Fluorination of Graphene, Gas Sensing of Carbon-based Materials, and Spectral Analysis of Water/Oxides Surface: Physics of Adsorption and Interfaces

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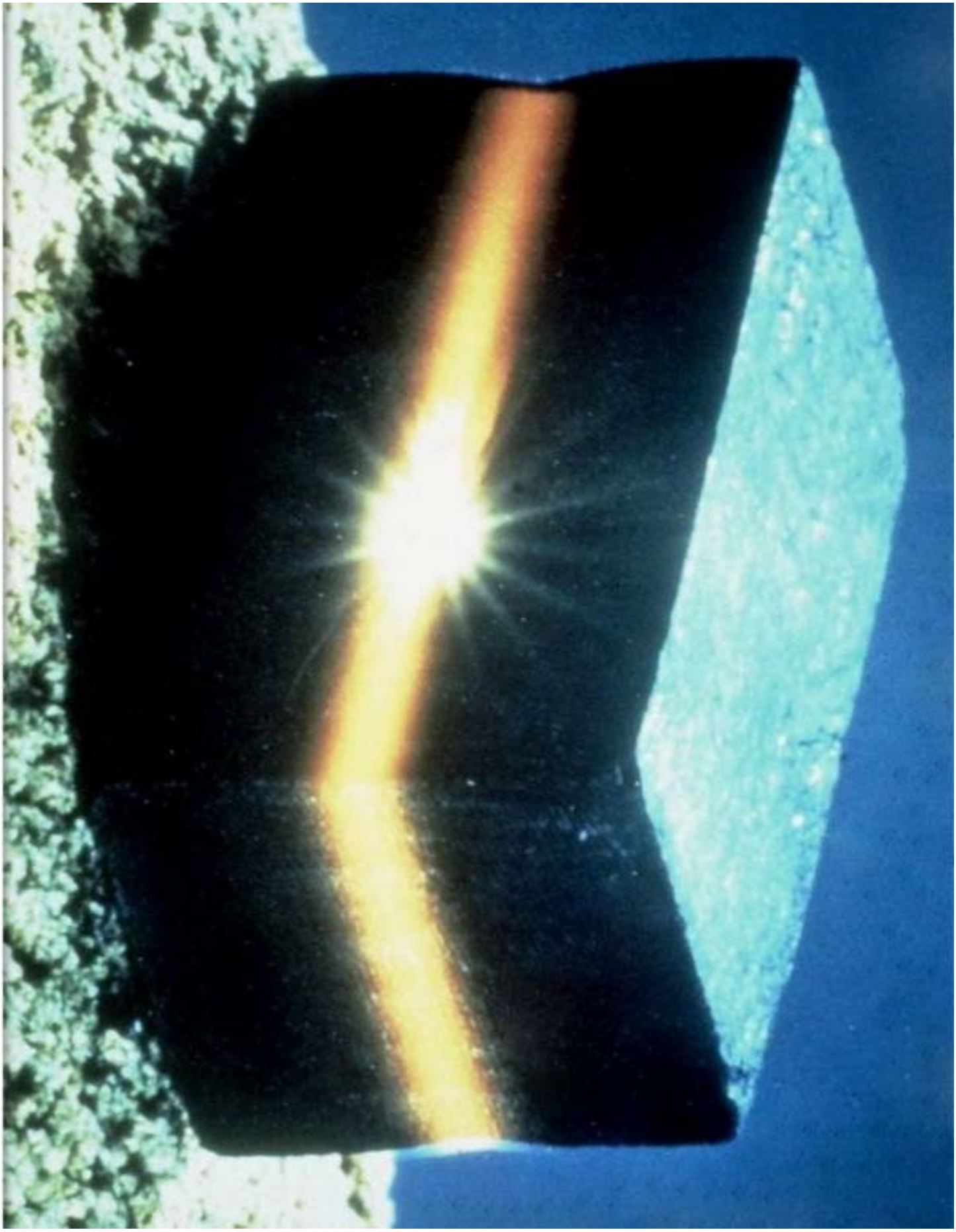
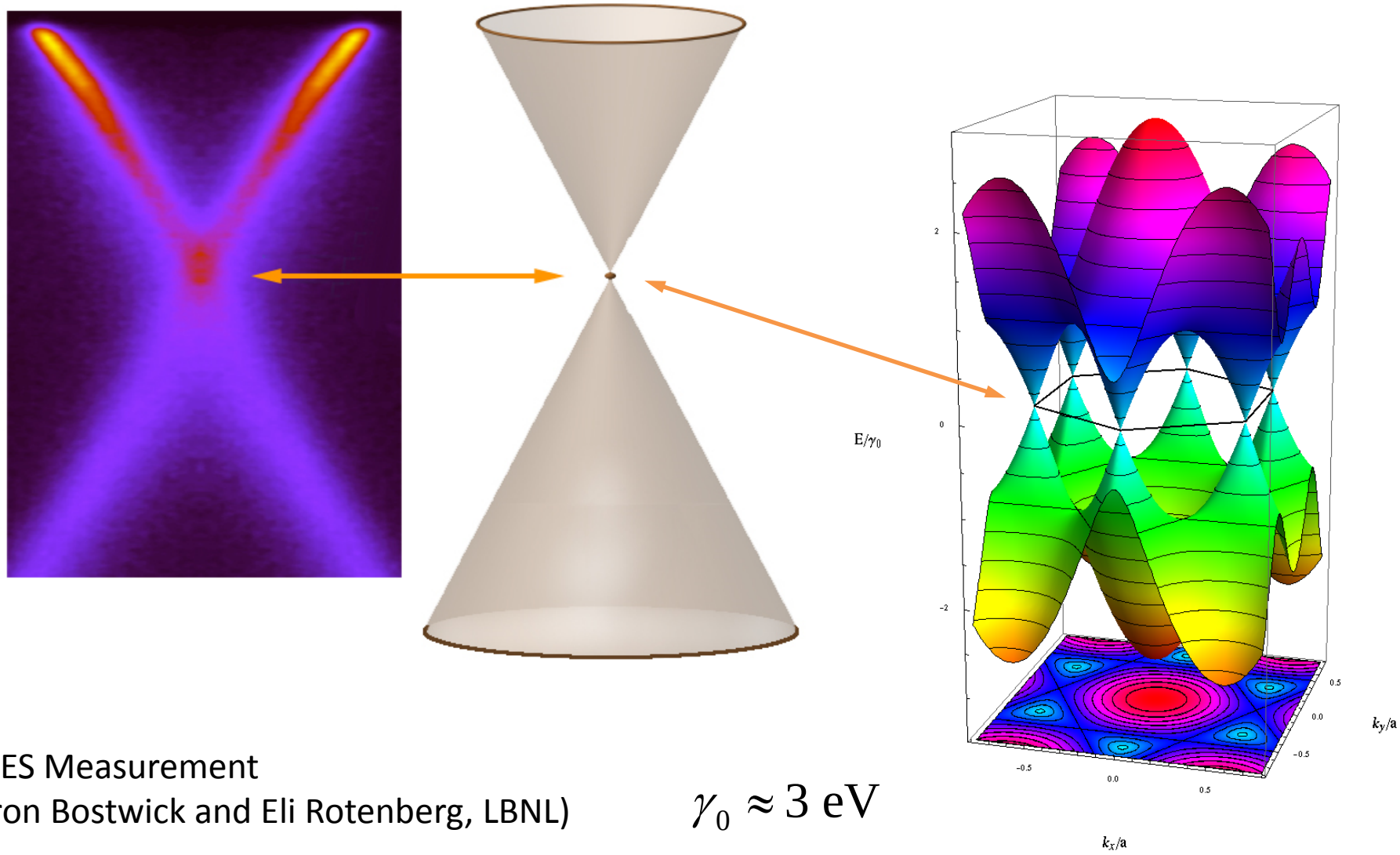
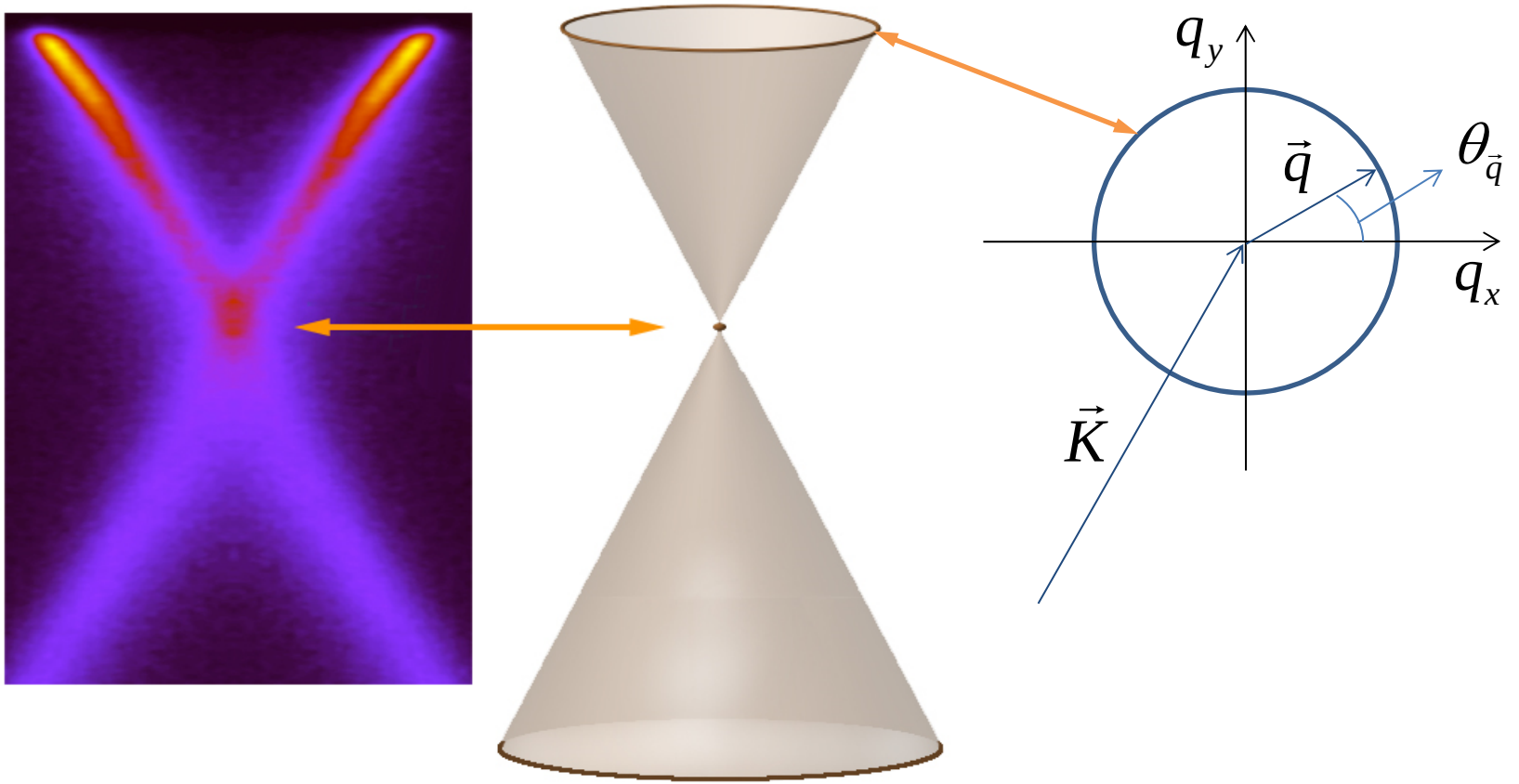
Courtesy: Richard Kaner, UCLA





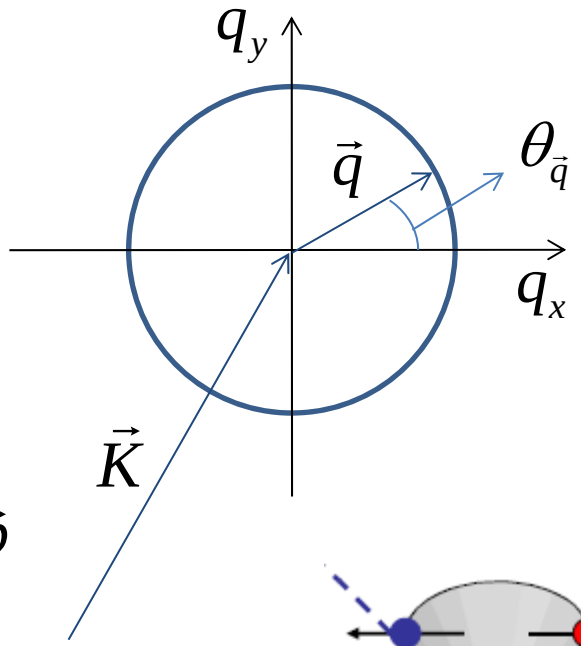
ARPES Measurement
(Aaron Bostwick and Eli Rotenberg, LBNL)

$\gamma_0 \approx 3$ eV


q_y
$\vec{q}$
$\theta_{\vec{q}}$
q_x
$\vec{K}$

Massless Dirac Fermions

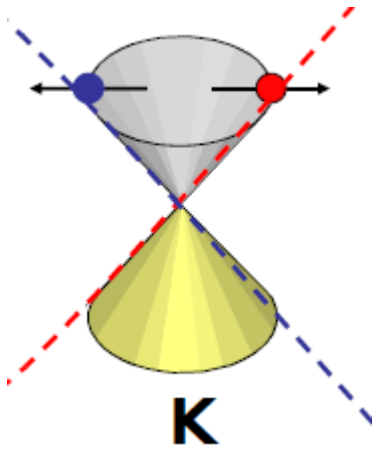
$$H_{\vec{k}} = \begin{bmatrix} 0 & -\gamma_0 \phi\left(\vec{k}\right) \\ -\gamma_0 \phi^*\left(\vec{k}\right) & 0 \end{bmatrix} \qquad \vec{k} = \vec{K} + \vec{q} \qquad \left|\vec{K}\right| >> \left|\vec{q}\right|$$



$$H_{\vec{q}} = \begin{bmatrix} 0 & -\frac{3\gamma_0 a}{2}\left|\vec{q}\right| e^{i\theta_{\vec{q}}} \\ -\frac{3\gamma_0 a}{2}\left|\vec{q}\right| e^{-i\theta_{\vec{q}}} & 0 \end{bmatrix} = v_F \vec{\sigma}\cdot\vec{p}$$

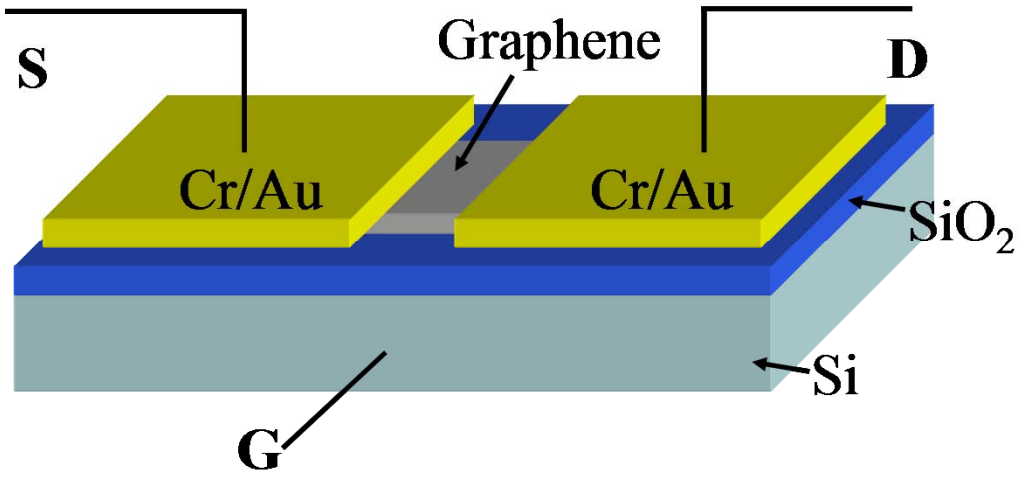
$$\varepsilon_{\pm}\left(\vec{q}\right) = \pm\frac{3\gamma_0 a}{2}\left|\vec{q}\right| = \pm\hbar v_F \left|\vec{q}\right|$$

Transport:
Backscattering is suppressed

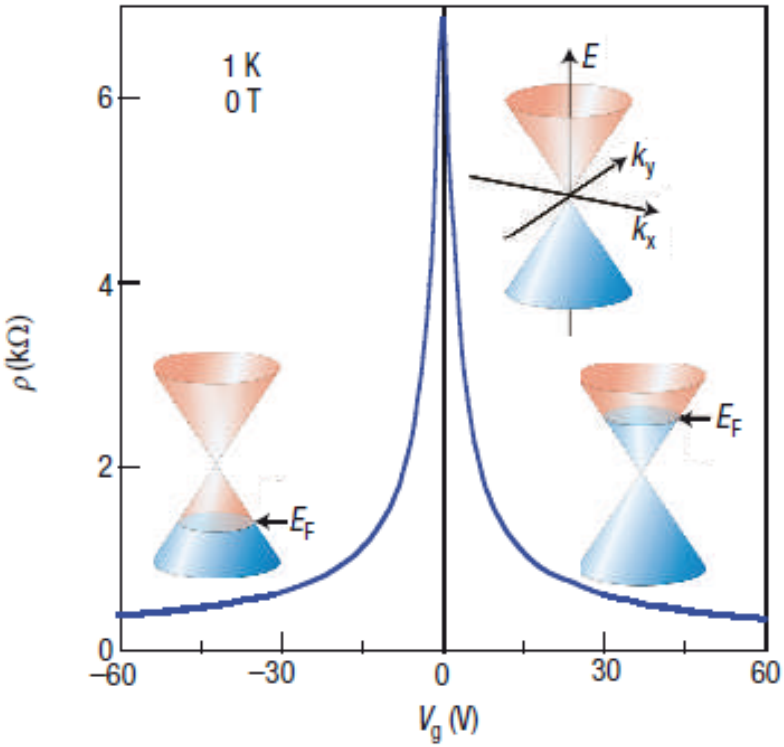


$$\left|\pm,\vec{q}\right\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} e^{-i\frac{\theta_{\vec{q}}}{2}} \\ \pm e^{i\frac{\theta_{\vec{q}}}{2}} \end{pmatrix} \qquad \left\langle +,\vec{q}\middle|+,-\vec{q}\right\rangle = 0 \quad !!$$

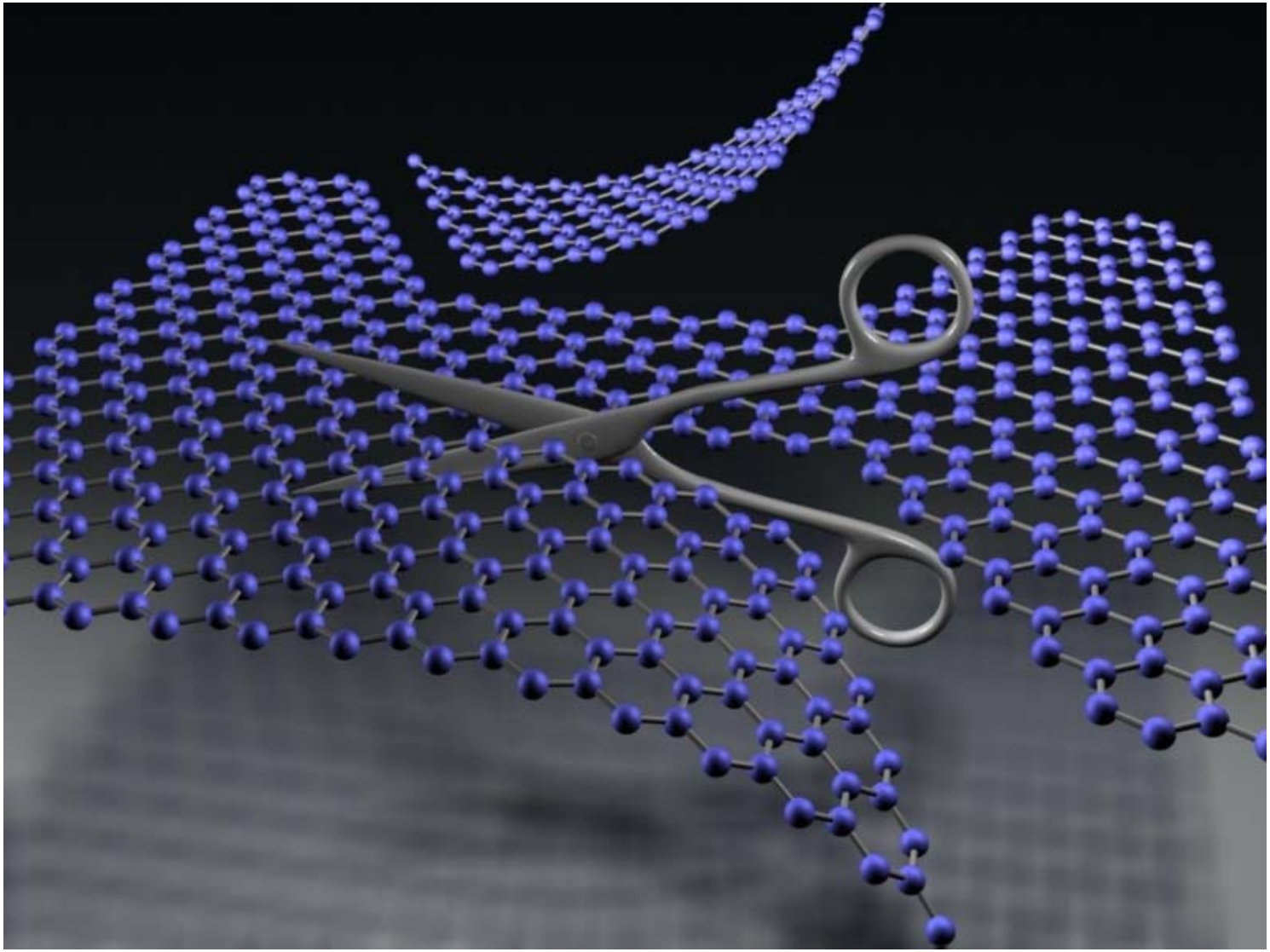
Carrier density controlled by gate voltage



Hugo Romero, et al., *ACS Nano* (September 30, 2008).



A. Geim and K. Novoselov.
"The rise of graphene."
Nat Mater 6, 183 (2007)



Graphics courtesy of
Kostya Novoselov

PHYSICAL REVIEW B **75**, 153401 (2007)

Graphane: A two-dimensional hydrocarbon

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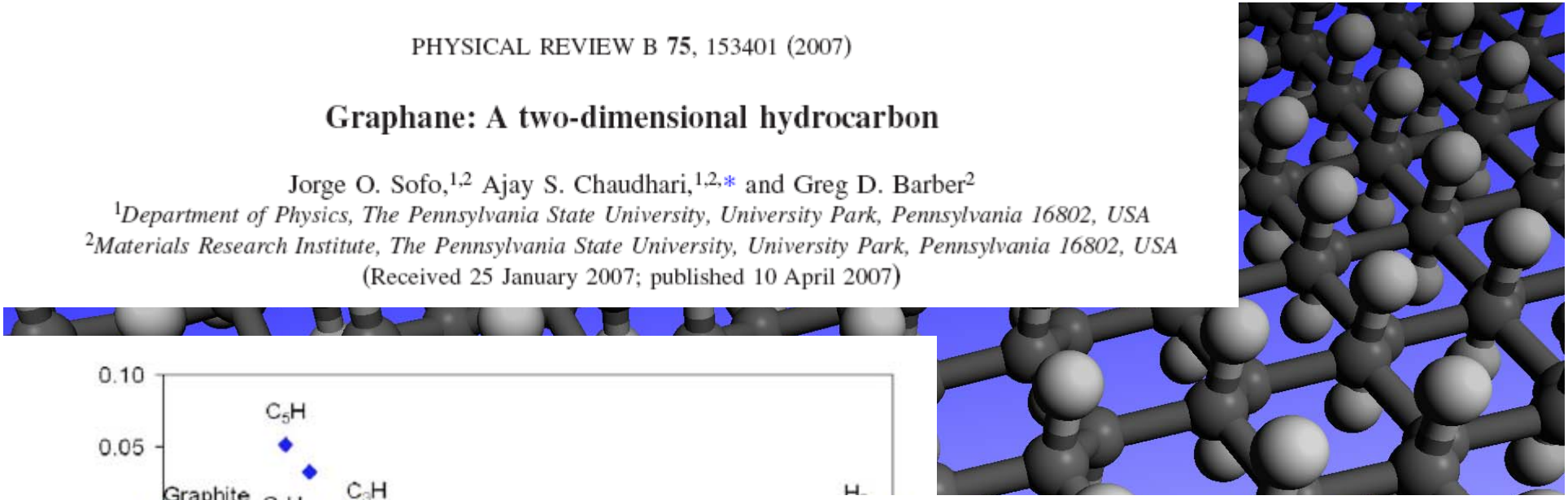
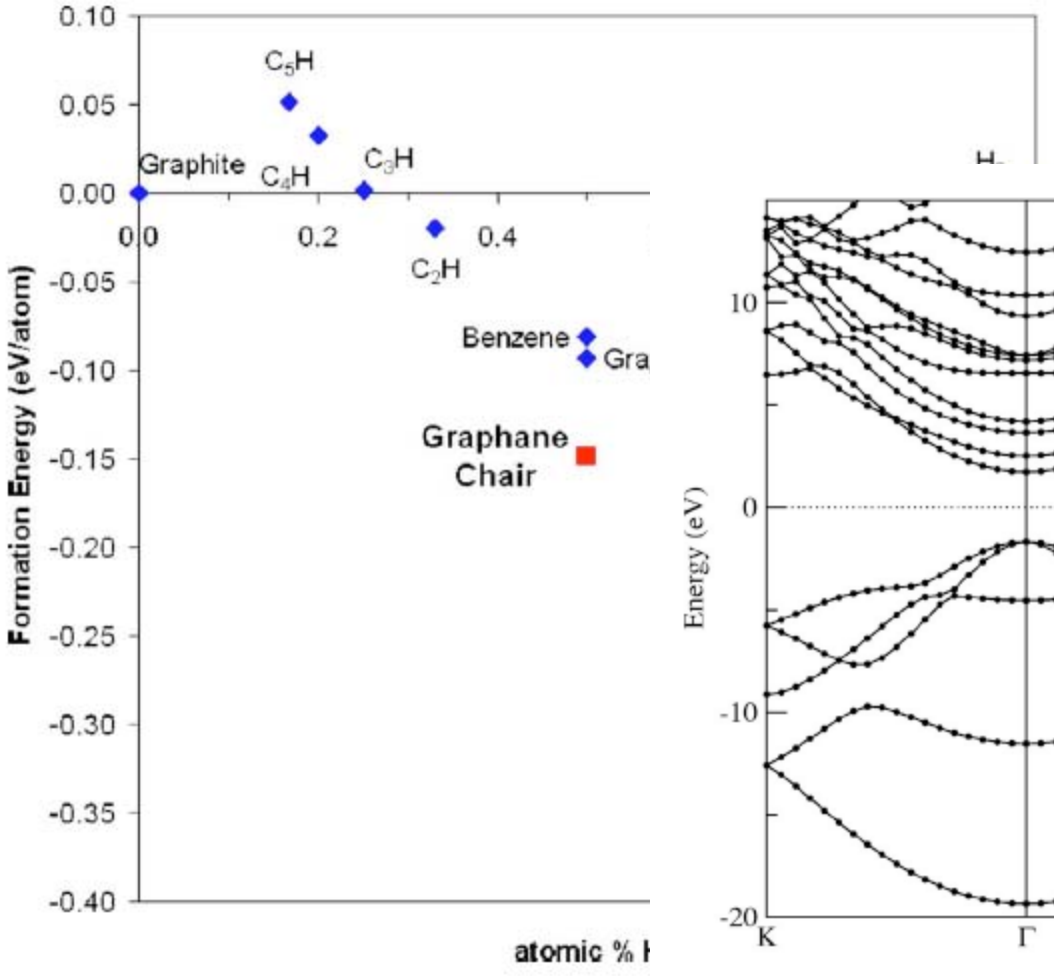
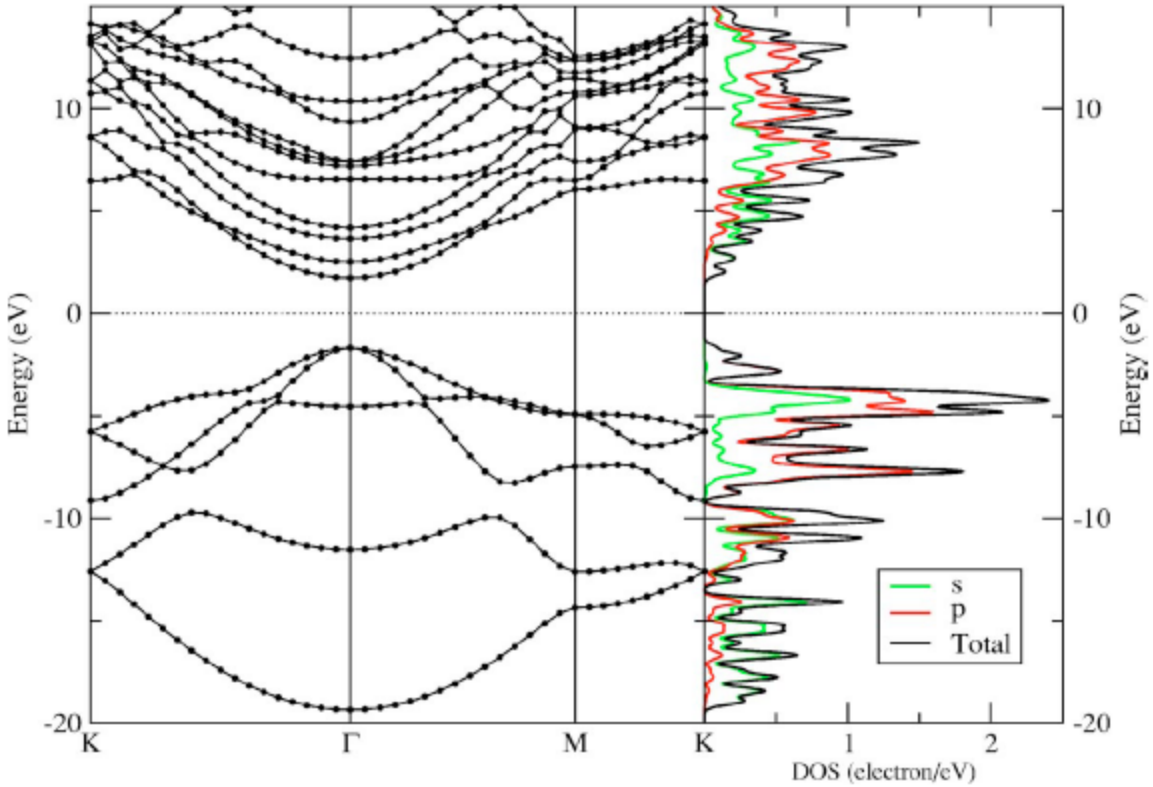
(Received 25 January 2007; published 10 April 2007)







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Control of Graphene's Properties by Reversible Hydrogenation: Evidence for Graphane

D. C. Elias,[1*] R. R. Nair,[1*] T. M. G. Mohiuddin,[1] S. V. Morozov,[2] P. Blake,[3] M. P. Halsall,[1] A. C. Ferrari,[4] D. W. Boukhvalov,[5] M. I. Katsnelson,[5] A. K. Geim,[1,3] K. S. Novoselov[1]†

Although graphite is known as one of the most chemically inert materials, we have found that graphene, a single atomic plane of graphite, can react with atomic hydrogen, which transforms this highly conductive zero-overlap semimetal into an insulator. Transmission electron microscopy reveals that the obtained graphene derivative (graphane) is crystalline and retains the hexagonal lattice, but its period becomes markedly shorter than that of graphene. The reaction with hydrogen is reversible, so that the original metallic state, the lattice spacing, and even the quantum Hall effect can be restored by annealing. Our work illustrates the concept of graphene as a robust atomic-scale scaffold on the basis of which new two-dimensional crystals with designed electronic and other properties can be created by attaching other atoms and molecules.

Graphene, a flat r
tightly packed
continues to attr
ly because of its unu
and effects that arise fi
ness (*1*). Chemical mo
been less explored, eve
bon nanotubes suggest
tered chemically without
bonds. For example, graphene oxide is graphene densely covered with hydroxyl and other groups (*2*–*6*). Unfortunately, graphene oxide is strongly disordered, poorly conductive, and difficult to

rial. Particularly elegant is the idea of attaching atomic hydrogen to each site of the graphene lattice to create graphane (*7*), which changes the hybridization of carbon atoms from sp^2 into sp^3,

thus removing the conducting π-bands and opening an energy gap (*7*, *8*).

Previously, absorption of hydrogen on graphitic surfaces was investigated mostly in conjunction with hydrogen storage, with the research focused on physisorbed molecular hydrogen (*9*–*11*). More recently, atomic hydrogen chemisorbed on carbon nanotubes has been studied theoretically (*12*) as well as by a variety of experimental techniques including infrared (*13*), ultraviolet (*14*, *15*), and x-ray (*16*) spectroscopy and scanning tunneling microscopy (*17*). We report the reversible hydrogenation of single-layer graphene and observed dramatic changes in its transport properties and in its electronic and atomic structure, as evidenced by Raman spectroscopy and transmission electron microscopy (TEM).

Graphene crystals were prepared by use of micromechanical cleavage (*18*) of graphite on top of an oxidized Si substrate (300 nm SiO_2) and then identified by their optical contrast (*1*, *18*) and distinctive Raman signatures (*19*). Three types of samples were used: large (>20 μm) crystals for Raman studies, the standard Hall bar devices 1 μm in width (*18*), and free-standing membr TEM. For details of sample er to earlier work (*18*, *20*, *21*).

Astronomy, University of Manchester, UK. [2]Institute for Microelectronics Tech- ogolovka, Russia. [3]Manchester Centre anotechnology, University of Manches- ster, UK. [4]Department of Engineering, 9 JJ Thomson Avenue, Cambridge CB3 OFA, UK. [5]Institute for Molecules and Materials, Radboud University Nijmegen, 6525 ED Nijmegen, Netherlands.

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†To whom correspondence should be addressed. E-mail: Kostya@manchester.ac.uk

7. J. O. Sofo, A. S. Chaudhari, G. D. Barber, *Phys. Rev. B* **75**, 153401 (2007).

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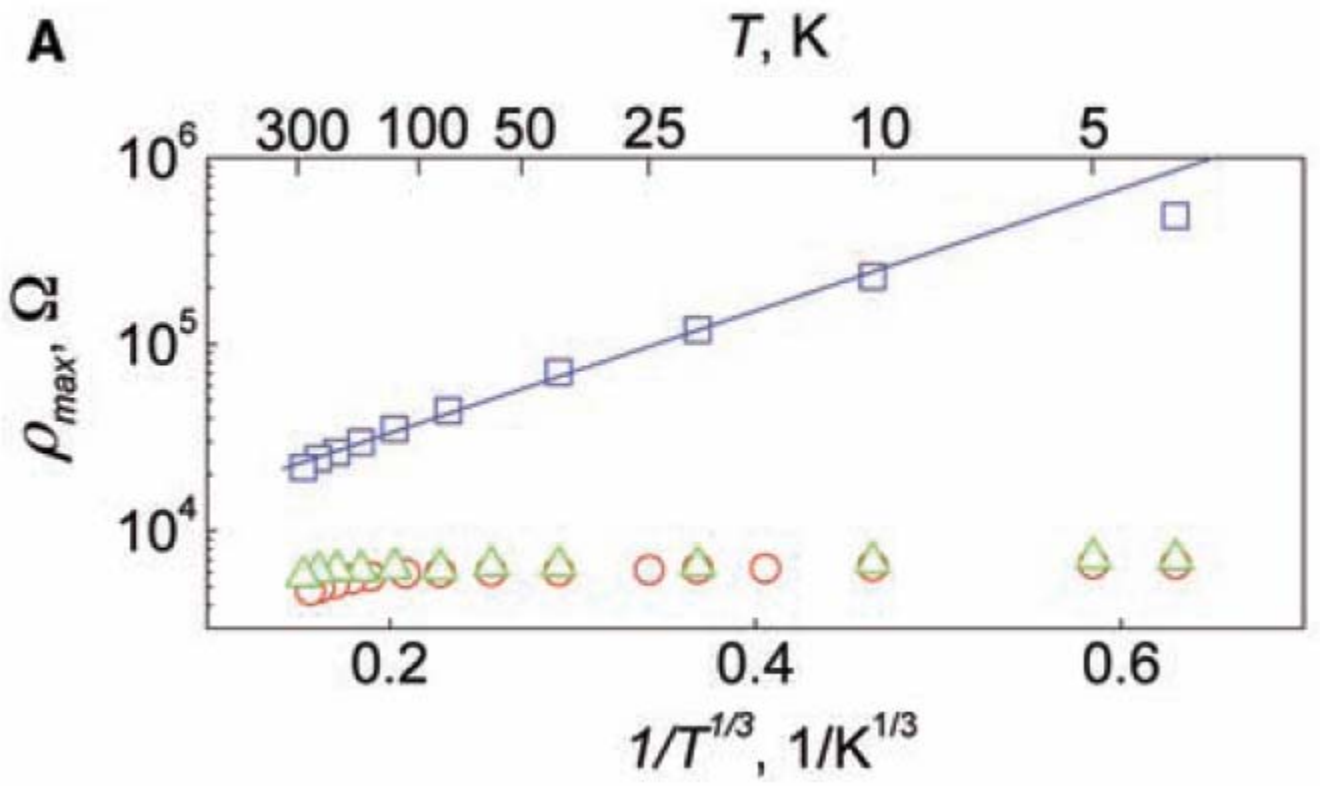

Graphe
tightl
conti
ly because c
and effects th
ness (*1*). Che
been less exp
bon nanotube
tered chemica
bonds. For ex
densely cove
(*2*–*6*). Unfort
disordered, p

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M).
by use of
raphite on
SiO_2) and
ast (*1*, *18*)
Three types
n) crystals
all bar de-
ding mem-
of sample
8, *20*, *21*).

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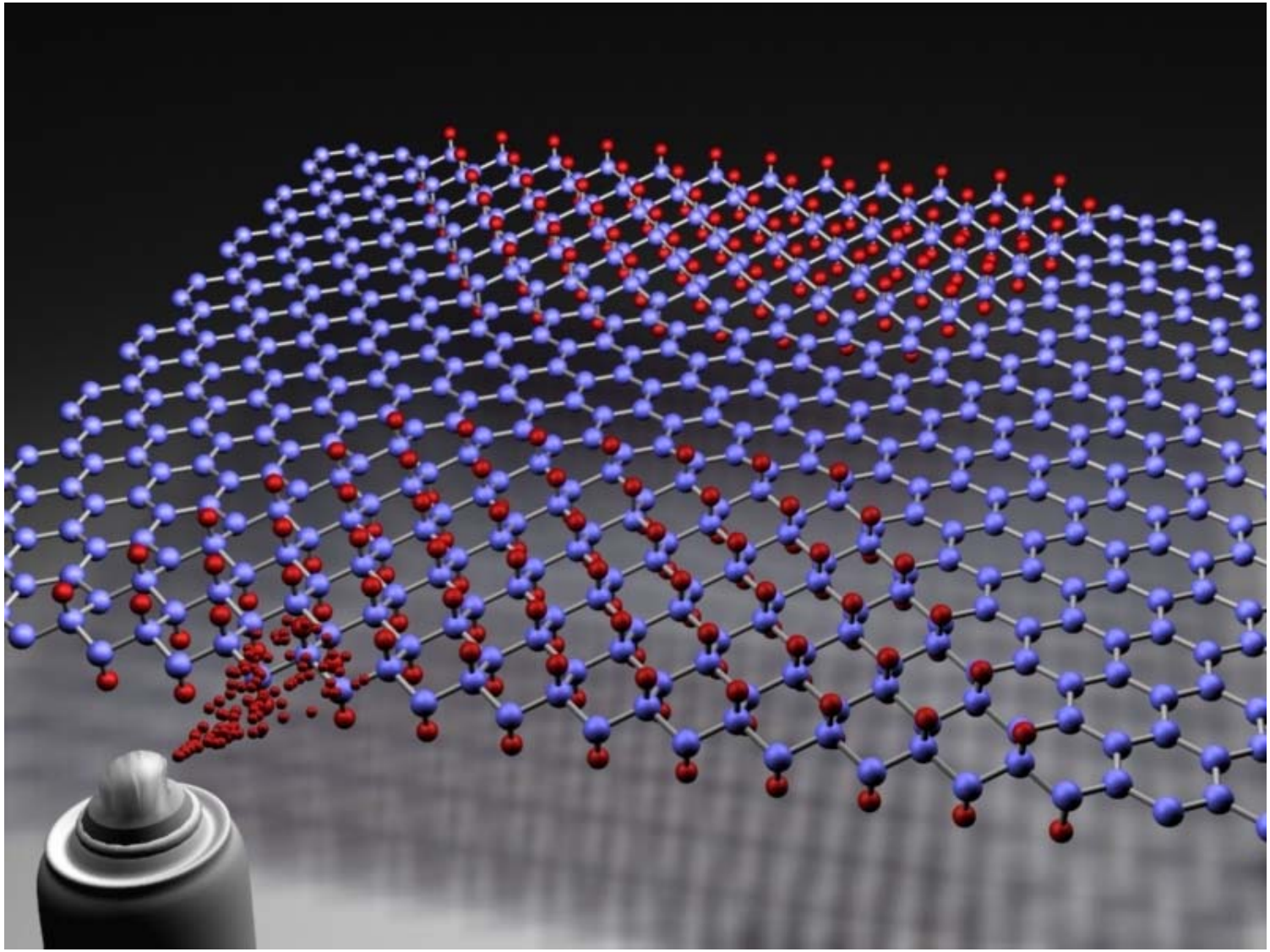
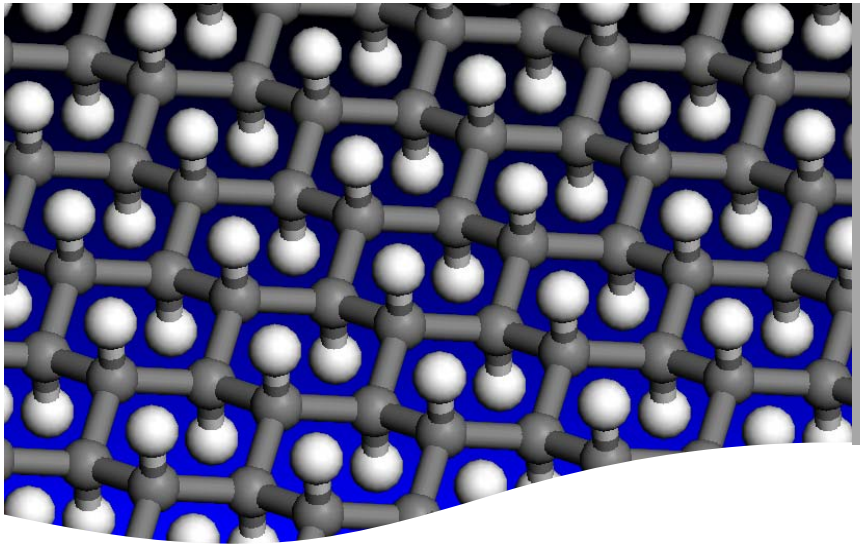


Graphics courtesy of
Kostya Novoselov



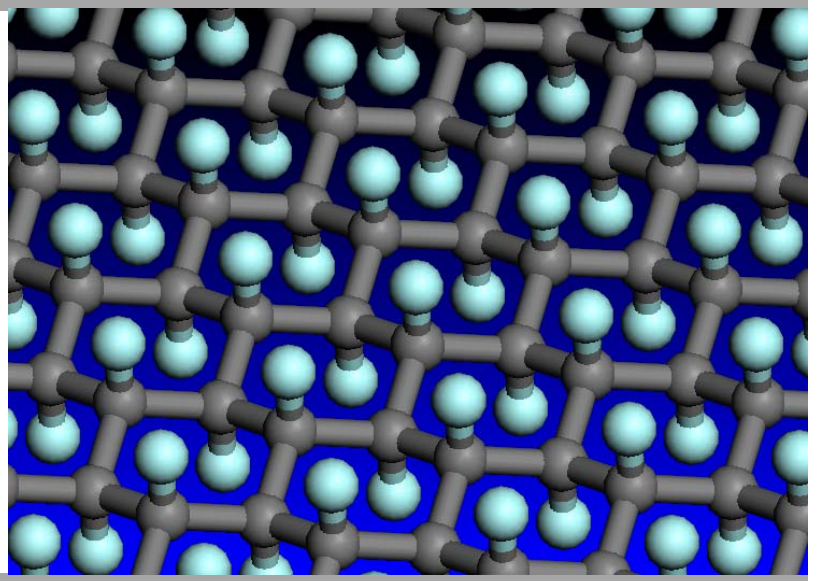
CH → Graphane

Predicted by

JOS, A. Chaudhari, and G. Barber PRB **75**,153401 (2007)

Some evidence shown by

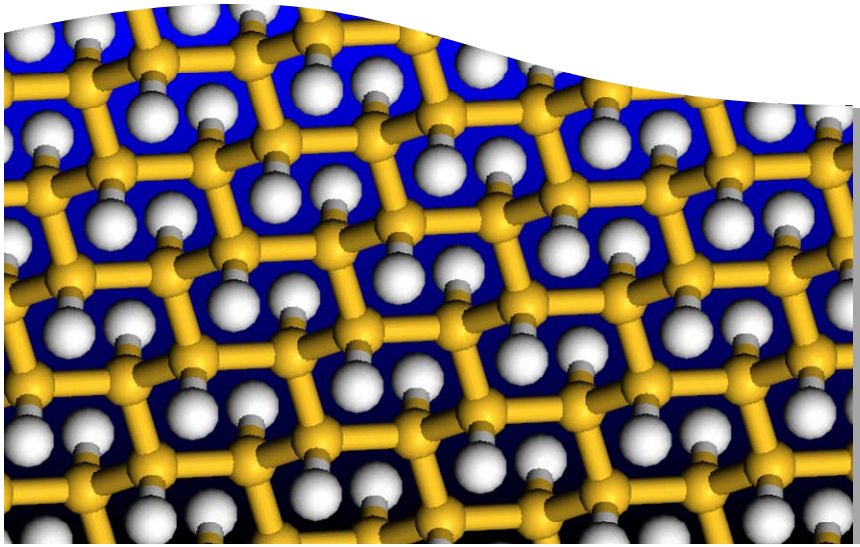
D. C. Elias, et al. Science **323**, 610 (2009)



CF → Carbon Monofluoride

Discovered by

O. Ruff and O. BretshneiderZJOS1rg. Allg. Chem. **217**, 1 (1934)



SiH → Polysilane

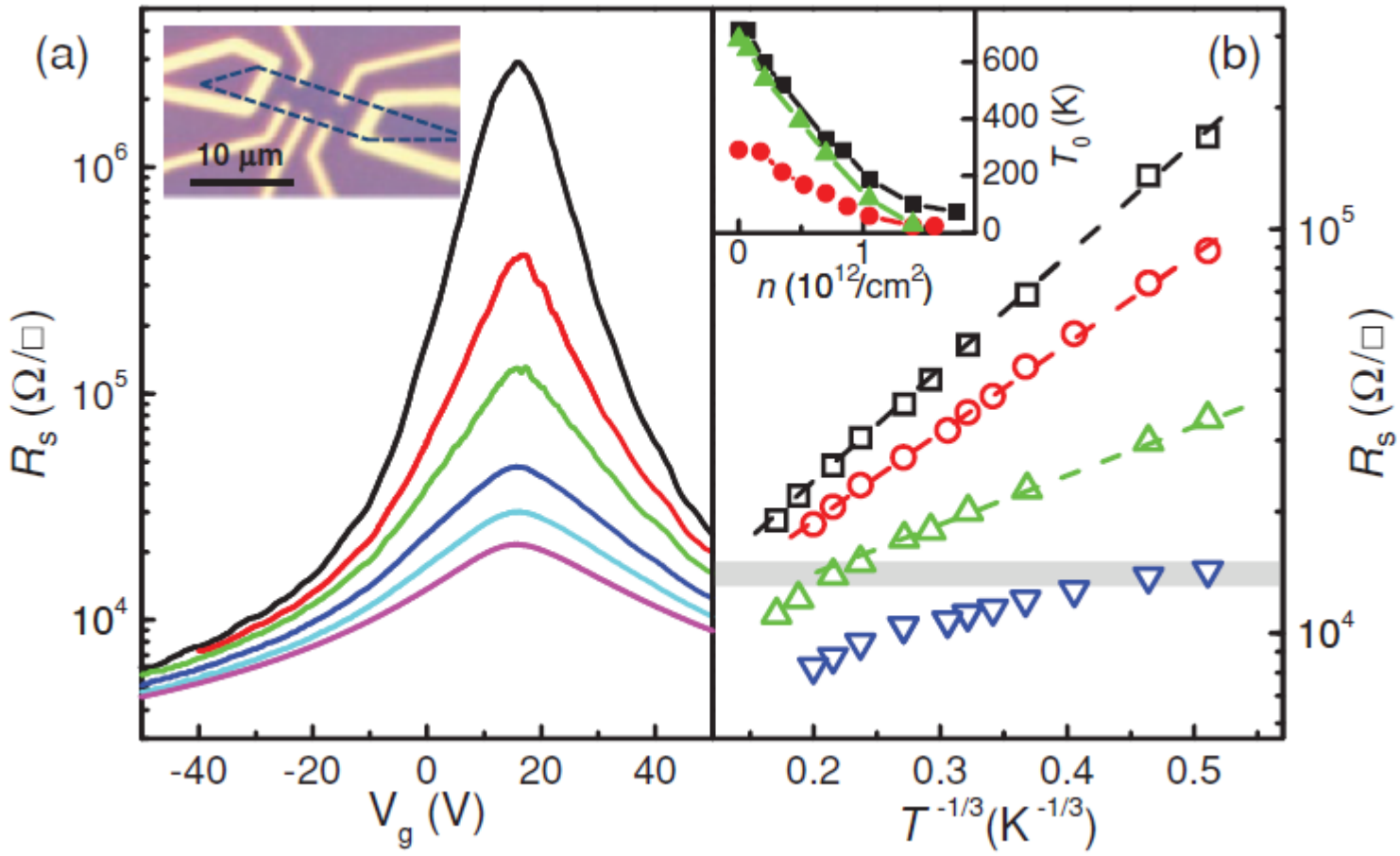
Predicted by

K. Takeda and K. Shiraishi, PRB **39**, 11028 (1989)

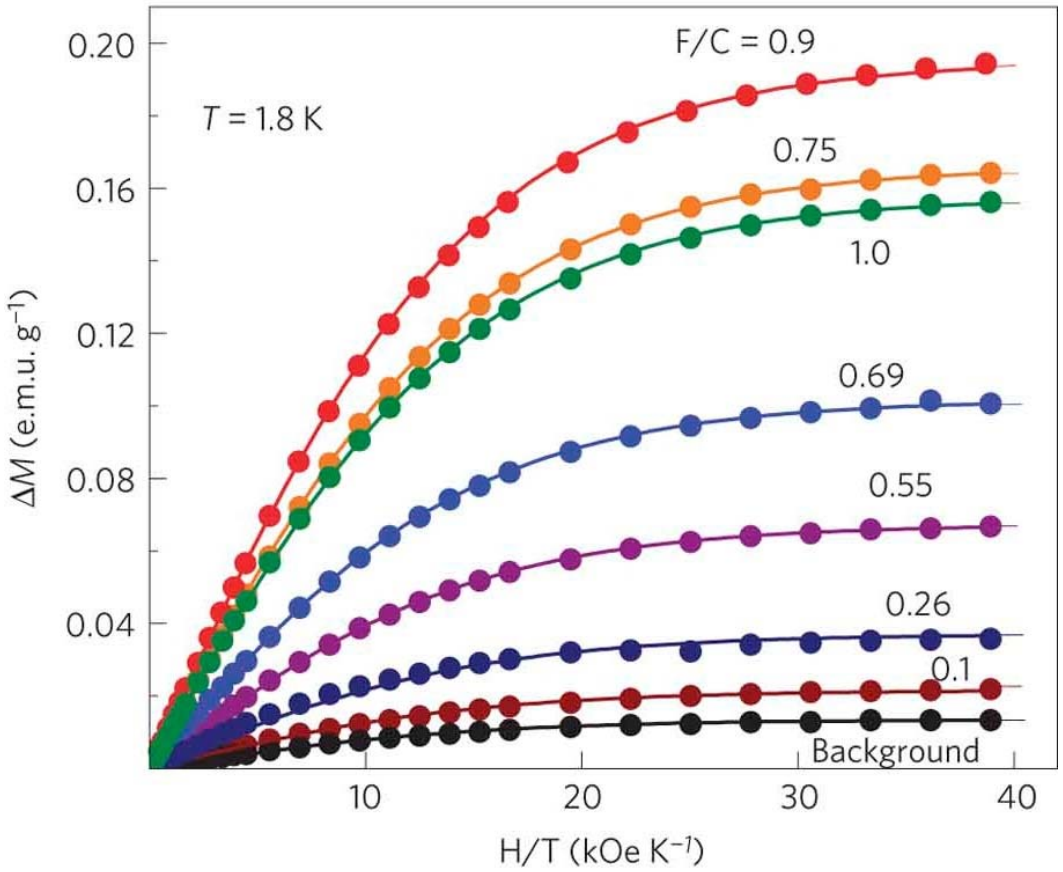
Synthesized by

J. Dahn, B. Way, E. Fuller, and J. Tse PRB **48**, 17872 (1993)

Partially fluorinated graphene



X. HONG, S.-H. CHENG, C. HERDING, AND J. ZHU
PHYSICAL REVIEW B **83**, 085410 (2011)



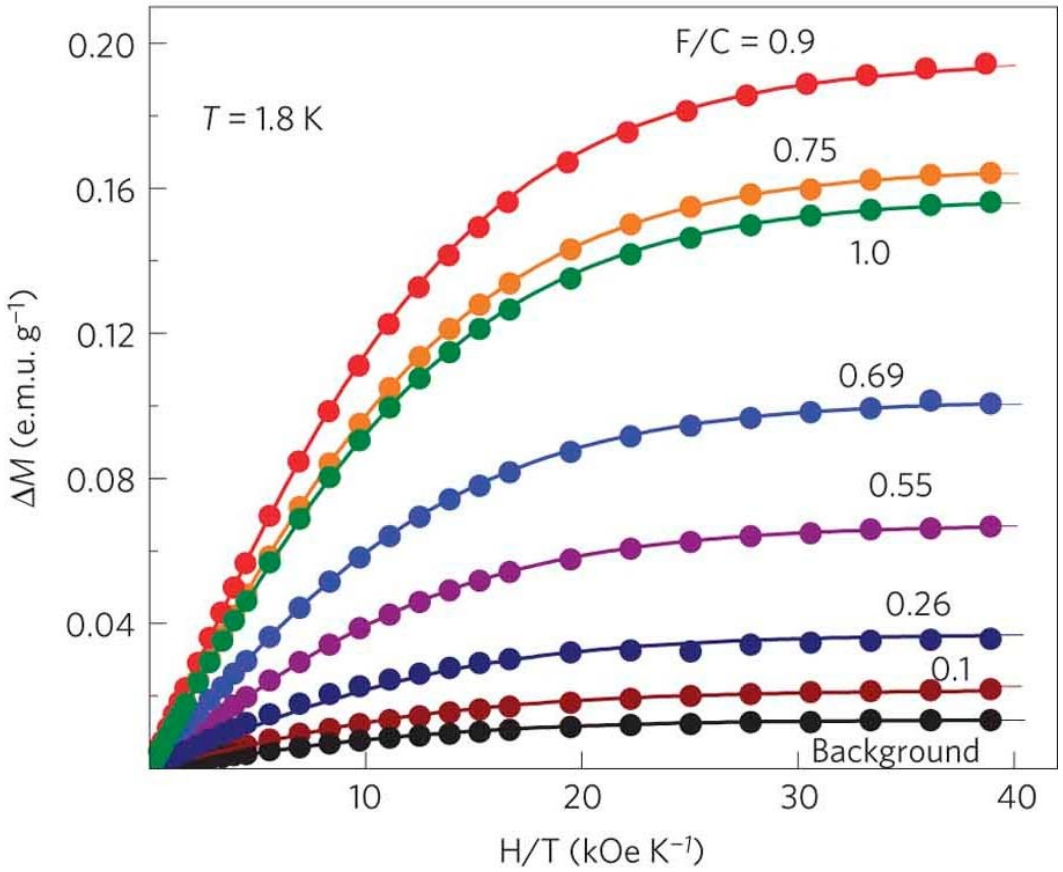
$$M = NgJ\mu_B \left[\frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} z \right) - \frac{1}{2J} \coth\left(\frac{z}{2J} \right) \right]$$

$$z = \frac{gJ\mu_B H}{k_B T}$$

R. R. Nair, et al., Nat. Phys. **8**, 199 (2012).

What about adsorbing more atoms…

IS FLUORINATED GRAPHENE MAGNETIC?



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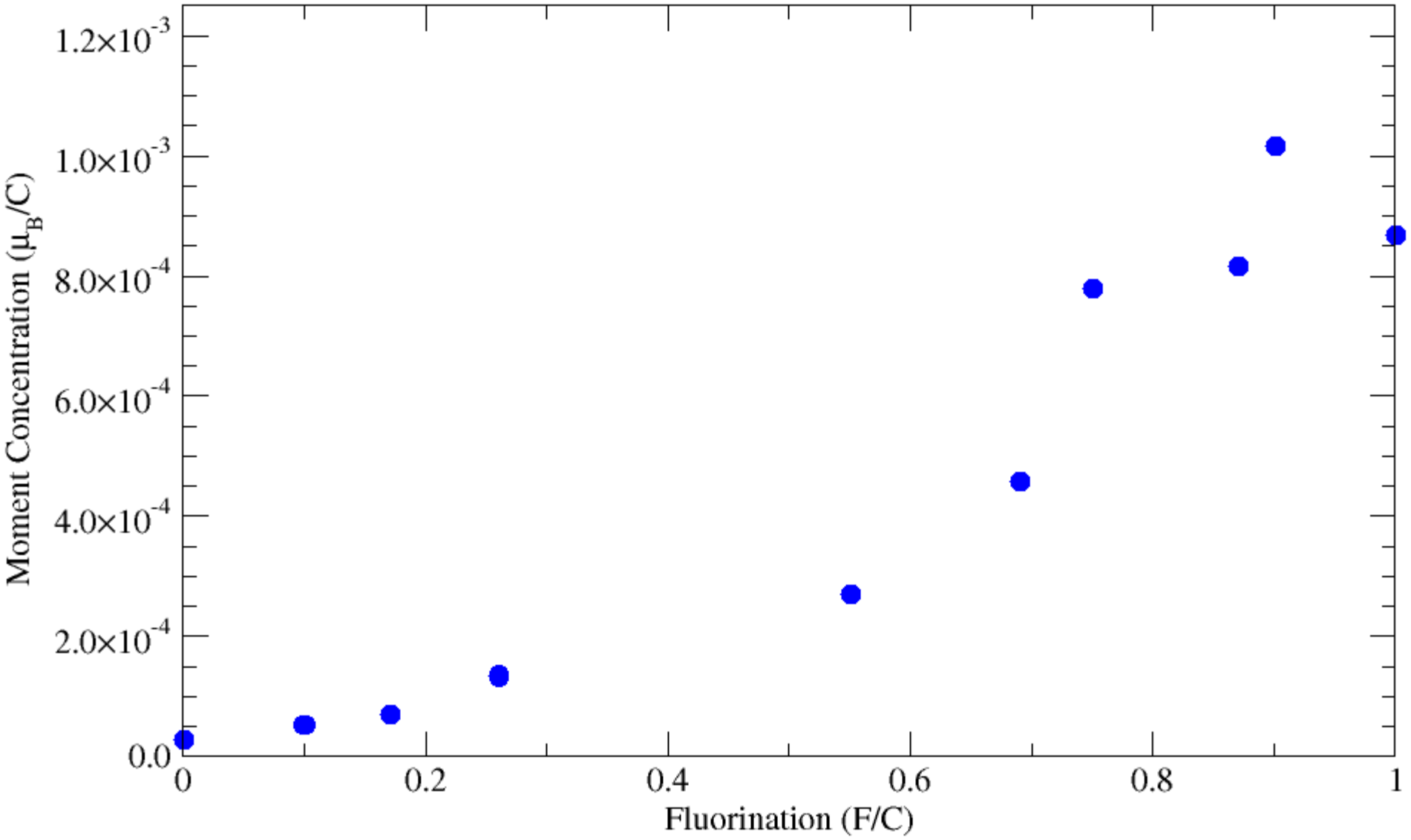
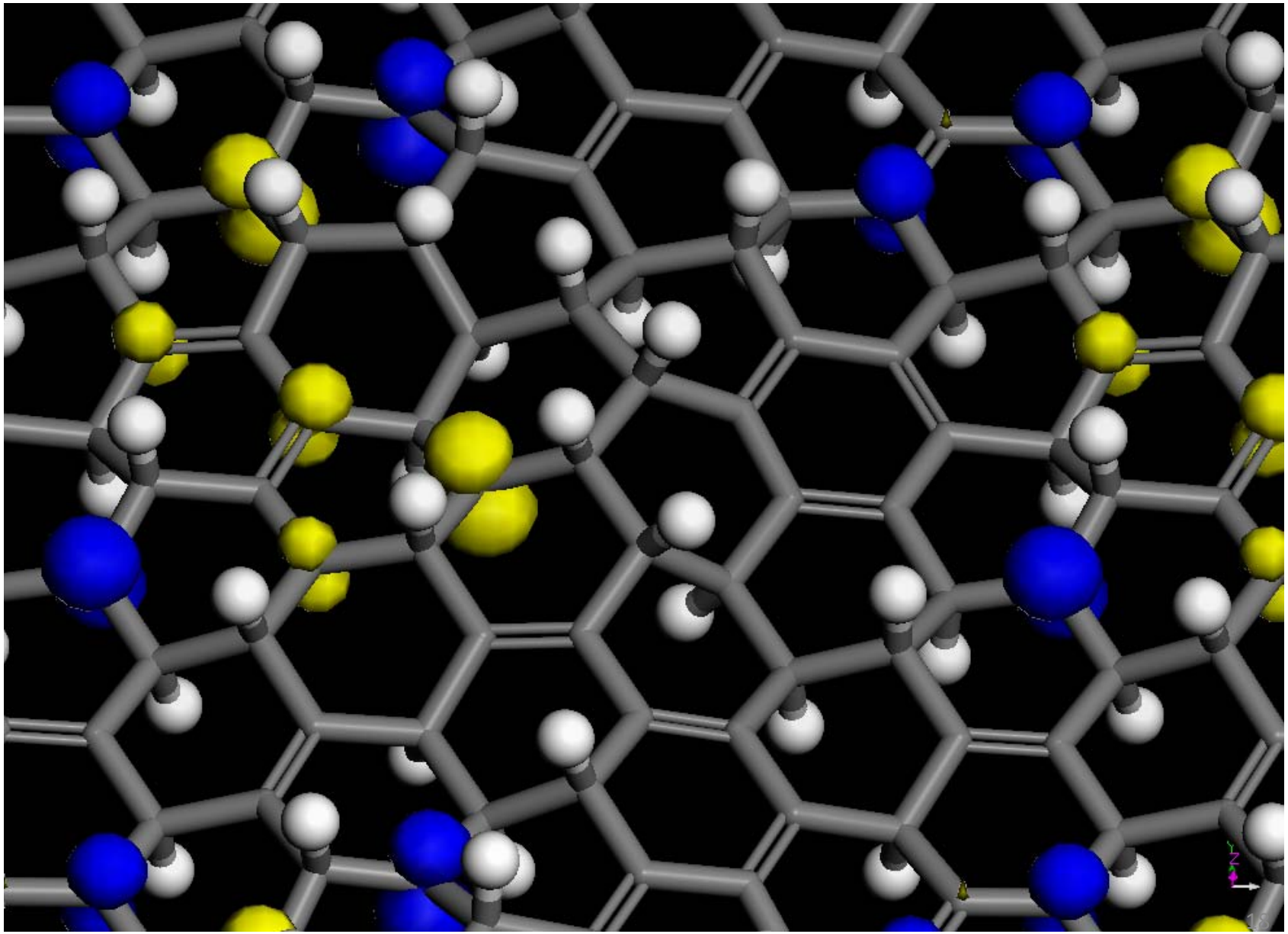
$$z = \frac{gJ\mu_B H}{k_B T}$$

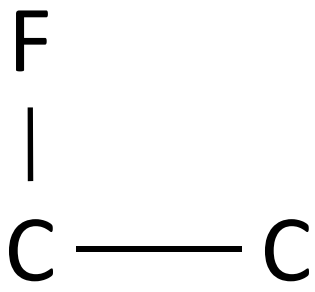
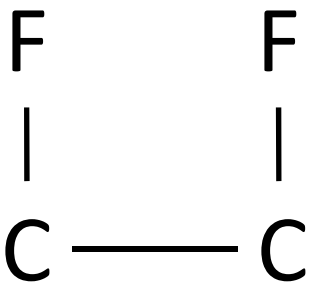
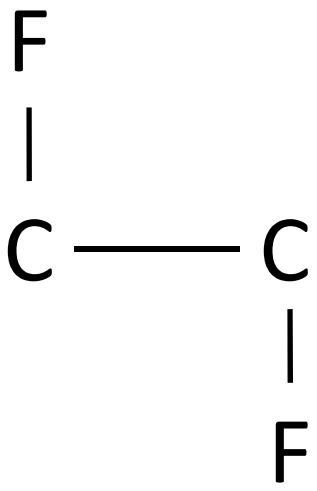
R. R. Nair, et al., Nat. Phys. **8**, 199 (2012).

Experimental fluorination sees magnetism…

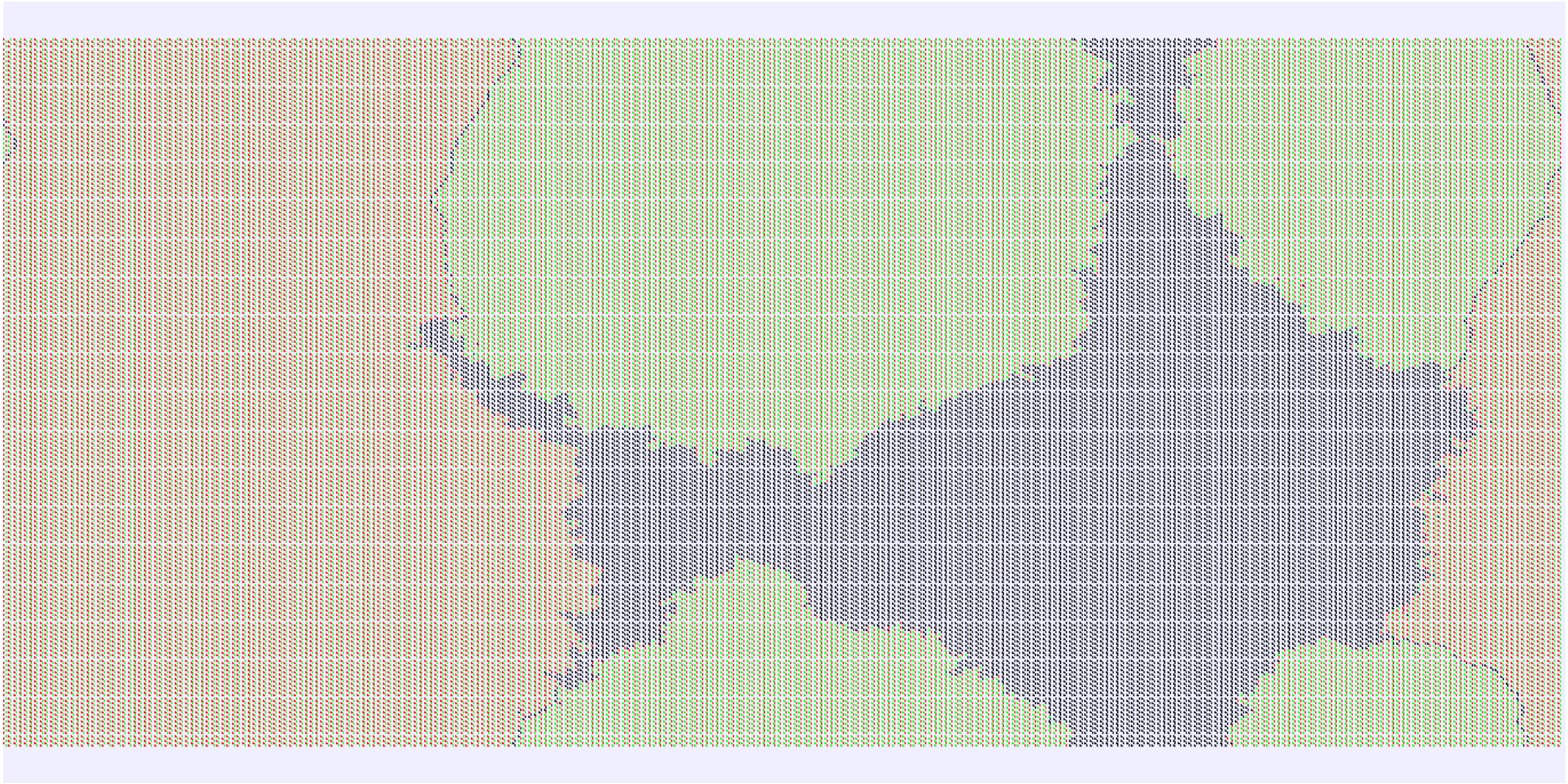


R. R. Nair, et al., Nat. Phys. **8**, 199 (2012).



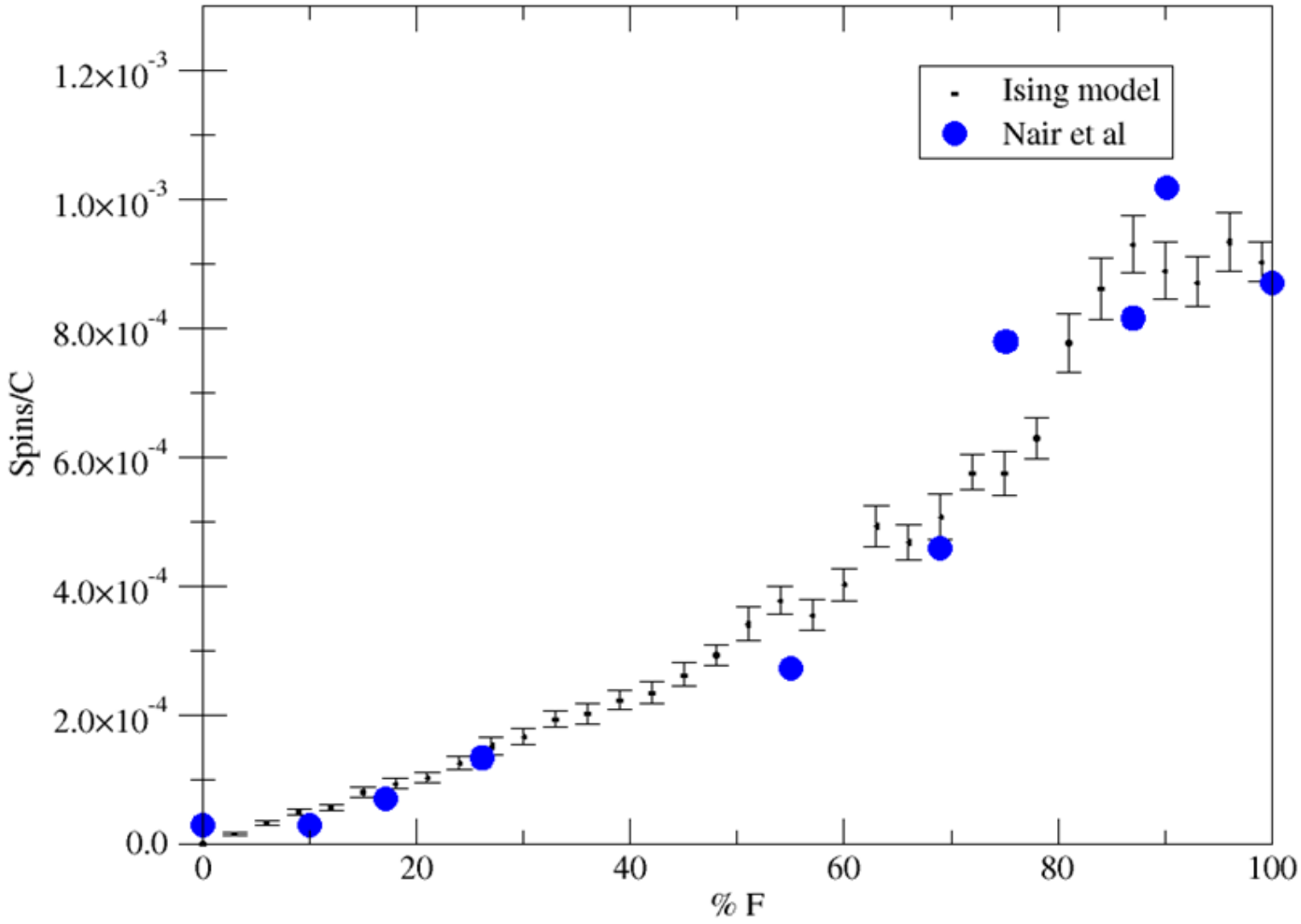
a)	b)	c)
		
$dE = 0$	$dE = J_{same}$	$dE = J_{opp}$

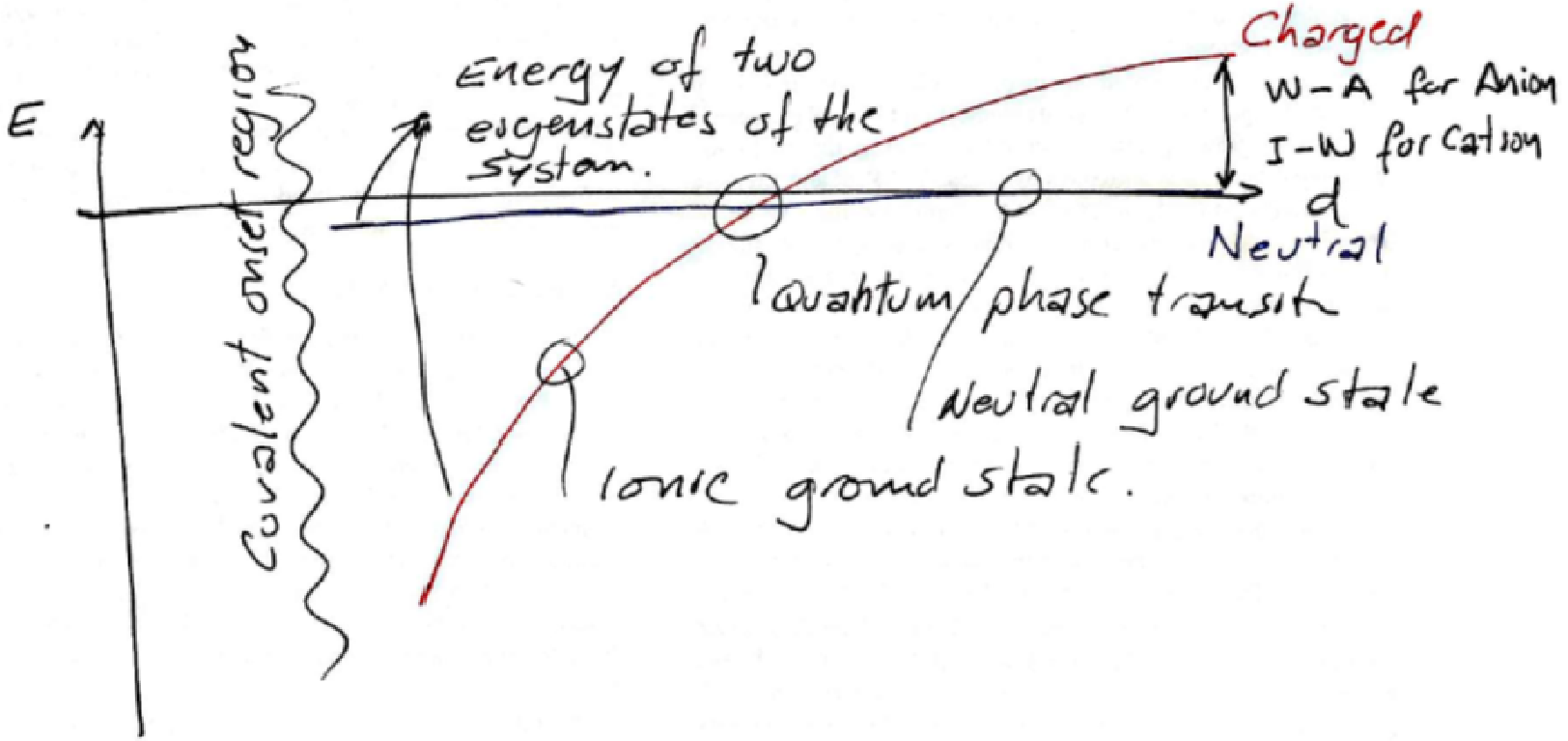
$$H^{IL} = \sum_{<i,j>} (J_{opp} + (J_{same} - J_{opp})\delta_{s_i s_j}) s_i s_j - \mu \sum_i |s_i|$$



Ising Model $J_{same} = 1, J_{opp} = -1, \mu = -1, T = 0.07$

F/C = 0.75


Ising model
Nair et al
Spins/C
% F
0.0
2.0×10-4
4.0×10-4
6.0×10-4
8.0×10-4
1.0×10-3
1.2×10-3
0
20
40
60
80
100


E
Covalent onset region
Energy of two eigenstates of the system.
Charged
W-A for Anion
I-W for Cation
d
Neutral
Quantum phase transit
Neutral ground state
Ionic ground state.

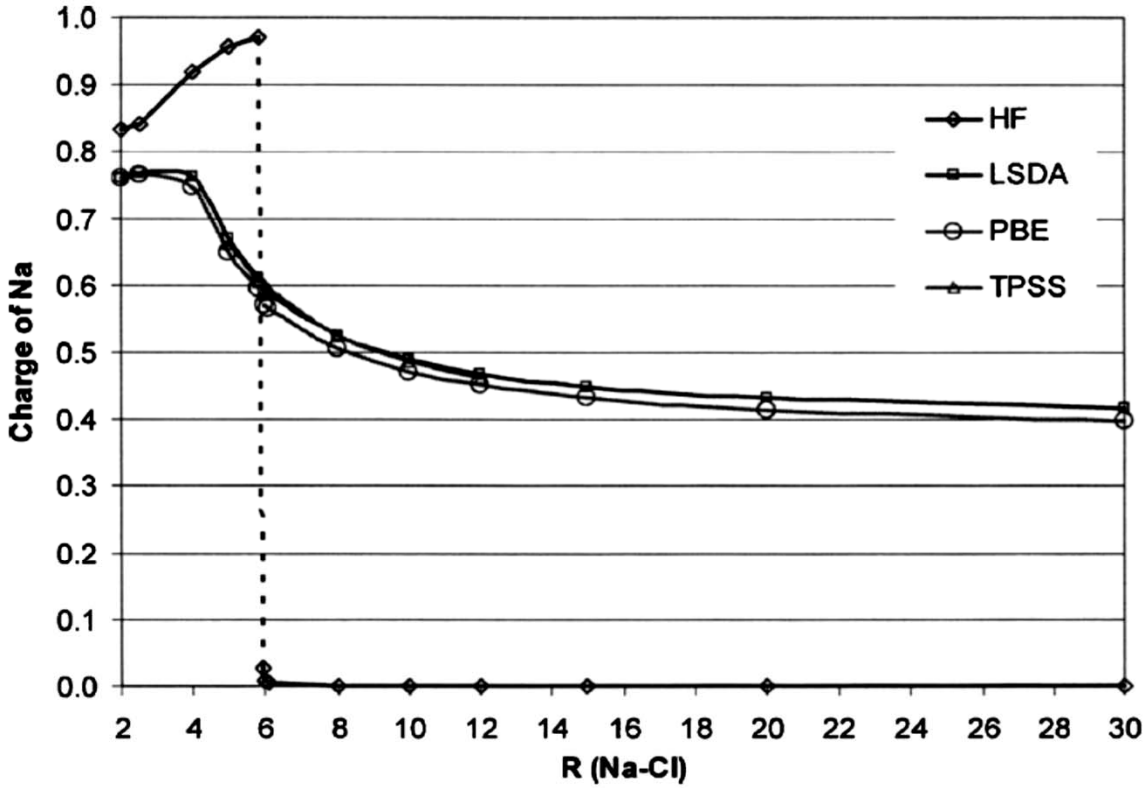


FIG. 3. Fractional (ChelpG) (Ref. 35) charge q on Na in NaCl as a function of bond length R (in Å). The Hartree-Fock "quantum phase transition" is qualitatively right, as discussed in the text.

Ruzsinszky, J. P. Perdew, G. I. Csonka, O. A. Vydrov, and G. E. Scuseria. 2006. "Spurious Fractional Charge on Dissociated Atoms:
Pervasive and Resilient Self-Interaction Error of Common Density Functionals." *The Journal of Chemical Physics* 125 (19): 194112. doi:10.1063/1.2387954.

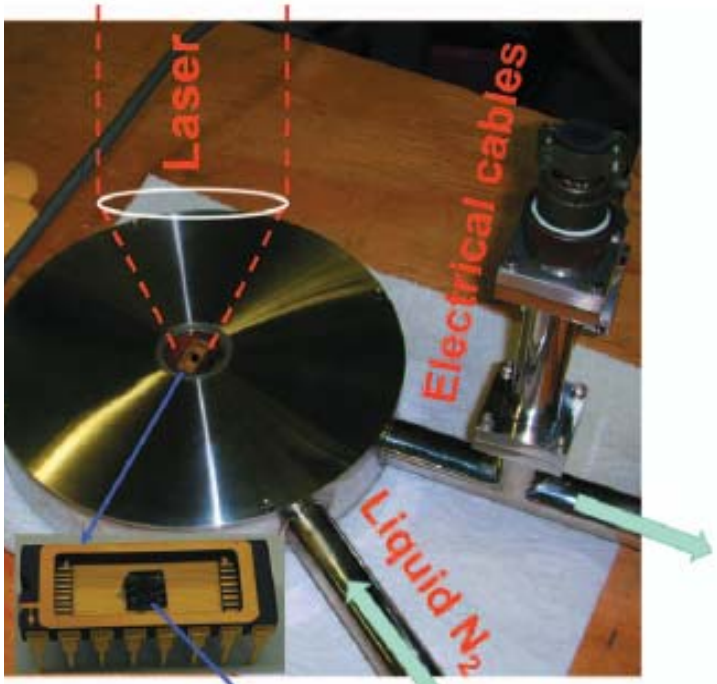
What about gas detection…

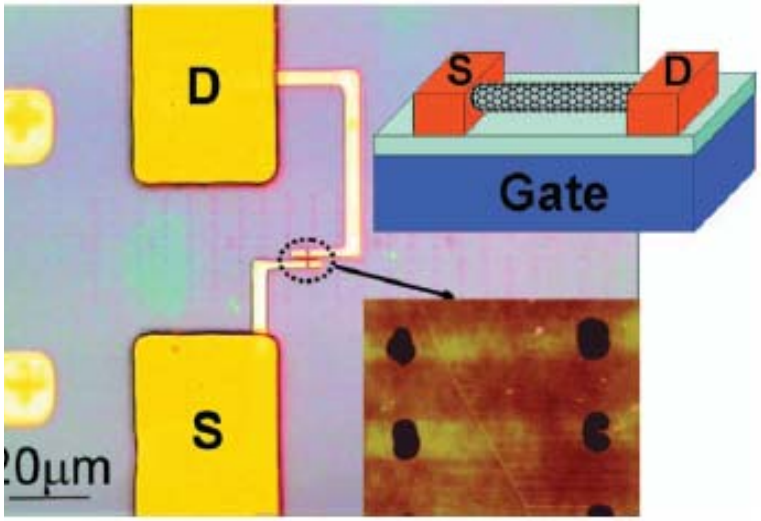
VERY TINY AMOUNTS OF GAS DETECTED

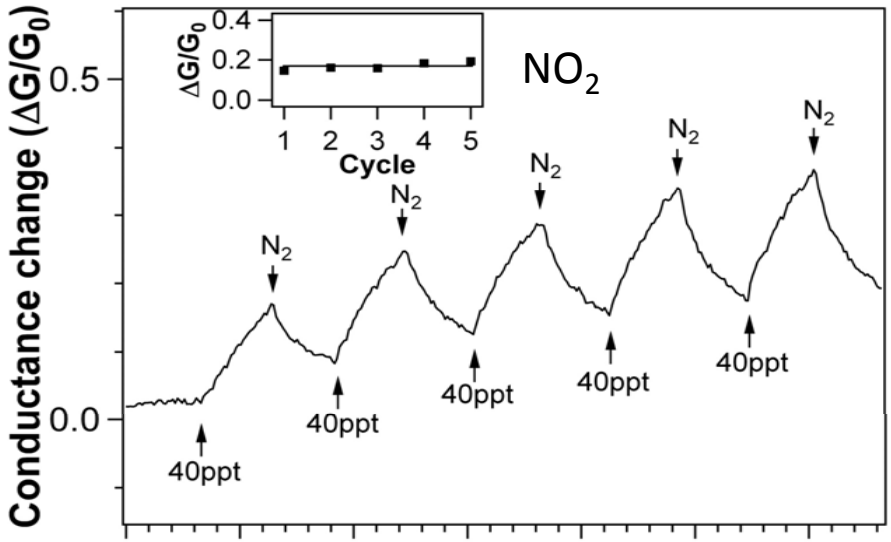
HONDA

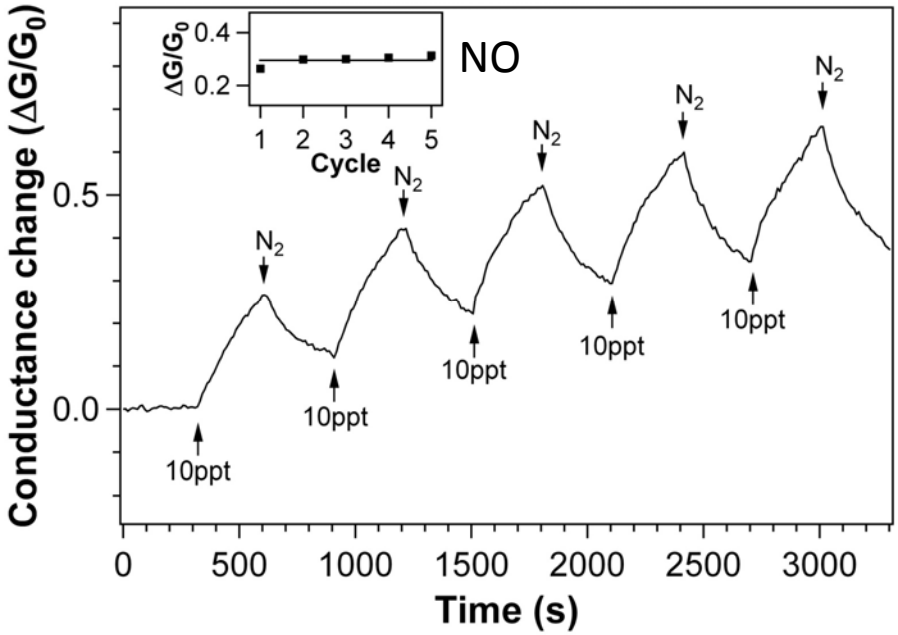
The Power of Dreams

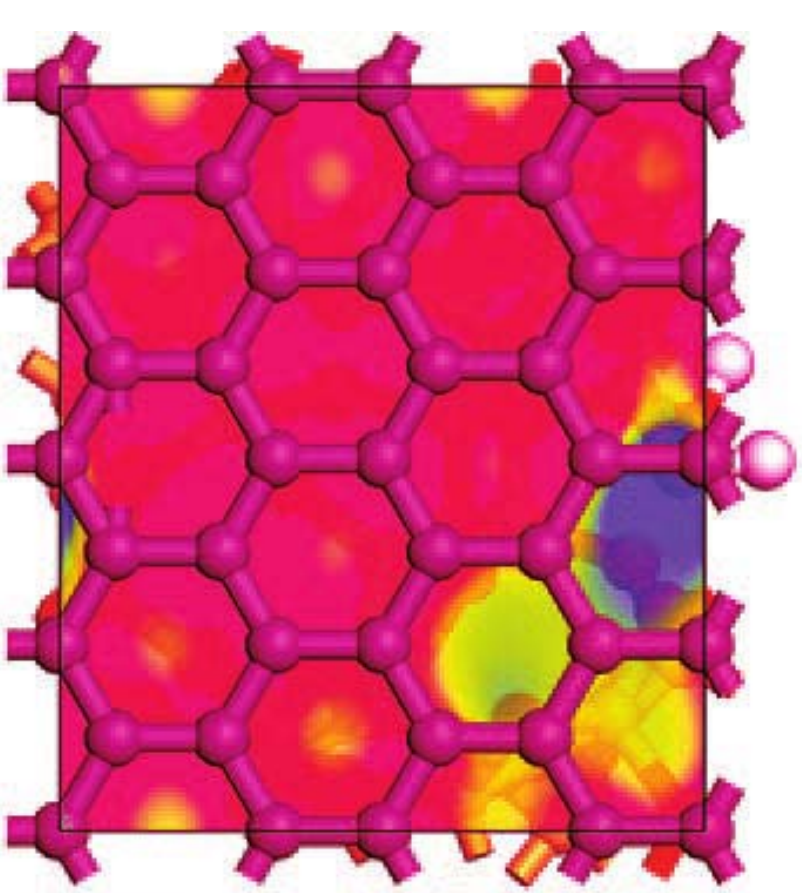
PENNSTATE

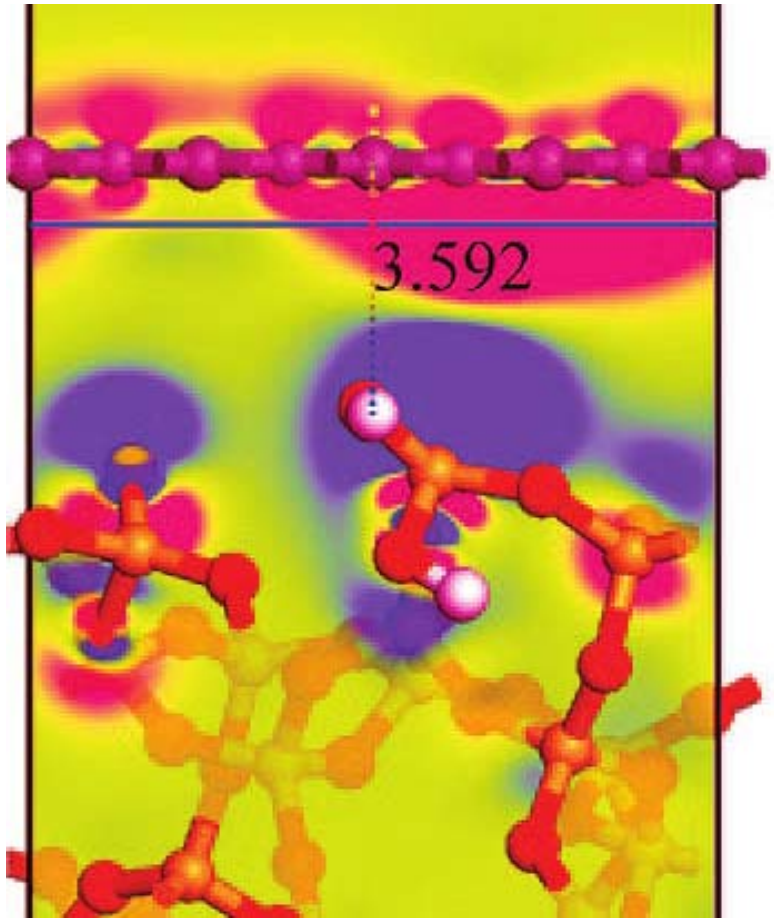




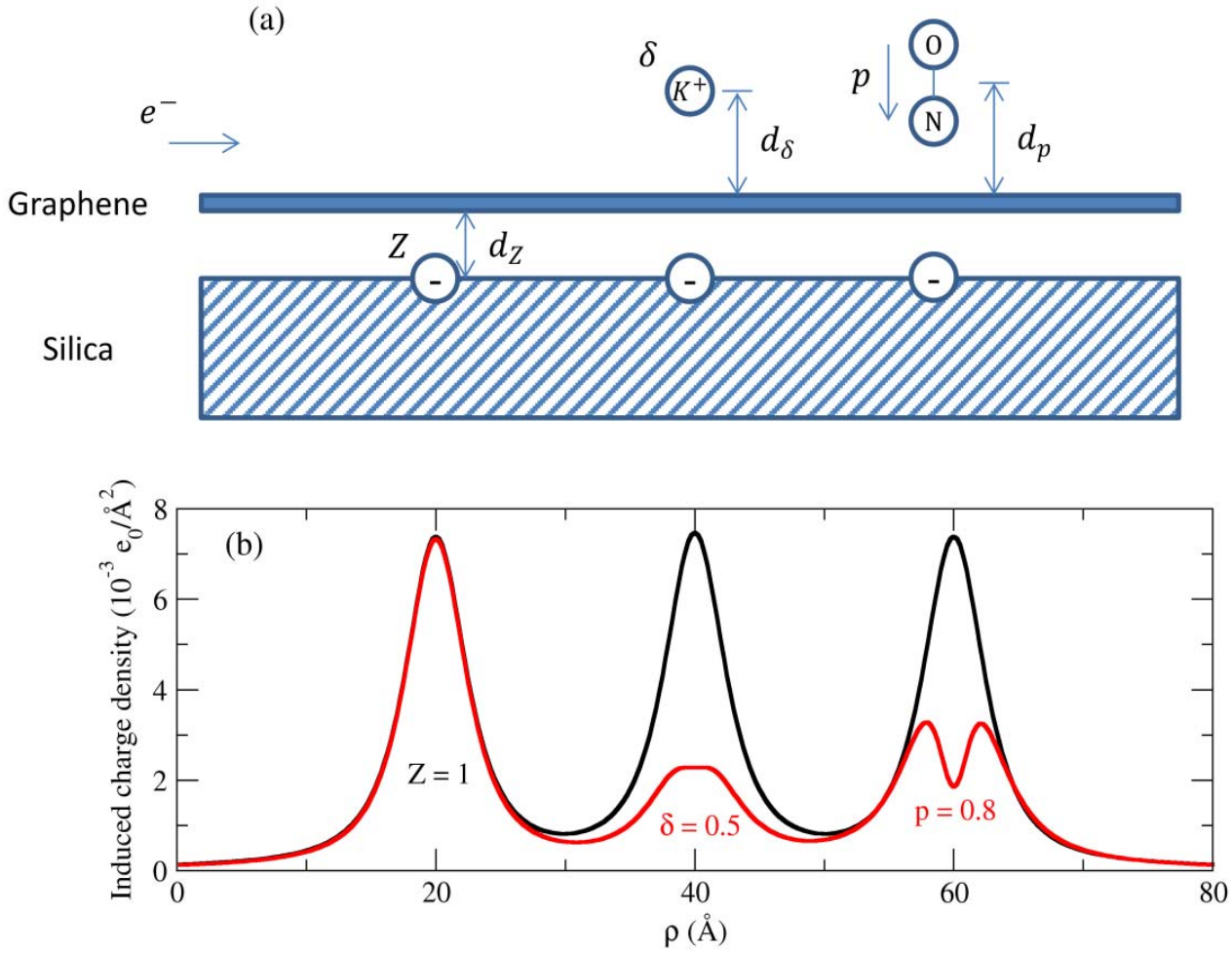






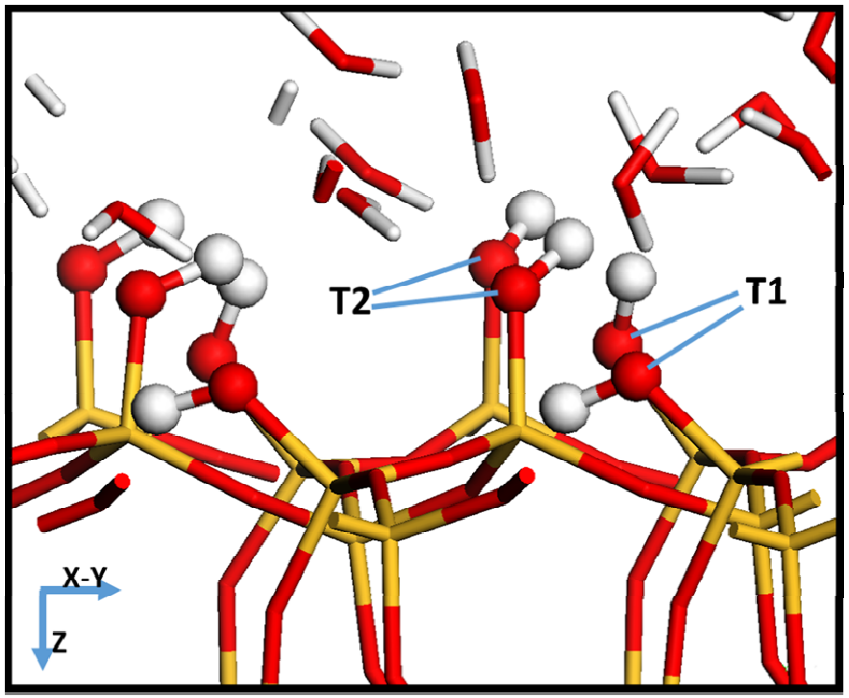


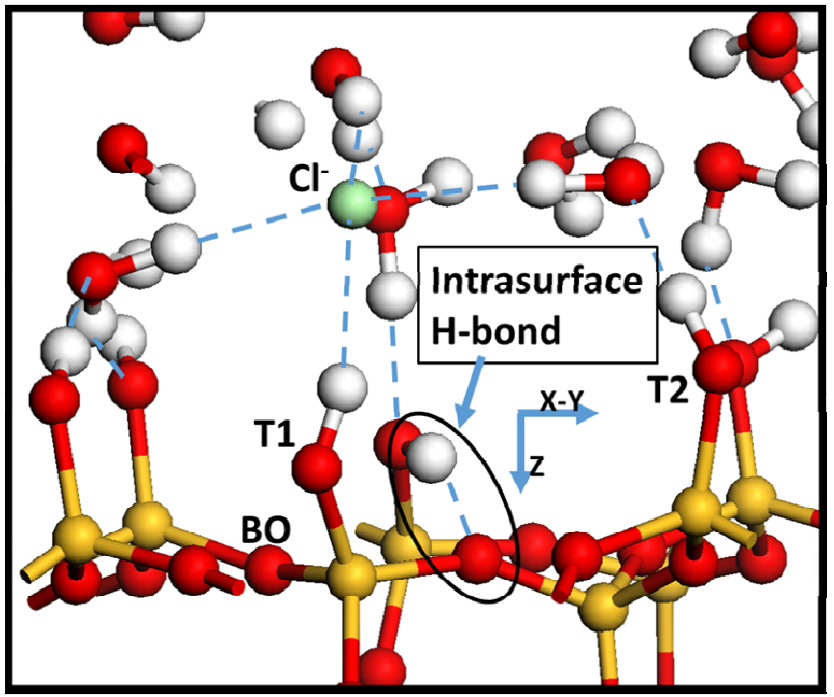
H. E. Romero, N. Shen, P. Joshi, H. R. Gutierrez, S. A. Tadigadapa, J. O. Sofo, and P. C. Eklund. "N-Type Behavior of Graphene Supported on Si/SiO2 Substrates." ACS Nano **2,** 2037 (2008)

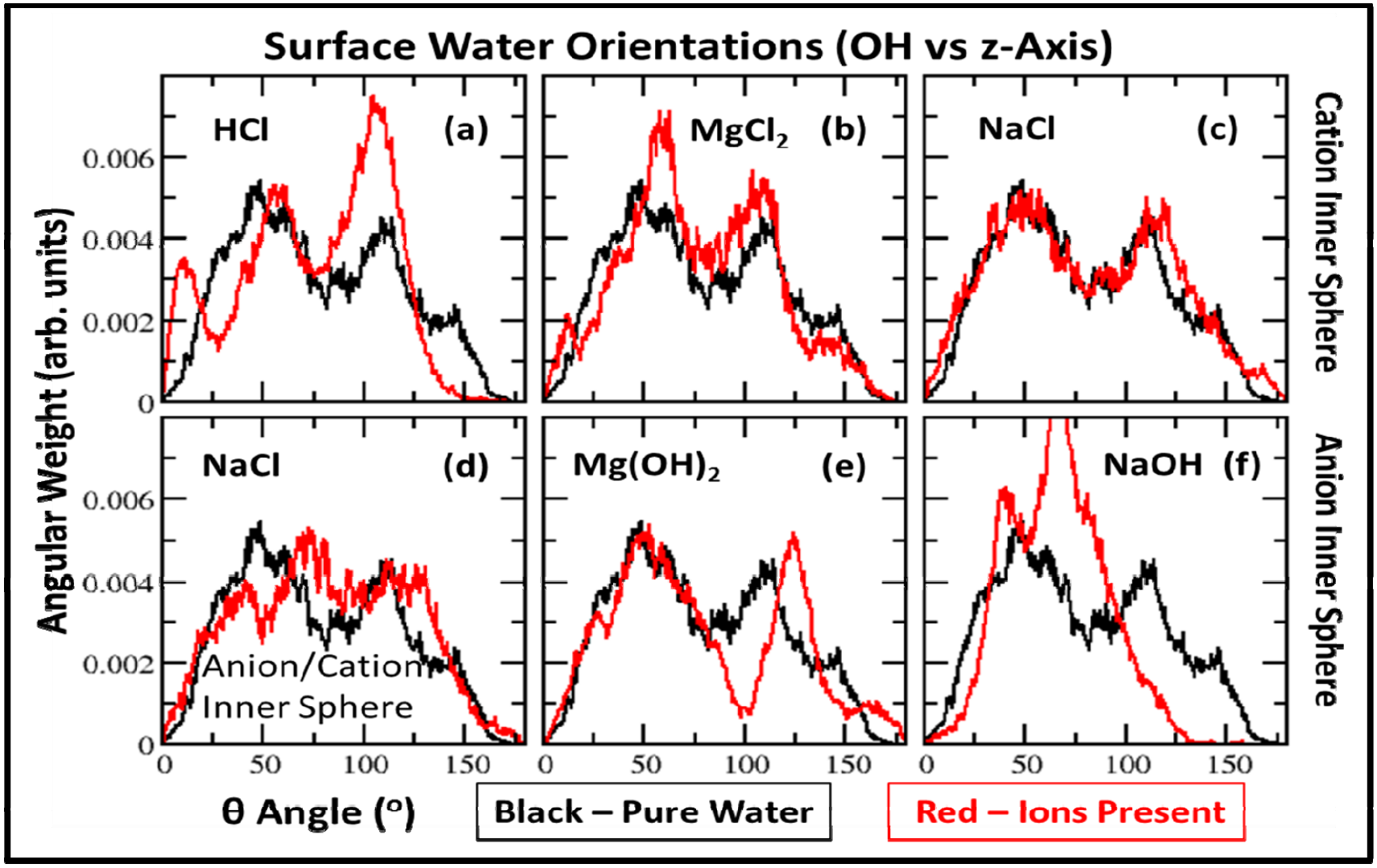

(a)
e^-
δ
K^+
d_δ
p
O
N
d_p
Graphene
Z
d_Z
Silica
(b)
Induced charge density (10^{-3} $e_0/Å^2$)
Z = 1
δ = 0.5
p = 0.8
ρ (Å)
0
2
4
6
8
0
20
40
60
80

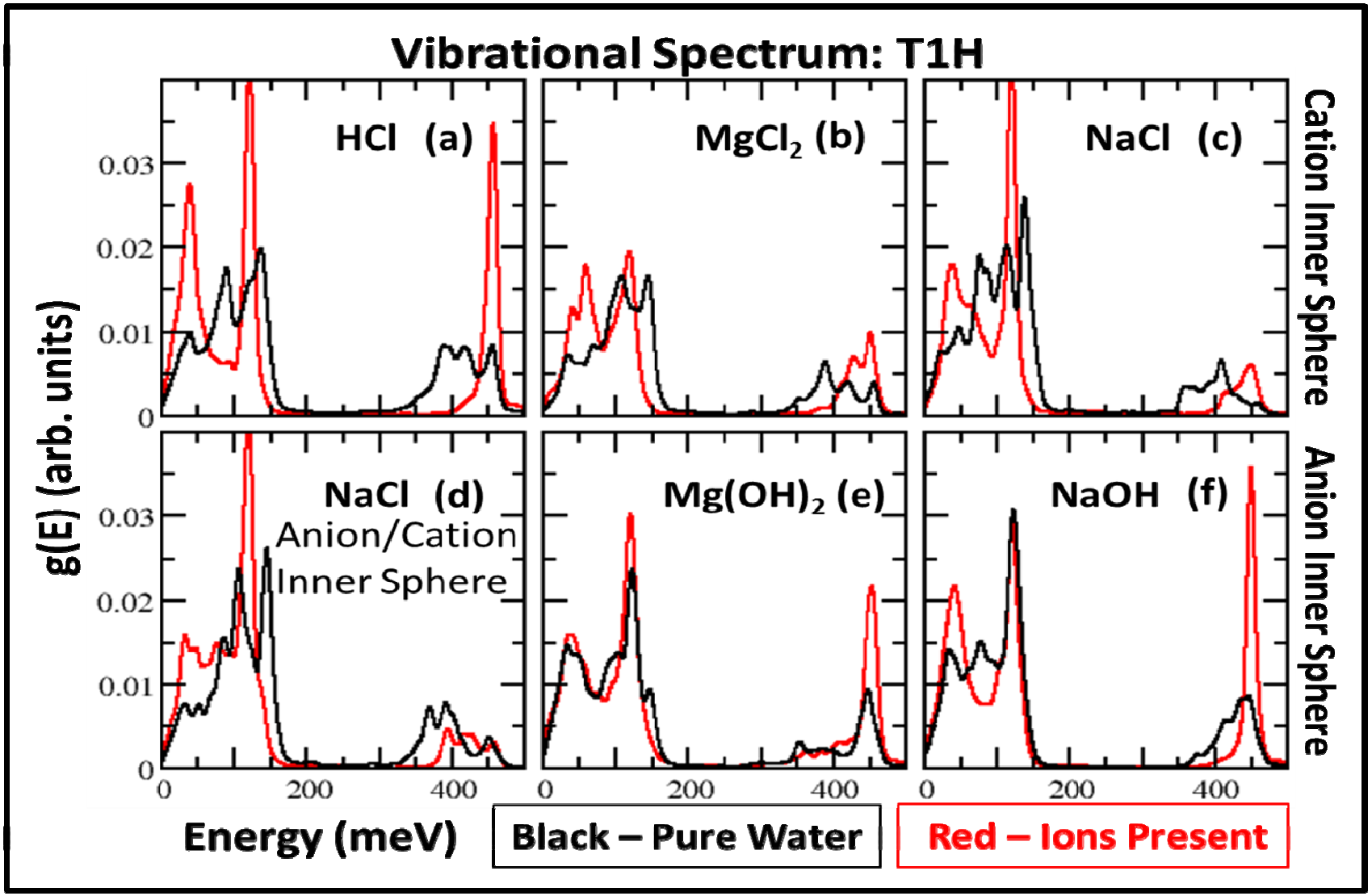
Silica dissolution…

WHAT CAN WE SAY WITH ONE PICOSECOND


T2
T1
X-Y
Z


Cl-
Intrasurface
H-bond
T2
X-Y
T1
Z
BO

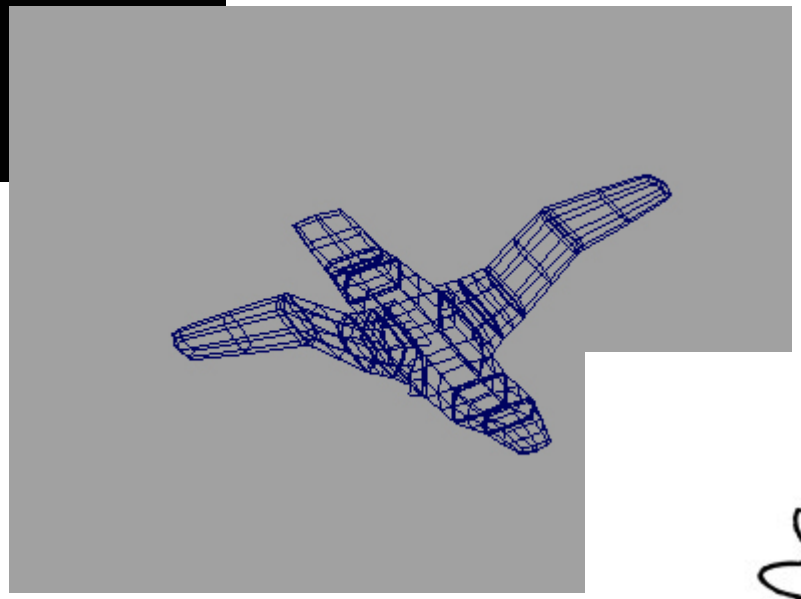

Surface Water Orientations (OH vs z-Axis)
HCl (a)
MgCl2 (b)
NaCl (c)
NaCl (d)
Mg(OH)2 (e)
NaOH (f)
Cation Inner Sphere
Anion Inner Sphere
Anion/Cation Inner Sphere
Angular Weight (arb. units)
0.006
0.004
0.002
0
0 50 100 150
θ Angle (°)
Black – Pure Water
Red – Ions Present


Vibrational Spectrum: T1H
HCl (a)
MgCl2 (b)
NaCl (c)
NaCl (d)
Anion/Cation
Inner Sphere
Mg(OH)2 (e)
NaOH (f)
Cation Inner Sphere
Anion Inner Sphere
g(E) (arb. units)
0.03
0.02
0.01
0
0
200
400
Energy (meV)
Black – Pure Water
Red – Ions Present

PENNSTATE

A final comment:

EXPERIMENT<-> SIMULATION<->THEORY



Simulations describe complexity. Our theoretical work is to make it simple.