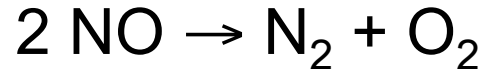




# Example reaction

Dream reaction: Low-T direct decomposition of NO



NO is unstable (  $\Delta G_f^0 = -1.53 \text{ eV}$  at  $25^\circ\text{C}$  )

Large reaction activation barrier ( approximately  $3.8 \text{ eV}$  )

## Catalytic Conversion Today

➤ Chemical plants and power plants:

Selective catalytic reduction (SCR) with ammonia

➤ Gasoline motor vehicles:

Catalytic reduction in the presence reductants such as hydrocarbons and CO

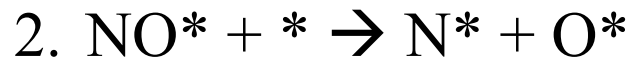
# Micro-kinetic Expressions



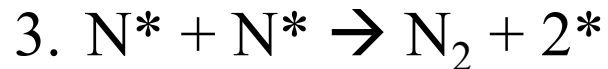
## Direct decomposition on a metal catalyst



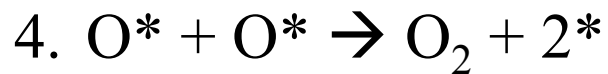
$$r_1 = k_1 \theta_* p_{\text{NO}} (1 - \gamma_1)$$



$$r_2 = k_2 \theta_* \theta_{\text{NO}} (1 - \gamma_2)$$

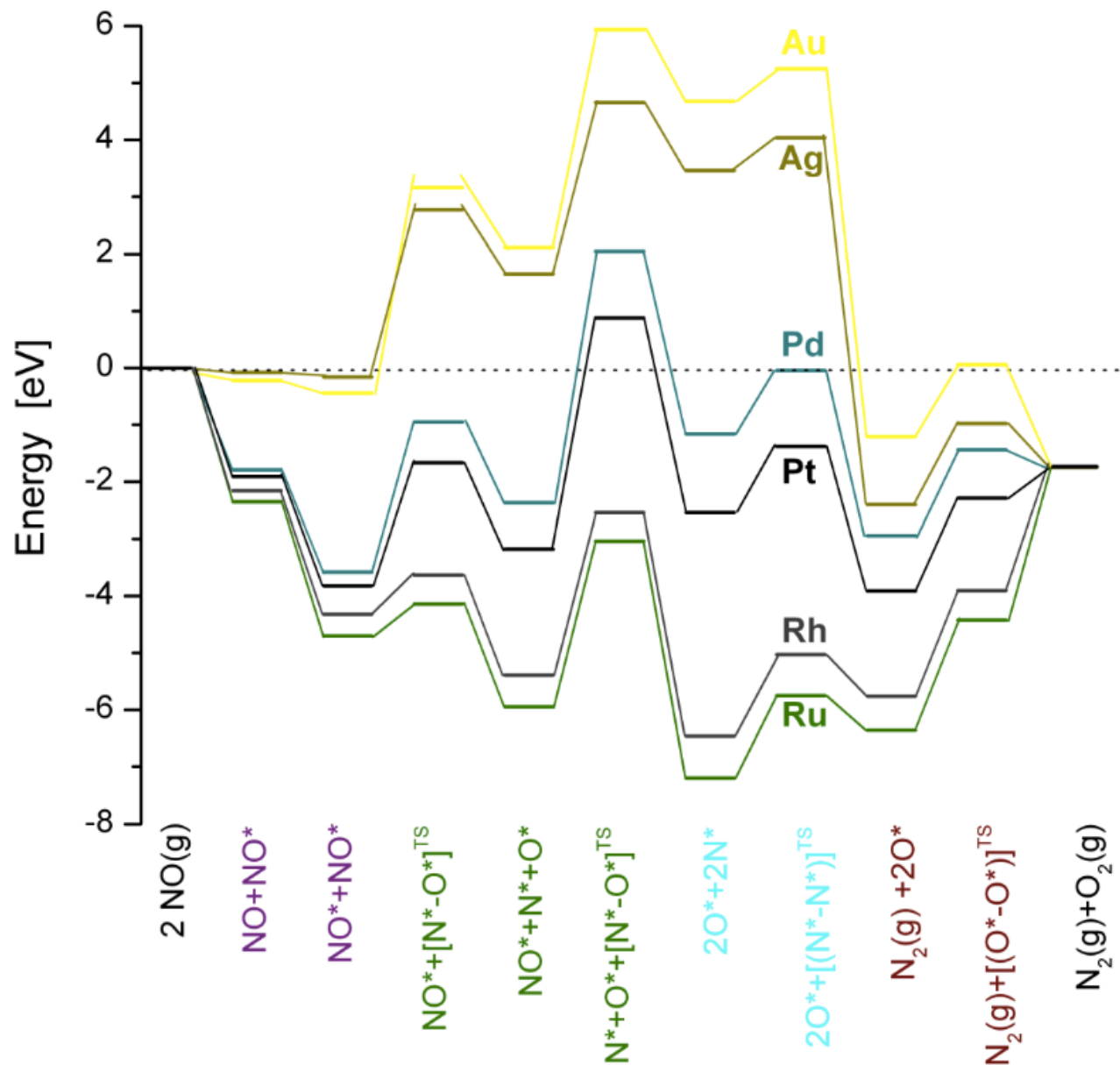


$$r_3 = 2 k_3 \theta_{\text{N}}^2 (1 - \gamma_3)$$



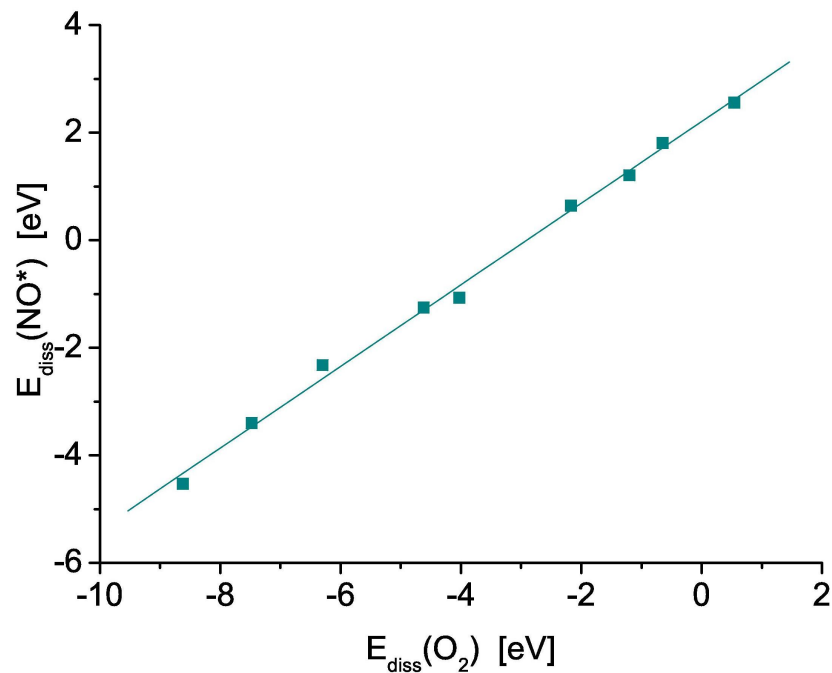
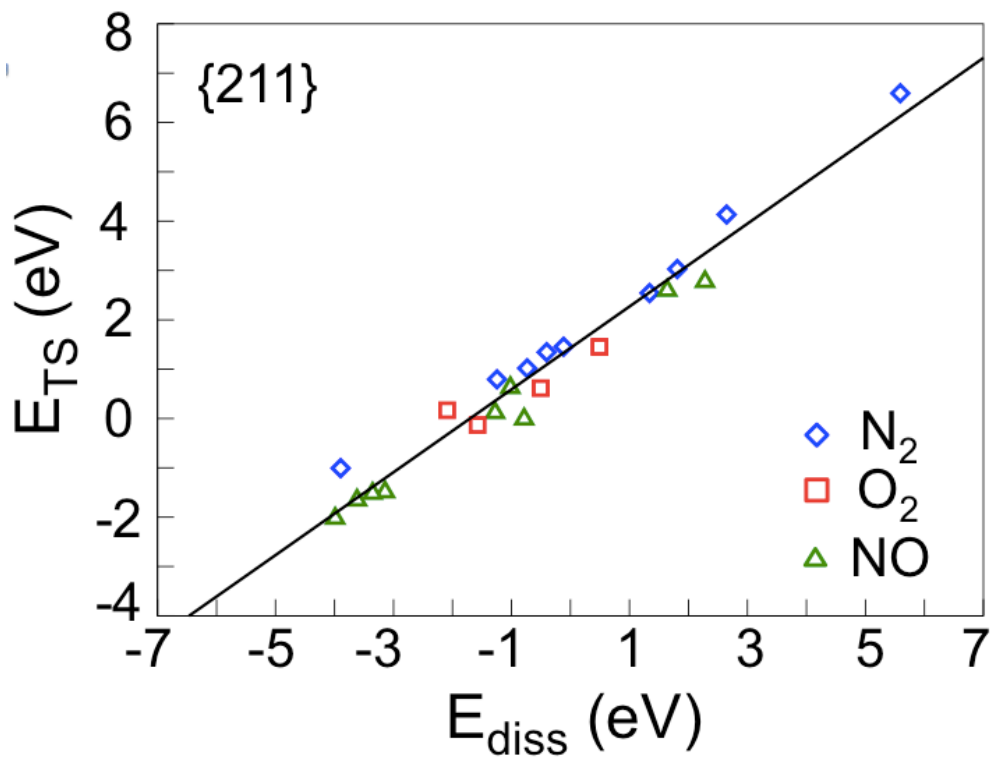
$$r_4 = 2 k_4 \theta_{\text{O}}^2 (1 - \gamma_4)$$

# Energy diagrams



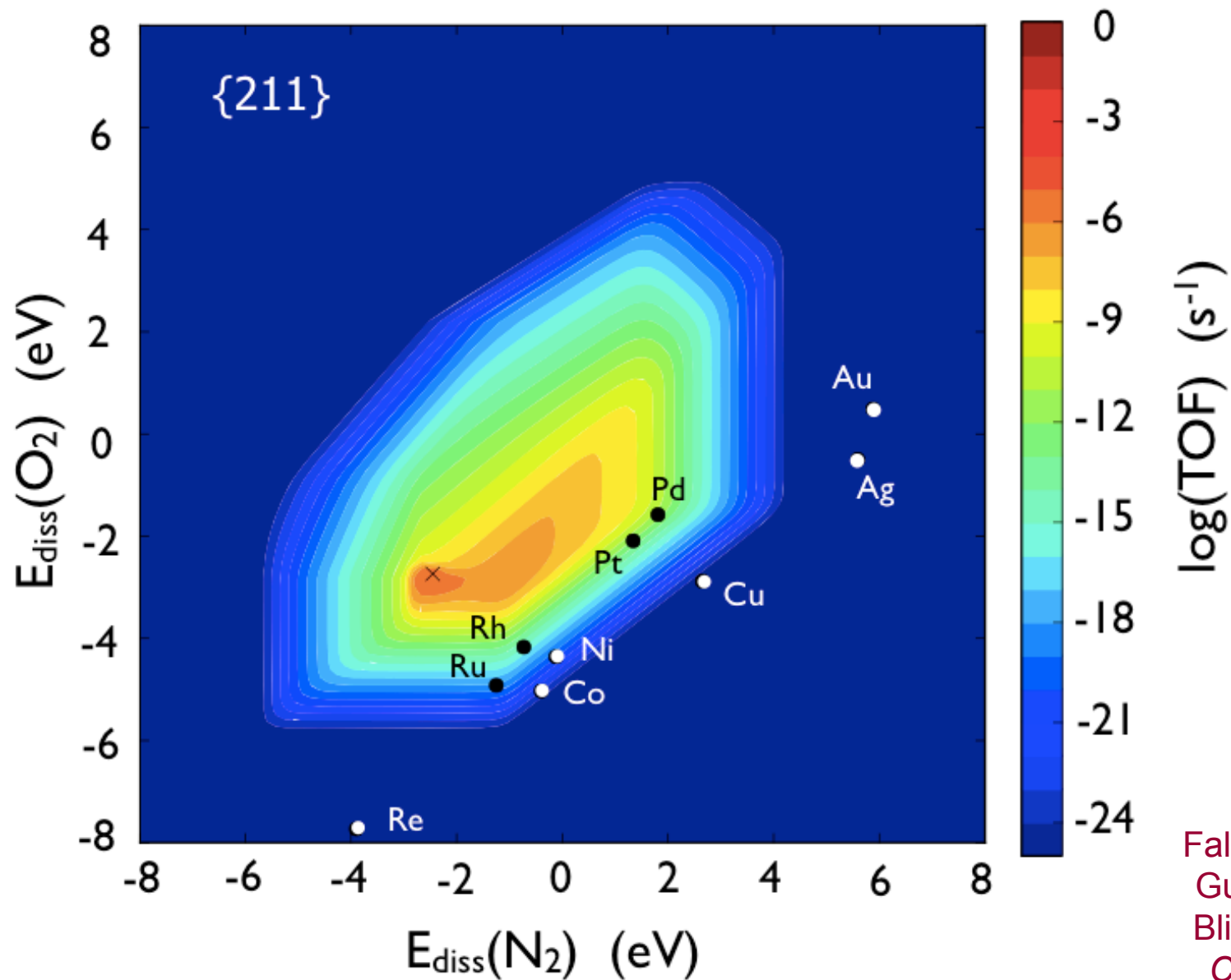
Falsig, Bligaard,  
Christensen, Nørskov,  
*Pure & Appl. Chemistry*  
**79**, 1895 (2007)

# Linear Energy Relationships



Falsig, Bligaard,  
Christensen, Nørskov,  
*Pure & Appl. Chemistry*  
**79**, 1895 (2007)

# Steady-state microkinetics



Falsig, Shen, Khan,  
Guo, Jones, Dahl,  
Bligaard, *Topics in  
Catalysis* (2013)

# Error analysis in catalysis

3 knowledge prerequisites for establishing confidence in a *Standard Model*:

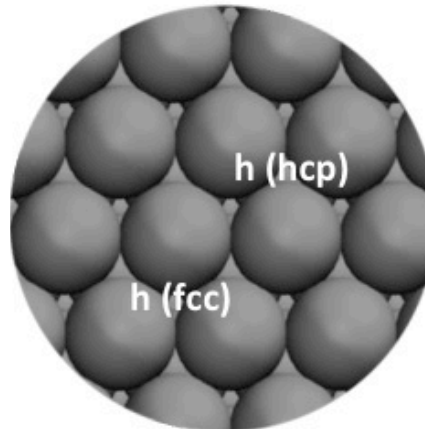
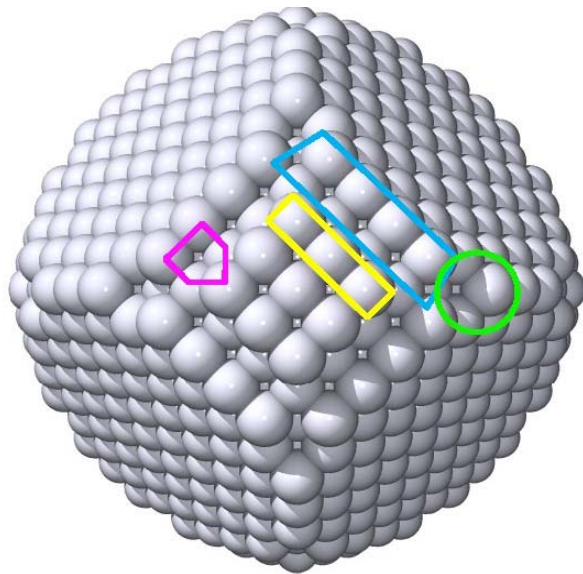
- Error sources
- Sensitivity of scientific conclusions
- Uncertainties

Error Sources:

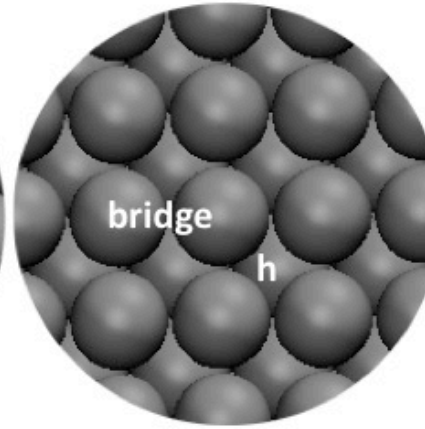
- Poor kinetics
- Structure & mechanistic assumptions
- Dimensionality reduction (TS and adsorbate scaling)
- Adsorbate-adsorbate interactions
- Uncertainty in the electronic structure calculations
- ...

# Errors introduced by Structural assumptions

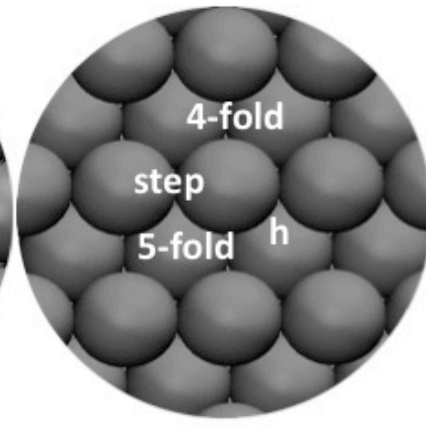
# Surface structure



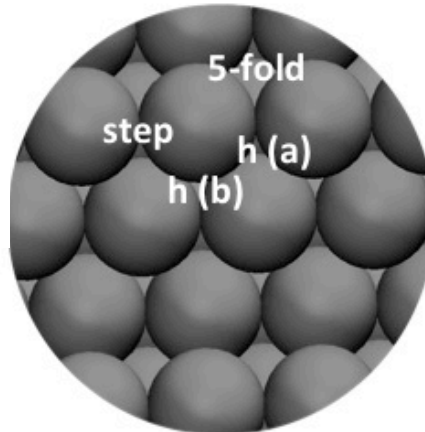
(111) closed packed surface



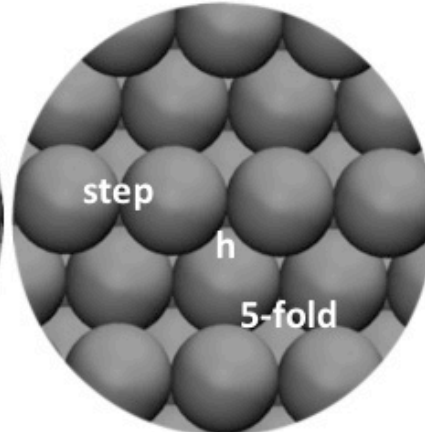
(100) closed packed surface



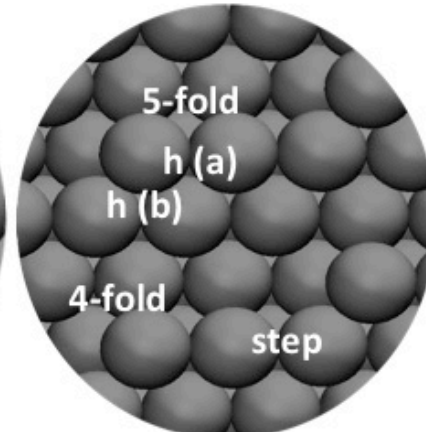
(110) closed packed surface



(211) stepped surface



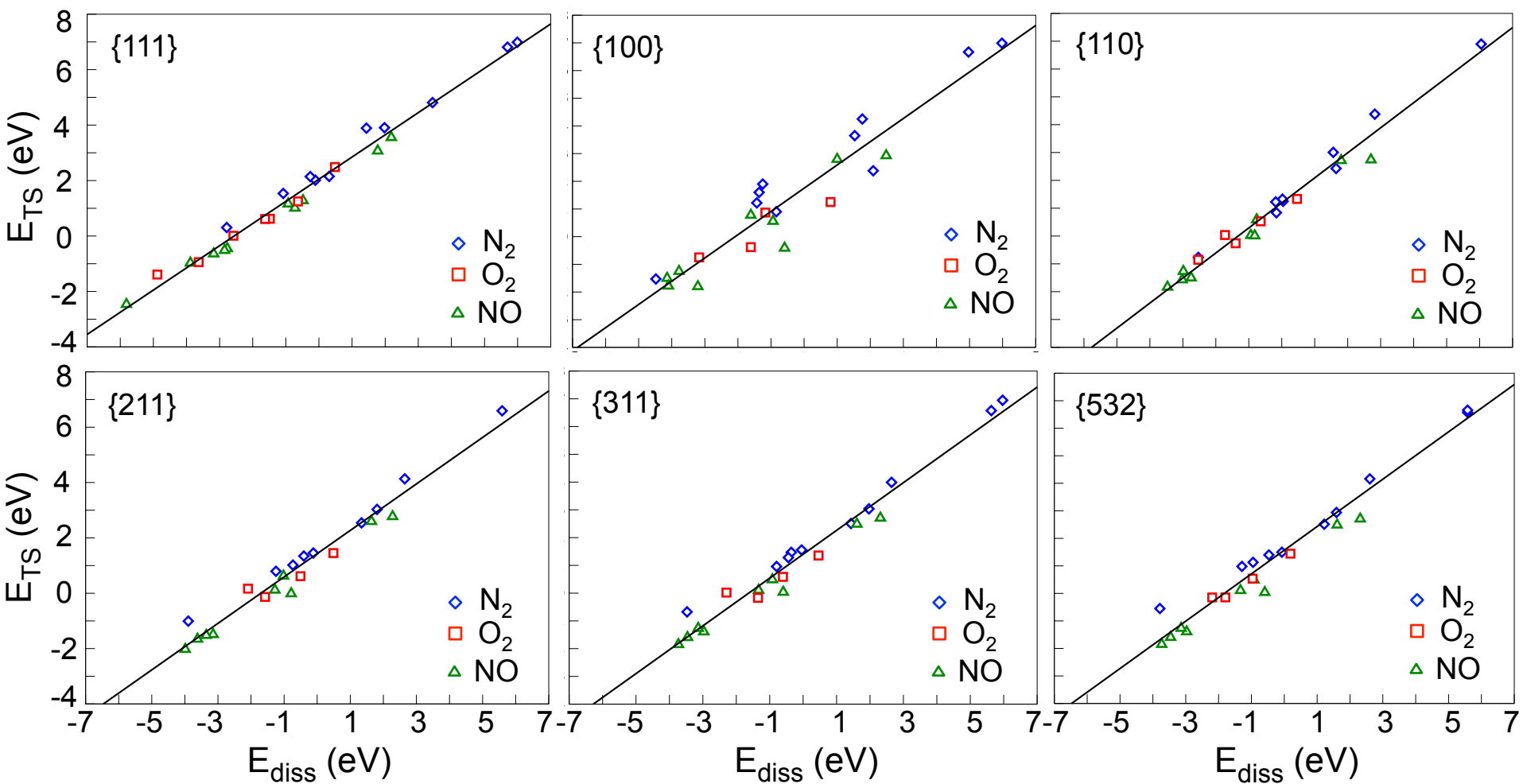
(311) stepped surface



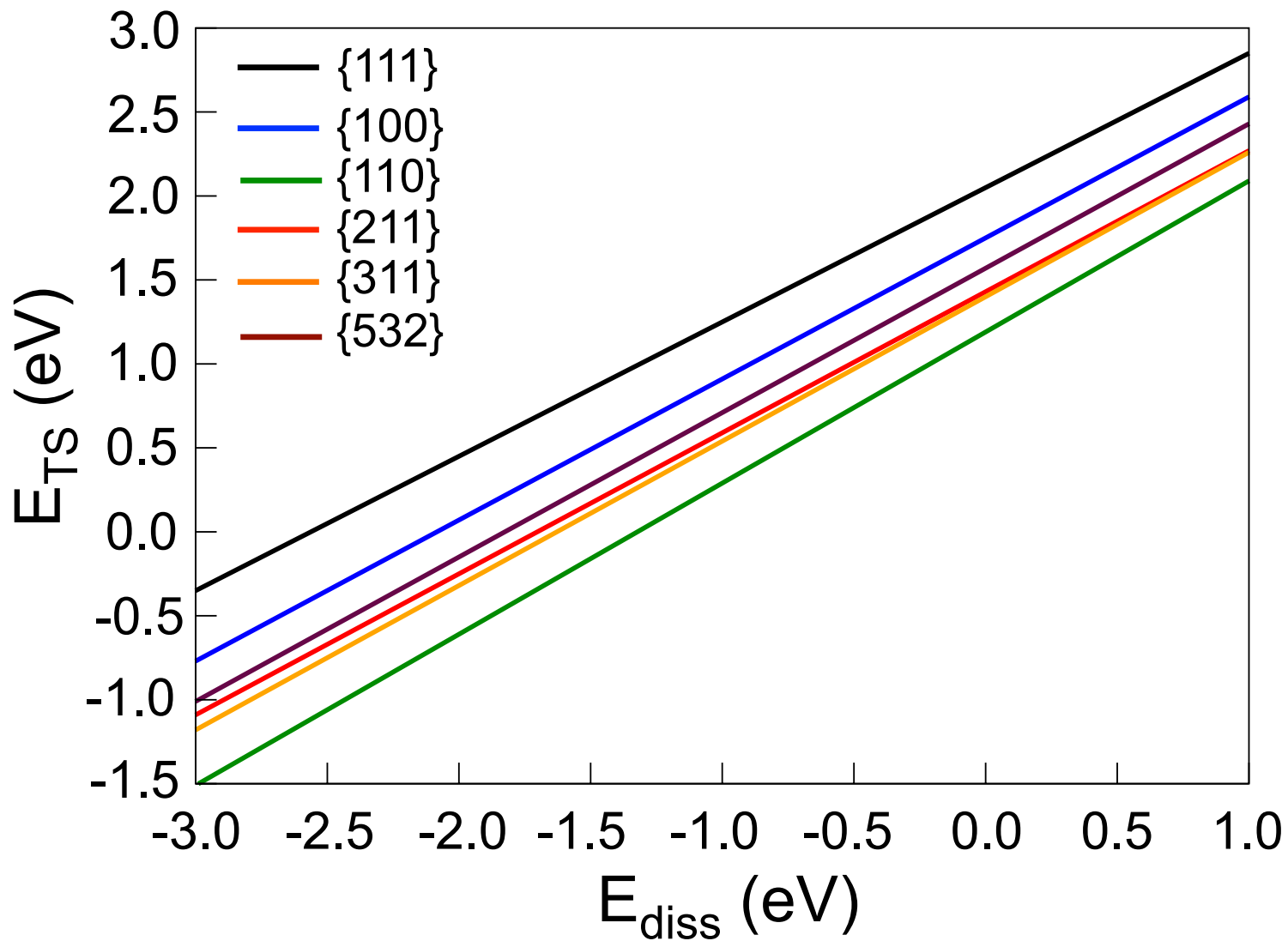
(532) kinked surface

# Structure dependence of BEP-relations

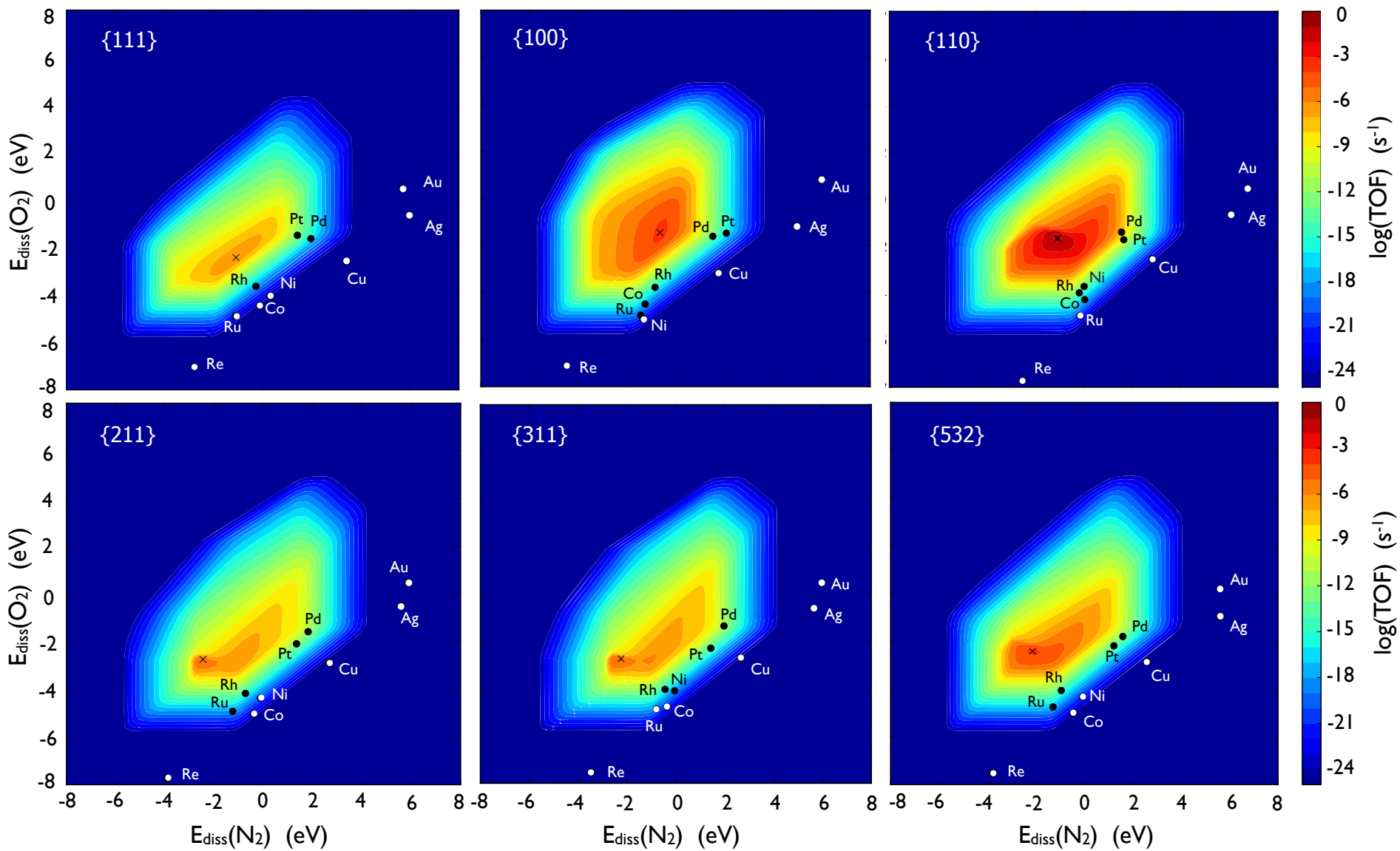
We consider the following metals: Au, Ag, Co, Cu, Ni, Pd, Pt, Rh, Ru, Re



# Structure dependence of BEP-relations

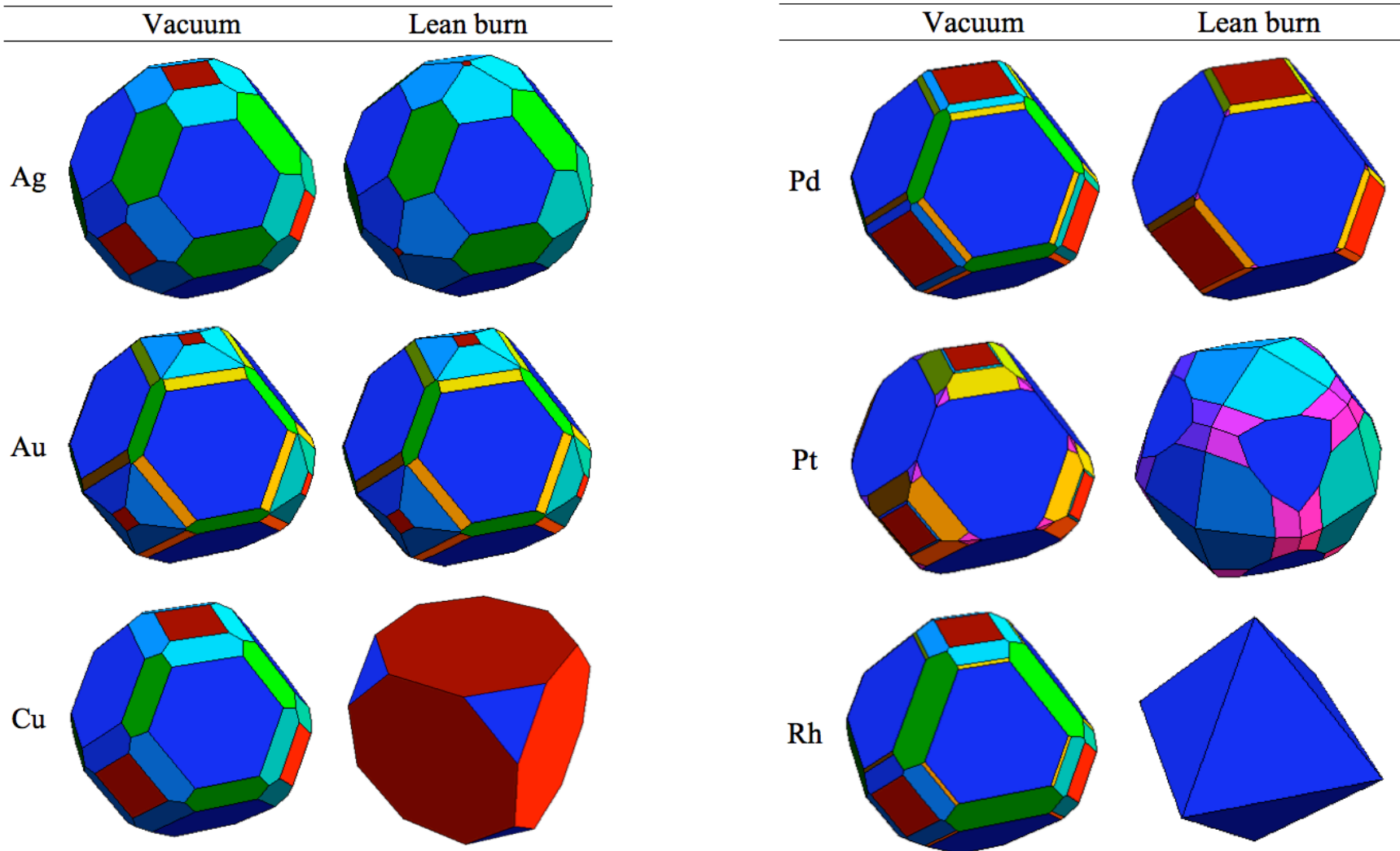


# Structure-dependent activity trends



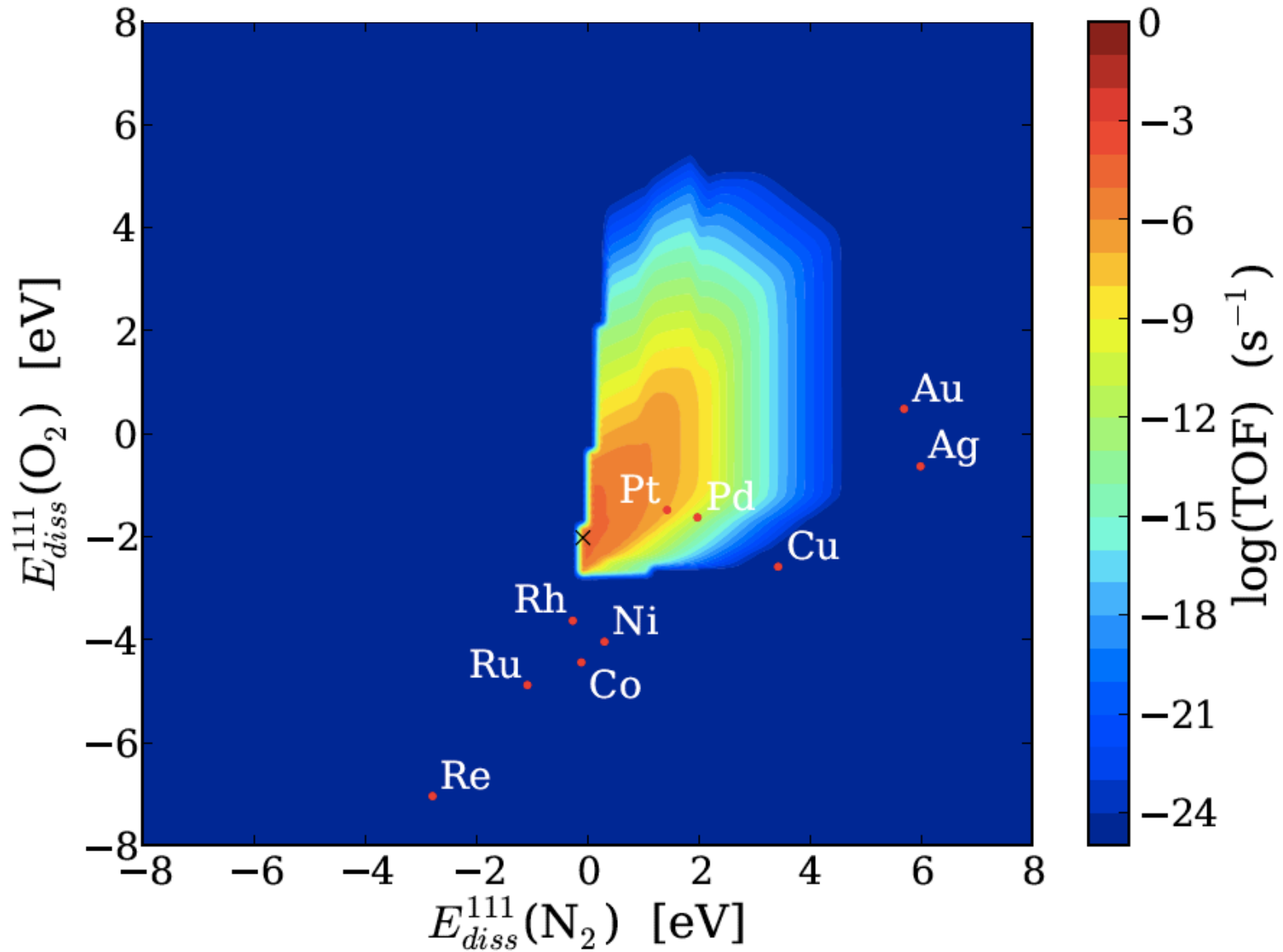
Falsig, Shen, Khan, Guo, Jones, Dahl, Bligaard, *Topics in Catalysis* (2013)

# Kinetics-consistent Morphology



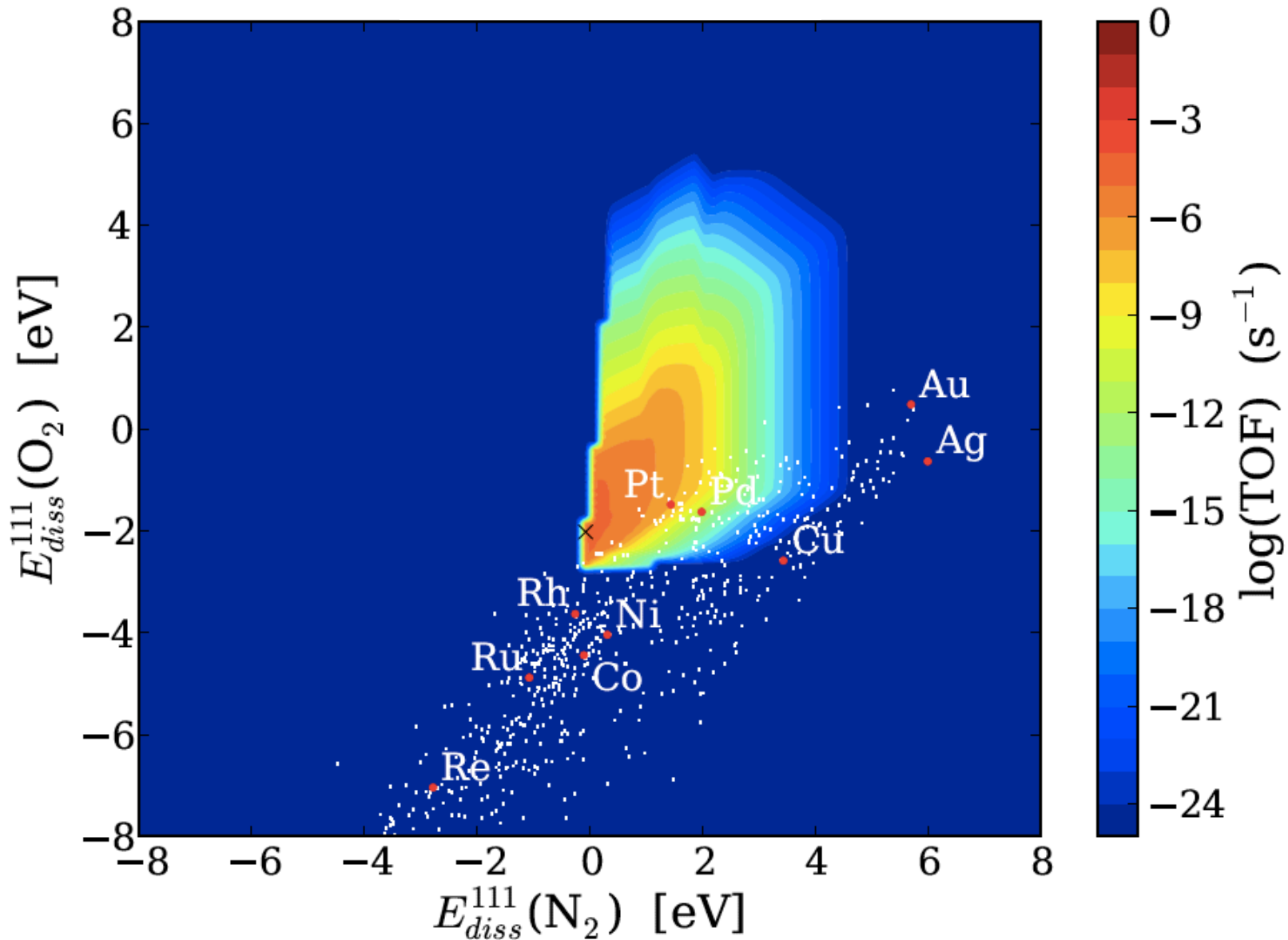
Brodersen, Khan, Falsig, Schiøtz, Bligaard, *In preparation*

# Morphologically-consistent rate



Brodersen, Khan, Falsig, Schiøtz, Bligaard, *In preparation*

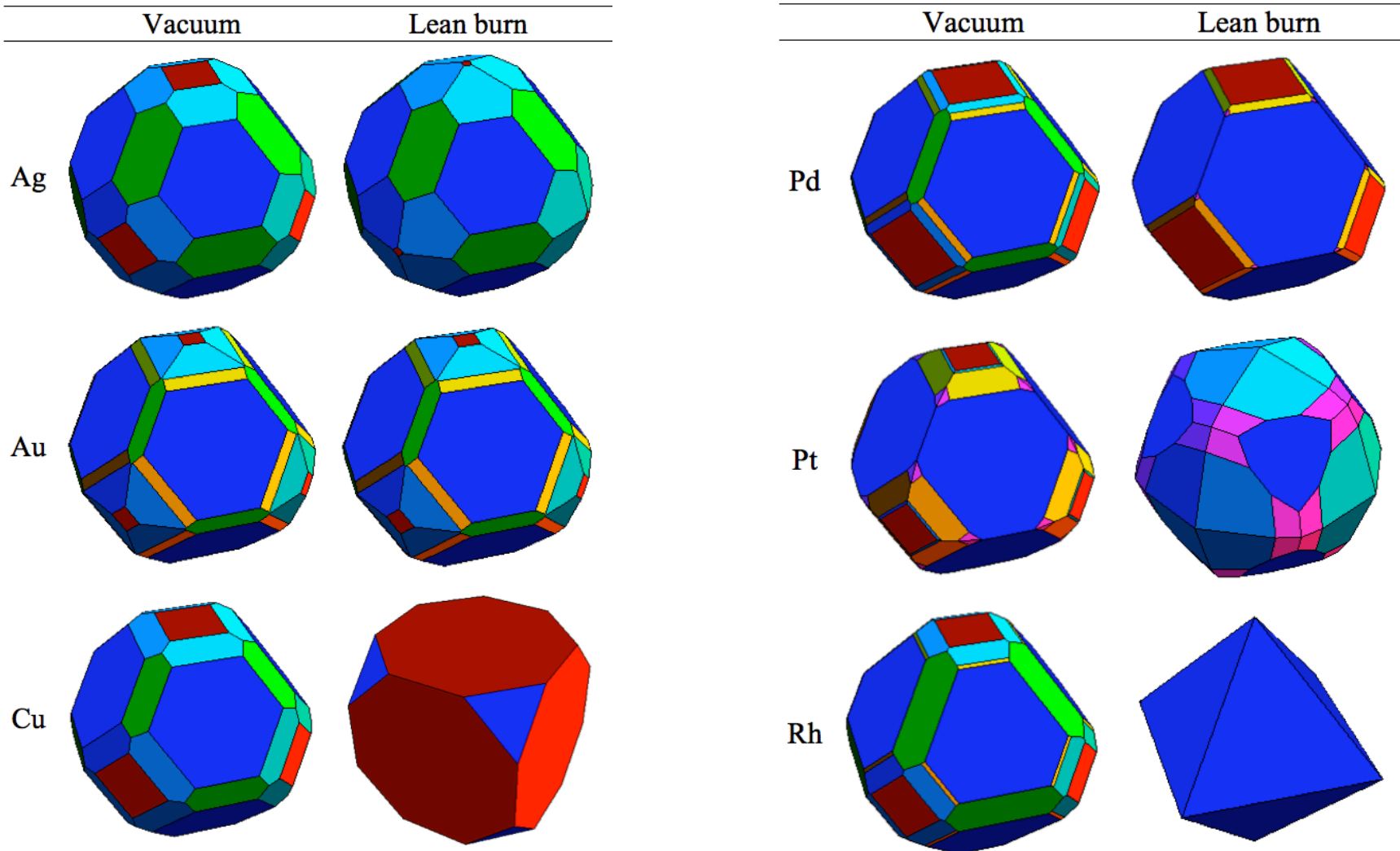
# Alloy screening – Catastrophic sensitivity



Brodersen, Khan, Bligaard (2013)

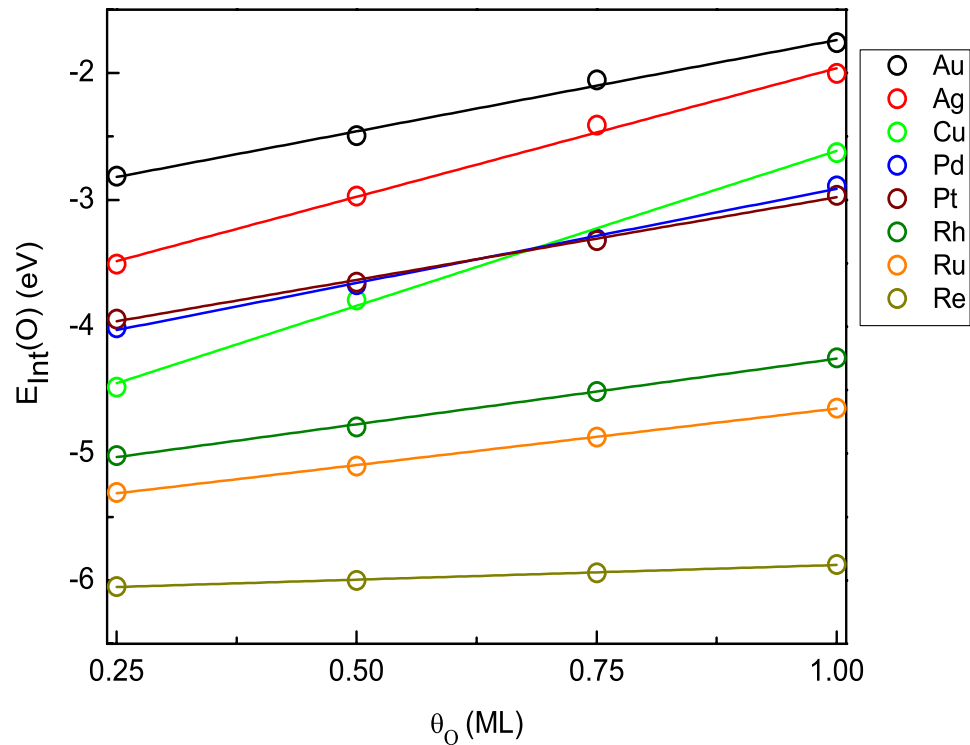
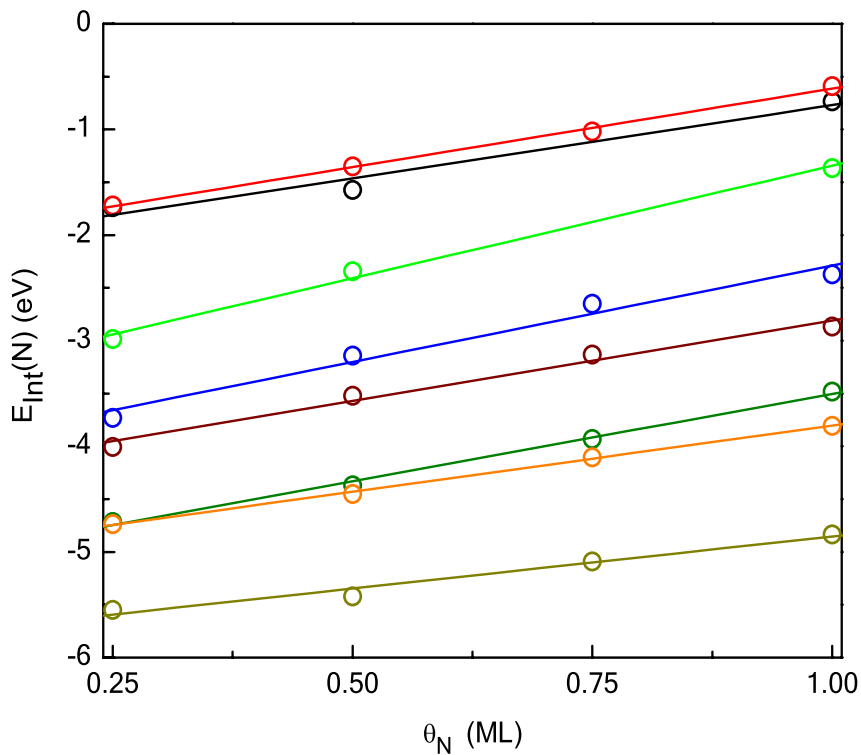
# Errors introduced by Adsorbate-adsorbate interactions

# Kinetics-consistent Morphology



Brodersen, Khan, Falsig, Schiøtz, Bligaard, *In preparation*

# Coverage-dependent adsorption energy



S.D. Miller, J. Kitchin, Surface Science 603, 794 (2009)

Khan, Falsig, Wang, Guo, Dahl, Bligaard (2013)

# Definition of an adsorbate-adsorbate interaction model

$$E_T(\underline{\theta}) = \underline{E}^0 \underline{\theta} + 1/2 \underline{\theta}^T \underline{\epsilon} \underline{\theta}$$

$$E_{Int}(\underline{\theta}) = \left( \frac{\underline{E}^0 \underline{\theta} + 1/2 \underline{\theta}^T \underline{\epsilon} \underline{\theta}}{\sum \underline{\theta}} \right)$$

$$E_{Int}(\theta_i) = \frac{E_{n-ads+slab(N)} - n \cdot E_{gas} - E_{slab(N)}}{n}$$

$$E_{dif}^i(\underline{\theta}) = \frac{dE^T(\underline{\theta})}{d\theta_i} = E_i^0 + \sum_j \epsilon_{ij} \cdot \theta_j$$

$$\epsilon_{ii} = 2 \left( \frac{E_{Int}(\theta_1) - E_{Int}(\theta_2)}{(\theta_1 - \theta_2)} \right)$$

$$\epsilon_{ij} = \frac{(\theta_i + \theta_j)E_{Int}(\theta_i, \theta_j) - E_i^0 \theta_i - E_j^0 \theta_j - 1/2 \epsilon_{ii} \theta_i^2 - 1/2 \epsilon_{jj} \theta_j^2}{\theta_i \theta_j}$$

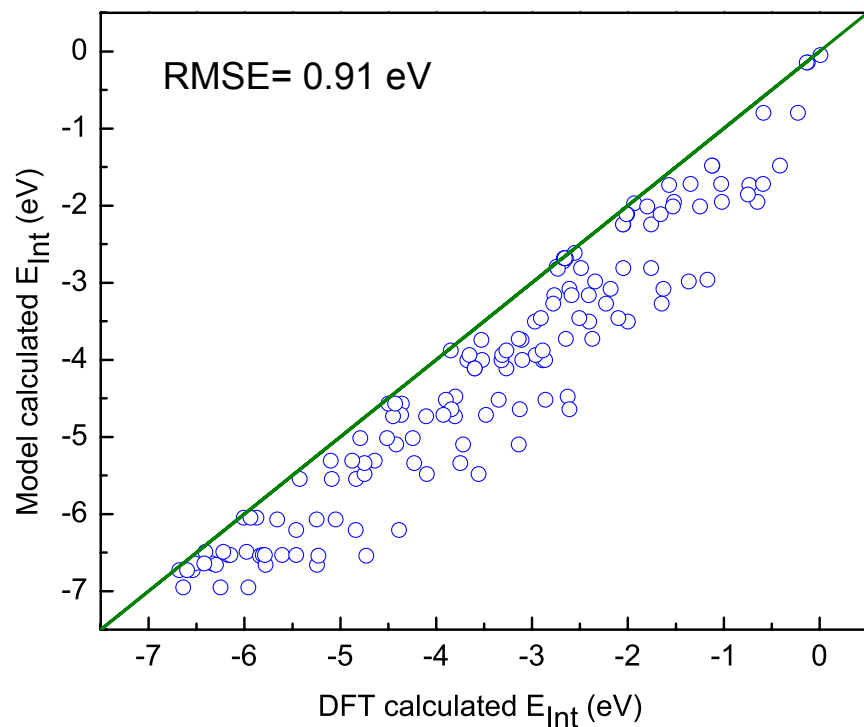
$$E^T(\theta) = (\theta_N \quad \theta_O \quad \theta_{NO}) \begin{pmatrix} E_{\theta_N=0}^M \\ E_{\theta_O=0}^M \\ E_{\theta_{NO}=0}^M \end{pmatrix} + 1/2 (\theta_N \quad \theta_O \quad \theta_{NO}) \begin{pmatrix} \epsilon_{N-N} & \epsilon_{N-O} & \epsilon_{N-NO} \\ \epsilon_{N-O} & \epsilon_{O-O} & \epsilon_{O-NO} \\ \epsilon_{N-NO} & \epsilon_{O-NO} & \epsilon_{NO-NO} \end{pmatrix} \begin{pmatrix} \theta_N \\ \theta_O \\ \theta_{NO} \end{pmatrix}$$

# Comparison of simulated adsorption energy models

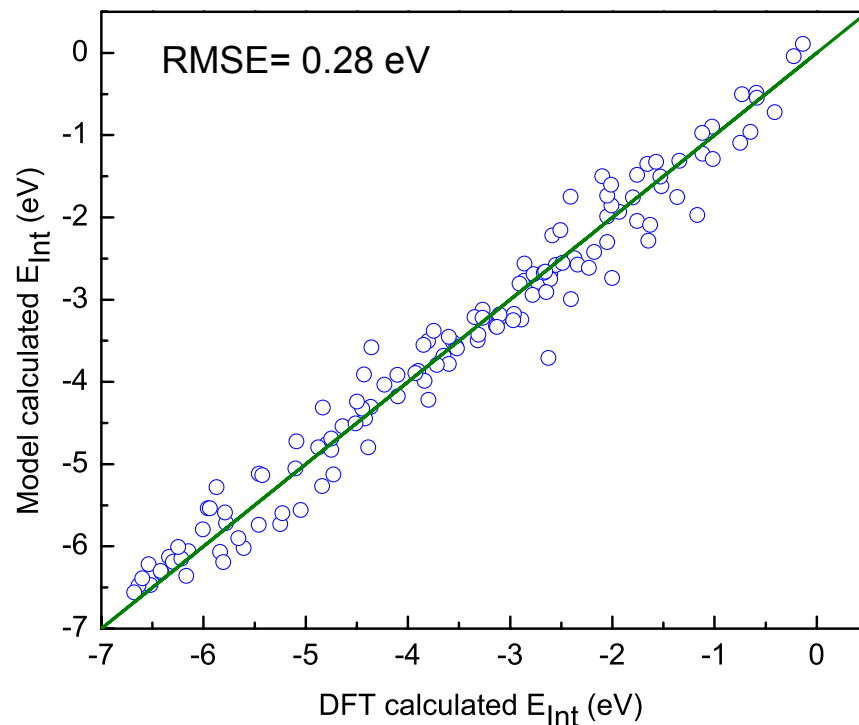


Adsorbates: H, C, N, O, S, NO, NH, CH, and NO

Fcc(111) metals: Au, Ag, Cu, Pd, Pt, Rh, Ru, and Re

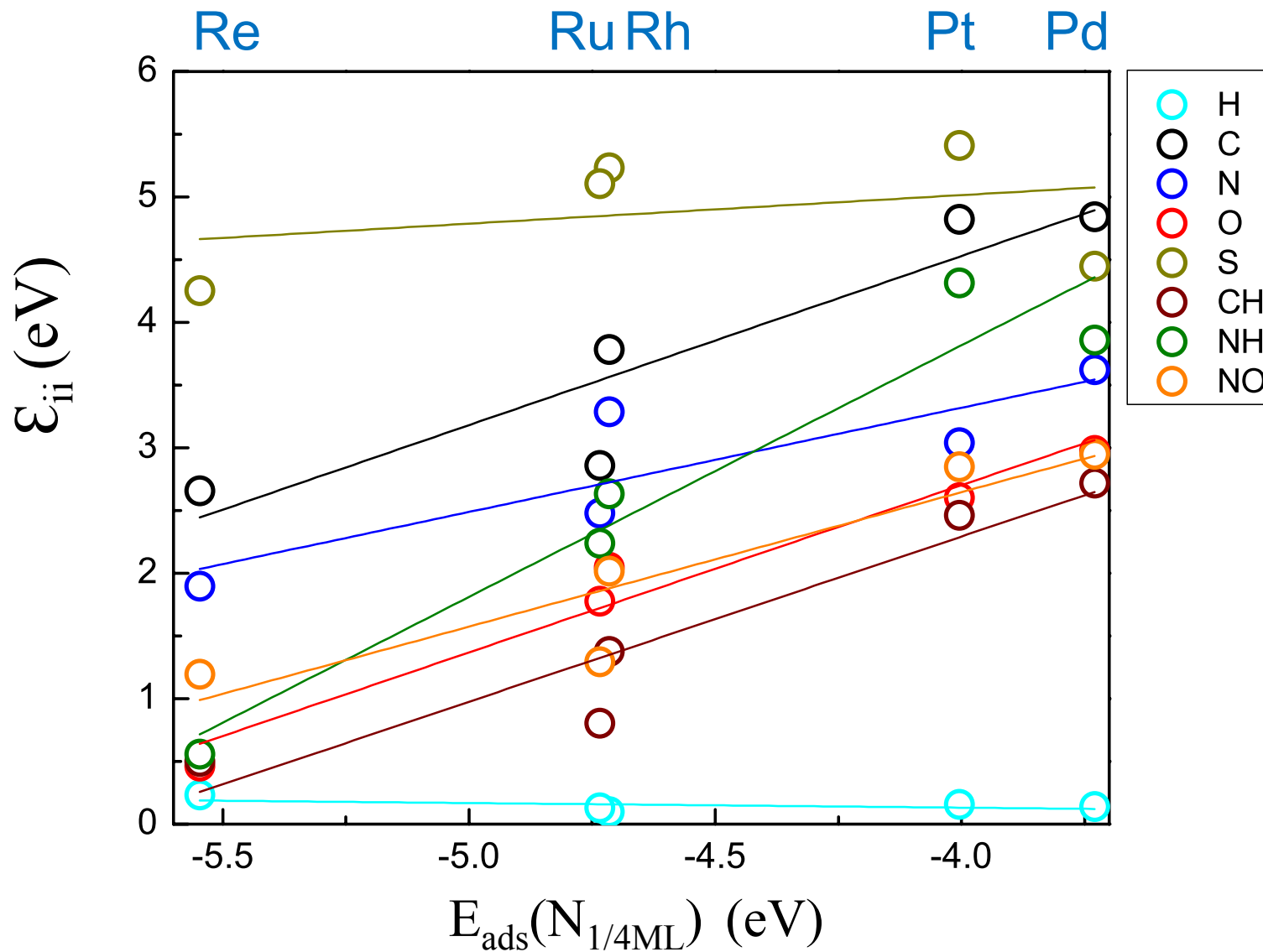


Adsorption energy calculated using the adsorption energy at  $\frac{1}{4}$  ML coverage without any interaction correction



Adsorption energy calculated using the interaction model and the interaction parameters from Rh{111}

# Adsorbate interaction scaling with reactivity



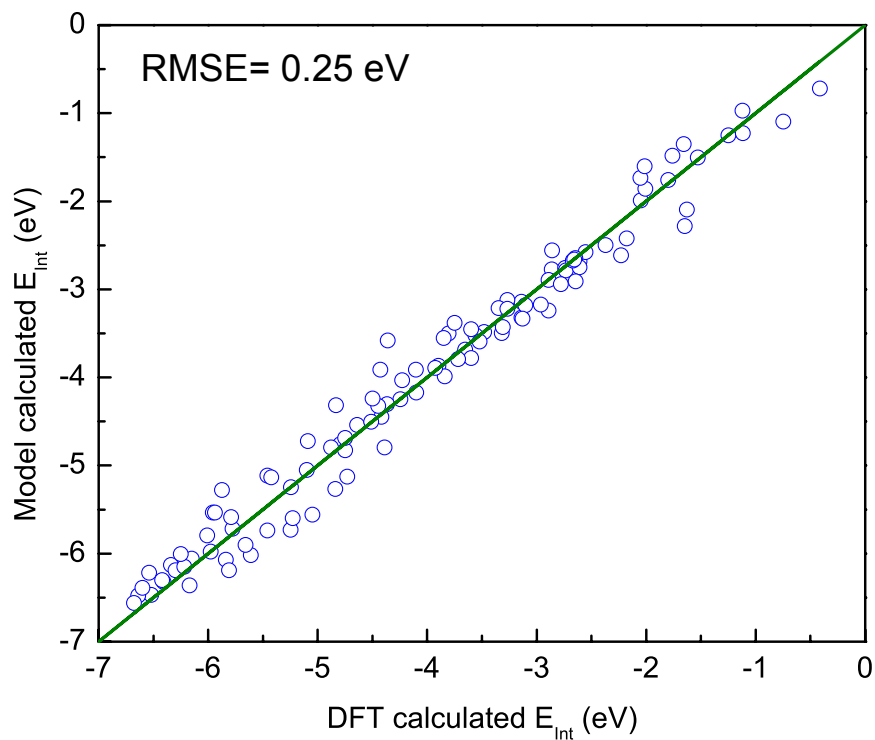
# Comparison of simulated adsorption energy models



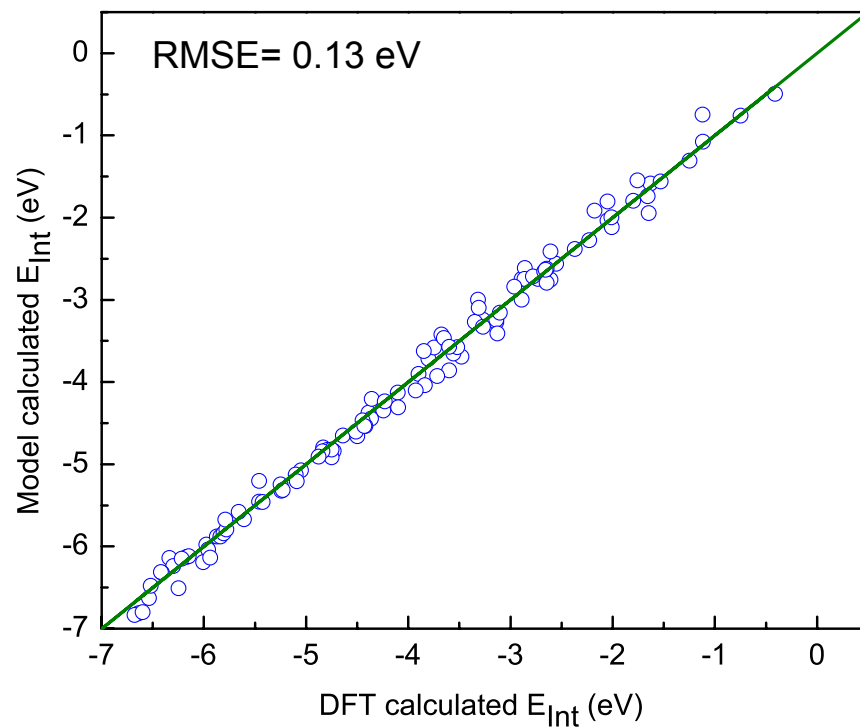
Adsorbates: H, C, N, O, S, NO, NH, CH, and NO

Metals: Pd{111}, Pt{111}, Rh{111}, Ru{111}, and Re{111}

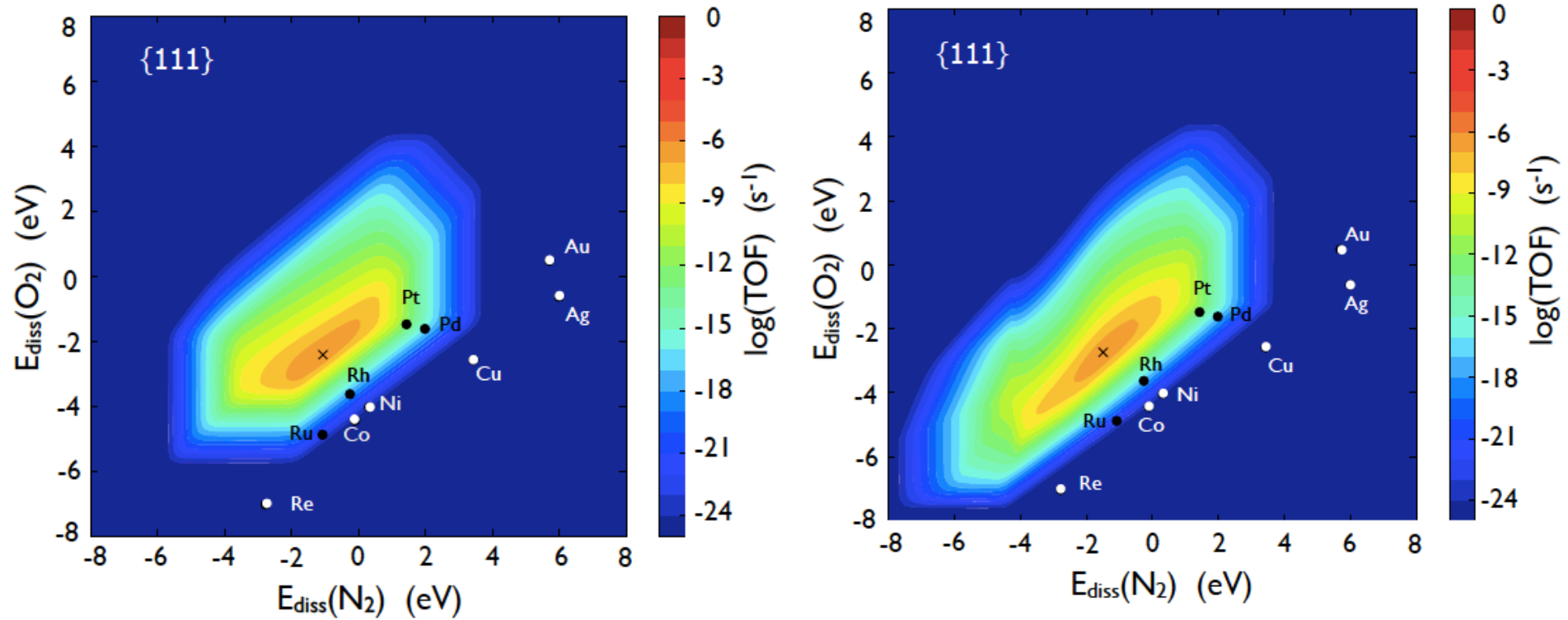
Adsorption energy calculated using the interaction model and the interaction parameters from Rh{111}



Adsorption energy calculated using the interaction model and the scaled interaction parameter



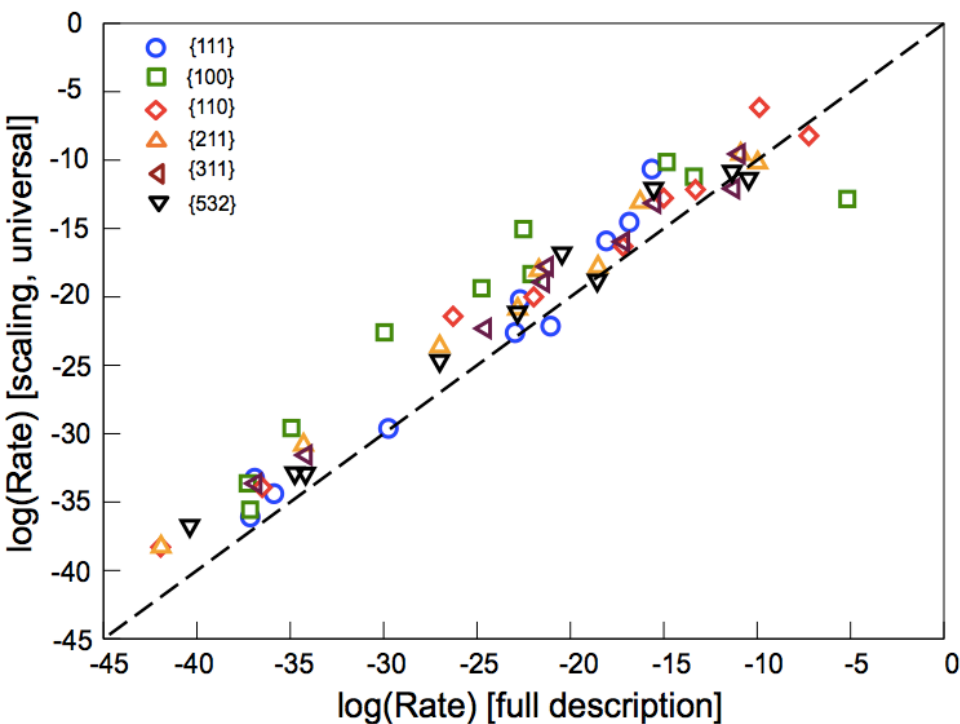
# Interaction-effects on volcanoes



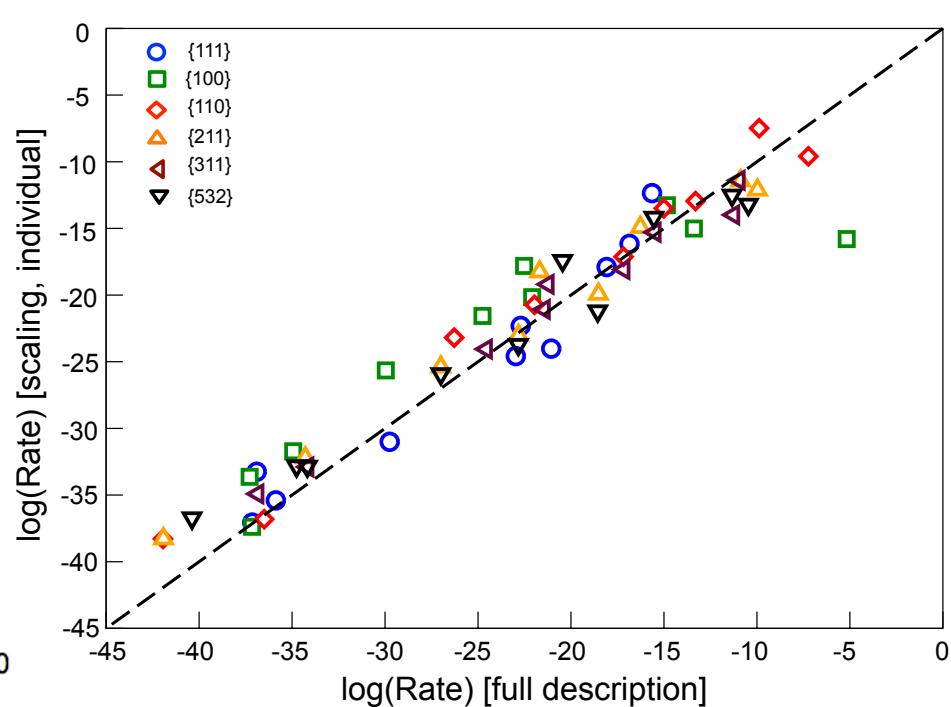
# Errors introduced by Dimensionality Reduction

# Errors introduced through the scaling relations

## Universal BEPs

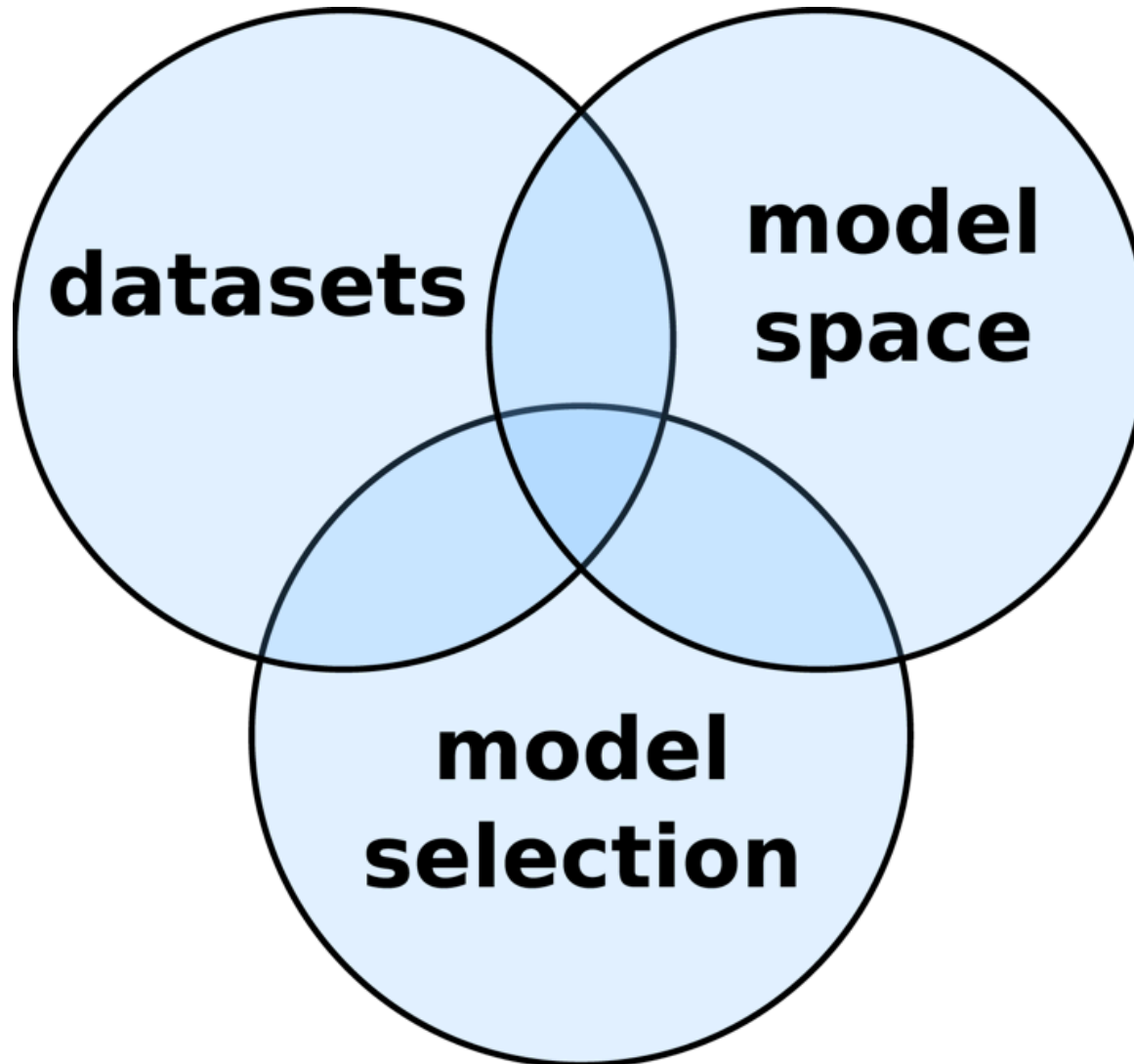


## Individual BEPs



Errors introduced by  
Uncertainties in the electronic structure  
simulations

# Fitting of Exchange - Correlation Functionals



# Data sets – Catalysis relevant!?

G3:	Molecular atomization energies
CE27:	Chemisorption on TM surfaces
DBH24:	Gas-phase reaction barriers
RE42:	Gas-phase reaction energies
Sol27Ec:	Solid cohesive energies
Sol27Lc:	Solid lattice constants
S22x5:	Non-covalent (vdW) bonding

Typical GGA exchange expansion:

$$s = \frac{|\nabla n|}{2k_F n}, \quad 0 \leq s \leq \infty,$$

$$\varepsilon_x^{\text{GGA}}(n, \nabla n) = \varepsilon_x^{\text{UEG}}(n) F_x[s(n, \nabla n)],$$

$$E^{\text{GGA-x}}[n, \nabla n] = \int \varepsilon_x^{\text{UEG}}(n) F_x[s(n, \nabla n)] d\mathbf{r},$$

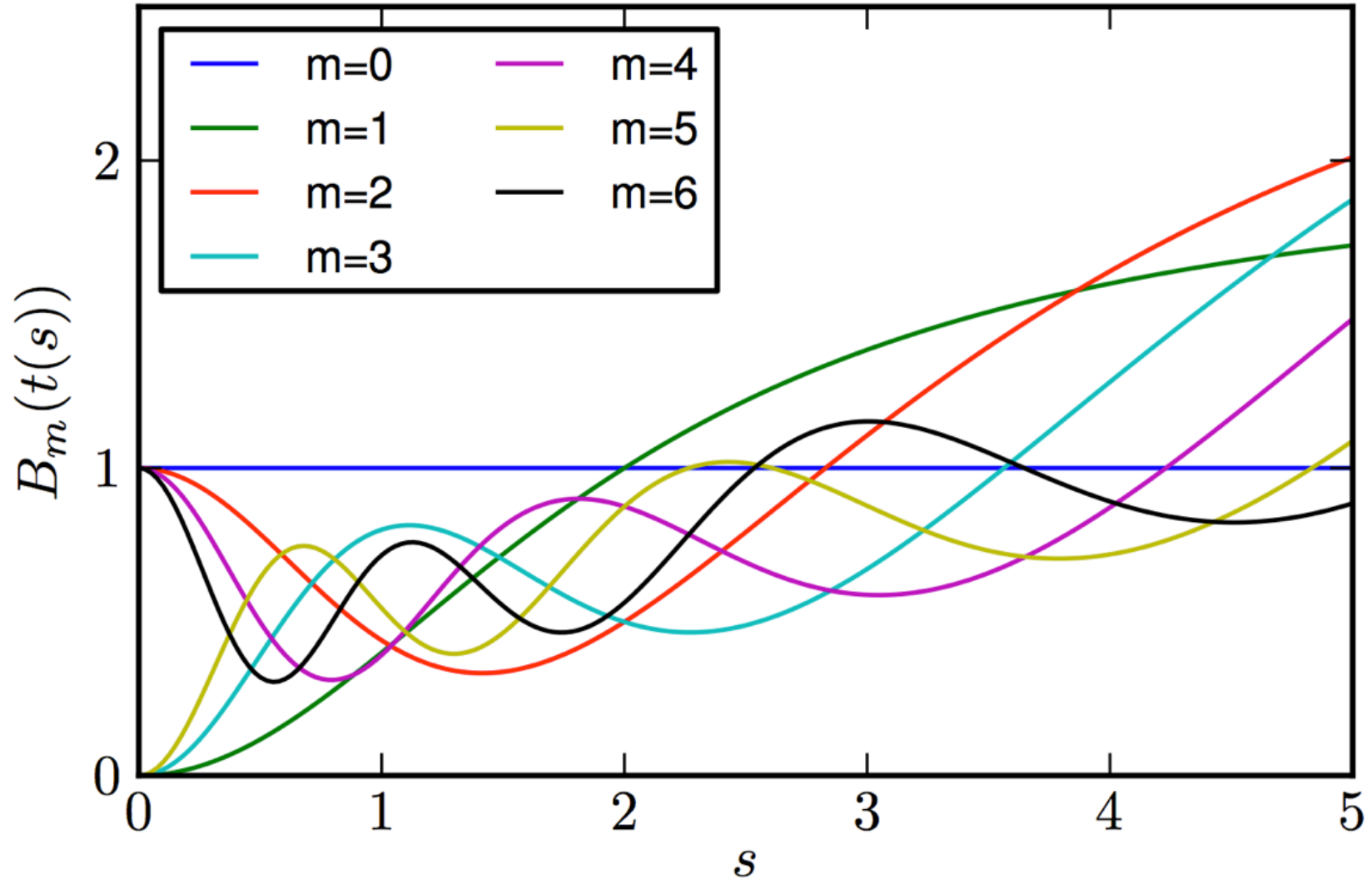
Significance-transformed reduced gradients:

$$t(s) = \frac{2s^2}{4 + s^2} - 1, \quad -1 \leq t \leq 1$$

$$F_x^{\text{GGA}}(s) = \sum_m a_m B_m[t(s)],$$

$$\begin{aligned} E^{\text{GGA-x}}[n, \nabla n] &= \sum_m a_m \int \varepsilon_x^{\text{UEG}}(n) B_m[t(s)] d\mathbf{r} \\ &= \sum_m a_m E_m^{\text{GGA-x}}[n, \nabla n], \end{aligned}$$

# Model Space – the complete GGA basis



## Model Space

$$E^{\text{nl-c}} [n] = \frac{1}{2} \int n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$E_{xc} = \sum_{m=0}^{M_x-1} a_m E_m^{\text{GGA-x}} + \alpha_c E^{\text{LDA-c}} \\ + (1 - \alpha_c) E^{\text{PBE-c}} + E^{\text{nl-c}},$$

# Model Selection

Smoothness as a “transferability criterion”

$$E_x[n] = \int n(\mathbf{r}) \varepsilon_x(n(\mathbf{r})) f_x(s(\mathbf{r})) d^3 r$$

$$f_x(\mathbf{a}; s) = \sum_{n=1}^P a_n f_x(n; s)$$

$$P_1^{\text{smooth}}(\mathbf{a}) := \int (f''(s; \mathbf{a}))^2 ds$$

# Model Selection – Practical Implementation

## Ridge Regression:

$$C_i(\mathbf{a}) = (\mathbf{X}_i \mathbf{a} - \mathbf{y}_i)^2 + \omega^2 \Gamma^2 (\mathbf{a} - \mathbf{a}_p)^2$$

$$\Gamma_{ij}^2 = \int_{-1}^1 \frac{d^2 B_i(t)}{dt^2} \frac{d^2 B_j(t)}{dt^2} dt$$

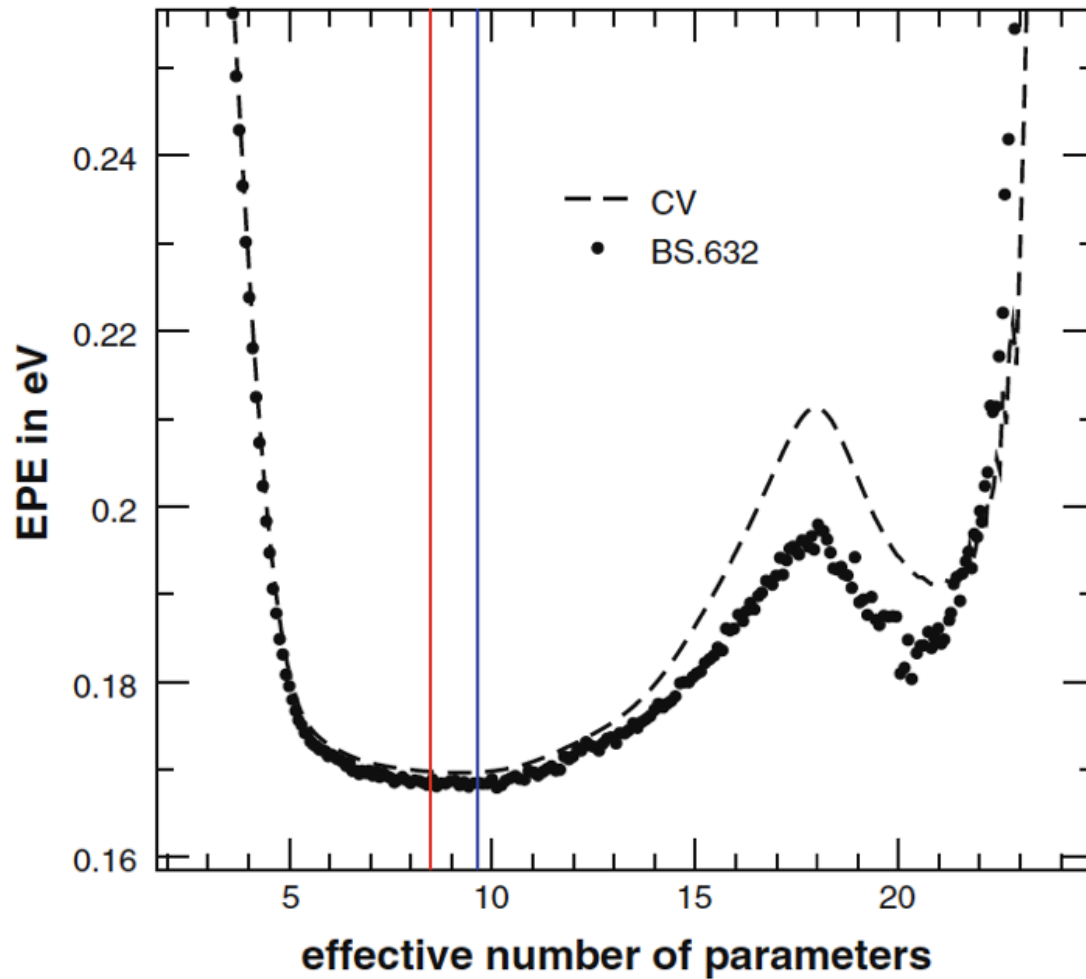
$$\mathbf{X}'_i = \mathbf{X}_i \Gamma^{-1}, \mathbf{a}'_p = \Gamma \mathbf{a}_p$$

$$\mathbf{a}_i = \Gamma^{-1} (\mathbf{X}'_i{}^T \mathbf{X}'_i + \mathbf{L}^2 \omega_i^2)^{-1} (\mathbf{X}'_i{}^T \mathbf{y}_i + \omega^2 \mathbf{L}^2 \mathbf{a}'_p)$$

But how do we choose the regularization parameter,  $\omega_i$  ???

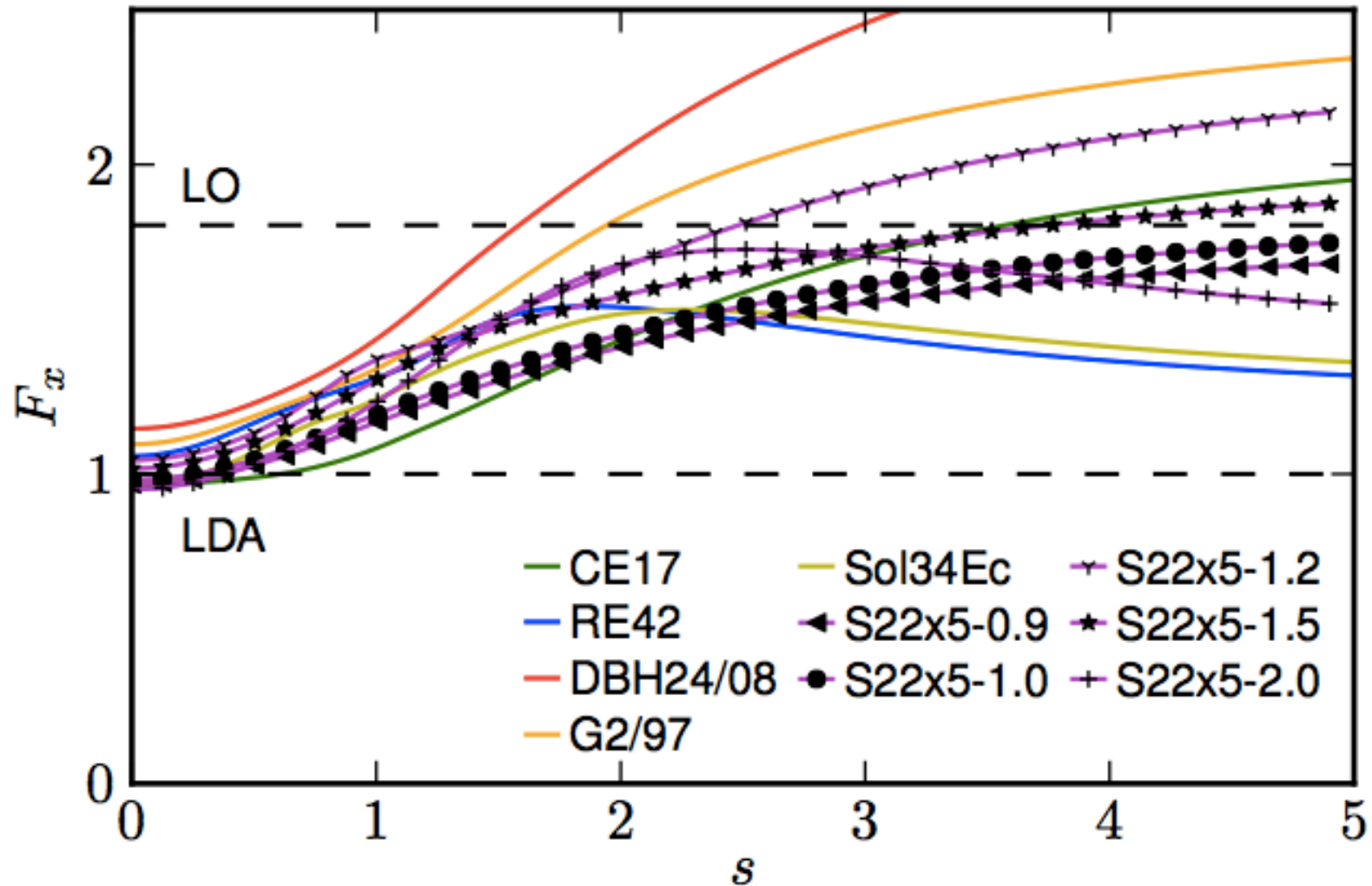
# Model Selection

## Cross Validation to choose optimal model complexity



Petzold, Bligaard, Jacobsen, *Top. Catal.* 55, 402 (2012)

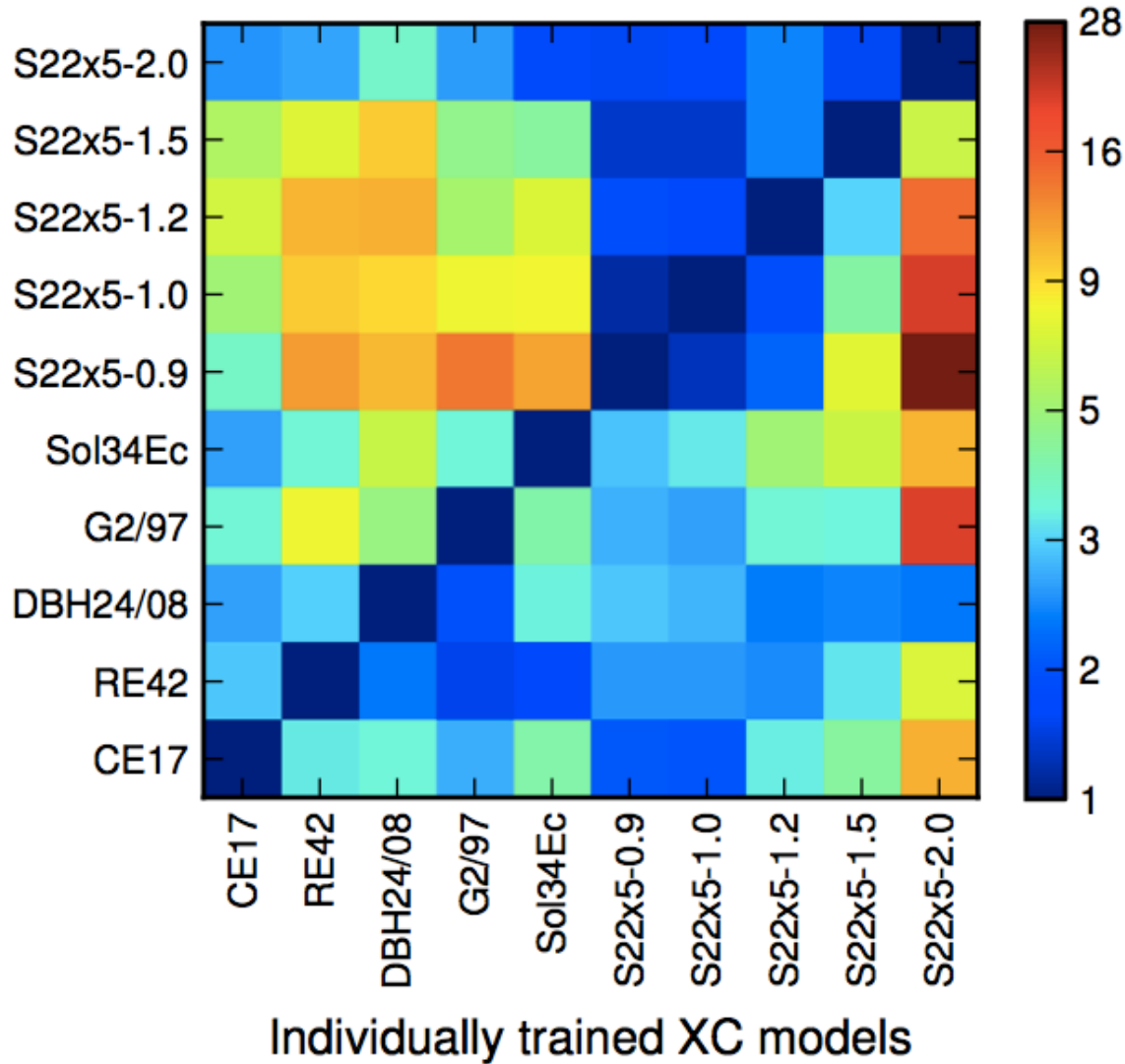
# Fits of the individual data sets



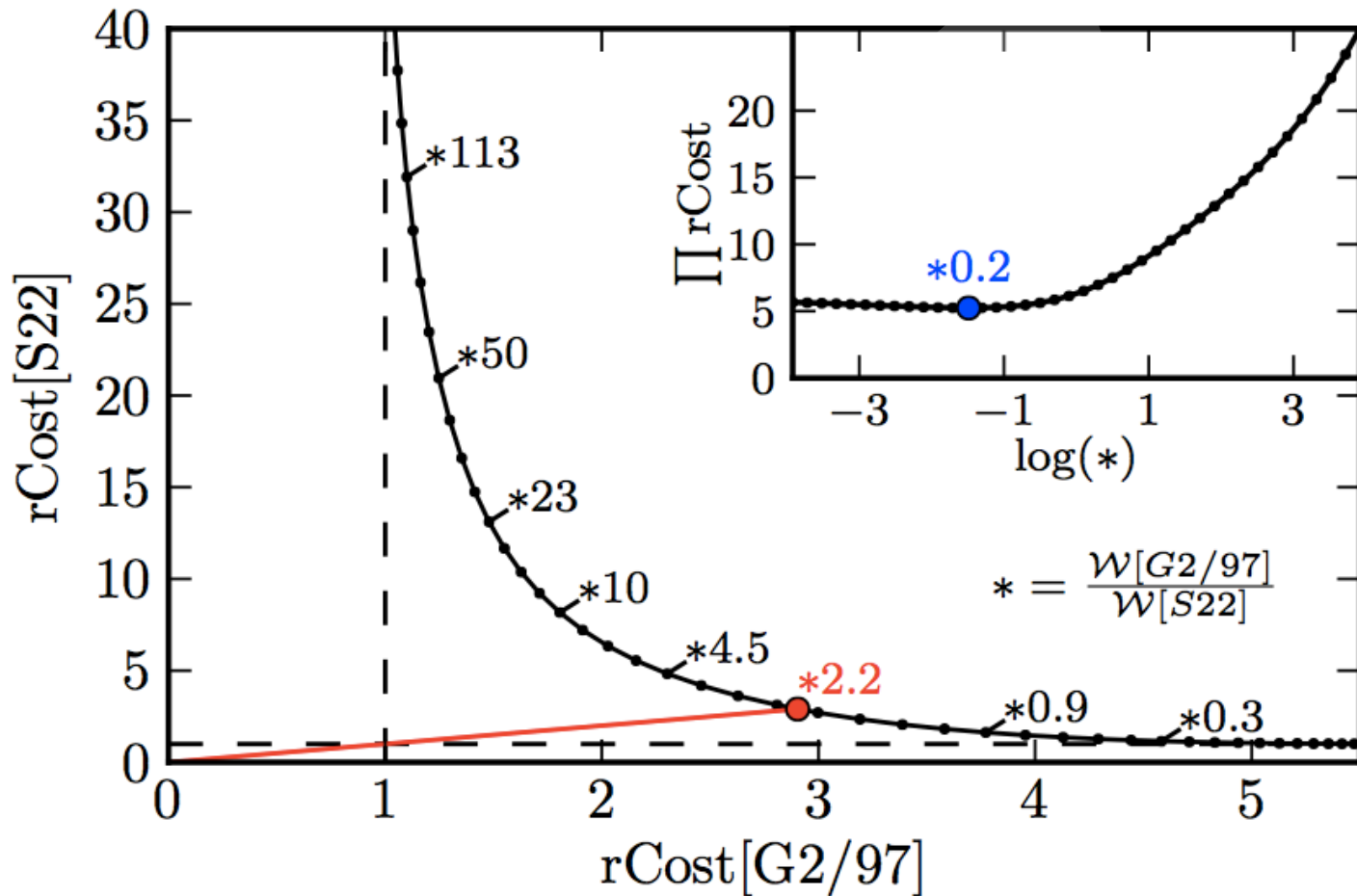
## Fits of the individual data sets

	$\alpha_c$	$M_{\text{eff}}$	$F_x(0)$	$F_x(\infty)$
CE17	0.90	4.7	0.97	2.15
RE42	1.00	4.2	1.06	1.21
DBH24/08	0.00	3.7	1.14	3.14
G2/97	0.27	7.2	1.10	2.53
Sol34Ec	0.00	7.7	0.97	1.25
S22x5-0.9	0.81	3.2	0.96	1.68
S22x5-1.0	0.82	3.1	0.98	1.87
S22x5-1.2	0.40	5.7	1.04	2.38
S22x5-1.5	0.85	4.0	1.02	1.91
S22x5-2.0	1.00	3.3	0.95	1.37

# Relative cost compensation between data sets



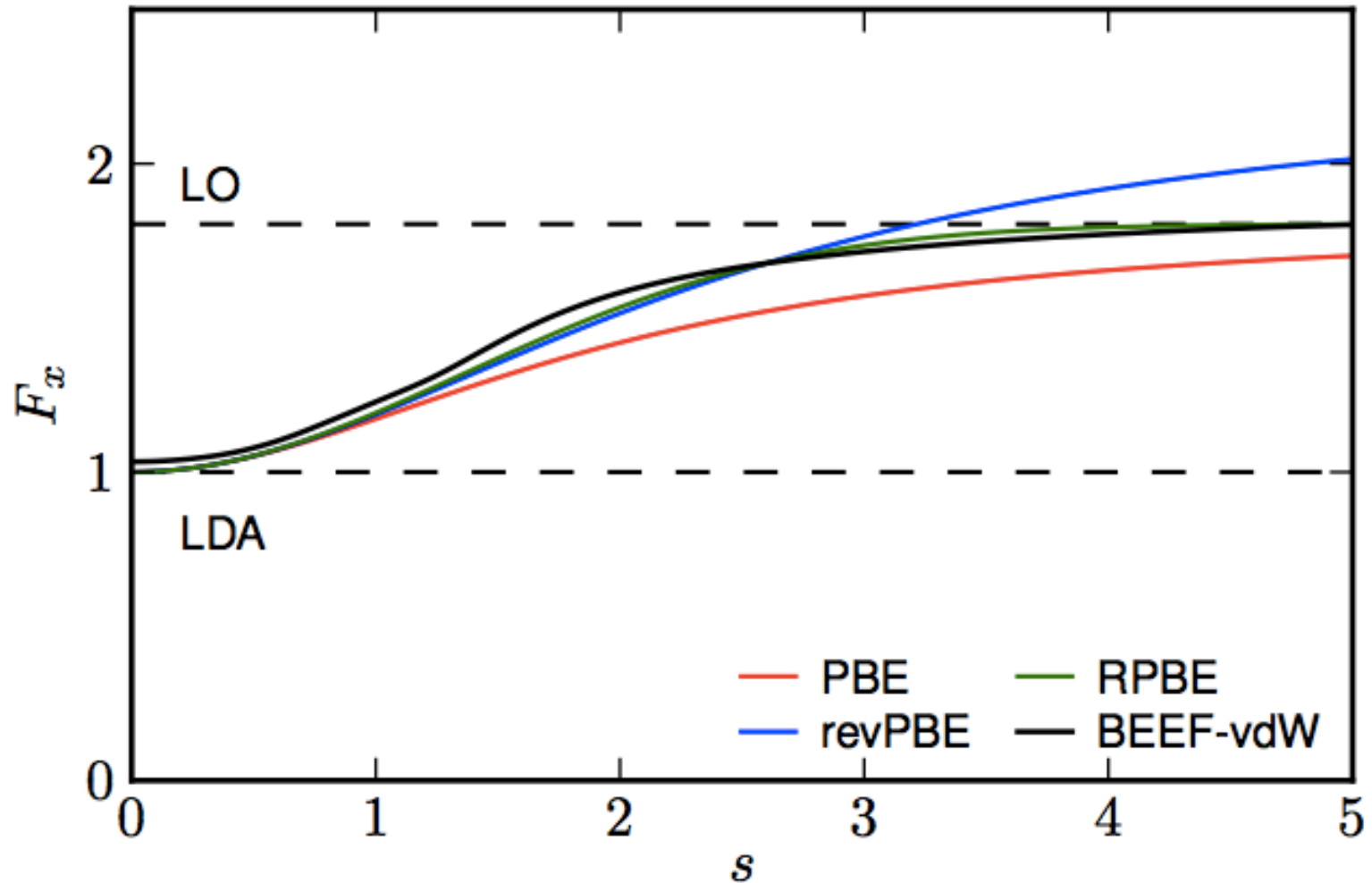
# Relative cost compensation between data sets



$$\Phi(\mathbf{a}) = \prod_i C_i(\mathbf{a})^{w_i} \quad \sum_i \frac{w_i}{C_i} \frac{dC_i}{d\mathbf{a}} = 0$$

# Functional Fitting of several data bases

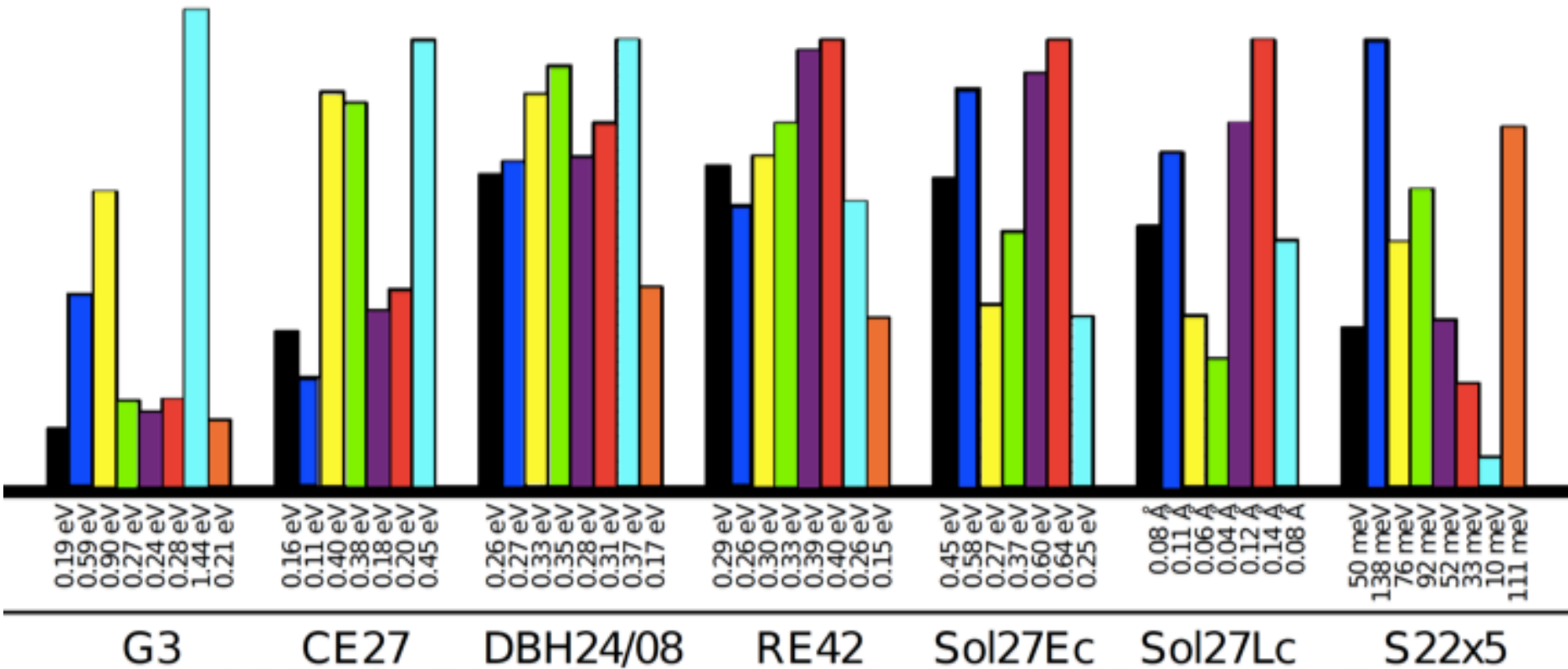
## BEEF-vdW functional



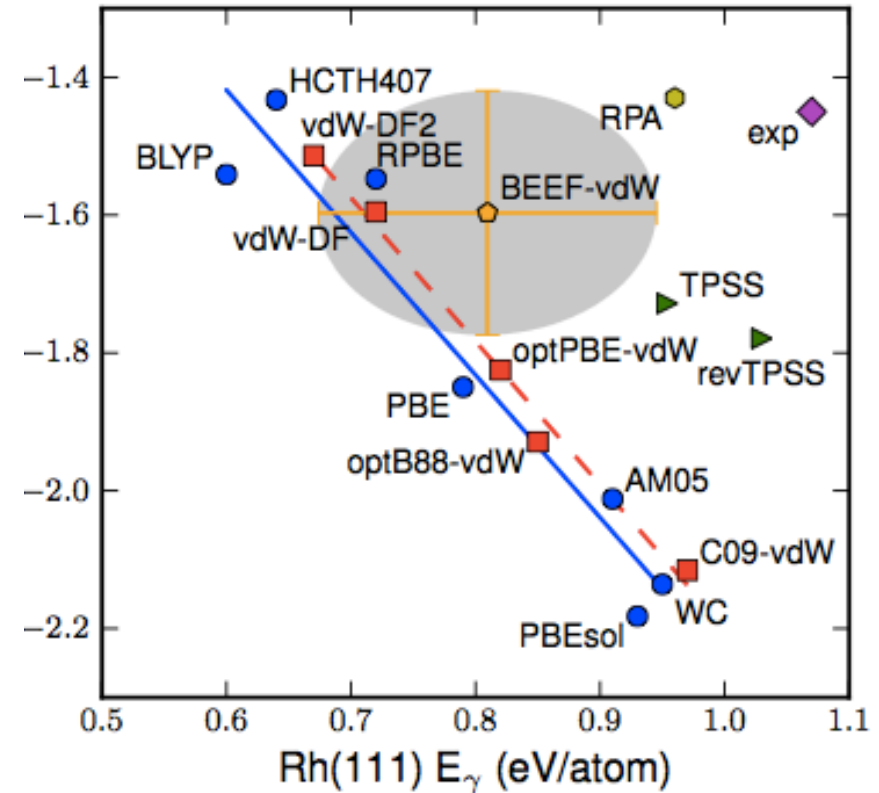
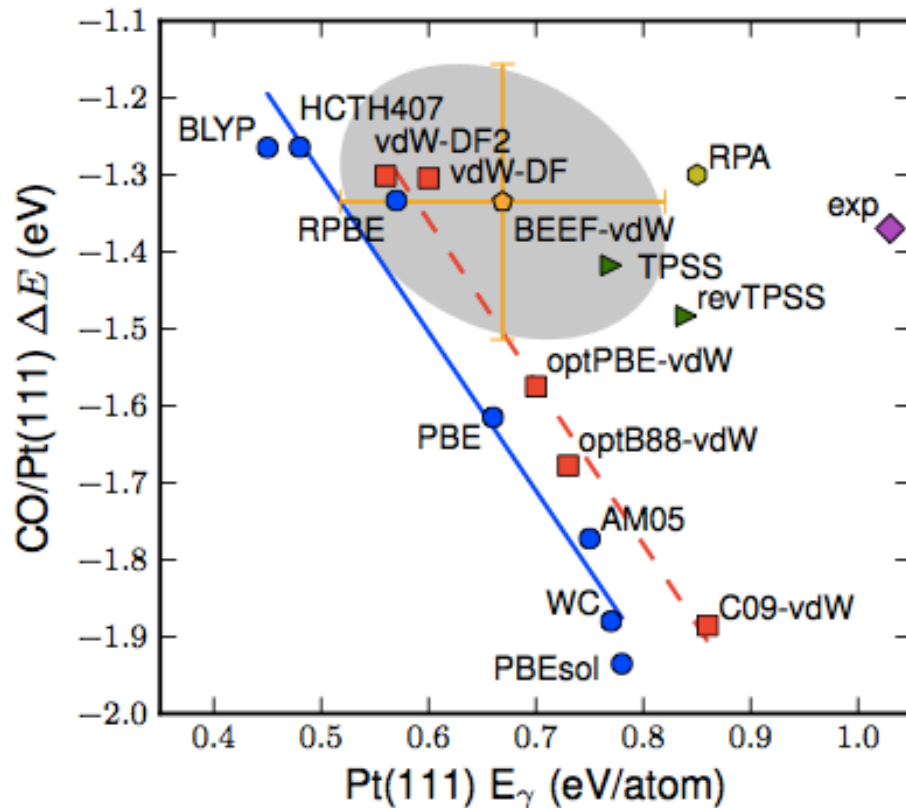
# Functional Fitting of several data bases

## BEEF-vdW functional

Scaled MAD



# BEEF-vdW: surface and chemisorption energies

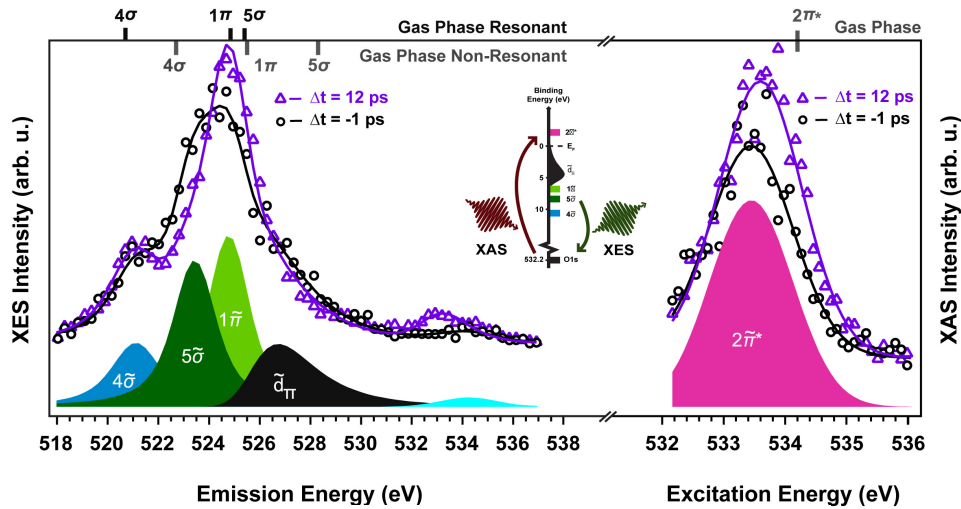


[Ref. data](#): Schimka, Harl, Stroppa, Gruneis, Marsman, Mittendorfer, Kresse, Nature Materials, 9, 741 (2010)

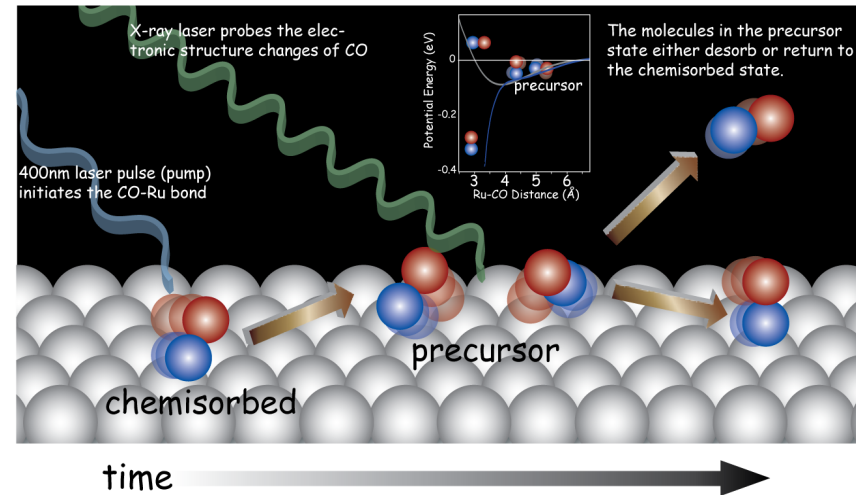
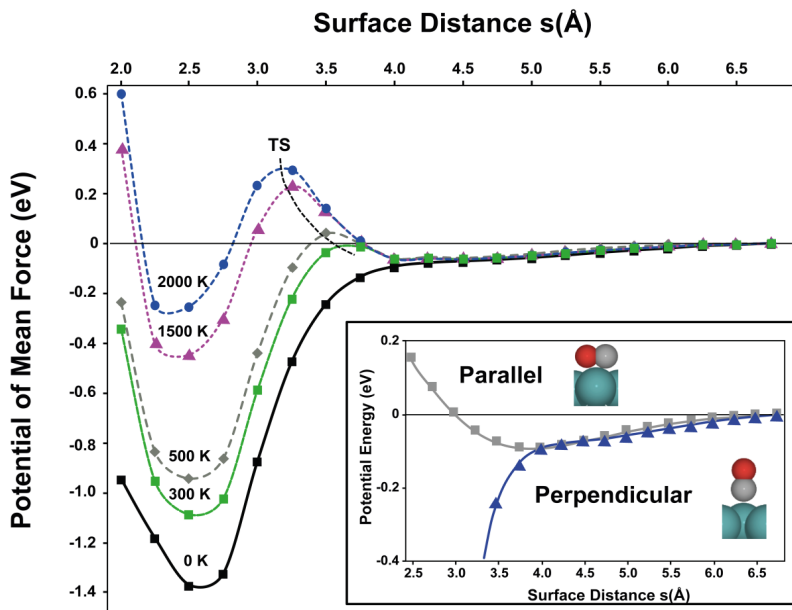
Wellendorff, Lundgaard, Møgelhøj, Petzold, Landis, Nørskov, Bligaard, Jacobsen, Phys. Rev. B 85, 235149 (2012)

# Application: Ultrafast Surface Chemistry

New experiments + new theory → new fundamental insight



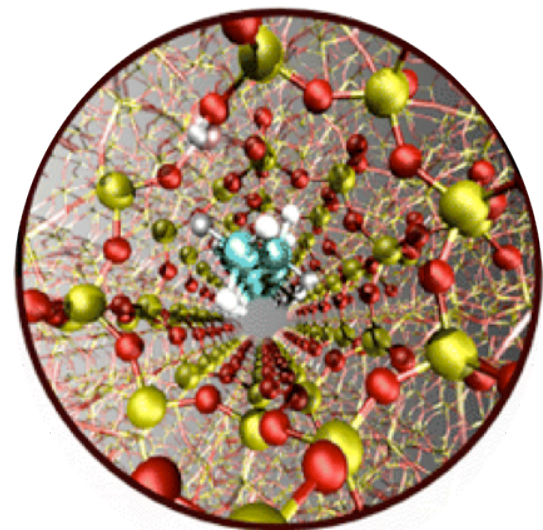
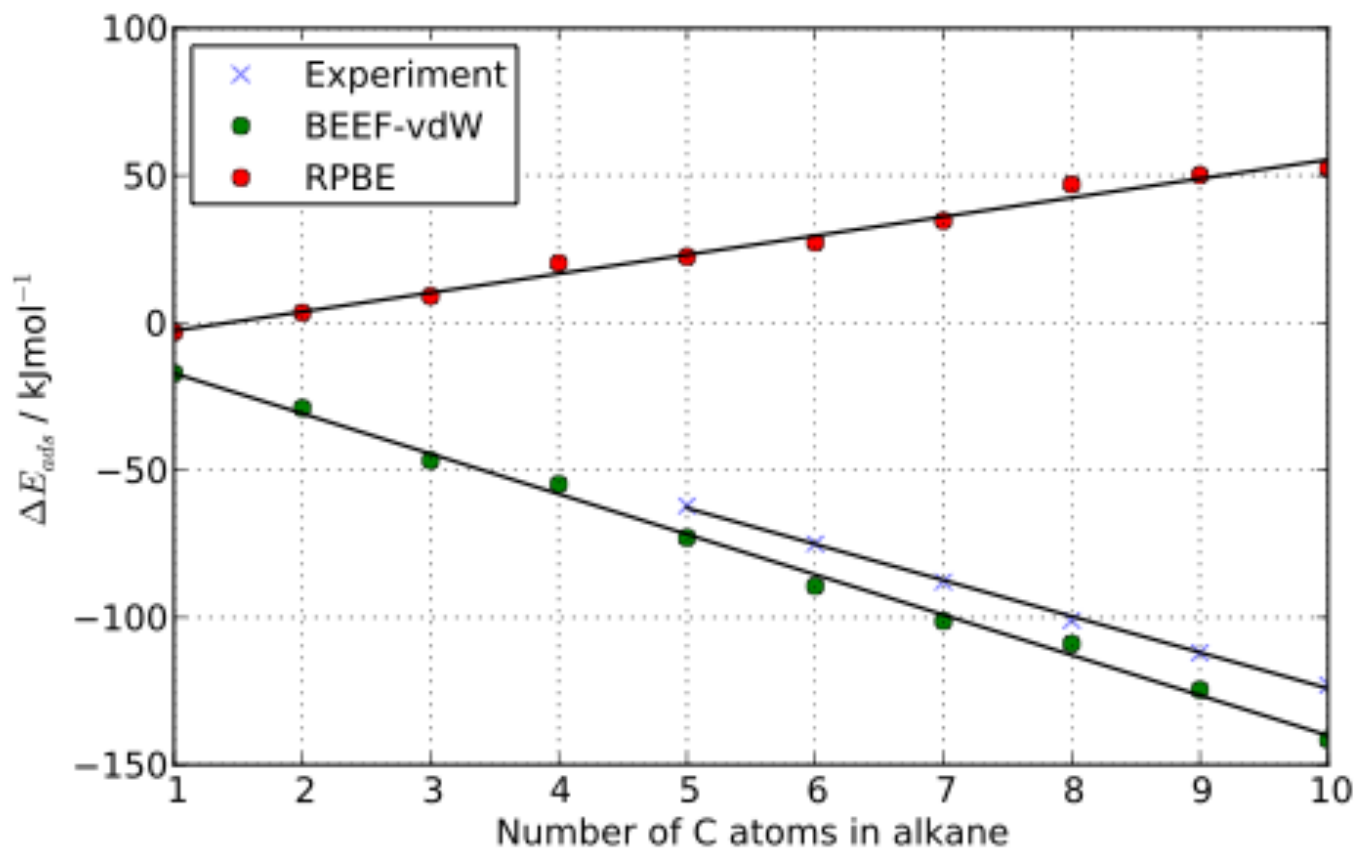
- 400nm pump pulse
- FEL induced O K edge x-ray emission and absorption spectroscopies as probes



Dell'Angela, Anniyev, Beye, Coffee, Föhlisch, Gladh, Katayama, Kaya, Krupin, LaRue, Møgelhøj, Nordlund, Nørskov, Öberg, Ogasawara, Öström, Pettersson, Schlotter, Sellberg, Sorgenfrei, Turner, Wolf, Wurth, Nilsson, *Science* **339**, 1302 (2013)

# Application: Weak interactions in surface chemistry

## Alkane adsorption in H-ZSM-22

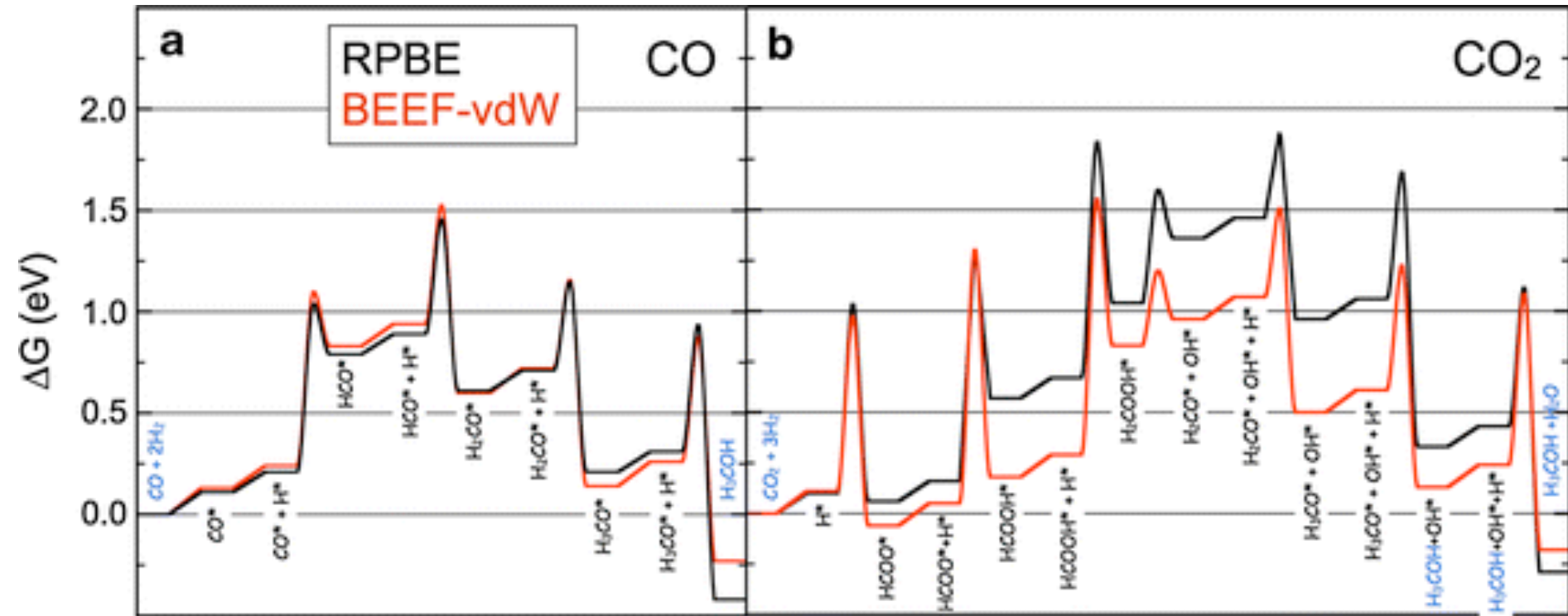


BEEF-vdW calculations: Brogaard, Moses, Nørskov, Catal. Lett. 142, 1057 (2012)

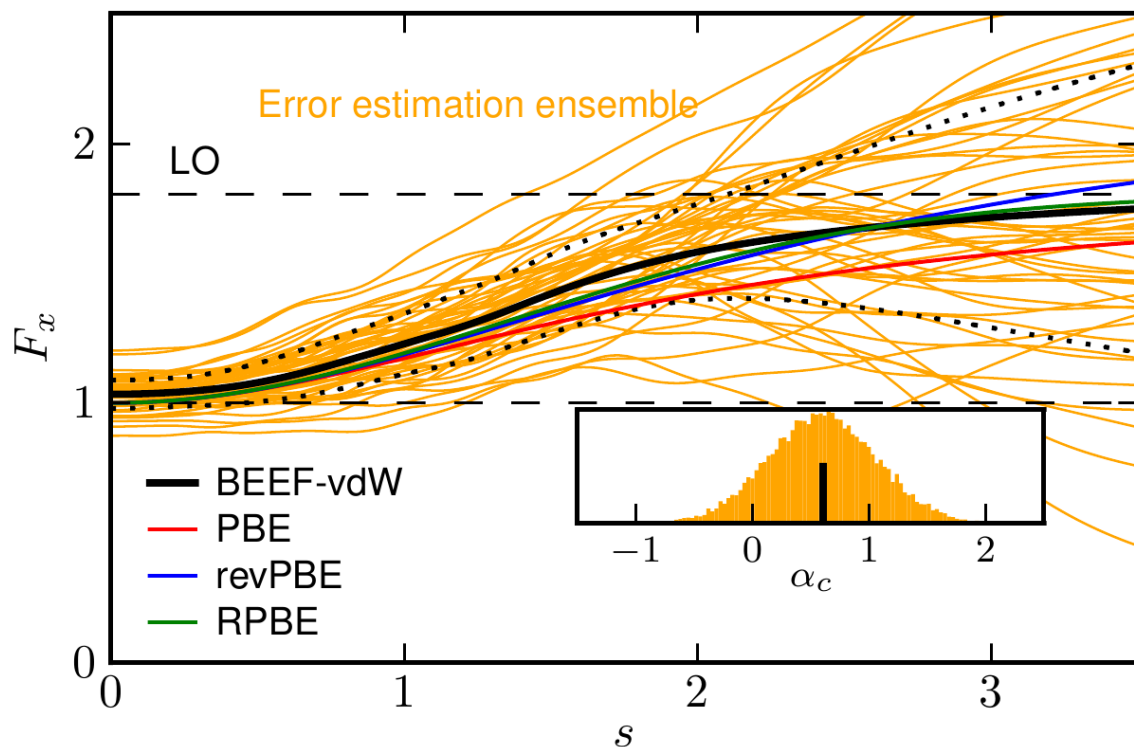
Experiment: Ocakoglu, Denayer, Marin, Martens, Baron, J. Phys. Chem. B 107:398 (2003)

# Application: Methanol Synthesis

## CO and CO<sub>2</sub> hydrogenation over Cu(211)



# The BEEF-vdW Ensemble of Functionals



- A Bayesian ensemble of functionals gives a *probability distribution* for the model parameters and offers a computationally cheap estimate of the prediction error on any calculated quantity.

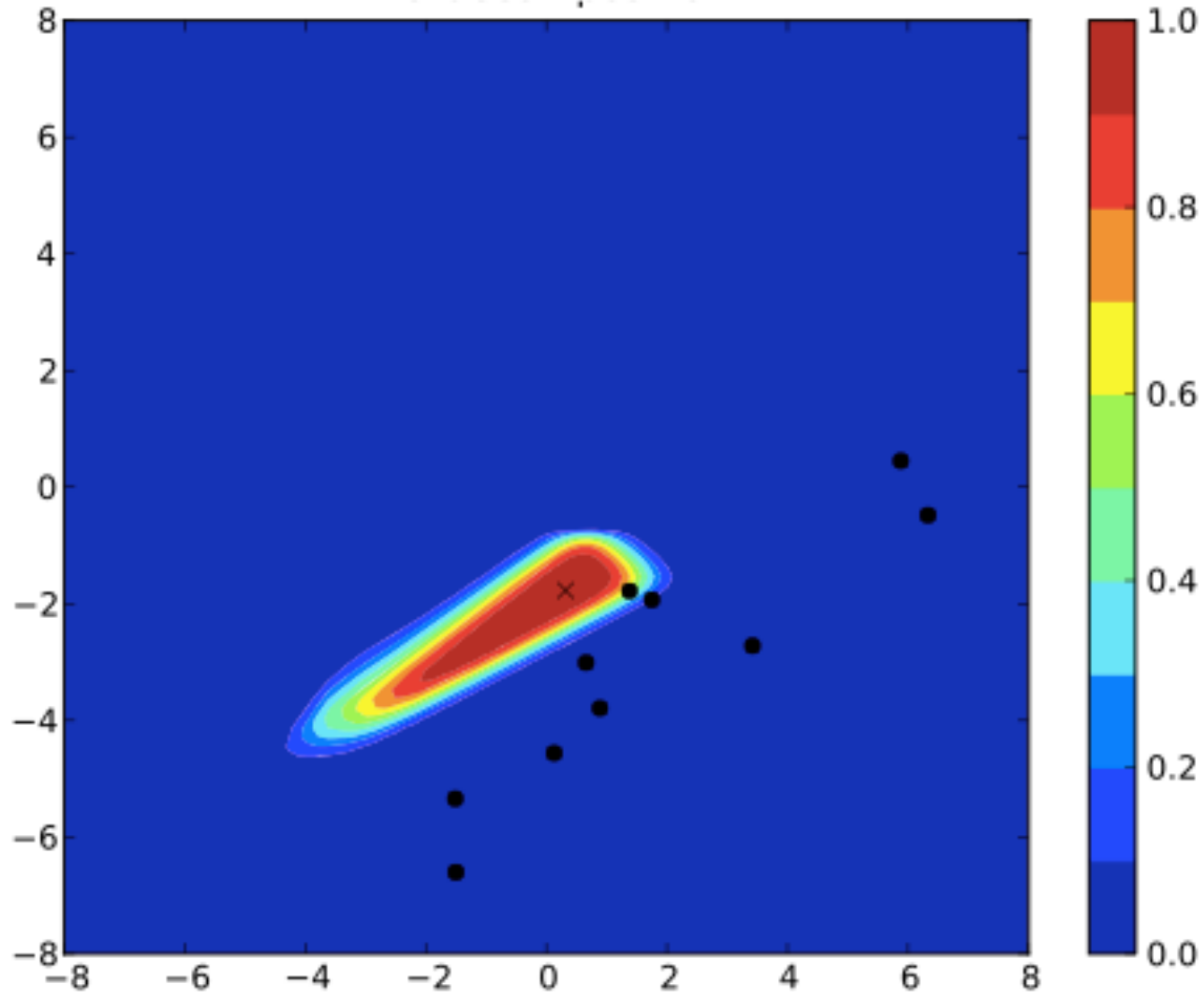
# The BEEF-vdW Ensemble of Functionals

## BEEF-vdW Quantitative Error Estimation (std. in meV)

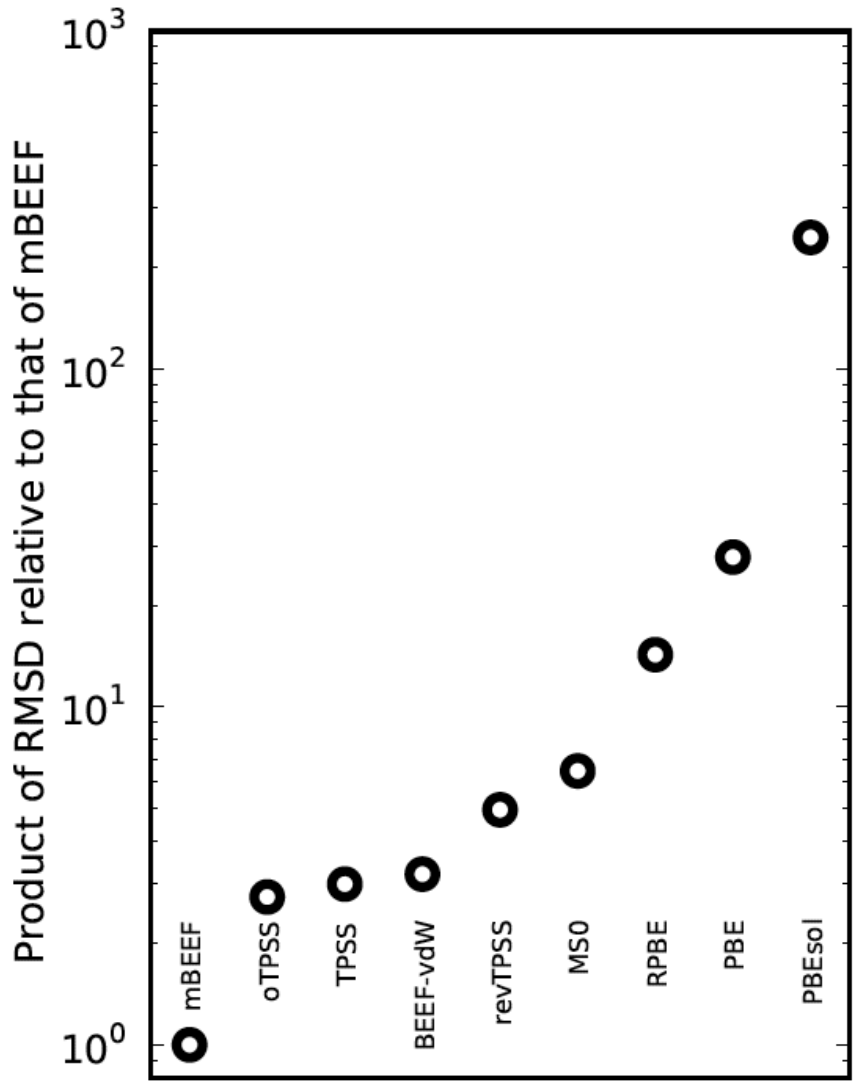
	BEEF-vdW	Ensemble estimate
CE17	143	209
RE42	372	253
DBH24	331	144
G2/97	242	312
SolEc34	576	436
s22x5-0.9	171	197
s22x5-1.0	94	181
s22x5-1.2	36	137
s22x5-1.5	8	67
s22x5-2.0	5	18

# Application: Probability volcano plots (NO decomposition)

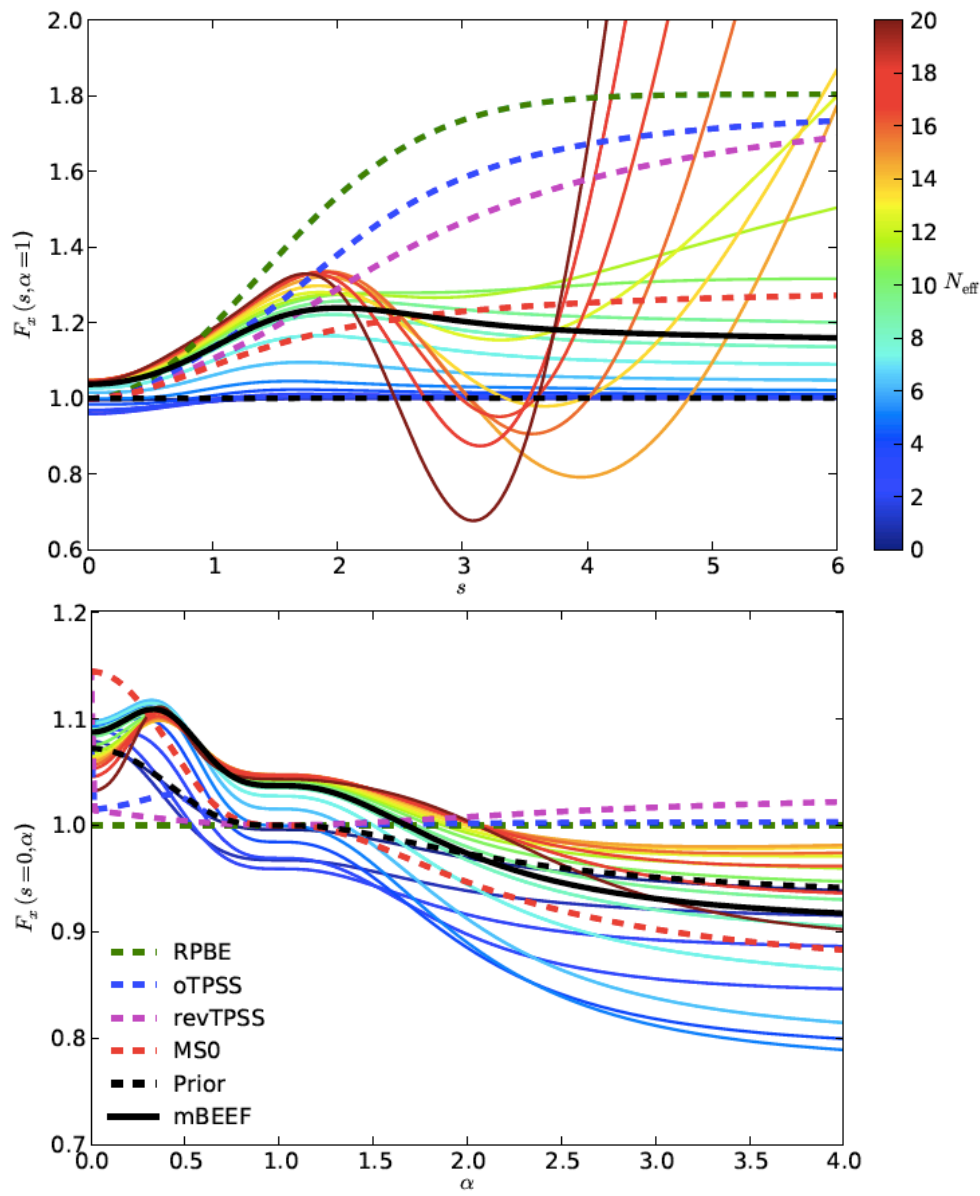
What is the probability that I can find an alloy that is 10,000 times more active than Pt for NO decomposition?



# Improved functional flexibility – toward second derivatives



Wellendorff, Lundgaard, *Preliminary*



Thanks !

