Nanoscience: fact or fiction?

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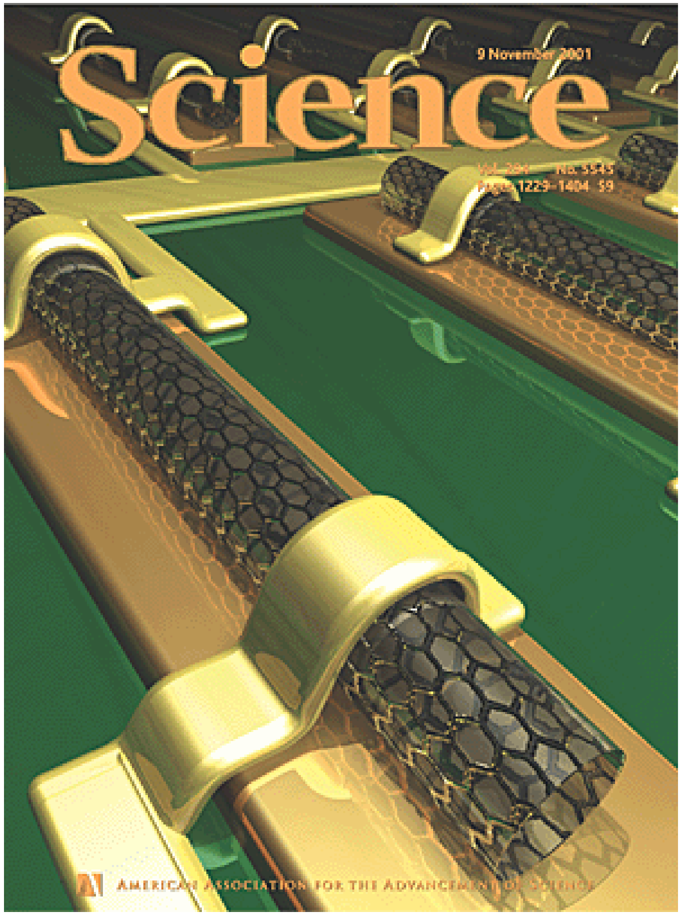


International Symposium on Contemporary Physics, NCP, Islamabad, March 07

Promise of Nanoscience

- Use Interdisciplinary research

to

- Understand & exploit novel properties

of

- Materials at the nanoscale

to

- Address grand challenge problems

in

- Health, Environment, Energy, etc.

Outline

- **Pedigree of Nanoscience:**

  -- *from Microphysics to Macrophysics?*
- **Two inventions that changed the way we do business: *the transistor & STM***
- **A peek at Surface Physics**
- **Some results from Nanoscience**
- **Back to the origins (*in more than 1 way*)**

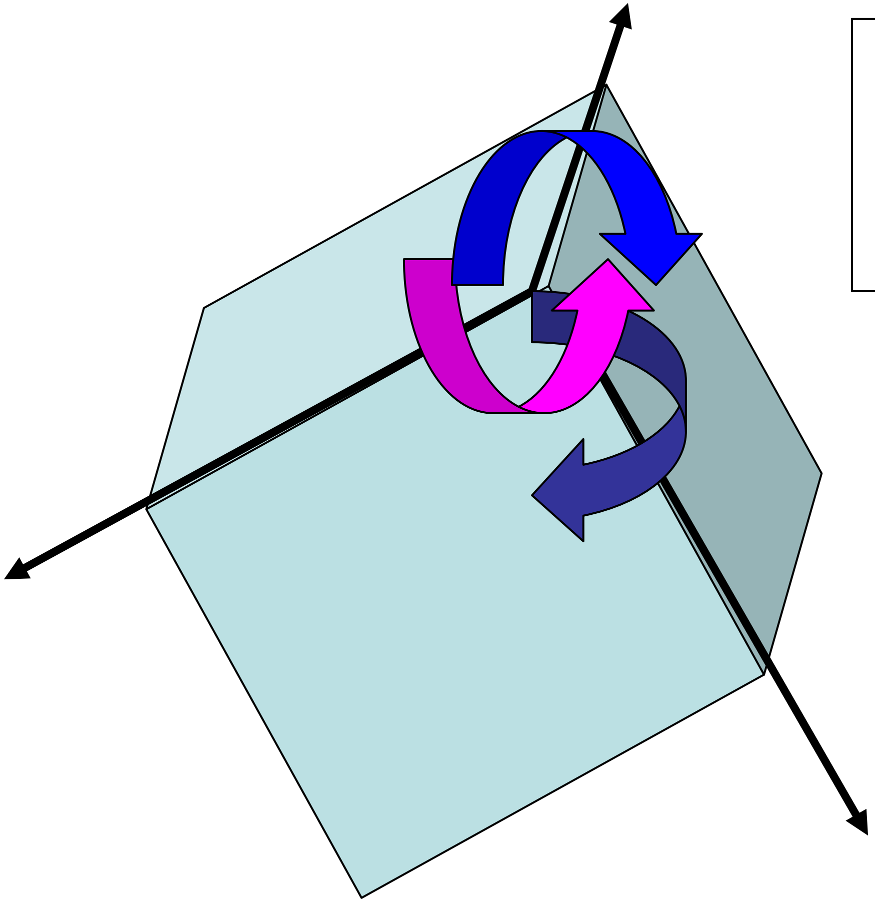
Physics in Perspective
in this interdisciplinary era

- **Maxwell Equations**
- **Lagrangian Dynamics**
- **Quantum Mechanics**
- **Quantum Field Theory**

Simplicity, Symmetry, Beauty, Charm

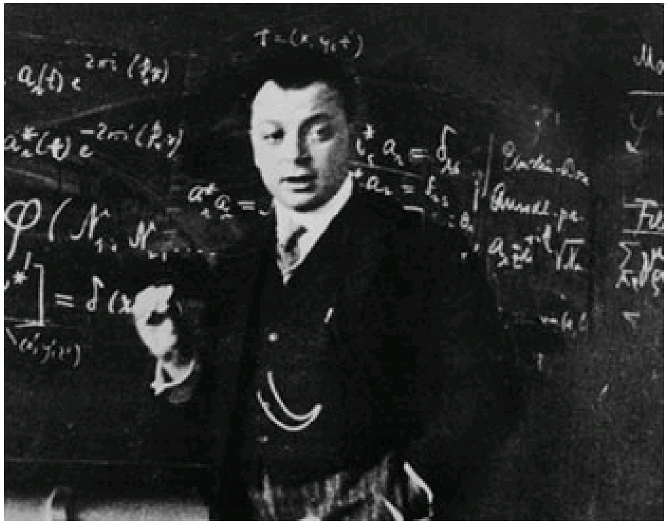
But then there is periodicity!

Bulk Solid



- High Symmetry
- Low Complexity
- All atoms equivalent

Converting Problem into Opportunity

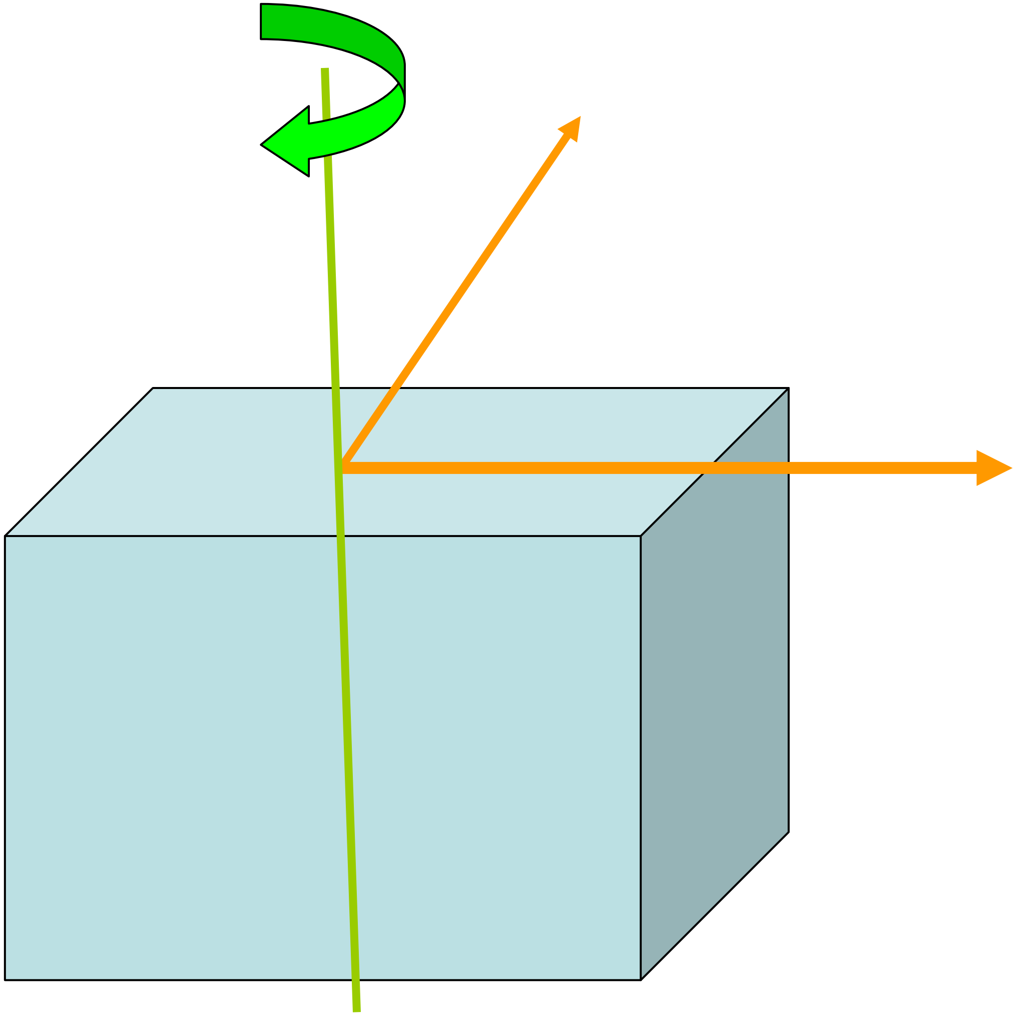


"God created the solids, the devil their surfaces"

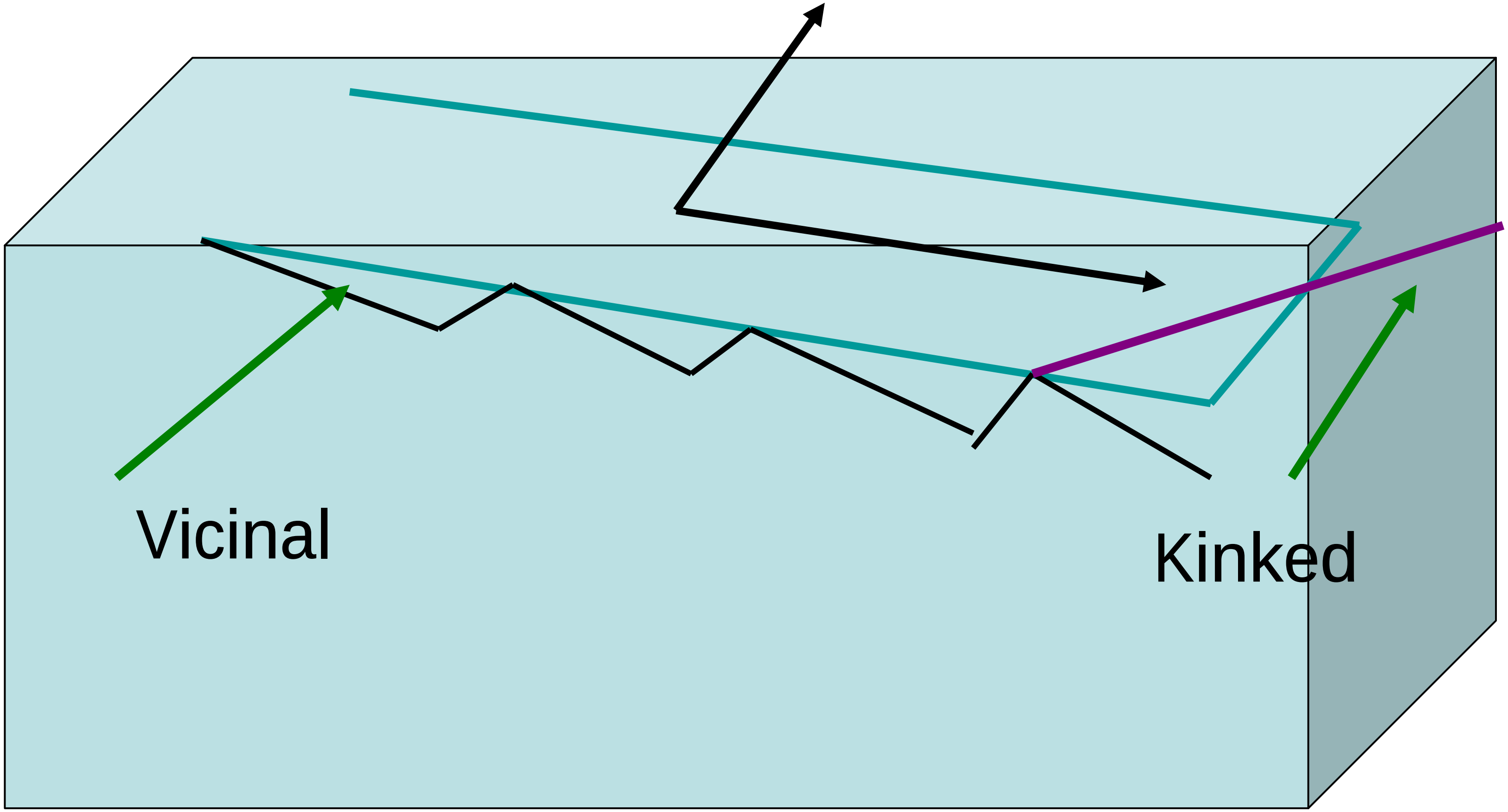
-Wolfgang Pauli (1900-1958)

- Materials symmetry defined by atomic-scale features
- Achieving materials control to atomic-scale

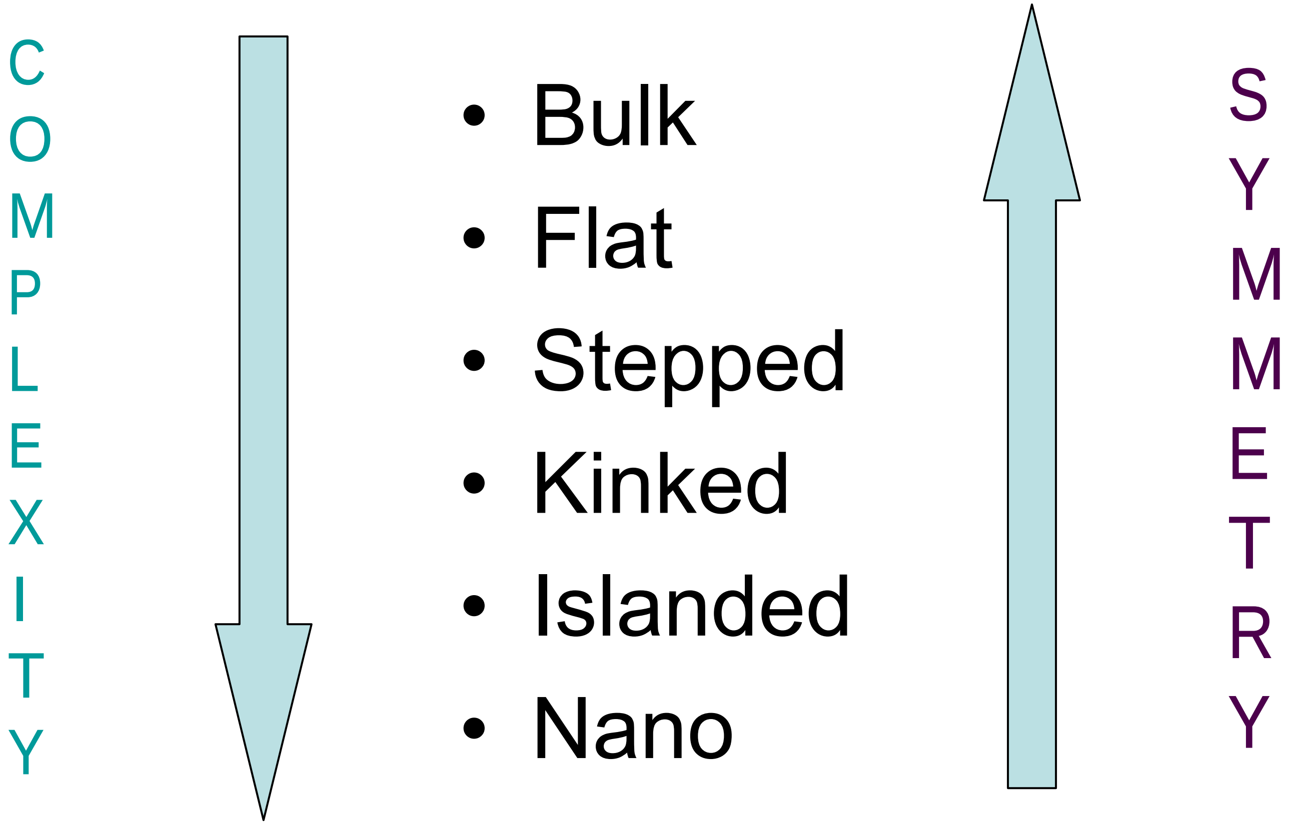
Low Miller Index Surfaces



High Miller Index Surfaces



An area of increasing complexity and decreasing symmetry



COMPLEXITY

- Bulk
- Flat
- Stepped
- Kinked
- Islanded
- Nano

SYMMETRY

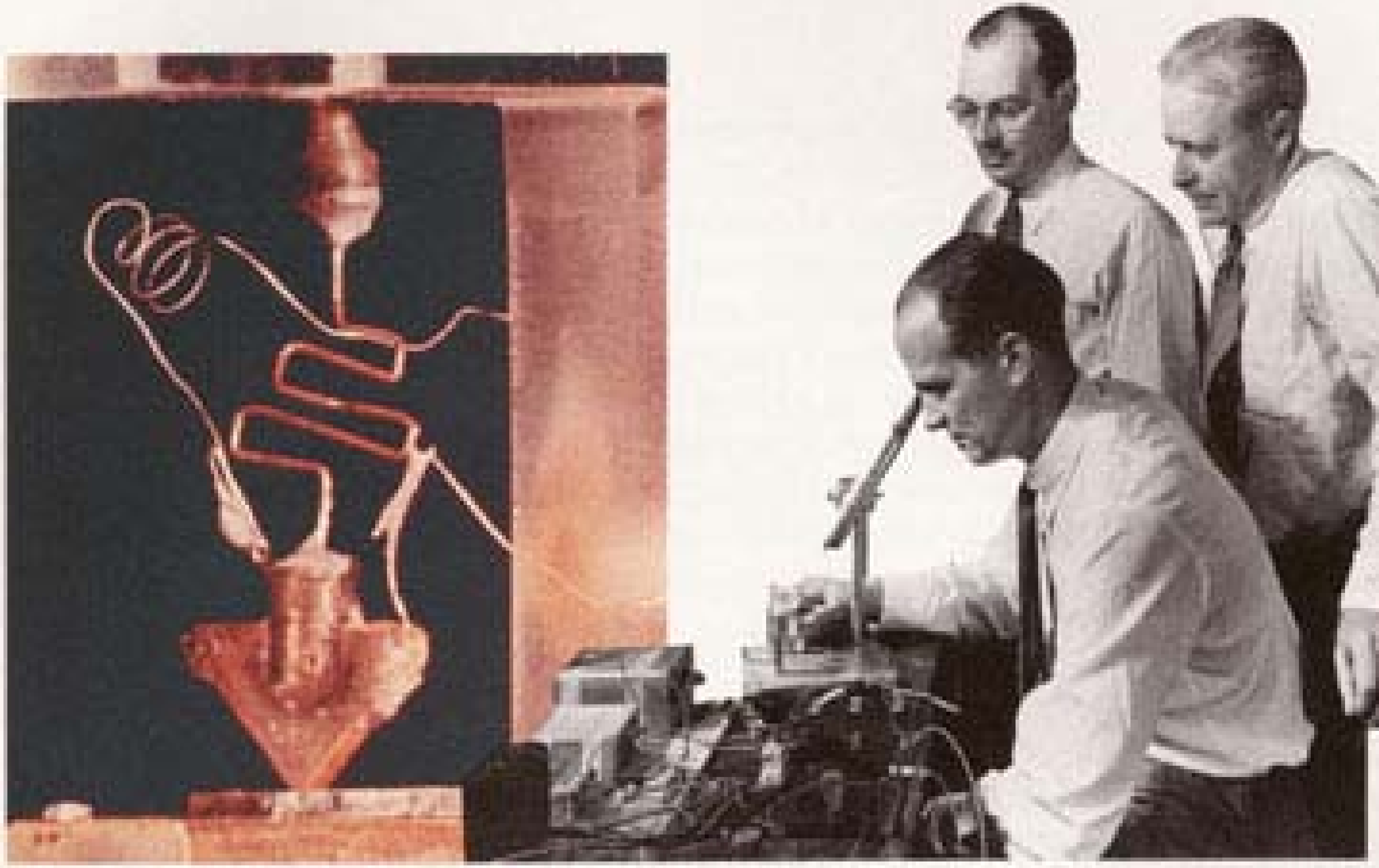
Two Important Inventions

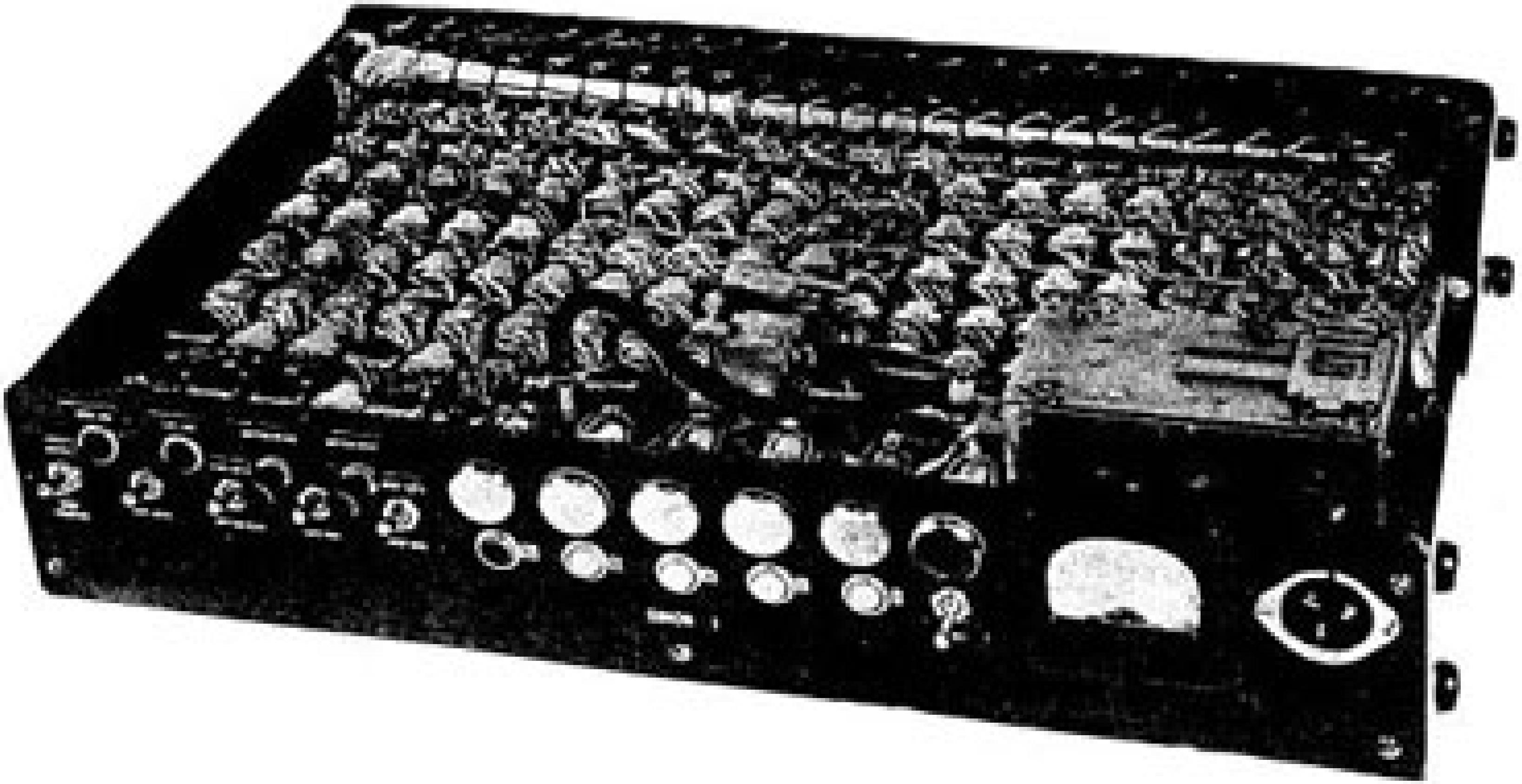
- **Then: The Transistor**

  --- *miniaturization*

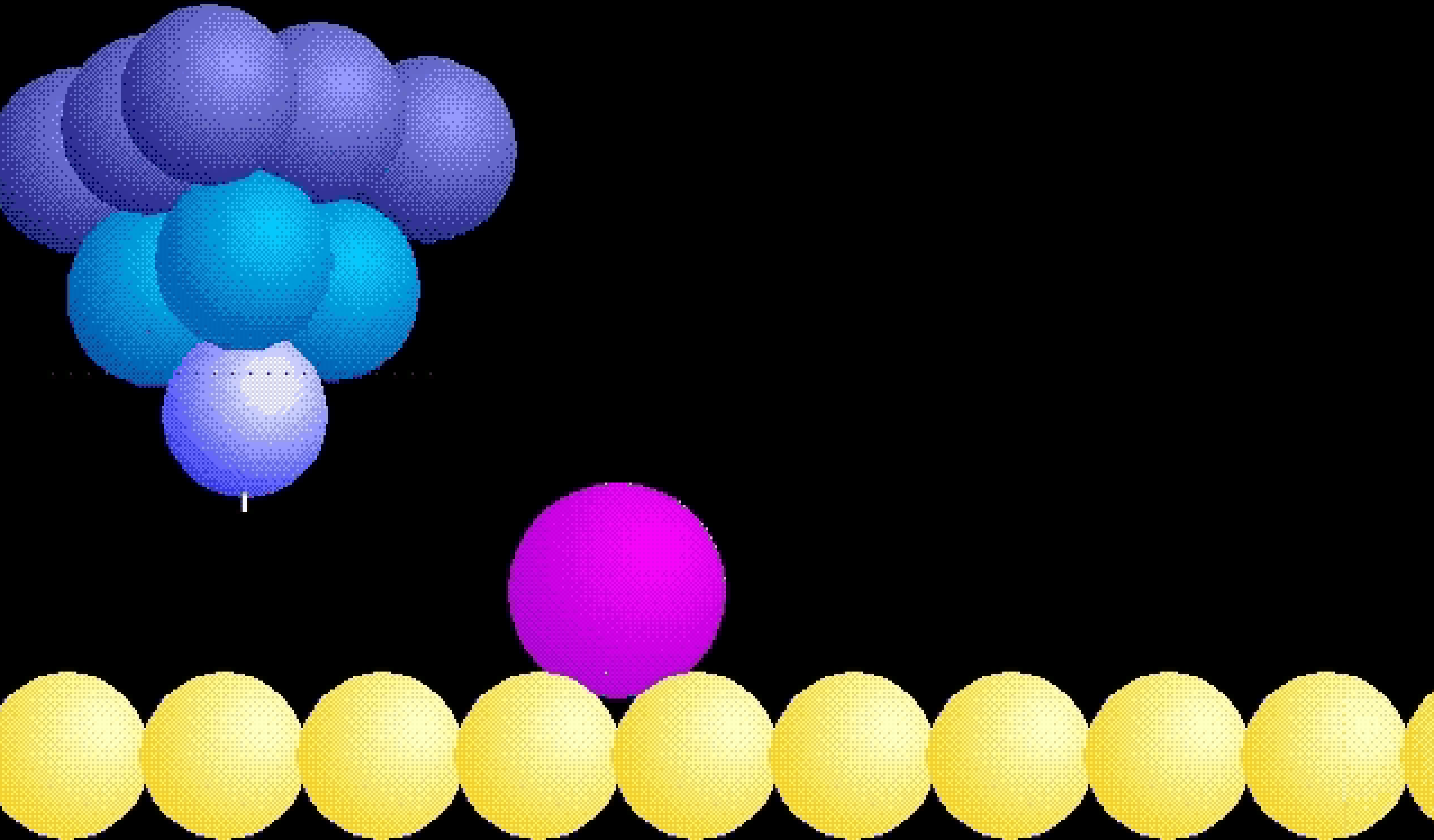
- **Now: Scanning Tunneling Microscope**

  --- *seeing the world atom by atom*





**We are not the only ones changing the world:
a predecessor with tremendous impact**



Examples from Surface Physics

- **Reactivity of an oxide surface**

  CO oxidation on cuprous oxide
- **Walking Molecules**

  Dithiolanthracene (DTA) on Cu(111)
- **Walking Molecule learns to carry a load**

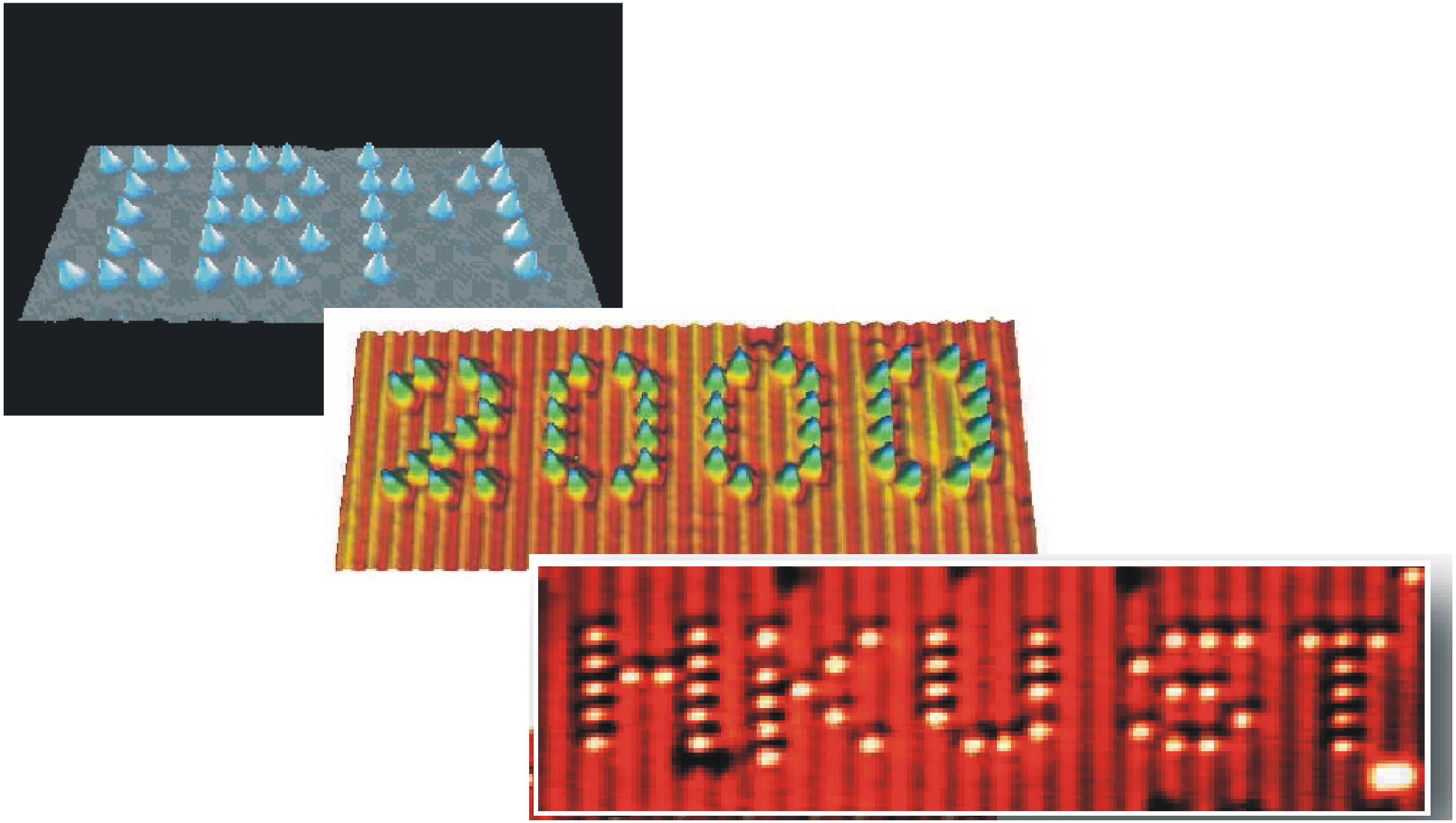
  Anthraquinone with CO_2 on Cu(111)

One of the Milestones in Nanoscience

Building the world atom by atom

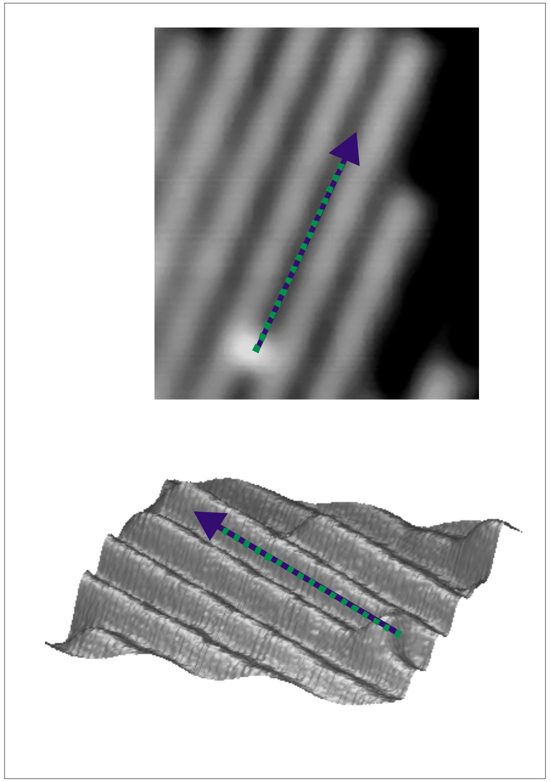
The power of Scanning Tunneling Microscope: some examples

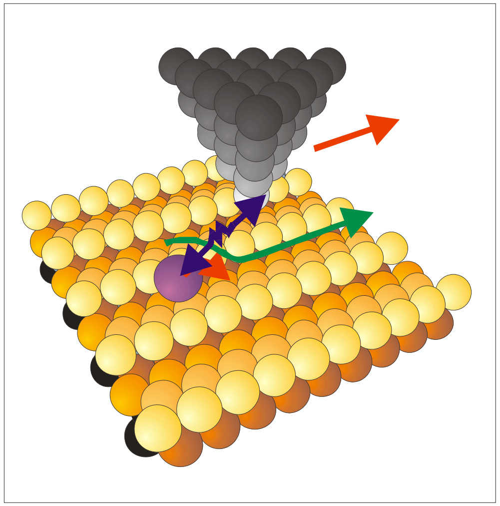
Lateral Manipulation



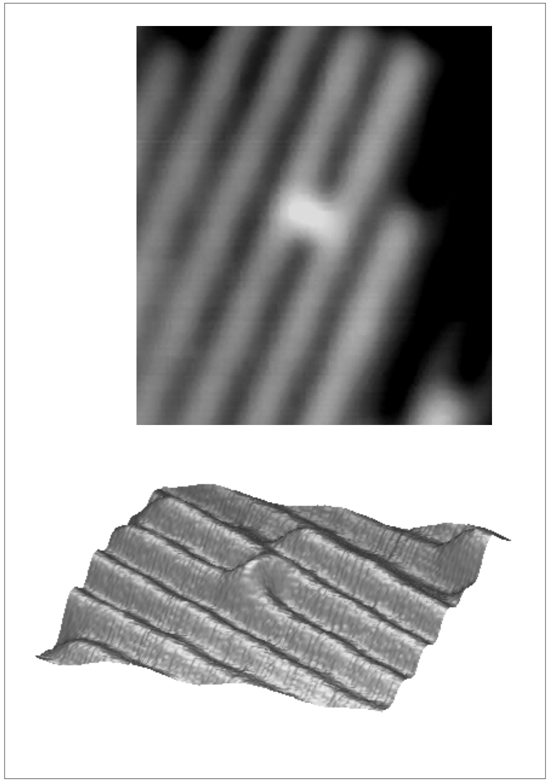
Lateral Manipulation of a Pb atom on Cu(211)

Bartels L., et al.,
PRL 79, 697 (1997)

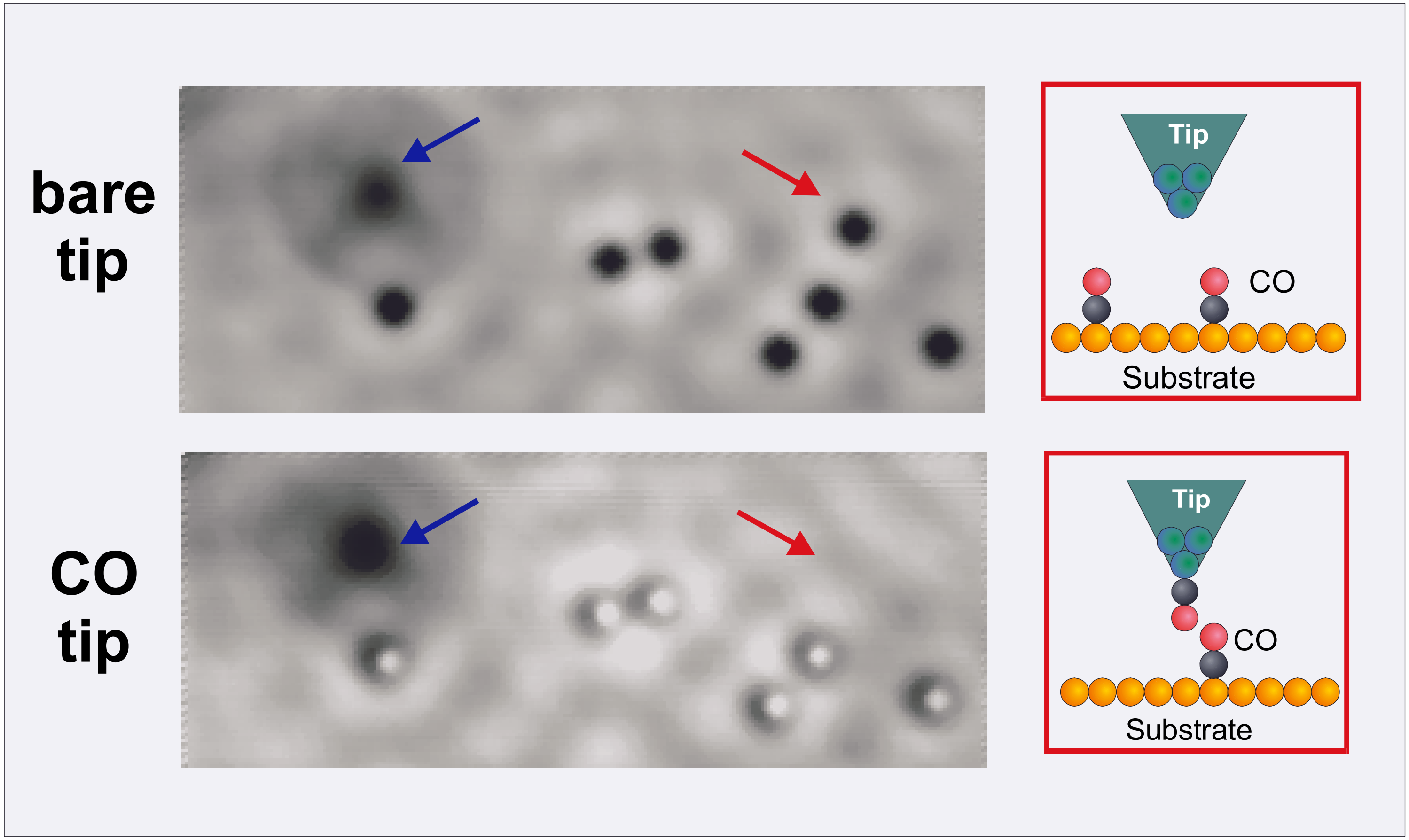




1. Initial image
2. Choosing line
3. Measuring contour
4. Decreasing gap resistance=approaching sample with tip
5. Manipulation
6. Measuring contour



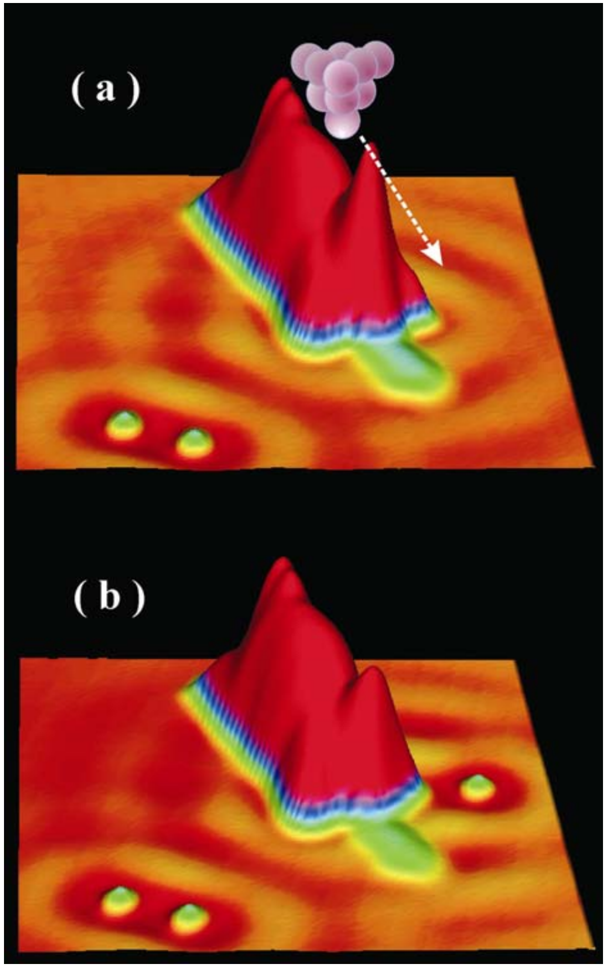
Vertical Manipulation

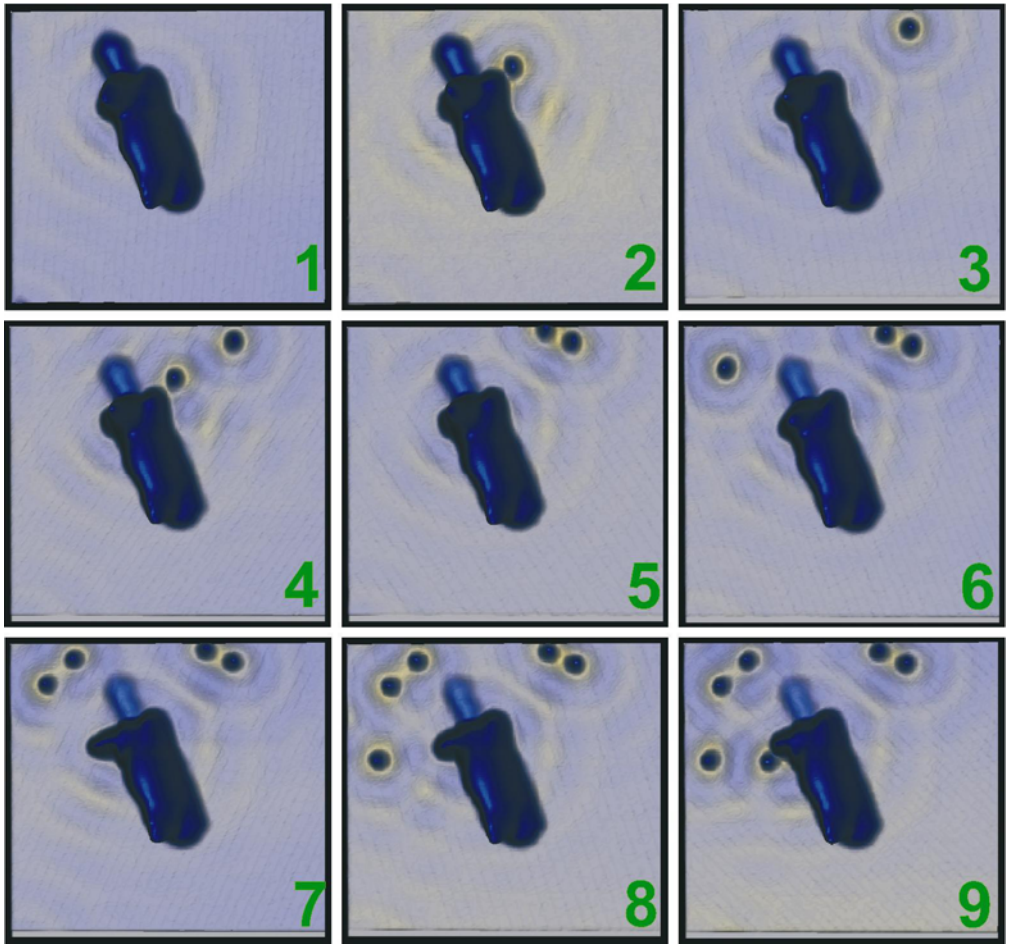


bare tip

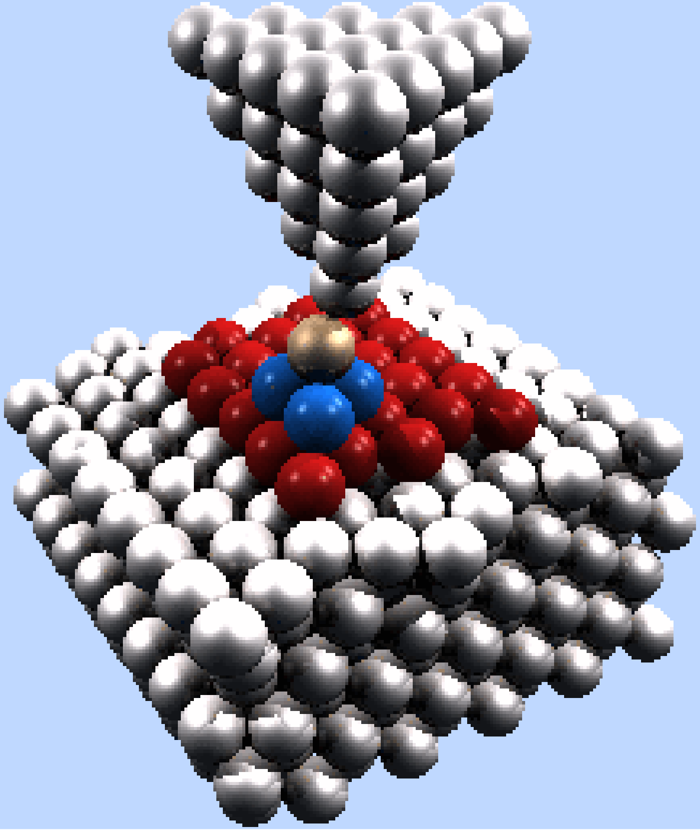
CO tip

Extraction of atoms
Hla et al(PRL, 2007)





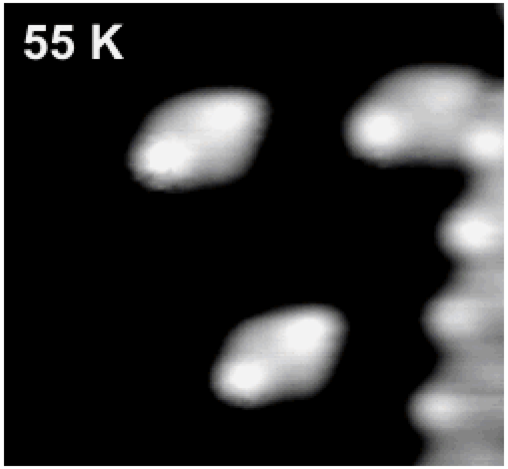
Manipulation with a sharp Ag tip



Molecular Dynamics Simulations, Yildirim, et al, PRL 2007

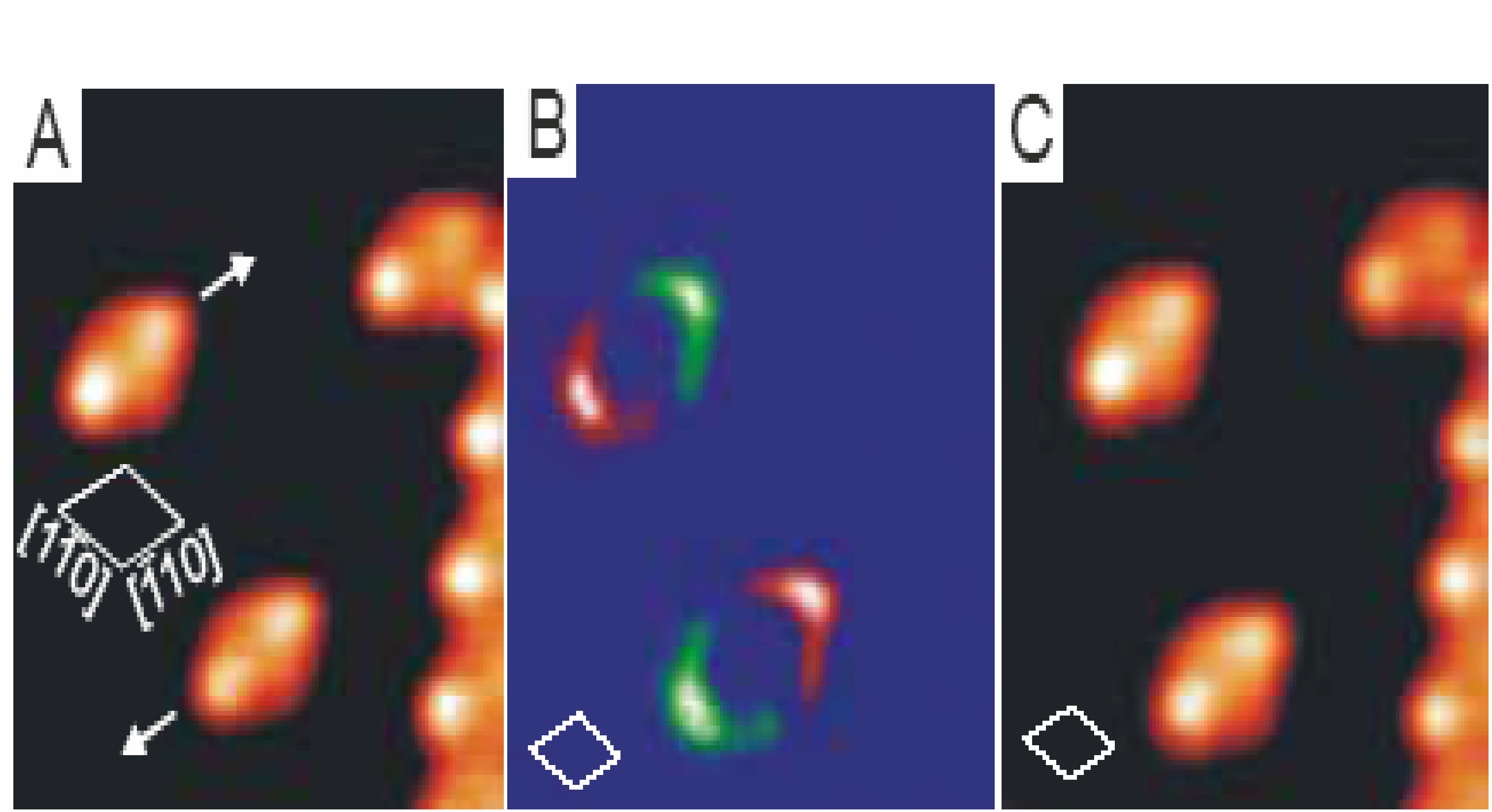
Movie of DTA motion on Cu(111):

a 2005 top 25 story in physics

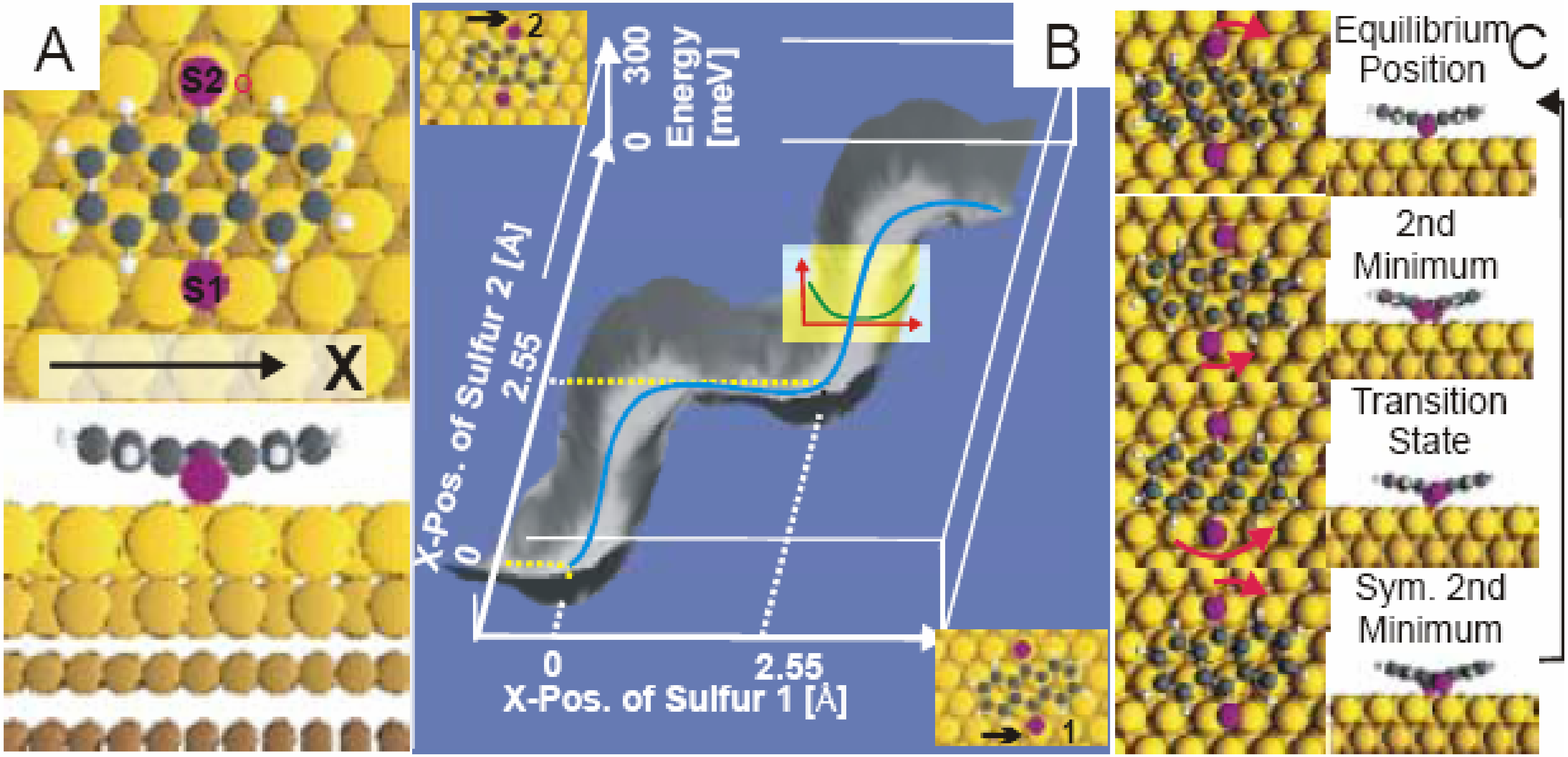


Movement of DTA Molecule on Cu(111)

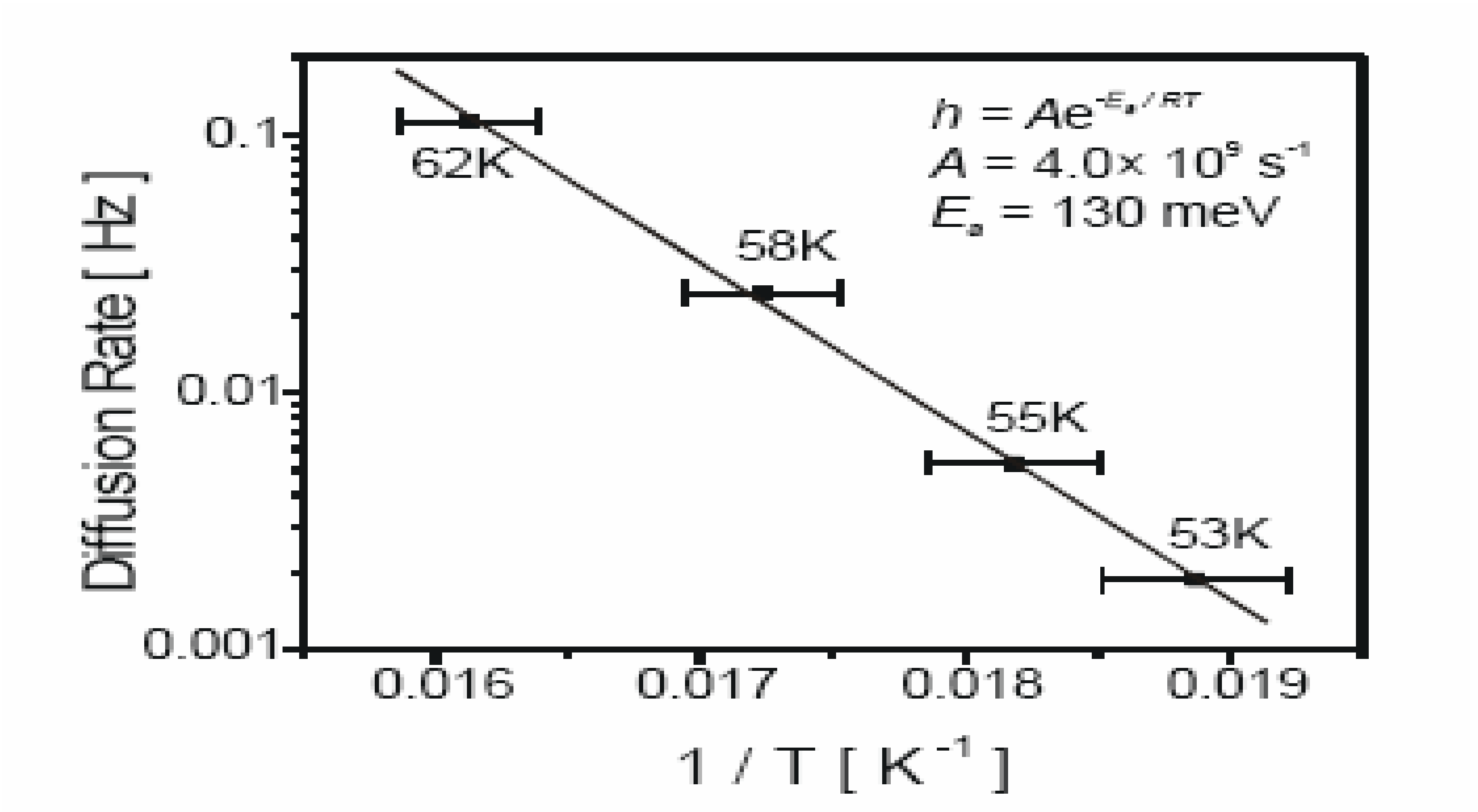
as measured by STM (by Bartels et al.)



Insights from theory

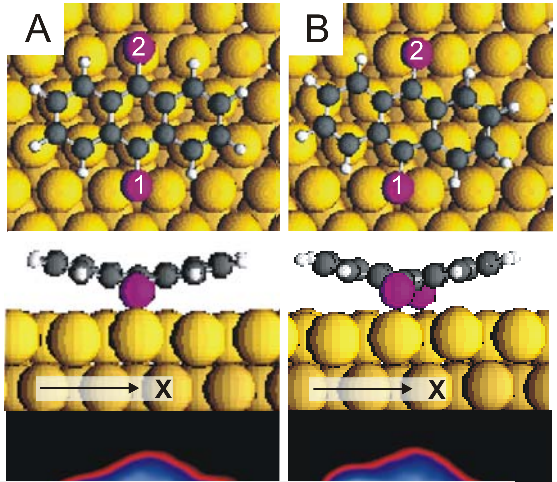


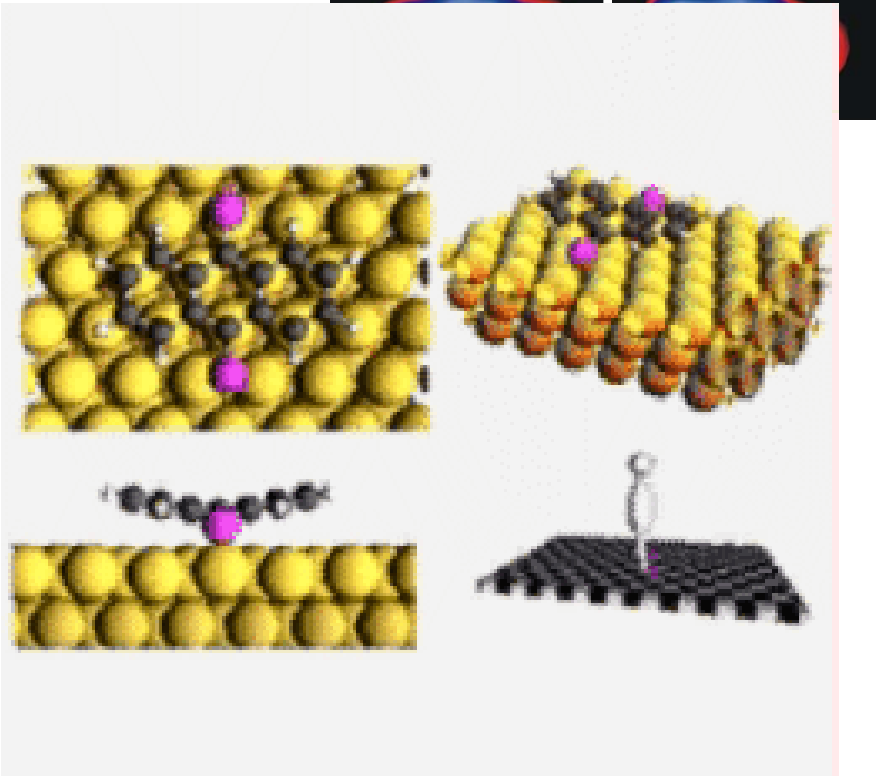
Temperature Dependence of DTA diffusion



K.-Y. Kwon, K. L. Wong, G. Pawin, L. Bartels, S. Stolbov, and T. S. Rahman, *Phys. Rev. Lett.*, 95 166101 (2005); see also *Physics Today* 58, No.12, p. 9 (2005).

A molecule – called 9,10-dithioanthracene (DTA) – has been created with three linked benzene rings and two "sulfur feet". Activated by heat on Cu(111), DTA is found to move straight along the [110] axis. In tests DTA has taken 10,000 steps without faltering.

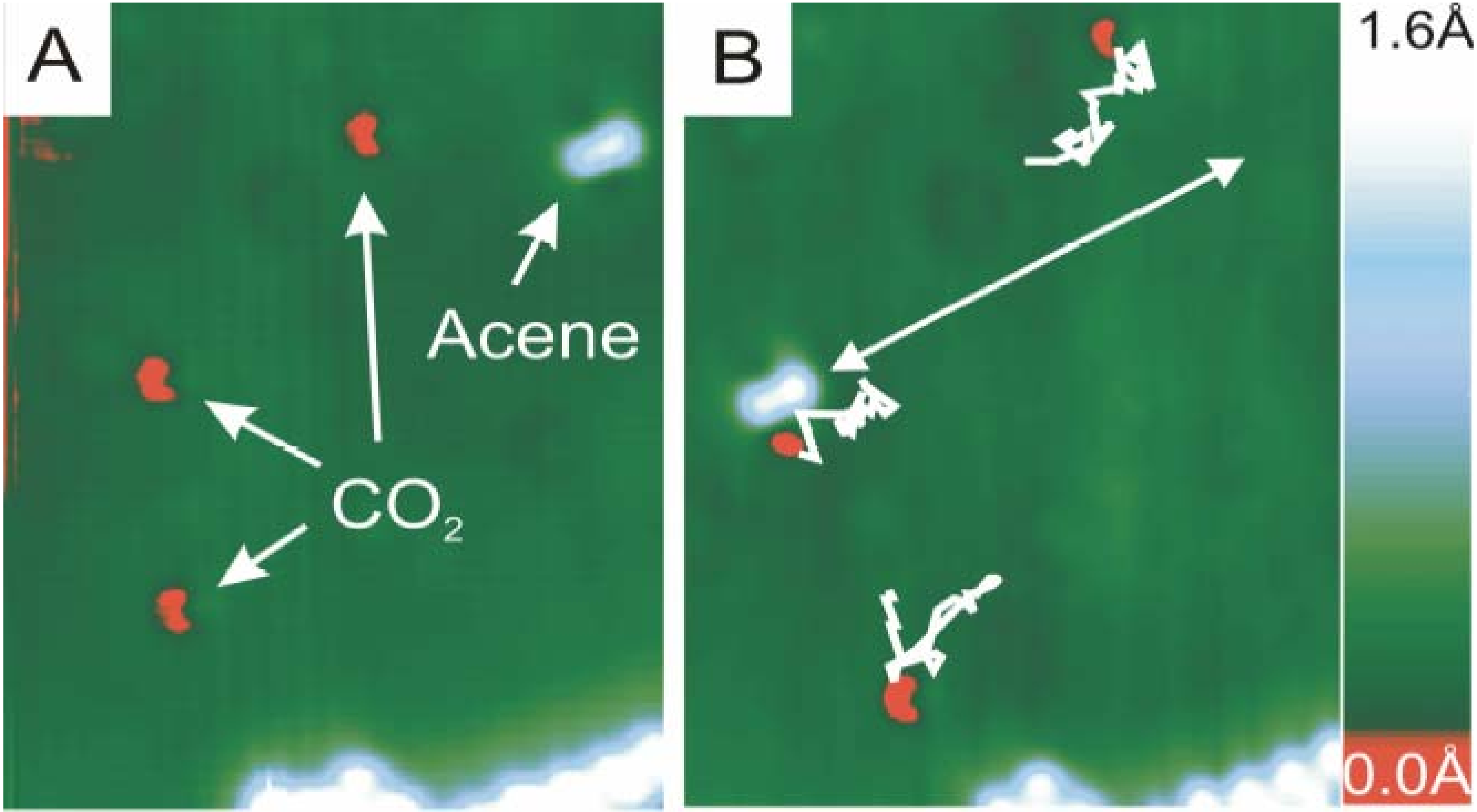




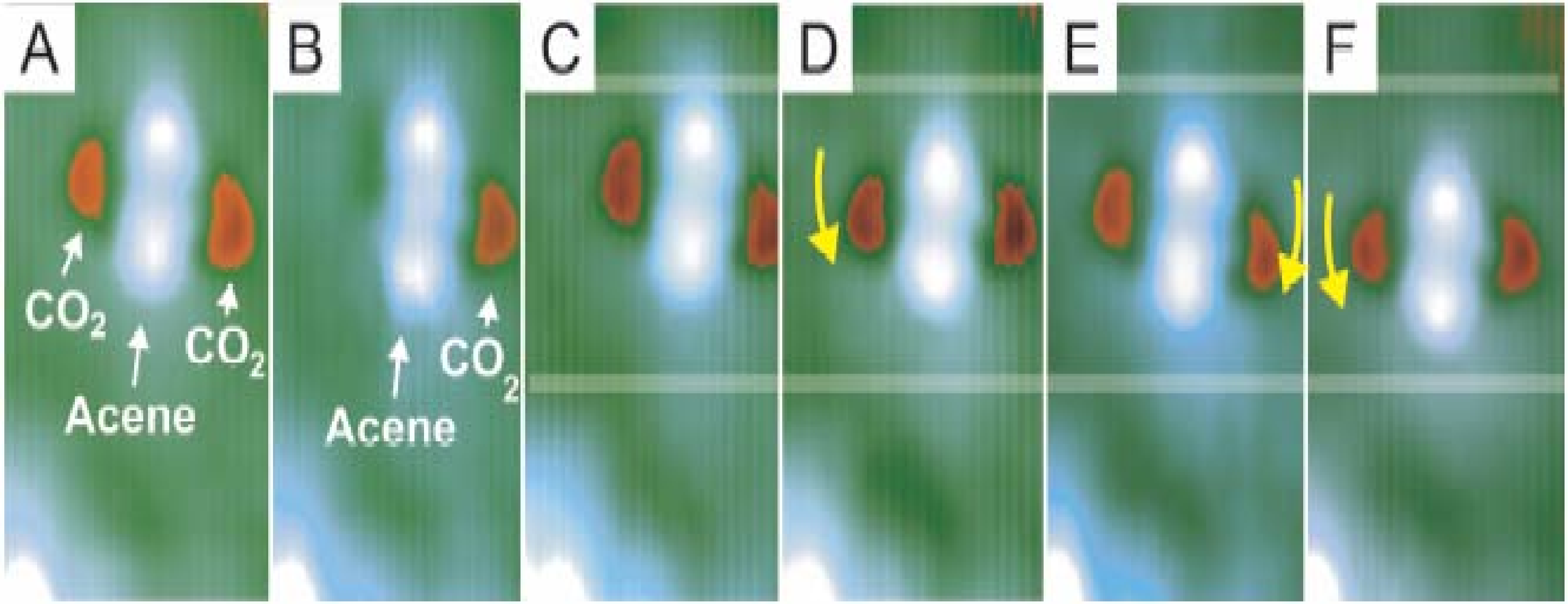
Cartoon of the Walking Molecule

Walking Molecule Carries a Load

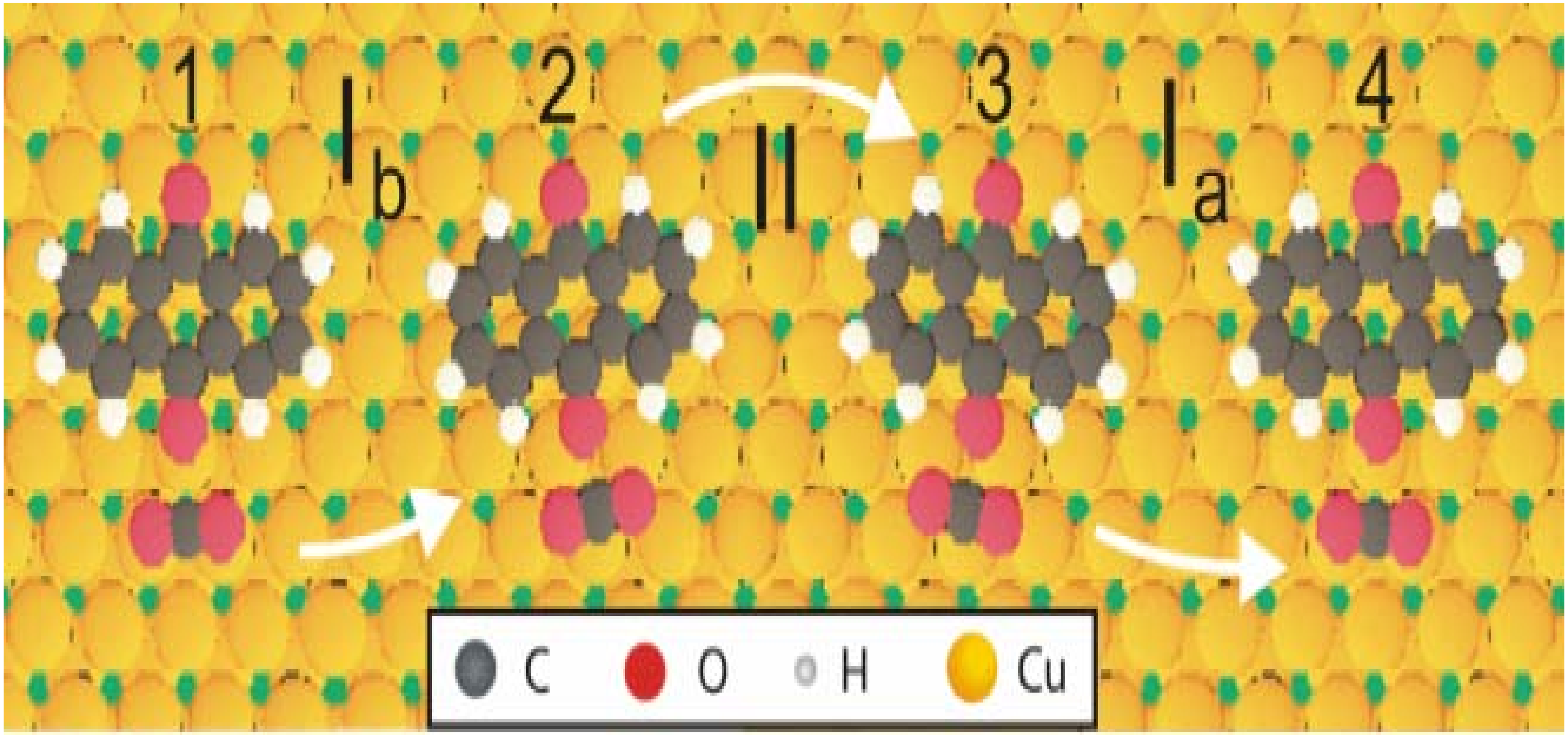
Wong et al, Science, 315 (2007)



Free Ride for CO_2



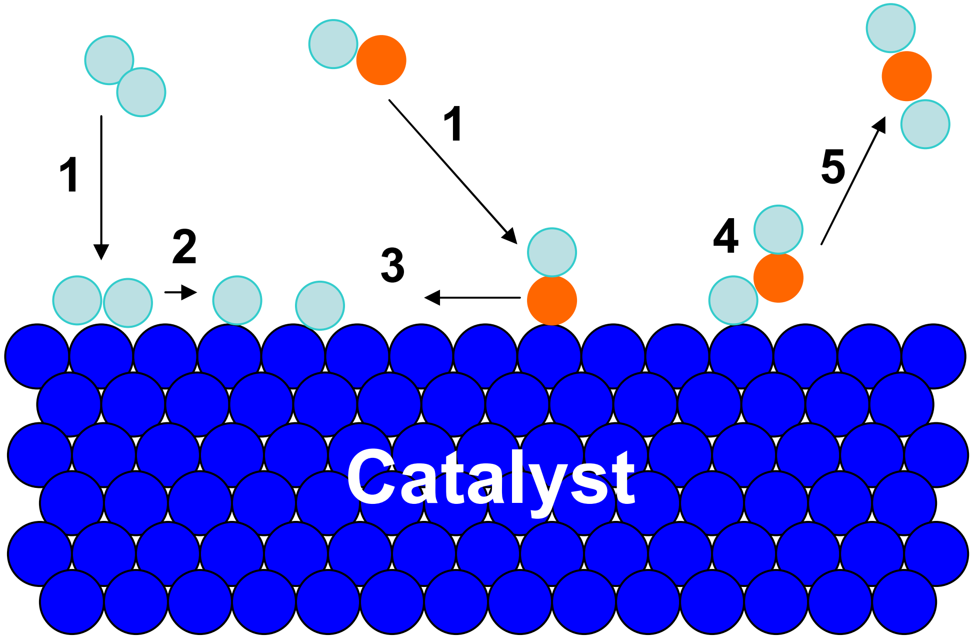
Modeling Adsorbate-Substrate Dynamics



Example: CO oxidation - $2CO+O_2 = 2CO_2$

● C

○ O

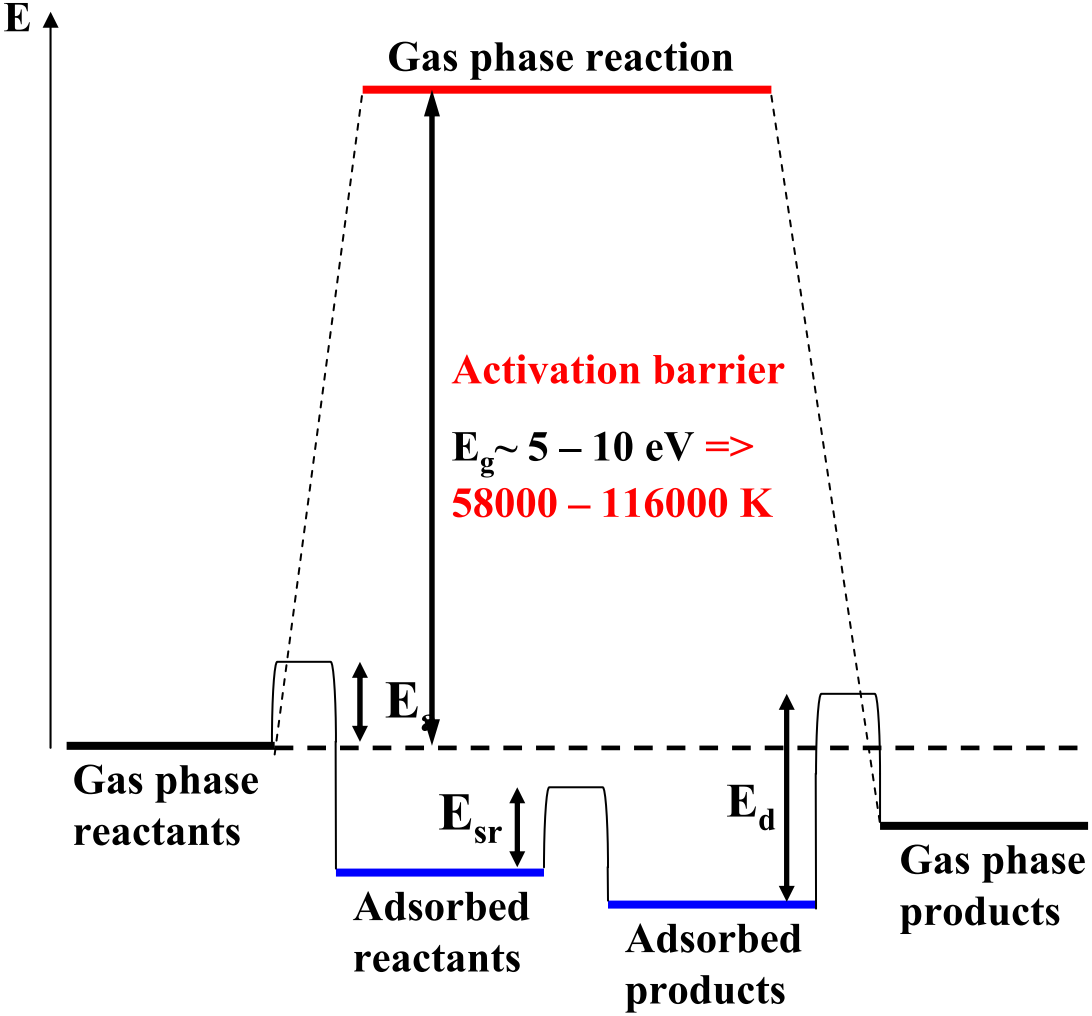


Elementary processes:

1. Adsorption;
2. Dissociation;
3. Diffusion;
4. Bonding;
5. Desorption;

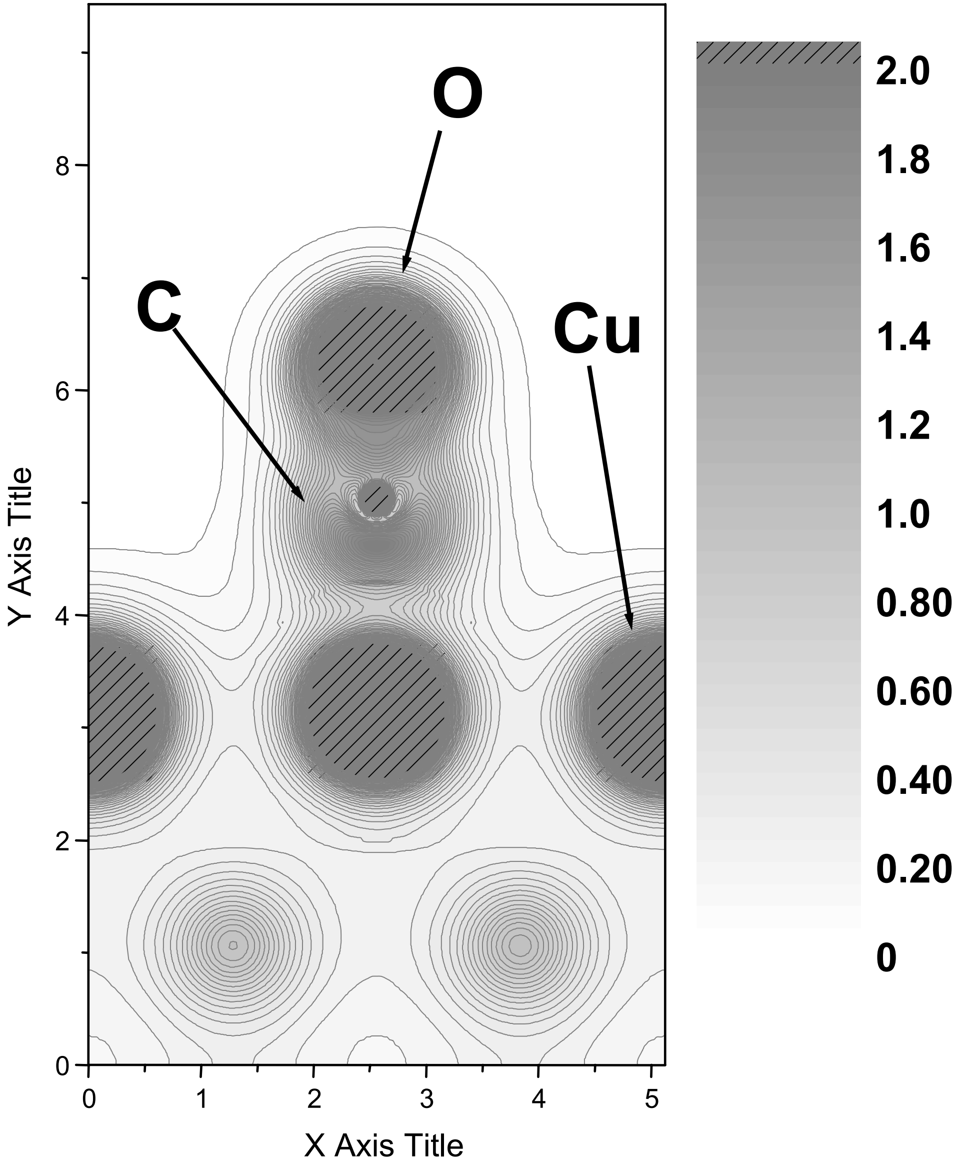
Everything is about breaking and making bonds.
This thus requires a quantum mechanical description.

How it works:



Why does it work?

Valence charge density of the Cu(111) surface adsorbed with CO (our calculations)



Computational details

We use first principles methods based on the density functional theory (DFT)

$$\boxed{\left\{-\frac{1}{2}\nabla^2 + V_{\text{eff}}[n(\mathbf{r})]\right\}\varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r})}$$

Reciprocal space representation for wave functions - developed for periodic crystals.

Surface breaks periodicity perpendicular to the surface.

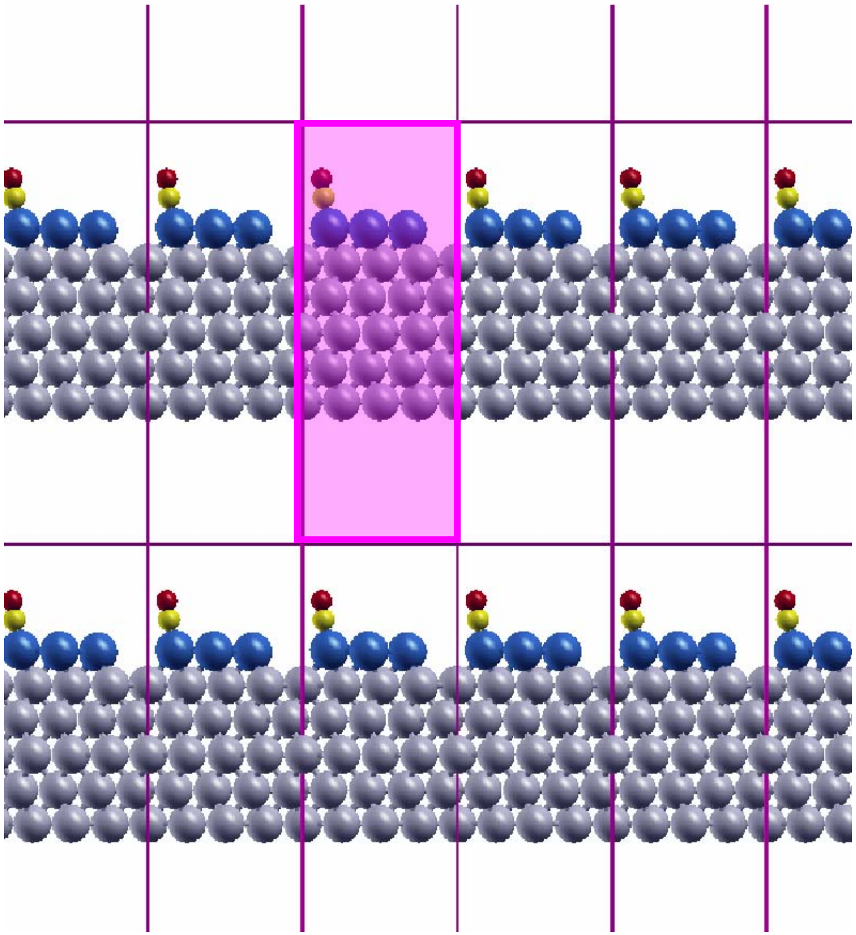
Adsorbates break the periodicity along the surface.

Supercell restores the 3D periodicity.

Output:

1. Ground state wave function;
2. Electronic charge density, LDOS;
3. Total energy;
4. Forces acting on each atom – structural relaxation;
5. Phonons;
6. Many other characteristics.

A supercell and 3D periodic structure prepared for the first principles studies of adsorption and diffusion of CO molecules on small Pt islands pre-adsorbed on the Ru(0001) surface.



First principles studies of CO adsorption and oxidation on the $Cu_2O(100)$ surface

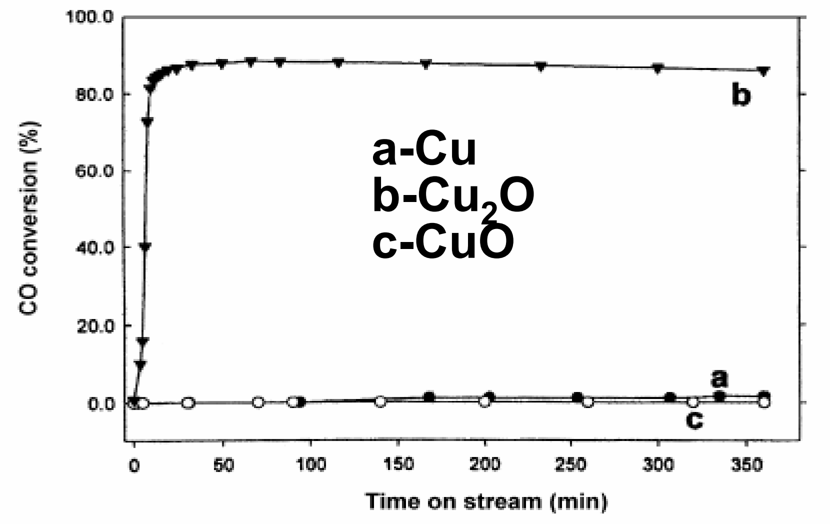
Duy Le, Sergey Stolbov, and TSR

In collaboration with:
B. White, M. Yin, A. Hall, N. Turro, S. O'Brien **Columbia University**

Nanoletters 2006

CO oxidation at T=140°C

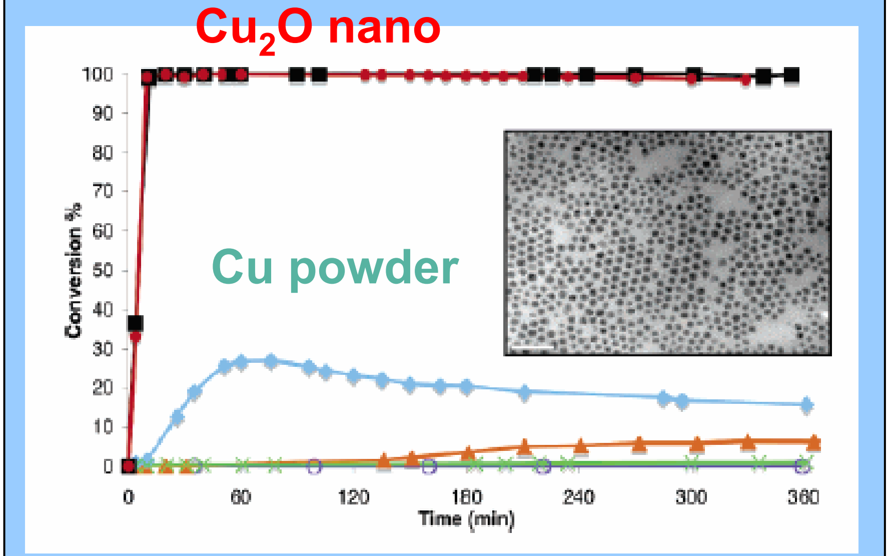
More than 85% CO converse to CO_2 over Cu_2O powder



T. Huang and D. Tsai, *Catal. Lett.* **87**, 173 (2003)

CO oxidation at T=240°C

More than 99.5% CO converses to CO_2 over Copper (II) oxide nanoparticles



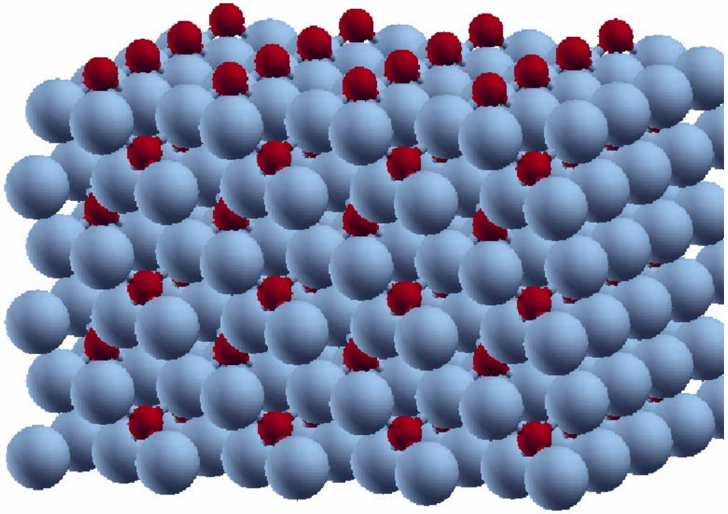
B. White, M. Yin, A. Hall, D. Le, S. Stolbov, T. Rahman, N. Turro, S. O'Brien, S. *Nano Lett.* **6**(9), 2095 (2006).

Copper (II) oxide may be a good, cheap catalyst for CO oxidation

First principles studies

For the $Cu_2O(100)$ surface we calculate a surface *(p,T)* phase diagram applying *ab initio* thermodynamics, DFT – energetics and pathways for CO adsorption, diffusion and oxidation on $CuO_2(100)$.

A fragment of the slab modeling the O-terminated $Cu_2O(100)$ surface



DFT – GGA – PBE (1996)

Slab:

O-terminated – 6 Cu_2 layers; 7 O-layers

Cu-terminated – 7 Cu_2 layers; 6 O layers

~13Å vacuum.

Used 2D supercells: 2x2.

Surface phase diagram

Free energy: $\gamma(T,\{p_i\}) = \frac{1}{A}\left[G_{DFT} - \sum_i N_i \mu_i(T,p_i)\right]$

Applying $2\mu_{Cu} + \mu_O = g^{bulk}_{Cu_2O}$ **for equilibrium**

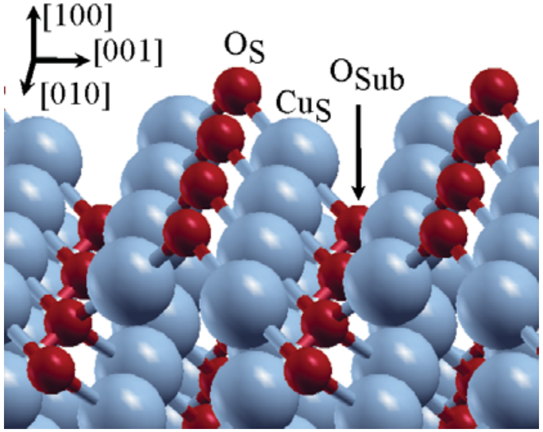
=> only one independent variable μ_O:

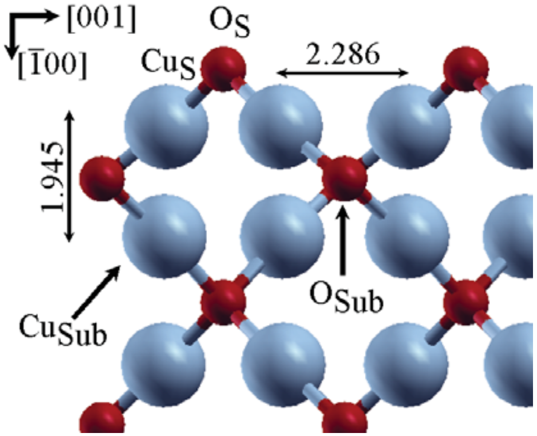
$$\mu_O(T,p_{O_2}) = \frac{1}{2}\left[E^{tot}_{O_2} + \tilde{\mu}_{O_2}(T,p^0) + k_B T \ln\left(\frac{p_{O_2}}{p^0}\right)\right]$$

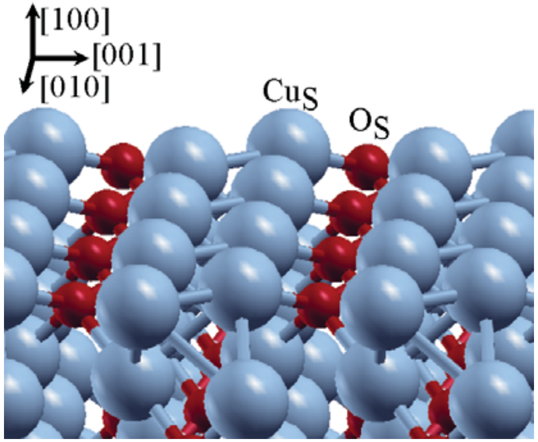
$$\boxed{\gamma(T,p_{O_2}\} = \frac{1}{2A}\left\{G^{surf}_{slab} - \frac{1}{2}\left[N_{Cu} g_{Cu_2O} + (2N_O - N_{Cu})\mu_O\right]\right\}}$$

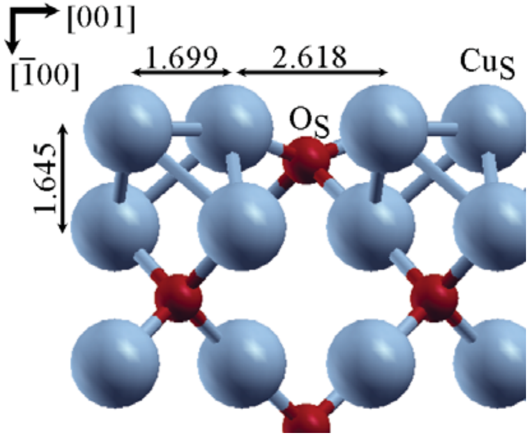
Ref: K.Reuter and M. Scheffler, *PRB* **65**,035406 (2001)

Surface structure

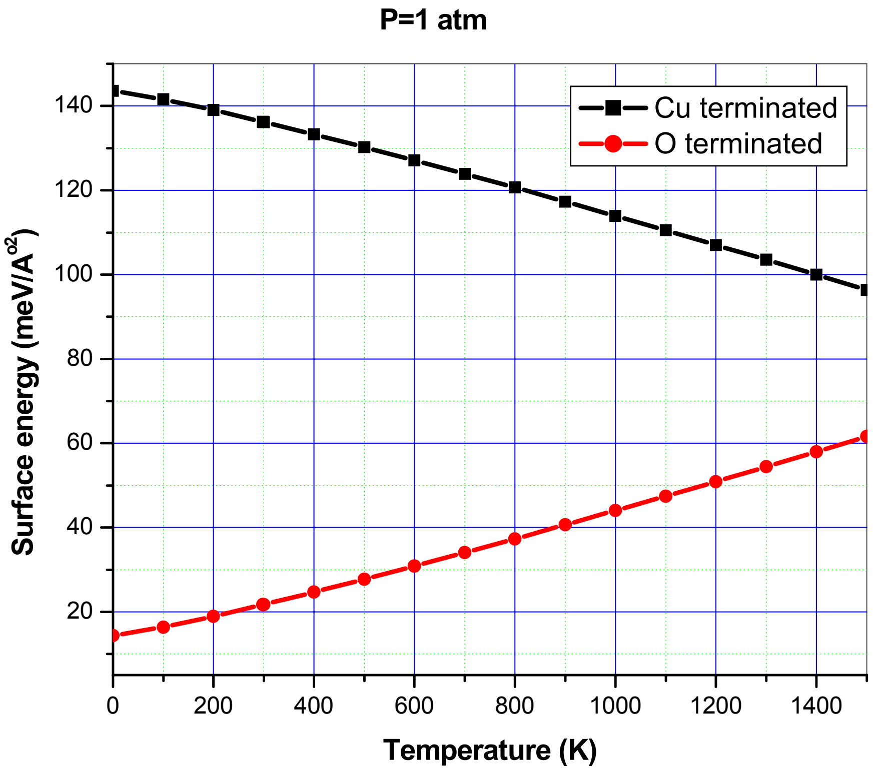


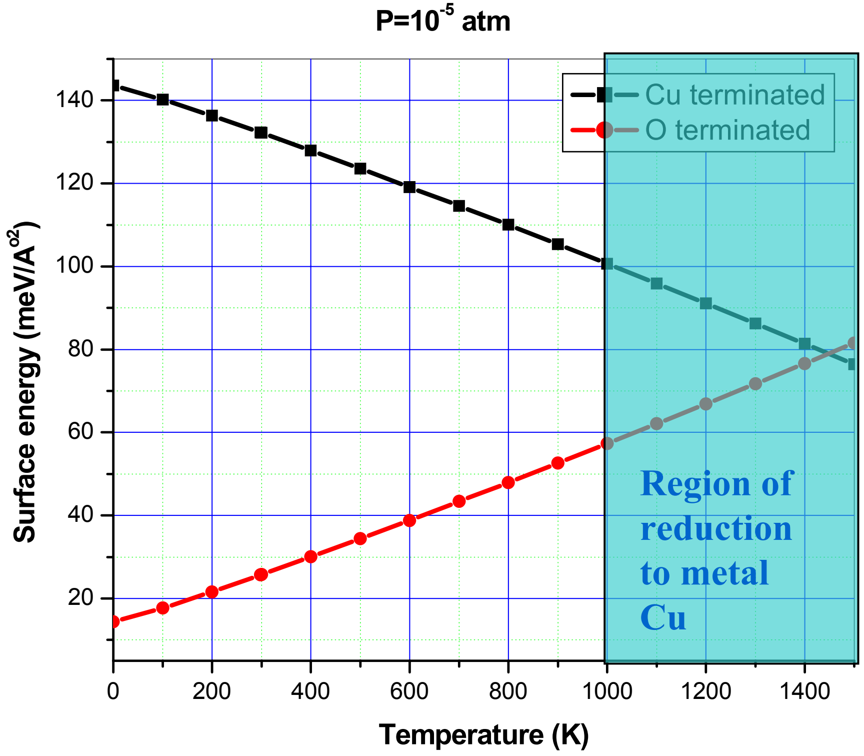






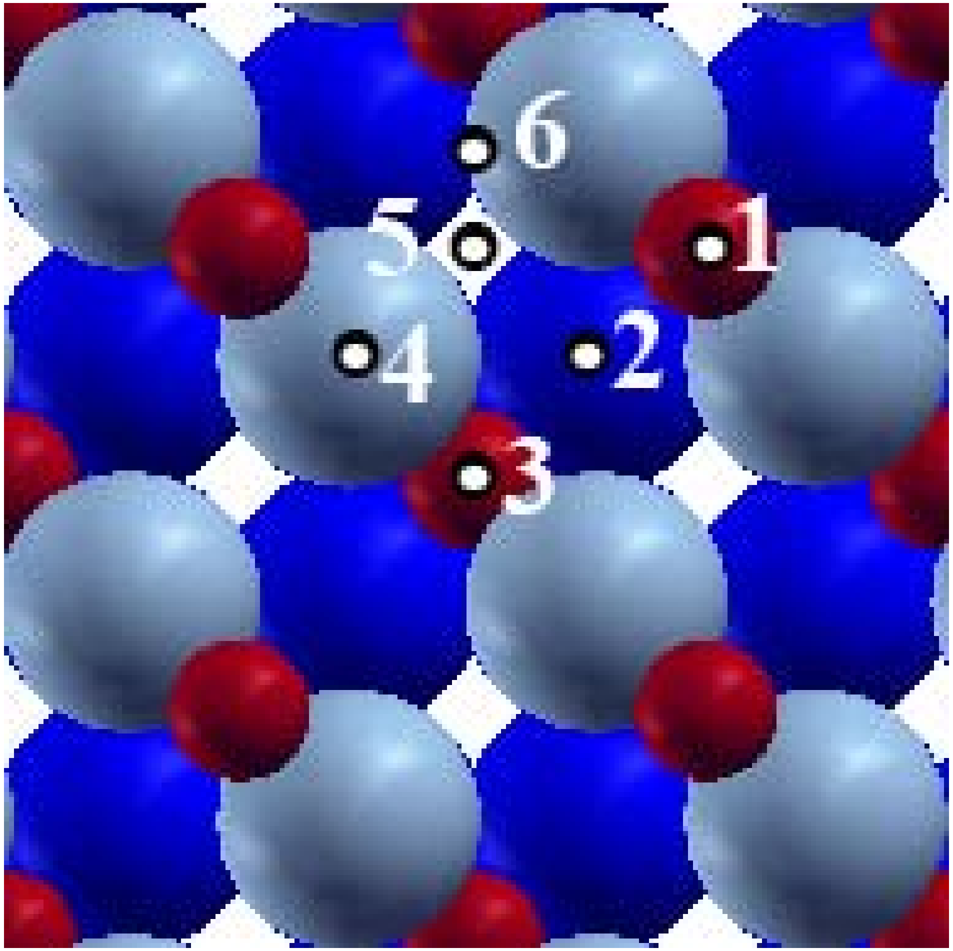
Surface phase diagram

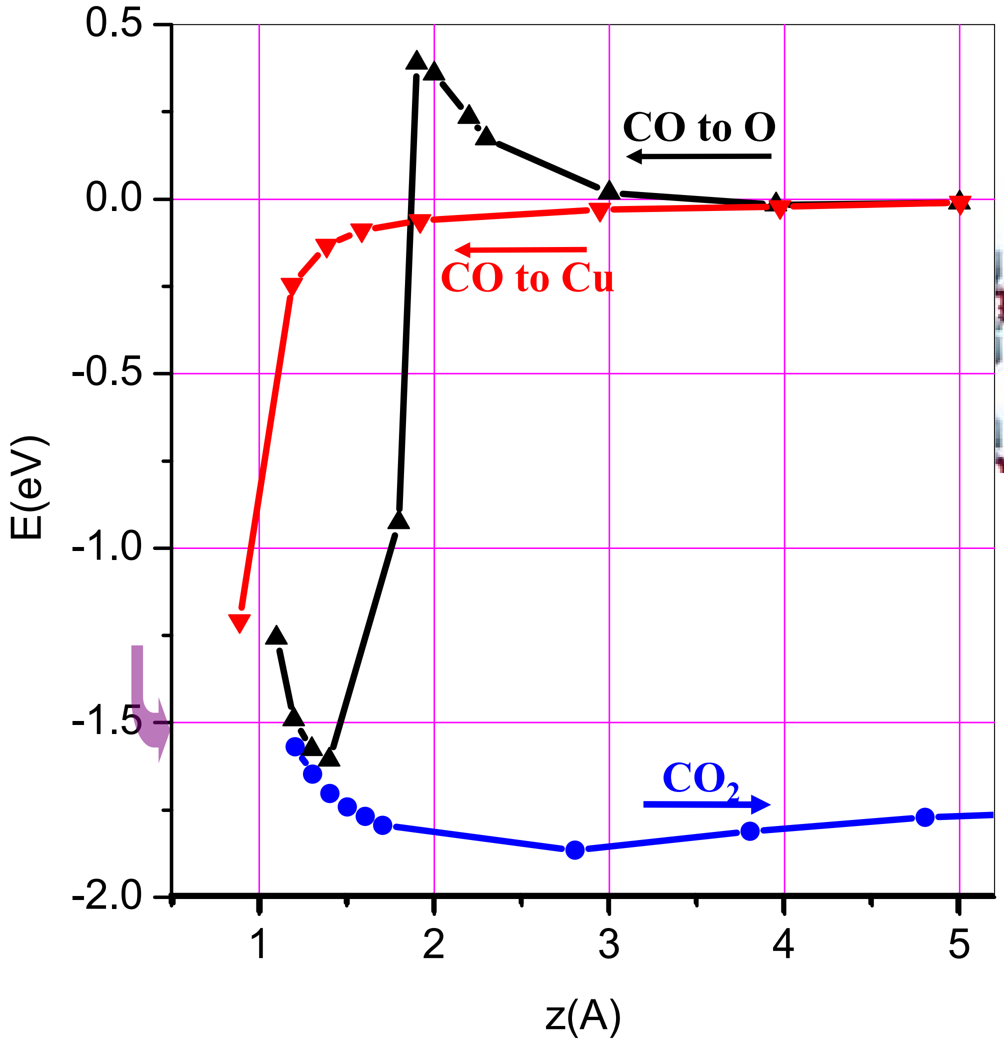

P=1 atm

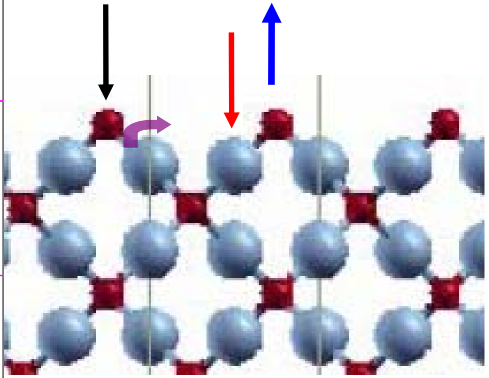

P=10^{-5} atm

In entire *(p,T)* region of existence of Cu_2O the O-terminated $Cu_2O(100)$ is more stable than Cu-terminated $Cu_2O(100)$

CO adsorption & reaction on $Cu_2O(100)$







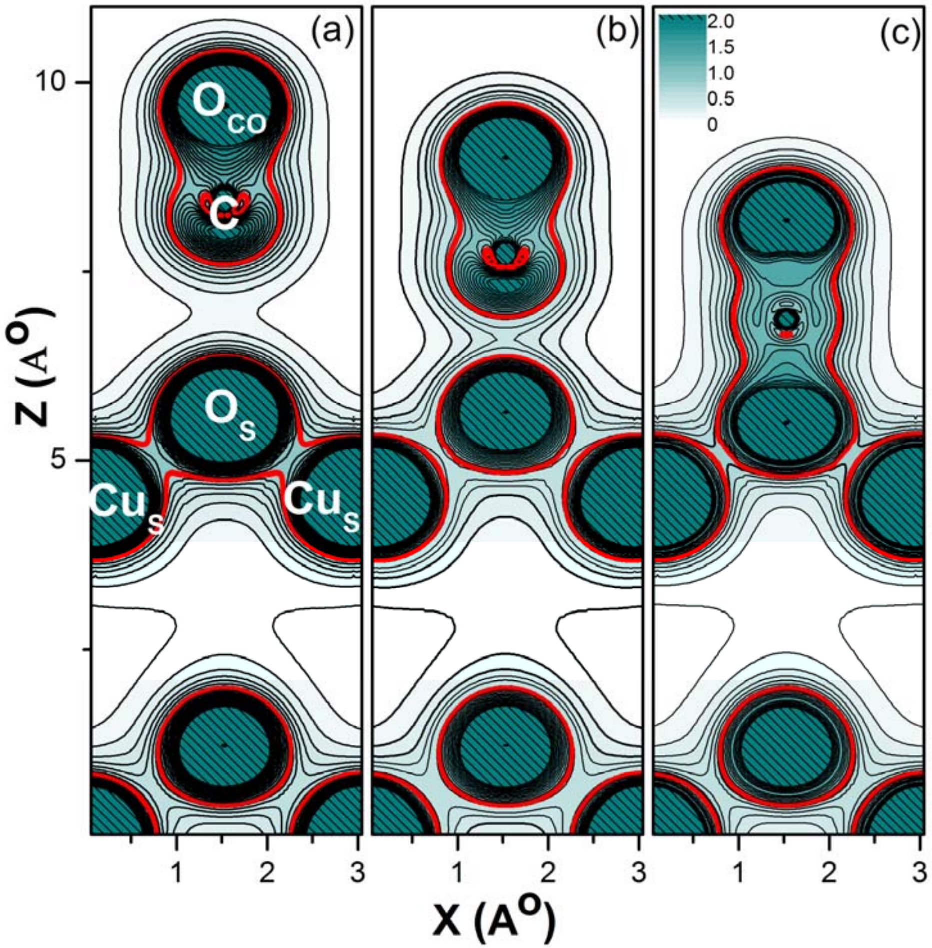
To land on surface oxygen, CO needs to overcome an energy barrier of ~ 0.4 eV.

Once CO adsorbs on the surface oxygen it forms CO_2 that spontaneously departs from the surface leaving an oxygen vacancy.

CO adsorbs on Cu without any barrier.

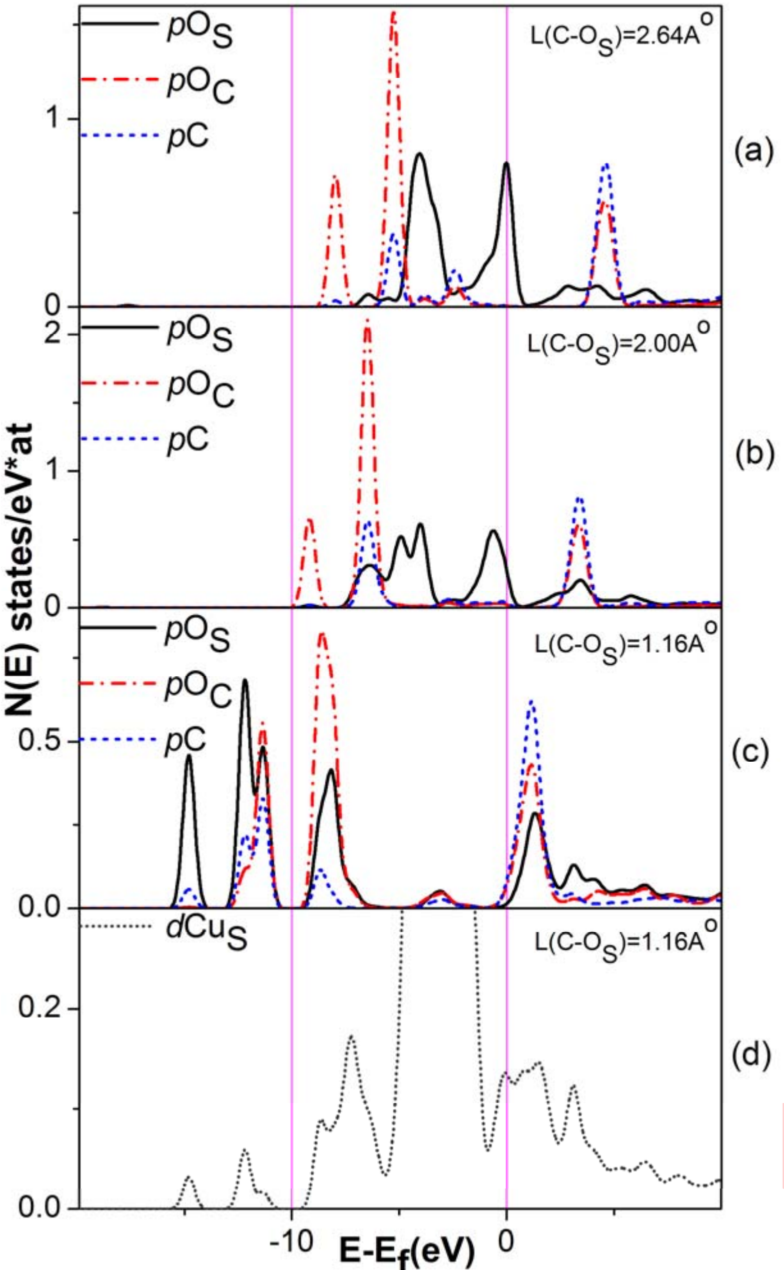
As CO adsorbs on Cu, it diffuse spontaneously to neighboring surface oxygen to be oxidized spontaneously as explained above.

Valence charge density



As CO is approaching the surface, a strong covalent bond is formed between C and surface oxygen that makes CO_2 ready to desorb

Local Density of Electronic States



As CO is approaches the surface, *p*-states of surface oxygen (black lines) and *p*-states of C (red lines) strongly hybridize (see substantial splitting).

Occupied bonding states of O_{surf} and non-occupied anti-bonding states of C formed, causing strong covalent C – O_{surf} bonding

Cu *d*-states are only slightly admixed to the band indicating weak Cu-O_{surf} bonding

What next?

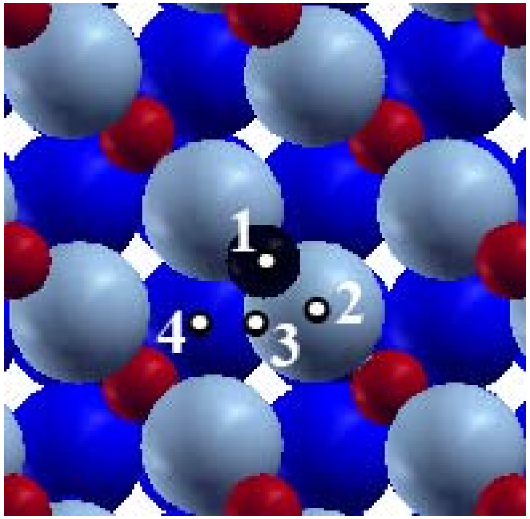
CO is oxidized on $Cu_2O(100)$ by consuming surface oxygen. O-vacancies left on the surface and change its properties.

The composition of $Cu_2O(100)$ and its catalytic activity may be restored by dissociative adsorption of gaseous O_2 on the surface.

To model this important process we need to:

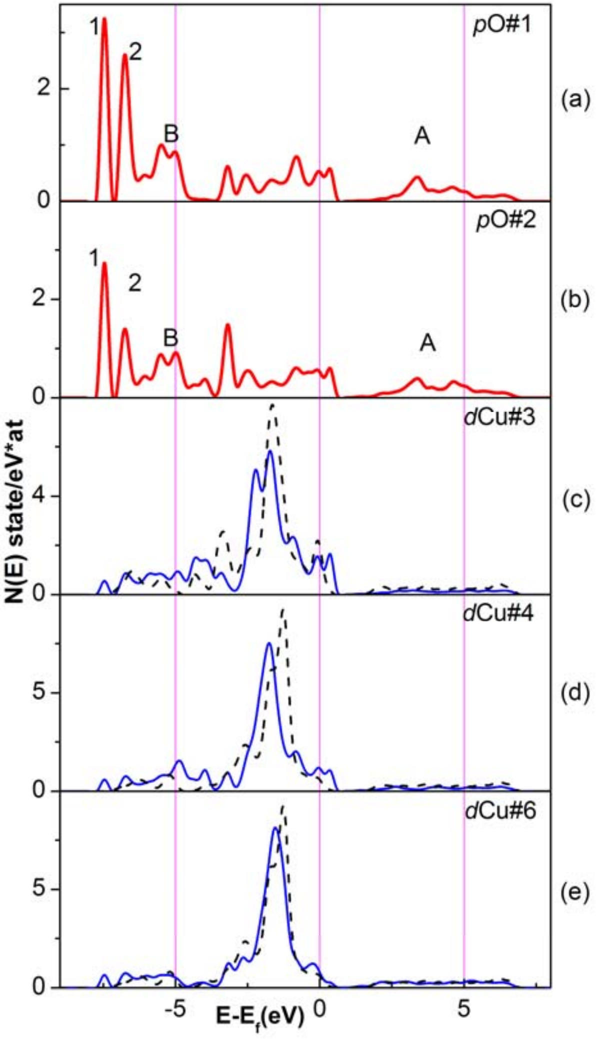
1. Calculate the electronic and geometric structure of the surface with O-vacancies;
2. Obtain geometry and energy of molecular O_2 on the defected surface;
3. Locate the final state of O_2 dissociation on the surface;
4. Calculate the pathway and activation energy barrier for O_2 dissociation on the defected surface.

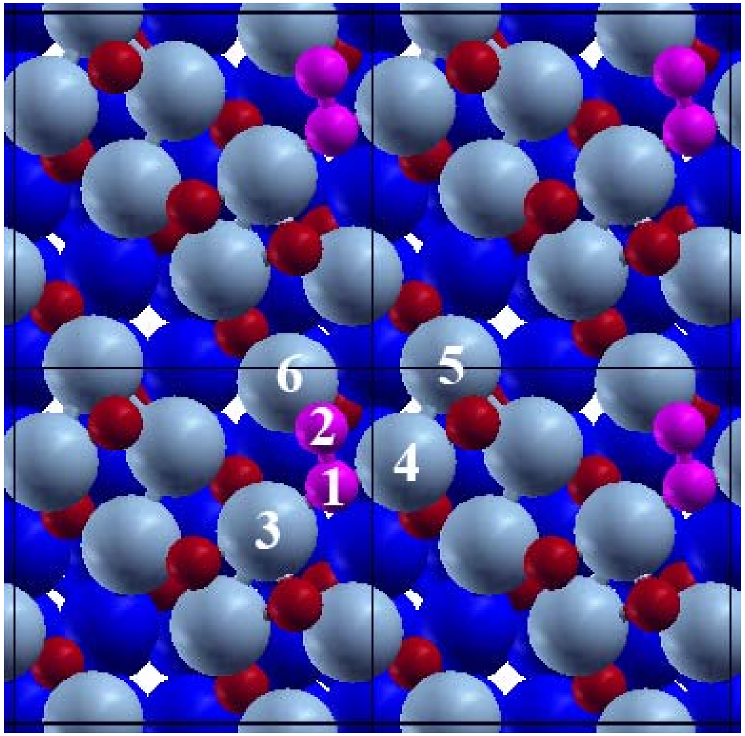
O_2 adsorption sites on $Cu_2O(100)$ with O-vacancies



Site	Landing	Adsorption energy
1	Perpendicular Parallel	-1.66 -2.08
2	Perpendicular Parallel	-0.87 No adsorption
3	Perpendicular Parallel	No adsorption -3.37
4	Perpendicular	No adsorption

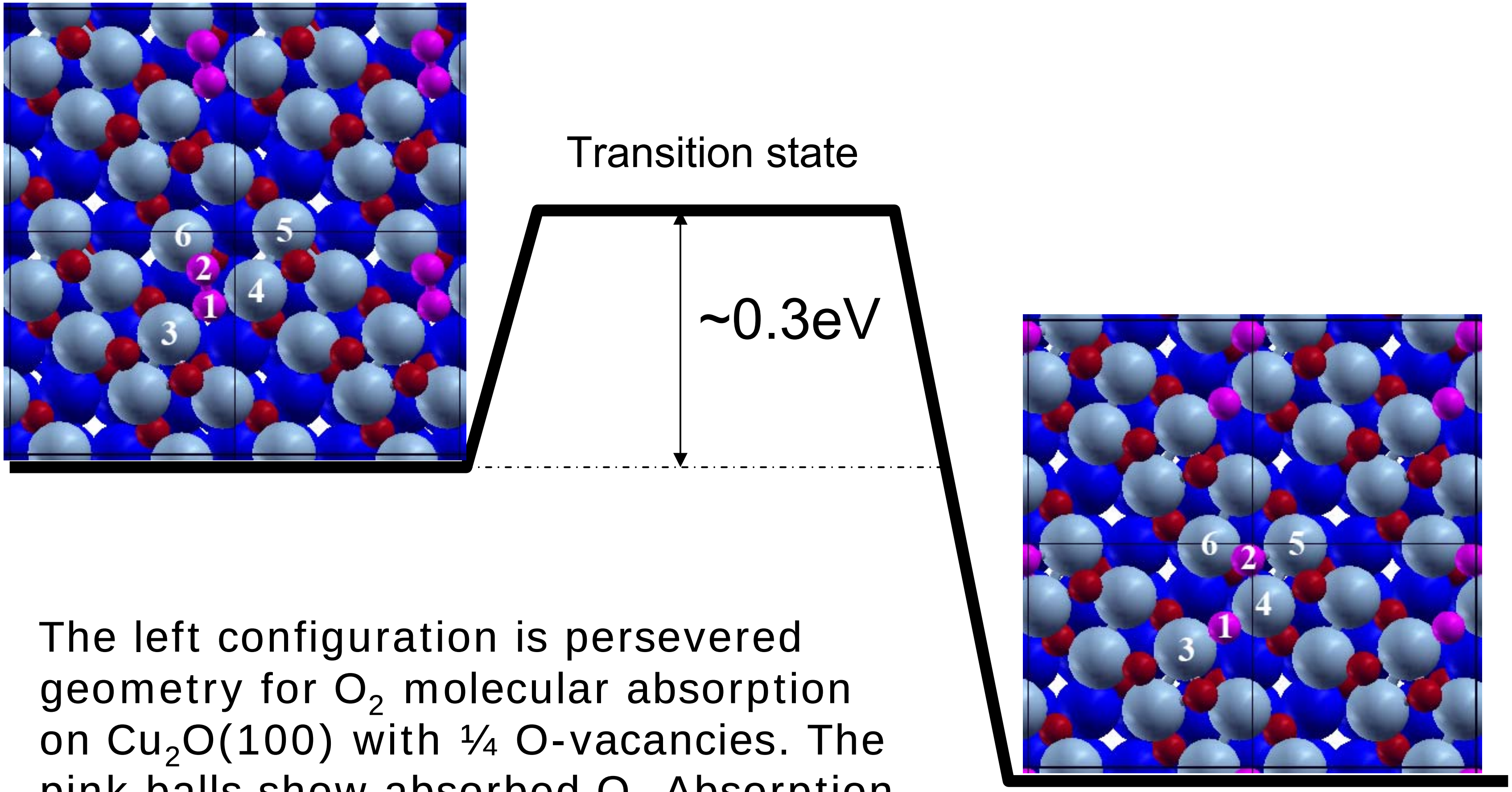
O_2 absorption on $Cu_2O(100)$





Adsorption energy is found to be -3.37 eV.

Activation Barrier



The left configuration is persevered geometry for O_2 molecular absorption on $Cu_2O(100)$ with ¼ O-vacancies. The pink balls show absorbed O_2.Absorption energy is found to be -3.37eV.

The right configuration is preferred geometry for dissociated O_2.

Activation barrier is about 0.3eV.

Conclusion

- **O-termination is preferred for entire *(p,T)* region of existence of Cu2O**
- **Adsorbing on surface oxygen, CO overcomes a ~ 0.4 eV activation barrier;**
- **CO adsorbs on Cu without any barrier;**
- **Once CO adsorbs on Cu, it diffuse spontaneously to neighboring surface oxygen;**
- **CO is spontaneously oxidized on Cu_2O(100) by consuming surface oxygen.**
- **O_2 adsorbs on the defected Cu_2O with the adsorption energy of -3.37 eV.**
- **O_2 dissociation barrier is found to be ~0.3 eV**

Examples from Nanoscience

- **Reactivity of a nanosystem**

  Pt islets on Ru(0001)
- **Vibrational dynamics of a nanosystem**

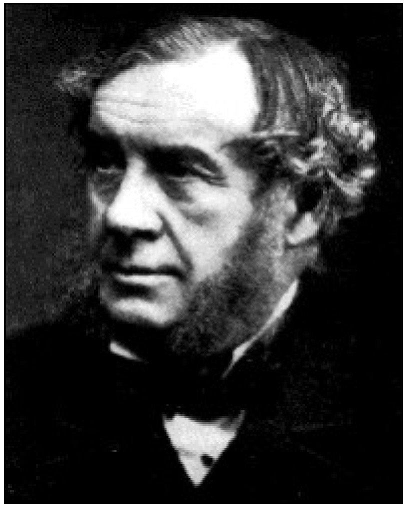
  Transition metal nanoparticles
- **Electronic Structure of a nanoalloy**

  Ag/Cu nanoparticles

Fuel Cells

Basic principles like for electrochemical battery.
Difference – in a fuel cell, the chemical energy is provided by a fuel and an *oxidant* stored outside

Despite their modern high-tech aura, fuel cells have been known for more than 150 years.



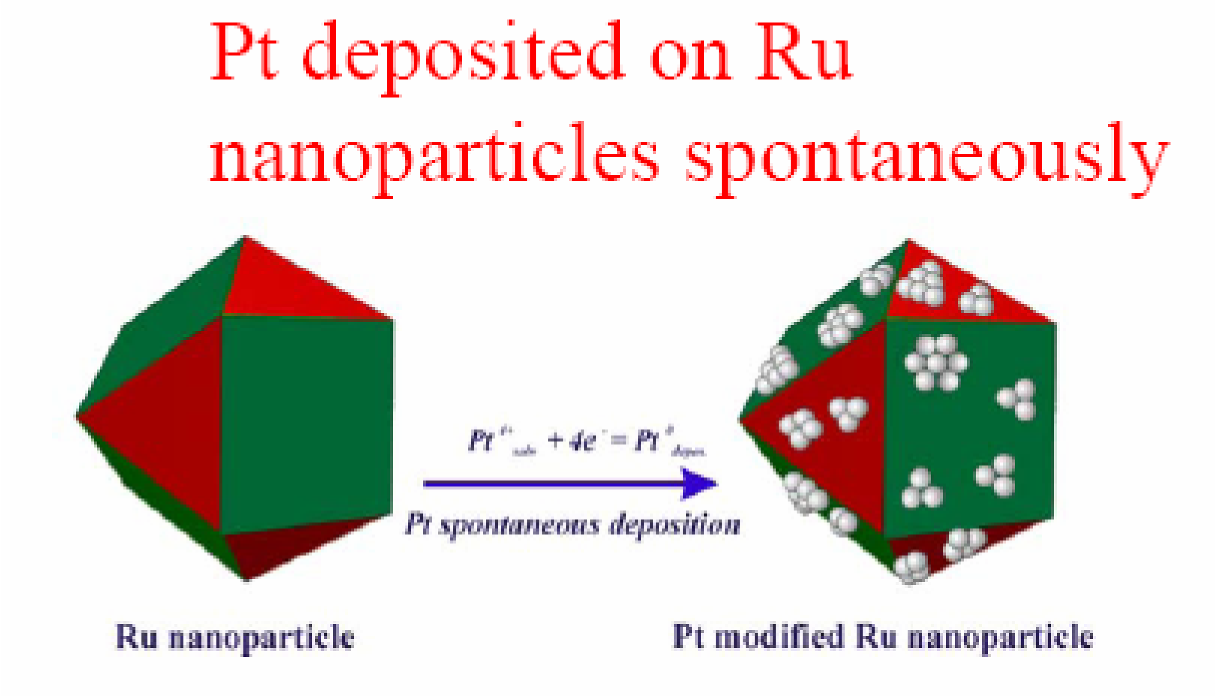
Sir William Robert Grove is known as “Father of the ***Fuel Cell***.” **(1839)**

A real fuel cell

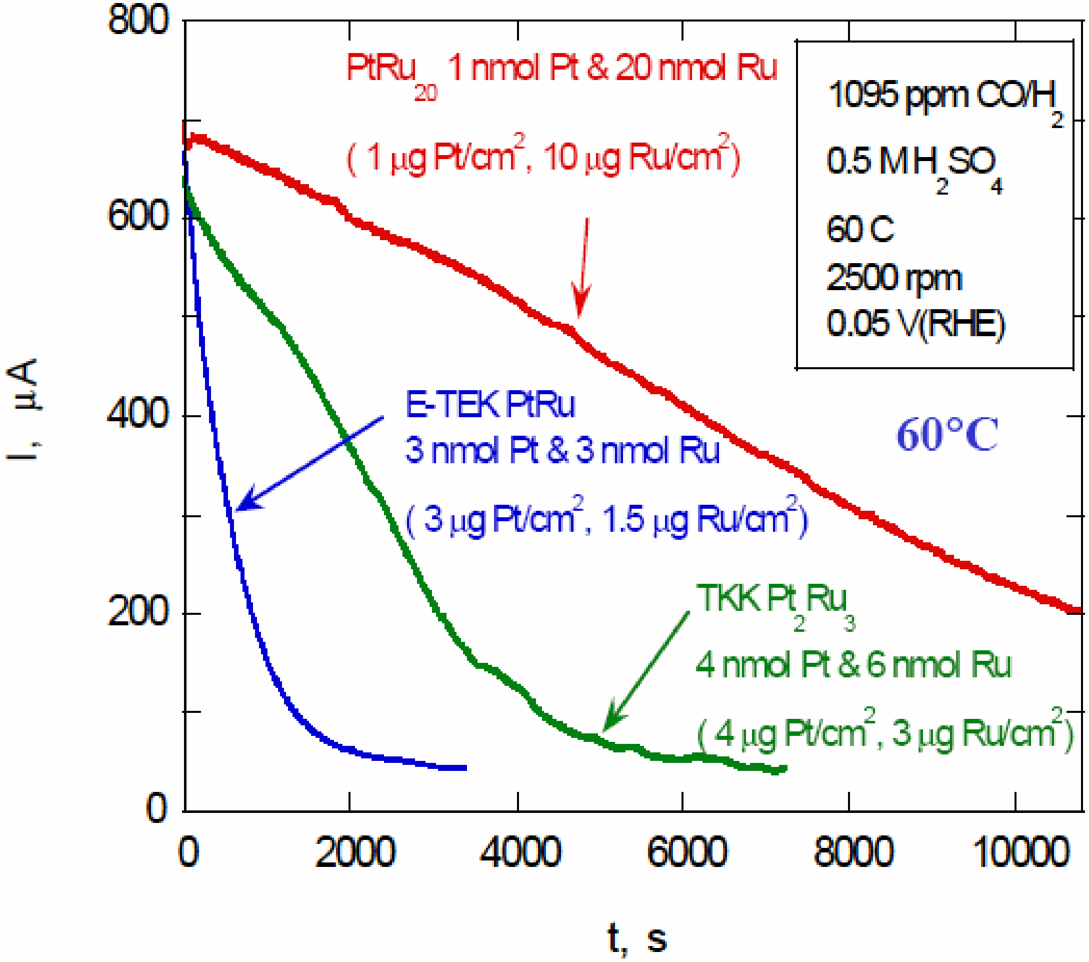

necar 5
methanol powered fuel cell ca

Traces of CO inevitably present in hydrogen obtained from natural gas block active sites of Pt anode of hydrogen fuel cell and this way suppress hydrogen oxidation. Alloying Ru or some other metals just slightly improve the CO tolerance of the anode.

S. R. Brankovic, et al., Electrochem. Sol.-St. Lett. 4 (12) A217-A220 (2001):

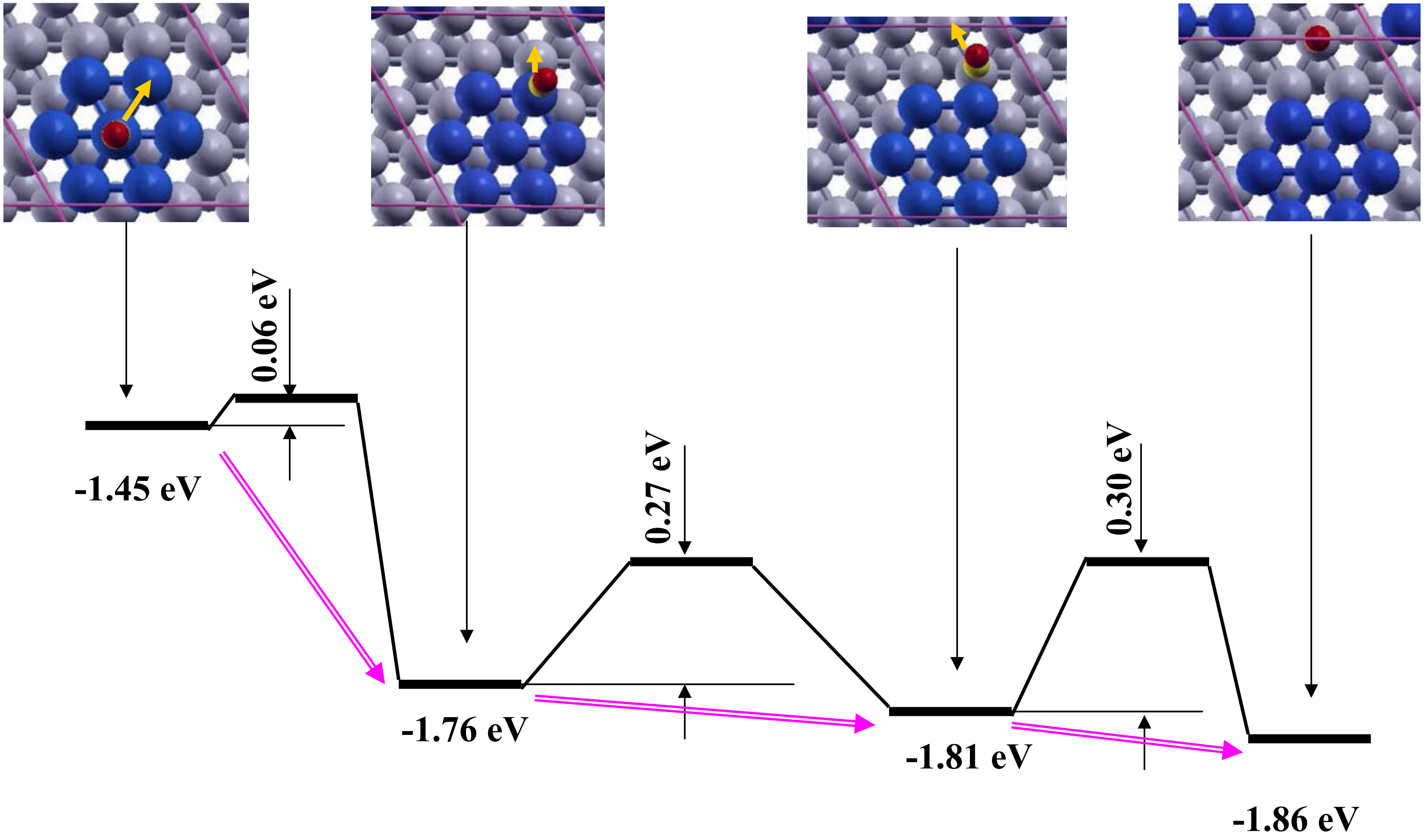


COMPARISON OF THREE ELECTROCATALYSTS FOR CO TOLERANCE



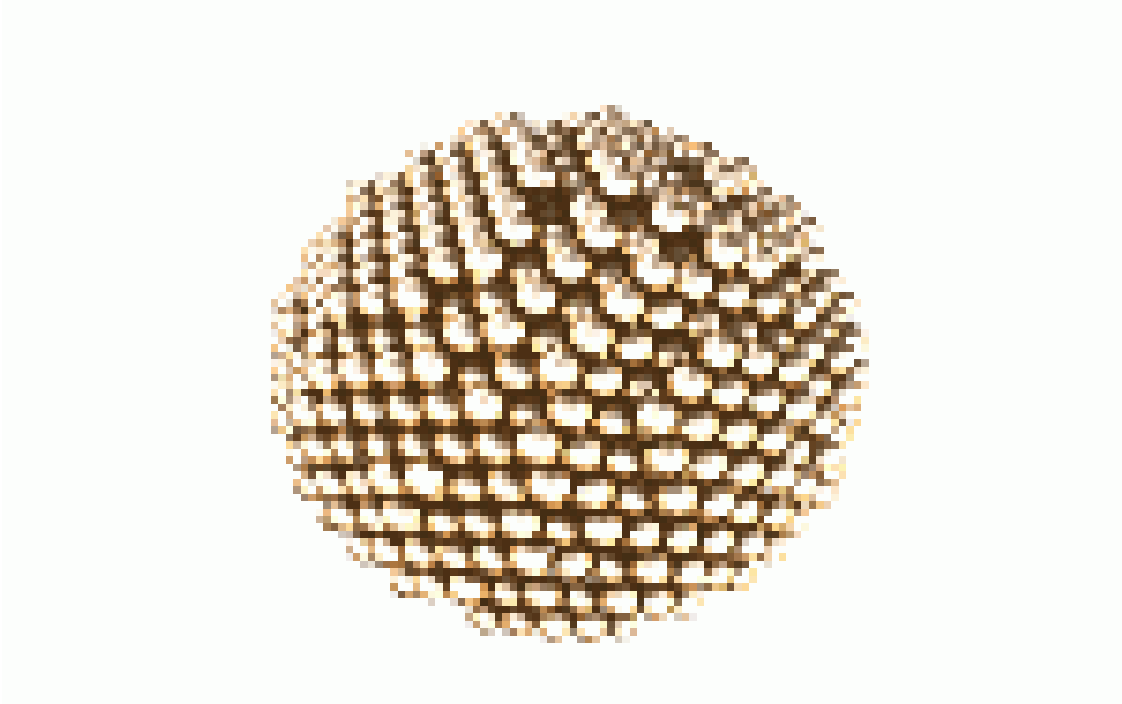
Ru nanoclusters with deposited Pt islands demonstrate much higher tolerance to CO than commercial alloys.

Why?

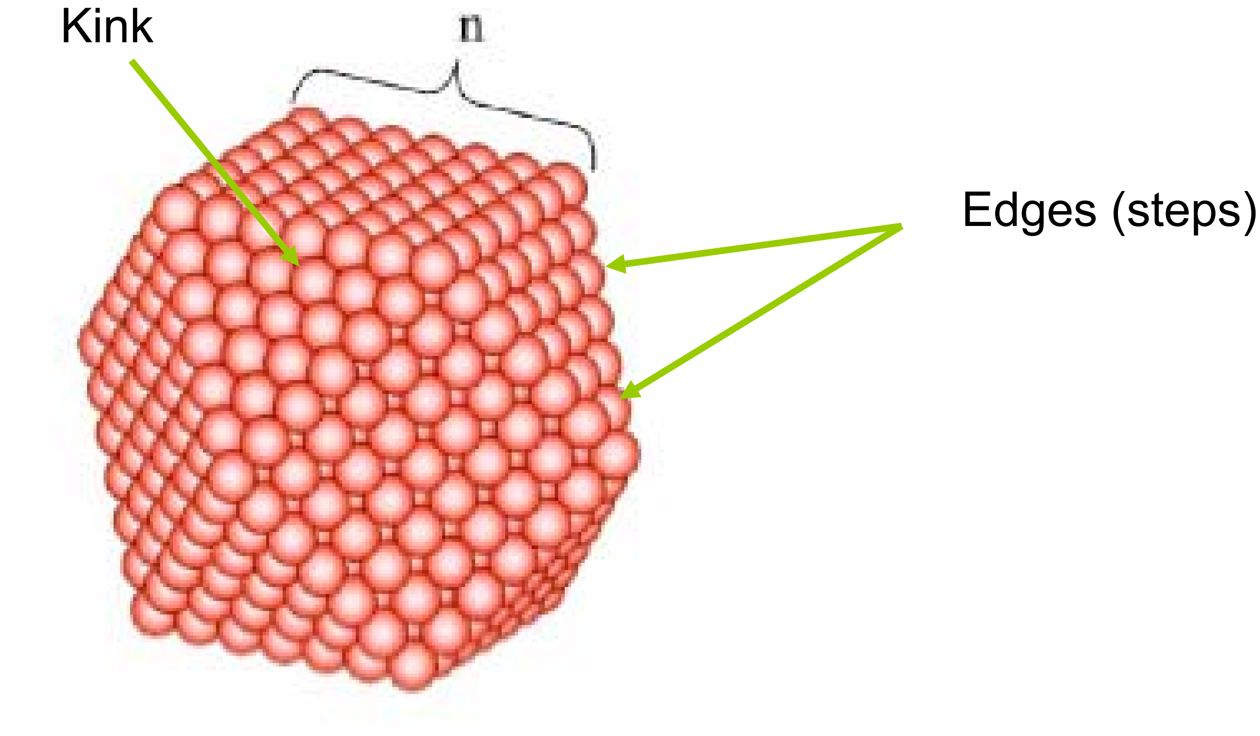


Adsorption and diffusion of CO (C-yellow, O-red) on Pt (blue) island and Ru(0001) (grey) substrate.

Thermodynamics of Metallic Nanoparticles: lattice heat capacity



A. Kara and T.S. R., Phys. Rev. Letters 81, 1453 (1998);
A. Kara, A. Al-Rawi, and T. S. R.,
J. Comp. and Theo. Nanoscience 1, 216 (2004).

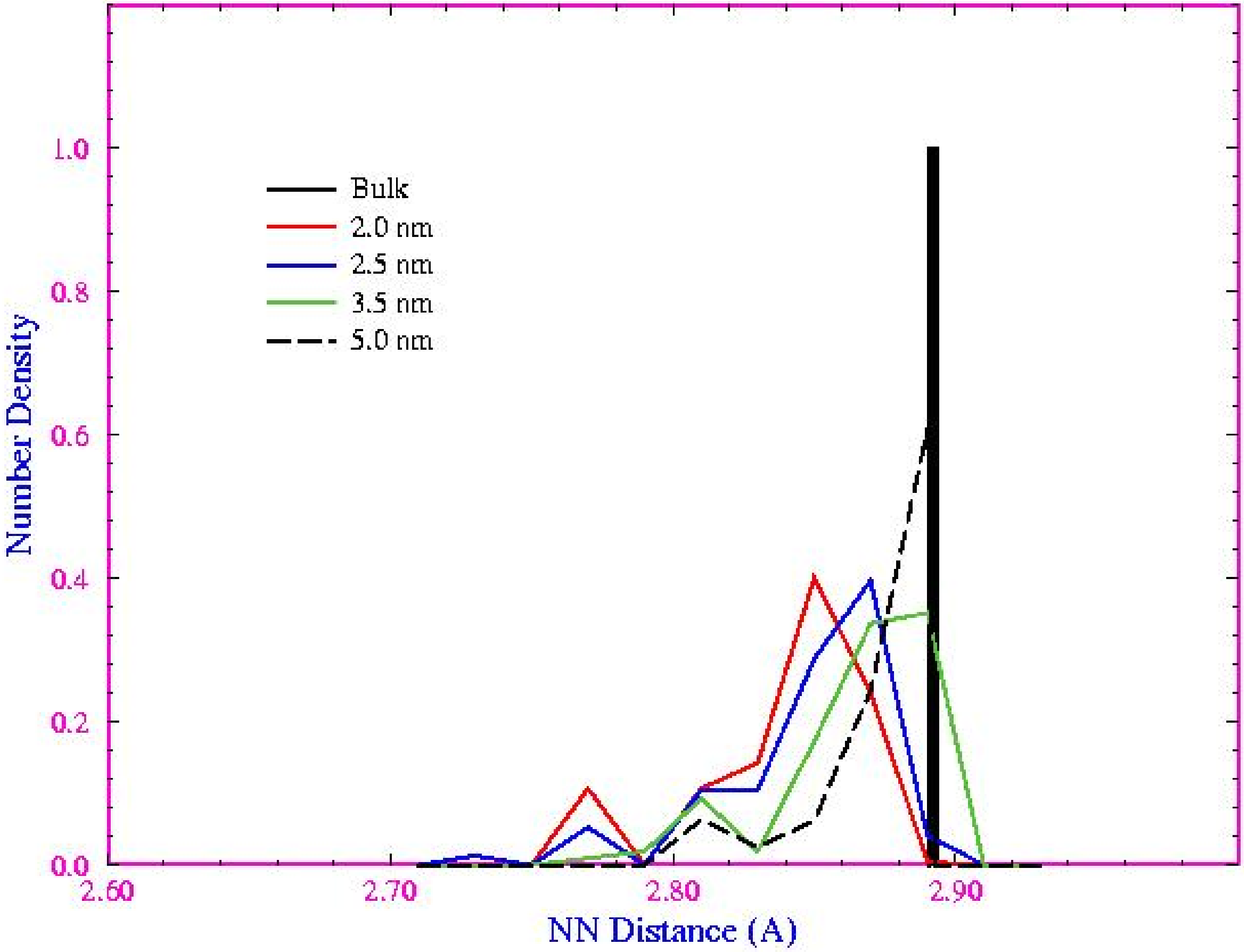


Kink

Edges (steps)

Ag Nanoclusters EAM–VC

NN distance distributions



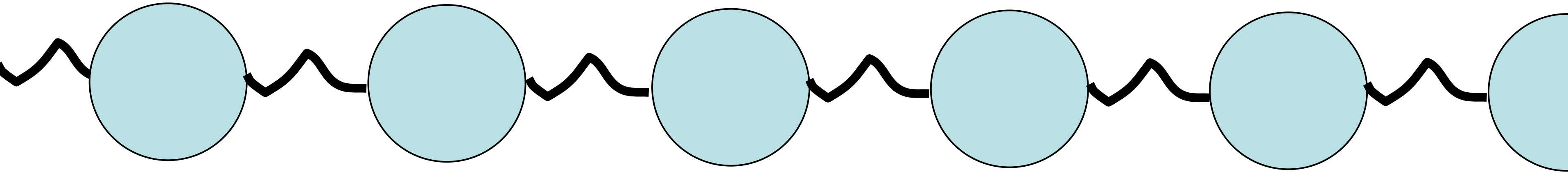
Are the forces that bind atoms and molecules in nanoparticles similar to those in bulk systems?

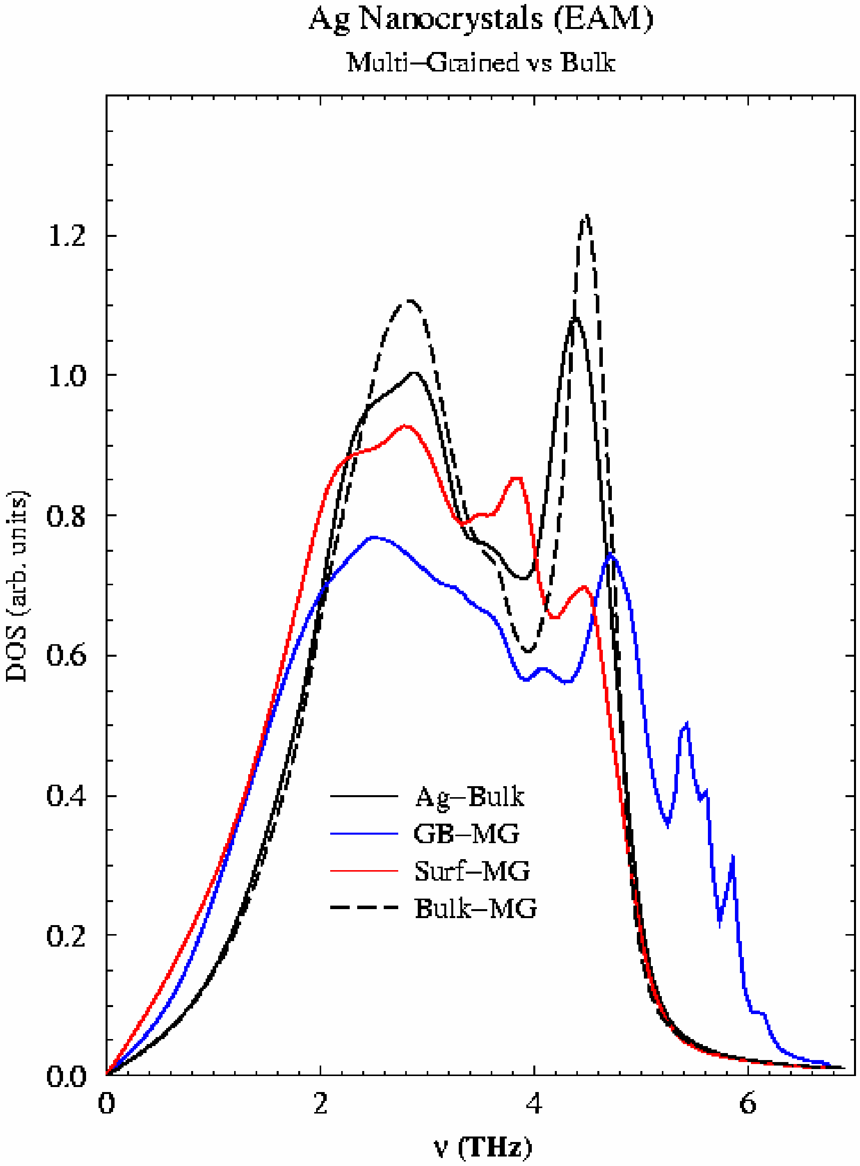
Let us look at vibrational modes in nanoparticles

We know that for a system of linear chain of atoms:

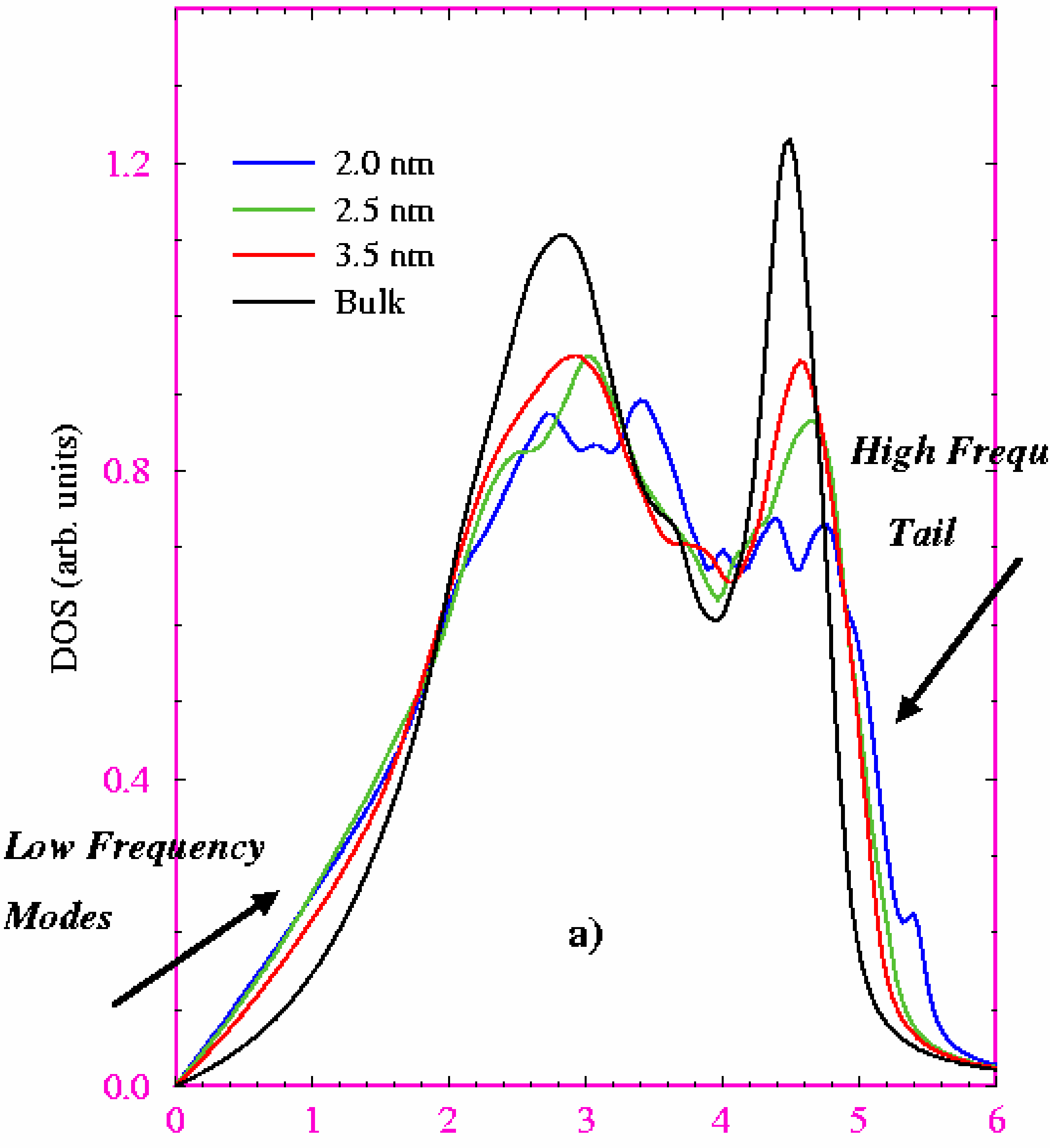
$$\omega^2 = k/m$$

(k is the force constant and m mass)




Ag Nanocrystals (EAM)
Multi–Grained vs Bulk
DOS (arb. units)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
2
4
6
ν (THz)
Ag–Bulk
GB–MG
Surf–MG
Bulk–MG

Ag Nanocrystallines EAM_VC/RSGF
Total Density Of States

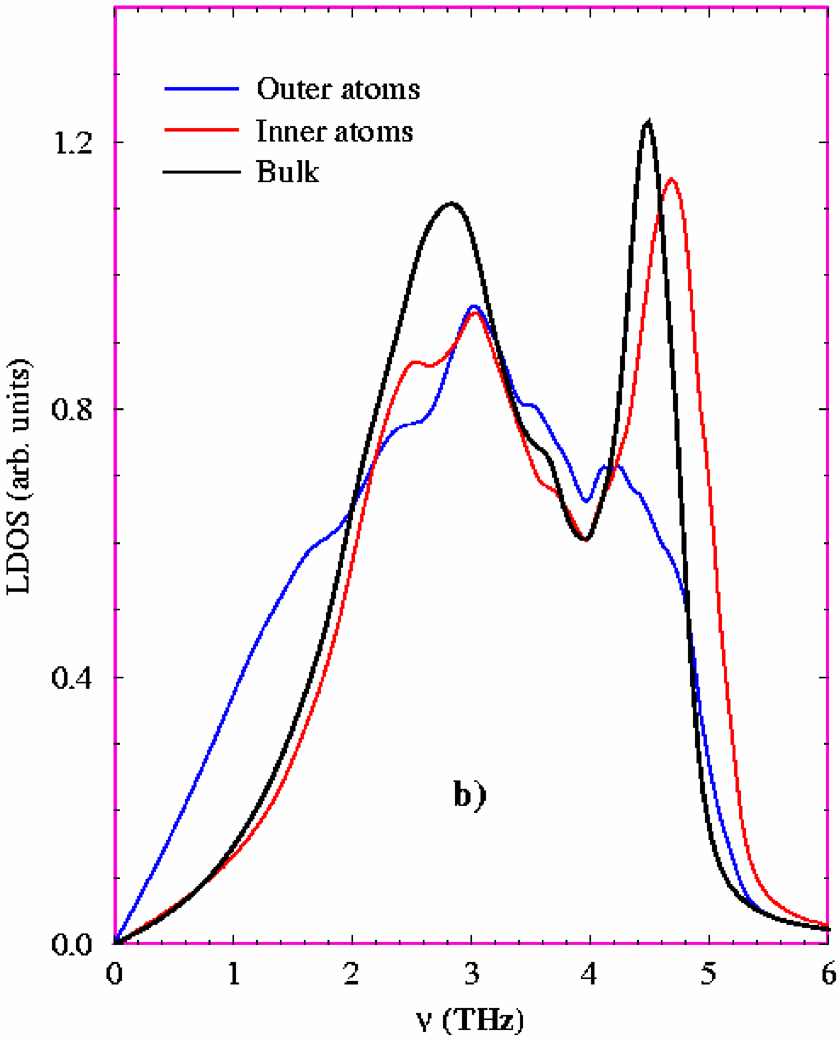


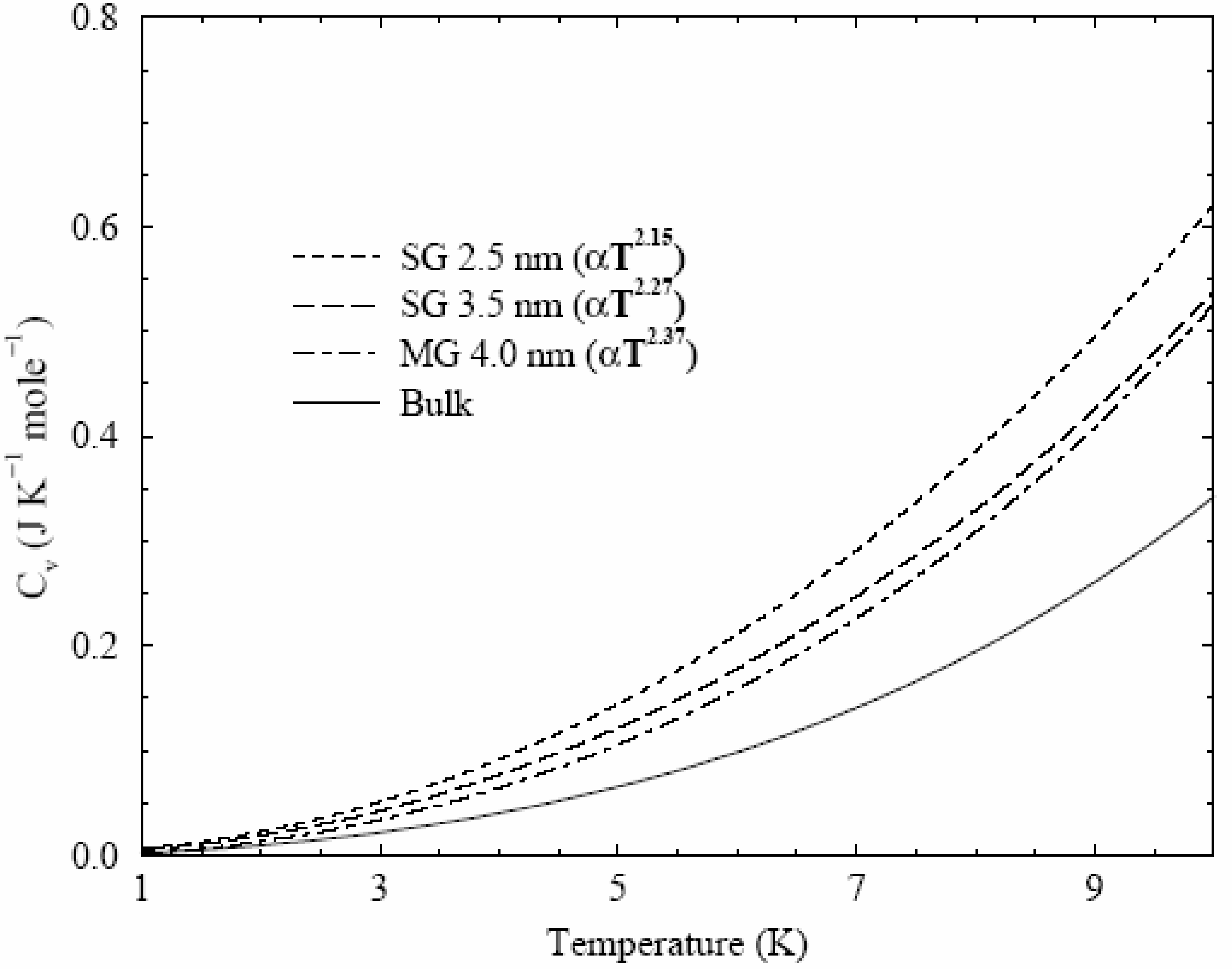
Low Frequency Modes

High Frequency Tail

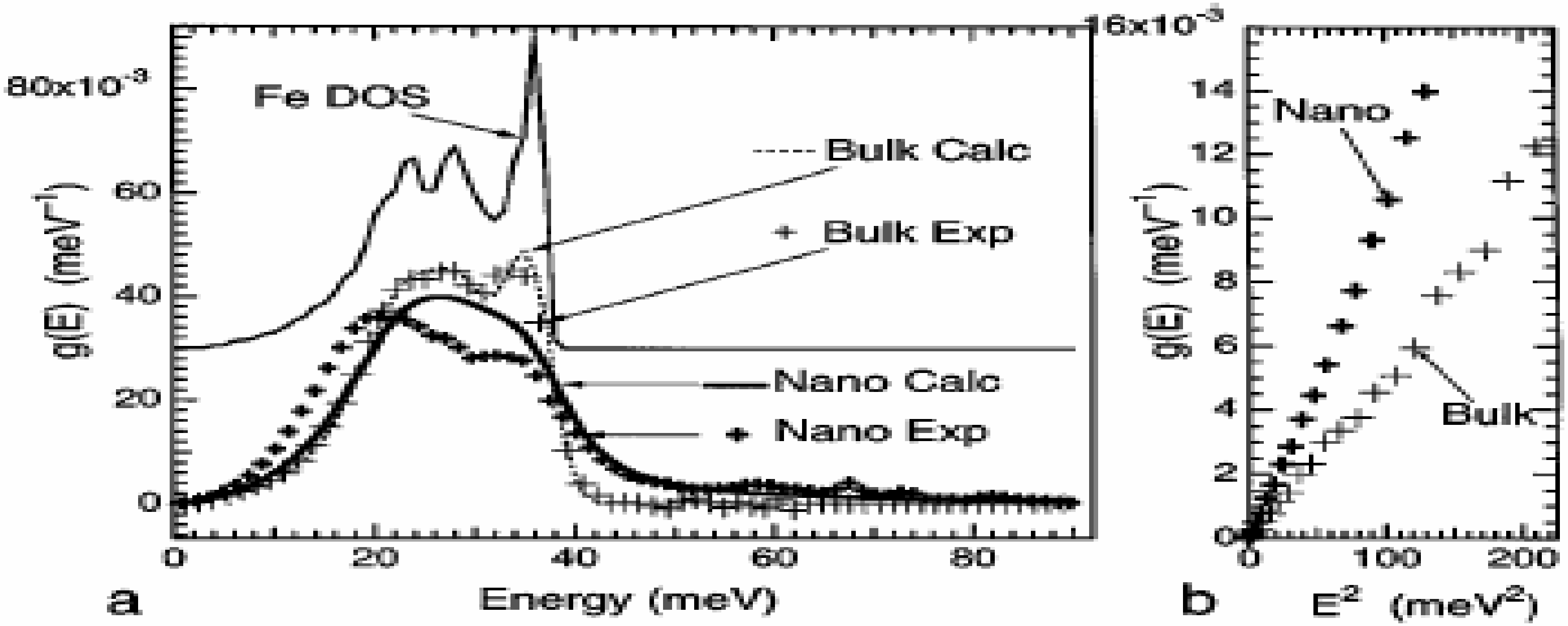
Ag Nanocrystals

Linear Behavior at Low Frequencies





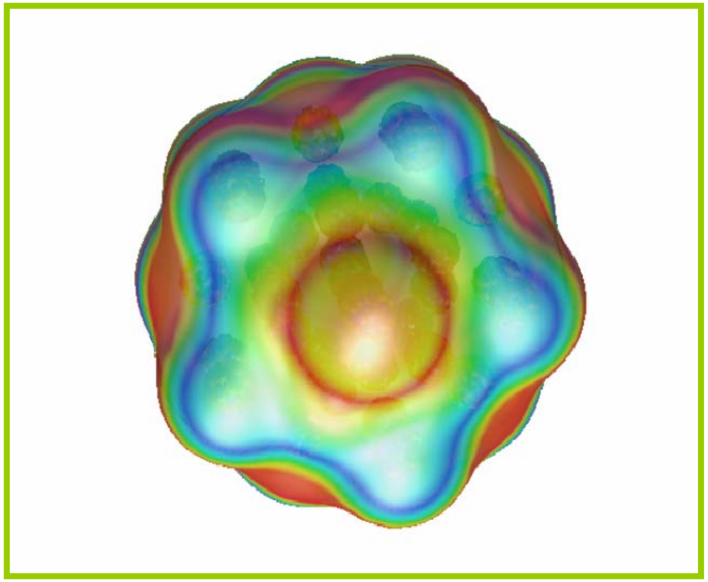
Temperature Variation of Heat Capacity of Nanoparticles

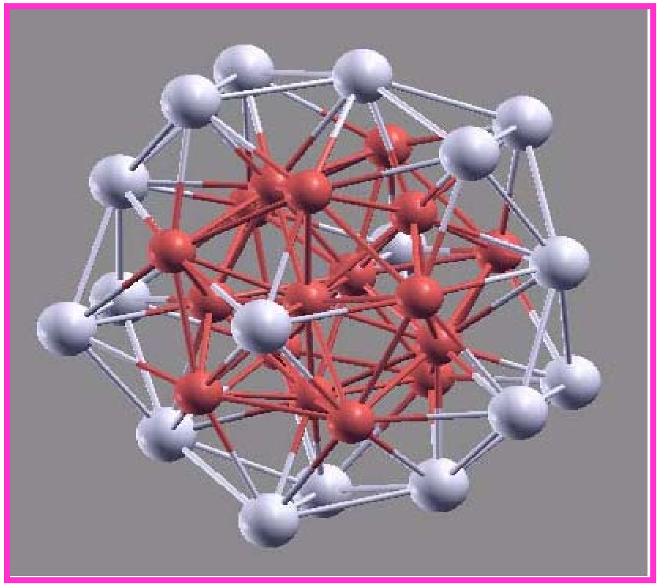


G. 4. (a) Top: phonon DOS of bulk bcc Fe, calculated with rce constants from inelastic neutron scattering [18]. Bottom: osses are phonon DOS curves extracted from experimental ta of Fig. 4. Solid curves are calculated as described in text.) Enlargement of low energy part of the experimental phonon OS curves of Fig. 4(a).

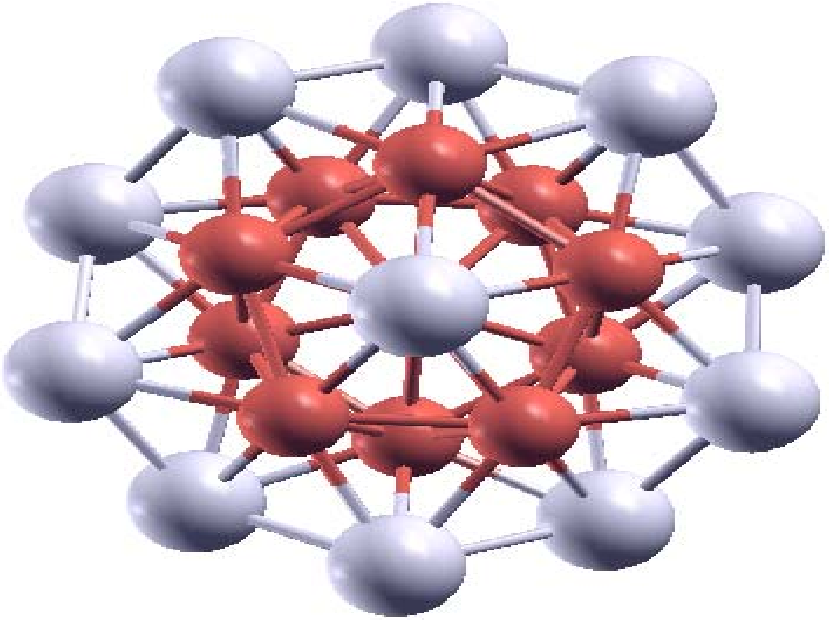
Ag_nCu_{34-n}, Ag_nCu_{38-n}, and Ag_nNi_{34-n}, Alloy Nanoparticles

A. Kara, H. Yildirim, M. A. Ortigoza, R. Ferrando and TSR

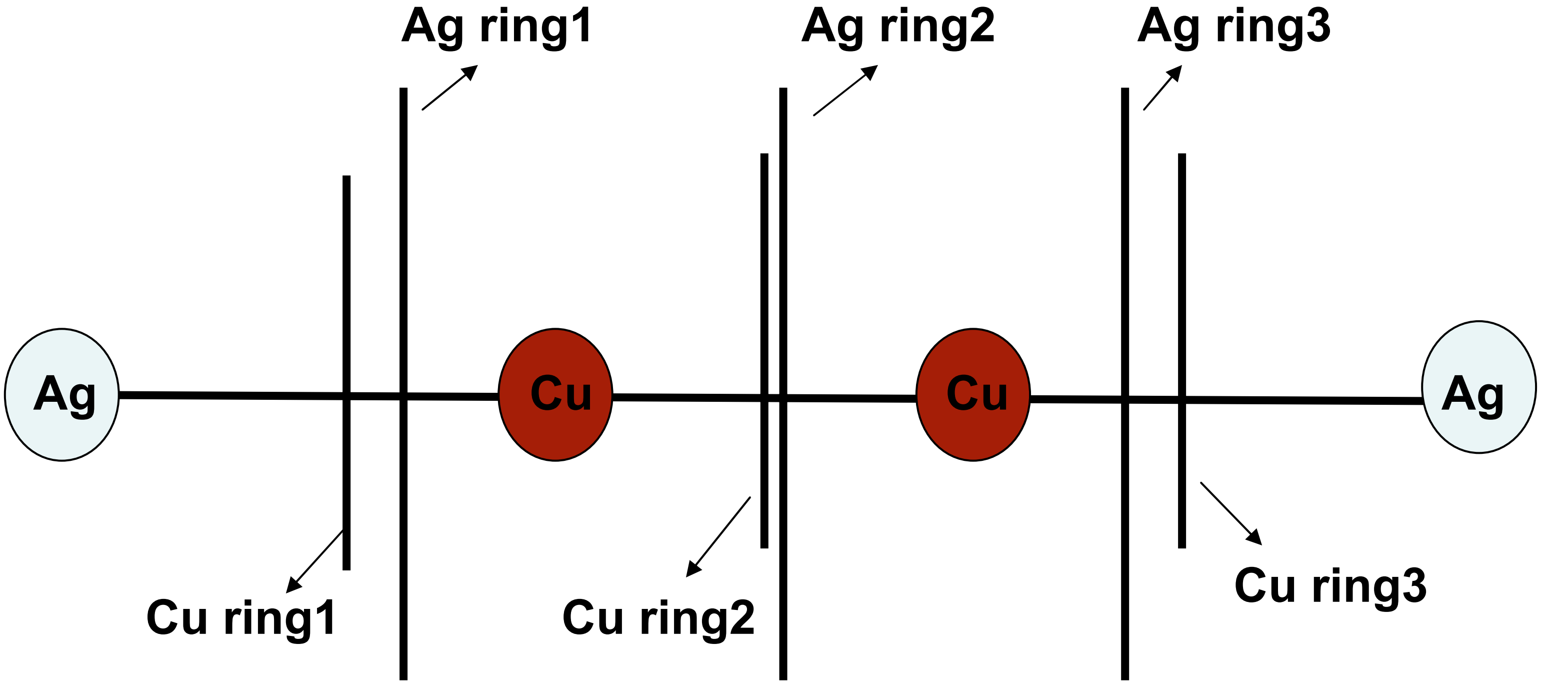




Ag17Cu17



$Ag_{17}Cu_{17}$



Ag ring1

Ag ring2

Ag ring3

Ag

Cu

Cu

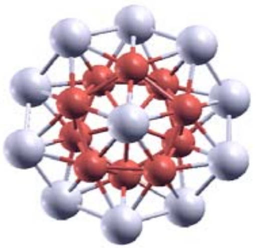
Ag

Cu ring1

Cu ring2

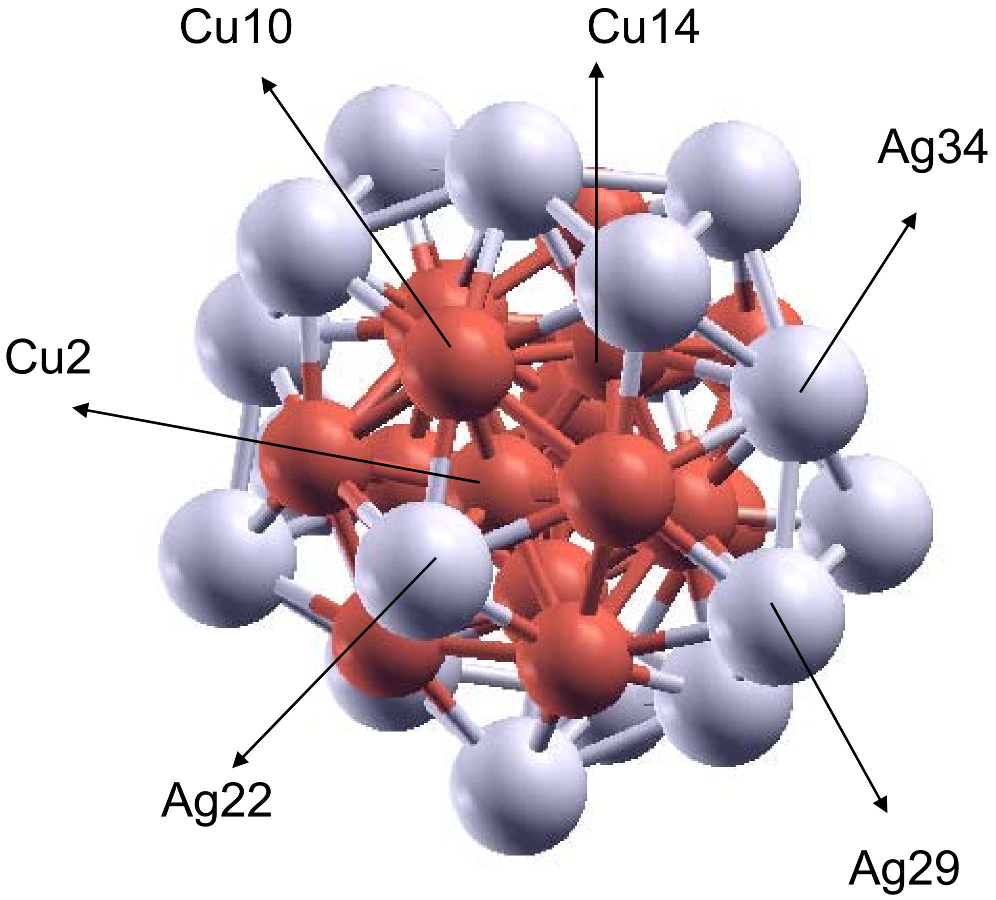
Cu ring3

Ag17Cu17



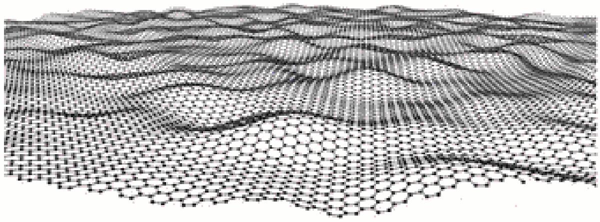
atom	tot-nn	Cu-nn	Ag-nn
Cu2	12	11	1
Cu10 R1	9	5	4
Cu14 R2	12	8	4
Ag22	6	6	0
Ag29	5	3	2
Ag34	8	4	4

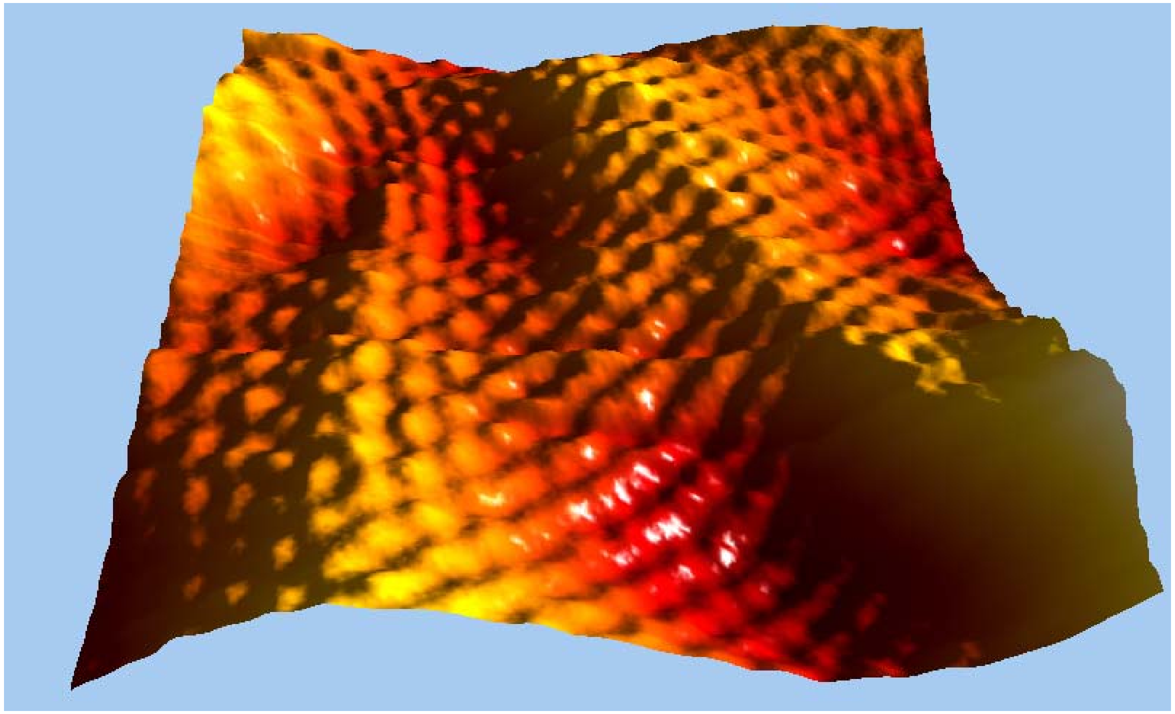
The 6 non-equivalent atoms in Ag17Cu17



Back to the origins

The ever-unfolding story of Graphene

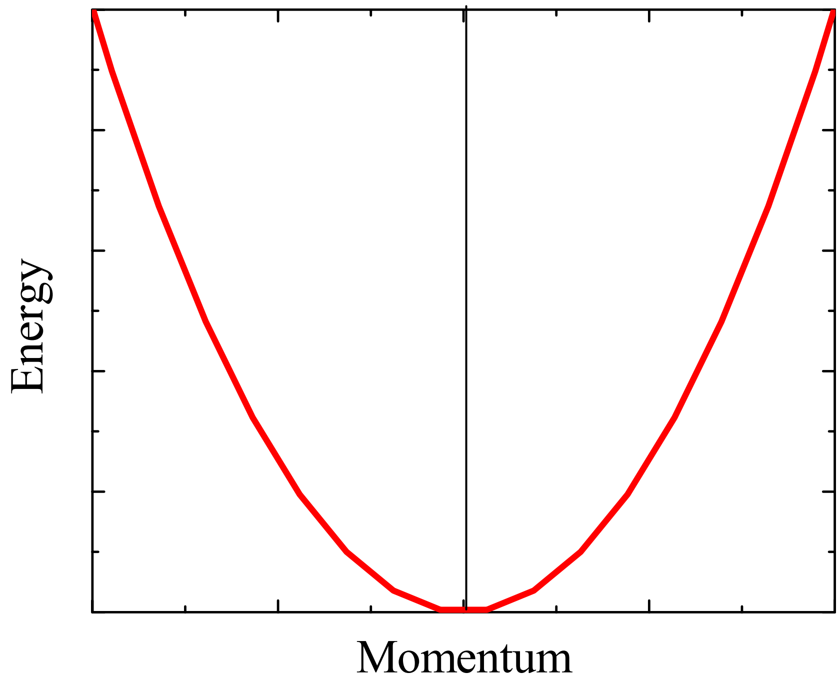




Observations of structural and electronic disorder

– from von Klitzing et al and Ishigami et al

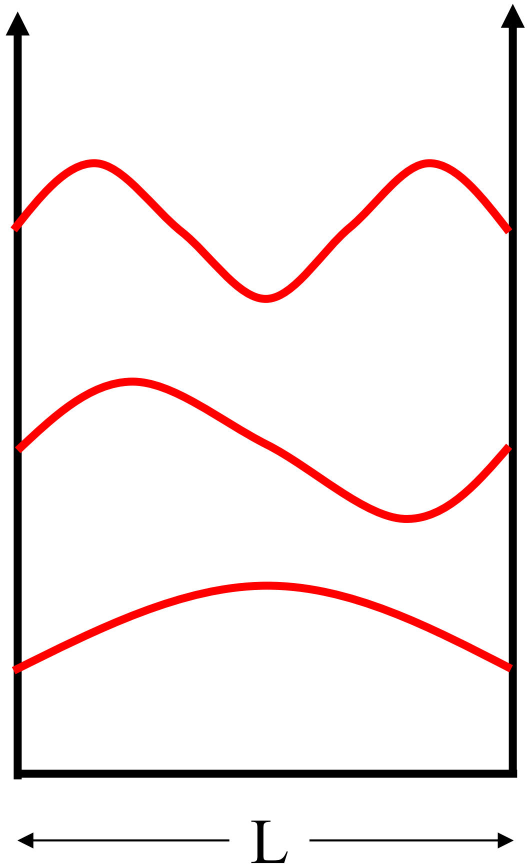
DOS and Dispersion Relationship



$$E = \frac{\eta^2 k^2}{2m}$$

Electronic Densities of States

Example: Quantum Well



$$\psi(x) \sim \sin(kx)$$

$$k = \frac{n\pi}{L} \qquad n = 1,2,3.....$$

$$E = \frac{\eta^2 k^2}{2m} \qquad (\frac{2mE}{\eta^2})^{\frac{1}{2}} = k$$

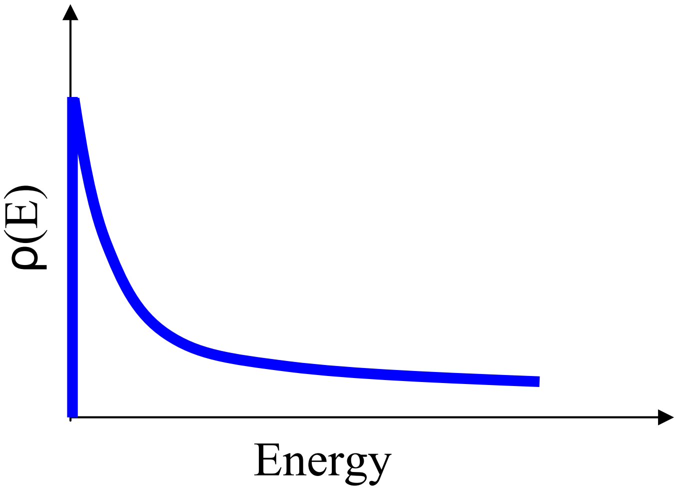
$$(\frac{2m}{\eta^2})^{\frac{1}{2}} E^{-\frac{1}{2}} dE = dk = dn\frac{\pi}{L}$$

$$dn \sim dE \times E^{-\frac{1}{2}}$$

$$\frac{dn}{dE} \sim E^{-\frac{1}{2}}$$

Densities of States = ρ(E)

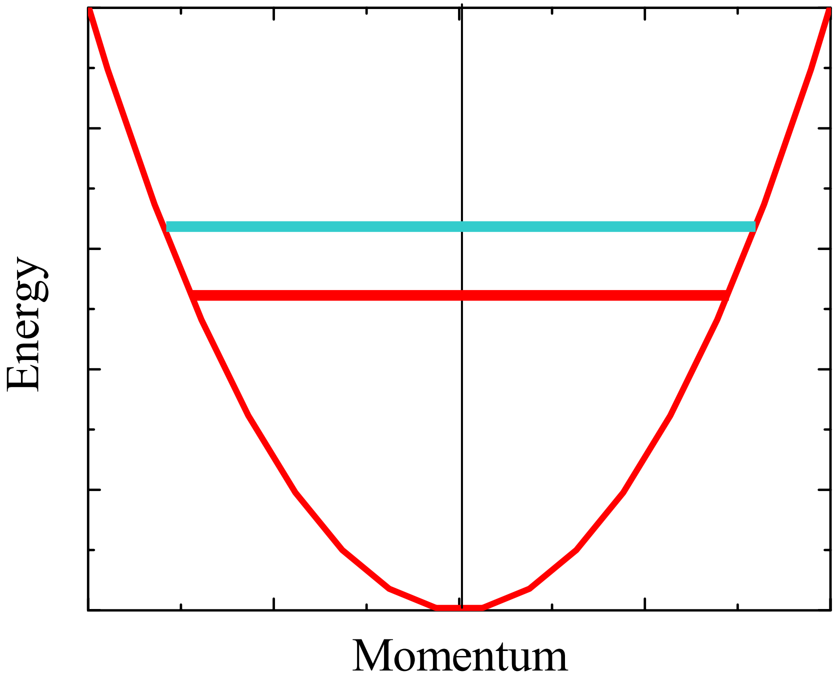
Number of quantum states available at a particular energy E

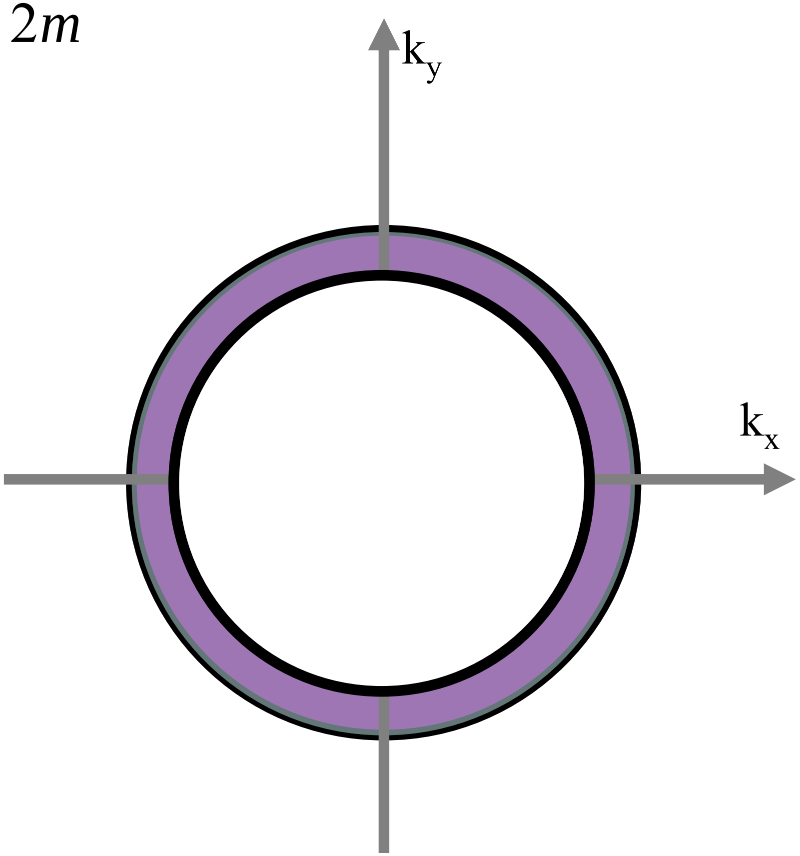


Dispersion Relationship of Free Electrons

Example: Free Electron Gas in 2D

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



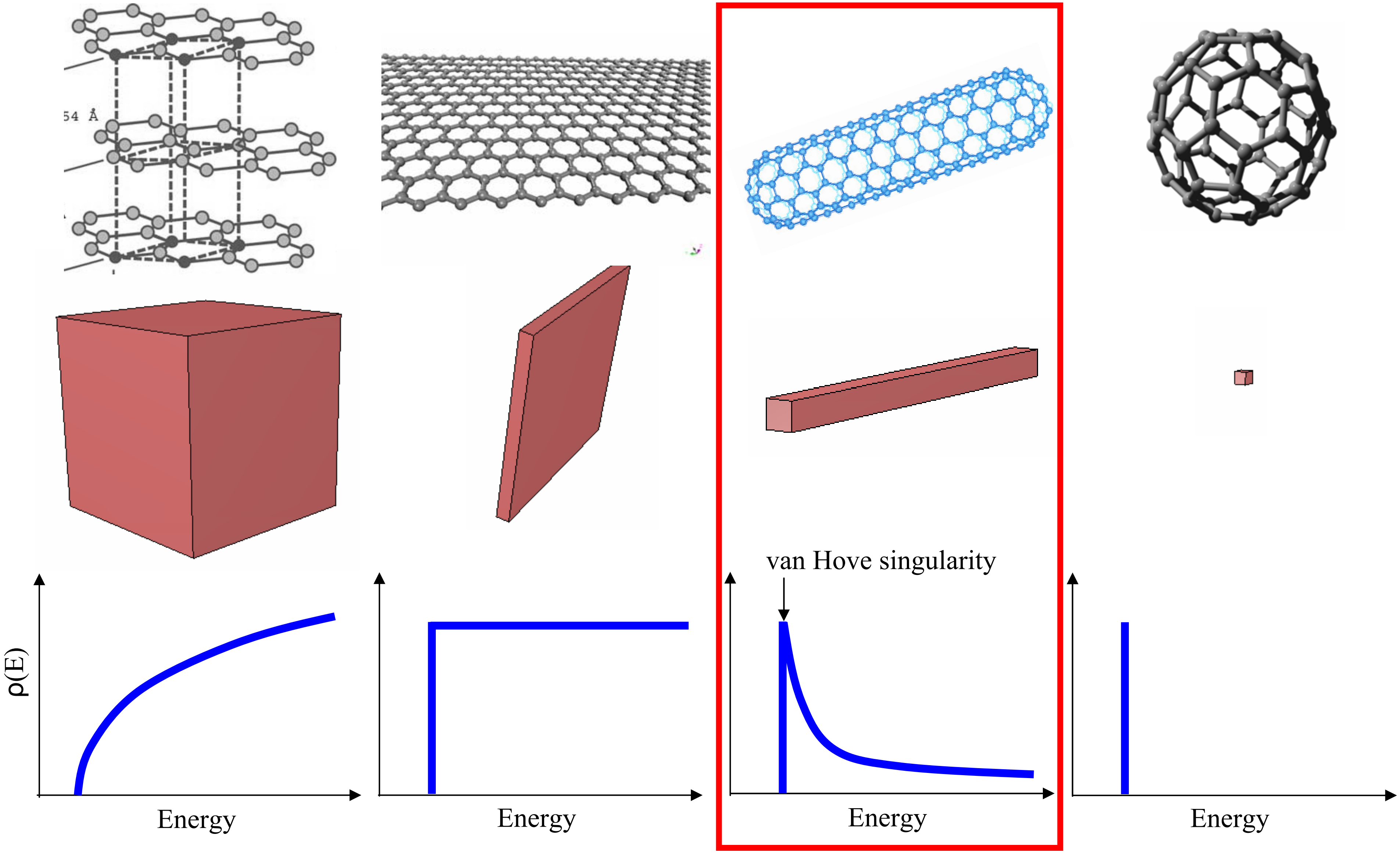


ρ(E)dE = the number of allowed states between E and E+dE

$$\rho(E) \sim \oint \frac{dS}{|\nabla E(k)|}$$

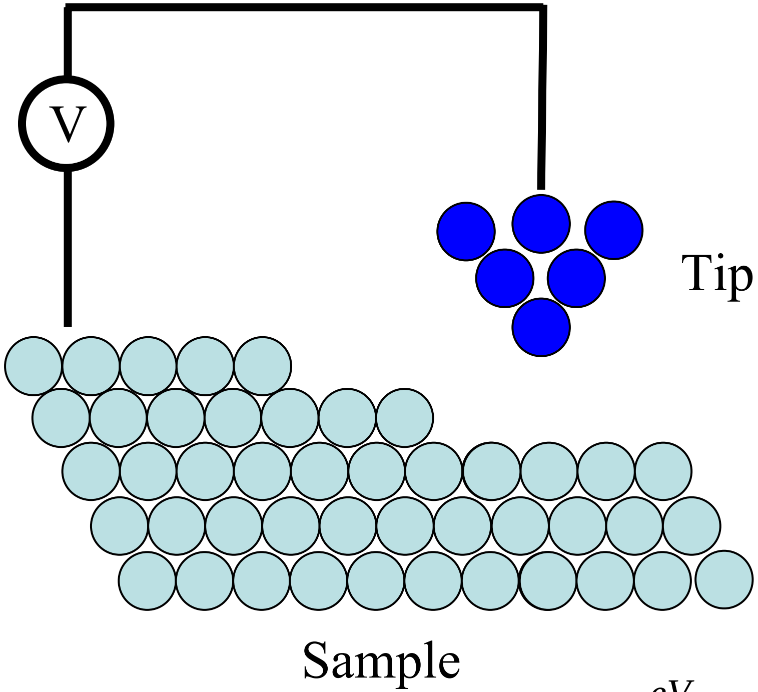
Electronic Densities of States

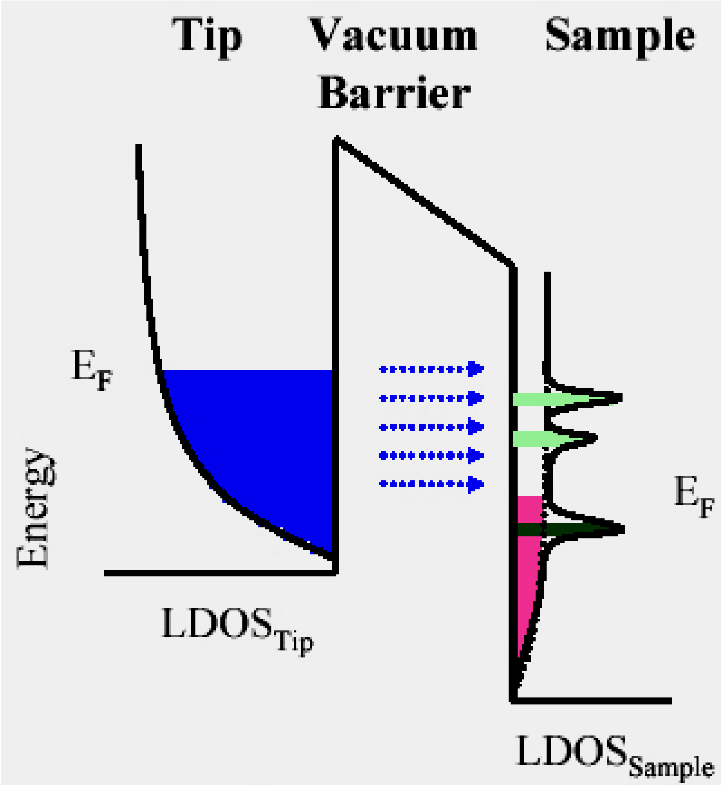
Densities of States = ρ(E) : number of quantum states available at a particular energy E



- van Hove singularities at band edges in 1-D materials

Scanning Tunneling Microscopy

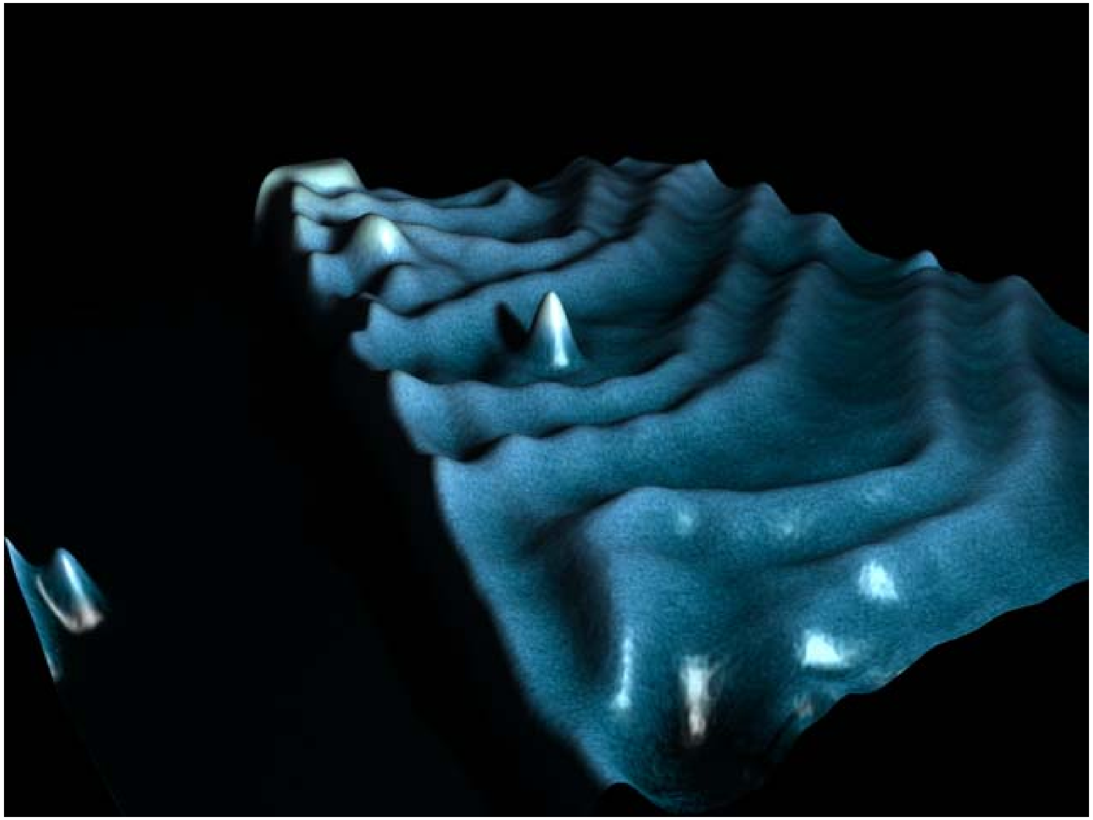




$$I \sim e^{-kz} \int_{0}^{eV} dE \times LDOS\,(E_F + E)$$

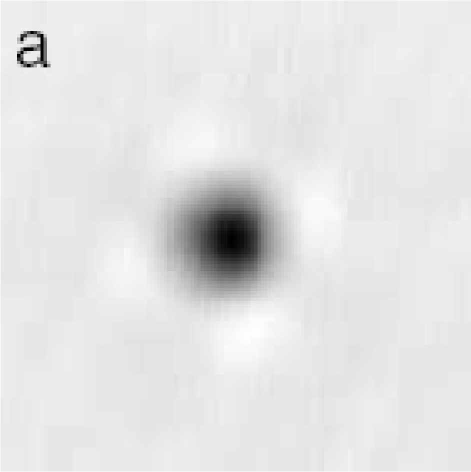
- Capable of atomic scale resolution
- dI/dV ~ Local Densities of States (LDOS)

STM Maps Electronic Densities of States



300 Angstrom square: Sample Bias 100 mV; current 0.20 nA

Hydrogen atom on copper

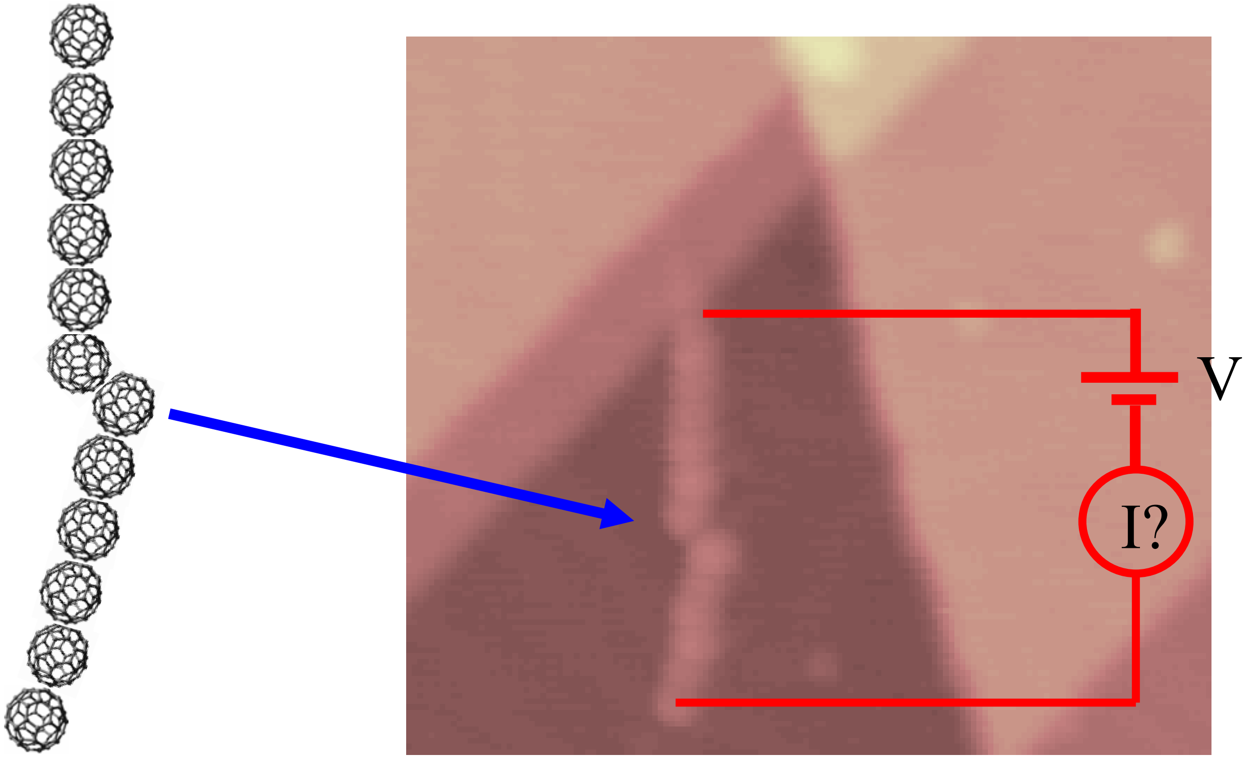


[L. J. Lauhon and W. Ho, PRL 2000]

- Sensitive to electronic properties
- Not direct observation of atomic structures

M. Ishigama et al (to be published)

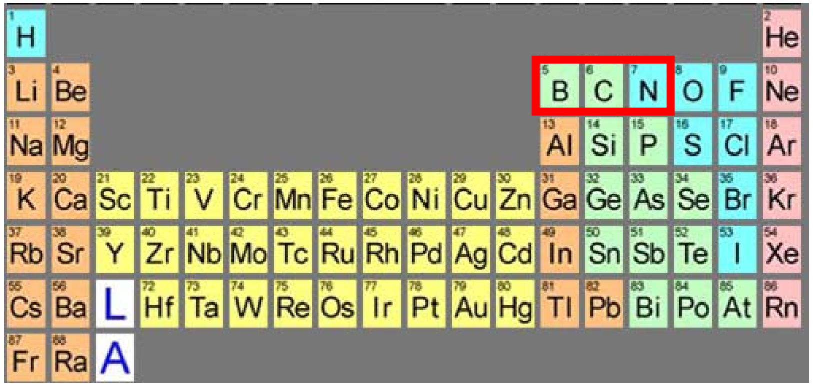
Nanoscale Materials: Ideal Proving Ground for Solid State Physics



Fabricated Fullerene Chain on Surface

- Controlling materials composition/structure down to atomic scale
- Availability of testable theory for electronic, transport, thermal, and mechanical properties
- **Every atom/molecule counts**

sp^2-Bonded Nanoscale Materials

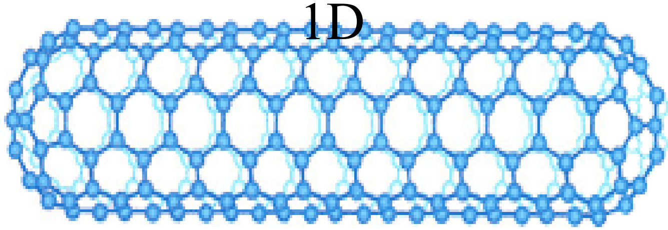


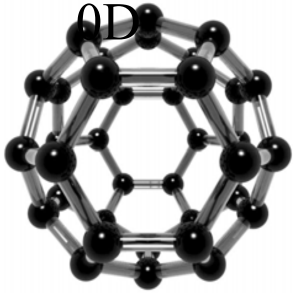
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	L	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	A															

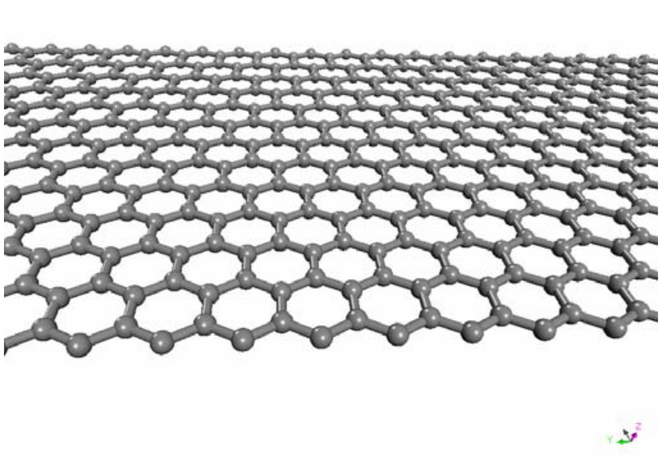
2D

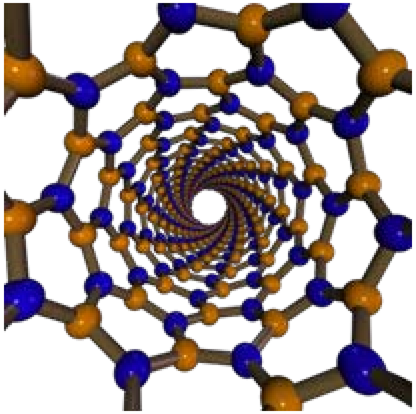
1D

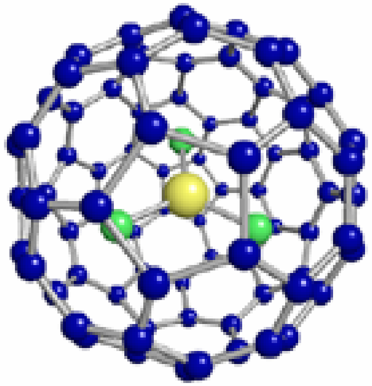
0D





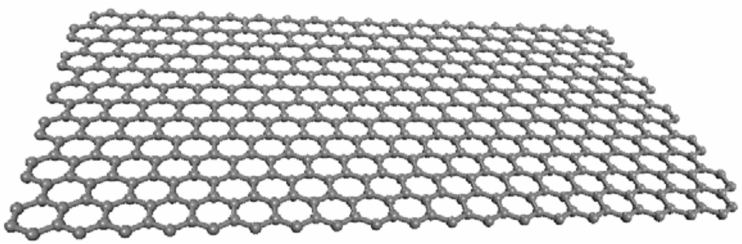


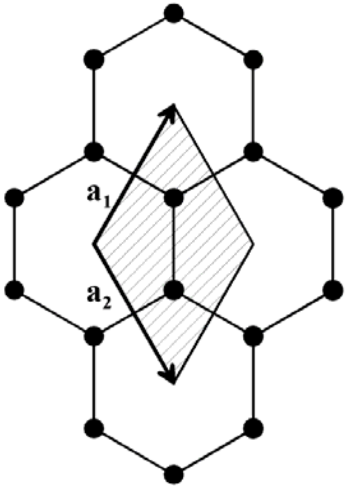


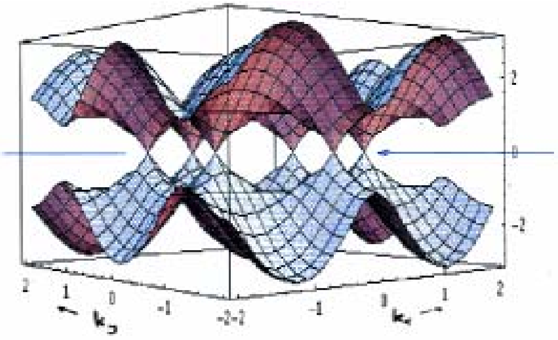


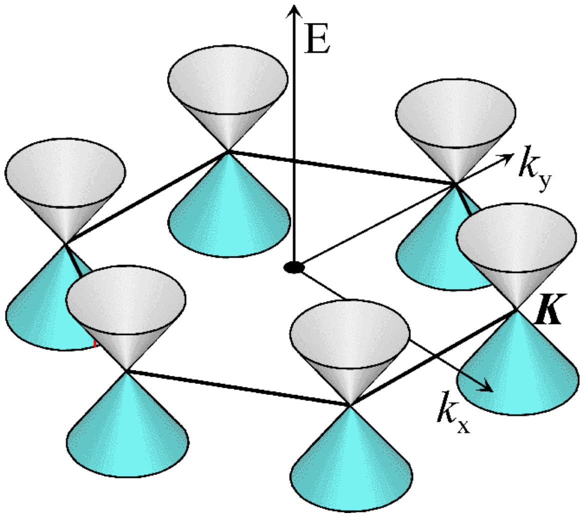
- Composed of robust sp^2-bonds
- There are no dangling bonds i.e. very well-ordered

Graphene: a semi-metal





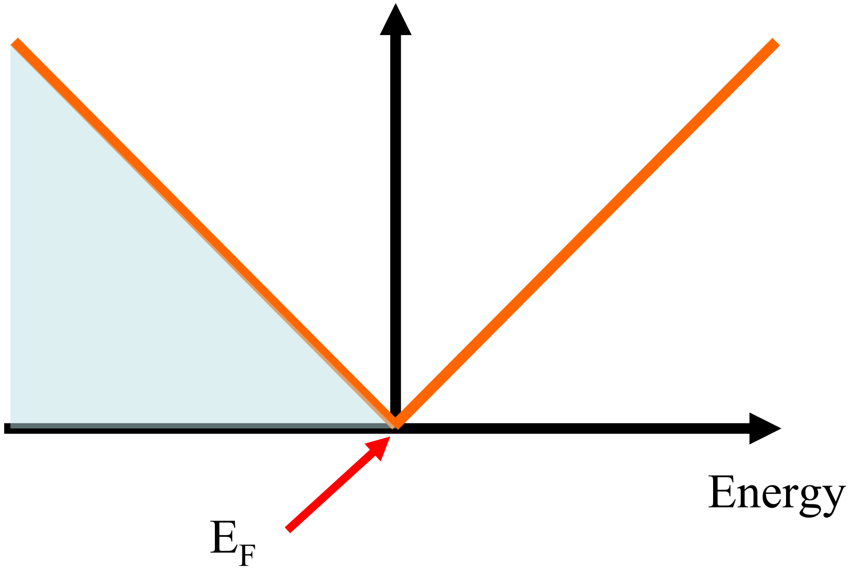




$$E = h v_F |k|$$

$$v_F = 9.3\times10^7\, cm/s$$

Electronic Densities of state

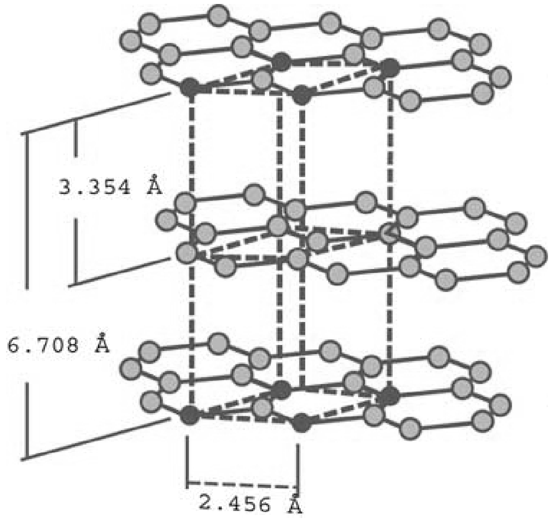


Vanishing DOS @ E_F

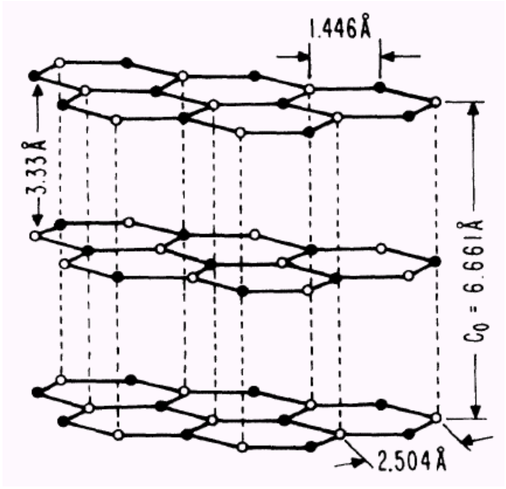
World Year of PHYSICS 2005
www.physics2005.org

Graphite: Unique Band Crossing at Fermi Level

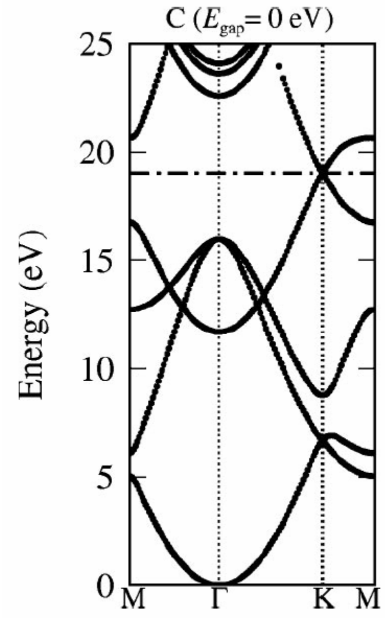
Graphite

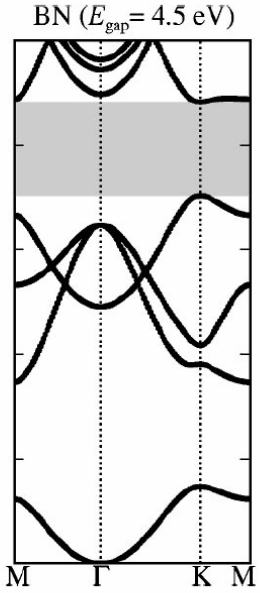


h-BN



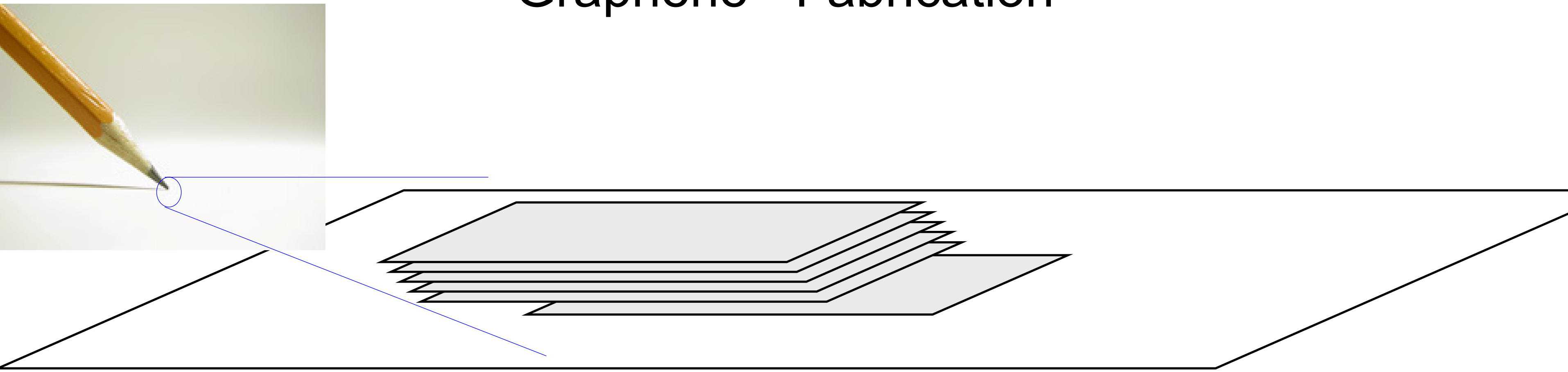
E. K. Sichel et al., PRB 13, 4607 (1976)





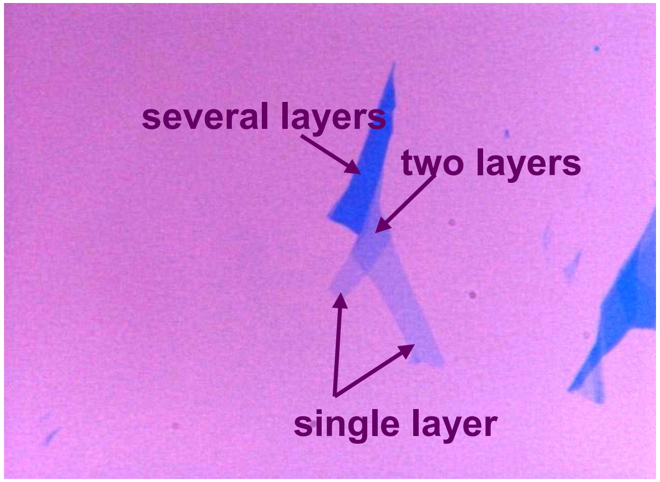
Yong-Hyun Kim, K. J. Chang, and S. G. Louie Physical Review B **63** 205408 (2001)

Graphene - Fabrication

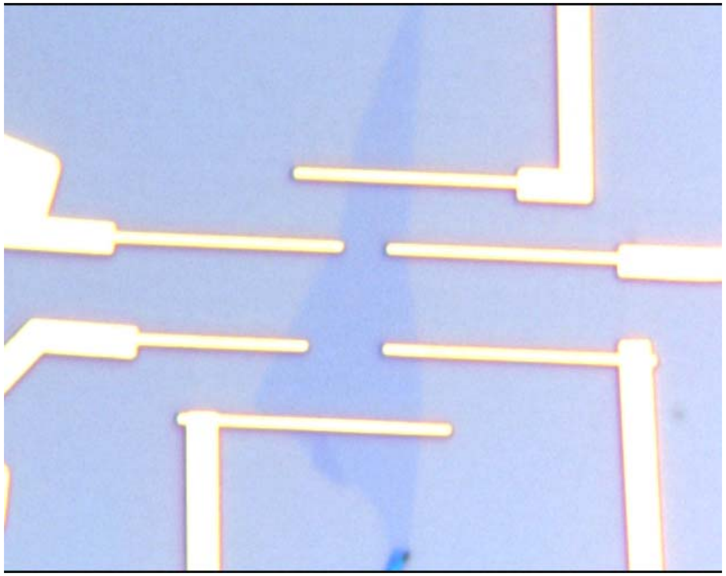


Only a little more complicated:

- Starting material is single-crystal Kish graphite
- Exfoliate to obtain very small flakes
- Rub on **flat** SiO_2/Si chips



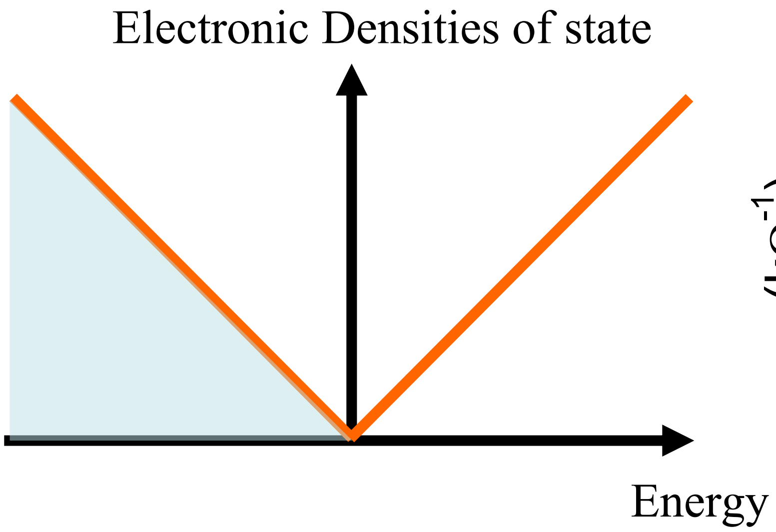
Optical micrograph (layer thickness verified by AFM)

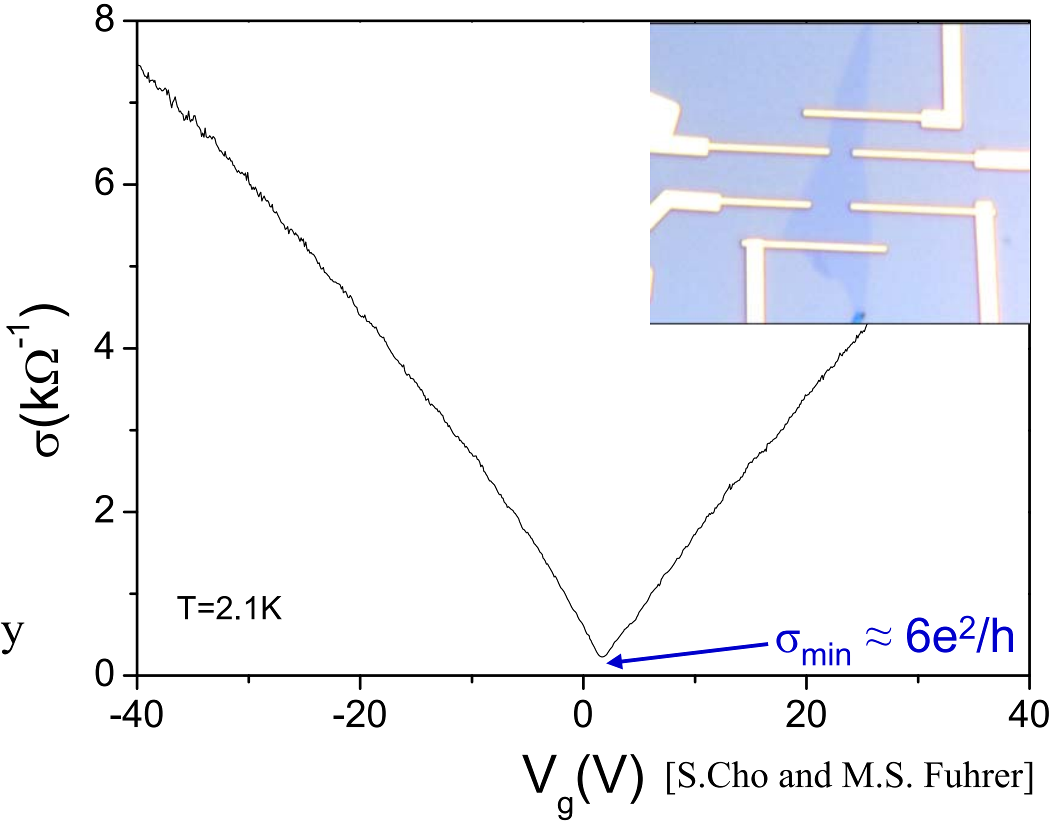


Single layer device after e-beam lithography

Alternatively, graphene may be prepared epitaxially on SiC wafers - see Walt De Heer's group at GaTech

Transport Properties of Graphene



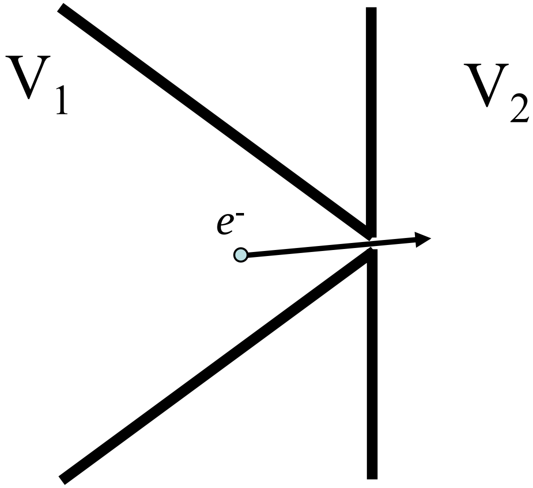


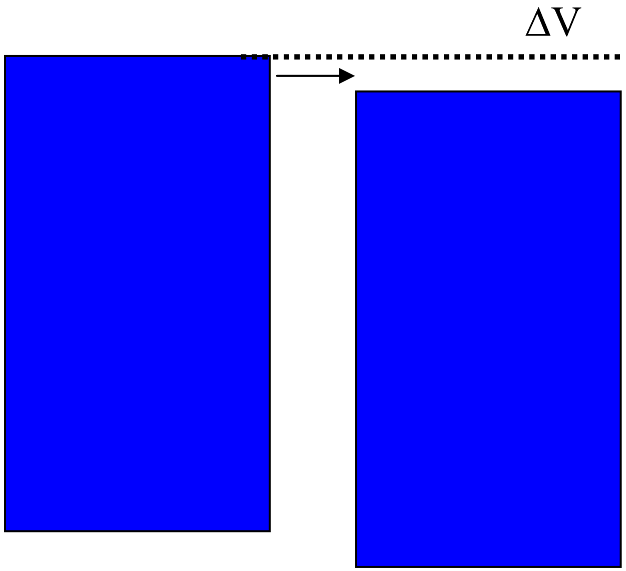
[S.Cho and M.S. Fuhrer]

- High mobility
- Strange non-zero minimum conductivity
- Perfect material for transparent, flexible electronics

Conductance Quantum

Point Contact Geometry





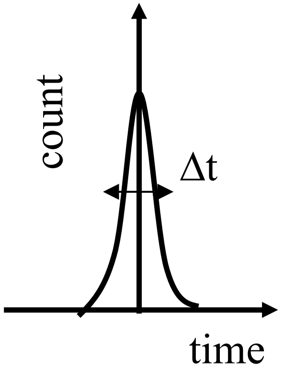
ΔE: Spread in electron energy at constriction

Δt : Spread in time spent at the junction

$$\Delta E \Delta t \sim h$$

$$\Delta E = e\Delta V$$

$$\Delta V \Delta t \sim \frac{h}{e}$$

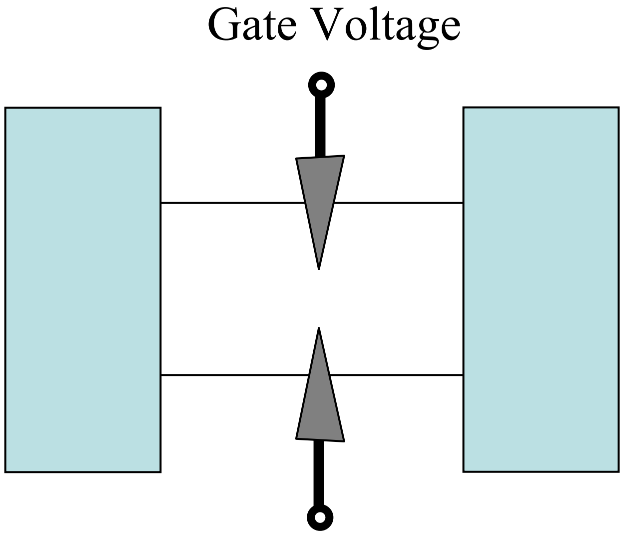


$$\Delta I \sim e / \Delta t$$

$$\frac{\Delta V}{\Delta I} \sim \Delta R \sim \frac{h}{e^2}$$

or $$G \sim \frac{e^2}{h}$$

Quantized Conductance: what it means



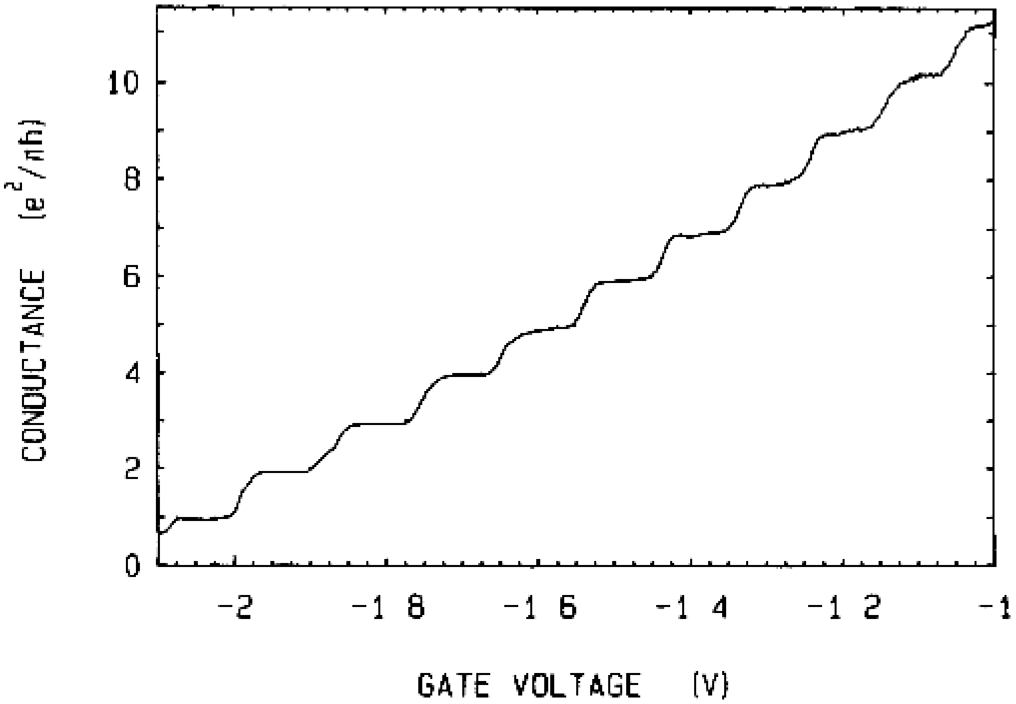
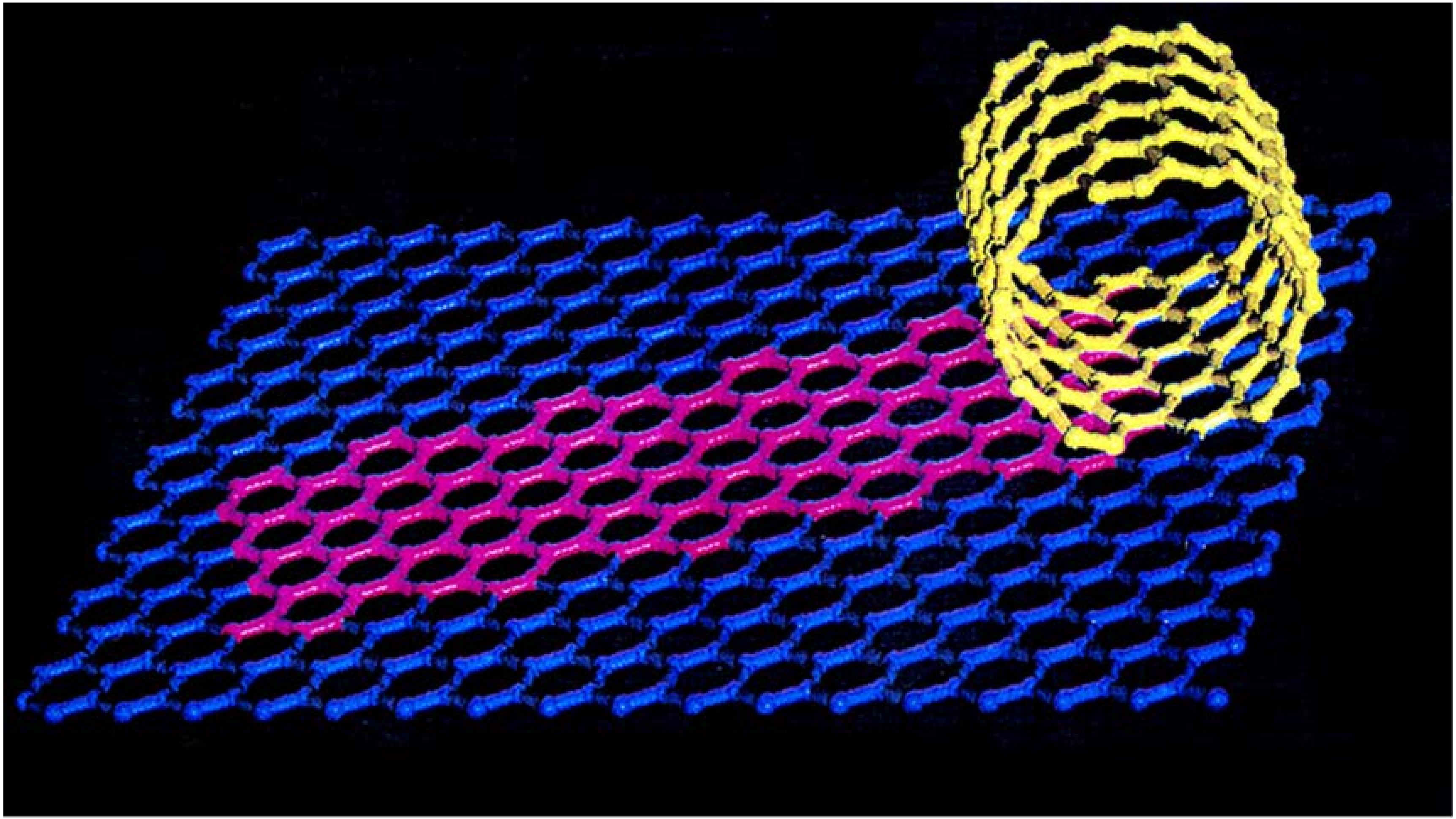


FIG. 2. Point-contact conductance as a function of gate voltage, obtained from the data of Fig. 1 after subtraction of the lead resistance. The conductance shows plateaus at multiples of $e^2/\pi\hbar$.

$$G = \frac{2e^2}{h}$$

Single-wall Carbon Nanotubes

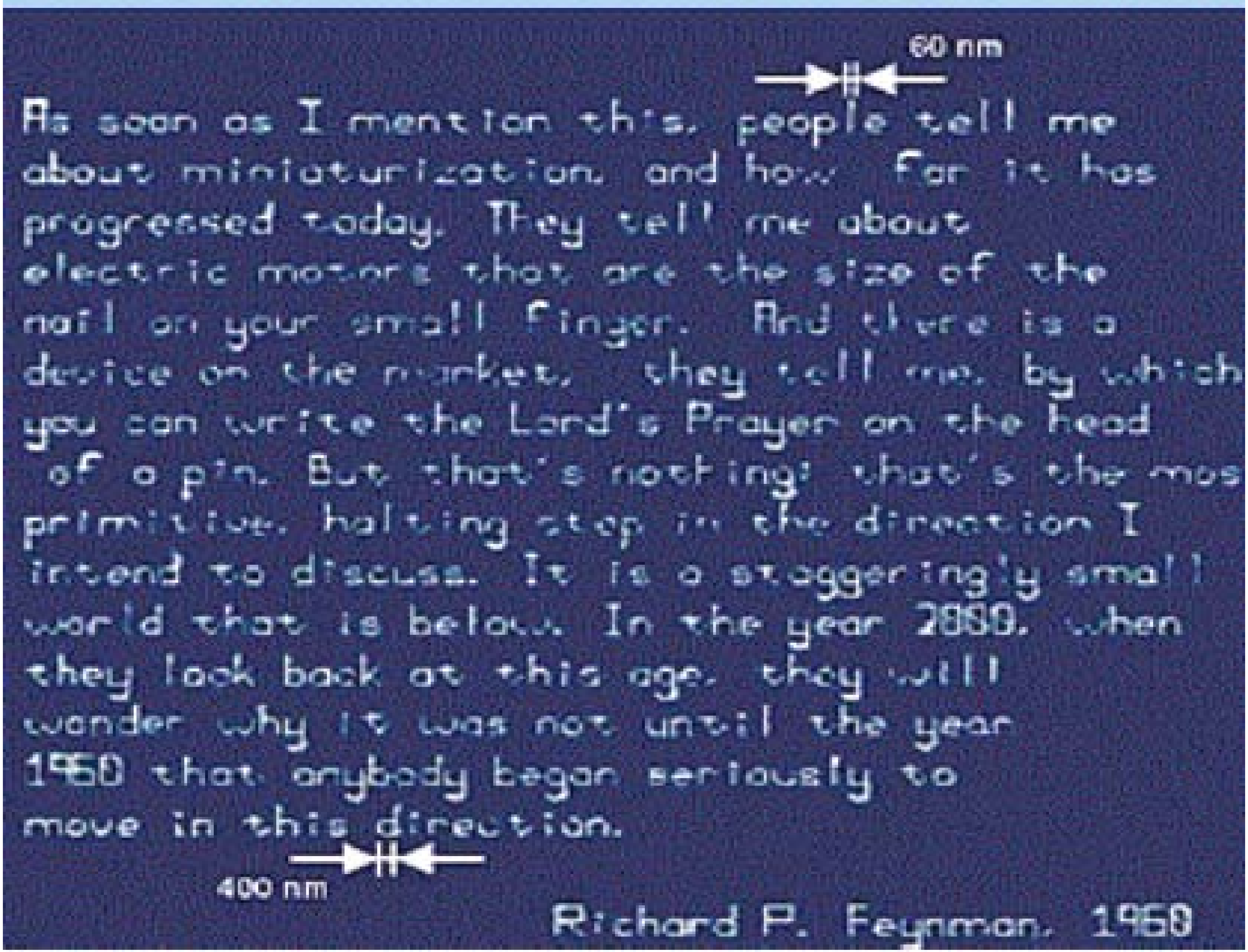


Acknowledgments

- Chandana Ghosh
- Sampyo Hong
- Altaf Karim
- Faisal Mehmood
- Marisol Alcantara Ortegoza
- Handan Yildrim
- Sergei Stolbov
- Ahlam Al-Rawi
- Abdel Kader Kara
- John Spangler
- Oleg Trushin

- Matti Alatalo
- Petri Salo
- Ilja Makkonen
- Tapio Ala Nissila
- Klaus Peter Bohnen
- Rolf Heid
- F. Baumberger
- T. Greber
- J. Osterwalder
- Ludwig Bartels

$$ NSF, DOE, CRDF



As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

Richard P. Feynman, 1960