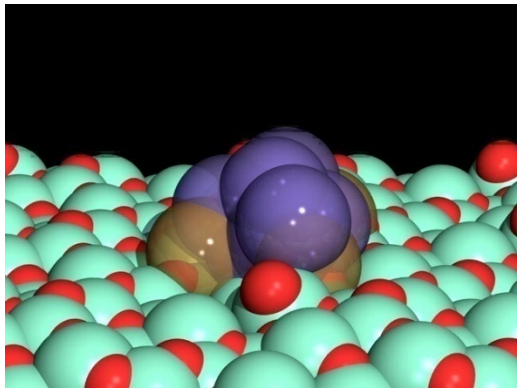
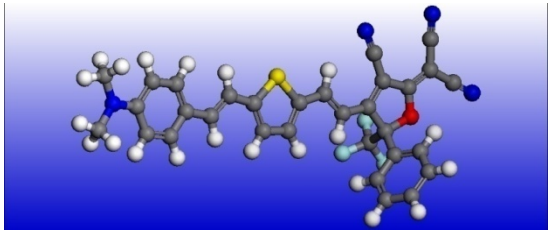
Excitations in Condensed Matter: From Basic Concepts to Real Materials

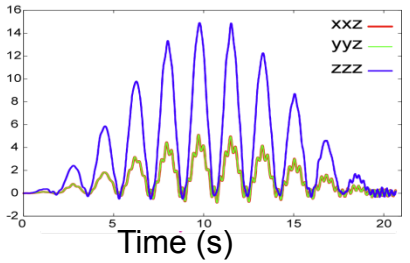
Real-time approaches for *linear* and *nonlinear* optical & xray response

J. J. Rehr, Y.Takimoto, and F. Vila

Department of Physics
University of Washington
Seattle, WA USA







UNIVERSITY OF WASHINGTON

KITP, UCSB November 17, 2009

Goals: Real-time response of complex and non-equlibrium systems

Beyond linear response and harmonic approximations

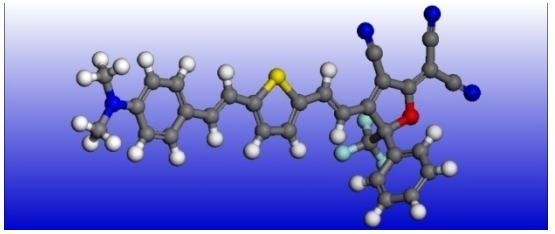
Talk:

- **I.** Non-linear Optical Response – RT-TDDFT
  Codes: RT-SIESTA

- **II. Real time** XAS of non-equlibrium system
  Finite Temperature DFT/MD + RSGF XAS
  Codes: VASP + FEFF8

I. Non-linear Optical Response

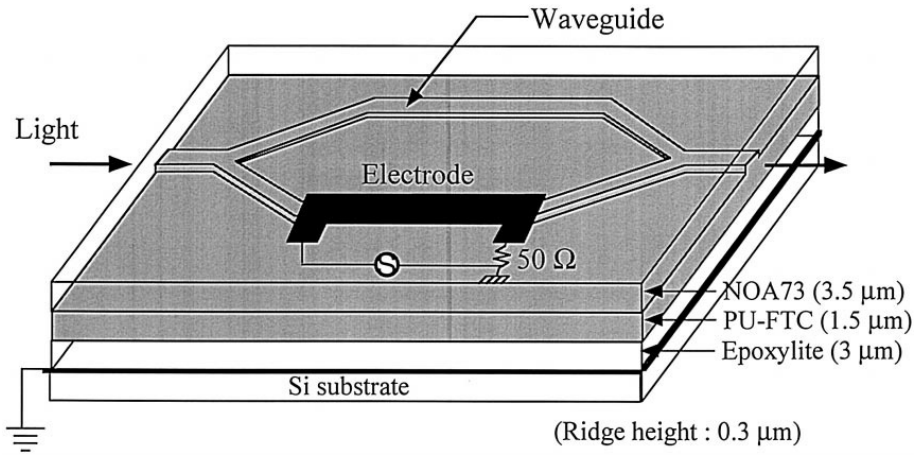
- Goal: *non-linear* optical response of *organic-photonic* systems

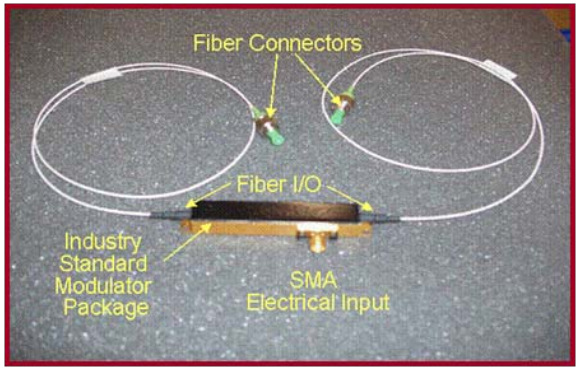


- Difficulty: frequency-space is computationally demanding - **too-many** excited states

- Strategy: extend linear RT-TDDFT/ SIESTA approach
  Sanchez-Portal, Tsolakidis, and Martin, Phys. Rev. B**66**, 235416 (2002)

Motivation: Polymeric Electro-optic devices for **integrated photonics**





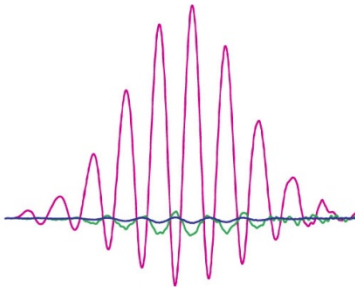
The **electro-optic** coefficient $r_{33} \sim \beta_{zzz}$

change of the refractive index induced by an applied 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 ~ 450 pm/V, more than 15x higher than the best inorganic materials!

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



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

Y. Takimoto, F. D. Vila, and J. J. Rehr[a)]
Department of Physics, University of Washington, Seattle, Washington 98195, USA

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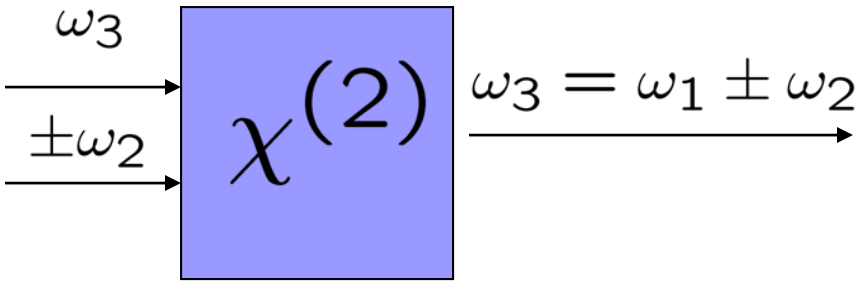
We present *ab initio* calculations of frequency-dependent linear and nonlinear optical responses based on real-time time-dependent density functional theory for arbitrary photonic molecules. This approach is based on an extension of an approach previously implemented for a linear response using the 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]

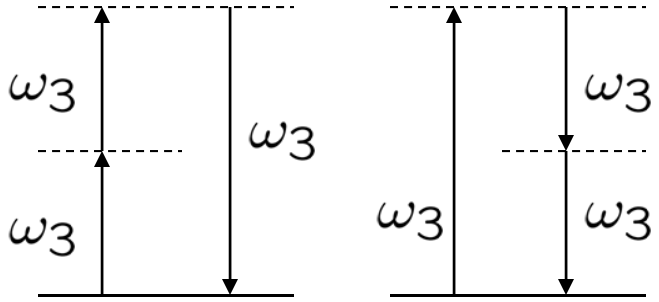
J. Chem. Phys. **127**, 154114 (2007)

Nonlinear Polarizabilities

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

- 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. B**54**, 4484 (1996)

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

- 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** $\Delta H(t) = -\boldsymbol{E}(t)\cdot\boldsymbol{x}.$

- Optical properties determined from **total dipole moment**:

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

MORE EFFICIENT THAN FREQUENCY -SPACE METHODS !

Calculation of $\Psi(t)$ at each time step using 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 for excited states**

*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

$$i\frac{\partial c(t)}{\partial t} = S^{-1}H(t)c(t)$$

Coefficients of Orbitals

- Crank-Nicholson time-evolution: **unitary**, **time-reversible**

  stable for long time-steps

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

- Adiabatic GGA exchange-correlation (PBE) functional

Review: Real time Linear Response

- Standard relations…

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

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

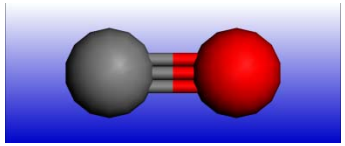
$$\chi_{ij}^{(1)}(\omega) = \delta p_i(\omega)/E_j(\omega) = \alpha_{ij}(\omega)$$ Linear Response Function

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

$$\sigma(\omega) \sim \omega \langle \alpha(\omega) \rangle / E(\omega)$$ Optical Absorption

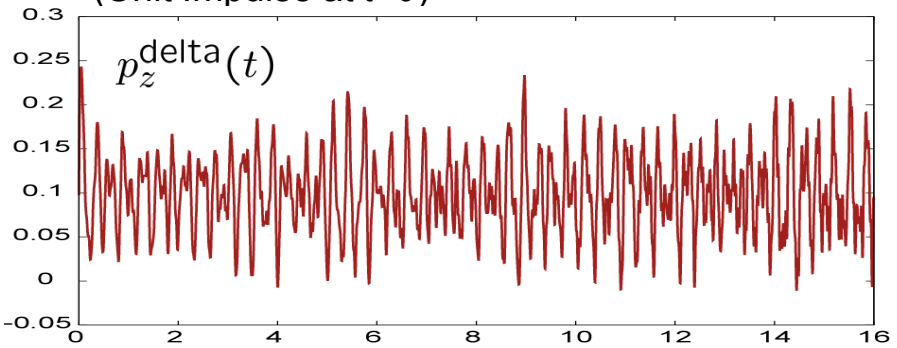
Example: Linear Response

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



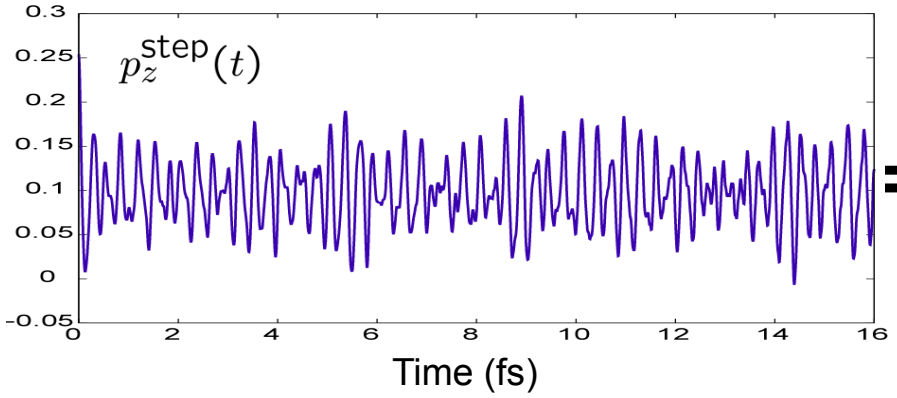
- Delta Function

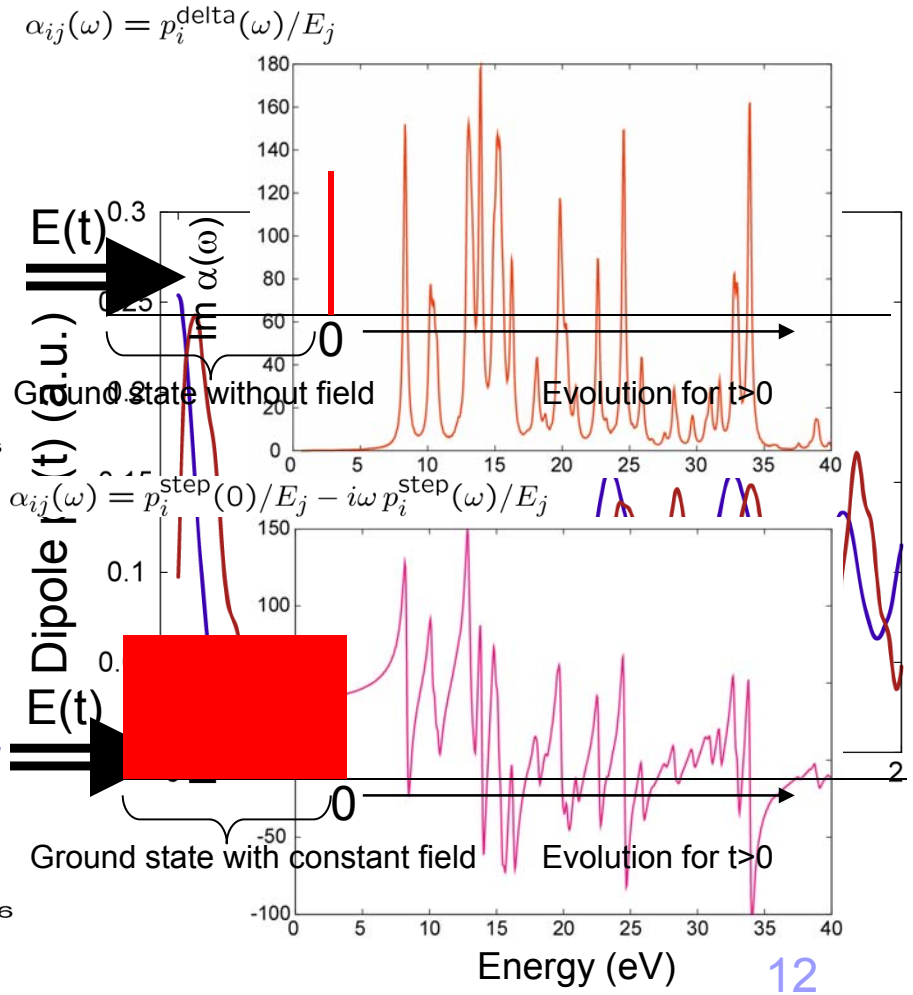
(Unit Impulse at *t=0*)



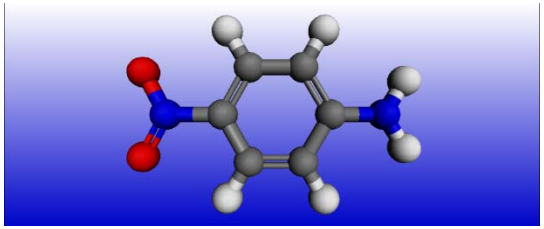
- Step Function

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





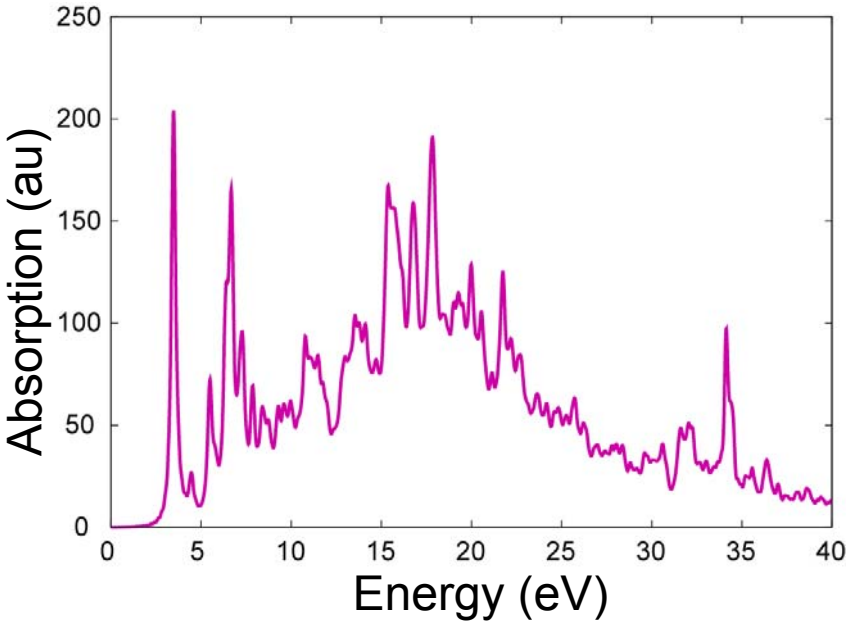
Example:Small molecules
p-Nitroaniline (pNA)



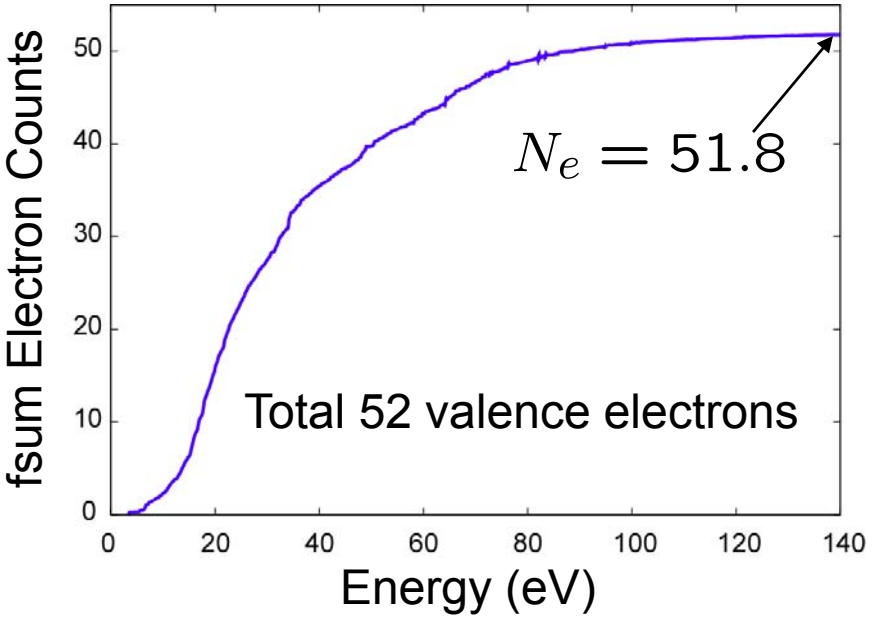
- Linear absorption

$\lambda_0 = 356\text{nm}$ $\quad$ $\lambda_0^{\text{exp.}} = 347\text{nm}$

$\omega_0 = 3.49\ \text{eV}$ $\quad$ (in chloroform)

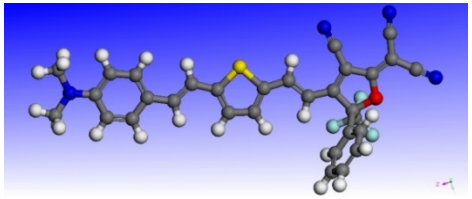


- Sum rule



$$\int_0^\infty d\omega\, S(\omega) = \lim_{\omega\to\infty} f_{\text{sum}}(\omega) = \sum_i f_i = N_e,$$

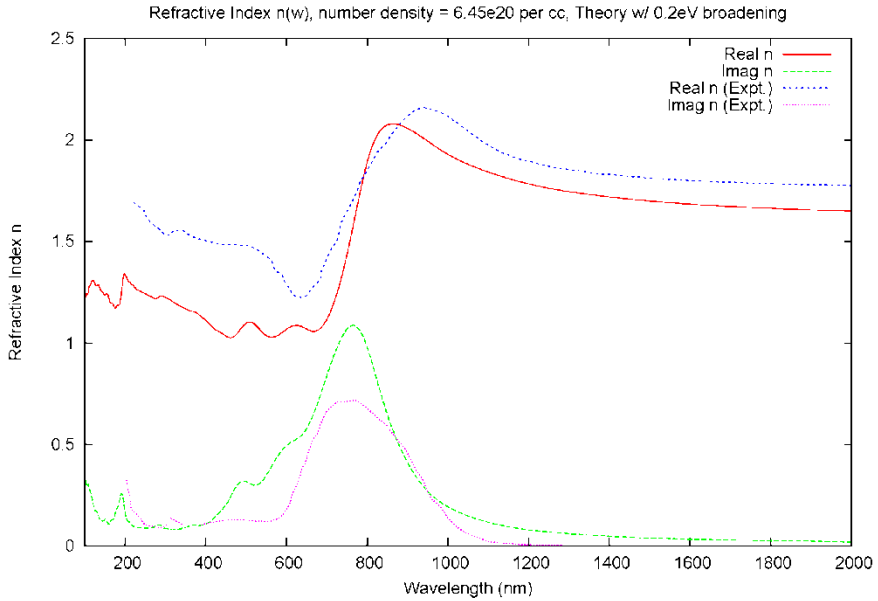
Linear response of Large Photonic molecules "YLD156"



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

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

- Accounting for time lag in system response

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

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

Extraction of **Static** Nonlinear Polarizabilities

- Standard technique: fit to static expansion

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

Either finite-difference or polynomial fitting $p_i(E)$ *e.g.*,

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

Extraction of **Dynamic** Nonlinear Polarizabilities

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

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

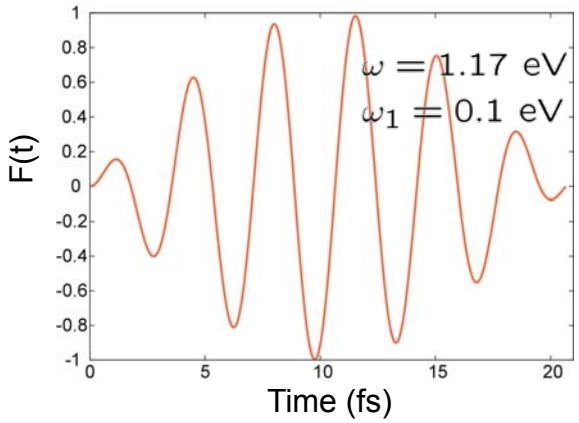
where $p^{(1)}$ yields linear response, $p^{(2)}$ first non-linear quadratic response, ….

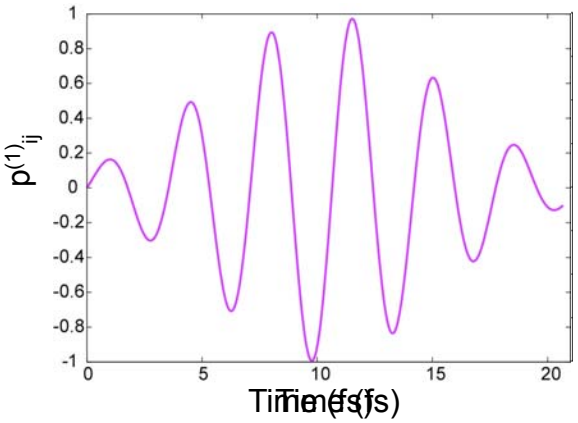
- The quadratic response $\chi^{(2)}$ is then given by

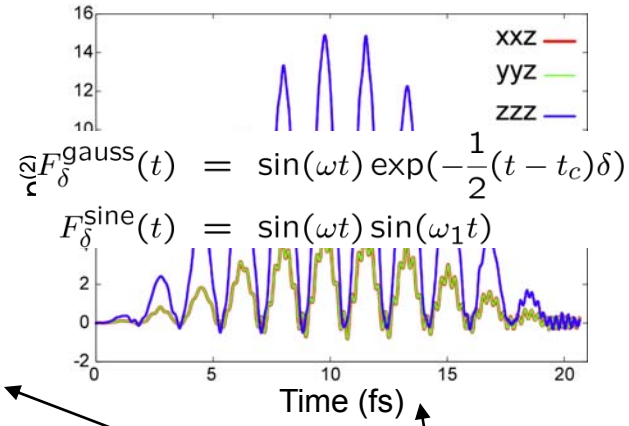
$$p_{ijk}^{(2)}(t) = \int dt_1 \int dt_2 \; \chi_{ijk}^{(2)}(t - t_1, t - t_2)F(t_1)F(t_2)$$

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

- Sine wave enveloped by another sine wave or Gaussian





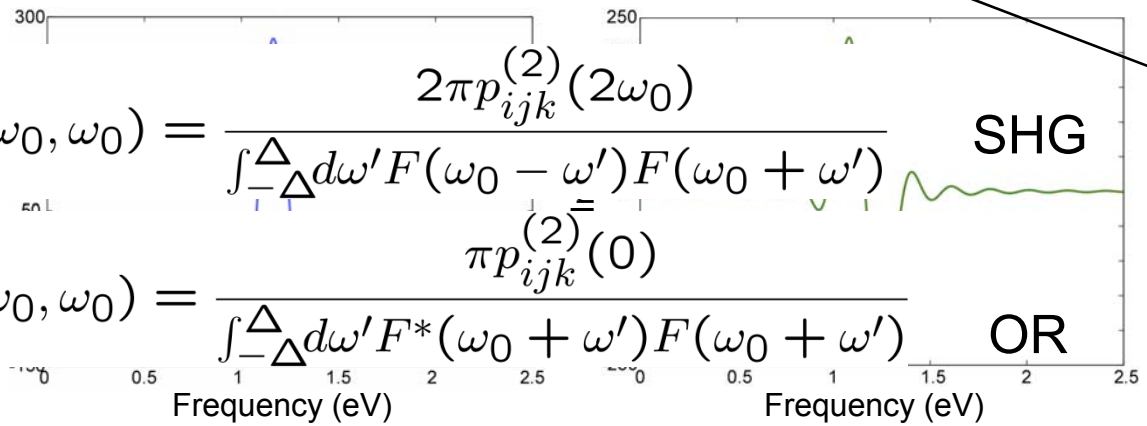


$$\chi^{(2)}_{ijk}(-2\omega_0;\omega_0,\omega_0) = \frac{2\pi p^{(2)}_{ijk}(2\omega_0)}{\int_{-\Delta}^{\Delta} d\omega' F(\omega_0-\omega')F(\omega_0+\omega')}$$

SHG

$$\chi^{(2)}_{ijk}(0;-\omega_0,\omega_0) = \frac{\pi p^{(2)}_{ijk}(0)}{\int_{-\Delta}^{\Delta} d\omega' F^*(\omega_0+\omega')F(\omega_0+\omega')}$$

OR



Linear and Nonlinear response of CO

Real time vs Frequency space Nonlinear Response

- Operation cost
  - Sternheimer equation (frequency space)

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

  - Real time

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

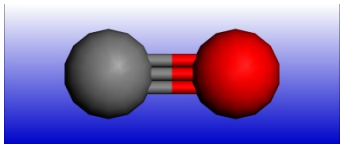
- Memory cost
  - Sternheimer equation (frequency space)

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

  - Real time

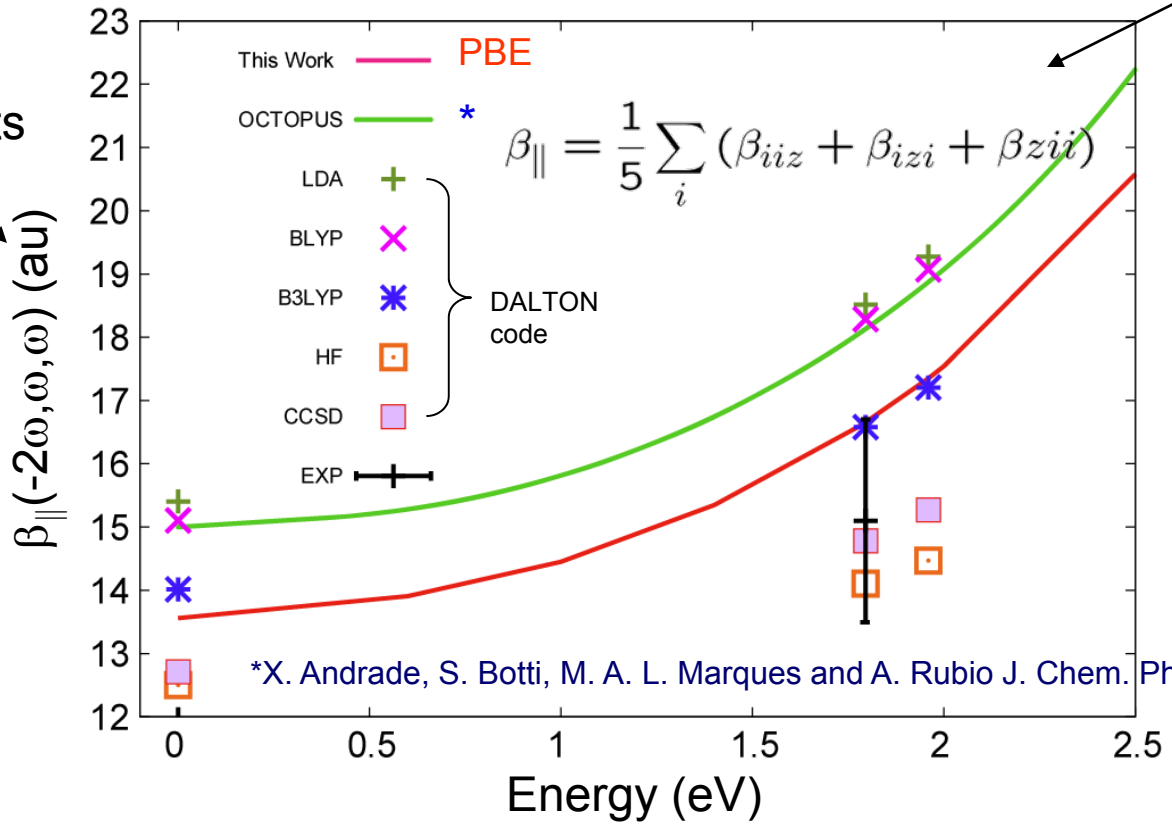
$$\mathcal{O}(N_{\mathsf{occ}}\, N_{\mathsf{basis}})$$

Example: CO: Nonlinear Second Harmonic Generation (SHG)



- Comparison with other methods

atomic units

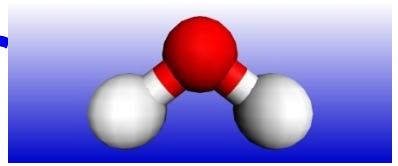


"Vector" average, related to EFISH experiment

$$\Gamma = \gamma + \frac{\mu_0 \beta_{\parallel}}{3kT}$$

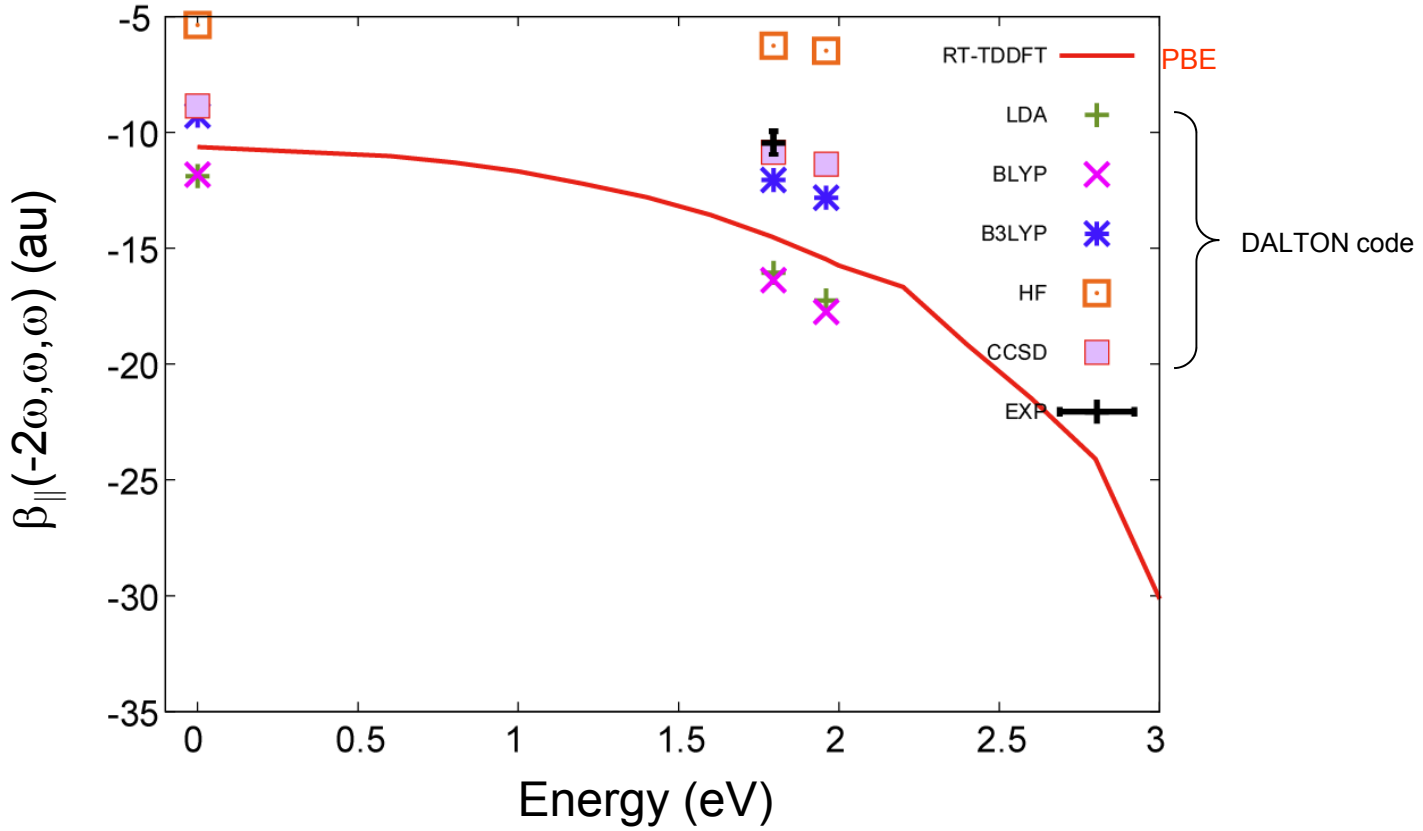
*X. Andrade, S. Botti, M. A. L. Marques and A. Rubio J. Chem. Phys. **126**, 184106 (2007)

Example: H_2O: Nonlinear

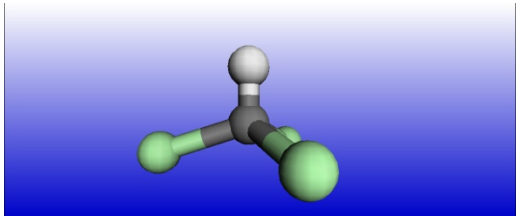


Second Harmonic Generation (SHG)

- Comparison with other methods



Chloroform $CHCl_3$
Hyperpolarizability



Basis-set effects on the hyperpolarizability of $CHCl_3$: Gaussian-type orbitals, numerical basis sets and real-space grids

Fernando D. Vila,[1] David A. Strubbe,[2] Yoshinari Takimoto,[3,1] Xavier Andrade,[4] Angel Rubio,[4,5] Steven G. Louie,[2] and John J. Rehr[1]

[1] *Department of Physics, University of Washington, Seattle, WA 98195*

[2] *Department of Physics, University of California, Berkeley, and Materials Sciences Division, Lawrence Berkeley National Laboratory*

[3] *Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*

[4] *Nano-Bio Spectroscopy group and ETSF Scientific Development Centre, Dpto. Física de Materiales, Universidad del País Vasco, Centro de Física de Materiales CSIC-UPV/EHU-MPC and DIPC, Av. Tolosa 72, E-20018 San Sebastián, Spain*

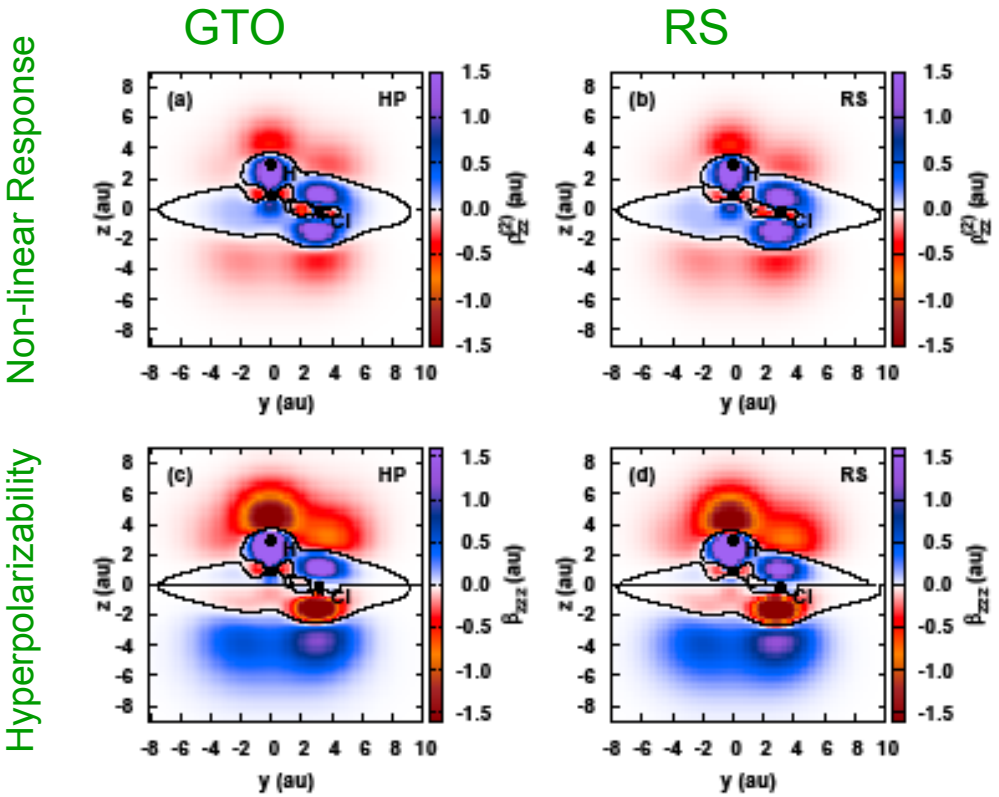
[5] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*

(Dated: October 26, 2009)

All 3 methods with **large basis sets** are **consistent**

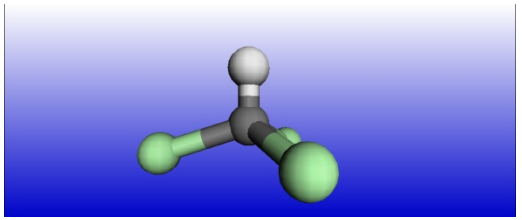
Preprint Submitted to J. Chem Phys (October 2009)

Local Response Densities



Contributions from Cl and HC are **opposite** in sign

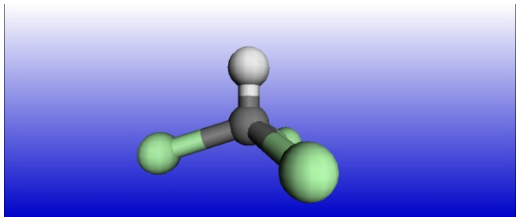
$CHCl_3$: Effect of basis



- *Nonlinear* calculation require ***large*** basis especially for small molecules

		DZP (default)	5Z4P	5Z4P	5Z4P	5Z4P
"radius"	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	μ z	0.26	**0.41**	**0.40**	**0.40**	**0.40**
	α	44.39	60.18	60.39	60.15	60.09
Nonlinear	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 ‖	-13.28	-3.59	-1.86	-0.88	-0.90

Chloroform ($CHCl_3$)



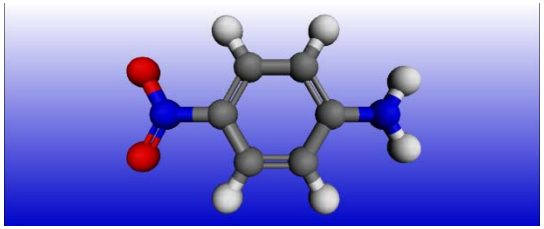
Static calculation comparison

GTO
Num
RS

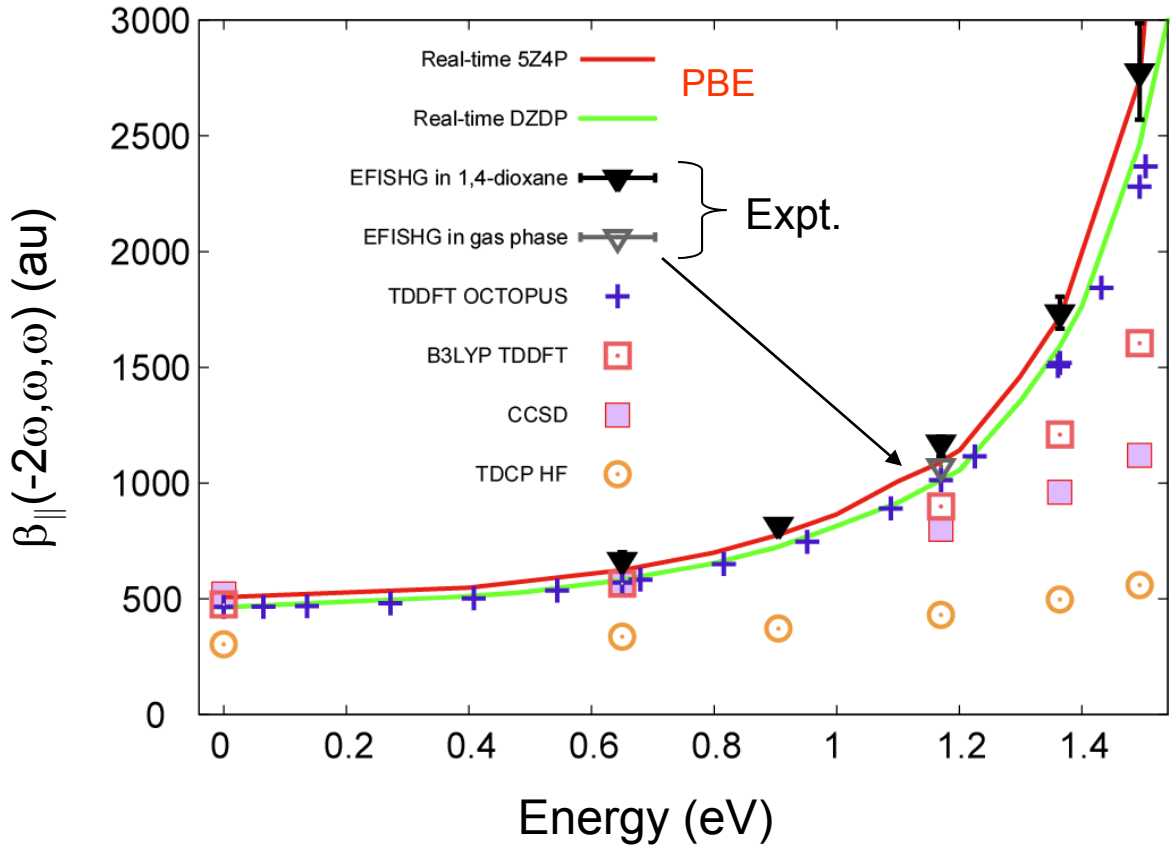
Basis Set	μ_z	α_{yy}	α_{zz}	β_{yyy}	β_{yyz}	β_{zzz}	$\bar{\alpha}$	$\beta_{\|\|}$	β^{VV}_{HRS}
GTO 5Zsa	0.404	65.70	46.79	27.35	−15.31	22.27	59.40	−5.01	16.90
NBS 5Z4Pe8	0.398	65.45	46.28	24.54	−14.90	21.37	59.06	−5.07	15.68
RS lr	0.399	66.02	47.00	27.12	−16.36	26.94	59.68	−3.47	17.44
RS fd	"	66.46	47.07	24.22	−15.66	25.50	60.00	−3.52	16.14
RS 1064 nm	"	66.69	47.34	30.35	−18.95	31.56	60.24	−4.01	19.91
Expt.	0.409±0.008 [32]	61±5 [33]	45±3 [33]				56±4 [33]	1±4 [1]	

Preprint Submitted to J. Chem Phys (October 2009)

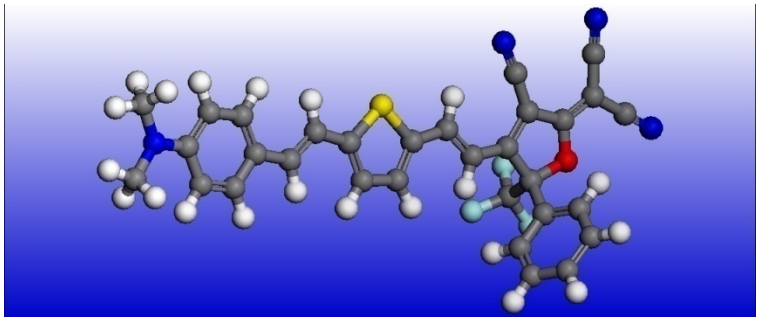
*p*NA: Nonlinear (SHG)



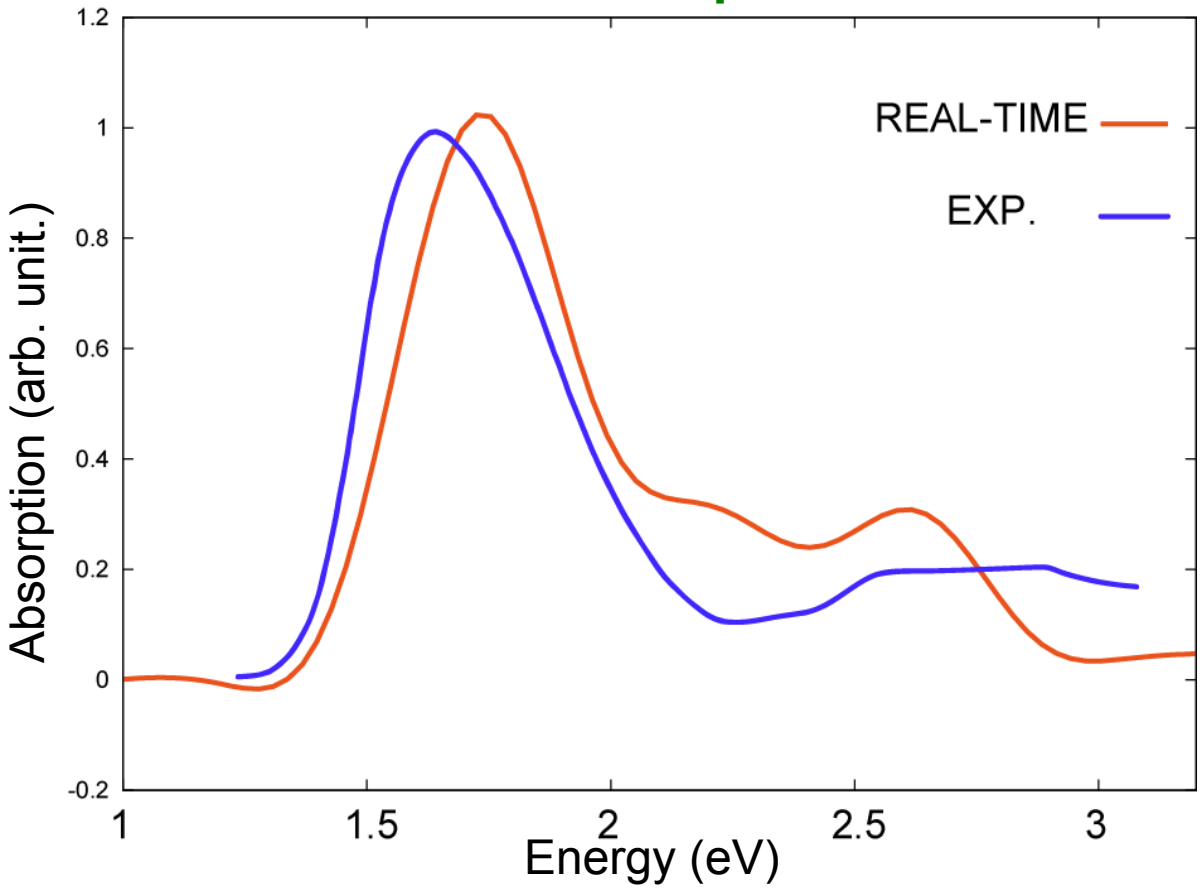
- Comparison with other methods



NLO Molecule



- YLD156 chromophore



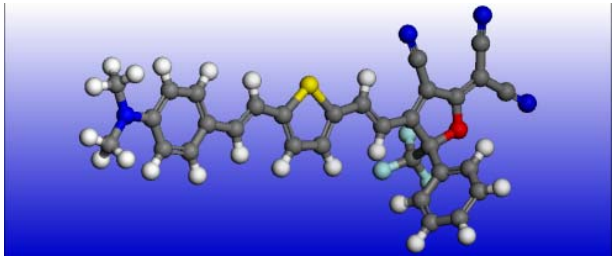
Real-time Absorption peak of YLD_156 (GAS)

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

Experimental Absorption peak of YLD_156 in Chloroform solution

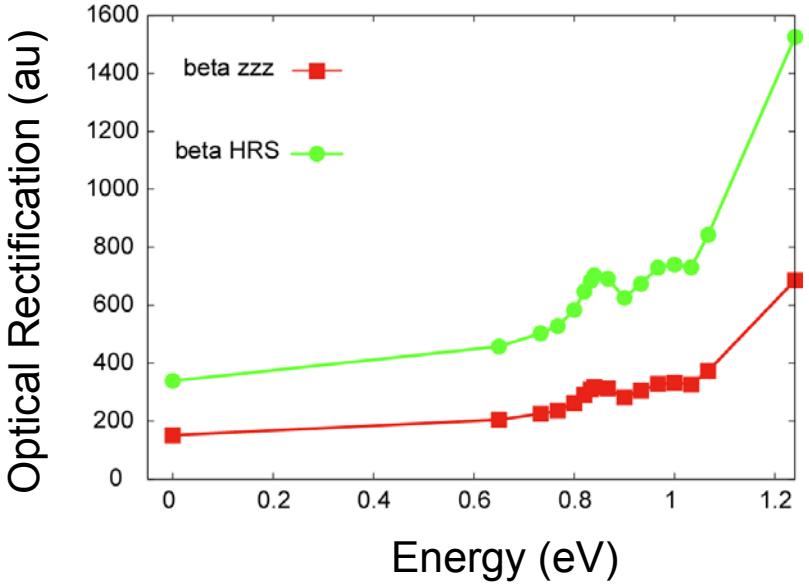
$$\omega_0 = 1.65 \text{ eV}$$
$$(\lambda_0 = 753\text{nm})$$

YLD156

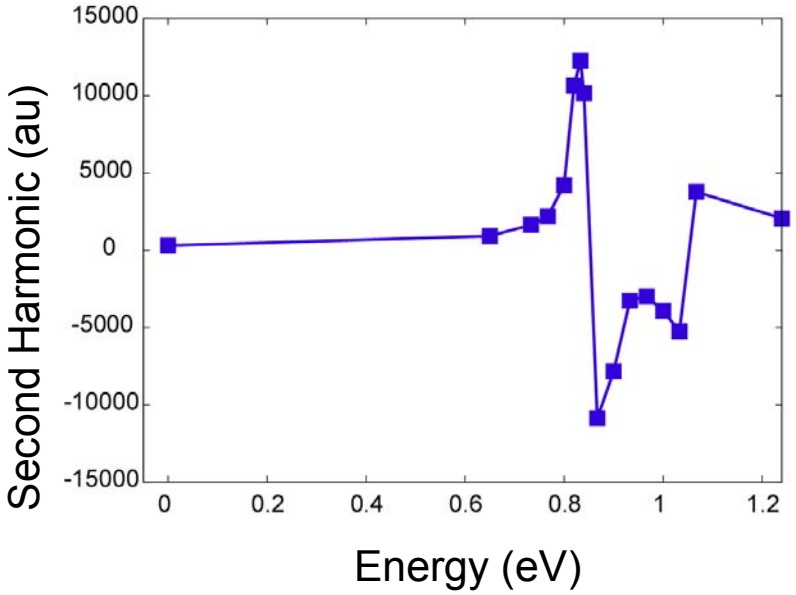


- Nonlinear results

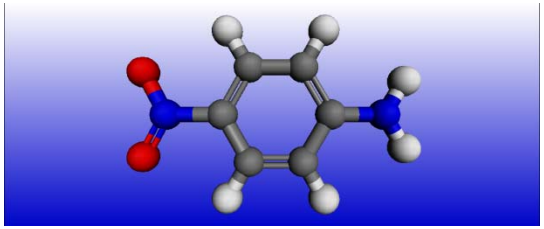
$\beta_{||}(0;-\omega;\omega)$ **OR**

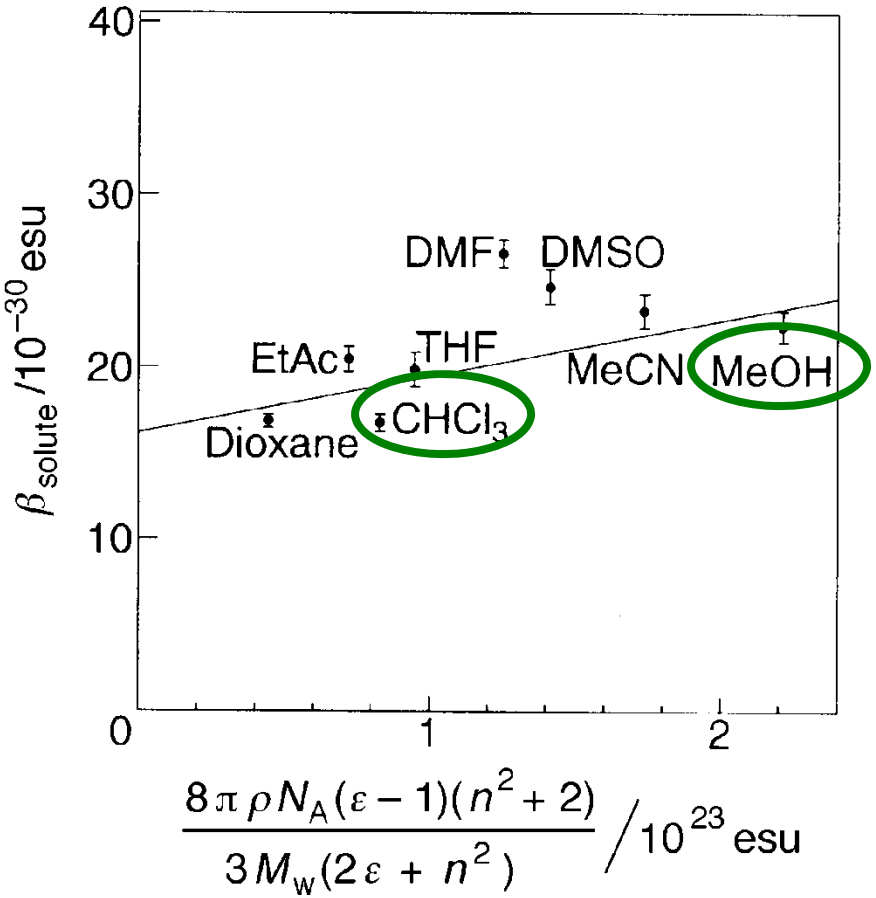


$\beta_{||}(-2\omega;\omega,\omega)$ **SHG**



Solvent Effects – HRS Experiment



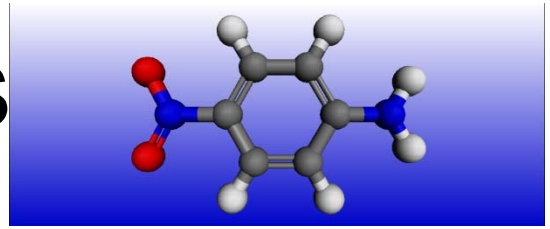


solvent	β_{solute} /10^{-30} esu	λ_{max} /nm
chloroform	16.80 ±0.50	347
p-dioxane *	16.90 ±0.40	352
tetrahydrofuran (THF)	19.90 ±1.00	363
ethyl acetate (EtAc)	20.50 ±0.70	356
acetonitrile (MeCN)	23.30 ±1.00	364
methanol (MeOH)	22.40 ±0.90	356
dimethyl sulfoxide (DMSO)	24.70 ±1.00	388
N,N-dimethylformamide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

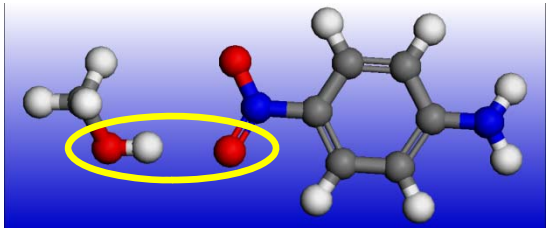


β_{HRS} 798.6 (au)

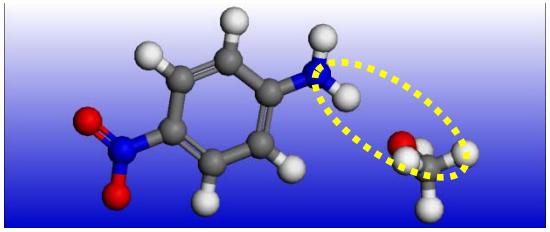
- Large local contact effects with methanol (polar) or chloroform (non-polar)

"Adjusted" Expt. Values.

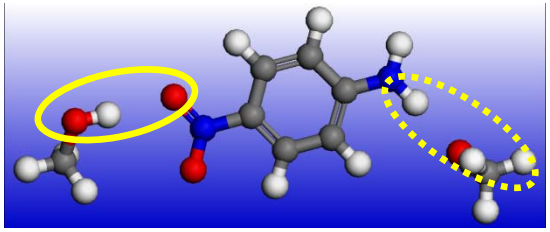
1900 ± 100



β_{HRS} 1556 (21.3)

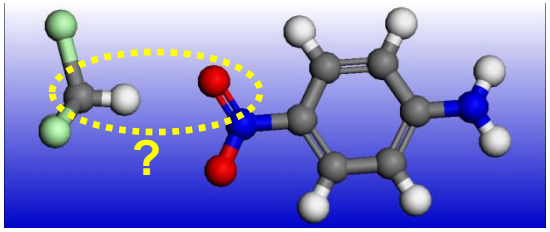


869.3 (19.9)

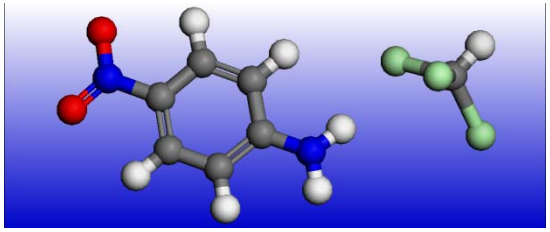


1812 (31.4)

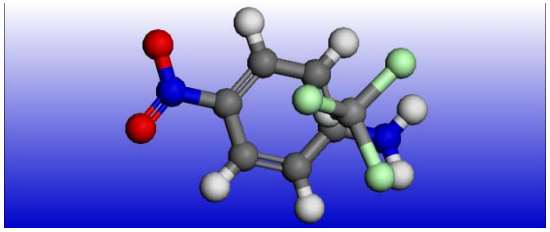
1400 ± 40



β_{HRS} 1081 (10.8)



797.5 (8.79)



746.1 (6.36)

Conclusions I

- 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.

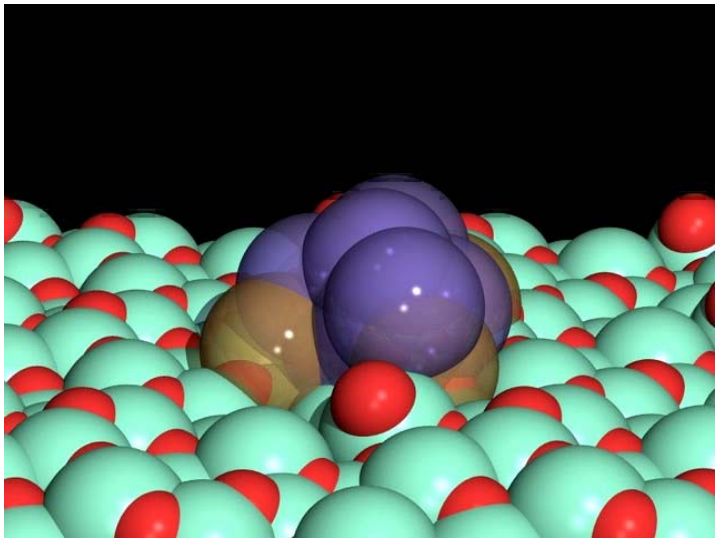
Part II: X-ray Spectra – DFT/MD - Dynamic Structure in Supported Pt nanoclusters*

MYSTERY: Unusual thermal properties of Pt_{10} /γ-Al_2O_3

NTE, disorder, redshift in XAS

Approach: Real-time Finite temp DFT/MD

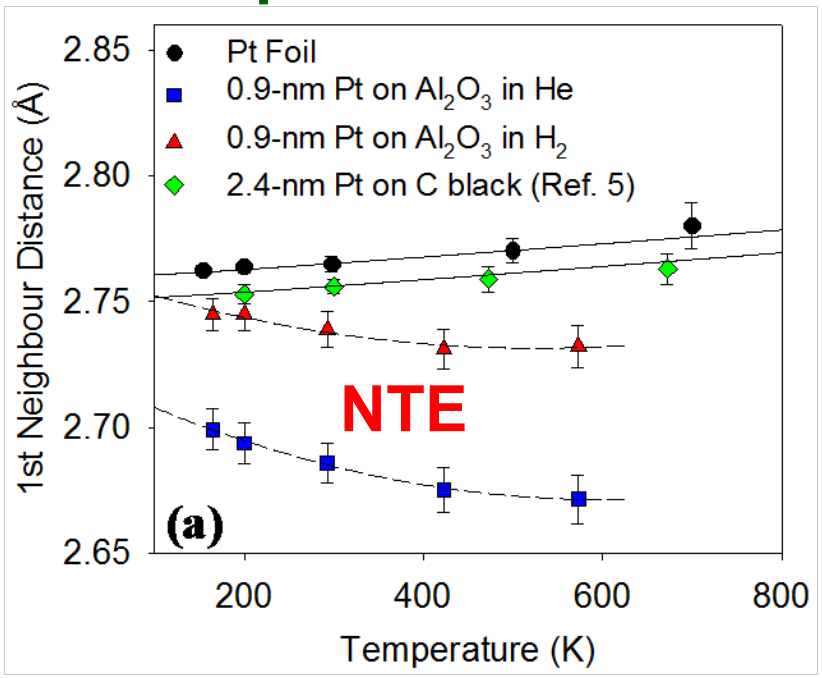
Pt_{10} Cluster on [110] γ-Al_2O_3

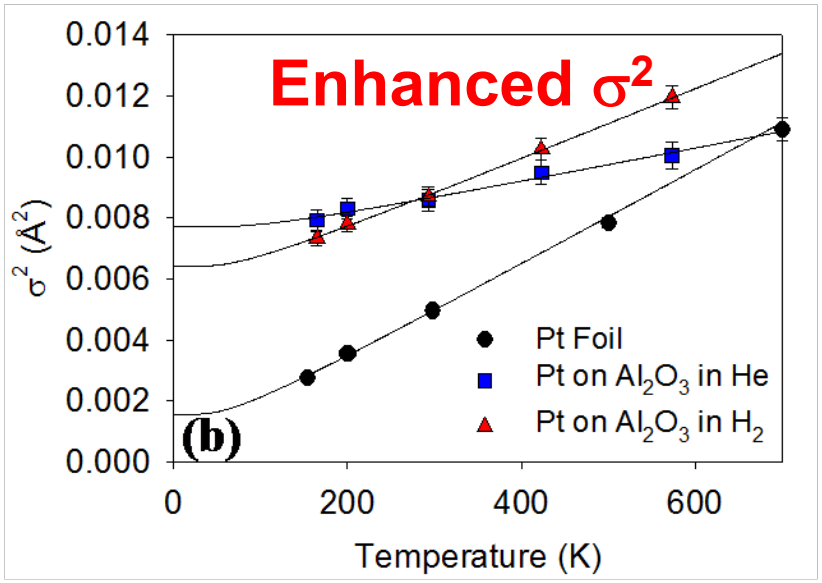


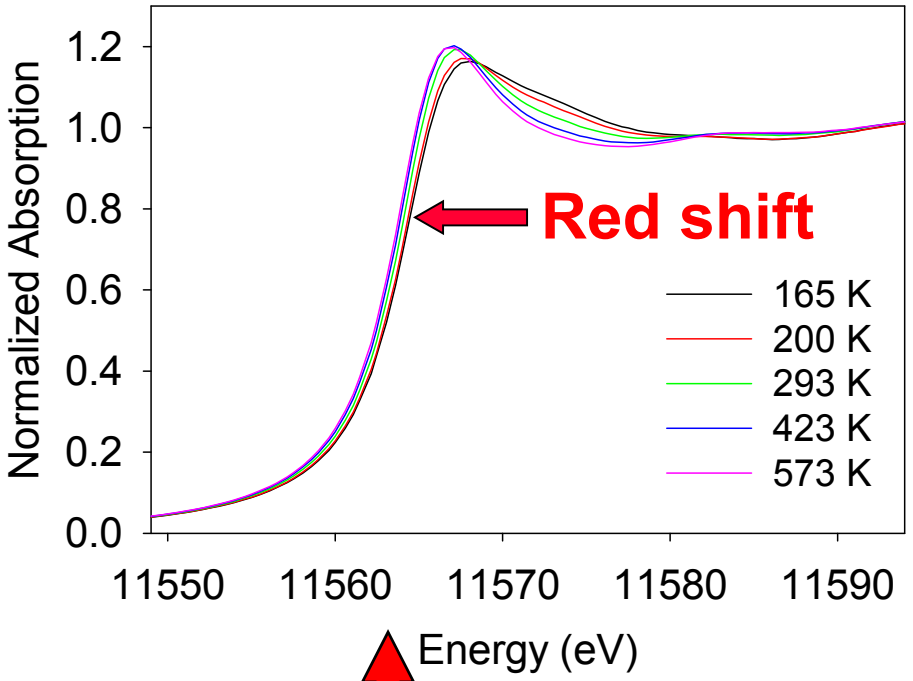
metallic Pt Al oxidized Pt O

*F. Vila, J. Rehr, A. Frenkel, R. Nuzzo, J. Kas, Phys Rev. B **78**, 121404(R), (2008).

Experimental XAS Observations*







Surprising anomalies

*Kang, Menard, Frenkel, Nuzzo., JACS Commun. **128**, 12068 (2006)

Pt-Pt bond **expansion** going from He to H_2 atmosphere ❶

Pt-Pt bond **negative thermal expansion NTE** ❷

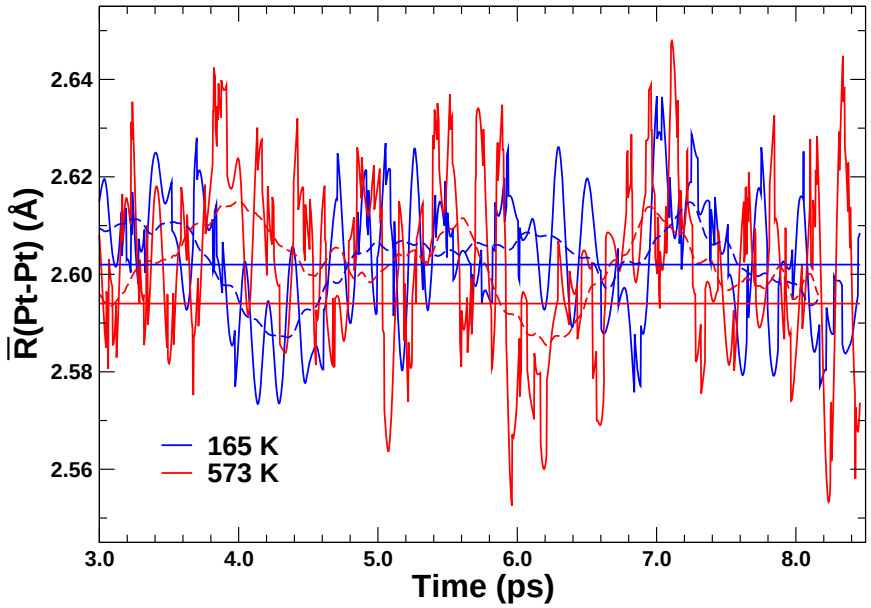
High Pt-Pt **disorder** ❸

Increased whiteline and **redshift** of XANES with increasing T ❹

Calculation - VASP + 10^4 cpu-hrs

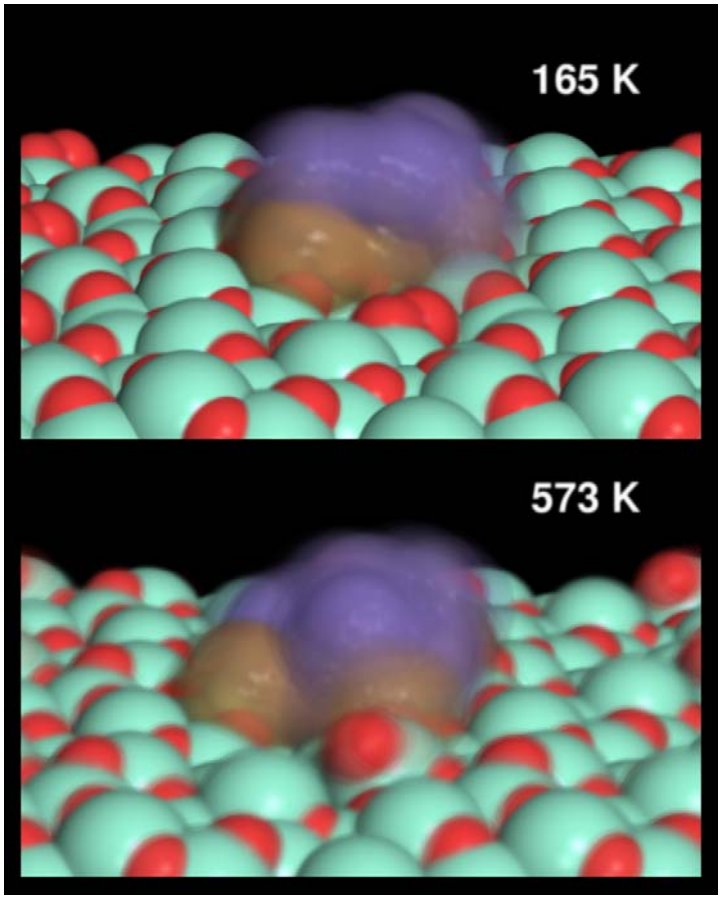
Calculation 10 atom Pt/ γ-Al_2O_3

Mean nn distance $R_{Pt\text{-}Pt}$



2500 3 fs steps

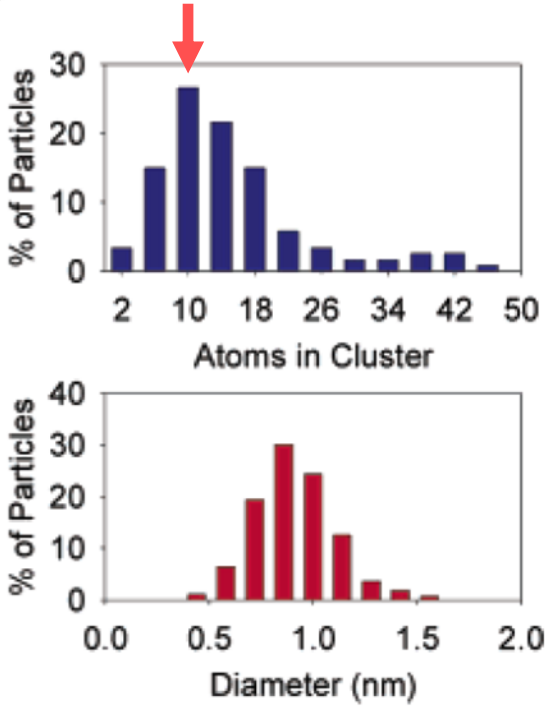
NTE



time-elapsed rendering

Computational Details

Study prototypical Pt_{10} cluster on [110] surface of γ-Al_2O_3



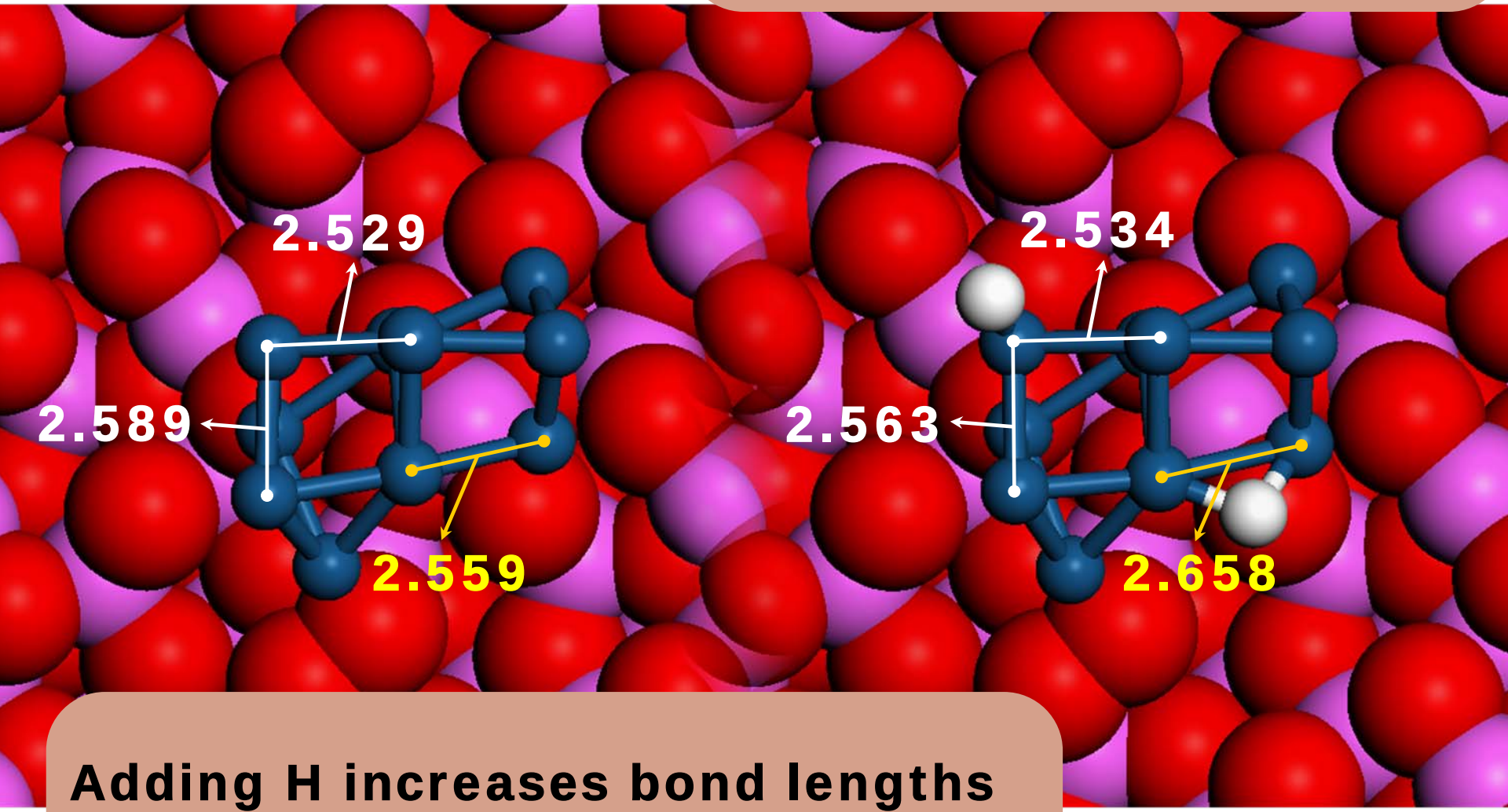
DFT / MD

VASP
PBE Functional
396 eV Cutoff
3 fs time step
3 ps Equilibration
5 ps Runs (3)
165 K & 573 K

XANES

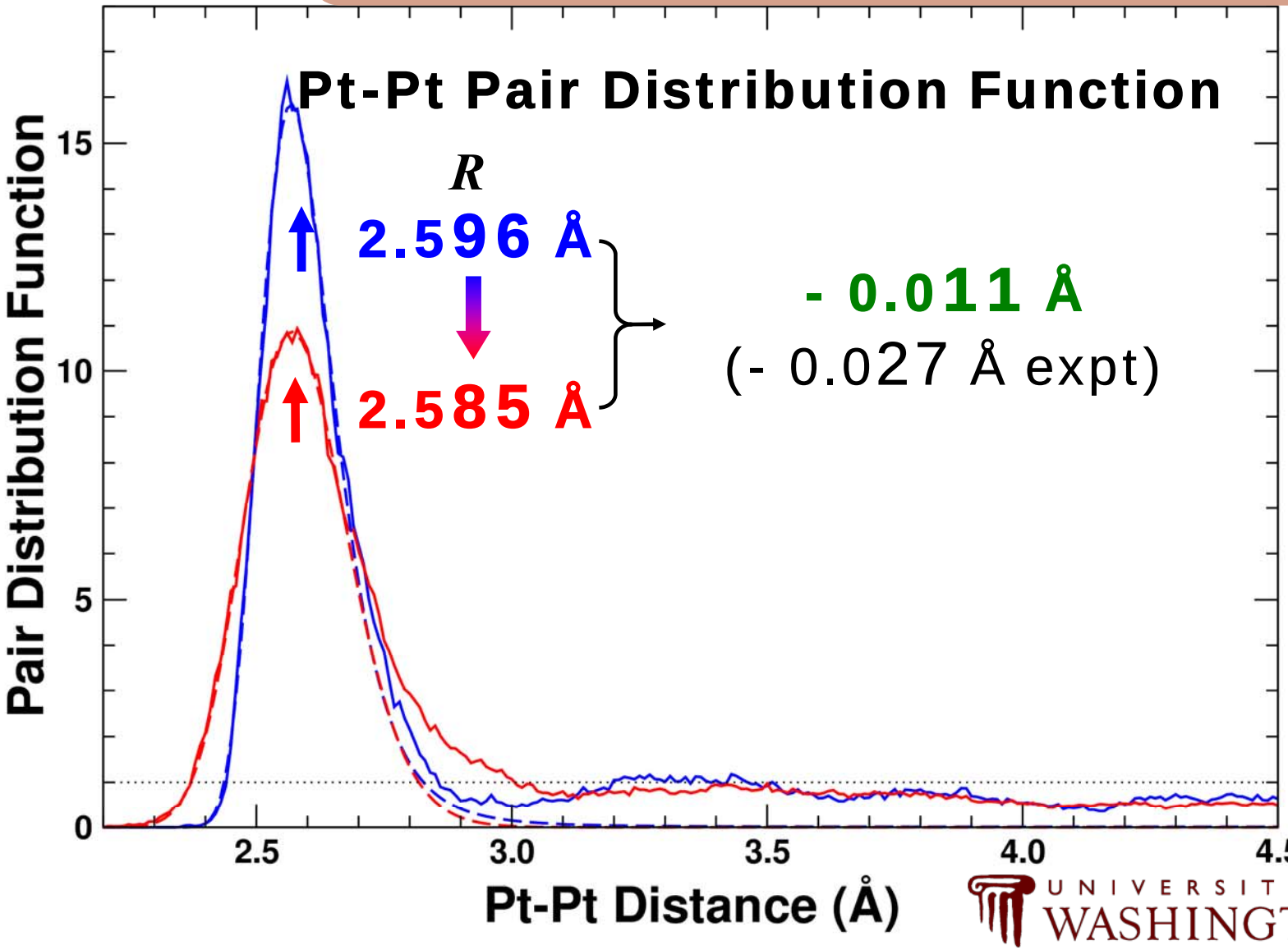
FEFF8
Full Multiple Scattering
32 Configurations from MD
7 Å Clusters (~150 atoms)

❶ Bond expansion in H_2 atmosphere



Adding H increases bond lengths

❷ Negative Thermal Expansion



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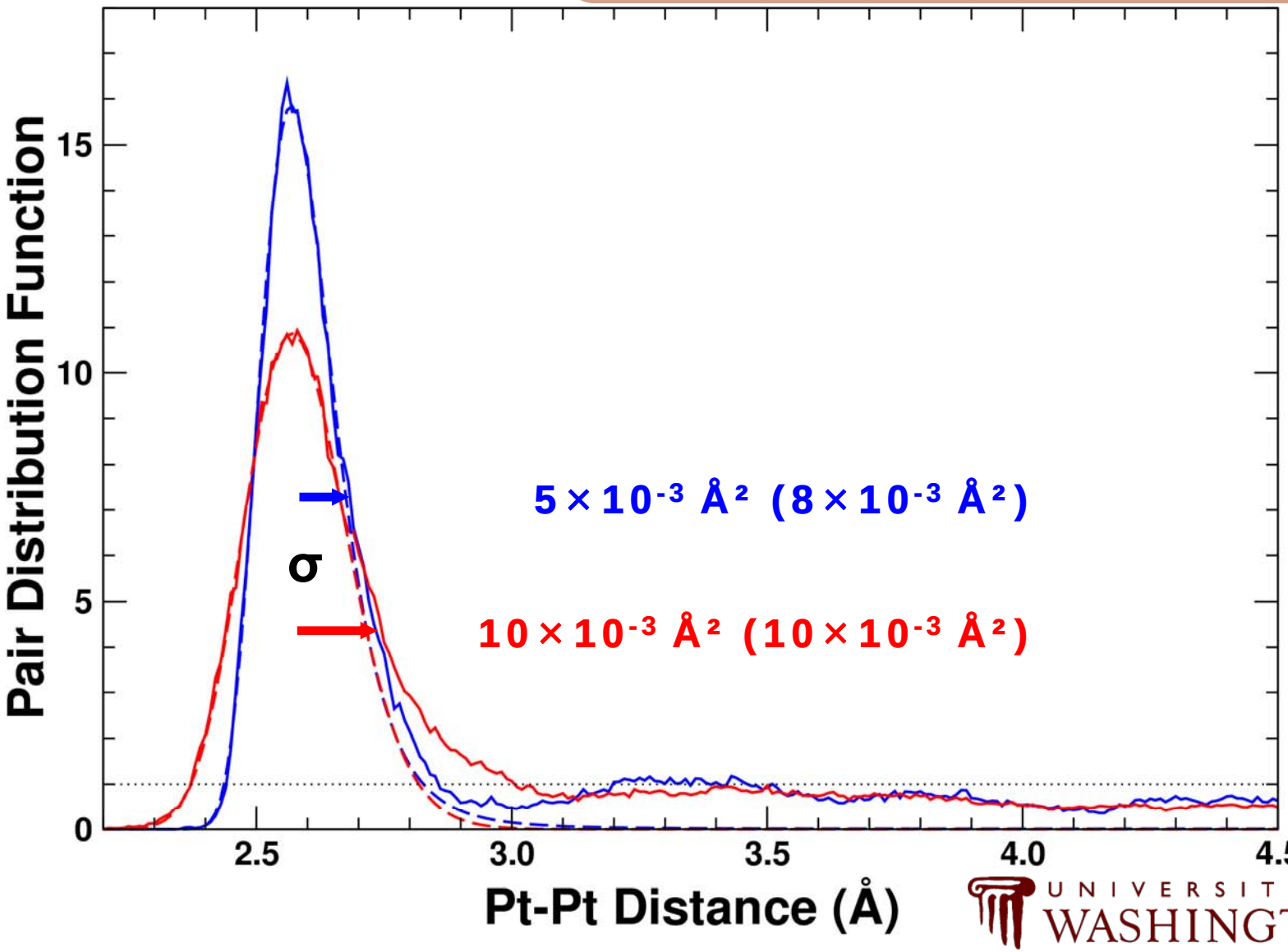
❸ High Pt-Pt Disorder



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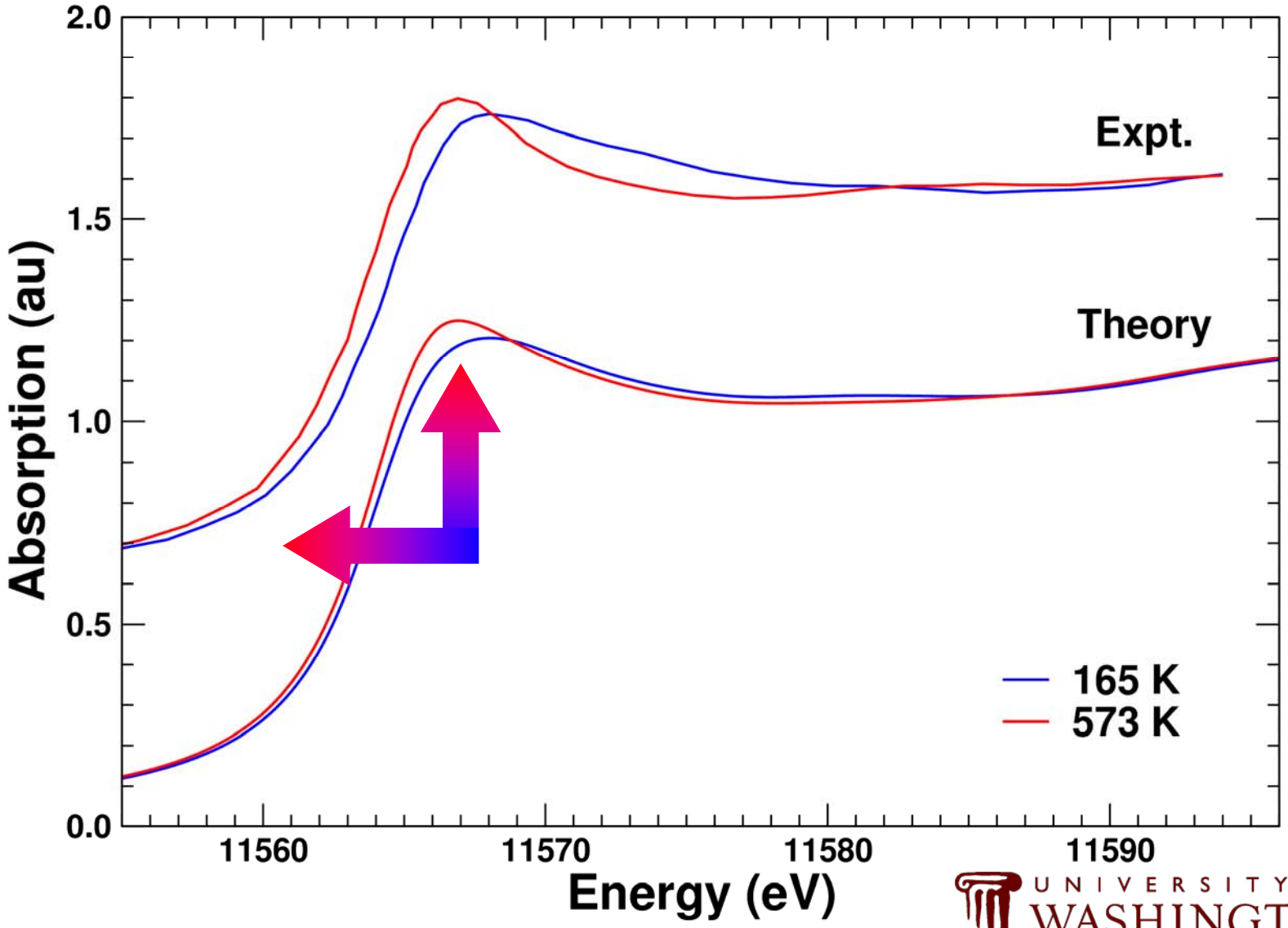
❹ Increased intensity and redshift at high T



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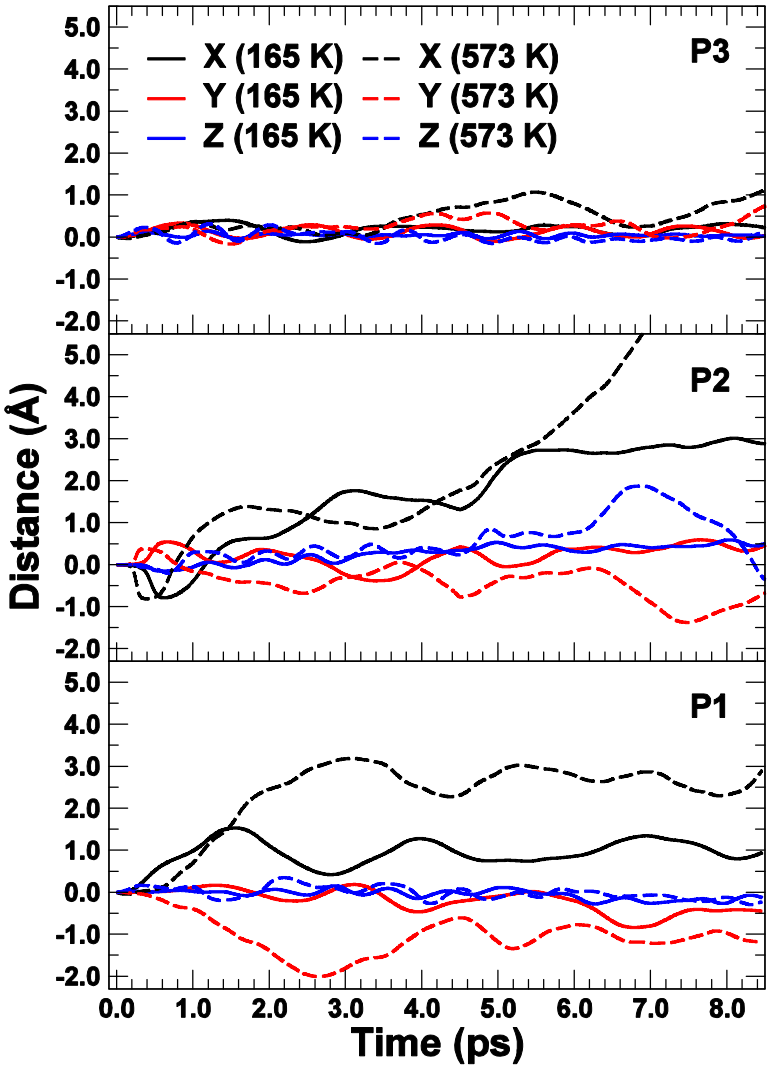
Physical Interpretation

Center of Mass Motion

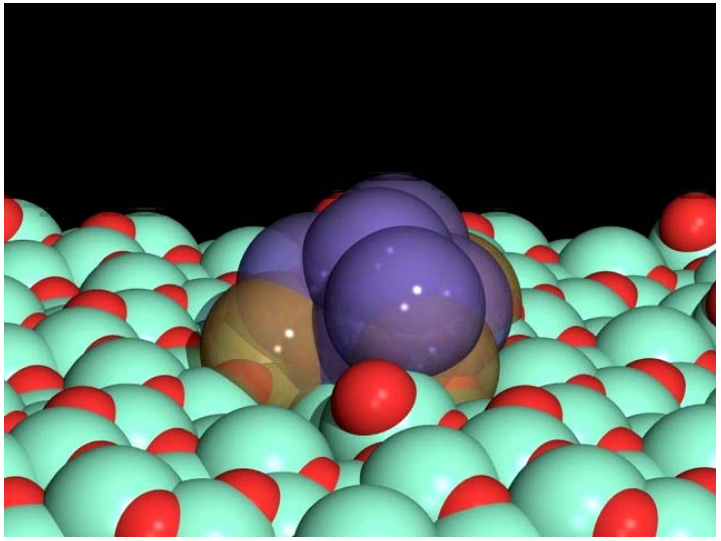
Librational motion of center of mass

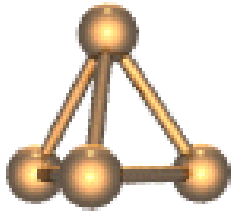
Period ~ 2 ps
Amplitude ~ 1 Å

Hindered Brownian motion

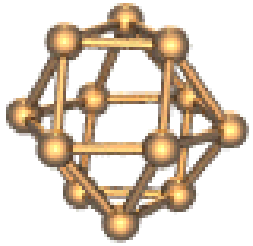


Librational motion





$Co_4(CO_{12})$

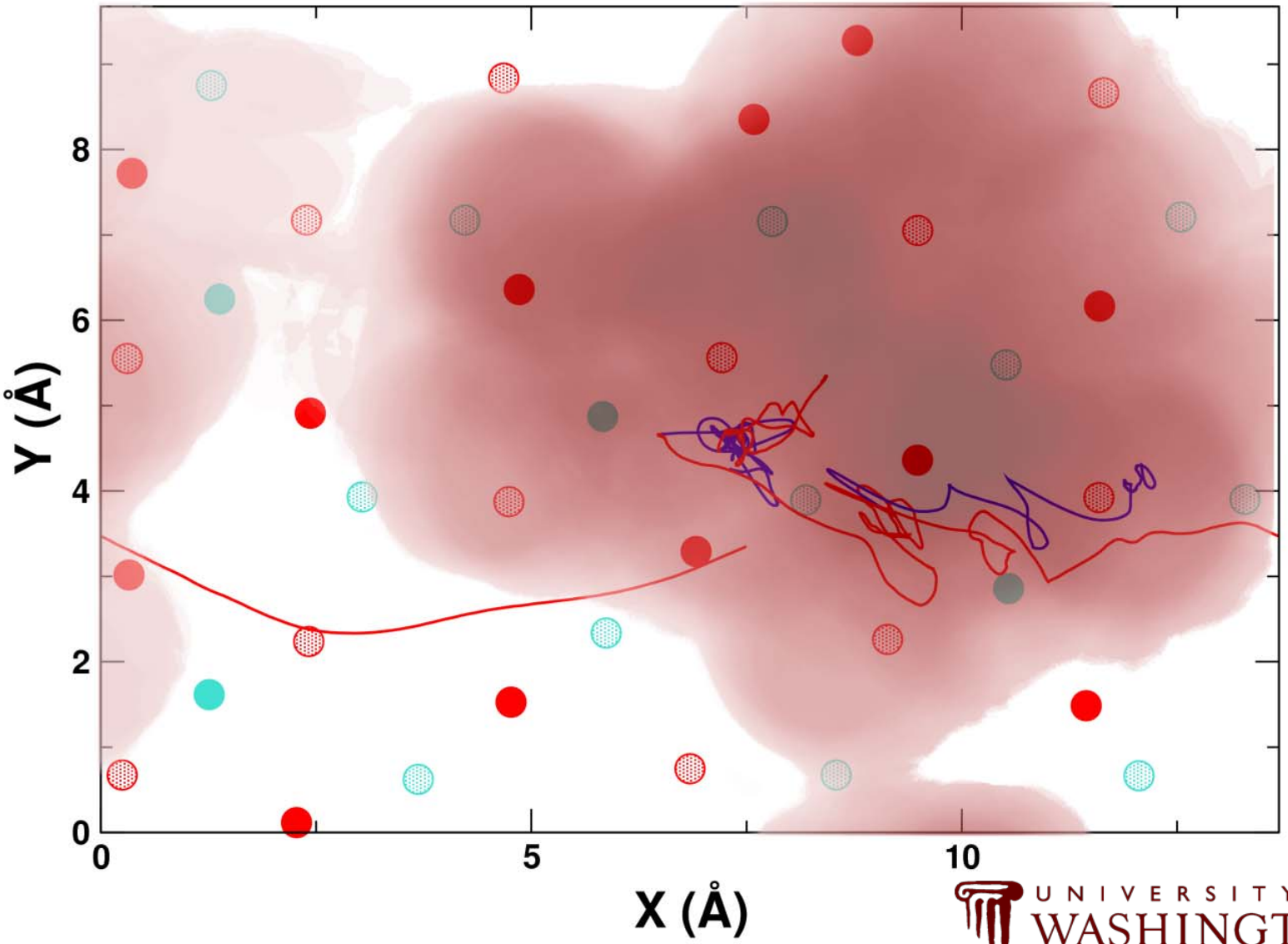


Fluxional behavior in tetrahedral clusters with carbonyl ligands

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

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

Cluster footprint @ 573 K



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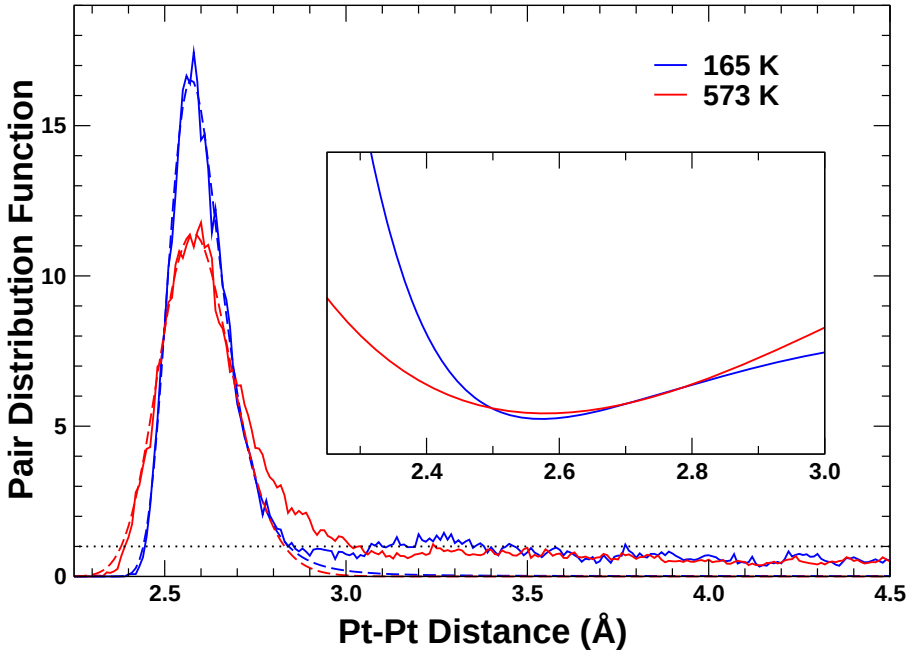
Configurational avg time-series

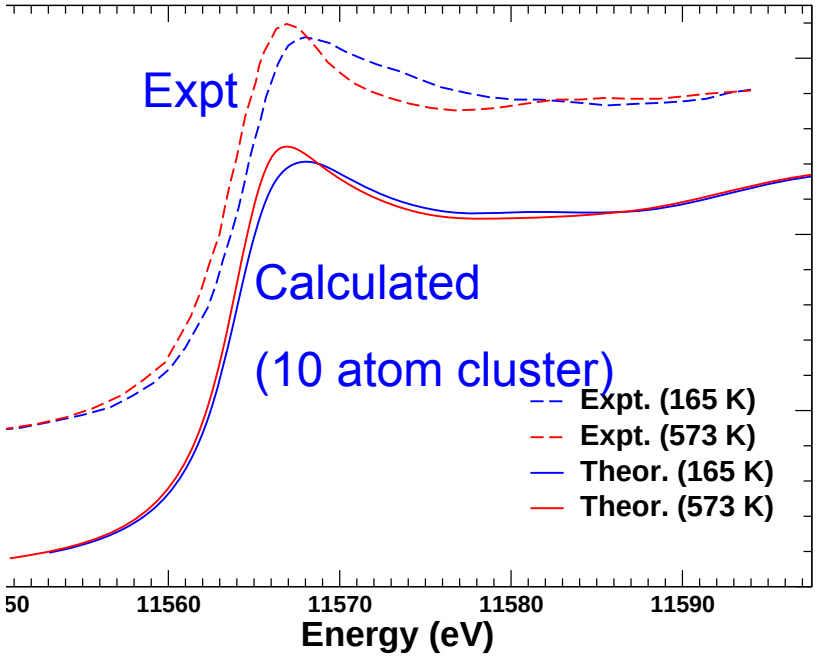
Accounts for ***dynamic structural fluctuations:***

vibrations, charge fluctuations, libration, …

Calculated PDF



RT-FEFF8 XAS Calculations



Cannot be treated as mean structure + Debye-Waller factors !

Conclusions II

Dynamic structure explains **all four** experimental observations:

Structural and spectroscopic

Novel interpretation

Librational & Hindered Brownian motion

Non-equlibrium behavior modeled well by real-time, finite temp DFT/MD

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That's all folks