Density Functional Theory Applied to the Sudy of Clusters, Surfaces, and Solids

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-Prof. Dr. Su-Huai Wei

-Prof. Dr. Guilherme M. Sipahi

-Prof. Dr. Germano Tremiliosi-Filho

-Prof. Dr. Victor Richard-Lopez

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Theoretical Approach

Ab initio Potentials: Density Functional Theory

$$h\phi_i^{KS}(\mathbf{r}) = \varepsilon_i^{KS}\phi_i^{KS}(\mathbf{r}) \qquad h = -\frac{1}{2}\nabla_i^2 + V_{eff}(\mathbf{r})$$

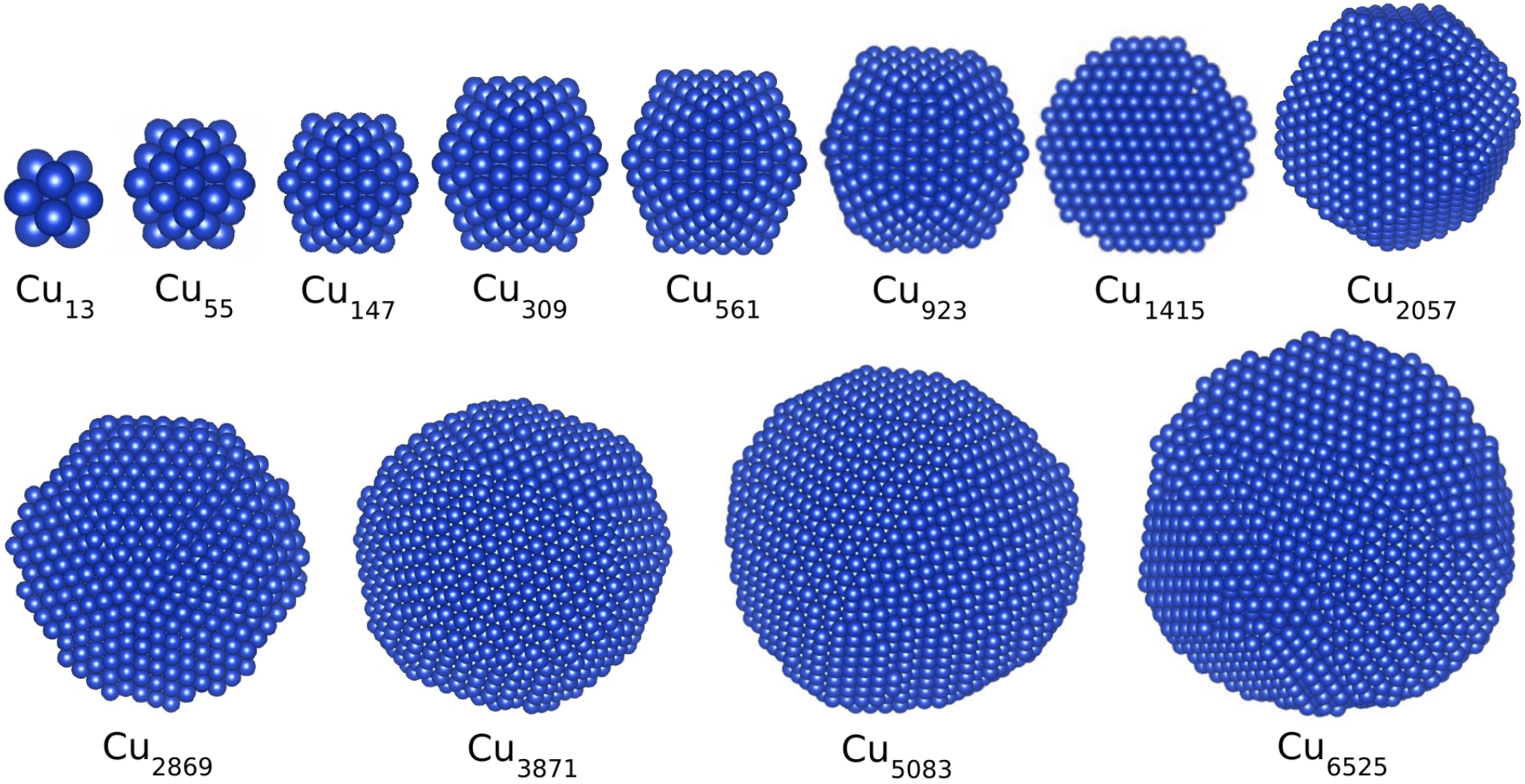
Force-Fields: pair-potentials, many-body, ReaxFF, ….

$$E_{tot}\left(\{\mathbf{R}_i\}\right) = \sum_{i=1}^{N} U_1\left(\mathbf{R}_i\right) + \sum_{i=1,j>i}^{N} U_2\left(\mathbf{R}_i,\mathbf{R}_j\right) + \sum_{i=1,j>i,k>j}^{N} U_3\left(\mathbf{R}_i,\mathbf{R}_j,\mathbf{R}_k\right) +$$

$$+ \sum_{i=1,j>i,k>j,l>k}^{N} U_4\left(\mathbf{R}_i,\mathbf{R}_j,\mathbf{R}_k,\mathbf{R}_l\right) + \cdots,$$

LAMMPS
GOTNano

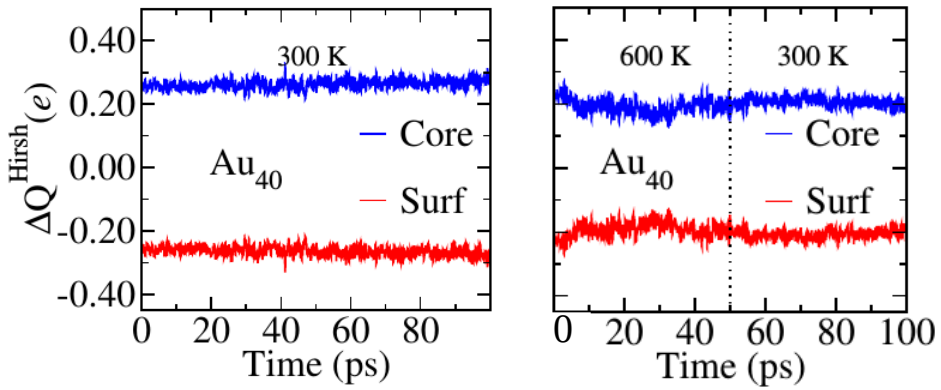
GOTNano: Atomic Structure



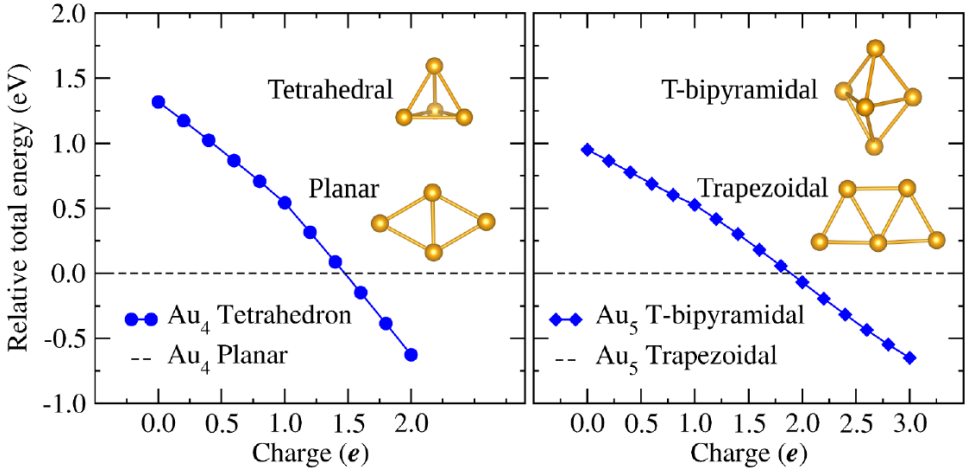
We are able to obtain the putative global-minimum configuration for a given number of atoms for particles with few to 10000 atoms combined with LAMMPs, etc.

Temperature Effects on Au_n

Charge Hirshfeld Analysis



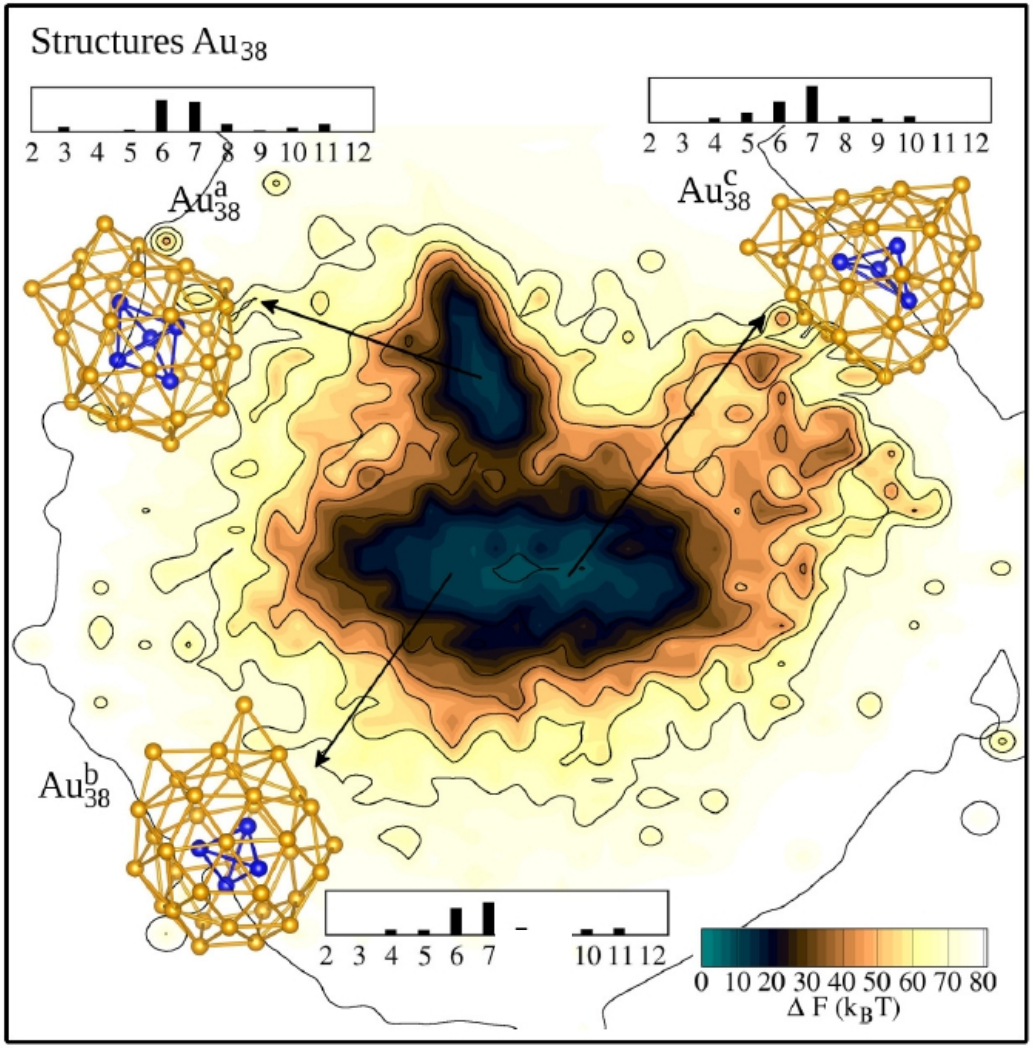
Stability vs. Charge State



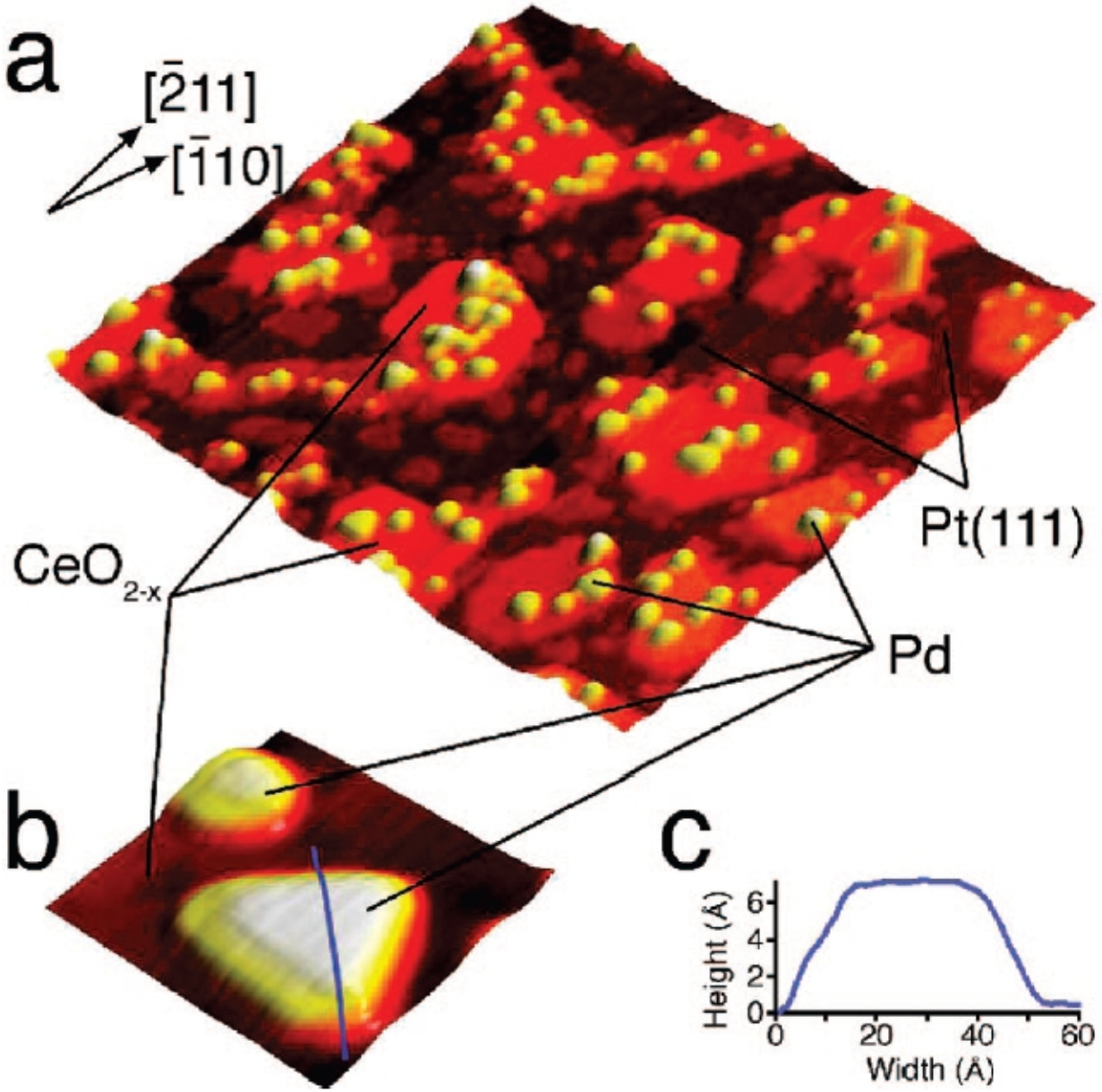
Guedes-Sobrinho D. *et al.*
Manuscript in preparation

Ab-initio Molecular Dynamics

Temperature: 300 K



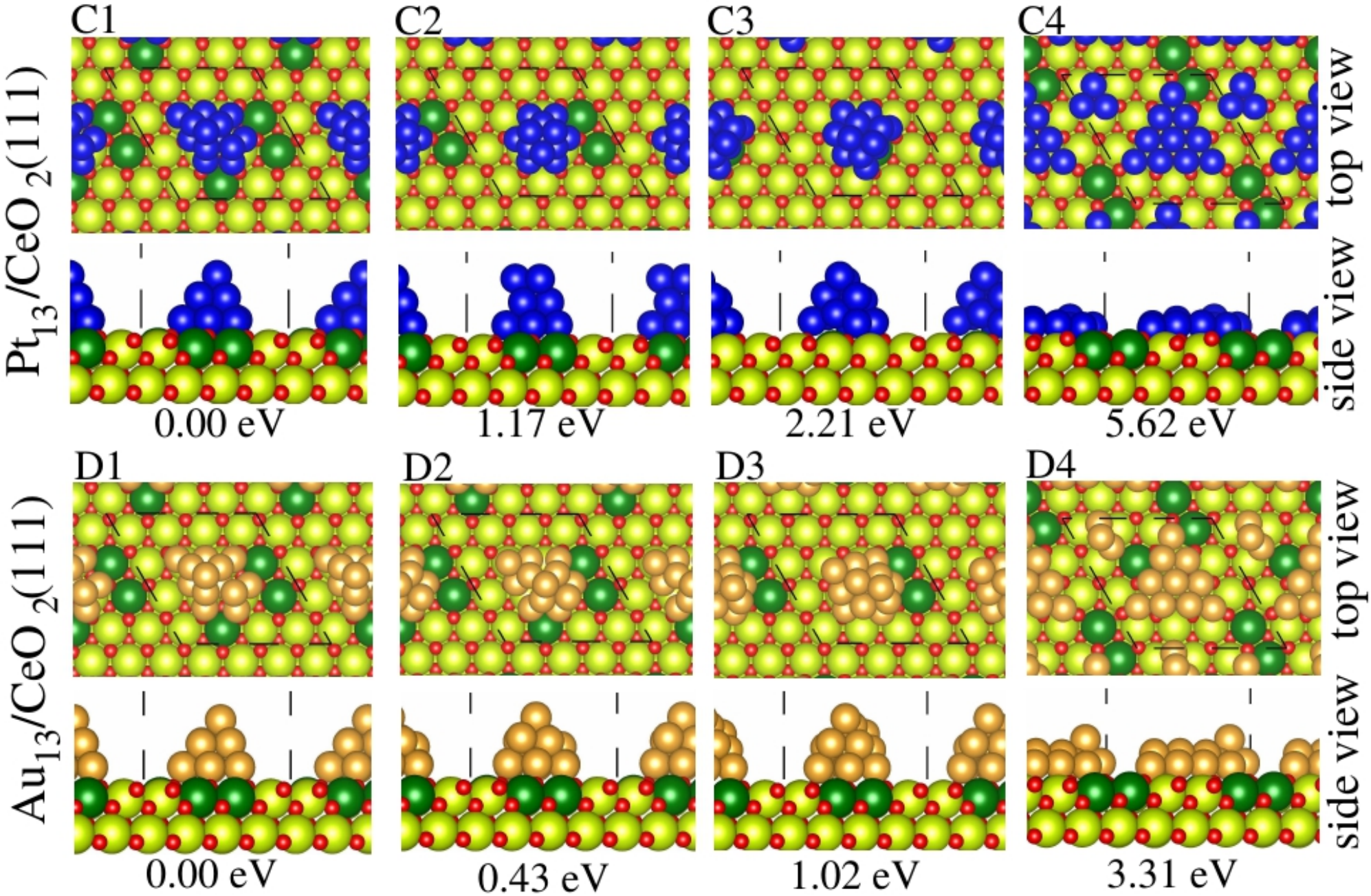
$Pd/CeO_{2-x}/Pt(111)$: Ce^{III} Cations



Pd particles supported on the CeO_{2-x} surfaces contributes to increase the transition from Ce^{IV} to Ce^{III}. Thus, it contributes to increase the amount of Ce^{III} on the CeO_{2-x} surfaces.

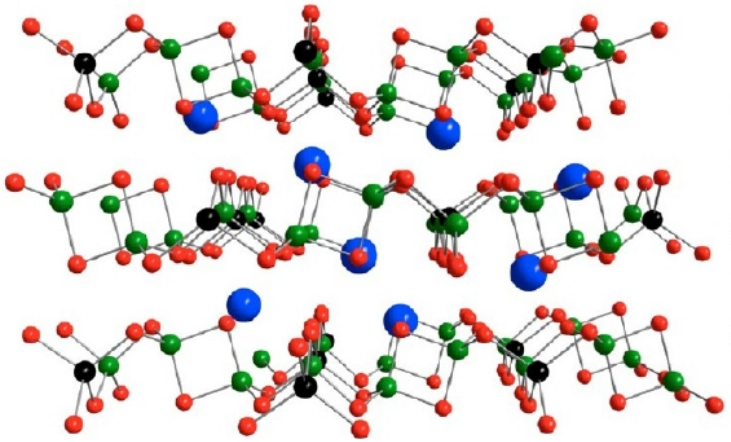
Wilson et al, J. Phys. Chem. C **112**, 10918 (2008).

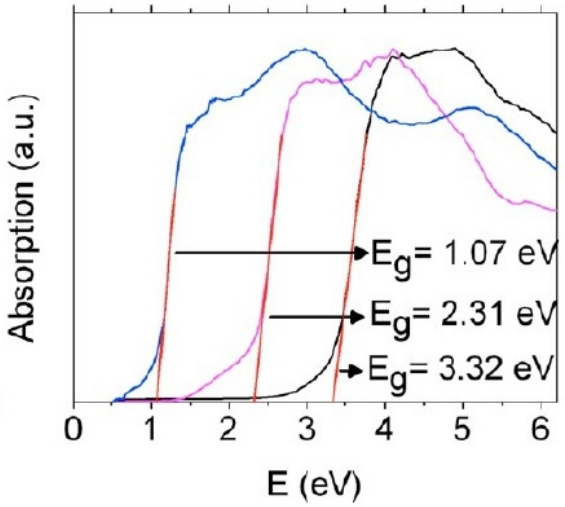
TM_{13} Clusters on $CeO_2(111)$



Chalcogenides: Band Gap Engineering

$Cs_2M^{II}M^{IV}{}_3Q_8$, 11 synthesized compounds (M^{II} = Mg, Zn, Cd, Hg; M^{IV} = Ge, Sn; Q = S, Se, Te). Quaternary semiconductors with layered crystal structure(Orthorhombic lattice, Space group $P2_12_12_1$, Z = 4).





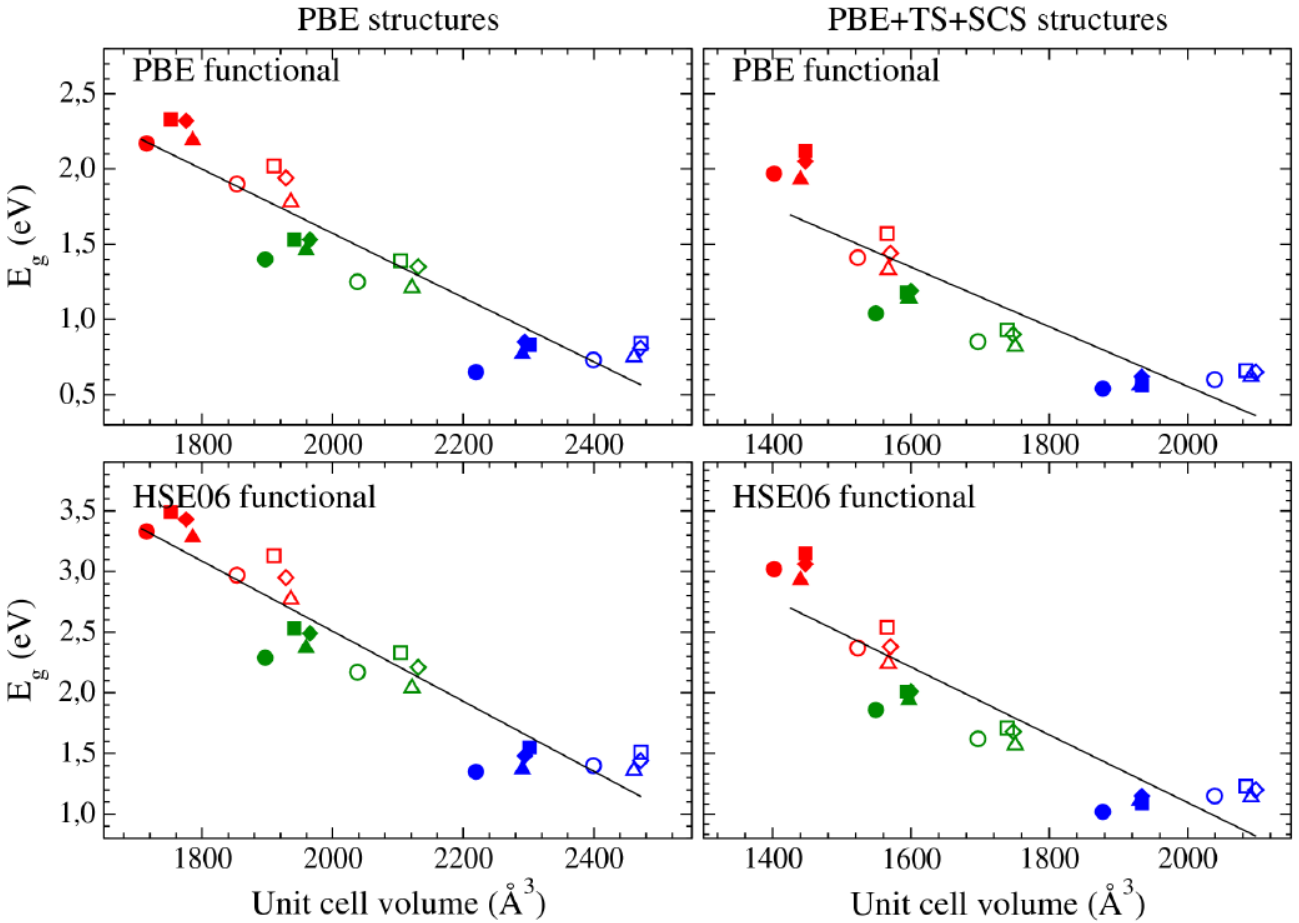
Morris, C. D. *et al.*, *Chem. Mater.* **2013**, 25, 3344.

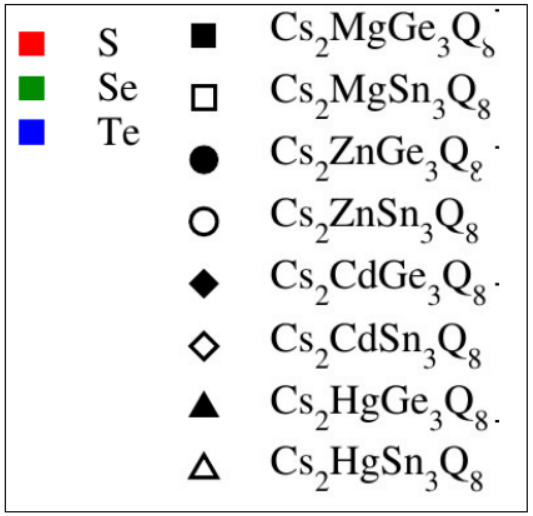
Measured band gaps vary from 1.0 eV to 3.4 eV, indicating potential for band gap engineering.
Only 11 of the 24 possible compositions were synthesized and characterized.

Objective: characterize all the compounds of this family and understand the effects of composition.

R. Besse, F. P. Sabino, J. L. F. Da Silva, Phys. Rev. B 93, 165205 (2016).

Chalcogenides: Band Gap Engineering





Approximate linear correlation between band gap and cell volume.

Large variety of band gaps consistent with experimental observation.

The change in the Q species leads to the largest variations in the band gap: decrease as atomic number gets larger, known trend in families of chalcogenides (higher VBM due to increase in energy of Q p states).

Band gaps obtained with HSE06 and PBE structures agree very well with experimental results for most of compounds with available experimental data: errors smaller than 0.1 eV.

Cs2MgGe3Se8, Cs2MgSn3Se8, Cs2ZnGe3Te8: overestimated by 0.28 eV to 0.50 eV (better than PBE)

Publications: 2014 - 2016

26 Publications + 6 Submitted manuscripts.

- **1 ACS Catalysis**
- **5 Journal of Physical Chemistry C**
- **3 Physical Chemistry Chemical Physics**
- **1 Dalton Transactions**
- **4 Physical Review B**
- **2 RSC Advances**

- **2 Journal of Chemical Physics**
- **3 Journal of Physical Chemistry A**
- **3 Journal of Physics: Condensed Matter**
- **1 Computational Material Science**
- **1 Semiconductor Science and Technology**