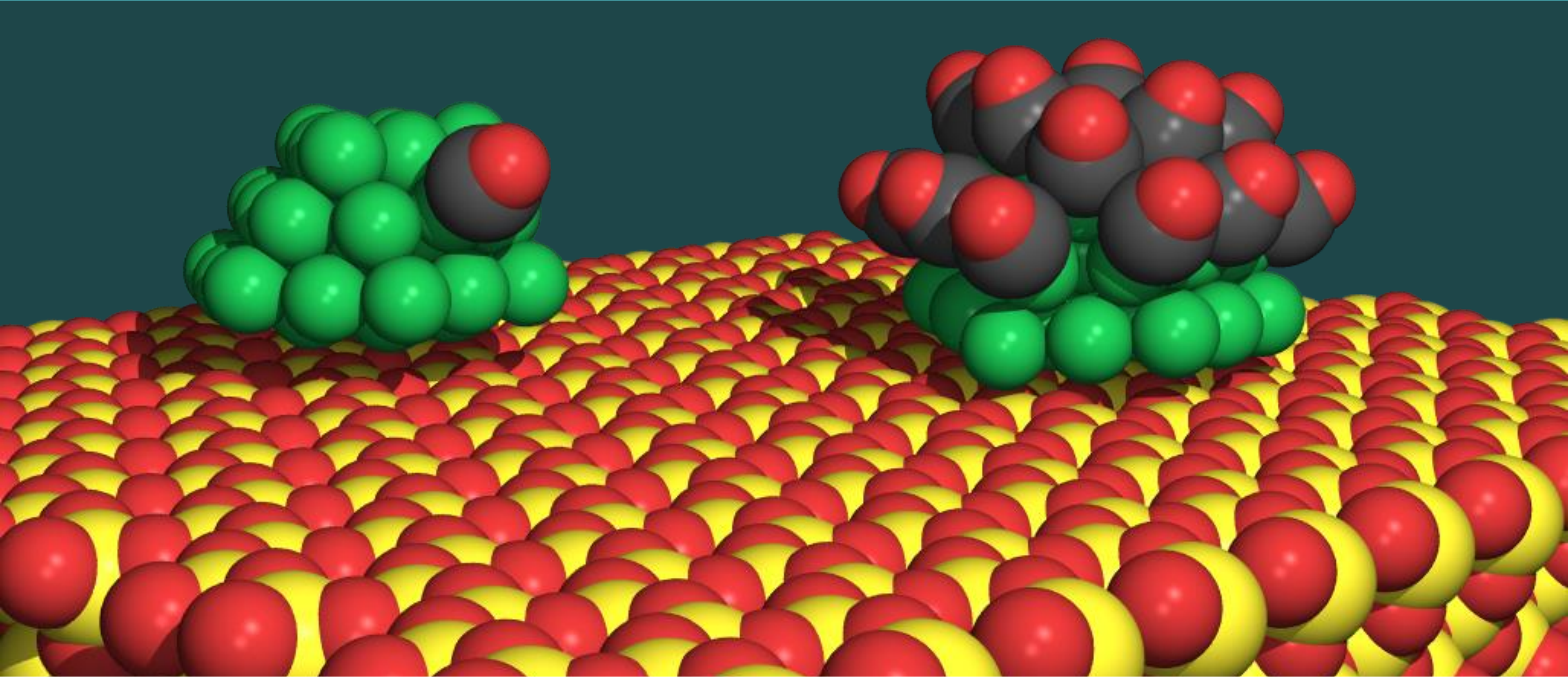
Dynamic structural disorder and reactivity in supported metal nanocatalysts

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



UNIVERSITY OF WASHINGTON

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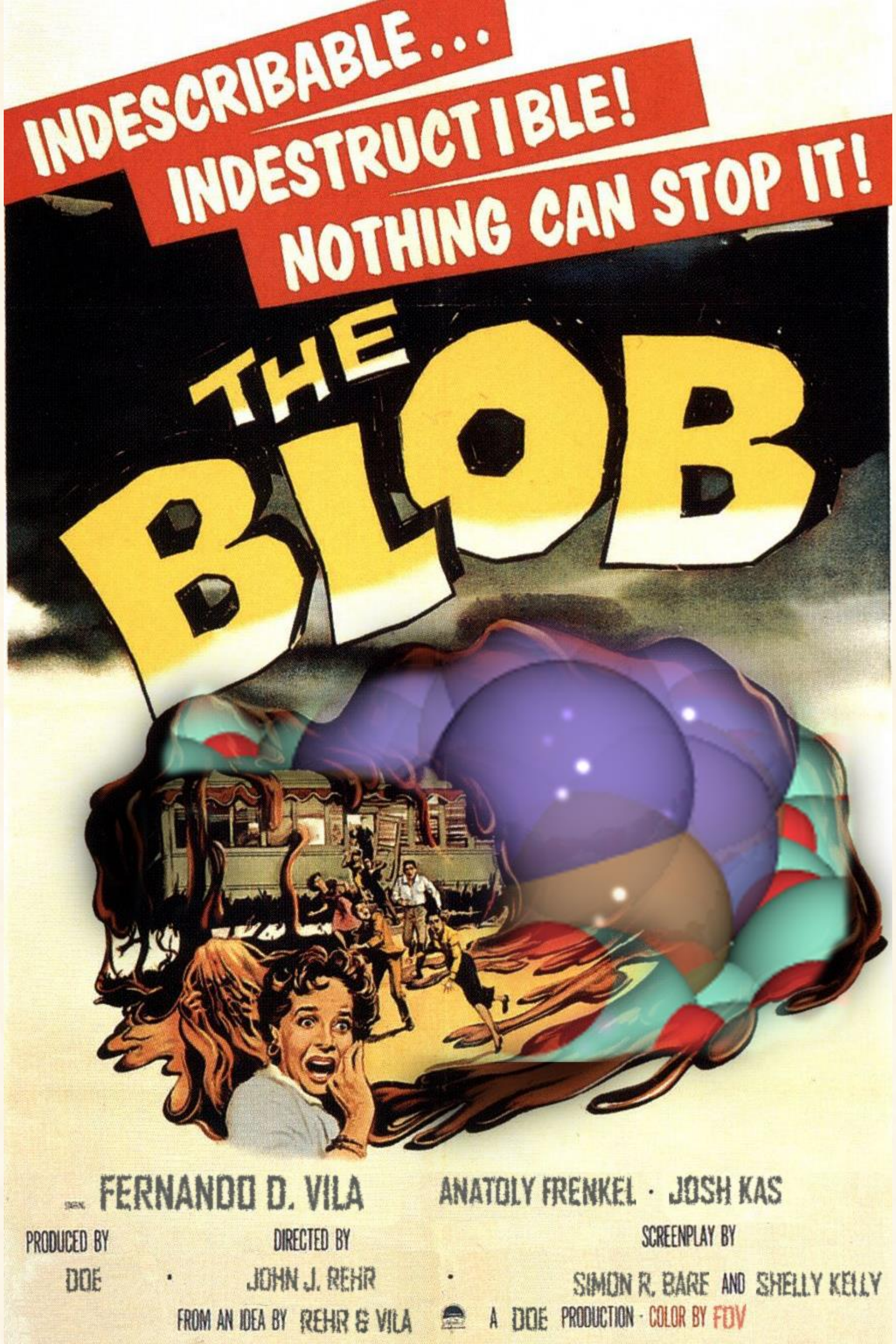


“A theoretical tour de force”
J. Horr. Phys. A

“Love it..”
An anonymous referee

“Hate it..”
Nature editor

An Evolving Picture of Metal Nanocatalysts

Metal nanocatalysts:

- Keystone of heterogeneous catalysis in industry

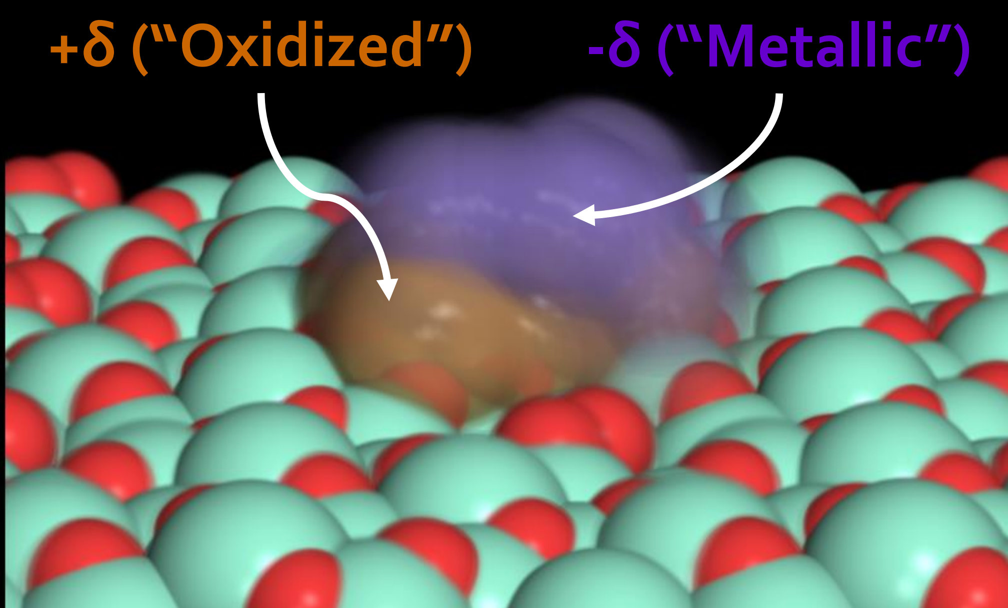
Theoretical studies of nanocatalysts used to:

- Use static structures
- Sample few conformations
- Not account for realistic temperature

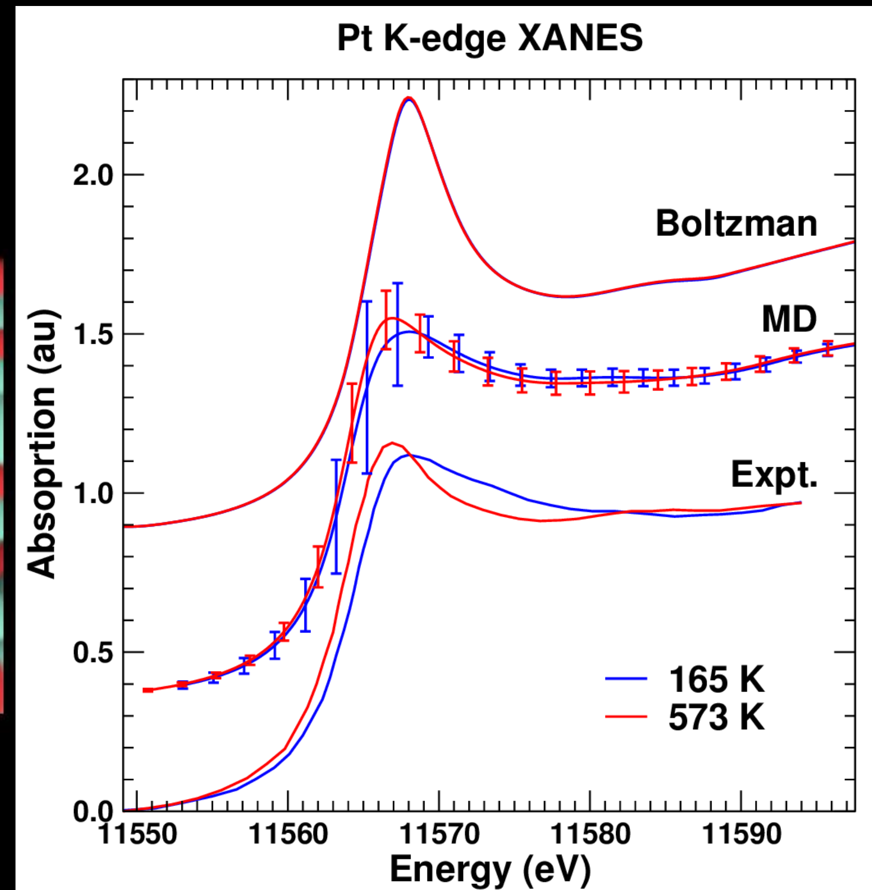
More recently:

- Finite temperature DFT/MD simulations
- Highlight importance of disorder

Static Simulations are Usually Not Sufficient



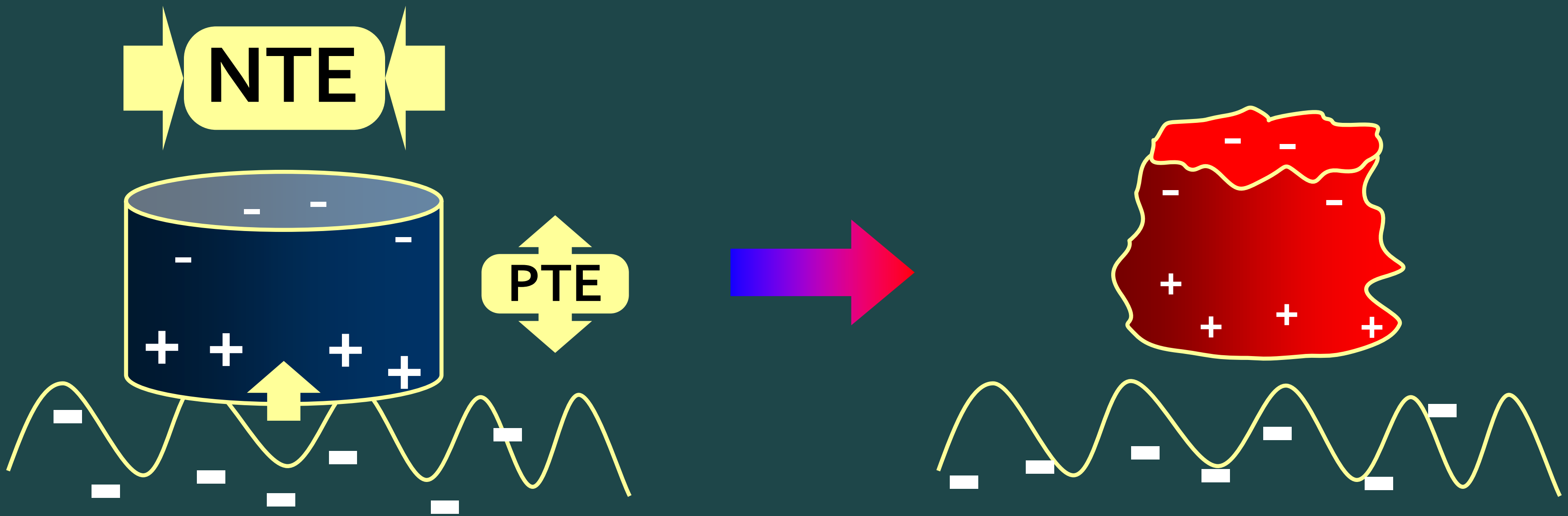
Pt_{10} on γ-Al_2O_3 @ 165 K



Need dynamics to reproduce experiment

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

Model of Negative Thermal Expansion (NTE)



Low T High T

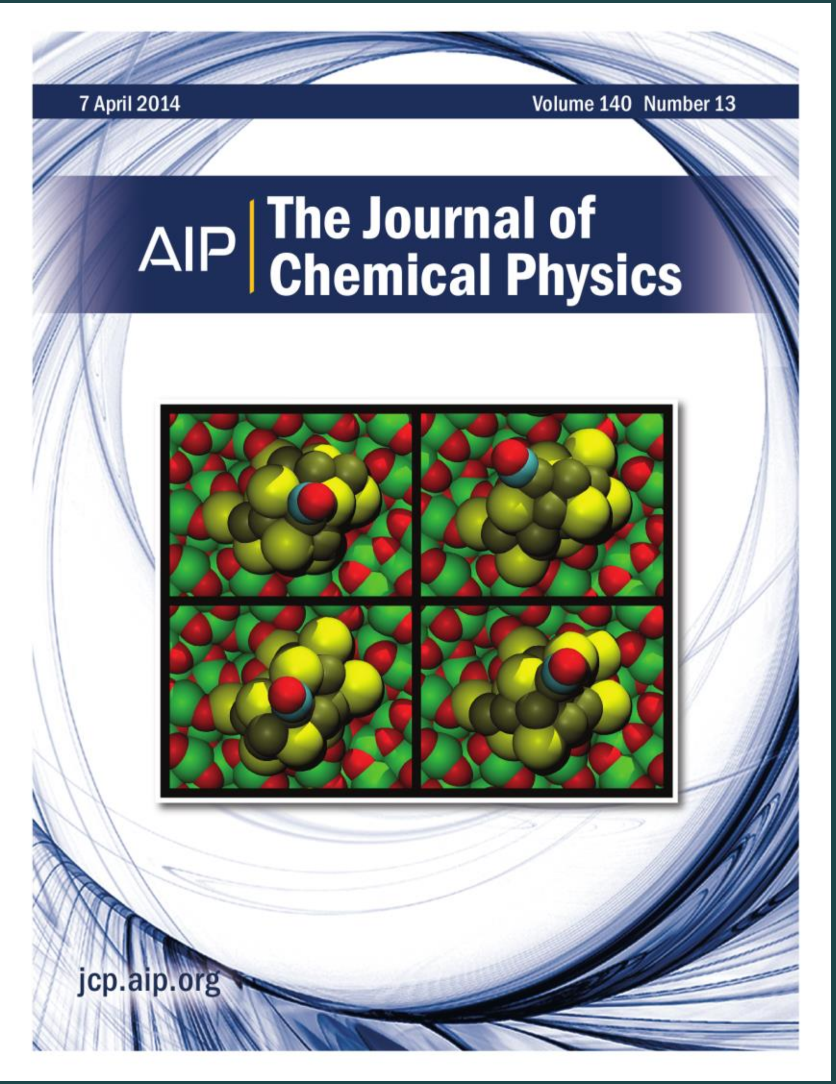
Overall behavior: Results from inhomogeneous changes
Driven by dynamic fluctuations

Dynamic Structural Disorder (DSD) in Nanoparticles

DSD drives:

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

Inhomogeneity



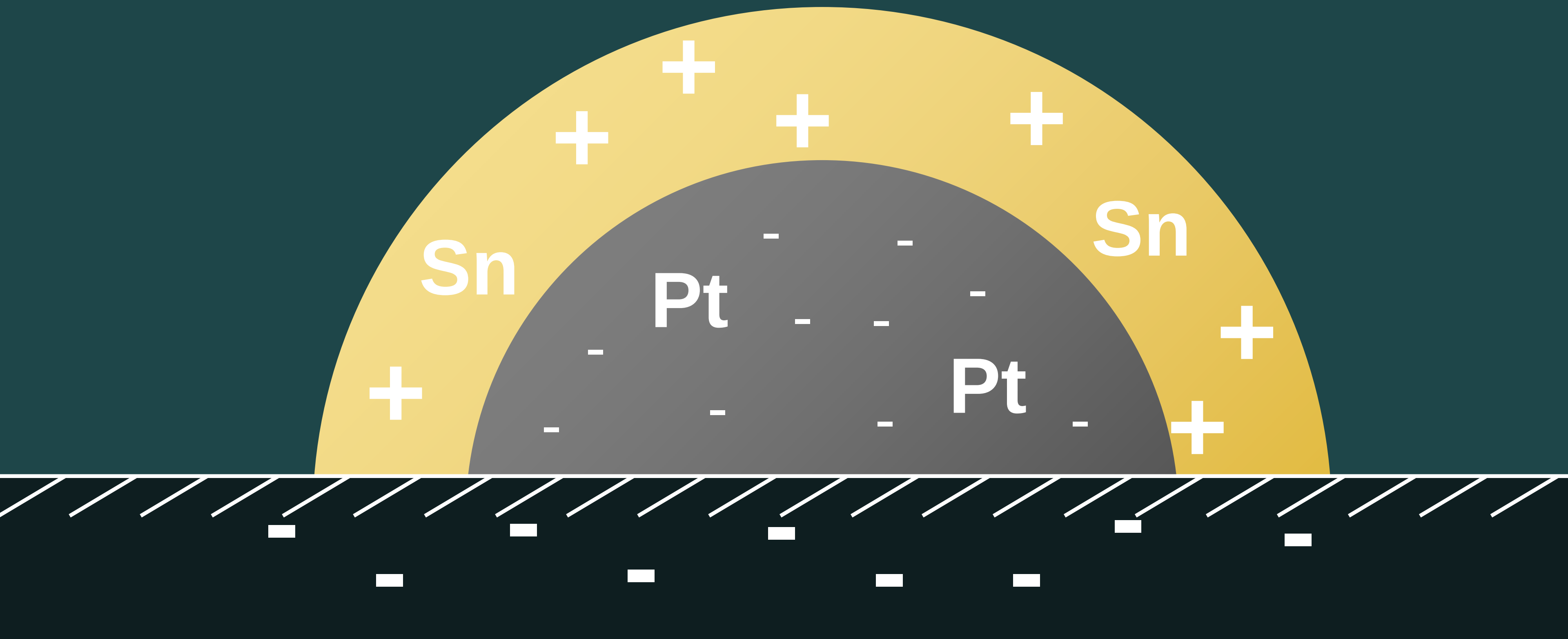
CO dynamics on $Pt_{10}Sn_{10}$

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

Model of Charge Segregation

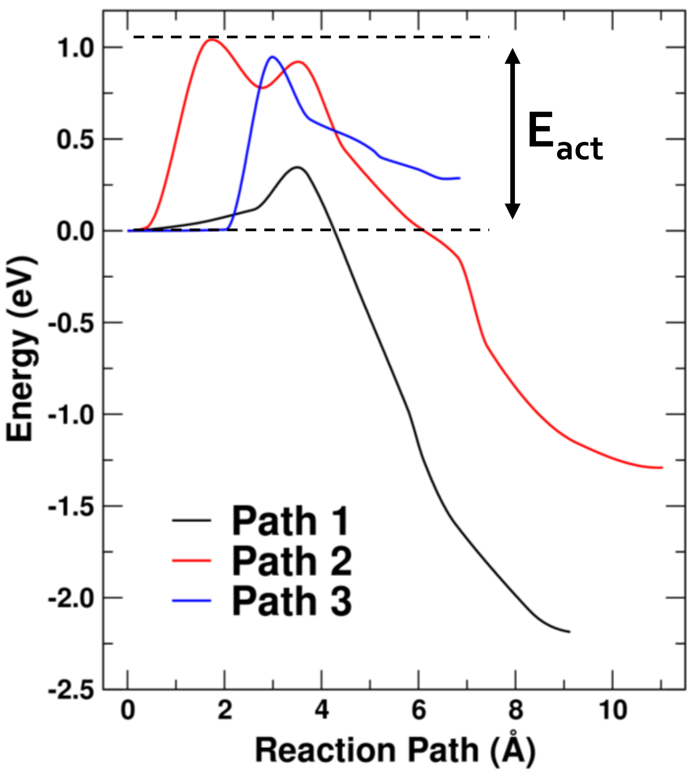
In PtSn alloy nanoparticles:

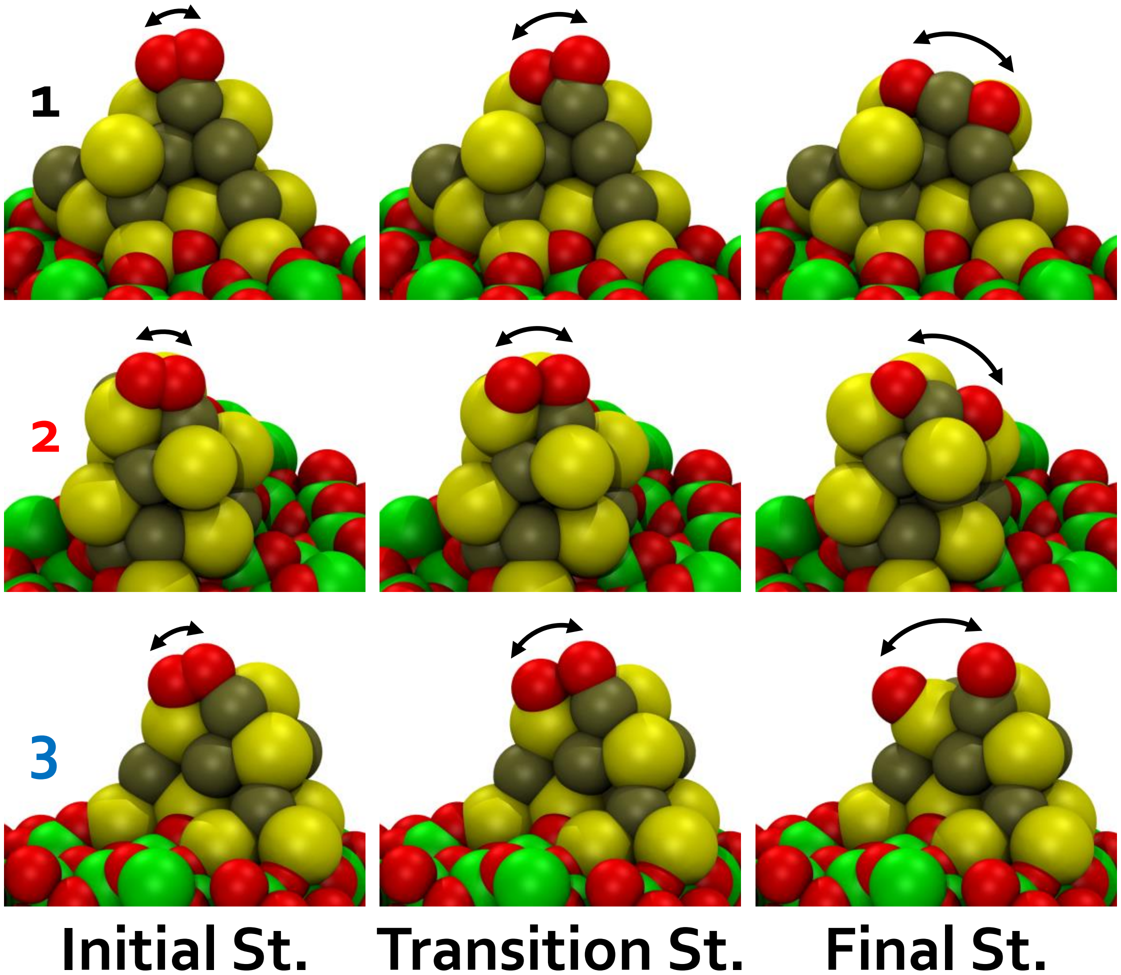
- Sn segregation to particle surface
- Driven by Coulomb repulsion
- Less charged Pt atoms in particle core



Disorder Affects Reactivity

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

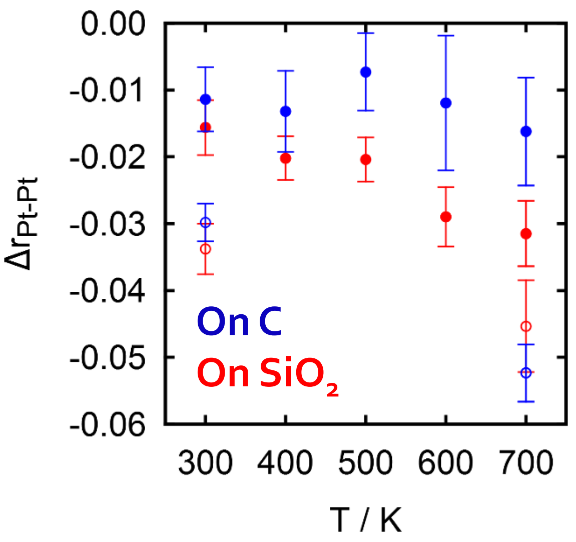


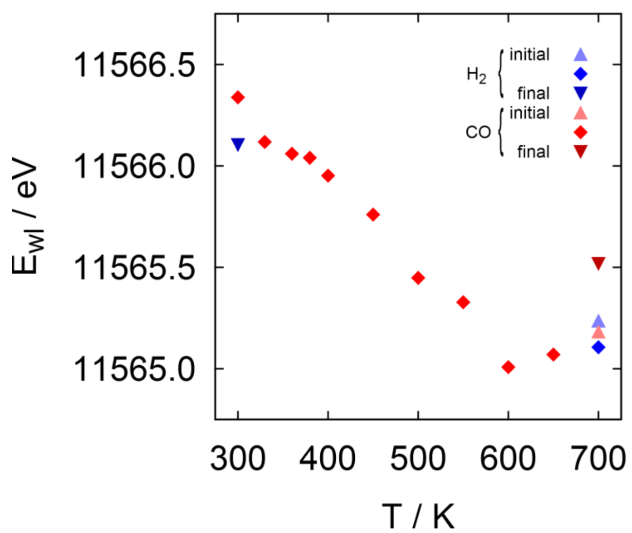


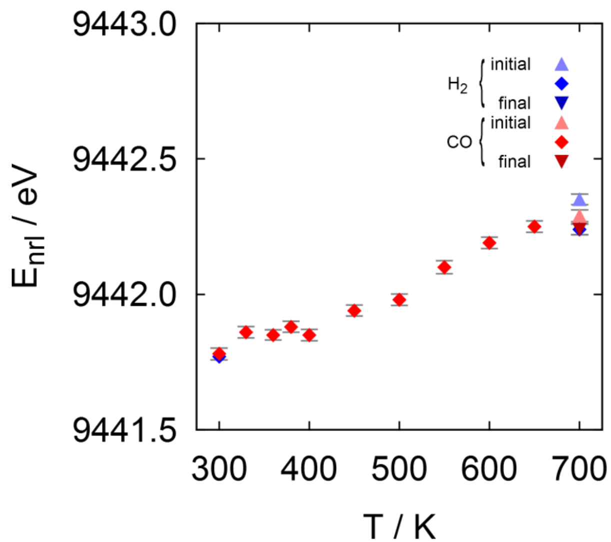
Large differences in activation energy (E_{act})

Reaction path depends on DSD

Inhomogeneity in Well-defined(?) Nanoparticles







Bond contraction with heating/desorption

White line: redshift, Emission line: blueshift

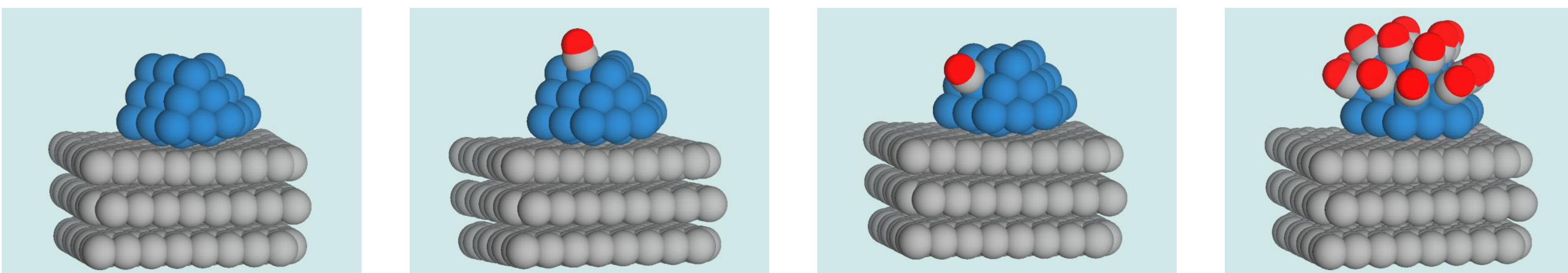
EXAFS measurements: Predict truncated cuboctahedron Pt_{37}

Hypothesis: Both phenomena related to desorption

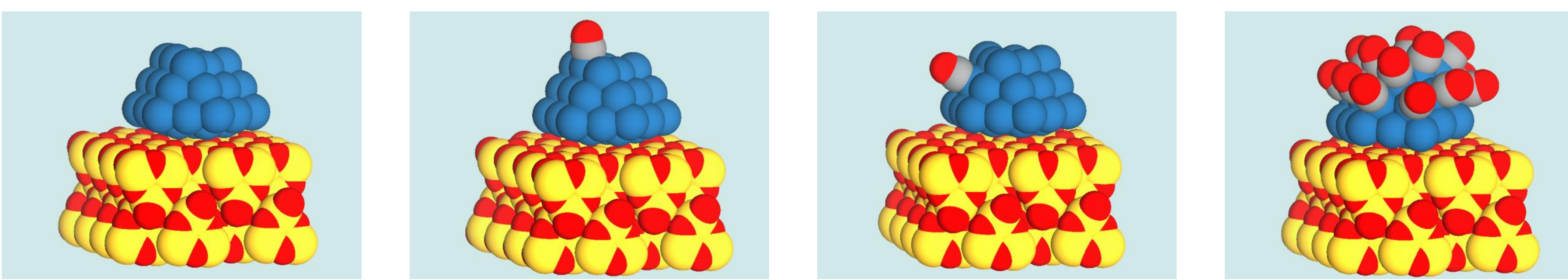
Is inhomogeneity important to these phenomena too?

Preliminary Methods and Models

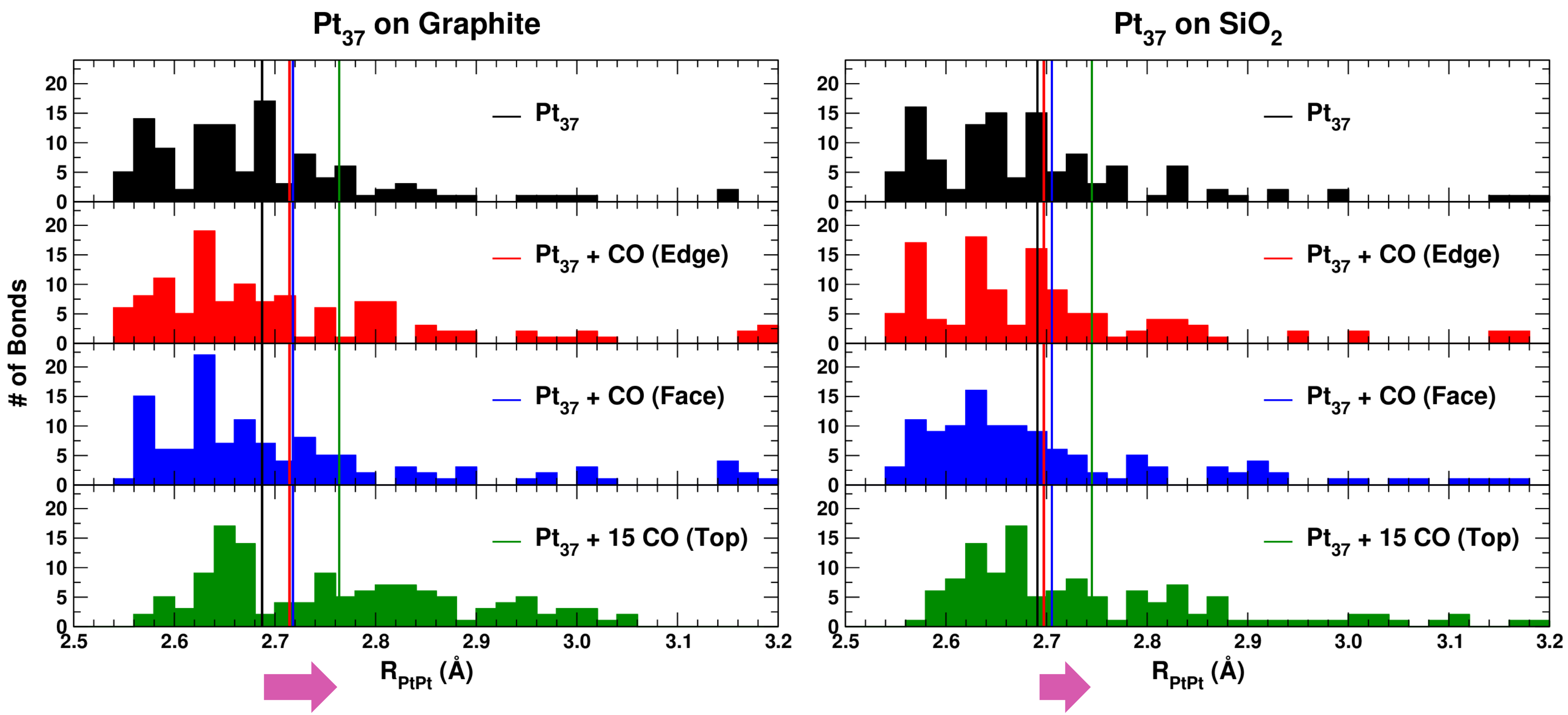
- Pt_{37} on C and SiO_2:
  - PBE/PAW optimization with 400 eV planewave cutoff
  - C surface: 3 graphite layers (4 x 4, 384 atoms)
  - SiO_2: reconstructed (001) α-quartz (2 x 4, 278 atoms)



Clean | Edge | Face | High Cov.



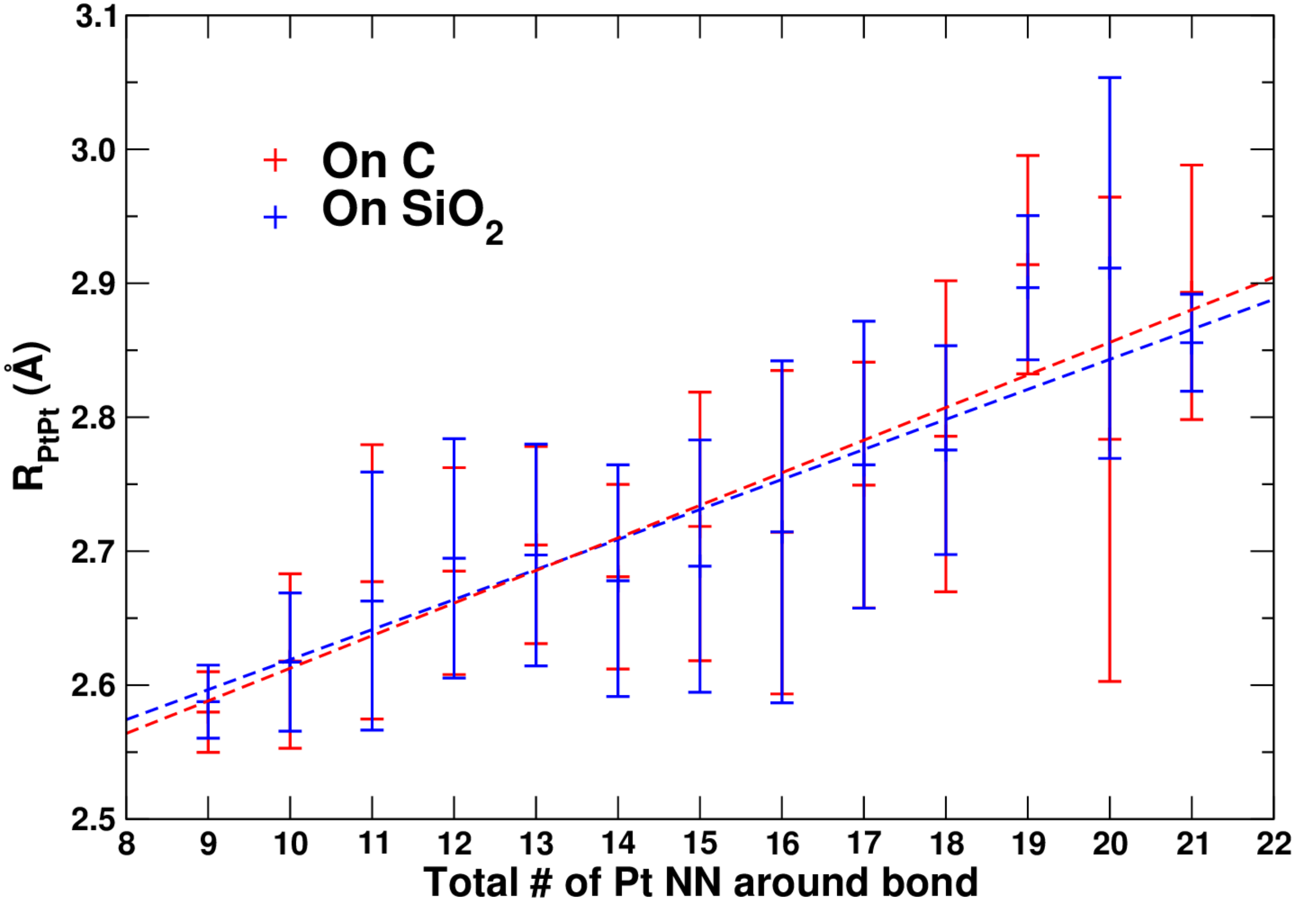
Bond Expansion



PtPt mean expansion (*vs* H-covered, not shown):

1.2% on C and 0.4% on SiO_2 (Expt. 1% and 0.4%)

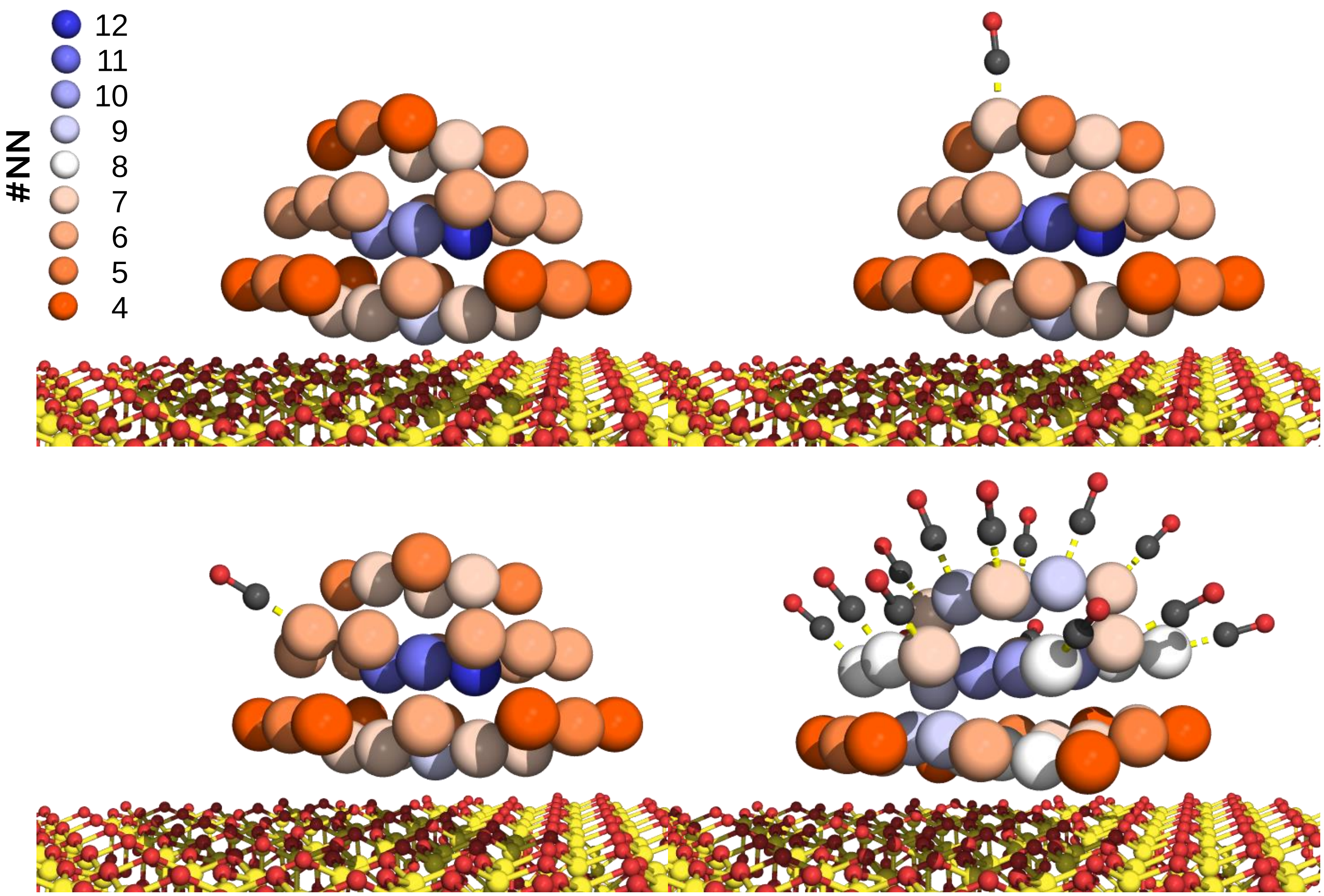
Bond Distance *vs* # of NN



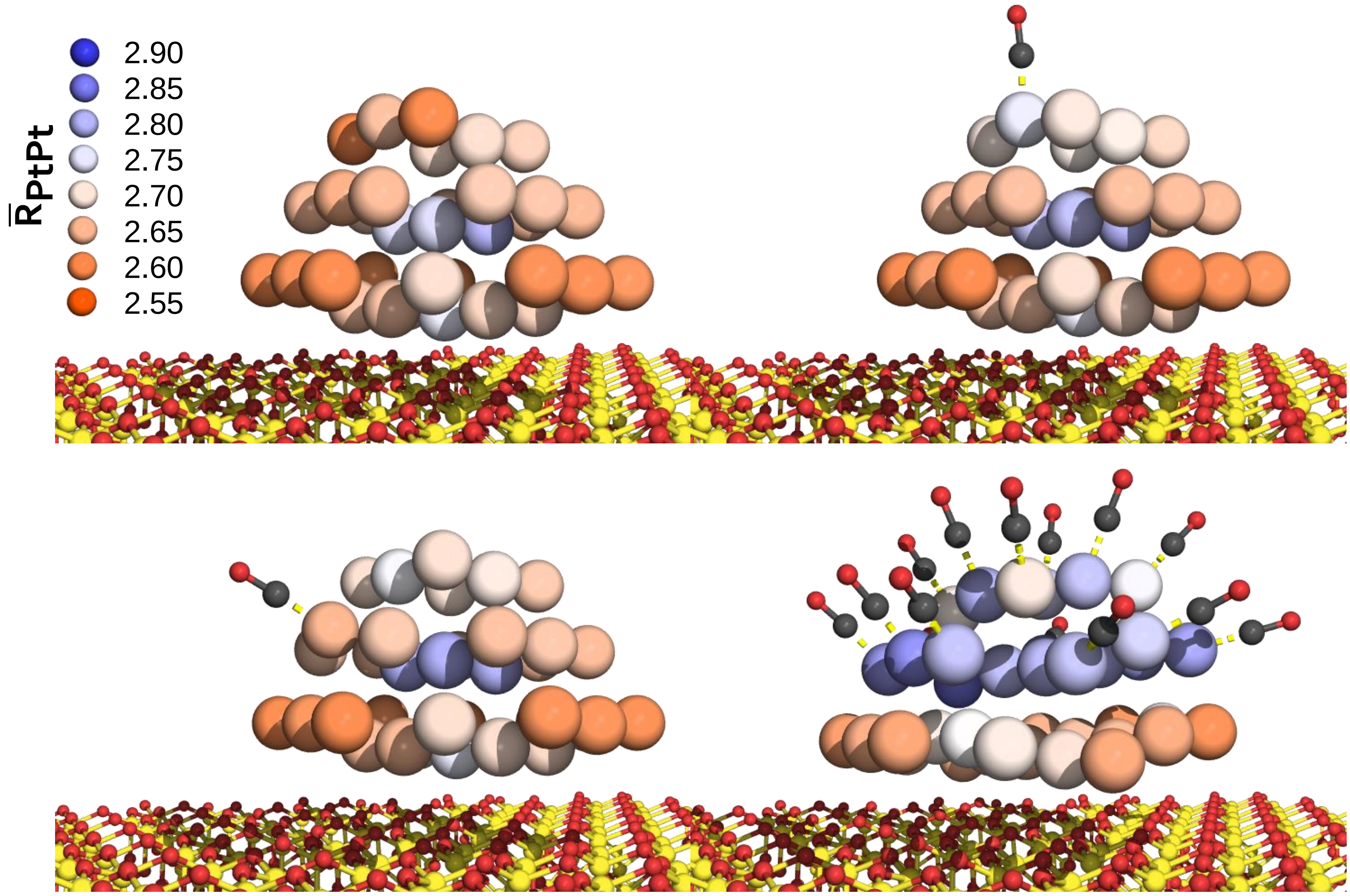
Higher coordination ⇔ Longer bonds

Similar behavior on both supports

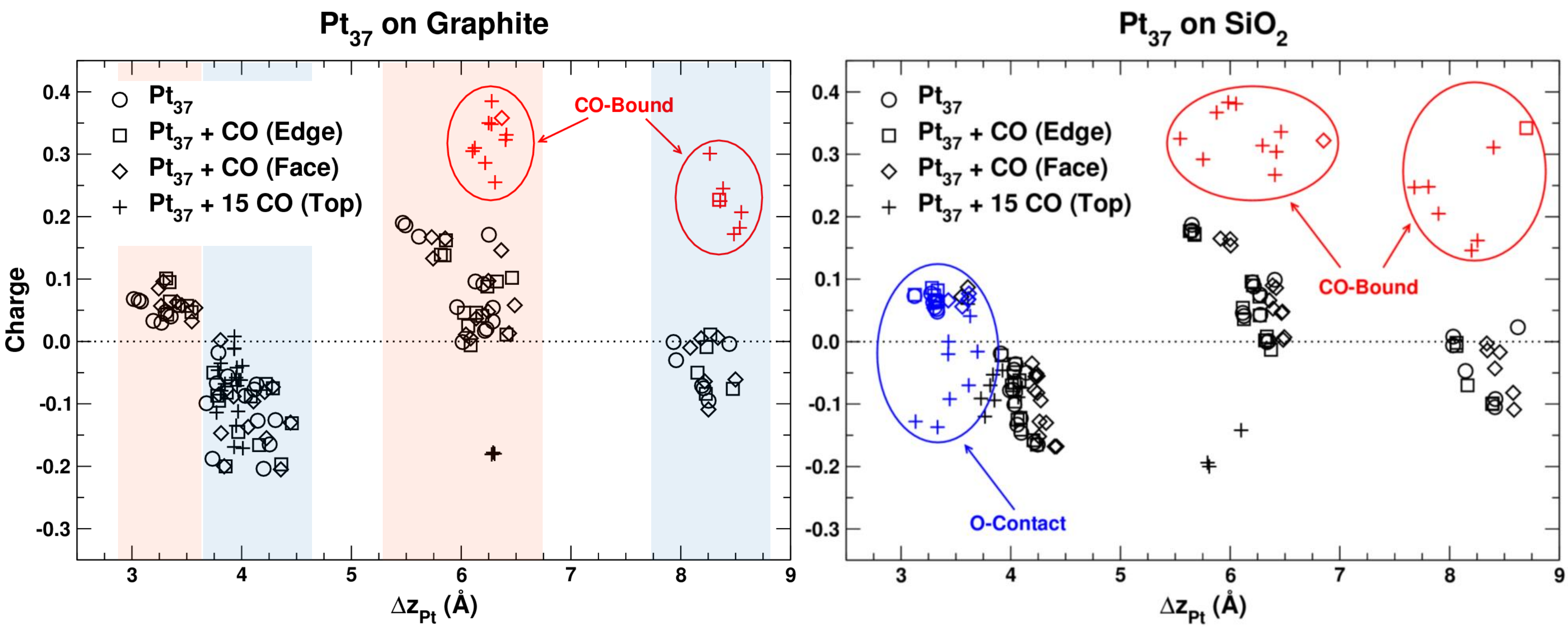
of Pt NN on SiO_2



Mean PtPt Bond Lengths on SiO_2



Charge Inhomogeneity

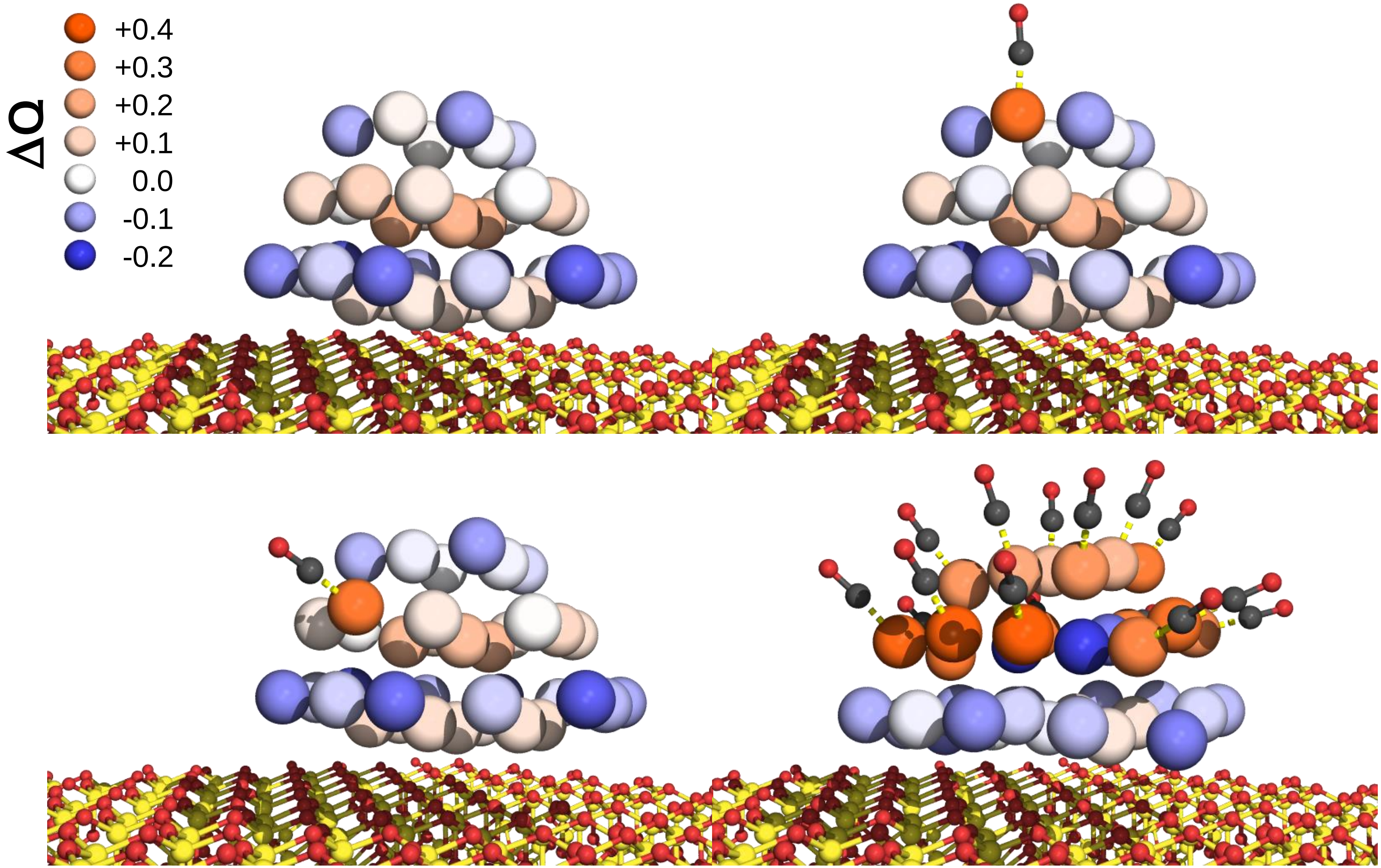


CO-bound Pt atoms loose 0.2-0.3*e* each

Layer charge alternation

Bond expansion due to charge loss

Charge inhomogeneity on SiO_2



Ab initio Vibrational Properties

Projected Vibrational DOS: Use efficient pole model

$$\rho_R(\omega) = -\frac{2\omega}{\pi}\,\mathrm{Im}\left\langle 0\left|\frac{1}{\omega^2 - \mathbf{D} + i\varepsilon}\right|0\right\rangle \cong \sum_{v=1}^{N} w_v \delta(\omega - \omega_v)$$

Dynamical Matrix (D) from VASP:

$$D_{jl\alpha,j'l'\beta} = \left(M_j M_{j'}\right)^{-1/2} \frac{\partial^2 E}{\partial u_{jl\alpha}\partial u_{j'l'\beta}}$$

Properties: DW factors and mean Einstein temperatures:

$$\sigma_R^2(T) = \frac{\hbar}{2\mu_R}\int_0^\infty \frac{1}{\omega}\coth\left(\frac{\beta\hbar\omega}{2}\right)\rho_R(\omega)\,d\omega$$

$$T_E = \frac{\hbar\langle\omega^2\rangle^{-\frac{1}{2}}}{k_B} = \frac{\hbar}{k_B}\left(\sum_{v=1}^{N}\frac{w_v}{\omega_v^2}\right)^{-\frac{1}{2}}$$

Bond Stiffness Inhomogeneity on SiO_2

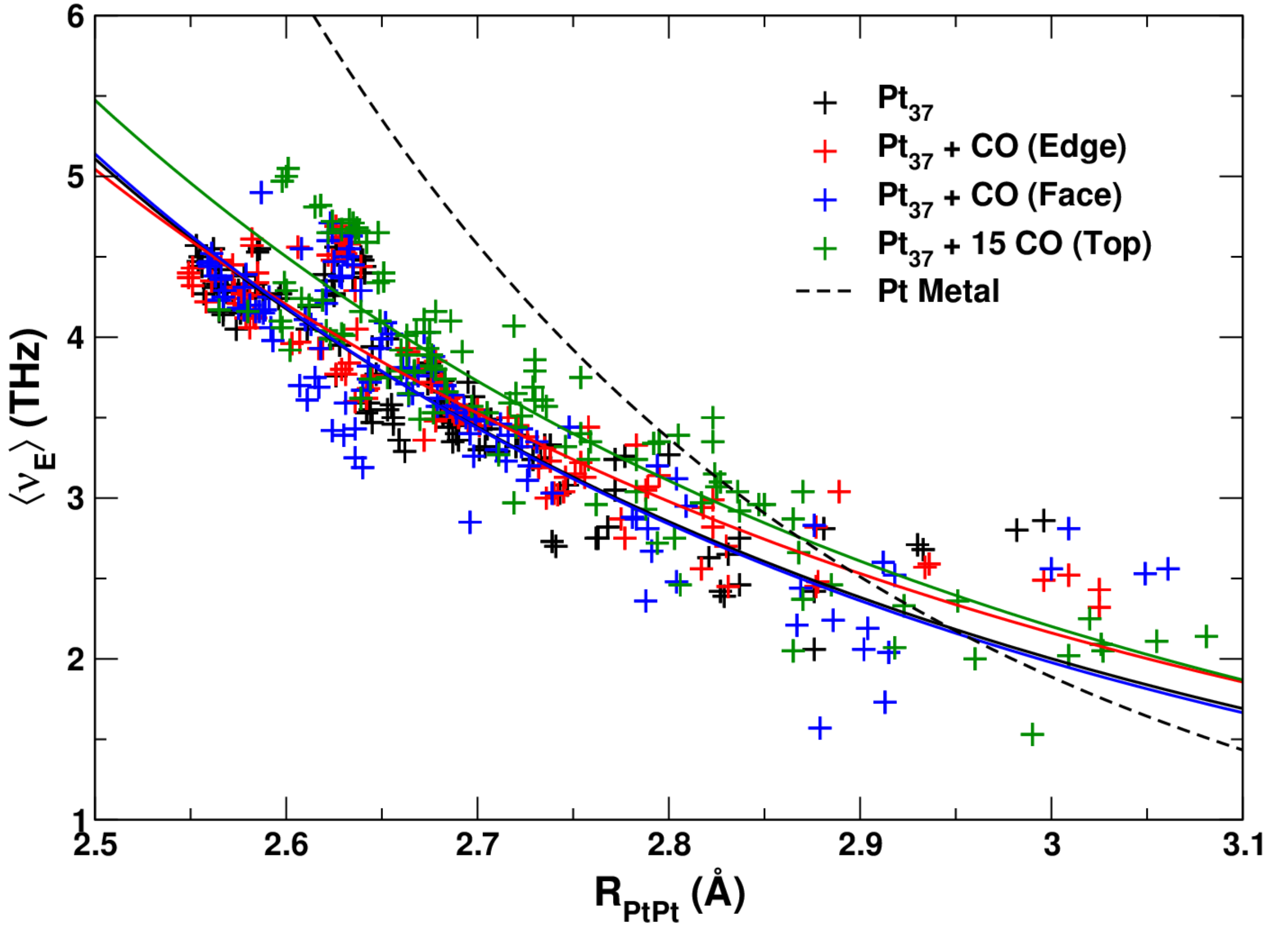
$$\gamma = -\frac{1}{3}\frac{d\ln\langle\nu_E\rangle}{d\ln R_{PtPt}}$$

Pt metal:

$\gamma = 2.8$

Nanoparticle:

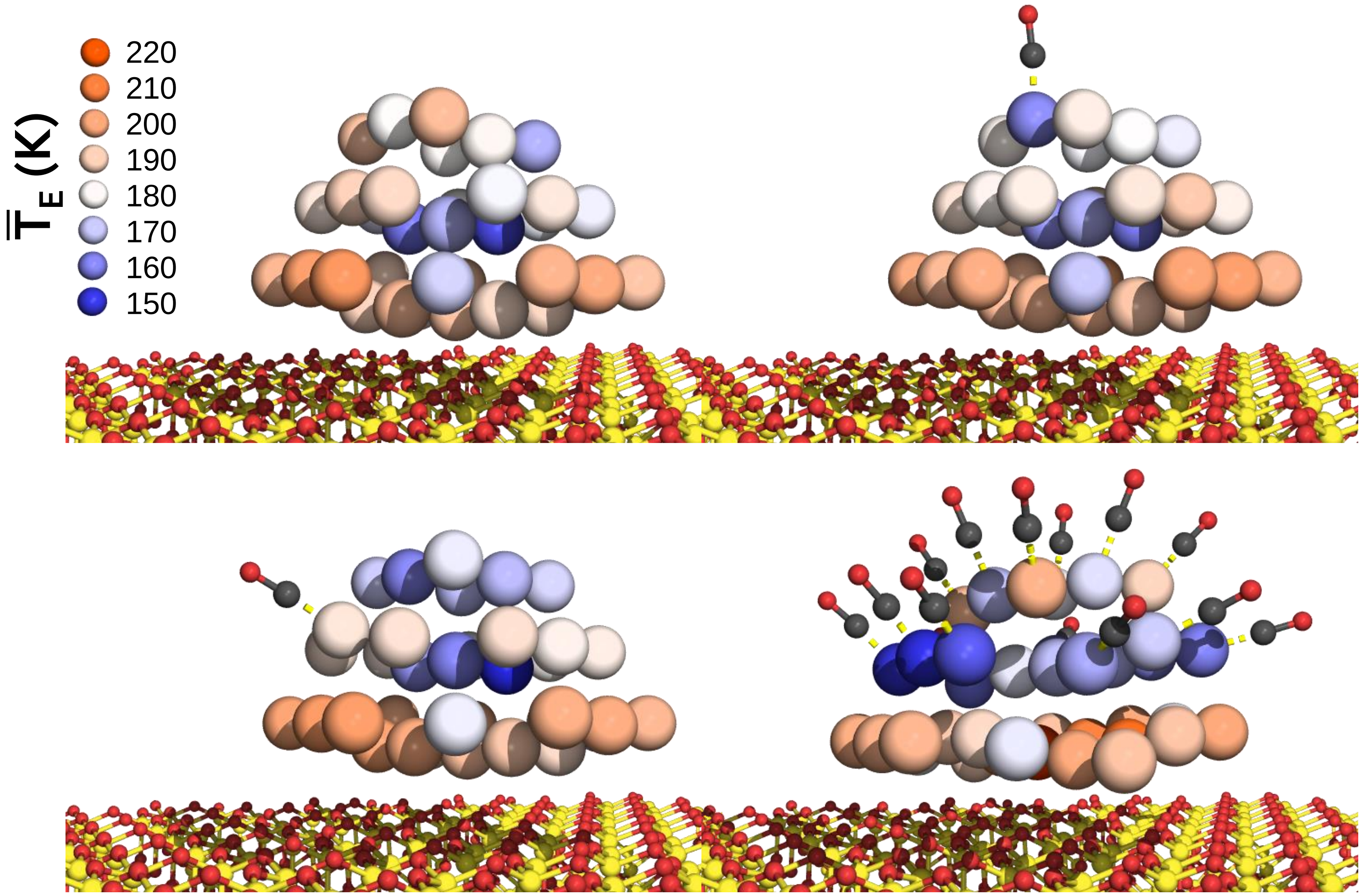
$\gamma \cong 1.7$



Broad range of stiffness over single nanoparticle

Reduced Gruneisen parameter (γ) *vs* metal

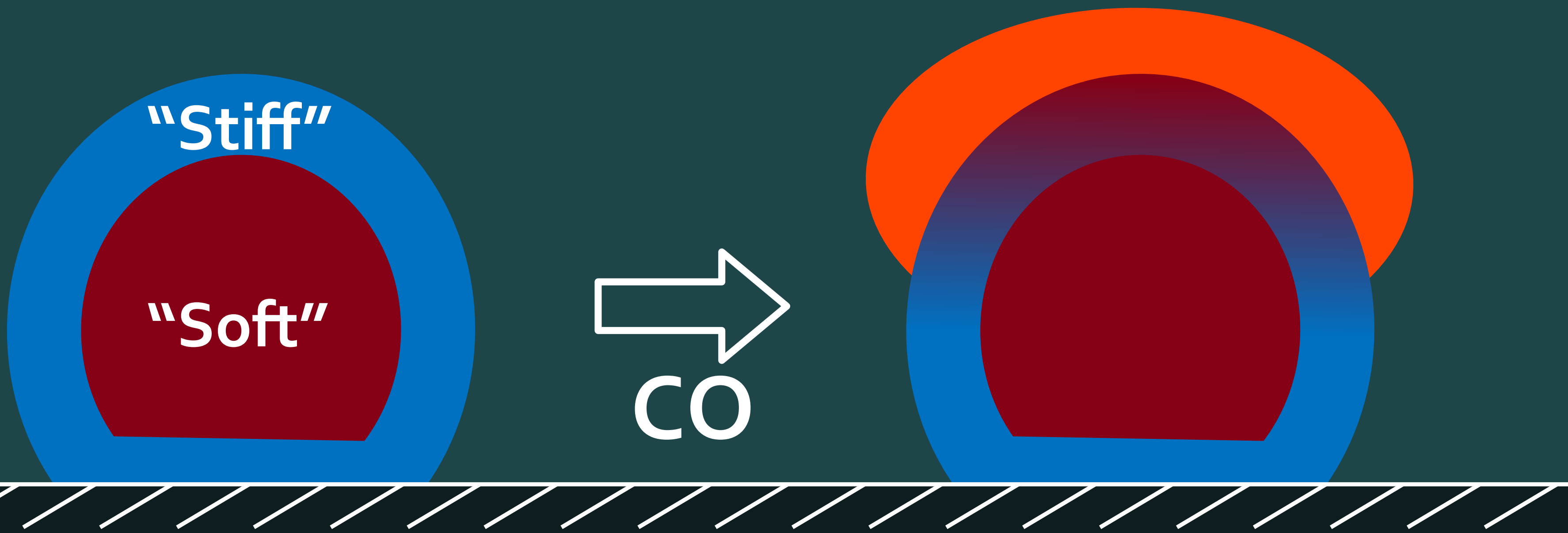
Mean PtPt Einstein Temperatures on SiO_2



Model of Stiffness

Pt nanoparticles have:

- Stiff outer shell (Shorter R_{PtPt}, less #NN)
- Soft core (Longer R_{PtPt}, more #NN)
- Outer shell weakens upon CO adsorption



Conclusions

- Inhomogeneity encompasses nanoparticle behavior:
  - Changes reactivity
  - Modulates charge distribution
  - Modulates structure and vibrations
  - Coupled to adsorbate interaction

- Correlations between XAFS parameters
  - #NN $\Leftrightarrow$ R_{PtPt} $\Leftrightarrow$ ν_E $\Leftrightarrow$ σ^2_{PtPt}

- Future work
  - Finite temperature dynamics
  - Local x-ray spectroscopy

Structural and charge inhomogeneity in supported Pt clusters

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