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Control and Assembly of Nanoscale Structures: Chemistry and Light

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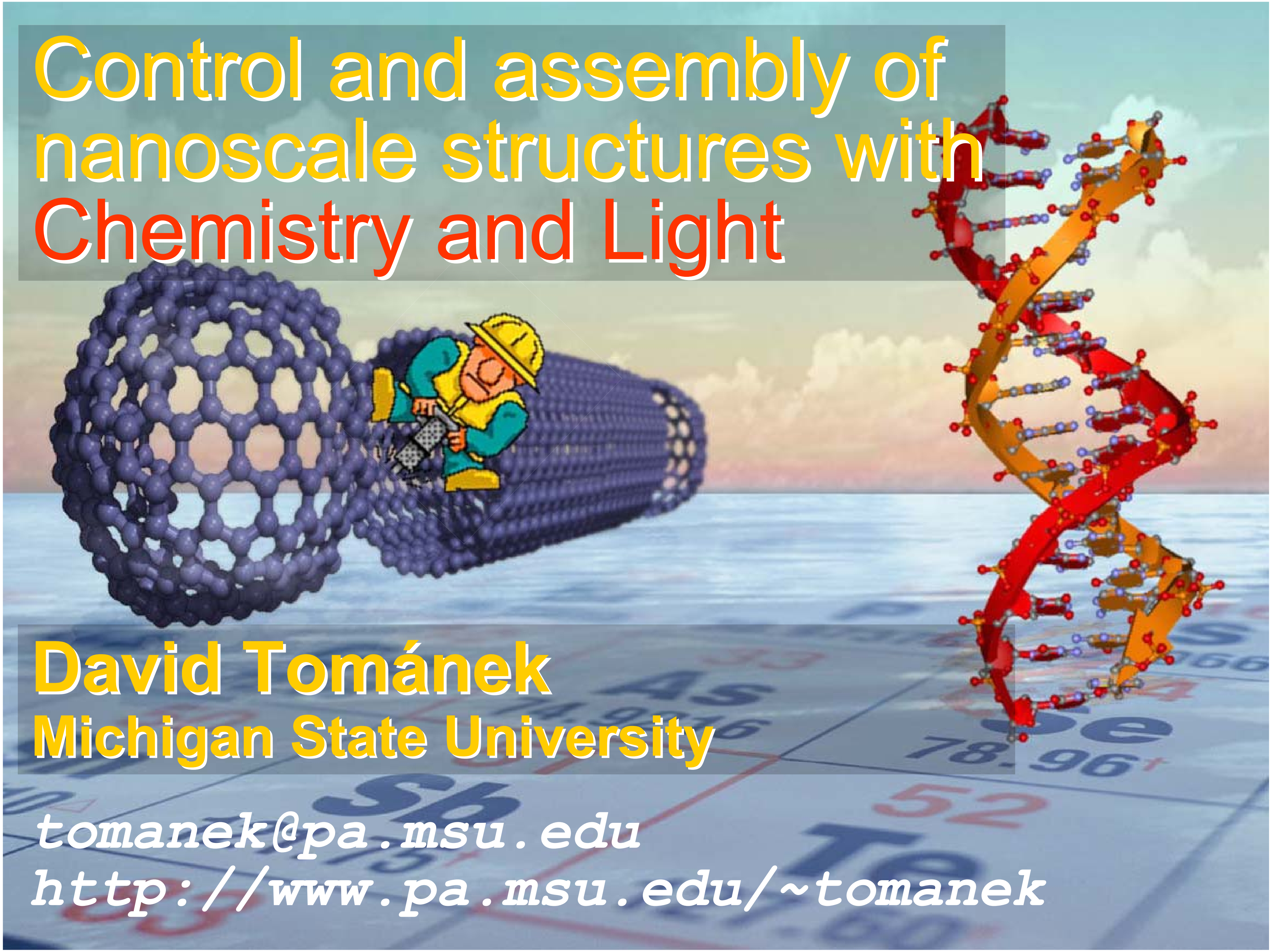

Control and assembly of nanoscale structures with Chemistry and Light

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Acknowledgements

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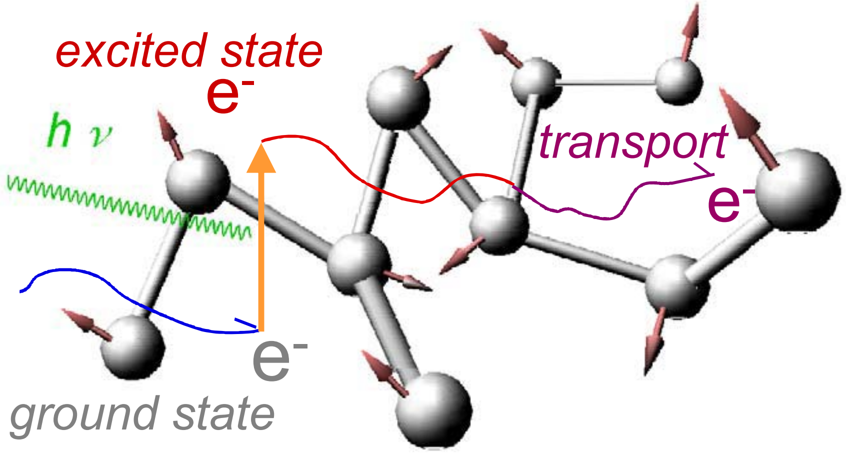
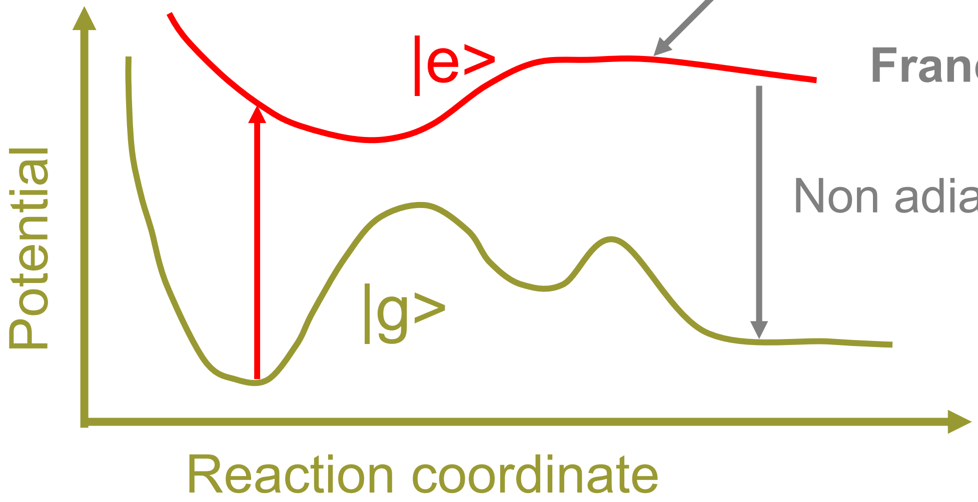
RIST (Japan)

Outline

- Introduction
  - **Dynamics of ground state and excited state processes**
  - **State of the art computer simulations**
  - **Long lifetime of electronic excitations**
- Chemical modification of nanocarbons
  - **Hydrogenation of nanocarbons by wet chemistry**
  - **Peeling fullerenes by hydrogen**
  - **Unzipping nanotubes by hydrogen**
- Excited state engineering of nanocarbons
  - **Transforming graphite to diamond by light**
  - **Photo-exfoliation of graphite to graphene**
  - **Focused Ion Beam (FIB) lithography for nano-architectonics**
- Removing atomic-scale defects
  - **Defect tolerance of nanotubes**
  - **Selective deoxidation of defective nanotubes**
- Summary and Conclusions

Dynamics of ground state and excited state processes





To follow right adiabatic surfaces of excited states is rather difficult

Franck-Condon effect

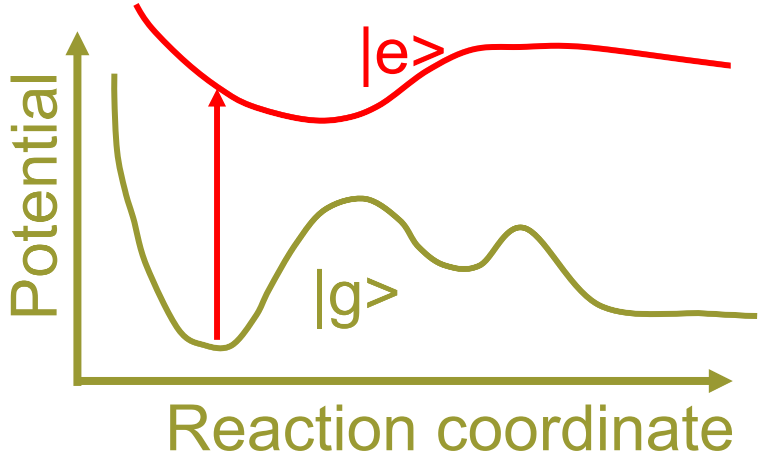
Non adiabatic decay (finite lifetime)

Can be calculated by *ab initio* simulation

State of the art computer simulations

- 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 eigenvalue problem

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

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

Excited state dynamics:
Solve the time-dependent problem

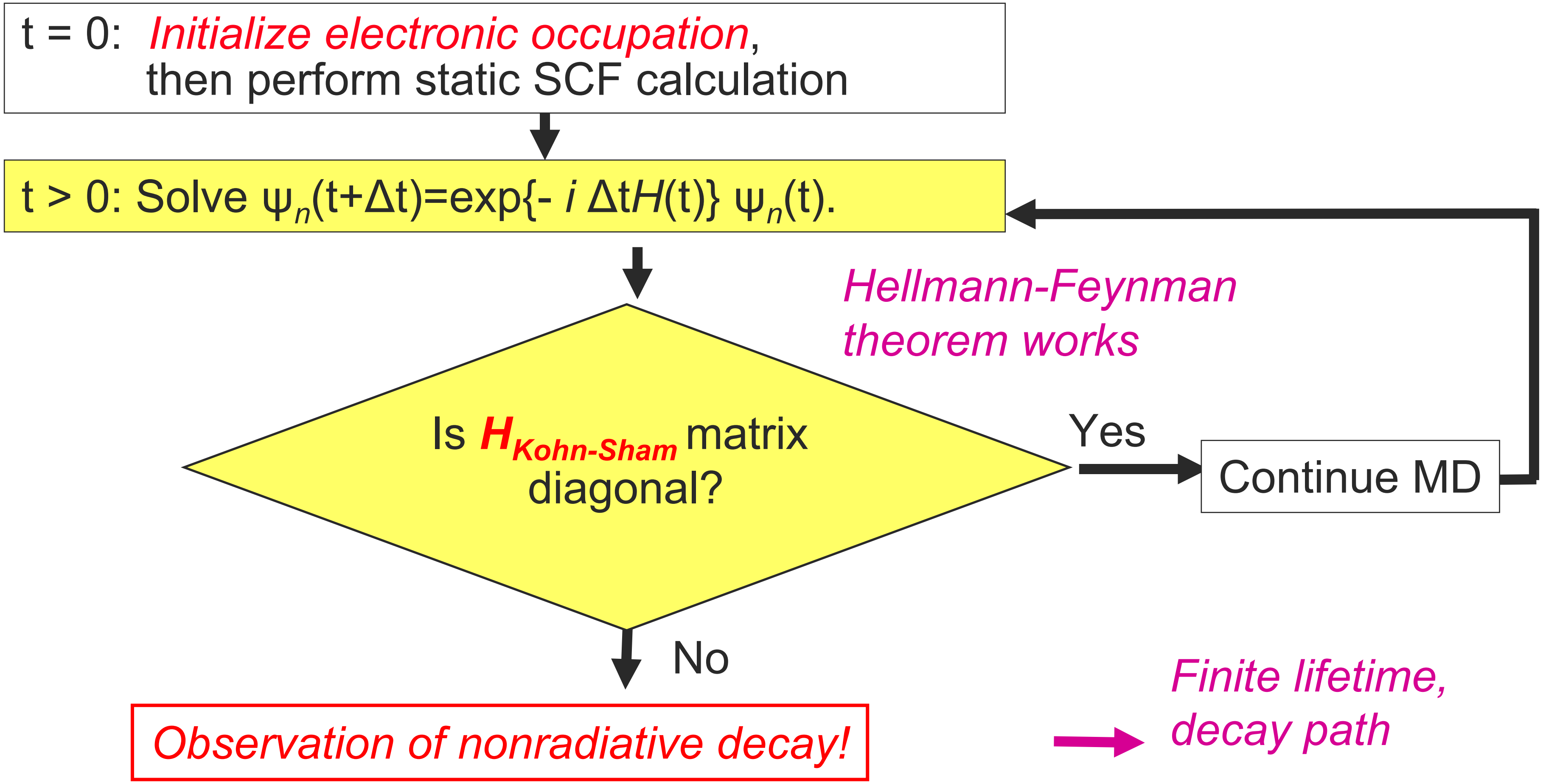
$$i\hbar \frac{d\psi_n}{dt} = H\psi_n$$

FPSEID (éf-psái-dí:)

First-**P**rinciples **S**imulation tool for **E**lectron-**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 $\psi_n(t+\Delta t)=\exp\{-i\,\Delta t H(t)\}\,\psi_n(t)$.

Hellmann-Feynman theorem works

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

Yes

Continue MD

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

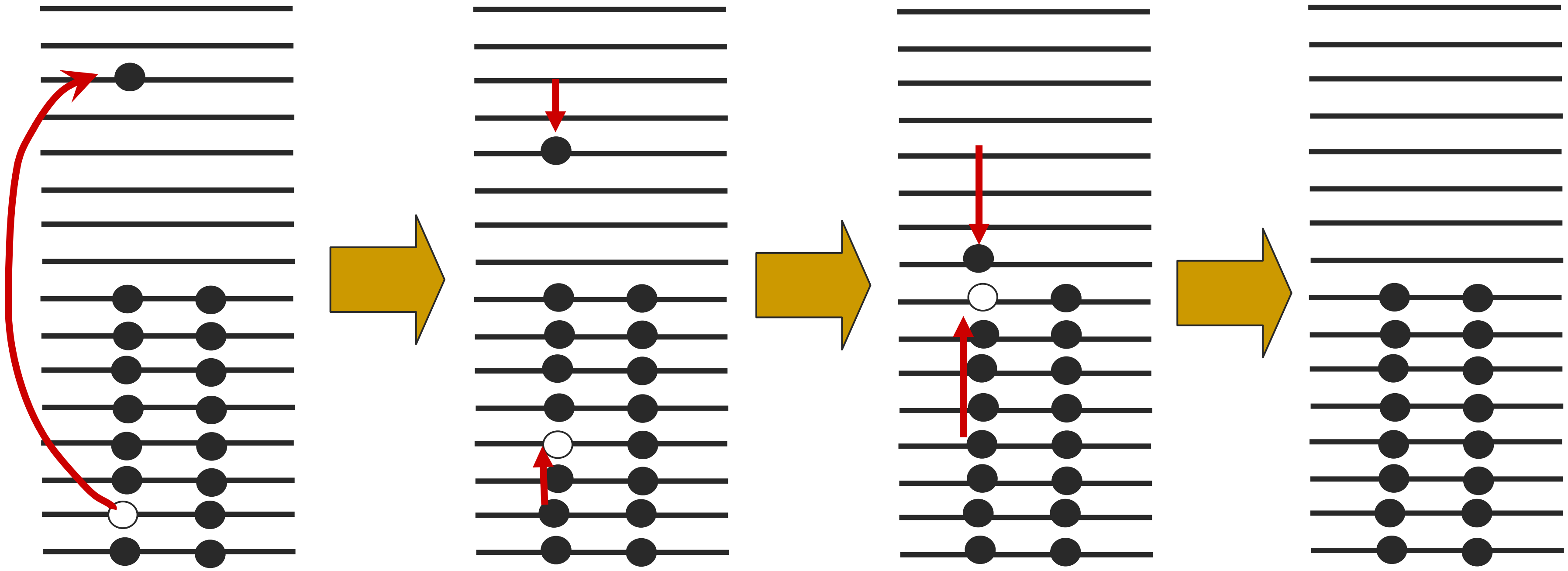
SAN FRANCISCO, April 19 — A Japanese laboratory has built the world's fastest computer, a machine so powerful that it matches the raw processing power of the 20 fastest American computers combined and far outstrips the previous leader, an I.B.M.-built machine.

Cost: $500,000,000

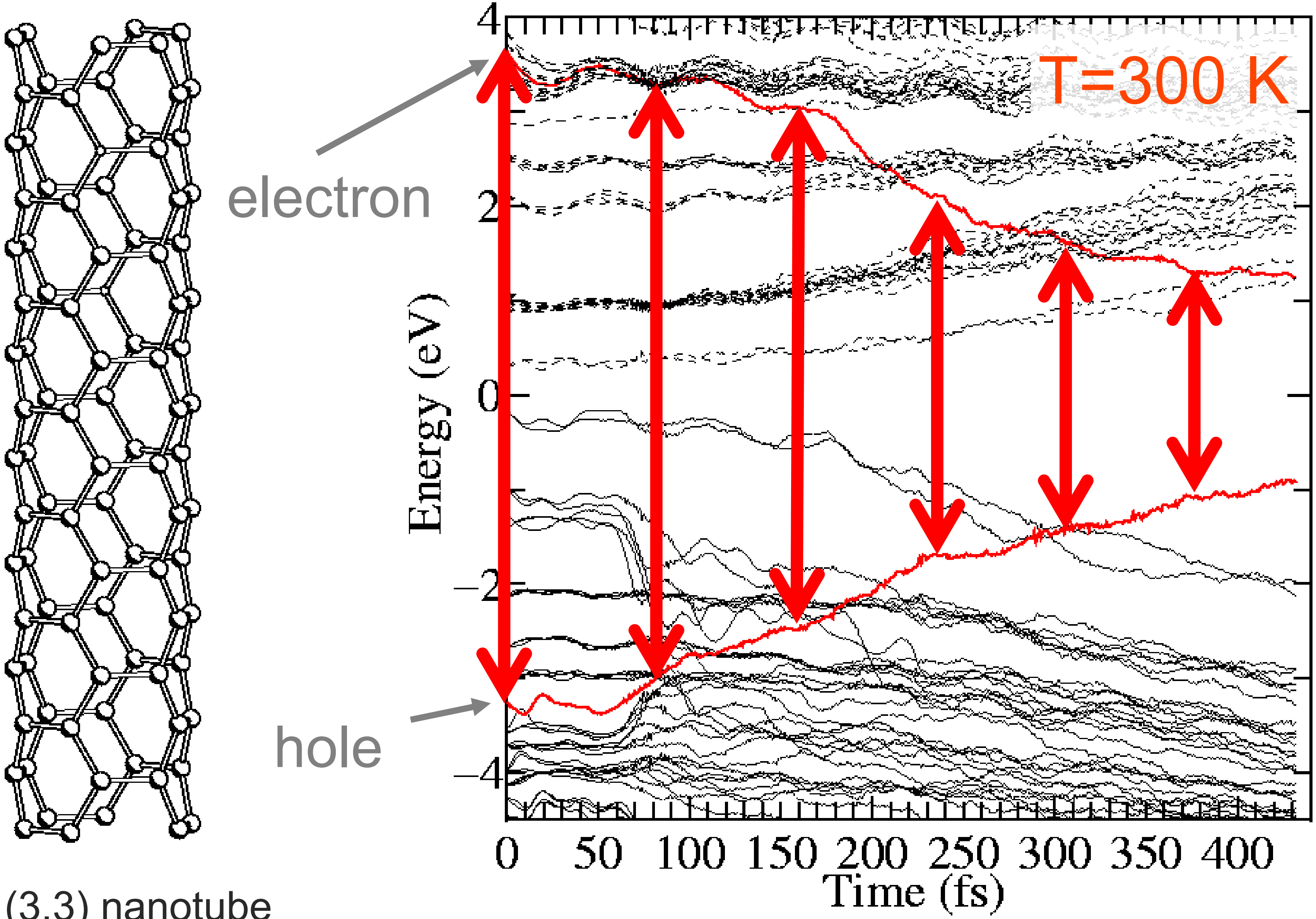
Maintenance: $50,000,000/year

<70% used for nano-carbons

Creation and decay of an electron-hole excitation



Long lifetime of electronic excitations



(3,3) nanotube

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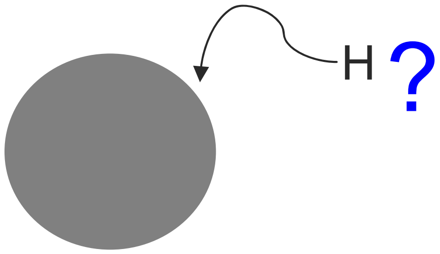
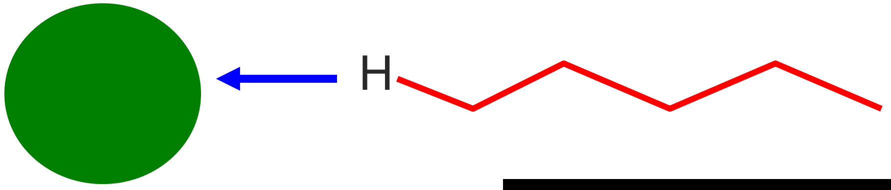
Chemical modification of nanocarbons

Hydrogenation of nanocarbons by wet chemistry

- Can fullerenes, nanotubes be hydrogenated by wet chemistry?
- Which is the reaction mechanism ?
- Does hydrogen cause structural changes?

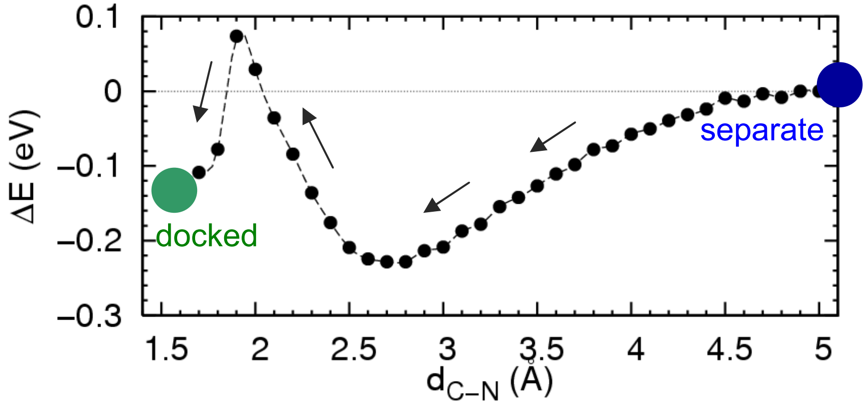


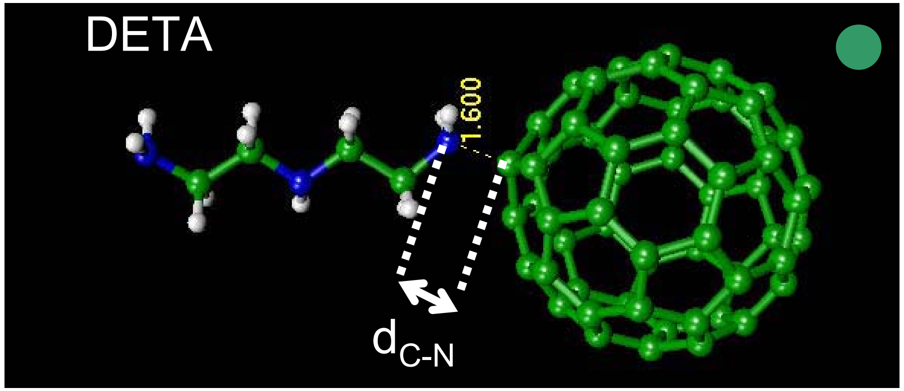
Hydrogenation of C_{60} by DETA: possible pathway



DETA is a source of H

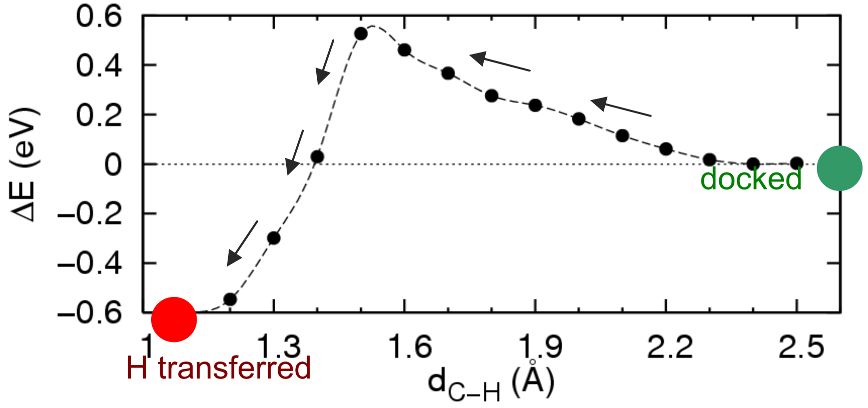
Step 1: docking



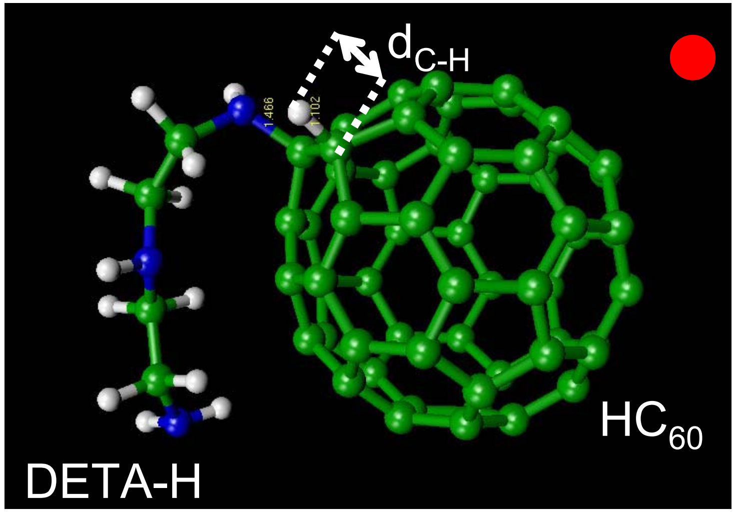


DETA docking on C_{60} is exothermic

Step 2: H transfer



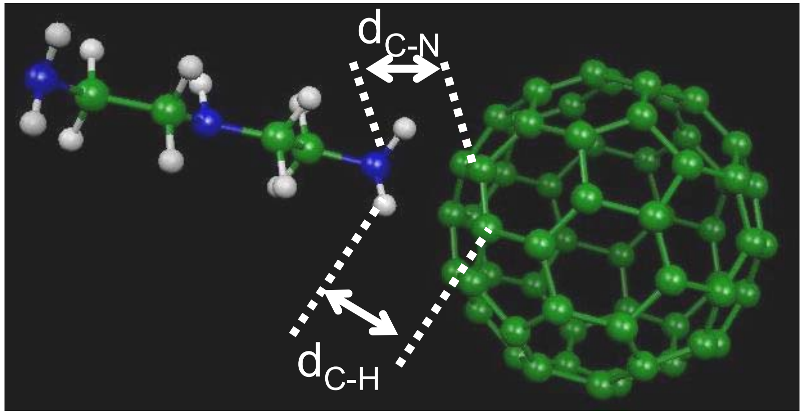
Moderate barrier, exothermic reaction



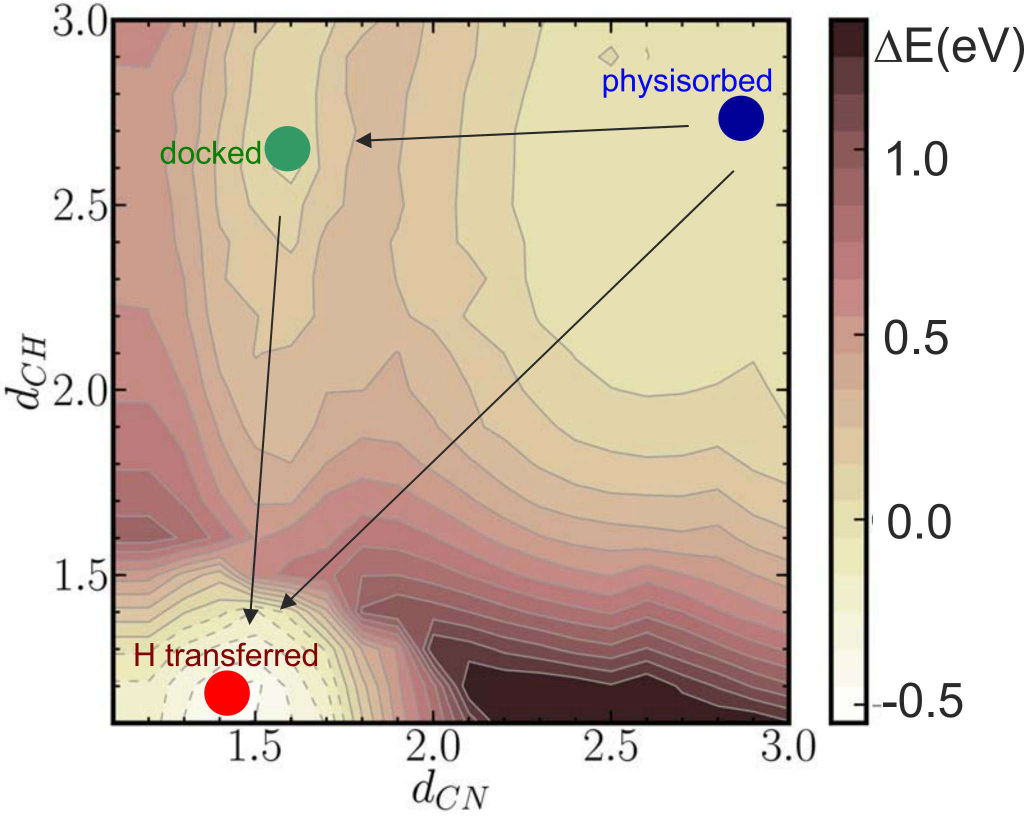
Is this the best reaction pathway?

Optimum hydrogenation pathway of C_{60} by DETA

Full energy landscape search



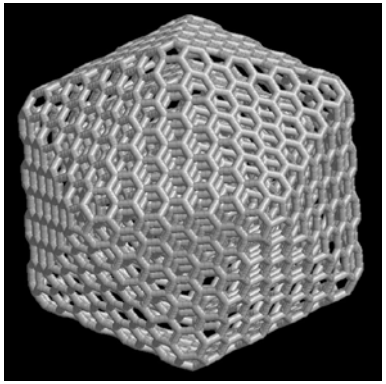
- Reaction must end with adsorbed radical, regardless of pathway
- Hydrogenation of C_{60} by wet chemistry is feasible and may apply also to other nanocarbons



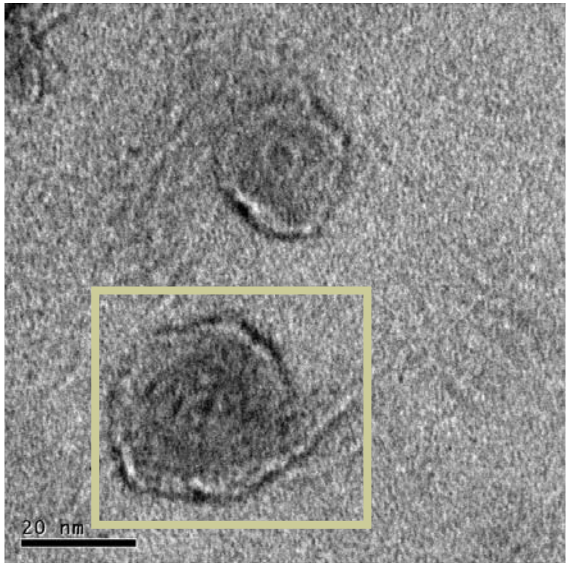
Docked DETA has a shallow energy landscape → efficient H transfer

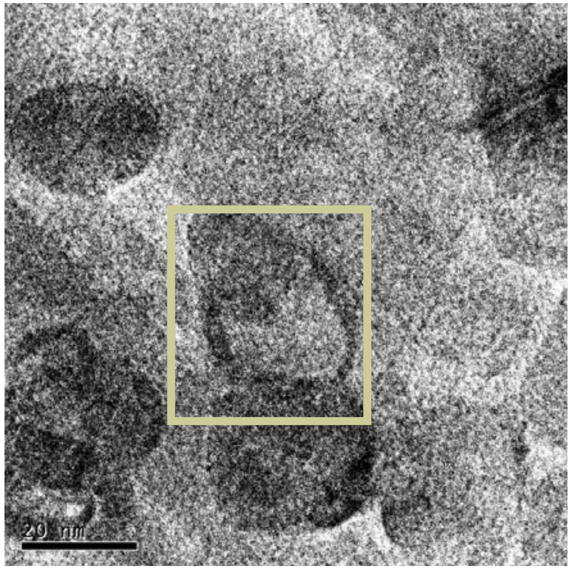
Peeling fullerenes by hydrogen

- Opening a multi-wall fullerene (bucky onion)



- Carbon onions (from arcing) hydrogenated by DETA

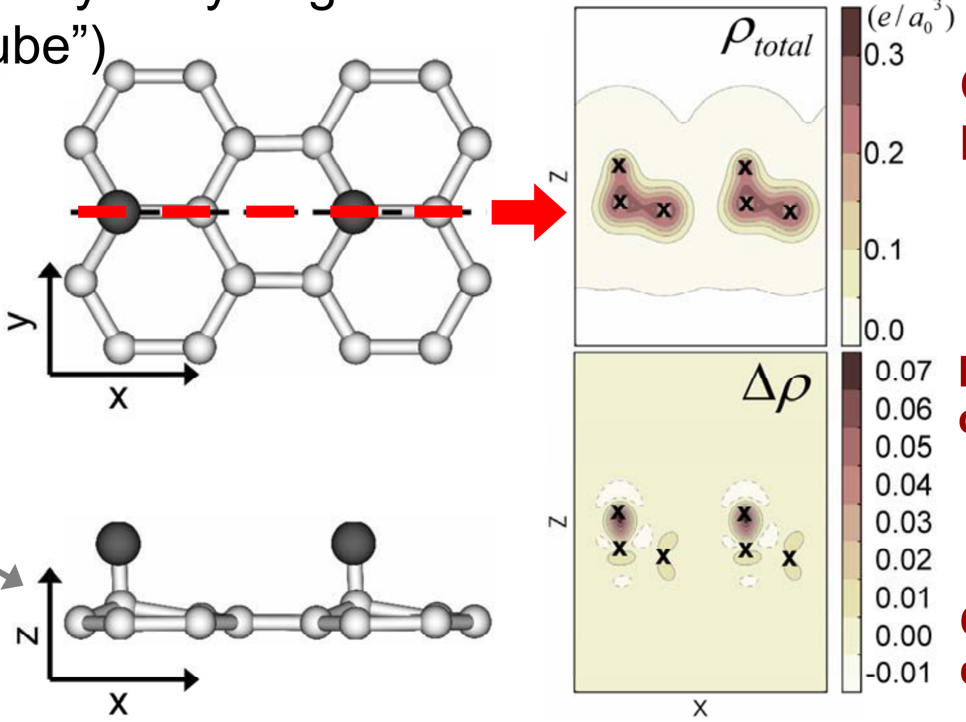




Glen P. Miller
(University of
New Hampshire)

Hydrogen adsorption on sp^2 carbon

Optimum adsorption geometry of hydrogen on graphene ("very fat nanotube")



Top view

Pyramidalization due to sp^3 bonding

Side view

Covalent bonds

Excess charge

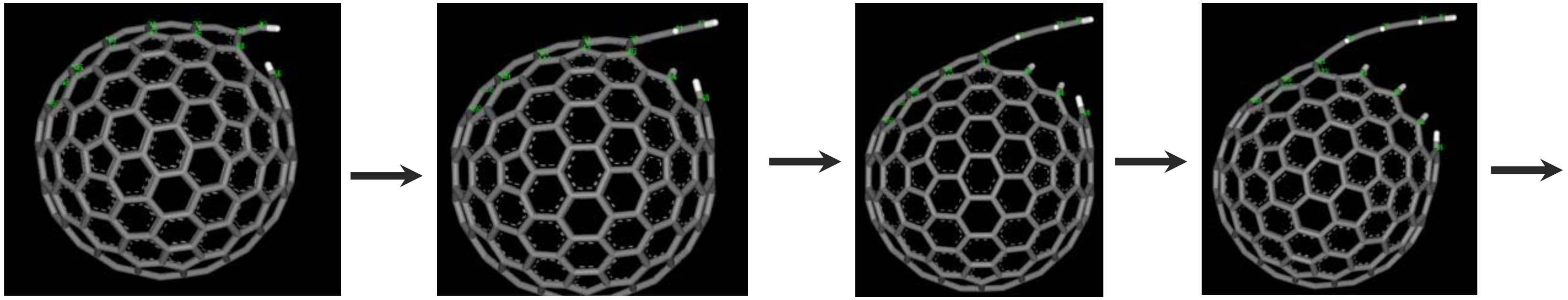
Charge deficiency

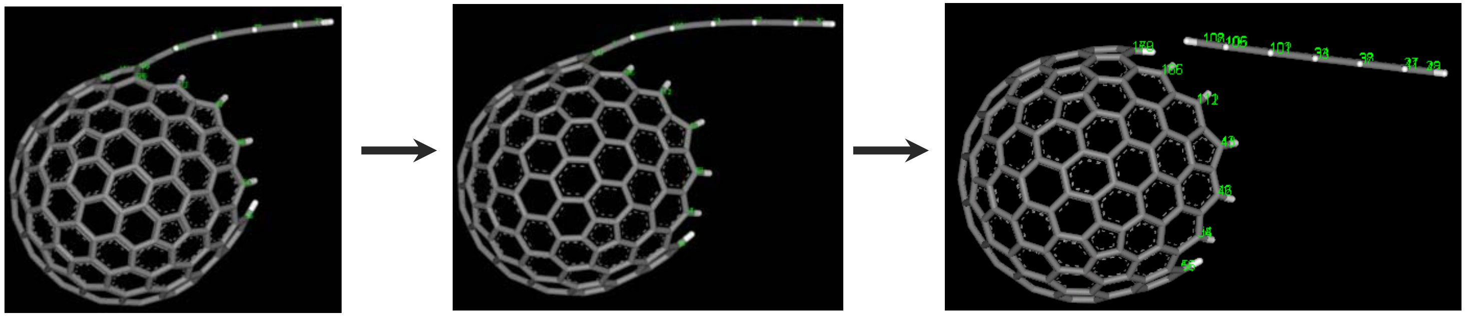
Charge density difference: $\Delta\rho = \rho_{tot}(H/CNT) - [\rho_{tot}(CNT)+\rho_{tot}(H)]$

Hydrogen bonding to sp^2 bonded nanocarbons:

Additional *sp^3* character due to finite curvature → **Strong covalent bonds especially in narrow nanotubes**

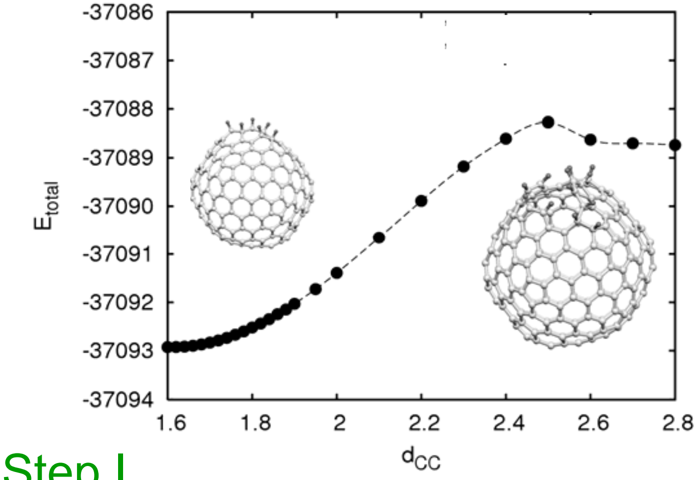
Dreams about ways to peel a large fullerene



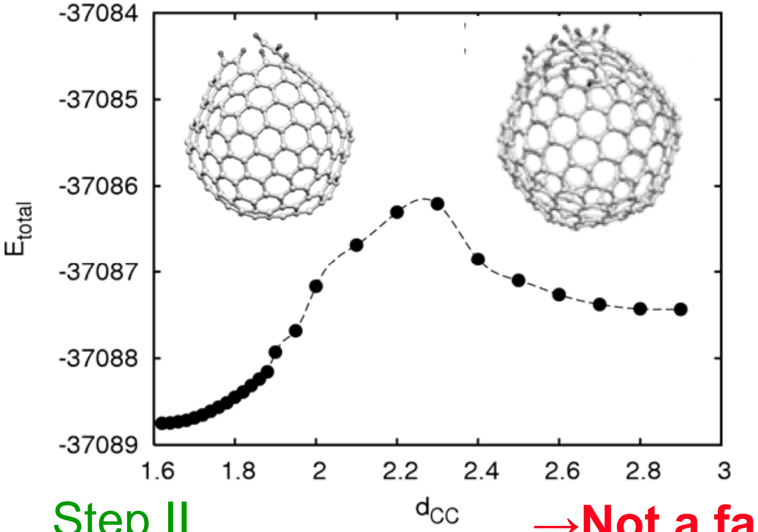


Two H pairs added in each step

Energetics is less promising



Step I

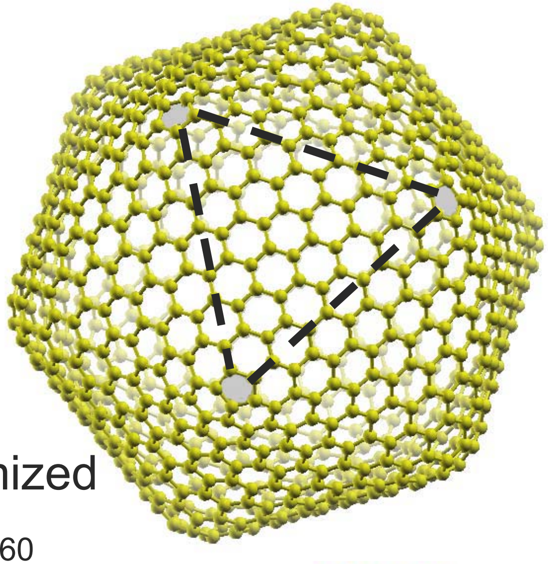


Step II

→Not a fast reaction

Favorable adsorption sites for hydrogen

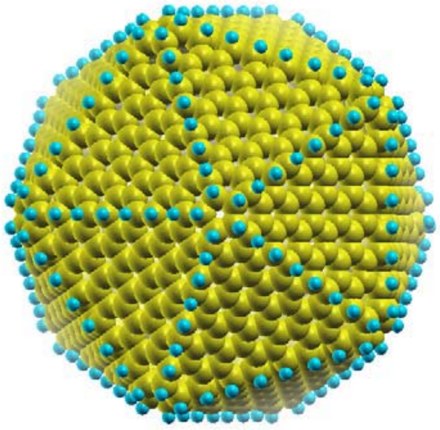
Hydrogens prefers to adsorb in pairs



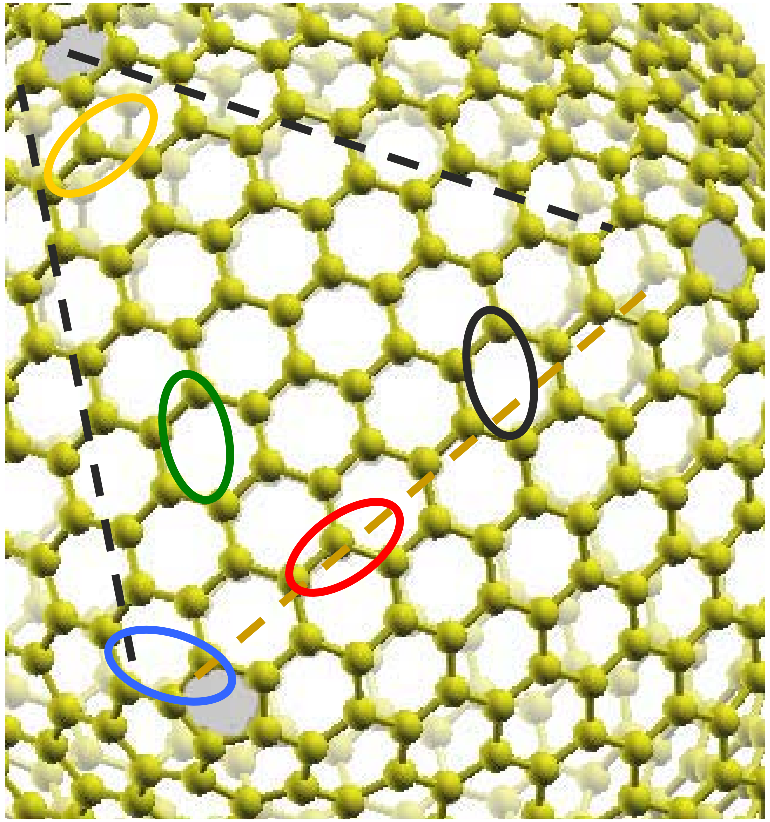
Optimized
C_{960}

● C

● H



Optimized
H-C_{960}



$\Delta E=-1.351$ eV

$\Delta E=-1.203$ eV

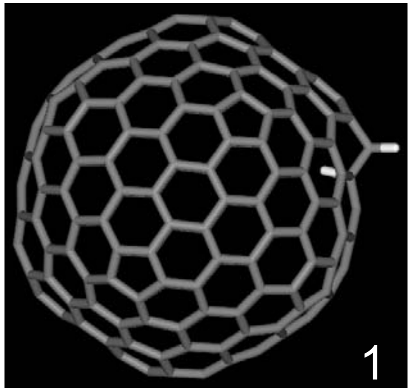
$\Delta E=-0.555$ eV

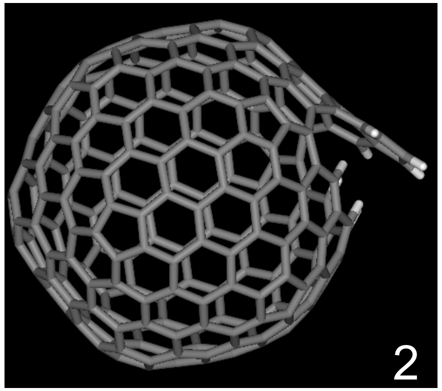
$\Delta E=-0.672$ eV

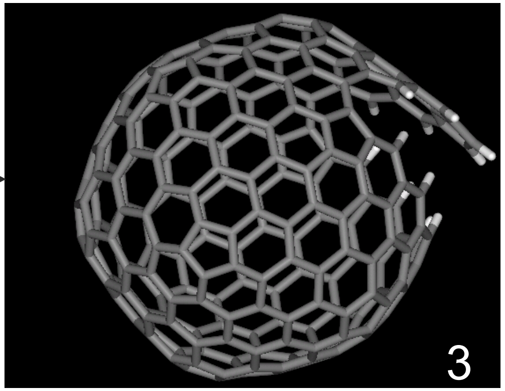
$\Delta E=-1.203$ eV

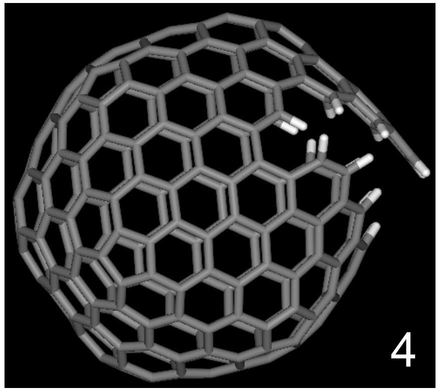
Adsorption first on edge, then near edge

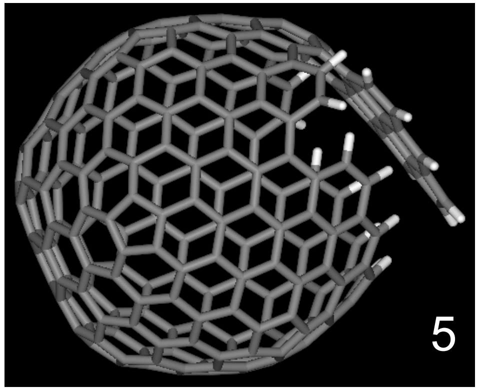
Peeling a large fullerene using edge hydrogenation

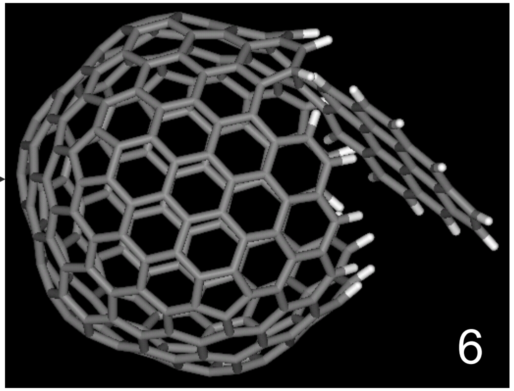


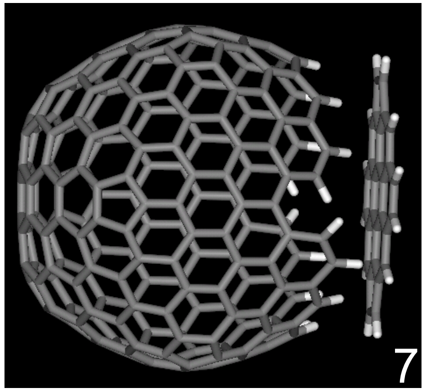




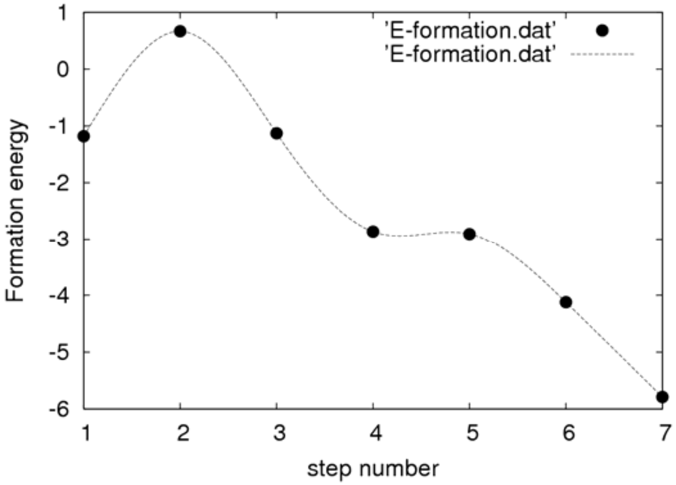






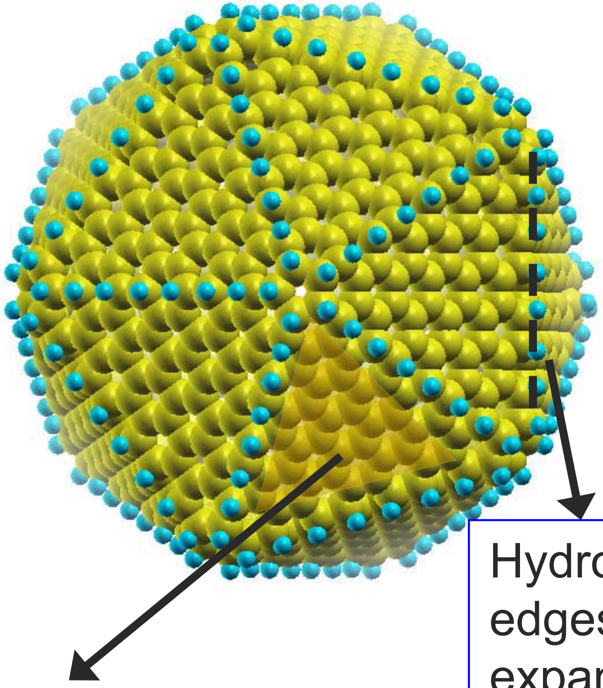


- Formation energies of intermediate steps are promising!
- What about energy barriers?



Modeling edge hydrogenation

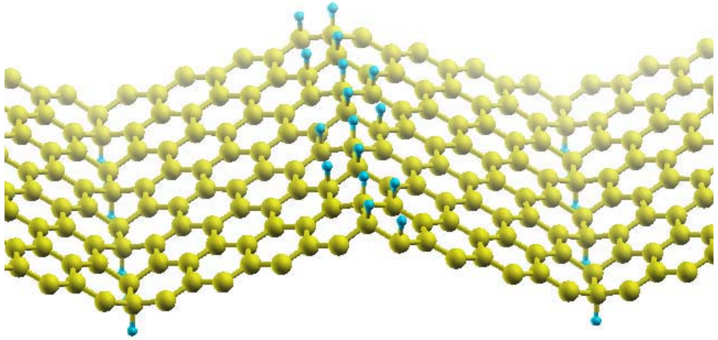
Regions with different relaxation requirements



Hydrogenated edges want to expand!

Facets are rigid graphene pieces: Unwilling to expand!

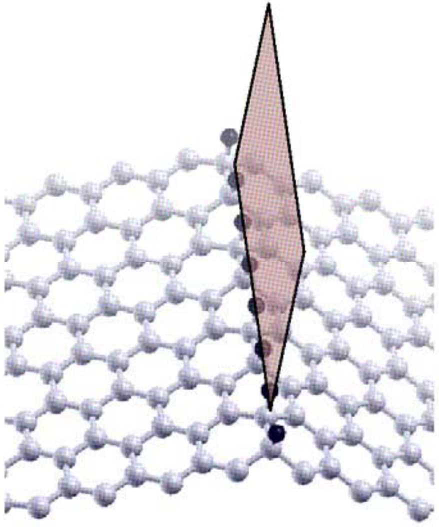
- Edge strain energy increases with edge length
- Large fullerenes more likely to burst by hydrogenation
- Very large systems necessary → calculations on model system
- Zipper-like edge opening most likely

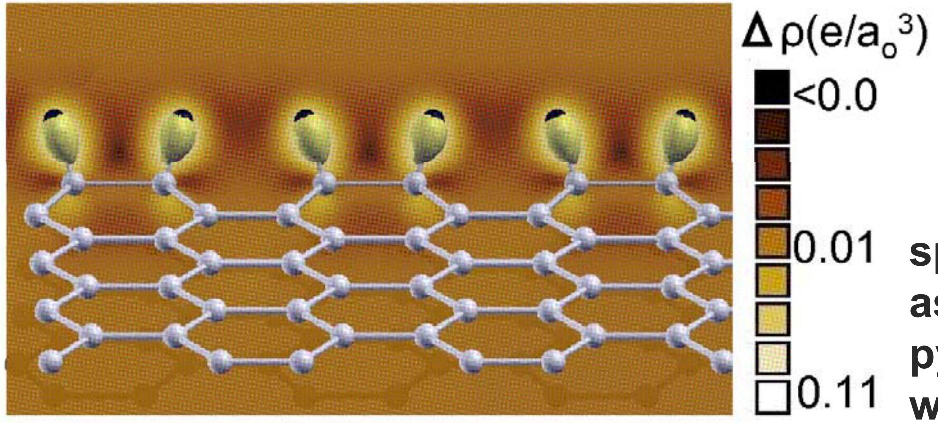


Structure used to model edge hydrogenation

Hydrogen-induced decohesion

Charge redistribution near a bent edge



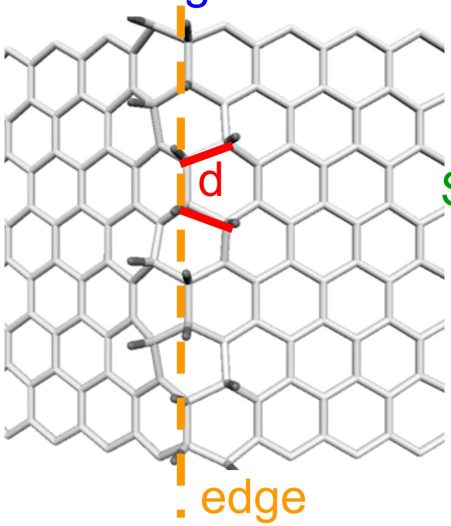


sp^3 hybridization associated with pyramidalization weakens bonds

Savas Berber and David Tománek, Hydrogen-induced exfoliation of fullerenes and nanotubes: An ab initio study, Phys. Rev. B **80**, 075427 (2009).

Energetics of an unzipping step

The length of the C-C bond d is taken as reaction coordinate



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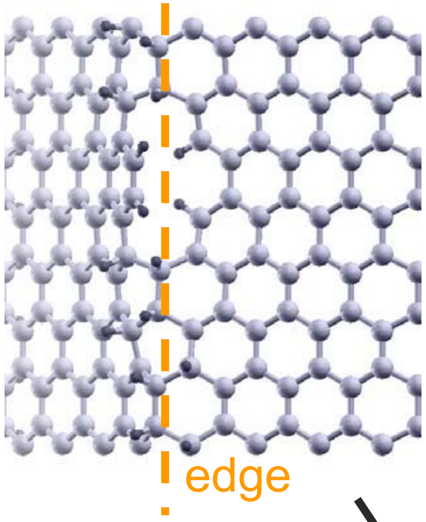
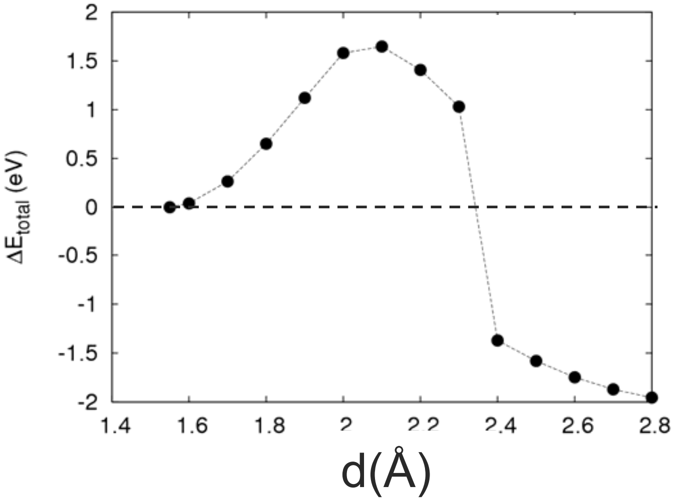
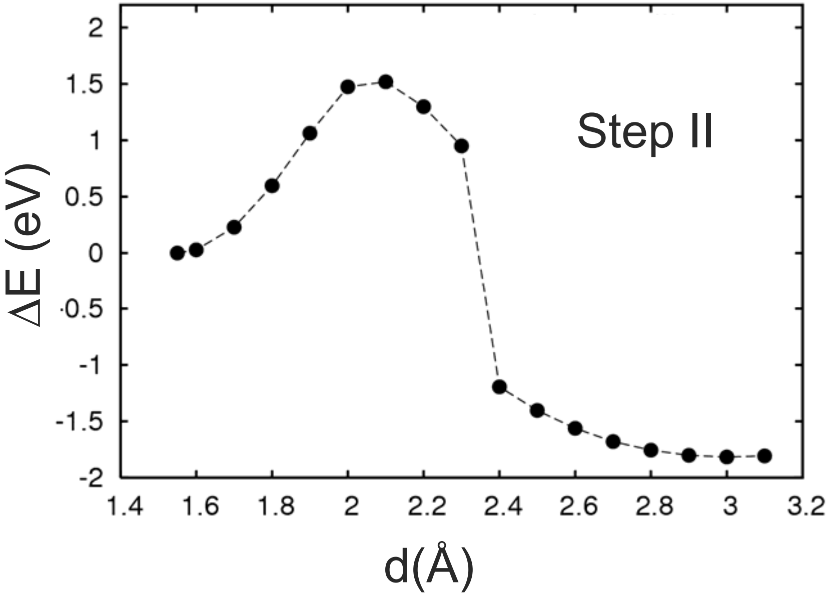
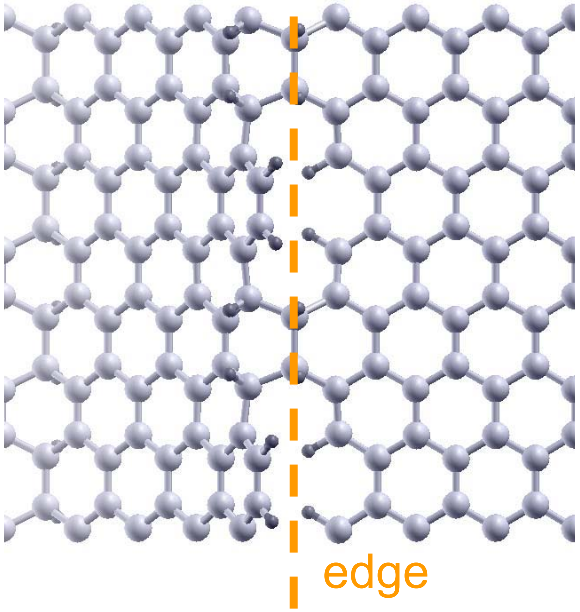


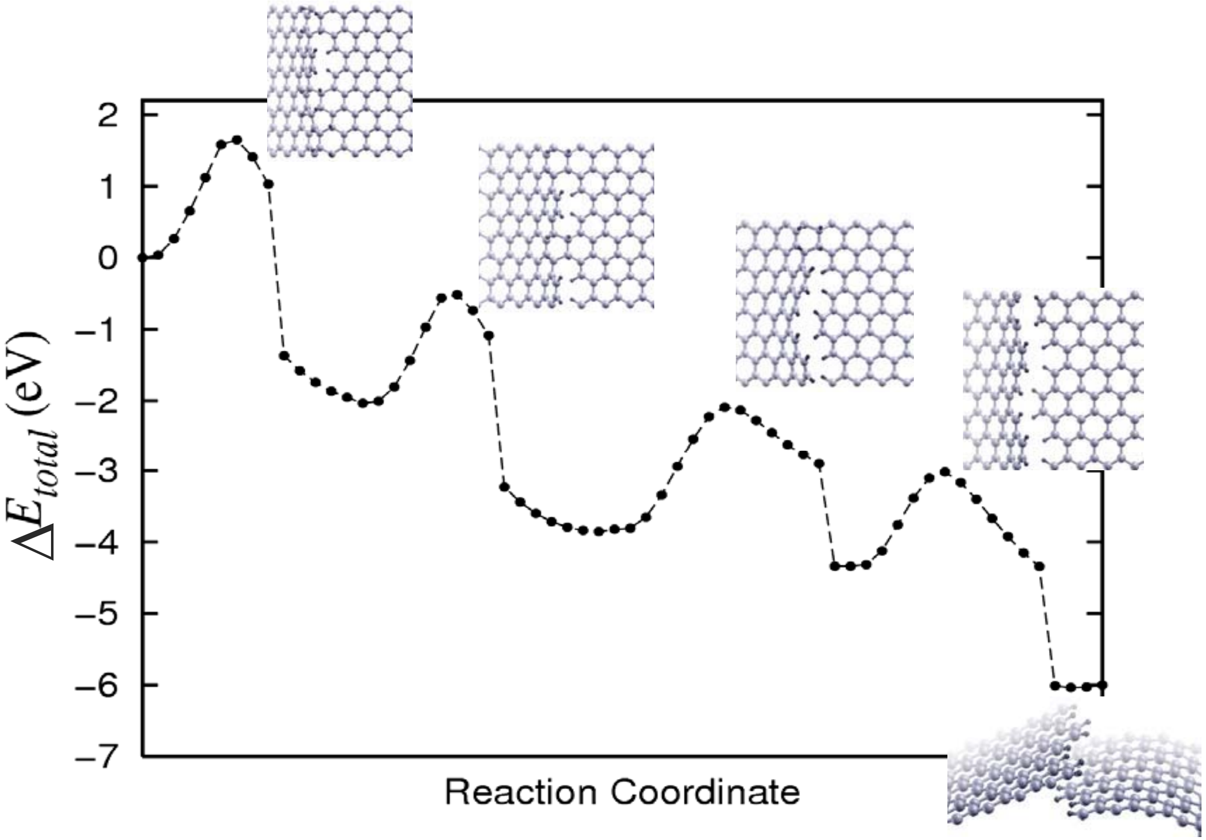


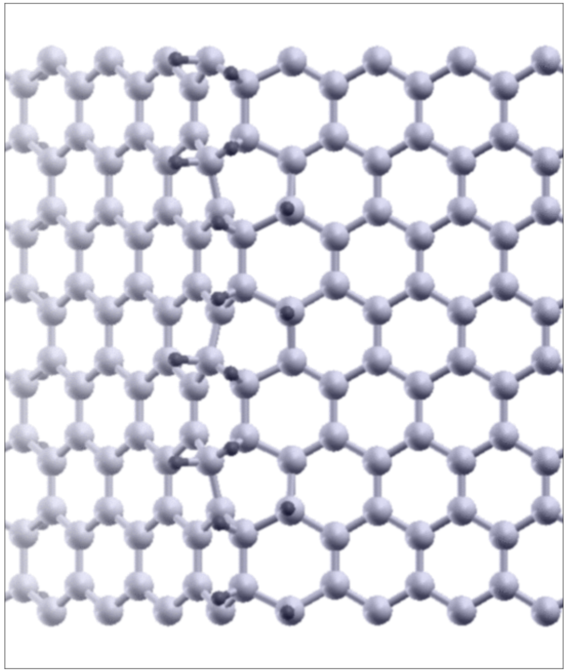
Step II





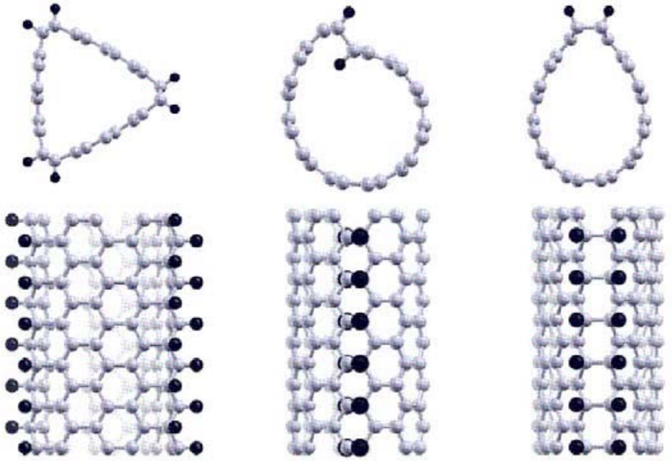
Energetics along the complete unzipping path





- ❖ C-C bonds break in pairs
- ❖ Net exothermic process, once started, is likely to continue

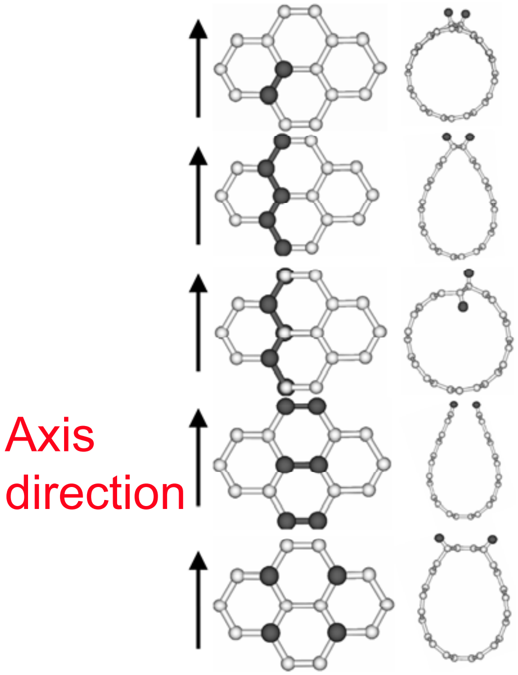
Unzipping nanotubes by hydrogen



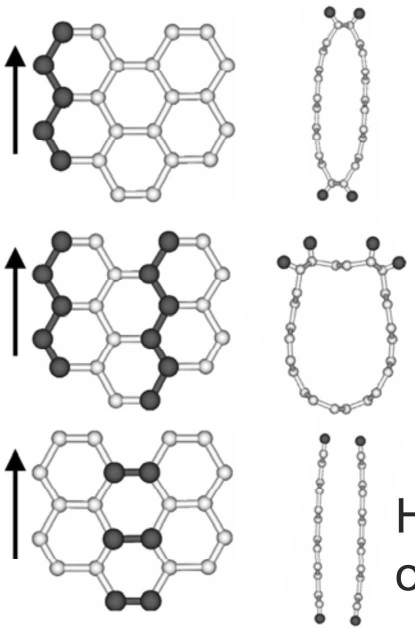
Preferred adsorption geometry: axially aligned chains of hydrogen

(6,6) nanotube deformation
following hydrogen adsorption

Optimum adsorption geometries



Low H coverage
on a (6,6) CNT

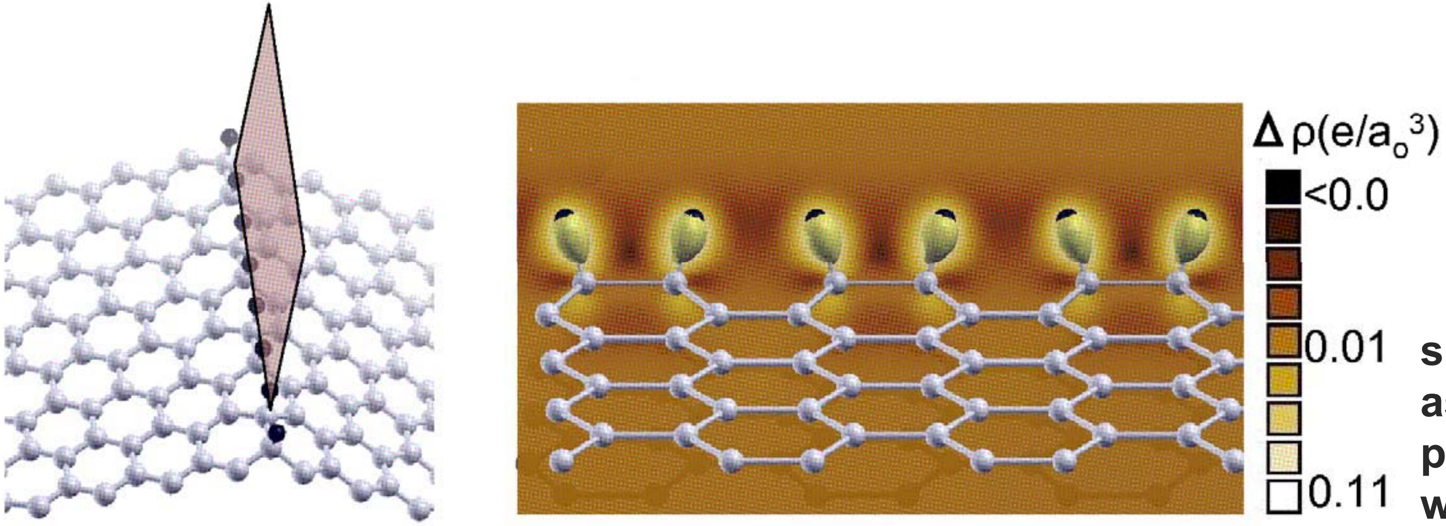


High H coverage
on a (6,6) CNT

Glen P. Miller, Jeremy Kintigh, Eunja Kim, Philippe F. Weck, Savas Berber, and David Tománek, J. Am. Chem. Soc. 130, 2296 (2008).

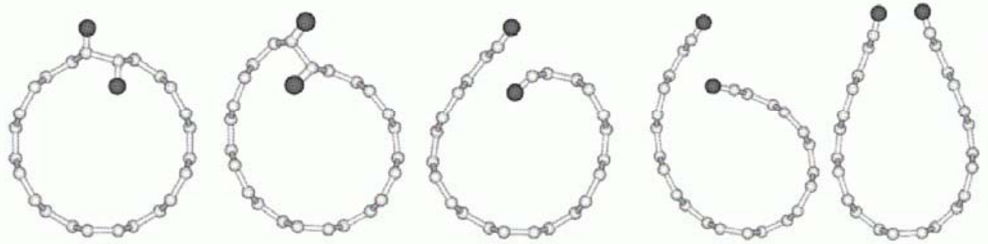
Worst-case scenario: irreversible reconstruction

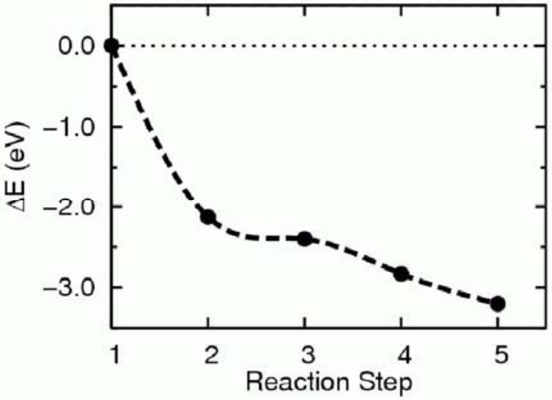
Charge redistribution near a bent edge



sp^3 hybridization associated with pyramidalization weakens bonds

Activation-free unzipping





Savas Berber and David Tománek, Hydrogen-induced exfoliation of fullerenes and nanotubes: An ab initio study, Phys. Rev. B **80**, 075427 (2009).

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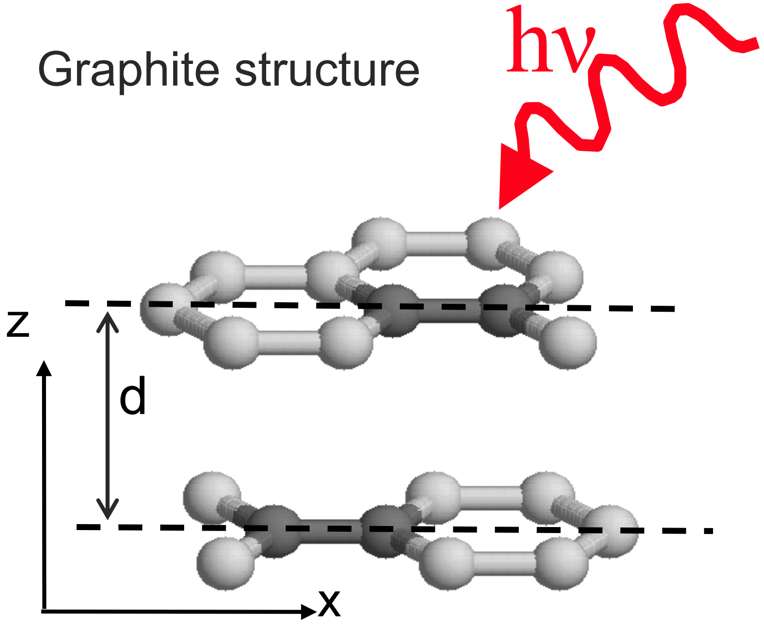
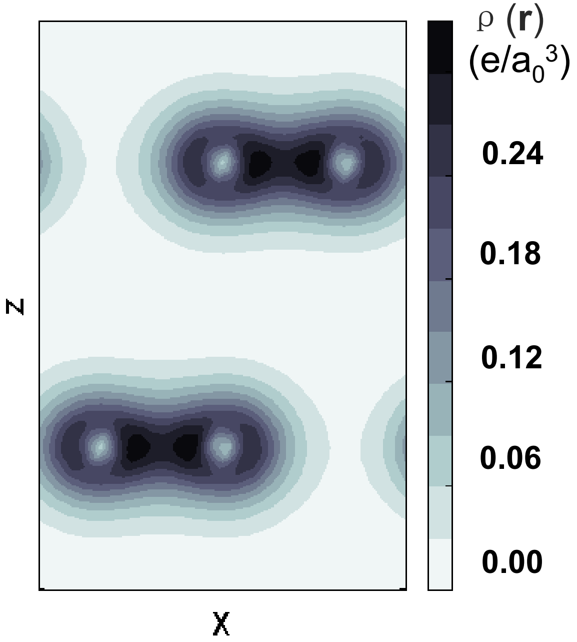
Excited state engineering of nanocarbons

Transforming graphite to diamond by photons

Graphite structure



Total charge density

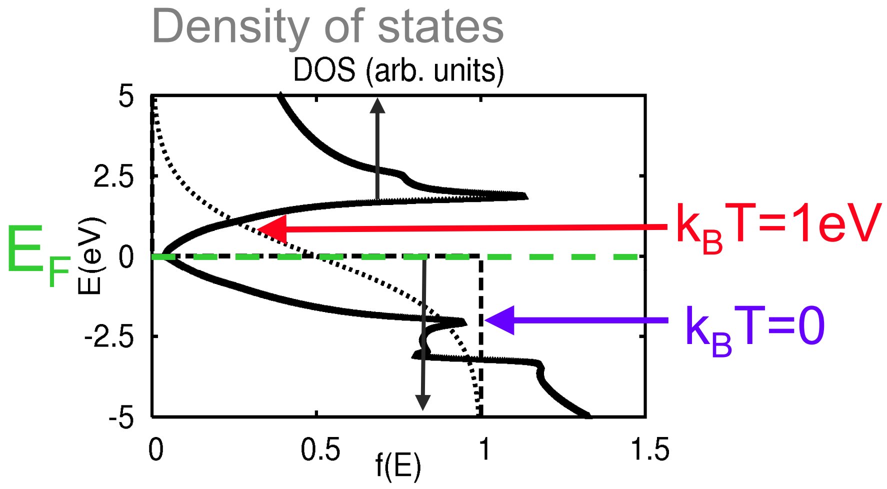


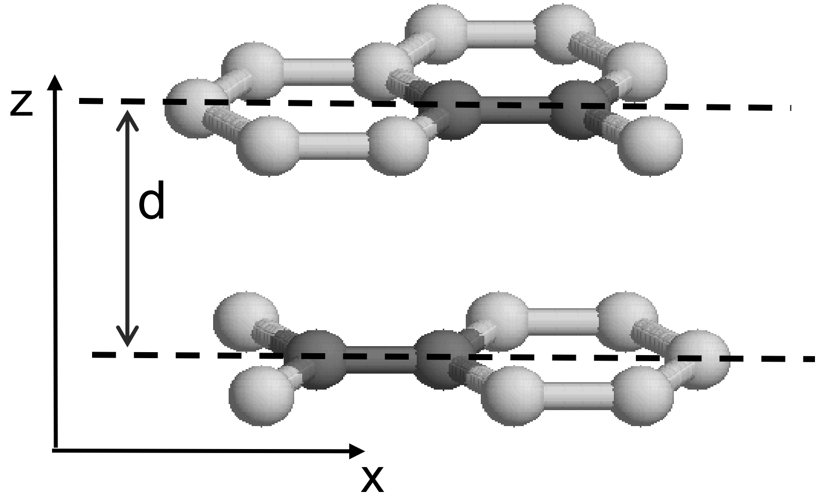
- Can light transform graphite to diamond?

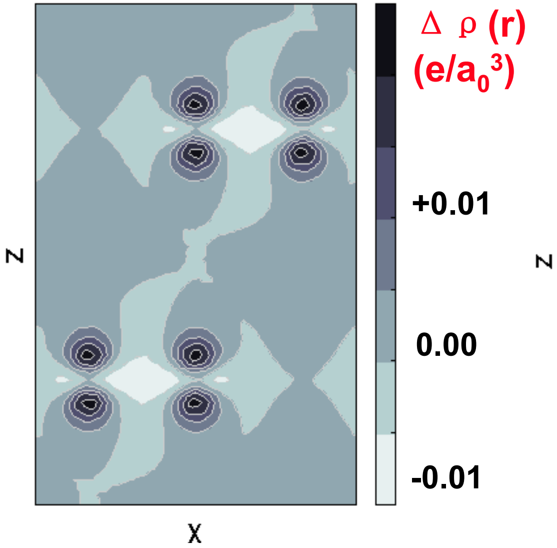
K. Raman, Yoshie Murooka, Chong-Yu Ruan, Teng Yang, Savas Berber, Y. Miyamoto and David Tománek, Phys. Rev. Lett. 101, 077401 (2008).

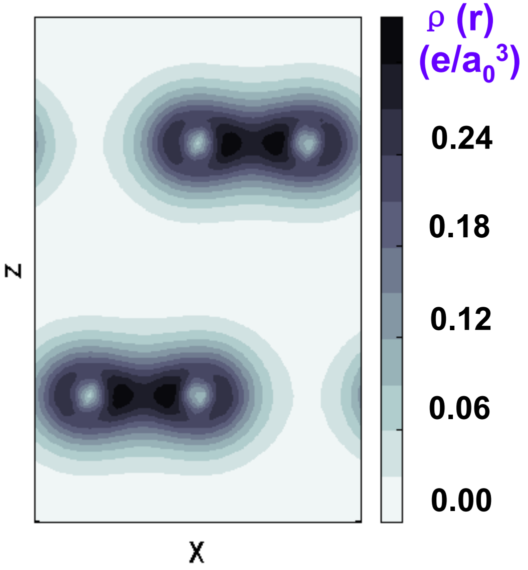
Nonthermal heating of the electron gas

- Occupy previously empty states in the DOS above E_F
- Occupying $2p_z$ states causes interlayer attraction
- Net contraction: $\Delta d_z \approx -0.04$Å





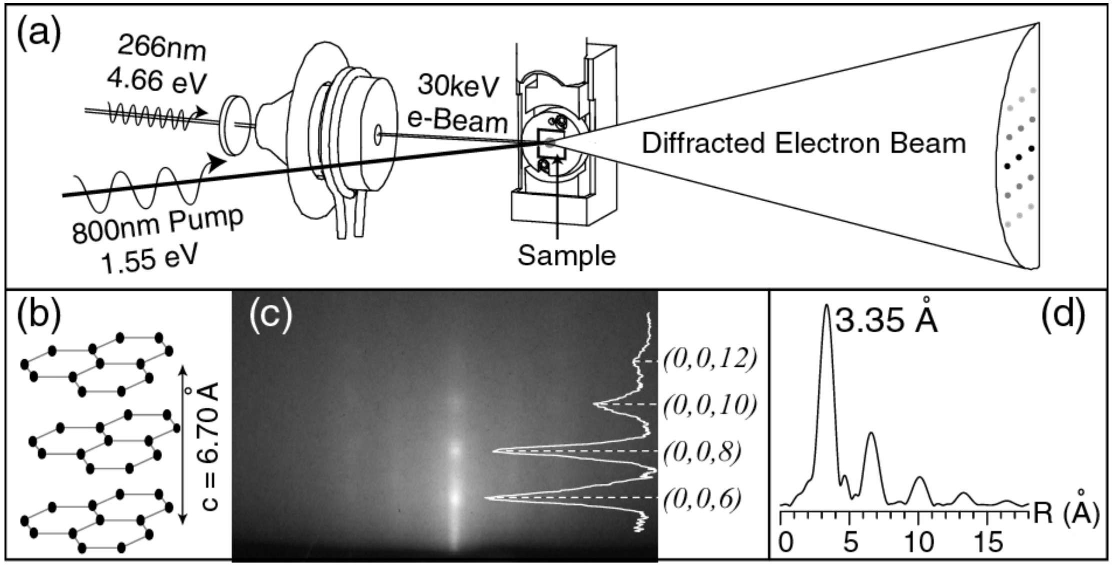




Charge density difference: $\Delta\rho = \rho_{tot}(k_BT=1eV) - \rho_{tot}(k_BT=0)$

Ultrafast electron crystallography results

- Time-resolved electron diffraction following laser pulse:
- Initial small interlayer expansion
- Sizeable interlayer contraction follows



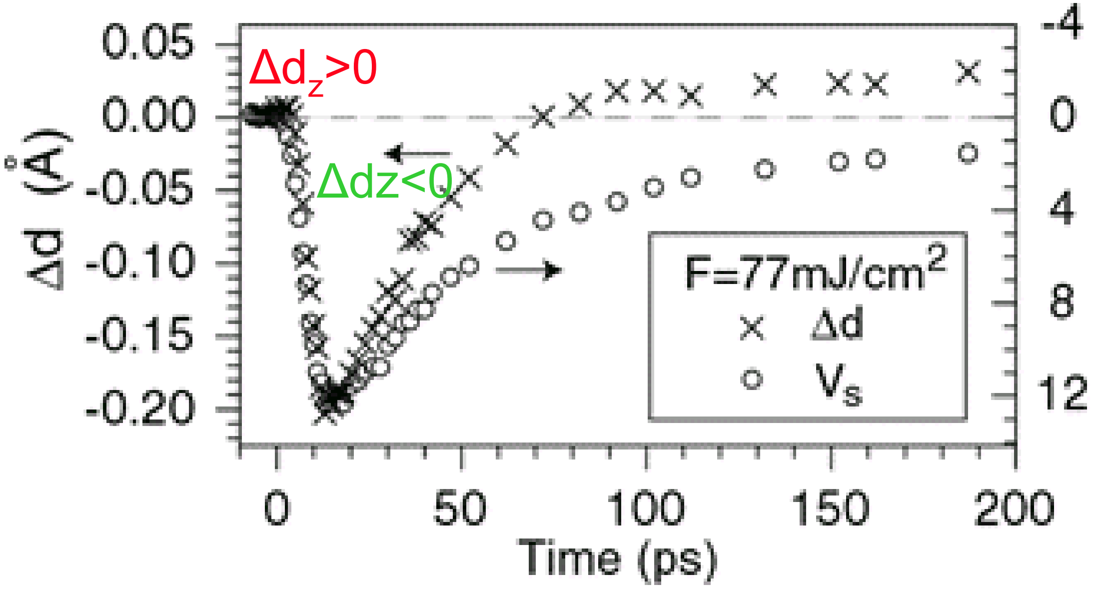
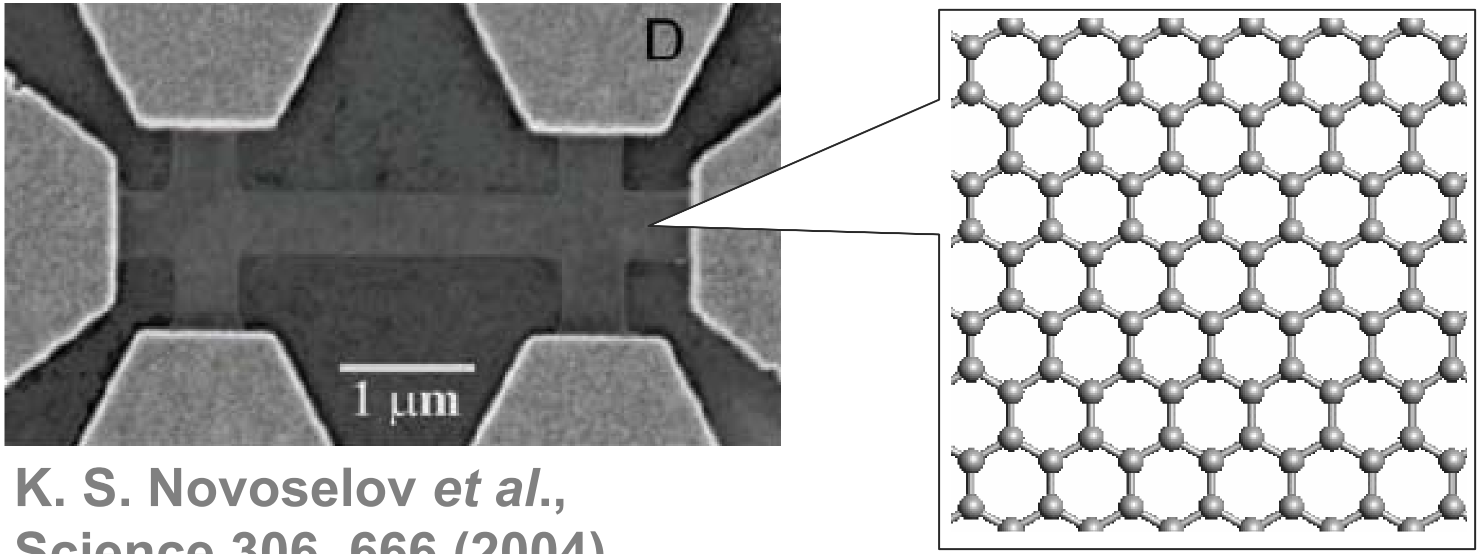


Photo-exfoliation of graphite to graphene

Graphene channel transistor: Real alternative to Si?



K. S. Novoselov *et al*., Science 306, 666 (2004)

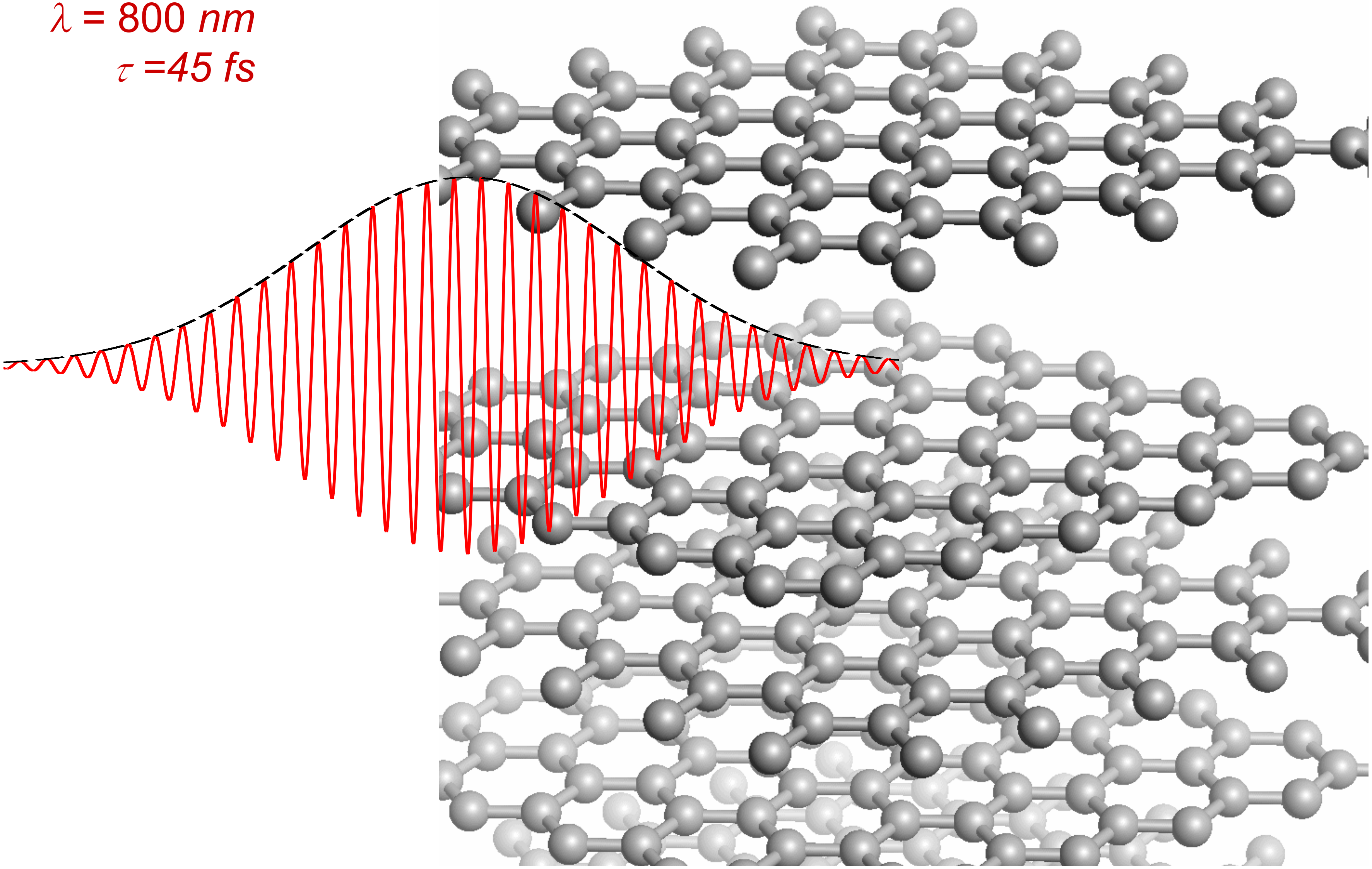
How to make this?

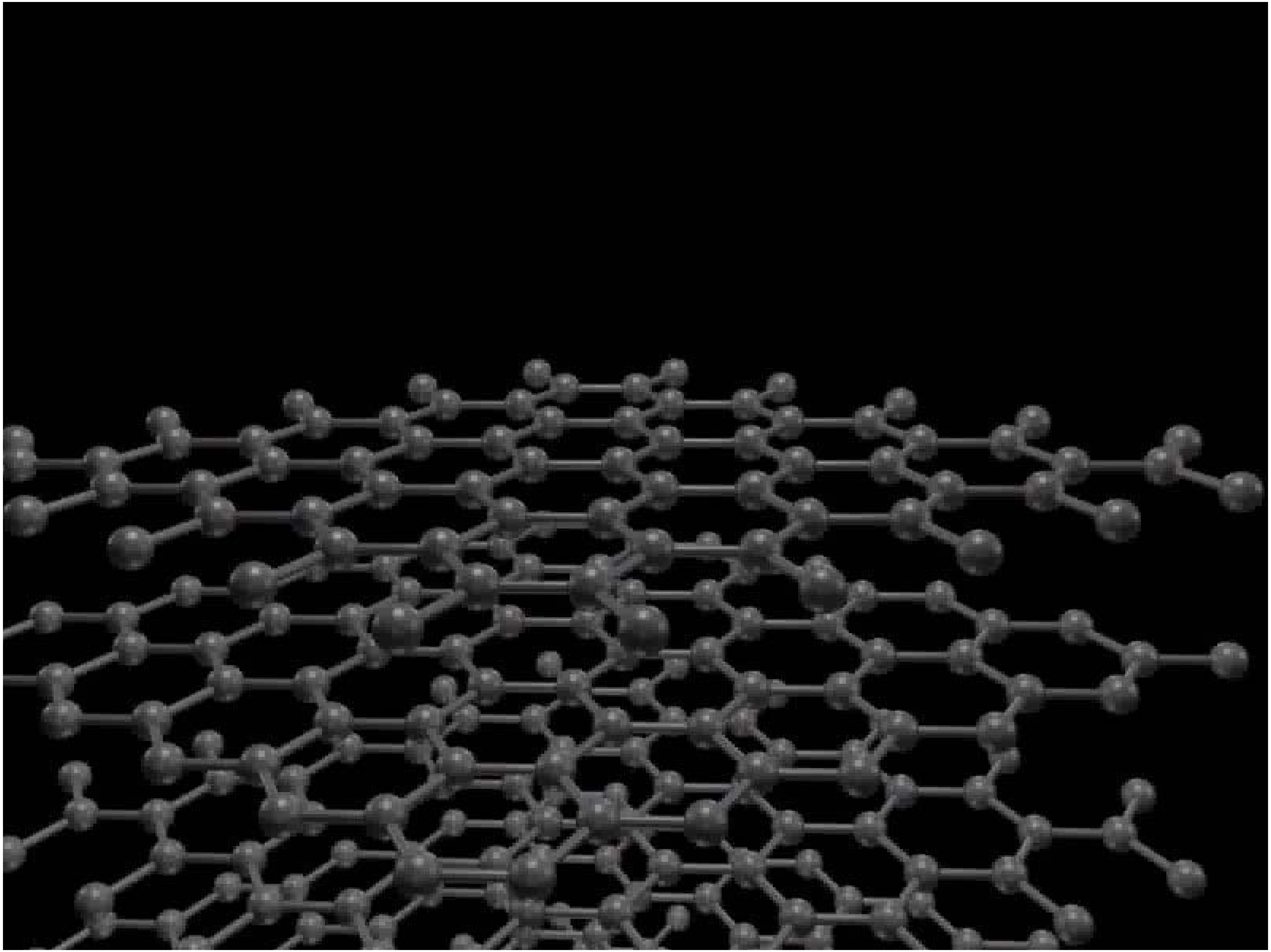
1. CVD on metal substrate
2. Exfoliation from graphite
   - Wet chemical process?
   - Scotch tape?
   - Other alternatives?

Laser irradiation

λ = 800 *nm*

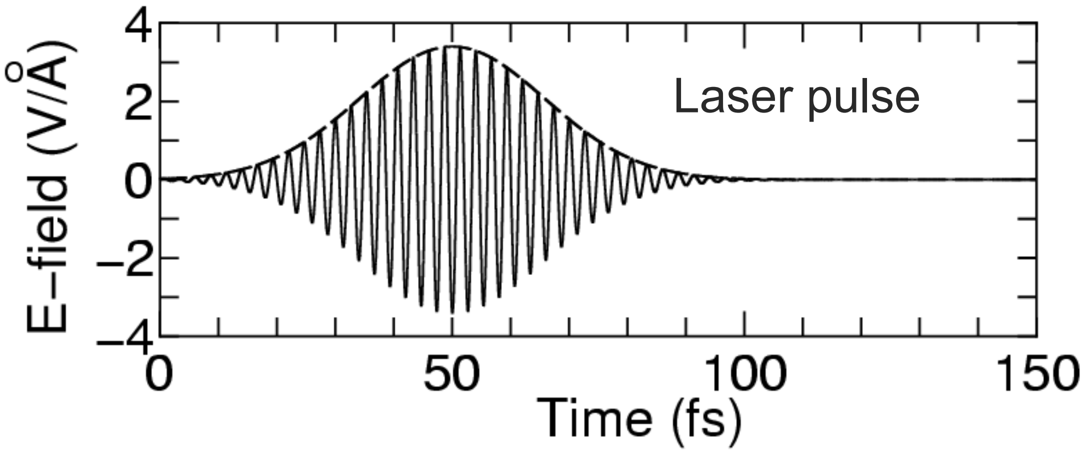
τ =*45 fs*

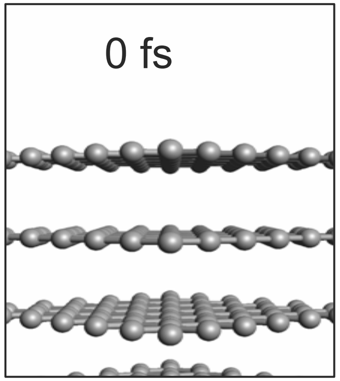




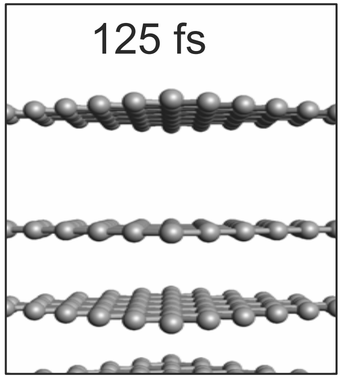
Expected graphene monolayer detachment following a laser pulse

- Describe coupling to laser field directly in the coupled TDDFT-MD formalism
- Yields both
    - charge redistribution among layers: Coulomb attraction/repulsion
    - Nonequilibrium occupation of electronic levels





Before irradiation

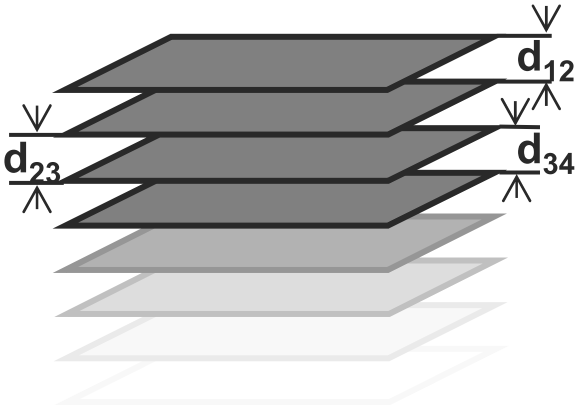


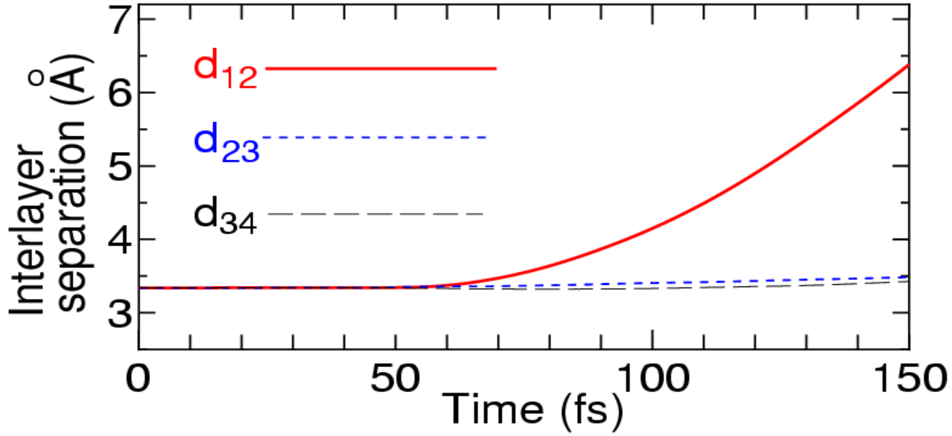
After irradiation: graphene detaches

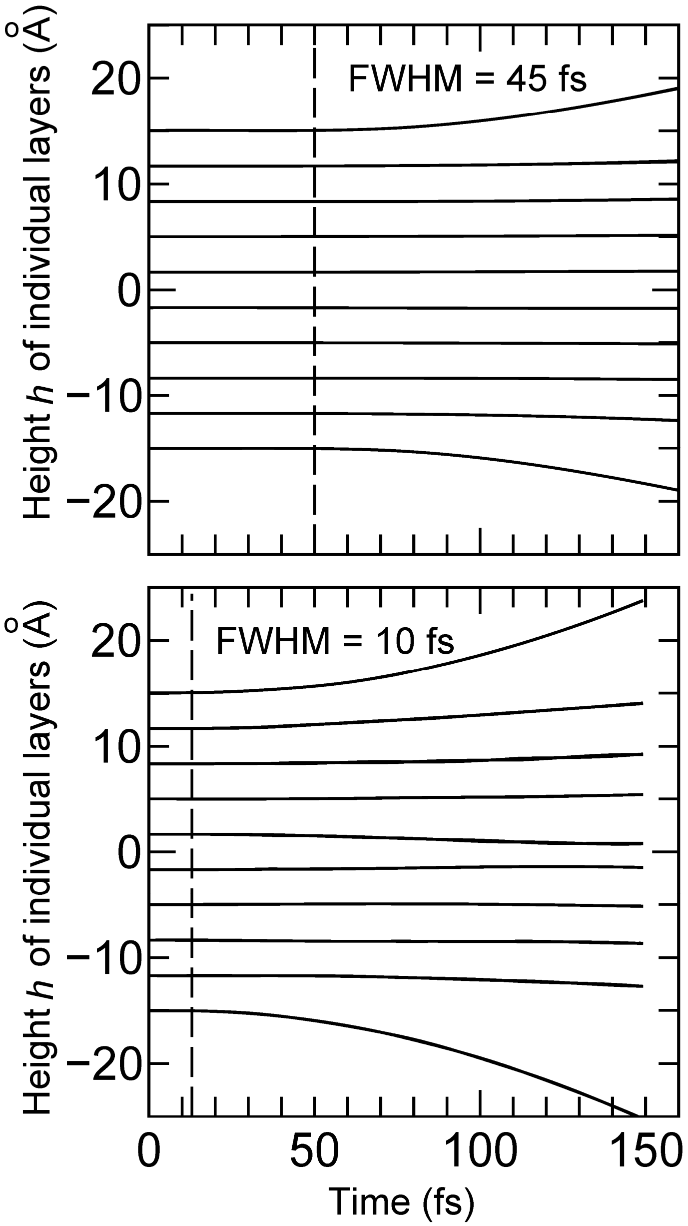
Yoshiyuki Miyamoto, Hong Zhang, and David Tománek, Photo-exfoliation of graphene from graphite: An *ab initio* study, Phys. Rev. Lett. (28 May 2010)

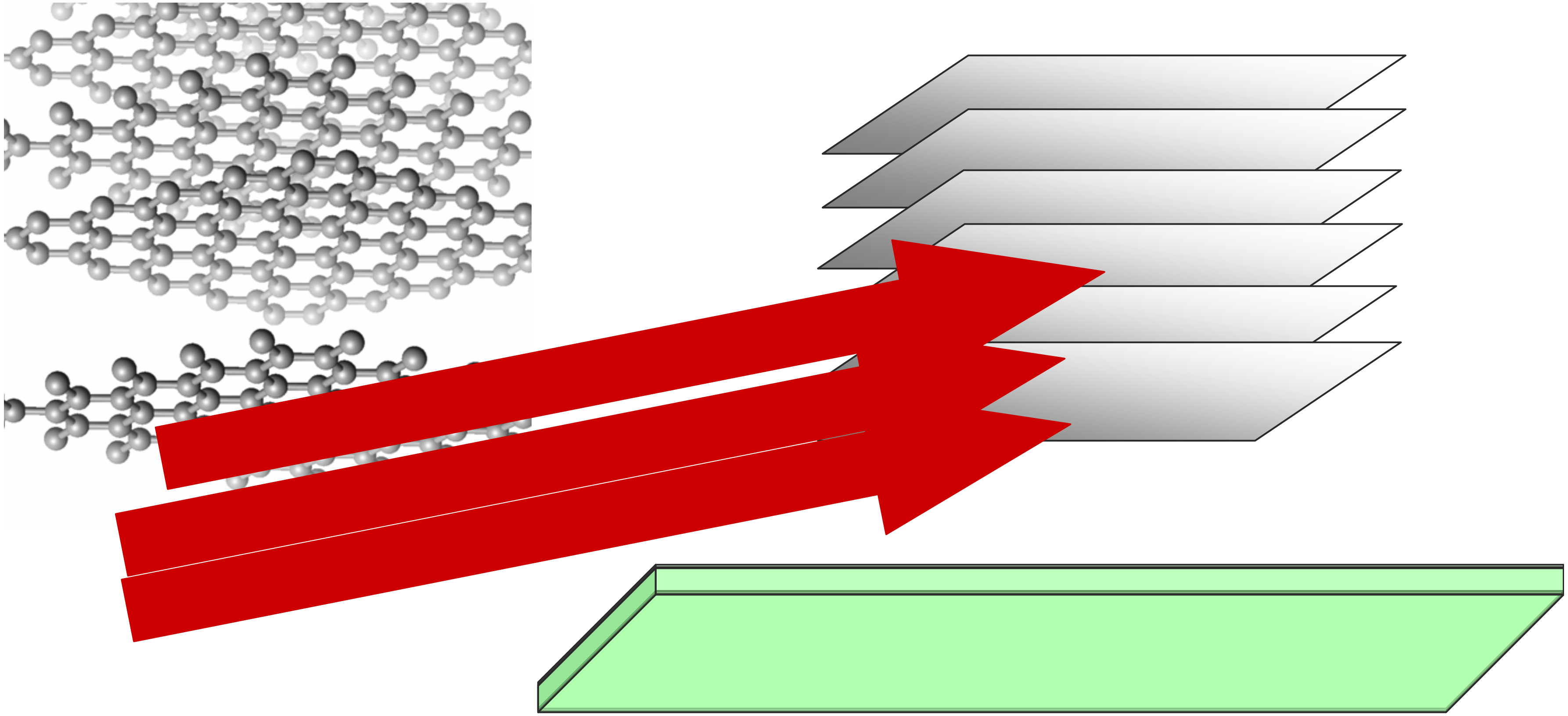
Results of coupled TDDFT-MD calculations

- Potential energy increases due to laser energy absorption
- Inter-layer distances change in time
- Initial inter-layer expansion causes exfoliation by detaching a graphene monolayer



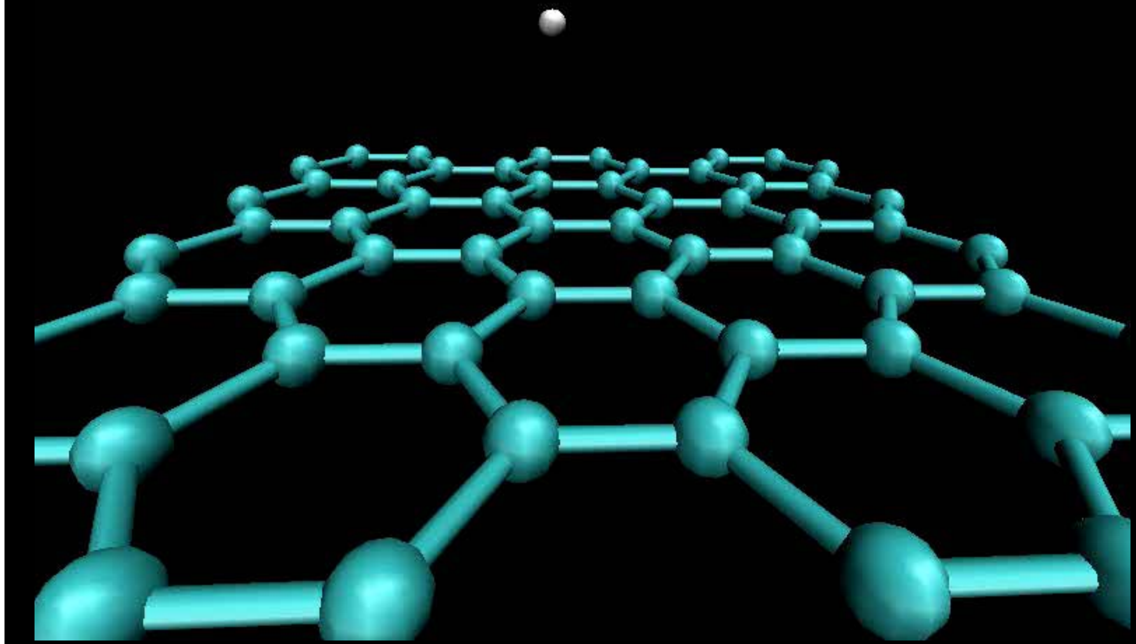






Possible mass production of graphene monolayers free of chemical contaminants!

Focused Ion Beam (FIB) lithography for nano-architectonics



Arkady Krasheninnikov, Yoshiuki Miyamoto, David Tománek,
Phys. Rev. Lett. **99**, 016104 (2007)

Beyond Black Magic:

❖*How much do we* ***REALLY*** *know about FIB lithography?*

❖*Can ion beam irradiation be used for precise structural control?*

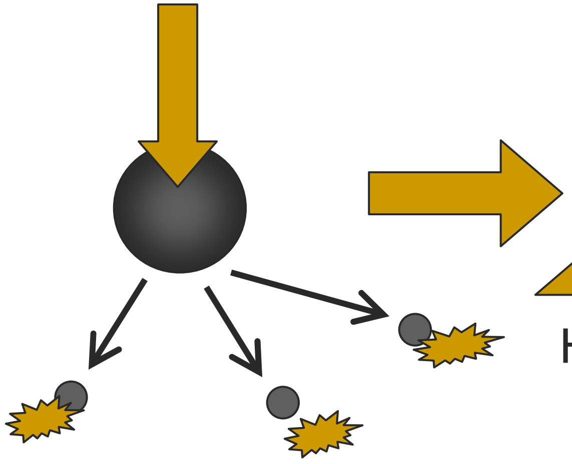
❖How large is the threshold displacement energy?

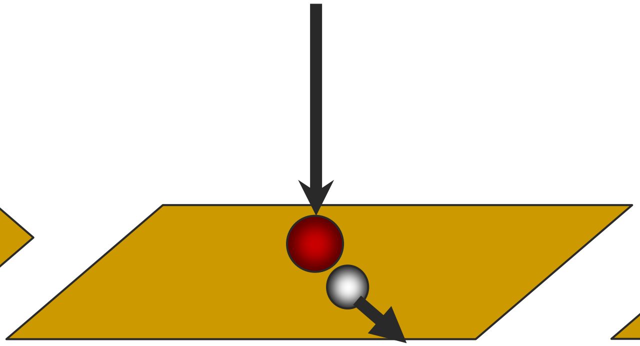
❖How much energy is transferred from the projectile (H)?

❖Which fraction goes to electronic excitations?

Which are the dominant processes during collisions?

Microscopic processes during sputtering

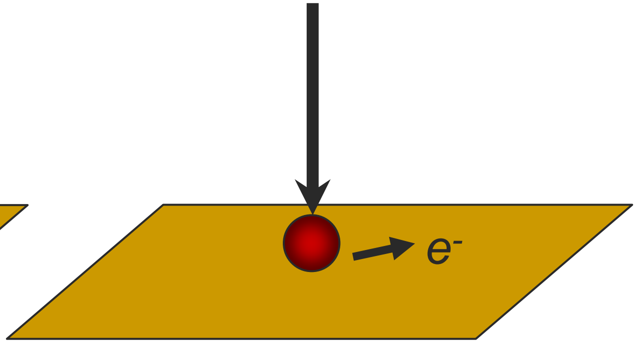




Head-on collisions:

→ Heat

→ Sputtering

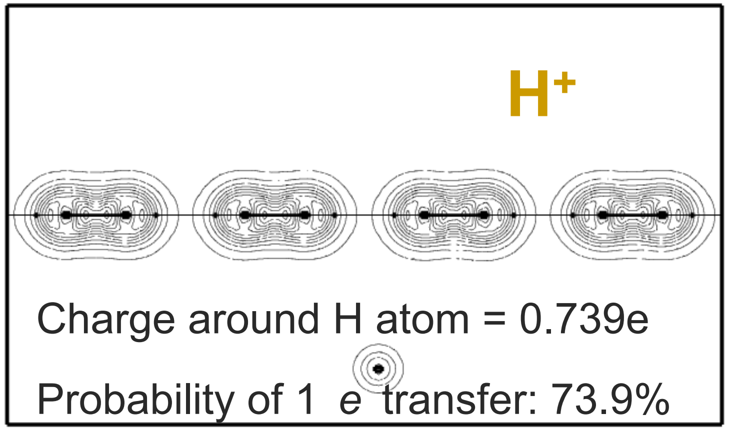


Off-center collisions:

→ Shakeup of electrons

→ Island evaporation

H^+ ion irradiation *(E_{kin}=100 eV)*



Charge around H atom = 0.739e

Probability of 1 e^- transfer: 73.9%

⇓ Quick neutralization

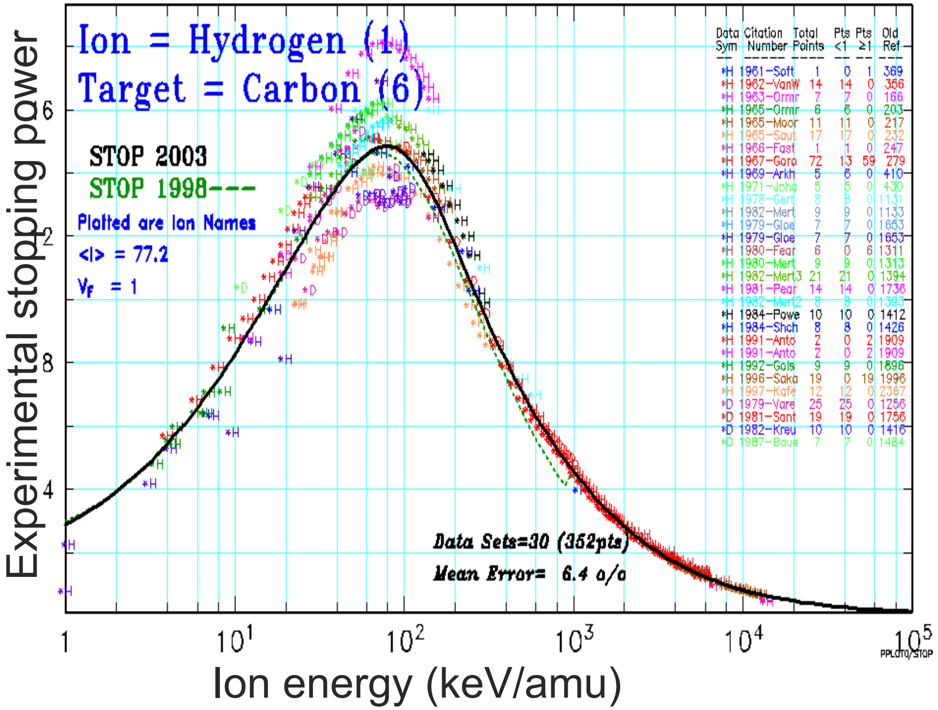
H atom irradiation

- ❖Electronic excitations dominate for ion velocities $v_I > v_F$(*sp*^{2} carbon)
- ❖Protons with E_{kin}=100 eV: $v_I = 1.7\text{x}10^5$ m/s< v_F(graphite)=$8\text{x}10^5$ m/s

How much do excitations affect energy deposition in target?

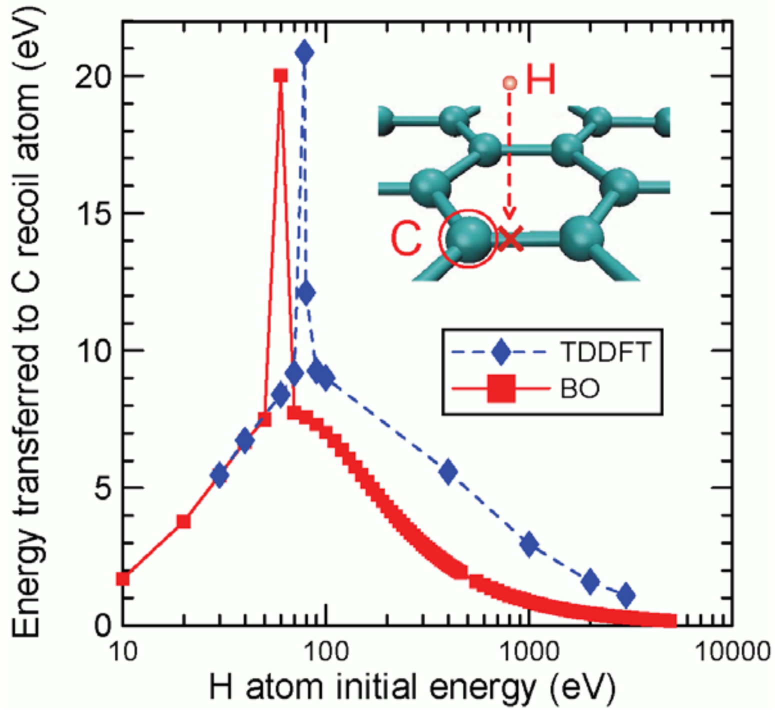
Energy deposition in graphene and nanotubes

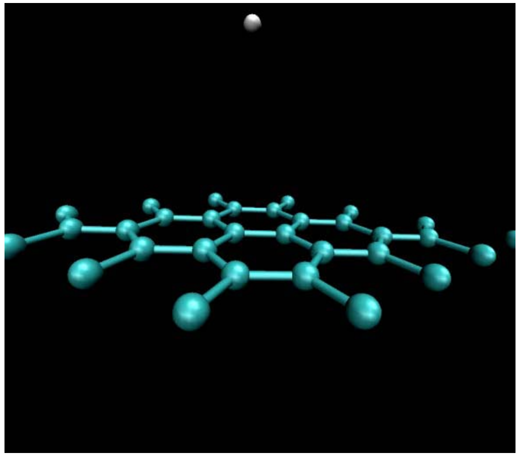
Experiment:
Average of many collisions



Data Sym	Citation Number	Total Points	Pts <1	Pts ≥1	Old Ref
*H	1961–Soft	1	0	1	369
*H	1962–VanW	14	14	0	356
*H	1963–Ormr	7	7	0	166
*H	1965–Ormr	6	6	0	203
*H	1965–Moor	11	11	0	217
*H	1965–Saut	17	17	0	232
*H	1966–Fast	1	1	0	247
*H	1967–Goro	72	13	59	279
*H	1969–Arkh	5	6	0	410
*H	1971–Joha	5	5	0	430
*H	1978–Gert	8	8	0	1131
*H	1982–Mert	9	9	0	1133
*H	1979–Gloe	7	7	0	1653
*H	1979–Gloe	7	7	0	1653
*H	1980–Fear	6	0	6	1311
*H	1980–Mert	9	9	0	1313
*H	1982–Mert3	21	21	0	1394
*H	1981–Pear	14	14	0	1736
*H	1982–Mert2	8	8	0	1393
*H	1984–Powe	10	10	0	1412
*H	1984–Shch	8	8	0	1426
*H	1991–Anto	2	0	2	1909
*H	1991–Anto	2	0	2	1909
*H	1992–Gols	9	9	0	1896
*H	1996–Saka	19	0	19	1996
*H	1997–Kafe	12	12	0	2367
*D	1979–Vare	25	25	0	1256
*D	1981–Sant	19	19	0	1756
*D	1982–Kreu	10	10	0	1416
*D	1987–Baue	7	7	0	1484

Theory:
ground state and excited state

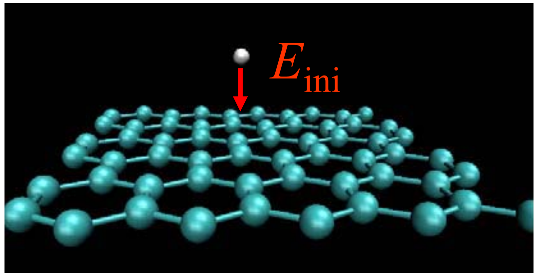


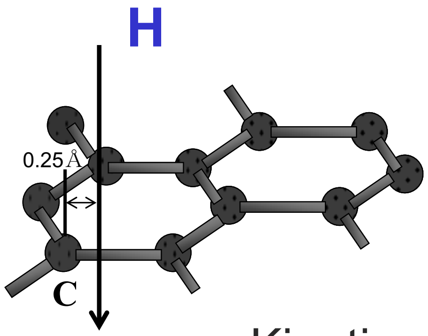


- ❖Strongest effect of excitations: Impact in the bond region
- ❖Qualitative agreement between theory and experiment
- ❖Intriguing pinball motion at 80 eV
- ❖Threshold displacement energy:
  84 eV (TDDFT), 80 eV (BO-MD)
- ❖Electronic excitations matter for E_I>100 eV

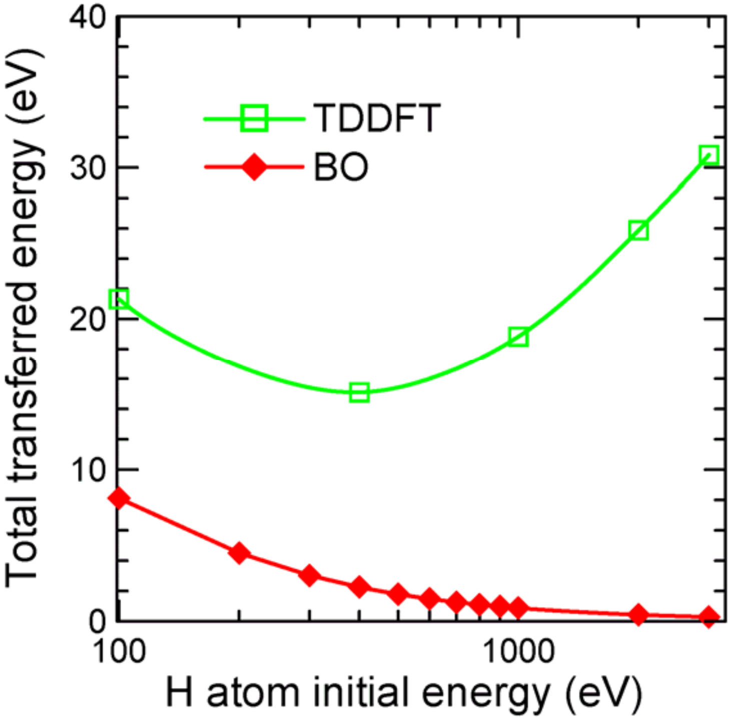
What happens microscopically at E_I>100 eV?

Microscopic accommodation of the impact energy

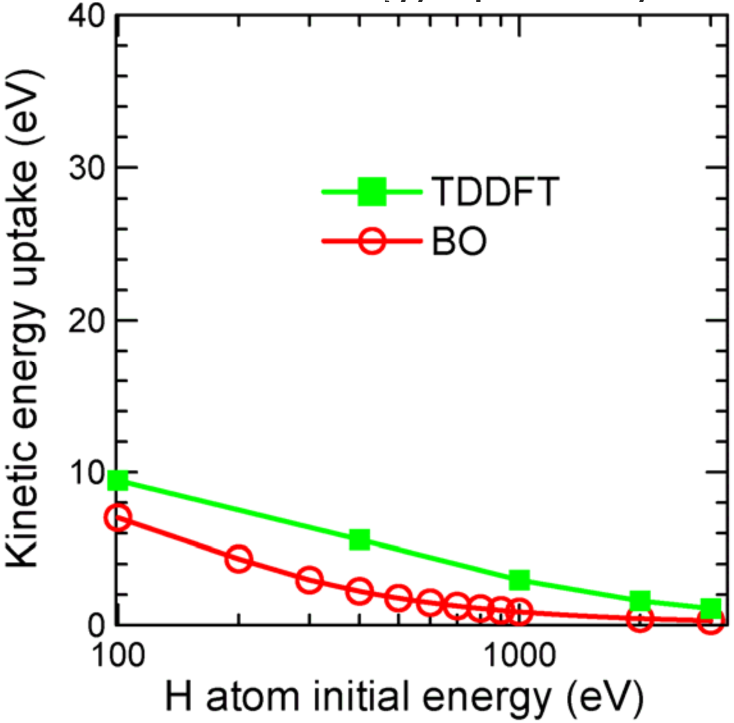




Total energy uptake



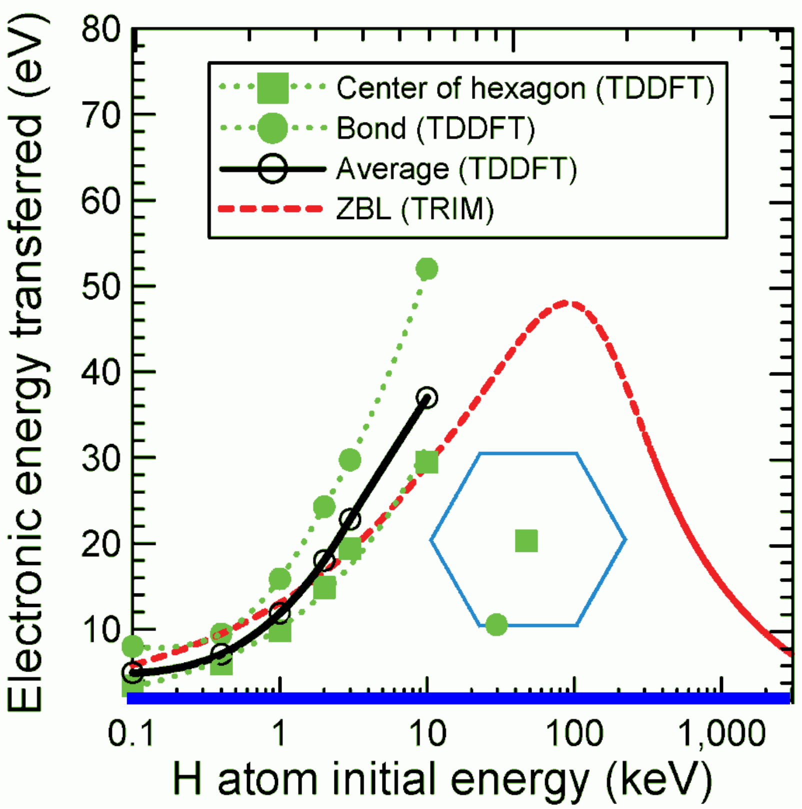
Kinetic energy uptake by C



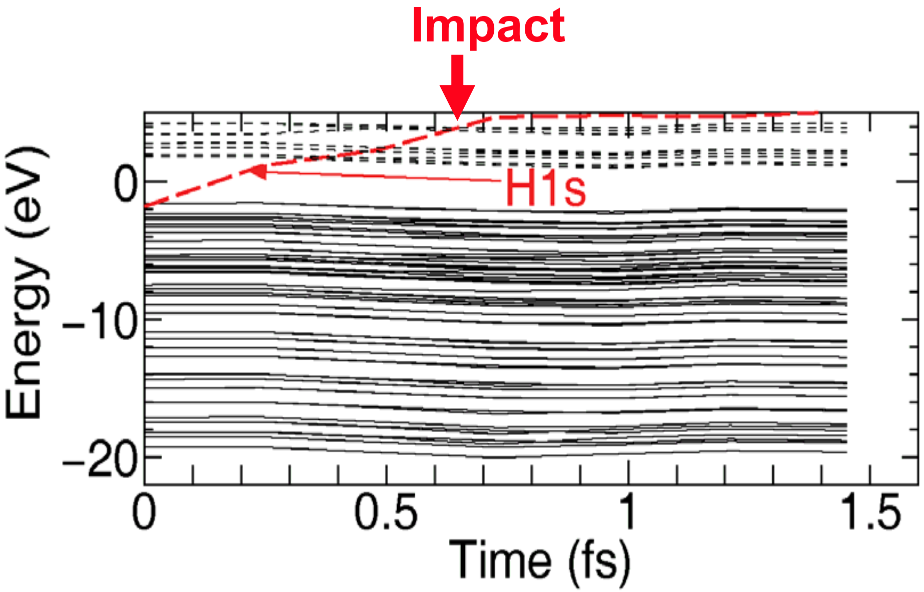
- ❖**Large difference between BO-MD and TDDFT-MD**
- ❖**Very small difference between BO-MD and TDDFT-MD**

How much goes to electronic excitations?

Energy uptake by electronic excitations



Time evolution of energy eigenvalues (E_{kin}=3 keV)



❖TDDFT-MD, experiment:
Electronic excitations accommodate <50 eV at high energies

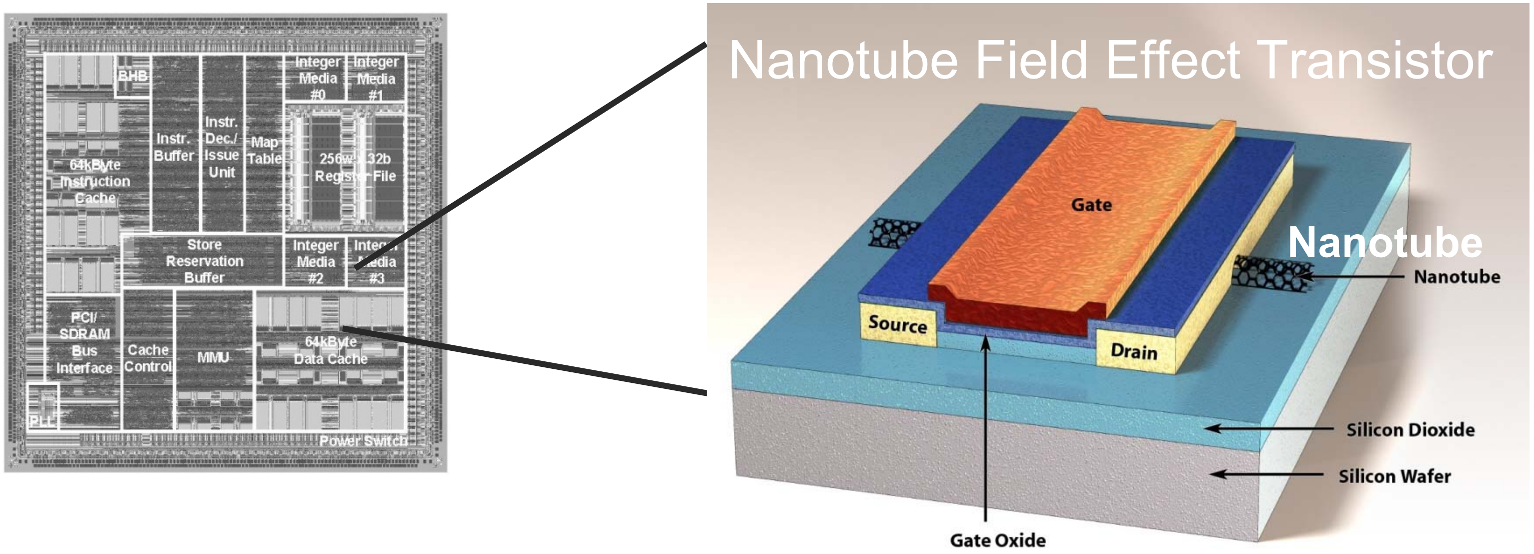
❖ BO-MD: excitations suppressed

❖ Conclusion:
Non-adiabatic effects play an important role at high ion impact energies

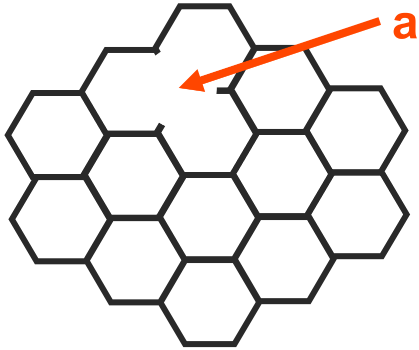
Outline

- Introduction
  - **Dynamics of ground state and excited state processes**
  - **State of the art computer simulations**
  - **Long lifetime of electronic excitations**
- Chemical modification of nanocarbons
  - **Hydrogenation of nanocarbons by wet chemistry**
  - **Peeling fullerenes by hydrogen**
  - **Unzipping nanotubes by hydrogen**
- Excited state engineering of nanocarbons
  - **Transforming graphite to diamond by light**
  - **Photo-exfoliation of graphite to graphene**
  - **Focused Ion Beam (FIB) lithography for nano-architectonics**
- Removing atomic-scale defects
  - **Defect tolerance of nanotubes**
  - **Selective deoxidation of defective nanotubes**
- Summary and Conclusions

Removing atomic-scale defects



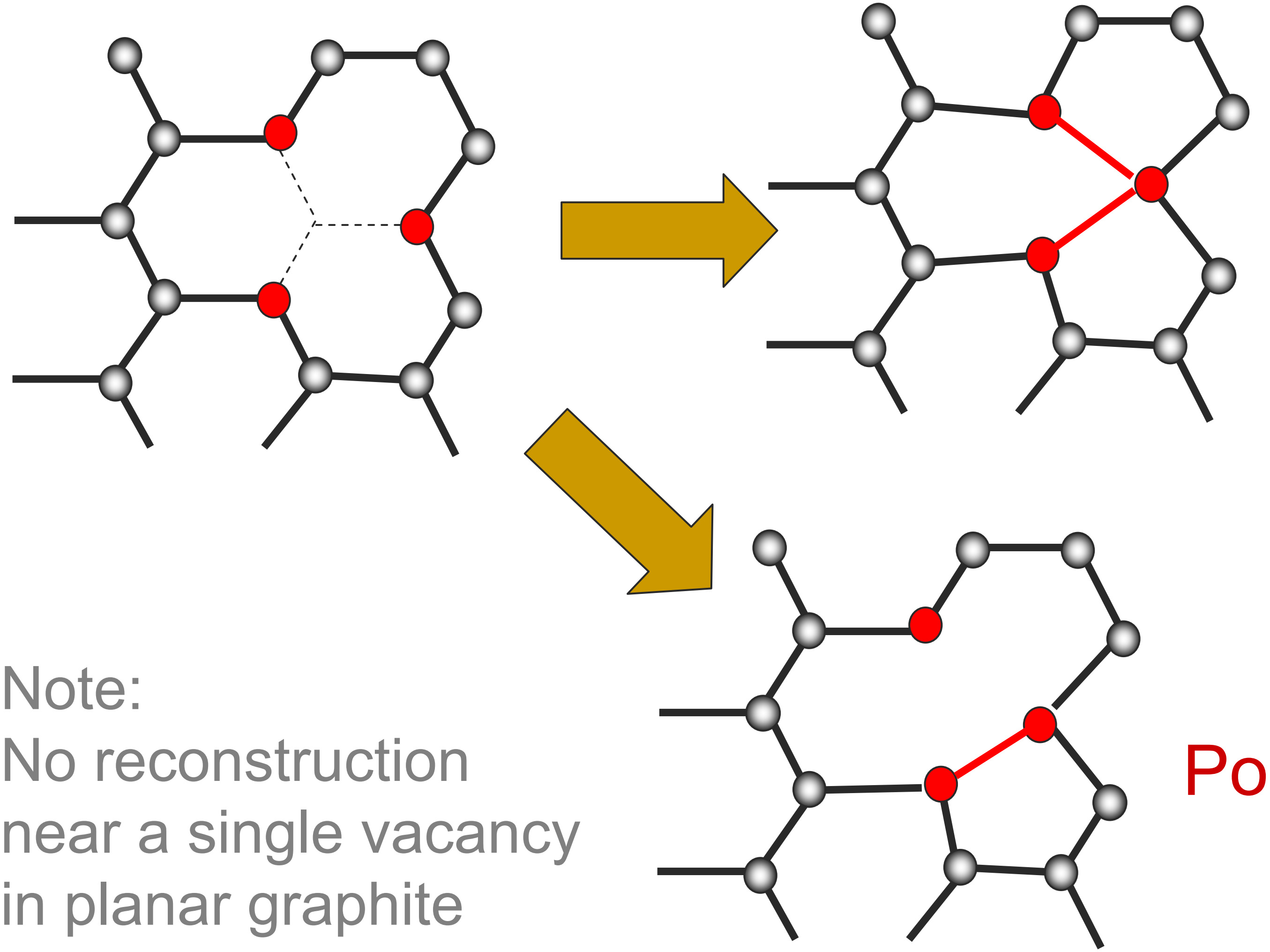
- Defects limit performance, lifetime of devices
- Are CNT devices as sensitive to defects as Si-LSI circuits?



Will atomic vacancies trigger failure under

- high temperatures?
- illumination?

Equilibrium structure near a monovacancy in sp^2 carbon



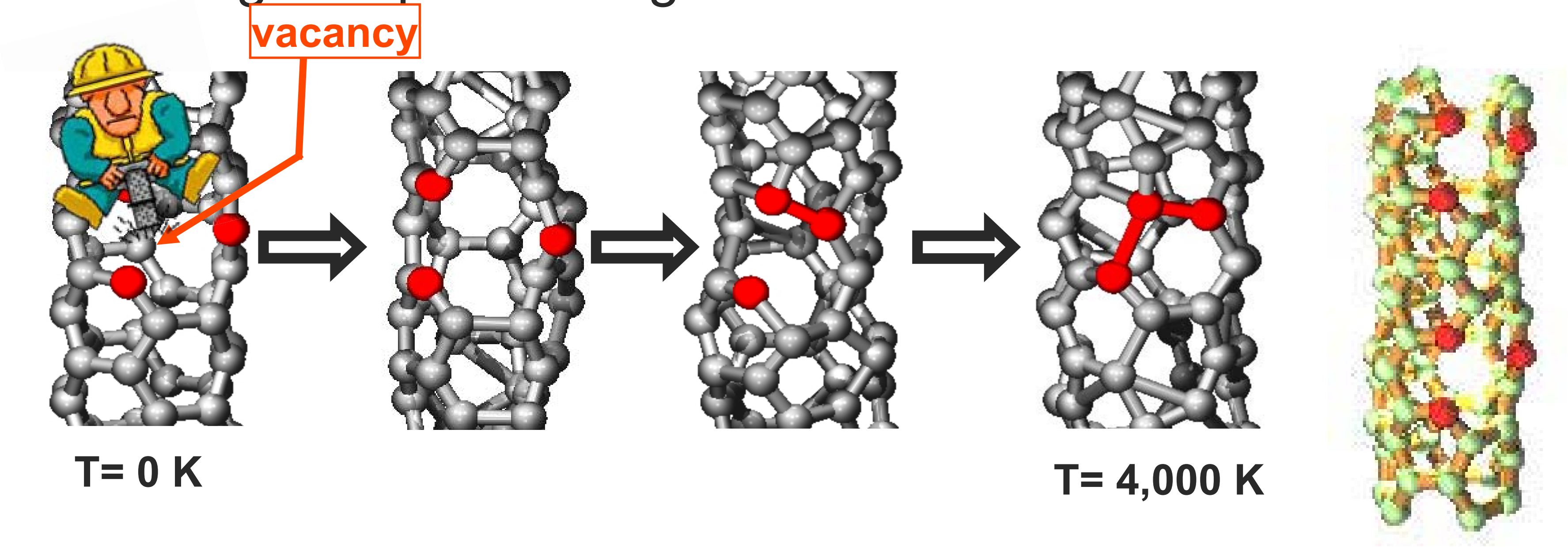
Strain too large

Possible?

Note:
No reconstruction near a single vacancy in planar graphite

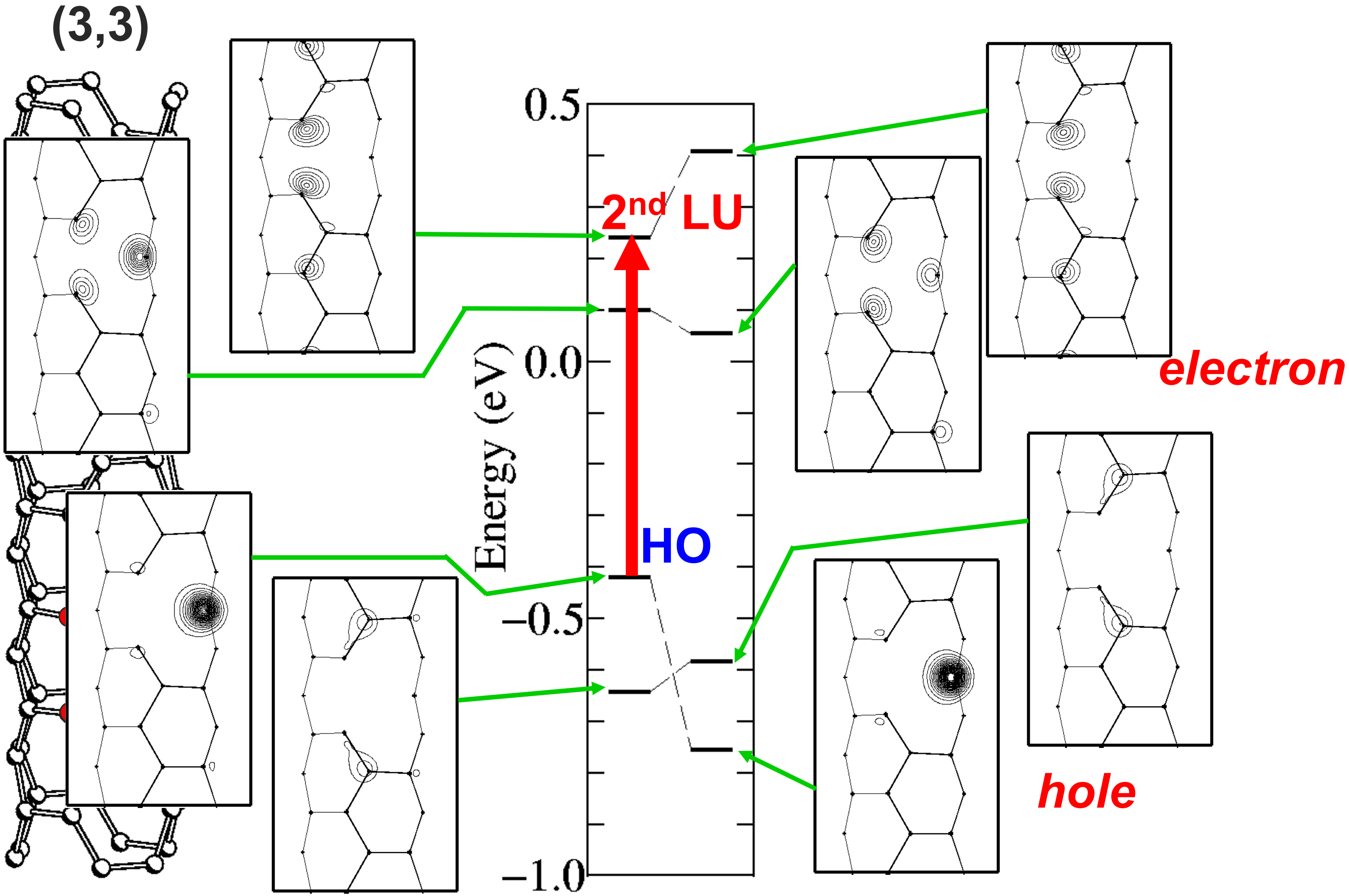
Stability of defective tubes at high temperatures

- Danger of pre-melting near vacancies?

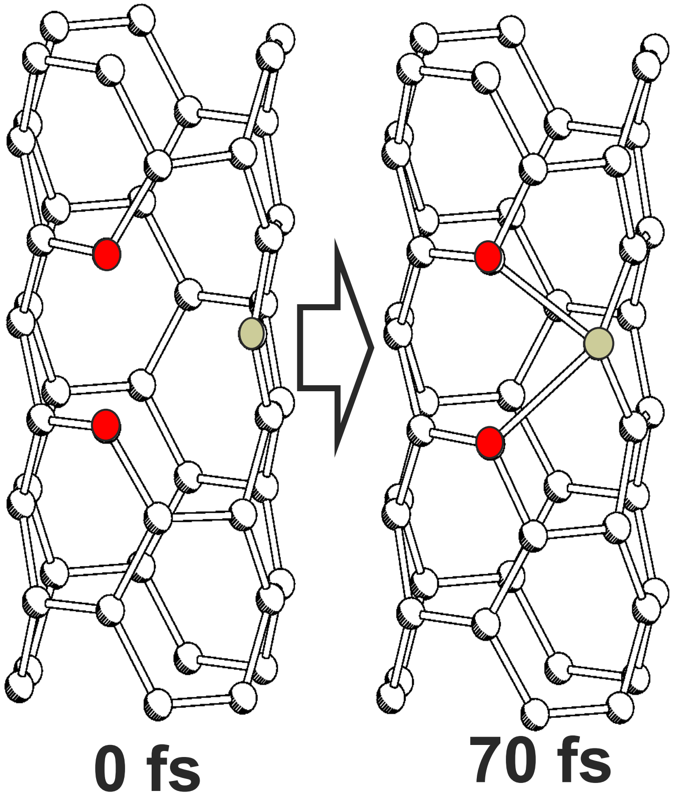


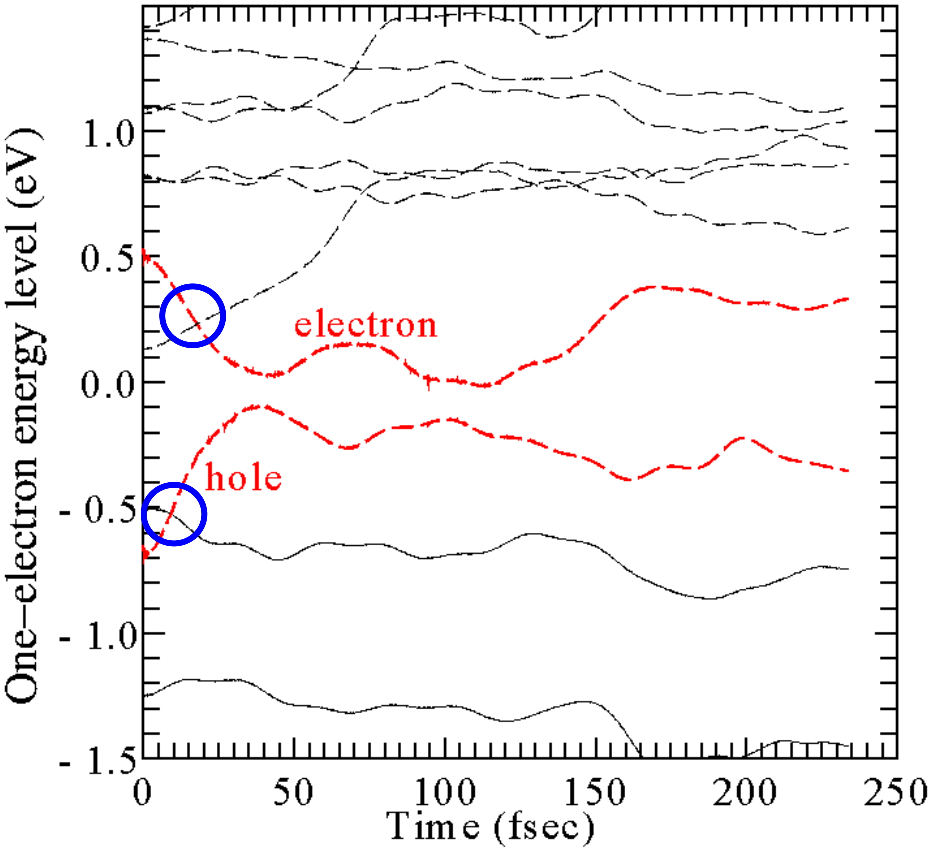
- Nanotube remains intact until 4,000 K
- Self-healing behavior:
  Formation of new bond helps recover
  - structural stiffness
  - conductance

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



Time evolution of the electronic states

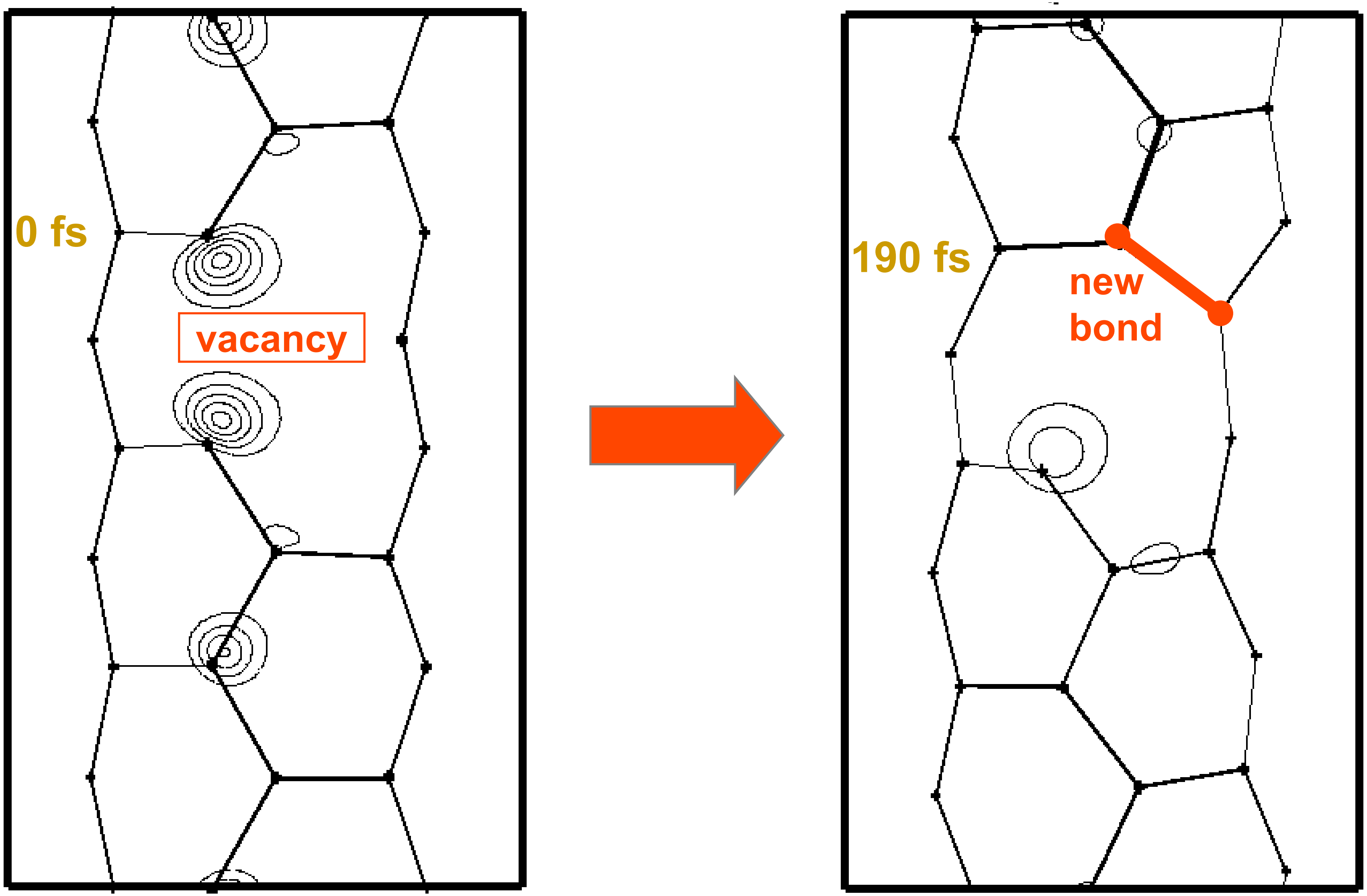




$$\Psi_n\,(t+\Delta t)=\exp(-i/h\ H\Delta t\,)\ \Psi_n(t)$$

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

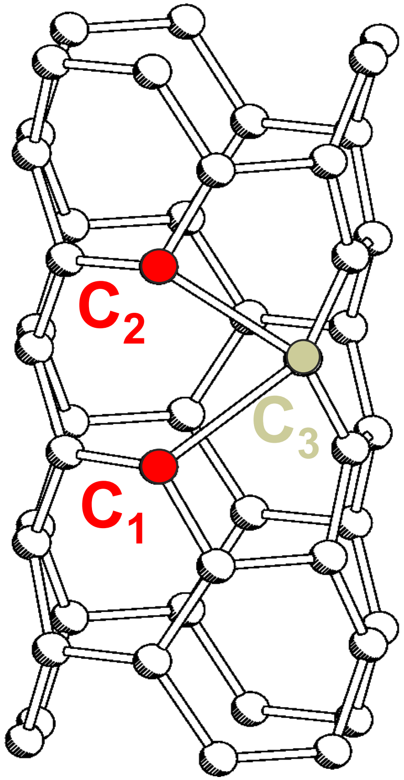
Structural changes under illumination



- 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)

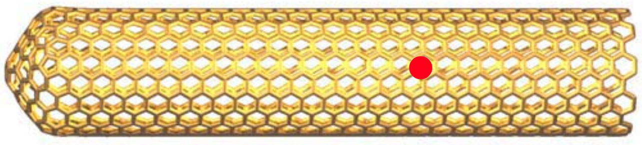
Reconstructed geometry



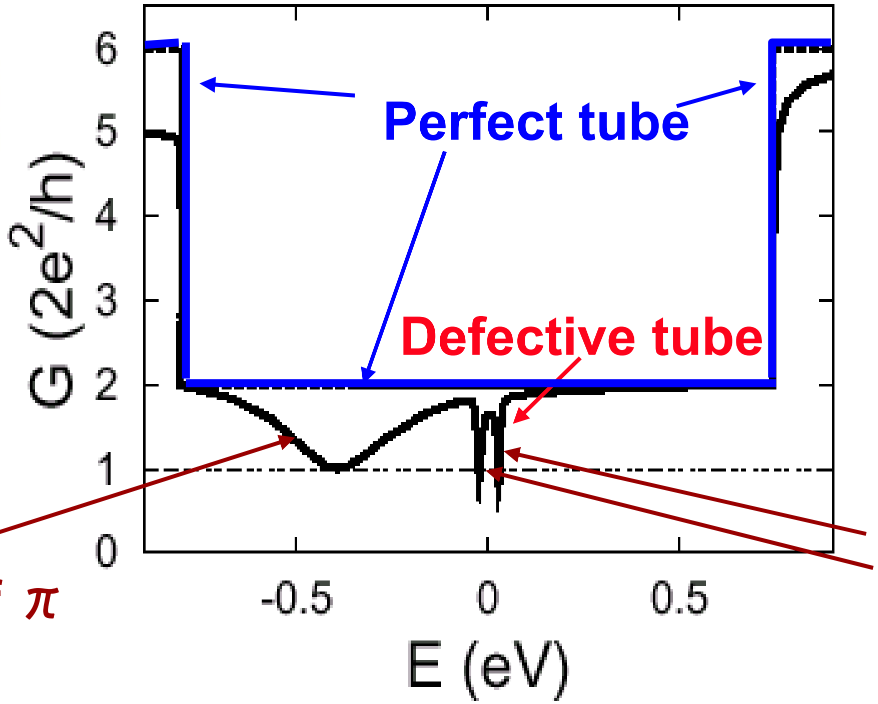
Stability increase due to reconstruction
(bond formation across vacancy)

Does reconstruction affect favorably transport in defective tubes?

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



(10,10) nanotube with a monovacancy



Missing network of π electrons

Dangling bonds: σ electrons

H.J. Choi, J. Ihm, S.G. Louie, M.L. Cohen, Defects, quasibound states, and quantum conductance in metallic carbon nanotubes, Phys. Rev. Lett. 84, 2197 (2000).

- A single vacancy seriously disrupts the quantum conductance of a nanotube
- Good news for applications: Self-healing by reconstruction may remove one of the sharp dips

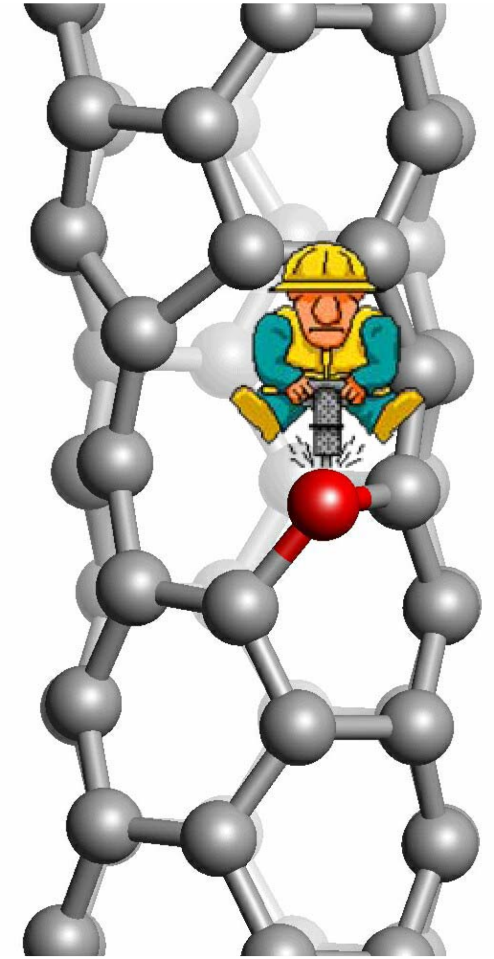
Selective deoxidation of defective nanotubes

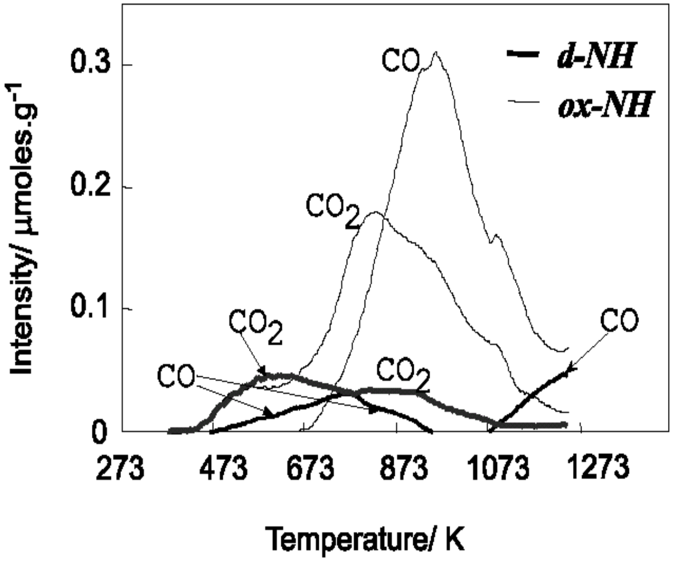
How to deoxidize?

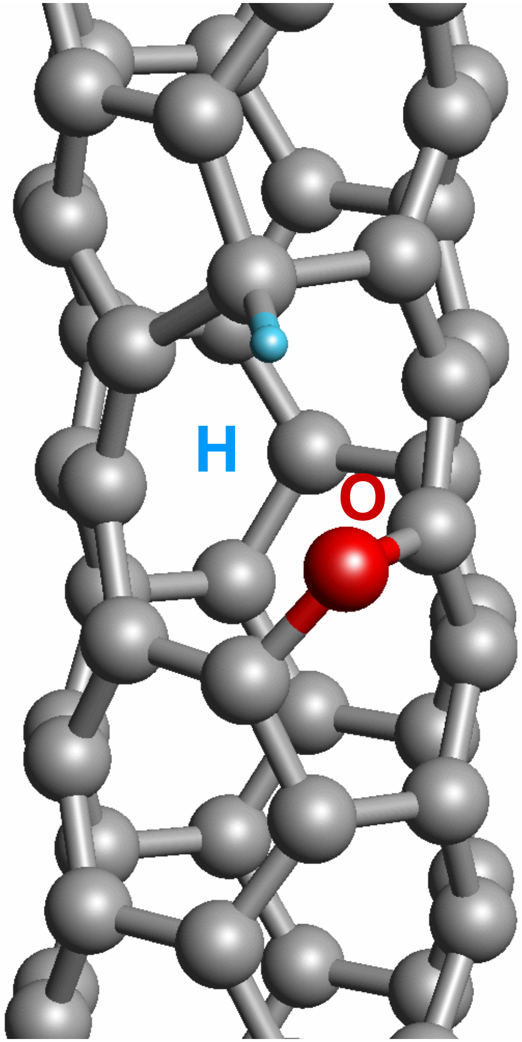
- **By heat treatment?**

⇒No: Larger damage to nanotube

- **By chemical treatment** with H?



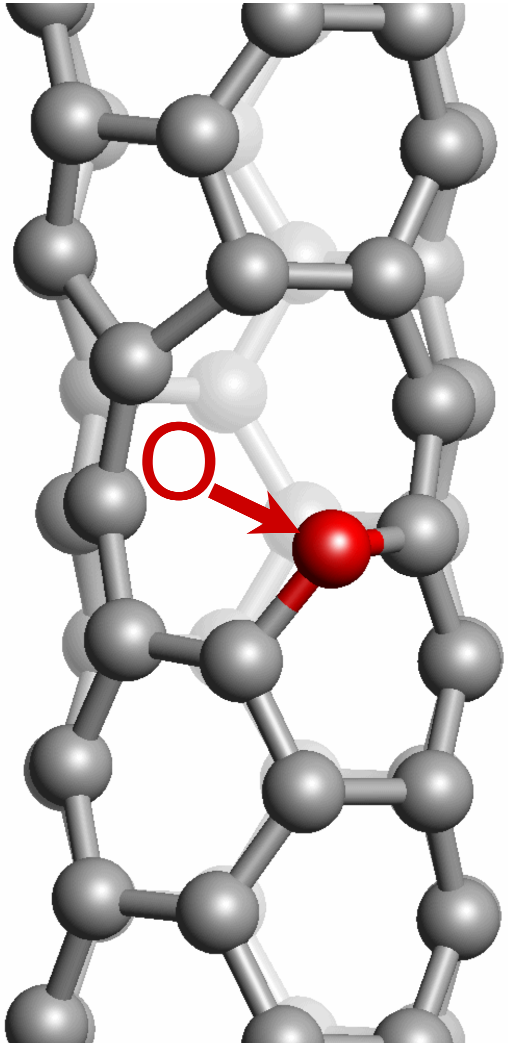


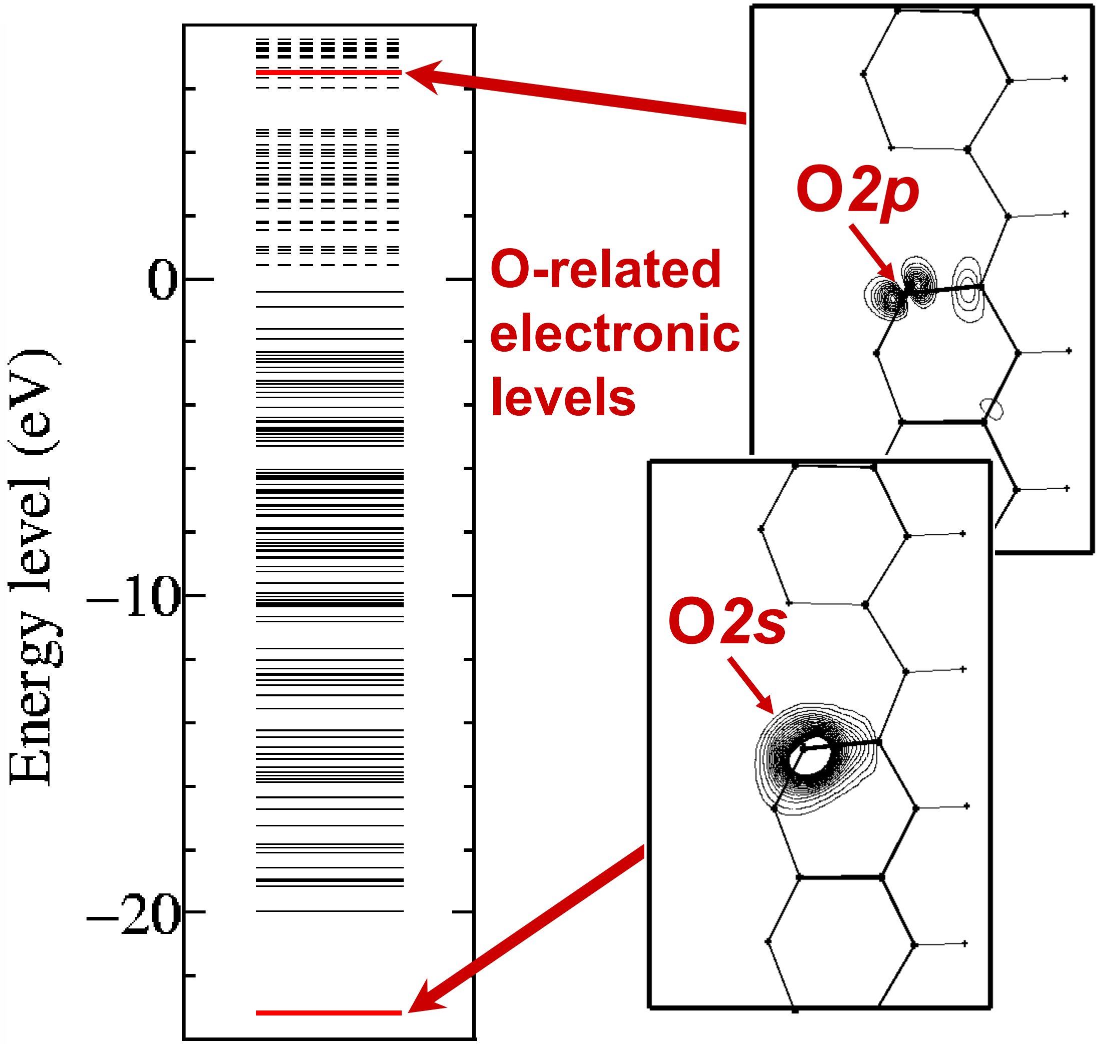


Y. Miyamoto, N. Jinbo, H. Nakamura, A. Rubio, and D. Tománek, Phys. Rev. B 70, 233408 (2004).

Alternative to thermal and chemical treatment

Electronic excitations!

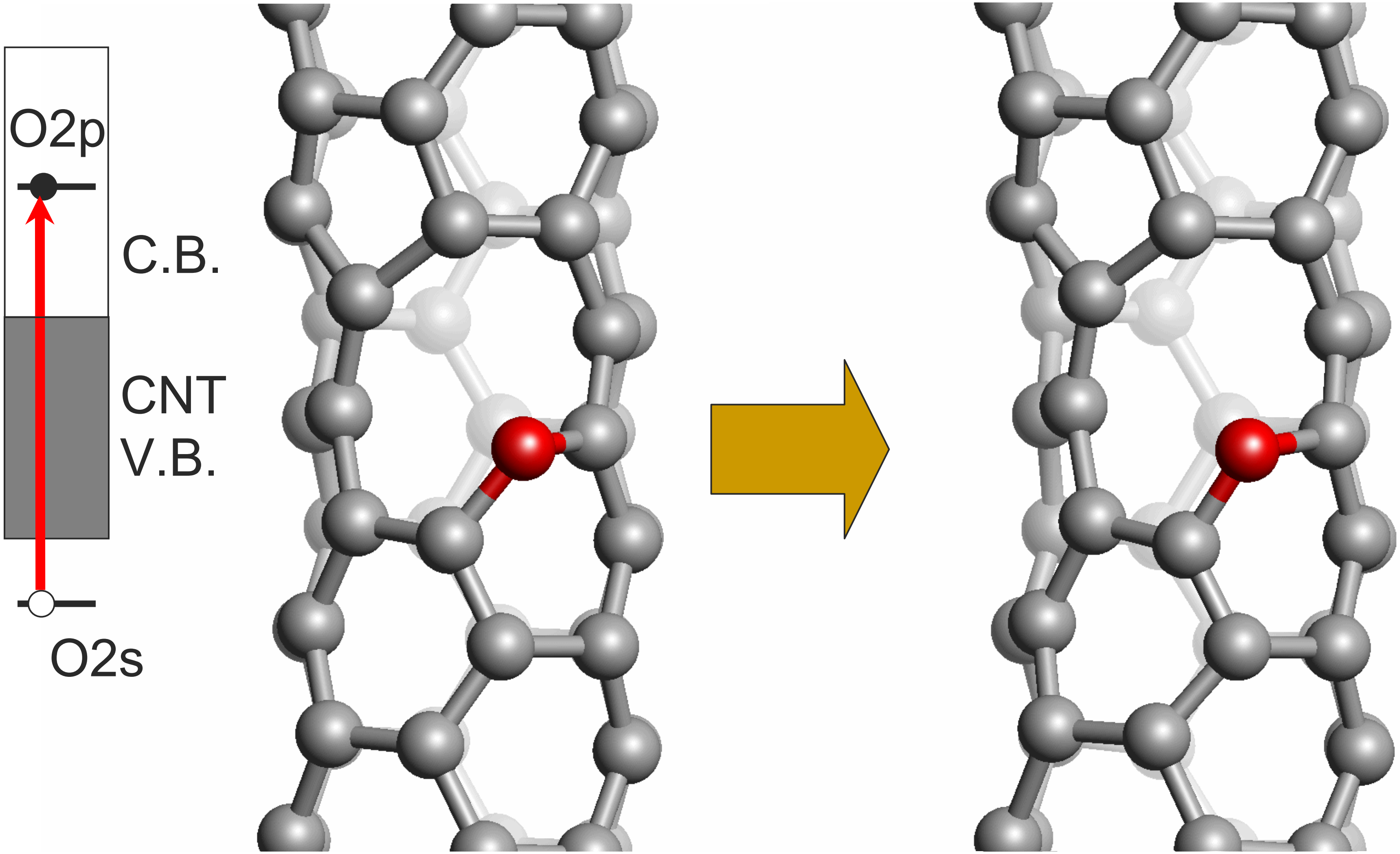




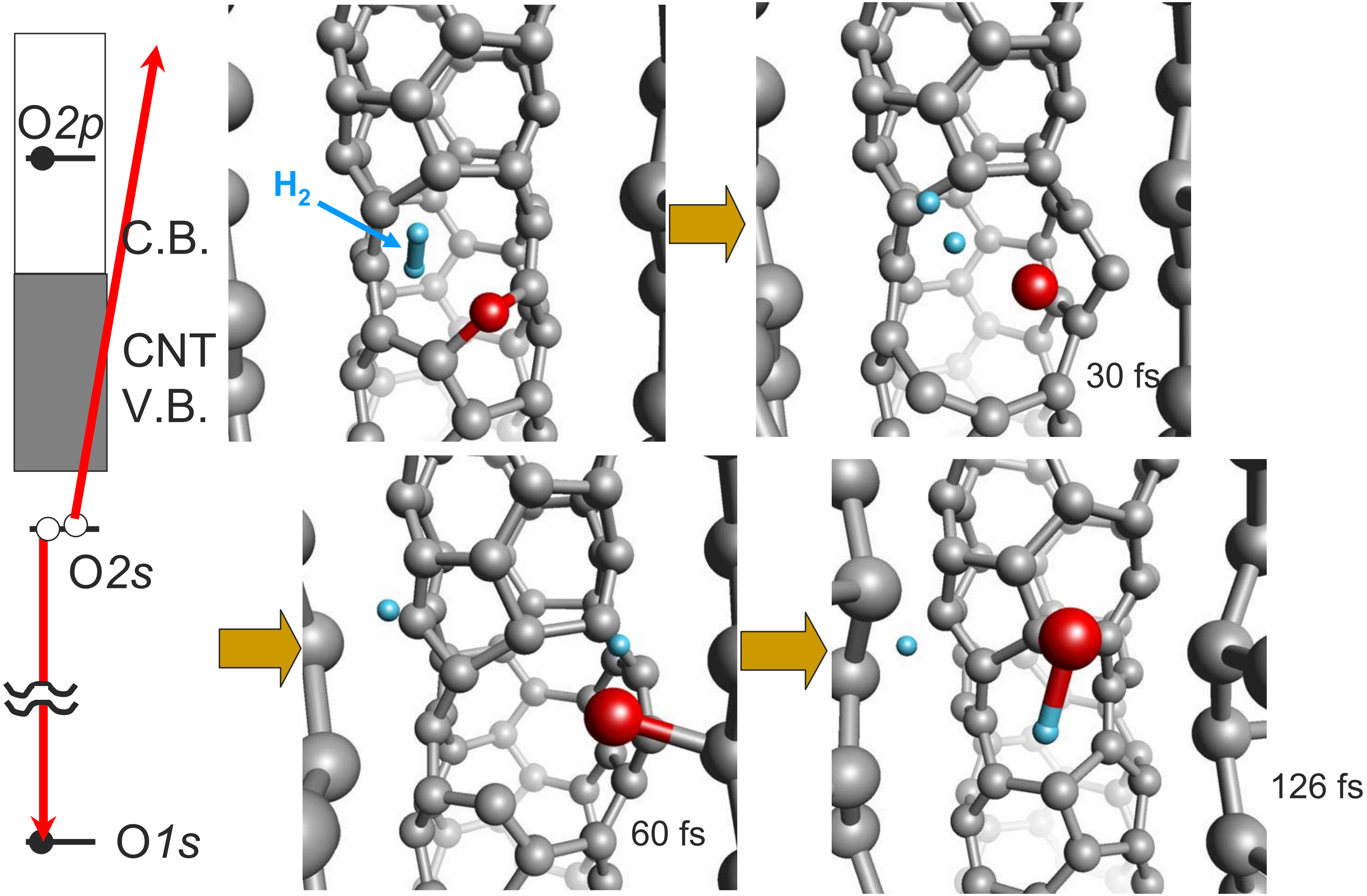
O-related electronic levels

O2s → O2p excitation (33 eV)

hopeless



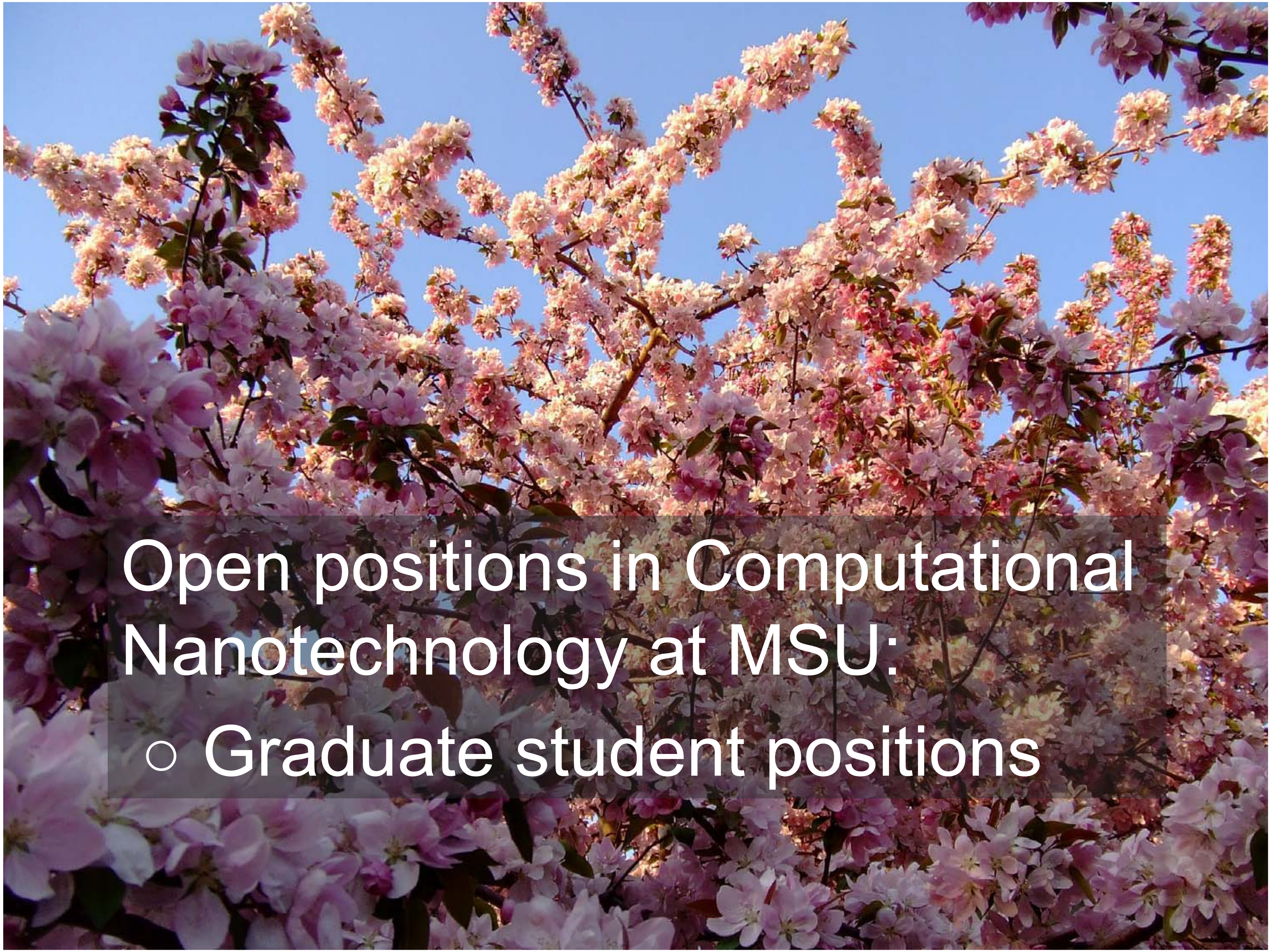
Auger decay following the O1s → 2p excitation (~520 eV)



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

Summary and Conclusions

- *Ab initio* calculations provide microscopic insight into structural transformations induced by chemical reactions and light.
- Fullerenes and nanotubes can be hydrogenated by wet chemical reactions.
- Hydrogen can efficiently peel and unzip fullerenes and nanotubes.
- Time-dependent DFT simulations, combined with classical MD simulations, provide insight into the dynamics in excited carbon nanostructures.
- Electronic excitations in nanostructures are long-lived and can induce structural changes:
  - transform graphite to diamond
  - detach graphene monolayers one-by-one from graphite
  - affect threshold energy for sputtering.
- Thermal and electronic excitations may induce self-healing in defective nanotubes or selectively remove impurities.



Open positions in Computational Nanotechnology at MSU:

- ○ Graduate student positions

End
of
Lecture 2