Construction of an Anchored and Decoupled Single Molecular Rotor Array

H.-J. Gao Group (-À/I2\ ), IOP-CAS, China

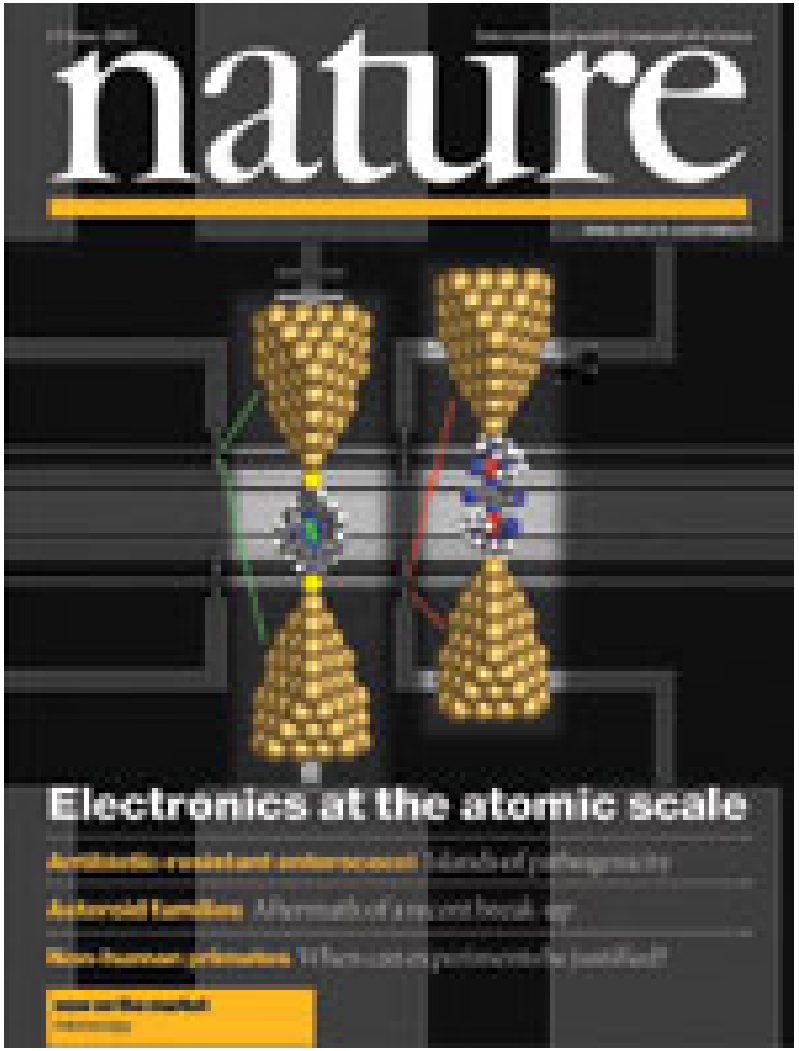
m
m

Top down

Bottom up

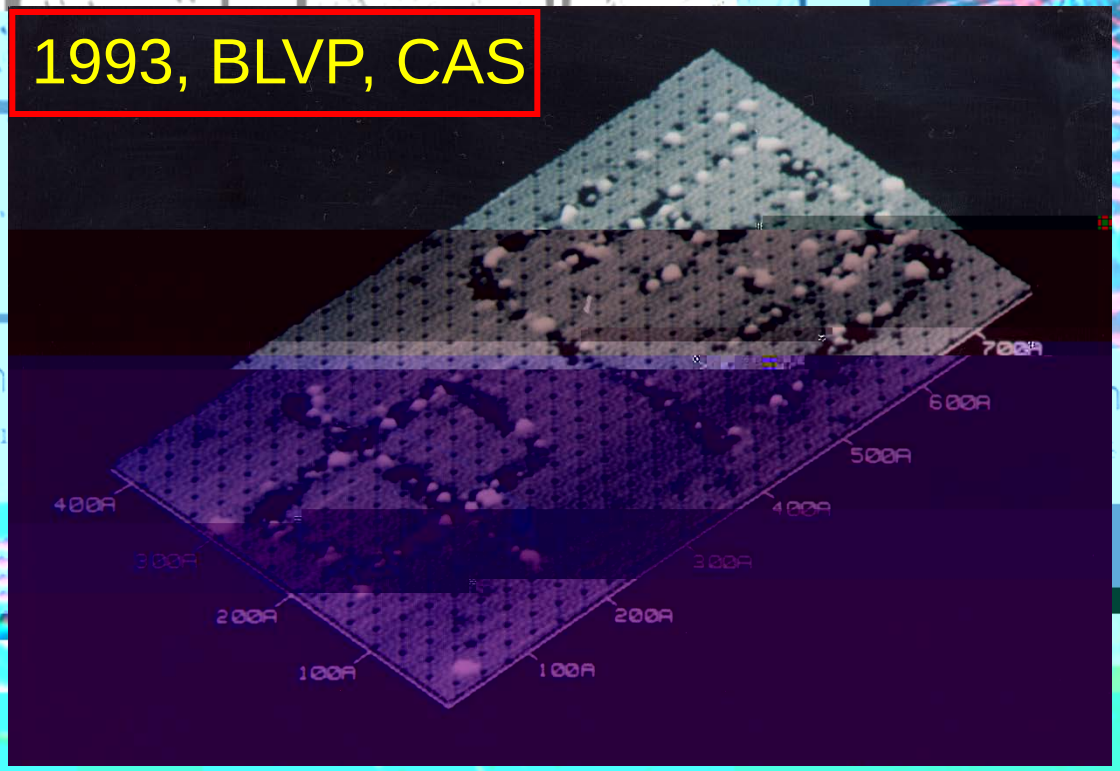
nm

Nature, 413,619(2001)



Challenges:

1) Novel Nanostructures and nanomaterials × 2) Interface and self-assembly × 3) Physical properties of the unit cells


1993, BLVP, CAS
700A
600A
500A
400A
400A
300A
300A
200A
200A
100A
100A

Growth System with *in situ* Analysis Techniques

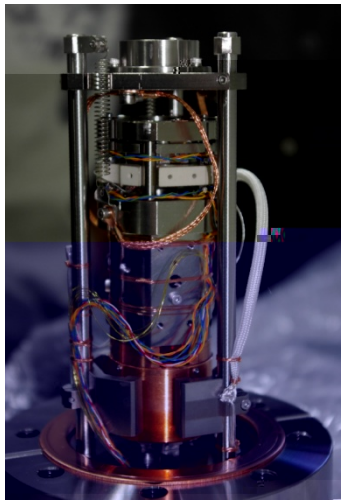
Analysis Chamber

- LEED
- AES
- STM

Growth Chamber

- Carbon Source
- Ar+ Ion gun
- Sample Heater
- Evaporator

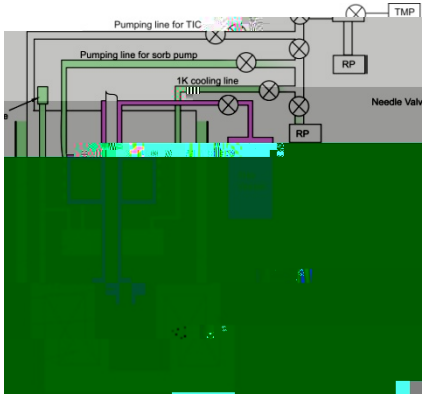
Ru, Pt, Ni, Cu, Ir metal crystals have been used



RT-STM Head

USM 1300S-^{3}He
STM System

LT-STM Head

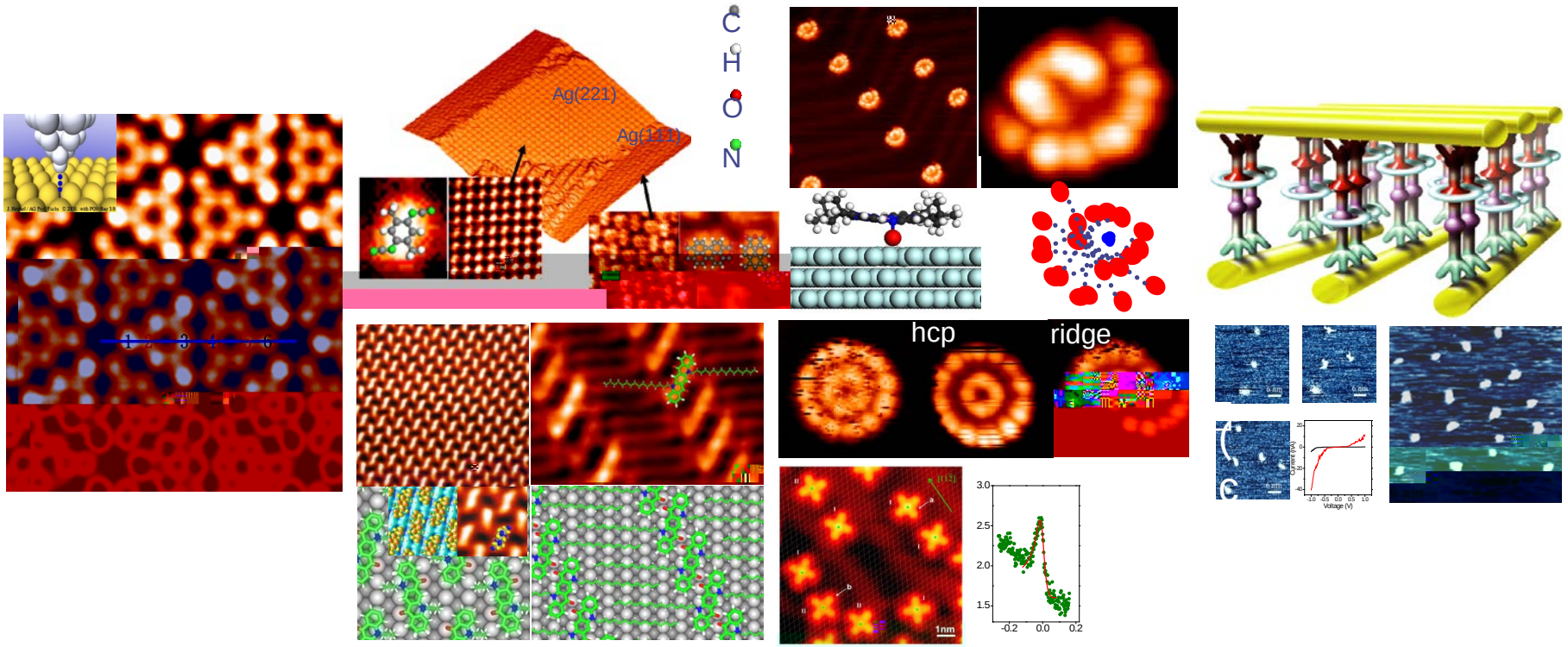


^{3}He Circulatory
Refrigeration

Cleaving and
Cooling Stage

6ª5ø.G6½1,.Z0‘8E+FB‹>P3Î?µD+

¶ q ” r “ 8 r “ 8 Å r þ q _ Ÿ $ r



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PRL 95, 076103(2005)	PRL 96, 226101(2006)	PRL 99, 106402(2007)	PRL 100, 186104(2008)
PRL 94, 106101(2005)	PRL 96, 156102(2006)	PRL 99, 059602(2007)	PRL 101, 216102(2008)
PRL 95, 156803(2005)	PRL 97, 156105(2006)	JACS 129, 2204(2007)	PRL 101, 197209(2008)
JACS 127, 15338(2005)	PRL 97, 246101(2006)	JACS 129, 11674(2007)	Adv. Mater. 20, 2609(2008)
Adv. Mater. 17, 1893(2005)	Nano Lett. 6, 1141(2006)	Adv. Mater. 19, 4480(2007)	Adv. Mater. 20, 1-4 (2008)

2014

SCI 25

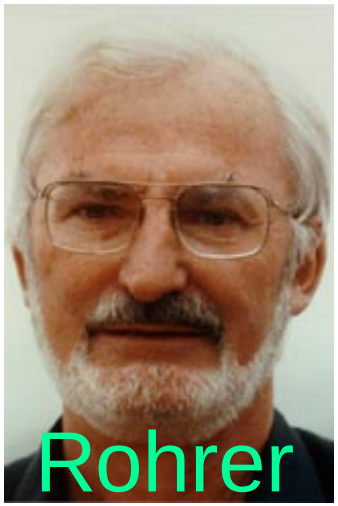
- Nature Physics 1 1›
- Adv. Mater. 1 1›
- Nano Lett. 2 1›
- J. Am. Chem. Soc. 1 1›
- Scientific Reports 2 1›

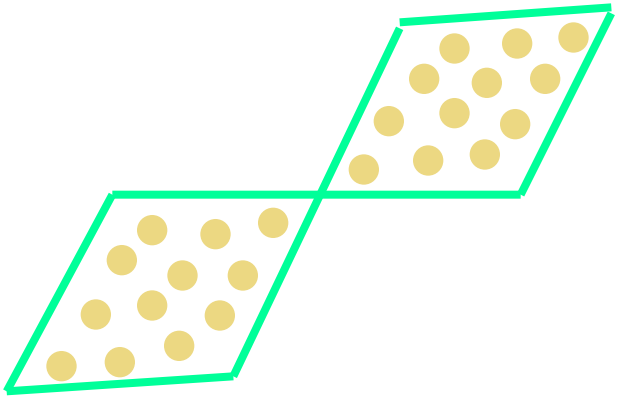
Plenary / Invited Talk: 15

- MRS , Boston, Invited talk
- AVS , Baltimore, Invited talk
- The 2014 International Conference on Nanoscience + Technology (ICN+T) , Colorado, USA, Invited talk
- ……

STM

Si(111)-7 × 7 STM



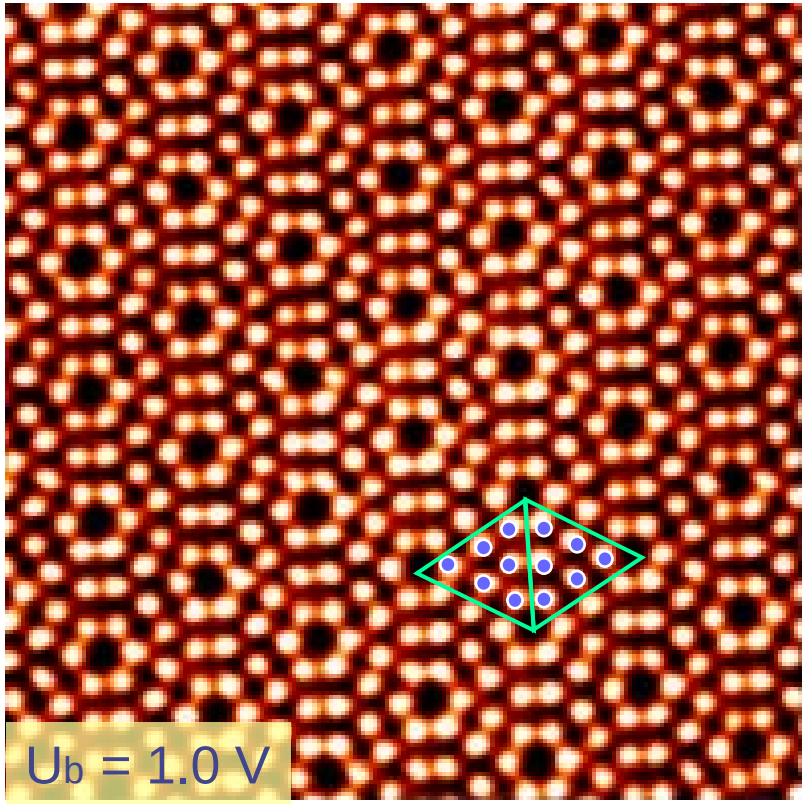


G. Binnig et al. Phys. Rev. Lett. 50,120(1983)

Si(111)-7 × 7 STM

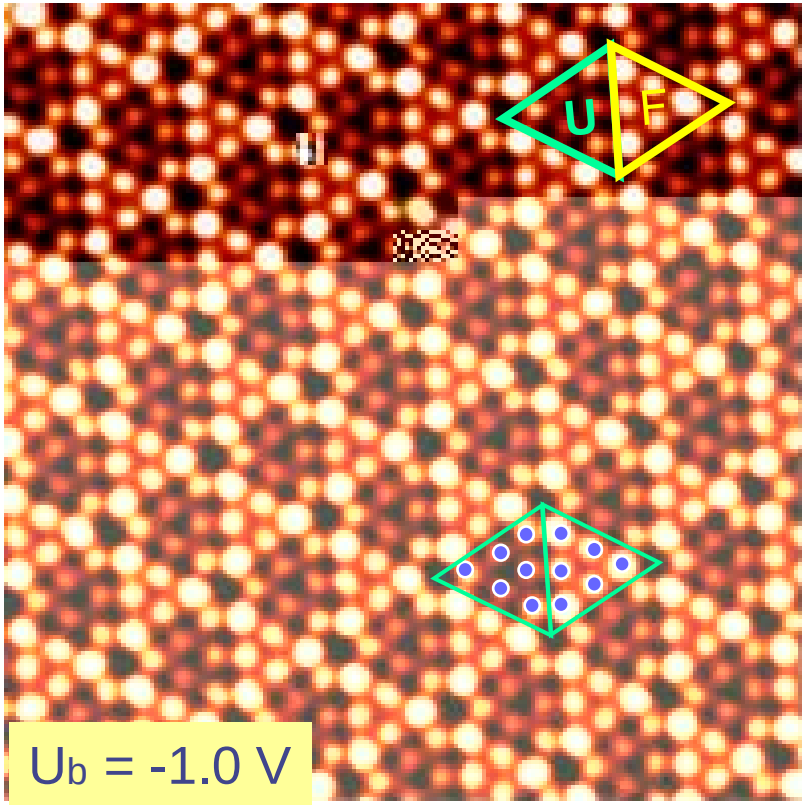
Si(111)7 × 7	12	(adatom)

STM



16 nm × 16 nm

STM



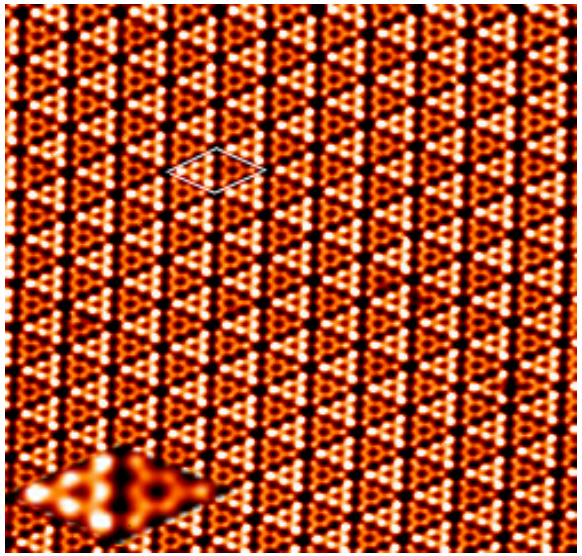
16 nm × 16 nm

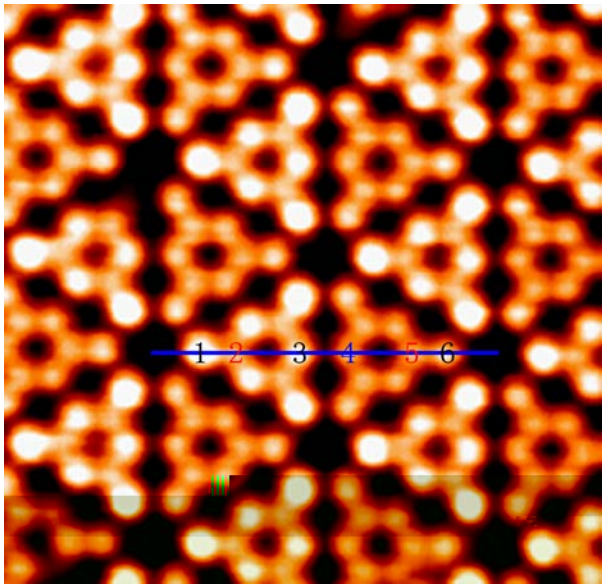
Seeing the Rest Atoms and Adatoms Simultaneously

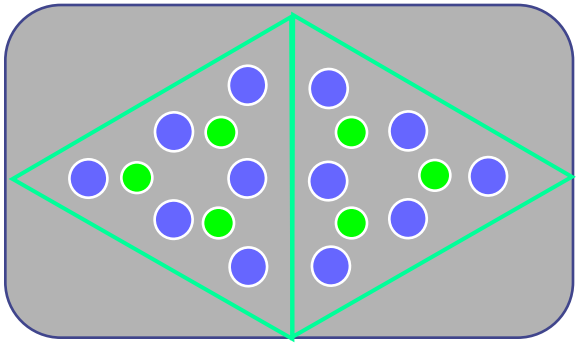
30 nm × 30 nm

8 nm × 8 nm

U_b = - 1.5 V
I_t =0.4 nA



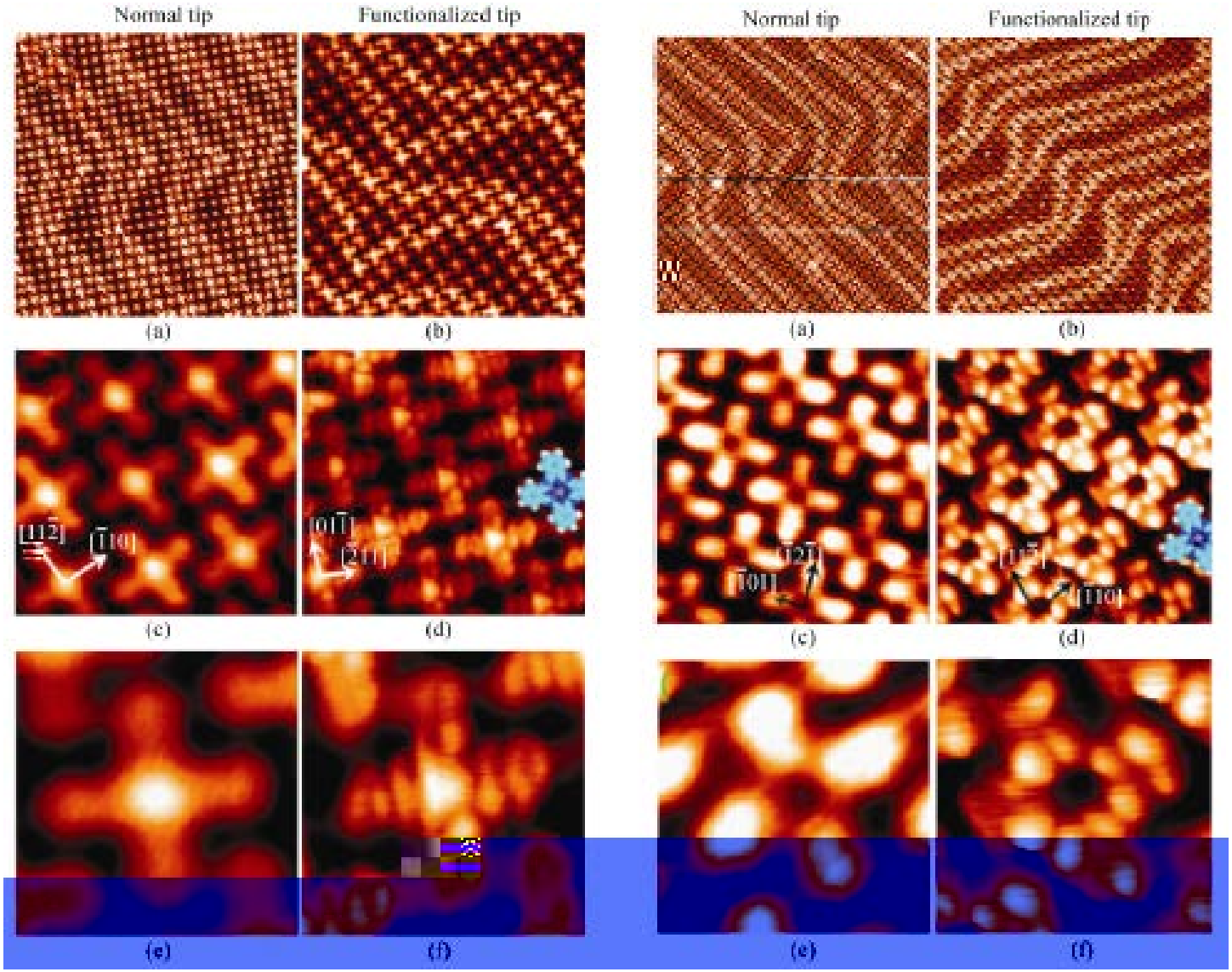




Adatom

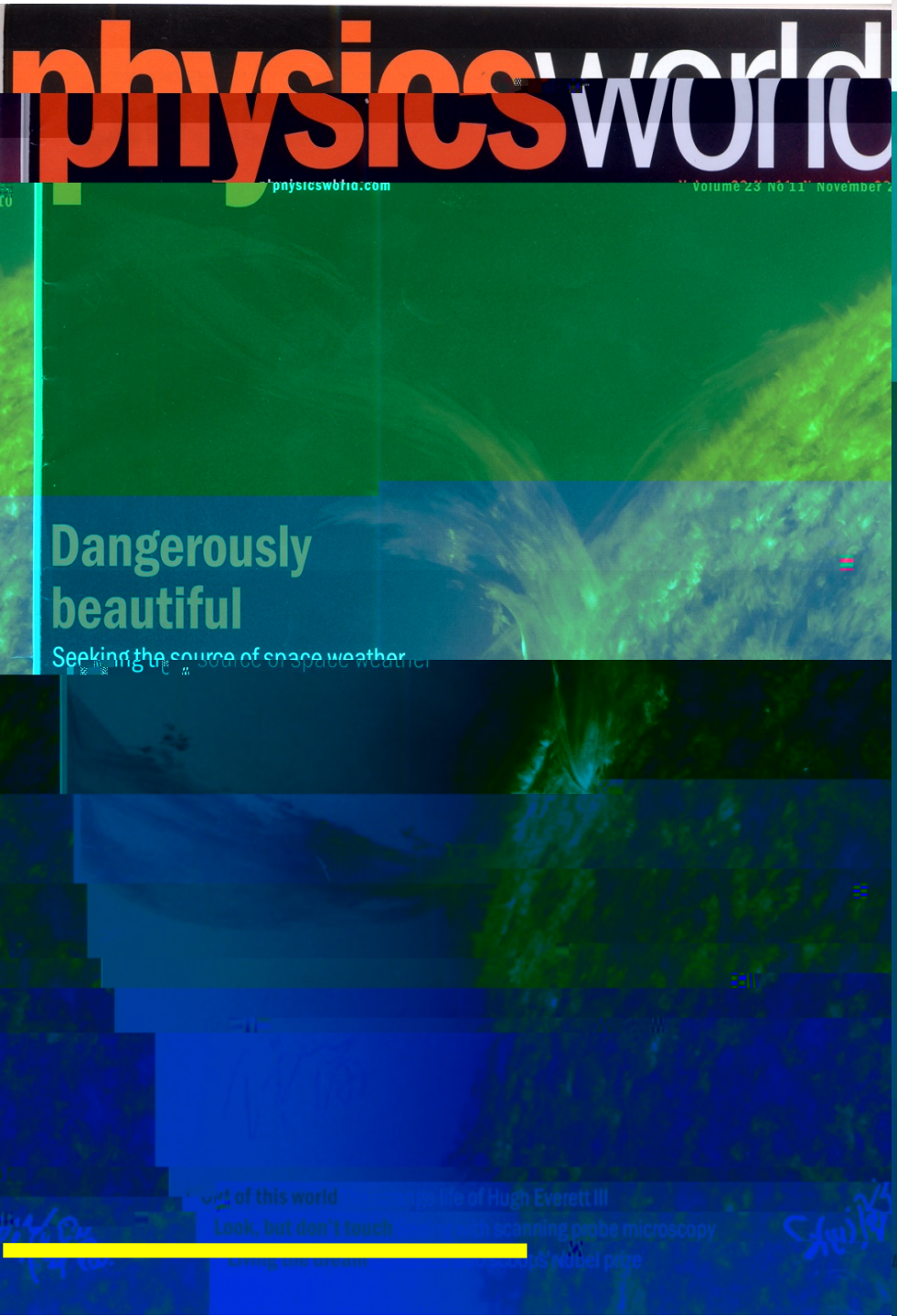
Rest atom

YL Wang, H.J.Gaoet al., Phys. Rev. B70, 073312 (2004)



Z.T. Deng/H.-J. Gao *et al*., Phys. Rev. Lett. 96, 156102(2006)

Z.H. Cheng/H.-J. Gao *et al*., Nano Res. 4, 780(2011)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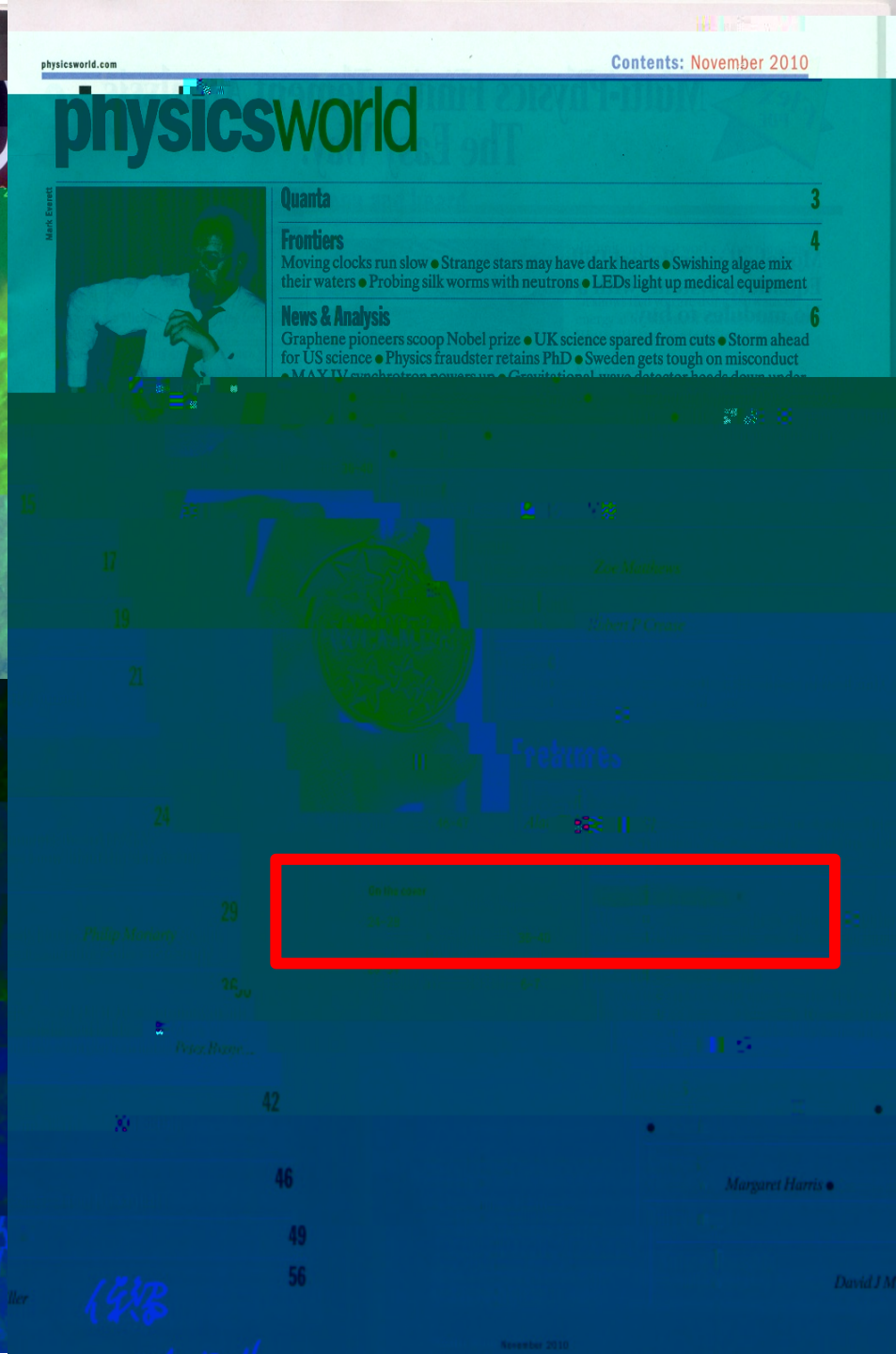
Volume 23 No 11 November 2
Dangerously beautiful
Seeking the source of space weather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physicsworld
Mark Everett
Quanta 3
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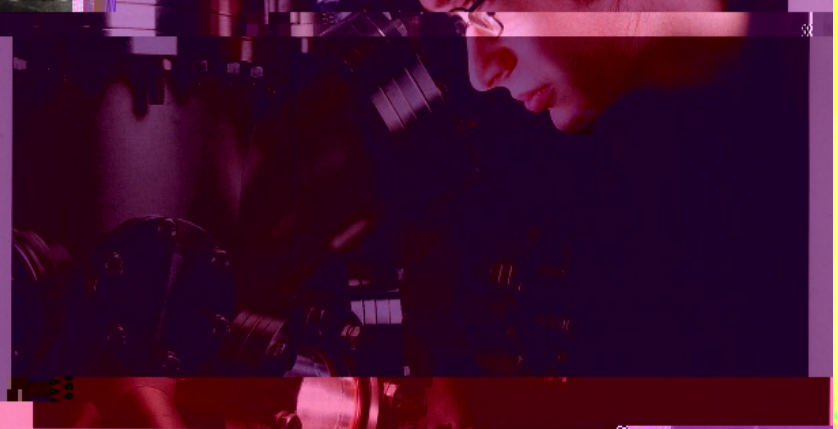
Moving clocks run slow • Strange stars may have dark hearts • Swishing algae mix their waters • Probing silk worms with neutrons • LEDs light up medical equipment
News & Analysis 6
Graphene pioneers scoop Nobel prize • UK science spared from cuts • Storm ahead for US science • Physics fraudster retains PhD • Sweden gets tough on misconduct
Margaret Harris
November 2010

University of Nottingham



Resolution frontiers

ace, keep smashing the record for how small we can see. Philip M
explains how these instruments let us explore the nanoworld, and what it really means to "see" anyw

Philip Moriarty
is a professor of physics at the
University of Nottingham, UK, e-mail philip.moriarty@nottingham.ac.uk

"I know what the atom looks like!" Ernest Rutherford ... means "to see small". But the tradition ... micr
excited announcement at a Sunday evening dinner party almost a century ago stemmed from his remarkable ability to distil the results of a series of painstaking scattering experiments into an elegant and appealing model of the atom. Despite the revolution in our understanding of the atom brought about by quantum mechanics, Rutherford's iconic model persists. It is the Rutherford–Bohr picture of the atom that non-scientists, and quite a few scientists ... tend to hold in their ... head, rather than the ... distributions for s, p, d and other ... In the minds of most, an atom is a solar system writ small.

To see small things, we, of course, use a microscope. Indeed, the word microscope, which has Greek origins,

scopes many of us have used to bring small structure into focus have a basic problem when it comes to reso ving something as small as an atom: the wavelength of photon of visible light is *huge* on the atomic scale. Visib light spans from about 400–750 nm and there is a fu damental limit – the diffraction limit – that dictates ju how small an object we can resolve using photons these wavelengths. It turns out that about the best w can do with traditional optical microscopy is t objects about 200 nm across – magnitude larger than the diam

In order to get anywhere clos length scales, a radically differen with the most logical step bein

licon(111)-(7 × 7) diamonds are a scanning tunnelling microscopist's best friend

STM

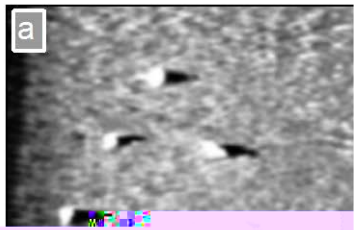
¾ STM ,

STM

¾

STM

Molecular Recording: Toward the Next Generation CD



Sunday, February 20, 2000 Toward the Next Generation CD Page: 1

Physical Review Focus

Reversible, Nanometer-Scale Conductance Transitions in an Organic Complex

S. M. Hou, L. P. Ma, X. W. Fang, S. J. Pang, and S. J. Pennycook

Toward the Next Generation CD

16 February 2000

Andrew Gannon

From punch cards to floppy disks to CD-ROM's, data storage devices continue to evolve. Researchers at the Oak Ridge National Laboratory (ORNL) in Tennessee don't know what the next device will look like, but they believe they know what it will be made of: thin films of complex organic compounds. They report in the 21 February *PRL* that they have produced reversible changes in electrical resistance in molecule-sized regions of organic thin films. The results help pave the way for making thin-film storage devices because they mark the first time anyone has demonstrated reversibility needed for "writing" and then "erasing" data--at a molecular level.

Other researchers have shown they could induce changes in conductance--the equivalent of "writing"--to a thin film, says Karl Sohlberg, a theoretician with the Oak Ridge group. But using only heat or laser pulses, they haven't been able to "erase," or reverse, the transition without clearing entire regions of the film, as if shaking clear a whole Etch-a-Sketch.

Sohlberg says organic compounds have peaked the interest of data-storage makers because of their incredible storage capacity. A typical CD-ROM, for example, has a storage density of perhaps 10^8 bits per cm^2. The thin films used by the ORNL group and their colleagues at the Chinese Academy of Sciences in Beijing and the University of Chicago can store 10^{14} bits per cm^2--a million-fold increase. Sohlberg says that organic-based data storage will "ultimately create headaches for the engineers who have to design the machine fast enough to read from and write to such materials, but "that's the engineering hurdle."

"Today's technology, like punch cards and floppy disks, CD-ROM's may become obsolete if organic thin films live up to their potential for storing a million times more data.

The team made films of a complex of two organic molecules on a graphite surface. By applying a range of voltages

http://focus.aps.org/v5/st7.html

The Weekly Newsmagazine of Science

SCIENCE NEWS

February 26, 2000
Vol. 157, No. 9
Pages 129-144

Manhandled molecules, midget memories

Gangsters break someone's arm to deliver a message, leaving a powerful impression. Researchers at the Oak Ridge National Laboratory in Tennessee and the University of Chicago, in a series of experiments, the collaborators discovered that roughing up organic molecules also can create an enduring, though small, memory. In this case, however, some researchers have strong arguments that the molecules have positively and negatively charged ends. This polarization makes it possible to store information a million times more densely than CD-ROMs do and top even hard disks by a factor of nearly 100,000. However, the lab accomplishment remains limit," Sohlberg says. —P. Weiss

form an A shape (left) on a novel chemical coating. After researchers zap the A's peak with a negative voltage pulse, the spot there vanishes (right), indicating restored high resistivity.

investigating substances that have potential for high-density data storage and molecular-scale electronics. In particular,

Power plants: Algae churn

Could the green scum that grows on the walls of a fish tank produce the fuel of the future? Some scientists think so. They've found a way to coax green algae into producing significant amounts of hydrogen gas. In these researchers' view, large pools of algae could generate clean-burning hydrogen fuel for cars and other applications.

As microscopic

sensitivity to oxygen to protect against that danger, he says.

Melis and his coworkers discovered a way around this dilemma. By depriving the algae of sulfur, which the cells need to make several important proteins, the researchers can turn off normal photosynthesis. This shuts down the algae's oxygen production and forces the cells to make hydrogen instead. Melis presented his group's findings this week in Washington, D.C., at the annual meeting of the American Association for the Advancement of Science.

Hydrogen bubbles rise to the surface in a flask containing green algae.

To prevent algae from dying during the hydrogen production, the researchers

carbon dioxide, and have the biochemical machinery to produce hydrogen, Melis and his colleagues at the University of California, Berkeley. Under conditions—in the absence of oxygen

engineer at the National Renewable Energy

On NBMN/pDA thin films, “A” pattern voltage pulse: 3.5 V Ë 6

Erasing voltage: 4.5 V Ë 6

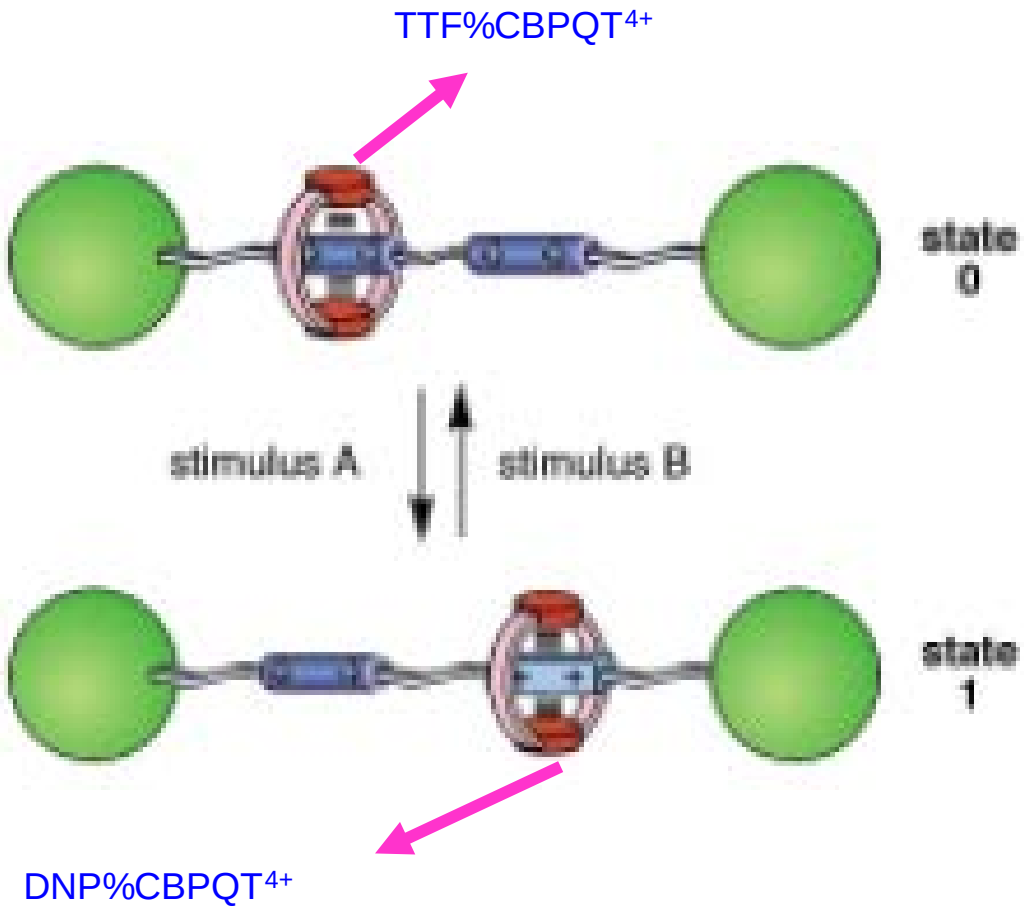
– **Program Contact:** Iran L. Thomas, SC-10 (301) 903-3081

– **The Library of Congress on a Single Disk:** Disordering and re-ordering tiny regions of a thin film shows promise for storing a million times more information than with today's computer disks and CD's, and with no increase in space. This is the conclusion from work performed in a collaboration between H.J. Gao, K. Sohlberg, and S.J. Pennycook of Oak Ridge National Laboratory and the Beijing Laboratory for Vacuum Physics [Phys. Rev. Lett., Vol. 84, p 1780 (2000)]. The film is made of organic material and supported by graphite. It is so thin that 40,000 layers would be only as thick as a sheet of paper. Exposing the film to voltage pulses with a scanning tunneling microscope (STM), nano-meter sized regions were switched from crystalline to disordered, changing their electrical conductivity by 10,000 times. Each tiny spot is one bit of information, not much bigger than a single molecule of the film. This is the first demonstration that information can be written and erased in a film at or near the single molecule limit. Drs. Gao, Sohlberg, and Pennycook are supported by the Office of Basic Energy Sciences/Division of Materials Sciences and Engineering.

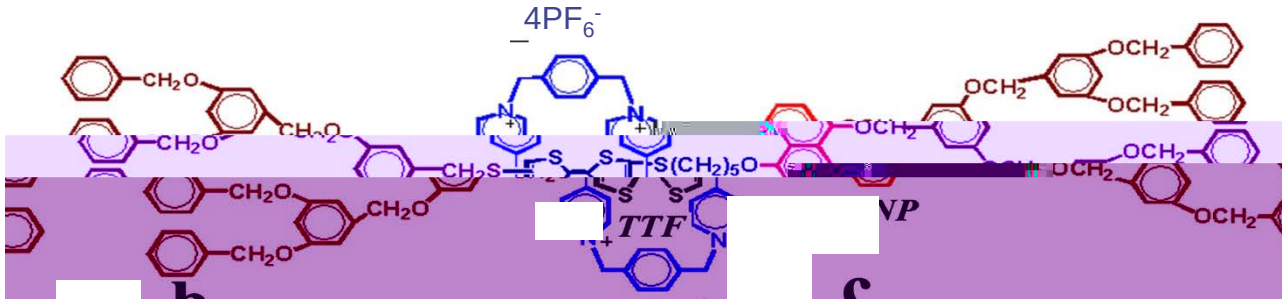
– **Program Contact:** Iran L. [illegible] 3081

2000

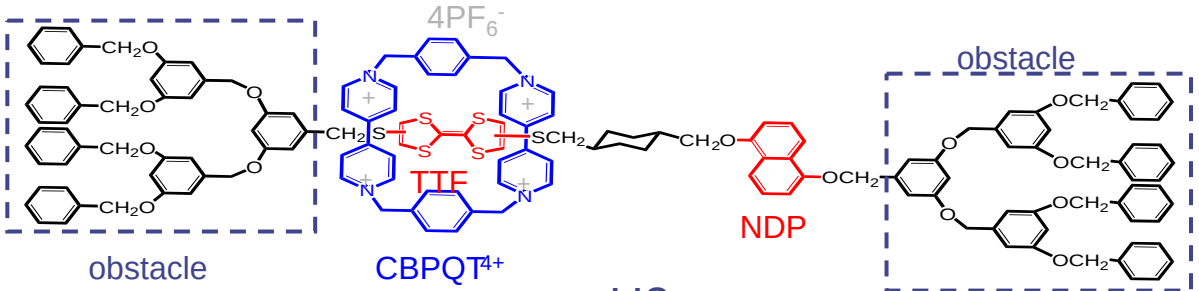
“0” “1” Bistability of Rotaxane Molecule



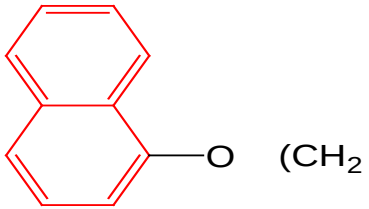
when the TTF unit be oxidized or reduced, the $CBPQT^{4+}$ ring will move along the axe and stay on different position



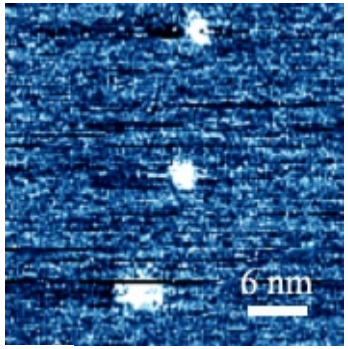
H1

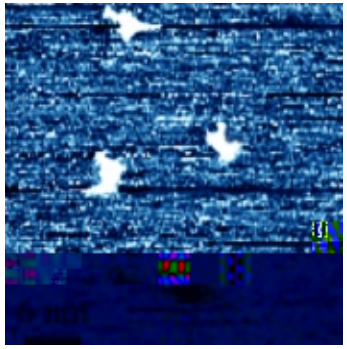


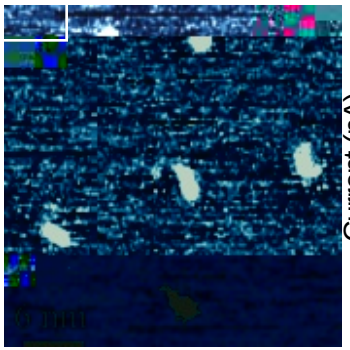
H2

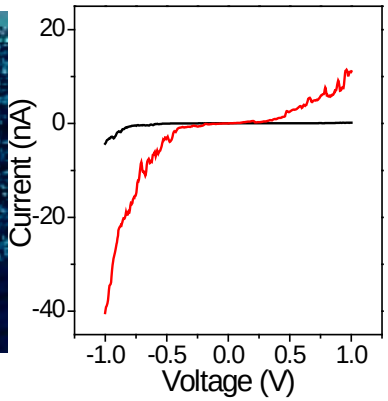


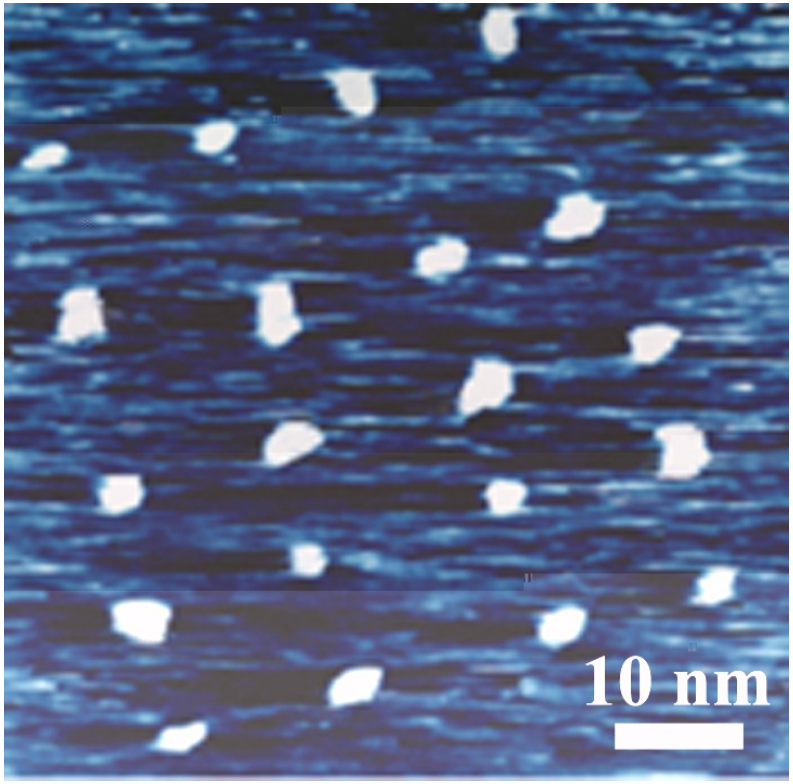
Stable, Reproducible Conductance Transition and Ul
Density Data Storage









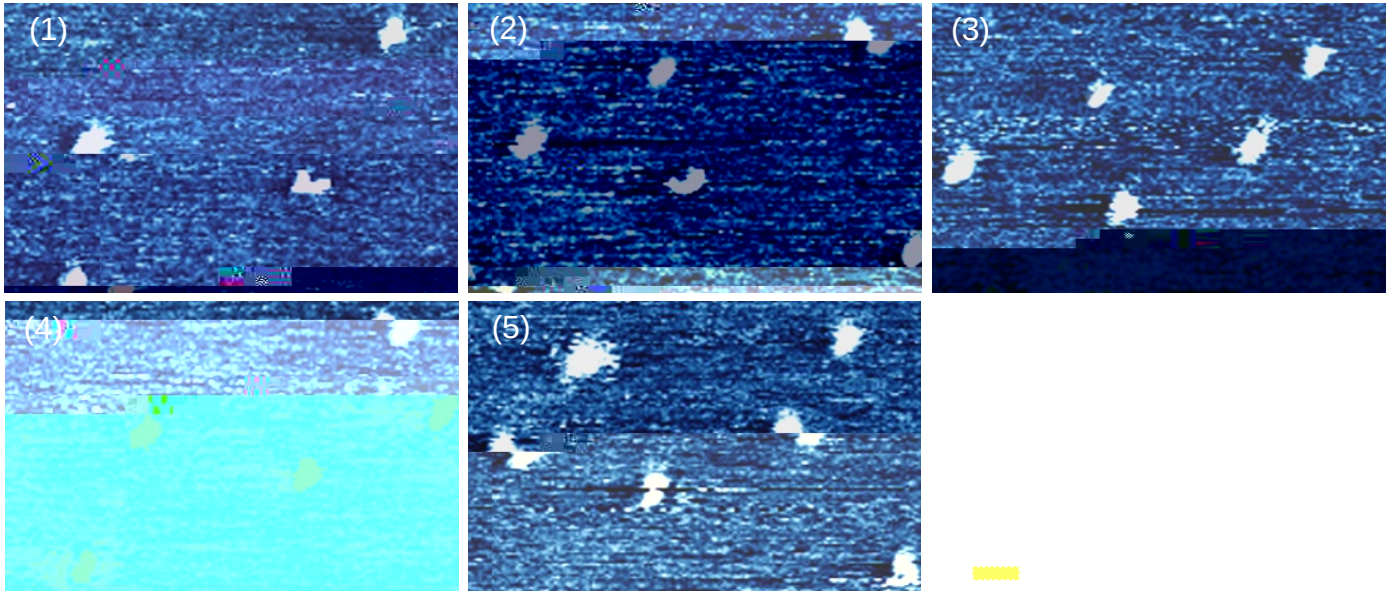


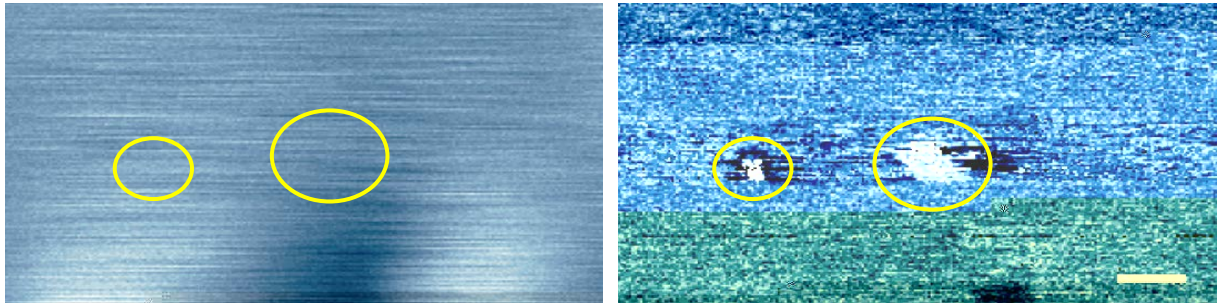
Reproducible nano- recording on H1 thin films: writing one by one

Stable reproducible nano-recording

M. Feng, H.-J. Gao *et al*., JACS 127, 15338 (2005)

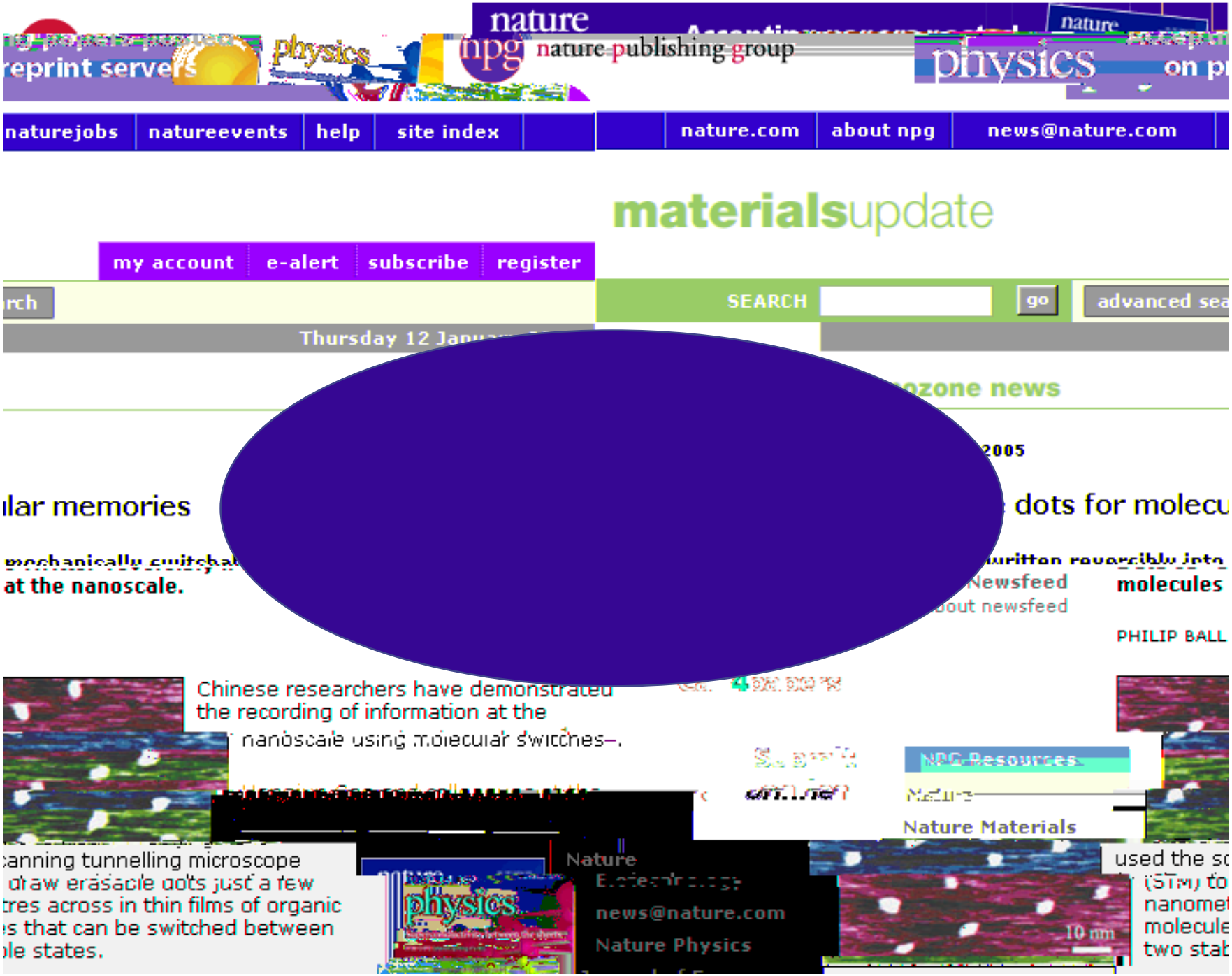
Erasable, Rewritable, Reerasable Nanorecording





Reproducible and reversible erasing and writing of recording marks of about 3 nm in diameter on H2 thin films

M. Feng, H.-J. Gao *et al*., JACS 127, 15338 (2007)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the recording of information at the
nanoscale using molecular switches–.
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draw erasable dots just a few
tres across in thin films of organic
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(STM) to
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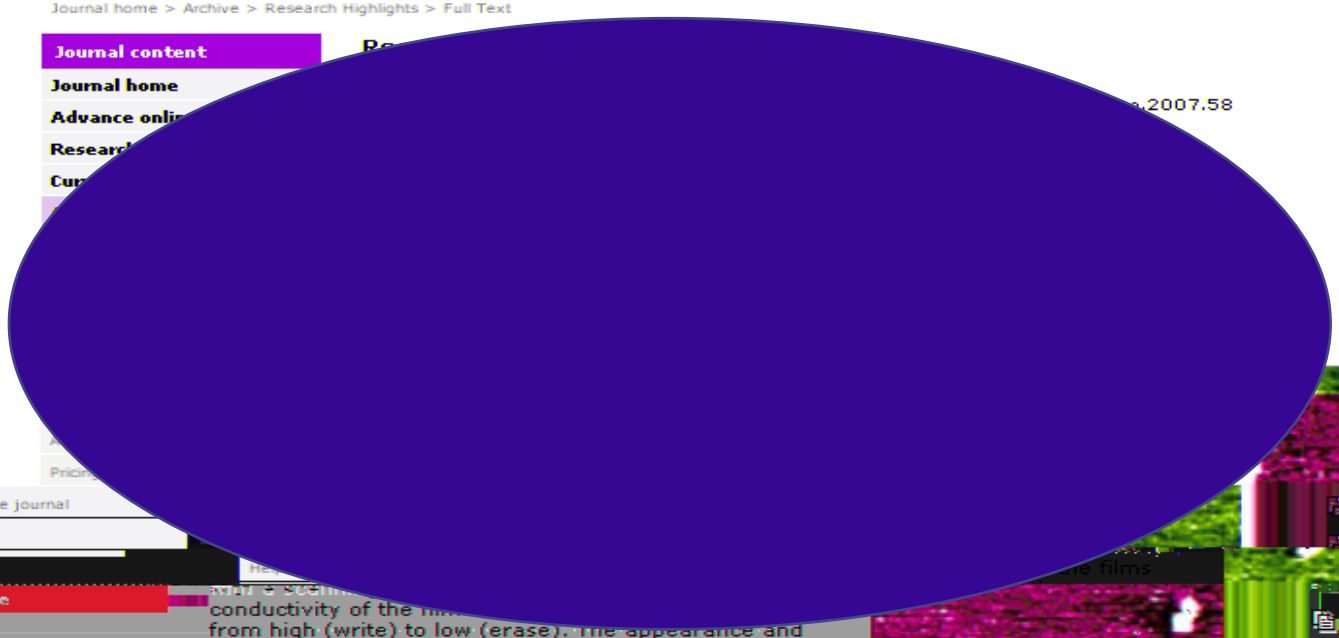

conductivity of the film
from high (write) to low (erase). The appearance and erasure of 'written' dots can be seen in atomic force microscope images, which are sensitive to the surface conductivity. However, topographic images show that there is no change in the height of the surface, suggesting that the changes are purely electronic.

The rotaxane in this study has a dumbbell-shaped axle component encircled by an electron-deficient ring-shaped molecule. The ring can move between two different

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Samia Mantoura
Samia Mantoura

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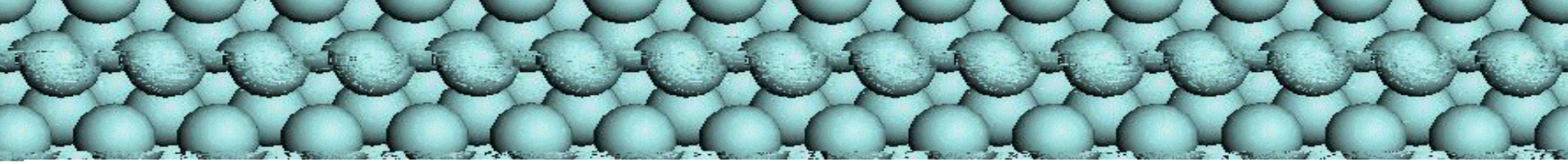
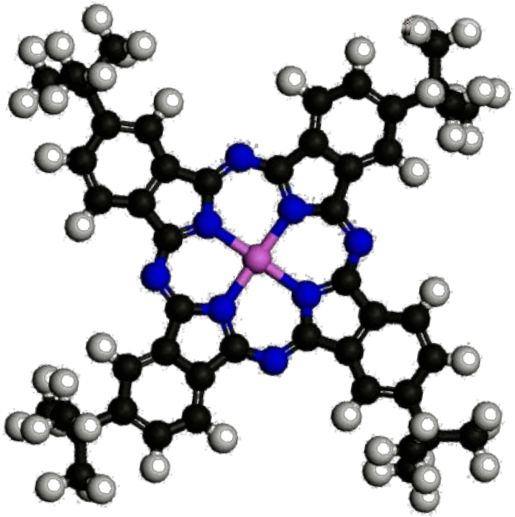


H.-J. Gao Group, IOP-CAS, China

$(t\text{-}Bu)_4$-ZnPc Molecule

Carbon
Nitrogen
Zinc
Hydrogen



- Full name: tetra-tert-butyl zinc phthalocyanine ($C_{48}H_{48}N_8Zn$)
- STM image of single stationary molecule: four bright lobes

Array of Single Molecular Rotors

$(t\text{-}Bu)_4$-ZnPc on Au(111), 78 K

20 nm

4 nm

L. Gaoet al. Phys. Rev. Lett. 101, 197209 (2008).

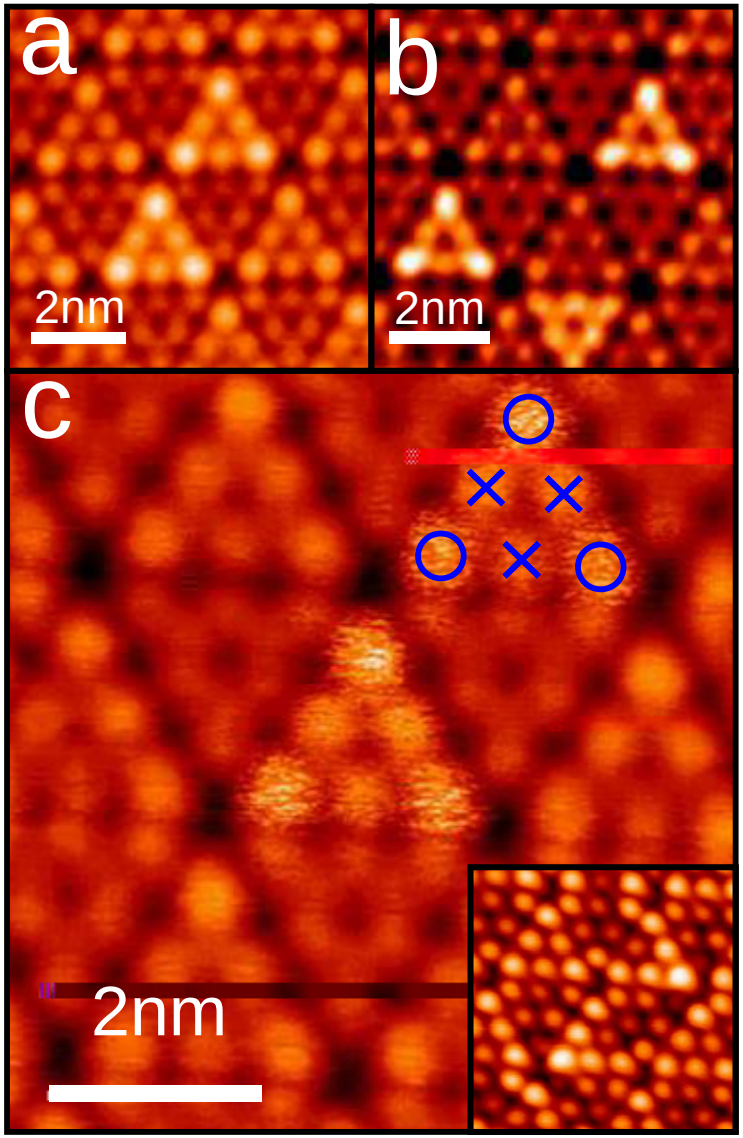
Diffusion Induced STM Images

Ag

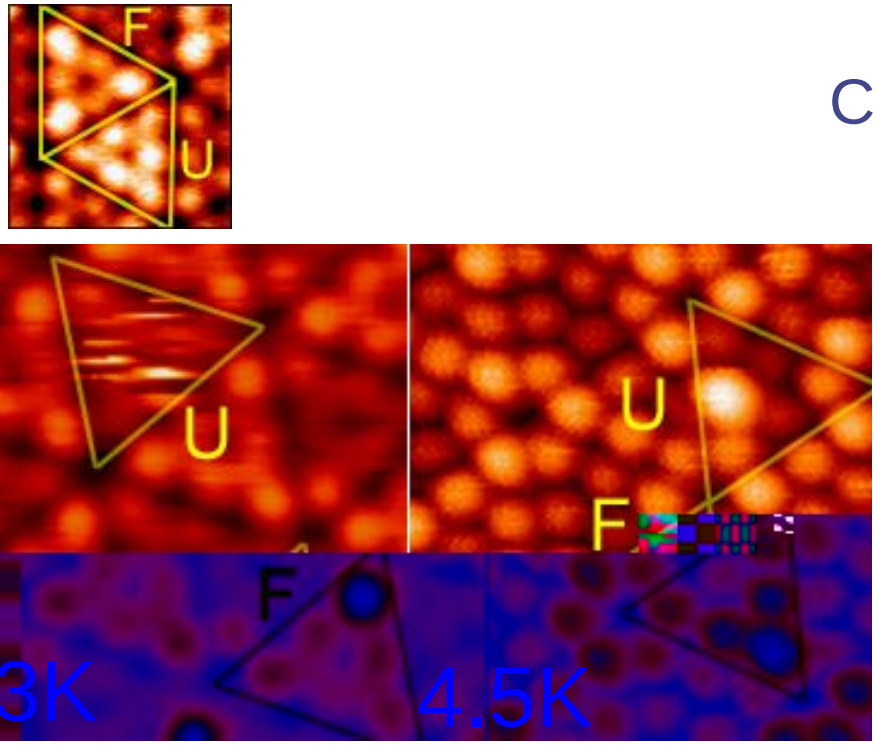
at RT

a

Au

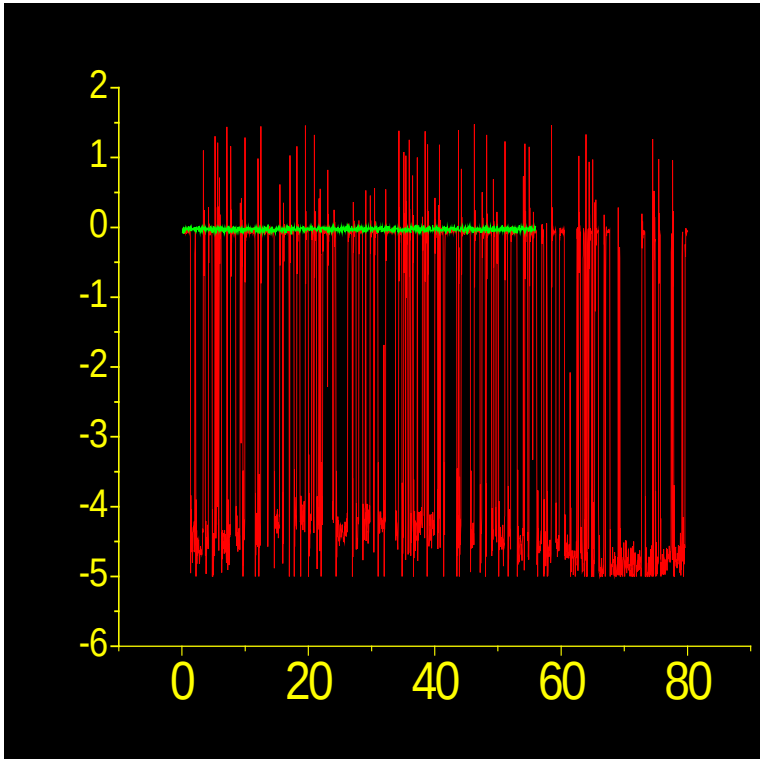


Cu



X.D. Xiao (6j Á ð Å *et al*., Phys. Rev. B

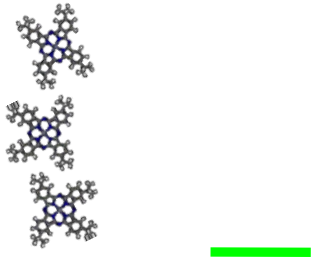
Tunneling Current Oscillation



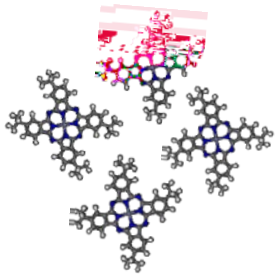
STMImaging of Molecular Aggregates at Surfaces

A

B



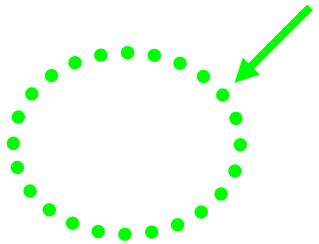
C



D

A, B, C, D: at 4.5K

Real Physical Process



2 nm

2 nm

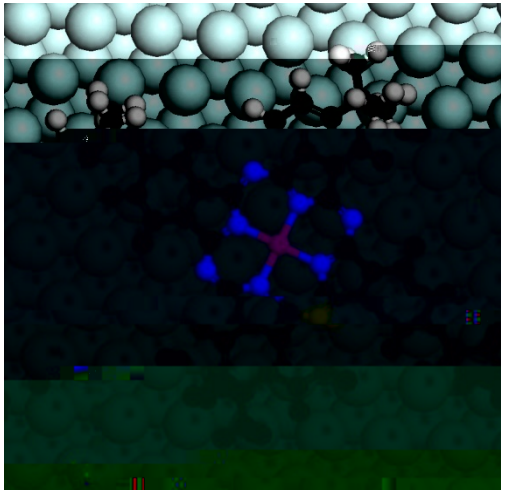
- Stationary single molecule attached to molecular cluster
- Instable single molecule isolated from molecular clusters
-

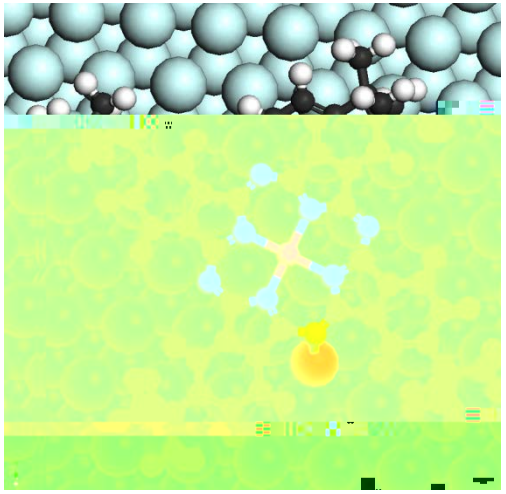
Underlying Au Adatom

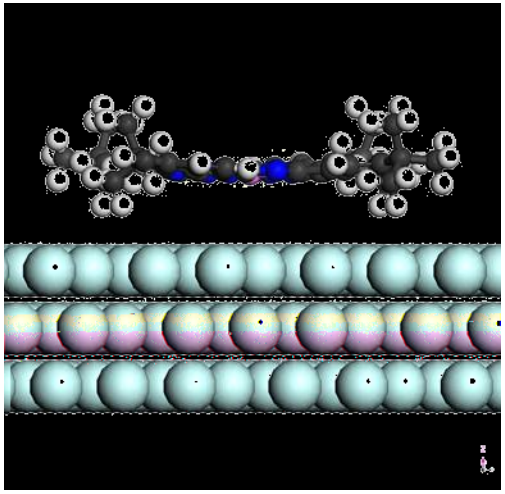
- Bright Spots Left After Removing Molecules
- Center Position of Molecular Rotor

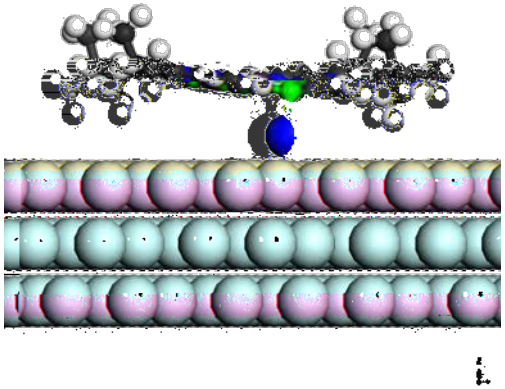
¾Gold Adatoms*

Molecular Configurations on a Au Adatom of Au(111)

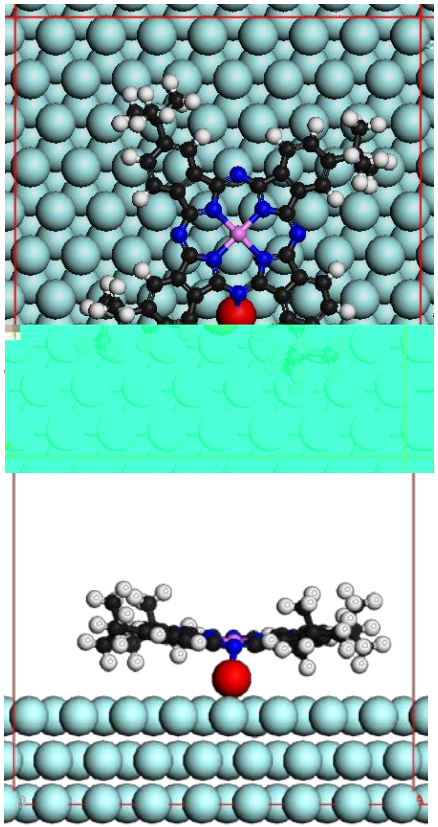








Lateral Translation Energy of the Molecule: Adsorptio
Rotation around Au Adatom



E_{ad}=804meV

Lateral Translation

Energy (meV)

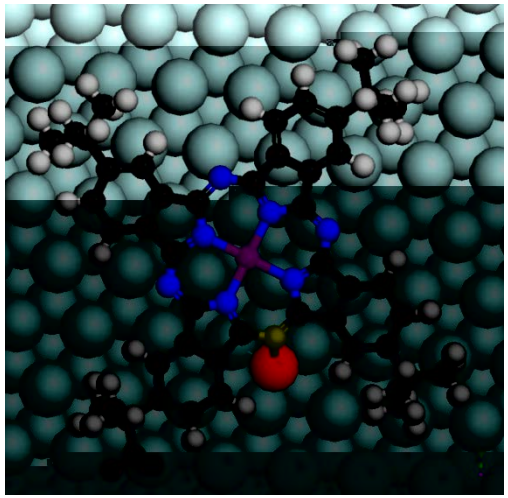
Distance (A)

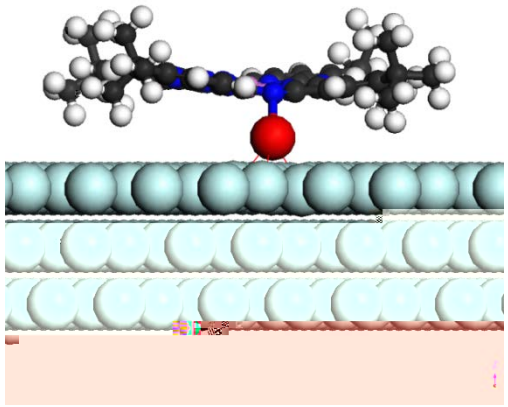
The diffusion barrier along different directions is still high (30°)

L. Gao/ H.-J. Gao et al. Phys. Rev. Lett. 101, 197209(2008)

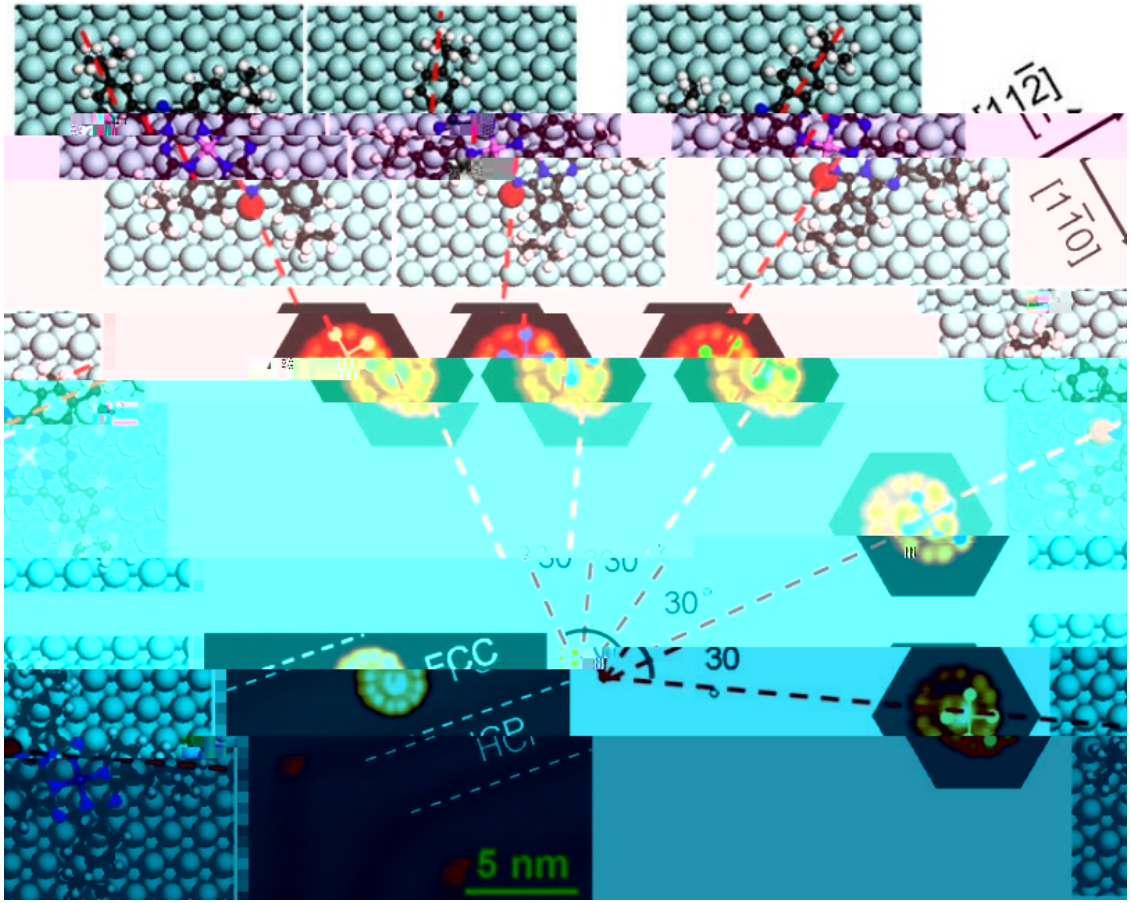
Ab Initio Calculations of Metastable Configurations and Comparison with Experimental Observations

E_{ad} = 804 meV

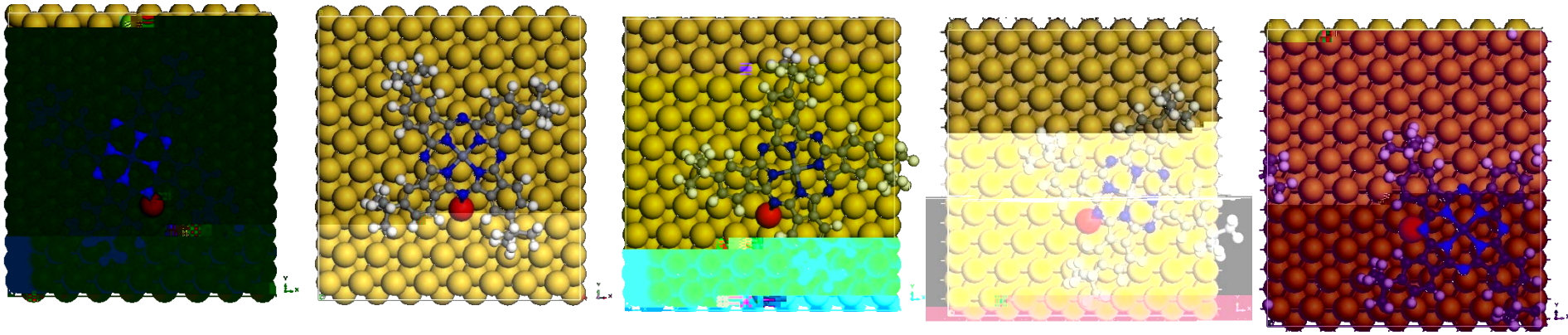




Barrier ~20meV

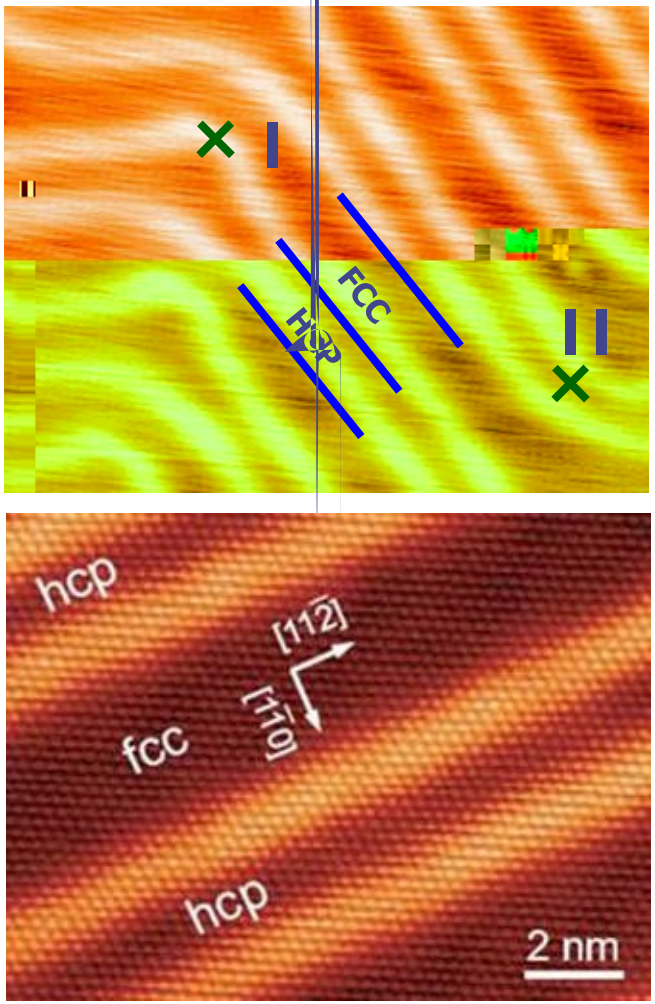


Energy Barriers between Molecular Configurations of Rot
Au Adatom



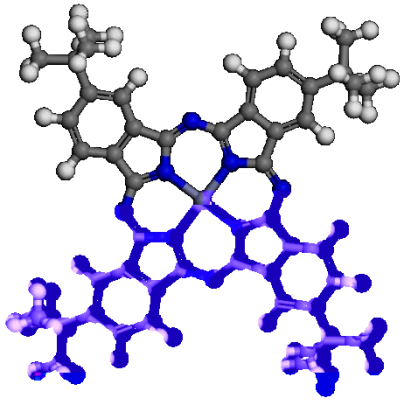
-16meV 9 meV -22 meV 18 meV

Manipulating Single Molecular Rotors Locations using Different

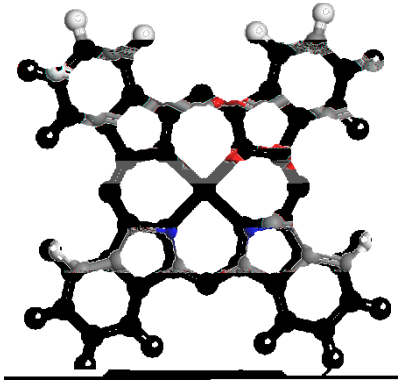


H.-J. Gao *et al.*, Phys. Rev. Lett.

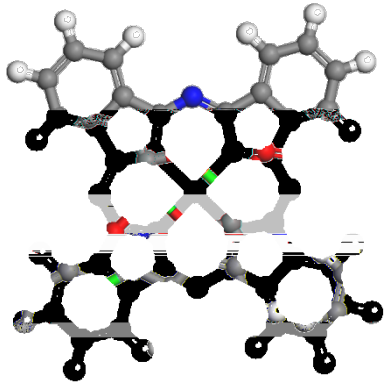
Change Structure of Molecule



(t-Bu)4-ZnPc
FePc



ZnPc



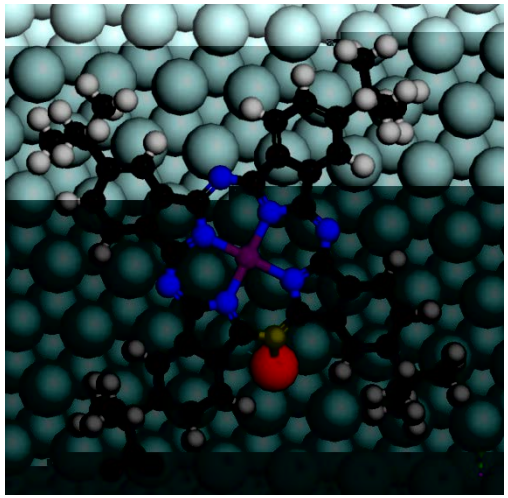
1nm

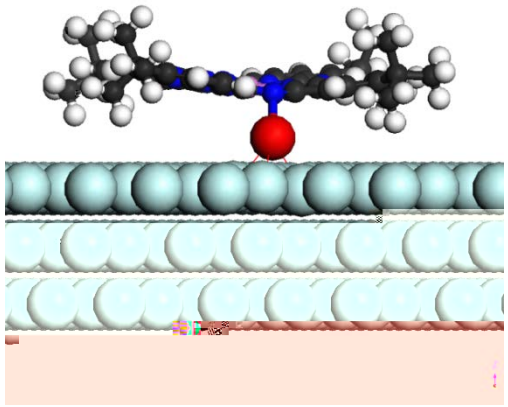
1nm

1nm

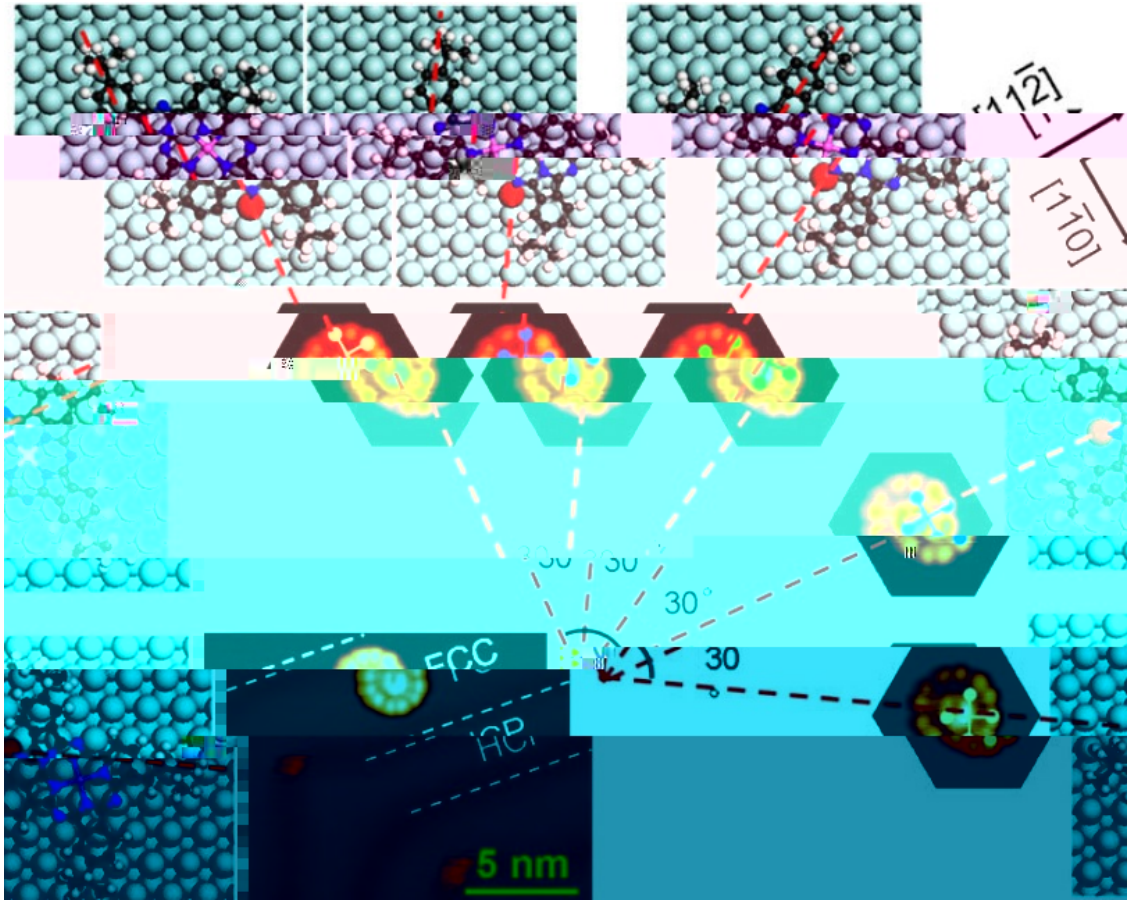
Ab Initio Calculations of Metastable Configurations and Comparison with Experimental Observations

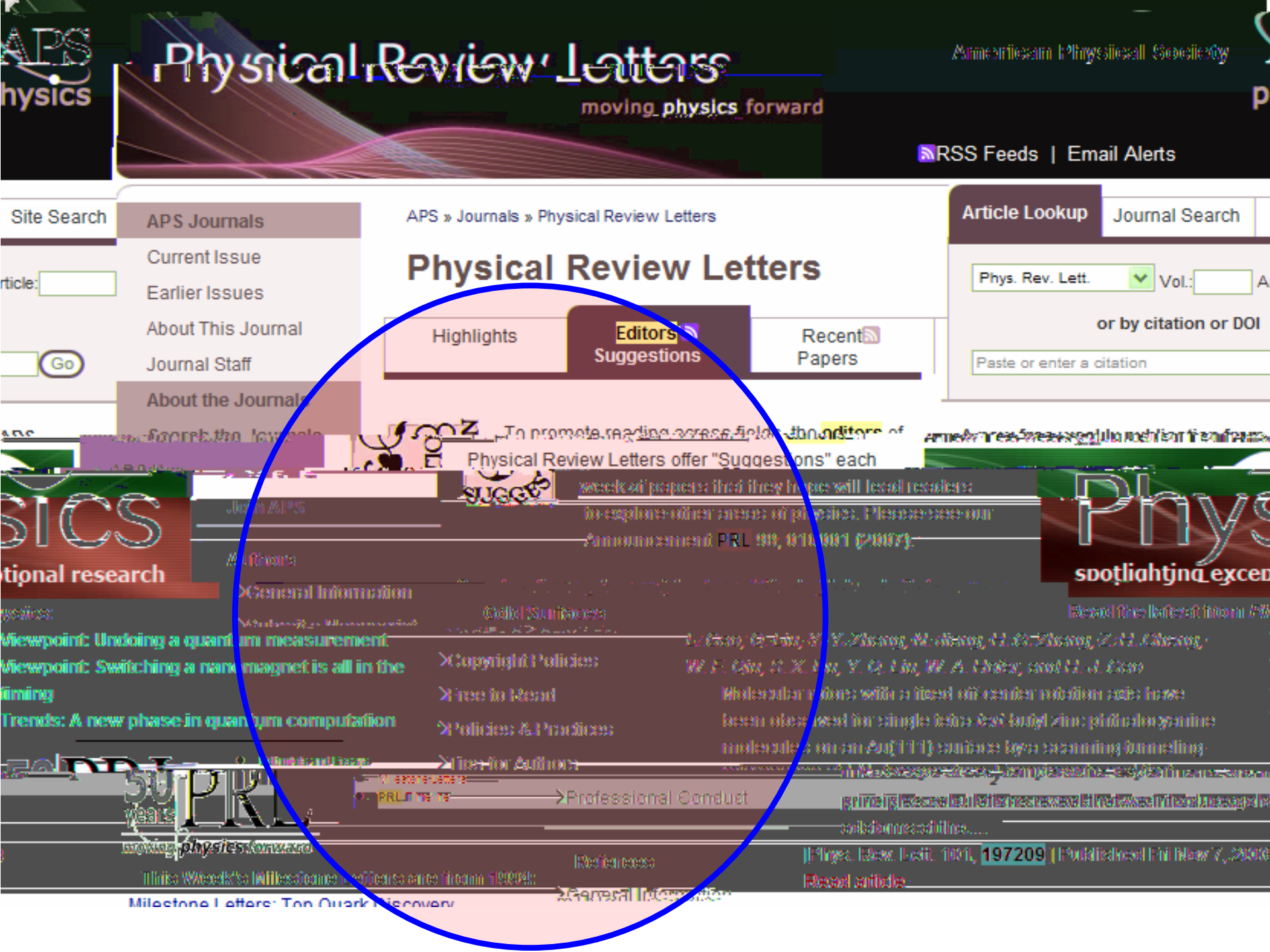
E_{ad} = 804 meV





Barrier ~20meV

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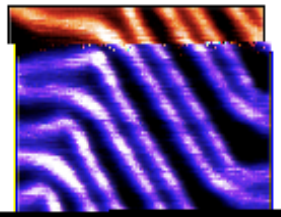
Spinning on a gold atom



Constructing an Array of Anchored Single-Molecule Rotors on Gold Surfaces

L. Gao, Q. Liu, Y. Y. Zhang, N. Jiang, H. G. Zhang, Z. H. Cheng, W. F. Qiu, S. X. Du, Y. Q. Liu, W. A. Hofer, and H.-J. Gao

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D STORIES
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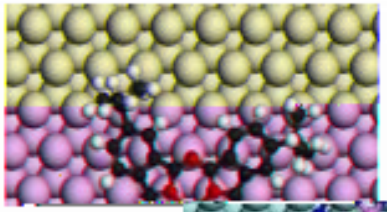
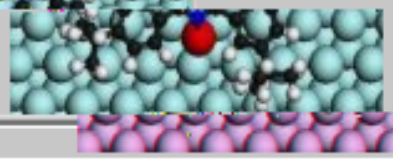
nanomotors
ght for nanomotors
LINKS
Gao Research group
RESTRICTED LINKS
have also made arrays
of the devices that spread over
distances as large as micrometres.
rotors in the arrays
ert, something that the team believes will be
ial for making molecular machines. Such machines could
onomous nanorobots in the future that
uits or delivering drugs to specific parts of the

NEWS
Nov 18, 2008
Physics Research Highlights

Researchers in China and the UK have made a new type of nanometre-sized rotor with an off-centre axis of rotation. The





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rch highlight

cular machines: Rows of rotors

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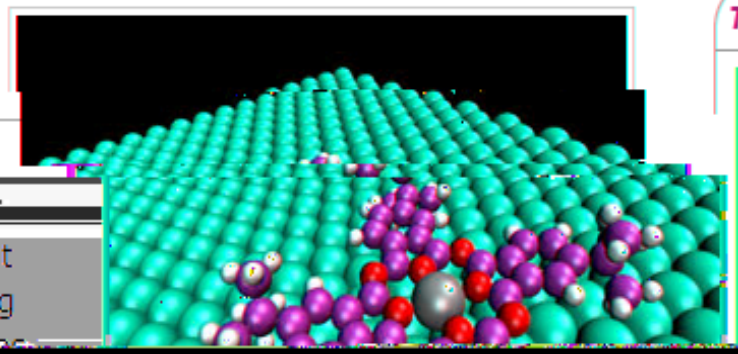
ty to move individual atoms with the tip
nning tunneling microscope is a powerful
ep towards building complex molecular
ns at the atomic scale. But for practical
pplications of such molecular machinery, it
ust be possible to construct it easily and at
w cost, on a large-scale. The key satisfying



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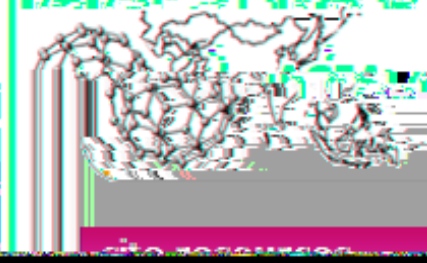

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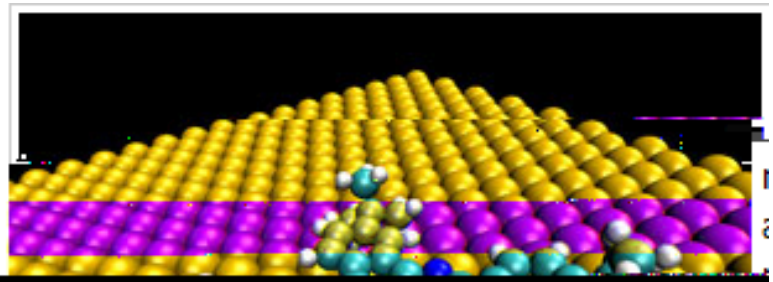
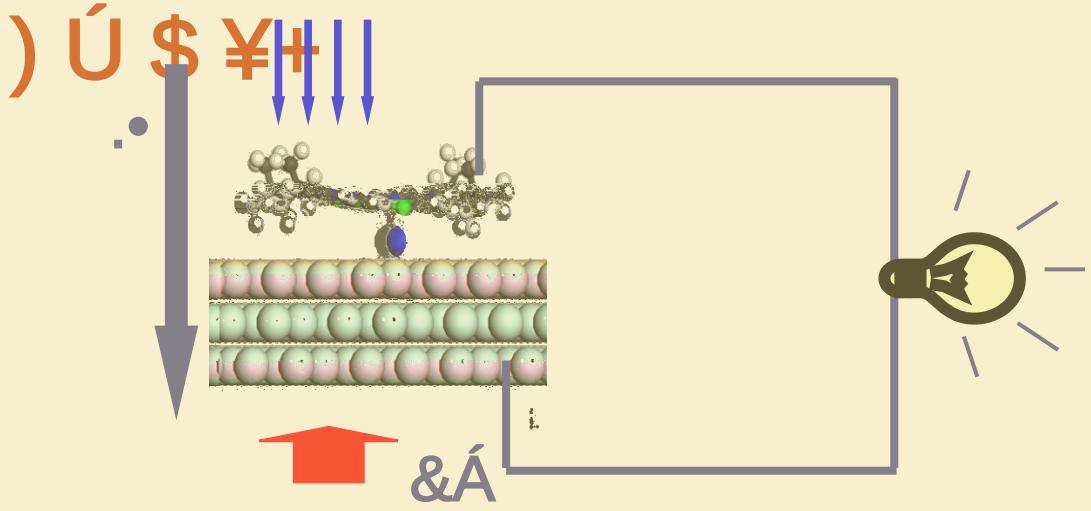
The ability to move individual atoms with the tip of a scanning tunneling microscope is a powerful [illegible] machines at the atomic scale. But for practical applications of such molecular machinery, it must be possible to construct it easily and at



t-Bu)4-ZnPc

78K



Reversible Single Spin Control of Magnetic Molecule by H Atom Adsorption

L.W. Liu/H.J. Gao *et al*., Scientific Report **3**, 1210(2013)

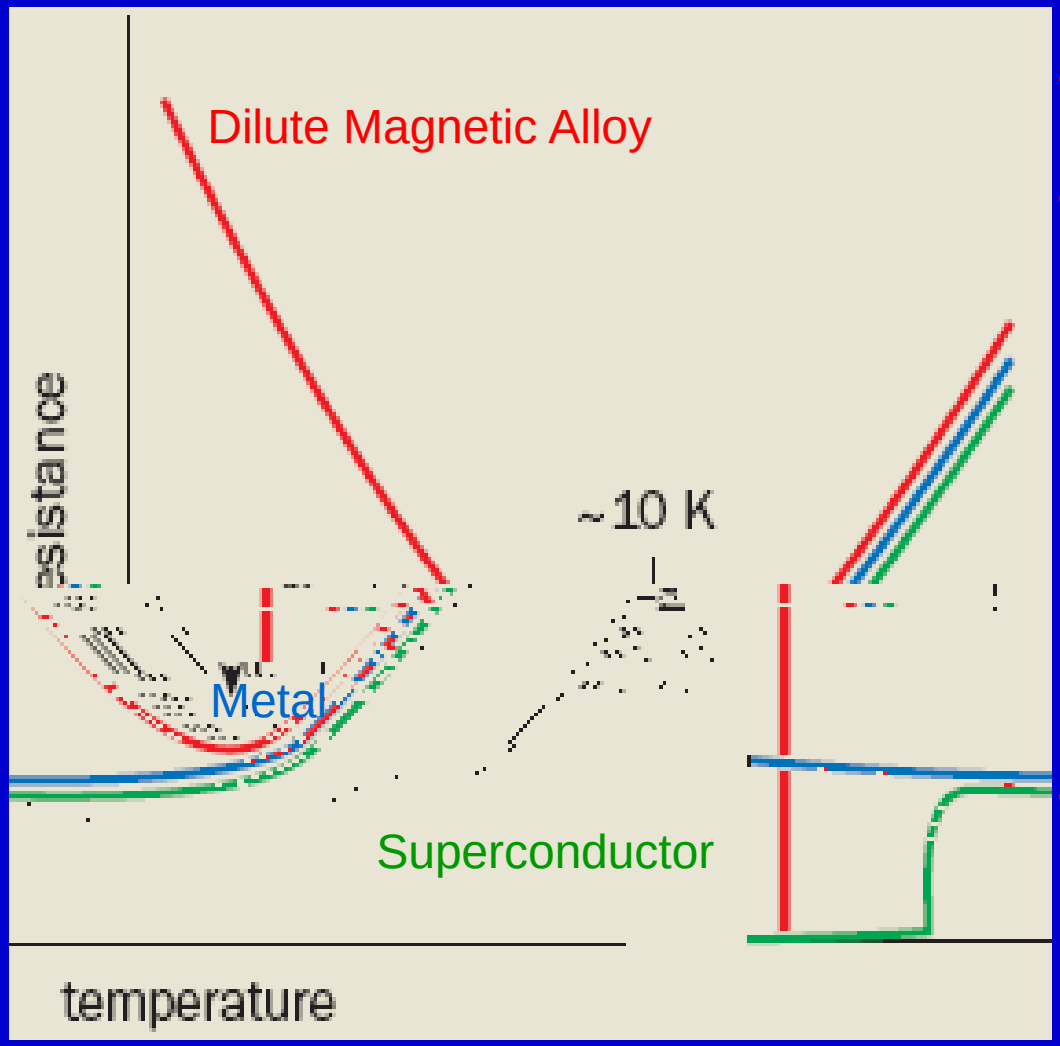
Kondo

- Molecular structure of the magnetic impurities.
  - cut off ligands from impurities.
  - attach ligands to impurities.
- Changing the substrate properties.
  - different materials.
  - film thickness, Pb/Si(111).

Nondestructive and Reversible Control

A. Zhao et al., Science 309, 1542 (2005).
P. Wahl et al., Phys. Rev. Lett. 95, 166601 (2005).
V. Iancu et al., Nano Lett. 6, 820 (2006).
P. Wahl et al., Phys. Rev. Lett. 98, 056601 (2007).

Kondo Effect



- Discovered in 1930s.
- Dilute magnetic alloys:

  Metals: Au, Ag, Cu, Mg, Zn.

  Magnetic Impurities: Cr, Mn, Fe, Co, Ni, V, Ti.

  No inter-impurity interaction.
- Electrical resistance minimum at low temperatures for dilute magnetic alloys.

L. Kouwenhoven, L. Glazman, Physics World, January 2001

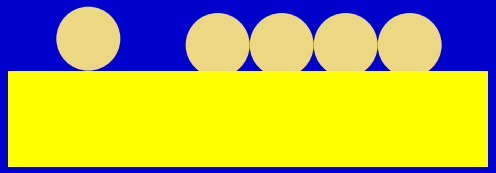
Magnetism of Nanostructures

Nanostructures
at surfaces !

„Single Spin Objects”

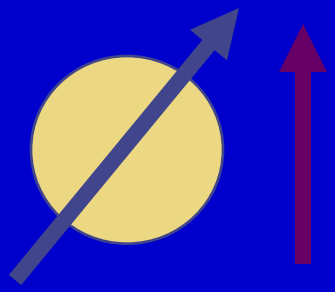
Atoms, Molecules

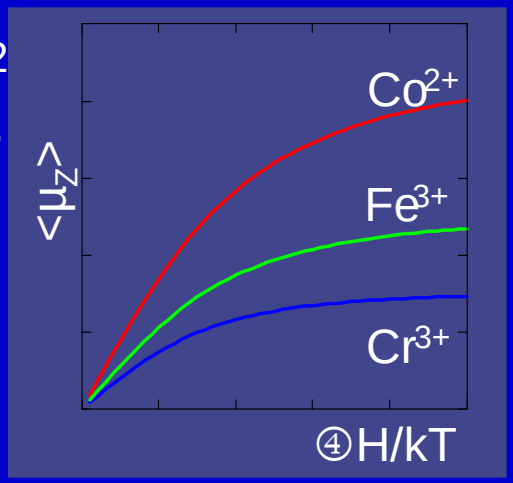
???



$^4F_{9/2}$

S=3/2 L=3 J=9/2





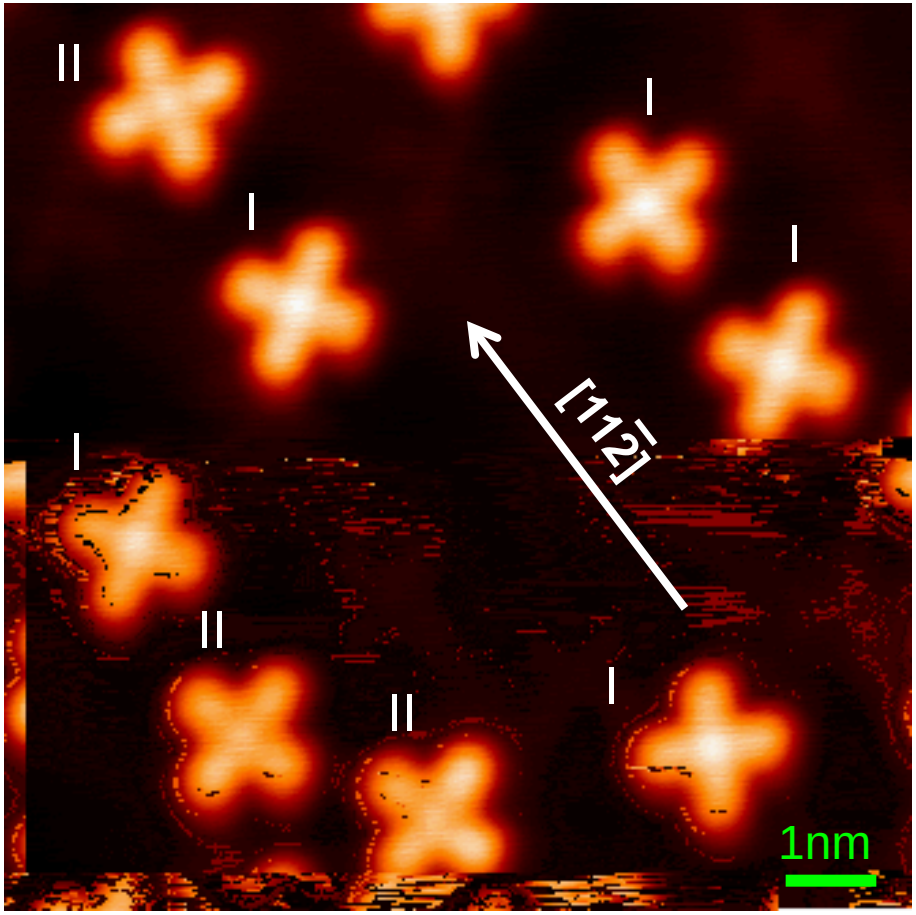
magnetic moment ?

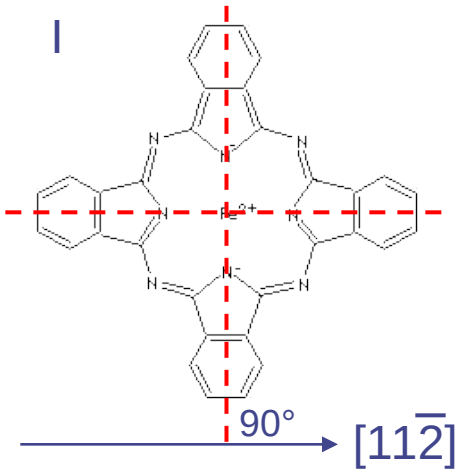
anisotropy ?

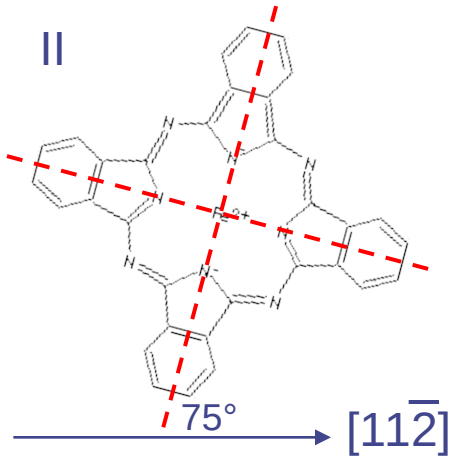
magnetic order ?

Kondo

Two Molecular Orientations



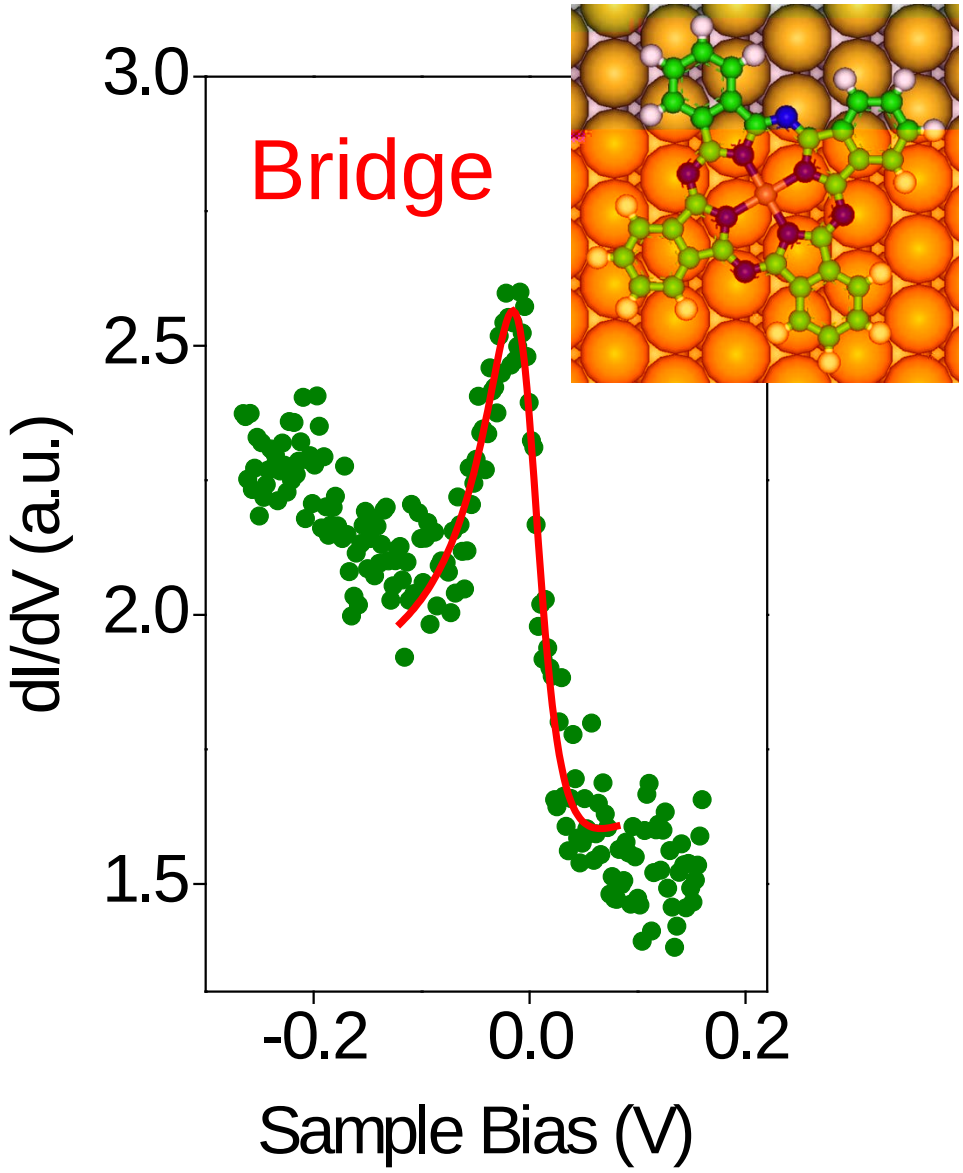


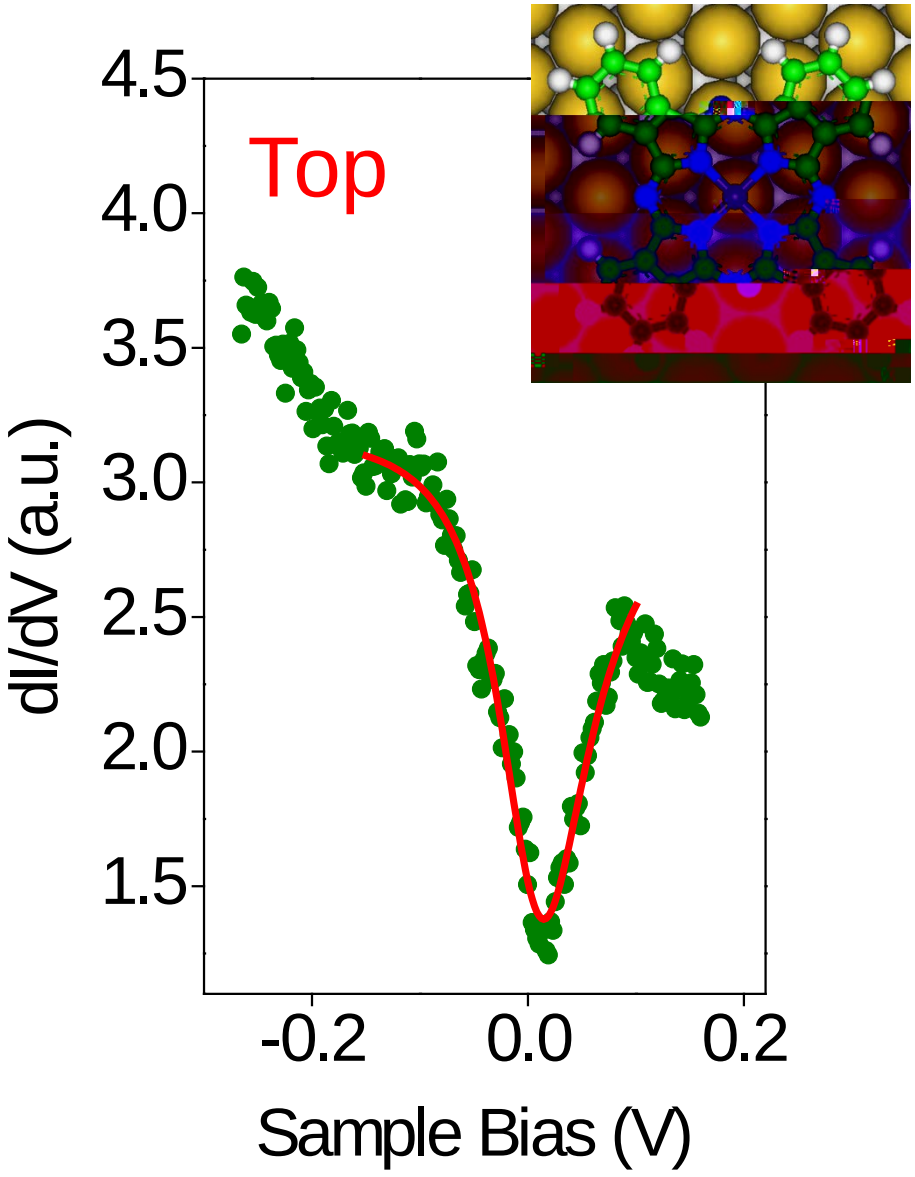


5 K

L. Gaoet al. Phys. Rev. Lett. 99, 106402 (2007).

dI/dV Spectra at Molecular Center

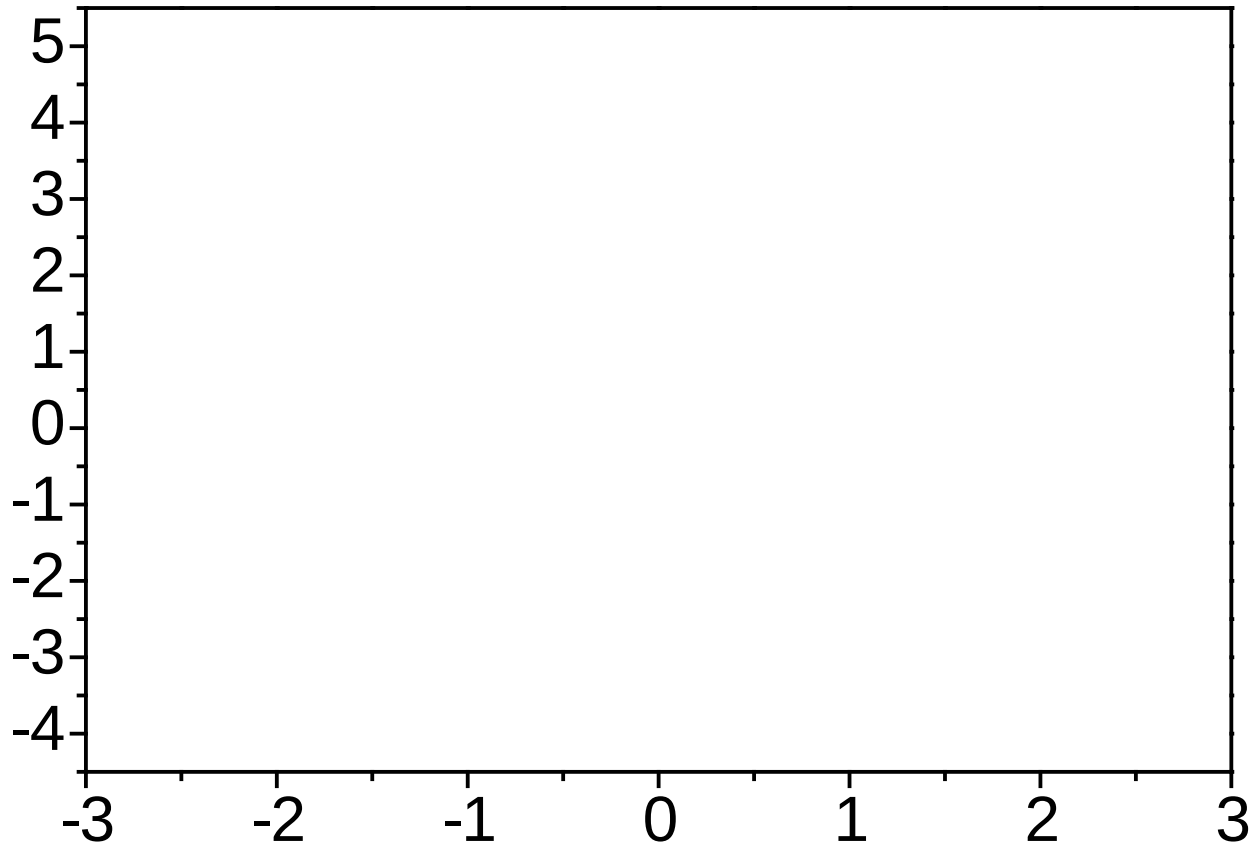




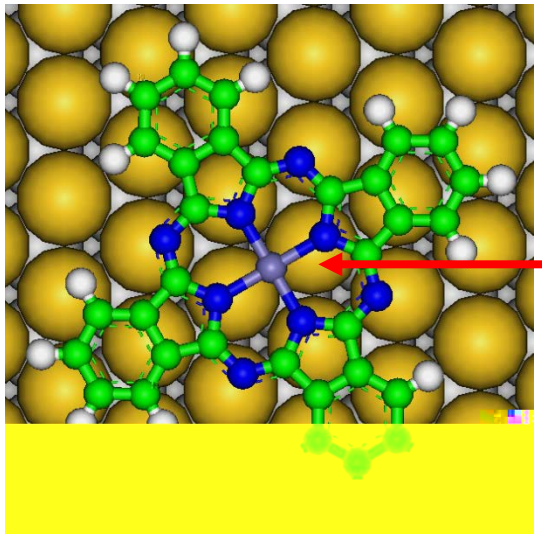
Fano Function Fit

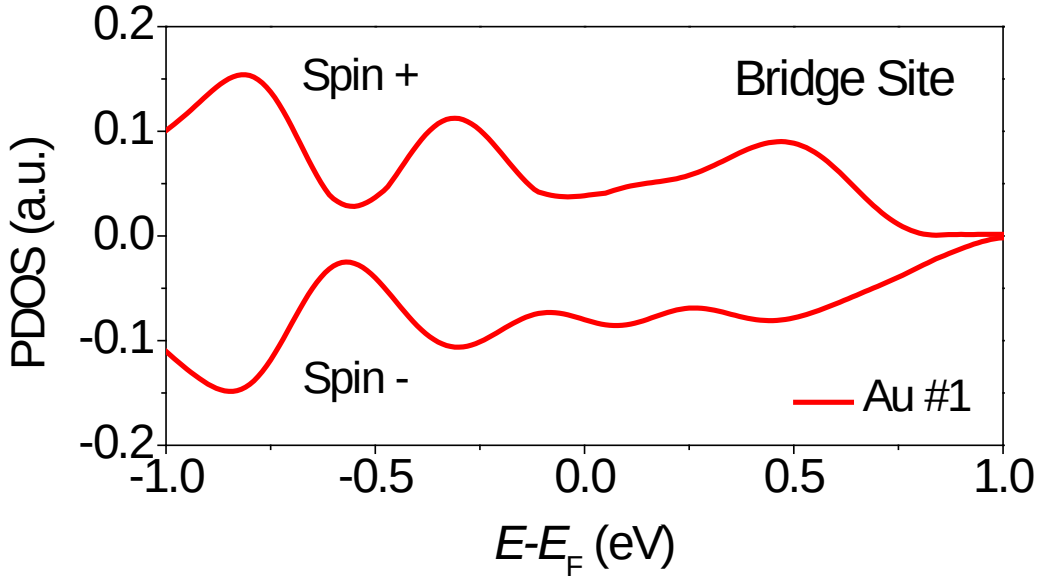
$$\frac{dI}{(\quad)} \qquad \frac{(\quad q)^2}{1 \quad ^2}$$

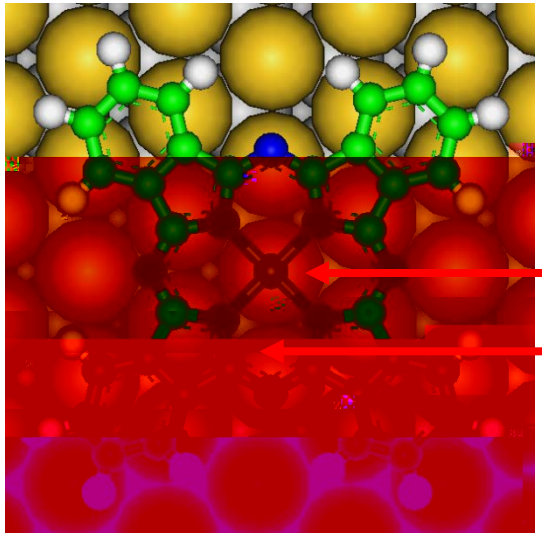
Spin Polarized PDOS of Fe(2+)

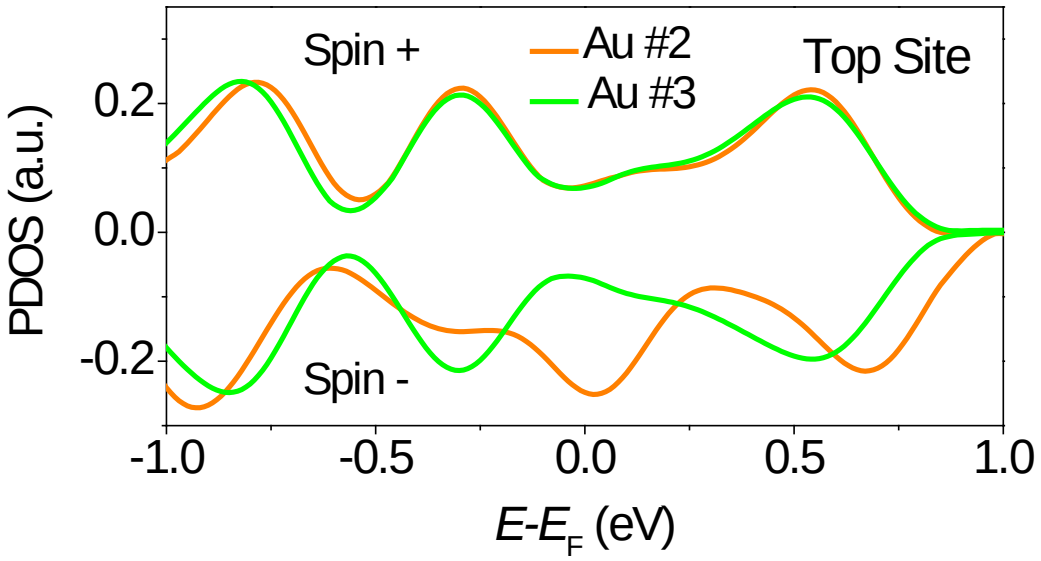


PDOS of Neighboring Au Atoms

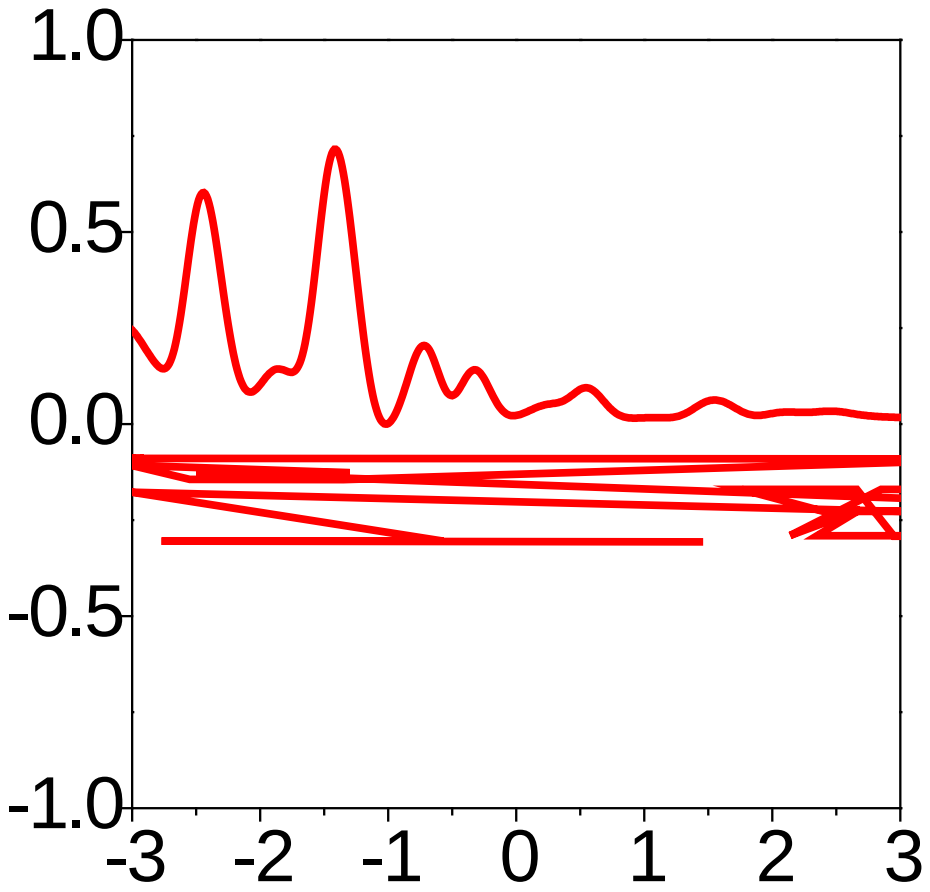


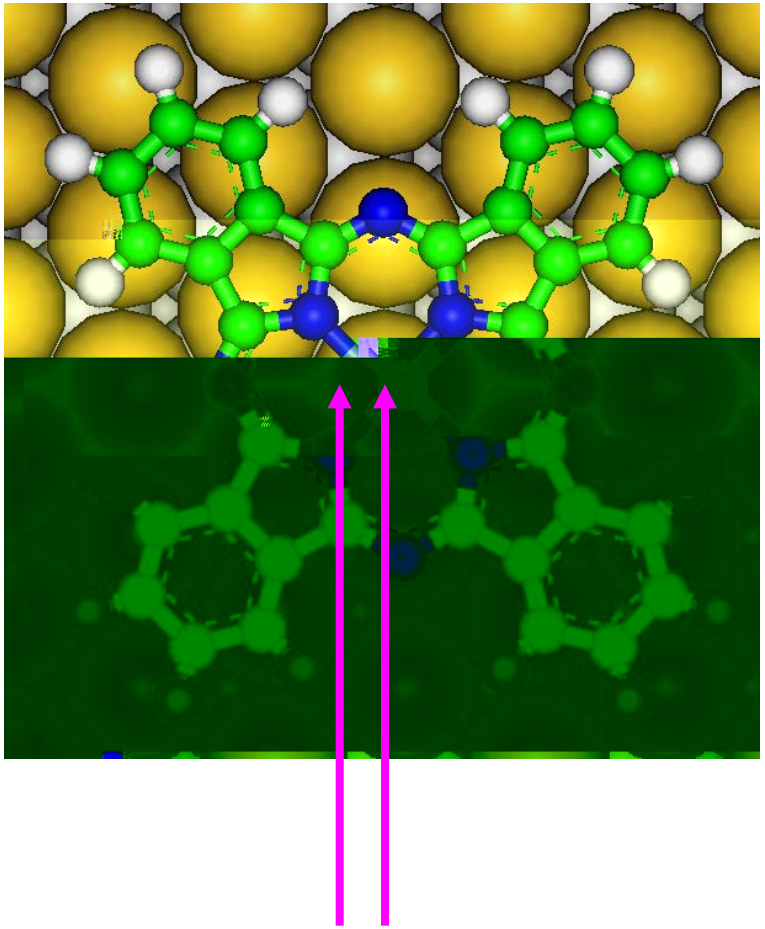






Top Site: d-level Hybridization

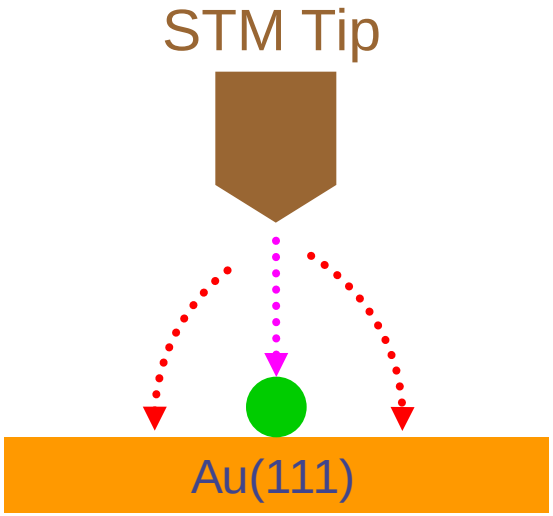


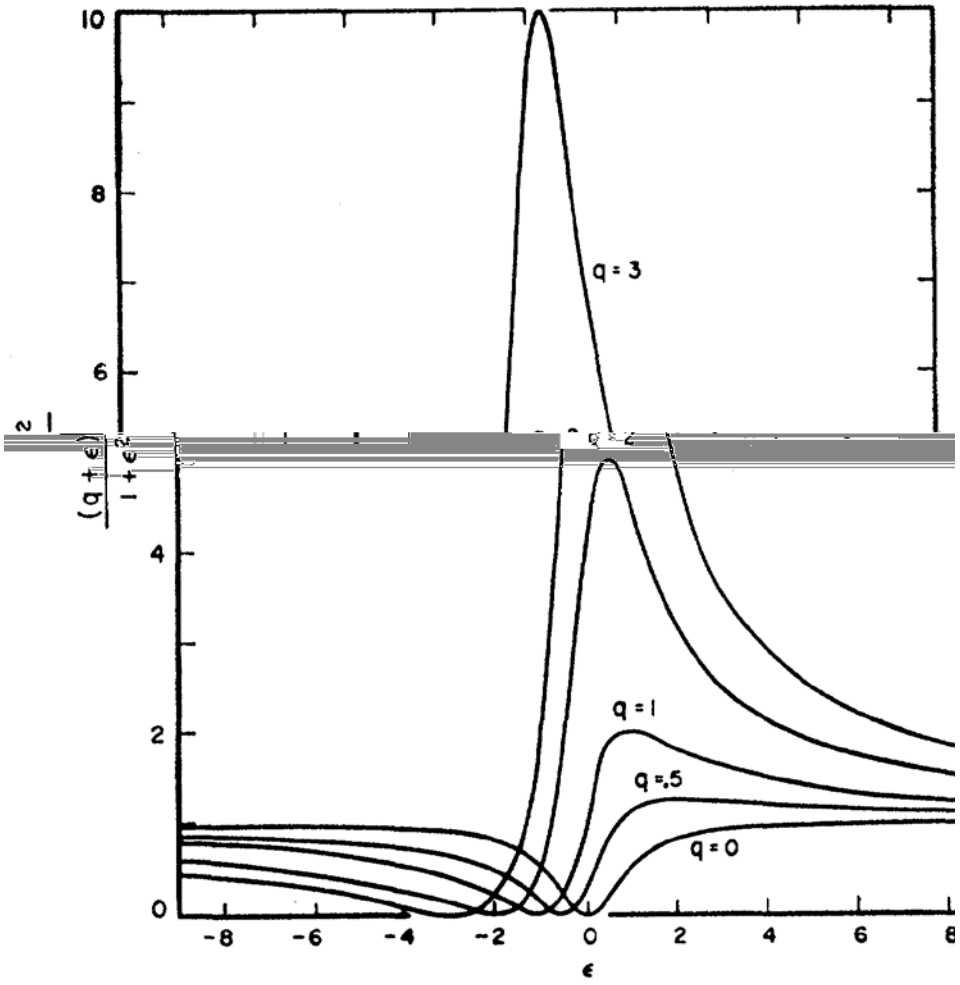


Line Shape of Kondo Resonance

- Bridge site:q = 2.20±0.19
- Top site:q = 0.12±0.03

$$\frac{1}{2}\rho q^2 = \frac{\left|\left(\quad |T|i\right)\right|^2}{\left|\left(\psi_E|T|i\right)\right|^2 G}$$

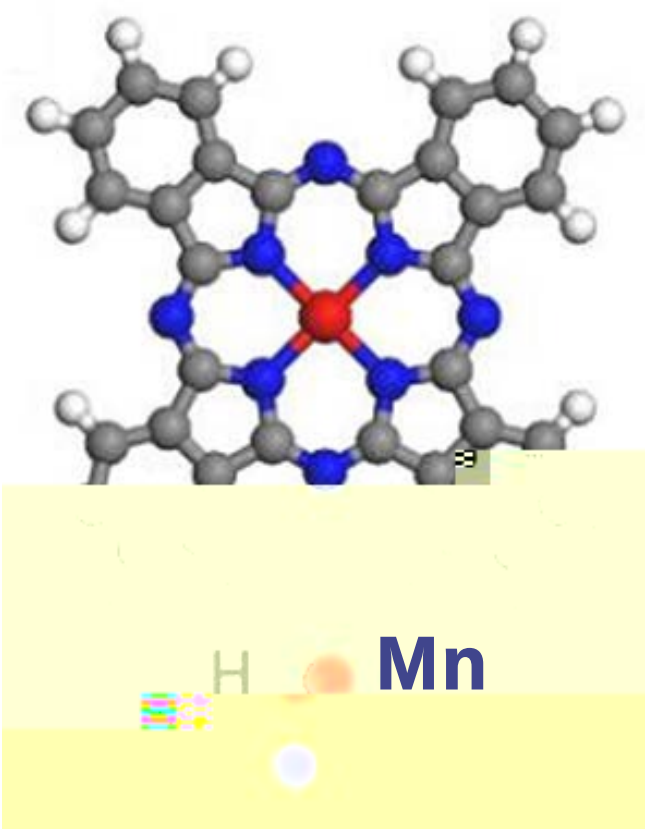




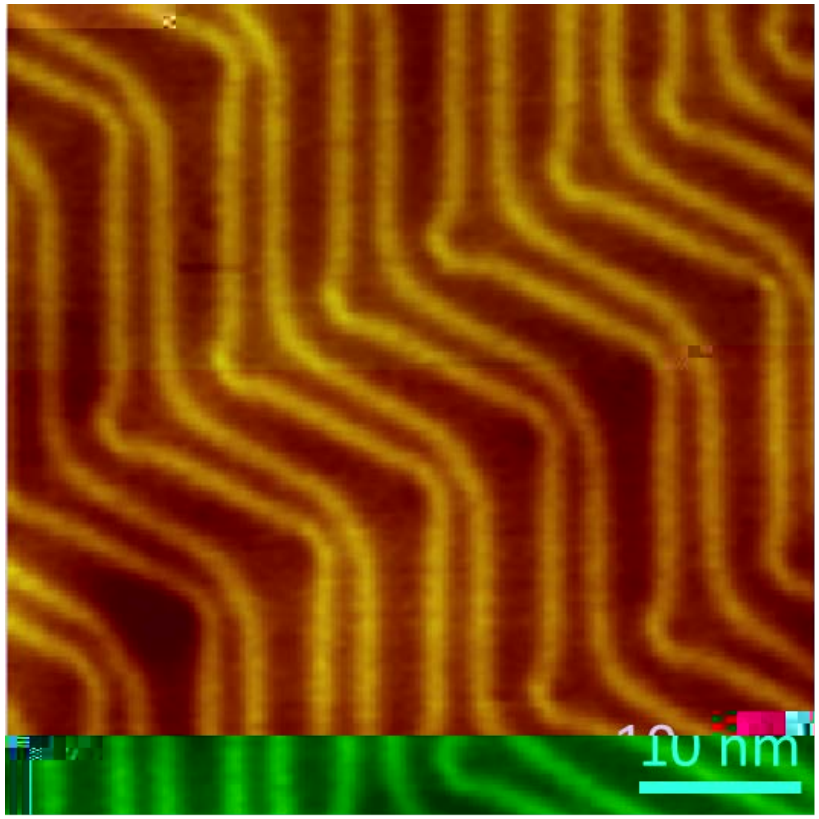
U. Fano,Phys. Rev124, 1866 (1961).

Studied Systems: MnPc+Au(111)

MnPc S=3/2

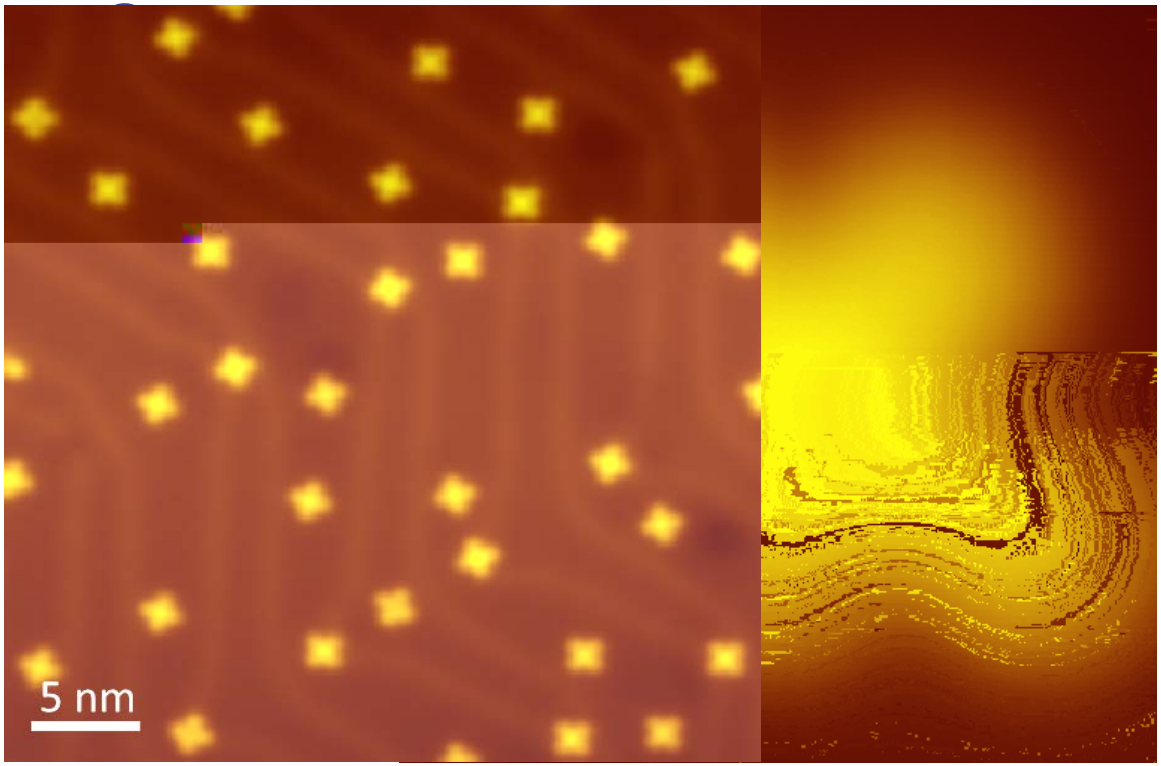


Au(111)



STM Image of the MnPc/Au(111)

“ Protrusion ” at the Molecular

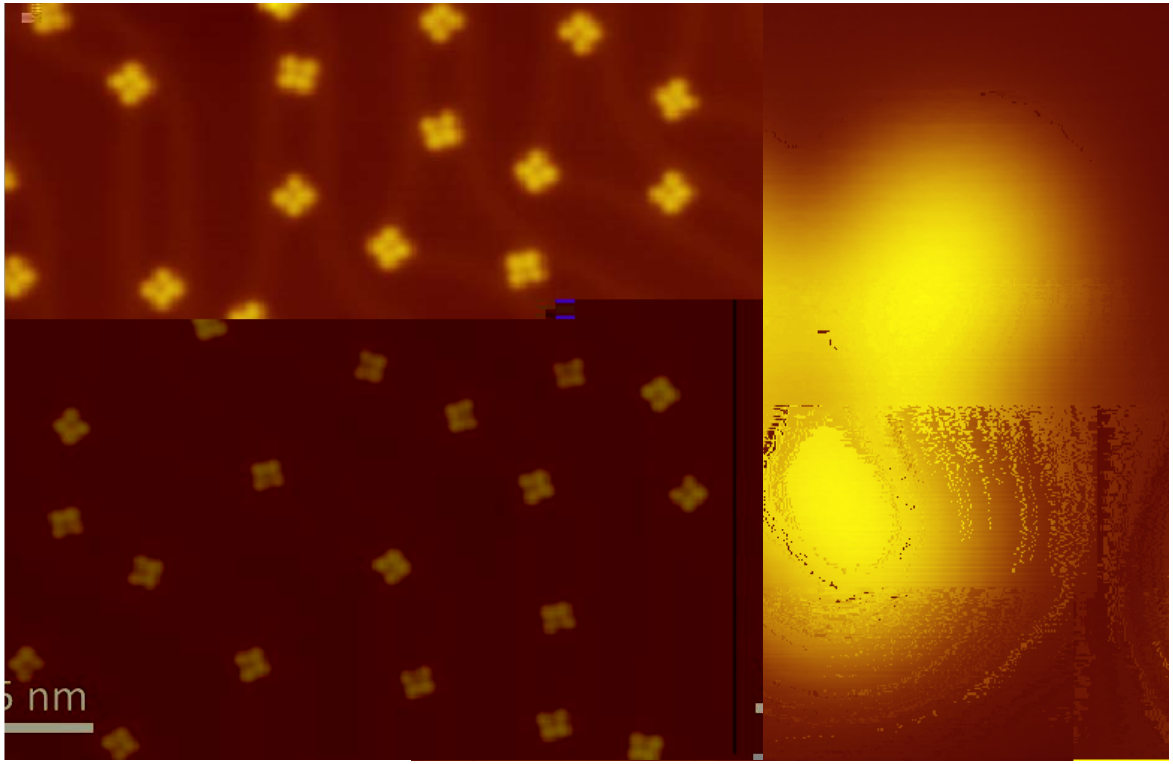


MnPc/Au(111)

H induced at room Temperature in the UHV

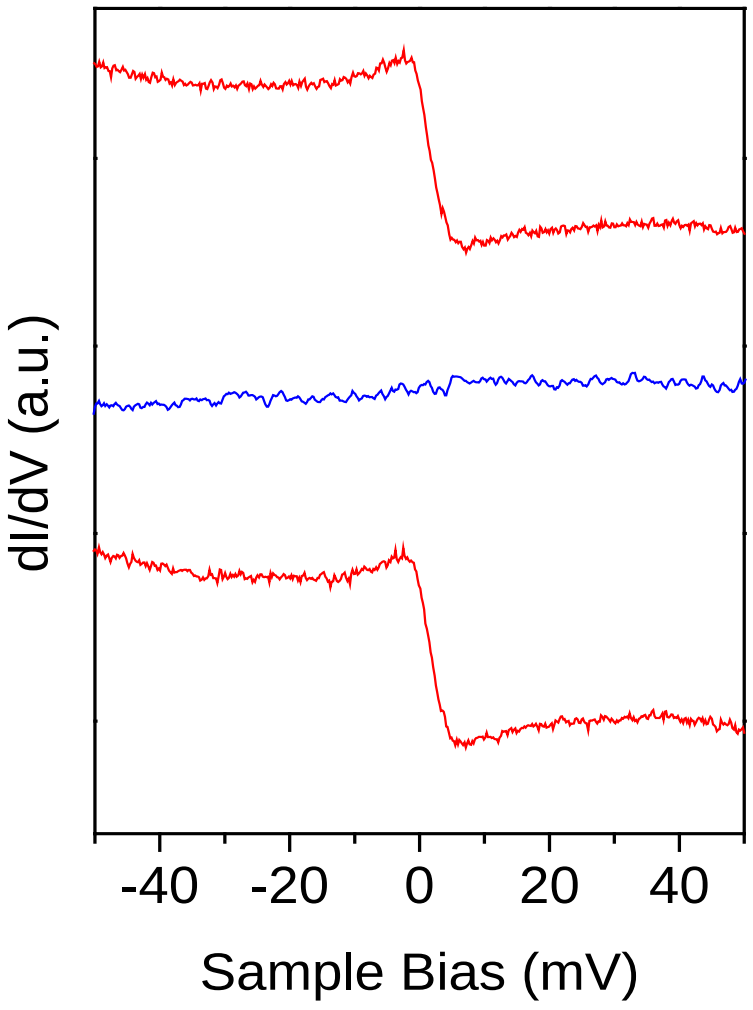
STM Image of the MnPc/Au(111) after H adsorption

"Depression" at the Molecular



H-MnPc/Au(111)

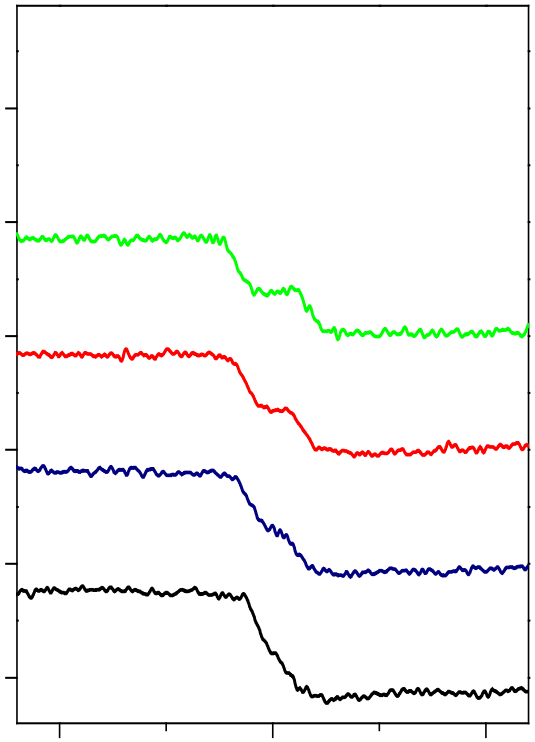
Reversible Peak Feature at the Fermi Level



¾MnPdAu(111): A pronounced step shaped feature at zero bias---- which can be attributed to Kondo effect

¾H-MnPdAu(111): are featureless in this energy range

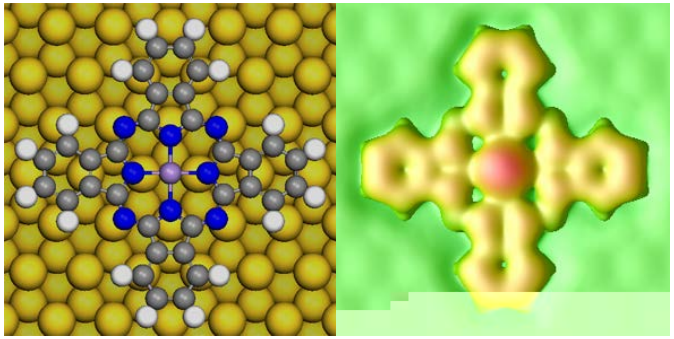
¾once the H-MnPc state was switched back to the MnPc state, its electronic structure including the Kondo resonance can be fully recovered in addition to the recovery of the topographic feature.



DFT Calculation: Larger Spacing with H

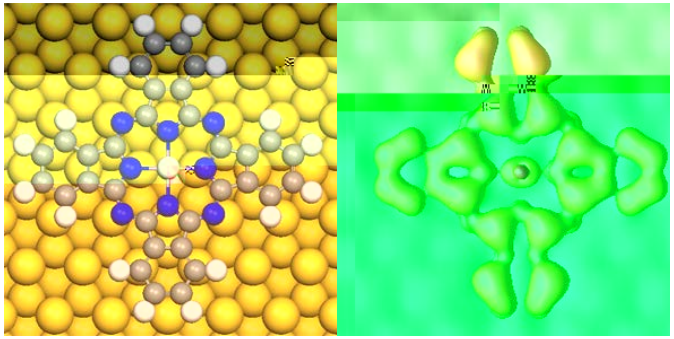
A

MnPd⁄Au(111)

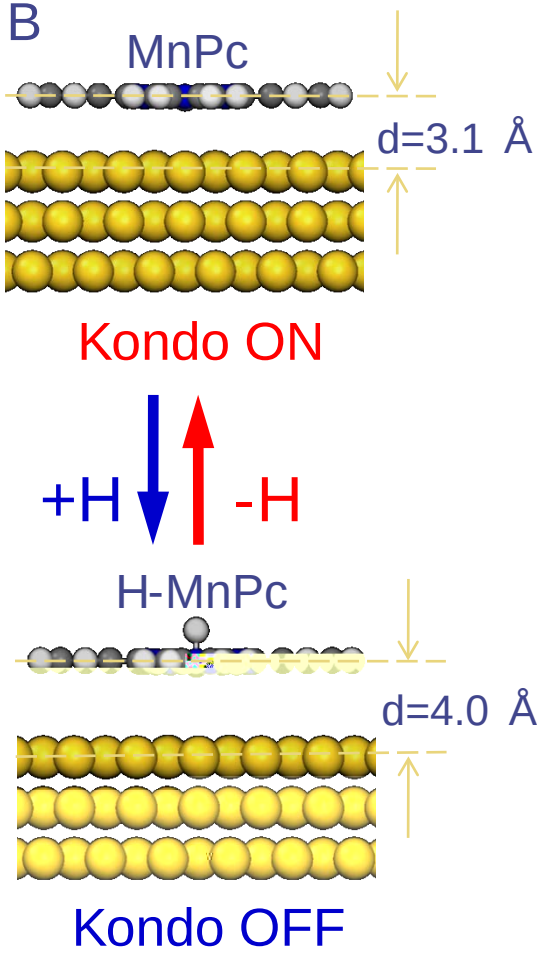


+H -H

H-MnPd⁄Au(111)

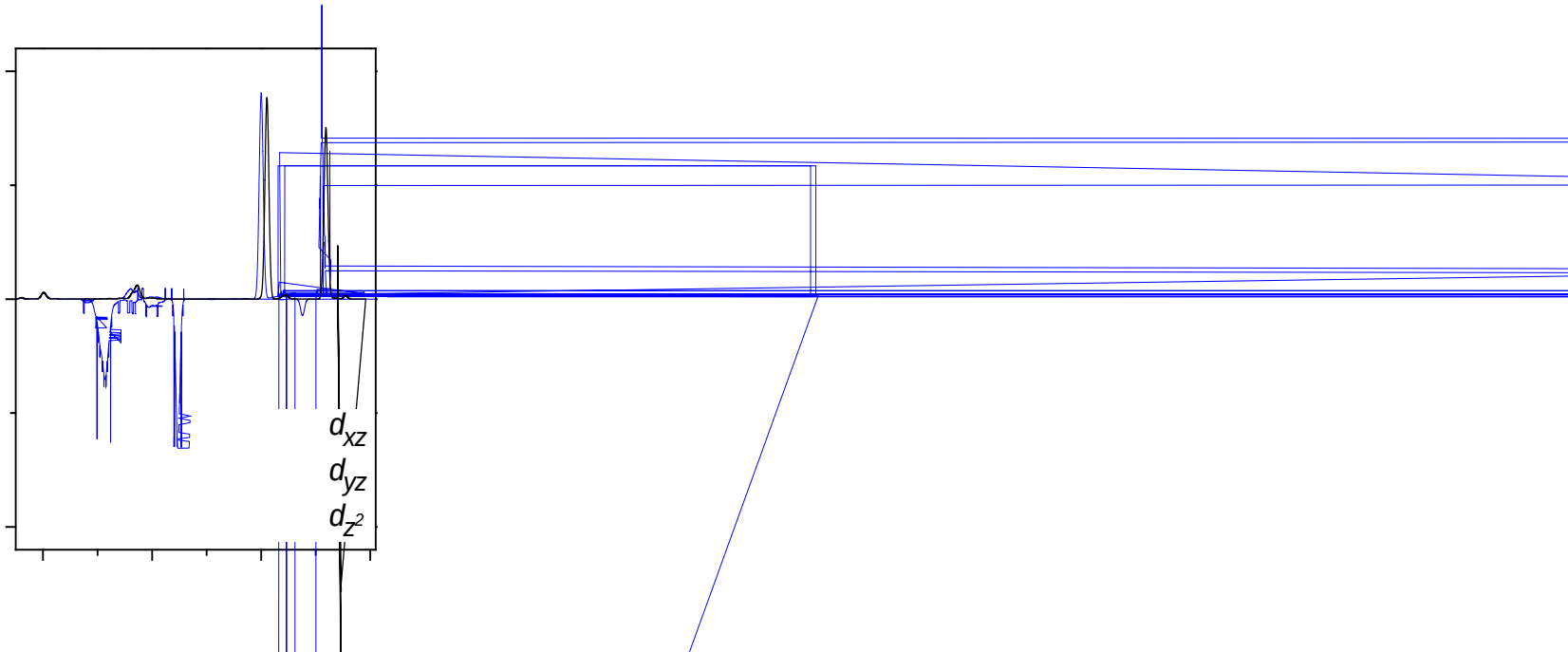


B



Topographic features of both the MnPc and H-MnPcstates can be well reproduced by STM simulations

The separation between the molecular plane of the MnPcand the Au(111) surface increases after the H decoration


d_{xz}
d_{yz}
d_{z^2}

Quench of Kondo Effect---Switching

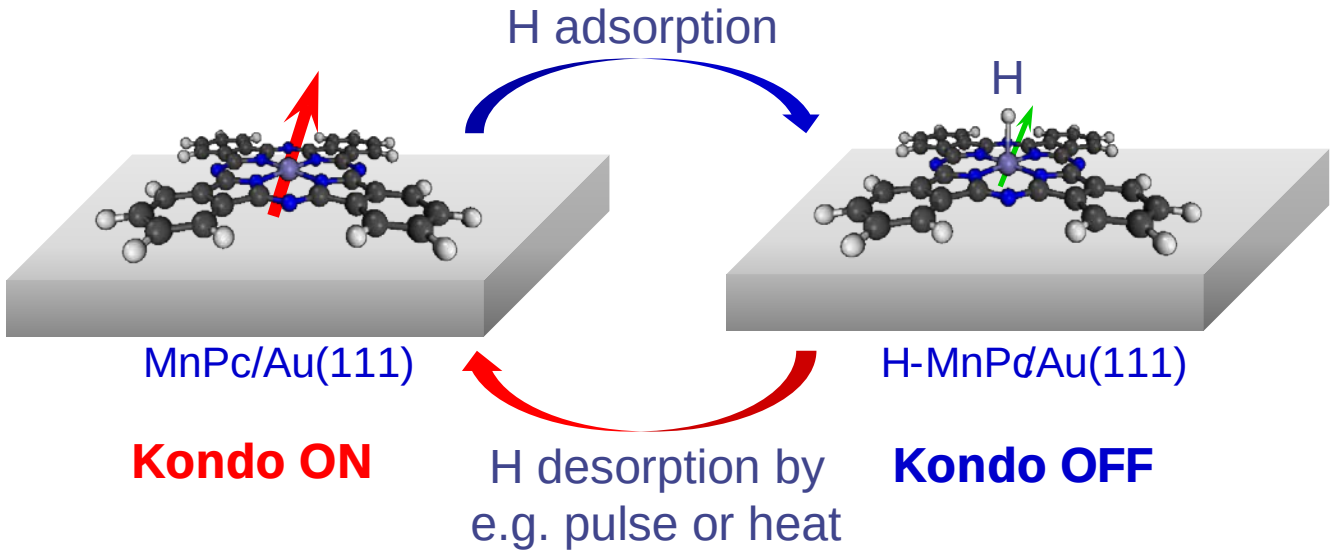
What Can be Done Using the Kondo Switching ?

1. Reduction of spin
2. Larger distance between Mn and Au

Both of the two factors lead to a lower interaction J and a lower Kondo temperature (T_K) below our measurement temperature.

$$T_K \sim e^{-1/\rho J}$$

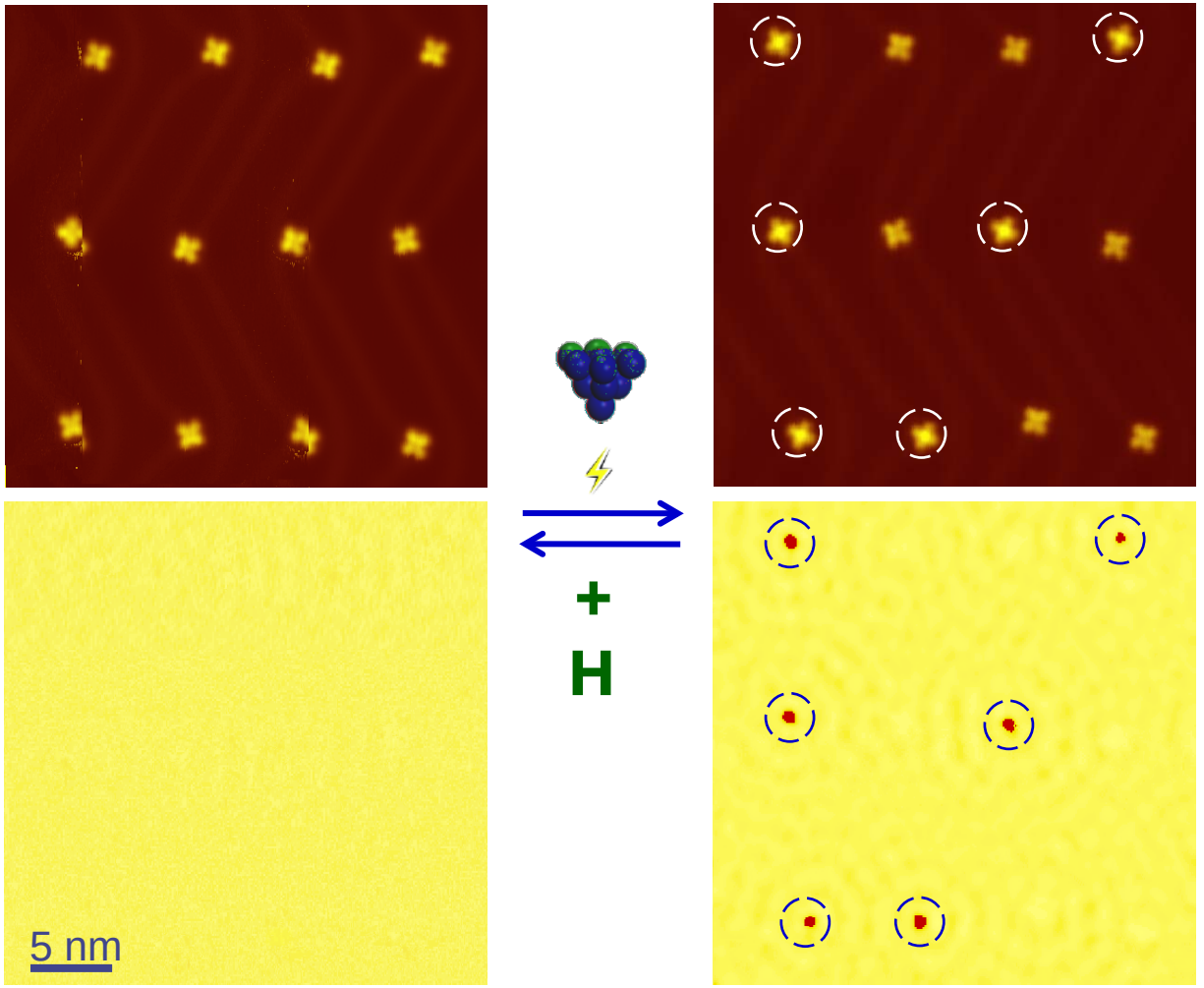
where ρ and J are the density of states at the Fermi energy and the exchange coupling between the spin of the adsorbed molecule and that of the host, respectively



Implication: Quantum Recording and Processing?

Topography

dI/dV mapping

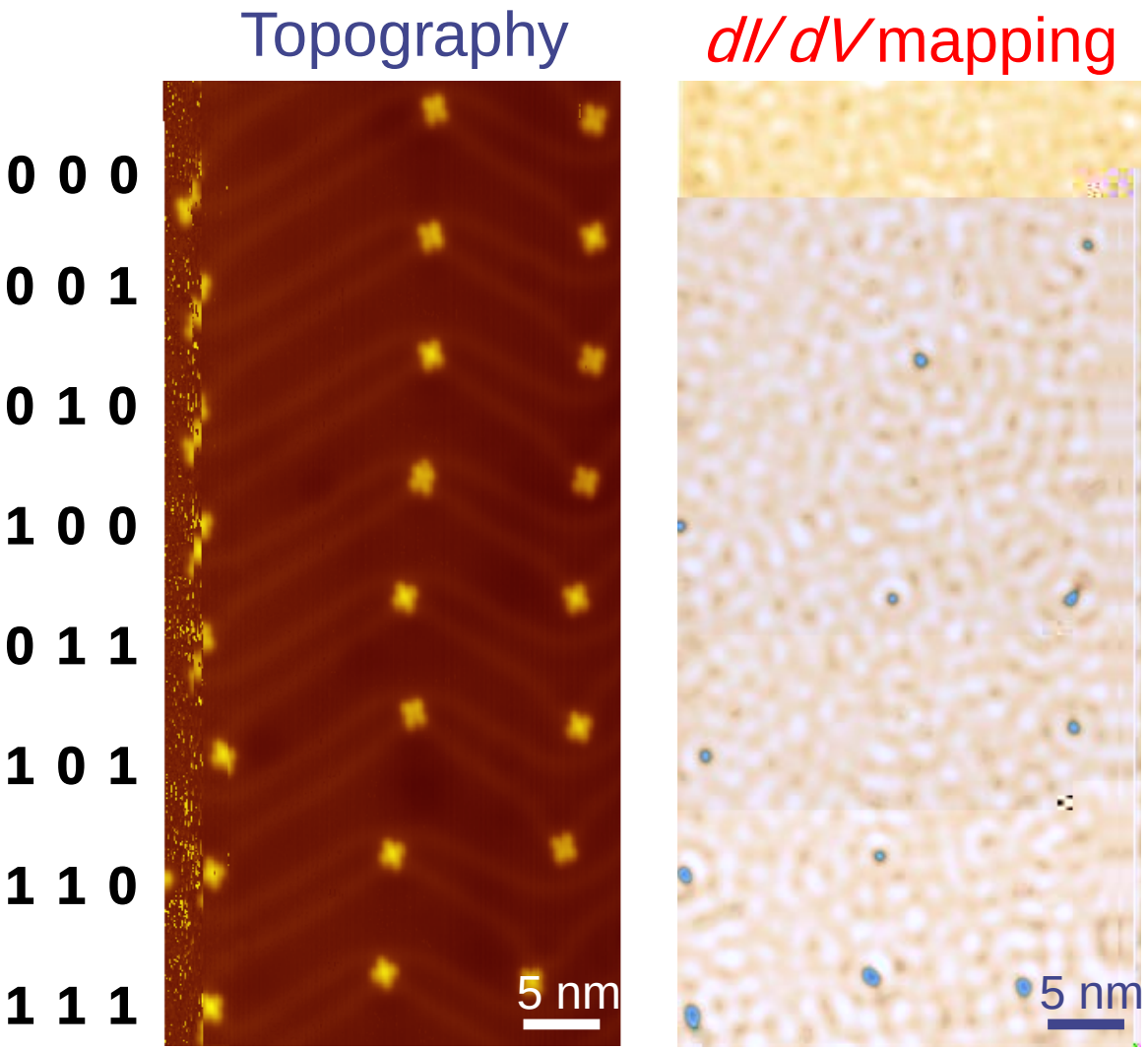


Data Density: 6Tb/inch^2

¾ Kondo On/OFF on this magnetic molecule: a single bit of information recording and storage at the ultimate molecular limit!

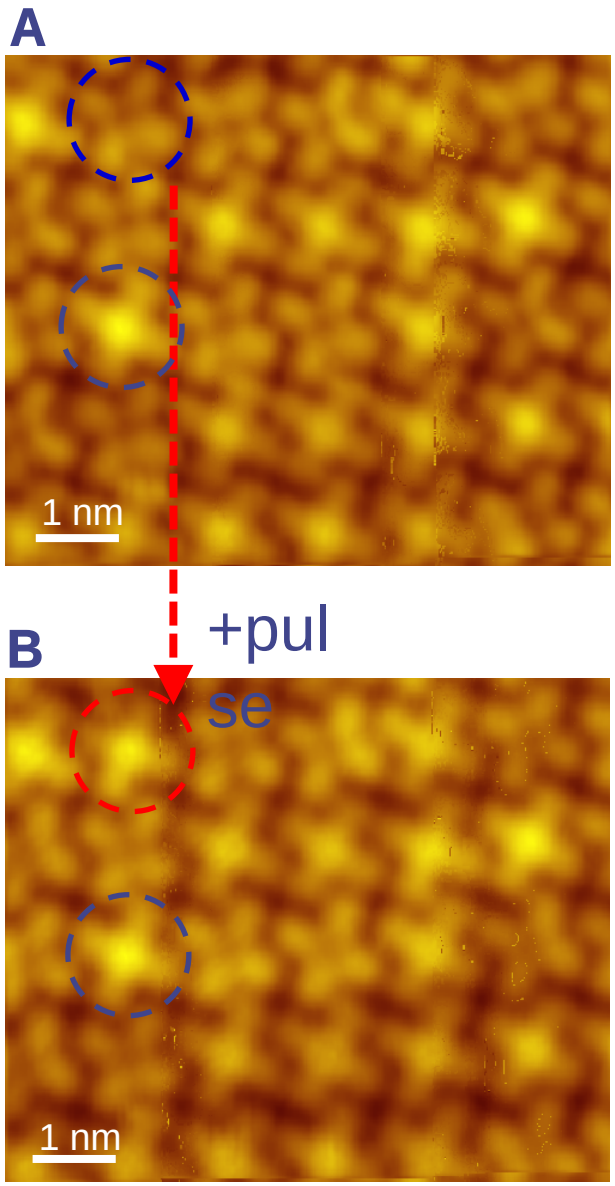
¾ This process can be realized in an ordered molecular array, patterns

Reversible Spin OFF-ON Switching in 3× 8 Molecular Arrays by Kondo Effect and Data Recording



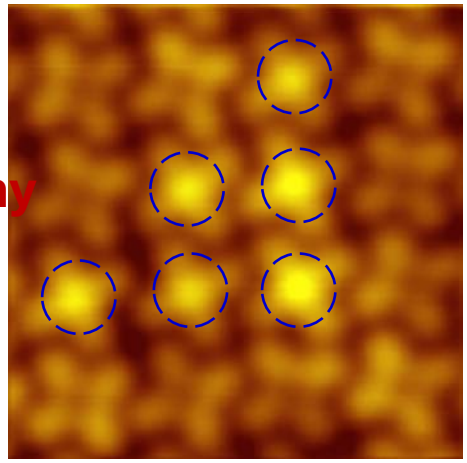
In Closely-packed Molecular Arrays

Reversible Spin OFF-ON Switching by Kondo Effect

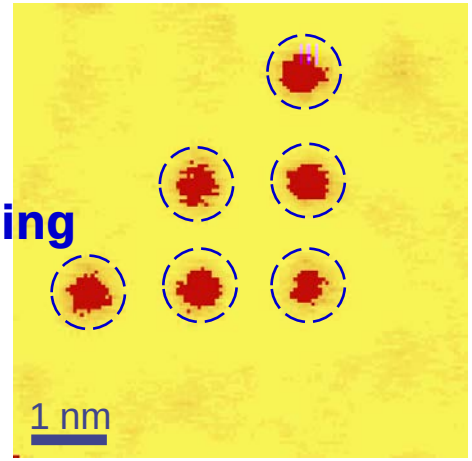


C

Topography

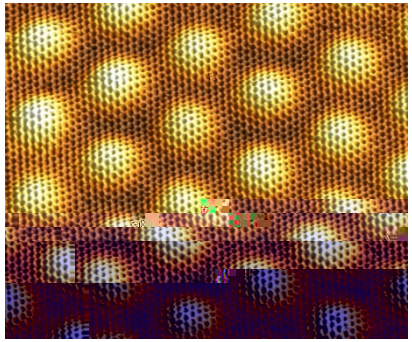


dI/dV mapping



Spacing: 1.5 nm

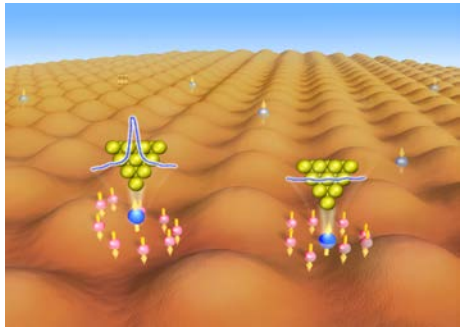
Density: 280 Tb/inch^2

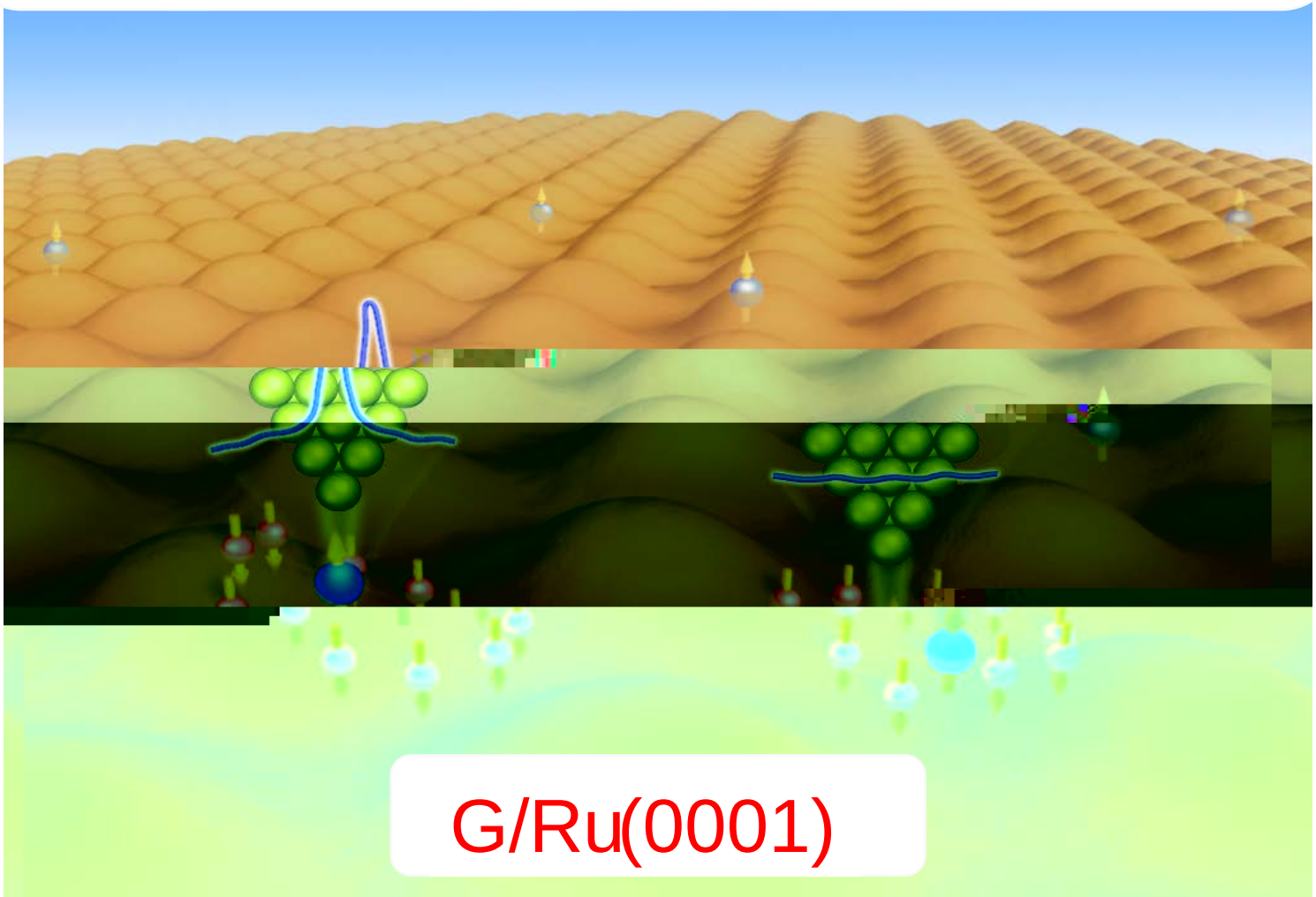


Co

mK-

STM

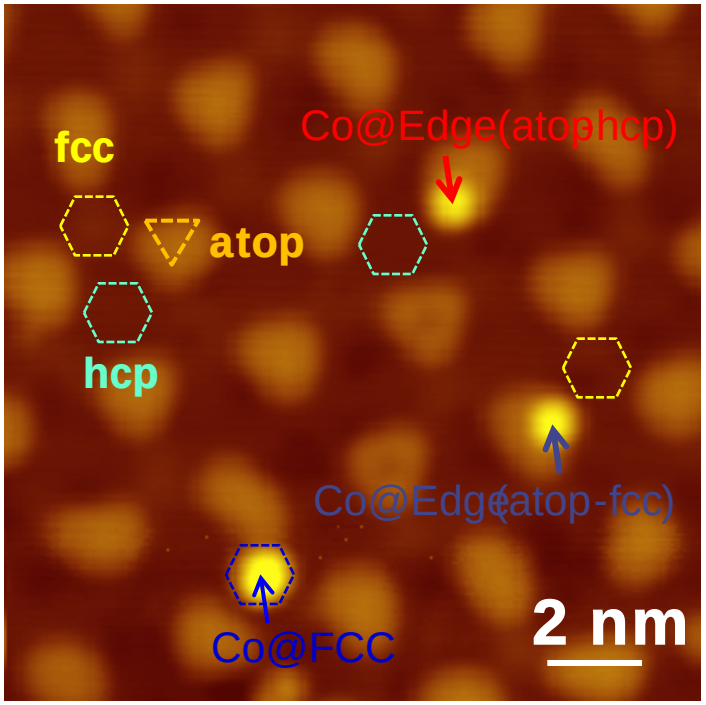


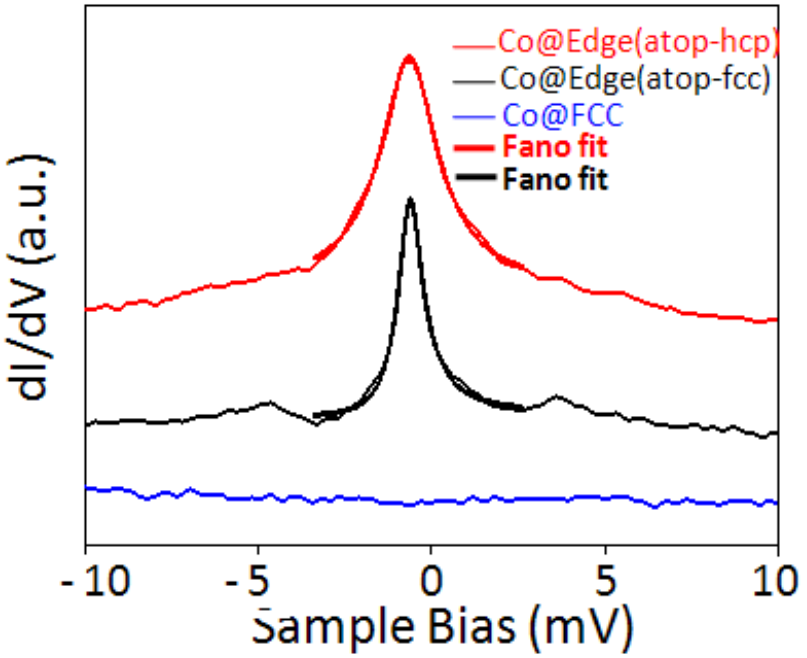


G/Ru(0001)

Co Atoms at Different Sites of G/Ru: STM & STS

Co atoms are deposited onto G/Ru(0001) at ~ 20 K.



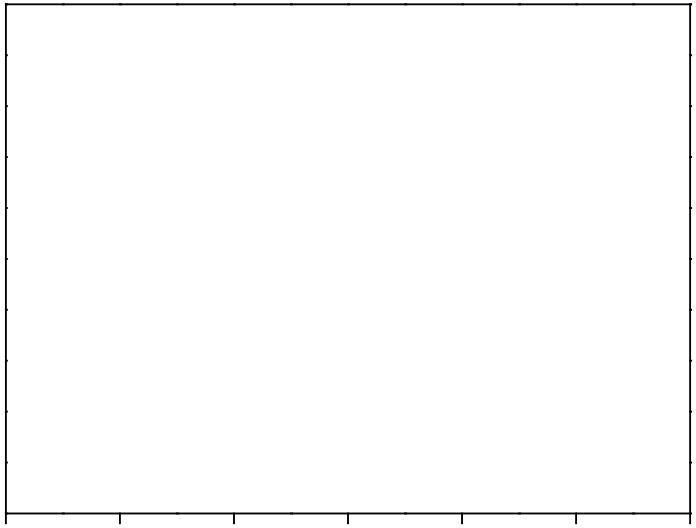


¾ Three Co adsorption regions: hcp, fcc, and edge of atop regions (>50%)

¾ Co@edge can be divided into two different kinds of species: facing to the fcc side (Co@edge(atop-fcc)) or to the hcp side (Co@edge(atop-hcp)).

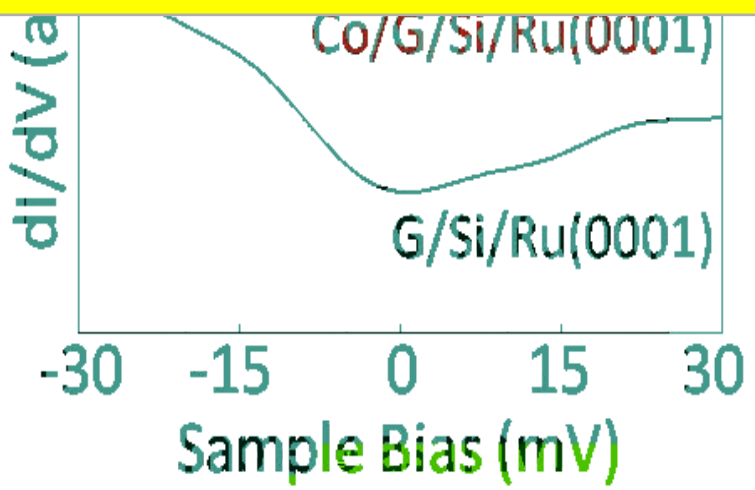
¾ Only Co adatoms at edge sites show Kondo peaks around E_F;

¾ T_K of Co@edge(atop-hcp) and Co@edge(atop-fcc) is 12.10 ± 0.10 K and 5.39 ± 0.06 K by fitting the Fano formula, respectively.



dI/dV Spectra of Co Adatom on G/Si/Ru(0001)

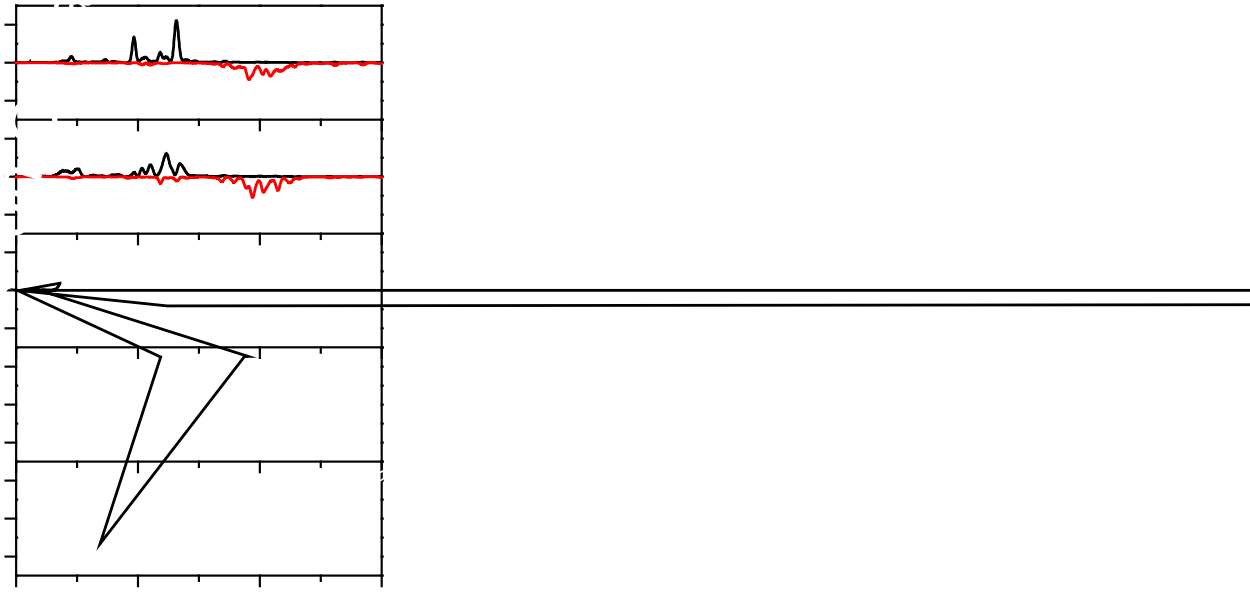
- Si Ru Si
- Co Kondo



¾ The intercalation of Si weakens the interaction between graphene and substrate.

¾ It makes the DOS at the E_F vanish as in freestanding graphene, thus quenching the Kondo effect.

Electronic Structures of Co



	atop	edgesatop	
		/hcp	/fcc
d/nm	0.51	0.46	0.47
E_b/eV	4.20	4.30	4.28
B	1.0	1.0	1.0
LDOS/a.u	0.1	0.8	0.7
Tc/K	no	12.10± 0.10	5.39± 0.06

¾ G/Ru(0001) ,X

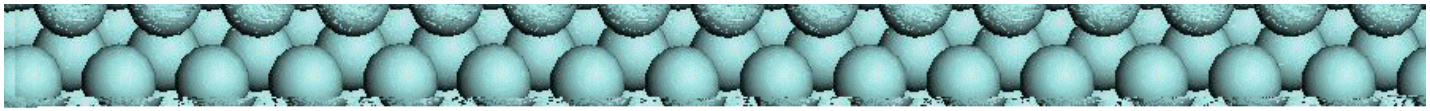
atopE•

+ !5B Þ L ,X Co s $ K ÝEW û.•-½ `EÖ Ü,X Õ š z È ü "#ý ß Ä4.2 K Å?–# E¥;¸ h Ä

¾E- ü

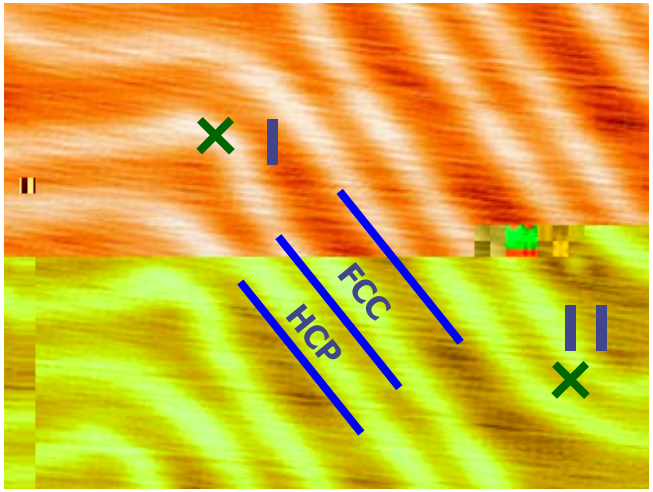
Ä

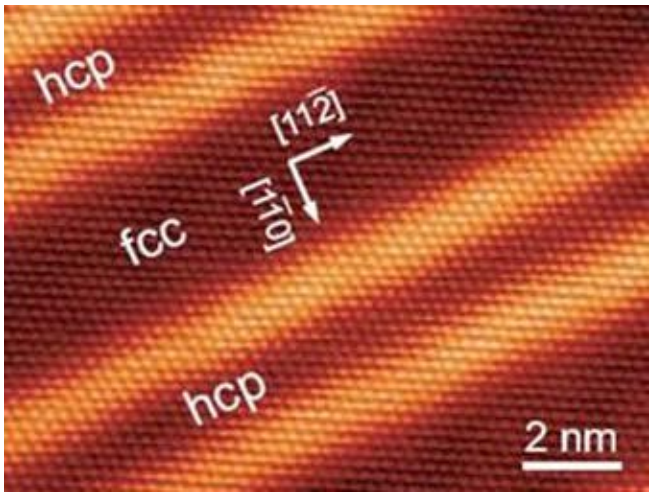
Conclusions and Outlook



- Construction of an Anchored and Offtered Single Molecular Rotor Array

Conclusions and Outlook

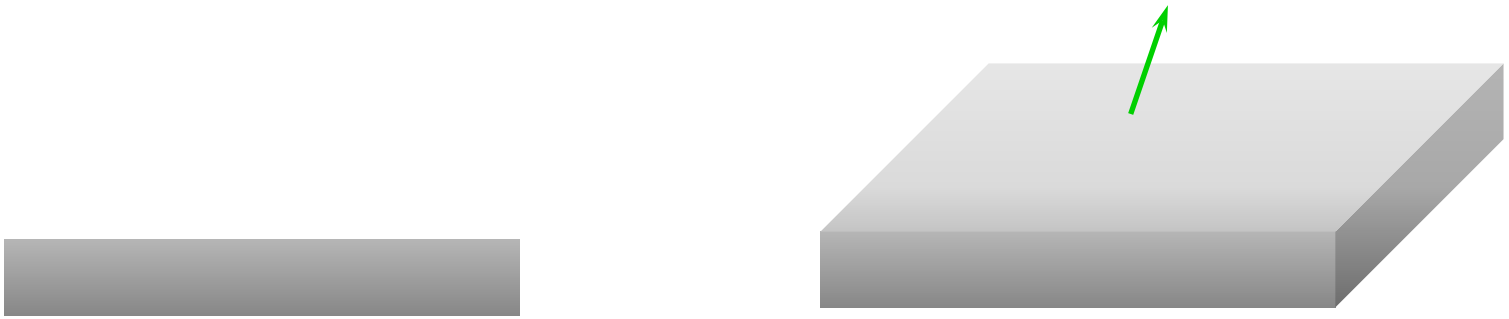




- Manipulating Single Molecular Rotors using Different Locations

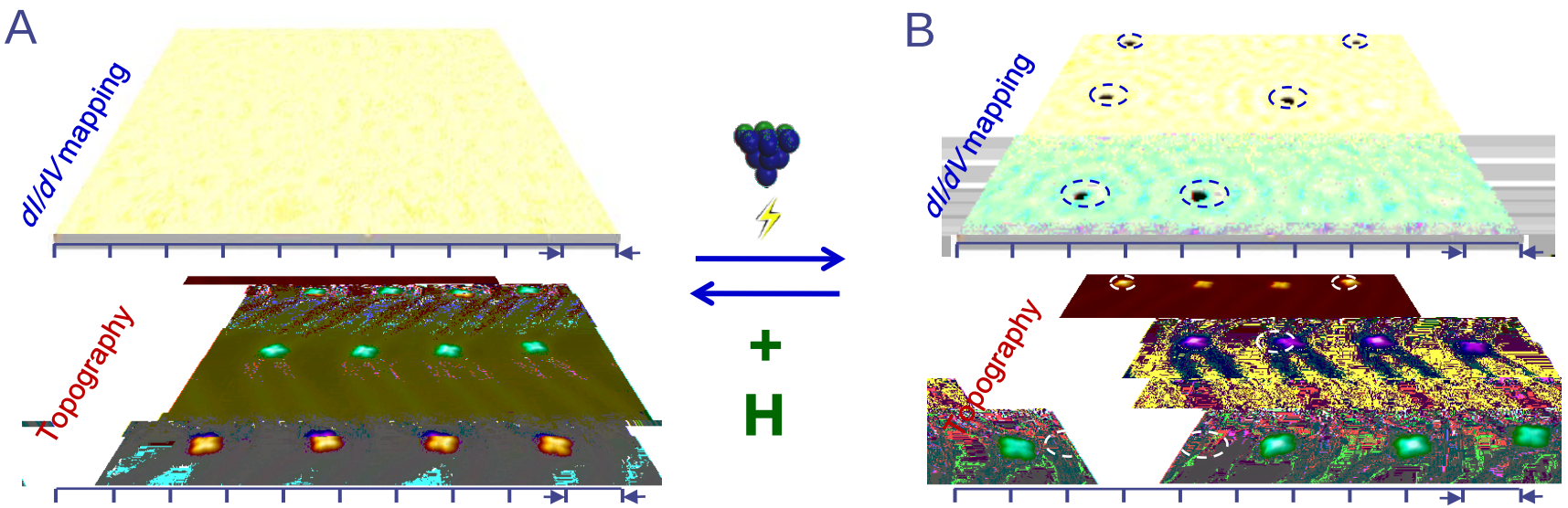
Conclusion and Outlook

- Reversible single spin control has been demonstrated on individual molecules



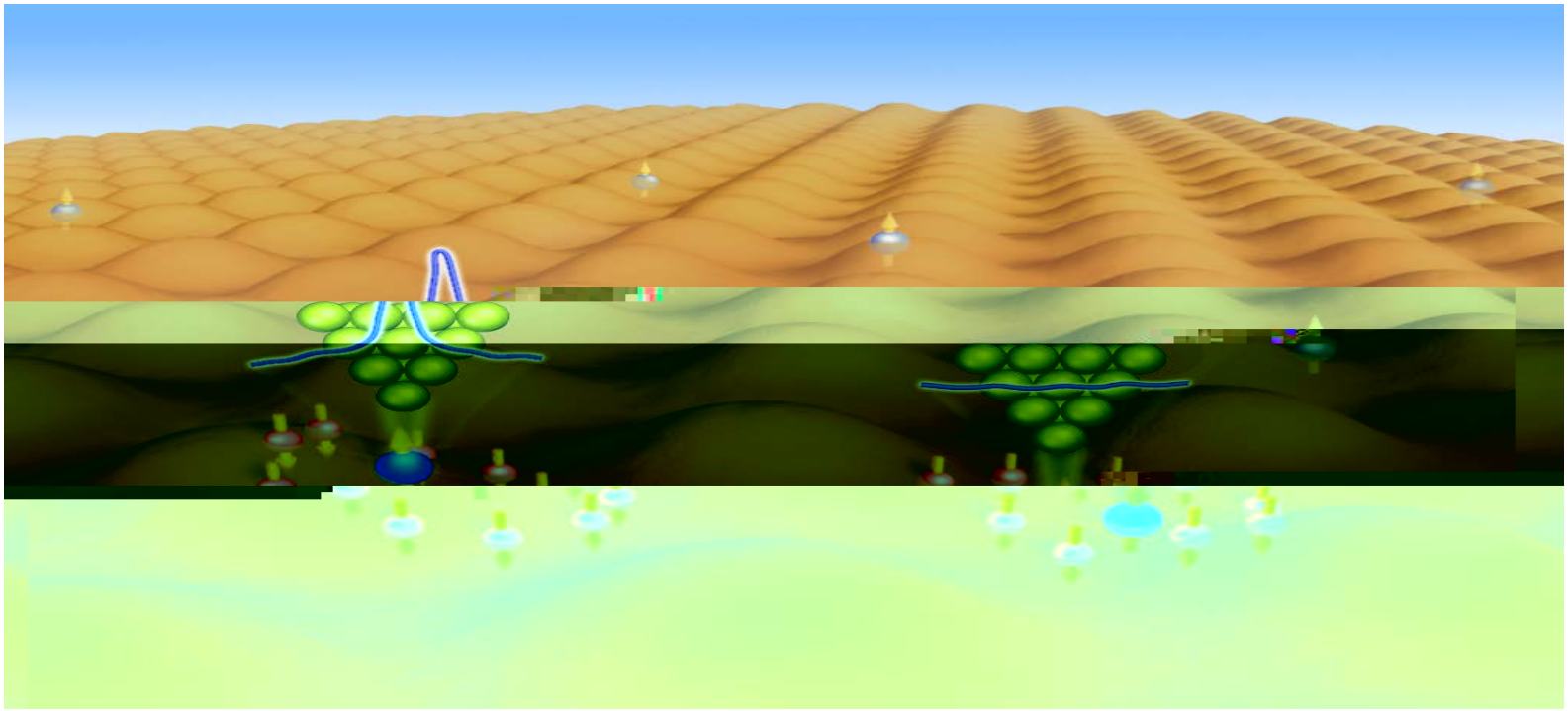
Conclusion and Outlook

- Potential application in quantum data recording or processing.



Conclusions and Outlook

- We observed the site-specific Kondo effect of Co adatoms on a rippled graphene at a Ru(0001) surface.
- DFT calculations show that the delicate balance among the local spin, the LDOS at the Fermi energy, and their coupling are crucial factors in generating the Kondo effect for magnetic impurities on graphene.

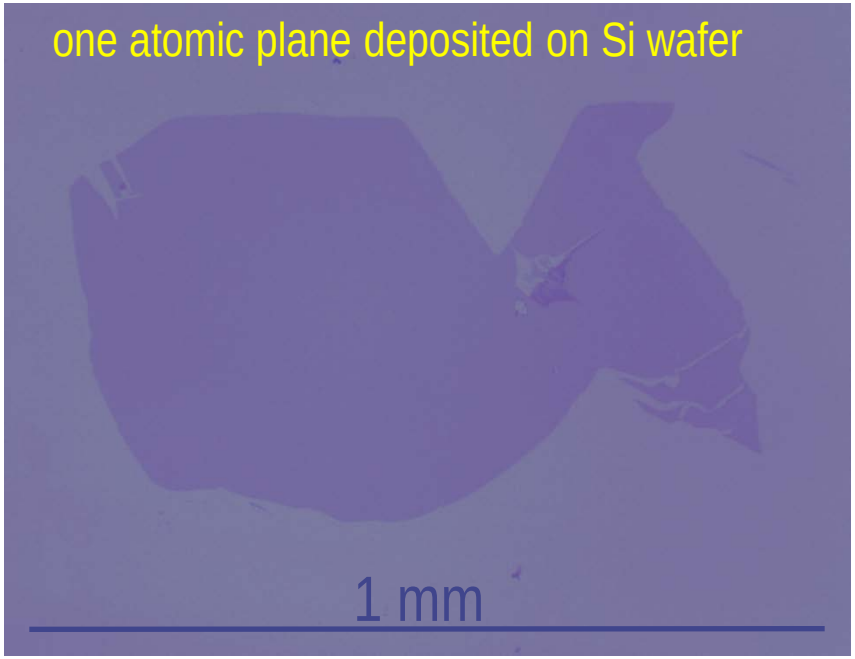


Exploration of Novel 2D Atomic Crystals

- Graphene
- Silicene
- Hafnene
- ...??? and beyond

Starting with graphite

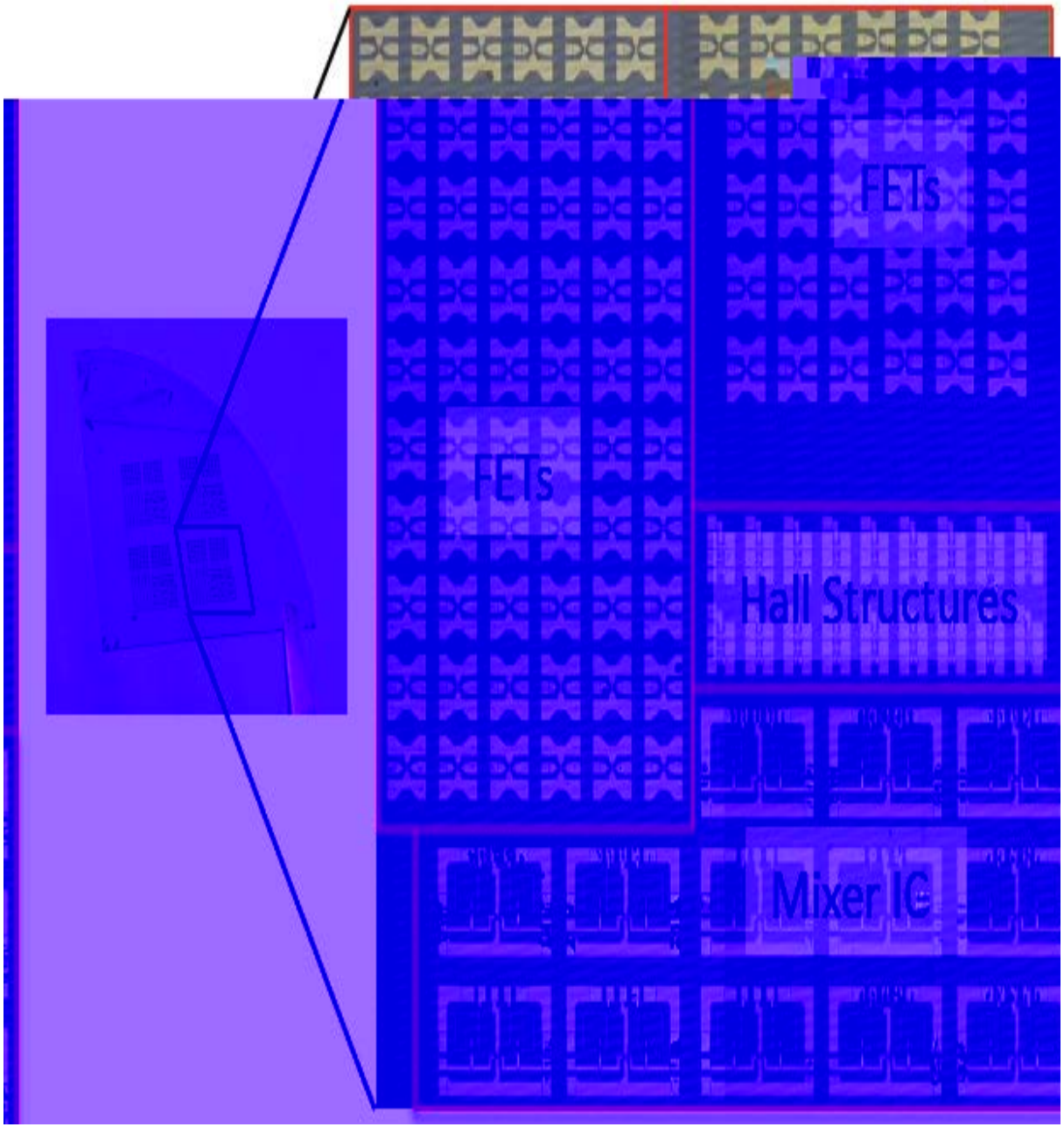
Split into increasingly thinner “pancakes”



Split off
a single layer
called GRAPHENE

Geim *et al*., Manchester, *Science* 2004

5 nm
(e)


FETs
FETs
Hall Structures
Mixer IC

Operation of Graphene Transistors at Gigahertz Frequencies

Yu-Ming Lin,* Keith A. Jenkins, Alberto Valdes-Garcia, Joshua P. Small, Damon B. Farmer, and Phaedon Avouris

IBM T.J. Watson Research Center, Yorktown Heights, New York 10598

Received November 3, 2008; Revised Manuscript Received December 9, 2008

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422-426

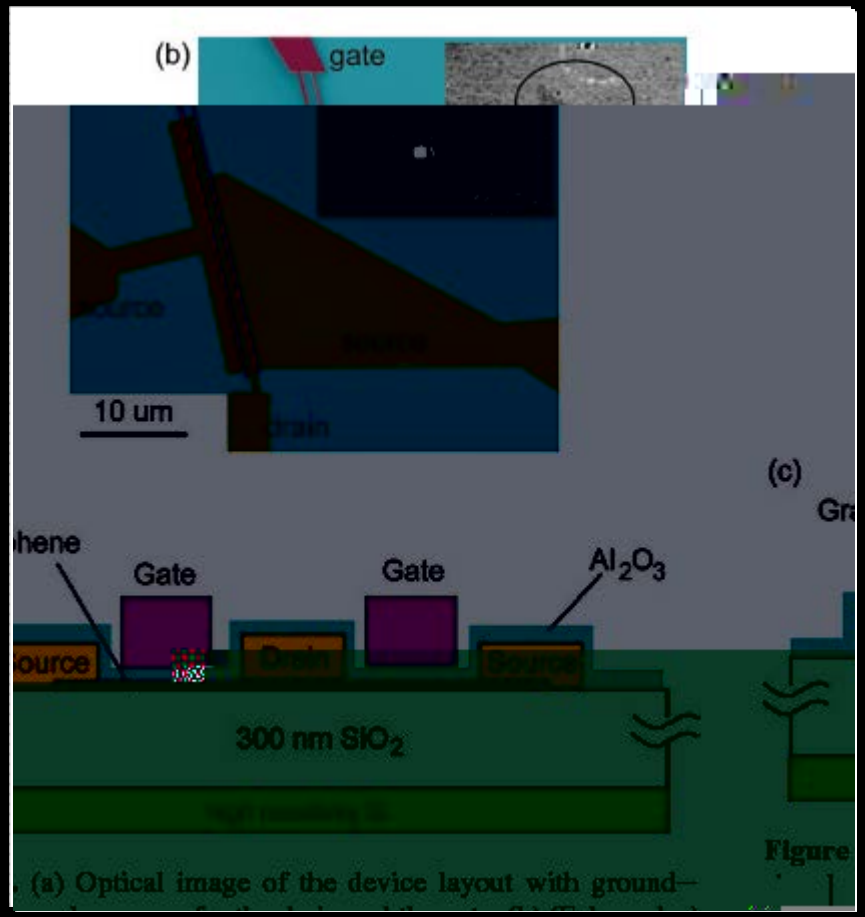
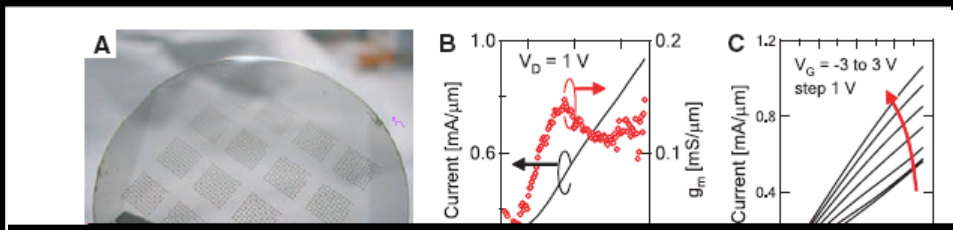


Figure 1. (a) Optical image of the device layout with ground–



Main Challenges about Graphene Applications in Future Electronics

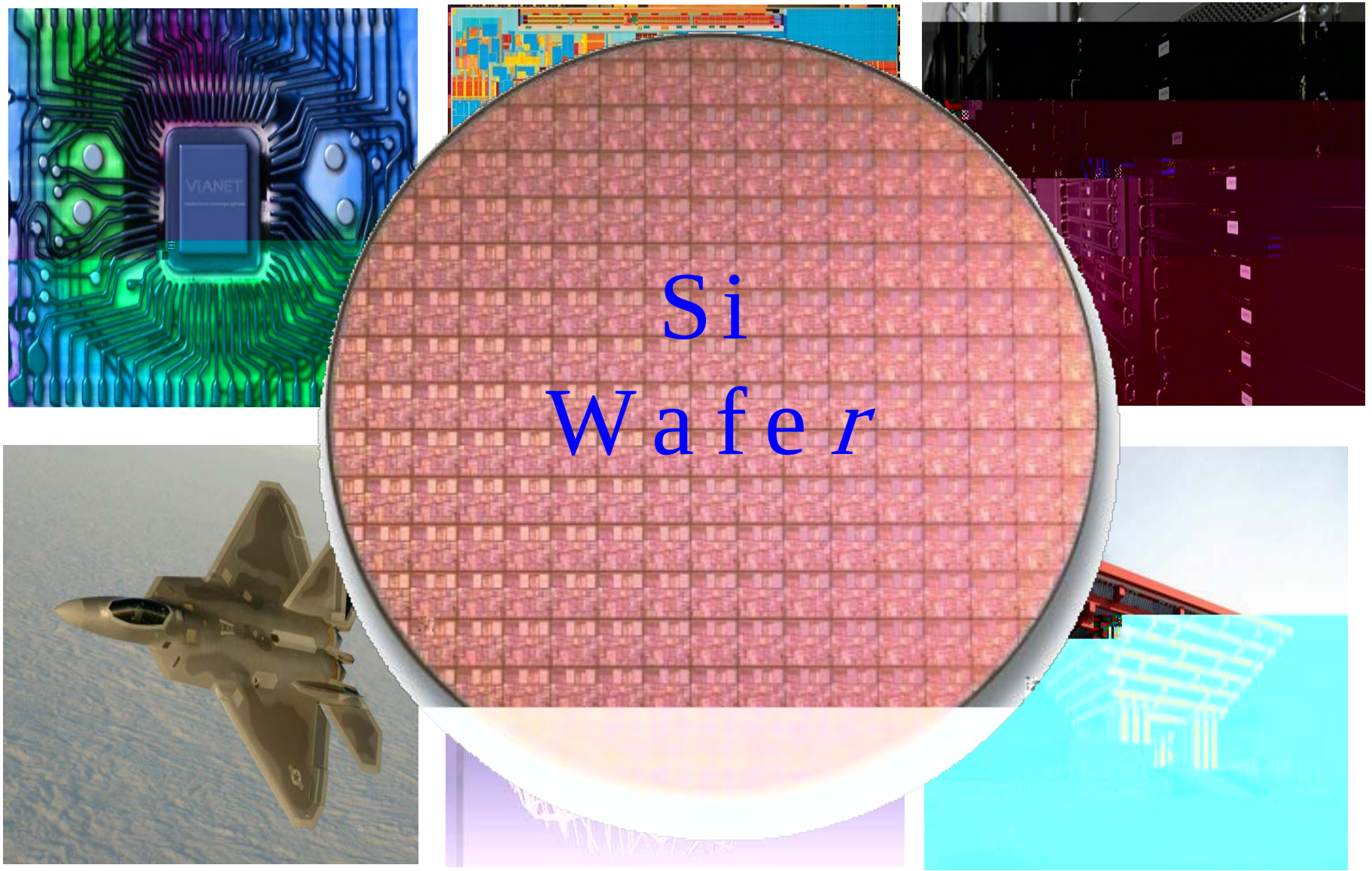
- Fabrication of large-scale, highly-ordered, singe crystalline graphene layers of "High Quality".

m^2

- Compatible to Si Processing Technology.

- Without Transfer Technique.

Similar to the Single Crystal Si Based Science, and Industrial Applications



Highly Ordered, Millimeter-scale, Single Crystalline Graphene Monolayer Epitaxy on Ru (0001)

Y. Pan/H.J. Gao *et al*., Adv. Mater. 21, 2777(2009)

Growth System with *in situ* Analysis Techniques

Analysis Chamber

- LEED
- AES
- STM

Growth Chamber

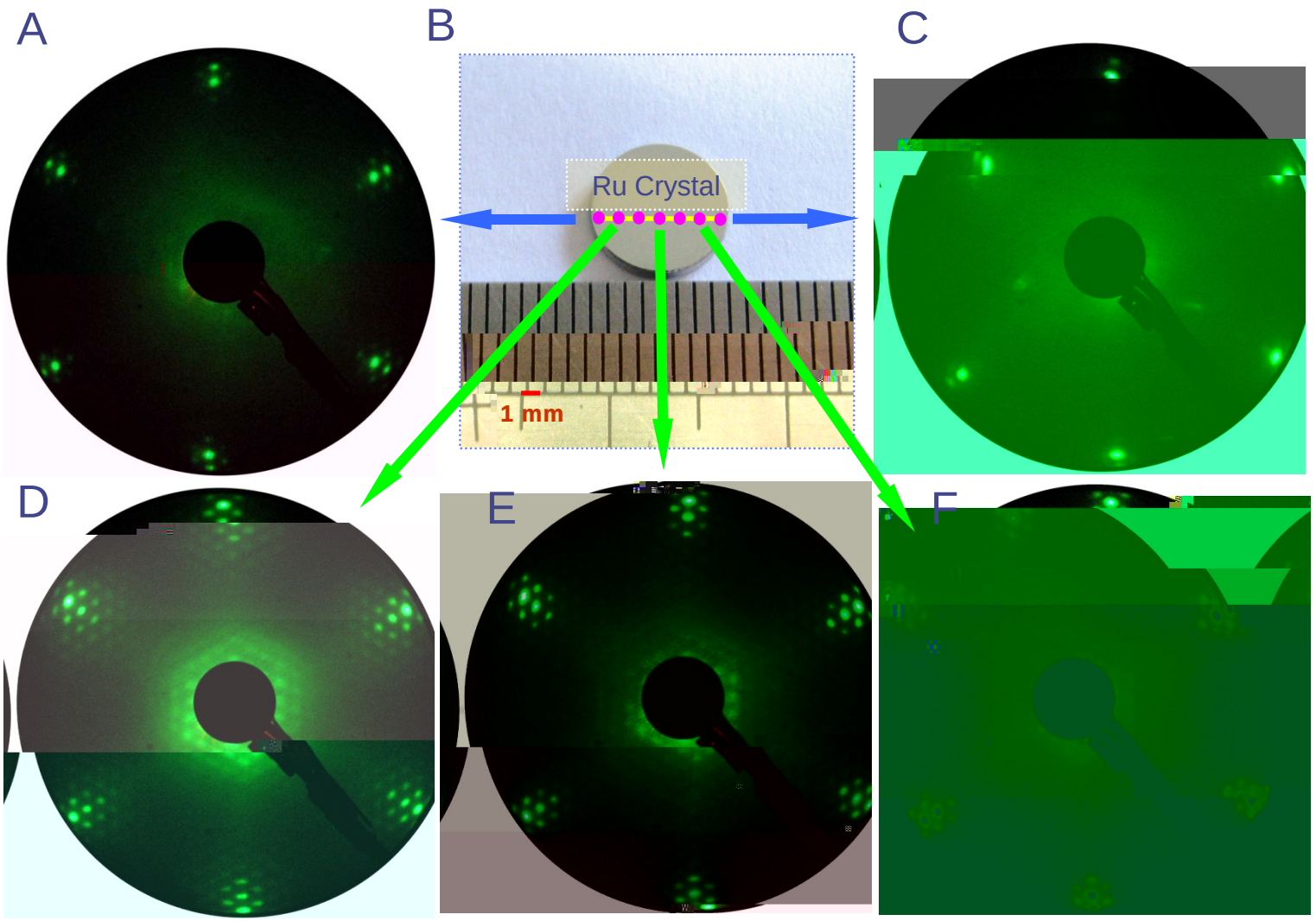
- Carbon Source
- Ar+ Ion gun
- Sample Heater
- Evaporator

Ru, Pt, Ni, Cu, Ir metal crystals have been used

ys. Soc. Vol. 16 No 11, November 2007 Chinese Physics © 2007 Chin. Ph
hing Ltd 1009-1963/2007/16(11)/3151-03 and IOP Publis

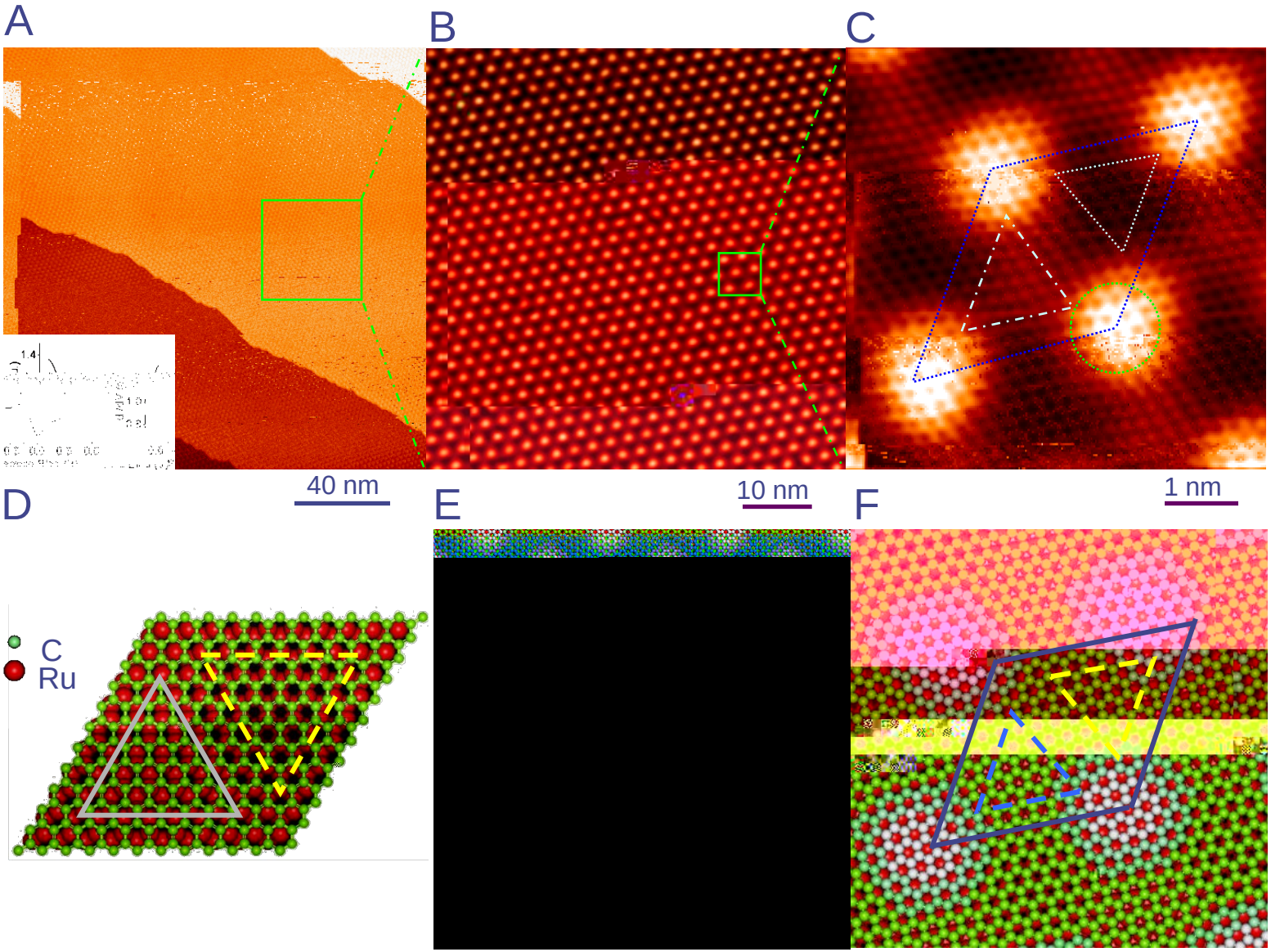
Formation of graphene on Ru(0001) surface*

LEED Patterns of the Graphene/Ru(0001)



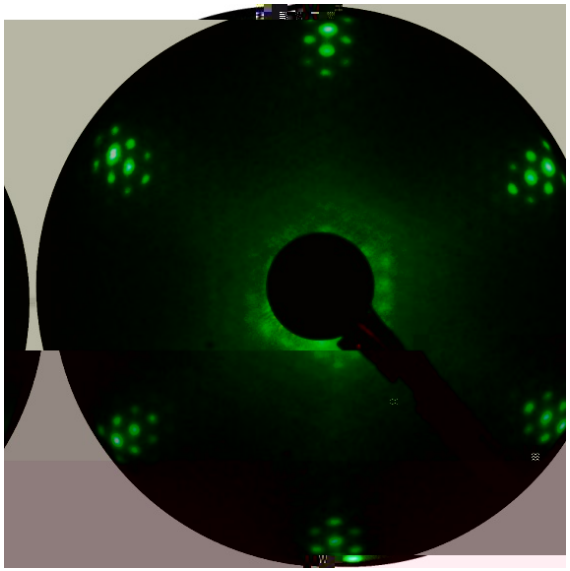
Y. Pan/H.-J. Gao et al., Adv. Mater. **21**, 2777(2009)

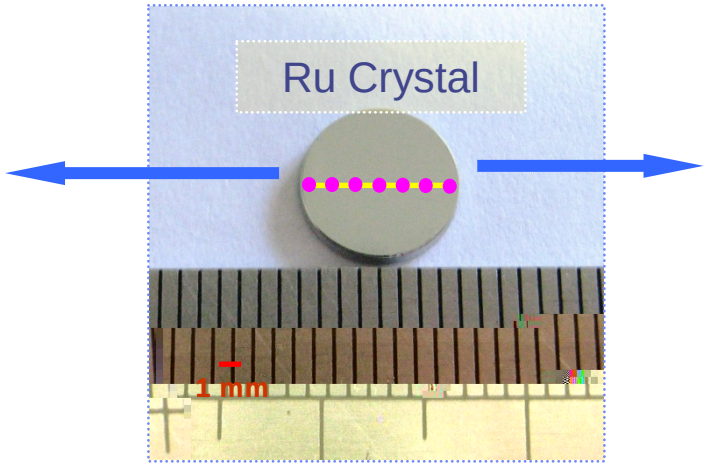
STM Images of Graphene/Ru(0001) and DFT Theoretical Calculations



Y. Pan/H.-J. Gao et al., Adv. Mater. **21**, 2777(2009)

Challenges





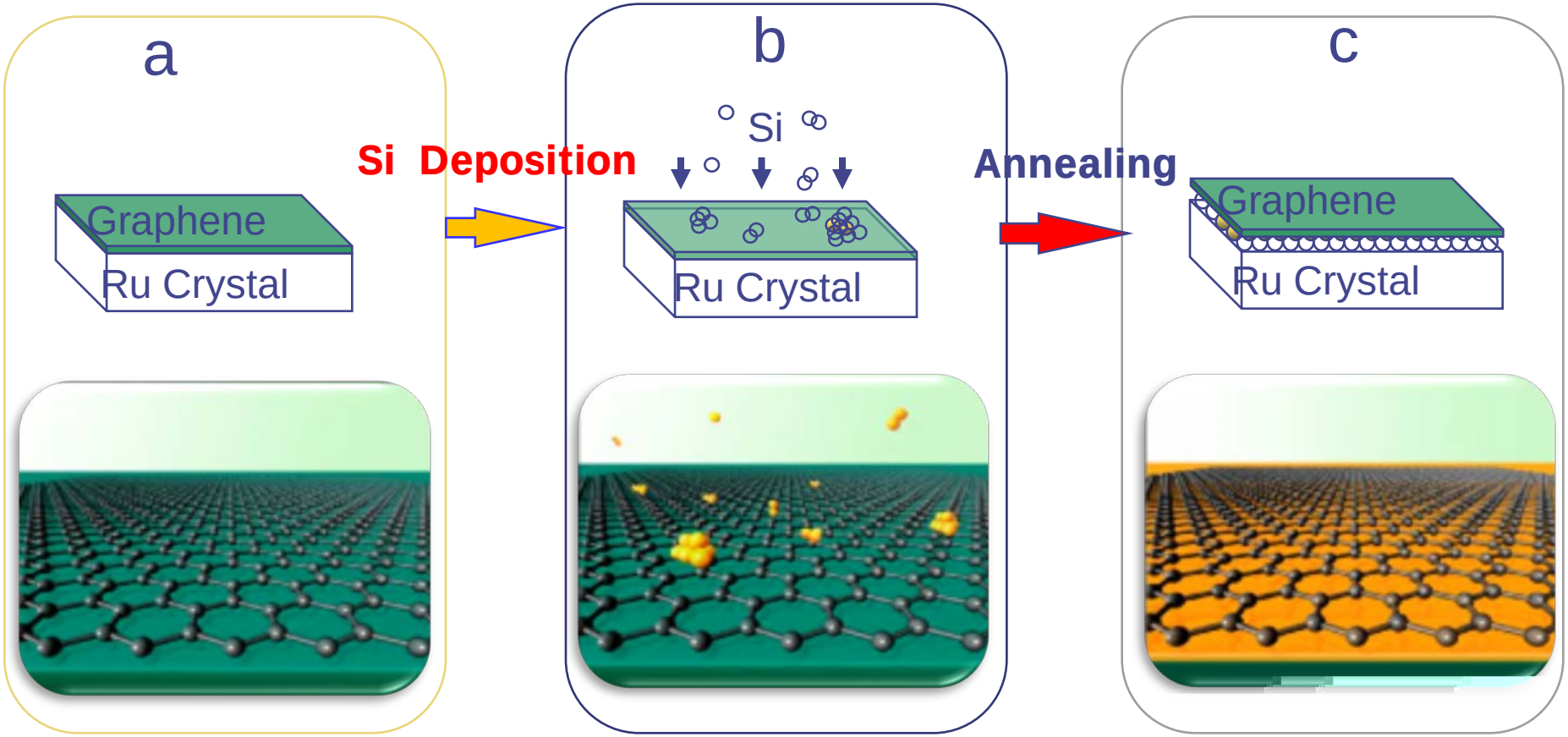
Large-scale Single Crystalline Graphene Monolayer

High Quality !
However,
...

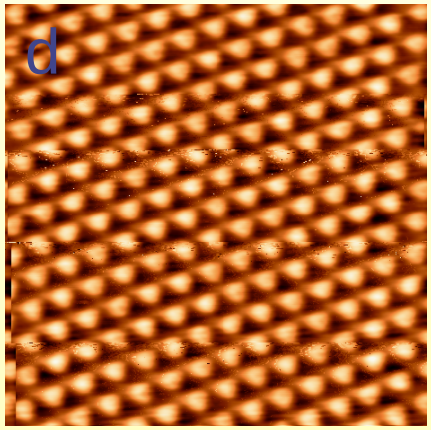
&

1) On insulator or semiconductor
2) Without Transfer ???

Procedure of Silicon-layer Intercalation Approach

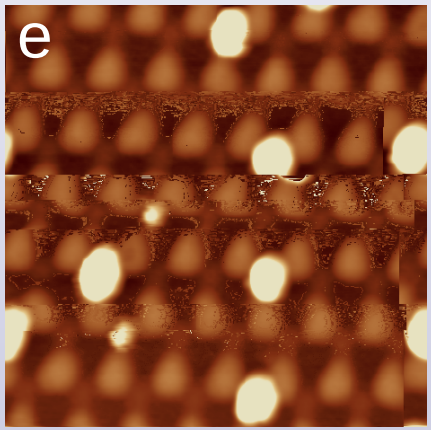


Procedure of Silicon-layer Intercalation Approach



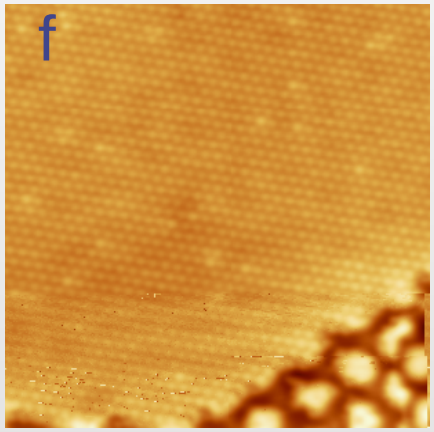
Moiré pattern of Gr./Ru(0001)

Si Deposition



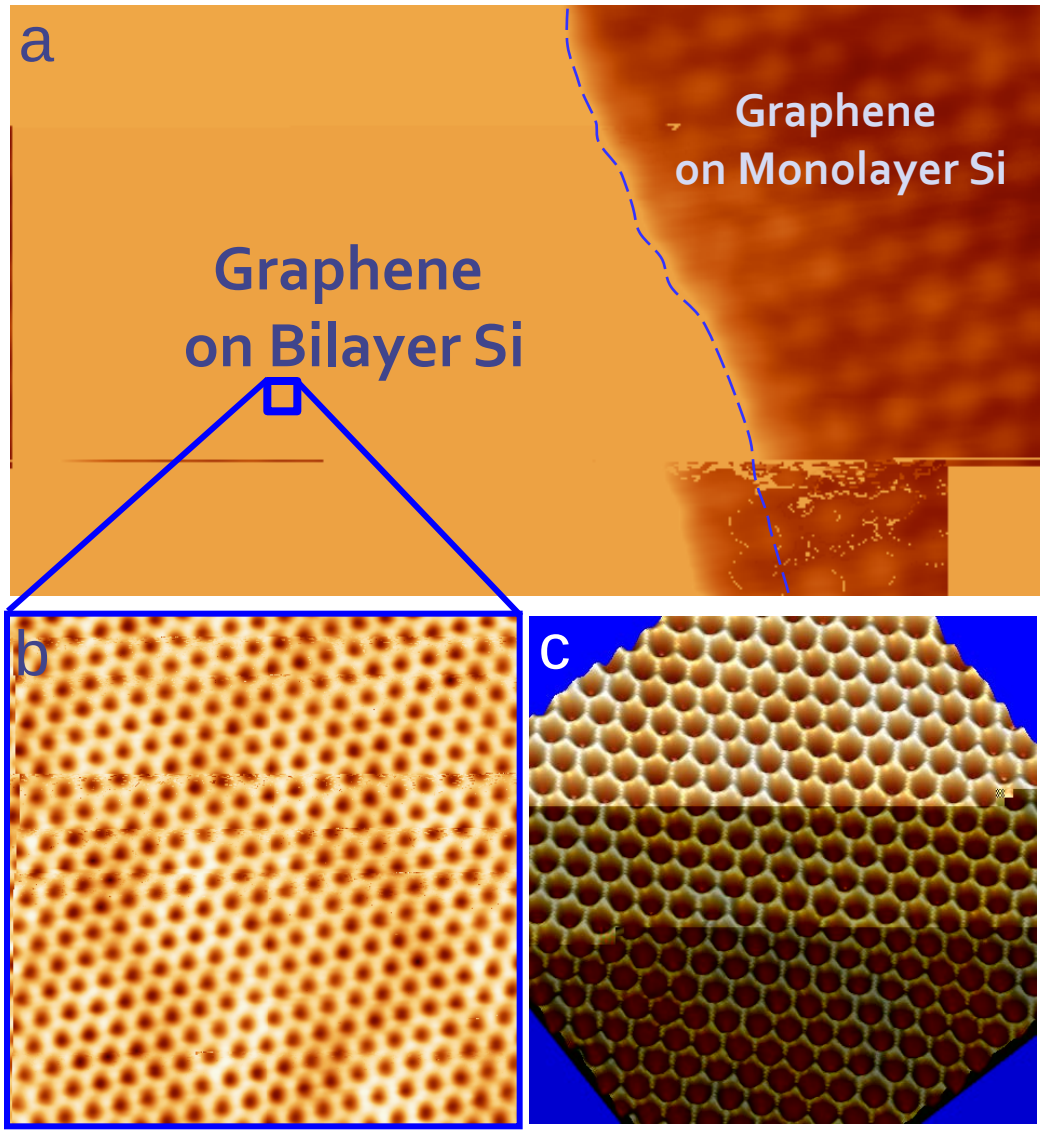
Si clusters at RT

Annealing

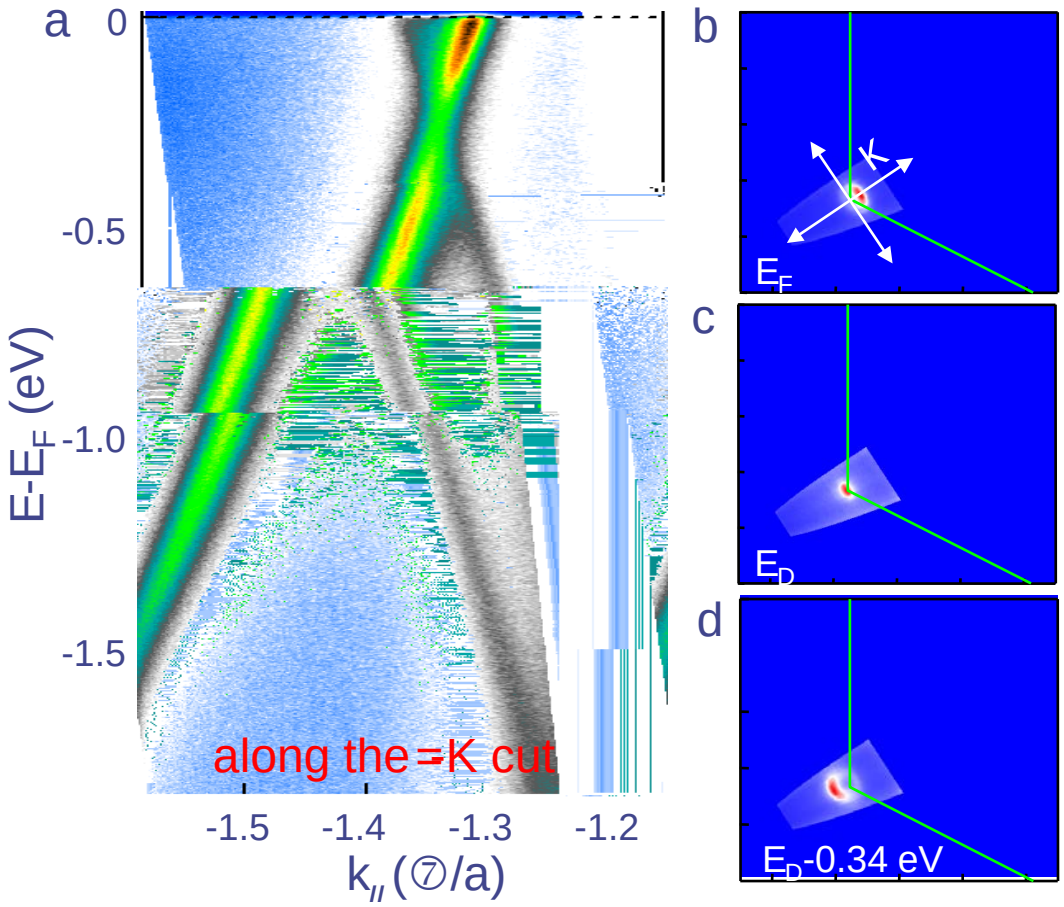


Uniform and flat

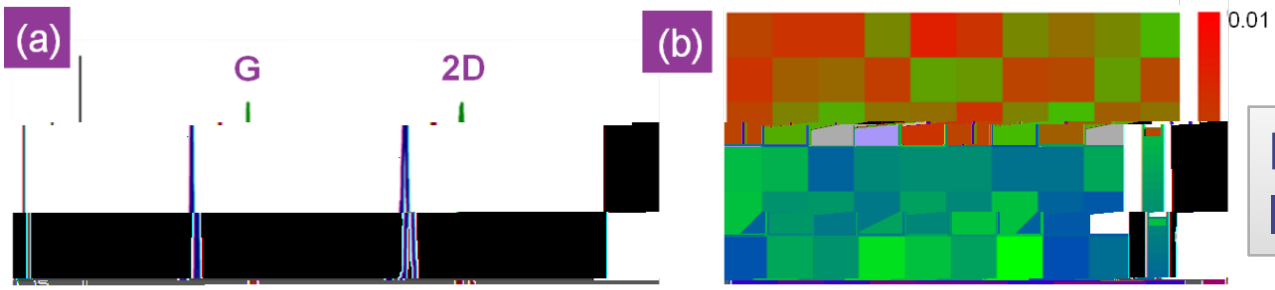
Under Silicon-layer Intercalation



- Graphene becomes uniform and atomic flat.
- Atomic control of the distance between graphene and metal.


a
0
-0.5
-1.0
-1.5
E-E$_F$ (eV)
along the Γ-K cut
-1.5
-1.4
-1.3
-1.2
k$_{//}$ (Å^{-1})
b
K
E$_F$
c
E$_D$
d
E$_D$-0.34 eV

Raman data of GFS i/



Extremely low I(D)/I(G)

Uniform G position

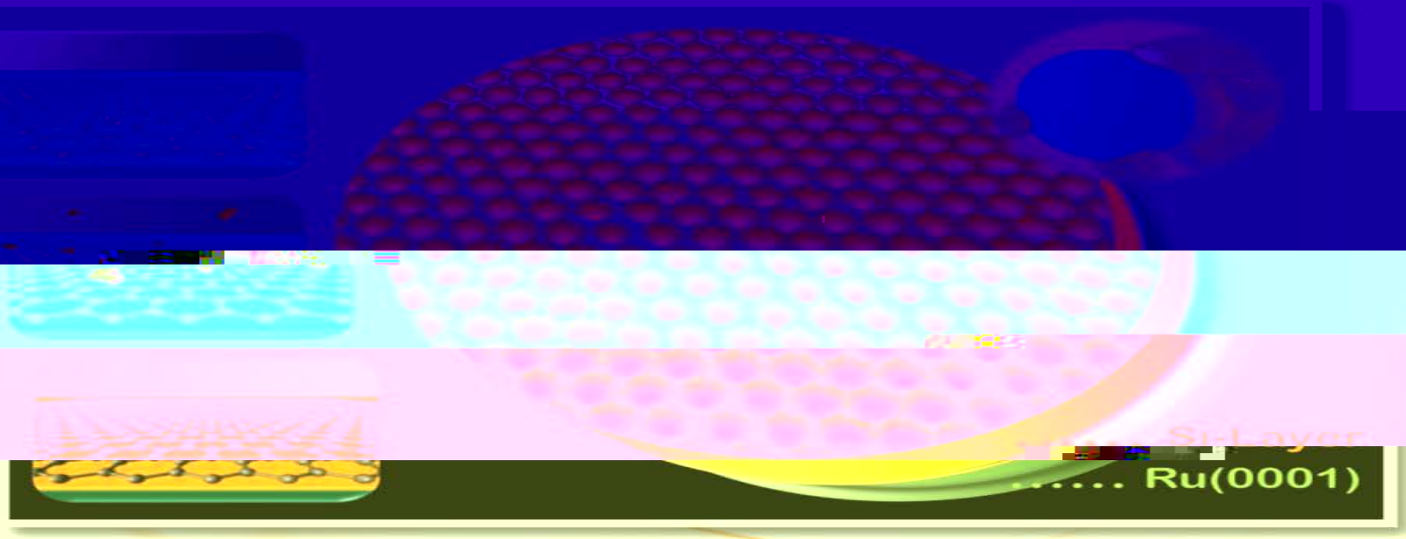
Locate among 1-layer graphene region

After thick silicon-layer intercalation:

¾ **G and 2D peaks are visible and sharp, no D peak.**

27 February 2012 Volume 100 Number 9

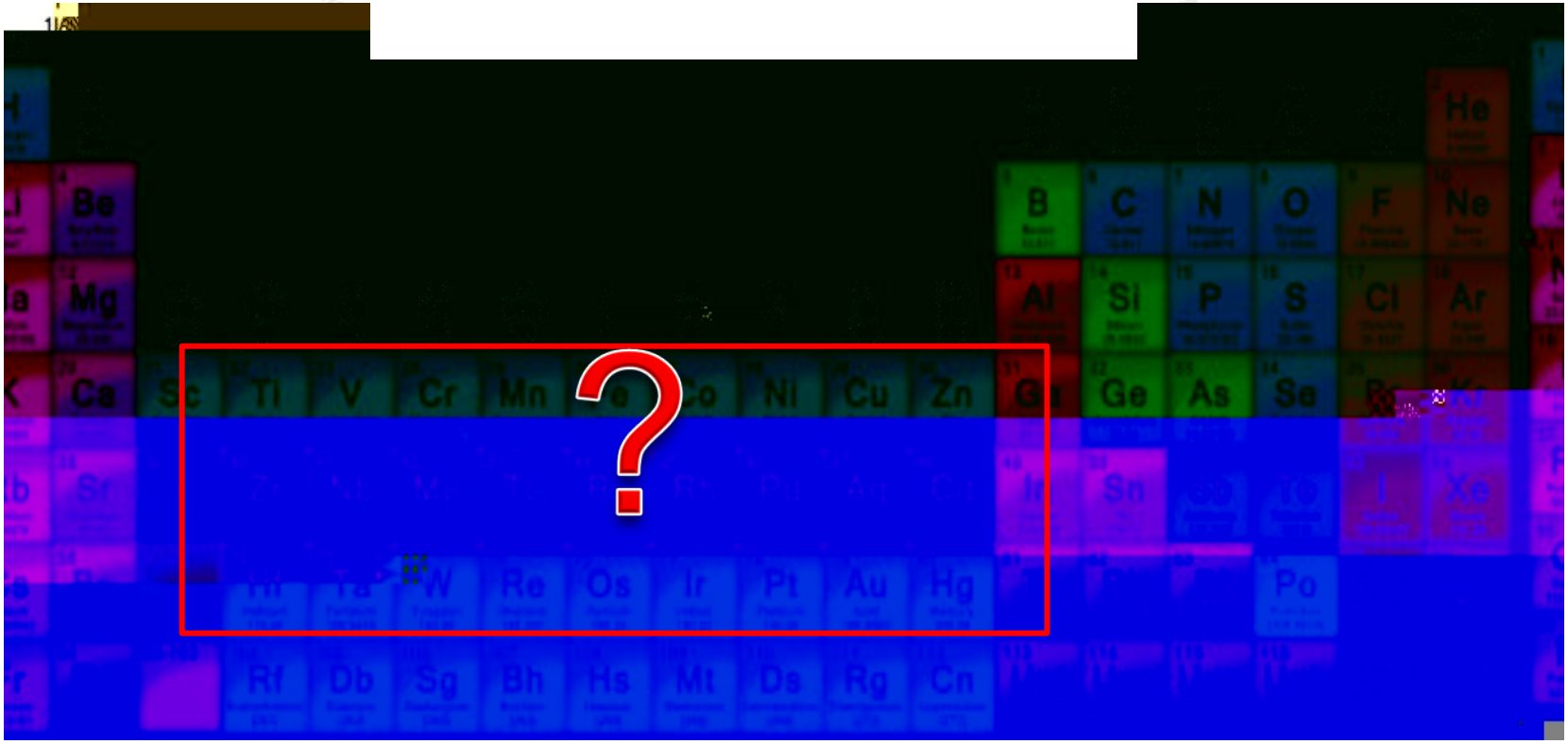
AIP | Applied Physics Letters



Silicon-Layer Intercalation of Epitaxially-grown Graphene on Metal Crystals

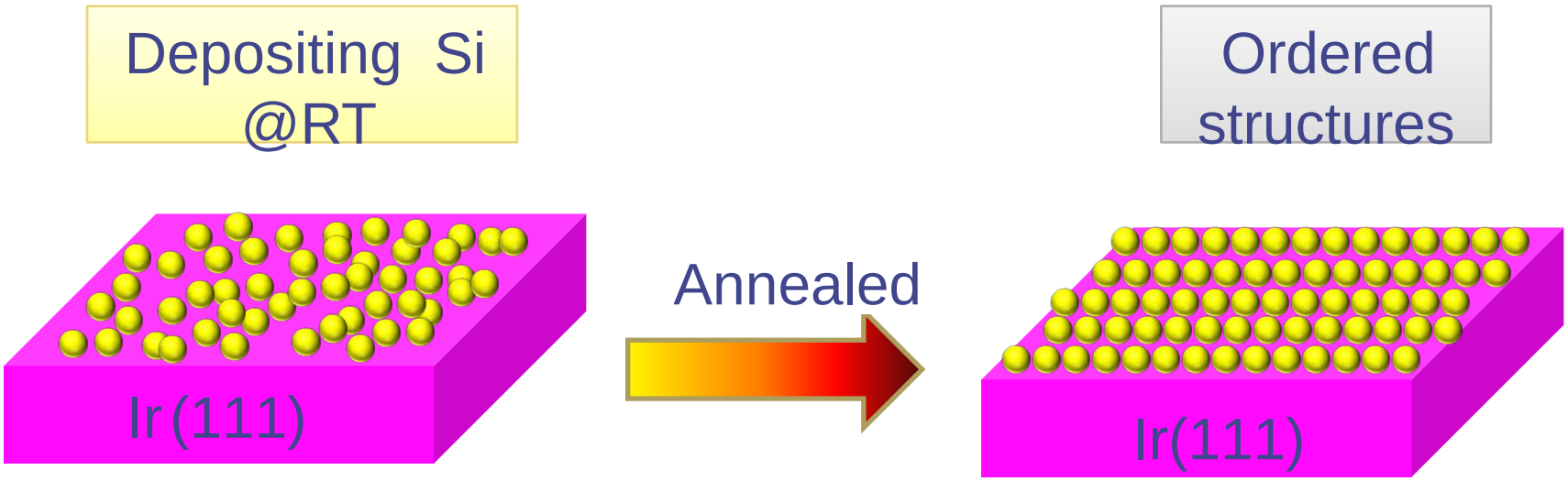
apl.aip.org

Two-dimensional Materials Based on d-block Elements



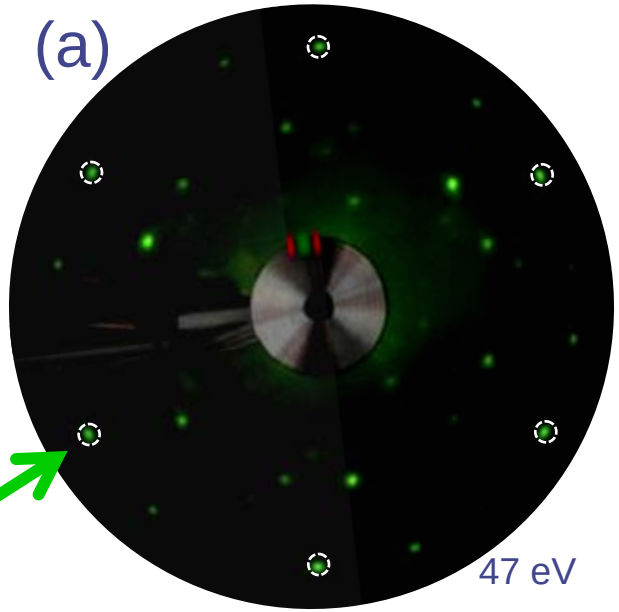
- The reported 2D honeycomb materials are made of elements with p-orbital electronic structure
- with d electrons have not been reported before

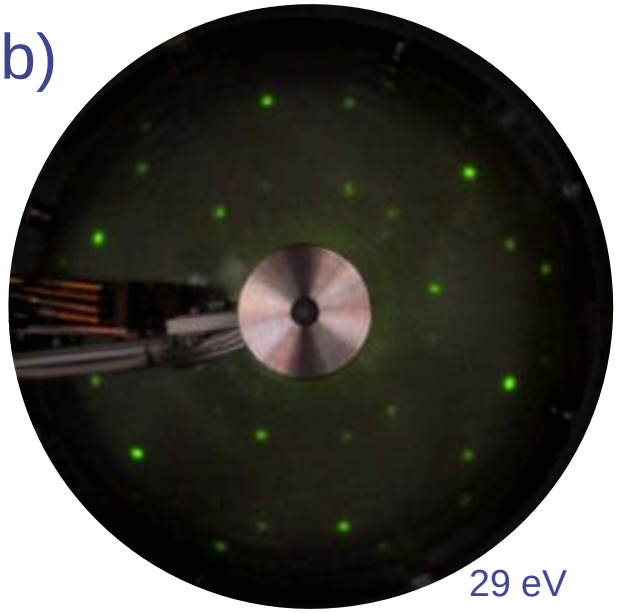
Silicene on Ir(111)



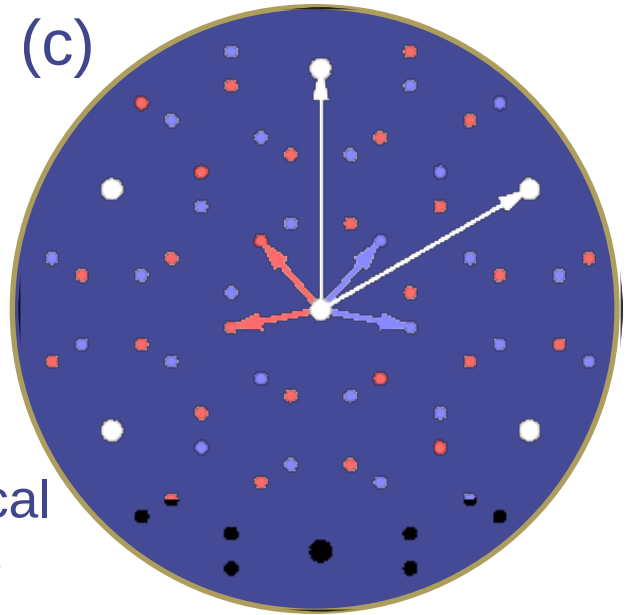
L. Meng *et al.,* Nano Letters **13**, 685 (2013).

LEED Patterns of Si Adlayer on Ir(111)

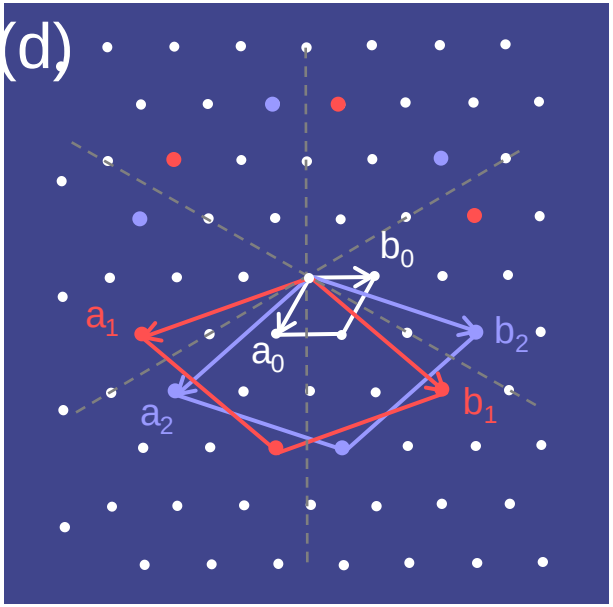




$(\sqrt{7}x\sqrt{7})$
superstructur

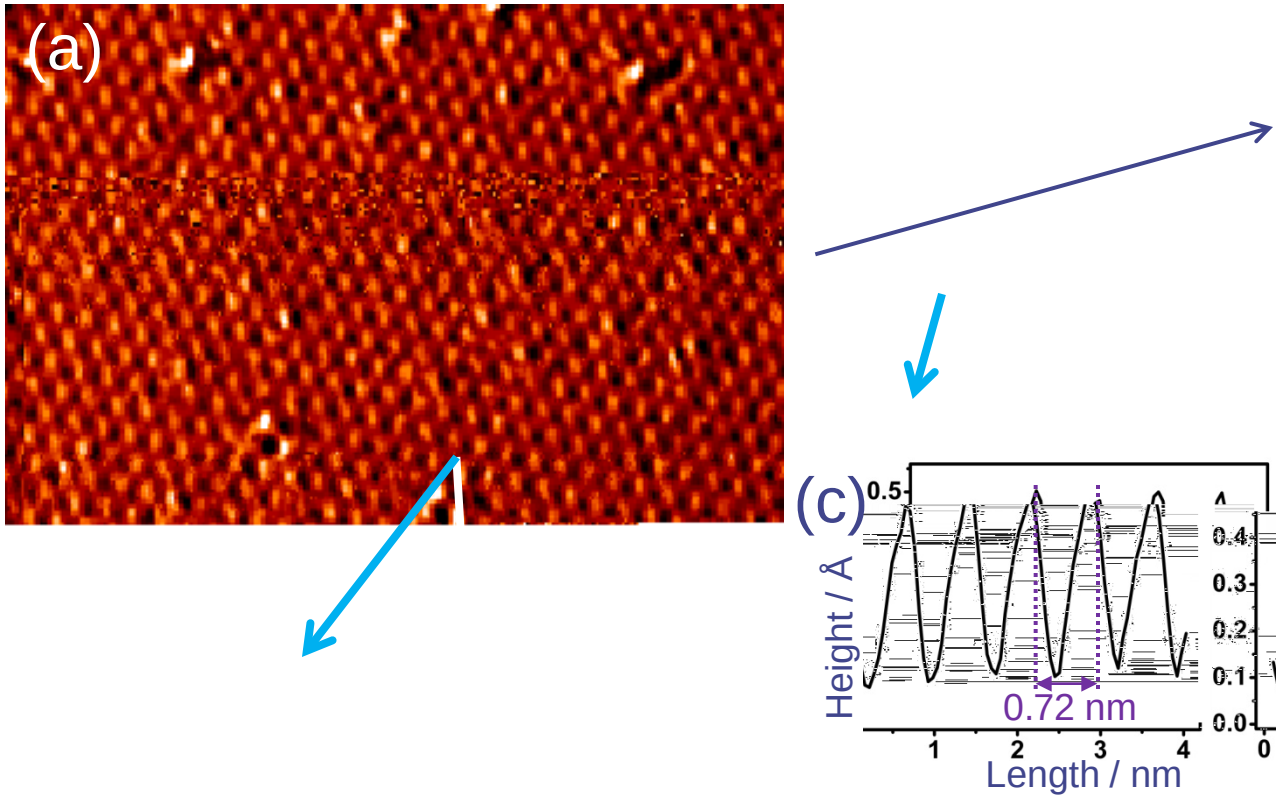


Reciprocal space



Real space

STM Characterization: Buckled Si Adlayer



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nm

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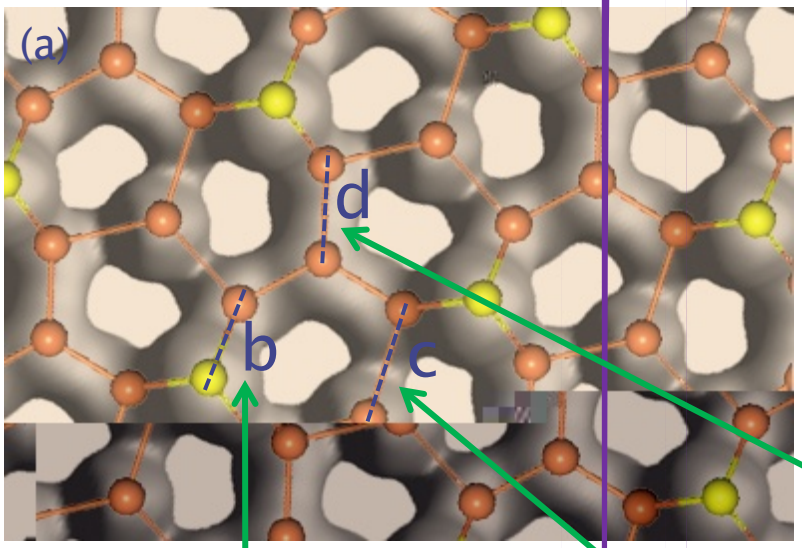
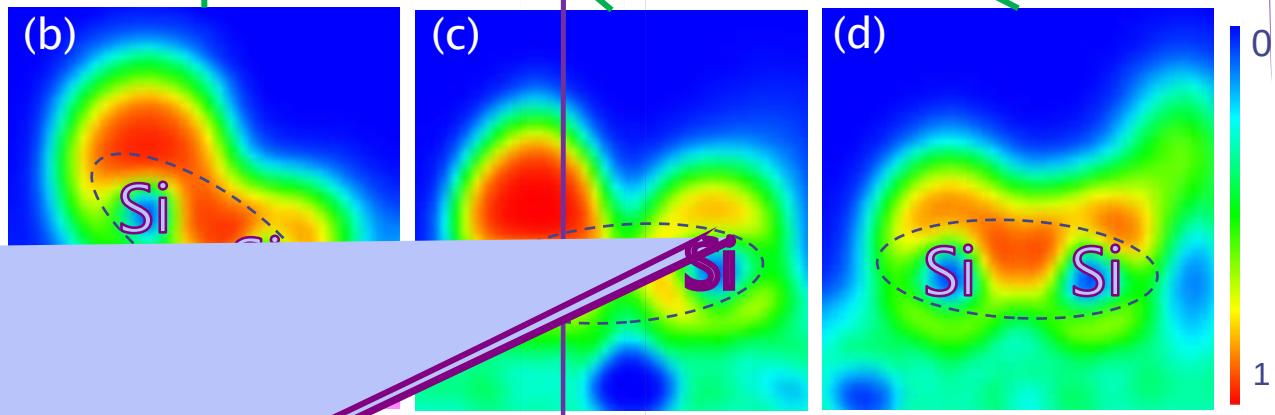


(a)Top view of ov ELF (electron localization funct f 0.6, showing a continuity of the yer.

(b-d) Cross sect of ELFs along each Si pair: cova nt interaction existing between -Si atoms.



Electron Localization Function (ELF) :
Red: electrons highly localized;
Blue: almost no localization.

nature International weekly jo

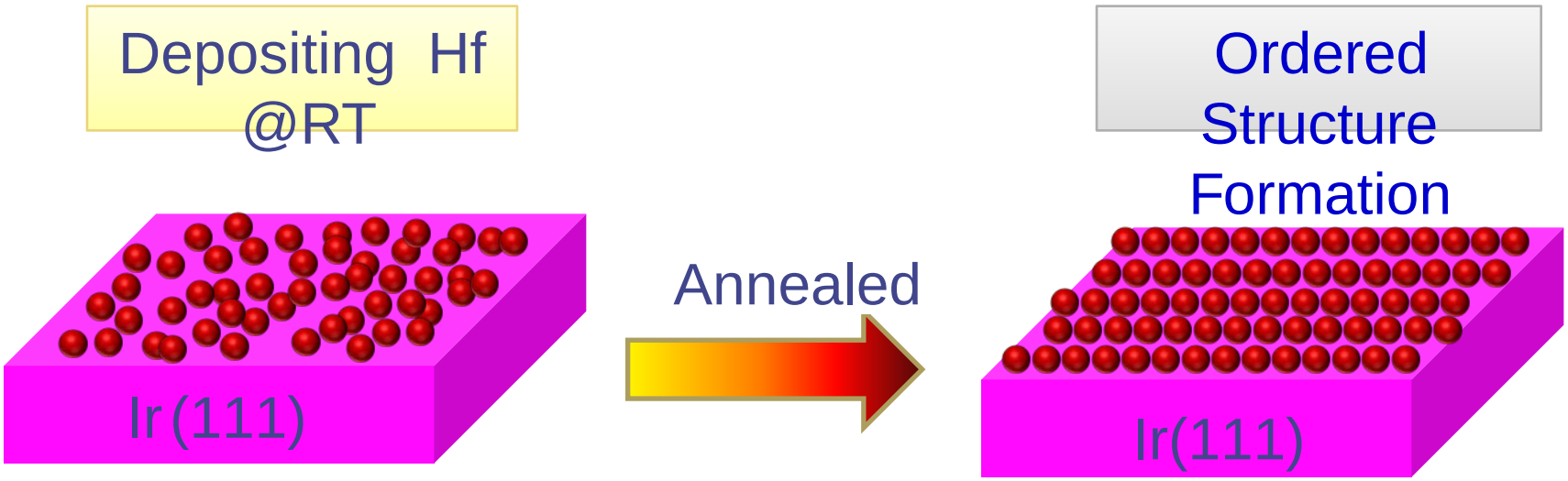
References

1. Vogt, P. *et al. Phys. Rev. Lett.* **108**, 155501 (2012).
+ Show context

2. Fleurence, A. *et al. Phys. Rev. Lett.* **108**, 245501 (2012).
+ Show context

has the advantage of naturally sucking silicene onto its surface from a block of silicon positioned below[2].

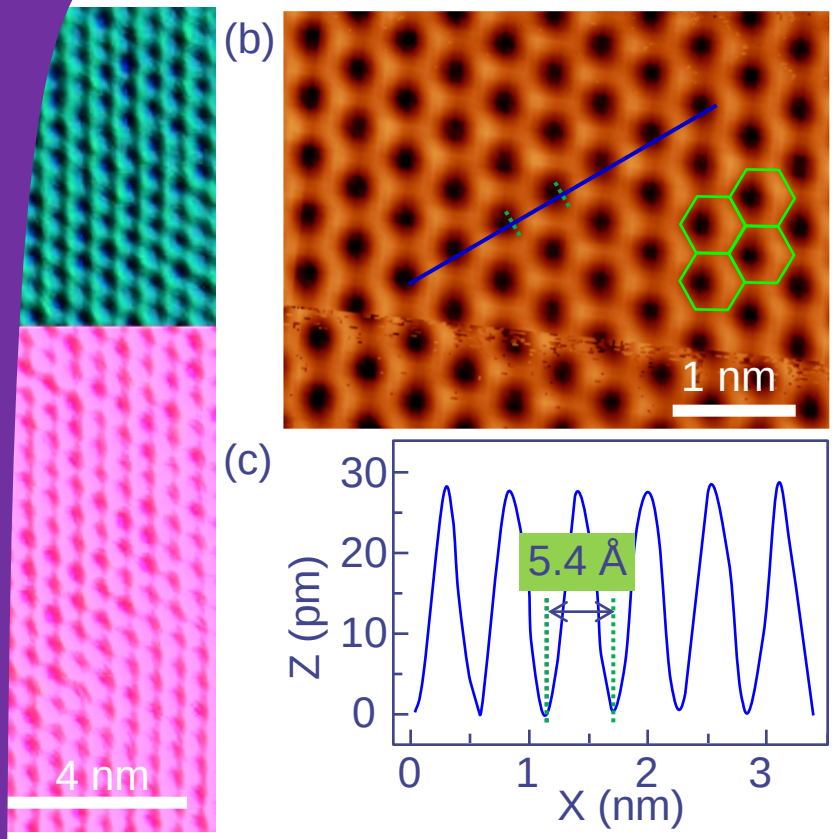
Hafnene on Ir(111)

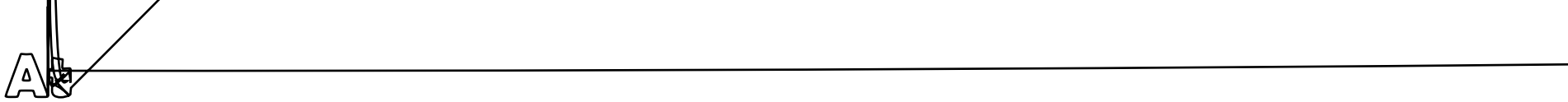


L. F. Li *et al.,* Nano Letters 13, 4671 (2013).

Ir

STM Images of

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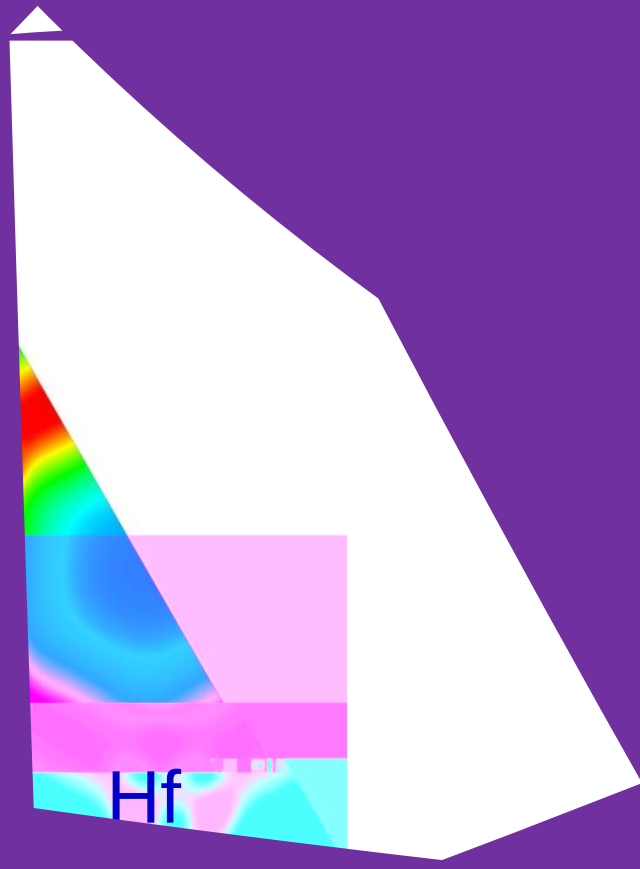
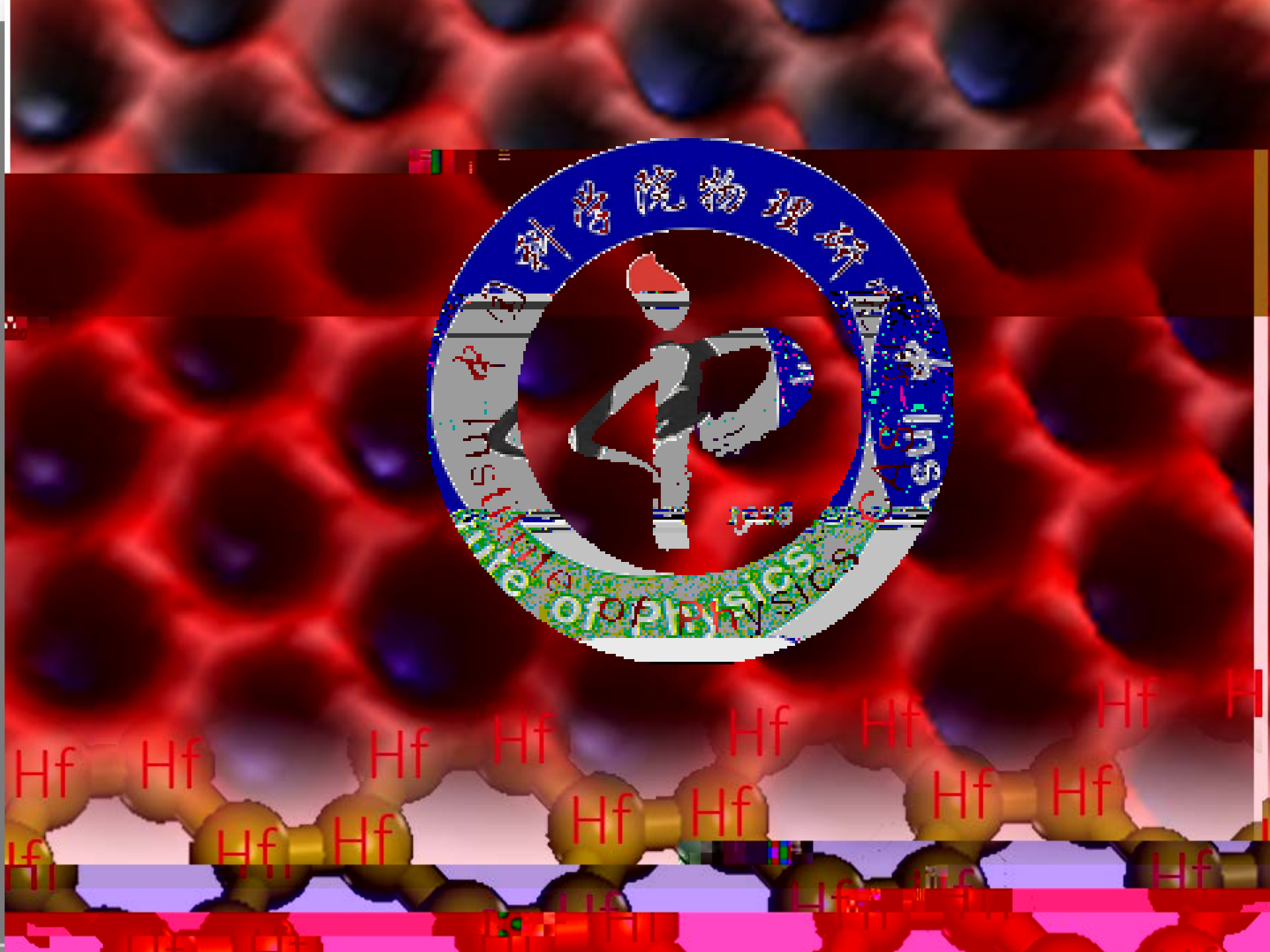
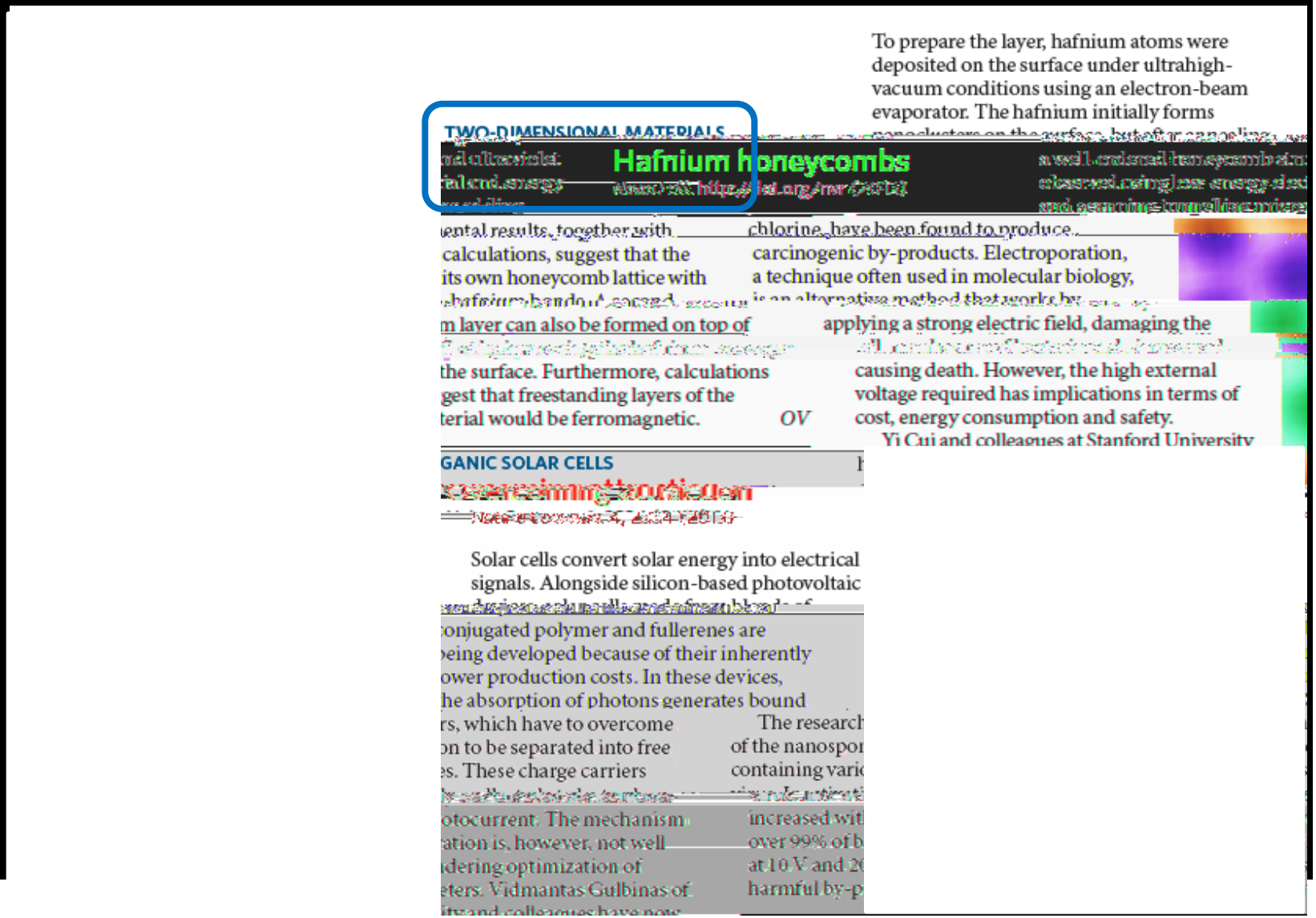

Hf


Hf

Research Highlights



nature

To prepare the layer, hafnium atoms were deposited on the surface under ultrahigh-vacuum conditions using an electron-beam evaporator. The hafnium initially forms

TWO-DIMENSIONAL MATERIALS

Hafnium honeycombs

ental results, together with calculations, suggest that the its own honeycomb lattice with m layer can also be formed on top of the surface. Furthermore, calculations gest that freestanding layers of the terial would be ferromagnetic. *OV*

chlorine, have been found to produce carcinogenic by-products. Electroporation, a technique often used in molecular biology, applying a strong electric field, damaging the causing death. However, the high external voltage required has implications in terms of cost, energy consumption and safety.

Yi Cui and colleagues at Stanford University

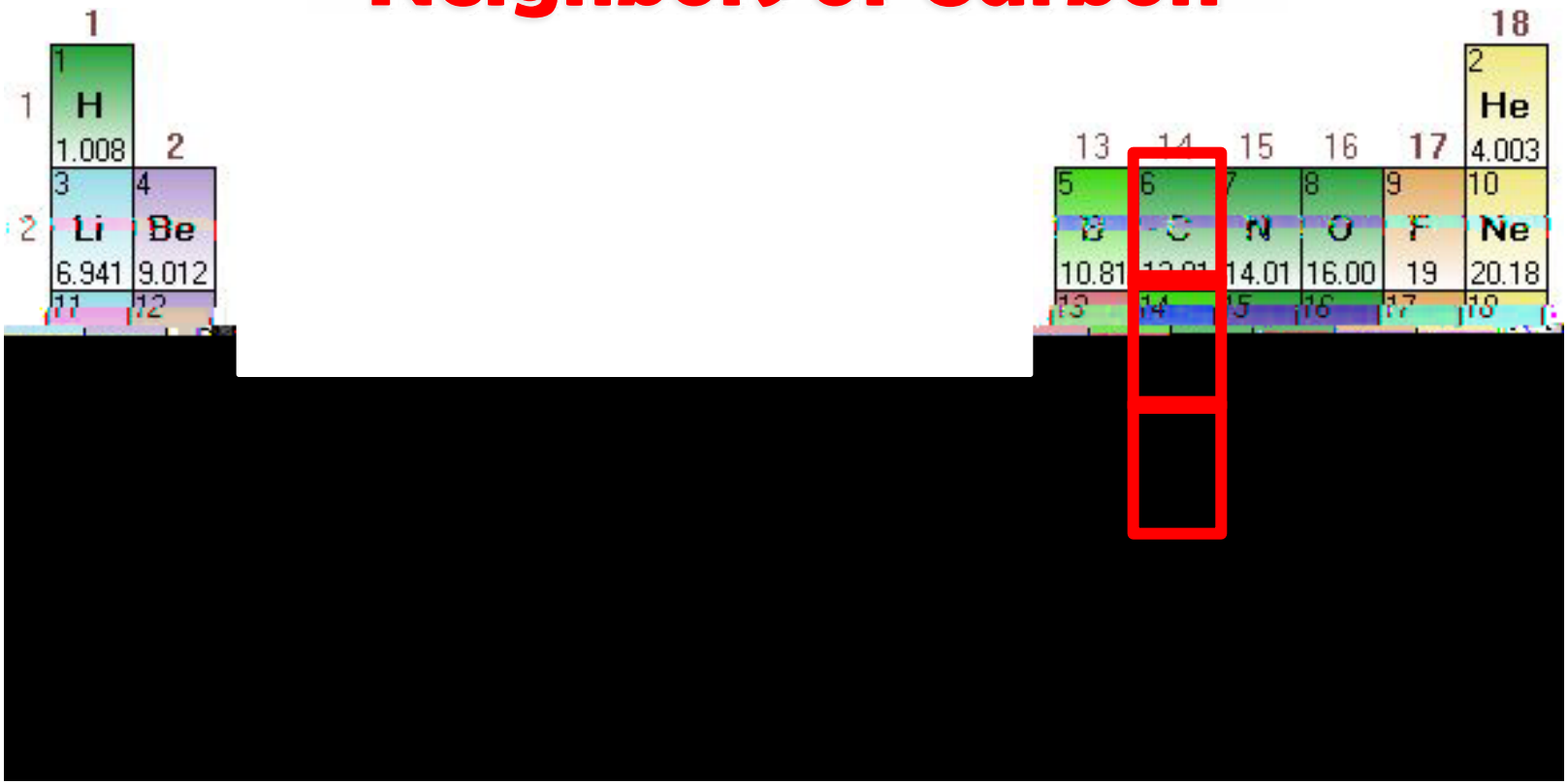
GANIC SOLAR CELLS

Solar cells convert solar energy into electrical signals. Alongside silicon-based photovoltaic

onjugated polymer and fullerenes are being developed because of their inherently ower production costs. In these devices, he absorption of photons generates bound rs, which have to overcome on to be separated into free s. These charge carriers otocurrent. The mechanism ation is, however, not well dering optimization of eters. Vidmantas Gulbinas of

The research of the nanospor containing vari increased wit over 99% of b at 10 V and 2 harmful by-p

Neighbors of Carbon



- 2D crystalline sheet materials by Si (Ge)?
- Honeycomb lattice like graphene?

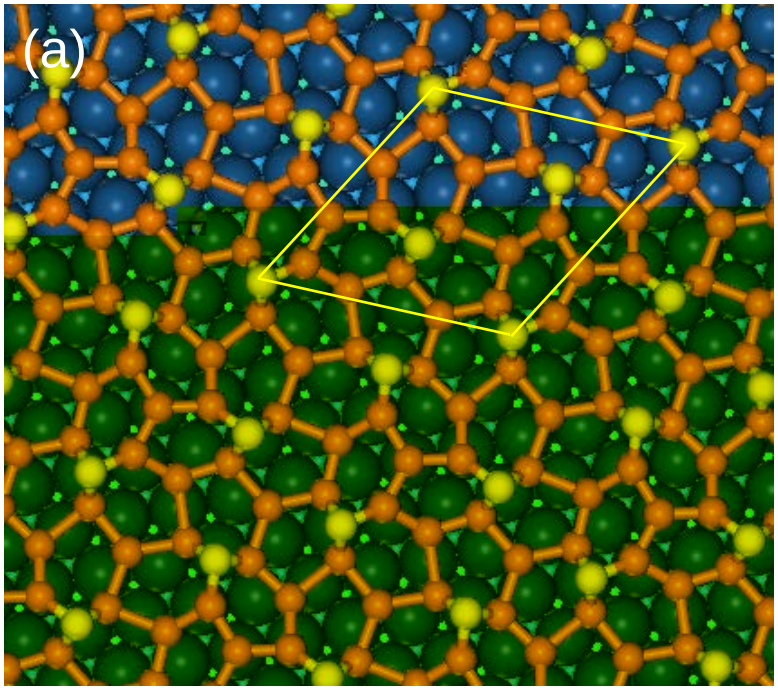
Silicene & Germanene

(Theoretical & Experimental)

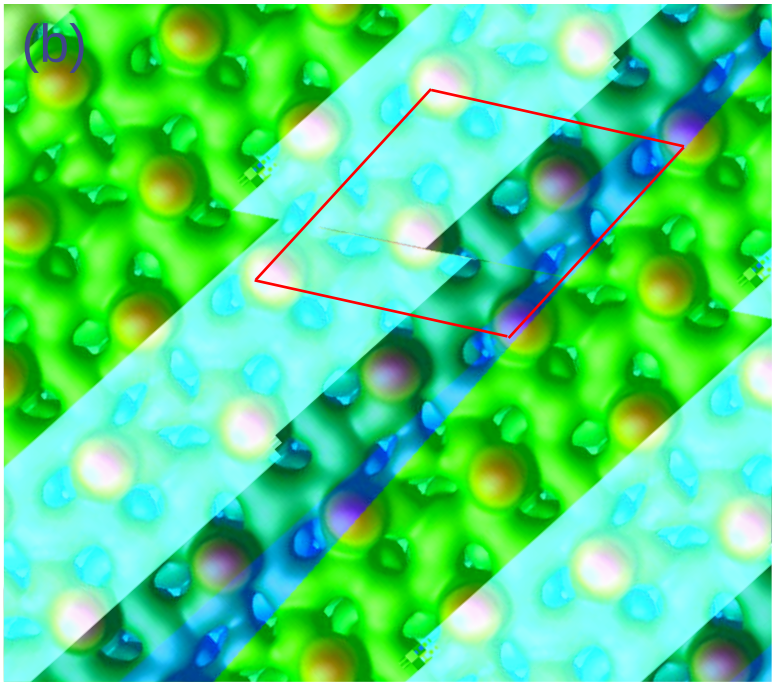
Germanene on Pt(111)

L.F. Li, Y.L. Wang/H.J.Gao *et al*., Adv. Mater. 26, 4820(2014)

Atomic configuration of germanene lattice on Pt(111)



Relaxed structure



DFT-simulated

¾(3×3) Germanene ¥ × ¥ 3 W superstructure

¾The simulated results are in remarkable agreement with exp. data

Theoretical

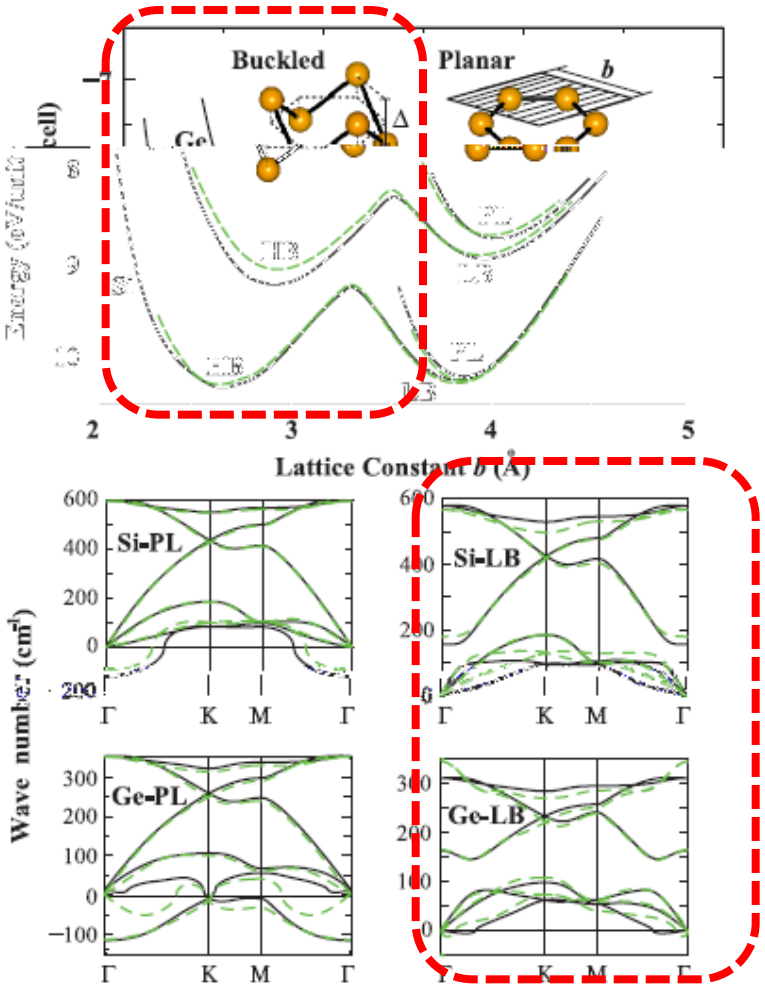
PRL 102, 236804 (2009) PHYSICAL REVIEW LETTERS week ending 12 JUNE 2009

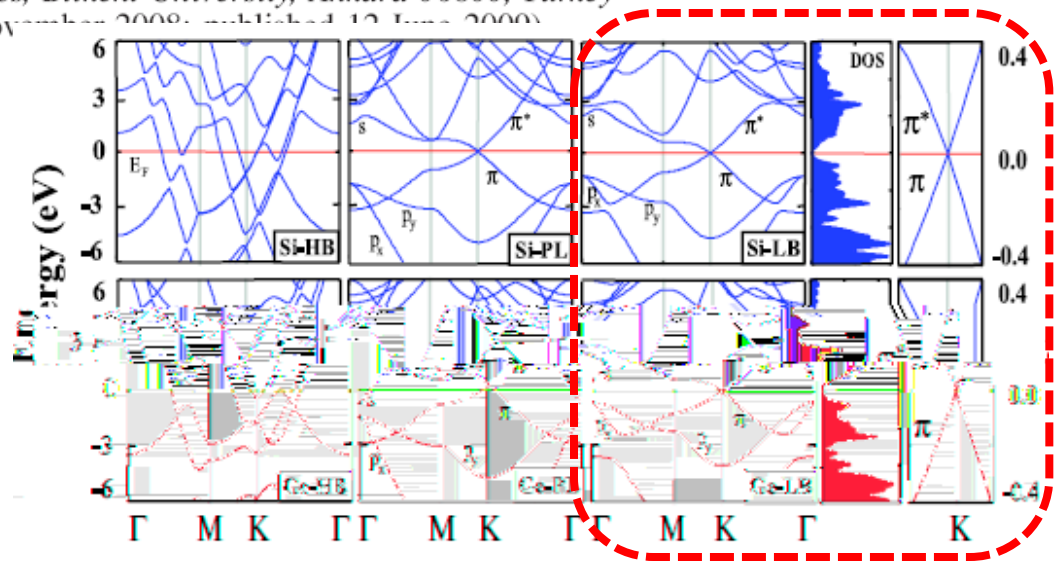
Two- and One-Dimensional Honeycomb Structures of Silicon and Germanium

S. Cahangirov,[1] M. Topsakal,[1] E. Aktürk,[1] H. Şahin,[1] and S. Ciraci[1,2,*]

ınd Nanotechnology, Bilkent University, Ankara 06800, Turkey

cs, Bilkent University, Ankara 06800, Turkey





¾ab initio studies revealed that a buckled honeycomb structure of Si & Ge can exist.

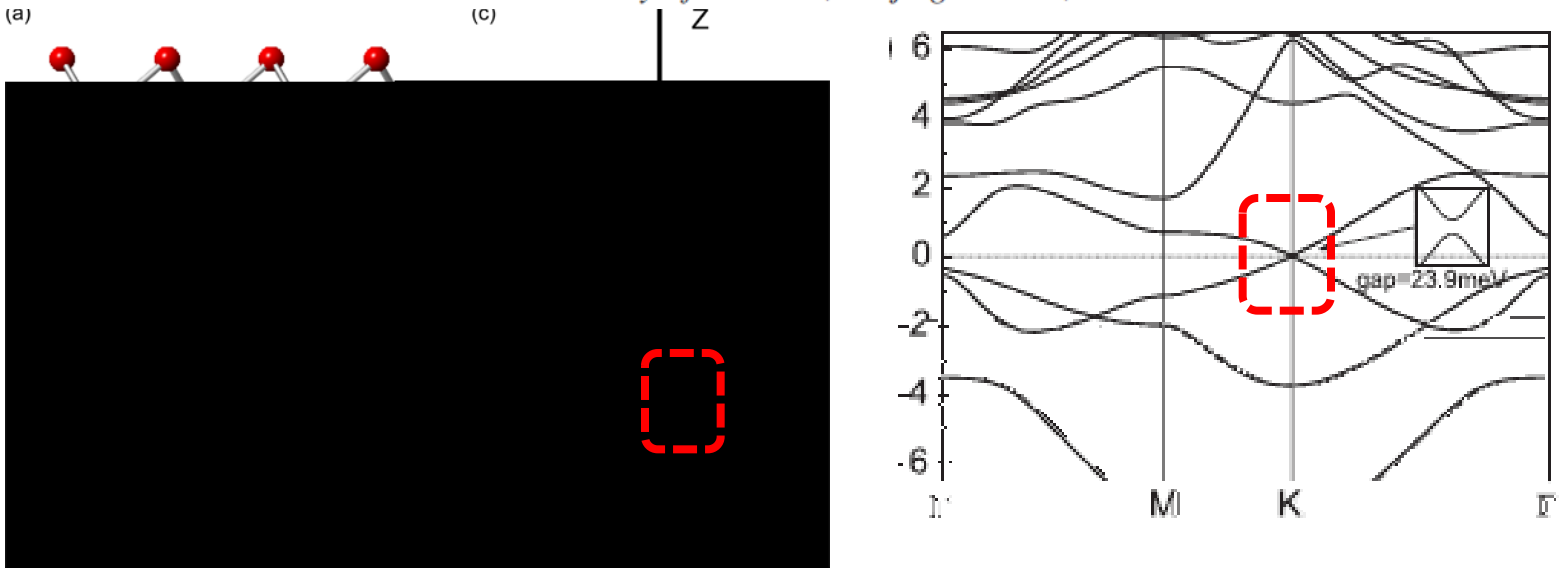
Theoretical

PRL 107, 076802 (2011) PHYSICAL REVIEW LETTERS week ending 12 AUGUST 2011

Quantum Spin Hall Effect in Silicene and Two-Dimensional Germanium

Cheng-Cheng Liu, Wanxiang Feng, and Yugui Yao*

Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

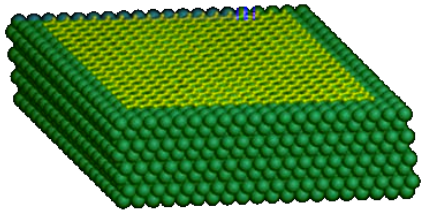


- QSHE can be observed in silicene andgermanene.
- Spin-orbit band gap (1.55 meV in silicene,23.9 meV in germanene), much higher than that of graphene (ËeV).

Experimental

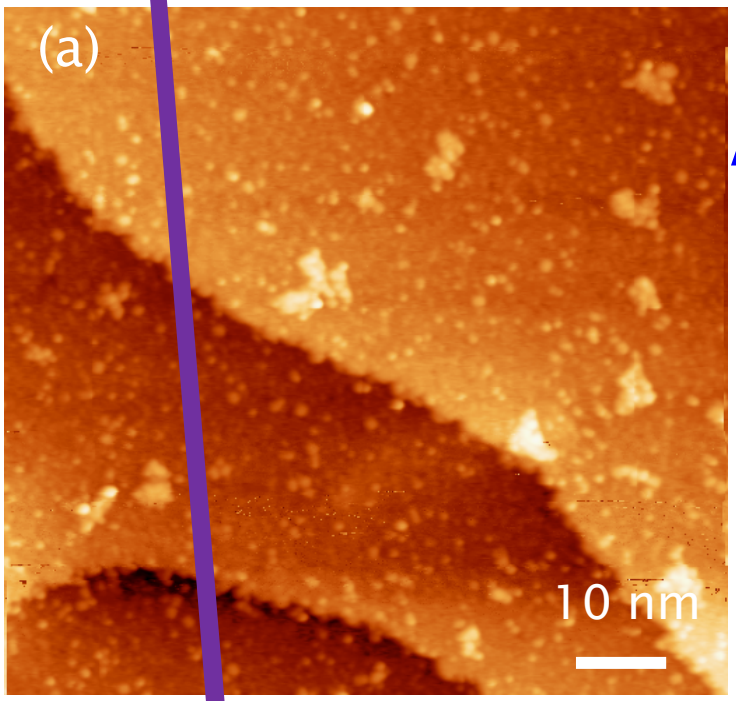
Fabrication Methods: Graphene vs Silicene & Germanene

- Micromechanical cleavage of HOPG
- Thermal decomposition of SiC
- Chemical-based methods (chem-cleave HOPG, …)
- Upzip carbon nanotubes
- Epitaxial growth on solid surfaces

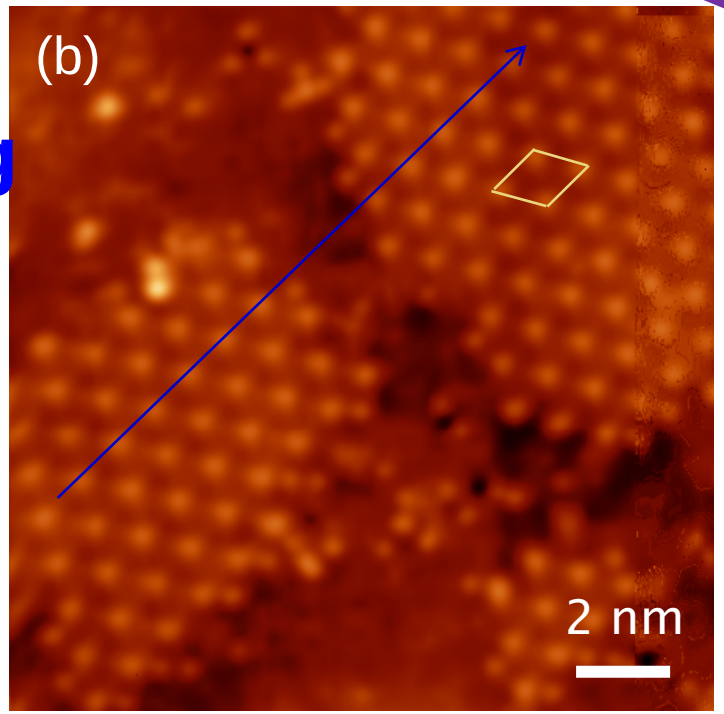


Depositing Ge @RT

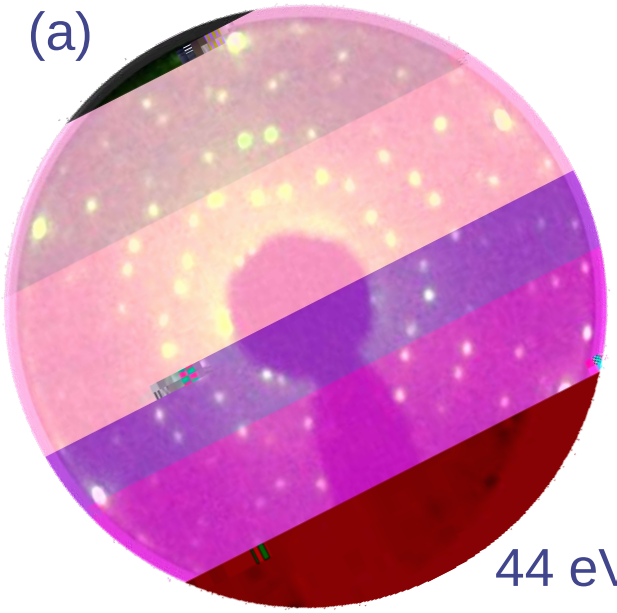
Ordered str

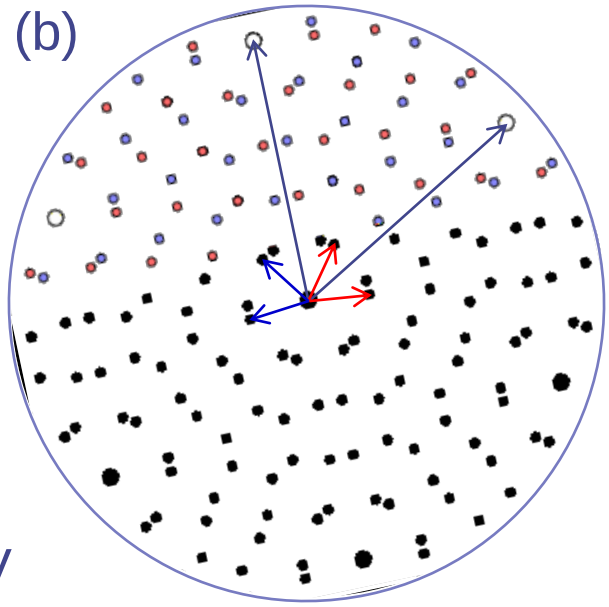


Annealing

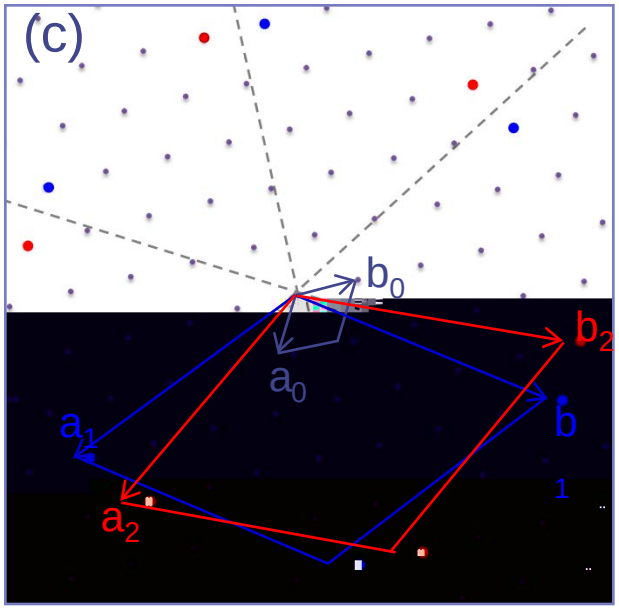


LEED Patterns of Ge Adlayer on Pt(111)





Reciprocal space

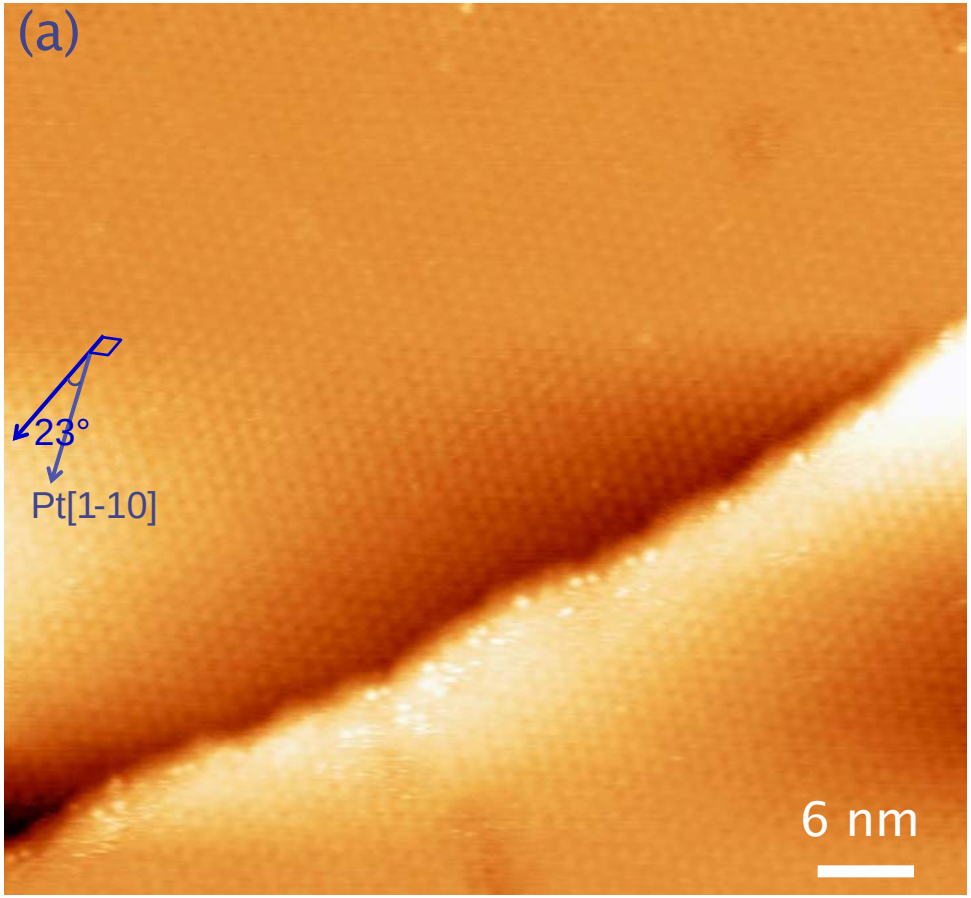


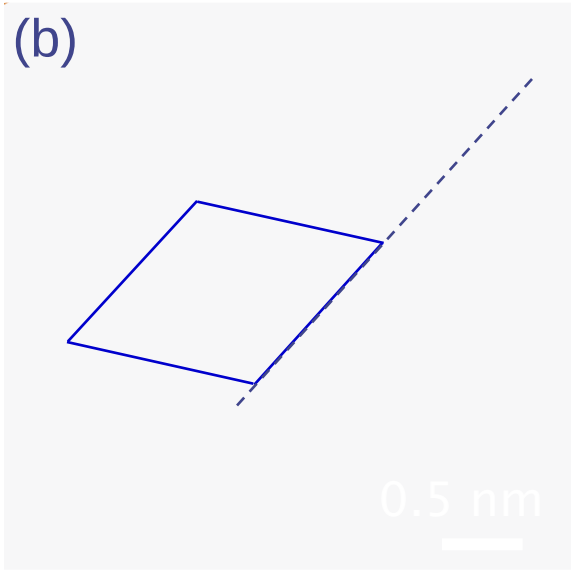
Real space

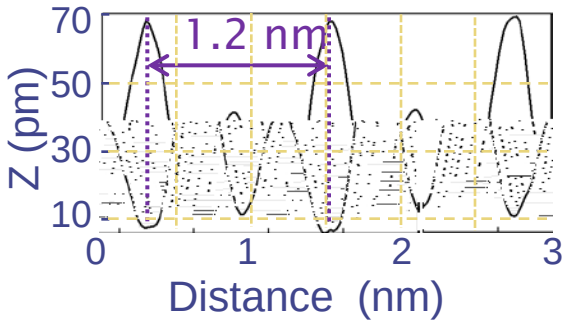
¾ (¥ [¥ V X S H U V W U X F W X U H Z L W K U H

lattice

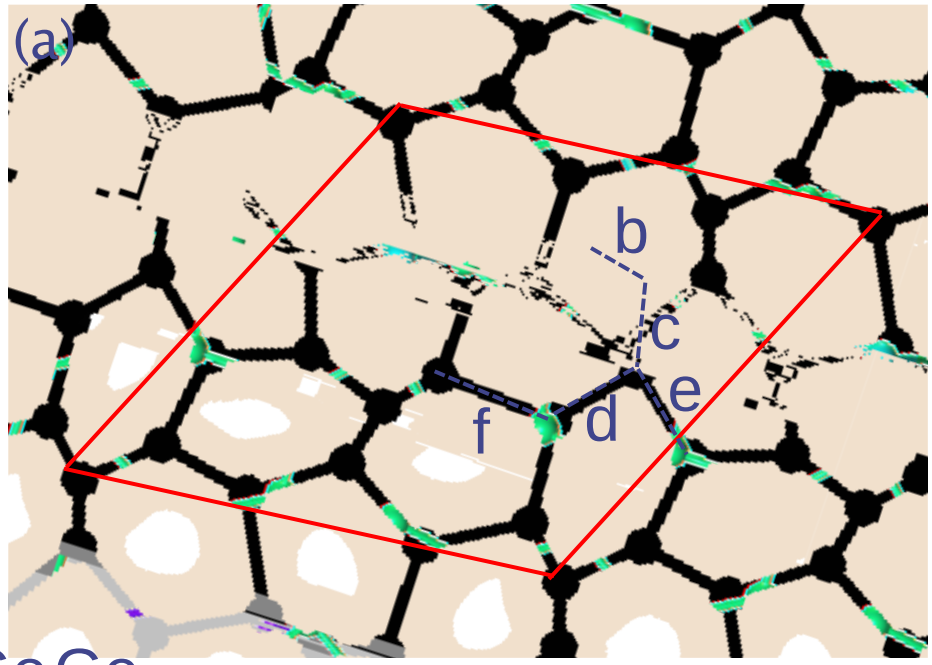
STM: buckle

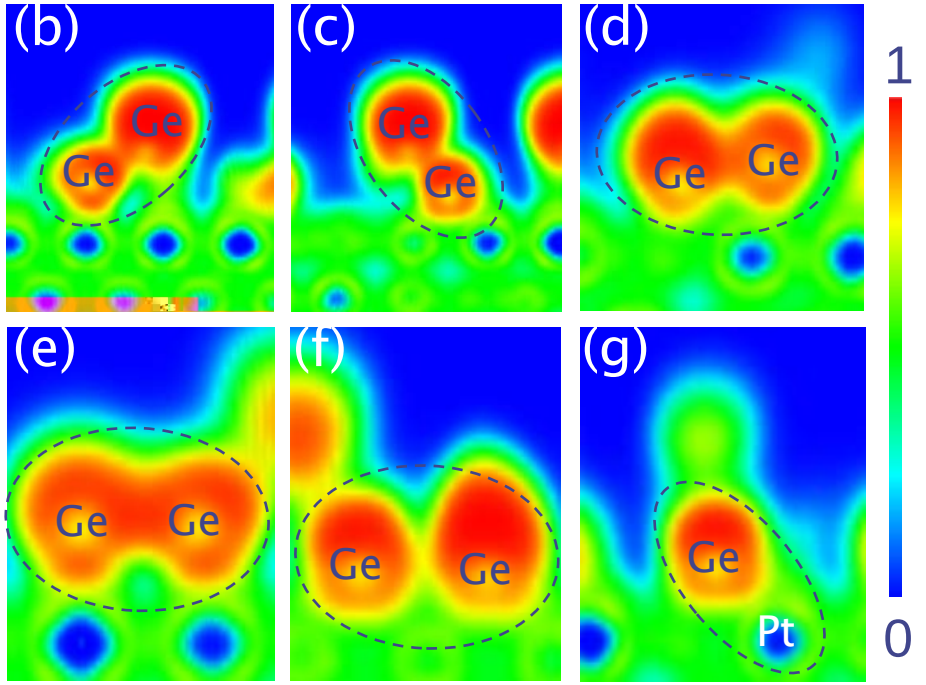






Evidence of covalent interaction between Ge atom pairs





(a) Top view of overall ELF (electron localization function) of 0.5, showing a continuity of the Ge layer.

(b-f) Cross section of ELFs along each Ge pair: covalent interaction existing between Ge-Ge atoms.

A 2D continuous Ge layer, **Germanene,** was successfully fabricated on Pt(111).

http://www.popsci.com/article/technology/meet-germanene-graphenes-newest-2-d-

Meet Germanene, Graphen

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Meet Germanene, Graphene's Newest 2-D Competitor

It's a single-atom-thick array of germanium atoms that could r
super fast transistors.

By Francie Diep Posted 09.10.2014 at 10:00 am

19

atoms of germanium, the next element down the list.

The report from Le Lay, a professor emeritus of nanotechnology at the Aix-Marseilles University in France, comes just a month after a Chinese team became the first to create germanene. The coincidental publishing highlights the work scientists have put into making two-dimensional materials.

……comes just a month after a Chinese team became the first to create germanene.

do across graphene.

It's ha

L.F.Le *et al.*, Adv. Mater. 26, 4820 (2014)

Germanene? Tinene, a 2-D array of tin atoms,

which Le Lay wants to make next? (Yes, tin is

Under the Microscope: A scanning tunneling microscope image of

Guy Le Lay says he's working his way down the pe

atoms with a number of potential applications

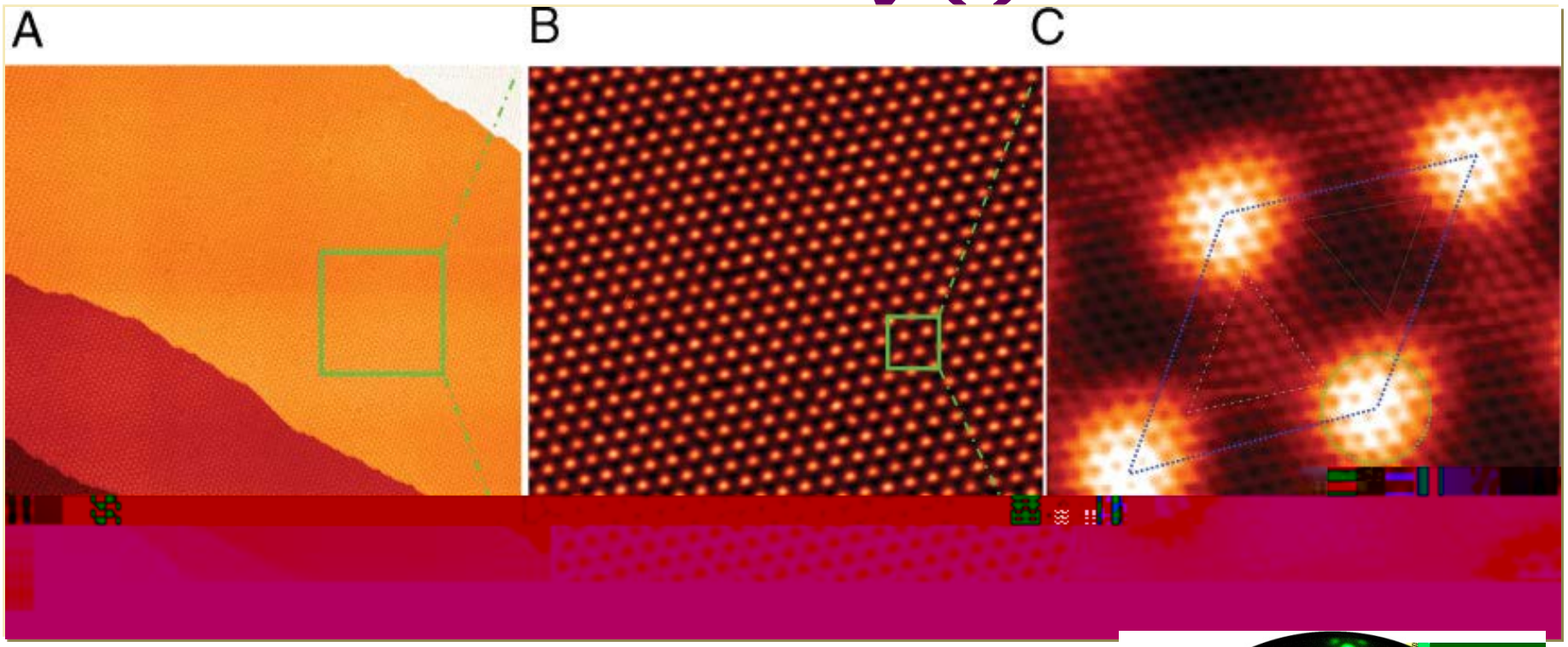
Silicon also happens to be just below carbon

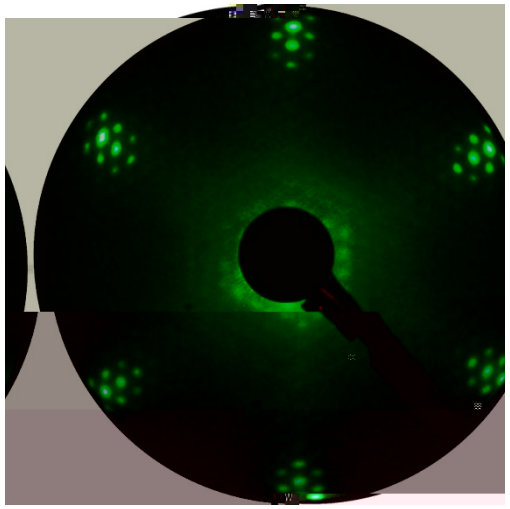
publishing

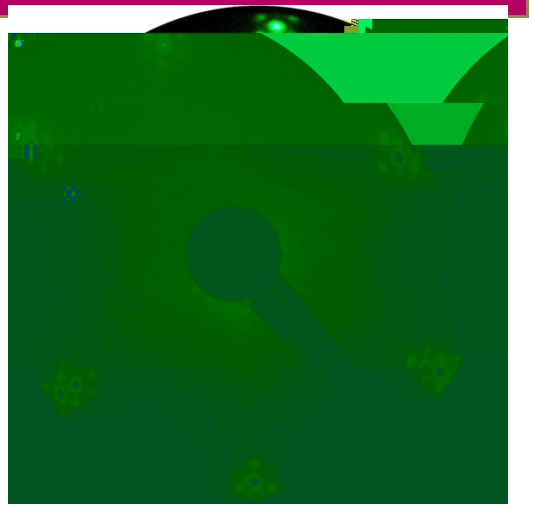
Germanene on Au(111)

http://www.popsci.com/article/technology/meet-germanene-graphenes-newest-2-d-competitor

Summary (I)

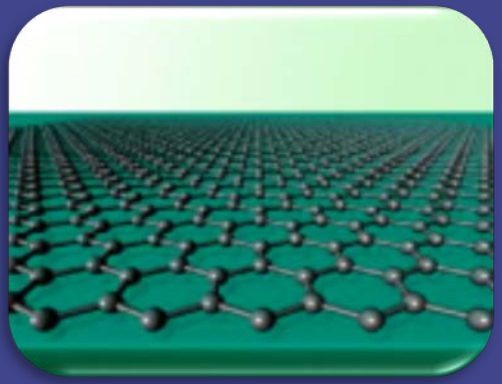


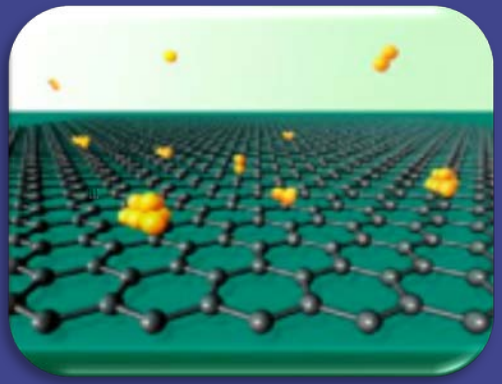


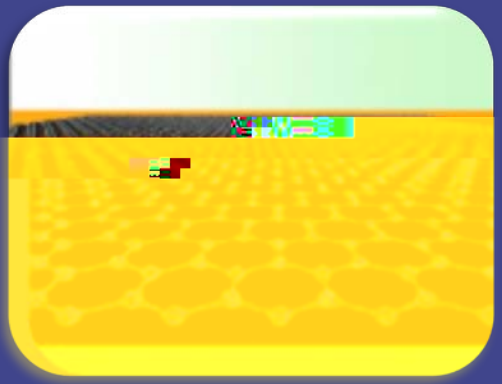


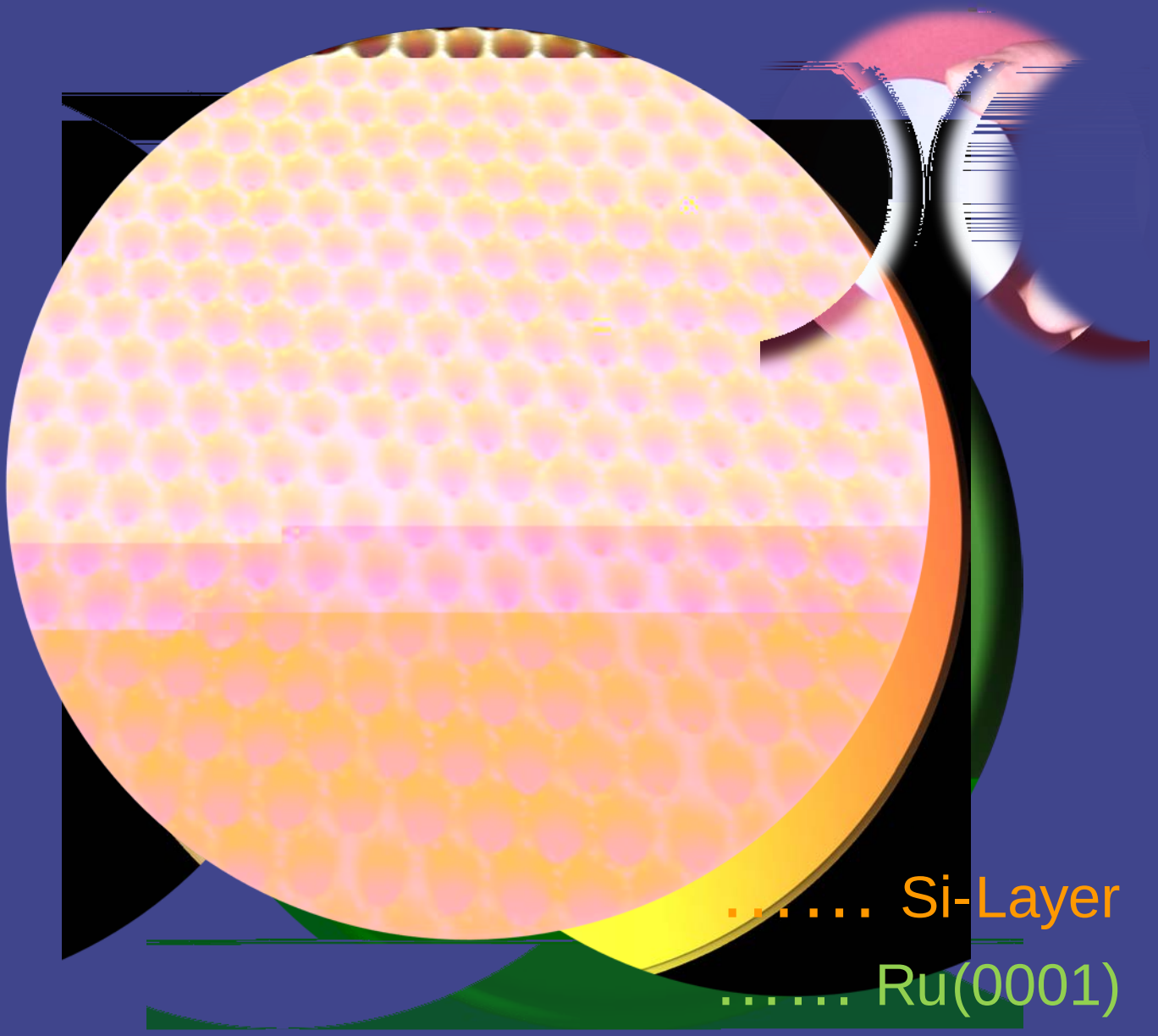
Formation of Large-scale Single Crystalline Graphene Monolayer

Summary (II)



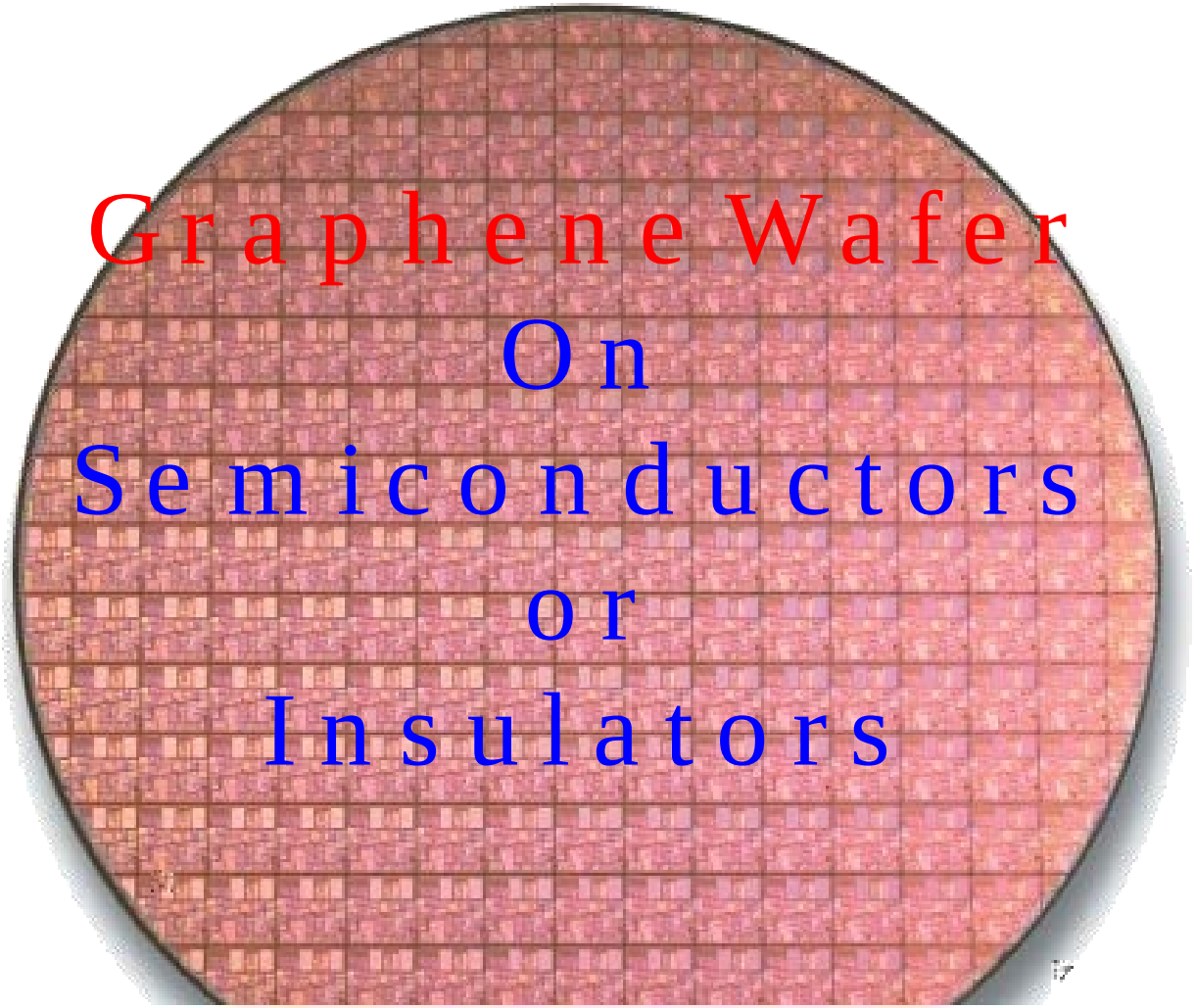






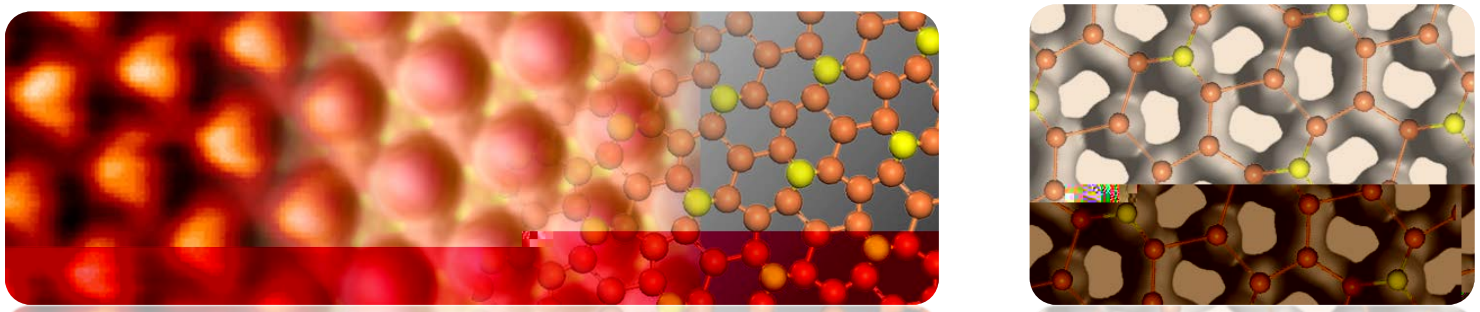
Outlooks

Graphene Wafer and Graphene Complex Systems for the Future Nano-Electronics or Mol-tronics



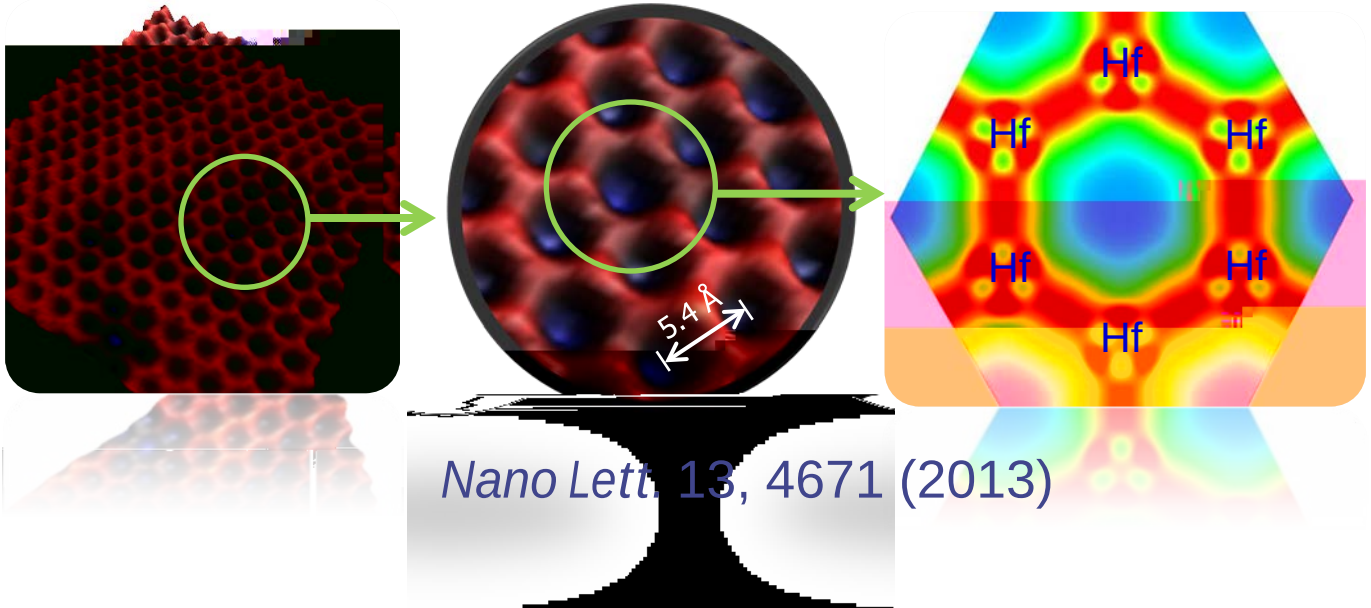
Summary (III)

Buckled Silicene Formation on Ir(111)

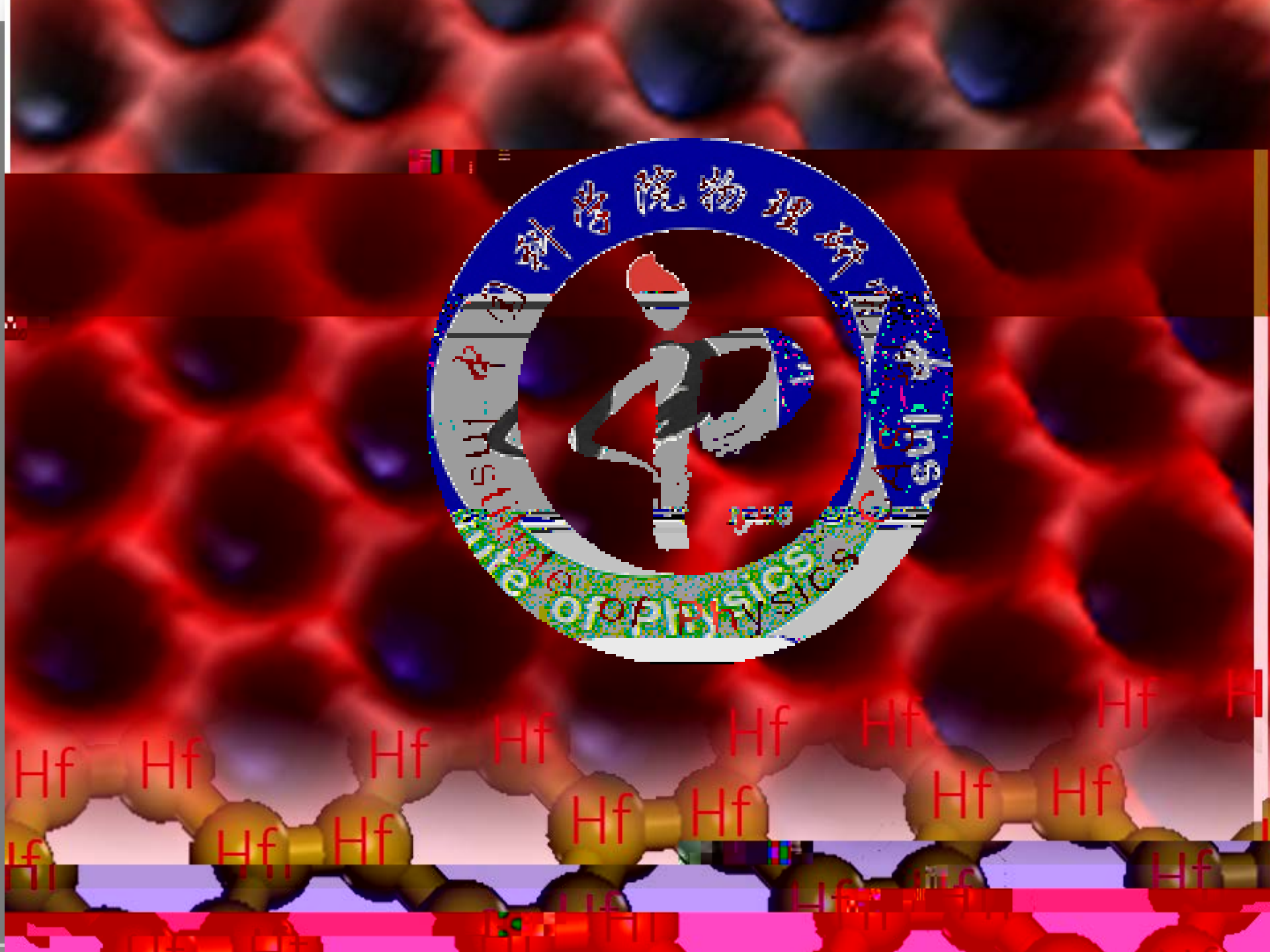


Nano Lett. 13, 685 (2013)

2D Transition Metal Honeycomb Lattice: Hafnene on Ir(111)



Nano Lett. 13, 4671 (2013)


Hf

Summary (IV)

Germanene on Pt( )

L.F. Li, Y.L. Wang/H.J.Gao *et al*., Adv. Mater. 26, 4820(2014)

What Else for Graphene/Ru(0001) ?

- It can be as a
  Graphene-based Quantum Dots
- It can provide a way of
  Direct Imaging of Intrinsic Molecular Orbitals
- It can provide a way of
  Formation and Tunning of Kagome Lattices
  of Magnetic Molecules
- It can provide a way of
  Selective Adsorption of Monodisperse metal clusters
  and Magnetic Molecules

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Featured in this issue

Surface, Interface and Atomic-Scale Science

Special section

Atom-surface scattering

Guest Editor: Salvador Miret-Artés

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J. Phys.: Condens. Matter 22 (2010) 302001 (4pp) doi:10.1088/0953-8984/22/30/302001

FAST TRACK COMMUNICATION

Graphene based quantum dots

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S X Du[1], T Greber[2] and H-J Gao[1]

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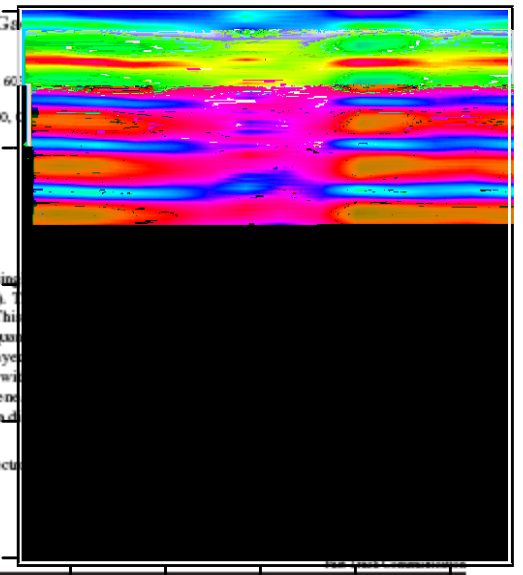
Published 2 July 2010
Online at stacks.iop.org/JPhysCM/22/302001

Abstract

Laterally localized electronic states are ide
low temperature scanning tunneling spectroscopy (STS).
3 nm and comprise regions of about 90 carbon atoms. Thi
dot-array with molecular precision. It is evidenced by qua
energies that relate to the corrugation of the graphene laye
are modeled by a layer height dependent potential-well wi
describes the barrier for electron penetration into graphen
and lowest in energy on the isolated 'hill' regions w
is decoupled from the surface.

(Some figures in this article are in colour only in the elect



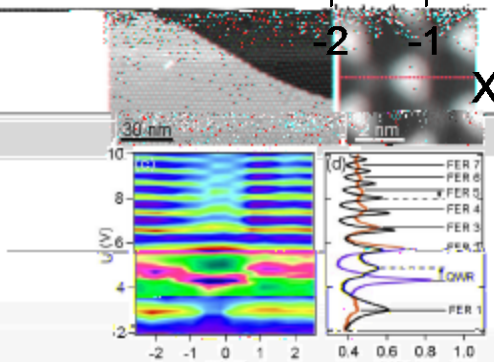


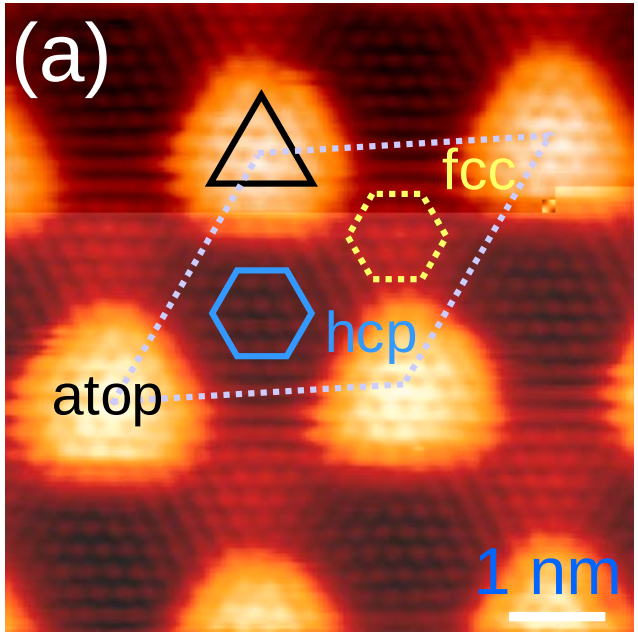
Figure 1. STM image and STS for monolayer graphene on Ru(0001). (a) Large-scale ($U_t = -2.0$ V, $I_t = 100$ pA) STM

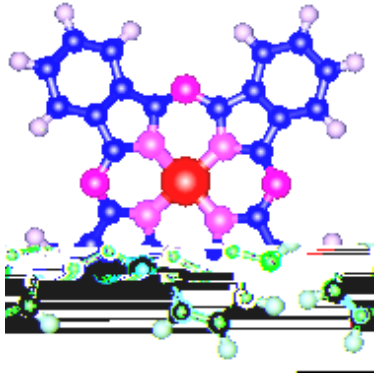
Selective Molecular Adsorption at the Initial Stage

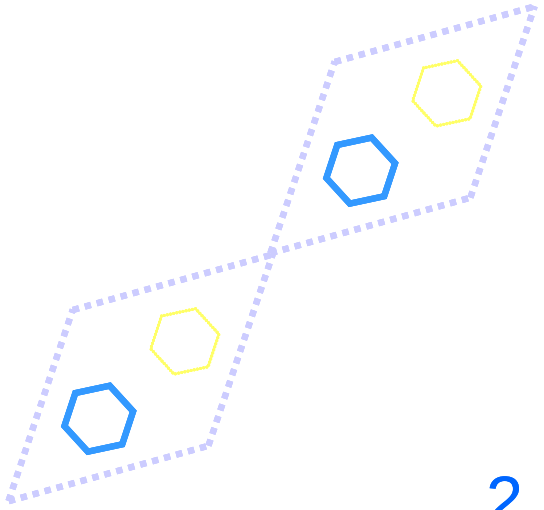
Graphene/Ru(0001)

FePc

FePc/Graphene/Ru(0001)





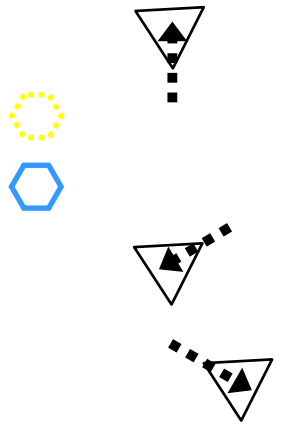


Fe N C H

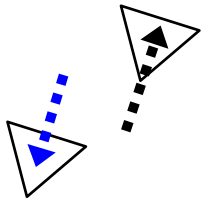
2 nm

(H.G. Zhang/H.J. Gao *et al*., PR B 84, 245436(2011)

Adsorption Sites and Orientations with Increas Coverage



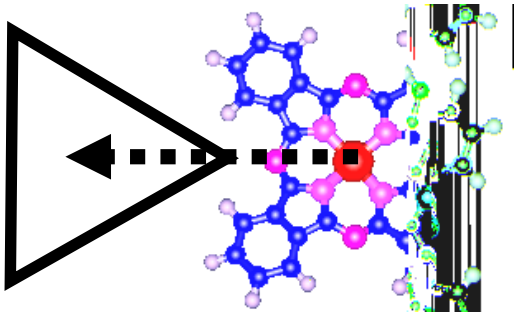
3 nm

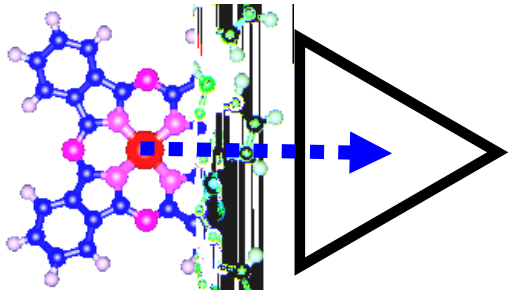


2 nm

"A" type at fcc

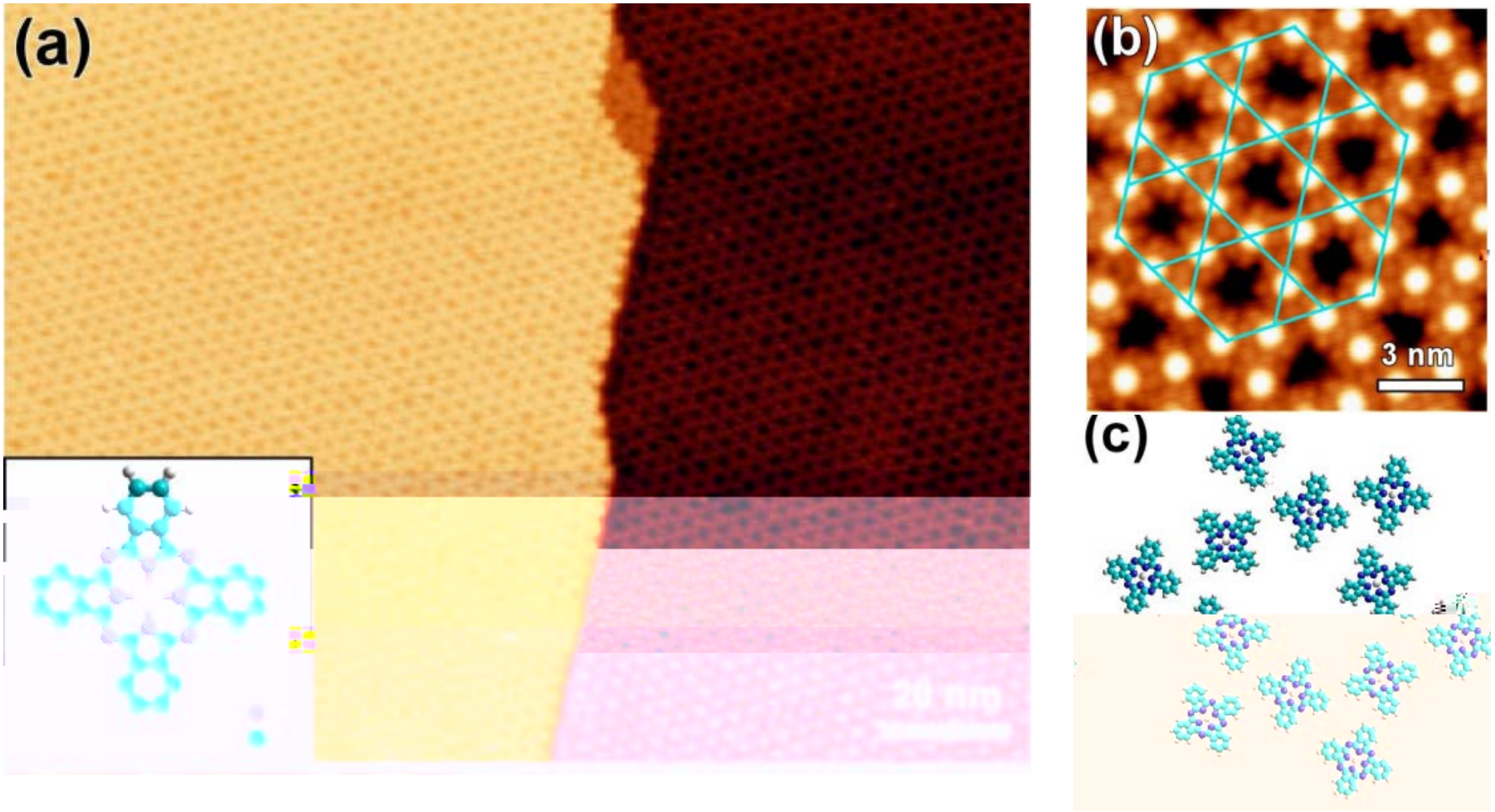
"B" type at edge of atop





Fe N C H

Kagome Lattice: FePc/MG/ Ru(0001)

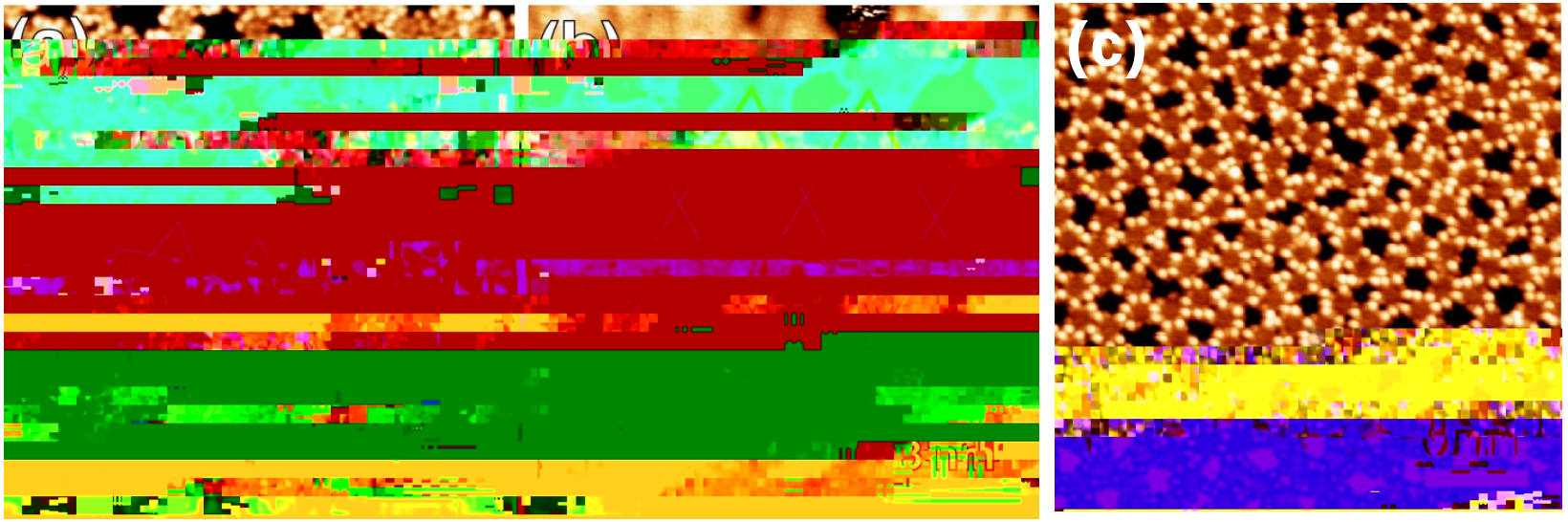


(a) Kagome lattice of FePcacross steps of the Ru(0001) substrate.
(b) Details of the Kagome lattice of FePc
(c) Structural model of the Kagome lattice: molecular orientation disorder.

(J.H. Mao/H.J. Gao et al., JACS, 131, 14136(2009)

Kagome Lattice:

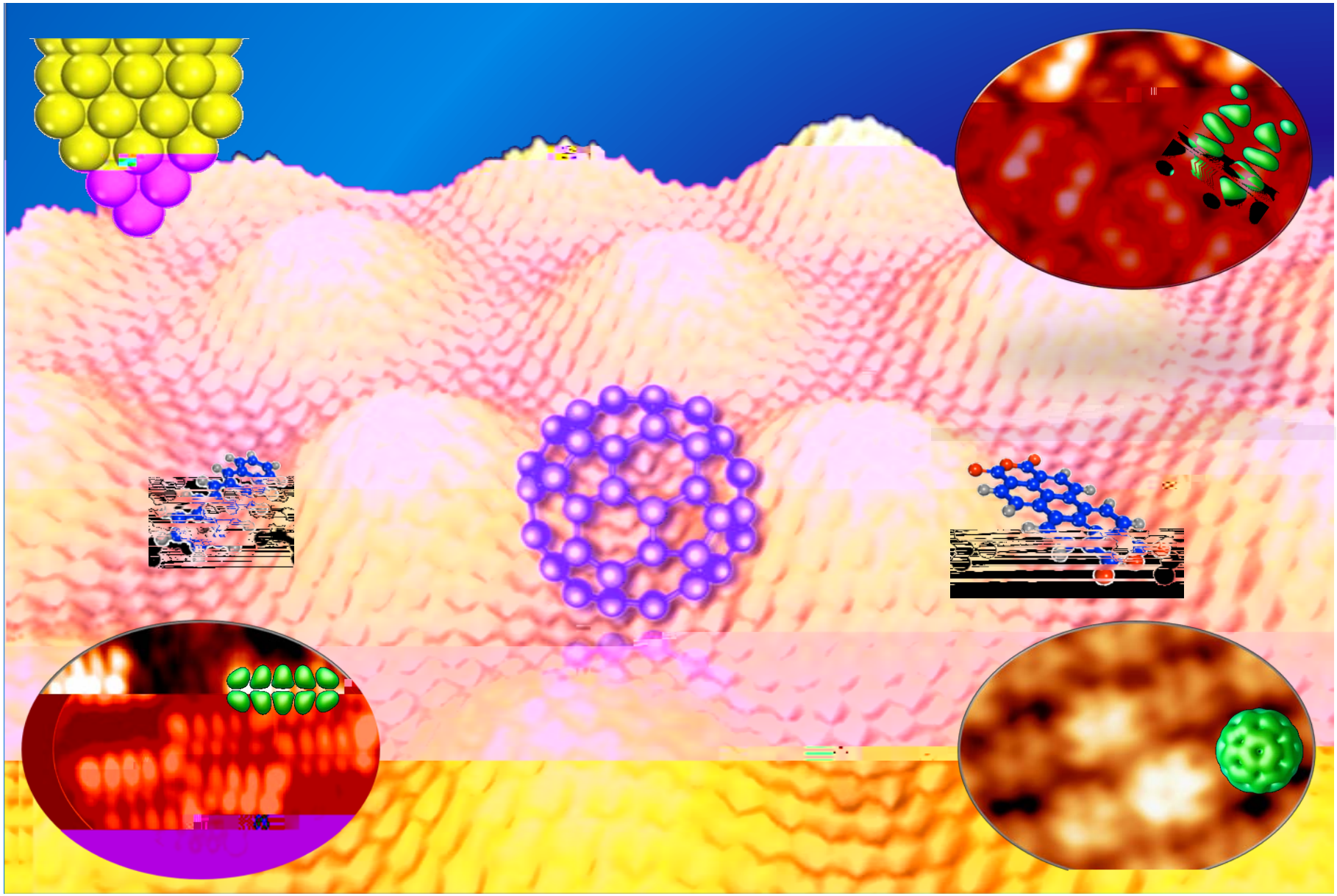
H_2Pc,NiPc, $(t\text{-}Bu)_4$-ZnPc/MG/ Ru(0001)



H_2Pc NiPc $(t\text{-}Bu)_4$-ZnPc

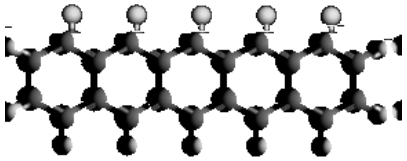
(J.H. Mao / H.J. Gao et al., JACS, 131, 14136(2009)

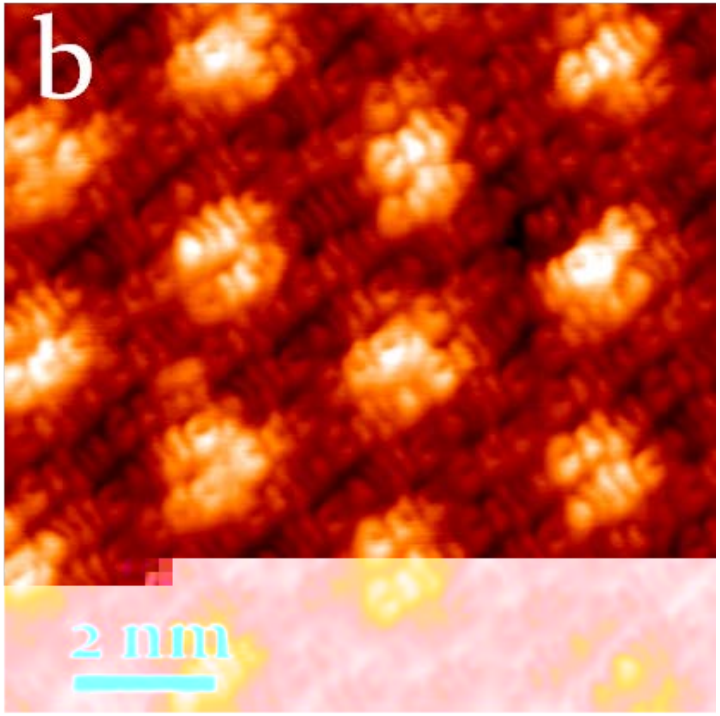
Direct Imaging of Intrinsic Molecular Orbitals Using Epitaxially Grown Graphene For Study of Single Molecules

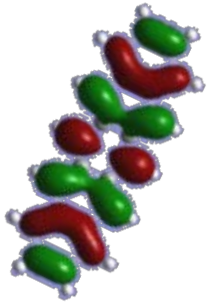


Intrinsic Molecular Orbitals Observed after Graphene Reserves as a buffer layer

Pentacene







1 nm

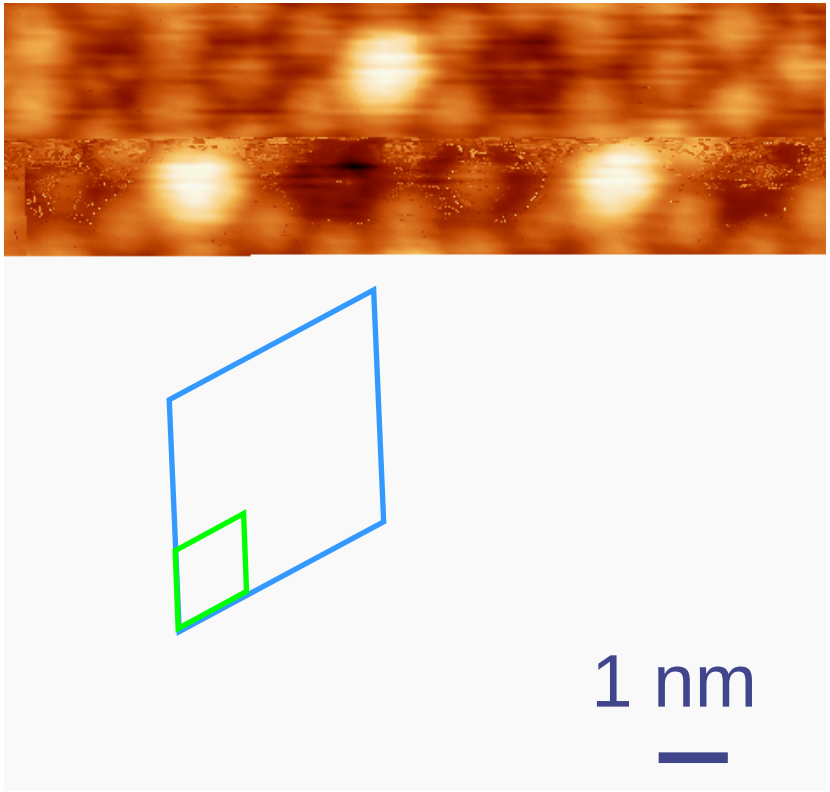
-2.0V

1 nm

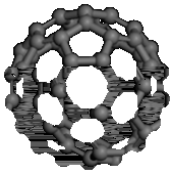
HOMO

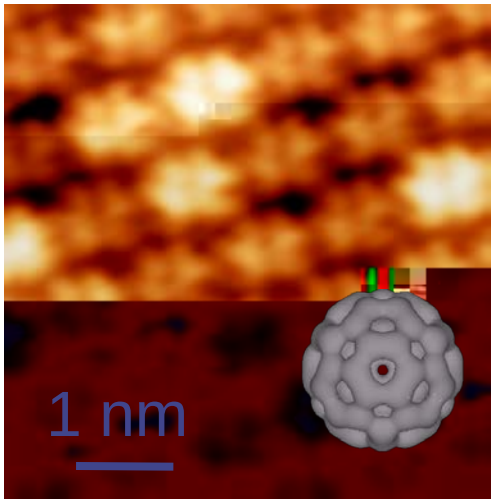
LUMO

Intrinsic Molecular Orbitals Observed after Graphene/Ir Reserves as a buffer layer



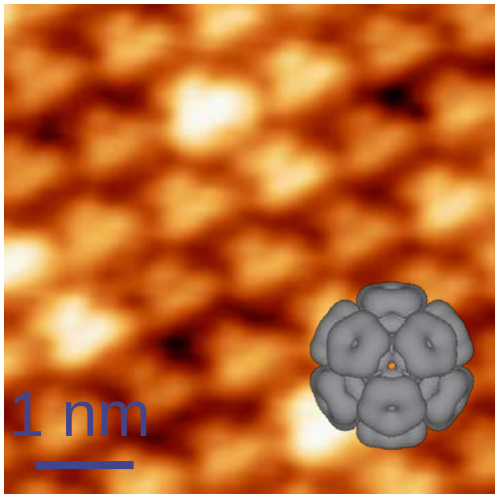
C_{60}





-2.0 V

HOMO



+1.4 V

LUMO

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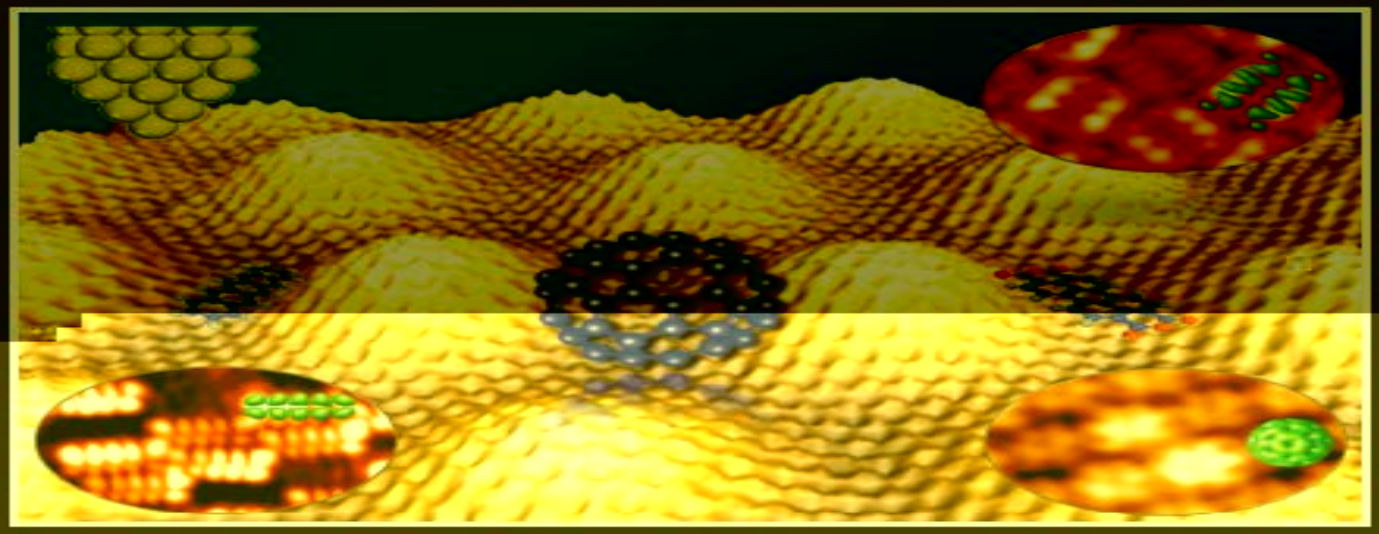
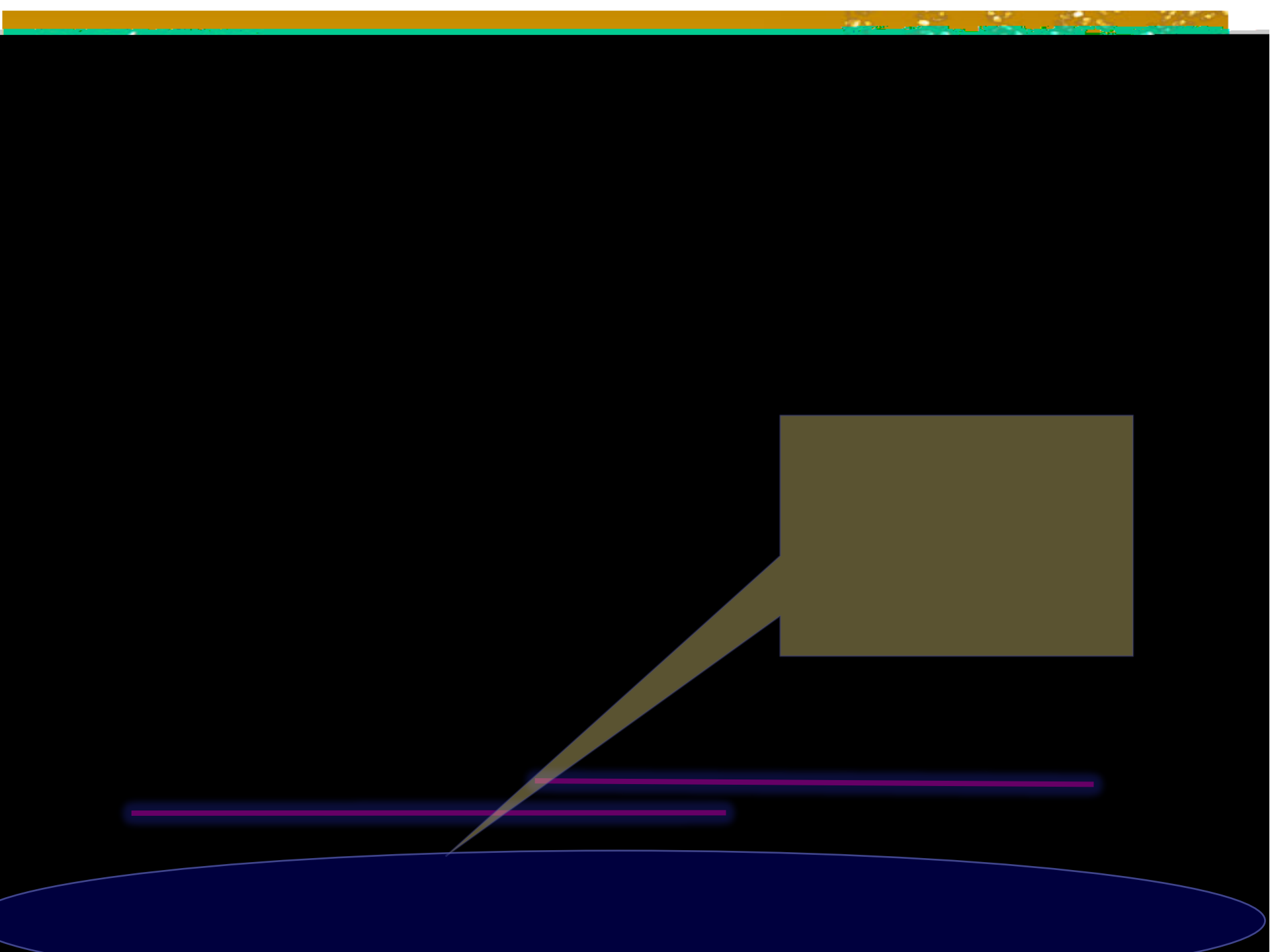
Volume 99 Number 15

APPLIED PHYSICS LETTERS



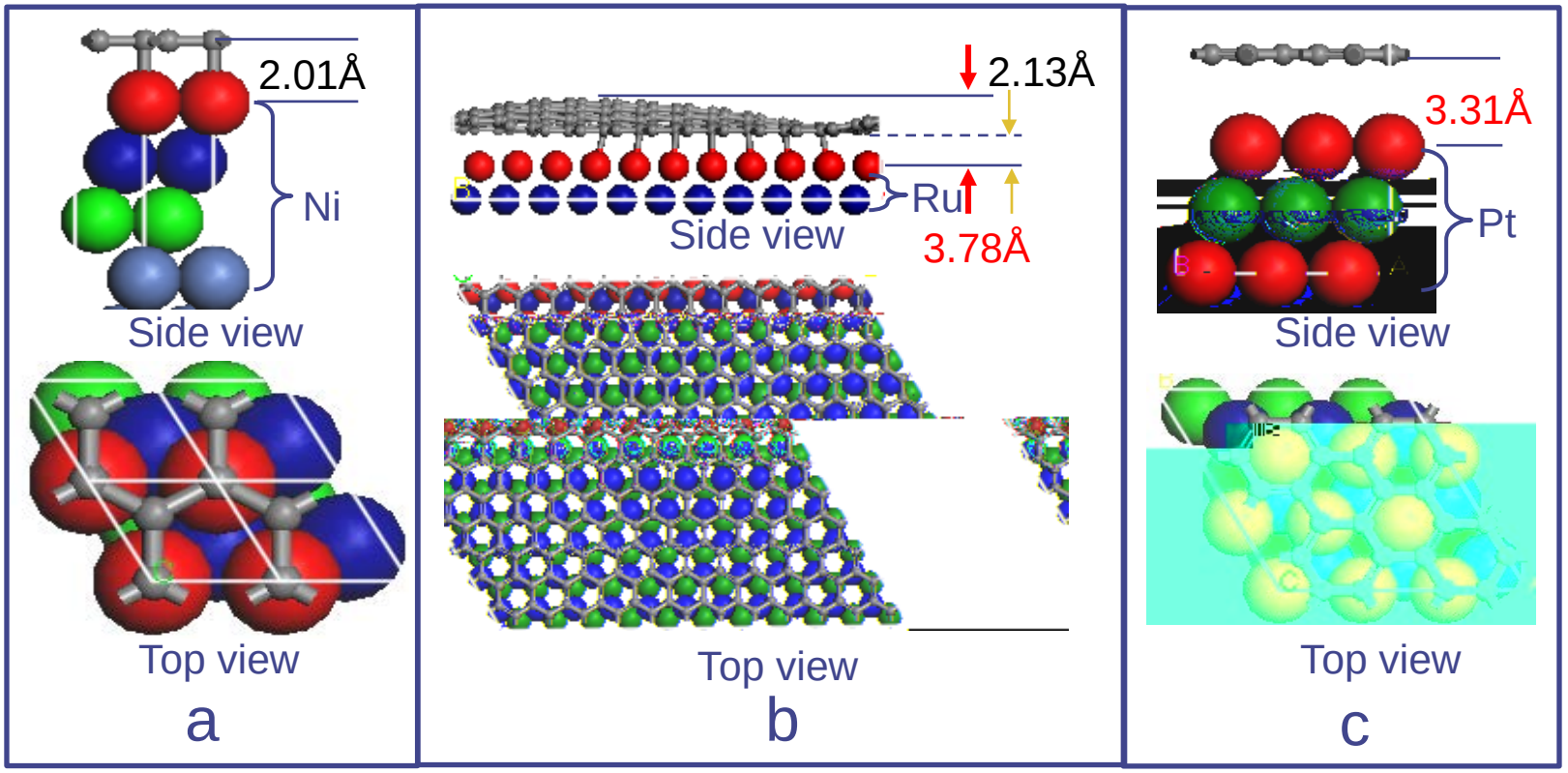
AIP



Tunable Interfacial and Physical Properties of Epitaxial Graphene on Metal Substrates

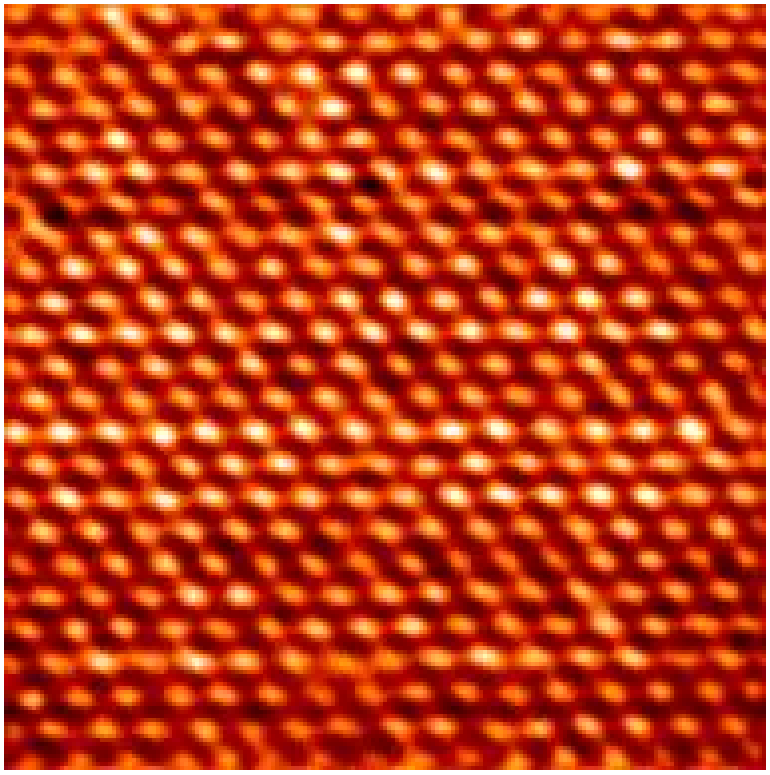
M. Gao, H.J. Gao et al., APL, 2010
M. Gao, H.J. Gao et al., APL, 2011

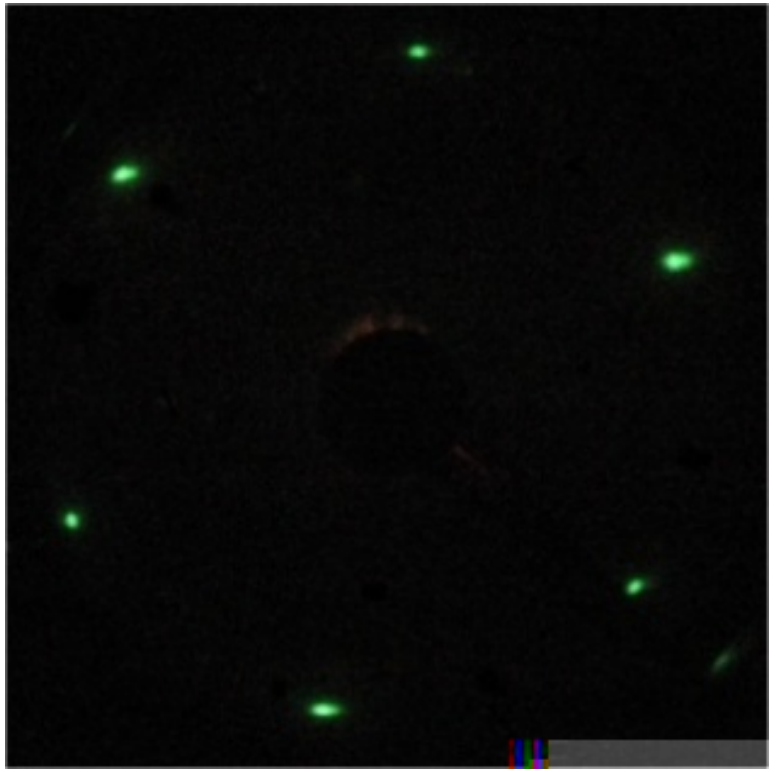
Idea and Calculation Results of Graphene Interfacial Structure on Ni(111), Ru(0001) and Pt(111)



- The atomic model of graphene on Ni(111), Ru(0001) and Pt(111).
- OnNi(111). The interfacial distance is 2.01 Å.
- OnRu(0001). *The distance is 2.13 Å and 3.79 Å.*
- OnPt(111). The distance is 3.31 Å.

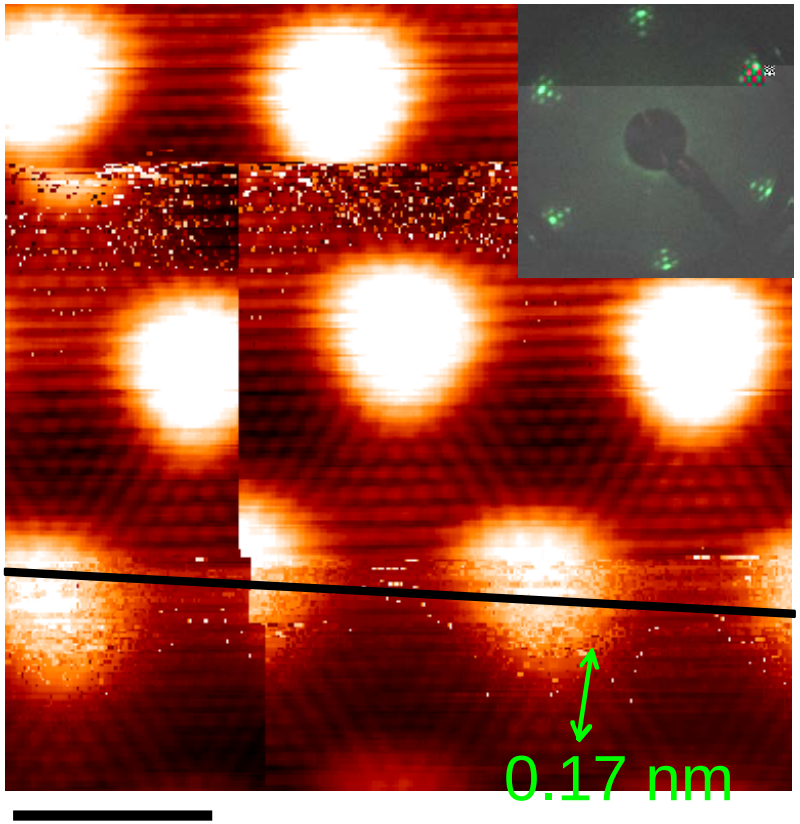
STM Image of Graphene on Ni(111)





- Atomic resolution STM image of graphene on Ni(111) grown at 700 .
- The inset is the LEED pattern of the sample. The beam energy is 60 eV.
- The image was taken with a sample bias voltage of Vs=-40 mV and a tunneling current of I=1.5 nA.

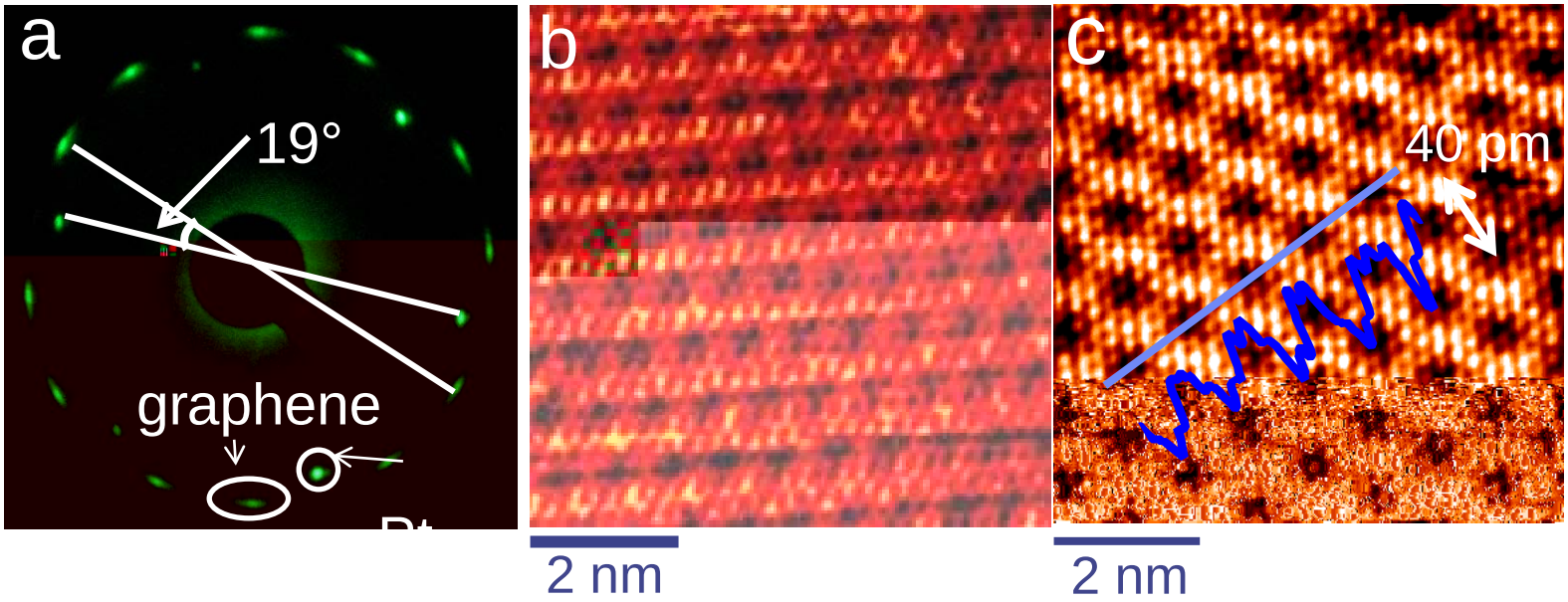
STM Image Of Graphene on Ru(0001)



¾ Atomic resolution STM image of graphene on Ru(0001) grown at 800 . The image was taken with a sample bias voltage of Vs= -300 mV and a tunneling current of I=1.3 nA.

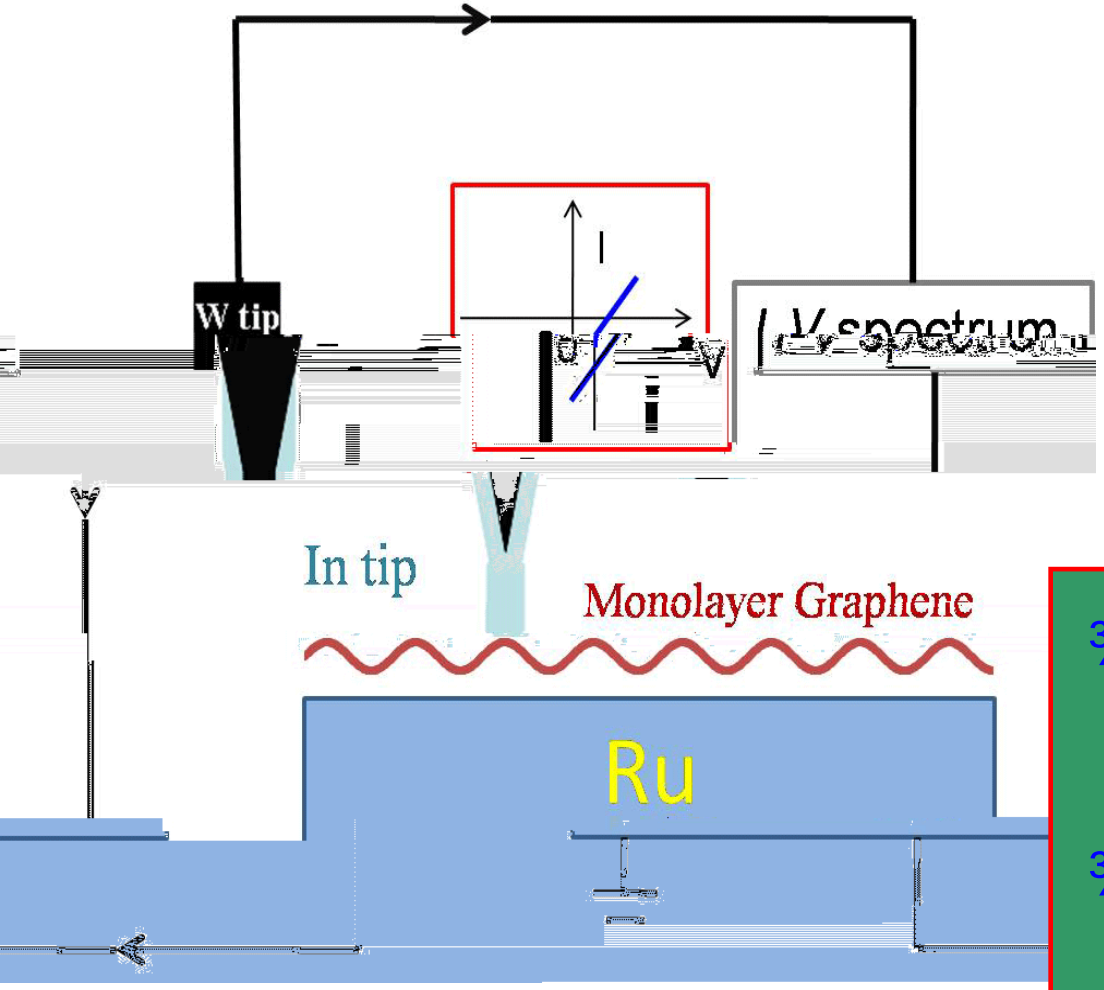
¾The height profile is taken along the black line in the STM image, showing the fluctuation of graphene on Ru(0001) is 0.17 nm.

LEED Pattern and STMN images of Graphene on Pt(111)



- LEED pattern of graphene on Pt(111) grown at 600 . The circular and the elliptical lines indicate the Pt and graphene pattern, respectively.
- Atomic resolution STM images show moiré patterns of two graphene domains of different rotational angles with respect to Pt(111) surface.
- All images were taken at Vs=-0.4 V, I=0.2 nA.

The Schematic of Thermoelectric Voltage Measureme

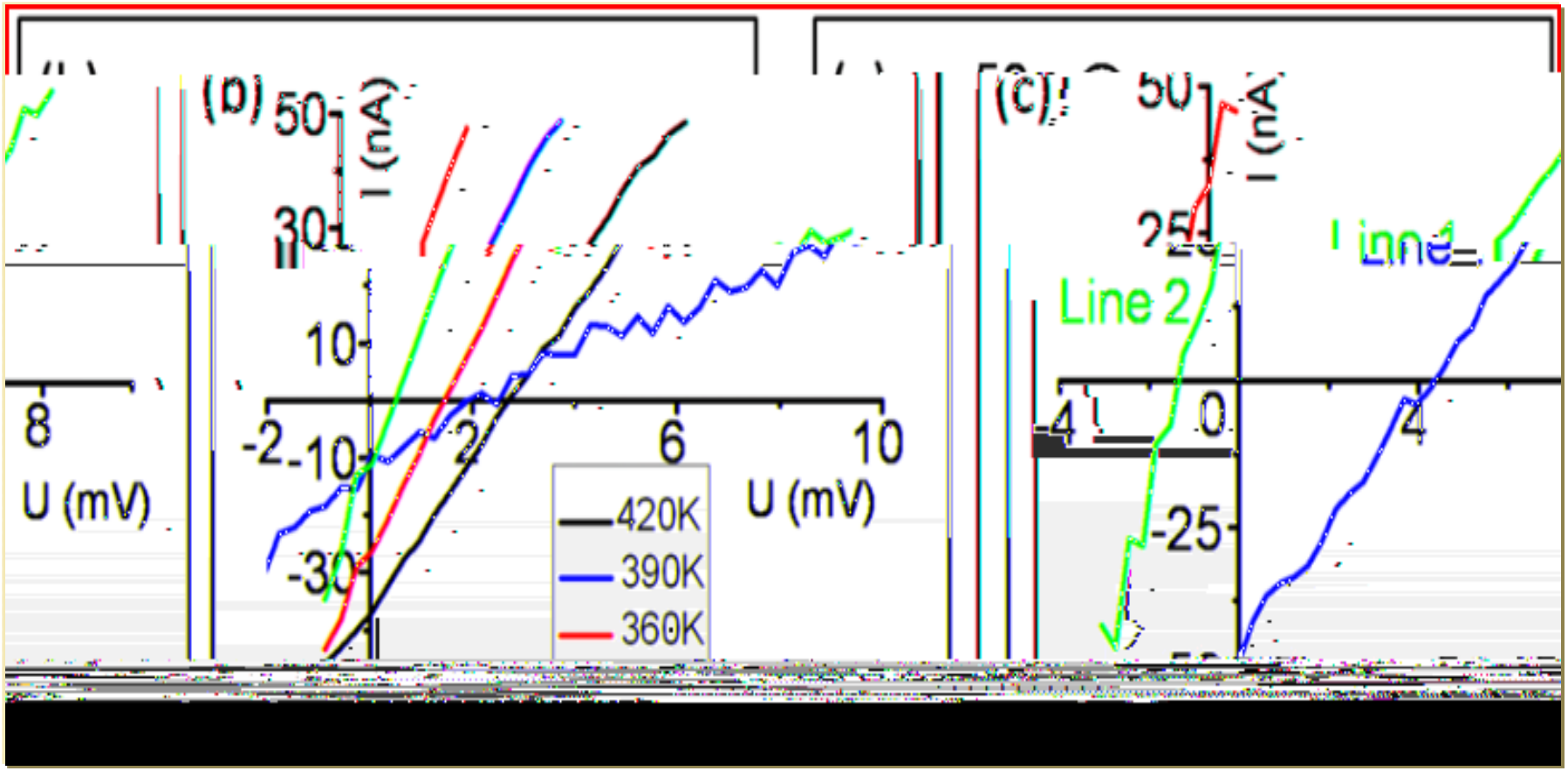


The substrate is heated

- Sketch of thermoelectric measurement.
- The W tip is coated with indium.

- The I-V curve shows V_{bias}.
- Thermoelectric voltage: $V = V_{bias}$

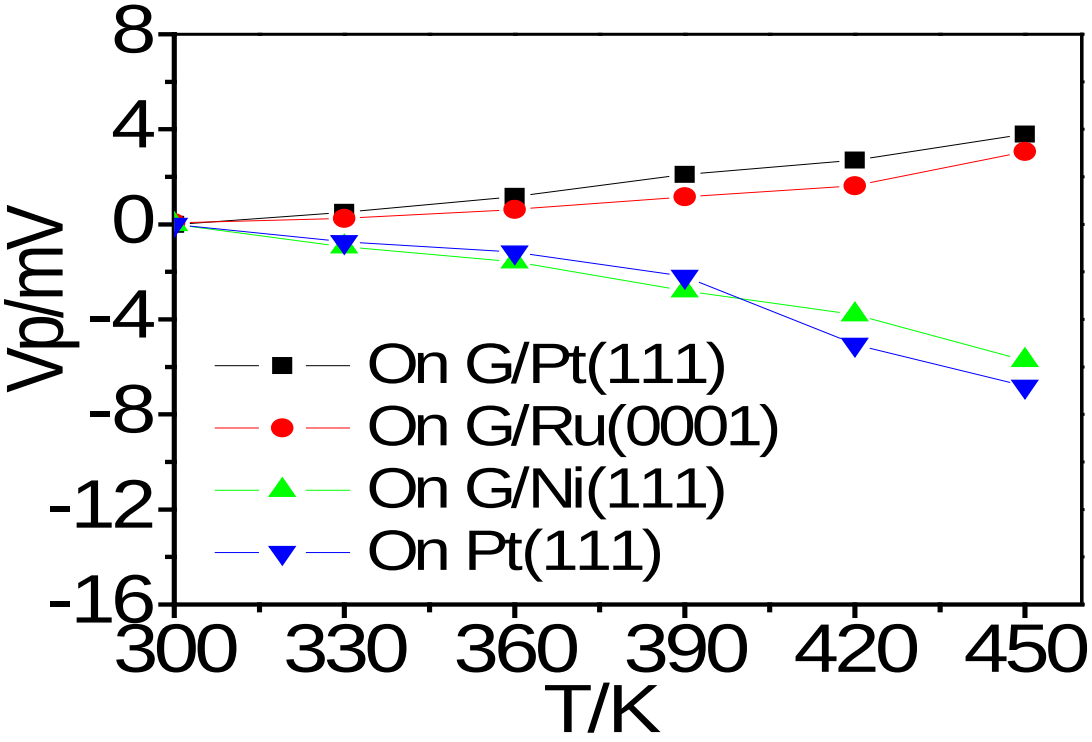
The Measurement of Thermoelectric Voltage



¾(b) The *I*-*V* curve of graphene on Pt(111) at 330 K, 360 K, 390 K and 420 K.

¾(c) The *I*-*V* curve of graphene on Ru(0001) at 450 K: two typical states: **positive** thermoelectric potential and **negative** thermoelectric potential, showing the variation from positive state (line 1) to negative state (line 2) when the tip approaches by a step.

Thermoelectric Properties of Graphene on Metals



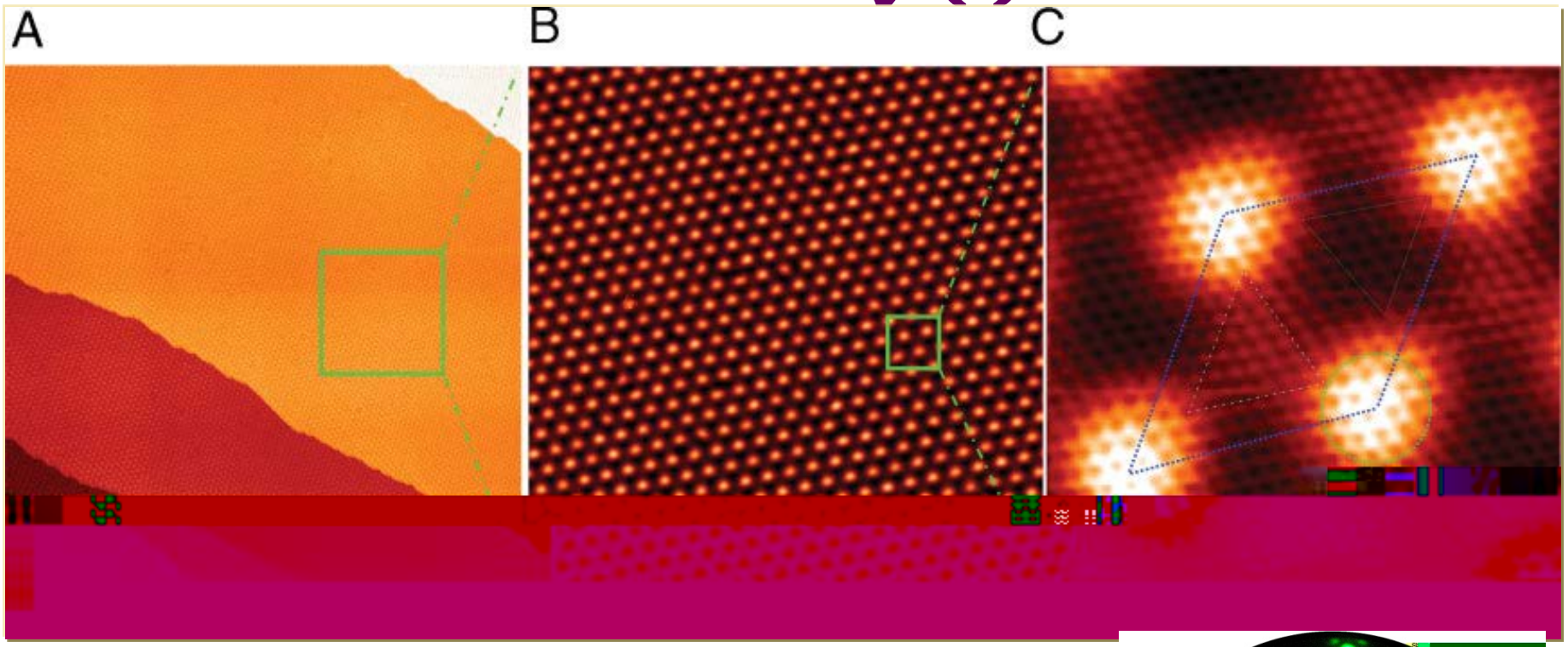
- Theoretical consideration was collaborated with (Qian Niu, UT-Austin X.C. Xie, OSU/IOP)

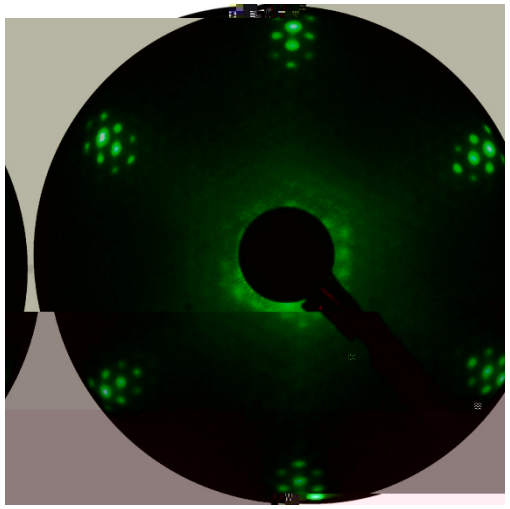
¾The voltage-temperature (V-T) relationship of graphenes on different metal surfaces, in comparison with the V-T curve of bare Pt(111) surface.

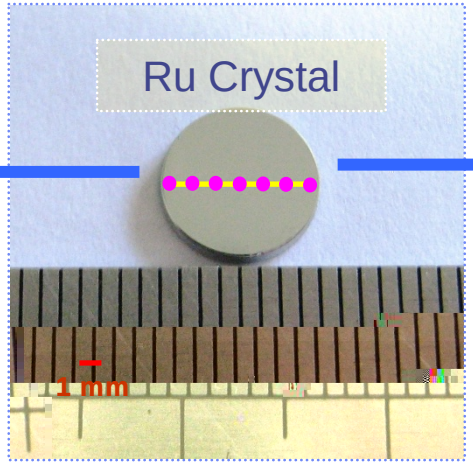
¾Voltage polarity gets changed.

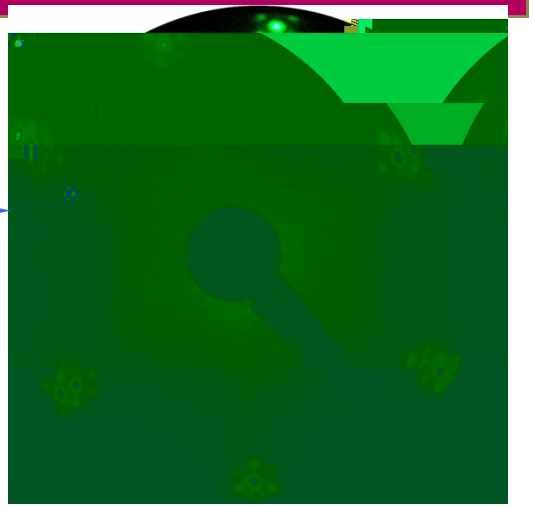
¾High Seebeck co-efficiency.

Summary (I)



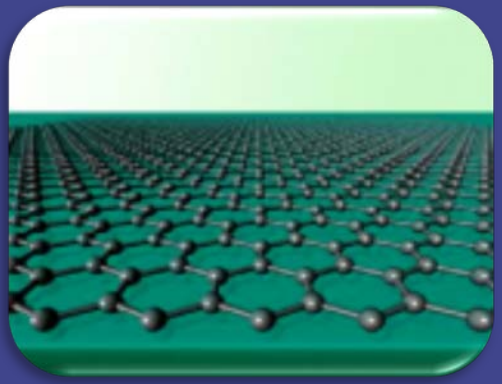


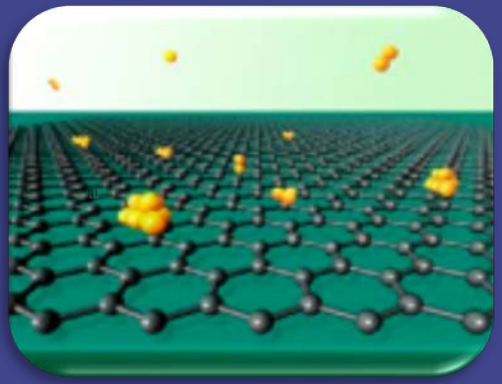


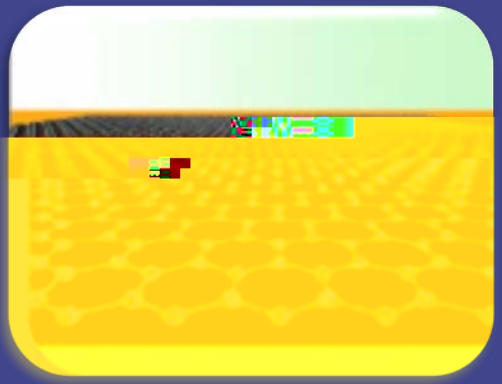


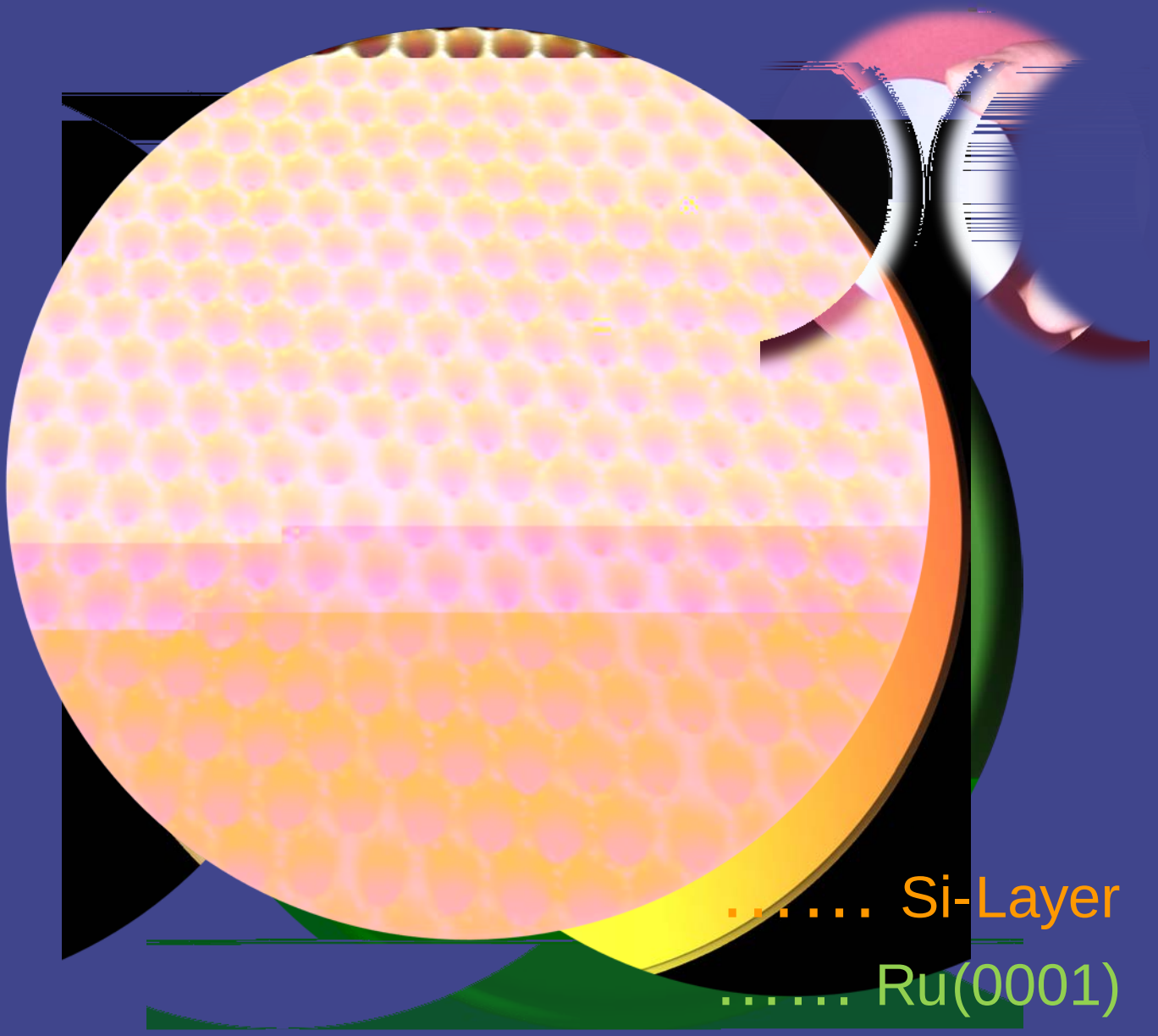
Formation of Large-scale Single Crystalline Graphene Monolayer

Summary (II)

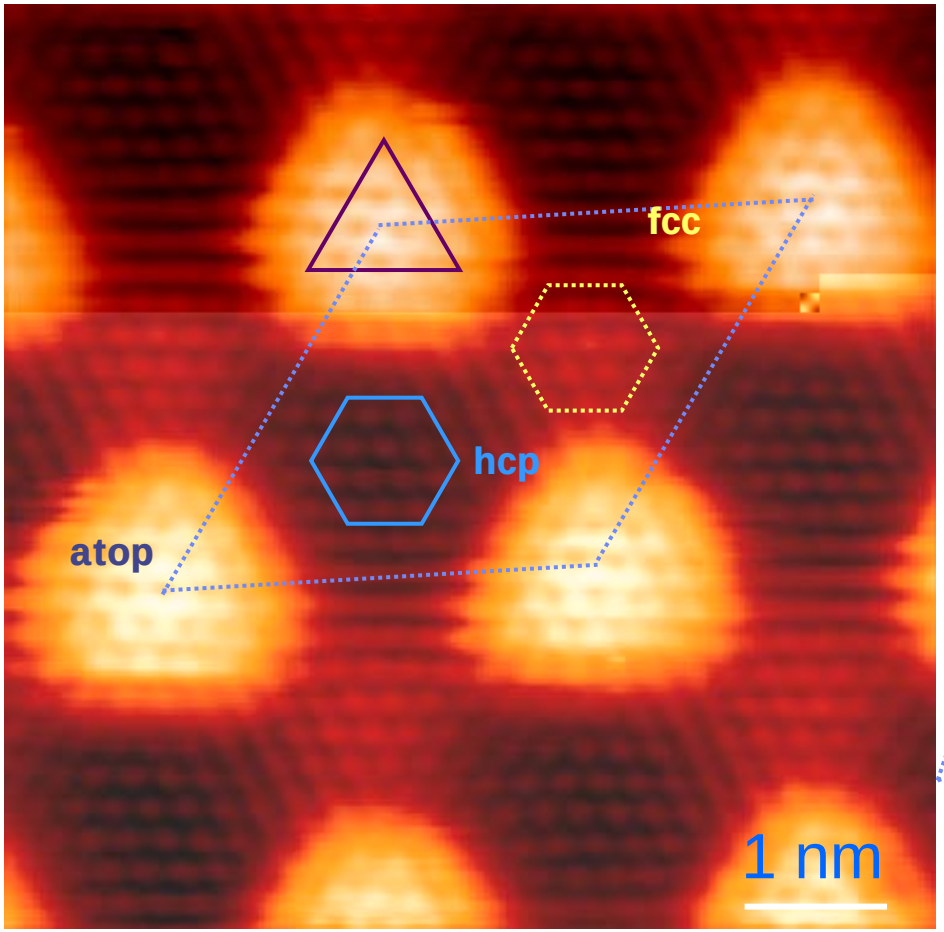


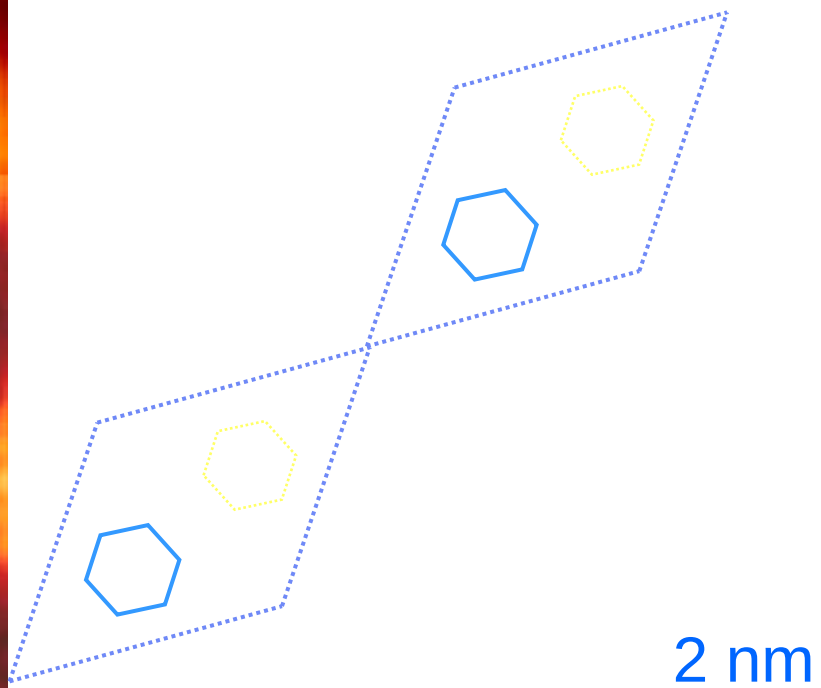




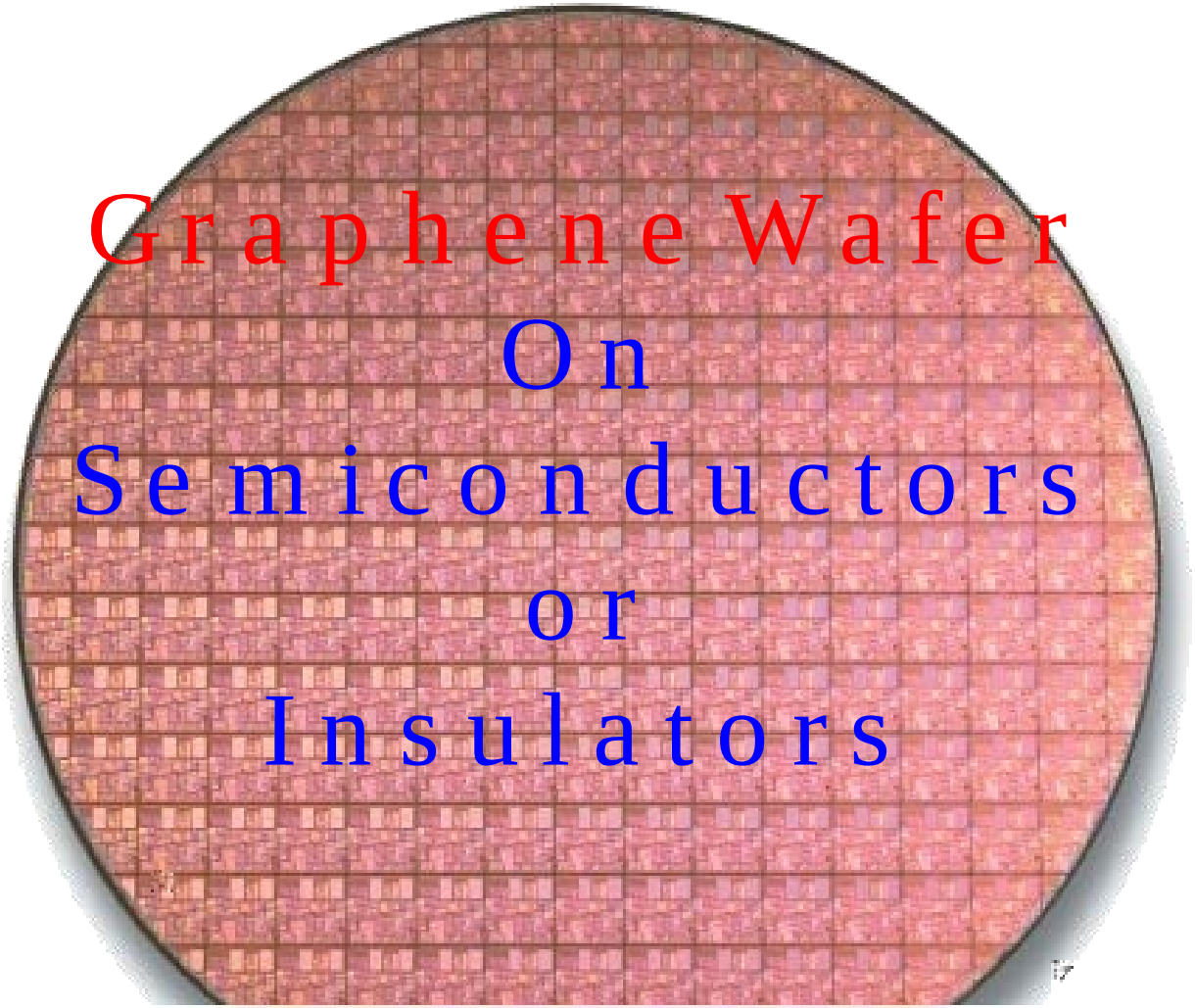


Summary (III)





Ordered Morie Pattern Used for Ordered Molecular/cluster Array Formation and Tunablity

Outlooks

Graphene Wafer and Graphene Complex Systems for the Future Nano-Electronics or Mol-tronics