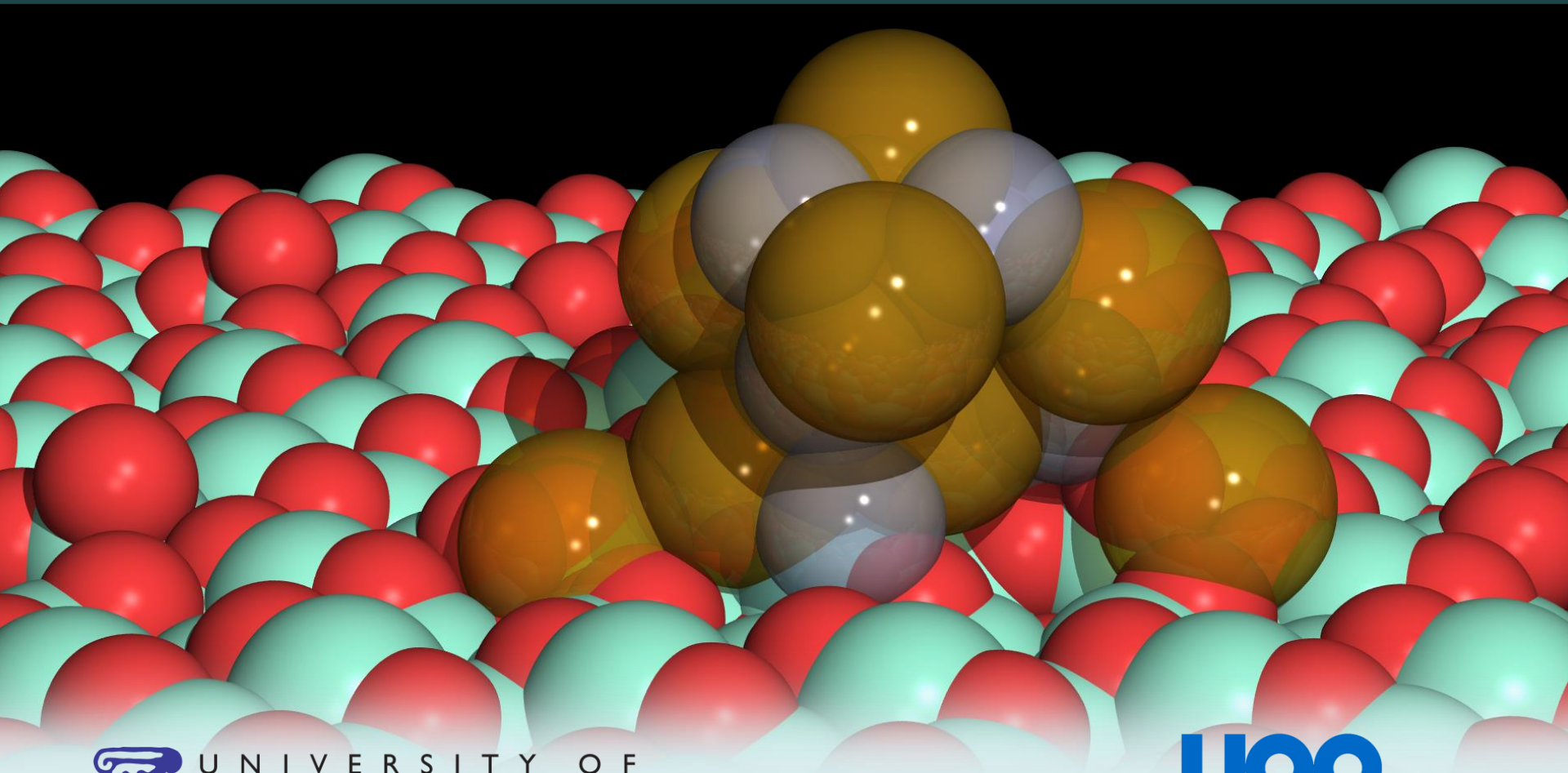
Dynamic structure of supported Pt and Pt-Sn nanocatalysts: Real-time DFT/MD and X-ray Spectroscopy simulations

F. Vila, May 8th 2013



UNIVERSITY OF WASHINGTON

UOP
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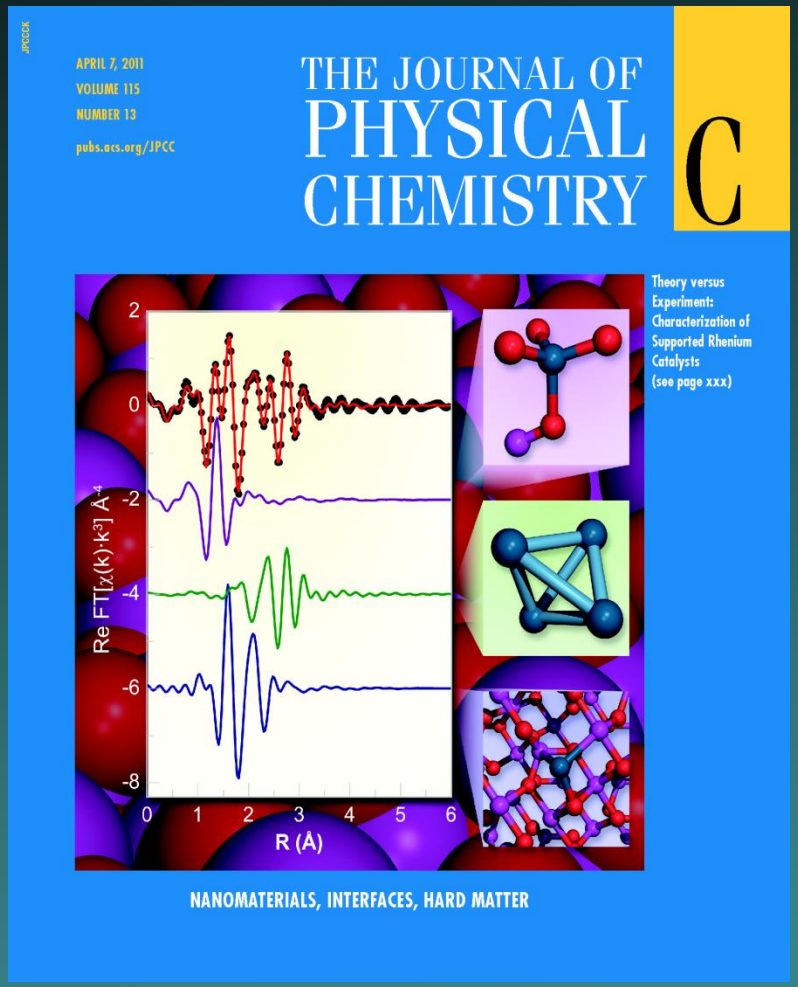
Previous Work



Experimental (XAS, STEM, TPR, and XPS) and Theoretical (DFT) Characterization of Supported Rhenium Catalysts

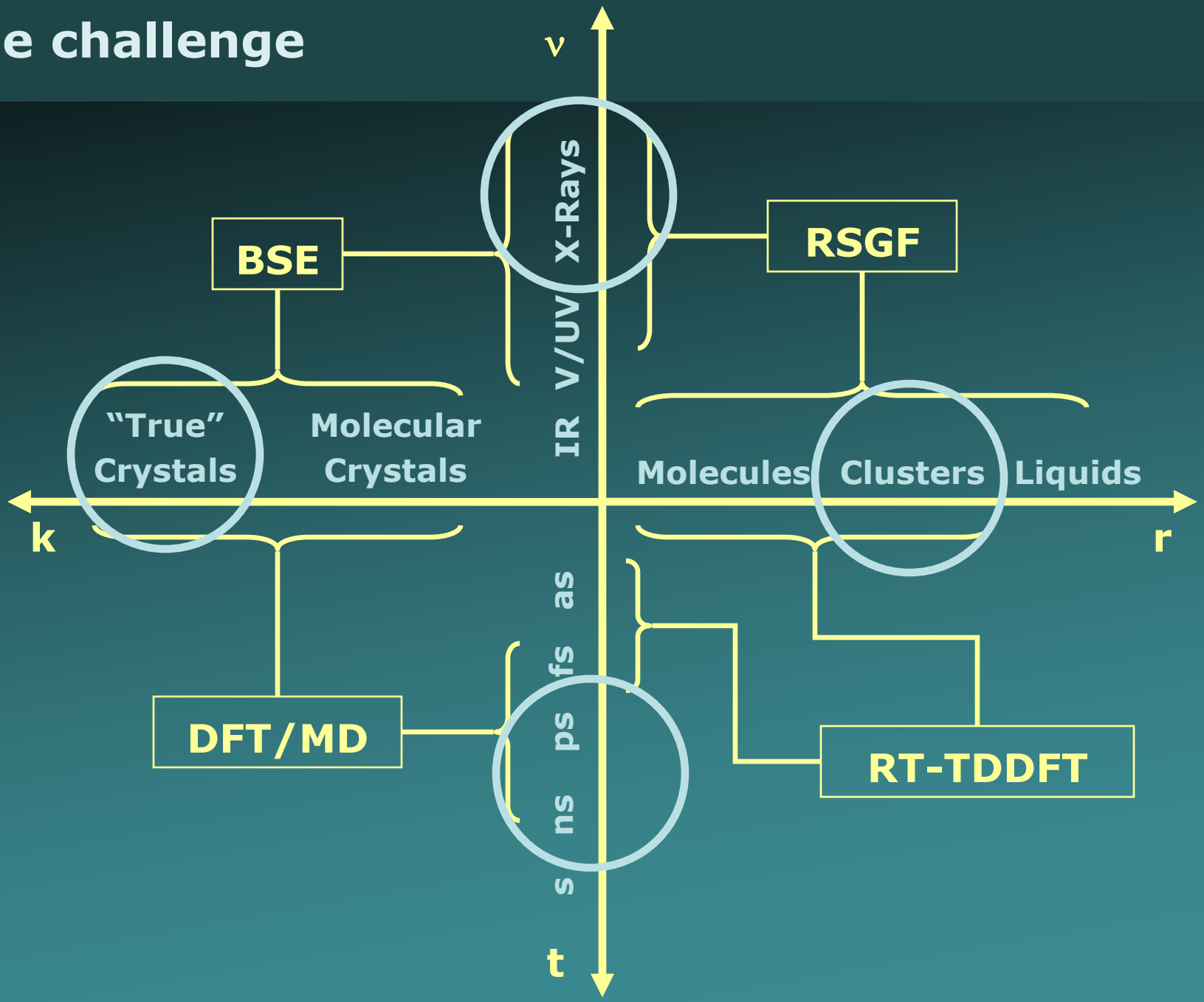
S. Bare, S. Kelly, F. D. Vila, D. Boldingh, E. Karapetrova, J. Kas, G. Mickelson, F. Modica, N. Yang, J. J. Rehr

J. Phys. Chem. C **115**, 5740, 2011

DFT/EXAFS model with three species was used to identify the dominant Re adsorption site on the alumina surface.

Re on γAl_2O_3

The challenge



Outline

Pt_{10} on γ-Al_2O_3:

Negative Thermal Expansion and Disorder

PtSn Alloy Clusters on γ-Al_2O_3:

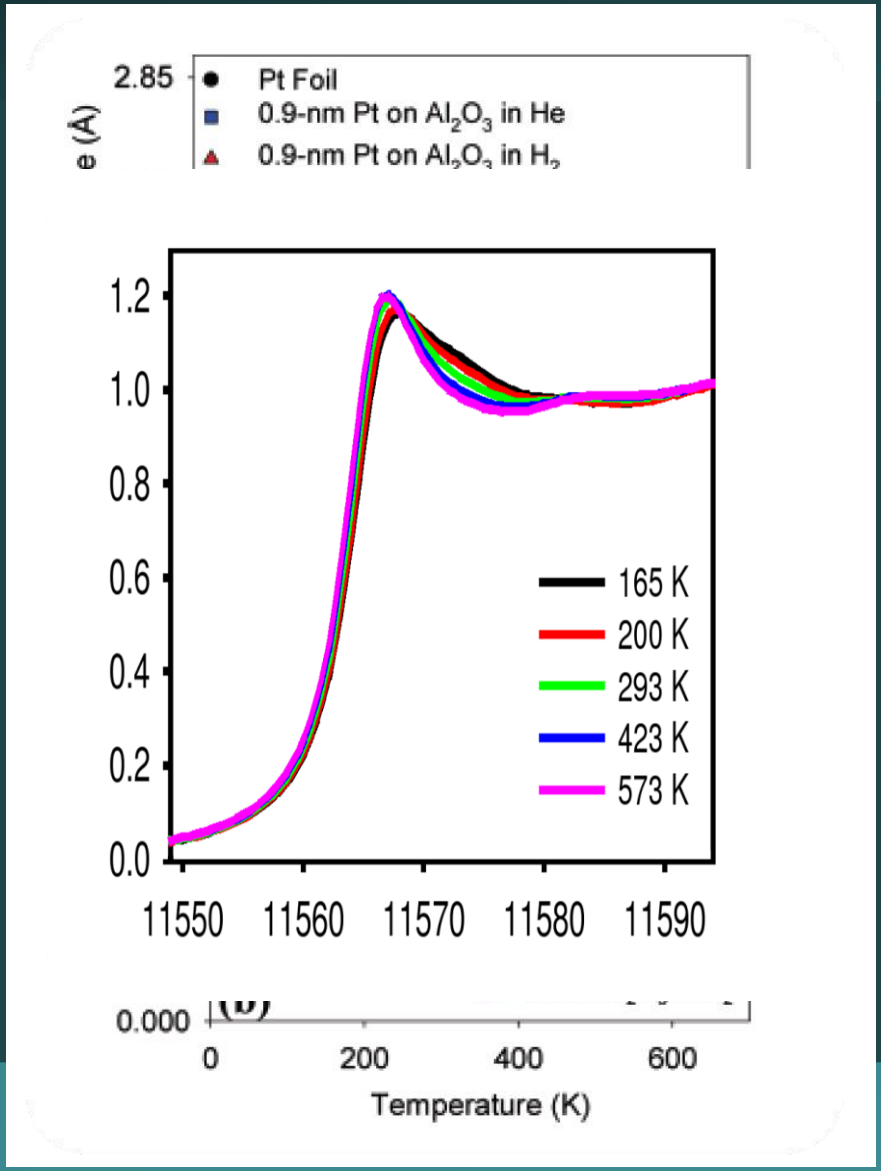
Structure and Dynamic Disorder

Adsorbates and Reactivity on
PtSn Clusters on γ-Al_2O_3

Pt_{10} on γ-Al_2O_3:
Negative Thermal Expansion and Disorder

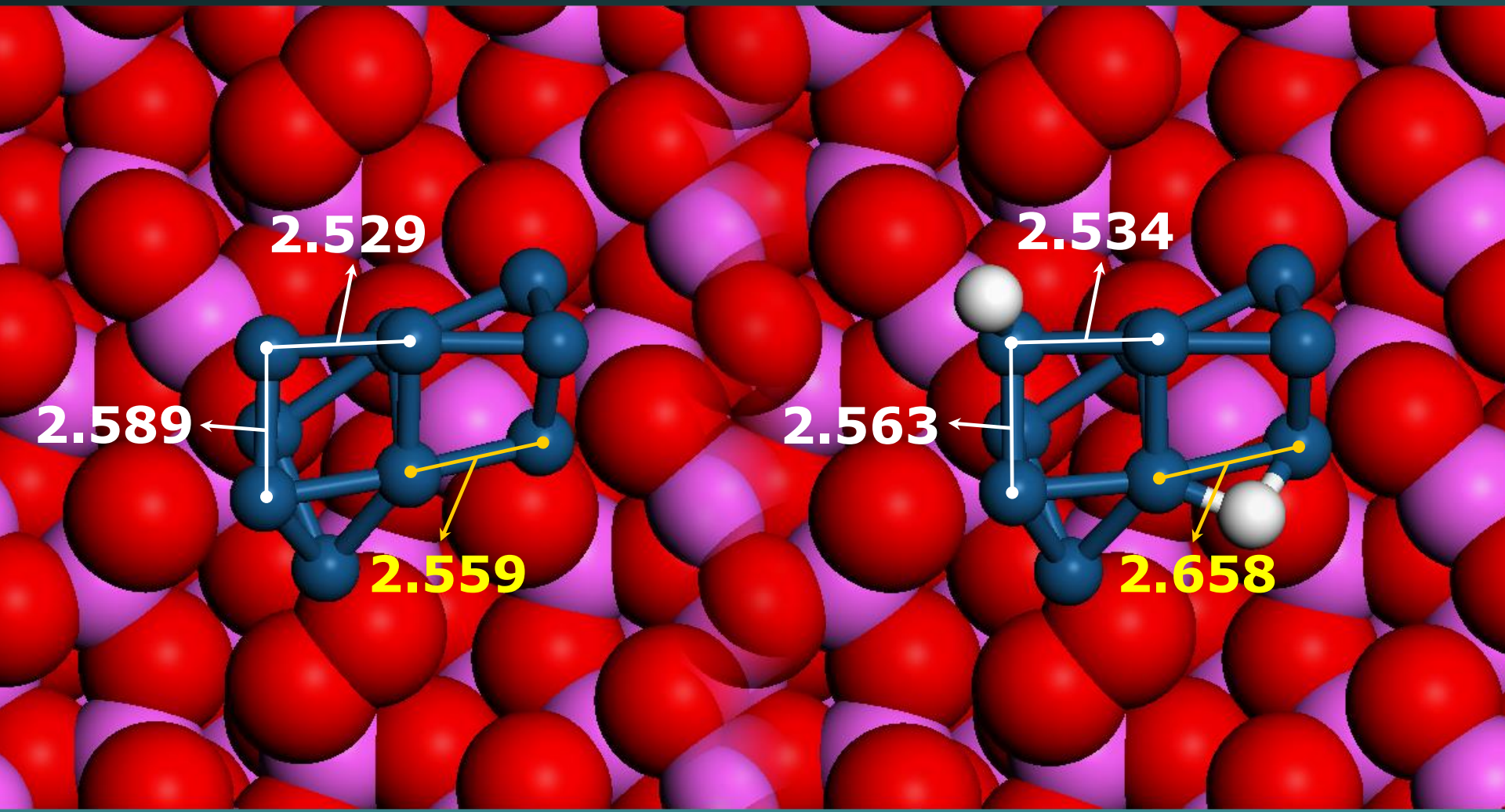
Experimental Results

- Pt-Pt expansion going from He to H_2 atmosphere
- Pt-Pt negative thermal expansion
- High Pt-Pt disorder
- Increased intensity and redshift of XANES with increasing T



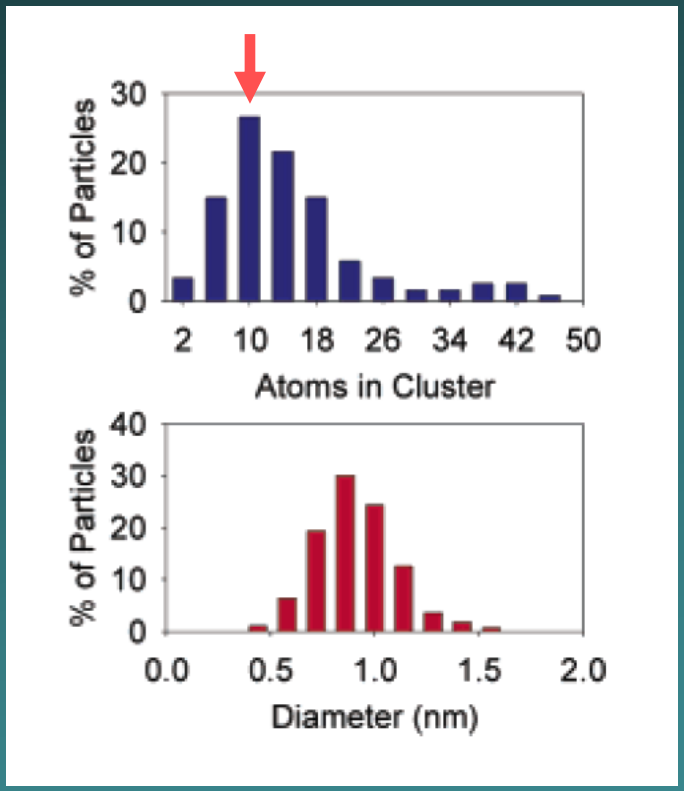
Kang *et al.* JACS 2006, *128*, 12068

Bond expansion in H_2 atmosphere



Computational details

Study prototypical Pt_{10} clusters on γ-Al_2O_3



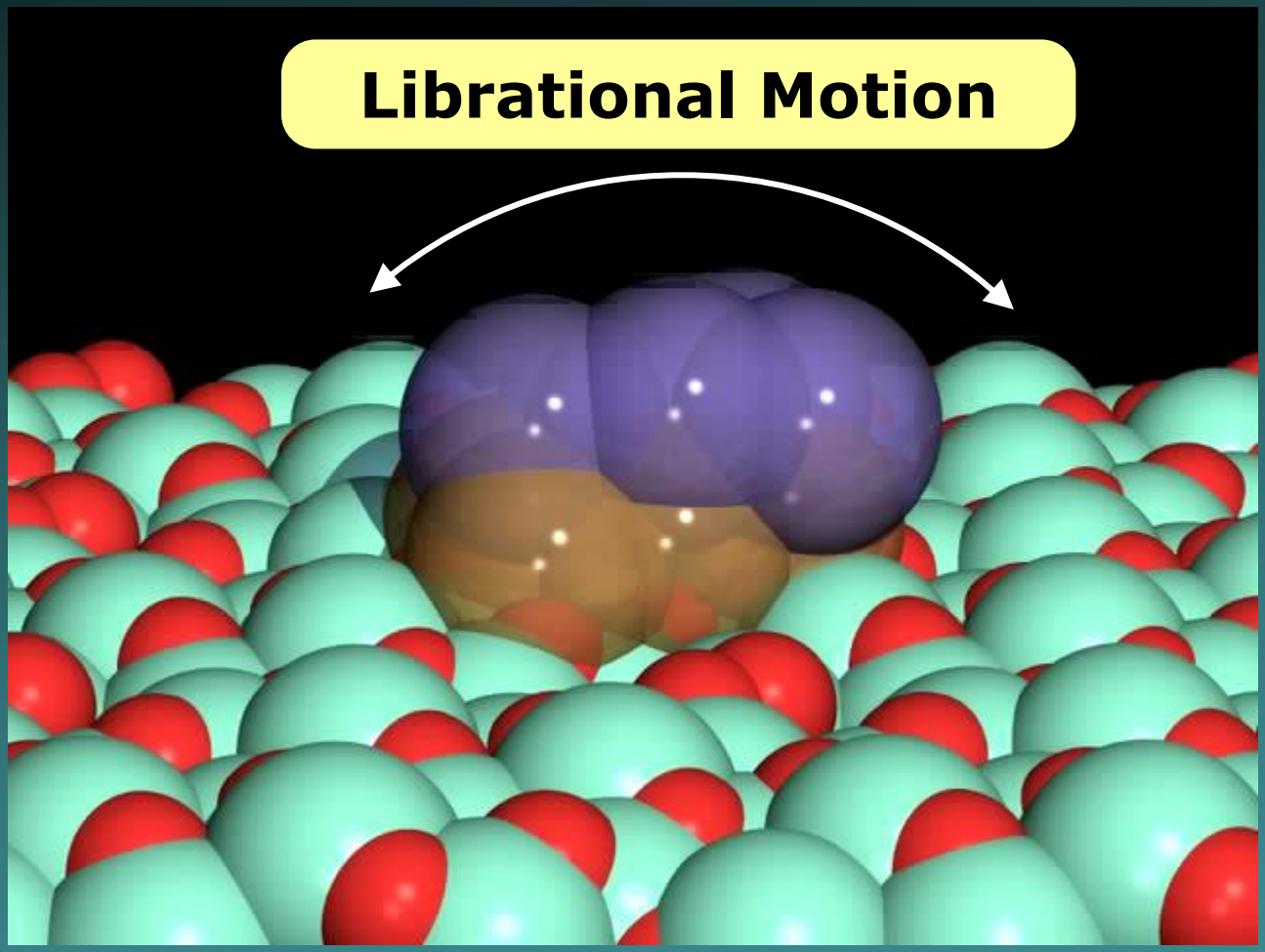
DFT/MD

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)

MD @ 165 K



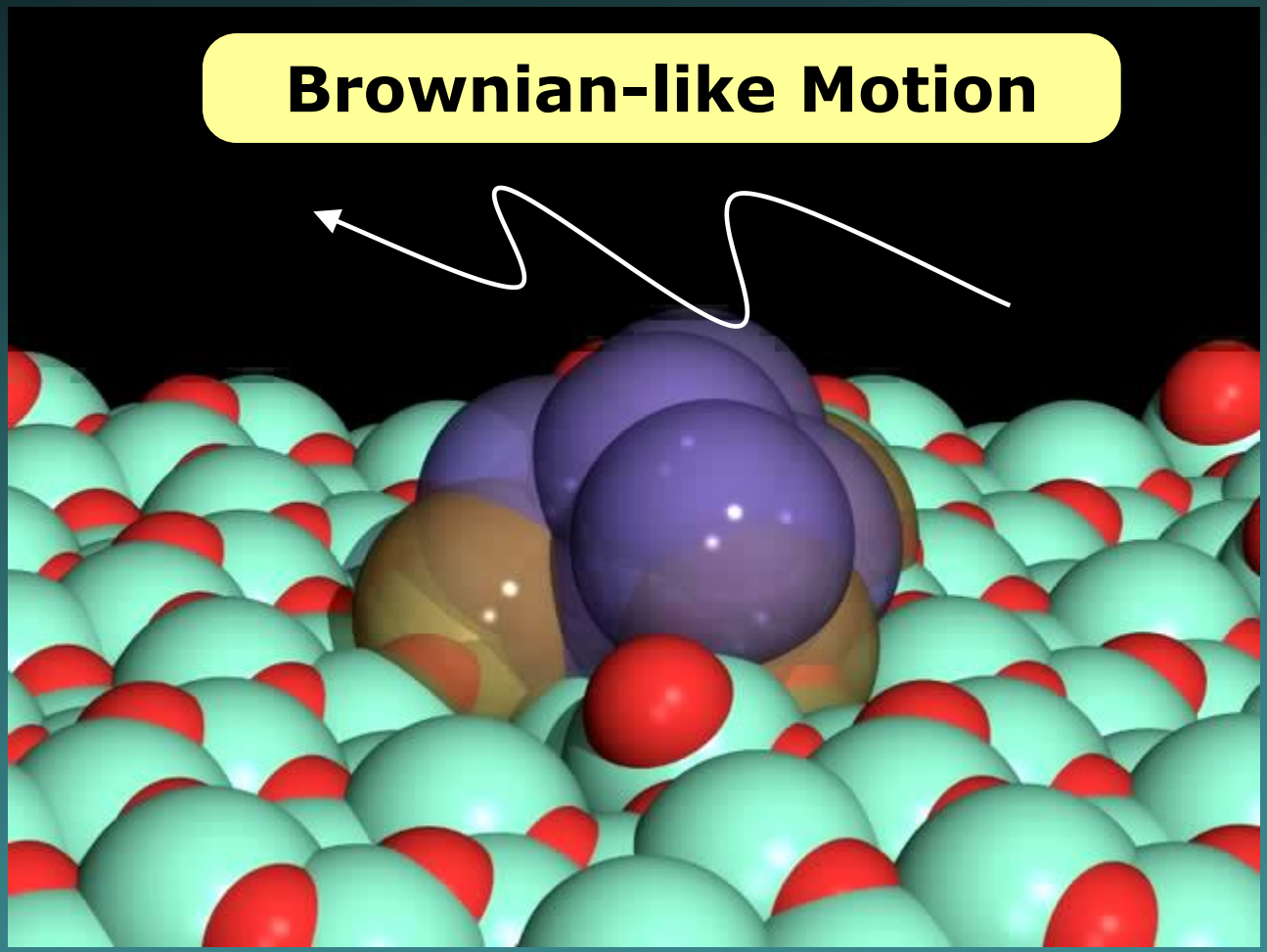
Pt (Ox)

Pt (Me)

O

Al

MD @ 573K



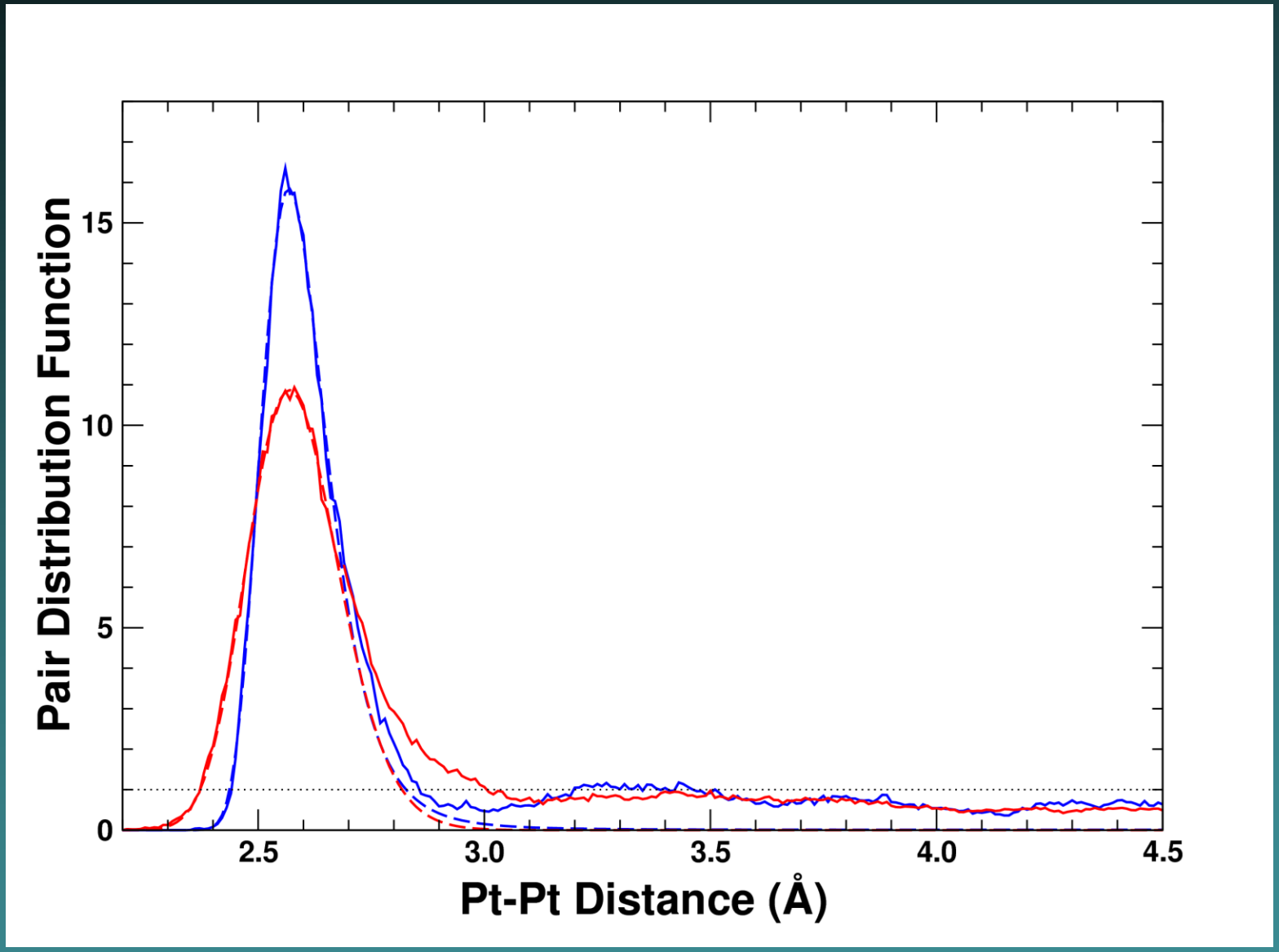
Pt (Ox)

Pt (Me)

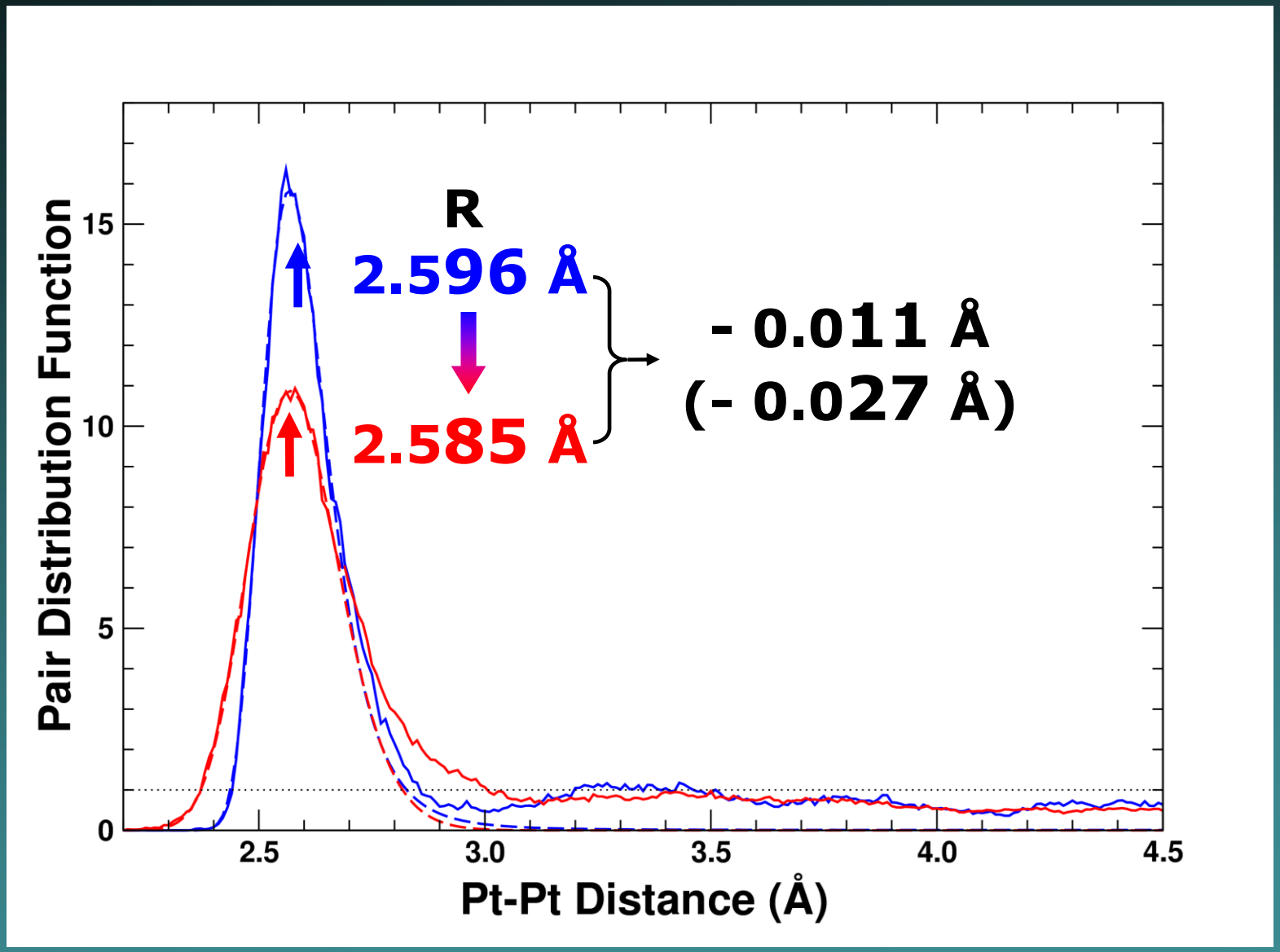
O

Al

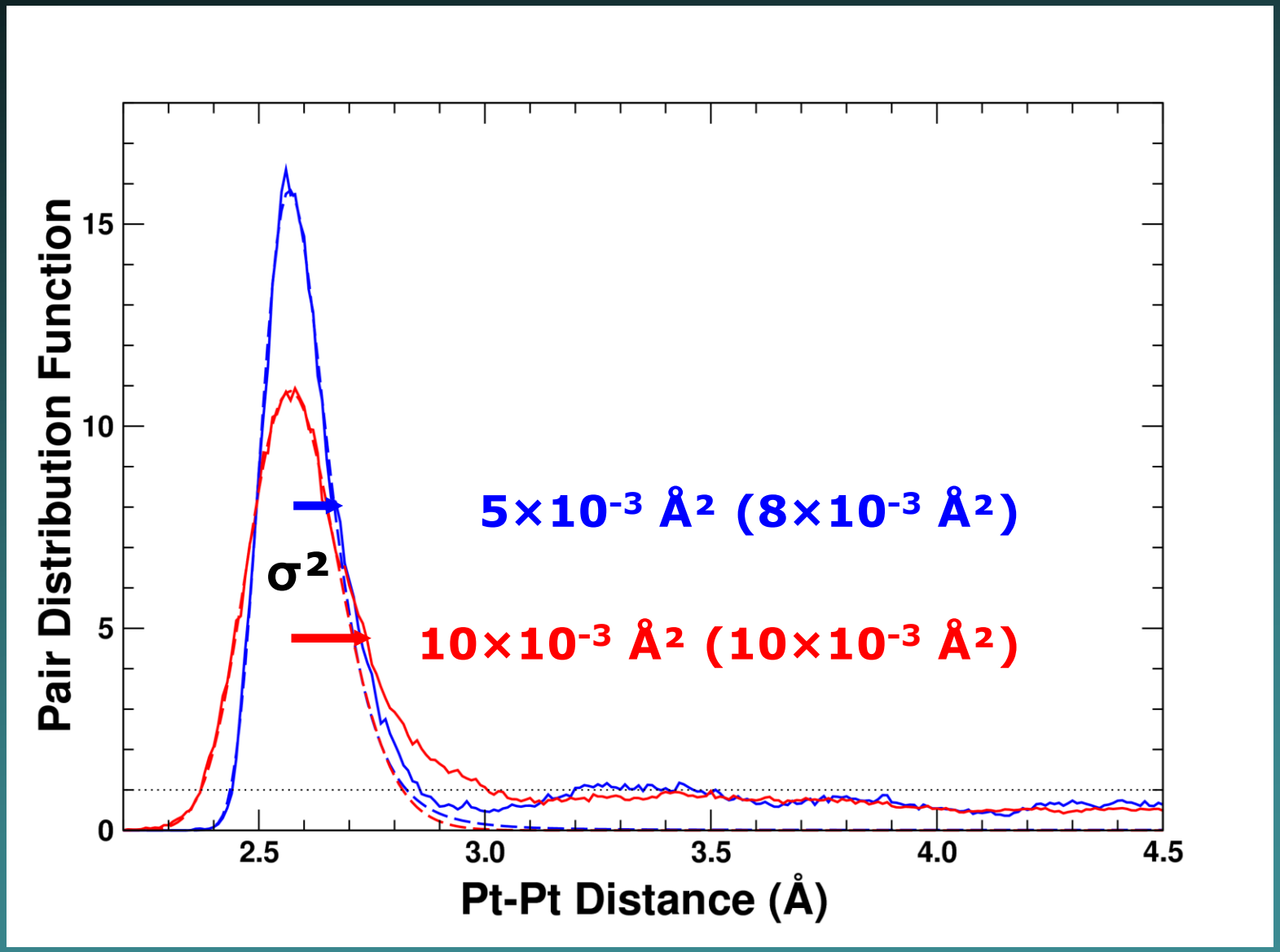
Pt-Pt Pair Distribution Function



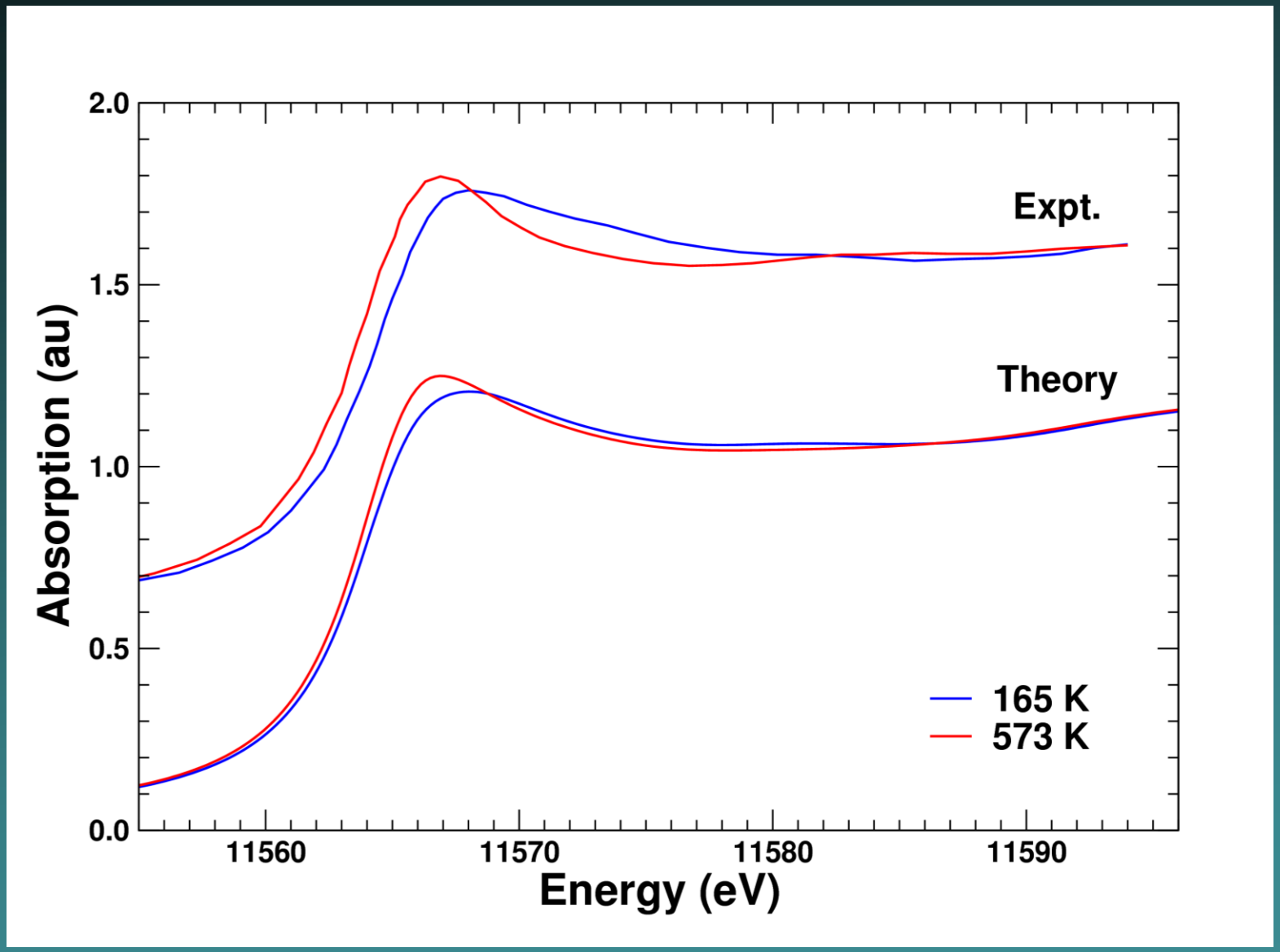
Negative Thermal Expansion



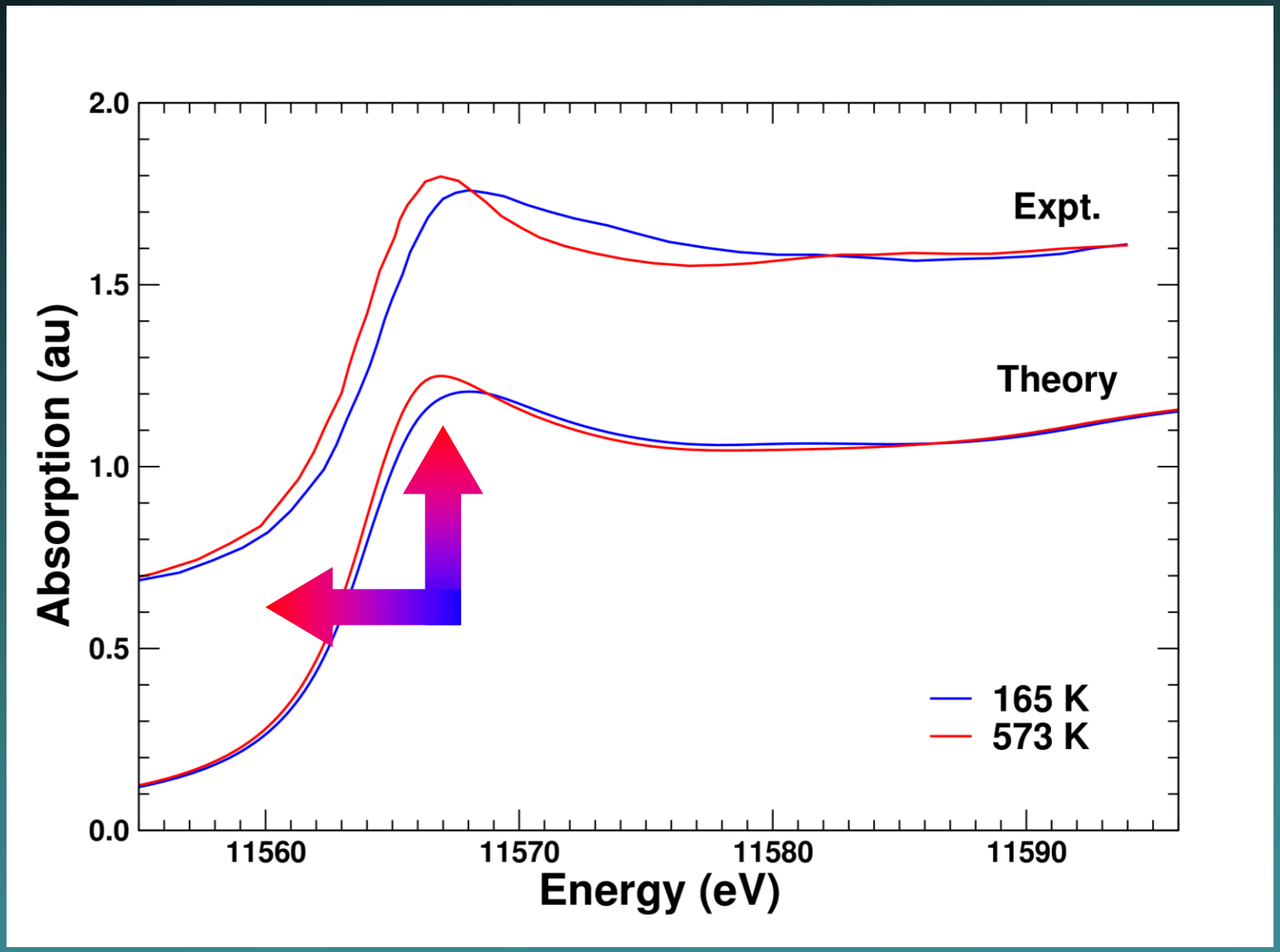
High Pt-Pt Disorder



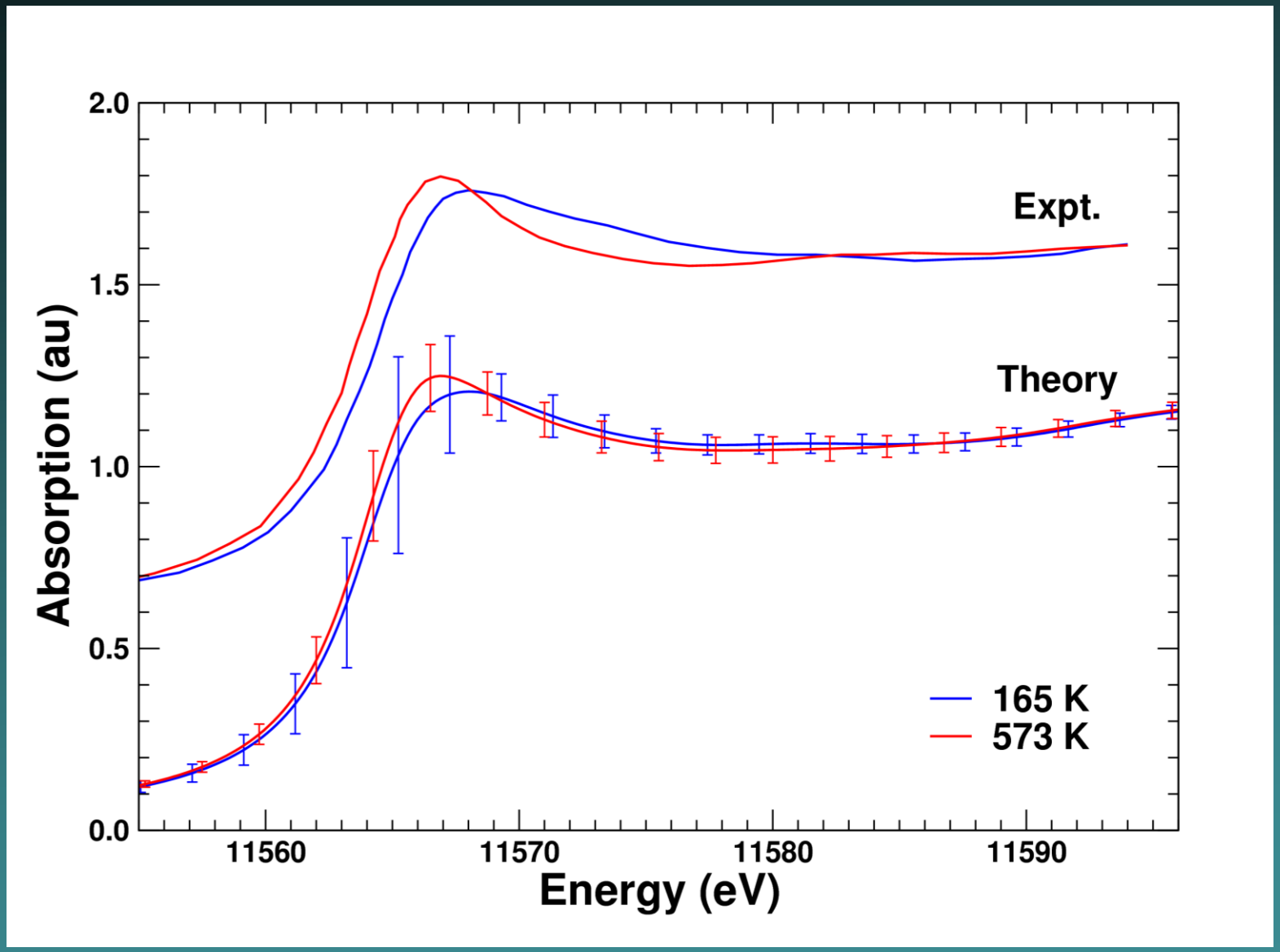
Pt L_3 XANES


2.0
1.5
1.0
0.5
0.0
Absorption (au)
11560
11570
11580
11590
Energy (eV)
Expt.
Theory
165 K
573 K

Increased intensity and redshift at high T



Increased intensity and redshift at high T



Summary

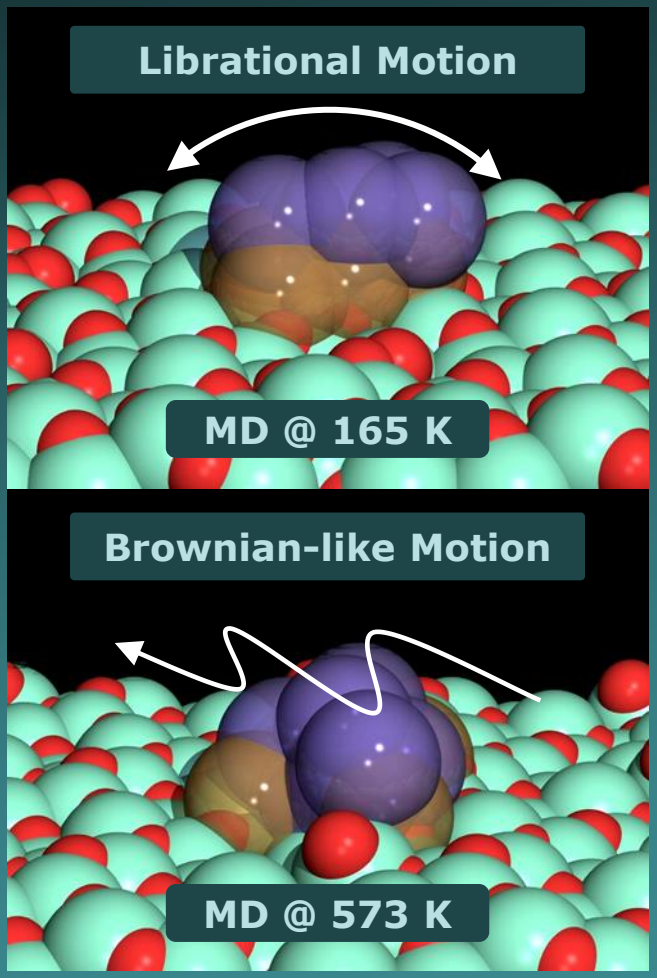
Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

F. D. Vila, J. J. Rehr, J. Kas, R. G. Nuzzo, A. I. Frenkel

Physical Review B **78**, 121404(R), 2008

Complex dynamics:
multiple-time scales, librational motion, fluctuating bonding

Simulations explain:
large structural disorder, Negative Thermal Expansion (NTE).



Pt_{10} on γ-Al_2O_3

PtSn Alloy Clusters on γ-Al_2O_3: Structure and Dynamic Structural Disorder

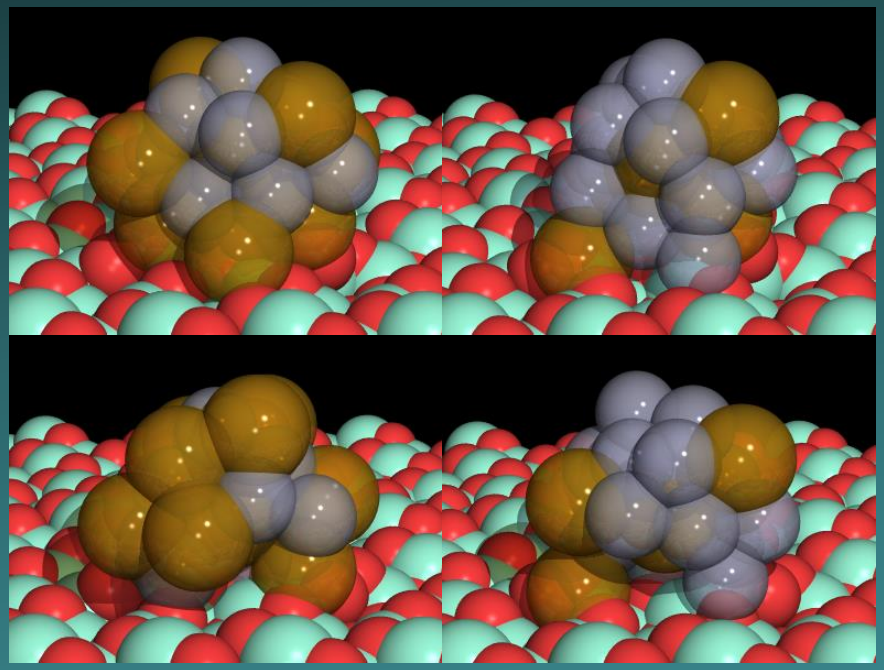
Motivation

- Alumina-supported Pt-based catalysts:
  - Used for: Reforming of light petroleum distillate
  - Modifiers (Sn, Re and Ir): profound effect on stability, reduce carbon deposition
- Knowledge of structure and dynamics: Understanding and improvement of catalytic activity

Theory in Operando Conditions: Study thermal and composition effects on the structure and reactivity of PtSn clusters on γ-Al_2O_3 under realistic conditions

Theoretical Probe: DFT/MD

Atomistic electronic and structural information

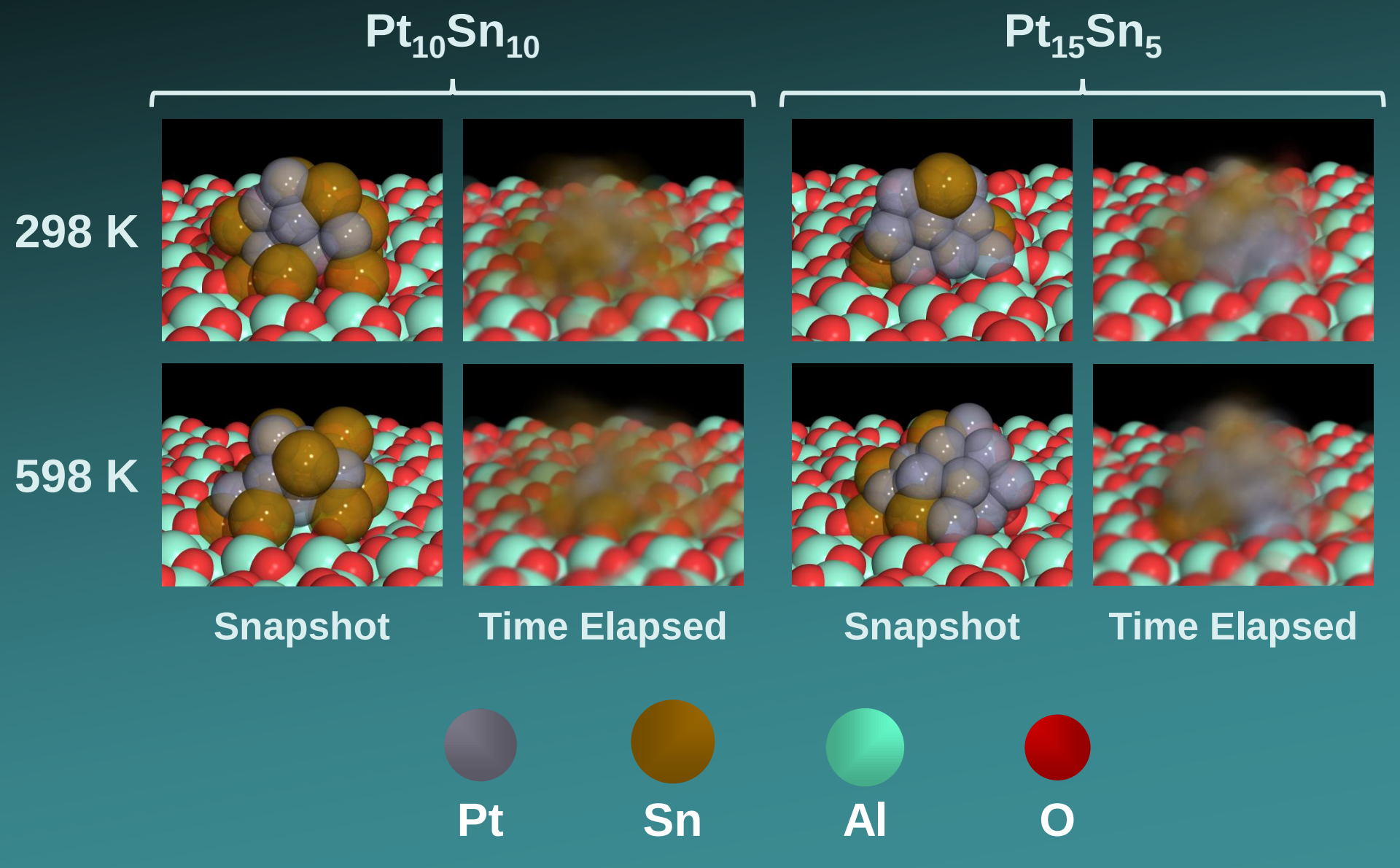


Initial structures: Randomly Sn-substituted Pt_{20} cluster

DFT/MD

VASP
PBE Functional
396 eV Cutoff
3 fs Steps
3 ps Equilibration
9 ps Runs (4/Temp)
298 and 598 K

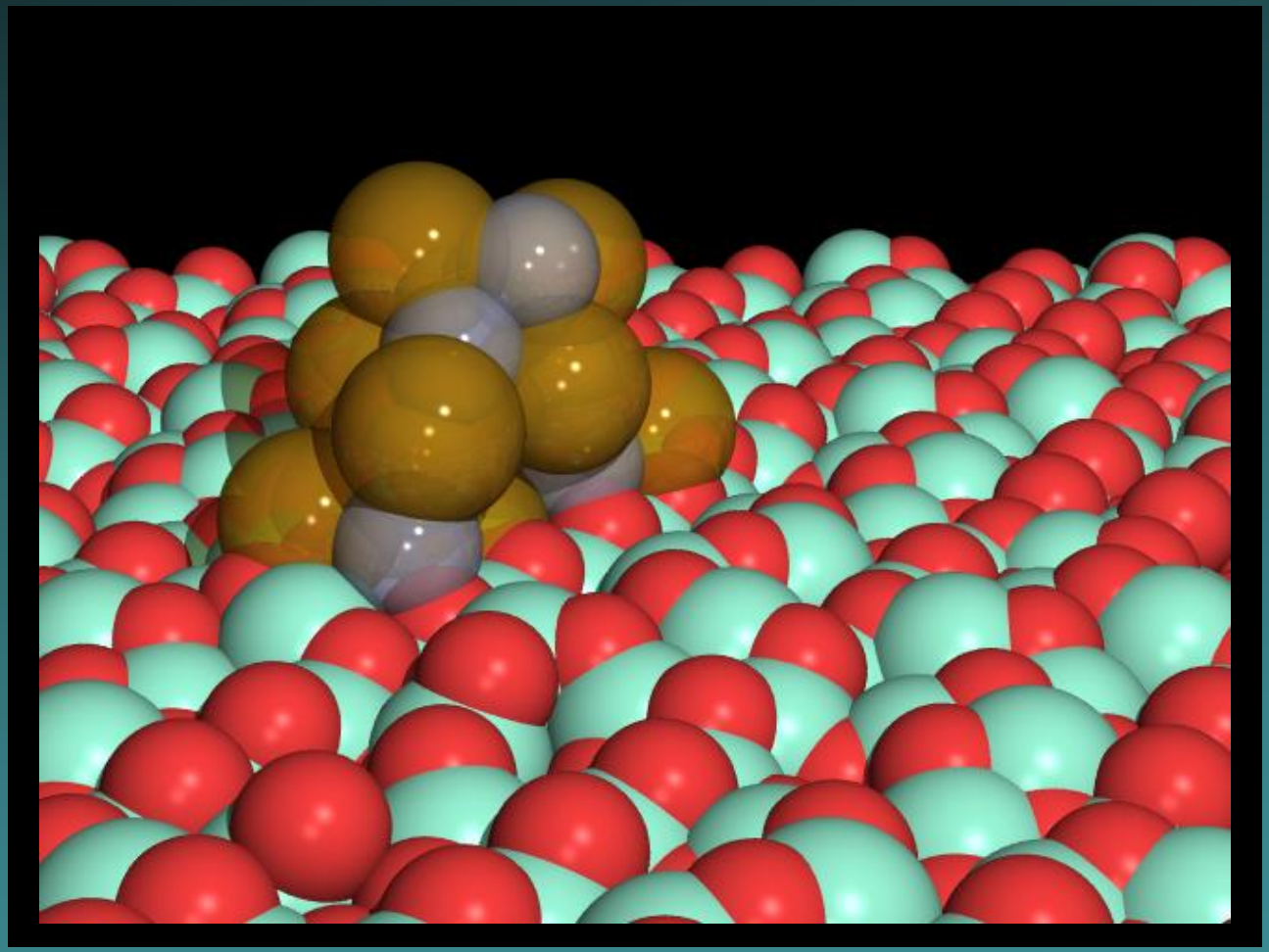
Structure: Segregation and Disorder



Dynamical Properties: Molecular Dynamics

Sn

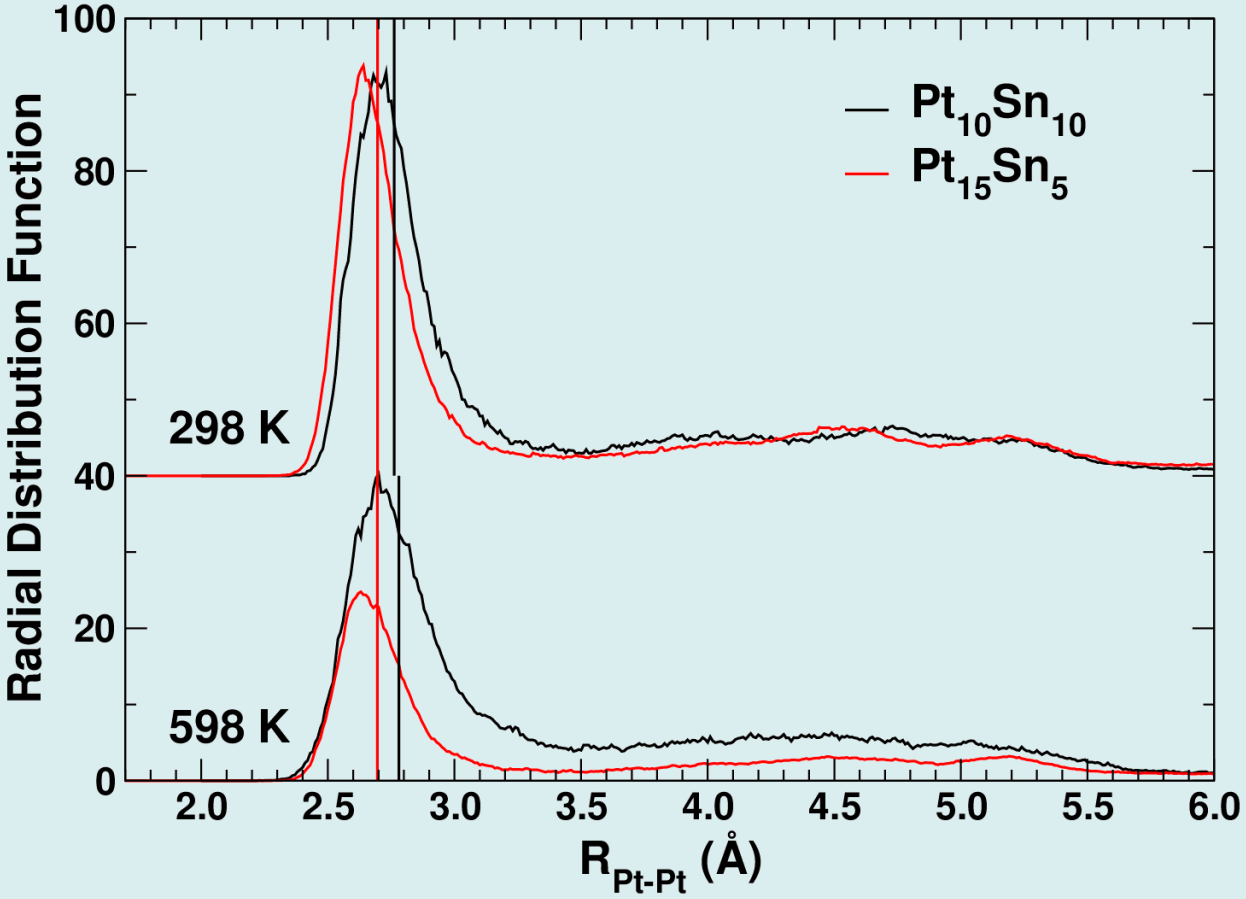
Pt



O

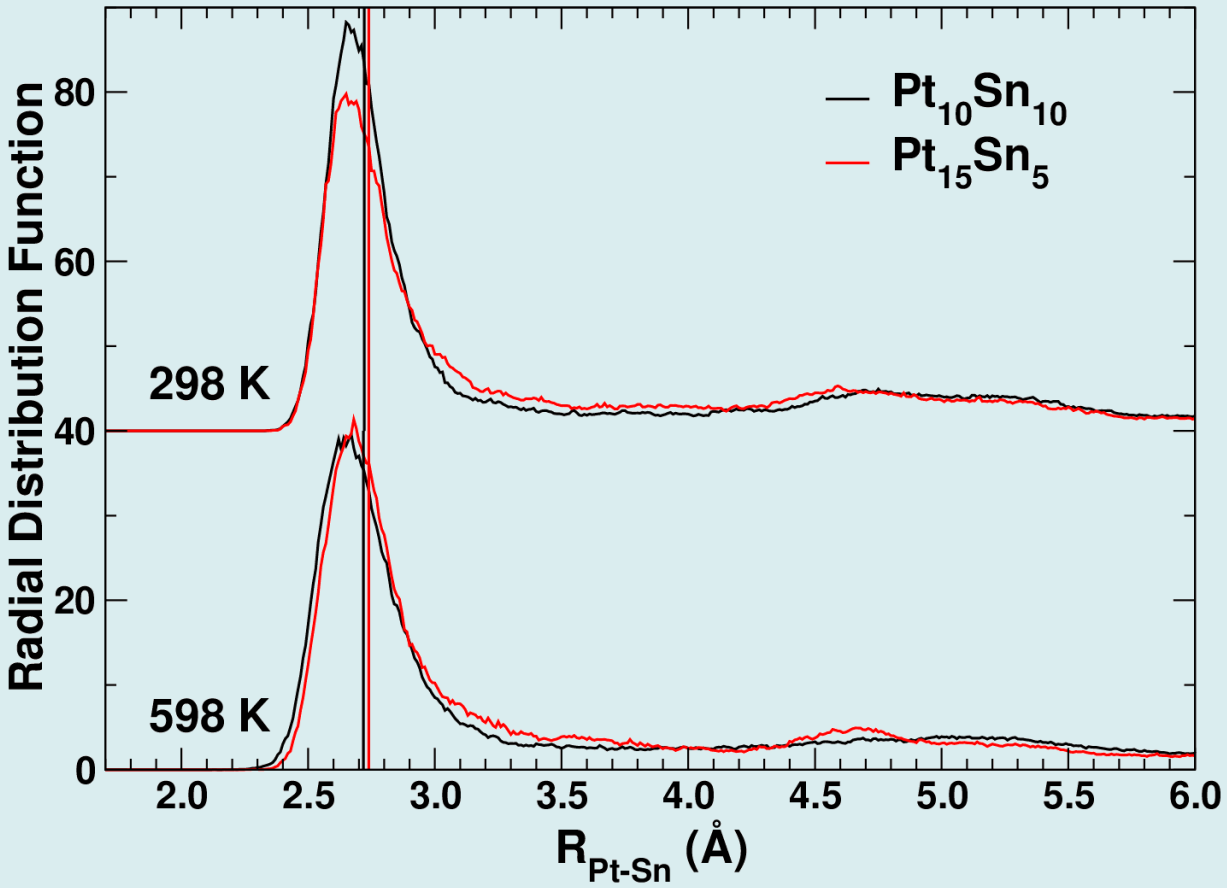
Al

Cluster Internal Structure: Pt-Pt



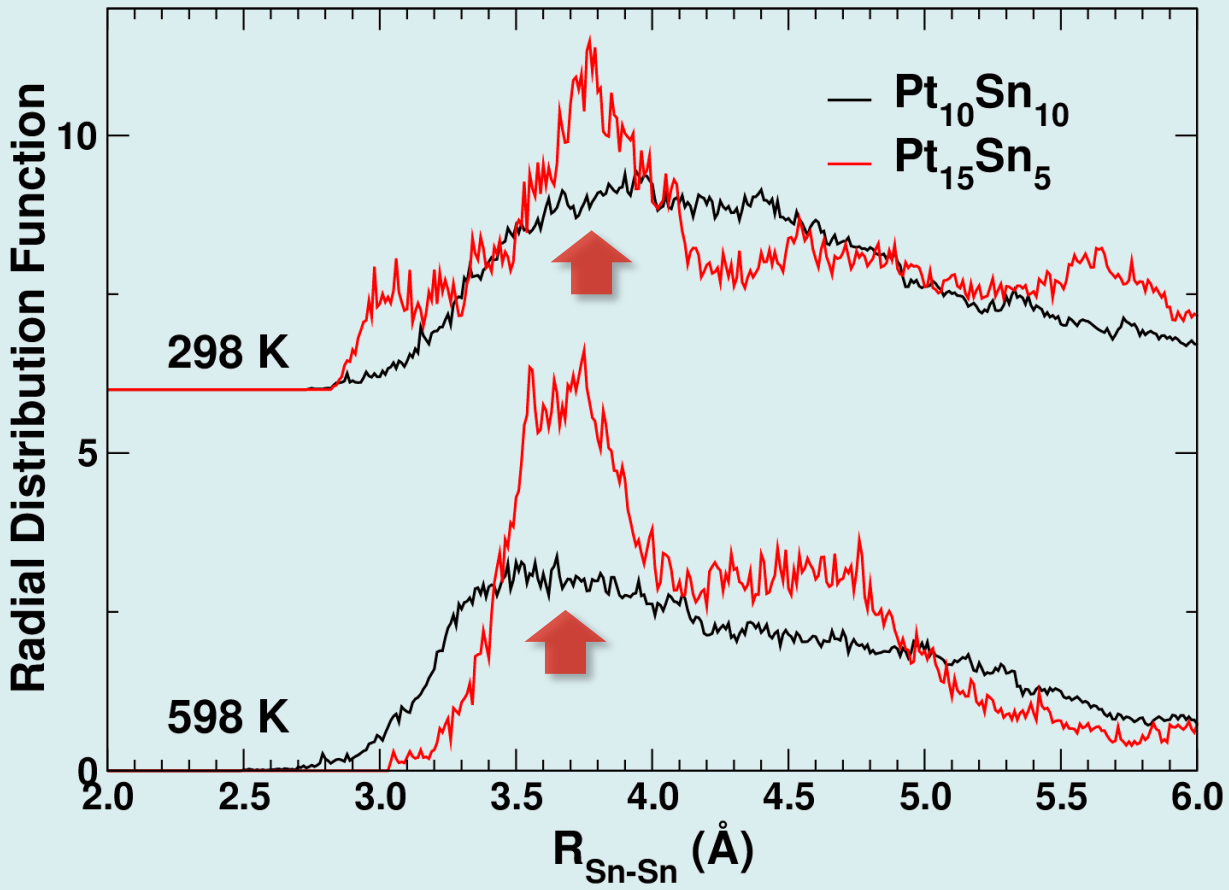
Shorter R_{Pt-Pt} and NTE trend at higher Pt concentration

Cluster Internal Structure: Pt-Sn



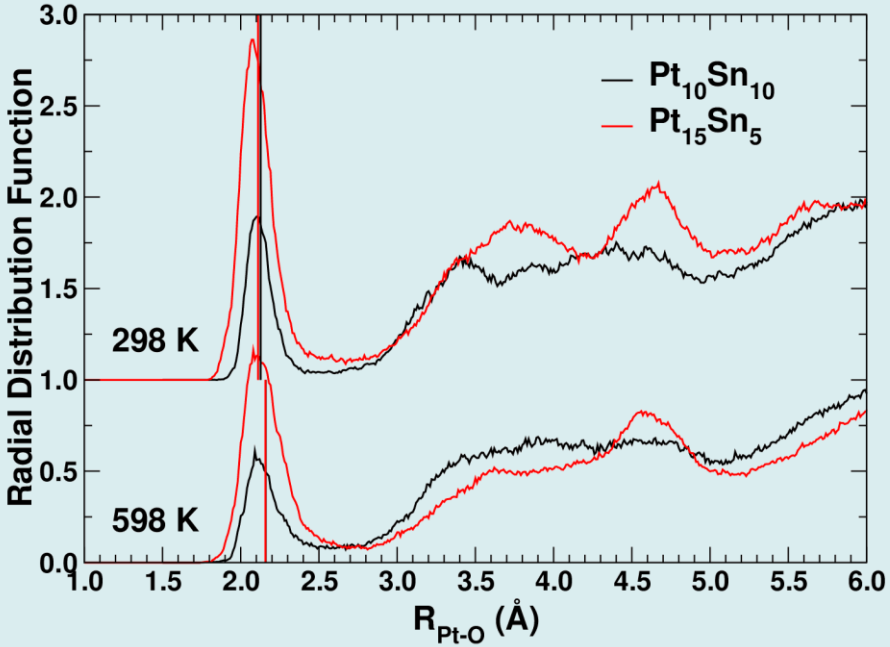
Pt-Sn shell: Unaffected by temperature and concentration

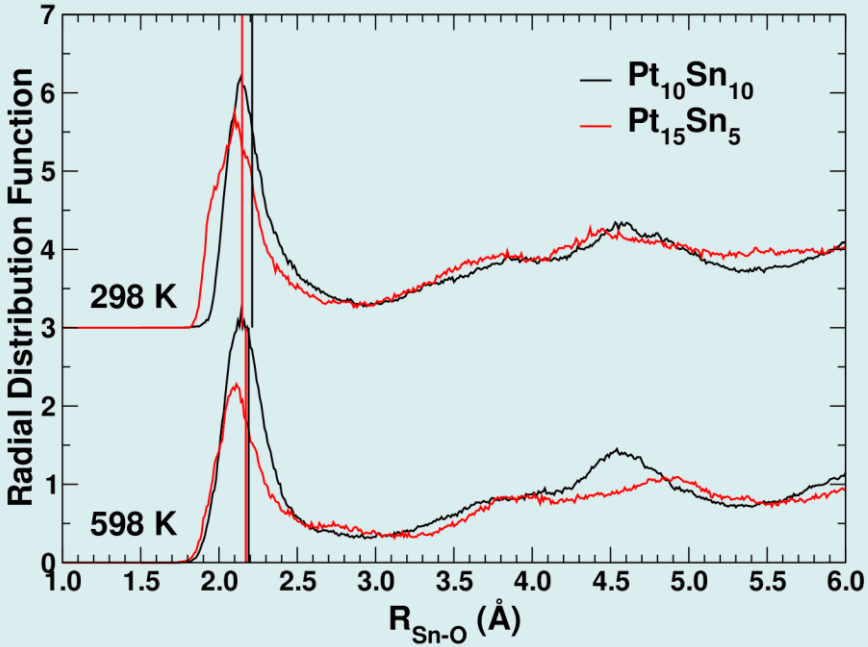
Cluster Internal Structure: Sn-Sn



Sn-Sn shell: Structure develops at high Pt concentration

Cluster-Surface Interaction: Pt-O and Sn-O





Pt-O shell: More O per Pt in Sn-poor clusters

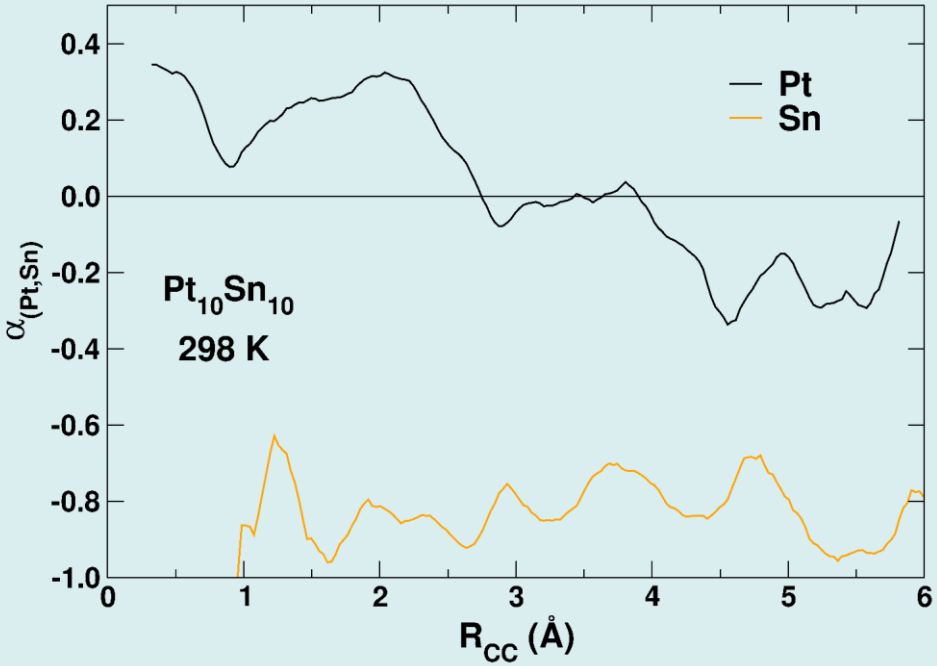
Sn-O shell: Very similar except for O uptake shoulder

Inhomogeneous Structure: Surface Segregation

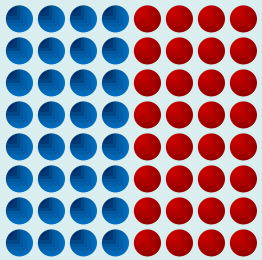
Cowley short-range order parameter

$$\alpha_A = 1 - {}^{n_{AB}}/_{n_{AM}x_B}$$

$$n_{AM} = n_{AA} + n_{AB}$$

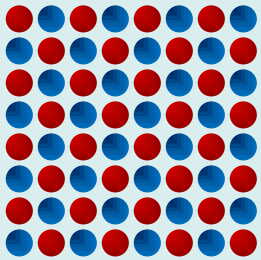


Correlated



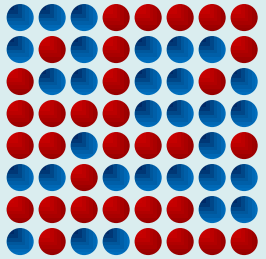
$0 < \alpha_A \leq 1$

Anticorrelated



$-1 \leq \alpha_A < 0$

Random

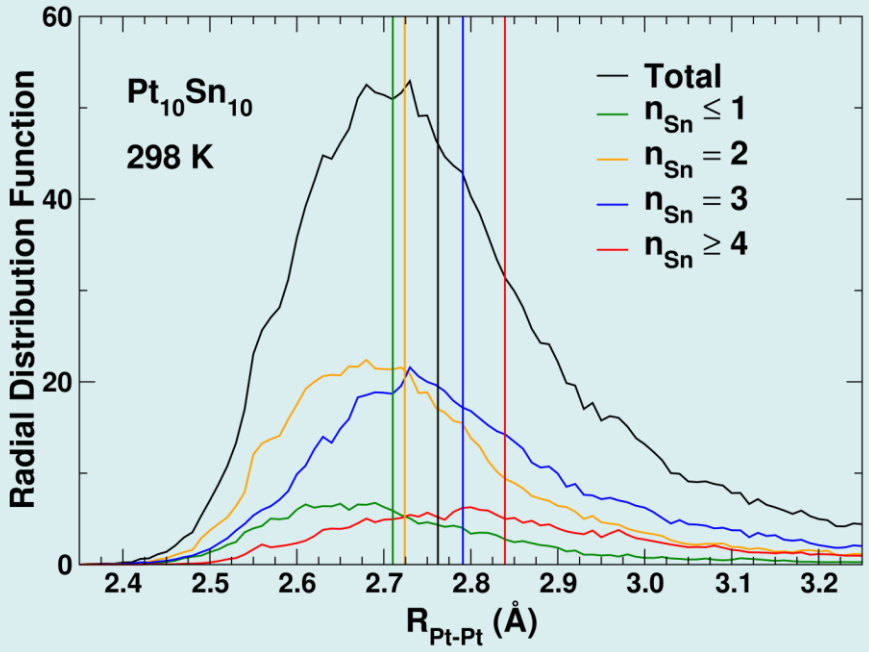


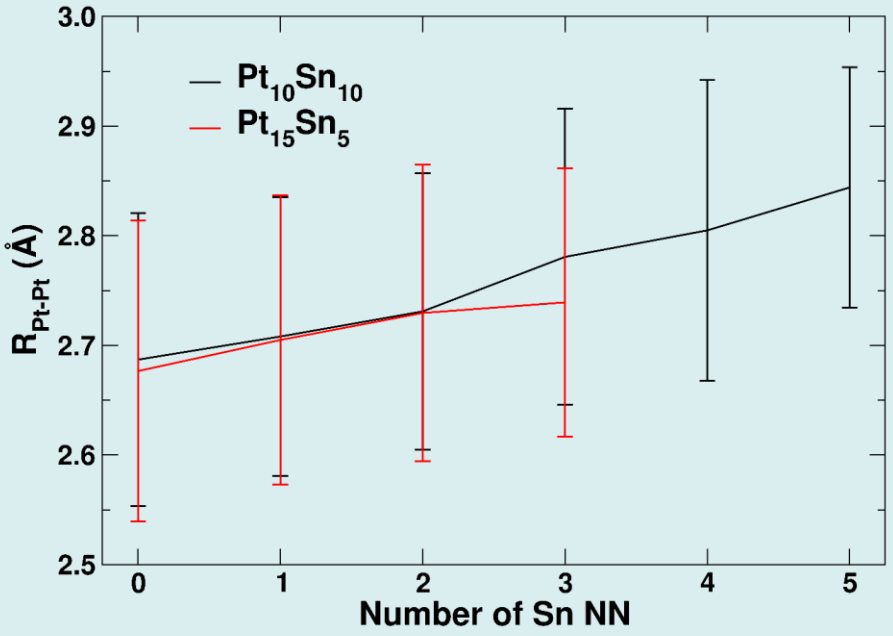
$\alpha_A \cong 0$

Pt – Favors Pt NN in core and Sn NN near surface

Sn – Always favors Pt NN

Inhomogeneous Structure: Pt-Pt Interaction

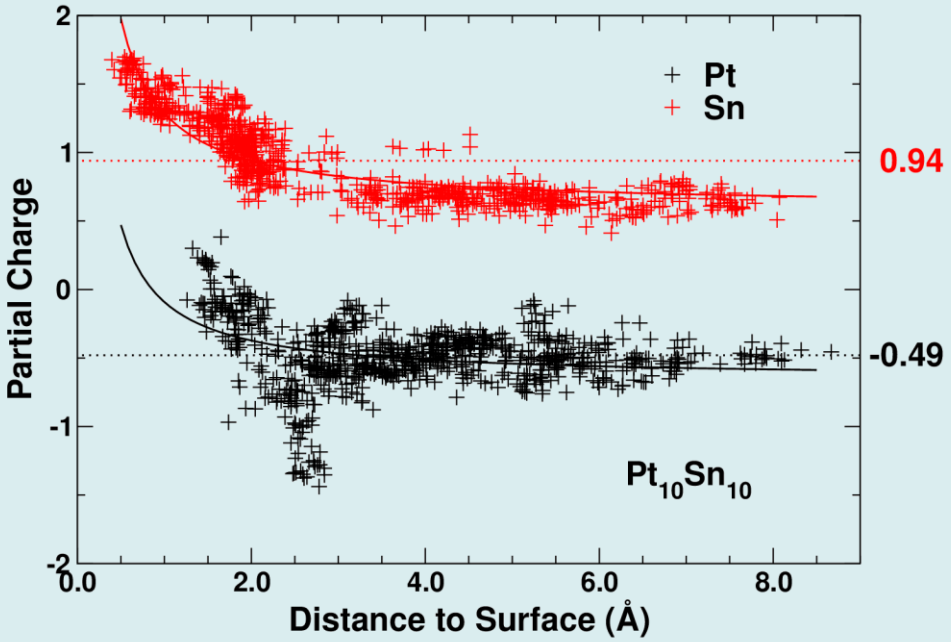


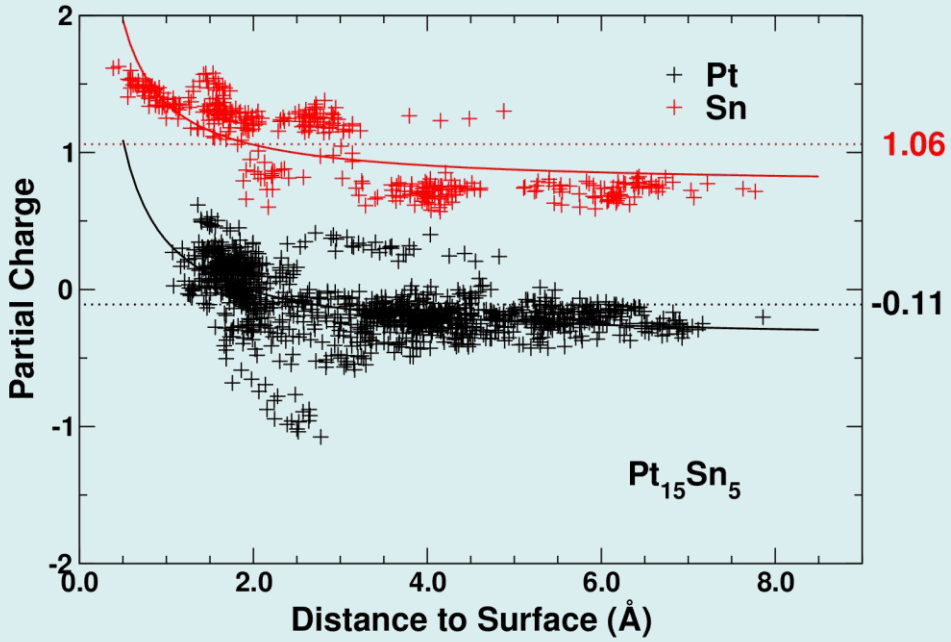


Pt-Pt RDF composed of different populations

Mean Pt-Pt distance linearly modulated by # of Sn NN

Electronic Properties: Net Atomic Charge





Near surface: Both species more positive

Far from surface: Clusters nearly neutral

Pt mean net charge: Controlled by Sn

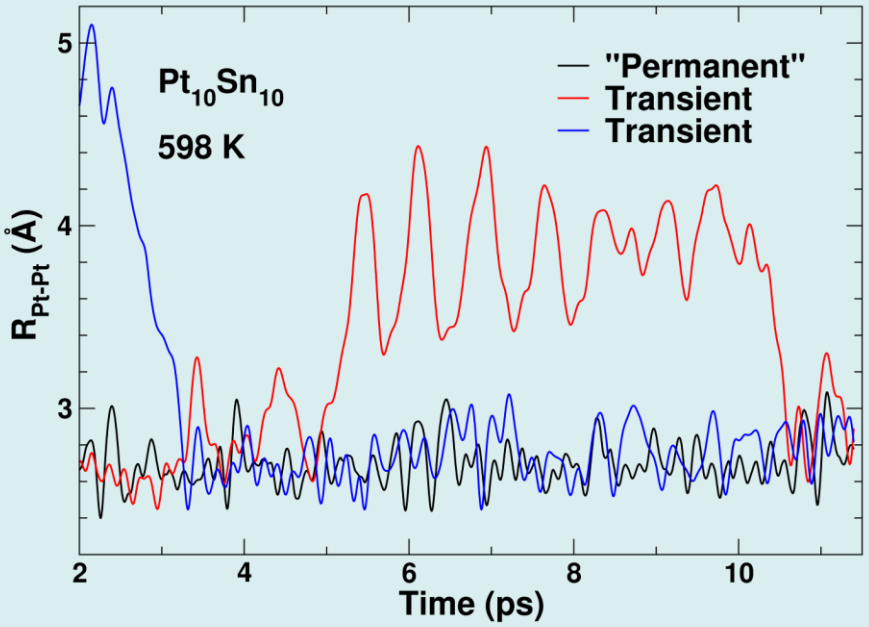
Dynamic Disorder

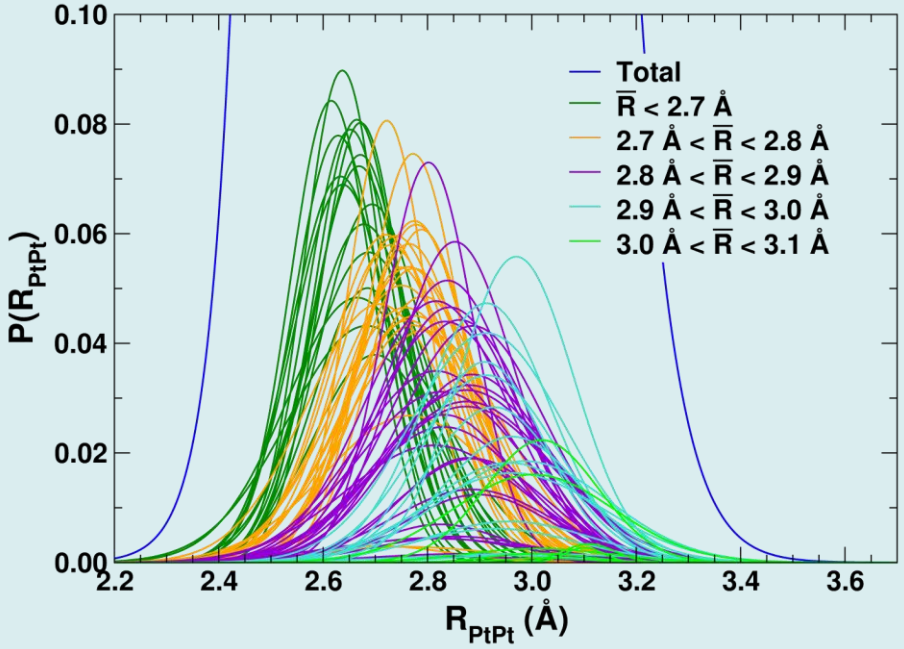
- Nanoscale physics:
  - Differ from condensed matter
  - Experience surface effects, inhomogeneous

- Experimental probes:
  - Yield only averaged properties

- Need better understanding of:
  - Dynamical segregation
  - Transient bonding

Dynamic Disorder: Fluxional Bonds

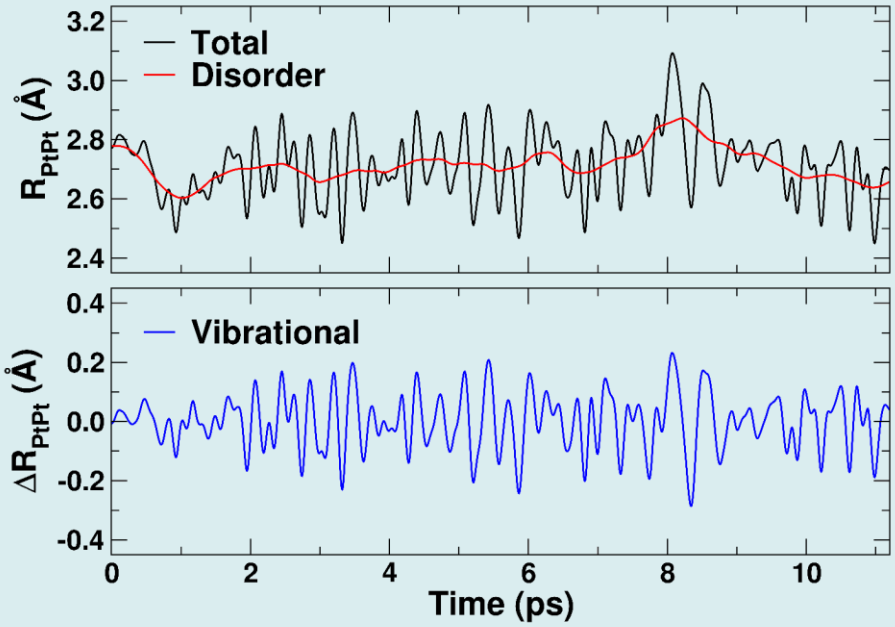


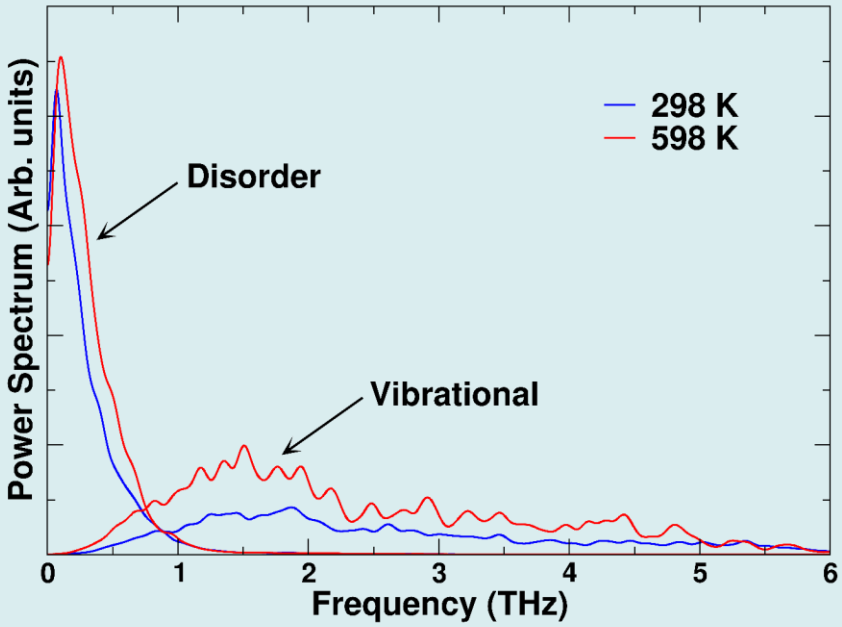


Fluxional Pt-Pt bonds (period > 6-8 ps) – Large DSD

Complex R_{PtPt} distribution – Many inhomogeneous bonds

Dynamic Disorder: Anomalous Behavior



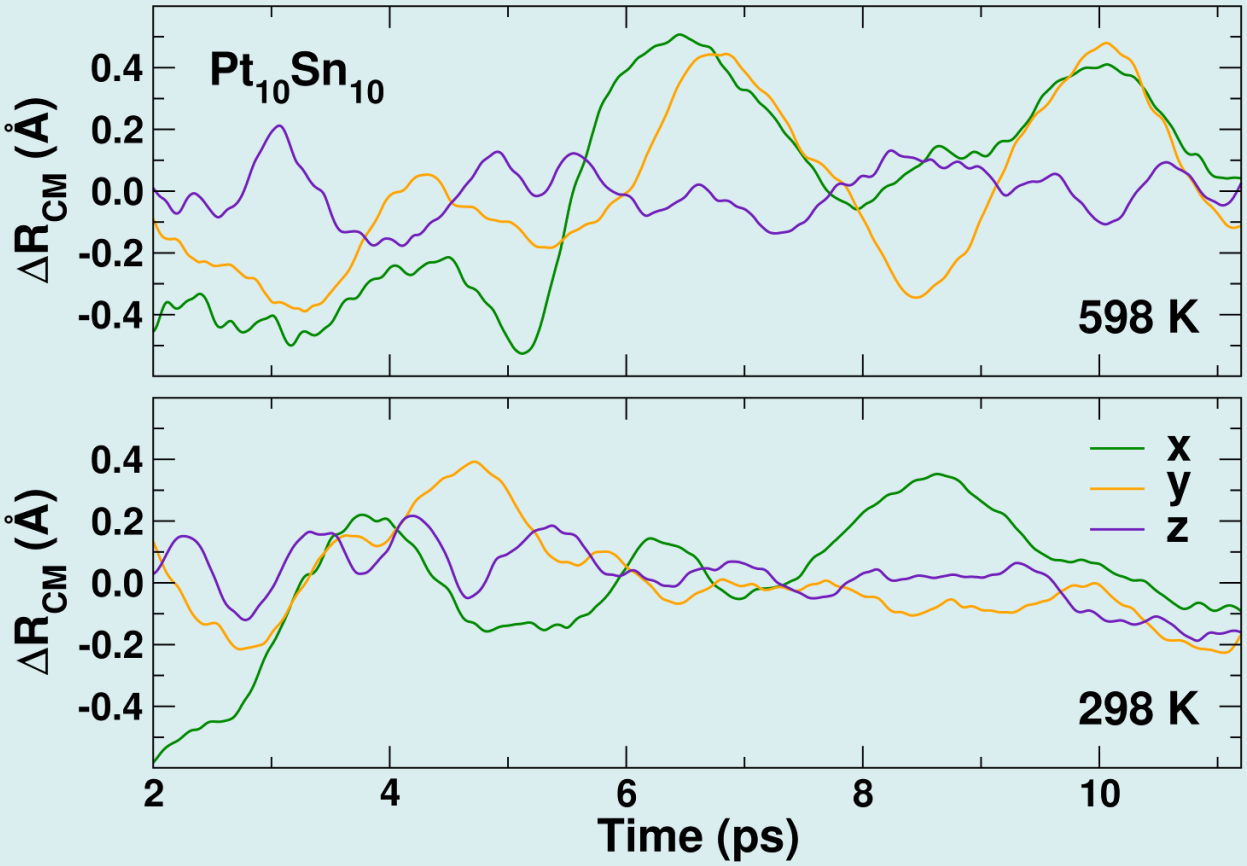


Traj. decomp. into Vibrational and Disorder components

Vibrational – Normal behavior (200-400 fs periods)

Disorder – Large, anomalous

Dynamic Disorder: Center of Mass Fluctuations



Librational (CM) motion mainly parallel (x,y) to support Sub-THz regime (2-4 ps periods)

Summary

- Sn atoms:
  - Modulate Pt-Pt interaction
  - Preferentially on cluster surface
  - Act as "barrier" between support and Pt
  - Differential charging of Pt and Sn atoms

- Three dynamic regimes:
  - Fast bond vibrations
  - Stochastic CM motion
  - Slow fluxional bonding

- Dynamic, anomalous disorder

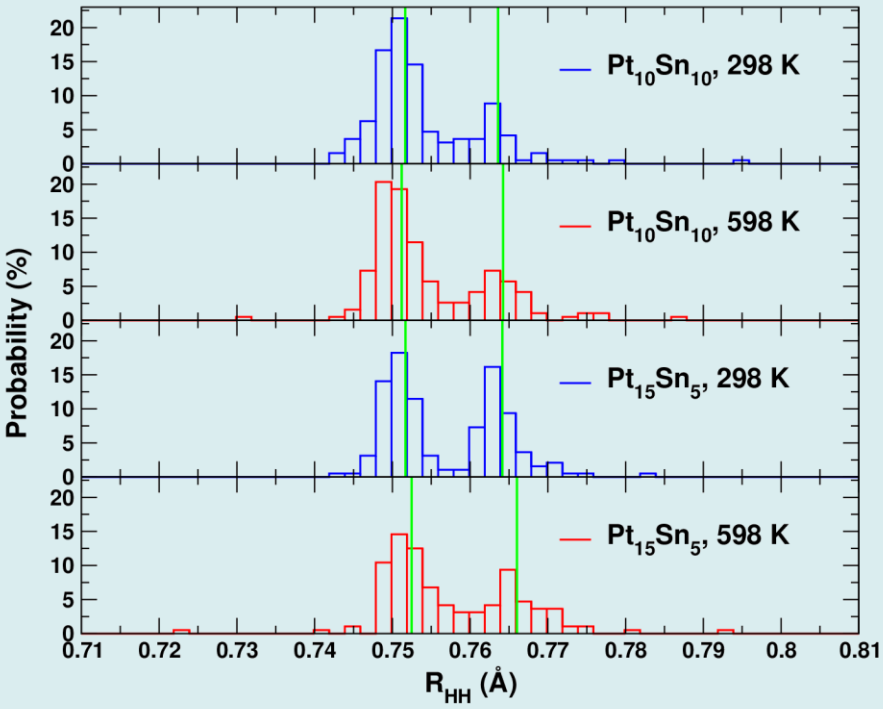
- Need better models for DSD in XAFS?

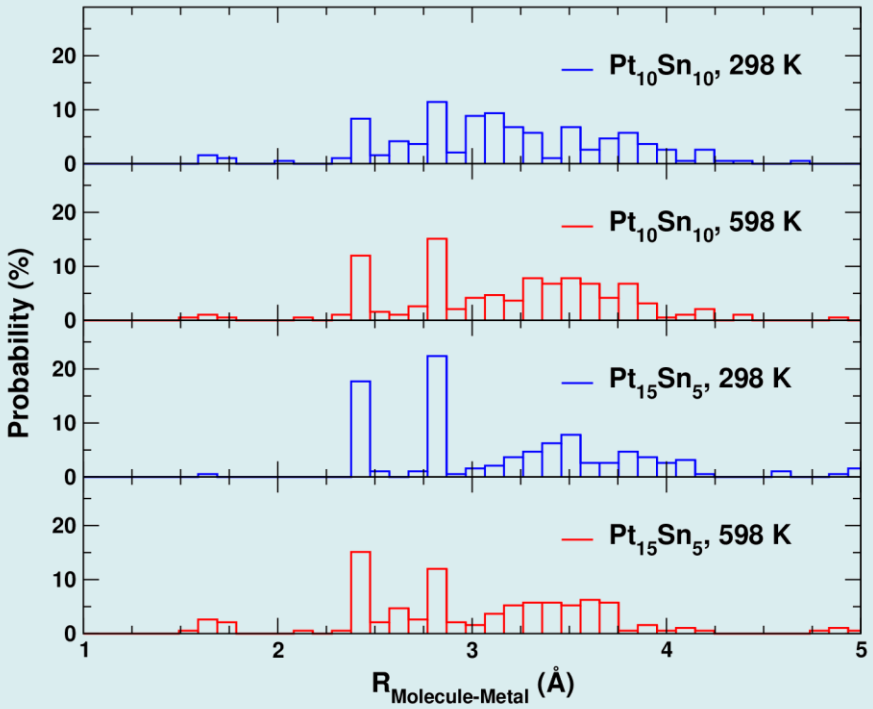
Adsorbates and Reactivity on PtSn Alloy Clusters on γ-Al_2O_3

Reactivity: Static Thermal Sampling (STS)

- MD reactivity sampling:
  - Computationally demanding
  - Difficult to capture relevant events
- Need efficient alternative: STS
  - Extract snapshots from MD
  - "Drop" adsorbate on cluster
  - Optimize adsorbate interaction while keeping cluster fixed

Reactivity: R_{H-H} and $R_{Molecule-Metal}$ Distribution

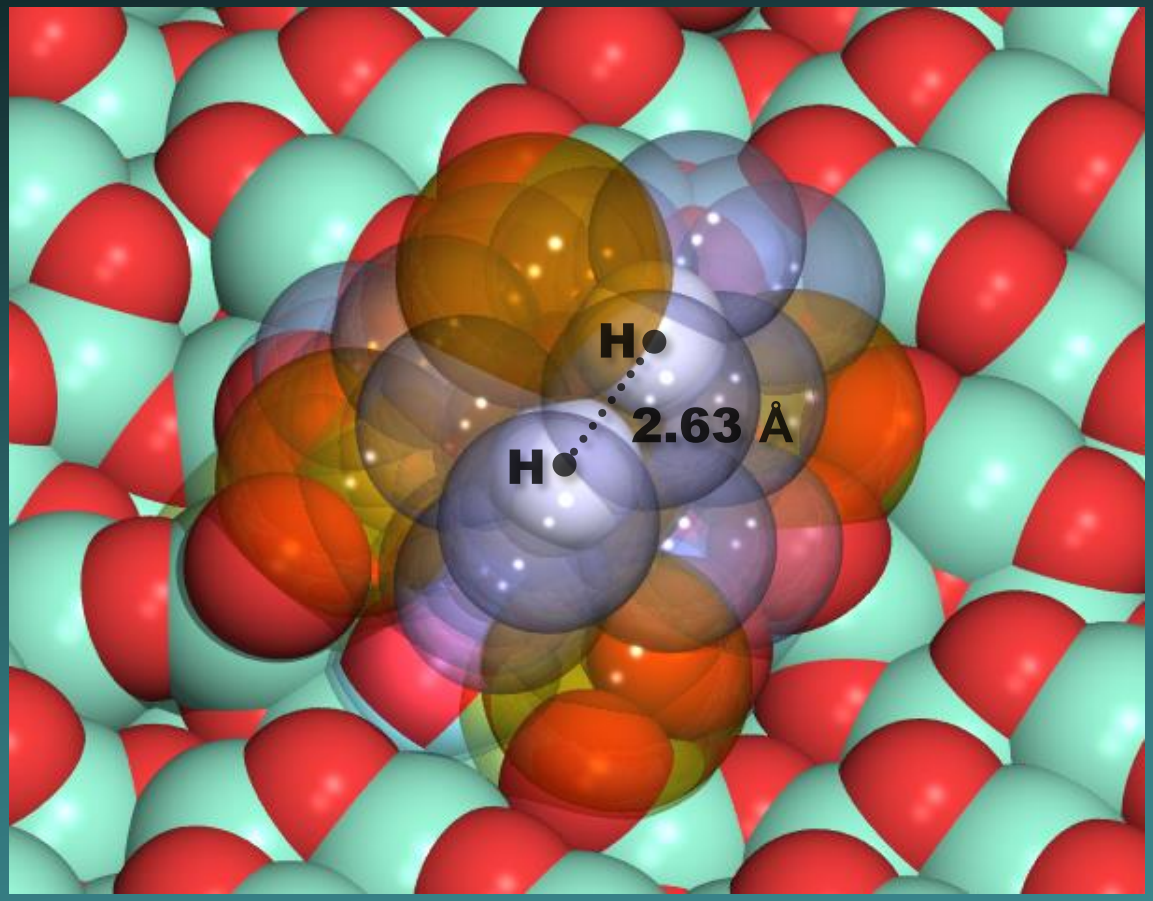




Two H_2 interactions: Weak and strong

Strong interaction: Shorter $R_{Molecule-Metal}$ distance

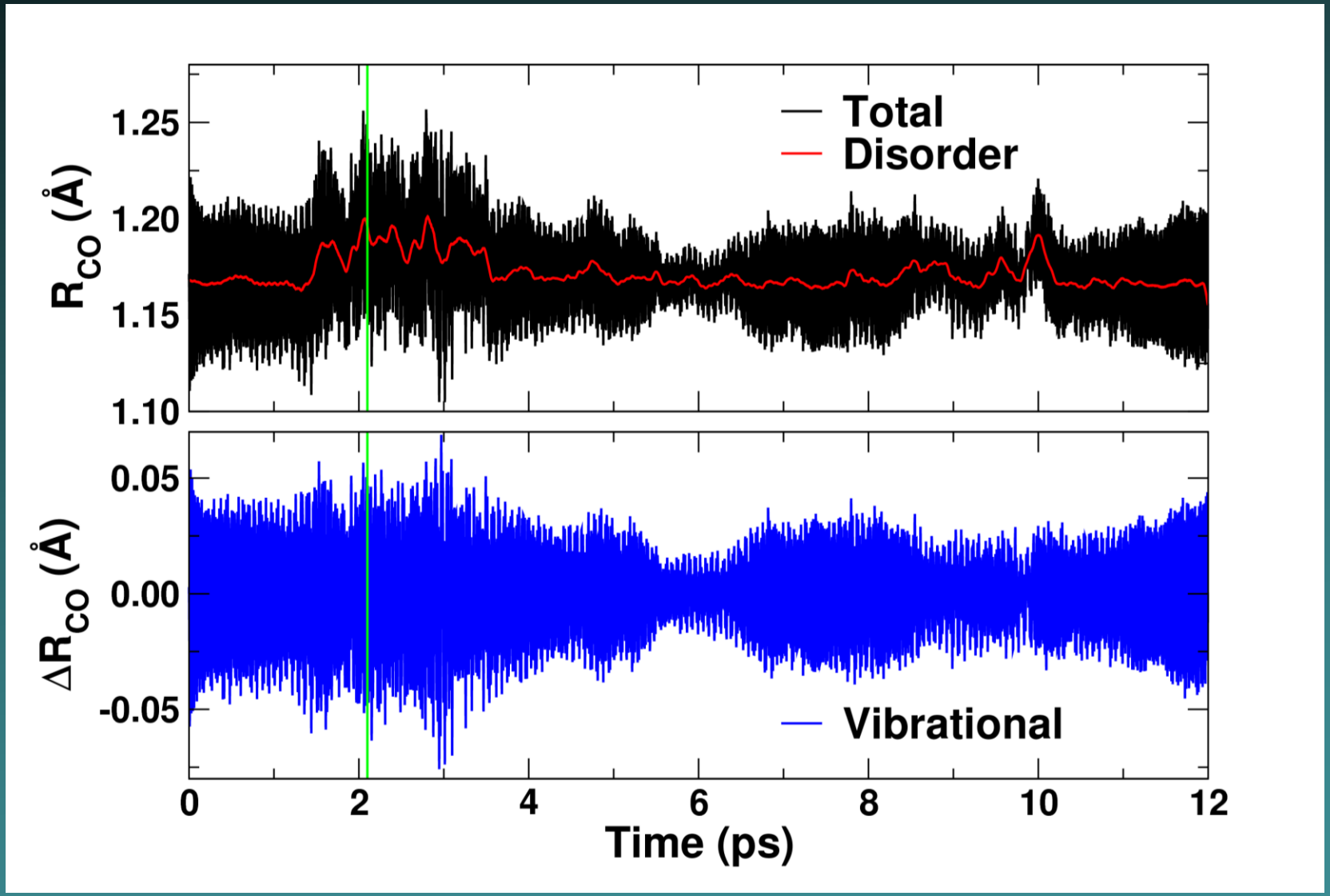
Reactivity: H_2 Dissociation Probability



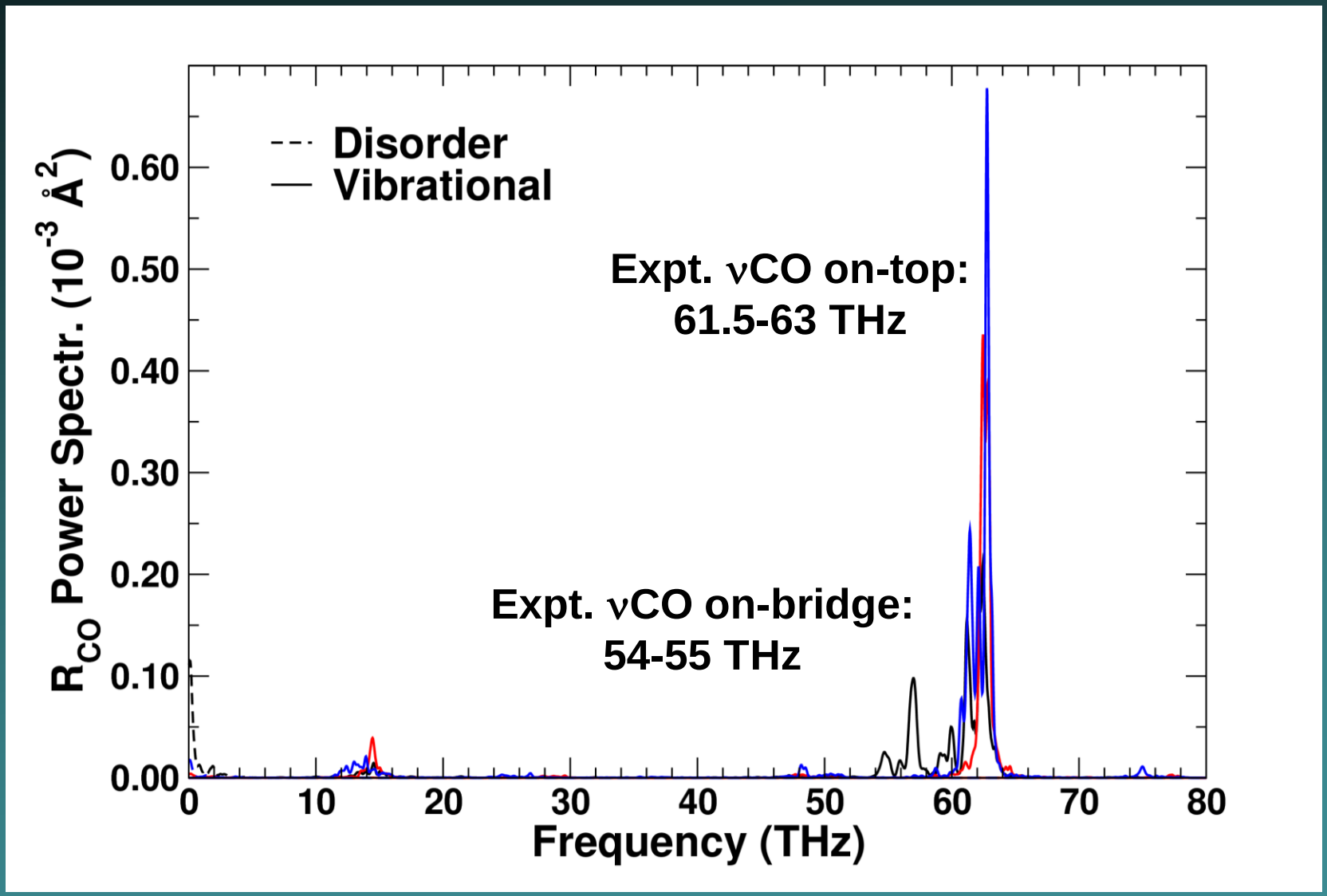
On $Pt_{10}Sn_{10}$: Low probability (<1%) at both 298 and 573K

On $Pt_{15}Sn_5$: 5% at 298K and 10% at 598K

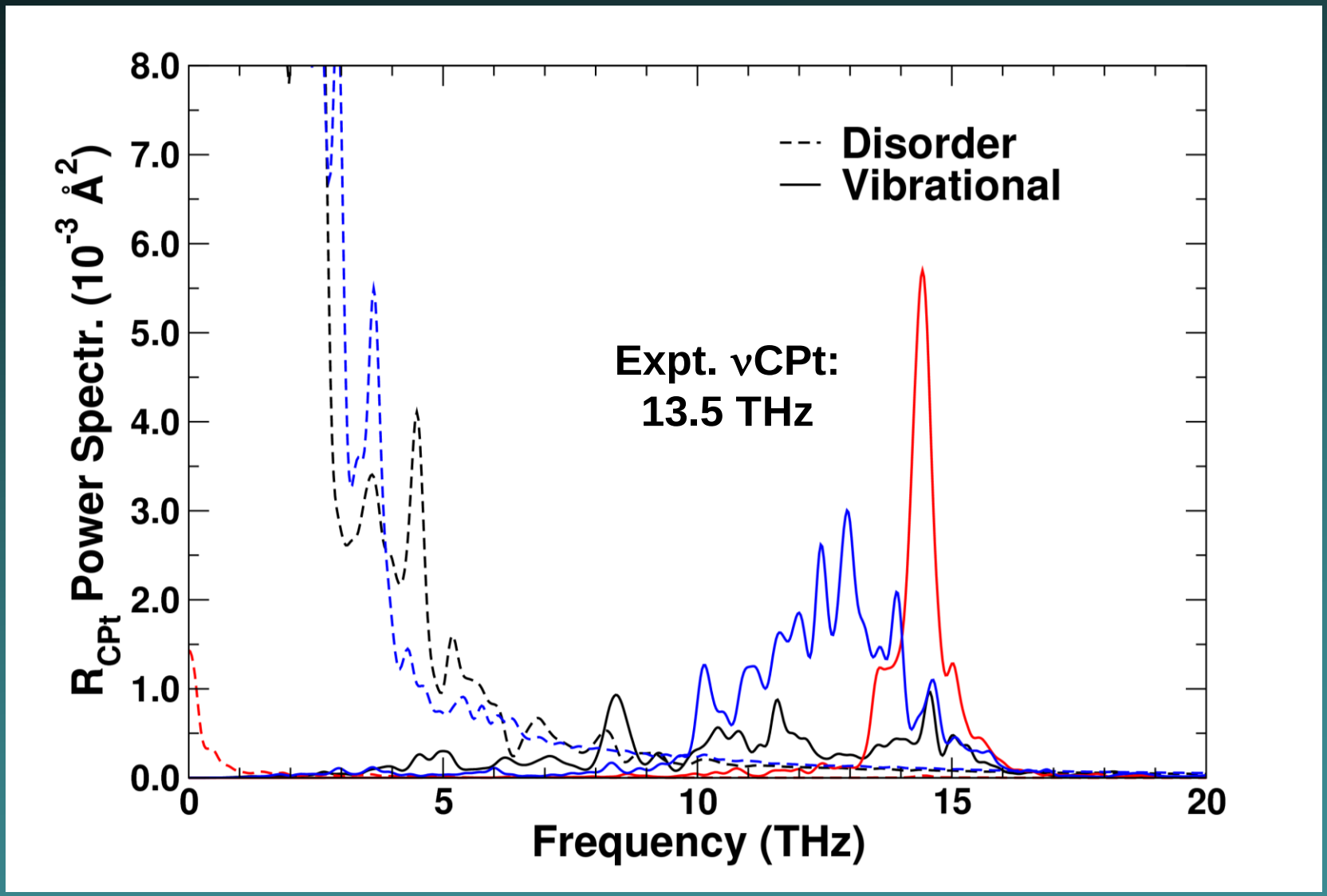
Adsorbate Dynamics: CO Internal Motion



Adsorbate Dynamics: CO Internal Motion



Adsorbate Dynamics: CO Surface Motion



Summary

- STS reveals:
  - Different cluster-H_2 interaction types
  - Preferential H_2 dissociation on Pt-rich clusters
- Adsorbate dynamics:
  - DFT/MD gives good frequencies
  - Little coupling with internal motion
  - Big coupling with cluster surface

Conclusions

- DFT/MD provides deep understanding of supported nanoparticles
- Simulations under realistic conditions are now possible
- "The devil is in the ~~details~~ sampling"

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F. Vila, May 8th 2013

Acknowledgements:

Simon Bare and Shelly Kelly

A. Frenkel

The Rehr Group at the UW

Supported by:

NSF Grant PHY-0835543

UOP LLC, a Honeywell Company

With computer support from NERSC

UNIVERSITY OF WASHINGTON

UOP A Honeywell Company