Is the adsorption free energy a good criterion to distinguish between physisorption & chemisorption

Anton Kokalj
Department of Physical and Organic Chemistry

Jožef Stefan Institute

The "20/40" rule

Many studies utilize the following criteria to distinguish between physisorption and chemisorption:

- **physisorption:** $\Delta G^{\circ}_{\mathrm{ads}} > -20$ kJ/mol
- **mixed physisorption/chemisorption:** $\Delta G^{\circ}_{\mathrm{ads}} \in [-20, -40]$ kJ/mol
- **chemisorption:** $\Delta G^{\circ}_{\mathrm{ads}} < -40$ kJ/mol

($\Delta G^{\circ}_{\mathrm{ads}} \equiv$ standard free energy of adsorption)

The "20/40" rule

Many studies utilize the following criteria to distinguish between physisorption and chemisorption:

- **physisorption:** $\Delta G^{\circ}_{\text{ads}} > -20$ kJ/mol
- **mixed physisorption/chemisorption:** $\Delta G^{\circ}_{\text{ads}} \in [-20, -40]$ kJ/mol
- **chemisorption:** $\Delta G^{\circ}_{\text{ads}} < -40$ kJ/mol

($\Delta G^{\circ}_{\text{ads}} \equiv$ standard free energy of adsorption)

This "20/40" rule is based on the fundamental premise:

chemisorption interaction is strong & physisorption interaction is weak

The "20/40" rule

Many studies utilize the following criteria to distinguish between physisorption and chemisorption:

- **physisorption:** $\Delta G^{\circ}_{\text{ads}} > -20$ kJ/mol
- **mixed physisorption/chemisorption:** $\Delta G^{\circ}_{\text{ads}} \in [-20, -40]$ kJ/mol
- **chemisorption:** $\Delta G^{\circ}_{\text{ads}} < -40$ kJ/mol

($\Delta G^{\circ}_{\text{ads}} \equiv$ standard free energy of adsorption)

This "20/40" rule is based on the fundamental premise:

chemisorption interaction is strong & physisorption interaction is weak

This premise is true, but still ...

Contention

The "20/40" rule is not a reliable criterion to distinguish between physisorption and chemisorption.

Arguments against the "20/40" rule

(i) $\Delta G^\circ_{\mathrm{ads}}$ is "intricate" $\Rightarrow$ $\Delta H^\circ_{\mathrm{ads}}$ is a more direct measure of the molecule–surface interaction

(ii) physisorption is weak only for small molecules

(iii) due to bond-breaking (dissociative adsorption), the chemisorption enthalpy can be weak*

(iv) due to substantial molecular distortion during chemisorption, the chemisorption enthalpy can be weak*

*A note on wording (stable energies/enthalpies are "negative"):

stronger adsorption $\Rightarrow$ lower adsorption energy } "stronger" energy
weaker adsorption $\Rightarrow$ higher adsorption energy } "weaker" energy

Arguments against the "20/40" rule

(i) $\Delta G^\circ_{\mathrm{ads}}$ is "intricate" $\Rightarrow$ $\Delta H^\circ_{\mathrm{ads}}$ is a more direct measure of the molecule–surface interaction

(ii) physisorption is weak only for small molecules

(iii) due to bond-breaking (dissociative adsorption), the chemisorption enthalpy can be weak*

(iv) due to substantial molecular distortion during chemisorption, the chemisorption enthalpy can be weak*

*A note on wording (stable energies/enthalpies are "negative"):

stronger adsorption $\Rightarrow$ lower adsorption energy } "stronger" energy
weaker adsorption $\Rightarrow$ higher adsorption energy } "weaker" energy

Arguments against the "20/40" rule

(i) $\Delta G^\circ_{\mathrm{ads}}$ is "intricate" $\Rightarrow$ $\Delta H^\circ_{\mathrm{ads}}$ is a more direct measure of the molecule–surface interaction

(ii) physisorption is weak only for small molecules

(iii) due to bond-breaking (dissociative adsorption), the chemisorption enthalpy can be weak*

(iv) due to substantial molecular distortion during chemisorption, the chemisorption enthalpy can be weak*

*A note on wording (stable energies/enthalpies are "negative"):

stronger adsorption $\Rightarrow$ lower adsorption energy } "stronger" energy
weaker adsorption $\Rightarrow$ higher adsorption energy } "weaker" energy

Arguments against the "20/40" rule

(i) $\Delta G^\circ_{\mathrm{ads}}$ is "intricate" $\Rightarrow$ $\Delta H^\circ_{\mathrm{ads}}$ is a more direct measure of the molecule–surface interaction

(ii) physisorption is weak only for small molecules

(iii) due to bond-breaking (dissociative adsorption), the chemisorption enthalpy can be weak*

(iv) due to substantial molecular distortion during chemisorption, the chemisorption enthalpy can be weak*

*A note on wording (stable energies/enthalpies are "negative"):

stronger adsorption $\Rightarrow$ lower adsorption energy } "stronger" energy
weaker adsorption $\Rightarrow$ higher adsorption energy } "weaker" energy

Free energy vs. enthalpy

Definition

Gibbs free energy: G = E + pV − TS = H − TS (enthalpy: H; energy: E; entropy: S)

$p \equiv$ pressure, $V \equiv$ volume, $T \equiv$ temperature

- pV term:
  - For ideal gas: $pV = RT = 2.5$ kJ/mol at room T
    For solids at ambient pressure: about 1000-times smaller
  - Hence: $E \approx H \quad \Rightarrow$ E and H will be used interchangeably
- TS term:
  - cannot be neglected (at room T)
    [it is significantly larger than the pV term]

Free energy vs. enthalpy

Definition

Gibbs free energy: G = E + pV − TS = H − TS (enthalpy: H; energy: E; entropy: S)

$p \equiv$ pressure, $V \equiv$ volume, $T \equiv$ temperature

- pV term:
  - For ideal gas: $pV = RT = 2.5$ kJ/mol at room T

    For solids at ambient pressure: about 1000-times smaller
  - Hence: $E \approx H \quad \Rightarrow$ E and H will be used interchangeably
- TS term:
  - cannot be neglected (at room T)

    [it is significantly larger than the pV term]

Free energy vs. enthalpy

Definition

Gibbs free energy: G = E + pV − TS = H − TS (enthalpy: H; energy: E; entropy: S)

$p \equiv$ pressure, $V \equiv$ volume, $T \equiv$ temperature

- pV term:
  - For ideal gas: $pV = RT = 2.5$ kJ/mol at room T

    For solids at ambient pressure: about 1000-times smaller
  - Hence: $E \approx H \quad \Rightarrow$ E and H will be used interchangeably
- TS term:
  - cannot be neglected (at room T)

    [it is significantly larger than the pV term]

Free energy vs. enthalpy

Definition

Gibbs free energy — enthalpy

$$G = E + pV - TS = H - TS$$

energy — entropy

$p \equiv$ pressure, $V \equiv$ volume, $T \equiv$ temperature

- pV term:
  - For ideal gas: $pV = RT = 2.5$ kJ/mol at room T

    For solids at ambient pressure: about 1000-times smaller
  - Hence: $E \approx H \quad \Rightarrow$ E and H will be used interchangeably
- TS term:
  - cannot be neglected (at room T)

    [it is significantly larger than the pV term]

Adsorption free energy vs. adsorption enthalpy

Definition

Gibbs free energy: G = energy: E + pV − TS = enthalpy: H − T entropy: S

$p \equiv$ pressure, $V \equiv$ volume, $T \equiv$ temperature

For chemical reactions:

$$\Delta X = X(\text{products}) - X(\text{reactants}), \qquad \text{where } X \equiv E, H, G, V, S$$

For adsorption:

$$\Delta G^\circ_{\text{ads}} = \Delta H^\circ_{\text{ads}} - T\Delta S^\circ_{\text{ads}}$$

- $T\Delta S^\circ_{\text{ads}}$ is sizable and strongly depends on the adsorption reaction type, and masks the molecule–surface interaction
- **better and simpler to consider $\Delta H^\circ_{\text{ads}}$ instead**

Adsorption free energy vs. adsorption enthalpy

Definition

Gibbs free energy

enthalpy

$$G = E + pV - TS = H - TS$$

energy

entropy

$p \equiv$ pressure, $V \equiv$ volume, $T \equiv$ temperature

For chemical reactions:

$$\Delta X = X(\text{products}) - X(\text{reactants}), \qquad \text{where } X \equiv E, H, G, V, S$$

For adsorption:

$$\Delta G^\circ_{\text{ads}} = \Delta H^\circ_{\text{ads}} - T\Delta S^\circ_{\text{ads}}$$

- $T\Delta S^\circ_{\text{ads}}$ is sizable and strongly depends on the adsorption reaction type, and masks the molecule–surface interaction
- **better and simpler to consider $\Delta H^\circ_{\text{ads}}$ instead**

Adsorption free energy vs. adsorption enthalpy

Definition

Gibbs free energy: G = energy: E + pV − TS = enthalpy: H − T entropy: S

$p \equiv$ pressure, $V \equiv$ volume, $T \equiv$ temperature

For chemical reactions:

$$\Delta X = X(\text{products}) - X(\text{reactants}), \qquad \text{where } X \equiv E, H, G, V, S$$

For adsorption:

$$\Delta G^\circ_{\text{ads}} = \Delta H^\circ_{\text{ads}} - T\Delta S^\circ_{\text{ads}}$$

- $T\Delta S^\circ_{\text{ads}}$ is sizable and strongly depends on the adsorption reaction type, and masks the molecule–surface interaction
- **better and simpler to consider $\Delta H^\circ_{\text{ads}}$ instead**

The "20/40" rule and adsorption enthalpy

$\Delta H^\circ_{\mathrm{ads}}$ is a more direct measure of the molecule–surface interaction than $\Delta G^\circ_{\mathrm{ads}}$

But:

- $\Delta H^\circ_{\mathrm{ads}}$ and $\Delta G^\circ_{\mathrm{ads}}$ can differ significantly due to $T\Delta S^\circ_{\mathrm{ads}}$
- the "20/40" rule was "parameterized" for $\Delta G^\circ_{\mathrm{ads}}$

$\Downarrow$

- phys/chem threshold values for $\Delta H^\circ_{\mathrm{ads}}$ are different

Yet according to the "20/40" rule:

- *weak* $\Delta H^\circ_{\mathrm{ads}}$ values $\Rightarrow$ physisorption
- *strong* $\Delta H^\circ_{\mathrm{ads}}$ values $\Rightarrow$ chemisorption

The "20/40" rule and adsorption enthalpy

$\Delta H^\circ_{\mathrm{ads}}$ is a more direct measure of the molecule–surface interaction than $\Delta G^\circ_{\mathrm{ads}}$

But:

- $\Delta H^\circ_{\mathrm{ads}}$ and $\Delta G^\circ_{\mathrm{ads}}$ can differ significantly due to $T\Delta S^\circ_{\mathrm{ads}}$
- the "20/40" rule was "parameterized" for $\Delta G^\circ_{\mathrm{ads}}$

$\Downarrow$

- phys/chem threshold values for $\Delta H^\circ_{\mathrm{ads}}$ are different

Yet according to the "20/40" rule:

- *weak* $\Delta H^\circ_{\mathrm{ads}}$ values $\Rightarrow$ physisorption
- *strong* $\Delta H^\circ_{\mathrm{ads}}$ values $\Rightarrow$ chemisorption

The "20/40" rule and adsorption enthalpy

$\Delta H^\circ_{\mathrm{ads}}$ is a more direct measure of the molecule–surface interaction than $\Delta G^\circ_{\mathrm{ads}}$

But:

- $\Delta H^\circ_{\mathrm{ads}}$ and $\Delta G^\circ_{\mathrm{ads}}$ can differ significantly due to $T\Delta S^\circ_{\mathrm{ads}}$
- the "20/40" rule was "parameterized" for $\Delta G^\circ_{\mathrm{ads}}$

$\Downarrow$

- phys/chem threshold values for $\Delta H^\circ_{\mathrm{ads}}$ are different

Yet according to the "20/40" rule:

- *weak* $\Delta H^\circ_{\mathrm{ads}}$ values $\Rightarrow$ physisorption
- *strong* $\Delta H^\circ_{\mathrm{ads}}$ values $\Rightarrow$ chemisorption

Adsorption modes: definitions

Physisorption

IUPAC: *physisorption involves intermolecular van der Waals forces, which do not involve a significant change in the electronic orbital patterns of the species involved.*

Wikipedia: *physisorption is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption.*

ionic bonding $\neq$ physisorption

although with respect to ions, electron-charge distribution is little affected

(but it is significant effected with respect to neutral species)

physisorption = (permanent) dipolar, induction, and dispersion interactions

Adsorption modes: definitions

Physisorption

IUPAC: *physisorption involves intermolecular van der Waals forces, which do not involve a significant change in the electronic orbital patterns of the species involved.*

Wikipedia: *physisorption is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption.*

Chemisorption

IUPAC: *adsorption which results from chemical bond formation (strong interaction) between the adsorbent and the adsorbate.*

ionic bonding $\neq$ physisorption

although with respect to ions, electron-charge distribution is little affected

(but it is significant effected with respect to neutral species)

physisorption = (permanent) dipolar, induction, and dispersion interactions

Adsorption modes: definitions

Physisorption

IUPAC: *physisorption involves intermolecular van der Waals forces, which do not involve a significant change in the electronic orbital patterns of the species involved.*

Wikipedia: *physisorption is a process in which the electronic structure of the atom or molecule is barely perturbed upon adsorption.*

Chemisorption

IUPAC: *adsorption which results from chemical bond formation (strong interaction) between the adsorbent and the adsorbate.*

ionic bonding $\neq$ physisorption

although with respect to ions, electron-charge distribution is little affected

(but it is significant effected with respect to neutral species)

physisorption = (permanent) dipolar, induction, and dispersion interactions

Phyisorption vs. chemisorption

- Physisorption interaction is weak:
  1 – 10 kJ/mol (for atom or diatomic molecule)

- Chemisorption interaction is strong:
  several 100 kJ/mol (strong chemisorption)

However:

- **chemisorption interaction is short ranged and directional**
  (a chemisorbed molecule forms one or a few chemical bonds with the surface)

- **physisorption interaction is long ranged and non-directional**
  (a large molecule forms many weak physisorption interactions)
  $\Downarrow$
  physisorption energy scales with the molecular size

Physisorption energy of an elephant is stronger than super strong chemisorption energy. But, it is an elephant!

Phyisorption vs. chemisorption

- Physisorption interaction is weak:
  1 – 10 kJ/mol (for atom or diatomic molecule)

- Chemisorption interaction is strong:
  several 100 kJ/mol (strong chemisorption)

However:

- **chemisorption interaction is short ranged and directional**
  (a chemisorbed molecule forms one or a few chemical bonds with the surface)

- **physisorption interaction is long ranged and non-directional**
  (a large molecule forms many weak physisorption interactions)
  $\Downarrow$
  physisorption energy scales with the molecular size

Physisorption energy of an elephant is stronger than super strong chemisorption energy. But, it is an elephant!

Phyisorption vs. chemisorption

- Physisorption interaction is weak:
  1 – 10 kJ/mol (for atom or diatomic molecule)

- Chemisorption interaction is strong:
  several 100 kJ/mol (strong chemisorption)

However:

- **chemisorption interaction is short ranged and directional**
  (a chemisorbed molecule forms one or a few chemical bonds with the surface)

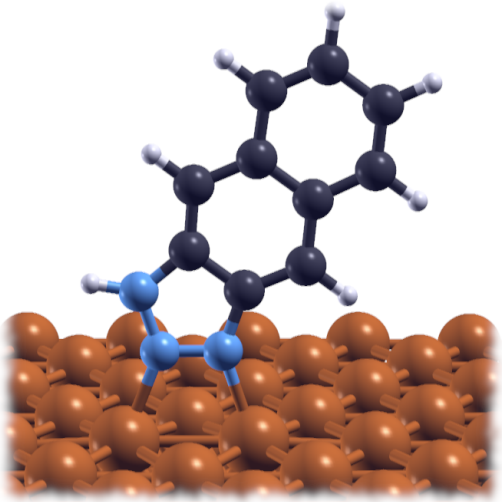
- **physisorption interaction is long ranged and non-directional**
  (a large molecule forms many weak physisorption interactions)
  $\Downarrow$
  physisorption energy scales with the molecular size

Physisorption energy of an elephant is stronger than super strong chemisorption energy. But, it is an elephant!

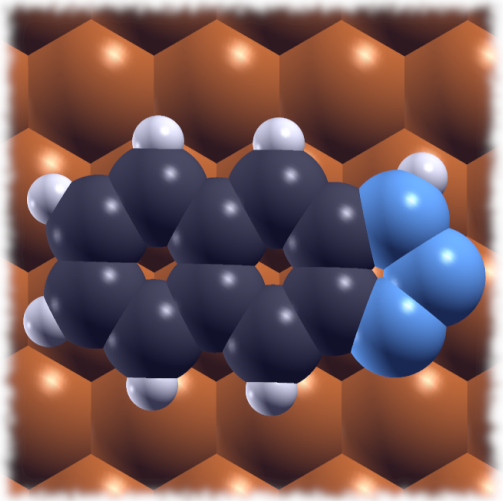
Molecular adsorption on metal surfaces (based on DFT)

Kokalj et al., ChemPhysChem **12**, 3547–3555

naphthotriazole @ Cu(111)



$\Delta E_{ads} = -66$ kJ/mol

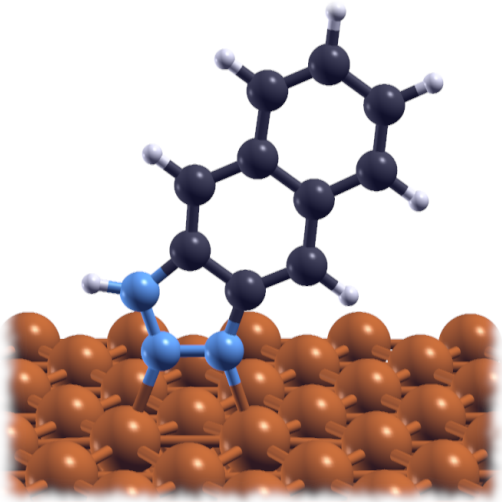


$\Delta E_{ads} = -99$ kJ/mol

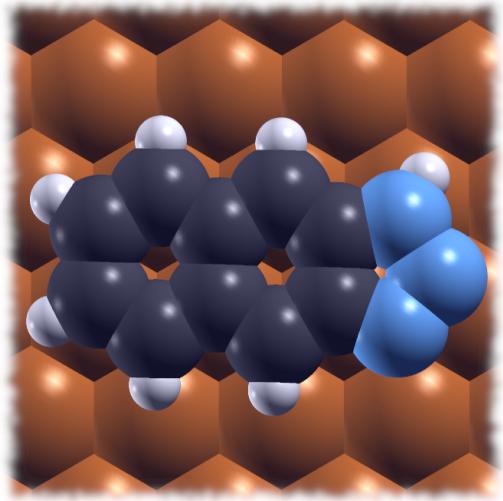
Molecular adsorption on metal surfaces (based on DFT)

Kokalj et al., ChemPhysChem **12**, 3547–3555

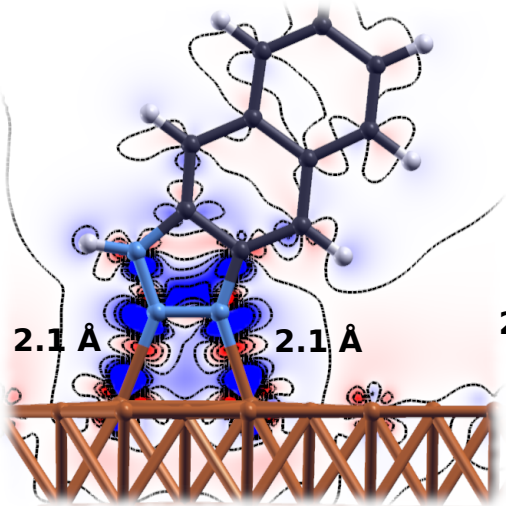
naphthotriazole @ Cu(111)

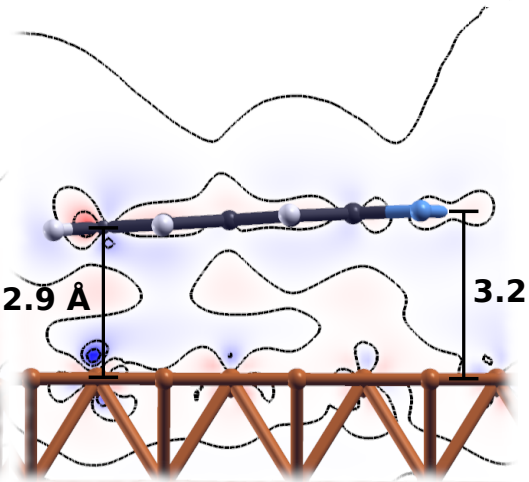


$\Delta E_{ads} = -66$ kJ/mol



$\Delta E_{ads} = -99$ kJ/mol



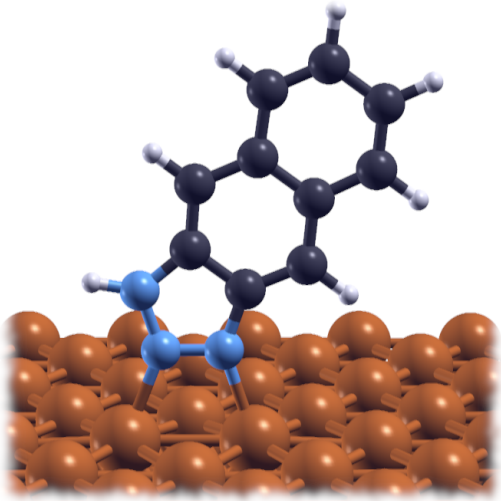


electron-density difference: $\Delta\rho(\boldsymbol{r}) = \rho_{\mathrm{mol/surf}}(\boldsymbol{r}) - \rho_{\mathrm{mol}}(\boldsymbol{r}) - \rho_{\mathrm{surf}}(\boldsymbol{r})$

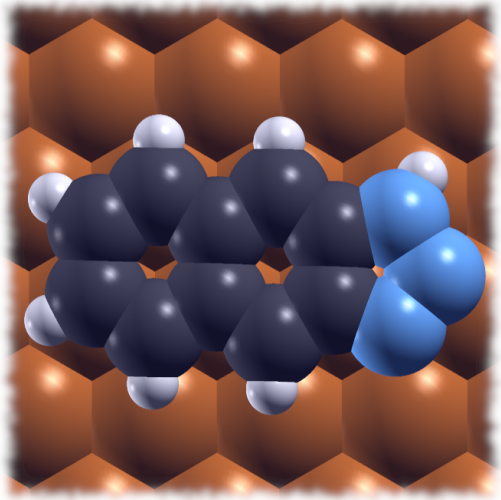
Molecular adsorption on metal surfaces (based on DFT)

Kovačević et al., Mater. Chem. Phys. **137**, 331–339

naphthotriazole @ Cu(111)

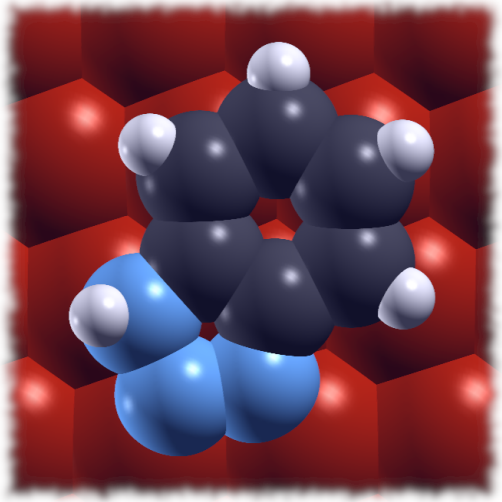


$\Delta E_{ads} = -66$ kJ/mol

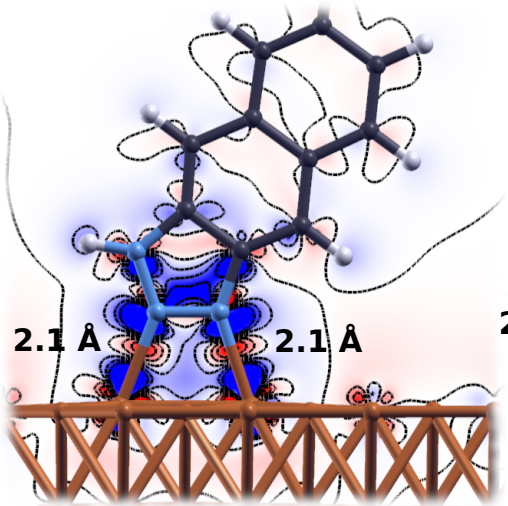


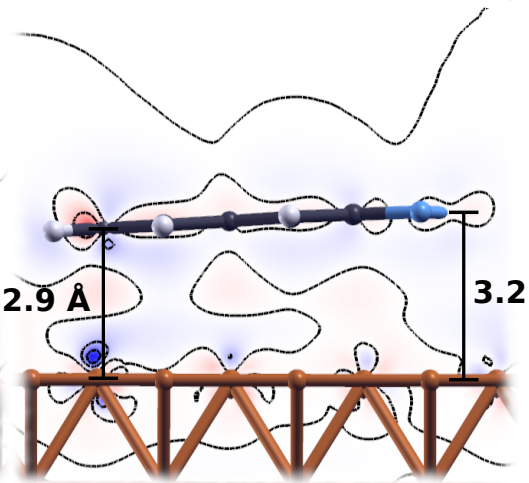
$\Delta E_{ads} = -99$ kJ/mol

benzotriazole @ Fe(110)

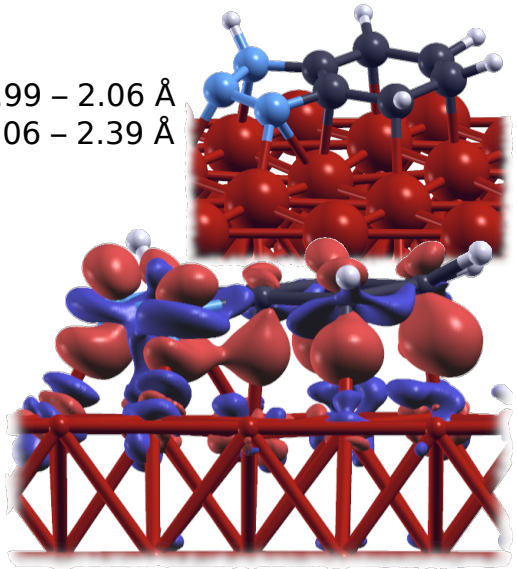


$\Delta E_{ads} = -130$ kJ/mol





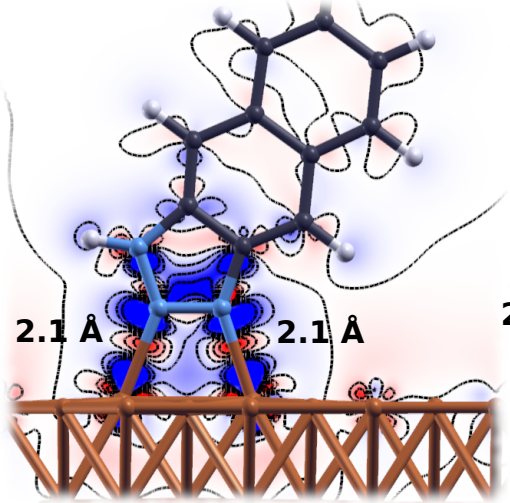
$d_{N–Fe} = 1.99 – 2.06$ Å
$d_{C–Fe} = 2.06 – 2.39$ Å



electron-density difference: $\Delta\rho(\boldsymbol{r}) = \rho_{\mathrm{mol/surf}}(\boldsymbol{r}) - \rho_{\mathrm{mol}}(\boldsymbol{r}) - \rho_{\mathrm{surf}}(\boldsymbol{r})$

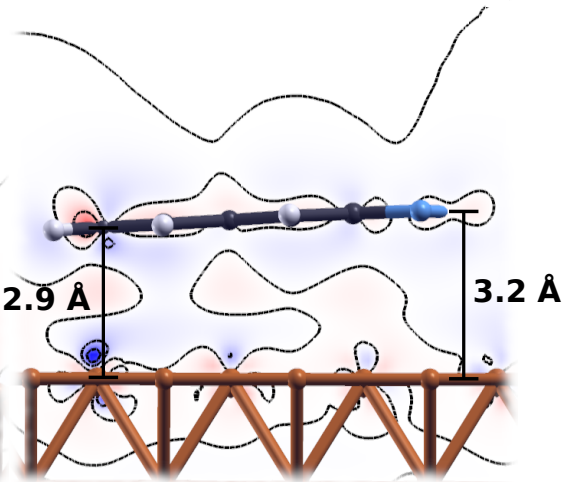
Molecular adsorption on metal surfaces

weak chemisorption



$\Delta E_{ads} = -66$ kJ/mol

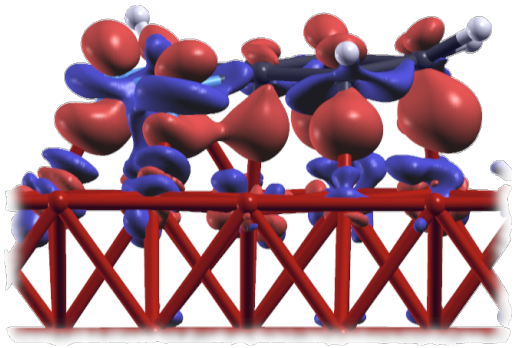
physisorption



$\Delta E_{ads} = -99$ kJ/mol

chemisorption

$d_{N–Fe} = 1.99 – 2.06$ Å
$d_{C–Fe} = 2.06 – 2.39$ Å



$\Delta E_{ads} = -130$ kJ/mol

⇓

physisorption energy can be strong for larger molecules

⇓

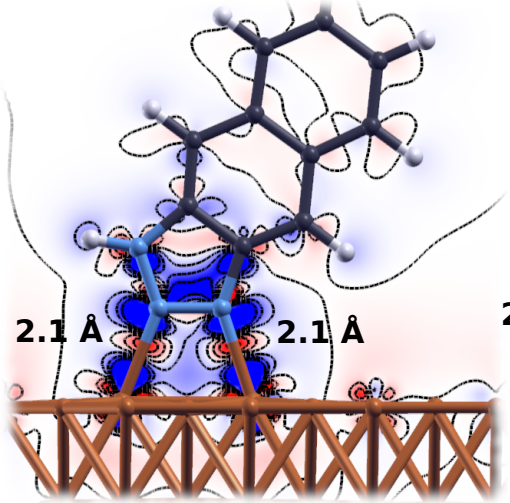
physisorption can become stronger than chemisorption

Experimental confirmation:

- G. Scoles et al., J. Phys. Chem. B 102 (1998) 3456–3465
  J. Phys. Chem. B 102 (1998) 9266–9275
- F. Schreiber, Prog. Surf. Sci. 65 (2000) 151–257

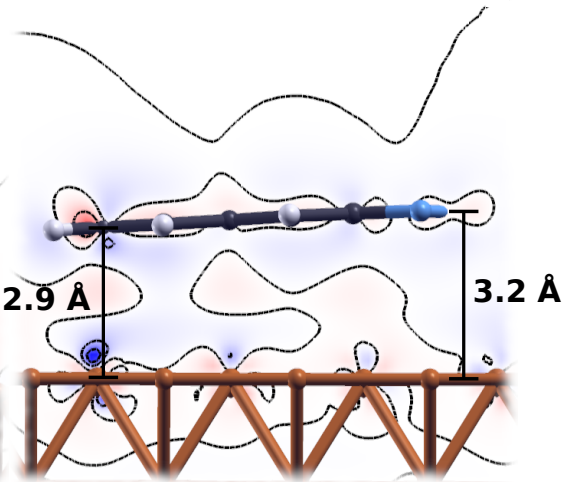
Molecular adsorption on metal surfaces

weak chemisorption



$\Delta E_{ads} = -66$ kJ/mol

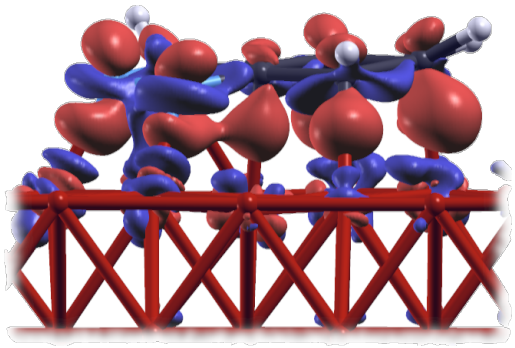
physisorption



$\Delta E_{ads} = -99$ kJ/mol

chemisorption

$d_{N–Fe} = 1.99 – 2.06$ Å
$d_{C–Fe} = 2.06 – 2.39$ Å



$\Delta E_{ads} = -130$ kJ/mol

$\Downarrow$

physisorption energy can be strong for larger molecules

$\Downarrow$

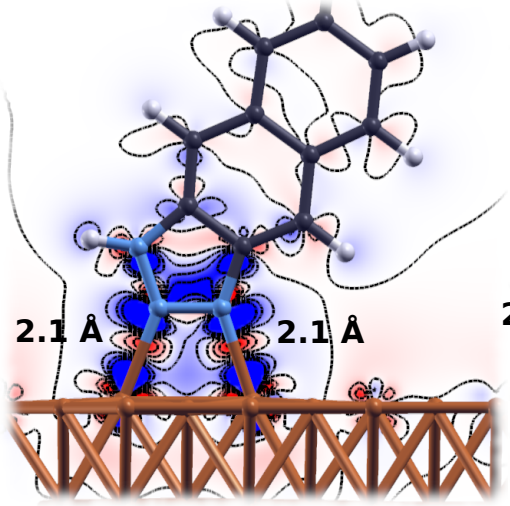
physisorption can become stronger than chemisorption

Experimental confirmation:

- G. Scoles et al., J. Phys. Chem. B 102 (1998) 3456–3465
  J. Phys. Chem. B 102 (1998) 9266–9275
- F. Schreiber, Prog. Surf. Sci. 65 (2000) 151–257

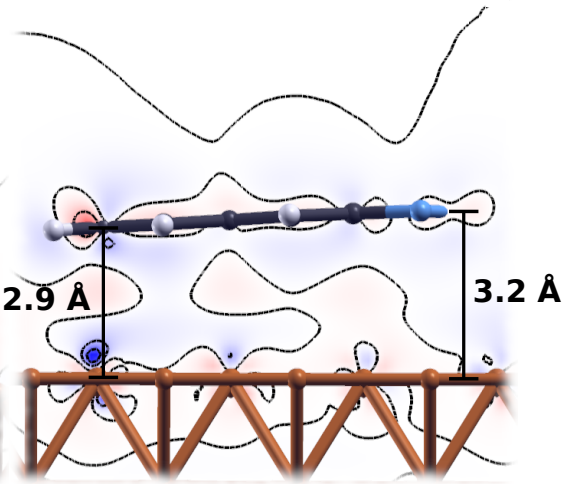
Molecular adsorption on metal surfaces

weak chemisorption



$\Delta E_{ads} = -66$ kJ/mol

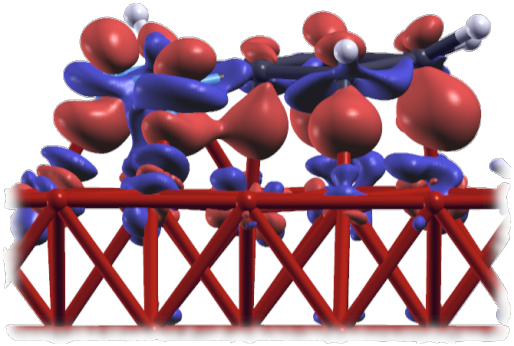
physisorption



$\Delta E_{ads} = -99$ kJ/mol

chemisorption

$d_{N–Fe} = 1.99 – 2.06$ Å
$d_{C–Fe} = 2.06 – 2.39$ Å



$\Delta E_{ads} = -130$ kJ/mol

$\Downarrow$

physisorption energy can be strong for larger molecules

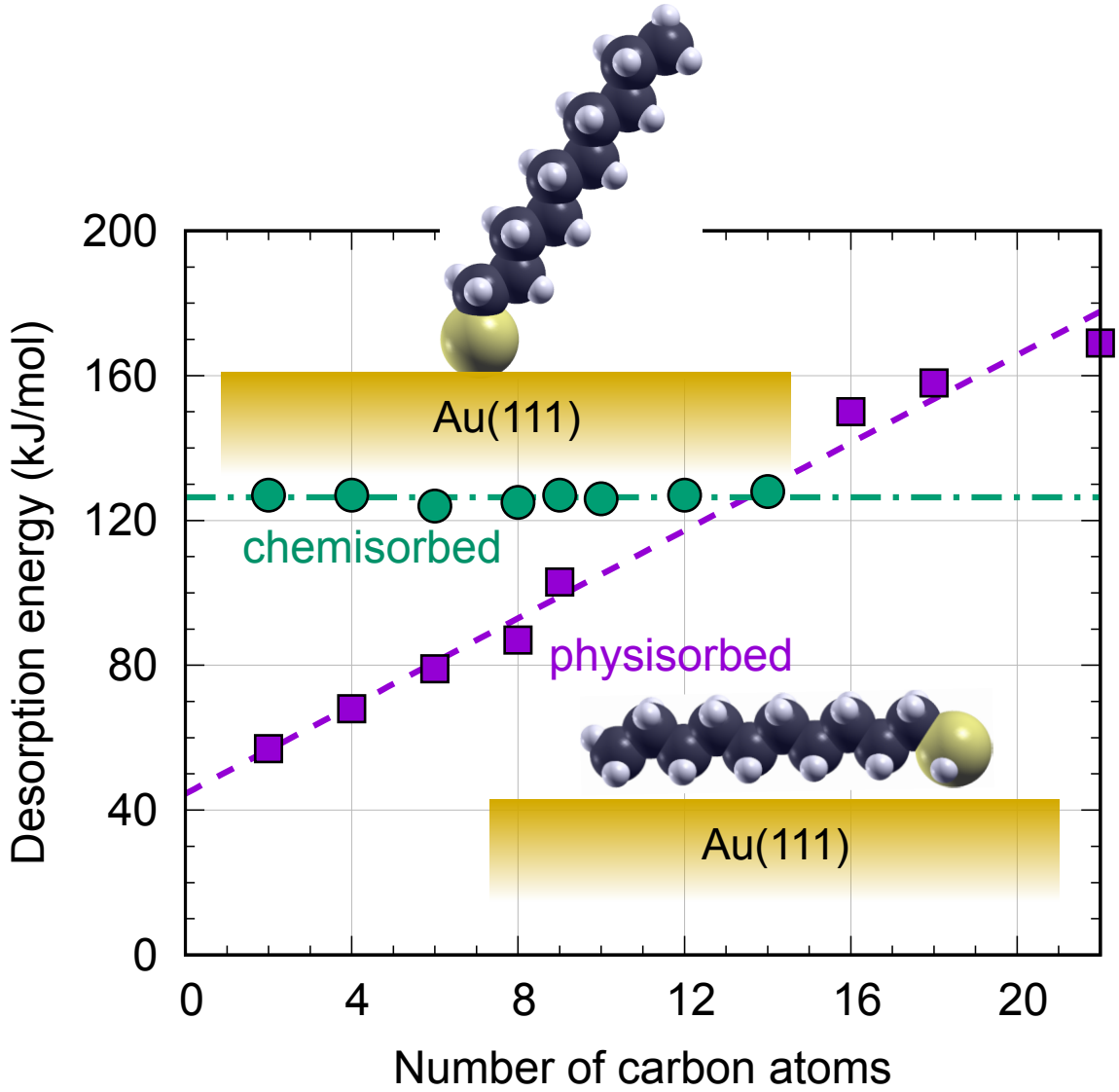
$\Downarrow$

physisorption can become stronger than chemisorption

Experimental confirmation:

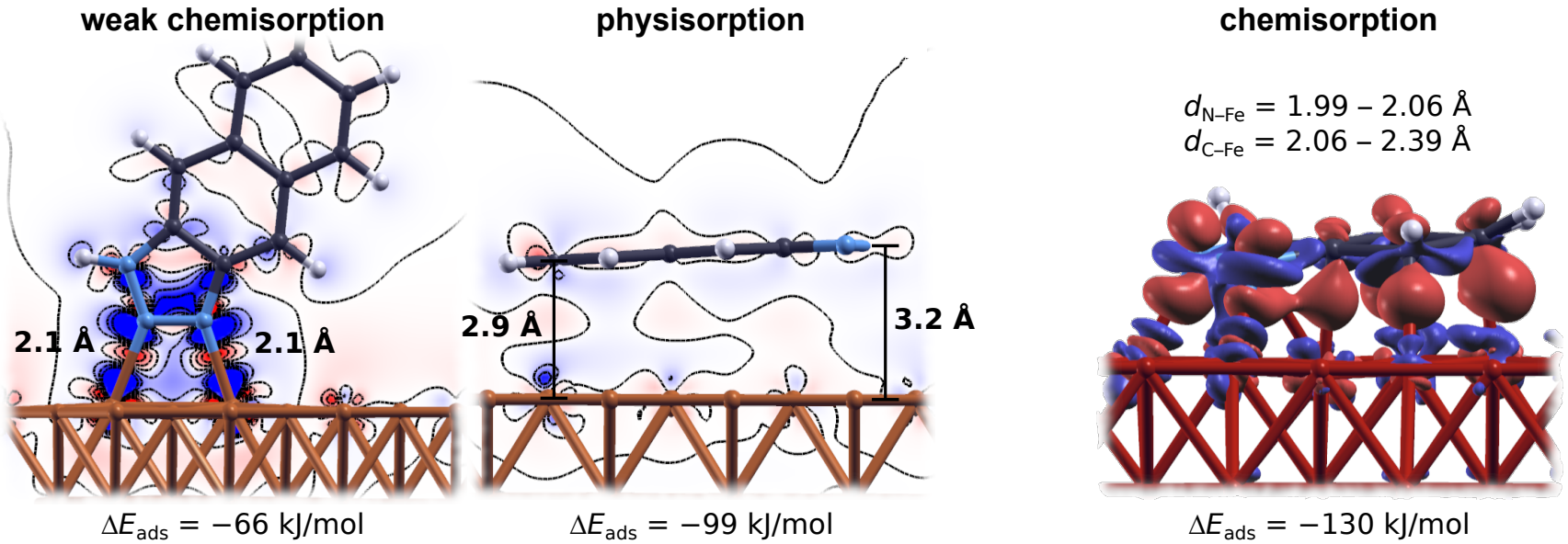
- G. Scoles et al., J. Phys. Chem. B 102 (1998) 3456–3465
  J. Phys. Chem. B 102 (1998) 9266–9275
- F. Schreiber, Prog. Surf. Sci. 65 (2000) 151–257

Alkanthiols @ Au(111): experimental data



G. Scoles et al., J. Phys. Chem. B 102 (1998) 3456–3465, doi: 10.1021/jp980047v

Molecular adsorption on metal surfaces



Good criteria to distinguish between physisorption and chemisorption:

(i) electron-density difference: $\Delta\rho(\boldsymbol{r}) = \rho_{\mathrm{mol/surf}}(\boldsymbol{r}) - \rho_{\mathrm{mol}}(\boldsymbol{r}) - \rho_{\mathrm{surf}}(\boldsymbol{r})$

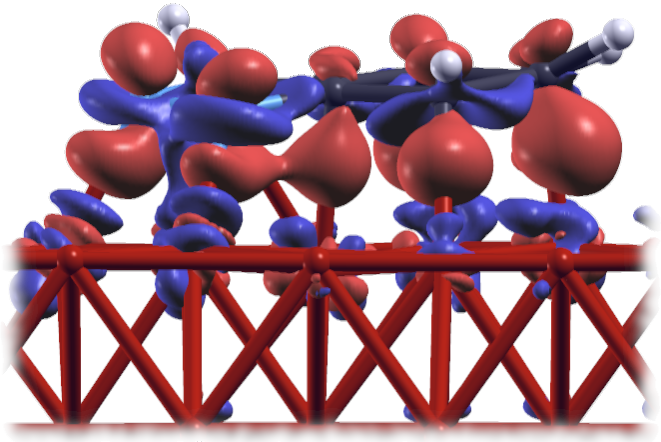
- **physisorption:** almost no electron-density redistribution
- **chemisorption:** strong electron-density redistribution (appearance of bonds)

(ii) molecule–surface distance: $d_{\mathrm{mol-surf}}$

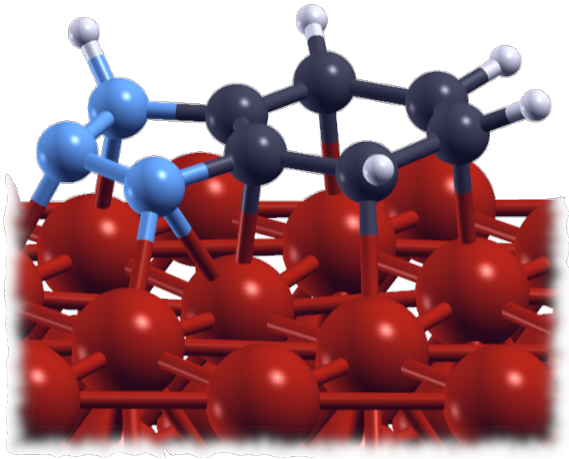
- **physisorption:** $d_{\mathrm{mol-surf}} \approx$ sum of van der Waals radii ≈ 3 Å
- **chemisorption:** $d_{\mathrm{mol-surf}} \approx$ sum of covalent radii ≈ 2 Å

Molecular distortion during adsorption

benzotriazole @ Fe(110)



$\Delta E_{\text{ads}} = -130$ kJ/mol



substantial $\Delta\rho(\boldsymbol{r})$ suggests a stronger bonding than ΔE_{ads} of -130 kJ/mol

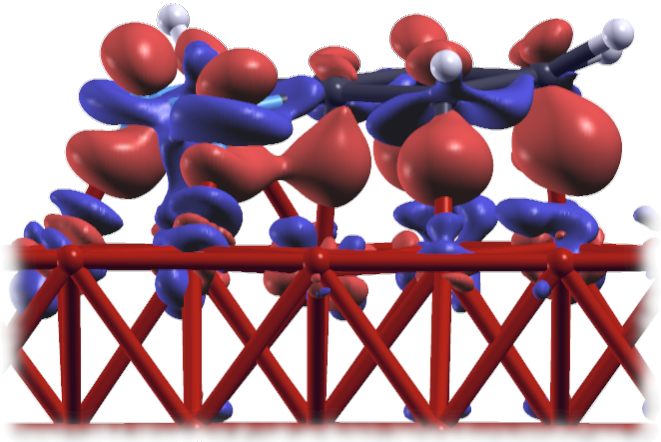
$\Downarrow$

relatively weak E_{ads} is due to a considerable molecular distortion

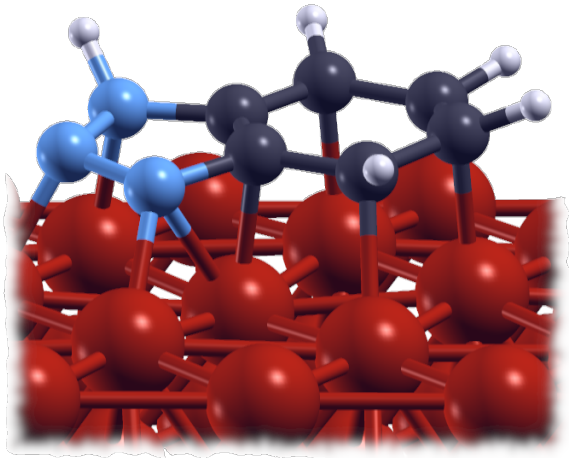
- rigid binding energy: -303 kJ/mol $\quad (E_{\text{b}}^{\text{rigid}} = E_{\text{mol/surf}} - E_{\text{mol}}^{\text{rigid}} - E_{\text{surf}}^{\text{rigid}})$
- cost of molecular distortion: 159 kJ/mol
- cost of substrate distortion: 14 kJ/mol

Molecular distortion during adsorption

benzotriazole @ Fe(110)



$\Delta E_{\text{ads}} = -130$ kJ/mol



substantial $\Delta\rho(\boldsymbol{r})$ suggests a stronger bonding than ΔE_{ads} of -130 kJ/mol

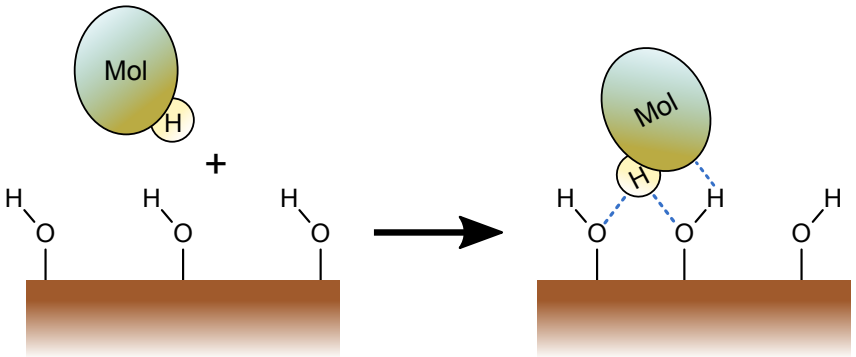
$\Downarrow$

relatively weak E_{ads} is due to a considerable molecular distortion

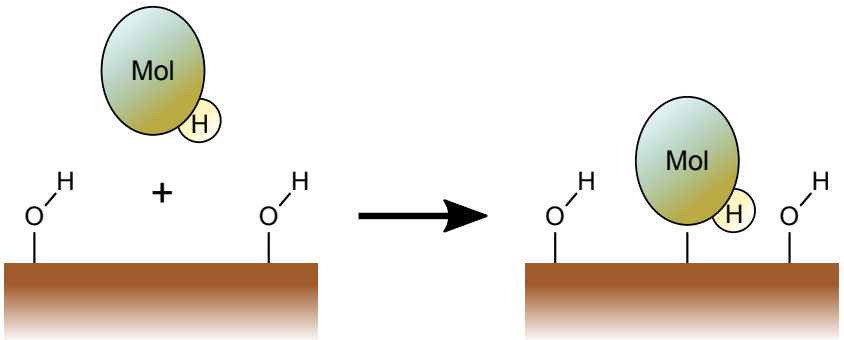
- rigid binding energy: -303 kJ/mol $\quad (E_{\text{b}}^{\text{rigid}} = E_{\text{mol/surf}} - E_{\text{mol}}^{\text{rigid}} - E_{\text{surf}}^{\text{rigid}})$
- cost of molecular distortion: 159 kJ/mol
- cost of substrate distortion: 14 kJ/mol

Bond-breaking and bond-making during adsorption

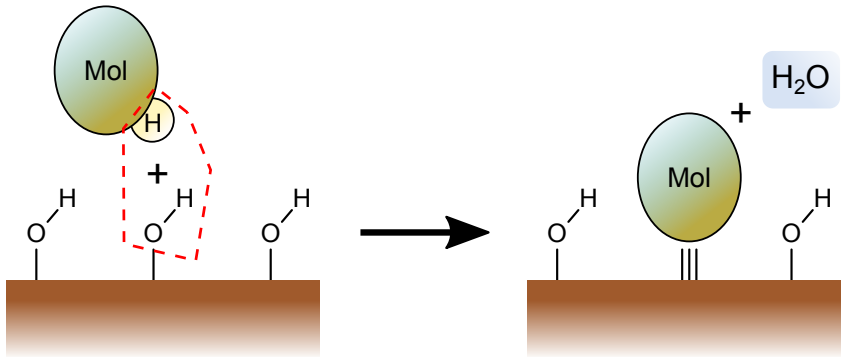
MolH + * → MolH*



plain adsorption (only bond-making)



MolH + OH* → Mol* + H_2O



condensation adsorption (also bond-breaking)

bond-breaking costs !

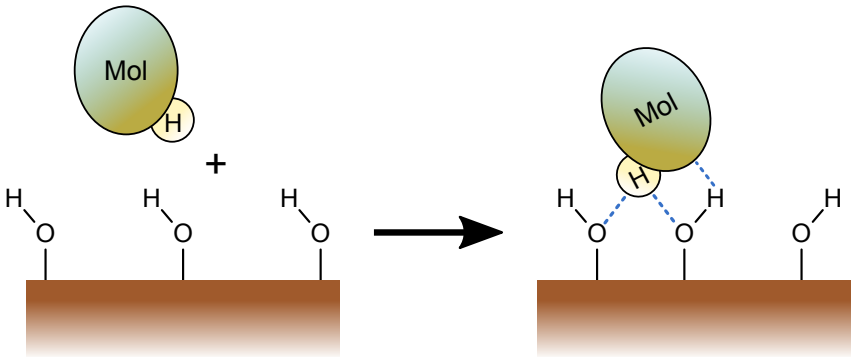
* = adsorption site

X* = adsorbed species

$$\Delta G^\circ_{\text{ads}} = \Delta H^\circ_{\text{ads}} - T\Delta S^\circ_{\text{ads}}$$

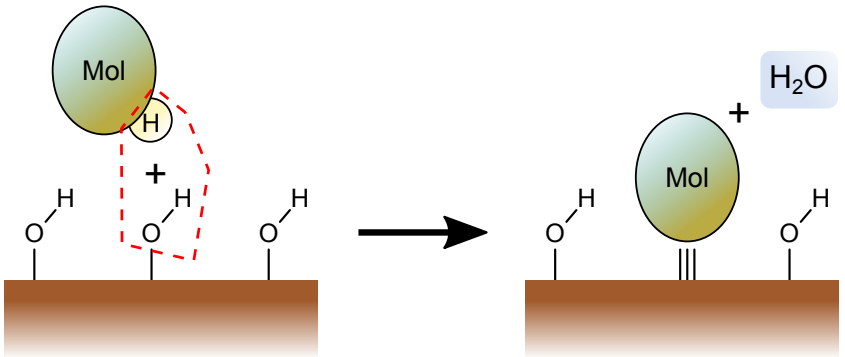
Bond-breaking and bond-making during adsorption

MolH + * → MolH*

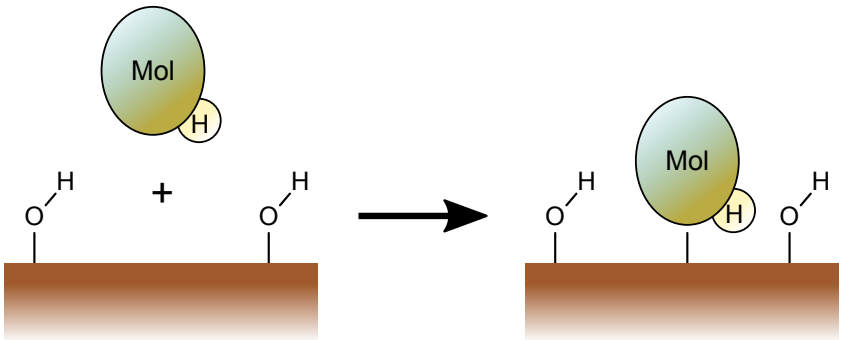


plain adsorption (only bond-making)

MolH + OH* → Mol* + H_2O



condensation adsorption (also bond-breaking)



bond-breaking costs !

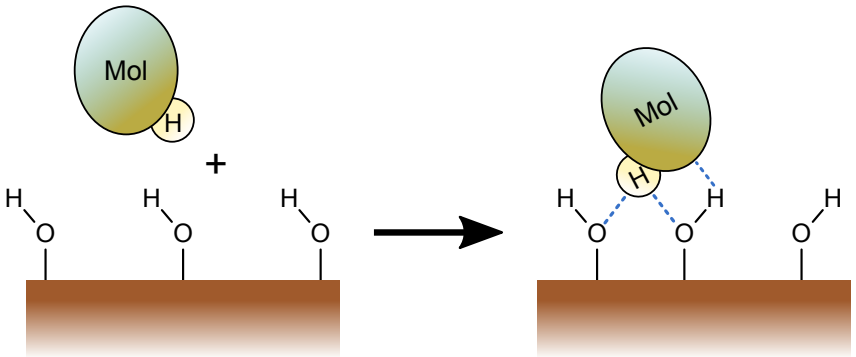
* = adsorption site
X* = adsorbed species

$$\Delta G^\circ_{\mathrm{ads}} = \Delta H^\circ_{\mathrm{ads}} - T\Delta S^\circ_{\mathrm{ads}}$$

considerably different for plain and condensation adsorption

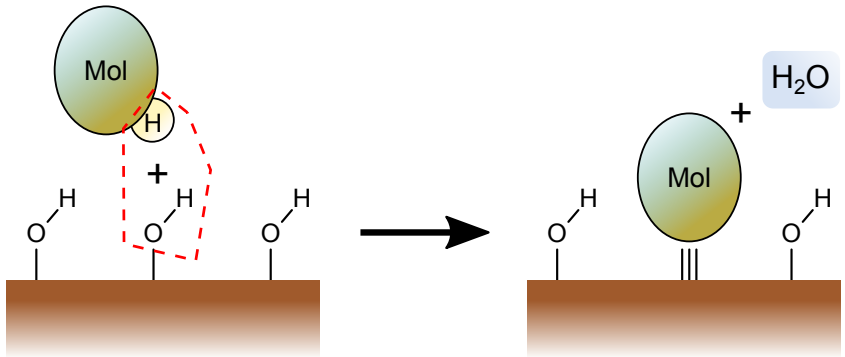
Bond-breaking and bond-making during adsorption

MolH + * → MolH*

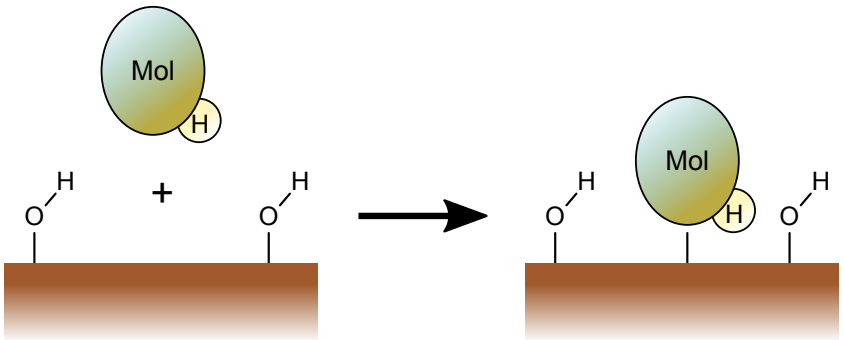


plain adsorption (only bond-making)

MolH + OH* → Mol* + H_2O



condensation adsorption (also bond-breaking)



bond-breaking costs !

* = adsorption site
X* = adsorbed species

$$\Delta G^\circ_{\text{ads}} = \Delta H^\circ_{\text{ads}} - T\Delta S^\circ_{\text{ads}}$$

TS of liberated $H_2O \approx 50$ kJ/mol at $p = 1$ atm, $T = 300$ K

About the entropy

Molecular species:

$$S = S_{\mathrm{tr}} + S_{\mathrm{rot}} + S_{\mathrm{vib}} + \cdots$$

rotational

translational

vibrational

Solids (surf & mol/surf)**:**

$$S = S_{\mathrm{vib}} + S_{\mathrm{configurational}} + \cdots$$

typically neglected

About the entropy

Molecular species:

$$S = S_{\mathrm{tr}} + S_{\mathrm{rot}} + S_{\mathrm{vib}} + \cdots$$

rotational

translational

vibrational

Solids (surf & mol/surf)**:**

$$S = S_{\mathrm{vib}} + S_{\mathrm{configurational}} + \cdots$$

typically neglected

Adsorption: mol + * $\rightarrow$ mol*

About the entropy

Molecular species:

$$S = S_{\mathrm{tr}} + S_{\mathrm{rot}} + S_{\mathrm{vib}} + \cdots$$

rotational; translational; vibrational

Solids (surf & mol/surf)**:**

$$S = S_{\mathrm{vib}} + S_{\mathrm{configurational}} + \cdots$$

typically neglected

Adsorption: mol + * → mol*

$$\Delta S_{\mathrm{ads}} = S(\mathrm{products}) - S(\mathrm{reactants})$$

$$= [S_{\mathrm{vib}}(\mathrm{mol/surf}) - S_{\mathrm{vib}}(\mathrm{surf}) - S_{\mathrm{vib}}(\mathrm{mol})] + [\,0 - S_{\mathrm{tr+rot}}(\mathrm{mol})\,] + \cdots$$

roto-transl. contribution of mol/surf & surf

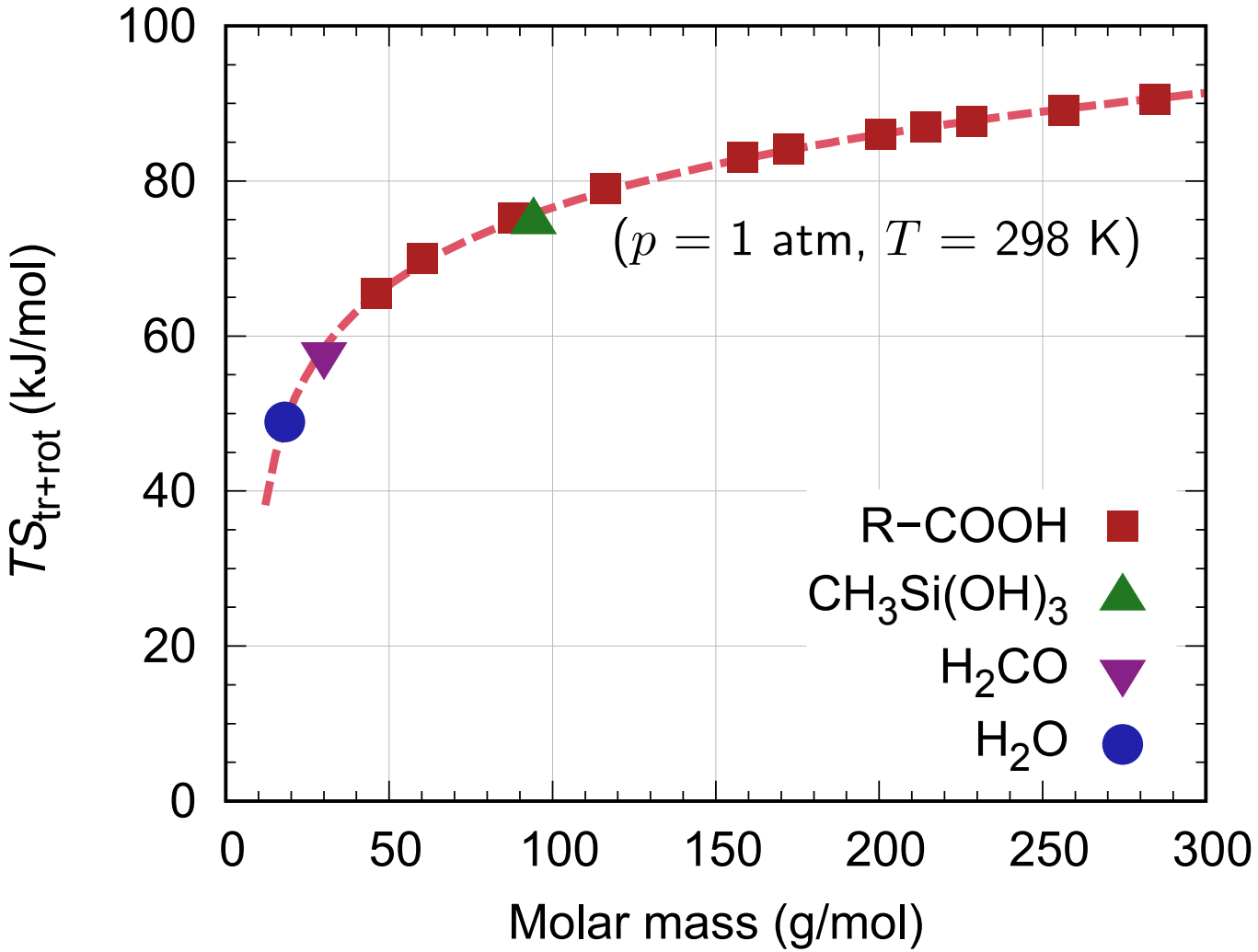
substantial cancellation ($T\Delta S_{\mathrm{vib}}$ usually within ±10 kJ/mol) (at $T = 300$ K)

$-T\Delta S_{\mathrm{ads}}^{\mathrm{tr+rot}} = TS_{\mathrm{tr+rot}}(\mathrm{mol}) > 0$ (sizable positive contribution)

Roto-translational contribution

For molecules: $S_{\mathrm{tr+rot}} \propto \log m$

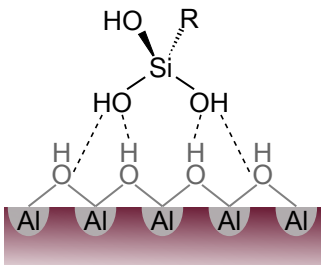
molecular mass



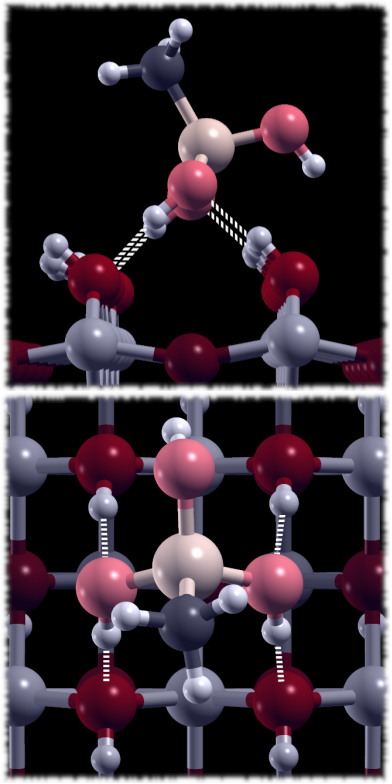
Plain vs. condensation adsorption

$CH_3Si(OH)_3$ @ γ–AlOOH(010)

$CH_3Si(OH)_3 + * \rightarrow CH_3Si(OH)_3*$

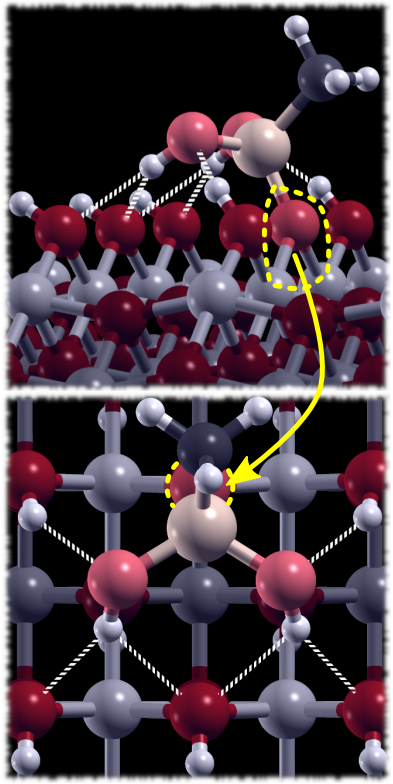


$CH_3Si(OH)_3$:
loss of roto-transl.: 75 kJ/mol

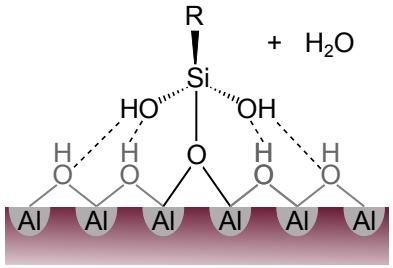


ΔH°_{ads} = −83 kJ/mol
ΔG°_{ads} = −4 kJ/mol

$CH_3Si(OH)_3 + OH* \rightarrow CH_3Si(OH)_2O* + H_2O$



ΔH°_{ads} = −46 kJ/mol
ΔG°_{ads} = −21 kJ/mol



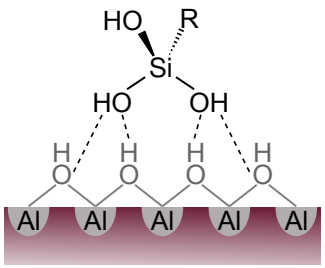
$CH_3Si(OH)_3$: loss of roto-transl.: 75 kJ/mol
H_2O: gain of roto-transl. −49 kJ/mol

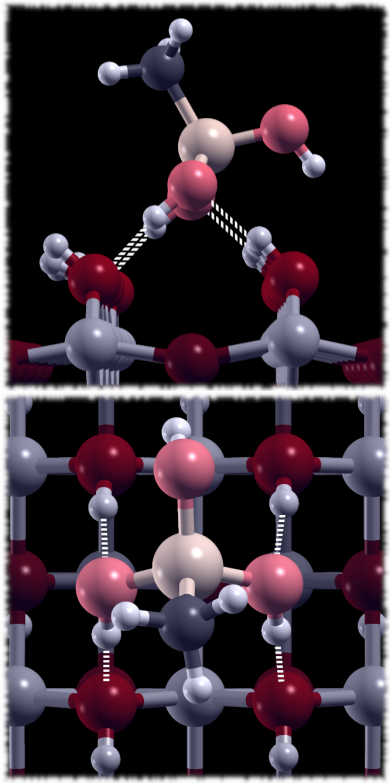
p = 1 atm, T = 298 K

Plain vs. condensation adsorption

$CH_3Si(OH)_3$ @ γ–AlOOH(010)

$CH_3Si(OH)_3 + * \rightarrow CH_3Si(OH)_3*$



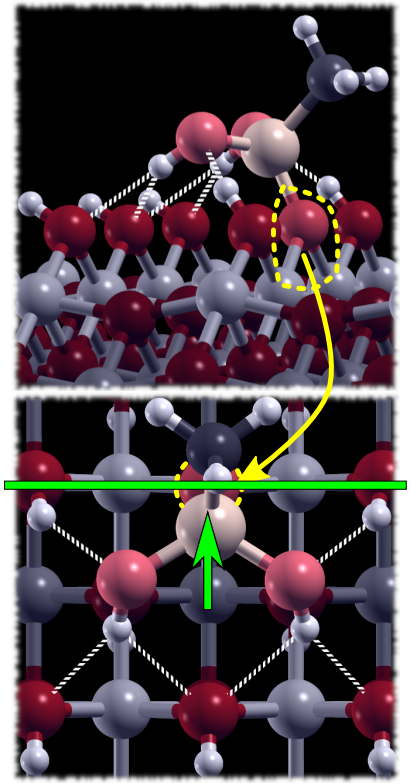


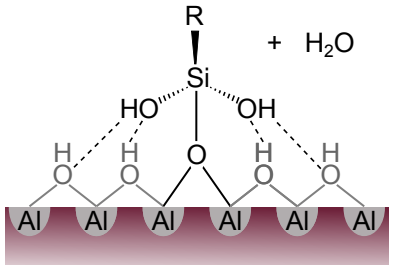
$CH_3Si(OH)_3$:
loss of roto-transl.: 75 kJ/mol

p = 1 atm, T = 298 K

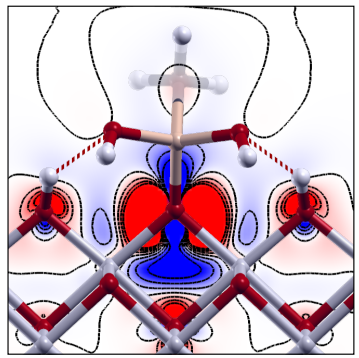
ΔH°_{ads} = −83 kJ/mol
ΔG°_{ads} = −4 kJ/mol

$CH_3Si(OH)_3 + OH^* \rightarrow CH_3Si(OH)_2O^* + H_2O$





$CH_3Si(OH)_3$: loss of roto-transl.: 75 kJ/mol
H_2O: gain of roto-transl. −49 kJ/mol



$\Delta\rho(\boldsymbol{r})$

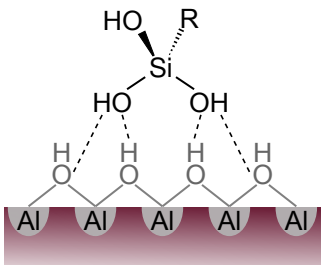
ΔH°_{ads} = −46 kJ/mol
ΔG°_{ads} = −21 kJ/mol

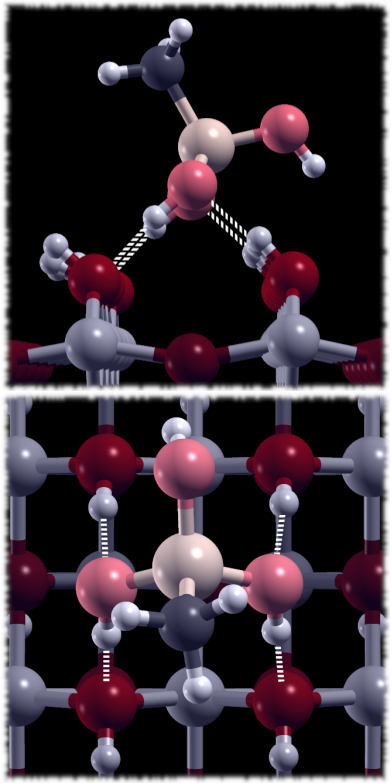
the "20/40" rule: physisorption

Plain vs. condensation adsorption

$CH_3Si(OH)_3$ @ γ–AlOOH(010)

$CH_3Si(OH)_3 + * \rightarrow CH_3Si(OH)_3*$



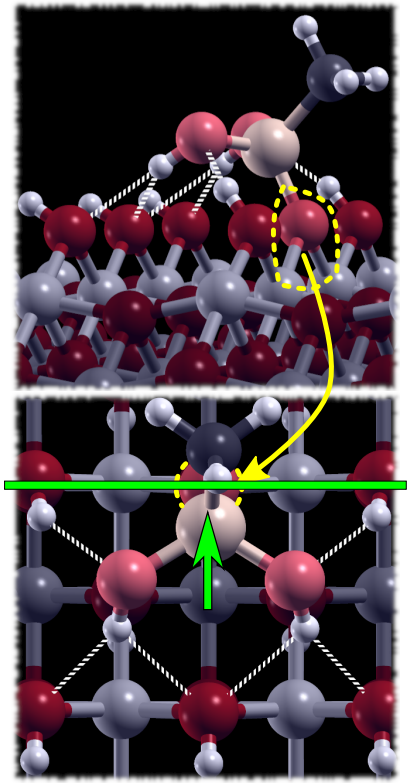


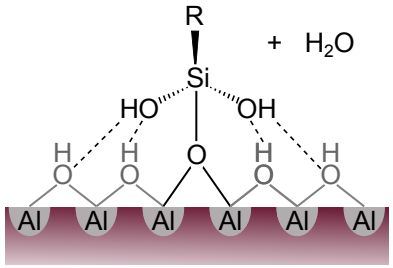
$CH_3Si(OH)_3$:
loss of roto-transl.: 75 kJ/mol

p = 1 atm, T = 298 K

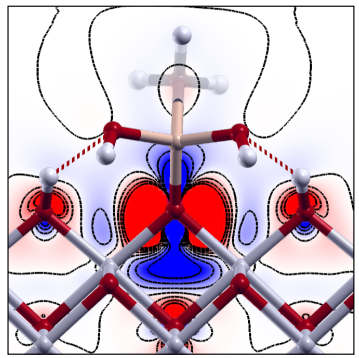
ΔH°_{ads} = −83 kJ/mol
ΔG°_{ads} = −4 kJ/mol

$CH_3Si(OH)_3 + OH^* \rightarrow CH_3Si(OH)_2O^* + H_2O$





$CH_3Si(OH)_3$: loss of roto-transl.: 75 kJ/mol
H_2O: gain of roto-transl. −49 kJ/mol



$\Delta\rho(\boldsymbol{r})$

ΔH°_{ads} = −46 kJ/mol
ΔG°_{ads} = −21 kJ/mol

the "20/40" rule: physisorption

Conclusions

- **$\Delta H^\circ_{\mathrm{ads}}$ and $\Delta G^\circ_{\mathrm{ads}}$ are not reliable criteria to distinguish between physisorption and chemisorption**

  (i) ΔG_{ads}: loss of "roto-translation" during adsorption
  (depends on the adsorption reaction type)

  (ii) physisorption energy scales with the size of the molecule
  (it is weak only for small molecules)

  (iii+iv) chemisorption can display "weak" $\Delta H^\circ_{\mathrm{ads}}$
  - (iii) due to bond-breaking
  - (iv) due to substantial molecular deformation

For further info, see: A. Kokalj, Corros. Sci. 196 (2022) 109939

Conclusions

- **$\Delta H^\circ_{\mathrm{ads}}$ and $\Delta G^\circ_{\mathrm{ads}}$ are not reliable criteria to distinguish between physisorption and chemisorption**

  (i) ΔG_{ads}: loss of "roto-translation" during adsorption
  (depends on the adsorption reaction type)

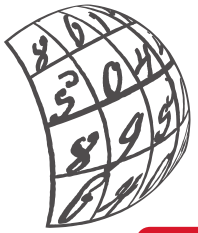
  (ii) physisorption energy scales with the size of the molecule
  (it is weak only for small molecules)

  (iii+iv) chemisorption can display "weak" $\Delta H^\circ_{\mathrm{ads}}$
  - (iii) due to bond-breaking
  - (iv) due to substantial molecular deformation

- **good criteria:**
  - modeling: molecule–surface bond distances & electronic structure analysis
    (electron-density difference, $\Delta\rho(\boldsymbol{r})$)
  - experiment: spectroscopy

For further info, see: A. Kokalj, Corros. Sci. 196 (2022) 109939

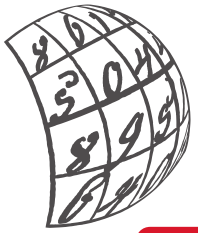
Acknowledgments



P2-0393

- Matic Poberžnik
- Nataša Kovačević

Acknowledgments



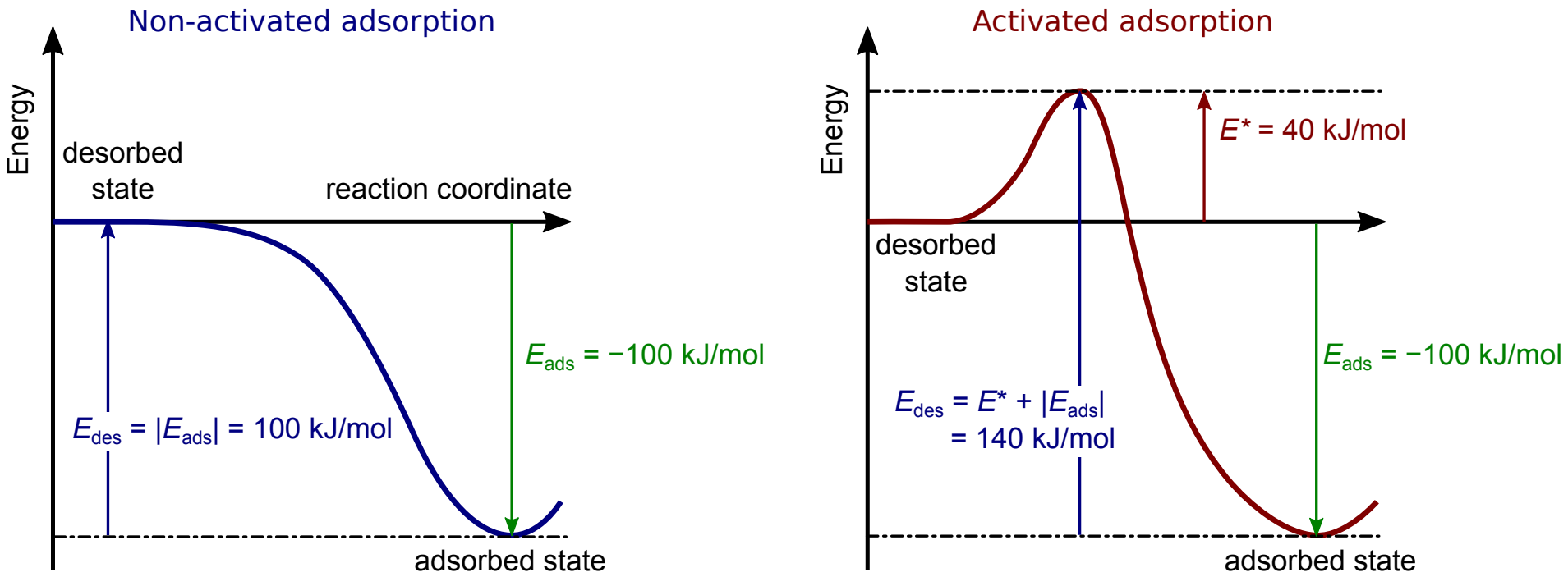
P2-0393

arrs
SLOVENIAN RESEARCH AGENCY

- Matic Poberžnik
- Nataša Kovačević

Thank you for your attention

Plain vs. activated adsorption

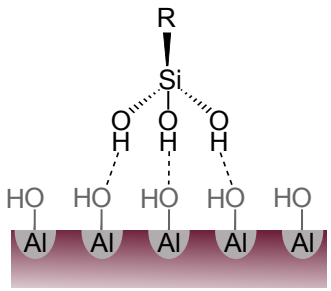


$\tau = \nu^{-1} \exp(\frac{E_{\mathrm{des}}}{RT}) \approx 30$ s ⟵ T = 298 K ⟶ $\tau = \nu^{-1} \exp(\frac{E_{\mathrm{des}}}{RT}) \approx 10$ years

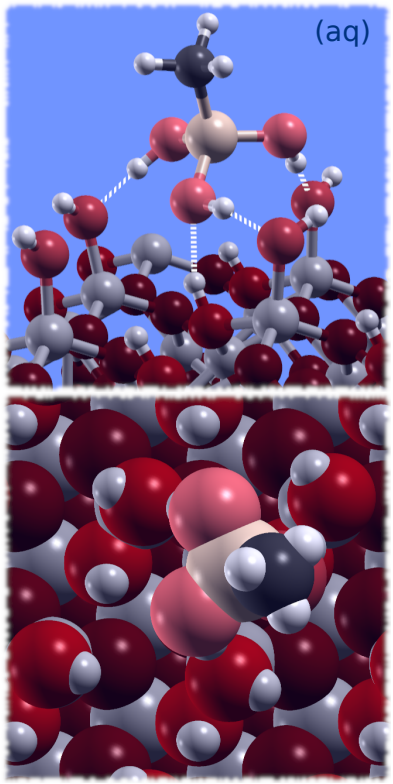
(assumed value for desorption: $\nu = 10^{16}$ s^{-1})

$CH_3Si(OH)_3$ @ α–$Al_2O_3(001)$ [solid/liquid interface]

$CH_3Si(OH)_3 + * \rightarrow CH_3Si(OH)_3*$

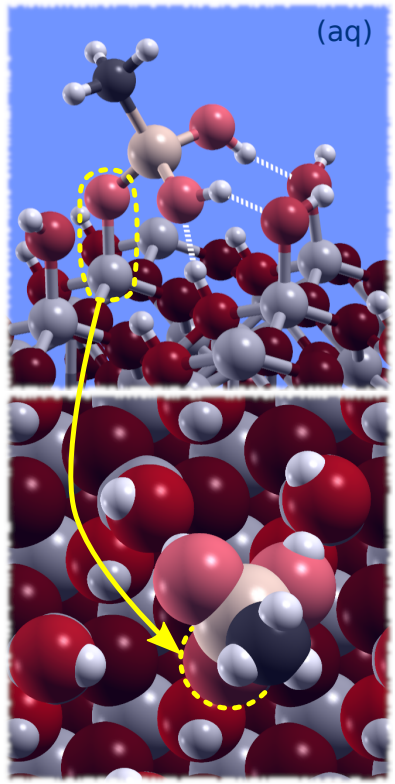


$CH_3Si(OH)_3$:
loss of roto-transl.: 67 kJ/mol

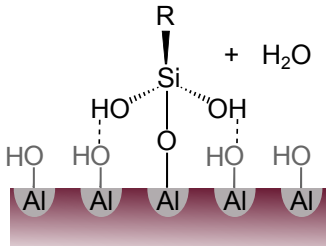


ΔH°_{ads} = −58 kJ/mol
ΔG°_{ads} = +2 kJ/mol

$CH_3Si(OH)_3 + OH* \rightarrow CH_3Si(OH)_2O* + H_2O$



ΔH°_{ads} = −73 kJ/mol
ΔG°_{ads} = −37 kJ/mol



$CH_3Si(OH)_3$: loss of roto-transl.: 67 kJ/mol
H_2O: gain of roto-transl. −31 kJ/mol

c = 1 M, T = 298 K

About the entropy

Molecular species:

$$S = S_{\mathrm{tr}} + S_{\mathrm{rot}} + S_{\mathrm{vib}} + \cdots$$

rotational

translational

vibrational

Approximations:

molecular mass

$$S_{\mathrm{tr}} + S_{\mathrm{rot}} \propto \ln m$$

- ideal gas: $S_{\mathrm{tr}} = R\Big(\ln \Big[\Big(\frac{m\, kT}{2\pi\hbar^2} \Big)^{\frac{3}{2}} V \Big] + \frac{5}{2} \Big)$

$V = kT/p \quad \Rightarrow \quad G(T) = G^{\circ}(T) + RT \ln \frac{p}{p^{\circ}}$

- rigid rotor: $S_{\mathrm{rot}} = R\Big(\ln \Big[\frac{\sqrt{8\pi (kT)^3\, I_{\mathrm{A}} I_{\mathrm{B}} I_{\mathrm{C}}}}{\sigma_{\mathrm{rot}} \hbar^3} \Big] + \frac{3}{2} \Big)$

moment of inertia eigenvalues

- harmonic oscillator: $S_{\mathrm{vib}} = R \sum_i \mathrm{f}(\nu_i, T)$

vibrational frequencies (computationally heavy)