Multidisciplinary Workshop on the Random Phase Approximation
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Real-time calculation for RPA response and nonlinear dynamics

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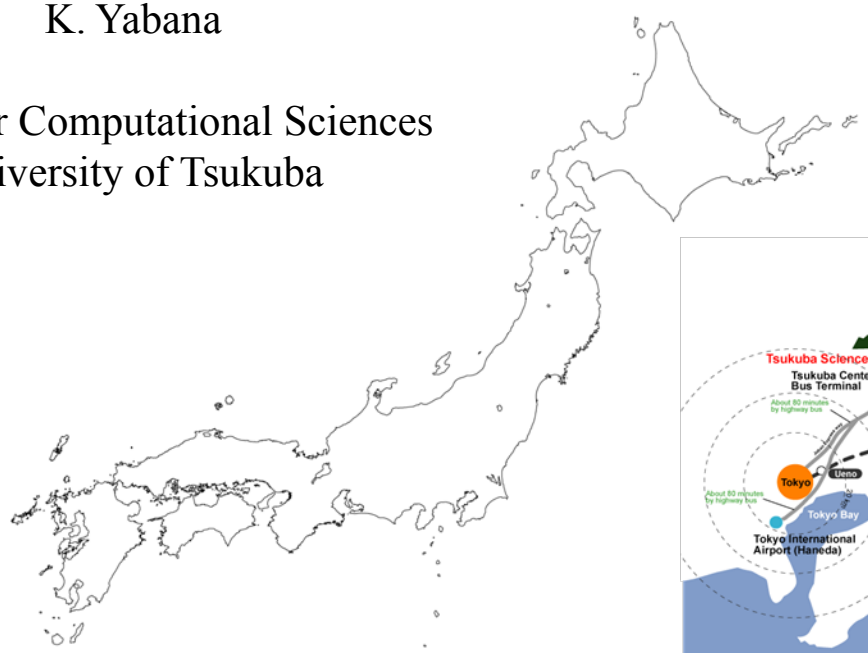

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Linearized TDHF (TDDFT) ~ RPA

Solve TDKS equation in real time

$$i\hbar\frac{\partial}{\partial t}\psi_i(t) = h_{KS}(n(t))\psi_i(t)$$

Response to external field of a given frequency

$$\chi(\omega) = \chi_0(\omega) + \chi_0(\omega)v_{ee}\chi(\omega)$$

Eigenvalue problem for excitations

$$\begin{pmatrix} A & B \\ B & A \end{pmatrix}\begin{pmatrix} X \\ Y \end{pmatrix} = E\begin{pmatrix} X \\ -Y \end{pmatrix}$$

Merit of real time approach

-Response of full spectral region from single real-time calculation

-Efficient for large systems

-Intuitive treatment of scattering boundary condition (Photoionization)

-Real-time measurements (with ultrashort laser pulse)

-Nonlinear dynamics beyond perturbation theory (with intense laser pulse)

Real-time, real-space calculation for nuclear TDHF

Nuclear fusion reaction of ^{16}O-^{16}O
Spatial grid: 30x28x16 (10^{-15}m), Time-step $4x10^{2}$ (10^{-22}s)

H. Flocard, S.E. Koonin, M.S. Weiss, Phys. Rev. 17(1978)1682.

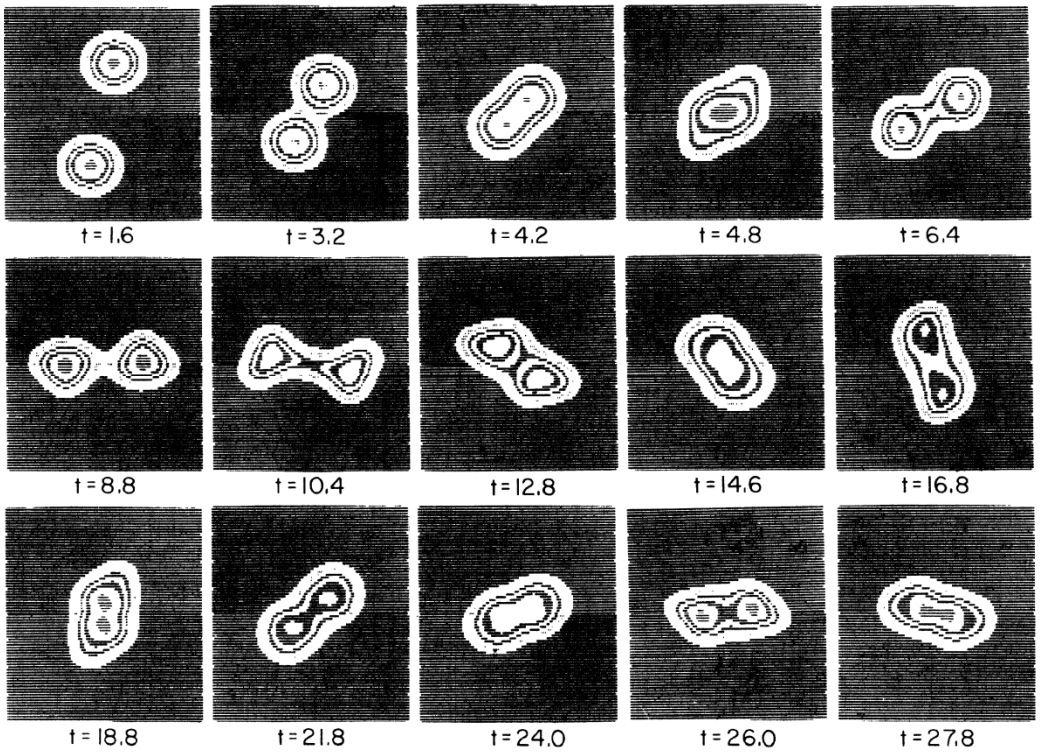


FIG. 2. Contour lines of the density integrated over the coordinate normal to the scattering plane for an $^{16}O + ^{16}O$ collision at $E_{lab} = 105$ MeV and incident angular momentum $L = 13\hbar$. The times t are given in units of 10^{-22} sec.

Electron dynamics solving TDKS equation in real-time to explore optical response

$$\left\{-\frac{\hbar^2}{2m}\vec{\nabla}^2+\sum_a V_{ion}(\vec{r}-\vec{R}_a)+e^2\int d\vec{r}'\frac{n(\vec{r}',t)}{|\vec{r}-\vec{r}'|}+\mu_{xc}(n(\vec{r},t))+V_{ext}(\vec{r},t)\right\}\psi_i(\vec{r},t)=i\hbar\frac{\partial}{\partial t}\psi_i(\vec{r},t)$$

$$n(\vec{r},t)=\sum_i|\psi_i(\vec{r},t)|^2$$

Contents

1. Oscillator strength distribution in molecules

   Scattering boundary condition, Large systems

2. Electron dynamics in crystalline solid
   - Dielectric function
   - Coherent phonon
   - Optical dielectric breakdown

   Intense and ultrashort laser pulse, Nonlinear dynamics

Linear Optical Response

Oscillator strength distribution of molecules

Real time calculation for polarizability

$$i\hbar\frac{\partial}{\partial t}\psi_i(t) = \{h_{KS}(n(t)) + V_{ext}(t)\}\psi_i(t)$$

$$n(\vec{r},t) = \sum_i |\psi_i(\vec{r},t)|^2$$

External field $V_{ext}(t) = E_j(t) r_j$

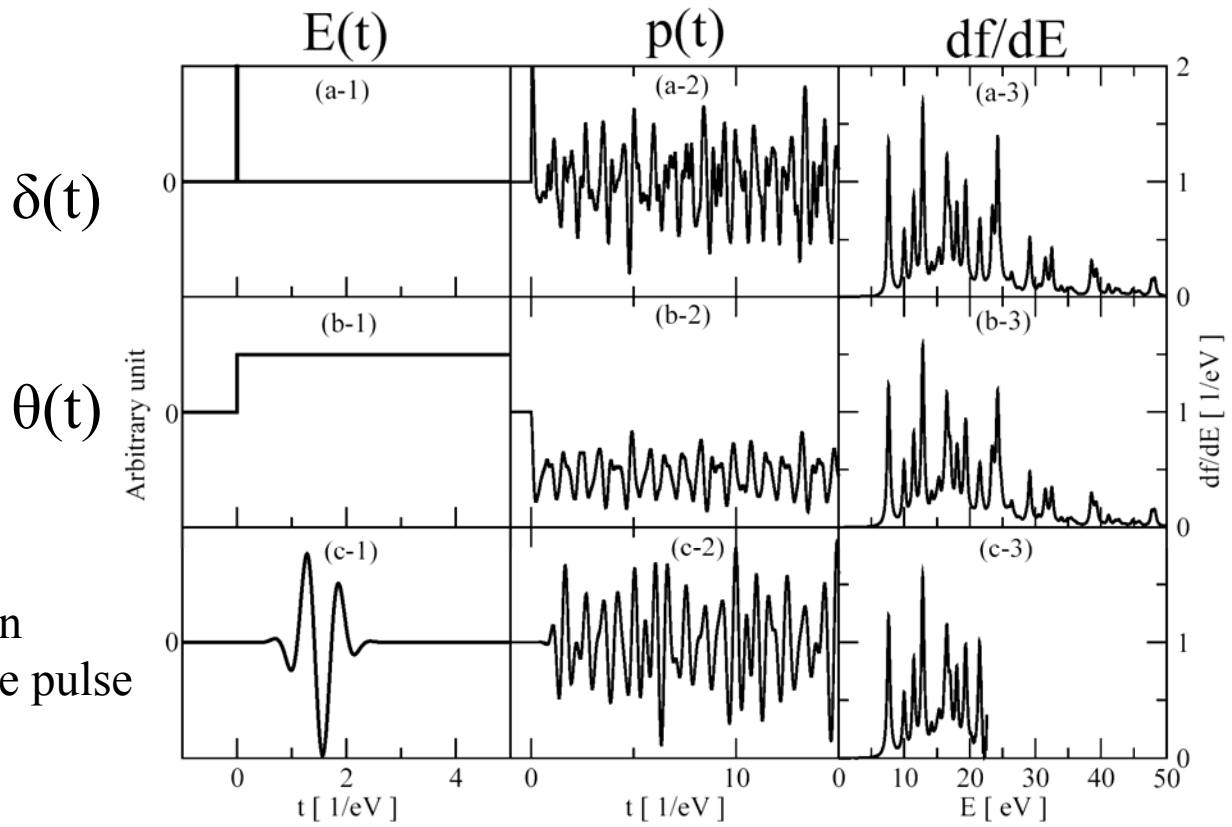
Induced polarization $p_i(t) = \int d\vec{r}\, r_i\, n(\vec{r},t)$

Polarizability $\int dt e^{i\omega t} p_i(t) = \alpha(\omega) \int dt e^{i\omega t} E_j(t) \Rightarrow \alpha(\omega) = \dfrac{\int dt e^{i\omega t} p_i(t)}{\int dt e^{i\omega t} E_j(t)}$

Three different choices of external electric field

$$\alpha(\omega) = \frac{\int dt e^{i\omega t} p_i(t)}{\int dt e^{i\omega t} E_j(t)}$$

Ethylene C_2H_4 molecule



Gaussian envelope pulse

Electron dynamics under δ(t) distortion

1. Apply impulsive external field

$$V_{ext}(\vec{r},t) = -k\delta(t)z$$

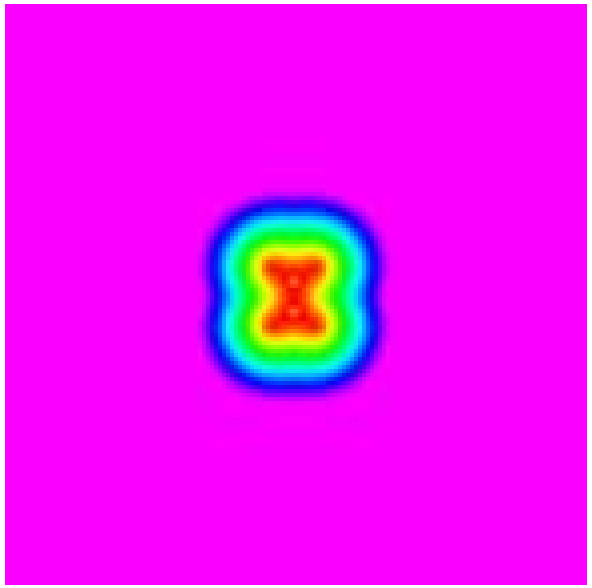
$$\psi_i(\vec{r},t=0) = \exp[ikz]\phi_i(\vec{r})$$

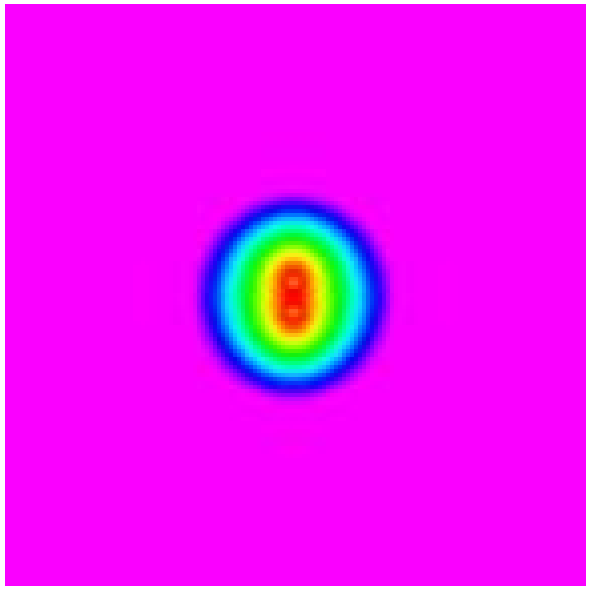
2. Calculate dipole moment in time d(t)

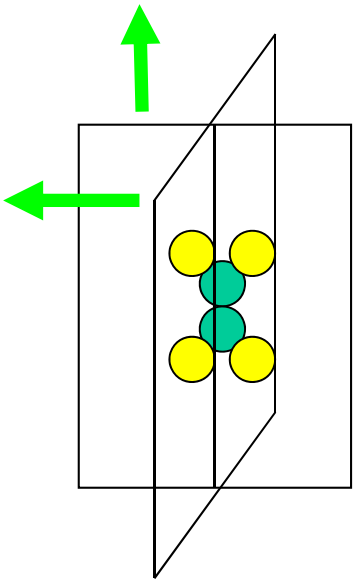
$$d(t) = \int d\vec{r} z n(\vec{r},t)$$

3. Time-frequency Fourier transformation gives frequency-dependent polarizability

$$\alpha(\omega) \propto \int_0^T dt\, e^{i\omega t} d(t)$$







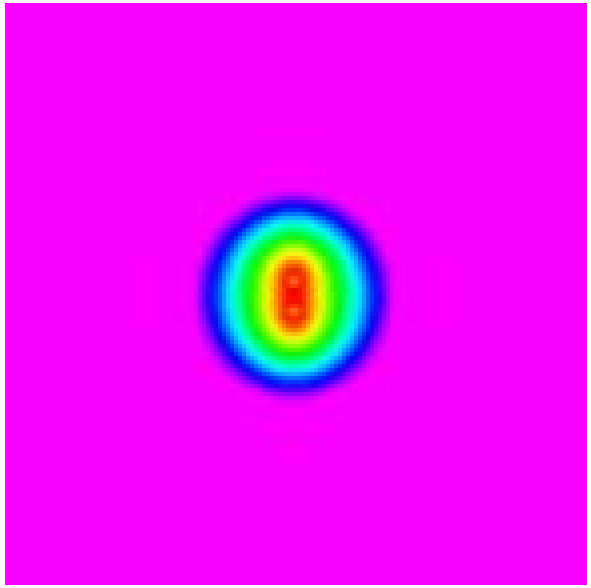
Ethylene molecule
After weak impulsive force

Immediately after distortion

⇨ photoemission

Steady oscillation

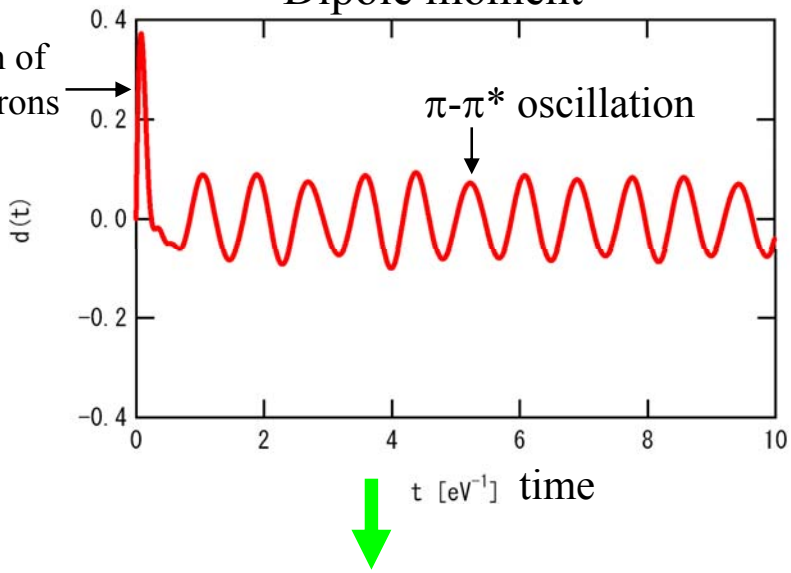
⇨ bound-bound transition



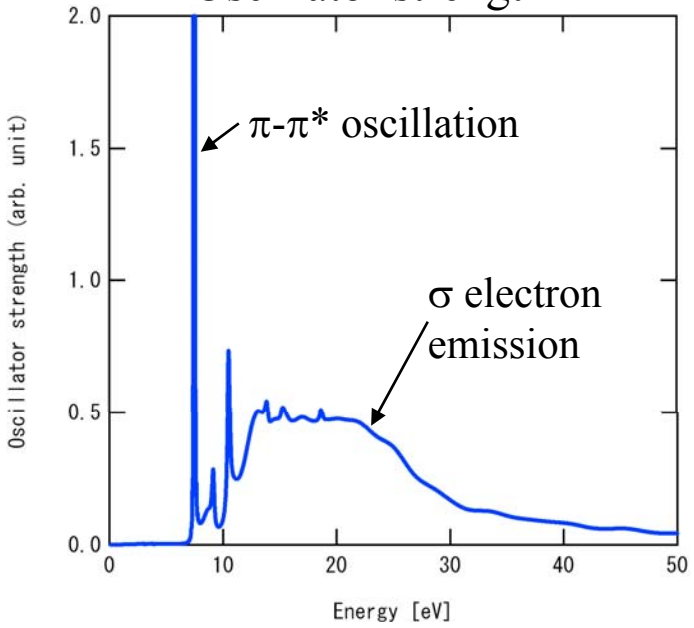
Whole spectrum from a single real-time calculation

Dipole moment

Coherent motion of all σ and π electrons

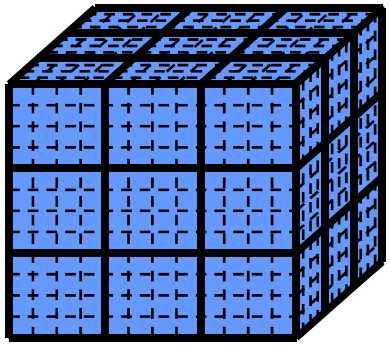


Oscillator strength



Excitation energy

Computational aspect



3D real-space grid

$$-\frac{\hbar^2}{2m}\left[\sum_{n_1=-N}^{N} C_{n_1}\psi(x_i+n_1h,y_j,z_k)+\sum_{n_2=-N}^{N} C_{n_2}\psi(x_i,y_j+n_2h,z_k)+\sum_{n_3=-N}^{N} C_{n_3}\psi(x_i,y_j,z_k+n_3h)\right]$$
$$+[V_{\text{ion}}(x_i,y_j,z_k)+V_H(x_i,y_j,z_k)+V_{\text{xc}}(x_i,y_j,z_k)]\psi(x_i,y_j,z_k)=E\psi(x_i,y_j,z_k)\,.$$

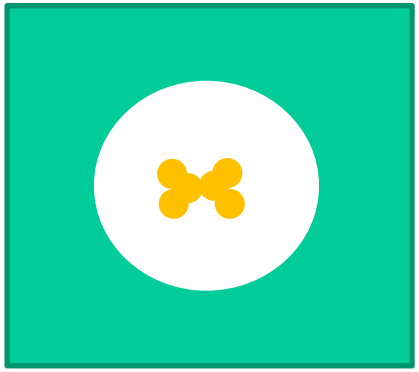
Time evolution: 4-th order Taylor expansion

$$\psi_i(t+\Delta t)=\exp\left[\frac{h_{KS}(t)\Delta t}{i\hbar}\right]\psi_i(t)\approx\sum_{k=0}^{N}\frac{1}{k!}\left(\frac{h_{KS}(t)\Delta t}{i\hbar}\right)\psi_i(t),\qquad N=4$$

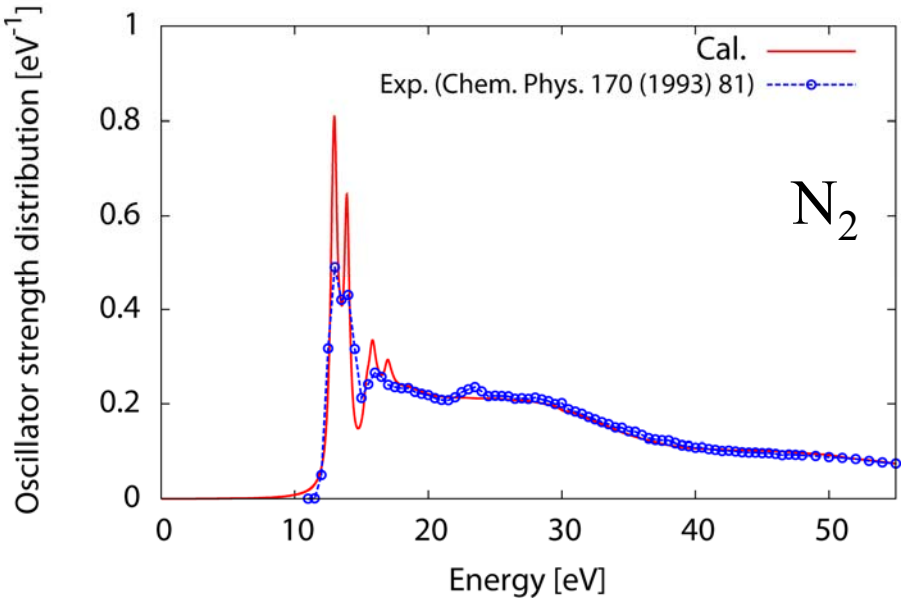
Parallelization: decompose spatial grids into many cubes

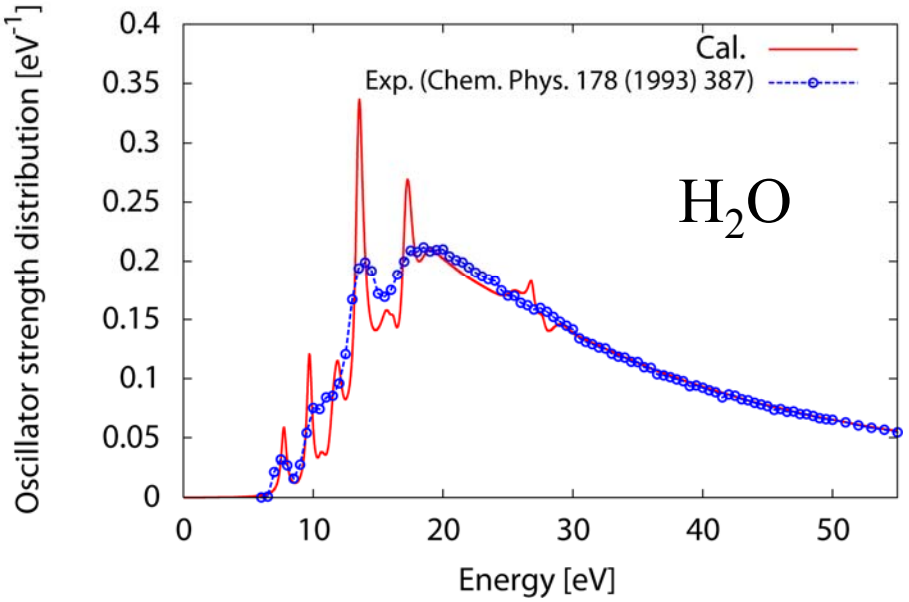
Absorbing potential outside molecule to mimic outgoing boundary condition

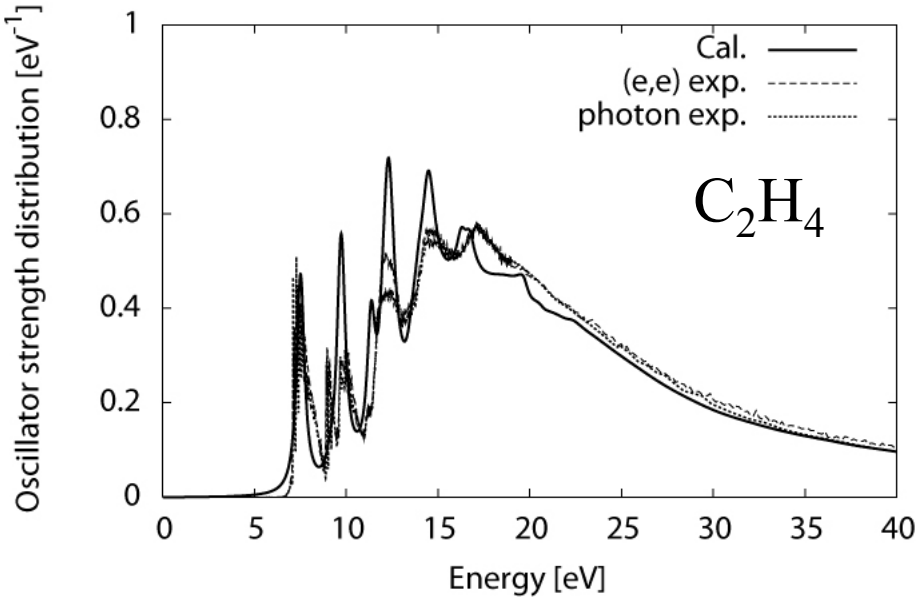
$$i\hbar\frac{\partial}{\partial t}\psi_i(t)=\{h_{KS}(n(t))+V_{ext}(t)+iW(r)\}\psi_i(t)$$

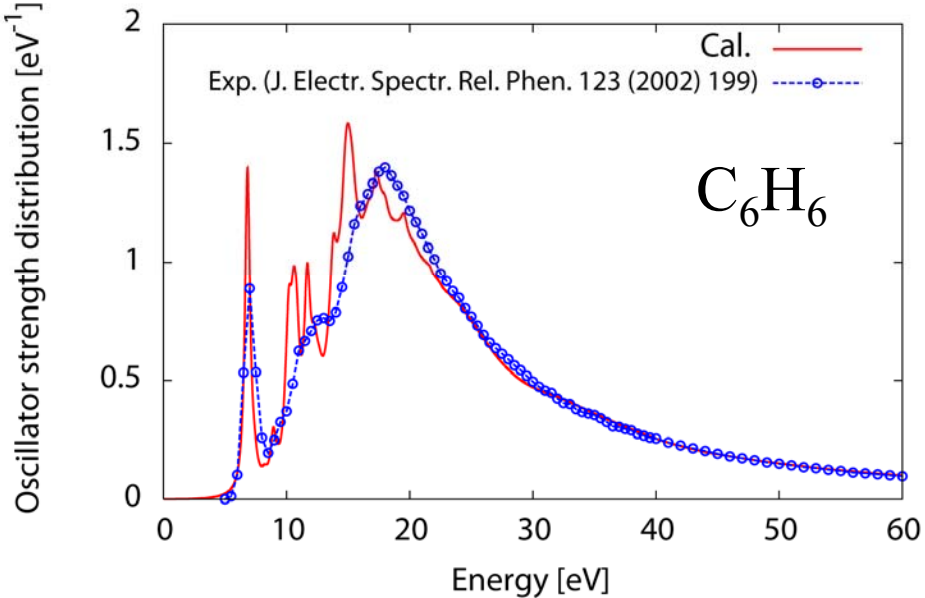


Oscillator strength distribution by TDDFT (LB94 functional)



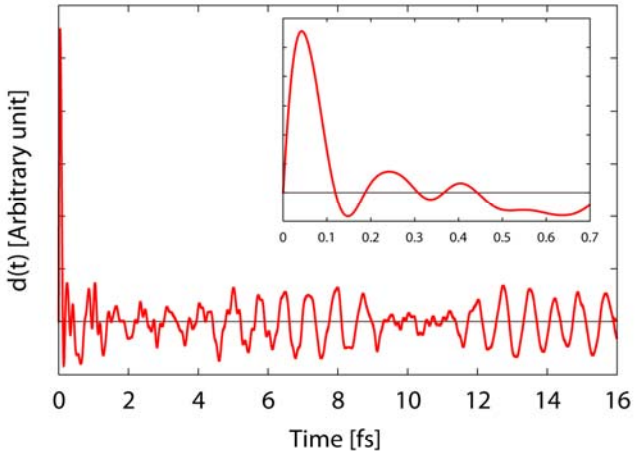




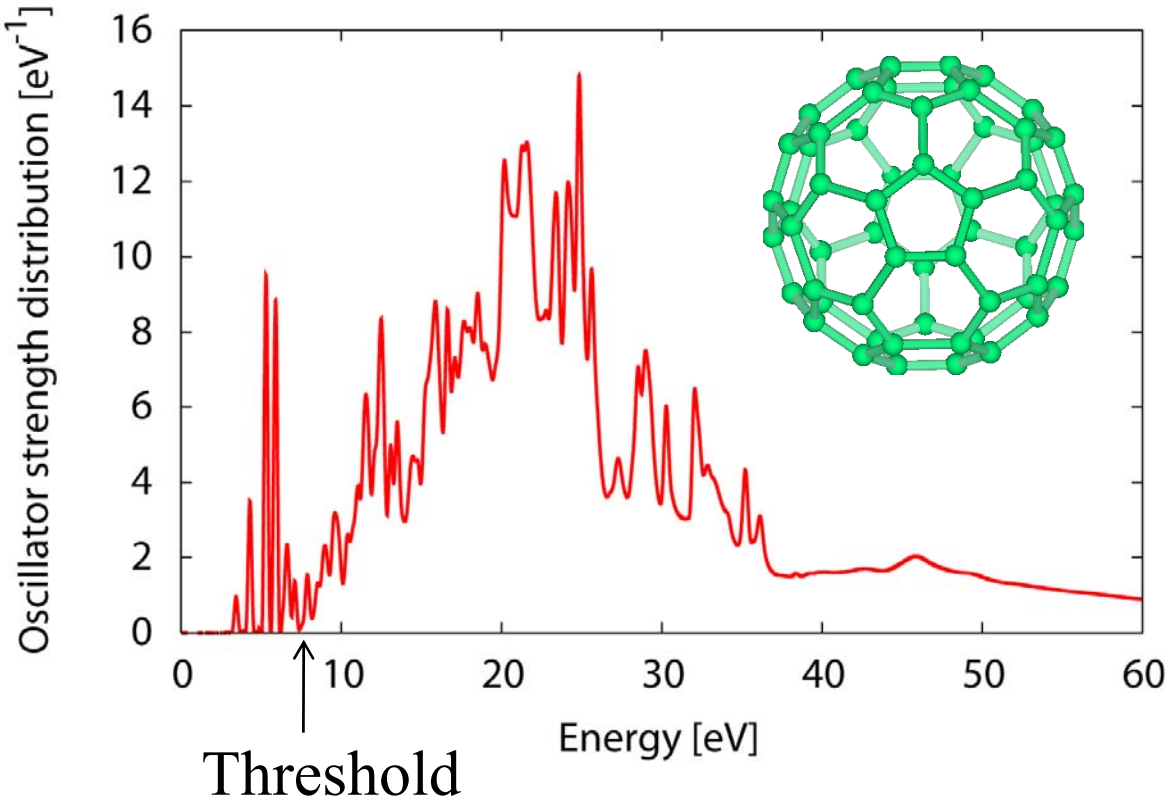


Example of large system: C_{60}

Kawashita, Yabana, Nobusada, Noda, Nakatsukasa,
J. Mol Struct. THEOCHEM 914, 130 (2009)



$$\alpha(\omega) = \frac{1}{k}\int dt e^{i\omega t} d(t)$$

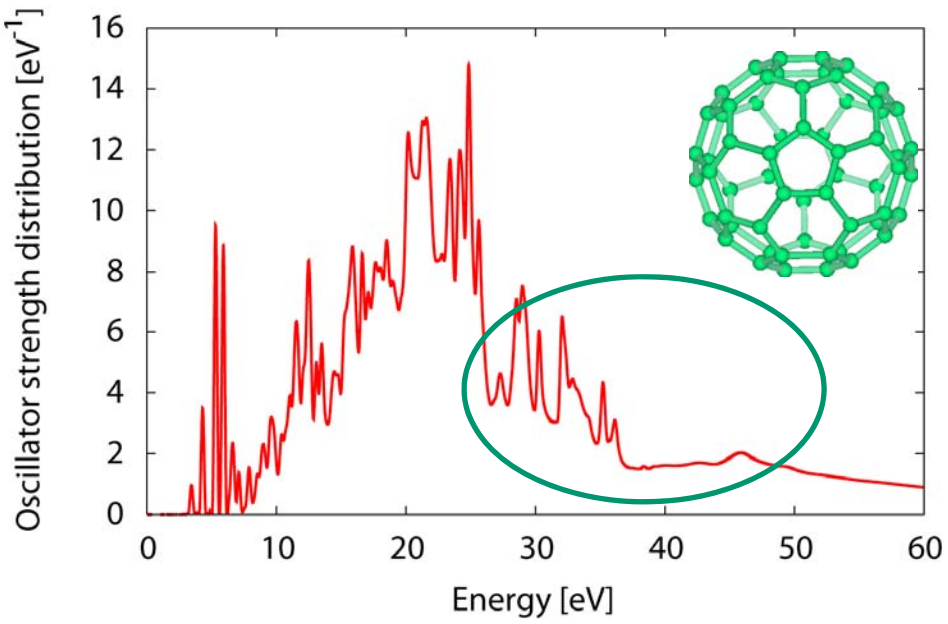


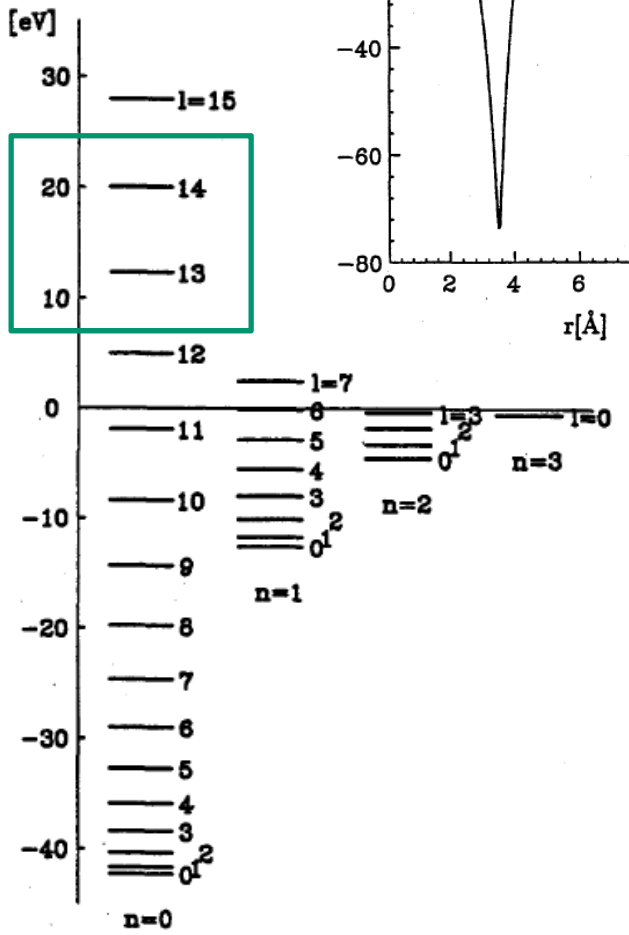
Fully convergent result
- for a fixed ion geometry
- within adiabatic local density approximation
- scattering boundary condition for emitted electrons is taken into account.

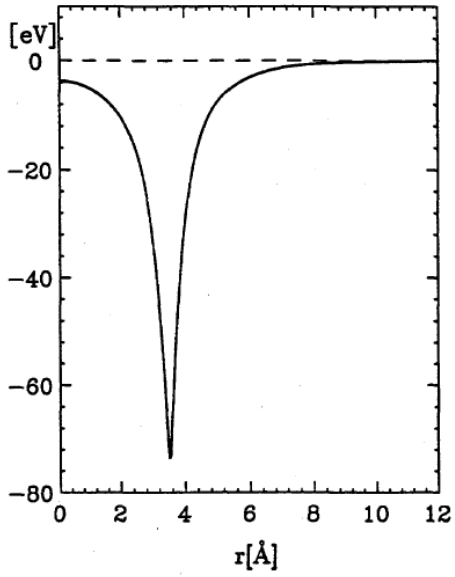
Origin of sharp structures at high excitation

Spherical shell model for fullerene

shape resonance
caused by centrifugal barrier

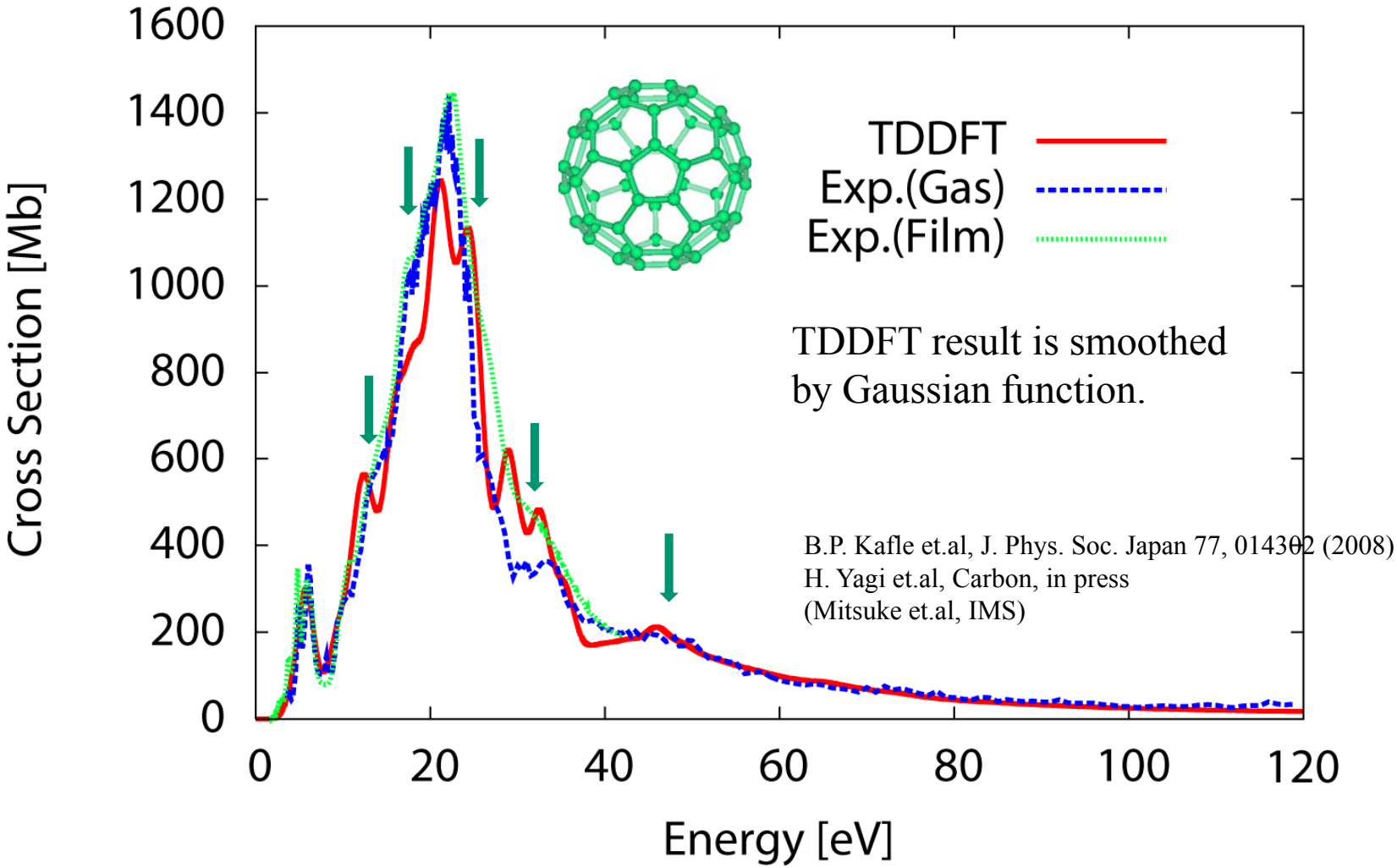






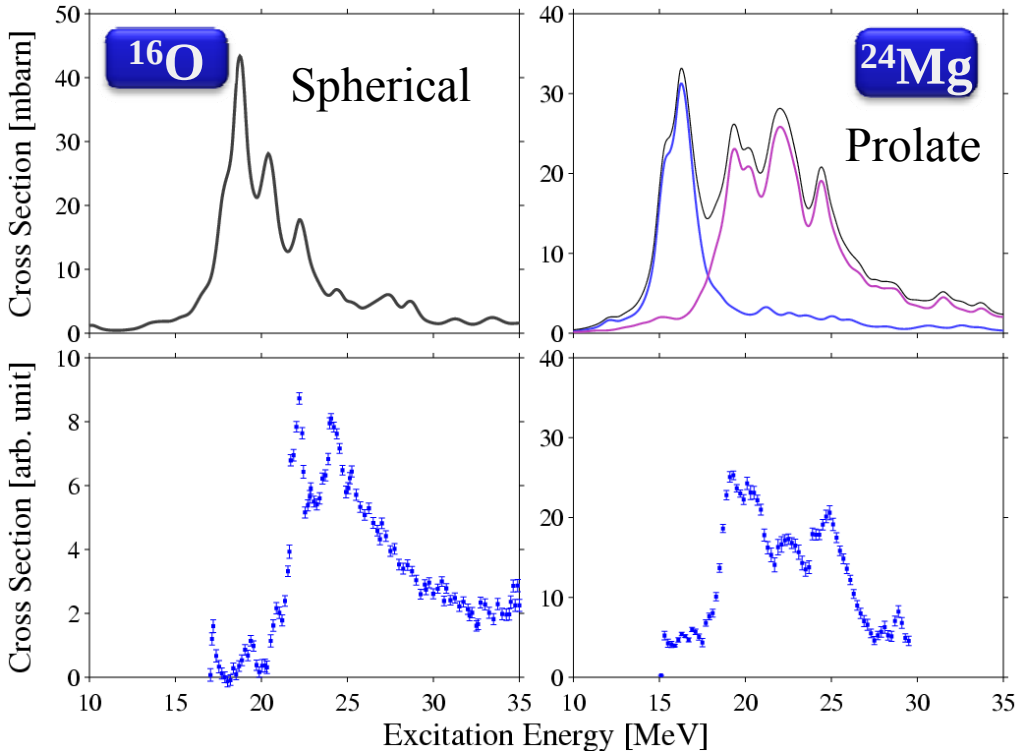
Comparison with measurements

Measured spectra do not show sharp resonance.
Significance of electron-vibration (phonon) coupling.



Nuclear dipole response

(Inakura, Nakatsukasa, K.Y.)



-Fine structures may be described with nuclear DFT-RPA

-Average excitation energy too low

-Strength at high excitations too low (tensor correlation?)

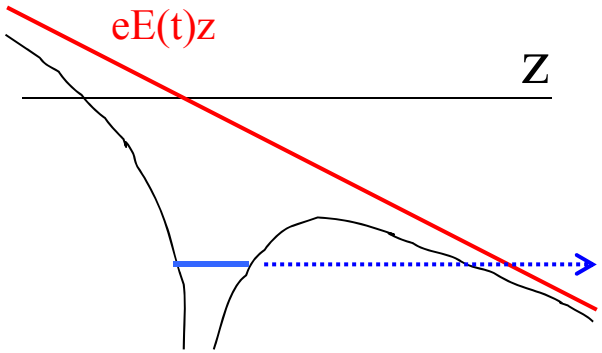
Electron dynamics in Crystalline Solid

Electron dynamics under
intense, ultra-short laser pulse

- Dielectric function
- Coherent phonon
- Optical breakdown

intense

One of frontiers of Laser Science: Intense and Ultrashort



Electric field of laser pulse
≅ Electric field inside materials

Intense field 10^{13}-10^{15} W/cm^2

Quantum
Nonlinear
Nonperturbative

Classical
Relativistic

Ultrashort 10^{-15}s (1 femto sec)

frozen ion

frozen electron

How to describe electron dynamics in periodic system under spatially-uniform electric field?

Bertsch, Iwata, Rubio, Yabana, Phys. Rev. B62(2000)7998.

Linear potential $V(\vec{r},t)=e\vec{E}(t)\vec{r}$ breaks periodicity, to avoid it…

So we use vector potential
spatially uniform, time-dependent

$$\vec{E}(t)=-\frac{\partial\vec{A}(t)}{\partial t} \qquad \vec{A}(t)=-\int^{t}\vec{E}(t)dt$$

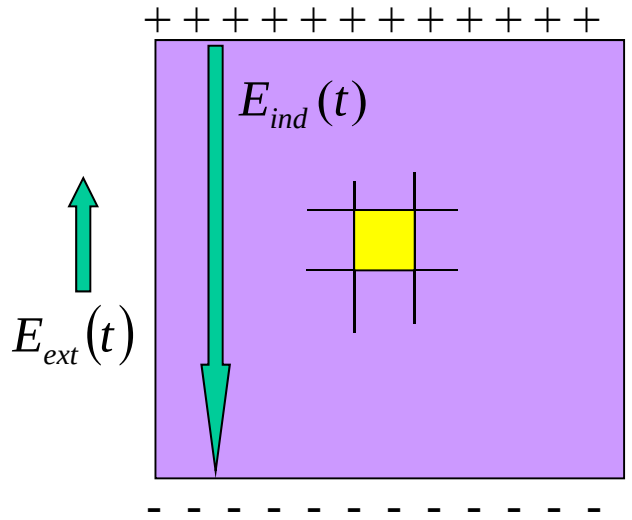
TD Schroedinger Eq. with periodic Hamiltonian

$$i\hbar\frac{\partial}{\partial t}\psi_i(t)=\left[\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}(t)\right)^2+V_{Periodic}(r,t)\right]\psi_i(t)$$

Time-dependent Bloch wave function

$$\psi_i(\vec{r},t)=e^{i\vec{k}\vec{r}}\phi_{nk}(\vec{r},t), \qquad \phi_{nk}(\vec{r}+\vec{R},t)=\phi_{nk}(\vec{r},t)$$

Polarization (Surface charge) effect



TD Kohn-Sham equation including polarization

$$i\hbar\frac{\partial}{\partial t}\psi_i(t)=\left[\frac{1}{2m}\left(\vec{p}-\frac{e}{c}\vec{A}_{tot}(t)\right)^2+V_{e-ion}(\vec{r})+\int d\vec{r}'\frac{e^2}{|\vec{r}-\vec{r}'|}n(\vec{r}',t)+\mu_{xc}[n]\right]\psi_i(t)$$

Polarization field is evaluated from average current in a cell

$$\vec{A}_{tot}(t)=\vec{A}_{ext}(t)+\vec{A}_{ind}(t) \qquad \frac{1}{4\pi}\frac{d^2\vec{A}_{ind}(t)}{dt^2}=\frac{dP}{dt}=\frac{4\pi}{V}\int_{cell}d\vec{r}\;\vec{j}(\vec{r},t)$$

Coupled equation of TD Bloch function and Polarization

Response to weak-field: dielectric function within TDDFT

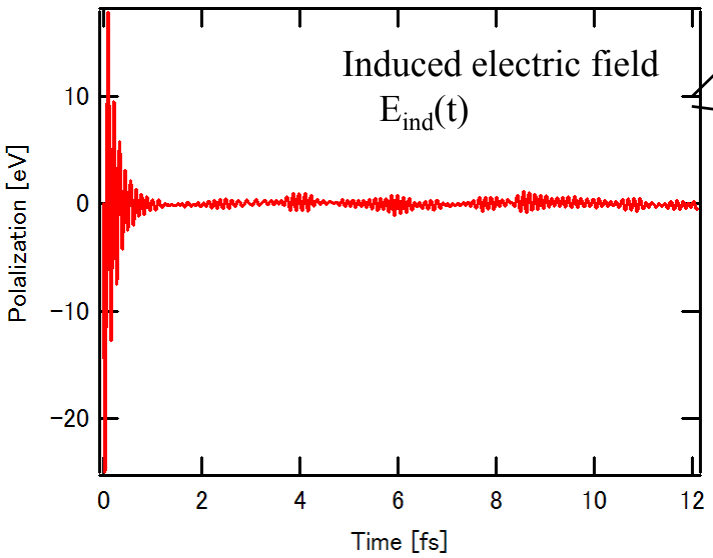
Bertsch, Iwata, Rubio, Yabana, Phys. Rev. B62(2000)7998.

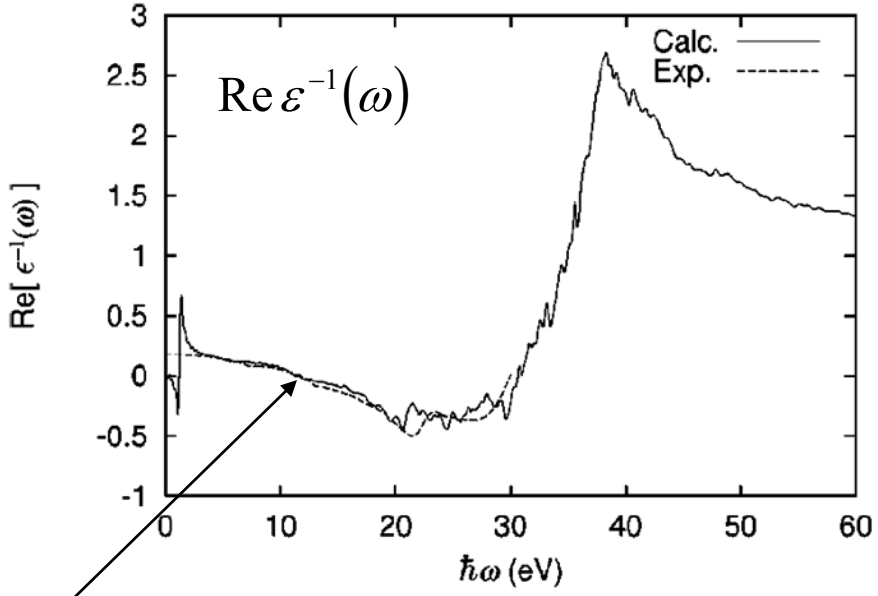
$$\frac{1}{\epsilon(\omega)} = \frac{\int dt e^{i\omega t} \frac{dA_{\rm tot}(t)}{dt}}{\int dt e^{i\omega t} \frac{dA_{\rm ext}(t)}{dt}}$$

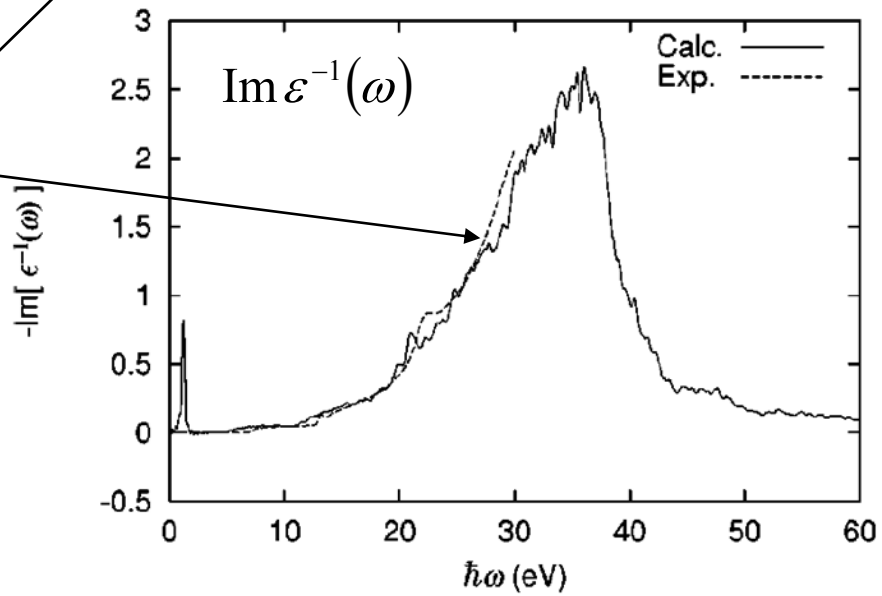
Response to inpulsive field

$$A_{ext}(t) = A_0\,\theta(t)$$

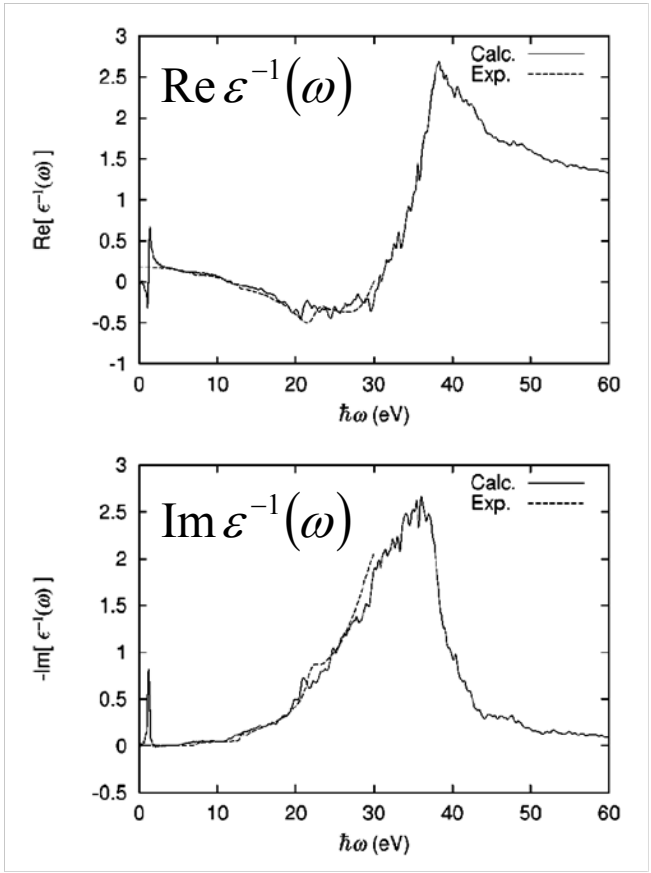
Example: diamond

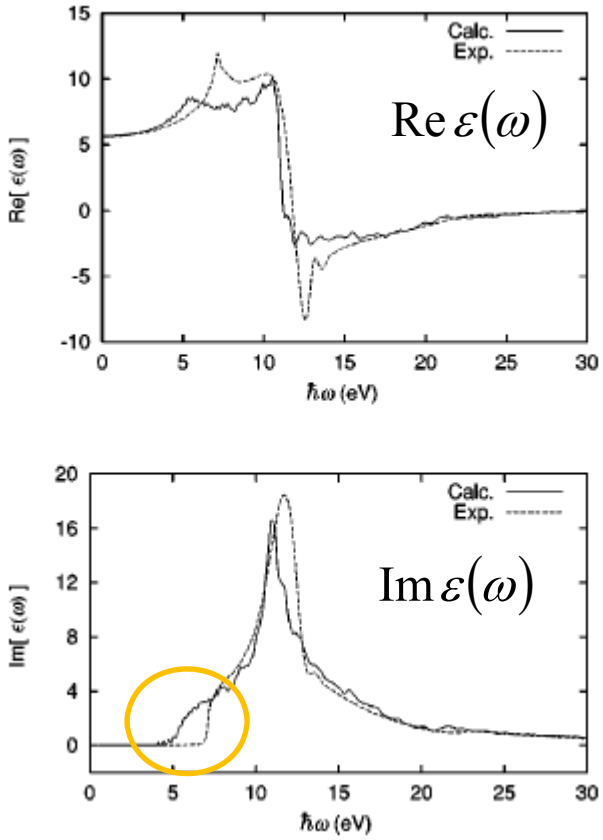






Dielectric function by TDDFT-ALDA



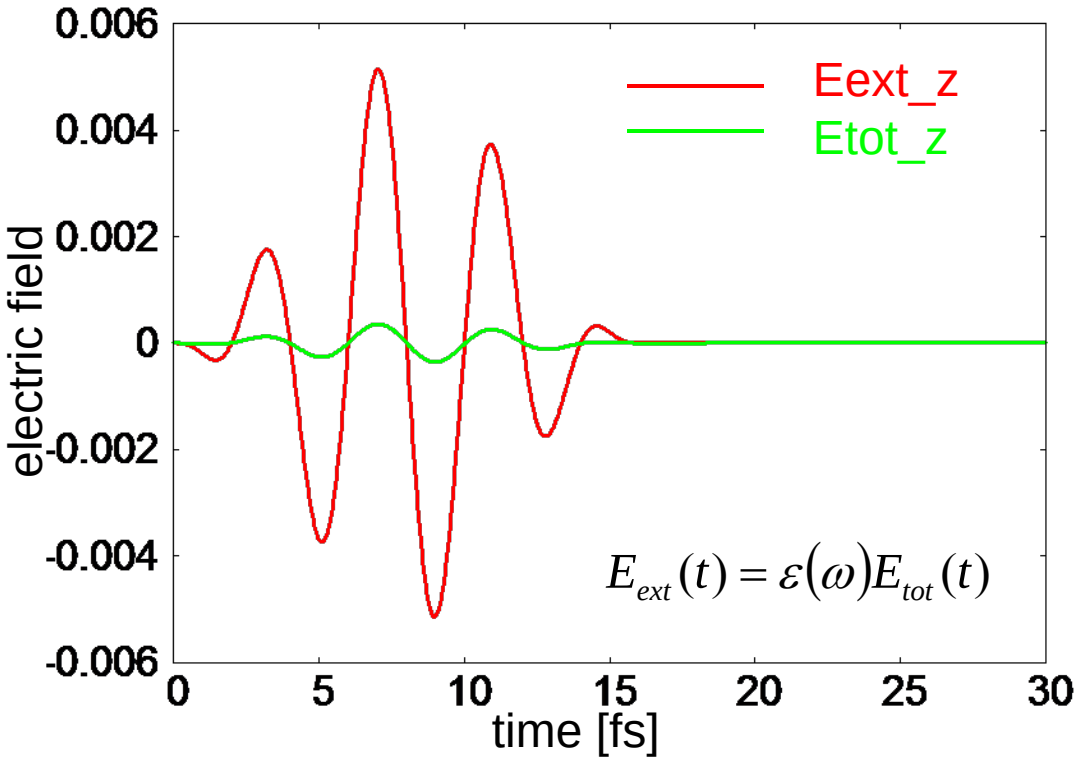


Limitation of TDDFT for Dielectric function

- lack of exciton effect
- too small bandgap

$E_{ext}(t)$ vs $E_{tot}(t)=E_{ext}(t)+E_{ind}(t)$

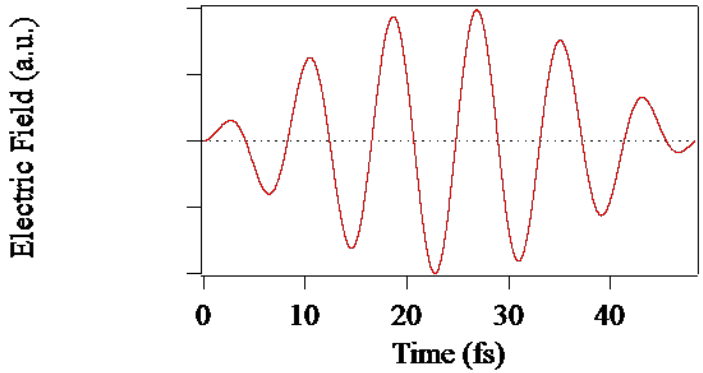
Calculations: $I=10^{12}W/cm^2$, $\langle\hbar\omega\rangle=1.03eV$

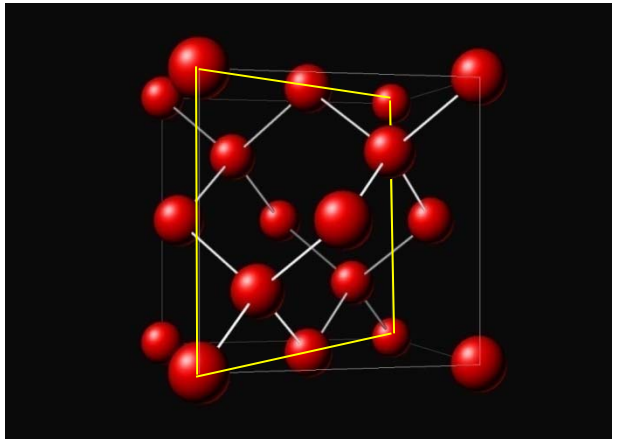


- Applied laser pulse (Red) vs total electric field (Green)
- The ratio is approximately 14, close to dielectric constant of silicon.

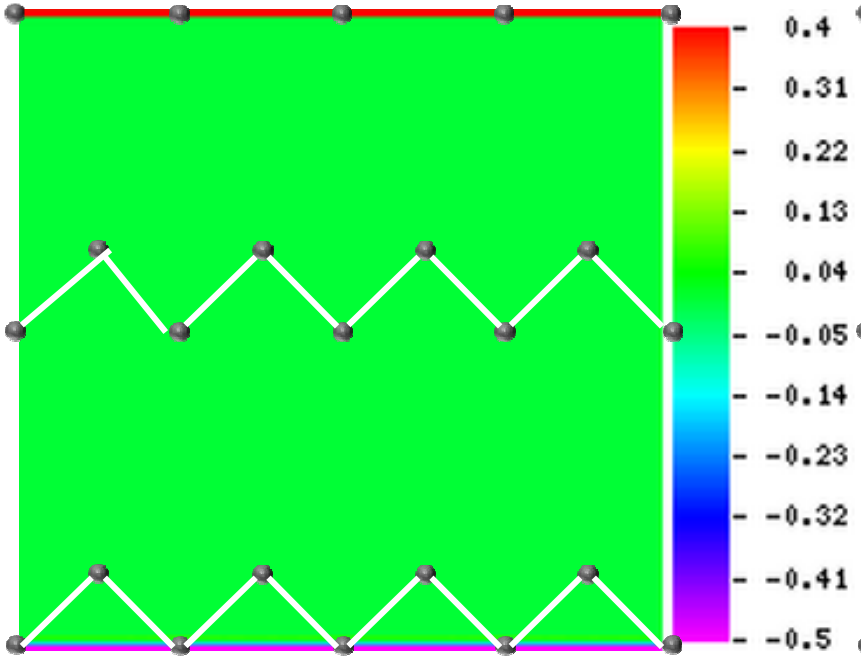
Electron dynamics under ultrashort pulse laser : bulk silicon

$I = 3.5 \times 10^{14}$ W/cm^2, T=50 fs, $\hbar\omega$=0.5 eV

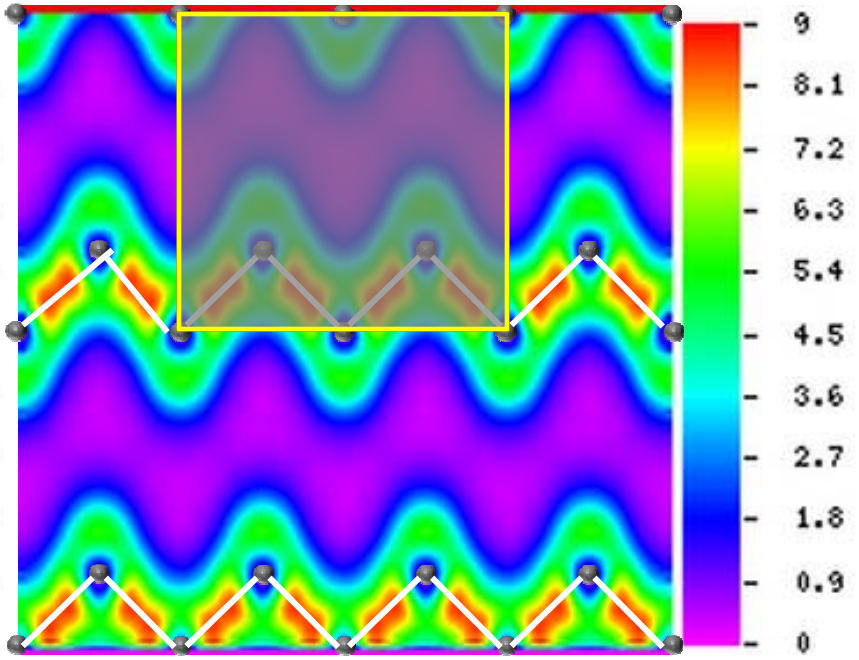




Density change from the ground state （110）



Ground state density （110）



Coherent phonon generation

Ehrenfest force for ion:

$$M_a \ddot{\vec{R}}_a = \vec{F}_a^{\text{ele-ion}} + \vec{F}_a^{\text{ion-ion}} + \vec{F}_a^{\text{ext}}$$

$$\vec{F}_a^{\text{ele-ion}} = -\sum_i \left\langle \psi_i \left| \frac{\partial V_{\text{ion}}(\vec{r}, \{\vec{R}_a\})}{\partial \vec{R}_a} \right| \psi_i \right\rangle$$

Two mechanisms proposed

Virtual excitation vs Real excitation

$$E(\omega, R) = E_0(R) + \frac{1}{2}\alpha(\omega, R)E^2$$

$$F = -\frac{dE_0(R)}{dR} - \frac{1}{2}\frac{d\alpha(\omega, R)}{dR}E^2$$

Impulsive Raman

$$F \approx C \,\mathrm{Im}\,\alpha(\omega)E^2 \quad ?$$

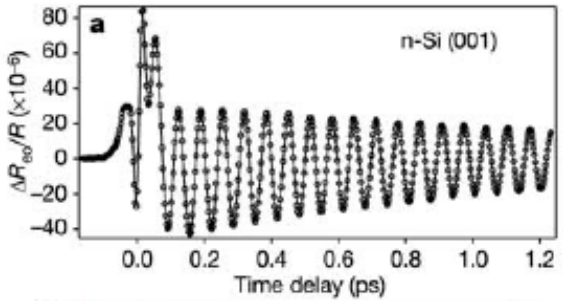
Displacive

Coherent phonon : bulk Si

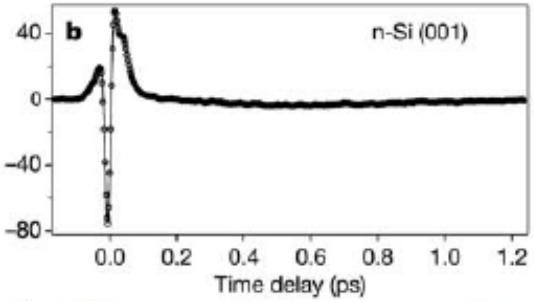
Measurement:
M. Hase, et.al, Nature 426, 51 (2003)

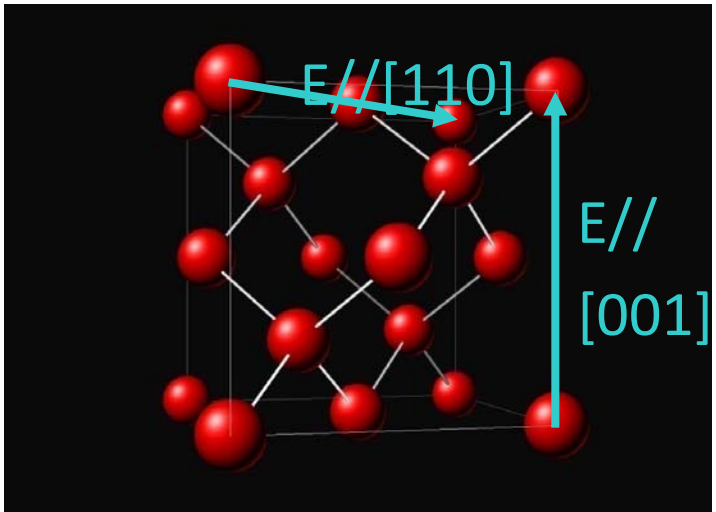
Selection rule

Raman active [110]



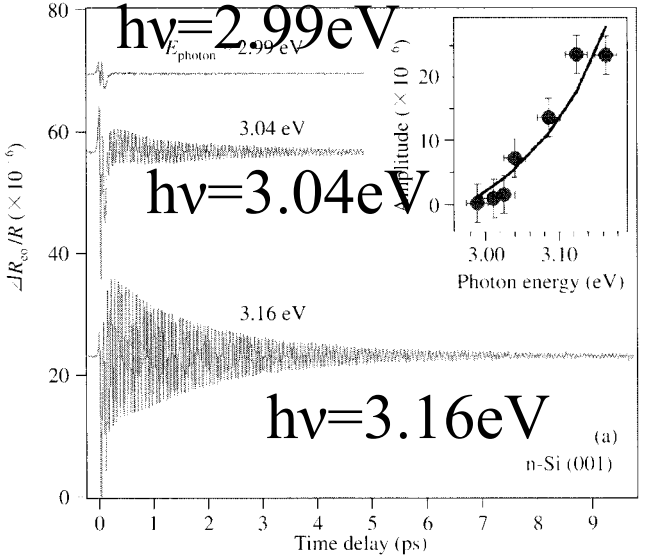
Inactive [001]





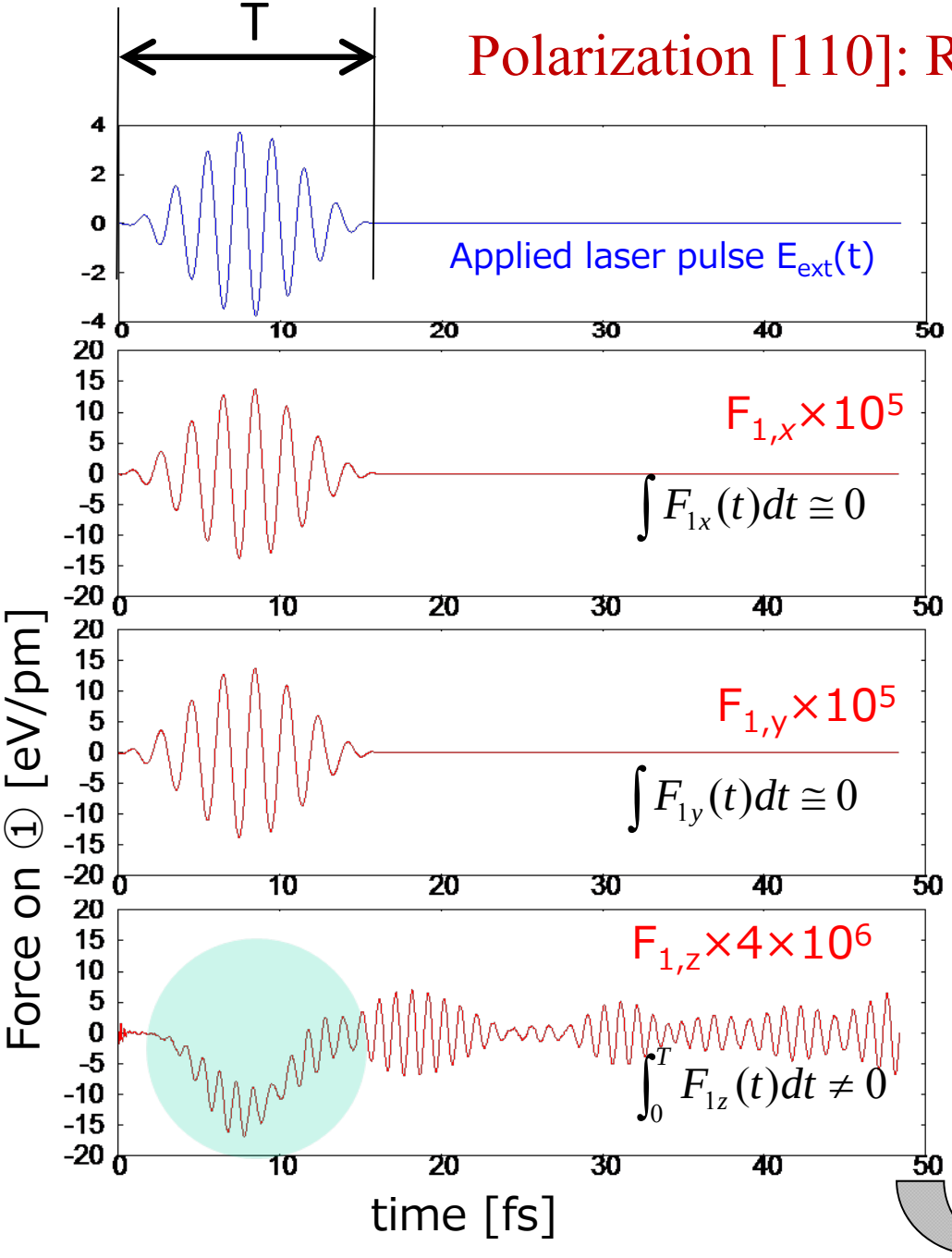
Amplitude

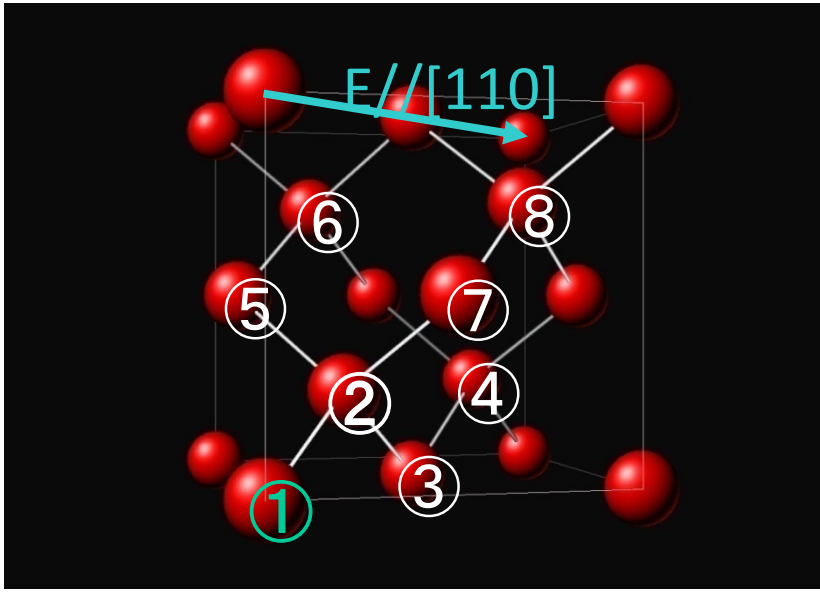
Sudden increase across
the direct bandgap
indicating one-photon absorption

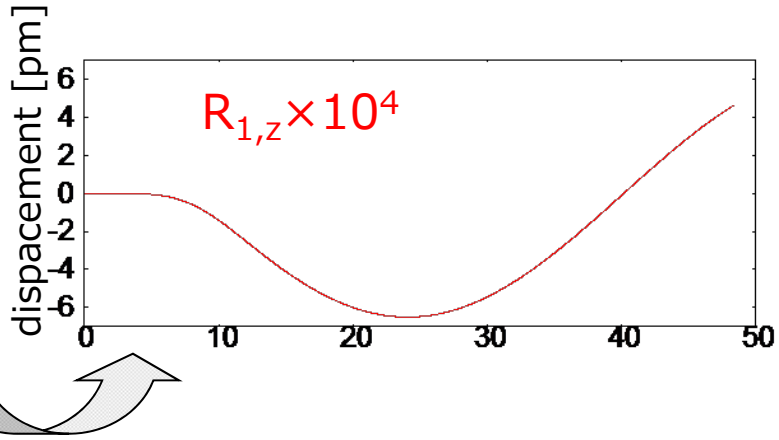


Polarization [110]: Raman active

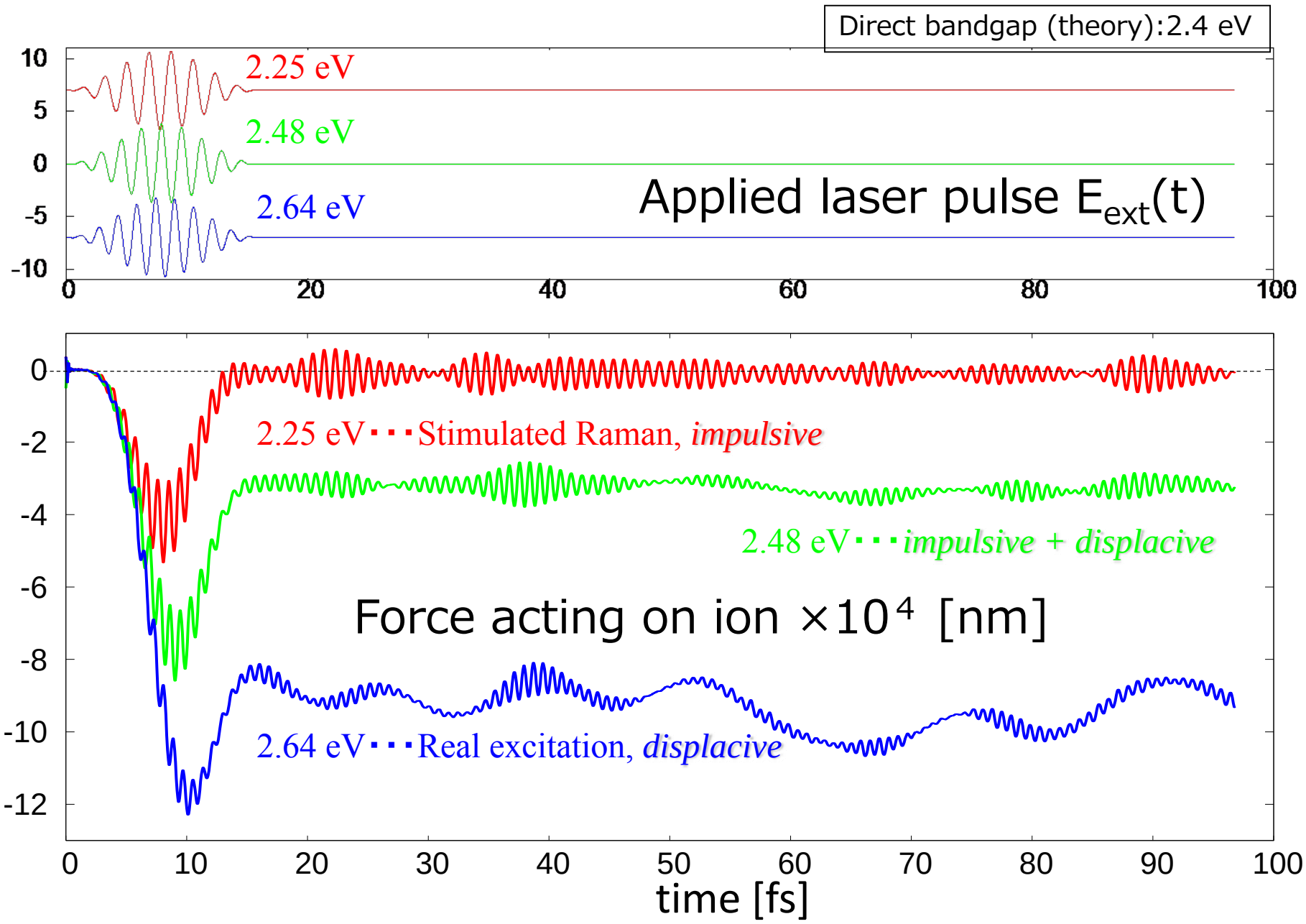
I= 1×10^{12} W/cm^2,
T=16 fs (8 mJ/cm^2),
ħω=2.06 eV







Dependence on laser frequency



Optical breakdown of dielectrics by intense laser pulse

T. Otobe, M. Yamagiwa, J.-I. Iwata, K.Y. T. Nakatsukasa,
G.F. Bertsch, Phys. Rev. B77, 165104 (2008)

As the laser intensity increases,

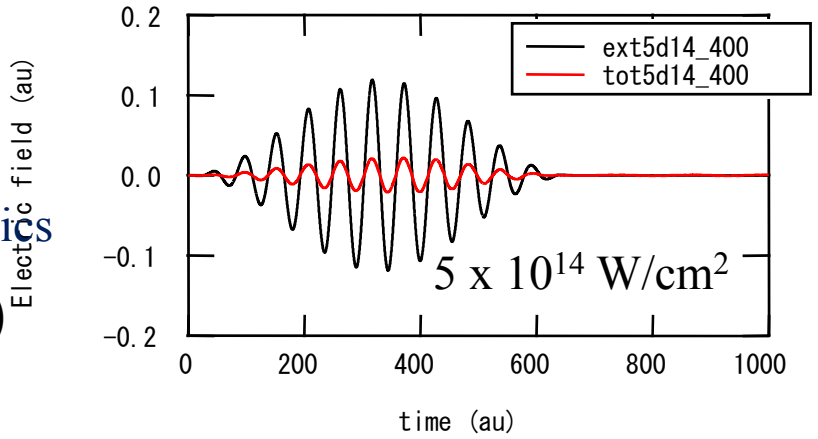
$E_{ext}(t)$ vs $E_{tot}(t)$

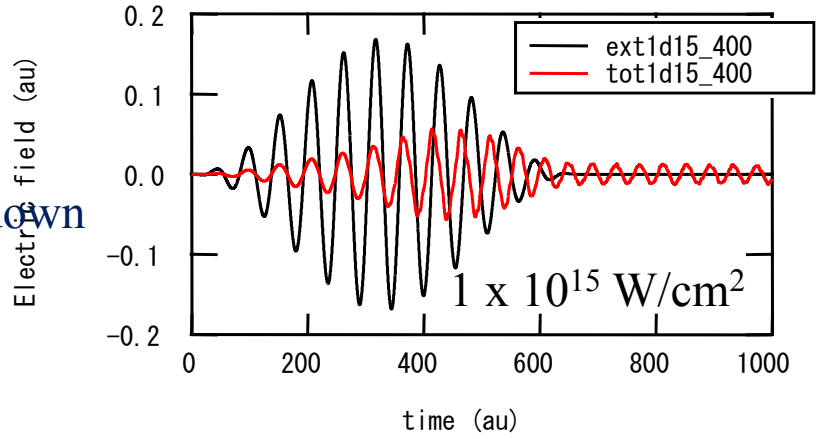
Weak field:
Dielectric dynamics

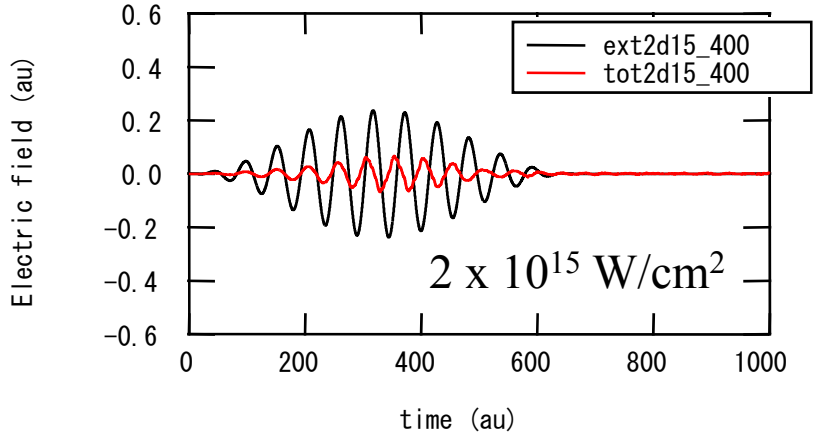
$$E_{tot}(t) \propto \frac{1}{\varepsilon(\omega)} E_{ext}(t)$$

Diamond
frequency: 3.1eV
pulse length: 16fs

Threshold
for breakdown







T. Otobe, M. Yamagiwa, J.-I. Iwata, K.Y. T. Nakatsukasa, G.F. Bertsch, Phys. Rev. B77, 165104 (2008)

Behavior around breakdown (1×10^{15} W/cm^2, 3.1eV, 40fs)

Initial stage < 15fs, dielectric screening

$$\varepsilon(0) \approx 5.7$$

Substantial excitation, 15-20fs

- phase difference between $E_{ext}(t)$ and $E_{tot}(t)$
- rapid increase of excited electron number and energy transfer

  $\Rightarrow$ Dielectric breakdown

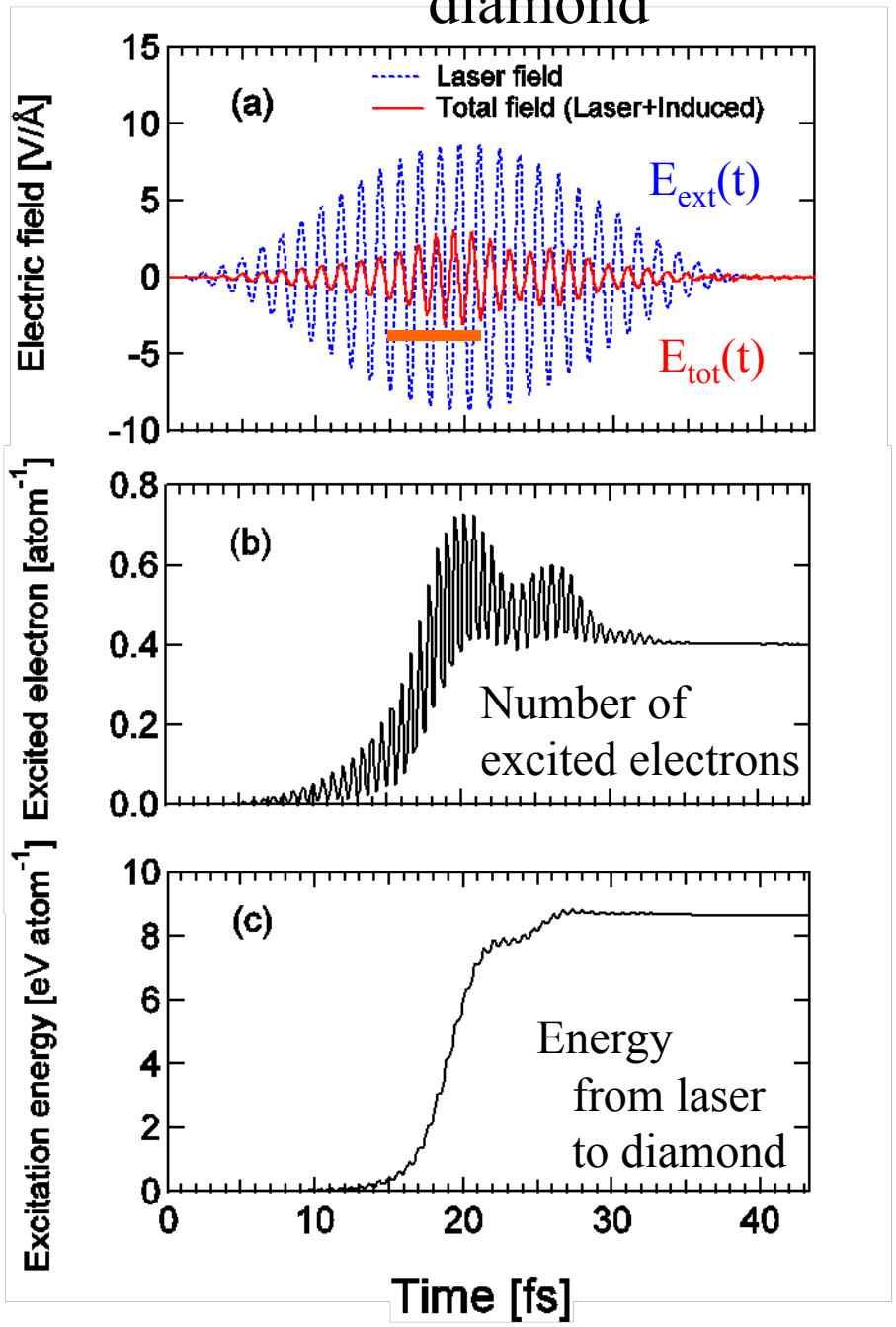
Metallic response, > 25 fs

- no further increase of excited electron number and energy transfer

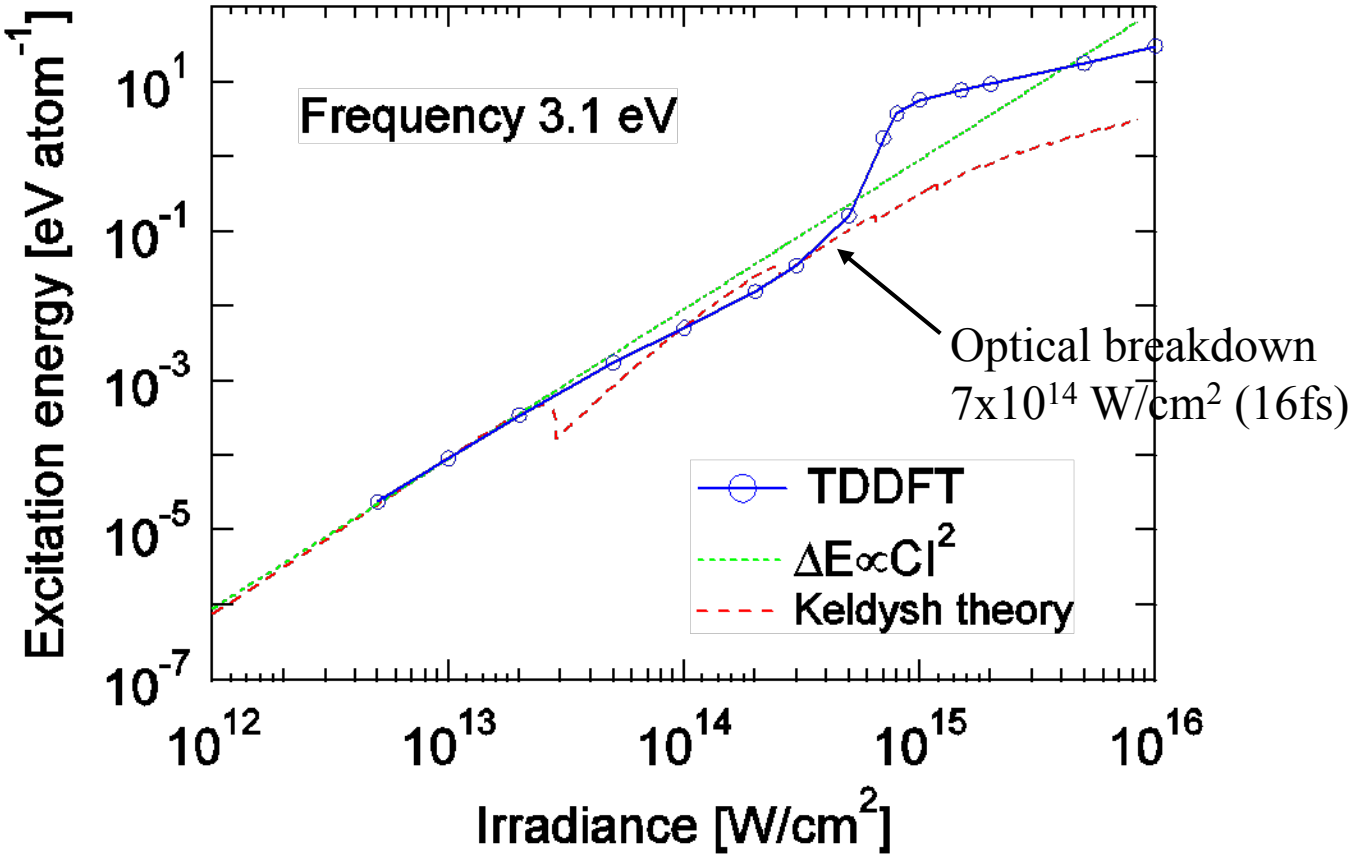
Note: plasma frequency for 0.4/atom

$$\omega_p = \left(\frac{4\pi n_{ex}}{m\varepsilon(0)}\right) \approx 4\text{eV}$$

close to frequency of laser pulse, 3.1eV



Energy transfer from laser pulse to diamond



Two photon curve (green)
Analytic theory by Keldysh (1965) (red)

Optical breakdown threshold: Comparison with measurements

Diamond:

TDDFT:
7×10^{14} W/cm^2, 16 fs $\Rightarrow$ 6 J/cm^2

Measurement
2eV, 90fs pulse 0.63 ± 0.15 J/cm^2
D.H. Reitze et.al, Phys. Rev. B45, 2677(1992)

Calculated threshold is systematically high by factor 10.

Possible significance of
- electron-electron collision
- self-focusing effect

Summary

Merit of real time approach

-Response of full spectral region from single real-time calculation

-Efficient for large systems

-Intuitive treatment of scattering boundary condition (Photoionization)

-Real-time measurements (with ultrashort laser pulse

-Nonlinear dynamics beyond perturbation theory (with intense laser pulse)

Linear response regime

accurate description for oscillator strength distribution

Nonlinear electron dynamics in ultrashort and ultraintense laser field

coherent phonon

optical dielectric breakdown