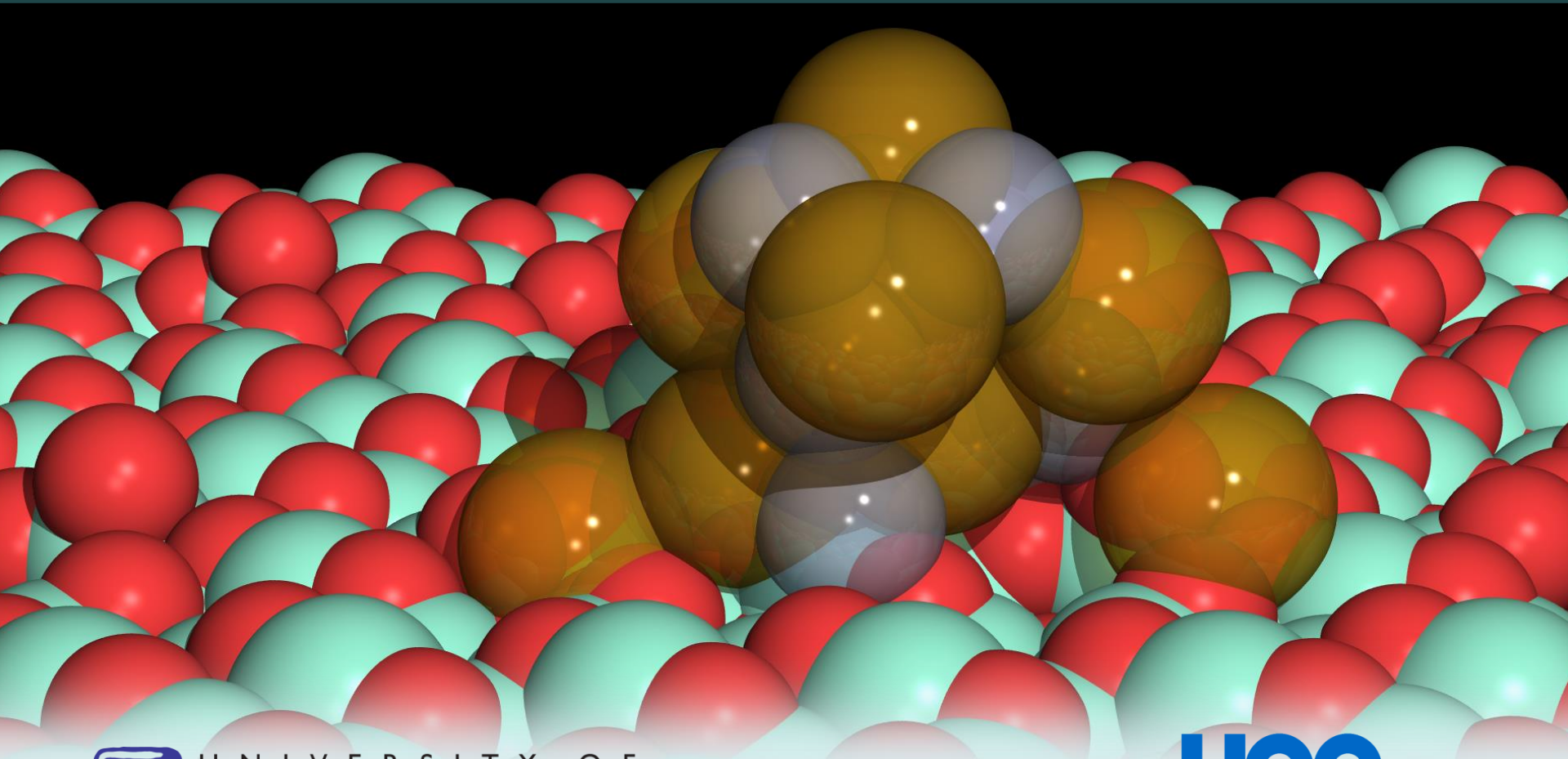
Thermal and composition effects on the structure, dynamics, and reactivity of PtSn bimetallic nanoparticles on γ-Al_2O_3

F. Vila, J. J. Rehr, S. D. Kelly and S. R. Bare



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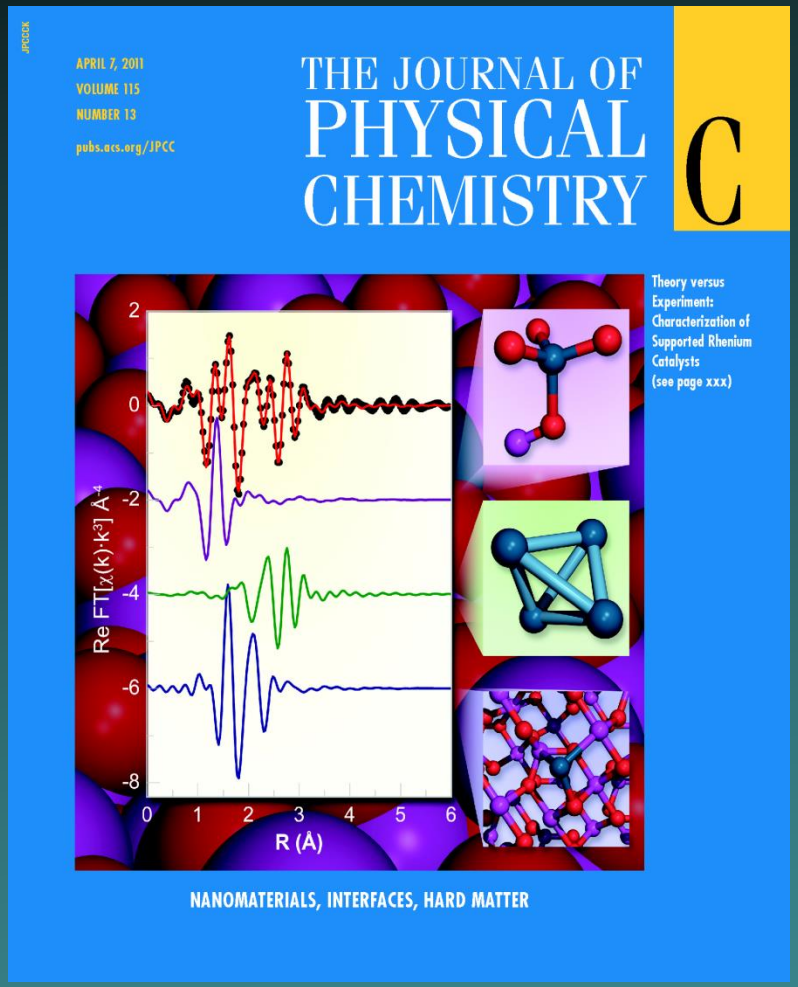
Motivation

- 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

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

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

Previous Work

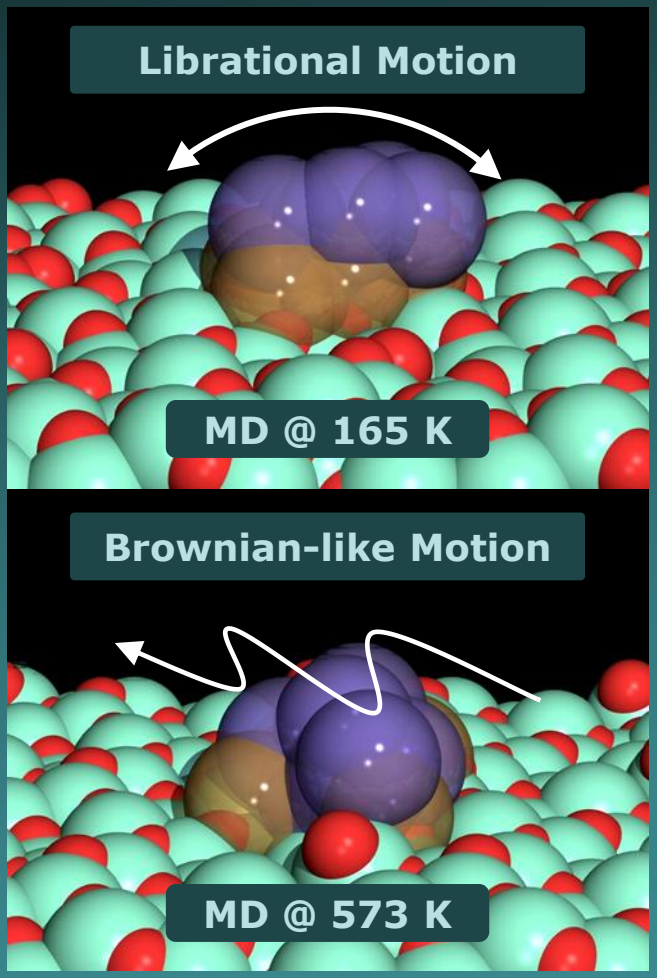
Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

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

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

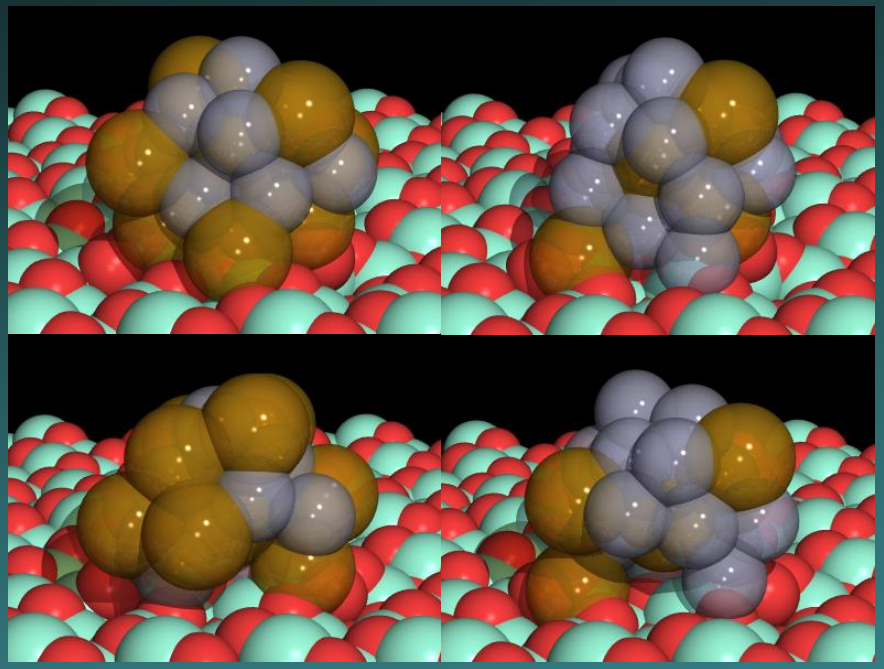
Complex dynamics on multiple-time scales including librational motion of the center of mass and fluctuating bonding.

Simulations explain unusual phenomena including large structural disorder and Negative Thermal Expansion (NTE).



Pt_{10} on γAl_2O_3

DFT/MD and XANES Computational Details



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

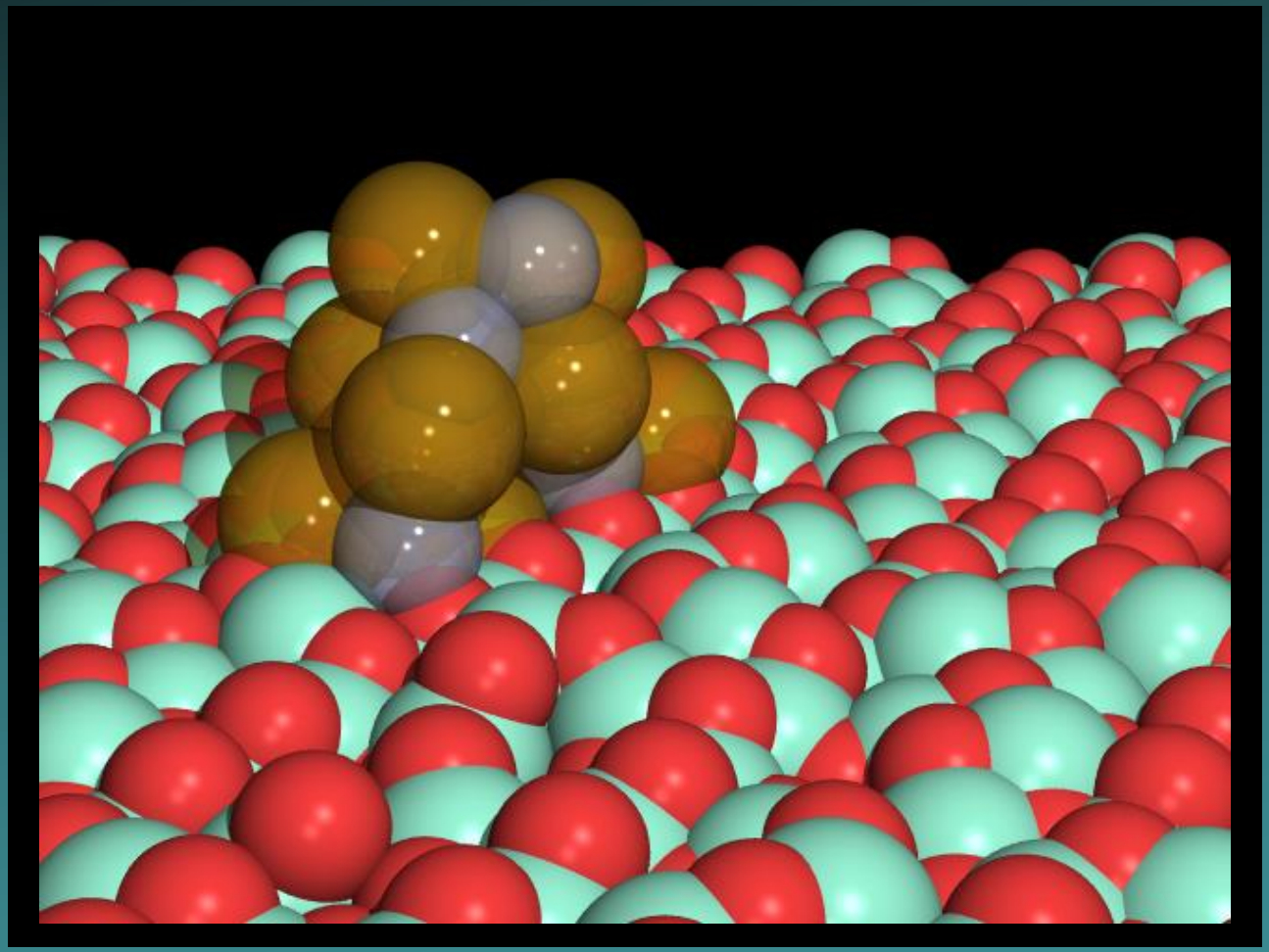
XANES

FEFF9
Full Multiple Scattering
15 MD Samples
7Å Clusters (~150 atoms)

Dynamical Properties: Molecular Dynamics

Sn

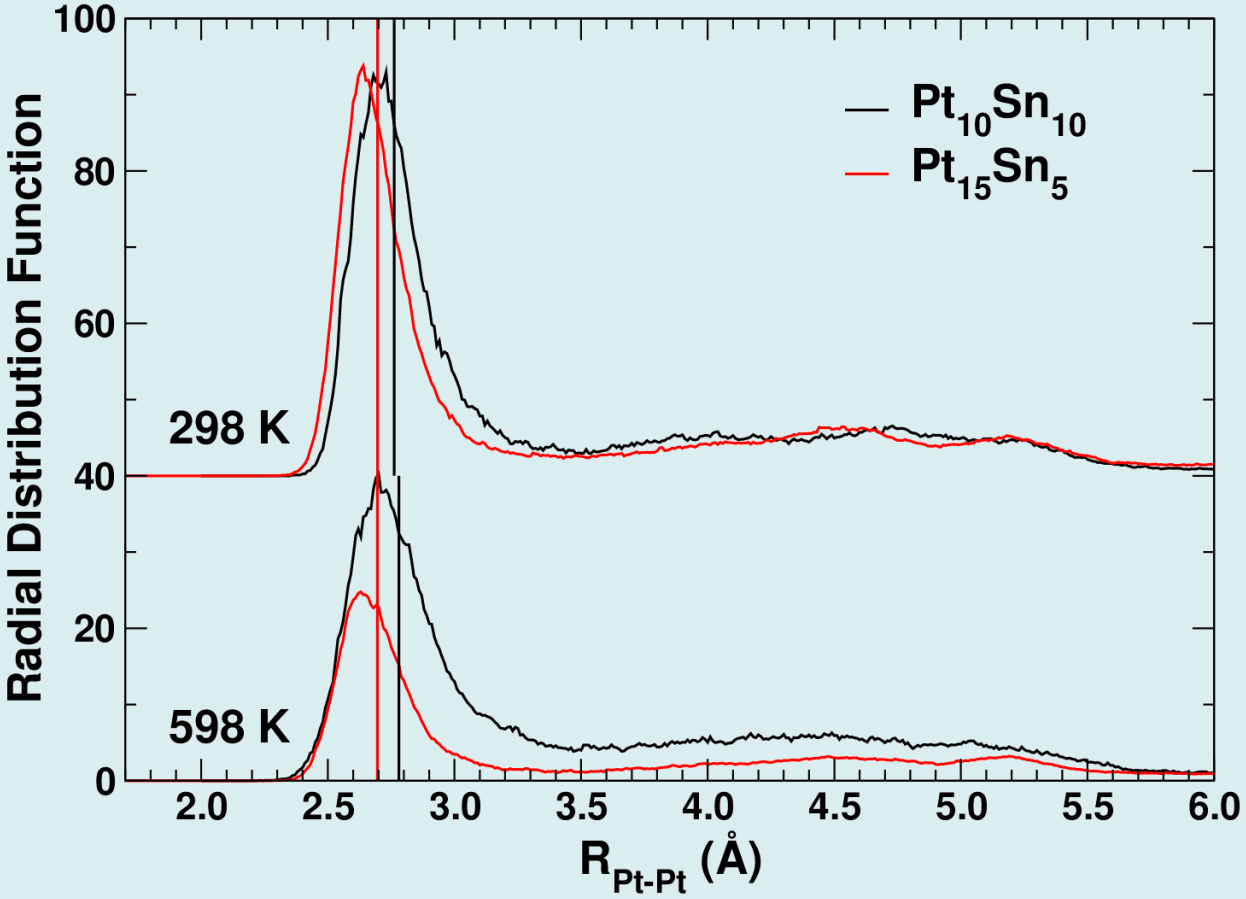
Pt



O

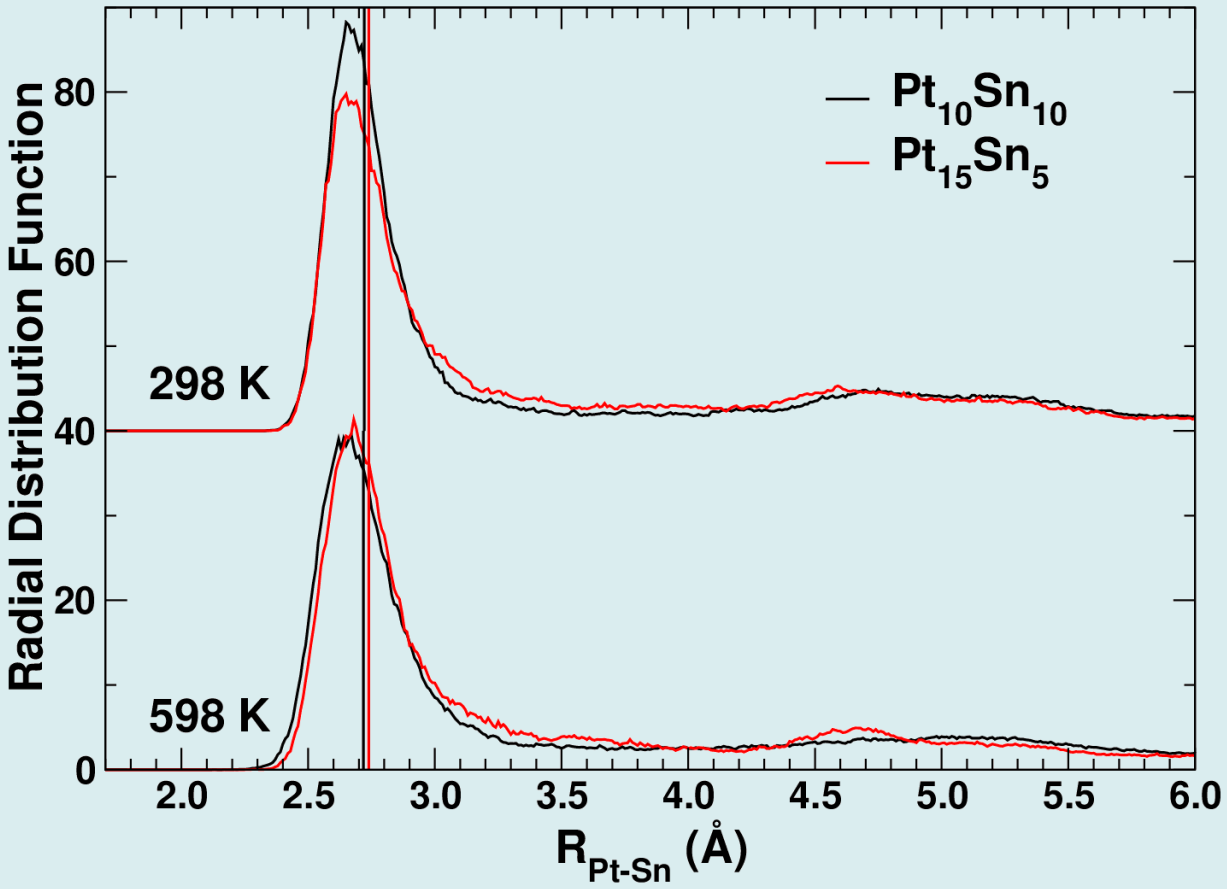
Al

Cluster Internal Structure: Pt-Pt



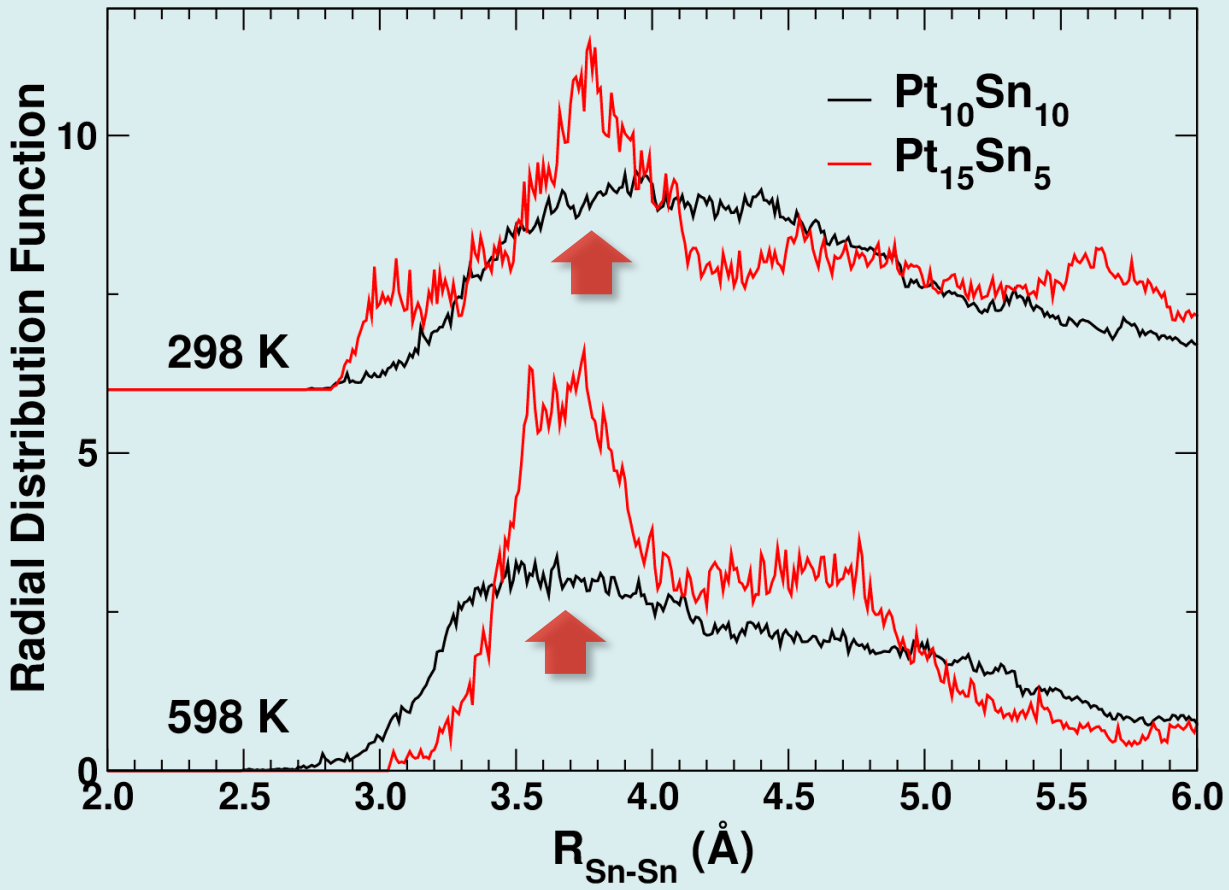
Shorter R_{Pt-Pt} and NTE trend at higher Pt concentration

Cluster Internal Structure: Pt-Sn



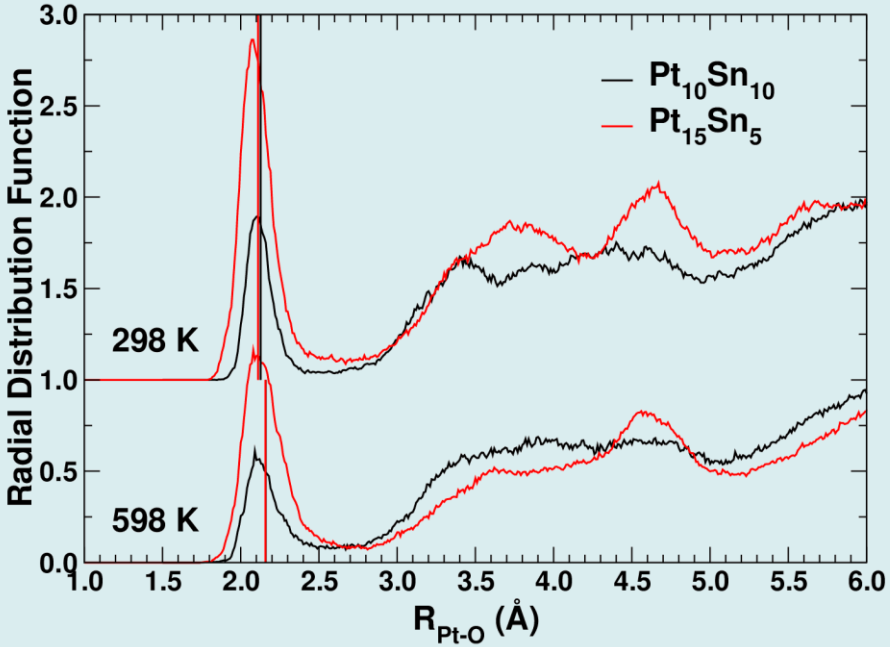
Pt-Sn shell: Unaffected by temperature and concentration

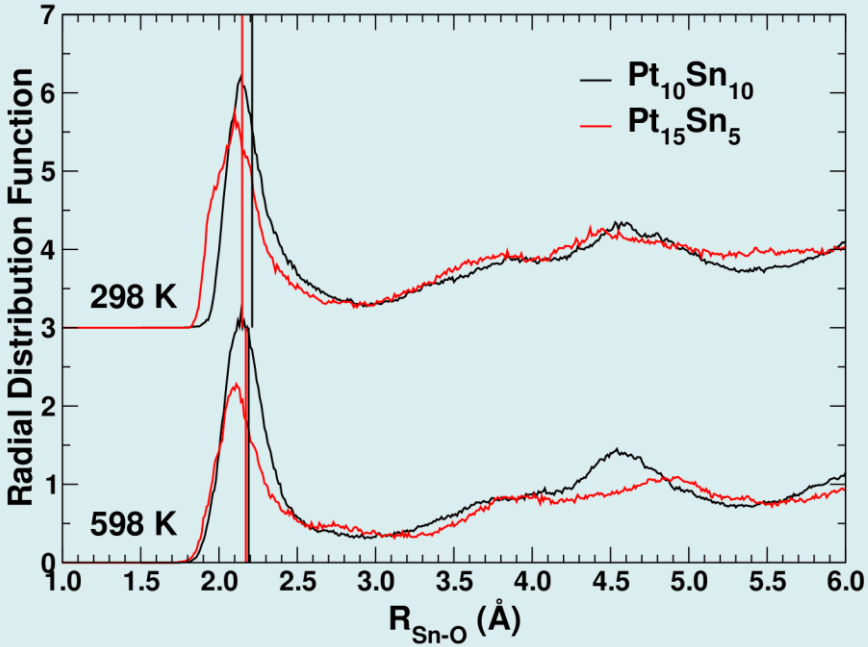
Cluster Internal Structure: Sn-Sn



Sn-Sn shell: Structure develops at high Pt concentration

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

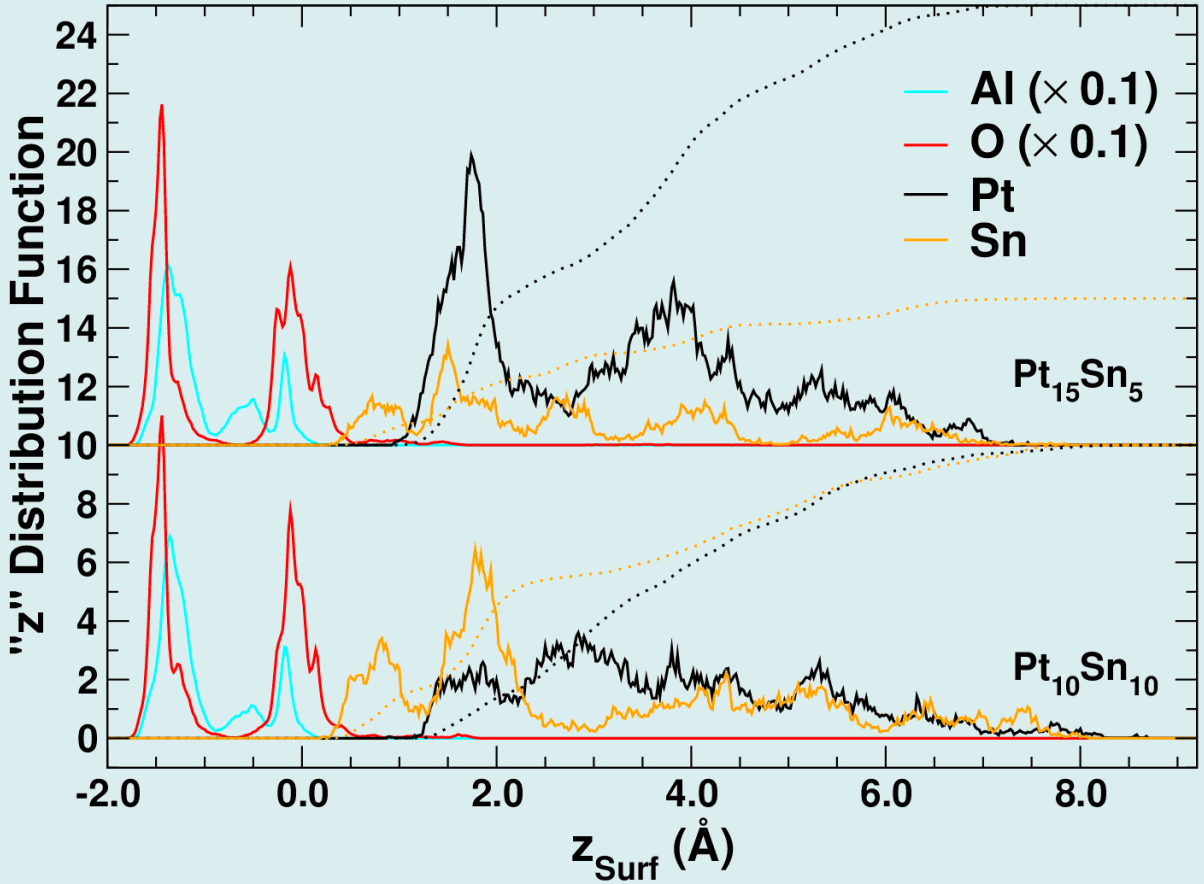




Pt-O shell: More O per Pt in Sn-poor clusters

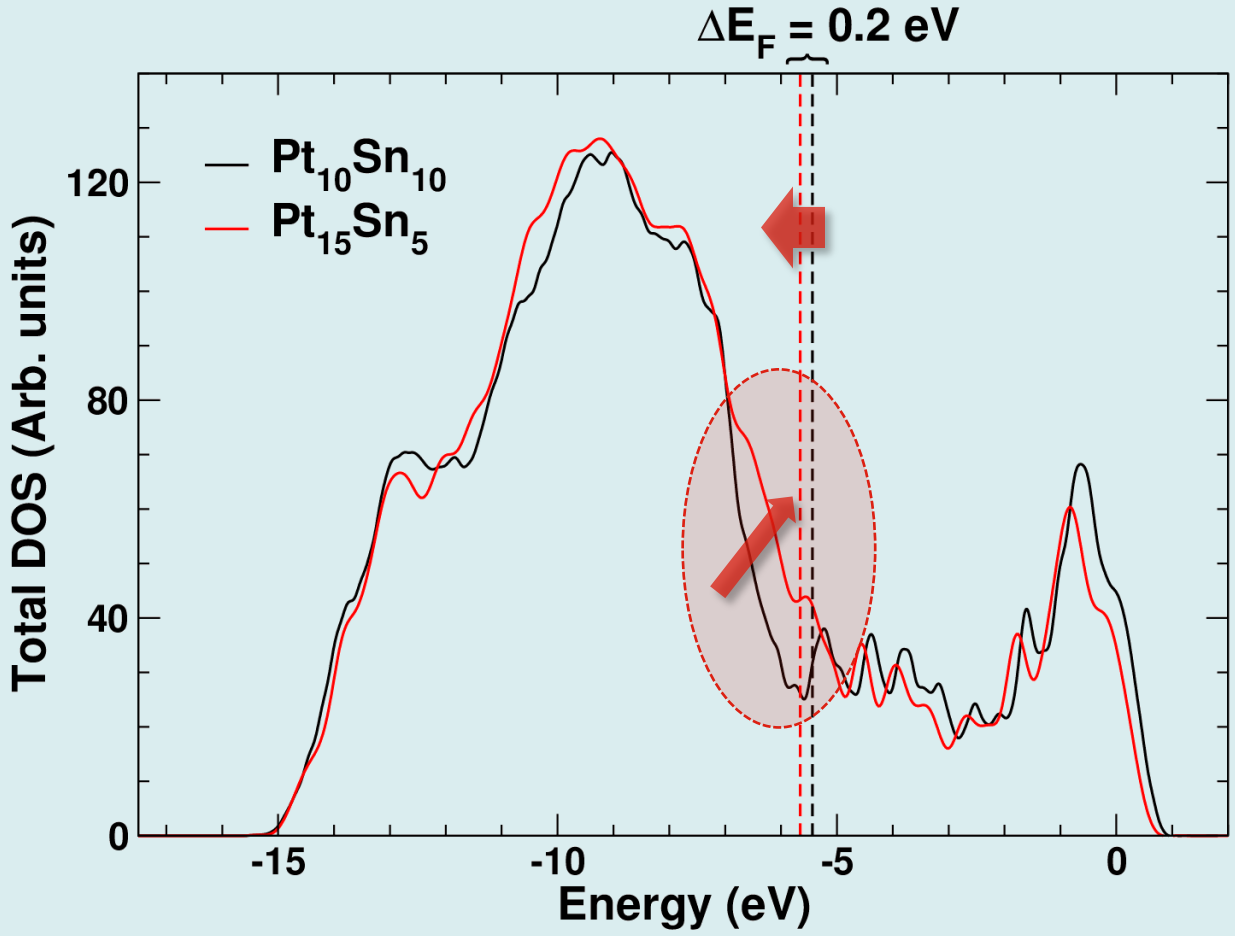
Sn-O shell: Very similar except for O uptake shoulder

Cluster-Surface Interaction: zDF



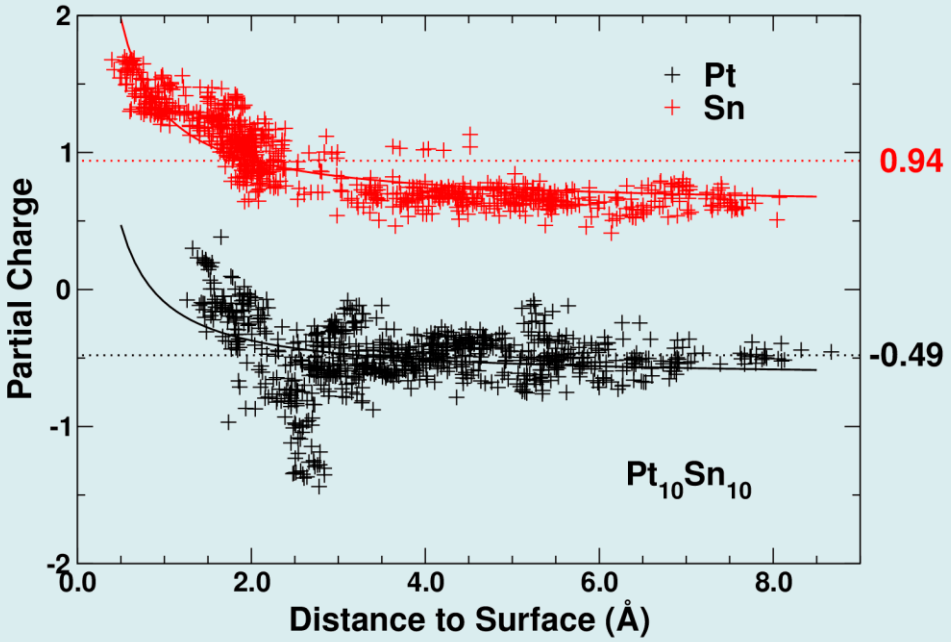
Surface-cluster interaction: Sn changes interface from Pt-rich to Pt-poor

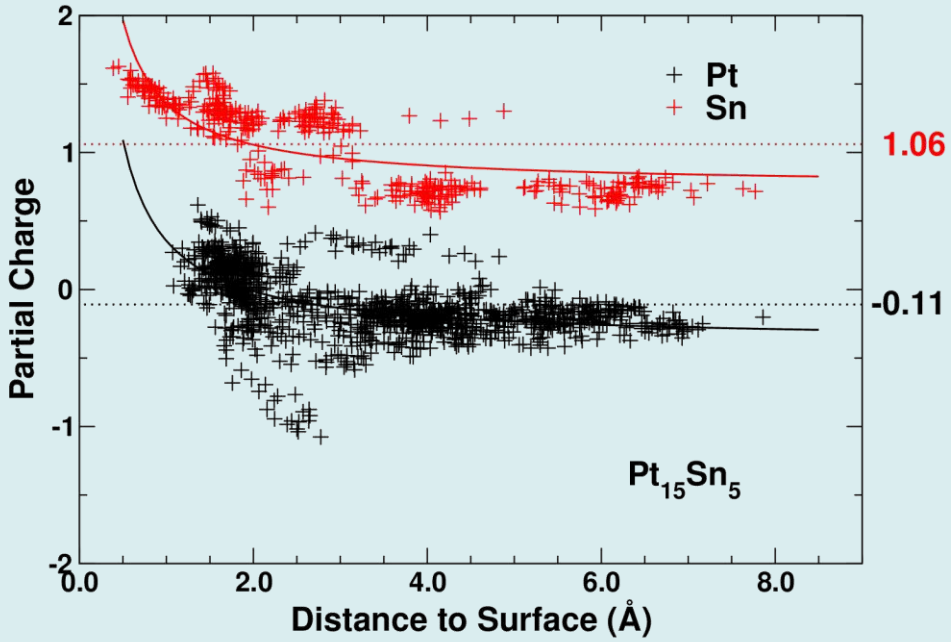
Electronic Properties: Total DOS



Small E_{Fermi} shift, change in DOS largest at E_{Fermi}

Electronic Properties: Net Atomic Charge



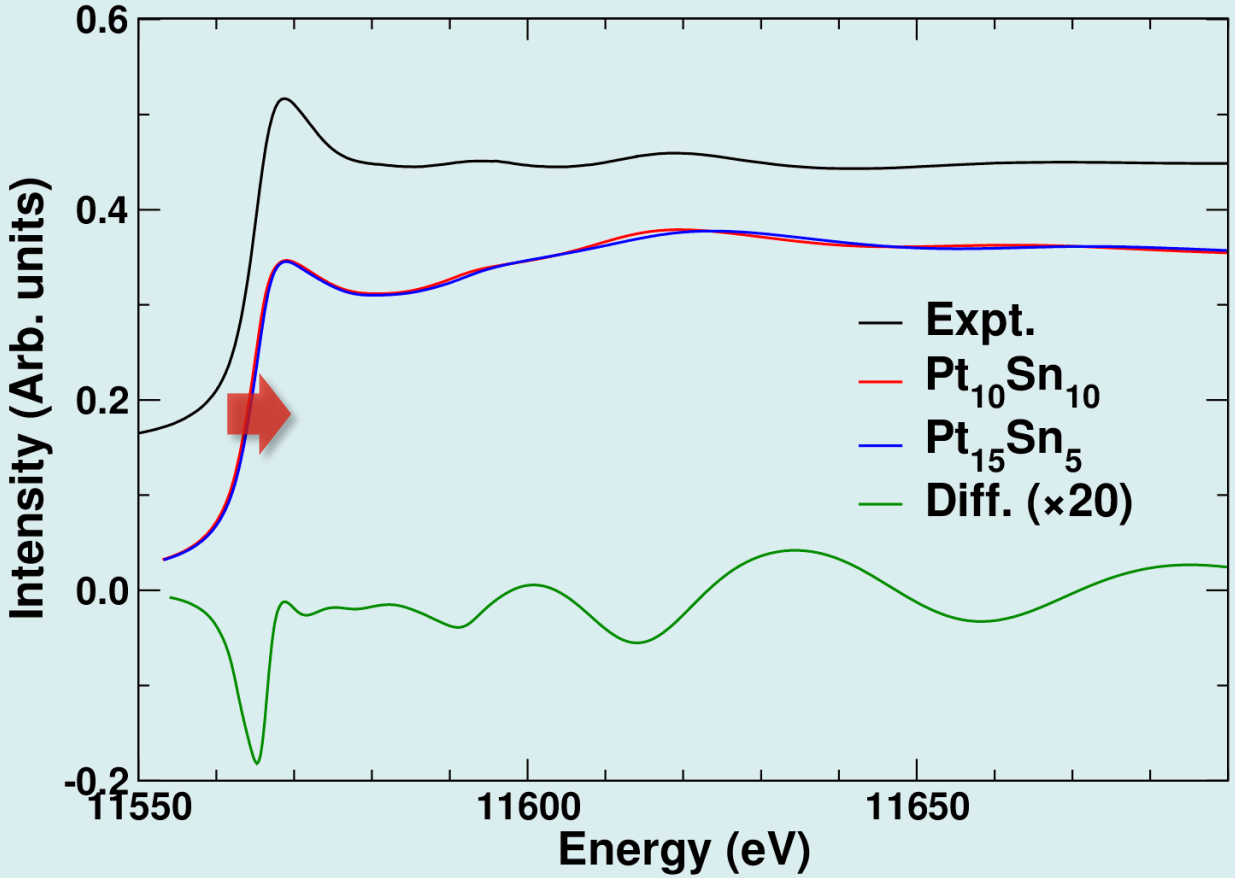


Near surface: Both species more positive

Far from surface: Clusters nearly neutral

Pt mean net charge: Controlled by Sn

Electronic Properties: Pt L3 XANES (298 K)



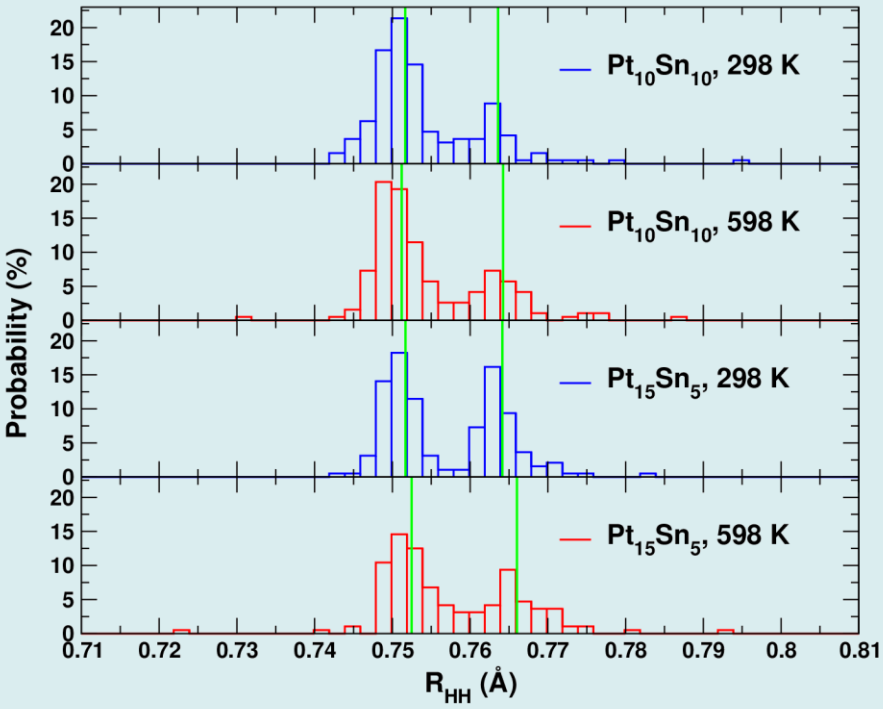
Edge shift: ~ to E_{Fermi} shift

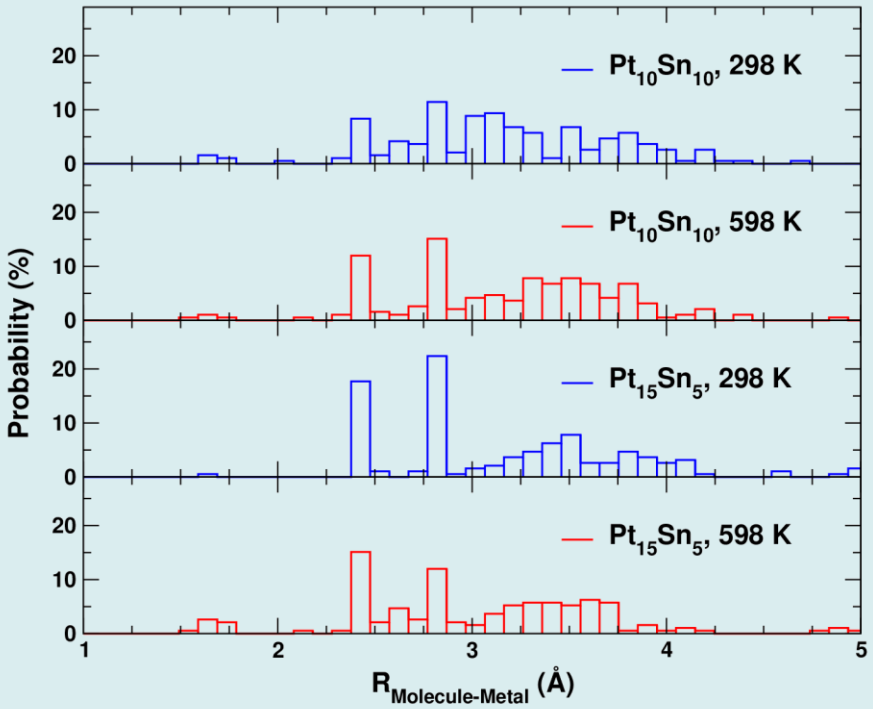
Phase shift in EXAFS: $R_{Pt\text{-}Pt}$ change

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

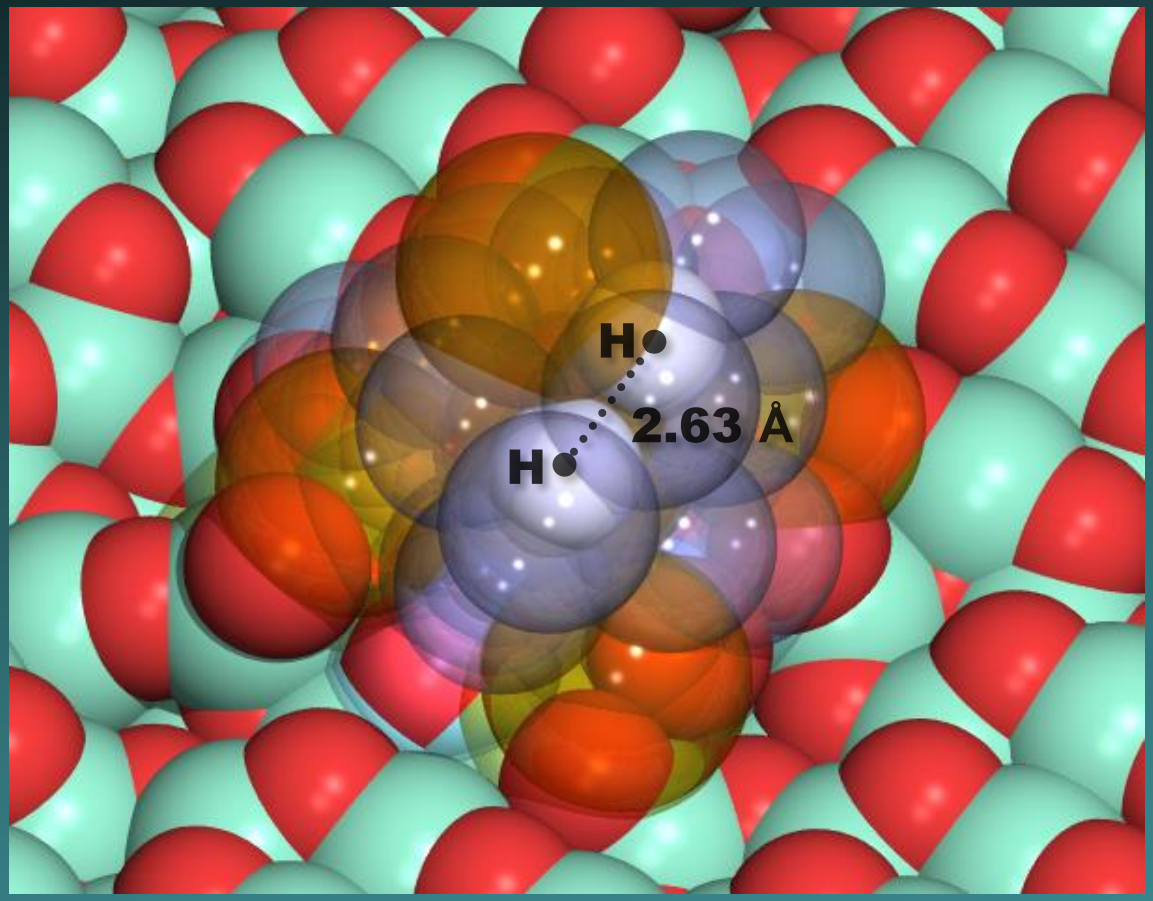




Two H_2 interactions: Weak and strong

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

Conclusions

- Operando DFT/MD provides a wealth of structural and dynamical information
- Sn atoms:
  - Modulate Pt-Pt interaction
  - Preferentially on surface layer
  - Act as "barrier" between surface and Pt
  - Differential charging of Pt and Sn atoms
- STS reveals:
  - Different cluster-H_2 interaction types
  - Preferential H_2 dissociation on Pt-rich clusters

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F. Vila, J. J. Rehr, S. D. Kelly and S. R. Bare

Supported by:

NSF Grant PHY-0835543

UOP LLC, a Honeywell Company

With computer support from NERSC

Thank you…

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