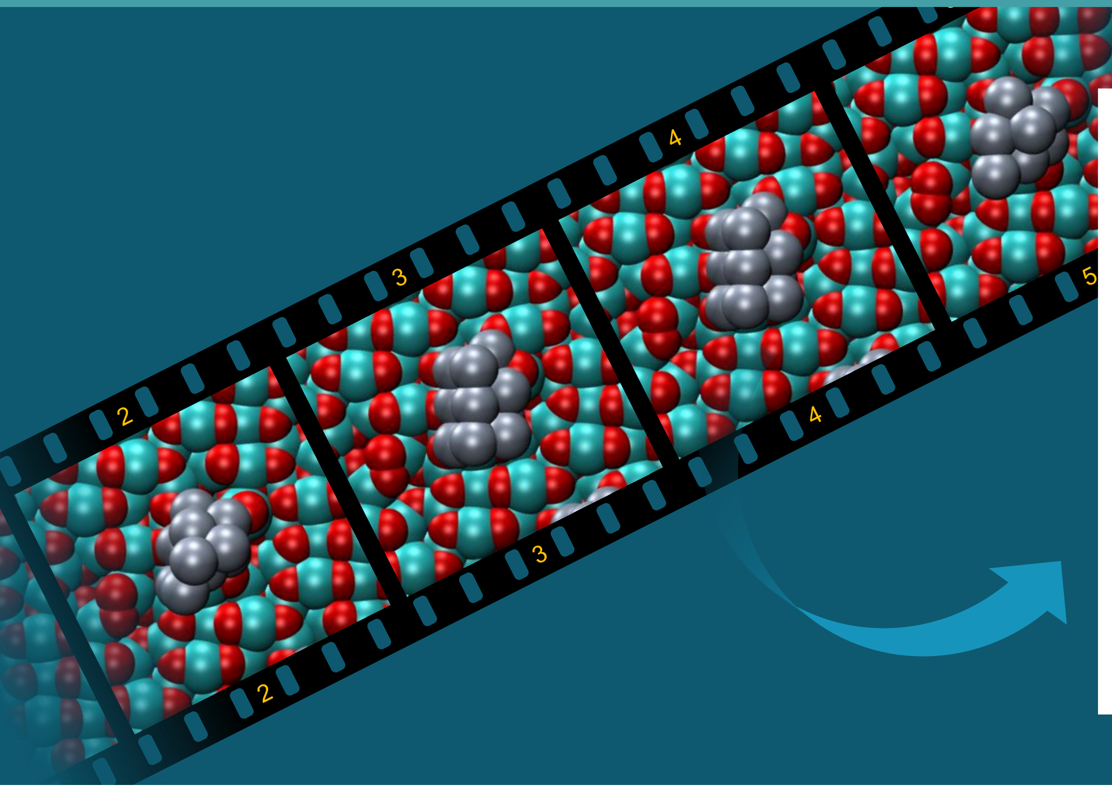
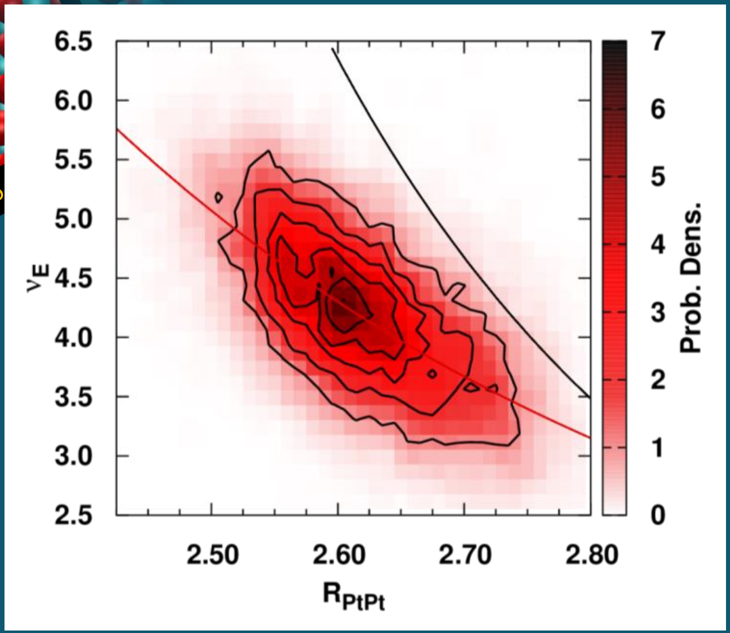
Dynamic Anomalies in the Nanoscale Structure and Disorder of Supported Metal Nanoparticles

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





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Dynamic Disorder in Nanosystems

Drives structural effects:

Fluctuating bonding

Cluster mobility

Affects electron distributions:

Charge separation

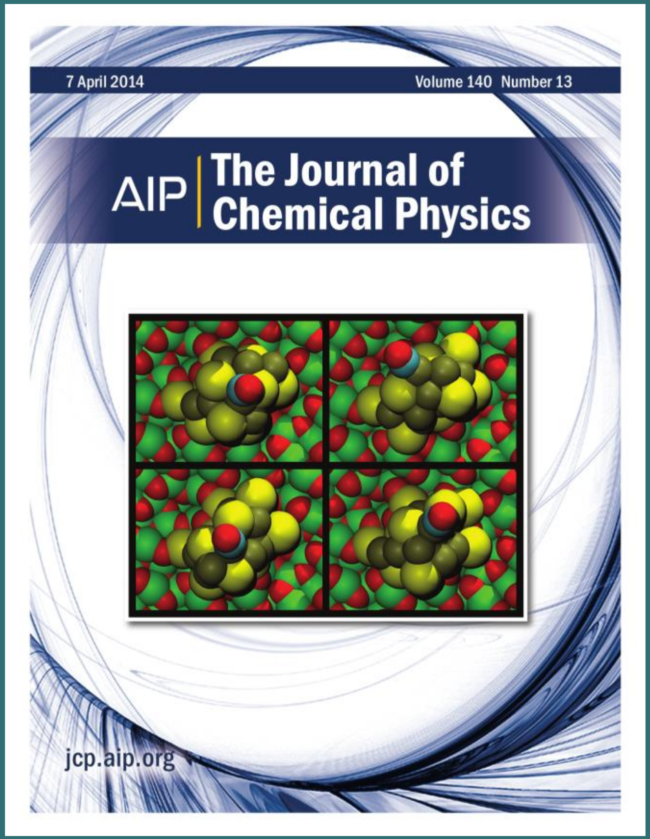
Layering and segregation

Enriches the catalytic landscape:

Changes adsorbate dynamics (right)

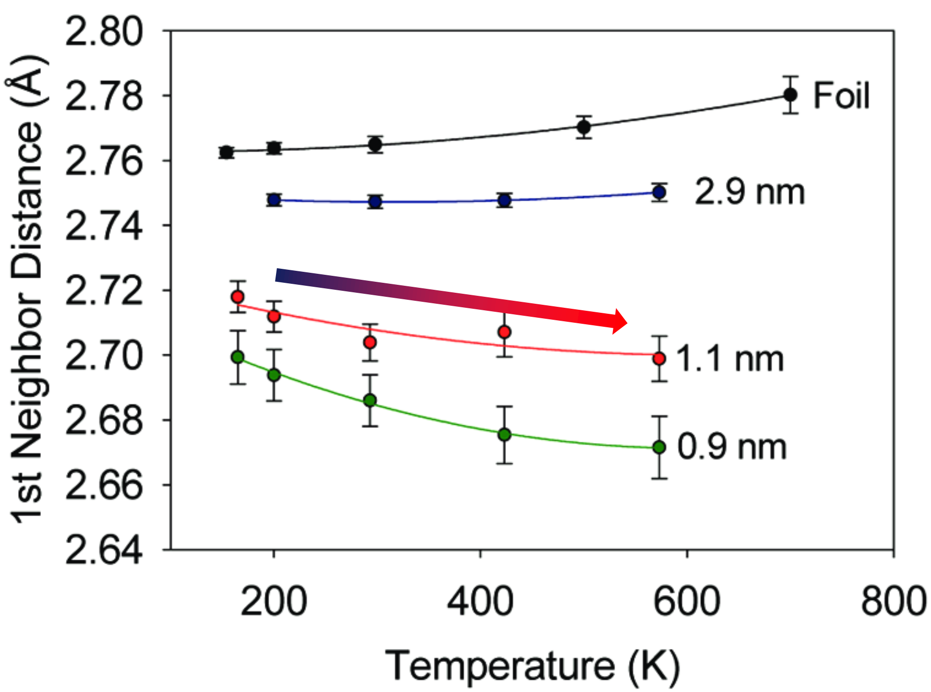
Opens new reaction channels

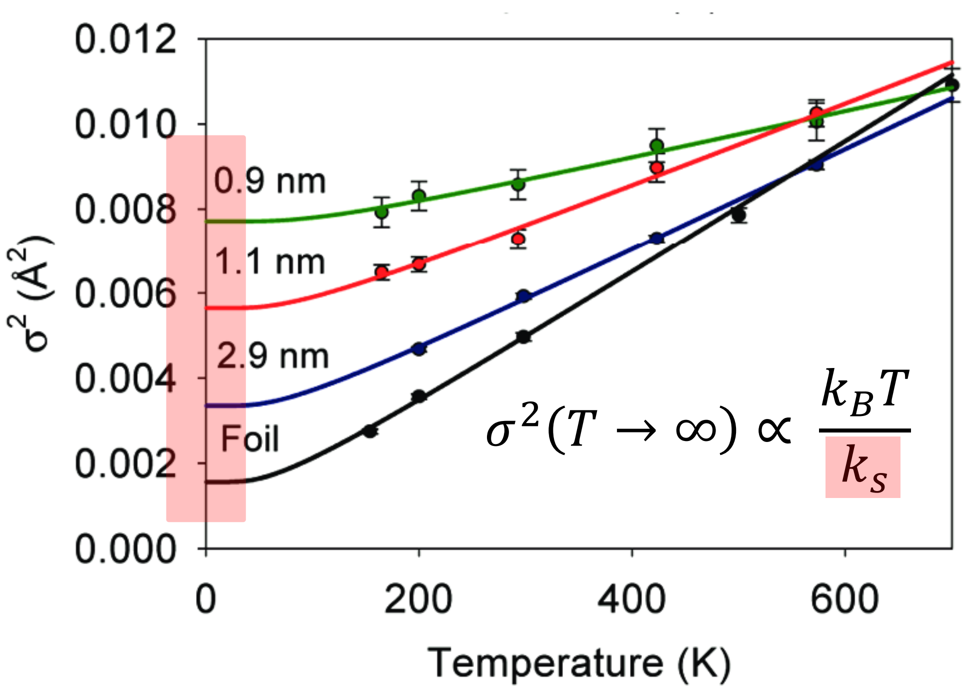
CO dynamics on $Pt_{10}Sn_{10}$



Rehr and Vila J. Chem. Phys. **140**, 134701 (2014)

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

Anomalous Effective Grüneisen Parameter?

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

Pt metal:

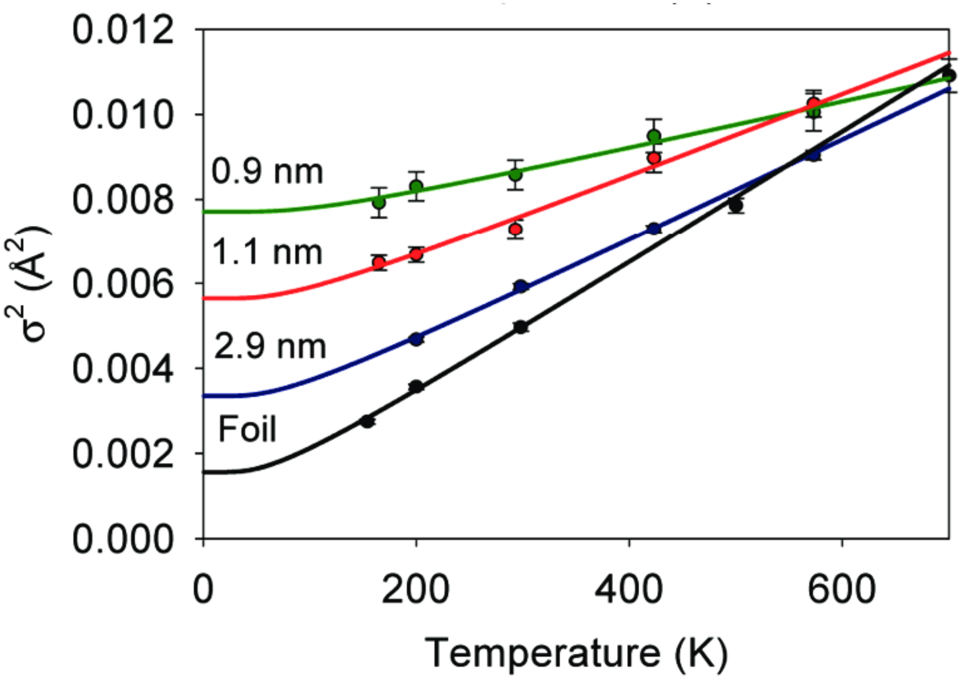
Expt: γ = 2.7

Theo: γ = 2.8

0.9-1.1 nm NPs:

From Einstein Model Fit:

Expt: γ ≅ 5±2



Einstein Model with Static Disorder

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

Effective Grüneisen parameter larger in NPs than bulk

Anomalous Effective Grüneisen Parameter?

$$\gamma = -\frac{1}{3}\frac{d\ln \nu_{\mathrm{E}}}{d\ln R_{\mathrm{PtPt}}} \quad \Longrightarrow \quad \gamma \cong -\frac{1}{3}\frac{\Delta \nu_{\mathrm{E}}}{\Delta R_{\mathrm{PtPt}}}\frac{R_{\mathrm{PtPt}}}{\nu_{\mathrm{E}}}$$

Pt metal:

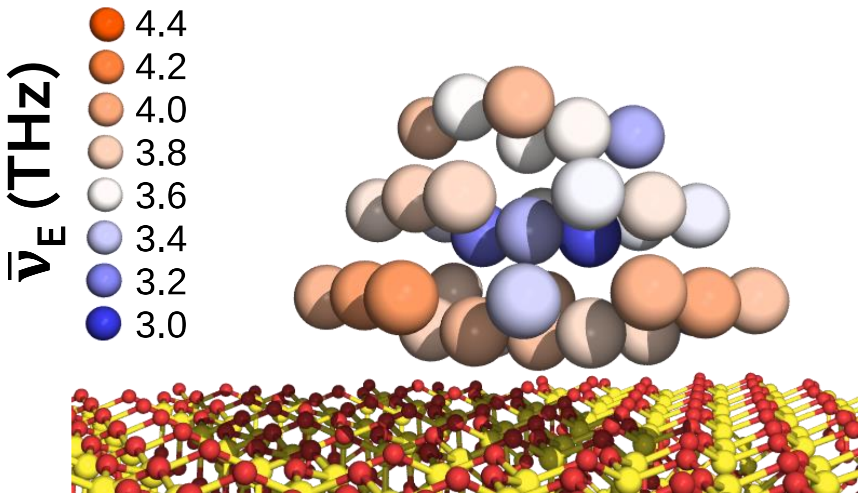
Expt: $\gamma = 2.7$

Theo: $\gamma = 2.8$

0.9-1.1 nm NPs:

From Einstein Model Fit:

Expt: $\gamma \cong 5\pm2$



$$\rho_R(\omega) \cong \sum_{i=1}^{N} w_i \delta(\nu - \nu_i)$$

$$\bar{\nu}_E = \langle \nu^{-2} \rangle^{-\frac{1}{2}} = \left(\sum_{i=1}^{N} \frac{w_i}{\nu_i^2} \right)^{-\frac{1}{2}}$$

We can estimate from *R*-dependent PDOS

A. Frenkel: Anomalous Effective Grüneisen Parameter?

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

Pt metal:

Expt: $\gamma = 2.7$

Theo: $\gamma = 2.8$

0.9-1.1 nm NPs:

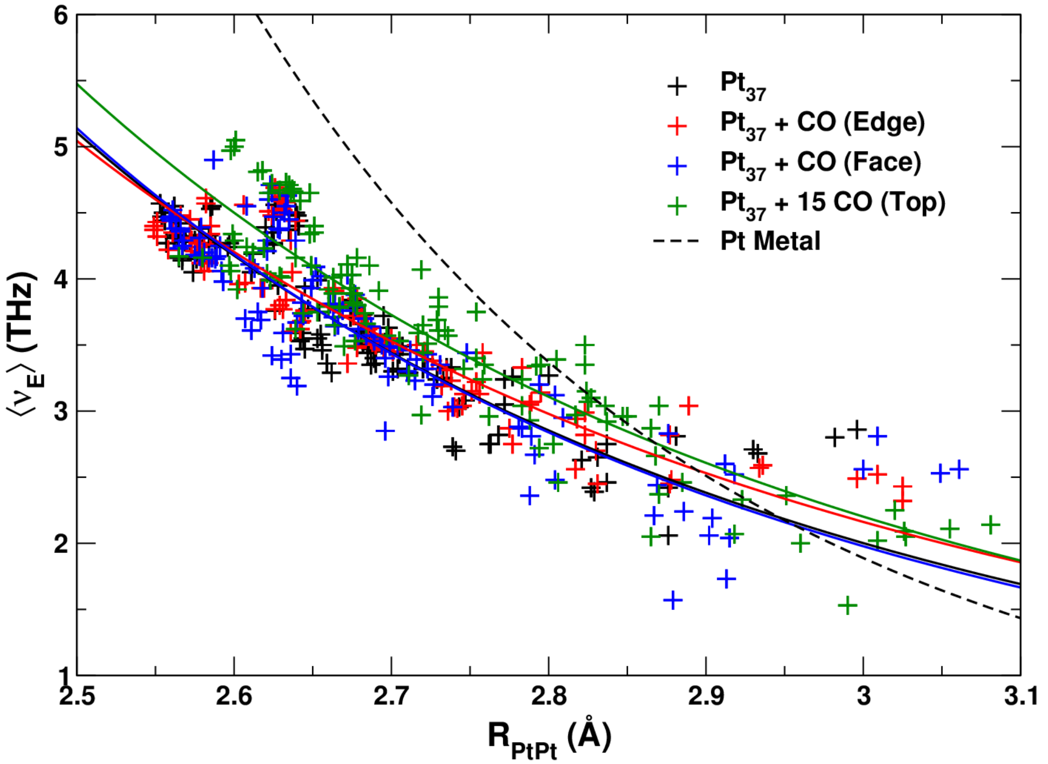
From Einstein Model Fit:

Expt: $\gamma \cong 5\pm2$

Pt_{37} on C:

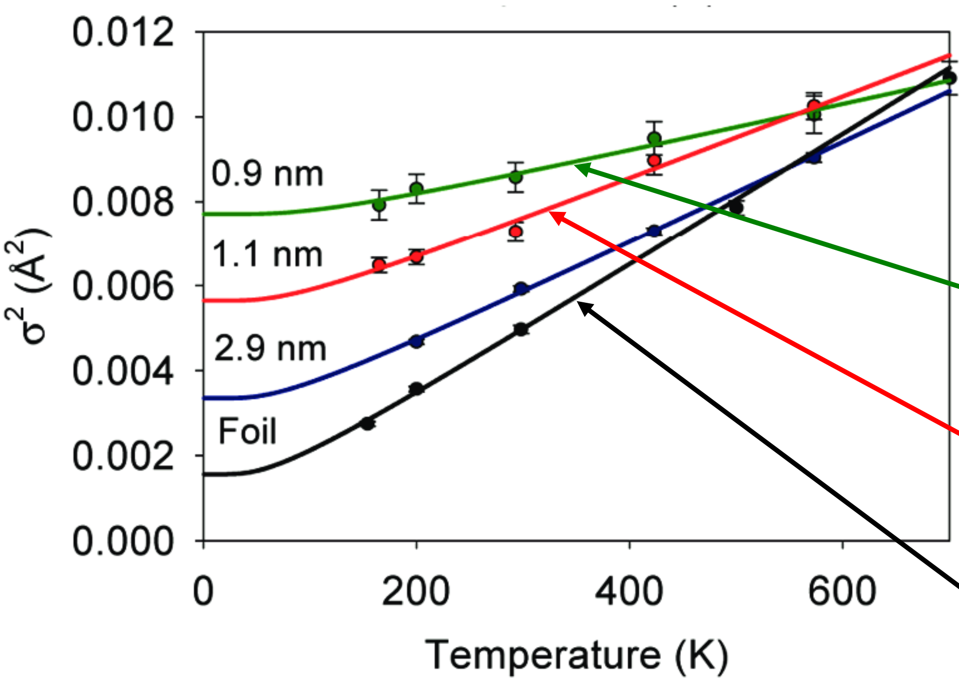
From Vib. Component:

$\gamma \cong 1.7$



What is the origin of this discrepancy?

The Problem: Anomalous Bond Strengths Einstein Model



Einstein Model with Static Disorder

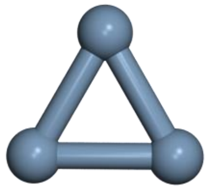
$$\sigma^2(T) = \sigma_S^2 + \frac{h}{8\pi^2\mu}\frac{1}{\nu_e}\coth\left(\frac{h\nu_E}{2k_BT}\right)$$

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

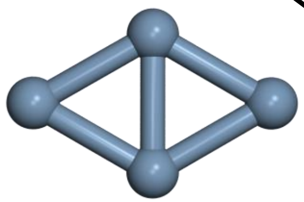
1.1 nm NPs:
$\nu_E \cong$ 4.6 THz

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

This Talk:

"The Mystery of the Superstrong Pt Nanoparticles"

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

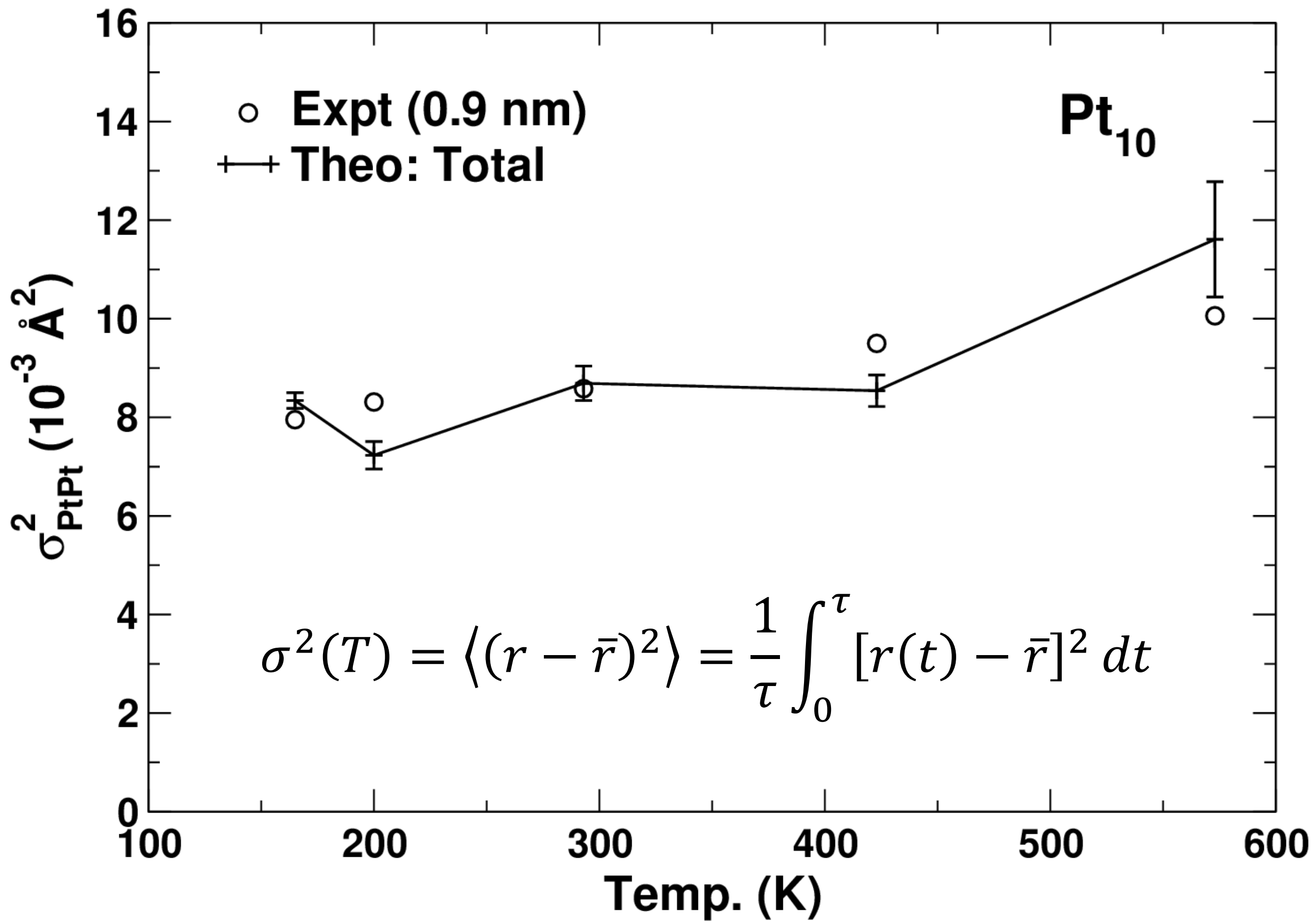
MD Setup:

- 6 initial conditions
- 20 ps runs:
  - 10 ps thermalization
  - 10 ps analysis
- 3 fs time-step
- Nosé-Hoover thermostat

Method:

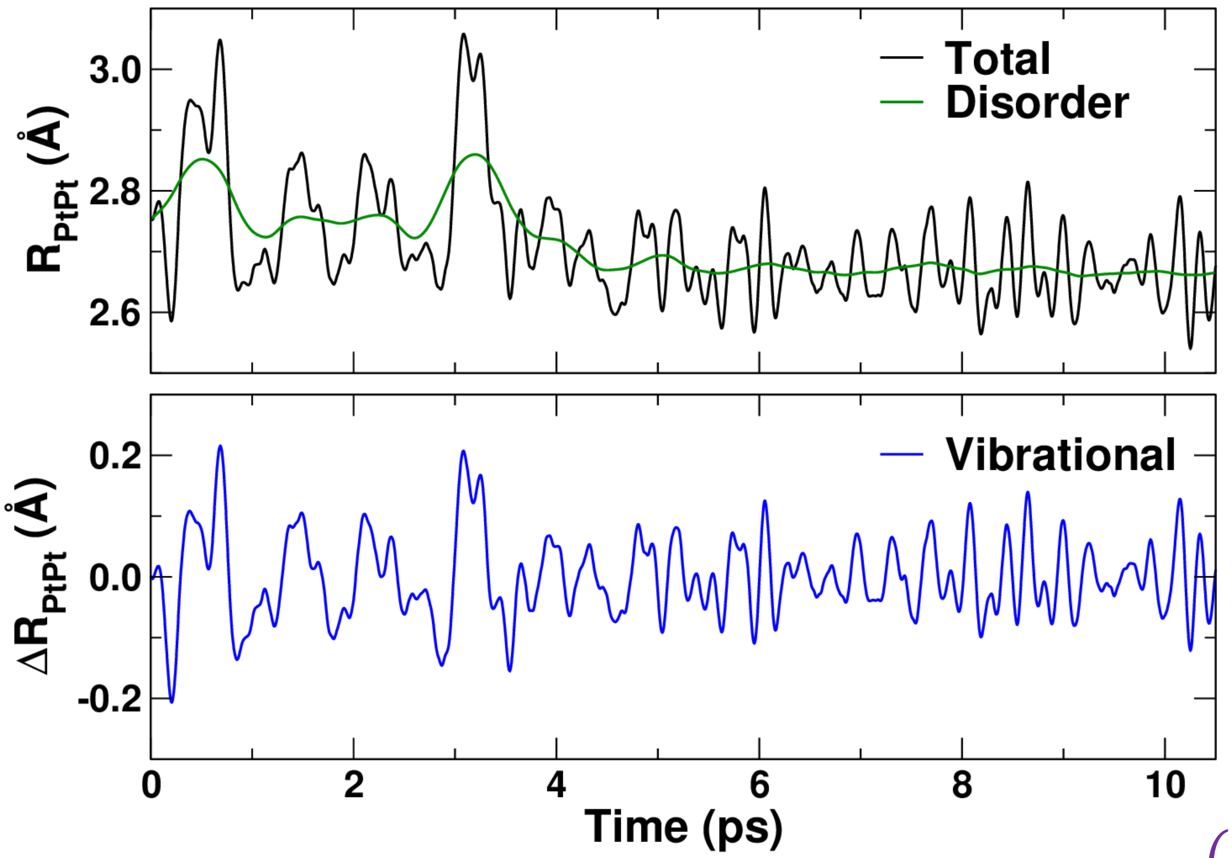
- PBE XC functional
- US PPs, 297 eV cutoff
- VASP

Total Mean Square Relative Displacement (MSRD)



Reasonable agreement between theory and expt.

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

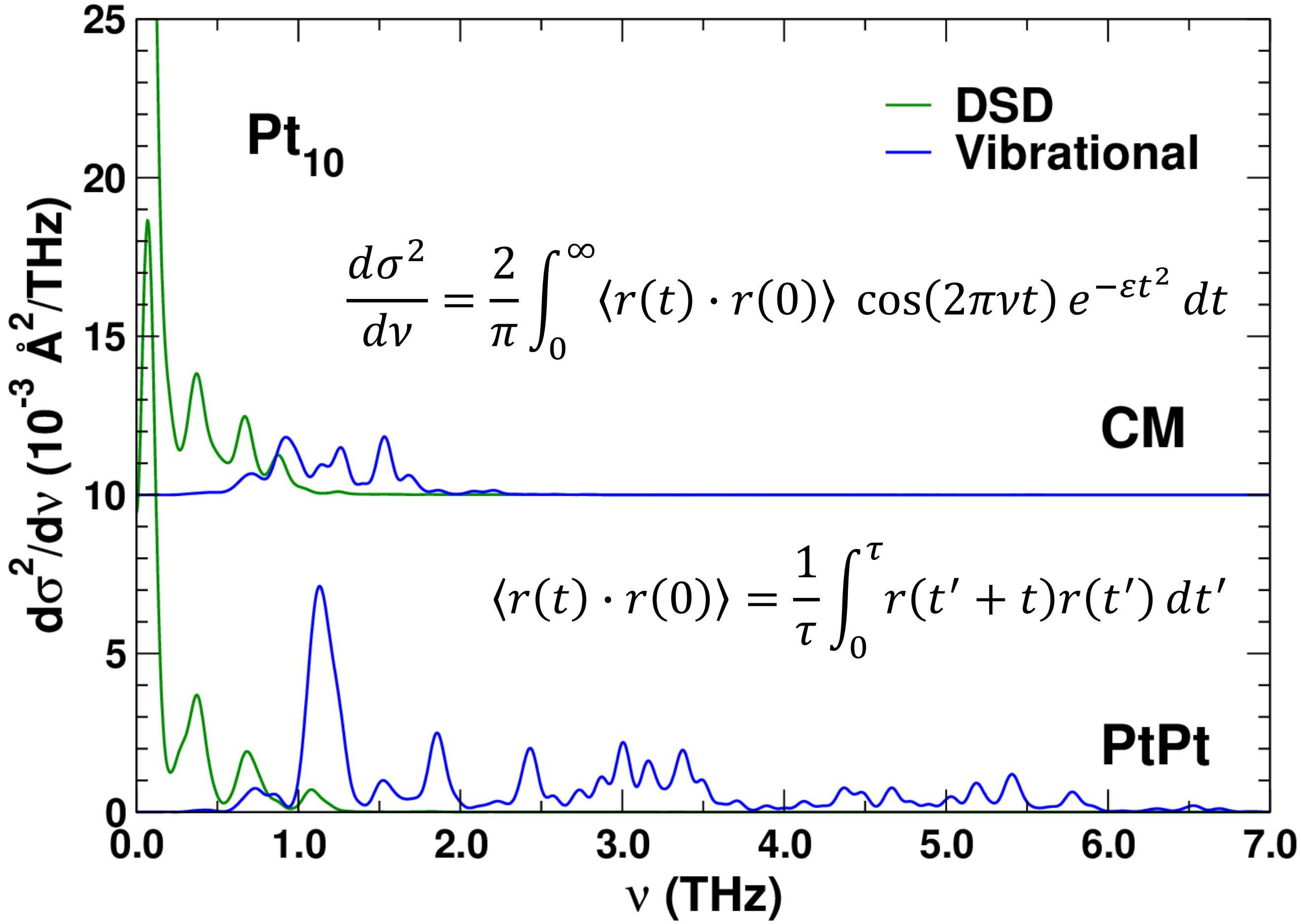


$$r_L(t) = \int_{-\infty}^{+\infty} r(\tau) F(t-\tau)\, d\tau$$

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

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

Power Spectra of CM and Pt-Pt Dynamics

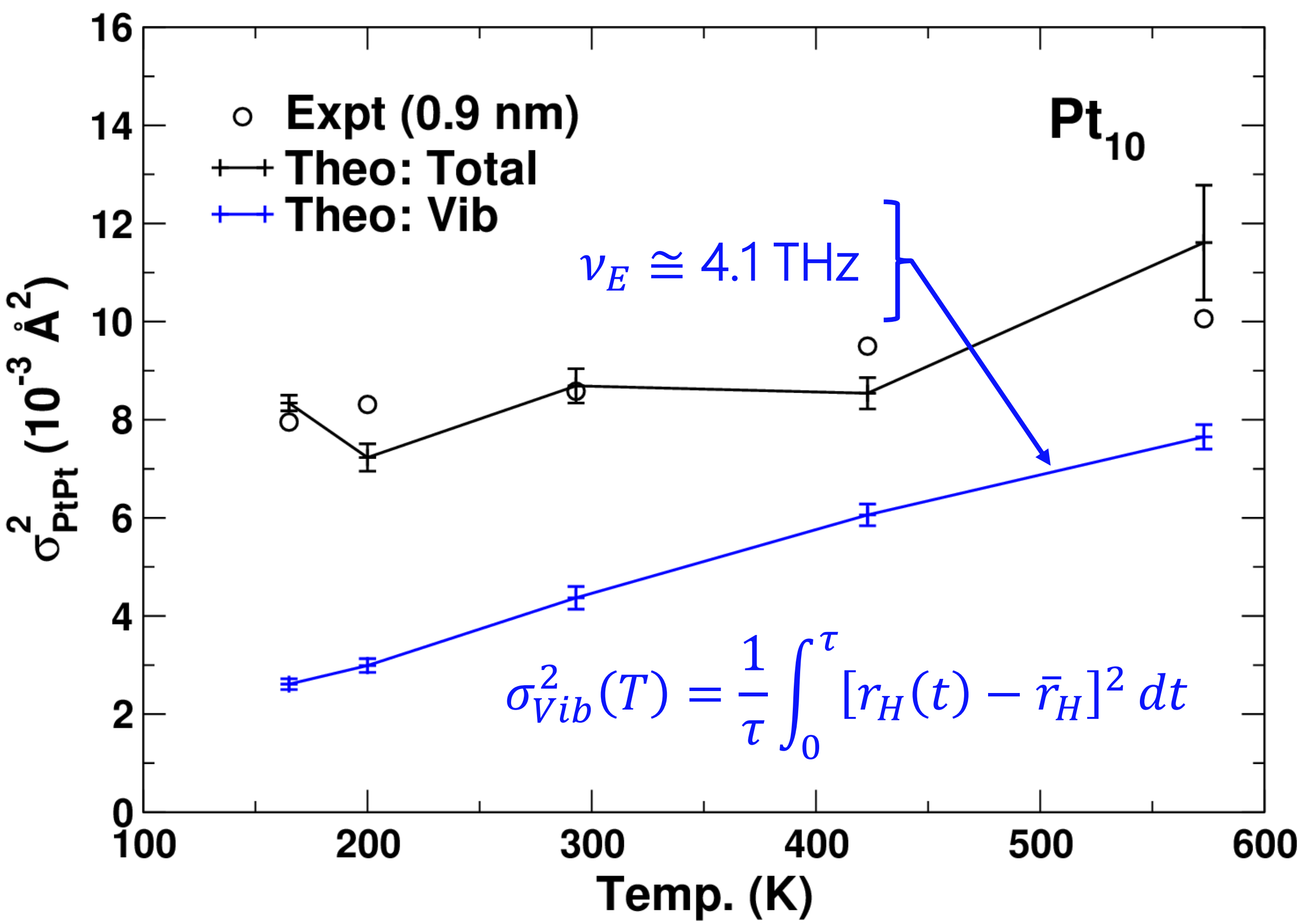


$$\frac{d\sigma^2}{d\nu} = \frac{2}{\pi}\int_0^\infty \langle r(t)\cdot r(0)\rangle\ \cos(2\pi\nu t)\, e^{-\varepsilon t^2}\, dt$$

$$\langle r(t)\cdot r(0)\rangle = \frac{1}{\tau}\int_0^\tau r(t'+t)r(t')\, dt'$$

Nice separation of slow and fast dynamic regimes

Vibrational MSRD

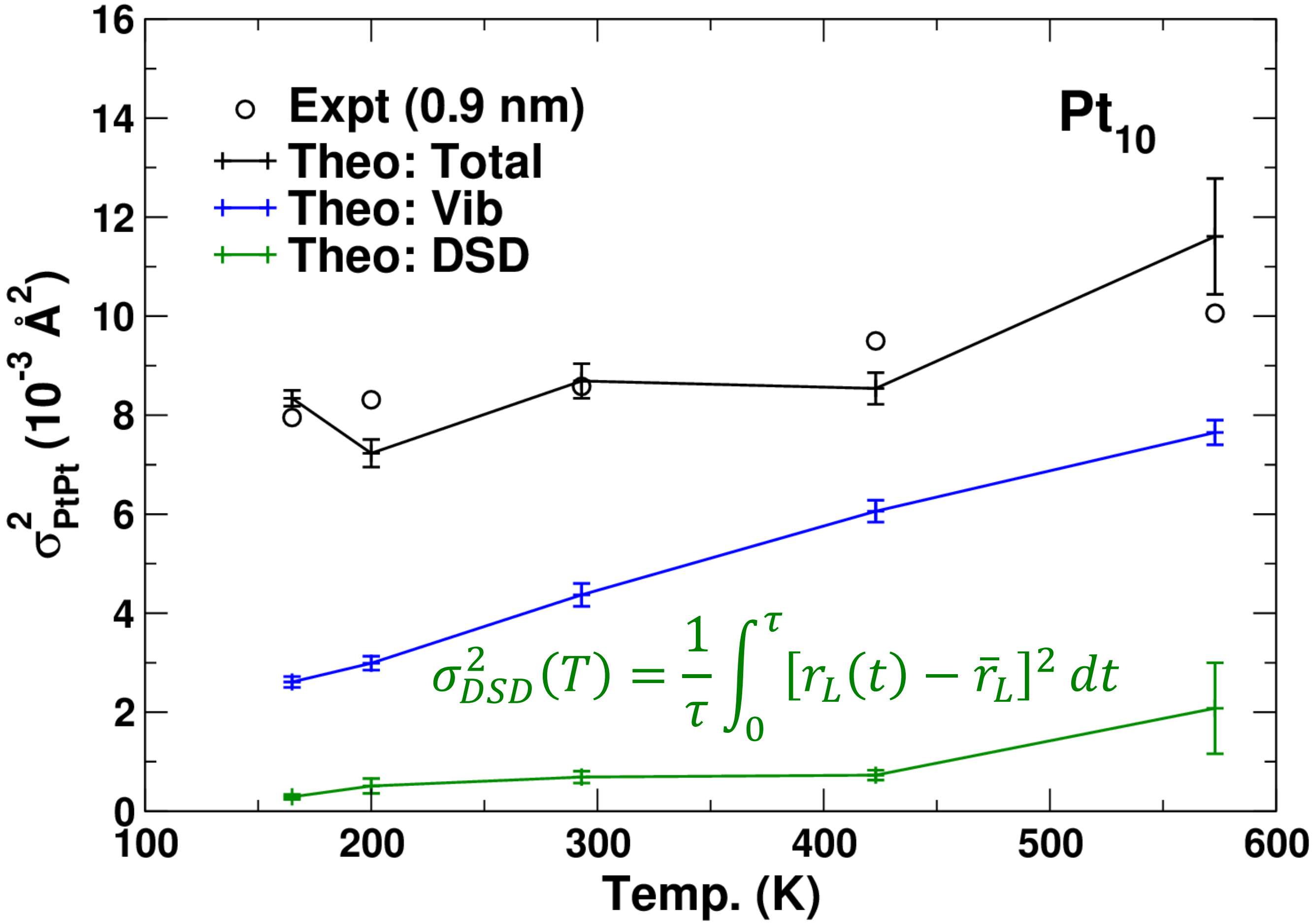


0.9 nm NPs:
$\nu_E \cong 6.3$ THz

Pt Foil:
$\nu_E \cong 3.8$ THz

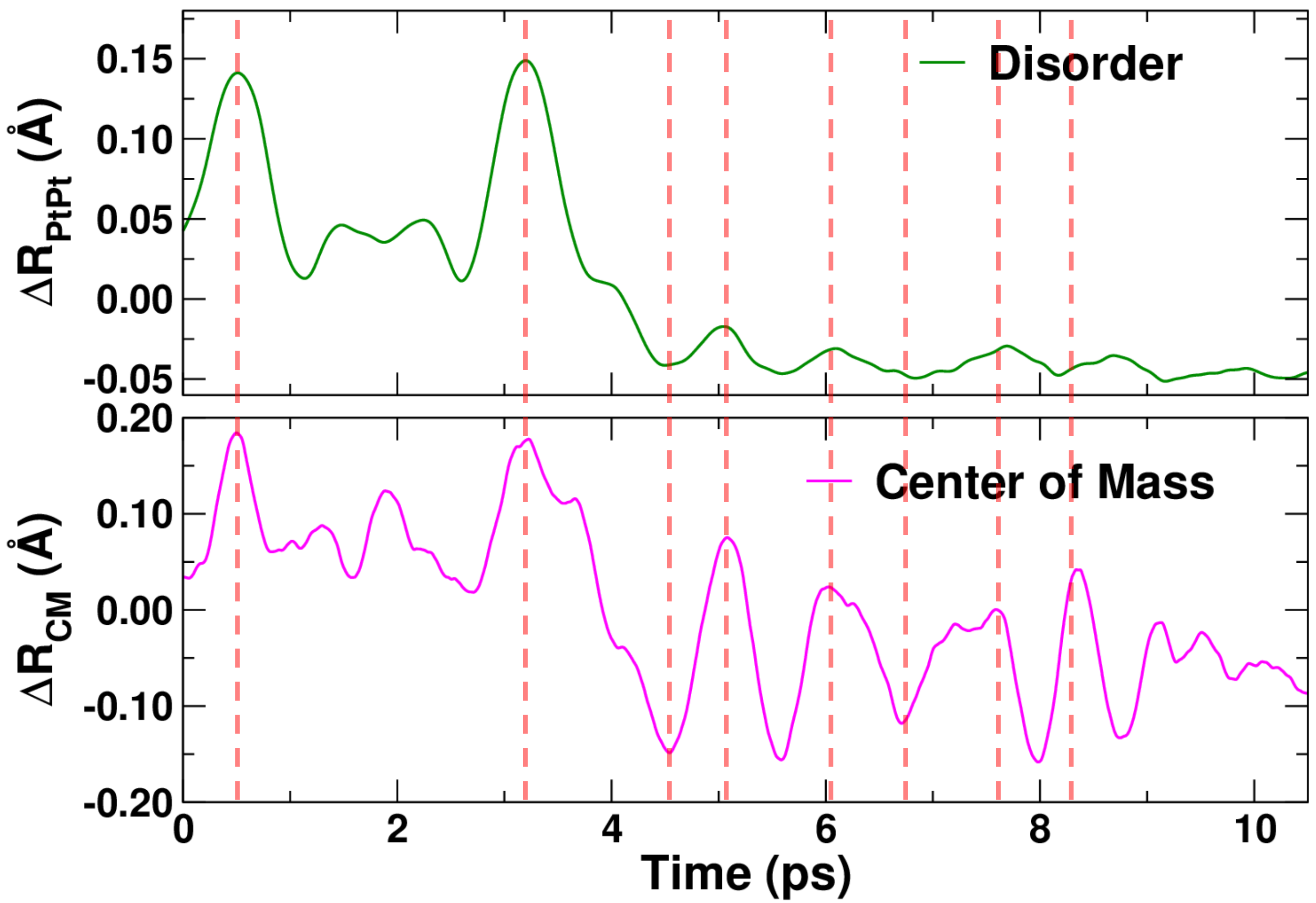
Normal linear vibrational behavior

Dynamic Structural Disorder (DSD) MSRD



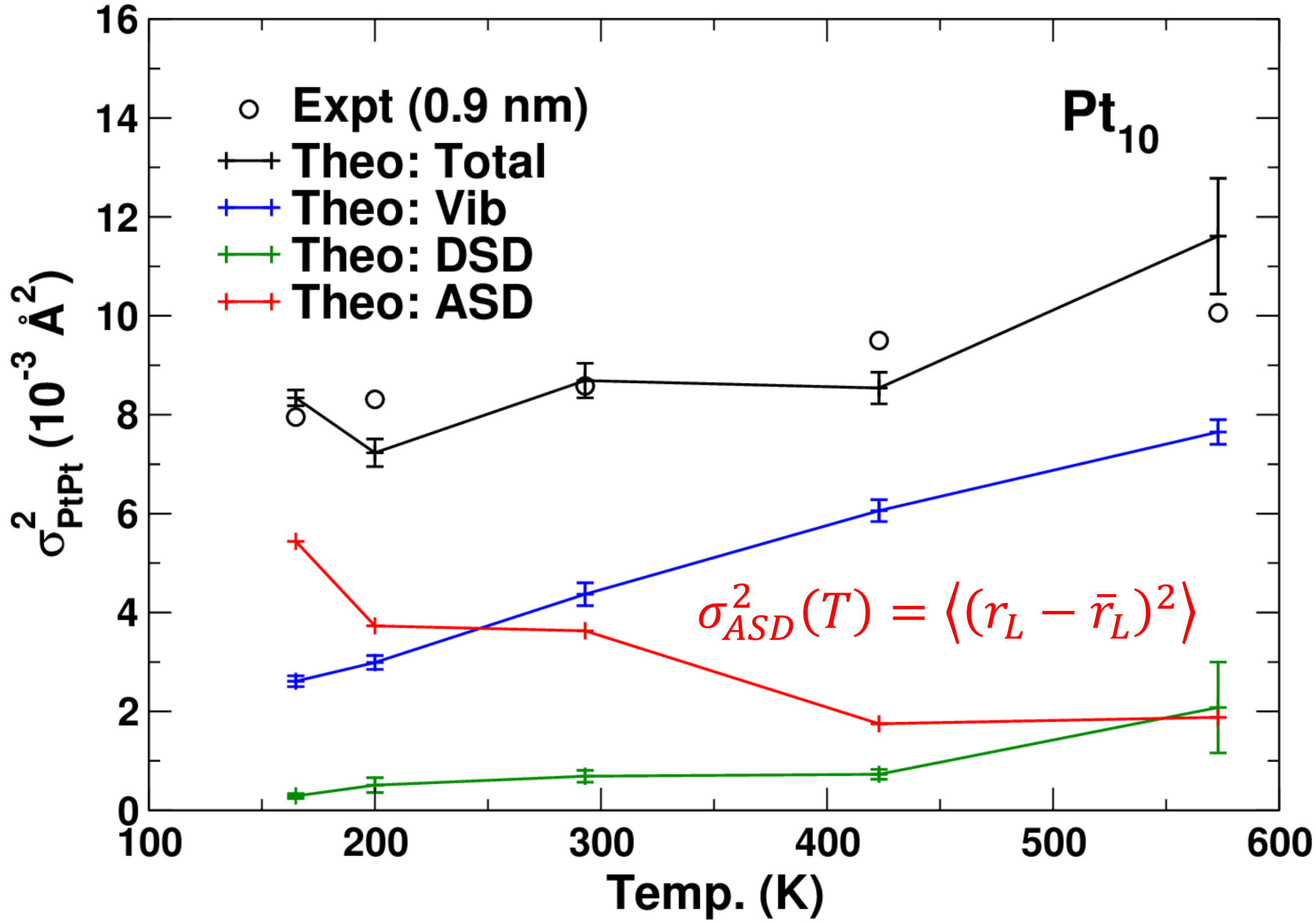
Normal linear behavior: Low frequency quasi-harmonic modes

DSD: Correlation Between CM and Pt-Pt Dynamics



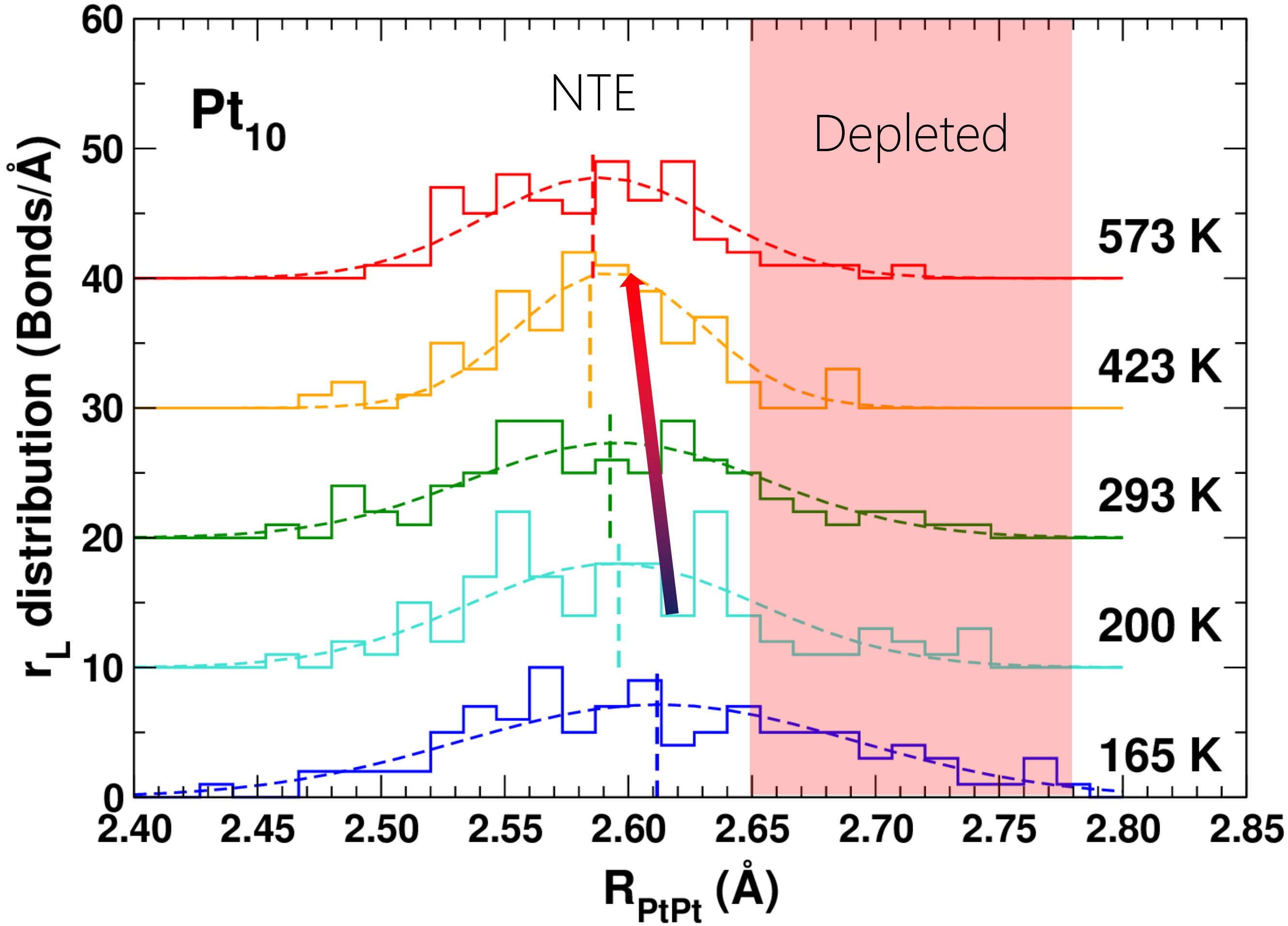
Moderate/strong correlation between CM libration and Pt-Pt bonds

Anomalous Structural Disorder (ASD) MSRD



Anomalous quasi-static disorder: Causes apparent strengthening

Temp. Dep. Anomalous Bond Distributions ($\sigma^2_{ASD}(T)$)



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:

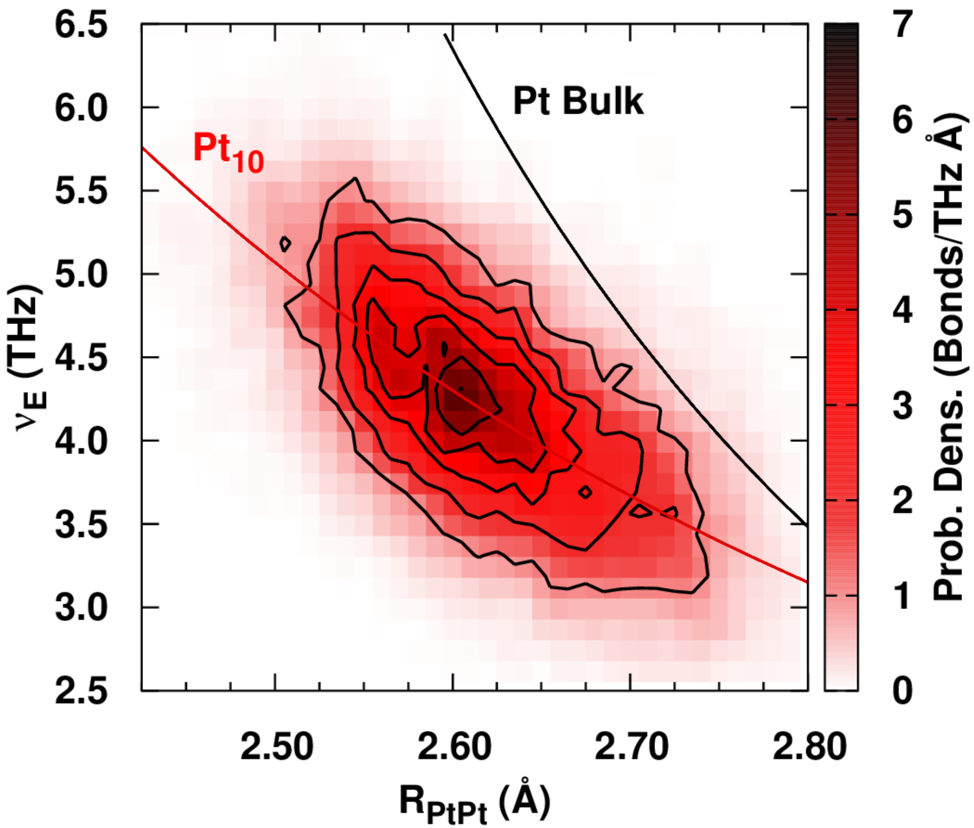
Expt: $\gamma \cong 5\pm2$

Theo: $\gamma \cong 4\pm2$

From Vib. Component:

Theo (Sta.) $\gamma \cong 1.7$

Theo (MD) $\gamma \cong 1.4 \pm 0.2$



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?: $\gamma_{NP} > \gamma_{Bulk}$

Dynamic anomalies in the nanoscale structure and disorder of supported metal nanoparticles

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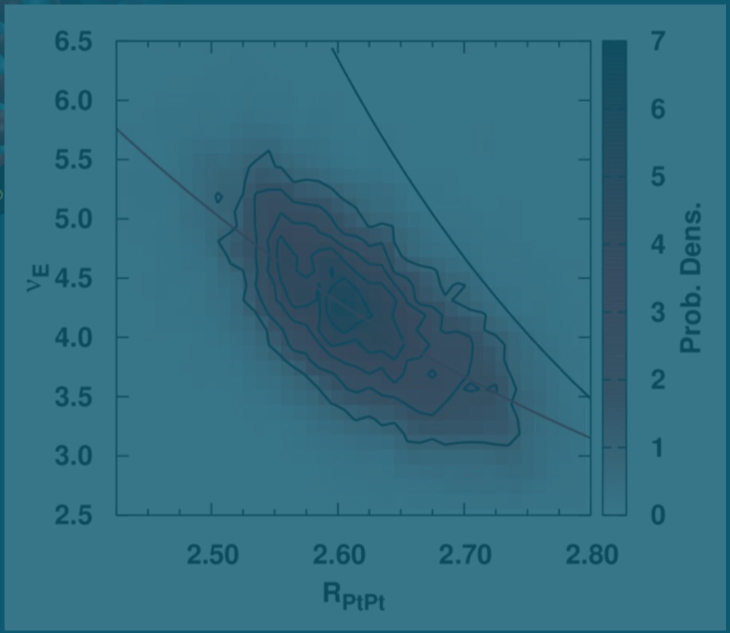

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