Concepts and perspectives on photo-induced structural phase transitions

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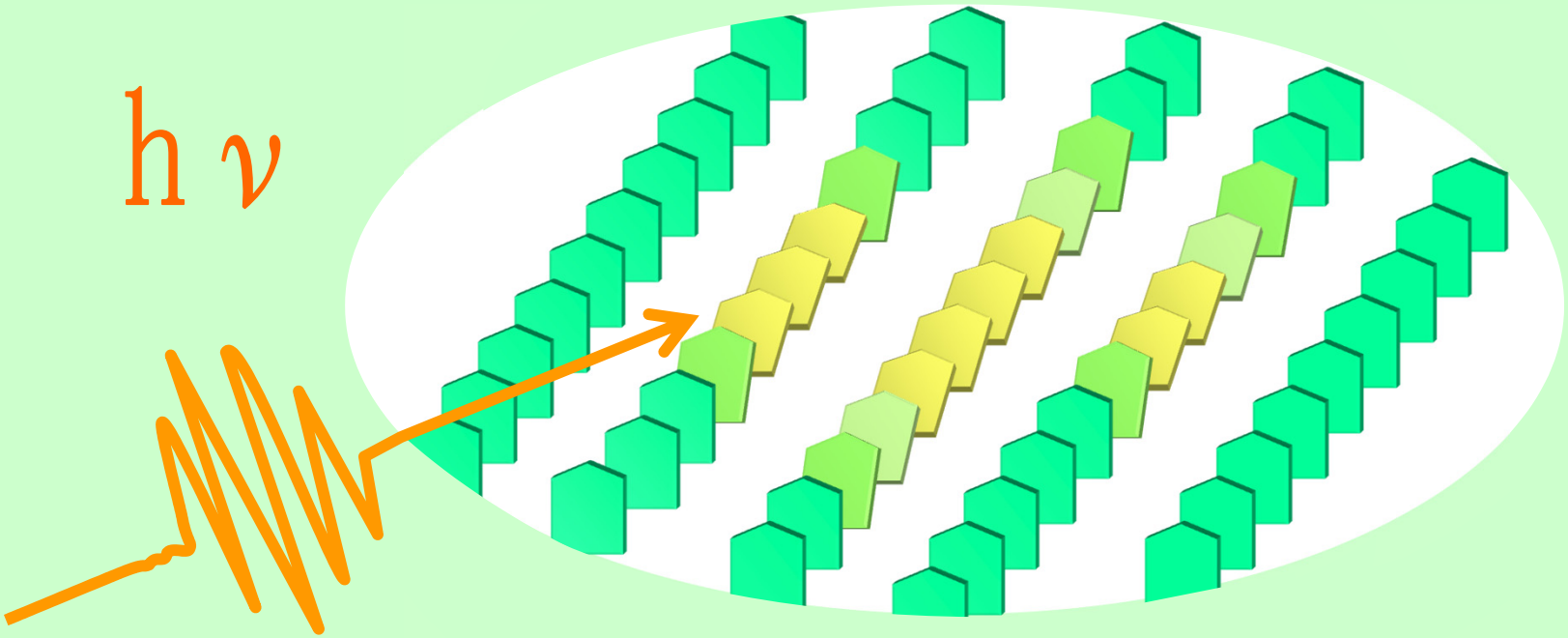
Photoinduced structural phase transitions



K. Nasu, Colloquium, European Physical Journal B 75(2010)415.

Photoinduced structural phase transition

There discovered a new class of solids, which, being shone only by a few visible photons, become pregnant with an excited nano ~ micron domain, that has new structural and electronic orders (, charge, spin and gauge), quite different from the starting ground state.

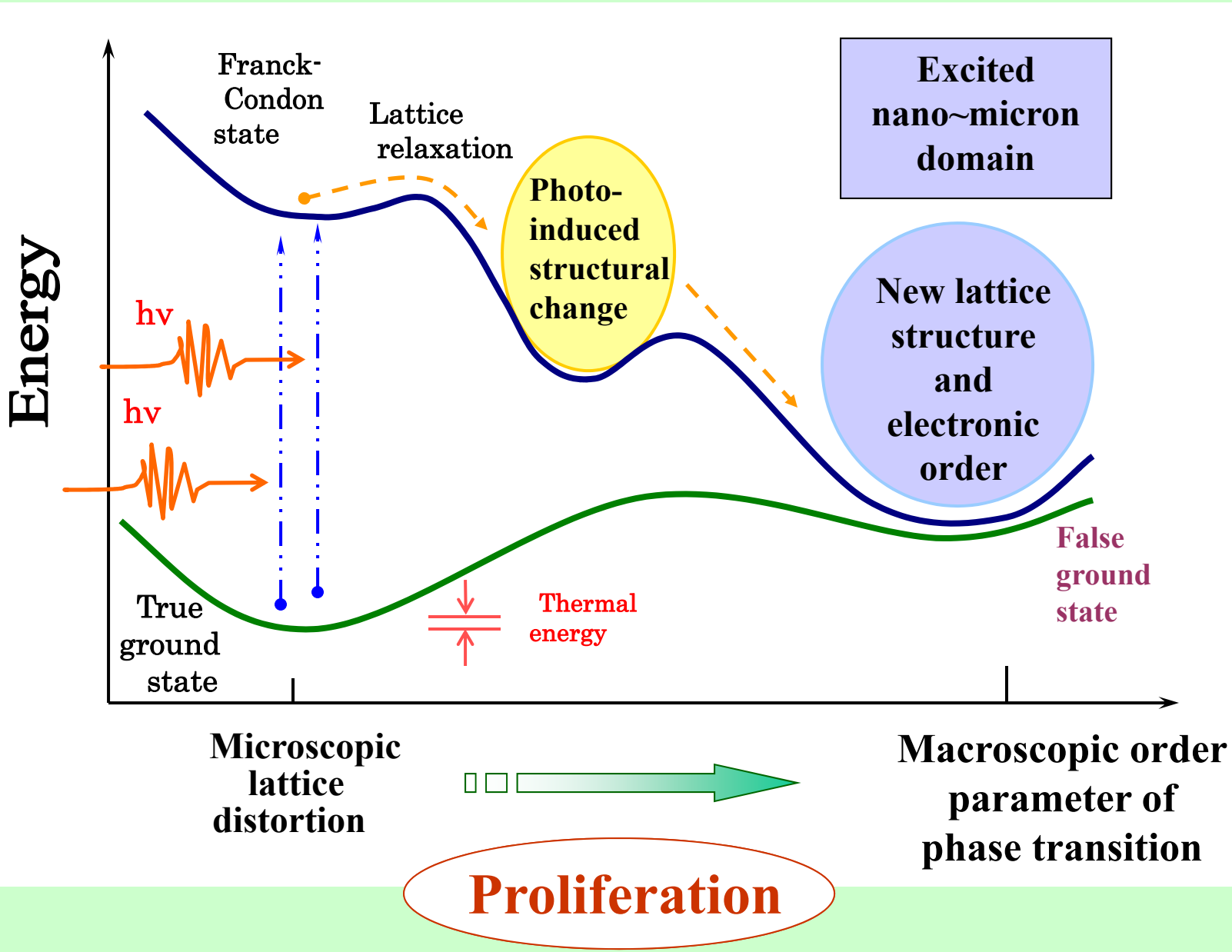
Purpose

Clarify,

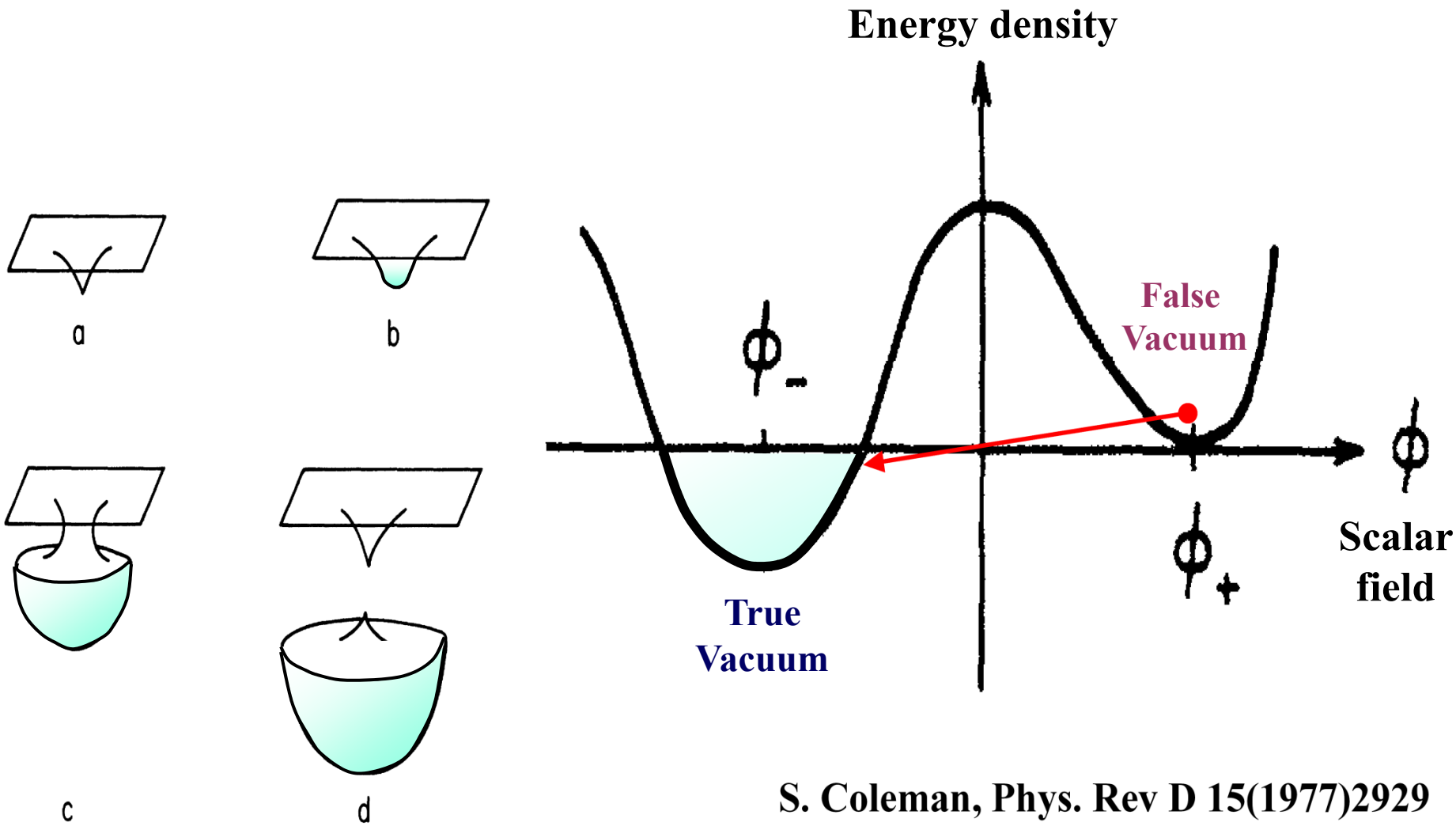
1) **conditions of its occurrence (, hidden multi-stability),**
2) **its mechanism (, criticality, initial condition sensitivity),**
3) **how different from thermally excited phases, and how to optically control nano-domains.**

Rep. Prog. Phys. **67**(2004)1607; Physics Report **465** (2008) 1

Hidden multistability and photoinduced phase transitions

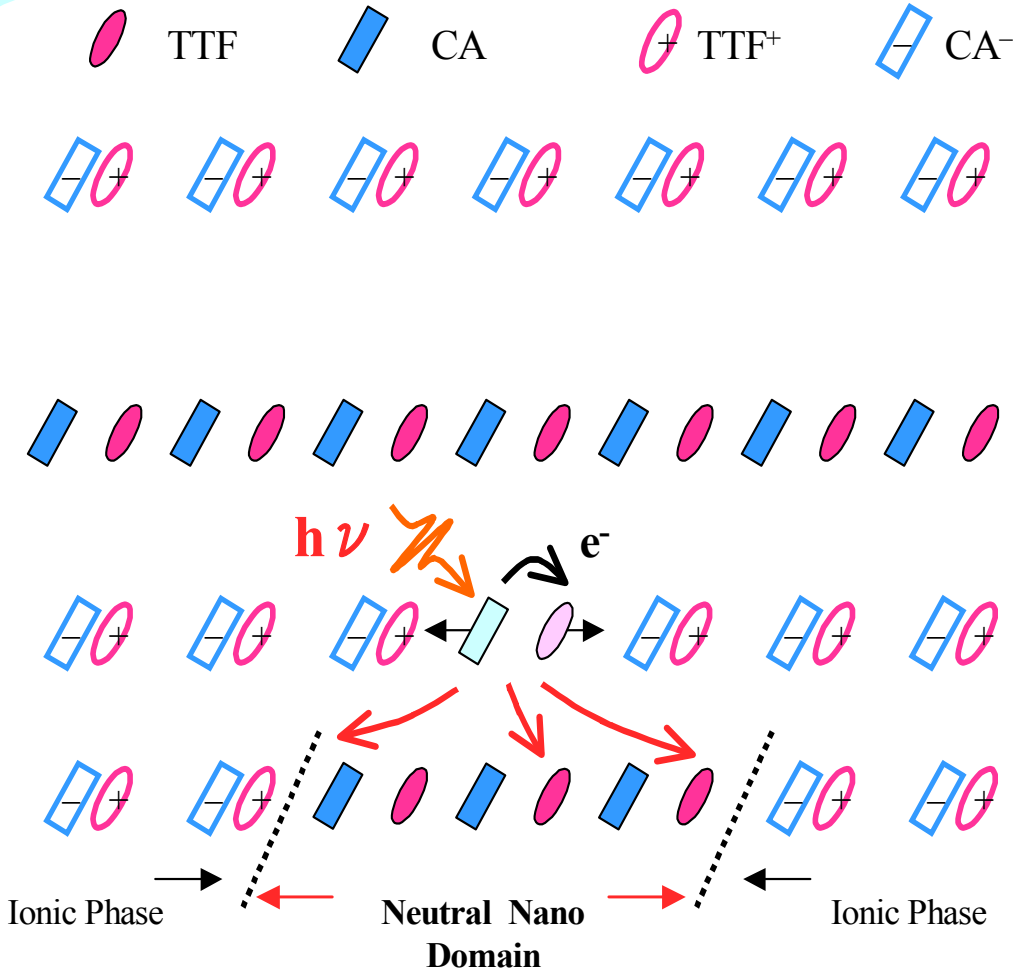


False vacuum and true vacuum in the scalar field theory related with the inflation universe



S. Coleman, Phys. Rev D 15(1977)2929

Photoinduced neutral nano domain in ionic phase of organic charge transfer crystal TTF-CA



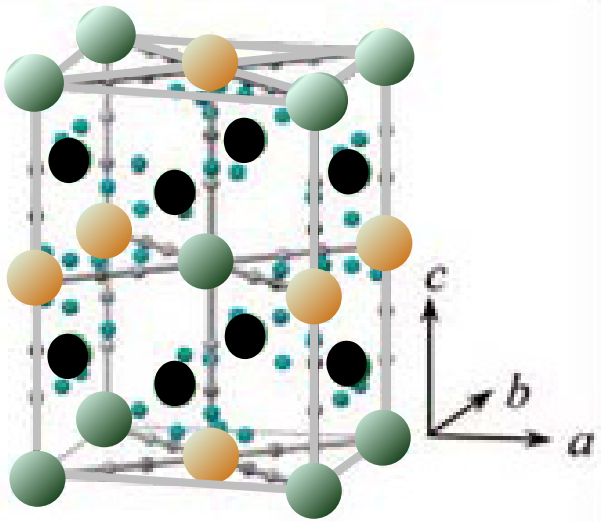
Ionic Phase (Dimer)
True ground state

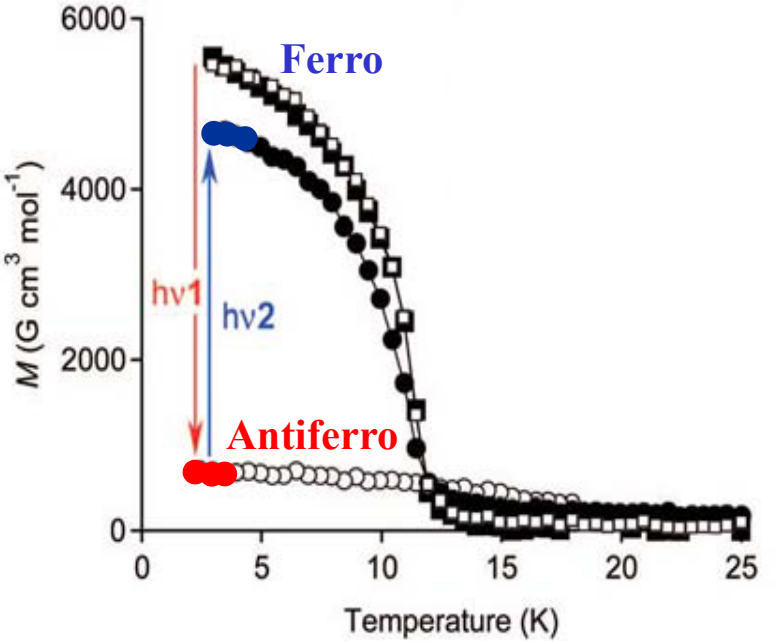
Neutral Phase (Monomer)
False ground state

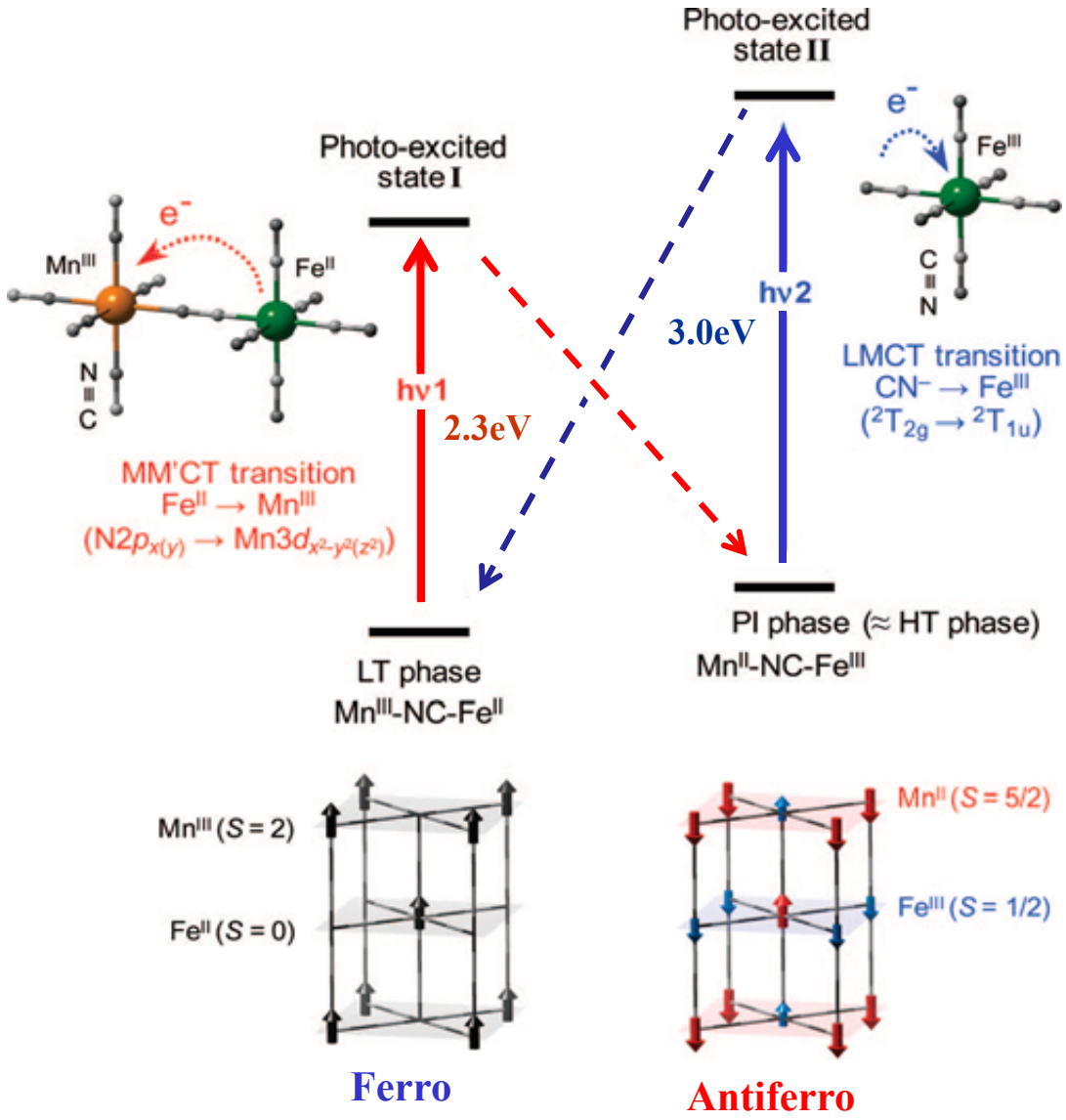
Charge Transfer Exciton

Neutral Nano Domain

Visible-light-induced reversible photo-magnetism in Rubidium Manganese Hexa-Cyano-Ferrate

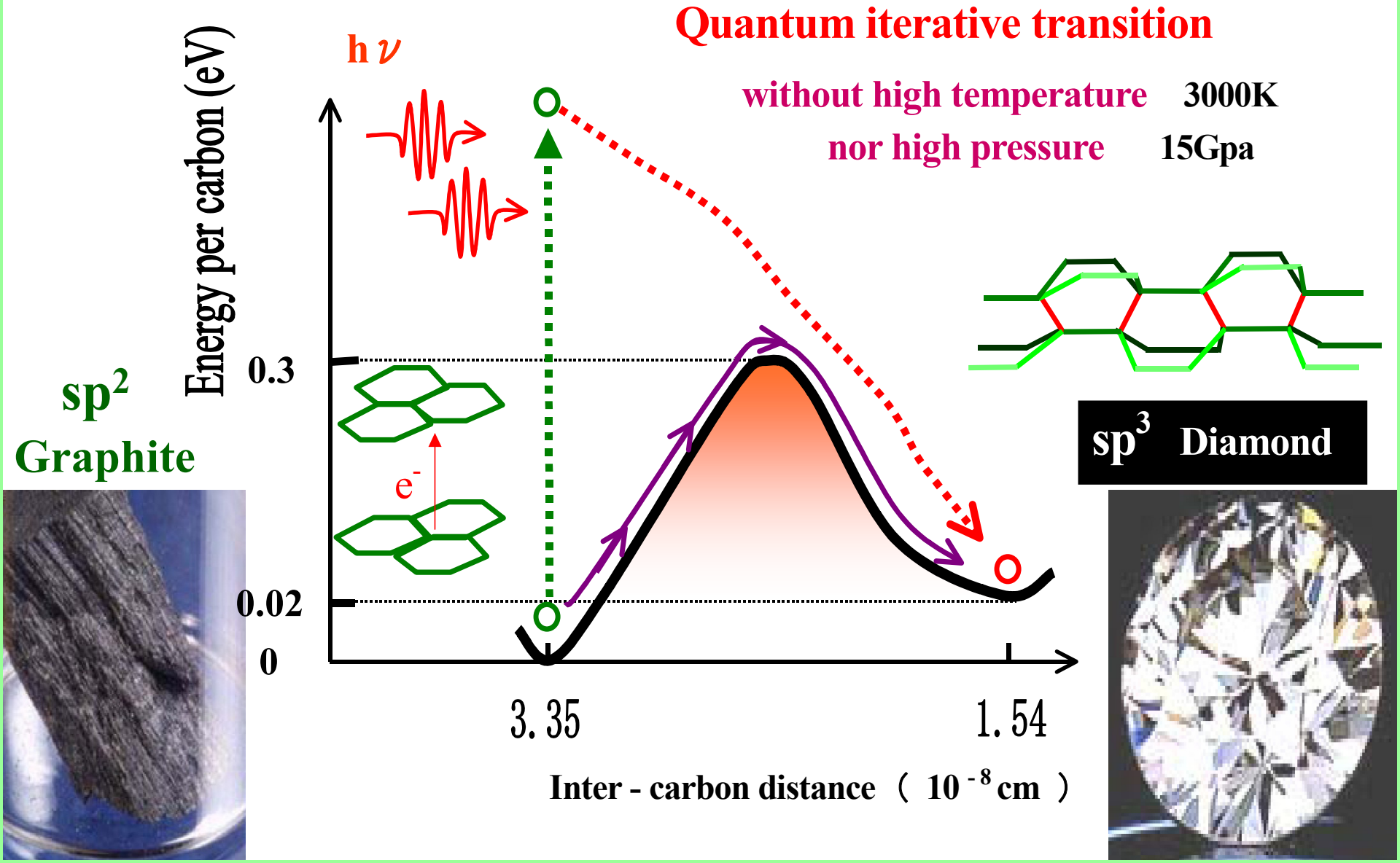






Tokoro, Matsuda, Nuida, Moritomo, Ohoyama, Dangui, Boukheddaden, Ohkoshi, Chem. Mater. 20 (2008) 423.

Early stage of graphite-diamond structural phase transition induced by inter-layer charge transfer excitations in the visible region



Experimental discoveries by Tanimura and Kanazaki

1. Exciting light (1.6 eV) should be polarized perpendicular to layer.

2. Nonlinear and multi-photon process, less than 10 photons.

3. Too strong excitation is rather harmful, resulting in two layers abrasion.

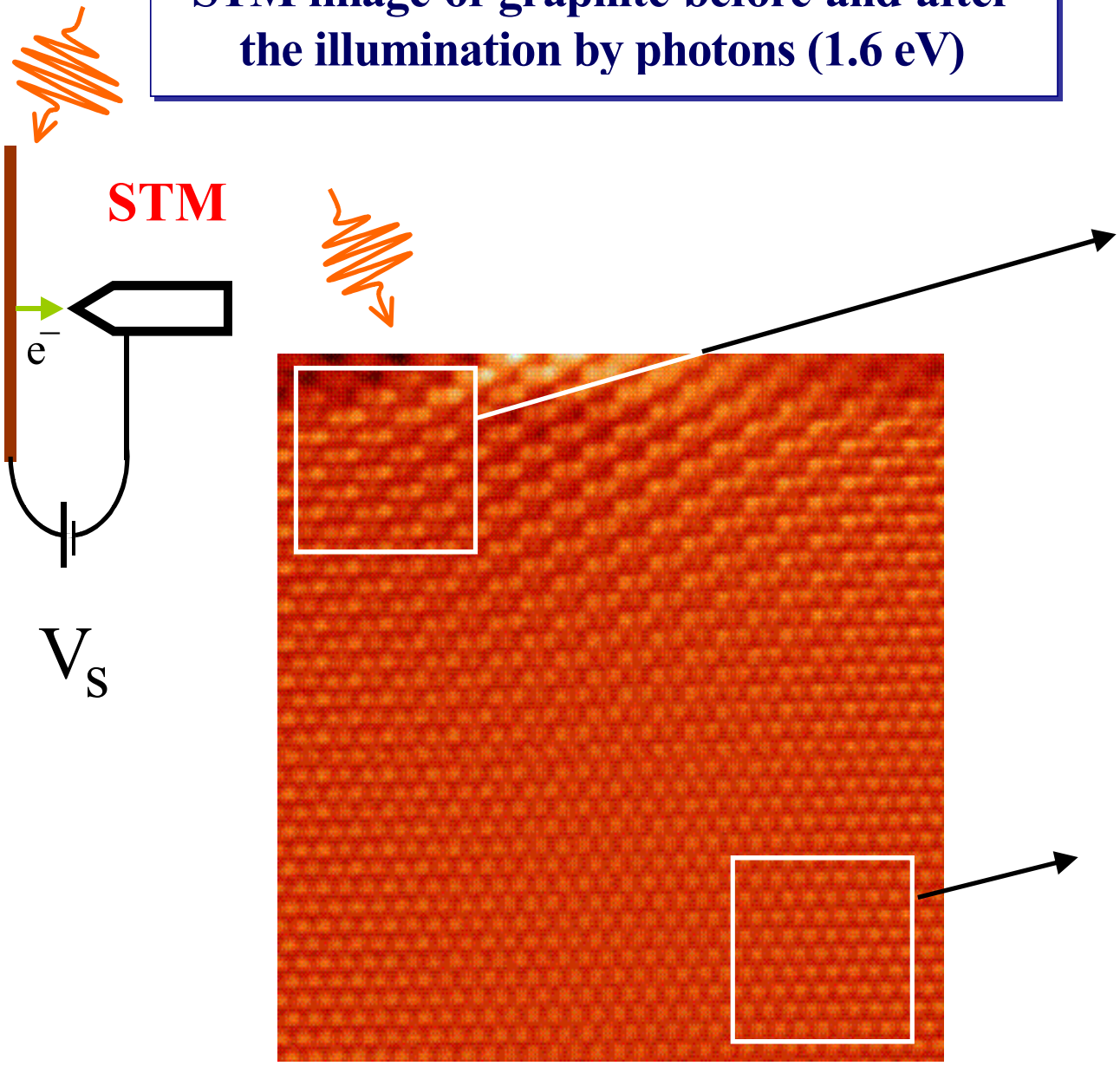
4. Femto-second pulse excitation, not nano-second

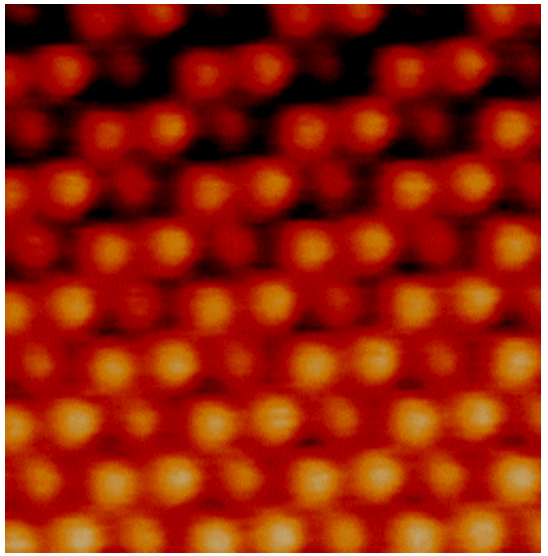
5. Resultant domain size includes about 1000 carbons

6. Structural phase transition due to inter-layer bond formation (STM image)

7. Resultant domain is quite stable(, more than 10 days)

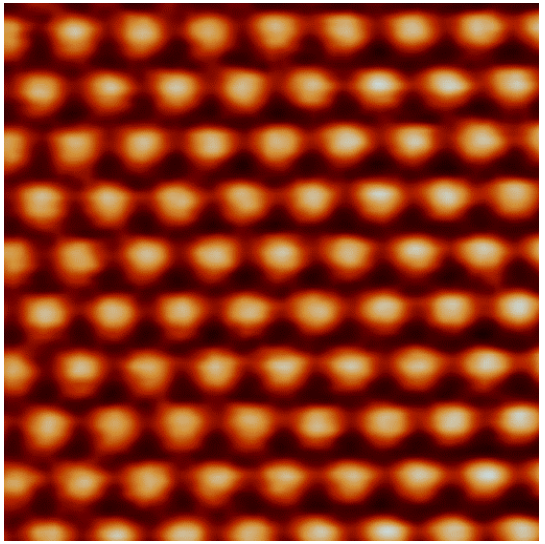
STM image of graphite before and after the illumination by photons (1.6 eV)



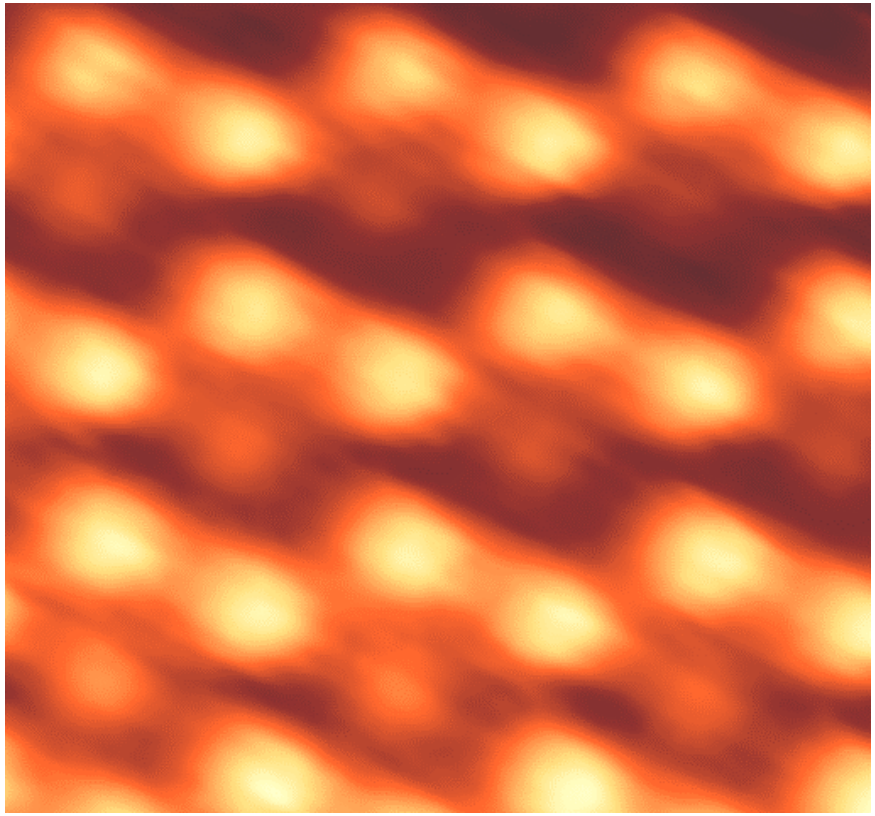


after

before



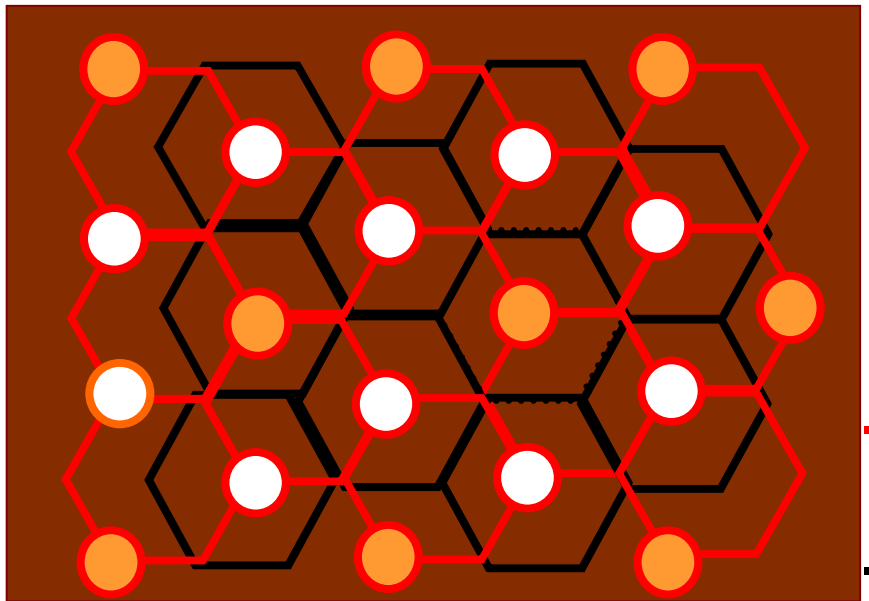
by Tanimura and Kanazaki



Vs = - 20 mV

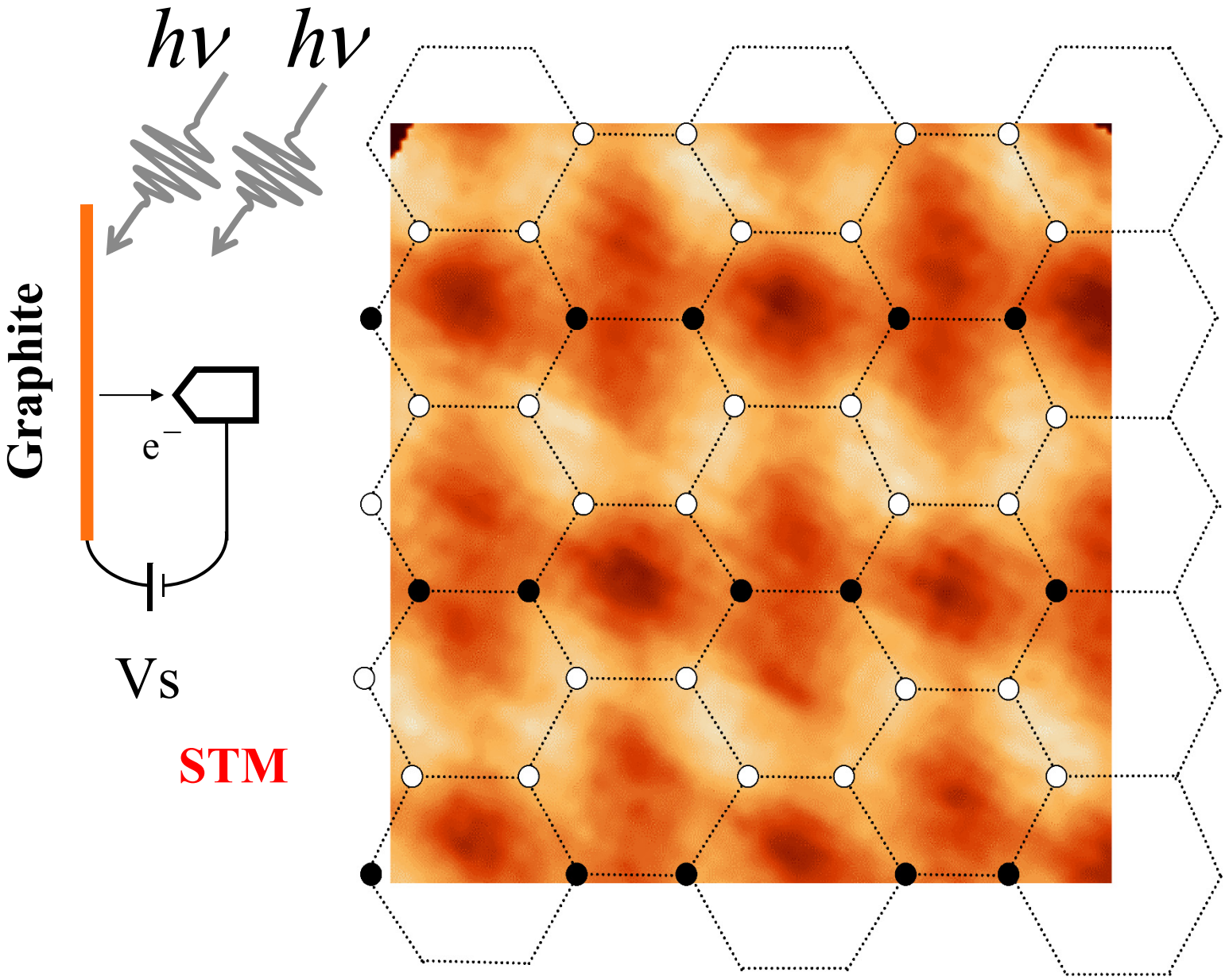
STM

by Tanimura
and Kanazaki

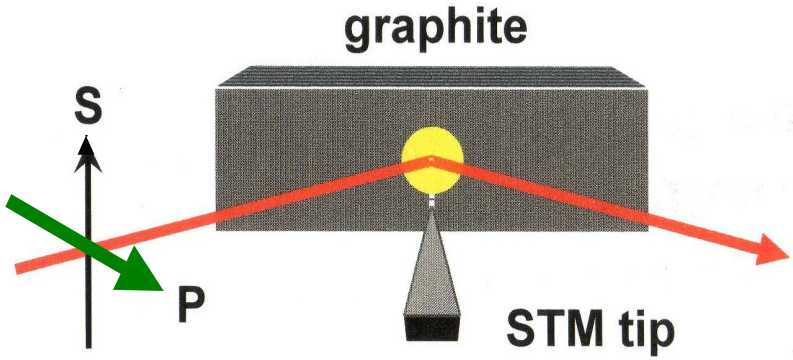


First layer

2’nd layer

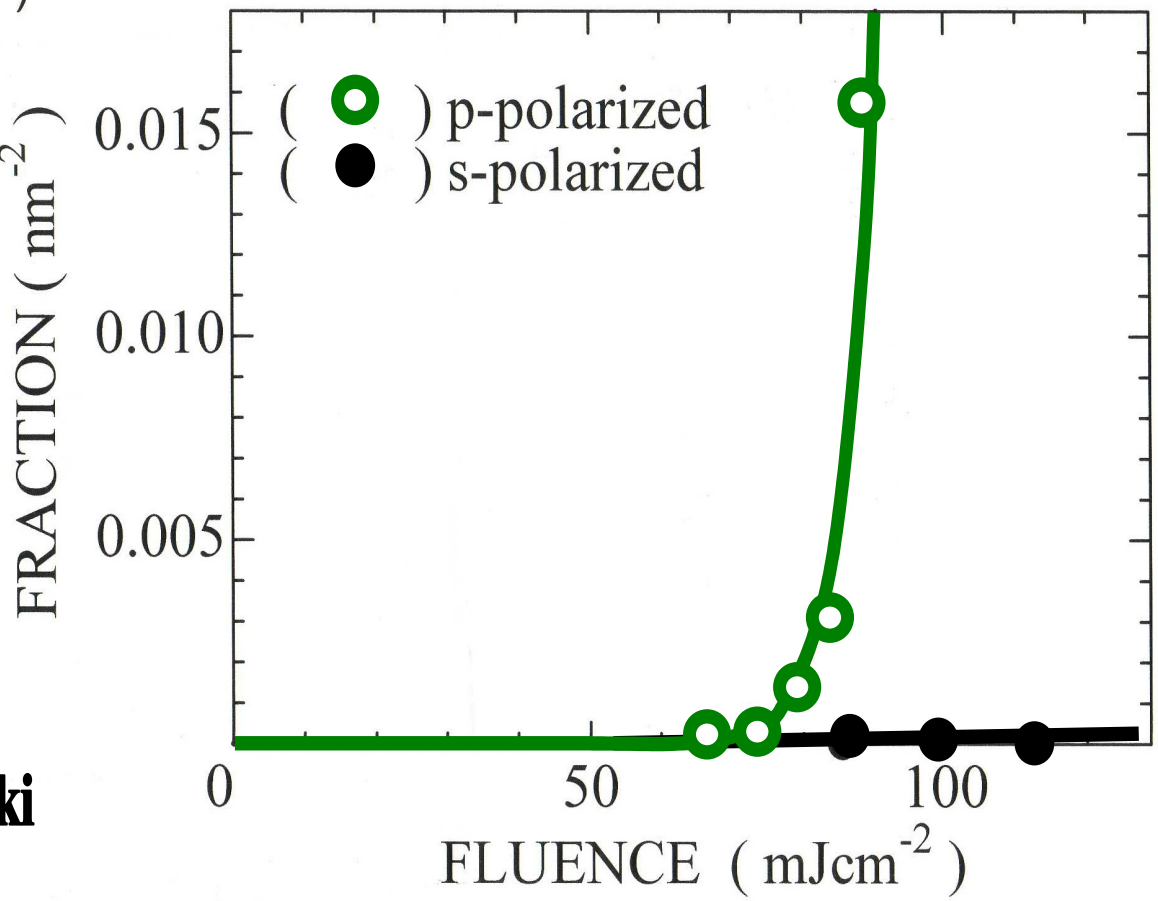


Kanasaki, Inami, Tanimura, Ohnishi, Nasu, PRL 102 (2009) 087402.



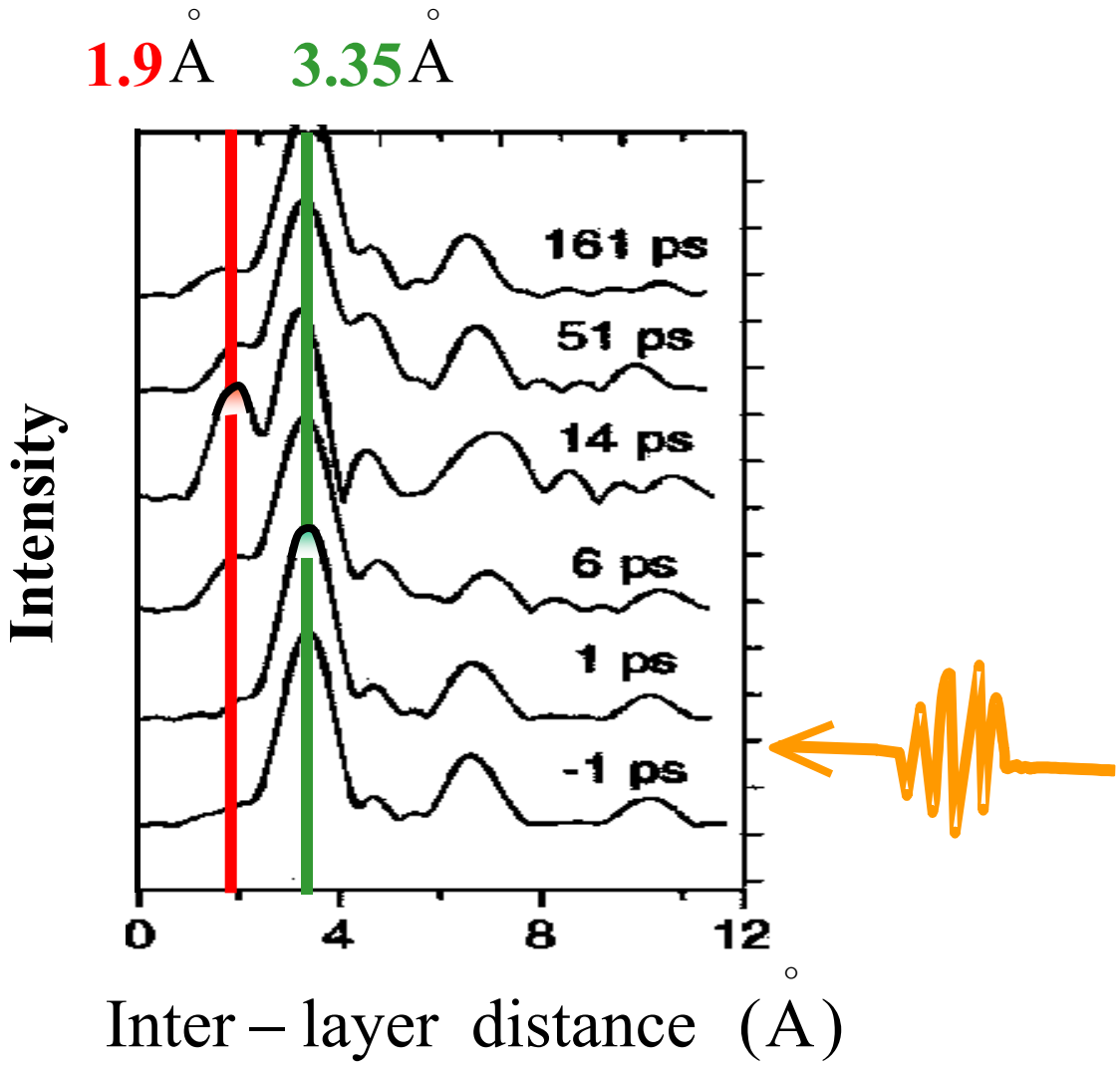
798nm (1.57eV)
80fs 1kHz

Exciting light should be polarized perpendicular to the layer, parallel component gives no effect.



by Tanimura and Kanazaki

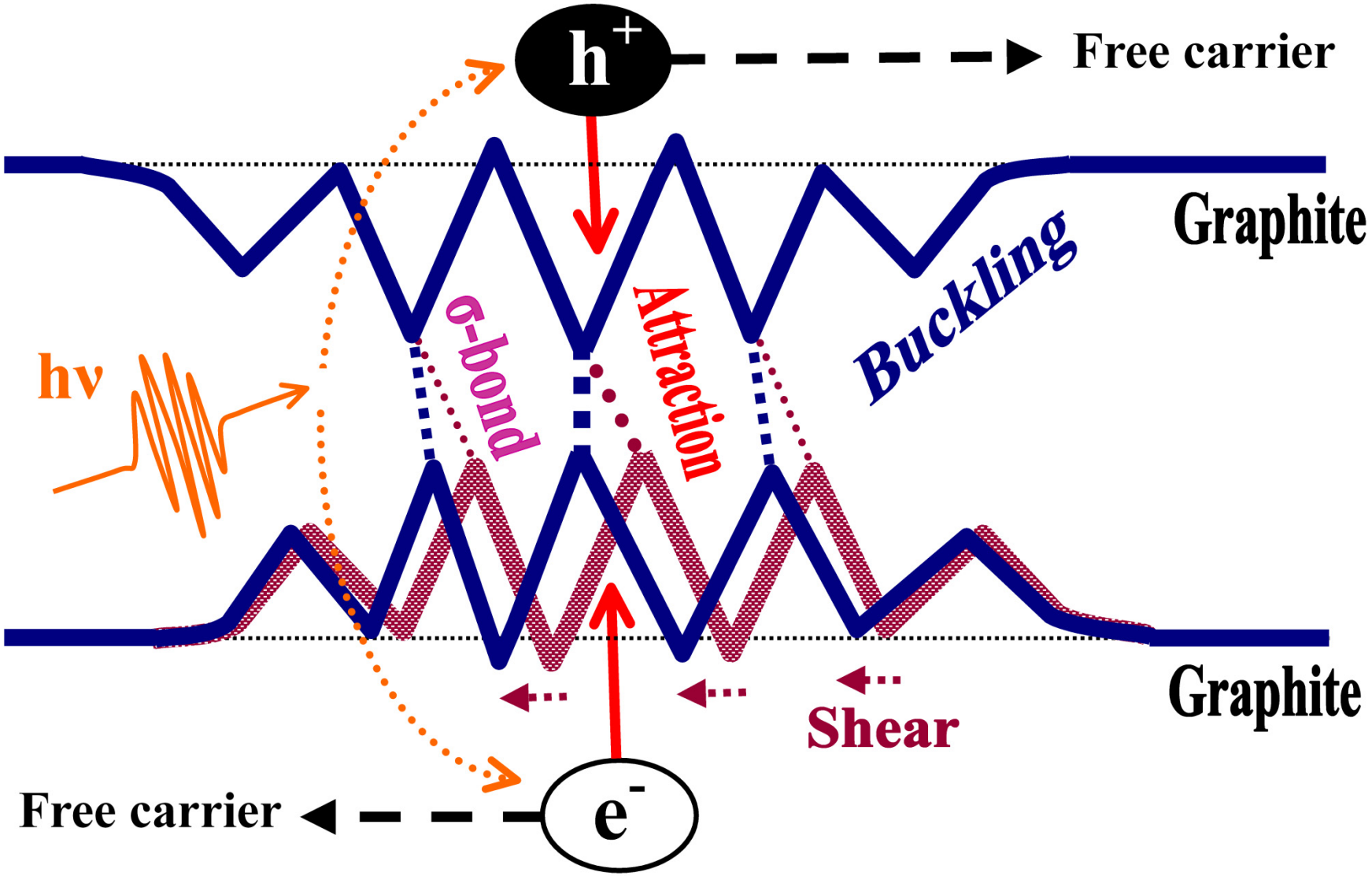
Direct observation of optically induced transient structures in graphite using ultrafast electron crystallography



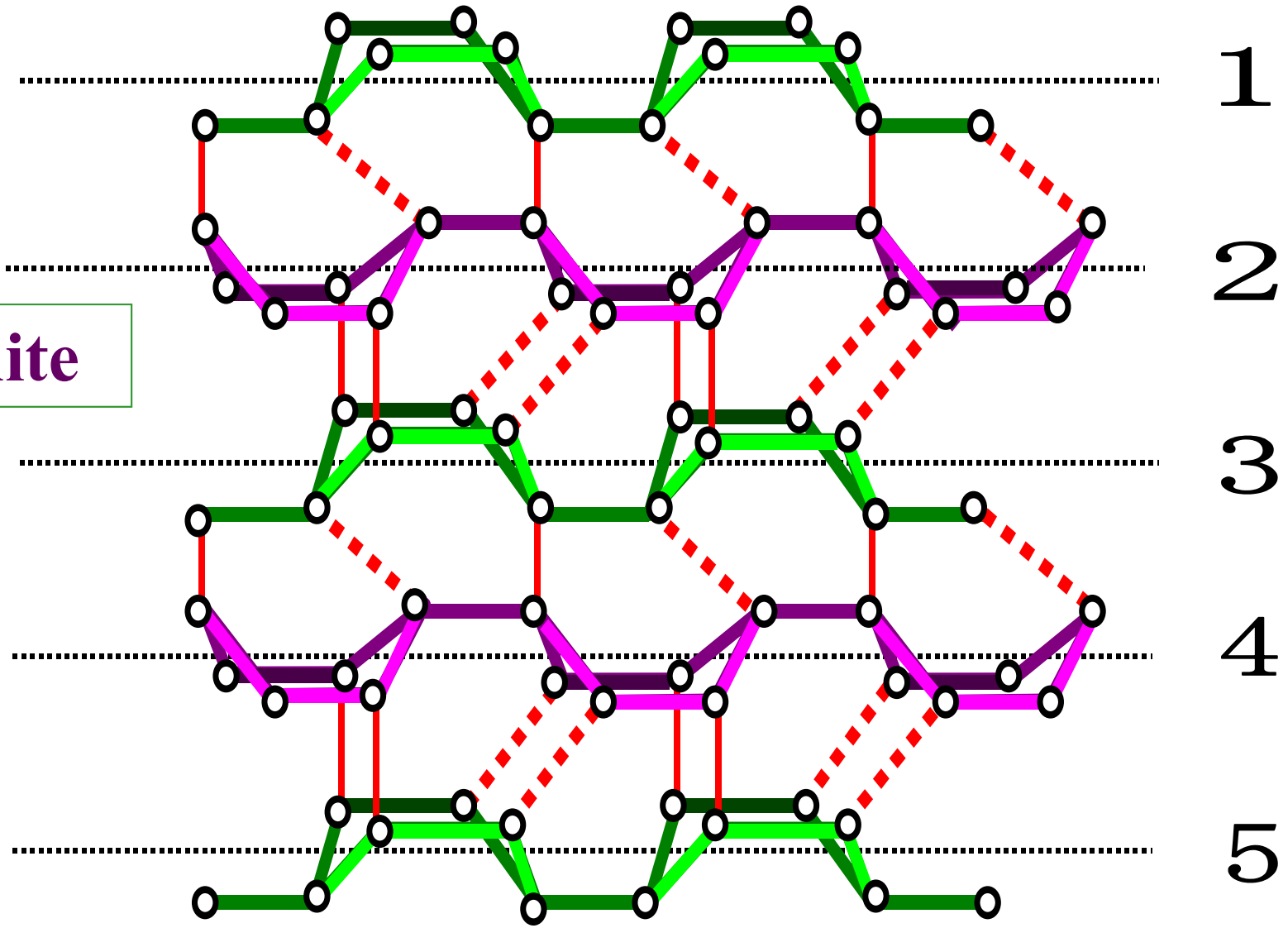
Raman, Murooka, Ruan, Yang, Berber and Tomanek, Phys.Rev.Lett. 101(2008) 077401.

Scenario for early stage

Spontaneous, successive broken symmetries



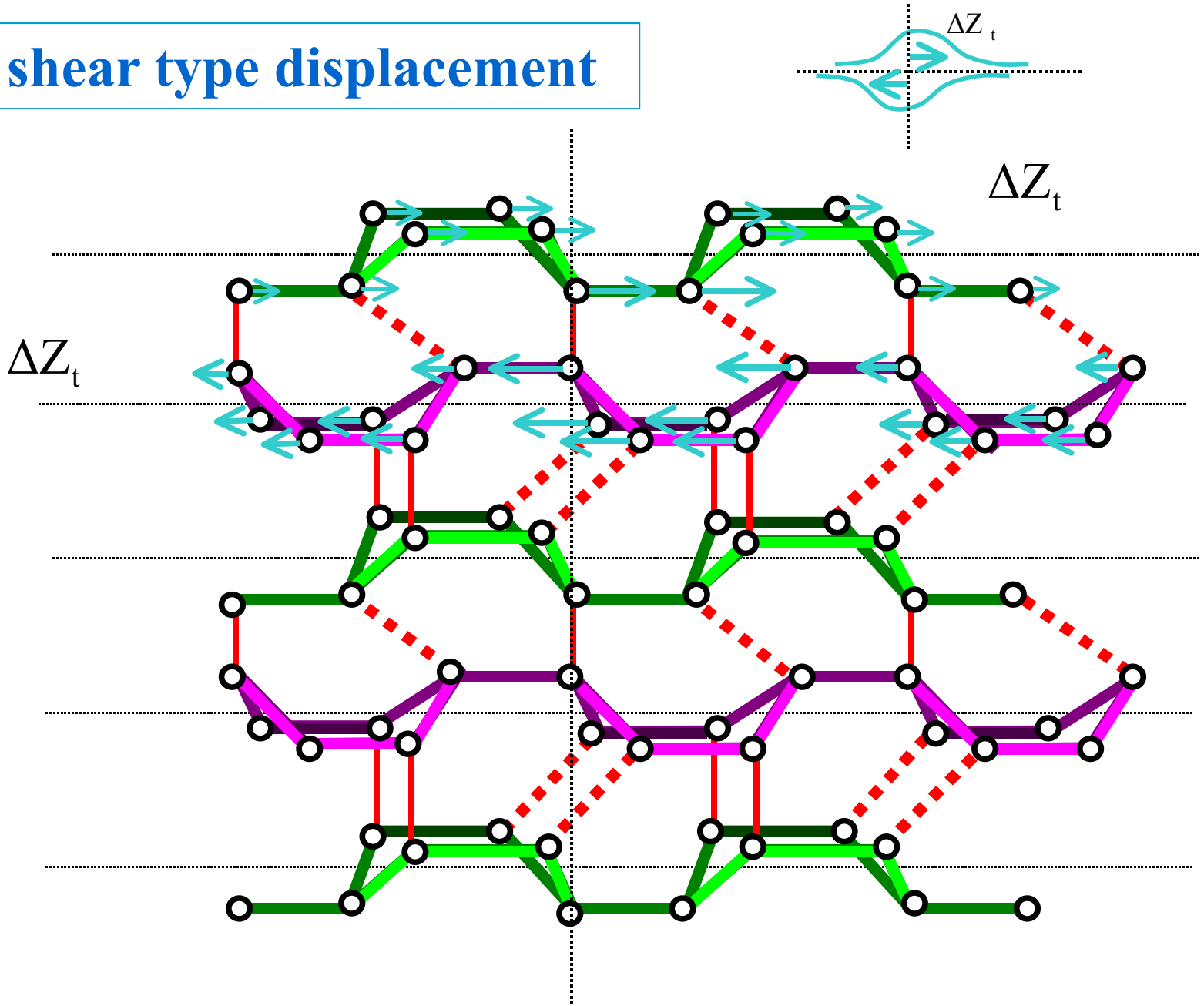
Inferred inter-layer bond structure



Diaphite

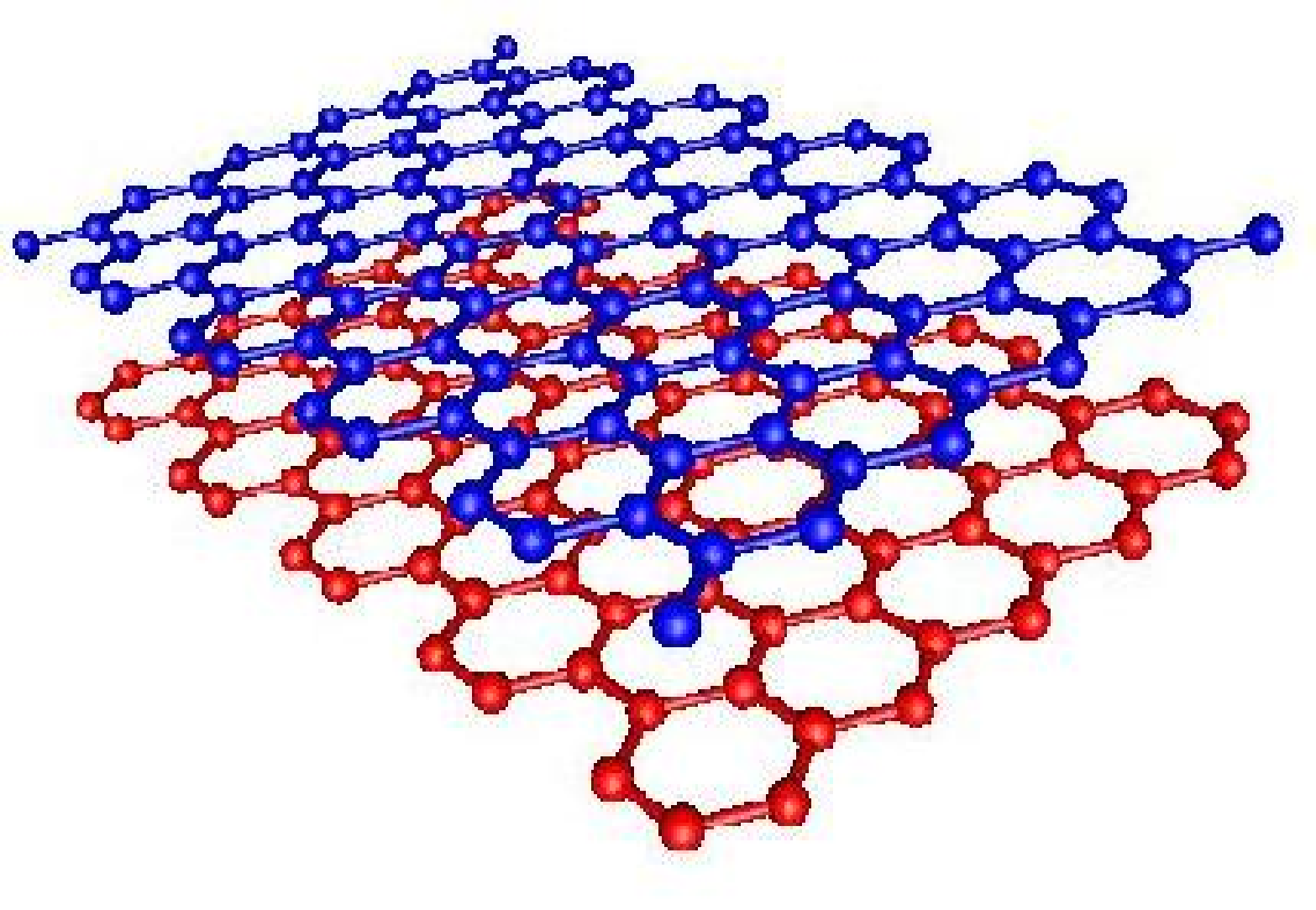
Research highlight, 2009, Nature (London) 458, 129.

Local shear type displacement

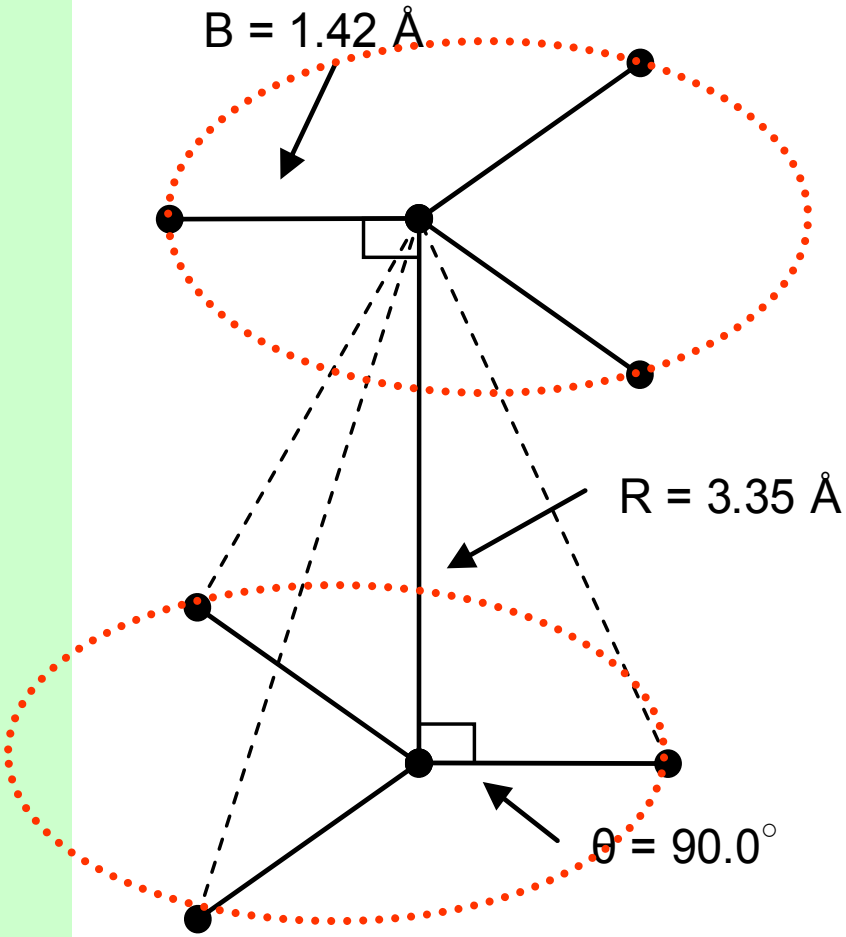


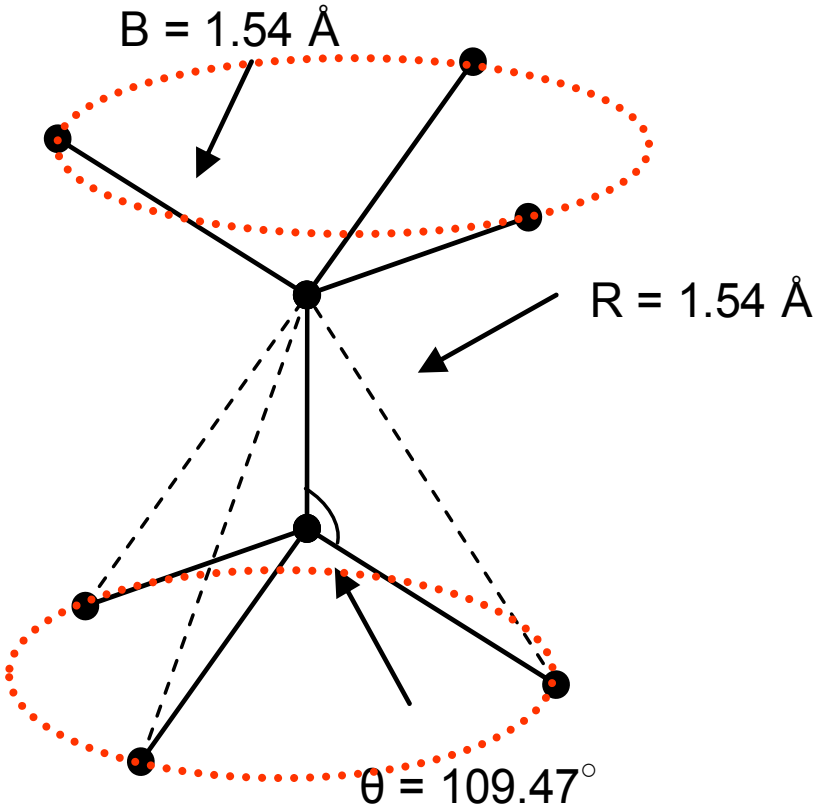
Shirotani, Inokuchi, Mol.Cryst.Liq.Cryst. 461(2007)93.

Hexagonal graphite – [ABAB] stacking



Graphite(sp^2) and diamond(sp^3) structures





LDF calculations by L. Cohen, S. Fahy and S.G. Louie

LDF calculation for graphite-diamond transition

S. Fahy et al, Phys. Rev. B35(1987)7623. Tateyama et al, Phys Rev.B54(1996)14994.

Energy barrier ~ 0.3 eV/carbon

However, it is a hypothetical uniform transformation.

All the macroscopic number of carbons are assumed to move simultaneously ?

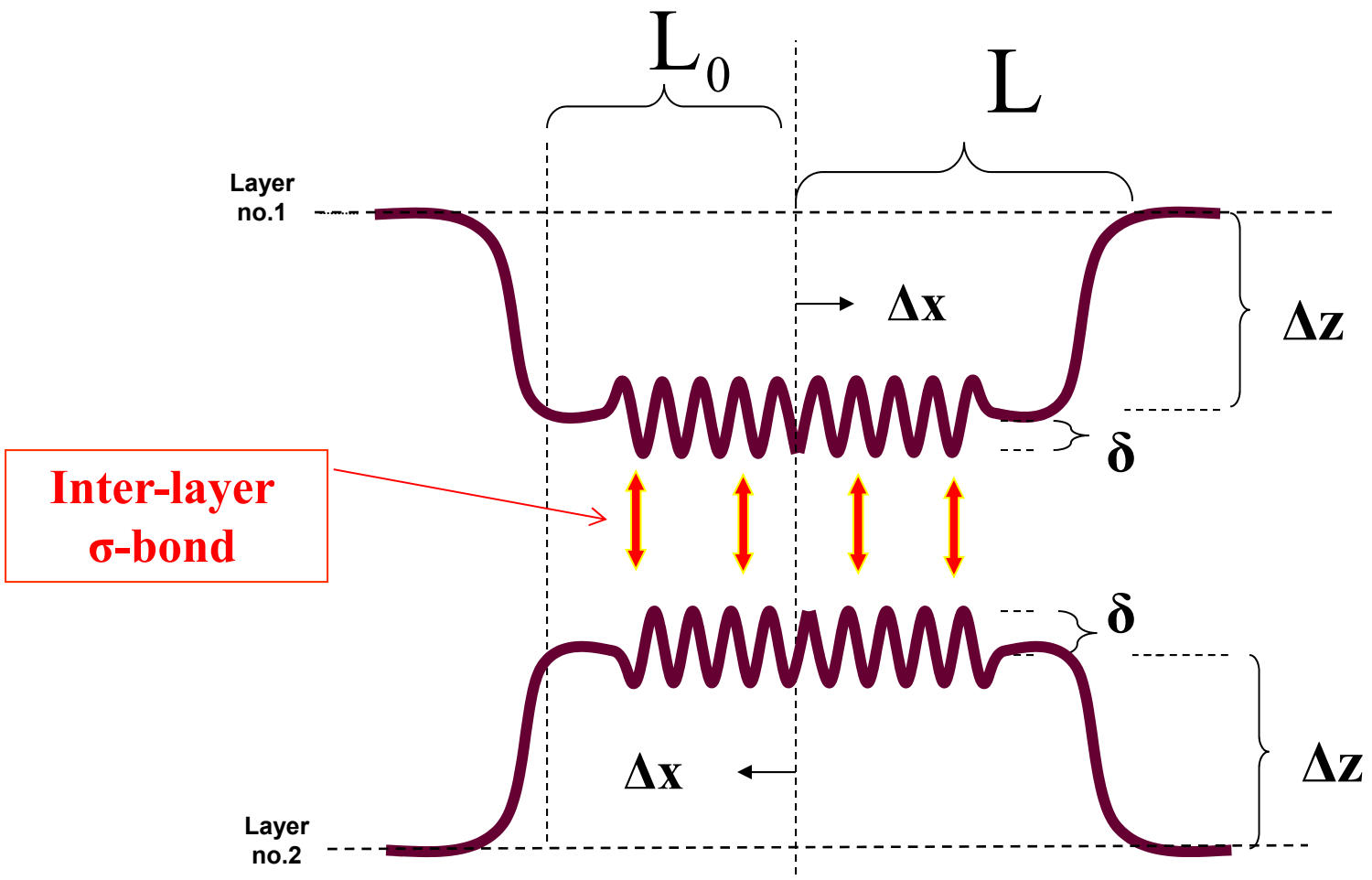
Real process is an iterative local domain formation, never be simultaneous.

More high barrier

Local domain formation is the essential process.

Local distortion of graphite layers

Trial distortion pattern



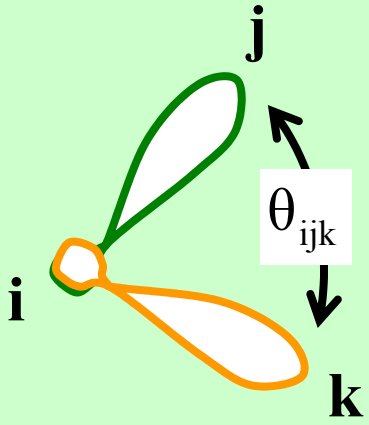
Brenner's 3-, 4-body potential

$$E = \sum_{i,\ j(>i)} \left[V_R(r_{ij}) - \overline{B}_{ij}(r_{ij}, \theta_{ijk})\, V_A(r_{ij}) \right]$$

Hard core repulsion

Attraction with chemical bond angle

θ_{ijk}



D.W. Brenner, Phys. Rev. B 42 (1990)9458.

Comparison

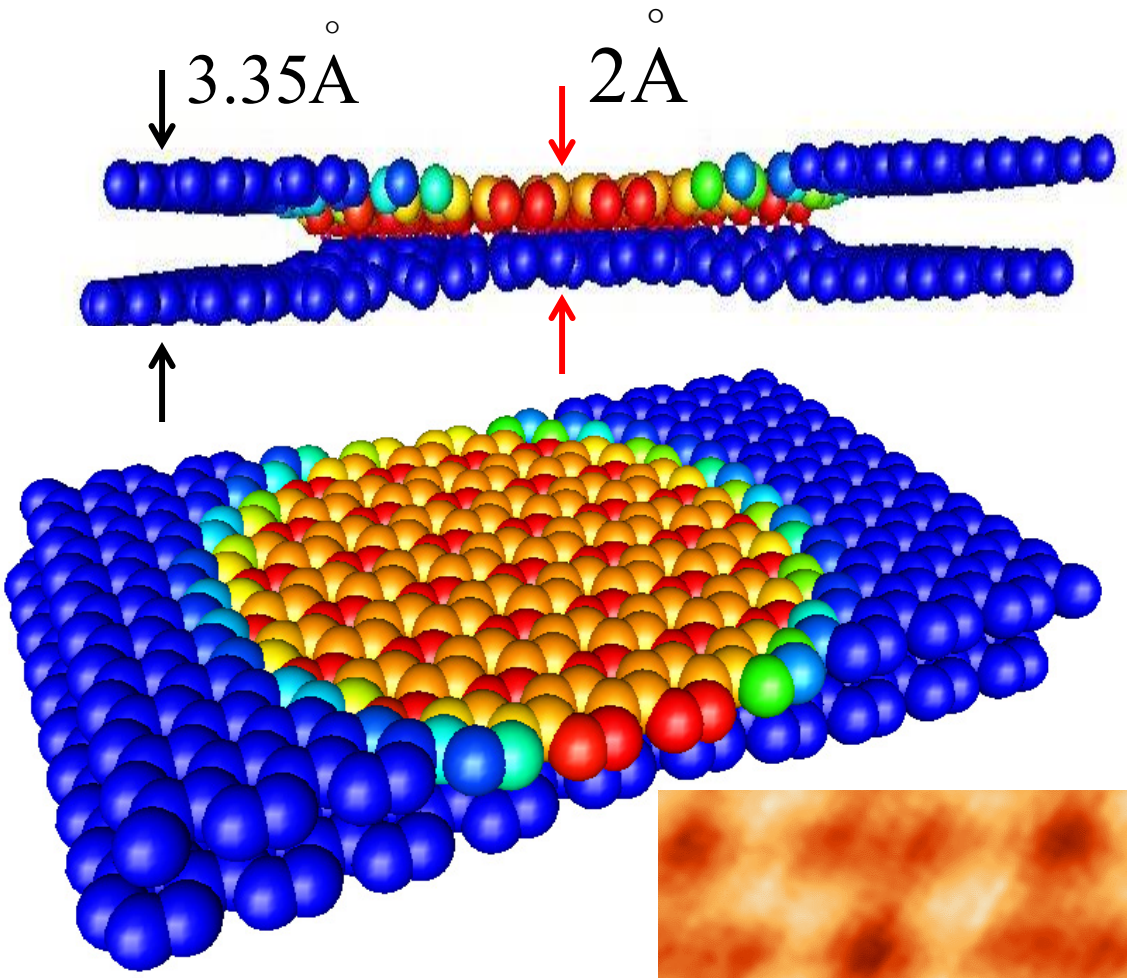
Brenner's potential

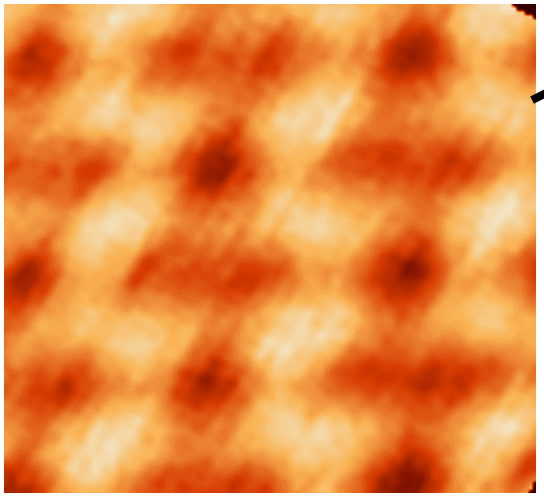
- Semi-empirical inter-atomic potential, 3- or 4- body force, Direction of chemical bonds,
- Gives proper data for both graphite and diamond structures,
  - Short range (2.0 $\mathring{A}$) – No information about interalyer coupling

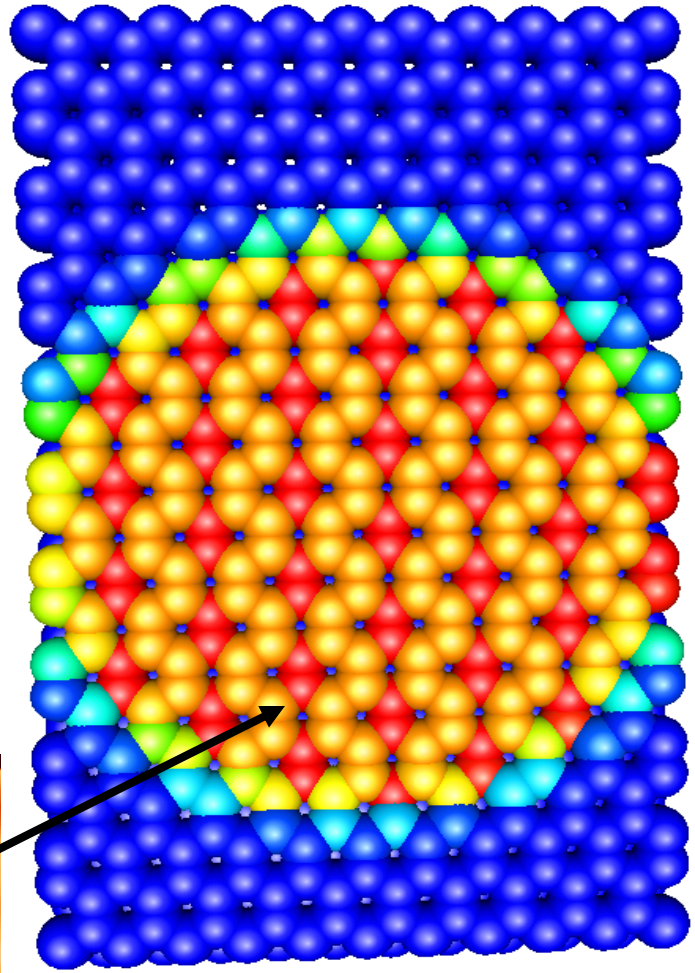
Lennard-Jones' potential

- Two body potential,
- Depends only on bond length
- No information for chemical bond structure

New domain structure by Brenner potential





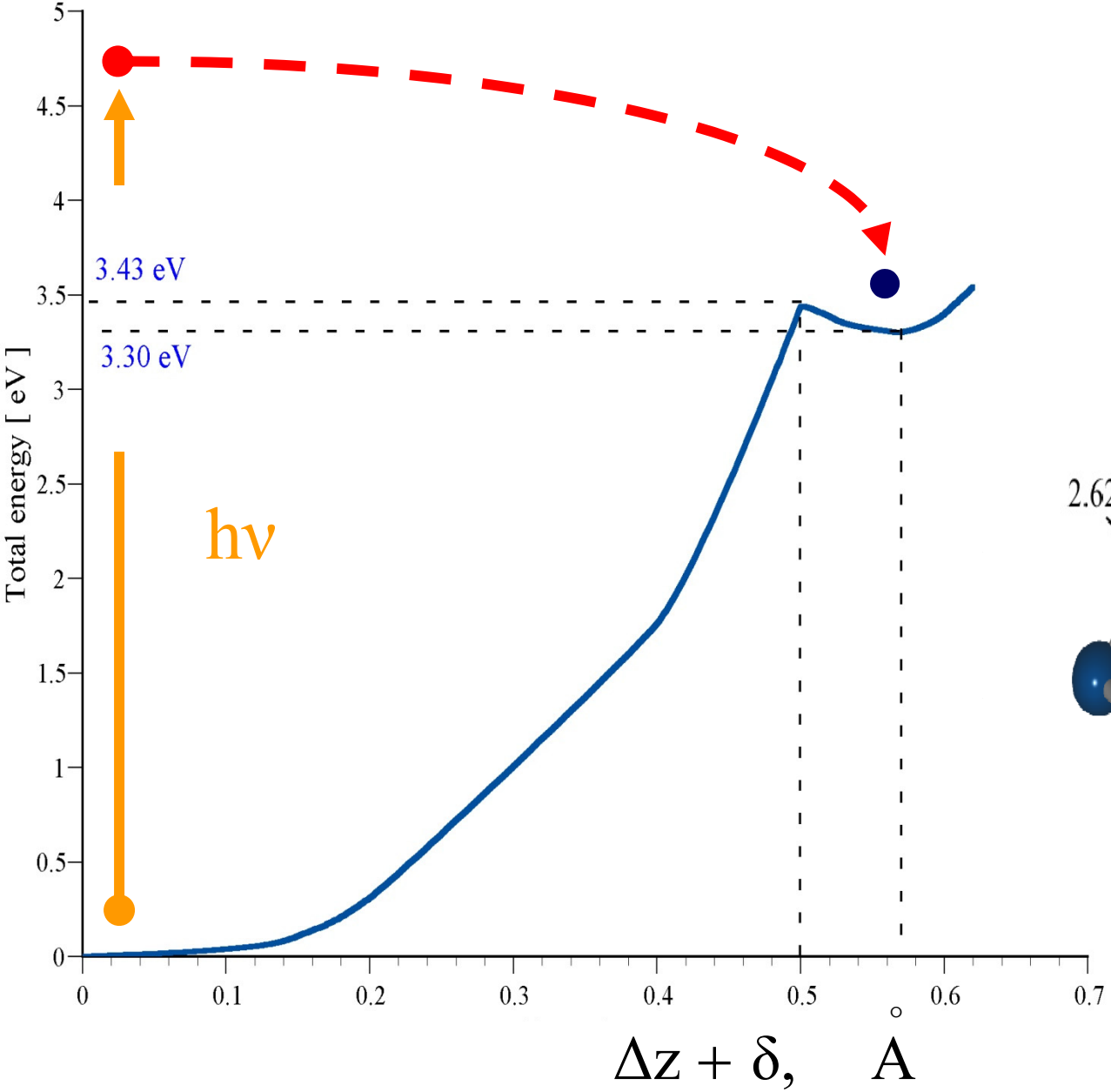


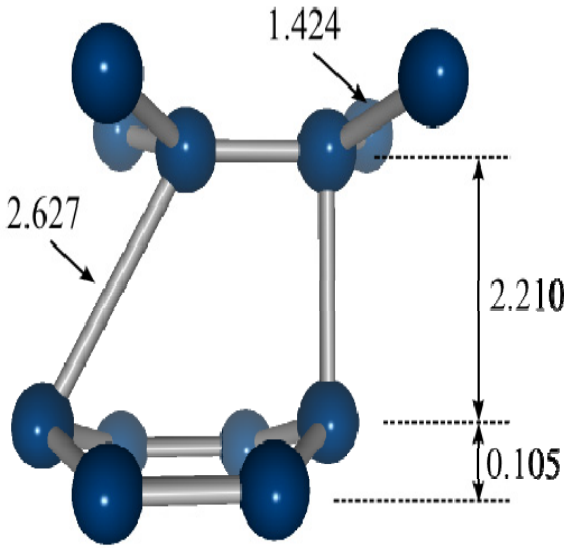
STM

Radosinski, Nasu, Luty
Radosz, PRB 81(2010) 035417.

LDF theory for new domain structure

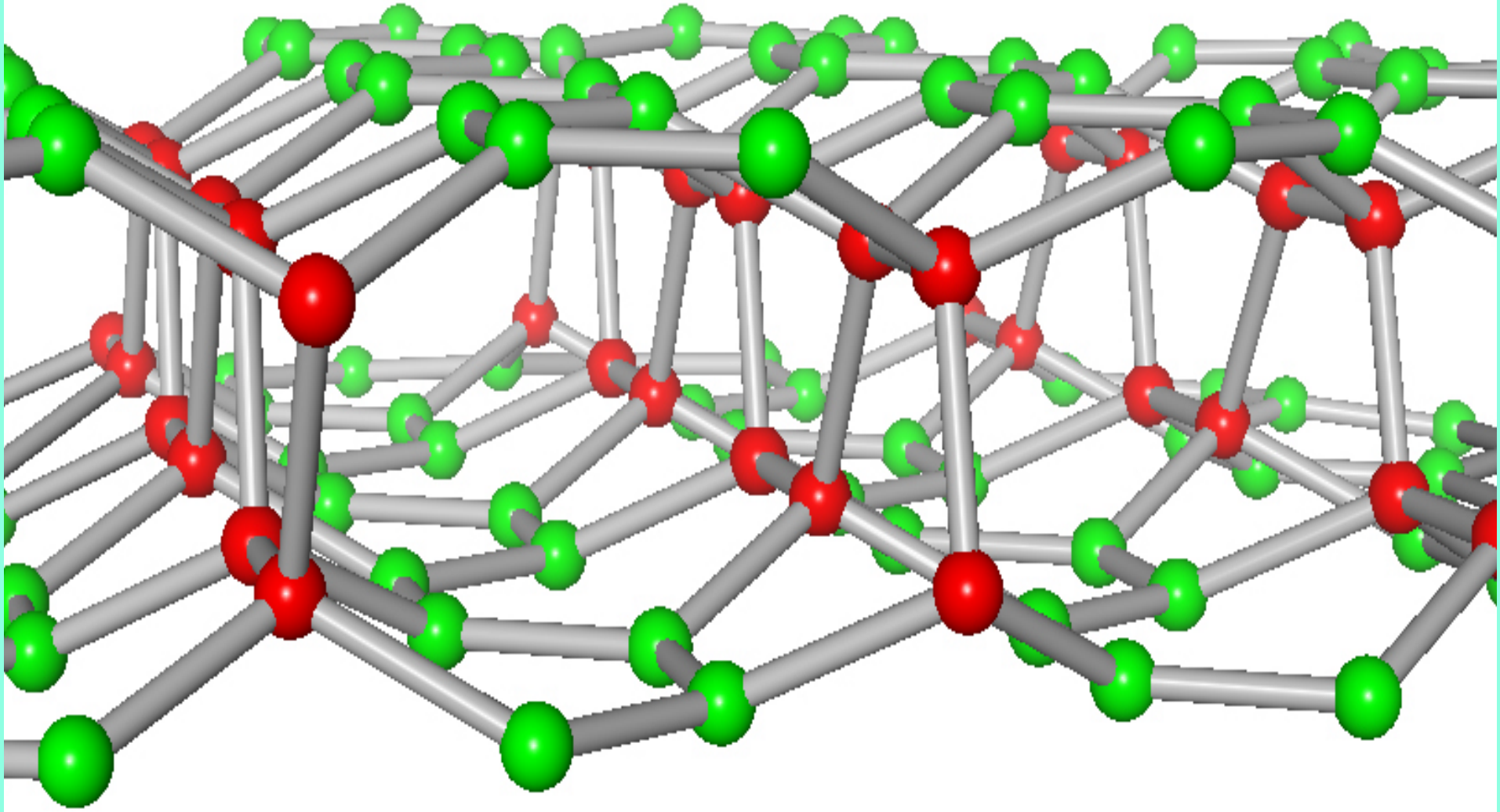
500 carbons





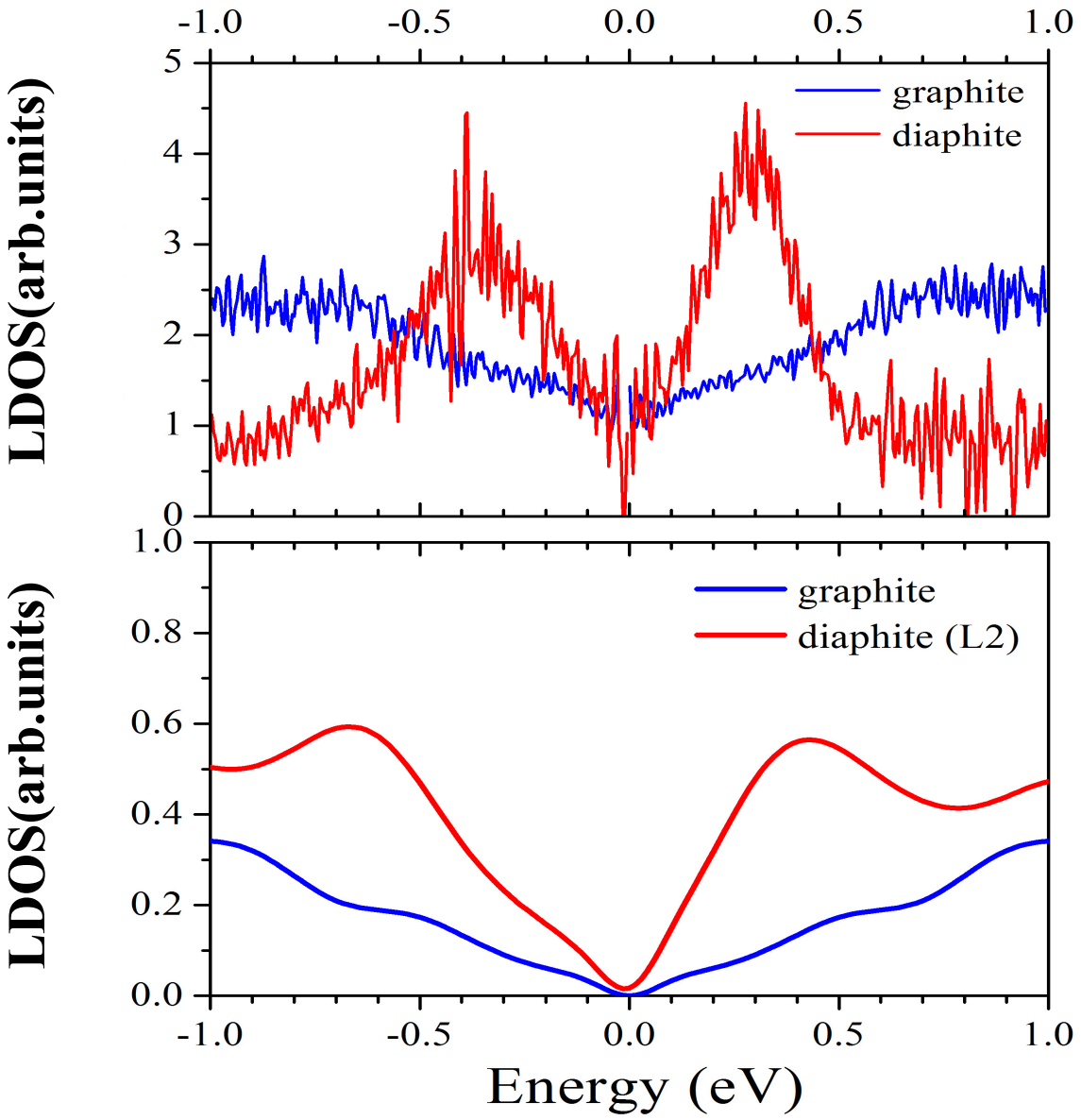
Ohnishi, Nasu, PRB 79 (2009) 054111.

High energy “L2” diaphite domain by Brenner



Ohnishi, Nasu, PRB 80 (2009)014112.

New localized states and pseudo gap



STM

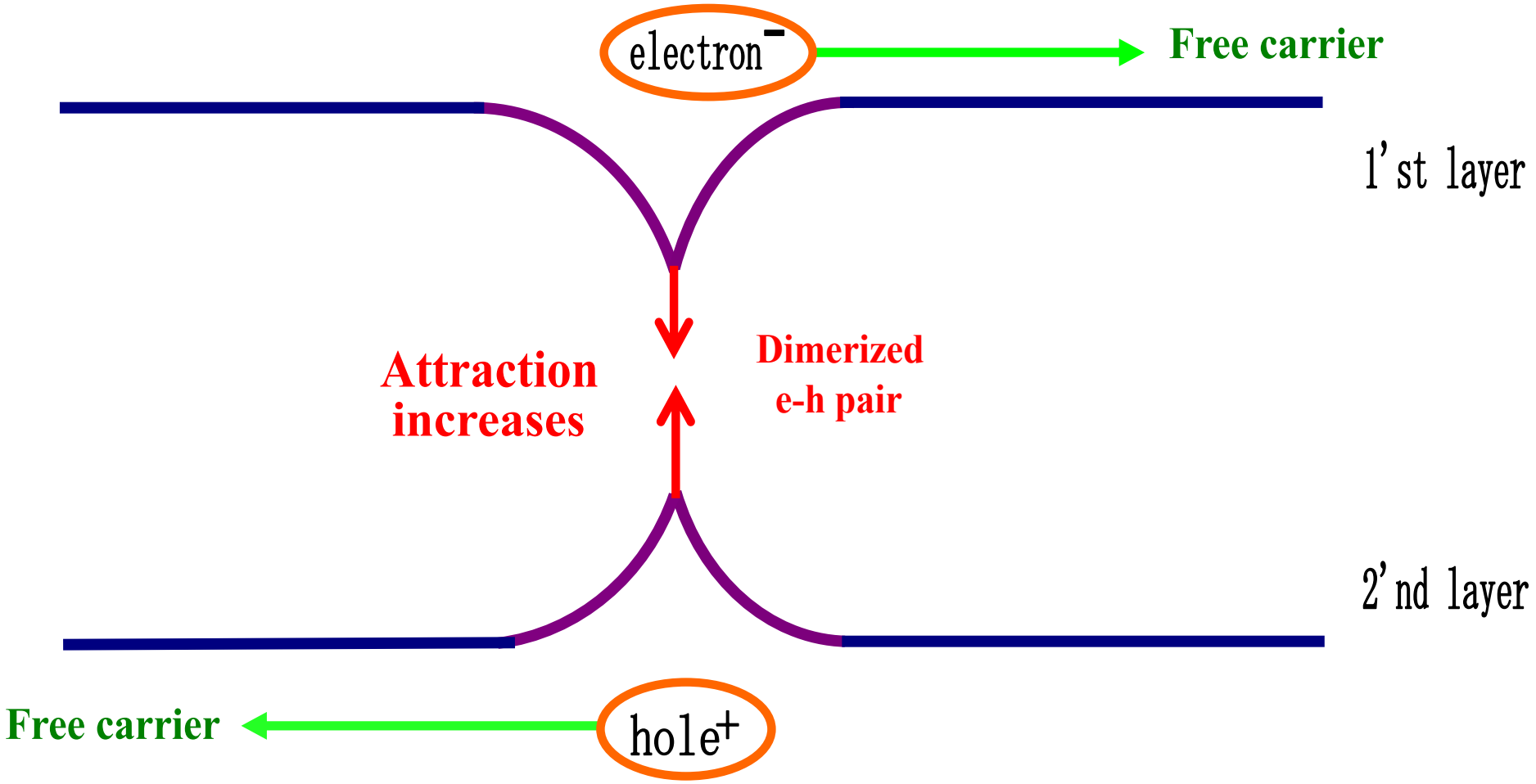
Kanasaki, Inami, Tanimura, Ohnishi, Nasu PRL 102 (2009) 087402.

Brenner

Koster Slater

Ohnishi, Nasu, PRB 80 (2009)014112.

Early time critical dynamics
Competition between
Electron-hole dimerization and Charge separation



V-shaped semi-metallic electron system

$$H_e = \sum_{j=1,2} \sum_{i=1,2} sign(i-3/2) \sum_{k,\sigma} E(k) a^{+}_{k\sigma ij} a_{k\sigma ij} \quad , \quad E(k) = \sqrt{k_x^2 + k_x^2}$$

j =1,2 Layer number,

i=1,2 Valence or conduction band,

k, $\sigma(=\alpha, \beta)$ wave vector and spin in a square lattice, lattice constant is unit of length

$$a_{k\sigma i j} \equiv N^{-1/2} \sum_{\ell} e^{-ik\cdot\ell} a_{\ell\sigma i j}$$

Inter-layer phonon

$$H_p = \frac{\omega}{2} \sum_{\ell} \left[-\frac{\partial^2}{\partial Q_\ell^2} + Q_\ell^2 \right]$$

Inter-layer Coulomb attraction between electron and hole, depending on Q_ℓ

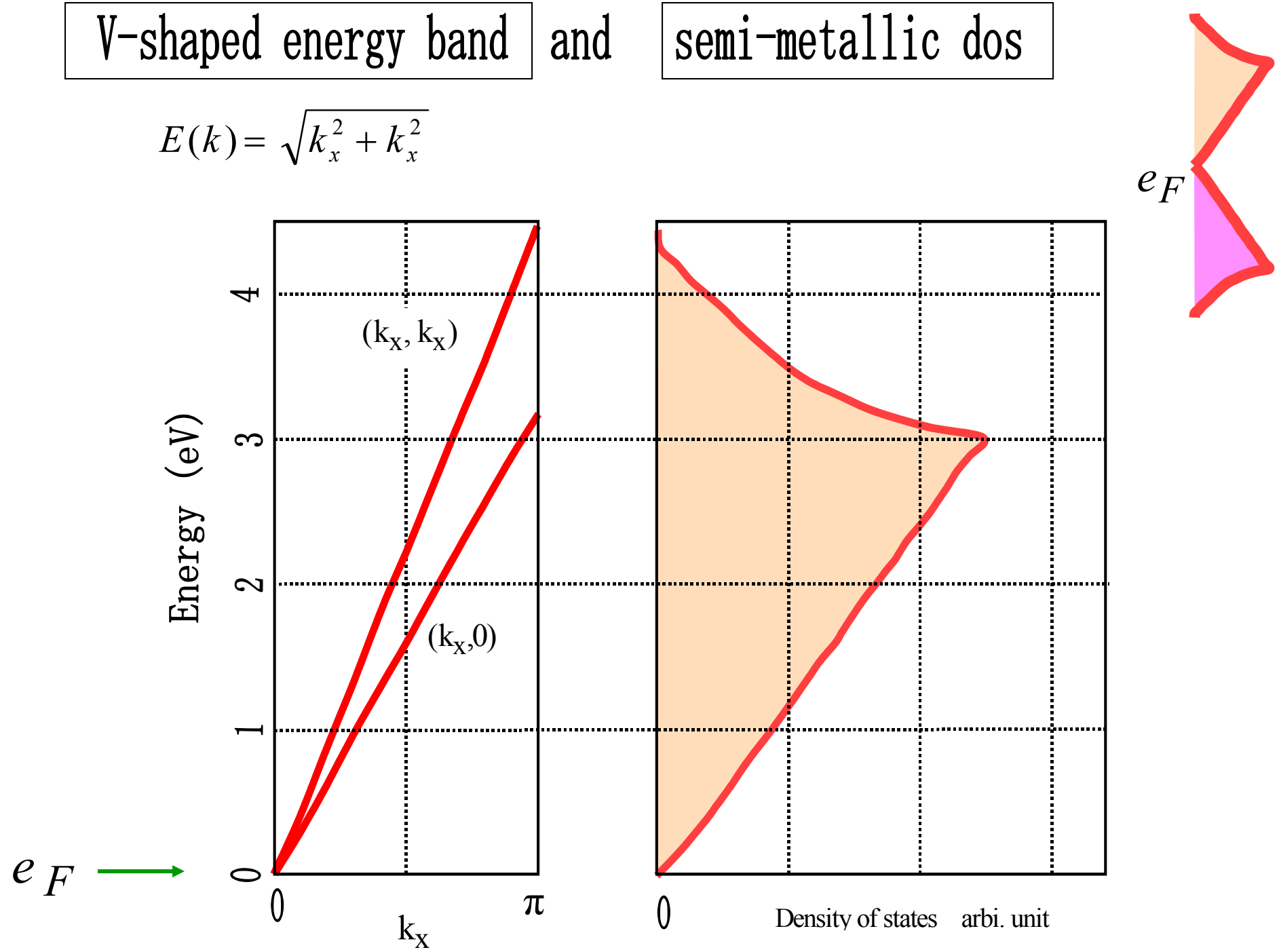
$$H_c = \sum_{\ell,\sigma,\sigma'} U(Q_\ell) \left[(n_{\ell\sigma 11} - <n_{\ell\sigma 11}>)(n_{\ell\sigma' 22} - <n_{\ell\sigma' 22}>) + (n_{\ell\sigma 21} - <n_{\ell\sigma 21}>)(n_{\ell\sigma' 12} - <n_{\ell\sigma' 12}>) \right]$$

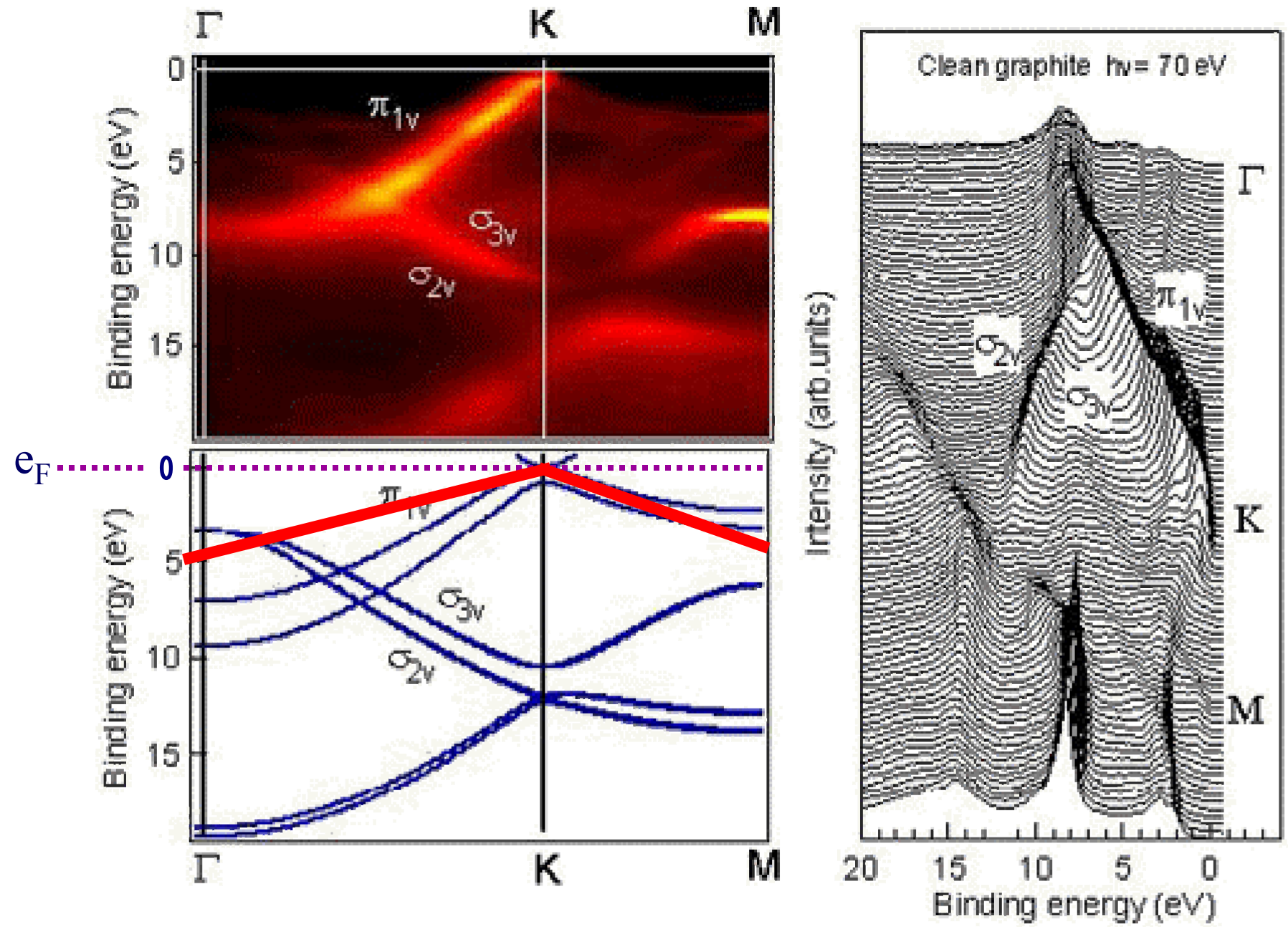
$$n_{\ell\sigma ij} \equiv a^{+}_{\ell\sigma ij} a_{\ell\sigma ij} \ ,$$

$$< \cdots > = \frac{Trace \ (e^{-H_0/k_B T_{em}} \cdots)}{Trace \ (e^{-H_0/k_B T_{em}})}, \qquad T_{em} \quad \text{absolute temperature,}$$

V-shaped energy band and semi-metallic dos

$$E(k) = \sqrt{k_x^2 + k_x^2}$$

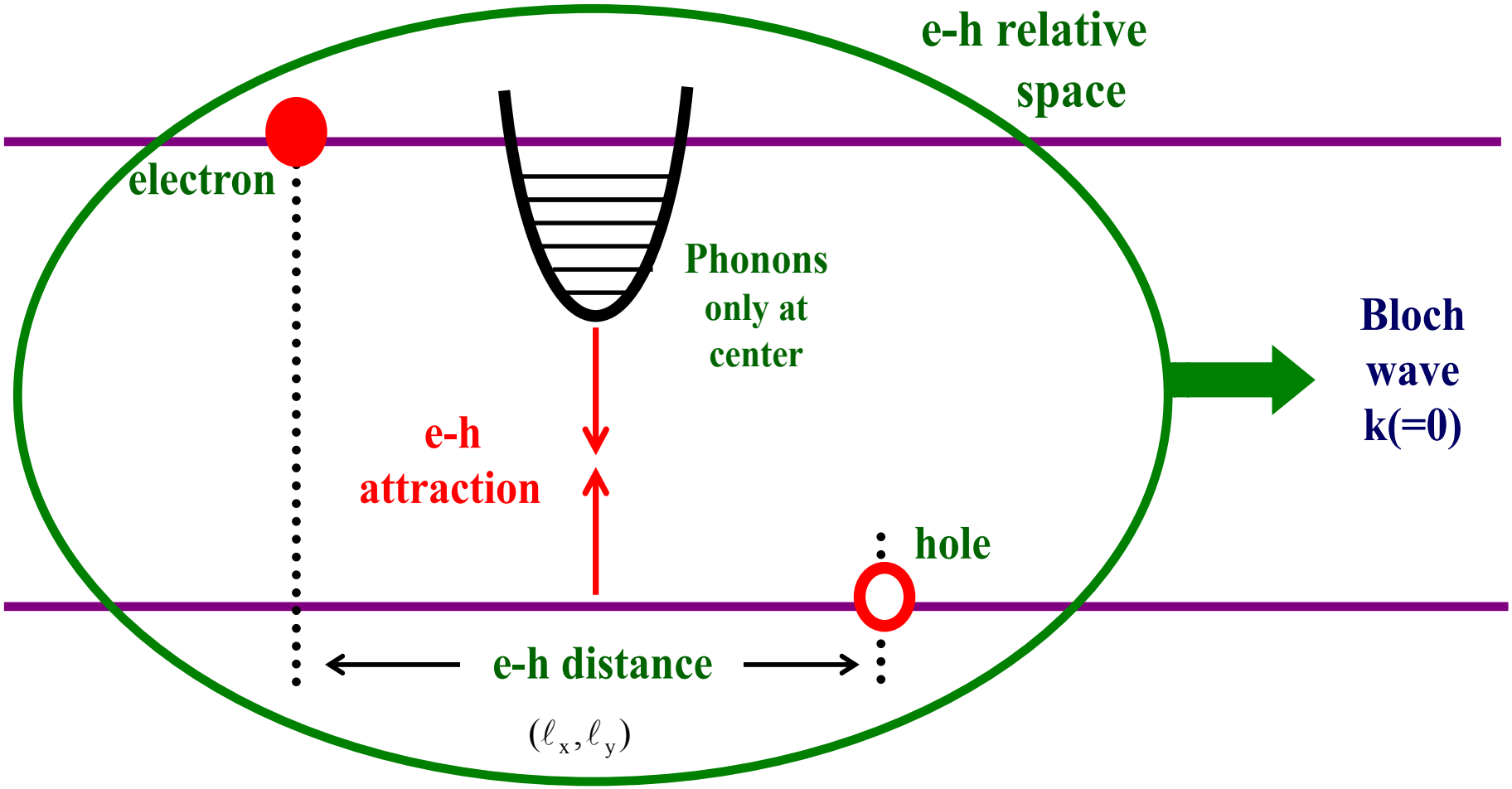



Γ
K
M
0
5
10
15
Binding energy (eV)
π_{1v}
σ_{3v}
σ_{2v}
e_F
0
Clean graphite hν = 70 eV
Intensity (arb.units)
20
15
10
5
0
Binding energy (eV)

Theory for dynamics

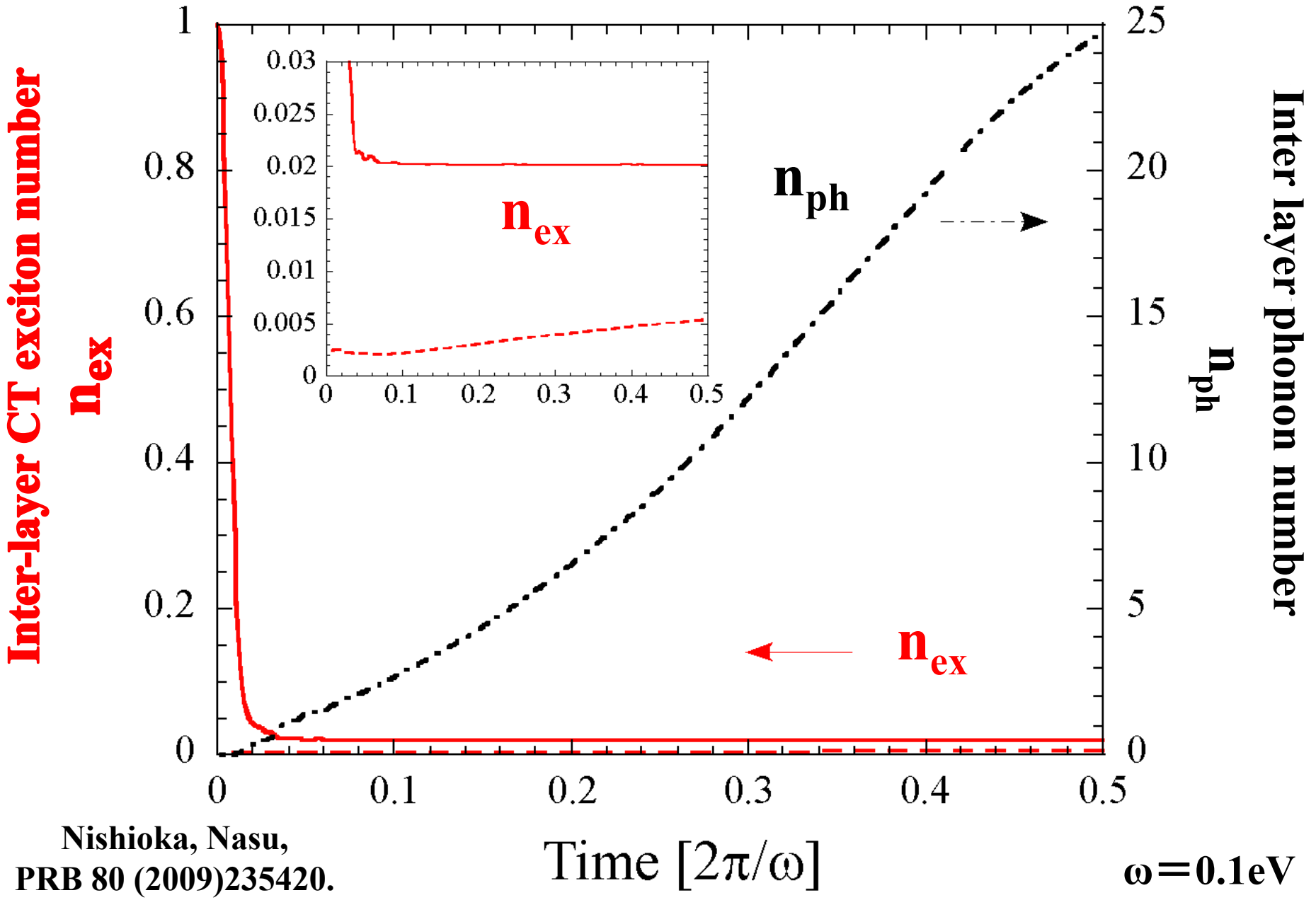
Bloch wave of (electron, hole and multi-phonon) coupled system with total momentum k (= 0)

Attraction depends on phonon



Cho, Toyozawa, JPSJ 30, 1555 (1971)

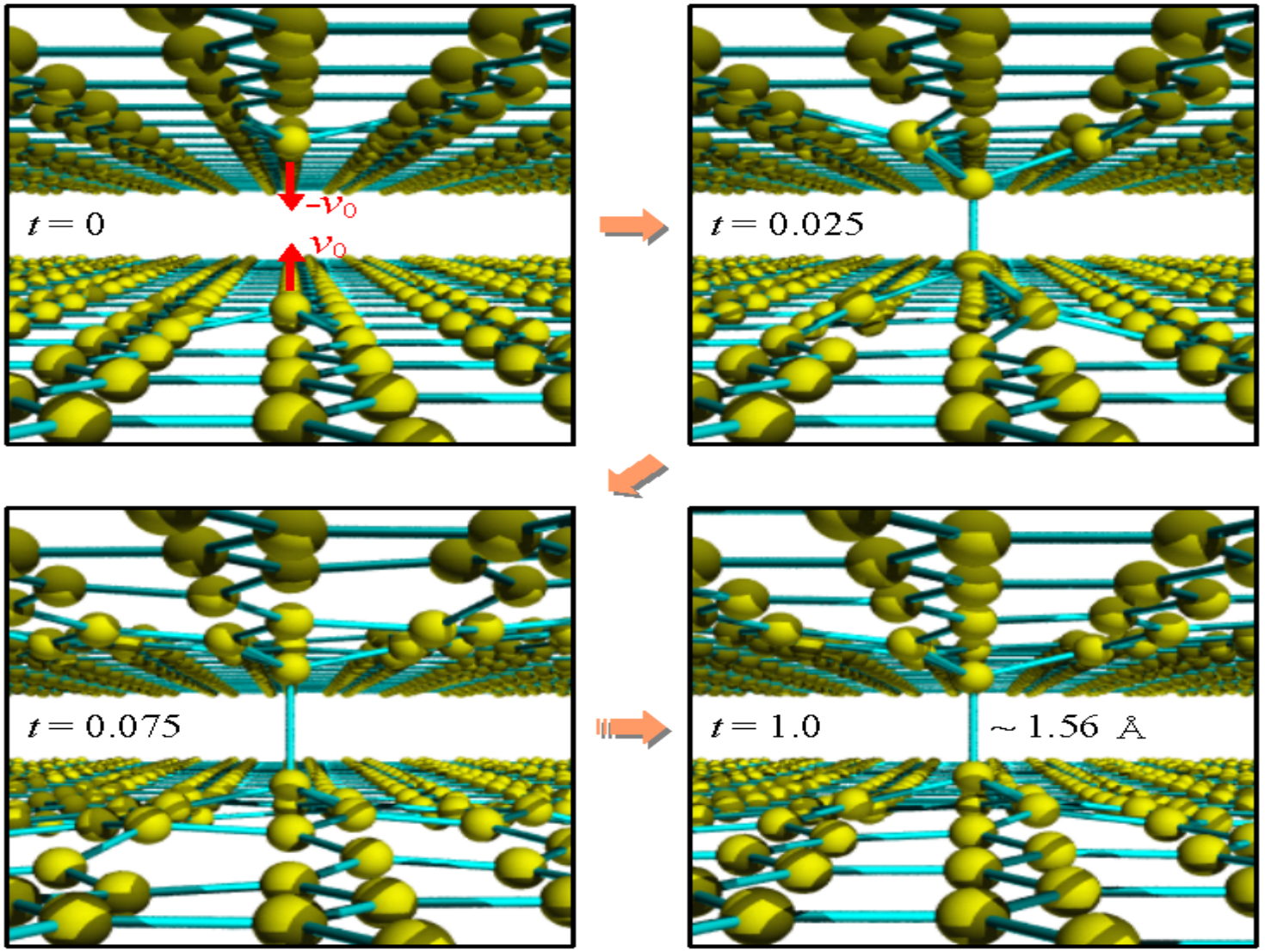
Free carrier dissipation and self-localization dynamics



Nishioka, Nasu,
PRB 80 (2009)235420.

ω=0.1eV

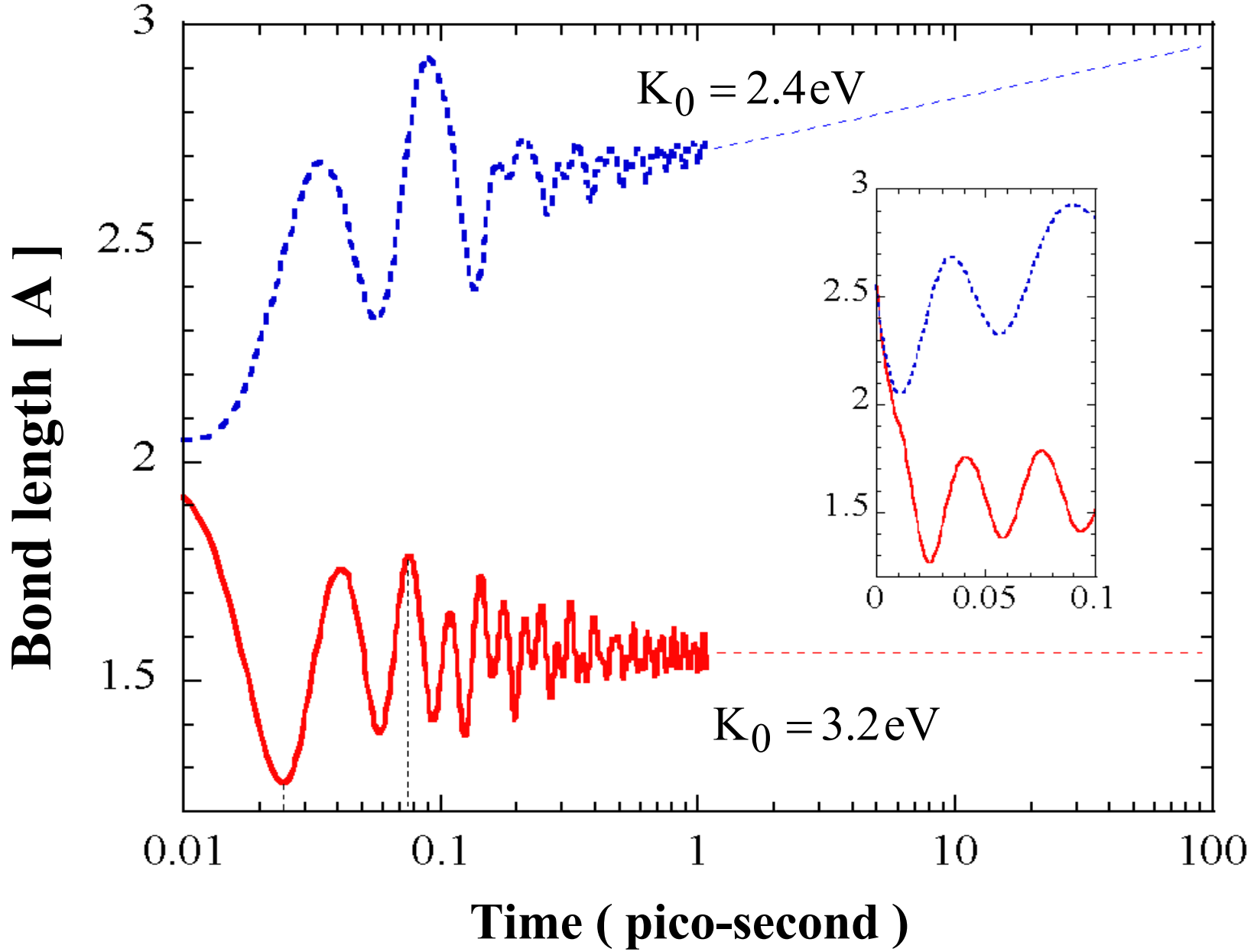
Classical dynamics of inter-layer σ-bond formation after self-localization



time: t pico-sec.

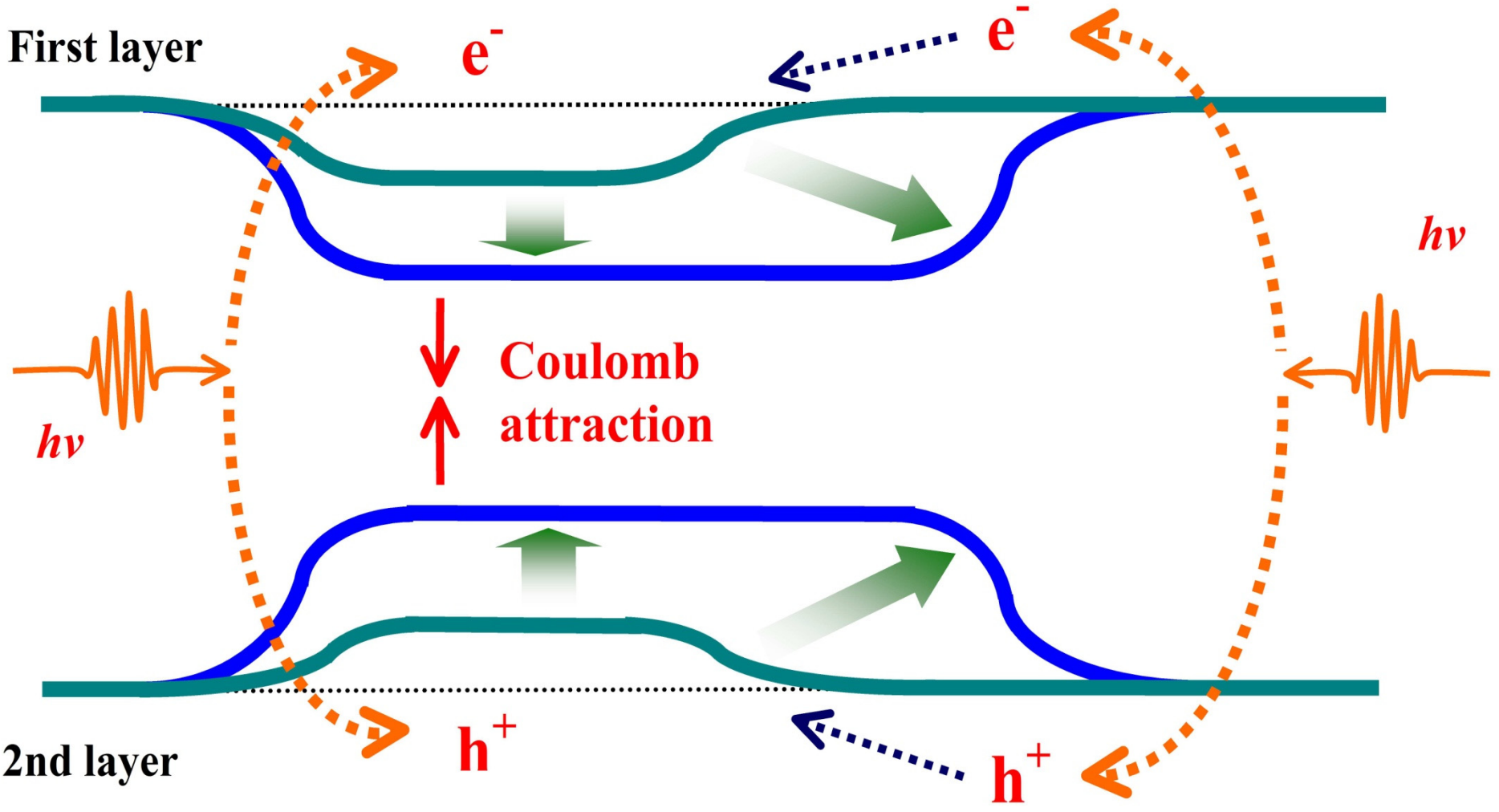
Nishioka, Nasu, PRB 80 (2009) 235420.

Dynamics of σ-bond formation after self-localization

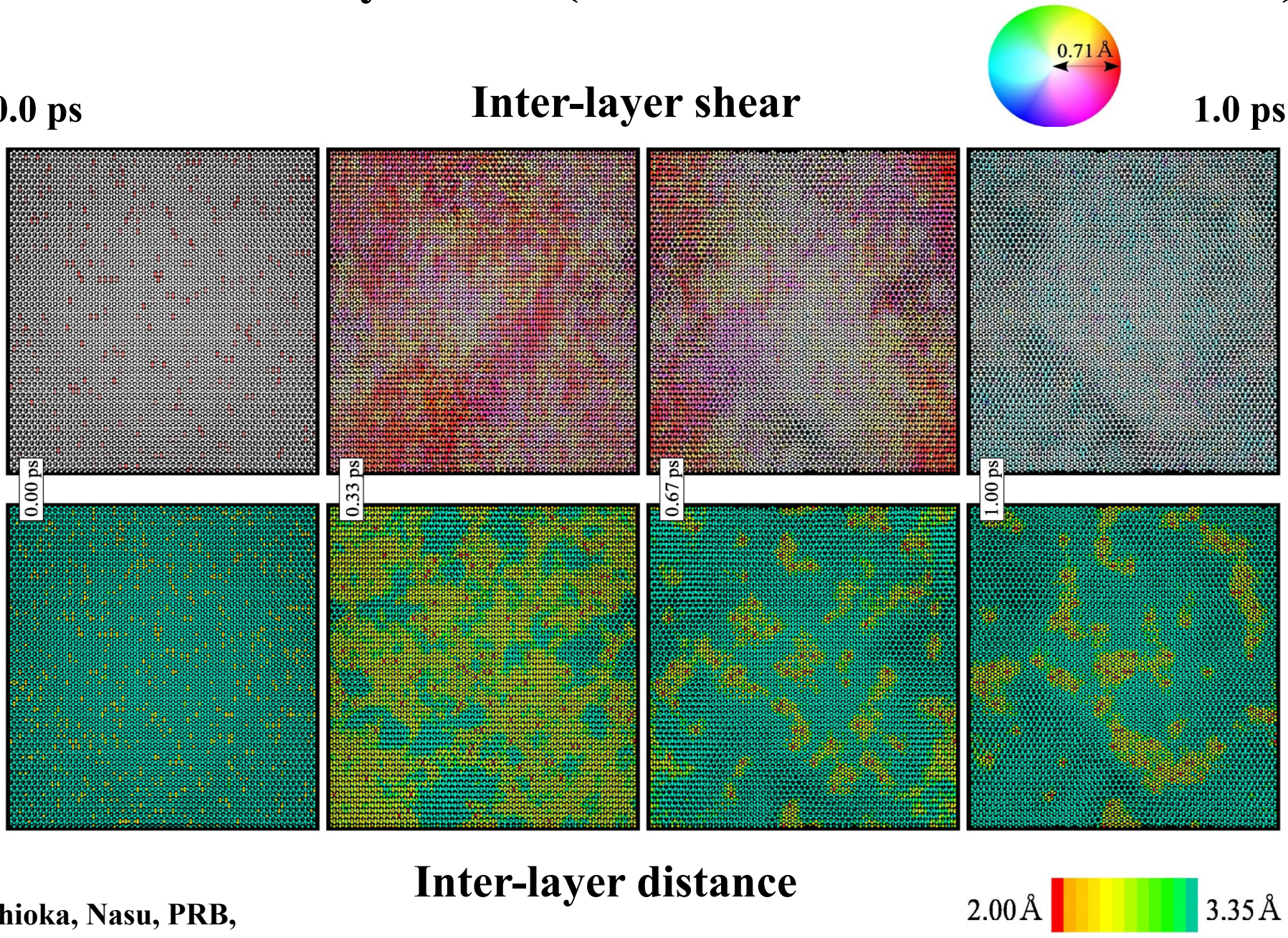


Nishioka, Nasu, PRB 80 (2009) 235420.

Cooperative nonlinear domain growth by random and multi-excitation



Excitation density : 10% (6240 × 0.1 = 624 excited sites)



Nishioka, Nasu, PRB, 82(2010)035440(1-7).

Importance of shear fluctuation at the time of pulse excitation

Two excitations, excitation density: 6%

First hν, (or quantum fluctuation)

Second hν

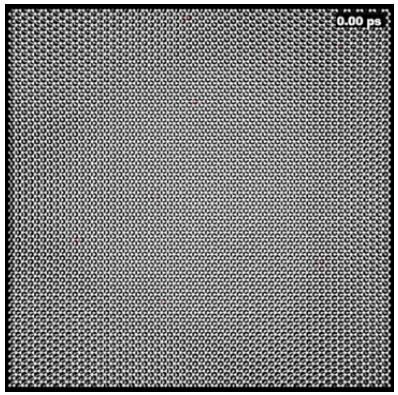
time 0

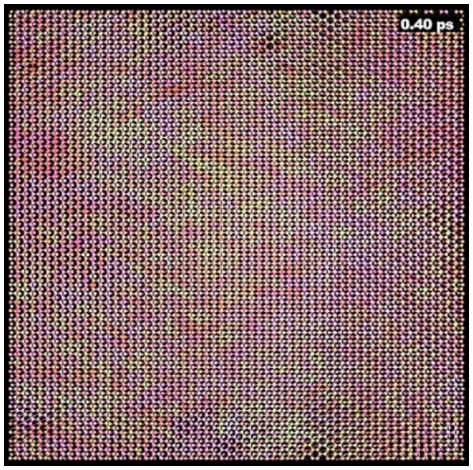
Δt

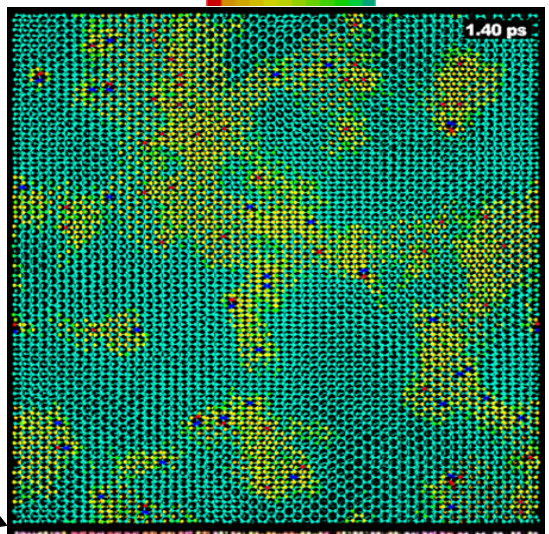
t

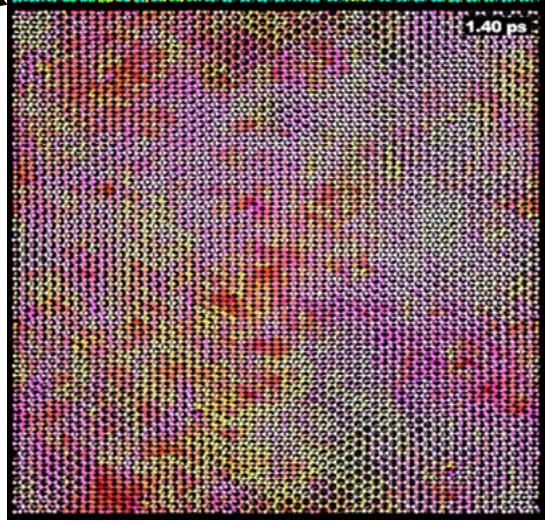
Inter layer distance

2.00Å **3.35Å**



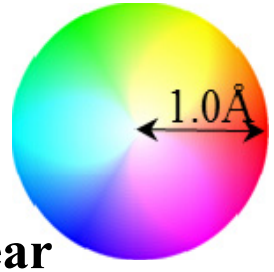






Frozen shear

Shear fluctuation by the first



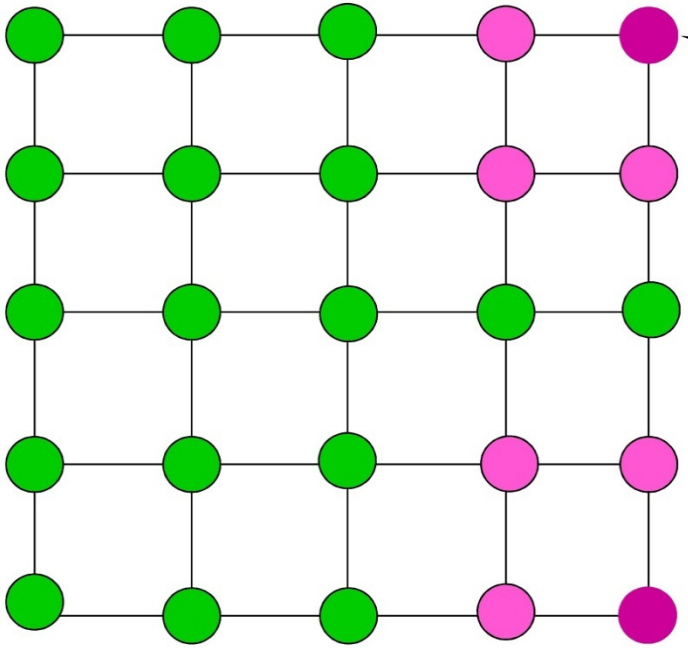
Inter layer shear

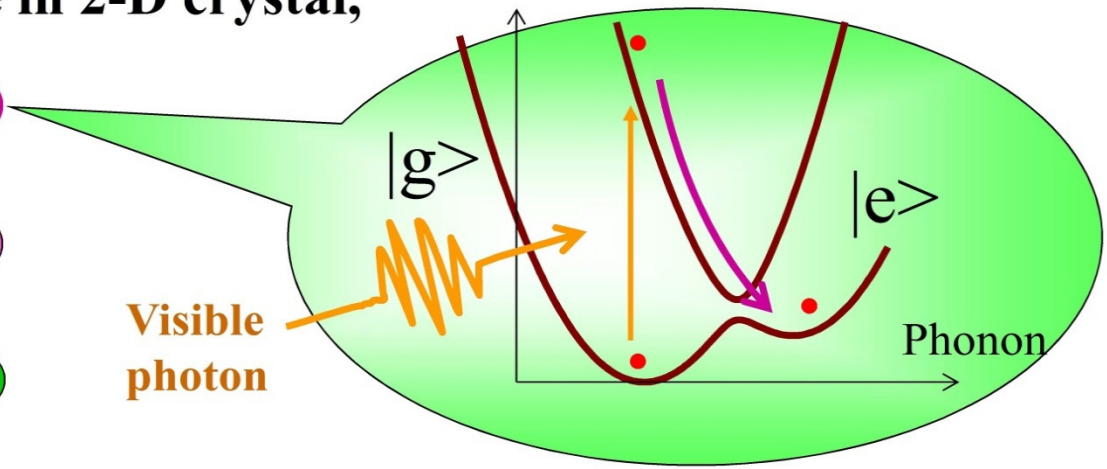
Nishioka, Nasu, Yonemitsu,
J. Phys. CM. 24 (2012) 205402.

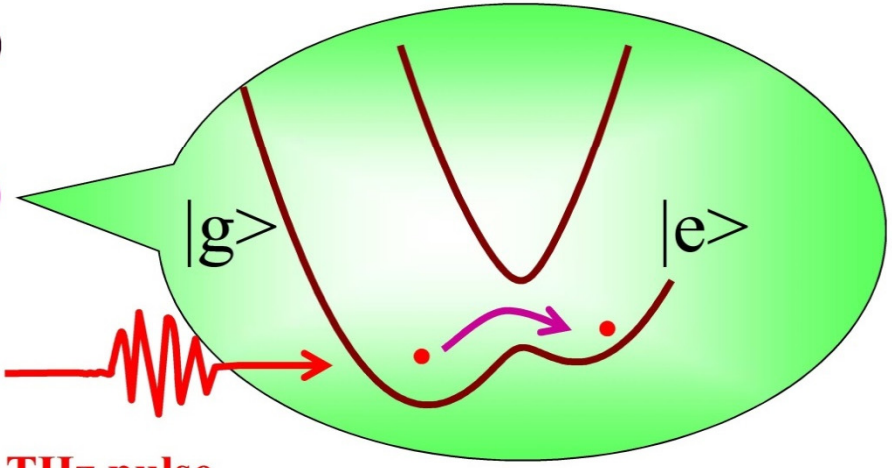
Two possible ways of excitation

Simulation by localized 2-level electron-phonon system

Ground |g > and excited |e > states in each lattice site interacting by dipole-dipole in 2-D crystal,





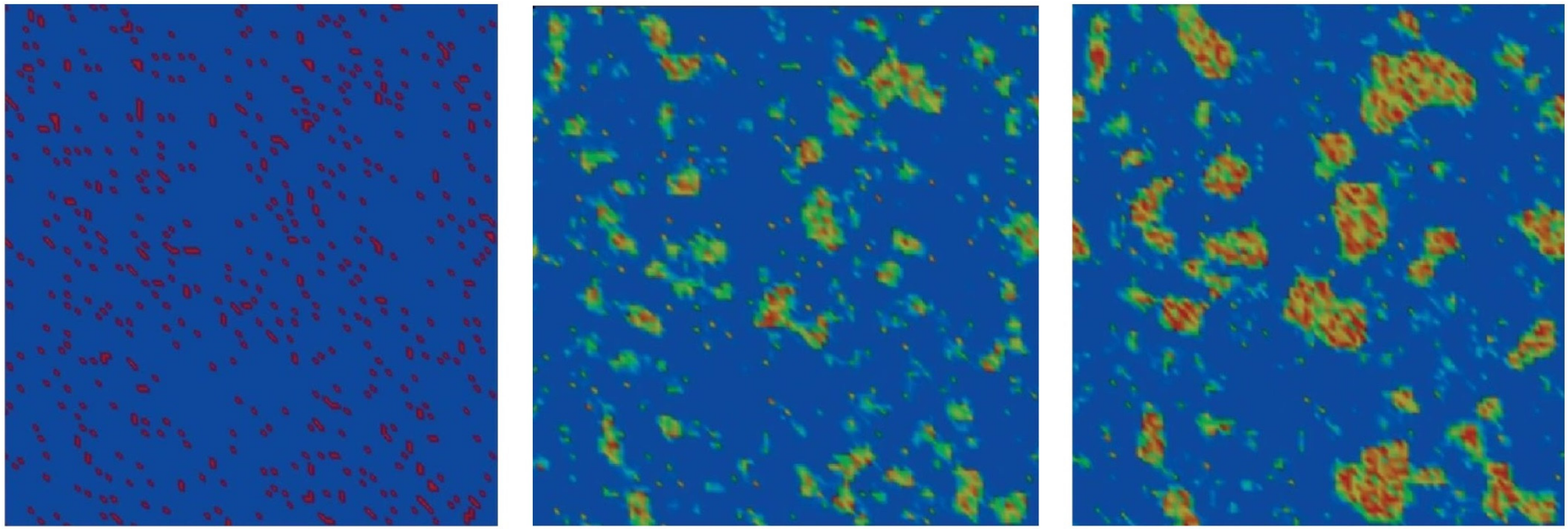


In both cases, excited electronic domain can proliferate.

Ishida,Nasu
Phys. Lett.
A**378** (2014)382

Excited electronic domain formation and proliferation in the case of visible photon

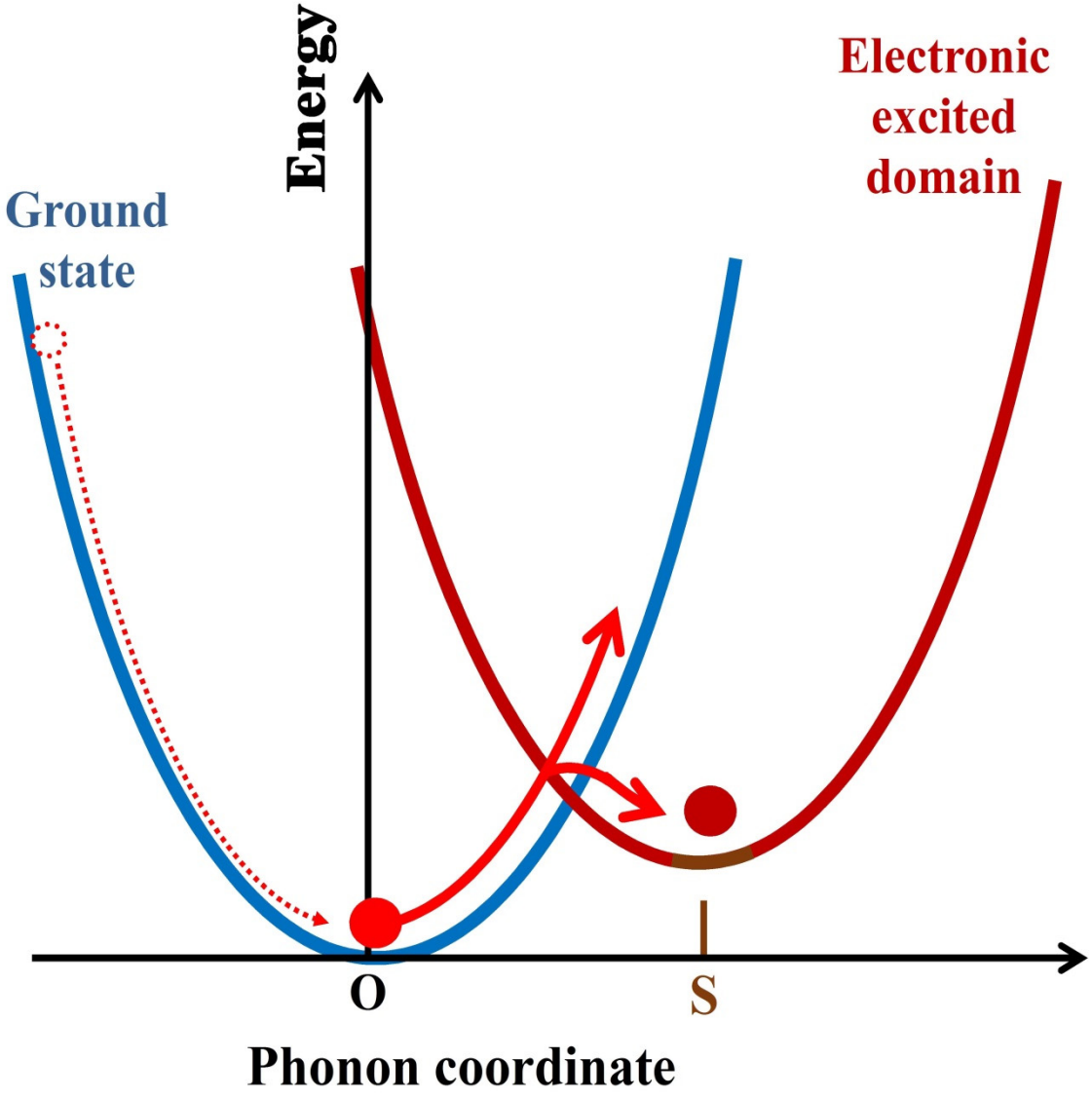
Ishida, Nasu, PRL **100**(2008)116403.

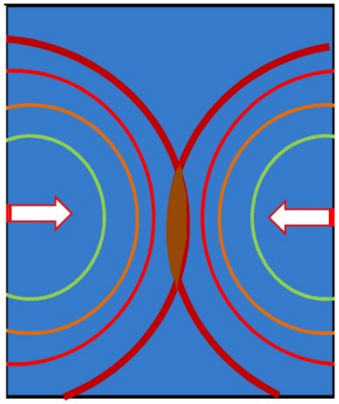


~ 0 ps ~ 3 ps ~ 6 ps

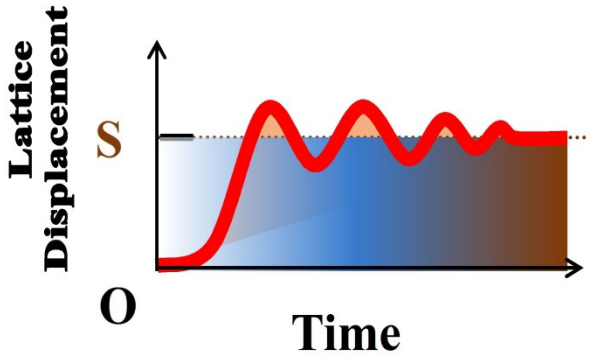
0 0.33 0.66 1

Excited electronic domain formation, not by visible photon, but by short giant phonon (THz) pulse and its nonlinear propagation





Excited electronic domain



Confer to KdV, Toda lattice,
Kru-Shu theories.