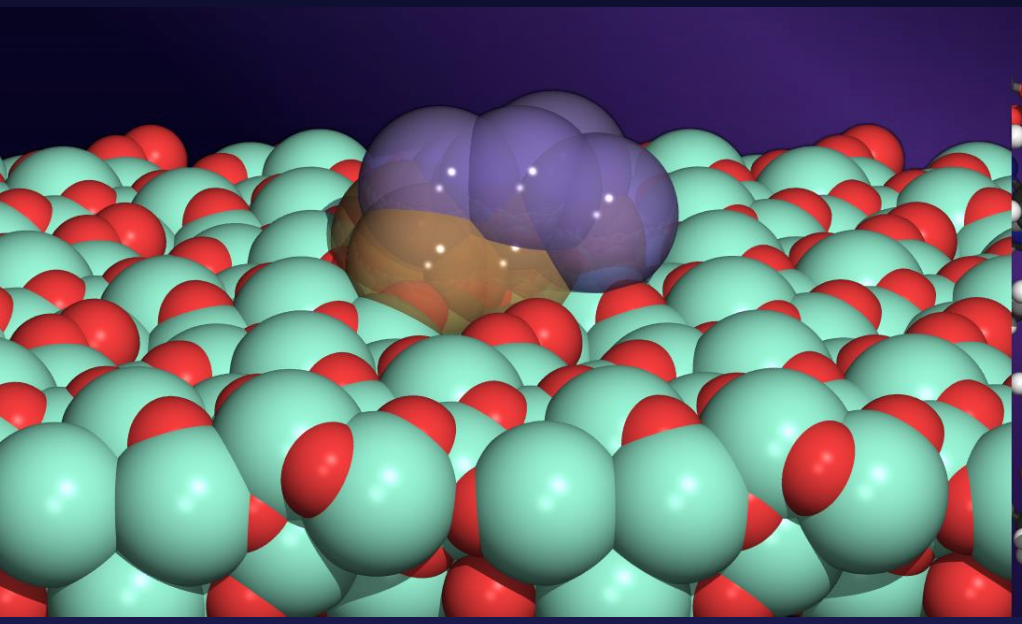
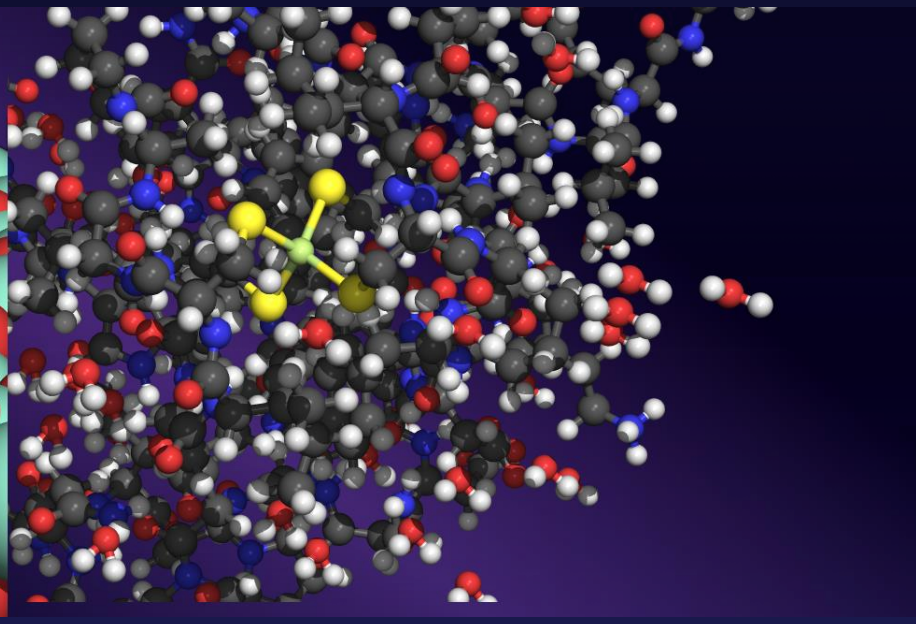
First Principles Structure, Dynamics and X-Ray Spectroscopy of Complex Systems





F. Vila

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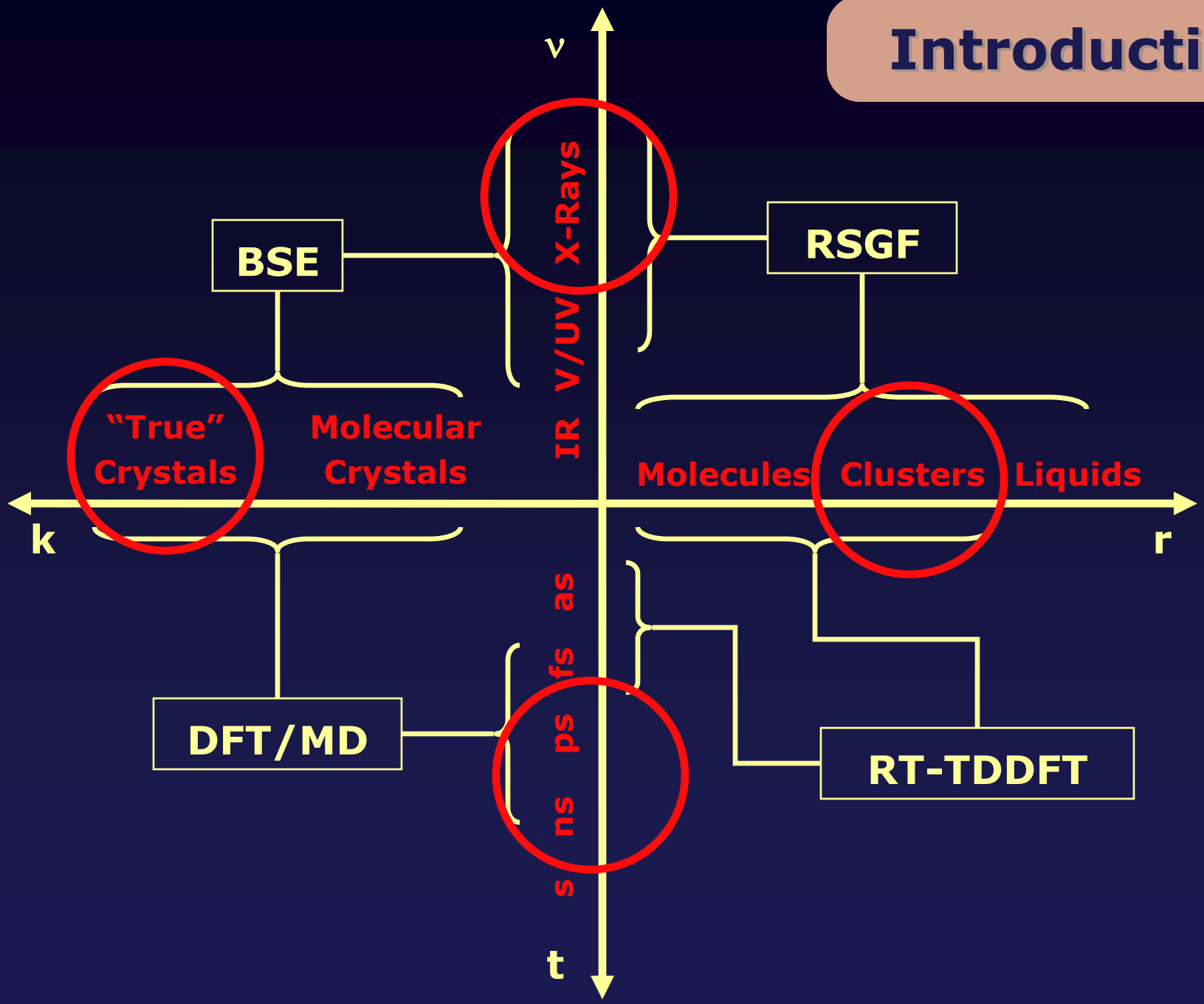
Molecular Foundry
June 2009

Introduction



Outline

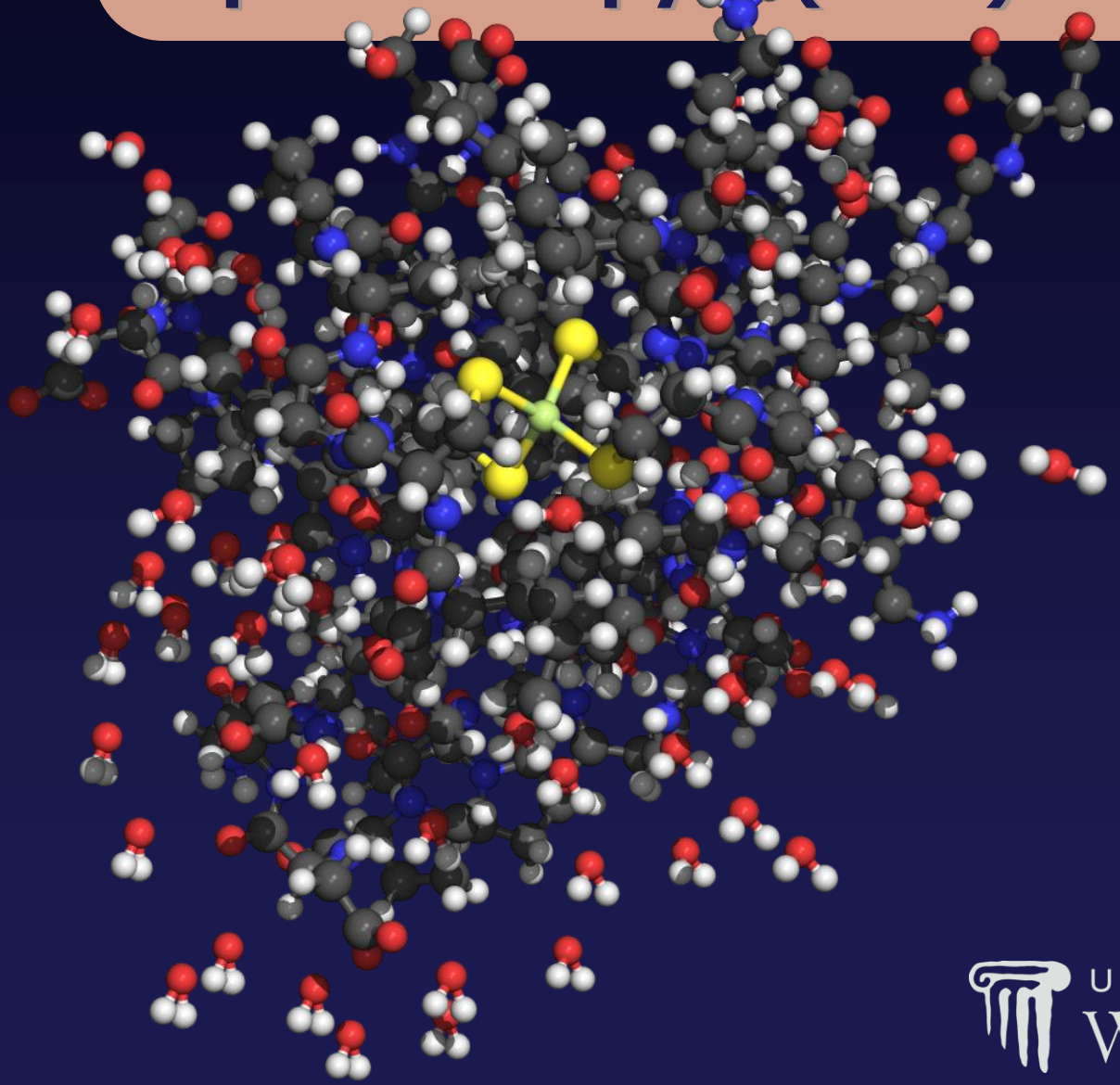
Thermal Effects in X-Ray Absorption Spectroscopy (XAS)

Vila *et al.* Phys. Rev. B 76, 014301 (2007)

Dynamic Structure in Pt Nanoclusters on γ–Al_2O_3

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

Thermal Effects in X-Ray Absorption Spectroscopy (XAS)



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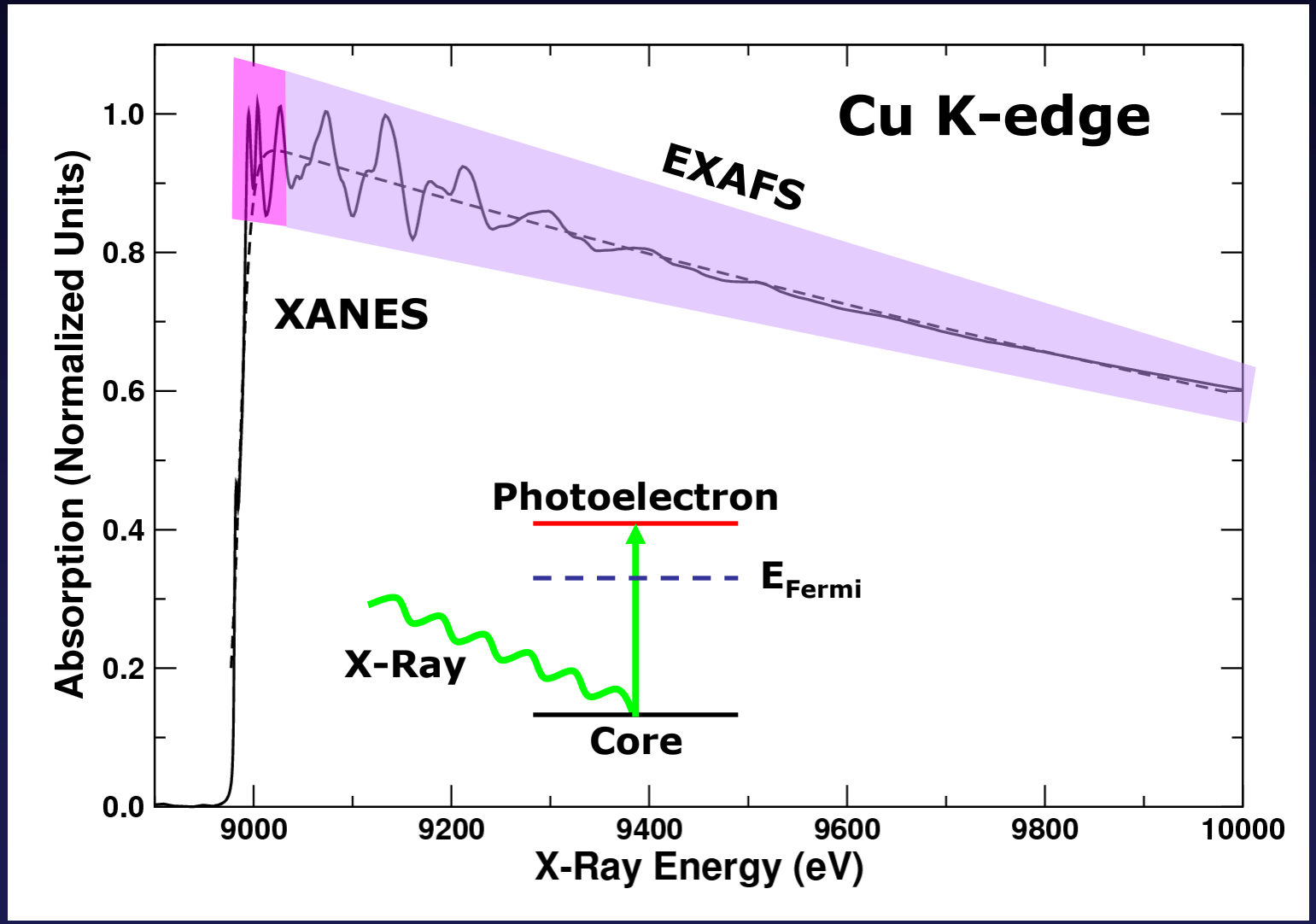
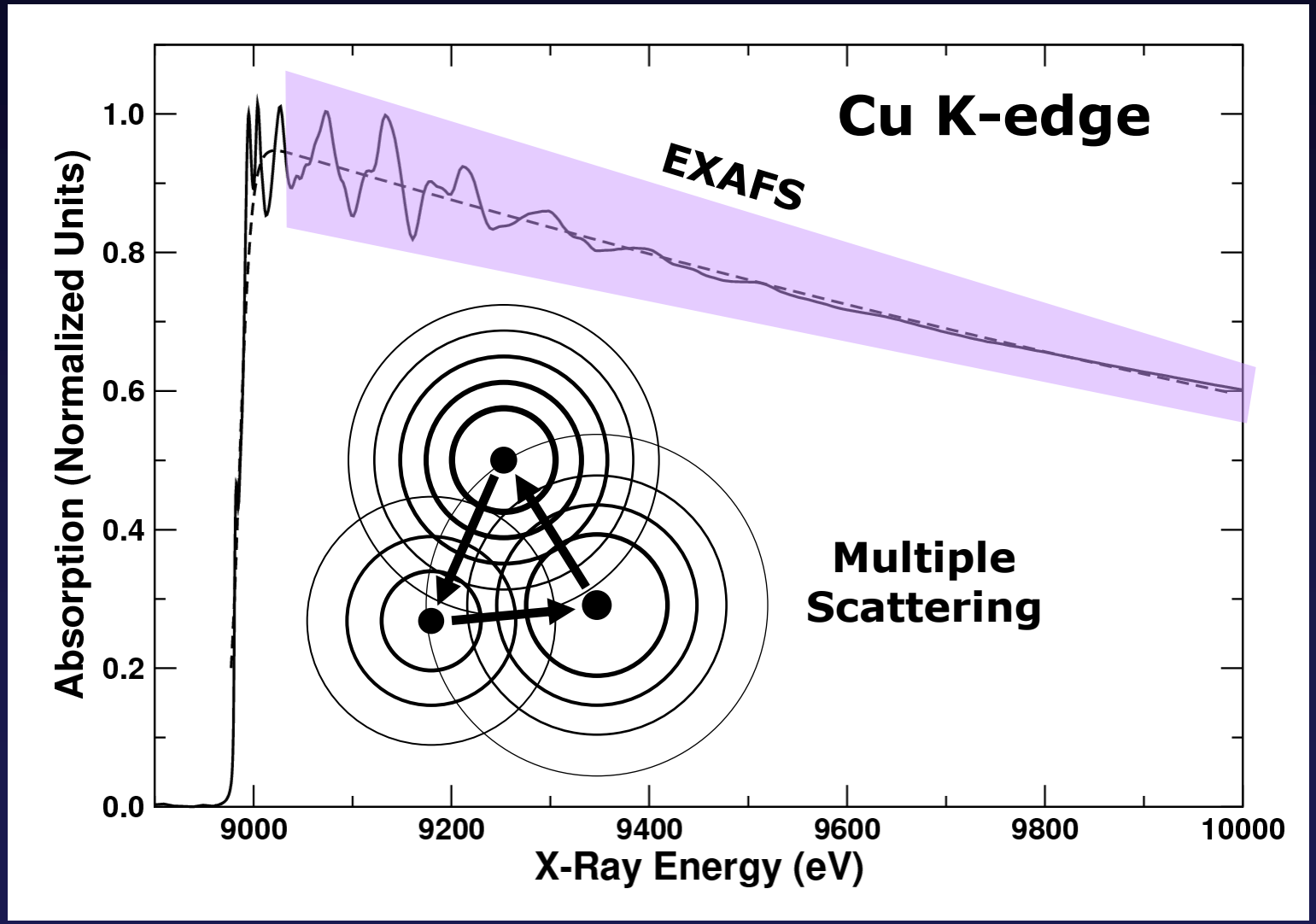
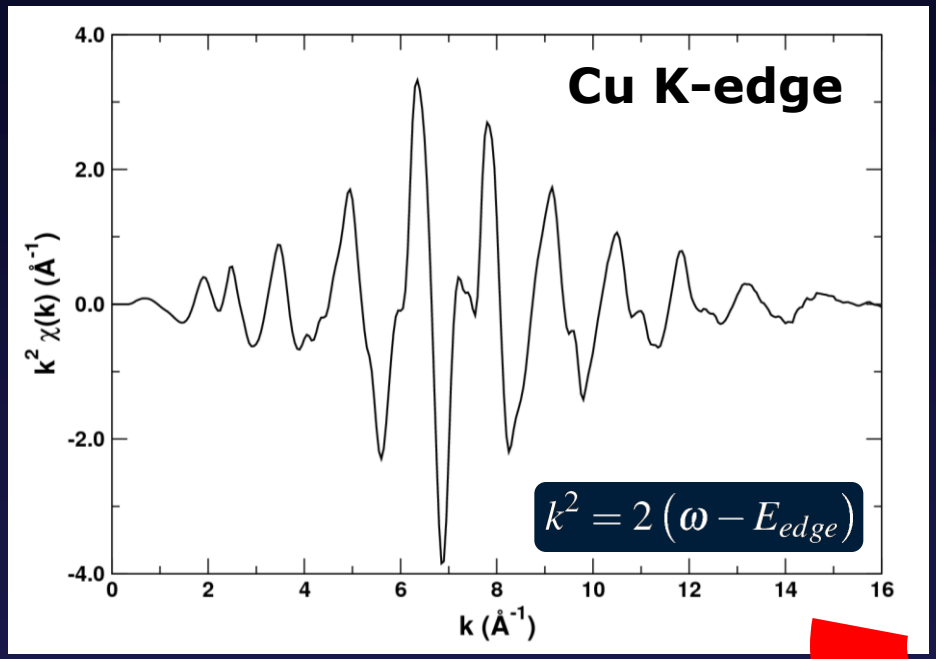
Typical XAS Spectrum

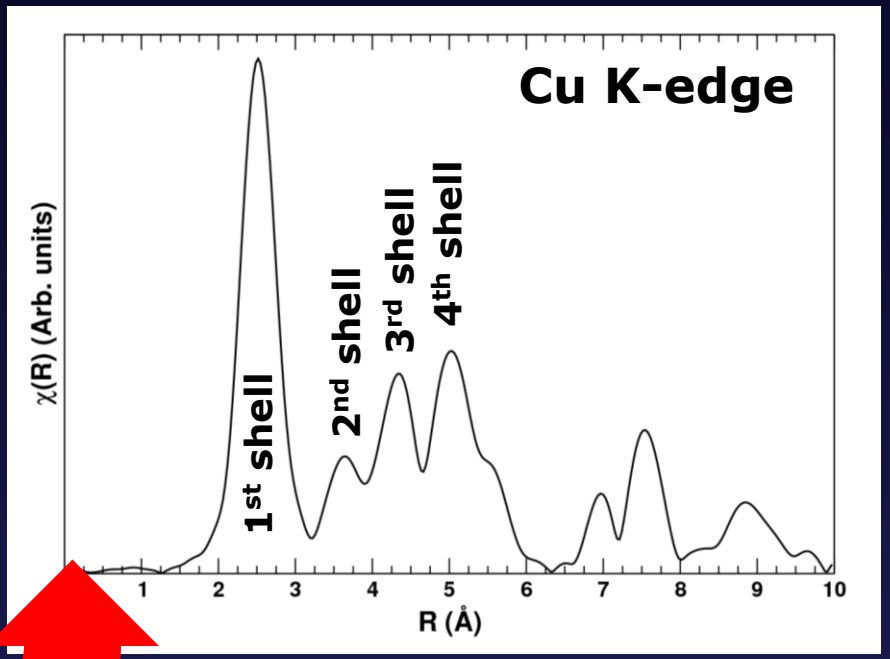


Typical XAS Spectrum



EXAFS Fine Structure





FT

$$\chi(k) = -k\sum_i S_0^2 N_i \frac{f_i^{eff}(k)}{R_i^2} e^{-R_i/\lambda} sin\left(2kR_i + 2\phi(k)\right) \boxed{e^{-\sigma_i^2 k^2/2}}$$

Sayers, Stern and Lytle (1970)

EXAFS Cumulants

$$\chi(k) = -k \sum_i S_0^2 N_i \frac{f_i^{eff}(k)}{R_i^2} e^{-R_i/\lambda} sin\left(2kR_i + 2\phi(k)\right) e^{-\sigma_i^2 k^2/2}$$

Multiple Scattering XAFS DW Factor:

$$\left\langle e^{i2kr} \right\rangle \equiv e^{2ikR_0} e^{-W(T)}$$

Configurational average: cumulant expansion

$$W(T) = -\sum_{n=1}^{\infty} \frac{(2ik)^n}{n!} \sigma^{(n)}(T)$$

EXAFS Cumulants

$$\sigma^{(1)} = \langle r - R_0 \rangle$$

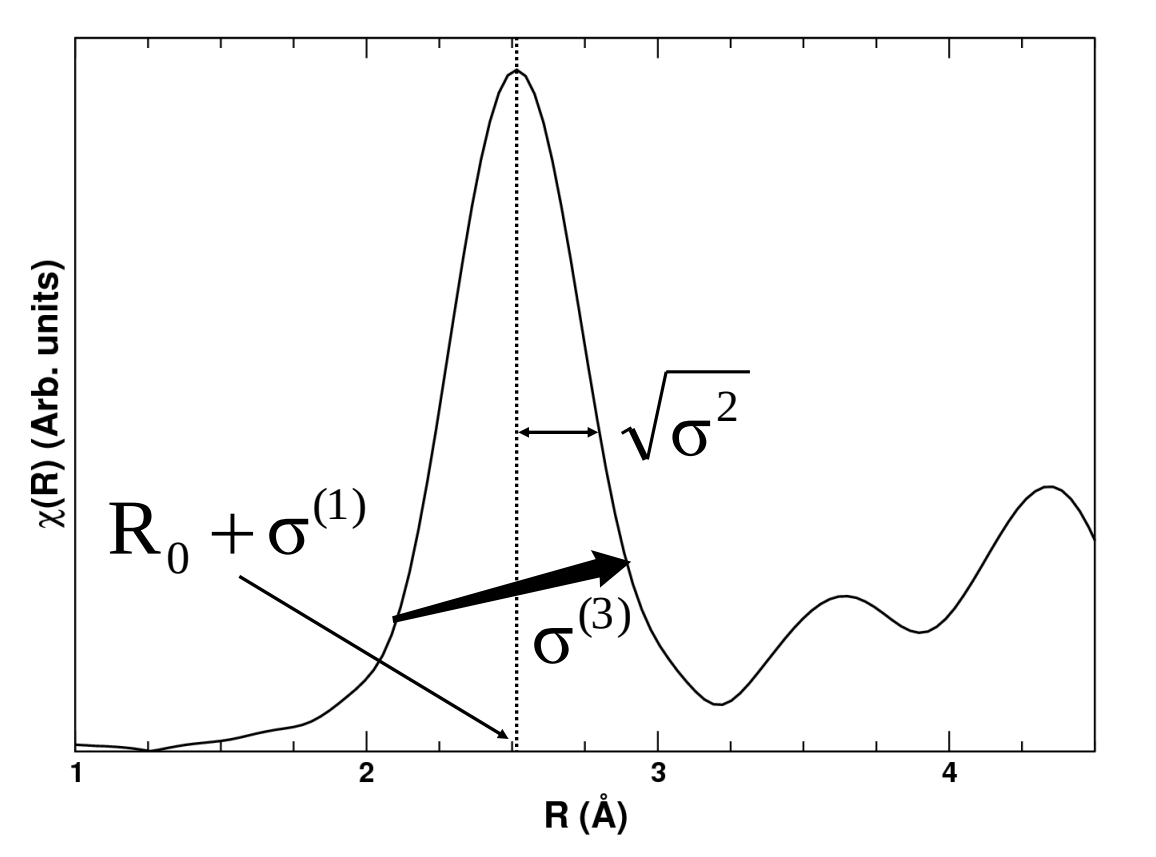
"Expansion"

$$\sigma^{(2)} = \langle (r - \bar{r})^2 \rangle \equiv \sigma^2(T)$$

"Width" (MSRD)

$$\sigma^{(3)} = \langle (r - \bar{r})^3 \rangle$$

"Skew"



The Problem

Can we **calculate** the **EXAFS MSRD** in **crystals** from **first principles**? ❶

How about **anharmonicity**-related **properties**, like lattice expansion and skew? ❷

Can we do the same for **systems** with **complex** force fields (*i.e.* **molecules**)? ❸

Calculation of the Vibrational DOS

XAFS MSRD for path R:

$$\sigma_R^2(T) = \frac{\hbar}{2\mu_R}\int_0^\infty \frac{1}{\omega}\coth\left(\frac{\beta\hbar\omega}{2}\right)\rho_R(\omega)\,d\omega$$

R-Projected VDOS: Imag. part of the phonon propagator

$$\rho_R(\omega) = -\frac{2\omega}{\pi}\mathrm{Im}\left\langle 0\left|\frac{1}{\omega^2 - \mathbf{D} + i\varepsilon}\right|0\right\rangle$$

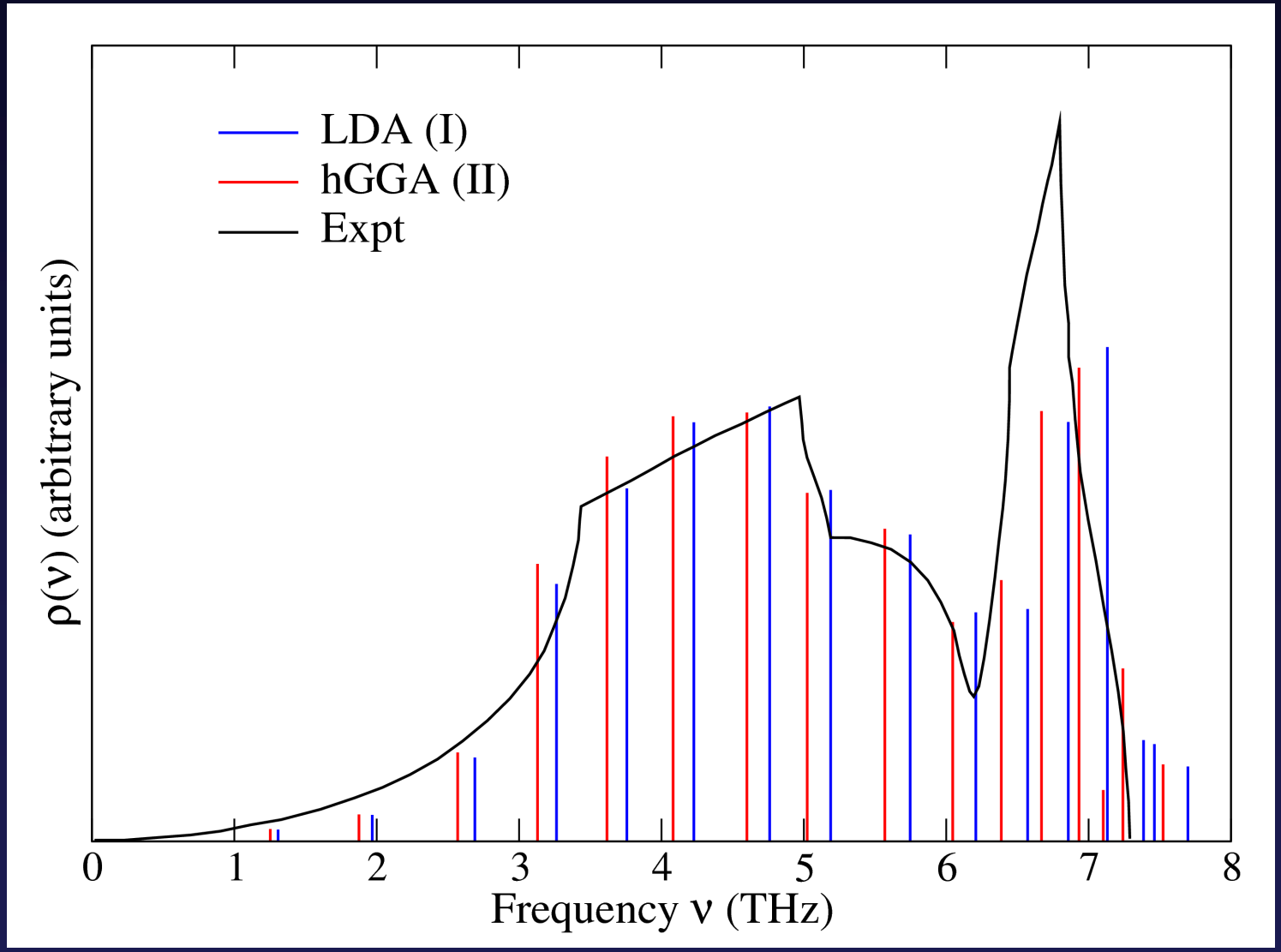
Dynamical Matrix or Hessian

Seed state: Displacement along R

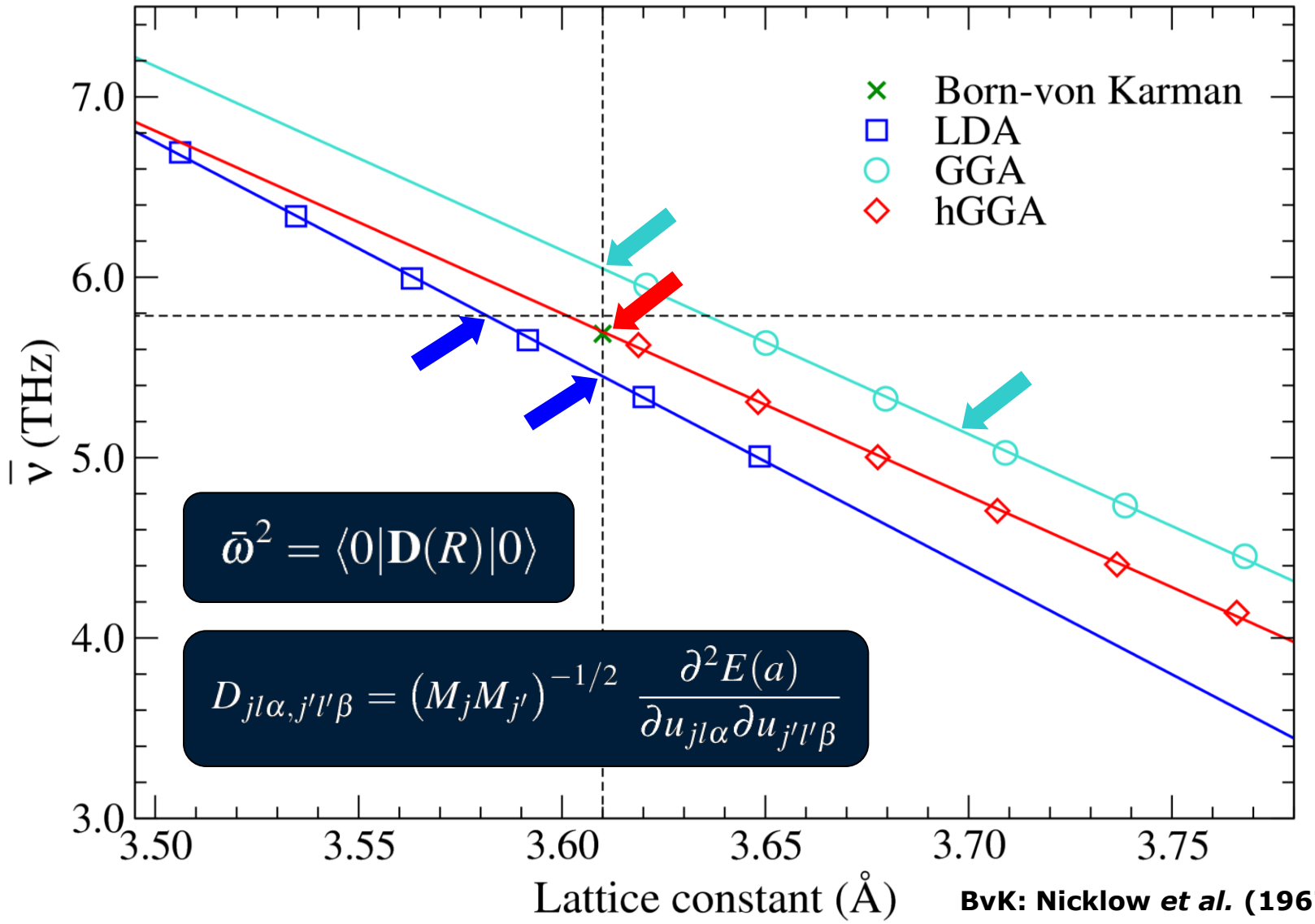
Lanczos *N*-Order Recursion: Convert integral to weighted sum

$$\sigma_R^2(T) = \frac{\hbar}{2\mu_R}\sum_{\nu=1}^{N}\frac{w_\nu}{\omega_\nu}\coth\frac{\beta\hbar\omega_\nu}{2}$$

Total VDOS of Cu



Anharmonicity on the Einstein Freq. of Cu



BvK: Nicklow *et al.* (1967)

Calculation of the Dynamical Matrix

I. **Calculate D with the LDA at the theoretical estimate of *a(T)***

- **Fully *ab initio***
- **Provides lattice expansion directly**

$$F(a,T) = E(a) + 3k_B T \int_0^\infty d\omega \ln\left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]\rho_a(\omega)$$

II. **Calculate *D* with the hGGA at the exp. estimate of *a(T)***

- **Uses a new functional (hGGA): 50% LDA + 50% GGA**
- **Requires experimental input**
- **Lattice expansion from Correlated Einstein model**

XAFS MSRDs (in 10^{-3} Å^2) for Pt and GaAs

	n	CD	LDA(I)	hGGA(II)	Expt
Pt (190 K)	1	3.55	3.23	3.23	3.22 ± 0.05
	2	4.38	4.64	4.78	4.7 ± 0.3
	3	4.50	4.44	4.49	4.3 ± 0.4
	4	4.56	4.60	4.66	4.5 ± 0.4
Pt (300 K)	1	5.41	4.98	4.90	4.83 ± 0.05
	2	6.69	7.23	7.34	6.8 ± 0.5
	3	6.91	6.92	6.89	6.7 ± 0.6
	4	7.01	7.17	7.16	7.0 ± 0.6
GaAs (295 K)	1	5.17	3.97	3.86	4.2 ± 0.1
	2	7.75	12.70	12.01	11.7 ± 0.14
	3	7.69	14.91	14.01	
GaAs (295 K)	1	5.15	3.96	3.86	4.2 ± 0.1
	2	7.20	10.80	10.19	9.6 ± 0.11
	3	7.68	14.83	14.00	

Expt: Stern *et al.* (1980)

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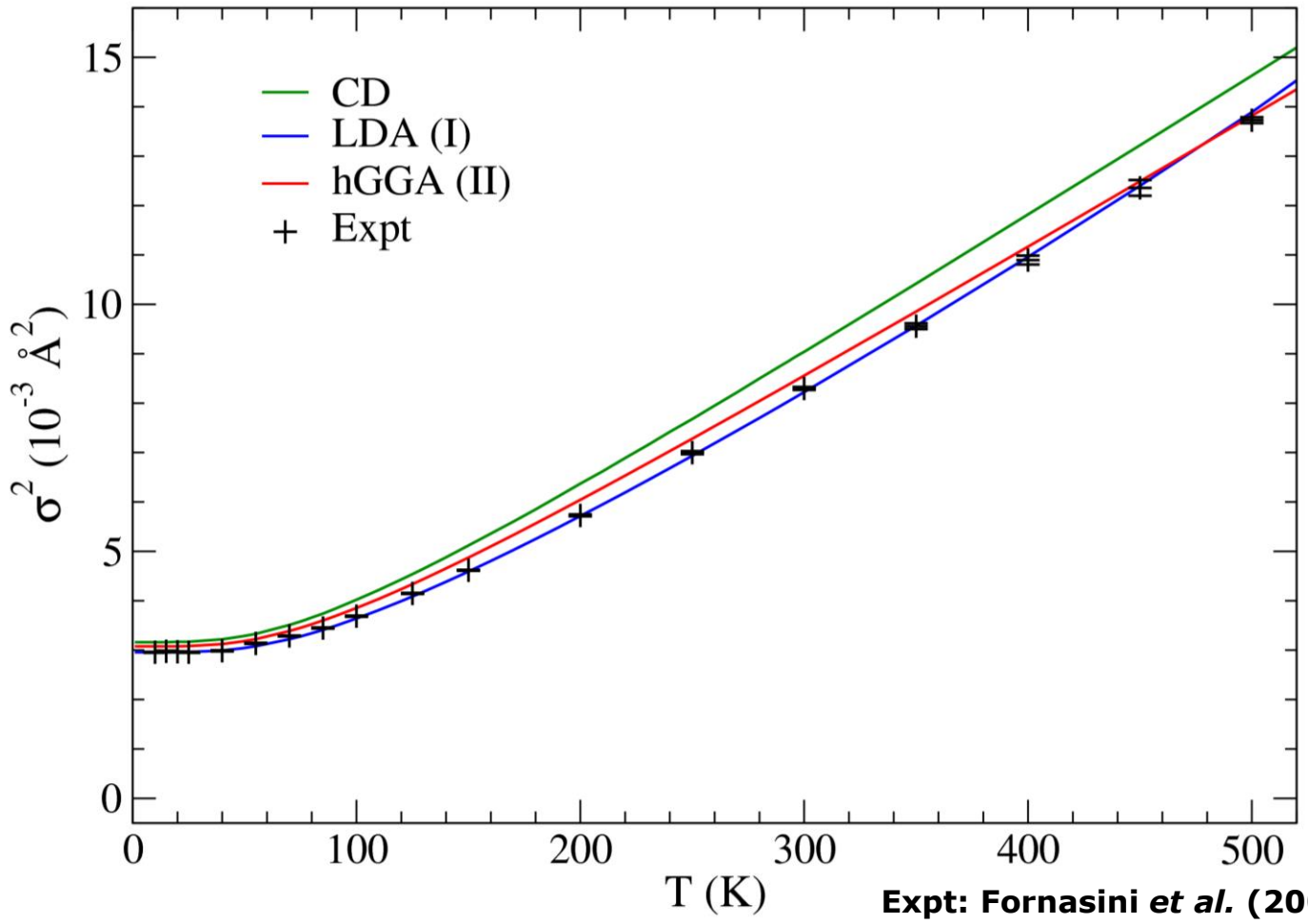
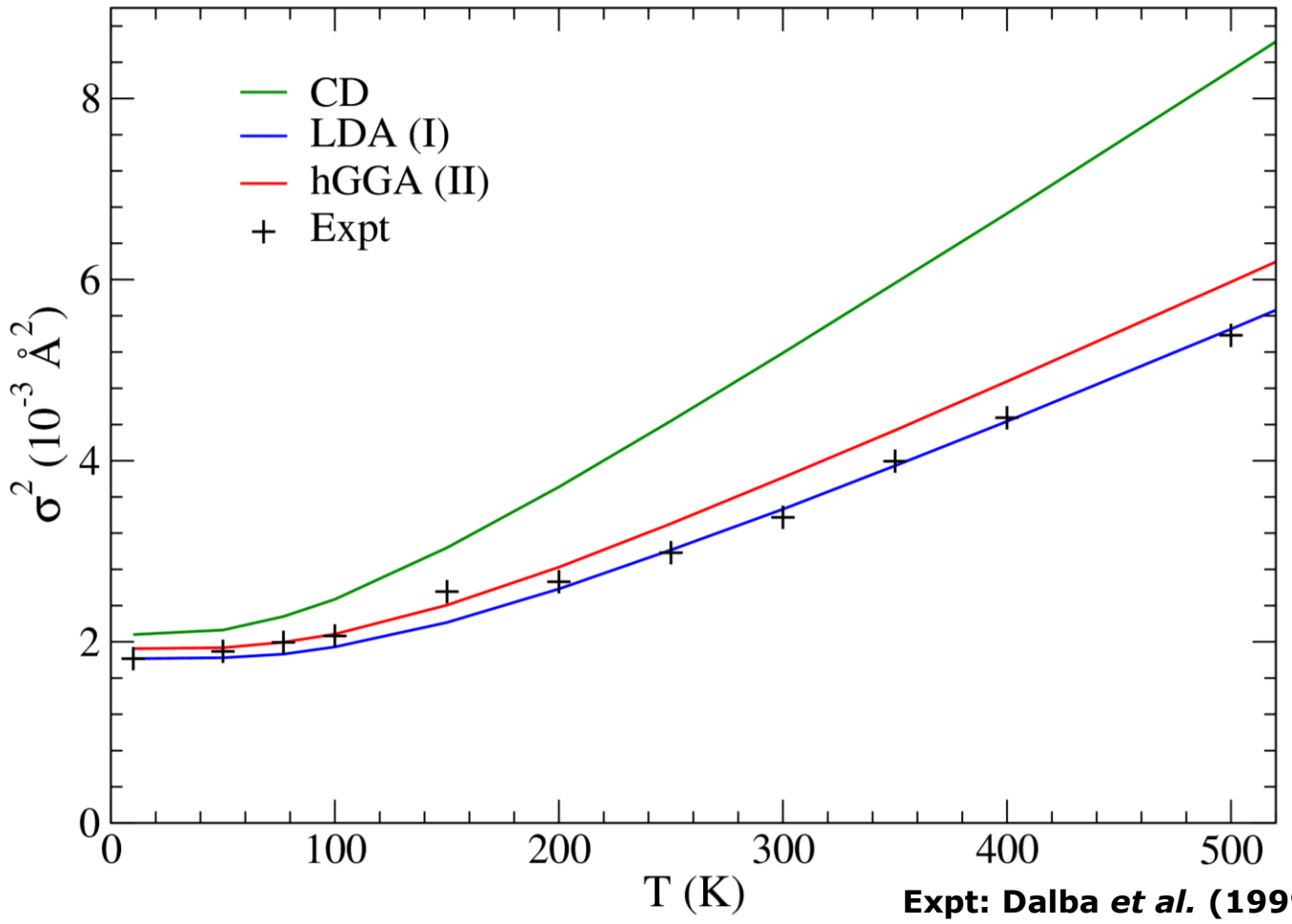
XAFS MSRD of Cu



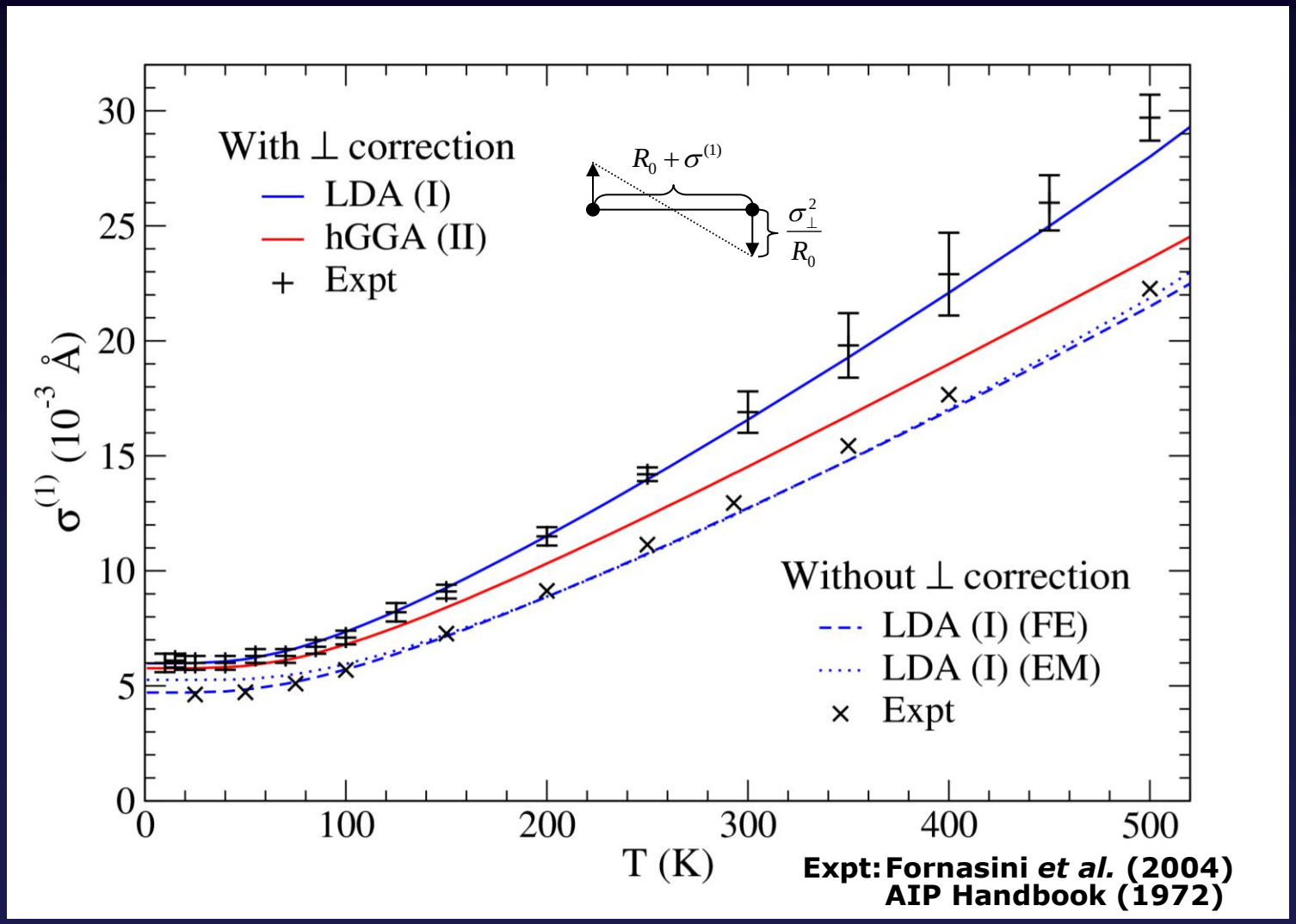
Expt: Fornasini *et al.* (2004)

XAFS MSRD of Ge

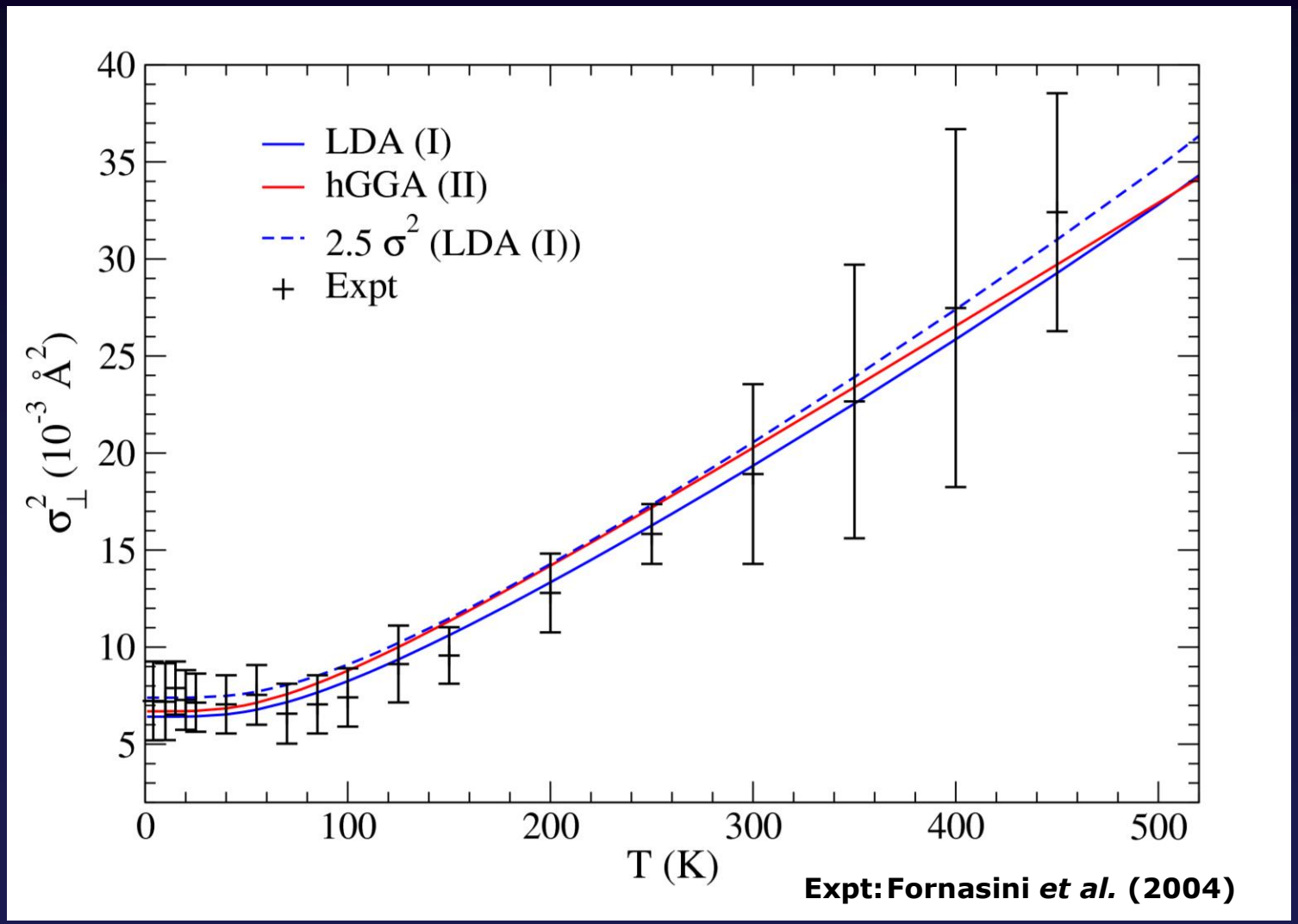


Expt: Dalba *et al.* (1999)

First XAFS Cumulant of Cu



Perpendicular Component of the XAFS MSRD of Cu



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EXAFS MSRDs (in 10^{-3} Å^2) of simple molecules

	N_2			C_6H_6		
Shell	**LDA**	**GGA**	**Exp.**	**LDA**	**GGA**	**Exp.**
1	1.003	0.983	1.033	2.240	2.230	2.009
2				2.770	2.730	2.942
3				2.970	2.900	3.856

	$GeCl_4$			GeH_3Cl		
Shell	**LDA**	**GGA**	**Exp.**	**LDA**	**GGA**	**Exp.**
1	2.040	2.160	2.070	2.200	2.300	3.000

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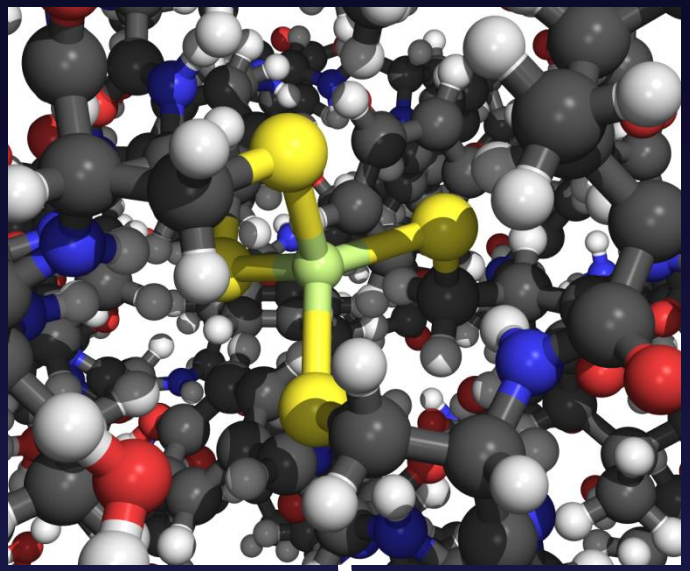
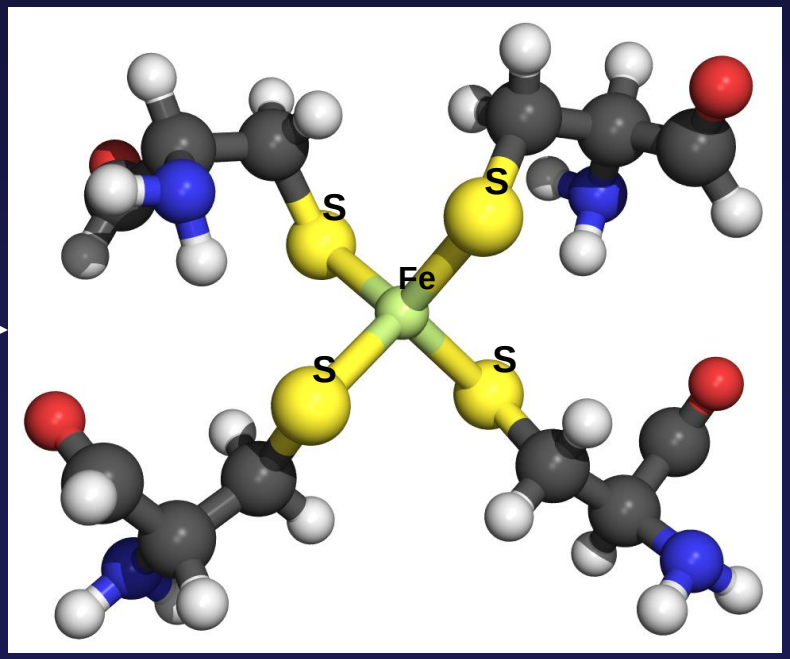
EXAFS MSRDs (in 10^{-3} Å^2) in rubredoxin



Path	Theory	Exp.
Fe-S_1	2.9	2.8±0.5
Fe-S_2	2.9	2.8±0.5
Fe-S_3	3.3	2.8±0.5
Fe-S_4	3.5	2.8±0.5



Convert Full System into Smaller Model

Summary

Method provides:
DW factors (XAS and cryst.), VDOS, lattice expansion and perp. correction ❶

General, applicable to crystalline and amorphous systems ❷

Accuracy dependent only on electronic structure calculation ❸

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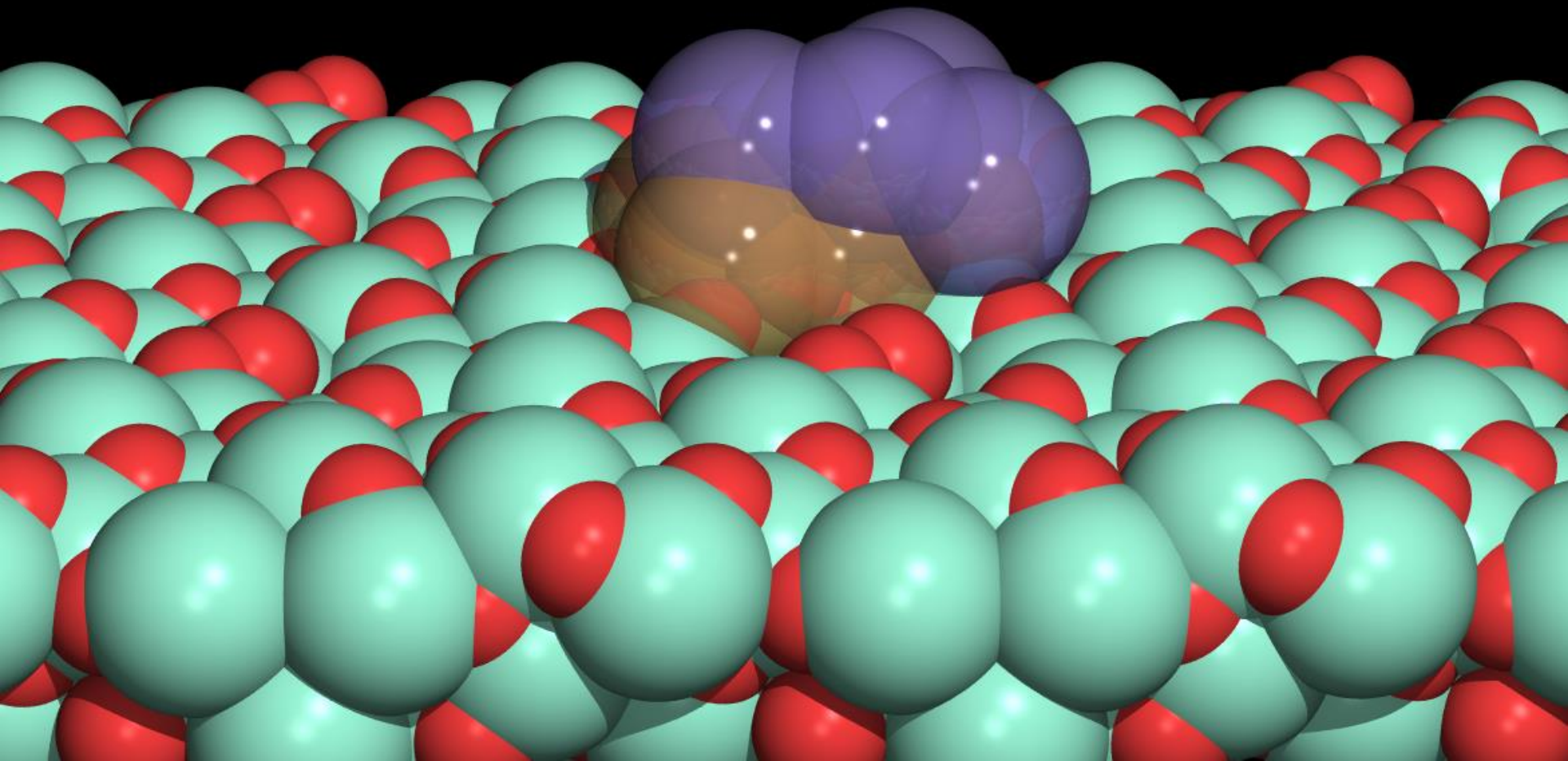
Dynamic Structure in Pt nanoclusters on γ–Al_2O_3



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

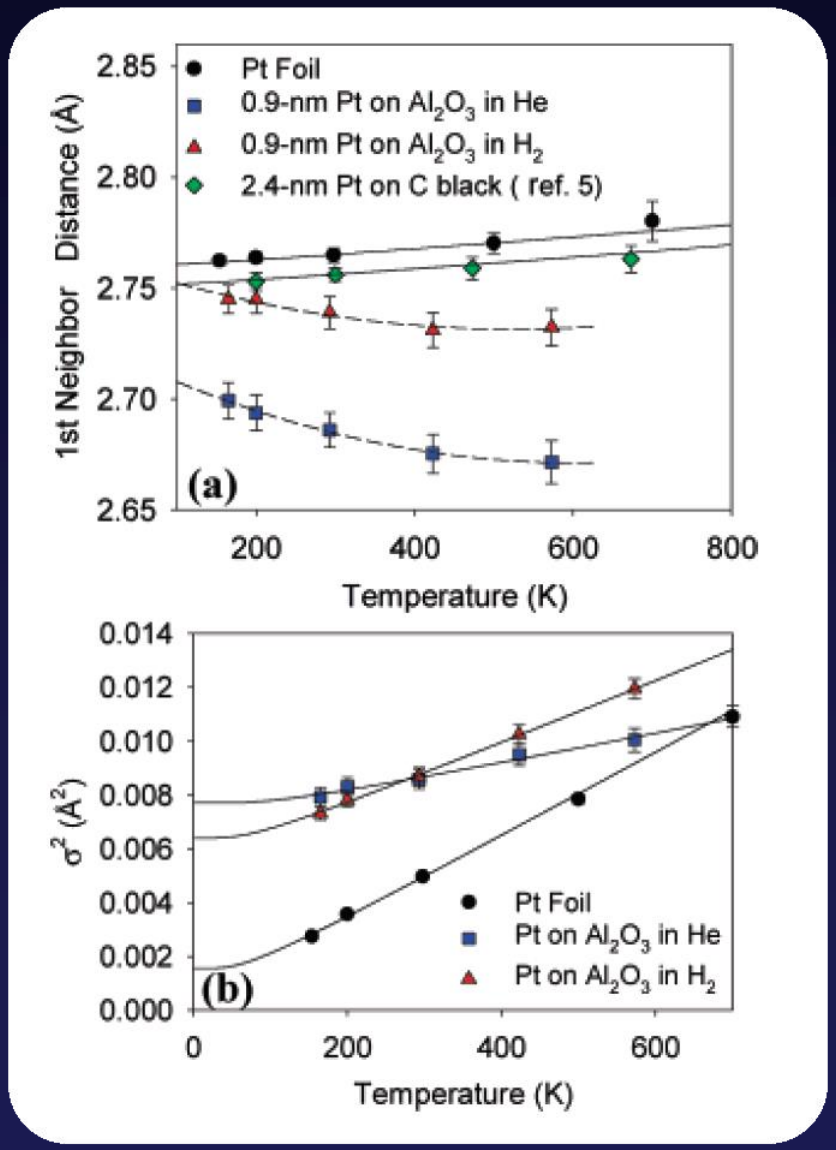
The Problem

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



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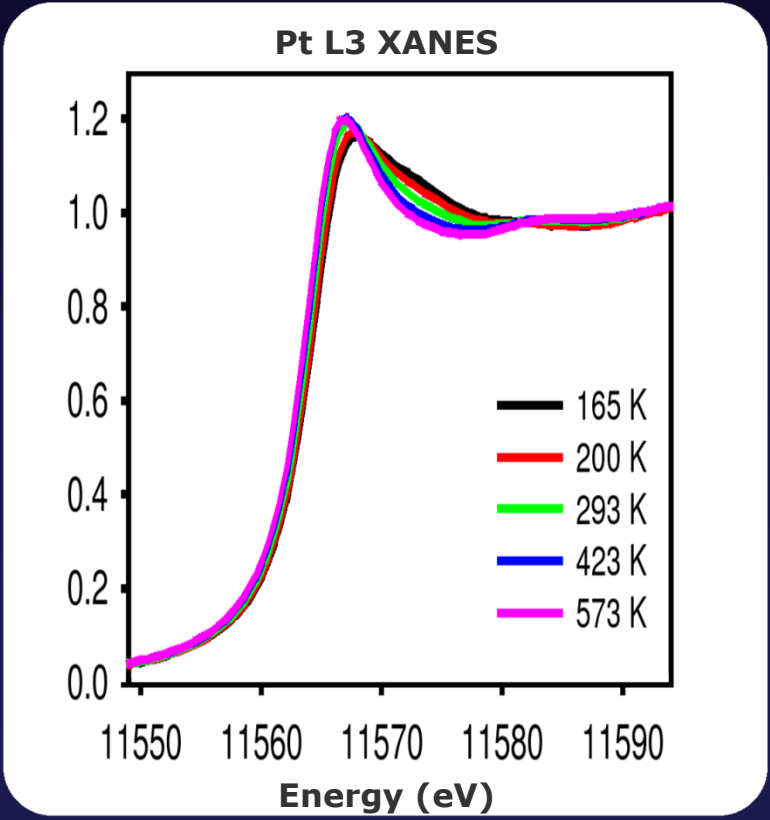
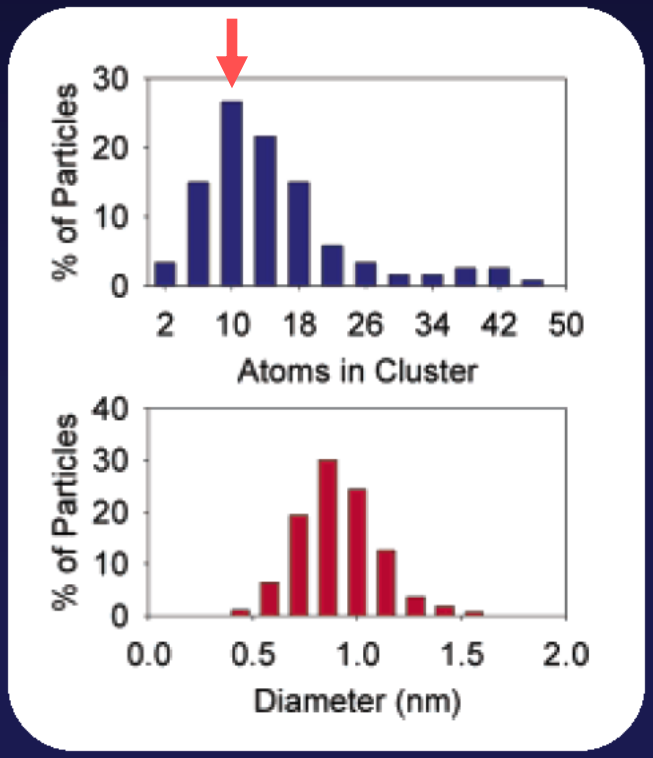


Computational Details

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



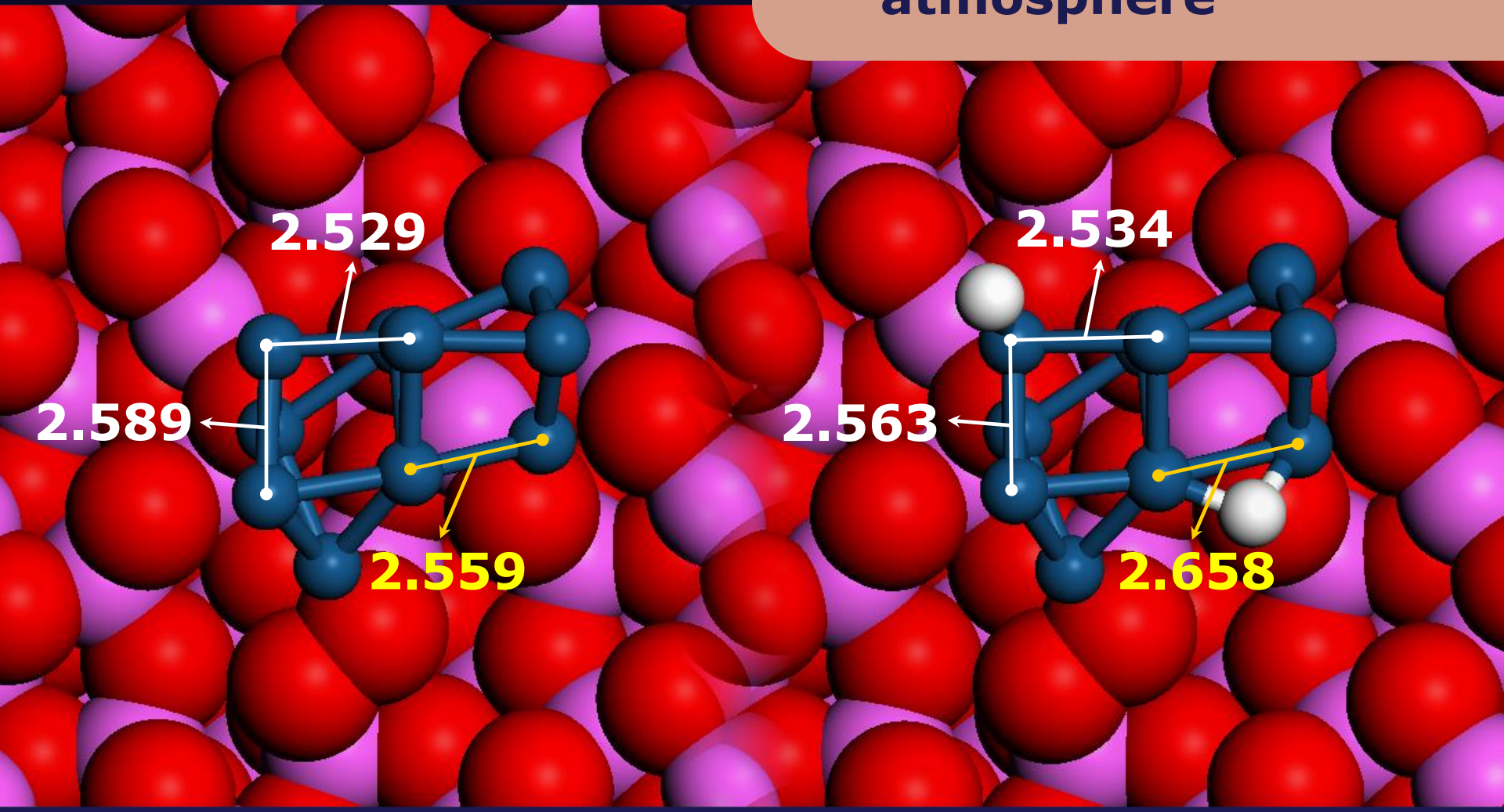
DFT/MD

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

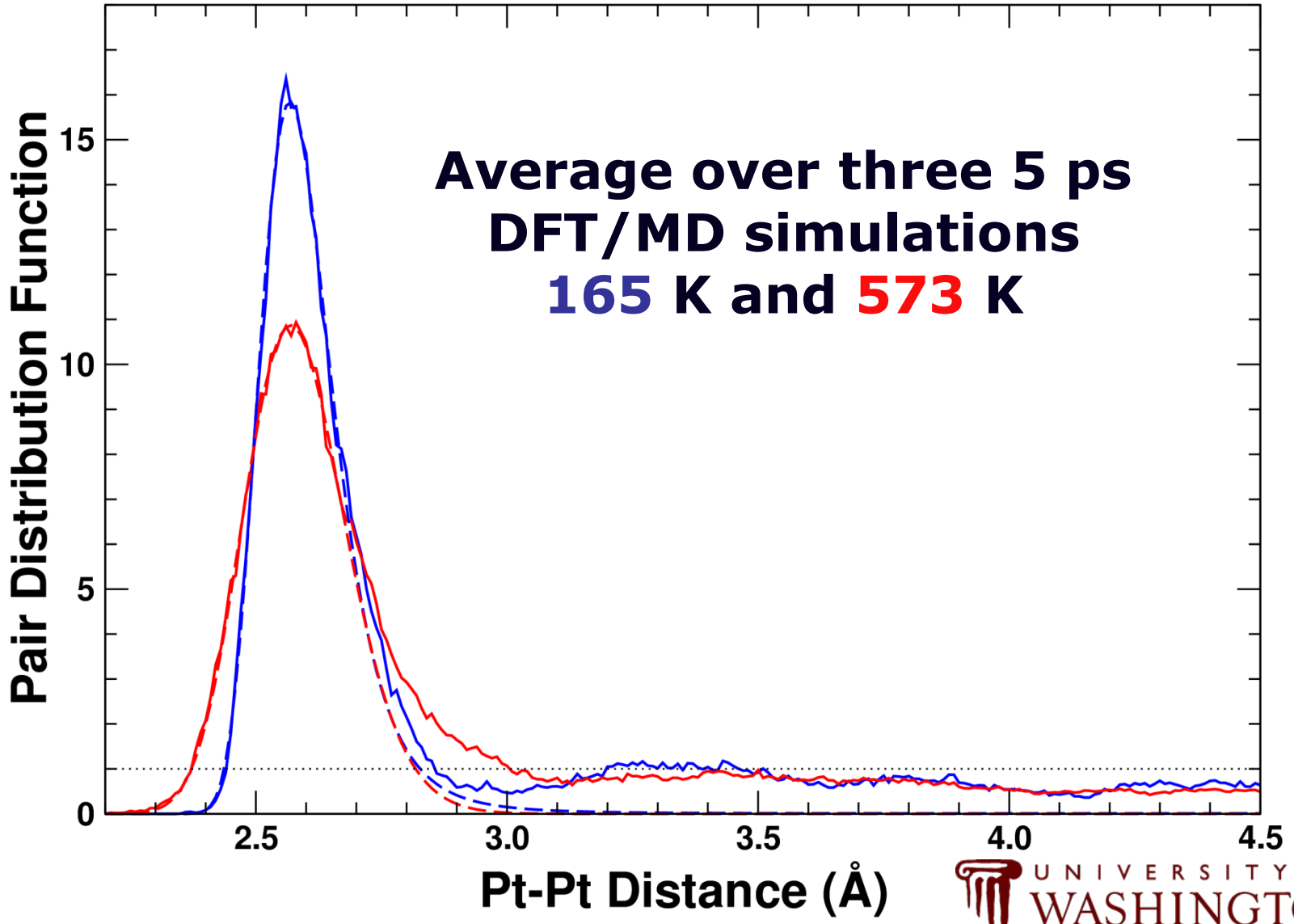
XANES

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

❶ Bond expansion in H_2 atmosphere



Pt-Pt Pair Distribution Function



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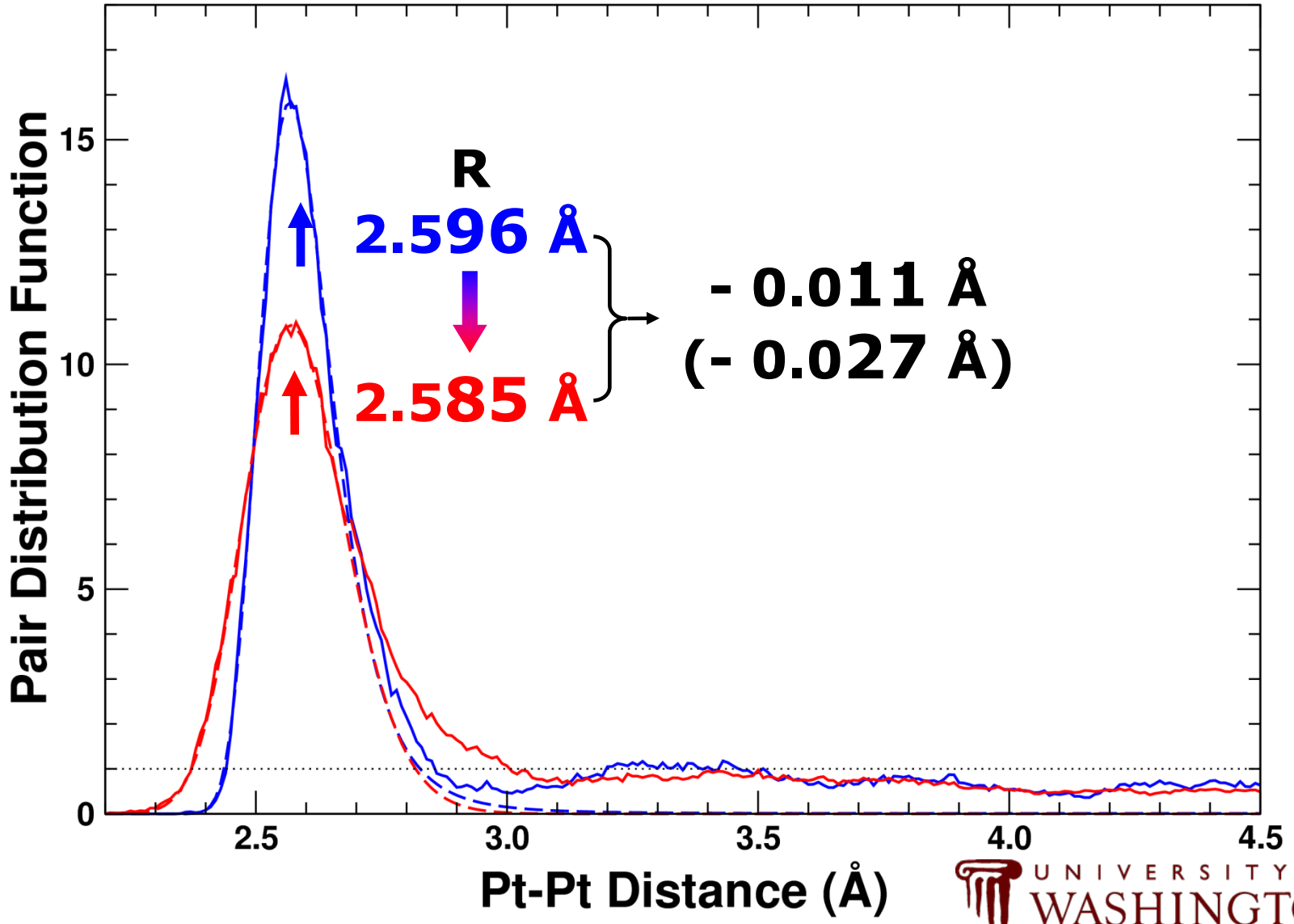
❷ Negative Thermal Expansion



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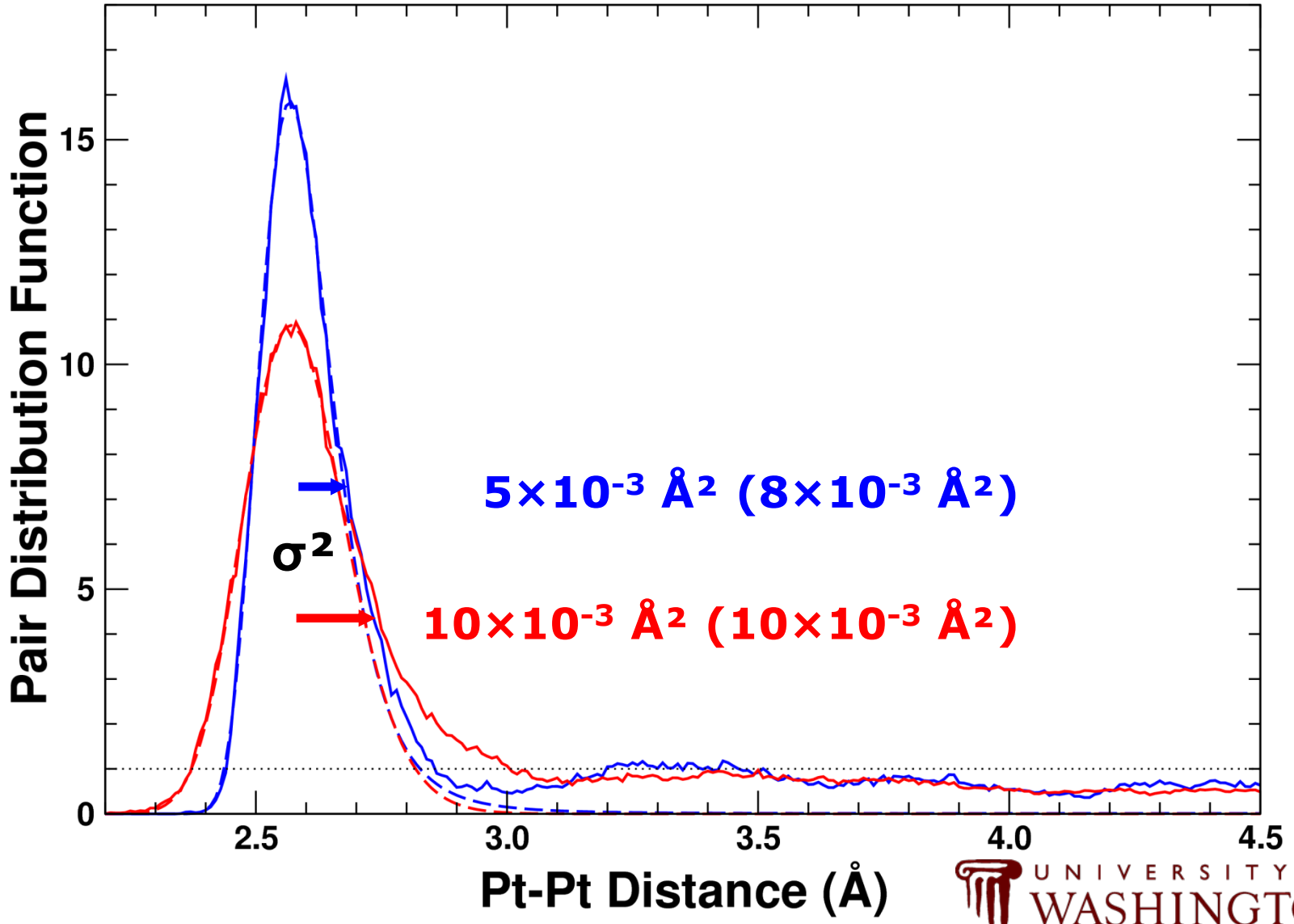
❸ High Pt-Pt Disorder



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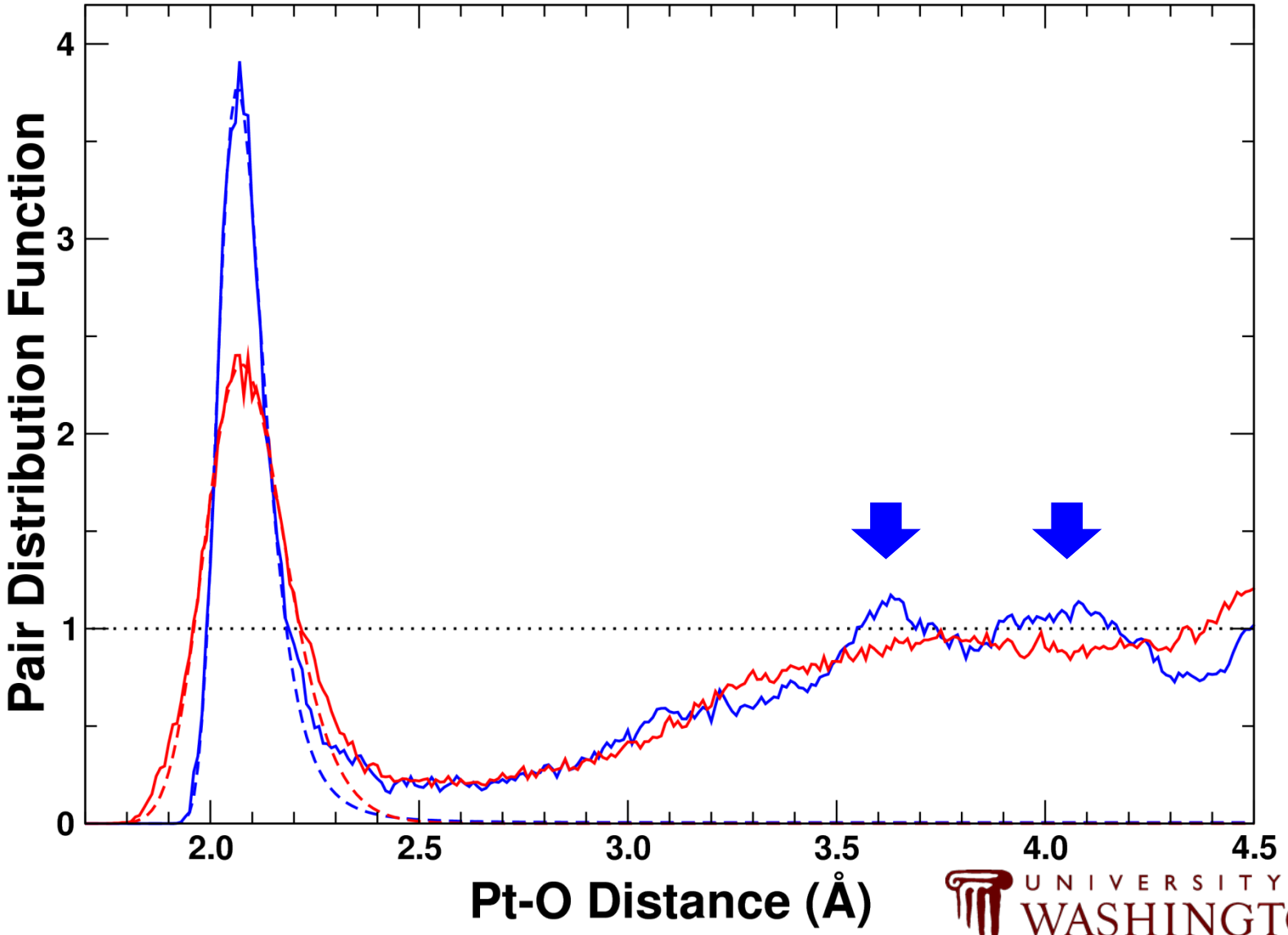
Pt-O Pair Distribution Function



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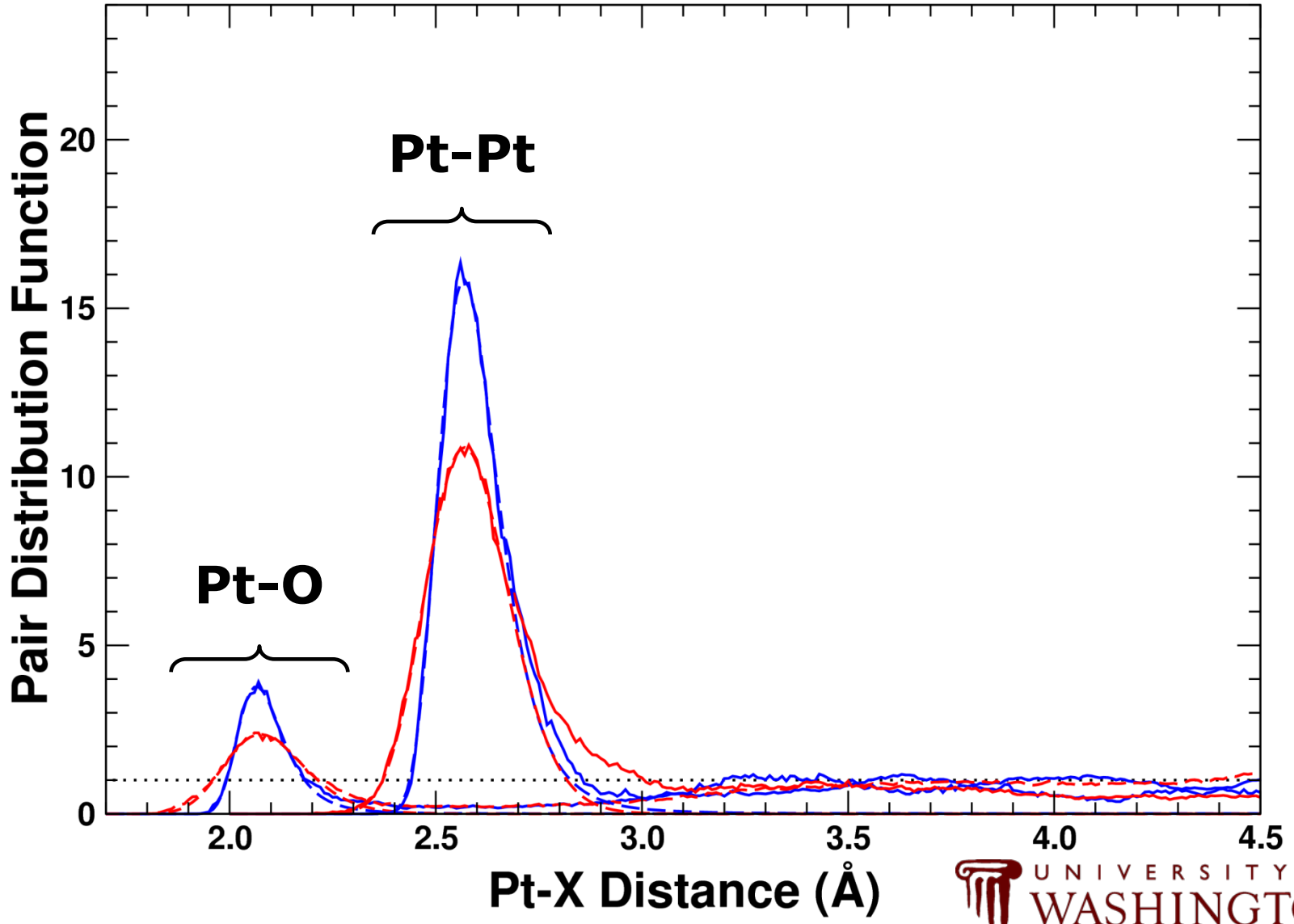
No O-signal in EXAFS



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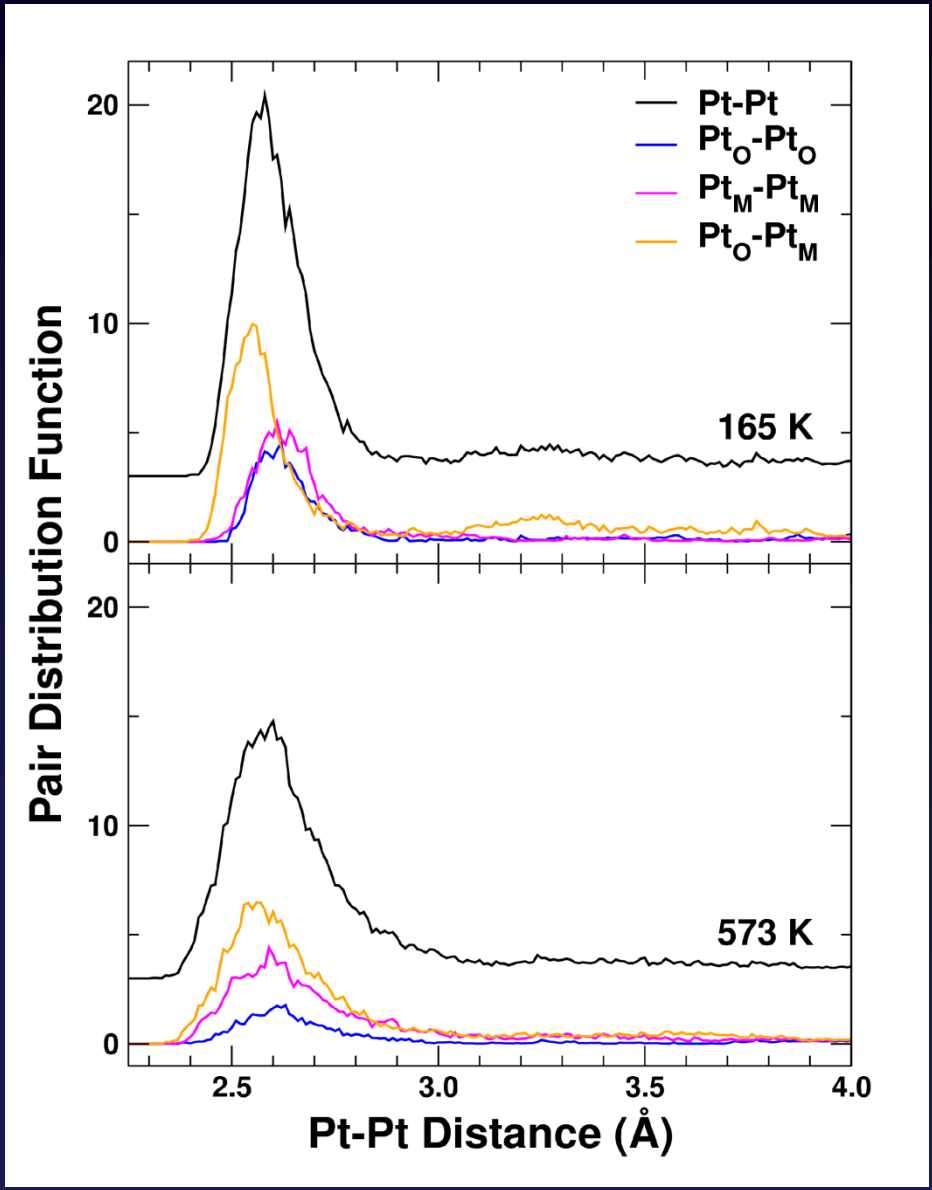
Decomposition of the Pt-Pt PDF



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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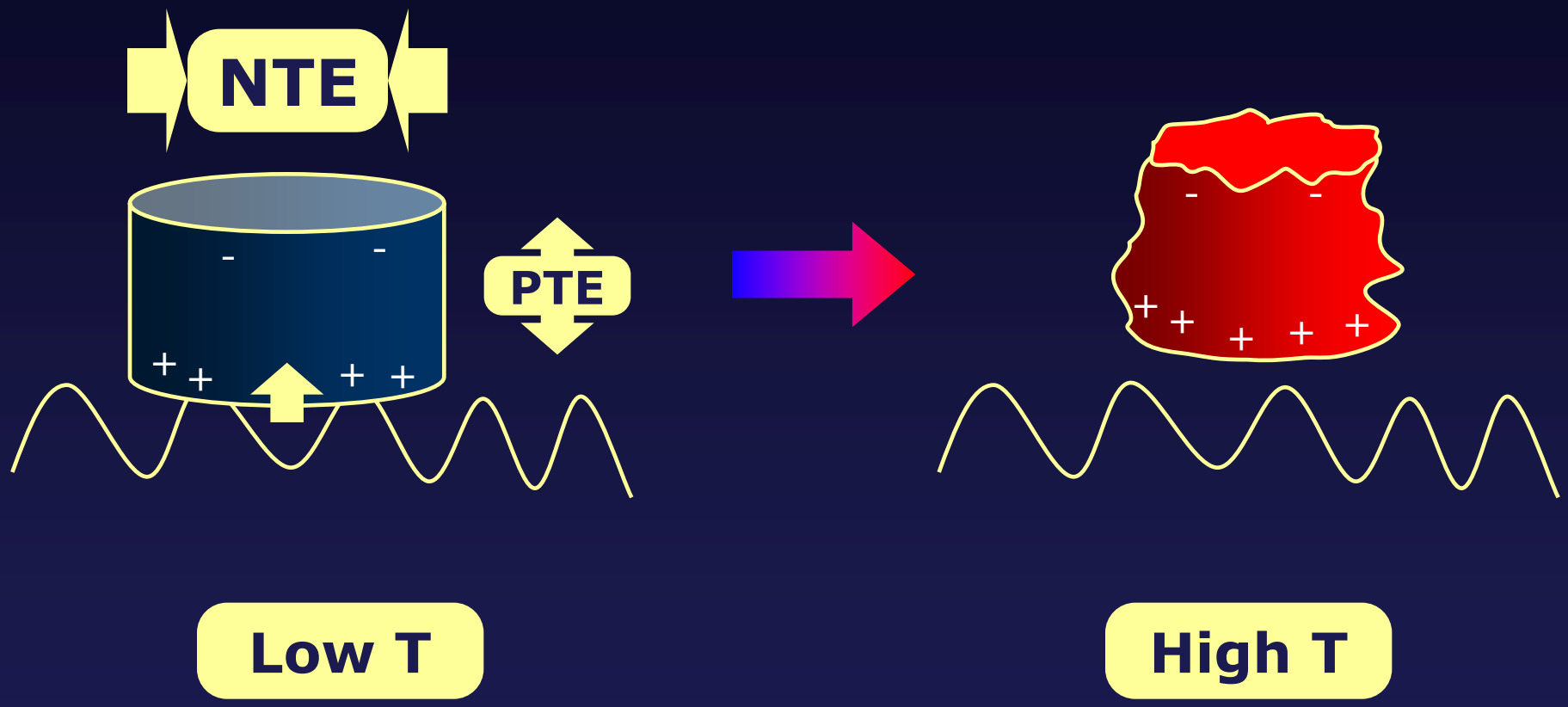
A Simple Model



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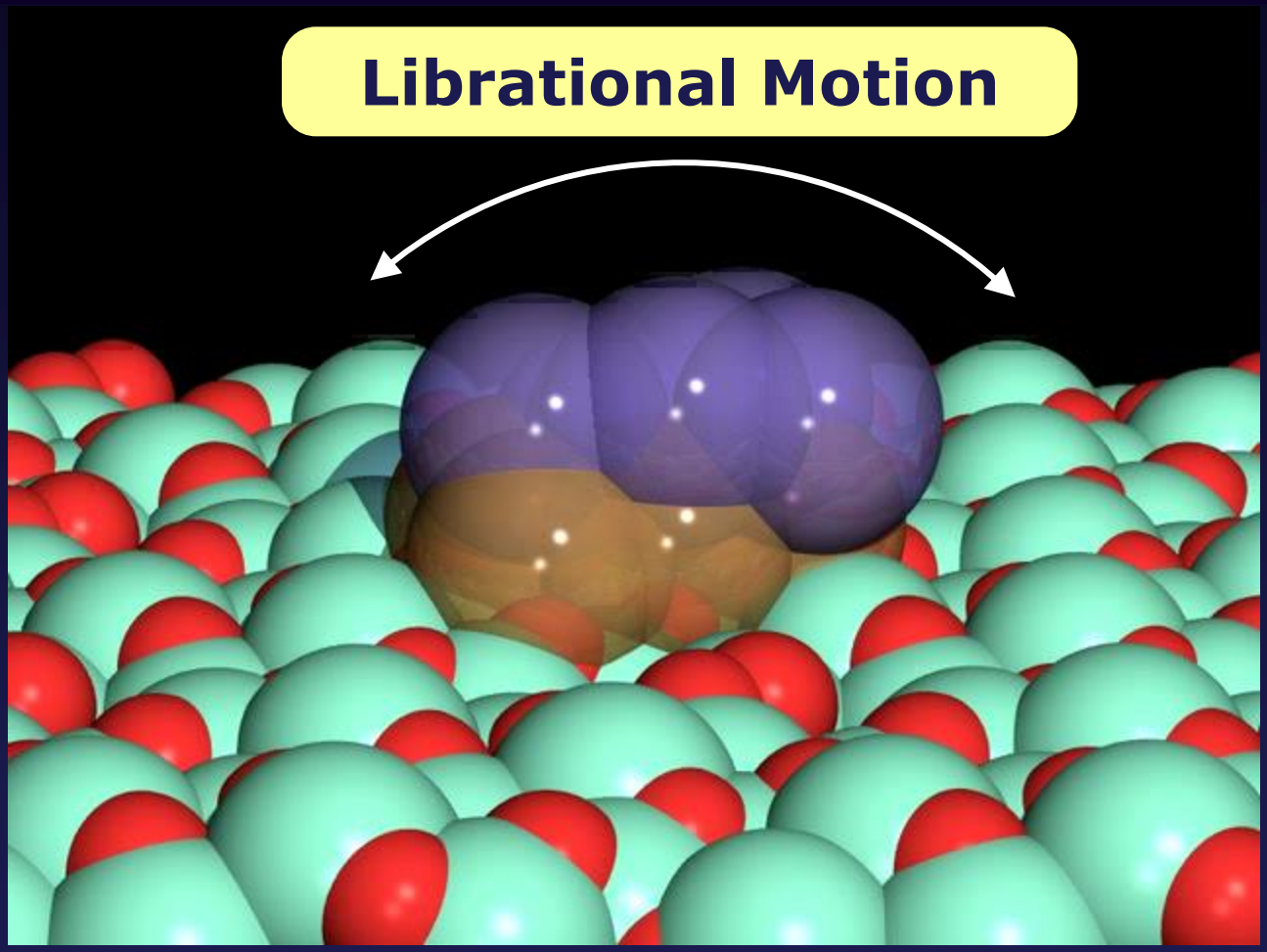
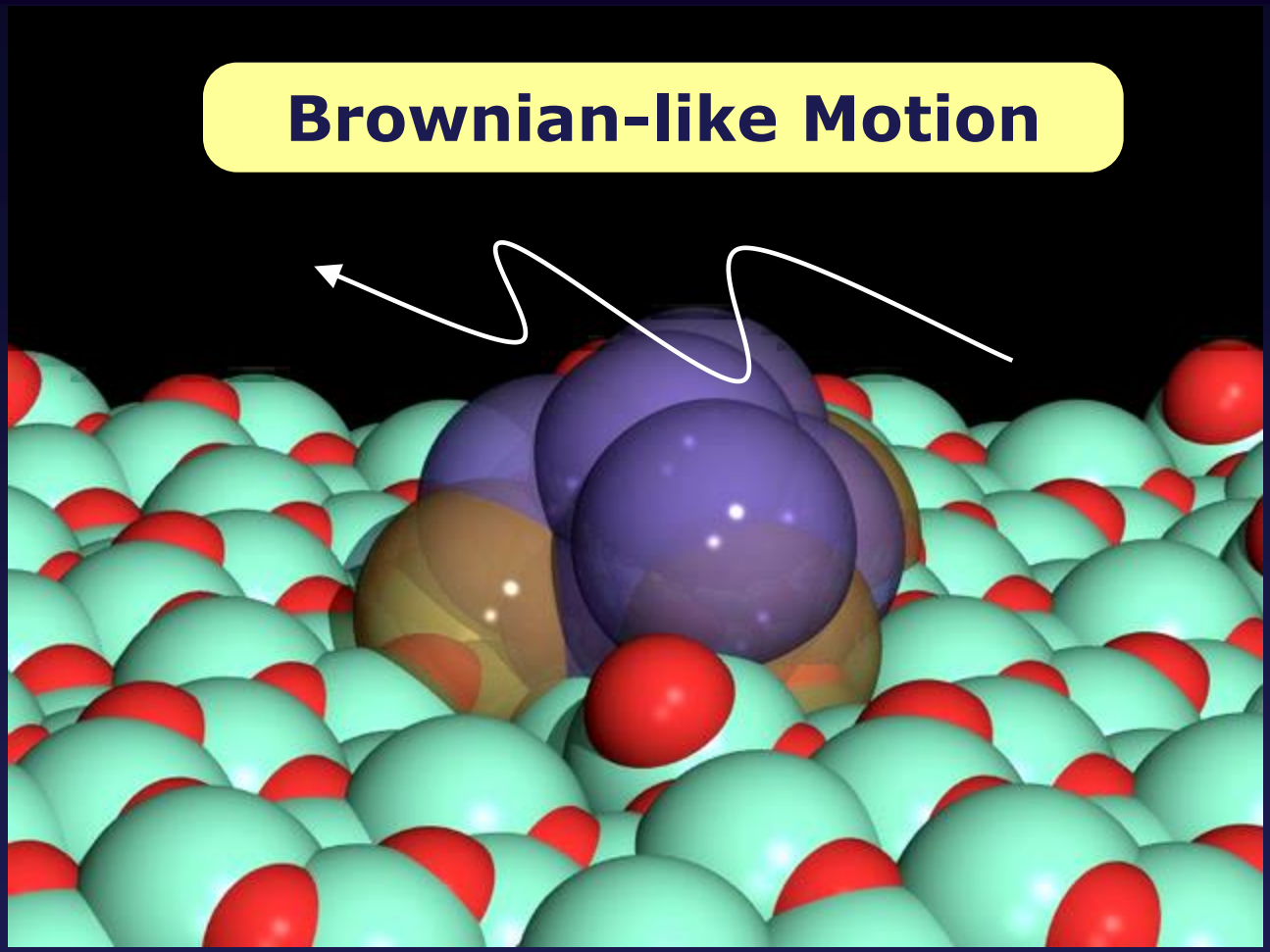
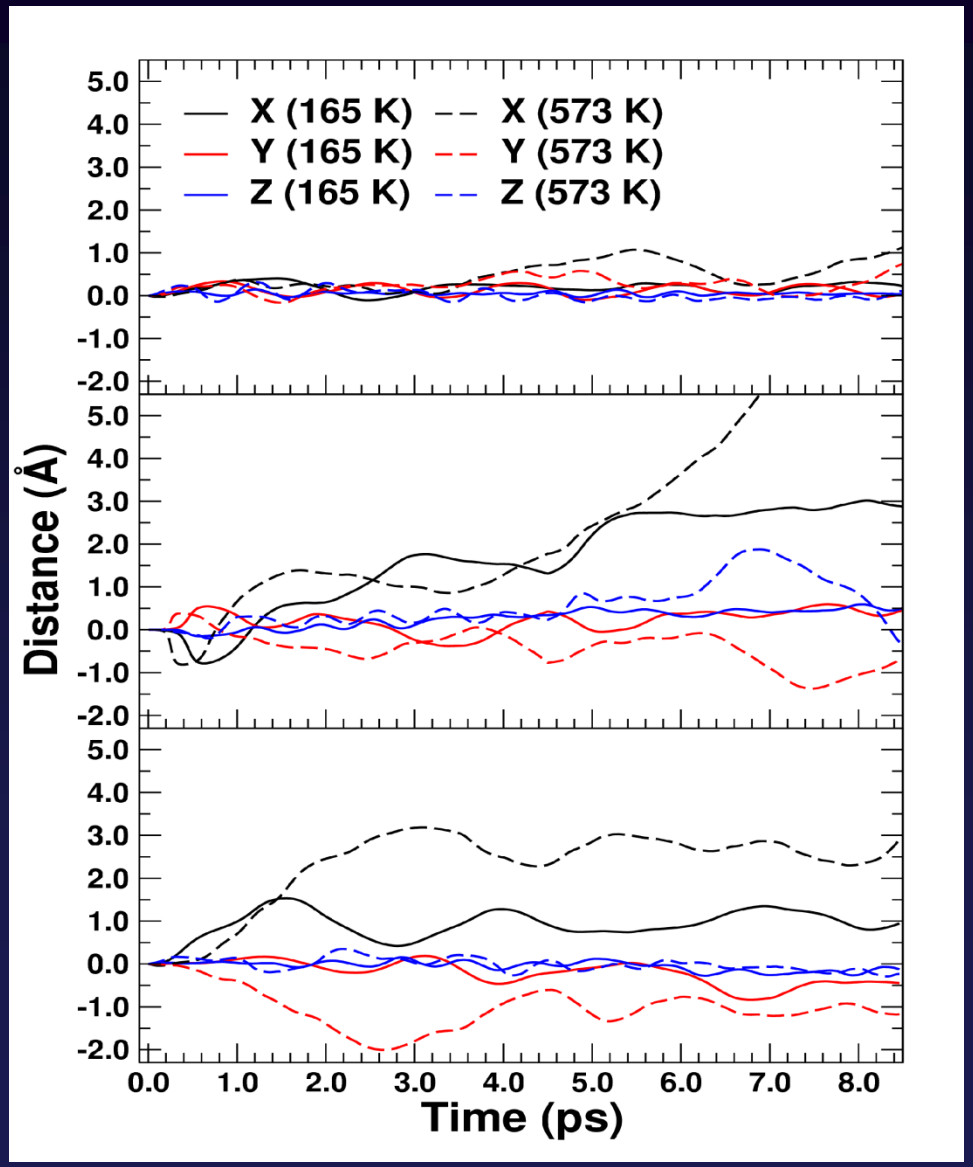
MD @ 165 K



MD @ 573 K



Drift of the cluster Center of Mass



Large amplitude motion on X-Y plane

Smaller amplitude on Z direction

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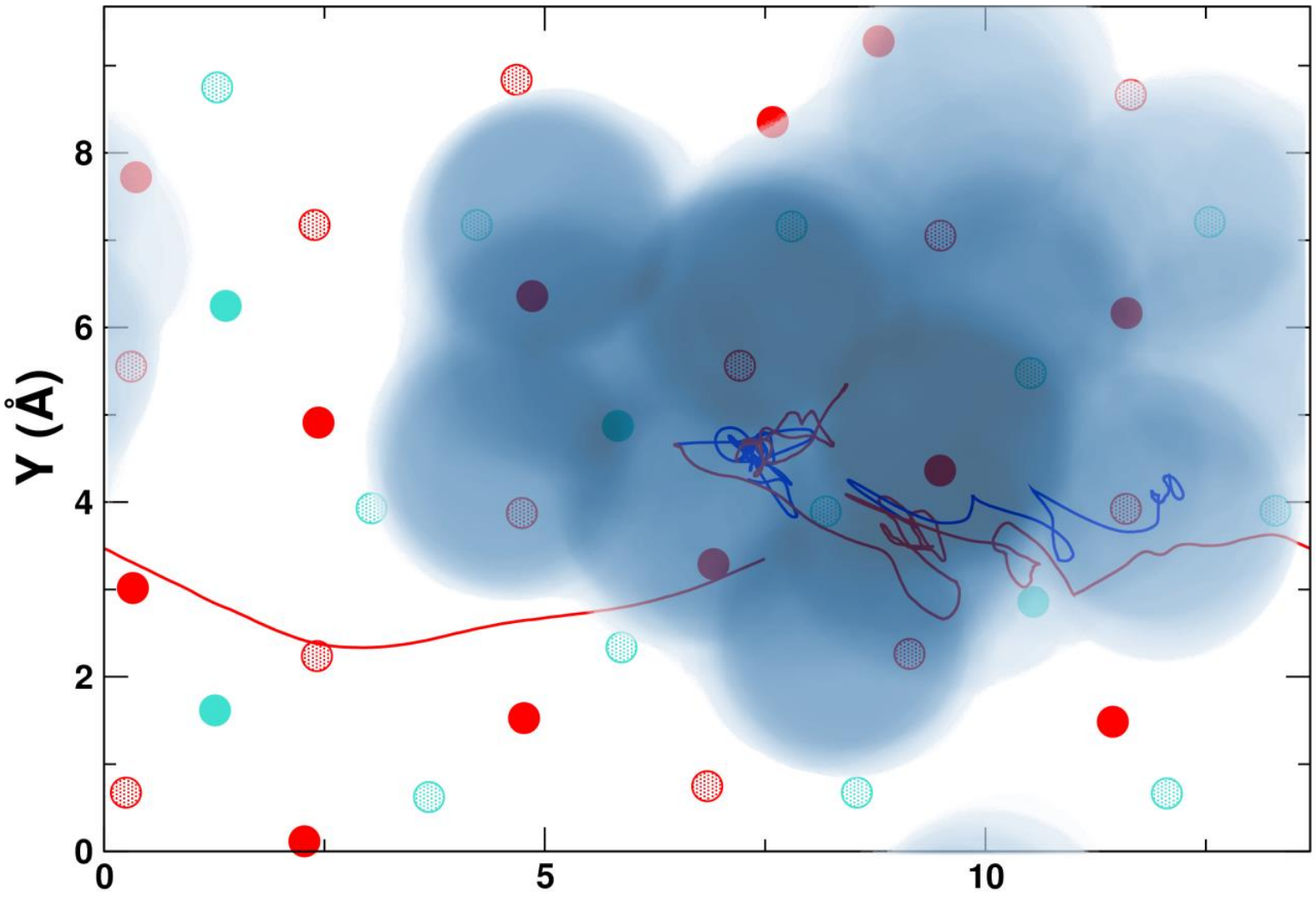
Cluster footprint @ 165 K



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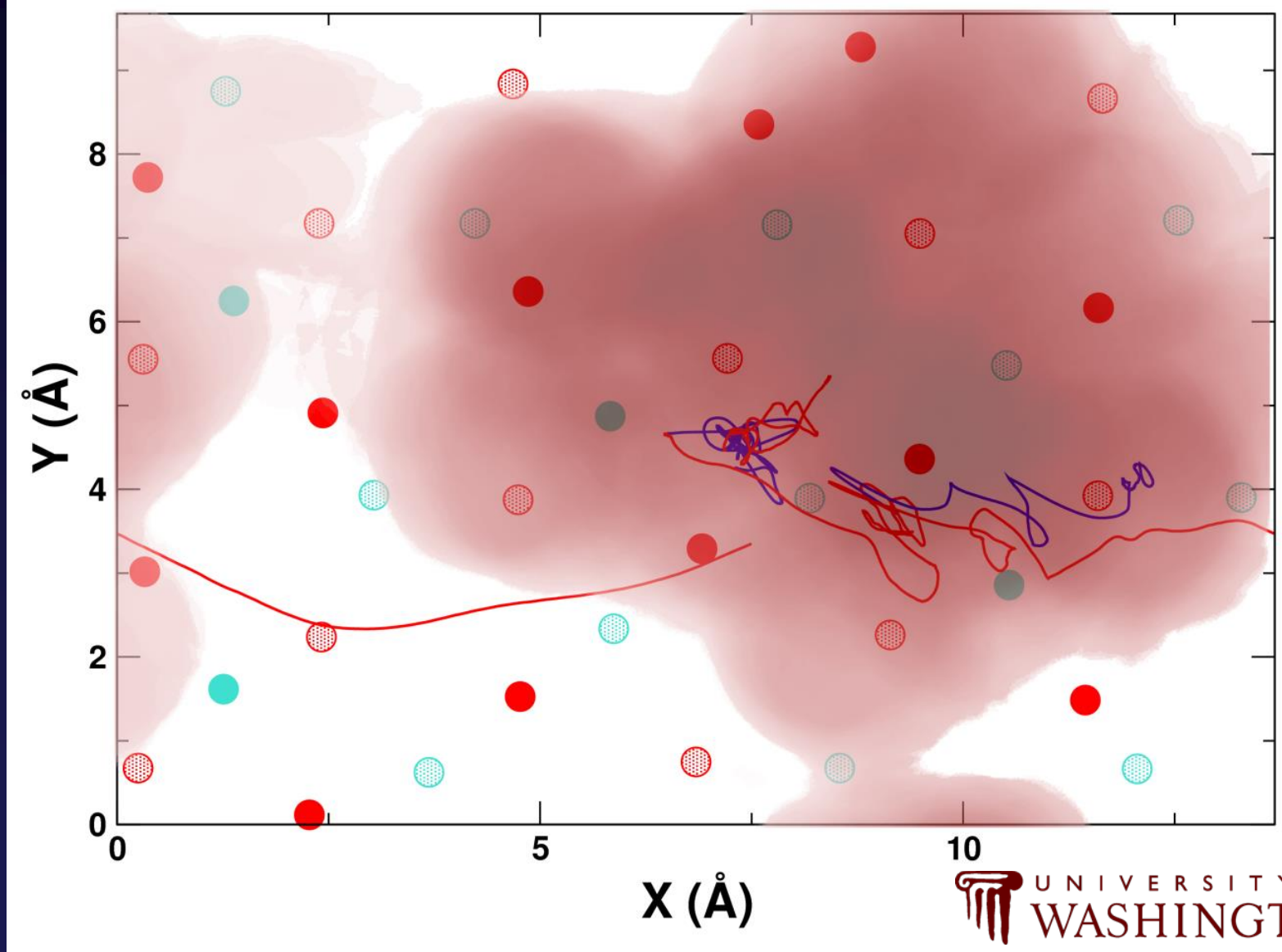
Cluster footprint @ 573 K



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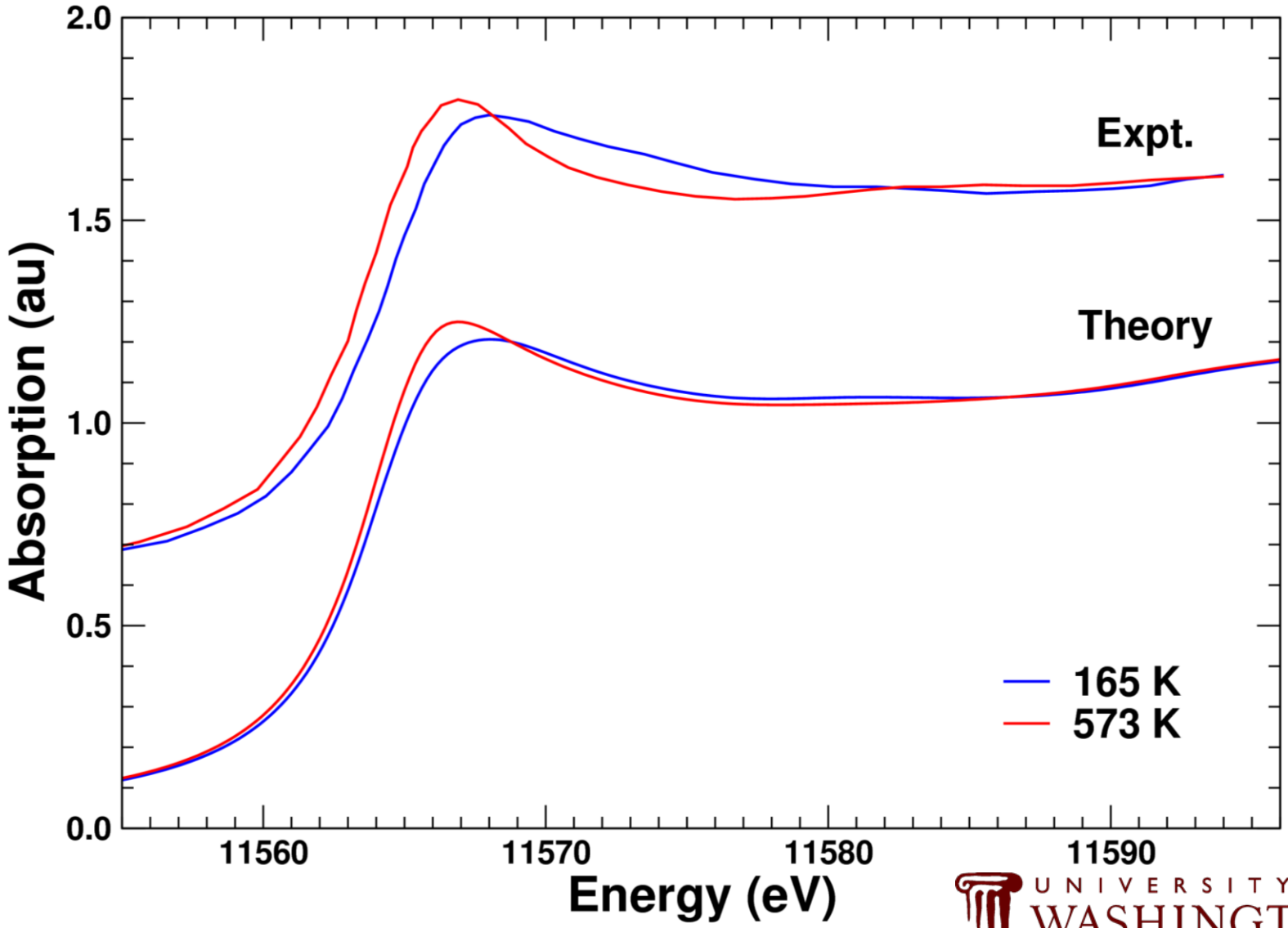
Pt L_3 XANES: Conf. Average over MD



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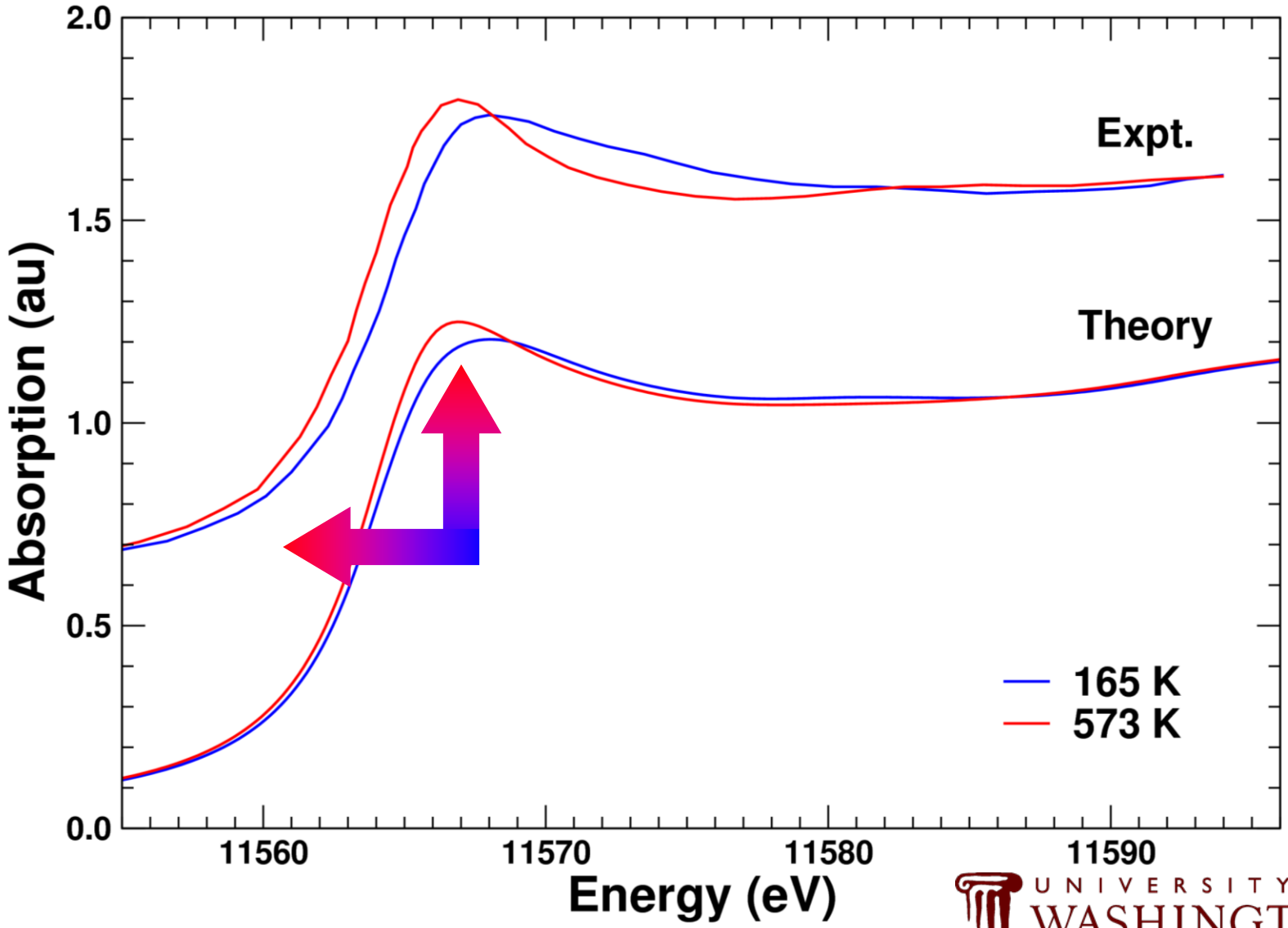
❹ Increased intensity and redshift at high T



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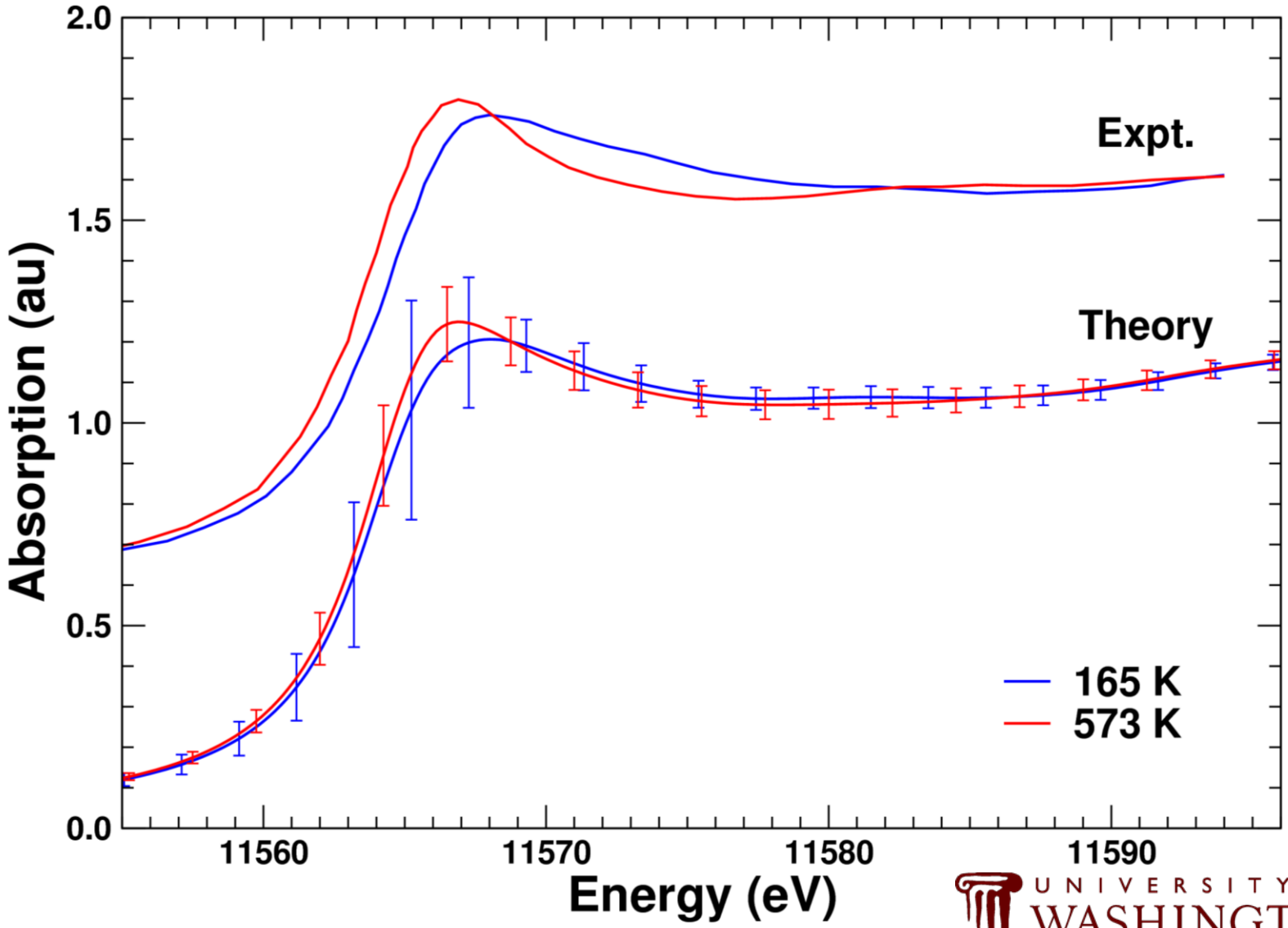

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Summary

Found 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

Conclusions

1. Real-Space Multiple-Scattering + DFT: Synergy works
2. Real time methods (MD), open a door to a new understanding of the XAS of complex systems
3. Many regions of the (νtkr) map are still inaccessible, so be patient

First Principles Structure, Dynamics and X-Ray Spectroscopy of Complex Systems

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

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

H. Rossner
H. Krappe

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

... and Thank You

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