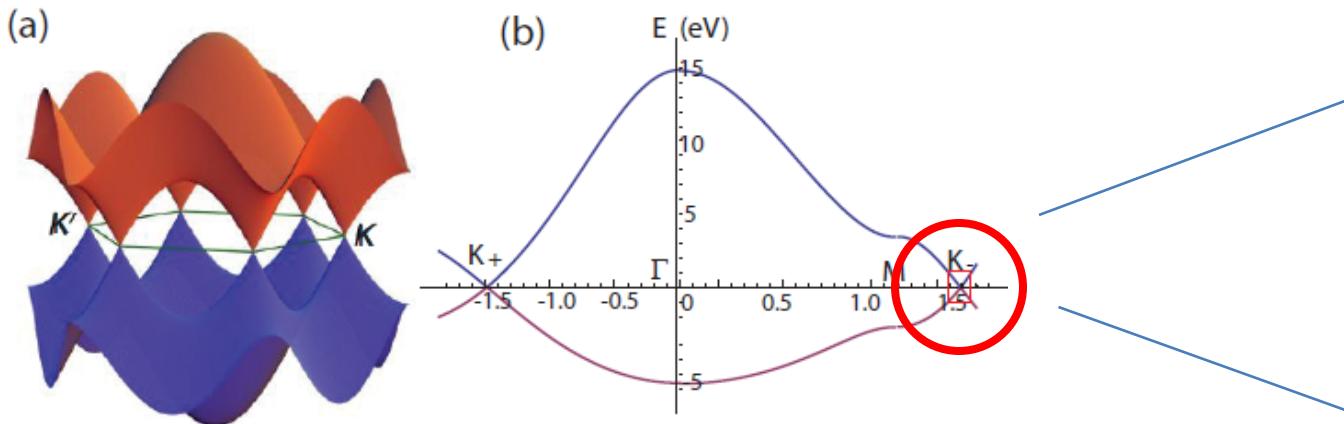
$$\det(H - ES) = 0$$

$$\det \begin{pmatrix} \varepsilon_0 - E & -(\gamma_0 + Es)f(\vec{k}) \\ -(\gamma_0 + Es)f^*(\vec{k}) & \varepsilon_0 - E \end{pmatrix} = 0$$

$$E = \frac{\varepsilon_0 \pm \gamma_0 |f(\vec{k})|}{1 \mp s |f(\vec{k})|}$$



Low Energy Properties



Expansion around K-points:

$$f(\vec{k}) = \sum_{\vec{\delta}_j=1}^3 e^{i\vec{k} \cdot \vec{\delta}_j} = e^{ik_y a / \sqrt{3}} + 2e^{-ik_y a / 2\sqrt{3}} \cos\left(\frac{k_x a}{2}\right) = -\frac{\sqrt{3}a}{2\hbar} (p_x - ip_y) + O(pa/\hbar)^2$$

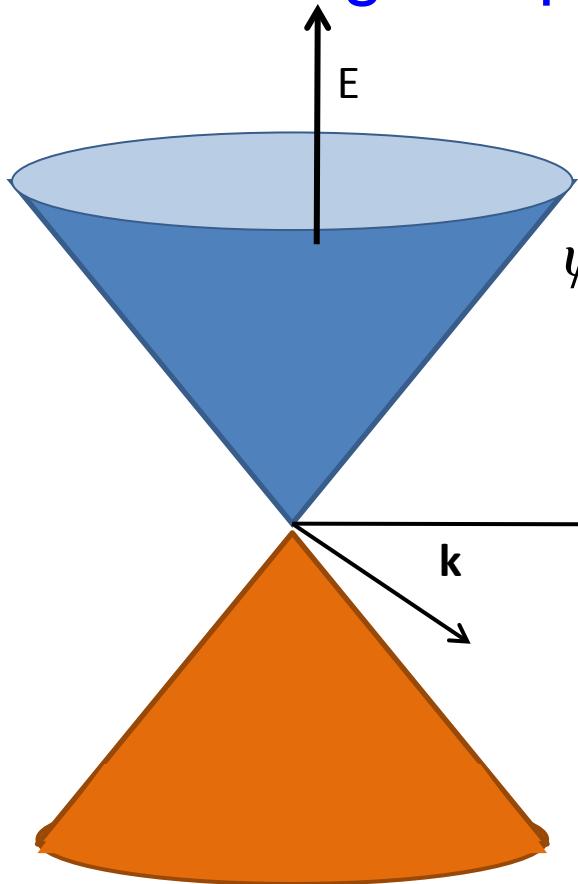
$$H = \begin{pmatrix} 0 & -\gamma_0 f(\vec{k}) \\ -\gamma_0 f^*(\vec{k}) & 0 \end{pmatrix} \approx v \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix} \quad S = \begin{pmatrix} 1 & sf(\vec{k}) \\ sf^*(\vec{k}) & 1 \end{pmatrix} \approx \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + O\left(\frac{spa}{\hbar}\right)$$

$$H = v \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix} = v \begin{pmatrix} 0 & \pi^+ \\ \pi & 0 \end{pmatrix} = v (\sigma_x p_x + \sigma_y p_y) = v \vec{\sigma} \cdot \vec{p}$$

$$v \begin{pmatrix} 0 & p_x - ip_y \\ p_x + ip_y & 0 \end{pmatrix} \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} = E \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix}$$

$$v = \frac{\sqrt{3}a\gamma_0}{2\hbar} \approx 10^6 m/s$$

Schrodinger equation to Dirac equation at low energy



$$\psi = \begin{pmatrix} \psi_{+A} \\ \psi_{+B} \end{pmatrix}$$

$$\psi = \begin{pmatrix} \psi_{-A} \\ \psi_{-B} \end{pmatrix}$$

$$\psi = \begin{pmatrix} \psi_{+A} \\ \psi_{+B} \\ \psi_{-A} \\ \psi_{-B} \end{pmatrix}$$

+,- valley index
A,B sublattice (pseudospin) index

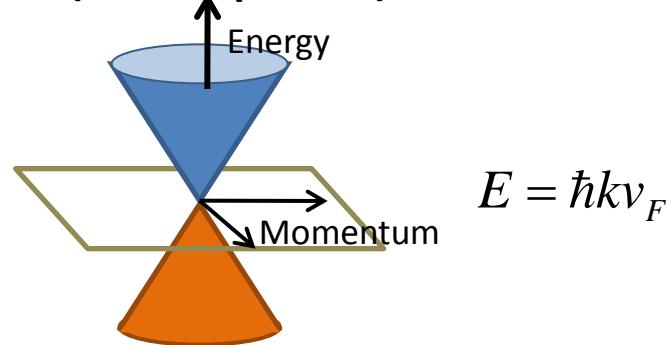
$$H = v \begin{pmatrix} 0 & p_x - ip_y & 0 & 0 \\ p_x + ip_y & 0 & 0 & 0 \\ 0 & 0 & 0 & -p_x - ip_y \\ 0 & 0 & -p_x + ip_y & 0 \end{pmatrix}$$

Electrons in usual solids (Schrodinger equation)



$$E = \frac{\hbar^2 k^2}{2m^*}$$

Electrons in graphene (Dirac equation)



$$E = \hbar k v_F$$

$$H = v \begin{pmatrix} 0 & \pi^+ \\ \pi^- & 0 \end{pmatrix} = v \vec{\sigma} \cdot \vec{p} = vp \ \vec{\sigma} \cdot \vec{n}$$

Electrons and holes in condensed matter physics are normally described by separate Schrödinger equations, which are not in any way connected (**Seitz sum rule**).

In contrast, electron and hole states in graphene are interconnected, analogous to the charge-conjugation symmetry in QED. This allows one to introduce **chirality** – formally a projection of pseudospin on the direction of motion – which is positive and negative for electrons and holes, respectively.

$$\vec{\sigma} \cdot \vec{n} = 1$$

$$\vec{\sigma} \cdot \vec{n} = -1$$

Electrons(holes) are chiral.

Electrons in conduction band and holes in valence band are entangled.

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Growth and Characterization Graphene



How we grow graphene monolayer

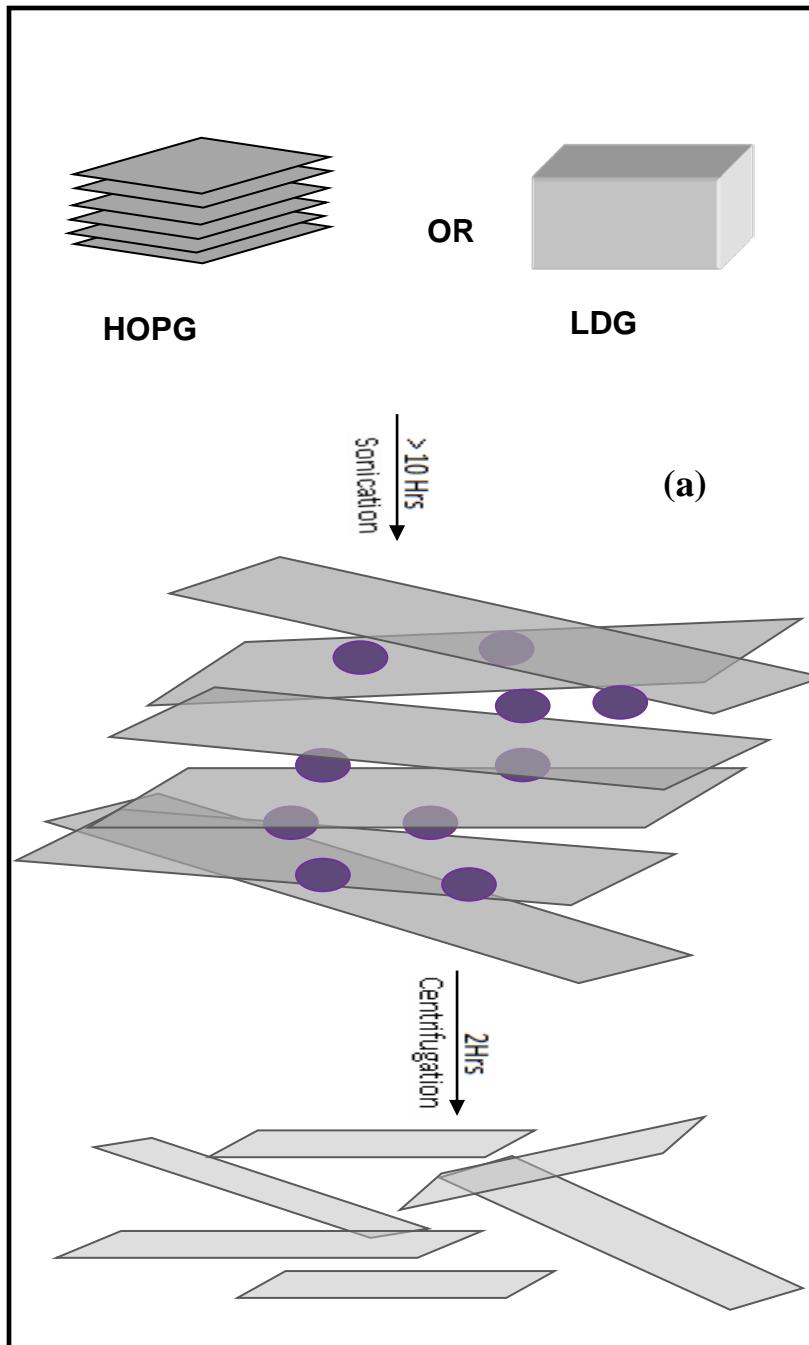
- Mechanical Exfoliation
- Chemical Exfoliation
- Chemical Vapor Deposition



A New (?) Method for Growth of High Quality Monolayer, Bilayer and Multilayer Graphene

Controllability & Reproducibility

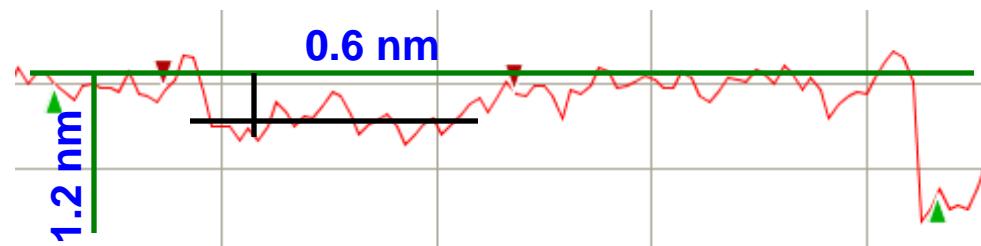
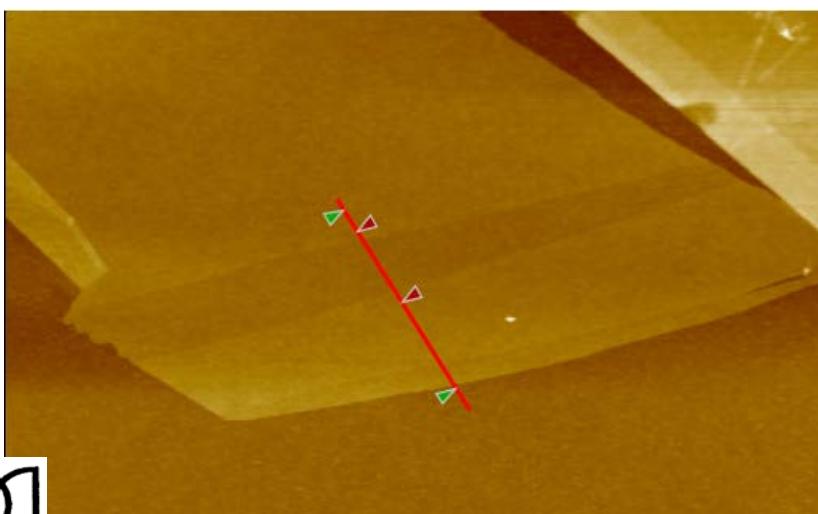
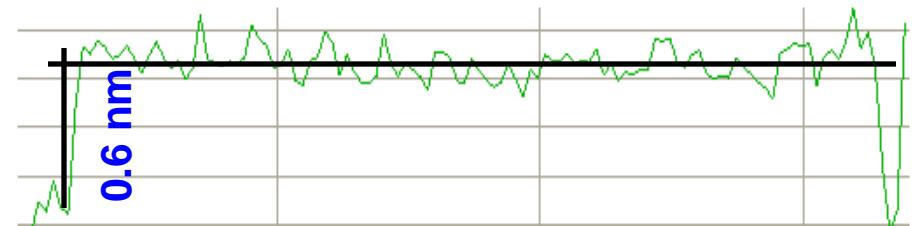
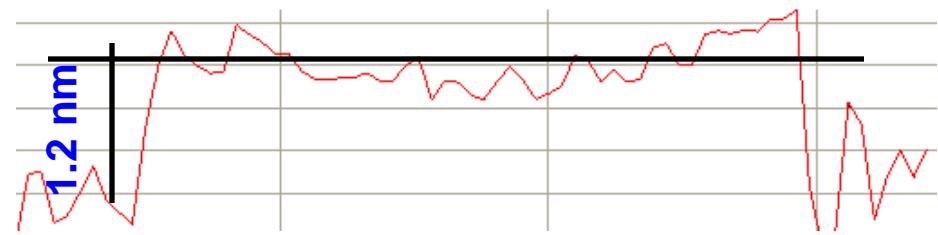
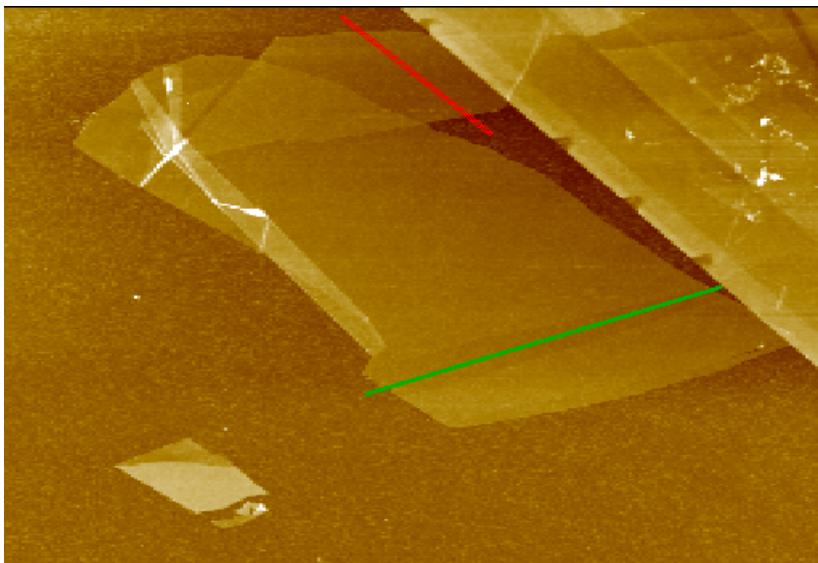




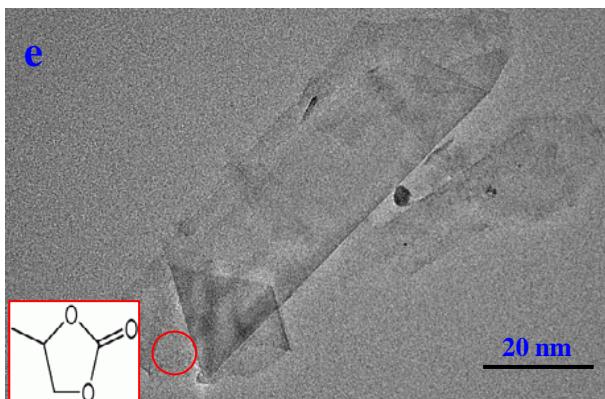
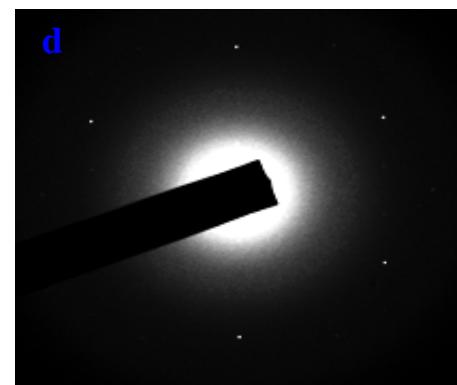
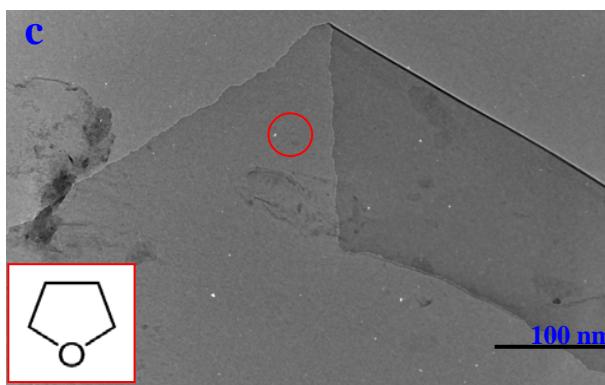
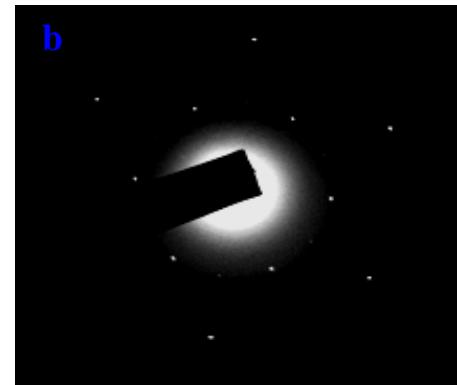
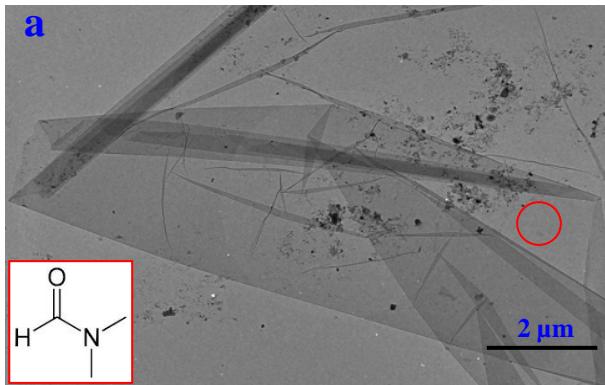
● → **Organic Molecules**
Also with water

Atomic Force Microscopy

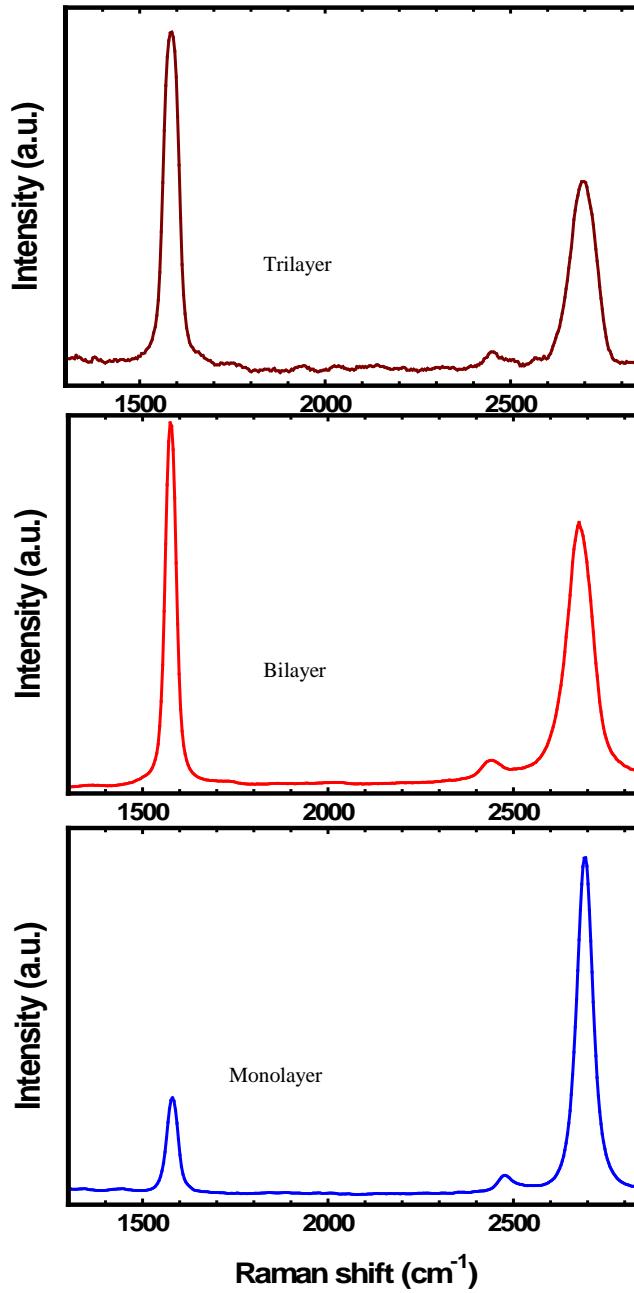
(Graphene sheet synthesized in Propylene carbonate)



Transmission electron microscopy



Excellent Control of No of Layers



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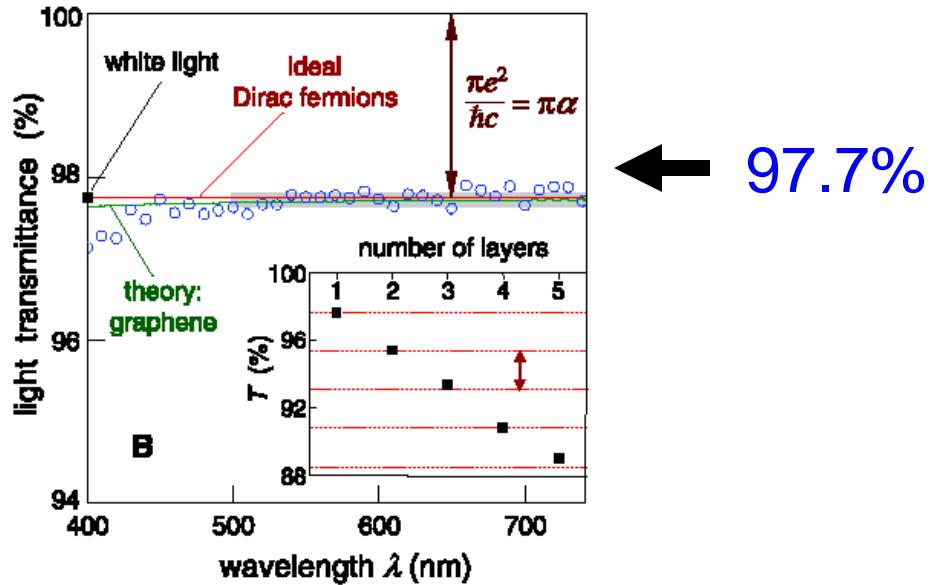
Fine Structure Constant Defines Visual Transparency of Graphene

R. R. Nair,¹ P. Blake,¹ A. N. Grigorenko,¹ K. S. Novoselov,¹ T. J. Booth,¹ T. Stauber,² N. M. R. Peres,² A. K. Geim^{1*}

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$$T = (1 - \pi\alpha)$$

$$\alpha = \frac{1}{137}$$

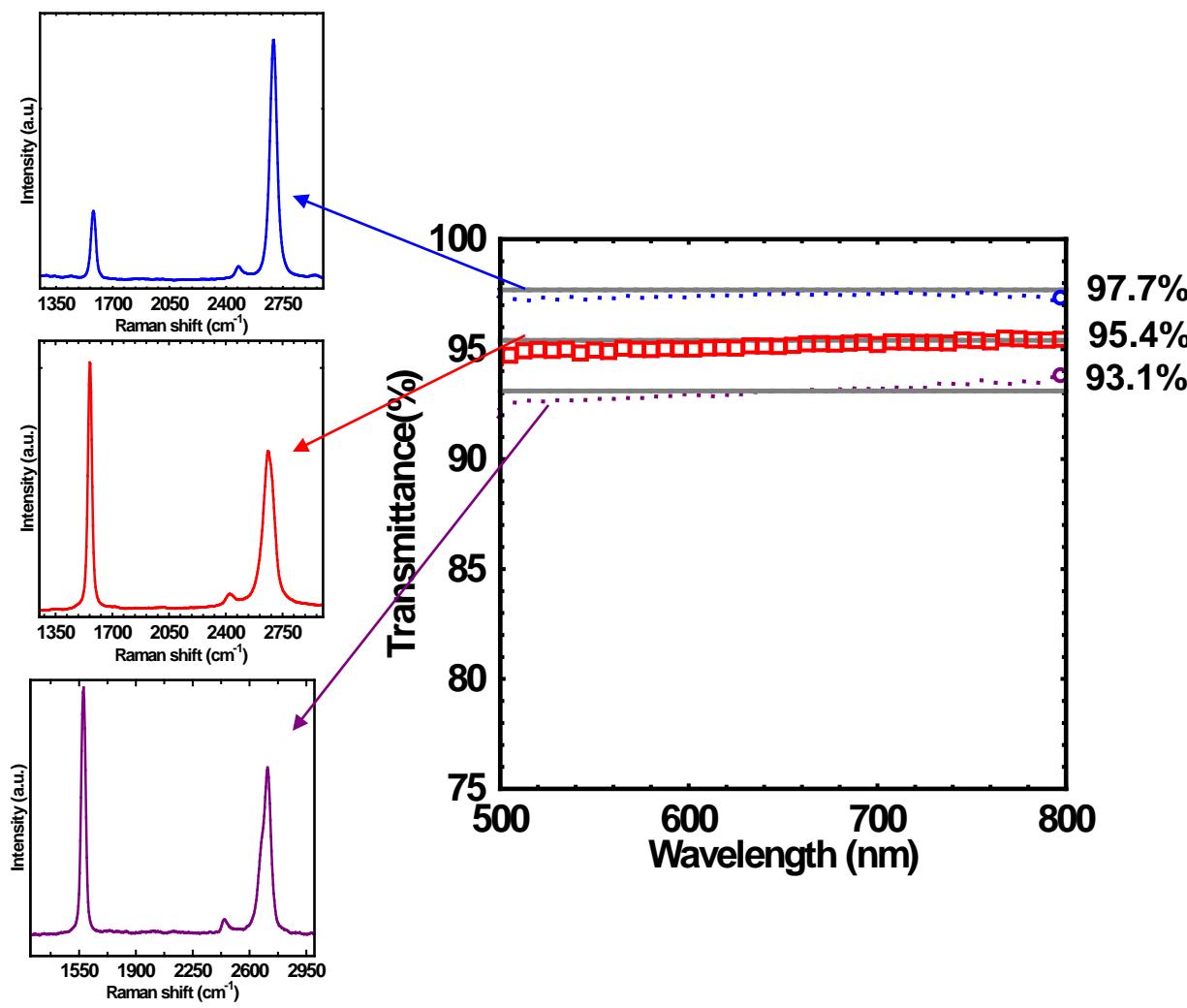


Origin: Dirac cone (linear dispersion) and optical properties are dictated by QED

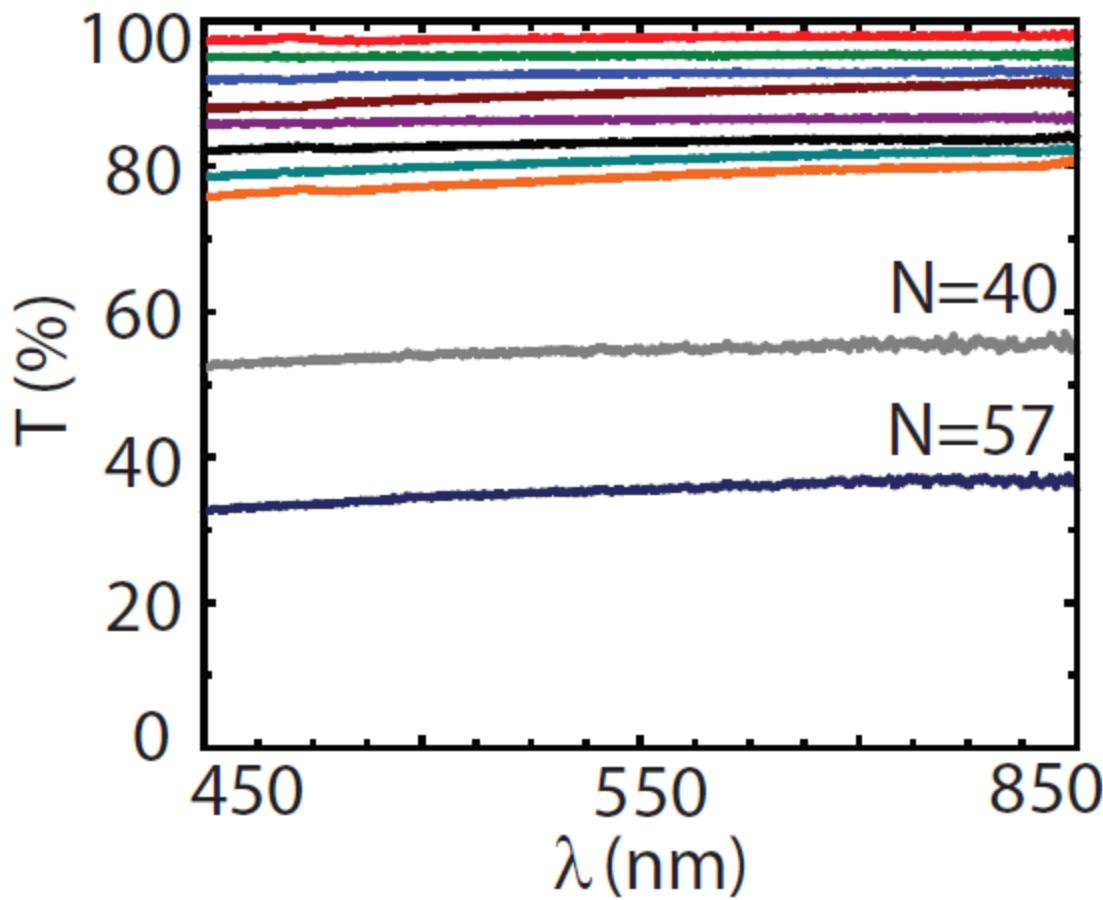
What about bilayer, trilayer.....multilayer ?

Does it depend on inter layer coupling ?





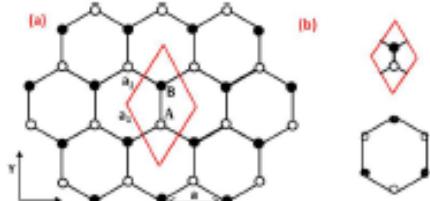
$$T = (1 - N\pi\alpha)$$



Universal in monolayer to multilayer graphene.

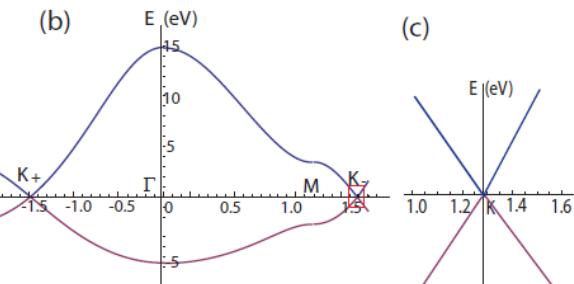
No effect of interlayer coupling.

Monolayer

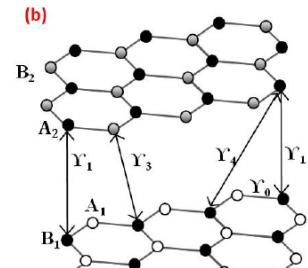


$$H_1 = \begin{bmatrix} \varepsilon_A & -\gamma_0 f(\mathbf{k}) \\ -\gamma_0 f^*(\mathbf{k}) & \varepsilon_B \end{bmatrix} \quad S_1 = \begin{bmatrix} 1 & s_0 f(\mathbf{k}) \\ s_0 f^*(\mathbf{k}) & 1 \end{bmatrix}$$

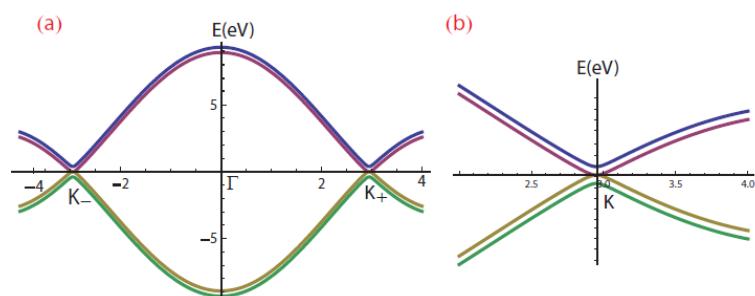
$$\det(H_1 - E_i S_1) = 0 \quad E_{\pm} = \frac{\varepsilon_{2p} \pm \gamma_0 |f(\mathbf{k})|}{1 \mp s_0 |f(\mathbf{k})|}$$



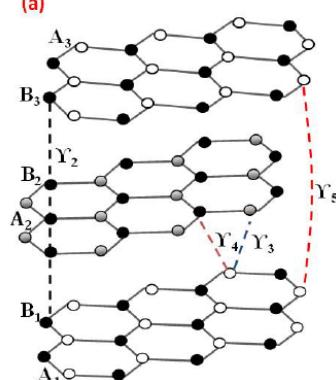
Bilayer



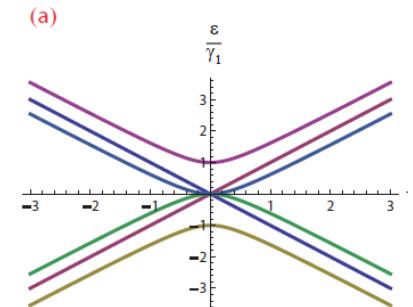
$$H_2 = \begin{array}{cccc} A_1 & B_1 & A_2 & B_2 \\ \begin{pmatrix} \varepsilon_{A_1} & -\gamma_0 f(\mathbf{k}) & \gamma_4 f(\mathbf{k}) & -\gamma_3 f^*(\mathbf{k}) \\ -\gamma_0 f^*(\mathbf{k}) & \varepsilon_{B_1} & \gamma_1 & \gamma_4 f(\mathbf{k}) \\ \gamma_4 f^*(\mathbf{k}) & \gamma_1 & \varepsilon_{A_2} & -\gamma_0 f(\mathbf{k}) \\ -\gamma_3 f(\mathbf{k}) & \gamma_4 f^*(\mathbf{k}) & -\gamma_0 f^*(\mathbf{k}) & \varepsilon_{B_2} \end{pmatrix} \end{array}$$



Trilayer

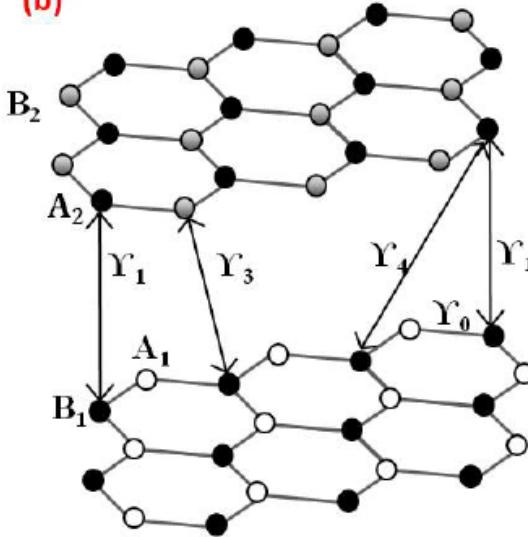


$$H_3 = \begin{array}{ccccccc} A_1 & B_1 & A_2 & B_2 & A_3 & B_3 \\ \begin{pmatrix} \varepsilon_{A_1} & -\gamma_0 f(\mathbf{k}) & \gamma_4 f(\mathbf{k}) & -\gamma_3 f^*(\mathbf{k}) & \gamma_2 & 0 \\ -\gamma_0 f^*(\mathbf{k}) & \varepsilon_{B_1} & \gamma_1 & \gamma_4 f(\mathbf{k}) & 0 & \gamma_5 \\ \gamma_4 f^*(\mathbf{k}) & \gamma_1 & \varepsilon_{A_2} & -\gamma_0 f(\mathbf{k}) & \gamma_4 f^*(\mathbf{k}) & \gamma_1 \\ -\gamma_3 f(\mathbf{k}) & \gamma_4 f^*(\mathbf{k}) & -\gamma_0 f^*(\mathbf{k}) & \varepsilon_{B_2} & -\gamma_3 f(\mathbf{k}) & \gamma_4 f^*(\mathbf{k}) \\ \gamma_2 & 0 & \gamma_4 f(\mathbf{k}) & -\gamma_3 f^*(\mathbf{k}) & \varepsilon_{A_3} & -\gamma_0 f(\mathbf{k}) \\ 0 & \gamma_5 & \gamma_1 & \gamma_4 f(\mathbf{k}) & -\gamma_0 f^*(\mathbf{k}) & \varepsilon_{B_3} \end{pmatrix} \end{array} \quad (2.38)$$



Bilayer Graphene : 4 atoms per unit cell

(b)



$$\mathbf{H}_2 = \begin{pmatrix} A_1 & B_1 & A_2 & B_2 \\ A_1 & \varepsilon_{A_1} & v\pi^\dagger & -v_4\pi^\dagger & v_3\pi \\ B_1 & v\pi & \varepsilon_{B_1} & \gamma_1 & -v_4\pi^\dagger \\ A_2 & -v_4\pi & \gamma_1 & \varepsilon_{A_2} & v\pi^\dagger \\ B_2 & v_3\pi^\dagger & -v_4\pi & v\pi & \varepsilon_{B_2} \end{pmatrix}$$

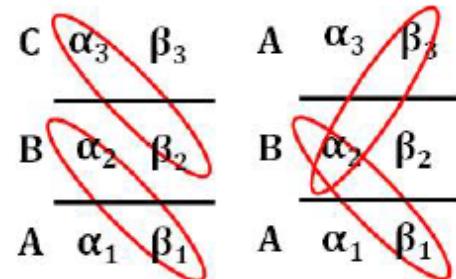
$$\mathbf{H}_2 = \begin{bmatrix} h_\theta & u \\ u^\dagger & h_\chi \end{bmatrix}$$

$$h_\theta = \begin{pmatrix} A_2 & B_1 \\ B_1 & A_2 \end{pmatrix} \begin{pmatrix} \varepsilon_{A_1} & v_3\pi \\ v_3\pi^\dagger & \varepsilon_{B_2} \end{pmatrix} h_\chi = \begin{pmatrix} A_2 & B_1 \\ B_1 & A_2 \end{pmatrix} \begin{pmatrix} \varepsilon_{A_2} & \gamma_1 \\ \gamma_1 & \varepsilon_{B_1} \end{pmatrix} u = \begin{pmatrix} A_1 & B_2 \\ B_2 & A_1 \end{pmatrix} \begin{pmatrix} -v_4\pi^\dagger & v\pi^\dagger \\ v\pi & -v_4\pi \end{pmatrix} u^\dagger = \begin{pmatrix} A_1 & B_2 \\ B_2 & A_1 \end{pmatrix} \begin{pmatrix} -v_4\pi & v\pi^\dagger \\ v\pi & -v_4\pi^\dagger \end{pmatrix}$$

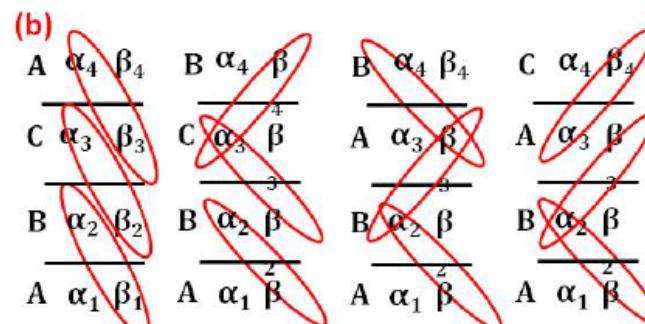
$$\mathbf{H}_2 = \frac{1}{2m} \begin{bmatrix} 0 & (\pi^\dagger)^2 \\ (\pi)^2 & 0 \end{bmatrix}$$

H. Min and A. H. MacDonald, Phys. Rev. Lett. 103, 067402 (2009).

$$\mathbf{H}_3 = \begin{bmatrix} h_\theta & u \\ u^\dagger & h_\chi \end{bmatrix}$$



$$\mathbf{H}_4 = \begin{bmatrix} h_\theta & u \\ u^\dagger & h_\chi \end{bmatrix}$$



$$\mathbf{H}_J = g_J \begin{bmatrix} 0 & (\pi^\dagger)^J \\ (\pi)^J & 0 \end{bmatrix} = \gamma_1 \left(\frac{v}{\gamma_1} \right)^J \begin{bmatrix} 0 & (\pi^\dagger)^J \\ (\pi)^J & 0 \end{bmatrix}$$

$$H_N^{eff} = H_{J_1} \otimes H_{J_2} \otimes H_{J_3} \otimes H_{J_4} \dots \dots \dots H_{J_N}$$

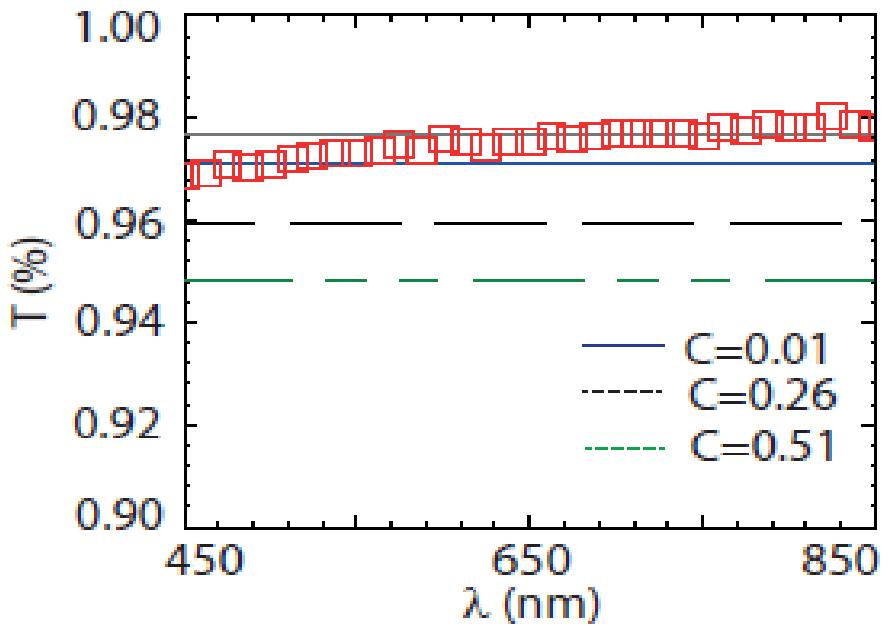
**Inspite of inter layer coupling ,
chirality is protected in
bilayer.....multilayerand graphite.**

**Hence it appears that chirality
and not linear dispersion is responsible
for optical transmittance universality.**

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**What is the effect of e-e interaction
on this universality ?**



$$\sigma(\omega) = \sigma(0) \left[1 + \frac{c \alpha}{\left(1 + \frac{\alpha}{4} \log(D/\omega) \right)} \right]$$

Europhys. Lett. 83, 17005 (2008) ($c=0.01$)

Phys. Rev. B 80, 193411 (2009) ($c=0.51$)

Phys. Rev. B 86, 115408 (2012). ($c=0.12$)

Phys. Rev. Lett. 114, 246801 (2015) ($c=0.26$)

Schrodinger Materials ($V \ll c$)

Galilean invariance

$$E_C = \frac{e^2}{\epsilon \langle r \rangle}$$

$$E_{KG} = \frac{p^2}{2m}$$

$$\alpha_G = \frac{E_C}{E_{KG}} = \frac{n_0}{n^{1/2}}$$

Dependent on carrier density

Dirac Materials ($V \leq c$)

Lorentzian invariance

$$E_C = \frac{e^2}{\epsilon \langle r \rangle}$$

$$E_{KL} = \hbar v_F \sqrt{\pi n}$$

$$\alpha_L = \frac{E_C}{E_{KL}} = \frac{e^2}{\epsilon \hbar v_F}$$

Independent on carrier density

How to dope graphene ?



Various routes to dope Graphene

Metal contacts

Phys. Rev. Lett.
101, 026803 (2008)
Phys. Rev. Lett.
104, 076807 (2010)

Substitutional

Nat. Commun. **6**:7123
doi: 10.1038/ncomms8123 (2015)
Nat. Commun. **6**:8098
doi: 10.1038/ncomms9098 (2015)

Covalent functionalization

Chem. Rev. **112**, 6156-6214
(2012)
J. Am. Chem. Soc. **135**, 8981-8988
(2013)

- graphene becomes disordered after doping
- difficult to dope both types(p and n)
- poor controllability
- low mobility

Substrate modification

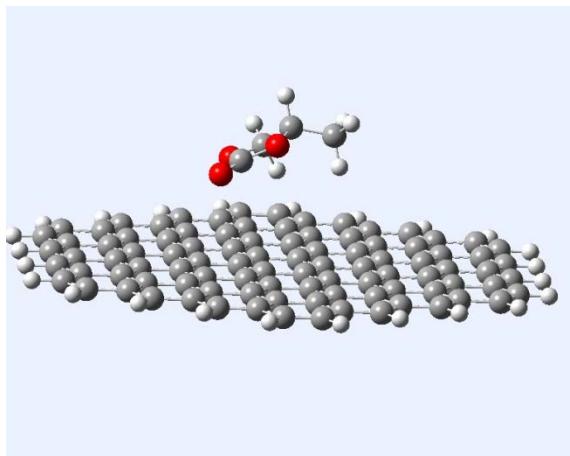
Adv. Mat. **26**, 8141-8146, (2014)
Sci. Rep. **6**, 21070, (2016)

Doping By Functionalization

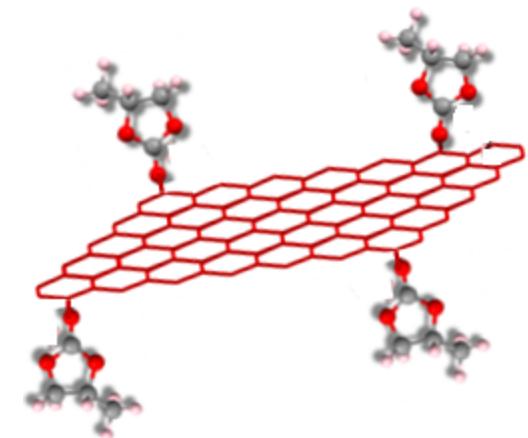
Weak
(supramolecular)

Medium

Covalent

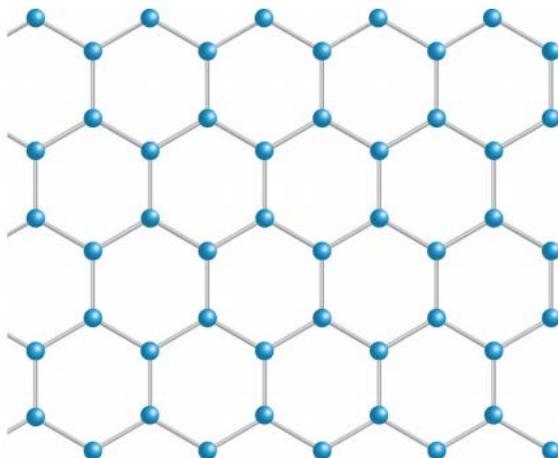


- high mobility
- no disorder



- low mobility
- disorder

Impermeability of Graphene

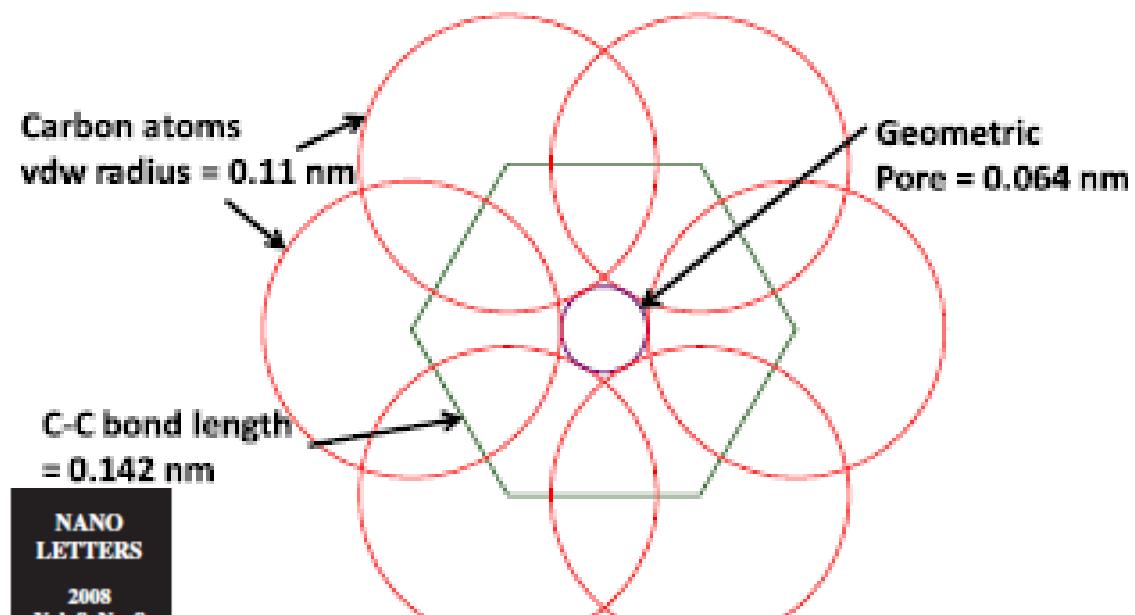


Impermeable Atomic Membranes from Graphene Sheets

J. Scott Bunch, Scott S. Verbridge, Jonathan S. Alden, Arend M. van der Zande, Jeevak M. Parpia, Harold G. Craighead, and Paul L. McEuen*

Cornell Center for Materials Research, Cornell University, Ithaca, New York 14853

Received May 21, 2008; Revised Manuscript Received June 12, 2008



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2008
Vol. 8, No. 8
2458-2462



ABSTRACT

We demonstrate that a monolayer graphene membrane is impermeable to standard gases including helium. By applying a pressure difference across the membrane, we measure both the elastic constants and the mass of a single layer of graphene. This pressurized graphene membrane is the world's thinnest balloon and provides a unique separation barrier between 2 distinct regions that is only one atom thick.

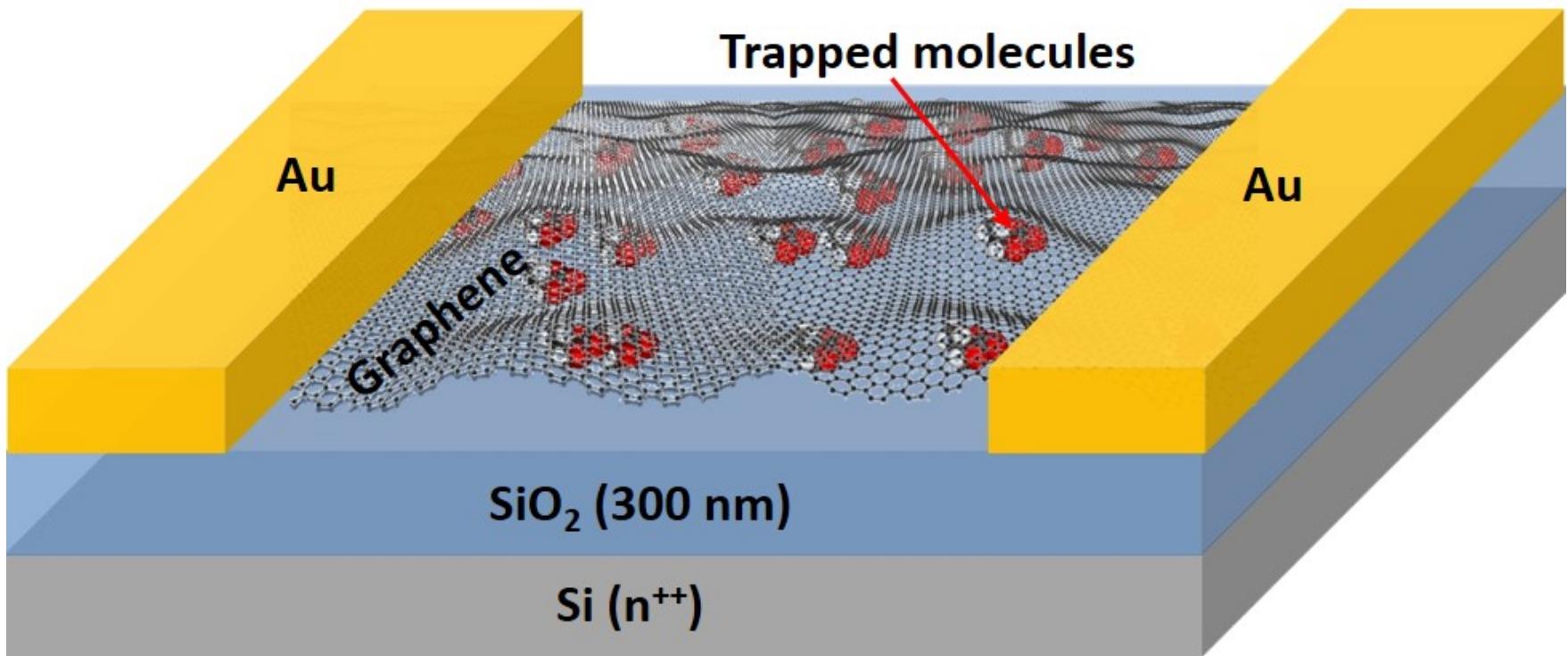
ARTICLE

Received 24 Apr 2014 | Accepted 29 Jul 2014 | Published 11 Sep 2014

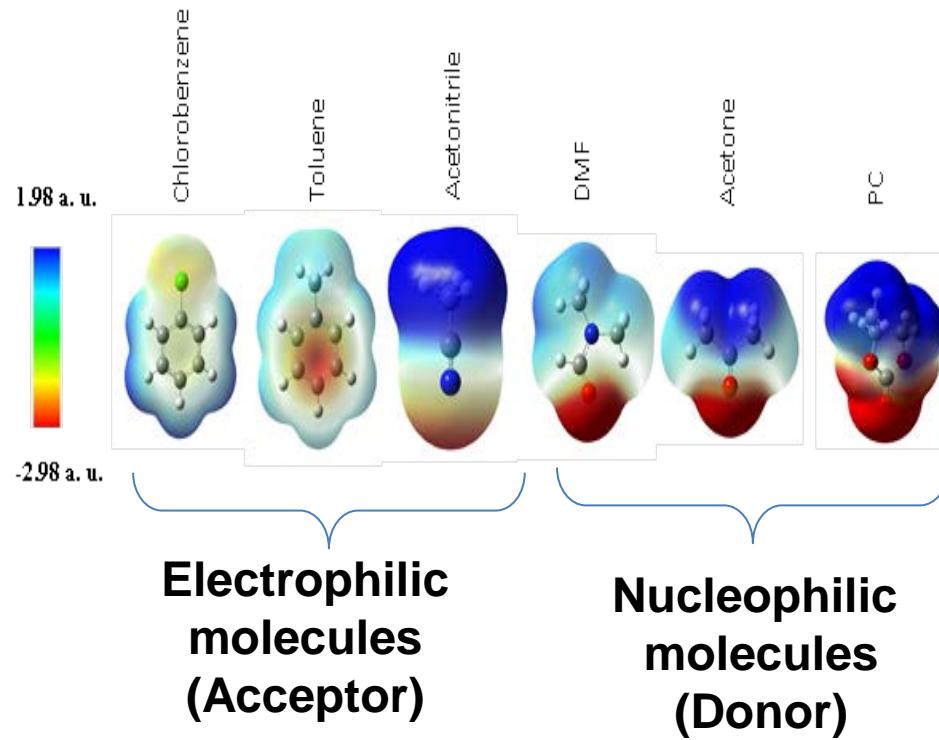
DOI: 10.1038/ncomms5843

Impermeable barrier films and protective coatings based on reduced graphene oxide

Y. Su¹, V.G. Kravets¹, S.L. Wong¹, J. Waters², A.K. Geim¹ & R.R. Nair¹

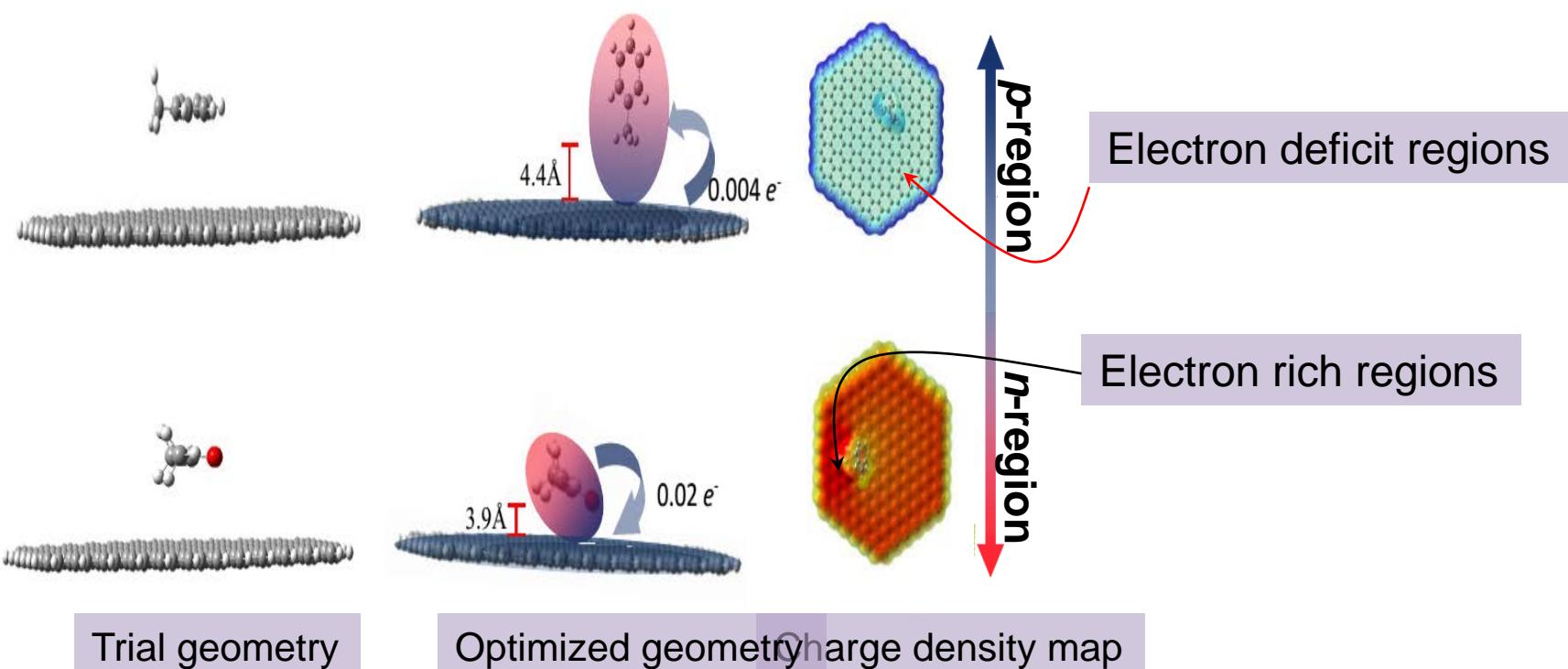


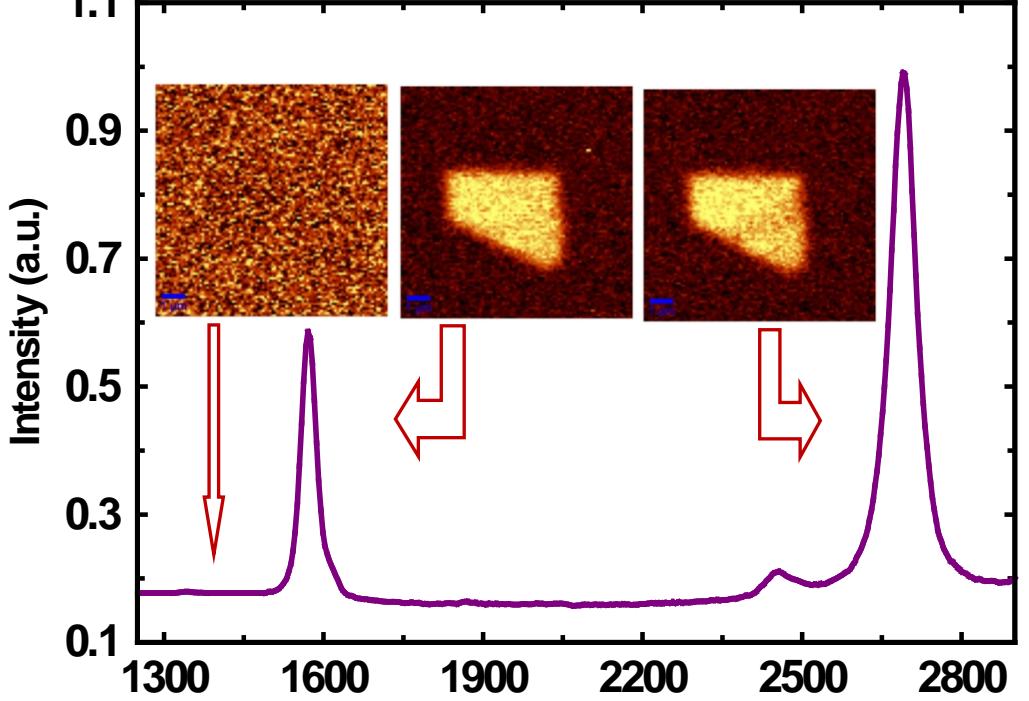
Doping tunability: Donor and acceptor nature of trapped molecules



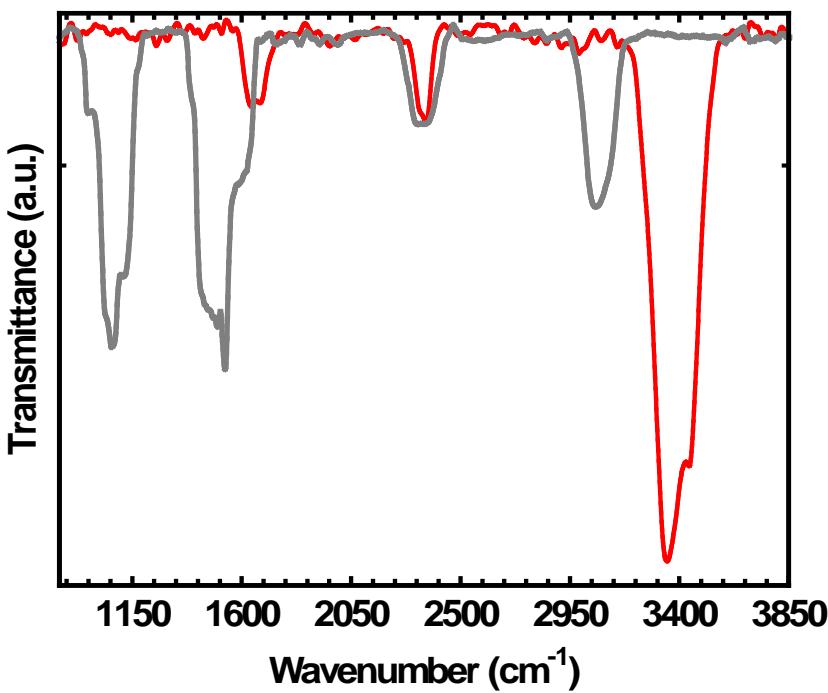
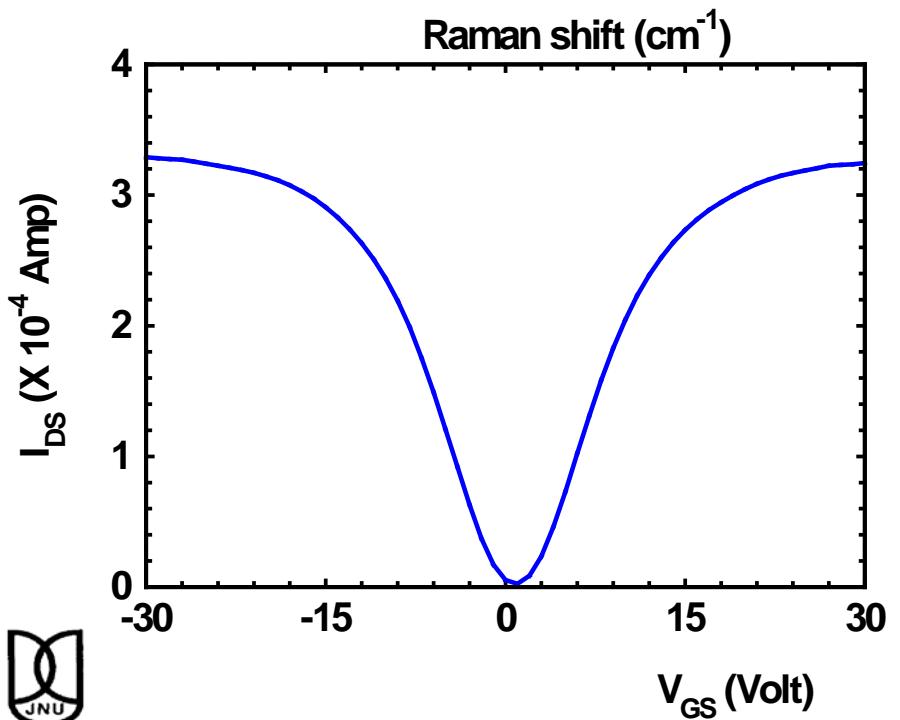
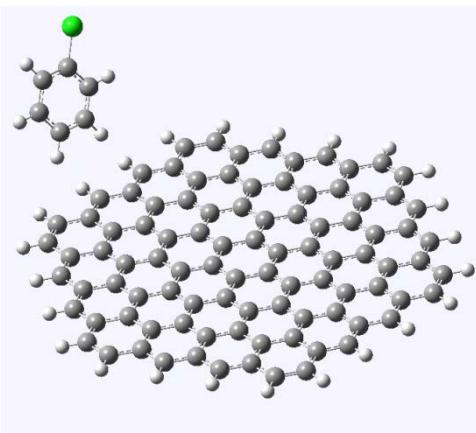
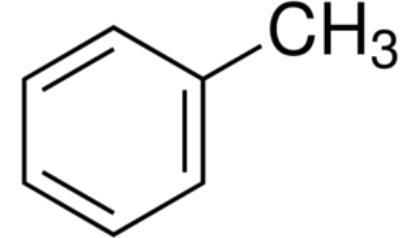
DFT calculations

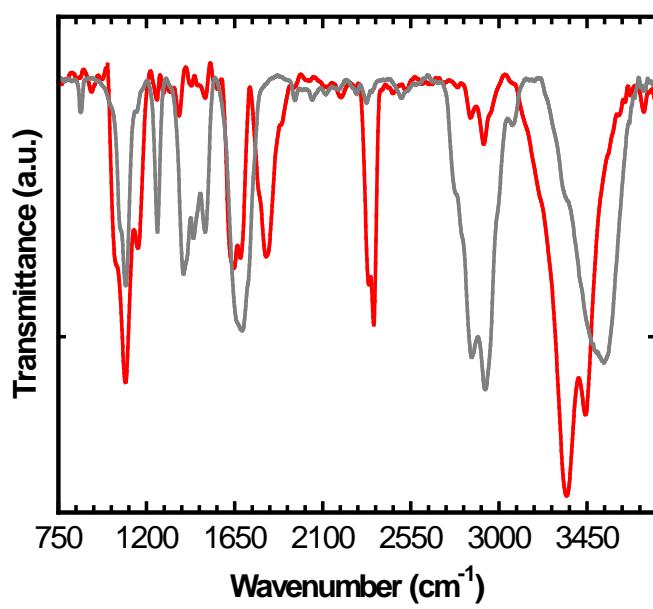
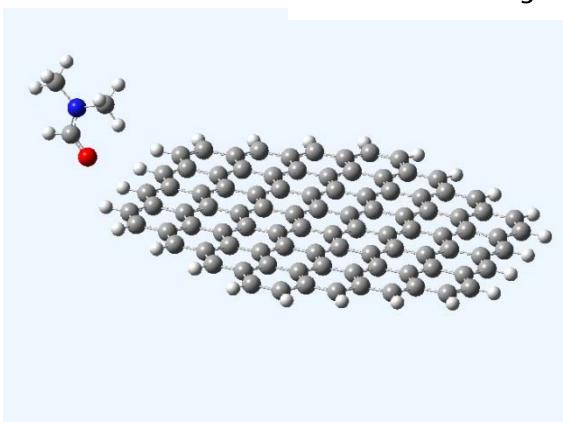
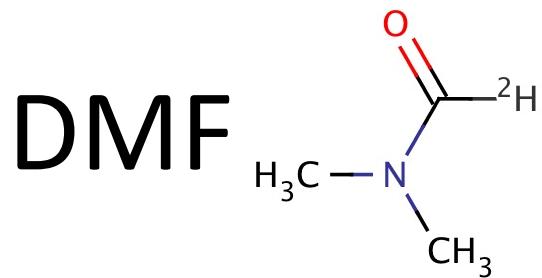
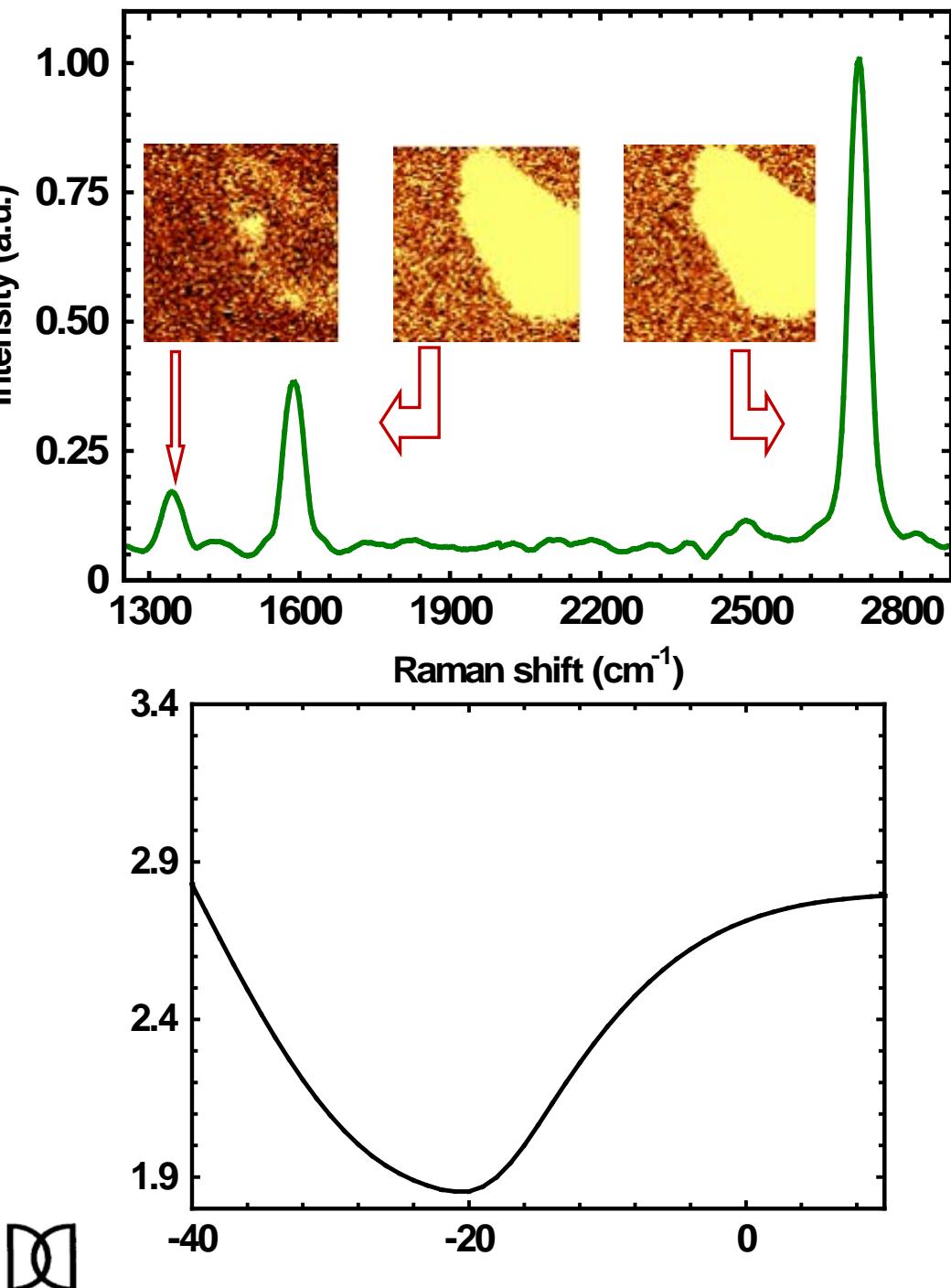
DFT calculations using Gaussian 9.0, using Lee-Yang-Parr correlation functional (B3LYP) with 631G-basis set

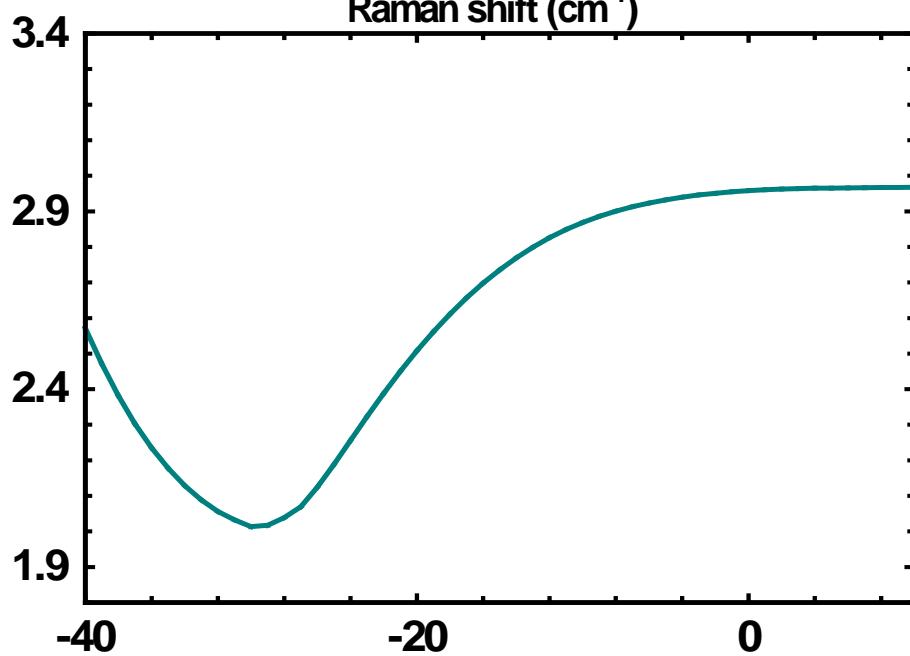
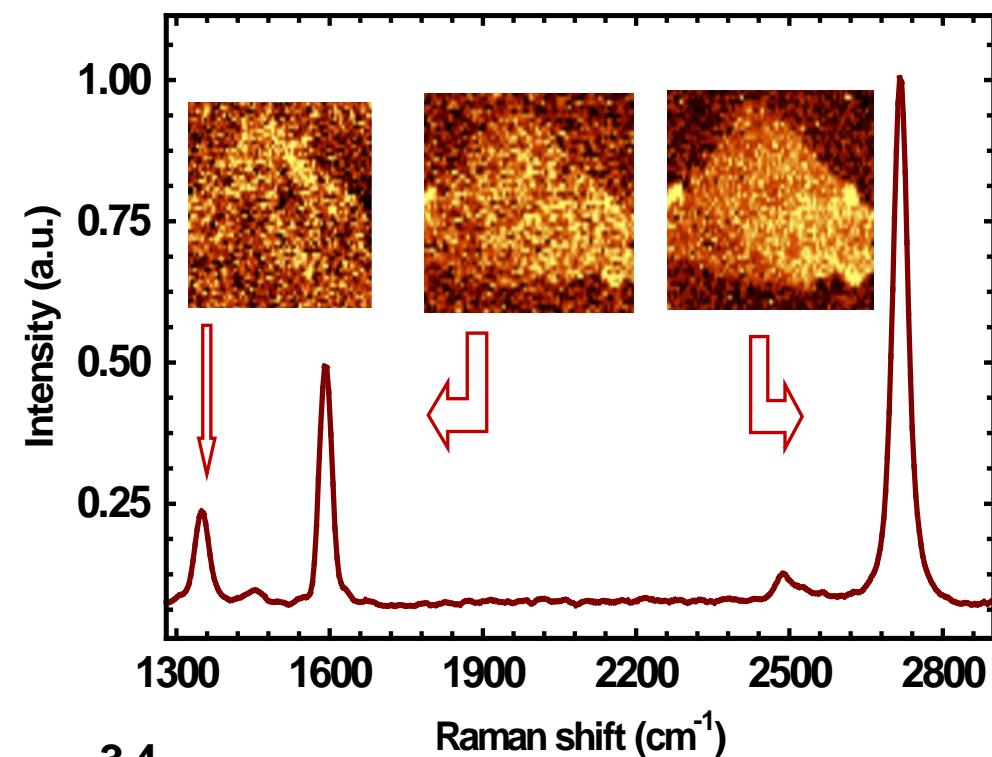




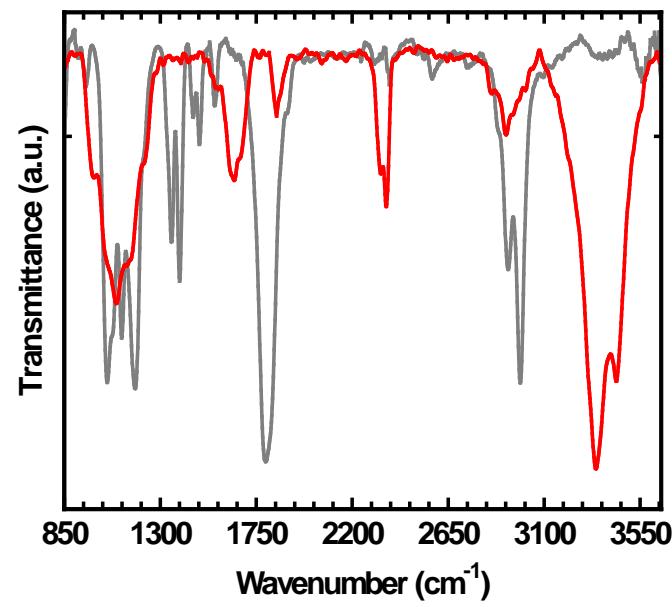
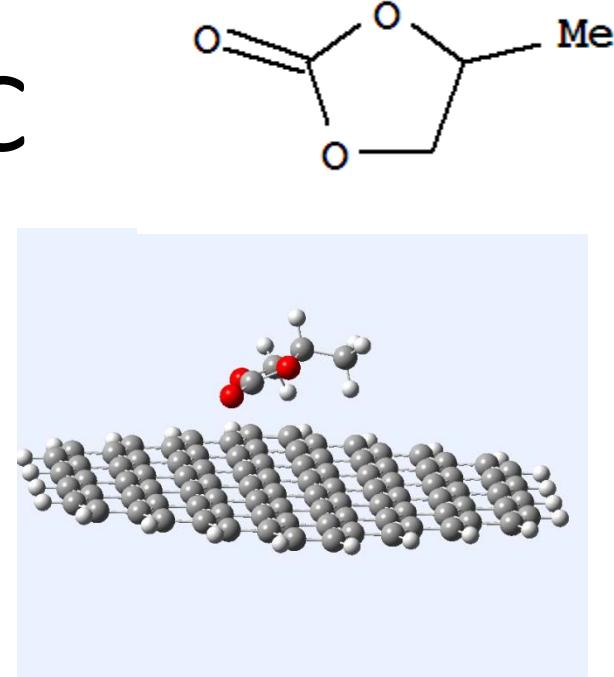
Toluene

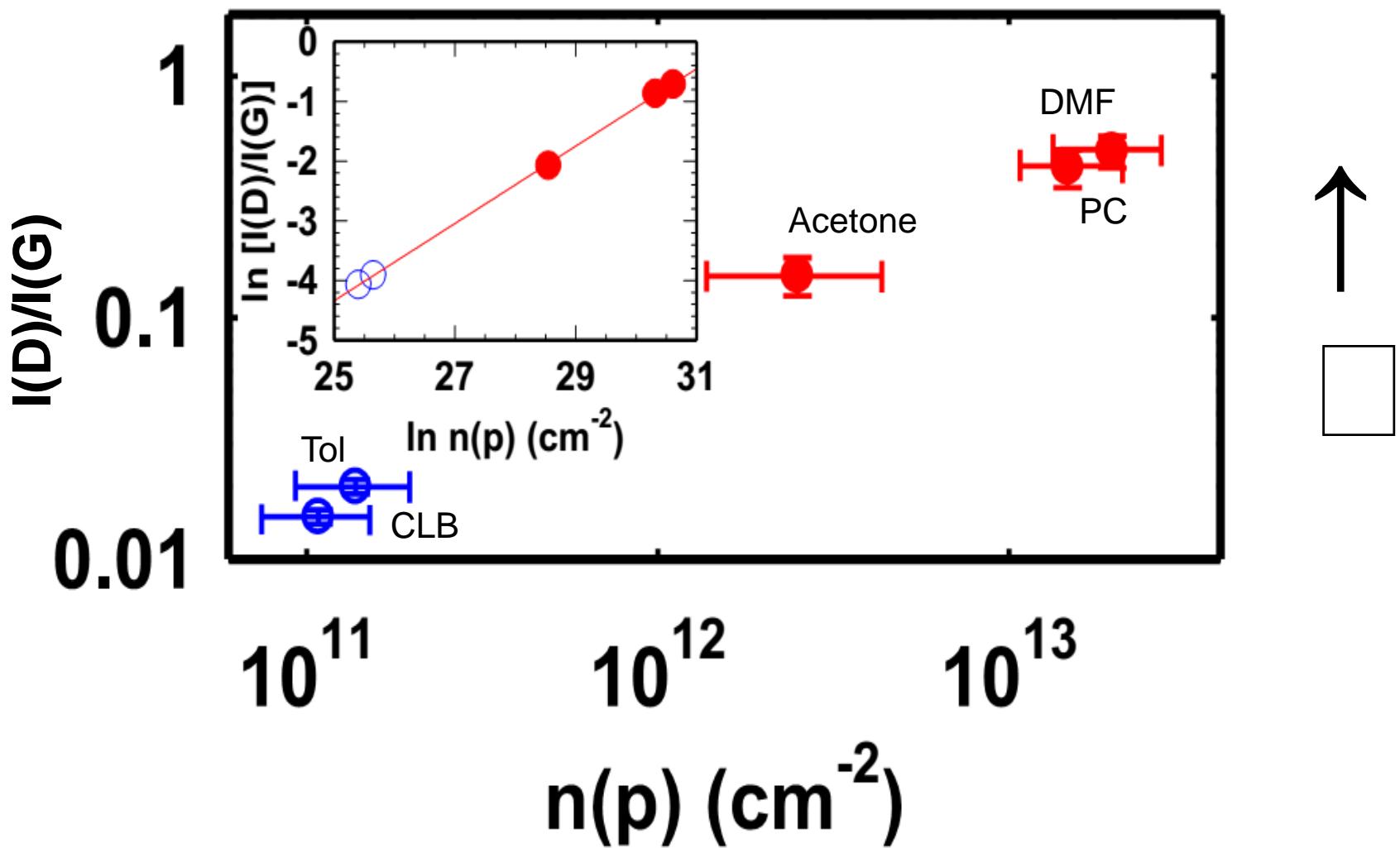


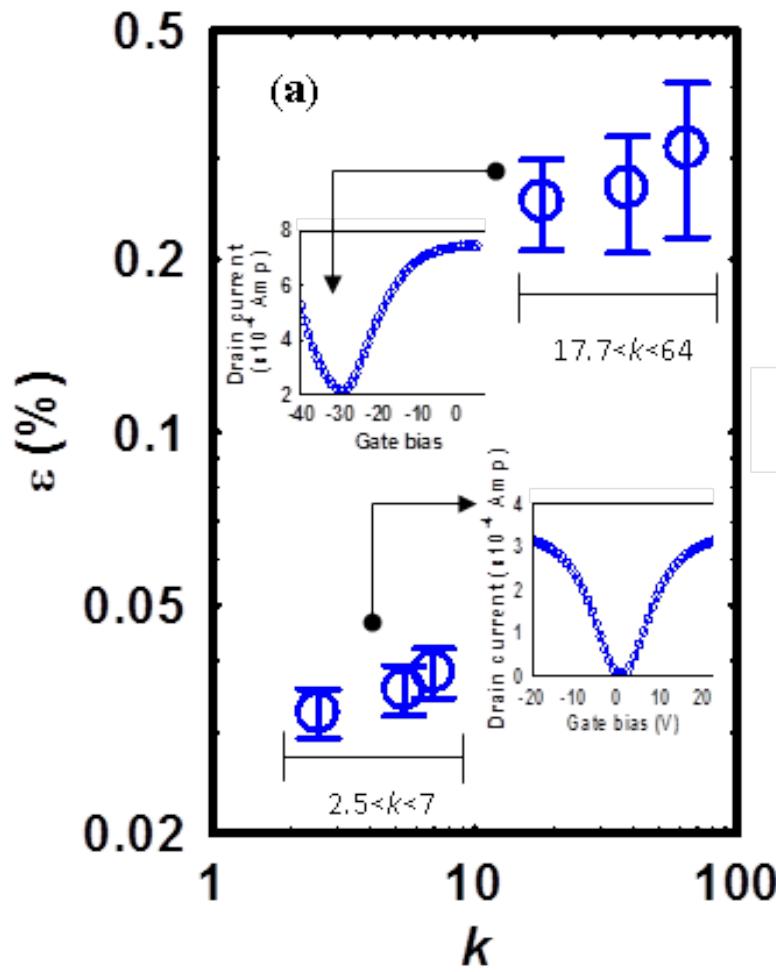
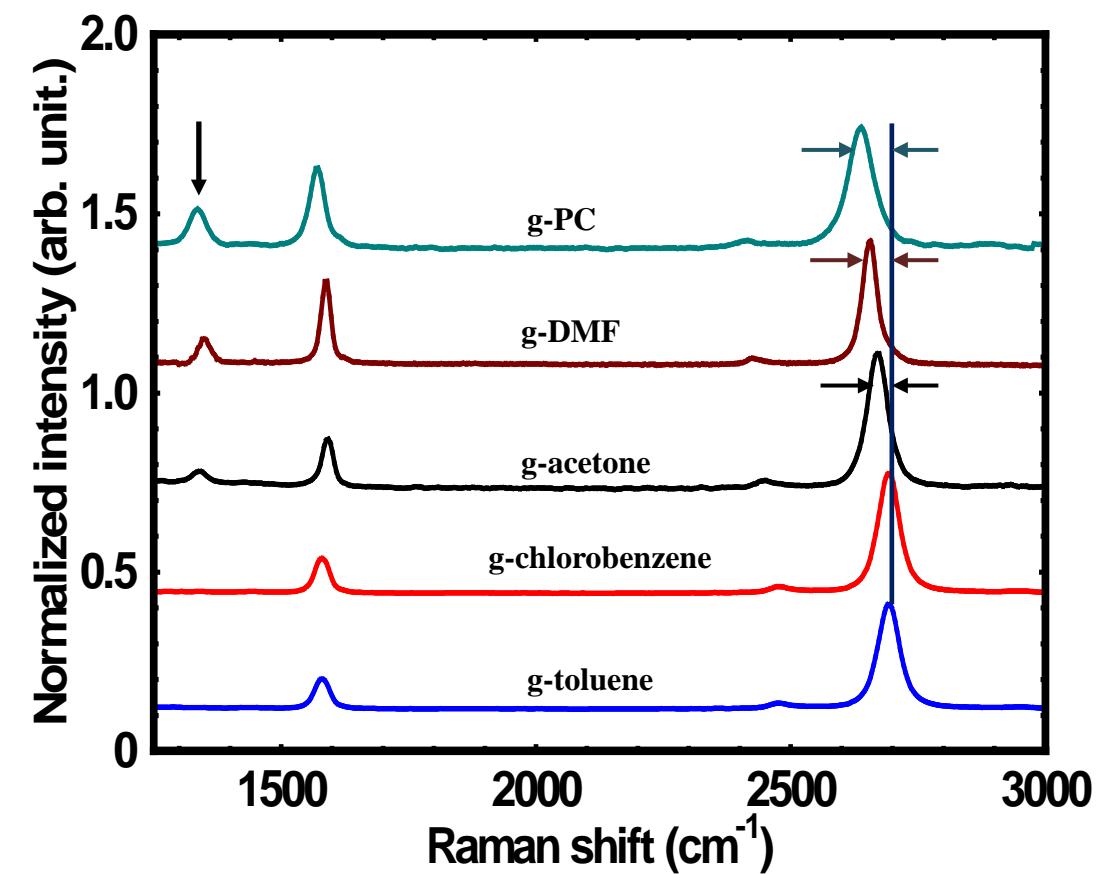
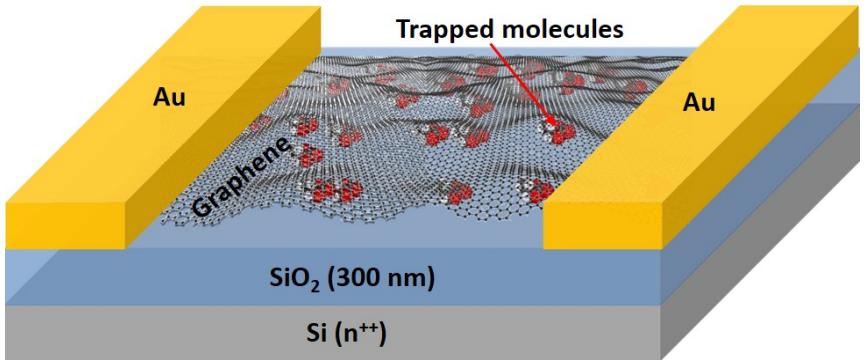




PC

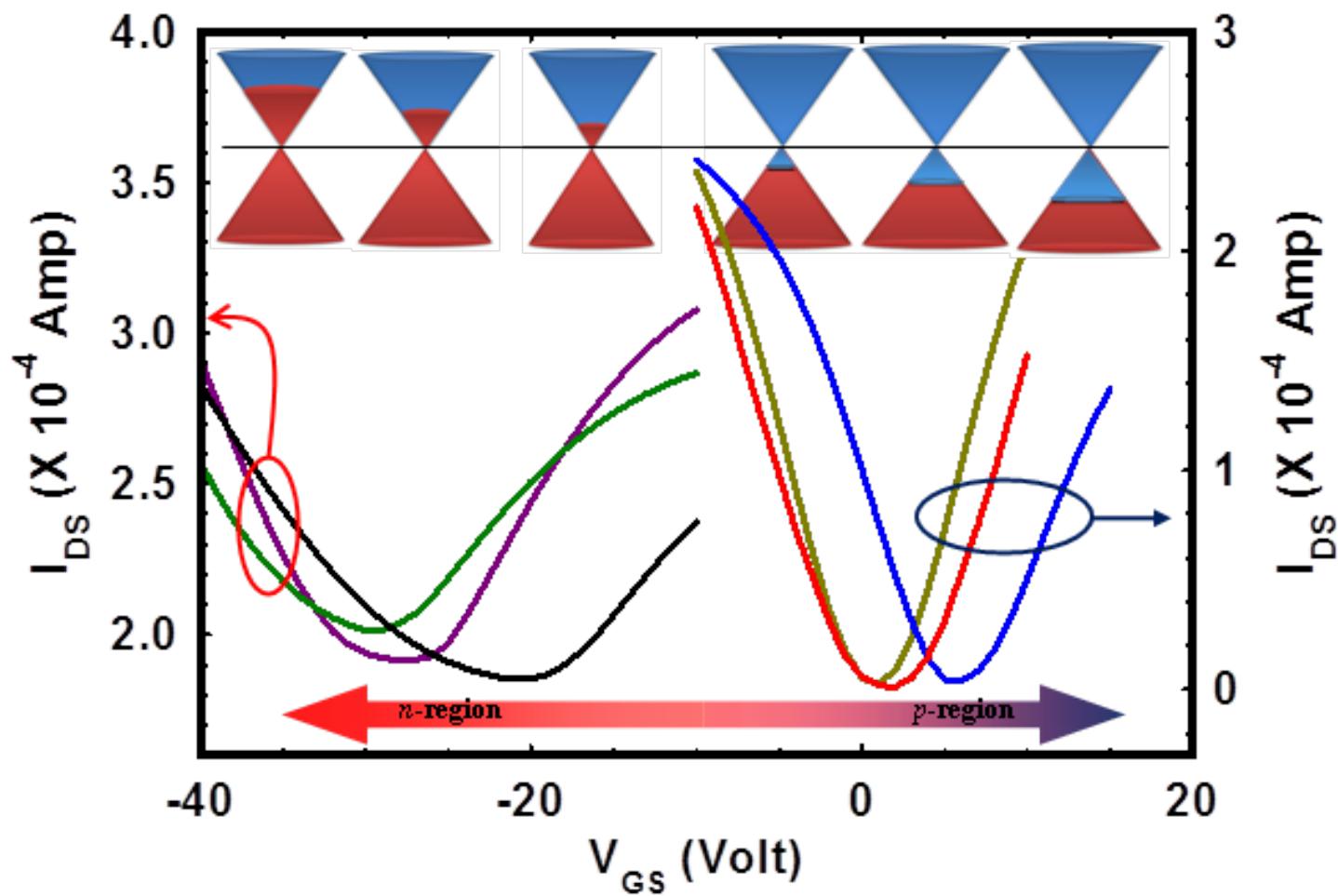


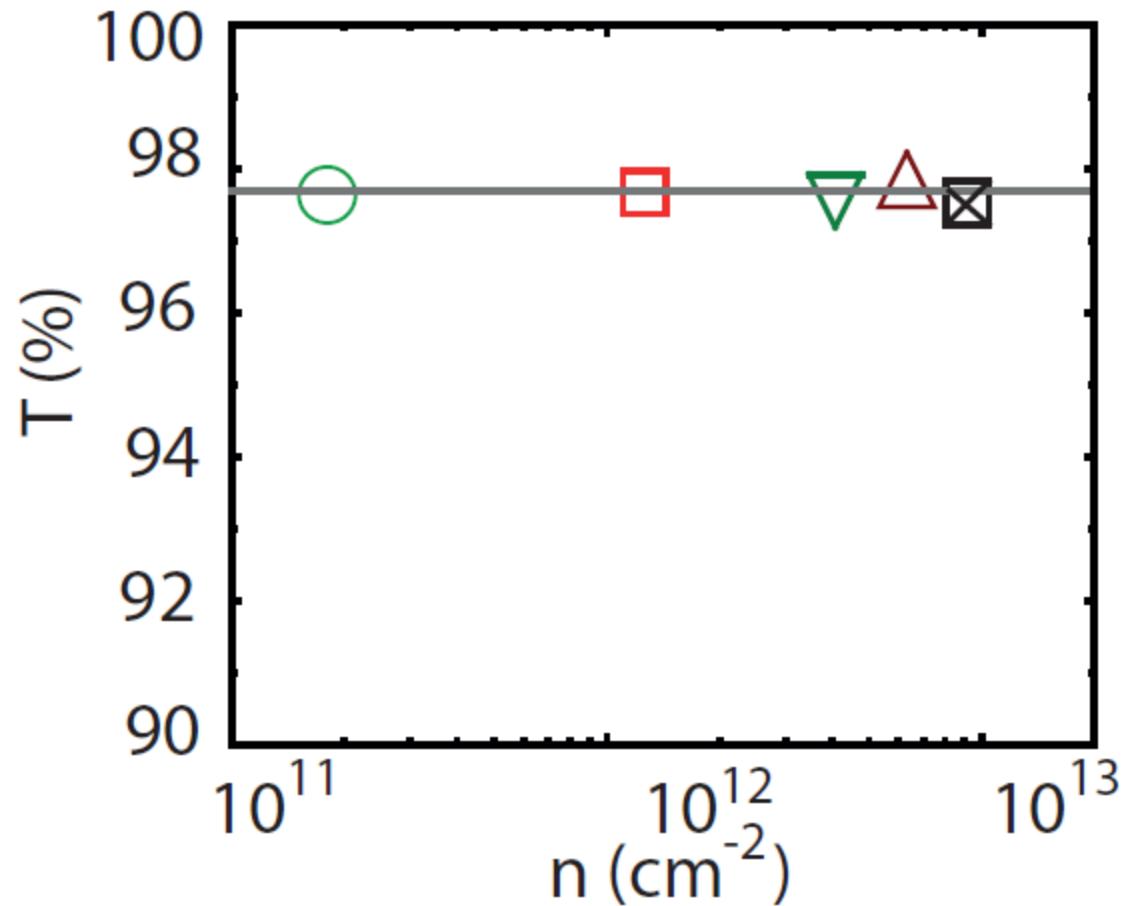


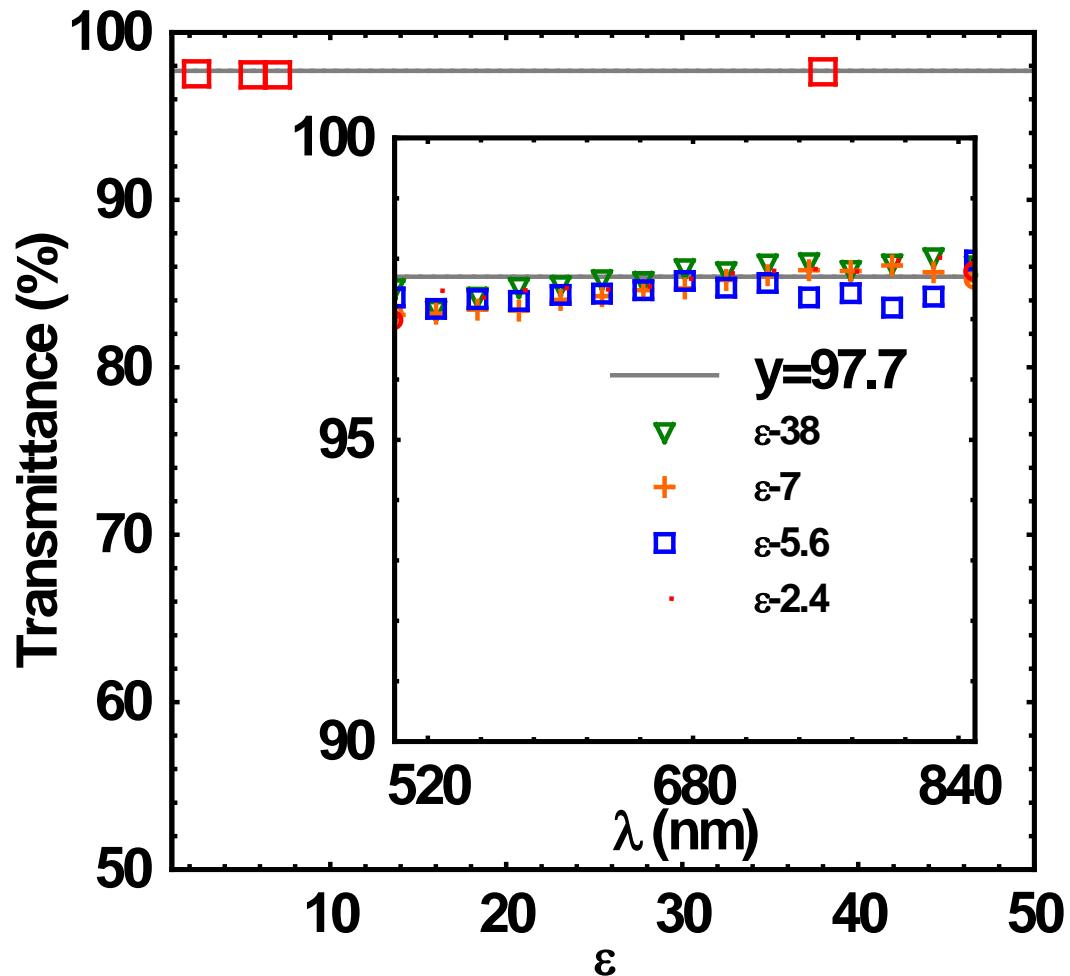


DFT Results

Solvents Used	Dielectric Constant	Adsorption Energy (eV)	Distance b/n Graphene & Molecule (A ⁰)	Charge Transfer (e)	Dirac Point (FET) (Volts)	Mobility (cm ² /Vs)
THF	7.5	-0.078694	3.81	0.021	~10	7632
Chlorobenzene	5.6	0.064171	4.0	0.014	~1	11650
DMF	37.5	-1.49501	3.44	-0.025	~25-27	5598
PC(propylene carbonate)	64	-2.48779	3.47	-0.035	~25-30	5530







Plan of this talk

- Introduction to graphene bandstructure and “chirality”.
- Growth and characterization of graphene.
- Robustness of universality under interlayer coupling and many body interactions.
- Doping of graphene to modulate the e-e interaction on universality
- How to break this universality ?



How to break universality ?

By breaking chiral symmetry?

Phys. Rev. Lett **99**, 226803, 2007

Phys. Rev. Lett **102**, 026802 (2009)

Phys. Rev. Lett. **107**, 016602 (2011)

Phys. Rev. Lett. **114**, 246801 (2015)

Phys. Rev. Lett. **115**, 186602 (2015)



How to break CHIRAL SYMMETRY in GRAPHENE ?

1. By electron-hole interaction (Exciton)

The attractive force that should be enough to create the electron – hole pairs that would break the chiral symmetry spontaneously. Excitonic condensate indicates opposite charges on sublattices

$$\langle \bar{\psi}^a \psi^a \rangle > 0$$

This would make quasiparticle massive and the phase insulating.

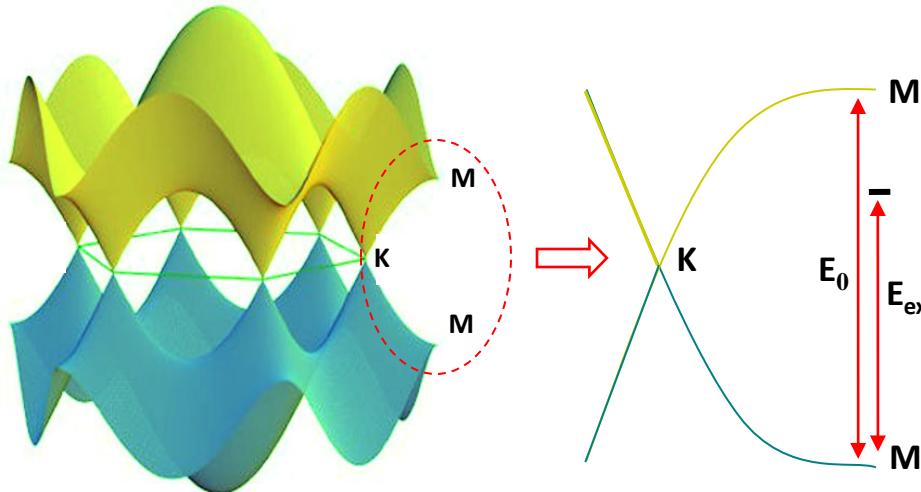
2. By antiferromagnetic ordering

Antiferromagnetic ordering of spins corresponds to opposite spin of electrons on different sublattices

$$\langle \bar{\psi}^a \sigma_{ab} \psi^b \rangle > 0$$

This also would make quasiparticle massive and should lead to metal-insulator transition.

Exciton in Graphene



Electron-hole bound state \equiv Exciton

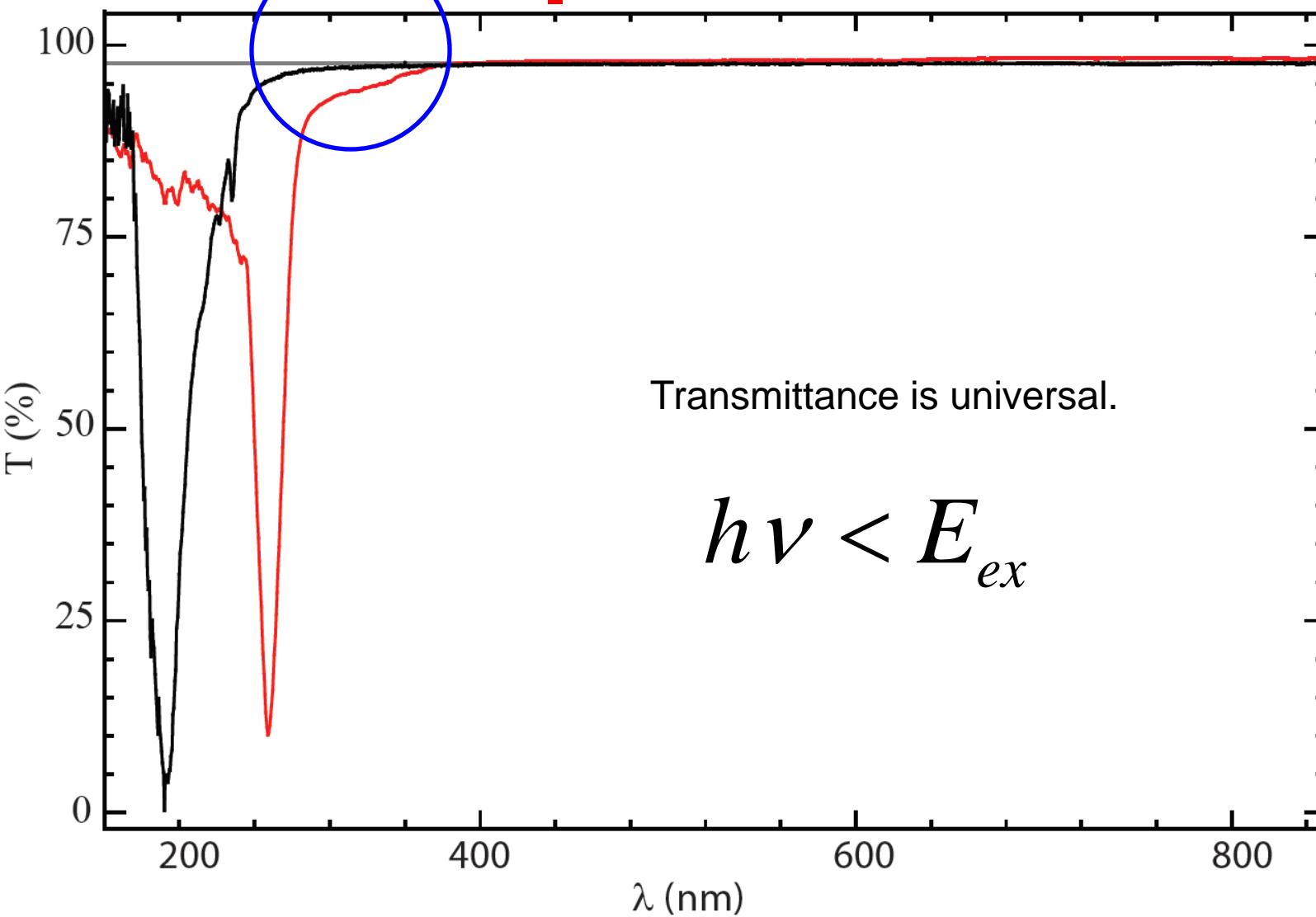
$$H \neq v \vec{\sigma} \cdot \vec{p}$$

Chirality is not conserved if electron-hole bound state exists

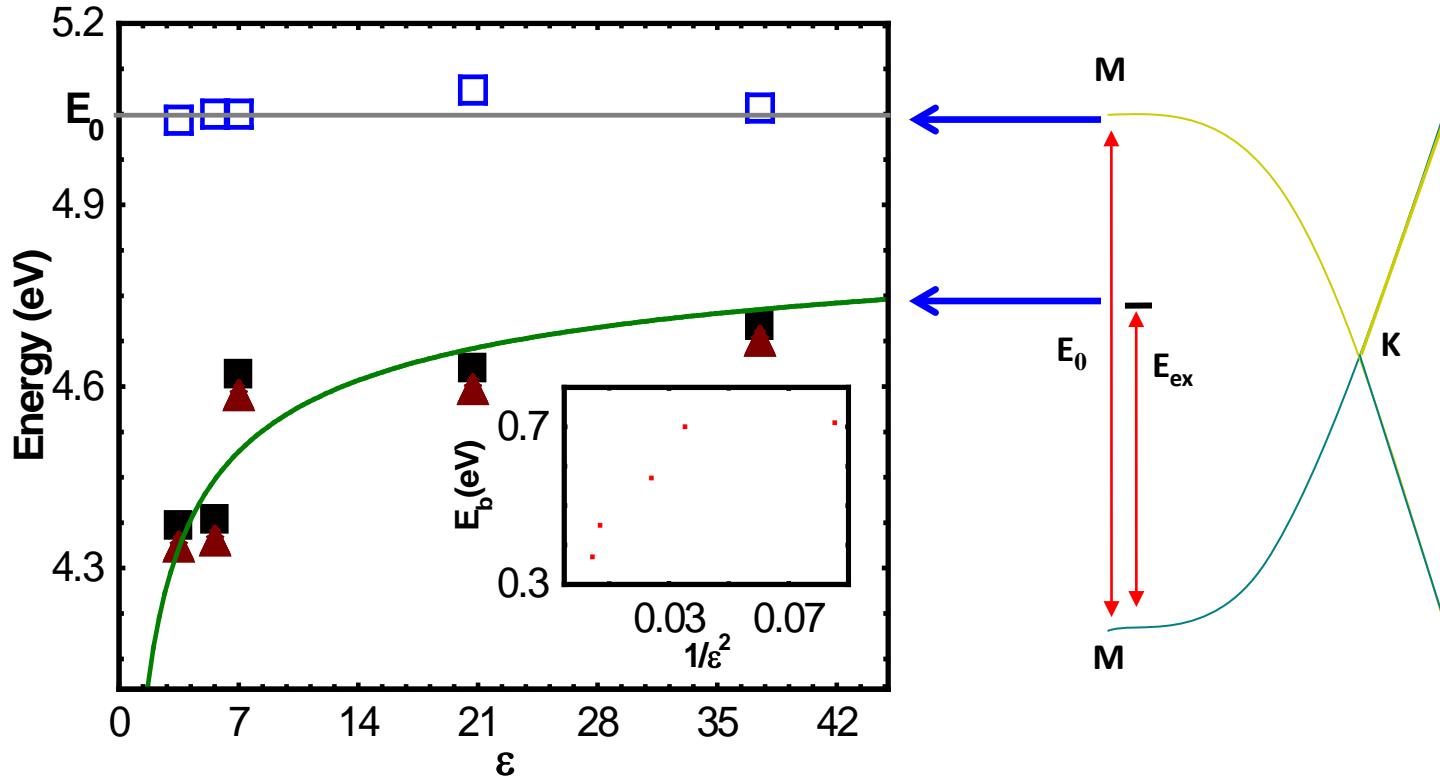
$$h\nu > E_{ex}$$

Universality is broken.

$$h\nu > E_{ex}$$



Strong Effect of e-e Interaction



Conclusions

- ✓ Universality is not affected by long range interactions.
- ✓ Chiral symmetry is responsible for optical transmittance universality.
- ✓ Strong many body interaction when $h\nu > E_{ex}$
- ✓ Phase transition due to breaking of Chirality is not yet observed.

Thank You

