# Designing Carbon-Based Nanotechnology on a Supercomputer


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# Acknowledgements


| | |
|---|---|
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# Outline

- Introduction
  - State of the Art of Computer Simulations: Where are We Now?
  - Challenging Problems: Microscopic Processes in Nanostructures
- Searching for Transition States in High-Dimensional Phase Spaces
  - Fusion of fullerenes in peapods
  - Fusion of nanotubes
- Ground State Molecular Dynamics Simulations
  - High thermal conductivity of nanotubes
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  - Detection of Stone-Wales defects
  - Hot carrier dynamics in carbon nanotubes
- What are Excitations Good for?
  - Defect tolerance of nanotubes
  - Deoxidation of defective nanotubes
- Summary and Conclusions

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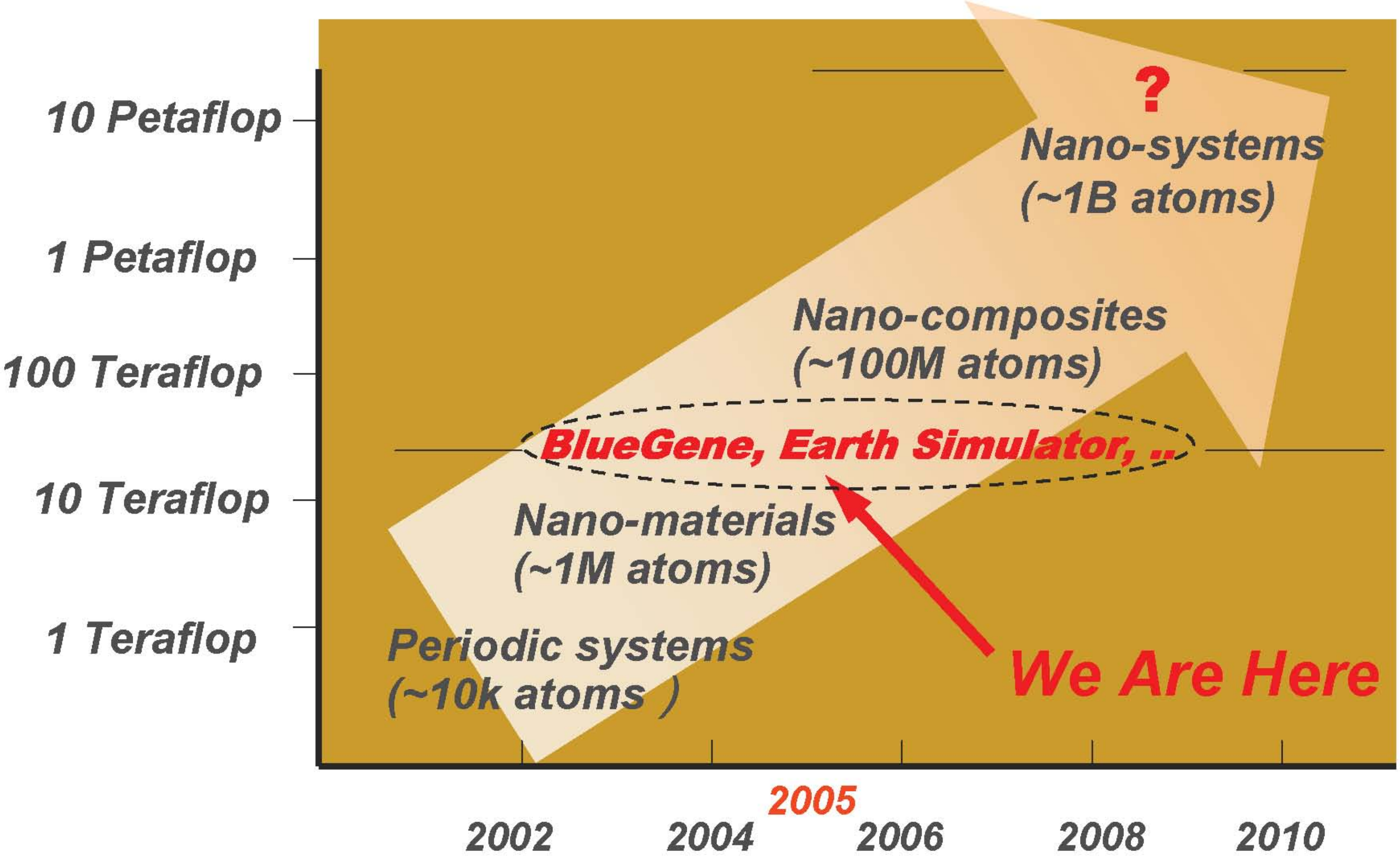
  *David Tománek, Carbon-based nanotechnology on a supercomputer, Topical Review in J. Phys.: Condens. Matter 17, R413-R459 (2005).*

# State of the Art Computer Simulations: Where Are We Now?



# The Nanocarbon Laboratory: Earth Simulator, Japan

www.nytimes.com

The New York Times ON THE WEB

April 20, 2002

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

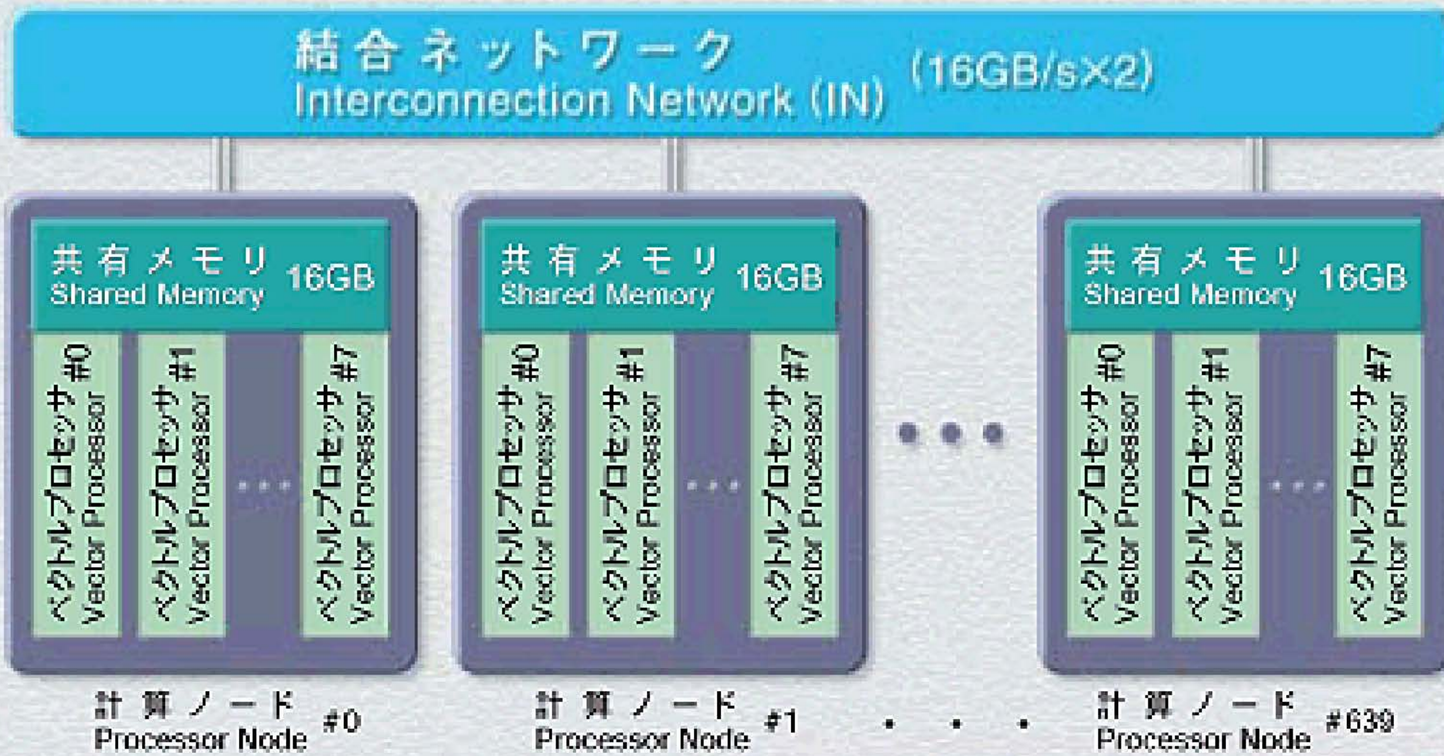
By JOHN MARKOFF

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.

# Earth Simulator Supercomputer

- Designed to model the Solid Earth (climate, earthquakes)
- Construction: 1997-2002
- Operation: since late 2002, by JAMSTEC
- Cost: 500M$
- Vendor: NEC
- Type:
  - Massively vector parallel architecture
  - 5120 processors/ 640 nodes
  - 40 TFLOPS, 10 TB
  - OS: Unix, MPI / OpenMP, FORTRAN77/90, C
- Location: Yokohama

# Earth Simulator Architecture

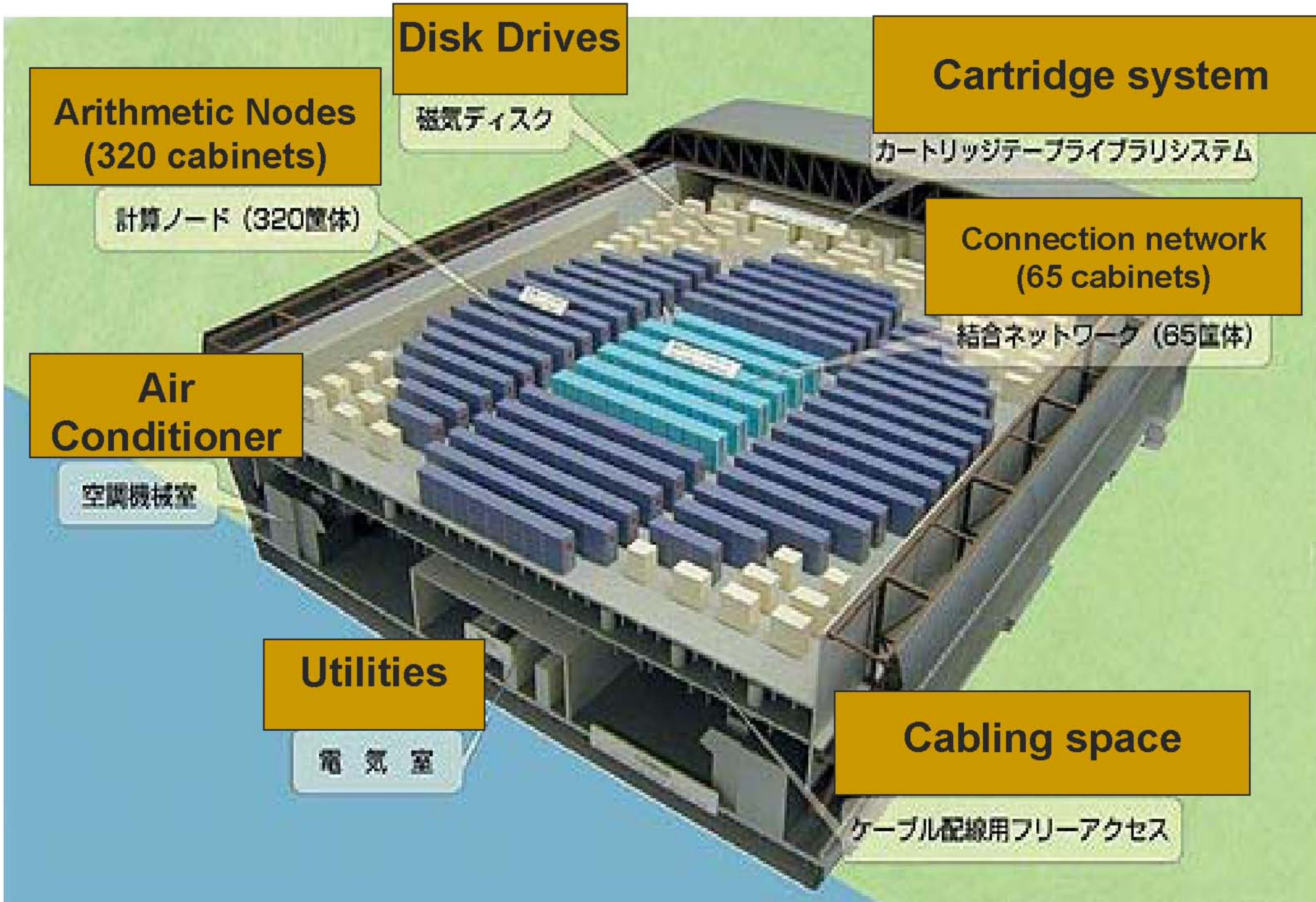



仕様
Specifications

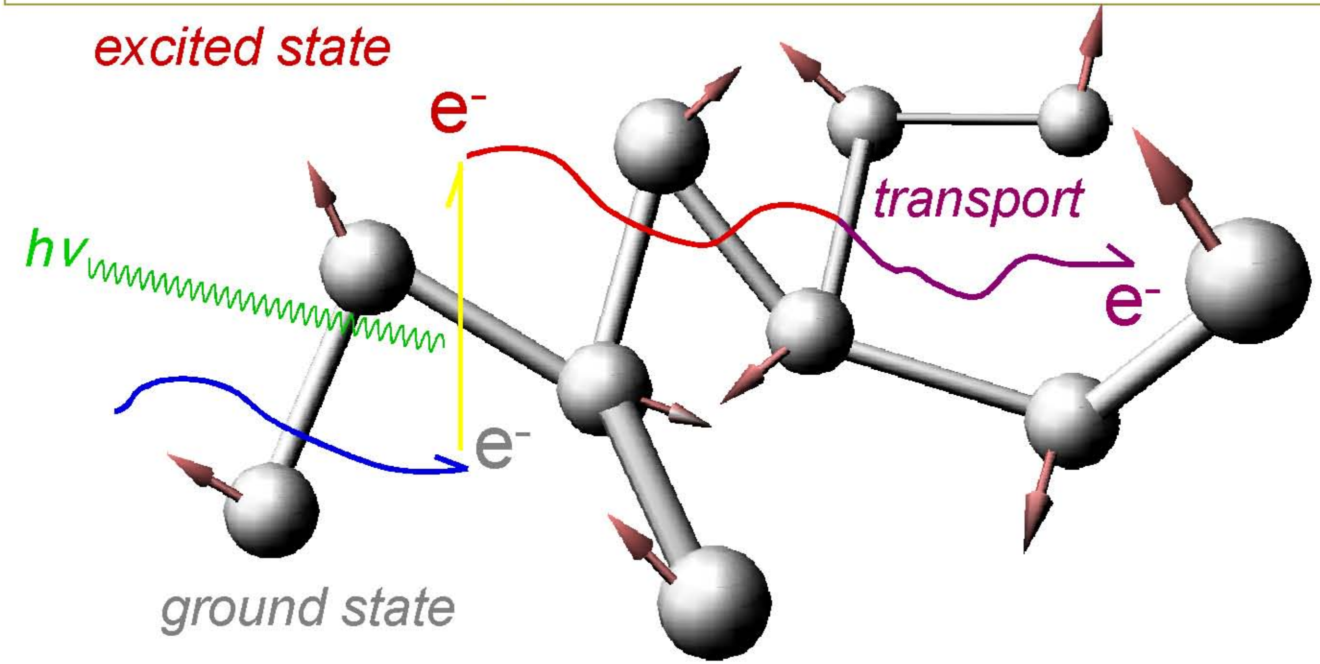
| | |
|---|---|
| 計算プロセッサのピーク性能<br>Peak performance/processor | 8 GFLOPS |
| 計算ノードのピーク性能<br>Peak performance/node | 64 GFLOPS |
| 計算ノードの主記憶容量<br>Shared memory | 16 GB |

| | |
|---|---|
| 総プロセッサ数<br>Total number of processors | 5,120 |
| 総計算ノード数<br>Total number of nodes | 640 |
| ピーク性能<br>Total peak performance | 40 TFLOPS |
| 主記憶容量<br>Total main memory | 10 TB |

# Earth Simulator Layout



# Challenging Problems: Microscopic processes in nanostructures




Which processes follow exposure to

- Heat?
- Photo-excitations?
- Carrier injection?
- Atomic collisions?

# Computational Approaches

- Electronic structure calculations based on the *ab initio* Density Functional formalism
- Atomic motion in the electronic ground state: Molecular dynamics simulations
- Forces from total energy expressions:

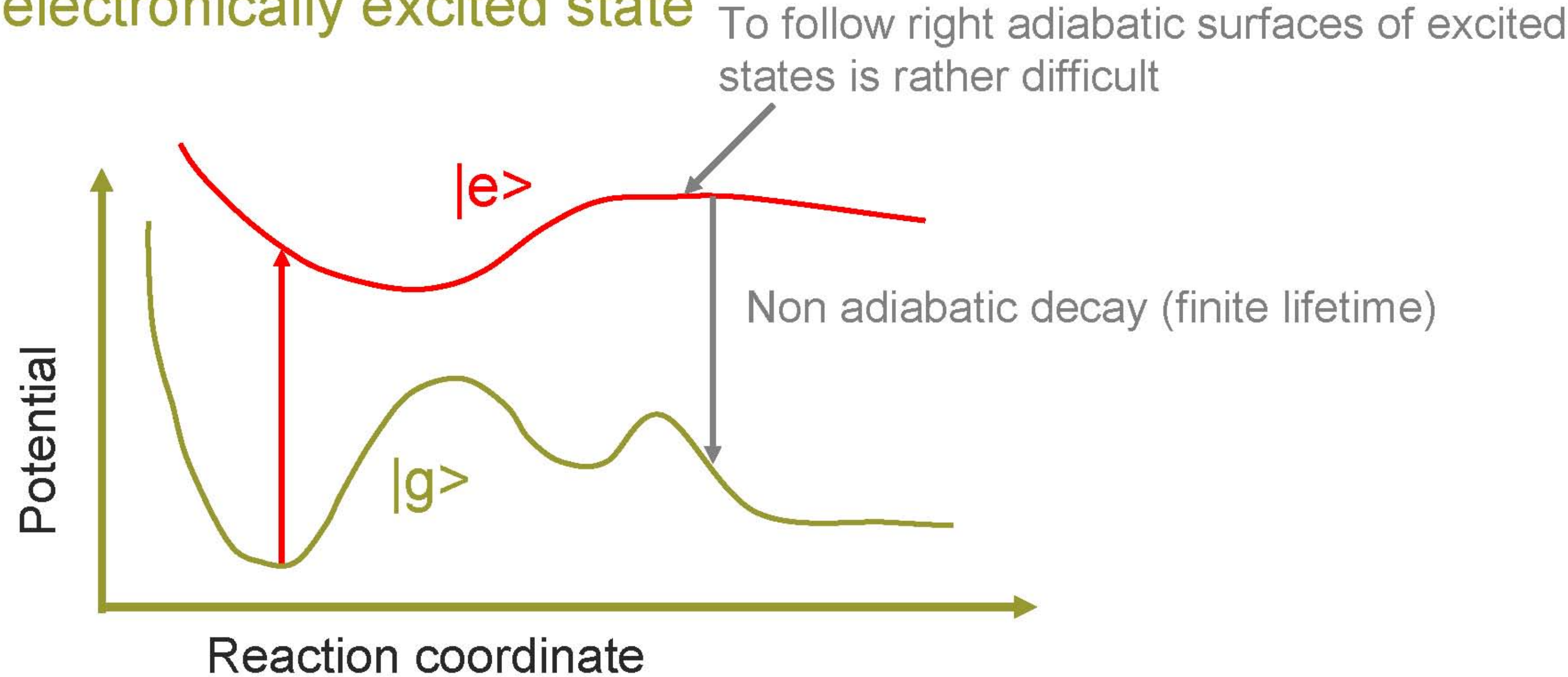
  $E_{tot} = E_{tot}(\{R_i\}) = E_{tot}\{\rho(r)\}$

  *ab initio* Density Functional formalism

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

  parametrized LCAO formalism (CRT)
- Dynamics of **atoms and electrons** under electronic excitations
- Massively parallel computer architectures and suitable algorithms distribute load over processors for speed-up

# System evolution on the adiabatic surface of an electronically excited state



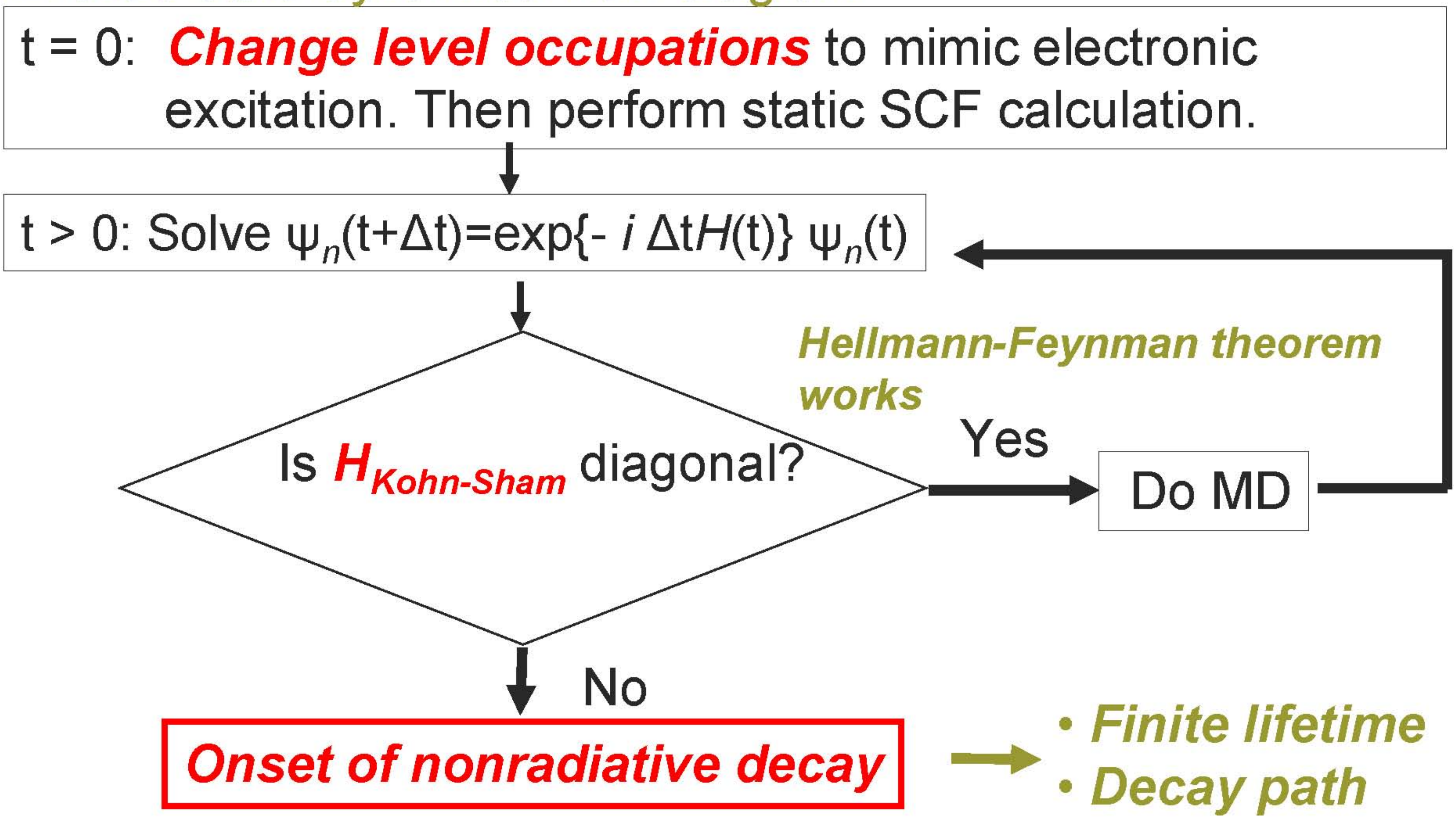

Challenges:

♦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 Simulation tool for Electron-Ion Dynamics
*Sugino & Miyamoto PRB* ***59****, 2579 (1999)*; *PRB* ***66****, 89901 (2002).*

# Excited state dynamics: flow diagram




1. No need of level assignment for a hole and an excited electron except at the beginning.
2. Automatic monitoring of the nonradiative decay (lifetime, decay path) without prejudice

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  - **Fusion of nanotubes**
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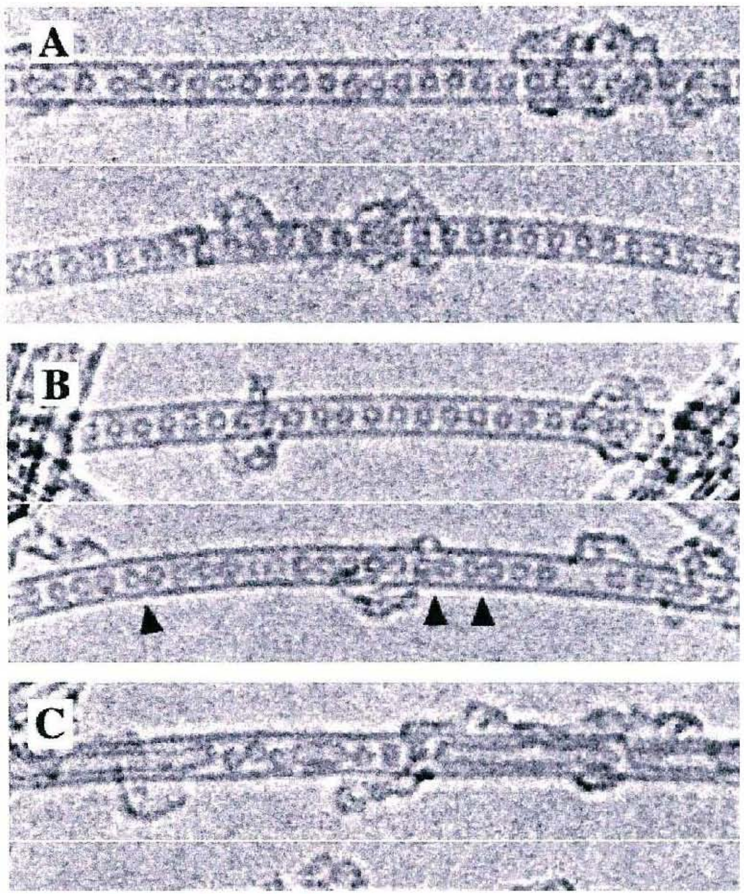
# Searching for Transition States in High-Dimensional Phase Spaces

## Fusion of fullerenes in peapods




T=1,100ºC

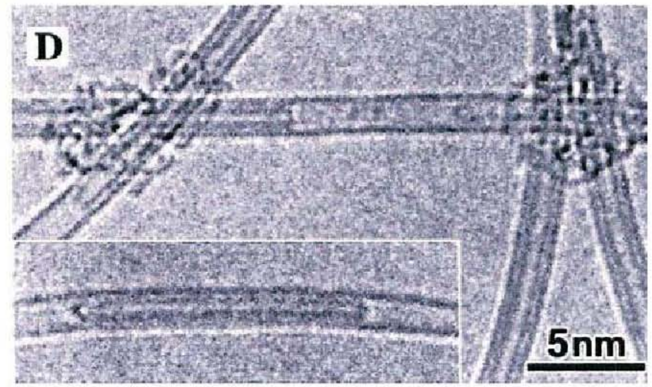
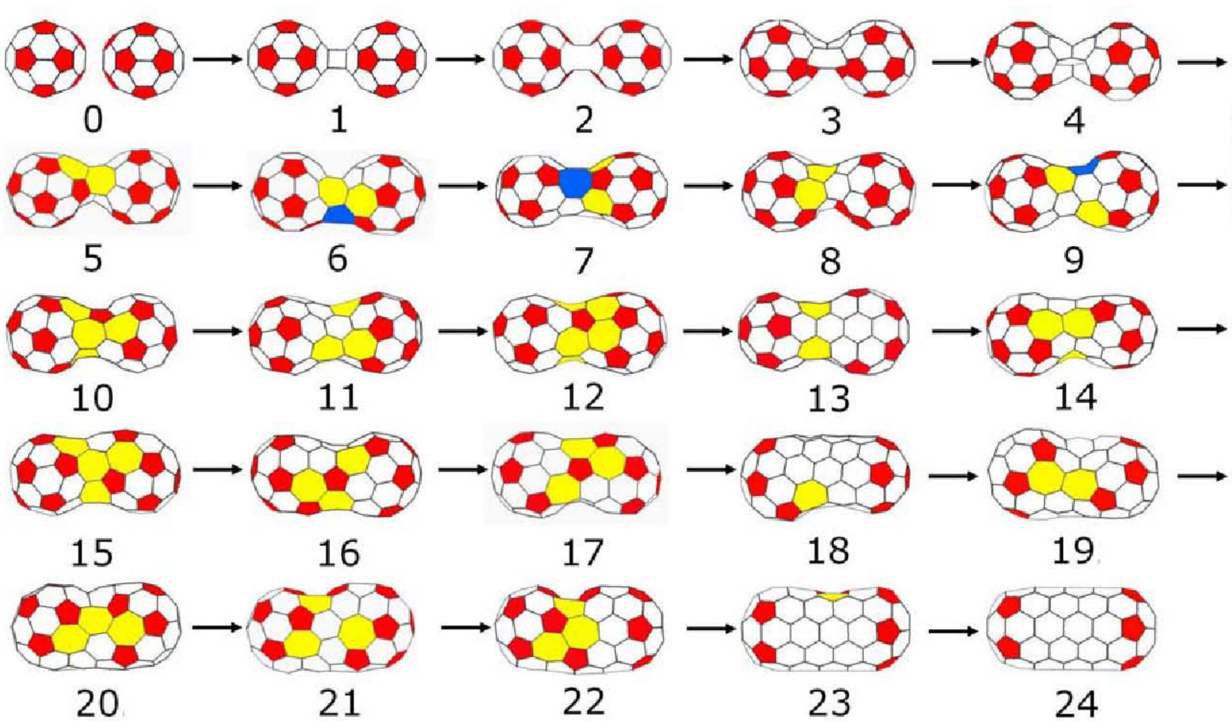


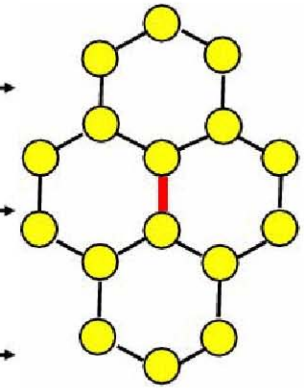

Fig. 1. Transmission electron microscopy images. (A) is for $(C_{60})_n$ @SWNTs, (B) for $(C_{60})_n$@SWNTs heated in ' (<$10^{-6}$ Torr) at 800°C for 14 h (HT800), (C) for HT100 (D) for HT1200. A and B indicate similar electron micro images, but in B we can occasionally find that some ( adjacent $C_{60}$ 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 ai 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) ]*



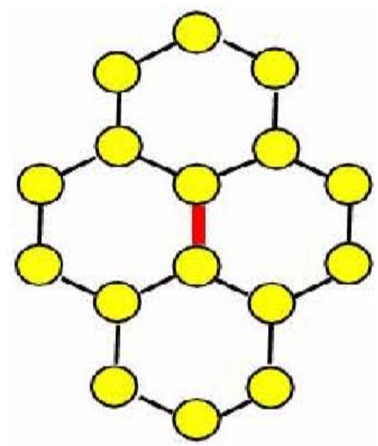



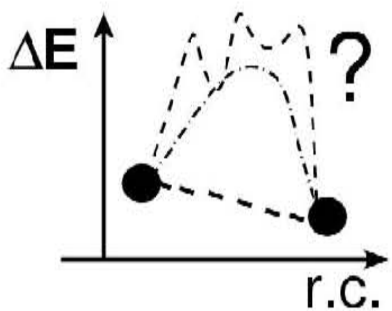
Stone-Wales transformation

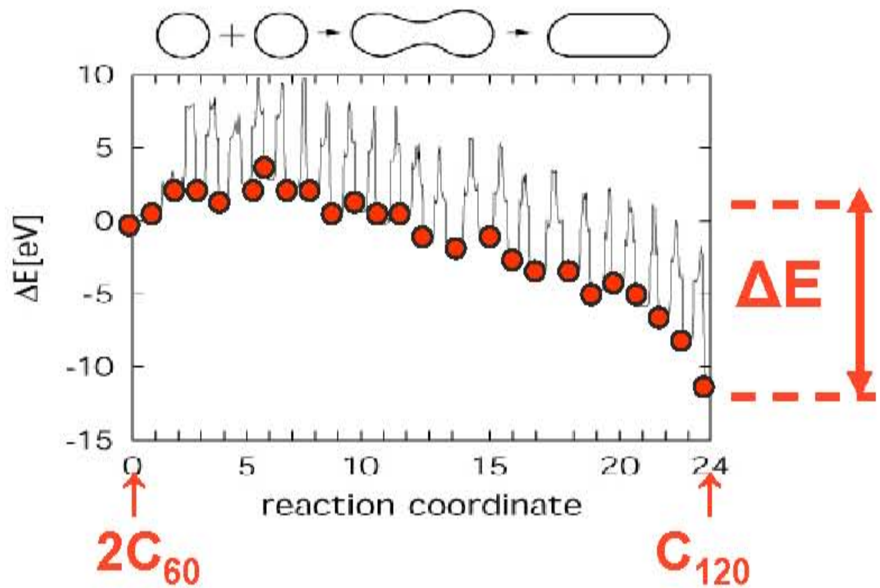
**Sequence of bond rotations: Solve 15x15x15 Rubik's Cube puzzle**

- Do we understand the energetics?

# Do we understand the Stone-Wales process?



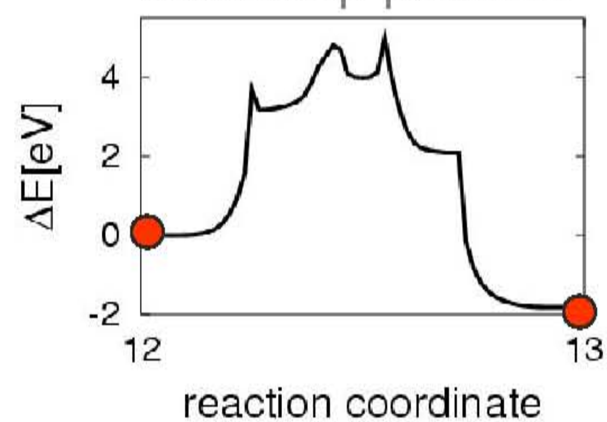


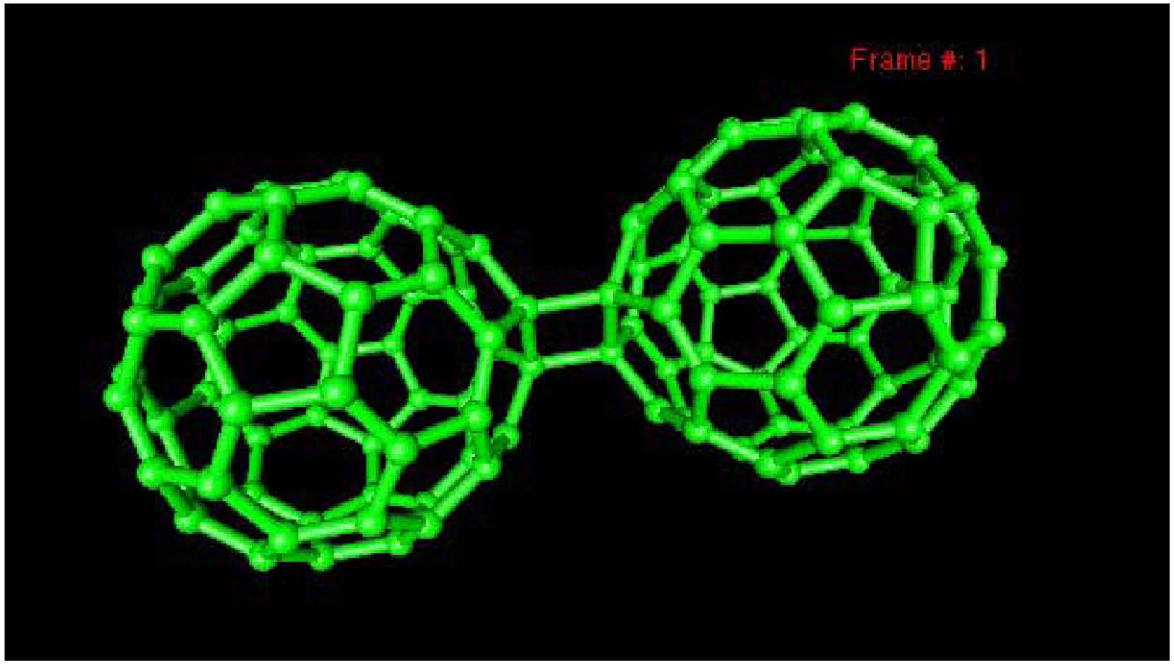

Search in 360-dimensional configuration space using string method:

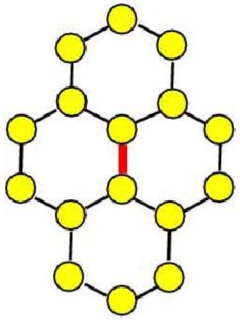
- Stone-Wales is a multi-step process
- Activation barriers do not exceed ≈ 5eV

Multi-step process

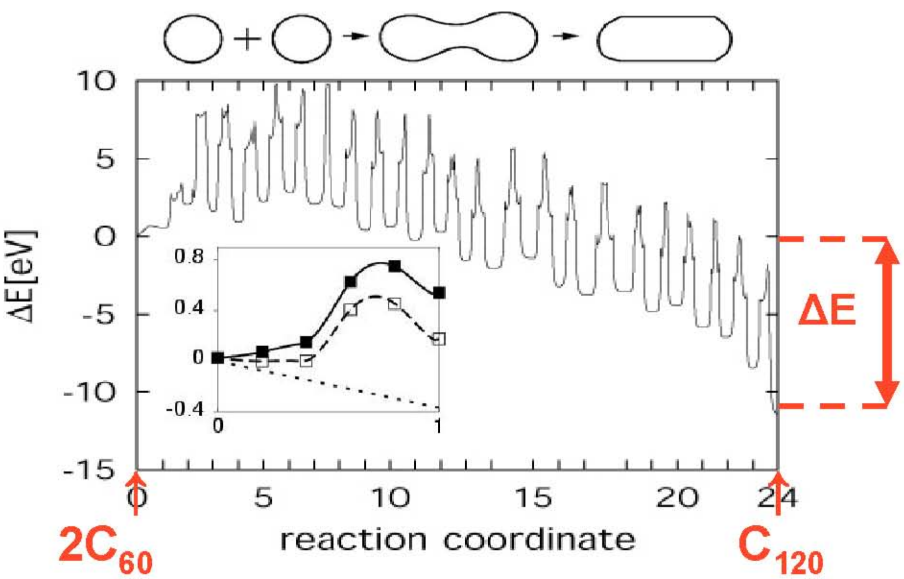


# Minimum energy path for the $2C_{60} \rightarrow C_{120}$ fusion



Sequence of Stone-Wales transformations



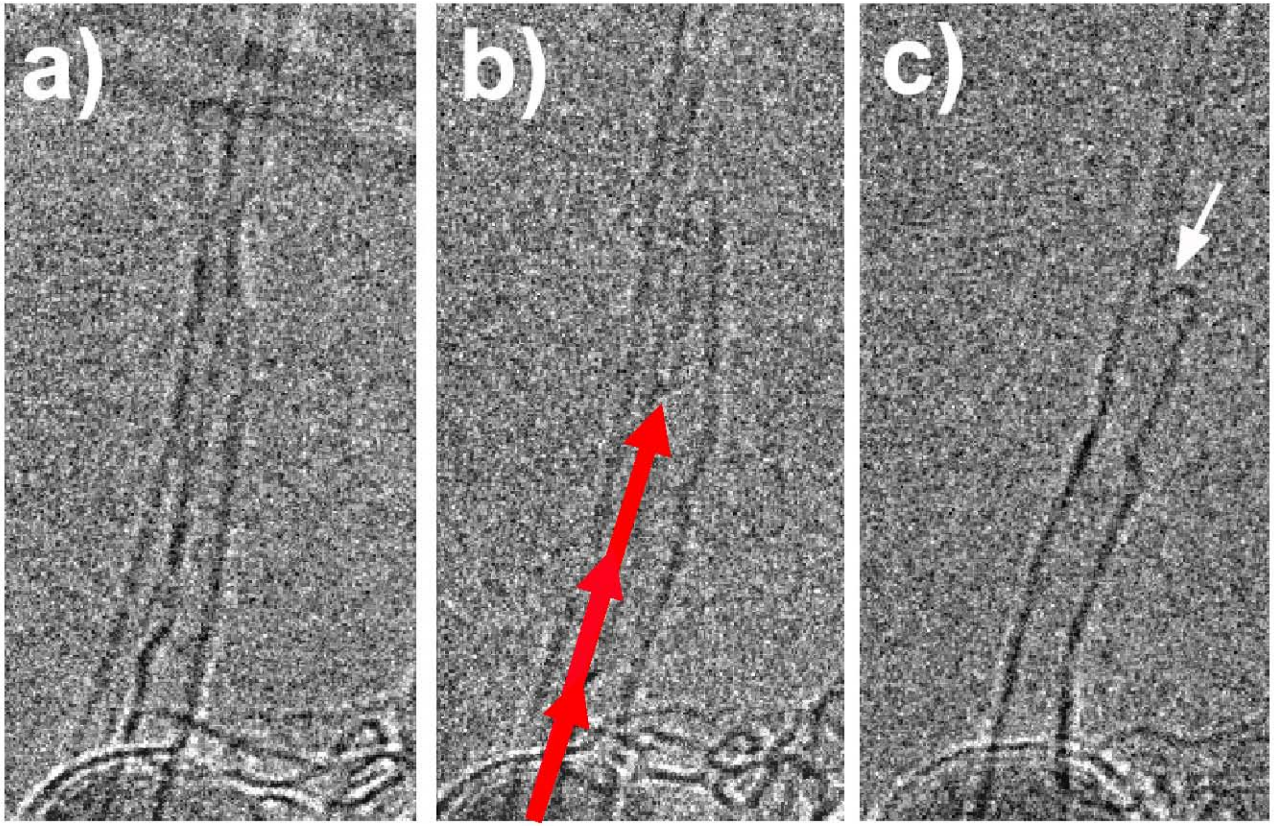

- Conclusions:
  - -Fusion is exothermic. Energy gain $\Delta E \approx 1$Ry.
  - -Essential initial step: (2+2) cycloaddition

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

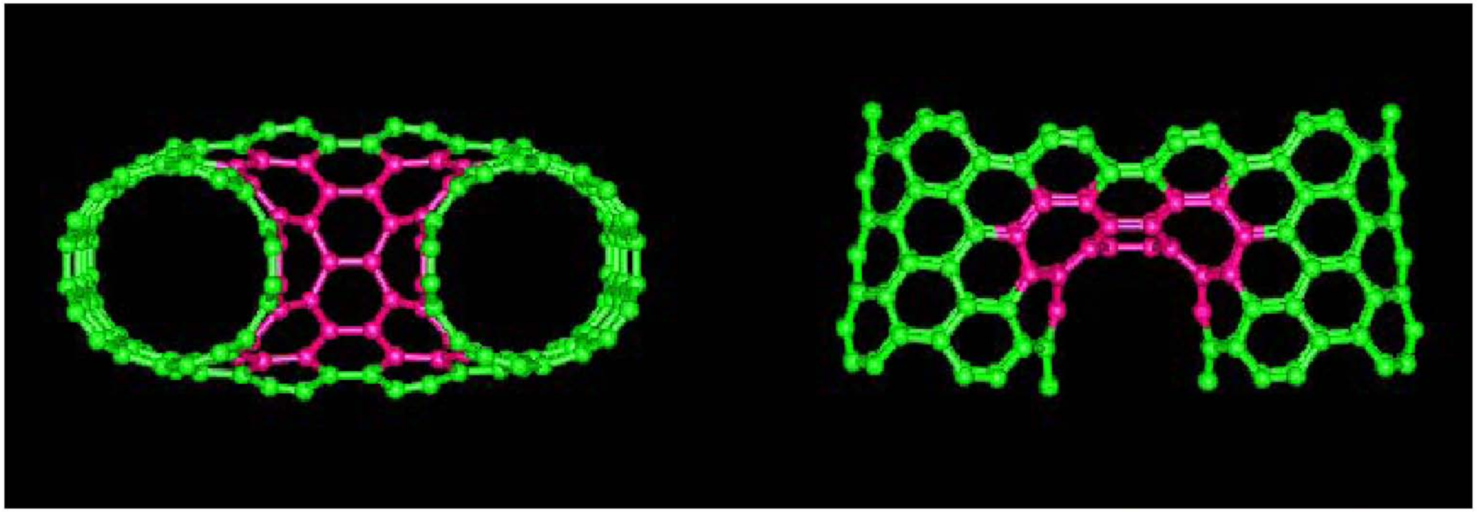
## The zipper mechanism

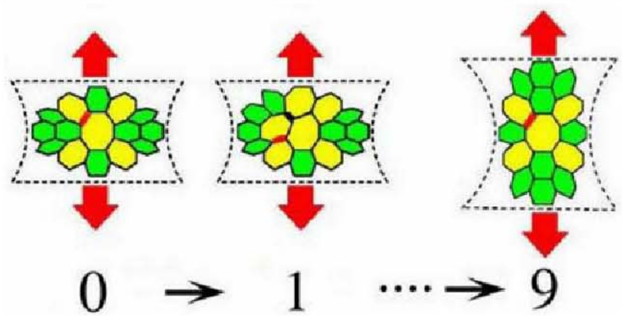
M. Yoon, S. Han, G. Kim, S. Lee, S. Berber, E. Osawa, J. Ihm, M. Terrones, F. Banhart, J.-C. Charlier, N. Grobert, H. Terrones, P. M. Ajayan, D. Tománek, Phys. Rev. Lett. **92**, 075504 (2004).

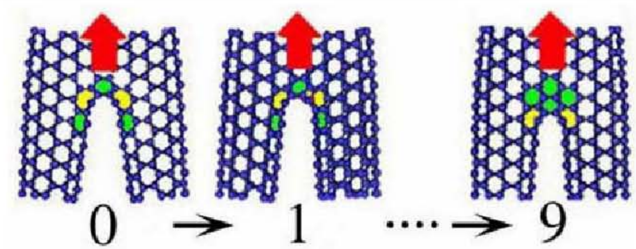


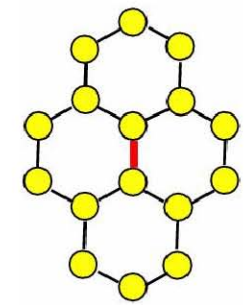

*Zipper*

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

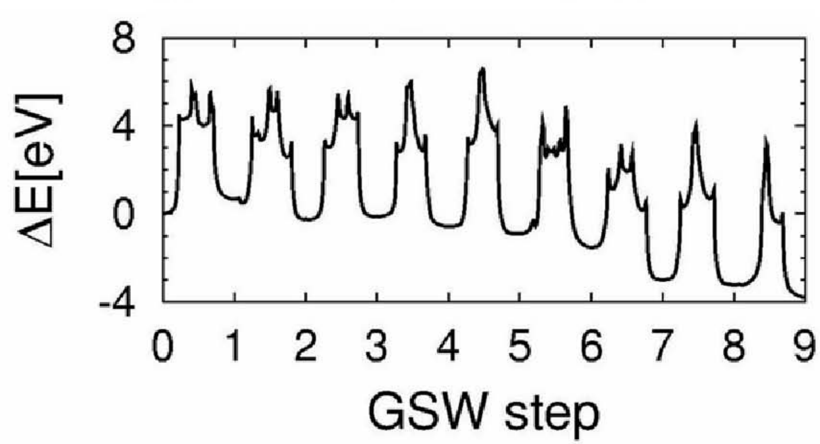




Sequence of Stone-Wales transformations

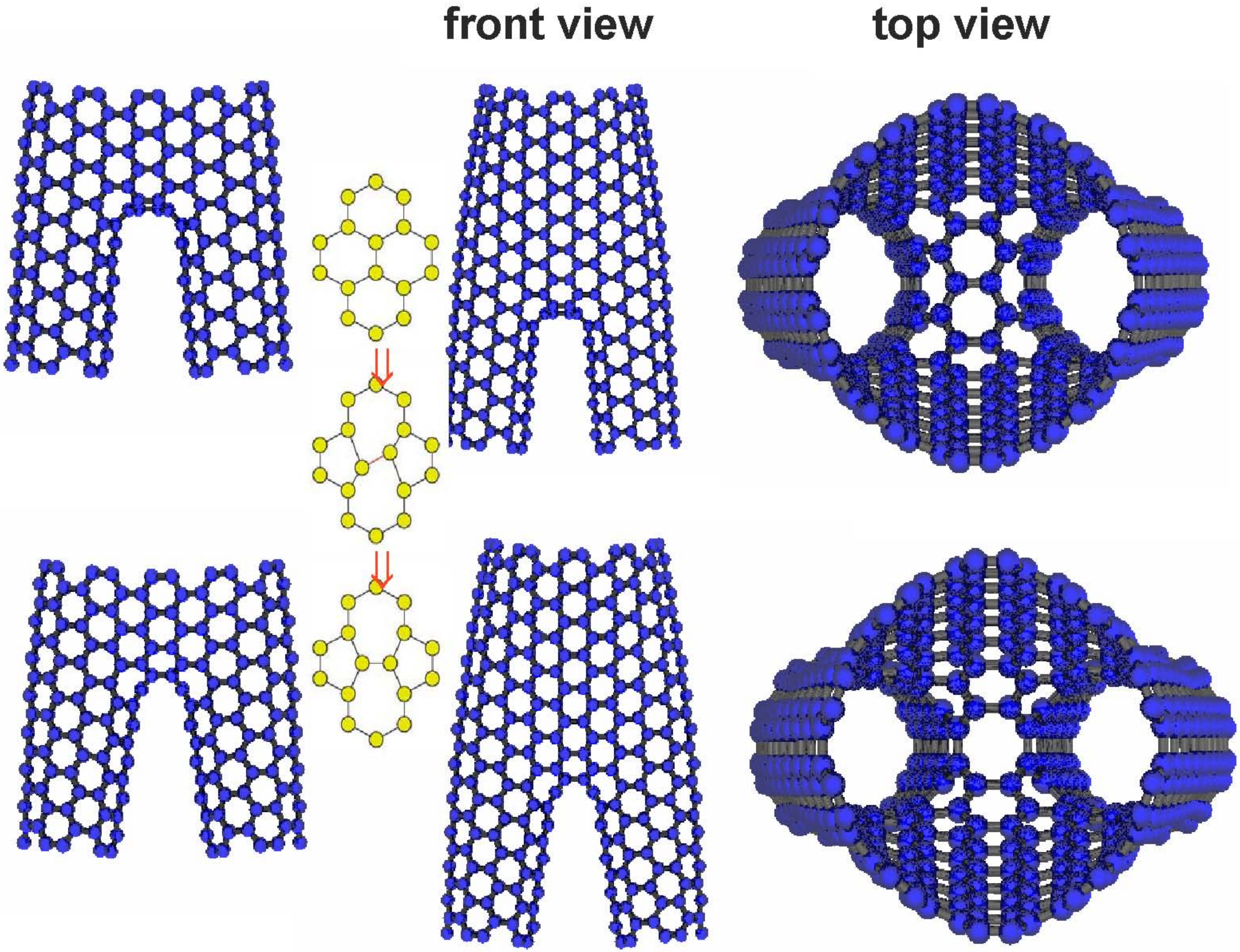



❖ **Conclusion: Fusion is exothermic**

# Geometry of fusing Nanopants

**Type A:**
*6 heptagons in junction area*

**Type B:**
*1 octagon, 4 heptagons in junction area*



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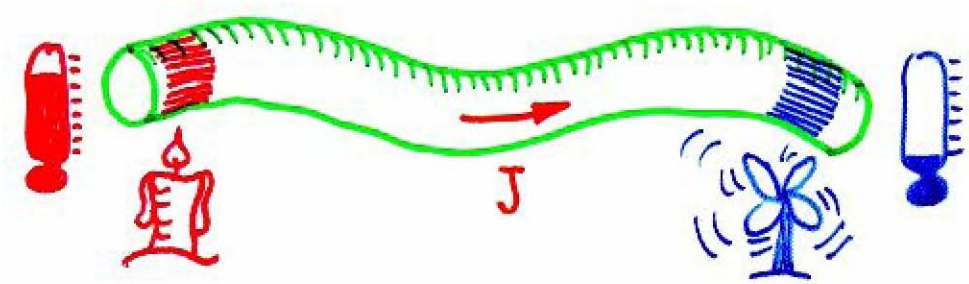
# Ground State Molecular Dynamics Simulations

## Thermal Conductivity of Carbon Nanotubes




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

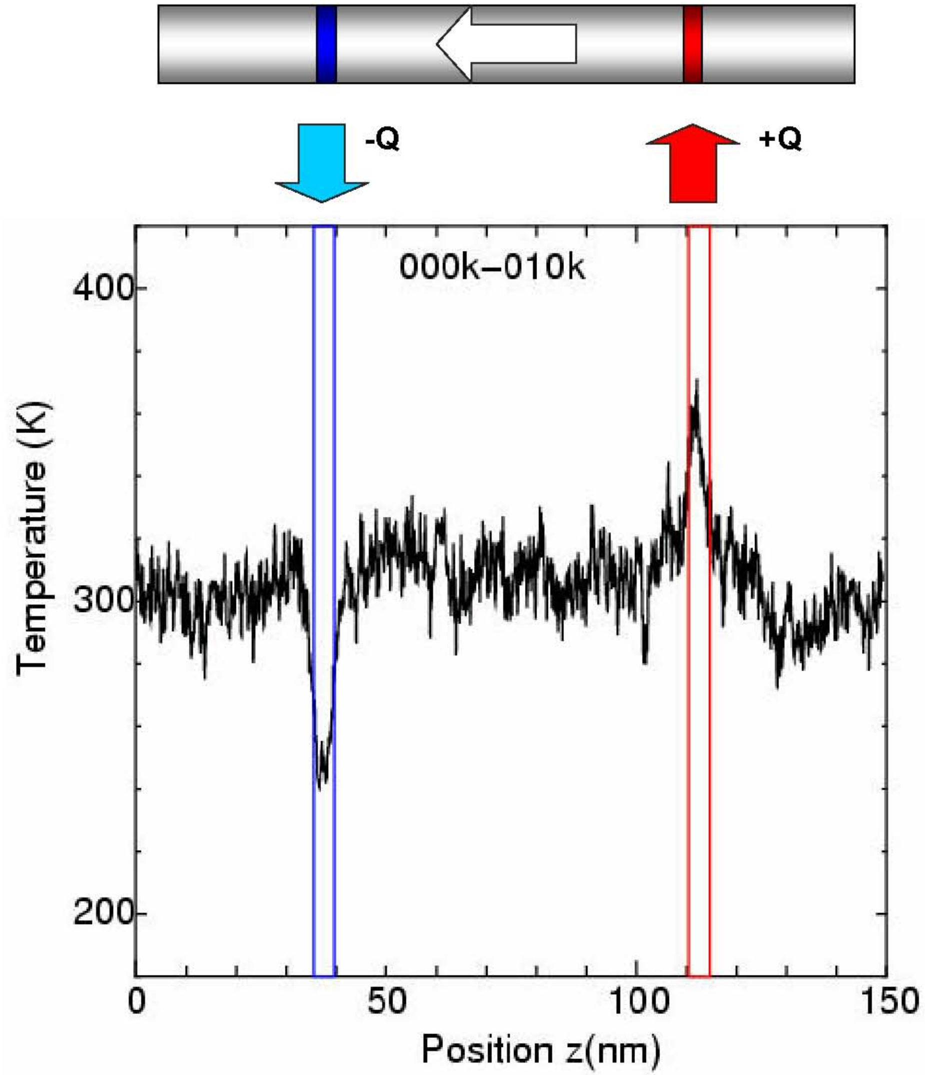
- Nanotubes may help solve the heat problem:
  Efficient conductors of electrons and heat
- Record Heat Conductivity:
  * Diamond
    (isotopically pure): 3320 W/m/K
  * Nanotubes: 6,600 W/m/K (theory, SWNT)
    >3,000 W/m/K (experiment, MWNT)

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

# Direct molecular dynamics simulation

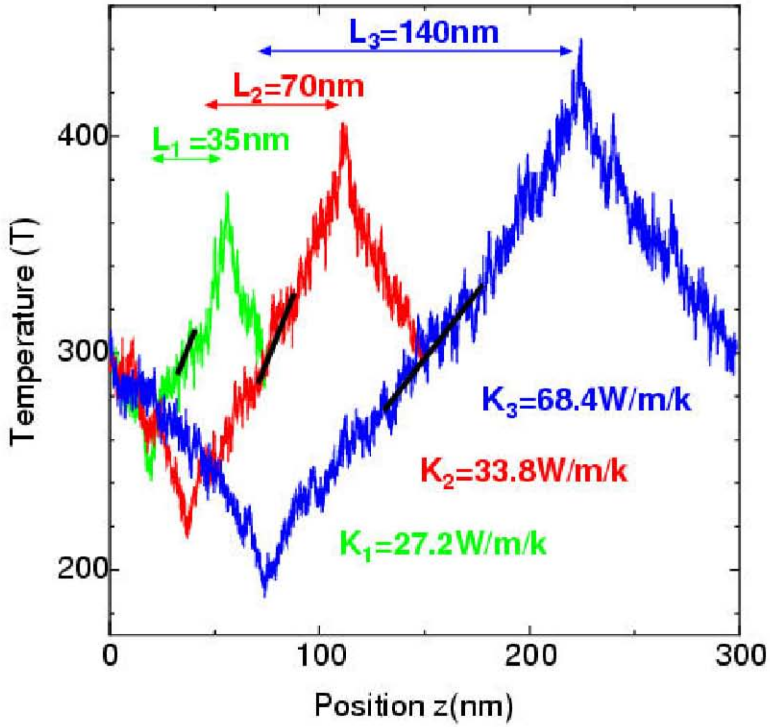
$$J = -\kappa S \frac{\partial T}{\partial x}$$ Fourier's law

J: Heat flux
S: Cross section area
κ: Thermal conductivity
  κ ∝ phonon mean free path λ
    (distance that phonons travel without scattering)




- Problem: Hot-cold spot separation > λ to avoid artifacts
- **How large is λ?**

# CPU resources for a large-scale simulation




**One time step in MD**
**∝ N (number of atoms)**

**Thermal flux propagation time along unit cell ∝ (unit cell length) ∝ N**

**Total CPU time ∝ $N^2$**

| | | | |
|---|---|---|---|
| CPU Time for $L_1$: | 2.5days | Simulation time: 60ps | N≈25,000 |
| $L_2$: | 10 days | 120ps | N≈50,000 |
| $L_3$: | 40 days | 240ps | N≈100,000 |

(Parametrized LCAO MD calculations)

1024 Processors / 2.5 Teraflops

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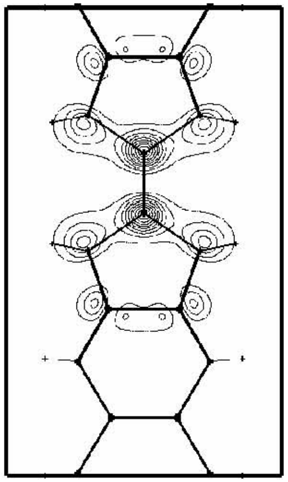
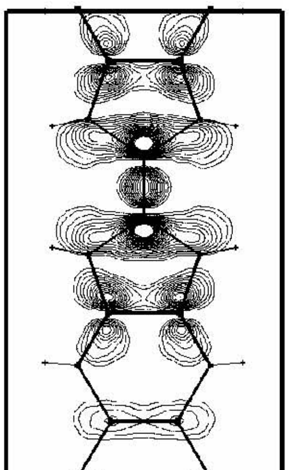
# Excited State Molecular Dynamics Simulations

## Detection of Stone-Wales defects

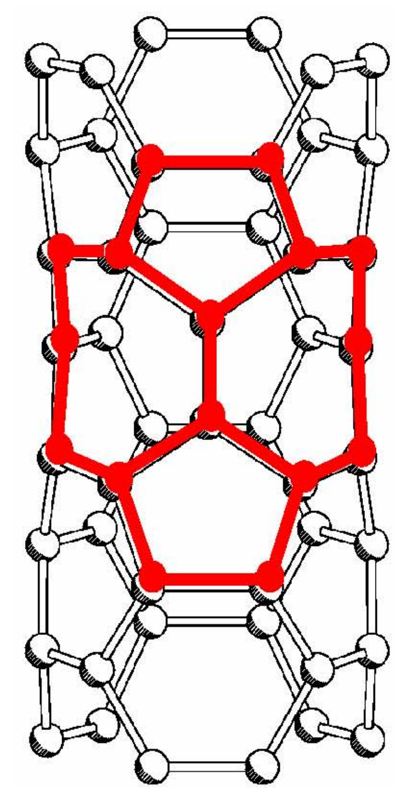


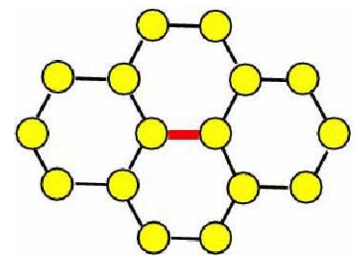


π* state (electron)

6 eV

σ-π hybridize d state (hole)

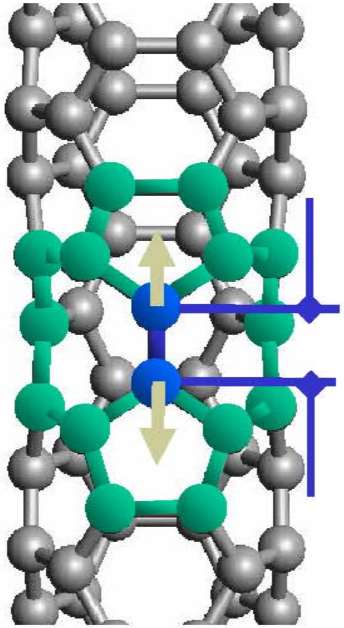


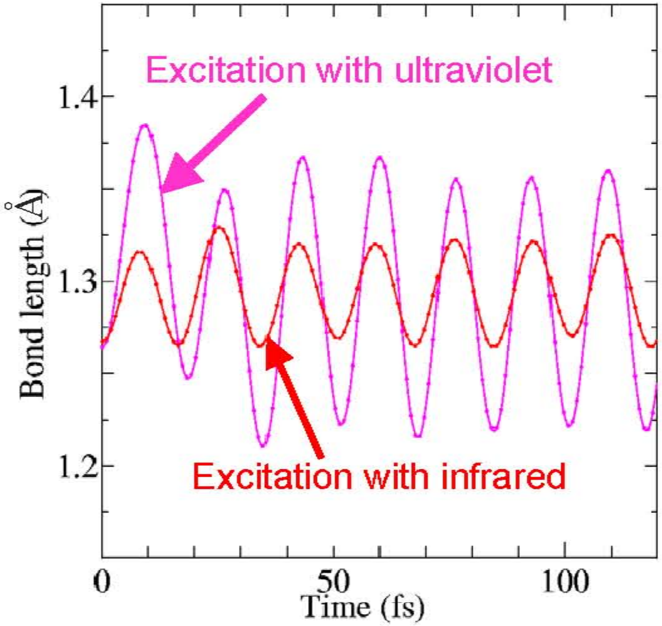


Origin of Stone-Wales defect

► How does a Stone-Wales defect react under photo-excitations?

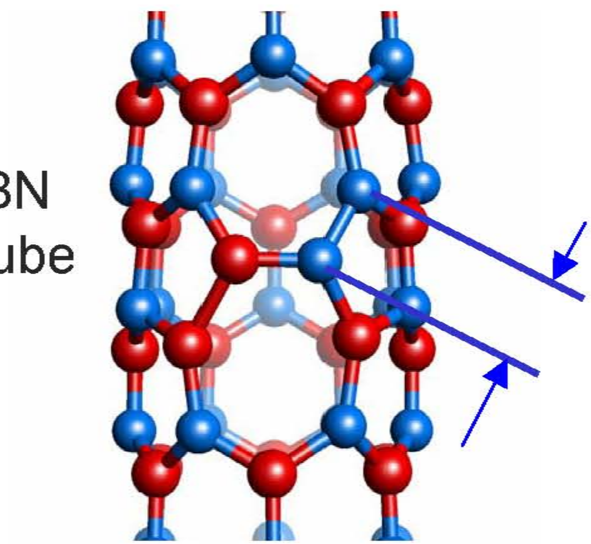
(3,3) carbon nanotube

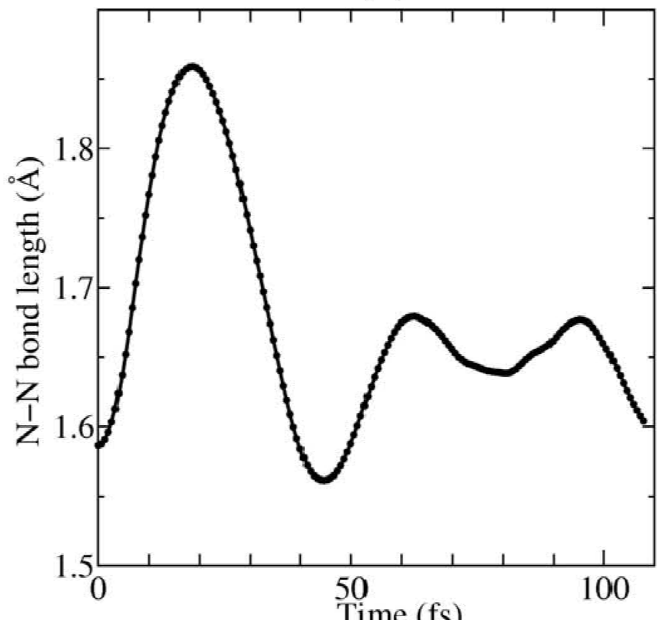





T=17 fs ($1962\ cm^{-1}$)

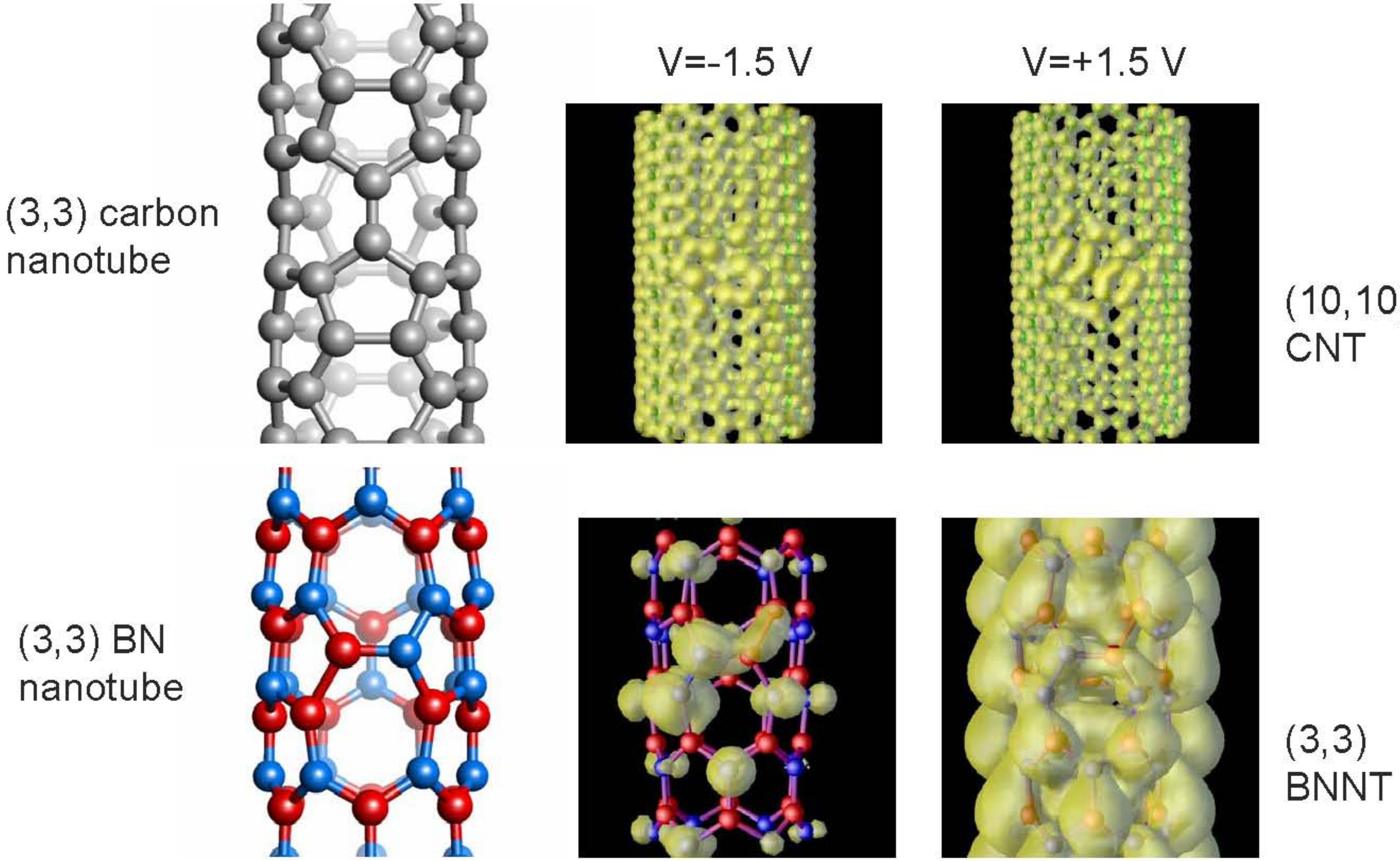
(3,3) BN nanotube






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

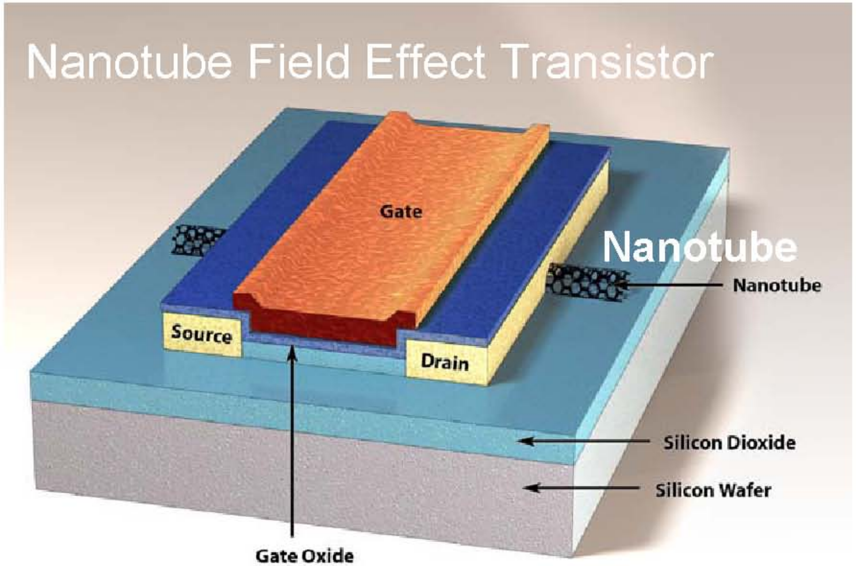
# STM characterization of Stone-Wales defects

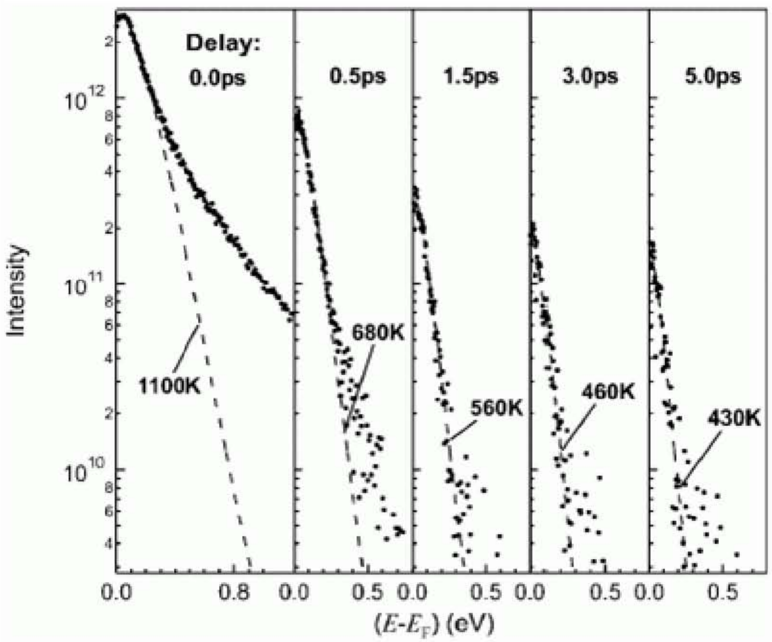



**Y. Miyamoto, A. Rubio, S. Berber, M. Yoon, and D. Tománek, Phys. Rev. BR 69, 121413 (2004).**

# Hot carrier dynamics in nanotubes

- How useful are carbon nanotube devices (field-effect transistors, non-linear optical devices)?
- Maximum switching frequency:
  ➡ lifetime of excited carriers
- How long do electronic excitations last?
- What dampens electronic excitations:
  - Electron gas?
  - Phonons?




Evolution of photoelectron spectra as a function of pump-probe delay. At pump-probe delays of over 200 fs, the spectra can be well described by a Fermi-Dirac distribution (dashed lines).

T. Hertel and G. Moos, PRL **84**, 5002 (2000)

Interpretation:
e-e comes before e-ph

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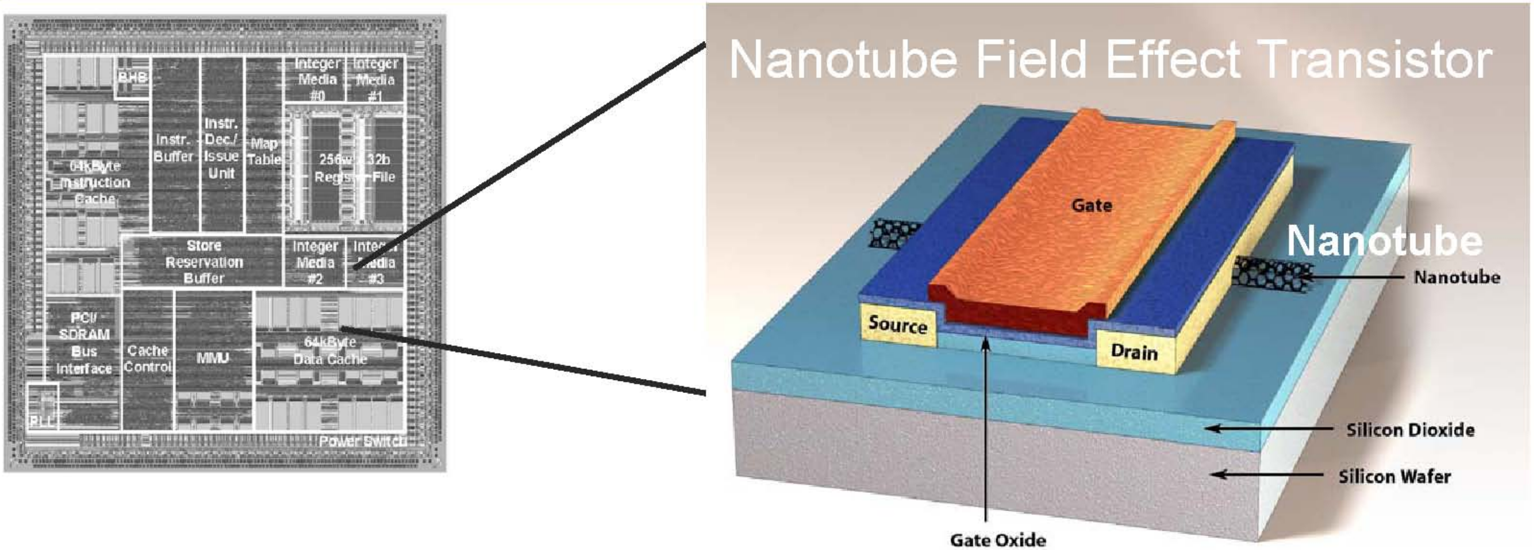
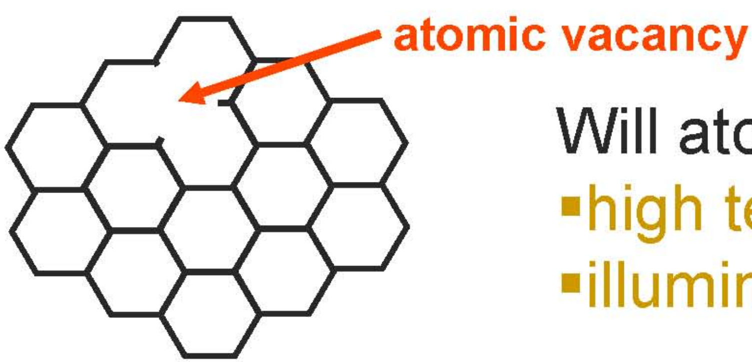
# What are Excitations Good for?

## Defect tolerance of nanotubes



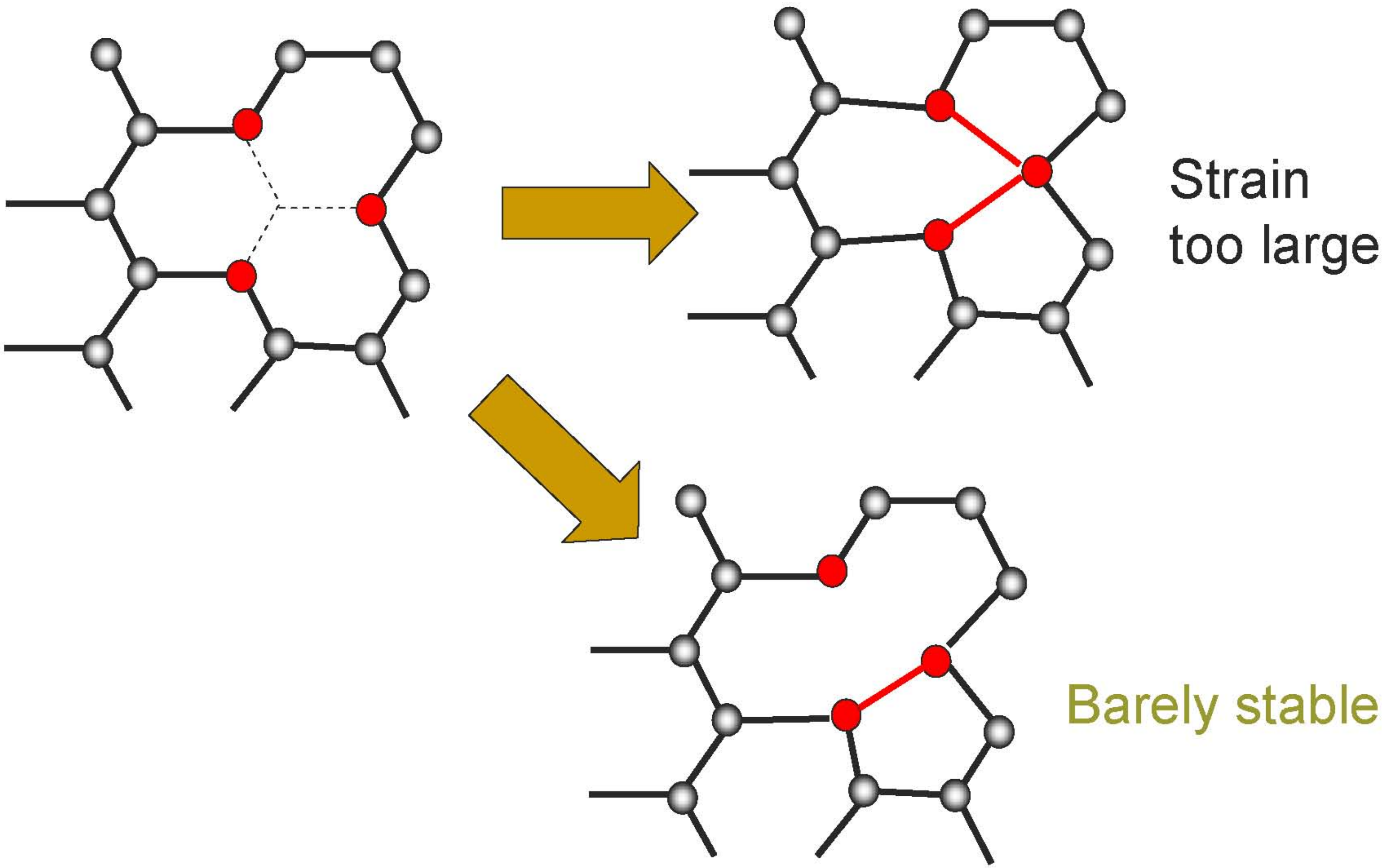

- Defects limit performance, lifetime of devices
- Are CNT devices as sensitive to defects as Si-LSI circuits?




Will atomic vacancies trigger failure under

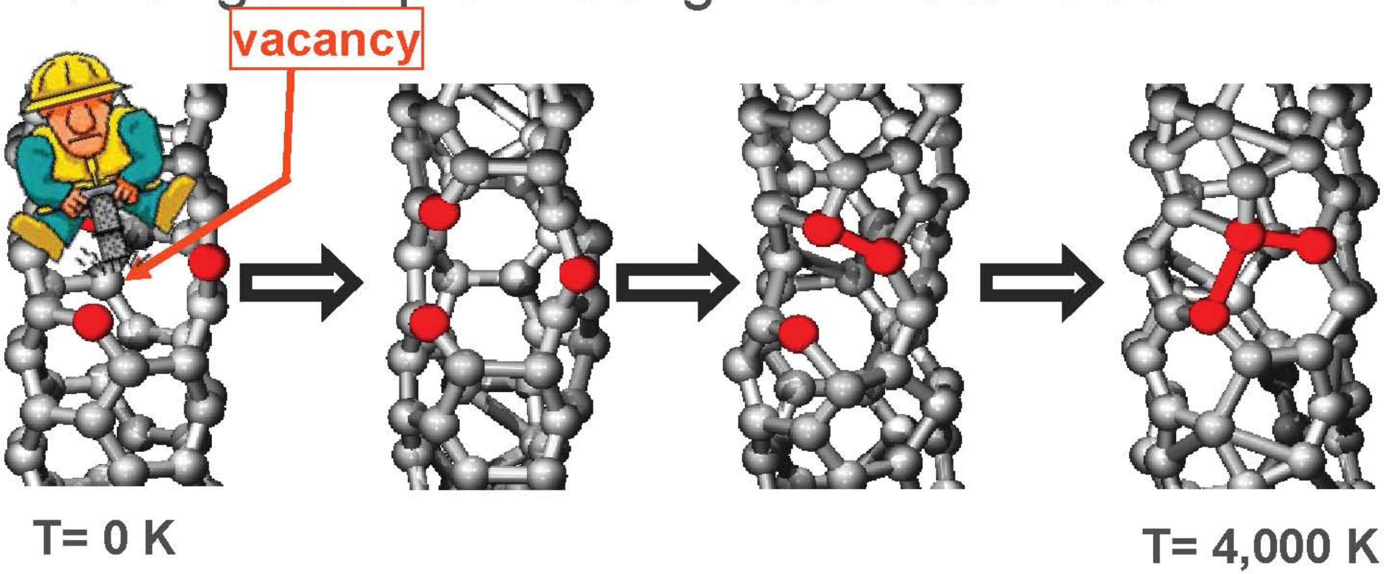
- high temperatures?
- illumination?

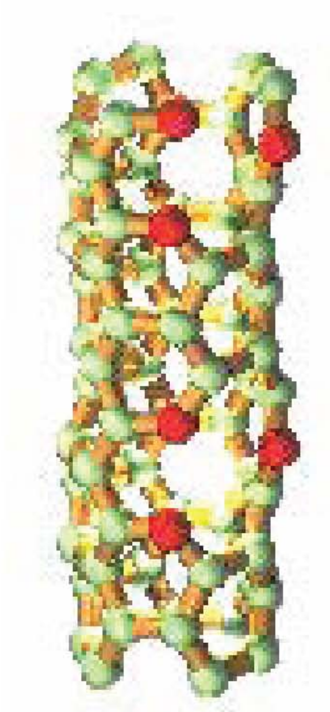
# Equilibrium structure near a monovacancy in *sp*$^2$ carbon



# Stability of defective tubes at high temperatures

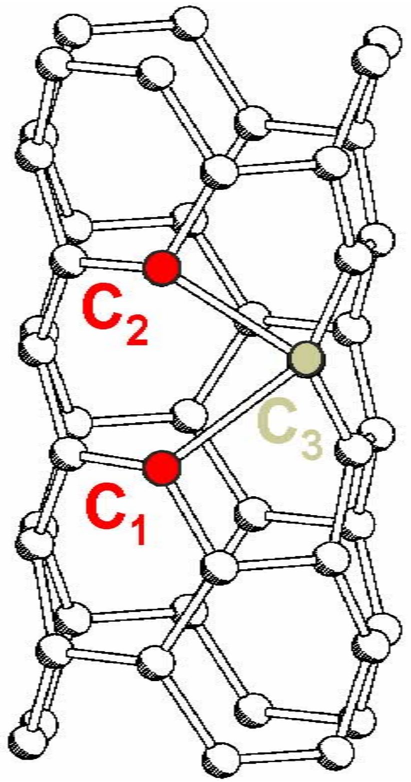
- Danger of pre-melting near vacancies?



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

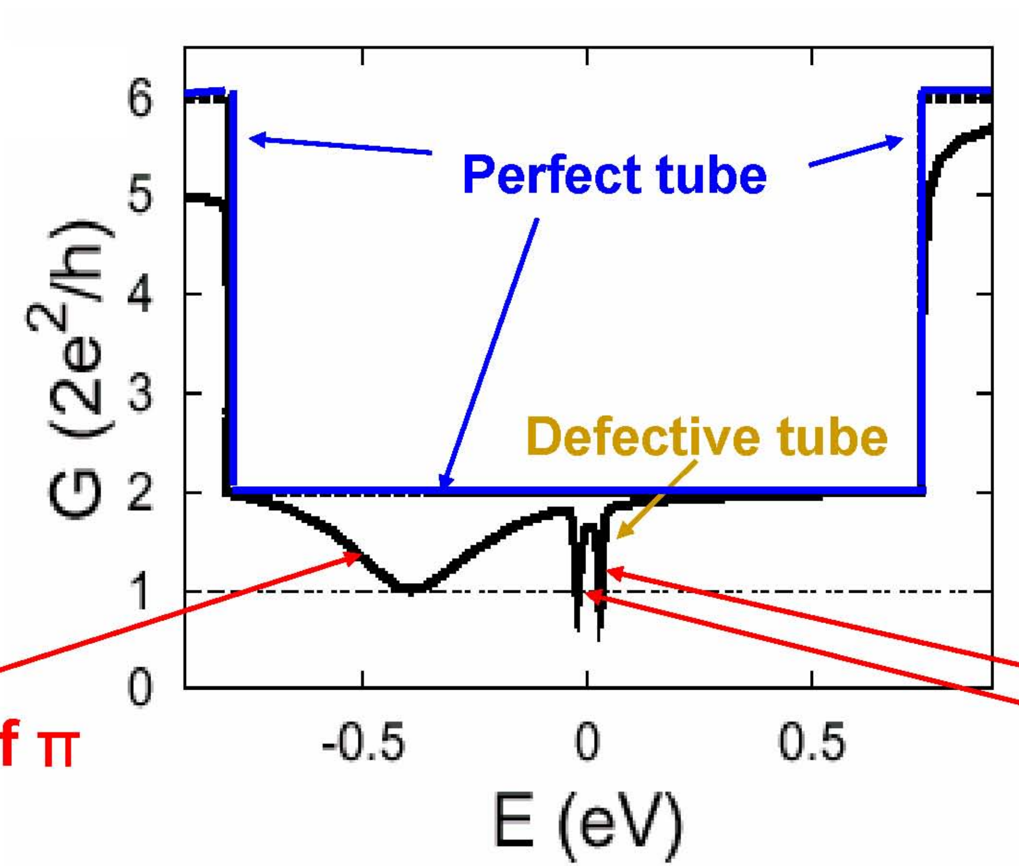
# Reconstructed geometry




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



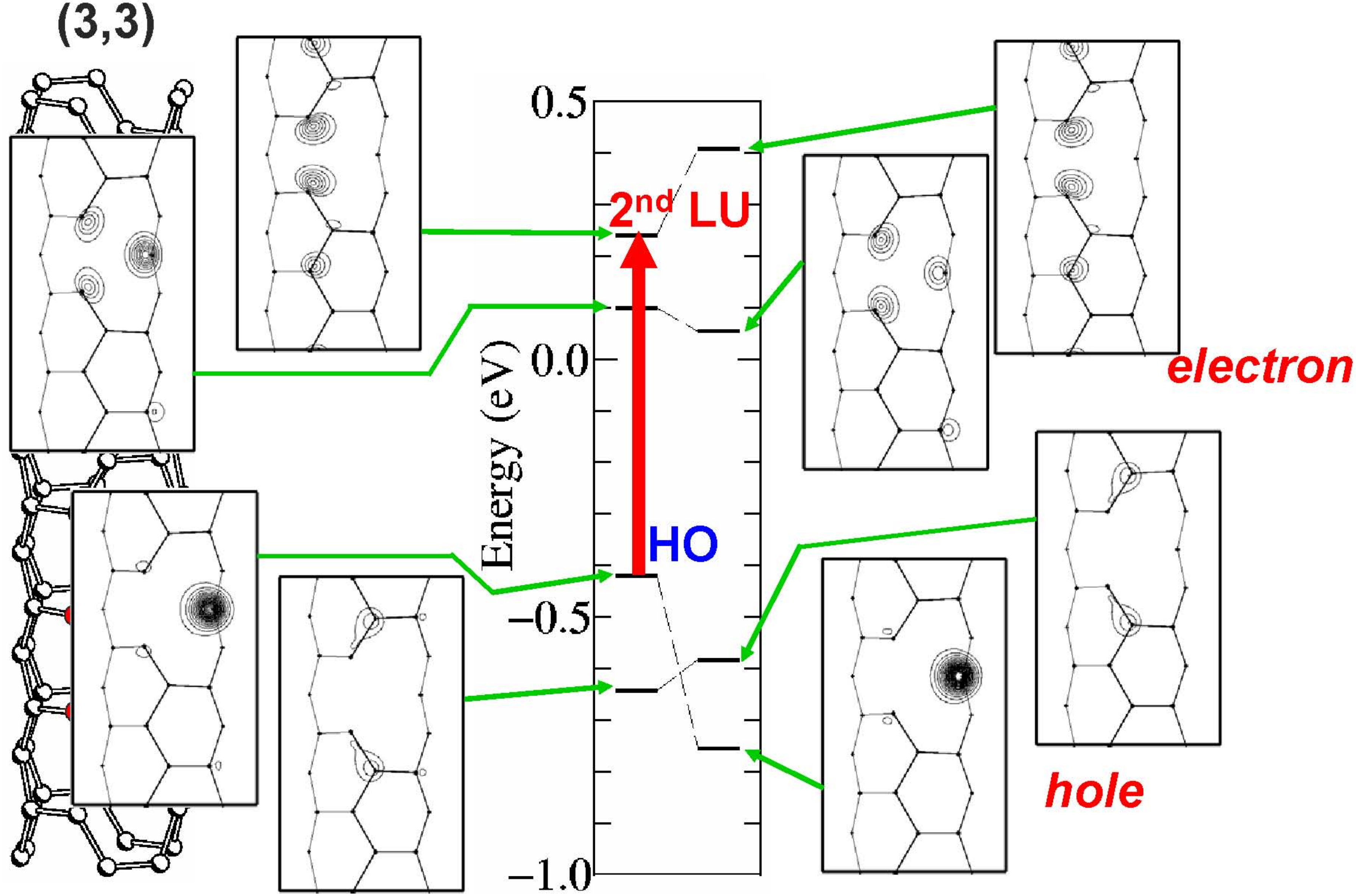

Choi, Ihm, Louie, Cohen, PRL (2000)

**Missing network of π electrons**

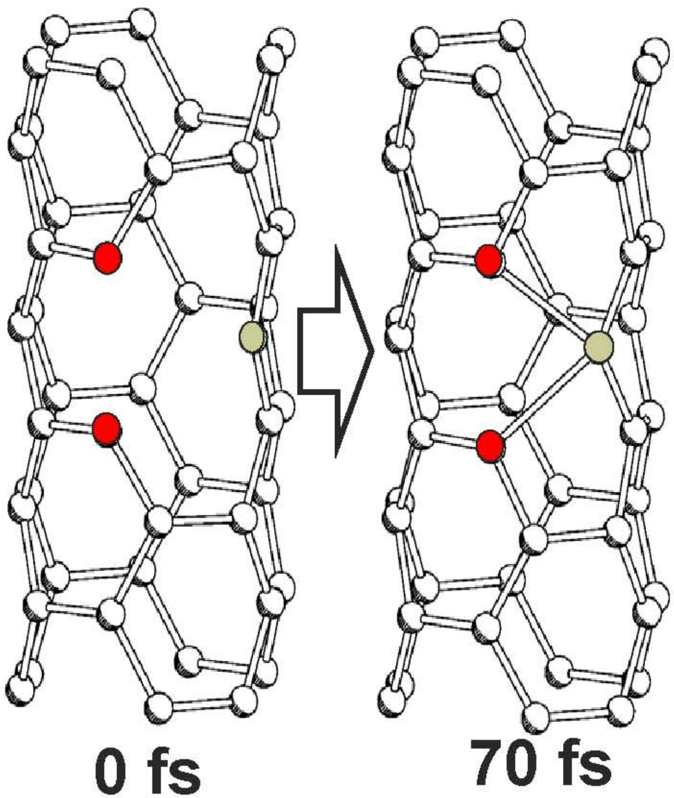
**Dangling bonds: σ electrons**

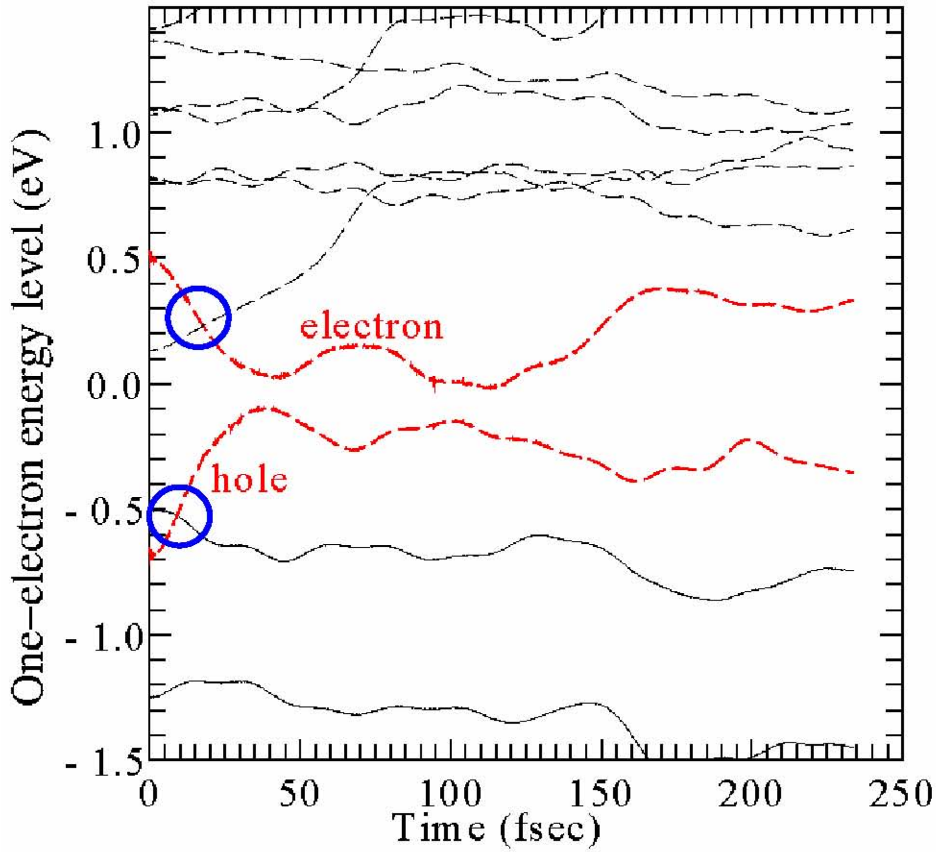
Good news for applications: Self-healing by reconstruction may remove one of the sharp dips

# Optical excitation (ΔE=0.9 eV)



# Time evolution of the electronic states

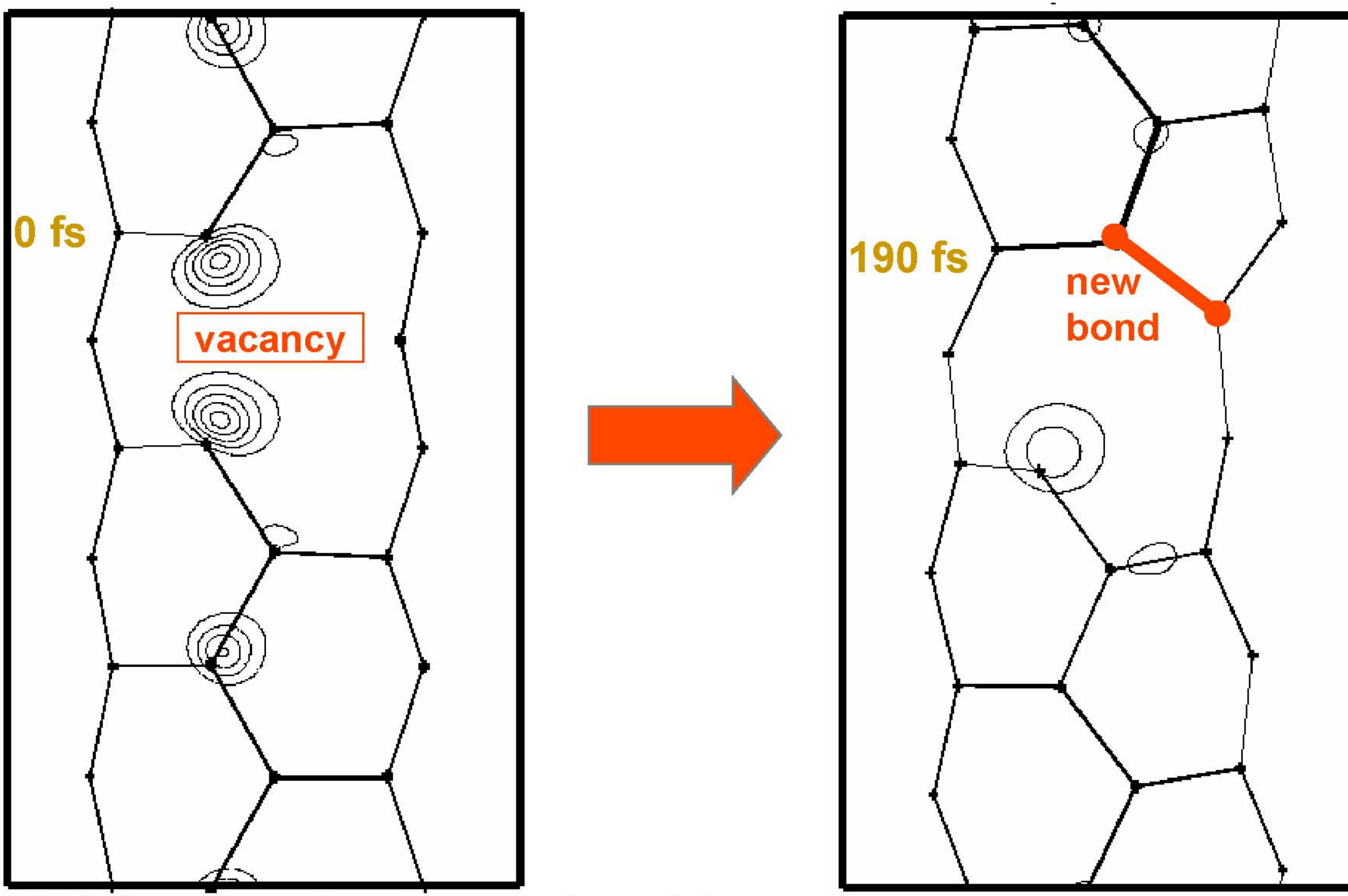



$\Psi_n(t+\Delta t)=\exp(-i/h\, H\Delta t)\, \Psi_n(t)$

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

# Structural changes under illumination

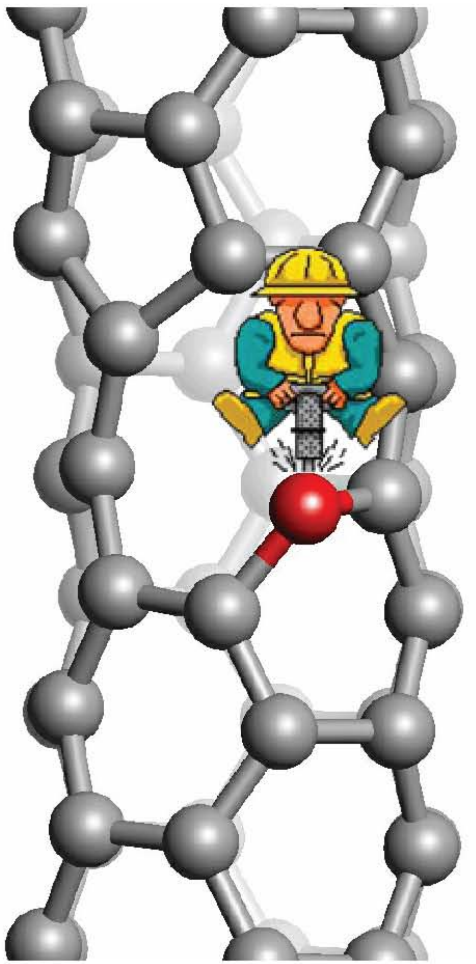



- Self-healing due to new bond formation

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)

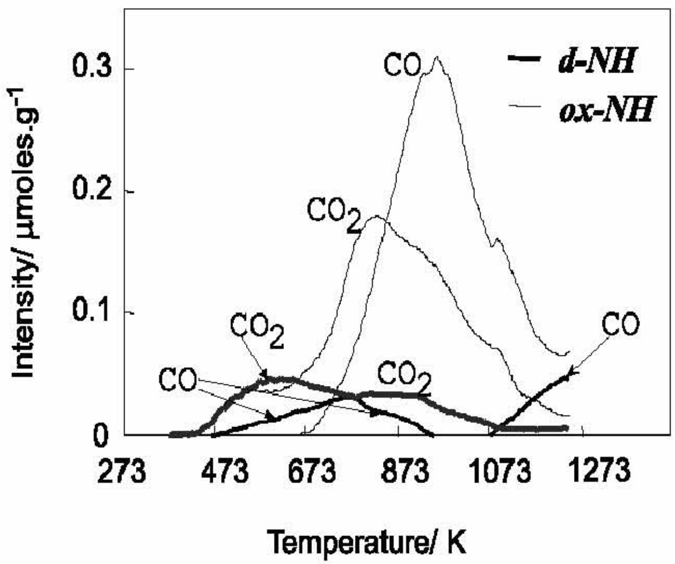
# Deoxidation of defective nanotubes

**How to deoxidize?**

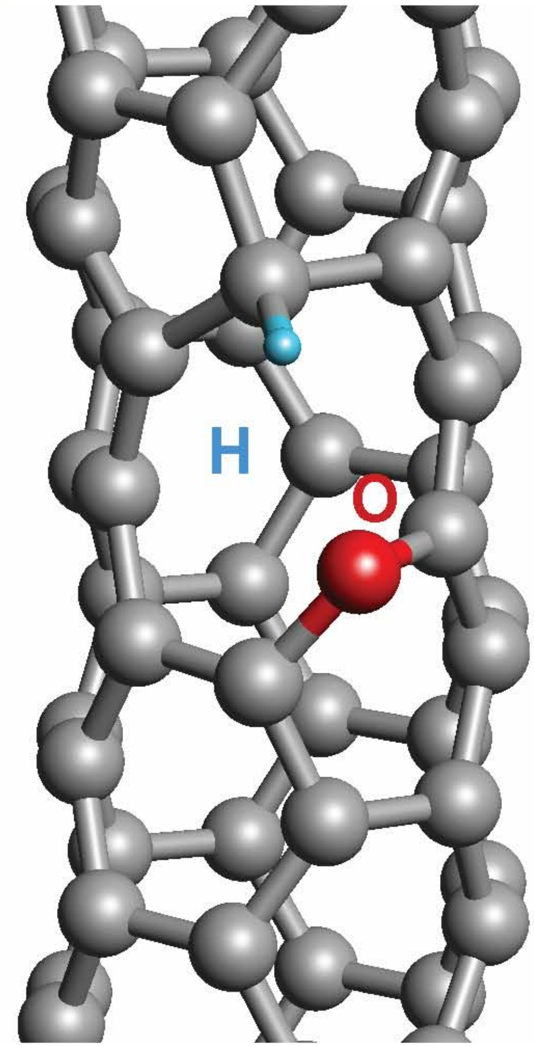


▪**By heat treatment?**

⇒No: Larger damage to nanotube




▪**By chemical treatment with H?**

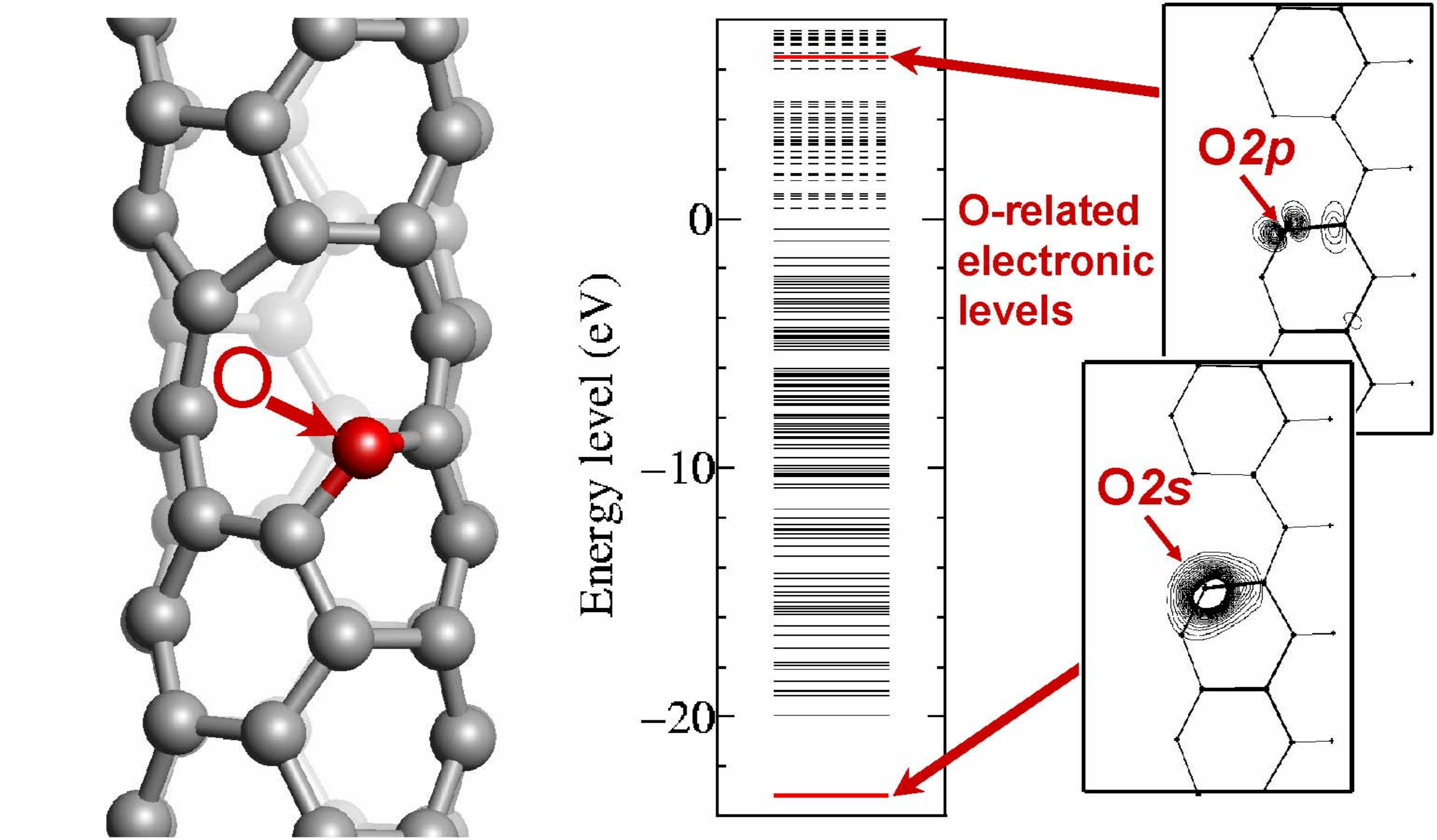




Yoshiyuki Miyamoto, Noboru Jinbo,
Hisashi Nakamura, Angel Rubio, and David Tománek,
Photosurgical Deoxidation of Nanotubes, Phys. Rev. B 70 (2004).

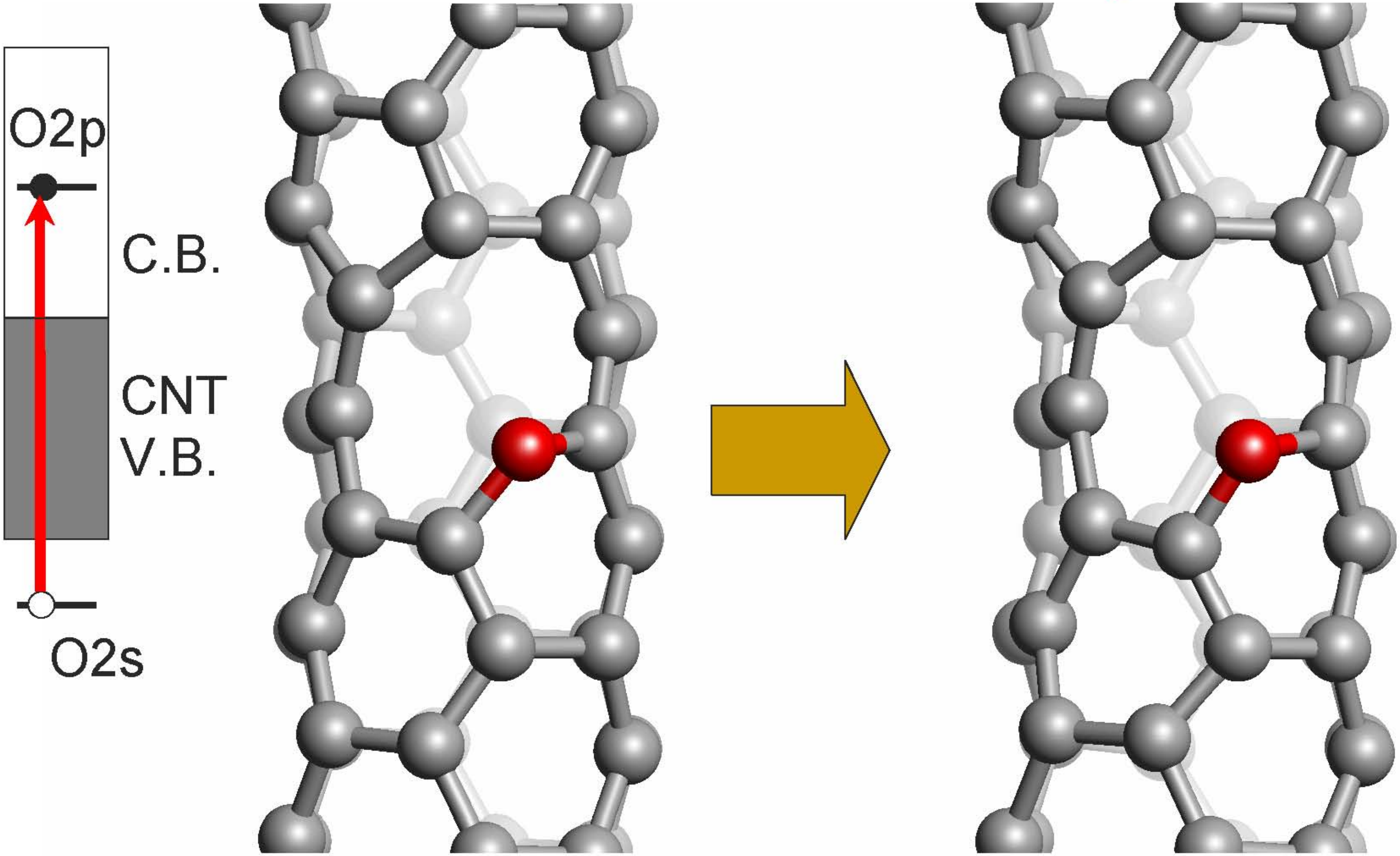
Alternative to thermal and chemical treatment

*Electronic excitations!*

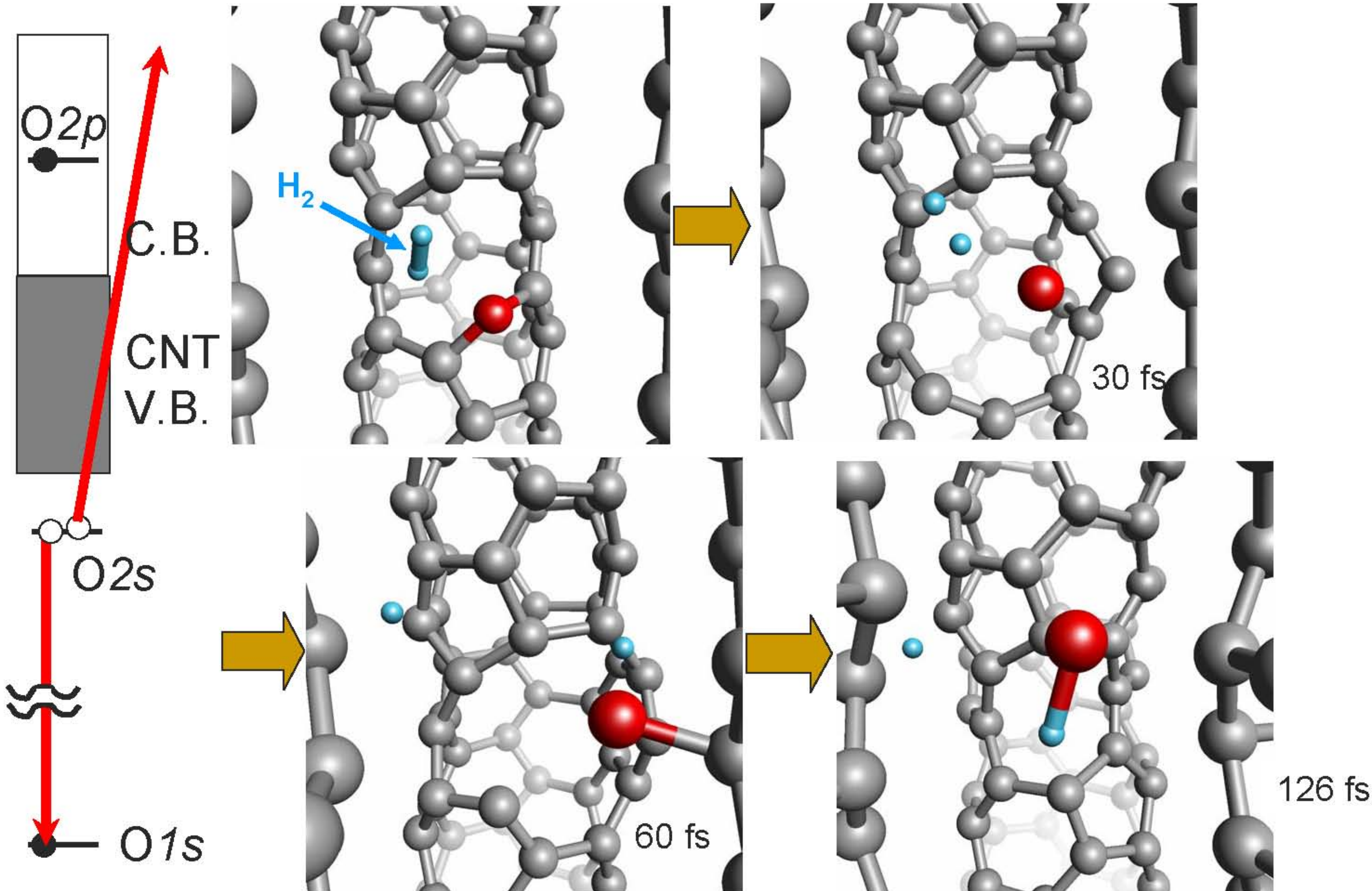


O2s → O2p excitation (33 eV)

hopeless



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




- Deoxidation by photo-surgery

# Summary and Conclusions

- 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.
- Carbon nanotubes are Nature's best thermal conductors.
- Photo-excitations may be used to detect specific defects by their vibrational signature.
- Hot carriers decay by electron-electron, subsequently by electron-phonon scattering.
- Heat and photo-excitations may induce self-healing behavior in defective nanotubes.
- Photo-excitations can be used to selectively remove oxygen impurities.

The End