

Water at α -Alumina Surfaces: Energetics, Dynamics and Kinetics

Disputation

Sophia Heiden



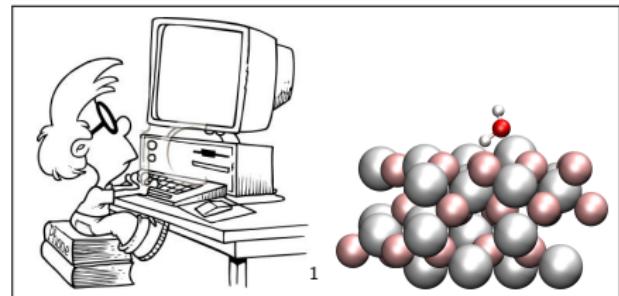
xy.0z.2019

Investigation of Water on α -Alumina Surfaces:

- **Motivation**
- $\text{H}_2\text{O}@\alpha\text{-Al}_2\text{O}_3(0001)$: Stability, Vibrational Frequencies, and Reactivity
- $\text{H}_2\text{O}@\alpha\text{-Al}_2\text{O}_3(0001)$: Molecular Beam Scattering with AIMD
- $\text{H}_2\text{O}@\alpha\text{-Al}_2\text{O}_3(11\bar{2}0)$: Stability, Reactivity, and Vibrational Frequencies
- **Summary and Outlook**

Motivation

- Surface science, catalysis
- Computer based modelling of processes

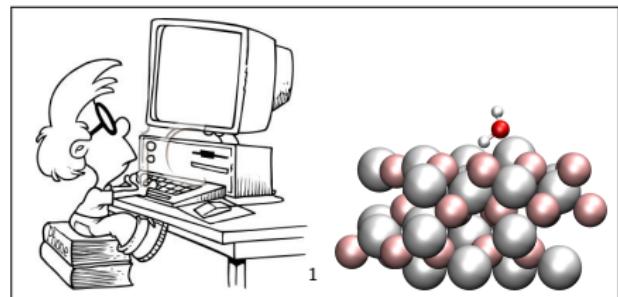


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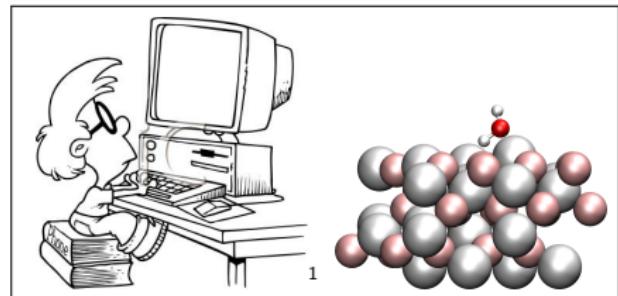
Applications of Al₂O₃

- Ruby laser
- Catalyst: Claus process
- Ceramic material
- Solid rocket exhaust, eject alumina particles



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Applications of Al₂O₃

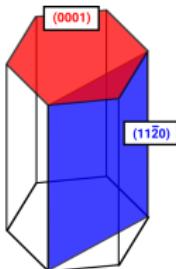
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→ Understanding processes on a microscopical scale!

¹ <https://mbtskoudsalg.com/images/scientist-clipart-nerd.jpg>, ² <https://external-preview.redd.it/raUdEwh8-J01prs80mqdLGG-sVTfg-80YXxwnfwVRtY.jpg?r=science&s=eabf5472b6d7a49b7a66ebfecade4f2b9d49dc2f>

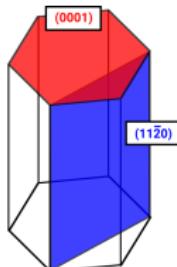
Properties of α -Al₂O₃



Schematic view of the (0001) and (11 $\bar{2}$ 0) surface cuts

- Hard
- Insulator
- Noncorrosive
- White solid, impurities can give color
- In UHV (0001) more stable than (11 $\bar{2}$ 0)

Properties of α -Al₂O₃

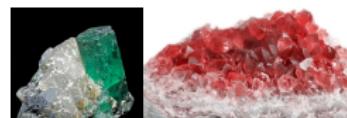


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Alumina crystal used in experimental setup (FHI Berlin)



Emerald (green, Cr/V); Ruby (red, Cr)

Methodology

- Electronic structure calculations (KS-DFT, HF, LMP2)

$$\left(-\frac{1}{2} \vec{\nabla}_1^2 + v_{ext}(\vec{r}_1) + v_H(\vec{r}_1) + v_{xc}(\vec{r}_1) \right) \psi_i^{KS}(\vec{r}_1) = \varepsilon_i^{KS} \psi_i^{KS}(\vec{r}_1)$$

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- Vibrational frequencies (harmonic approximation)

$$\mathbf{H} \vec{A}_i = \lambda_i \vec{A}_i; \quad \omega_i = \sqrt{\lambda_i}$$

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- *Ab-initio* molecular dynamics

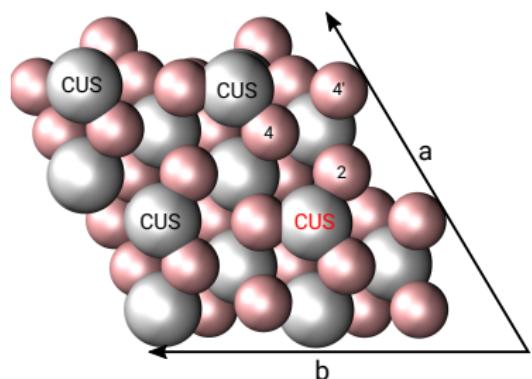
$$-\vec{\nabla}_A V(\{\vec{R}_i\}) = M_A \frac{d^2 \vec{R}_A(t)}{dt^2}$$

Methodology

- Periodic slab calculations
- Density functional theory
- GGA functional PBE with dispersion corrections in PW basis
- VASP program package
- PBE, B3LYP with dispersion corrections and LMP2, in AO basis
- CRYSTAL and CRYSCOR

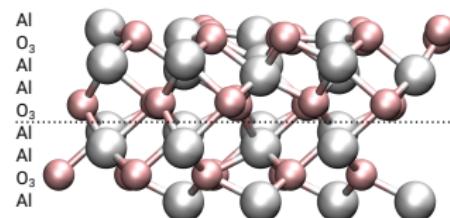


Model of the Al₂O₃(0001) Surface



Top view, Al gray, O pink.

Coordinatively Unsaturated Site



Side view, atomic layers sequence
Al-O₃-Al...

- UHV 0 K geometry optimized structure
- Al terminated surface cut
- 4 CUS Al atoms, 12 threefold coordinated O atoms
- (2 × 2) supercell

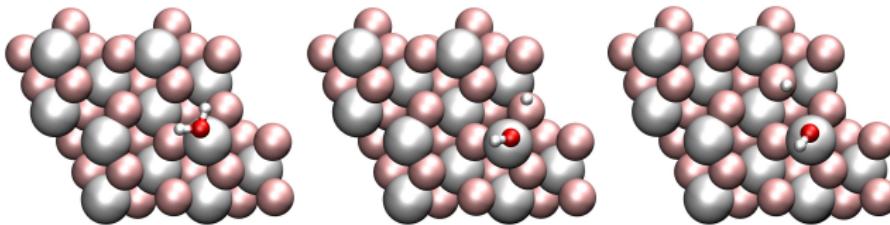
Adsorbed Species, Frequencies, and Reaction Path

- Adsorption Energies E_{ads} for most stable adsorbed species:

mol

1-2 diss

1-4 diss



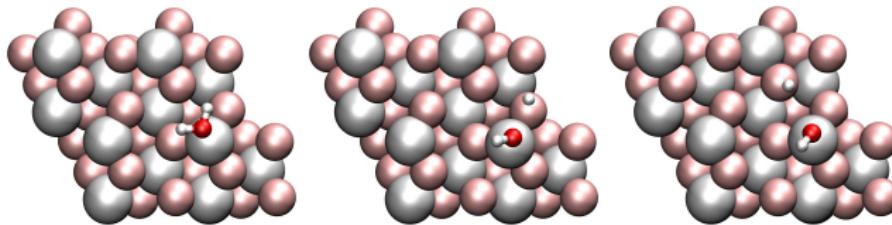
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- Vibrational frequencies for comparison with SFG spectroscopy

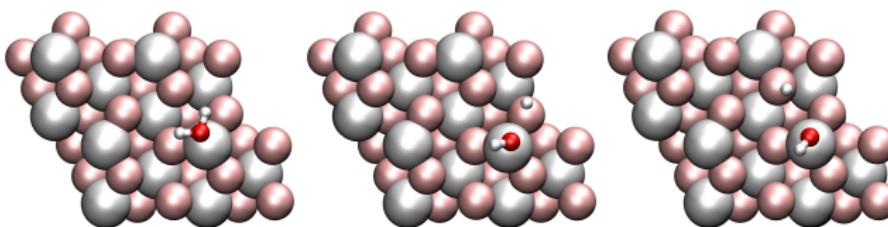
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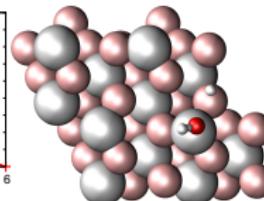
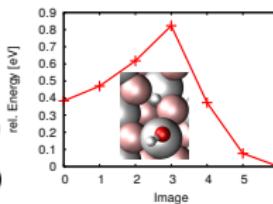
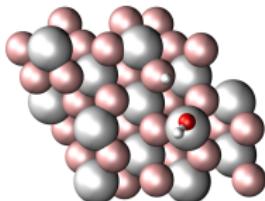
mol

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- Vibrational frequencies for comparison with SFG spectroscopy
- Diffusion reaction Df-H-4-2



1-4 to 1-2 hydrogen diffusion, NEB path with transition state

Adsorption Energies

Adsorption energies E_{ads} in eV of the molecular and two dissociated adsorption states of H₂O on the alumina(0001) surface, comparison of plane wave basis (PW) and atom orbital basis (AO).

$$E_{\text{ads}} = E_{\text{ads. species}} - (E_{\text{free water molecule}} + E_{\text{surface}})$$

basis	method	mol	1-2 diss	1-4 diss
PW	PW91	-1.25	-1.59	-1.25
	PW91+D2	-1.40	-1.81	-1.45
	PBE+D2	-1.31	-1.69	-1.21

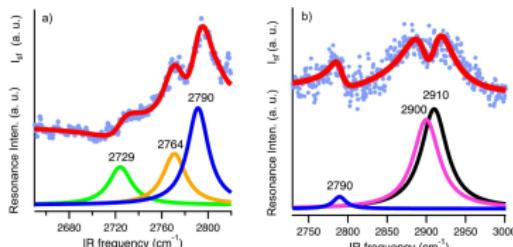
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AO	PBE+D3	-1.41	-1.68	-1.32
	B3LYP+D3	-1.43	-1.81	-1.40
	HF	-1.14	-1.67	-1.19
	LMP2	-1.34	-1.69	-1.26

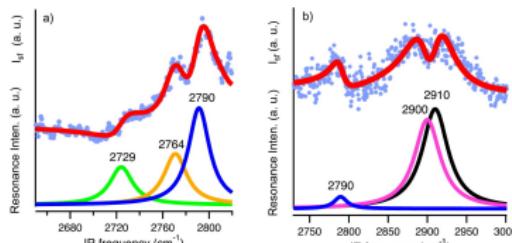
Vibrational Frequencies of Dissociated Water Species



J. Phys. Chem. C 2014, 118,
13623–13630.

stretch	B3LYP+D3/AO	Exp.
1-2 OD _{surf}	2697	2729
1-4 OD _{surf}	2715	2764
1-4 OD _{ads}	2873	2900
1-2 OD _{ads}	2883	2910

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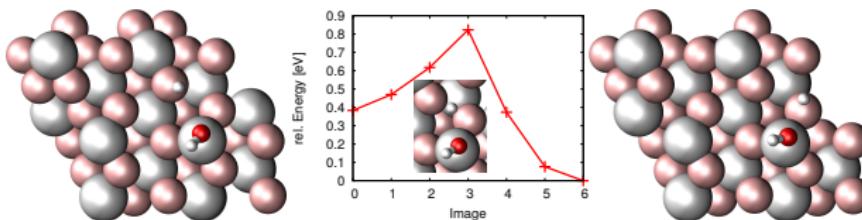
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Vibrational Frequencies $\Delta\tilde{\nu}$ of dissociated water species in cm⁻¹.

stretch	AO		PW	Exp.
	PBE+D3	B3LYP+D3	PBE+D2	
1-2 OD _{ads} –1-2 OD _{surf}	212	186	181	191
1-2 OD _{ads} –1-2 OD _{ads}	187	168	163	146
1-2 OD _{ads} –1-4 OD _{surf}	13	10	15	10

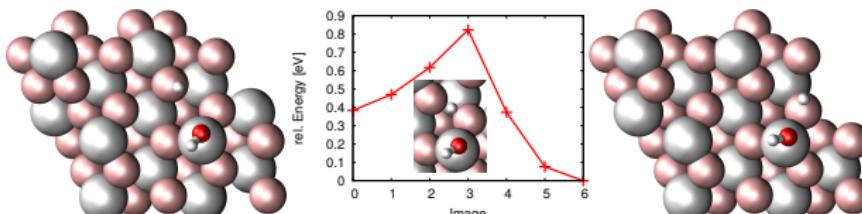
Activation Barriers with Hybrid Functionals and LMP2

- GGA functionals (here PBE) underestimate activation barriers
→ hybrid functional, perturbation theory



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$$k(T) = \frac{k_B T}{h} e^{-\Delta G^\ddagger(T)/(k_B T)}$$

method	B3LYP+D3/AO	LMP2/AO	PBE+D2/PW
ΔE^\ddagger [eV]	0.69	0.60	0.44
$\Delta G^\ddagger(300K)$ [eV]	0.58	0.49*	0.29
$k(300K)$ [s^{-1}]	1.2×10^3	$3.7 \times 10^{4*}$	9.1×10^7

* The contribution of the vibrations is estimated from B3LYP+D3, the corresponding rate is also affected by this approximation.

Achievements

- Recalculation of adsorption energies with atom centered orbital base
- Improvement of theoretical description of vibrational frequencies with respect to experimental values
- Improvement of activation barrier for diffusion reaction

S. Heiden, D. Usvyat, P. Saalfrank, **2018**, *in preparation*

Motivation: (0001) Molecular Beam Source

Water probing at the surface:

- MBS vs. pinhole dosing
- UHV, molecular beam onto surface vs. higher pressure
- non-equilibrium conditions vs. equilibrium situation
- enhanced dissociation probability with MBS

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- model adsorption/dissociation process with *ab initio* molecular dynamics simulations
 - Employing different surface and beam models

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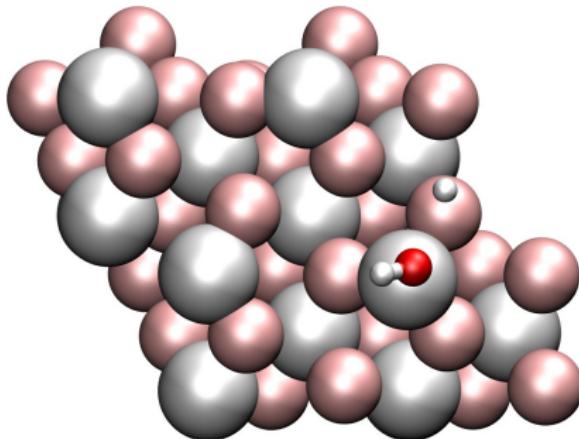
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Heiden, S.; Wirth, J.; Campen, R. K.; Saalfrank, P., *J. Phys. Chem. C* **2018**, 122 (27), 15494–15504.

(0001) Surface and Beam Model

Surface Models

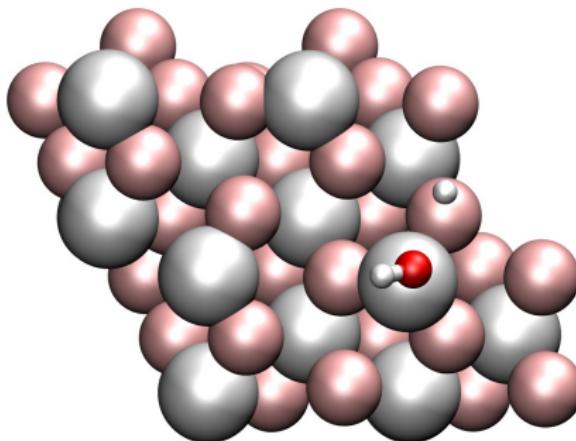
- Clean surface at 0 and 300 K
- Preadsorbed surface at 0 and 300 K



(0001) Surface and Beam Model

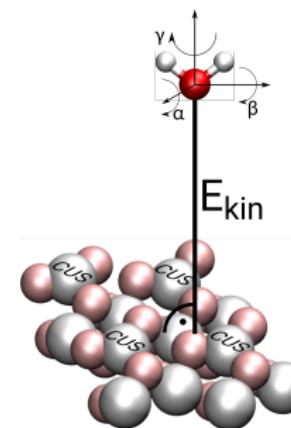
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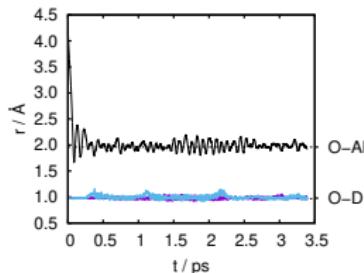
Beam Models

- Cold water molecule
- (D₂O)₄ cluster
- Rotationally/Vibrationally excited water

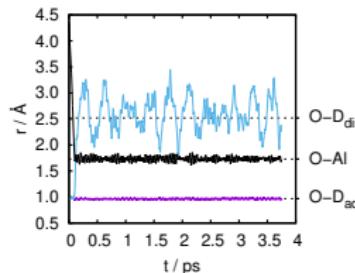


Adsorption and Dissociation Process

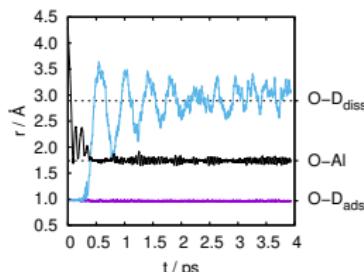
Example trajectories for molecular adsorption, dissociation



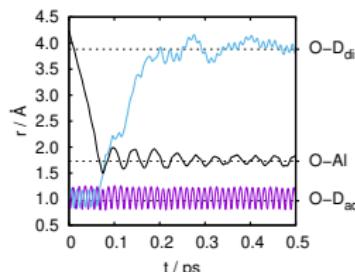
(a) molecular adsorption



(b) 1-2 dissociation

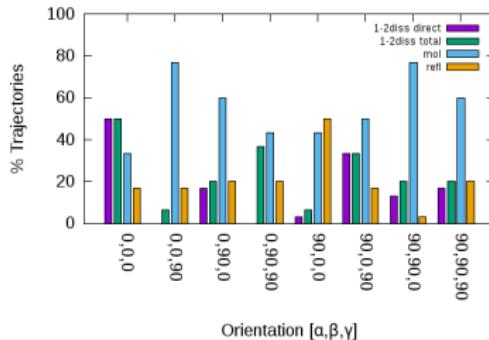
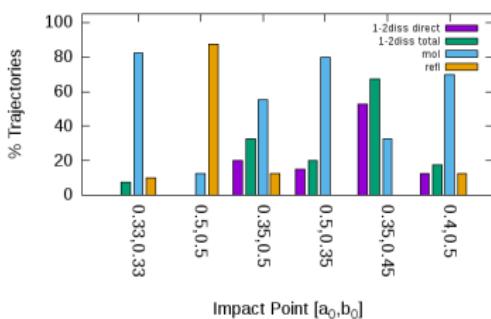


(c) 1-4 dissociation

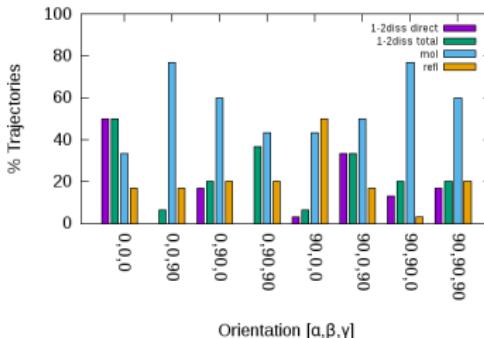
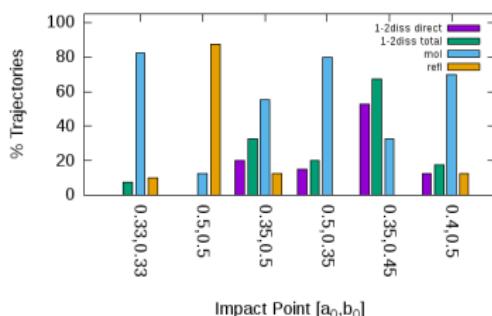


(d) 1-4' dissociation

Dissociation and Adsorption Probabilities



Dissociation and Adsorption Probabilities



strongly dependent on

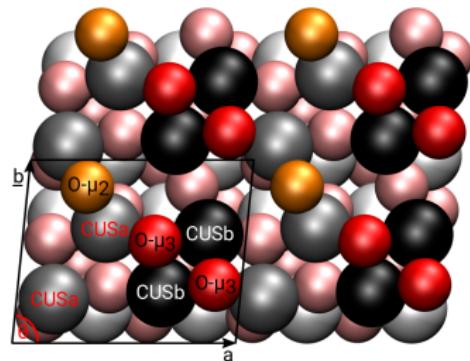
- impact site
- temperature effects
- precoverage
- vibrational excitation

less dependent on

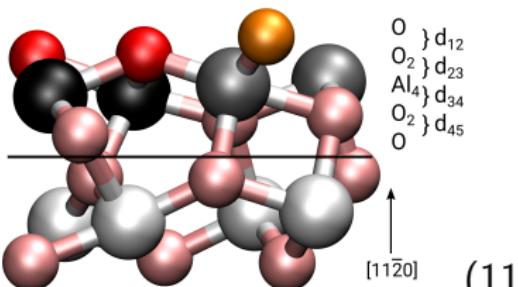
- kinetic energy of the beam
- orientation of the molecule

Heiden, S.; Wirth, J.; Campen, R. K.; Saalfrank, P., *J. Phys. Chem. C* **2018**, 122 (27), 15494–15504.

(11̄20) Surface



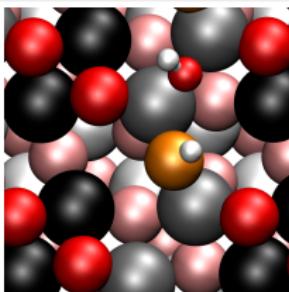
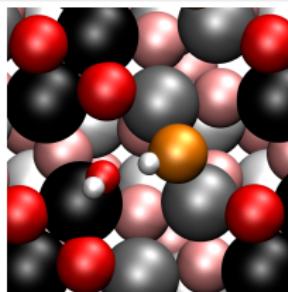
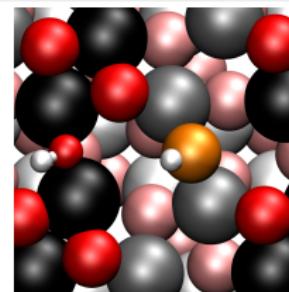
surface, top view



(11̄20) side view

- UHV 0 K geometry optimized structure
- O-I terminated surface cut
- 8 CUSa and 8 CUSb Al atoms, 8 threefold coordinated and 4 twofold coordinated O atoms
- (2 × 2) supercell

Water Adsorption at the (11̄20) Surface

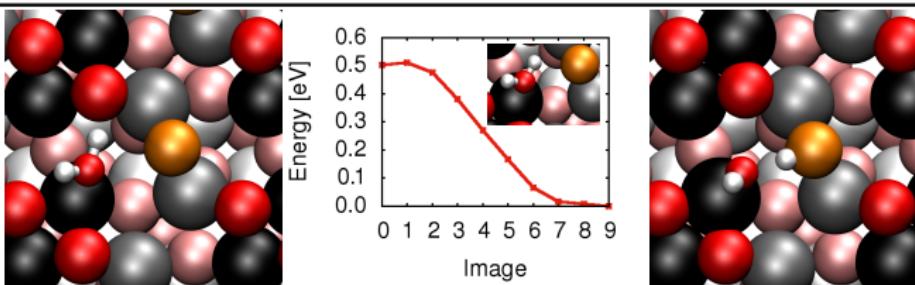
inter-CUSa||O- μ_2 CUSb||O- μ_2 inter-CUSb||O- μ_2

Adsorbed Species	E_{ads}
CUSb	-1.78
inter-CUSa O- μ_2	-2.50
inter-CUSa O- μ_3	-1.67
CUSb O- μ_2	-2.28
CUSb O- μ_3	-1.19
inter-CUSb O- μ_2	-2.09
inter-CUSb O- μ_3	-1.89

Dissociation and Diffusion Reactions

$$\text{Eyring equation: } k(T) = \frac{k_B T}{h} e^{-\Delta G^\ddagger/(k_B T)}$$

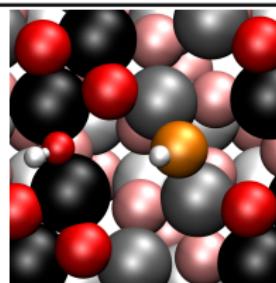
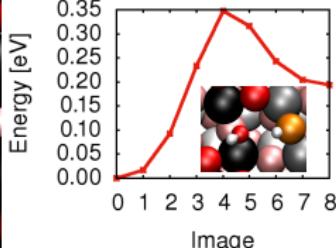
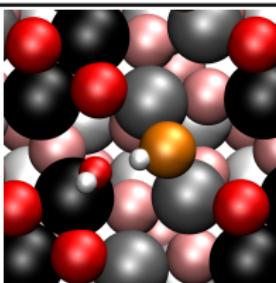
Reaction Type		ΔE^\ddagger (eV)	$\Delta G_{300\text{ K}}^\ddagger$ (eV)	$k_{300\text{ K}}$ (s ⁻¹)
H ₂ O dissociation	<i>D-I</i>	0.01	0.002	5.76×10^{12}
OH diffusion	<i>Df-OH-III</i>	0.35	0.39	1.88×10^6
H diffusion	<i>Df-H-V</i>	1.65	1.49	4.90×10^{-13}



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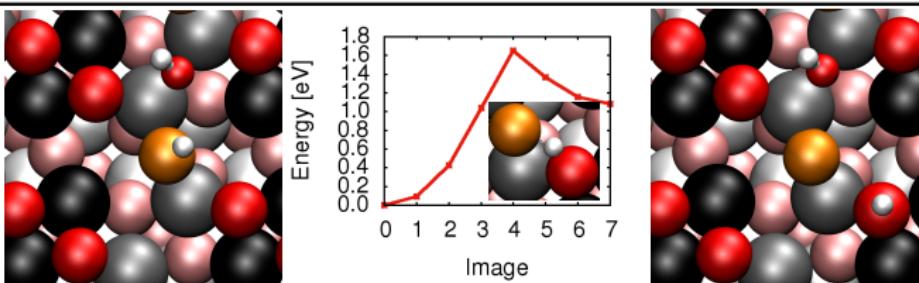
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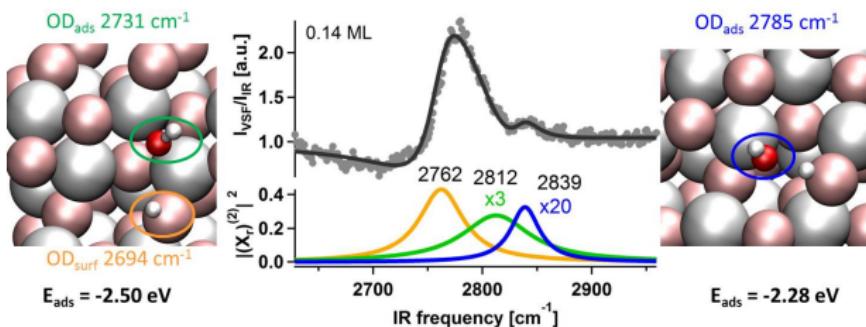


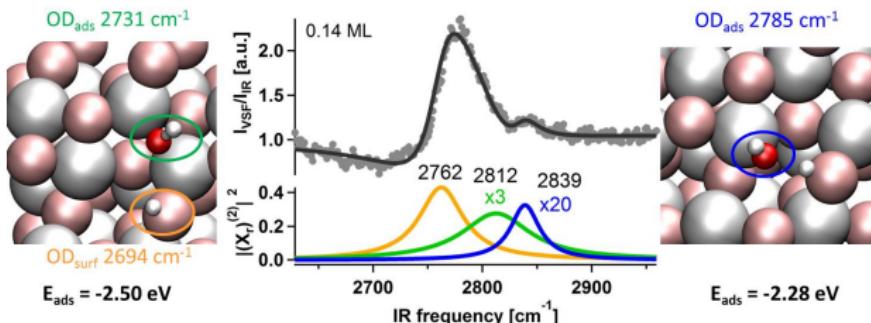
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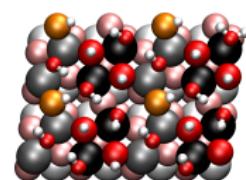
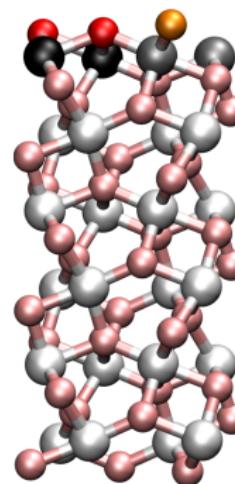
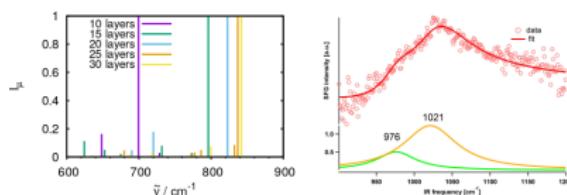


Assigned species	$\tilde{\nu}_{\text{calc.}}$	$\Delta\tilde{\nu}_{\text{calc.}}$	$\tilde{\nu}_{\text{exp.}}$	$\Delta\tilde{\nu}_{\text{exp.}}$
inter-CUSa O- μ_2 OD _{surf}	2694		2762	
inter-CUSa O- μ_2 OD _{ads}	2731	37	2812	50
CUSb O- μ_2 OD _{ads}	2785	91	2839	77

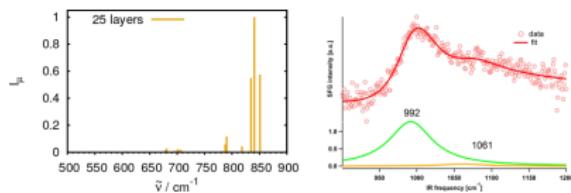
Heiden, S.; Yue, Y.; Kirsch, H.; Wirth, J.; Saalfrank, P.; Campen, R. K., *J. Phys. Chem. C* **2018**, *122* (12), 6573–6584.

Further Projects

• Lattice Al-O vibrations



• Higher water coverage



Yue, Y.; Heiden, S.; Kirsch, H.; Wirth, J.; Campen, R. K.; Saalfrank, P., in preparation

Summary and Outlook

(0001) Surface

- Recalculation of E_{ads}
- Vibrational frequency calculation improved w.r.t. experiment
- Activation and rate constant improvement

Summary and Outlook

(0001) Surface

- Recalculation of E_{ads}
 - Vibrational frequency calculation improved w.r.t. experiment
 - Activation and rate constant improvement
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 - Understand enhanced dissociation
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Summary and Outlook

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(11̄20) Surface

- Structure search and adsorption energies
- Vibrational frequencies of water and surface species
- Analyses of surface reactions

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