

BENASQUE Workshop TDDFT: Prospects and Applications Sept 10-15, 2008

Real-time TDDFT for *linear* and *nonlinear* optical response

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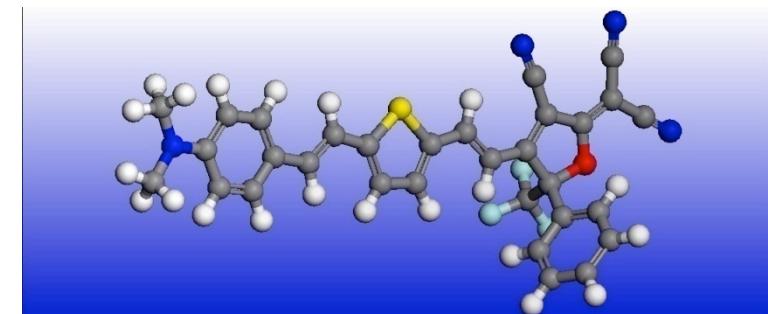
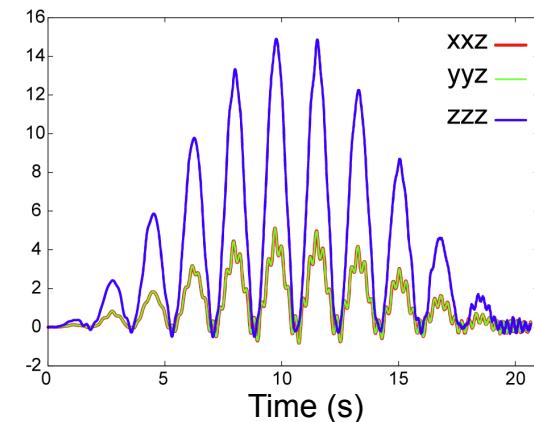
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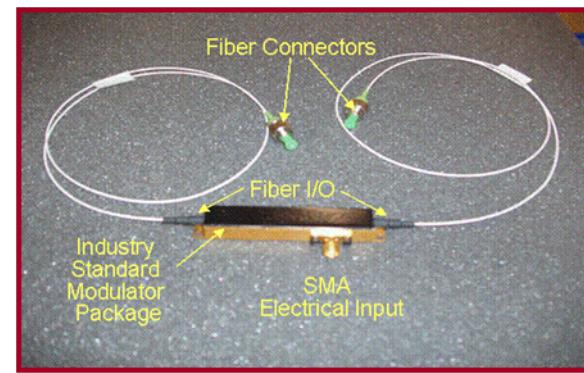
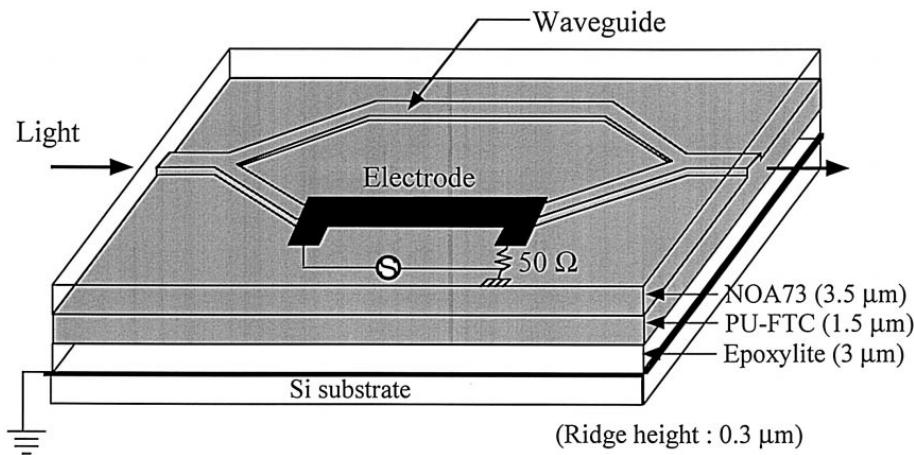
*Ph.D. Thesis 2008



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WASHINGTON



Motivation: Polymeric Electro-optic devices for integrated photonics



The electro-optic coefficient

(the change of the refractive index induced by applying an electric voltage)

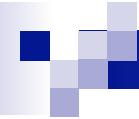
$$r_{33} = 2N\beta_{zzz}(-\omega; 0, \omega)\langle \cos^3 \theta \rangle \frac{g(\omega)}{n(\omega)^4}$$

NOTE: The best EO coefficient of organic polymer is about 450 pm/V, more than 15x higher than the best inorganic materials!

Acknowledgments

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Outline

- Objectives
- Approach: Real-time Time-dependent Density Functional Theory (RT-TDDFT)
- Results: *small* and **LARGE** molecules
- X-ray Spectra: real-time real-space methods
- Conclusions

Objective and Motivation

- Applications to *Organic-based photonics*
- Need: **non-linear** optical response in large organic molecular systems
- Difficulty: frequency-space is computationally difficult - **too-many** excited states
- Strategy: extend linear RT-TDDFT/ **SIESTA** approach [Sanchez-Portal, Tsolakidis, and Martin, Phys. Rev. B**66**, 235416 (2002)]
5

Reference: Real space, real time linear and non-linear optical response*

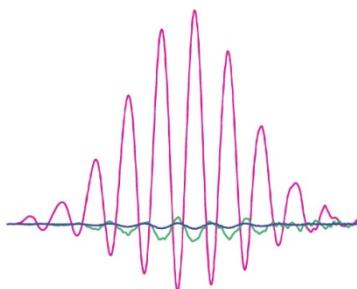
THE JOURNAL OF CHEMICAL PHYSICS 127, 154114 (2007)

Real-time time-dependent density functional theory approach for frequency-dependent nonlinear optical response in photonic molecules

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We present *ab initio* calculations of frequency-dependent linear and nonlinear optical responses based on real-time time-dependent density functional theory for arbitrary photonic molecules. This approach is based on an extension of an approach previously implemented for a linear response using the electronic structure program SIESTA. Instead of calculating excited quantum states, which can be a bottleneck in frequency-space calculations, the response of large molecular systems to time-varying electric fields is calculated in real time. This method is based on the finite field approach generalized to the dynamic case. To speed the nonlinear calculations, our approach uses Gaussian enveloped quasimonochromatic external fields. We thereby obtain the frequency-dependent second harmonic generation $\beta(-2\omega; \omega, \omega)$, the dc nonlinear rectification $\beta(0; -\omega, \omega)$, and the electro-optic effect $\beta(-\omega; \omega, 0)$. The method is applied to nanoscale photonic nonlinear optical molecules, including *p*-nitroaniline and the FTC chromophore, i.e., 2-[3-Cyano-4-(2-{5-[2-(4-diethylamino-phenyl)-vinyl]-thiophen-2-yl}-vinyl)-5,5-dimethyl-5H-furan-2-ylidene]-malononitrile, and yields results in good agreement with experiment. © 2007 American Institute of Physics.

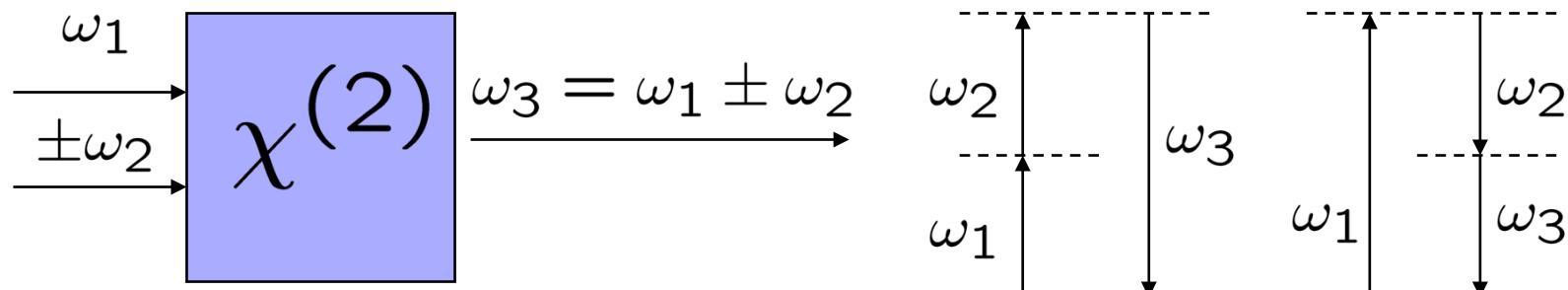
[DOI: [10.1063/1.2790014](https://doi.org/10.1063/1.2790014)]

Also: Y. Takimoto, Ph.D. Thesis, U. Washington 2008 (unpublished)

Nonlinear Polarizabilities

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + \dots$$

■ Second order nonlinearities



$\chi^{(2)}(-2\omega; \omega, \omega)$ Second Harmonic Generation (SHG)

$\chi^{(2)}(0; -\omega; \omega)$ Optical Rectification (OR)

$\chi^{(2)}(-\omega; 0; \omega)$ Electro-Optic effect (Pockel's effect)

Real time TDDFT

- Yabana and Bertsch Phys. Rev. B54, 4484 (1996)

$$i\frac{\partial \Psi}{\partial t} = H(t) \Psi \quad H = -\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}, t) + V_H[\rho](\mathbf{r}, t) + V_{xc}[\rho](\mathbf{r}, t)$$

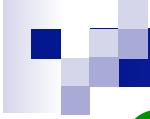
- Direct numerical integration of TD Kohn-Sham equations

$$\Psi(t) = T \exp \left(-i \int_0^t H(t') dt' \right) \Psi(0)$$

- The response to external field is determined by applying a **time-dependent electric field** $\Delta H(t) = -\mathbf{E}(t) \cdot \mathbf{x}$.
- Optical properties are determined from the **total dipole moment**:

$$\mathbf{p}(t) = \int \rho(\mathbf{r}, t) \mathbf{r} d^3\mathbf{r}$$

MORE EFFICIENT THAN EIGENSTATE METHODS !



Calculation of $\Psi(t)$ at each time step based on: SIESTA*

- Self-consistent DFT Ground State Code with LDA or GGA exchange/correlation
 - ***Ab-initio***
- LCAO and confined basis functions using pseudo potential
 - **Scalable**
- Projects the electron wavefunctions and density onto a real-space grid
 - **Flexible**
- Multiple zeta basis definition
 - **Accurate**

*Spanish Initiative for Electronic Simulations with Thousands of Atoms

Numerical Real time Evolution

- Ground state density ρ_0 , **overlap matrix S** , and $H(t)$ at each time-step evaluated with **SIESTA**

$$i\frac{\partial c(t)}{\partial t} = S^{-1}H(t)c(t) \quad \leftarrow \text{Coefficients of Orbitals}$$

- Crank-Nicholson time-evolution: **accurate, stable**

$$c(t + \Delta t) = \frac{1 - iS^{-1}H(t)\Delta t/2}{1 + iS^{-1}H(t)\Delta t/2}c(t) + \mathcal{O}(\Delta t^2)$$

- Adiabatic GGA exchange-correlation (PBE) functional used for **all** of our calculations

Review: Real time Linear Response

■ Well known relations...

$$\delta \mathbf{p}(t) = \mathbf{p}(t) - \vec{\mu}_0 \quad \text{Induced Dipole Moment}$$

$$\delta p_i(t) = \int dt' \chi_{ij}^{(1)}(t-t') E_j(t')$$

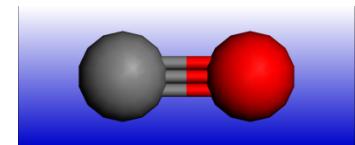
$$\chi_{ij}^{(1)}(\omega) = \delta p_i(\omega)/E_j(\omega) = \alpha_{ij}(\omega) \quad \text{Linear Response Function}$$

$$\epsilon_{ij}(\omega) = 1 + 4\pi N \alpha_{ij}(\omega) \quad \text{Linear Dielectric Function}$$

$$\sigma(\omega) \sim \omega \langle \alpha(\omega) \rangle / E(\omega) \quad \text{Optical Absorption}$$

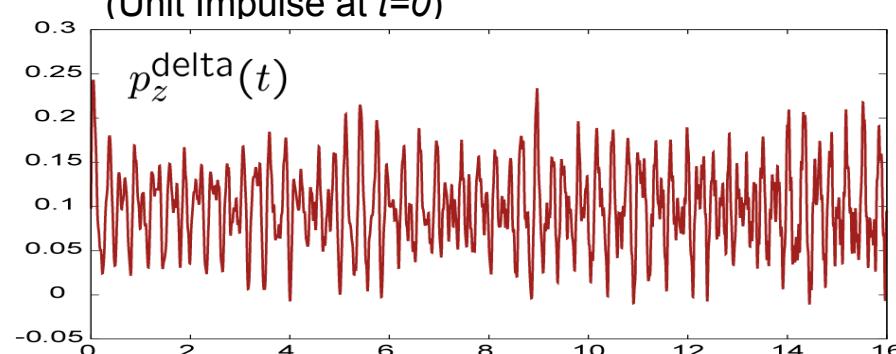
Example: Linear Response

Carbon Monoxide (CO), $p_z(t)$ response due to applied $E_z(t)$



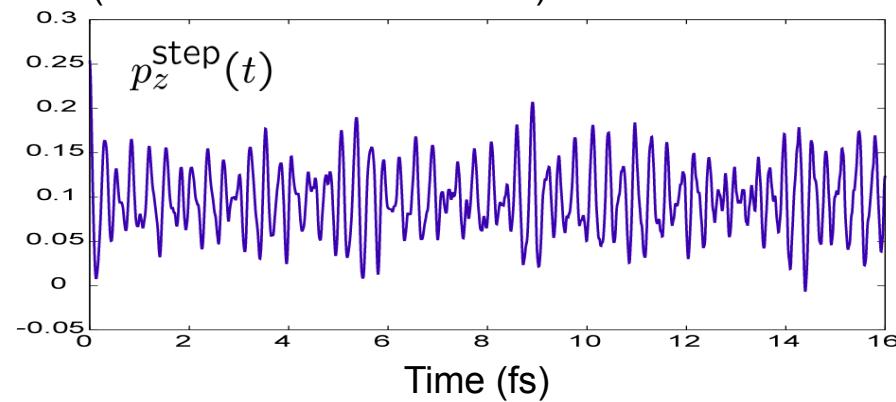
■ Delta Function

(Unit Impulse at $t=0$)

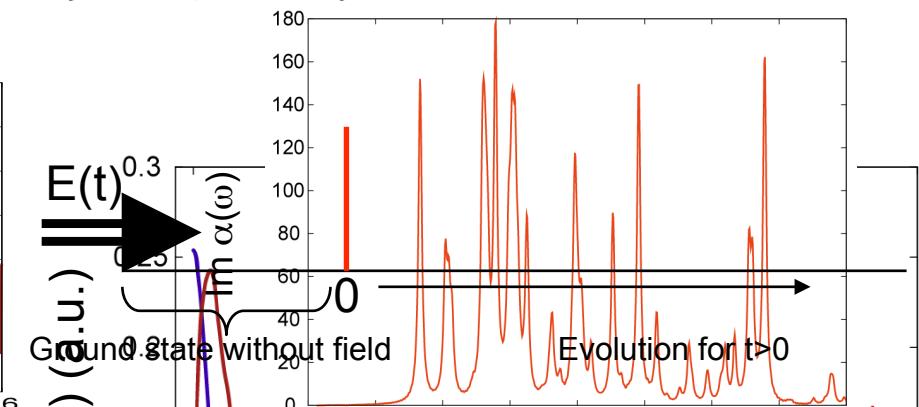


■ Step Function

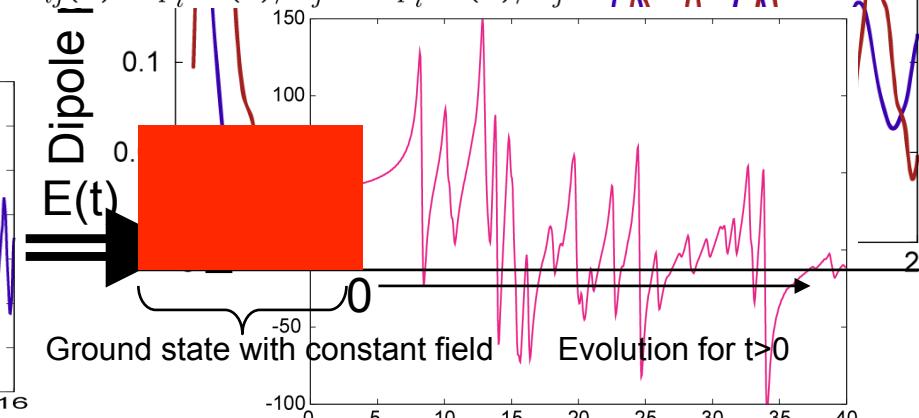
(Turn-off Constant E at $t=0$)



$$\alpha_{ij}(\omega) = p_i^{\text{delta}}(\omega)/E_j$$

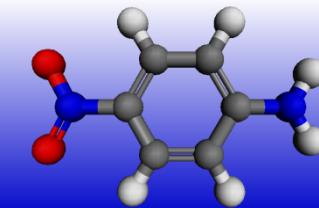


$$\alpha_{ij}(\omega) = p_i^{\text{step}}(0)/E_j - i\omega p_i^{\text{step}}(\omega)/E_j$$



Example: Small molecules

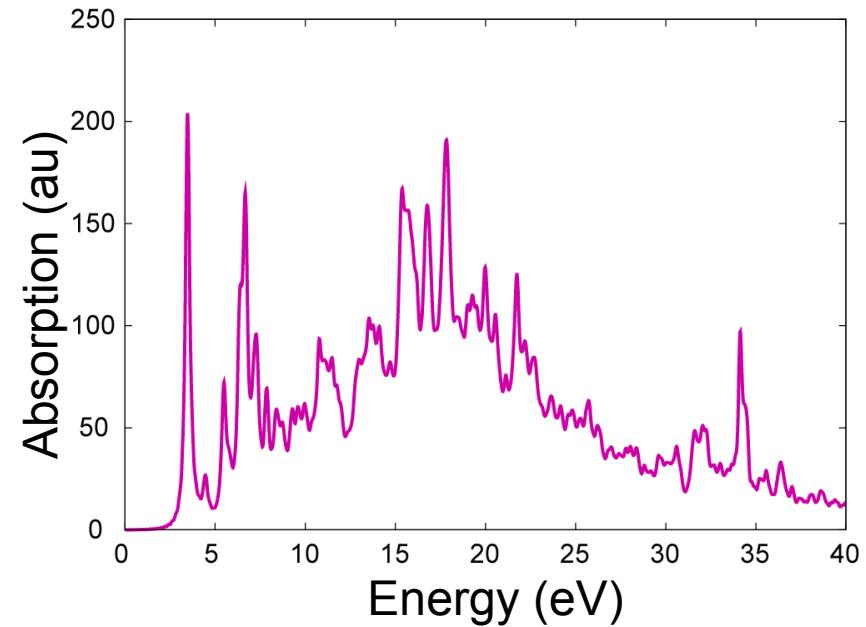
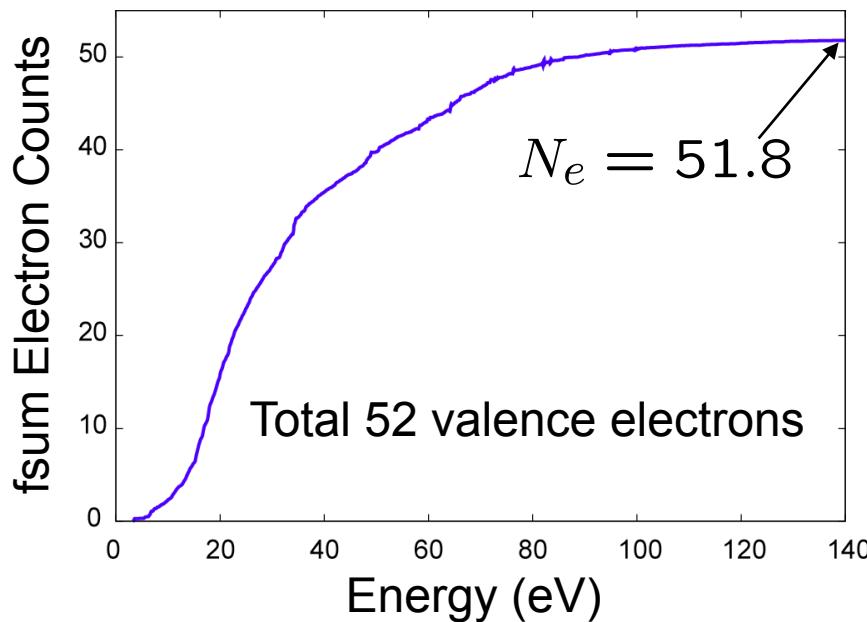
p-Nitroaniline (pNA)



■ Linear absorption

$$\lambda_0 = 356\text{nm} \quad \lambda_0^{\text{exp.}} = 347\text{nm}$$
$$\omega_0 = 3.49 \text{ eV} \quad (\text{in chloroform})$$

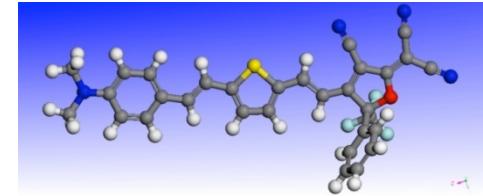
■ Sum rule



$$\begin{aligned} \int_0^\infty d\omega S(\omega) &= \lim_{\omega \rightarrow \infty} f_{\text{sum}}(\omega) \\ &= \sum_i f_i = N_e, \end{aligned}$$

Large Photonic molecules

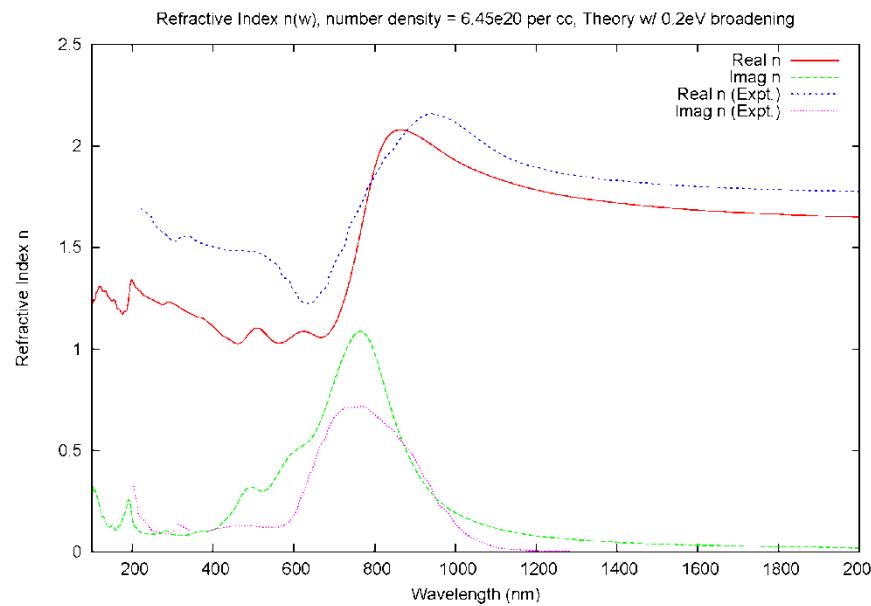
YLD156



Linear response, yields linear absorption spectra $\sigma(\omega)$ or the polarizability $\alpha(\omega)$, which is related to the refractive index through the Lorentz-Lorentz relation

$$\frac{4\pi}{3} N \alpha(\omega) = \frac{n^2(\omega) - 1}{n^2(\omega) + 2}$$

The figure below is the calculation of refractive index $n(\omega)$ from the linear polarizability calculation of RT-TDDFT for the YLD156 chromophore developed by the Dalton group (UW).



Real time Nonlinear Response

- The nonlinear expansion in field strength

$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots$$

- Accounting for time lag in system response

$$\begin{aligned} p_i(t) = & \mu_i^0 + \int dt_1 \chi_{ij}^{(1)}(t - t_1) E_j(t_1) \\ & + \int dt_1 \int dt_2 \chi_{ijk}^{(2)}(t - t_1, t - t_2) E_j(t_1) E_k(t_2) \\ & + \int dt_1 \int dt_2 \int dt_3 \chi_{ijkl}^{(3)}(t - t_1, t - t_2, t - t_3) E_j(t_1) E_k(t_2) E_l(t_3) \\ & + \dots \end{aligned}$$

¿ How can we invert the equation to get nonlinear response function?

Extraction of **Static** Nonlinear Polarizabilities

- Usual technique: fits to static expansion

$$p_i = \mu_i^0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots$$

Either finite-difference or fitting $p_i(E)$ to a polynomial

Example:

$$\beta_{ijj} = [-p_i(-2E_j) + 16p_i(-E_j) - 30p_i(0) + 16p_i(E_j) - p_i(2E_j)]/24E_j^2$$

Extraction of Dynamic Nonlinear Polarizabilities

- Set $E_j(t) = F(t)E_j$, and define expansion $p_i(E)$

$$p_i(t) = \mu_i^0 + p_{ij}^{(1)}(t)E_j + p_{ijk}^{(2)}(t)E_jE_k + \dots$$

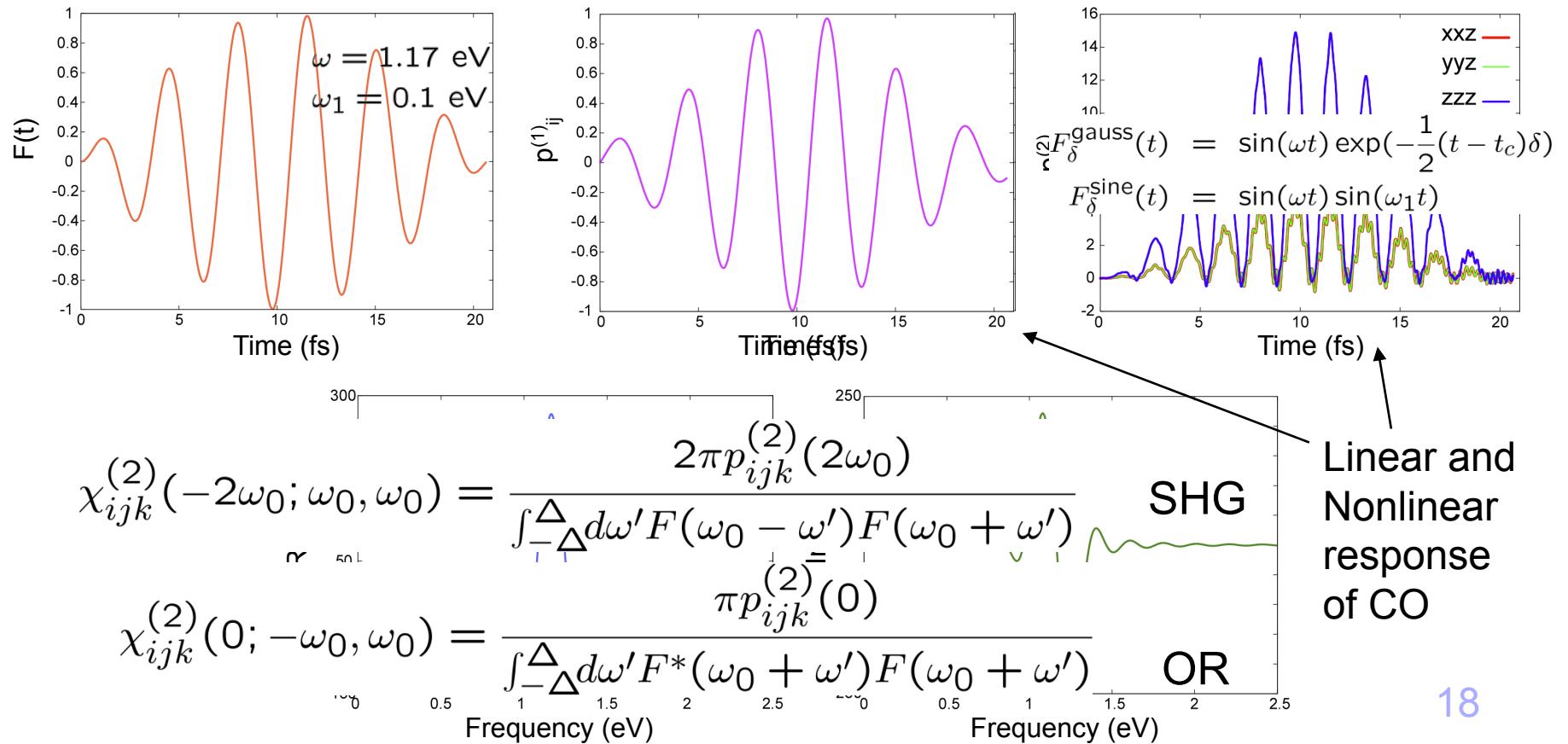
where $p^{(1)}$ yields linear response, $p^{(2)}$ first non-linear quadratic response,

- The quadratic response $\chi^{(2)}$ is then given by

$$p_{ijk}^{(2)}(t) = \int dt_1 \int dt_2 \chi_{ijk}^{(2)}(t - t_1, t - t_2) F(t_1) F(t_2)$$

Dynamic Nonlinear Response with Quasi-monochromatic Field $F_\delta(t)$

- Sine wave enveloped by another sine wave or Gaussian



Real time vs Frequency space Nonlinear Response

■ Operation cost

- Sternheimer equation (frequency space)

$$\mathcal{O}(N_{KS}^2 N_{\text{basis}} M_{\text{iterations}} M_{\omega})$$

- Real time

$$\mathcal{O}(N_{KS} N_{\text{basis}} N_{\text{evolve}} M_{\text{steps}} M_{\omega})$$

■ Memory cost

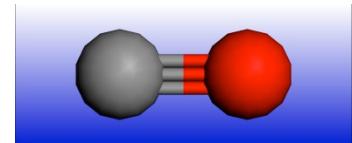
- Sternheimer equation (frequency space)

$$\mathcal{O}((N_{\text{occ}} + N_{\text{unocc}}) N_{\text{basis}})$$

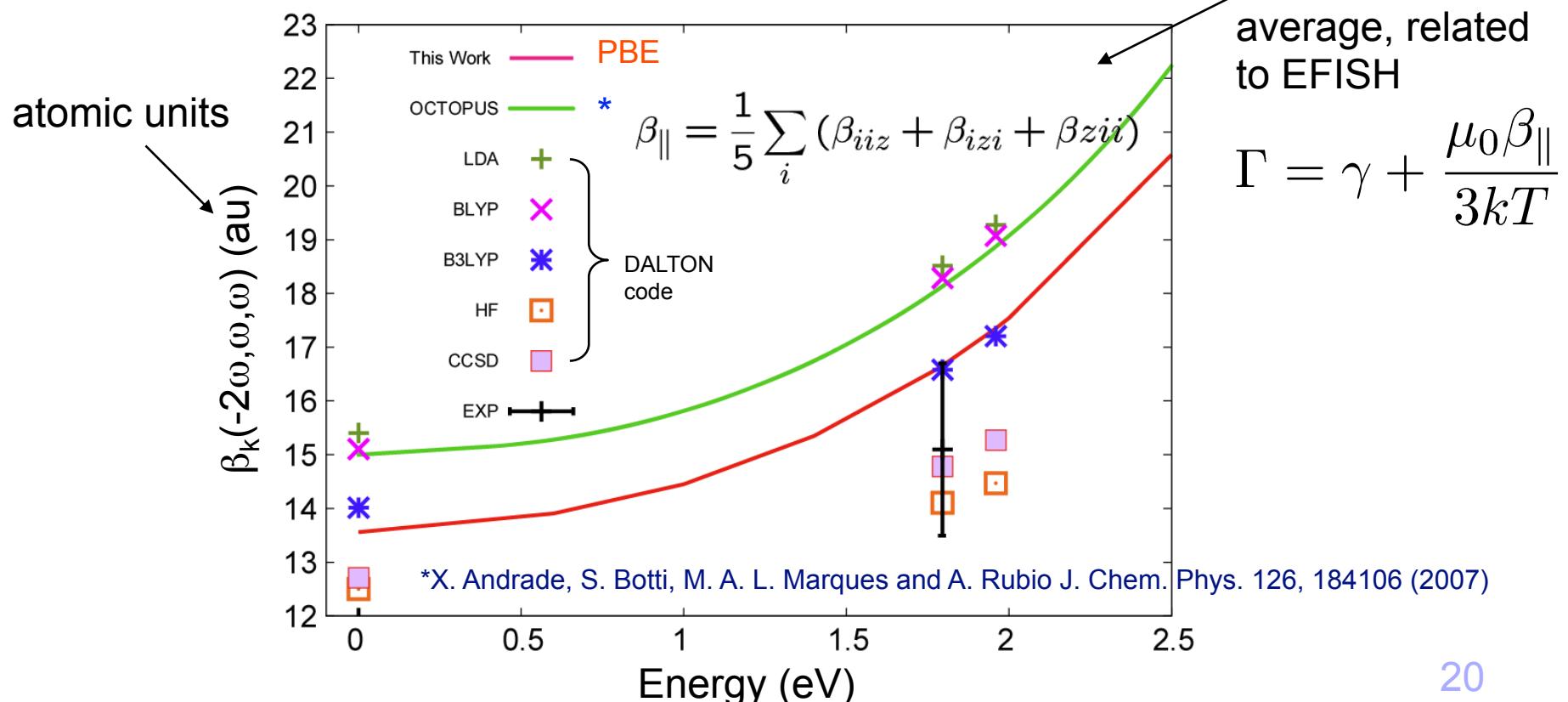
- Real time

$$\mathcal{O}(N_{\text{occ}} N_{\text{basis}})$$

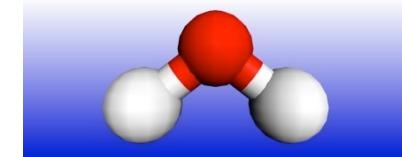
Example: CO: Nonlinear Second Harmonic Generation (SHG)



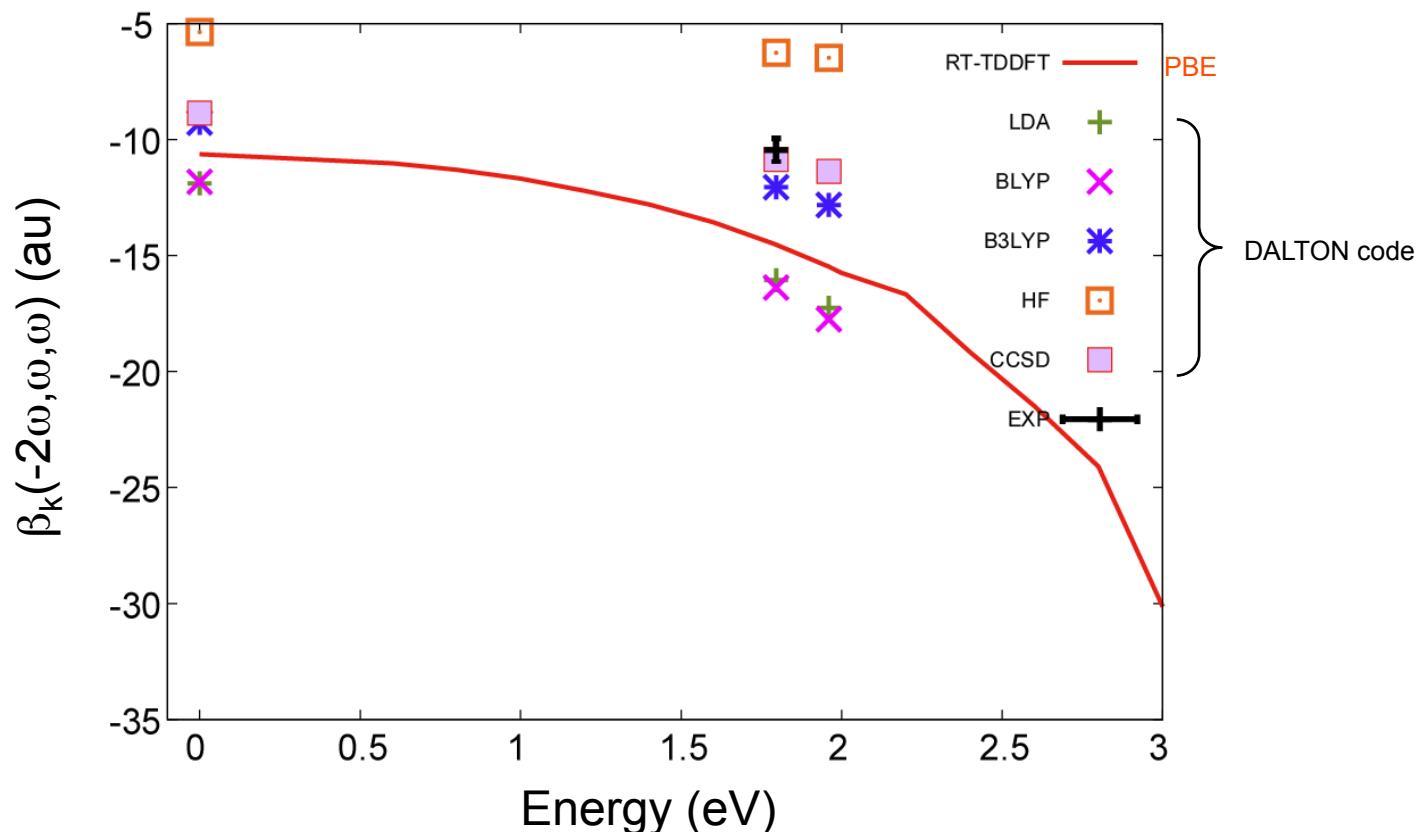
■ Comparison with other methods



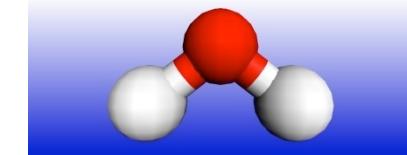
H_2O : Nonlinear Second Harmonic Generation (SHG)



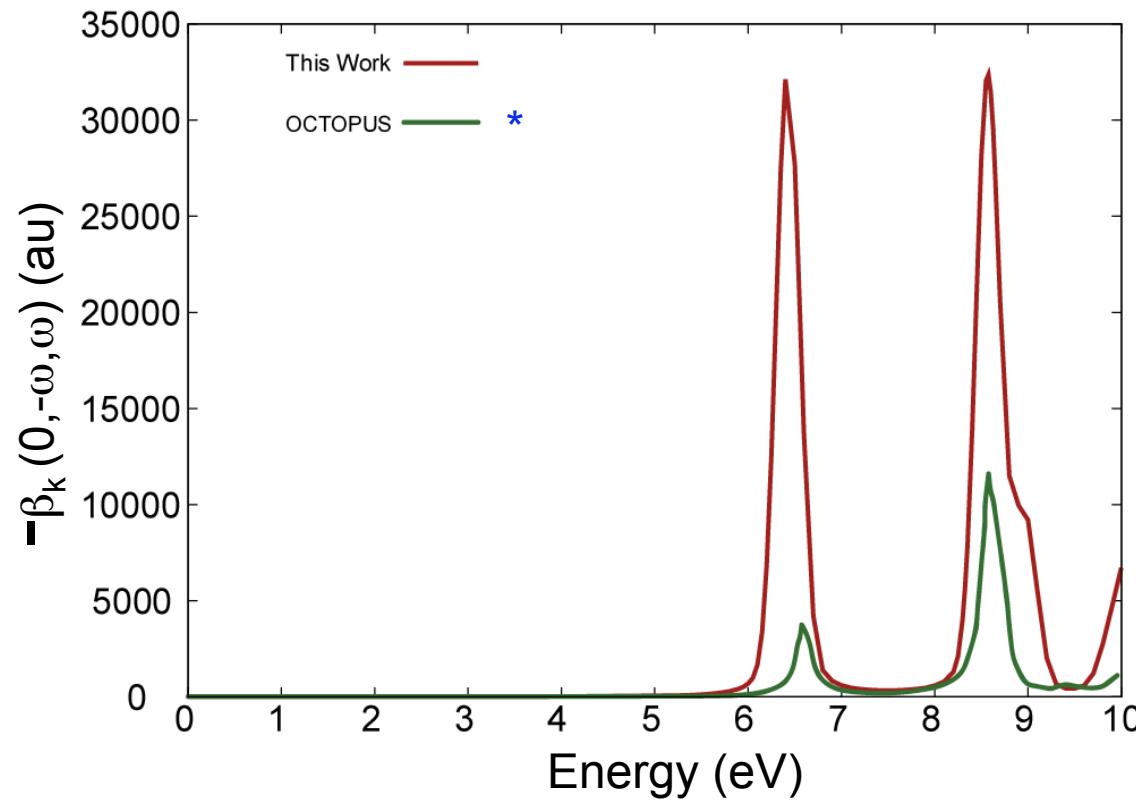
■ Comparison with other methods



H_2O : Nonlinear Optical Rectification (OR)

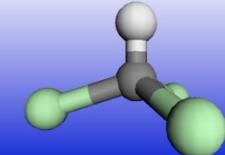


■ Resonant Frequencies



*X. Andrade, S. Botti, M. A. L. Marques and A. Rubio J. Chem. Phys. 126, 184106 (2007)

Chloroform (CHCl_3)

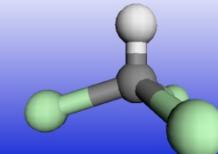


■ Static calculation comparison

	Gaussian03					
	This Work	PBE	B3LYP	HF	MP2	CCSD
μ_z	0.40	0.43	0.48	0.43	0.43	
α	60.15	58.52	54.50	57.35	56.90	
β_{xxy}	-12.19	-10.87	-6.60	-6.86	-7.70	
β_{xxz}	-6.40	-5.58	-3.22	-4.02	-4.33	
β_{zzz}	11.35	10.04	6.78	8.64	8.83	
β_k	-0.88	-0.68	0.21	0.36	+0.10	0.50 +/- 2. (EXPT.)



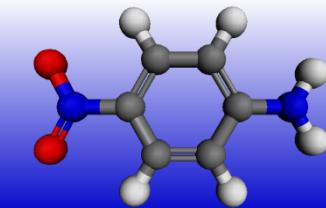
CHCl₃: Effect of basis



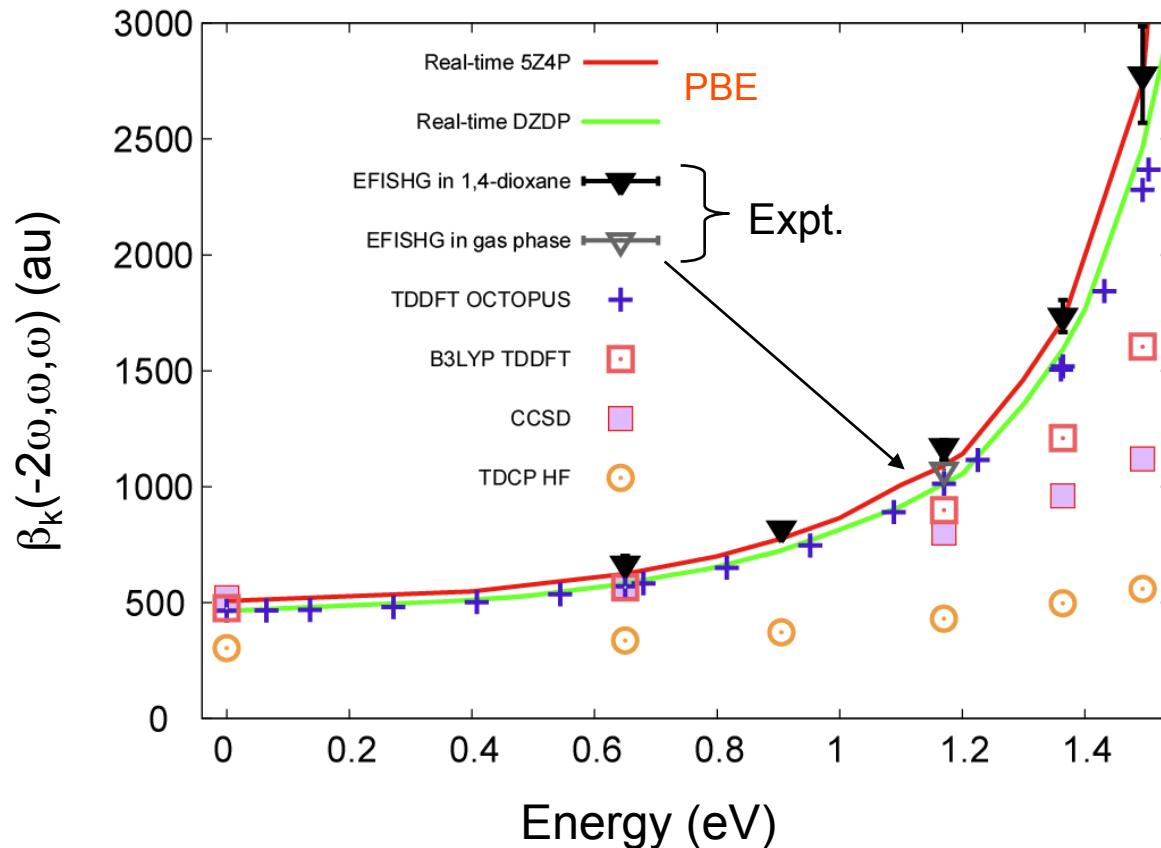
- *Nonlinear* calculation require “large” basis (especially for a small molecules)

	DZP (default)	5Z4P	5Z4P	5Z4P	5Z4P
r_s(C)	4.09	6.91	8.03	10.57	11.11
r_s(H)	4.71	8.80	10.48	13.80	14.88
r_s(Cl)	3.83	6.15	7.15	8.95	9.41
Linear					
<i>Nonlinear</i>					
μ_z	0.26	0.41	0.40	0.40	0.40
α	44.39	60.18	60.39	60.15	60.09
β_{xxy}	-7.62	-9.44	-11.67	-12.19	-12.18
β_{xxz}	-2.83	-4.97	-6.23	-6.40	-6.40
β_{zzz}	-16.40	3.98	9.39	11.35	11.28
β_k	-13.28	-3.59	-1.86	-0.88	-0.90

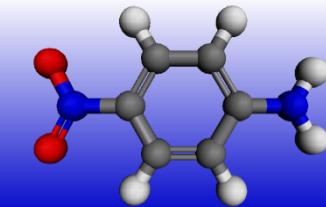
*p*NA: Nonlinear (SHG)



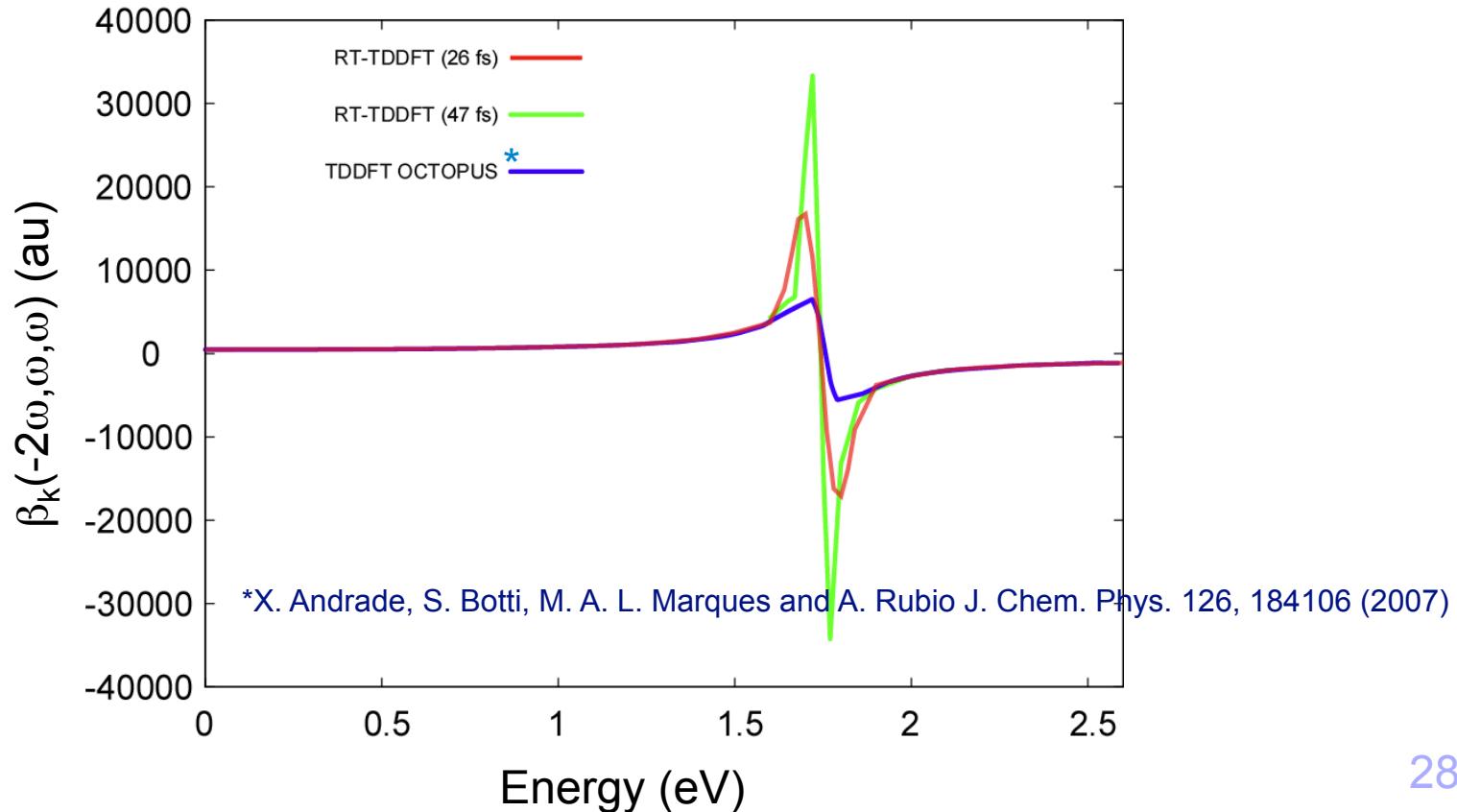
■ Comparison with other methods

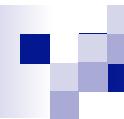


*p*NA: Nonlinear (SHG)



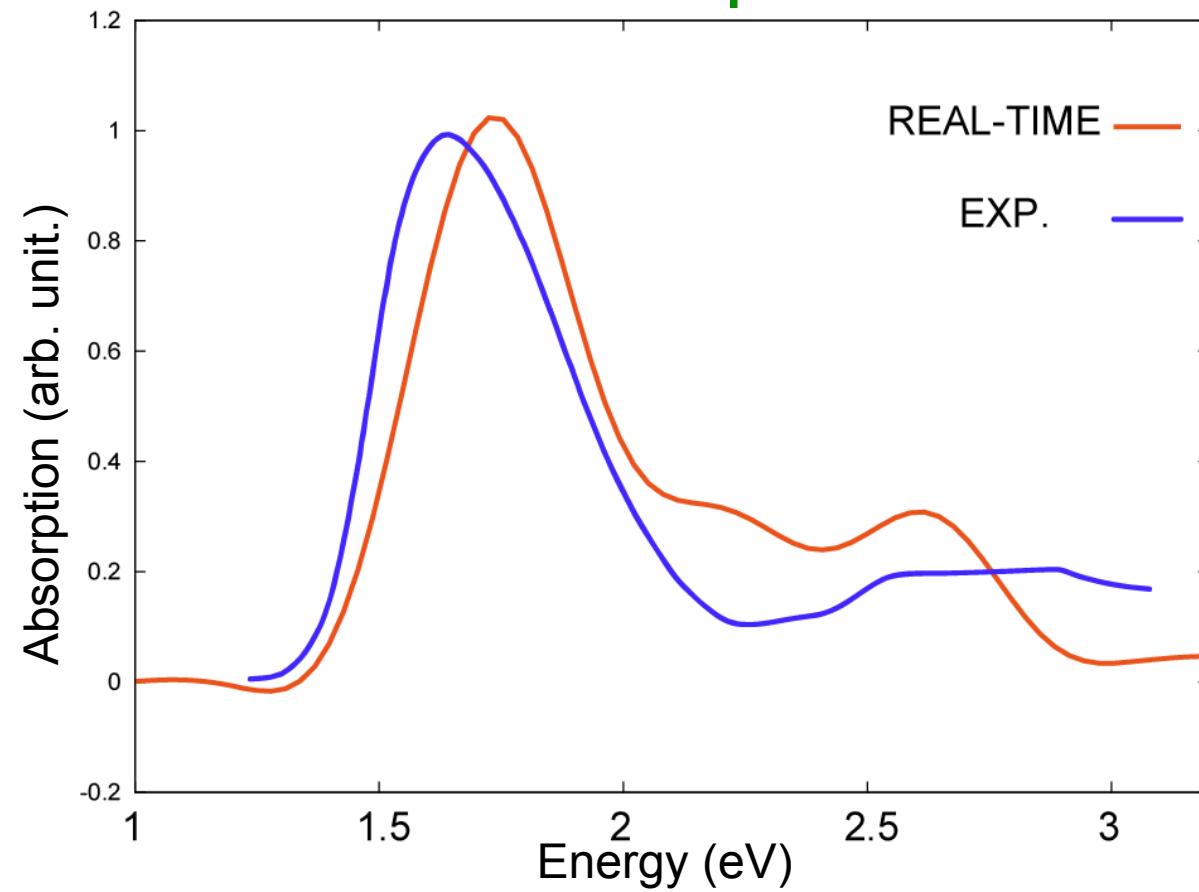
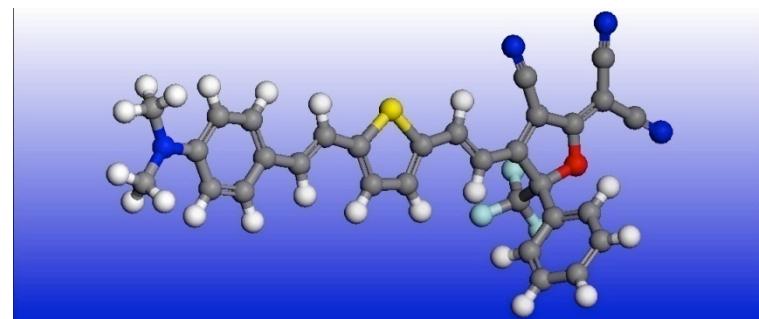
■ Resonant frequency





NLO Molecule

■ YLD156 chromophore

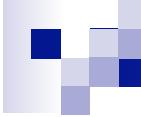


Real-time Absorption
peak of YLD_156 (GAS)

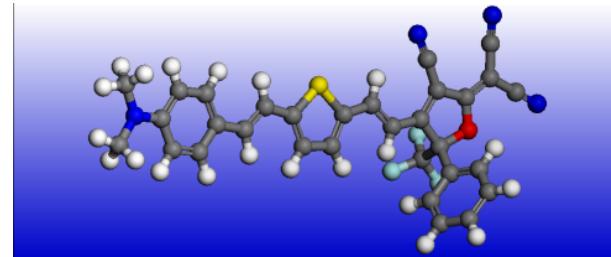
$$\omega_0 = 1.72 \text{ eV}$$
$$(\lambda_0 = 721\text{nm})$$

Experimental Absorption
peak of YLD_156 in
Chloroform solution

$$\omega_0 = 1.65 \text{ eV}$$
$$(\lambda_0 = 753\text{nm})$$

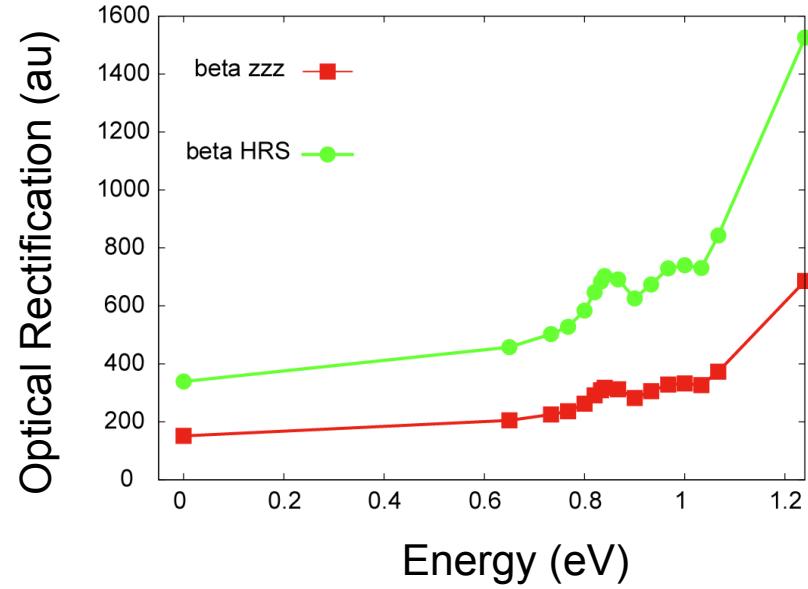


YLD156

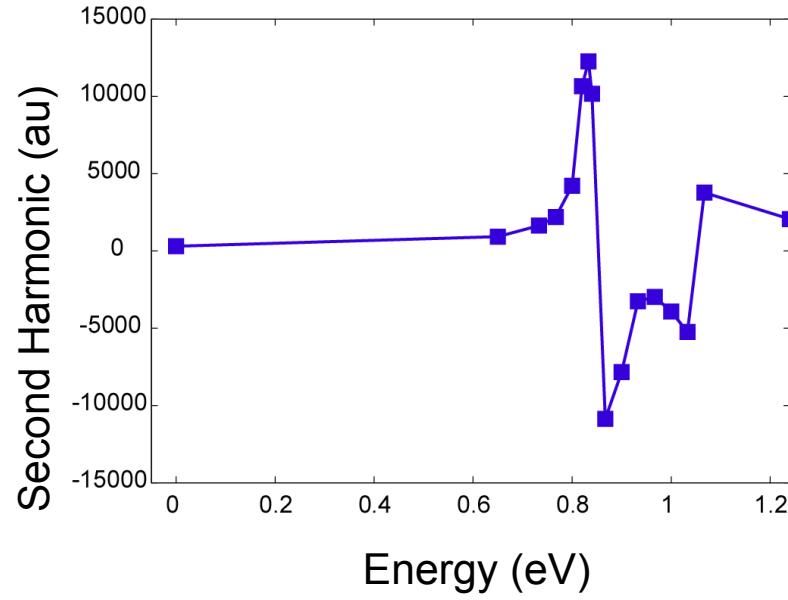


■ Nonlinear results

$\beta_{\parallel}(0; -\omega; \omega)$ OR



$\beta_{\parallel}(-2\omega; \omega, \omega)$ SHG



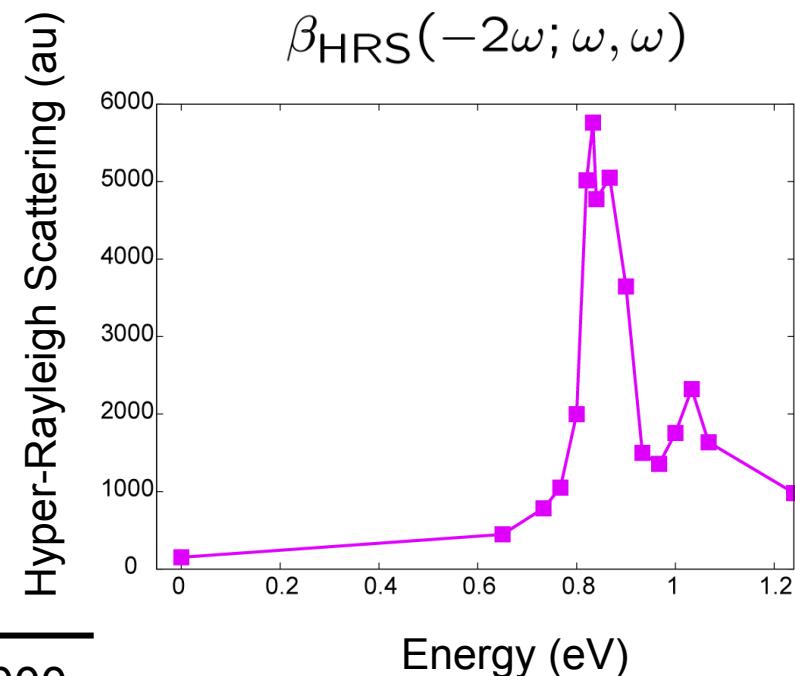
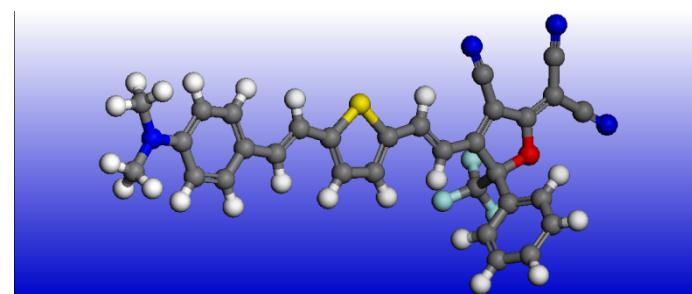
YLD_156

Hyper-Rayleigh Scattering (HRS) Experiment ($\langle \beta^2 \rangle$)

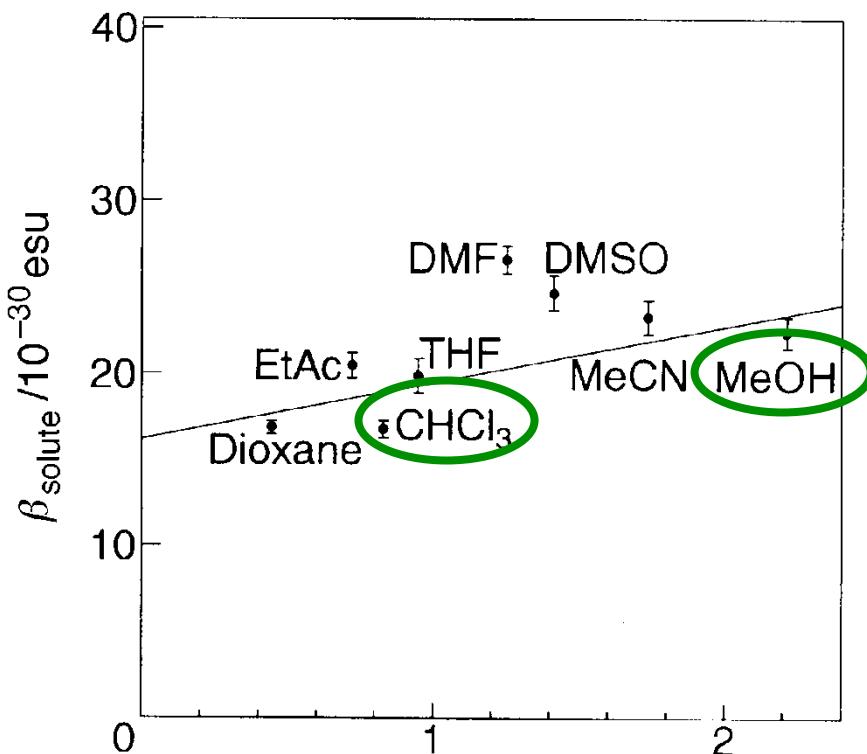
- HRS measurement
(in solution)

Absolute value (calc.)	YLD156	CHCl_3
0.65 eV ($\lambda = 1.9 \mu\text{m}$)	446	0.0866
1.24 eV ($\lambda = 1.0 \mu\text{m}$)	980	0.0962

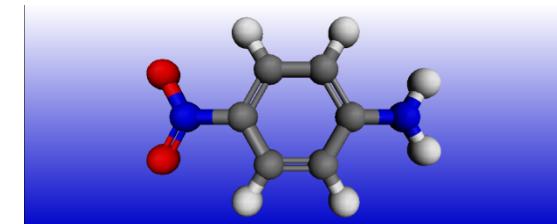
Relative value	This Work	Expt.
0.65 eV ($\lambda = 1.9 \mu\text{m}$)	5150	6100 ± 2000
1.24 eV ($\lambda = 1.0 \mu\text{m}$)	10190	7940 ± 500



Solvent Effects – HRS Experiment



$$\frac{8\pi\rho N_A(\epsilon - 1)(n^2 + 2)}{3M_w(2\epsilon + n^2)} / 10^{23} \text{ esu}$$



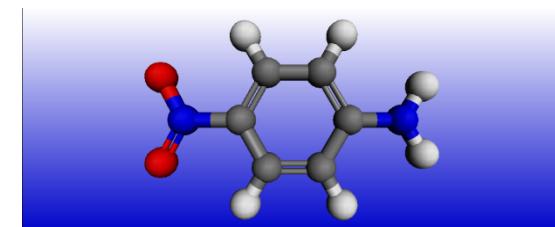
solvent	$\beta_{\text{solute}} / 10^{-30} \text{ esu}$	$\lambda_{\text{max}} / \text{nm}$
chloroform	16.80 ± 0.50	347
p-dioxane *	16.90 ± 0.40	352
tetrahydrofuran (THF)	19.90 ± 1.00	363
ethyl acetate (EtAc)	20.50 ± 0.70	356
acetonitrile (MeCN)	23.30 ± 1.00	364
methanol (MeOH)	22.40 ± 0.90	356
dimethyl sulfoxide (DMSO)	24.70 ± 1.00	388
N,N-dimethylformamide (DMF)	26.60 ± 0.80	381

* Reference value for HRS, measured by EFISH

T. Kodaira and *et al.*, J. Chem. Soc., Faraday Trans., 1997, Vol. 93



“Local” Solvent Effect

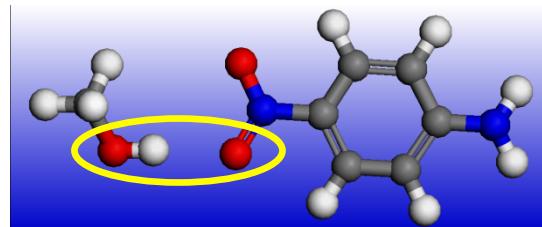


β_{HRS} 798.6 (au)

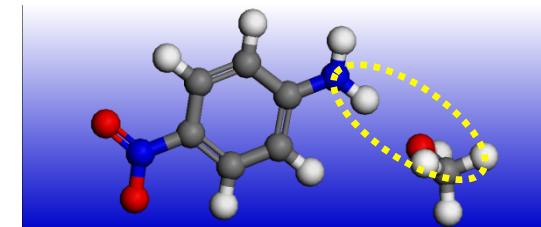
- Study of local contact with methanol (polar) or chloroform (non-polar)

← “Adjusted” Expt. Values.

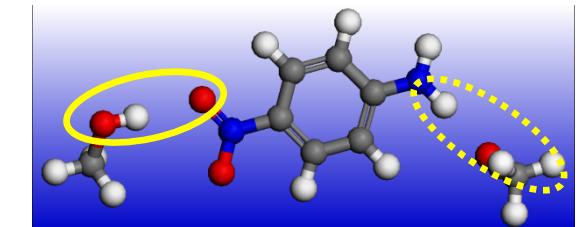
1900 ± 100



β_{HRS} 1556 (21.3)

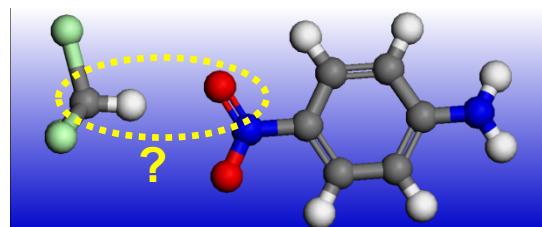


869.3 (19.9)

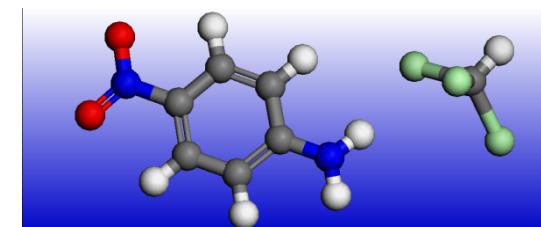


1812 (31.4)

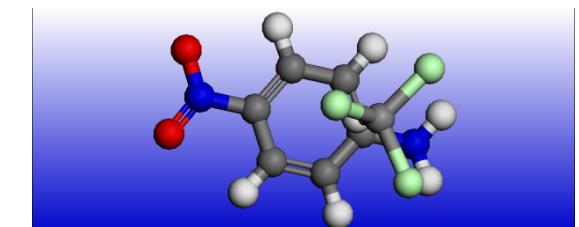
1400 ± 40



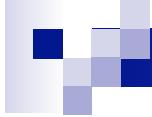
β_{HRS} 1081 (10.8)



797.5 (8.79)



746.1 (6.36) 33/35



RT-TDDFT Code* (Y. Takimoto, PhD Thesis 2008)

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Appendix B REAL TIME TDDFT PROGRAM MANUAL

B.1 Quick Start Guide

Real time TDDFT consists of following sets of files and you will find directories after unpacking the source distribution:

```
rt-tddft/examples
rt-tddft/patch
rt-tddft/utils
```

Script for pre-process and post-process:

```
utils/prepsti : TDDFT preparation script (Perl script)
utils/hypfits : TDDFT post process script (Octave script)
```

The directory 'patch' contains the patch 'diff' file tddft-current.diff to modify the original SIESTA source code for version 2.0.1.

Optional scripts to help running a set of jobs:

```
utils/submit.jobs : Script for running multiple jobs (require to edit)
utils/submit to queue : Used in together with the script above
```

The other utility scripts may be used for analysis that will be explained later.

B.1.1 Compilation

Create a working directory and untar SIESTA source code siesta-2.0.1.tgz.

```
$ tar zxf siesta-2.0.1.tgz
```

Unpack the Real time TDDFT distribution rt-tddft****.tar.gz where '****' is the version control number.

```
$ tar zxf rt-tddft****.tar.gz
```

*If interested, please contact ytakimot@u.washington.edu or jjr@phys.washington.edu

Conclusions

- Efficient RT-TDDFT approach for frequency dependent nonlinear optical response – extension of RT-SIESTA
- Accuracy comparable to frequency-domain methods for small systems
- Efficient on large systems (HPC ready)
- Can treat solvent effects etc.

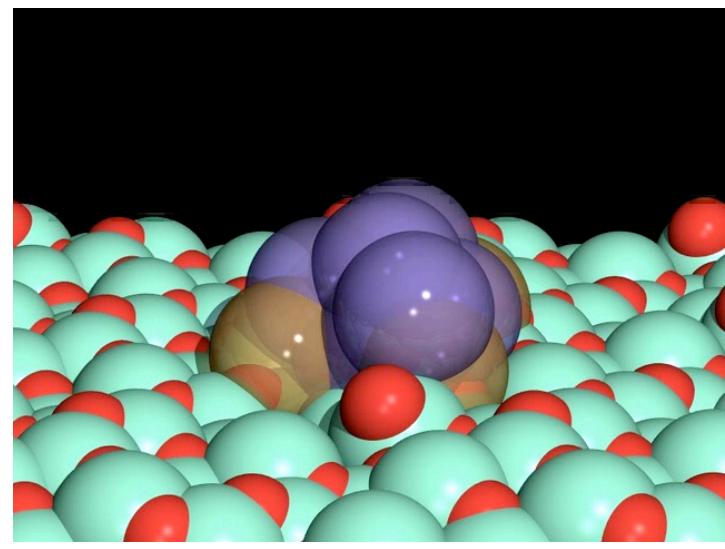
Part II: X-ray Spectra – DFT/MD - Dynamic Structure in Supported Pt nanoclusters*

MYSTERY: Unusual thermal properties of Pt_{10} / $\gamma\text{-Al}_2\text{O}_3$

NTE, disorder, redshift in XAS

Approach: Real-time DFT/MD

Pt_{10} Cluster on [110] $\gamma\text{-Al}_2\text{O}_3$



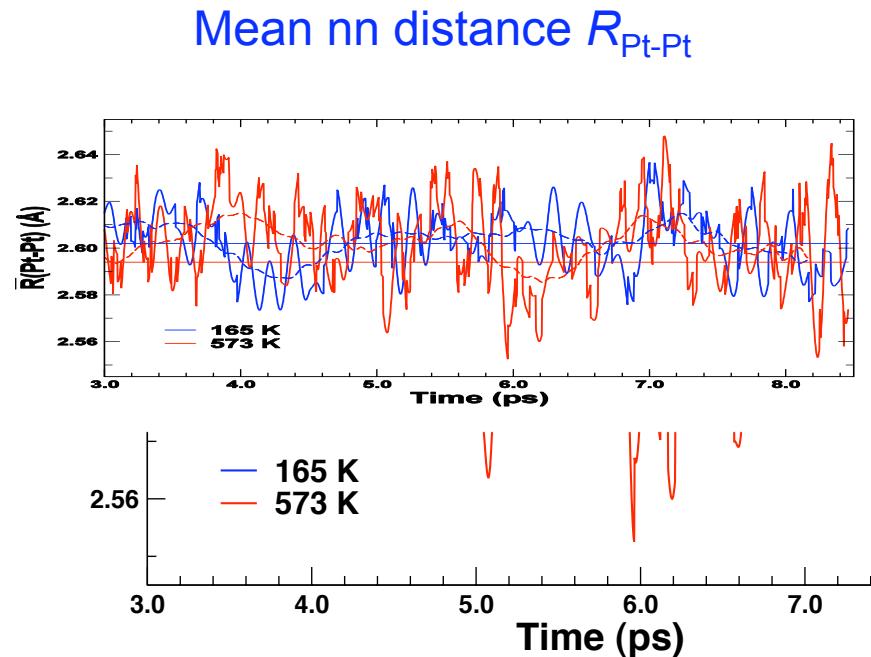
metallic Pt
Al

oxidized Pt
O

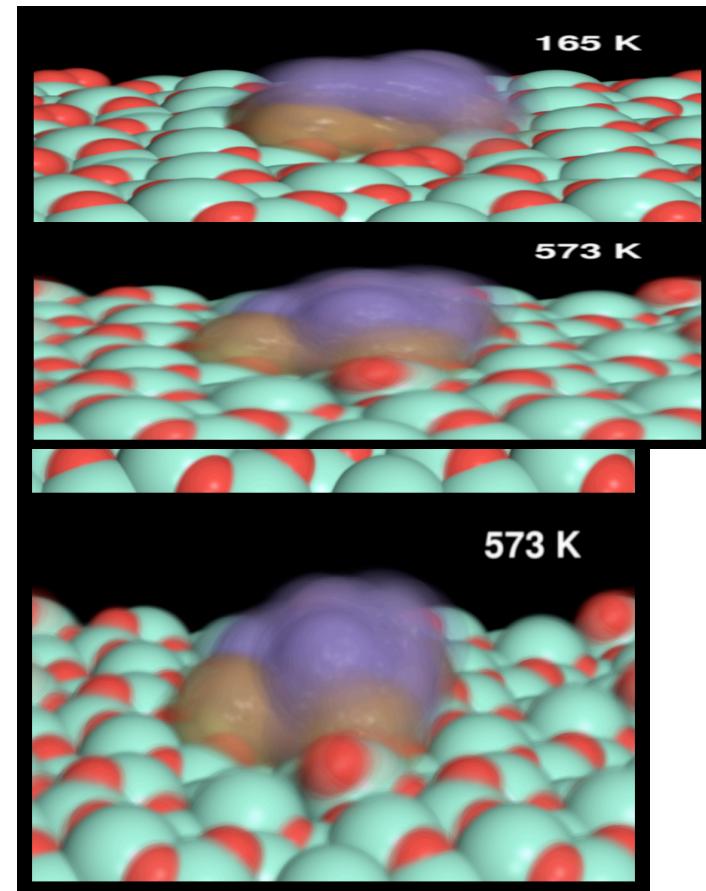
*F. Vila, J. Rehr, A. Frenkel, R. Nuzzo, J. Kas, Phys Rev. B in press (2008)

Calculation - VASP + 10^4 cpu-hrs

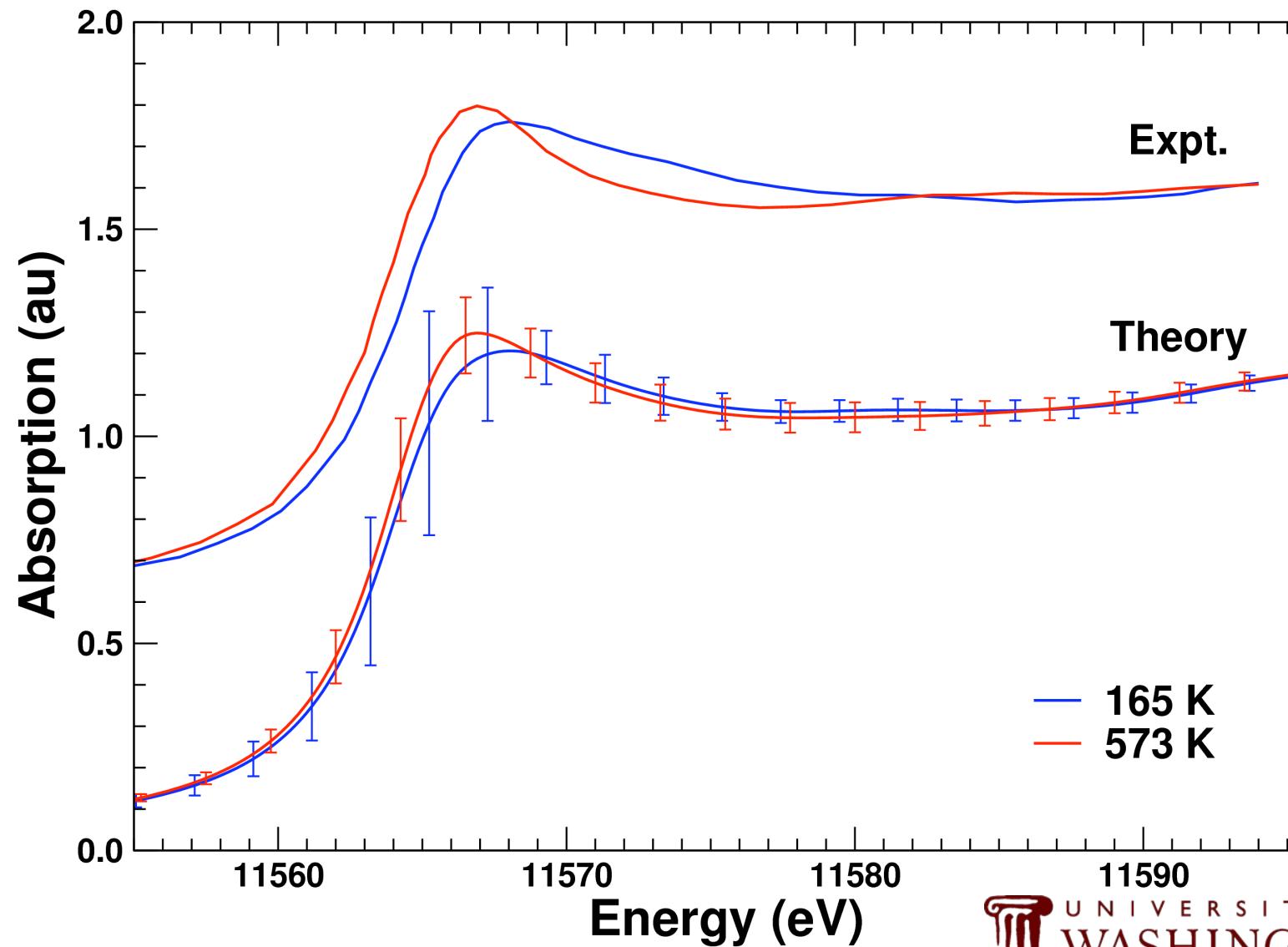
Calculation 10 atom Pt/ $\gamma\text{-Al}_2\text{O}_3$



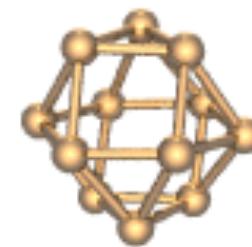
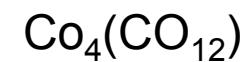
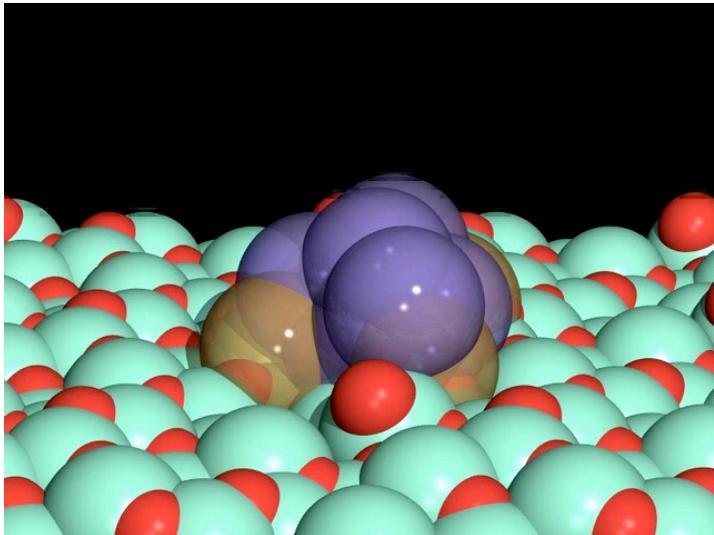
2500 3 fs steps



time-elapsed rendering



Librational motion



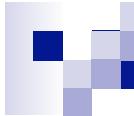
Fluxional behavior in tetrahedral clusters with carbonyl ligands

Y Roberts, BFG Johnson, RE Benfield,
Inorg. Chim. Acta 1995

Librational motion: long time-scale fluctuations of the center of mass

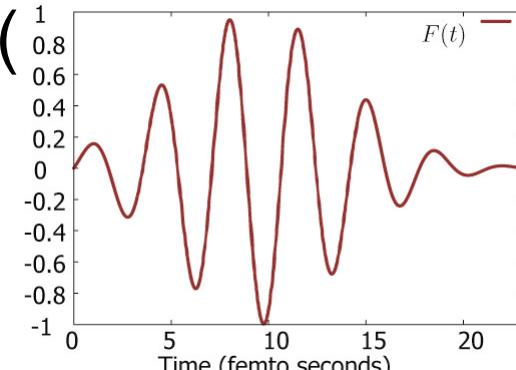
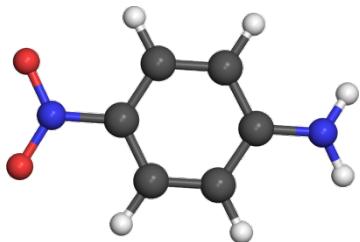


That's all folks



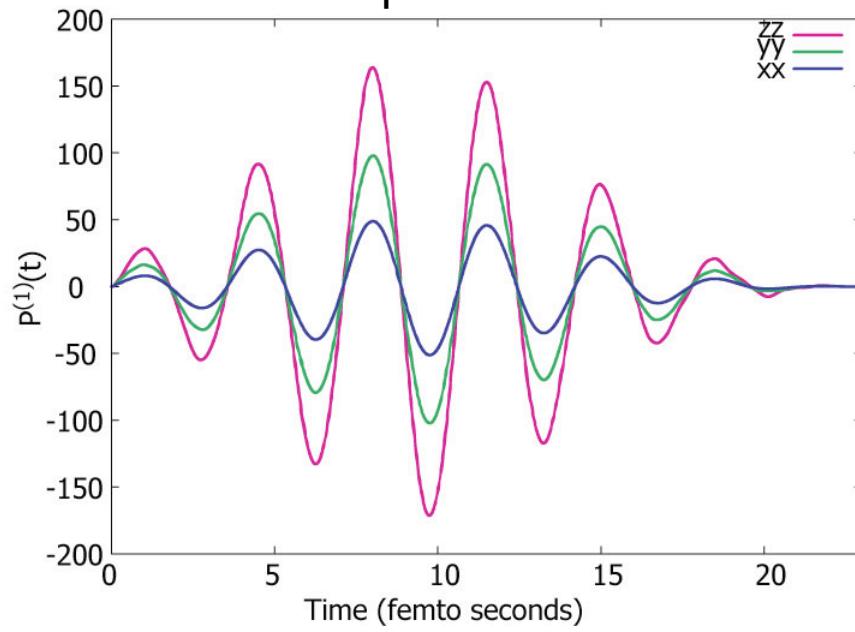
Applied *quasi-monochromatic field*

Results: Test case: p-nitroaniline (



$$F(t) = \sin(\omega_0) \exp(-\gamma(t - t_c)^2)$$

Linear response



First nonlinear response

