Time-dependent Density Functional theory at the limits

G.F. Bertsch*
University of Washington

ES2015 workshop

June 23, 2015

1. Goals, algorithms
2. Electron-phonon coupling
   a) molecules
   b) coherent phonon generation
3. Nonlinear regime
   a) Hyperpolarizability, Franz-Keldysh
   b) Rabi oscillations
   b) Intense laser pulses
   c) Simulating pump-probe experiments

*In collaboration with K. Yabana (Tsukuba)

Perspective

1. TDDFT is an effective Hamiltonian theory (adiabatic theory)
2. Utility of a predictive theory is a function of computational cost as well as accuracy.

Goals

1. Exploit the real-time method.
2. Determine the accuracy of the theory in different contexts.

Algorithm for TDDFT (Yabana code)

1. Uniform real-space mesh (~0.5 Bohr mesh)
2. Laplacian by 9-point difference
3. Time integration by 4-th order expansion of $\exp(-iH_{ks}\Delta t)$
4. Mixed gauge for crystalline lattices
5. multiscale for surface effects (~10^5 p.h.)

Electron-vibration coupling in molecules

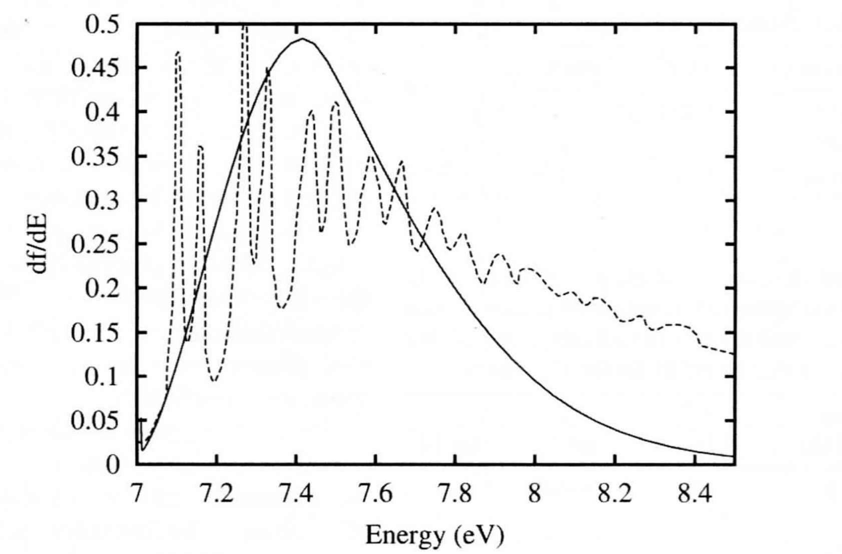
Vertical transitions in TDDFT:
Herzberg-Teller in benzene
LDA

$f/10^{-3}$	TDDFT	Expt.
$^1E_{1u}$	1100	900-950
$^1B_{1u}$	60	90
$^1B_{2u}$	1.6	1.3

J. Chem. Phys. 115 4051 (2001)

Vibronic coupling in ethylene

Main peak



Low-energy tail

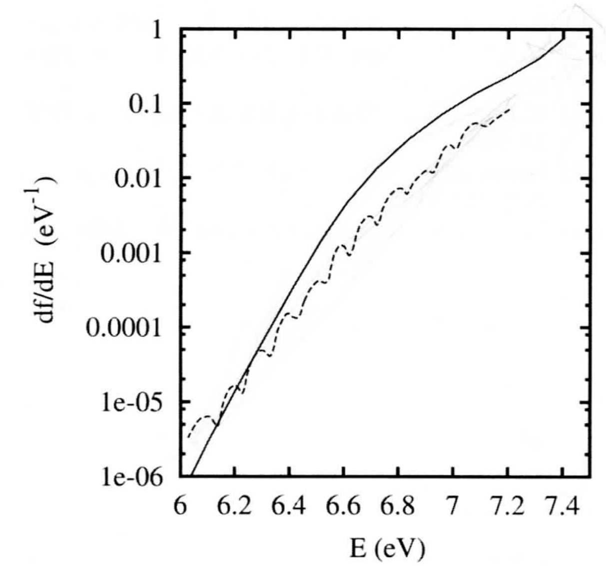


Fig. 4. Low energy absorption strength associated with the zero-point motion in the torsional coordinate. Solid: present theory; dashed: experiment.[19]

Israel J. Chem. 42 151 (2002)

Coherent phonon generation

Experiment in Sb

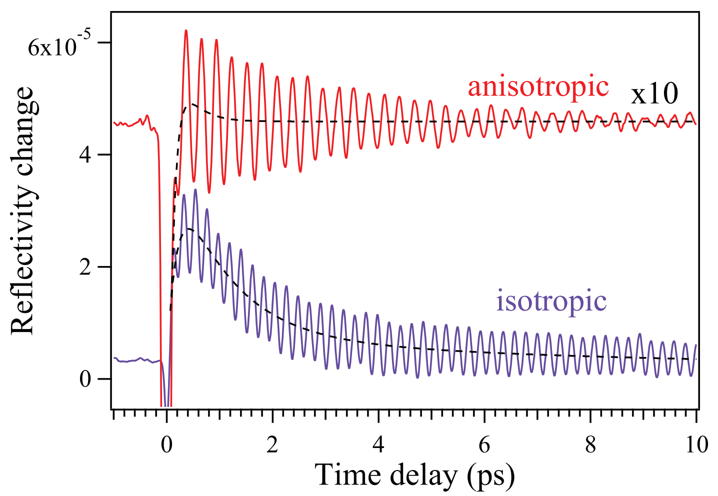
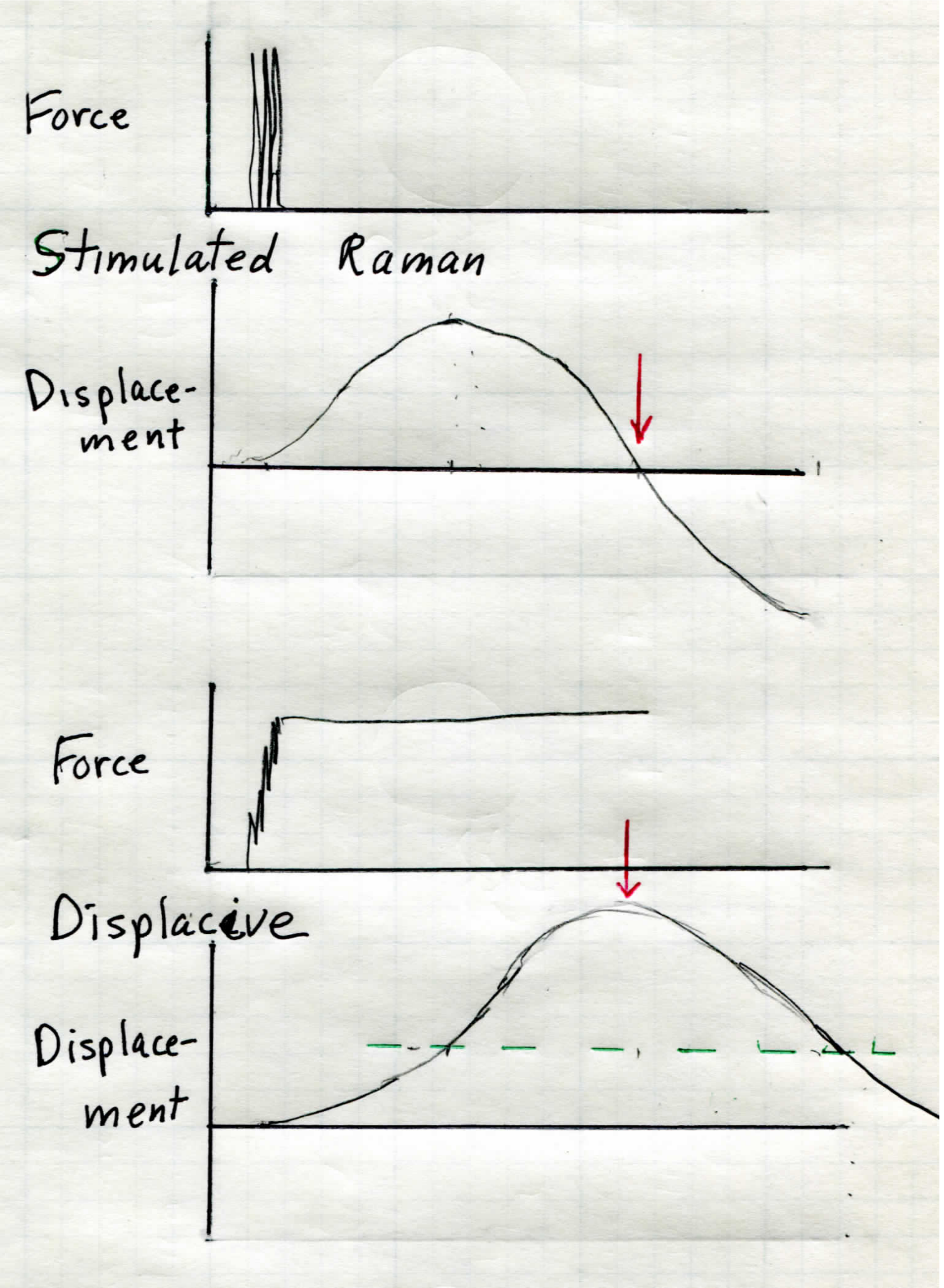
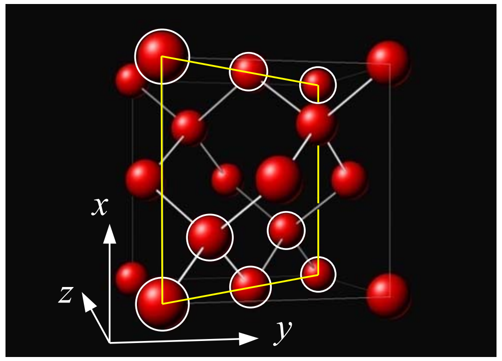


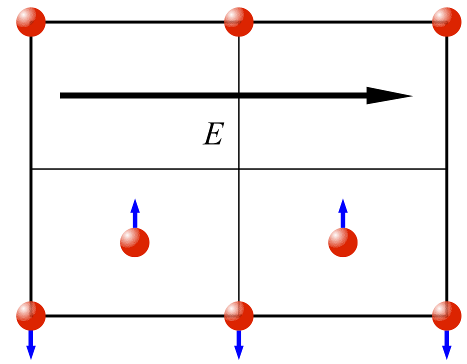
FIG. 1. Observation of coherent phonons in crystalline Sb generated by high-intensity laser pulses of 1.55 eV photon energy. Reprinted with permission from K. Ishioka, M. Kitajima, and O. Misochko, J. Appl. Phys. **103**, 123505 (2008). Copyright © 2008, American Institute of Physics.



Coherent phonon generation

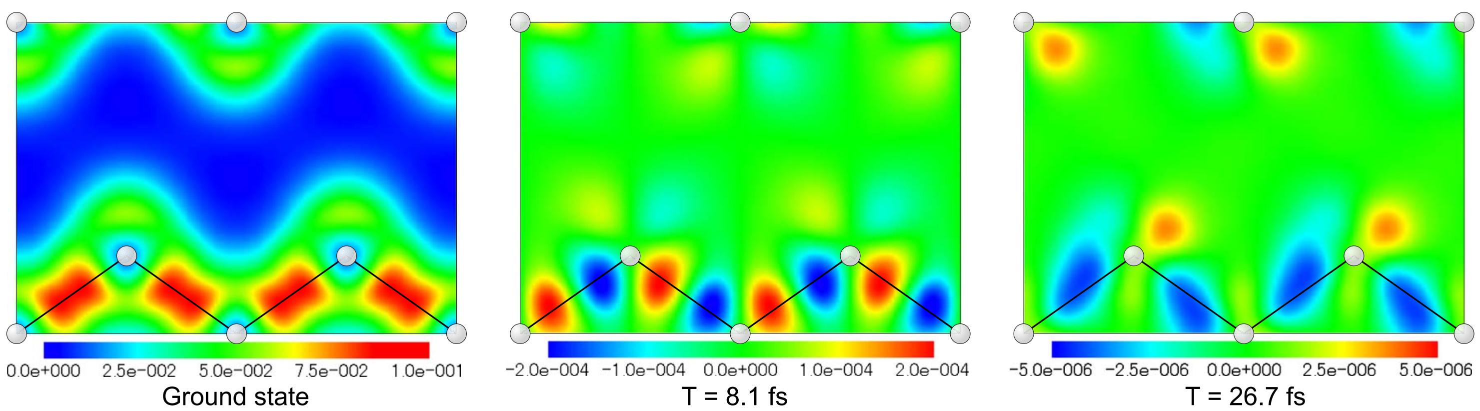
Silicon

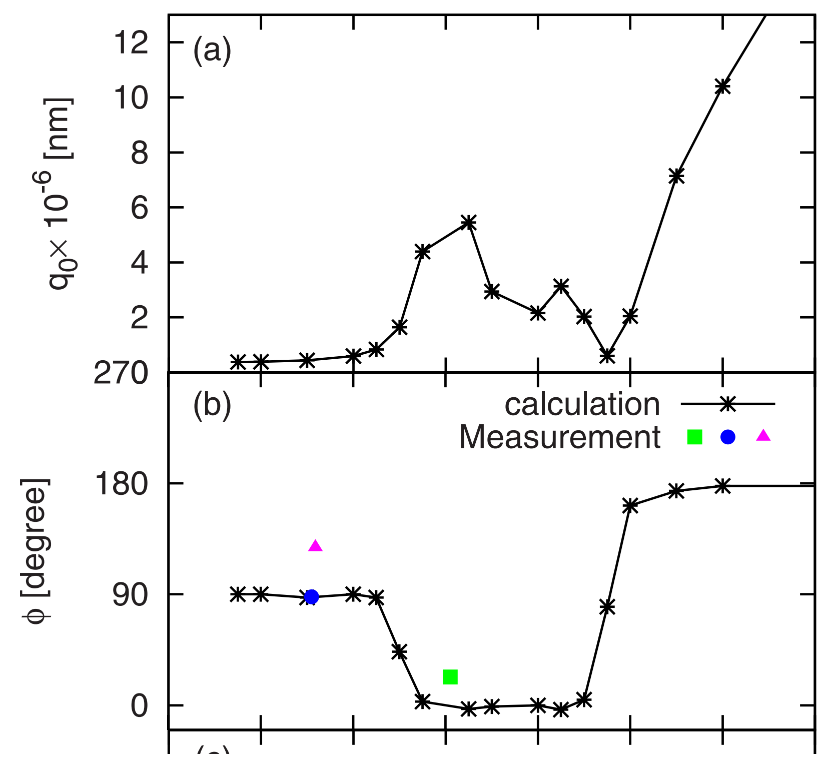




LDA

TDDFT: Phys. Rev. B **82** 15510 (2010)





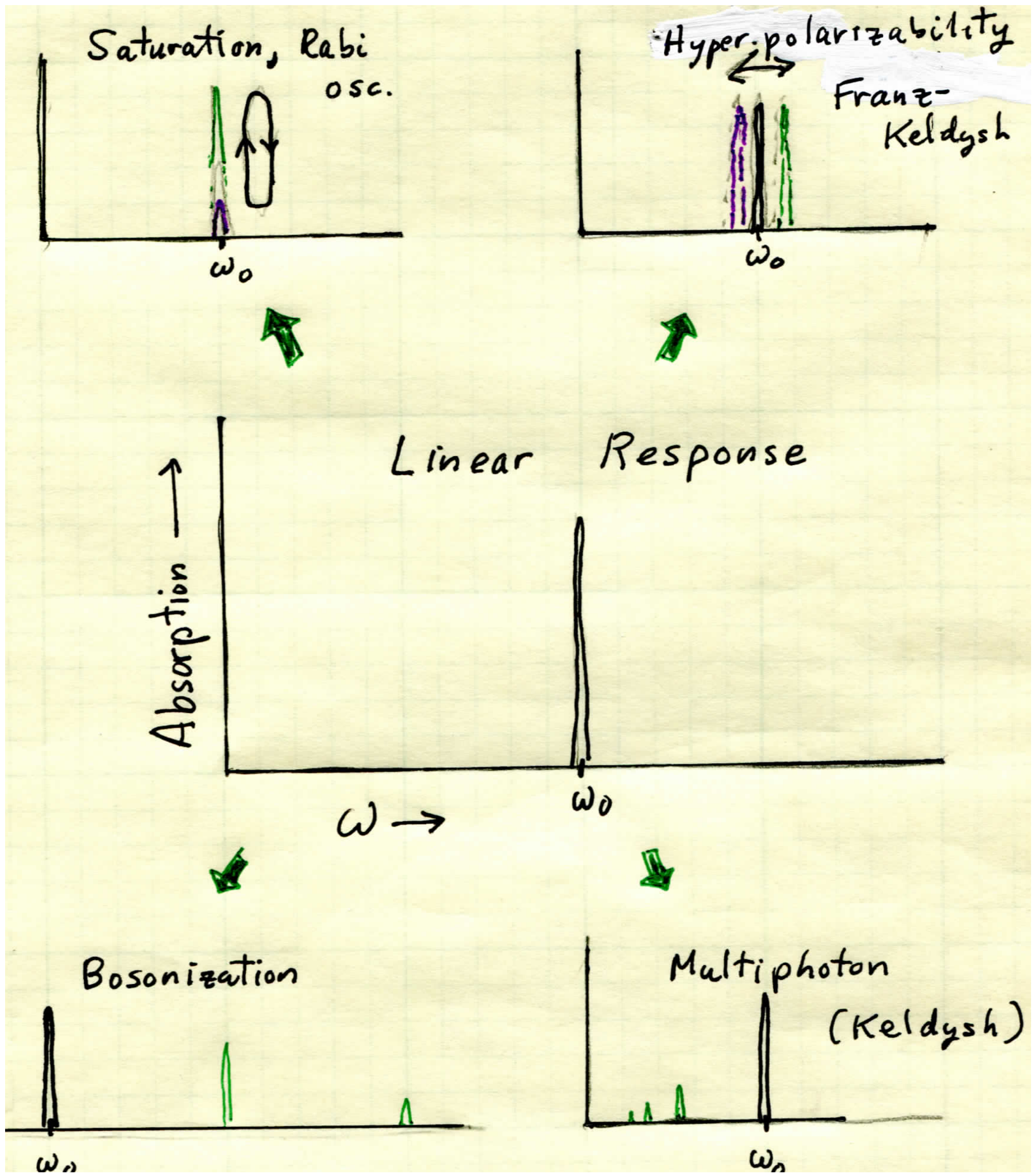
Equivalent to perturbative Raman when $\mathrm{Im}\,\varepsilon = 0$

Phonon amplitude is proportional to pulse fluence in both reactive and dissipative regions.

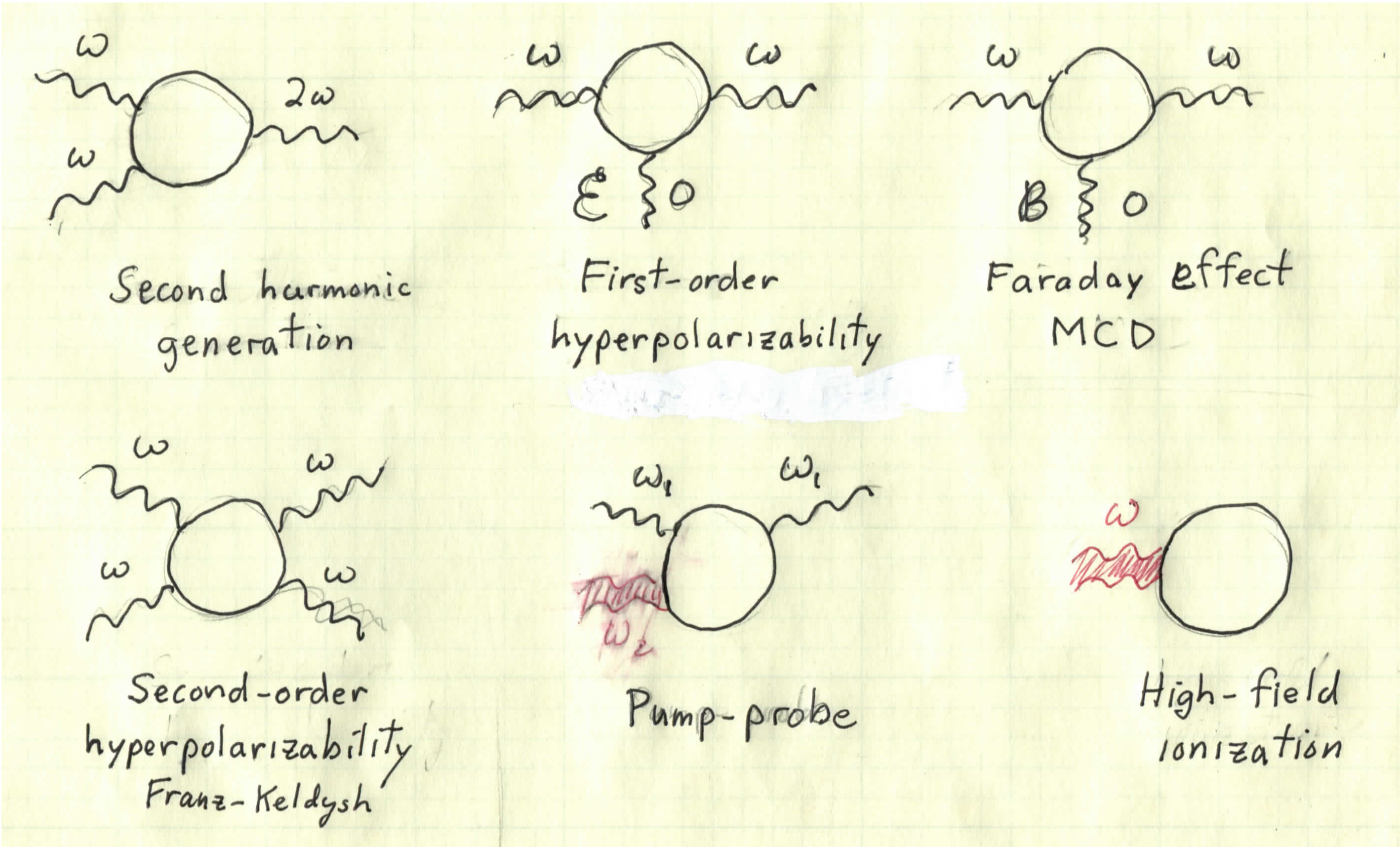
Amplitude in dissipative region agrees with phenomenological model of Stevens, Kuhl and Merlin, Phys. Rev. B 65 144304 (2002).

Physics beyond the linear response

Rabi: D. Bauer, PRL **102** 233001 (2009)

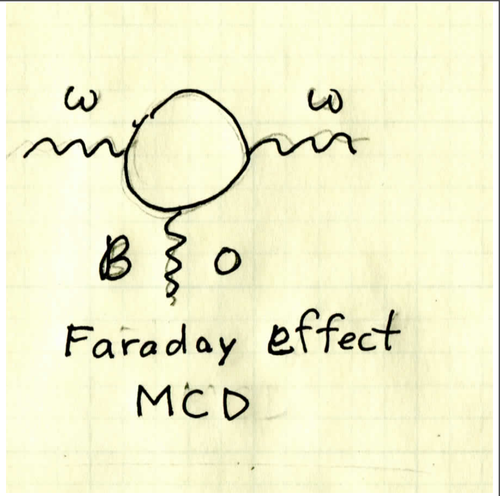


FOH: Takimoto, et al. J. Chem. Phys. **127** 154114 (2007)



Bozonization: J. Kas, et al., Phys. Rev. B **91** 121112 (2015).

Magnetic circular dichroism   Fullerine C_60



J. Chem. Phys **134** 144106 (2011)

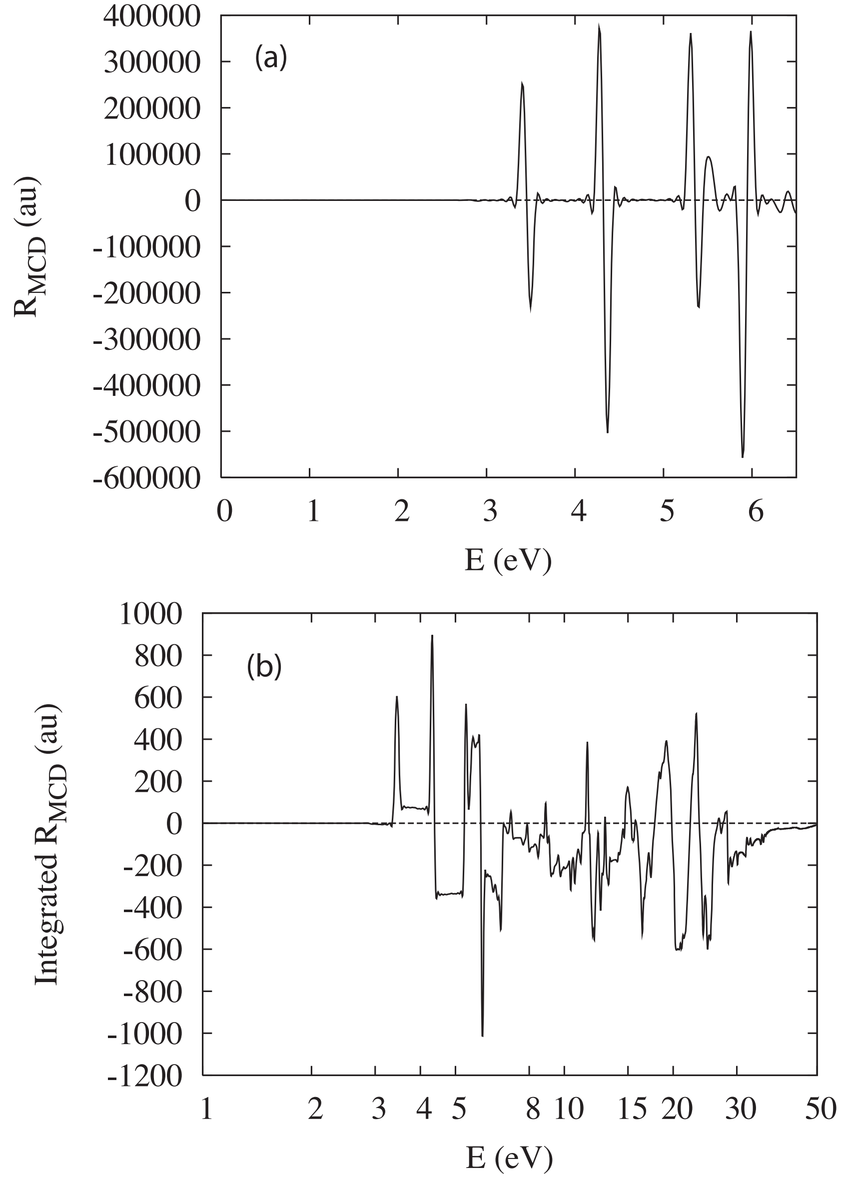
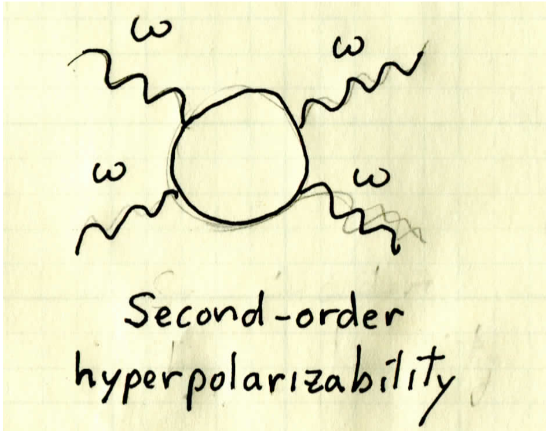


FIG. 4. MCD response $R_{MCD}(E)$ in C_{60}. Upper panel shows the strength function Eq. (4). The corresponding integrated strength function is shown in the lower panel.

$$\frac{R_{MCD}(\omega)}{B} \sim \mathcal{A}\frac{df(\omega)}{d\omega} + \mathcal{B}f(\omega)$$

Energy (eV)		$\mathcal{B}_n/\mathcal{D}_n$	
Exp.	TDDFT	Exp.	TDDFT
3.8	3.5	100	64
4.9	4.3	−700	−146
6.0	5.3		66
	5.9		−120

Second-order hyperpolarizability



Ethylene

J-I Iwata, et al., J. Chem. Phys. 115 8773 (2001)

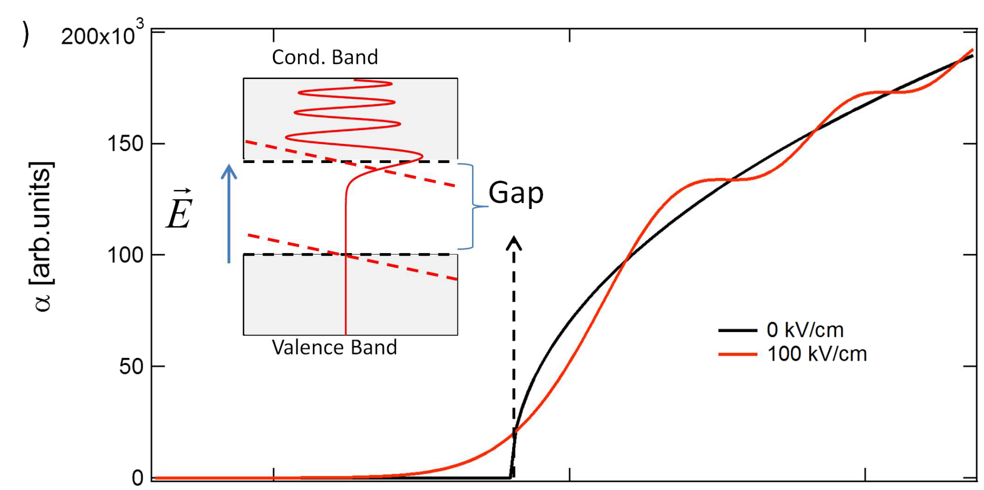
functional	VWN	BLYP	LB94	Exp.
$\alpha_{\|\|}/1000$	14.0	19.2	7.6	9.0+/-0.2

Experimental value is within the range of tested functionals.
There is a factor of 2-3 between functionals.

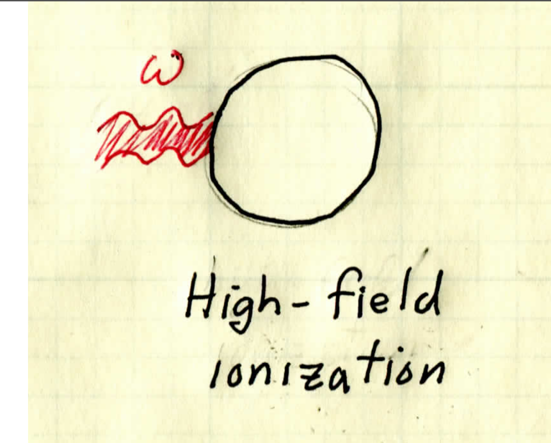
Dynamic Franz-Keldysh Effect

Experiment on GaAs:
Novelli, et al., Scientific Reports 3 1227 (2013)
TDDFT by Otobe, et al., arXiv:1504.01458:

not understood. To uncover the physics of time-resolved DFKE, we develop a pump-probe formalism in two different theoretical approaches: first-principles numerical simulations based on time-dependent density functional theory (TDDFT [25]) and analytic investigation for a two-band model. Combining two approaches, we can understand not only the strength of the modulation but the phase with respect to the pump field as well.



Intense laser pulses



1. Reflectivity diagnostics--silicon surface

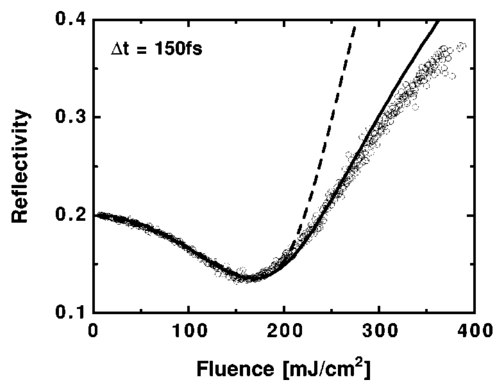


FIG. 6. Reflectivity of silicon as a function of laser fluence a

Sokolowski-Tinten and Linde, Phys. Rev. B **61** 2648 (2000).

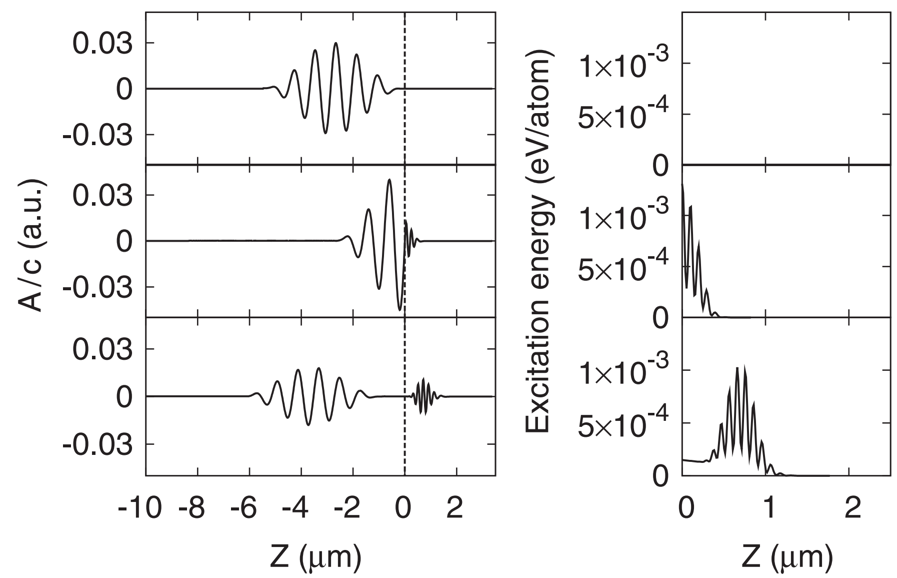


FIG. 1. Snapshots of the electromagnetic fields (vector potential divided by light speed, A/c; left panels) and of the electronic

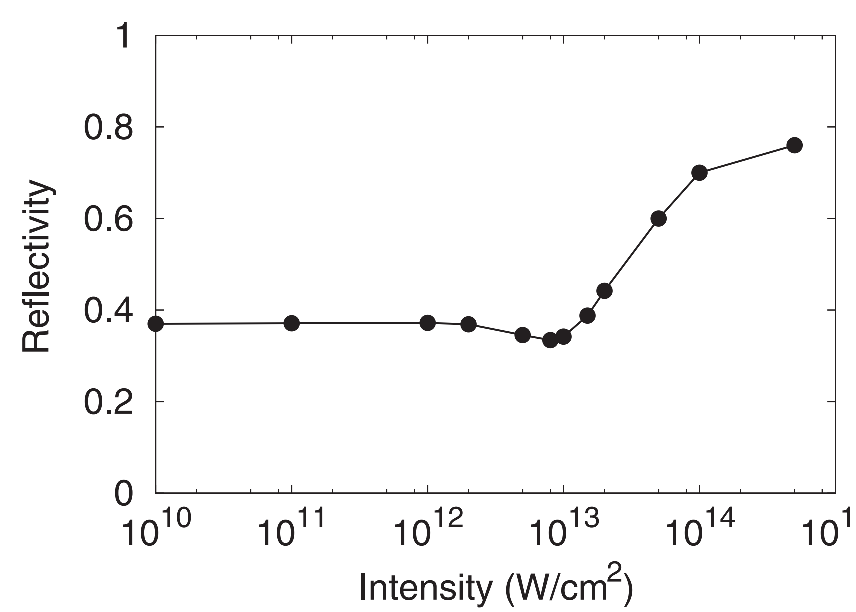


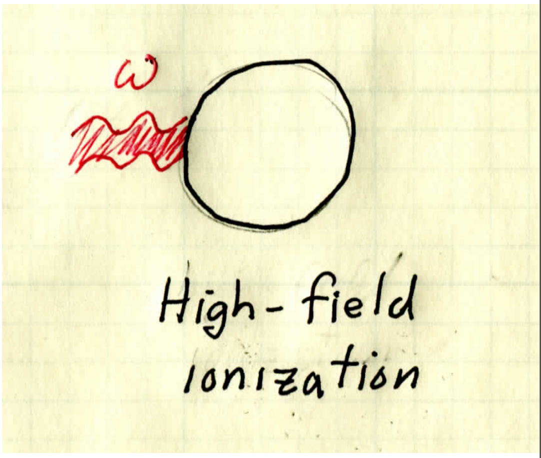
FIG. 4. The reflectivity of Si at normal incidence is shown as a function of peak laser intensity.

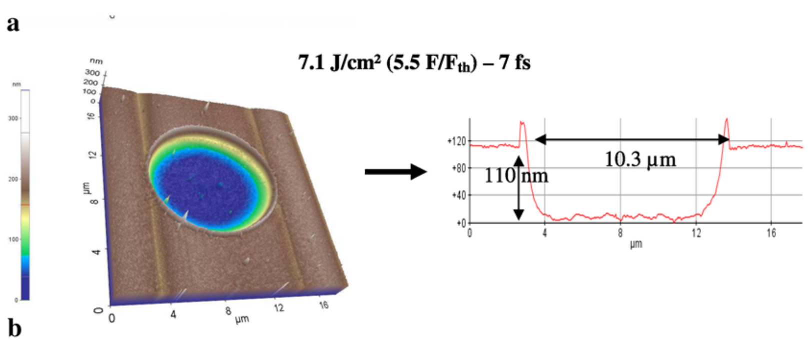
Yabana, et al., Phys. Rev. B **85** 045124 (2012)

Intense laser pulses

2. Surface damage and ablation

Of interest for nanoparticle production, cf.
Balling and Schou, Rep. Prog. Phys. 96 036502(2013)





Uteza, et al., App. Phys. A 105 131 (2011)

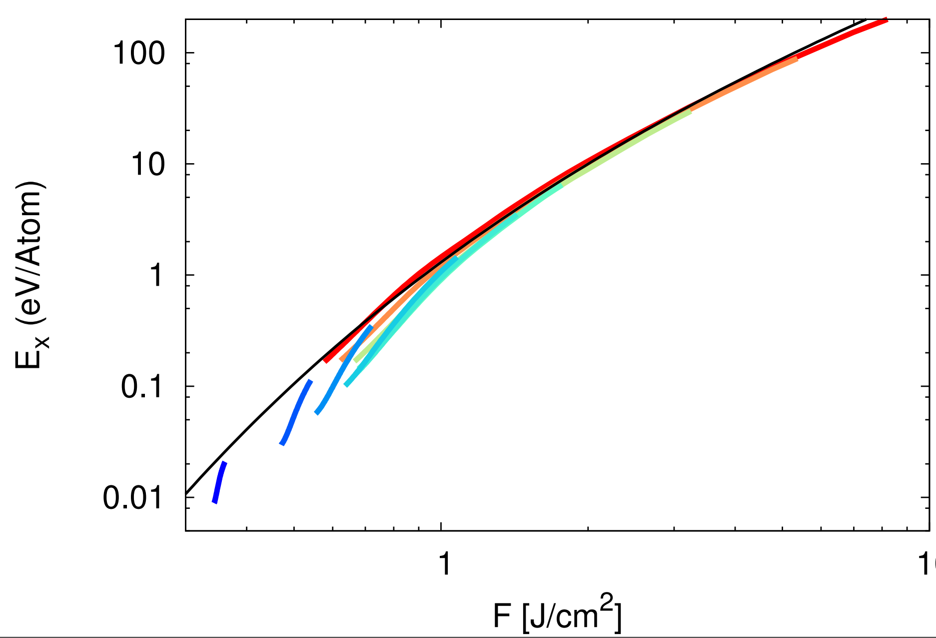
Keldysh:

$$W = \frac{4m^{1/4}\mathcal{E}^{5/2}}{9\pi^2\Delta^{5/4}} \exp(-\pi\Delta^{3/2}m^{1/2}/2e\mathcal{E})$$

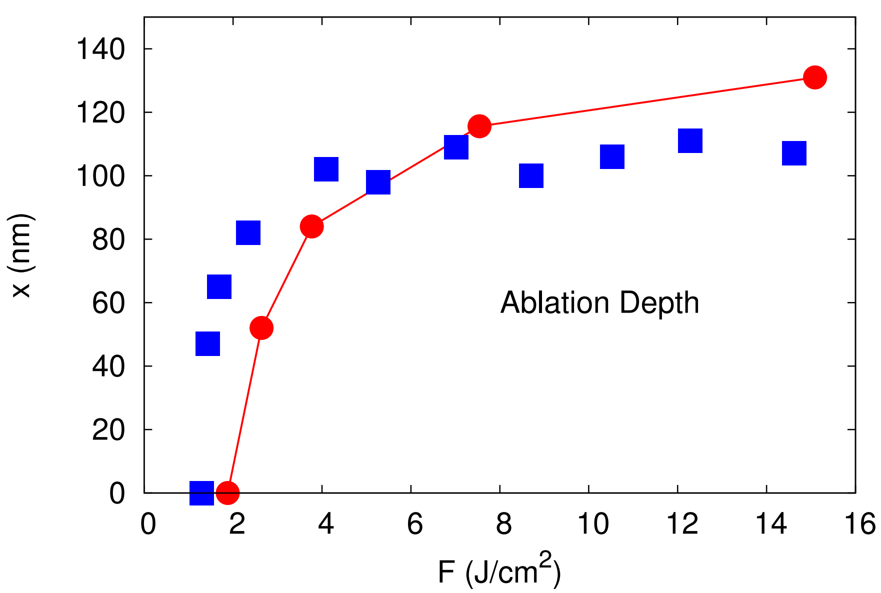
fits well with m an adjusted parameter

TDDFT with Becke-Johnson V_xc

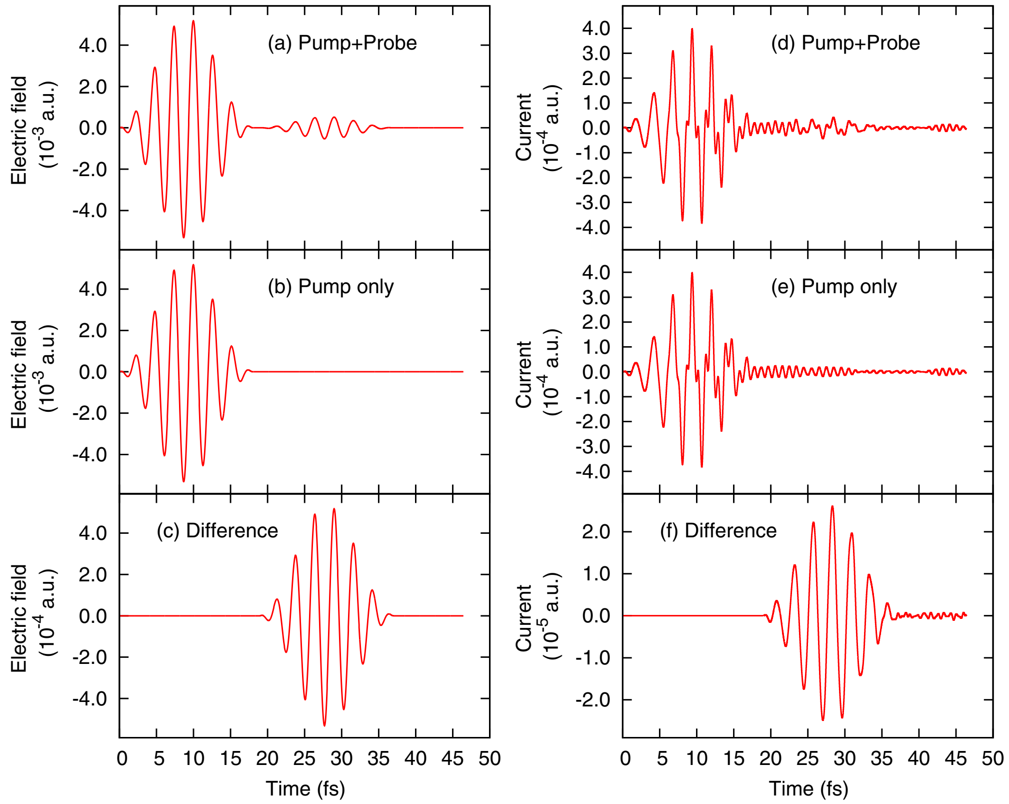
Sato, et al., arXiv:1412.1445 (2014)

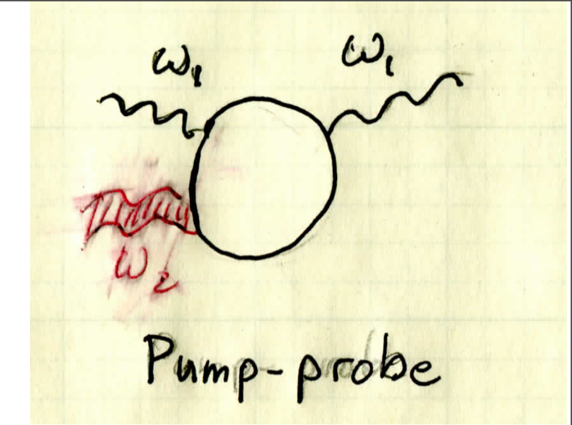


Depth of Ablation pit



Simulating pump-probe experiments





Sato, et al., Phys. Rev. B **89** 064304 (2014).

Dielectric function compared with thermal model in Sato, et al. Phys. Rev. B **90** 174303 (2014).

Summary

1. Electron-phonon coupling

2. First-order hyperpolarizability

2. Magnetic circular dichroism

3. Second-order hyperpolarizability

4. High-field ionization