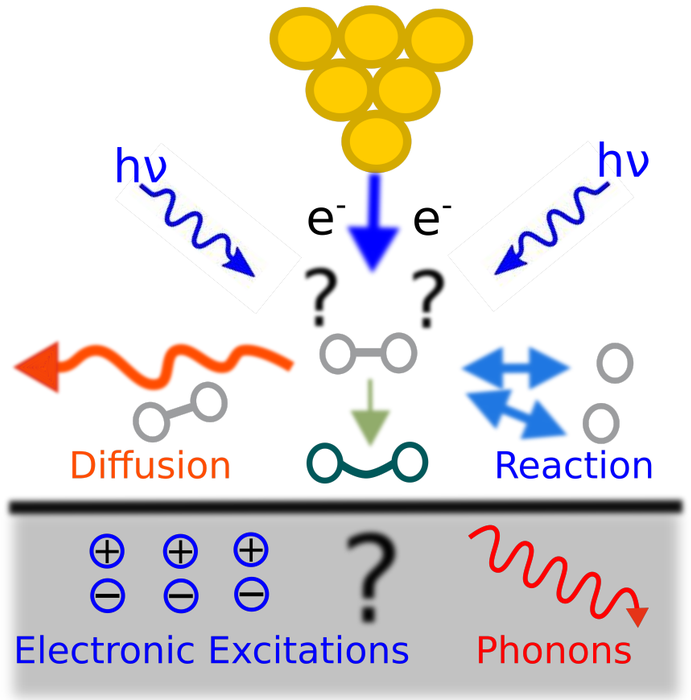
WARWICK

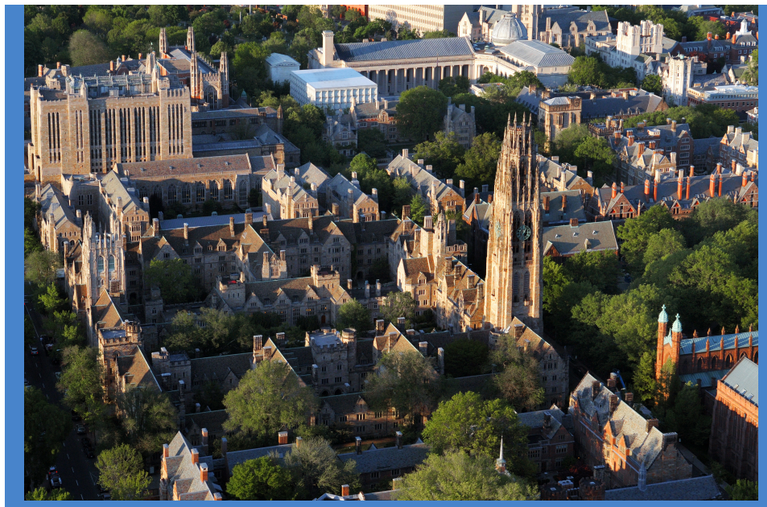
Controlled Self-Assembly, Switching, and Catalysis: Ab-Initio Insights into Stimulated Chemistry on Surfaces



Reinhard J. Maurer

Department of Chemistry, University of Warwick

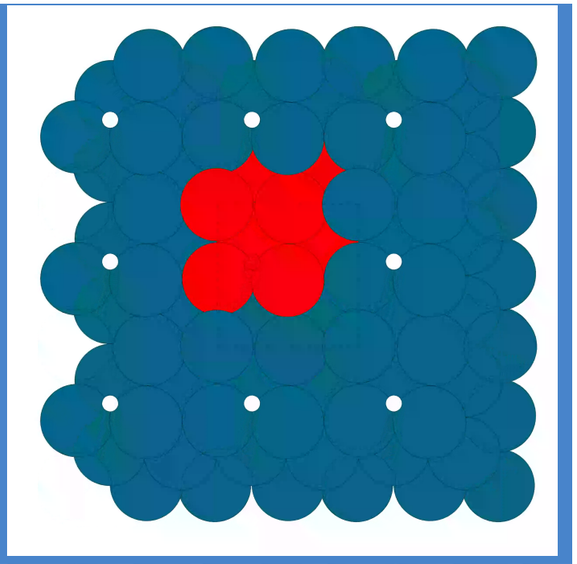
About Myself



PostDoc at Yale University

with Prof. John C. Tully

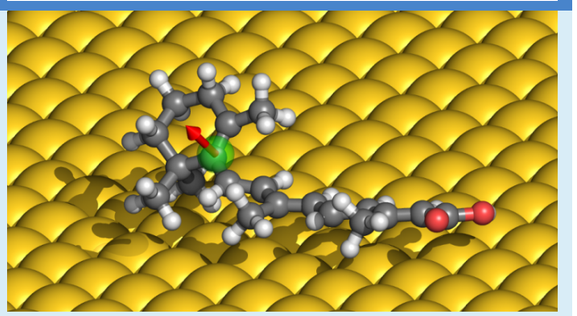
- 2014 - 2017
- Nonadiabatic and Quantum Nuclear Effects in Adsorbate Dynamics



PhD in Theoretical Chemistry

at Tech. University of Munich (Germany)

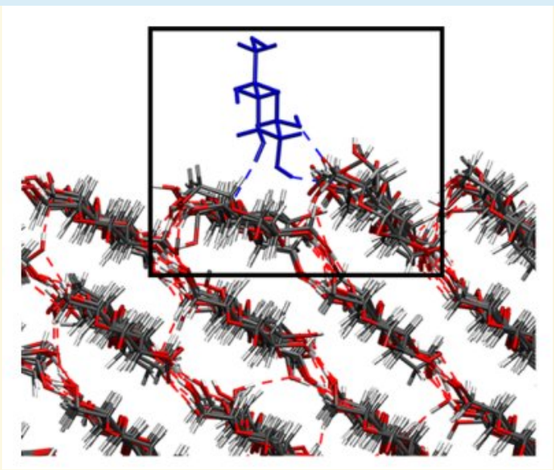
- 2010 - 2014
- Functional Molecules on Metal Surfaces
- Theoretical Spectroscopy/Photochemistry



Diploma (BSc/MSc) in Comp. Chemistry

at University of Graz (Austria)

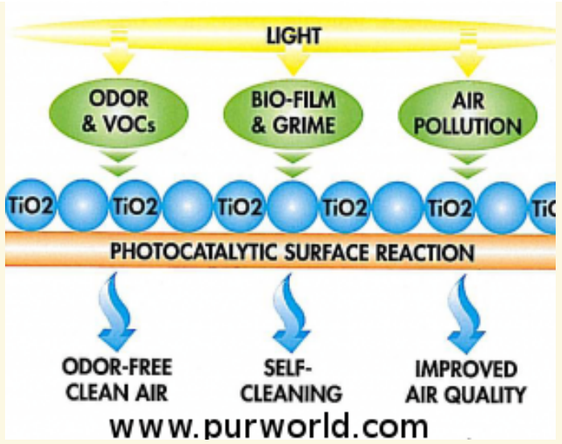
- 2005 - 2010
- Adsorption on and Wetting of Cellulose Crystal Surfaces



Stimulated Chemistry on Surfaces

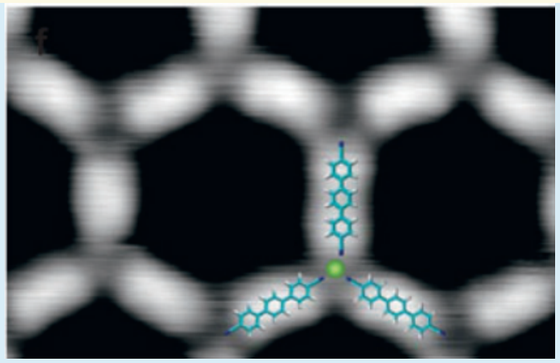
Surface Functionalization/Thin Films

- Smart Coated Surfaces e.g. Self-Cleaning Surfaces
- Photocontrolled Surface Function / Antimicrobial Surfaces
- Biocompatibility of Implants
- Device Physics of Hybrid Thin-Film Interfaces / Solar Cells



Energy Materials

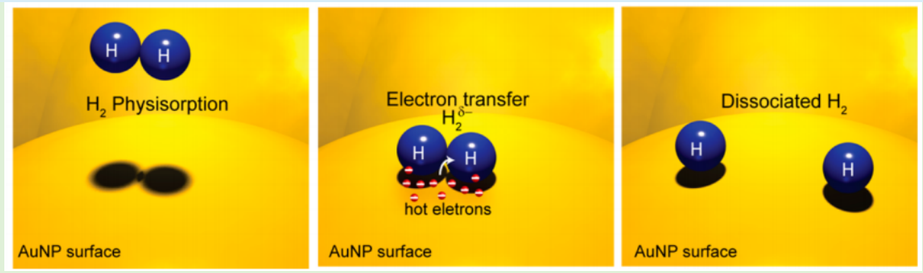
- Plasmonic Surfaces
- Surface Electrochemistry / Electron Transport
- Phase Change Materials
- Surface Self-Assembly in Hybrid Materials



Annu. Rev. Phys. Chem. 58, 375-407 (2007)

Catalysis and Surface Dynamics

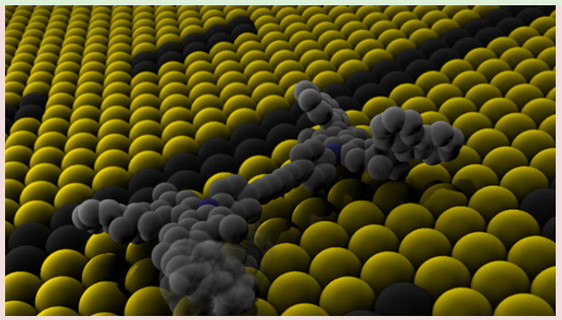
- Photon and Electron enhancement in Catalysis
- Energy Dissipation and Heat Transport
- Hot-electron Chemistry



Nano Lett., 13, 240-247 (2013)

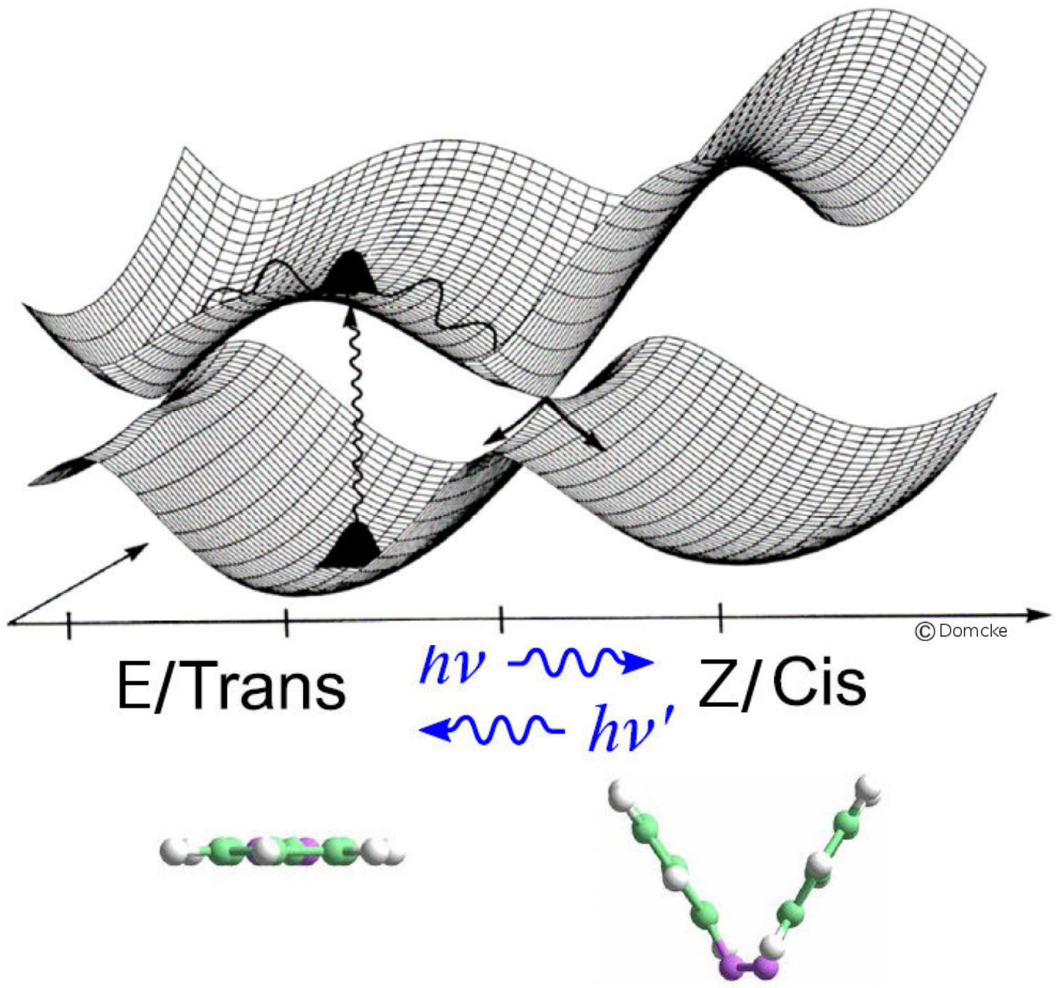
Nanotechnology

- Metal Nanoclusters for field-enhanced radiation treatment
- Nanomotors and Molecular Switches
- Nanomagnetism and Spintronics



Nature, 479, 208 (2011)

Example: Molecular Switches on Surfaces - Azobenzene

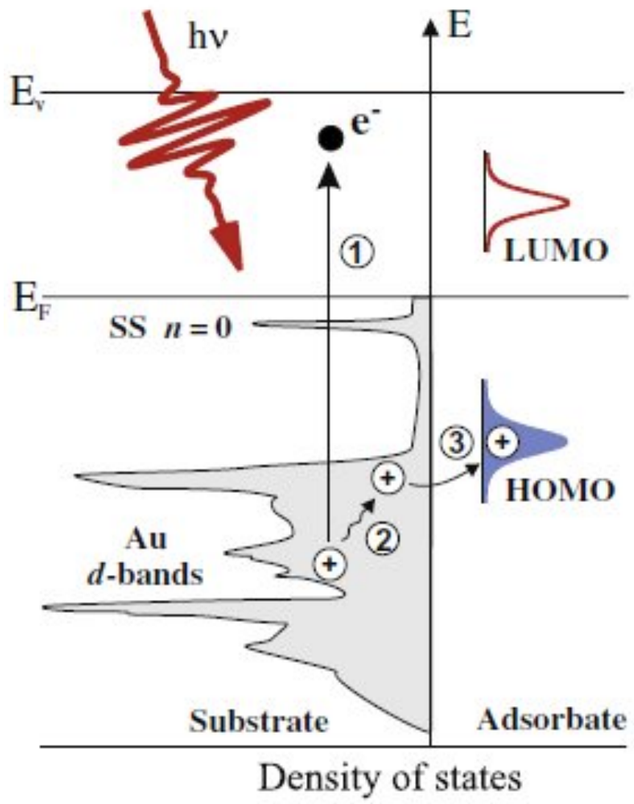


E. McNellis, Thesis (FU Berlin), 2010

1. two meta-stable states
2. reversible and **effi**cient light-induced switching

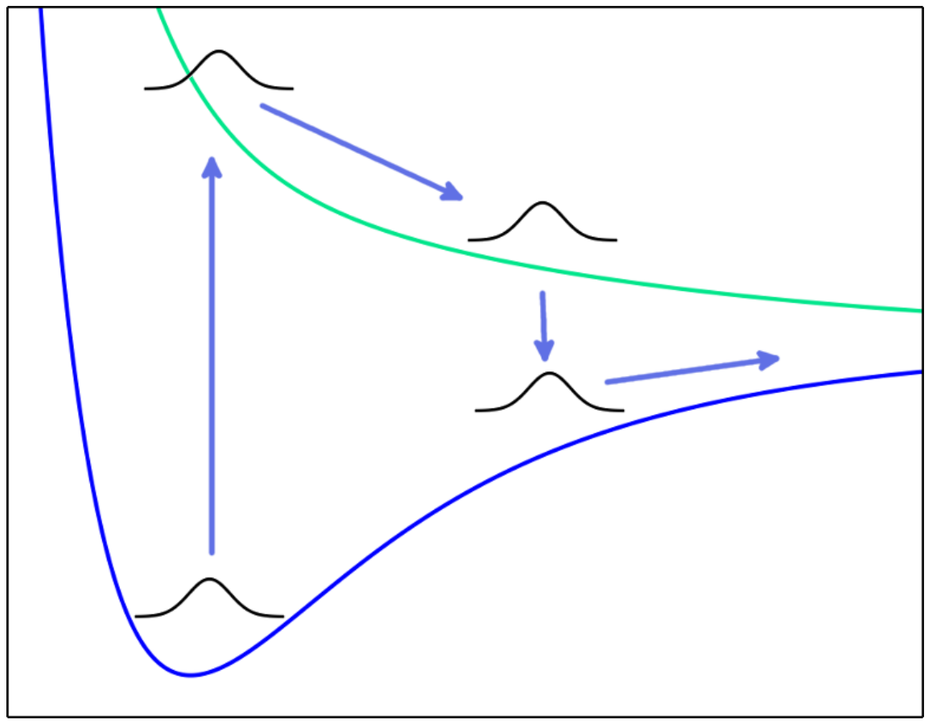
Mechanism: electronic excitation -> vibronic energy transfer -> molecular isomerization

Azobenzene on coinage metals



Wolf, Tegeder, Surf. Sci. 603, 1506-1516 (2009)

- ineffi**ci**ent photoswitching of TBA on Au
- no switching on Ag



Guo et al. , Progr. Surf. Sci. 62, 239-303 (1990)

Menzel, Gomer, J. Chem. Phys. 41, 3311 (1964)

- excited state induces motion to overcome ground state barrier

Questions for Ab Initio simulation

- what defines (non-)function
- what are the key design parameters
- what is the explicit mechanism
- coupling to surface electrons/phonons?

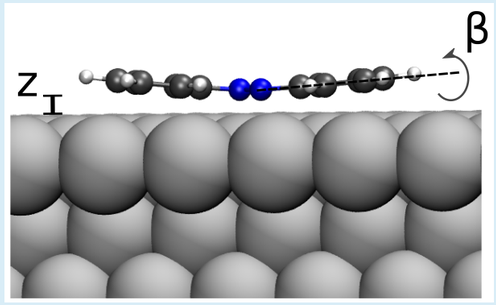
Challenges to Ab Initio simulation

- accurate structure/energetics
- be able to treat electronic excited states
- e**ffi**ciently describe surface spectroscopy
- computational feasibility

Ab Initio simulation of stimulated reactions on surfaces

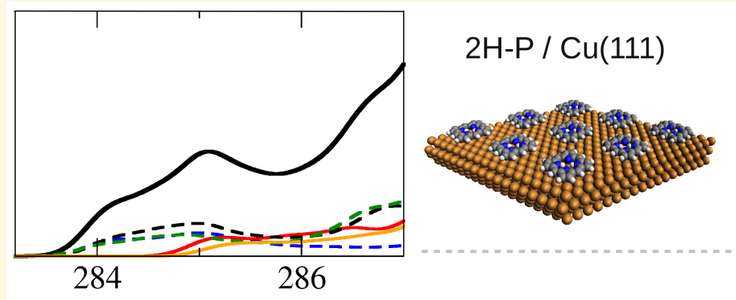
Accurate structure and energetics

- Density Functional Theory+beyond
- dispersion interactions
- finite-temperature effects



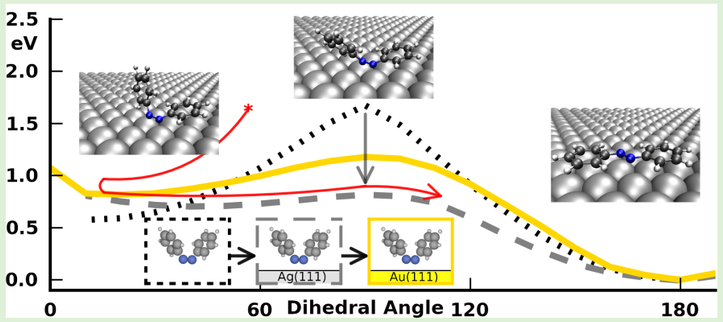
Excited States and Spectroscopy

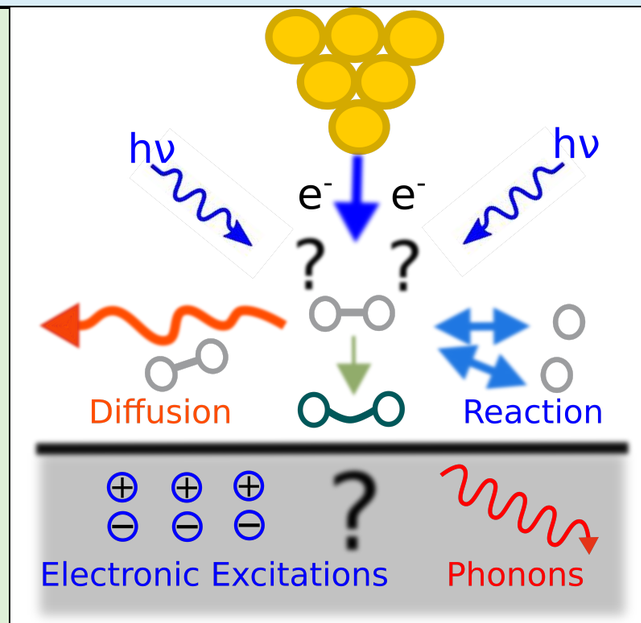
- excited states and couplings
- surface spectroscopy
- XPS,XAS,2PPE,SFG,SERS



Mechanistic Details / Reaction Dynamics

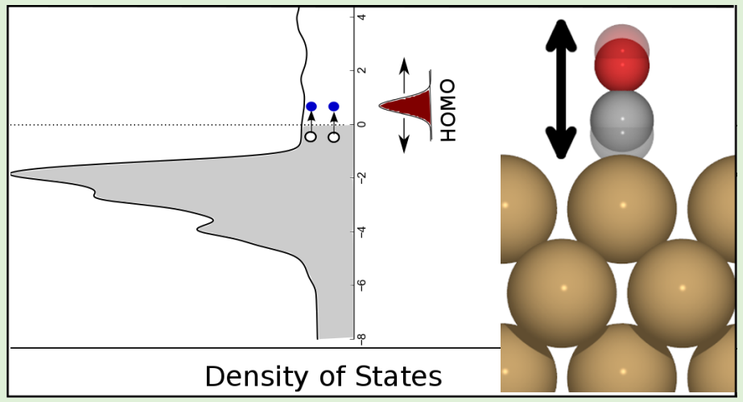
- general reaction mechanisms
- key design parameters





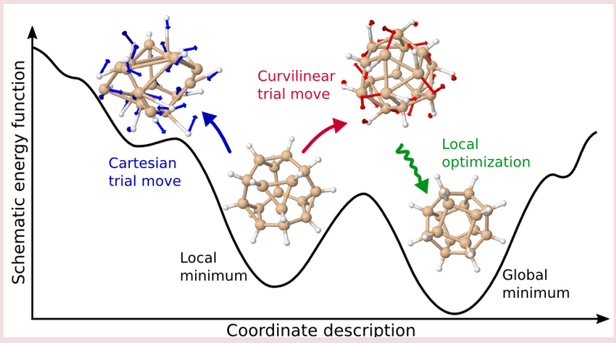
Energy Dissipation Nonadiabatic Dynamics

- role of nonadiabatic effects in surface dynamics
- electron-phonon coupling



Configurational Complexity / Computational Scaling

- enable treatment of larger systems
- address high dimensional systems
- identify structures/pathways in reaction networks



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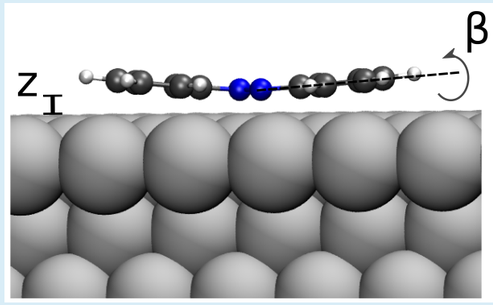
- dispersion interactions
- finite-temperature effects



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- surface spectroscopy
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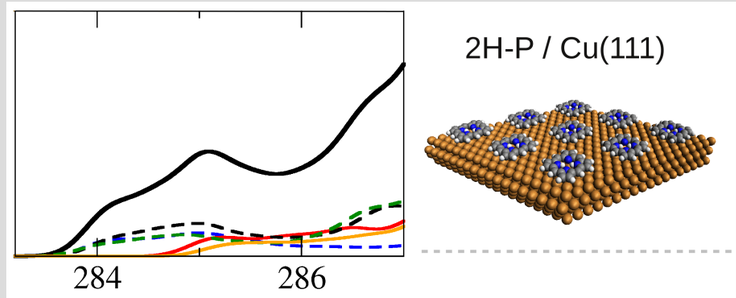

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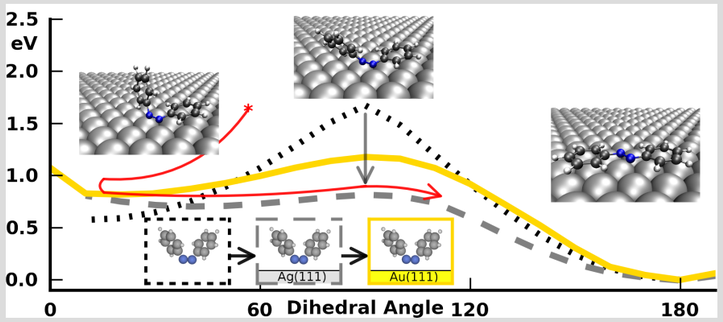

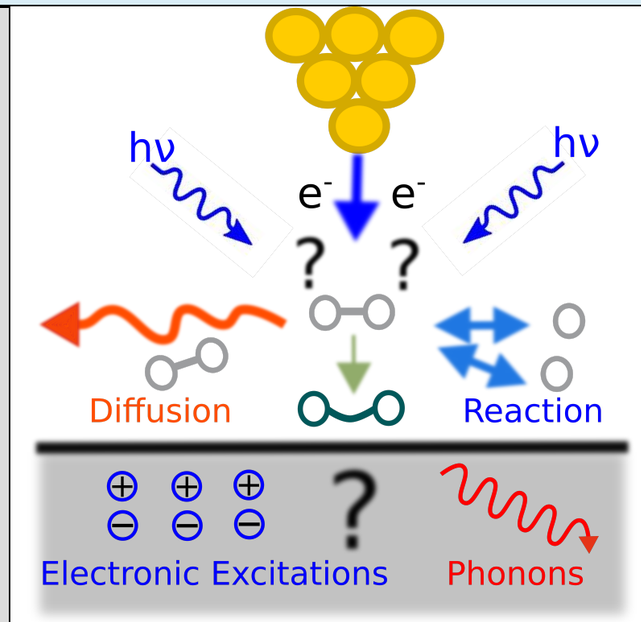

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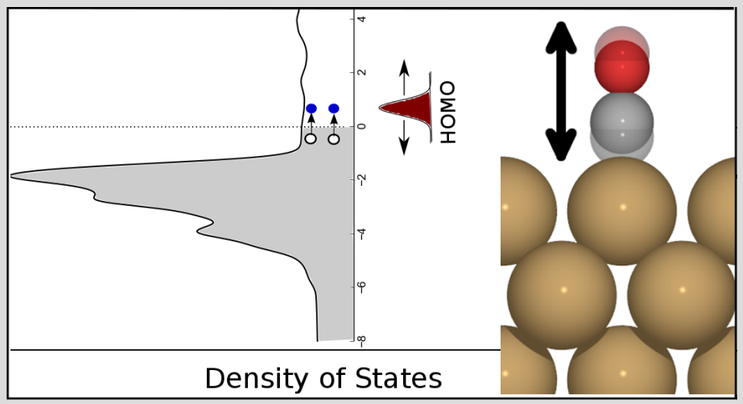

Configurational Complexity / Computational Scaling

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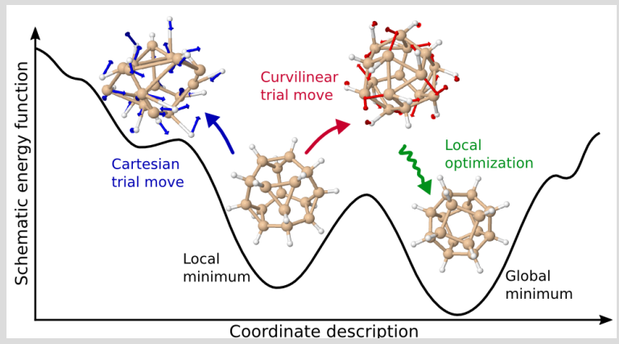
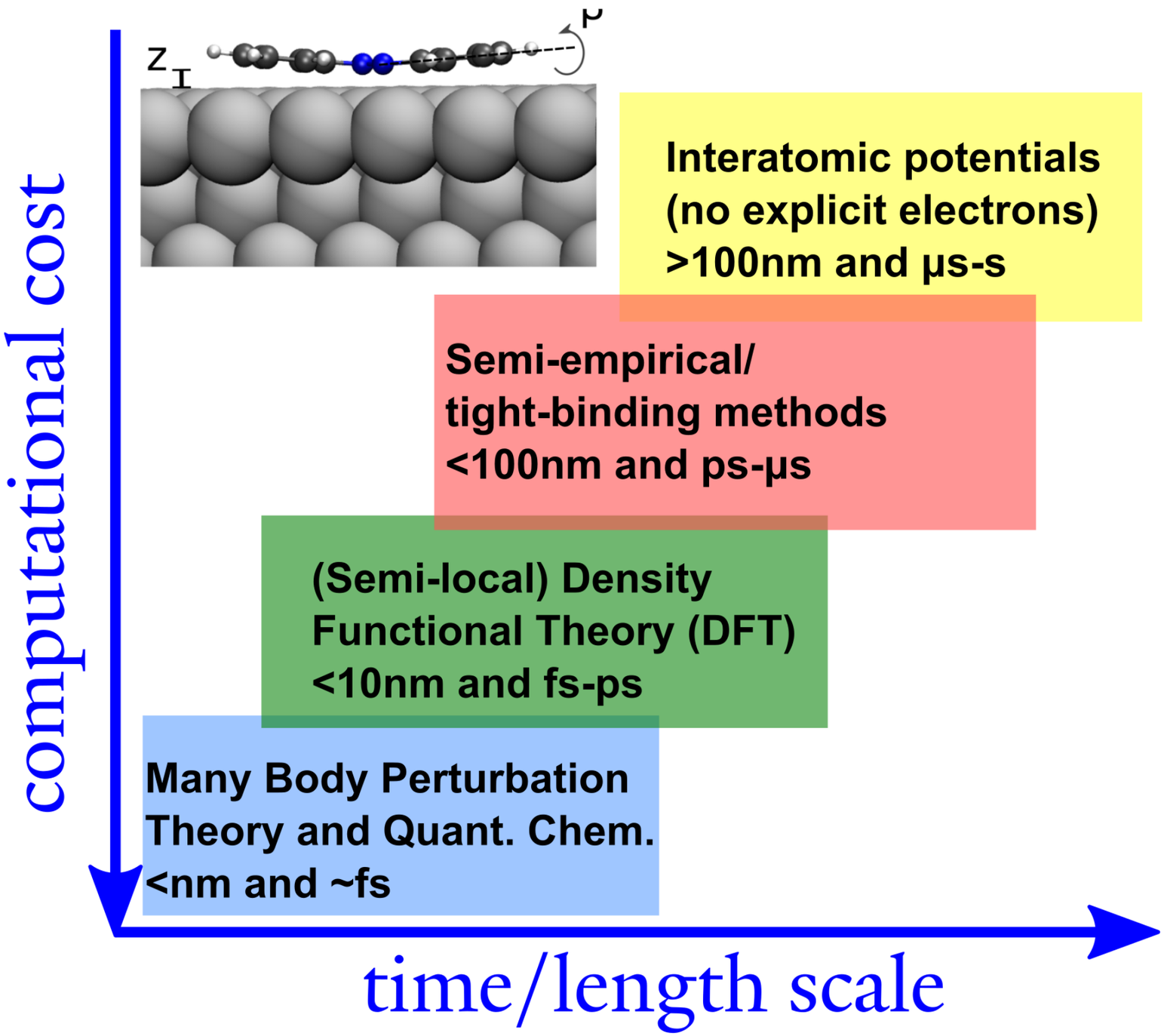
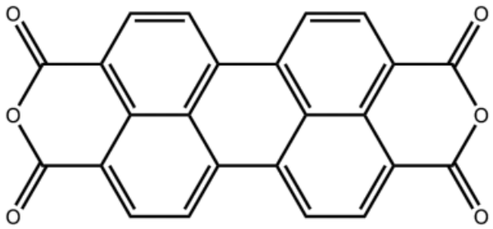


Atomistic simulation across different length and time scales



DFT performance in modeling molecules on metal surfaces

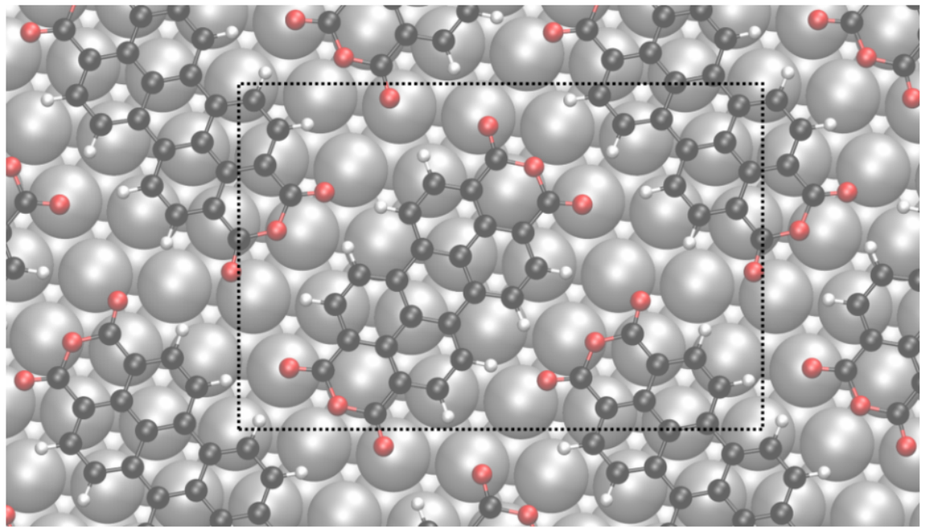


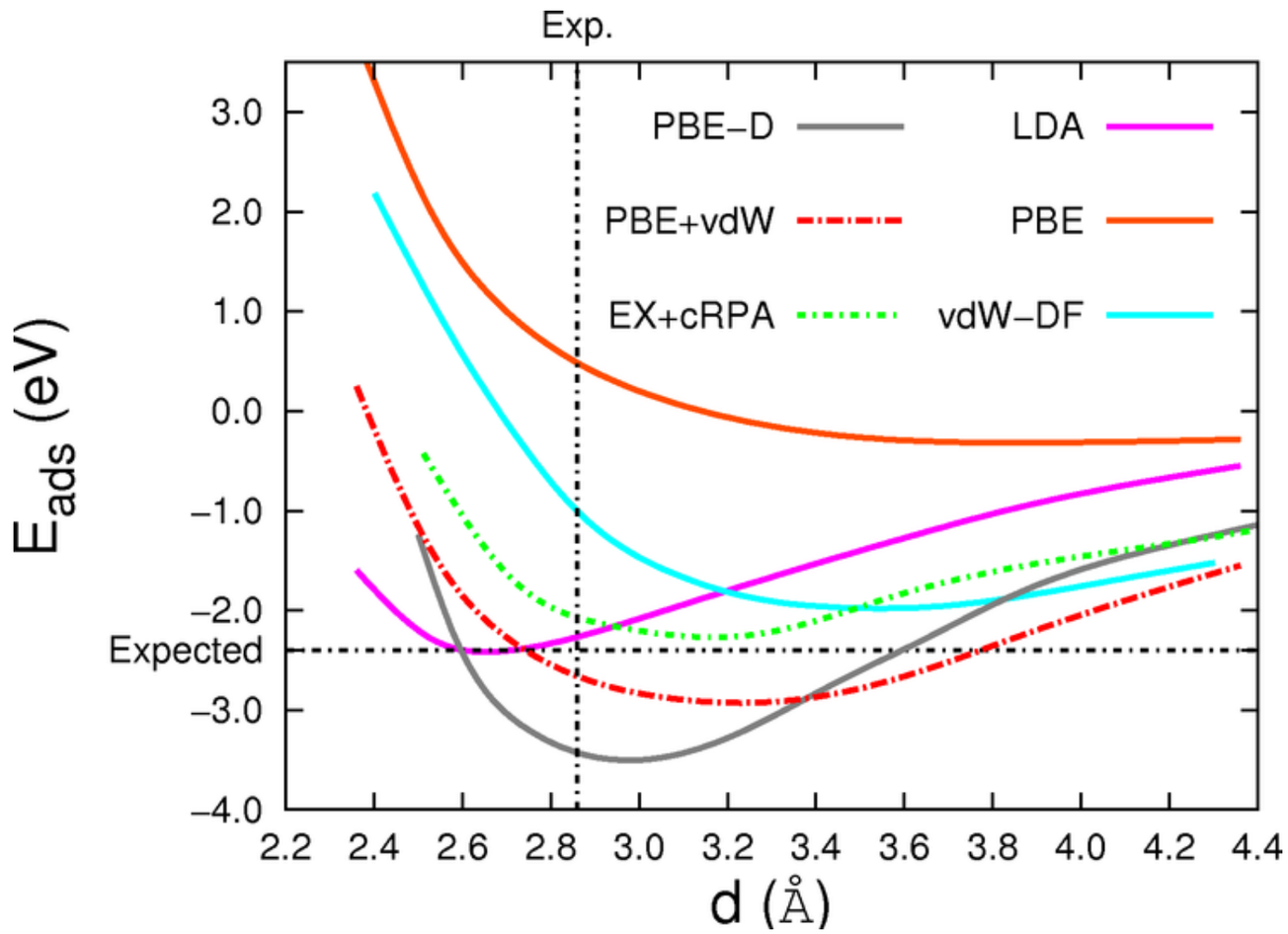
PTCDA molecule on Ag(111)

well-studied experimentally by

x-ray standing wave measurements[1]

E_{ads} estimated from smaller analogues[2]





Exact exchange and explicit correlation (EX+cRPA) correctly capture physics of long-distance correlation, but unfeasible for >100 atoms

! lack of efficient dispersion in semi-local Density Functional approximations !

Maurer, Ruiz, Camarillo-Cisneros, Liu, Ferri, Reuter, Tkatchenko, Progr. Surf. Sci. 91, 72-100 (2016)

[1] Phys. Rev. B 81, 125432 (2015) [2] J. Chem. Phys. 143, 102808 (2015)

Efficient Dispersion Interactions for Molecules at Surfaces

MAX-PLANCK-GESELLSCHAFT
Fritz-Haber-Institut

semi-empirical dispersion interactions

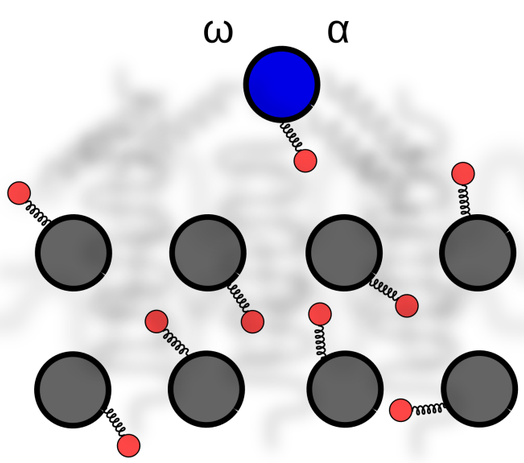
Grimme, J. Comput. Chem. 16, 1787 (2006)

$$E_{\mathrm{disp}} = -\sum_{A<B} f_{\mathrm{damp}}(R_{AB}) \frac{C_6^{AB}}{R_{AB}^6}$$

density-derived dispersion interactions

Tkatchenko, Scheffler, PRL 102, 073005 (2009)

1. vdW^{TS} : $\alpha = \alpha[n] \quad C_6 = C_6[n]$
2. vdW^{surf} : interaction screening in metal
3. MBD : full Many Body Dispersion with quantum oscillators



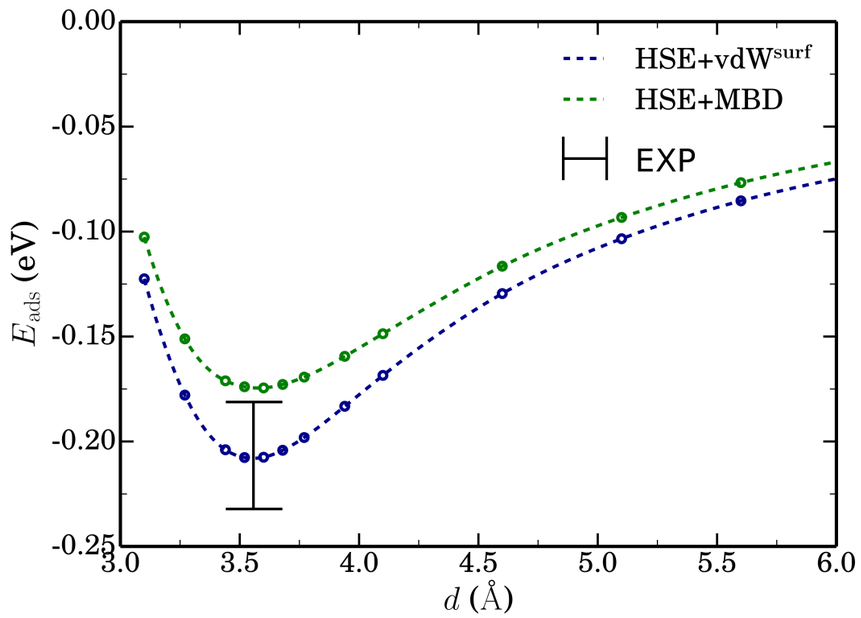
PBE+MBD, HSE+MBD

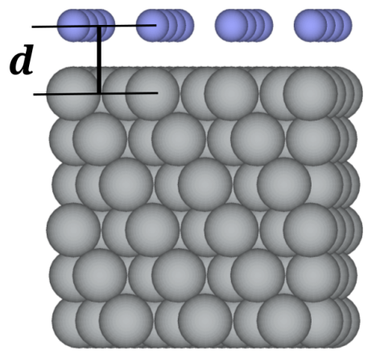
Collaboration with Tkatchenko group, FHI Berlin

Maurer, Ruiz, Tkatchenko, JCP 143, 102808 (2015)

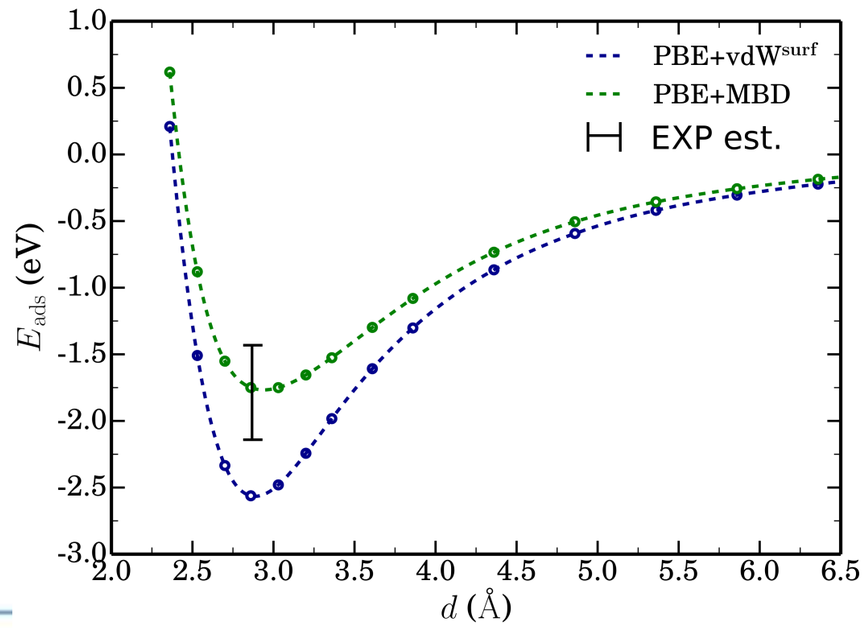
exp.: TPD, LEED, X-ray standing waves

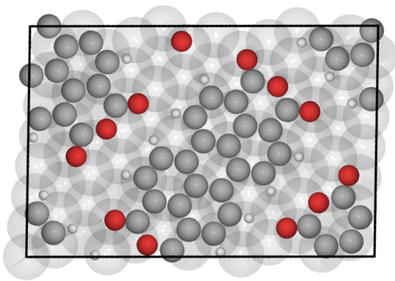
Xe@Ag(111)



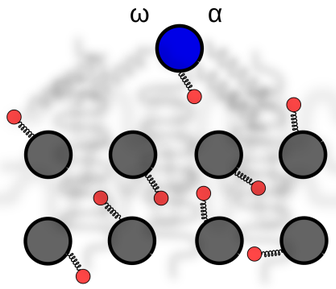


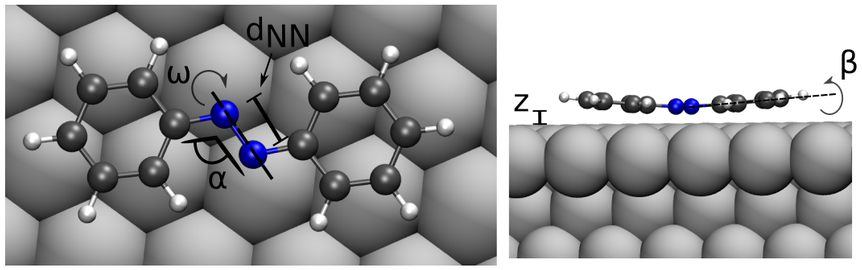
PTCDA@Ag(111)





Structure and Energetics of Azobenzene on Ag(111)





covalent interactions: DFT-PBE

z=3.64 Å, E=0.11 eV

+ pairwise dispersion interactions: PBE+vdW(surf)

z=2.61 Å, [Math Processing Error] eV

+ full Many-Body long-range Dispersion: PBE+MBD

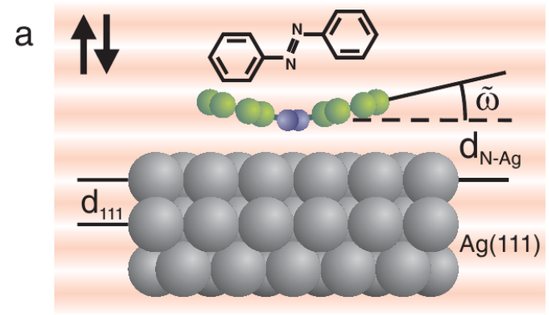
z=2.46 Å, E=1.24 eV

- What are we missing? finite temperature!

+ Ab Initio Molecular Dynamics

$z_{210K} \approx$ 2.98 Å, E_{400K}=0.99±0.17 eV

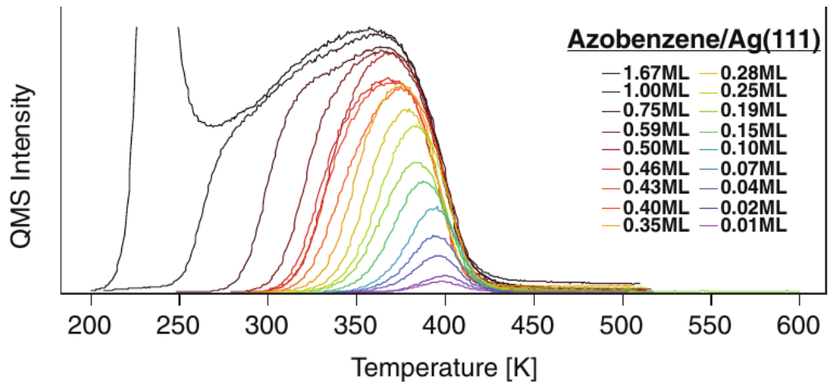
X-ray Standing Waves



z=2.97± 0.05 Å

T= 210 K

Temperature Programmed Desorption



E_{des}=1.02±0.06 eV

T ≈ 400 K

Collaboration with Prof. F.S. Tautz (FZ Jülich, NIXSW) and Prof. Tegeder (U Heidelberg, TPD)

XSW: Phys. Rev. Lett 104, 03610 (2010) TPD: J. Phys. Condens. Matter. 26, 35504 (2014)

Mercurio, Maurer et al., Phys. Rev. B 88, 035421 (2013), Maurer et al., Phys. Rev. Lett. 116, 146101 (2016)

Ab Initio Molecular Dynamics and Thermochemistry

Definition:

$$\Delta F_{\mathrm{des}}(T_{\mathrm{des}}) \leq 0$$

$$\Delta F_{\mathrm{des}} = \Delta U_{\mathrm{des}} - T\Delta S_{\mathrm{des}}$$

[Math Processing Error]

Thermodynamic Integration:

$$\Delta F = \int_{\mathrm{des}}^{\mathrm{ads}} d\lambda \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_{\lambda}$$

$$\Delta U = \Delta \langle E_{T=400\ K} \rangle$$

adding many-body dispersion: PBE+MBD

Free Energy Perturbation

$$\Delta F(PBE+MBD) = \Delta F(PBE+vdW^{\mathrm{surf}}) - k_B T \cdot [ln\langle -\beta \Delta E_{MBD,vdW} \rangle_f - ln\langle -\beta \Delta E_{MBD,vdW} \rangle_i]$$

Collaboration between

Reuter group, TU Munich and

Tkatchenko group, FHI Berlin

CASTEP

Ab Initio Molecular Dynamics

to simulate free energy of desorption

0:00

Maurer et al., Phys. Rev. Lett. 116, 146101 (2016)

Ab-initio prediction of functional interface properties is computationally challenging

Electronic and Thermal Fluctuations

Results

	T_{des} K	Δ U eV	Δ S eV/100K
PBE+MBD	495±99	0.99±0.17	0.20±0.04
exp	~400	1.02±0.05	-
PBE+vdW^{surf}	~600	1.58±0.08	0.24±0.02
PBE+MBD(harm.)	>1000	1.25	0.12

Role of MBD

- Using Pairwise Dispersion -> Overbinding

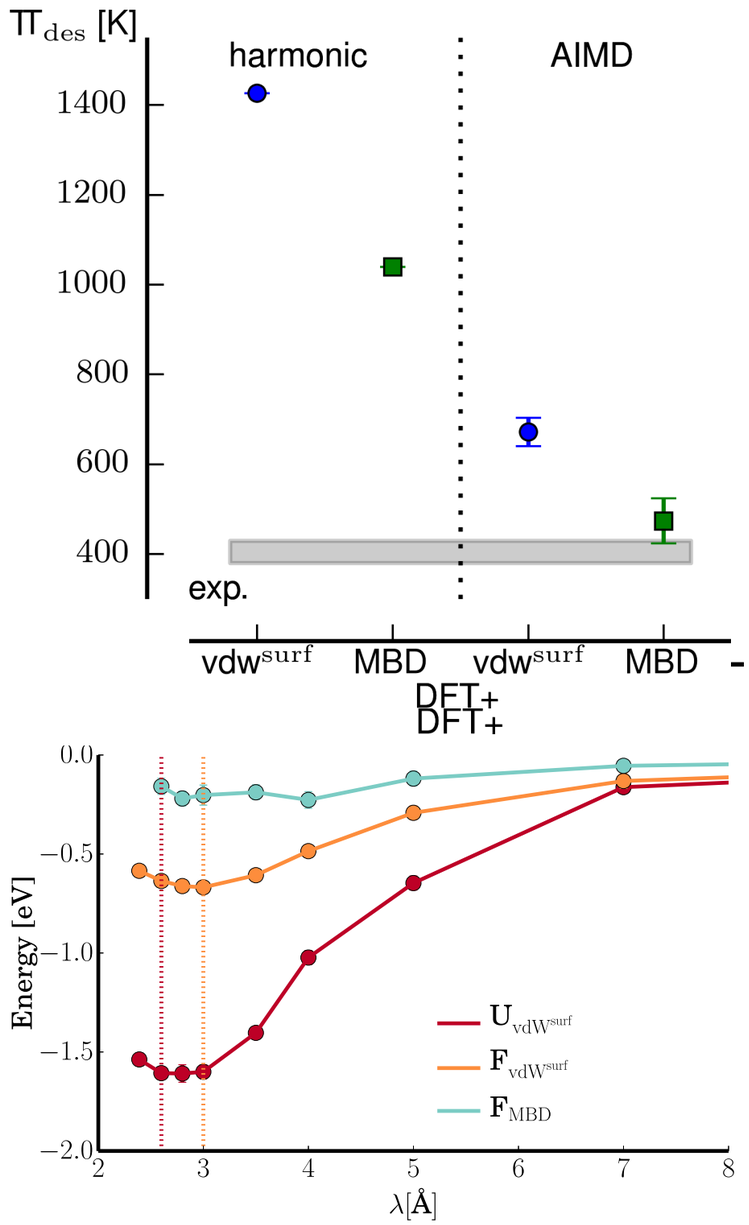
Electronic Fluctuations

Role of AIMD

- Harmonic Approximation
- $0\ K$ structure underestimates height

$$\Delta U = E_{T=0} + ZPE \quad \Delta S = \sum_j \frac{\hbar\omega_j \exp(-\hbar\omega_j/2k_BT)}{k_BT[1-\exp(-\hbar\omega_j/2k_BT)]} - \ln[1-\exp(-\hbar\omega_j/2k_BT)]$$

Thermal Fluctuations



exp: Schultze, Bronner, Tegeder,

J. Phys. Condens. Matter. 26, 35504 (2014)

Ab Initio simulation of stimulated reactions on surfaces

Accurate structure and energetics

- Density Functional Theory+beyond
- dispersion interactions
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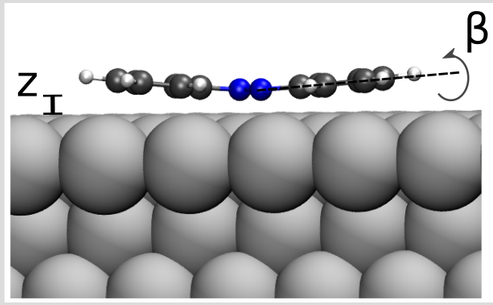

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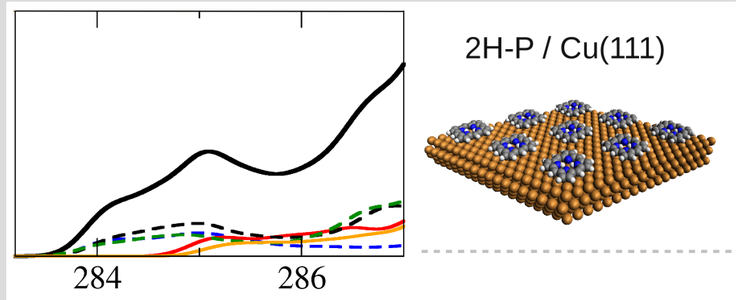

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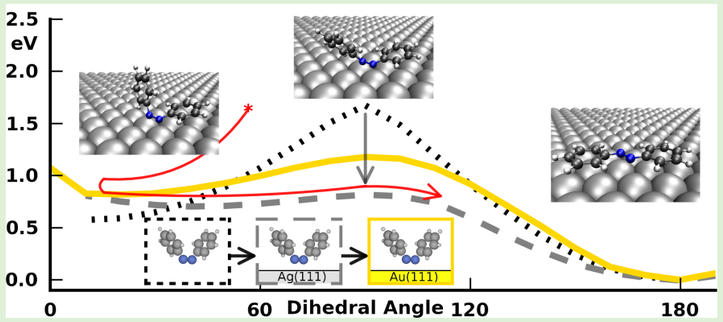

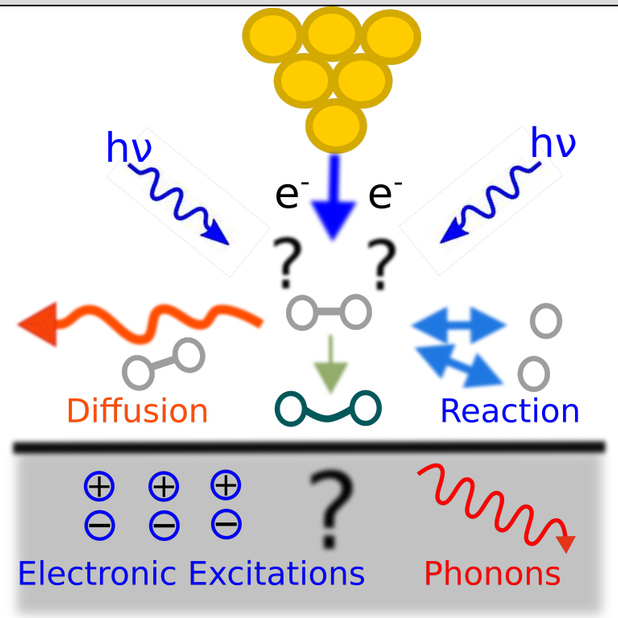

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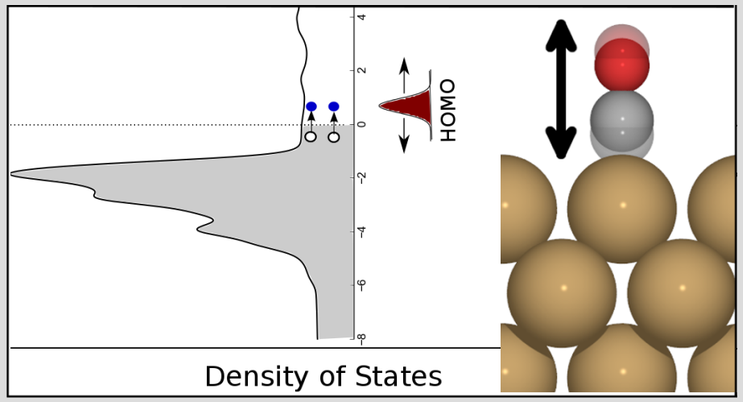
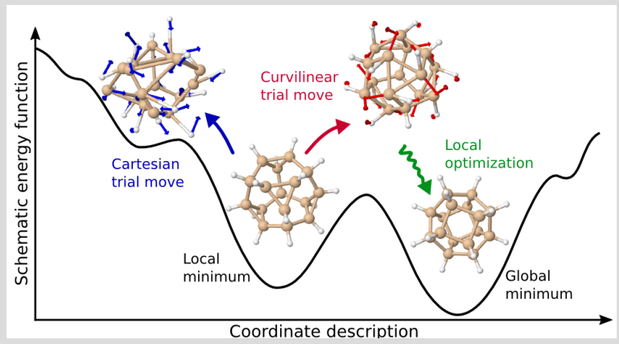
- role of nonadiabatic effects in surface dynamics
- electron-phonon coupling

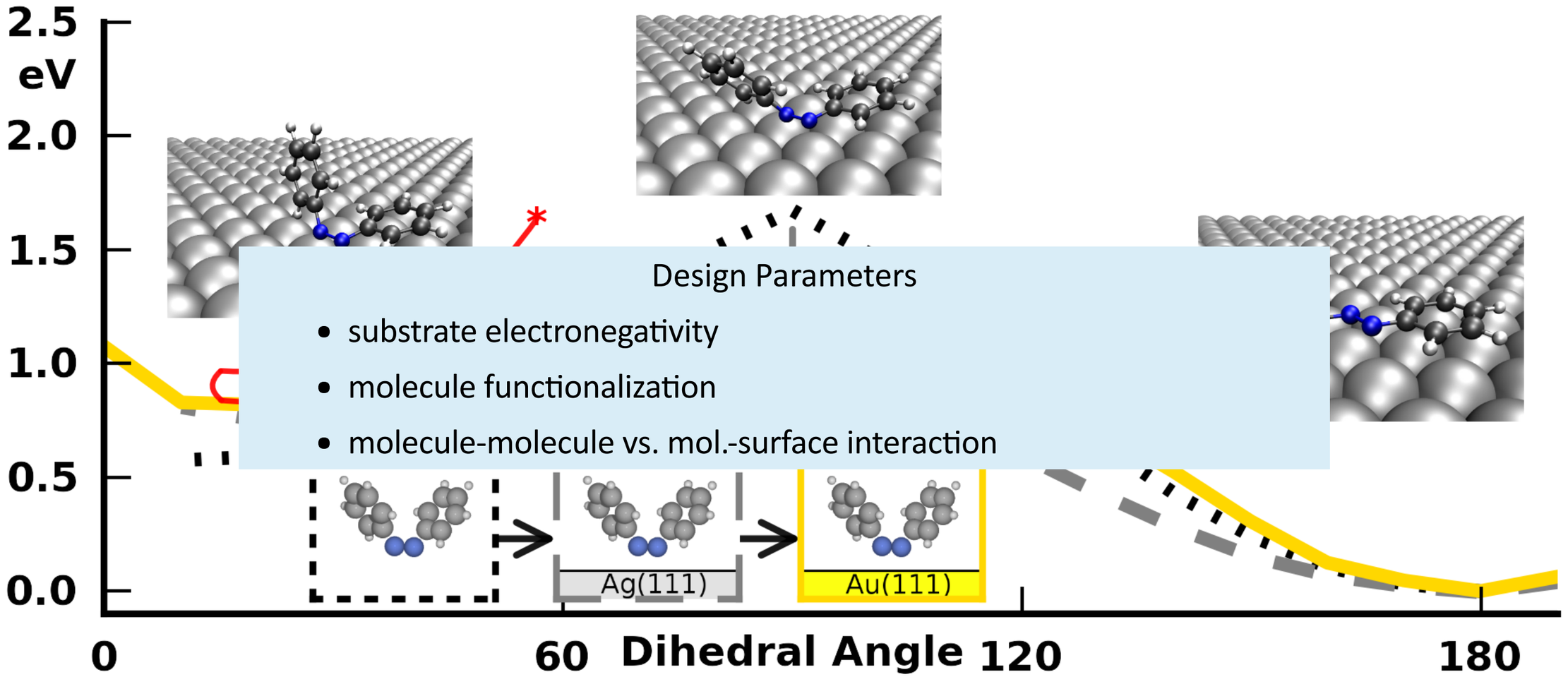


Configurational Complexity / Computational Scaling

- enable treatment of larger systems
- address high dimensional systems
- identify structures/pathways in reaction networks



Loss of Function = Loss of Bistability



Design Parameters

- substrate electronegativity
- molecule functionalization
- molecule-molecule vs. mol.-surface interaction

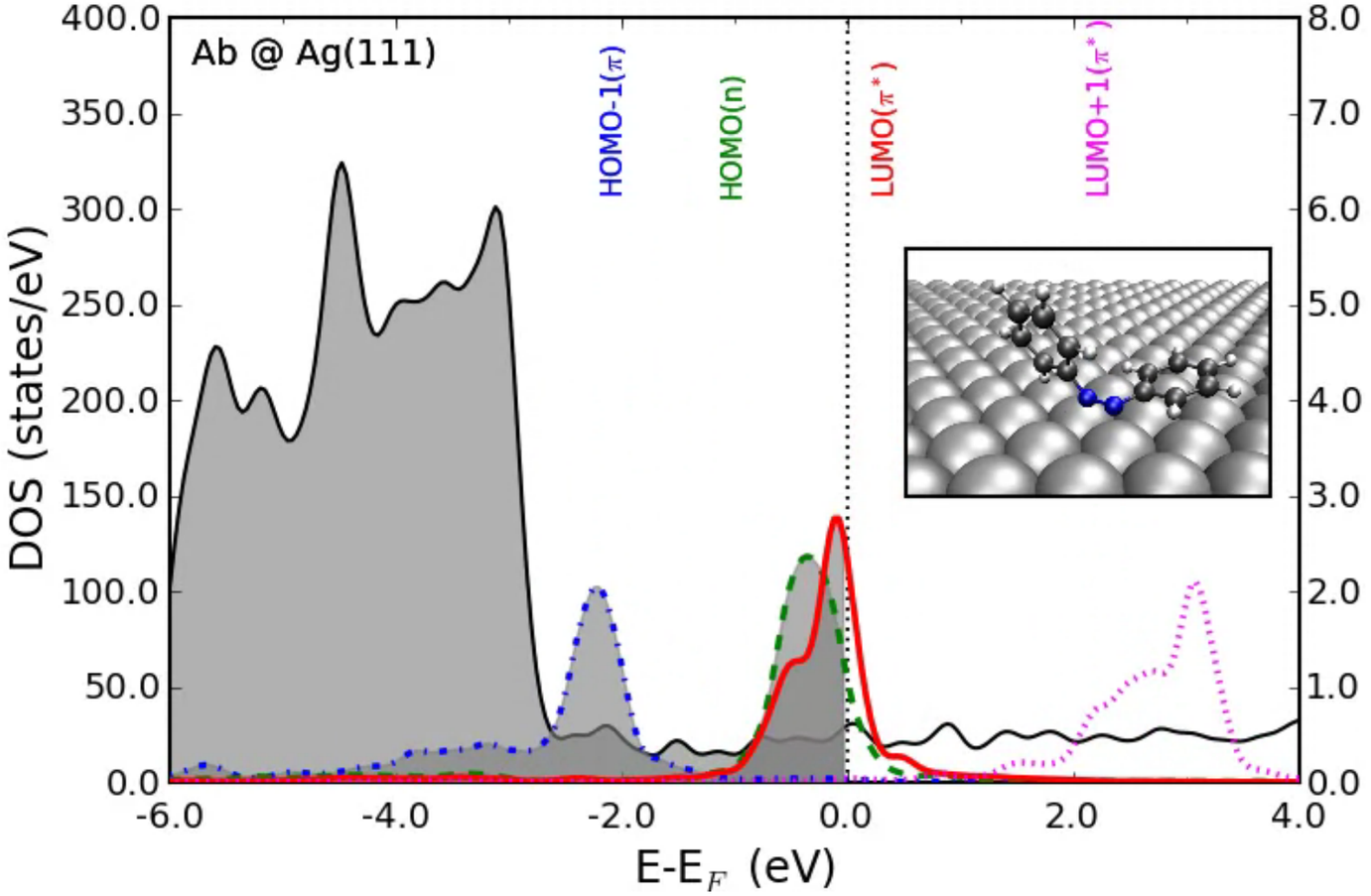
Switching:

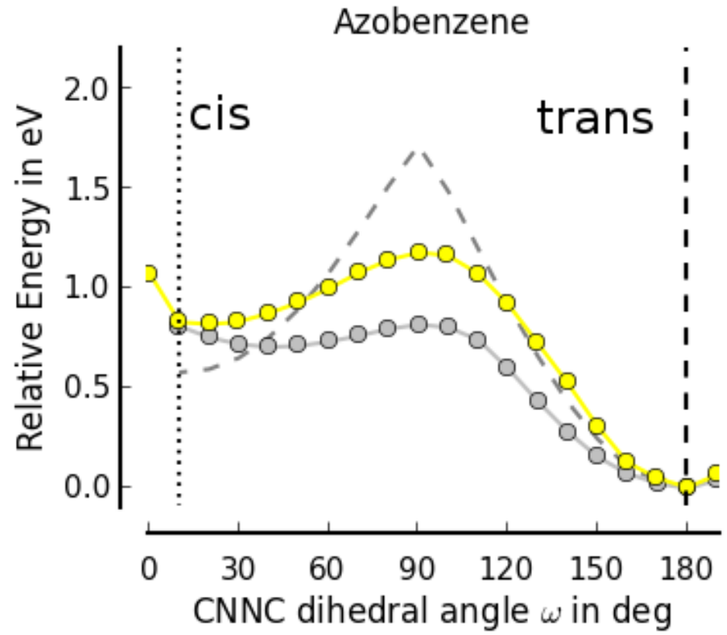
NO | with STM bias | NO | with hν

Maurer, Reuter, Angew. Chem. Int. Ed. 51, 12009-12011 (2012)

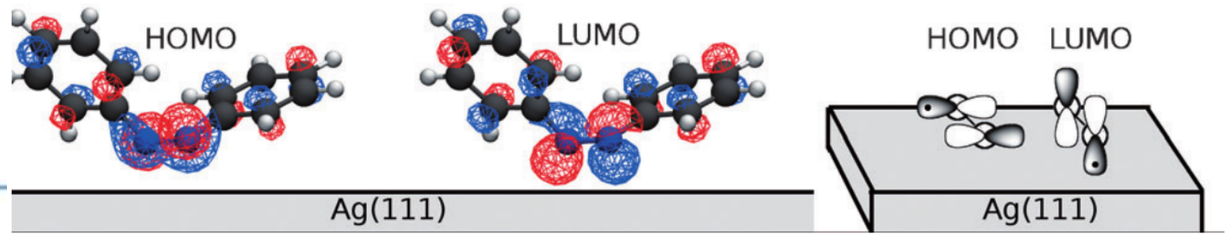
Azo@Au(111): Cho et al. PRL 96, 156106 (2006), TBA@Au(111): Comstock et al., PRL 99, 038301 (2007)

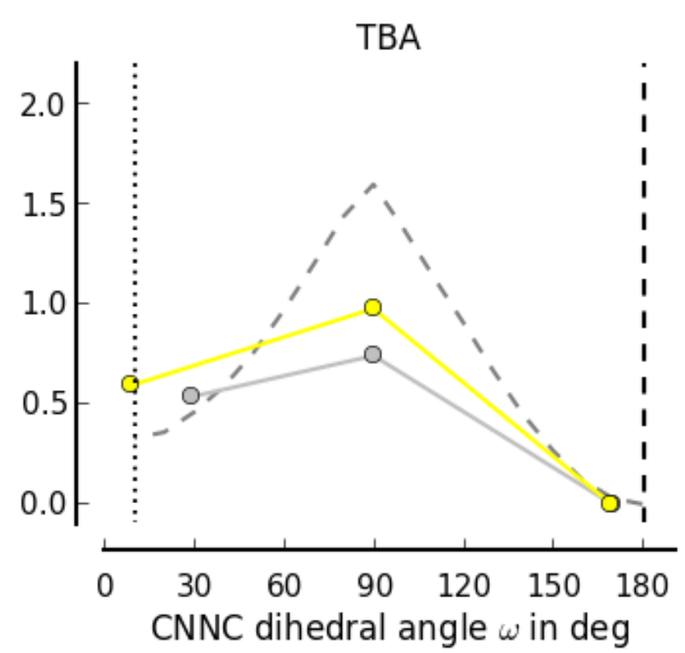
Looking closer at dihedral rotation





- Transition state strongly interacts with surface
- cis not stable on Ag(111) or more active surfaces

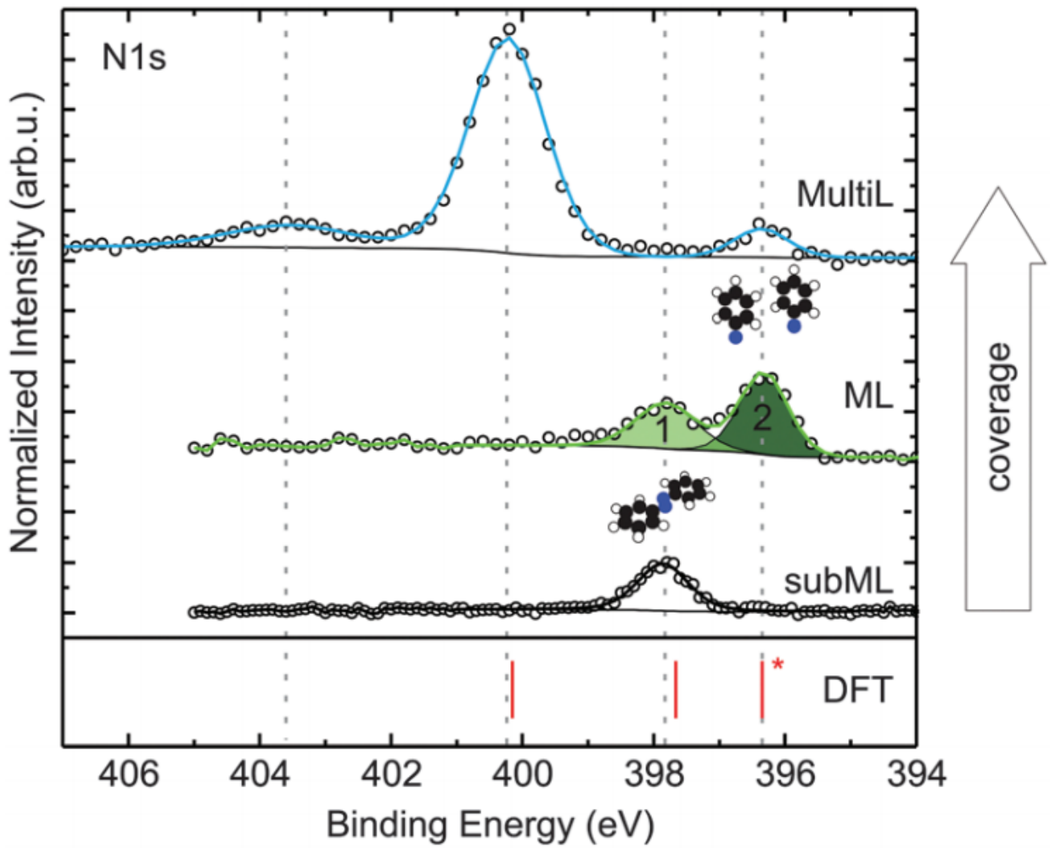


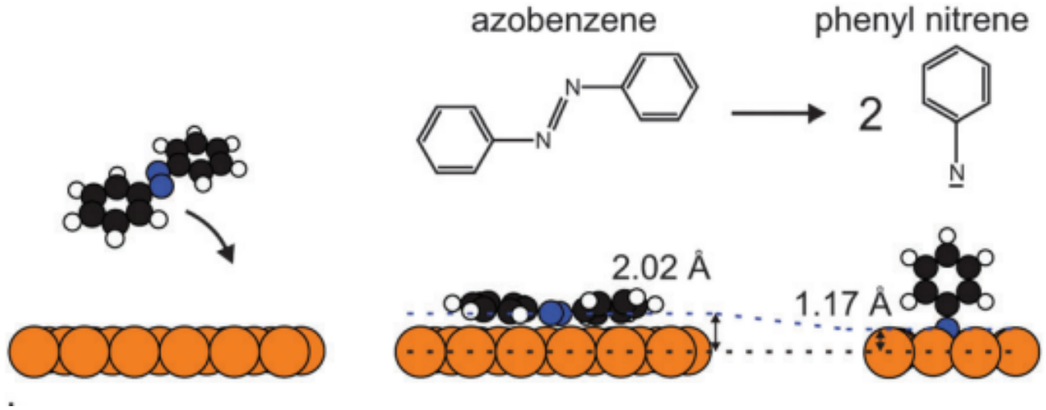


Maurer, Reuter,

Angew. Chem. Int. Ed. 51, 12009-12011 (2012)

Molecule-Substrate Interaction: Azobenzene/Cu(111)





- different phases characterized with
  X-ray photoelectron spectroscopy and
  X-ray standing wave measurements
- molecule-surface interaction too strong
- higher coverage induces dissociation

Adsorbate structure and function is very sensitive to molecule-surface interaction

Willenbockel, Maurer, Bronner, Schulze, Stadtmüller, Soubatch, Tegeder, Reuter, Tautz, Chem. Commun. 51, 15324 (2015)

Molecule Functionalization: TPAPA on Au(111) and Ag(111)

TPAPA: 3 connected Azo groups

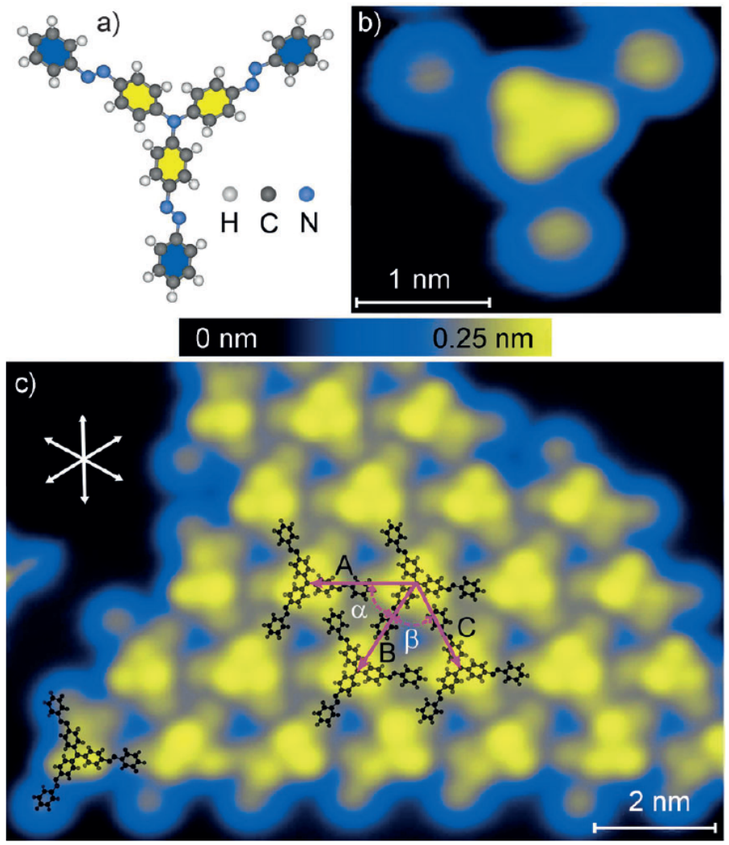
TPAPA on Au(111)

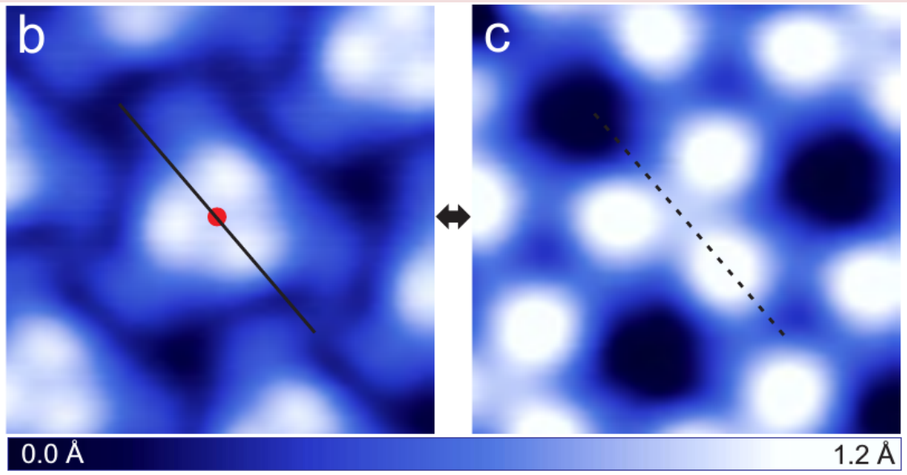
no molecular switching

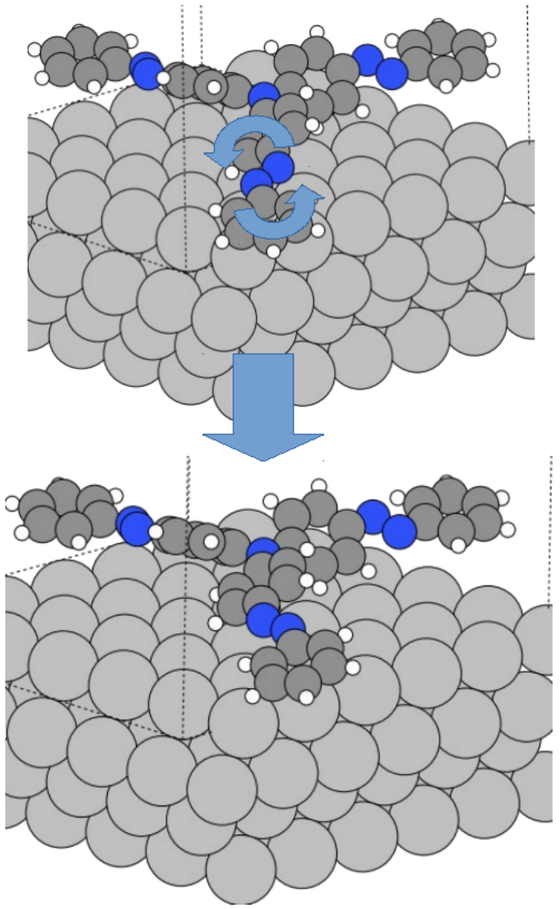
TPAPA on Ag(111)

STM-bias induced switching

!different mechanism!







0:00

Stronger binding on Ag(111)

induces new meta-stability

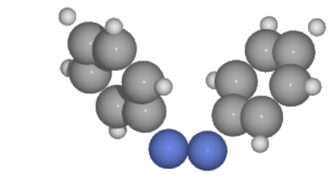
Gopakumar, Davran-Candan, Bahrenberg, Maurer, Temps, Reuter, Berndt, Angewandte Chem. Int. Ed. 52, 11007 (2013)

Scheil, Gopakumar, Bahrenberg, Temps, Maurer, Reuter, Berndt, J. Phys. Chem. Lett. 7, 2080-2084 (2016)

Details of Molecular Switching

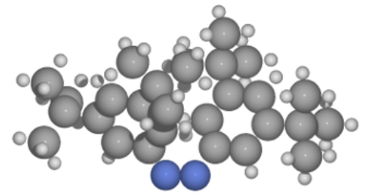
Switching:

Azo on Au(111)



with STM bias

TBA on Au(111)



with hν

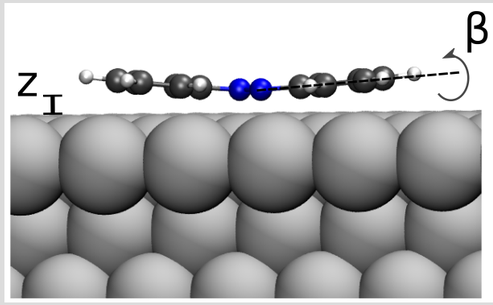
Details of excited state mechanism?

Maurer, Reuter, Angew. Chem. Int. Ed. 51, 12009-12011 (2012)

Ab Initio simulation of stimulated reactions on surfaces

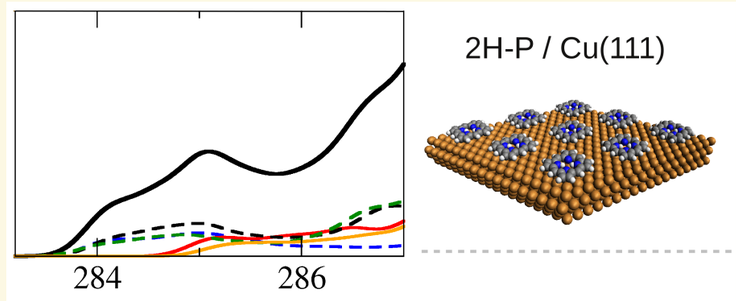
Accurate structure and energetics

- Density Functional Theory+beyond
- dispersion interactions
- finite-temperature effects



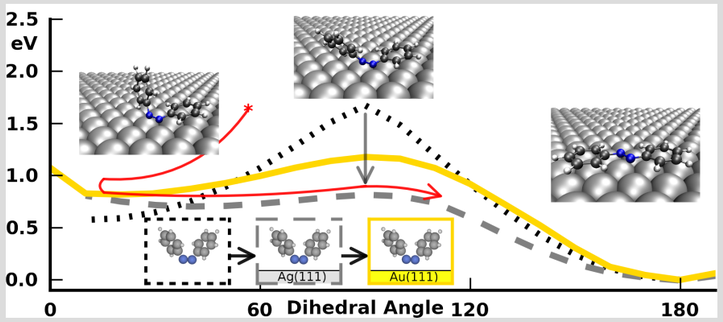
Excited States and Spectroscopy

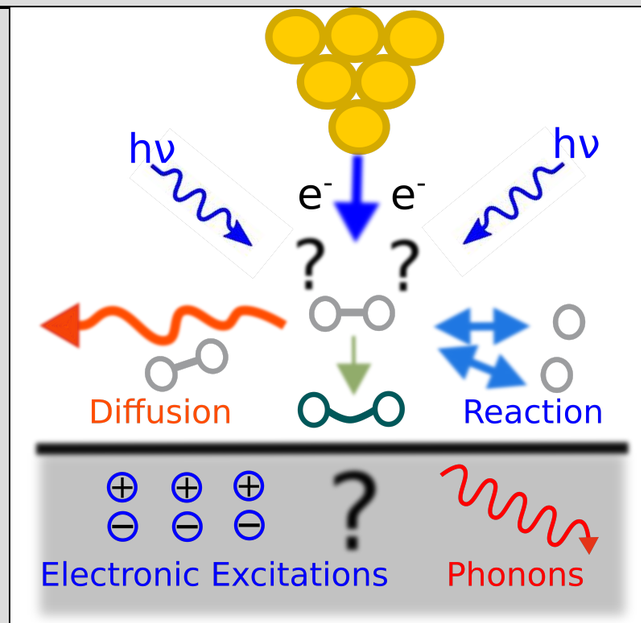
- excited states and couplings
- surface spectroscopy
- XPS,XAS,2PPE,SFG,TERS



Mechanistic Details / Reaction Dynamics

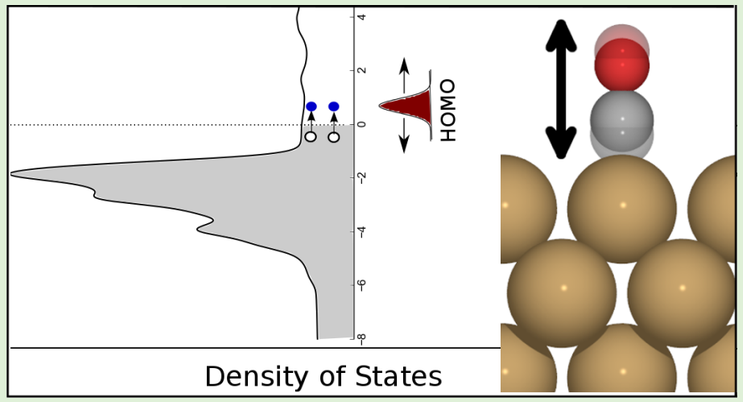
- general reaction mechanisms
- key design parameters





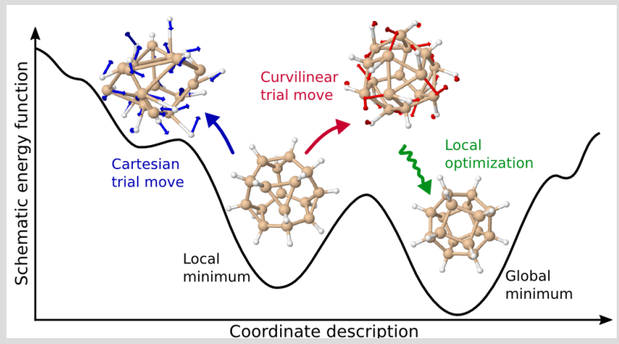
Energy Dissipation Nonadiabatic Dynamics

- role of nonadiabatic effects in surface dynamics
- electron-phonon coupling



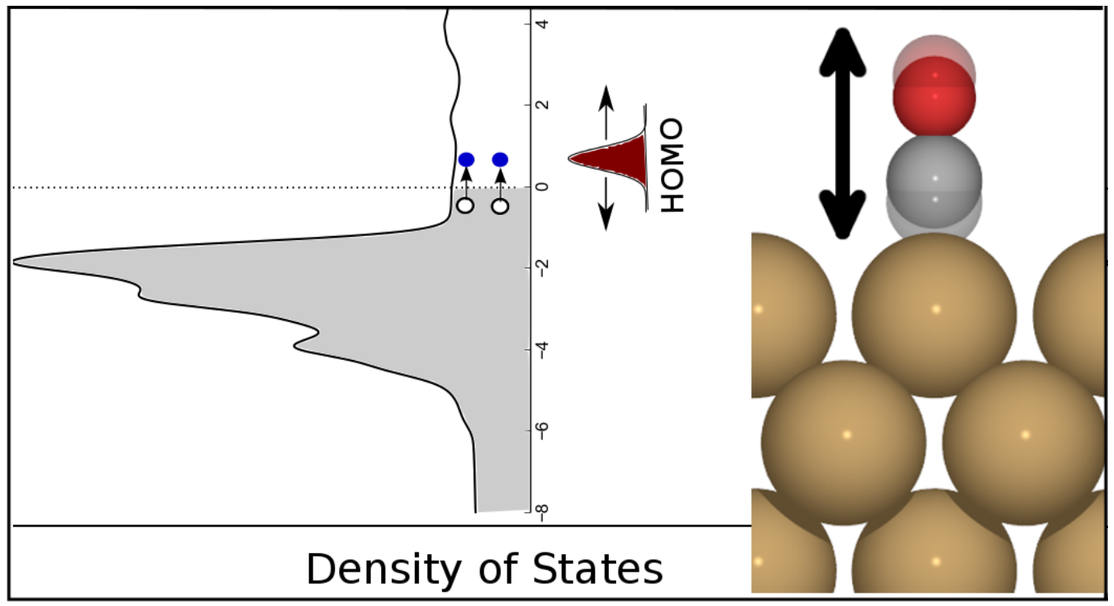
Configurational Complexity / Computational Scaling

- enable treatment of larger systems
- address high dimensional systems
- identify structures/pathways in reaction networks



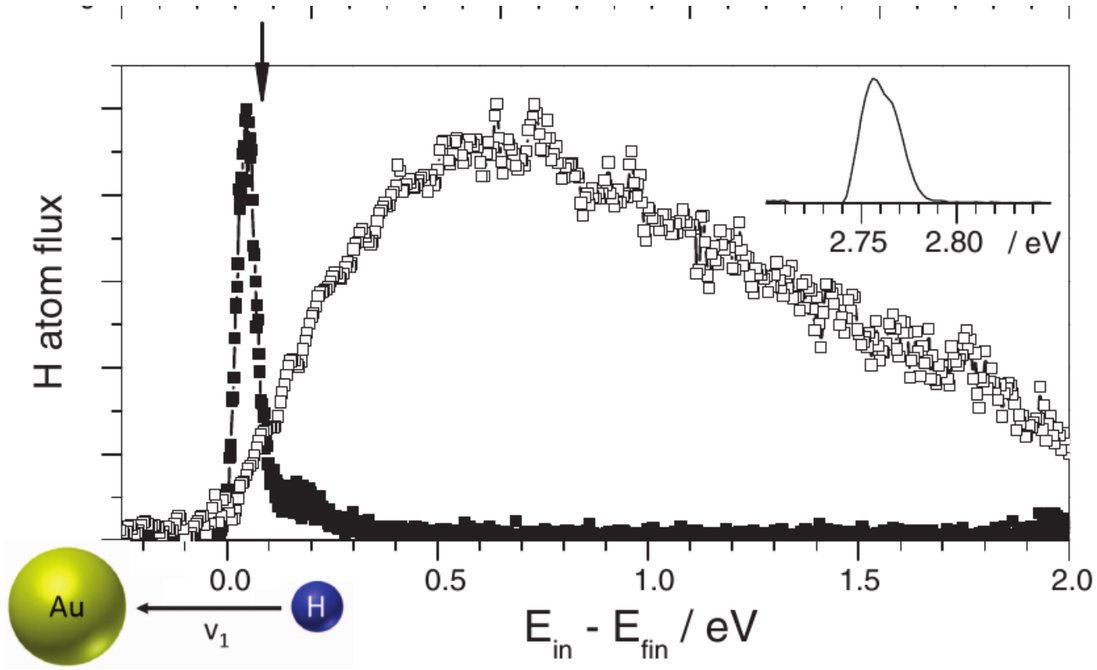
Examples of nonadiabaticity in metal surface chemistry

Vibrational energy dissipation



- Nonadiabatic vibrational energy loss at the picosecond level

Surface Scattering /Energy transfer

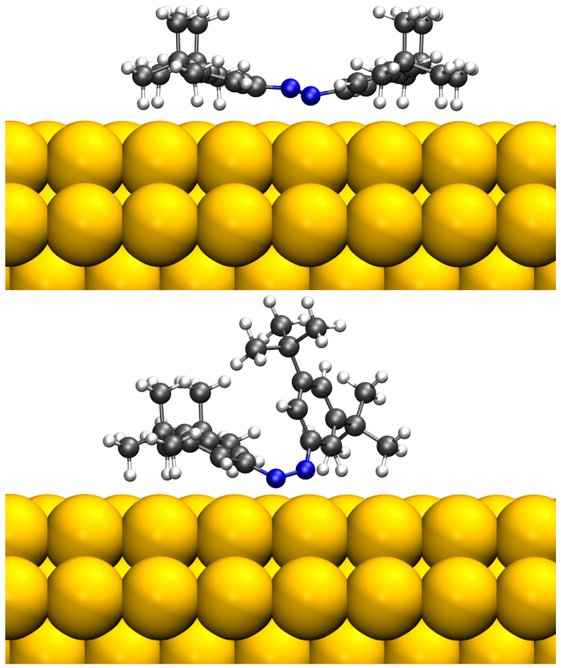


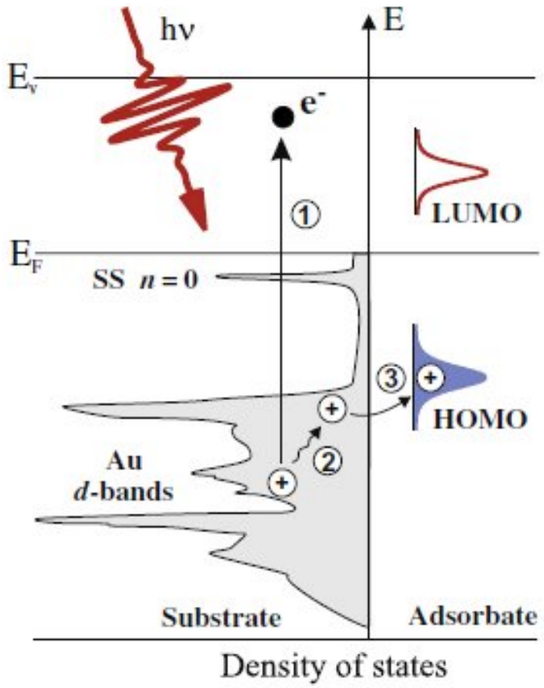
Science, 350, 1346-1349 (2015)

- Nonadiabatic inelasticity in atomic/molecular scattering

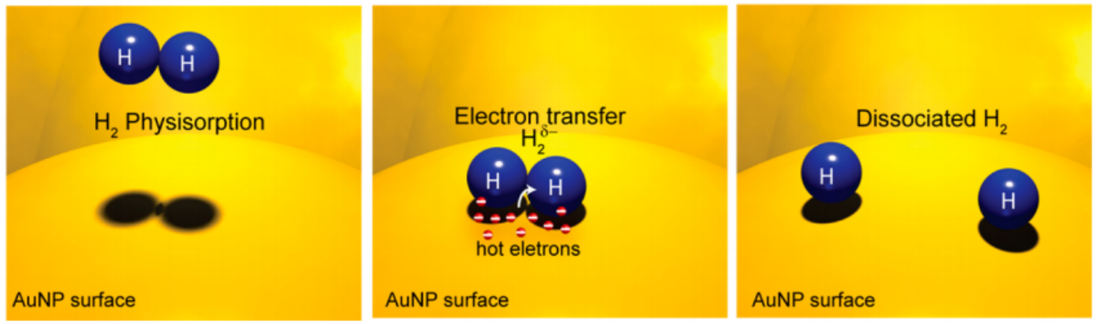
Examples of nonadiabaticity in metal surface chemistry

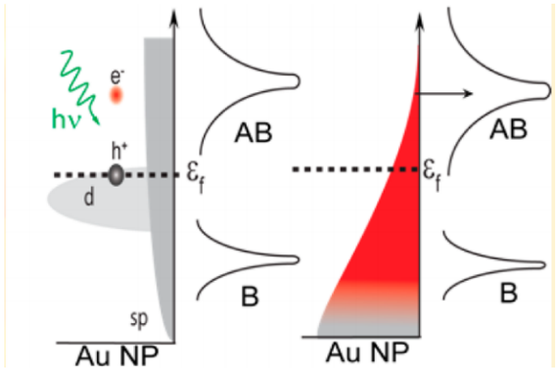
Photo-induced chemistry





Hot-electron chemistry

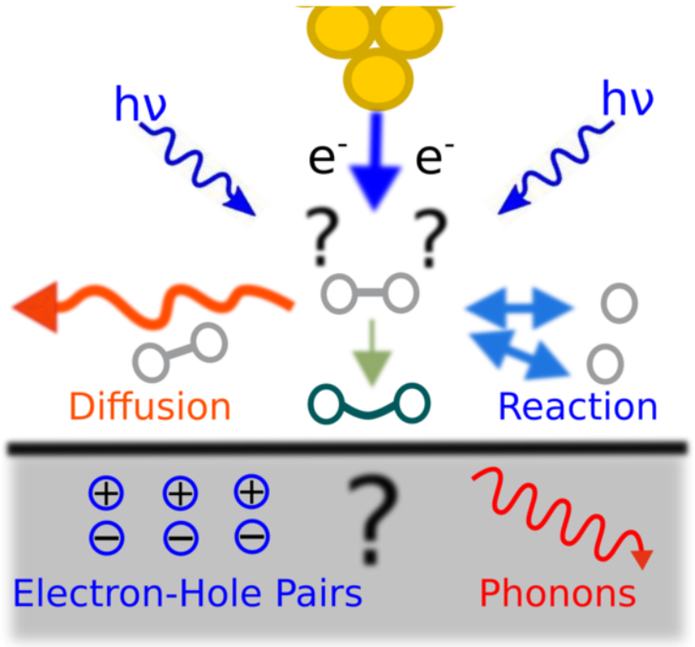


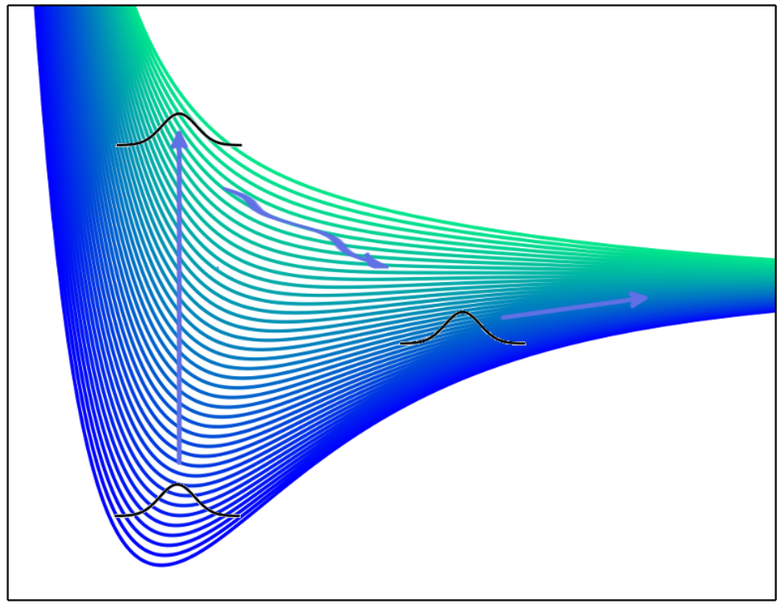


Nano Lett., 13, 240-247 (2013)

- Light- and electron-assisted surface chemistry
- Scanning Tunneling-induced chemical transformations

Nonadiabatic dynamics: beyond the Born-Oppenheimer approximation





'Friction Limit'

- electronic excitations: energy loss/gain channel
- they only slightly perturb ground state dynamics

'Surface-Hopping Limit'

- dynamics evolve on distinct electronic states
- molecule 'feels' different transient barriers

our developments

-ab-initio MD with DFT-based electronic friction

Phys. Rev. Lett. 116, 217601 (2016)

-e**ffi**cient electronic excited states

J. Chem. Phys. 139, 014708 (2013)

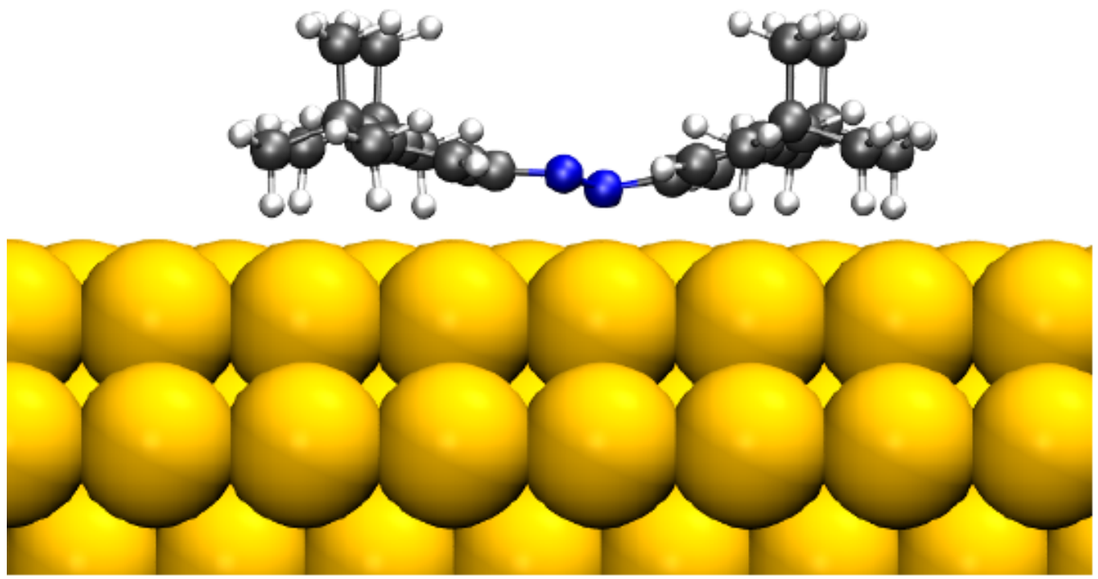
future work

-nonadiabatic dynamics beyond the friction limit

-excitonic/vibronic effects

-non-linear spectroscopic properties

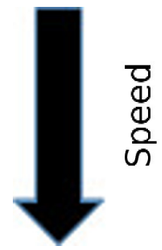
Excited States of Adsorbed Molecules



MBPT

TDDFT

ΔSCF DFT



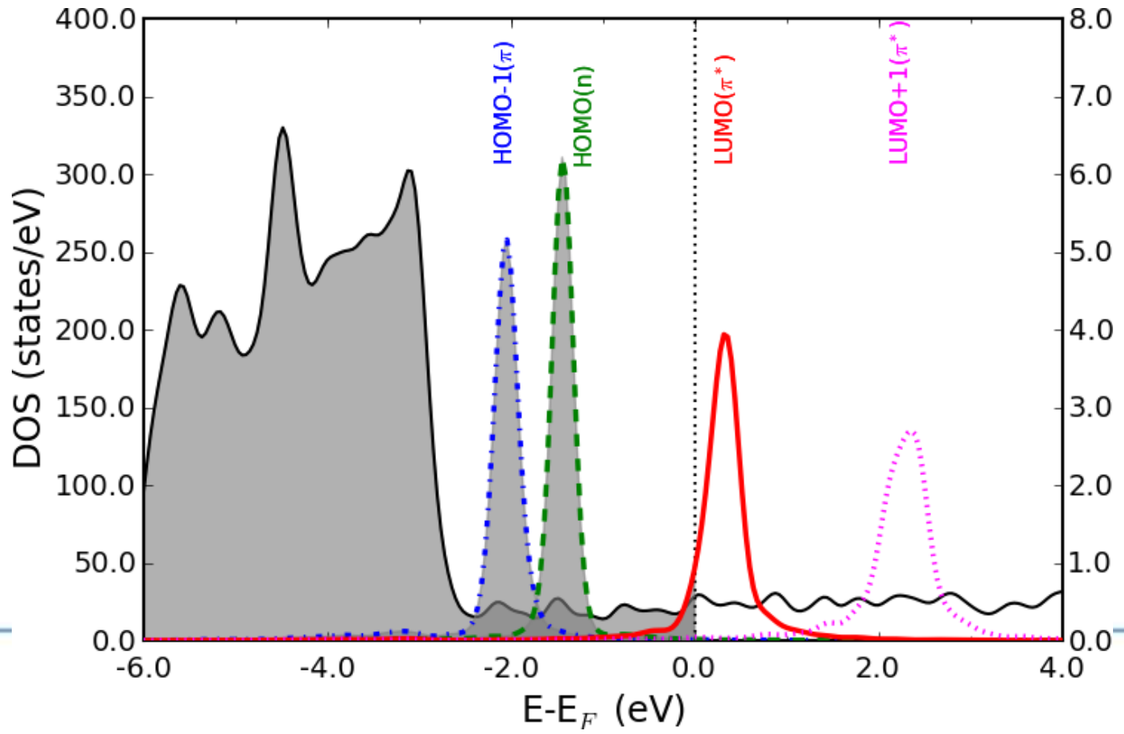
lin.exp. ΔSCF DFT

$$E_{\mathrm{ex}} = E(e^{-}\uparrow) - E(\mathrm{groundstate})$$

- speed of a DFT calculation
- can only handle single particle excitations
- Accuracy tested for isolated azobenzene

Maurer, Reuter, J. Chem. Phys. 135, 224303 (2011)

Constraining occupation of molecular states



$$|\psi_c\rangle = \sum_i |\psi_i\rangle\langle\psi_i|\phi_c\rangle$$

$$\rho_c = \sum_i f_i |\tilde{\psi}_i\rangle\langle\tilde{\psi}_i| + f_c |\tilde{\psi}_c\rangle\langle\tilde{\psi}_c|$$

ϕ_c . . . gasphase molecular reference orbital

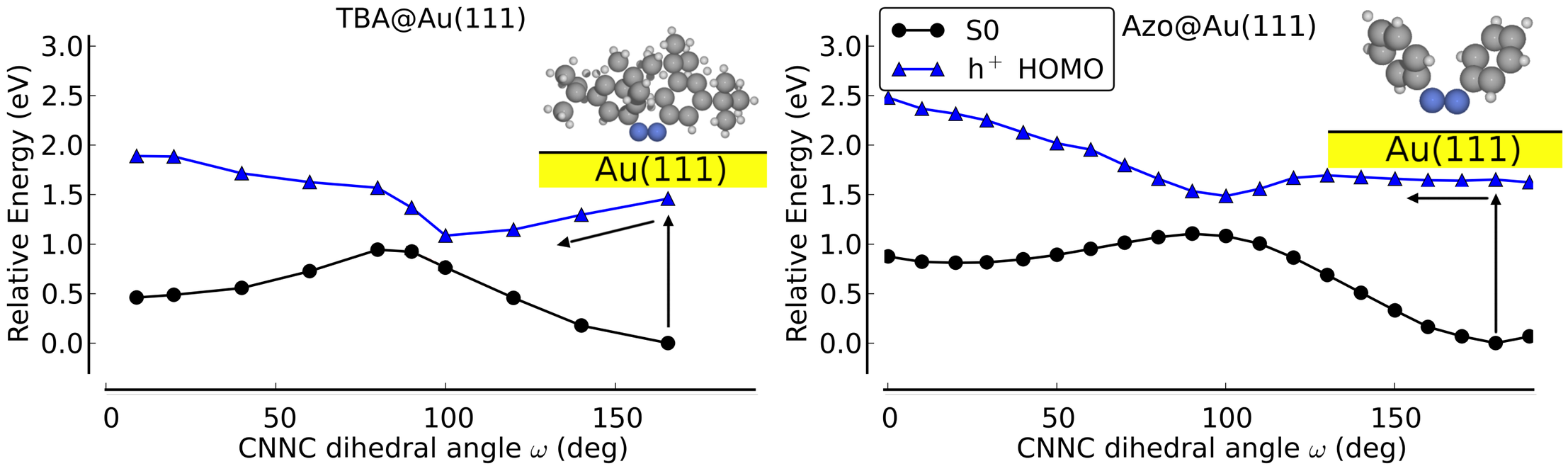
$$\sum_i f_i + \sum_c f_c = N_e$$

Gavnholt et al. , Phys. Rev. B 78, 075441 (2008)

Maurer, Reuter, J. Chem. Phys. 139, 014708 (2013)

CASTEP

Azo@Au(111) Isomerization: Excited States



cis trans cis trans

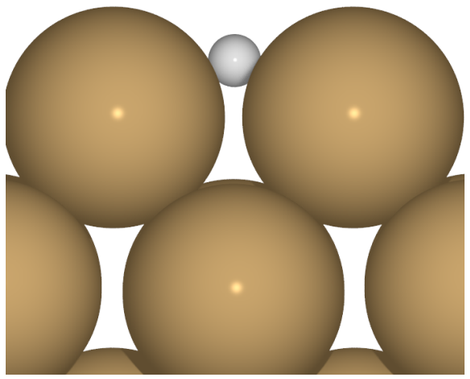
- TBA h+ state steeper at trans minimum: more vibronic coupling
- shorter path between minima for TBA
- Rationalization of photo-isomerization ability
- Feasible dynamics methods needed to study further details

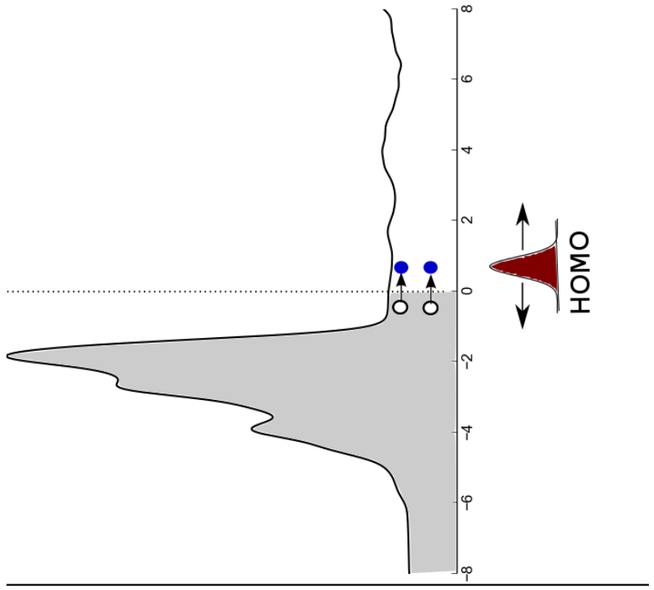
calculated using constrained excited state DFT(PBE)

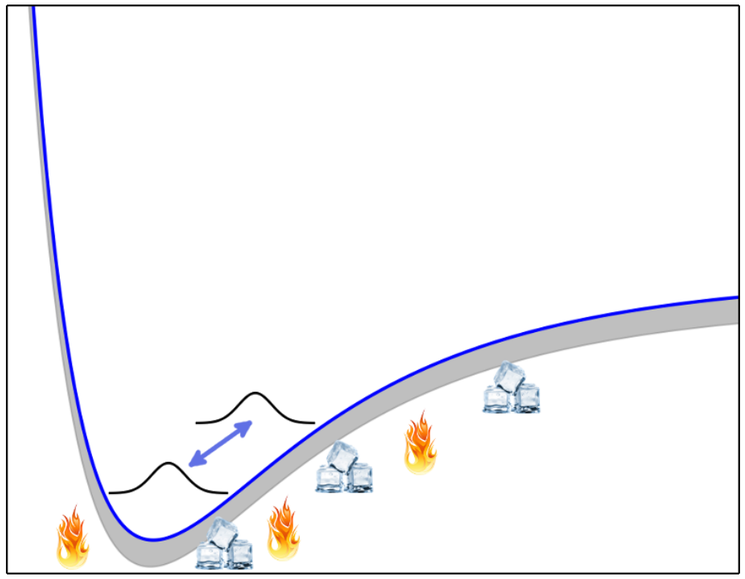
leΔSCF-DFT method: Maurer, Reuter, J. Chem. Phys. 139, 014708 (2013)

CASTEP

Ab-initio electronic friction for molecules on metals







PhD student:

Mikhail Askerka

$$\begin{pmatrix} \Lambda^{xx} & \Lambda^{xy} & \Lambda^{xz} \\ \Lambda^{yx} & \Lambda^{yy} & \Lambda^{yz} \\ \Lambda^{zx} & \Lambda^{zy} & \Lambda^{zz} \end{pmatrix}$$

Langevin Dynamics (MDEF) [1]

Idea: treat electrons as bath exerting fluctuation forces

$$M\ddot{R}_x = -\frac{\partial E_0}{\partial R} - \sum_y \Lambda_{xy}\dot{R}_y + \mathcal{R}_y(t)$$

Time Dependent Perturbation Theory

$$\mathbf{\Lambda}_{xy} = \pi\hbar^2 \sum_{\nu,\nu'} \langle\psi_\nu| \frac{\partial}{\partial_x \tilde{\mathbf{R}}} |\psi_{\nu'}\rangle \langle\psi_{\nu'}| \frac{\partial}{\partial_y \tilde{\mathbf{R}}} |\psi_\nu\rangle \Delta\epsilon \cdot \delta(\Delta\epsilon)$$

- full linear response up to 1st order PT
- accounts for molecular electronic structure

Implementation of tensorial MDEF [2]

- works in periodic and cluster mode
- directly implemented in FHI-aims
- coolvib supports FHI-aims and SIESTA input
- addresses 2 implementational issues

[1] J. Chem. Phys. 96, 3939 (1992)

[2] Phys. Rev. Lett. 116, 217601 (2016)

Electronic friction tensor from Fermi's Golden rule

$$\Lambda_{x,y}=\pi\hbar\sum_{\mathbf{k},\nu,\nu'>\nu}\langle\psi_{\mathbf{k}\nu}|\frac{\partial}{\partial R_x}|\psi_{\mathbf{k}\nu'}\rangle\langle\psi_{\mathbf{k}\nu'}|\frac{\partial}{\partial R_y}|\psi_{\mathbf{k}\nu}\rangle\cdot[f(\epsilon_{\mathbf{k}\nu})-f(\epsilon_{\mathbf{k}\nu'})]\cdot(\epsilon_{\mathbf{k}\nu'}-\epsilon_{\mathbf{k}\nu})\cdot\delta(\epsilon_{\mathbf{k}\nu'}-\epsilon_{\mathbf{k}\nu})$$

(1) how to evaluate [Math Processing Error] in local numerical orbital basis/FHI-aims?

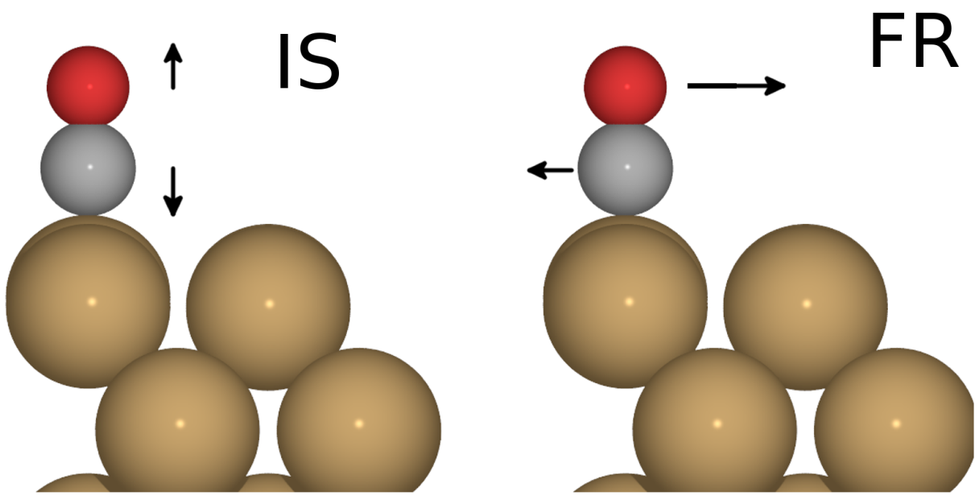
basis representation $|\psi_\nu\rangle=\sum_i c_\nu^i|\phi_i\rangle$ $\quad H_{ij}=\langle\phi_i|H|\phi_j\rangle$ $\quad S_{ij}=\langle\phi_i|\phi_j\rangle$

$$^{R}S_{i,j}^{na}=\langle\phi_i|\frac{\partial}{\partial R_{na}}\phi_j\rangle \quad ^{L}S_{i,j}^{na}=\langle\frac{\partial}{\partial R_{na}}\phi_i|\phi_j\rangle$$

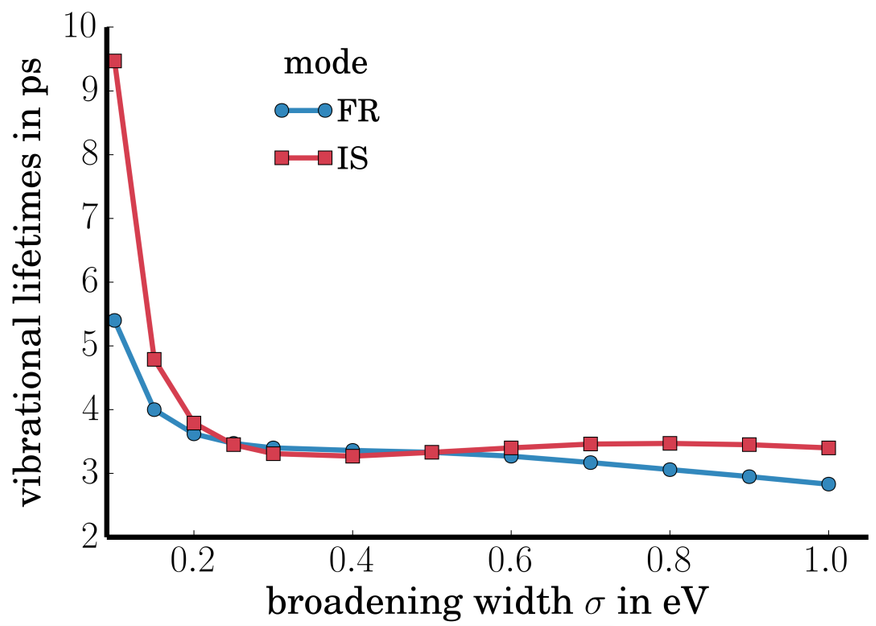
$$\langle\psi_\nu|\frac{\partial}{\partial R_{na}}|\psi_{\nu'}\rangle\approx\frac{1}{\epsilon_{\nu'}-\epsilon_\nu}\mathbf{c}_\nu^\dagger\cdot\underbrace{\left(\frac{\partial\mathbf{H}}{\partial R_{na}}-\epsilon_F\frac{\partial\mathbf{S}}{\partial R_{na}}\right)}_{\mathbf{G}^{\mathrm{HGT}}}\cdot\mathbf{c}_{\nu'}$$

(2) how to evaluate $\sum_{\mathbf{k},\nu,\nu'>\nu}\delta(\epsilon_{\mathbf{k}\nu'}-\epsilon_{\mathbf{k}\nu})$?

Simple Gaussian broadening: $\quad\delta(\epsilon_i-\epsilon_j)\approx\hat{\delta}(\epsilon_i-\epsilon_j)=\frac{1}{\sqrt{2\pi}\sigma}\exp\left\{\frac{-(\epsilon_i-\epsilon_j)^2}{2\sigma^2}\right\}$

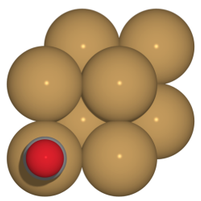
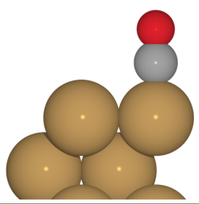
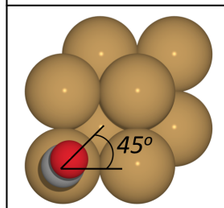
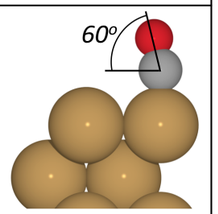


broadening dependence



Phys. Rev. B. 94, 15432 (2016)

CO on Cu(100): off-diagonal elements and mode coupling

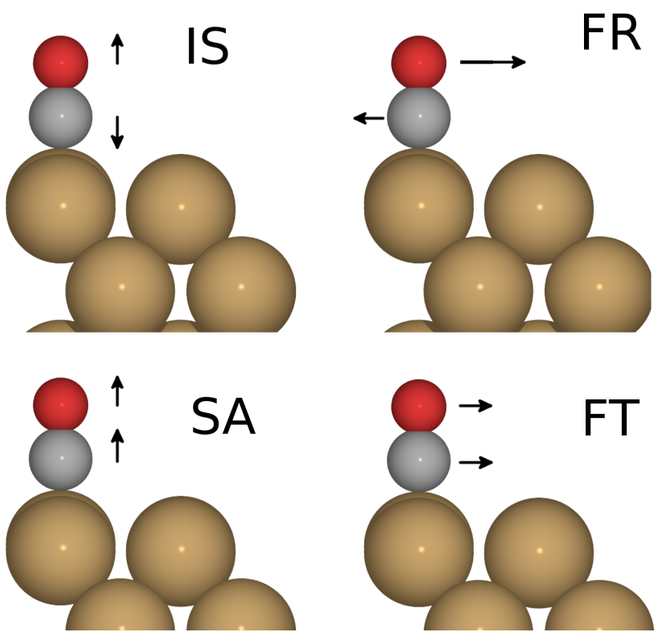
Top View	Side View	Mass-weighted Friction Tensor in ps^{-1}
Equilibrium Atop		
		C_x 0.248 0 0 −0.088 0 0 C_y 0.248 0 0 −0.088 0 C_z 0.245 0 0 −0.077 O_x 0.032 0 0 O_y 0.032 0 O_z 0.034
Non-equilibrium Tilted		
		C_x 0.248 0 0 −0.085 0 −0.011 C_y 0.248 0 0 −0.085 −0.011 C_z 0.245 0.021 0.021 −0.075 O_x 0.040 0 0 O_y 0.040 0 O_z 0.034

Langevin Dynamics

[Math Processing Error]

- off-diagonals of equal size as diagonals
- in general: tensor is non-diagonal

  in both cartesian and normal mode space



normal mode lifetime in ps	IS	SA	FT	FR
CO on Cu(100)	4.07 (2±1)*	17.0	70.5	3.61

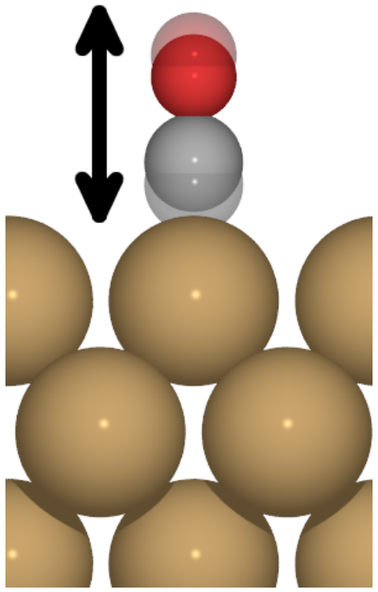
strong directional dependence of energy loss

Askerka, Maurer, Batista, Tully, Phys. Rev. Lett. 116, 217601 (2016)

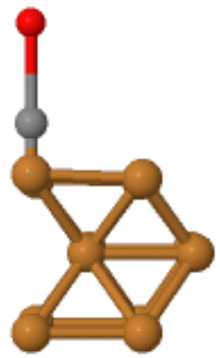
Maurer, Askerka, Batista, Tully, Phys. Rev. B 94, 115432 (2016)

* pump-probe experiments by Morin, Levinos, Harris, JCP 96, 3950 (1992);

vibrational modes vs. friction modes

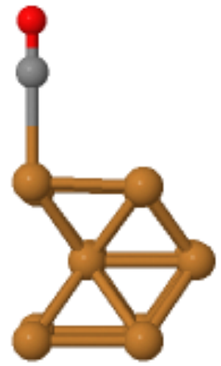


Vibrational normal modes



JSmol

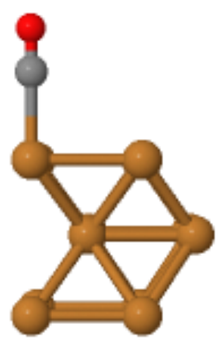
τ = 4.1 ps



JSmol

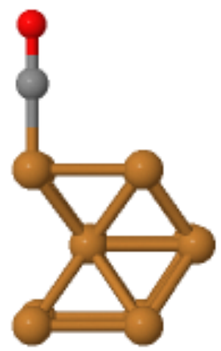
τ = 17.0 ps

Friction eigenvectors - Principal components of Λ



JSmol

τ = 3.7 ps



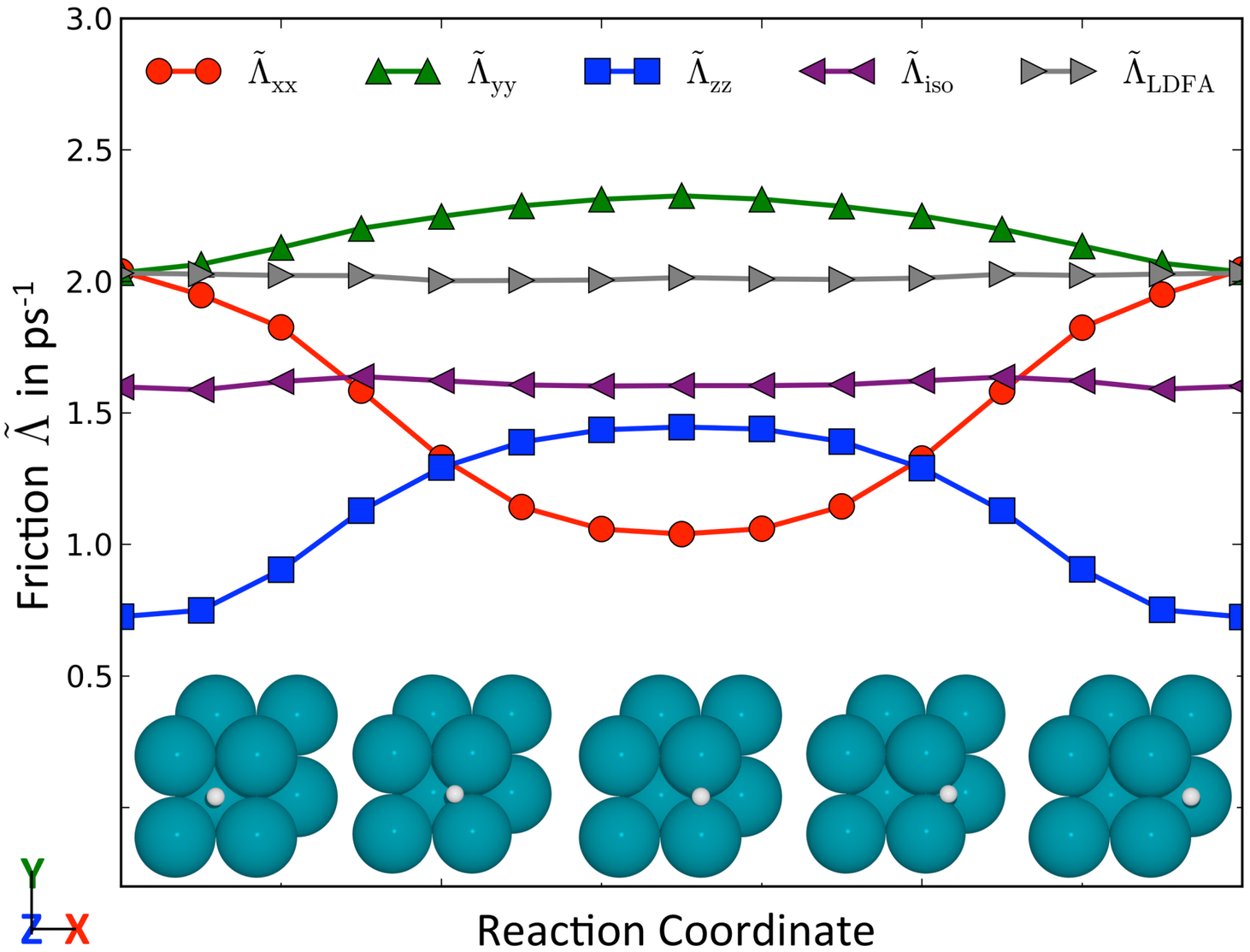
JSmol

τ = 108 ps

Electronic friction induces mode coupling! $\tau_{\mathrm{exp}} < \tau_{\mathrm{normal\ mode}}$

H on metals: the role of tensorial friction

H/Pd(100) diffusion: coordinate dependence



The current state-of-the-art: Local Density Friction Approximation [1]

$$\Lambda^{\mathrm{LDFA}} = \frac{4\pi\rho}{k_F}\sum_{l=0}^{\infty}(l+1)\sin^2[\delta_l^F - \delta_{l+1}^F]$$

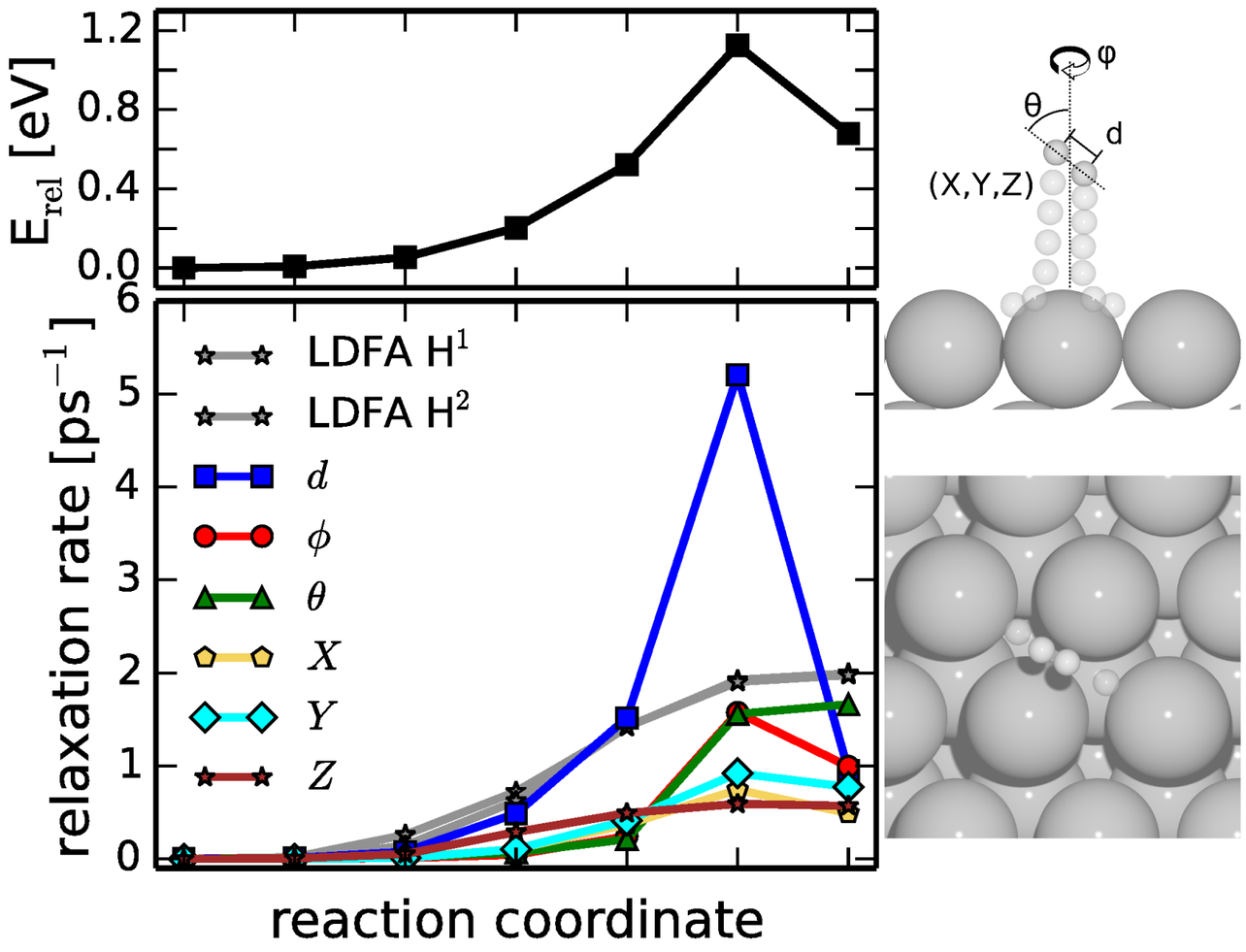
- atom in homogeneous electron gas
- 'Single scatterer model' - cartesian diagonal friction
- no directionality - isotropic friction in all directions
- LDFA: $\Gamma = f(\rho)$, isotropic friction
- LDFA does not capture directionality
- strong coordinate dependence

Askerka, Maurer, Batista, Tully, Phys. Rev. Lett. 116, 217601 (2016)

[1] Juaristi et al., Phys. Rev. Lett. 100, 116102 (2008)

H_2 dissociation on Ag(111): dynamical steering and energy loss

Minimum Energy Path

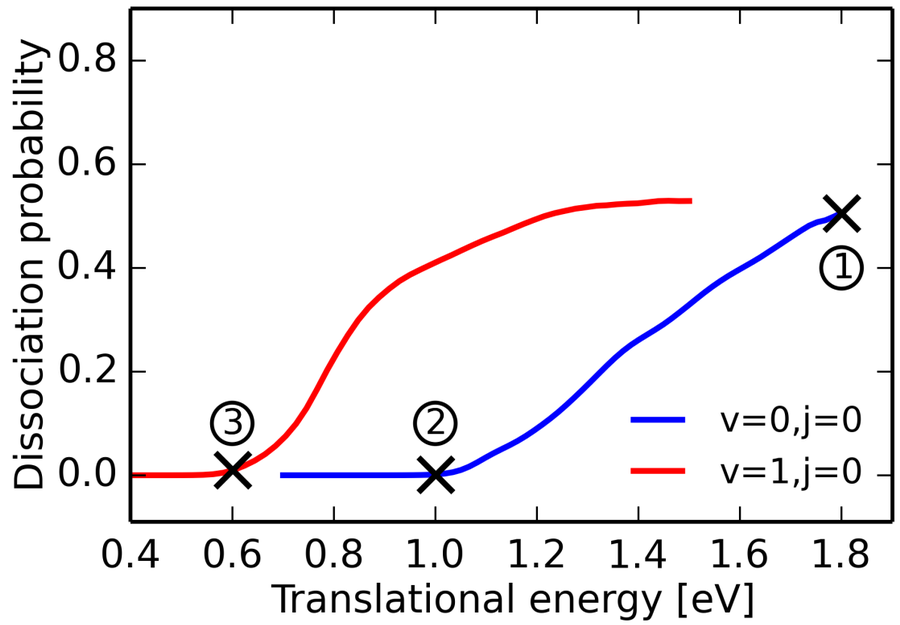


- strong frictional force along bond stretch d
- nonadiabatic energy transfer strongest at transition state
- coupling between these degrees of freedoms

Collaboration with Prof. Hua Guo, U New Mexico

Maurer et al., Phys. Rev. Lett. 118, 256001 (2017)

Molecular dynamics of dissociation



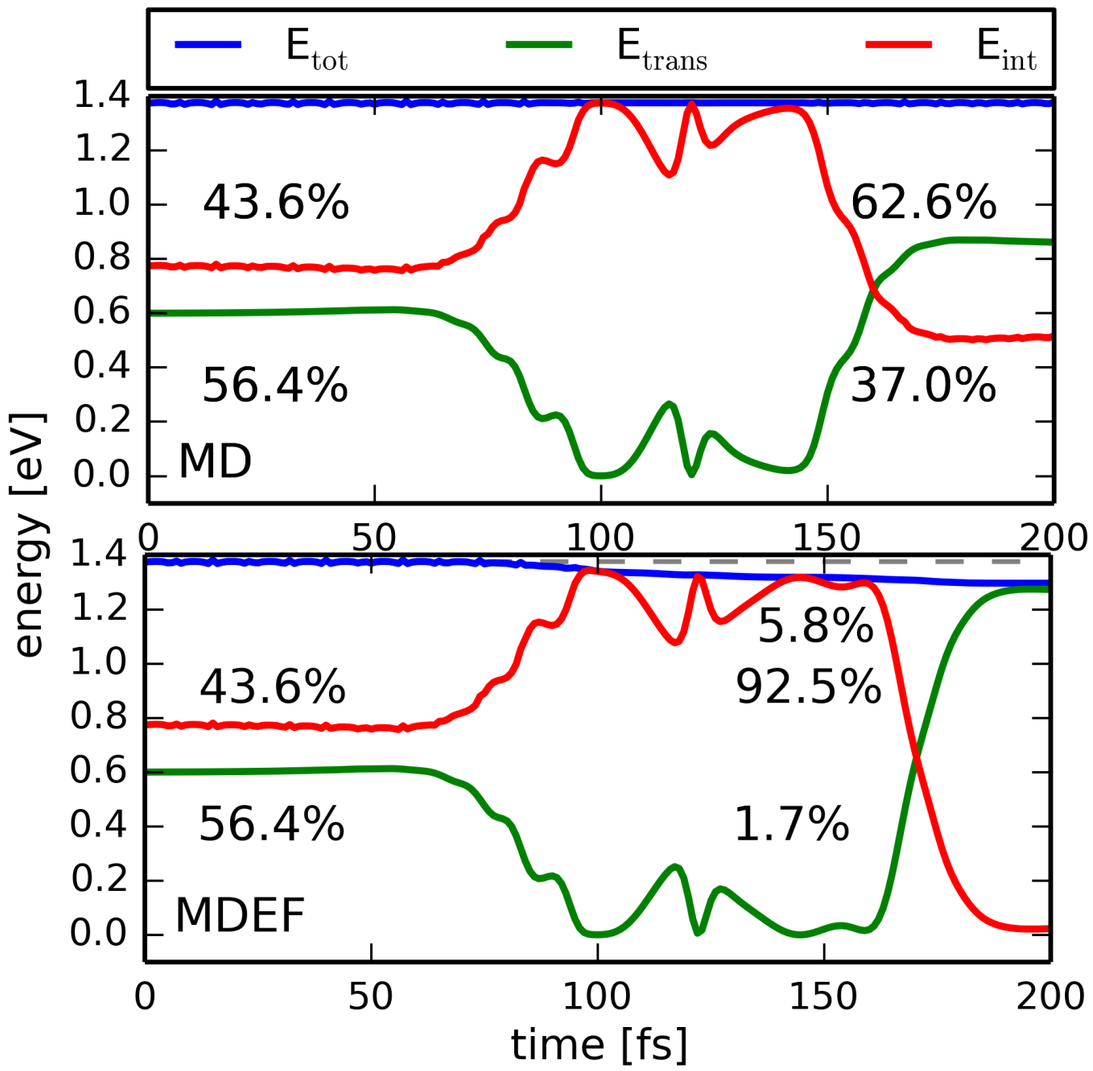
→ ab-initio molecular dynamics with electronic friction (MDEF)

- effects on reaction outcomes?
- effects on E_{vib},E_{trans} distribution?

Jiang, Guo, Phys. Chem. Chem. Phys. 16, 24704 (2014)

time step: 0.25~fs, friction tensor on-the-fly,
energies and forces based on interpolated PES

Energy distributions



- little nonadiabatic energy loss (ca. 5%)
- no significant effects for trajectories at E=1.8eV
- reaction outcomes affected at $E \approx E_{\mathrm{act}}$
- TDPT: hot electrons more effectively couple to rovibrational DoFs than translations

TABLE II. Initial (t=0) and final internal and translational energy contributions and EHP-induced energy loss for scattered trajectories in %. Columns without results correspond to DC events.

#	t=0		MD		MDEF(LDFA)			MDEF(TDPT)		
	E_{trans}	E_{int}	E_{trans}	E_{int}	E_{loss}	E_{trans}	E_{int}	E_{loss}	E_{trans}	E_{int}
1	87	13	69	31	7	64	30	3	67	30
2	87	13	48	52	5	48	47	3	49	48
4	87	13	76	24	7	71	22	3	75	22
5	87	13	29	71	4	28	68	3	29	68
10	79	21	-	-	5	62	32	4	72	24
11	44	56	63	37	-	-	-	6	92	2
14	44	56	-	-	5	66	29	4	73	23

Summary

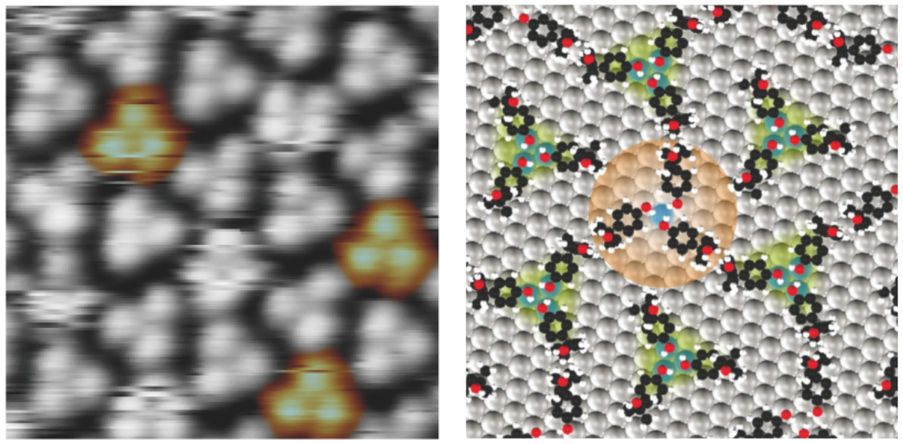
- effects on reaction outcomes? YES!
- effects on $E_{\mathrm{vib}}, E_{\mathrm{trans}}$ distribution? YES!
- hot-electrons selectively couple to rovibrations

Future projects in Warwick

Ab-initio surface nanochemistry at large length/time scales

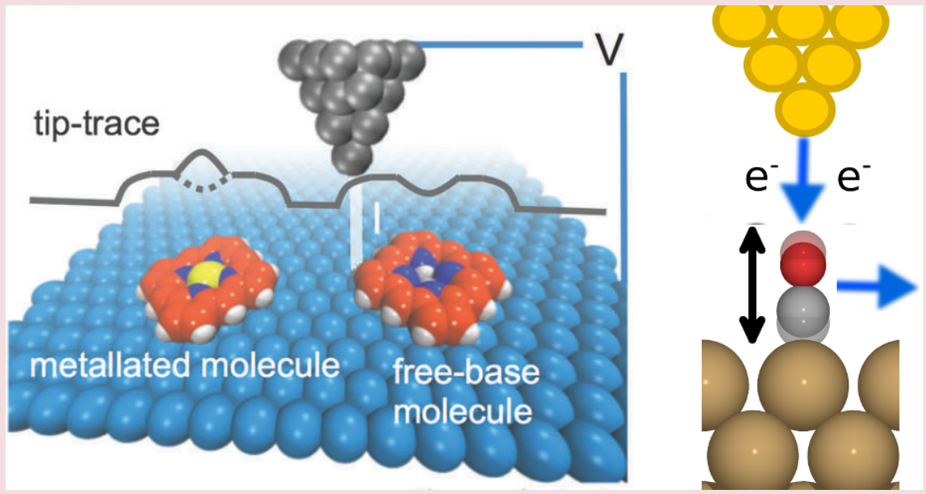
More e**ffi**cient methods to study

Surface Self Assembly/functional interfaces



molecular networks and phase transitions

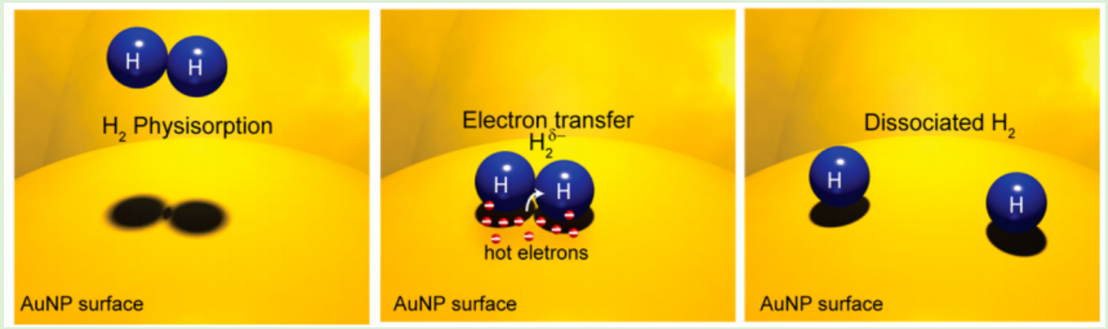
Molecular devices/Single-molecule control



Nano Lett. 16, 1884 (2016)

Photon/Electron-stimulated bond formation/breaking in catalysis

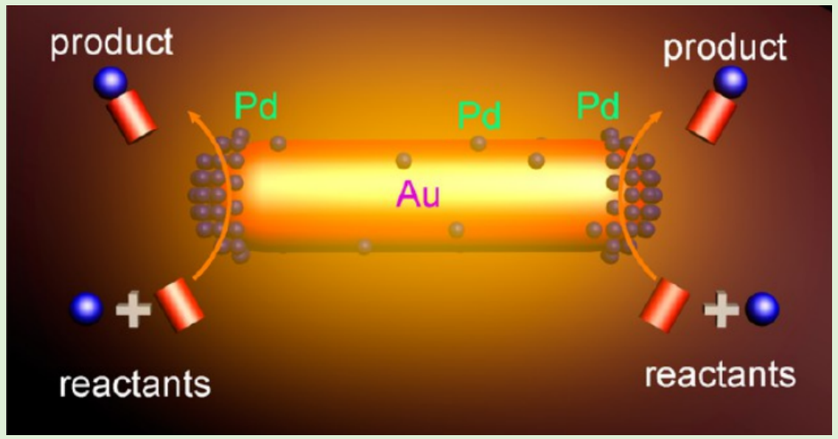
Hot-electron/plasmon surface chemistry



e.g. stimulated H-H dissociation

hot electrons in gas-surface dynamics

Surface Photochemistry



photostimulated C-C bond formation

mode-selective chemical conversions

Nano Lett. 13 240-247 (2013), JACS 135, 5588 (2013)

Getting faster: Towards surface chemistry with Tight-Binding Models

efficient electronic structure using tight-binding (TB)

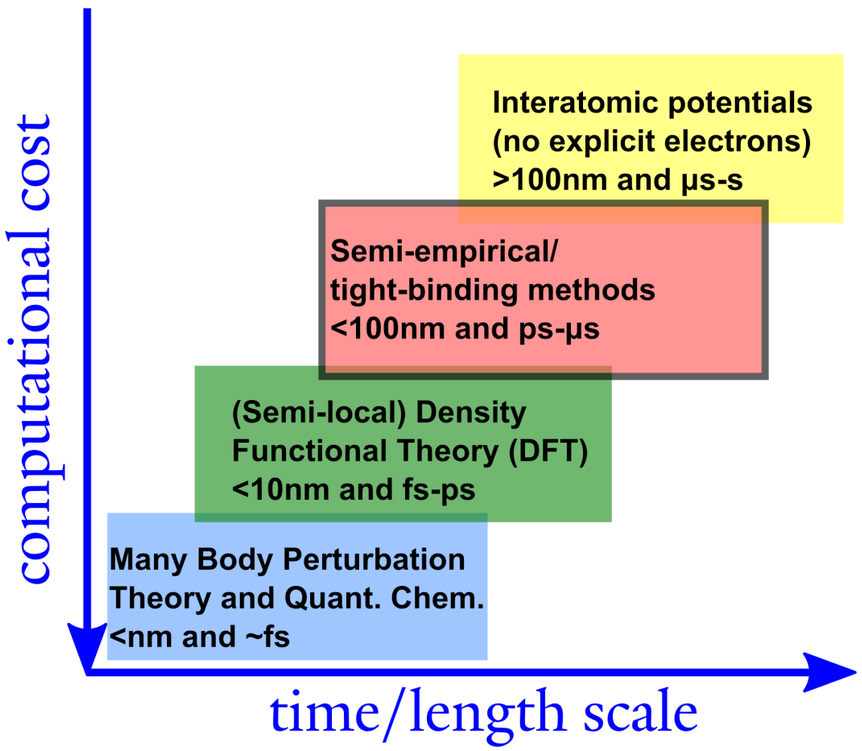
- 'tight-binding': precalculate integrals for speed-up
- modern TB approaches: DFTB[1] and FIREBALL[2]
- factor 100 increase in length/time scales
- DFT+vdW^{surf} [3] $\rightarrow$ DFTB+vdW^{surf} [4]

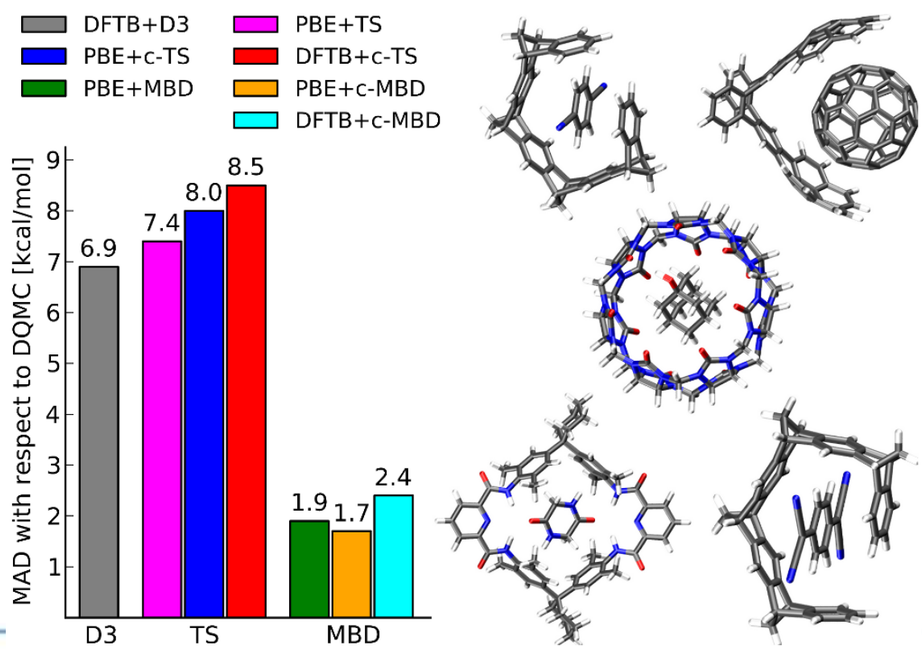
[1]: Elstner et al., Phys. Rev. B 58, 7260 (1998)

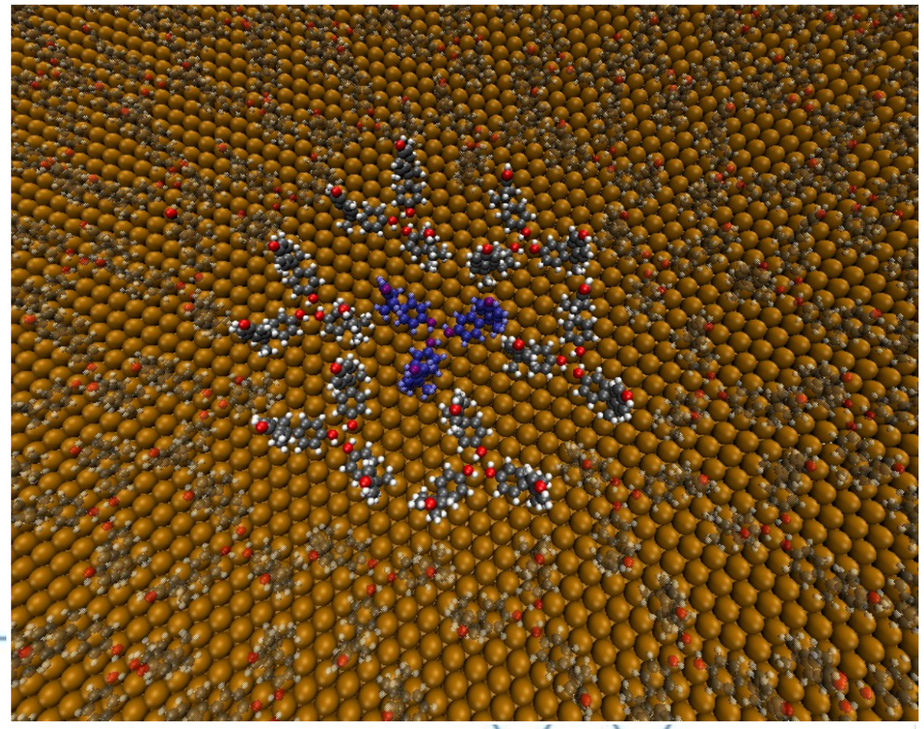
[2]: Lewis et al., Phys. Rev. B 64, 195103 (2001)

[3]: Tkatchenko, Scheffler, Phys. Rev. Lett. 102, 73005 (2009)

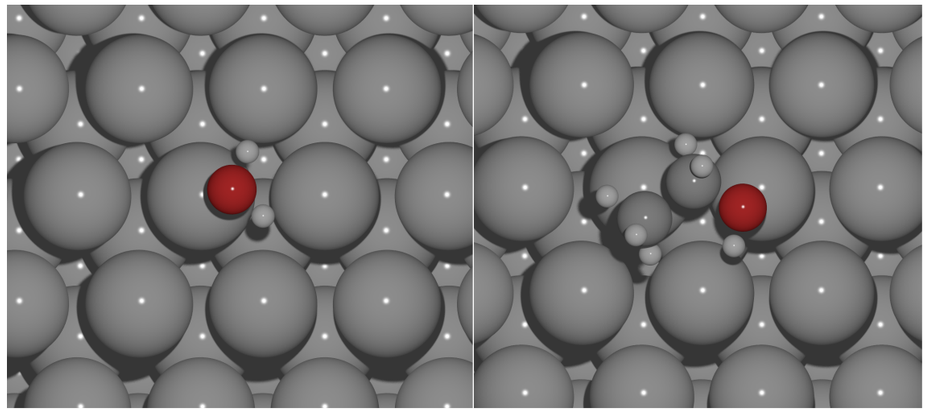
[4]: Stöhr, Michelitsch, Tully, Reuter, Maurer, J. Chem. Phys. 144, 151101 (2016)



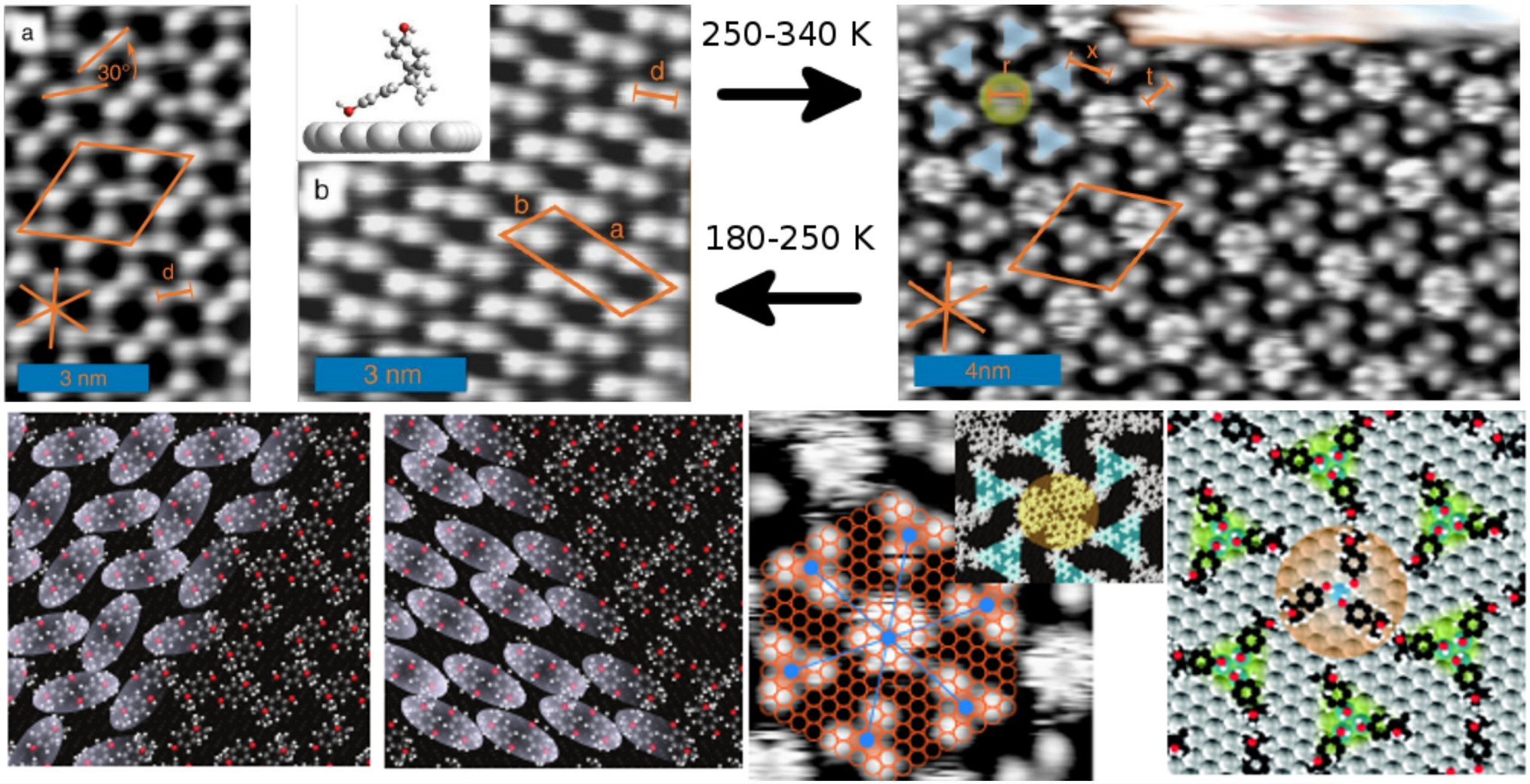




DFTB+vdW^{surf} Proof of Principle: Bisphenol A on Ag(111)



- using existing parameters for C,H,O and our own parameters for Ag
- parametrization on EtOH and H_2O on Ag(111)
- correct prediction of phase stability and entropic stabilization
- but better TB models are needed in the future

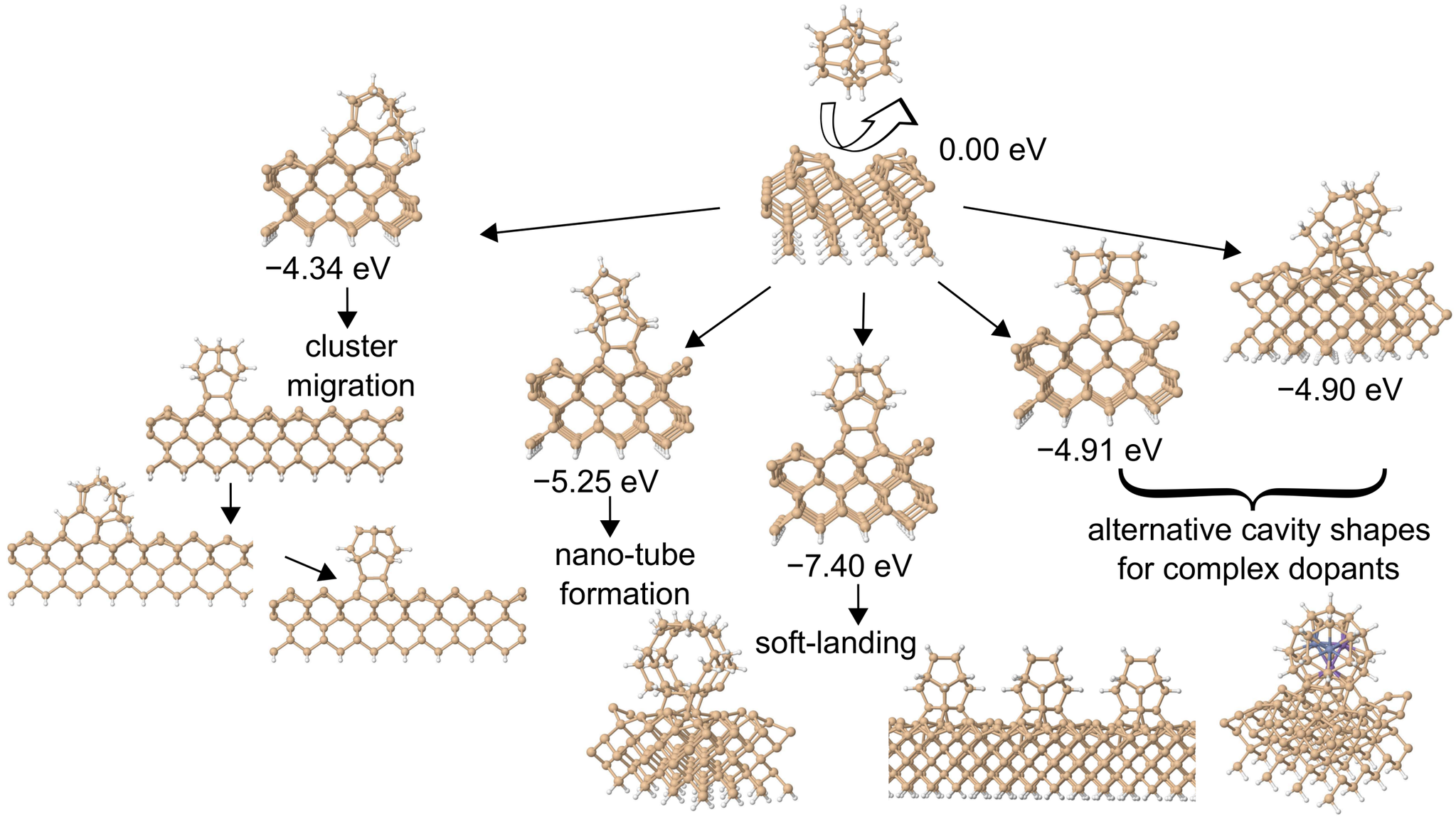


Lloyd et al., Nano Lett., 16, 1884-1889 (2016)

Getting smarter: Chemical reaction discovery and structure search

Example of soft-landing $Si_{16}H_{16}$ on a Si(001) surface

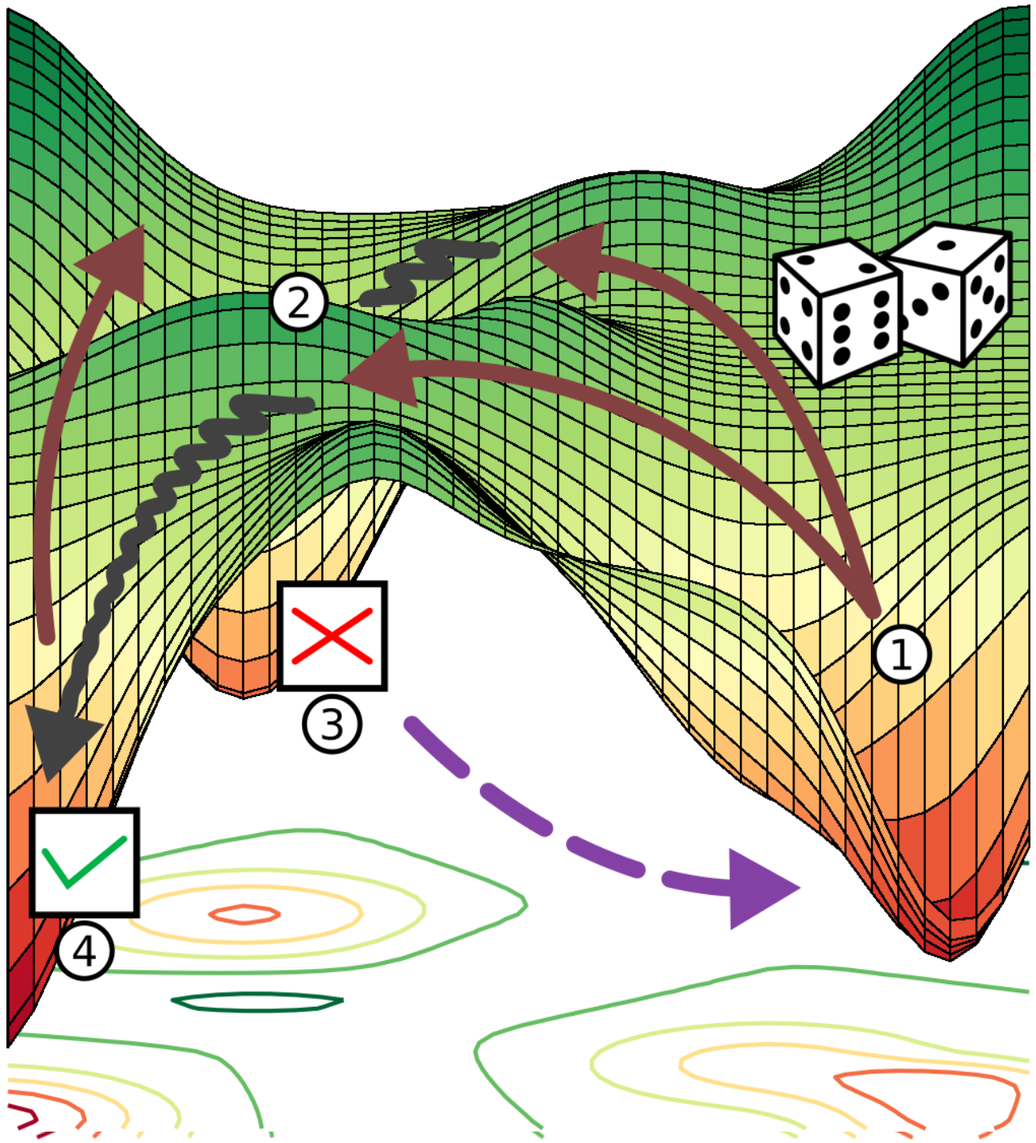
Materials structure search should identify all reaction avenues



Problem: Find all "chemically relevant" equilibrium structures and pathways

global optimization - unbiased structure search?

Finding local minima on high dimensional PES



Stochastic or heuristic sampling methods

Heuristic: genetic algorithms

Stochastic: basin hopping

Basin Hopping [1]

1. displace a geometry randomly by Δx
2. perform a local energy minimization: $\min\{E(\mathbf{X})\}$
3. calculate acceptance probability:

$$P(\Delta E_i) = \exp\left(-\frac{E_i - E_{\min}}{k_b T_{\text{eff}}}\right)$$

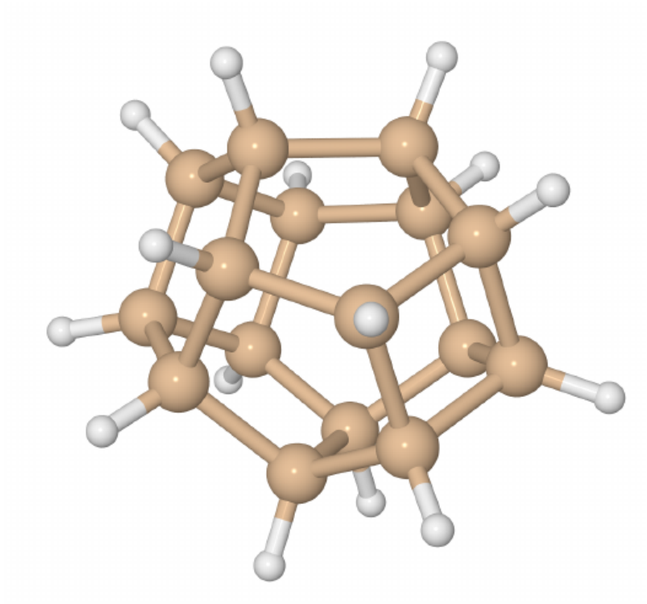
4. reject/accept new structure with probability P

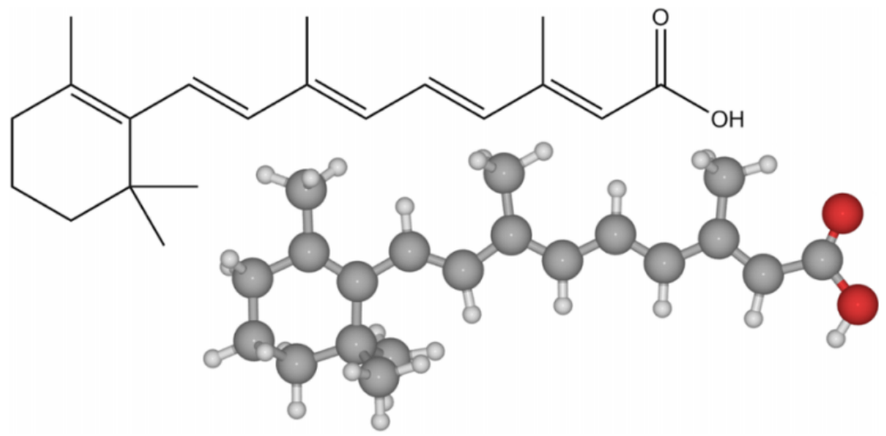
T_{eff} enables acceptance of higher energy structures

sequentially constructs a global map of "basins of attraction"

[1] Wales, Doye, J. Phys. Chem. A 75, 288-291 (1995)

global optimization of clusters and molecules





Optimization runs find less than 1%

intact stable geometries

99% of geometries are fragmented

0:00

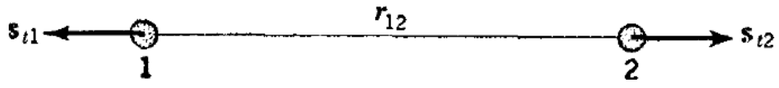
Question: Can we find an optimal choice of trial moves Δx?

global optimization of clusters and molecules

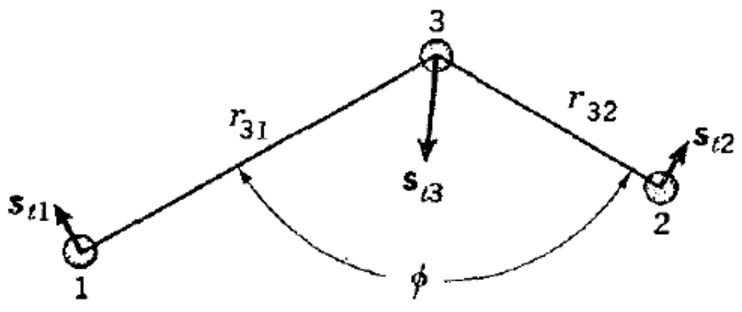
Wales, Miller, Walsh, Nature 394, 758-760 (1998)

What about simple internal coordinates?

bond stretch

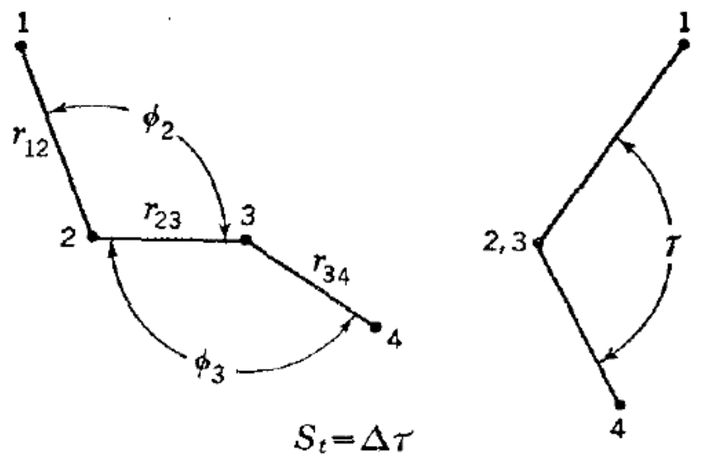


angle bend



$S_t = \Delta\phi$

dihedral torsion



$S_t = \Delta\tau$

coordinate	internal coordinates (IC) $\mathbf{q}$	$\mathbb{R}^3$ (CC) $\mathbf{x}$
bond	r_{12}	$\{\vec{s}_{t1}, \vec{s}_{t2}\}$
angle	ϕ_{123}	$\{\vec{s}_{t1}, \vec{s}_{t2}, \vec{s}_{t3}\}$
dihedral	τ_{1234}	$\{\vec{s}_{t1}, \vec{s}_{t2}, \vec{s}_{t3}, \vec{s}_{t4}\}$

Jacobi matrix: $B = \frac{dq}{dx}$ $\quad \Delta\mathbf{q} = \mathbf{B}\Delta\mathbf{x}$

- rotationally invariant, not permutationally invariant
- capture the local chemistry in covalent systems
- correspond to simple linear graphs with 2, 3, and 4 nodes

- z-matrix construction:
  non-unique, system- and geometry-specific
- redundant set of internal coordinates
- random mixing of ICs for Δx
  -> disconnected local changes

Wilson, Decius, Cross, Molecular Vibrations, Dover Books (2001)

Principal Component Analysis to the rescue!

Idea: Using these local graphs, we build a highly redundant coordinate set and performe a principal component analysis

$\mathbf{B}$ is $(M \times 3N)$ matrix

$M/3N \approx 2-40$

Singular Value Decomposition

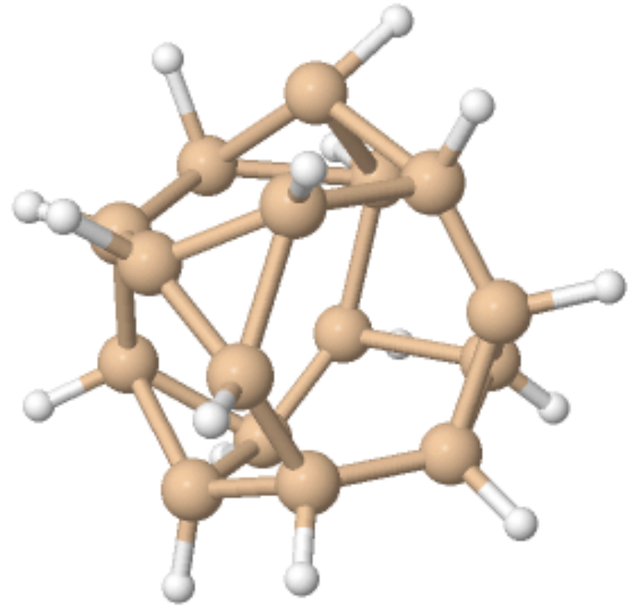
$$\mathbf{G} = \mathbf{B}^\dagger \mathbf{B} = \mathbf{U} \begin{bmatrix} \mathbf{\Lambda} & 0 \\ 0 & 0 \end{bmatrix} \mathbf{U}^\dagger$$

- $\mathbf{U}$ defines delocalized internal coordinate (DC) space
- subset of (3N-6) coordinates with singular value >0
- singular value spectrum reflects chemistry

$$\Delta\mathbf{d} = \mathbf{U}\Delta\mathbf{q} = \mathbf{U}\mathbf{B}\Delta\mathbf{x} = \mathbf{B}'\Delta\mathbf{x}$$

Pulay, Fogarasi, J. Chem. Phys. 96, 2856 (1992)

Baker, Kessi, Delley, J. Chem. Phys. 105, 192 (1996)



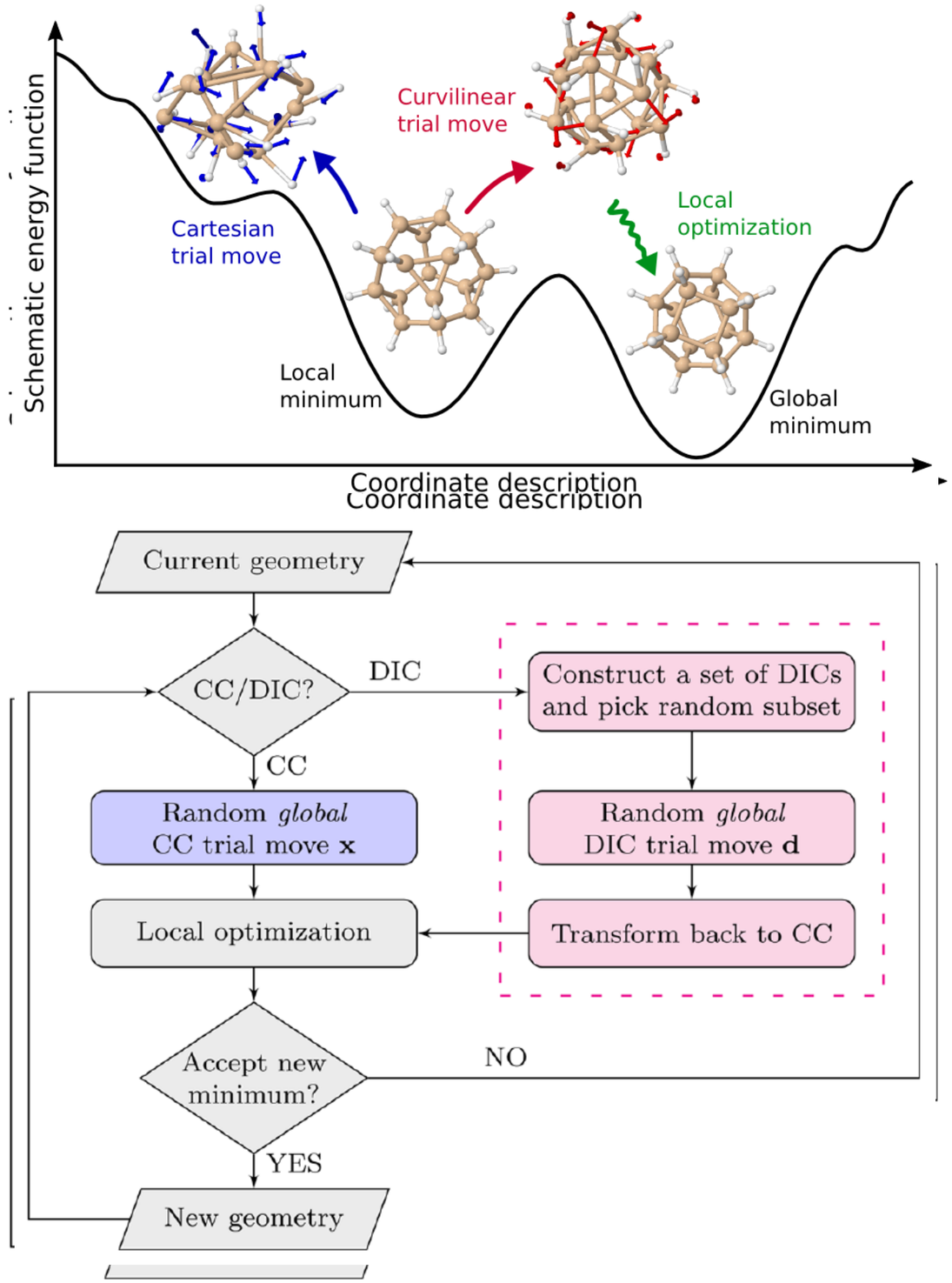
JSmol

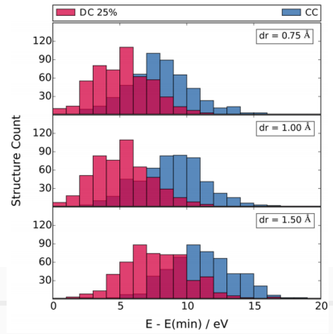
constructing displacement vectors in $\mathbb{R}^3$

$$\Delta\mathbf{x} = \mathbf{B}'^{-1}\Delta\mathbf{d}$$

generalized inverse: $\mathbf{B}'^{-1} = \mathbf{B}'^{T}\underbrace{(\mathbf{B}'\mathbf{B}'^{T})^{-1}}_{\mathbf{G}'^{-1}}$

Structure search with delocalized curvilinear coordinates





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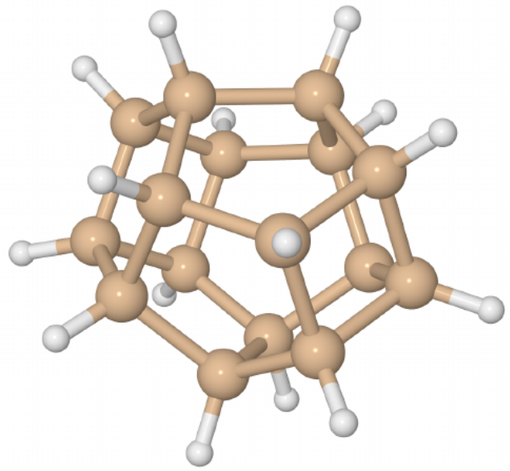
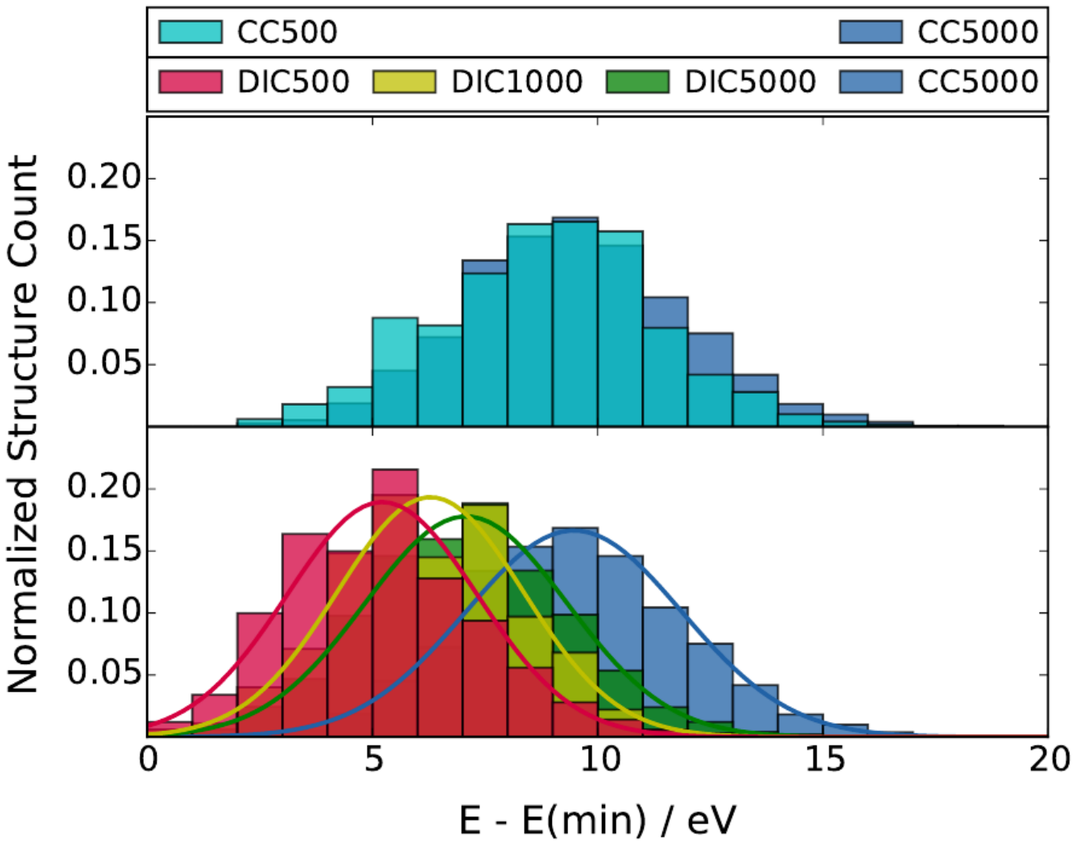


BSc/MSc thesis: Konstantin Krautgasser

Panosetti, Krautgasser, Palagin, Reuter, Maurer, Nano Lett. 15, 8044 (2015)

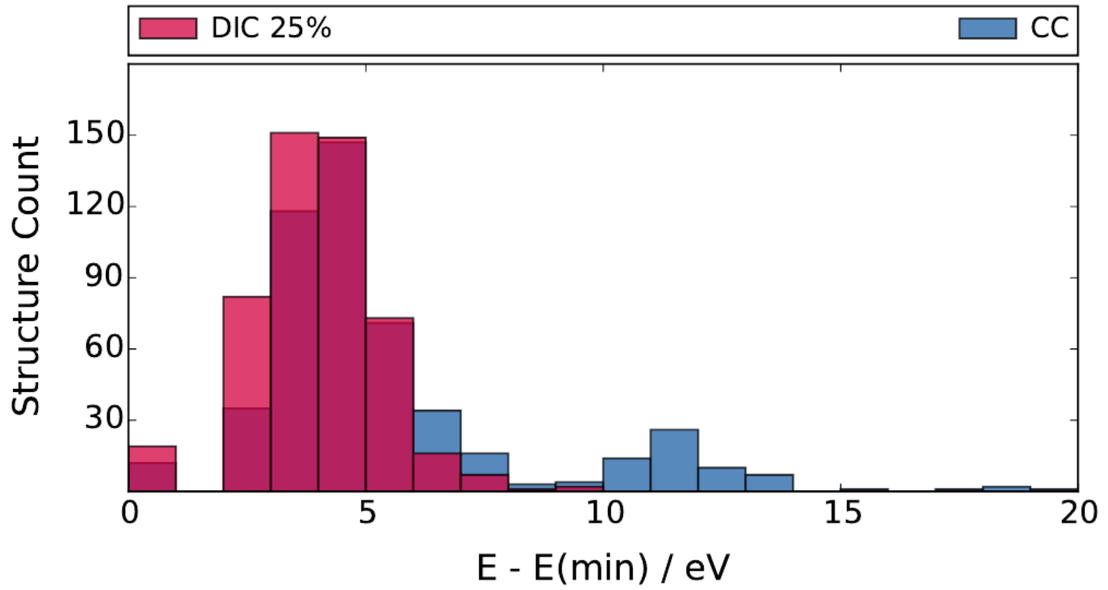
bias or constraint?

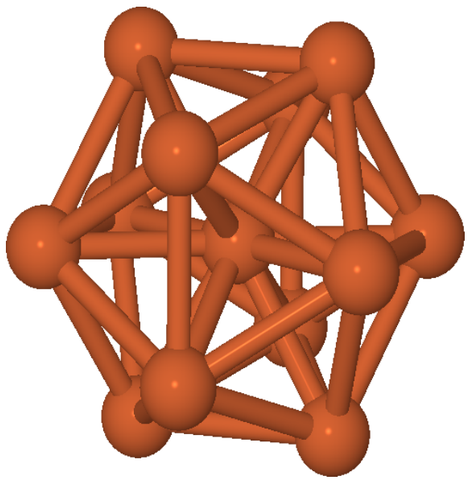
as $N_{\mathrm{step}} \rightarrow \infty$



- for large numbers of steps we retreive CC sampling
- DC trial moves do not constrain search
- they bias towards energetically lower lying structures

What about chemically isotropic systems?





Even without this bias, we are more e**ffi**cient

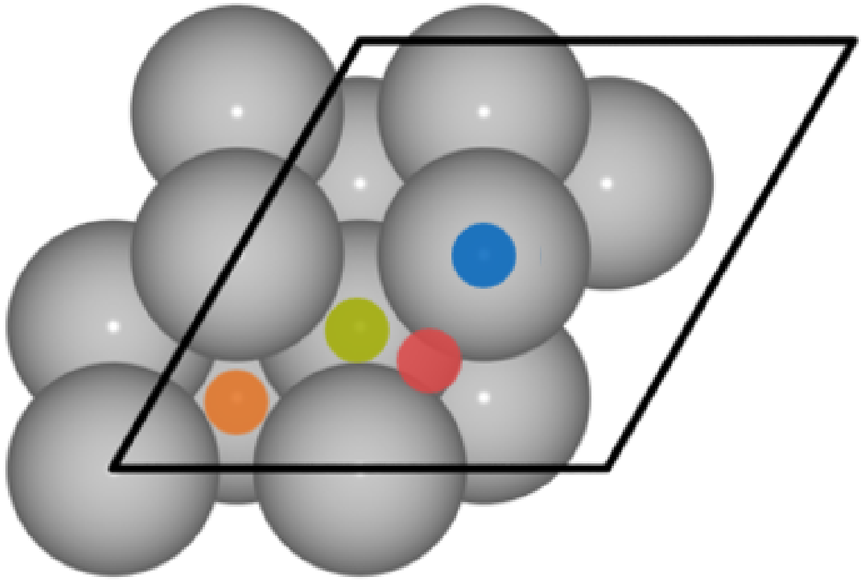
DC displaced structures are less strained

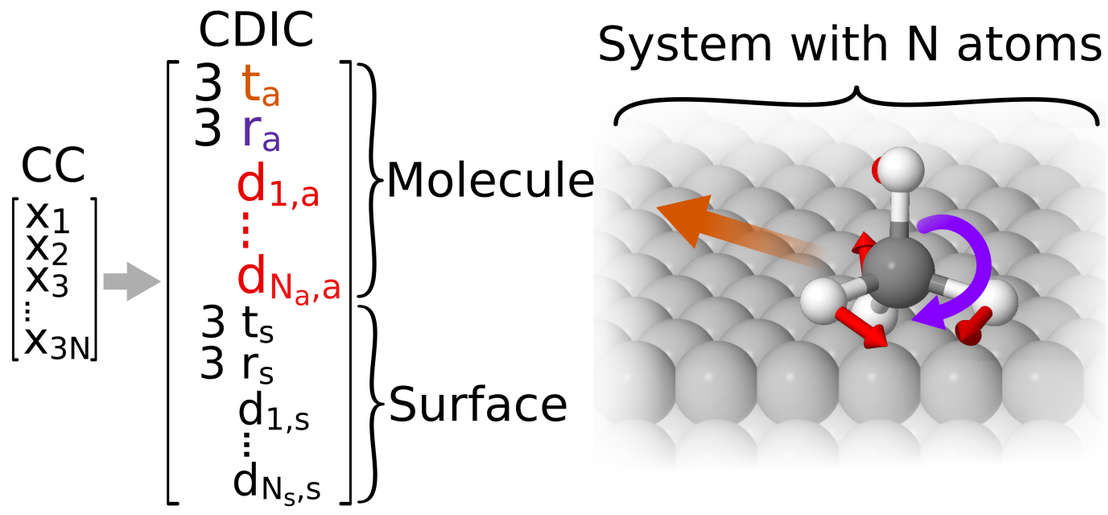
-> ~ -50% relaxation steps

molecules on surfaces: β-acid on Au(111)

CC dr=0.5	% of structures	25%cDC dr=1.5	% of structures
dissociations	93	dissociations	38
revisits	7	revisits	3
different site	0	different site	48
new structure	0	new structure	11

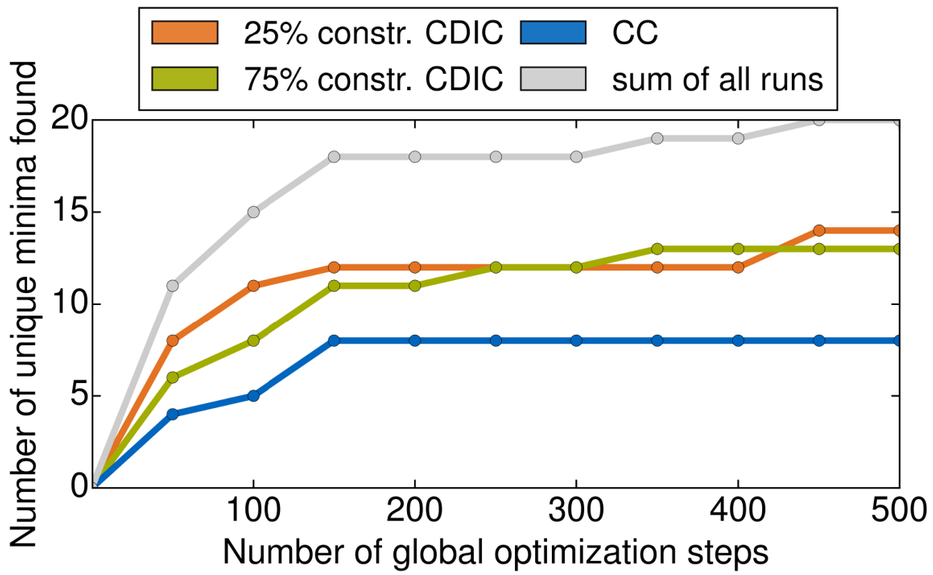
adding translations and rotations: CH_4/Ag(111) adsorption site sampling





surface-symmetry-adapted translations

quaternion description of rotation angles



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we sample the lateral PES more equally

we sample more unique minima

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U Heidelberg

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Konstantin Krautgasser, TUM

Georg Michelitsch, TUM

Moritz Müller, TUM

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Leibniz Supercomputing Center

Yale HPC

Thank you for your attention