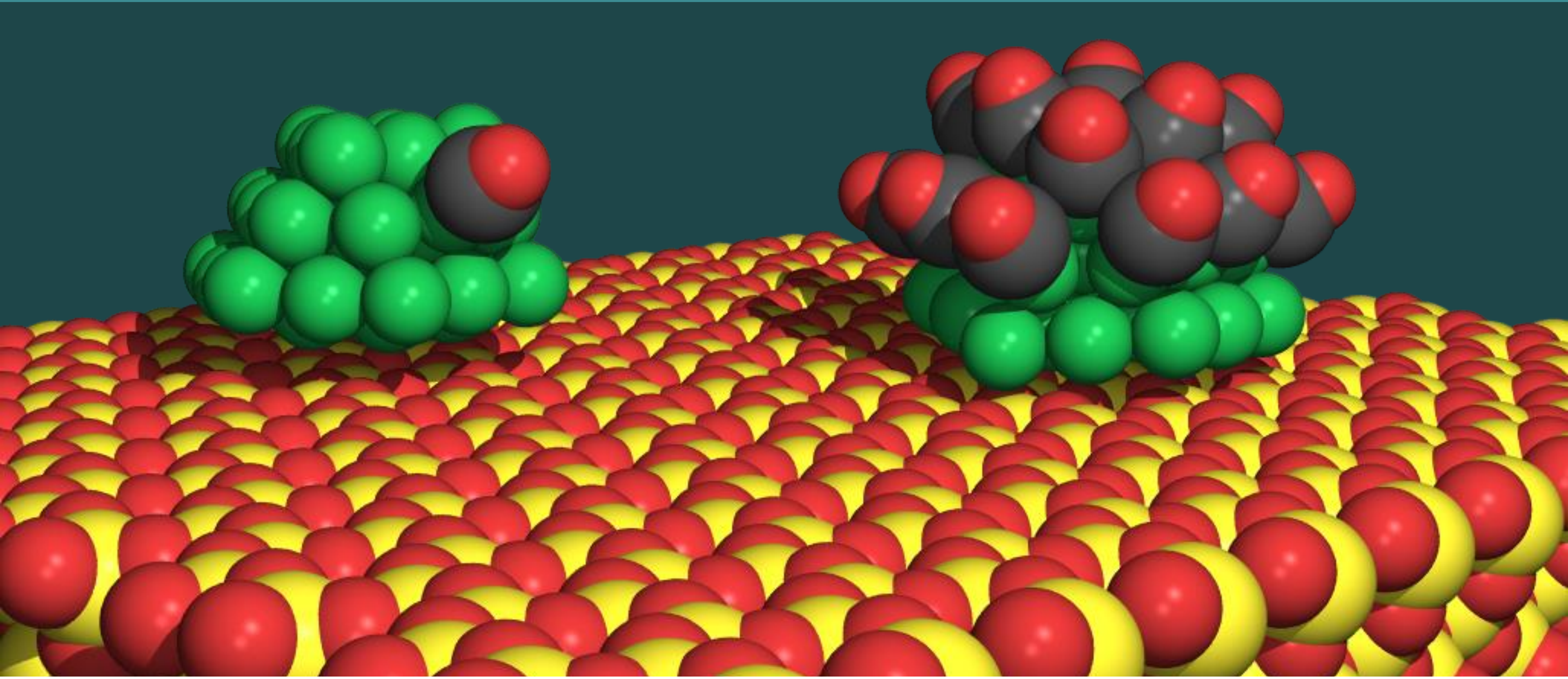
Structural and charge inhomogeneity in supported Pt clusters

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



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An evolving picture of metal nanocatalysts

Metal nanocatalysts:

- Keystone of heterogeneous catalysis in industry

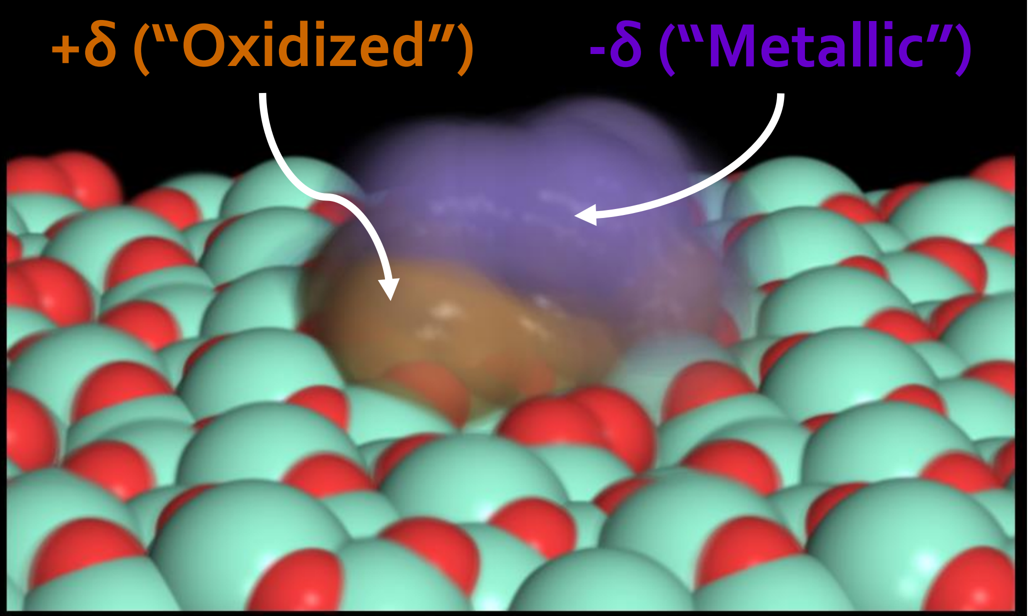
Theoretical studies of nanocatalysts used to:

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

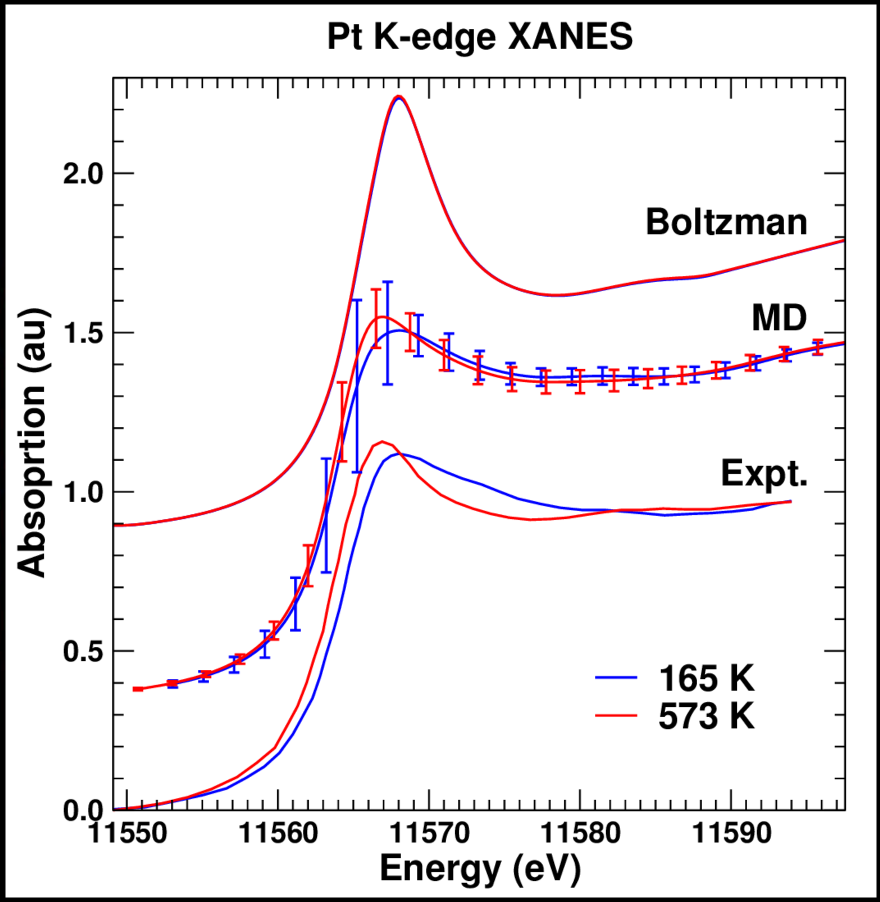
More recently:

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

Static simulations are not sufficient



Pt$_{10}$ on γ-Al_2O_3 @ 165 K



Need dynamics to reproduce experiment

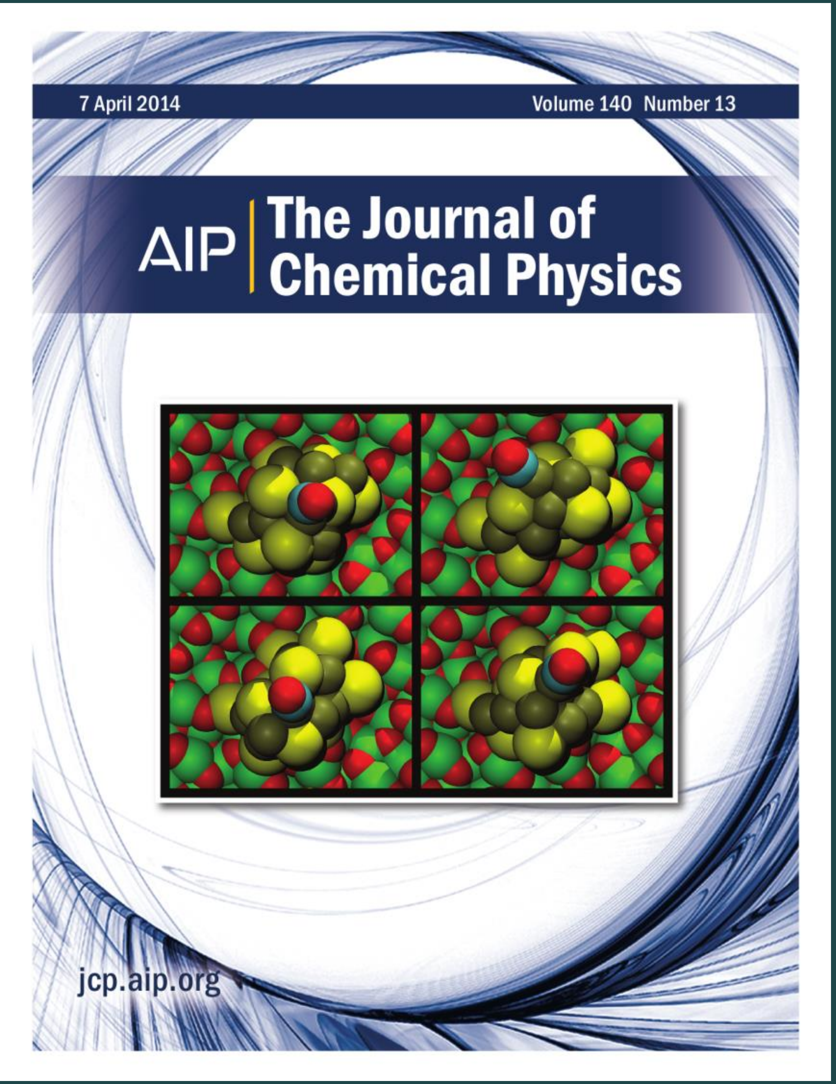
Vila *et al.* Physical Review B **78**, 121404(R), 2008

Dynamic Structural Disorder (DSD) in Nanoparticles

DSD drives:

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

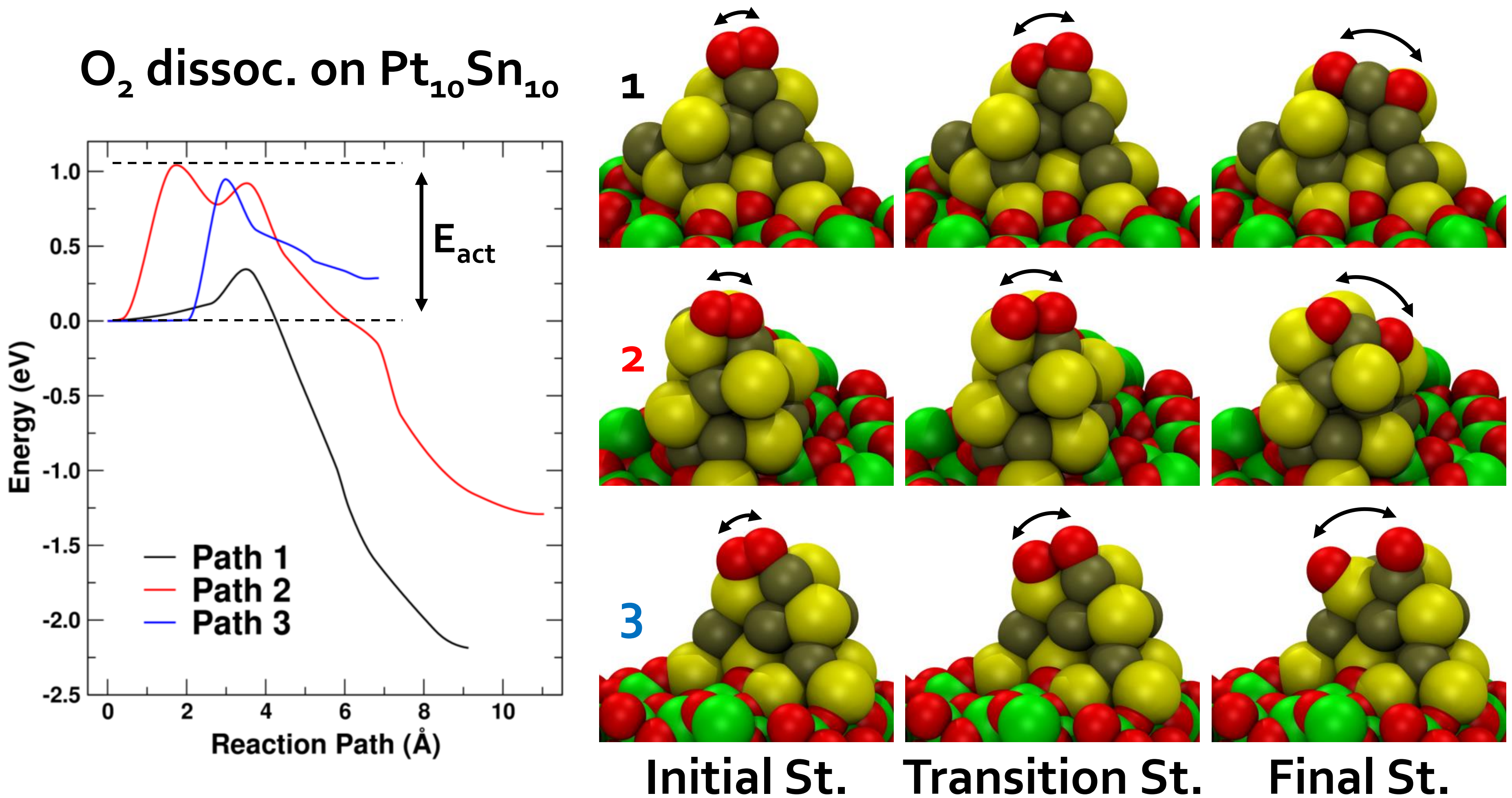
Inhomogeneity



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

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

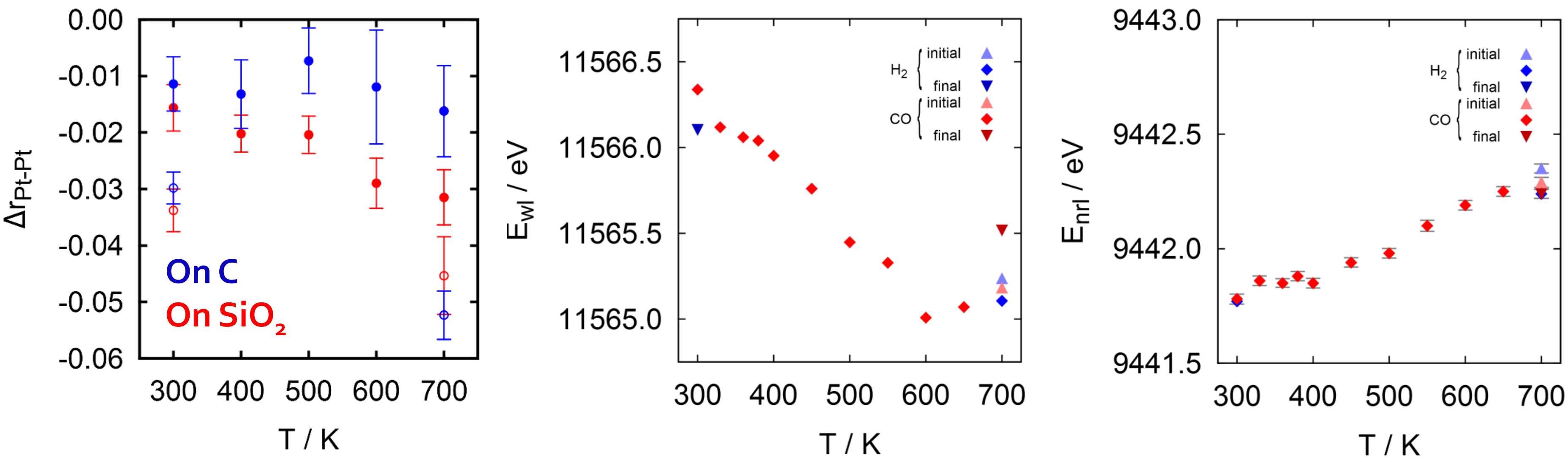
Disorder affects reactivity



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

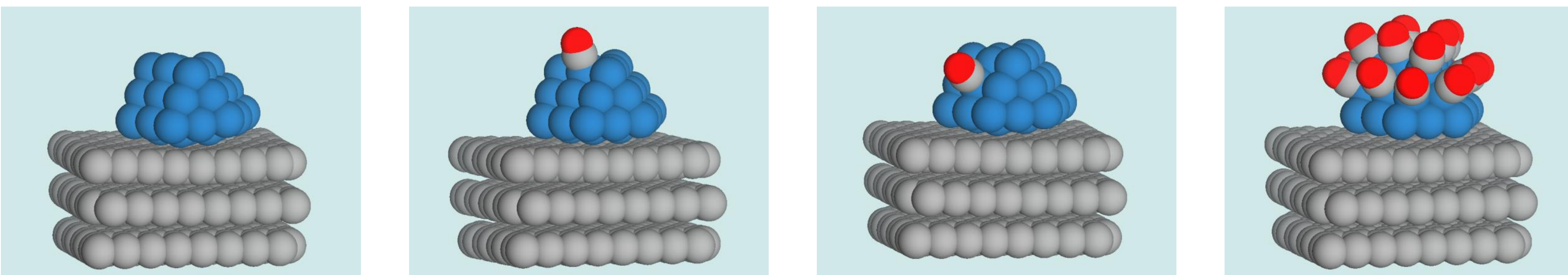
EXAFS measurements: Predict truncated cuboctahedron Pt_{37}

Hypothesis: Both phenomena related to desorption

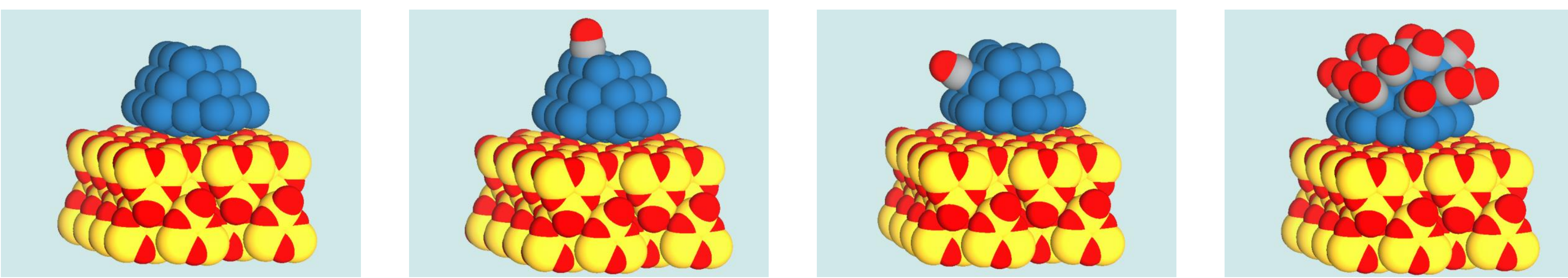
Is inhomogeneity important to these phenomena too?

Preliminary Methods and Models

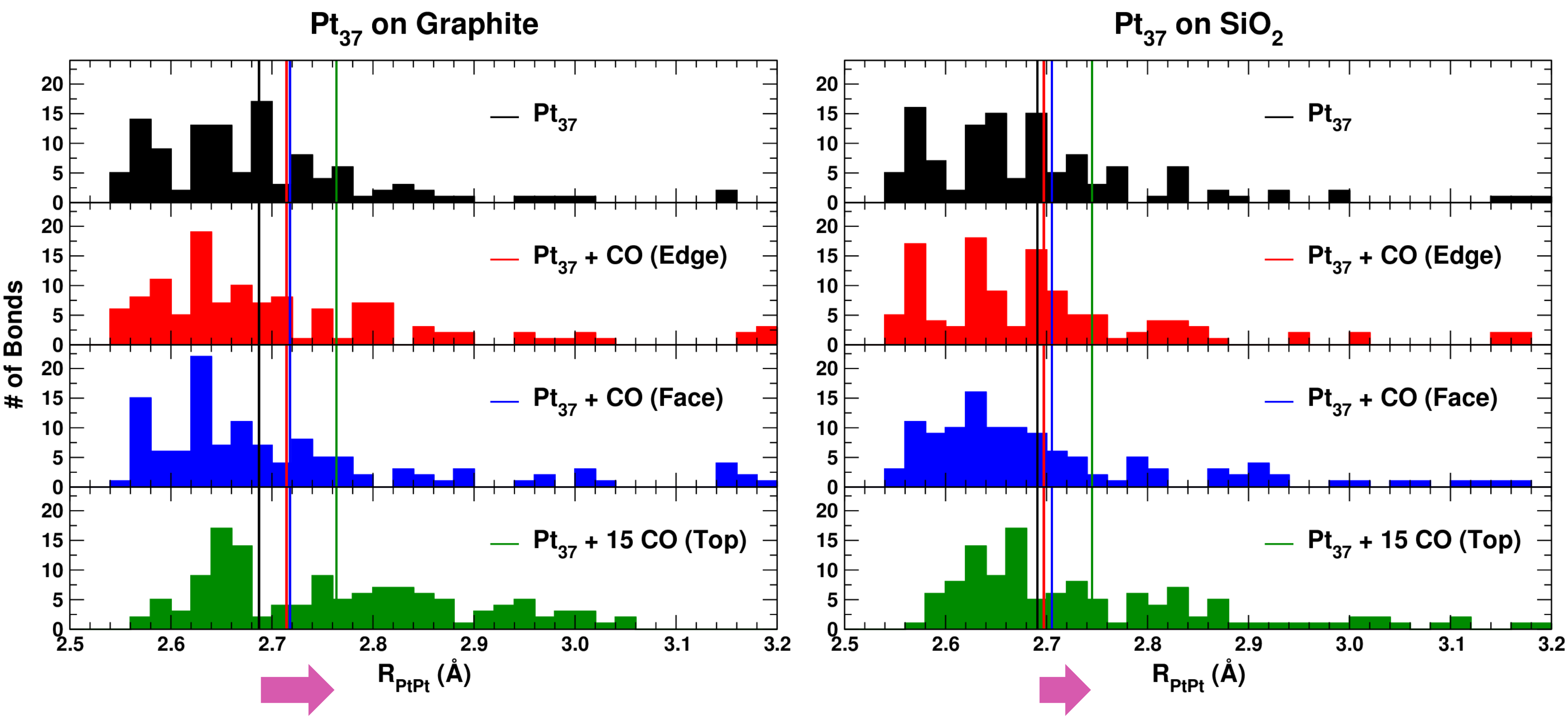
- Pt_{37} on C and SiO_2:
  - PBE/PAW optimization with 400 eV planewave cutoff
  - C surface: 3 graphite layers (4 x 4, 384 atoms)
  - SiO_2: reconstructed (001) α-quartz (2 x 4, 278 atoms)



Clean | Edge | Face | High Cov.



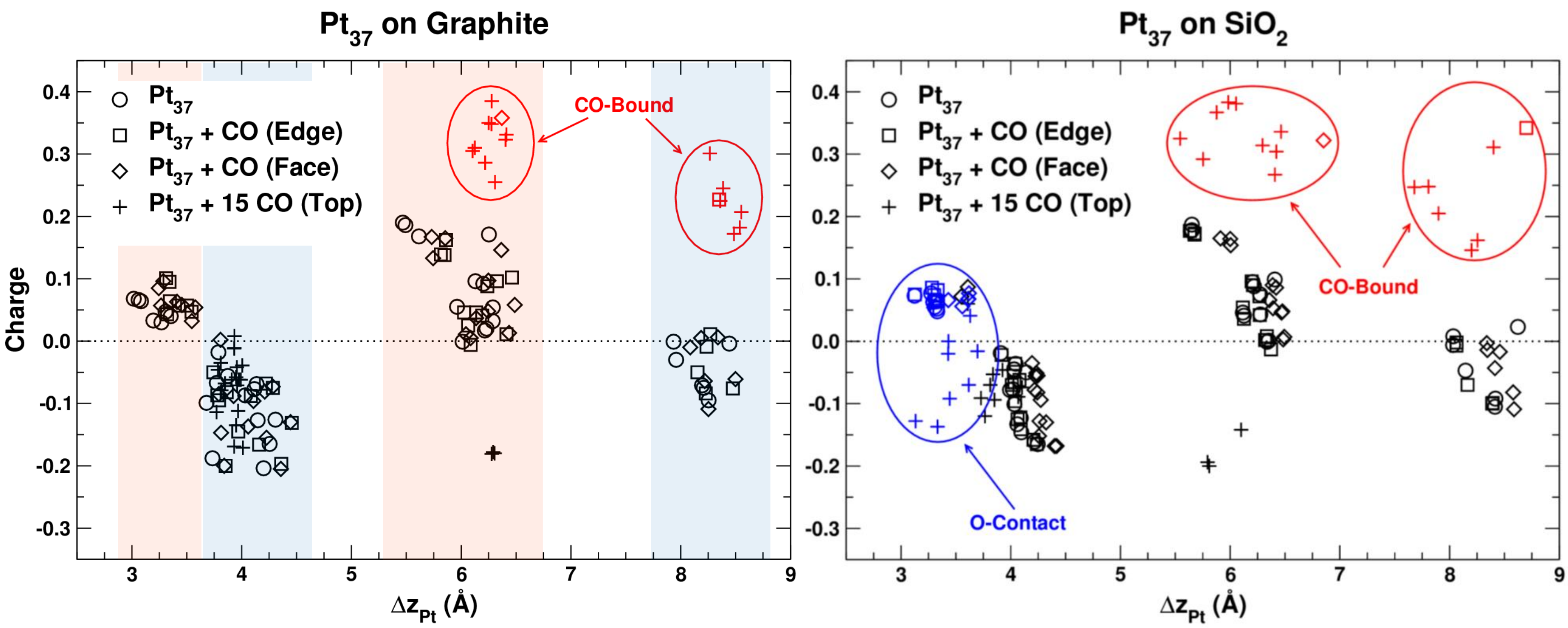
Bond expansion



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

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

Charge inhomogeneity

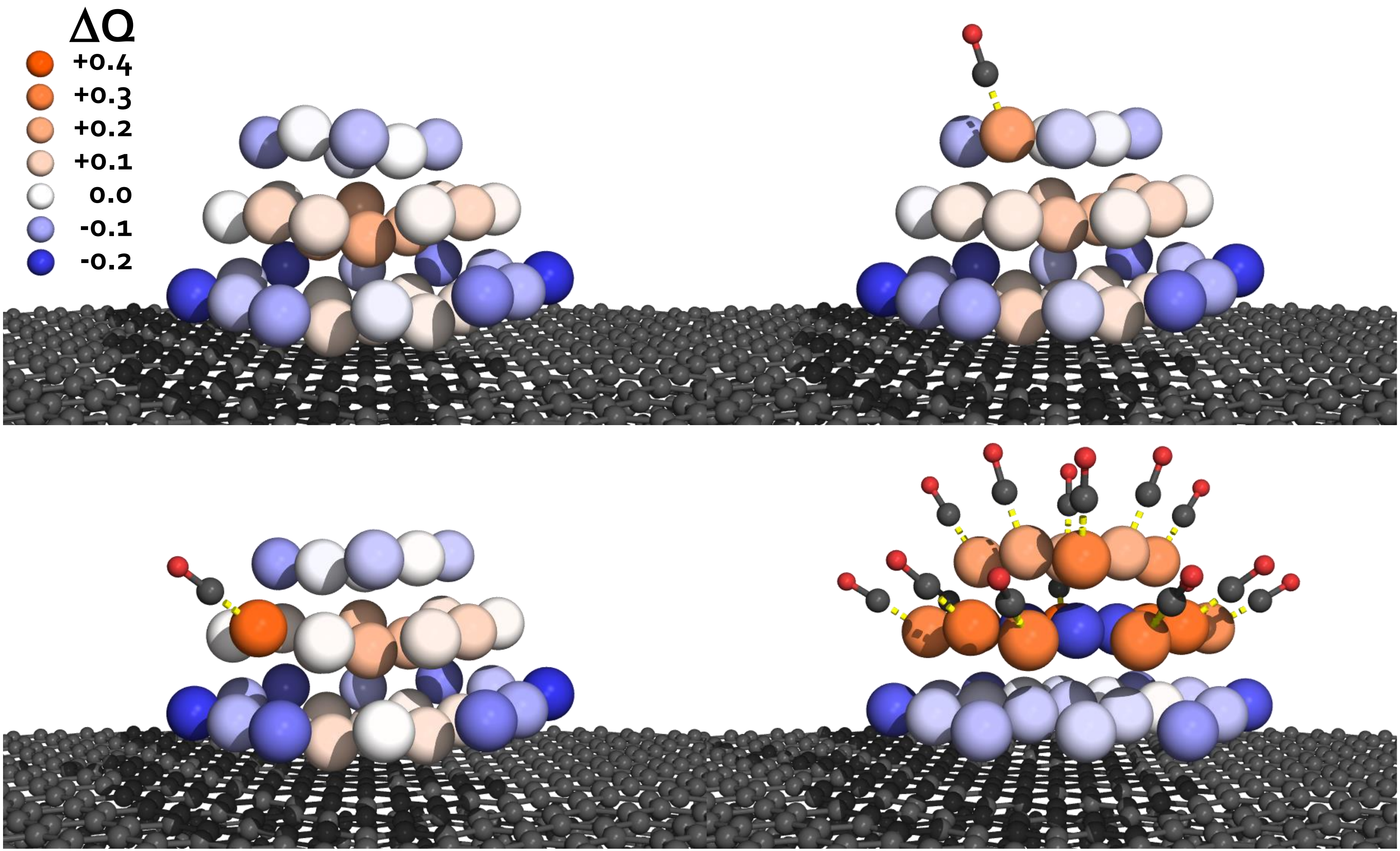


CO-bound Pt atoms loose 0.2-0.3*e* each

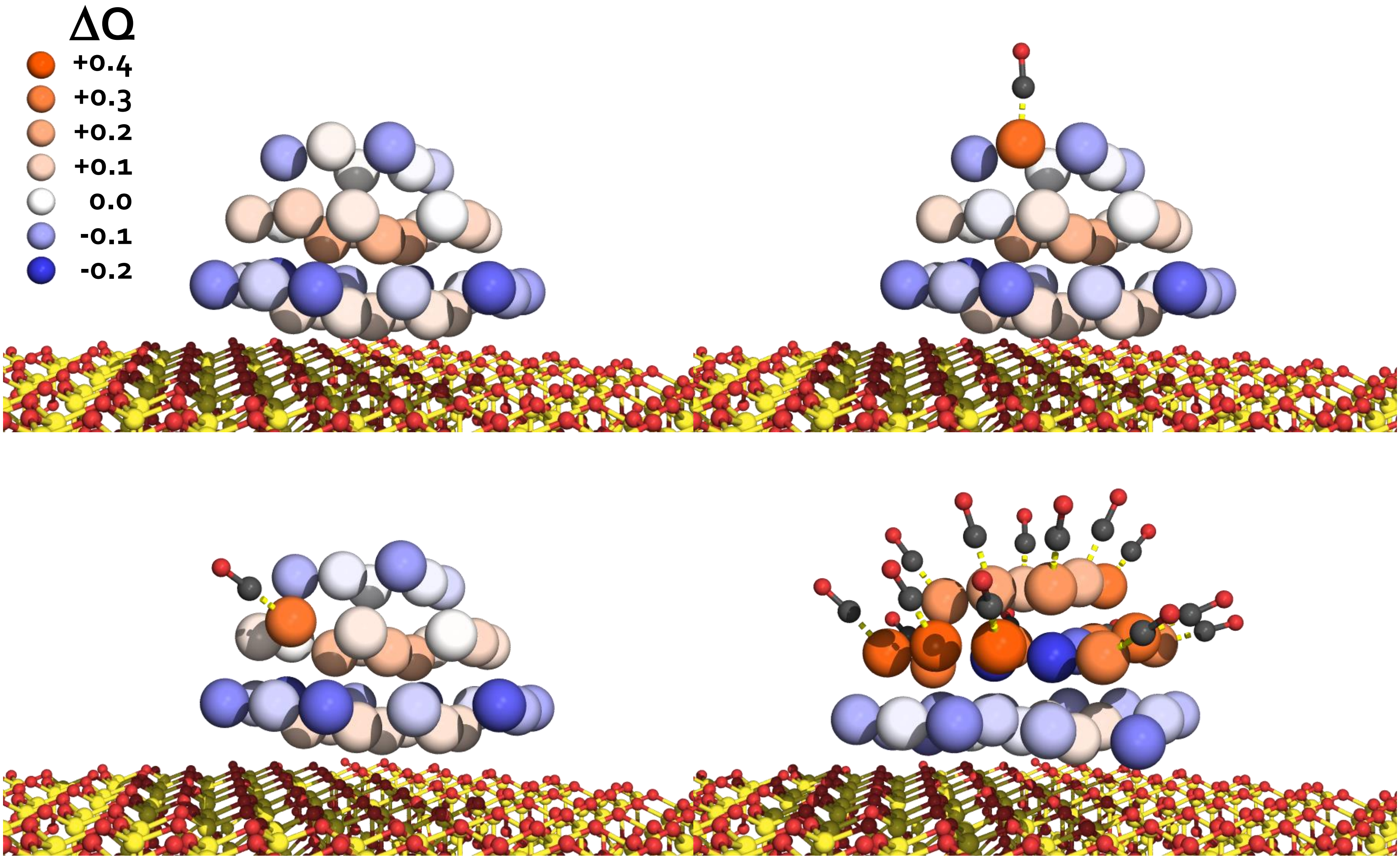
Layer charge alternation

Bond expansion due to charge loss

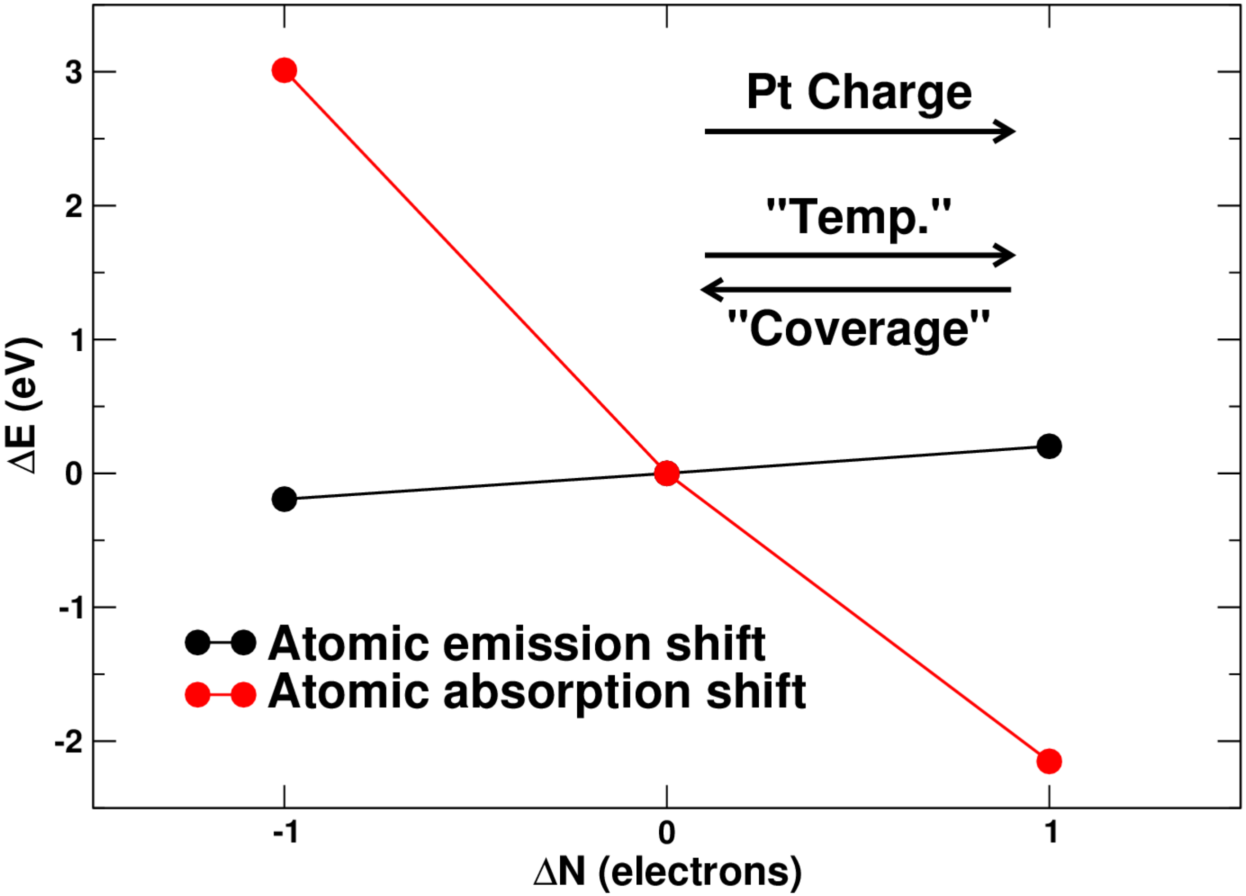
Charge inhomogeneity in C



Charge inhomogeneity in SiO_2



Atomic edge absorption and core emission shifts



Opposite trends: Qualitatively reproduce experiment

Conclusions

- Inhomogeneity encompasses nanoparticle behavior:
    - Changes reactivity
    - Modulates charge distribution
    - Coupled to adsorbate interaction
- Future work
    - Finite temperature dynamics
    - Better treatment of core energy shifts
    - Inhomogeneity in Debye-Waller factors
    - Local x-ray spectroscopy

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