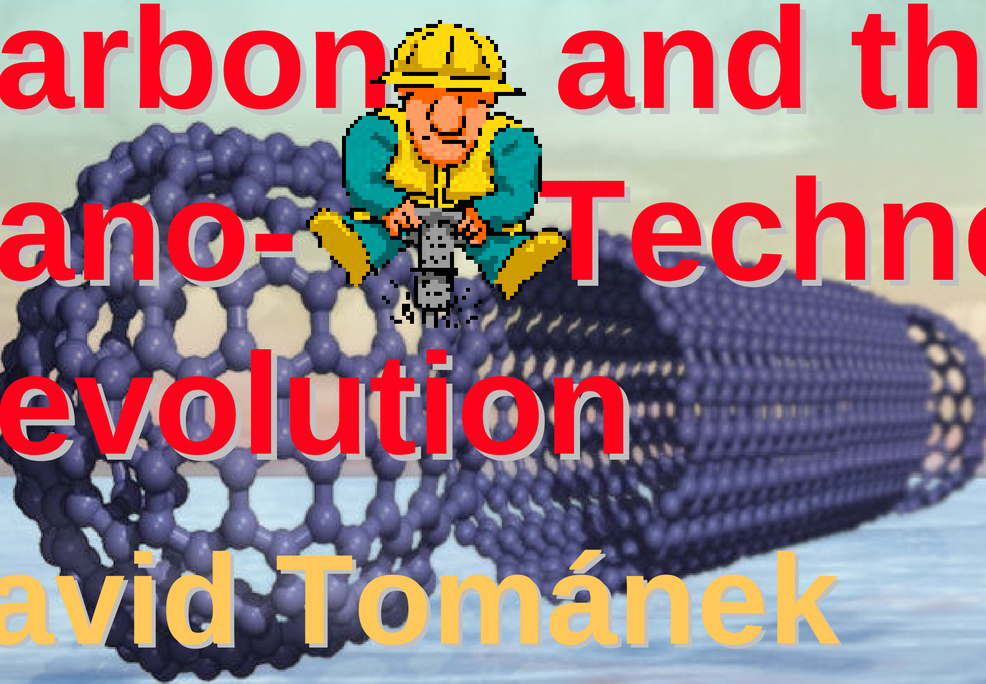
Nanostructured Carbon and the Nano-Technology Revolution



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Outline

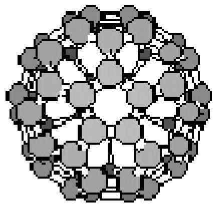
- Introduction
  - **Nanocarbon pioneers**
  - **What to expect from computer modeling**
  - **Computational tools**
- Curious Morphologies: Function Follows Form
  - **High thermal conductivity of nanotubes**
  - **Thermal contraction of nanotubes**
  - **Magnetism in foams and heterostructured tubes**
  - **Nanotube hooks as nano-velcro**
  - **Nanotube peapods: nano-memory and beyond**
- Structural transformations in fullerenes and nanotubes
  - **Fusion of fullerenes in peapods**
  - **Fusion of nanotubes**
- Technological challenges
  - **Defect tolerance of nanotubes**
  - **Deoxidation of defective nanotubes**
- Summary and Conclusions

It is never late …

… to get excited

Nanocarbon pioneers

- The C_{60} 'buckyball' and other fullerenes:



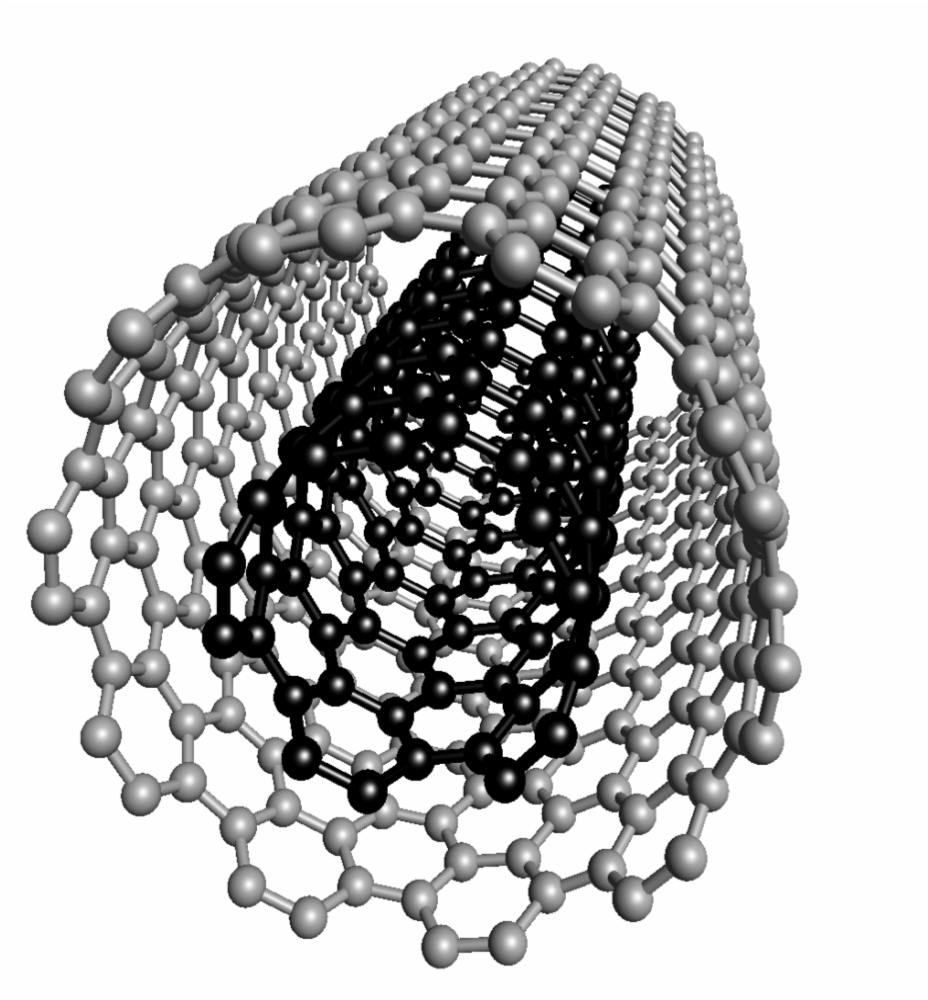
  - successful synthesis
  - potential applications:

lubrication	superconductivity

- Nanotubes:
  - successful synthesis
  - potential applications:

composites	flat-panel displays
Li-ion batteries	super-capacitors
medication delivery	fuel cells
EMI shielding	hydrogen storage

Carbon nanotubes



- 1-20 nm diameter
- Atomically perfect
- Chemically inert
- 100 times stronger than steel
- Extremely high melting temperature
- Ideal (ballistic) conductors of electrons, or insulators
- Ideal heat conductors
- Non-toxic

Commercial production of nanotubes

Rosseter

Rosseter Holdings Ltd

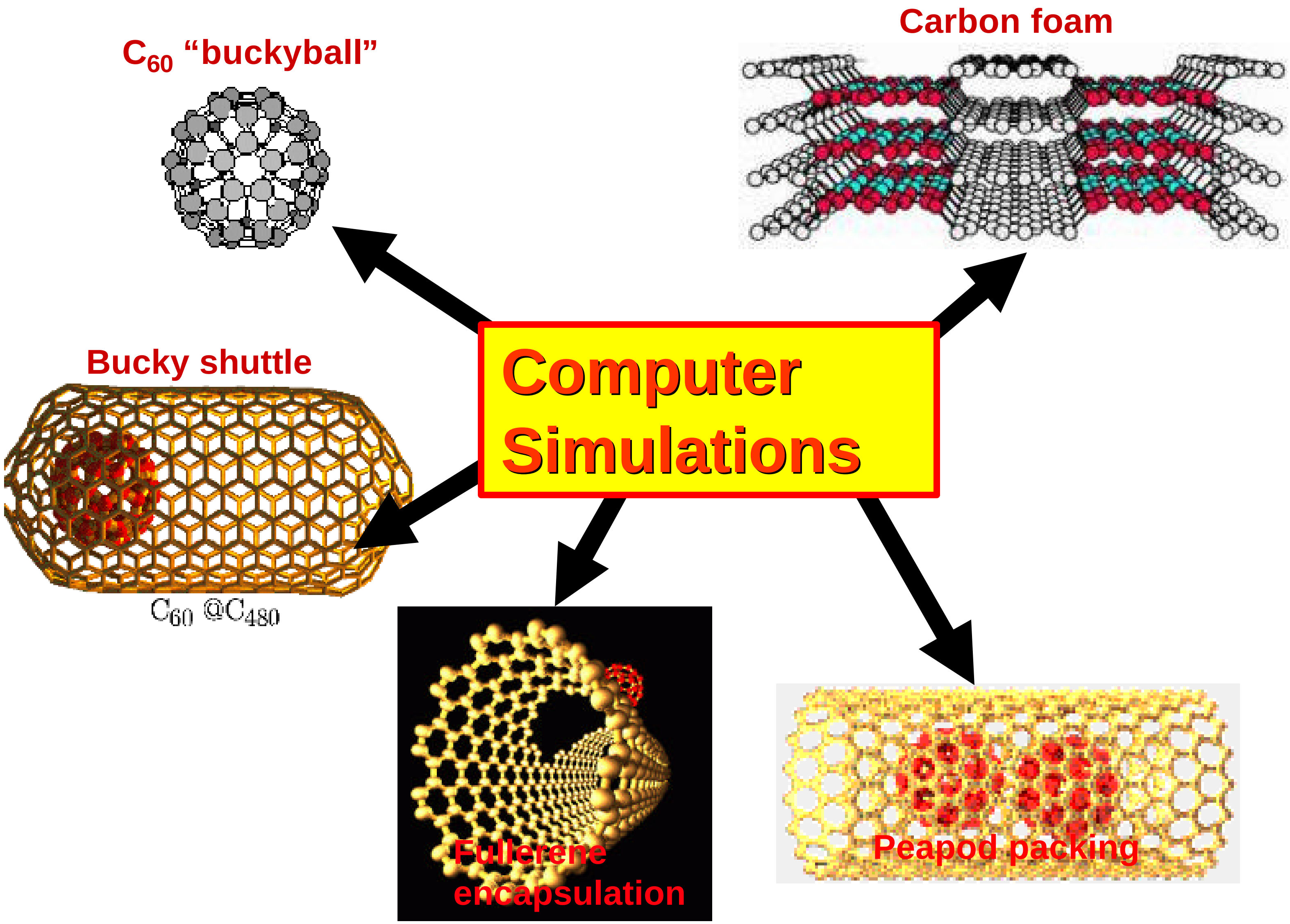
Building the nanoworld

Limassol, Cyprus

http://www.e-nanoscience.com

What to expect from computer modeling

Zooming in beyond observation



Computational tools

- Electronic structure calculations based on the *ab initio* Density Functional formalism
- Time evolution of electronic wave functions:

  Time-Dependent Density Functional formalism
- Atomic motion: Molecular dynamics simulations with electrons in the ground and excited state
- Forces from total energy expressions:

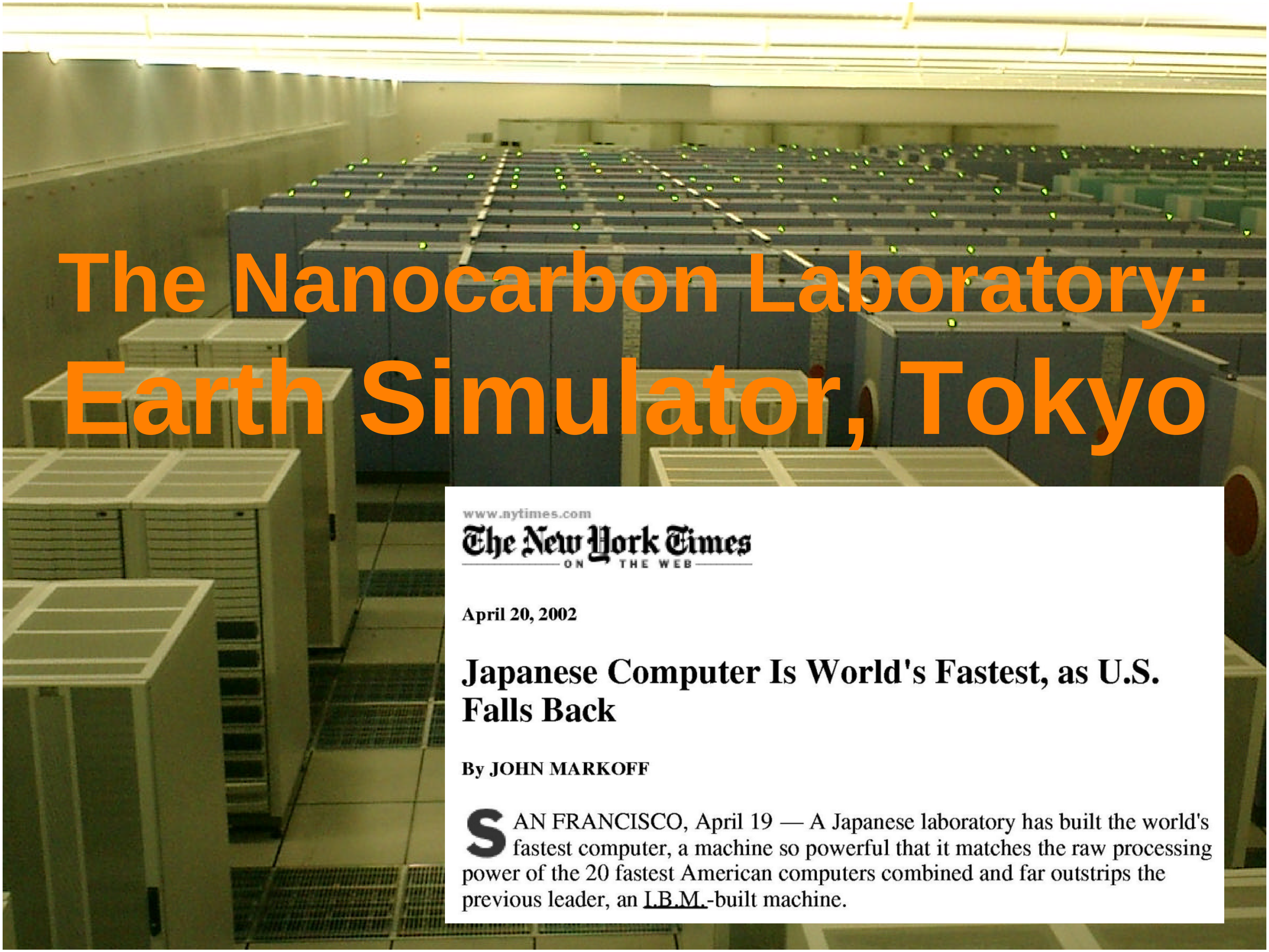
  $E_{tot} = E_{tot}(\{R_i\}) = E_{tot}\{?(r)\}$

  ab initio Density Functional formalism

  $E_{tot} = S_i\ E_{coh}(i) = S_i\ [E_{bs}(i) + E_{rep}(i)\ ]$

  parametrized LCAO formalism (CRT)
- Massively parallel computer architectures and suitable algorithms distribute load over processors for speed-up

The Nanocarbon Laboratory:
Earth Simulator, Tokyo



www.nytimes.com

The New York Times ON THE WEB

April 20, 2002

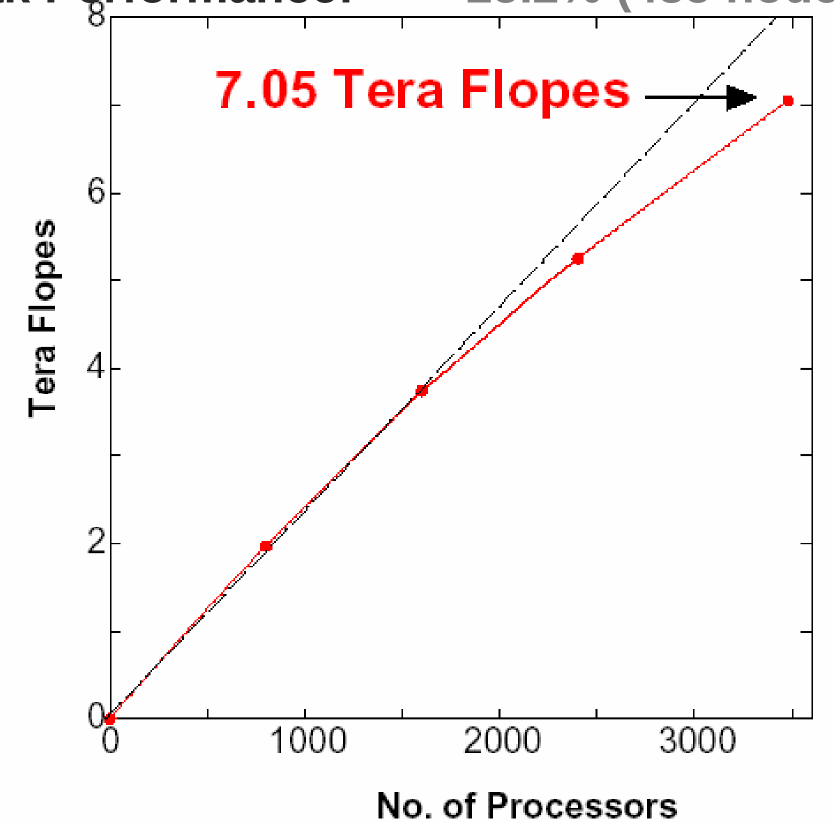
Japanese Computer Is World's Fastest, as U.S. Falls Back

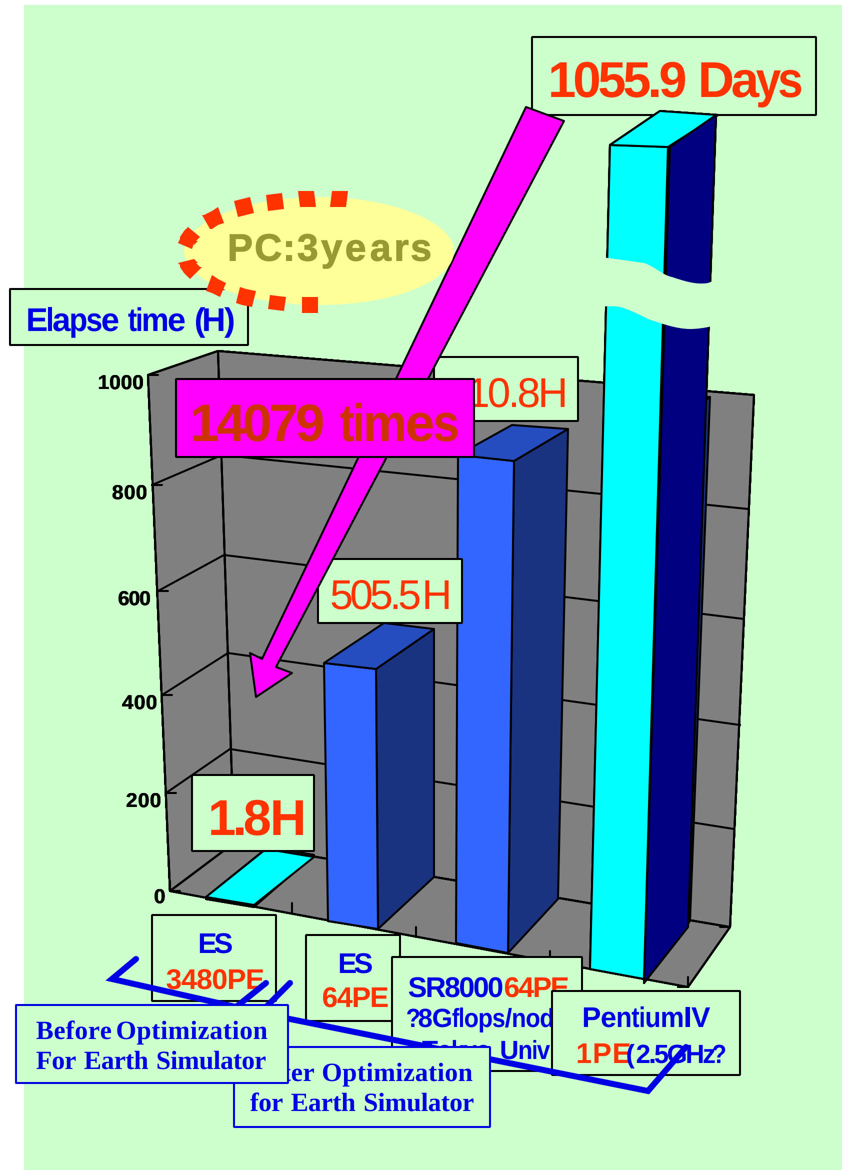
By JOHN MARKOFF

SAN FRANCISCO, April 19 — A Japanese laboratory has built the world's fastest computer, a machine so powerful that it matches the raw processing power of the 20 fastest American computers combined and far outstrips the previous leader, an I.B.M.-built machine.

Performance of MD Simulations on the Earth Simulator

Available no. of PE: 3480 PE(435 nodes)
Vector Op.: 97.7%
Parallel Op.: 99.99%
Total Performance: 7.05TeraFlops
Peak Performance: 25.2% (435 nodes)





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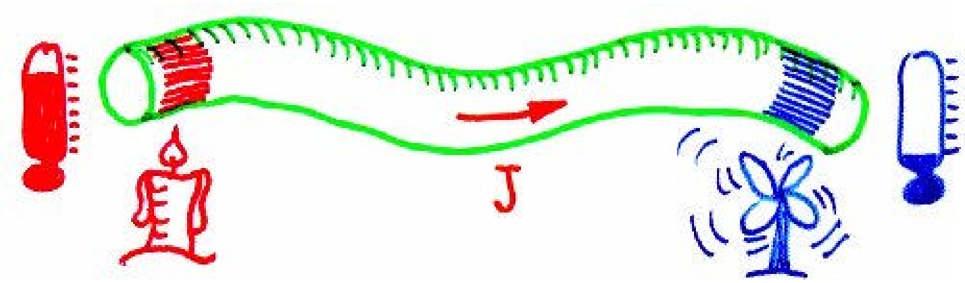
Curious Morphologies: Function Follows Form

High Thermal Conductivity of Nanotubes



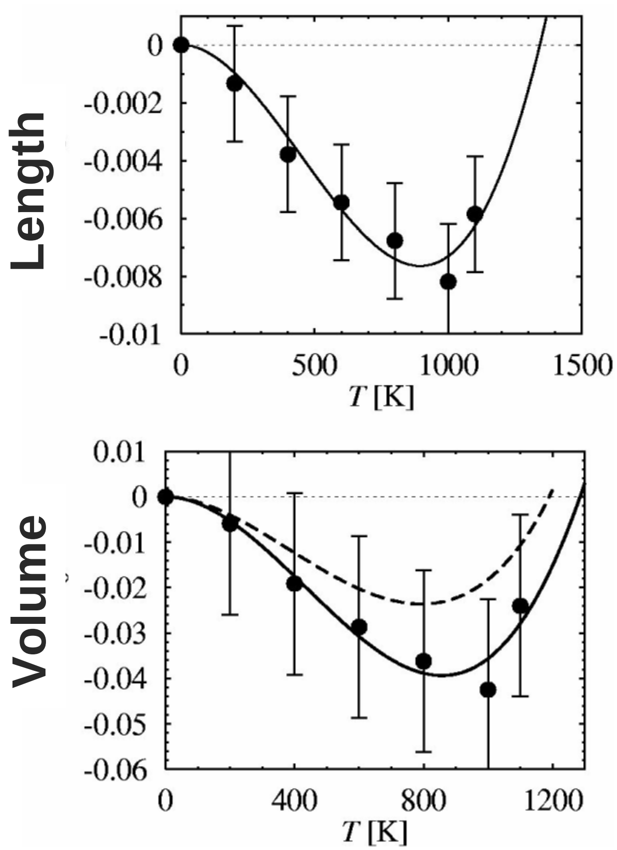
Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. 84, 4613 (2000)

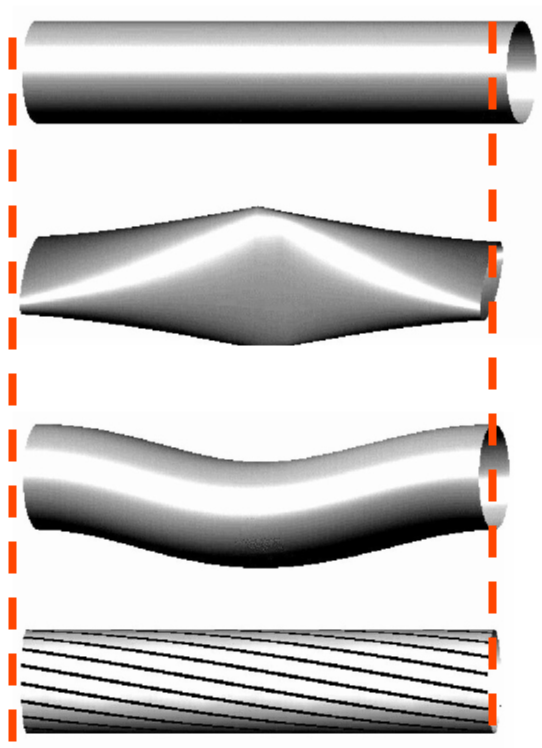
- Nanotubes may help solve the heat problem:
  Efficient conductors of electrons and heat
- Record Heat Conductivity:
  * Diamond
    (isotopically pure): 3320 W/m/K
  * Nanotubes: 6,600 W/m/K (theory, SWNT)
    >3,000 W/m/K (experiment, MWNT)

  (room temperature values)

  (combination of large phonon mean free path, speed of sound, Debye temperature)

Negative thermal expansion of nanotubes





Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. 92, 015901 (2004).

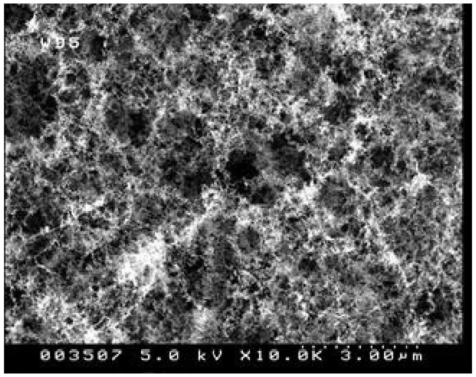
? Nanotubes contract rather than expand

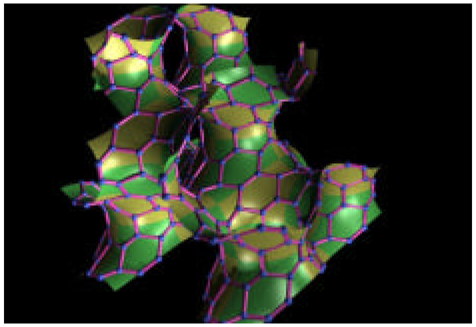
? Physical origin: length contraction due to a gain in configurational and vibrational entropy

? Challenge: Large unit cells with >100,000 atoms required

Magnetism in nanostructured carbon

- A. V. Rode, E. G. Gamaly, A. G. Christy, S. T. Hyde, R. G. Elliman, B. Luther-Davies, A. I. Veinger, J. Giapintzakis, J. Androulakis, Noejung Park, Mina Yoon, Savas Berber, Jisoon Ihm, Eiji Osawa, and David Tománek
- Synthesis by Laser Ablation of Amorphous Carbon





Scanning Electron Microscopy Image and possible structure of Nanostructured Carbon Foam

Ferromagnetic behavior (all known carbons are diamagnetic!)

Seite 10 / Süddeutsche Zeitung Nr. 70 WISSEN Mittwoch, 24. März 2004

Das fünfte Element

Leicht, luftig, locker: Physiker entwickeln einen magnetischen, halbleitenden Nanoschaum aus Kohlenstoff

Fifth form of carbon?

Fifth element?

nature physicsportal

researchhighlights

Scientists create fifth form of carbon

Jim Giles

Magnetic carbon 'nanofoam' could find medical applications.

Researchers have created a new form of carbon: a spongy solid that is extremely lightweight and, unusually, attracted to magnets. The foam could one day help treat cancer and enhance brain scans, say the inventors.

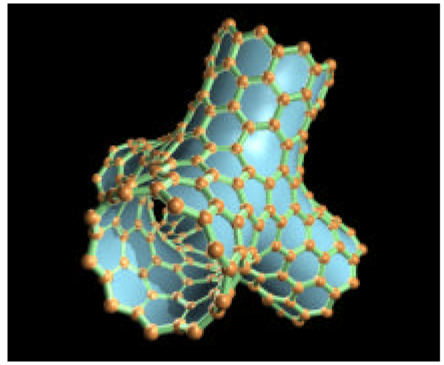
The new structure was created when physicists at the Australian National University in Canberra bombarded a carbon target with a laser capable of firing 10,000 pulses a second. As the carbon reached temperatures of around 10,000 ºC, it formed an intersecting web of carbon tubes, each just a few billionths of a metre long. The researchers have called the solid a 'nanofoam'.

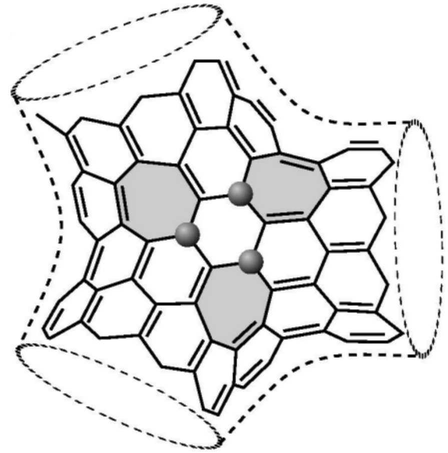
John Giapintzakis of the University of Crete has used an electron microscope to study the structure of the nanofoam. He says it is the fifth form of carbon known after graphite, diamond and two recently discovered types: hollow spheres, known as buckminsterfullerenes or buckyballs, and nanotubes.

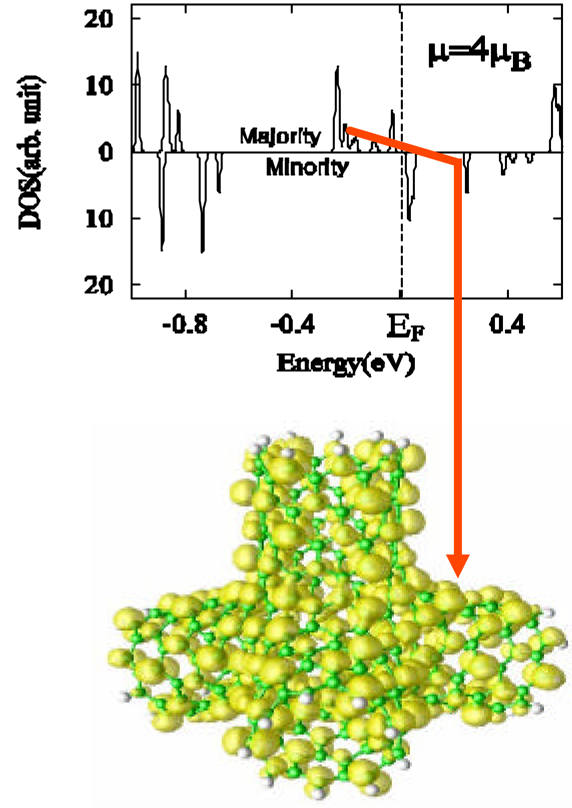
The new carbon foam is unusually attracted to magnets.
© Photodisc

It could help treat tumours, says David Tománek of Michigan State University, who has also worked with the foam. He points out that the new structure is very bad at transferring heat. So Tománek proposes that the foam could be injected into tumours, and the tumours exposed to infrared radiations. The foam would absorb the radiation and kill the tumour as it heated up, he suggests, without heating the surrounding tissue.

Why should carbon foam be magnetic?





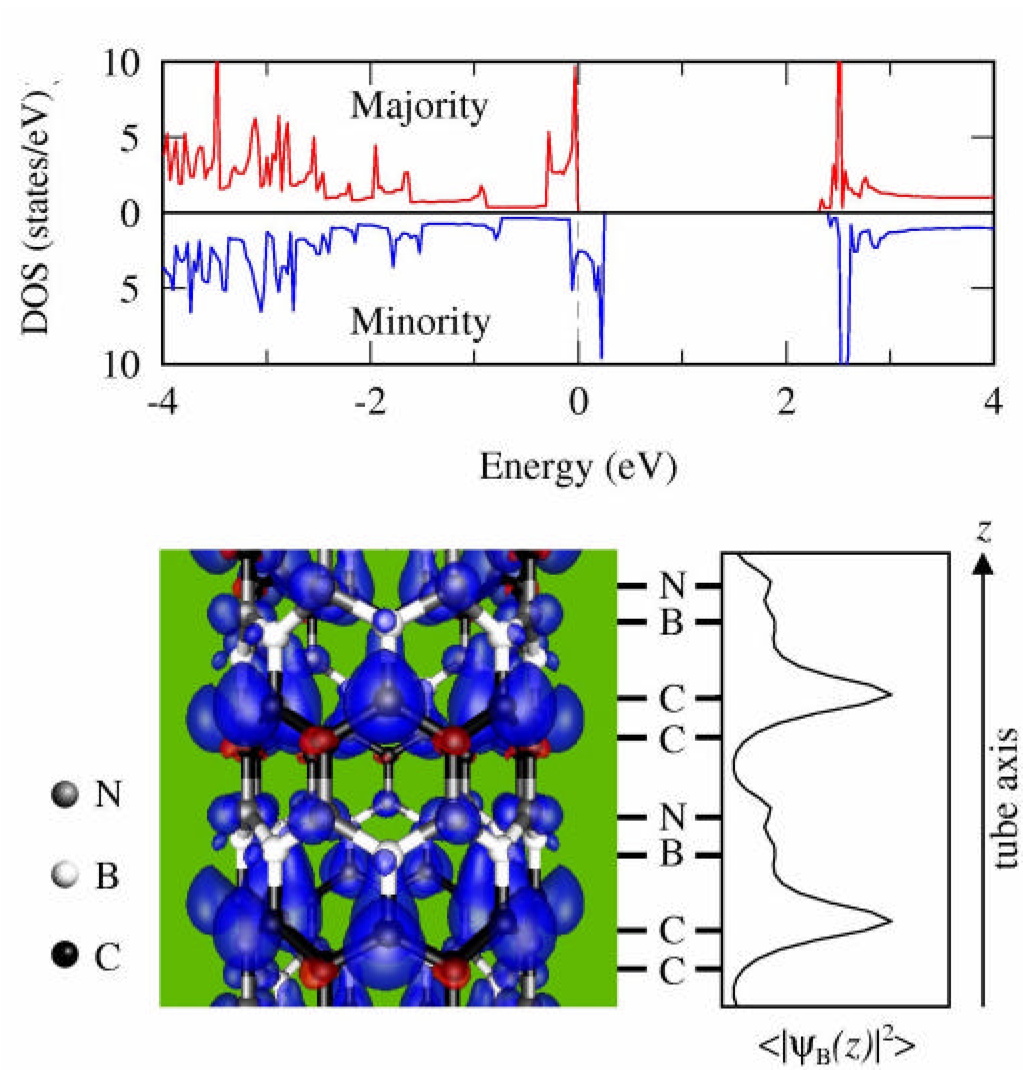


? Physical origin:
Sterically protected carbon radicals are stabilized in surfaces with a negative Gaussian curvature

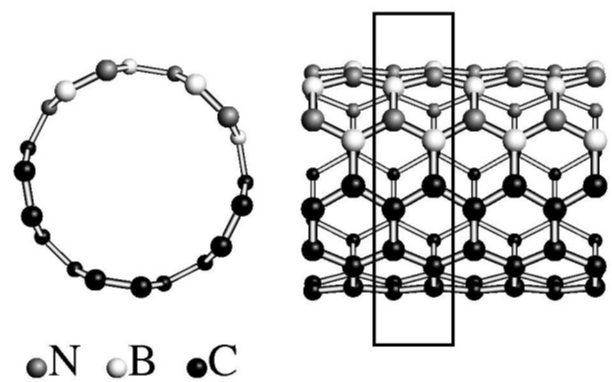
? Spin polarized electrons are delocalized across entire structure

Noejung Park, Mina Yoon, Savas Berber, Jisoon Ihm, Eiji Osawa, and David Tománek, Phys. Rev. Lett. 91, 237204 (2003).

Itinerant ferromagnetism in C/BN heterostructured nanotubes

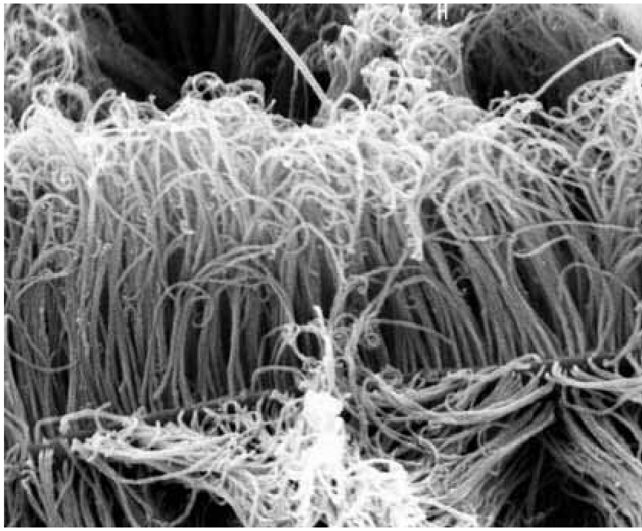


- Heterostructured C/BN nanotubes can become magnetic
- Magnetic ordering determined by heterostructure



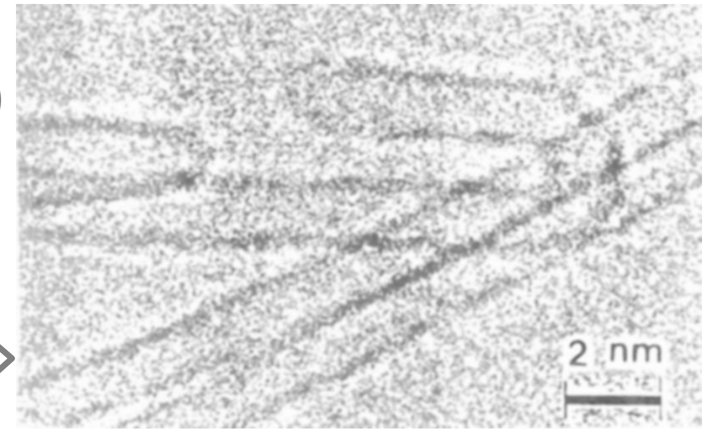
Jin Choi, Yong-Hyun Kim, Keejoo Chang, David Tománek, Phys. Rev. B 67, 125421 (2003)

Nanotube hooks as nano-velcro

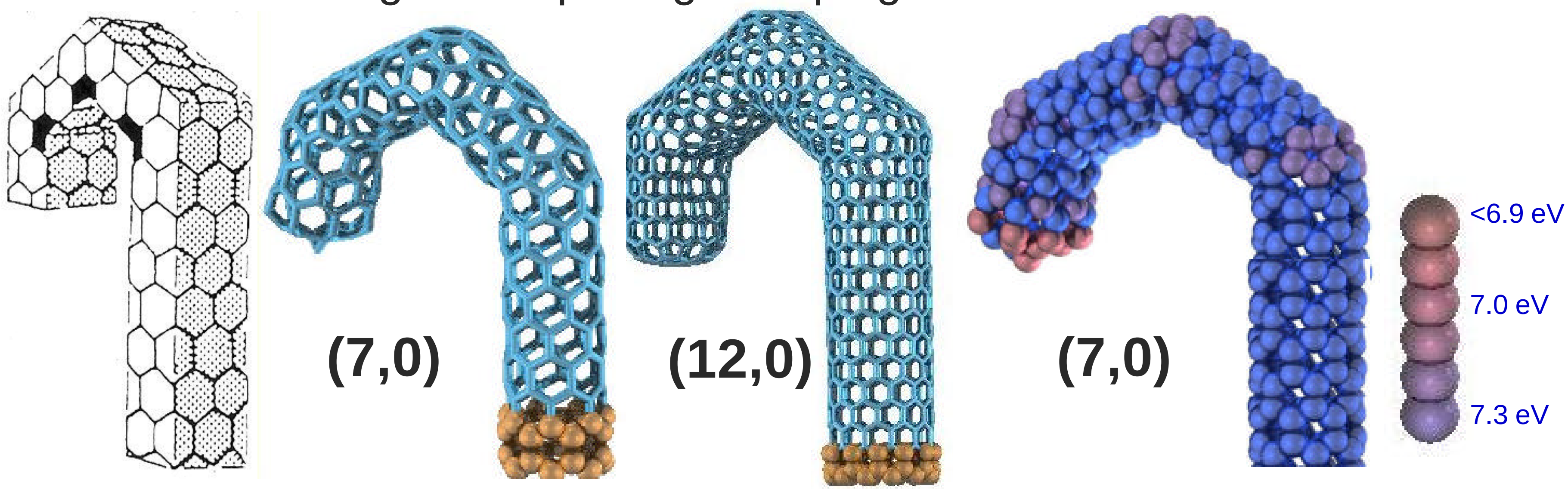


SEM of curly nanotubes (J.-C. Gabriel)

HRTEM of a nanohook (S. Iijima)

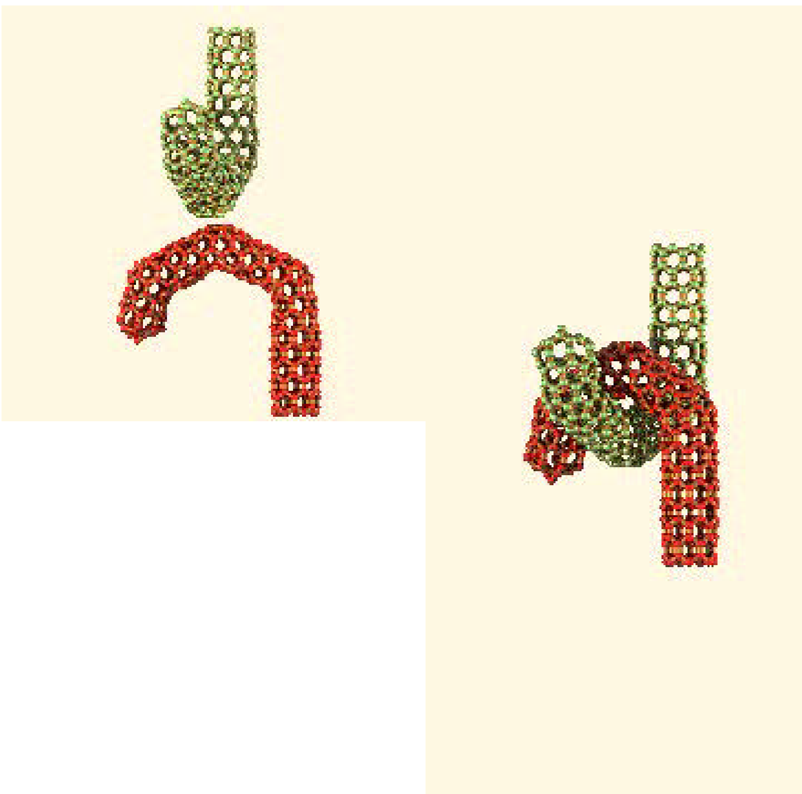


✍Permanent bending due to pentagon-heptagon insertion creates hooks:



nano*VELCRO* bond

Engage **Disengage**

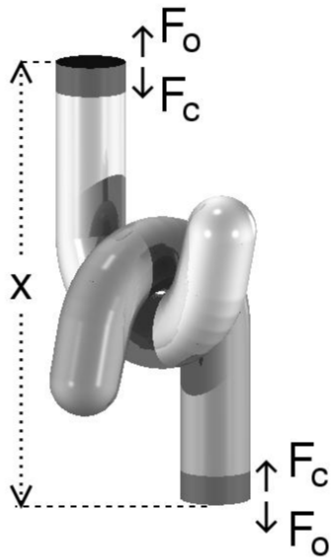


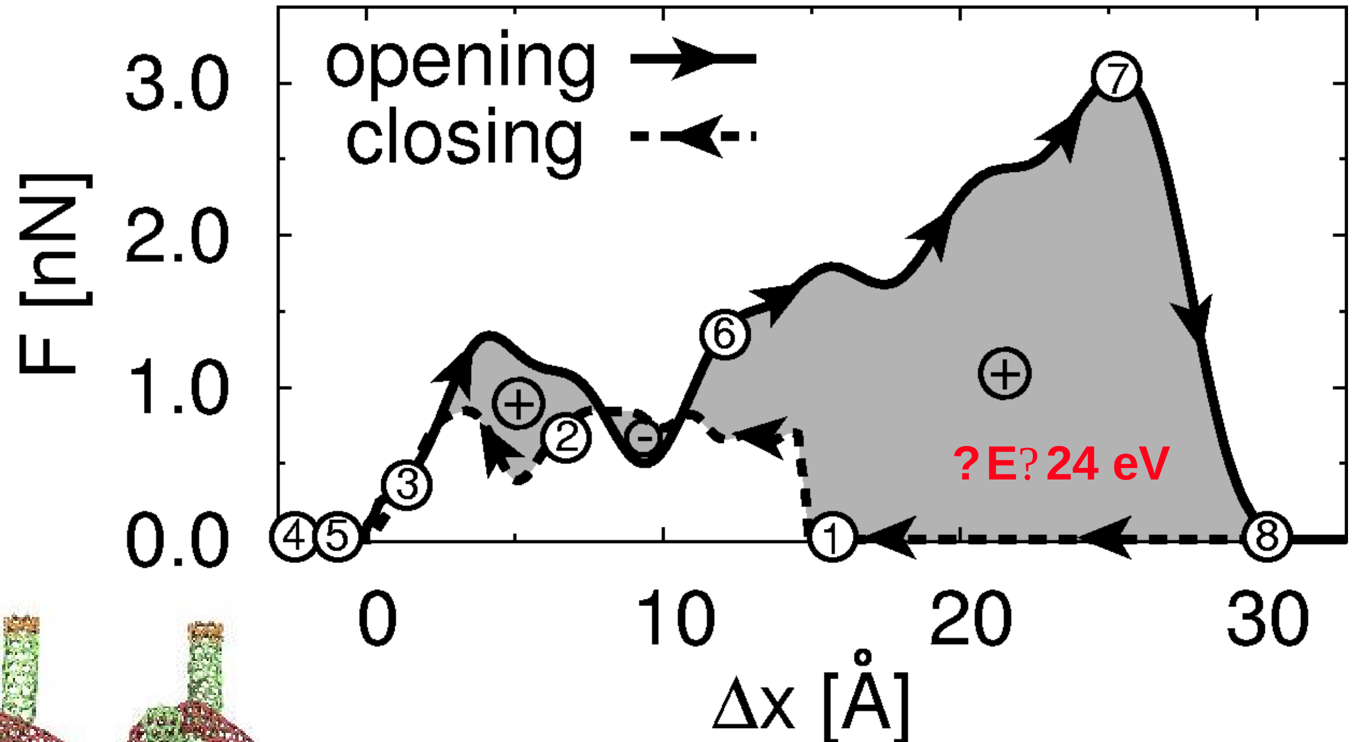
Mating nanotube hook elements

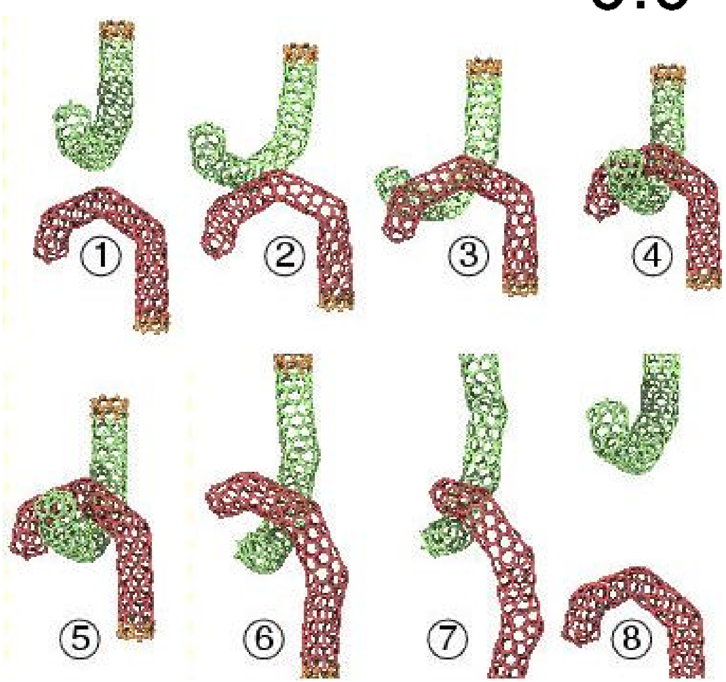
- Strong, permanent bonds
- Self-repairing bonds
- Chemically inert and non-toxic
- Thermally stable
- Good thermal and electrical conductors
- U.S. Patent pending (Tomanek/Enbody/Kwon)

Savas Berber, Young-Kyun Kwon, and David Tománek, Bonding and Energy Dissipation in a Nanohook Assembly, Phys. Rev. Lett. 91, 165503 (2003).

Toughness of nano*VELCRO*

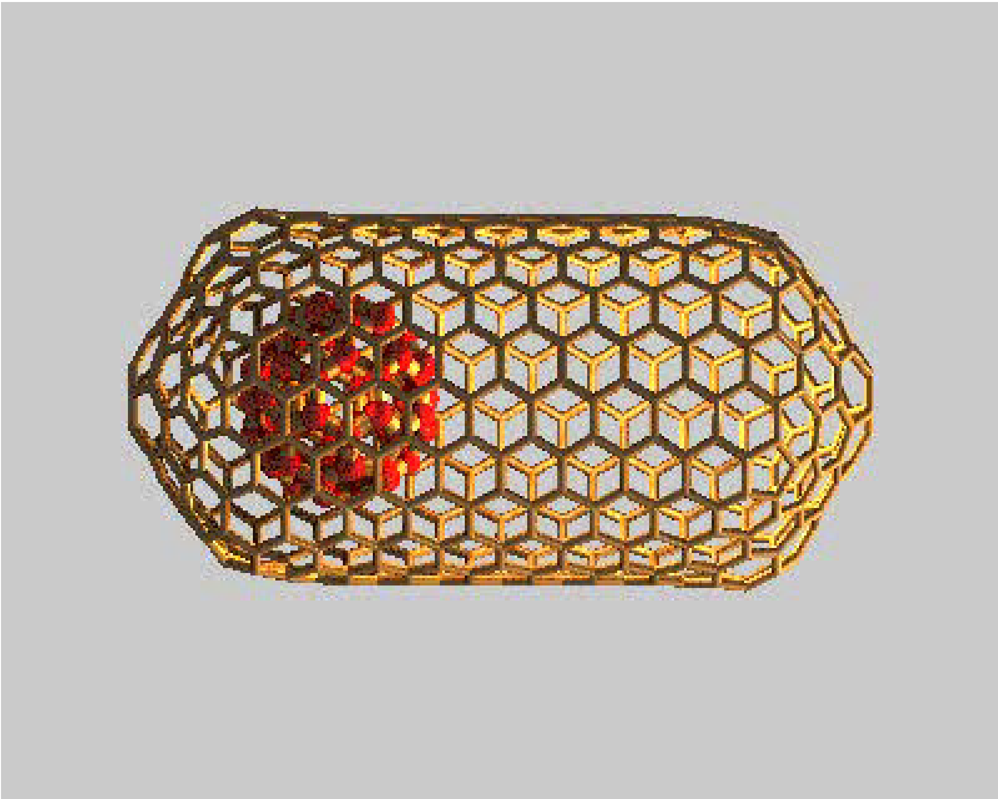






- Average opening force = 1.7 nN
- Average closing force = 0.9 nN
- Toughness of (7,0) nano*VELCRO* = 30 eV
- Cleavage energy of (7,0) CNT = 15.4 eV
- Ultimate strength up to 3 GPa

Nanotube peapods: nano-memory and beyond



A Pea in a Pod:
The Bucky Shuttle

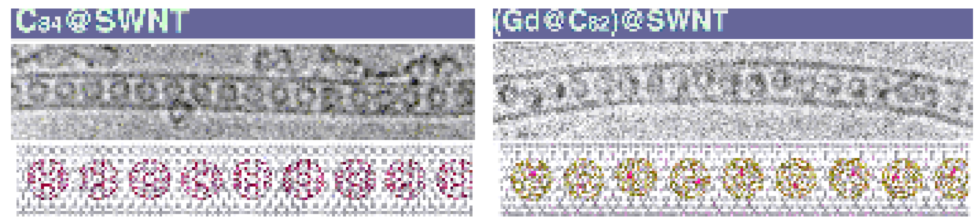
Young-Kyun Kwon, David Tománek, and Sumio Iijima, Phys. Rev. Lett. **82**, 1470 (1999)

C_{60}@nano-capsule: Non-volatile memory

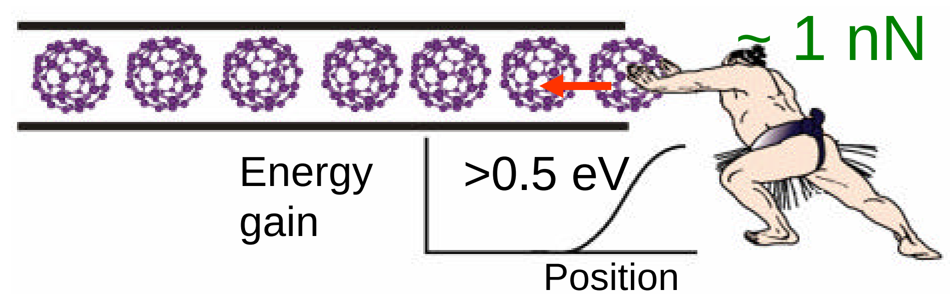
- Left/Right=Bit 0/Bit 1
- Packing density: <5 TB/cm^2
- Writing speed: <1 THz
- U.S. Patent 6,473,351

Uses beyond computer memory

•Intercalation of other species (Sumio Iijima)



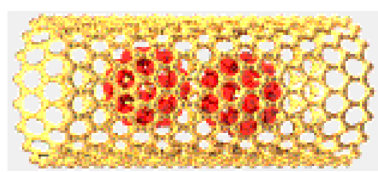
•Possible New Applications:

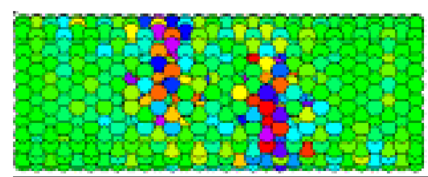


-Pressure container (e.g. Li, hydrogen storage)

p>1 GPa

-Chemical reaction vessel

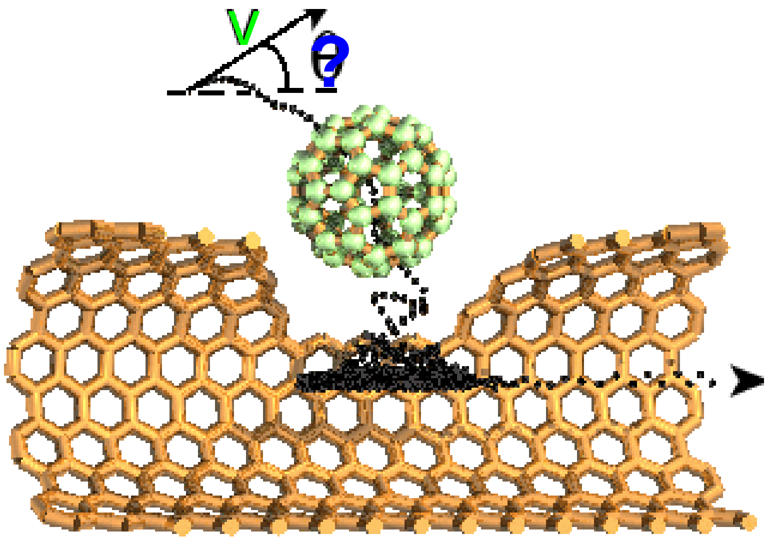




Stress visualization

Insertion of fullerenes into peapods

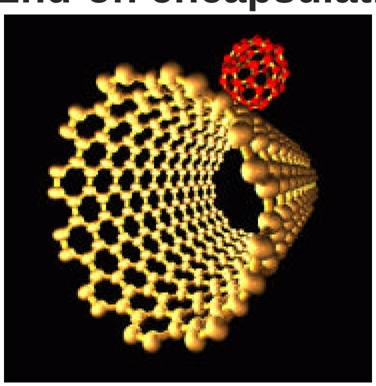
Savas Berber, Young-Kyun Kwon, and David Tománek,
Microscopic Formation Mechanism of Nanotube Peapods,
Phys. Rev. Lett. 88, 185502 (2002).



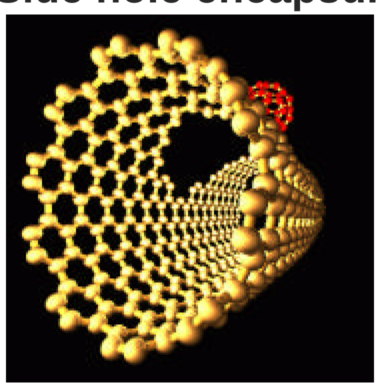
Microscopic mechanism:

- Through a nanotube end?
- Through a side hole?
- Dependence on initial conditions:
  C_{60} take-off velocity?
  C_{60} take-off angle?

End-on encapsulation



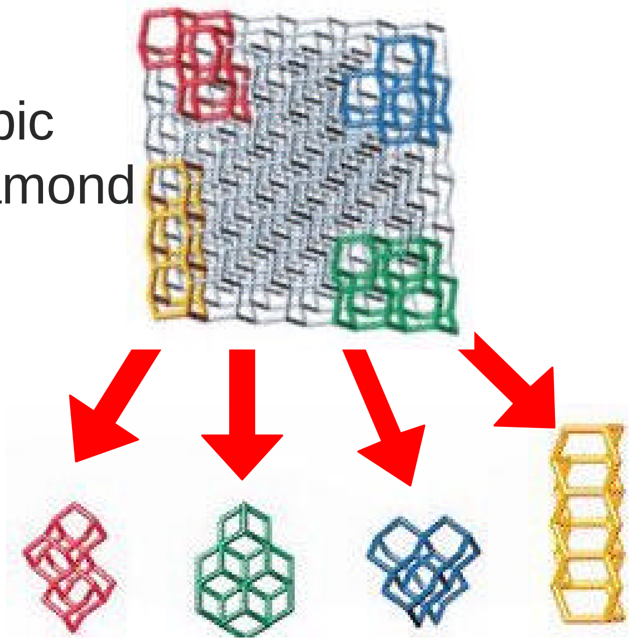
Side hole encapsulation



Simulations show that encapsulation through a large defect is most efficient

Diamondoids@Nanotubes

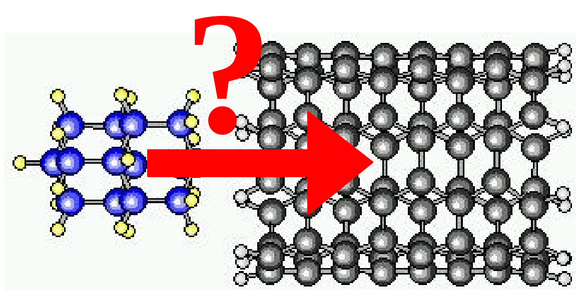
cubic diamond



diamondoid particles

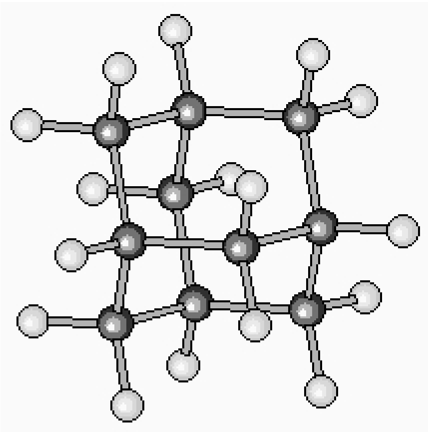
•Hydrogen-terminated, nanometer-size diamondoid particles were isolated experimentally *[J.E. Dahl et al., Science* ***299****,96-99(2003)]*

•Possible application in nanotechnology: functional building blocks with tunable electronic, structural properties

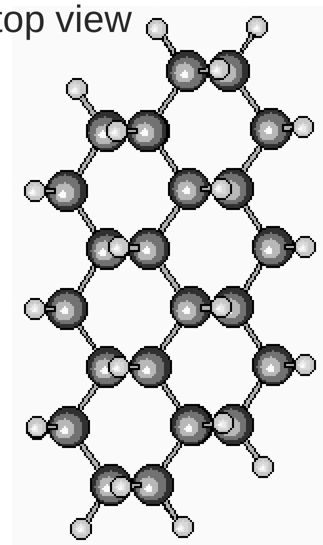


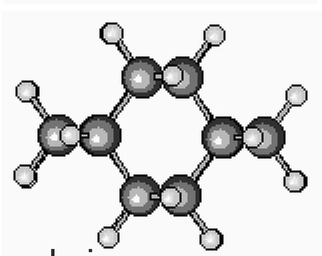
•Possible encapsulation in nanotubes provides for more complex nanostructures

Properties of lower diamondoids



top view





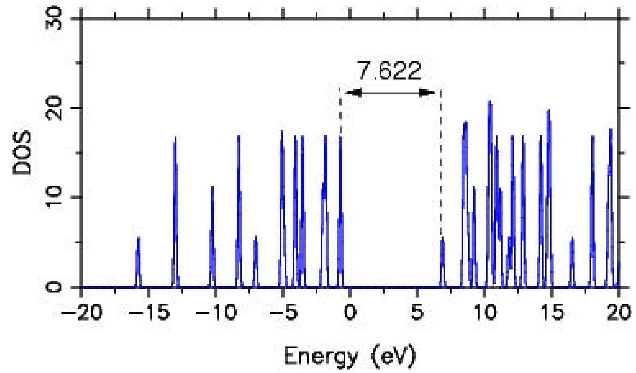
end view

Adamantane:$C_{10}H_{16}$ *(G.C. McIntosh)*

? E = -170.530 eV (atomization energy)

? $?_f$ = -60.51 eV (formation energy w.r.t. H_2, diamond)

? E_f/N_c = -6.051 eV (formation energy per carbon atom w.r.t. H_2, diamond)

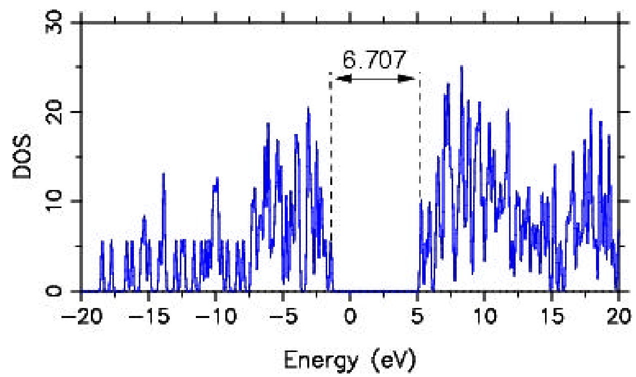


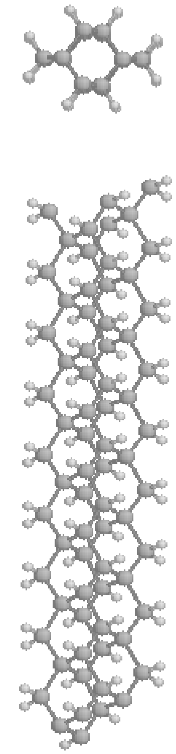
Hexamantane:$C_{30}H_{36}$ *(G.C. McIntosh)*

? E = -467.905 eV (atomization energy)

? E_f = -165.09 eV (formation energy w.r.t. H_2, diamond)

? E_f/N_c = -5.503 eV (formation energy per carbon atom w.r.t.H_2, diamond)

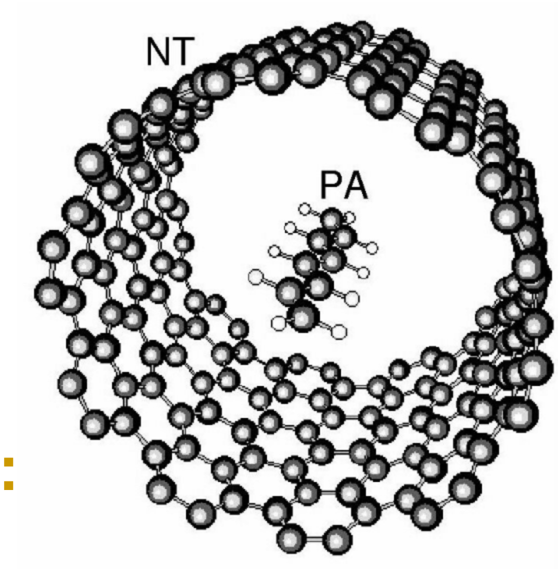




Diamodoid chain: C_nH_n *(N. Park)*

Polyacetylene@Nanotubes

A designer superconductor?

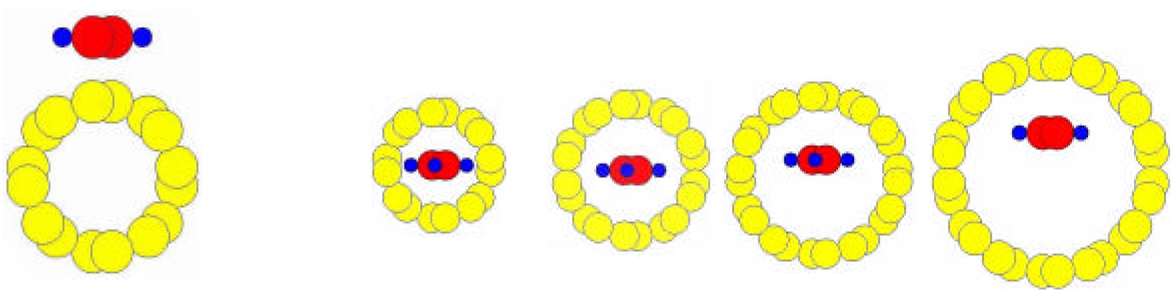


Facts:

- Undoped metallic nanotubes are superconductors
- Doped polyacetylene ropes are conductors

Exo- and endohedral PA/CNT system:

- **Potential superconductor?**

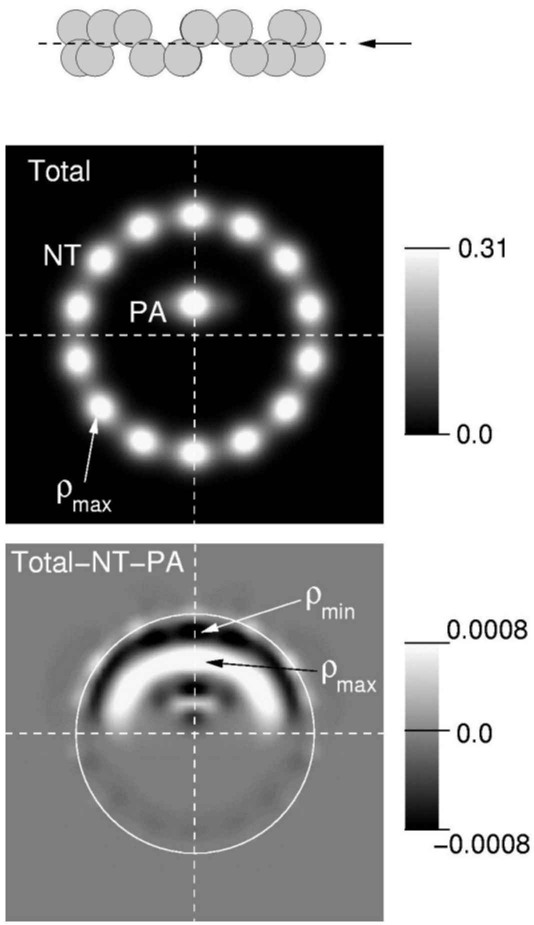


Exohedral **Endohedral**

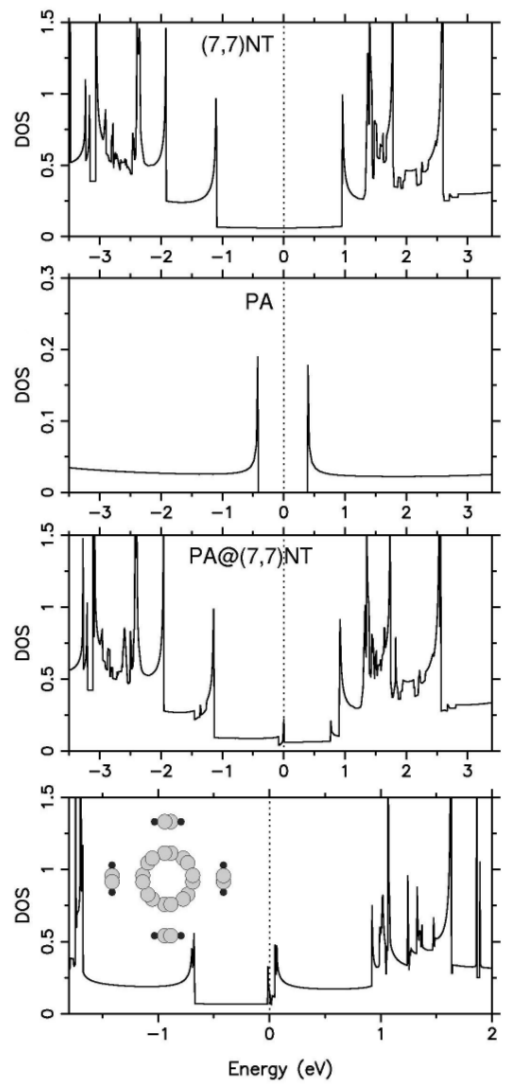
*Gregory McIntosh, Yung Woo Park, and David Tománek, Phys. Rev. B **67**, 125419 (2003)*

Electronic structure changes

Charge redistribution



Density of states



Findings:

- A small CNT/PA hybridization modifies electronic structure near E_F
- van Hove singularities of PA appear near the CNT Fermi level
- One of the PA-induced singularites is pinned at E_F, thus increasing $N(E_F)$
- This effect may increase T_c of undoped CNTs

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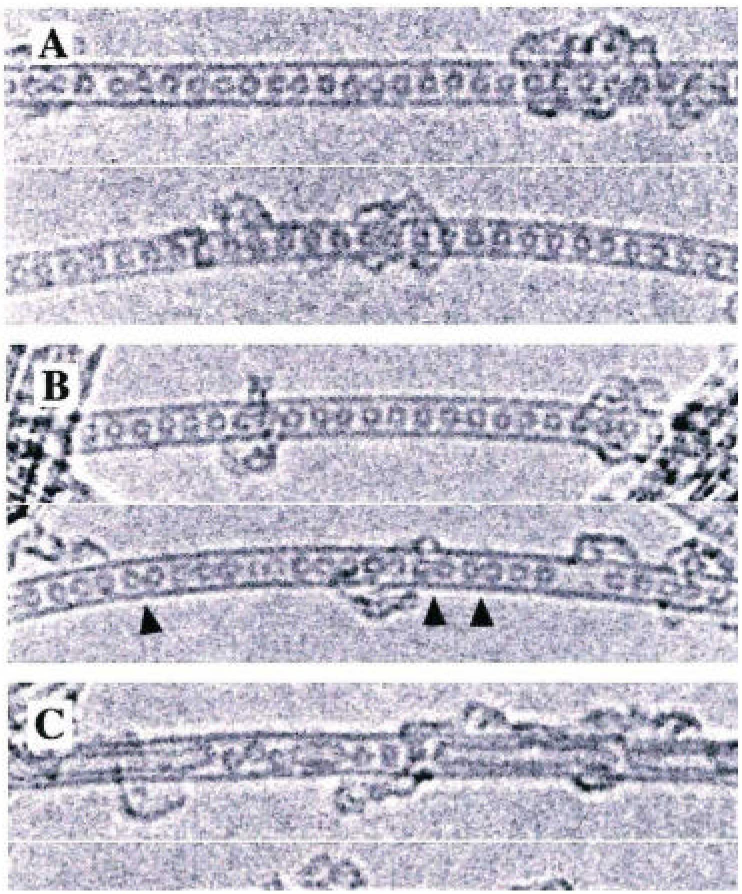
  - **Fusion of nanotubes**
- Technological challenges
  - **Defect tolerance of nanotubes**
  - **Deoxidation of defective nanotubes**
- Summary and Conclusions

Structural transformations in fullerenes and nanotubes

Fusion of fullerenes in peapods



T=1,100ºC

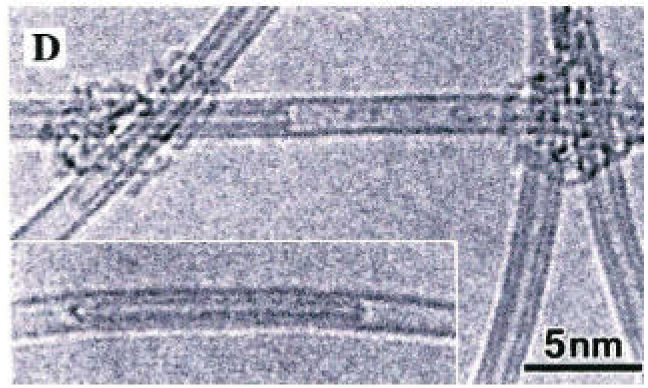
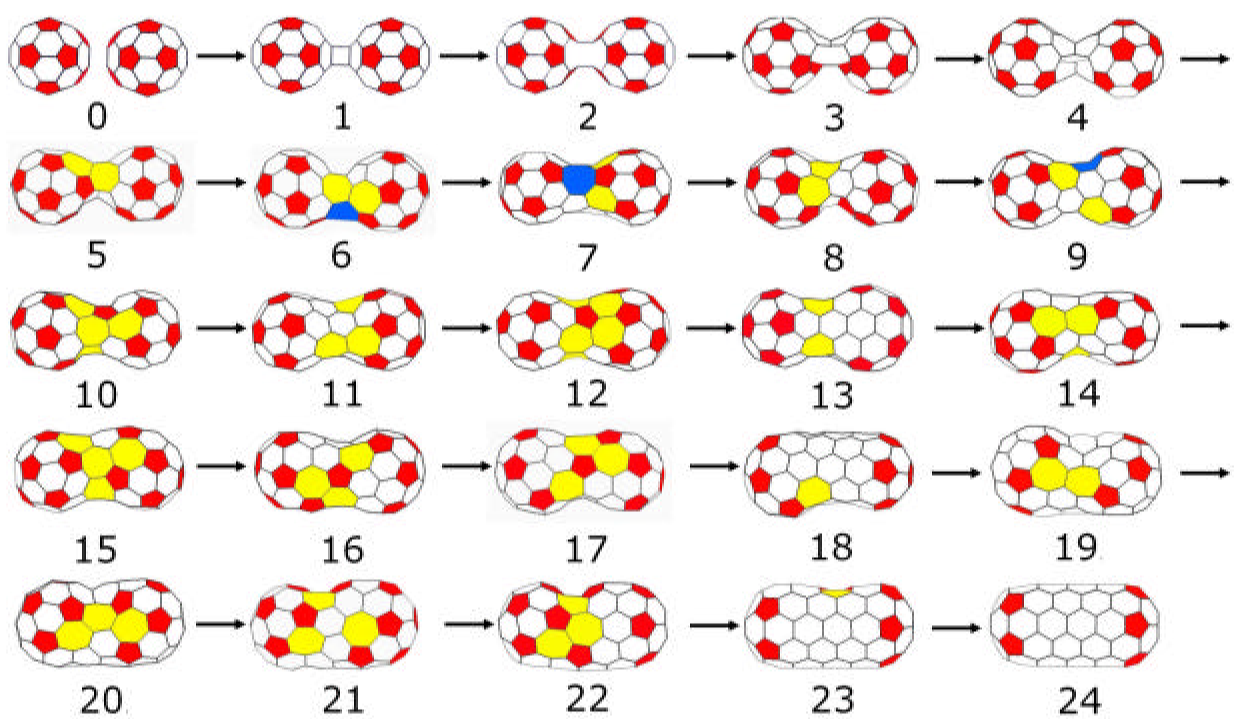


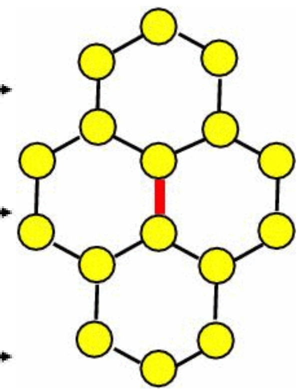
Fig. 1. Transmission electron microscopy images. (A) is
for $(C_{60})_n$ @SWNTs, (B) for $(C_{60})_n$@SWNTs heated in
(<10^{-6} Torr) at 800°C for 14 h (HT800), (C) for HT100
(D) for HT1200. A and B indicate similar electron micro
images, but in B we can occasionally find that some
adjacent C_{60} molecules are linked together as indicat
arrowheads. In C, some of the C_{60} molecules coalesce tog
and transform to a tubular structure. In D, no C_{60} molecu
be observed but we easily find DWNTs; in some of ther
inside-tubes are terminated by caps and the lengths ar
order of ~10 nm.

[S. Bandow, M. Takizawa, K. Hirahara, M. Yudasaka, and S. Iijima, Chem. Phys. Lett. 337, 48 (2001)]

Stone-Wales rearrangement pathway for fusion of fullerenes

[Hiroshi Ueno, Shuichi Osawa, Eiji Osawa, and Kazuo Takeuchi, Fullerene Science And Technology **6**, 319-338 (1998)]



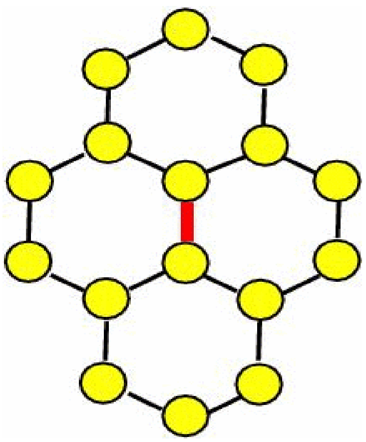


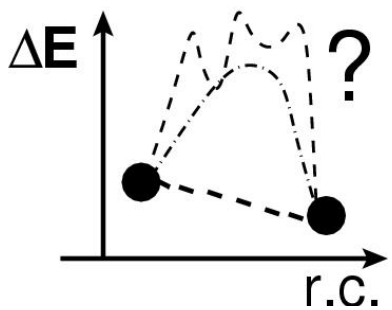
Stone-Wales transformation

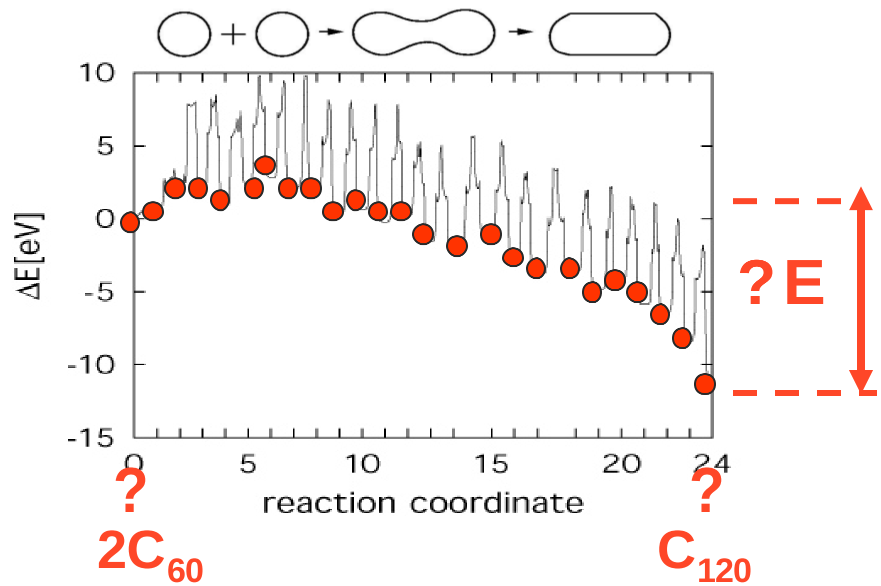
Sequence of bond rotations: Solve "11x11x11 Rubik's Cube" puzzle

- Do we understand the energetics?

Do we understand the Stone-Wales process?



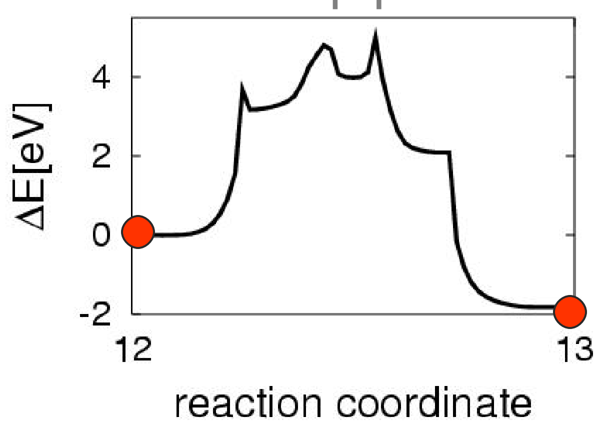




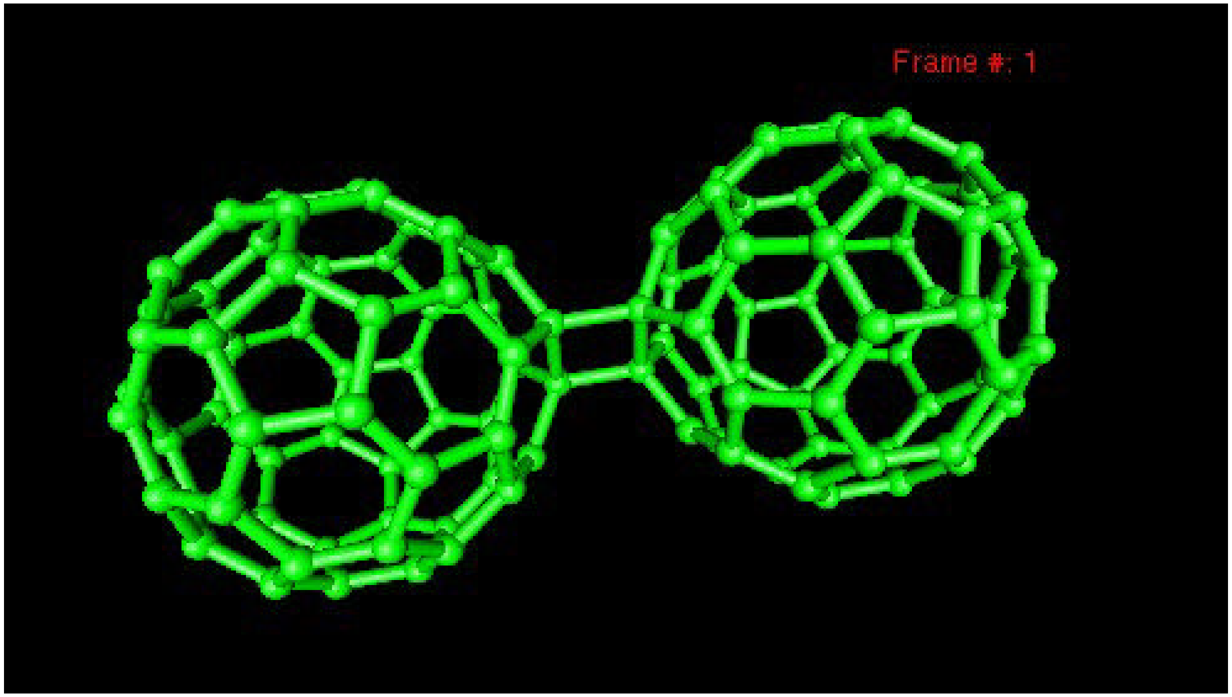
Search in 360-dimensional configuration space using string method:

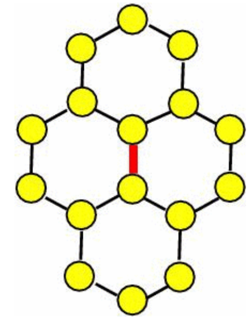
Stone-Wales
 is a multi-step process
•Activation barriers
 do not exceed ~ 5eV

Multi-step process

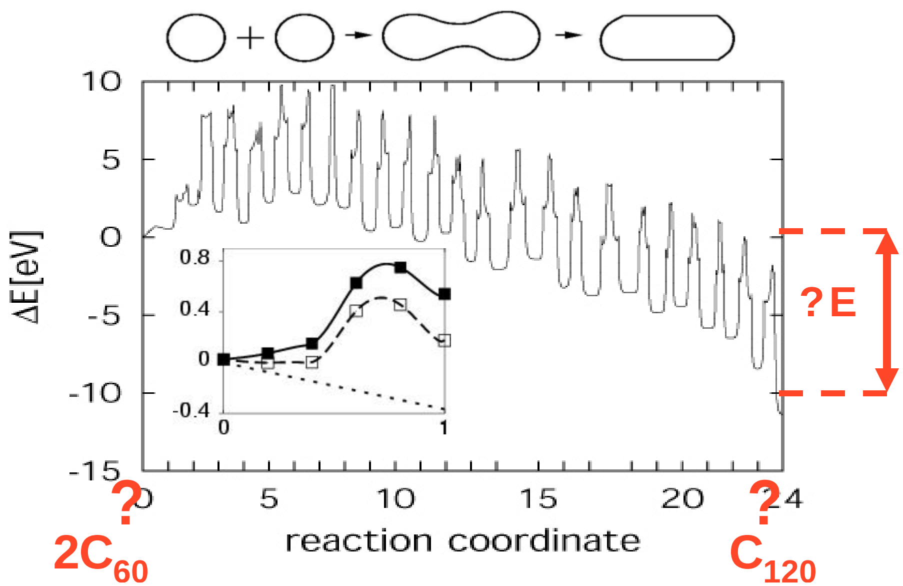


Minimum energy path for the $2C_{60}$? C_{120} fusion





Sequence of Stone-Wales transformations



✍ Conclusions:

-Fusion is exothermic. Energy gain ?E˜ 1Ry.

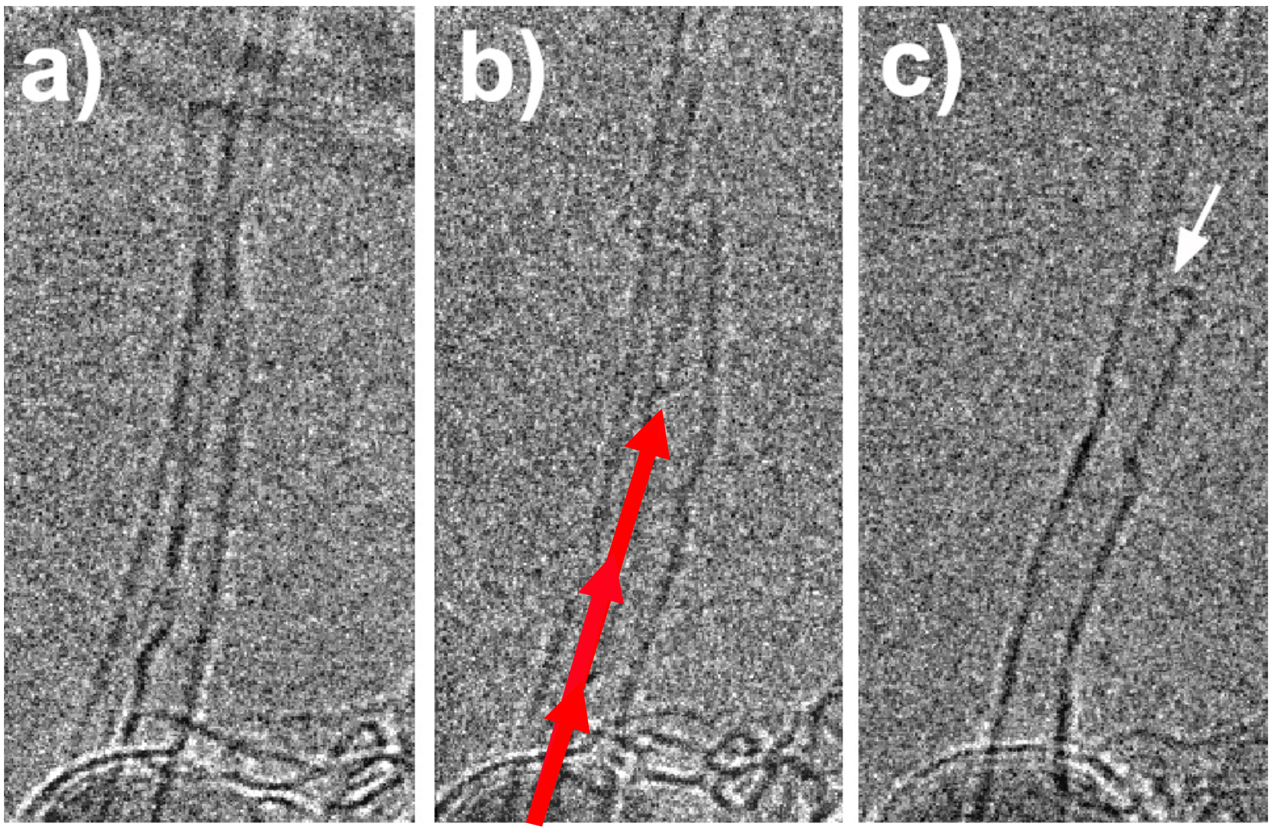
-Essential initial step: (2+2) cycloaddition

-Initial step facilitated by internal pressure

Fusion of nanotubes

The zipper mechanism

M. Yoon, S. Han, G. Kim, S. Lee, S. Berber, E. Osawa, J. Ihm, M. Terrones, F. Banhart, J.-C. Charlier, N. Grobert, H. Terrones, P. M. Ajayan, D. Tománek, Phys. Rev. Lett. **92**, 075504 (2004).



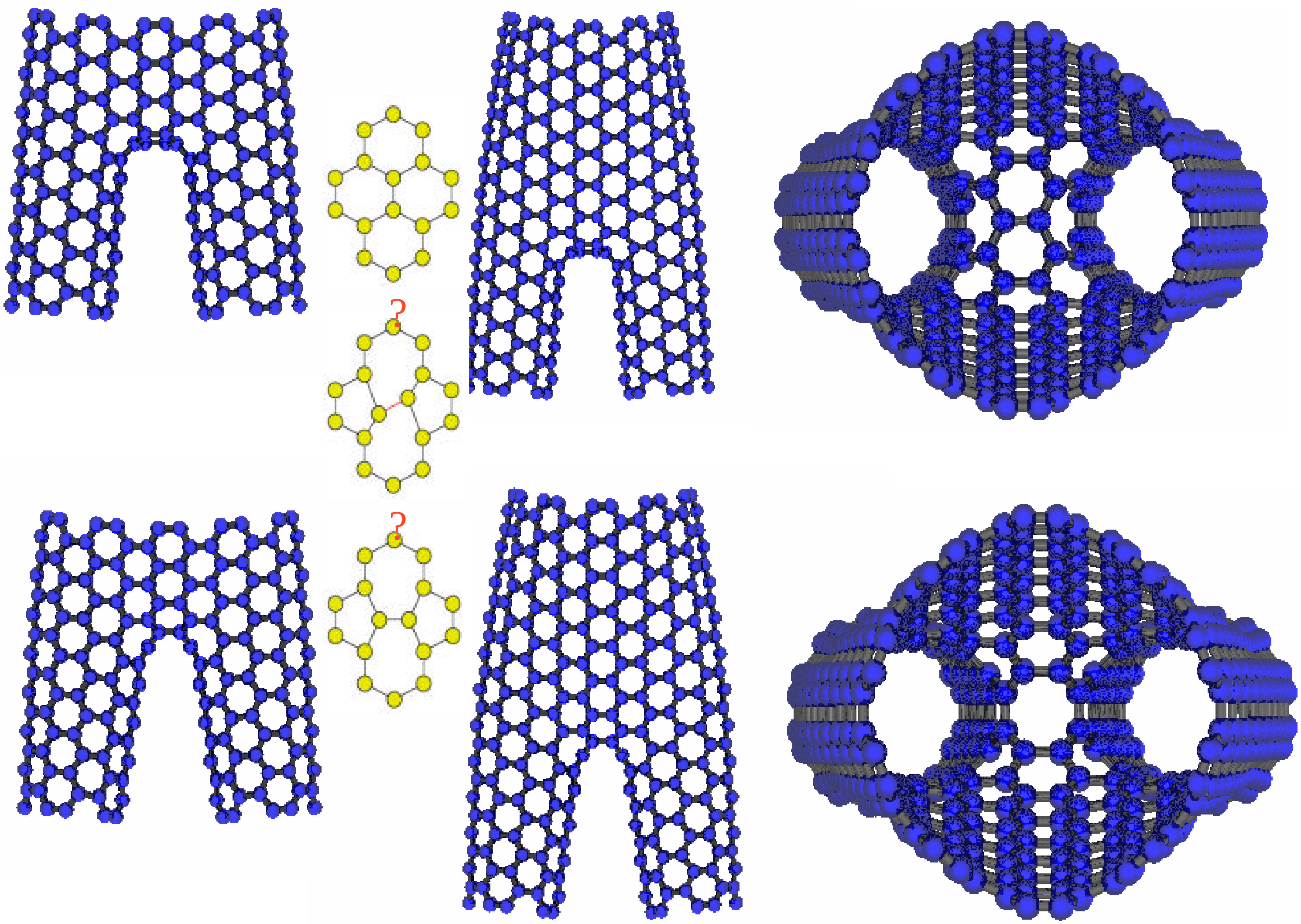
Zipper

Geometry of fusing Nanopants

front view **top view**

Type A:
6 heptagons in junction area

Type B:
1 octagon, 4 heptagons in junction area

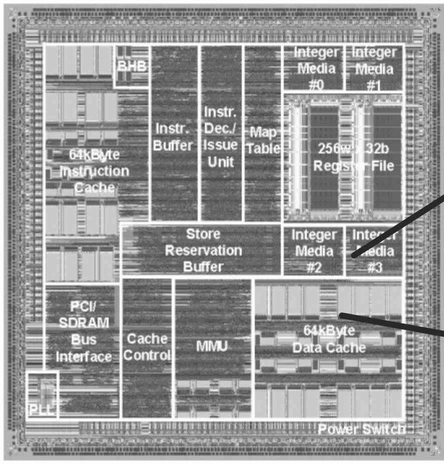


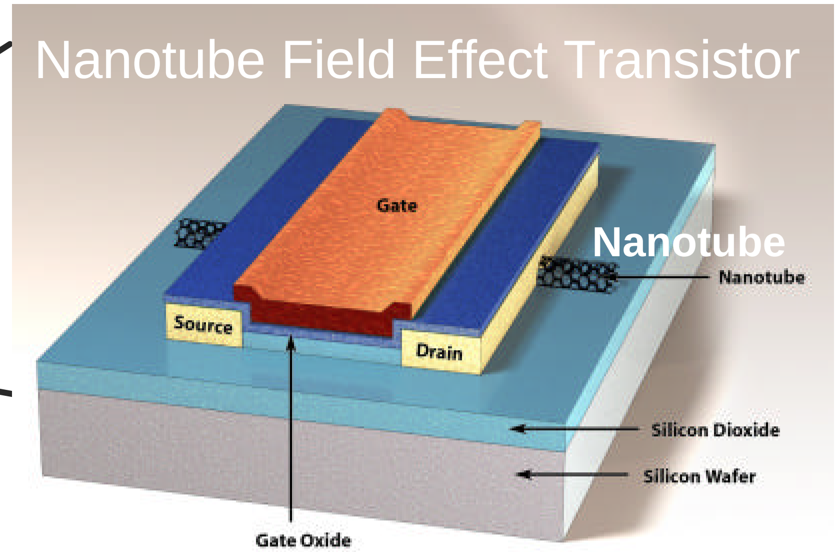
Outline

- Introduction
  - Nanocarbon pioneers
  - What to expect from computer modeling
  - Computational tools
- Curious Morphologies: Function Follows Form
  - High thermal conductivity of nanotubes
  - Thermal contraction of nanotubes
  - Magnetism in foams and heterostructured tubes
  - Nanotube hooks as nano-velcro
  - Nanotube peapods: nano-memory and beyond
- Structural transformations in fullerenes and nanotubes
  - Fusion of fullerenes in peapods
  - Fusion of nanotubes
- Technological challenges
  - Defect tolerance of nanotubes
  - Deoxidation of defective nanotubes
- Summary and Conclusions

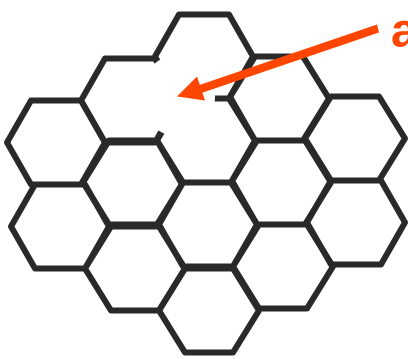
Technological challenges

Defect tolerance of nanotubes





- Defects limit performance, lifetime of devices
- Are CNT devices as sensitive to defects as Si-LSI circuits?



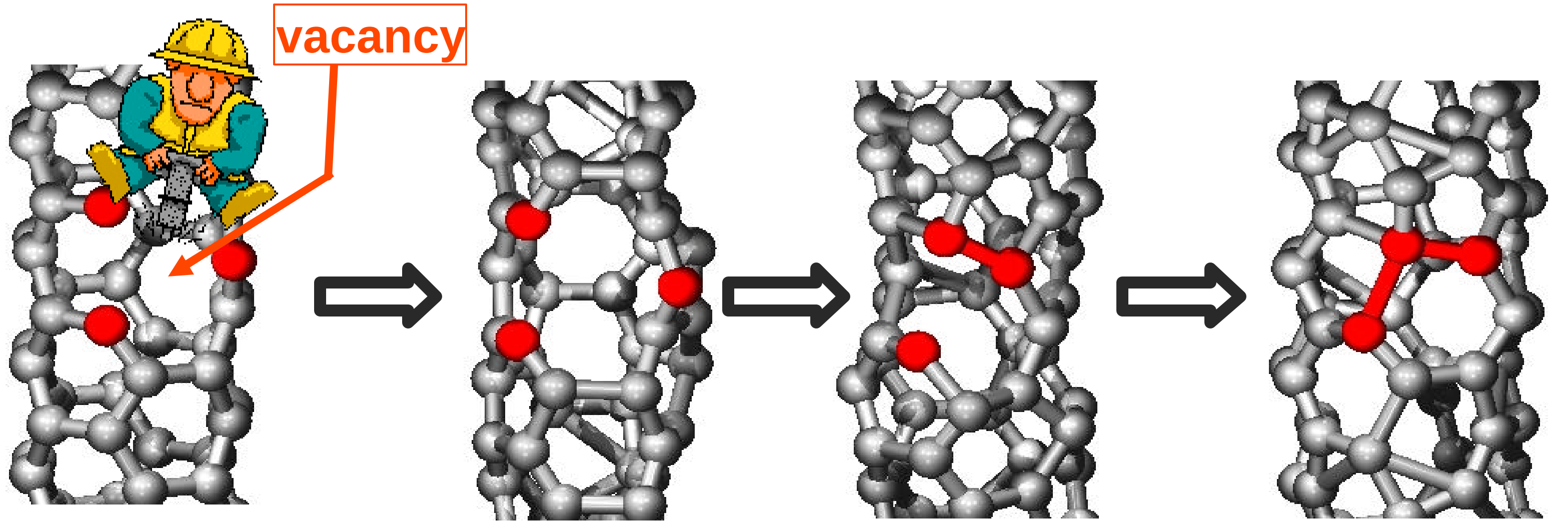
atomic vacancy

Will atomic vacancies trigger failure under

- high temperatures?
- illumination?

Stability of defective tubes at high temperatures

? Danger of pre-melting near vacancies?

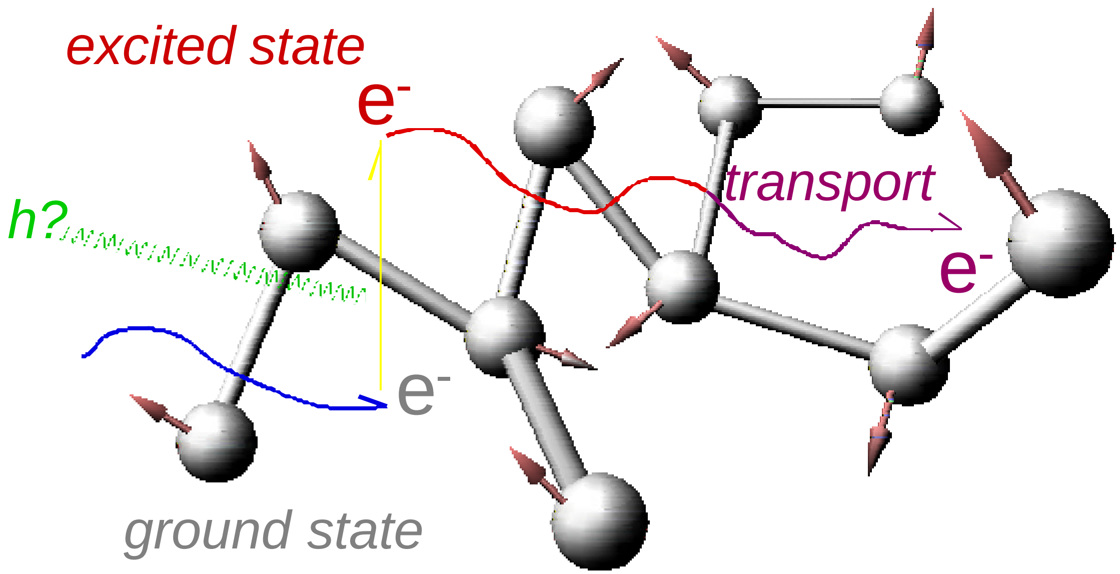


T= 0 K **T= 4,000 K**

? Nanotube remains intact until 4,000 K

? Self-healing behavior:
Formation of new bond helps recover
- structural stiffness
- conductance

Stability of defective tubes during electronic excitations

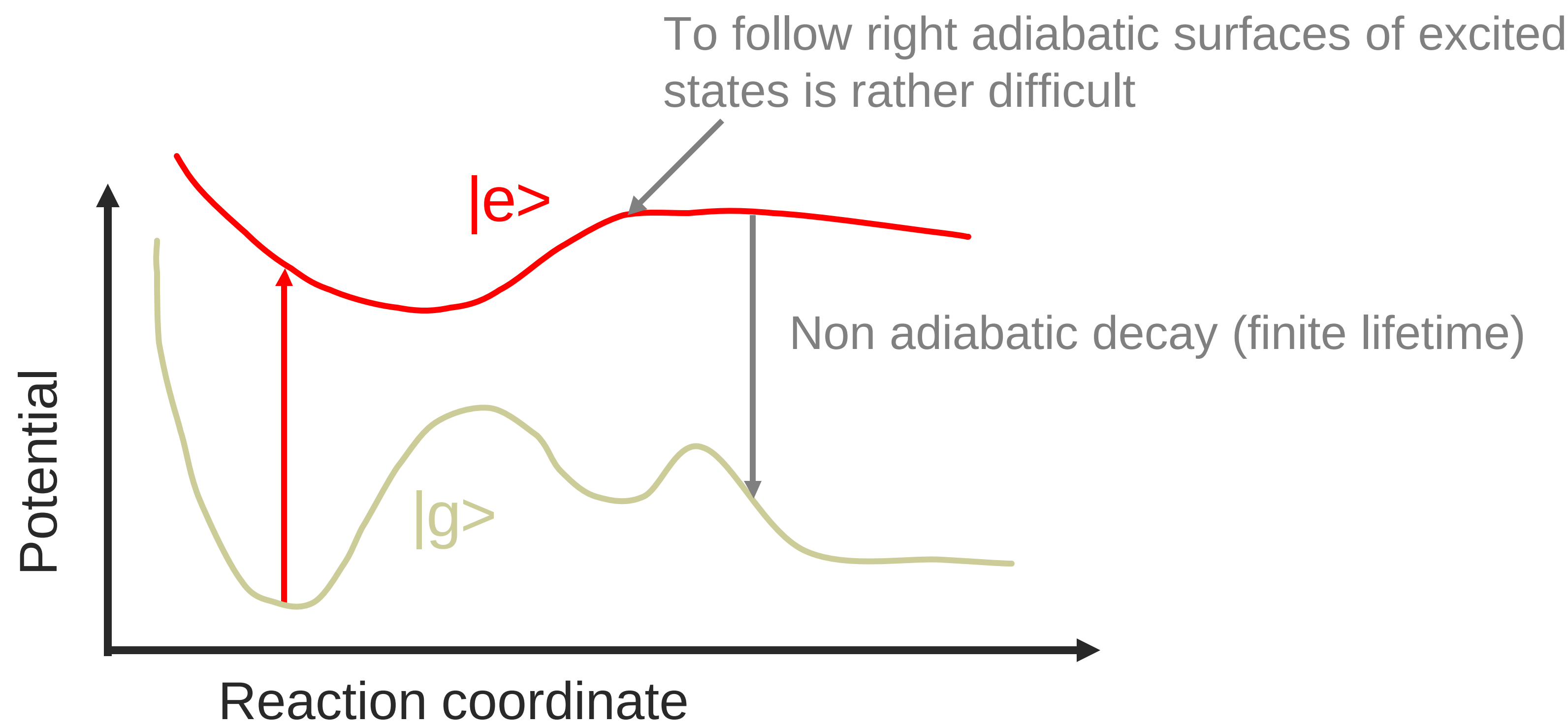


Challenges:

? Perform Molecular Dynamics simulations on the adiabatic surface of an electronically excited state

? Solve the time-dependent Schrödinger equation for electrons during ionic motion

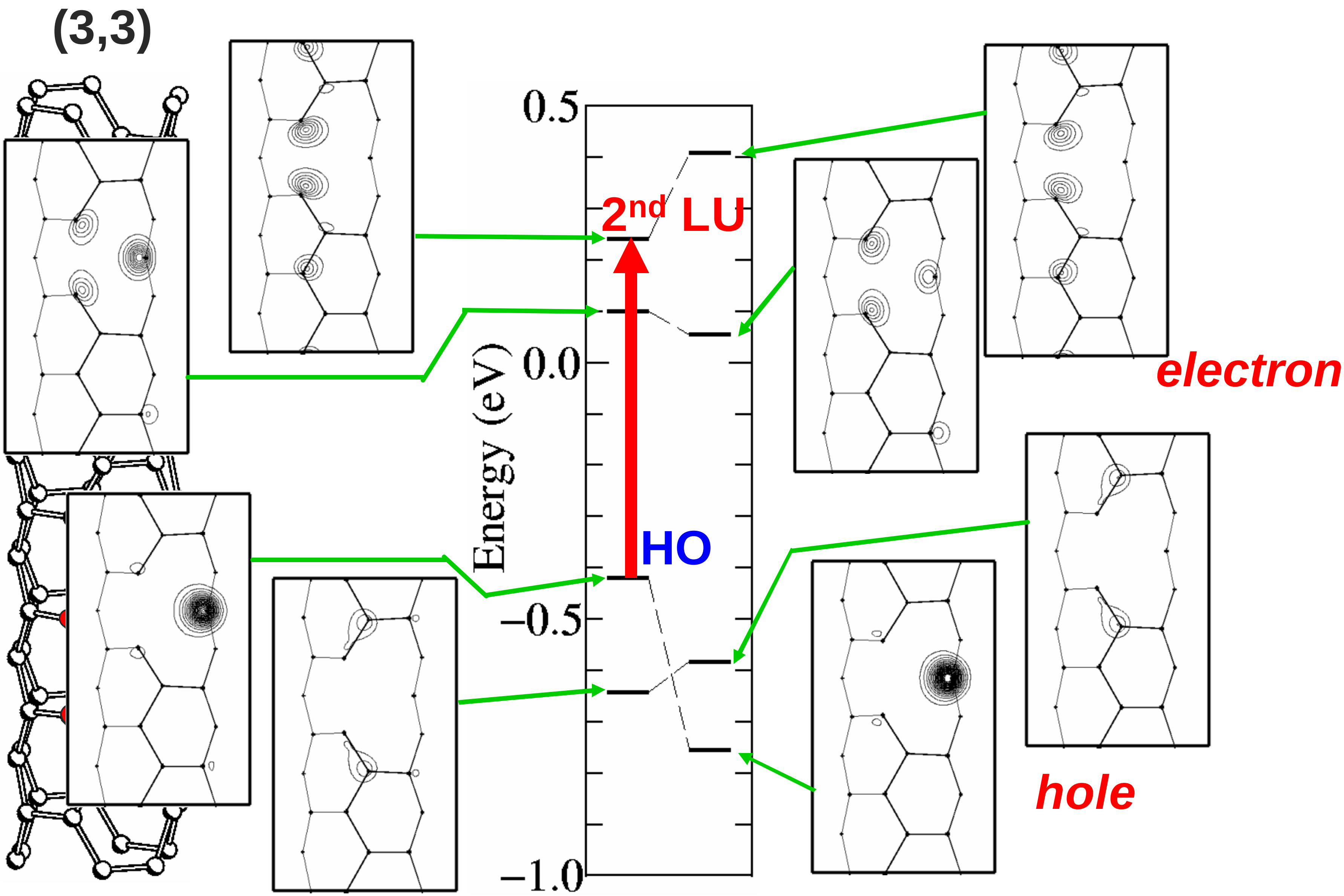
First-principles Molecular Dynamics simulation on the adiabatic surface of an electronically excited state



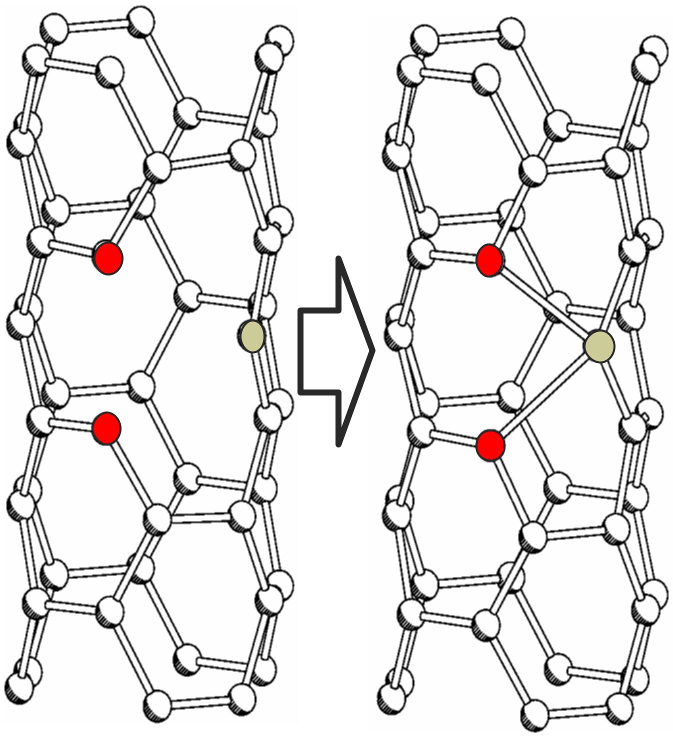
? First-Principles Simulation tool for Electron-Ion Dynamics

? Details: *Sugino & Miyamoto PRB **59**, 2579 (1999)*; *PRB **66**, 89901 (2002).*

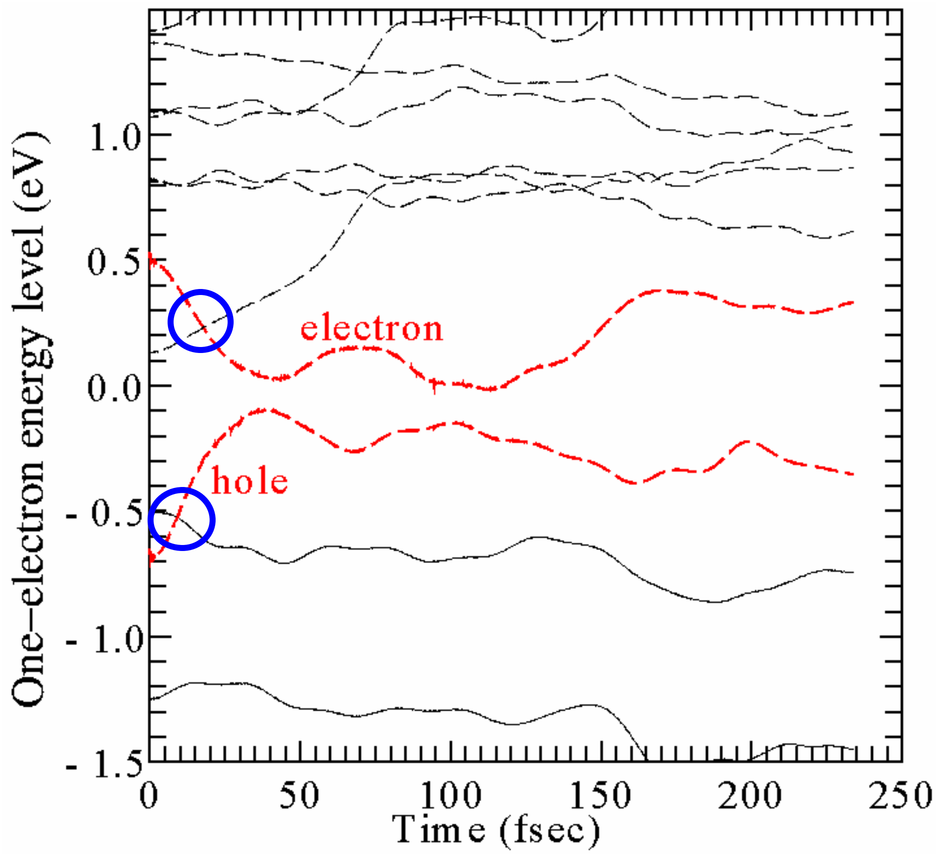
Optical excitation (?E=0.9 eV)



Time evolution of the electronic states



0 fs 70 fs

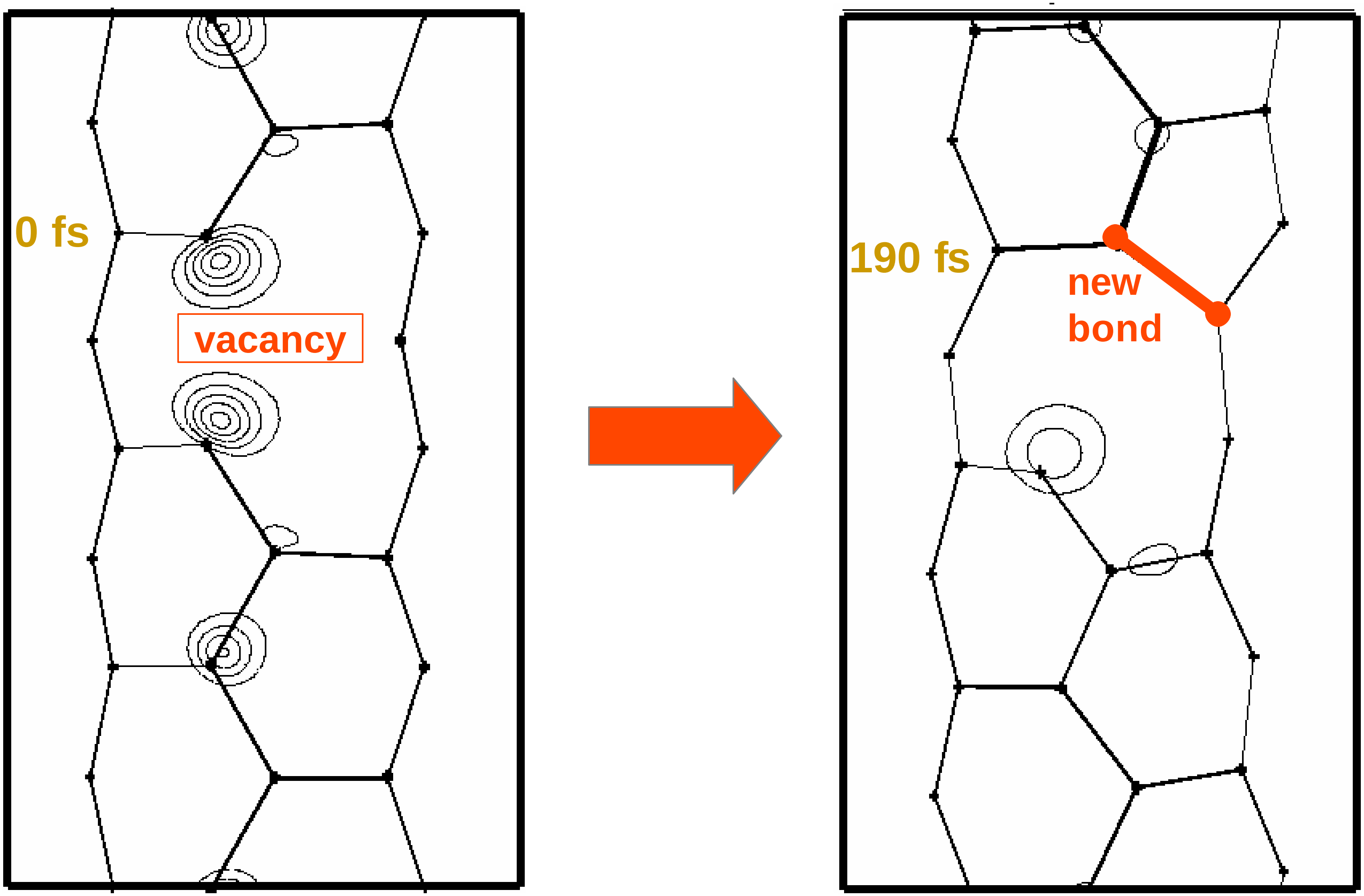


$?_n (t+?t)=\exp(-i/h\ H?t)\ ?_n(t)$

? Very long-lived excitation

? Correct PES is followed in case of level alternation

Structural changes under illumination

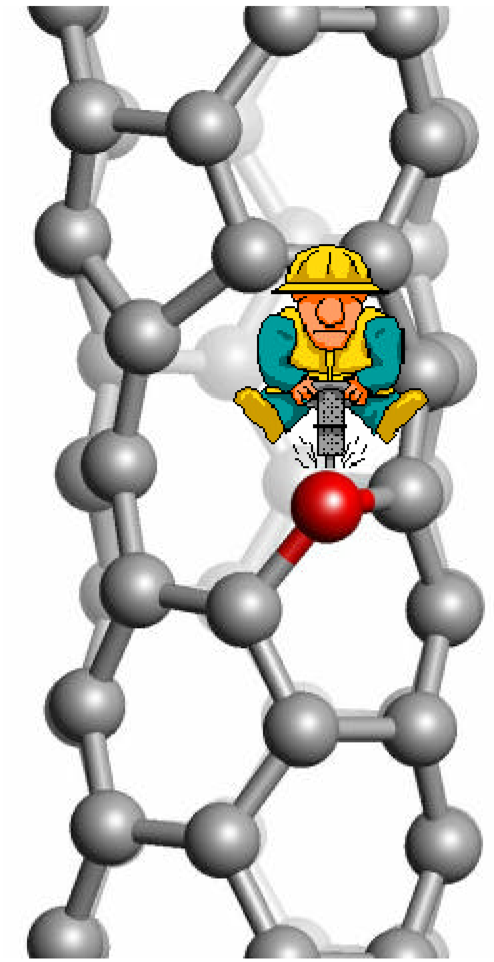


? Self-healing due to new bond formation

Y. Miyamoto, S. Berber, M. Yoon, A. Rubio, D. Tománek, Can Photo Excitations Heal Defects in Carbon Nanotubes? Chem. Phys. Lett. 392, 209–213 (2004)

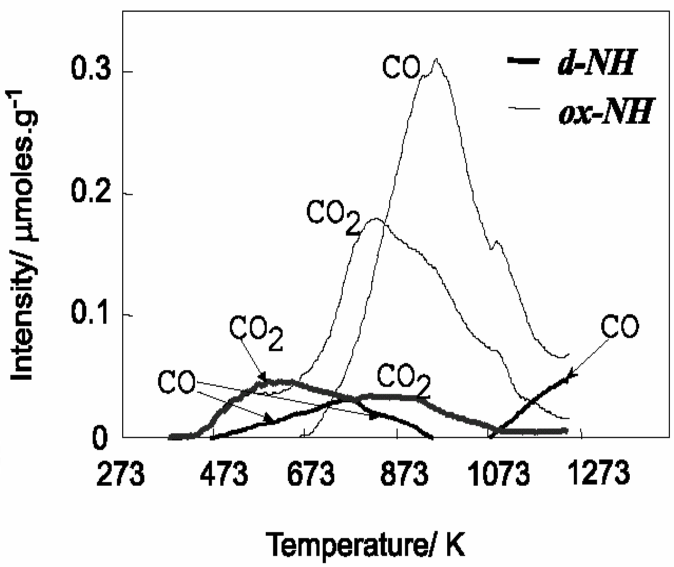
Deoxidation of defective nanotubes

How to deoxidize?

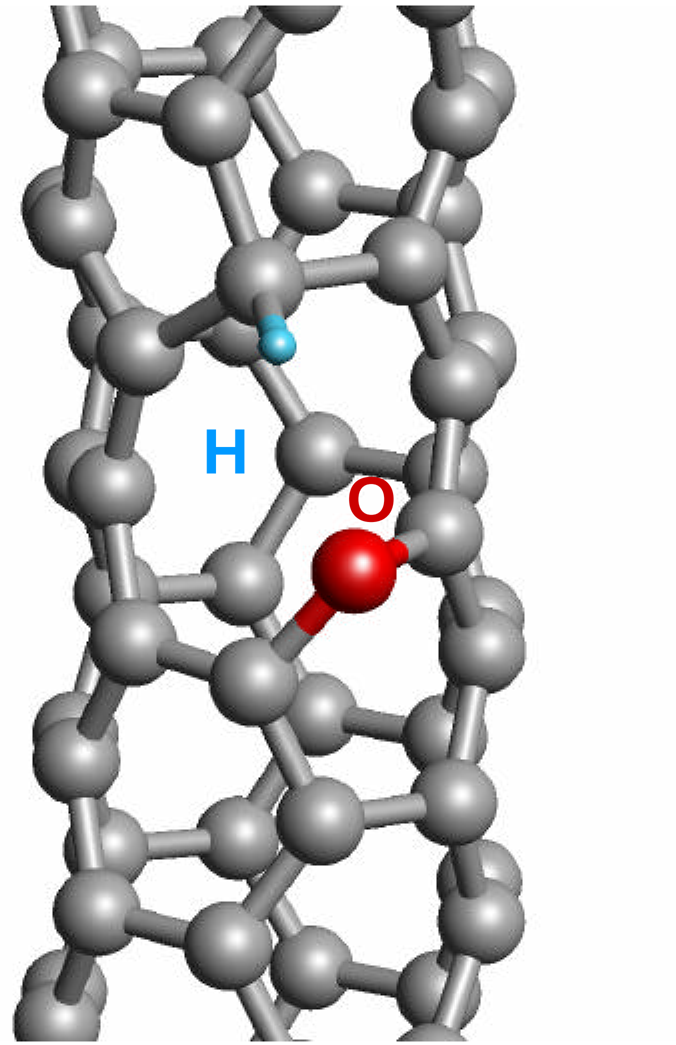


By heat treatment?

? No: Larger damage to nanotube



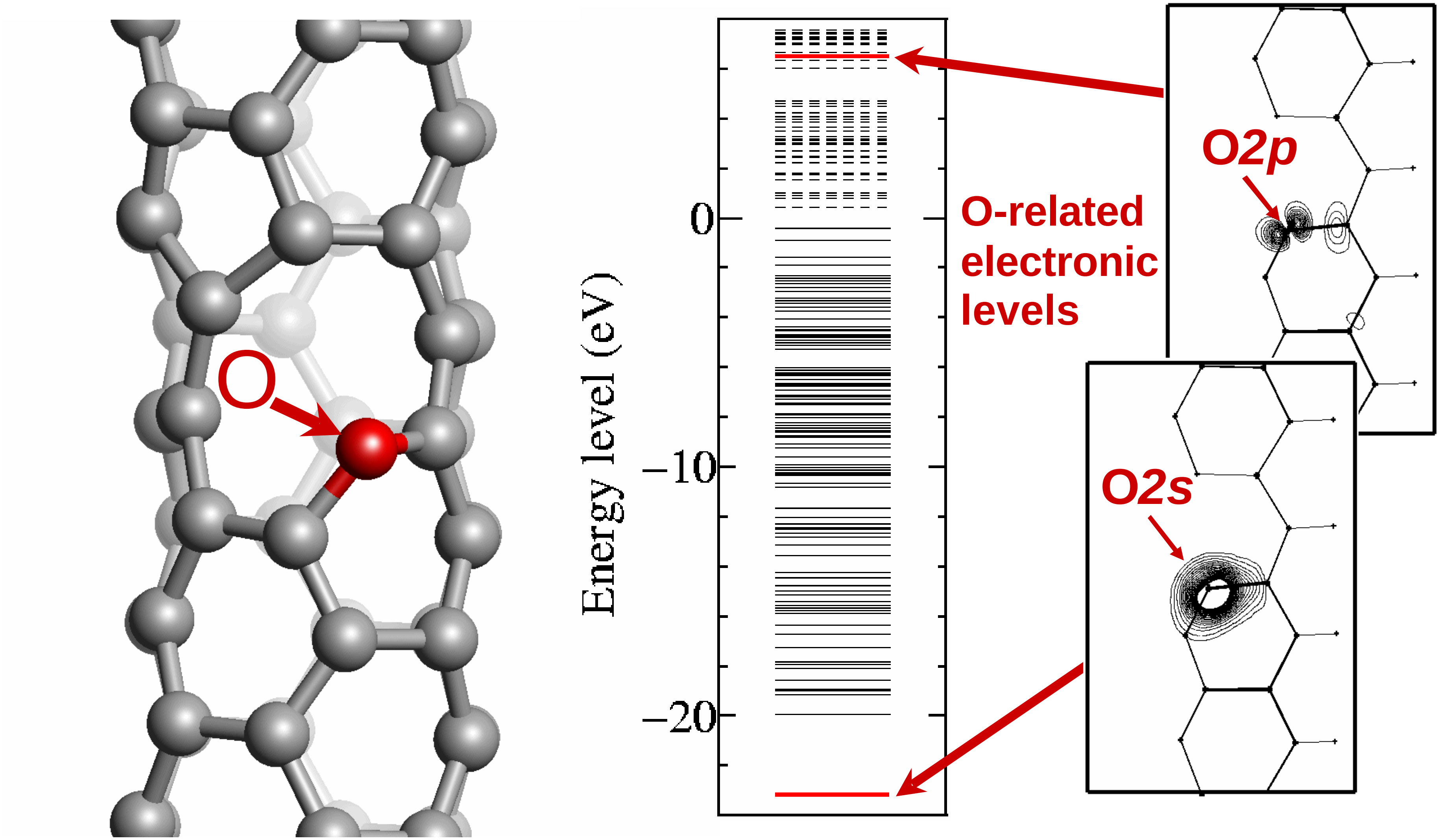
By chemical treatment with H?



Yoshiyuki Miyamoto, Noboru Jinbo,
Hisashi Nakamura, Angel Rubio, and David Tománek,
Photosurgical Deoxidation of Nanotubes, Phys. Rev. B 70 (2004).

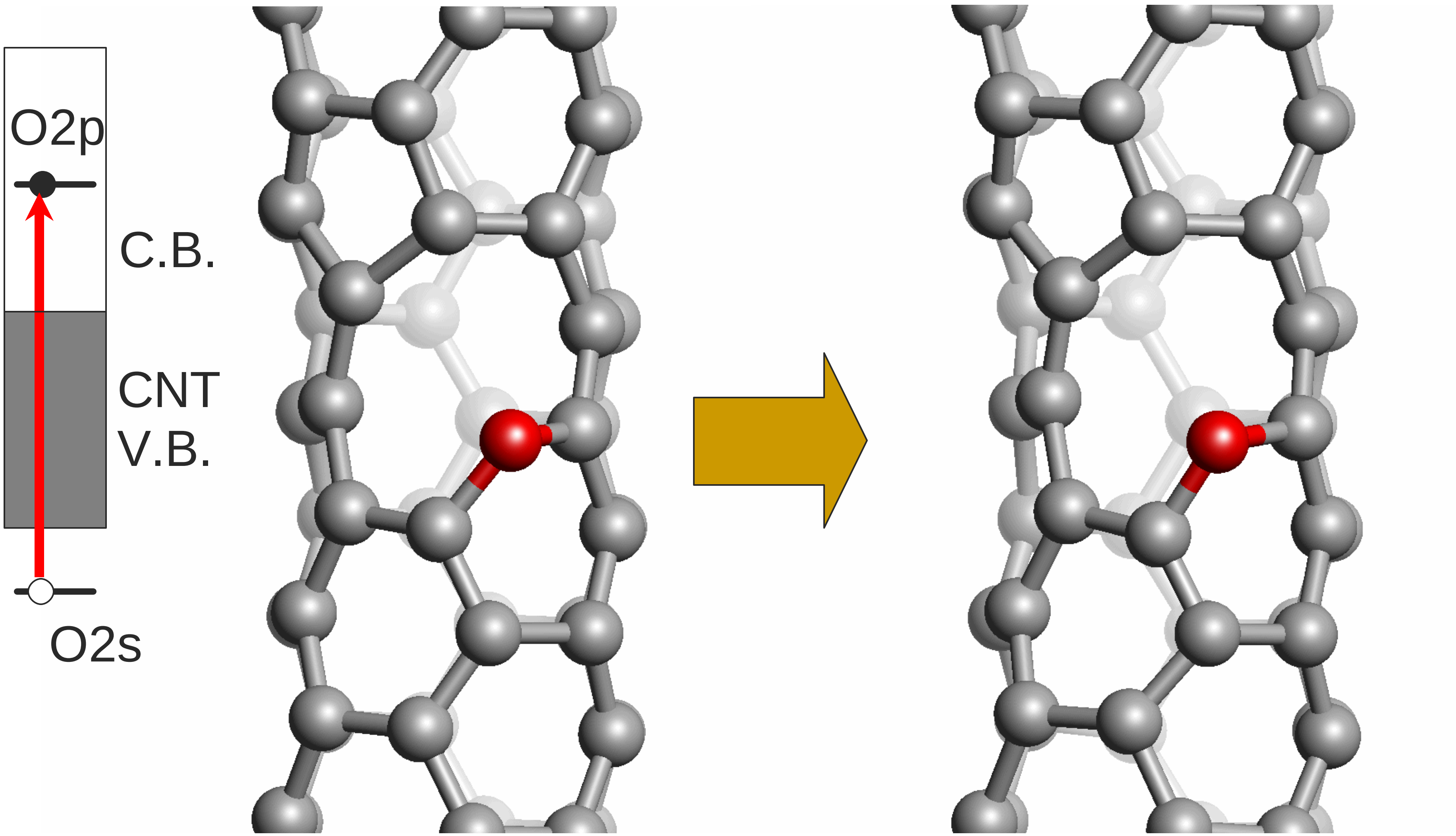
Alternative to thermal and chemical treatment

Electronic excitations!

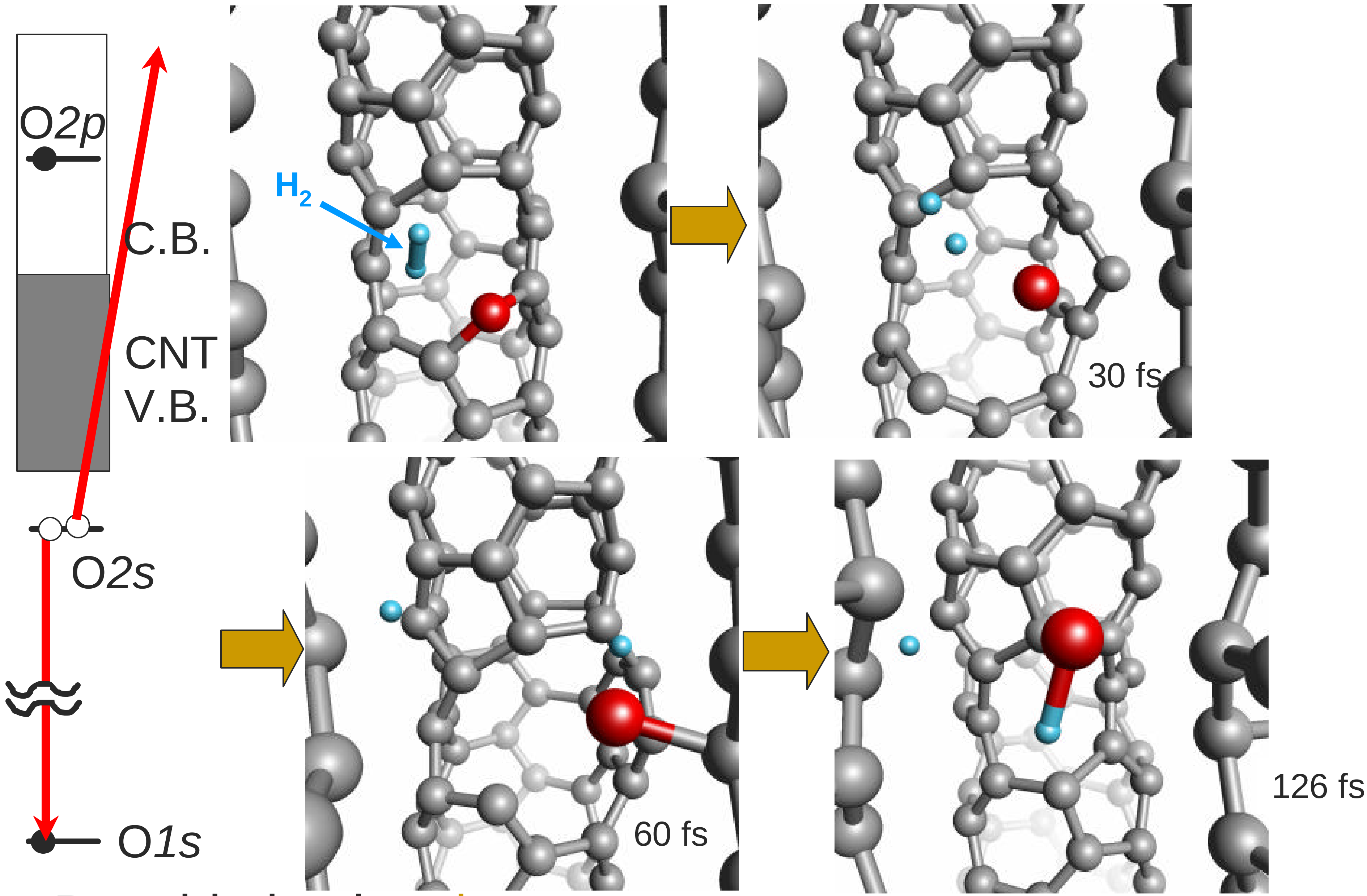


O2s ? O2p excitation (33 eV)

hopeless

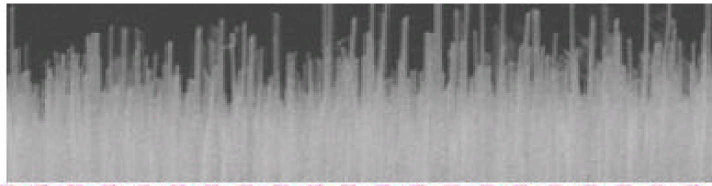


Auger decay following the O1s ? 2p excitation (~520 eV)



? Deoxidation by photo-surgery

Nanotube 2005



NT05

6th International Conference on the Science and Application of Carbon Nanotubes

26 June - 1 July 2005

URL: **http://www.fy.chalmers.se/conferences/nt05**
or **http://nanotube.msu.edu/nt05/**

Chalmers Conference Center
Gothenburg Sweden

Summary and Conclusions

- Exceptionally high thermal conductance of nanotubes results from the 1D structure and large phonon mean free path.
- Nanotubes exhibit thermal contraction.
- Nanostructured carbon may become magnetic.
- Insertion of fullerenes in nanotubes yields new nanostructures with intriguing properties.
- Nanotubes act as an autoclave to facilitate reactions between encapsulated molecules.
- Fusion of fullerenes inside a nanotube starts with a cycloaddition and continues exclusively with Stone-Wales transformations.
- Fusion of nanotubes occurs efficiently via a zipper mechanism.
- Self-healing behavior occurs in defective nanotubes.
- Electronic excitations can selectively remove impurities.

The End