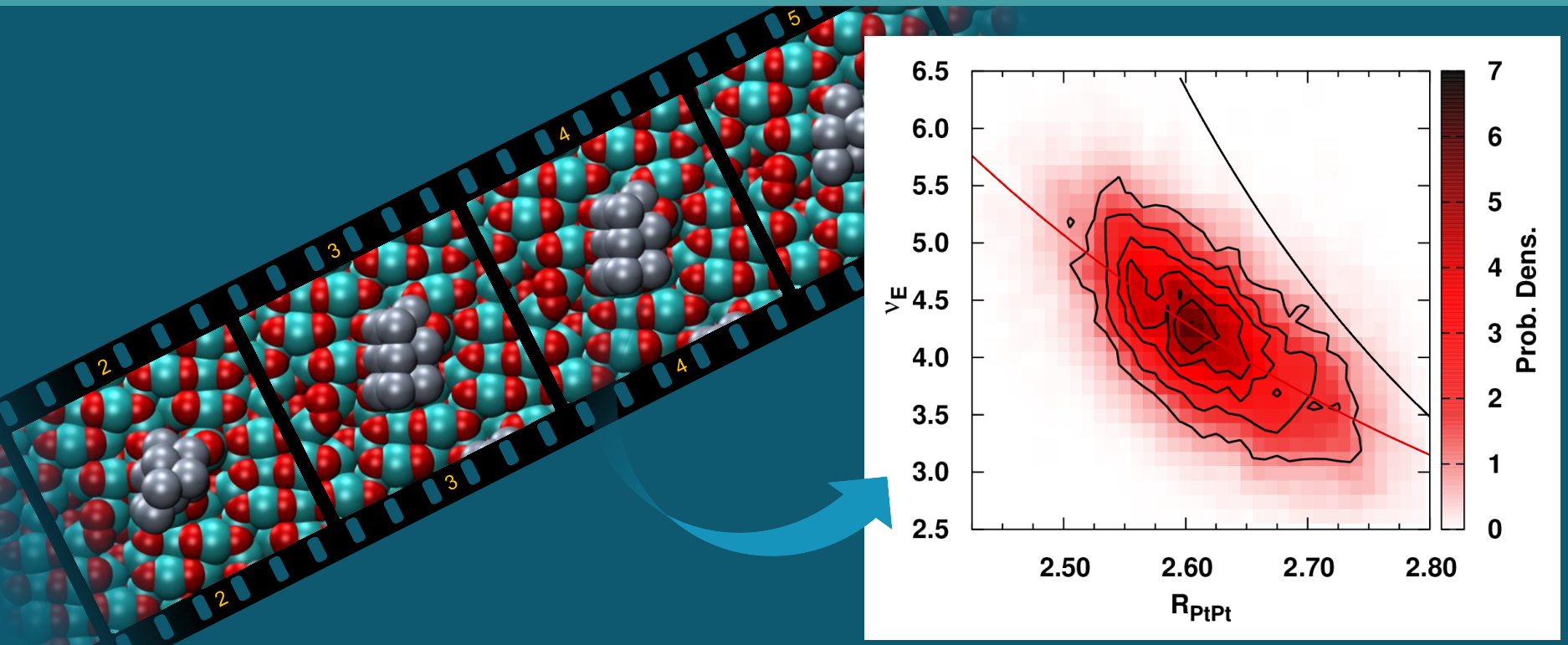
Exploring the anomalous behavior of metal nanocatalysts with finite temperature AIMD and x-ray spectra

F.D. Vila



UNIVERSITY OF WASHINGTON

DOE grant DE-FG02-03ER15476
With computer support from DOE - NERSC.

Importance of Theoretical Simulations

Why Theory?

- Access to structural and electronic properties
- Separation of local and global domains

In particular, why Ab Initio Molecular Dynamics (AIMD)?

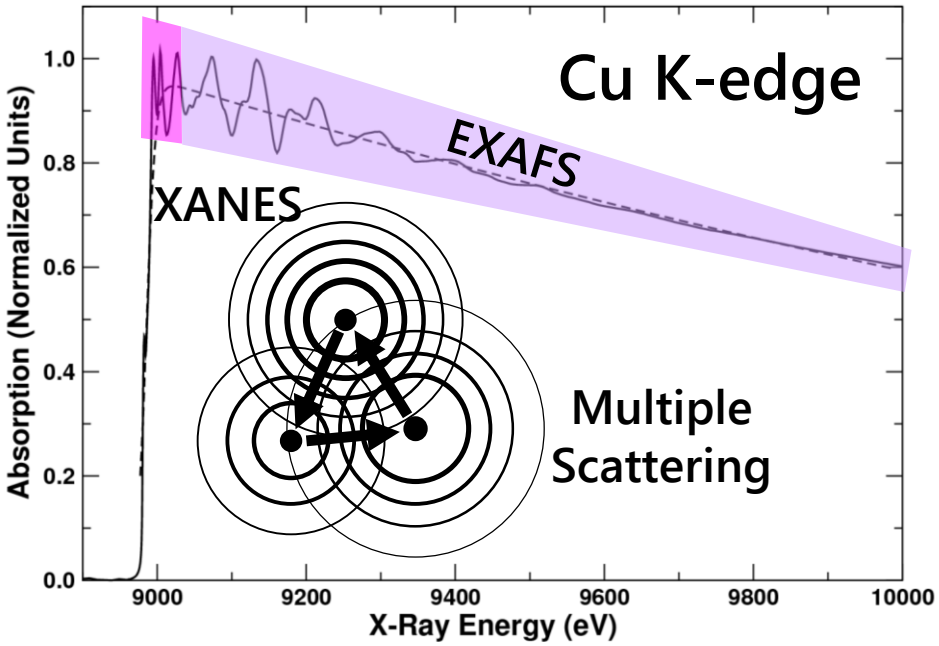
- Importance of non-equilibrium states
- Access to time-domain

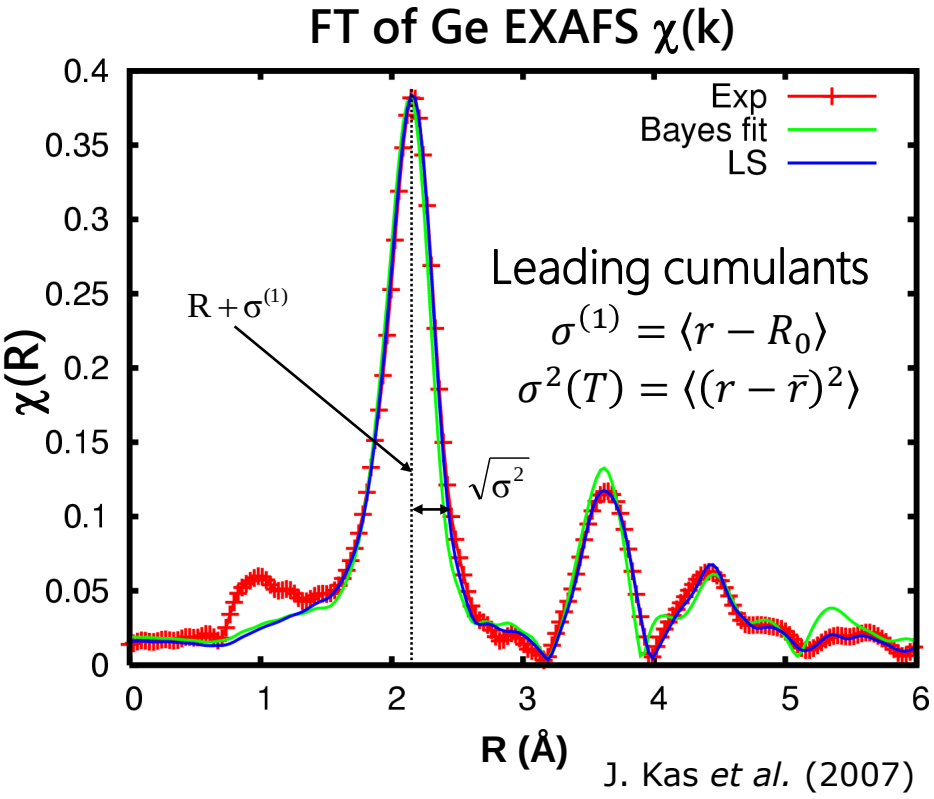
Outline:

- Importance of disorder in catalysis
- Dynamics and electronic structure in XANES
- Dynamics and structural disorder in EXAFS

Importance of Disorder in Catalysis

XAFS: Access to Average Local Properties



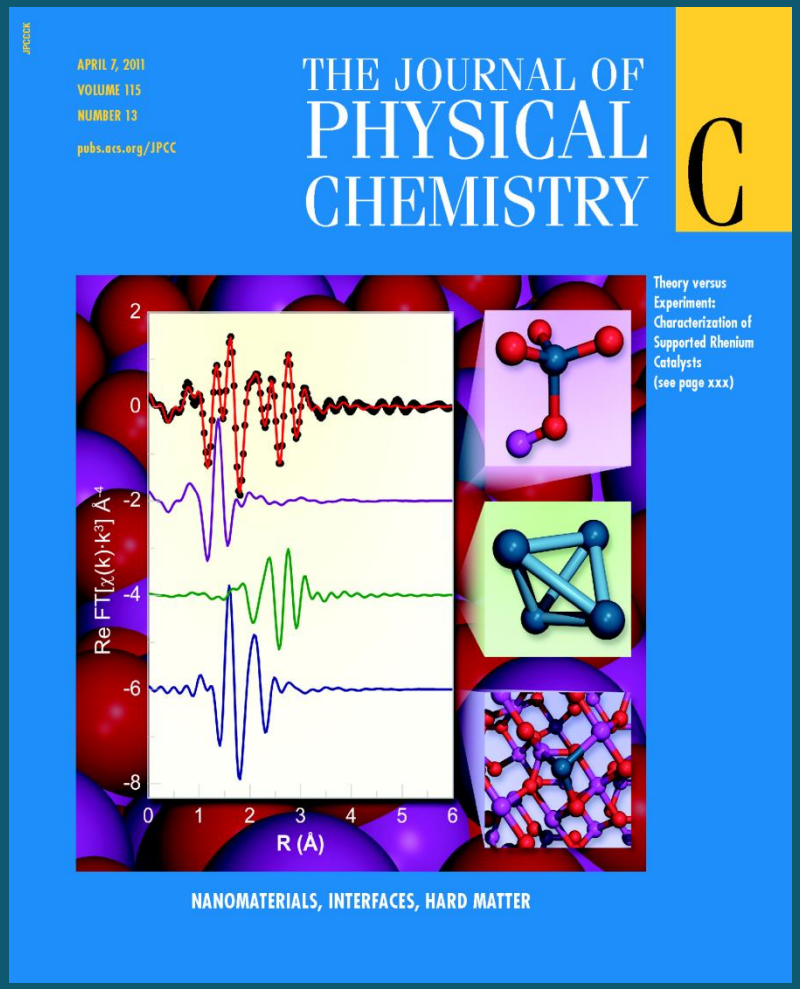


J. Kas *et al.* (2007)

XANES: Access to average electronic structure

EXAFS: Access to average bond distances and disorder

Early Success: EXAFS of Highly Dispersed Catalyst



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 γ-Al_2O_3

Early Success: Explaining Anomalous NP Properties

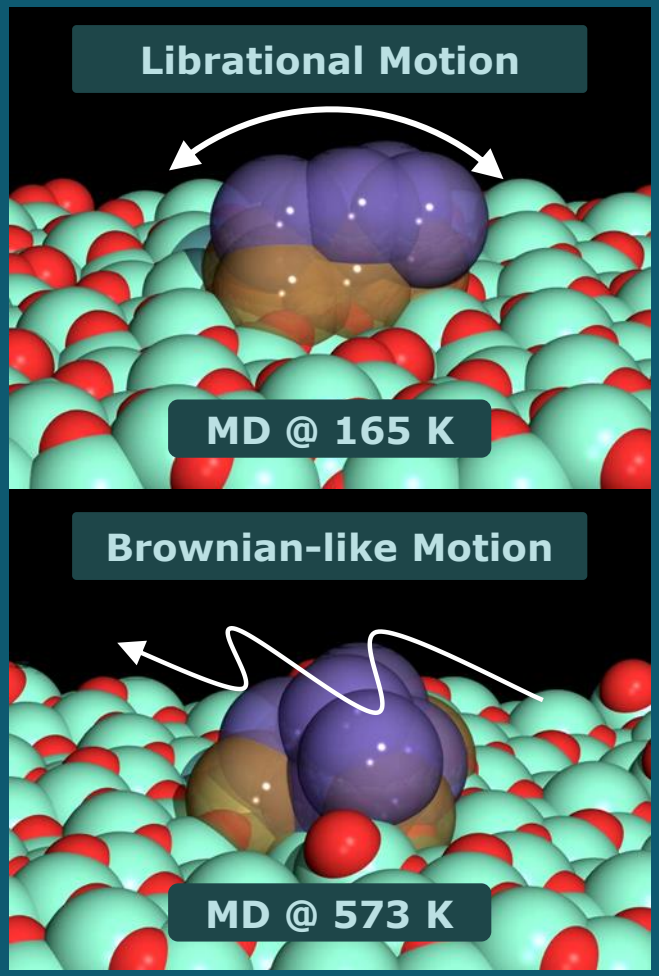
Dynamic structure in supported Pt nanoclusters: Real-time density functional theory and x-ray spectroscopy simulations

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).



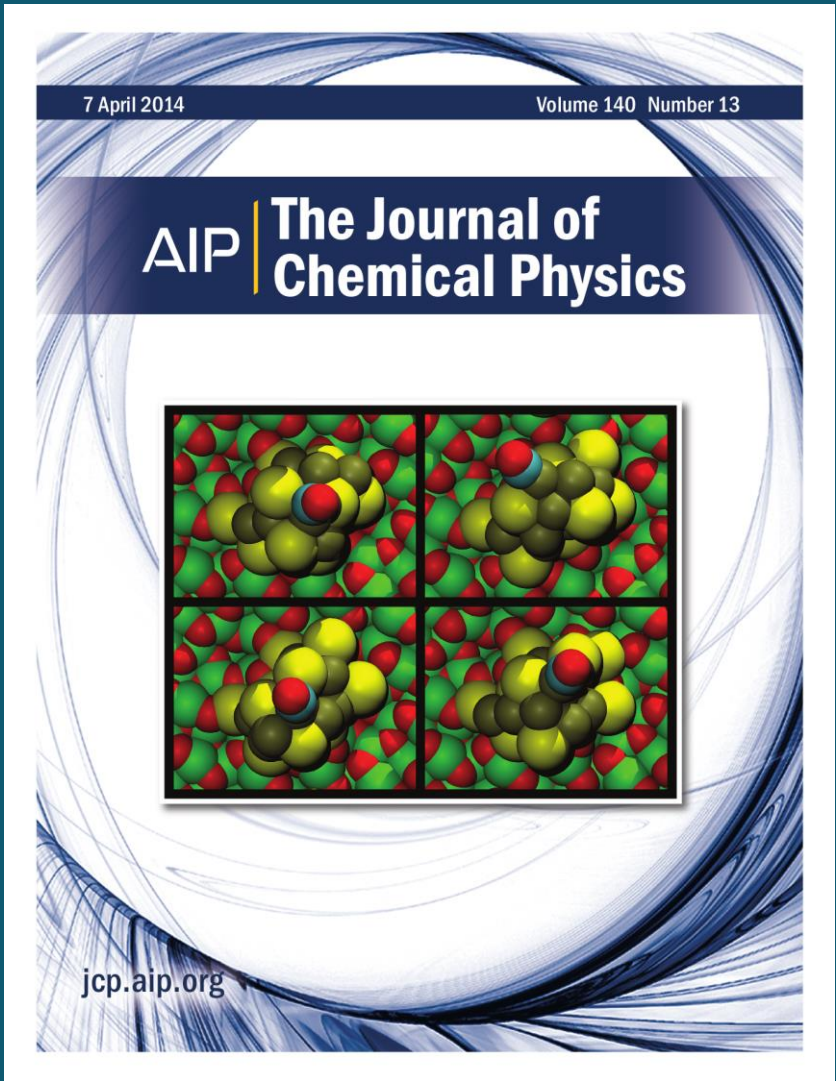
Pt_{10} on γ-Al_2O_3

New Concept: Dynamic Structural Disorder (DSD)

DSD drives:

- Fluctuating bonding
- Cluster mobility
- Charge separation
- Layering and segregation
- Adsorbate dynamics (right)
- Adsorbate reactivity

Inhomogeneity

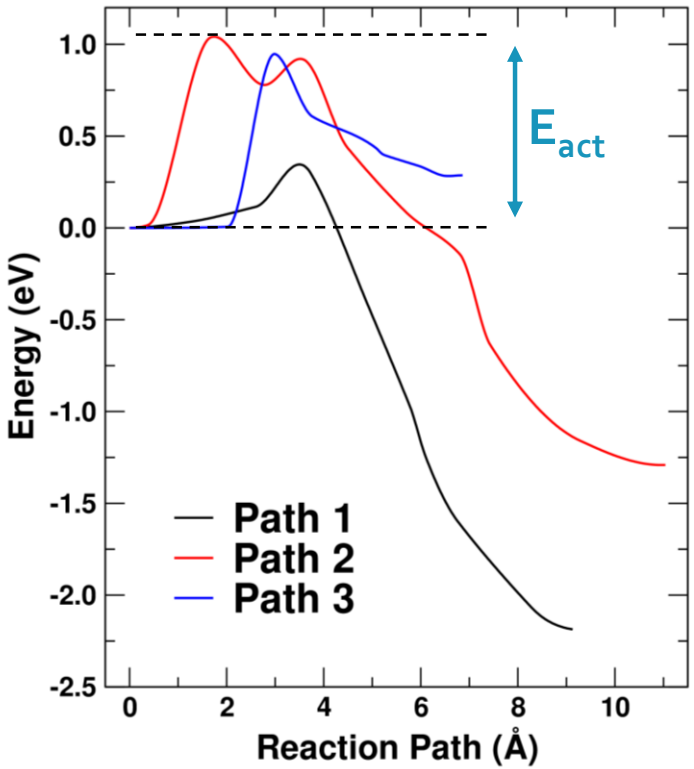


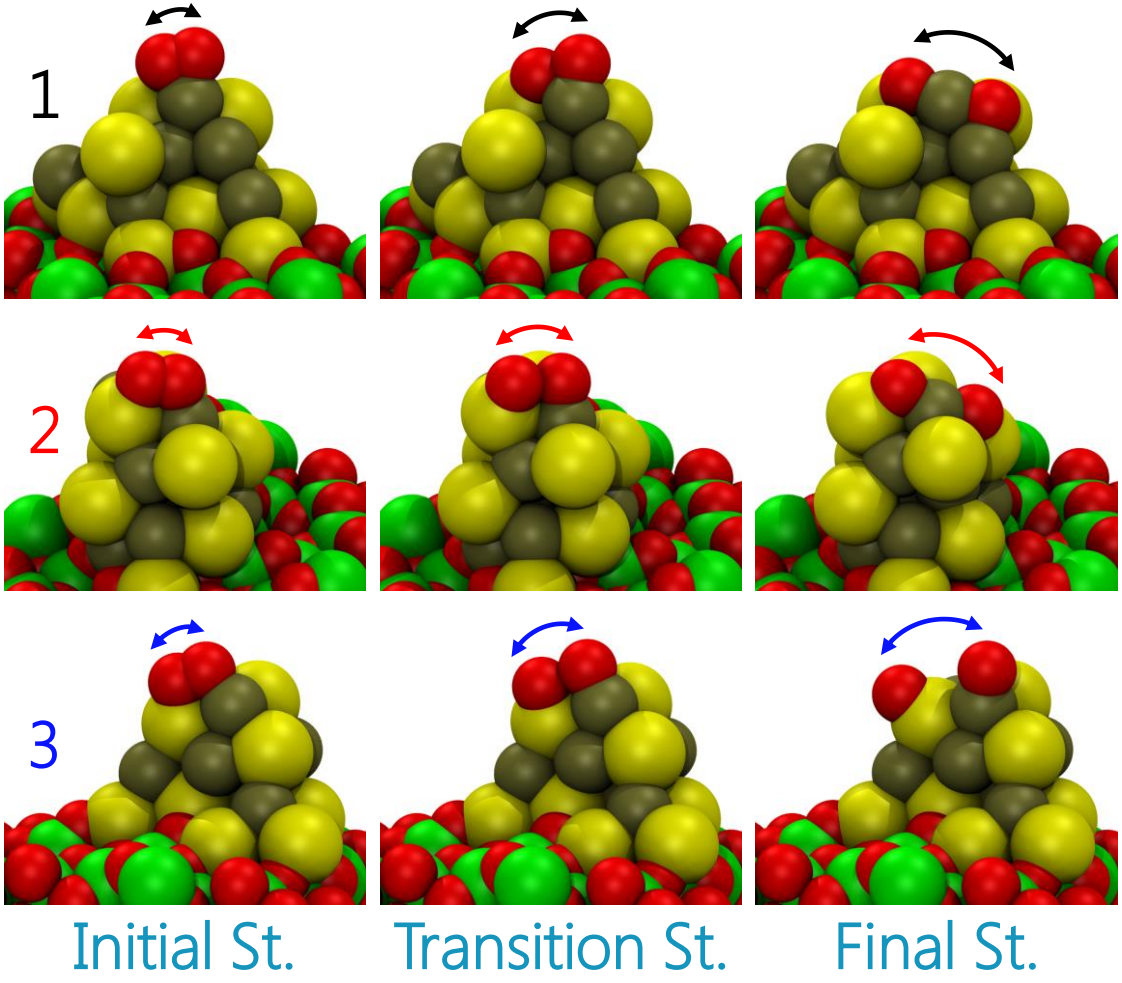
CO dynamics on $Pt_{10}Sn_{10}$

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

Disorder Affects Reactivity

O_2 dissoc. on $Pt_{10}Sn_{10}$

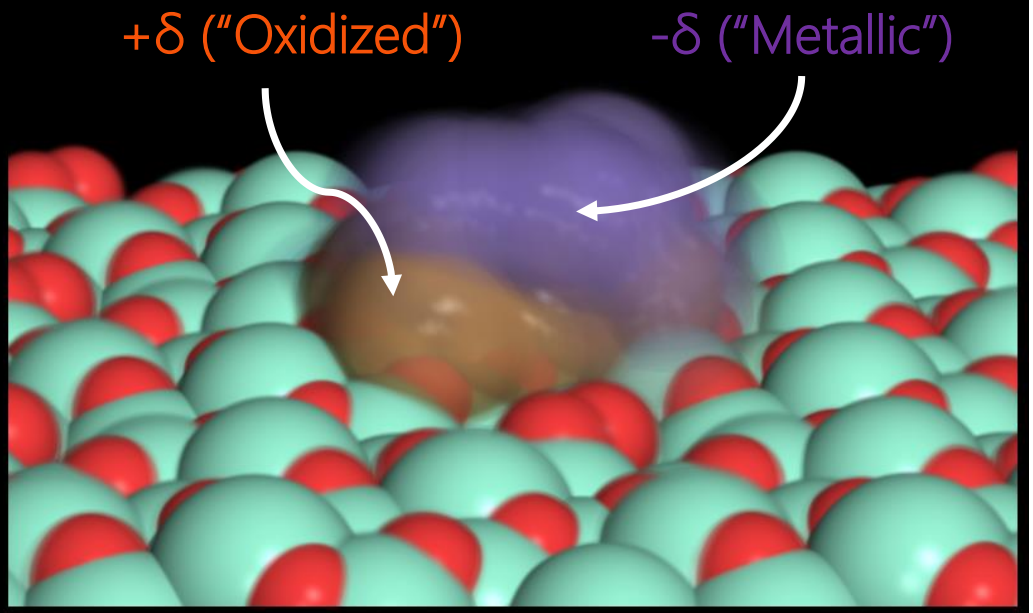




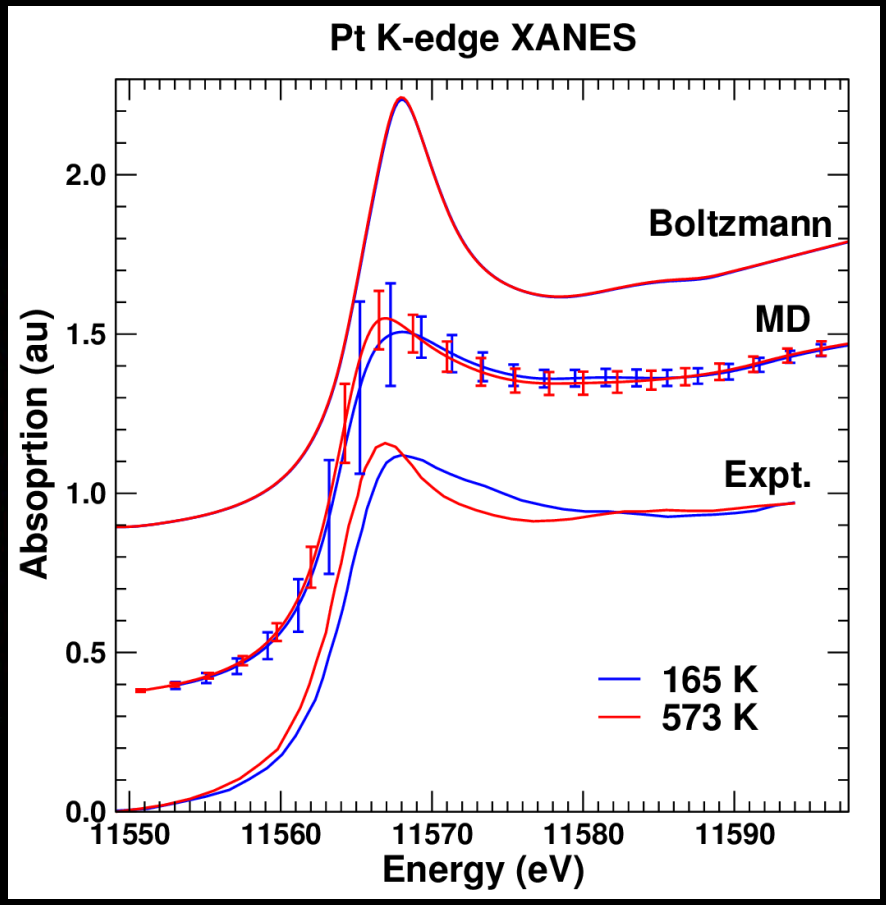
Large differences in activation energy (E_{act})
Reaction path depends on DSD

Dynamics and Electronic Structure in XANES

Theory: Static Simulations are Inadequate



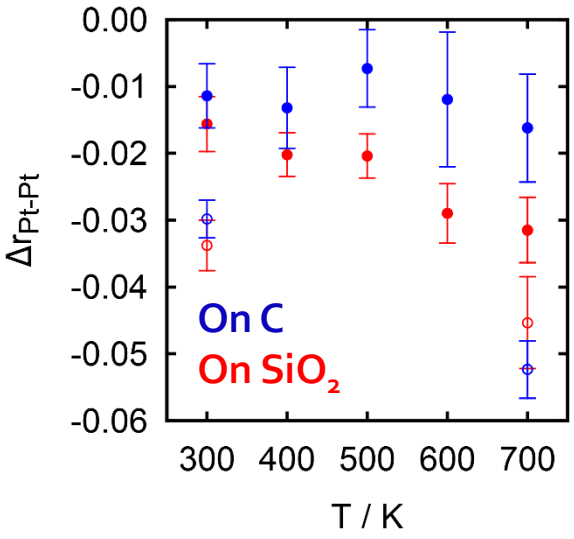
Pt_{10} on γ-Al_2O_3 @ 165 K

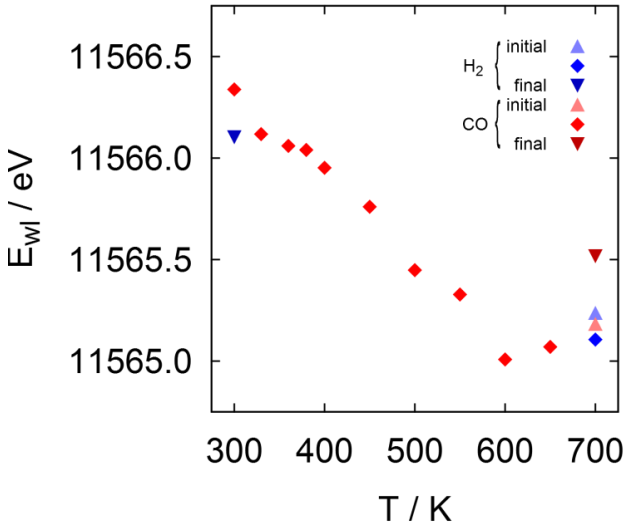


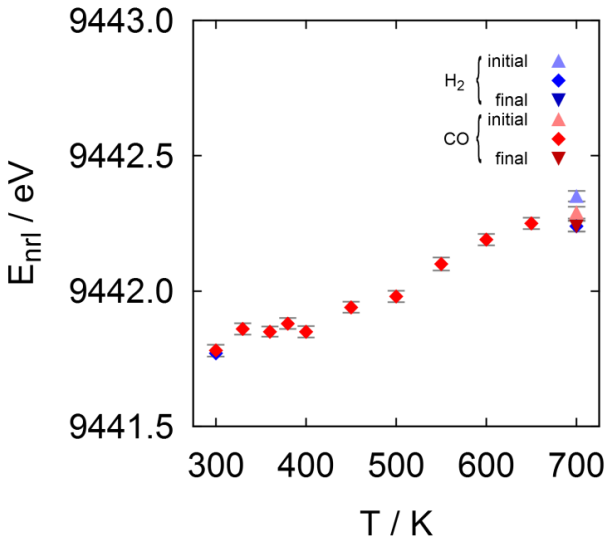
MD simulations reproduce experiment

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

Inhomogeneity in Well-defined(?) Nanoparticles



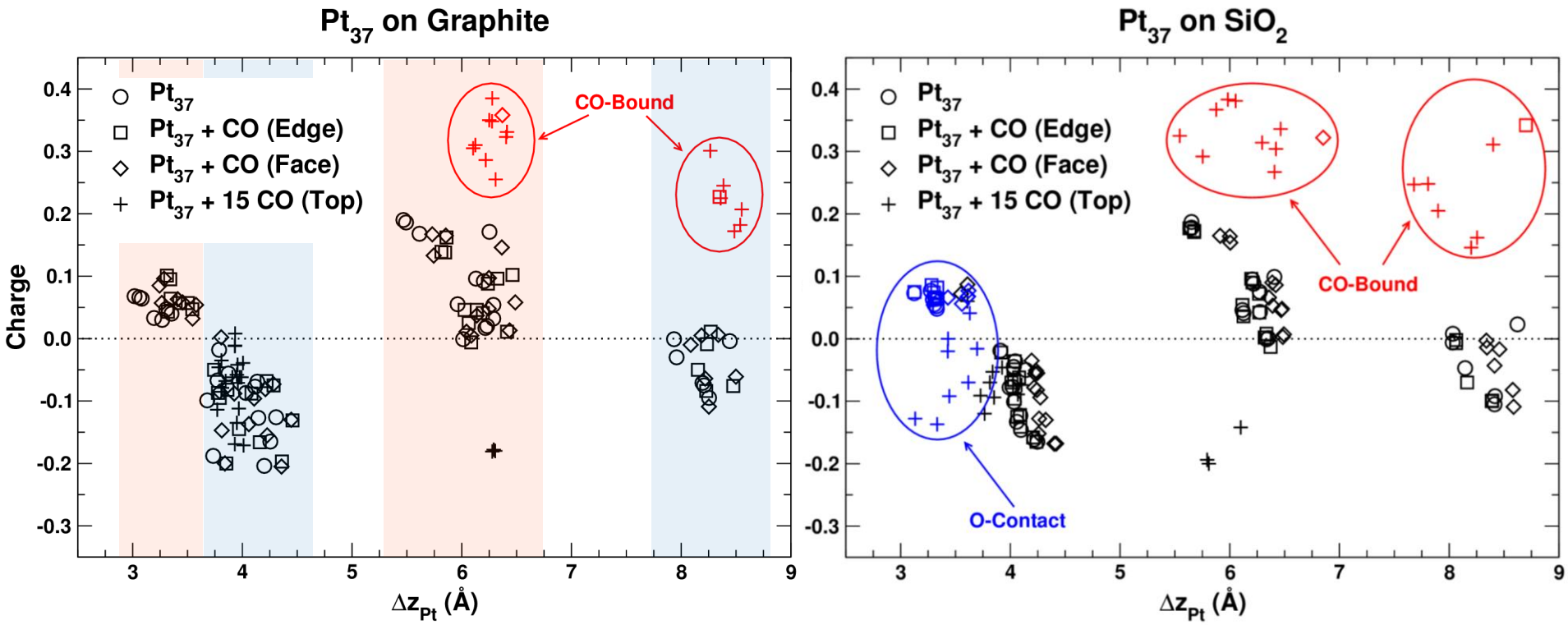




Bond contraction with heating/desorption
White line: redshift, Emission line: blueshift
EXAFS measurements: Predict truncated cuboctahedron Pt_{37}

Hypothesis: Both phenomena related to desorption
Is inhomogeneity important to these phenomena too?

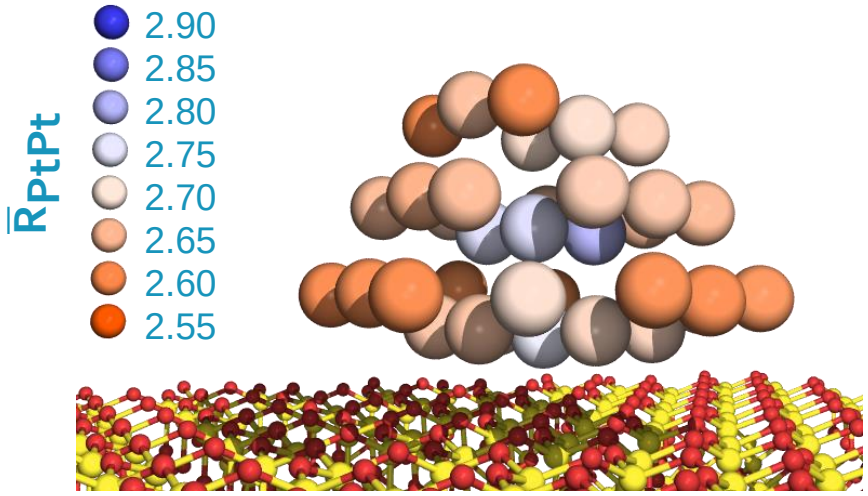
Charge Inhomogeneity

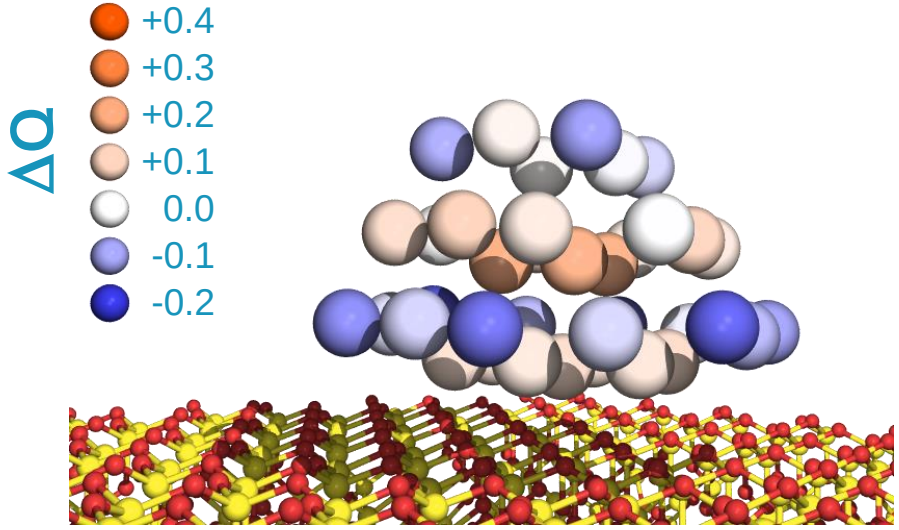


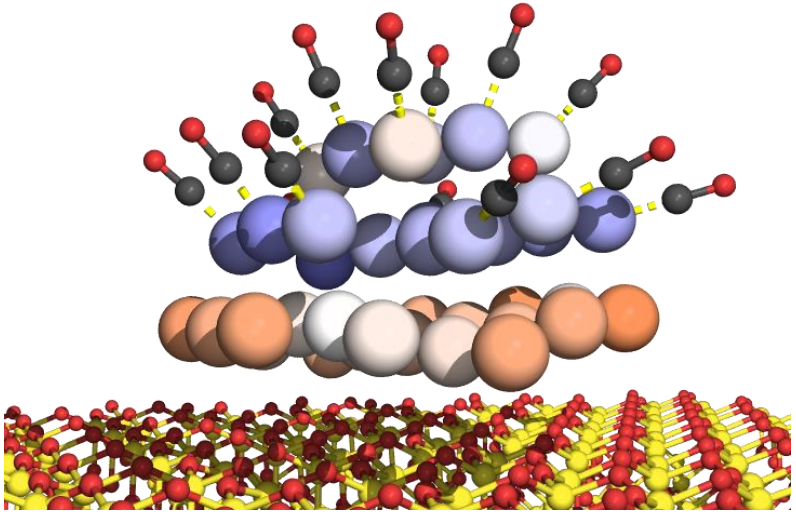
CO-bound Pt atoms loose 0.2-0.3e each

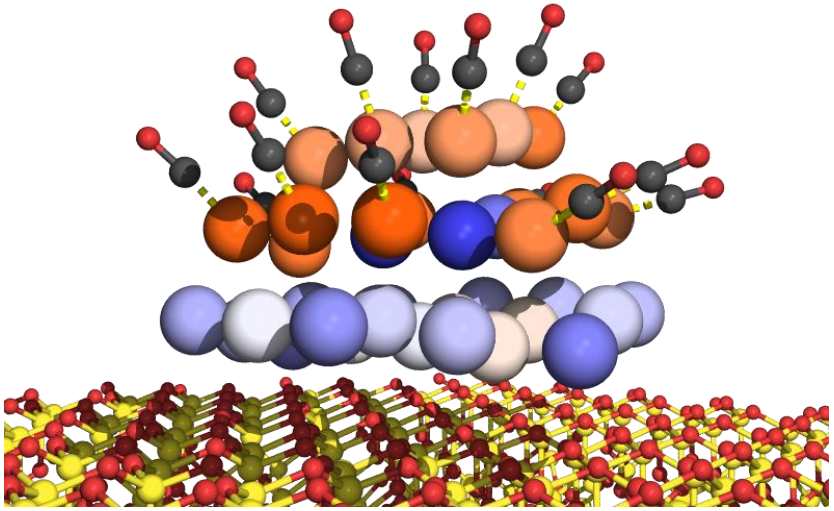
Layer charge alternation

Bond Length *vs* Charge Inhomogeneity

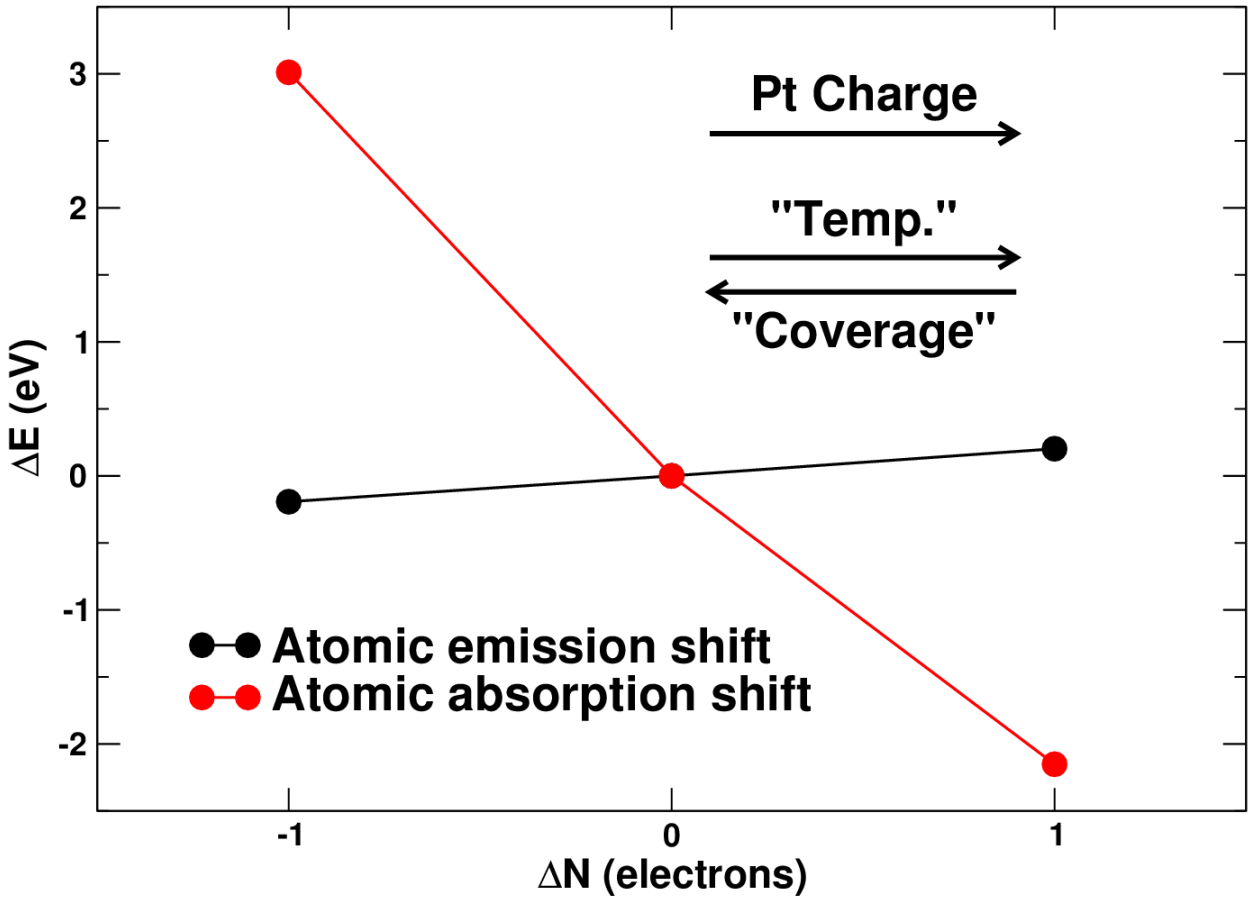








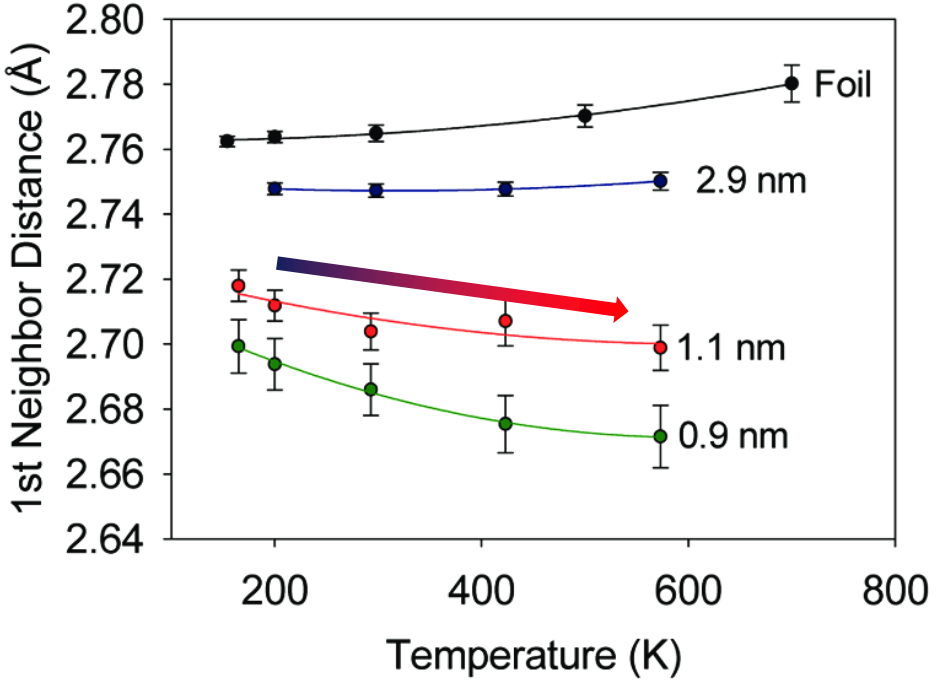
Atomic Edge Absorption and Core Emission Shifts

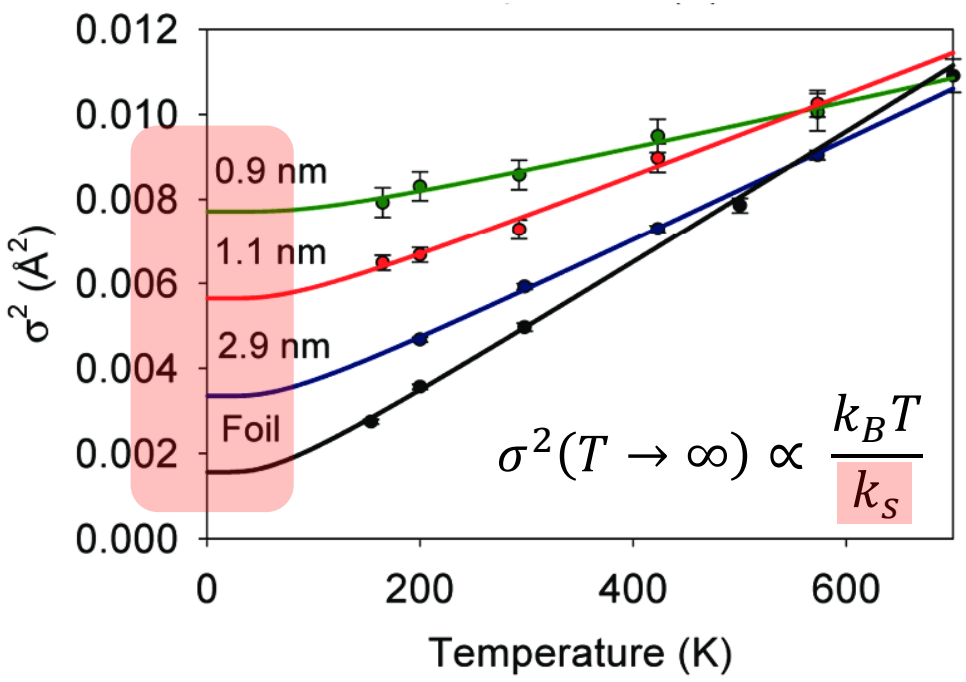


Opposite trends: Qualitatively reproduce experiment

Dynamics and Structural Disorder in EXAFS

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?

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

Pt metal:

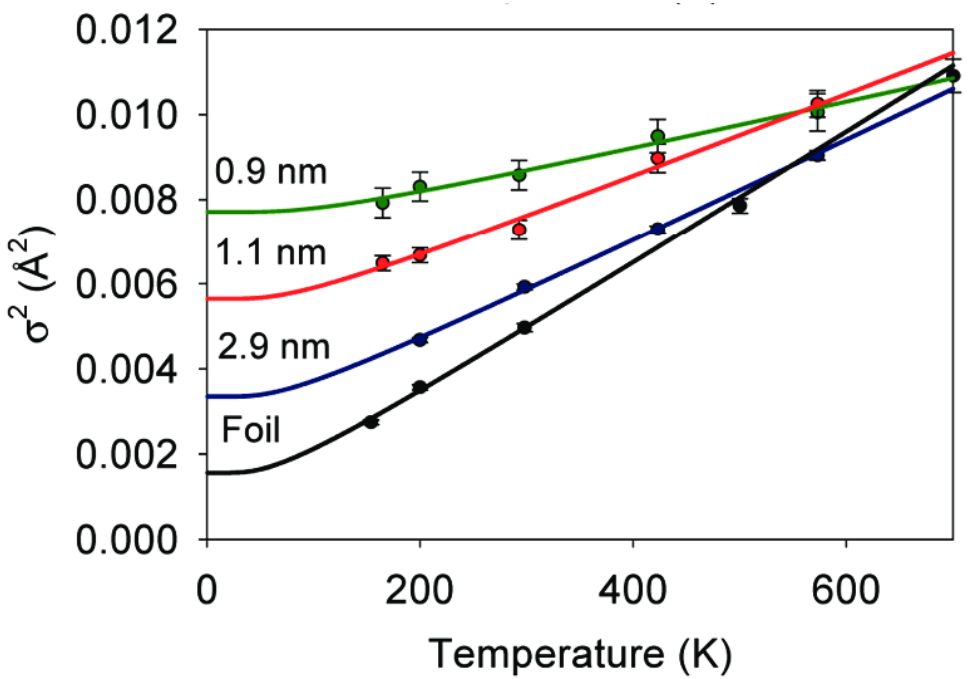
Expt: $\gamma = 2.7$

Theo: $\gamma = 2.8$

0.9-1.1 nm NPs:

From Einstein Model Fit:

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



Einstein Model with Static Disorder

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

Effective Grüneisen parameter larger in NPs than bulk

Anomalous Effective Grüneisen Parameter?

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

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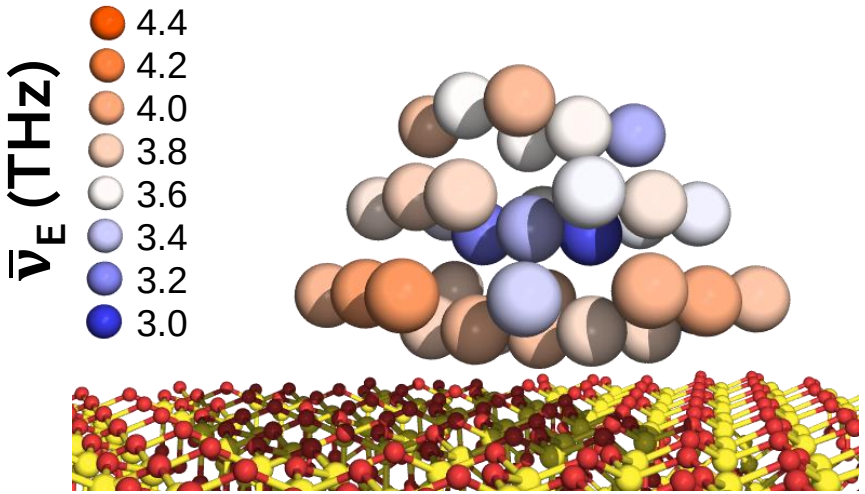

$$\rho_R(\omega) \cong \sum_{i=1}^{N} w_i \delta(\nu - \nu_i)$$

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

We can estimate from *R*-dependent PDOS

Anomalous Effective Grüneisen Parameter?

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Theo: $\gamma = 2.8$

0.9-1.1 nm NPs:

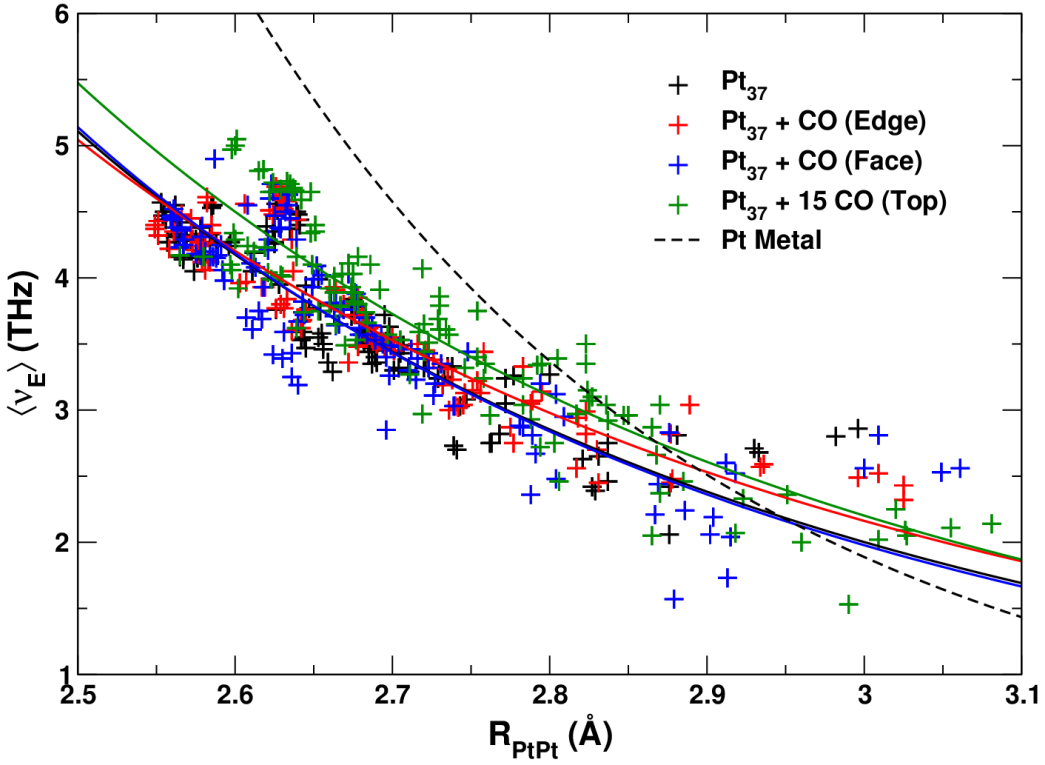
From Einstein Model Fit:

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

Pt_{37} on C:

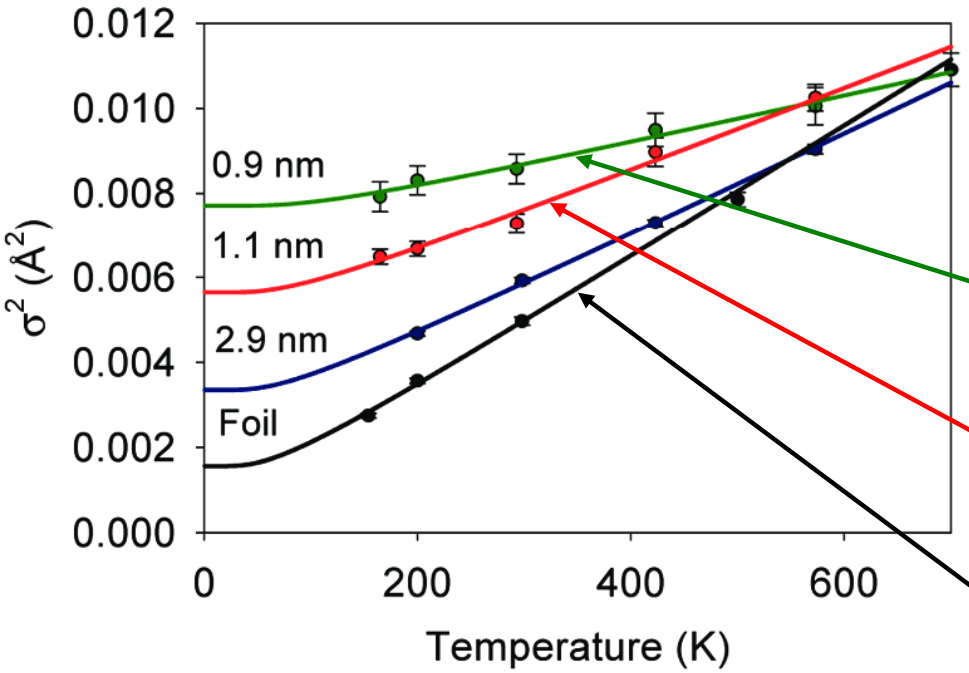
From Vib. Component:

$\gamma \cong 1.7$



What is the origin of this discrepancy?

Anomalous Bond Strength from Einstein Model Fits



Einstein Model with Static Disorder

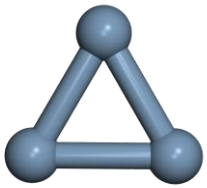
$$\sigma^2(T) = \sigma_S^2 + \frac{h}{8\pi^2\mu}\frac{1}{\nu_e}\coth\left(\frac{h\nu_E}{2k_BT}\right)$$

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

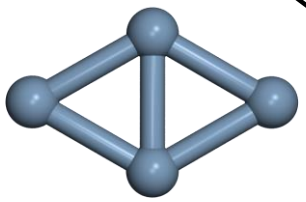
1.1 nm NPs:
$\nu_E \cong 4.6$ THz

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

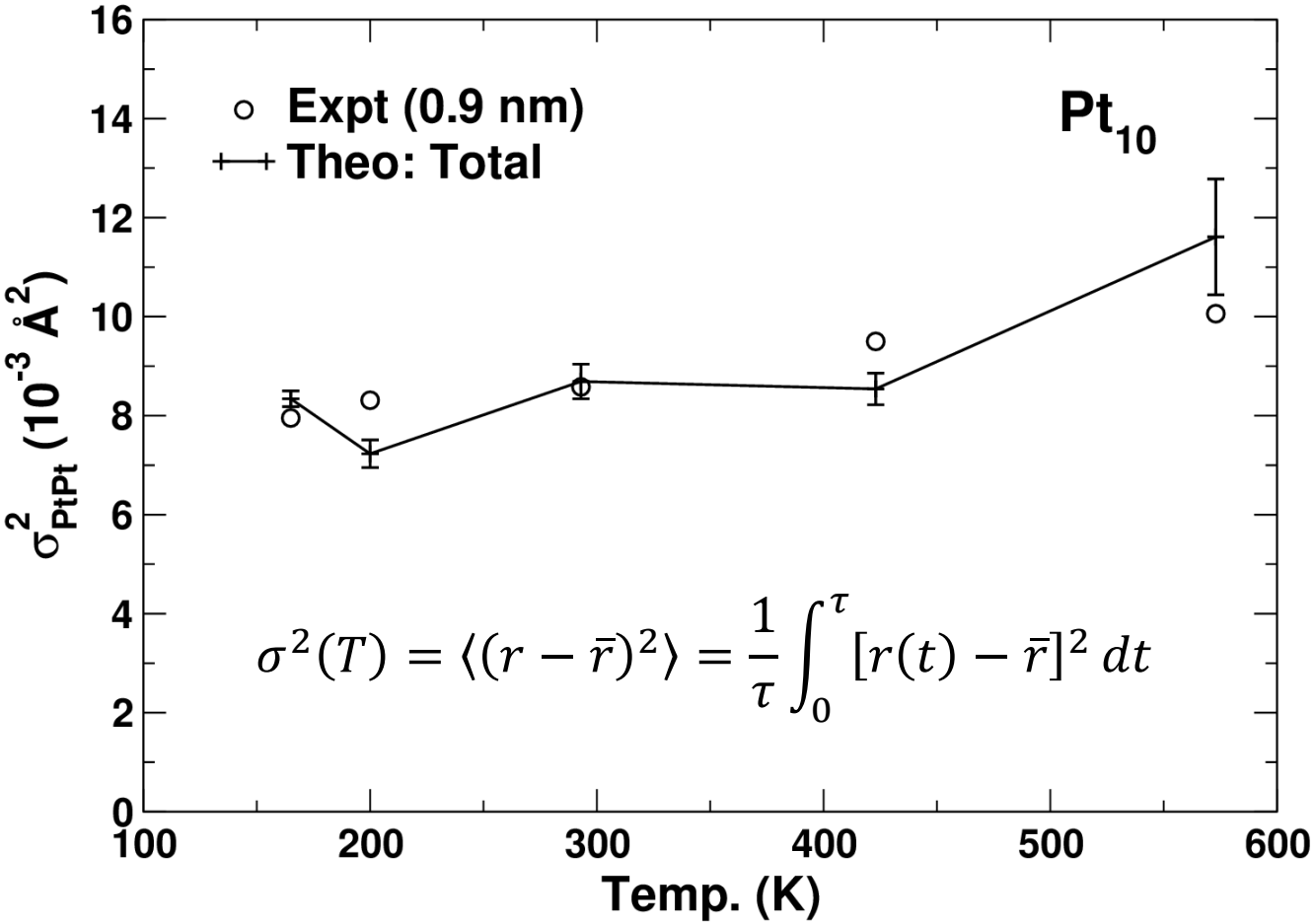
Method:

PBE XC functional

US PPs, 297 eV cutoff

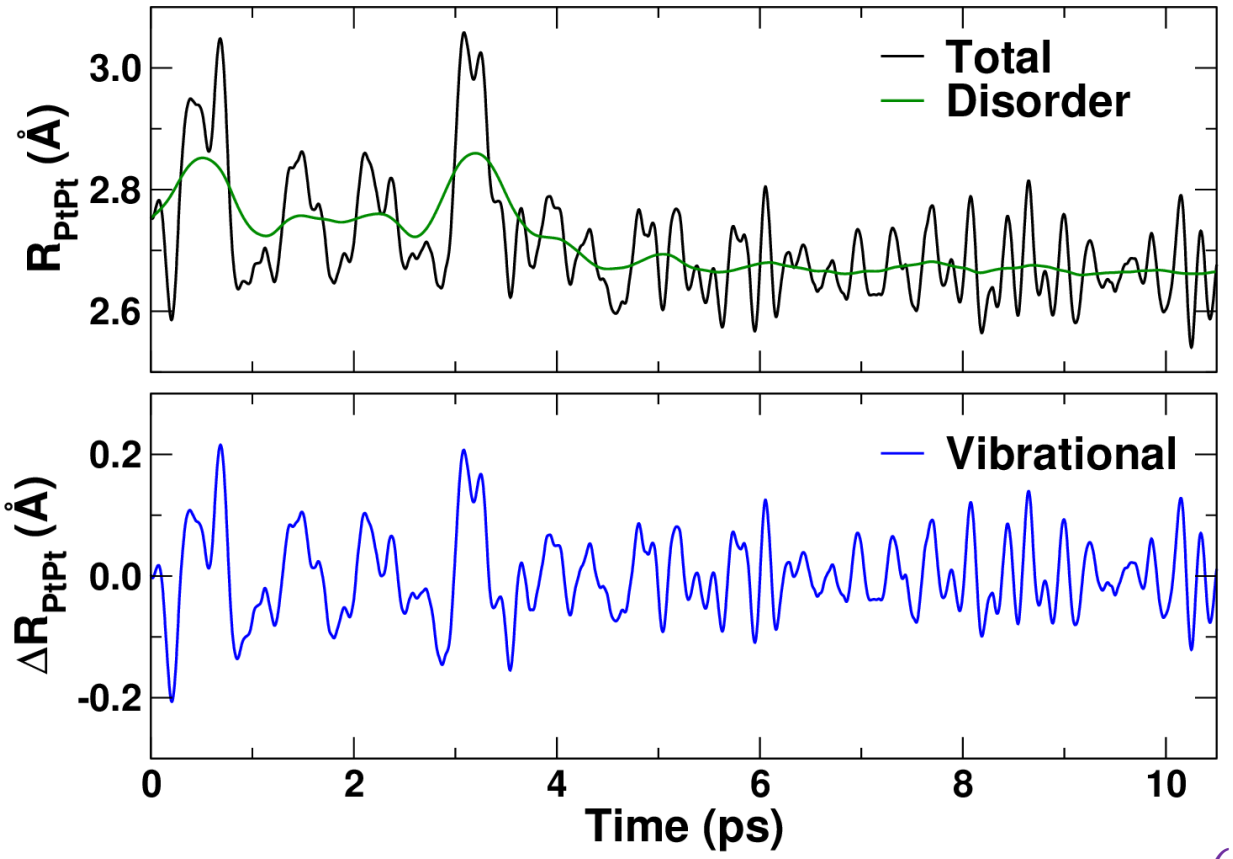
VASP

Total Mean Square Relative Displacement (MSRD)



Reasonable agreement between theory and expt.

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

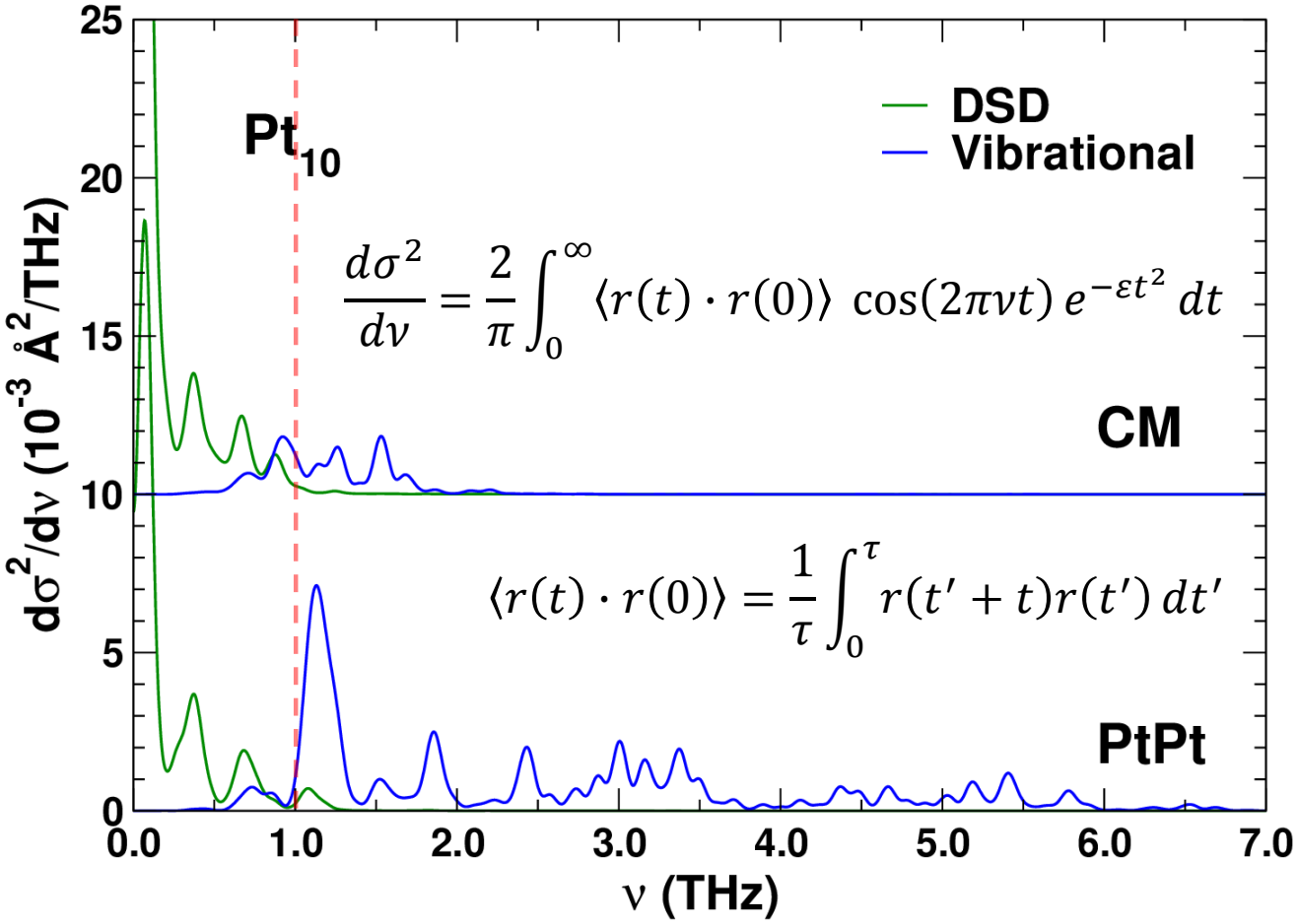


$$r_L(t) = \int_{-\infty}^{+\infty} r(\tau) F(t-\tau)\, d\tau$$

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

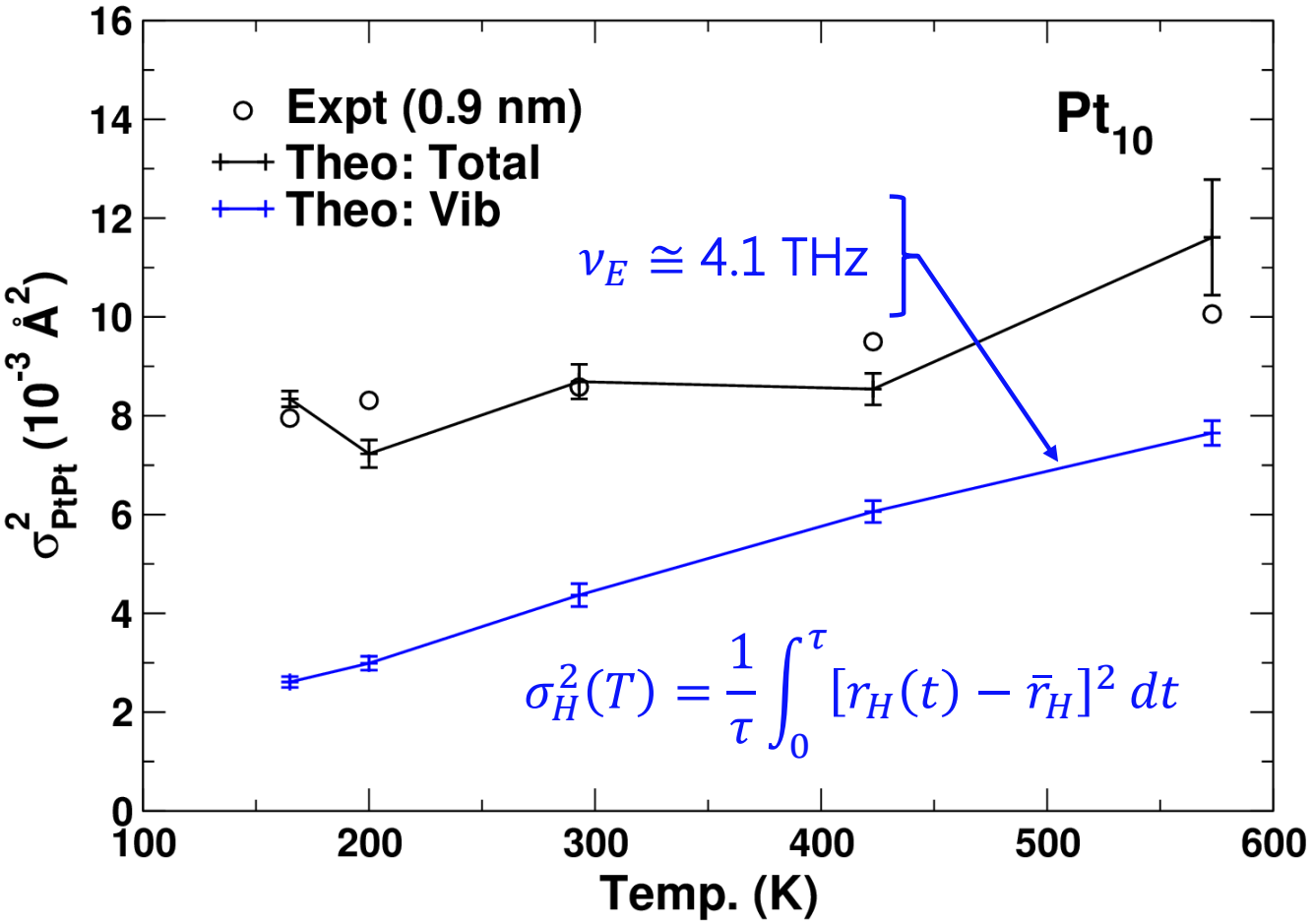
Filter Function: $$F(t) = \begin{cases} \frac{\pi}{2}\nu_L \cos(\pi\nu_L t), & |t| < {}^{1}/_{2\nu_L} \\ 0, & |t| \geq {}^{1}/_{2\nu_L} \end{cases}$$

Power Spectra of CM and Pt-Pt Dynamics



Nice separation of slow and fast dynamic regimes

Vibrational MSRD

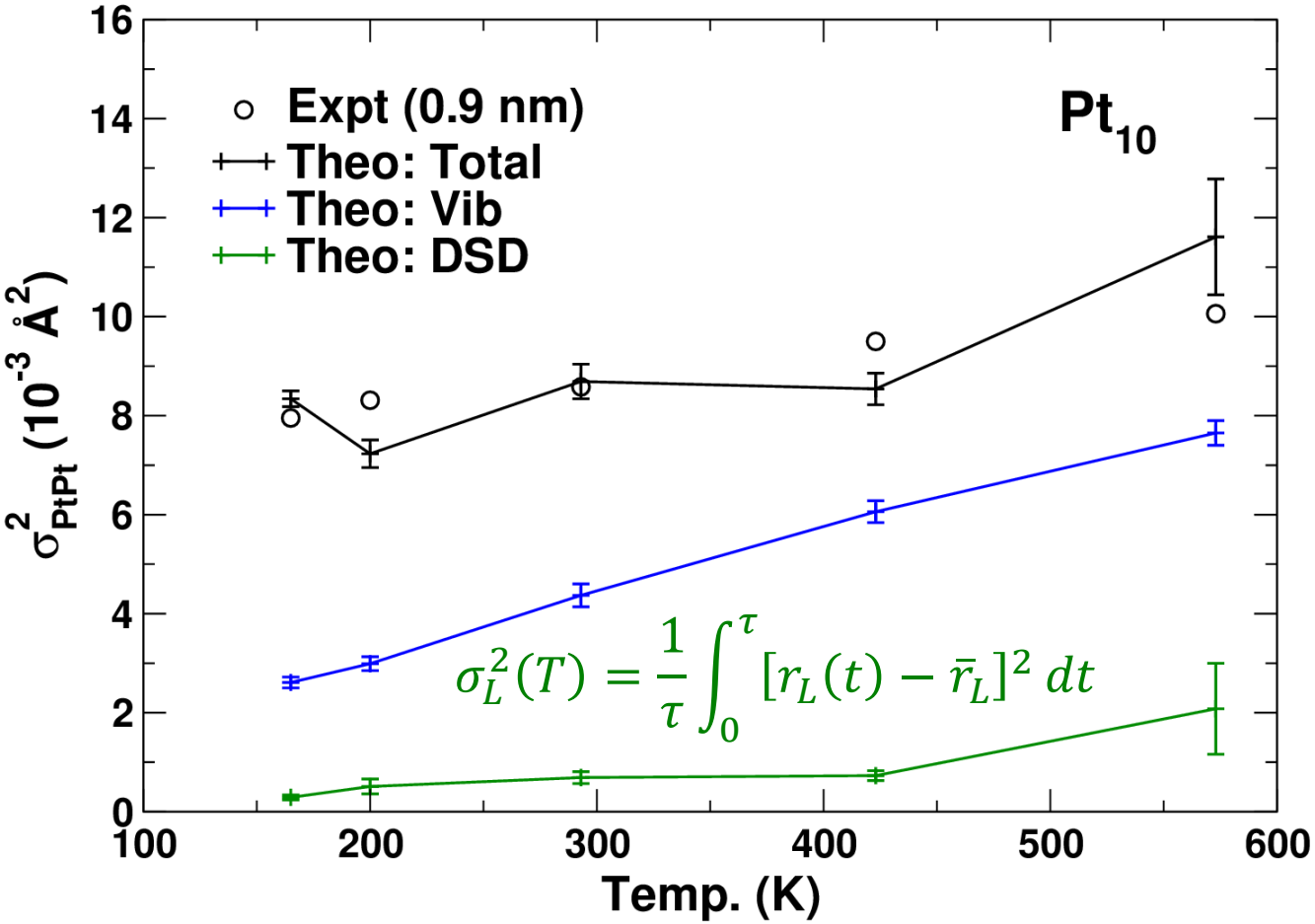


0.9 nm NPs:
$\nu_E \cong 6.3$ THz

Pt Foil:
$\nu_E \cong 3.8$ THz

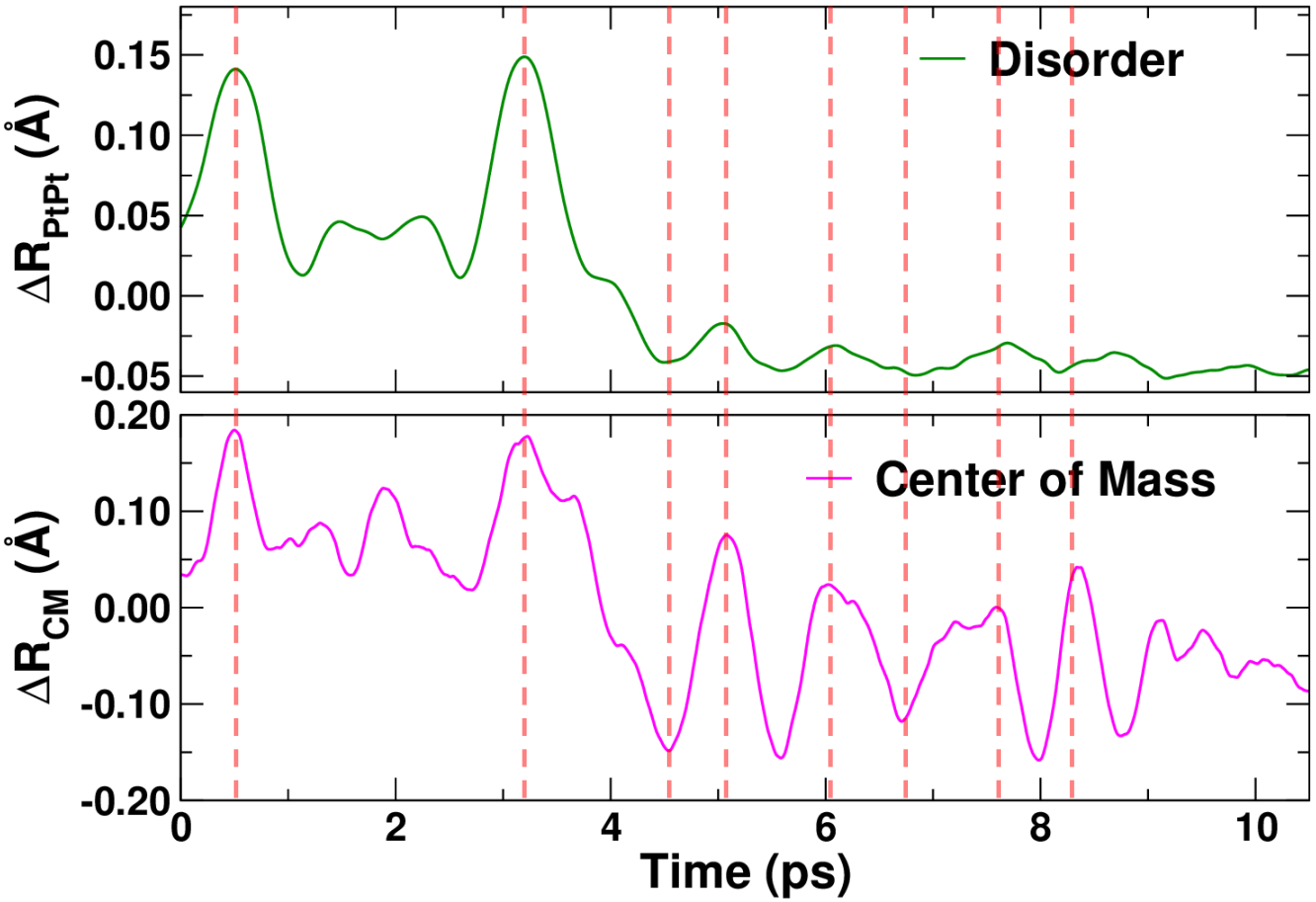
Normal linear vibrational behavior

Dynamic Structural Disorder (DSD) MSRD



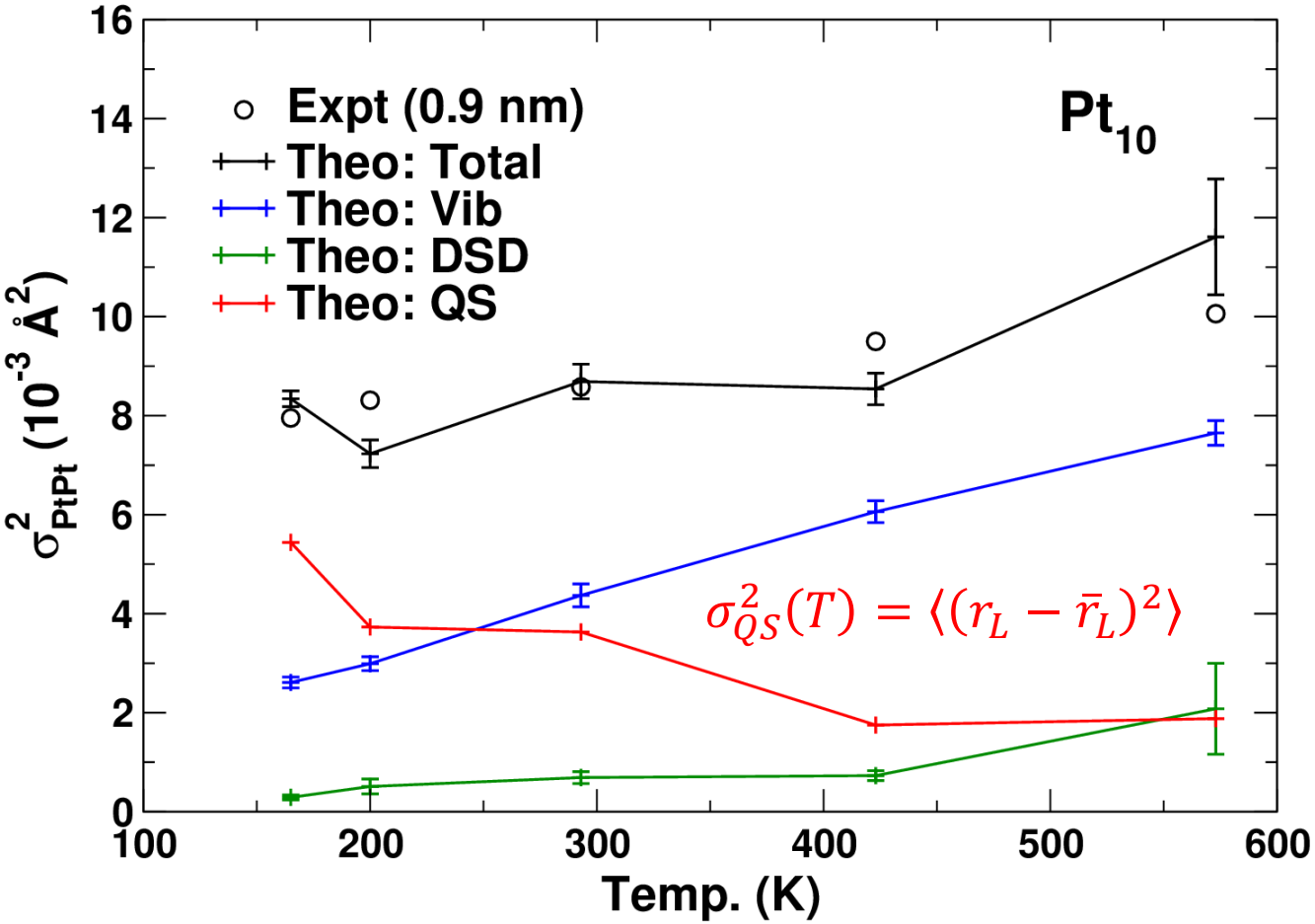
Normal linear behavior: Low frequency quasi-harmonic modes

DSD: Correlation Between CM and Pt-Pt Dynamics



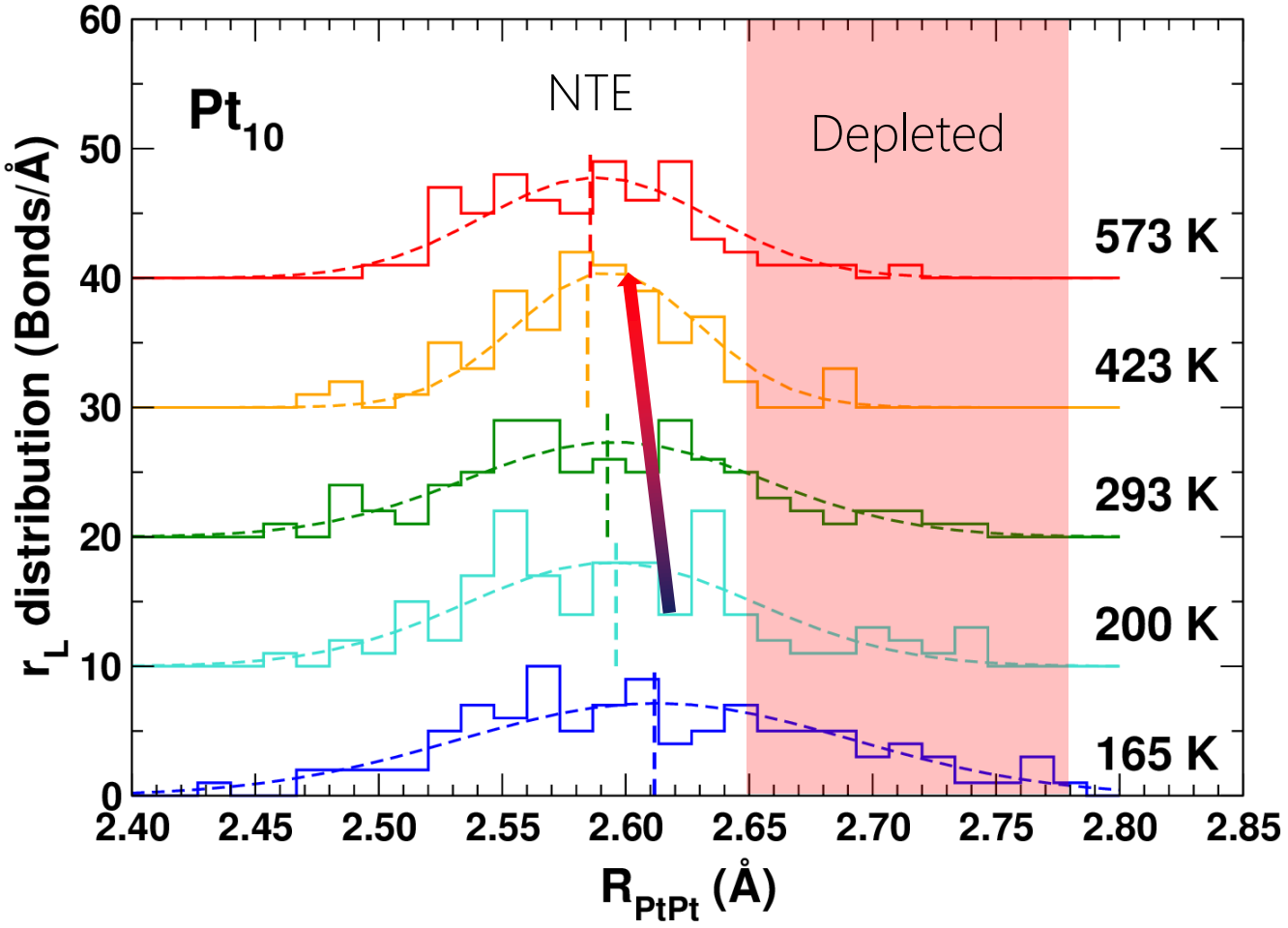
Moderate/strong correlation between CM libration and Pt-Pt bonds

Quasi-static MSRD: Anomalous Structural Disorder



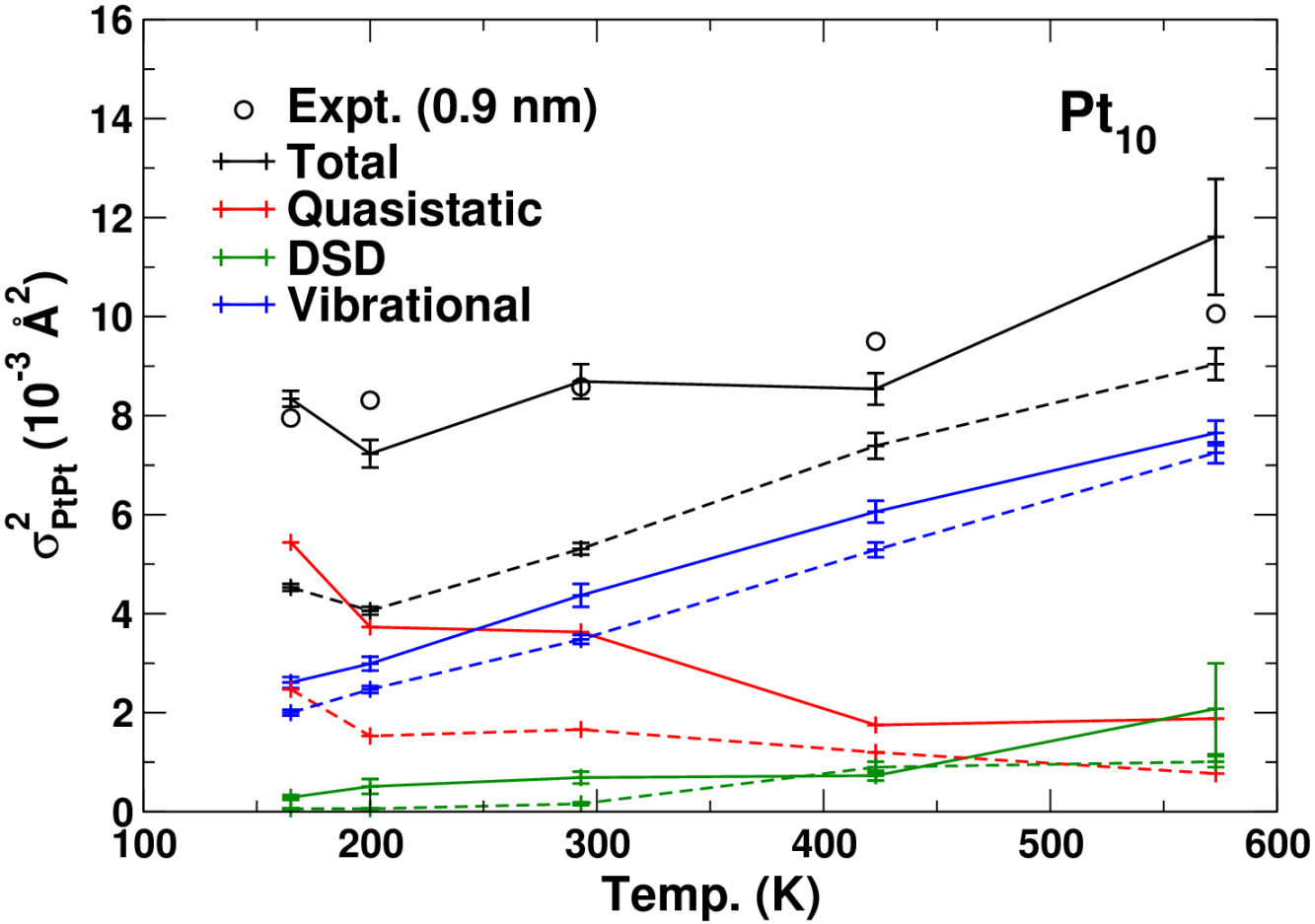
Anomalous disorder (ASD): Causes apparent strengthening

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



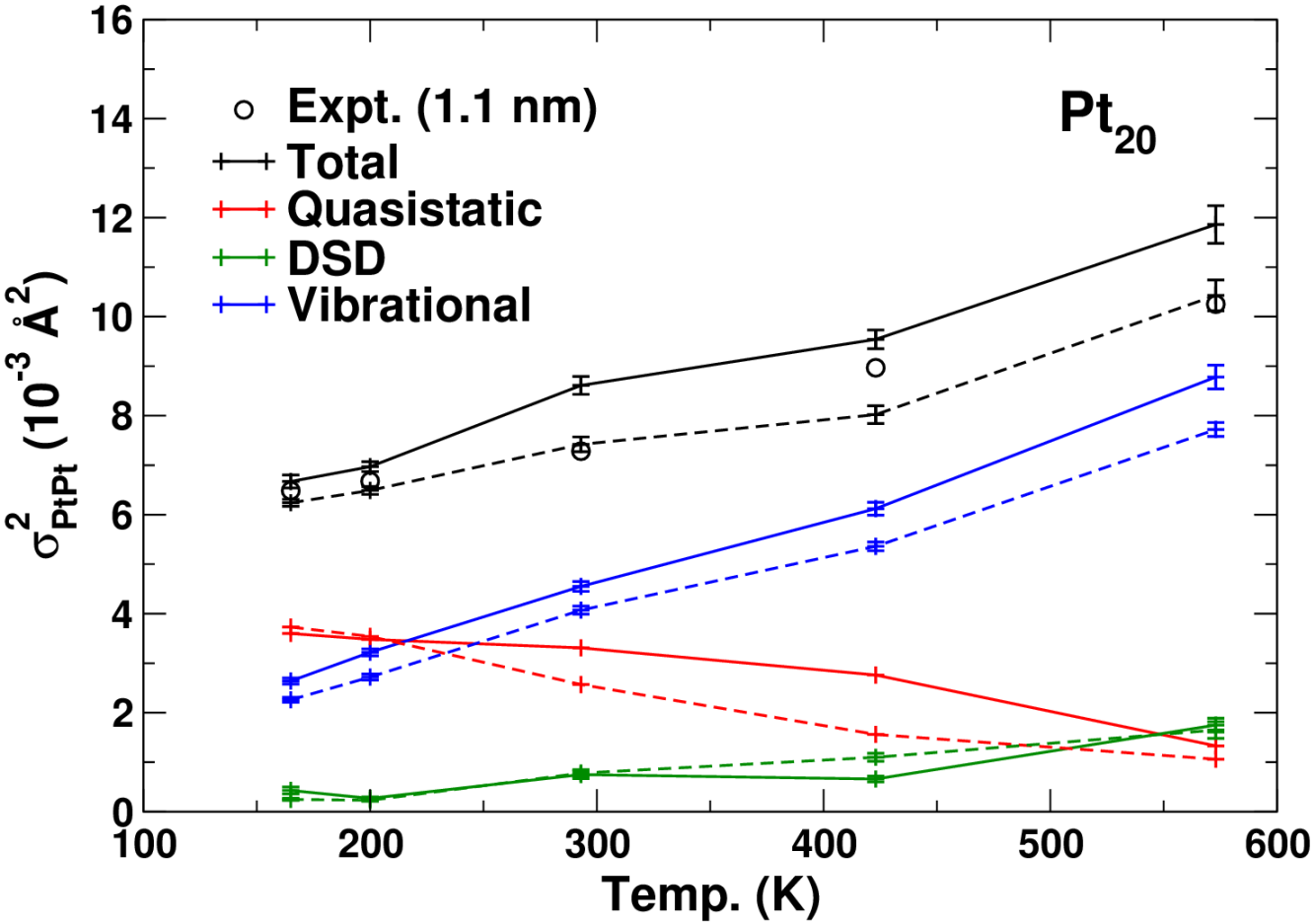
Dynamic activation and depletion of long bonds

Effect of Support



Support accounts for ~50% of disorder

Disorder in Pt_{20}



Support less important in Pt_{20}

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:

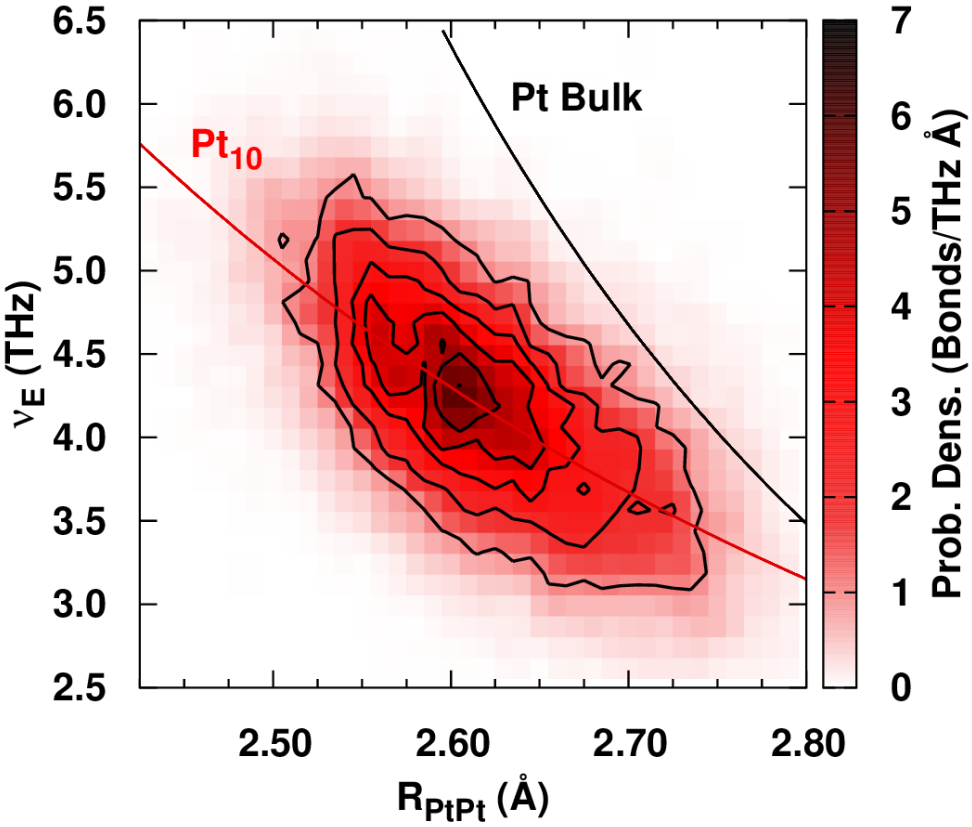
From Einstein Model Fit:

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

AIMD reveals:

Importance of Structural Disorder:

- In catalysis
- In EXAFS and XANES analysis

Single mechanism, dynamic activation, that 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: $\gamma_{NP} > \gamma_{Bulk}$

Exploring the anomalous behavior of metal nanocatalysts with finite temperature AIMD and x-ray spectra

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Acknowledgements:

J. J. Rehr
J. J. Kas
S. T. Hayashi
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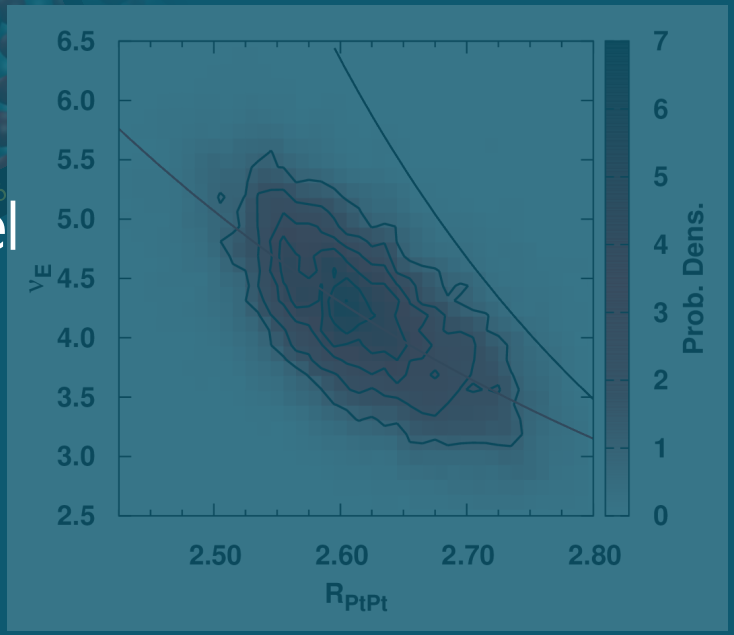
A. F. Frenkel
R. Nuzzo
S. R. Bare



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