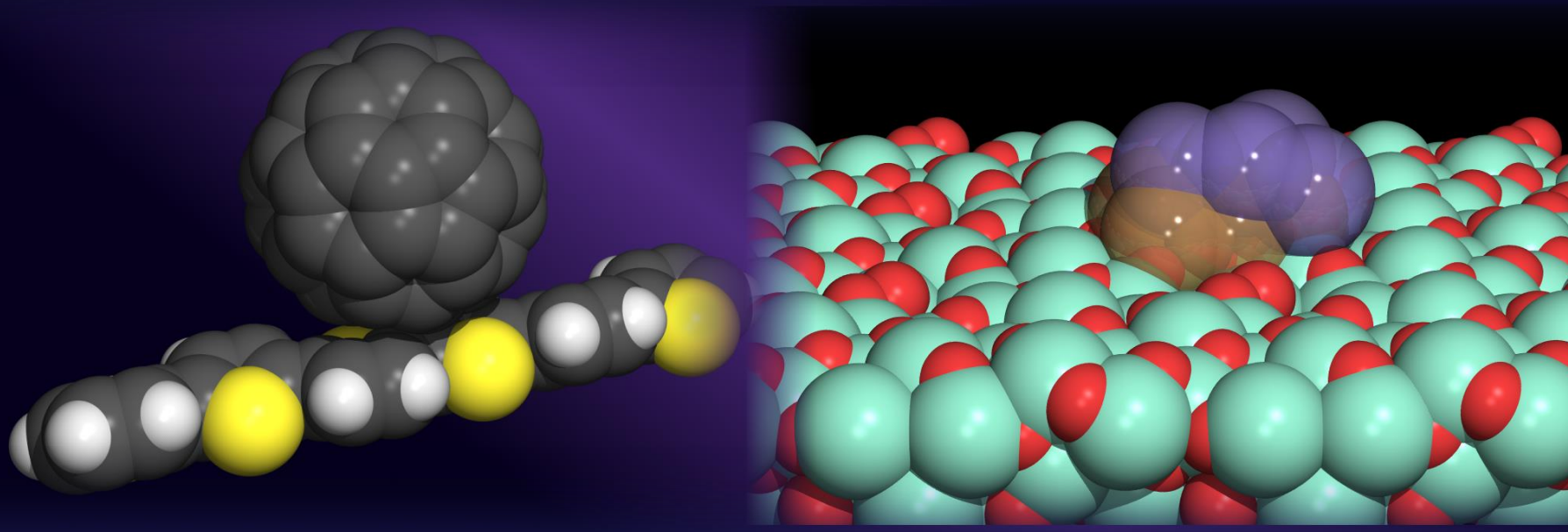
Real-Space and Real-Time Approaches for Energy-Related Materials



F. Vila

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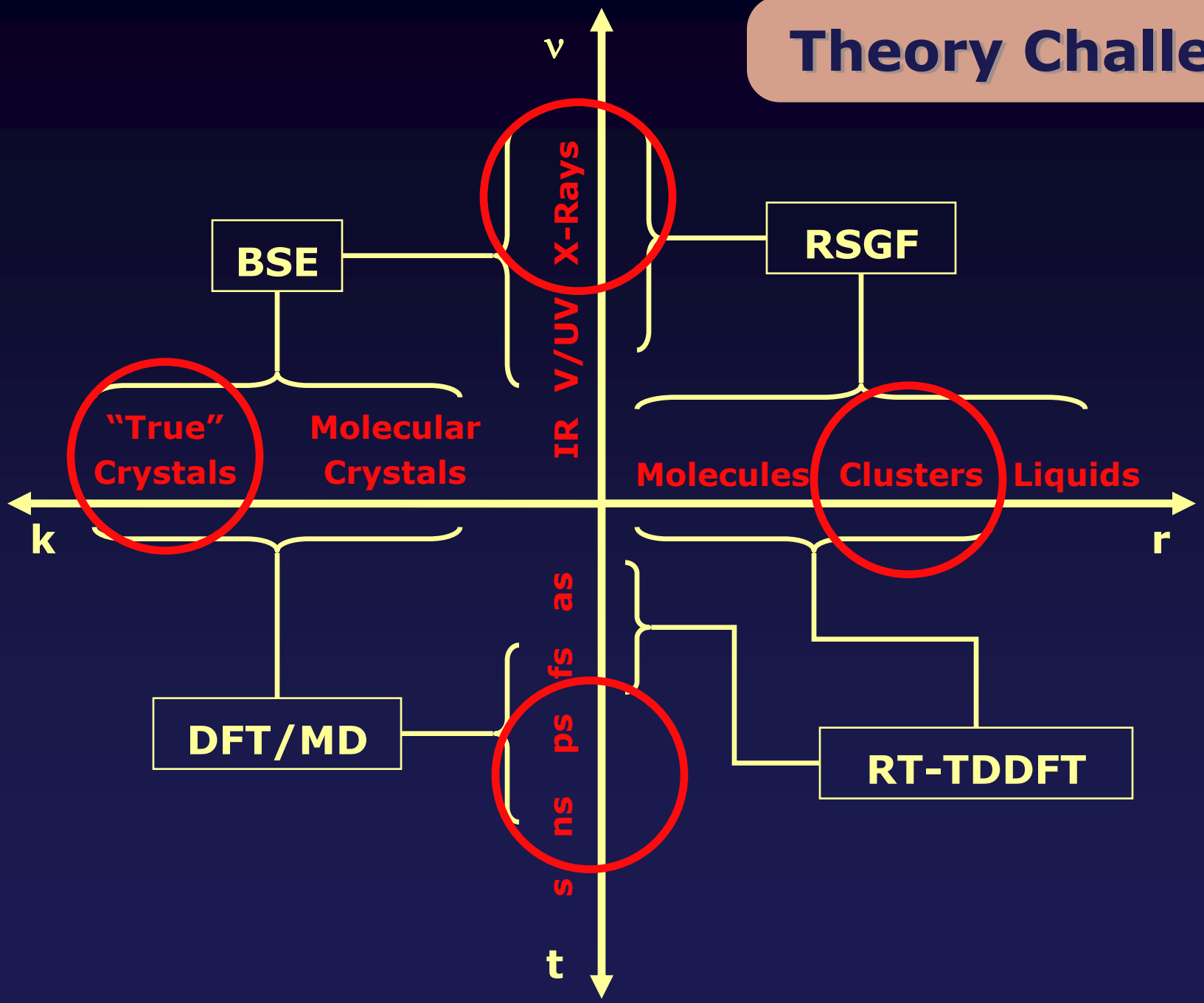
ALS Users Meeting
October 2009

Theory Challenges



Outline

Dynamic Structure in Pt Nanoclusters on γ–Al_2O_3

Vila *et al.* Phys. Rev. B 78, 121404(R) (2008)

Optical Properties of a Model Organic Photovoltaic Device

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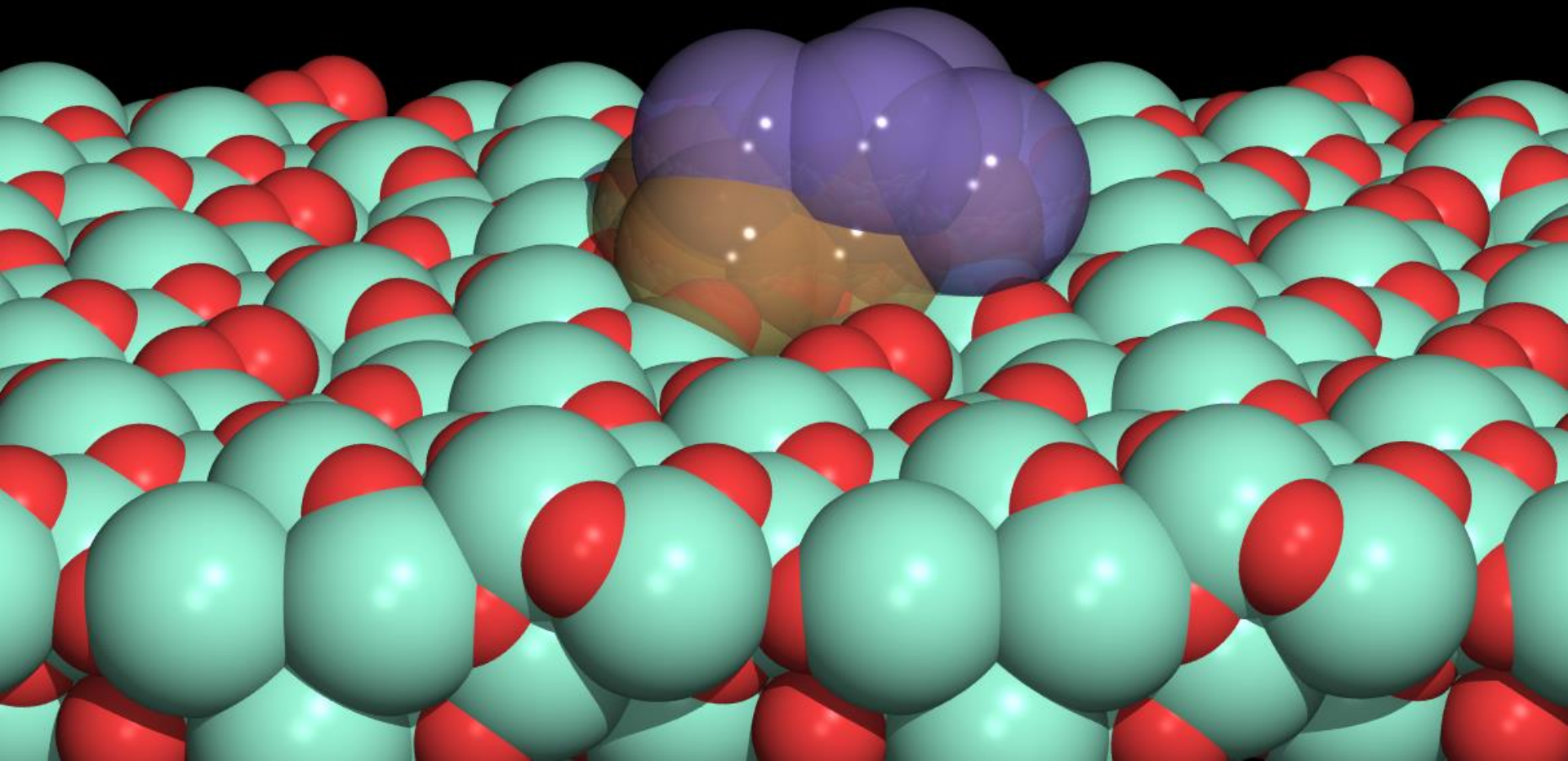
Dynamic Structure in Pt nanoclusters on γ–Al_2O_3



The Problem

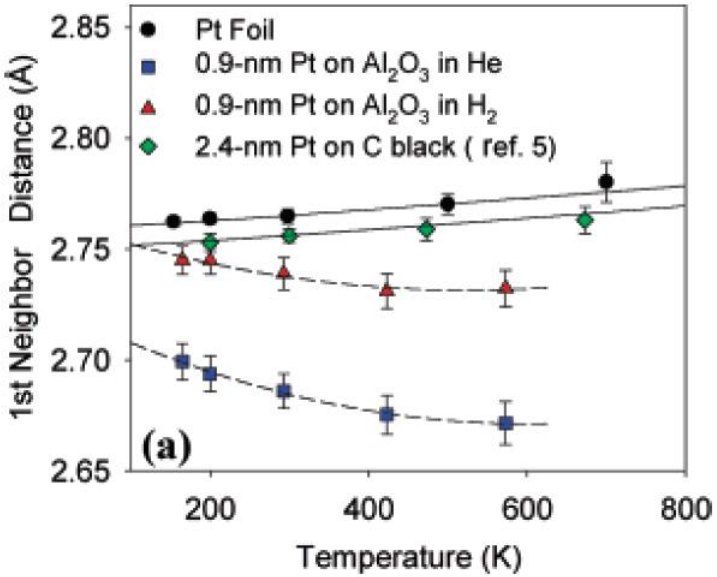
Kang *et al.* JACS 2006, *128*, 12068

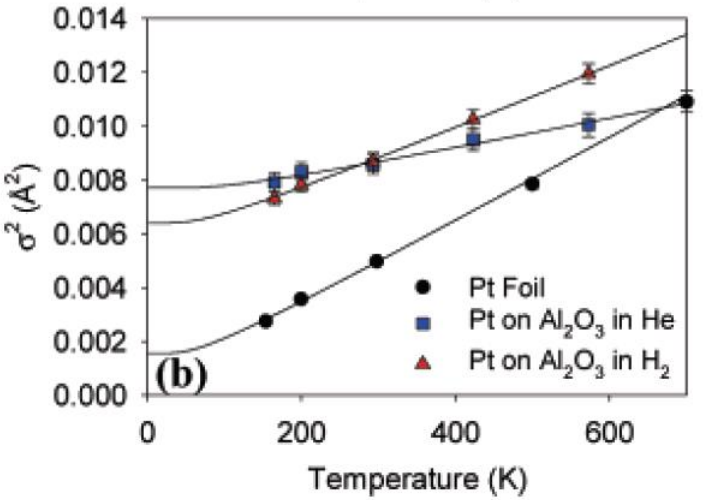
Pt-Pt bond expansion going from He to H_2 atmosphere ❶

Pt-Pt bond negative thermal expansion ❷

High Pt-Pt disorder ❸

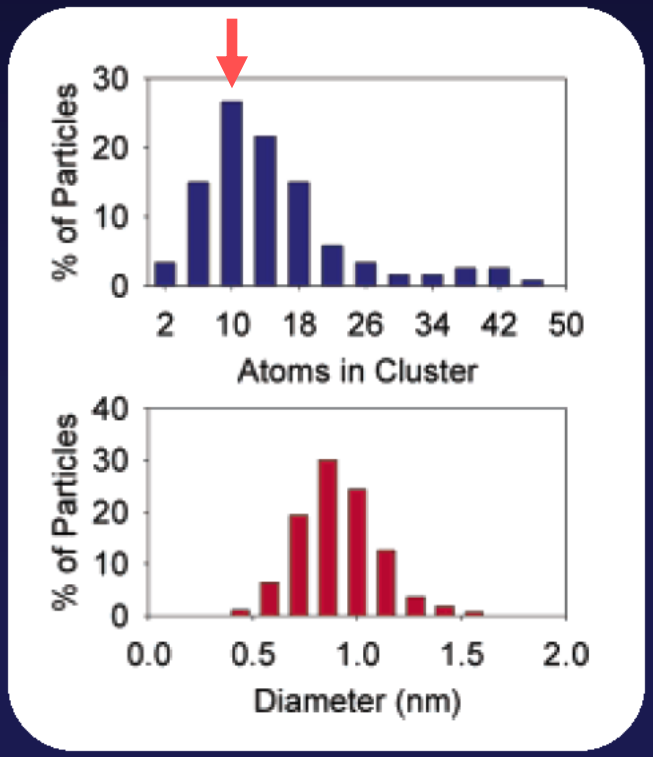
Increased intensity and redshift of XANES with increasing T ❹





Computational Details

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



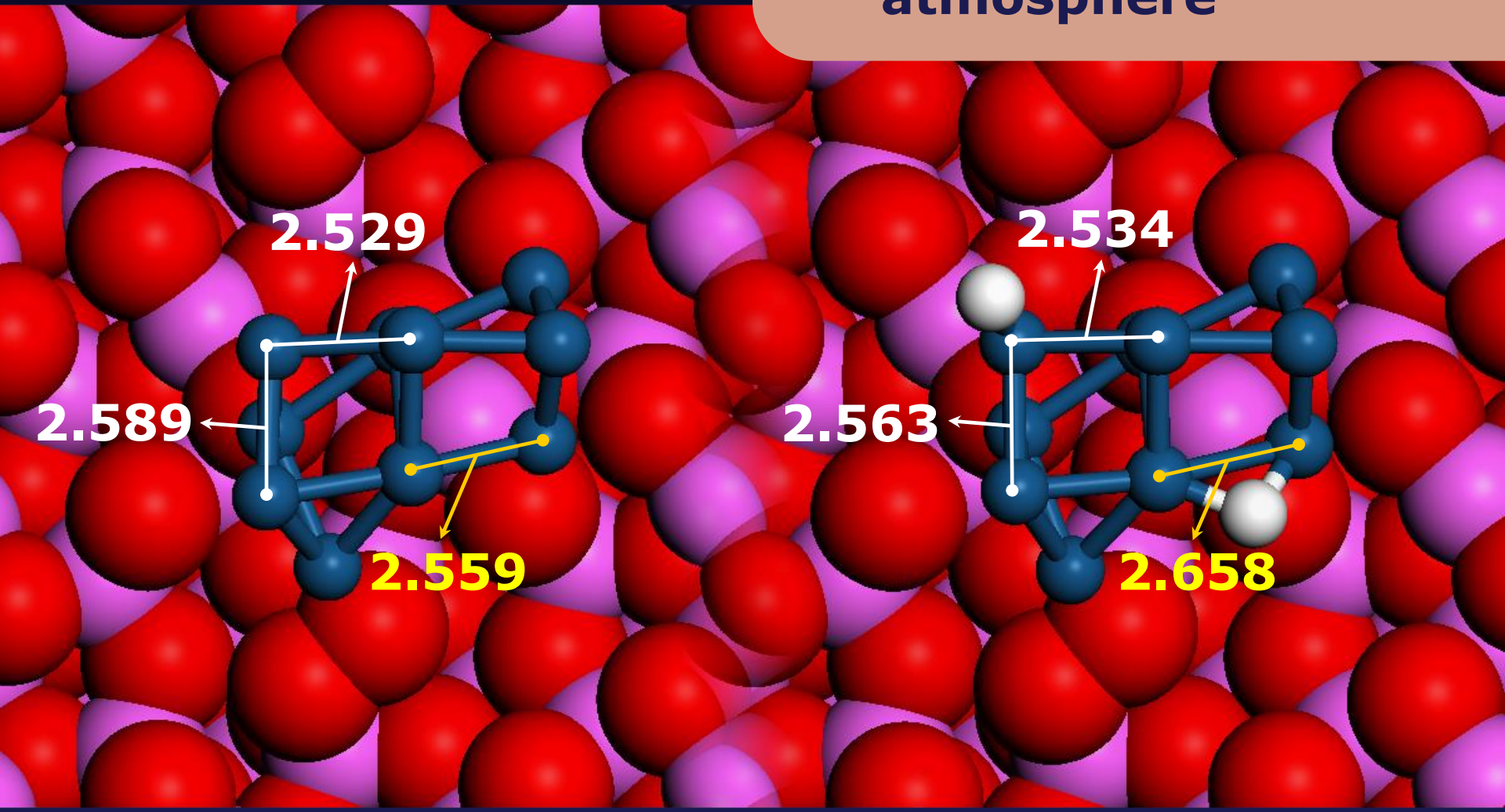
DFT/MD

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

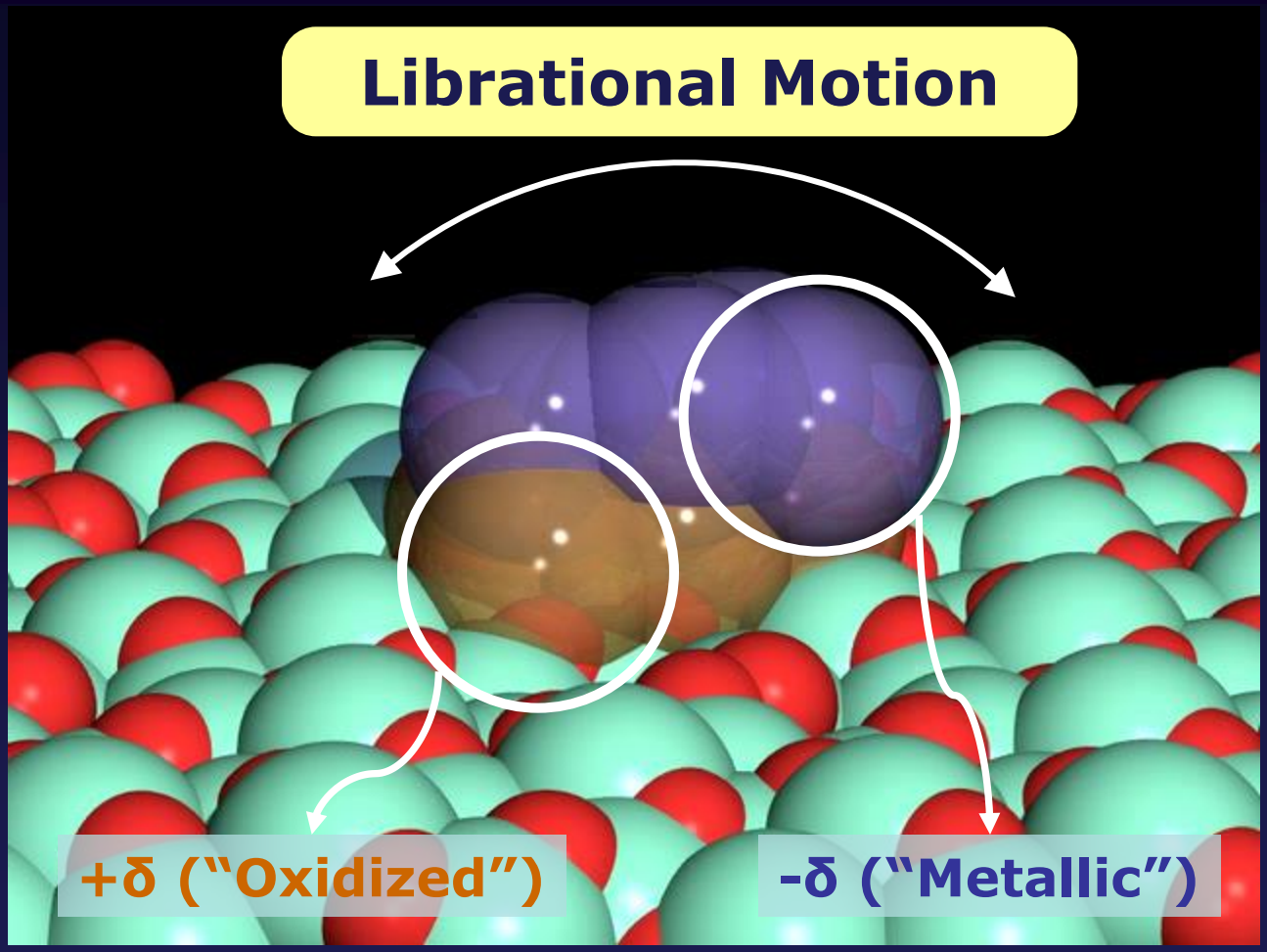
XANES

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

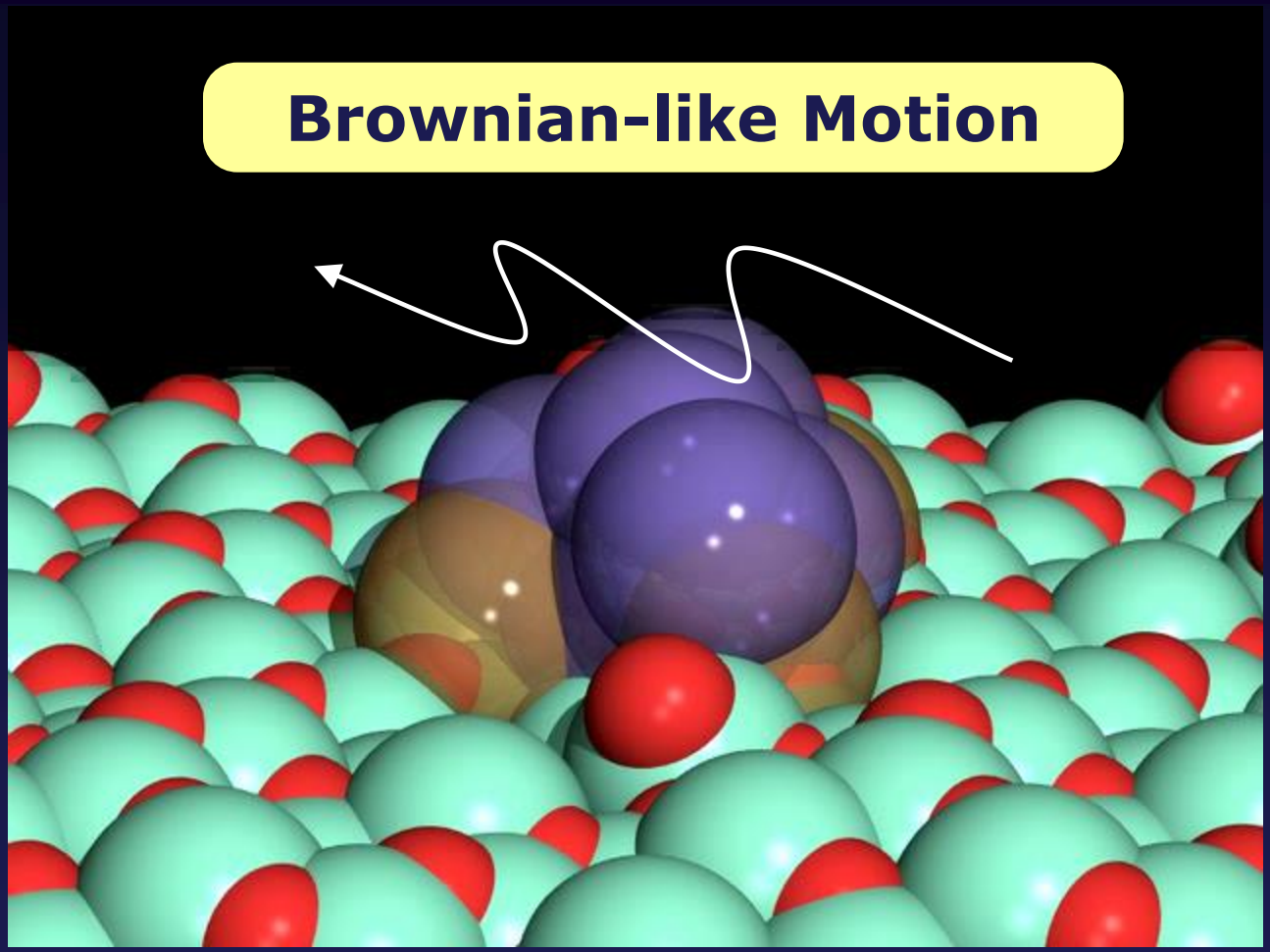
❶ Bond expansion in H_2 atmosphere



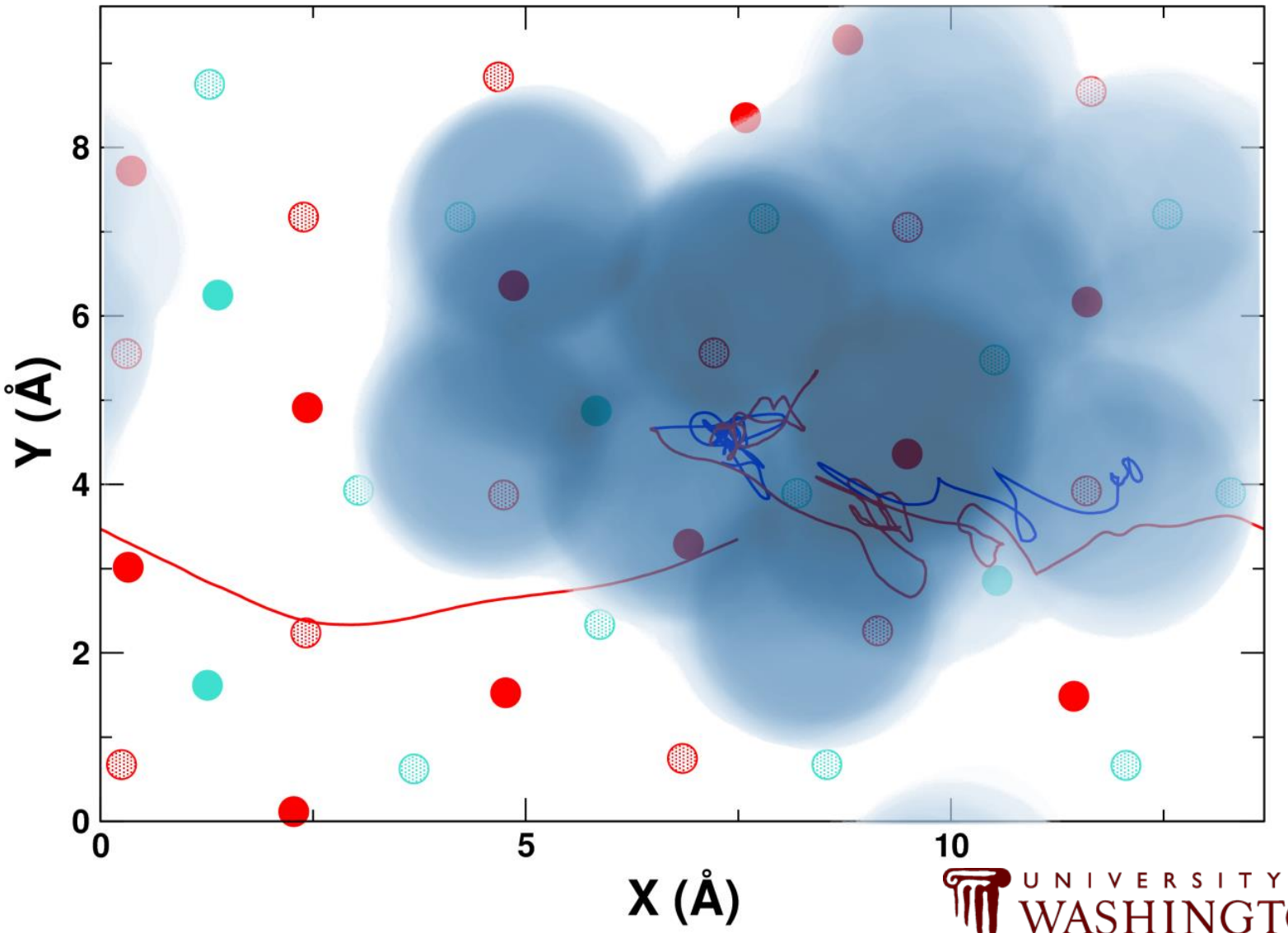
MD @ 165 K



MD @ 573 K



Cluster footprint @ 165 K



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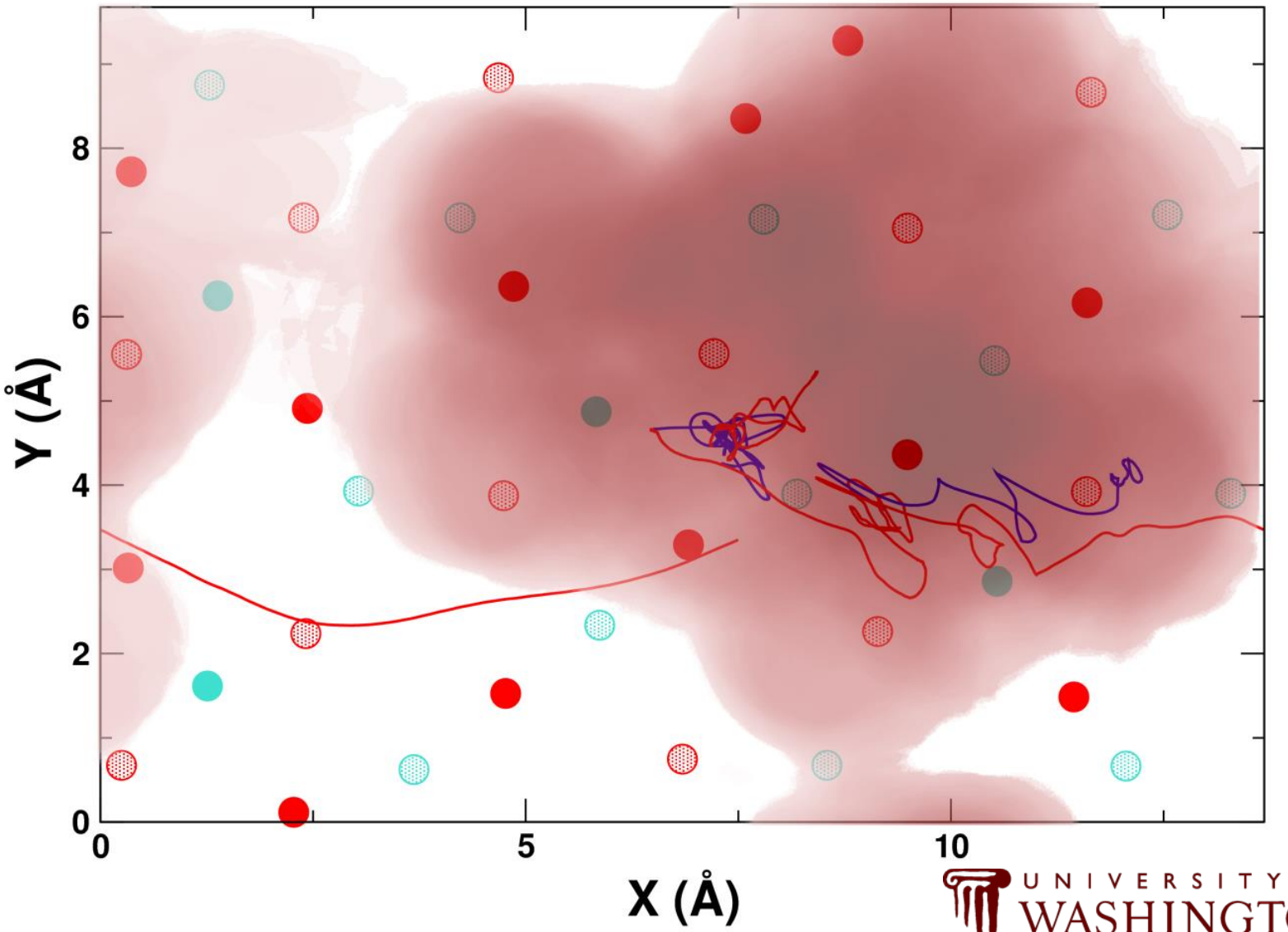
Cluster footprint @ 573 K



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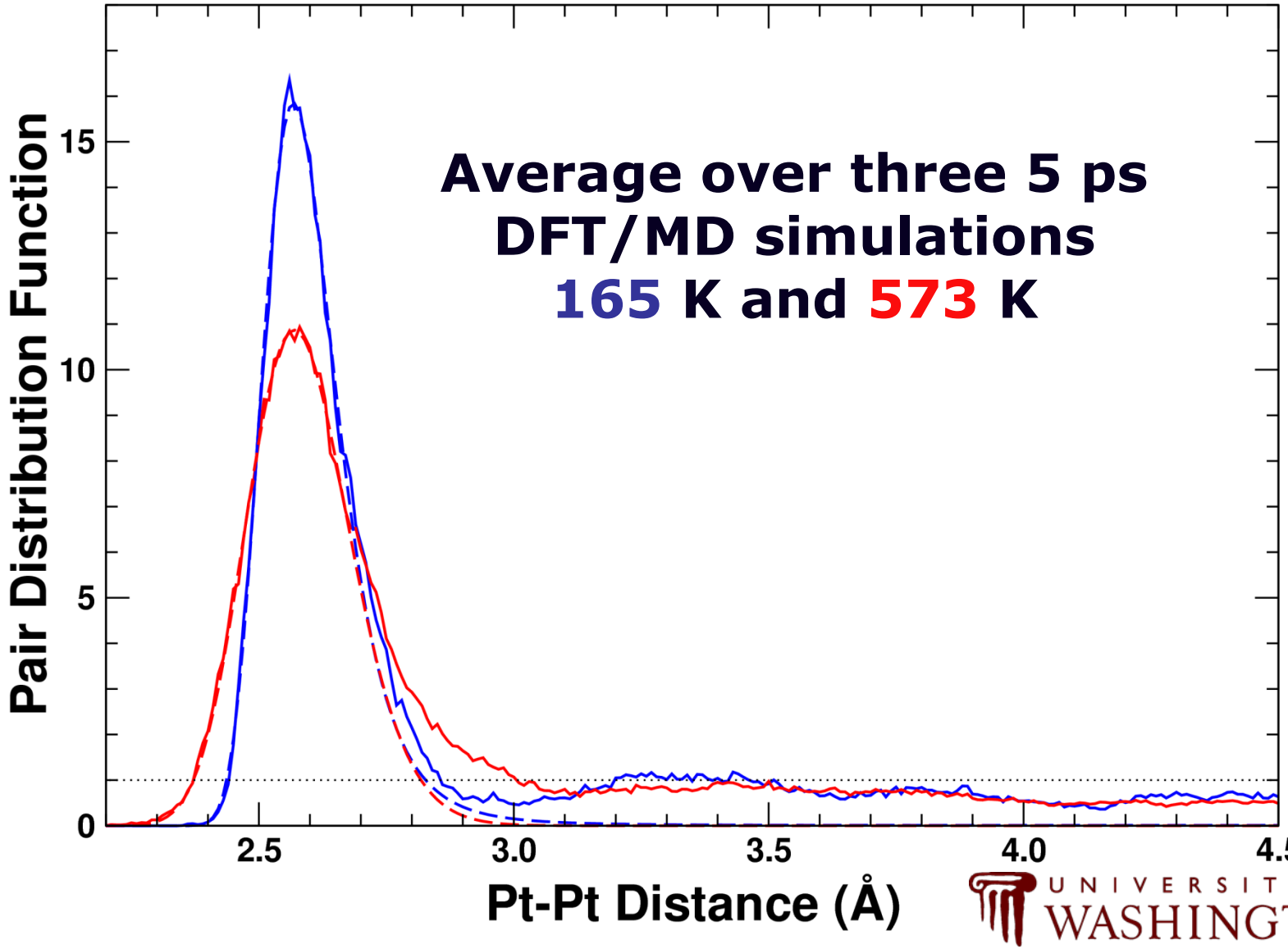
Pt-Pt Pair Distribution Function



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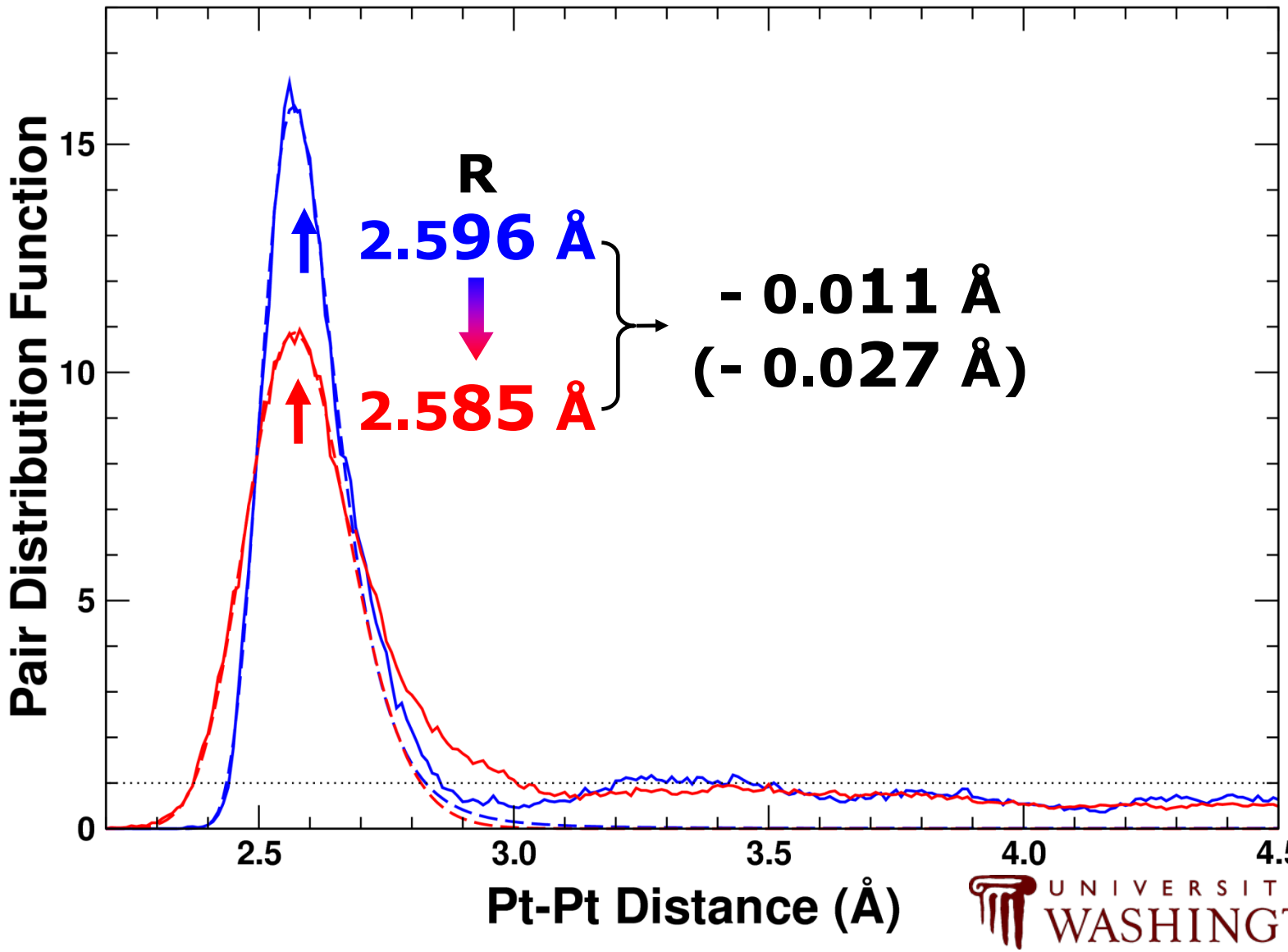
❷ Negative Thermal Expansion



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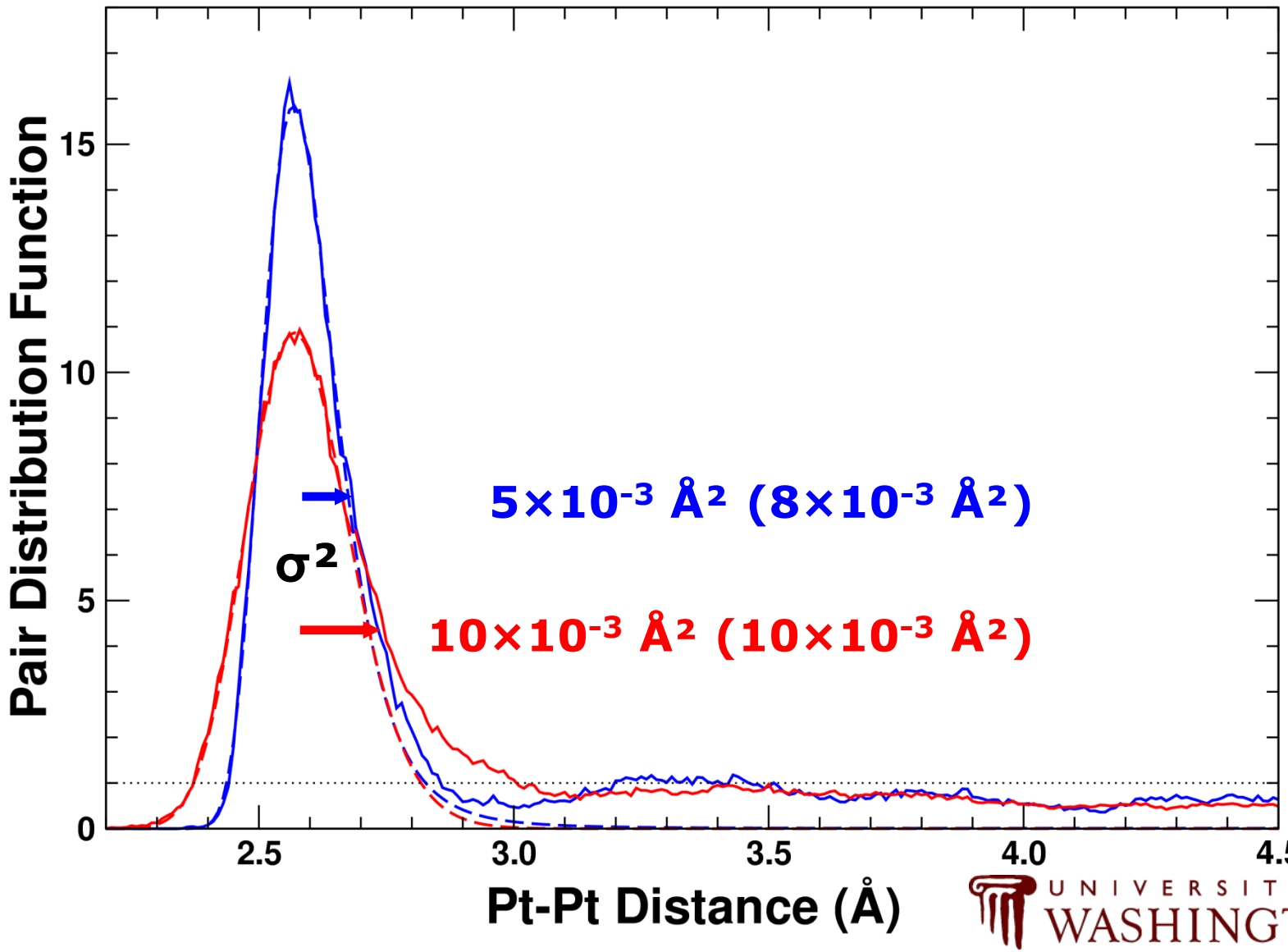
❸ High Pt-Pt Disorder



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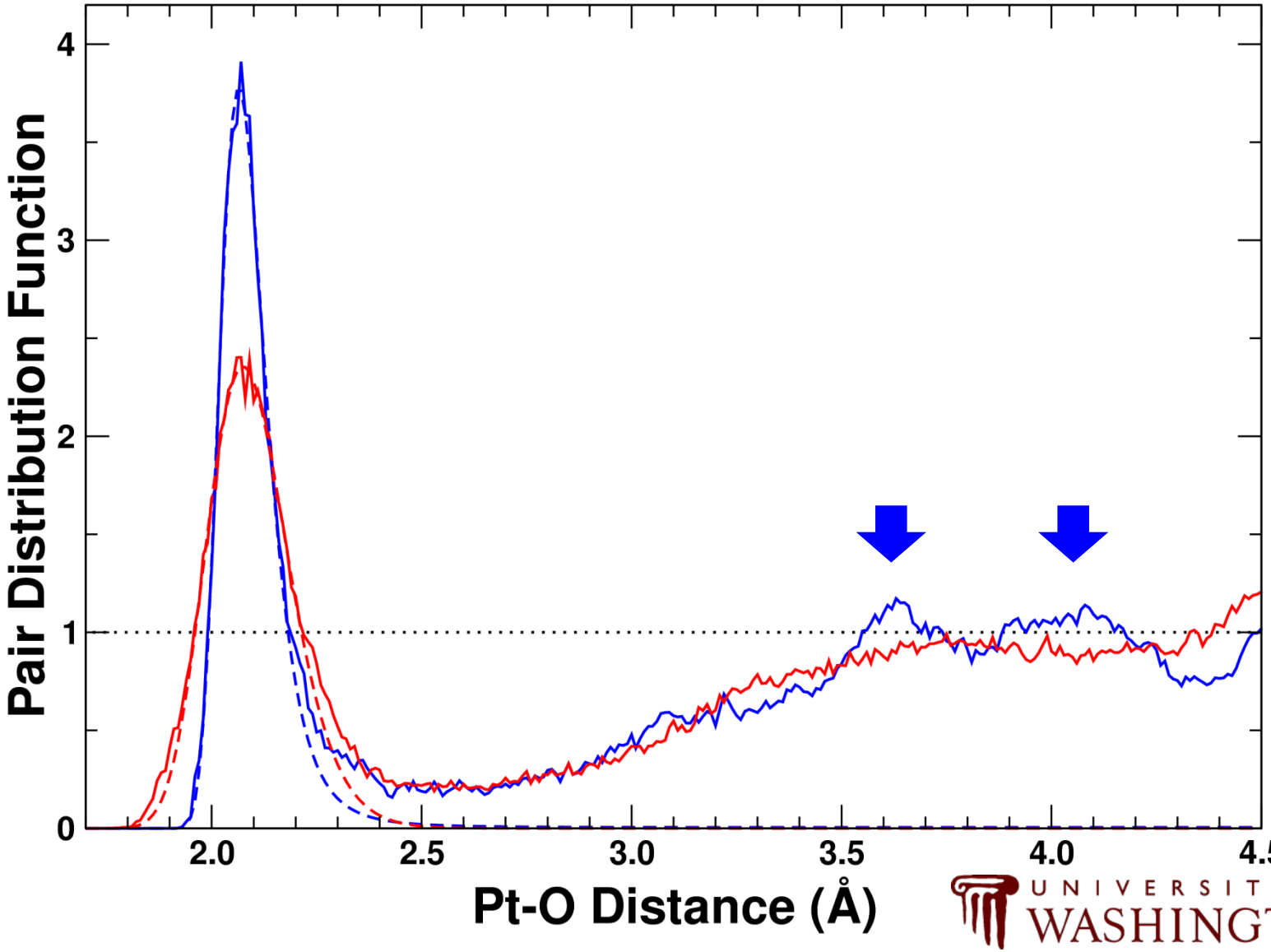
Pt-O Pair Distribution Function



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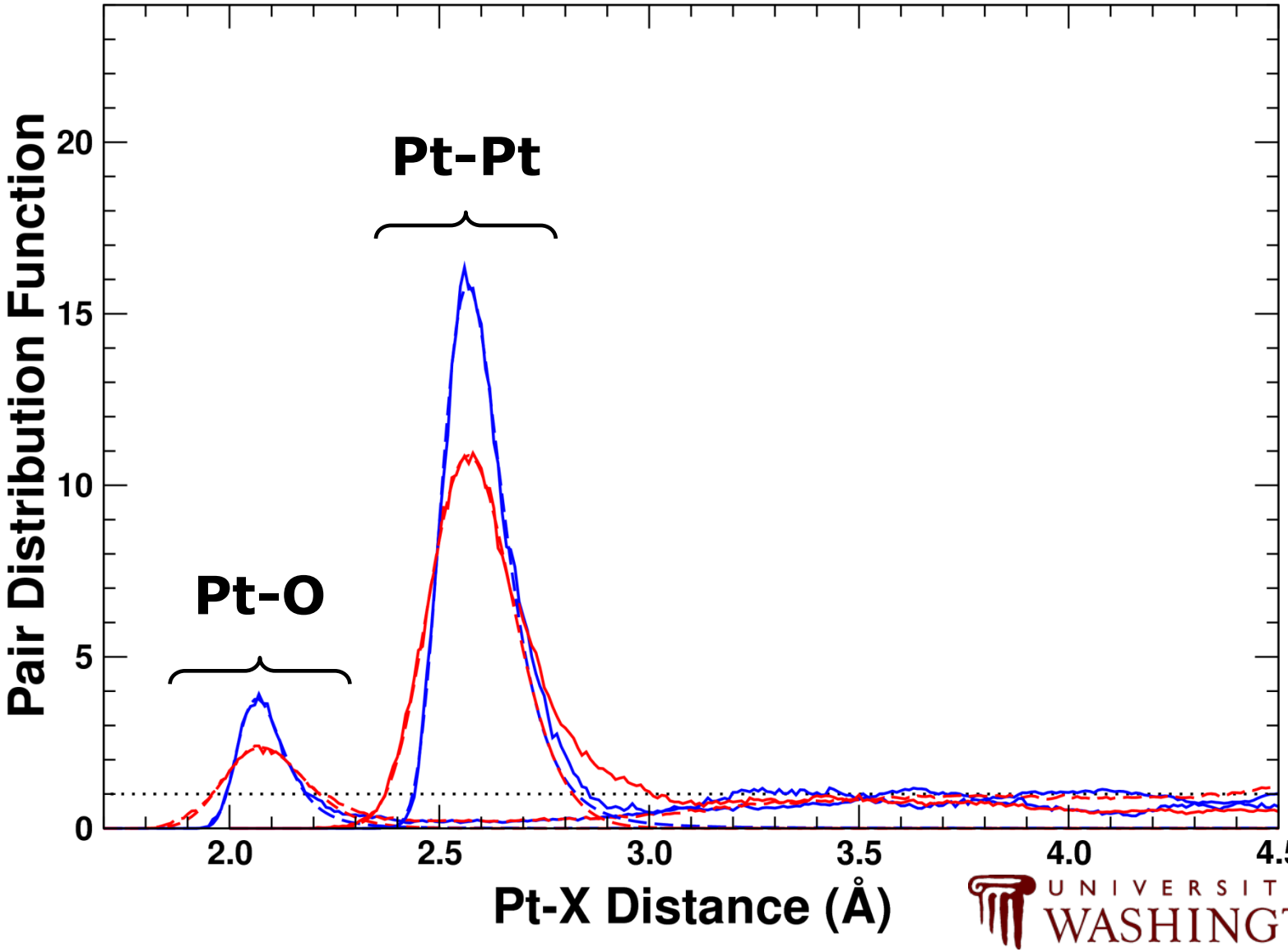
No O-signal in EXAFS



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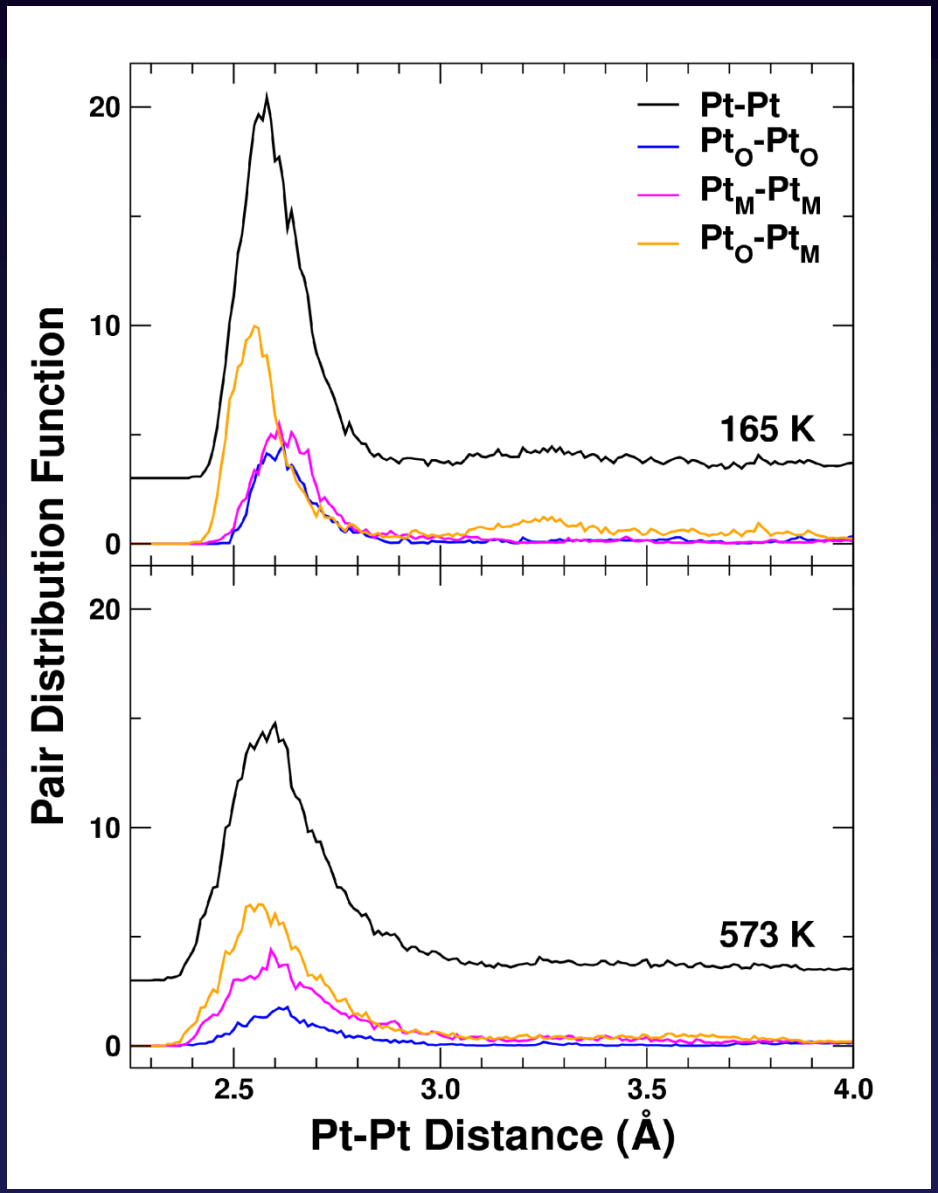
Decomposition of the Pt-Pt PDF



Bond Expansion

Pt$_O$-Pt$_M$: 0.036 Å

Pt$_M$-Pt$_M$: -0.039 Å

Pt$_O$-Pt$_O$: -0.014 Å

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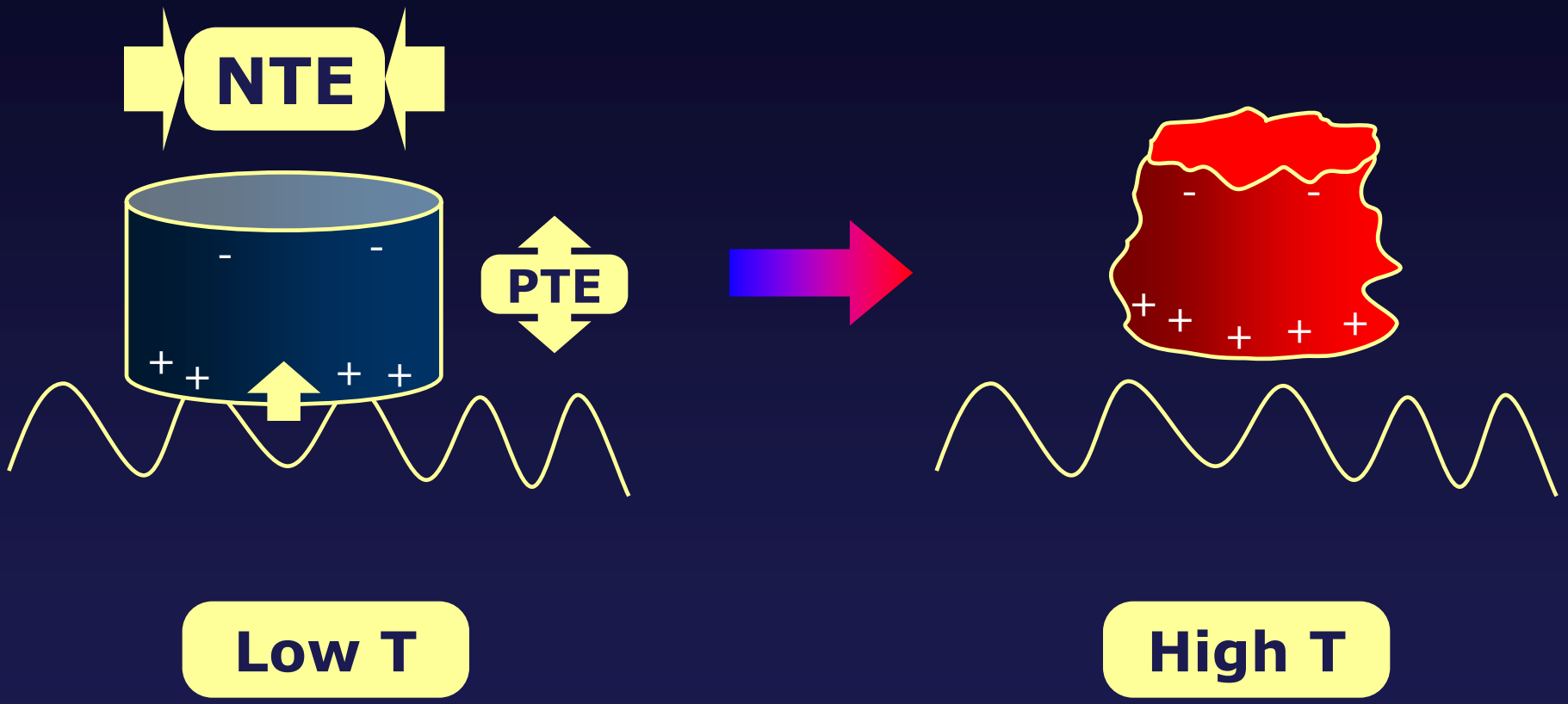
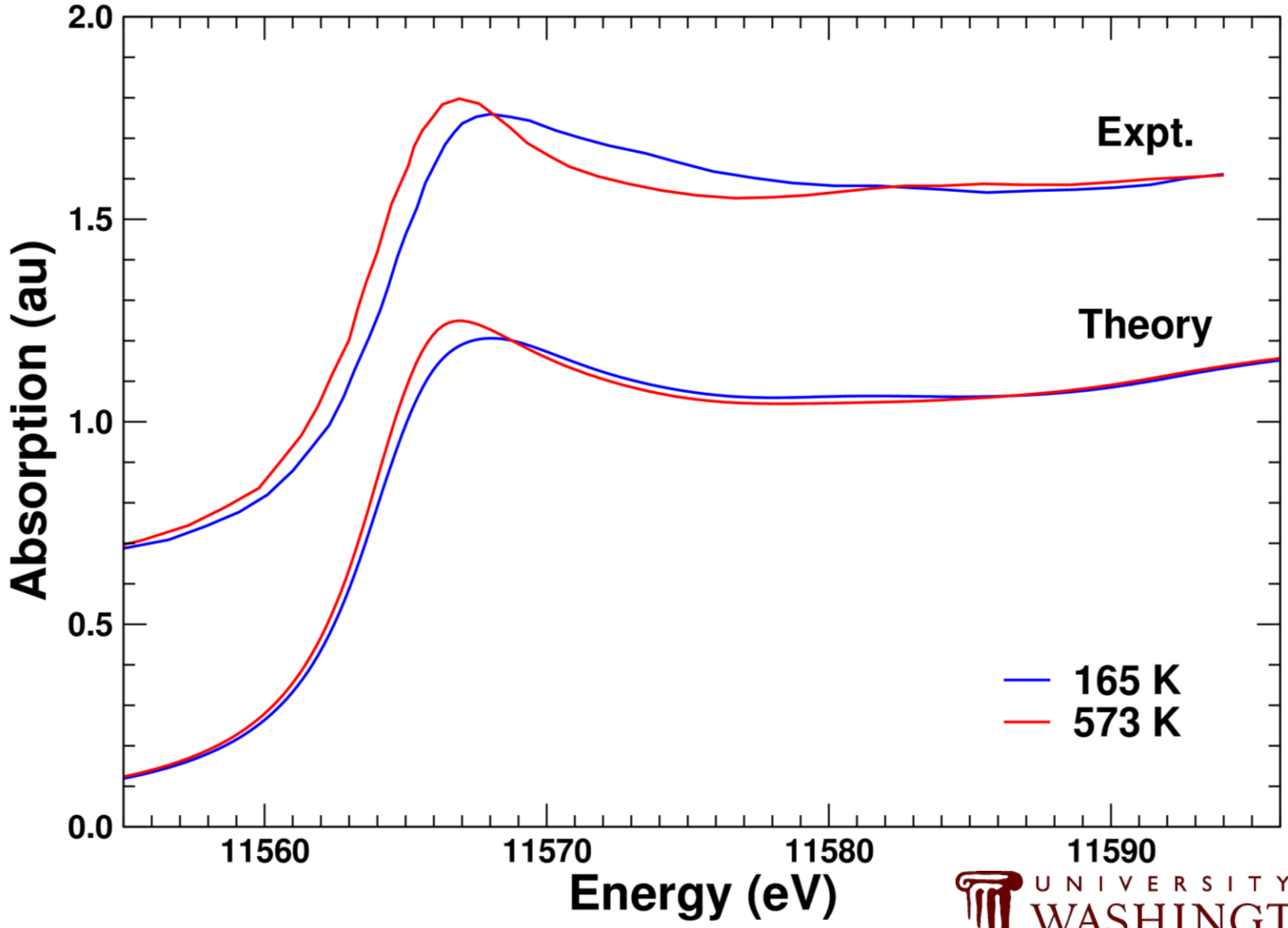
A Simple Model



Pt L_3 XANES: Conf. Average over MD



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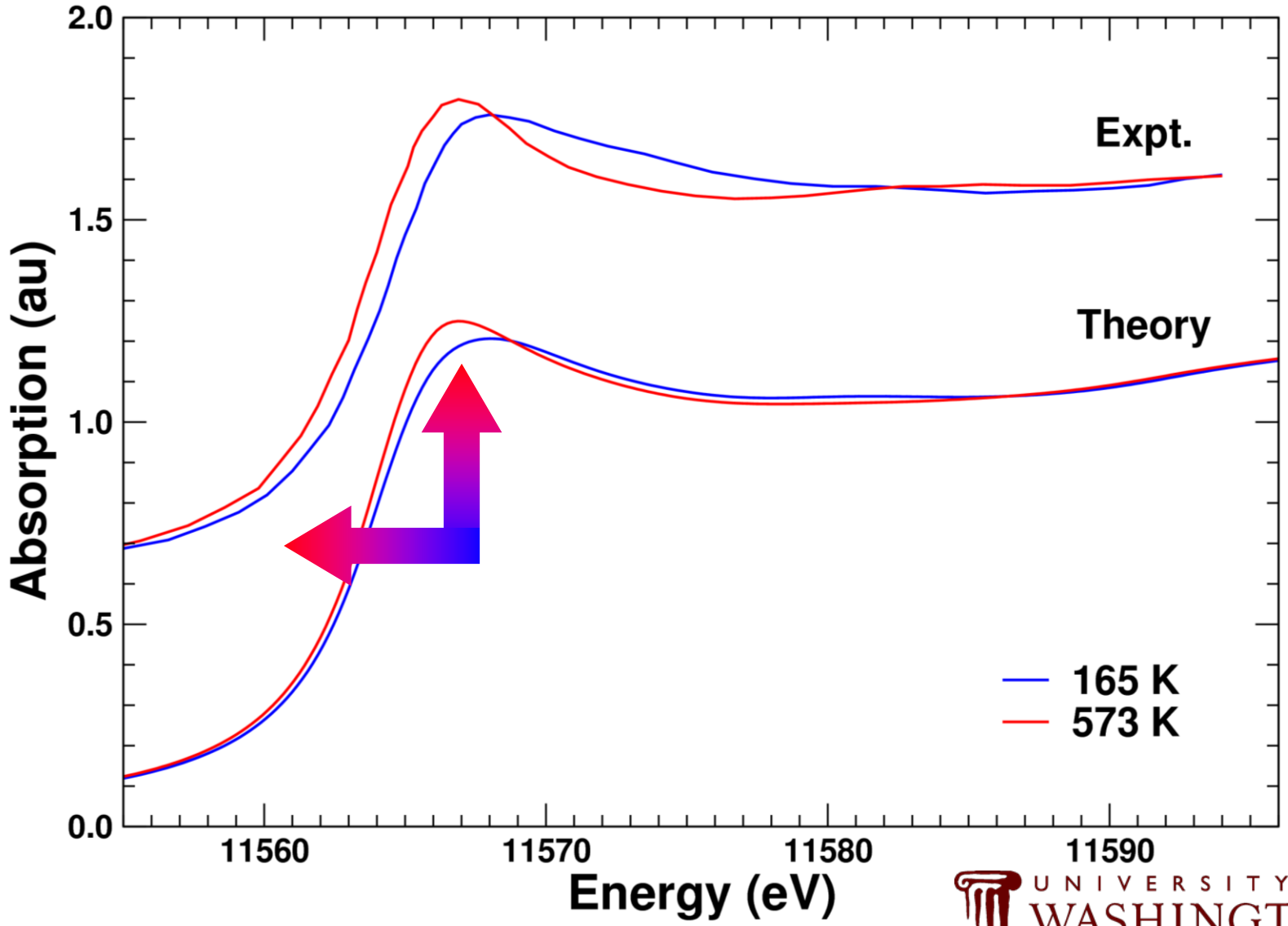
4 Increased intensity and redshift at high T



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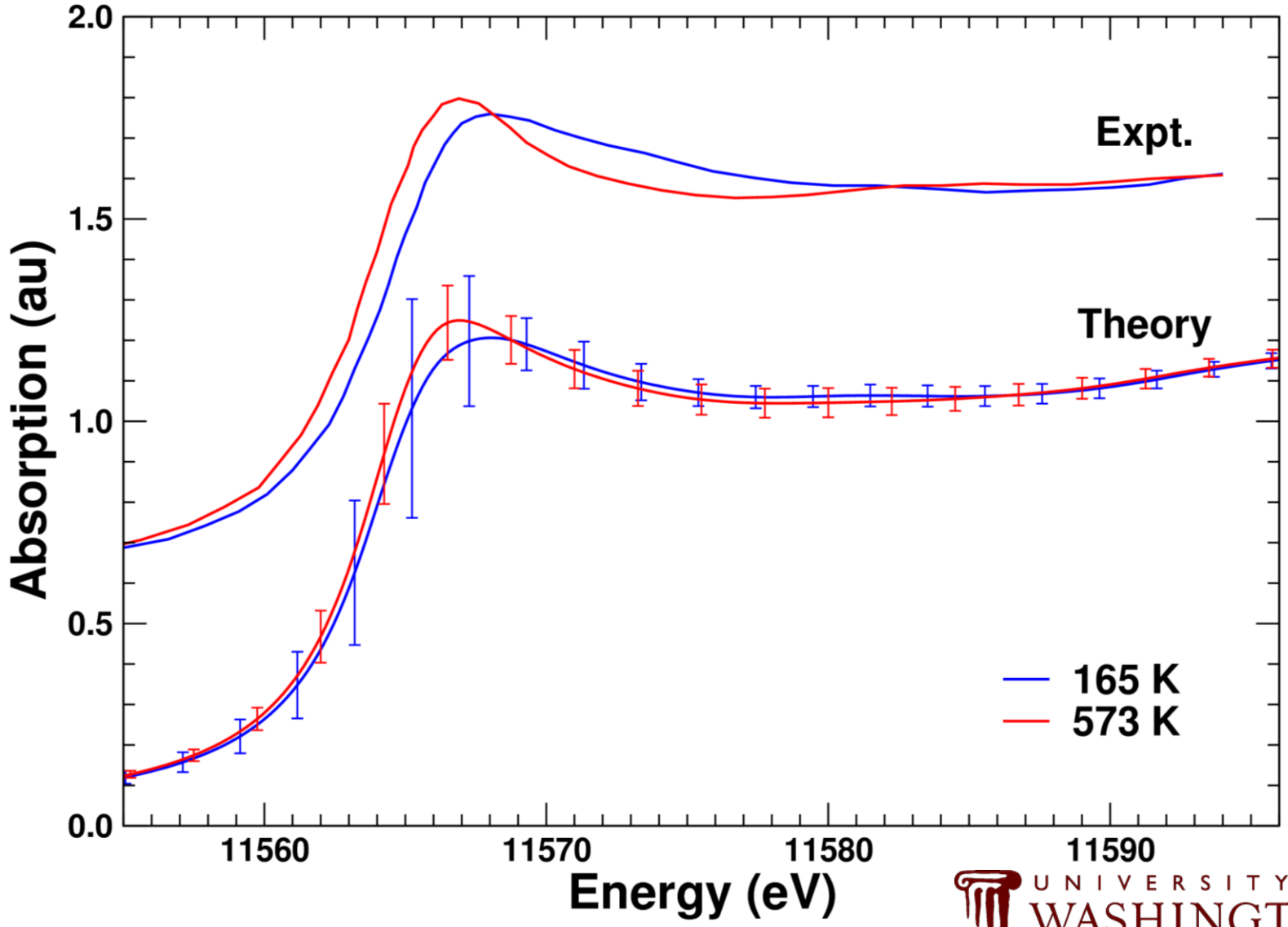

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Summary

Found qualitative agreement with all experimental observations:
structural and spectroscopic ❶

Discovered unusual dynamical behavior:
Librational and Brownian-like motion ❷

Possible implications in catalysis:
Activity affected by cluster mobility? ❸

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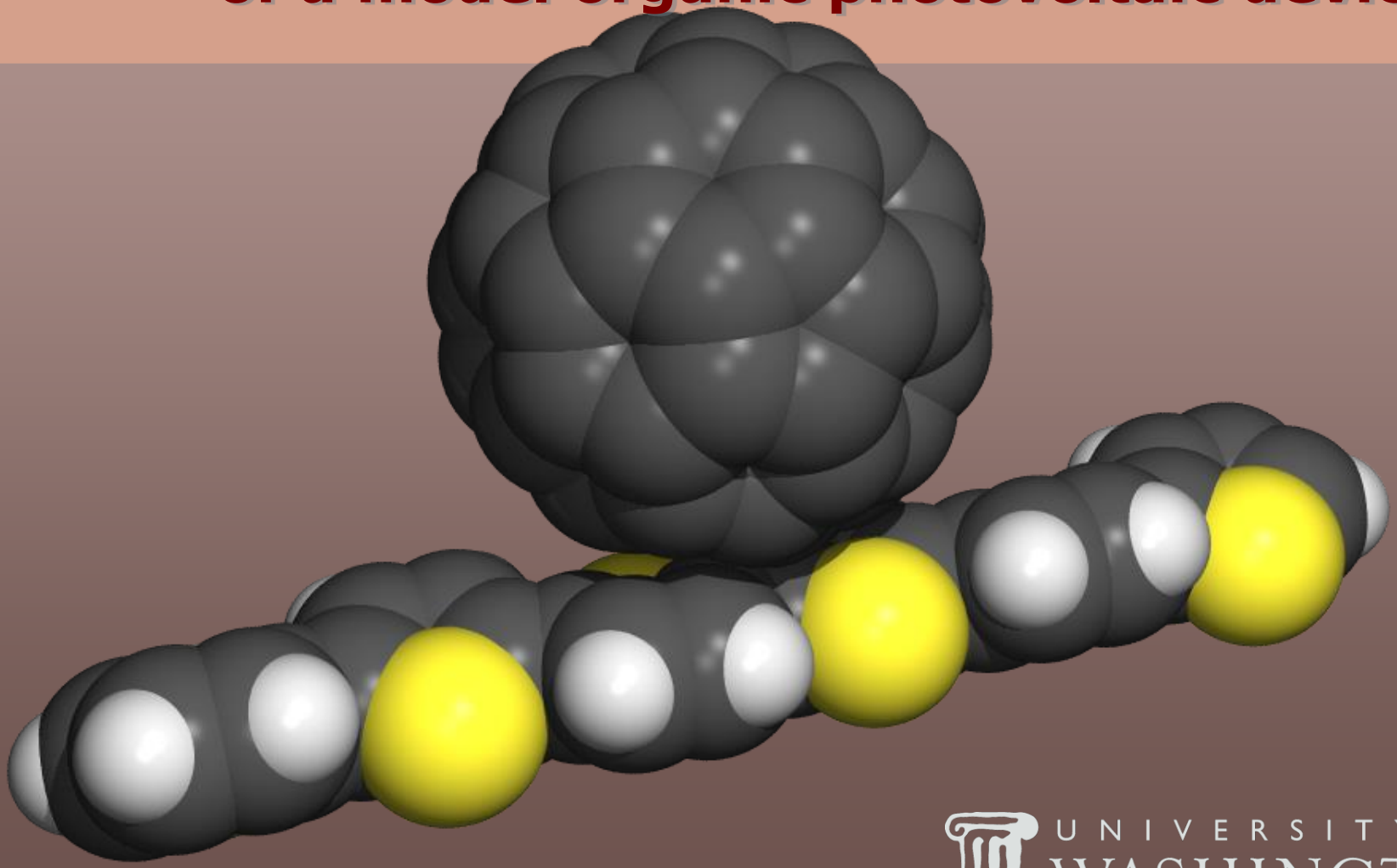
RT-TDDFT simulation of the optical properties of a model organic photovoltaic device



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The Problem

Theoretically study the initial process of light harvesting in organic photovoltaic devices:

Optical Absorption

1. **Develop simple structural models of organic photovoltaic devices**
2. **Calculate the optical absorption of photovoltaic components using RT-TDDFT**
3. **Explore spectral trends induced by changes in the structure of the components**

Real-Time Time Dependent DFT

Direct numerical integration of the time-dependent Kohn-Sham equations in a time-dependent external electric field:

$$i\frac{\partial \Psi}{\partial t} = H(t)\,\Psi \qquad \Psi(t) = T\,\exp\left(-i\int_0^t H(t')dt'\right)\Psi(0)$$

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

Optical properties are determined from the total dipole moment:

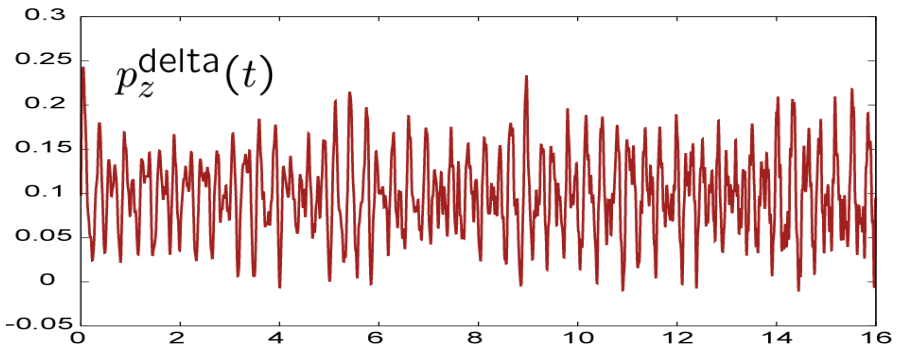
$$\mathbf{p}(t) = \int \rho(\mathbf{r},t)\,\mathbf{r}\,d^3\mathbf{r}$$

$$\underbrace{\chi^{(1)}_{ij}(\omega) = \delta p_i(\omega)/E_j(\omega) = \alpha_{ij}(\omega)}_{\text{Linear Response}} \qquad \underbrace{\sigma(\omega) \sim \omega\,\mathbf{Im}\,\langle\alpha(\omega)\rangle}_{\text{Absorption}}$$

Yabana and Bertsch, Phys. Rev. B 54, 4484 (1996)

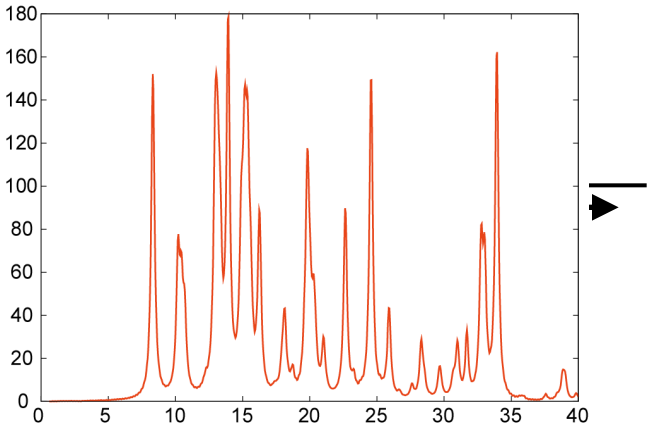
Optical Absorption in CO (Y. Takimoto)

Delta Function (Unit Impulse at t=0)

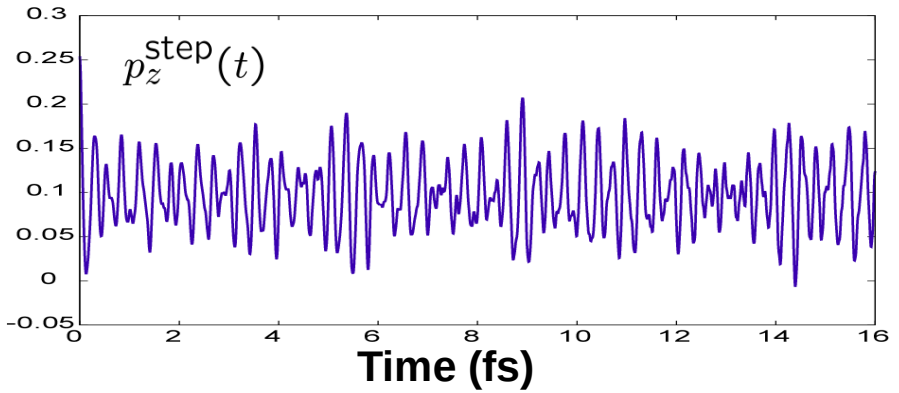


E(t)

Ground
without

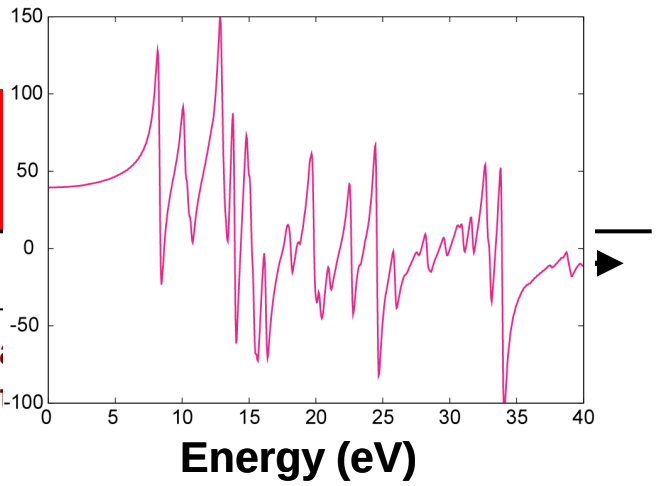


Step Function (Turn-off Constant E at t=0)



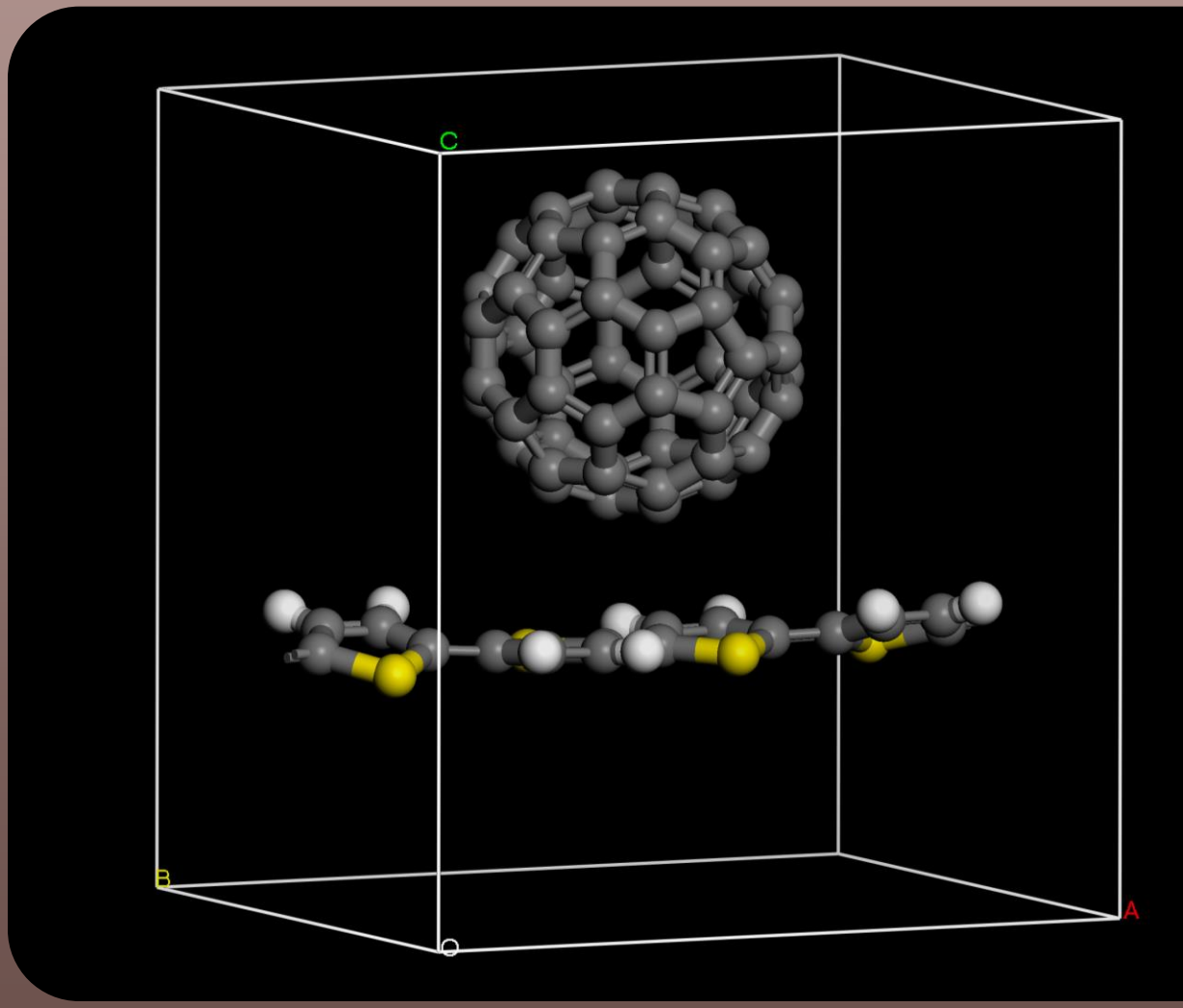
E(t)

Ground st
constan



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

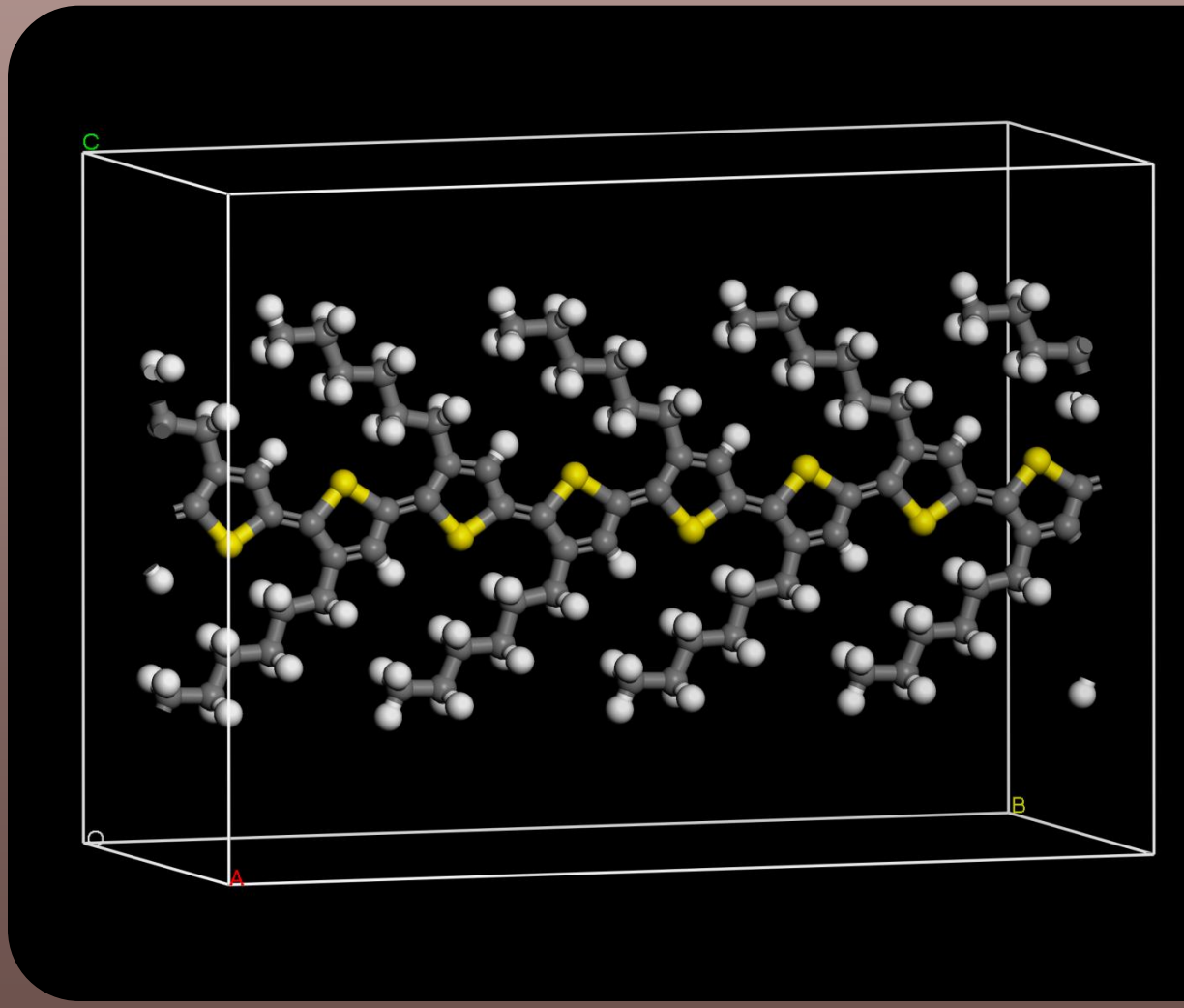
Model Structures (VASP, PBC)



C_{60} on poly-Thiophene (pT)

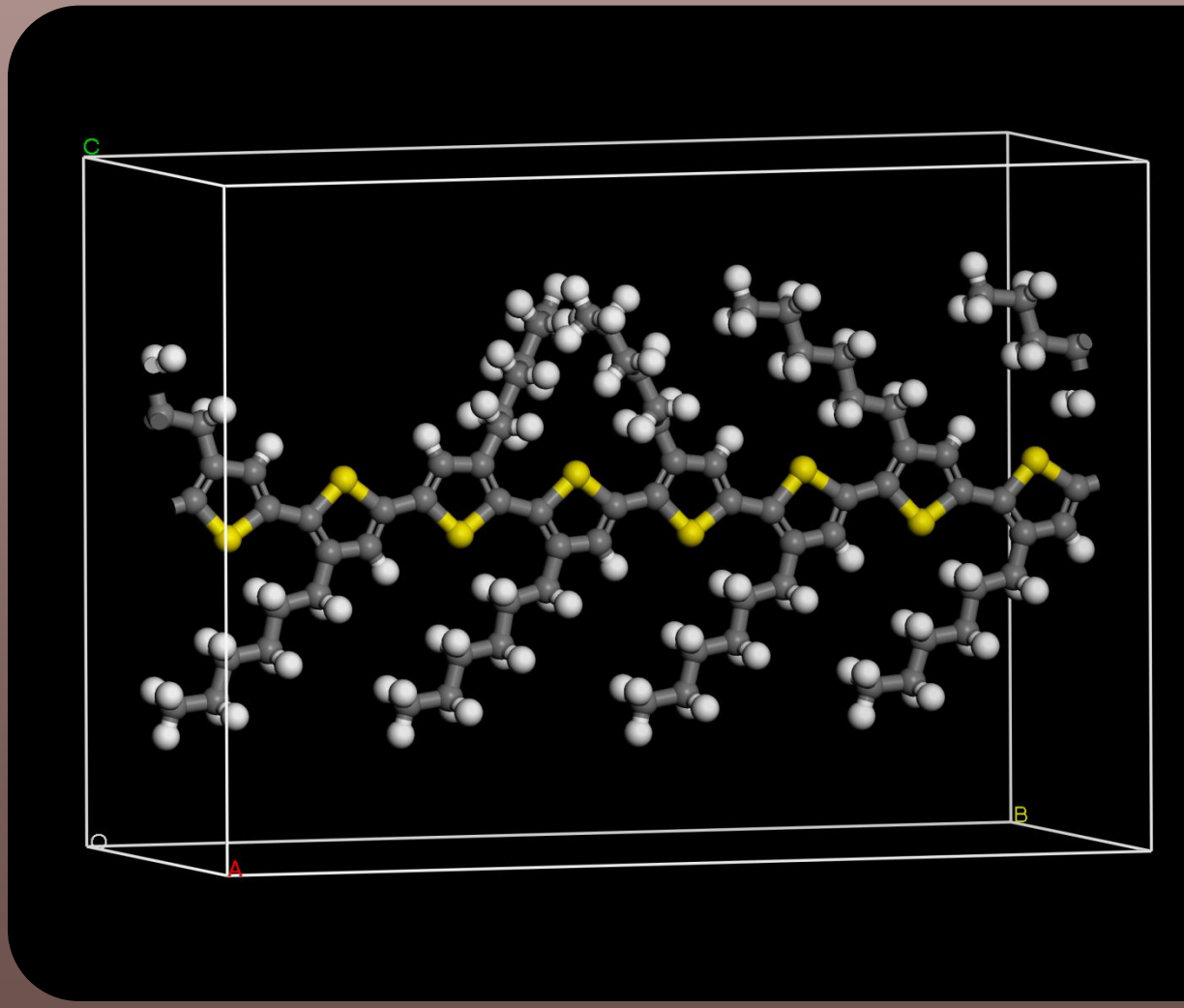
A model for a PCBM-p3TH heterojunction device

Model Structures (VASP, PBC)



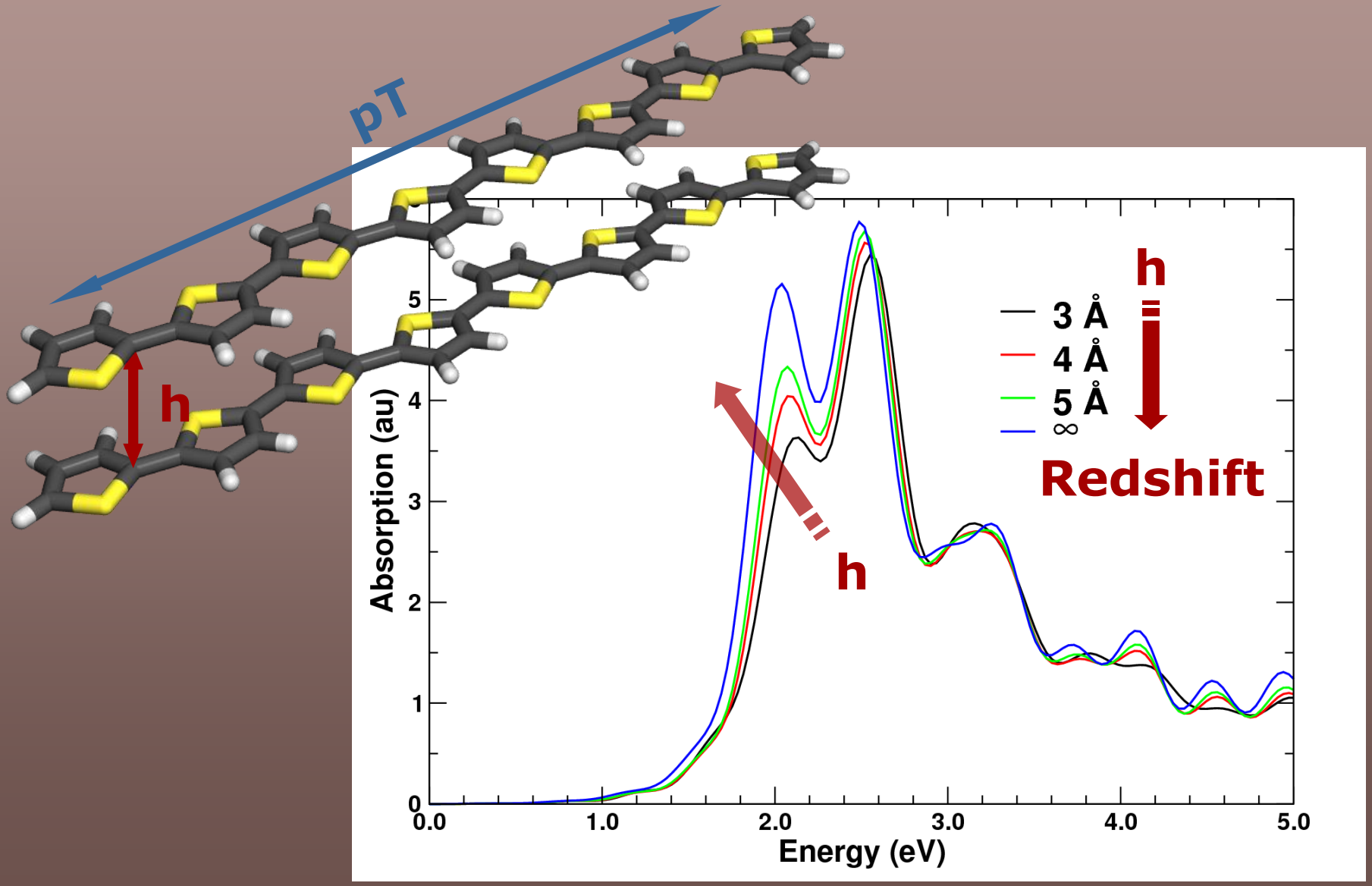
A model for a regioregular (rr) p3TH

Model Structures (VASP, PBC)

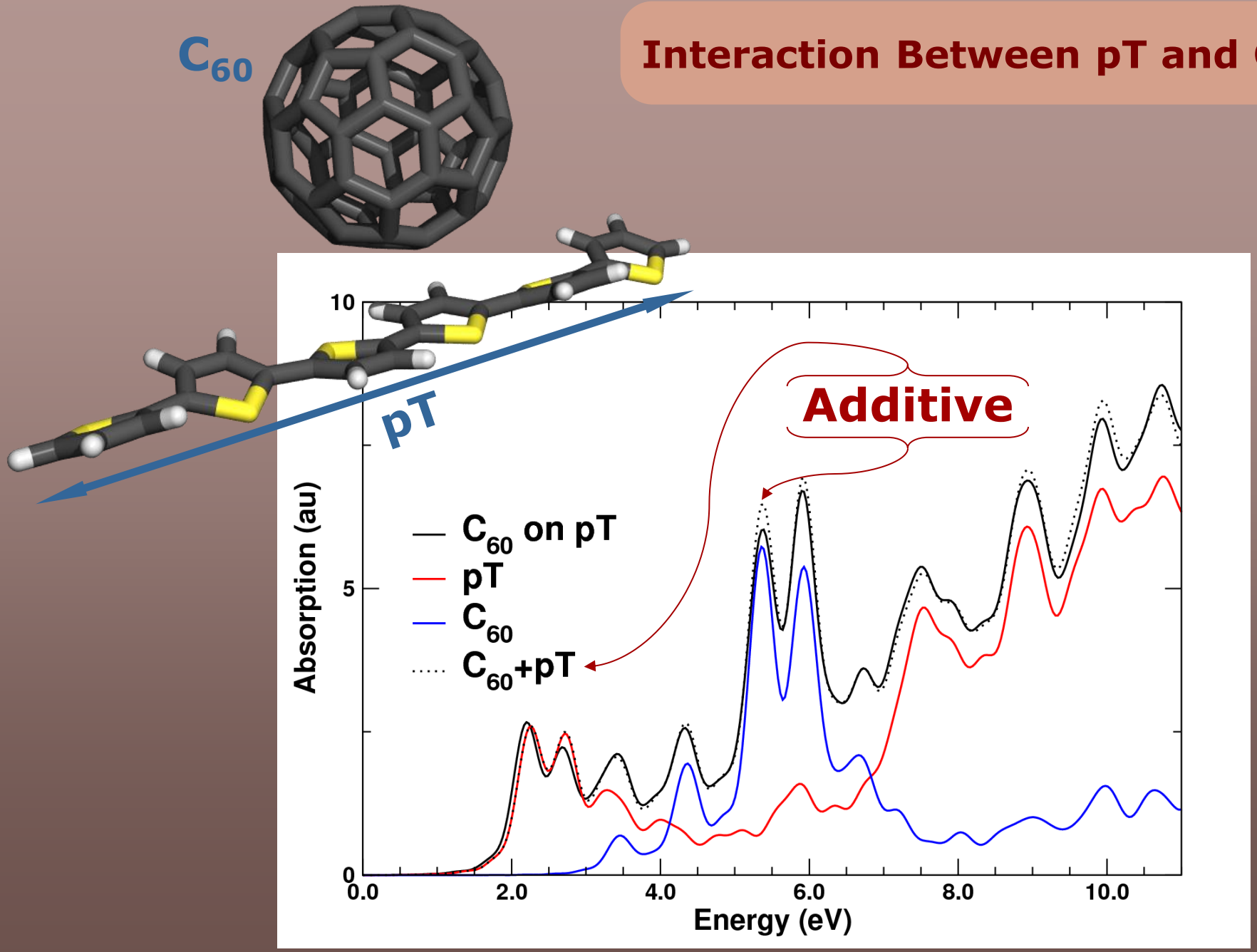


A model for a regiorandom (ra) p3TH

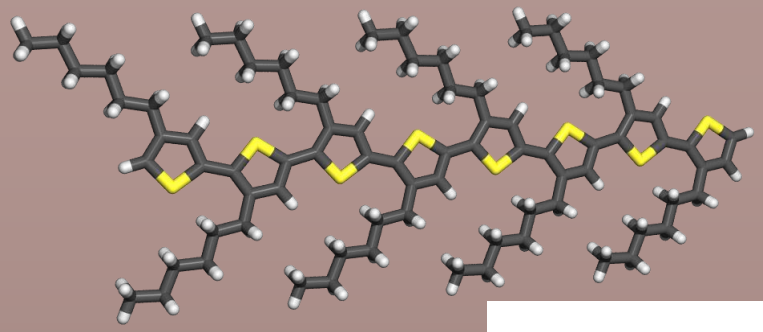
Interaction Between pT Chains



Interaction Between pT and C_{60}



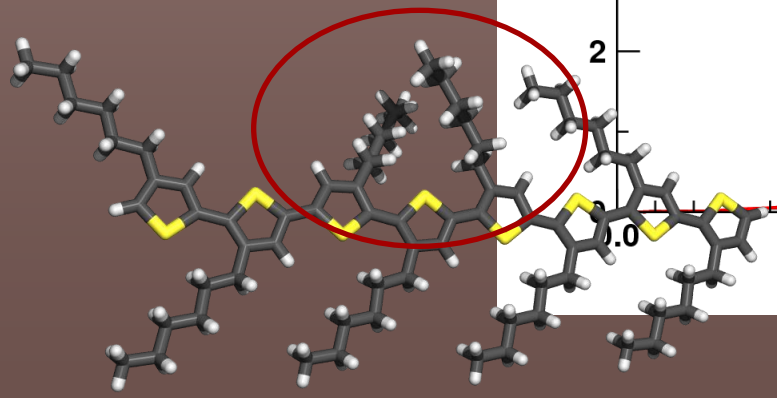
Effect of Hexyl Chains in p3HT

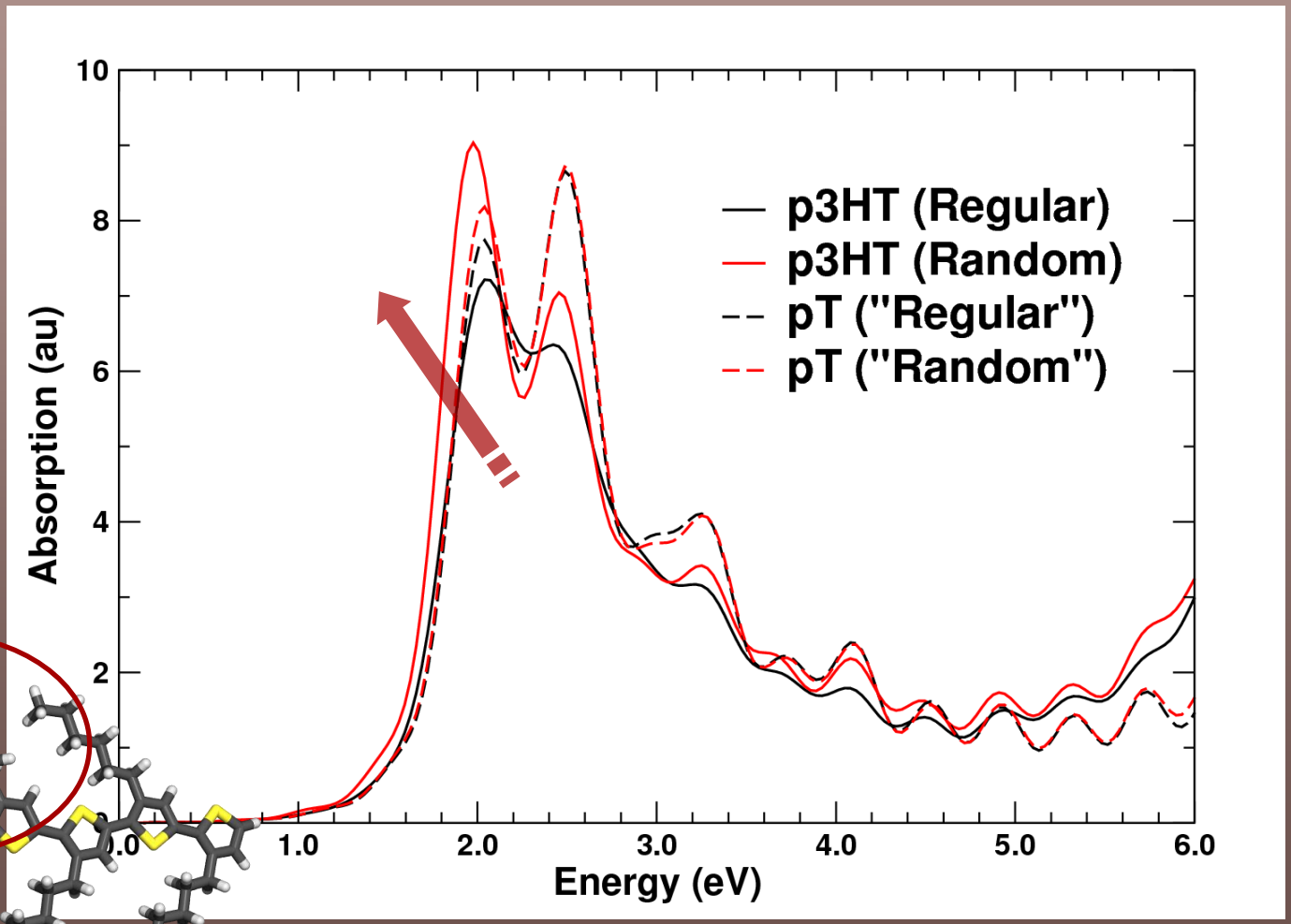


p3HT (Regular)

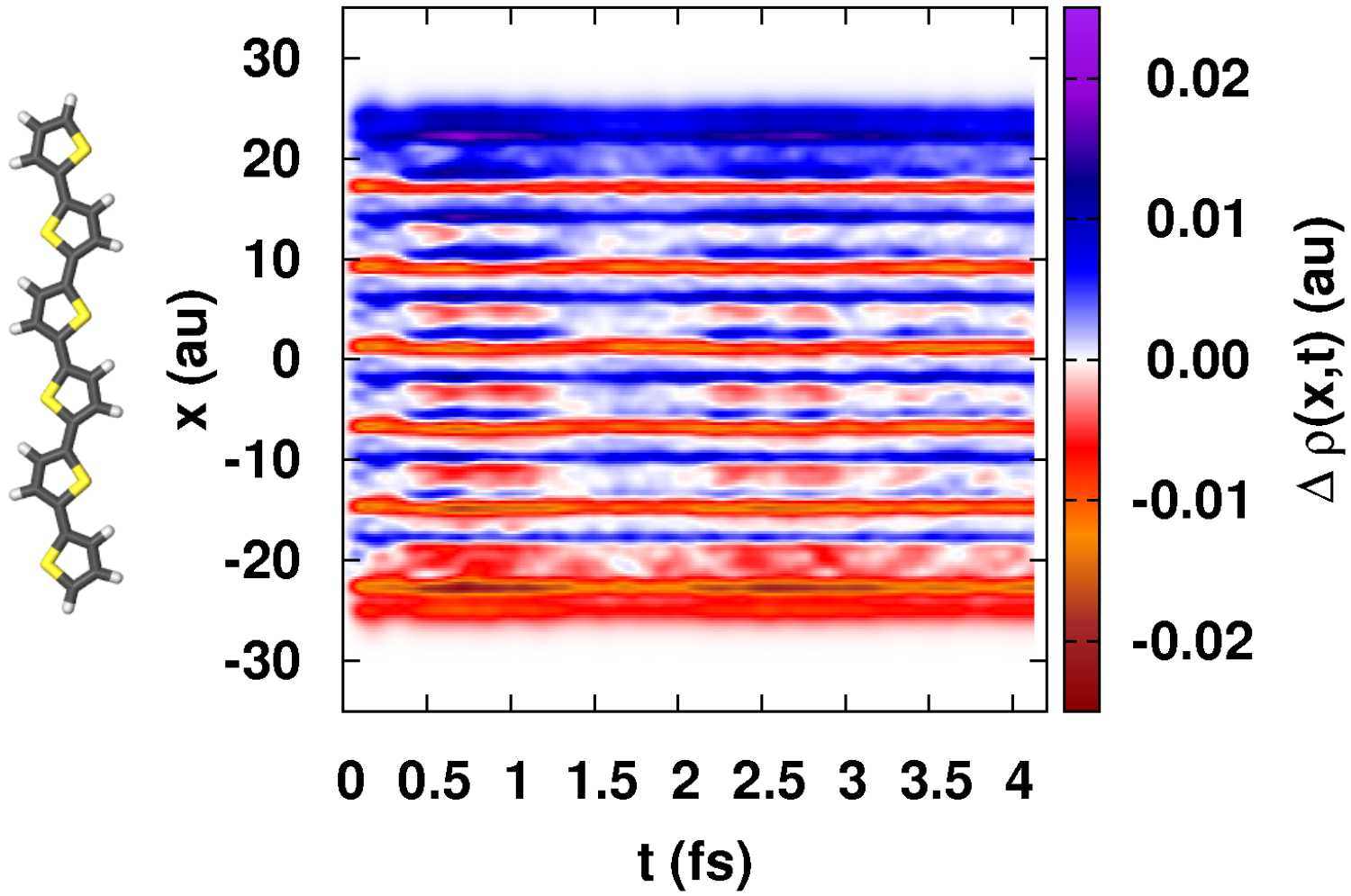
Redshift

p3HT (Random)





Electron Density Fluctuations



Summary

1. The effect of structural changes can be clearly observed in the simulated absorption spectrum

2. Simple device models give insights into the nature of light harvesting

3. RT-TDDFT is very efficient, making possible routine studies of device atomic morphology

Conclusions

Real-Space and Real-Time methods and their combination:

1. **Reveal the underlying relations between structure and spectra**
2. **Provide an efficient tool for the design of materials for energy applications**
3. **Open a door to a new understanding of complex systems**

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Real-Space and Real-Time Approaches for Energy-Related Materials

Y. Takimoto
T. Ahmed
C. Luscombe
A. Jen
D. Ginger

J. J. Rehr
A. Ankudinov
M. Prange
H. M. Lawler
J. Vinson
J. Seidler
T. Fister
K. Nagle

J. Kas
R. G. Nuzzo
A. I. Frenkel

DOE Grants
DE-FG35-08G018024, DE-FG02-04ER1599

... and Thank You

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