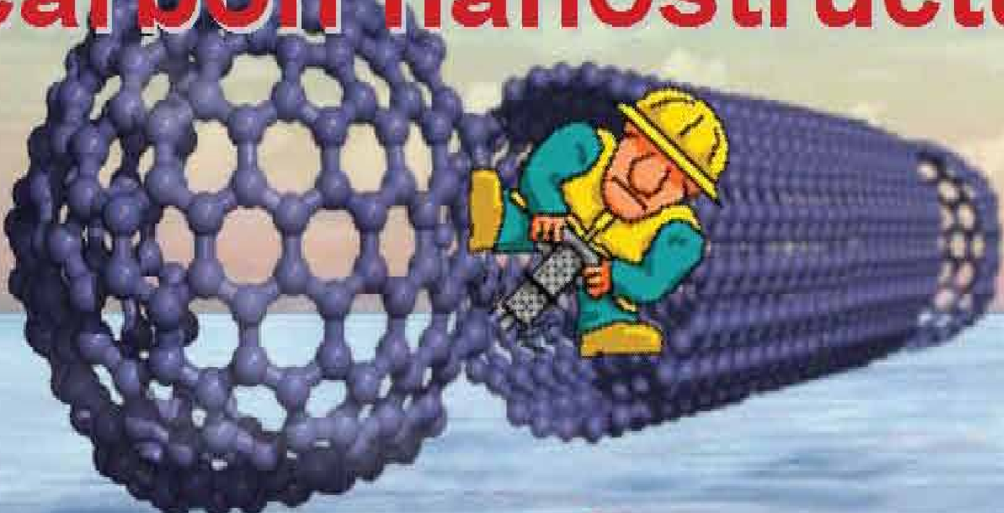
Real-time *ab initio* calculations of excited-state dynamics in carbon nanostructures



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Mina Yoon,	*Oak Ridge National Laboratory*

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NSF-NIRT

JAMSTEC-ESC (Japan)
RIST (Japan)

Outline

- Introduction
  - **Nanotechnology means more than small size**
  - **Nanocarbon pioneers**
  - **Carbon nanotubes: Ideal building blocks for nanotechnology?**
  - **What happens during electronic excitations?**
  - **Computational tools**
  - **State of the art of computer simulations**
  - **Limitations of quantum devices**
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  - **Defect tolerance of nanotubes**
  - **Detection of Stone-Wales defects in nanotubes**
  - **Selective deoxidation of defective nanotubes**
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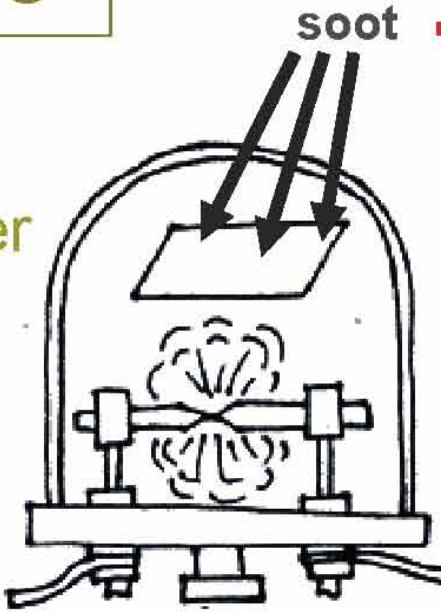
  David Tománek, Carbon-based nanotechnology on a supercomputer, Topical Review in J. Phys.: Condens. Matter ***17****, R413-R459 (2005).*

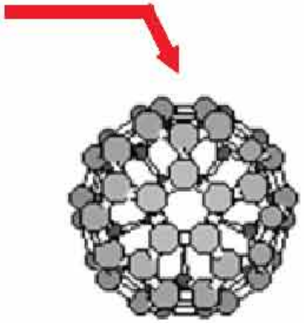
It is never late …

… to get excited

Nanocarbon pioneers

- The C_{60} 'buckyball' and other fullerenes:
  - successful synthesis
  - potential applications:
    - lubrication
    - superconductivity

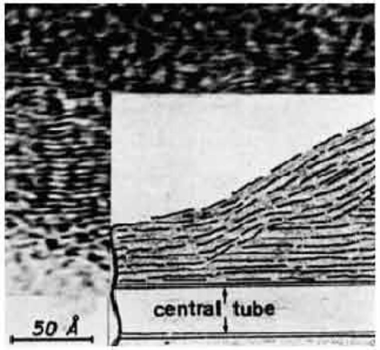




H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, and R.E. Smalley, Nature **318**, 162 (1985)

- Nanotubes:
  - successful synthesis
  - potential applications:

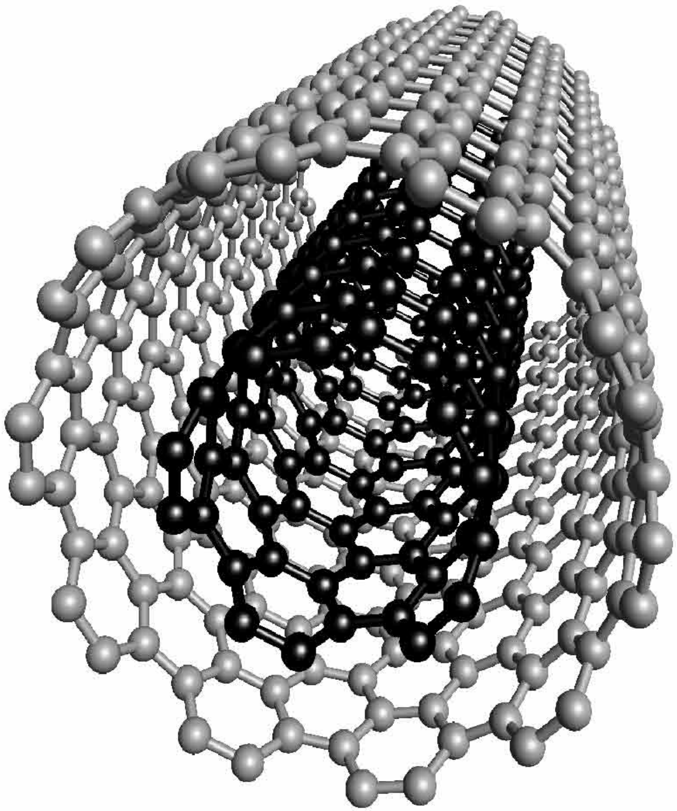
composites	flat-panel displays
Li-ion batteries	super-capacitors
medication delivery	fuel cells
EMI shielding	hydrogen storage



Nanotubes in the core of carbon fibers:
A. Oberlin, M. Endo, and T. Koyama, J. Cryst. Growth **32**, 335 (1976)

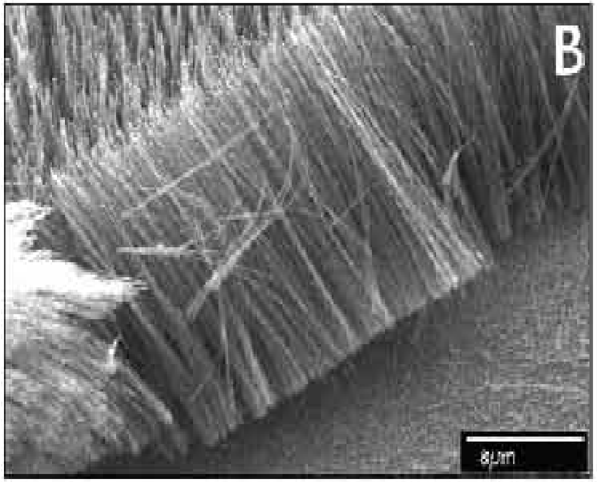
Nanotubes on the cathode in carbon arc:
S. Iijima, Nature **354**, 56 (1991)

Carbon nanotubes: Ideal building blocks for nanotechnology?

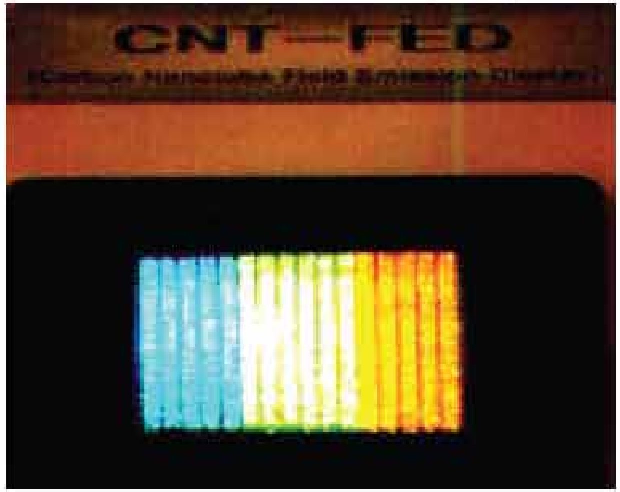


- 1-20 nm diameter
- Atomically perfect
- Chemically inert
- 100 times stronger than steel
- Extremely high melting temperature
- Ideal (ballistic) conductors of electrons, or insulators
- Ideal heat conductors
- Bio-compatible

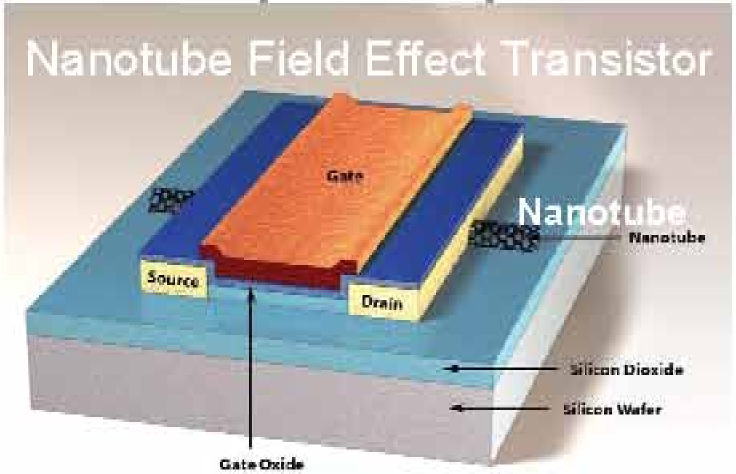
Nanotubes grow by decomposing carbon compounds …



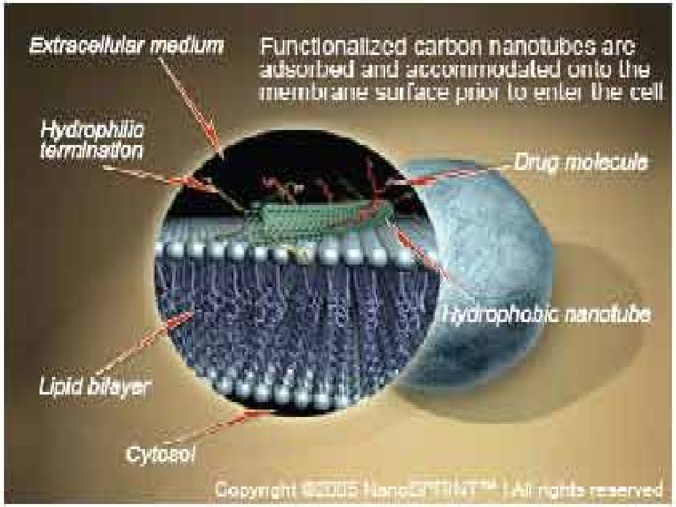
… to make bright flat-panel displays …



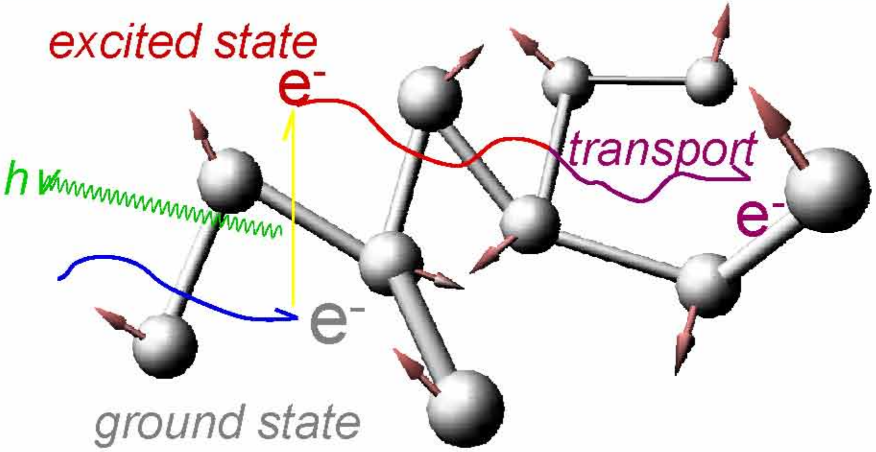
… field-effect transistors for the next generation of computer chips …

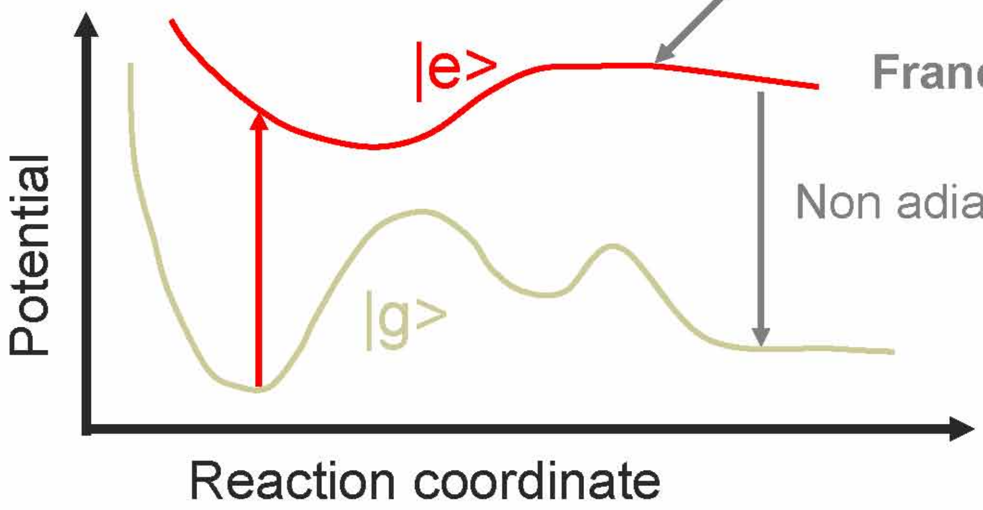


… or deliver drugs



What happens during electronic excitations?





To follow right adiabatic surfaces of excited states is rather difficult

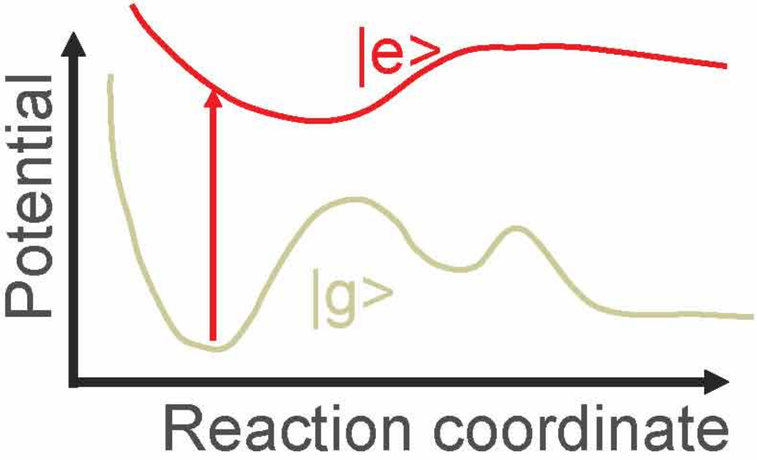
Franck-Condon effect

Non adiabatic decay (finite lifetime)

Computational tools

- Electronic structure calculations: *ab initio* Density Functional theory (DFT)
- Time evolution of electronic wave functions: Time-Dependent DFT
- Atomic motion: Molecular dynamics simulations (in ground & excited state)
- Forces from total energy expressions: $E_{tot} = E_{tot}(\{R_i\}) = E_{tot}\{\rho(r)\}$

What approach to use?



Ground state dynamics:
Solve the eigen-value problem

$$H\psi_n = \varepsilon_n \psi_n$$

Excited state dynamics:
Solve the time-dependent problem

$$i\hbar \frac{d\psi_n}{dt} = H\psi_n$$

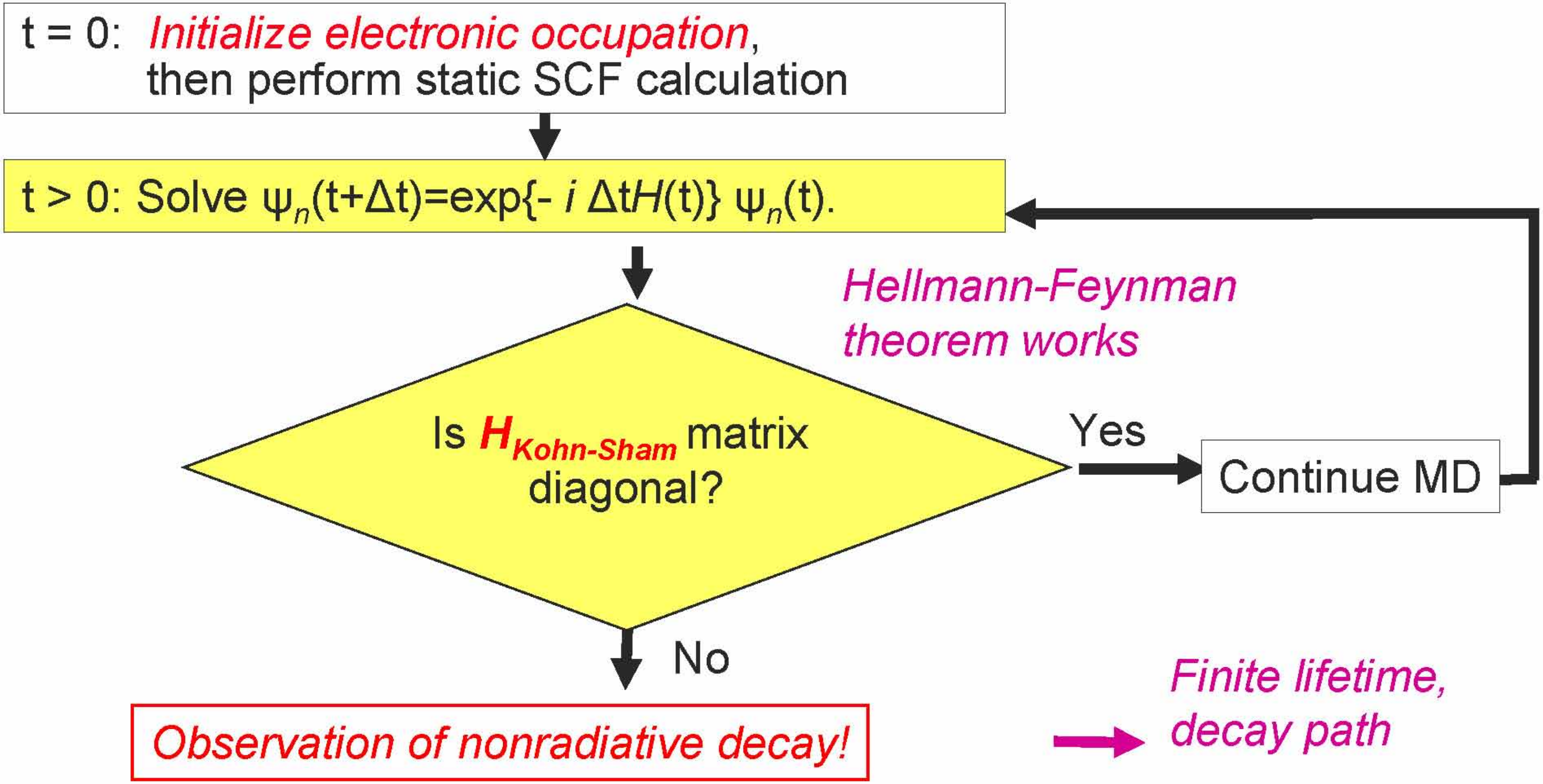
Density Functional Theory
(codes including SIESTA, VASP,
CASTEP, GAUSSIAN, etc.)

FPSEID (ef-psai-di:)

First-**P**rinciples **S**imulation tool for
Electron-**I**on **D**ynamics

- Computational details for real-time MD simulations:
Sugino & Miyamoto PRB 59, 2579 (1999) ; ibid, B 66, 89901(E) (2002)

Real-time electron dynamics during molecular dynamics



t = 0: *Initialize electronic occupation*, then perform static SCF calculation

t > 0: Solve $\psi_n(t+\Delta t)=\exp\{-i\,\Delta t H(t)\}\,\psi_n(t)$.

Is $H_{\text{Kohn-Sham}}$ matrix diagonal?

Yes → Continue MD

Hellmann-Feynman theorem works

No

Observation of nonradiative decay!

→ *Finite lifetime, decay path*

- Electronic state is fixed in the beginning, then evolves in time
- Continuous checking for nonradiative decay yields bias-free information about lifetime, decay path

Need massively parallel computer architectures and suitable algorithms distribute load over processors for speed-up

Computational Nanotechnology Laboratory: Earth Simulator, Tokyo

www.nytimes.com

The New York Times ON THE WEB

April 20, 2002

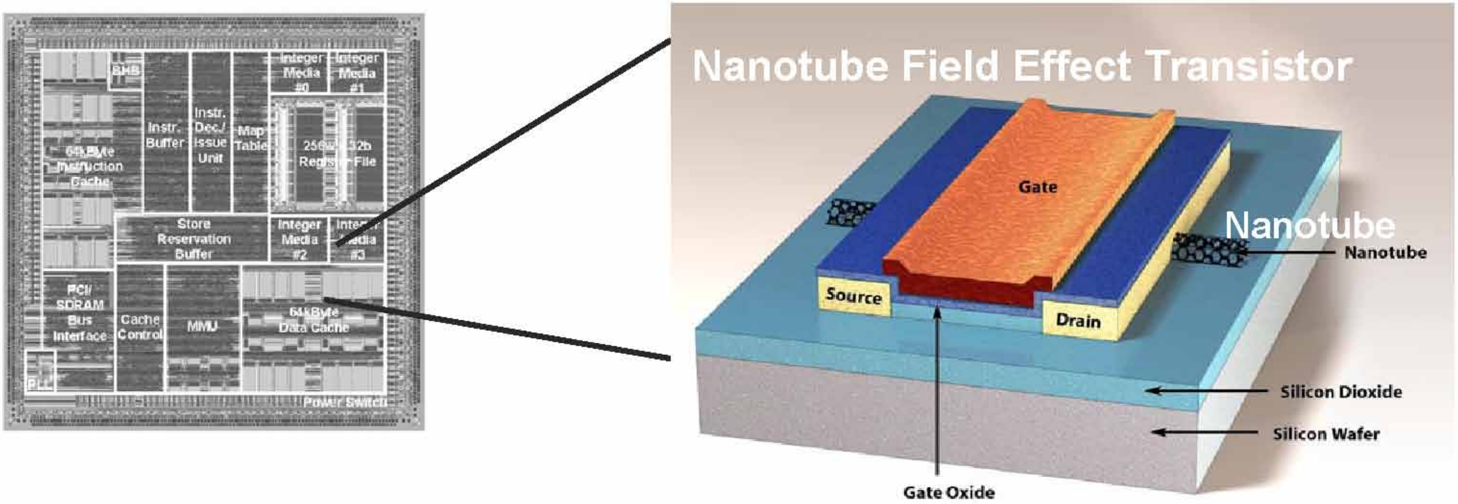
Japanese Computer Is World's Fastest, as U.S. Falls Back

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.

Cost: $500,000,000
Maintenance: $50,000,000/year
<70% used for nano-carbons

Limitations of quantum devices



- What limits the speed of nanotube-based electronics?
- What occurs microscopically during sputtering?
- Are nanotube devices as sensitive to defects as Si-LSI circuits?
- Can defects be identified spectroscopically?
- Can defects heal themselves?
- Are there ways to selectively remove defects?

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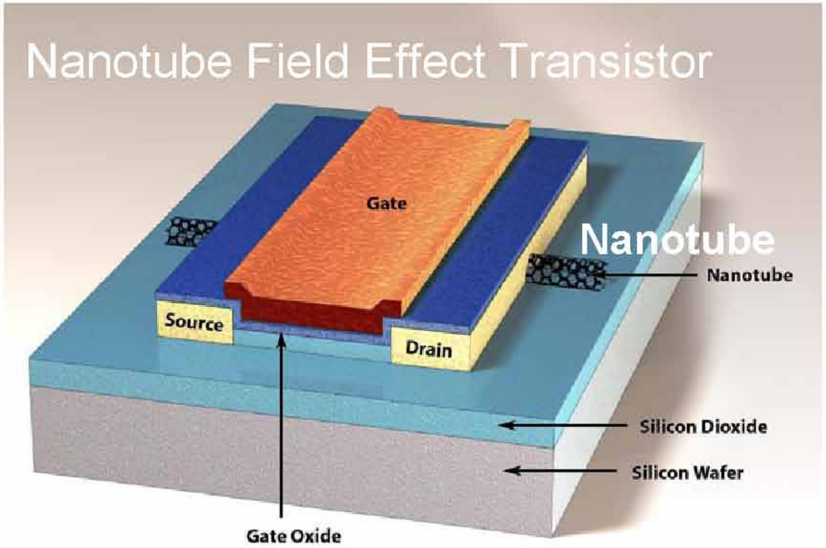
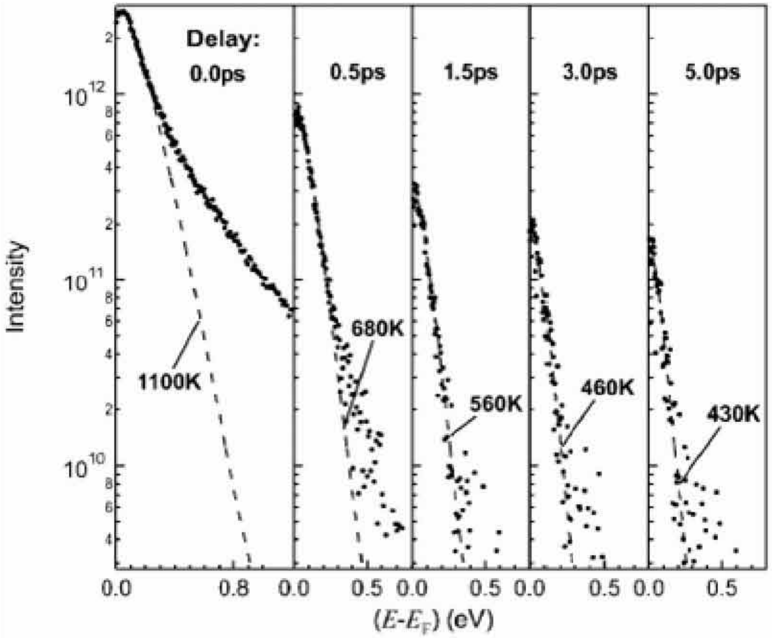
What limits the frequency response of nanotube electronics?

- 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?



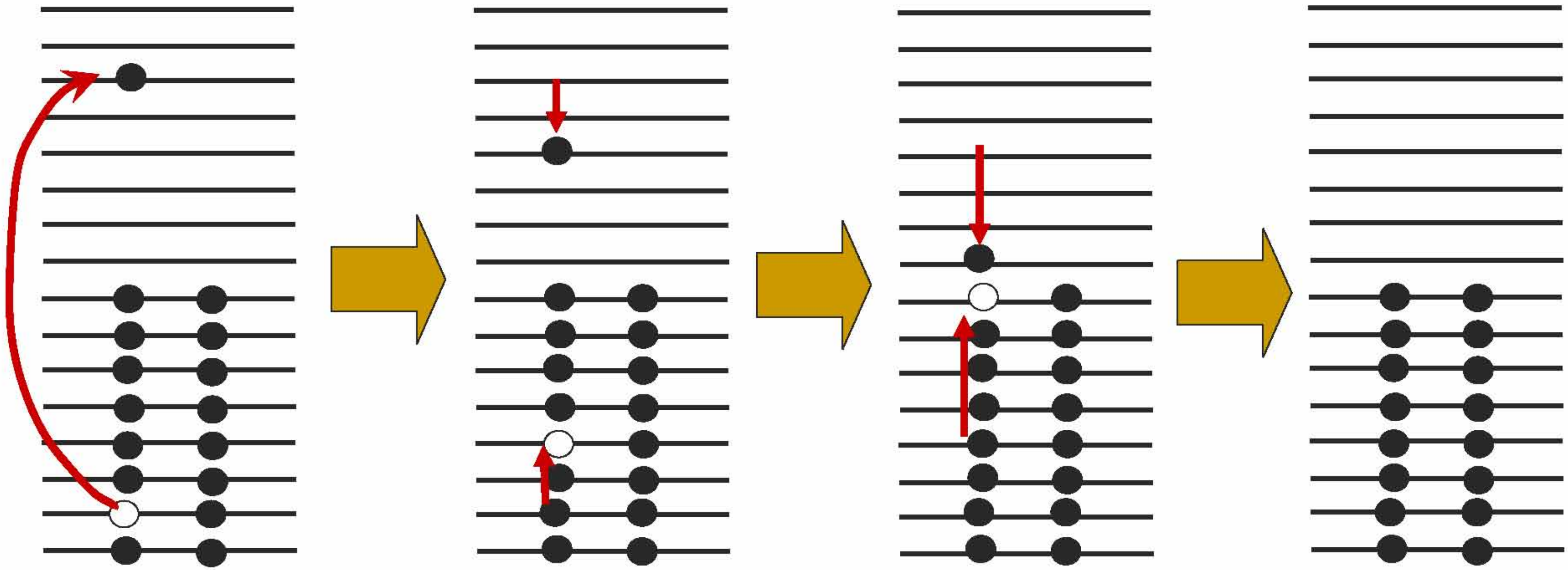


Evolution of photoelectron spectra as a function of pump-probe delay. At pump-probe delays of over 200 fs, the spectra can be well described by a Fermi-Dirac distribution (dashed lines).

Experiment: T. Hertel and G. Moos, PRL **84**, 5002 (2000)
Theory: Y. Miyamoto, A. Rubio, and D. Tománek, PRL **97**, 126104 (2006)

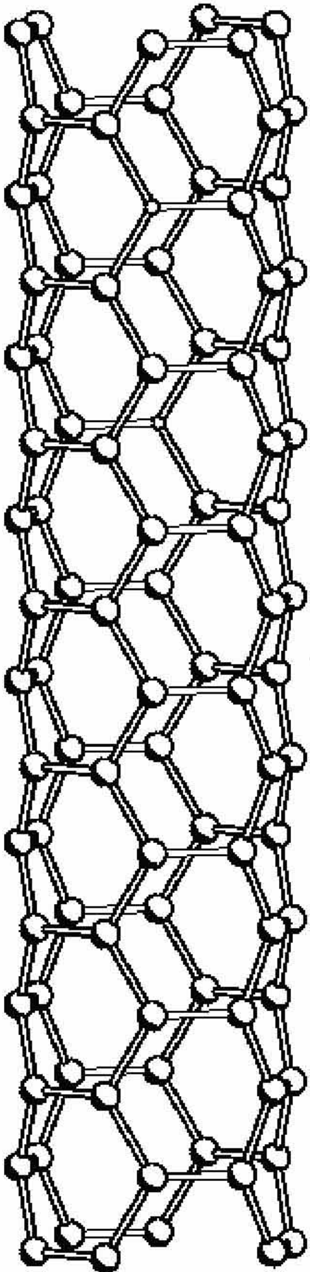
Interpretation:
e-e comes before e-ph

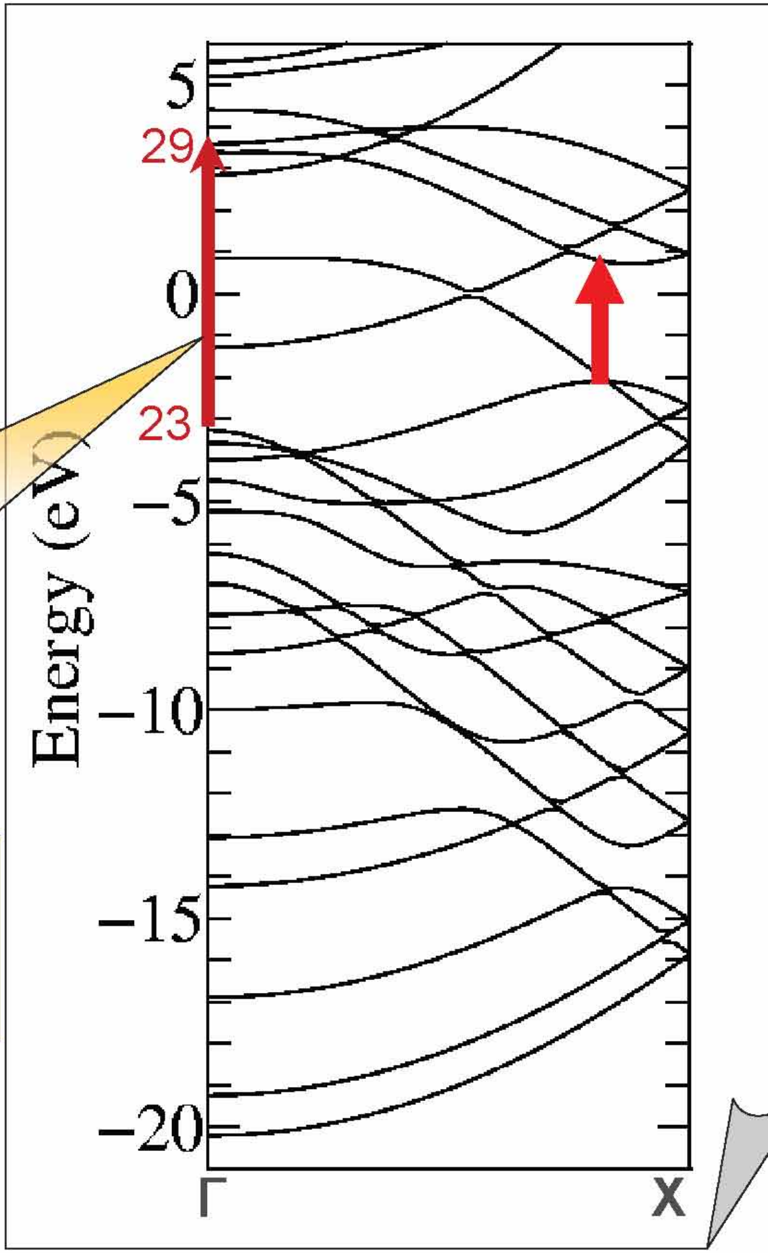
Relaxation of hot carriers after a photo-excitation



Test case: (3,3) nanotube

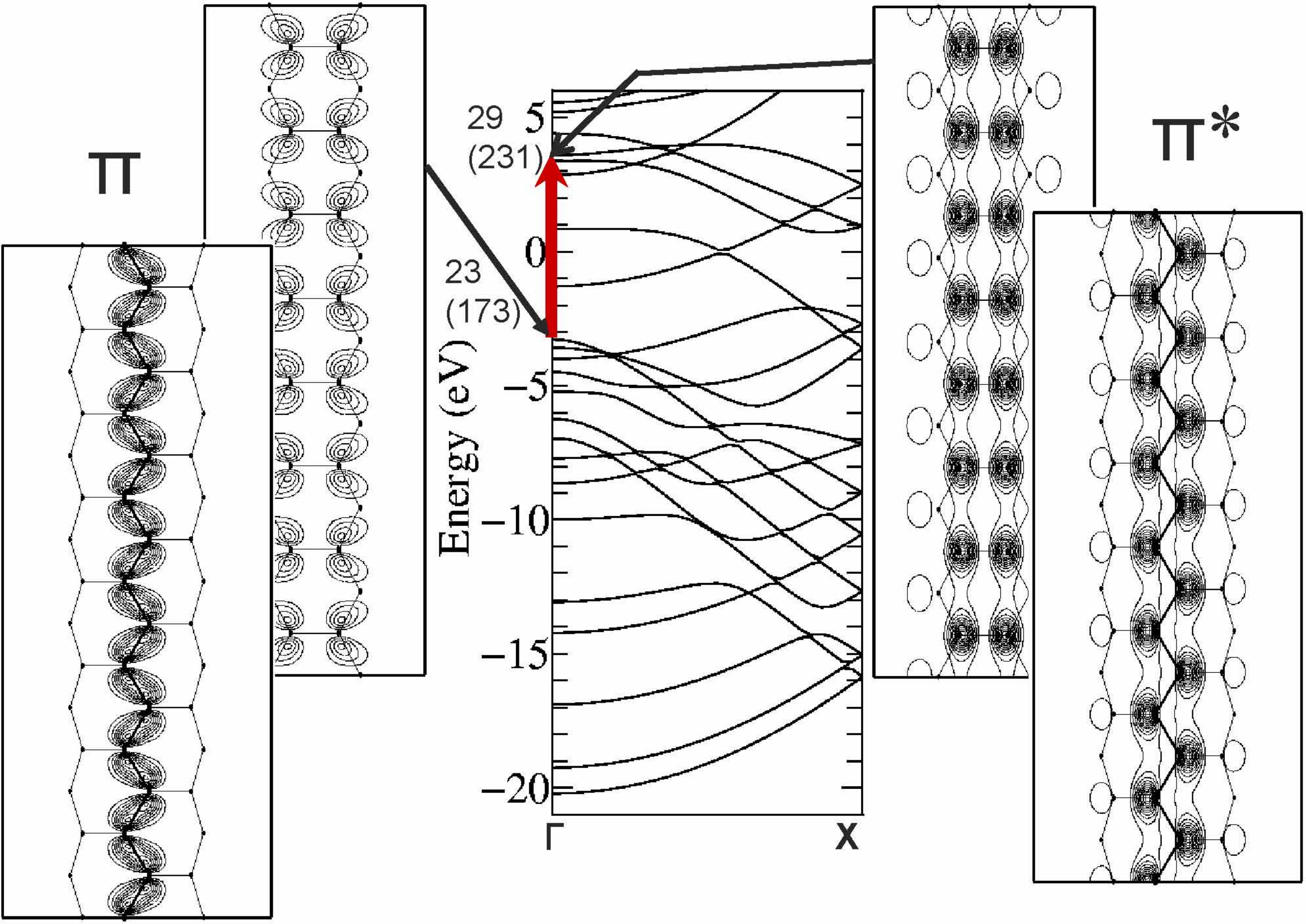
Observed photo-excitation:
[Z. M. Li et al., Phys. Rev. Lett. 87, 127401 (2001).]



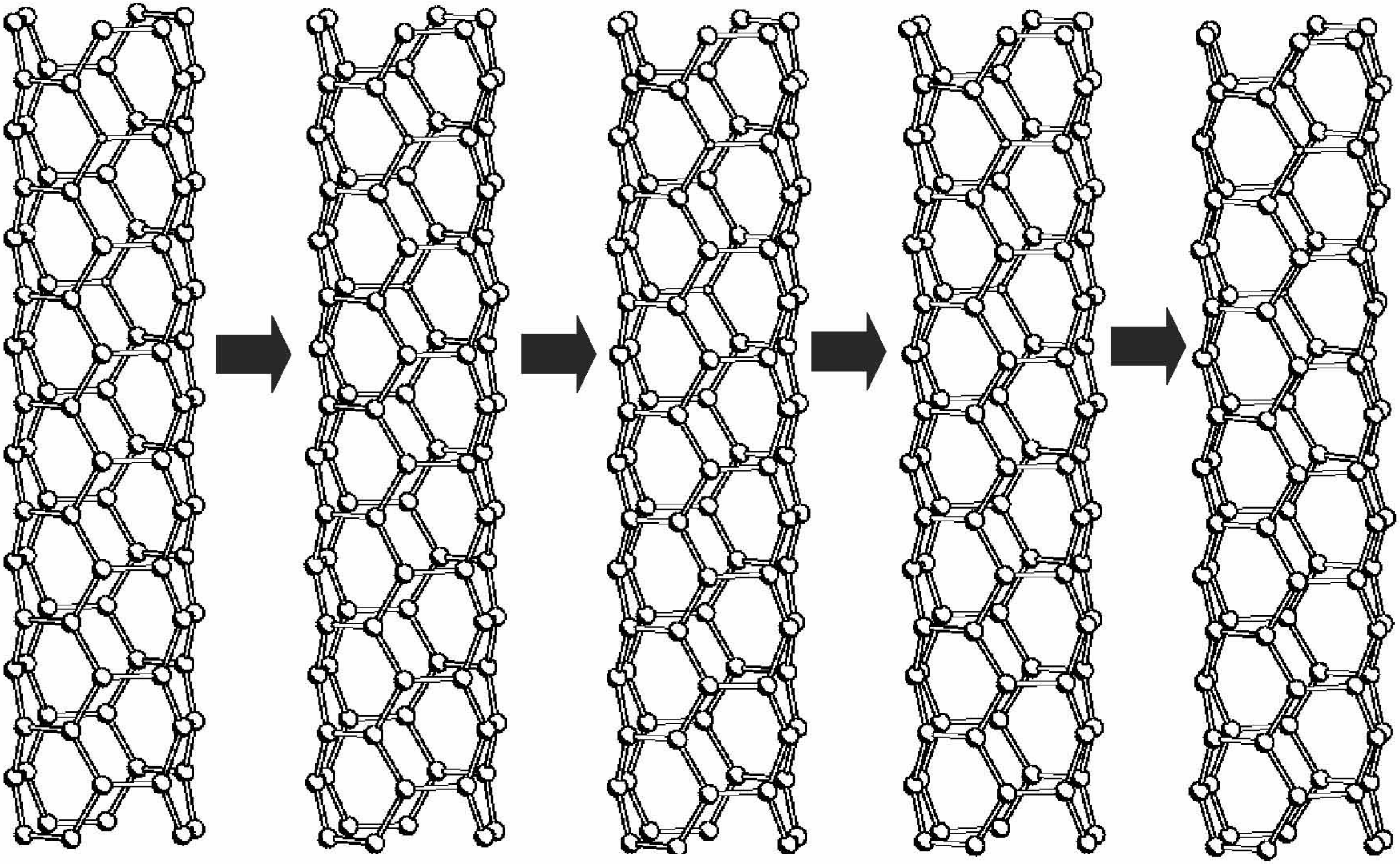


Focus on
#23→#29 transition:
Optically allowed, with
E∥(tube axis), *not yet reported*

Initial ionic velocities are randomized according to the Maxwell-Boltzmann distribution


π
π*
29
(231)
23
(173)
Energy (eV)
5
0
−5
−10
−15
−20
Γ
X

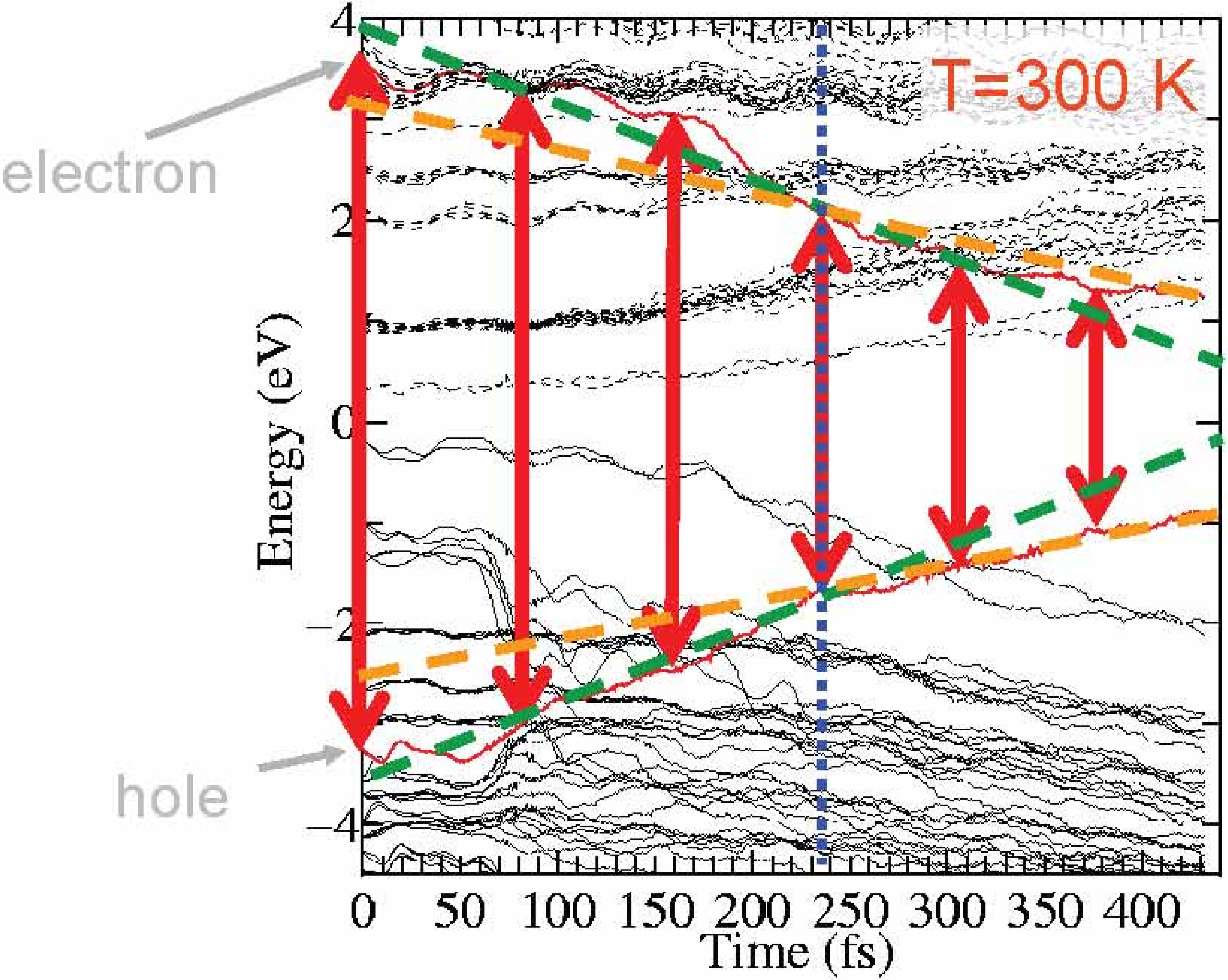
Atomic motion after excitation



0 fs
50 fs
100 fs
150 fs
200 fs

… very boring

Electron-hole excitation

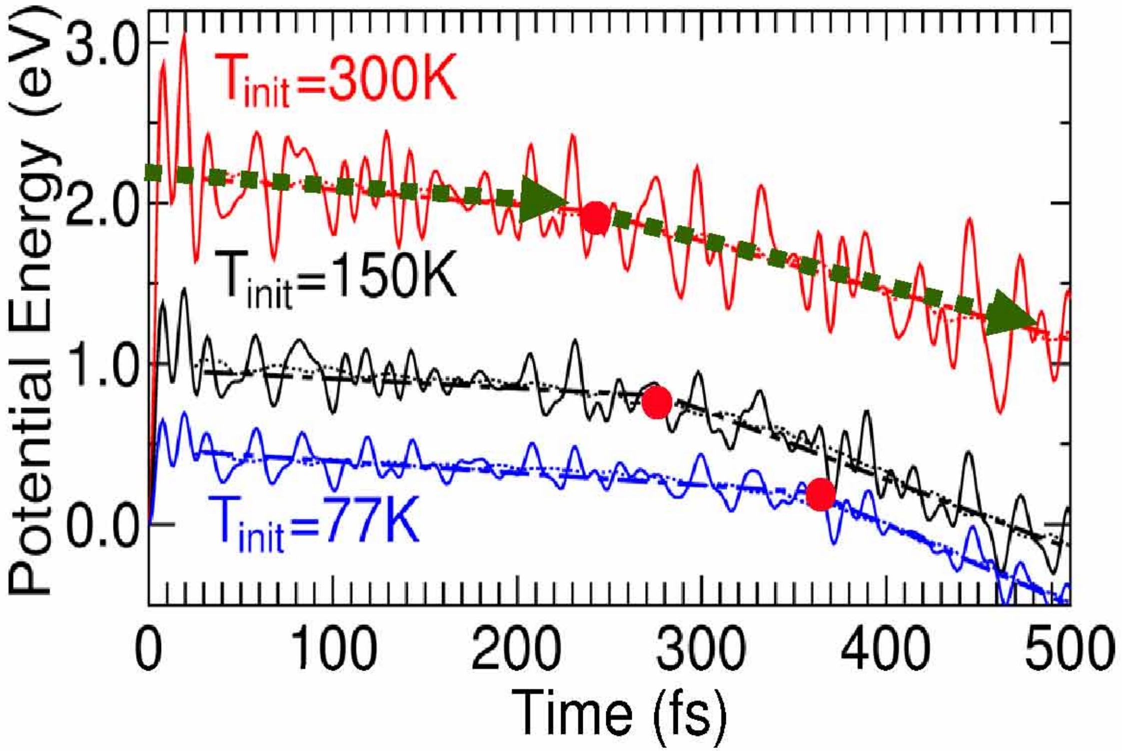


- Long lifetime (≤ps)
- Efficient damping

Energy transfer between electrons and ions

electron-electron dominates

electron-phonon dominates

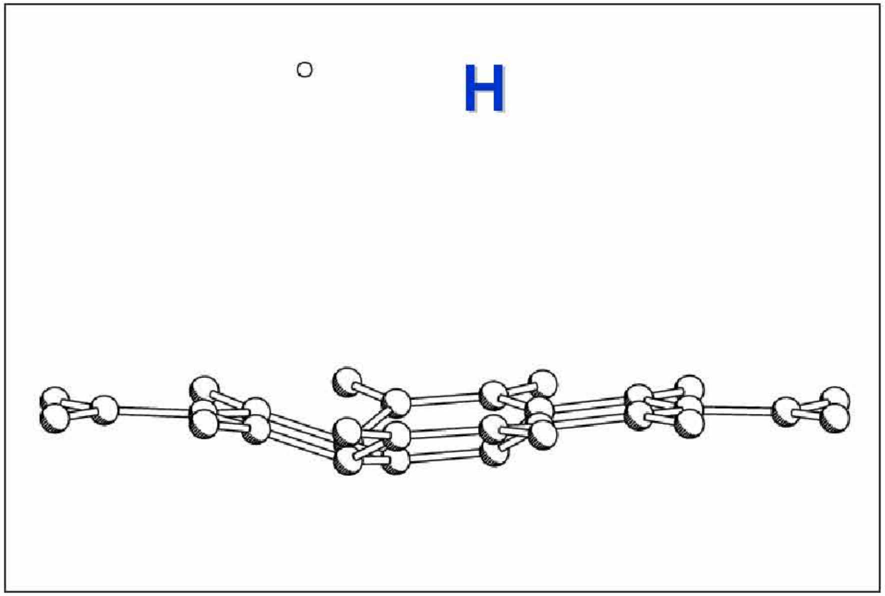


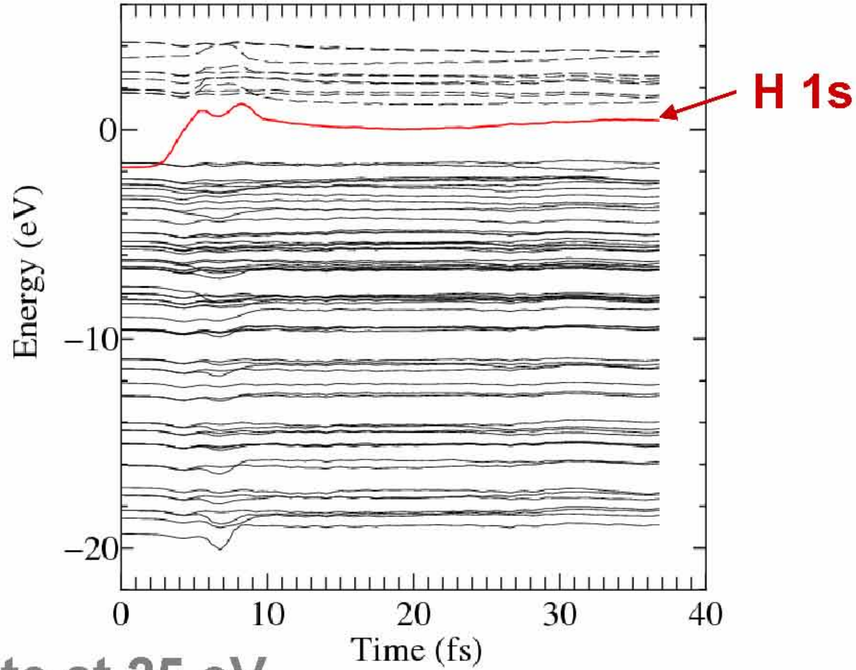
- Total energy is conserved
- Early: damping dominated electronic processes, temperature independent
- Later: damping dominated by coupling to phonons, temperature dependent
- Electron-phonon coupling is temperature dependent

Structural changes induced by sputtering

- Which atomic processes occur during sputtering?
- Deviation from the Born-Oppenheimer approximation are expected for ion velocities $v_I > v_F$(nanotubes)
- How important are electronic excitations in sputtering of nanotubes ($v_F = 8 \times 10^5$ m/s) by protons with $E_{kin} = 65$ eV ($v_I = 1.1 \times 10^5$ m/s)?

Impact of an H atom on a graphene sheet: $E_{kin}(H) = 25$ eV

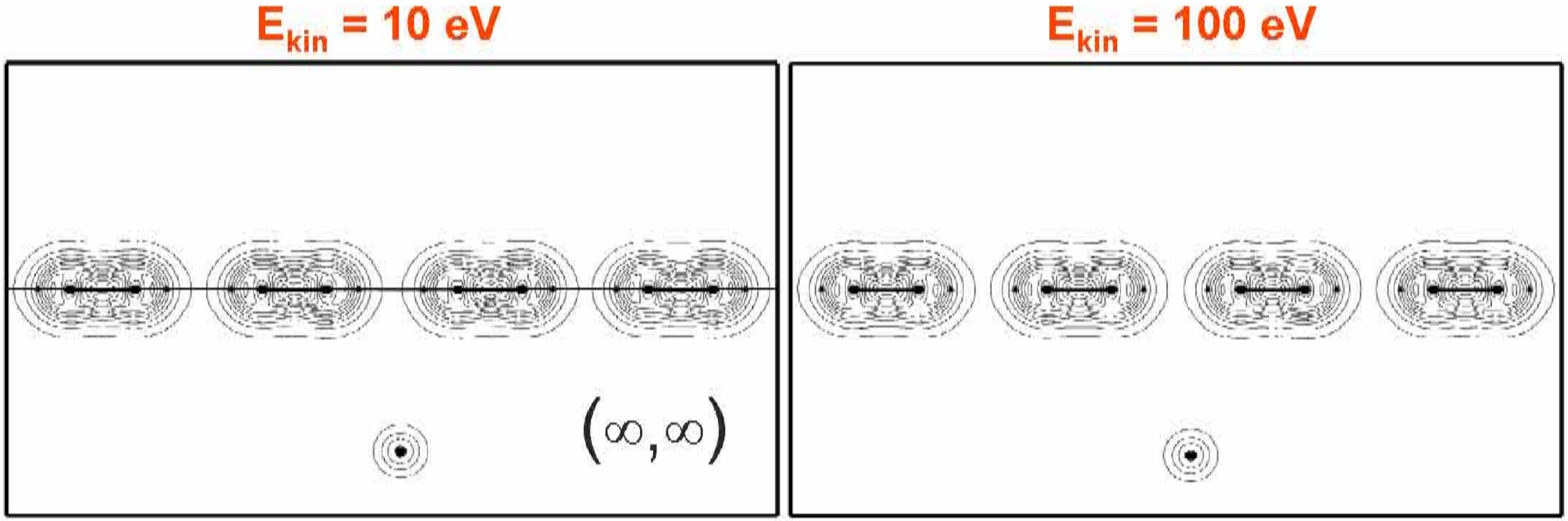




❖ **Conclusion: No damage to graphite at 25 eV**

Non-adiabatic effects in H^+/graphite collisions

- How adequate is the Born-Oppenheimer approximation in energetic H^+/graphite collisions?



E_{kin} = 10 eV

E_{kin} = 100 eV

Charge near H atom = 0.79e

Charge near H atom = 0.74e

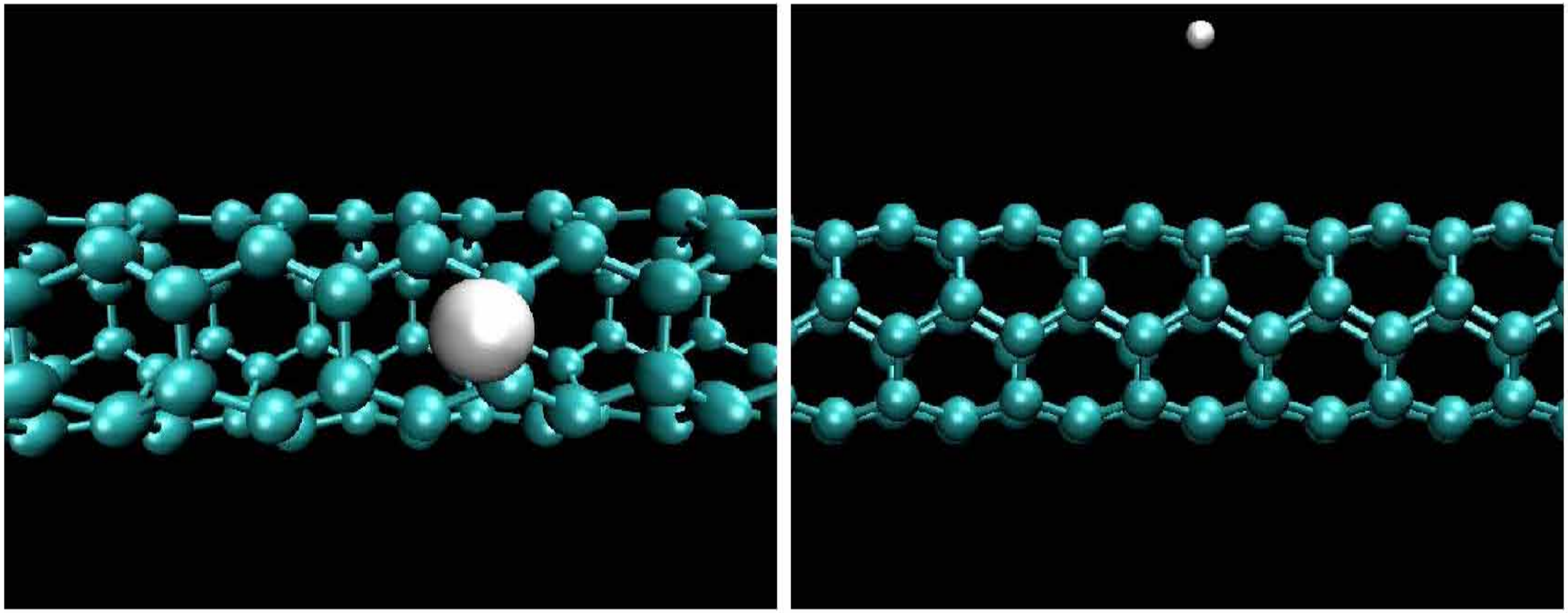
❖ **Conclusion:**
Non-adiabatic effects cause only small differences even at 100 eV

Yoshiyuki Miyamoto, Arkady Krasheninnikov, David Tománek (to be published)

Sputtering of nanotubes: Role of electronic excitations?

MD simulations for H^+/(3,3)CNT collisions with $E_{kin}(H)$=65 eV

- Born-Oppenheimer (ground state) dynamics: Sputtering occurs
- Allowing electronic excitations: Can sputtering occur?



Top view

Side view

- **Electronic excitations do affect threshold energy for sputtering**
- **Nanotubes have an amazing capability to heal defects**

Yoshiyuki Miyamoto, Arkady Krasheninnikov, David Tománek (to be published)

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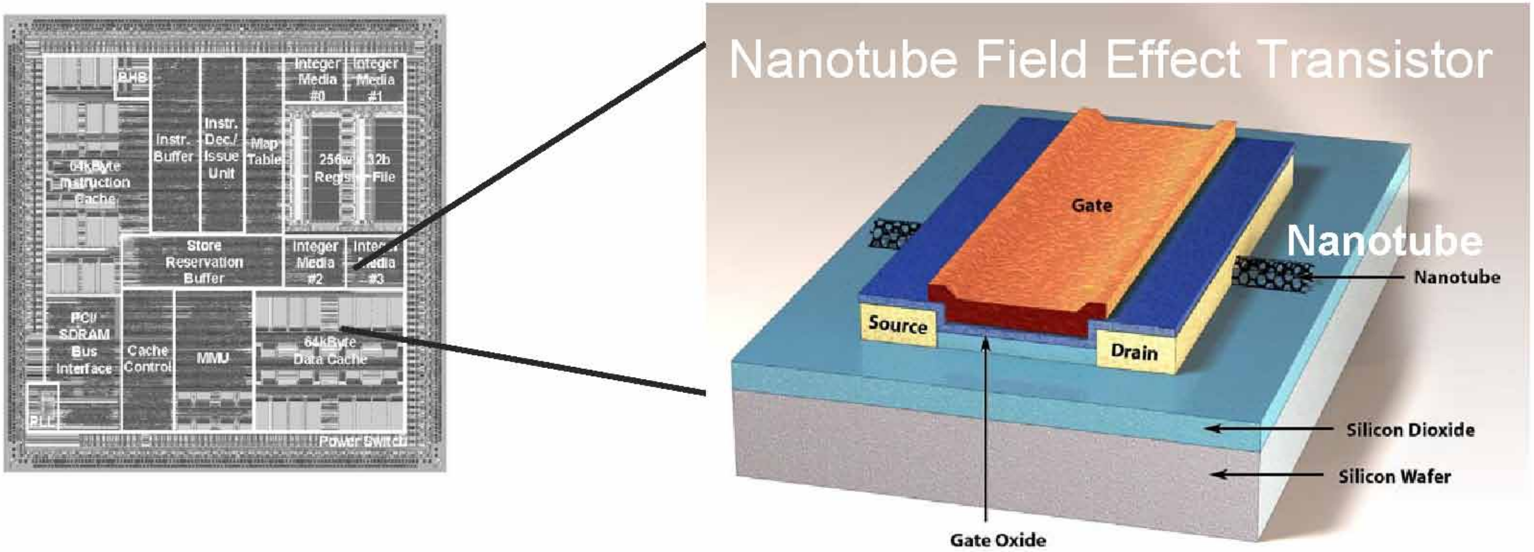
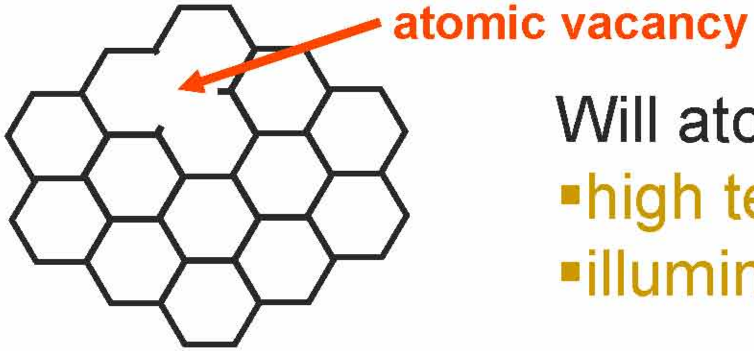
Dealing with atomic-scale defects



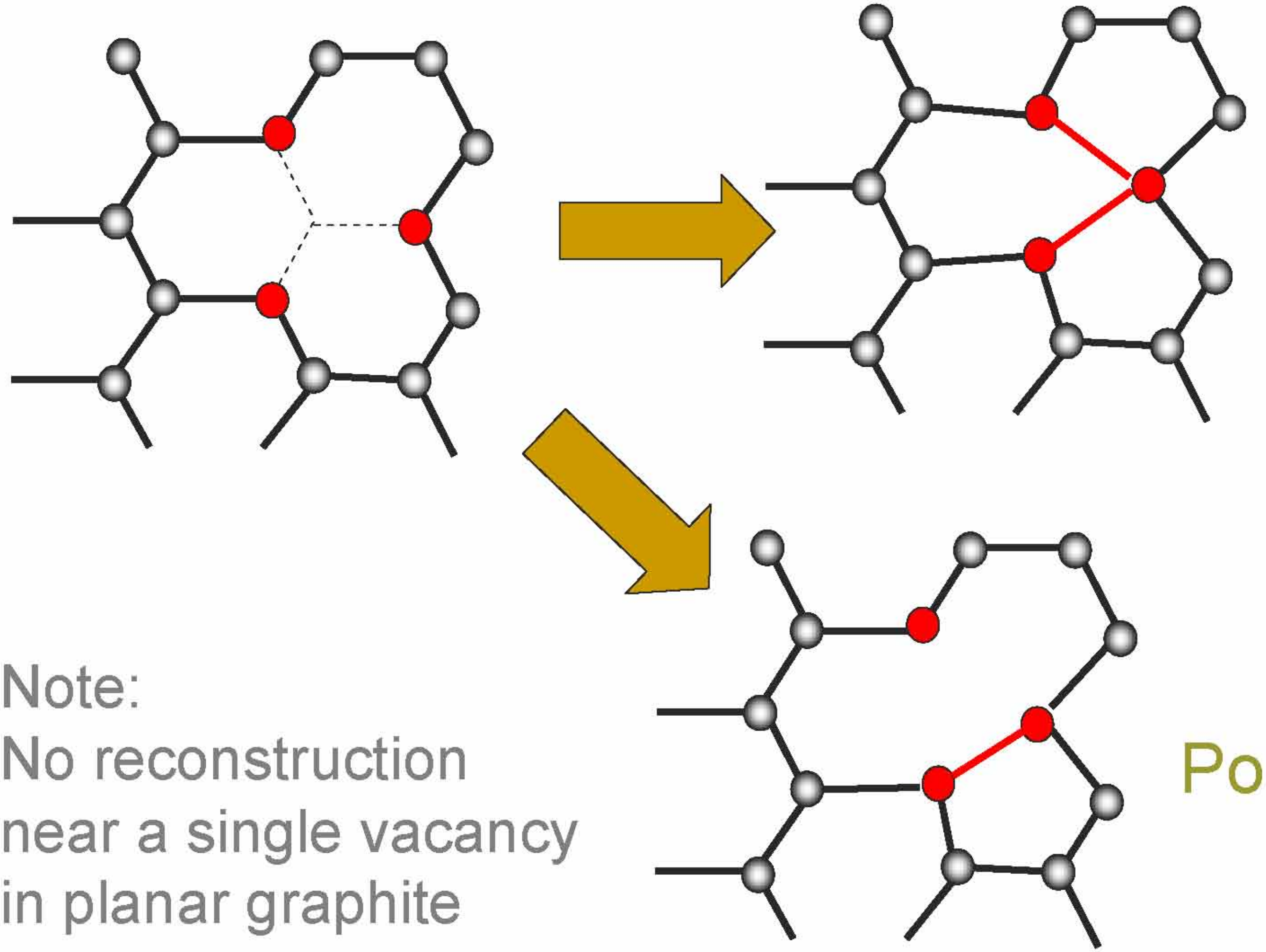
- Defects limit performance, lifetime of devices
- Are CNT devices as sensitive to defects as Si-LSI circuits?



Will atomic vacancies trigger failure under

- high temperatures?
- illumination?

Equilibrium structure near a monovacancy in *sp*^{2} carbon



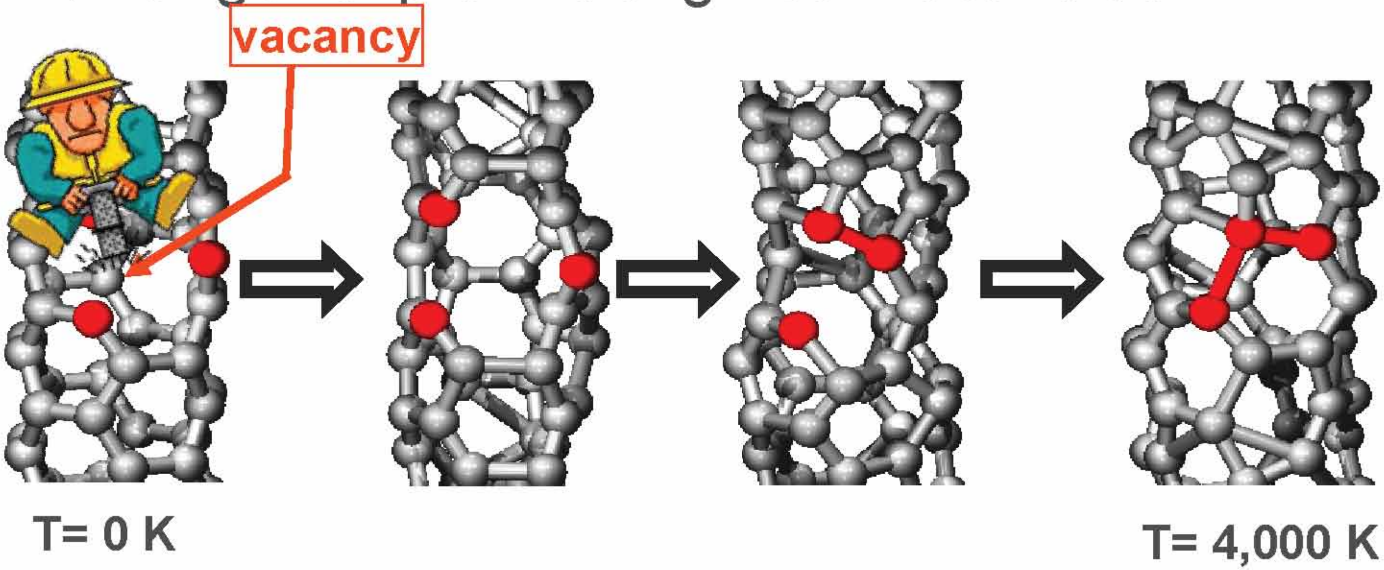
Strain too large

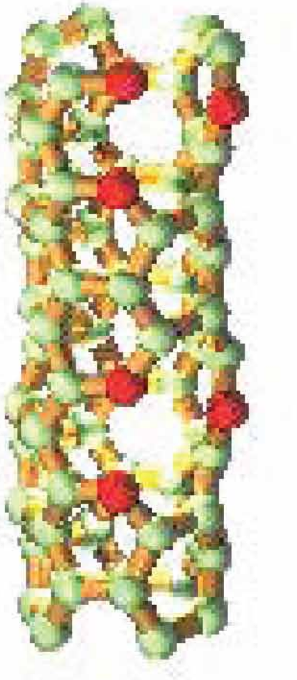
Possible?

Note:
No reconstruction near a single vacancy in planar graphite

Stability of defective tubes at high temperatures

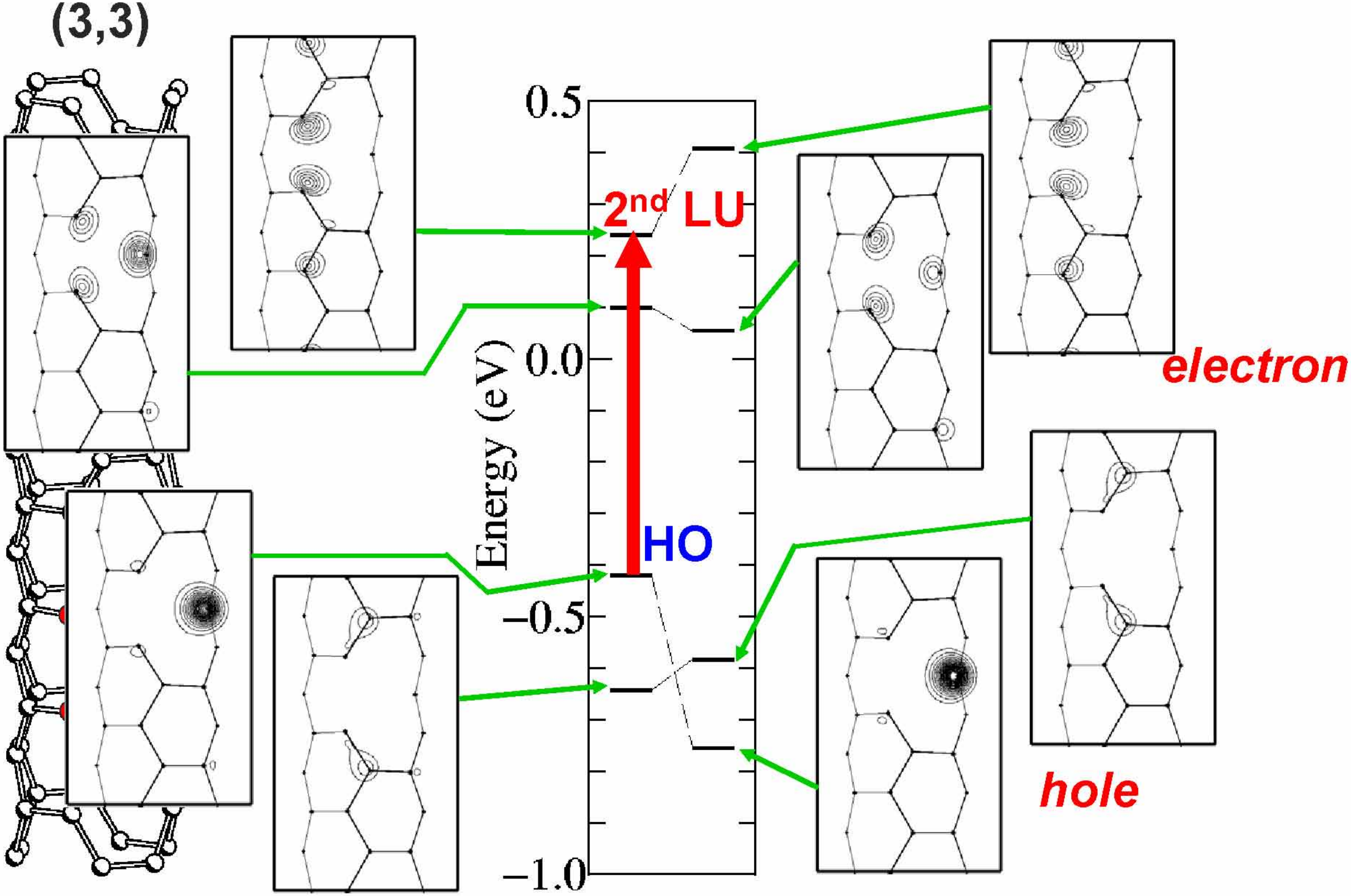
- Danger of pre-melting near vacancies?



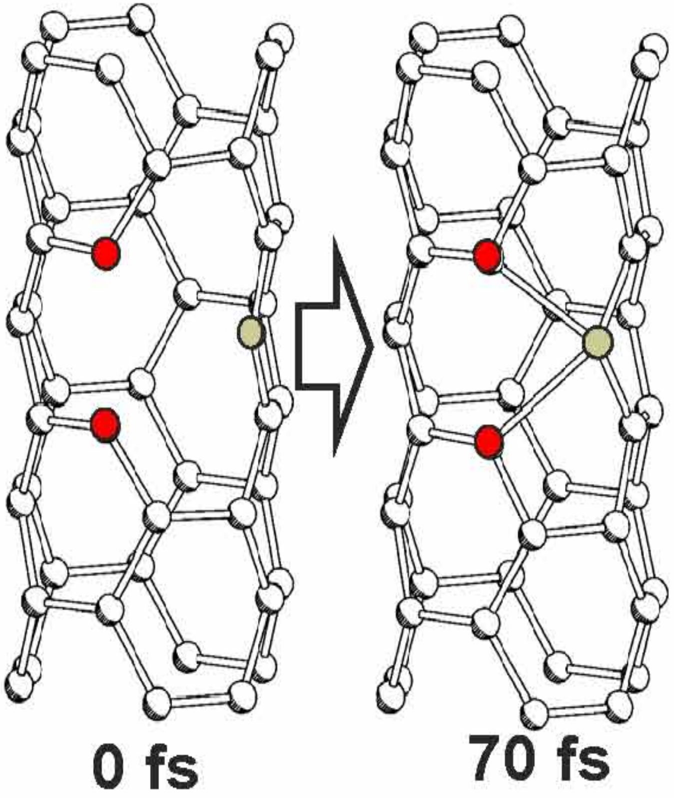


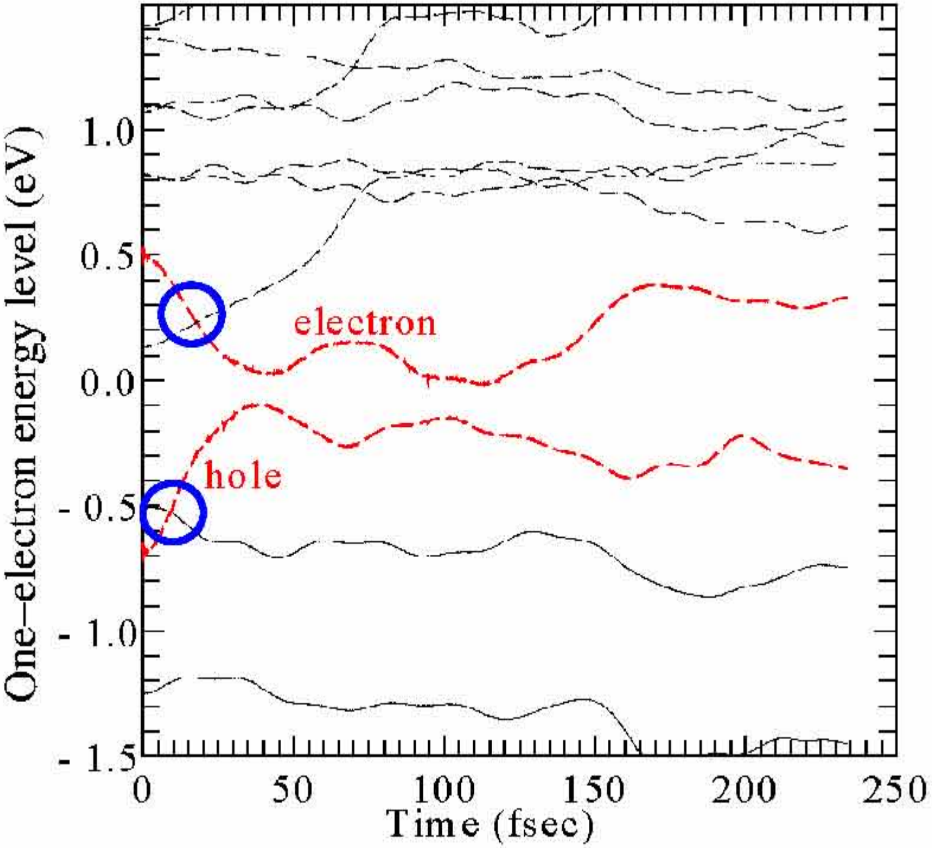
- Nanotube remains intact until 4,000 K
- Self-healing behavior:
  Formation of new bond helps recover
  - structural stiffness
  - conductance

Stability of defective tubes under optical excitations (ΔE=0.9 eV)



Time evolution of the electronic states

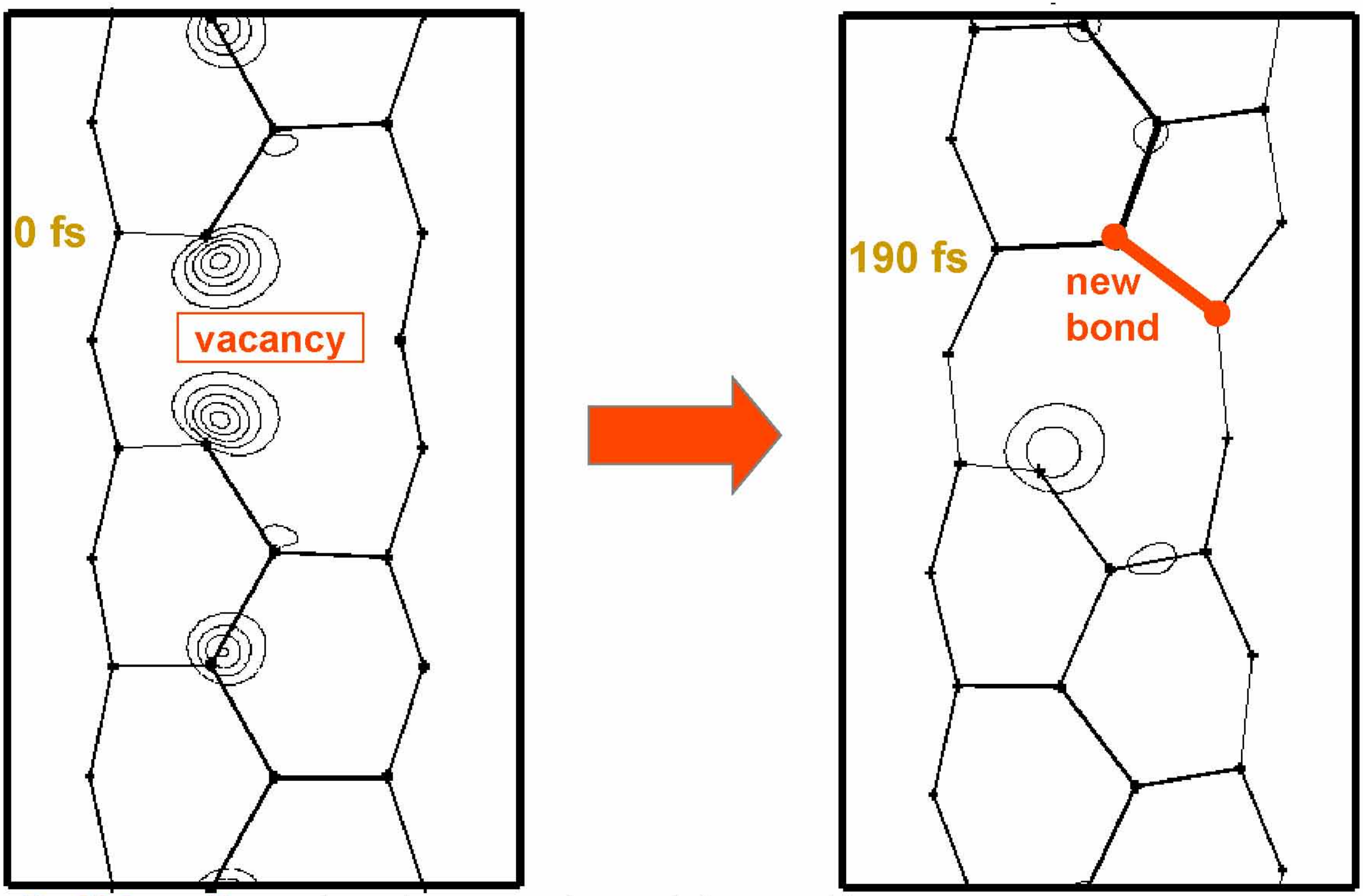




$$\Psi_n (t+\Delta t)=\exp(-i/h\ H\Delta t\ )\ \Psi_n(t)$$

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

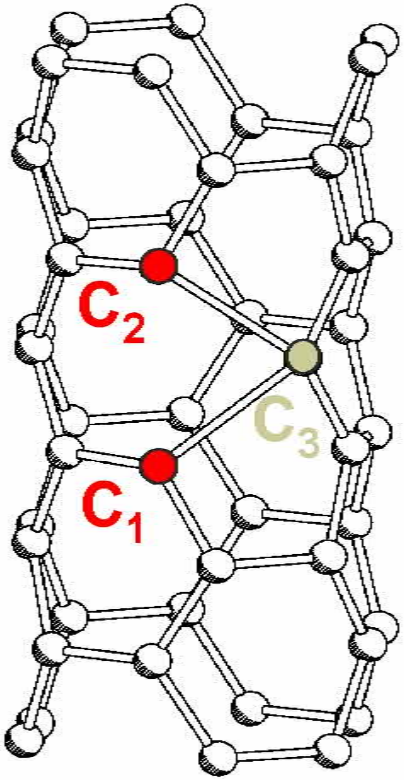
Structural changes under illumination



- 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)

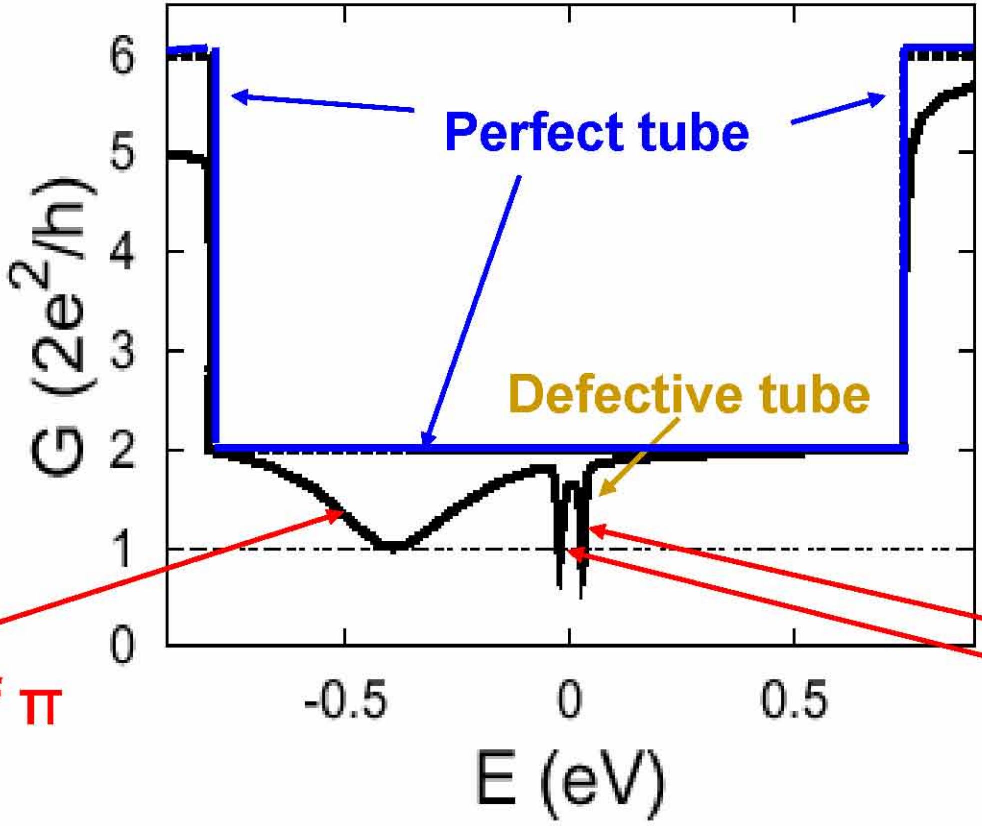
Reconstructed geometry



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



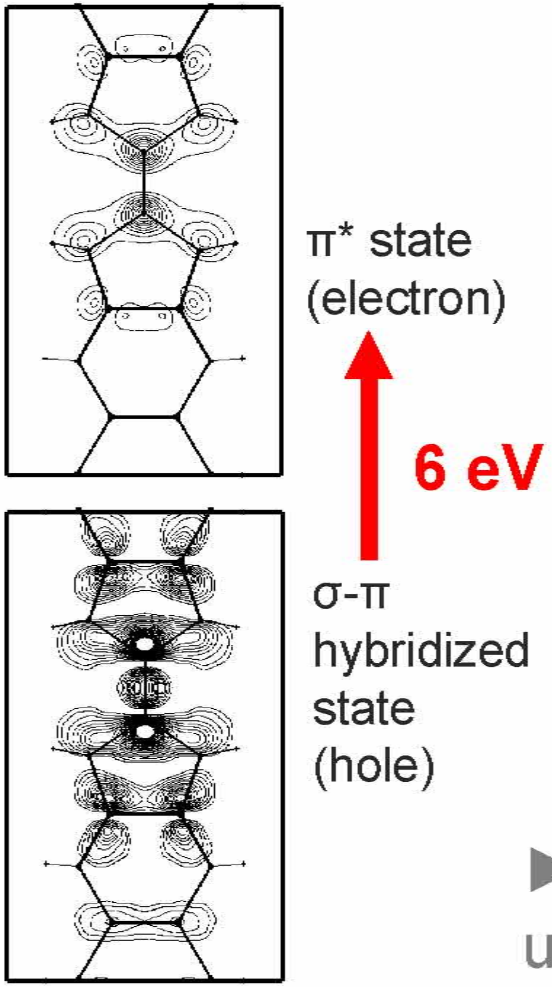
Choi, Ihm, Louie, Cohen, PRL (2000)

Missing network of π electrons

Dangling bonds: σ electrons

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

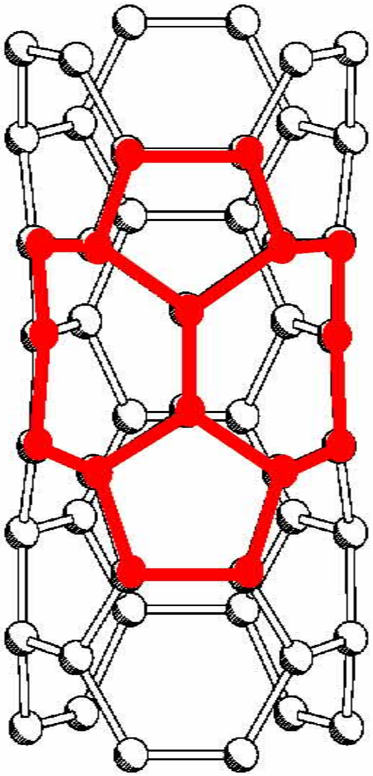
Detection of Stone-Wales defects in nanotubes

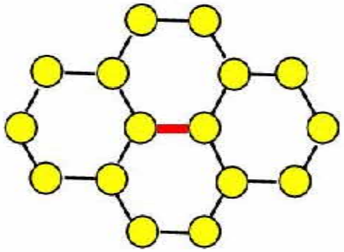


π* state
(electron)

6 eV

σ-π
hybridized
state
(hole)

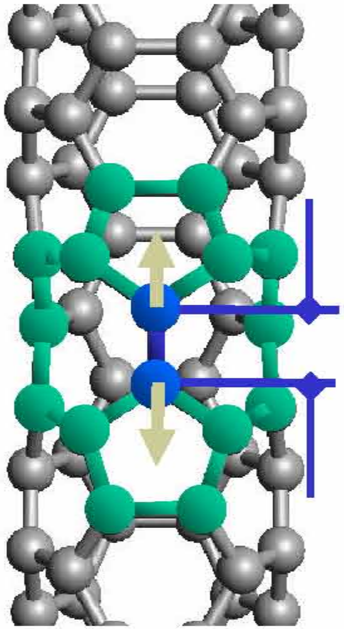


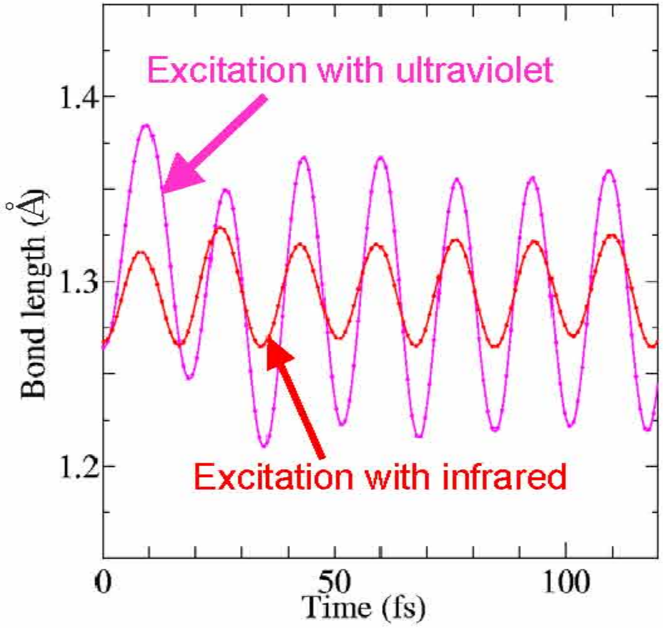


Origin of
Stone-Wales
defect

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

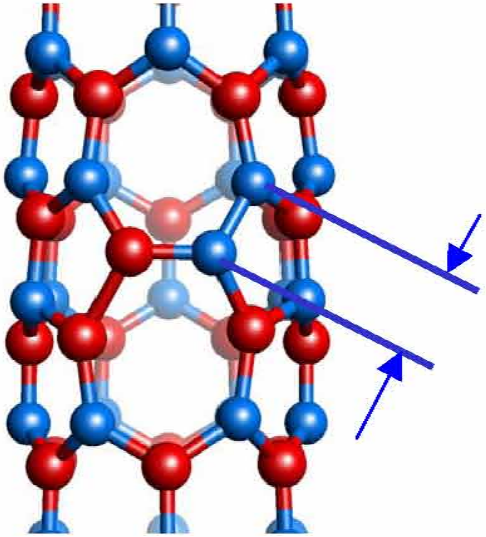
(3,3)
carbon
nanotube

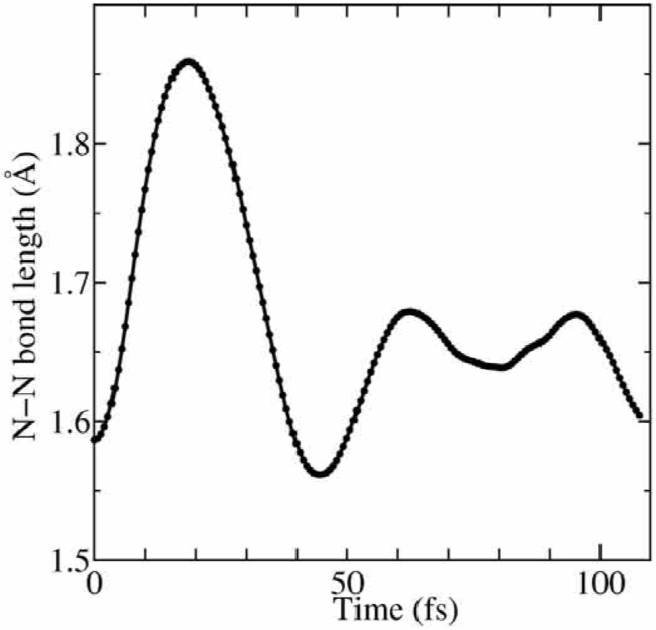




T=17 fs
(1962 cm^{-1})

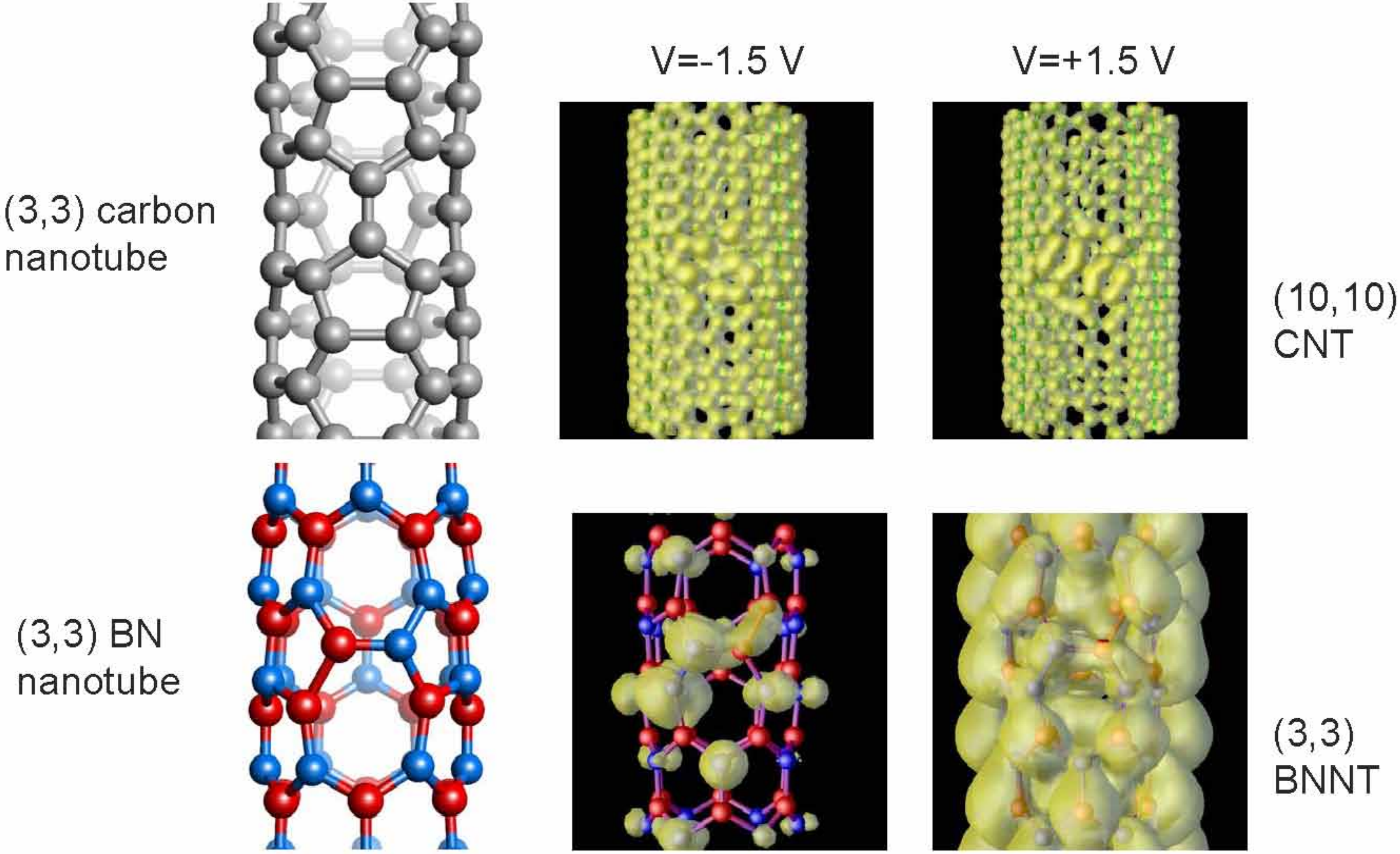
(3,3) BN
nanotube





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

STM characterization of Stone-Wales defects

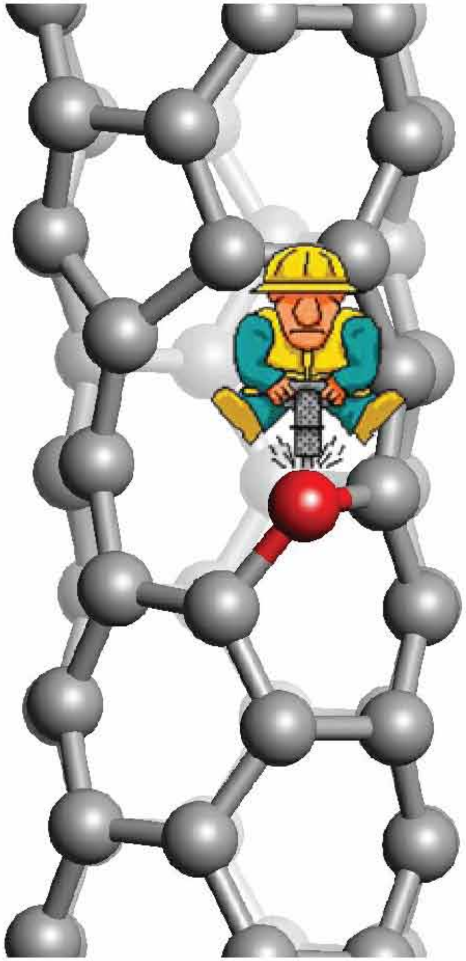


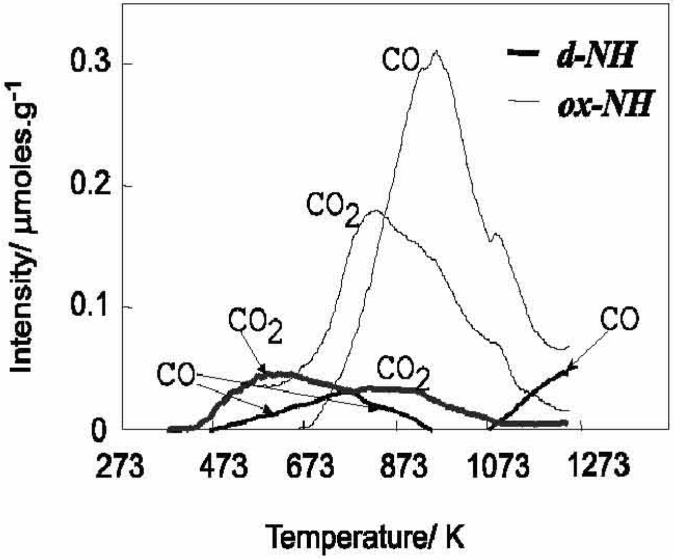
Y. Miyamoto, A. Rubio, S. Berber, M. Yoon, and D. Tománek, Phys. Rev. BR 69, 121413 (2004).

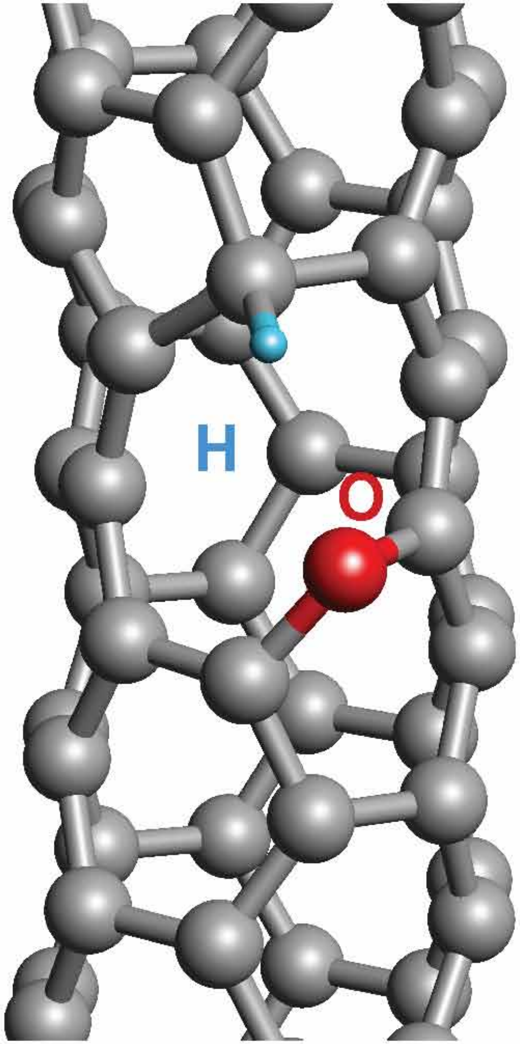
Selective deoxidation of defective nanotubes

How to deoxidize?

- **By heat treatment?**
  ⇒No: Larger damage to nanotube
- **By chemical treatment with H?**



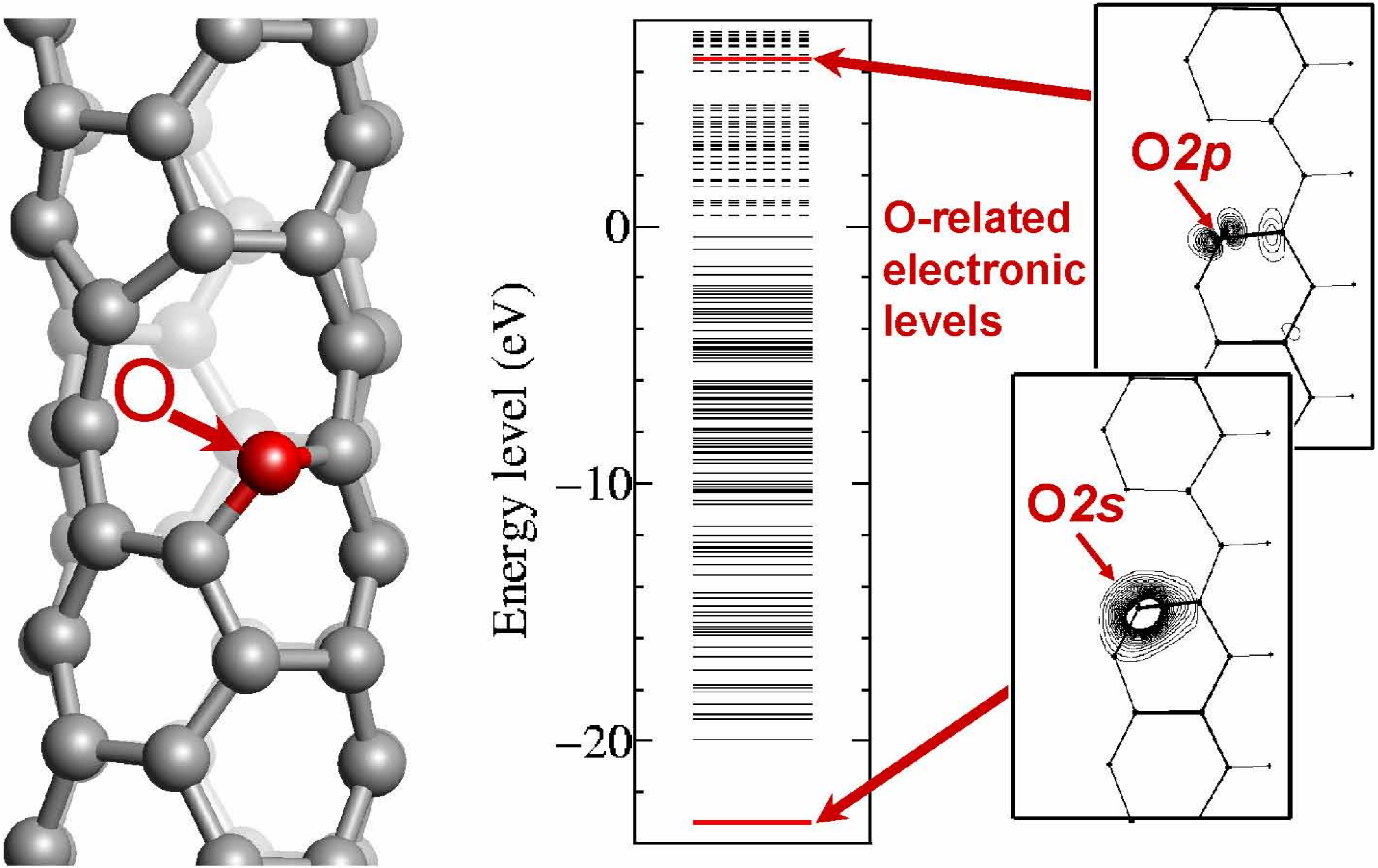




Y. Miyamoto, N. Jinbo, H. Nakamura, A. Rubio, and D. Tománek, Phys. Rev. B 70, 233408 (2004).

Alternative to thermal and chemical treatment

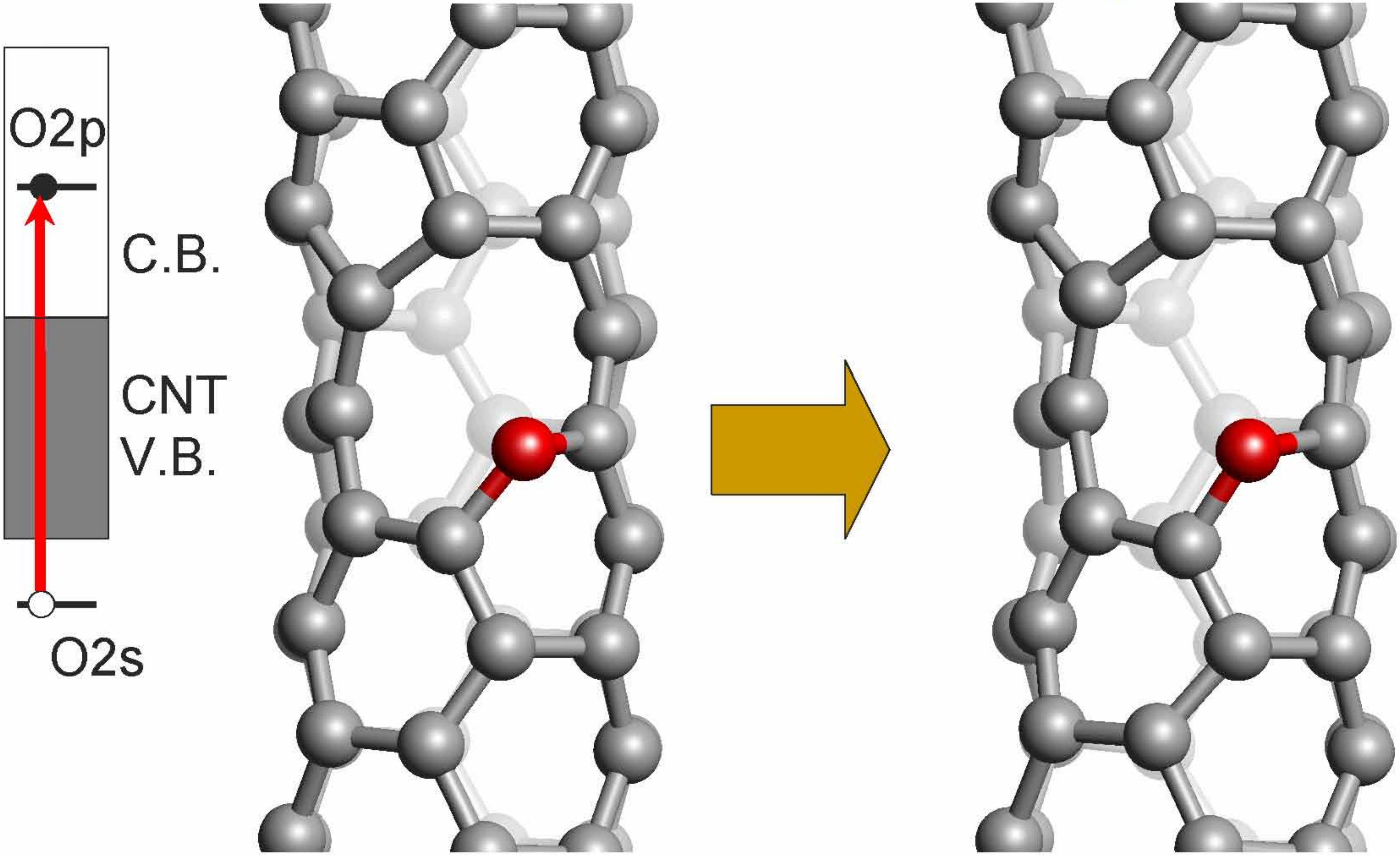
Electronic excitations!



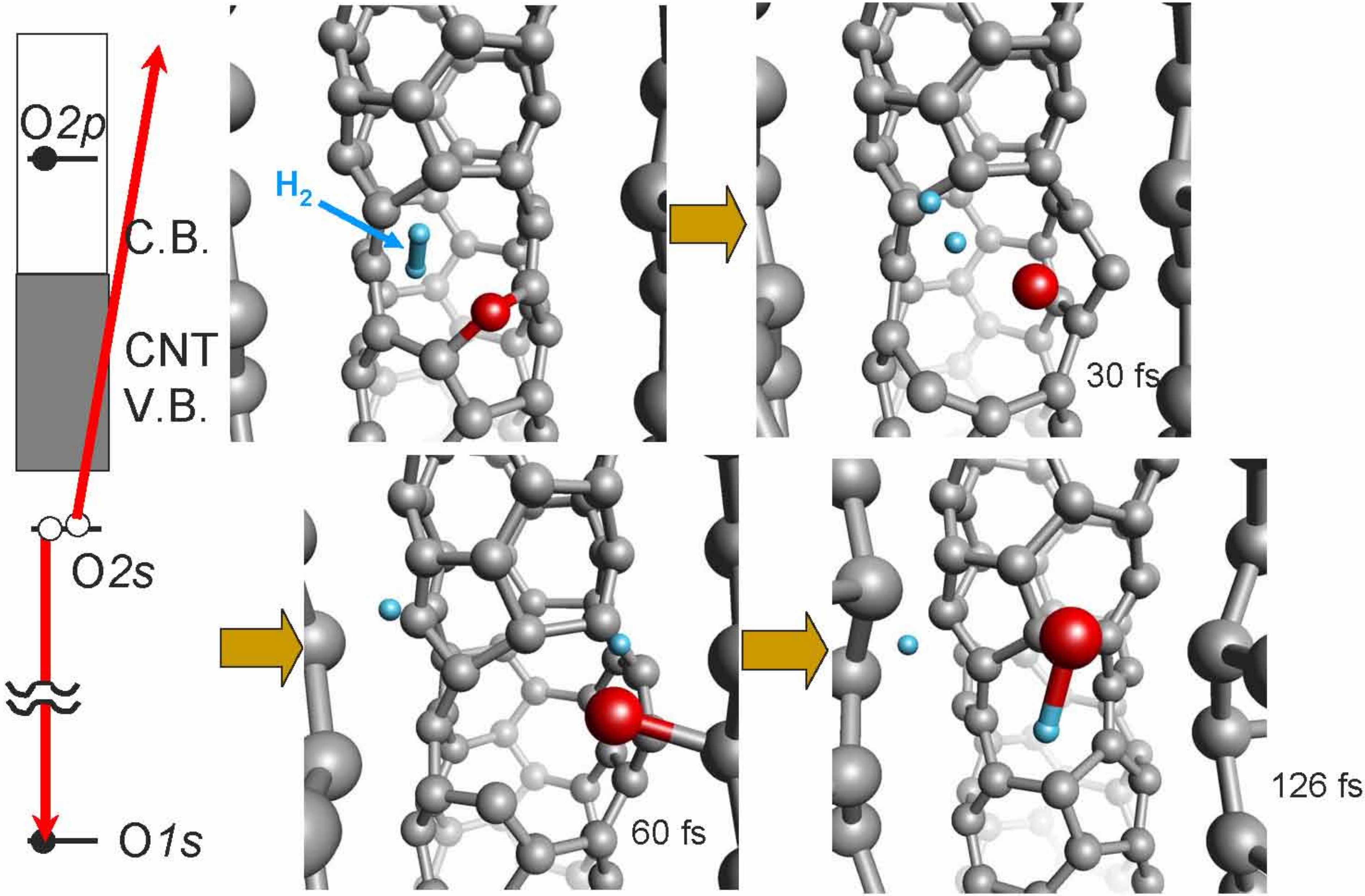
O-related electronic levels

O2s → O2p excitation (33 eV)

hopeless



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



◆Photoexcitations are long-lived ◆Deoxidation by photo-surgery

NT07

Eighth International Conference on the Science and Application of Nanotubes

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http://nanotube.msu.edu/nt07/

Summary and Conclusions

- Time-dependent DFT simulations have been combined with classical MD simulations to investigate the ultrafast dynamics in nanotubes under electronic excitations.
- The TDDFT scheme allows to monitor atomic motion and lifetime of the excitation.
- Electronic excitations in nanotubes exhibit ultrafast dynamics and decay by electronic and phonon channels.
- Photo-excitations may affect threshold energy for sputtering.
- Stone-Wales defects have a spectroscopic signature in the excited state.
- Thermal and electronic excitations may induce self-healing in defective nanotubes.
- Electronic excitations can selectively remove impurities.
- Electrons may be efficiently excited both by photons and electrons.