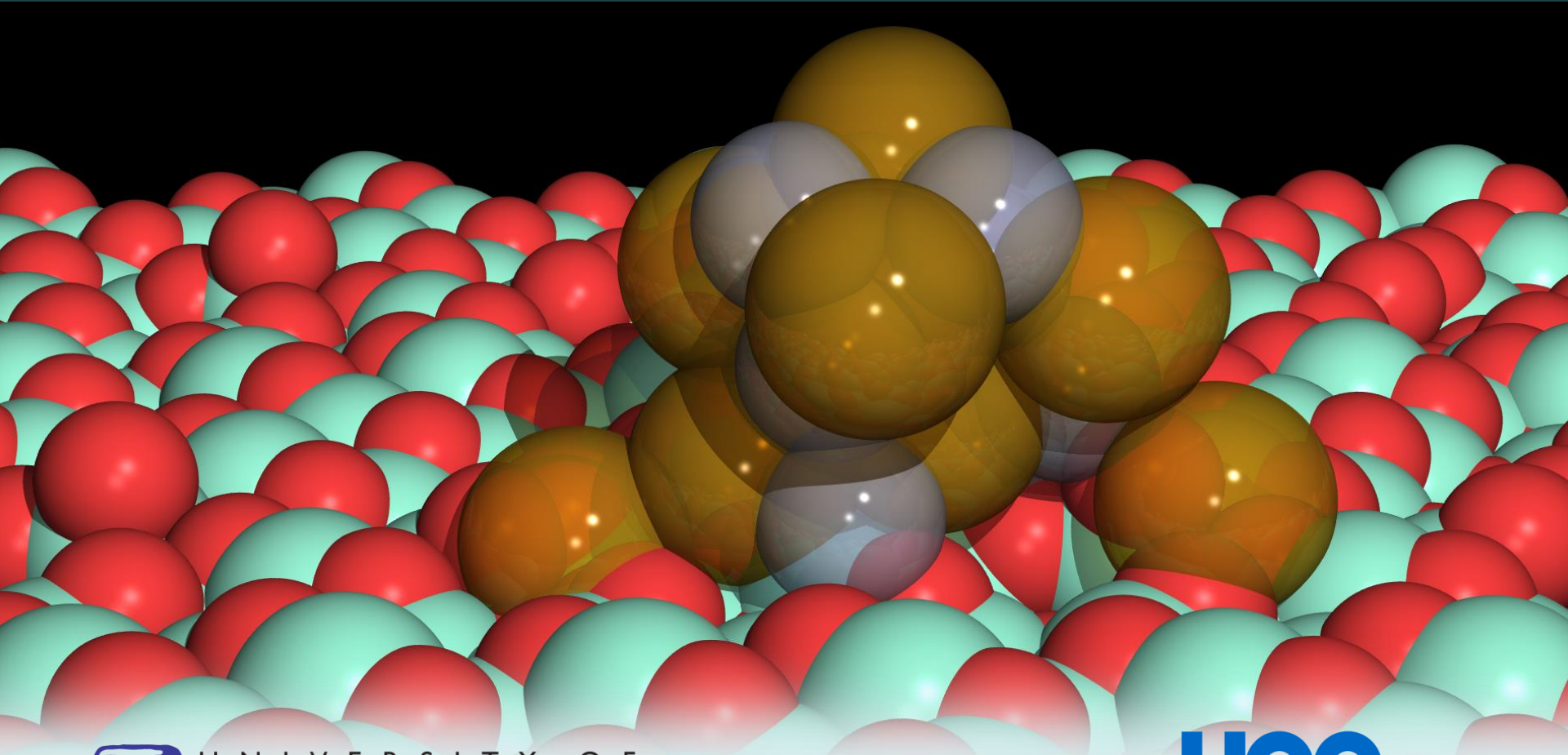
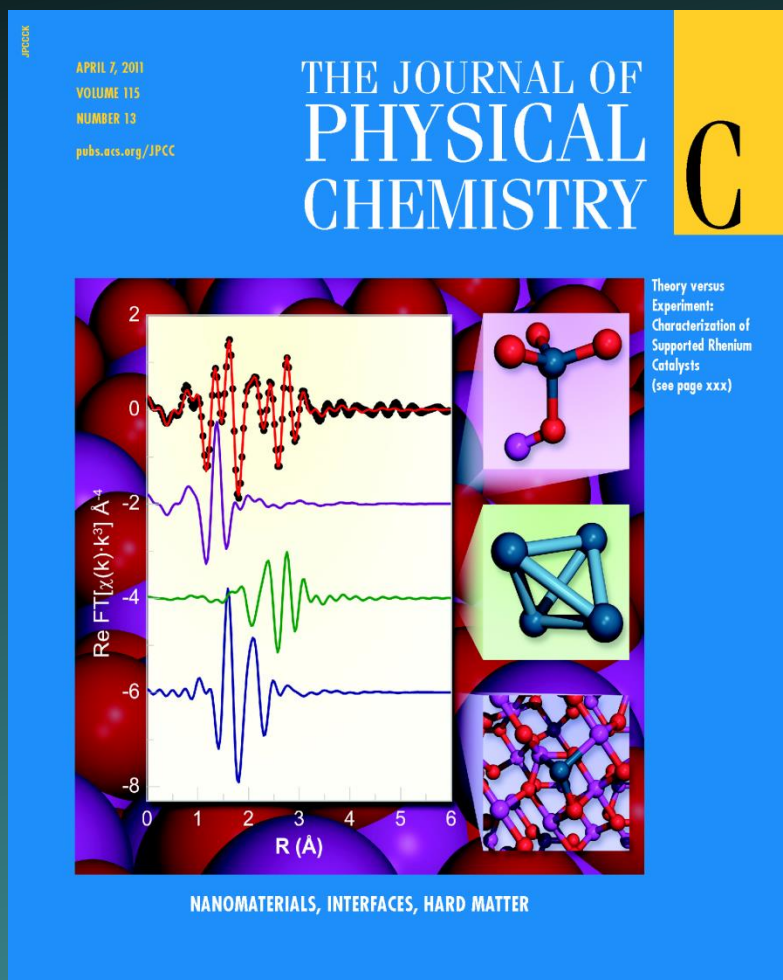


Estructura dinámica en nanopartículas de Pt y Pt-Sn

F. Vila, Montevideo, Uruguay, 26 de Agosto, 2013



Previous Work



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

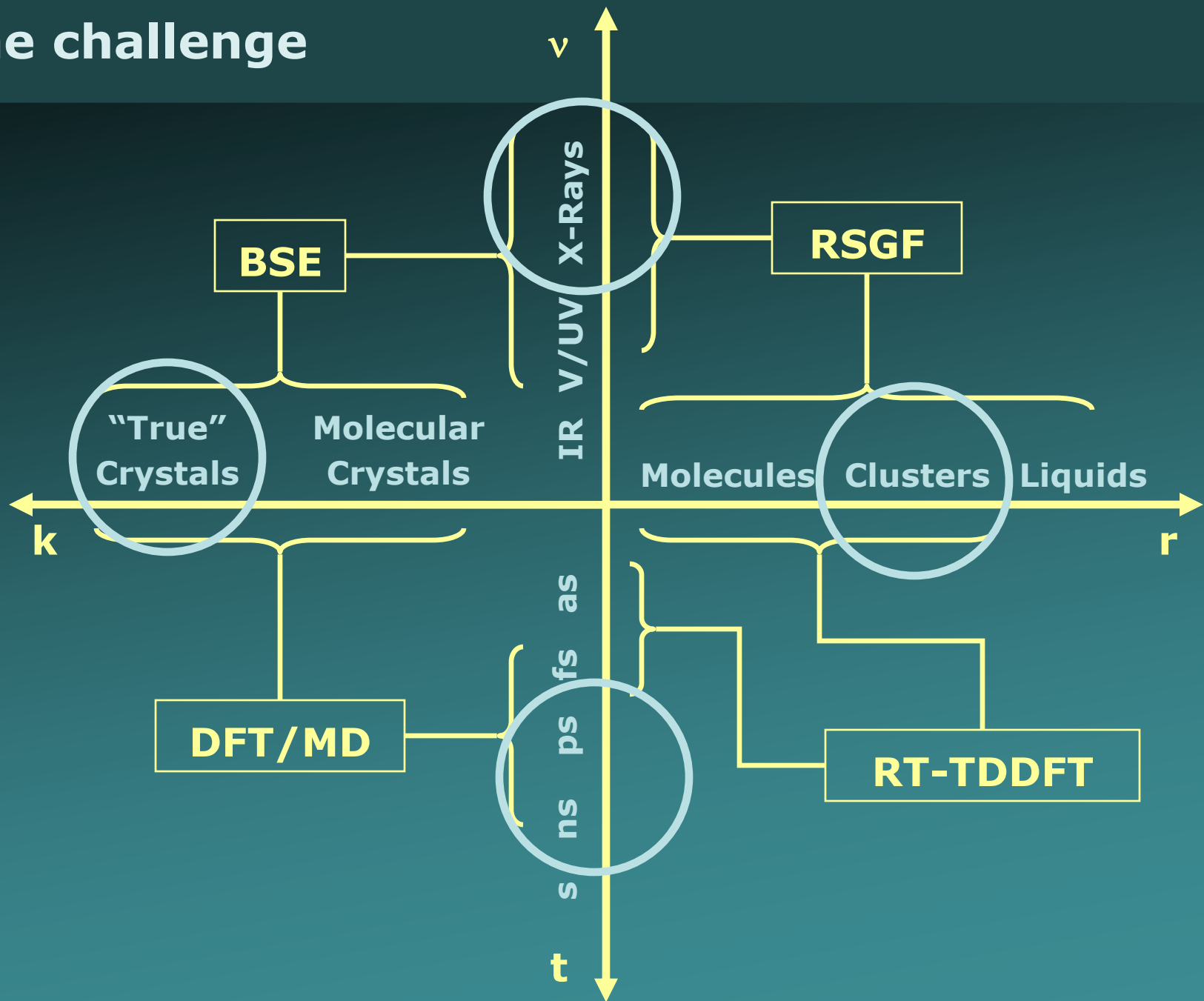
S. Bare, S. Kelly, F. D. Vila, D. Boldingh, E. Karapetrova, J. Kas, G. Mickelson, F. Modica, N. Yang, J. J. Rehr

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 $\gamma\text{Al}_2\text{O}_3$

The challenge



Outline

Pt₁₀ on γ -Al₂O₃:

Negative Thermal Expansion and Disorder

PtSn Alloy Clusters on γ -Al₂O₃:

Structure and Dynamic Disorder

Adsorbates and Reactivity on

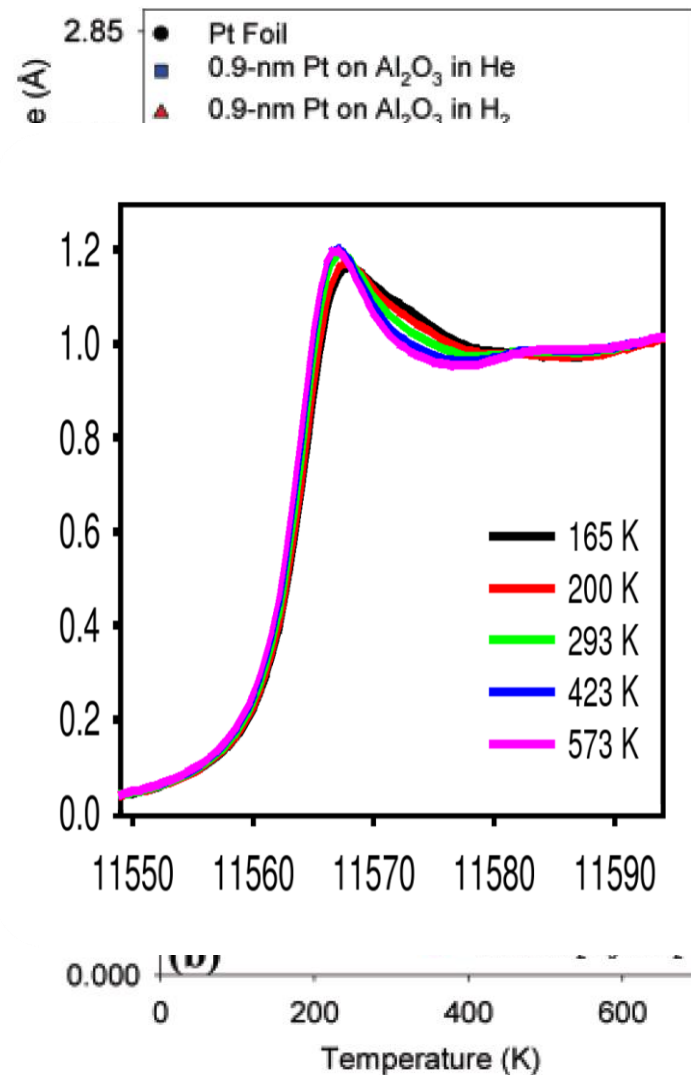
PtSn Clusters on γ -Al₂O₃

Pt₁₀ on γ -Al₂O₃:

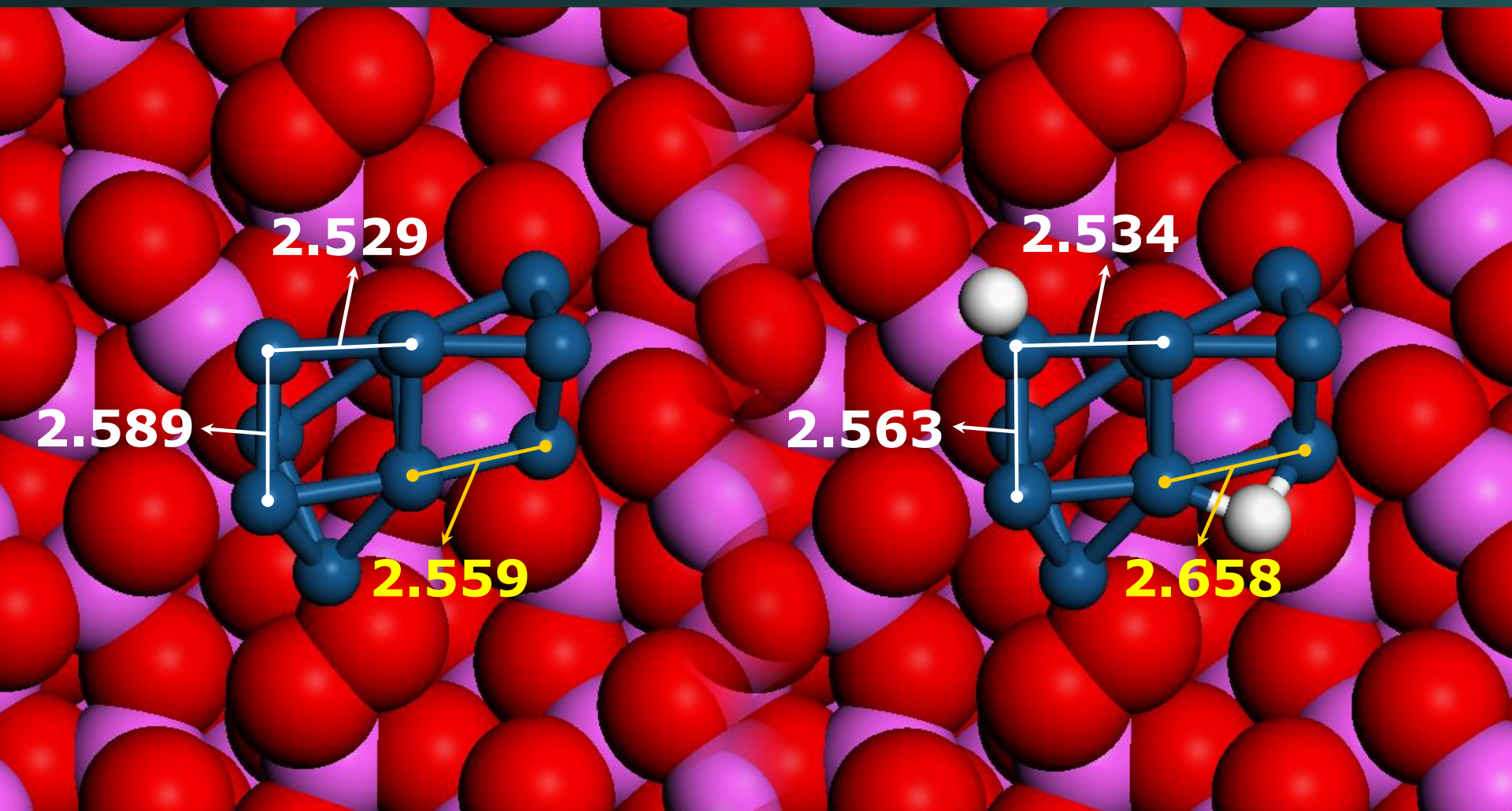
Negative Thermal Expansion and Disorder

Experimental Results

- **Pt-Pt expansion** going from He to H₂ atmosphere
- **Pt-Pt negative thermal expansion**
- **High Pt-Pt disorder**
- **Increased intensity and redshift of XANES** with increasing T



Bond expansion in H₂ atmosphere



Computational details

Study prototypical Pt_{10} clusters on $\gamma\text{-Al}_2\text{O}_3$

DFT/MD

VASP

PBE Functional

396 eV Cutoff

3 fs Step

3 ps Equilibration

5 ps Runs (3)

165 K & 573 K

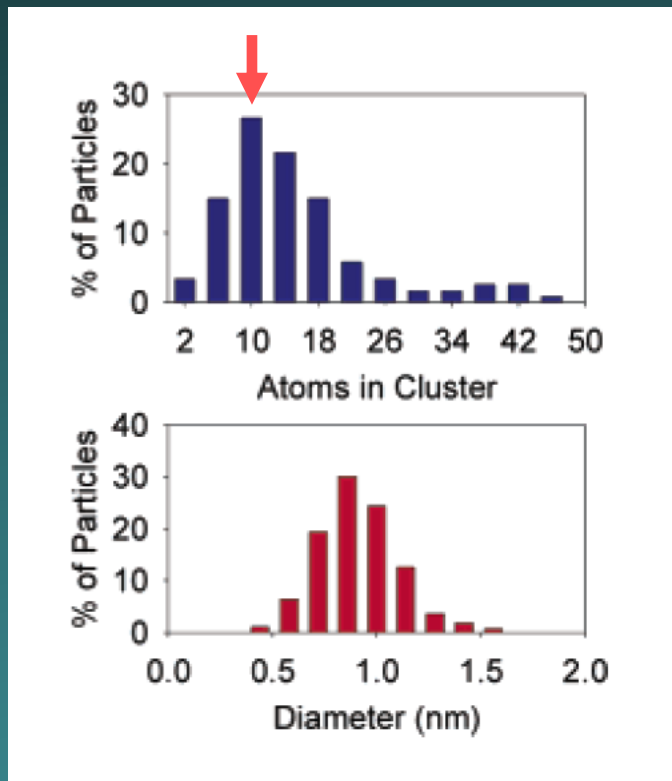
XANES

FEFF8

Full Multiple Scattering

32 Configurations from MD

7 Å Clusters (~150 atoms)



MD @ 165 K

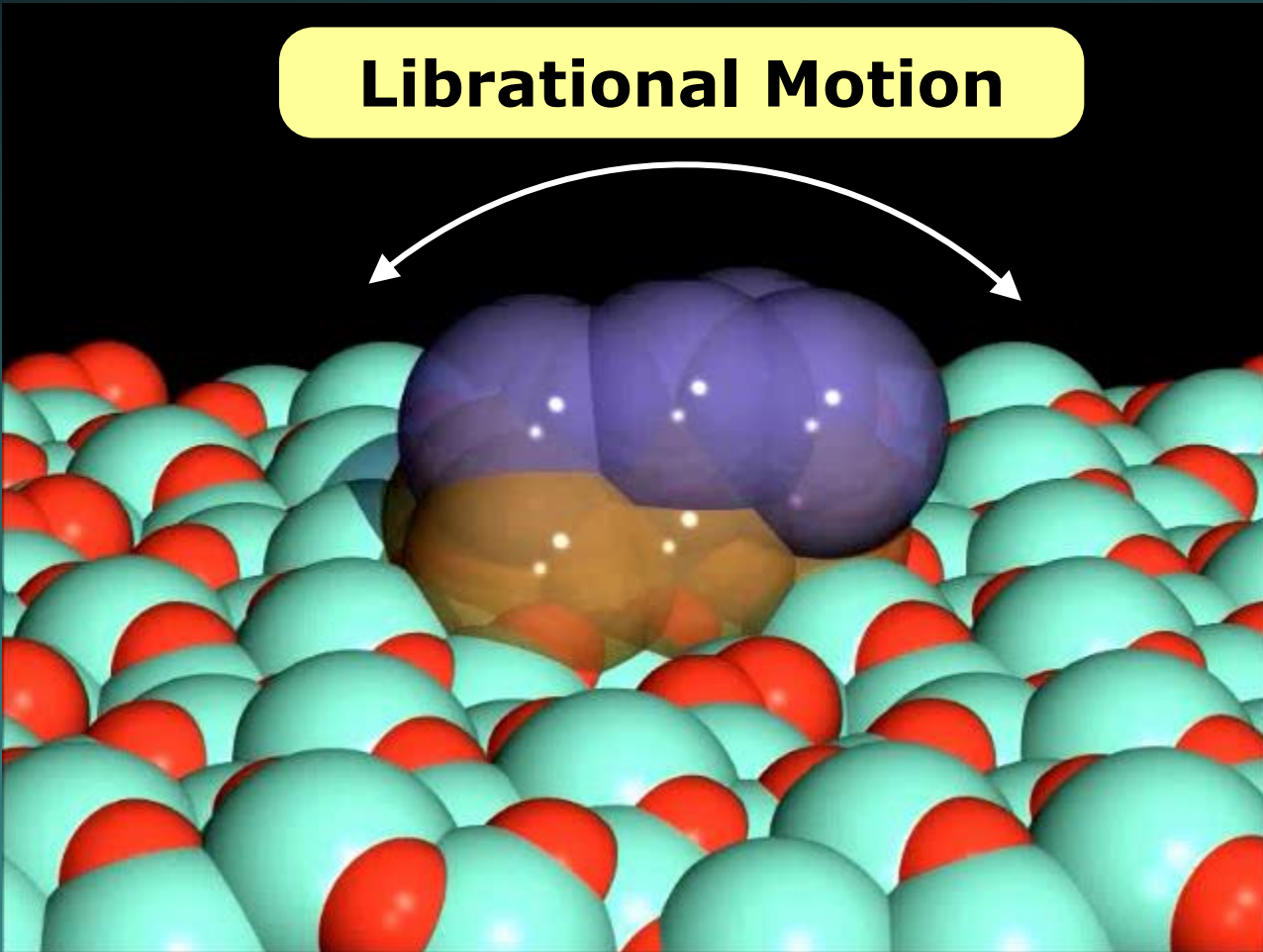
Librational Motion


Pt
(Ox)


Pt
(Me)


O


Al



MD @ 573K

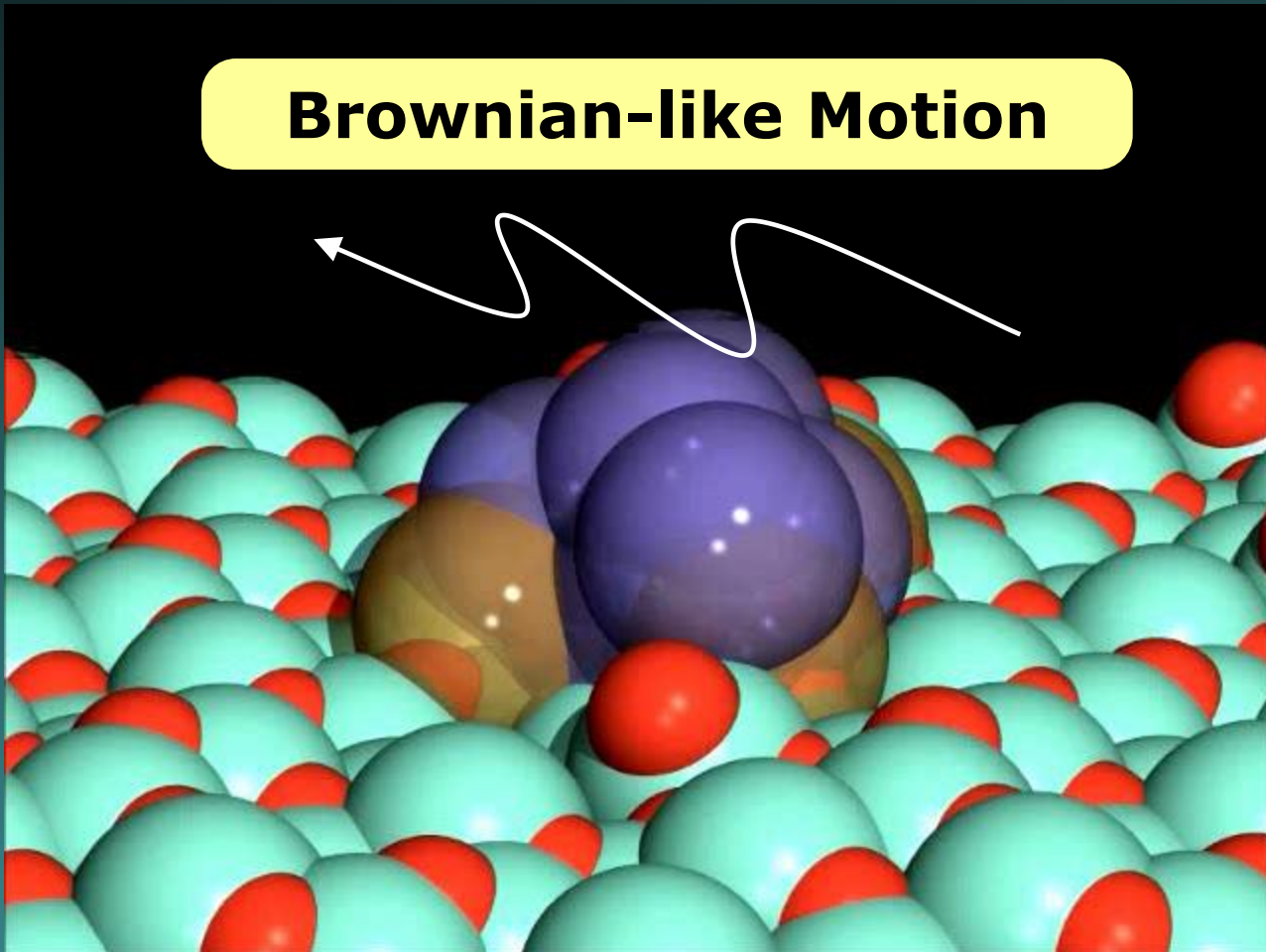
Brownian-like Motion


Pt
(Ox)

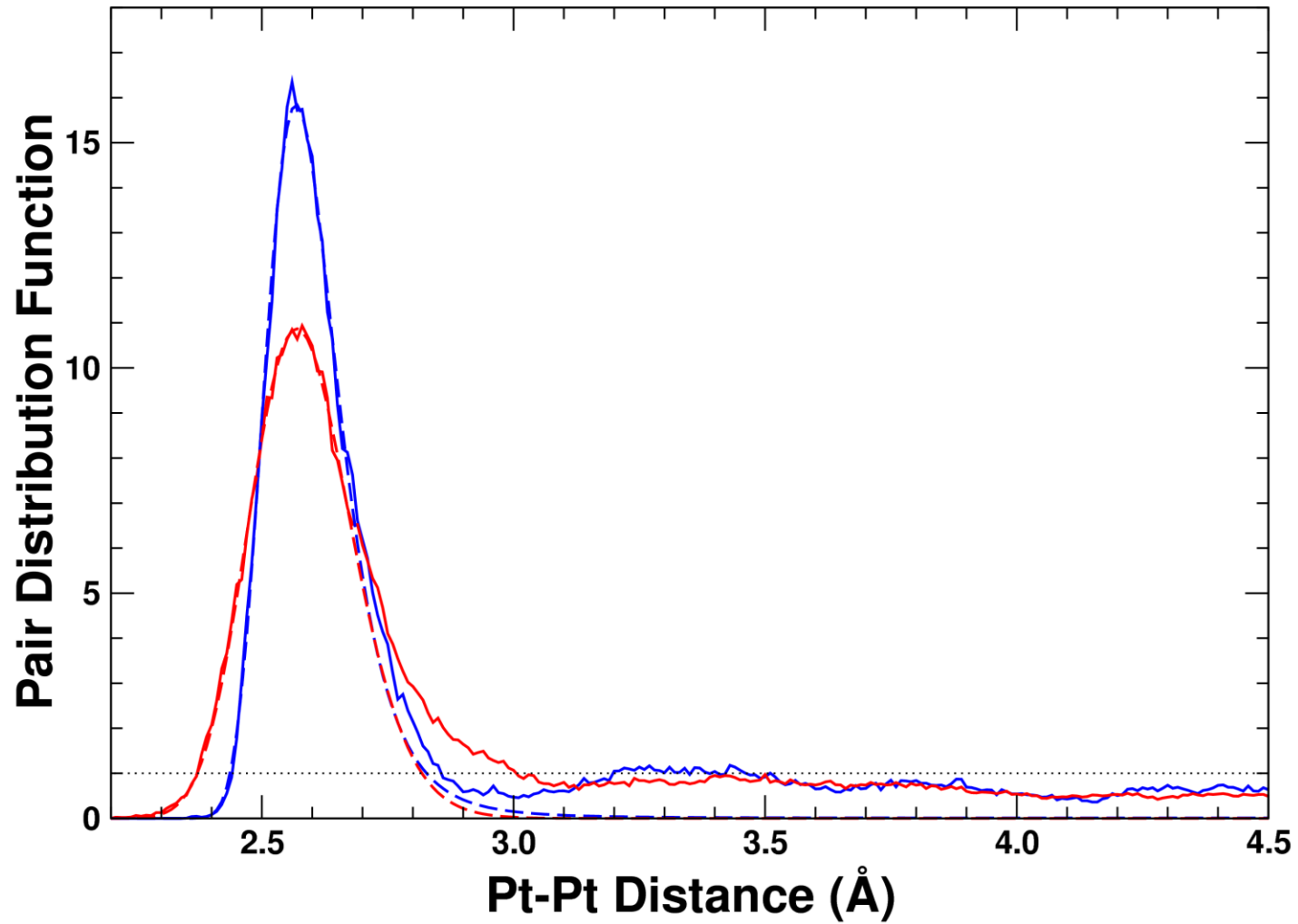

Pt
(Me)


O

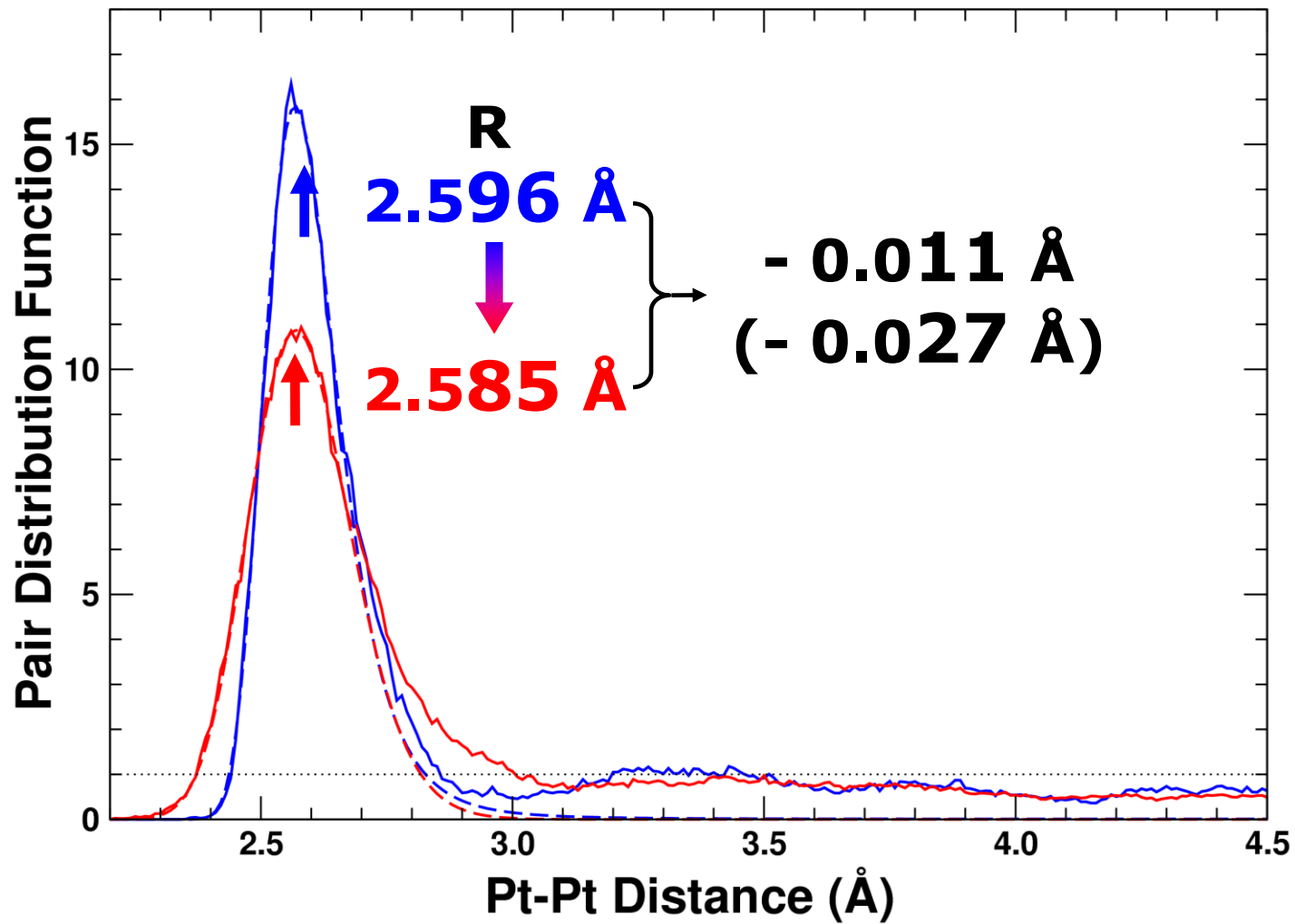

Al



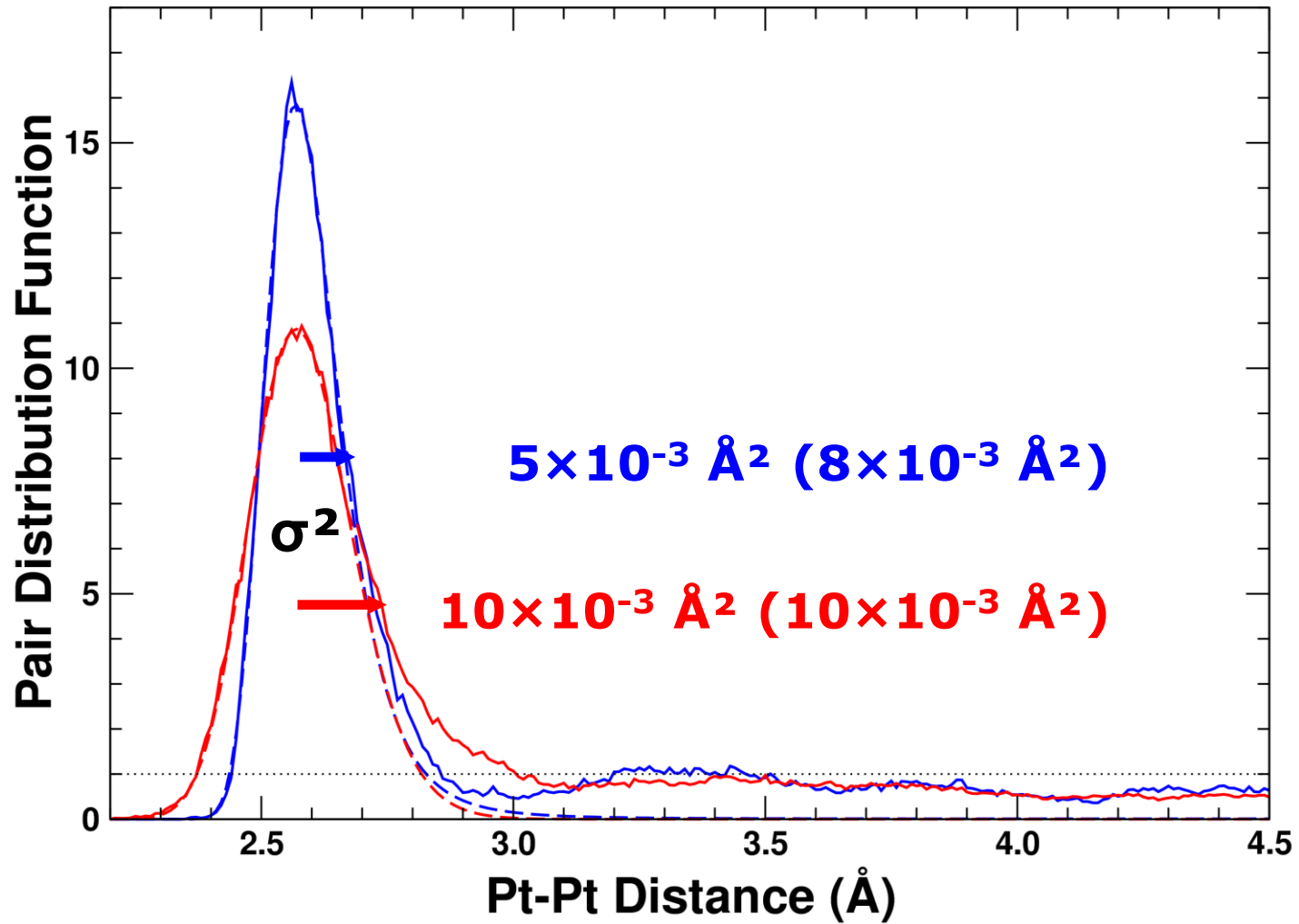
Pt-Pt Pair Distribution Function



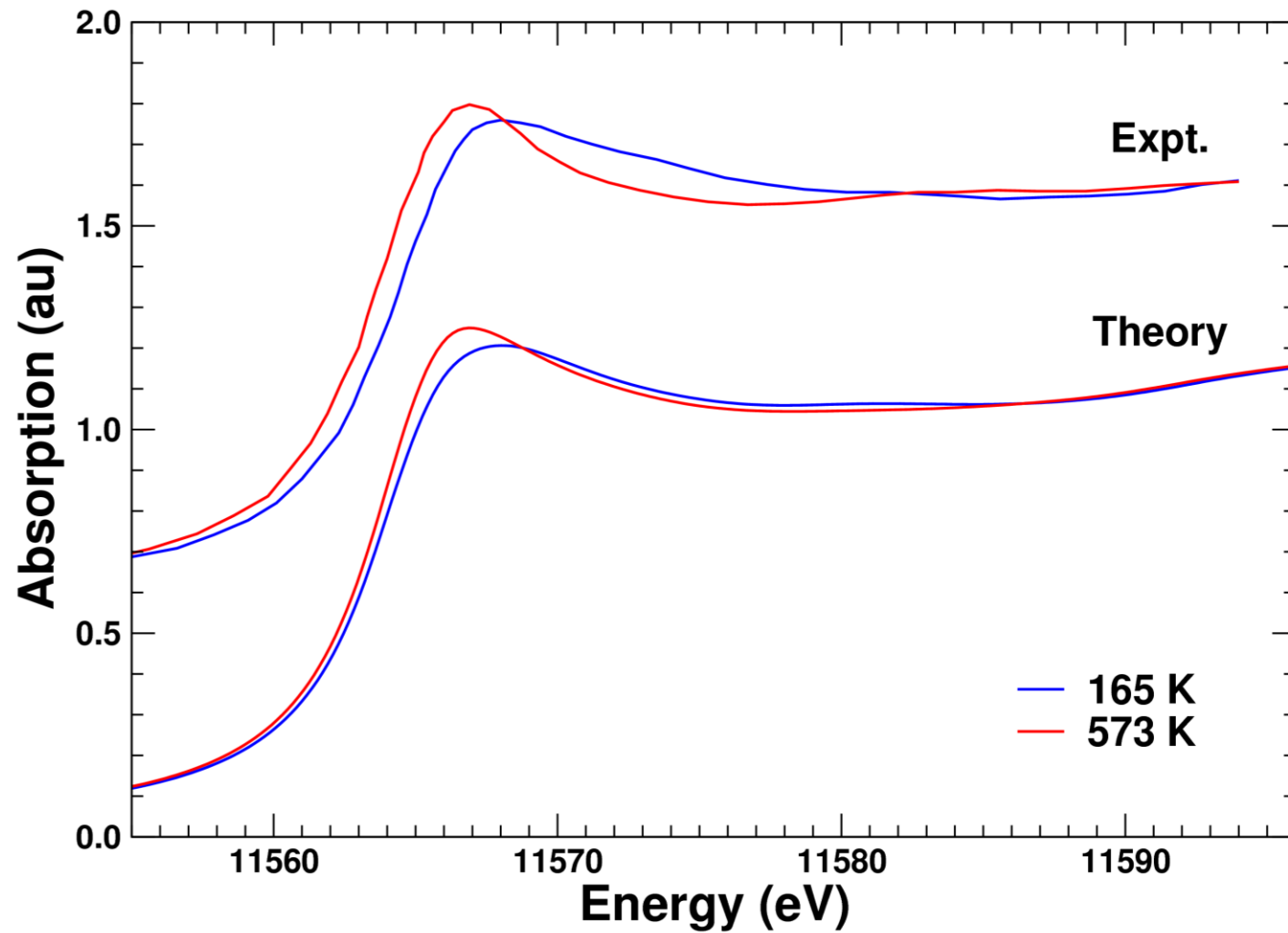
Negative Thermal Expansion



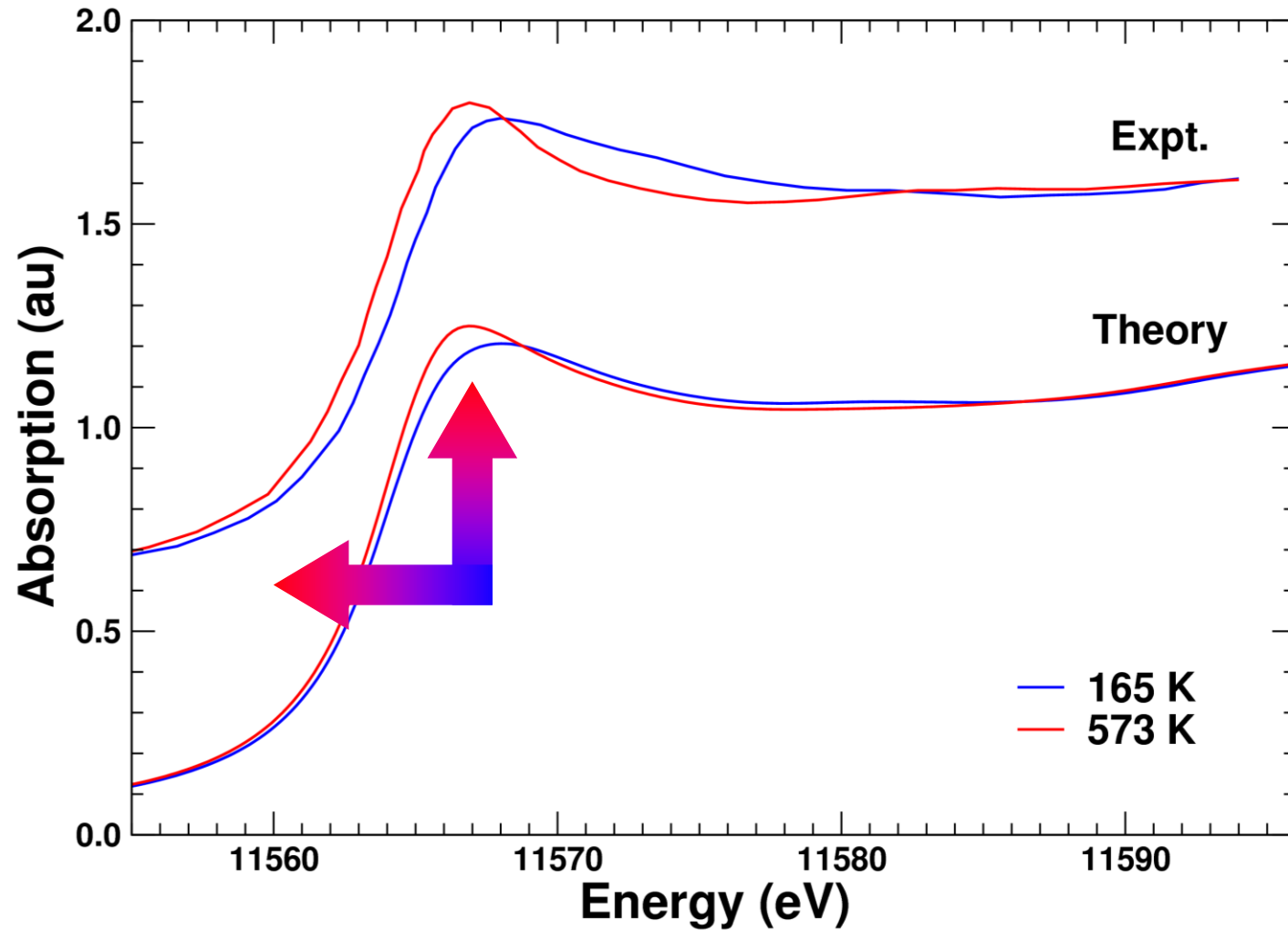
High Pt-Pt Disorder



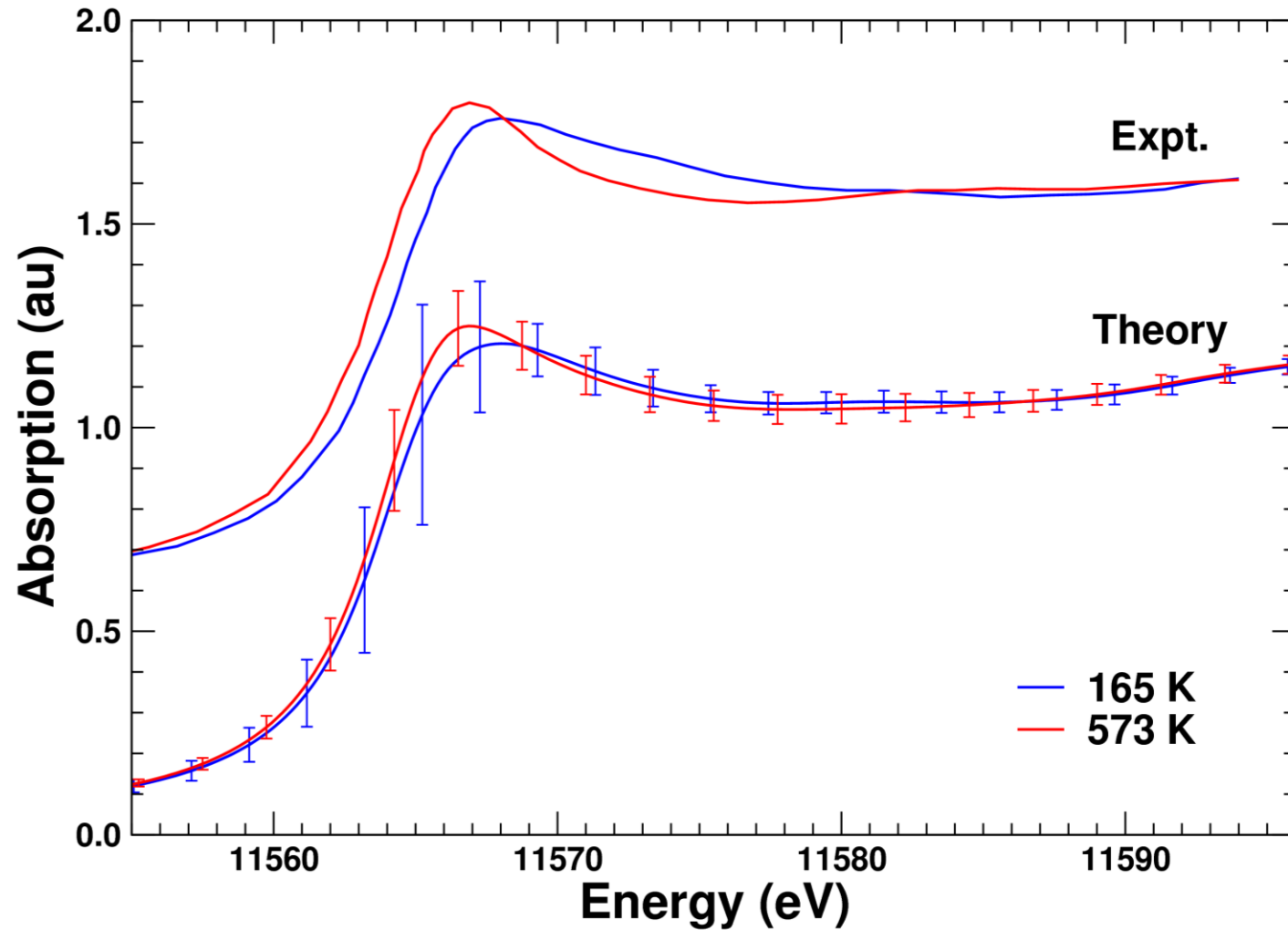
Pt L₃ XANES



Increased intensity and redshift at high T



Increased intensity and redshift at high T



Summary

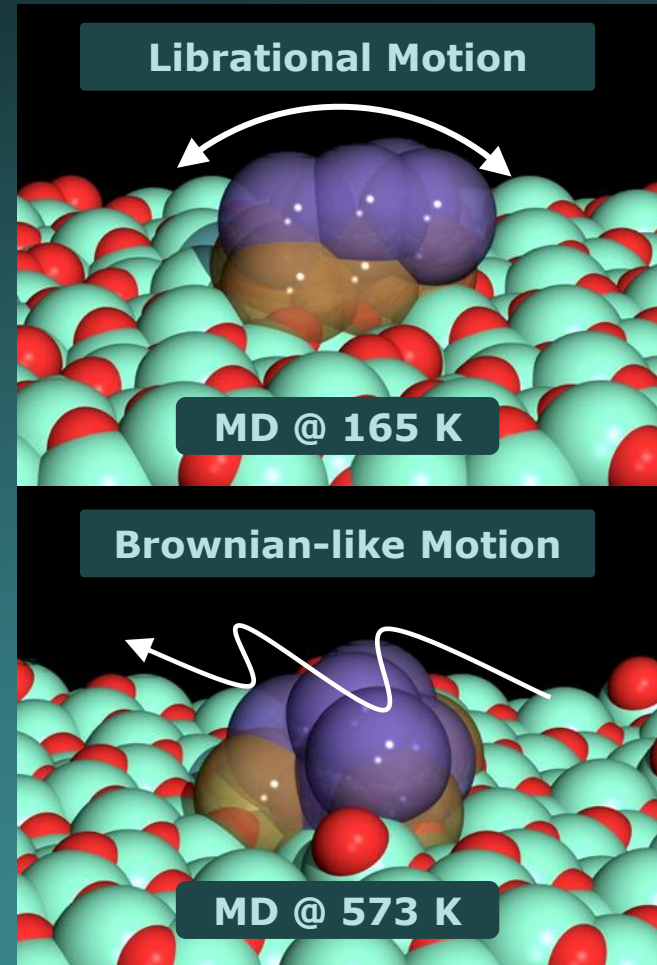
Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

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**).



Pt₁₀ on γ -Al₂O₃

**PtSn Alloy Clusters on γ -Al₂O₃:
Structure and Dynamic Structural Disorder**

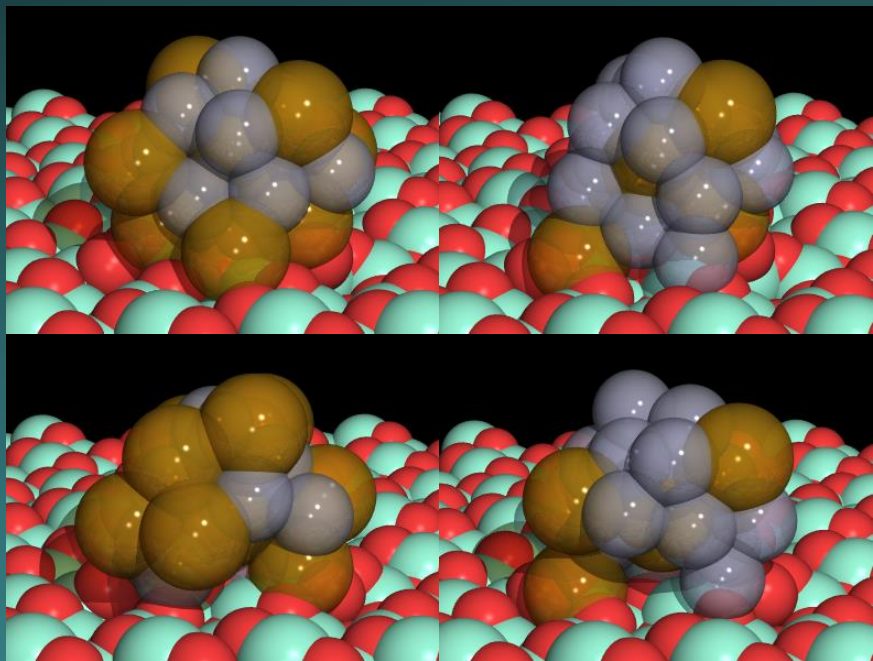
Motivation

- **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 $\gamma\text{-Al}_2\text{O}_3$ under realistic conditions

Theoretical Probe: DFT/MD

Atomistic **electronic** and **structural** information



Initial structures: Randomly
Sn-substituted Pt₂₀ cluster

DFT/MD

VASP

PBE Functional

396 eV Cutoff

3 fs Steps

3 ps Equilibration

9 ps Runs (4/Temp)

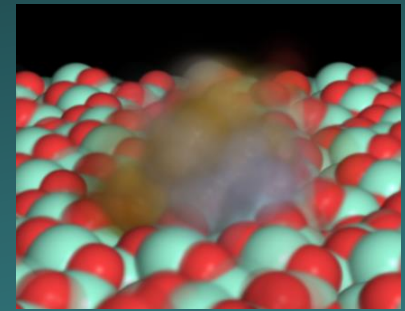
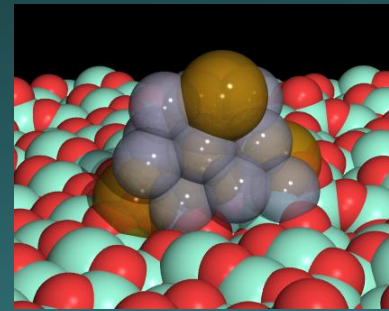
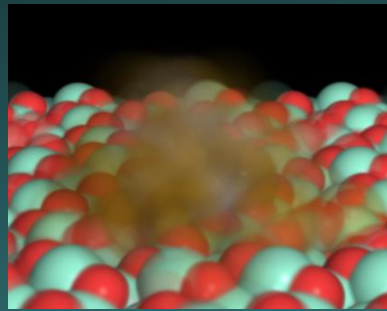
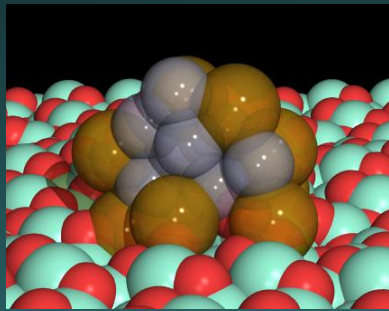
298 and 598 K

Structure: Segregation and Disorder

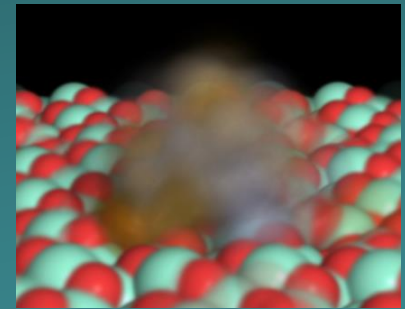
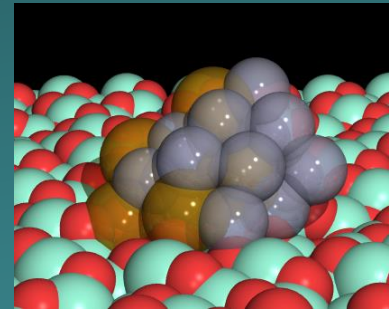
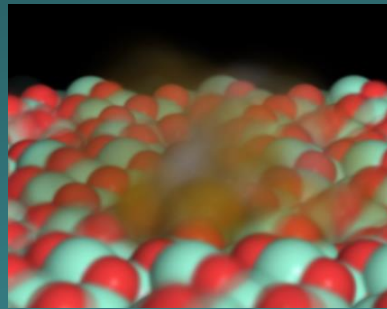
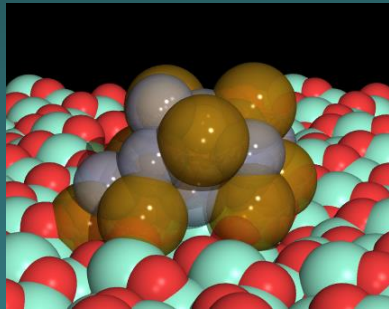
$\text{Pt}_{10}\text{Sn}_{10}$

$\text{Pt}_{15}\text{Sn}_5$

298 K



598 K



Snapshot

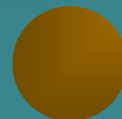
Time Elapsed

Snapshot

Time Elapsed



Pt



Sn



Al



O

Dynamical Properties: Molecular Dynamics



Sn



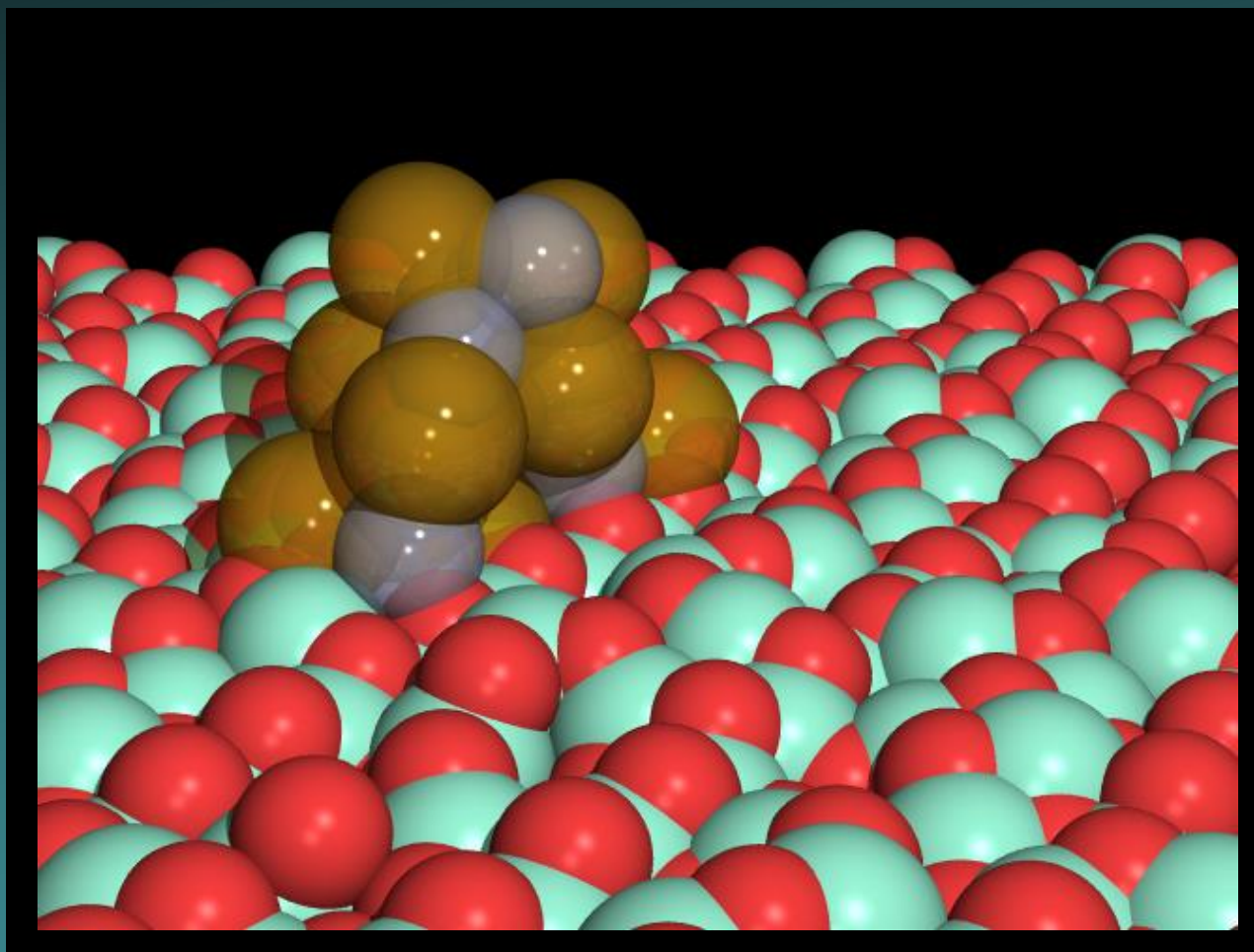
Pt



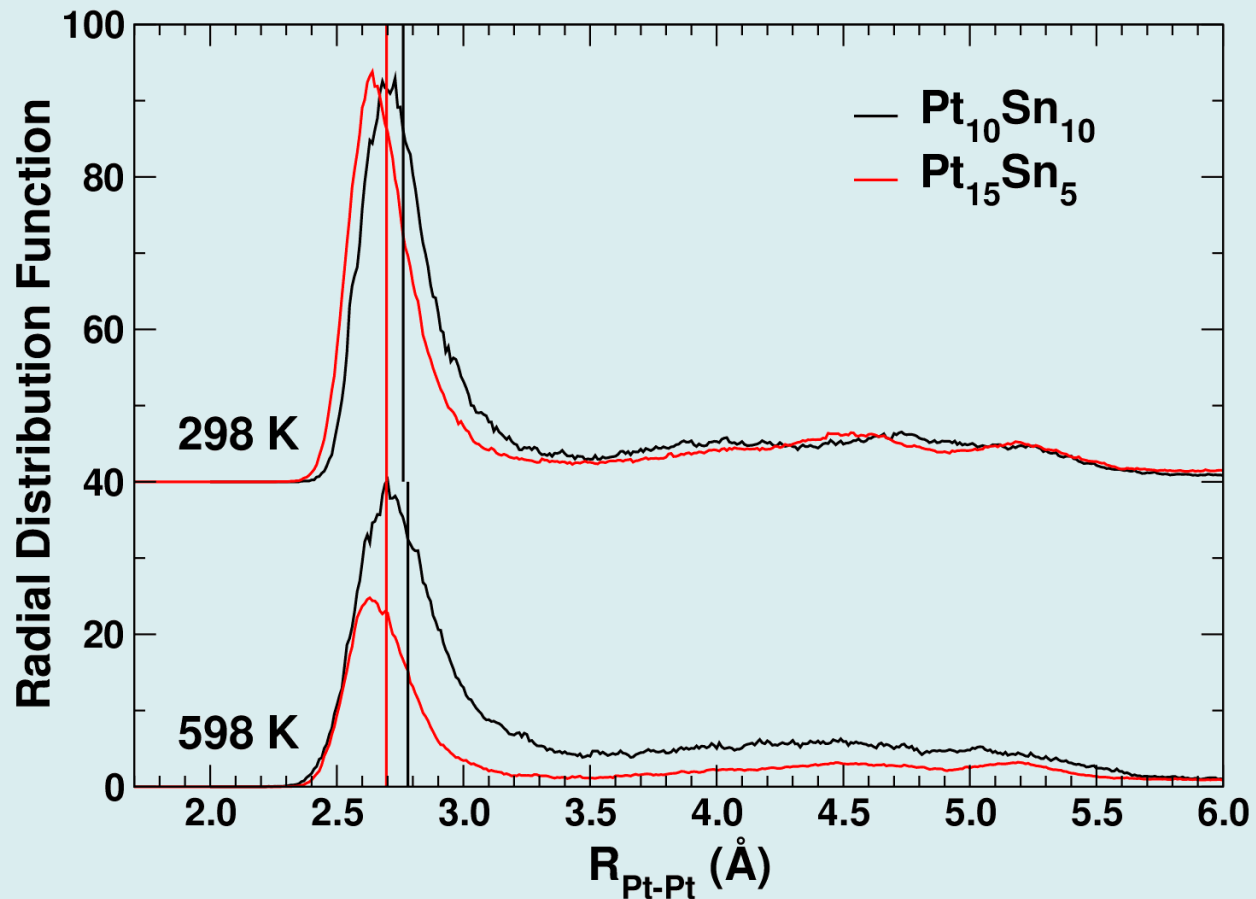
O



Al

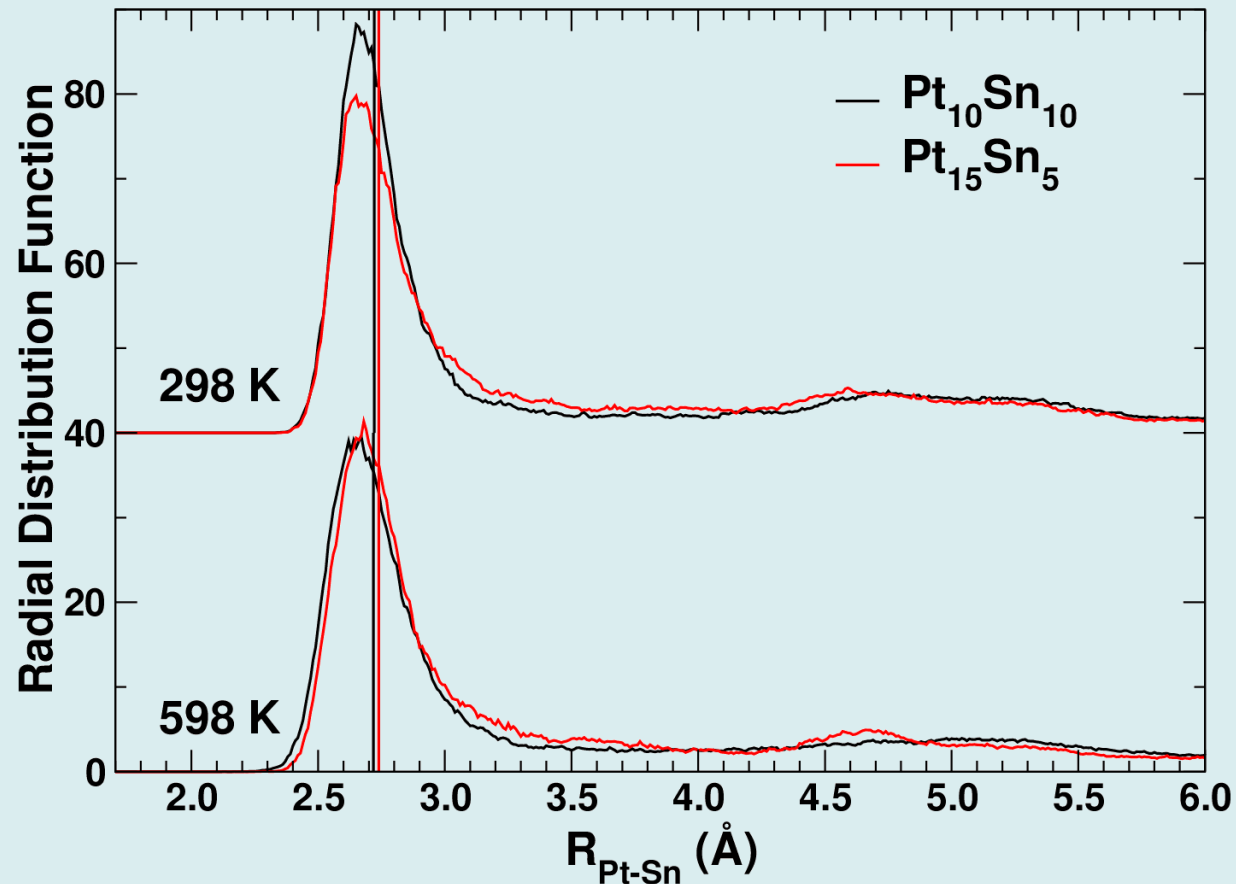


Cluster Internal Structure: Pt-Pt



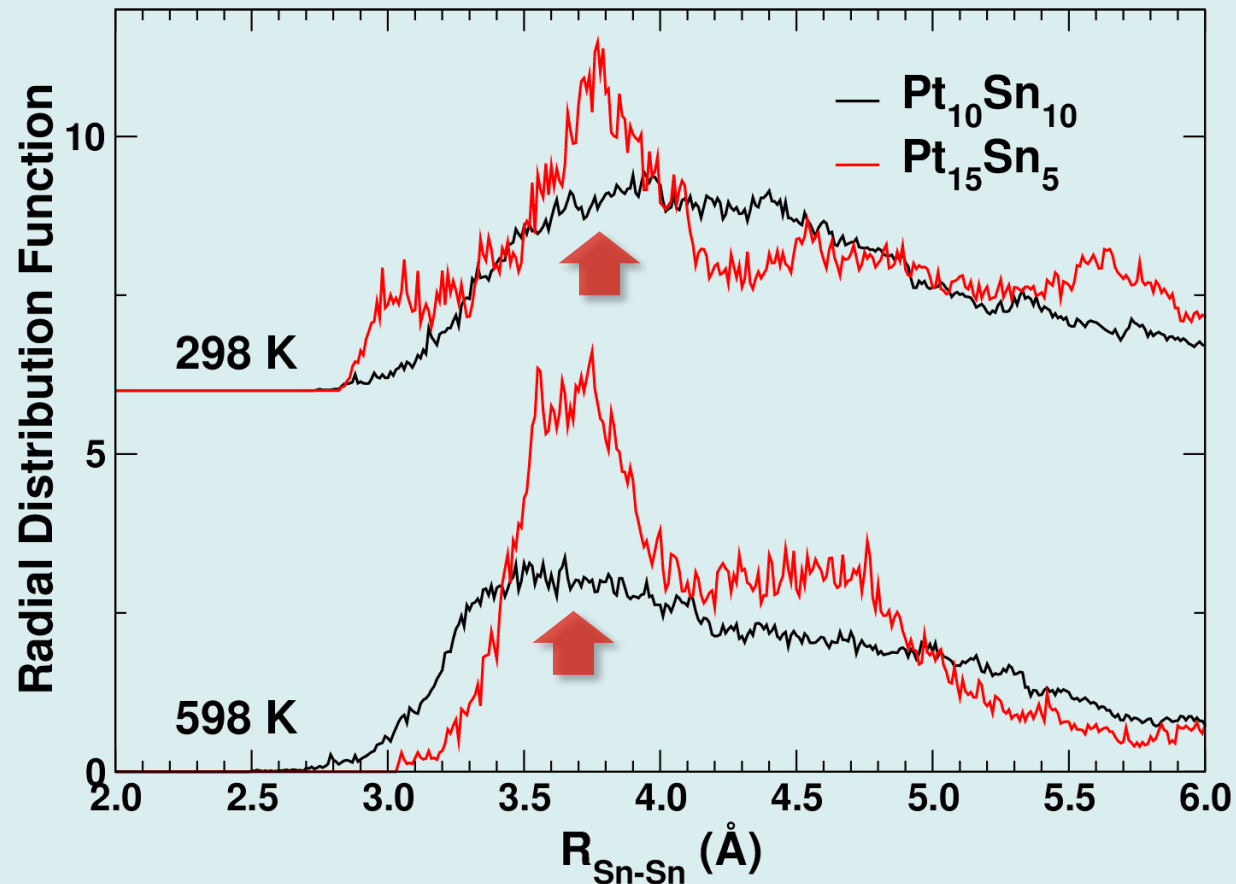
Shorter $R_{\text{Pt-Pt}}$ and NTE trend at higher Pt concentration

Cluster Internal Structure: Pt-Sn



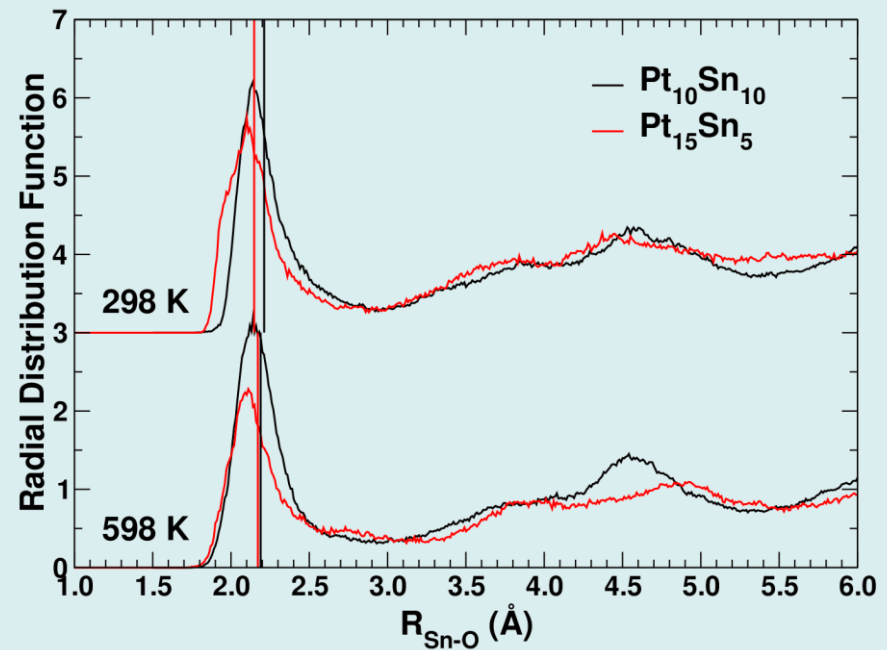
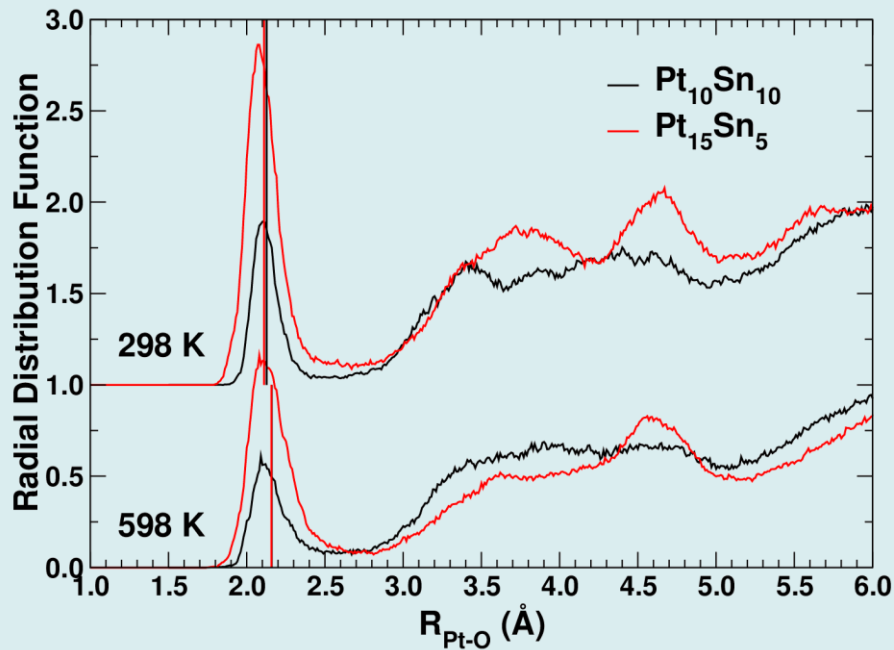
Pt-Sn shell: **Unaffected** by temperature and concentration

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

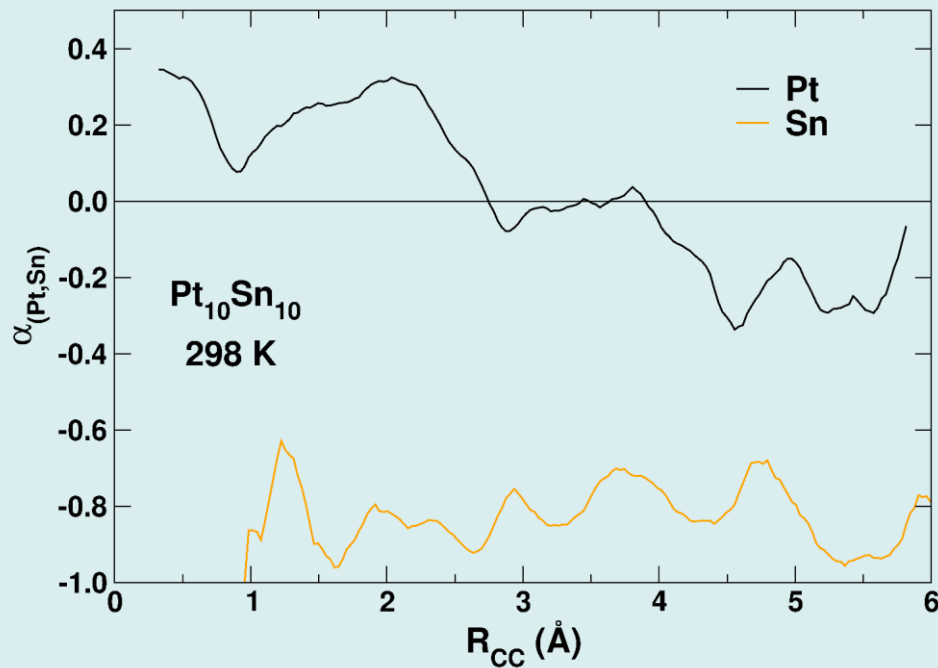
Sn-O shell: Very similar except for O uptake shoulder

Inhomogeneous Structure: Surface Segregation

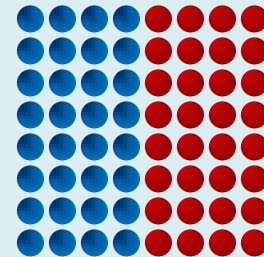
Cowley short-range order parameter

$$\alpha_A = 1 - \frac{n_{AB}}{n_{AM}x_B}$$

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

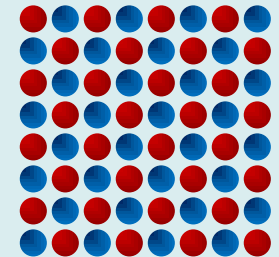


Correlated



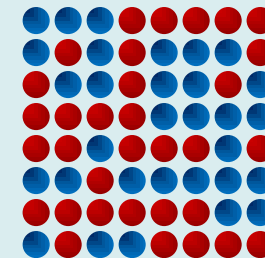
$$0 < \alpha_A \leq 1$$

Anticorrelated



$$-1 \leq \alpha_A < 0$$

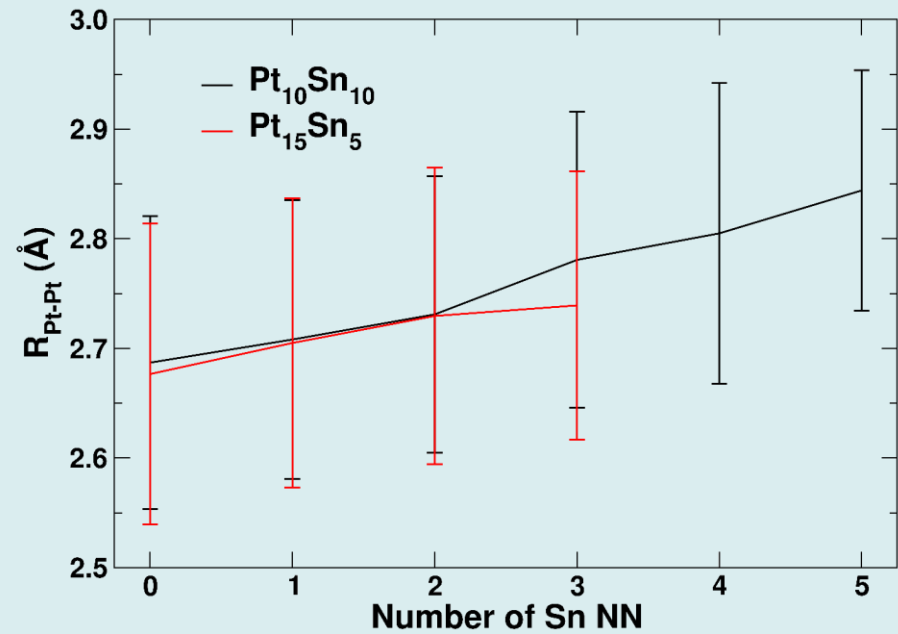
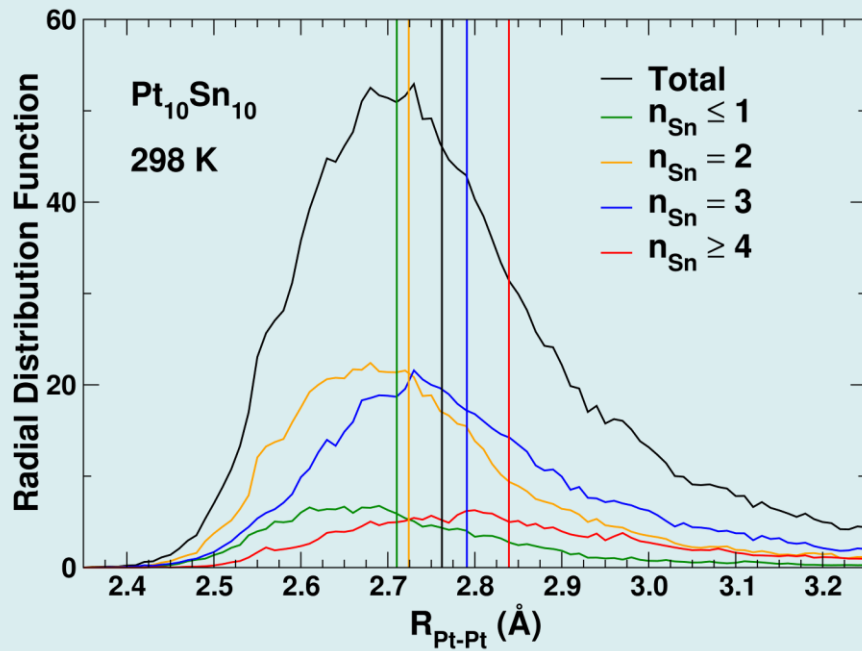
Random



$$\alpha_A \cong 0$$

- Pt – Favors Pt NN in core and Sn NN near surface
- Sn – Always favors Pt NN

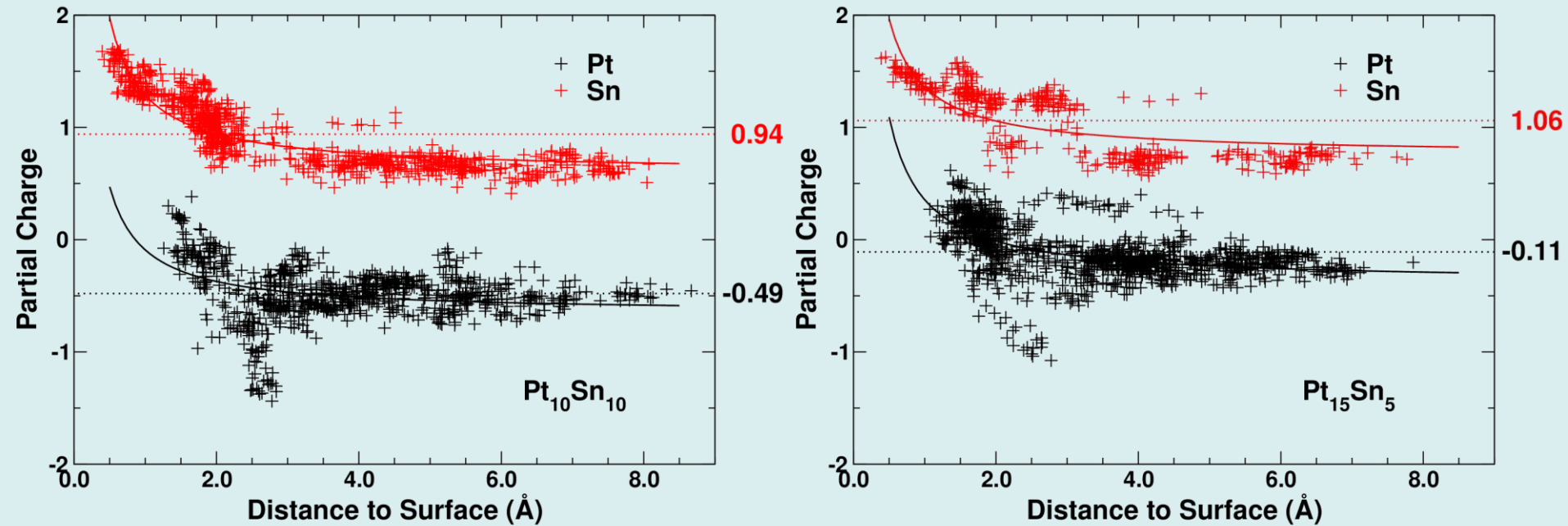
Inhomogeneous Structure: Pt-Pt Interaction



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

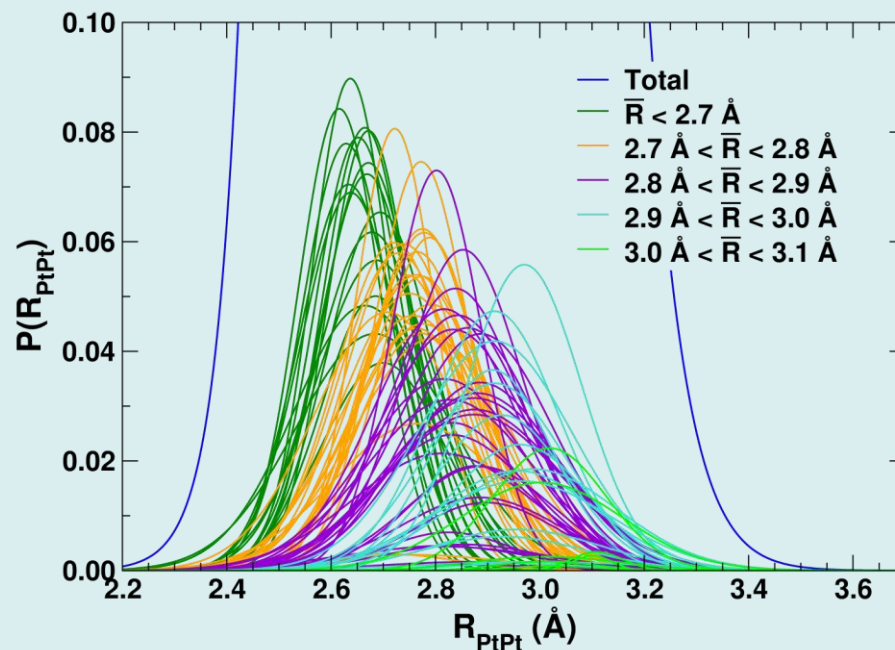
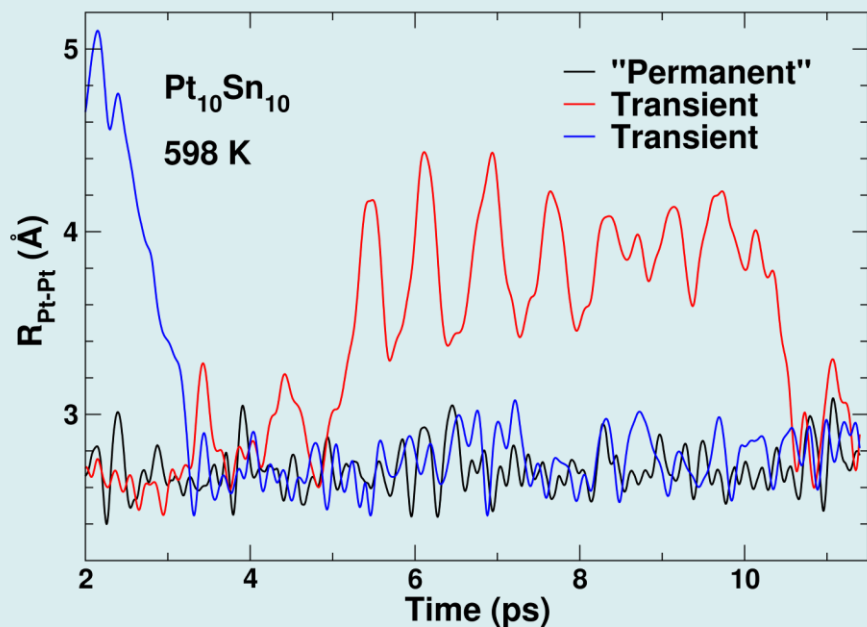
Dynamic Disorder

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

- **Experimental probes:**
 - Yield only **averaged** properties

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

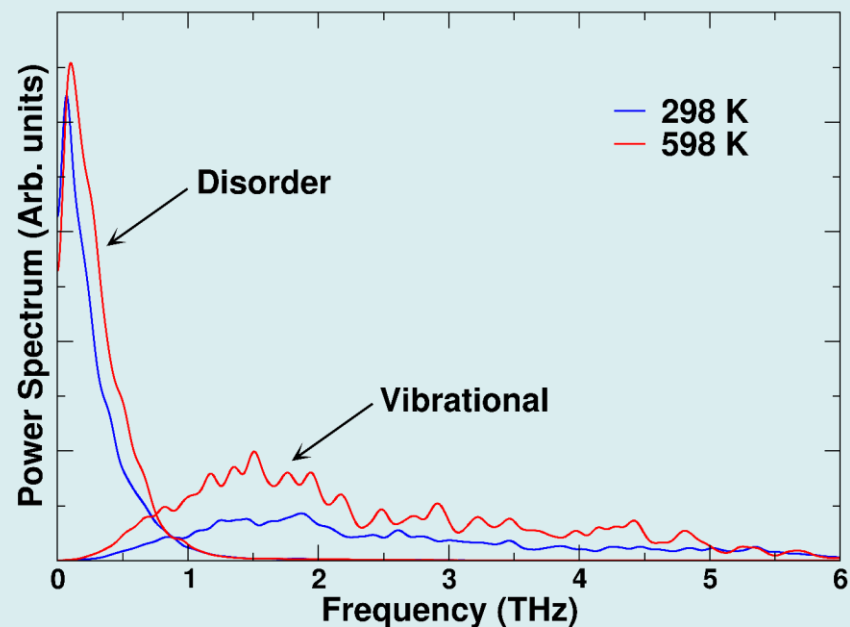
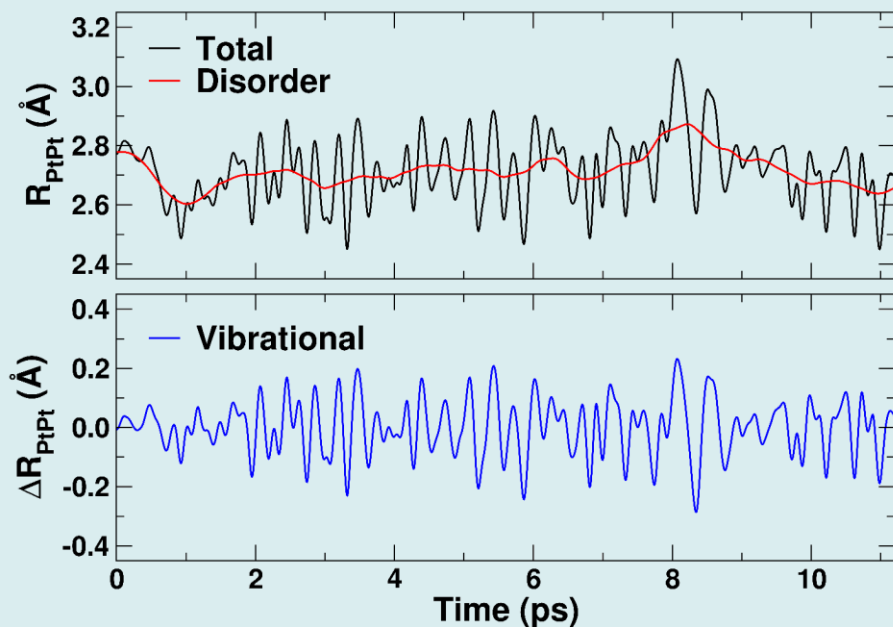
Dynamic Disorder: Fluxional Bonds



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

Complex R_{PtPt} distribution – Many **inhomogeneous** bonds

Dynamic Disorder: Anomalous Behavior

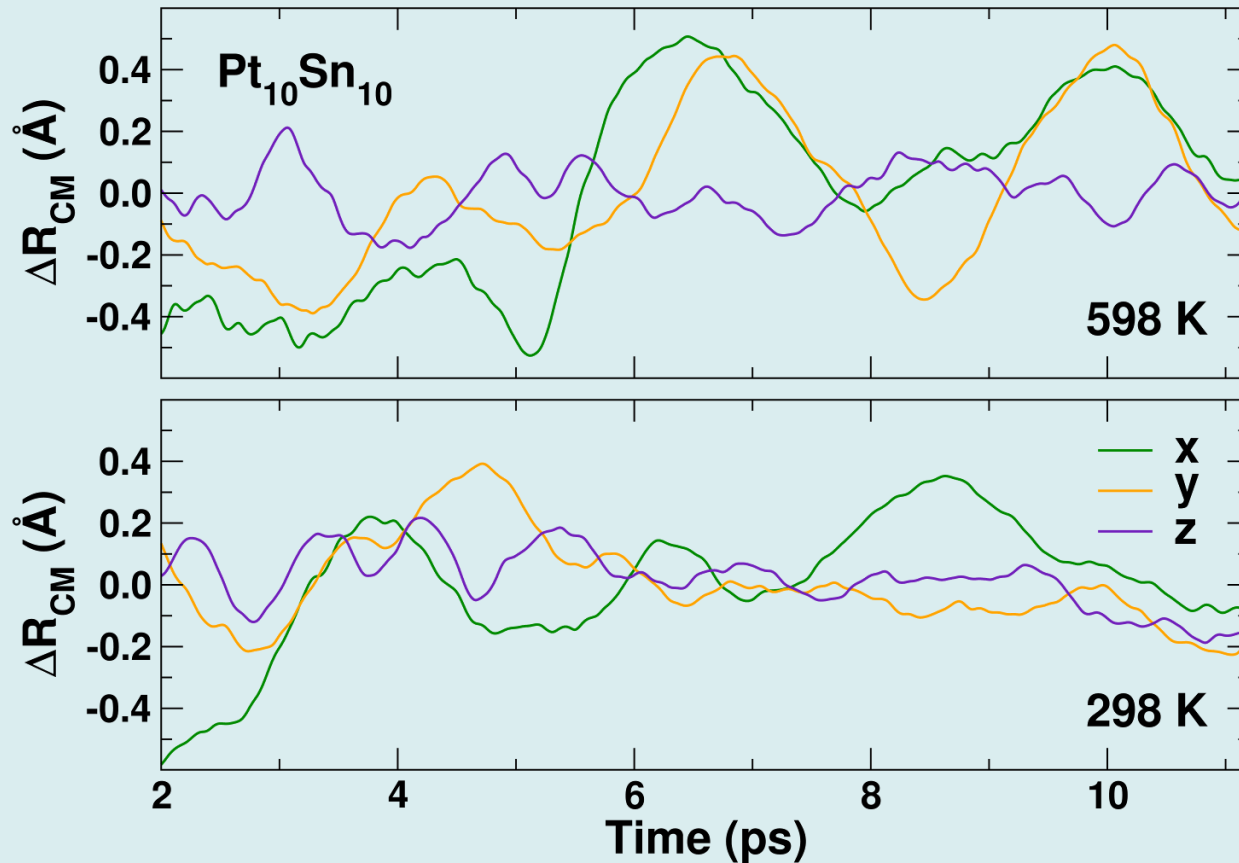


Traj. decomp. into **Vibrational** and **Disorder** components

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

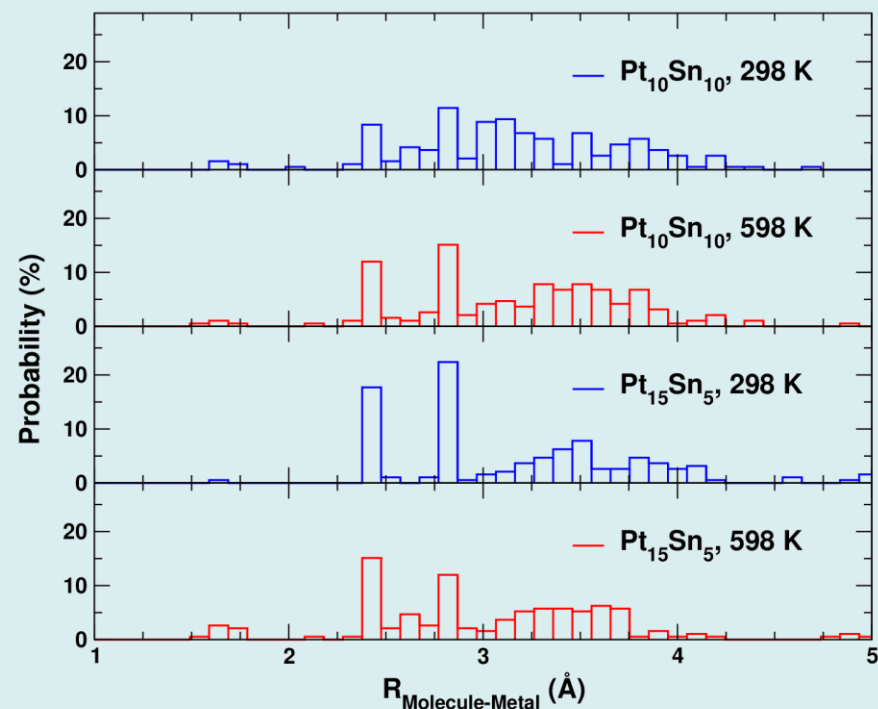
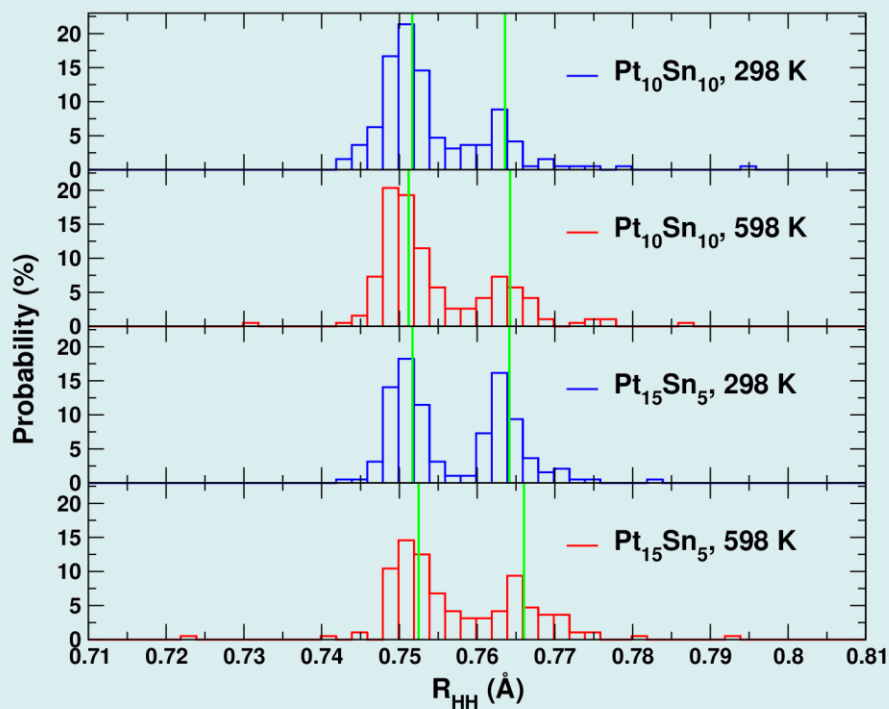
- **Sn atoms:**
 - **Modulate Pt-Pt interaction**
 - **Preferentially on cluster surface**
 - **Act as “barrier” between support and Pt**
 - **Differential charging of Pt and Sn atoms**
- **Three dynamic regimes:**
 - **Fast bond vibrations**
 - **Stochastic CM motion**
 - **Slow fluxional bonding**
- **Dynamic, anomalous disorder**
- **Need better models for DSD in XAFS?**

Adsorbates and Reactivity on PtSn Alloy Clusters on $\gamma\text{-Al}_2\text{O}_3$

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

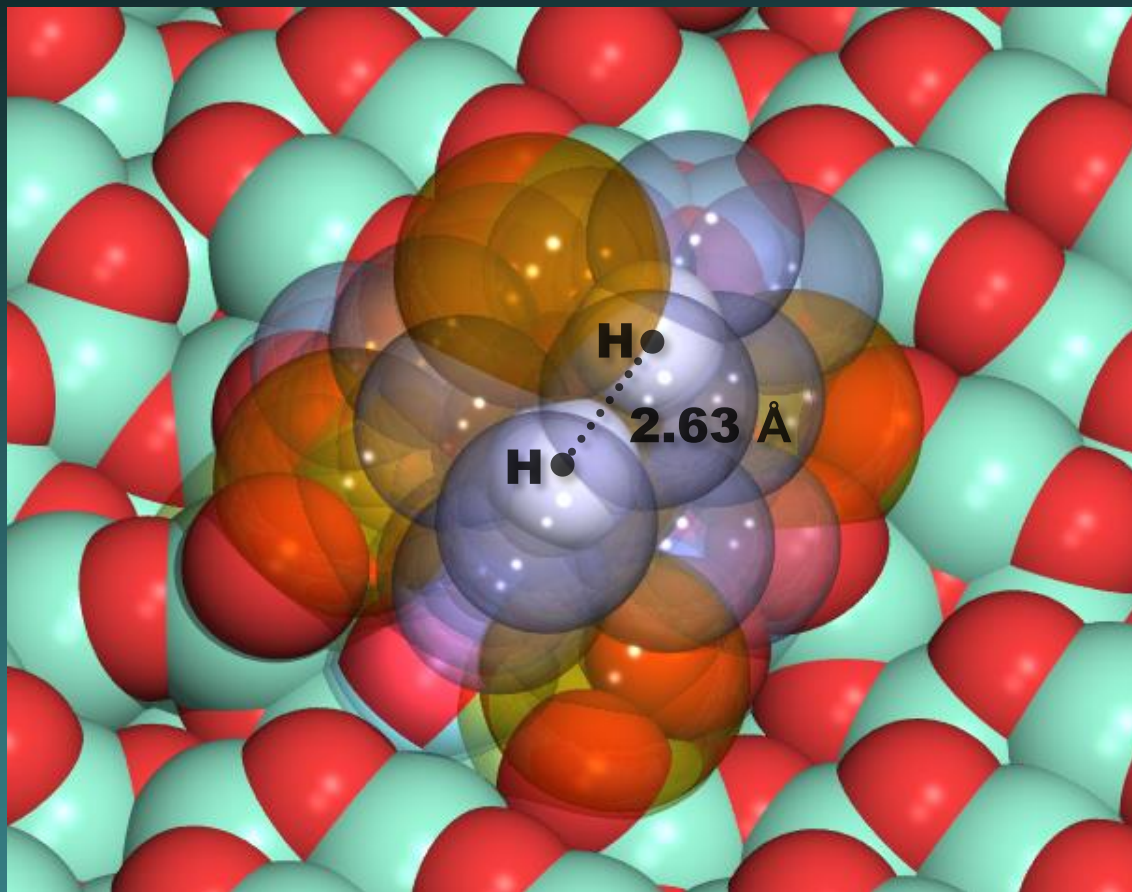
Reactivity: $R_{\text{H-H}}$ and $R_{\text{Molecule-Metal}}$ Distribution



Two H_2 interactions: Weak and strong

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

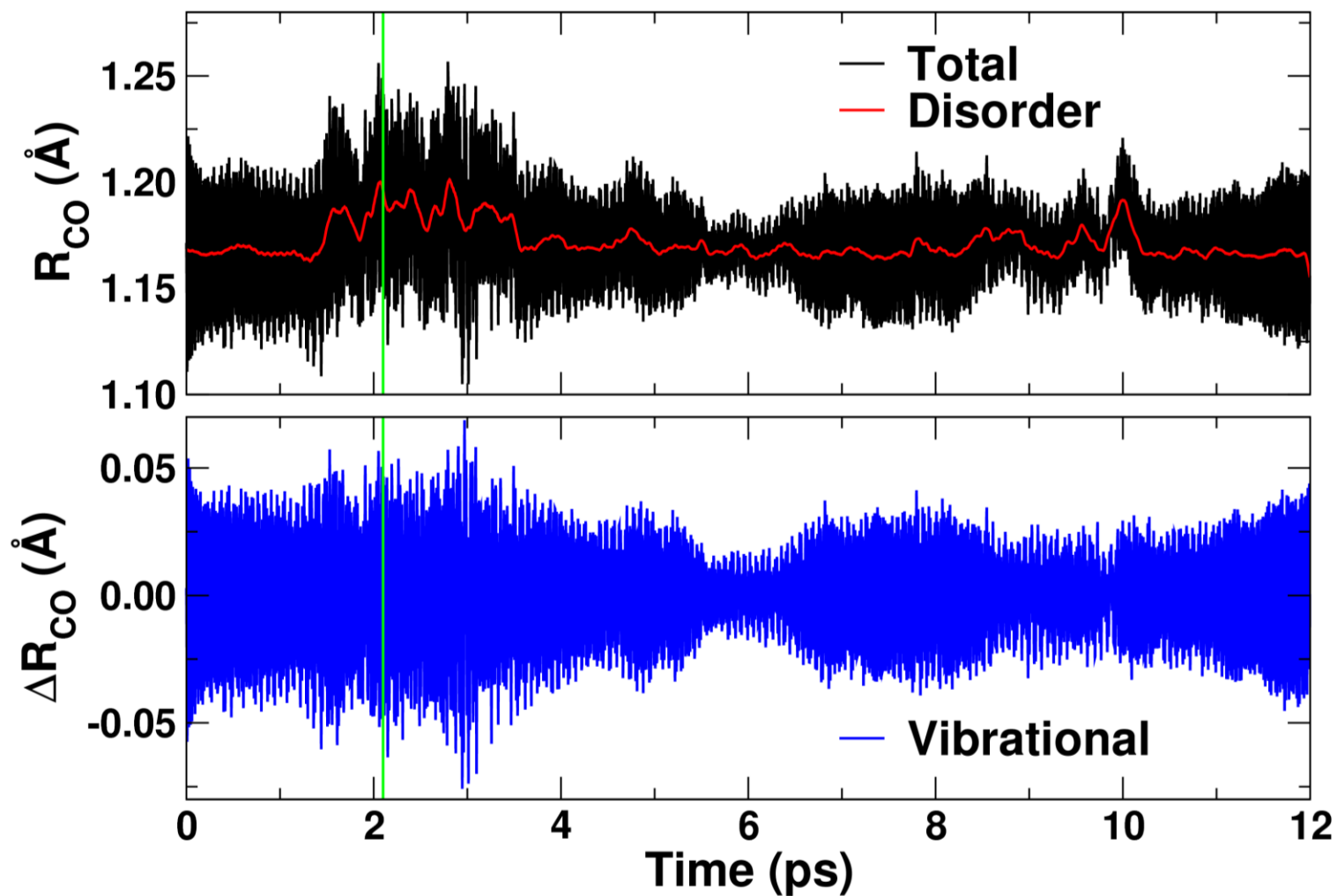
Reactivity: H₂ Dissociation Probability



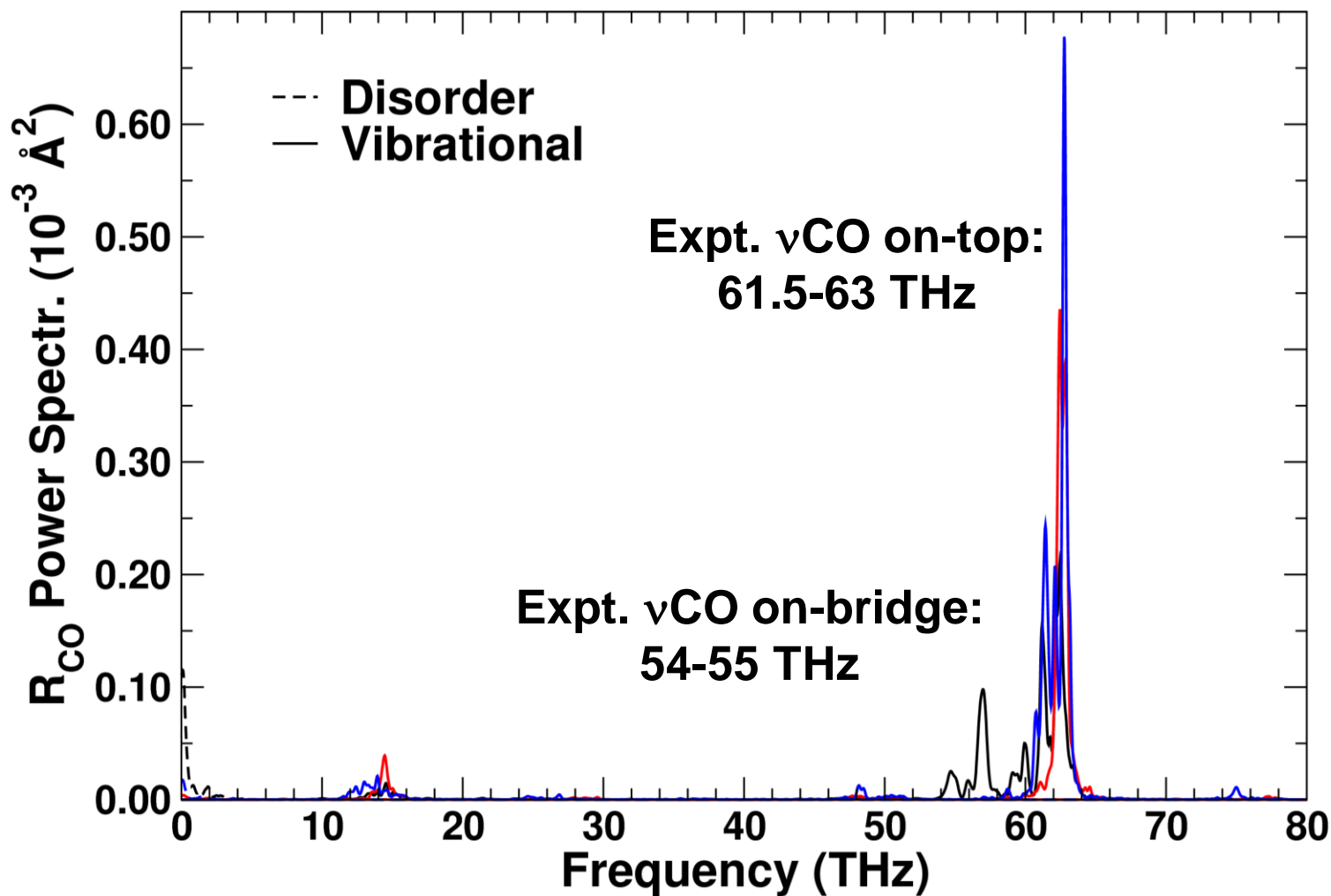
On Pt₁₀Sn₁₀: Low probability (<1%) at both 298 and 573K

On Pt₁₅Sn₅: 5% at 298K and 10% at 598K

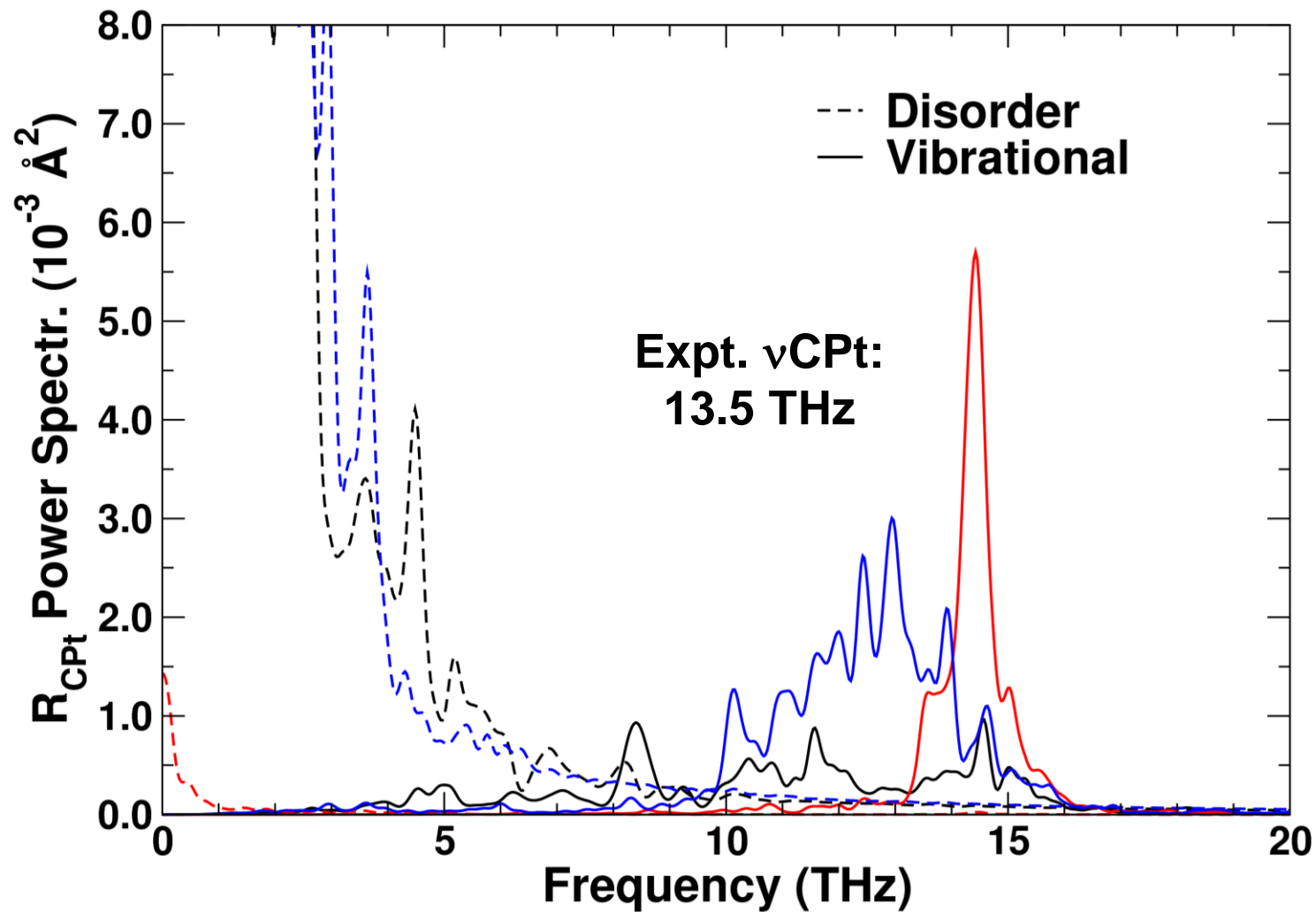
Adsorbate Dynamics: CO Internal Motion



Adsorbate Dynamics: CO Internal Motion



Adsorbate Dynamics: CO Surface Motion



Summary

- **STS reveals:**
 - Different cluster-H₂ interaction types
 - Preferential H₂ 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 *sampling* details”

Estructura dinámica en nanopartículas de Pt y Pt-Sn

F. Vila, Montevideo, Uruguay, 26 de Agosto, 2013

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