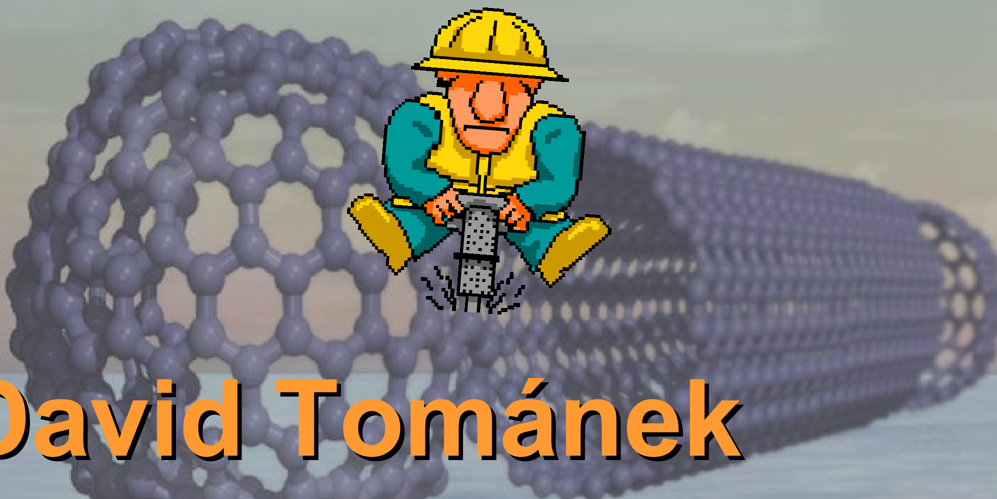
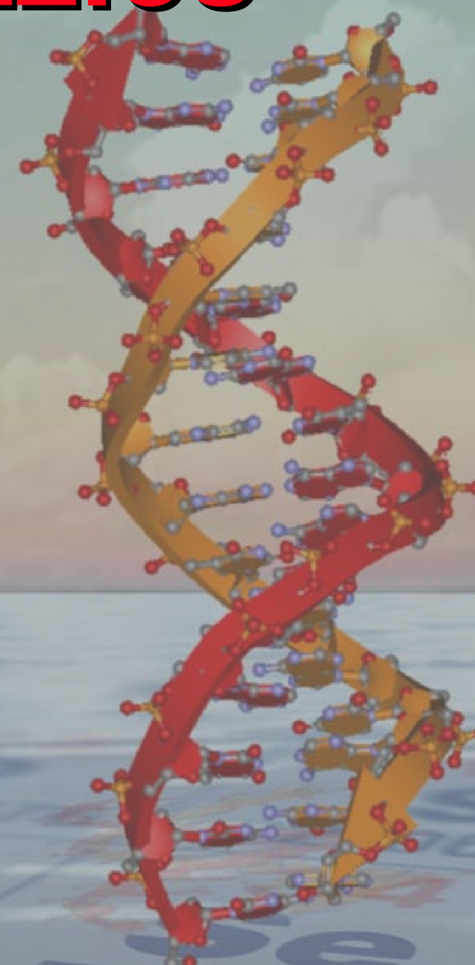
Solving Nanotube Puzzles on a Supercomputer





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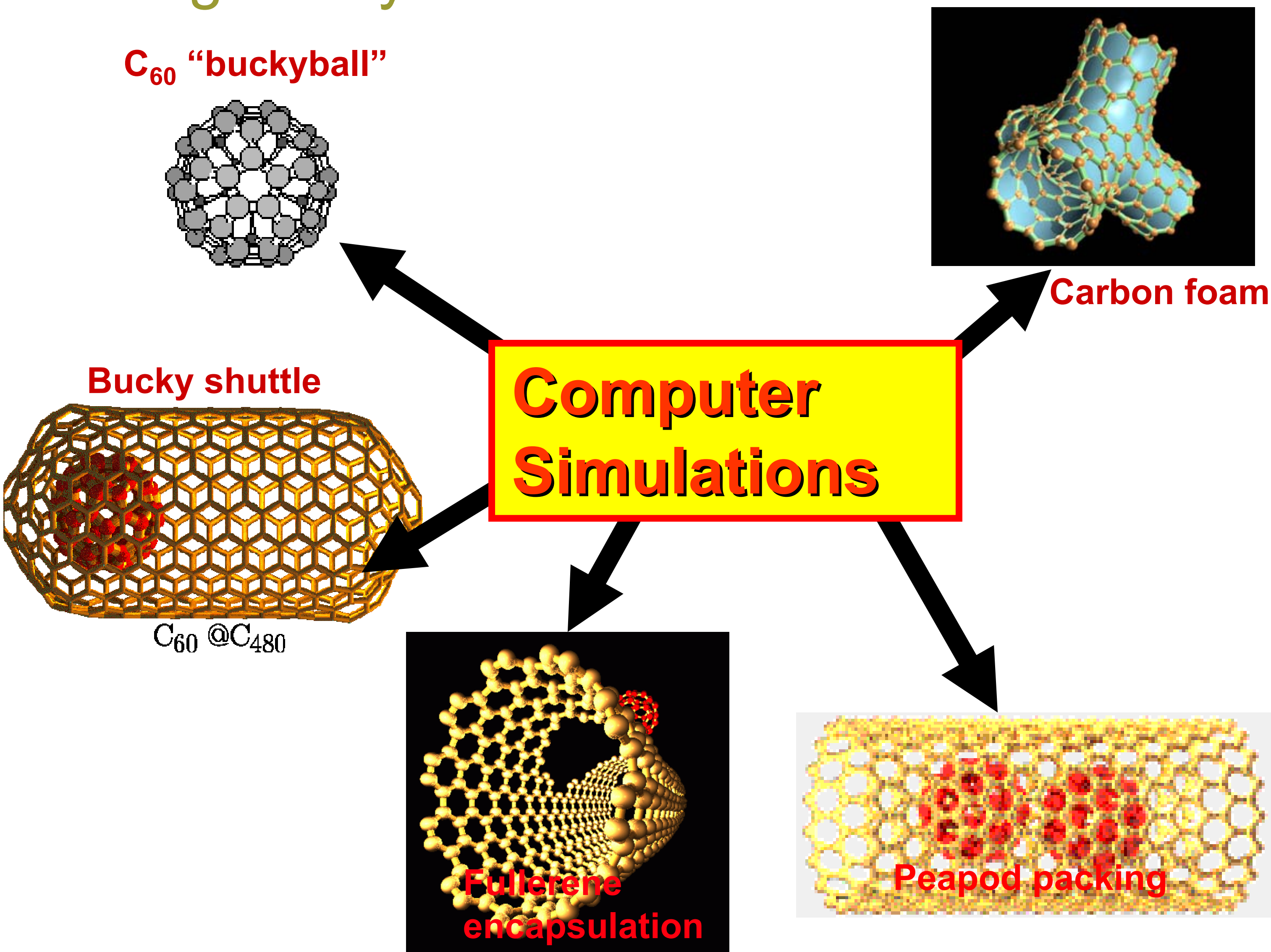
Outline

- **Introduction**
  - What to expect from computer modeling
  - Computational tools
- **Curious Morphologies: Function Follows Form**
  - High thermal conductivity of nanotubes
  - Thermal contraction of nanotubes
  - Magnetism in carbon foam
- **Structural Transformations in Fullerenes and Nanotubes**
  - Fusion of fullerenes in peapods
  - Fusion of nanotubes
  - Field-induced disintegration of nanotube electron emitters
  - Resilience of sputtered nanotubes
- **Behavior of Defective Nanotubes**
  - Defect tolerance of nanotubes
  - Detection of Stone-Wales defects
  - Deoxidation of defective nanotubes
- **Summary and Conclusions**

- **Review:**
  David Tománek, Carbon-based nanotechnology on a supercomputer, Topical Review in J. Phys.: Condens. Matter 17, R413-R459 (2005).

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:

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

  ab initio Density Functional formalism

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

  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.

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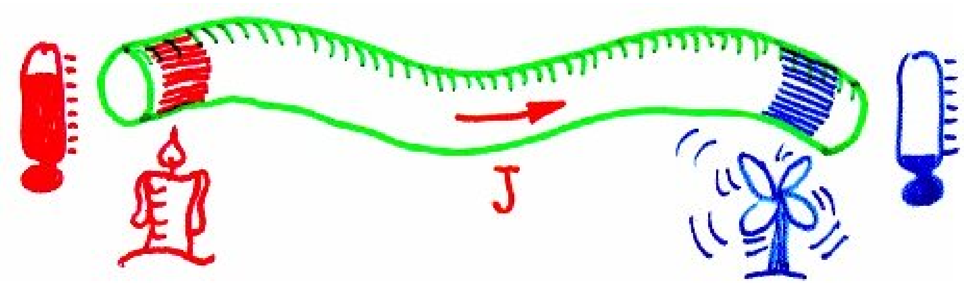
Curious Morphologies: Function Follows Form

High Thermal Conductivity of Nanotubes



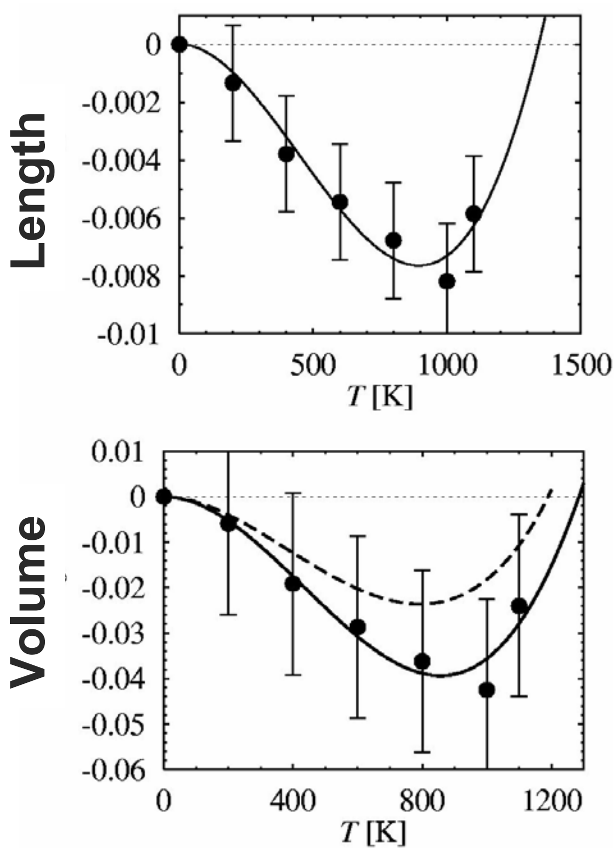
Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. 84, 4613 (2000)

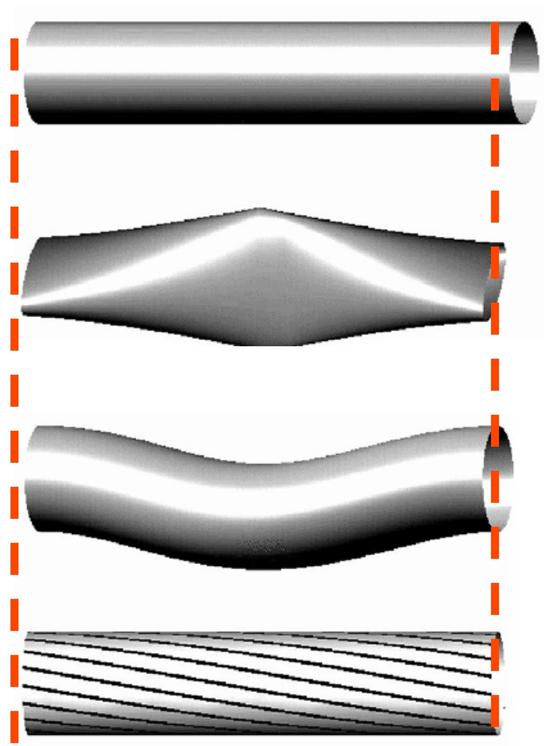
- ♦Nanotubes may help solve the heat problem:
  Efficient conductors of electrons and heat
- ♦Record Heat Conductivity:
  * Diamond
    (isotopically pure): 3320 W/m/K
  * Nanotubes: 6,600 W/m/K (theory, SWNT)
    >3,000 W/m/K (experiment, MWNT)

  (room temperature values)

  (combination of large phonon mean free path, speed of sound, hard optical phonon modes)

Thermal contraction of nanotubes





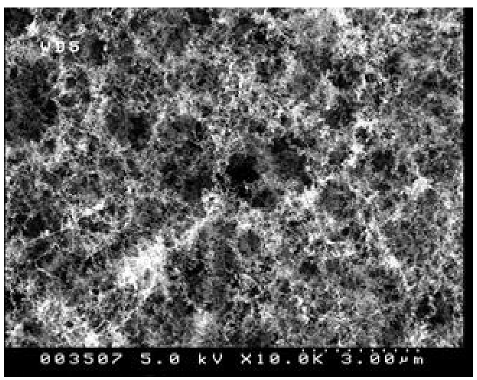
Savas Berber, Young-Kyun Kwon, and David Tománek, Phys. Rev. Lett. 92, 015901 (2004).

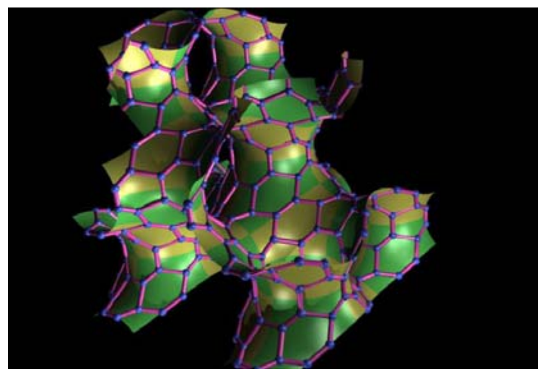
See also Comment: and Reply: Phys. Rev. Lett. 94, 209702 (2005).

- 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 carbon foam

- 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.

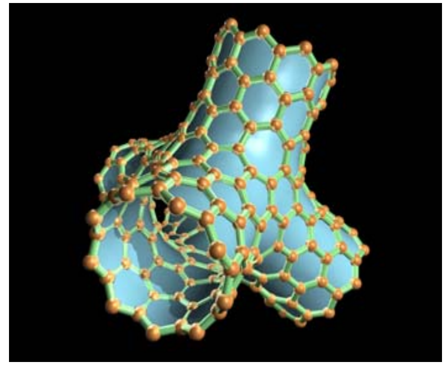
Researchers have created a new form of carbon: a spongy solid that is extremely lightweight and, unusually, attracted to magnets. The foam could one day help treat cancer and enhance brain scans, say the inventors.

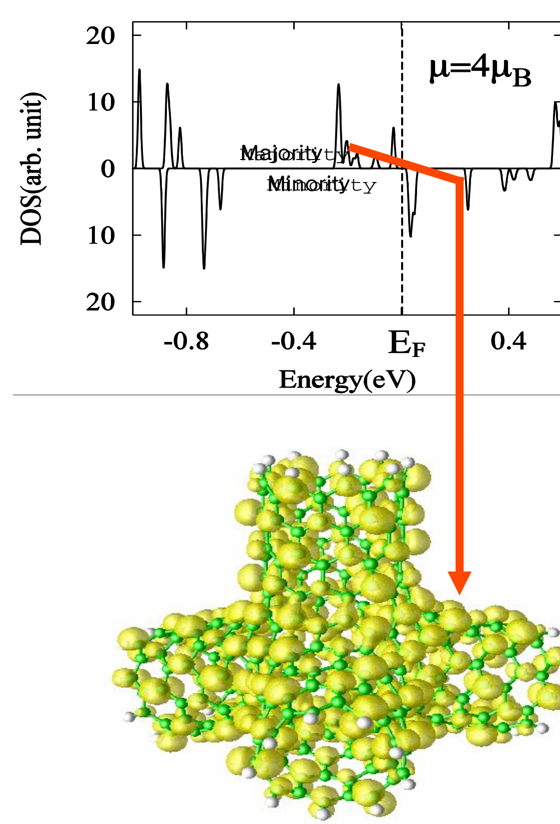
The new carbon foam is unusually attracted to magnets.
© Photodisc

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 °C, 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'.

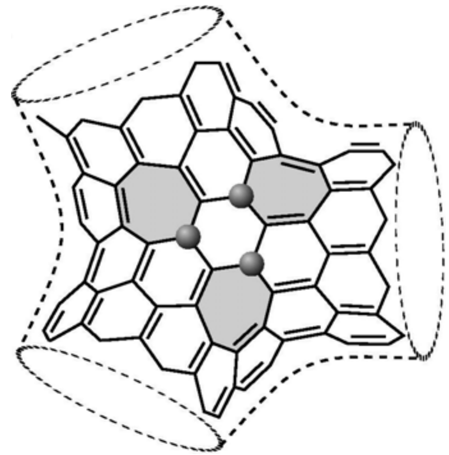
John Giapintzakis of the University of Crete has used an electron microscope to study the structure of the nanofoam. He says it is the fifth form of carbon known after graphite, diamond and two recently discovered types: hollow spheres, known as buckminsterfullerenes or buckyballs, and nanotubes.

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).

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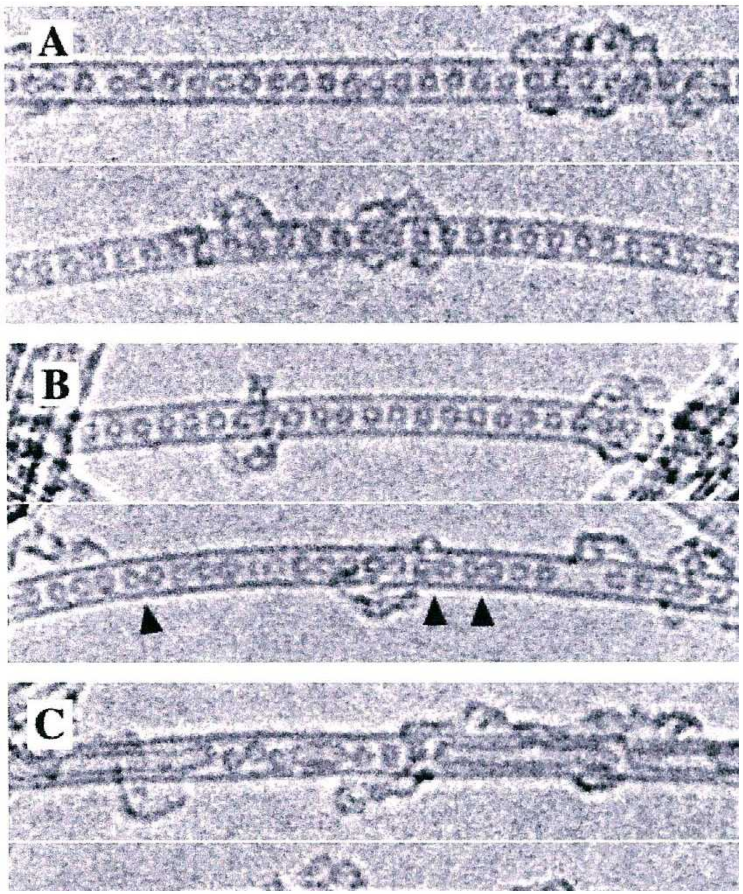
Structural Transformations in Fullerenes and Nanotubes

Fusion of fullerenes in peapods



T=1,100ºC

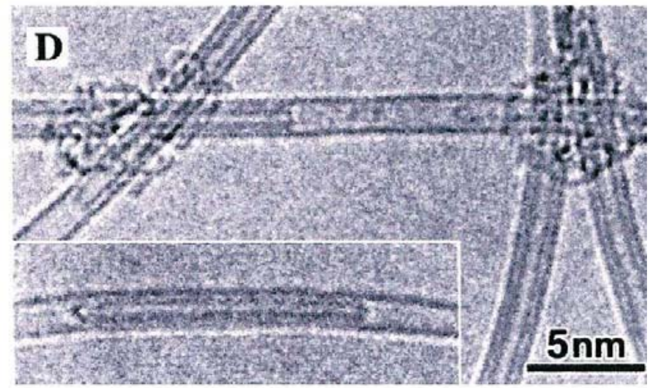
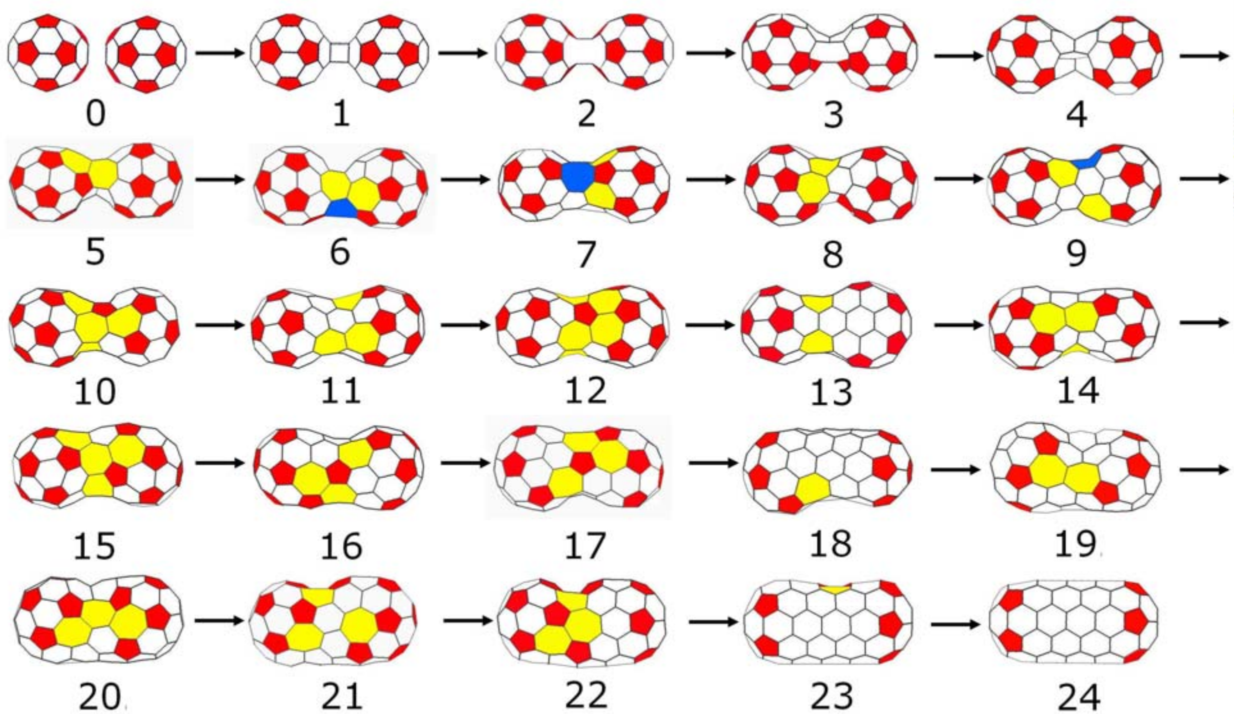


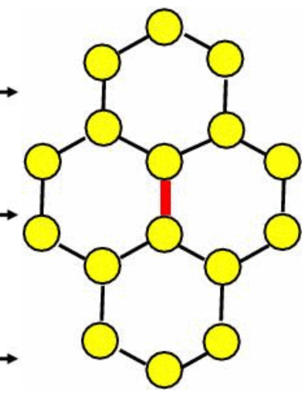
Fig. 1. Transmission electron microscopy images. (A) is
for $(C_{60})_n$ @SWNTs, (B) for $(C_{60})_n$@SWNTs heated in
($<10^{-6}$ Torr) at 800°C for 14 h (HT800), (C) for HT100
(D) for HT1200. A and B indicate similar electron micro
images, but in B we can occasionally find that some
adjacent C_{60}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



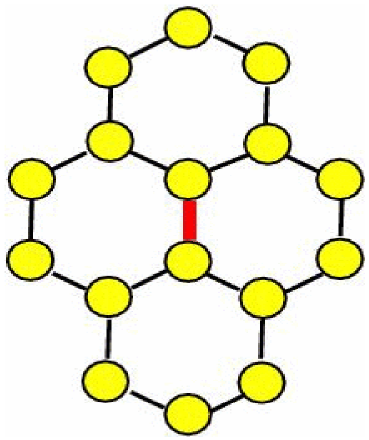


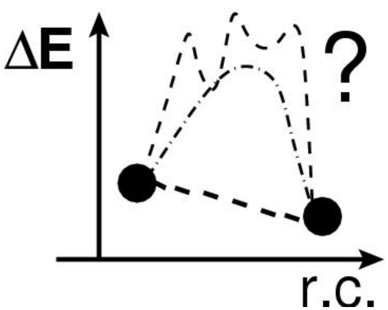
Stone-Wales transformation

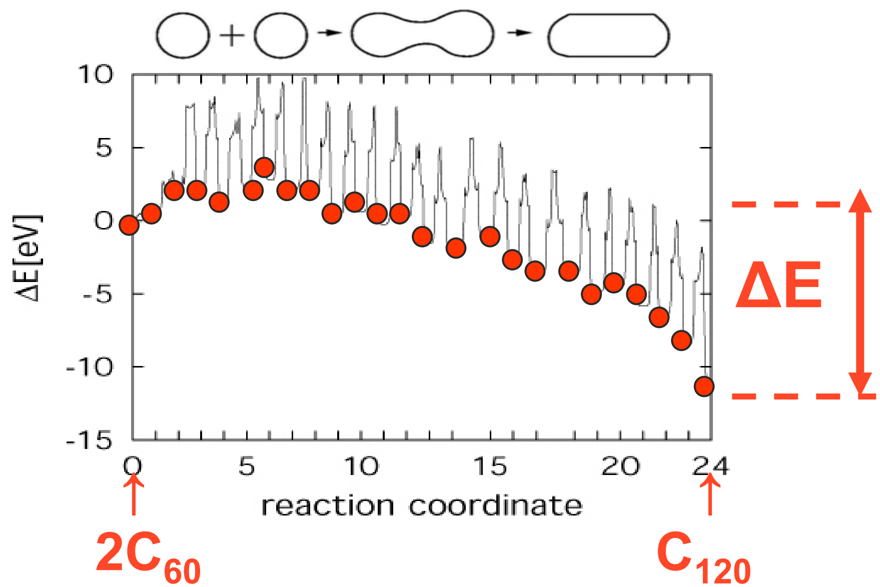
Sequence of bond rotations:
Solve 180x180x180 Rubik's Cube puzzle

- Do we understand the energetics?

Do we understand the Stone-Wales process?

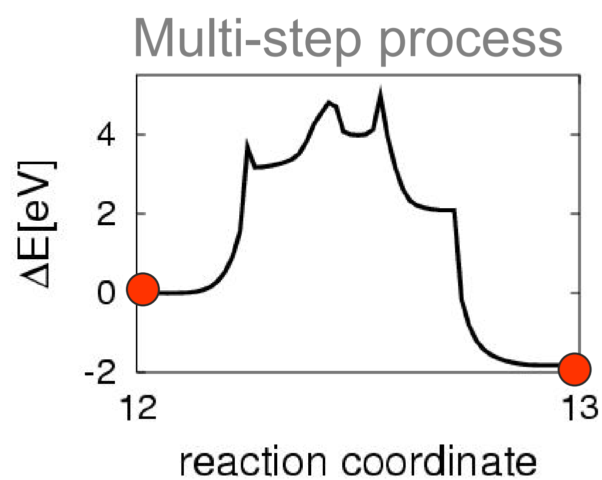




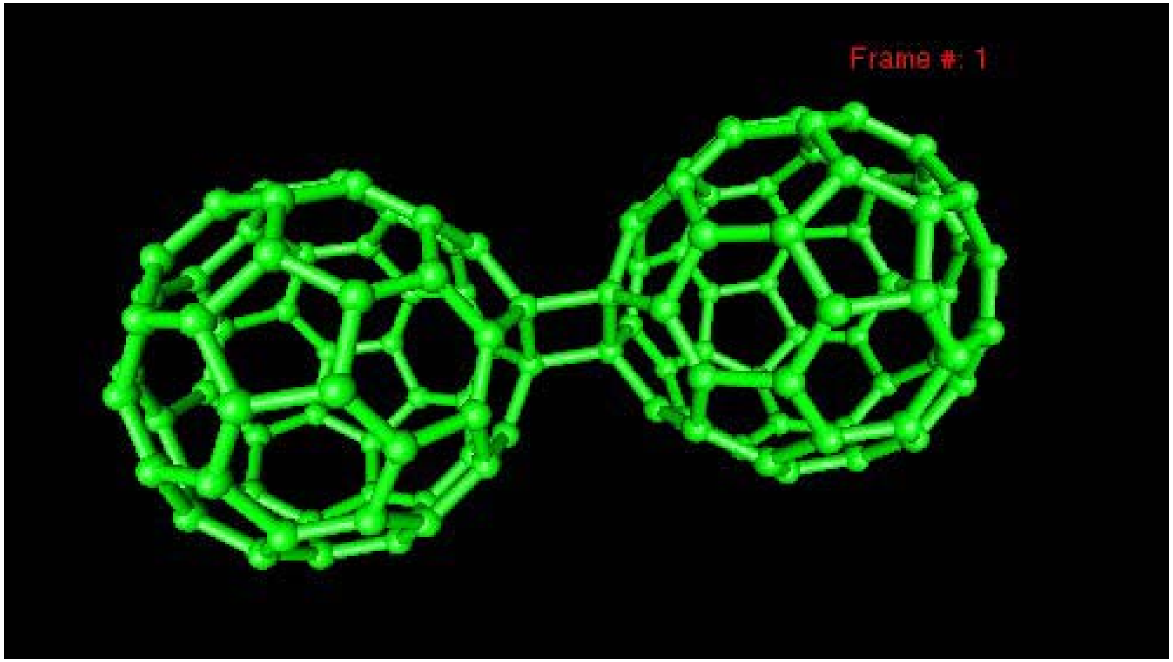


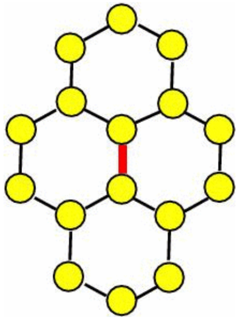
Search in 360-dimensional configuration space using string method:

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

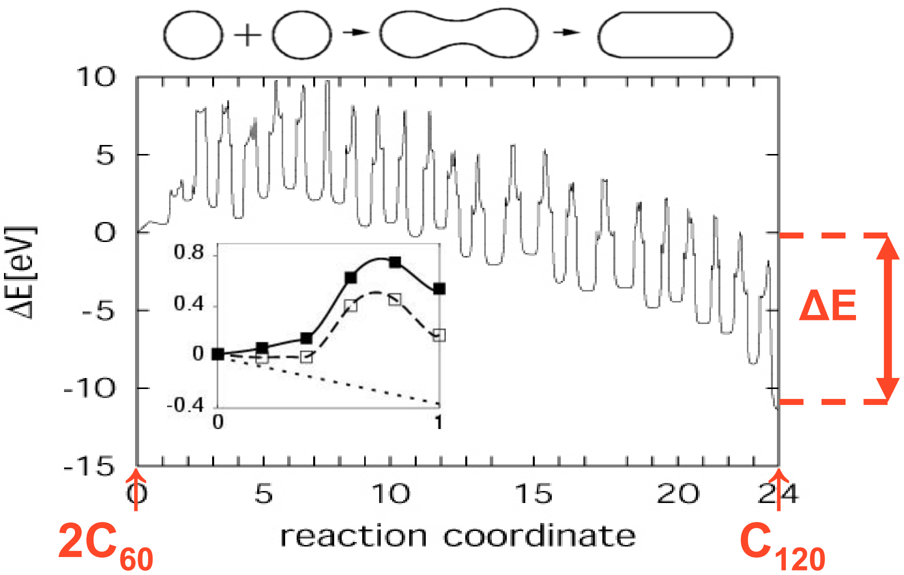


Minimum energy path for the $2C_{60} \rightarrow C_{120}$ fusion





Sequence of Stone-Wales transformations



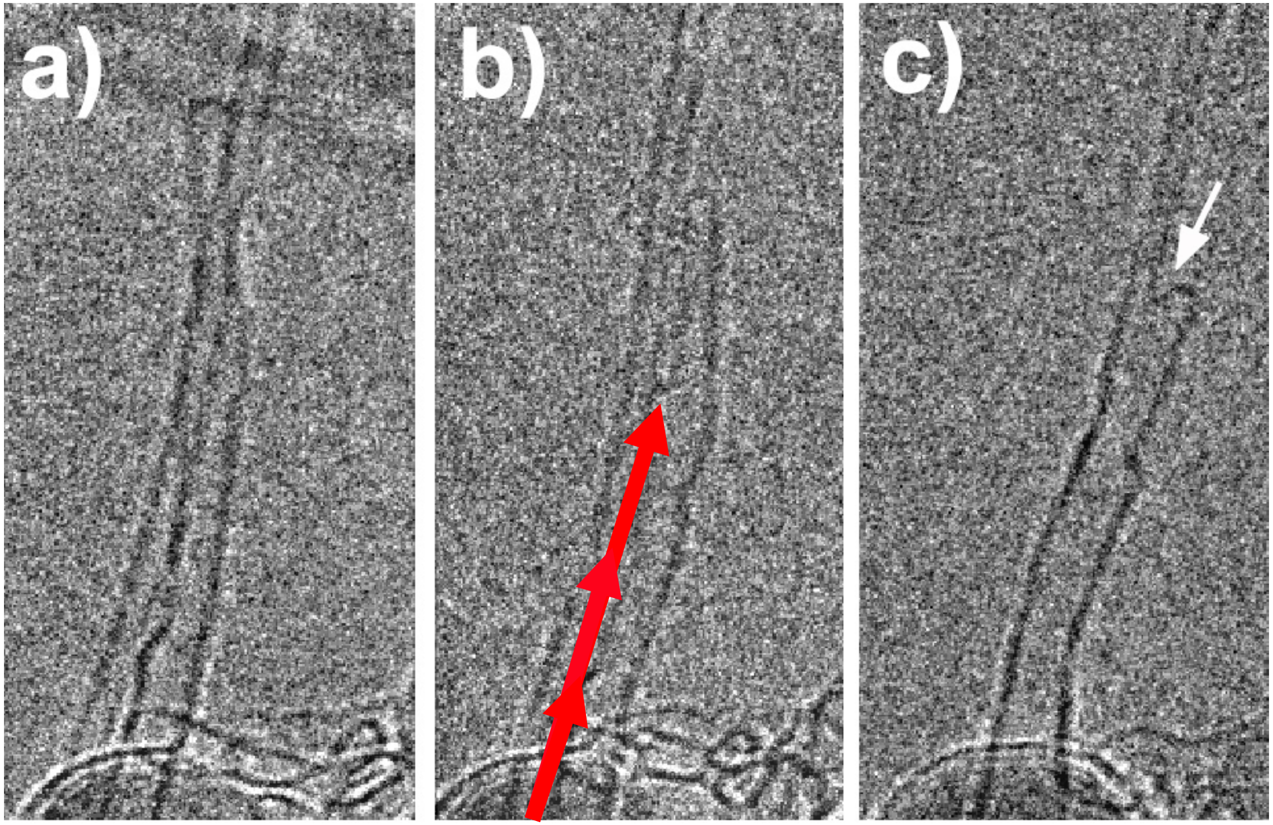
- Conclusions:
  - -Fusion is exothermic. Energy gain $\Delta E \approx 1$Ry.
  - -Essential initial step: (2+2) cycloaddition

Seungwu Han, Mina Yoon, Savas Berber, Noah Park, Eiji Osawa, Jisoon Ihm, and David Tománek, Microscopic Mechanism of Fullerene Fusion, Phys. Rev. B **70**, 113402 (2004).

Fusion of nanotubes

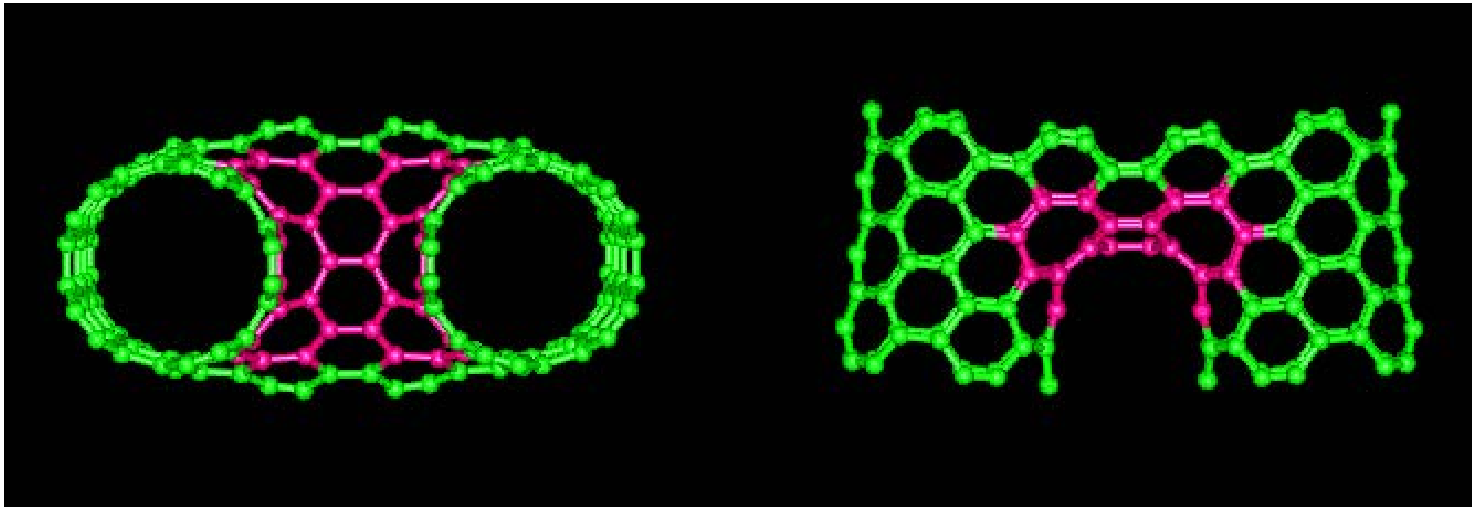
The zipper mechanism

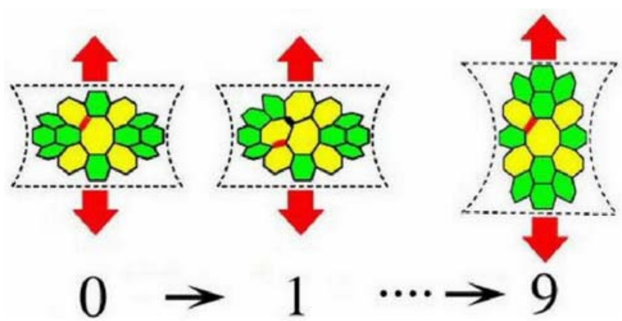
M. Yoon, S. Han, G. Kim, S. Lee, S. Berber, E. Osawa, J. Ihm, M. Terrones, F. Banhart, J.-C. Charlier, N. Grobert, H. Terrones, P. M. Ajayan, D. Tománek, Phys. Rev. Lett. **92**, 075504 (2004).

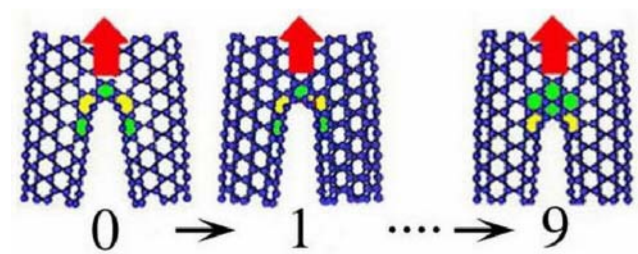


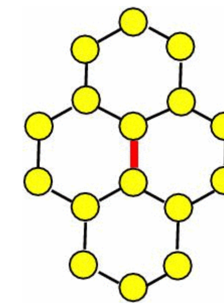
Zipper

Minimum energy path for the (5,5)+(5,5)→(10,10) fusion

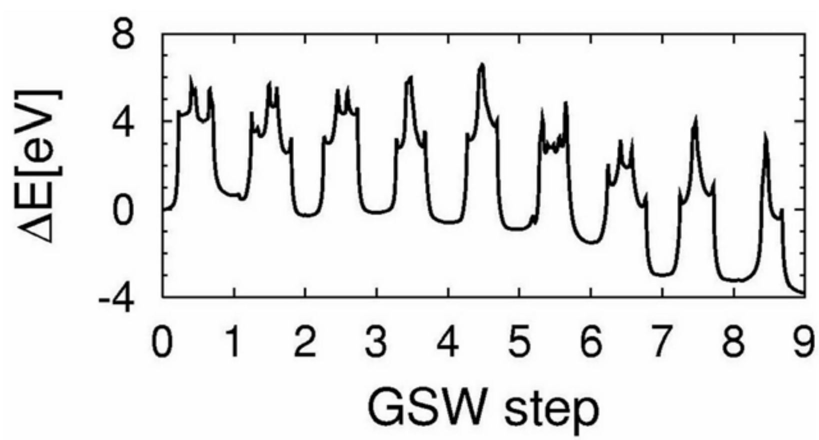








Sequence of Stone-Wales transformations

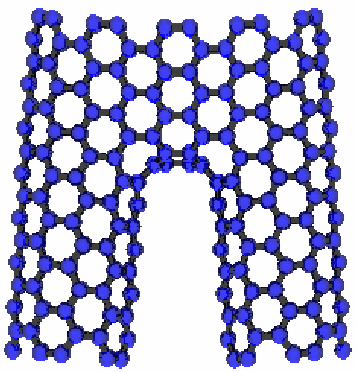


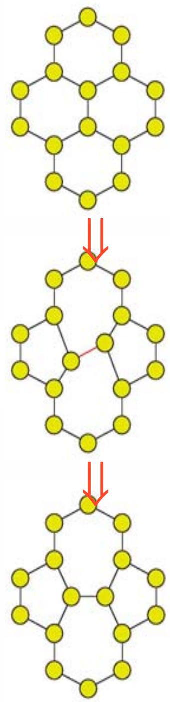
❖ **Conclusion: Fusion is exothermic**

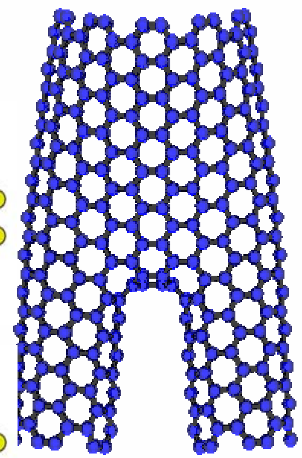
Geometry of fusing Nanopants

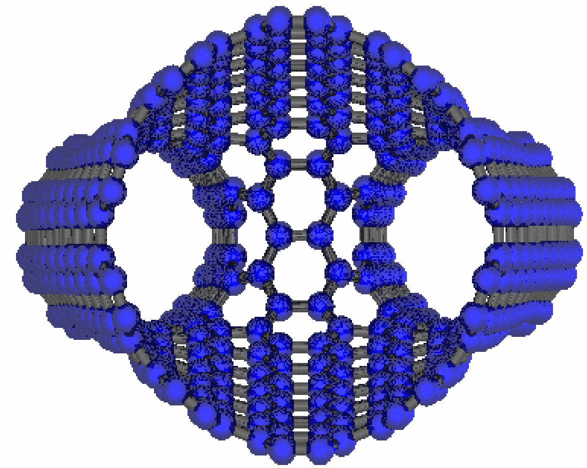
front view | **top view**

Type A:
6 heptagons in junction area

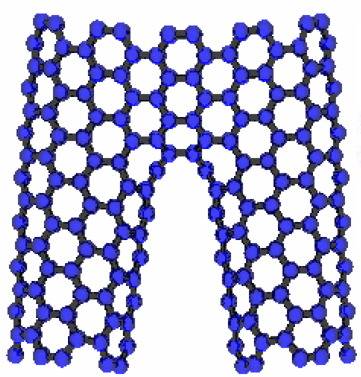


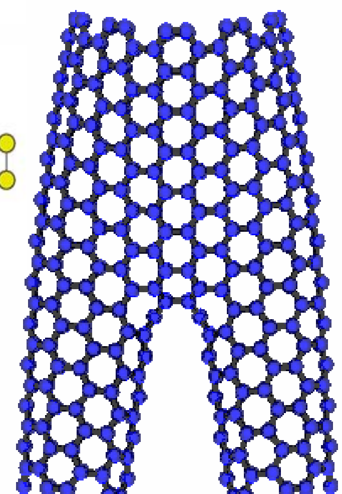


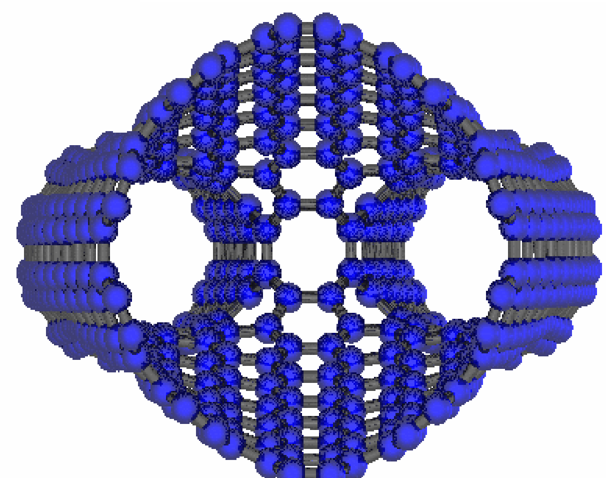




Type B:
1 octagon, 4 heptagons in junction area







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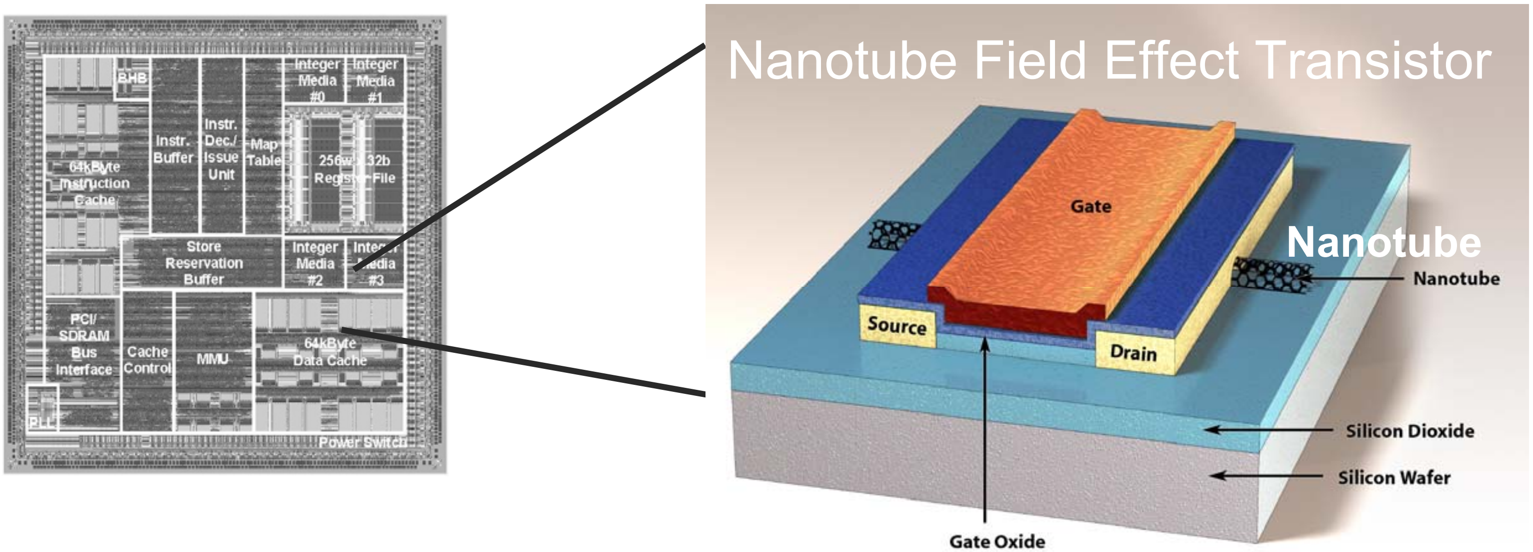
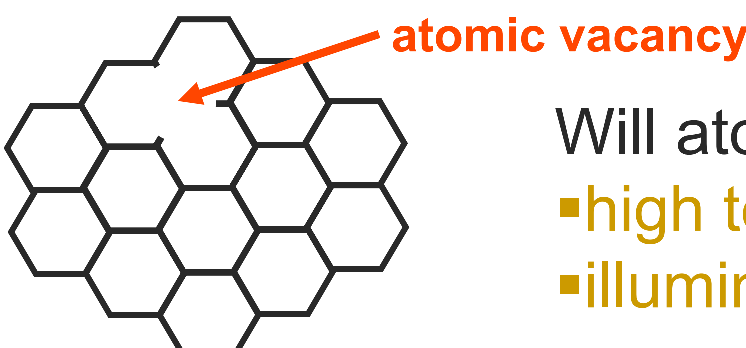
Behavior of Defective Nanotubes

Defect tolerance of nanotubes

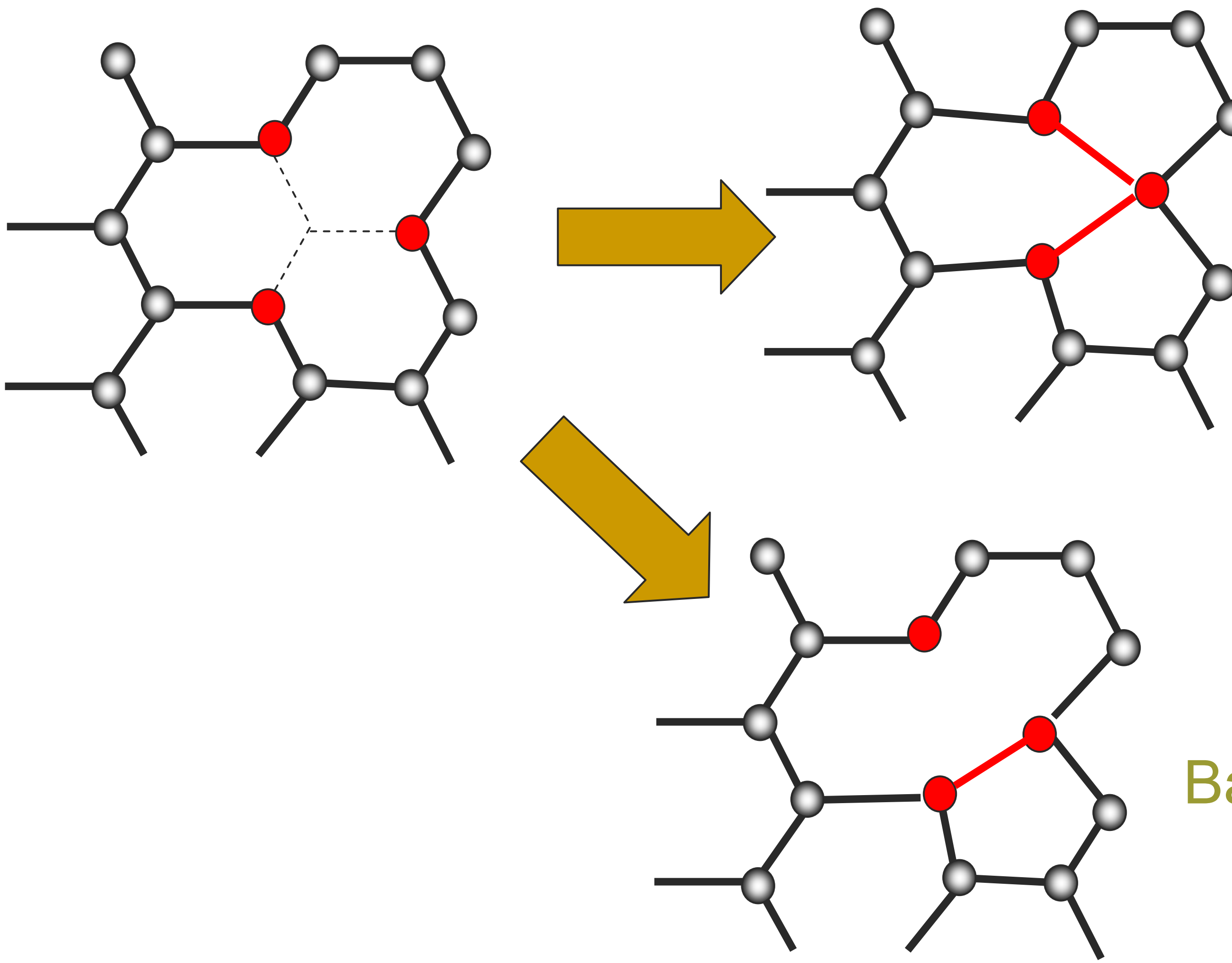


- Defects limit performance, lifetime of devices
- Are CNT devices as sensitive to defects as Si-LSI circuits?



Will atomic vacancies trigger failure under
- high temperatures?
- illumination?

Equilibrium structure near a monovacancy in sp^2 carbon

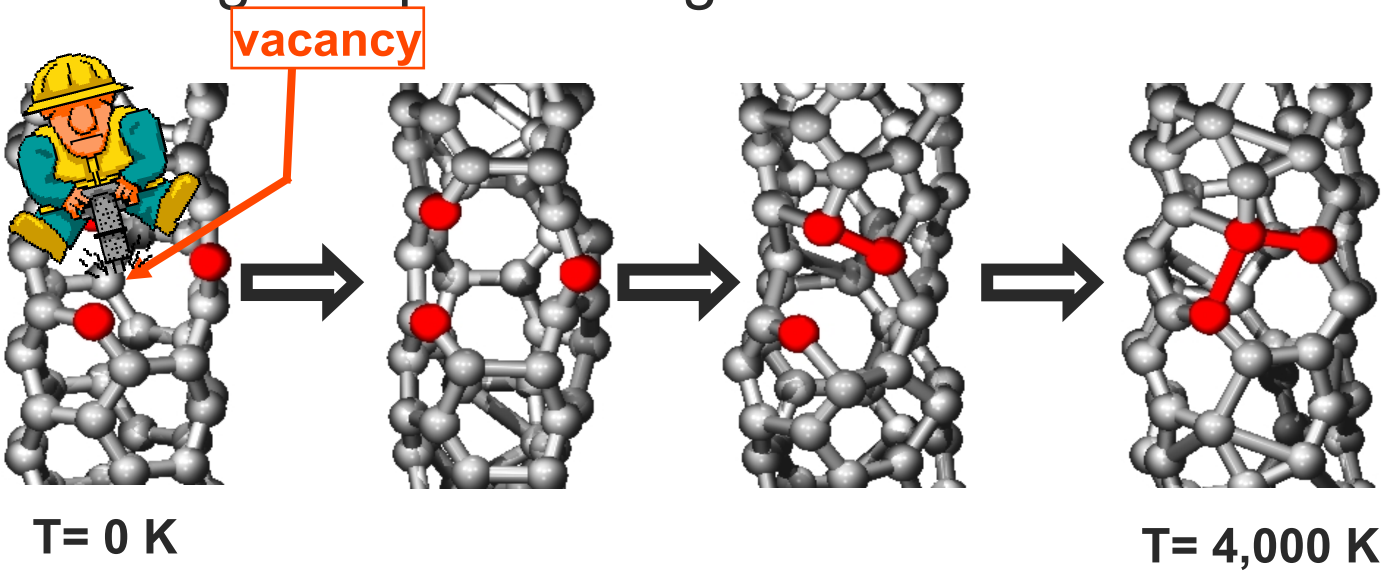


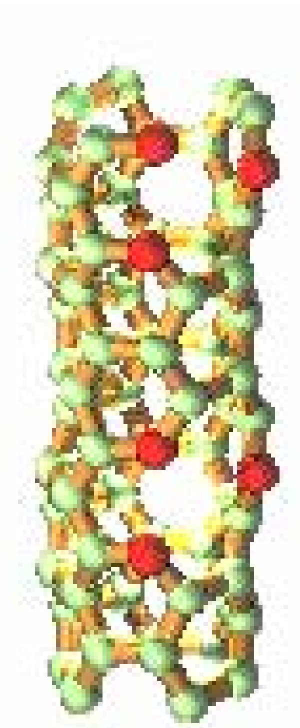
Strain
too large

Barely stable

Stability of defective tubes at high temperatures

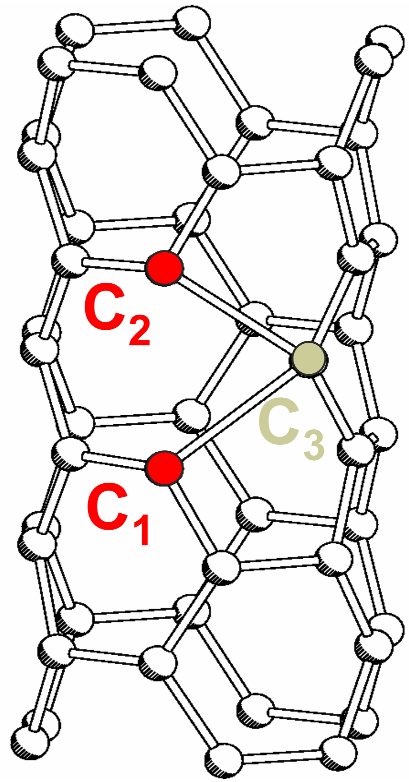
- Danger of pre-melting near vacancies?





- Nanotube remains intact until 4,000 K
- Self-healing behavior:
  Formation of new bond helps recover
  - structural stiffness
  - conductance

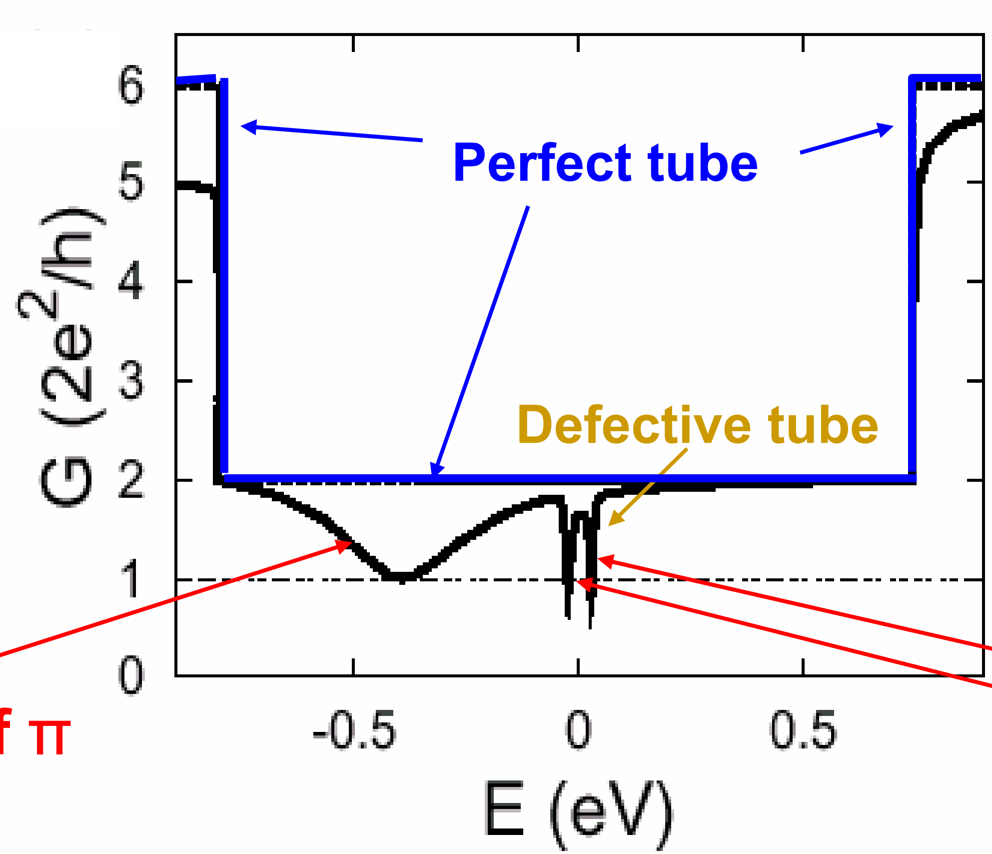
Reconstructed geometry



Stability increase due to reconstruction
(bond formation across vacancy)

Does reconstruction affect favorably transport in defective tubes?

Quantum conductance of a (10,10) nanotube with a single vacancy



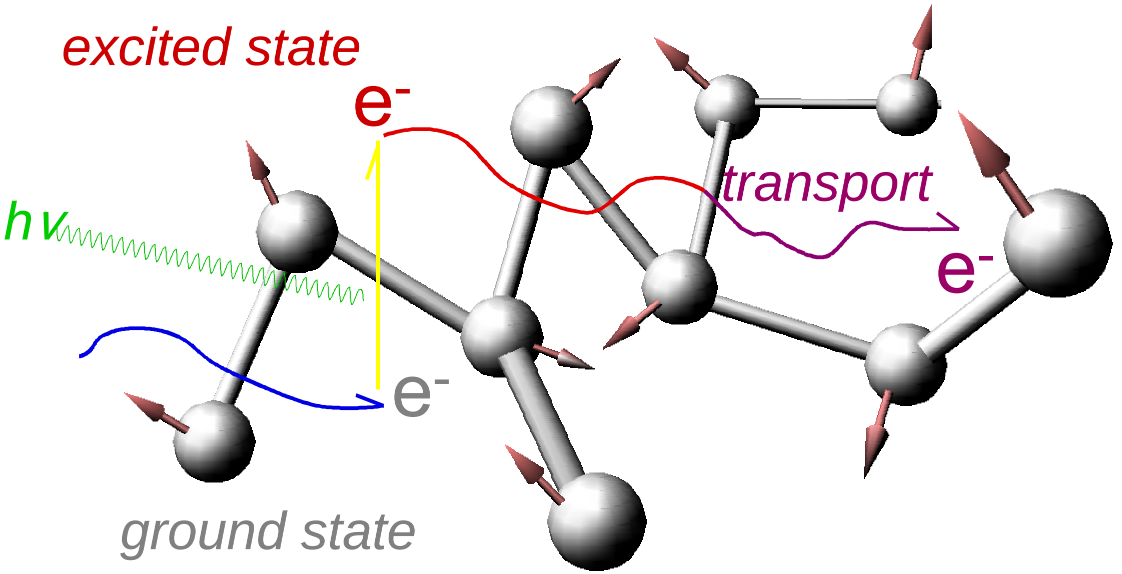
Missing network of π electrons

Dangling bonds: σ electrons

Choi, Ihm, Louie, Cohen, PRL (2000)

Good news for applications: Self-healing by reconstruction may remove one of the sharp dips

Stability of defective tubes during electronic excitations

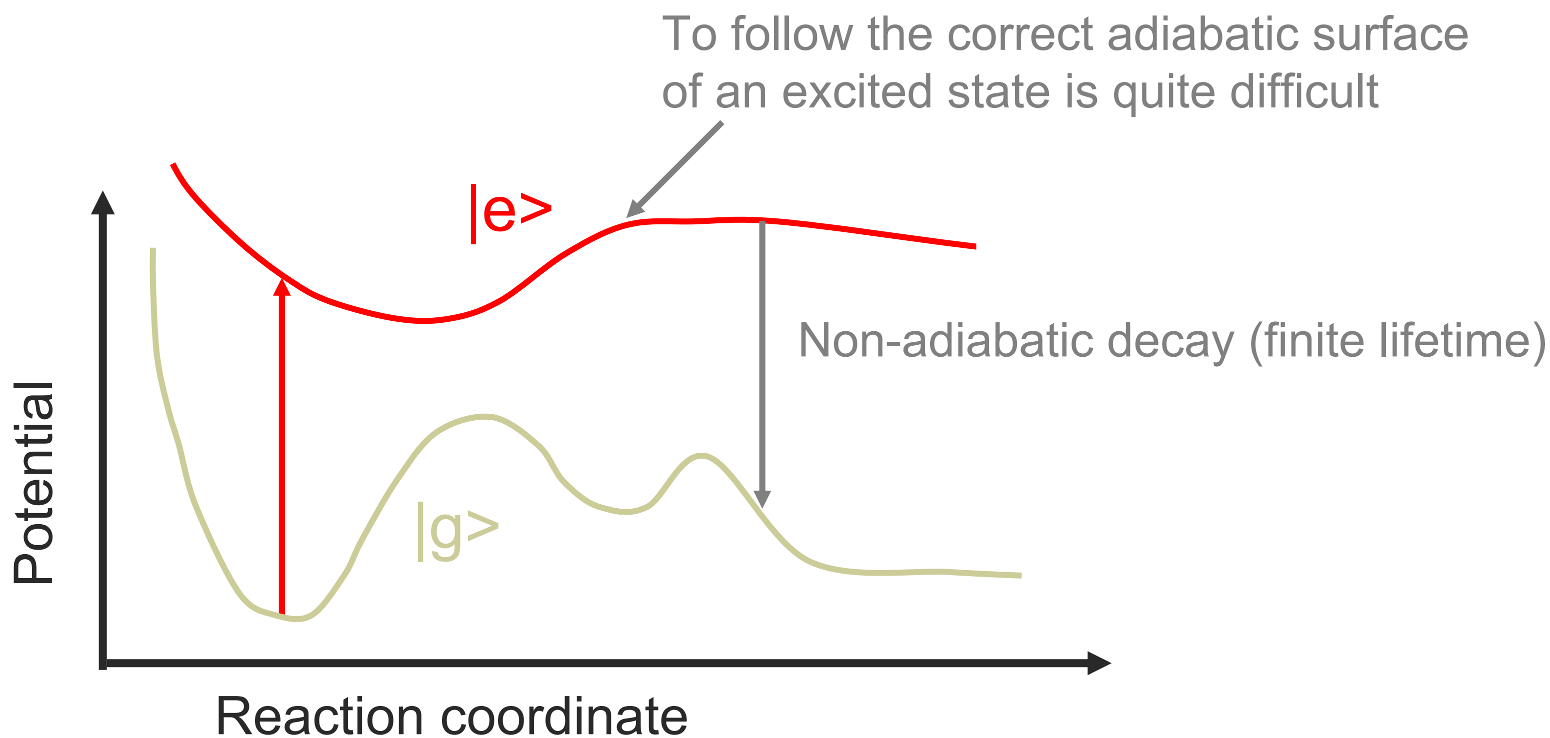


Challenges:

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

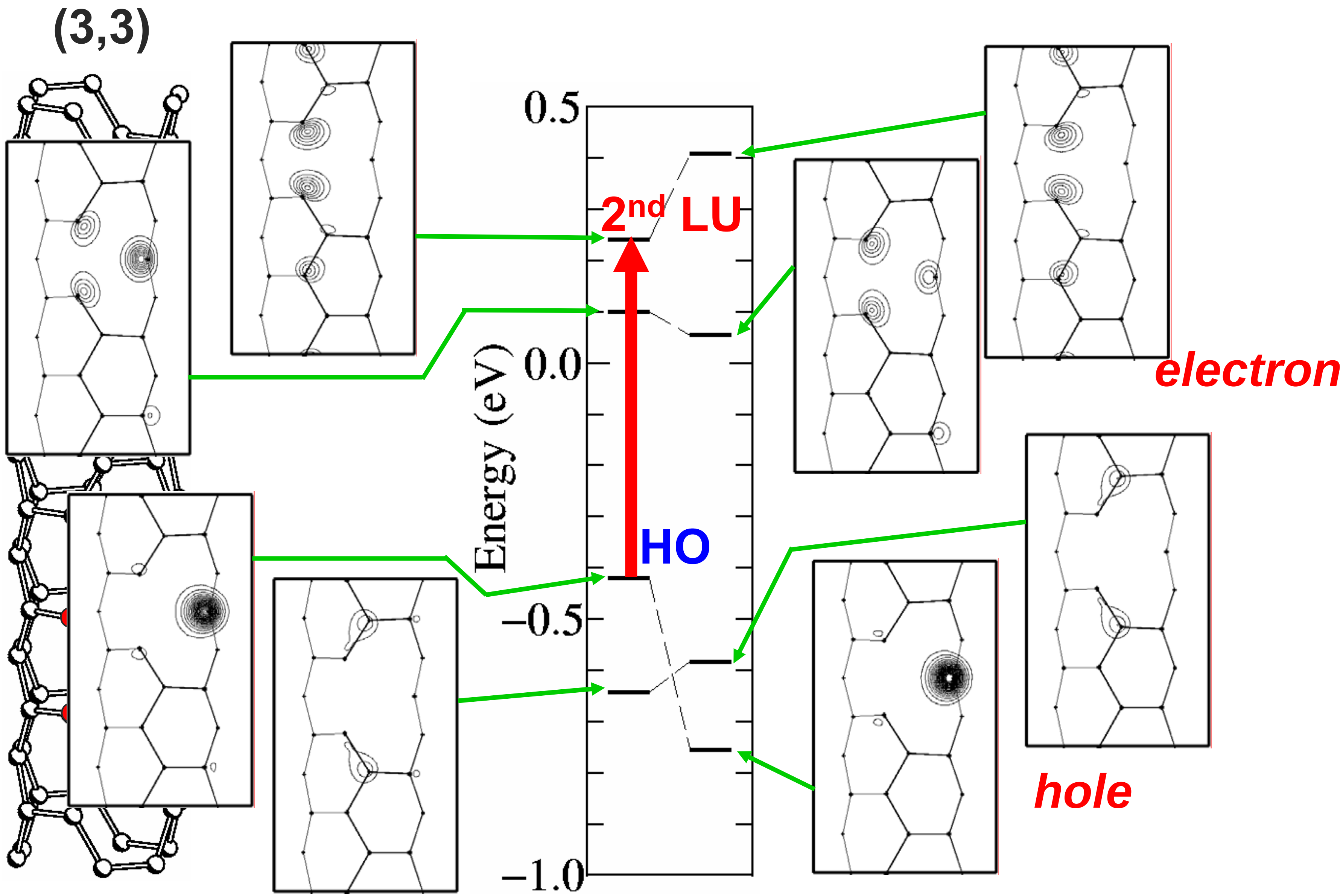
- Solve the time-dependent Schrödinger equation for electrons during ionic motion

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

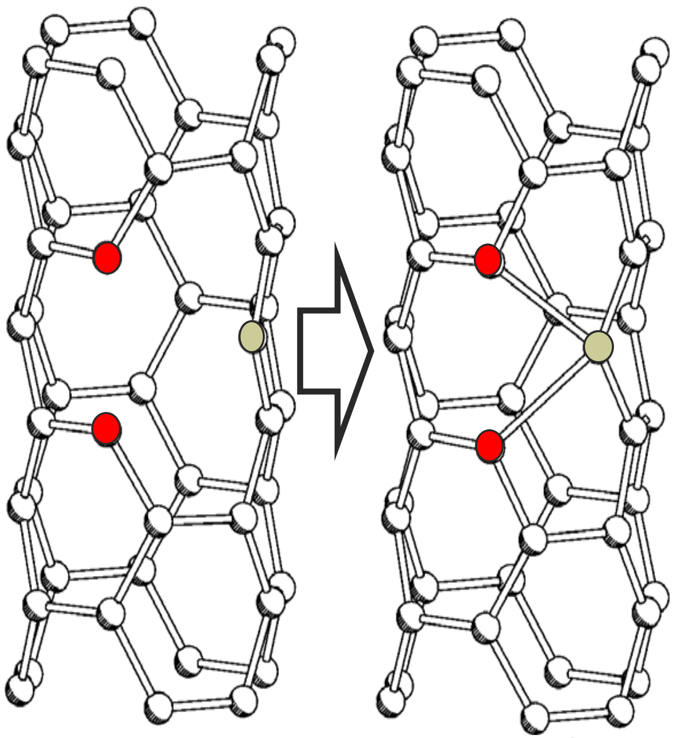


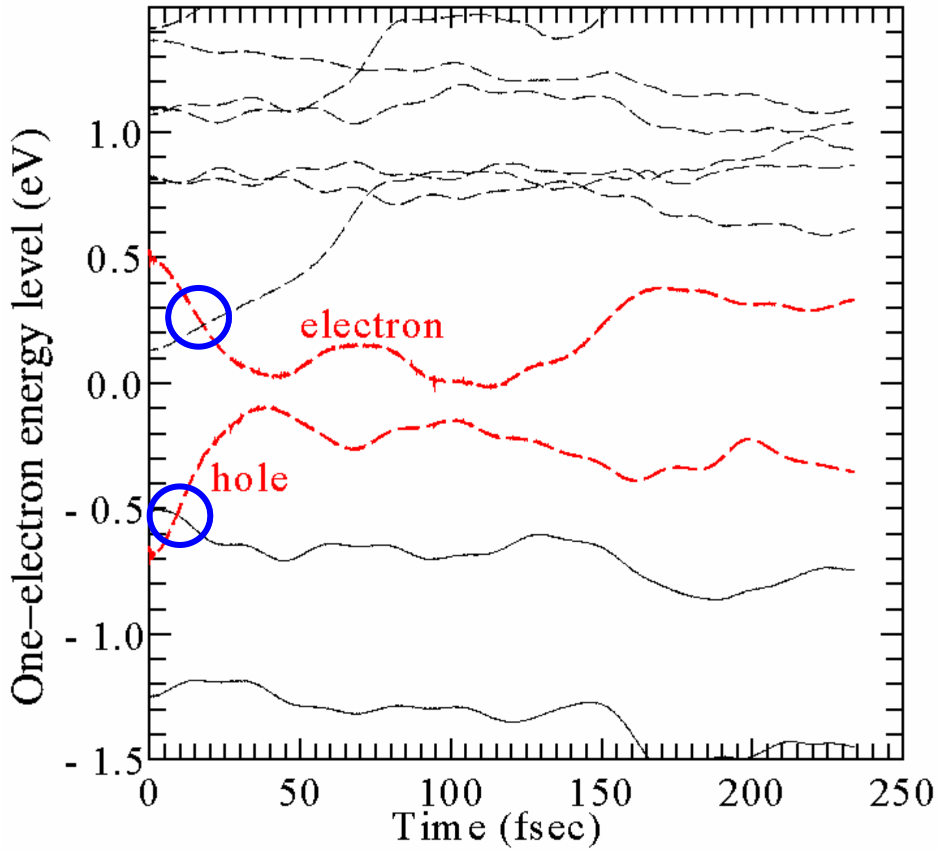
- **F**irst-**P**rinciples **S**imulation tool for **E**lectron-**I**on **D**ynamics
- Details: *Sugino & Miyamoto PRB **59**, 2579 (1999)*; *PRB **66**, 89901 (2002).*
- Results: *Yoshiyuki Miyamoto, Savas Berber, Mina Yoon, Angel Rubio, David Tománek, Can Photo Excitations Heal Defects in Carbon Nanotubes? Chem. Phys. Lett. **392**, 209–213 (2004).*

Optical excitation (ΔE=0.9 eV)



Time evolution of the electronic states

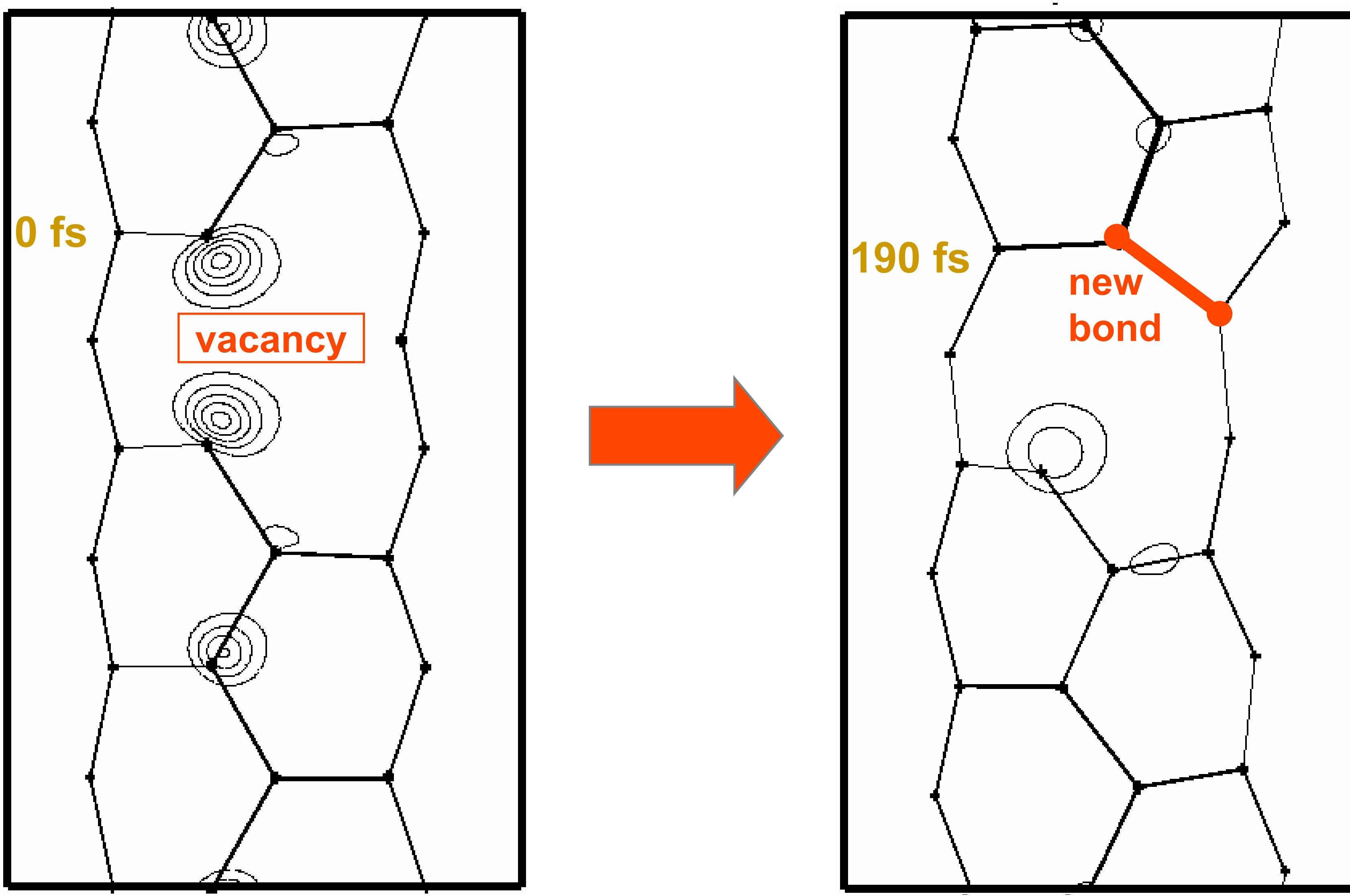




$$\Psi_n\,(t+\Delta t)=\exp(-i/h\; H\Delta t\;)\;\Psi_n(t)$$

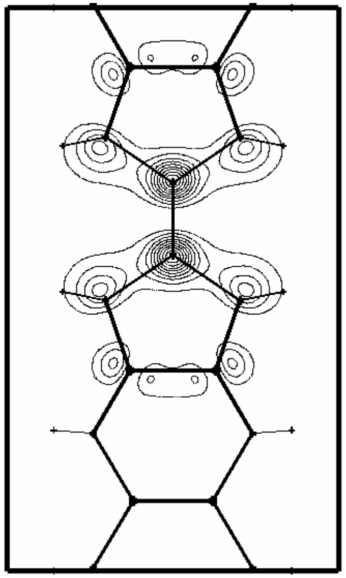
- Very long-lived excitation
- Correct PES is followed in case of level alternation

Structural changes under illumination



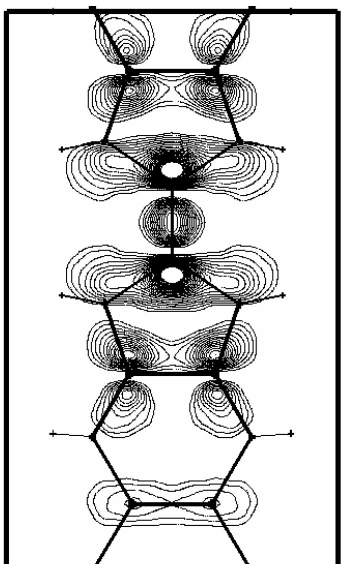
- Self-healing due to new bond formation

Detection of Stone-Wales defects

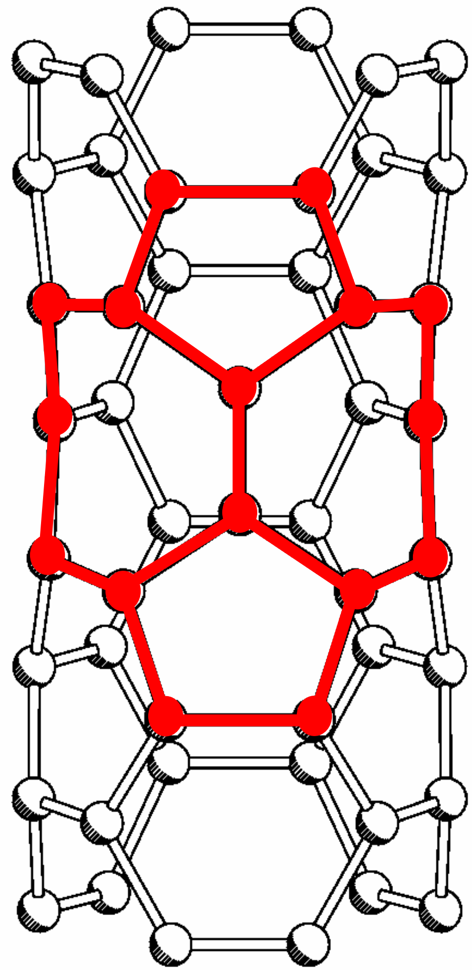


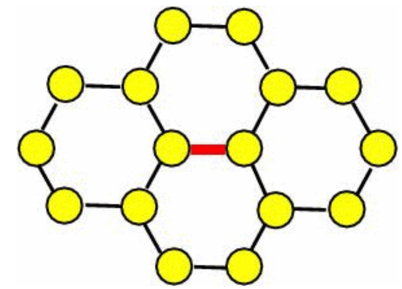
π* state
(electron)

6 eV



σ-π
hybridized
state (hole)

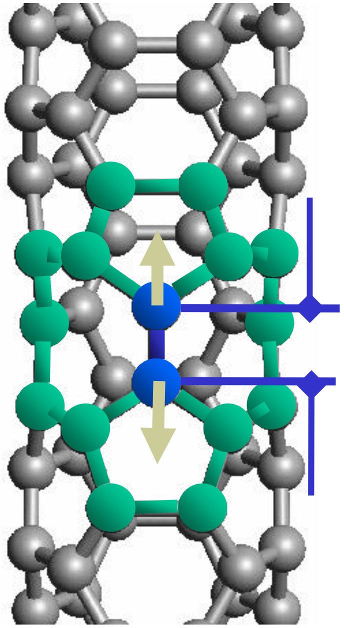


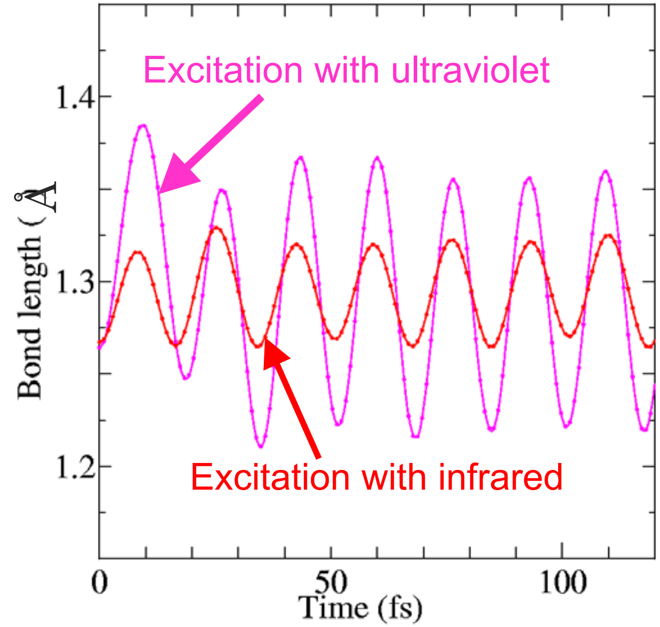


Stone-Wales
transformation

►Can Stone-Wales defects be removed by photo-excitations?

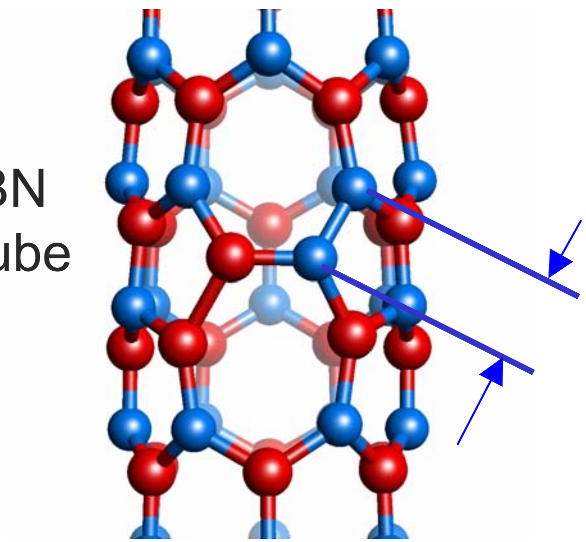
(3,3)
carbon
nanotube

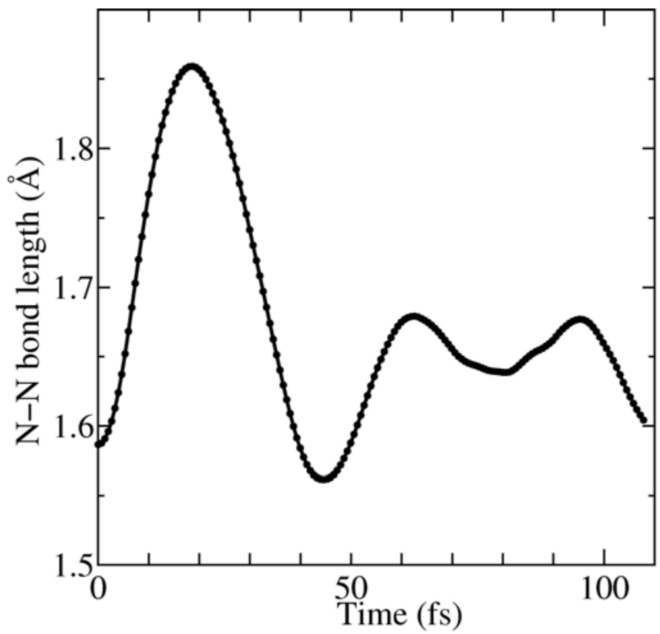




T=17 fs
(1962 cm^{-1})

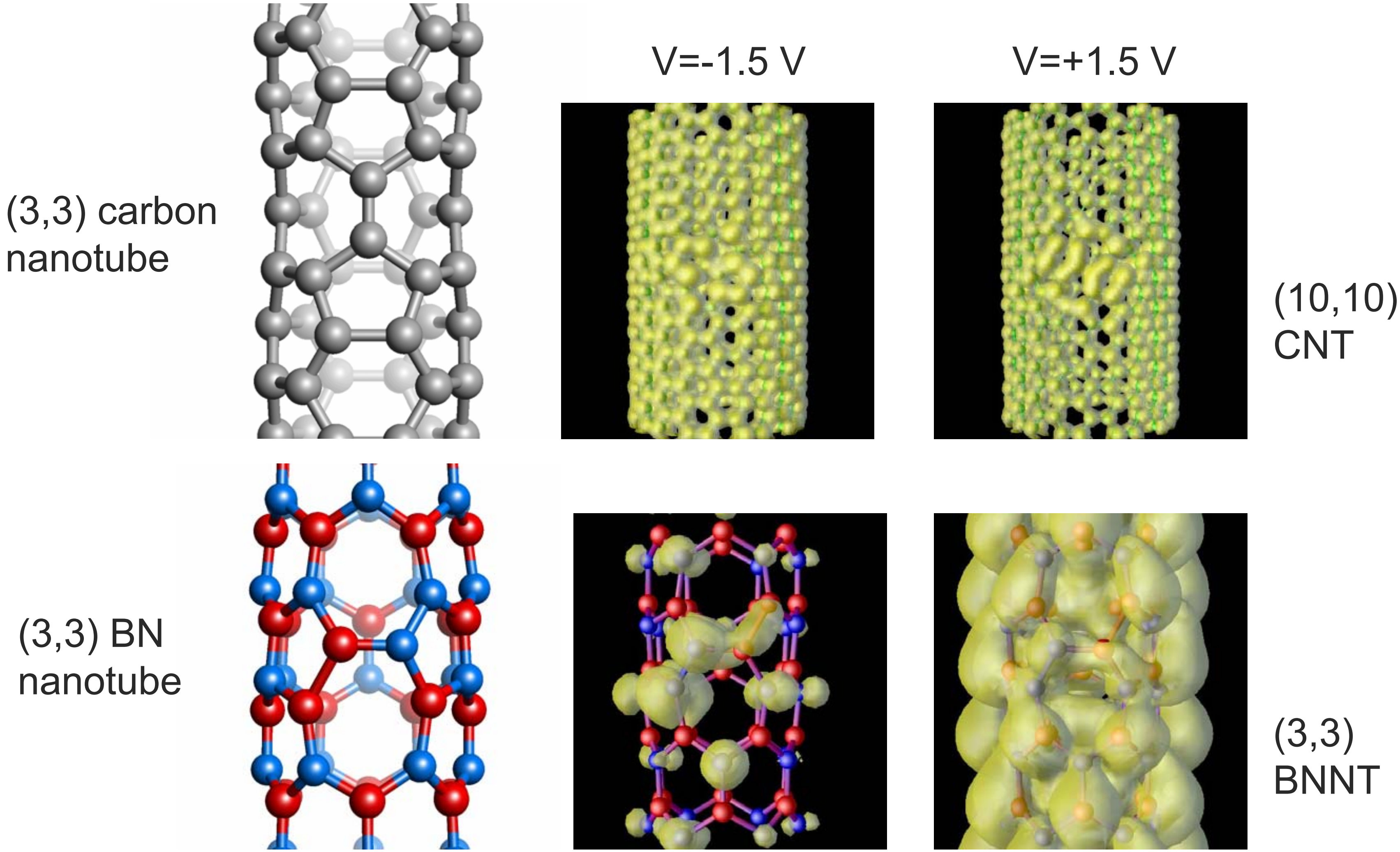
(3,3) BN
nanotube





Stone-Wales defects can not be removed, but can be identified using photo-excitations

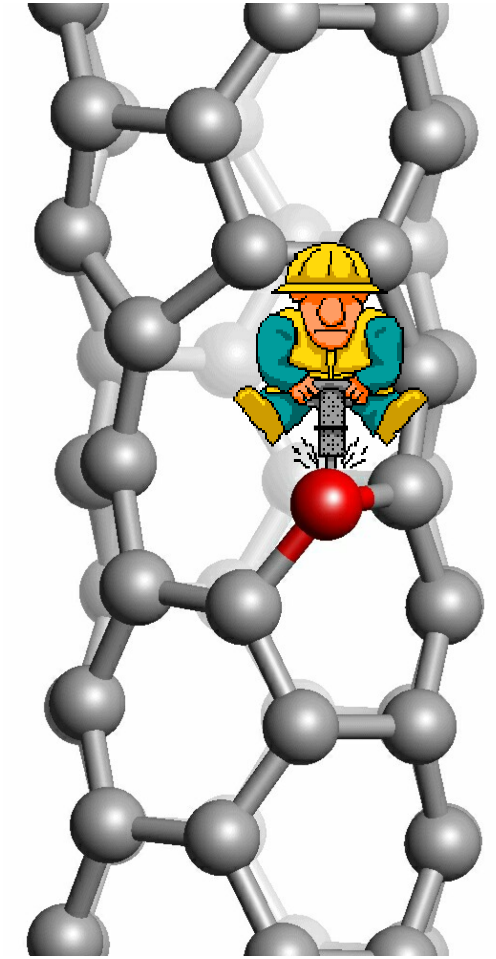
STM characterization of Stone-Wales defects



Y. Miyamoto, A. Rubio, S. Berber, M. Yoon, and D. Tománek, Phys. Rev. BR 69, 121413 (2004).

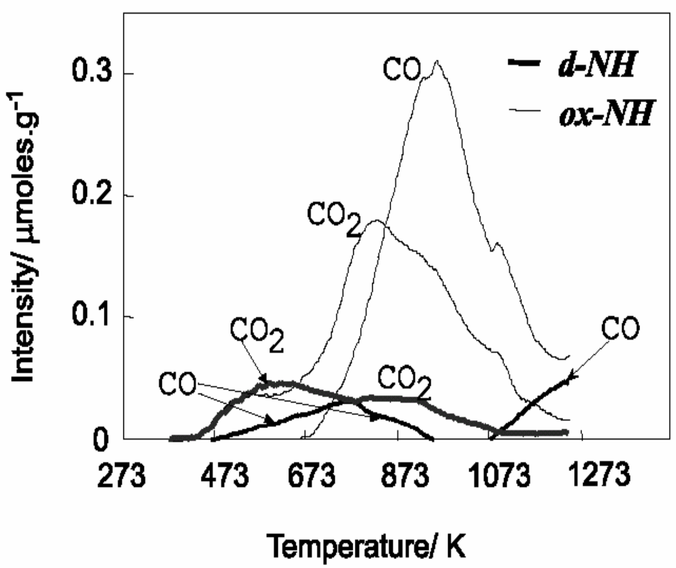
Deoxidation of defective nanotubes

How to deoxidize?

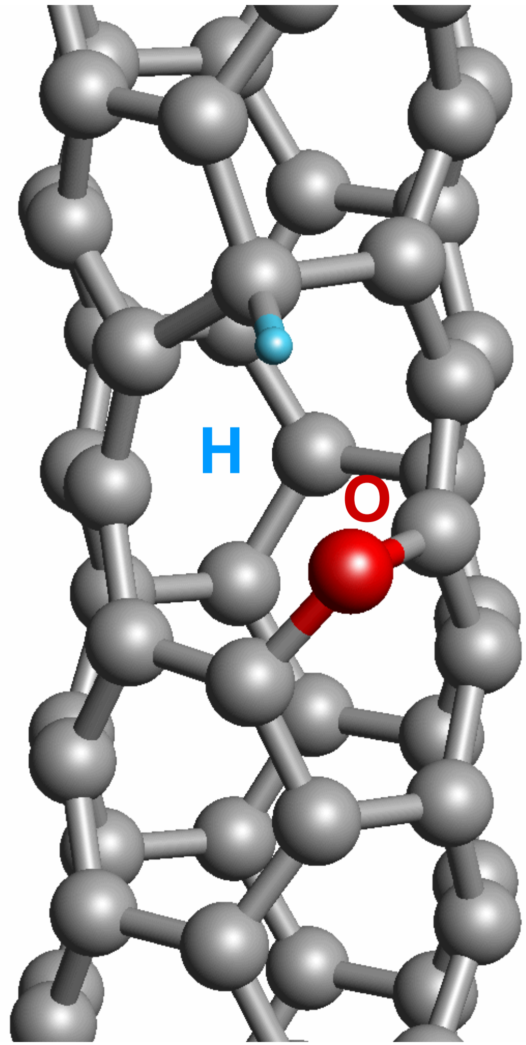


- **By heat treatment?**

⇒No: Larger damage to nanotube

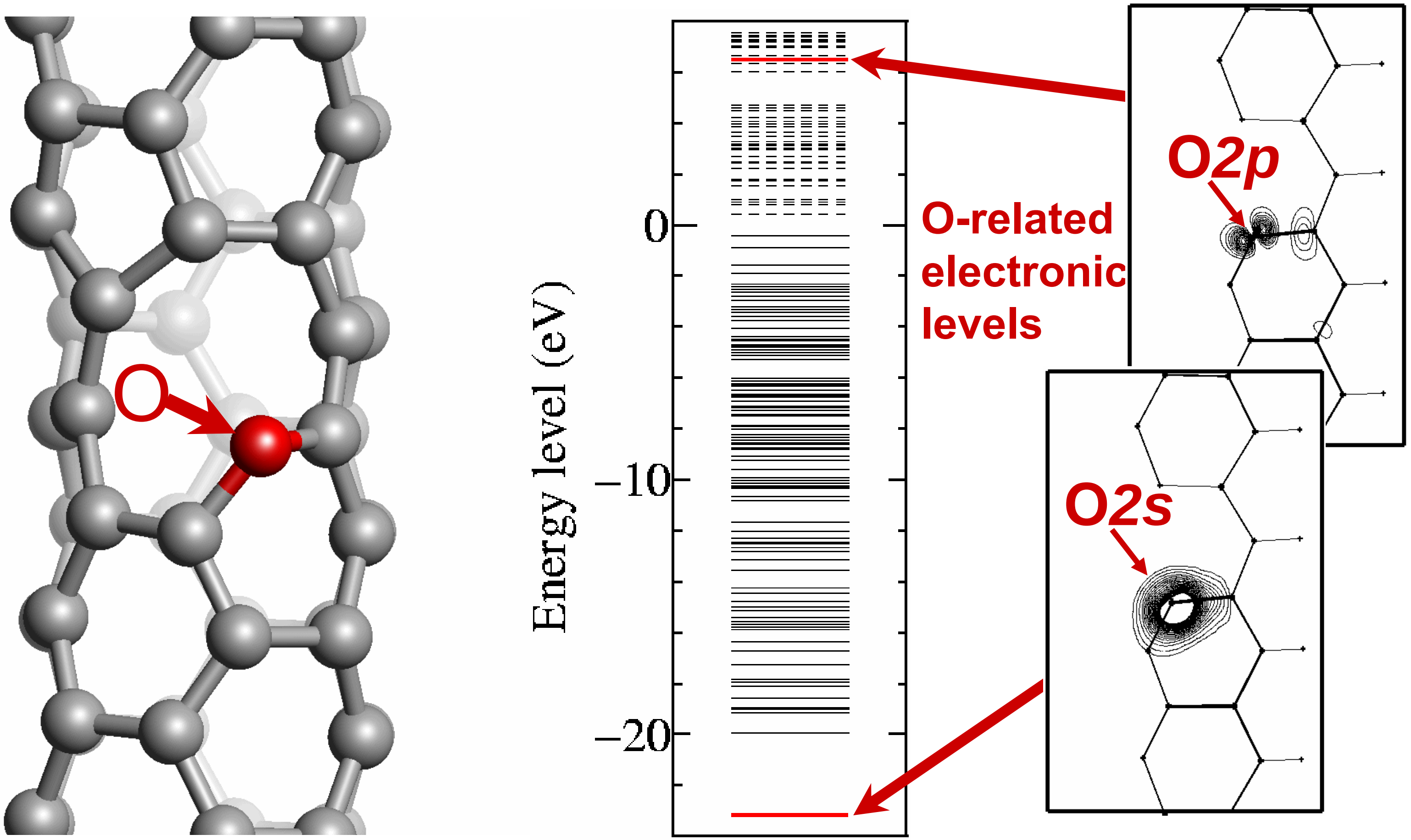


- **By chemical treatment with H?**



Alternative to thermal and chemical treatment

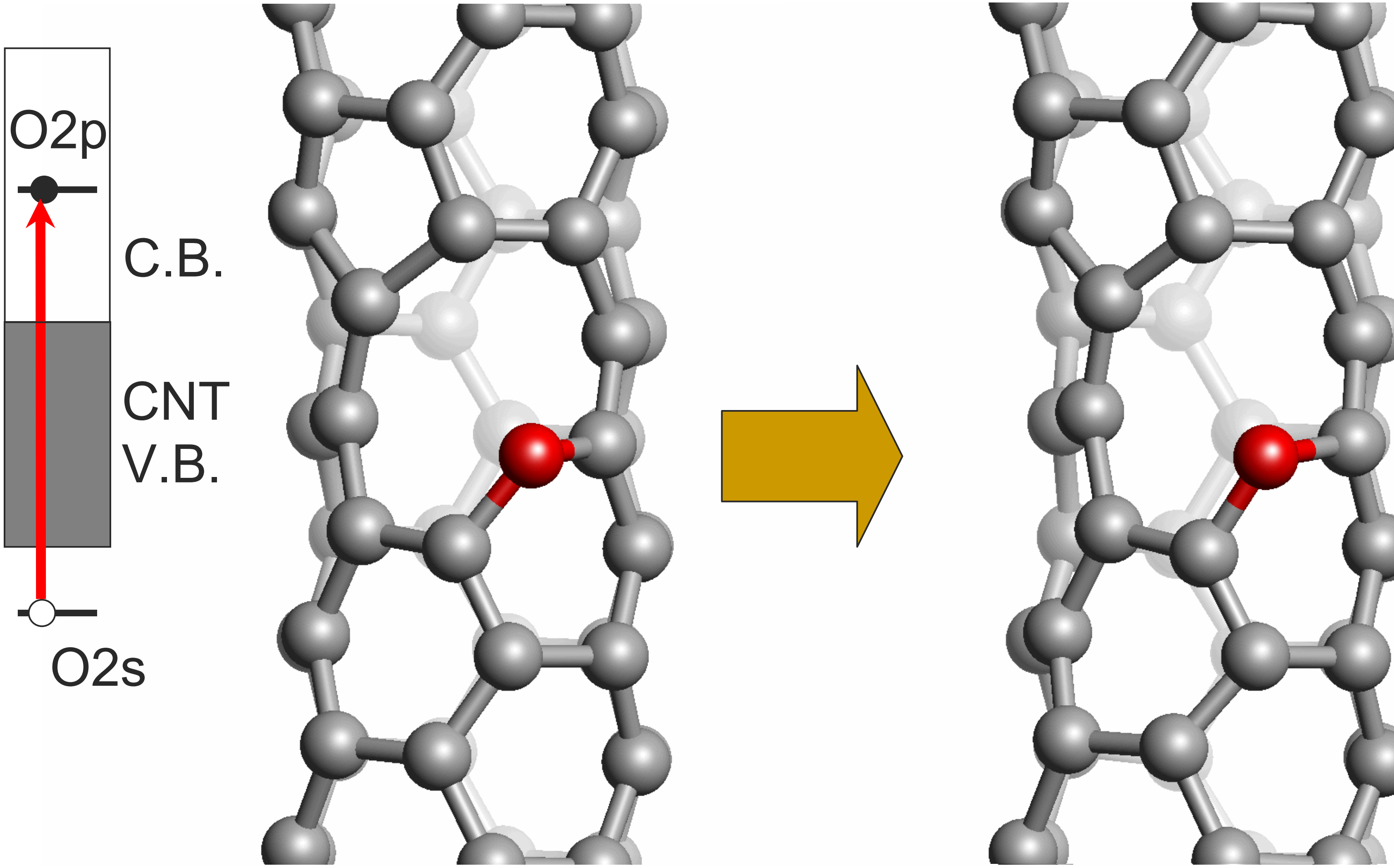
Electronic excitations!



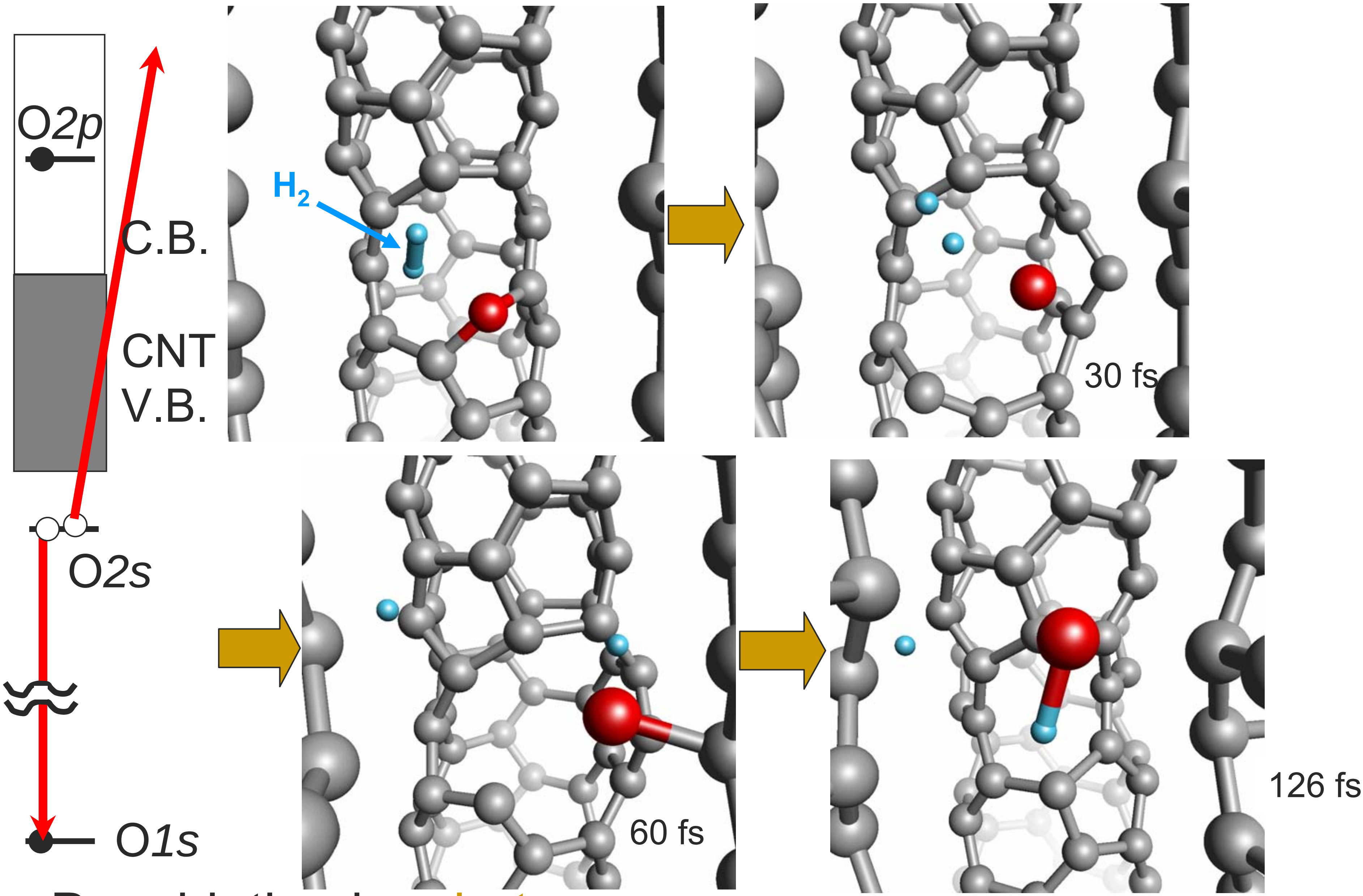
Yoshiyuki Miyamoto, Noboru Jinbo, Hisashi Nakamura, Angel Rubio, and David Tománek, Photodesorption of oxygen from carbon nanotubes, Phys. Rev. B **70**, 233408 (2004).

$O2s \rightarrow O2p$ *excitation (33 eV)*

hopeless



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



- Deoxidation by photo-surgery

Summary and Conclusions

- Carbon nanotubes are Nature's best thermal conductors.
- Carbon nanotubes contract thermally.
- Nanostructured carbon may become magnetic.
- 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.
- Nanotube field electron emitters decay by thermally assisted Coulomb explosion at the tip.
- Carbon nanotubes are unusually stable when sputtered.
- Heat and photo-excitations may induce self-healing behavior in defective nanotubes.
- Photo-excitations may be used to detect specific defects by their vibrational signature.
- Photo-excitations can be used to selectively remove oxygen impurities.

The End