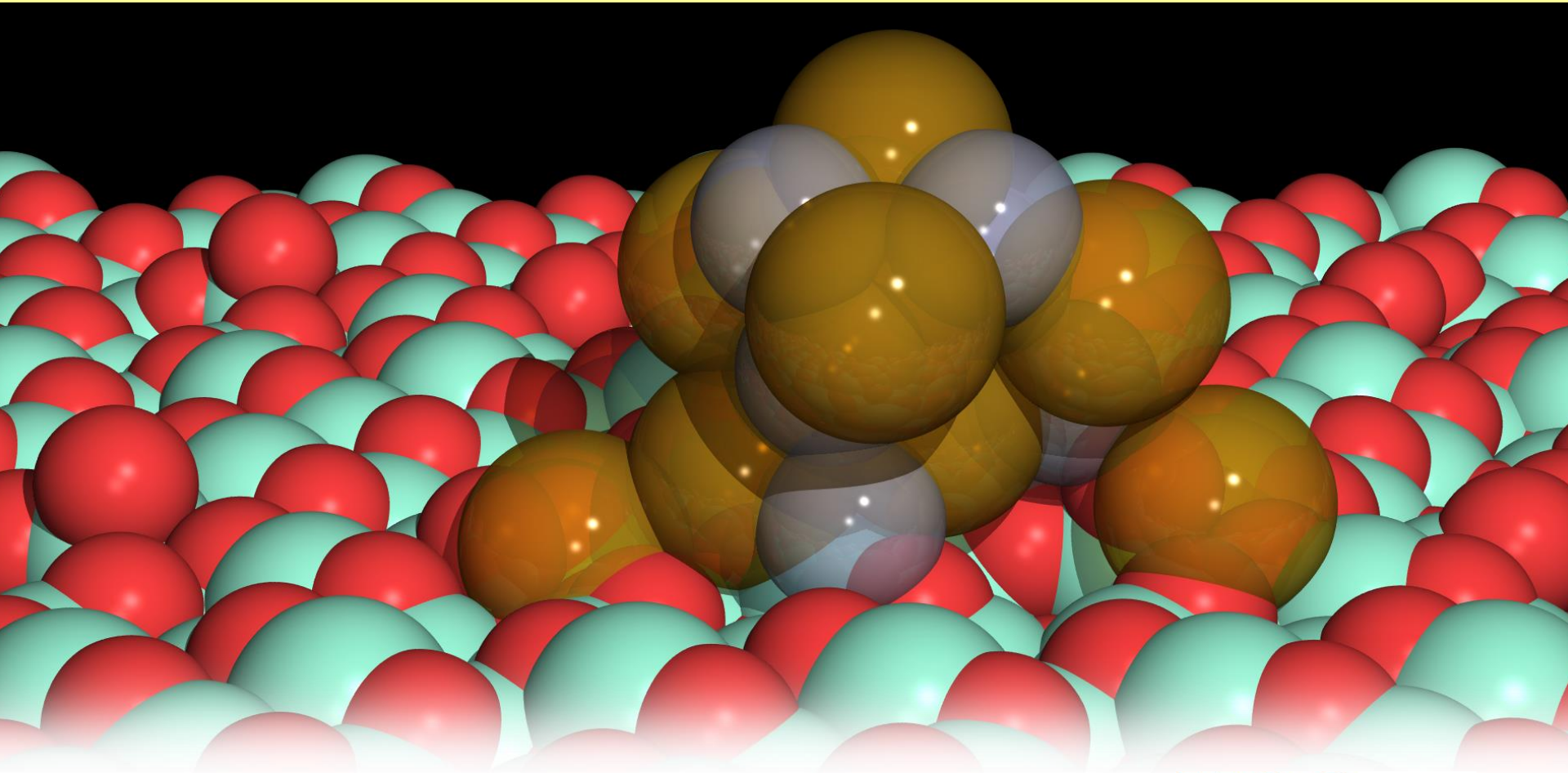
Structure and Dynamics of $PtSn/\gamma Al_2O_3$

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



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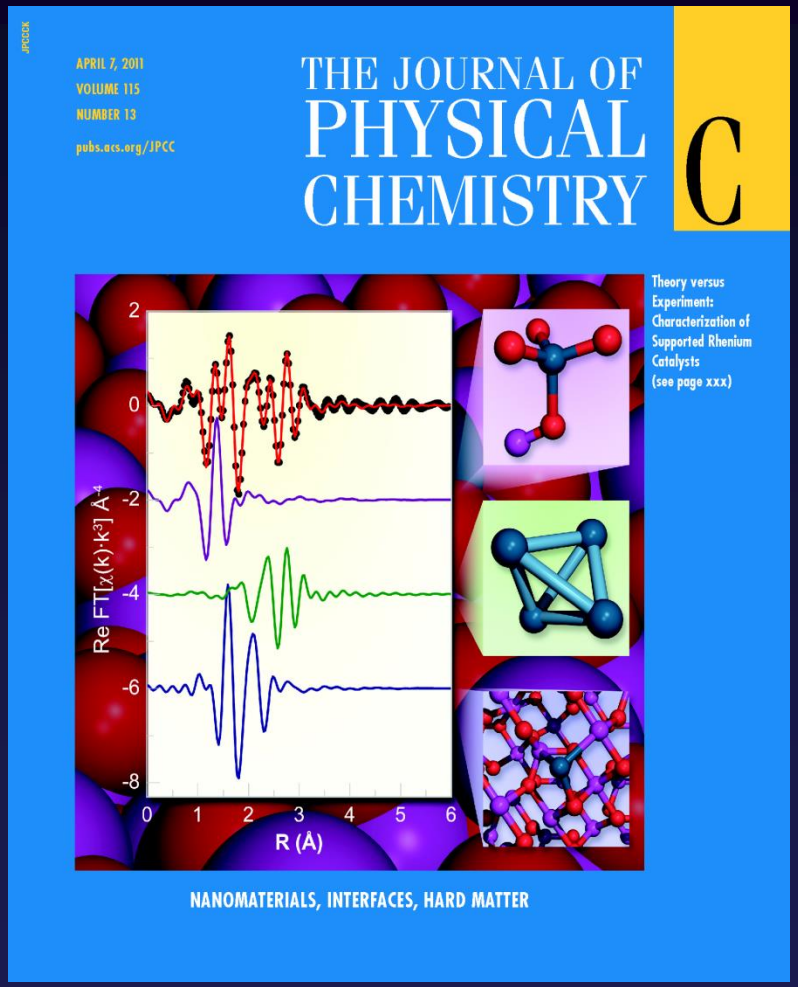
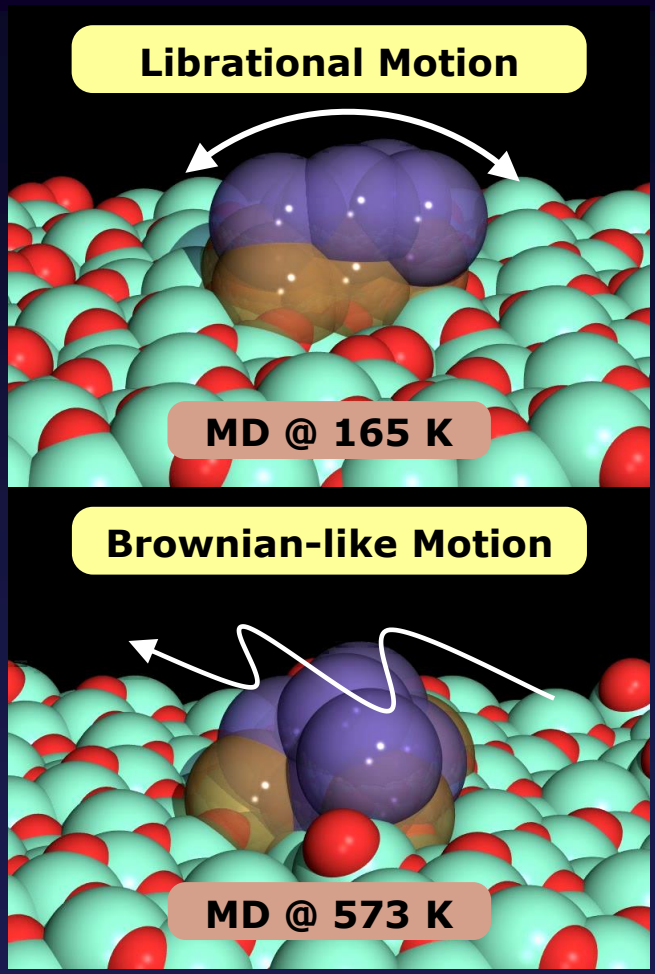
Motivation

- **Alumina-supported Pt-based catalysts:**
  - **Used for the reforming of light petroleum distillate**
  - **Modifiers (Sn, Re and Ir) have profound effect on catalyst stability, substantially reduce carbon deposition**
- **Knowledge of structure and dynamics: will contribute to understanding and improvement of catalytic activity**

Study dynamical and structural properties of $Pt_{10}Sn_{10}$ cluster on [110] surface of γ-Al_2O_3

Previous Work

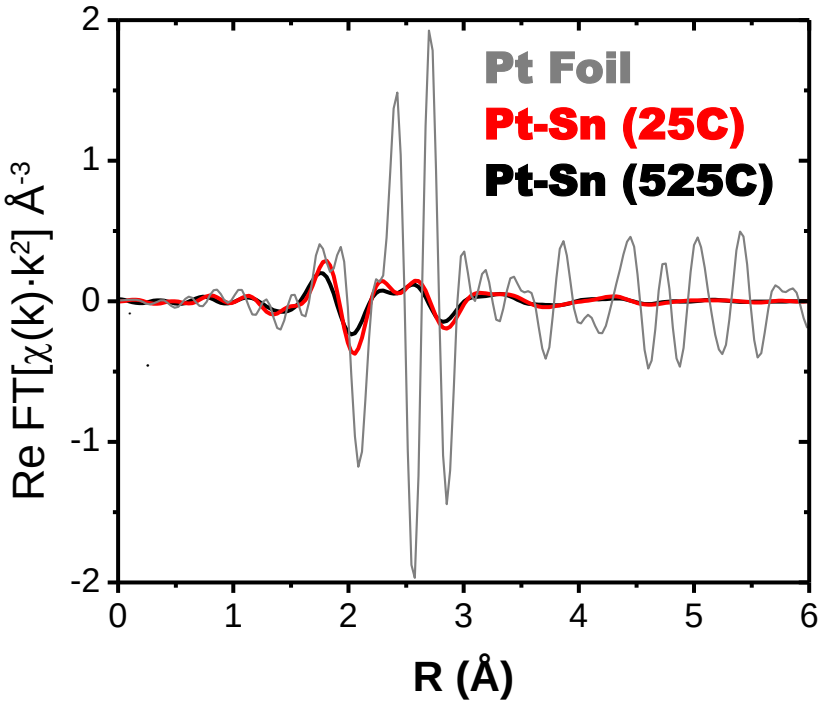


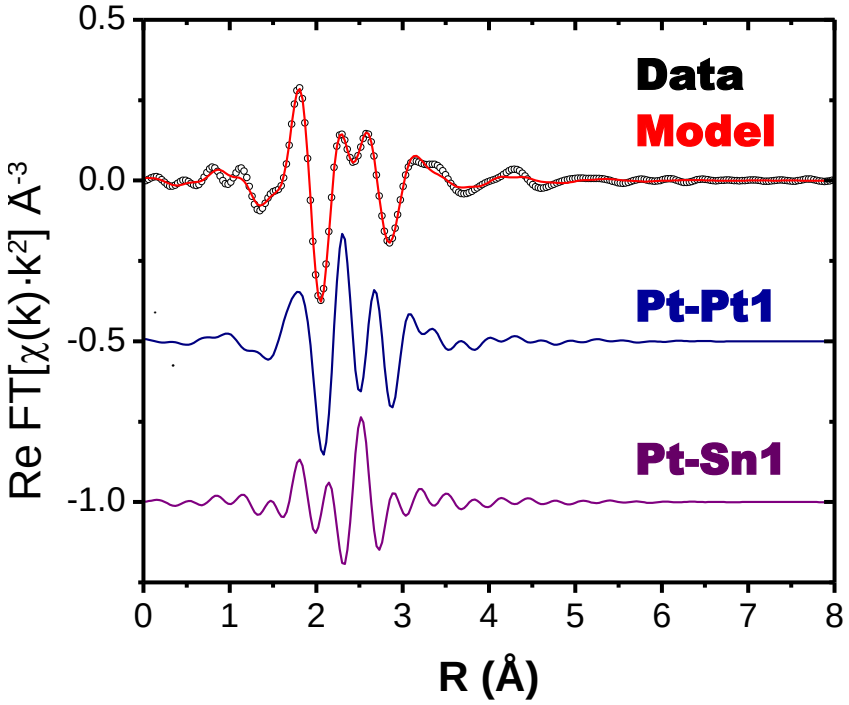


Re on γAl_2O_3

Pt_{10} on γAl_2O_3

Pt L_3 EXAFS on PtSn





Pt-Foil *vs* PtSn Signal

Smaller for clusters (smaller size)

Different between 2 and 3 Å due to Pt-Pt and Pt-Sn overlap

PtSn Clusters Modeling

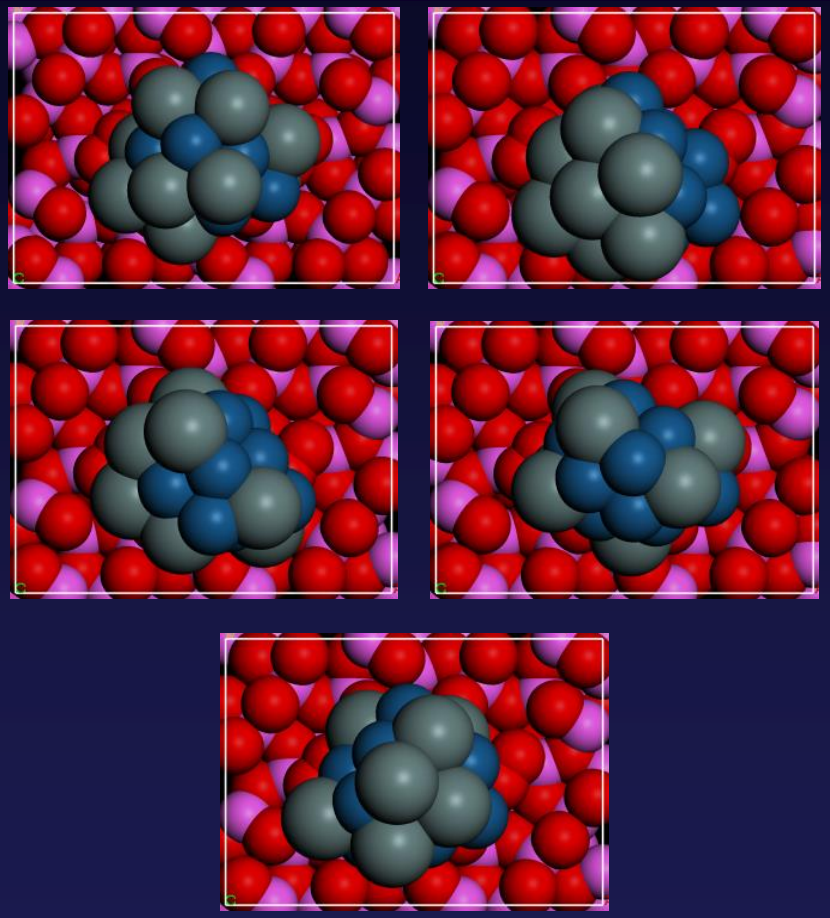
Clusters **~1.5 nm** in diameter

Composition **~10% Sn**

Contracted relative to bulk

Small C_3 (**asymmetric** Pt **bonds**)

DFT/MD and XANES Computational Details



Initial structures generated from randomly Sn-substituted Pt_{20} cluster

DFT/MD

VASP
PBE Functional
396 eV Cutoff
3 fs Steps
3 ps Equilibration
9 ps Runs (2)
298 K

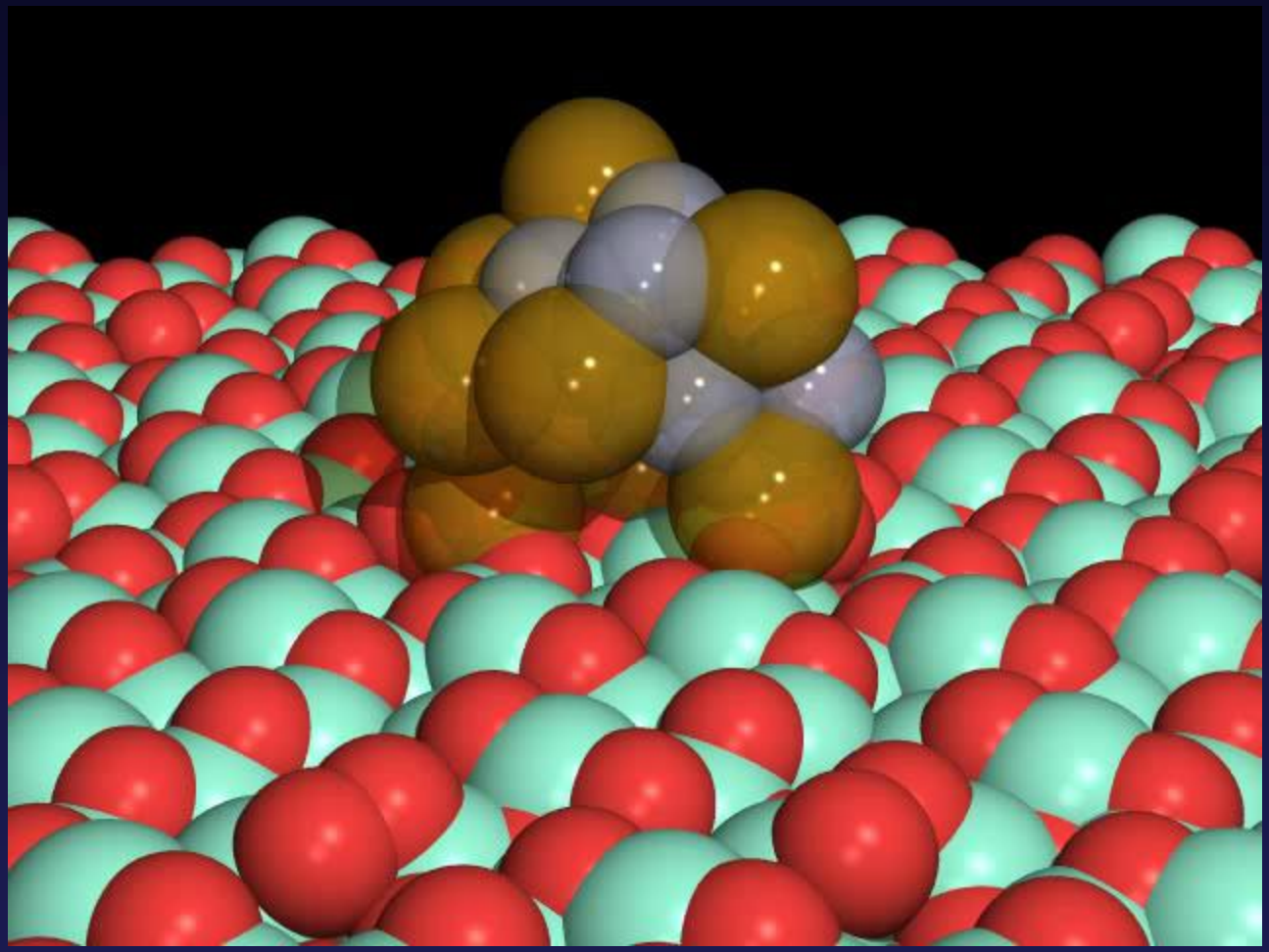
XANES

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

Dynamical Properties

Sn

Pt

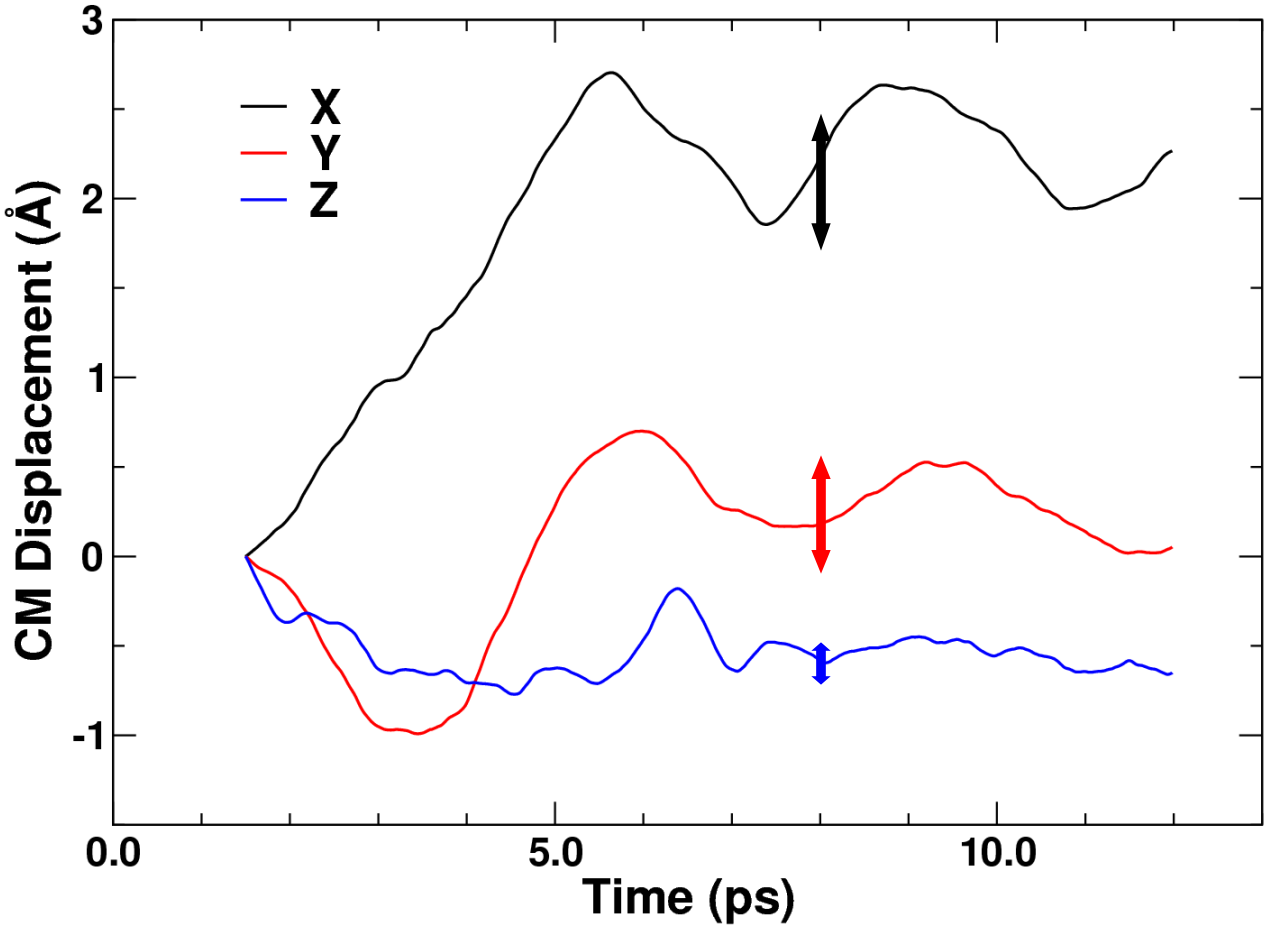


O

Al

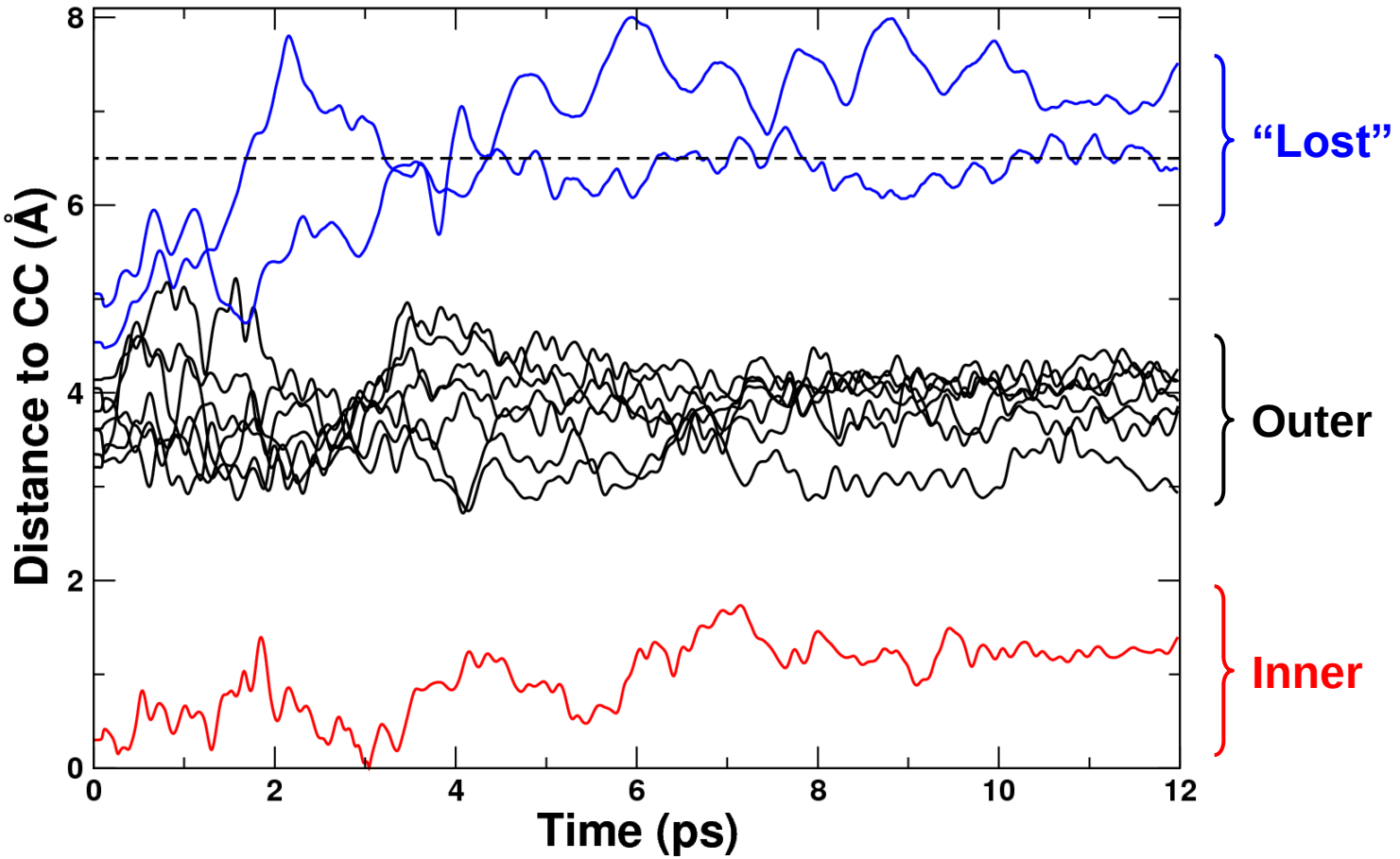
Example MD run @ 298 K

Dynamical Properties



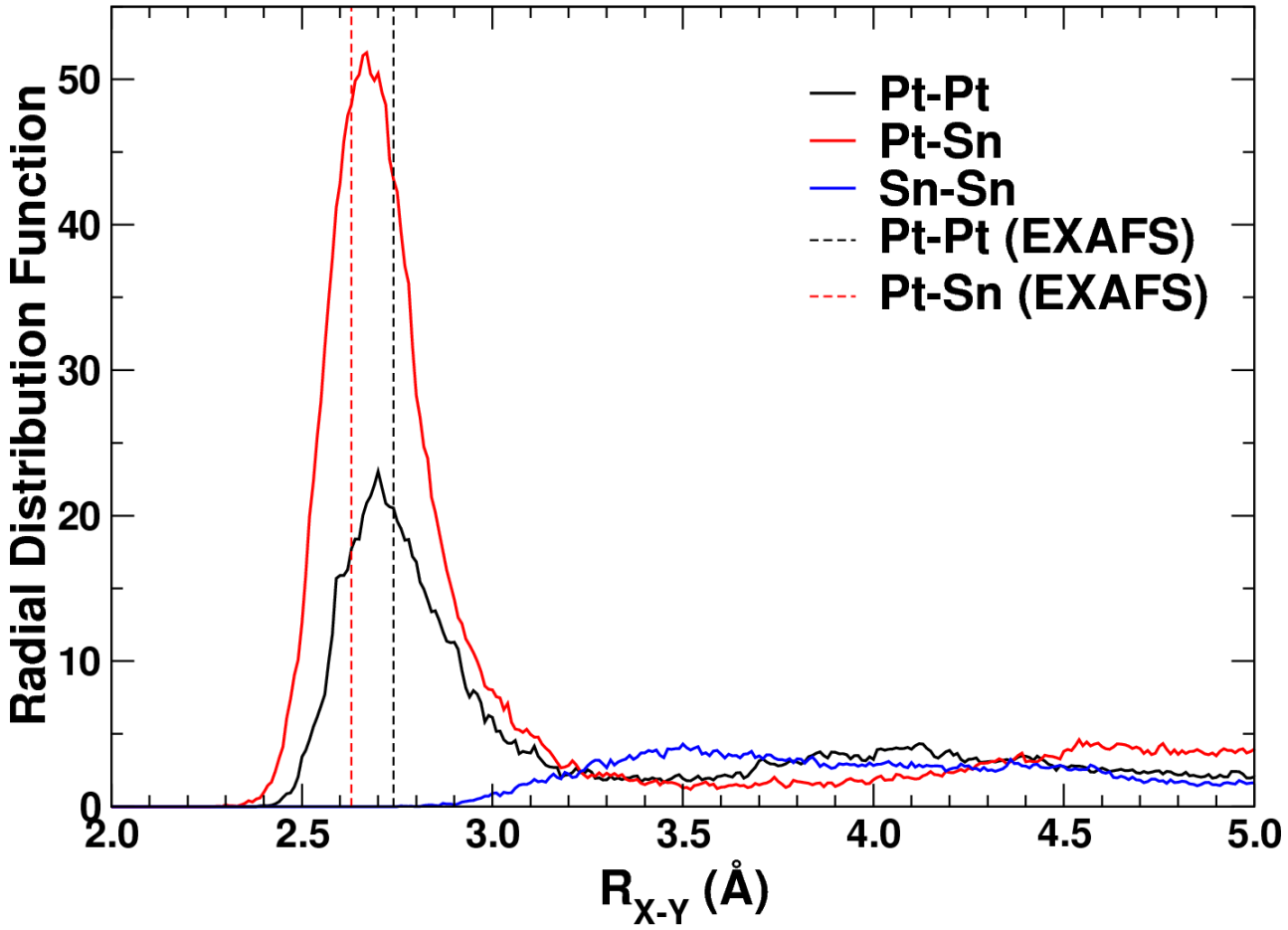
CM (Center of Mass) displacement: **fluctuations similar** to pure Pt_{10} cluster

Dynamical Properties



Sn-CC (Center of Coord.) distance: structuring and "loss" of Sn atoms

Structural Properties

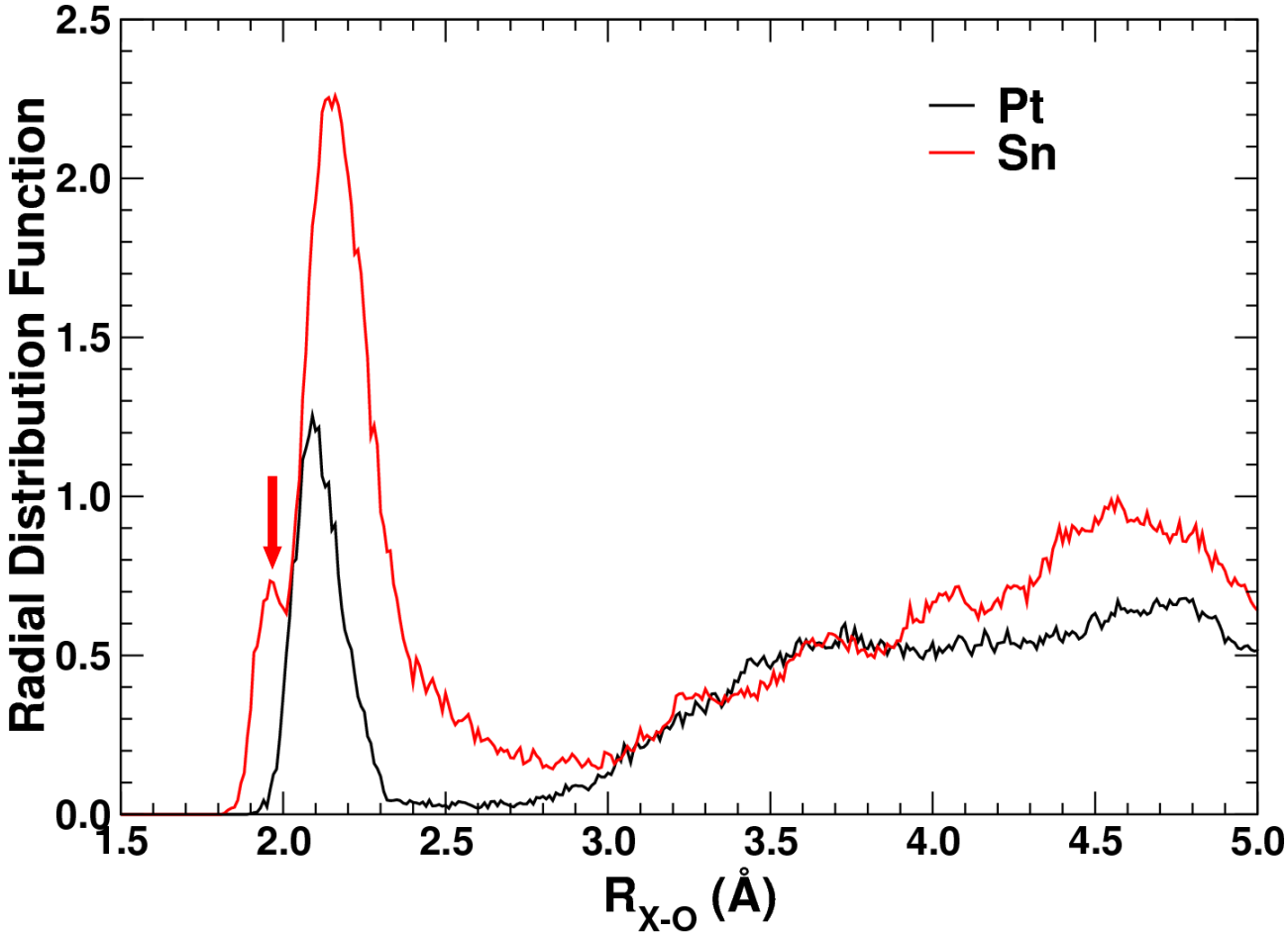


Pt-Pt distance: Good agreement with EXAFS

Pt-Sn distance: Slightly overestimated

Sn-Sn distance: Very broad distribution

Structural Properties

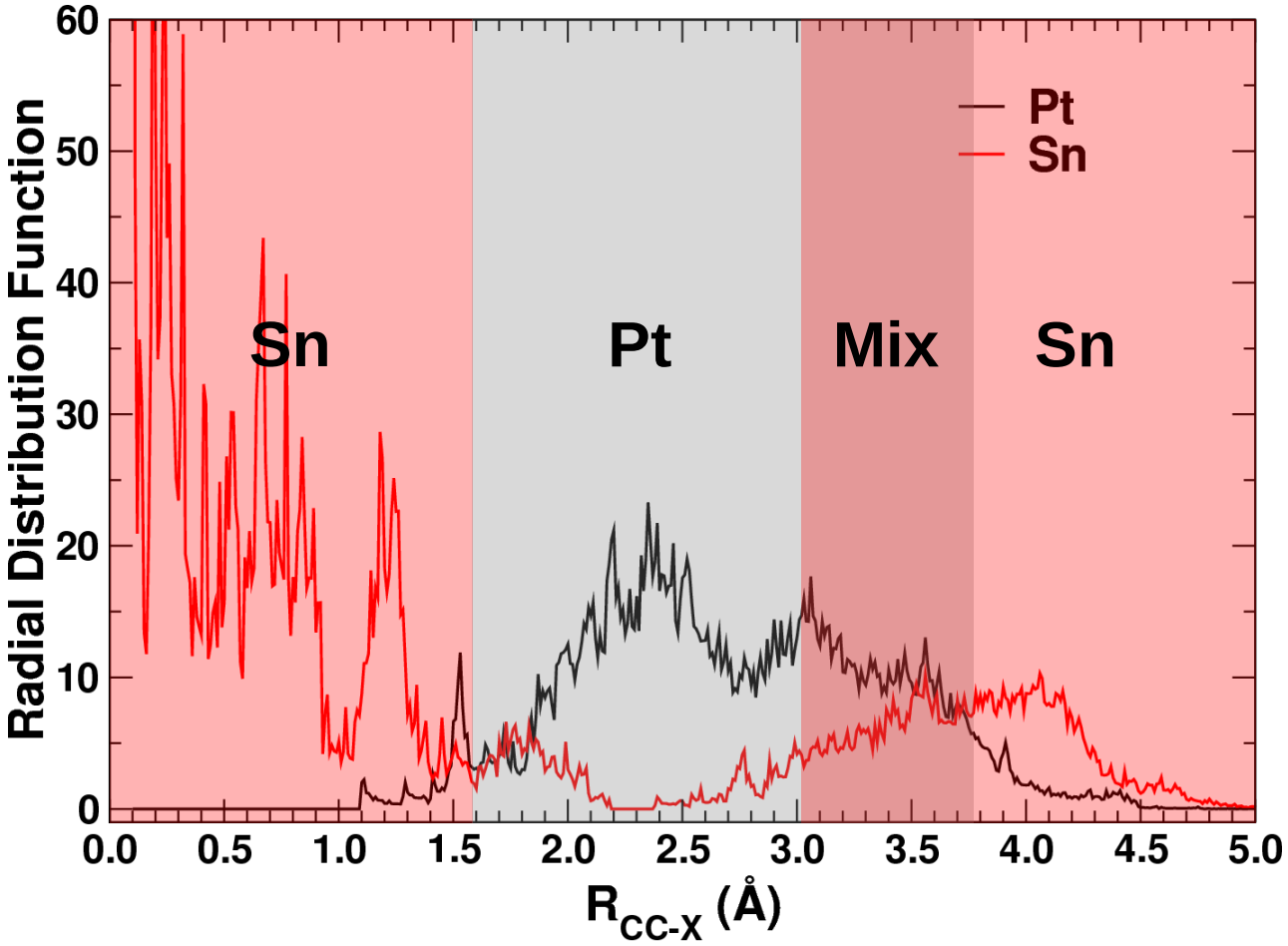


Pt atoms: Interacts less with surface than Sn

Sn atoms: Bimodal Sn-O RDF due to "lost" Sn atoms

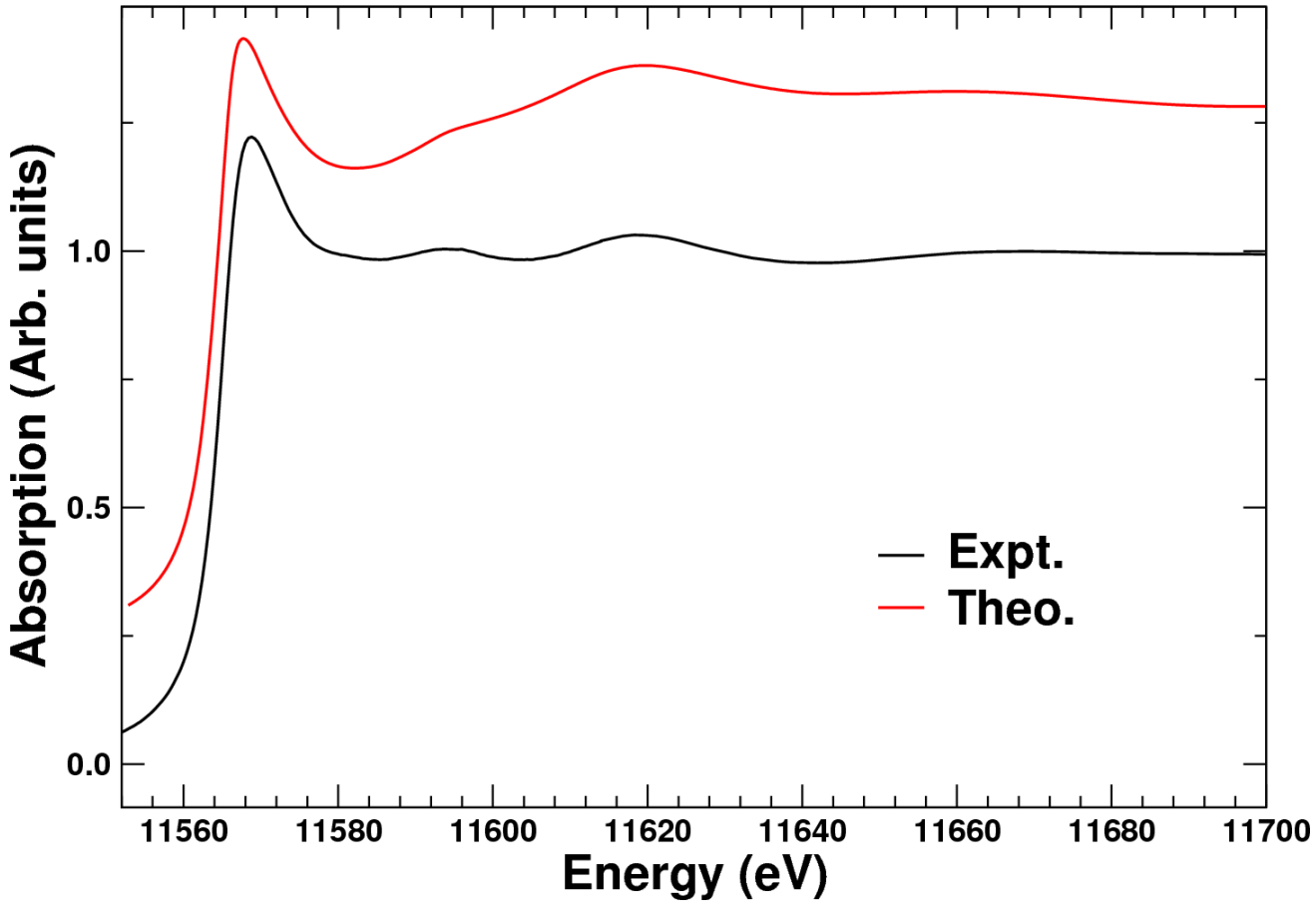
(Pt,Sn)-O RDFs: ~15x smaller than Pt-Pt, Pt-Sn

Structural Properties



CC-(Pt,Sn) RDF: "layered" Sn | Pt | Mix | Sn structure

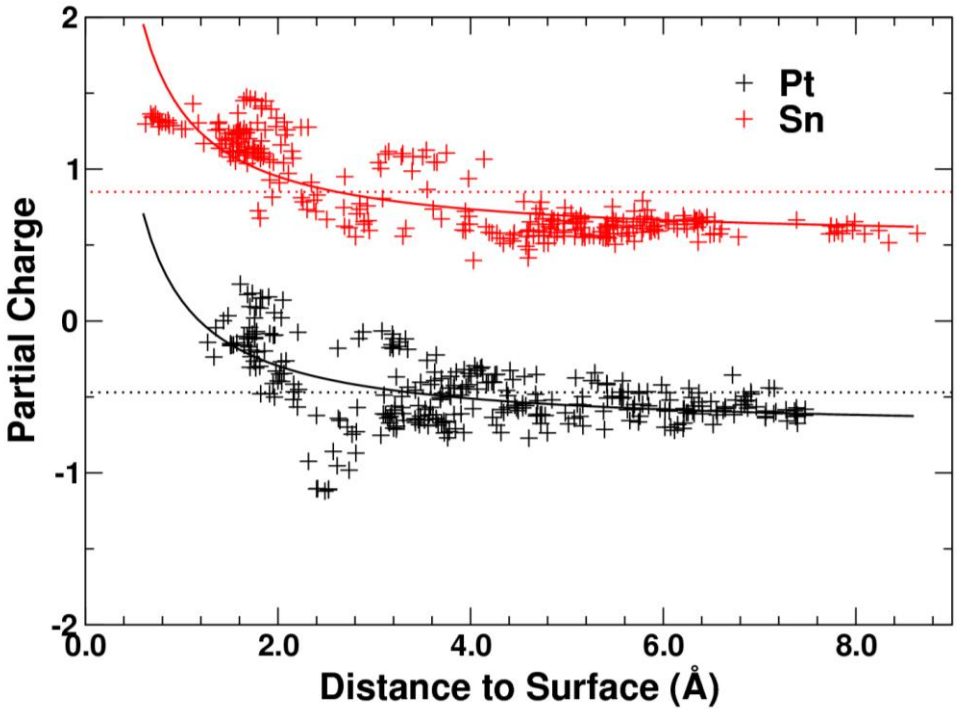
Electronic Structure



Pt L_3 XANES in qualitative agreement with expt.

Electronic Structure

System	Atom	Mean δQ	% bound to O
Pure Pt_{10}	Pt	0.1 ± 0.2	50 ± 5
Alloy $Pt_{10}Sn_{10}$	Pt	-0.5 ± 0.2	22 ± 4
	Sn	0.9 ± 0.3	33 ± 4

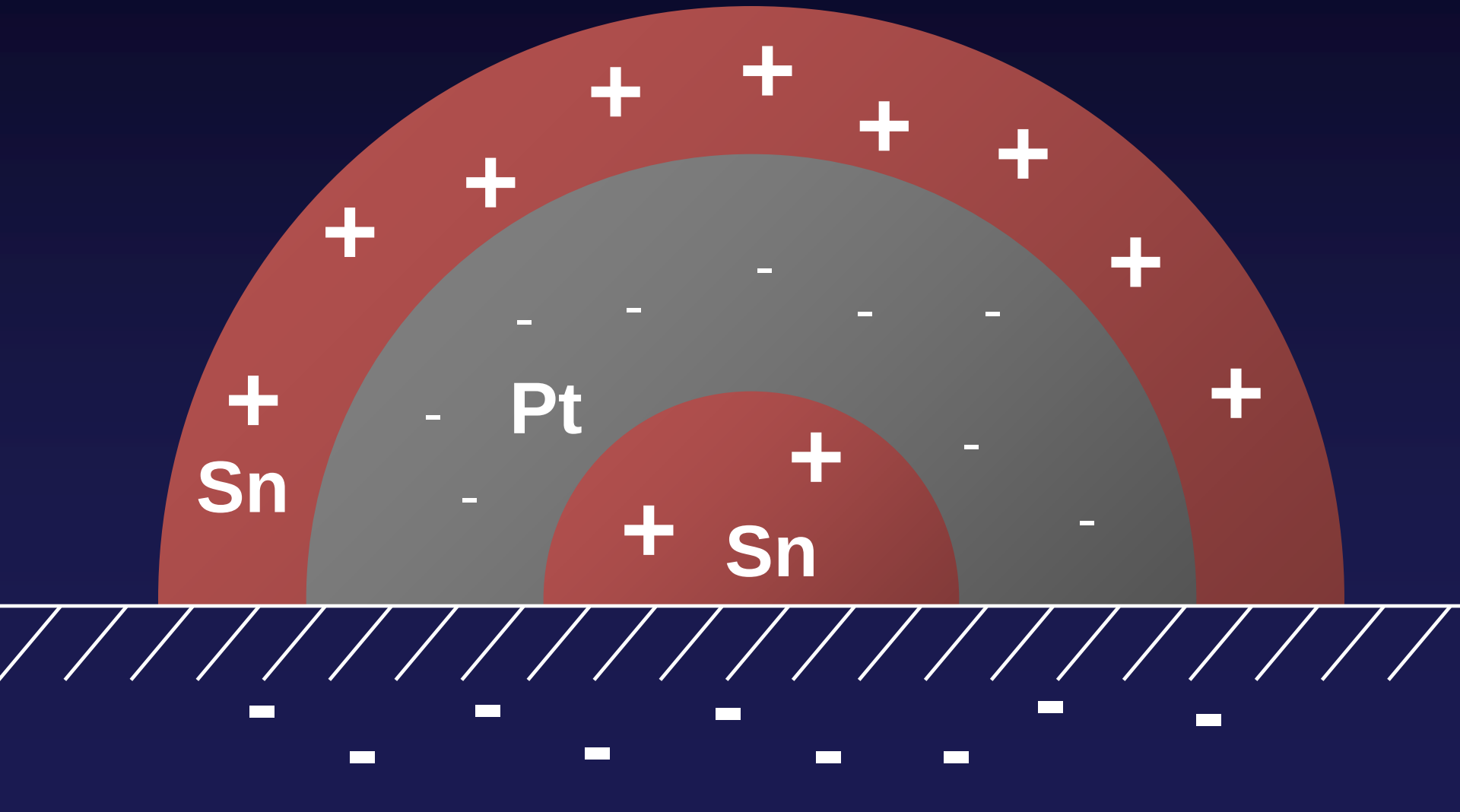


Pt atoms: Alloy more negative than pure cluster

Sn atoms: Very positively charged

Partial charges: More positive closer to the surface

Simplistic Nanoparticle Model



Conclusions

1. Simulations reveal clusters have a layered structure
2. Sn atoms are preferentially lost from the clusters
3. Differential charging of the Pt and Sn atoms explains Sn-loss and layered structure

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