

Semiempirical TDDFT – Chances and Challenges

Thomas Niehaus

Bremen Center for Computational Materials Science



Electron Dynamics in Complex Systems

The Gentner-Minerva Symposium on TDDFT, Winter 2007

Thesaurus

Legend: █ Synonyms █ Related Words █ Antonyms

Adj. 1. semiempirical - relying to some extent on observation or experiment

█ empirical, empiric - derived from experiment and observation rather than theory; "an empirical basis for an ethical theory"; "empirical laws"; "empirical data"; "an empirical treatment of a disease about which little is known"

Here:

*Relying to some extent on input from (more sophisticated)
theoretical methods*

Outline

- 1 DFTB: Ground state
- 2 TD-DFTB: Solution in frequency domain
 - Approximations for the coupling matrix
 - Luminescence of Silicon Quantum Dots
 - Excited state PES of organic compounds
- 3 TD-DFTB: Solution in time domain
 - Ehrenfest dynamics: Equations of motion
 - Vibrational excitation of C₆₀ by ultrashort laser pulses

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Density Functional based Tight-Binding

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$$H_{\mu\nu}^0 = \begin{cases} \epsilon_\mu & : \mu = \nu \\ \langle \phi_\mu | H_{KS}[\rho_A + \rho_B] | \phi_\nu \rangle & : \mu \in A, \nu \in B \\ 0 & : \text{otherwise} \end{cases}$$

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$$\gamma_{\mu\nu} = \iint |\phi_\mu(\mathbf{r})|^2 \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}[\rho_0] \right) |\phi_\nu(\mathbf{r}')|^2 d\mathbf{r} d\mathbf{r}'$$

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- Total energy

$$E_{\text{tot}} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu}^0 + \frac{1}{2} \sum_{\mu\nu} \gamma_{\mu\nu} \Delta q_\mu \Delta q_\nu + E_{\text{rep}}$$

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Linear response in DFTB: TD-DFTB

Equation to solve (singlets):

$$\sum_{kl} \left[\omega_{ij}^2 \delta_{ik} \delta_{jl} + 4 \sqrt{\omega_{ij}} K_{ij,kl}^S \sqrt{\omega_{kl}} \right] F_{kl}^I = \omega_I^2 F_{ij}^I$$
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Approximation:

$$K_{ij,kl}^S = \sum_{\mu\nu\alpha\beta} c_{\mu i} c_{\nu j} c_{\alpha k} c_{\beta l} \iint \phi_{\mu}(\mathbf{r}) \phi_{\nu}(\mathbf{r}) \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} + f_{xc}[\rho] \right) \phi_{\alpha}(\mathbf{r}') \phi_{\beta}(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

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$$\approx \sum_{\mu} q_{\mu}^{ij} q_{\mu}^{kl} M_{\mu} \quad \text{Onsite only, } M_{\mu} \text{ from atomic DFT}$$

TD-DFTB performance

Excitation energies (eV)

Molecule	State	Exp.	TD-DFTB		TDDFT ¹	
			ω_I	ω_{ij}	ω_I	ω_{ij}
Ethylen	$^3B_{1u}(\pi \rightarrow \pi^*)$	4.40	5.47	6.30	4.16	5.66
	$^1B_{1u}(\pi \rightarrow \pi^*)$	7.65	7.81	6.30	7.44	5.66
Propynal	$^3A''(n \rightarrow \pi^*)$	2.99	4.04	4.04	2.74	3.15
	$^1A''(n \rightarrow \pi^*)$	3.56	4.04	4.04	3.37	3.15

[1] BPW91//6-311+G**

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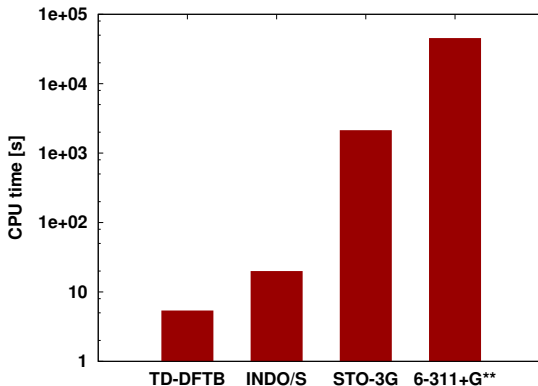
[1] BPW91//6-311+G**

Mean absolute error (eV)

	TD-DFTB	BPW91		INDO/S
		6-311+G**	STO-3G	
Sing. (16 Com.)	0.38	0.36	1.19	0.56
Trip. (13/11 Com.)	0.64	0.37	0.49	1.38

Numerical issues

Sum of CPU times (ground + excited state) for test set of 10 organic molecules (< 10 atoms). TDDFT results are for the BPW91 functional.

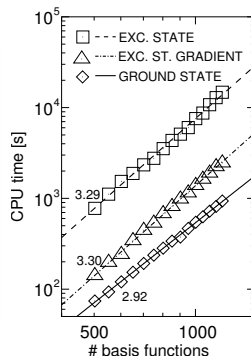


Numerical issues

Scaling

- Iterative subspace methods for diag.
- Formal scaling of N^6 reduced to N^3

$$\sum_{kl} \Omega_{ij,kl} v_{kl} = \omega_{ij}^2 v_{ij} + 4\sqrt{\omega_{ij}} \sum_{\mu} q_{\mu}^{ij} \left(\sum_{\nu} \gamma_{\mu\nu} \left(\sum_{kl} q_{\nu}^{kl} \sqrt{\omega_{kl}} v_{kl} \right) \right)$$



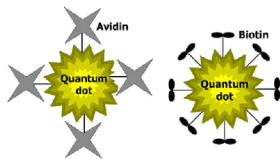
Analytical excited state gradients from auxiliary Lagrangian approach (Furche and Ahlrichs)

⇒ Heringer et al. JCC **28** 2589 (2007)

Outline

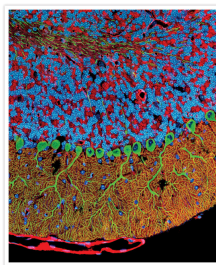
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Quantum dots as fluorescent markers in biology



Functionalization with
antibodies or aptamers

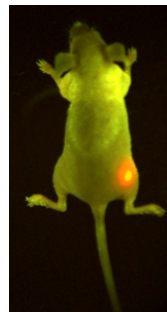
In vitro



Mouse cerebellum

<http://probes.invitrogen.com>

In vivo



Rat tumor

 Gao, Science (2004)

Biocompatibility of Cadmium based Dots

NANO
LETTERS

2004
Vol. 4, No. 1
11–18

Probing the Cytotoxicity of Semiconductor Quantum Dots

Austin M. Derfus, Warren C. W. Chan,[†] and Sangeeta N. Bhatia*

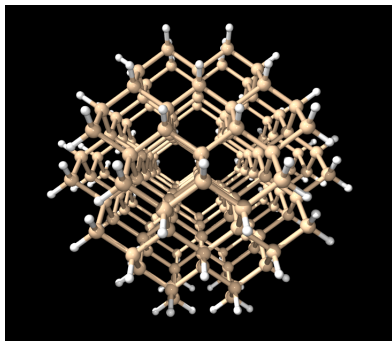
*Department of Bioengineering, University of California at San Diego,
La Jolla, California 92093*

Received September 3, 2003; Revised Manuscript Received November 7, 2003

ABSTRACT

With their bright, photostable fluorescence, semiconductor quantum dots (QDs) show promise as alternatives to organic dyes for biological labeling. Questions about their potential cytotoxicity, however, remain unanswered. While cytotoxicity of bulk cadmium selenide (CdSe) is well documented, a number of groups have suggested that CdSe QDs are cytocompatible, at least with some immortalized cell lines. Using primary hepatocytes as a liver model, we found that CdSe-core QDs were indeed acutely toxic under certain conditions. Specifically, we found that the cytotoxicity of QDs was modulated by processing parameters during synthesis, exposure to ultraviolet light, and surface coatings. Our data further suggest that cytotoxicity correlates with the liberation of free Cd²⁺ ions due to deterioration of the CdSe lattice. When appropriately coated, CdSe-core QDs can be rendered nontoxic and used to track cell migration and reorganization in vitro. Our results provide information for design criteria for the use of QDs in vitro and especially in vivo, where deterioration over time may occur.

Silicon Dots: Generation of models



- Spherical bulk fragments Si_{1-199}
- Si-Si bonds 2.33-2.38 Å
- T_d symmetry

Validation of TD-DFTB

$S_1 - S_0$ energy [eV]

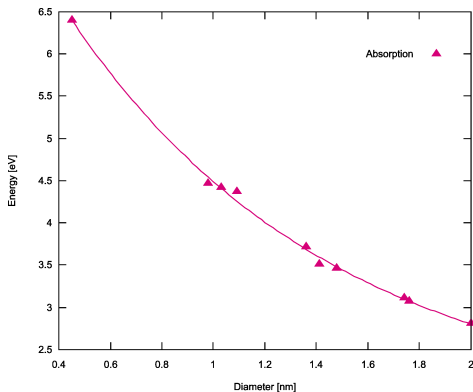
	DFTB	PBE ¹	B3LYP ²	MR-MP2 ²	exp ³
SiH ₄	10.3	8.76	9.25		8.8
Si ₅ H ₁₂	6.40	6.09	6.66	6.56	6.5
Si ₂₉ H ₃₆	4.42	3.65	4.52	4.45	
Si ₃₅ H ₃₆	4.37	3.56	4.42	4.33	

[1] Plane Wave, Degoli et al. PRB **69** 155411 (2004) [2] SV(P), Garoufalidis et al. PRL **87** 276402 (2001)

[3] Itoh et al. JCP **85** 4867 (1986)

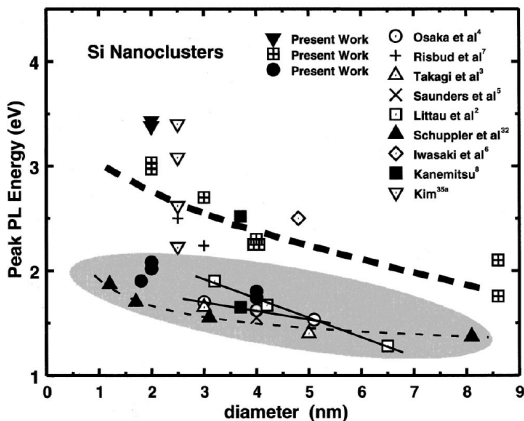
B3LYP functional of choice for SiQD
 DFTB is fine for larger dots

UV-Vis absorption energies of H-SiQD



Anticipated Particle-in-a-box behaviour

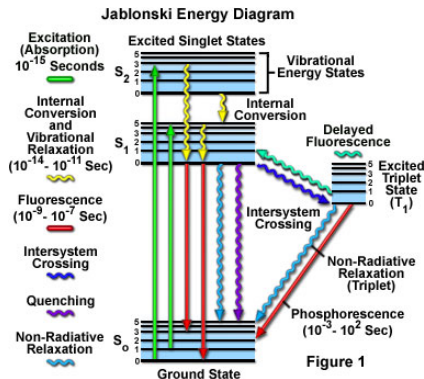
Experimental reports on SiQD photoluminescence



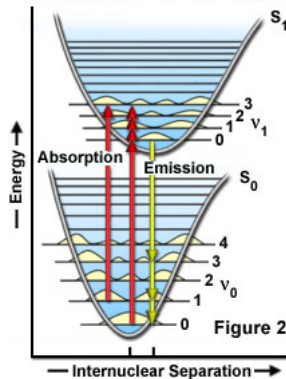
Peak PL versus Si nanocrystal size

Wilcoxon et al. PRB **60** 2704 (1999)

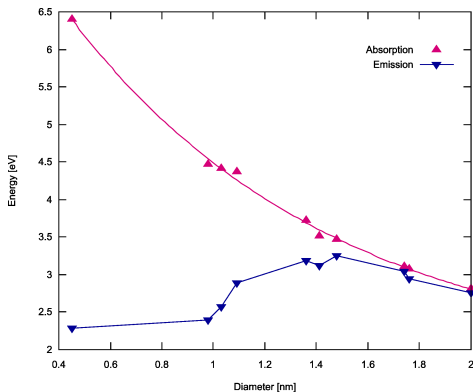
Luminescence and excited state processes



Franck-Condon Energy Diagram



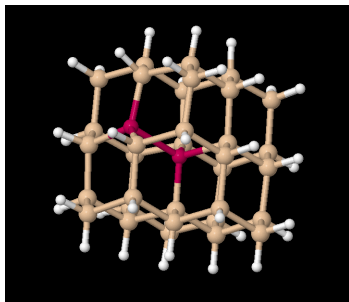
Luminescence properties of H-SiQD



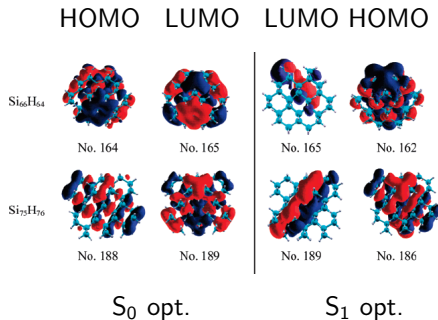
Huge Stokes shift for small particles

Wang et al. JPC C **111** 12588 (2007), APL **90** 123116 (2007)

Structure relaxation in the excited state



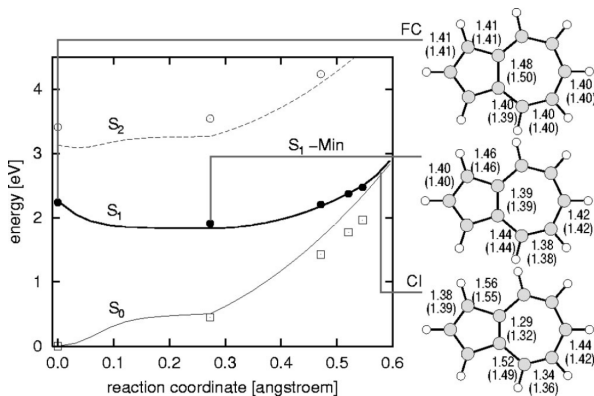
S_1 optimum of $\text{Si}_{35}\text{H}_{36}$



Outline

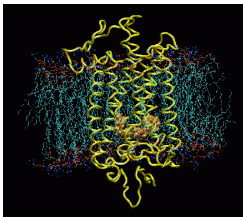
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Azulene

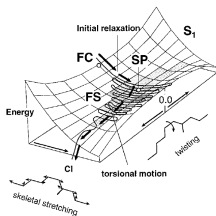


TD-DFTB minimum energy paths along the S_1
 Circles/Squares (BPW91/6-311+G**)

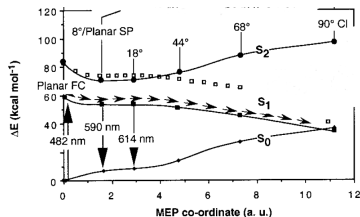
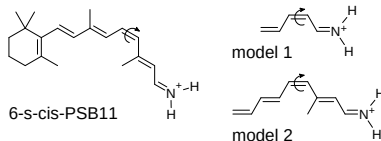
Retinal chromophores



Rhodopsin - Photoreceptor for colour vision
<http://www.ks.uiuc.edu>



Garavelli et al. JACS **121** 1023 (1999)



CASSCF/CASPT2 Minimum energy path
 Garavelli et al. PNAS **97** 9379 (2000)

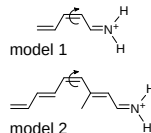
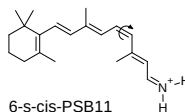
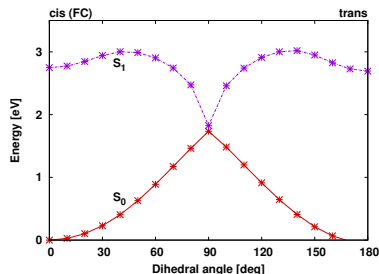
TD-DFT(B) treatment

Vertical excitation energy [eV] - Model 2, FC point

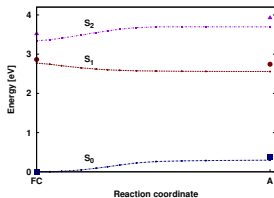
State	TD-DFTB	BP86 ¹	CASPT2 ²	exp ³
S ₁	2.77	2.89	2.58	2.92
S ₂	3.34	3.49	3.61	

[1] 6-311++G** [2] Garavelli et al. JACS **125** 12509 (2003)

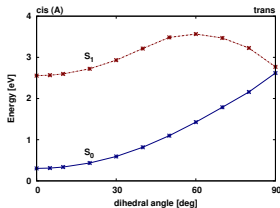
[3] PSB analogue in solution, Balogh-Nair et al. PCPB **33** 483 (1981)



Initial relaxation from the FC point

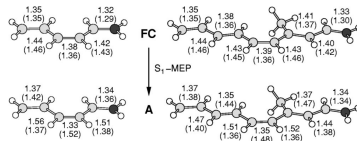


TD-DFTB S_1 minimum energy path from FC to planar minimum A. Circles/Squares (BP86/6-311++G**)

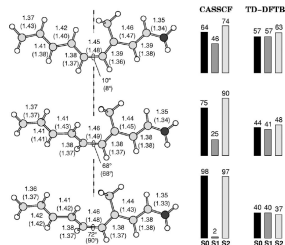


TD-DFTB PES scan along the isomerization coordinate starting at A

Wanko et al. JCP 120 1674 (2004)



Comparison of TD-DFTB and CASSCF (bondlengths in parentheses) geometries of structure A.



Outline

- 1 DFTB: Ground state
- 2 TD-DFTB: Solution in frequency domain
 - Approximations for the coupling matrix
 - Luminescence of Silicon Quantum Dots
 - Excited state PES of organic compounds
- 3 TD-DFTB: Solution in time domain
 - Ehrenfest dynamics: Equations of motion
 - Vibrational excitation of C₆₀ by ultrashort laser pulses

Quantum-classical Lagrangian approach

First-principles KS (adiabatic approximation):

$$\mathcal{L} = \sum_A \frac{1}{2} M_A \dot{\mathbf{R}}_A^2 - \sum_i^{\text{occ}} \langle \Psi_i(\mathbf{r}, t) | H[\rho](\mathbf{r}, t) | \Psi_i(\mathbf{r}, t) \rangle - E_{\text{DC}}[\rho](\mathbf{r}, t) - E_{ii} + \sum_i^{\text{occ}} \langle \Psi_i(\mathbf{r}, t) | i \frac{\partial}{\partial t} | \Psi_i(\mathbf{r}, t) \rangle$$

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DFTB case:

$$\Psi_i(\mathbf{r}, t) = \sum_{\mu} b_{\mu i}(t) \phi_{\mu}(\mathbf{r} - \mathbf{R}_A) \quad E_{\text{DFTB}} = \sum_{\mu\nu} b_{\mu i}^* b_{\nu i} H_{\mu\nu}^0 + \frac{1}{2} \sum_{\mu\nu} \gamma_{\mu\nu} \Delta q_{\mu} \Delta q_{\nu} + E_{\text{rep}}$$

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$$\mathcal{L}(b_{\mu i}, \mathbf{R}_A) = \frac{1}{2} \sum_A M_A \dot{\mathbf{R}}_A^2 - \frac{1}{2} \sum_{AB} \Delta q_A \gamma_{AB} \Delta q_B - E_{\text{rep}} \\ - \sum_i^{\text{occ}} \sum_{\mu\nu} \left[b_{\mu i}^* \left(H_{\mu\nu}^0 - i \langle \phi_{\mu} | \dot{\phi}_{\nu} \rangle \right) b_{\nu i} - i b_{\mu i}^* S_{\mu\nu} \dot{b}_{\nu i} \right]$$

Electronic equation of motion

Variation with respect to $b_{\mu i}^*$:

$$\dot{b}_{\nu i} = - \sum_{\delta\mu} S_{\nu\delta}^{-1} \left[iH_{\delta\mu} + \sum_A \dot{\mathbf{R}}_A \langle \phi_\delta | \frac{\partial}{\partial \mathbf{R}_A} \phi_\mu \rangle \right] b_{\mu i}$$

Conventional TD-KS equation in
non-orthogonal position dependent basis

Ionic equation of motion

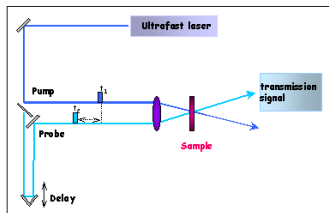
Variation with respect to $\mathbf{R}_A$:

$$\begin{aligned}
 M_A \ddot{\mathbf{R}}_A = & - \sum_i^{\text{occ}} \sum_{\mu\nu} b_{\mu i}^* \left(\frac{dH_{\mu\nu}^0}{d\mathbf{R}_\alpha} + \frac{dS_{\mu\nu}}{d\mathbf{R}_\alpha} \sum_B \gamma_{AB} \Delta q_B \right) b_{\nu i} \\
 & + \sum_i^{\text{occ}} \sum_{\mu\nu\delta\gamma} \left(b_{\mu i}^* \left\langle \frac{d\phi_\mu}{d\mathbf{R}_\alpha} \middle| \phi_\nu \right\rangle S_{\nu\delta}^{-1} H_{\delta\gamma} b_{\gamma i} + \text{c.c.} \right) \\
 & - \sum_i^{\text{occ}} \sum_{\mu\nu\delta\gamma} \left(i b_{\mu i}^* \left\langle \frac{d\phi_\mu}{d\mathbf{R}_\alpha} \middle| \phi_\nu \right\rangle S_{\nu\delta}^{-1} \langle \phi_\delta | \dot{\phi}_\gamma \rangle b_{\gamma i} + \text{c.c.} \right) + \sum_i^{\text{occ}} \sum_{\mu\nu} \left(i b_{\mu i}^* \left\langle \frac{d\phi_\mu}{d\mathbf{R}_\alpha} \middle| \dot{\phi}_\nu \right\rangle b_{\nu i} + \text{c.c.} \right) \\
 & - \Delta q_A \sum_B \frac{d\gamma_{AB}}{d\mathbf{R}_\alpha} \Delta q_B - \frac{dE_{\text{rep}}}{d\mathbf{R}_\alpha},
 \end{aligned}$$

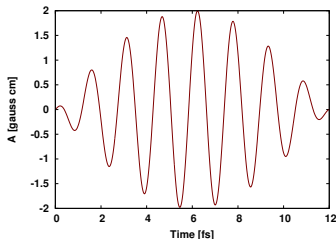
Conservation of total energy, momentum, norm and charge

■ Niehaus et al. EPJD **35** 467 (2005) ■ Todorov, JPCM **13** 10125 (2001)

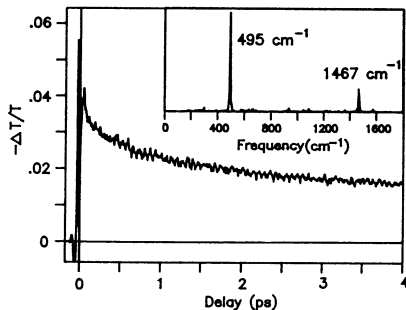
Pump-probe experiments on C_{60} films



Typical pump-probe experimental setup



Dexheimer et al. *Ultrafast Phenomena VIII*
 Springer, Berlin (1993).



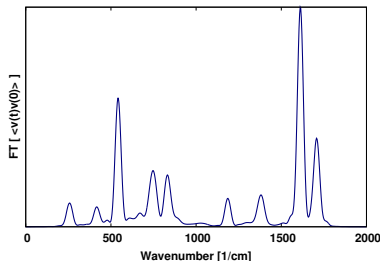
Negative differential transmittance of C_{60} film as function of delay between 12 fs/2 eV pump and probe pulses.

Simulation details

- Modified Cayley algorithm for time propagation
- Time step of 6 as during pulse, 25 as after
- Pulse length 12 fs, Gaussian envelope
- Carrier frequency 2.0 eV
- Sampling 1 ps, $\Delta E_{tot}/E_{tot} < 10^{-6}$
- Spectral density from $\text{FT}[\langle v(t)v(0) \rangle]$
- CPU time 13 h for one trajectory

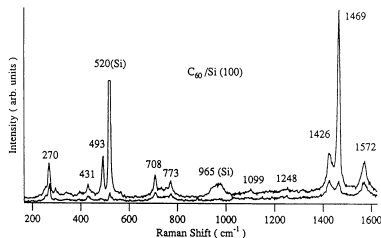
Weak intensity excitation

Theoretical spectral density



$$t_p = 12 \text{ fs}, \omega = 2.0 \text{ eV}, F = 4.7 \text{ mJ/cm}^2$$

Experimental spontaneous Raman spectrum

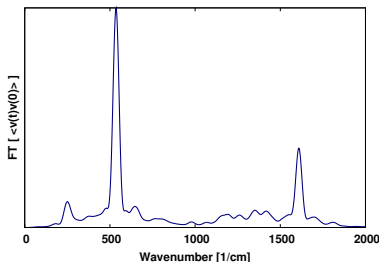


Eklund et al. JPCS **53**, 1391 (1992)

All Raman active modes excited

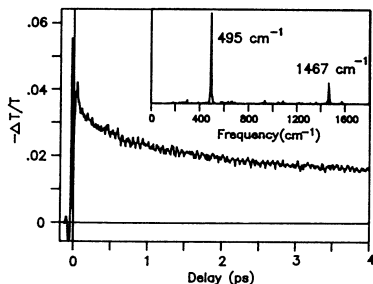
Medium intensity excitation

Theoretical spectral density



$$t_p = 12 \text{ fs}, \omega = 2.0 \text{ eV}, F = 9.5 \text{ mJ/cm}^2$$

Dexheimer et al. *Ultrafast Phenomena VIII*
 Springer, Berlin (1993).

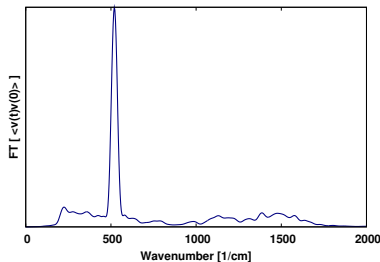


$$t_p = 12 \text{ fs}, \omega = 2.0 \text{ eV}, F \approx 10 \text{ mJ/cm}^2$$

Selective excitation of totally symmetric modes

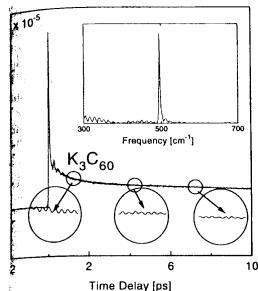
High intensity excitation

Theoretical spectral density



$$t_p = 12 \text{ fs}, \omega = 2.0 \text{ eV}, F = 19 \text{ mJ/cm}^2$$

Differential reflectivity of K_3C_{60} film



$$t_p = 10 \text{ fs}, \omega = 1.85 \text{ eV}, F \approx 10 \text{ mJ/cm}^2$$

■ Fleischer et al. APL 17 2734 (1997)

Selective excitation of the breathing mode

Summary TD-DFTB

Chances and challenges . . .

- Reproduces accuracy and trends of TDDFT
- Problems with triplet and Rydberg states
- Favourable scaling, low prefactor
- Allows for detailed investigation of PES

Thanks ∞

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Marius Wanko



Alessio Gagliardi



Chensheng Lin



Yong Wang