Computational Simulations of Electronic and Optical Properties of Nanomaterials

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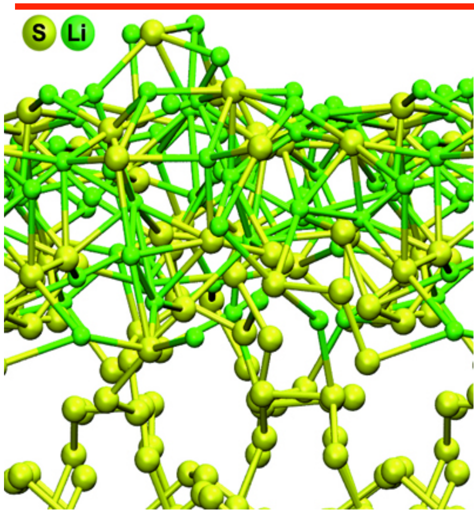
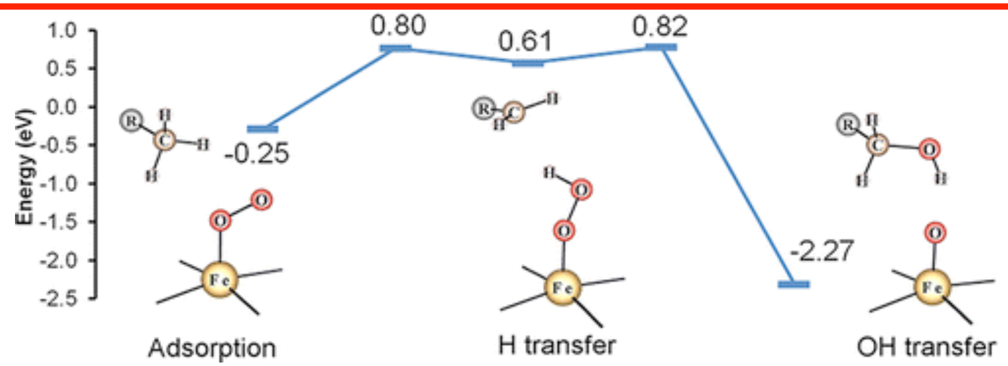
OKLAHOMA SUPERCOMPUTING SYMPOSIUM, Sept. 24th 2014

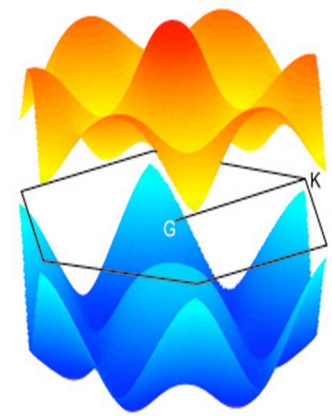
Computational Materials and Chemical Science
Advanced materials for energy



Lithium-ion batteries



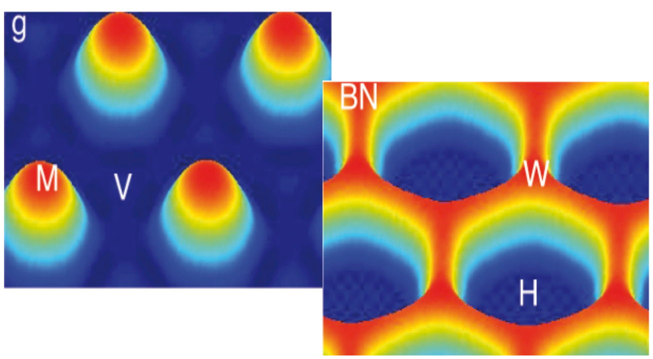
Molecular reaction and catalysis



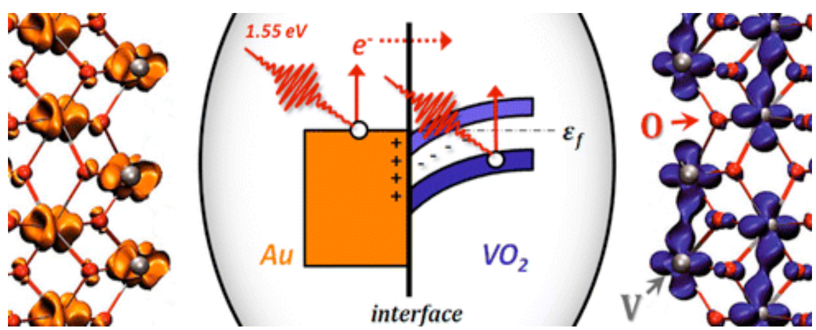
Optoelectronics

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + e^2\int\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r + \mu_{xc}\left[n(\vec{r})\right]\right\}\Phi_i(\vec{r}) = \varepsilon_i\Phi_i(\vec{r})$$

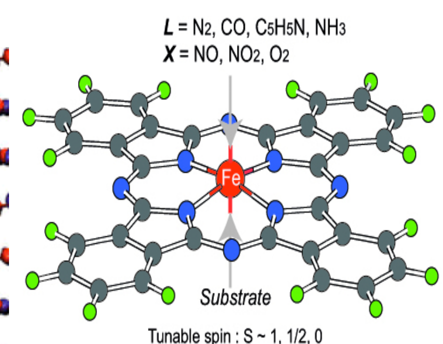
Density functional theory



2D materials (graphene, h-BN, MoS_2, etc)



Phase-change materials for molecular sensors



Molecular switch

What Can We Do ?

Density Functional Theory

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}) + e^2\int\frac{n(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}d^3r + \mu_{xc}\left[n(\vec{r})\right]\right\}\Phi_i(\vec{r}) = \varepsilon_i\Phi_i(\vec{r})$$

Electron density n(r); Total Energy

Ground State Properties

Structures

Chemical Reaction Barriers

Vibration

Band Structure

Core Levels

Spins

Optics

Temperature, time, scale

Molecular dynamics simulation

Kinetic Monte Carlo Simulation

Excitation, Conductance

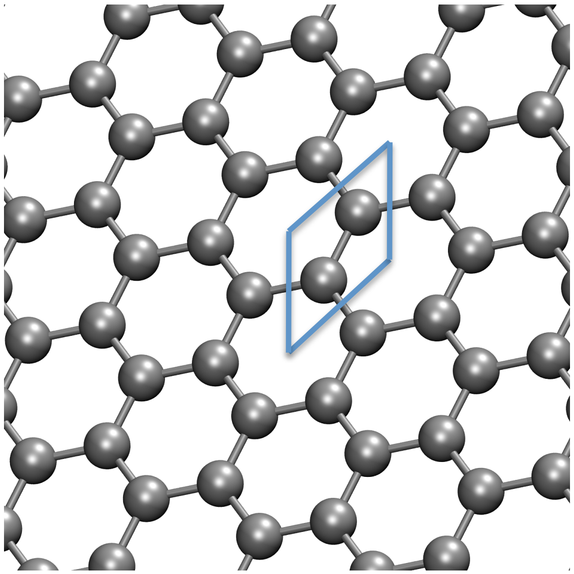
GW and BSE calculations

Non-equilibrium Green's Function

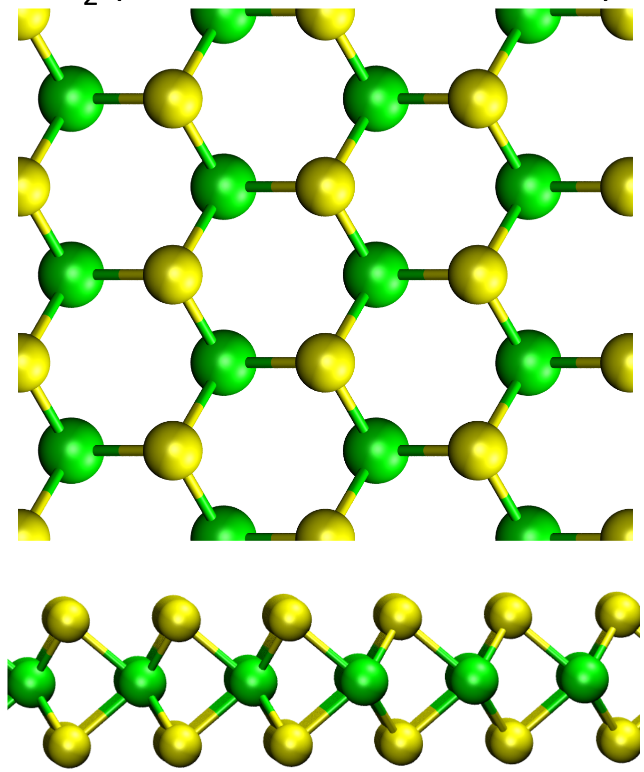
…

Two-Dimensional Materials

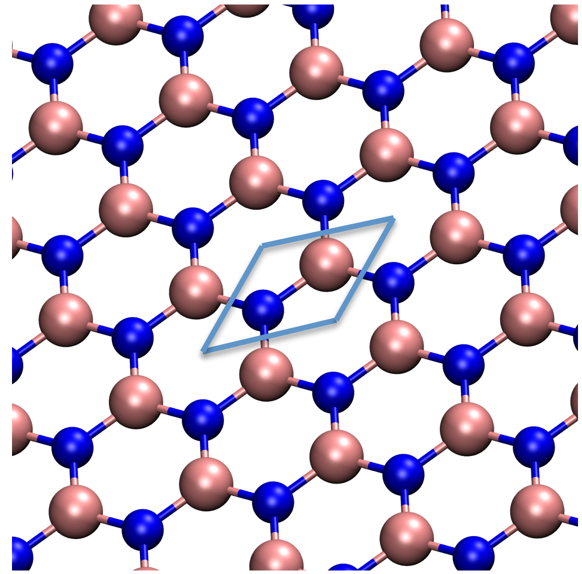
Graphene



Transition metal dichalcogenides
MX_2 (M=Mo, W, Ti; X=S, Se, Te)



h-BN

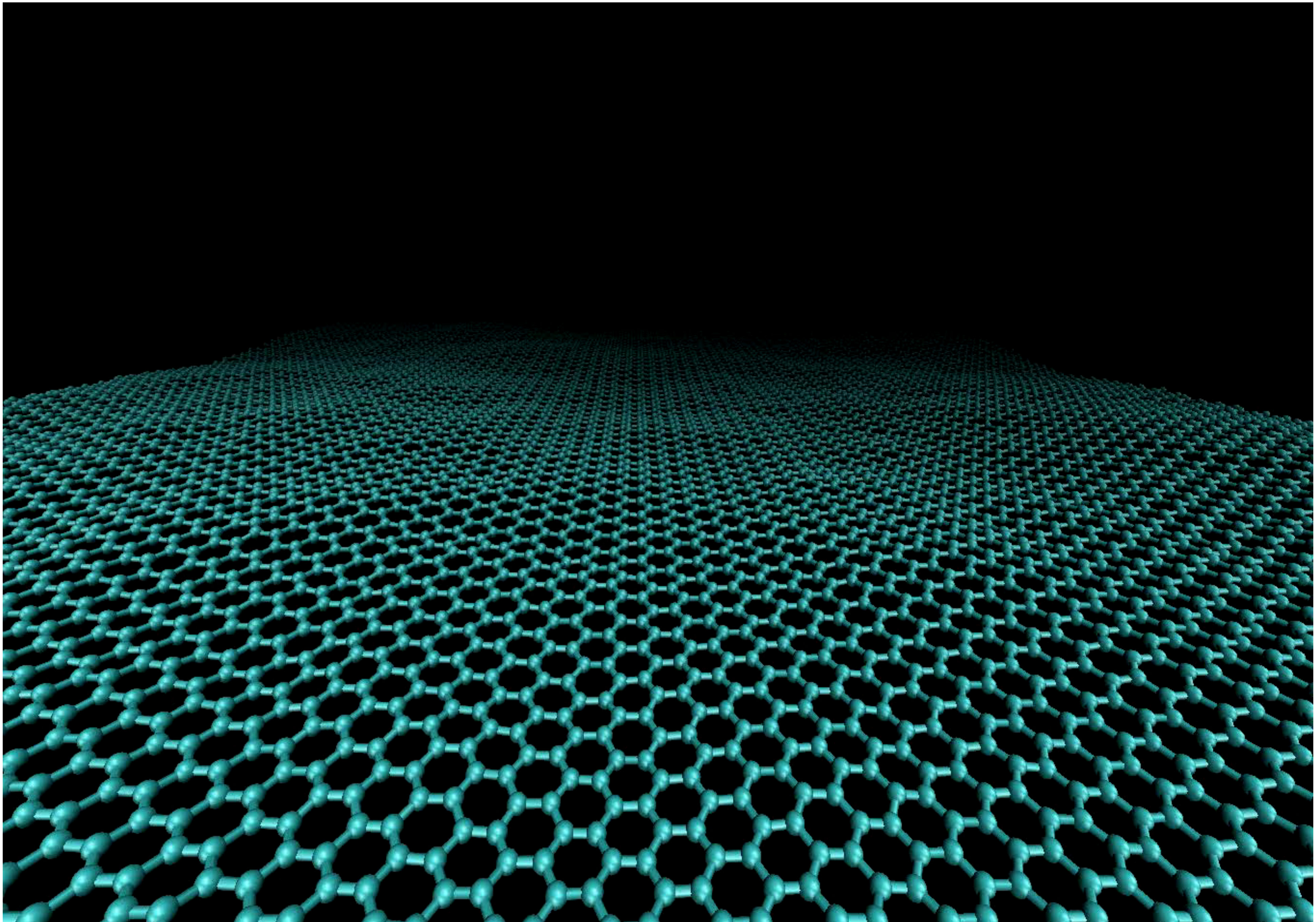


Metal

Semiconductor

Insulator

and a lot of others: Graphane, Silicene, Bi_2Se_3, β-FeSe, $Ti_3C_2(OH)_2$, transition metal oxides ….



A.K.M. Newaz, Y. S. Puzyrev, B. Wang, S. T. Pantelides, K. I. Bolotin, Nature Commun. 3, 734 (2012)

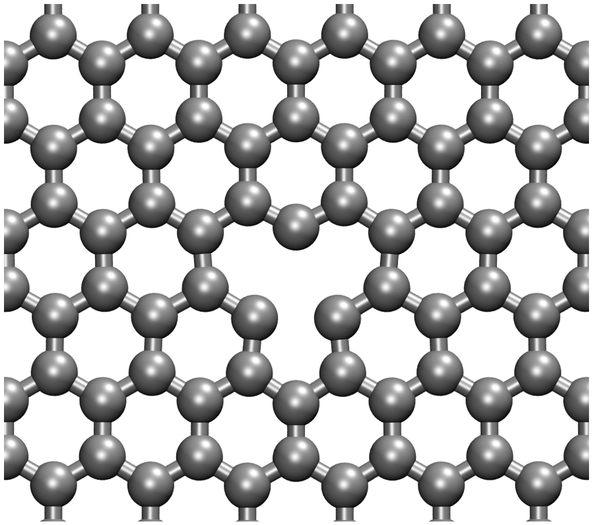
1. Defects and impurities in graphene

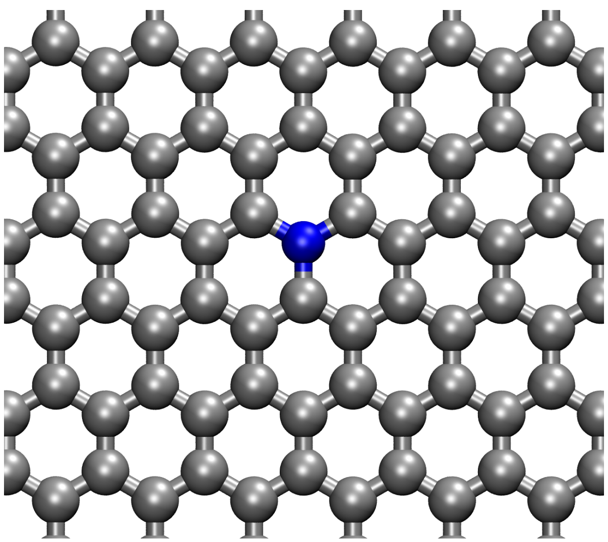
    Vacancies and chemical impurities : N, O

    Ripples, liquids, and transport

2. Exciton in MoS_2 under strain

Functionalization: Substitutional Doping





Vacancies:

Scatter electrons

Q: How to heal vacancies?

N-doping (substitution):

– enhanced carrier density; ($2s^2\ 2p^3$)

– enhanced chemical activity;

Oxygen reduction reaction : Pt/C

Liang et al. Nature Mater. 2012

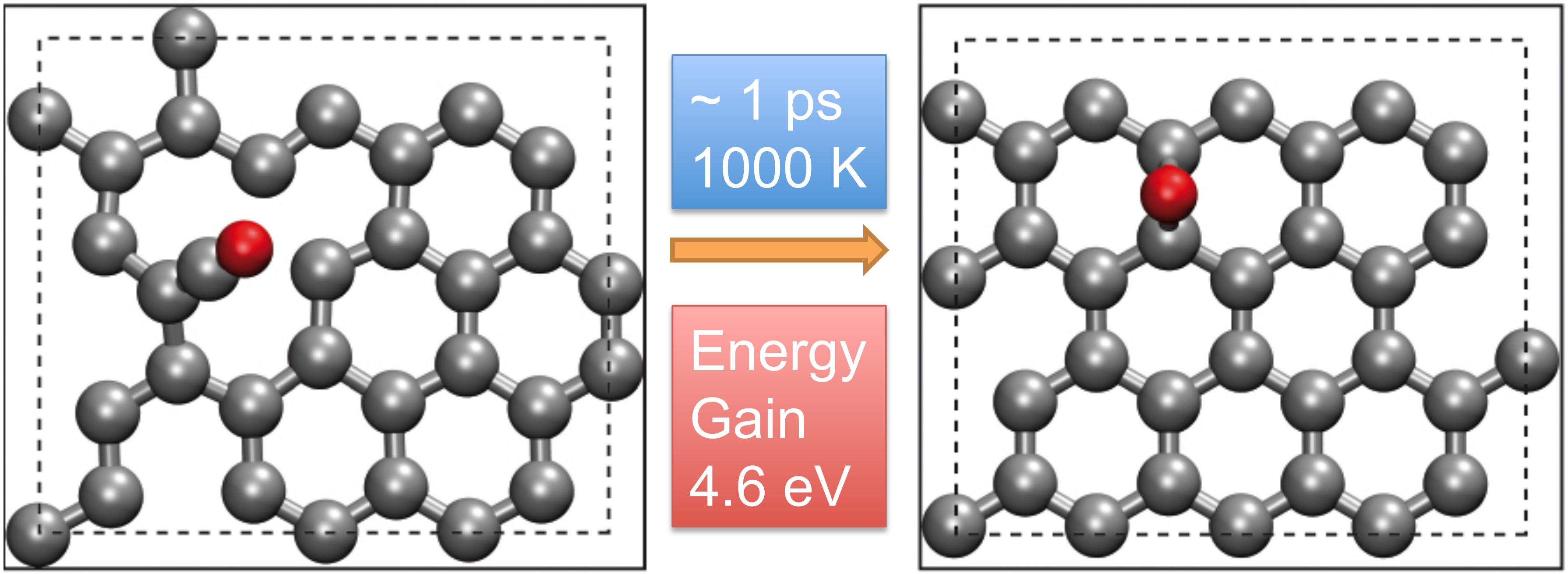
Cong et al. Science 2009

Qu et al. ACS Nano 2010

NH_3 : > 800 °C annealing; low mobility

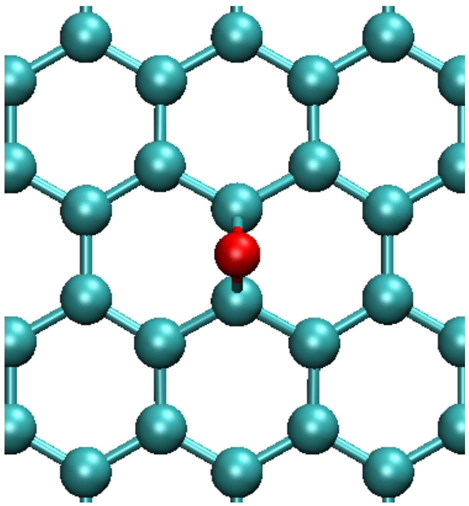
Q : Low-T process; improved mobility

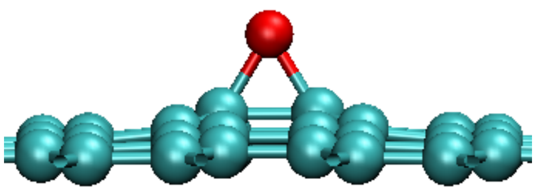
Incorporation of Carbon Using CO

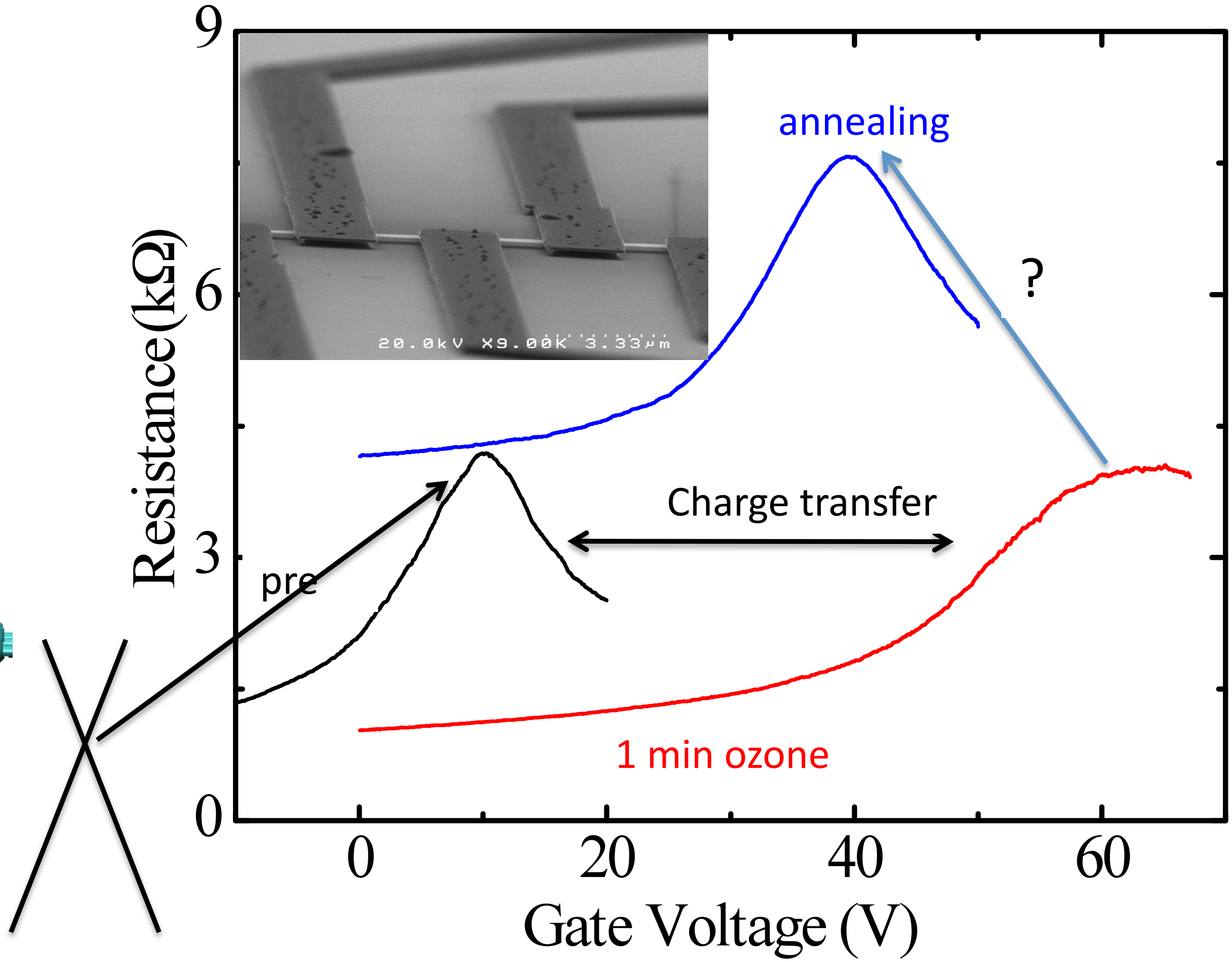


How to remove oxygen?

Removal of Oxygen – Thermal Annealing

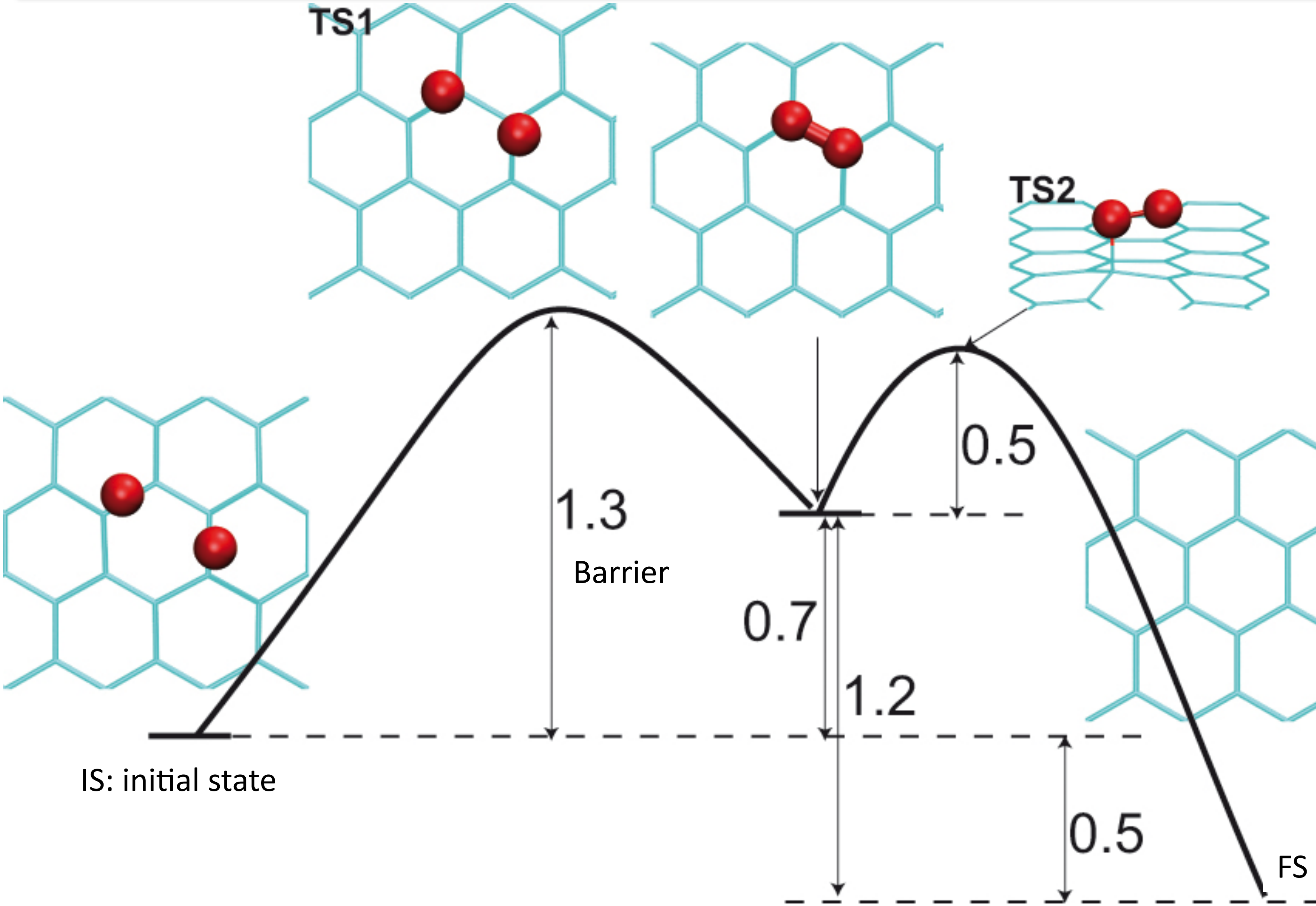




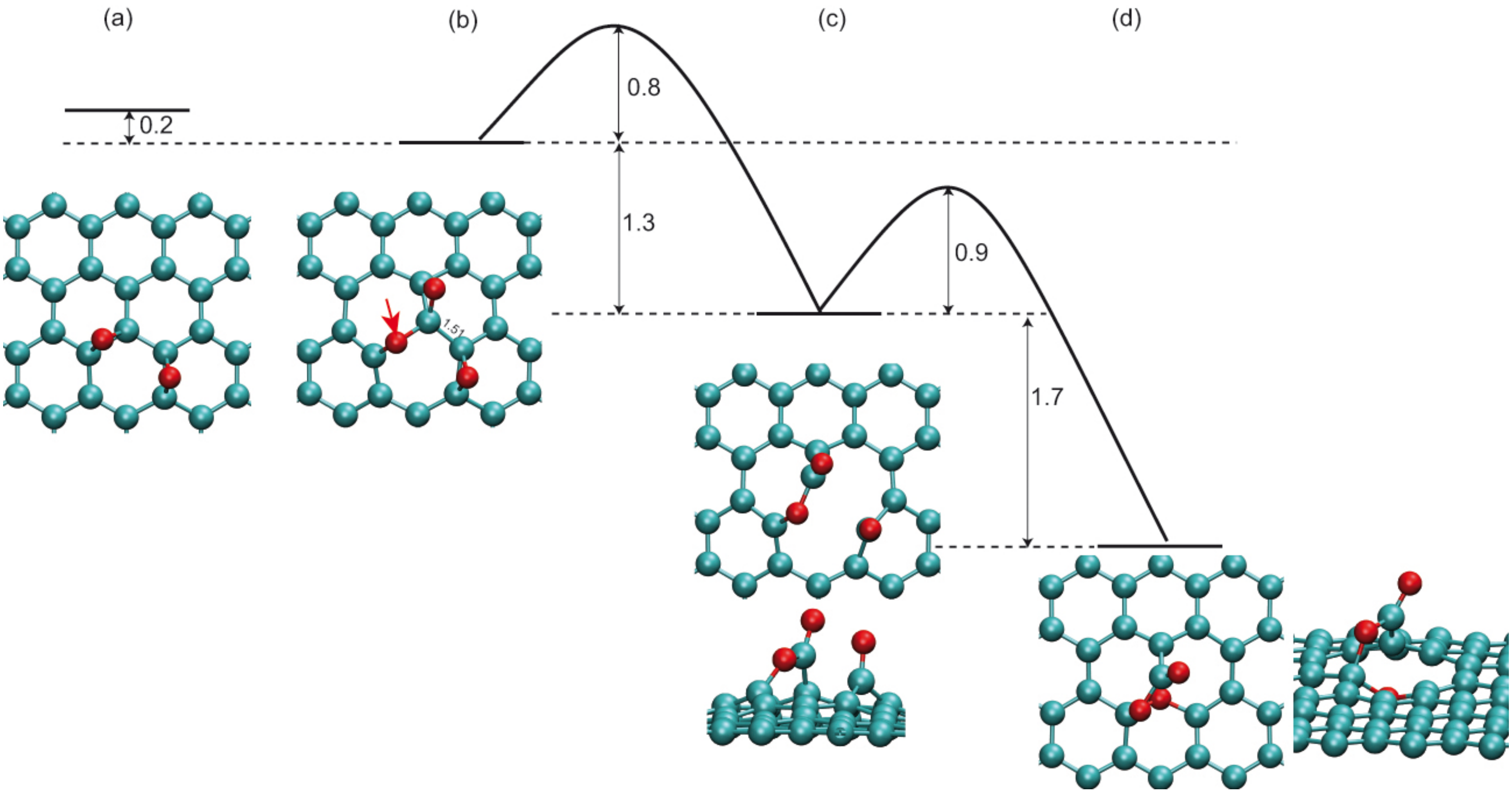


E. Zhang, AKM Newaz, B. Wang, C. Zhang, D. Fleetwood, K. Bolotin, R. D. Schrimpf, S. T. Pantelides, M. L. Alles, IEEE Transactions on Nuclear Science, 6, 2961 (2011); APL 101, 121601 (2012)

Removal of Oxygen



Removal of Oxygen



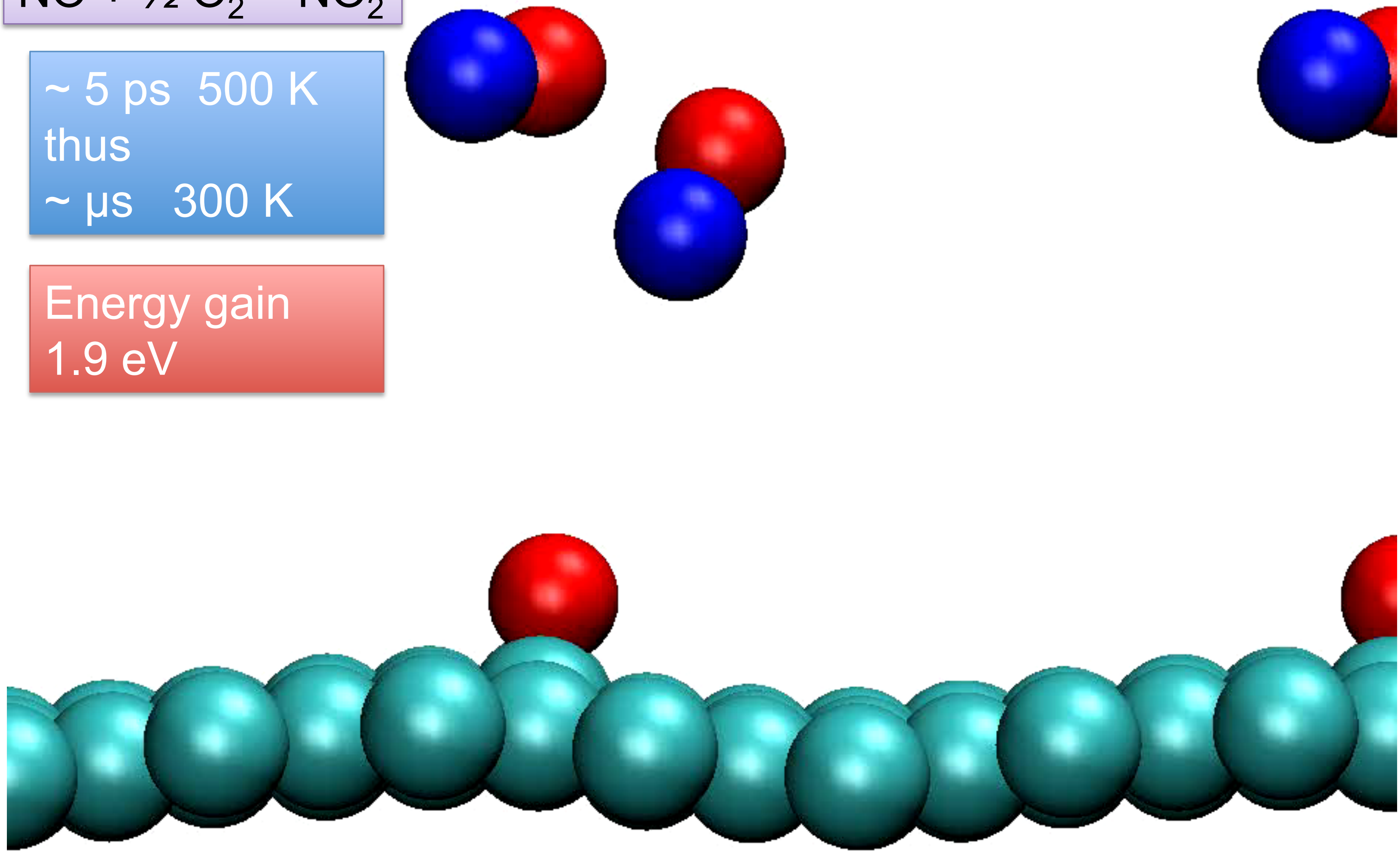
Vacancy created when removal of oxygen : scatter electrons

MD simulation

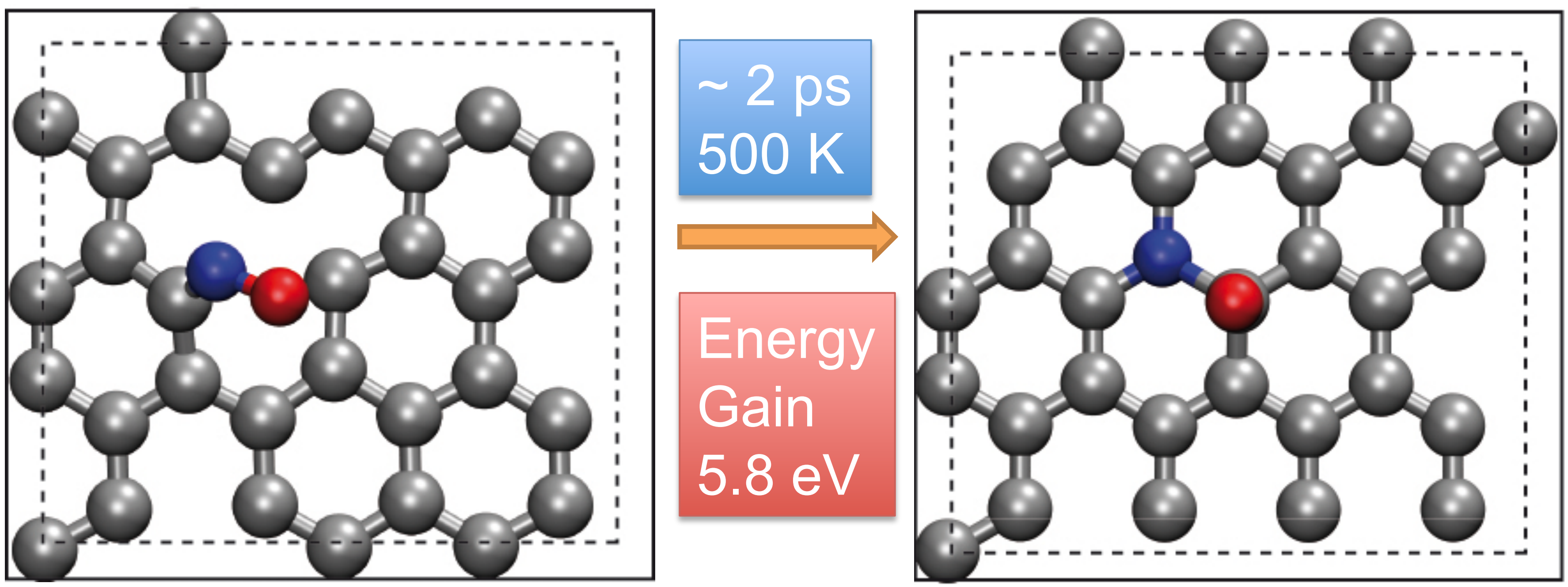
$NO + ½ O_2 = NO_2$

~ 5 ps 500 K
thus
~ μs   300 K

Energy gain
1.9 eV



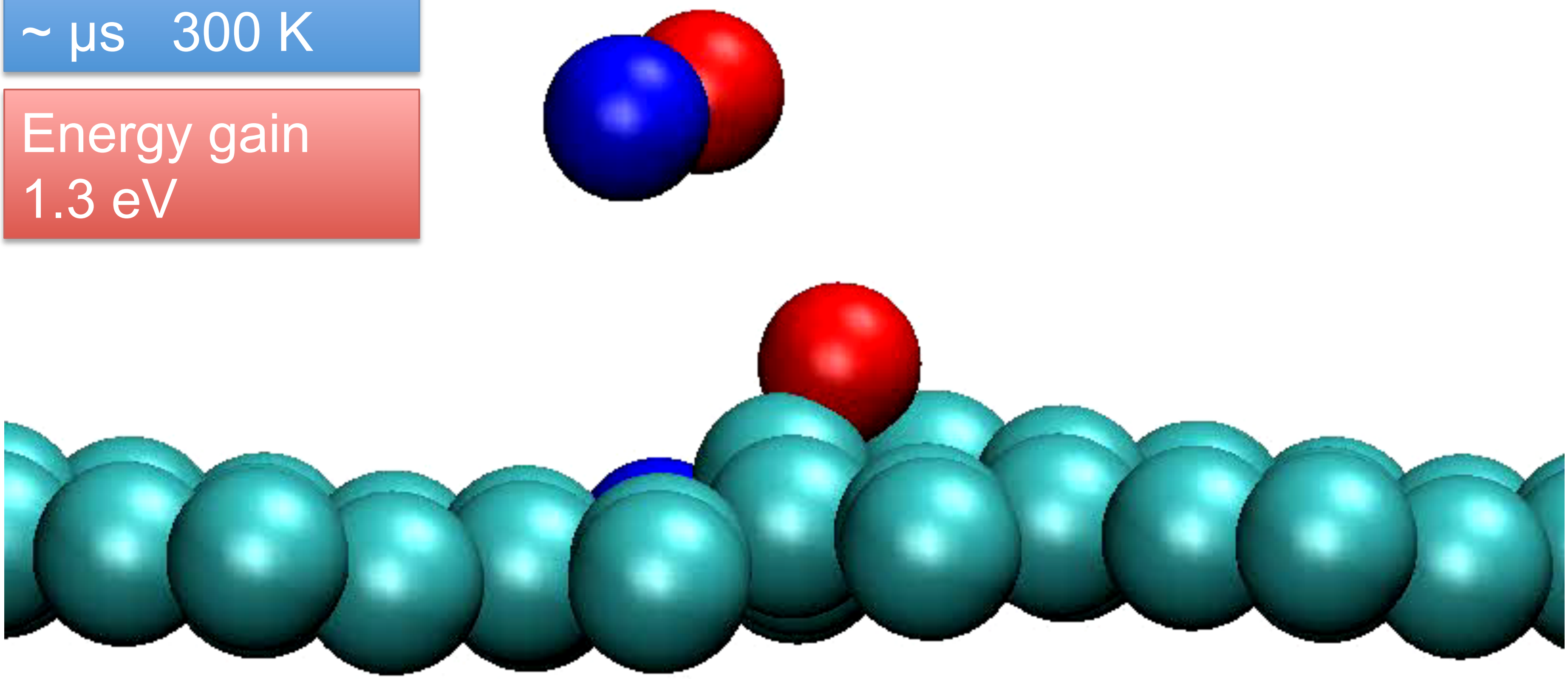
Incorporation of Nitrogen Using NO



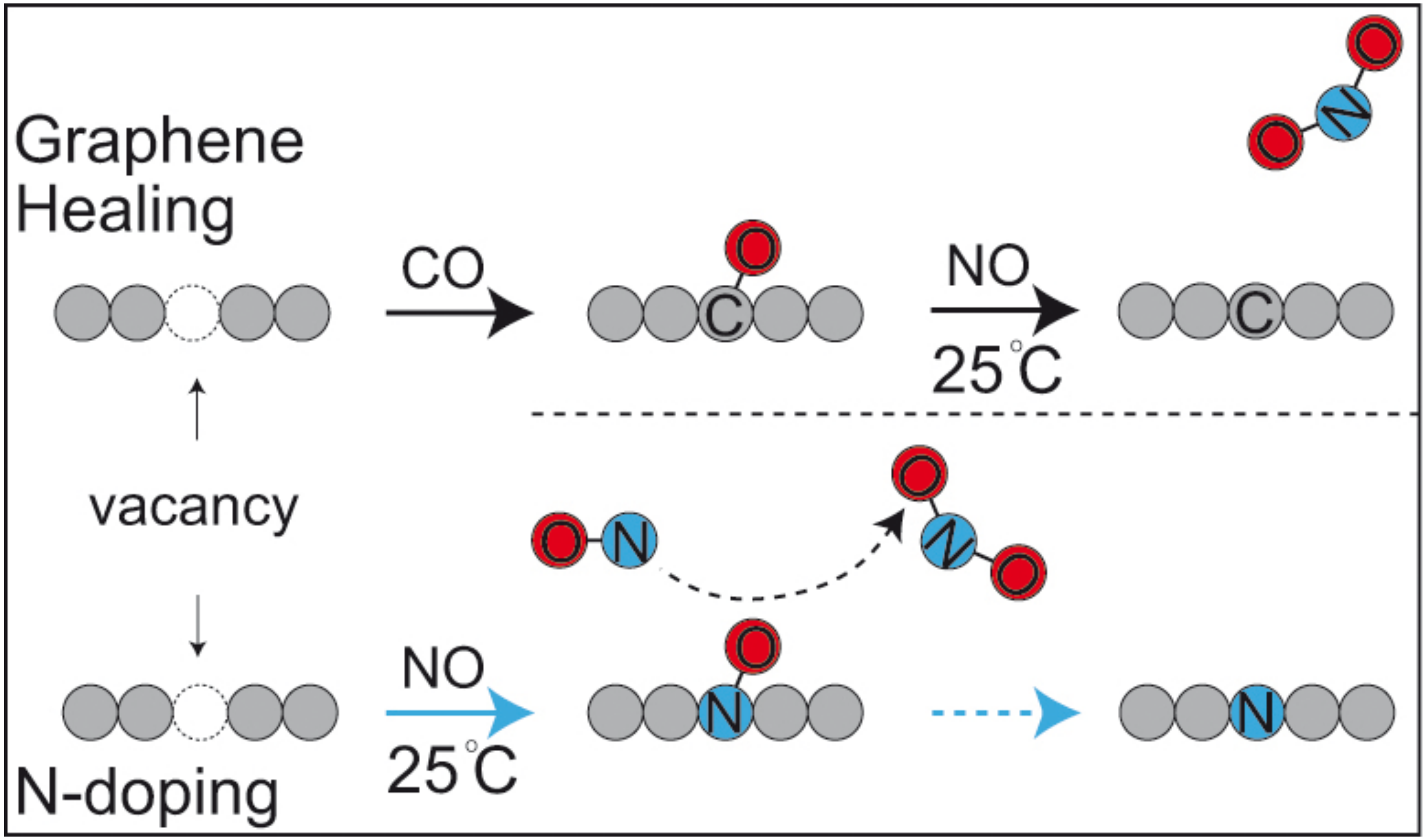
MD simulation

~ 1 ps 500 K
thus
~ μs   300 K

Energy gain
1.3 eV



Healing or Doping



Verified experimentally by Narayanan et al. JVST A, 2013

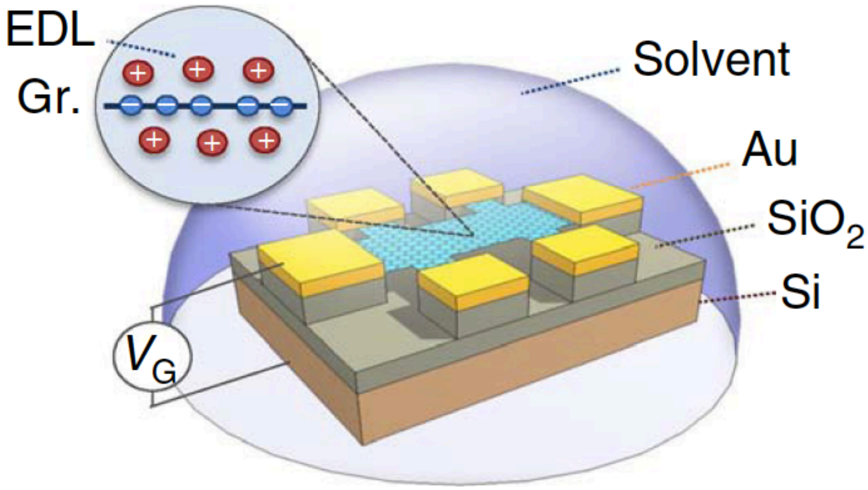
1. Defects and impurities in graphene

Vacancies and chemical impurities : N, O

Ripples, liquids, and transport

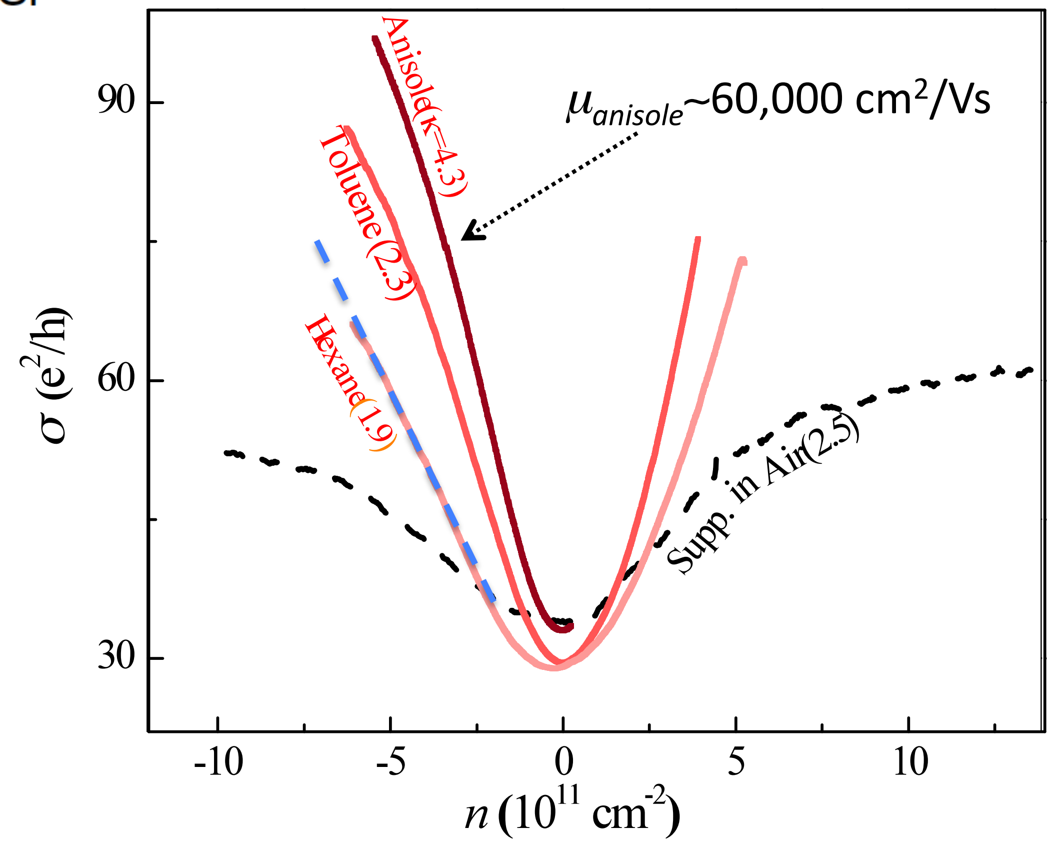
2. Exciton in MoS_2 under strain

Modification of Transport in Graphene



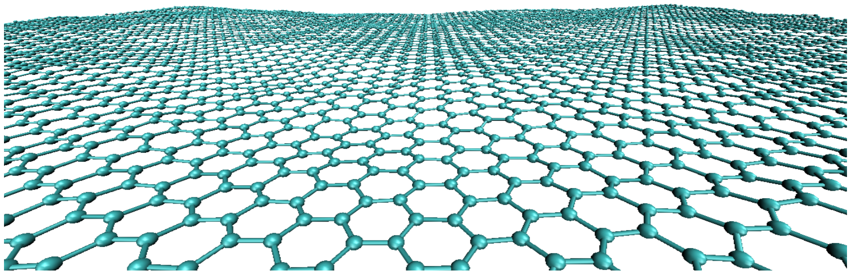
high mobility (clean, flat)
~ 200,000 cm^2/Vs at RT

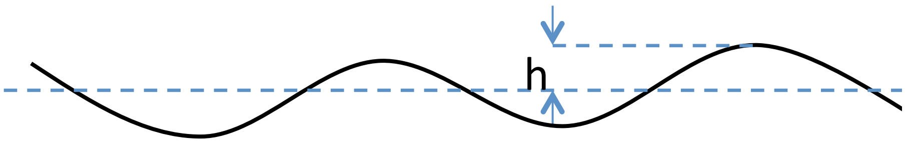
Reality
10,000 - 30,000 cm^2/Vs
(flexural phonon)
Q: How to enhance the mobility?



Modification of Transport in Graphene

Classical MD simulations

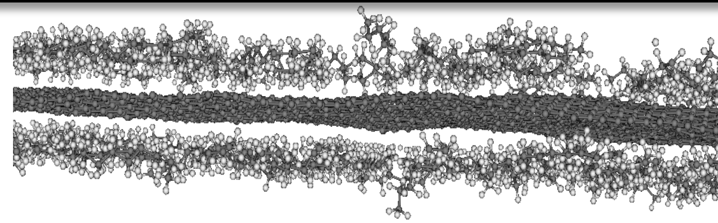


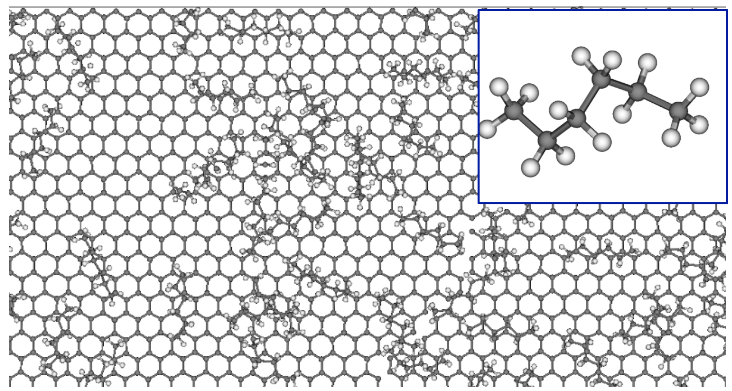


$<h^2> = 0.89$ Å^2

$$\mu \propto k^2 \propto (\frac{1}{\langle h^2 \rangle})^2$$

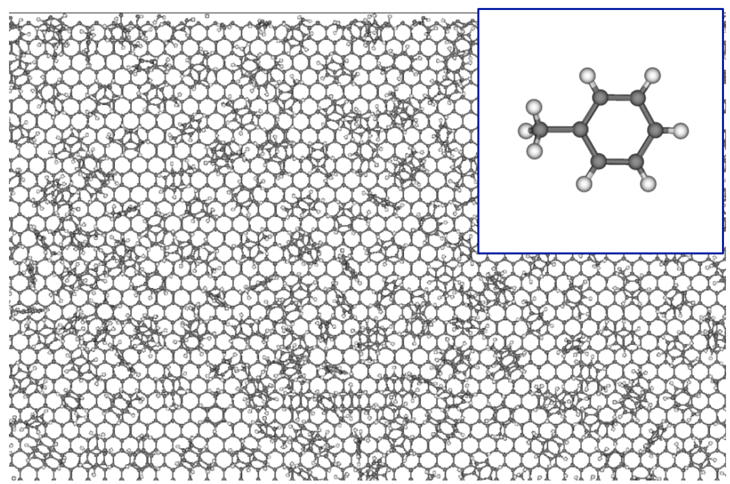
- ✓ *Vacuum μ ~30,000 cm²/V s*
- ✓ *Liquid μ ~ 200,000 cm²/V s*





$<h^2>_{\text{hexane}}$

$= 0.39$ Å^2

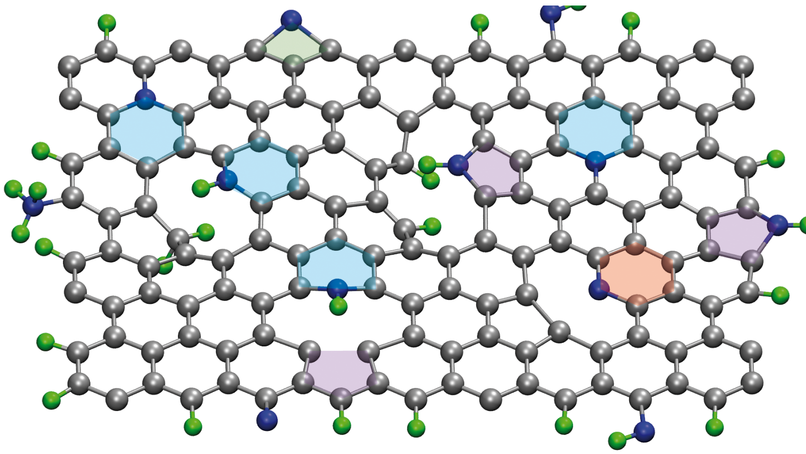


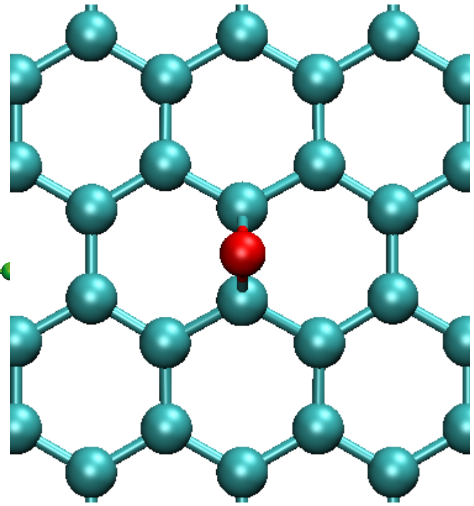
$<h^2>_{\text{toluene}}$

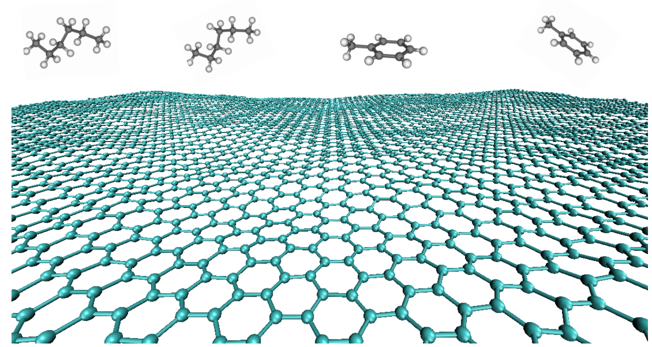
$= 0.42$ Å^2

A.K.M. Newaz, Y. S. Puzyrev, B. Wang, S. T. Pantelides, K. I. Bolotin, Nature Commun. 3, 734 (2012)

Take-home Message 1





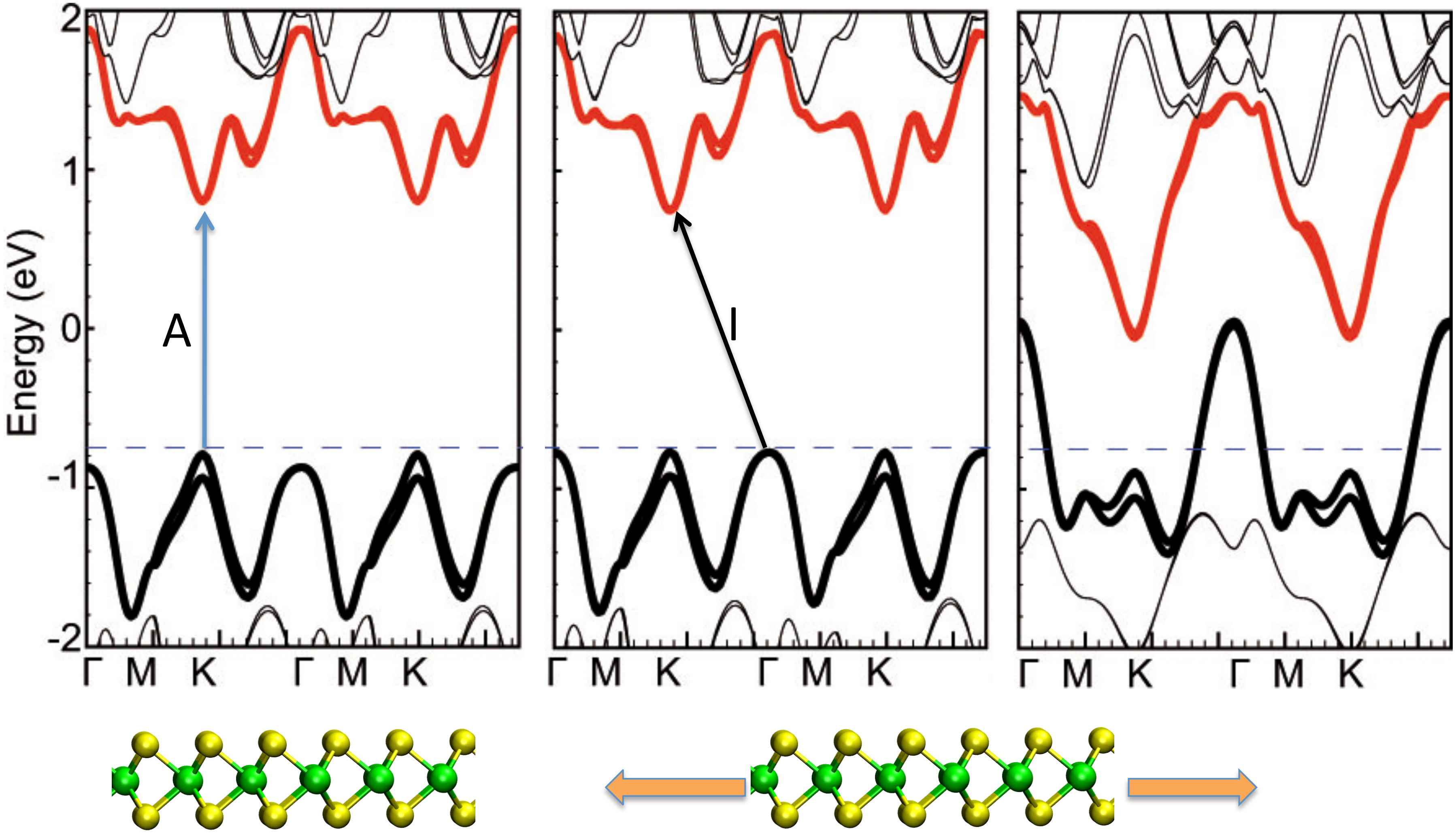


Functionalization methods : substitution, impurities, vdW

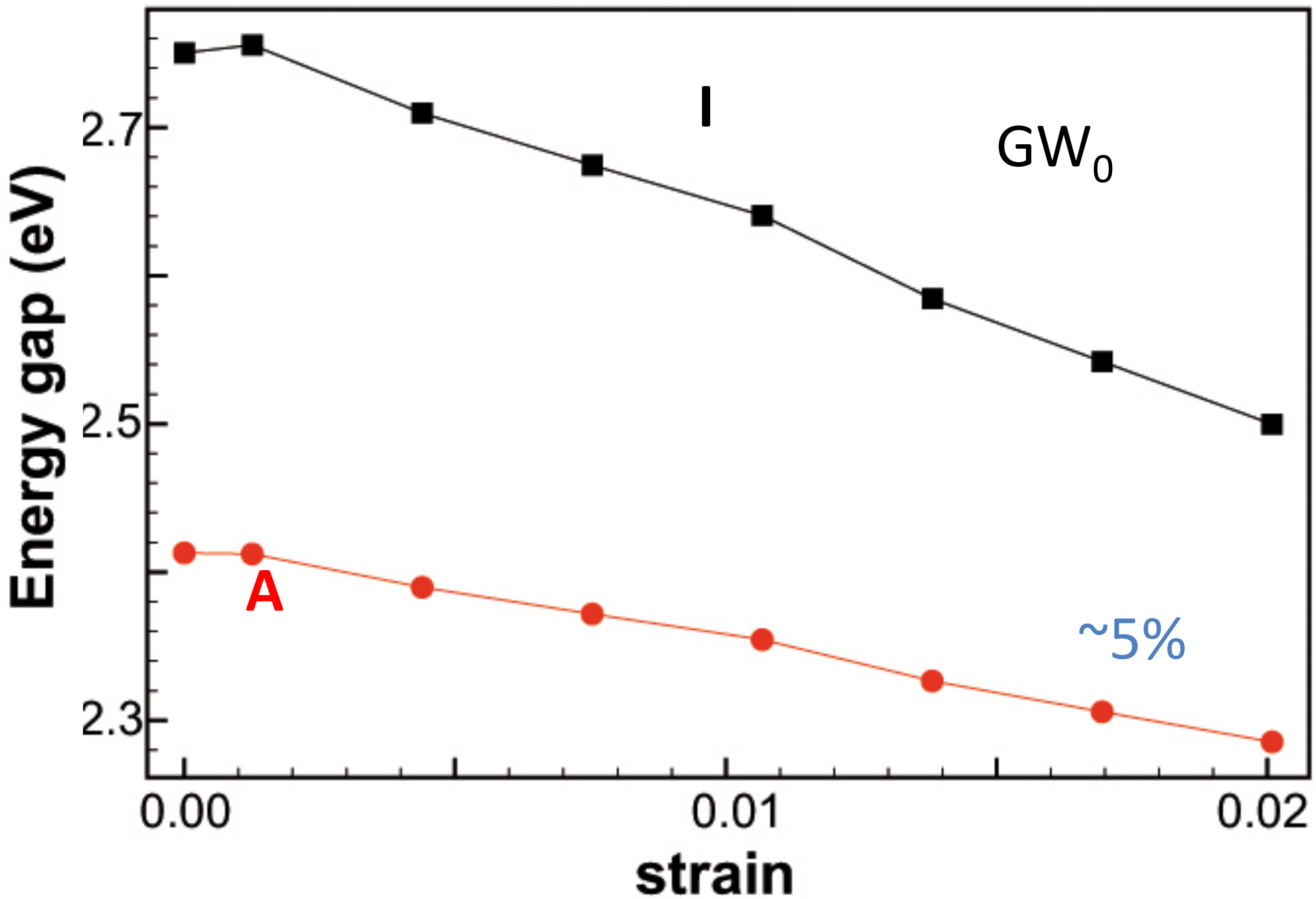
Benefits: enhanced conductivity, mobility, tunable WF, etc

S. T. Pantelides, Y. Puzyrev, L. Tsetseris, B. Wang, MRS Bulletin 37, 1187-1194 (2012)

Engineering of MoS_2 Band Structure

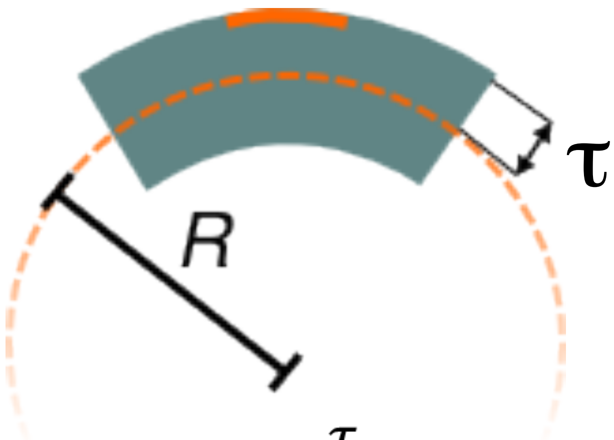


Direct to Indirect Optical Transition: Theory

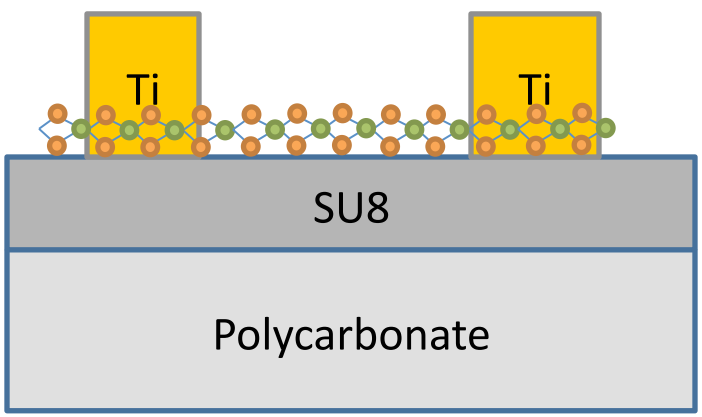


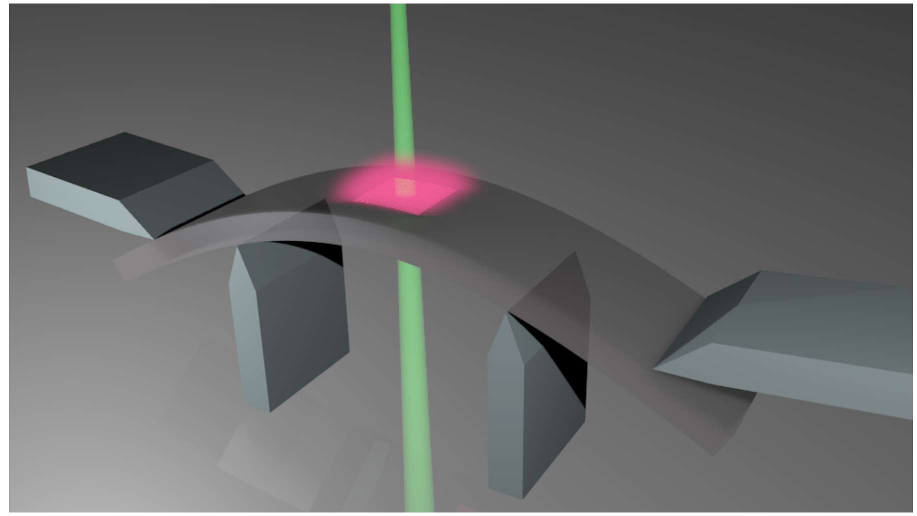
Q : achievable in experiments ?

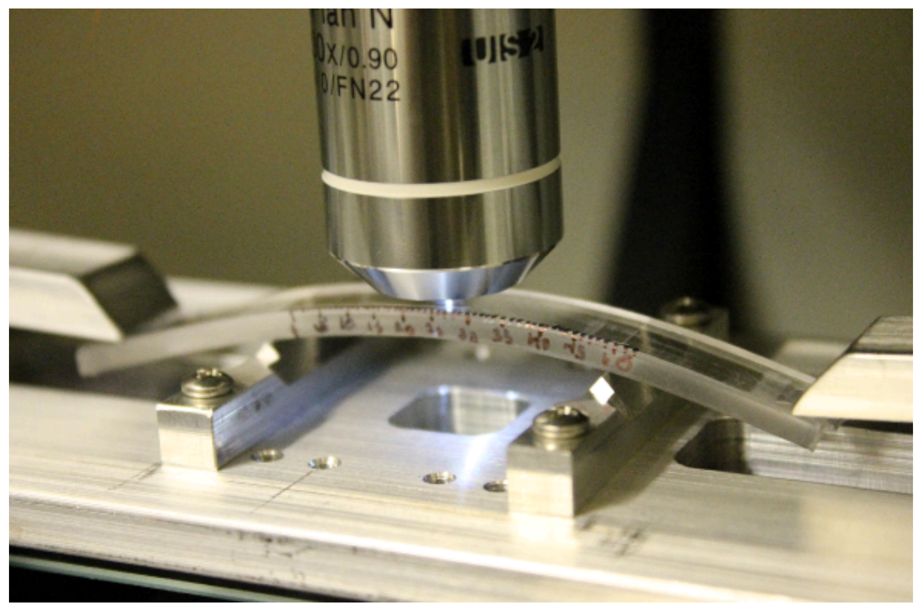
Direct to Indirect Optical Transition: Experiments



$$\varepsilon = \frac{\tau}{R}$$

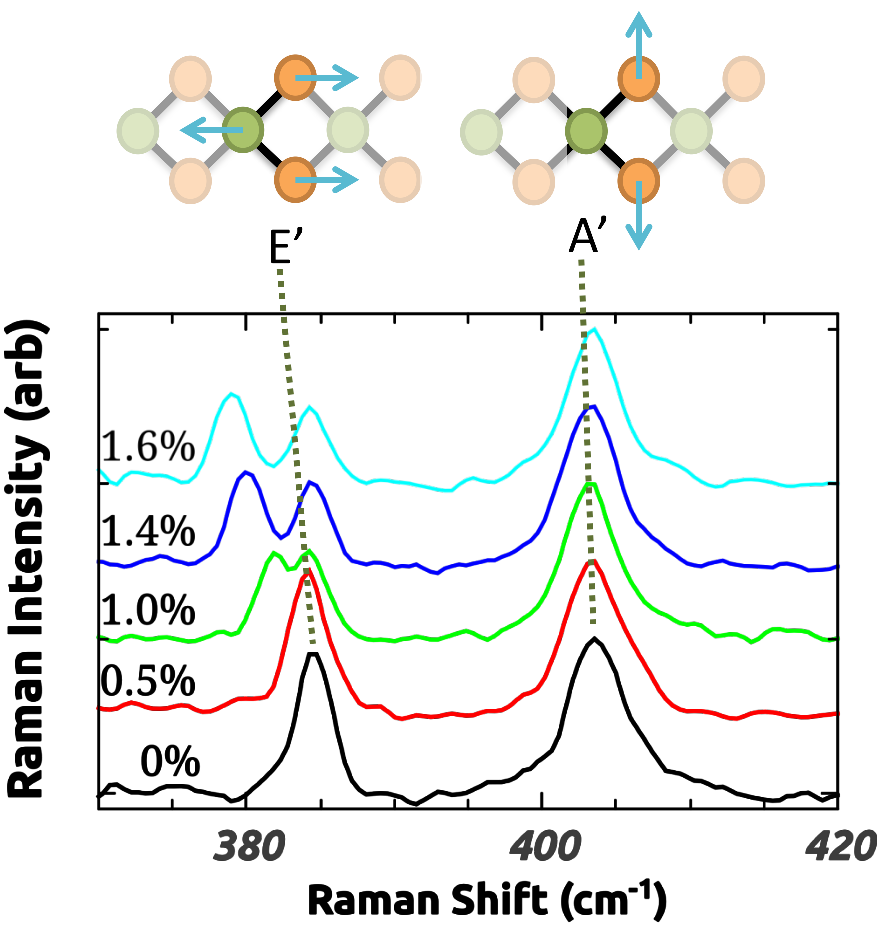


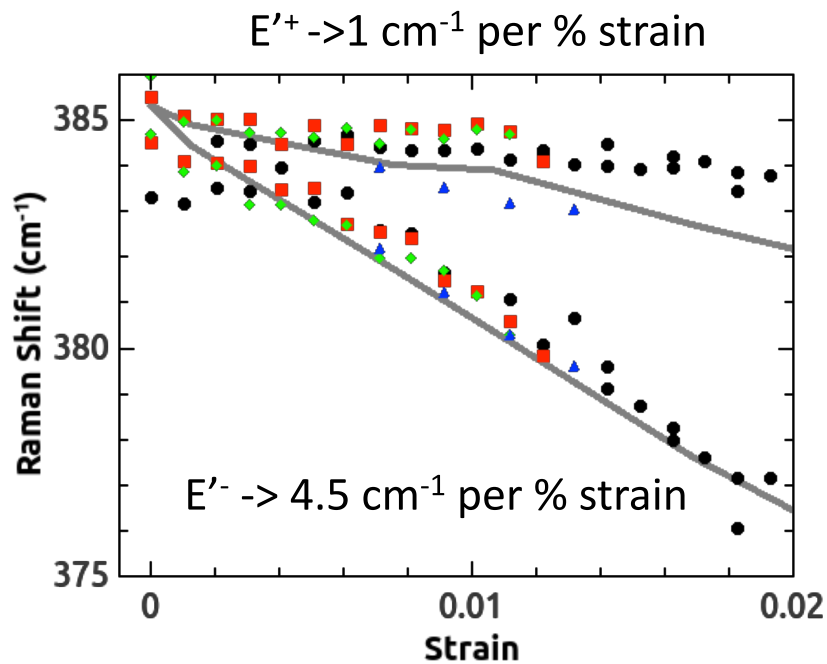




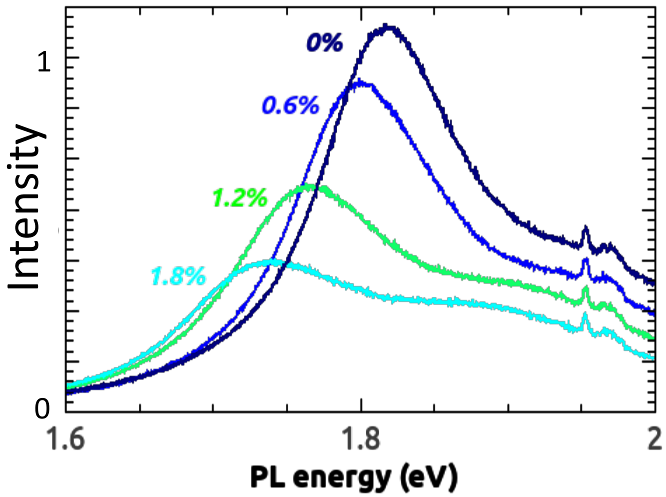
Phonon Softening : Experiments + Theory

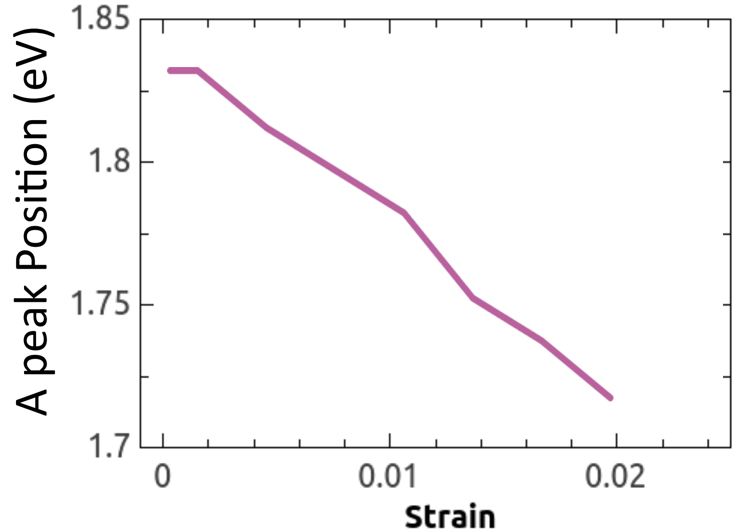
Q: How much MoS_2 is strained?

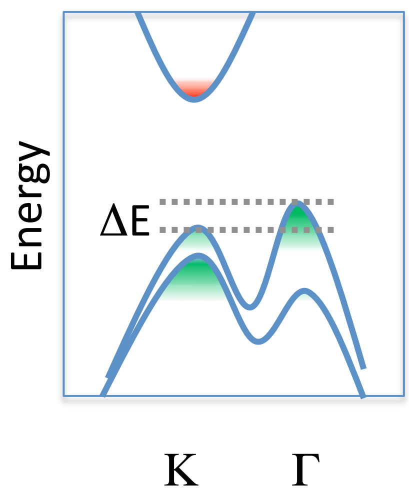


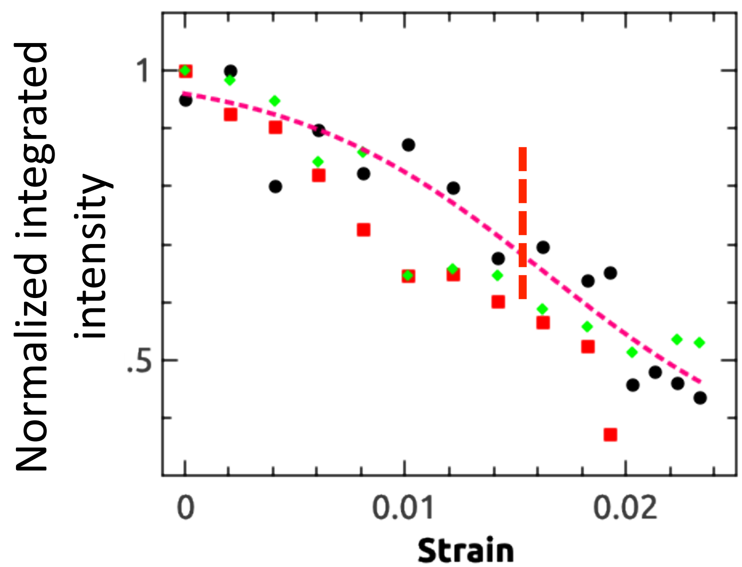


Combined Theory and Experiments







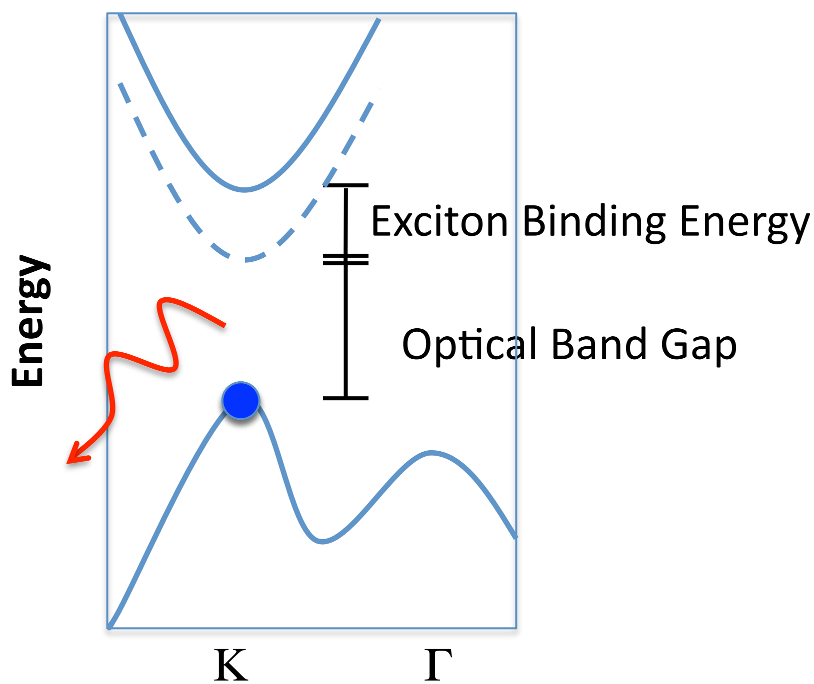


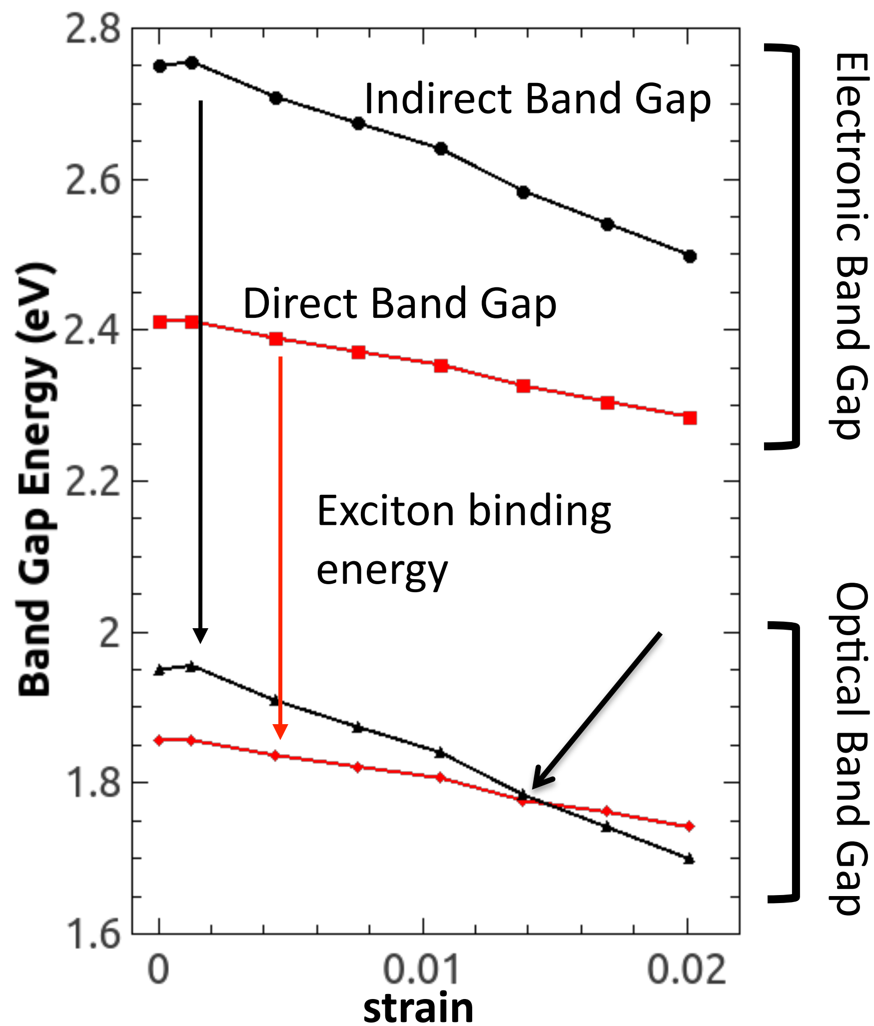
$$I \propto \frac{A}{e^{\Delta E / KT} + 1} + B$$

Δ E = 0 at 1.4 % strain

Theory: 5%

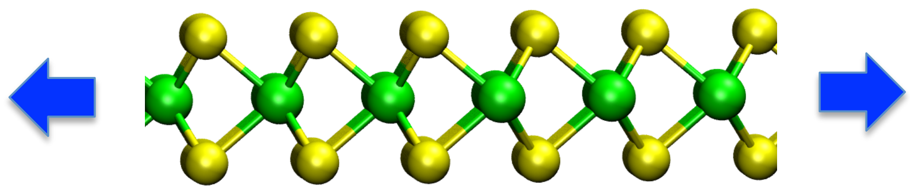
Optical Gap Switch





H. J. Conley, B. Wang, J. I. Ziegler, R. F. Haglund, S. T. Pantelides, K. I. Bolotin, Nano Lett. 13, 3626 (2013)

Take-home Message 2



- ✓Reduce the band gap
- ✓Optically direct → indirect
- ✓1.4% - 5%: optical switch

Thanks for your attention

HDTRA1-10-1-0016

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Prof. Ronald D. Schrimpf
Dr. Enxia Zhang