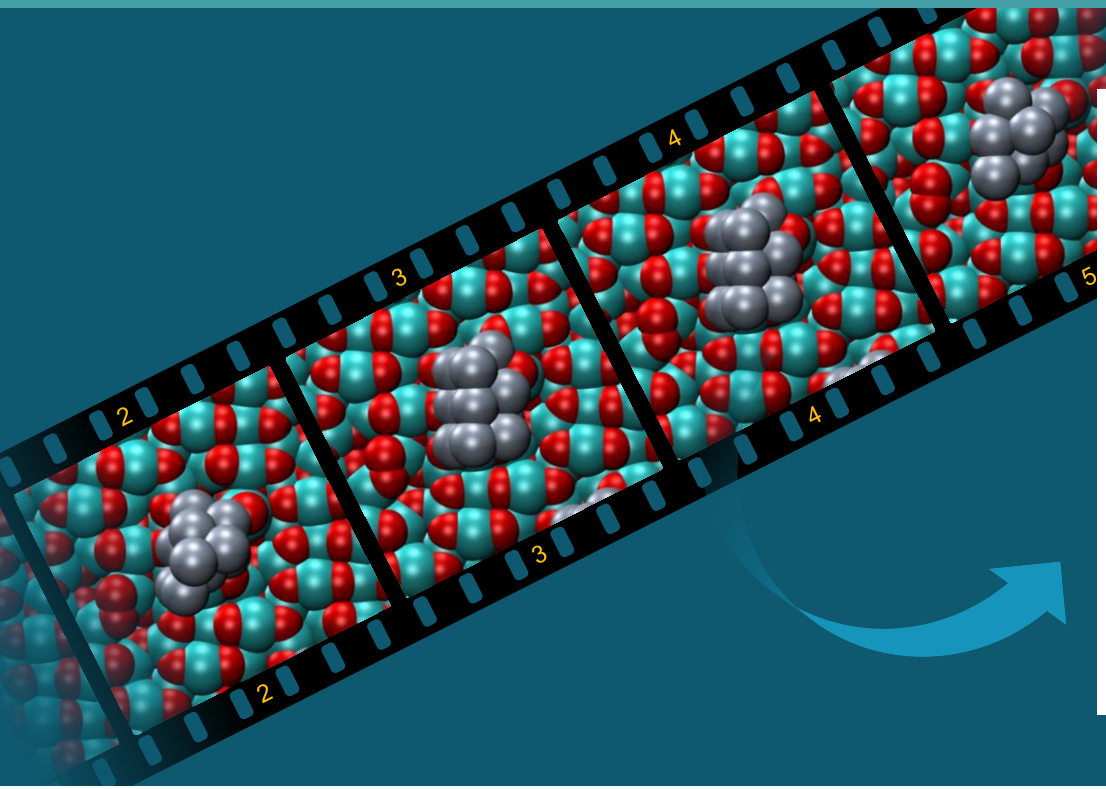
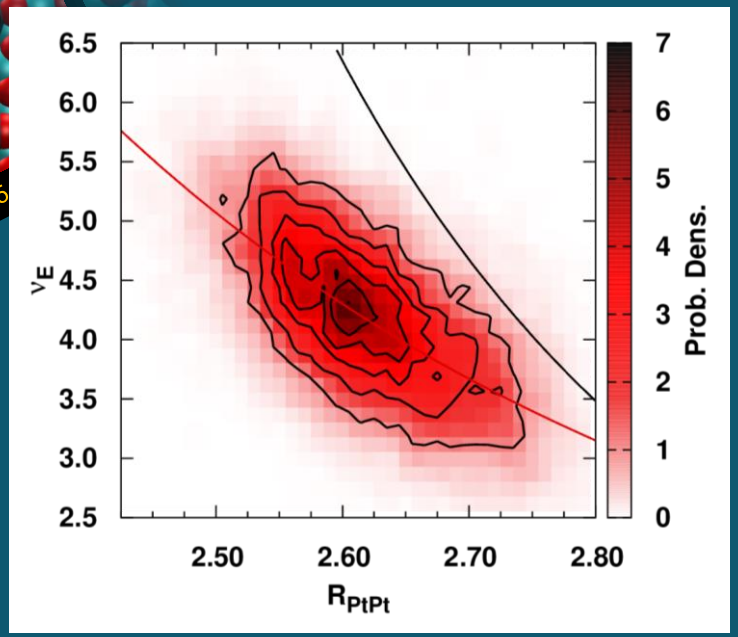
Dynamic and static disorder in supported Pt nanoparticles: when static is not static

F.D. Vila, J. J. Rehr and A. F. Frenkel





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Importance of Supported Nanoparticles (NPs)

Keystone of heterogeneous catalysis:

- Petroleum reforming, Fuel cells
- Broad range of reactions

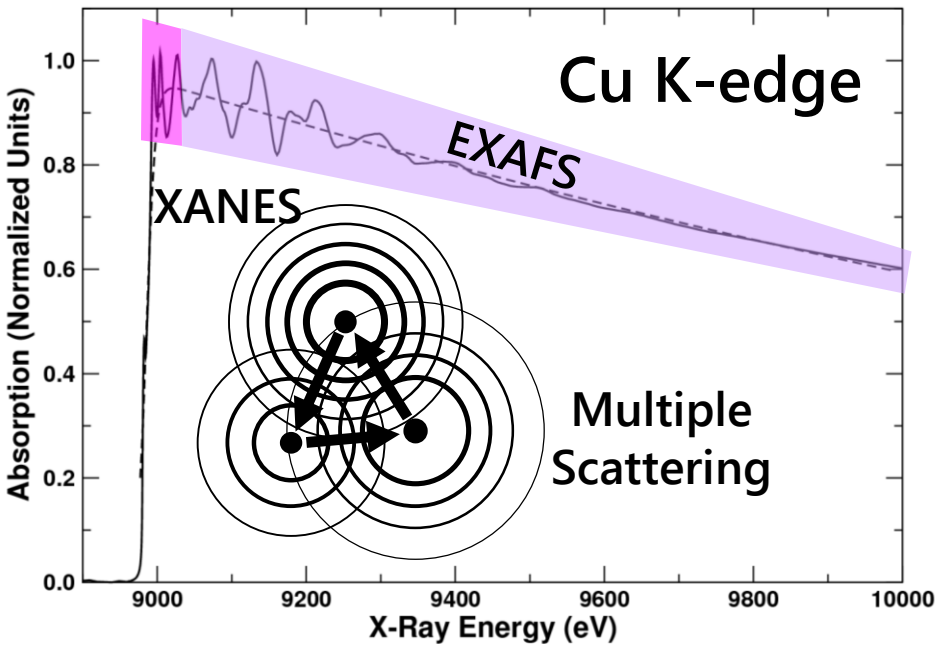
Chemistry and physics of supported NPs:

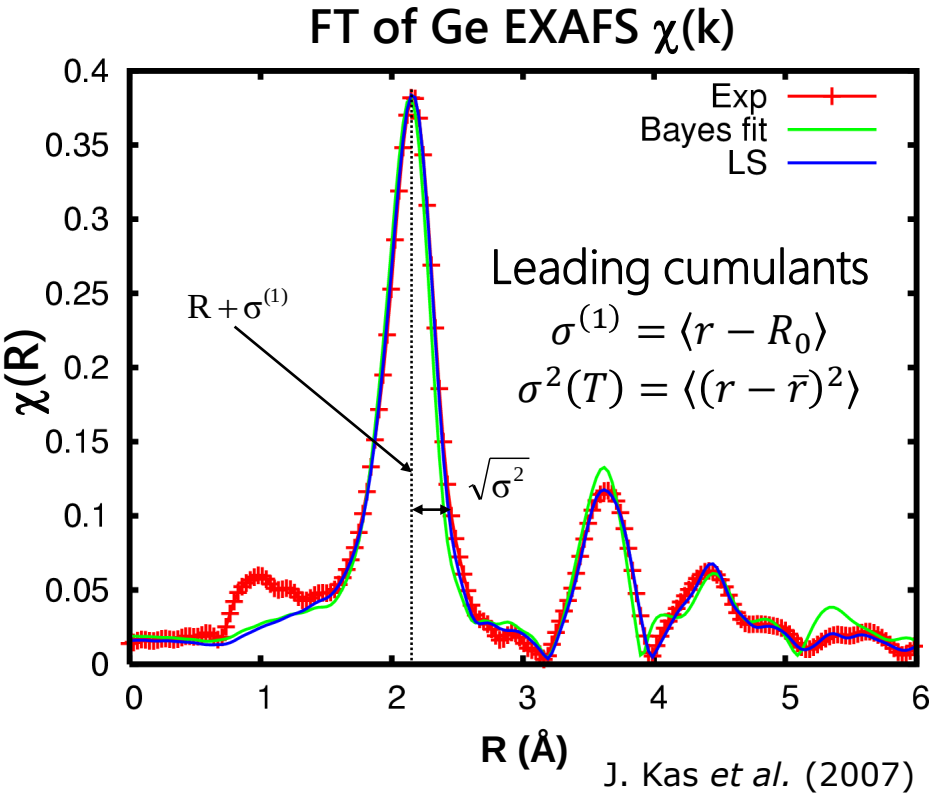
- Different from bulk: Anomalous Disorder
- Interesting at fundamental level

Typical experimental techniques:

- XPS, TEM
- X-ray absorption: XANES and EXAFS

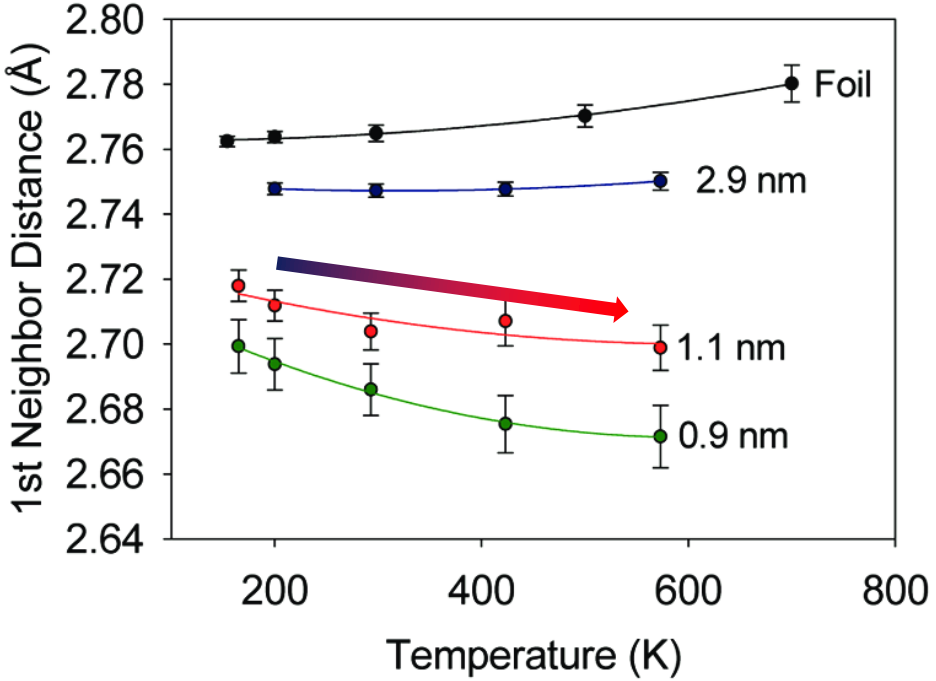
EXAFS: Access to Average Local Structure and Disorder

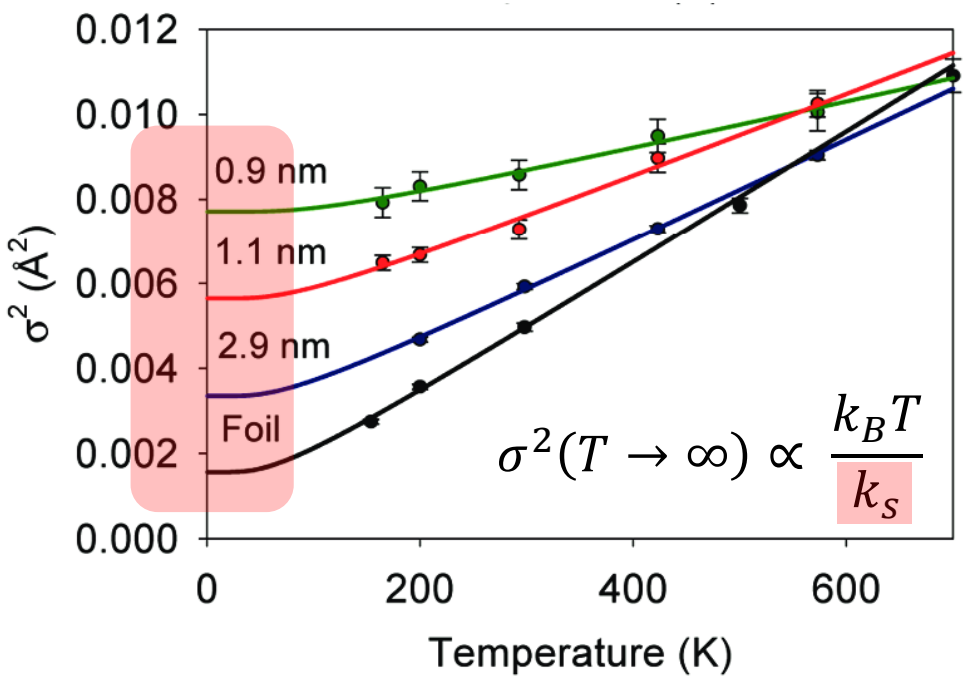




J. Kas *et al.* (2007)

Experiment: Anomalies in Supported Pt NPs





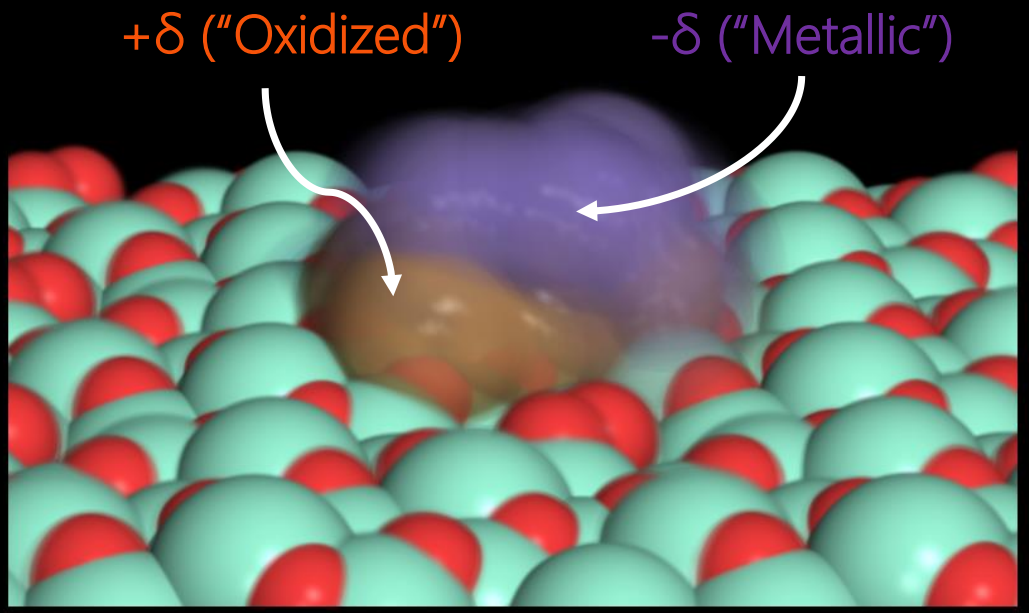
Negative Thermal Expansion (NTE) in smaller NPs

Large 0K ("static") disorder in smaller NPs

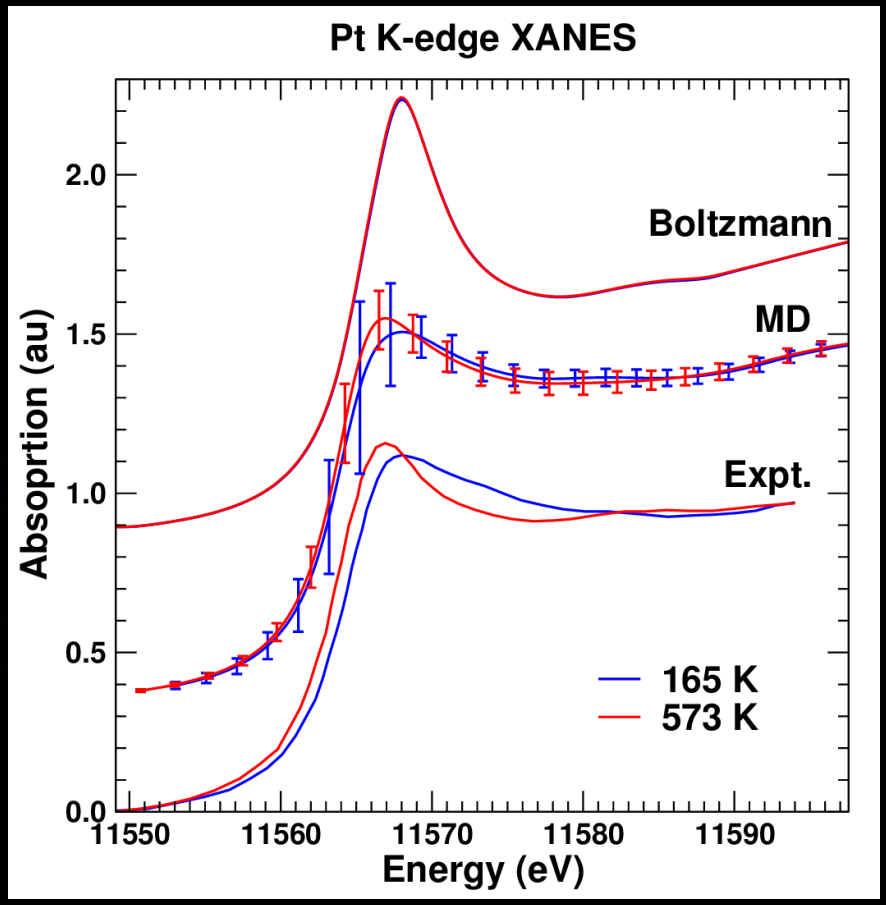
Apparent bond strengthening with NP size decrease

Sanchez *et al.* JACS **131**, 7040, 2009

Theory: Static Simulations are Inadequate



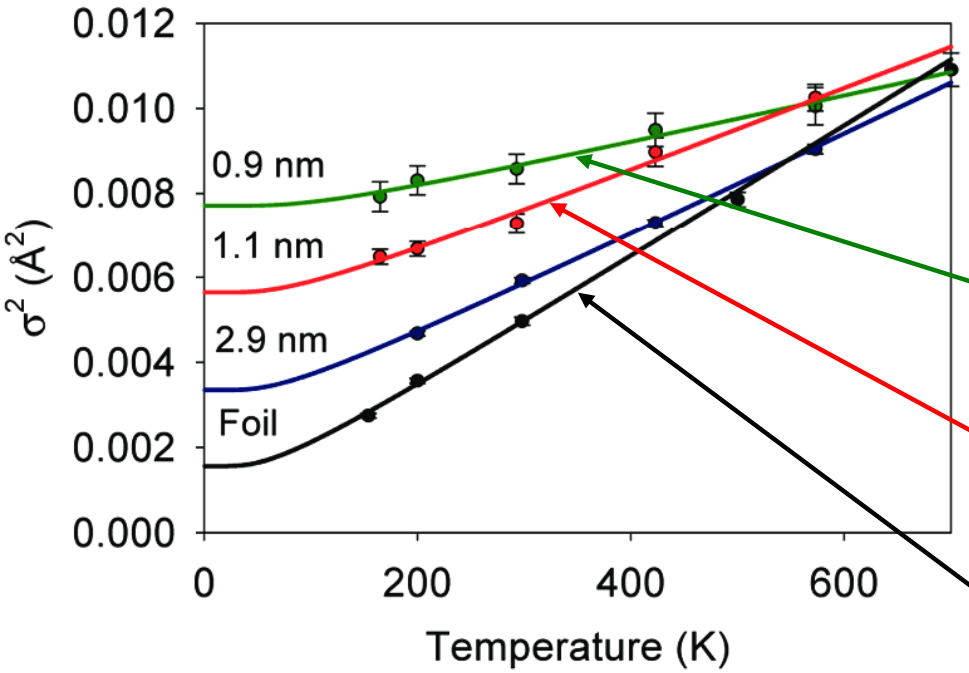
Pt_{10} on γ-Al_2O_3 @ 165 K



MD simulations reproduce experiment

Vila *et al.* Physical Review B **78**, 121404(R), 2008

Anomalous Bond Strength from Einstein Model Fits



Einstein Model with Static Disorder

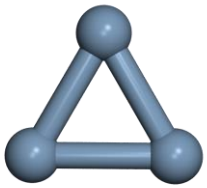
$$\sigma^2(T) = \sigma_S^2 + \frac{h}{8\pi^2\mu}\frac{1}{\nu_e}\coth\left(\frac{h\nu_E}{2k_BT}\right)$$

0.9 nm NPs:
$\nu_E \cong 6.3$ THz

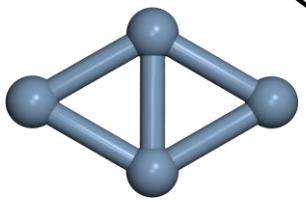
1.1 nm NPs:
$\nu_E \cong 4.6$ THz

Pt Foil:
$\nu_E \cong 3.8$ THz

$\nu_E \cong 6.4$ THz



$\nu_E \cong 6.4$ THz



$\nu_E \cong 4.5$ THz

Sanchez *et al.* JACS **131**, 7040, 2009

Computational Details

Systems:

Pt_{10} and Pt_{20} clusters

Support:

γ-Al_2O_3

4 layers

Dehydroxylated

Cell:

19.4 Å× 13.7 Å

16 Å vacuum

MD Setup:

6 initial conditions

20 ps runs:

10 ps thermalization

10 ps analysis

3 fs time-step

Nosé-Hoover thermostat

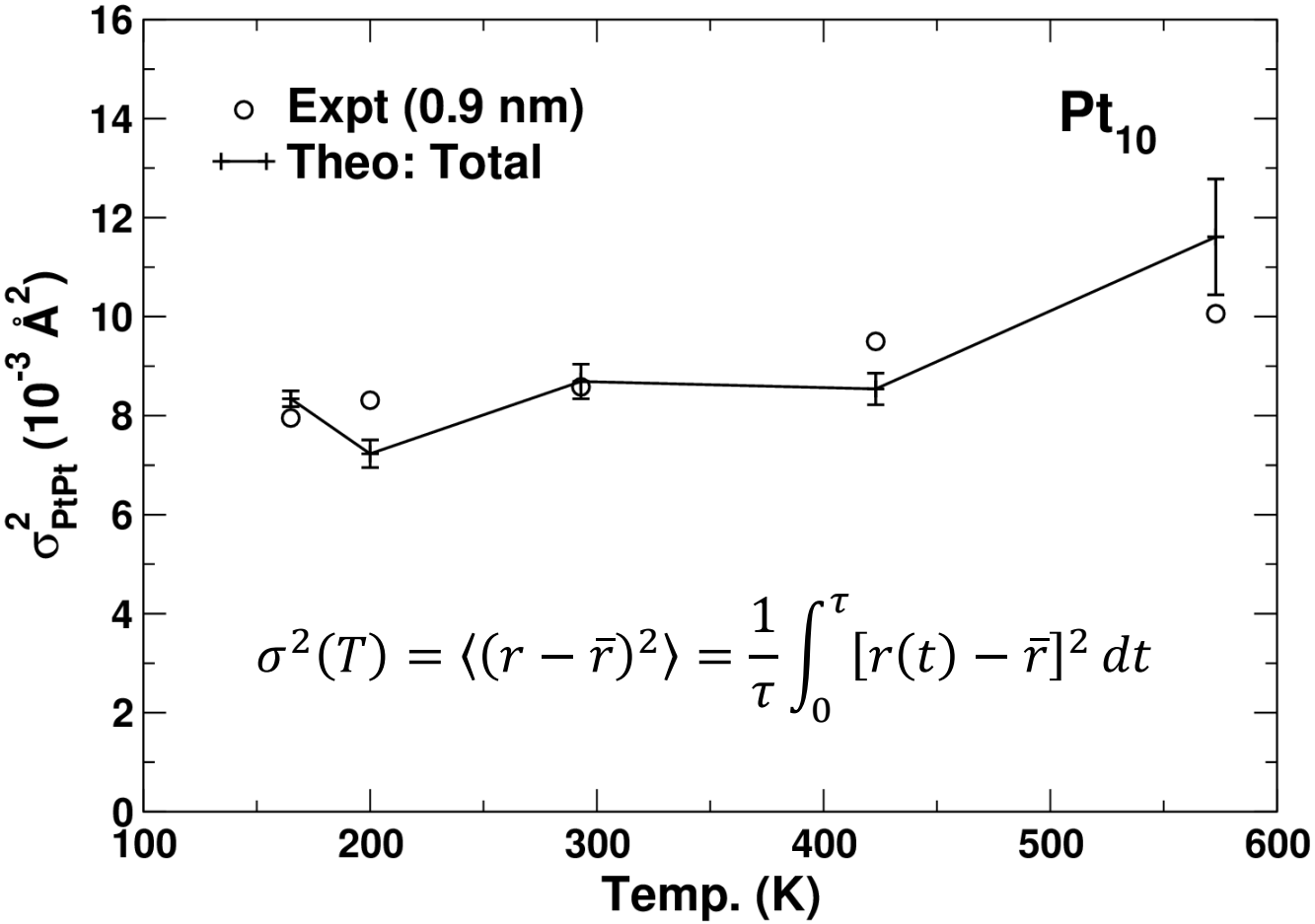
Method:

PBE XC functional

US PPs, 297 eV cutoff

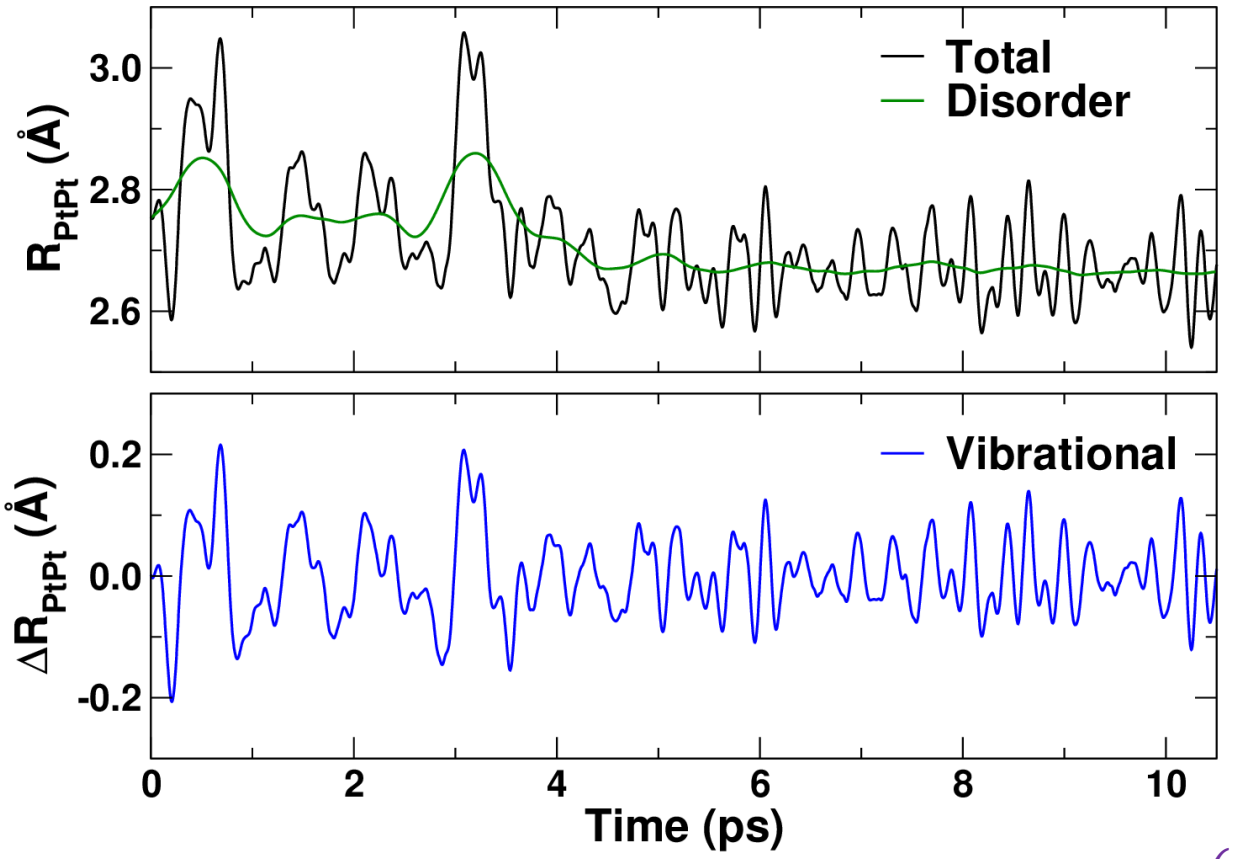
VASP

Total Mean Square Relative Displacement (MSRD)



Reasonable agreement between theory and expt.

High (> 1THz) and Low (< 1 THz) Frequency Filtering

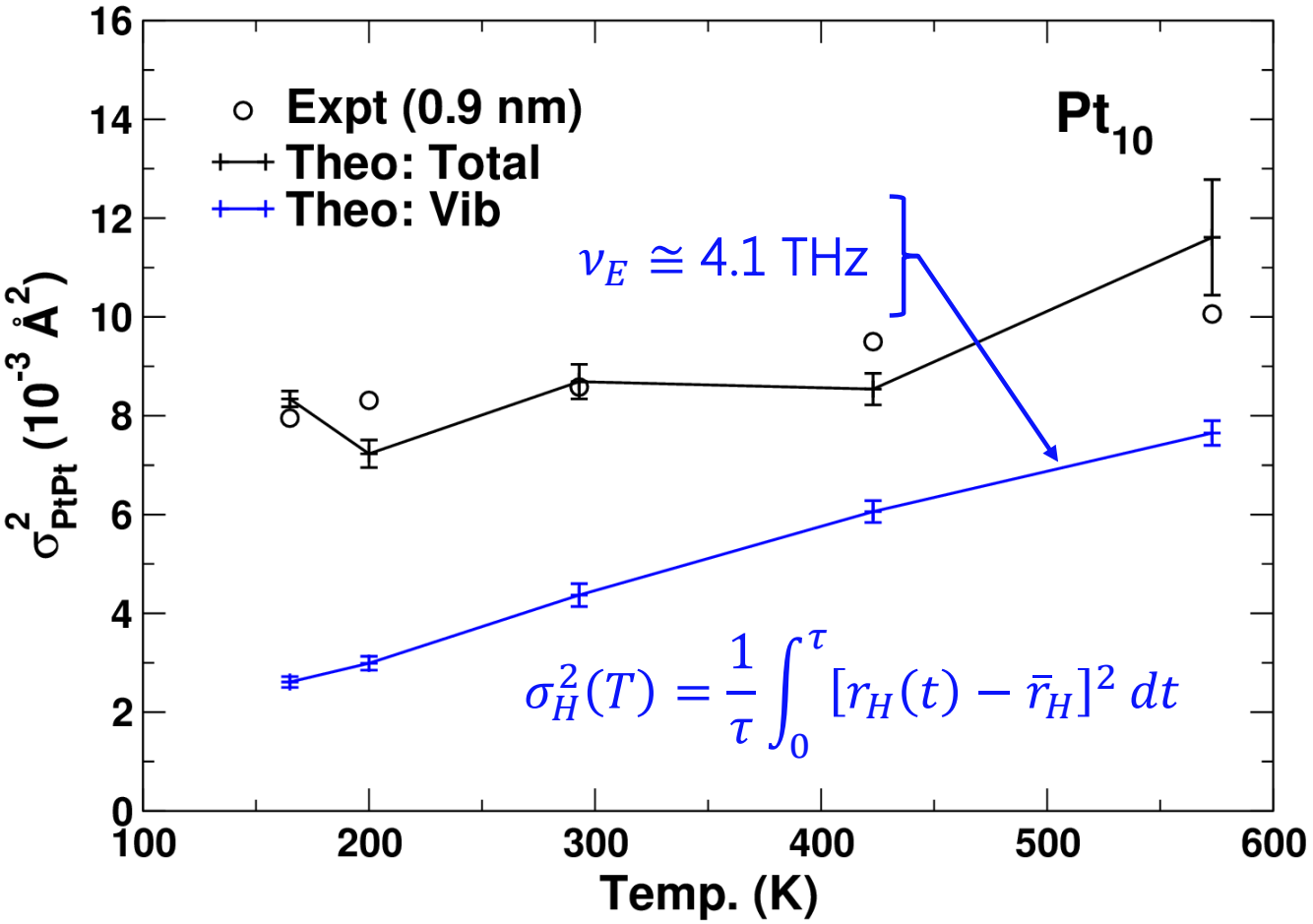


$$r_L(t) = \int_{-\infty}^{+\infty} r(\tau) F(t-\tau)\, d\tau$$

$$r_H(t) = r(t) - r_L(t)$$

Filter Function: $$F(t) = \begin{cases} \frac{\pi}{2}\nu_L \cos(\pi\nu_L t), & |t| < {}^{1}/_{2\nu_L} \\ 0, & |t| \geq {}^{1}/_{2\nu_L} \end{cases}$$

Vibrational MSRD

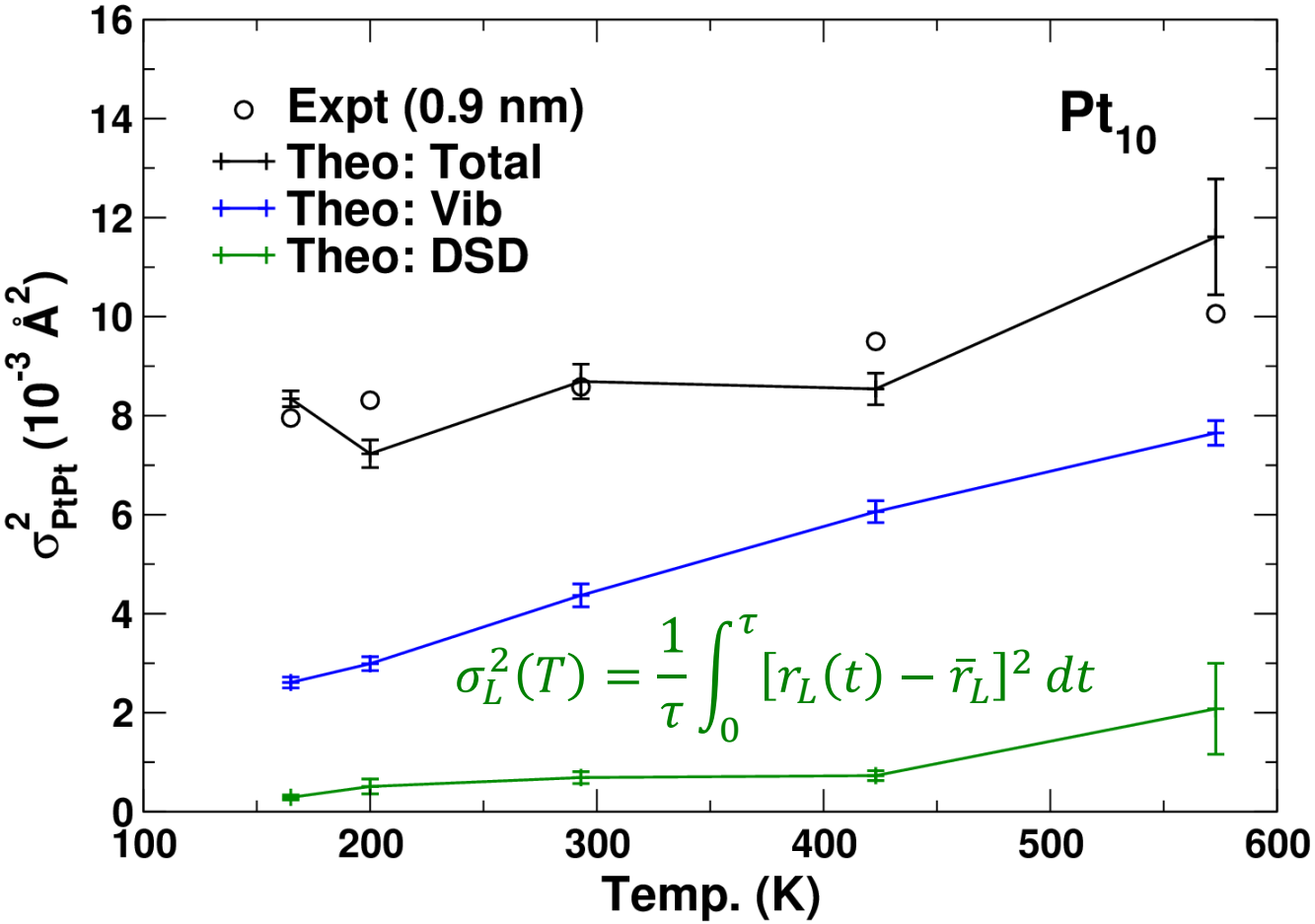


0.9 nm NPs:
$\nu_E \cong 6.3$ THz

Pt Foil:
$\nu_E \cong 3.8$ THz

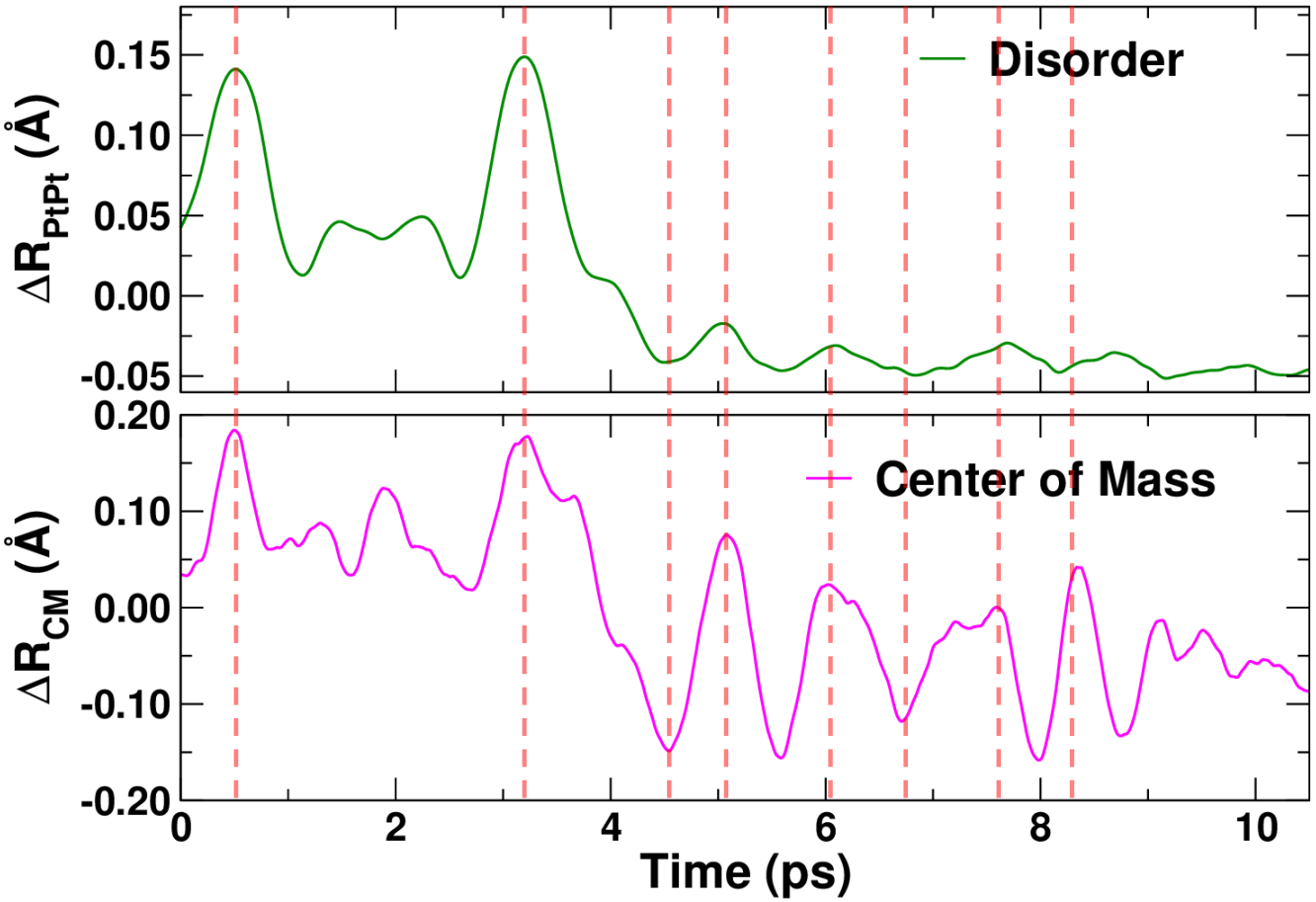
Normal linear vibrational behavior

Dynamic Structural Disorder (DSD) MSRD



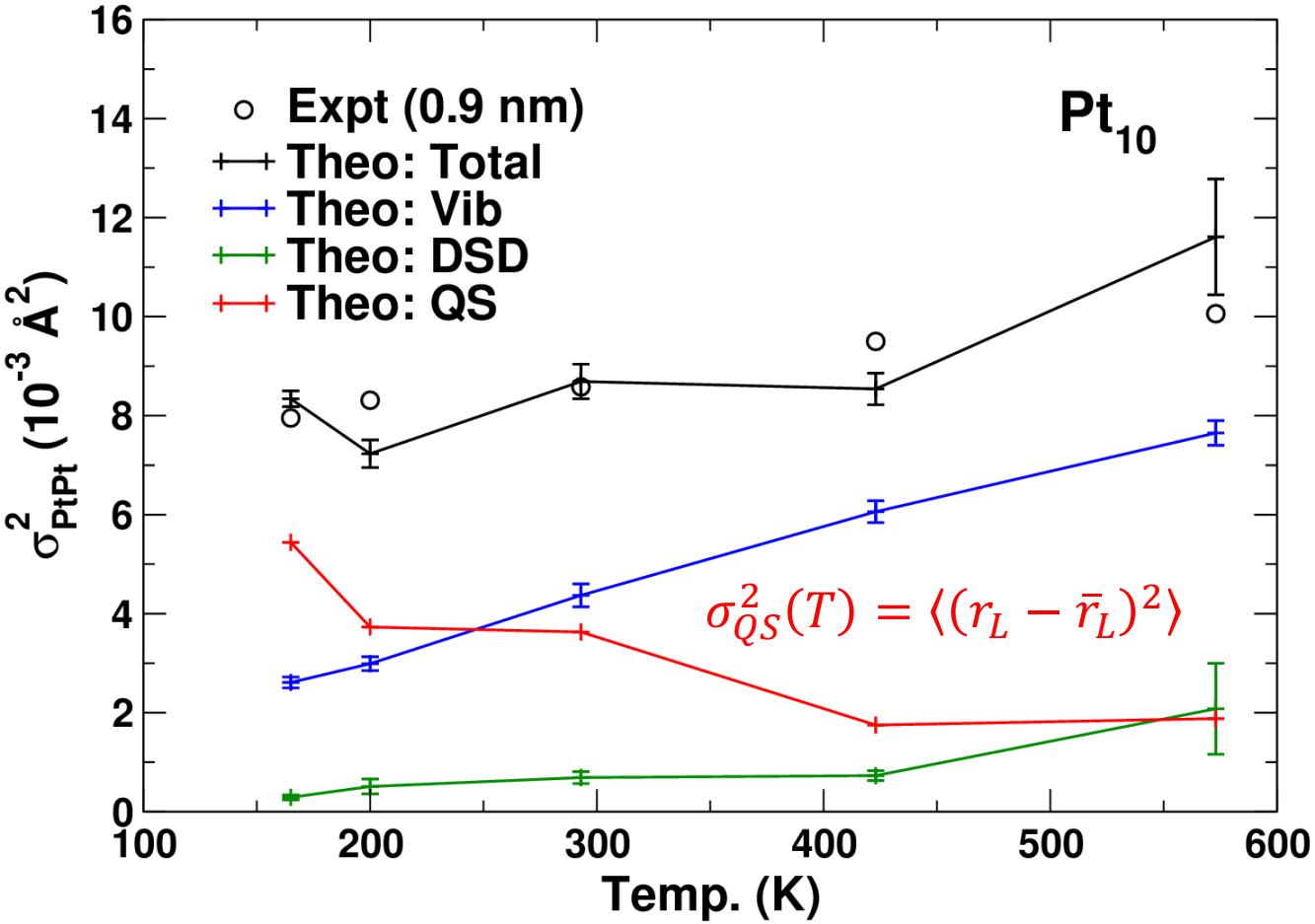
Normal linear behavior: Low frequency quasi-harmonic modes

DSD: Correlation Between CM and Pt-Pt Dynamics



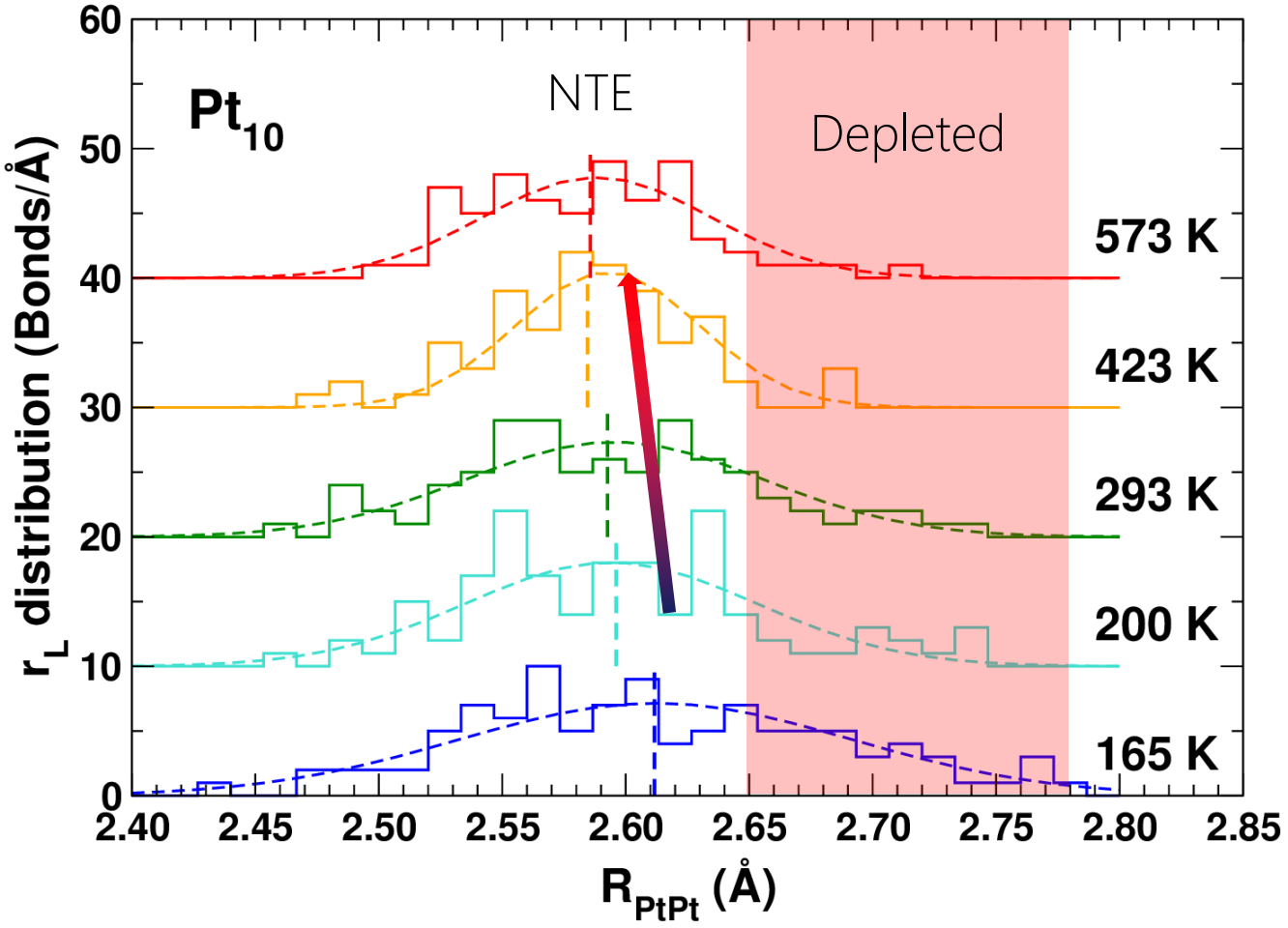
Moderate/strong correlation between CM libration and Pt-Pt bonds

Quasi-static MSRD



Anomalous quasi-static disorder: Causes apparent strengthening

Temp. Dep. Quasi-Static Bond Distributions ($\sigma^2_{QS}(T)$)



Dynamic activation and depletion of long bonds

Grüneisen Parameter: NPs *vs* Bulk

$$\gamma = -\frac{1}{3}\frac{d \ln \nu_E}{d \ln R_{PtPt}} \Rightarrow \gamma \cong -\frac{1}{3}\frac{\Delta \nu_E}{\Delta R_{PtPt}}\frac{R_{PtPt}}{\nu_E}$$

Pt metal:

Expt: $\gamma = 2.7$

Theo: $\gamma = 2.8$

Nanoparticle:

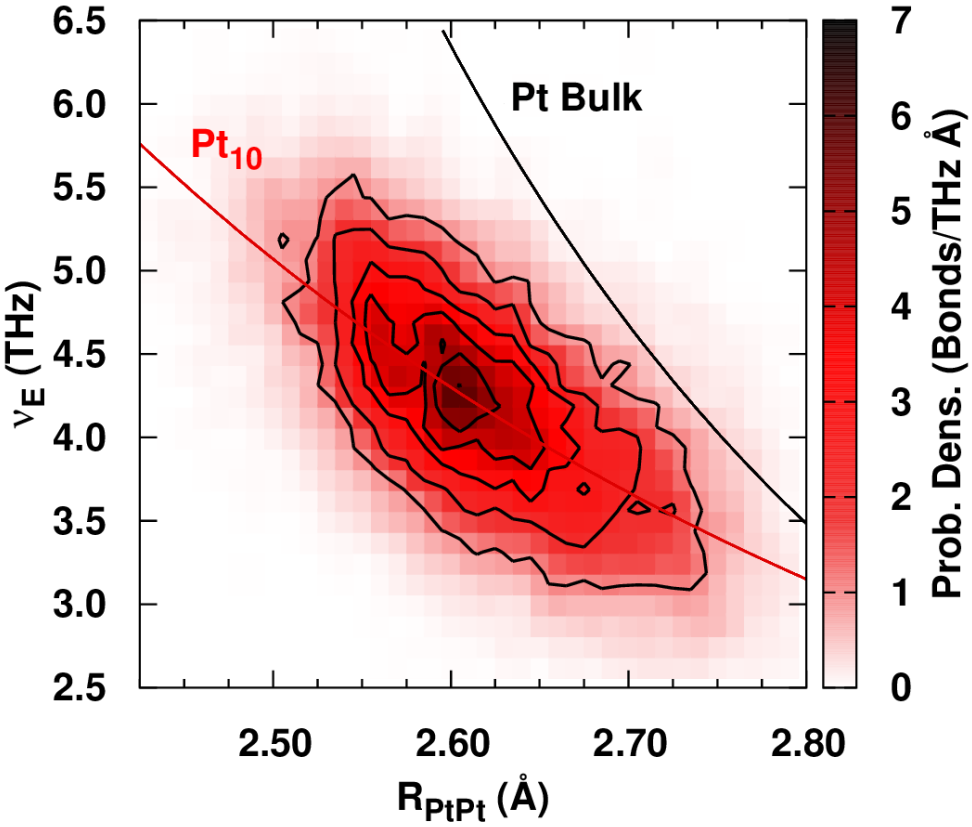
From Einstein Model Fit:

Expt: $\gamma \cong 5 \pm 2$

Theo: $\gamma \cong 4 \pm 2$

From Vib. Component:

$\gamma \cong 1.4 \pm 0.2$



Grüneisen Parameter: Enhanced by anomalous disorder

Summary

Partitioned MSRD from DFT/MD simulations reveals:

NEW concept:

- Anomalous Structural Disorder (ASD)
- Decreases with T

Single mechanism, dynamic activation, explains:

- NTE
- Large disorder
- Bond strengthening

Normal behavior of Pt-Pt vibrations, but slightly stronger bonds

Coupling to CM motion → Dynamic disorder

Implications for interpretation of EXAFS:

Analysis must account for both ASD and DSD

Need new ASD modelling approach

Anomaly signature: $\gamma_{NP} > \gamma_{Bulk}$

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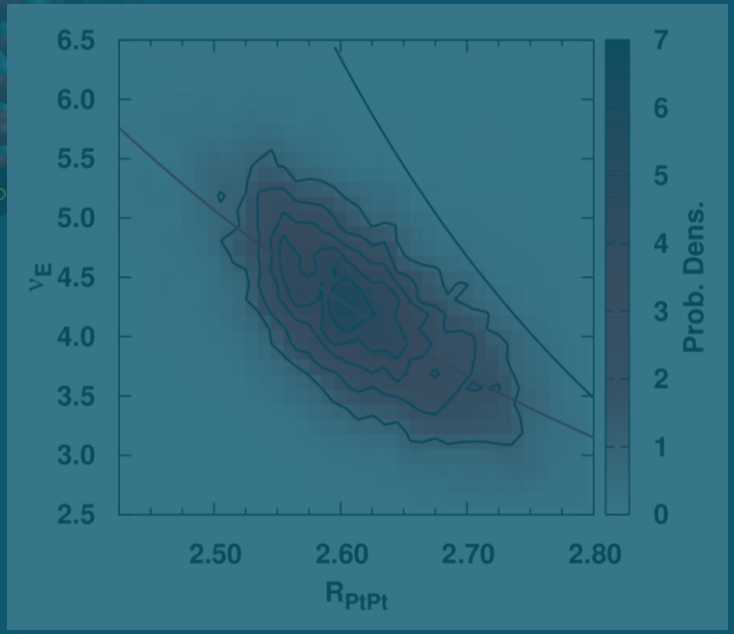

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