Y8 annual meeting of IRP $PACS_2$ @ IJS, 20 Sep 2022

The implausibility of bidentate bonding of silanols to oxidized aluminum surfaces

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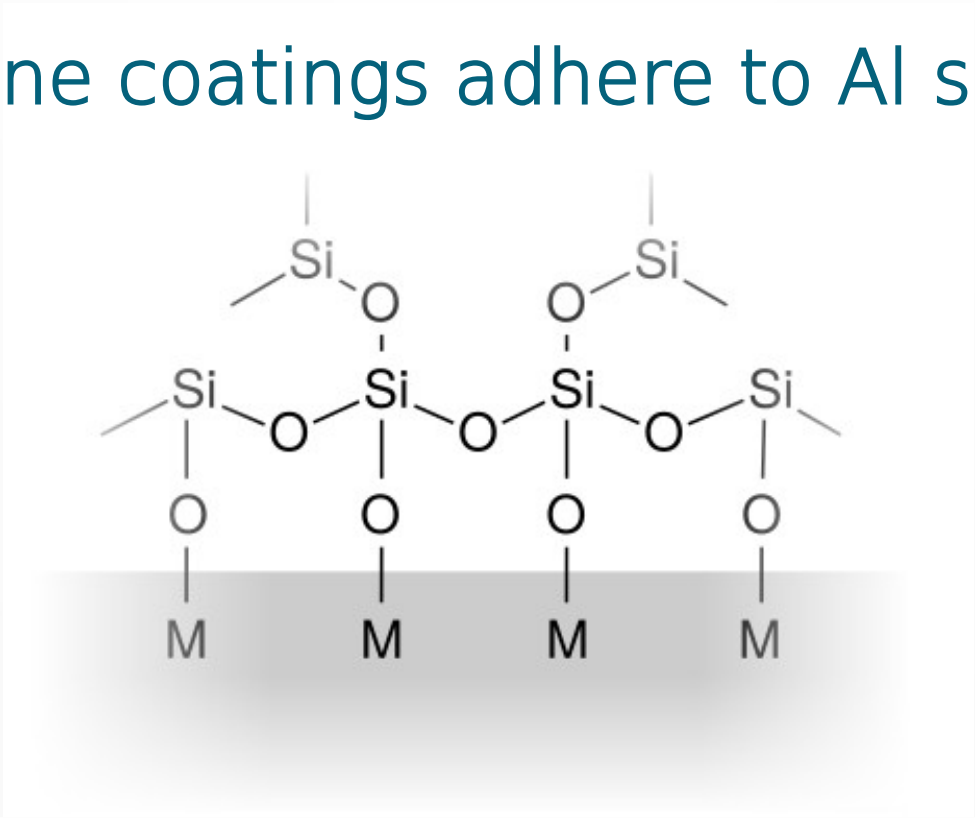
Department of Physical and Organic Chemistry

Jožef Stefan Institute

Aim of the study

How siloxane coatings adhere to Al surfaces?



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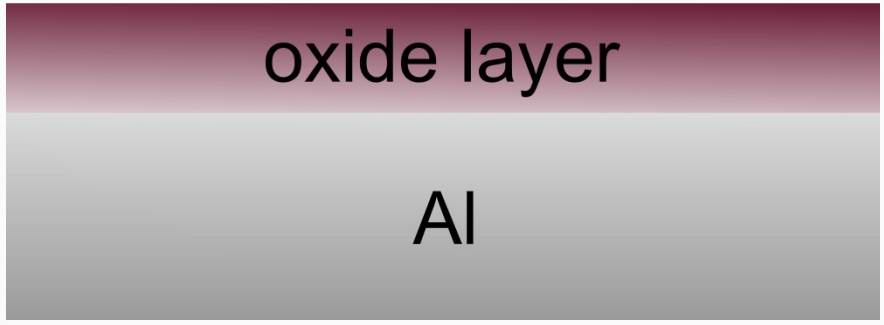

Premise: Al surface are oxidized

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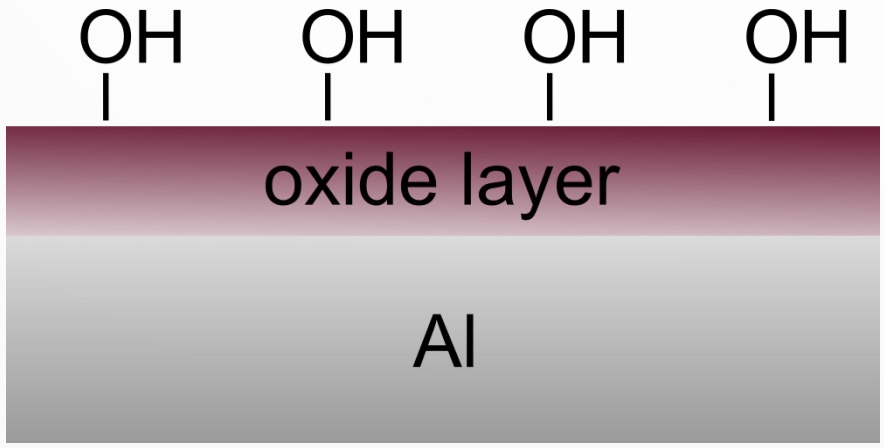
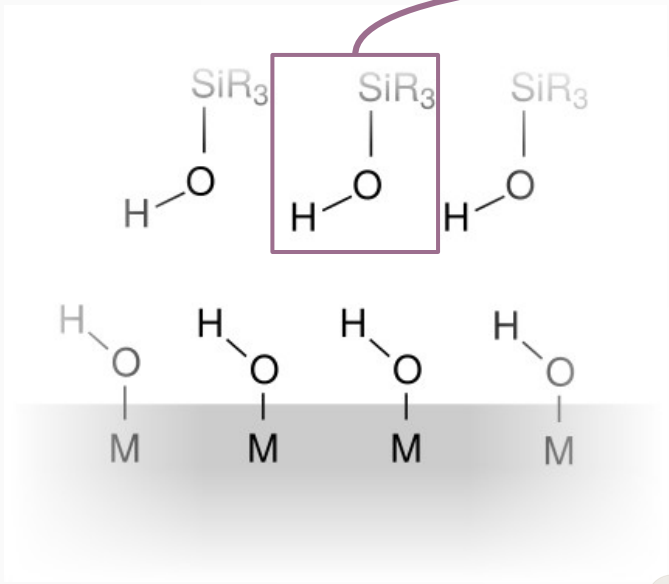


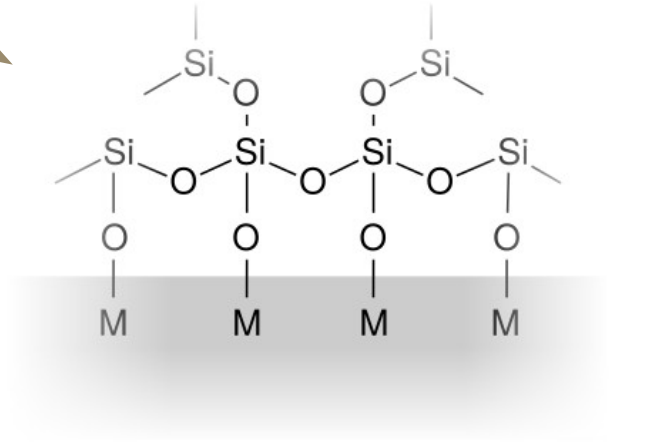
Premise: Al surface are oxidized and fully hydroxylated



precursor to siloxane coatings:

silanols: alcohols where C is replace by Si

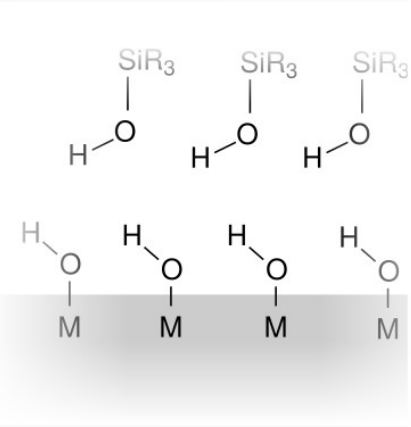
?

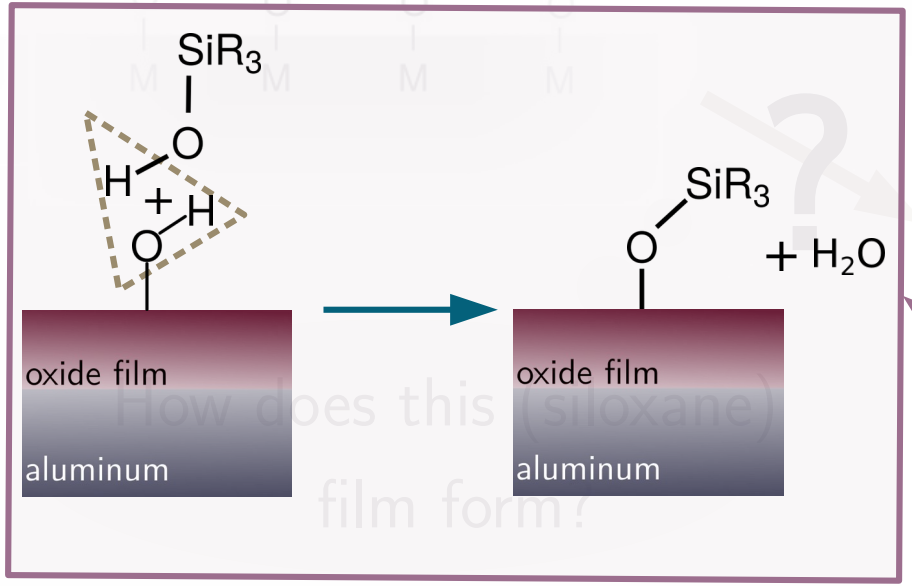


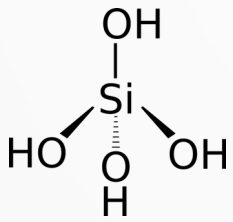
How does siloxane film form?

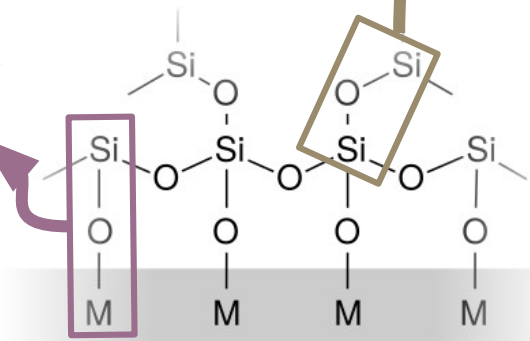
Condensation mechanism

Silanols react with each other or the surface, **water** is produced

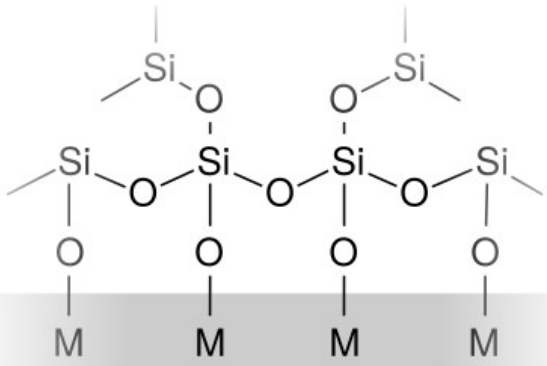




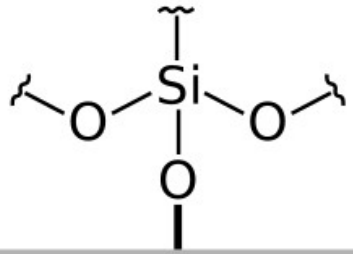




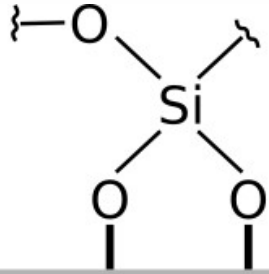
How siloxane coatings adhere to Al surfaces?



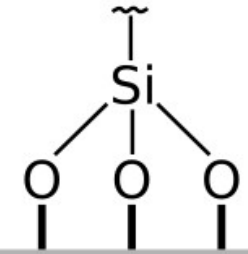
?



monodentate bonding

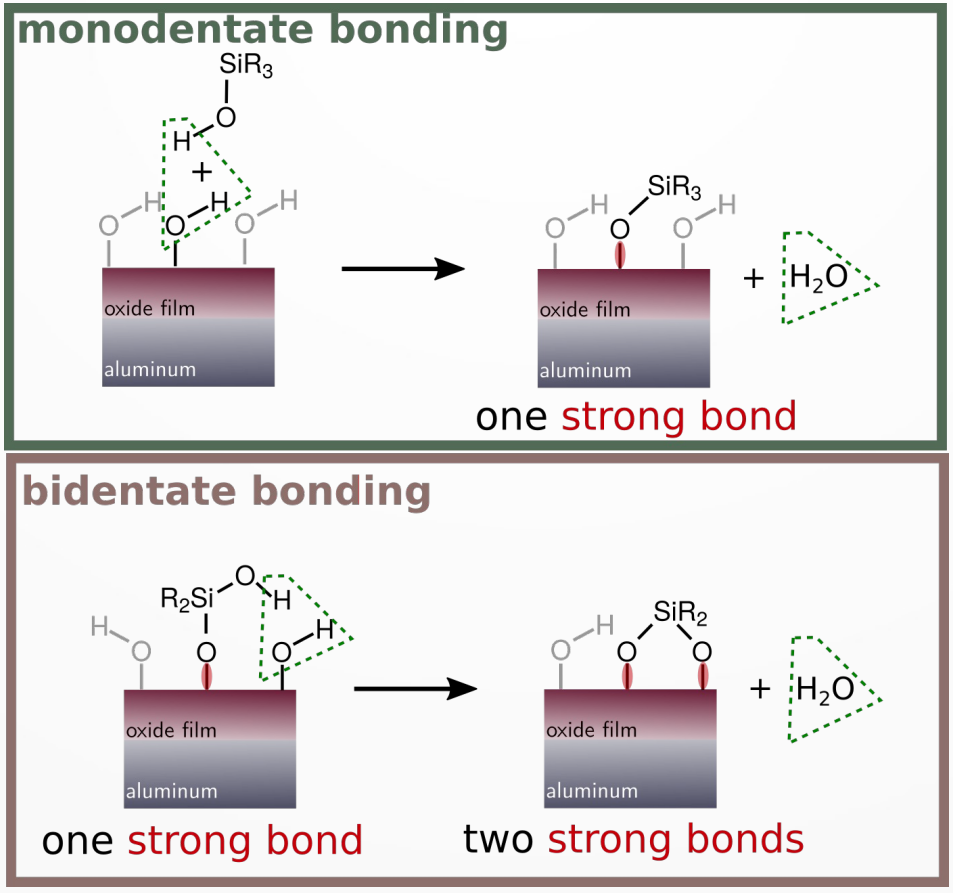


bidentate bonding



tridentate bonding

Fully hydroxylated surface

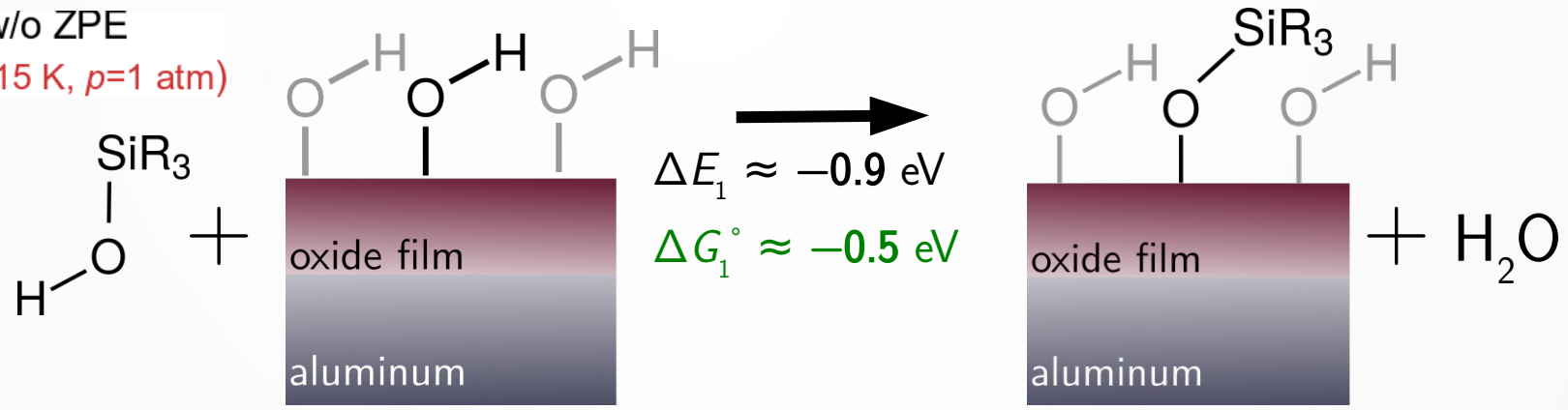


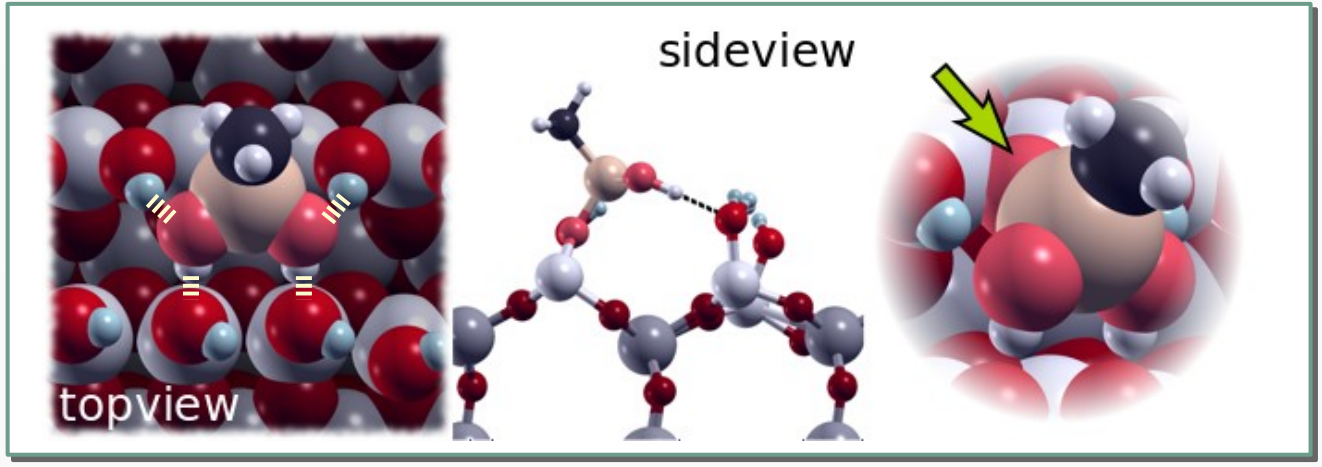
Reactions modeled by DFT calculations

Monodentate bonding

$\Delta E \equiv \Delta E(T=0\ \text{K})$ w/o ZPE

$\Delta G \equiv \Delta G$ (T=298.15 K, p=1 atm)





Poberžnik et al.,
J. Phys. Chem. C **122**,
9417–9431

Bidentate bonding

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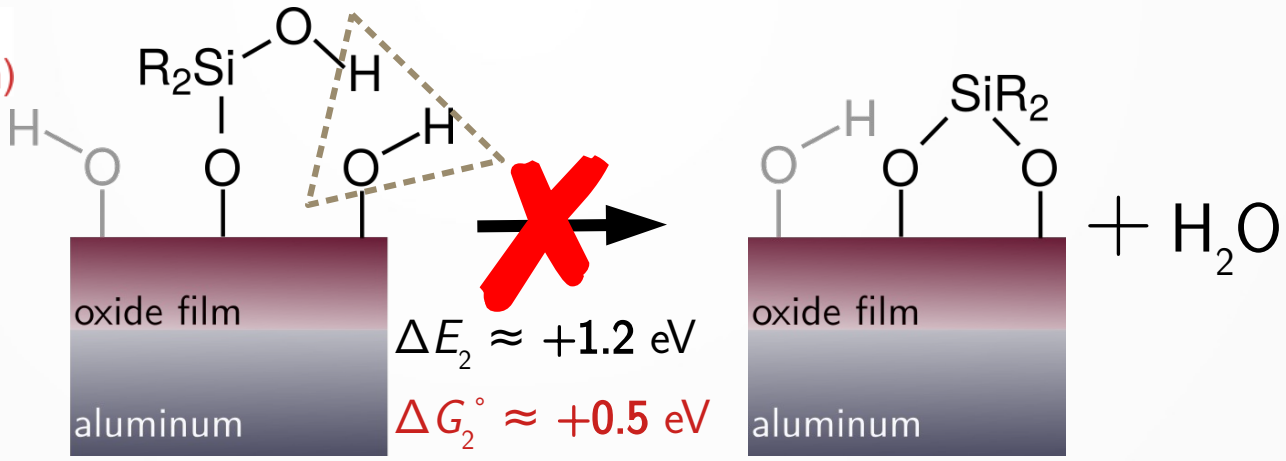

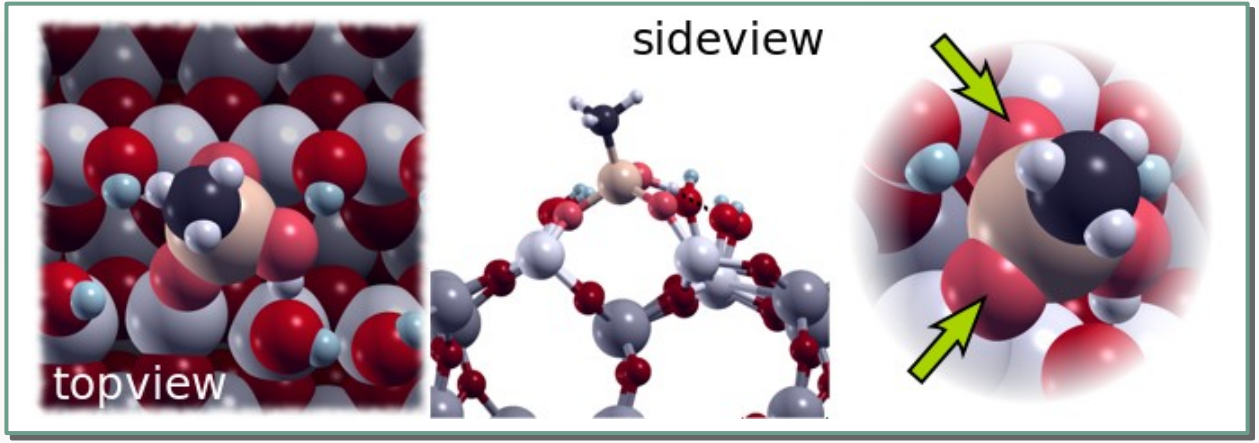

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Bidentates unfavorable?

- On the utilized model of oxidized-Al surface, bidentates are unstable … **is this results specific or general?**

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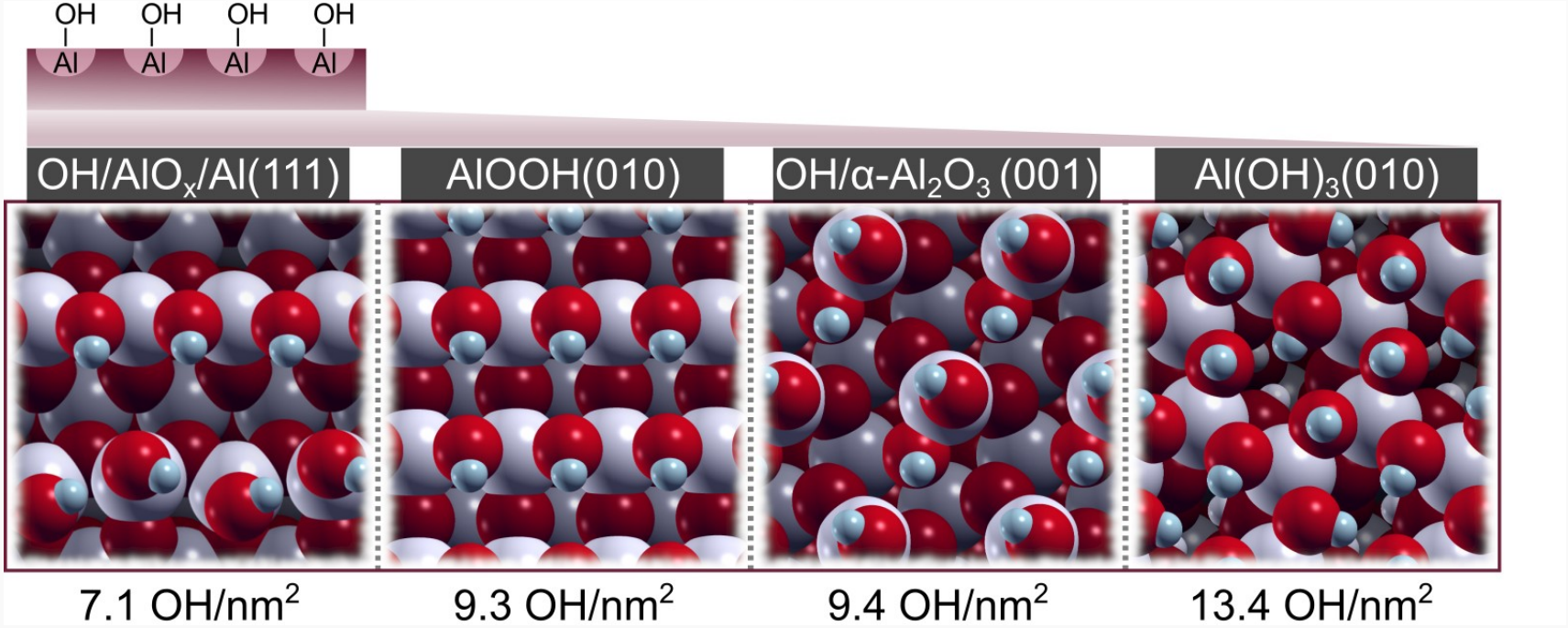
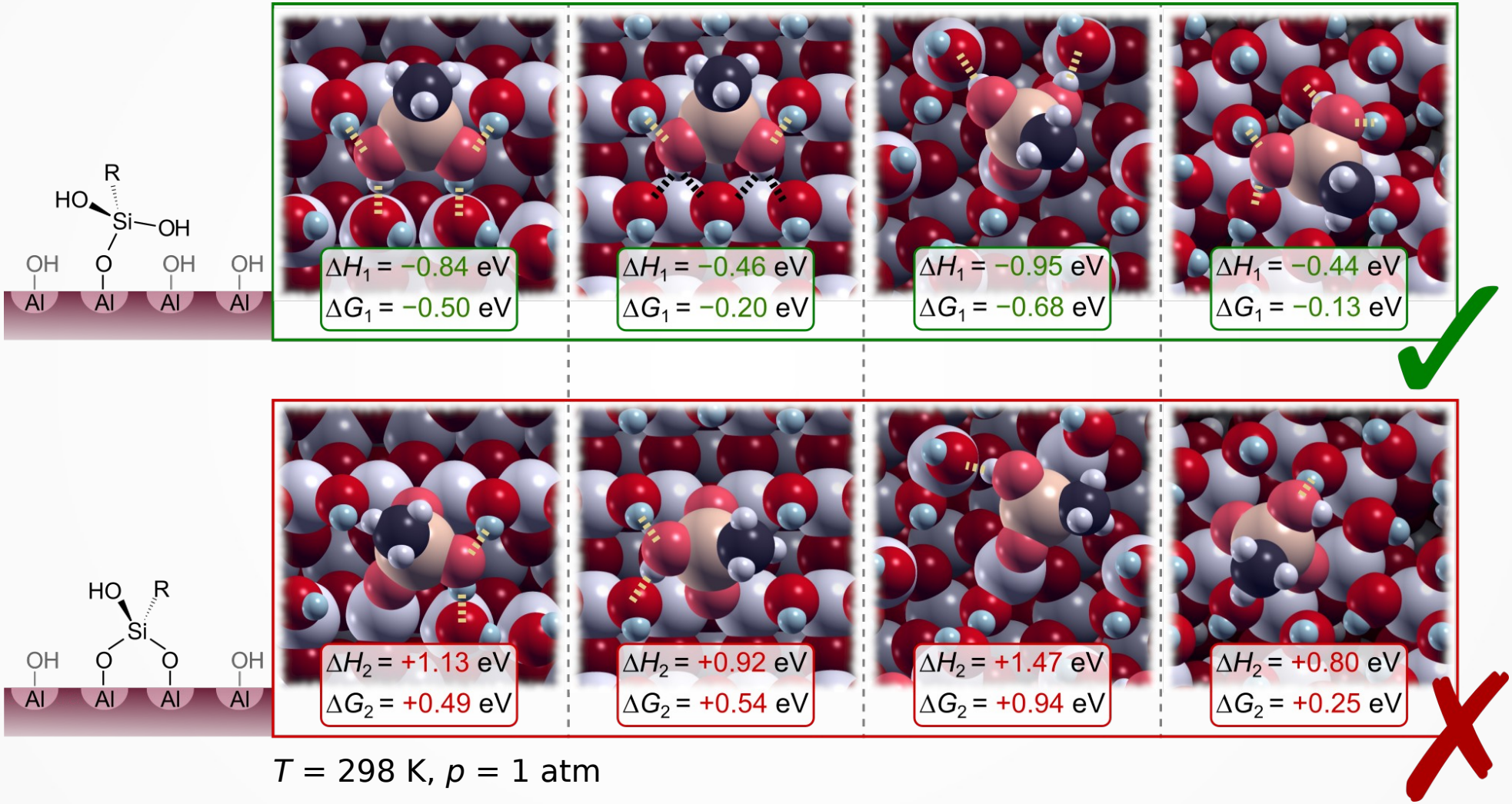


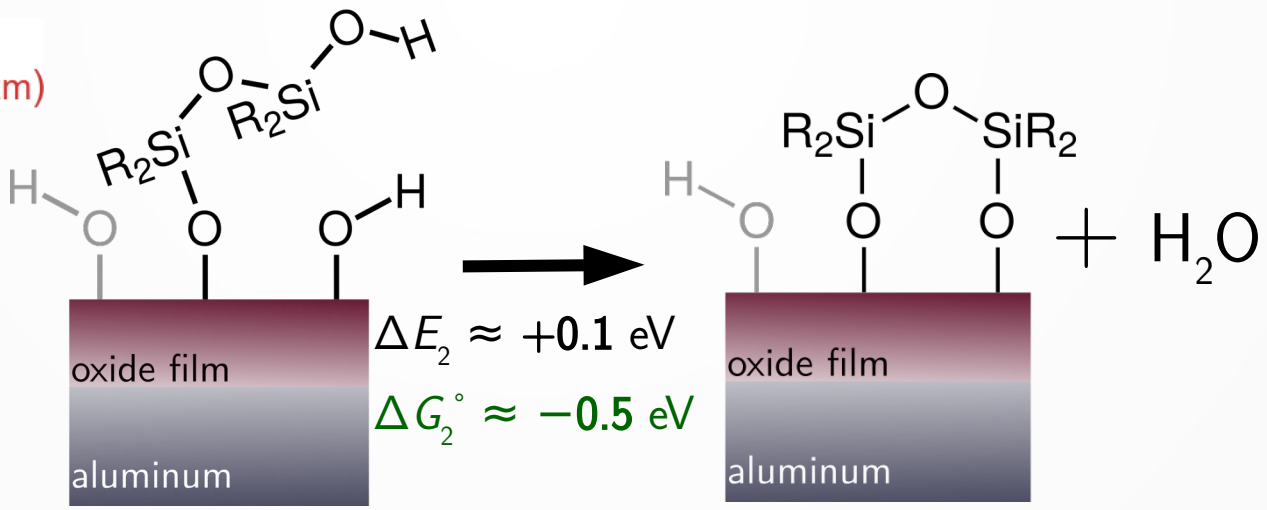

R
HO
Si
OH
OH
O
OH
OH
Al
Al
Al
Al
ΔH1 = −0.84 eV
ΔG1 = −0.50 eV
ΔH1 = −0.46 eV
ΔG1 = −0.20 eV
ΔH1 = −0.95 eV
ΔG1 = −0.68 eV
ΔH1 = −0.44 eV
ΔG1 = −0.13 eV
HO
R
Si
OH
O
O
OH
Al
Al
Al
Al
ΔH2 = +1.13 eV
ΔG2 = +0.49 eV
ΔH2 = +0.92 eV
ΔG2 = +0.54 eV
ΔH2 = +1.47 eV
ΔG2 = +0.94 eV
ΔH2 = +0.80 eV
ΔG2 = +0.25 eV

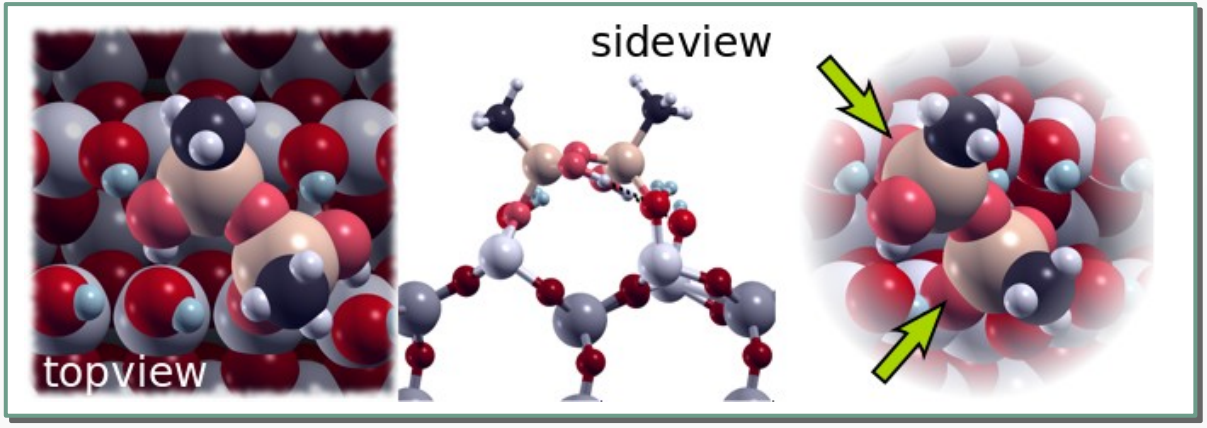
$T = 298$ K, $p = 1$ atm

Dimer: bidentate bonding

$\Delta E \equiv \Delta E(T=0\ \text{K})$ w/o ZPE

$\Delta G \equiv \Delta G\ (T=298.15\ \text{K}, p=1\ \text{atm})$





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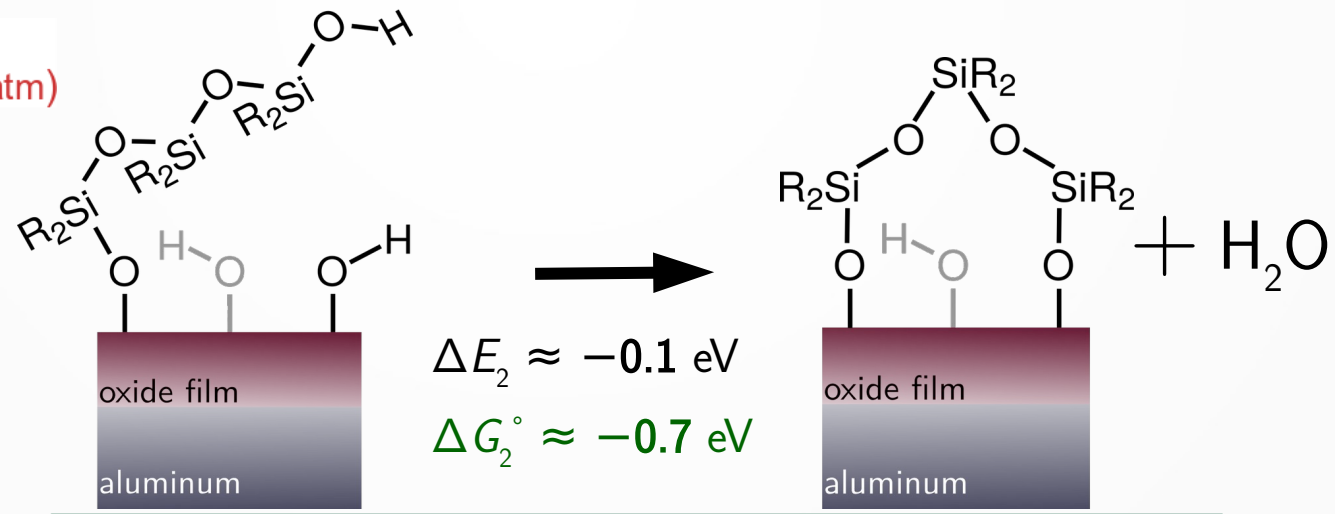
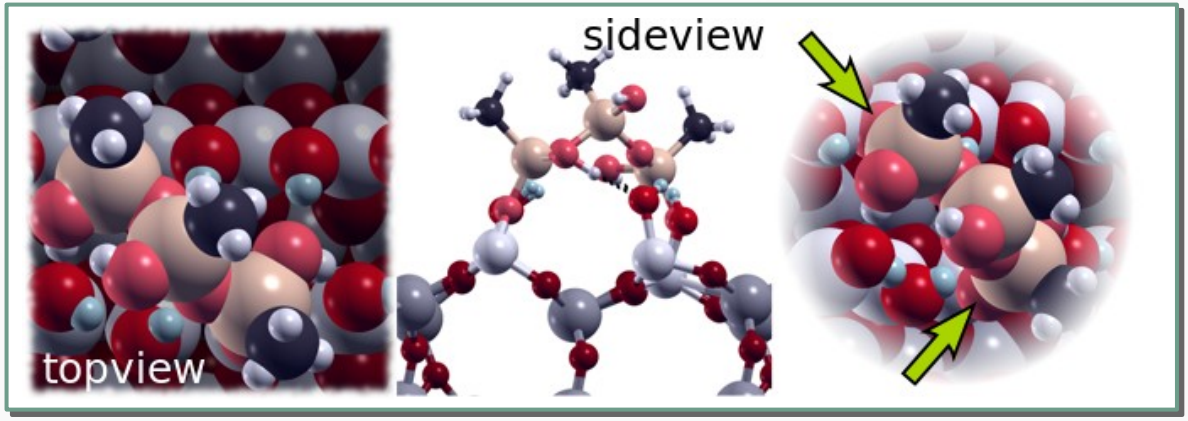
Trimer: bidentate bonding

$\Delta E \equiv \Delta E(T=0\ \text{K})$ w/o ZPE

$\Delta G \equiv \Delta G\ (T=298.15\ \text{K}, p=1\ \text{atm})$





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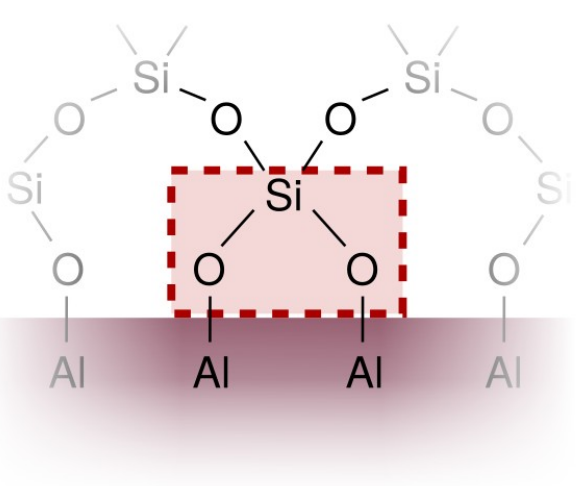
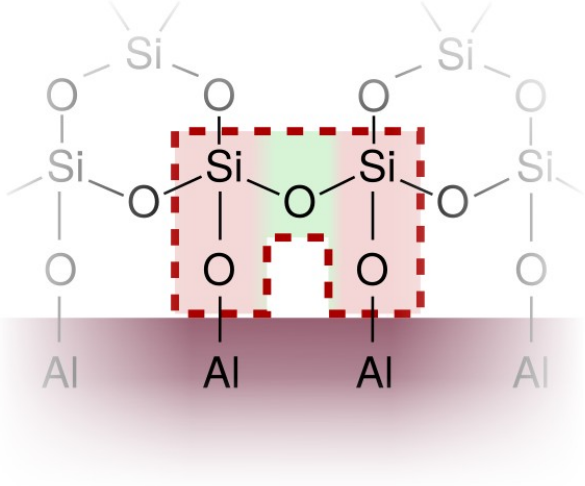
endothermic
endergonic



athermic
exergonic



exothermic
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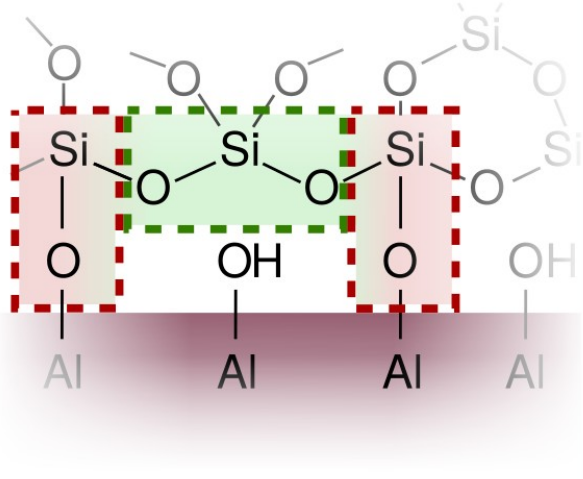
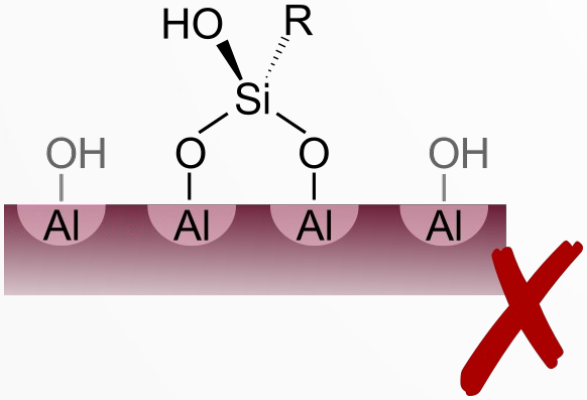


strain is reduced

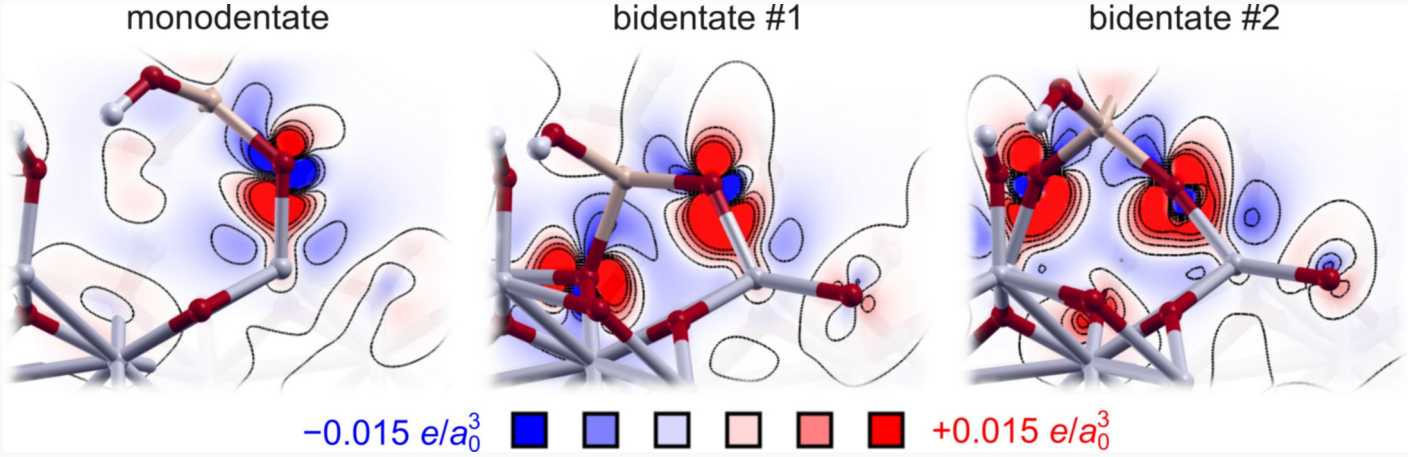
Why bidentate is unstable?

Why unstable?



Possibility #1:
the 2nd SiO—Al bond is weaker

Structural analysis: NO
Charge density difference $\Delta\rho(\boldsymbol{r})$: NO



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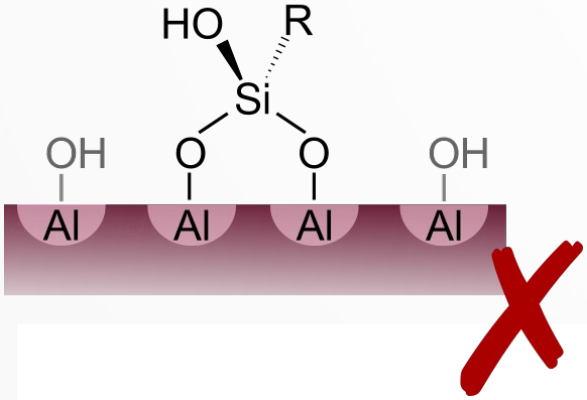
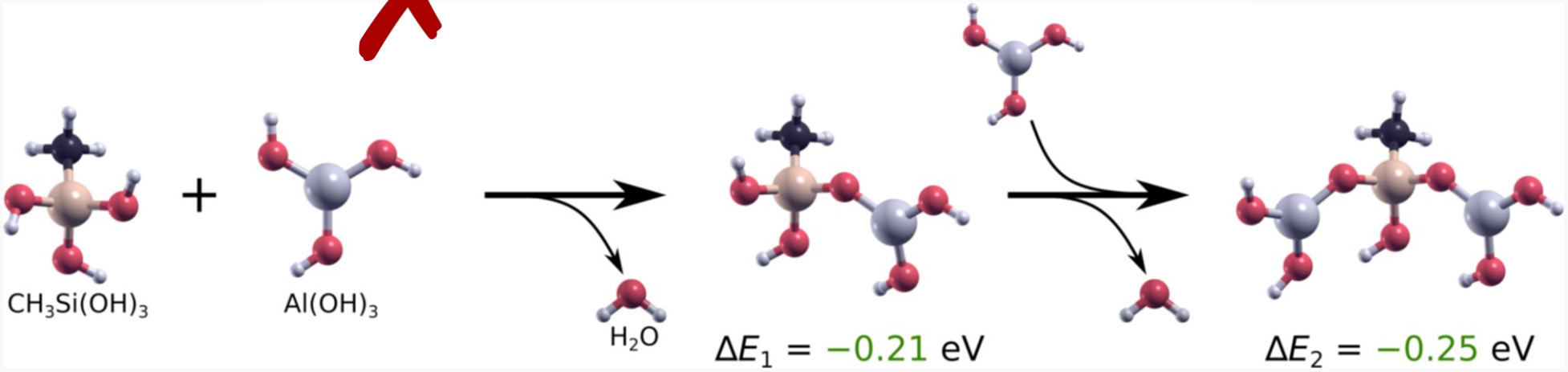


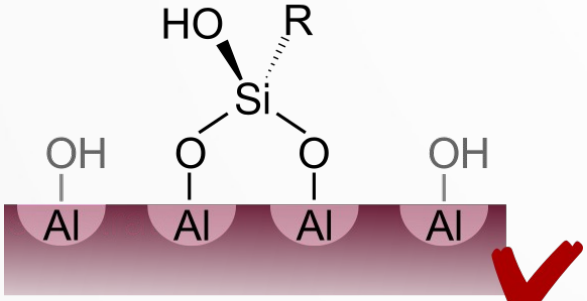
Possibility #1:
the 2nd SiO—Al bond is weaker

Structural analysis & $\Delta\rho(\boldsymbol{r})$: NO
Bonding with $Al(OH)_3$: NO



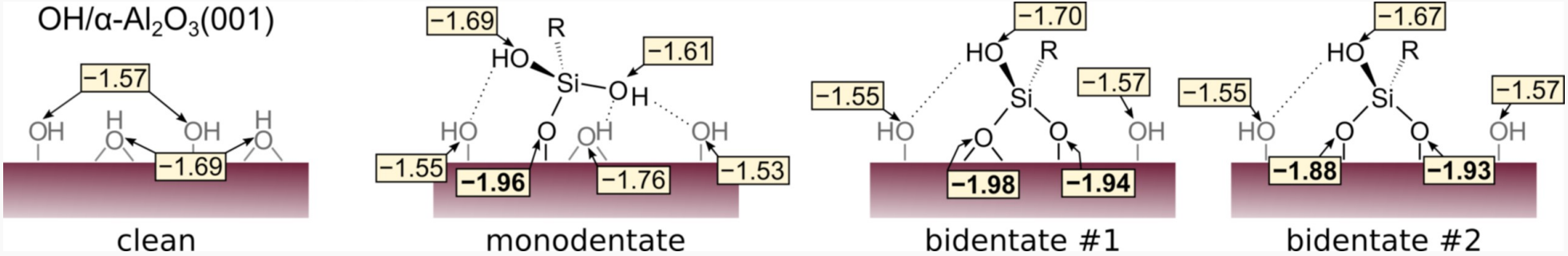
Why bidentate is unstable?

Why unstable?



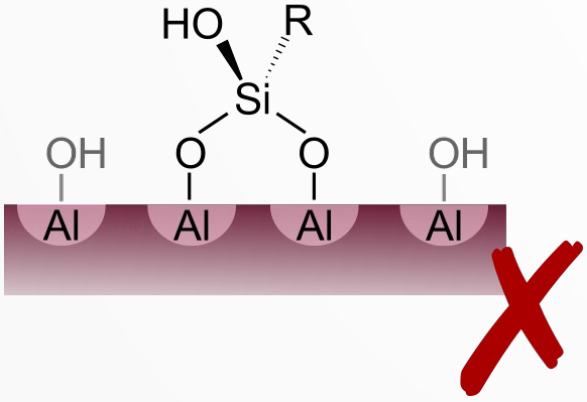
Possibility #1:
the 2nd SiO—Al bond is weaker ✗

Structural analysis & $\Delta\rho(\boldsymbol{r})$: NO
Bonding with $Al(OH)_3$: NO
Bader charges: NO

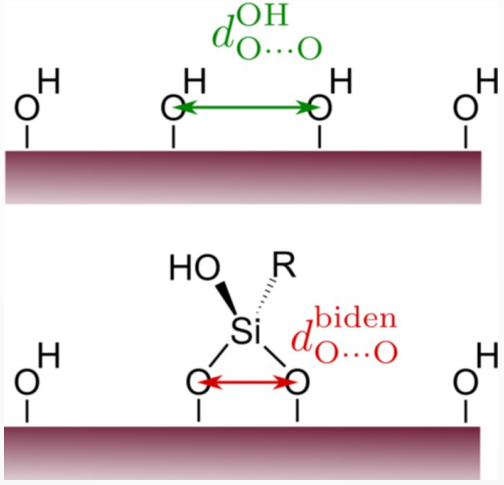


Why bidentate is unstable?

Why unstable?



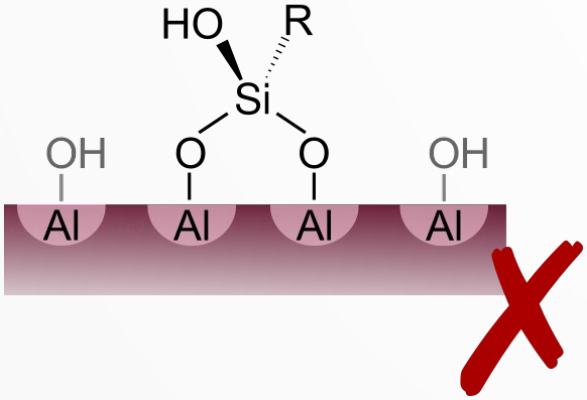
Possibility #2:
bidentate induced substrate deformation



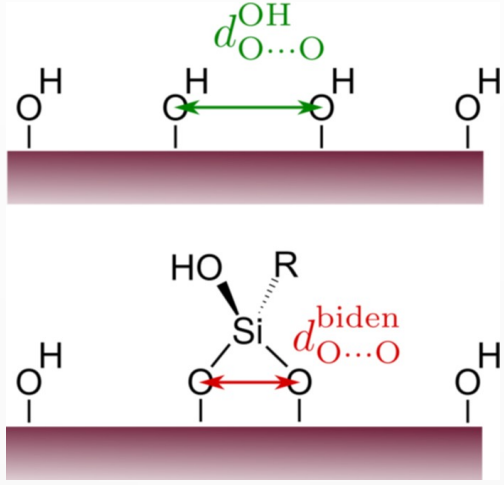
considerably reduced
O–O distance, by ~1 Å

Why bidentate is unstable?

Why unstable?



Possibility #2:
bidentate induced substrate deformation ✓

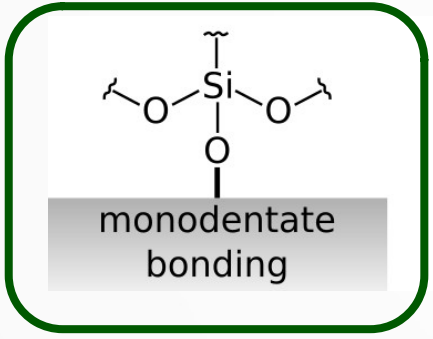


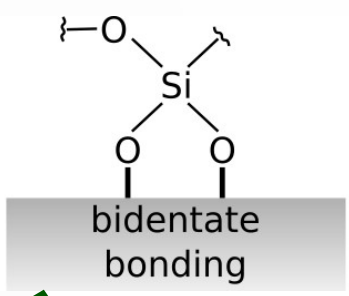
substrate deformation:

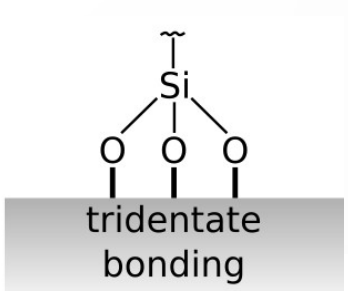
- monodentate: 0.3±0.2 eV
- bidentate: 1.7±0.2 eV

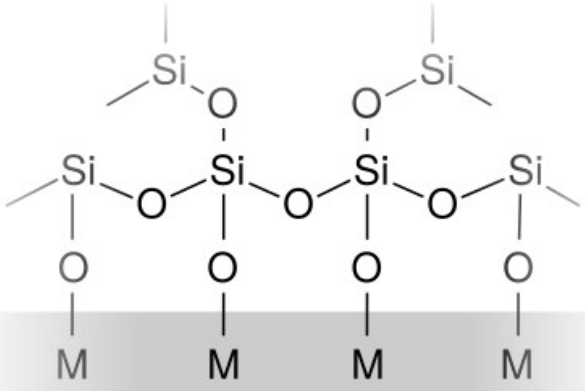
considerably reduced O–O distance, by ~1 Å

Summary

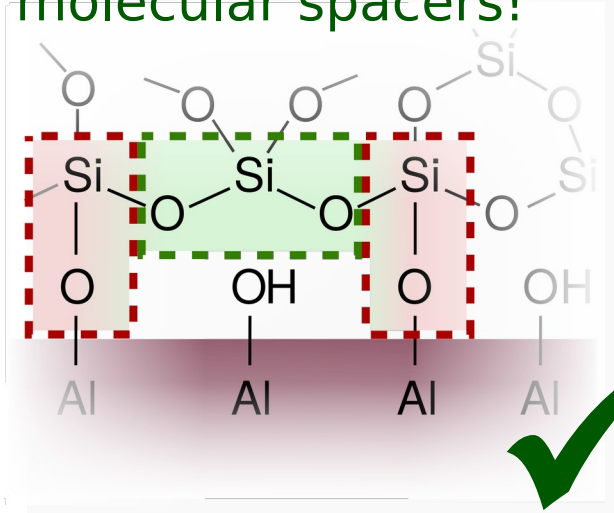








molecular spacers!



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Thank you for your attention!