X-Ray Science in the 21st Century

Calculations of X-ray Spectra in Real-space and Real-time

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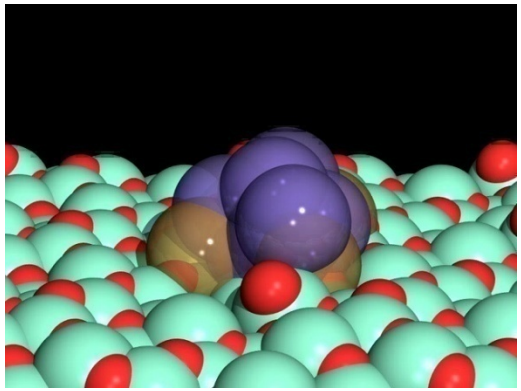
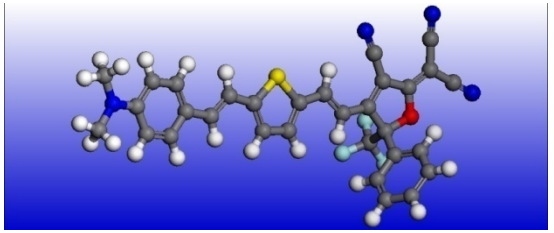
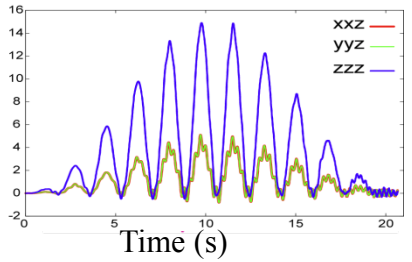






UNIVERSITY OF WASHINGTON

KITP, UCSB Aug 2-6, 2010

Calculations of X-ray Spectra in Real-space and Real-time

Goals: *Real-space & Real-time response beyond linear response & harmonic approx*

Talk: *Two approaches:*

- **I**. Linear & Non-linear Response RT-TDDFT

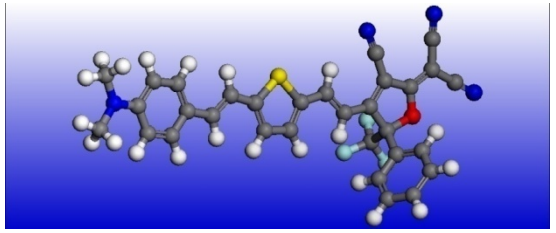
- **II.** Real space & time XAS of non-equlibrium system
  Finite Temperature DFT/MD + Real-Space Green's Function XAS

``If I can't calculate it,

I don't understand it."

R.P. Feynman

I. *Real-Space & Real-Time*
Linear and Non-linear Response

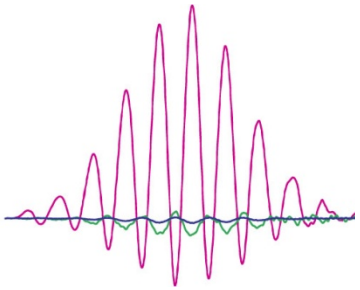


- Difficulty: frequency-space is computationally demanding - **too-many** excited states

- Strategy: extend RT-TDDFT/ SIESTA approach*

*Sanchez-Portal, Tsolakidis, and Martin, Phys. Rev. B**66**, 235416 (2002)

Approach I*:* RT-TDDFT



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]

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

RT-TDDFT Formalism

- 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 !

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

Real time *Linear* Response

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

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

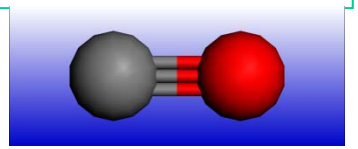
$$\chi_{ij}^{(1)}(\omega) = \delta p_i(\omega) / E_j(\omega) = \alpha_{ij}(\omega)$$ Linear Response Function

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

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

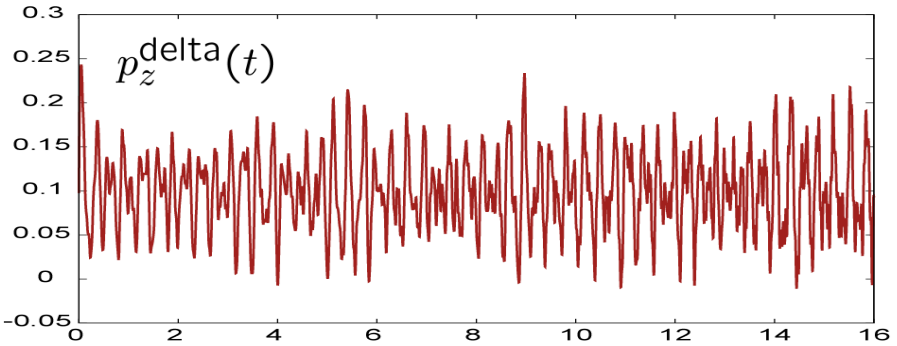
Example: CO Linear Response

$p_z(t)$ response due to applied $E_z(t)$

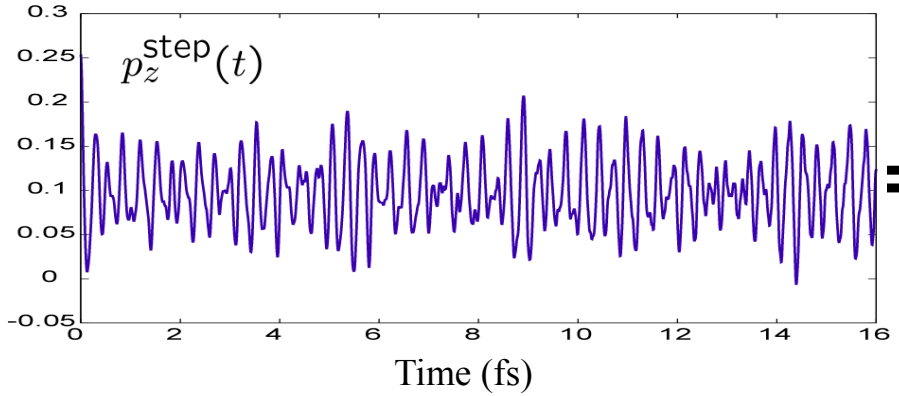


- Delta Function

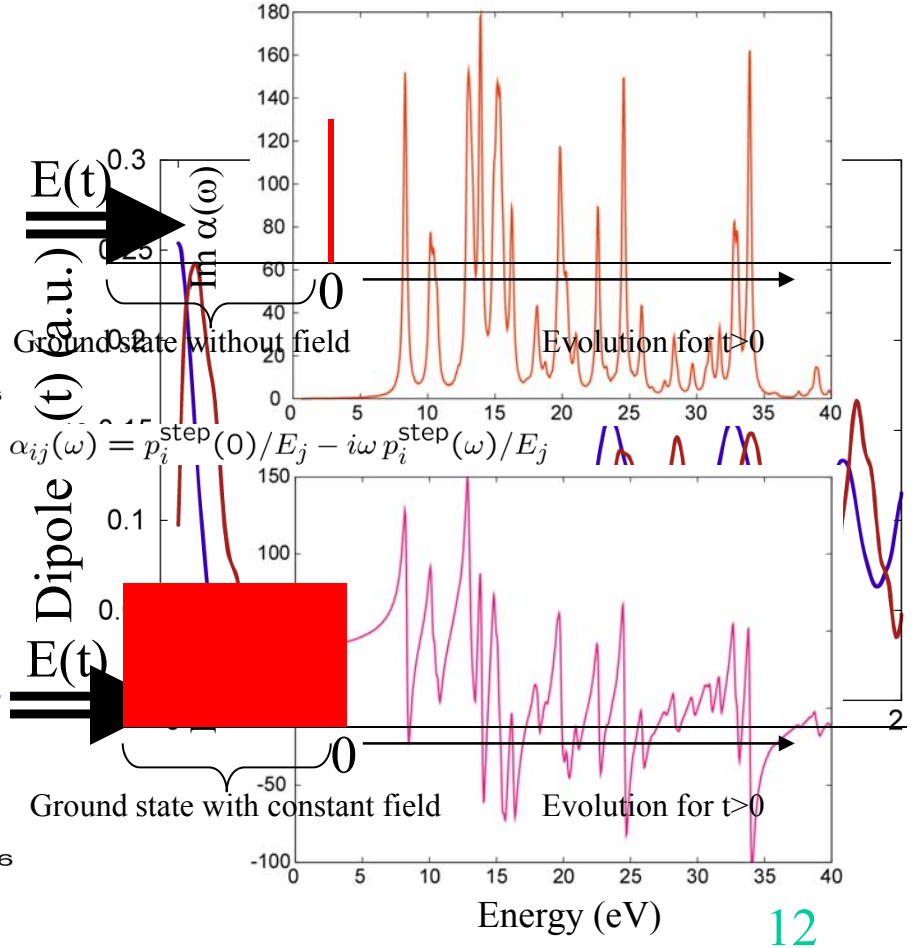
(Unit Impulse at *t=0*)



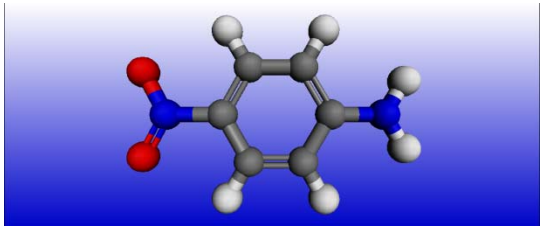
(Turn-off Constant E at *t=0*)



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



Example: Small molecule p-Nitroaniline (pNA)



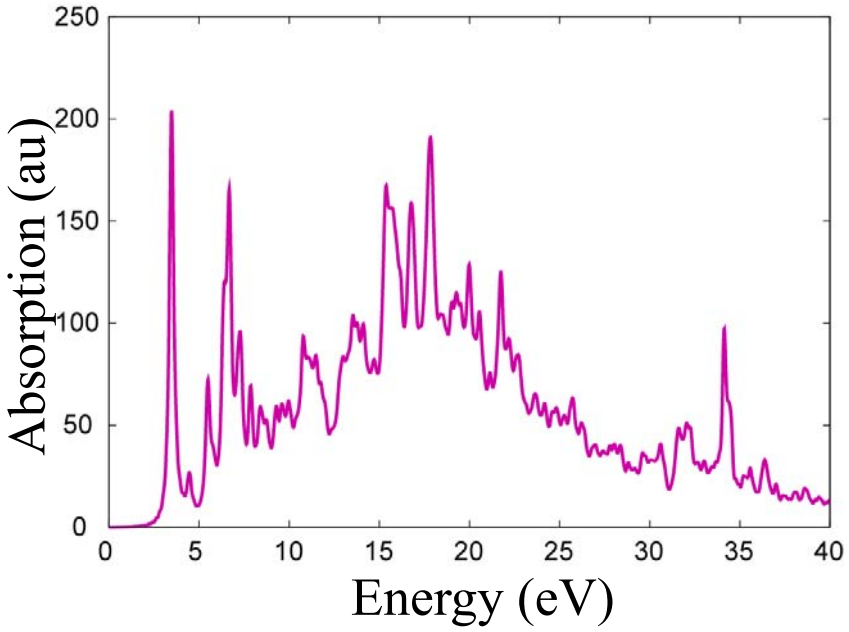
- Linear absorption

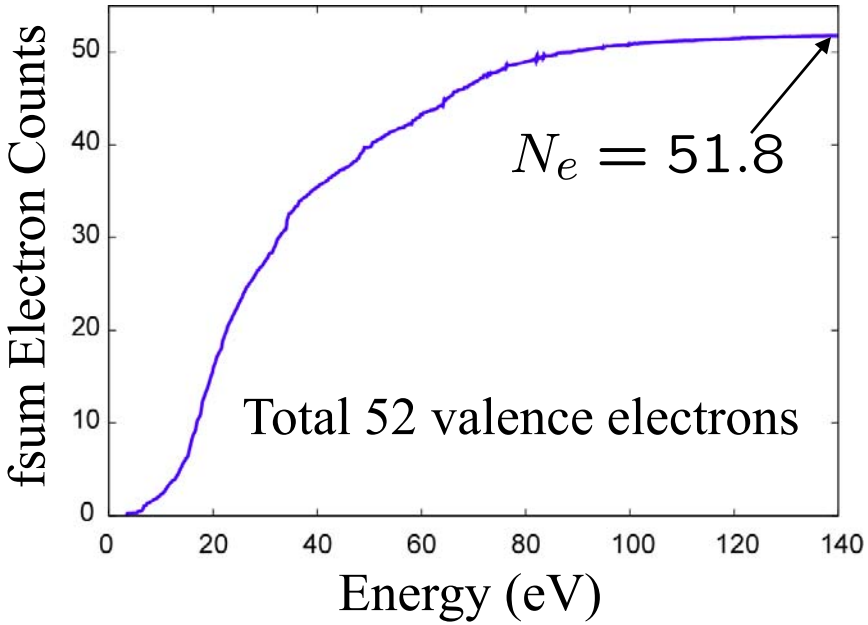
- Sum rule

$\lambda_0 = 356\text{nm}$

$\omega_0 = 3.49\ \text{eV}$

$\lambda_0^{\text{exp.}} = 347\text{nm}$
(in chloroform)



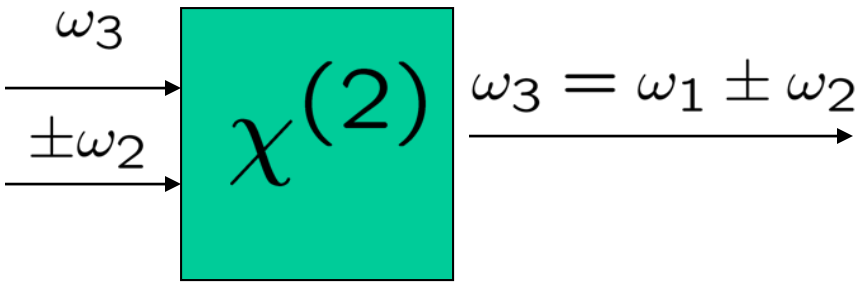


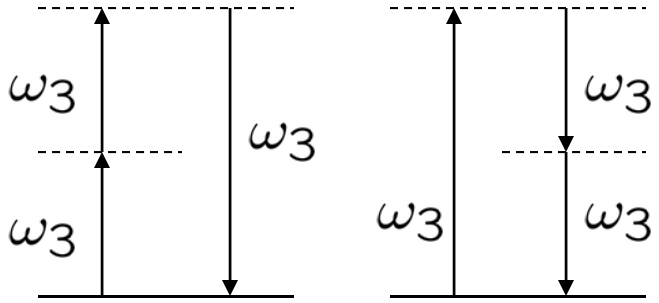
$$\int_0^\infty d\omega\, S(\omega) = \lim_{\omega\to\infty} f_{\text{sum}}(\omega) = \sum_i f_i = N_e,$$

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)

Extraction of Static Nonlinear Polarizabilities

- Standard technique: *static* nonlinearity

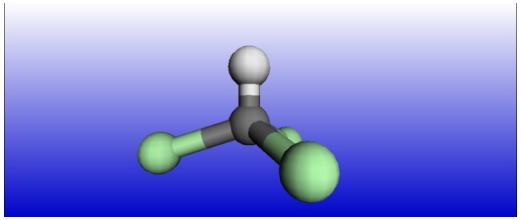
$$p_i = \mu_i^0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \cdots$$

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

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

Example: Static $CHCl_3$ Hyperpolarizability*

Difficult case: β very small!



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]

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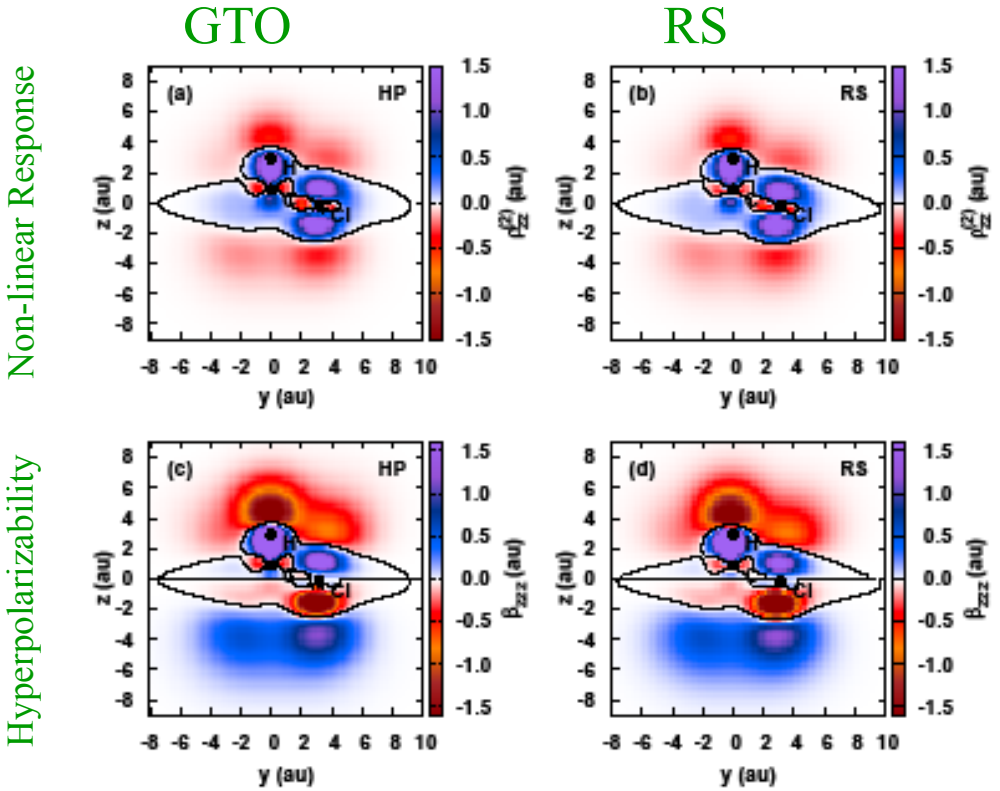
(Dated: October 26, 2009)

*J. Chem Phys **133**, 034111 (2010)

3 methods

All agree with large diffuse basis sets!

Local Response Densities



Note: Contributions from CI and HC are of **opposite sign** – **Explains smallness of β**

Real time Dynamic 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?

Dynamic Nonlinear Polarizabilities

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

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

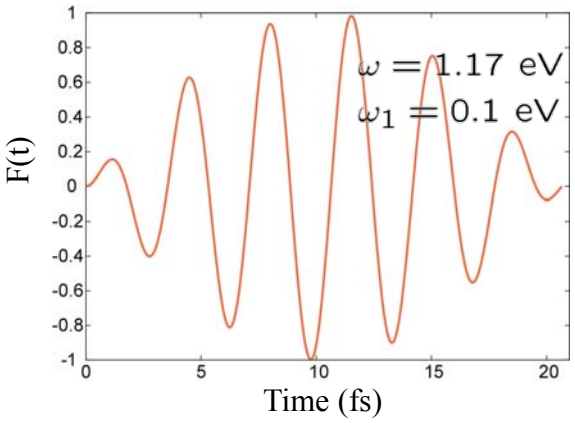
where $p^{(1)}$ yields linear response, $p^{(2)}$ first non-linear (quadratic) response, ….

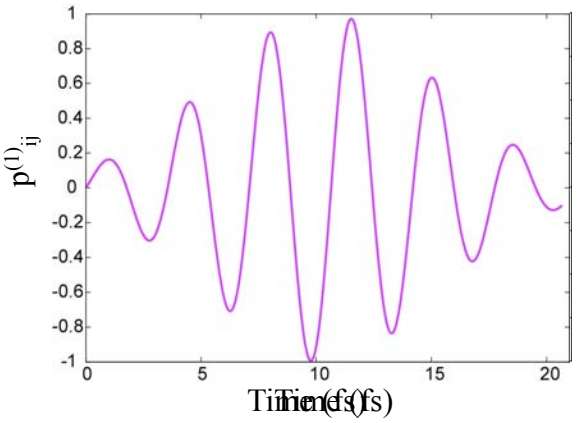
- Quadratic response $\chi^{(2)}$

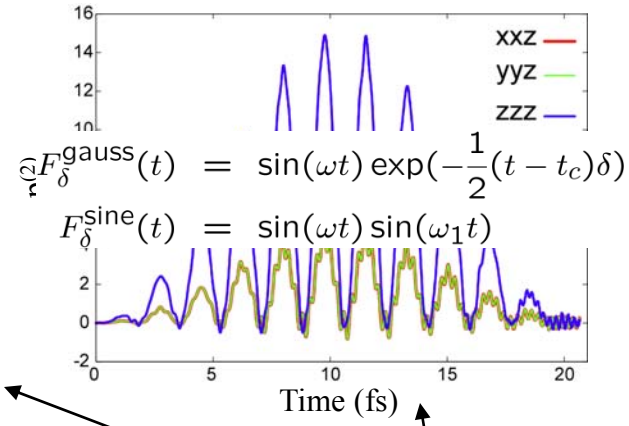
$$p_{ijk}^{(2)}(t) = \int dt_1 \int dt_2 \; \chi_{ijk}^{(2)}(t - t_1, t - t_2)F(t_1)F(t_2)$$

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

- Sine wave enveloped by another sine wave or Gaussian





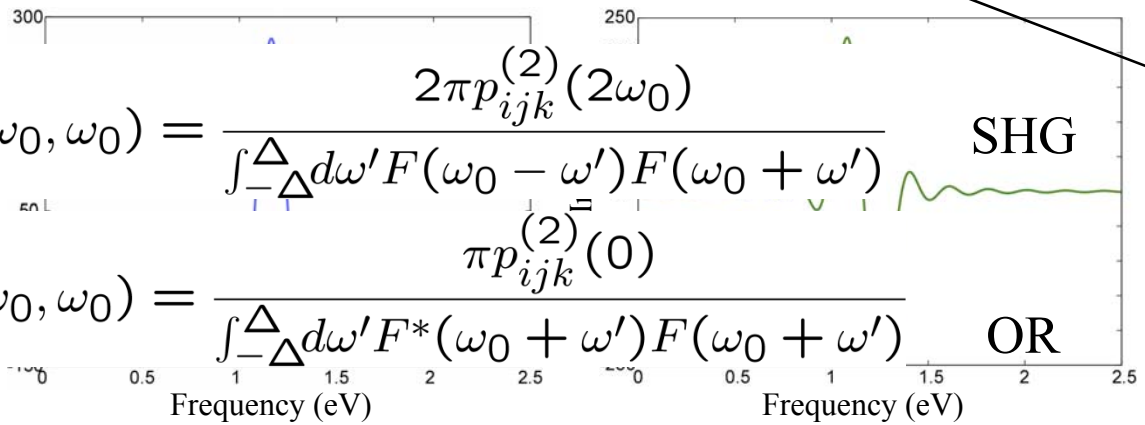


$$\chi^{(2)}_{ijk}(-2\omega_0;\omega_0,\omega_0) = \frac{2\pi p^{(2)}_{ijk}(2\omega_0)}{\int_{-\Delta}^{\Delta} d\omega' F(\omega_0-\omega')F(\omega_0+\omega')}$$

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



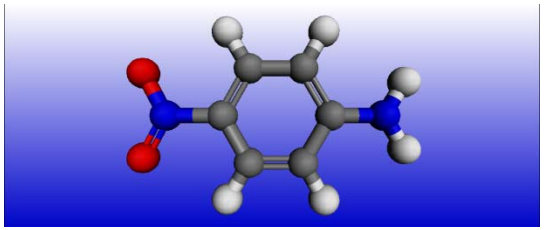
Linear and Nonlinear response of CO

Real time vs Frequency space Nonlinear Response

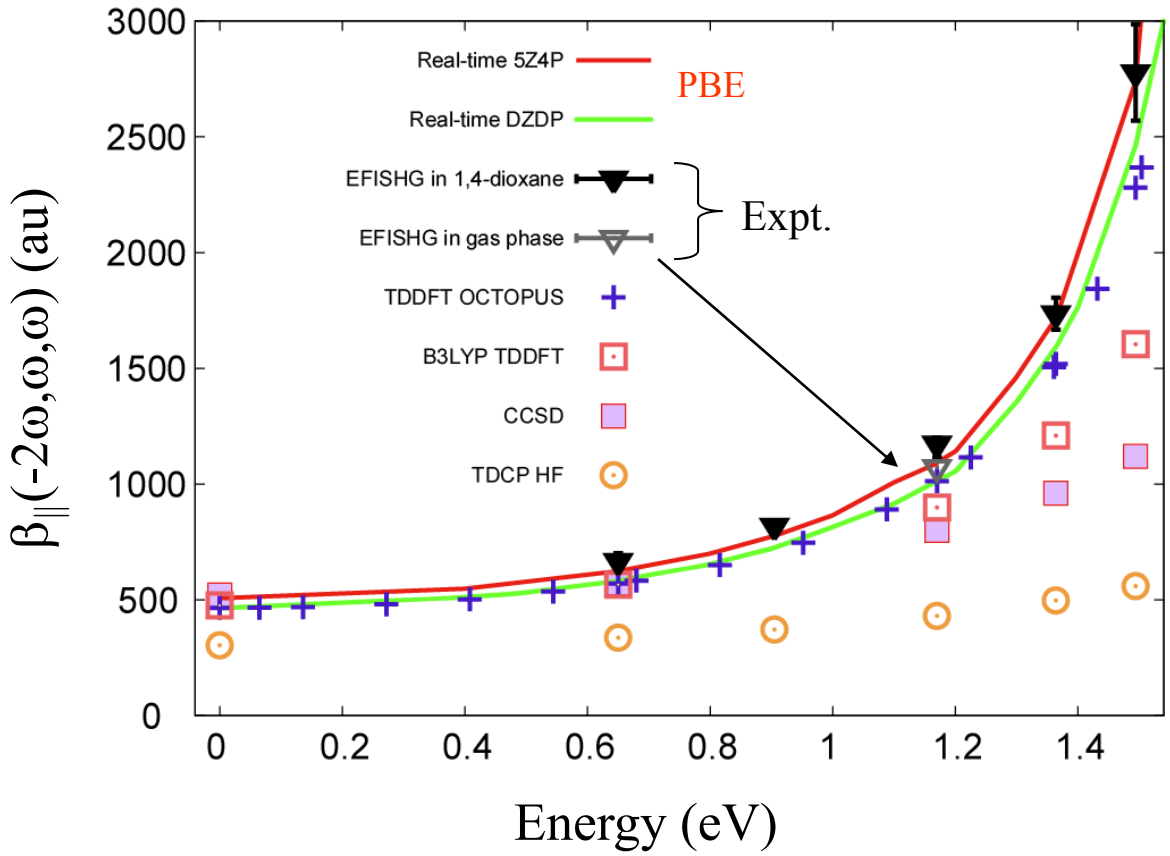
- Operation cost
  - Sternheimer equation (frequency space)
  - Real time $\mathcal{O}(N_{\mathsf{KS}}^2\, N_{\mathsf{basis}}\, M_{\mathsf{iterations}}\, M_\omega)$
- Memory cost $\mathcal{O}(N_{\mathsf{KS}}\, N_{\mathsf{basis}}\, N_{\mathsf{evolve}}\, M_{\mathsf{steps}}\, M_\omega)$
  - Sternheimer equation (frequency space)
  - Real time $\mathcal{O}((N_{\mathsf{occ}} + N_{\mathsf{unocc}}) N_{\mathsf{basis}})$

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

Example pNA: *Nonlinear SHG*

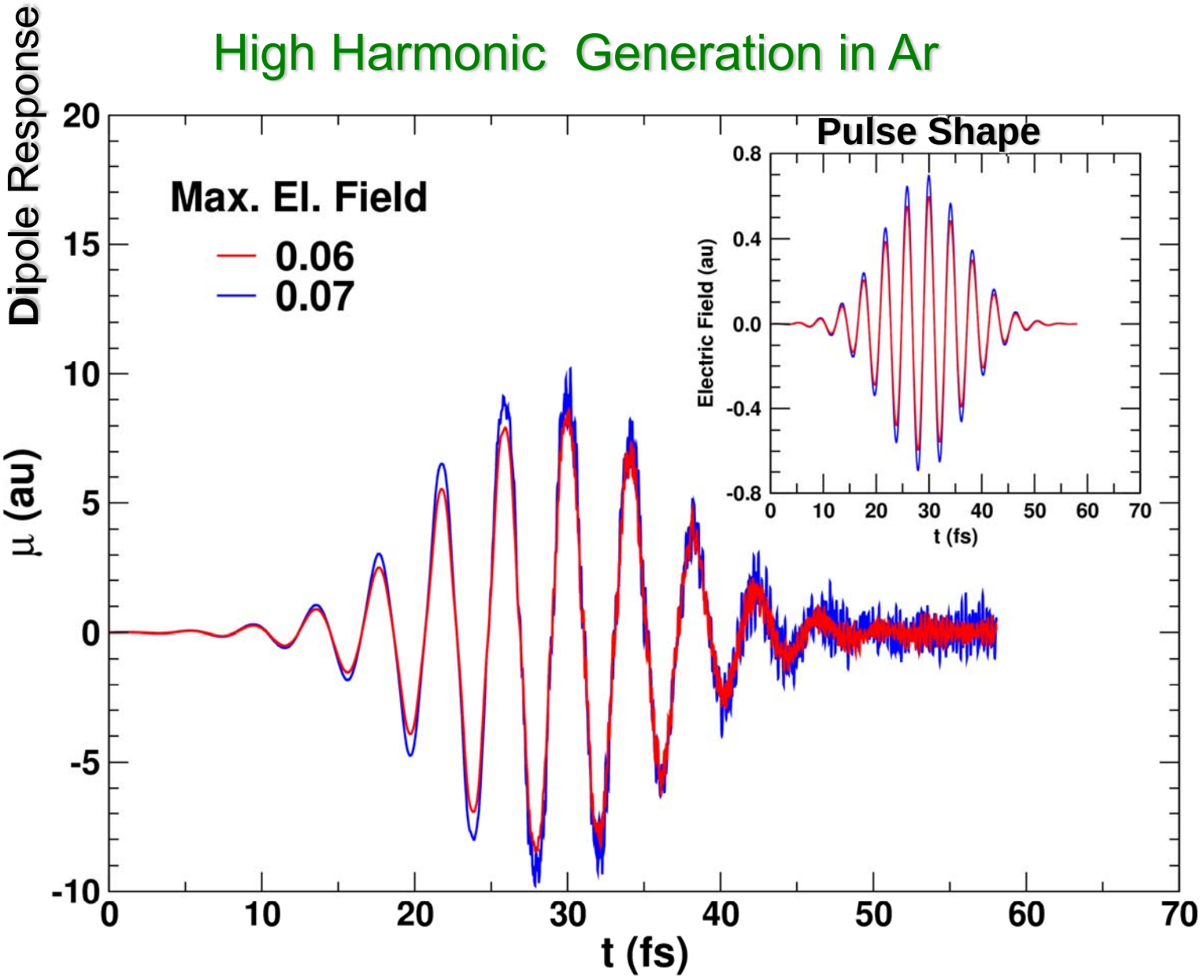


- Comparison with other methods



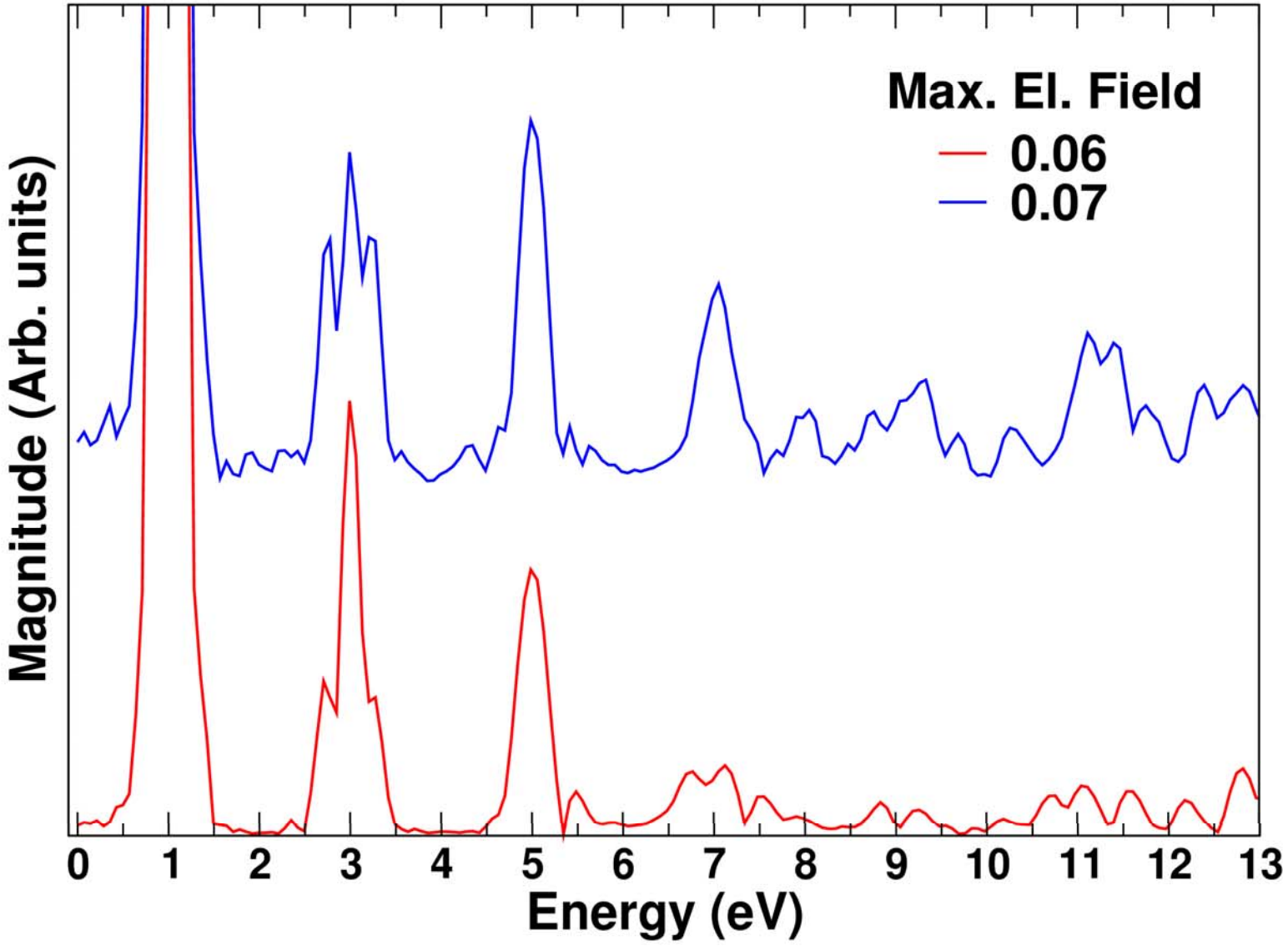
Extension to high fields:

High Harmonic Generation in Ar



RT-TDDFT High Harmonic Generation in Ar

Odd Harmonic Magnitude



II. Real-space & Real-time calculations of X–ray Response*

Dynamic structure in supported Pt nanoclusters

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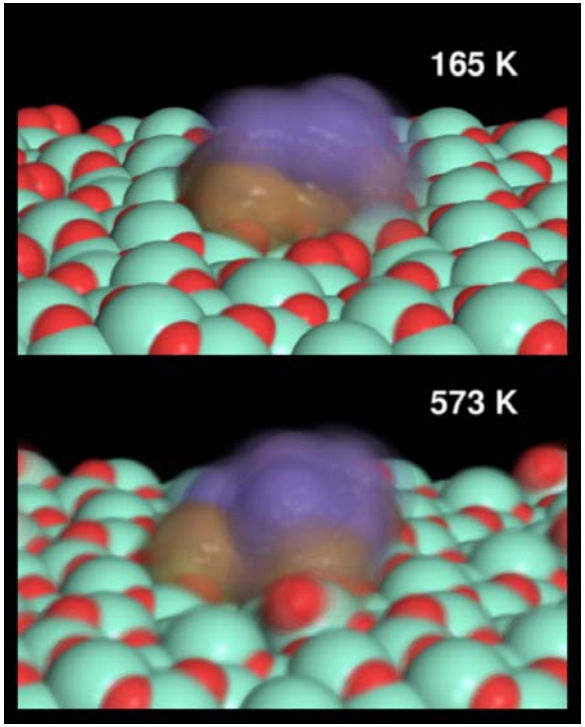
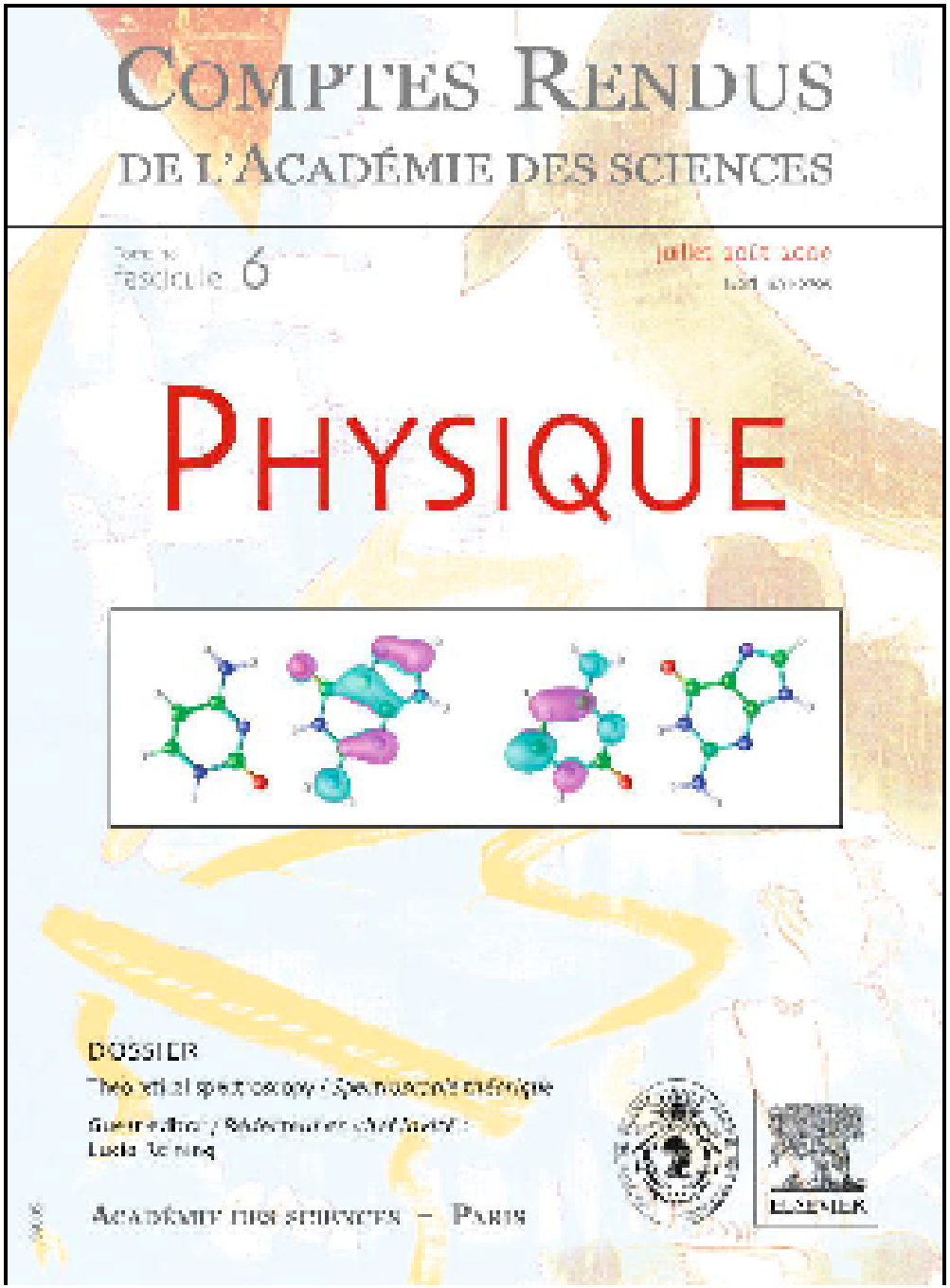
(Dated: May 20, 2008)

The nature of local atomic and electronic structure at the nano-scale is both of fundamental and technological importance. For example, supported metal nanoclusters exhibit a number of unusual phenomena including large structural disorder and bond-length contraction with increasing temperature. We investigate this behavior for a prototypical 10-atom Pt cluster supported on γ-alumina using temperature-dependent, real-time simulations based on density functional theory/molecular dynamics and x-ray spectroscopy theory. The simulations reveal a complex dynamical structure on multiple-time scales including librational motion of the center of mass and fluctuating bonding - characteristics which explain many of the unusual properties.



*Phys Rev B, Rapid Commun. **78**, 121404(R), (2008)



Real-space Green's Function theory

XAS, XES, IXS, XMCD…

FEFF9

JJR et al., Comptes Rendus Physique **10**, 548 (2009)

in Theoretical Spectroscopy
L. Reining (*Ed*) (2009)

Wave-function vs Green's functions

Paradigm shift:

Use Green's functions *not* **wave functions!**

- Golden rule via Wave functions

$$\mu(E) \sim \Sigma_f |\langle i|\hat{\epsilon}\cdot\mathbf{r}|f\rangle|^2 \delta(E-E_f)$$

- Golden rule via Green's functions *Efficient!*

Theorem: $-\frac{1}{\pi}\mathrm{Im}\, G(\mathbf{r}',\mathbf{r},E) = \Sigma_f |f\rangle\delta(E-E_f)\langle f|$

$$\mu(E) \sim -\frac{1}{\pi}\mathrm{Im}\,\langle \mathrm{i}|\,\hat{\epsilon}\cdot\mathbf{r}'\,\mathrm{G}(\mathbf{r}',\mathbf{r},\mathrm{E})\,\hat{\epsilon}\cdot\mathbf{r}\,|\mathrm{i}\rangle$$

FAST! Parallel Computation FEFFMPI

PHYSICAL REVIEW B, VOLUME 65, 104107

Parallel calculation of electron multiple scattering using Lanczos algorithms

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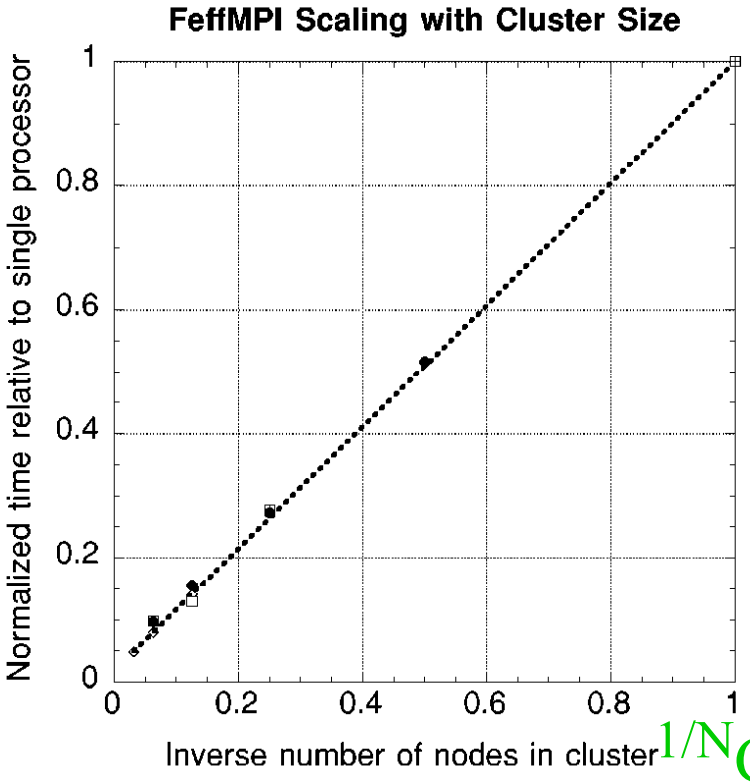
[2]*National Institute of Standards and Technology, Gaithersburg, Maryland 20899*



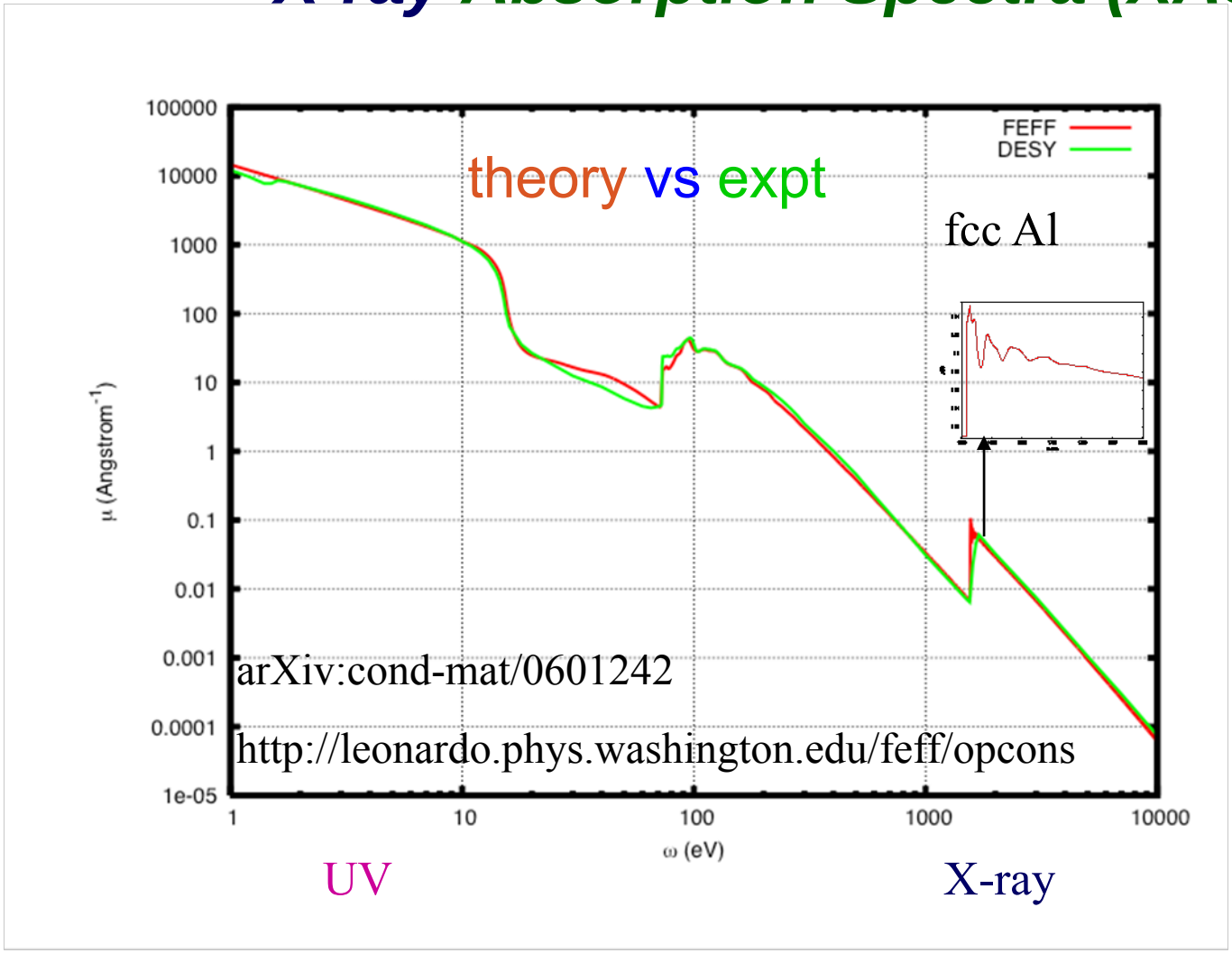
MPI: "Natural parallelization"

Each CPU does few energies

Lanczos: Iterative matrix inverse

$1/N_{CPU}$

Experiment vs Theory: Full spectrum
X-ray Absorption Spectra (XAS)



Photon energy (eV)

Example: Finite T Nano-scale Pt Clusters

MYSTERY: Unusual properties of

Pt_{10} /γ-Al_2O_3

Negative thermal expansion,

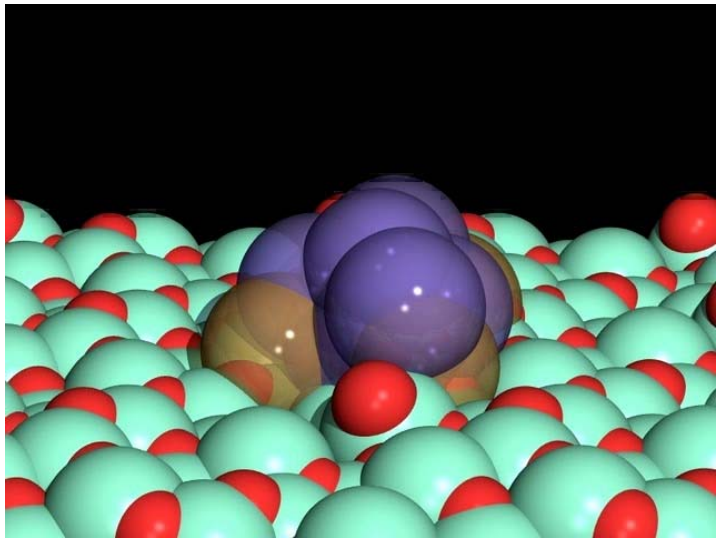
large disorder, …

Goals: Understand structure

Explain ***all*** properties

Method: Real-time DFT/MD

Pt_{10} Cluster on [110] γ-Al_2O_3

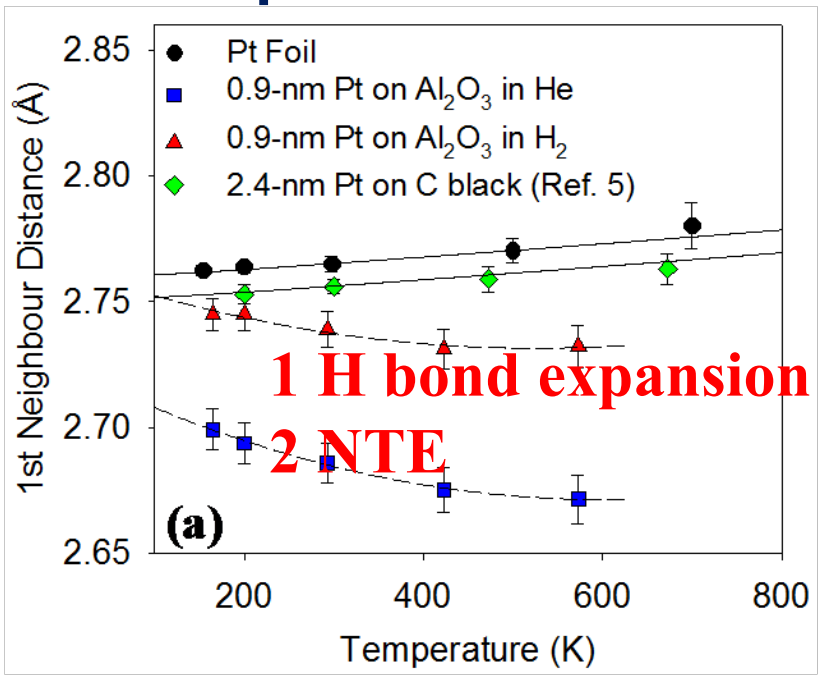


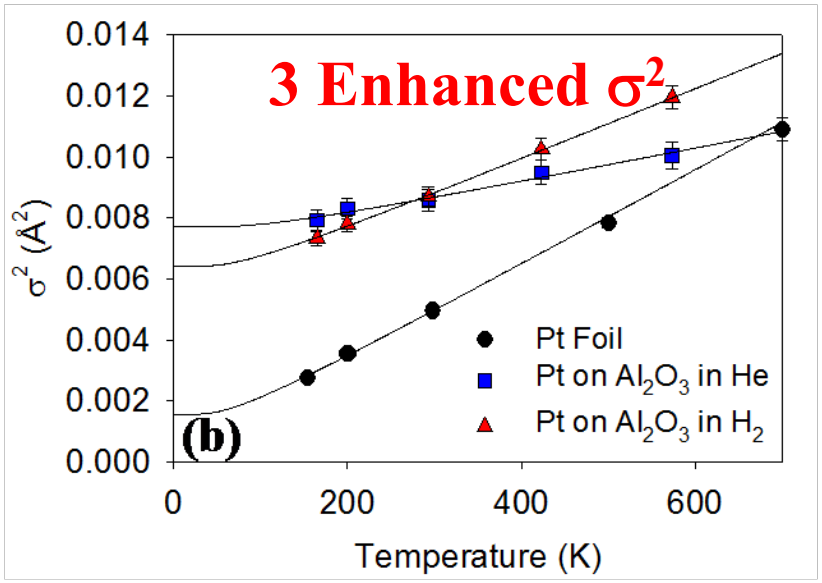
metallic Pt oxidized Pt

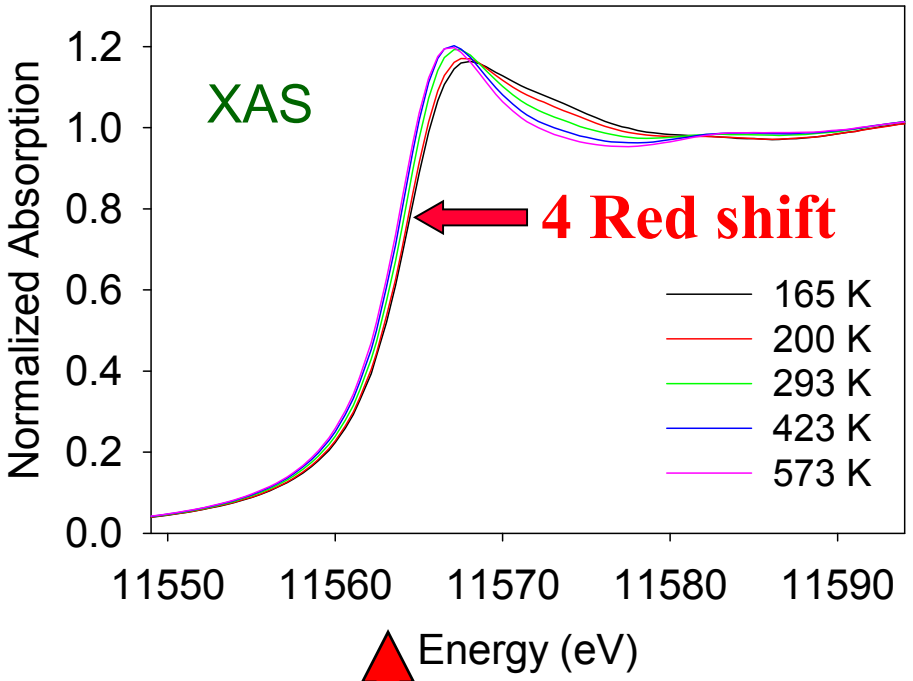
Al O

Alternative to conventional paradigm!

Experimental Observations (X-ray Absorption Expt)*







4 Anomalies

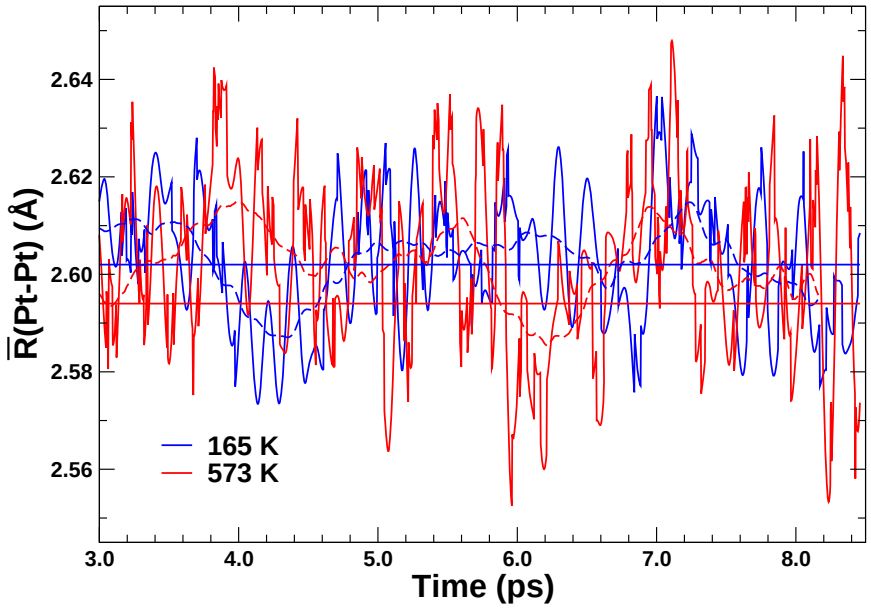
*Kang, Menard, Frenkel, Nuzzo., JACS Commun. 128, 12068 (2006)

Calculation – Finite-T DFT/MD

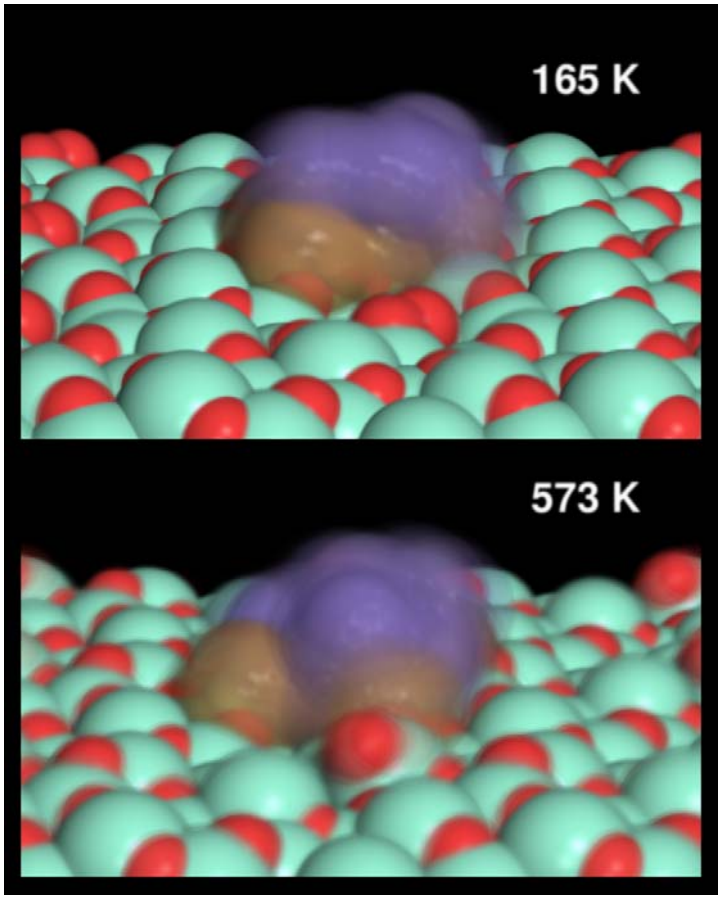
Non-equlilibrium Finite temperature

10 atom Pt/ γ-Al_2O_3

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



NTE



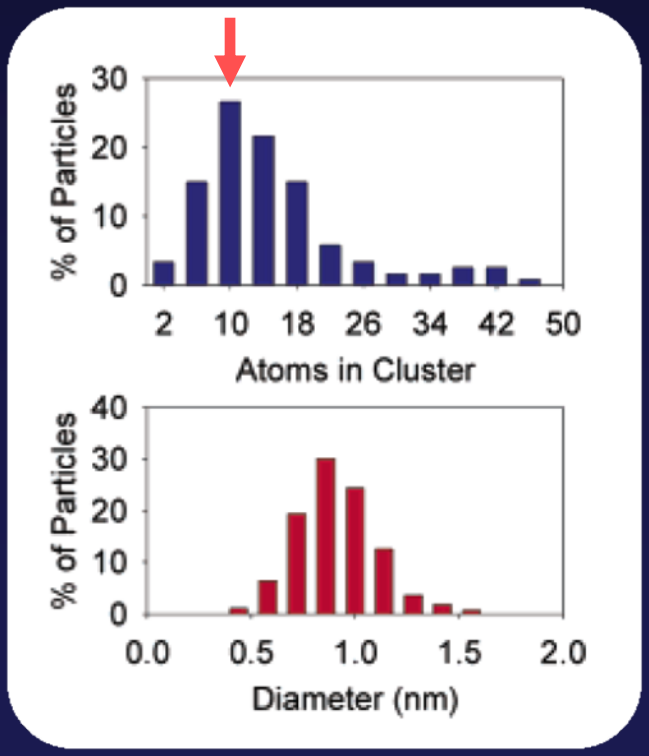
2500 3 fs steps

~ 10^4 cpu-hrs (VASP)

time-elapsed rendering

Computational Details

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



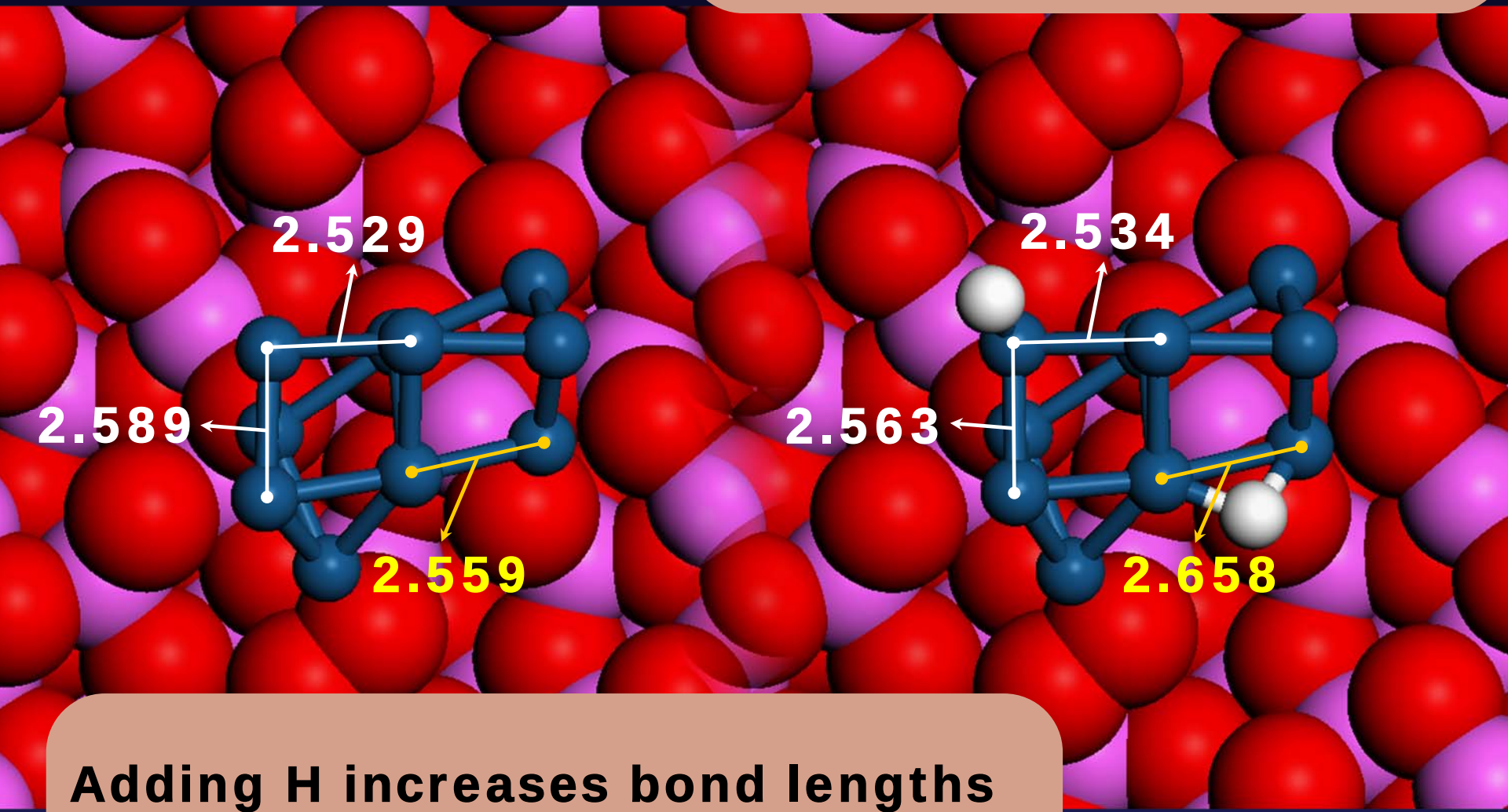
DFT / MD

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

XAS

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

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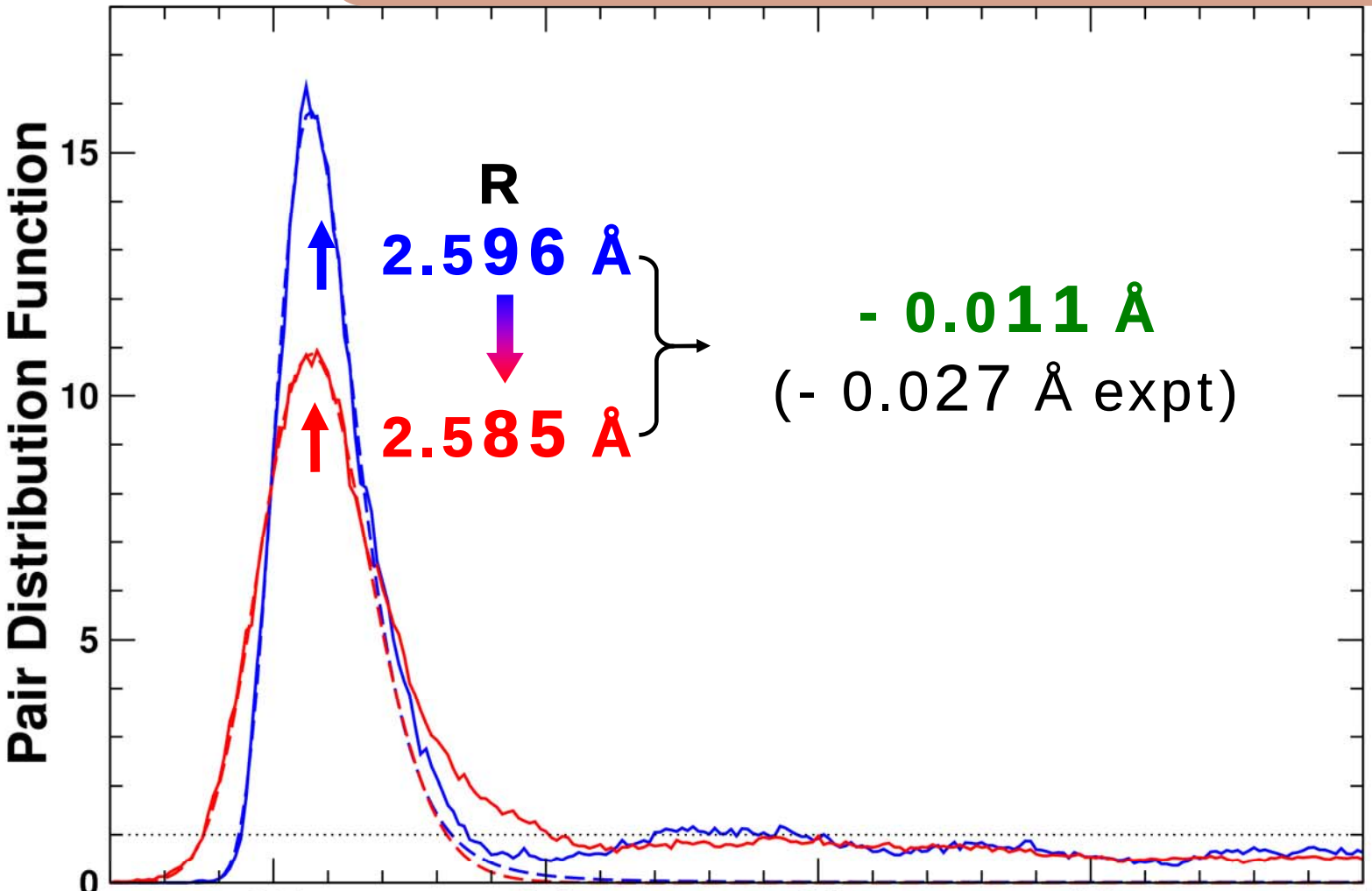
❷ Negative Thermal Expansion



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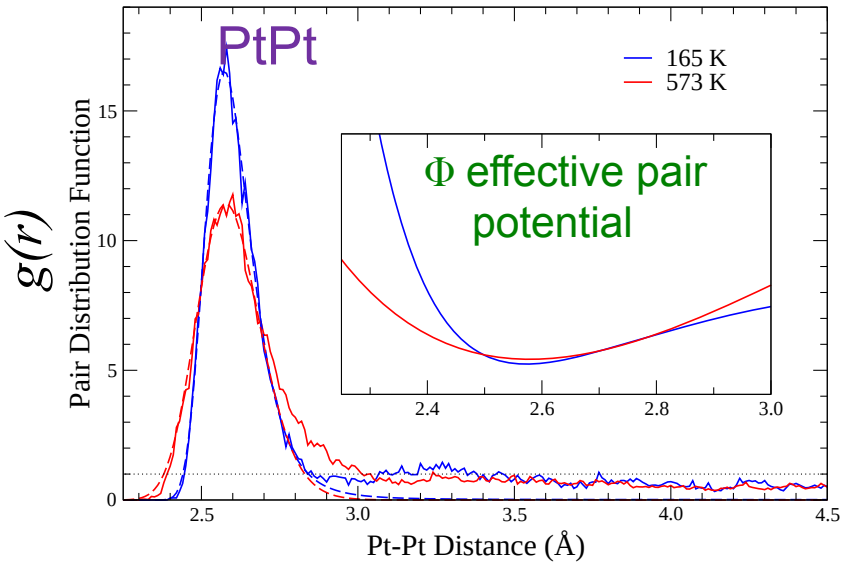
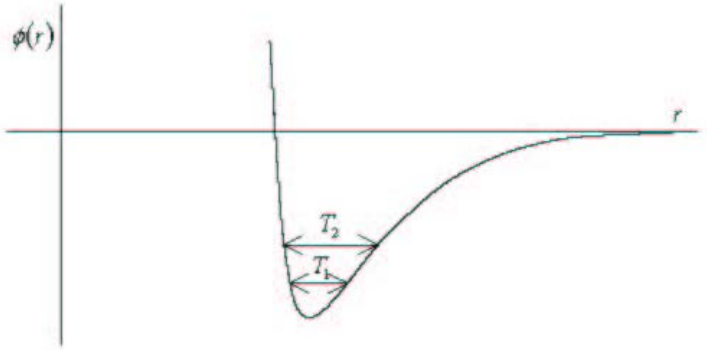
Morse-potential Fits to PDFs



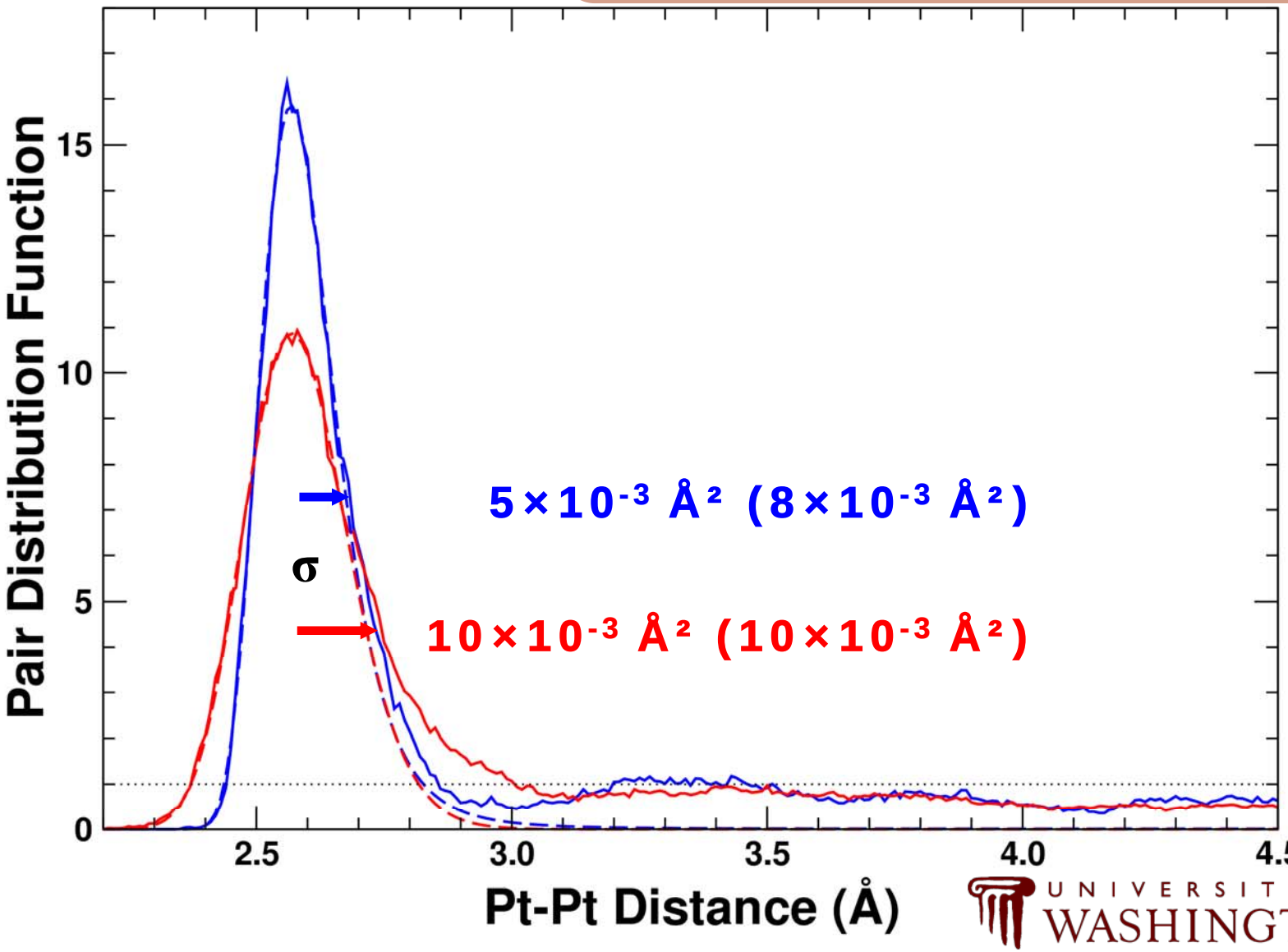
Note: increased low r width at HT implies PDF is ***non-vibrational.***

$$g(r) = Ae^{-\Phi(r)}$$

$$\Phi(r) = \beta D\left[e^{-\alpha(r-r_0)} - 1\right]^2$$



❸ High Pt-Pt Disorder



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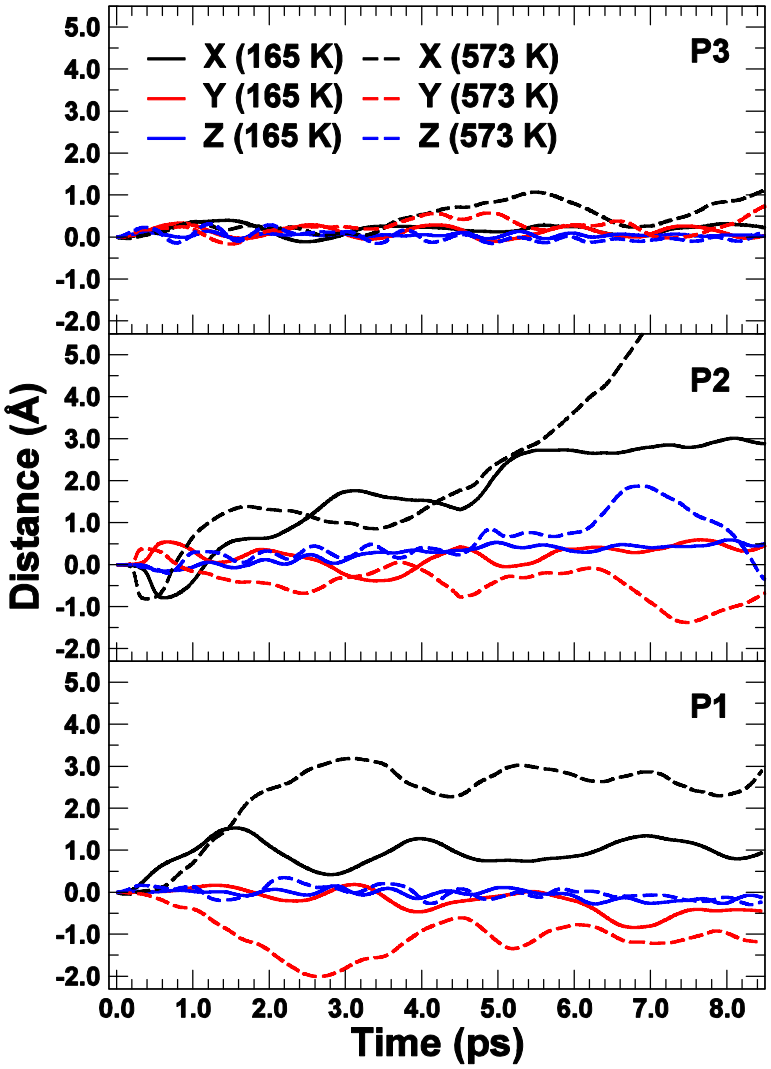
Physical Interpretation

Center of Mass Motion

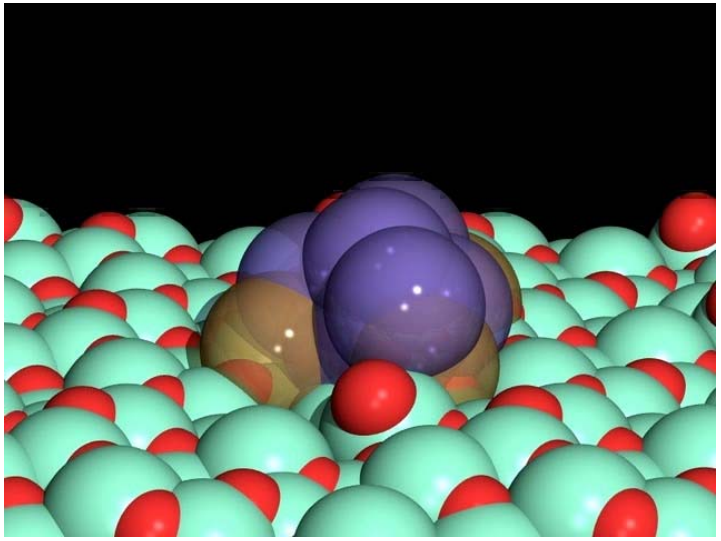
Librational motion of center of mass

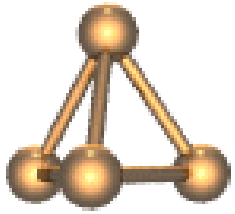
Period ~ 2 ps
Amplitude ~ 1 Å

Hindered Brownian motion

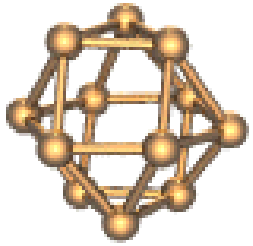


Librational motion





$Co_4(CO_{12})$

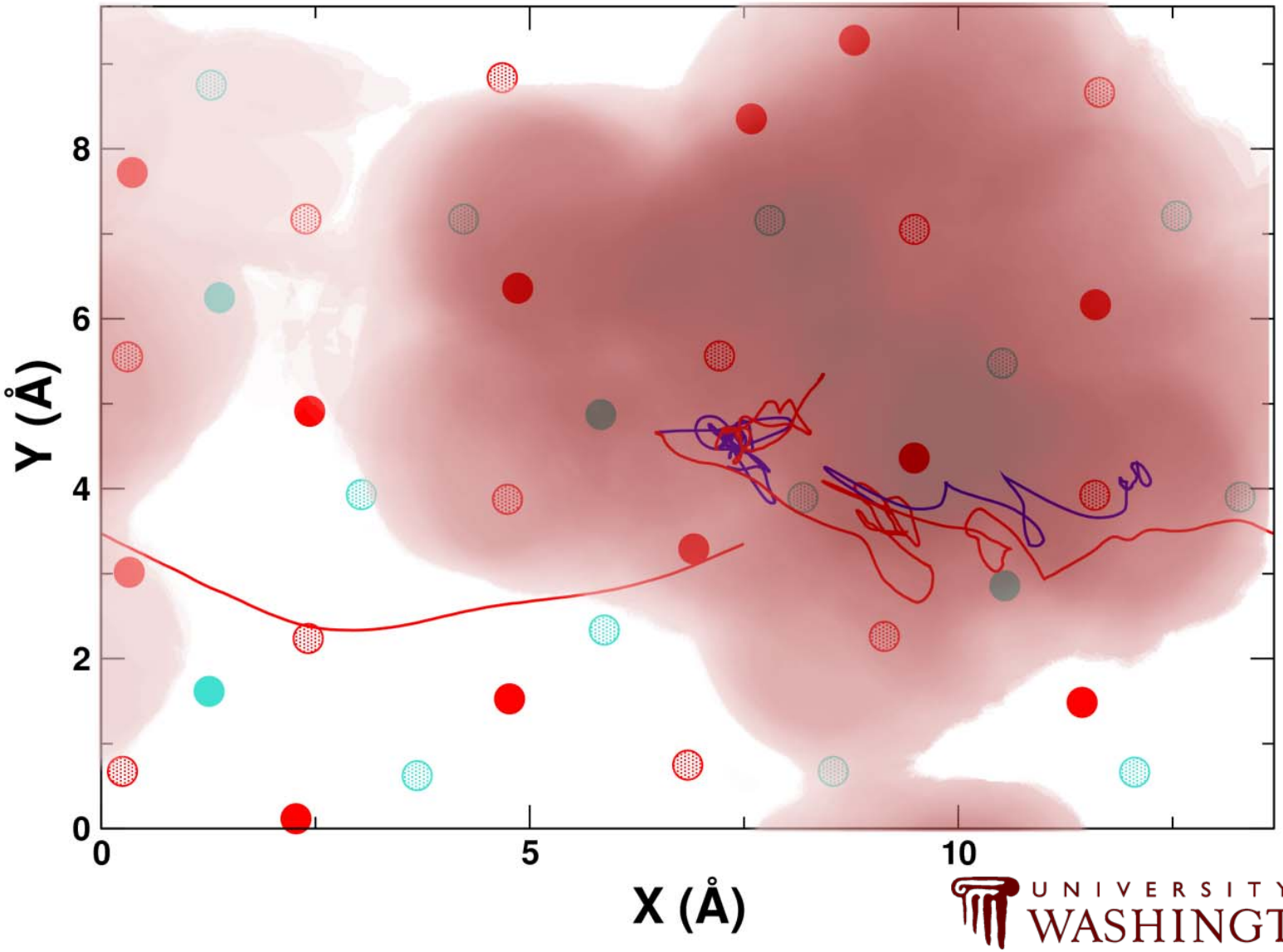


Fluxional behavior in tetrahedral clusters with carbonyl ligands

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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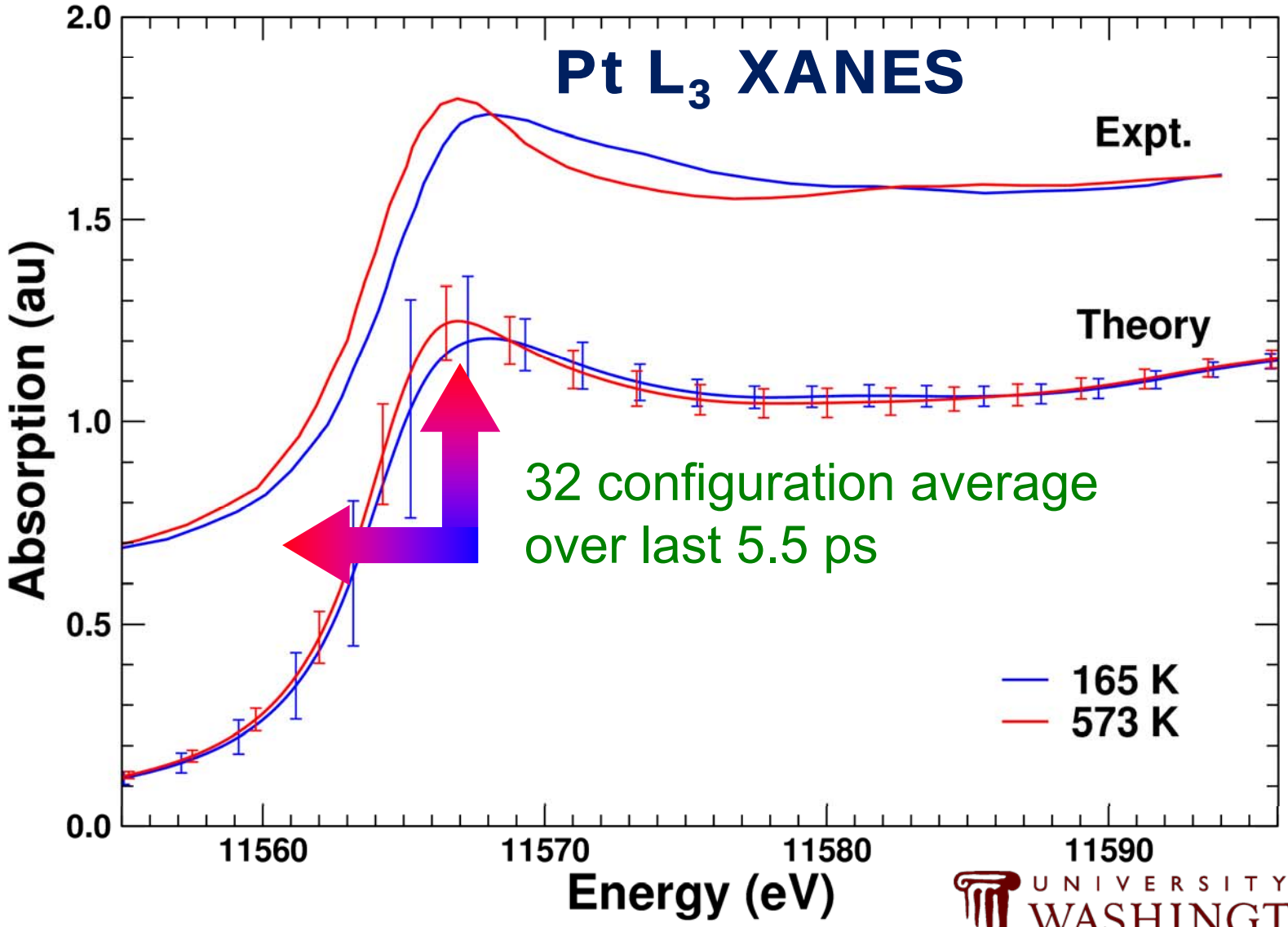
❹ Increased intensity and redshift at high T



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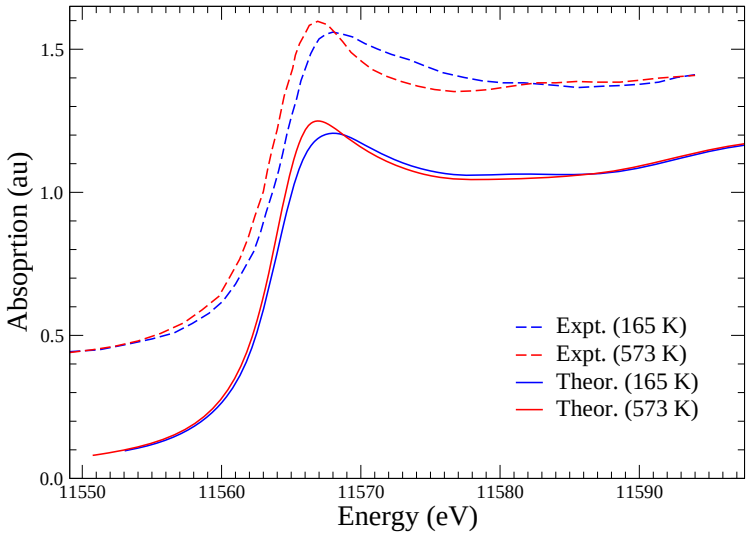
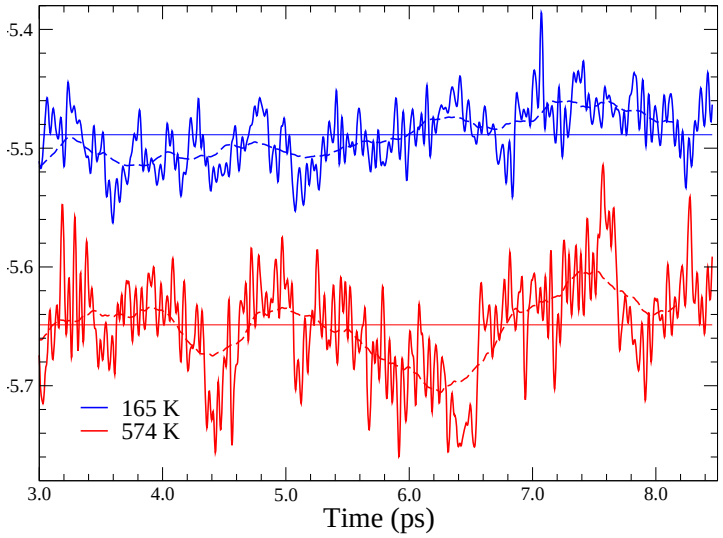
Interpretation of *red shift:*

Charge fluctuations due to transient bonding



Fermi energy vs time



Surface Pt-O bonds & charge fluctuate!

Conclusions

1. RT-TDDFT explains linear and non-linear response & high harmonic generation

Challenge: extension to core-XAS

(e.g. time-correlation function methods - in progress …)

2. RT-DFT/MD + RSGF XAS explains dynamic structure & experimental XAS of Pt nanoclusters

Novel nano-scale behavior: Brownian-like motion

Challenge: Extension to Faster, Hotter, Denser …

Acknowledgments

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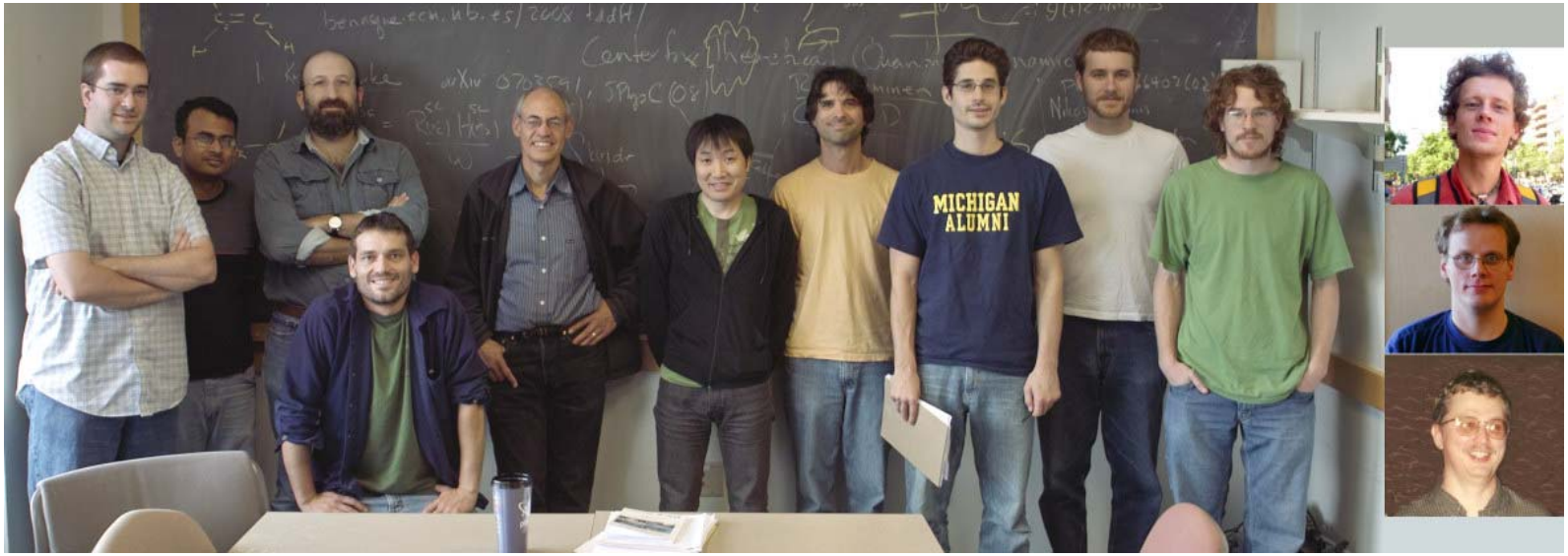
A. Frenkel (Yeshiva)
R. Nuzzo (UI)
R. Albers (LANL)



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That's all folks