Detecting Stable Surface Adsorbates with Bayesian Optimization

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Young Researcher's Workshop on Machine Learning
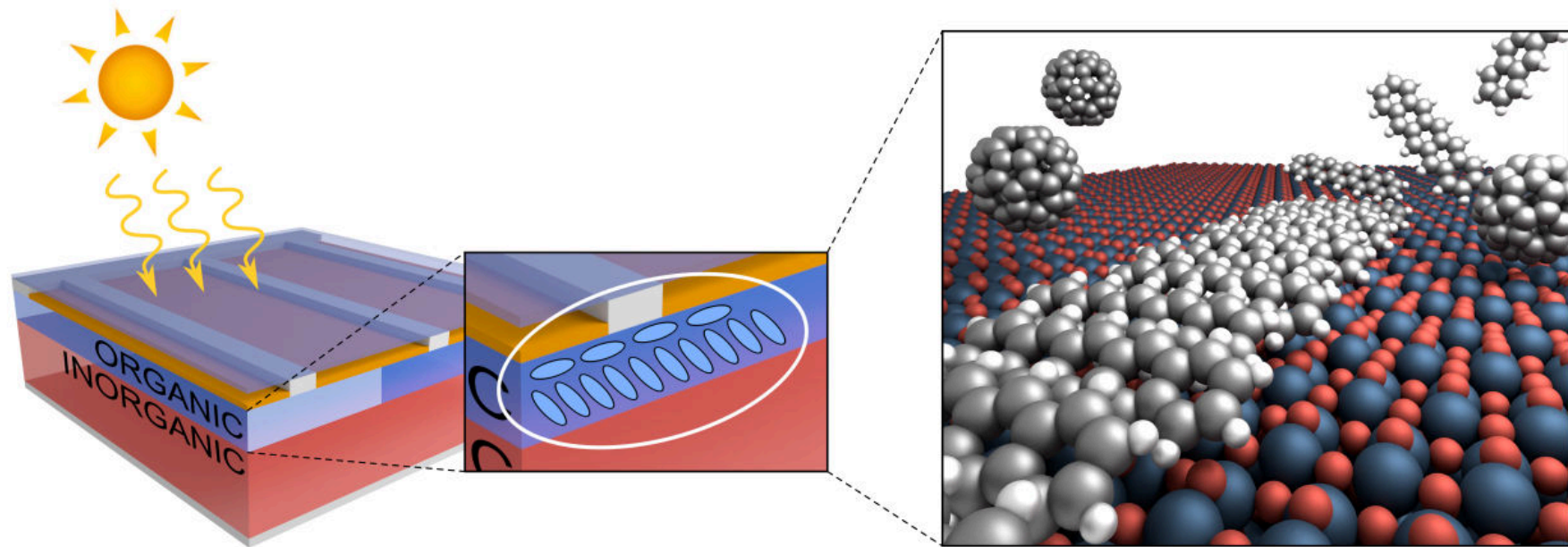for Materials Science 2019

08.05.2019

Functional materials

- Modern technologies based on functional materials
- Properties emerge from atomic structure
- Hybrid organic/inorganic

ORGANIC

INORGANIC

Hybrid solar cell

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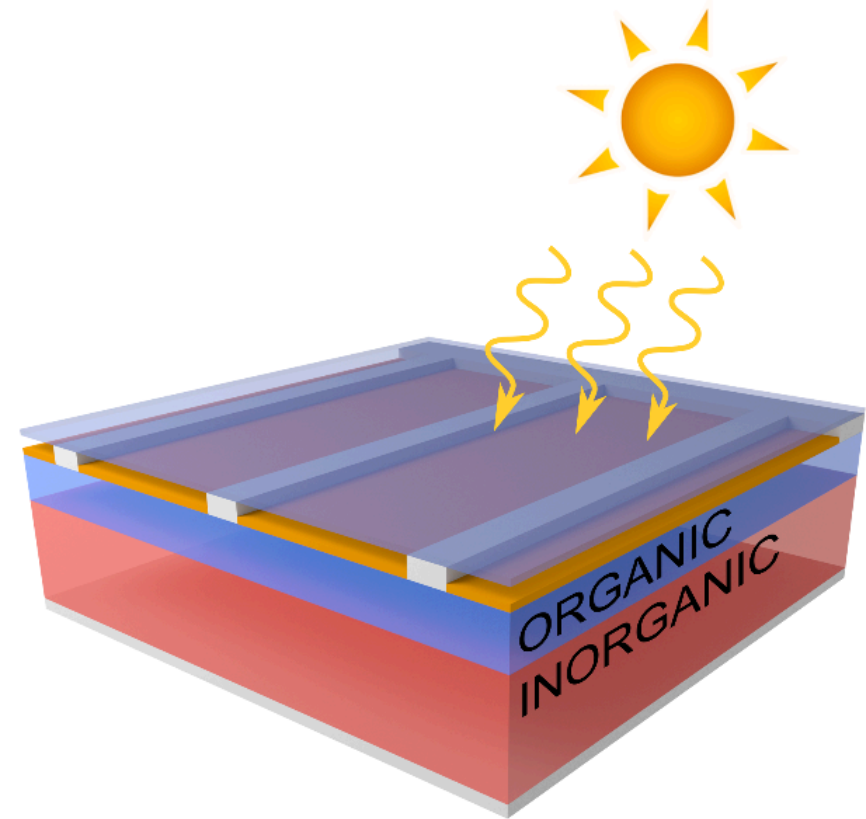
Organic-inorganic interface

Example: Assembly of C_{60} and pentacene on TiO_2

Focus: Molecular arrangement in hybrid interfaces

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Organic-inorganic interface

Organic

Inorganic

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Organic-inorganic interface

Organic

Inorganic

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Organic-inorganic interface

Organic

Inorganic

Challenges:

▶ **Experiments**
- Atomic Force Microscopy (AFM) images difficult to interpret

▶ **Simulations**
- Structure search with conventional methods too expensive
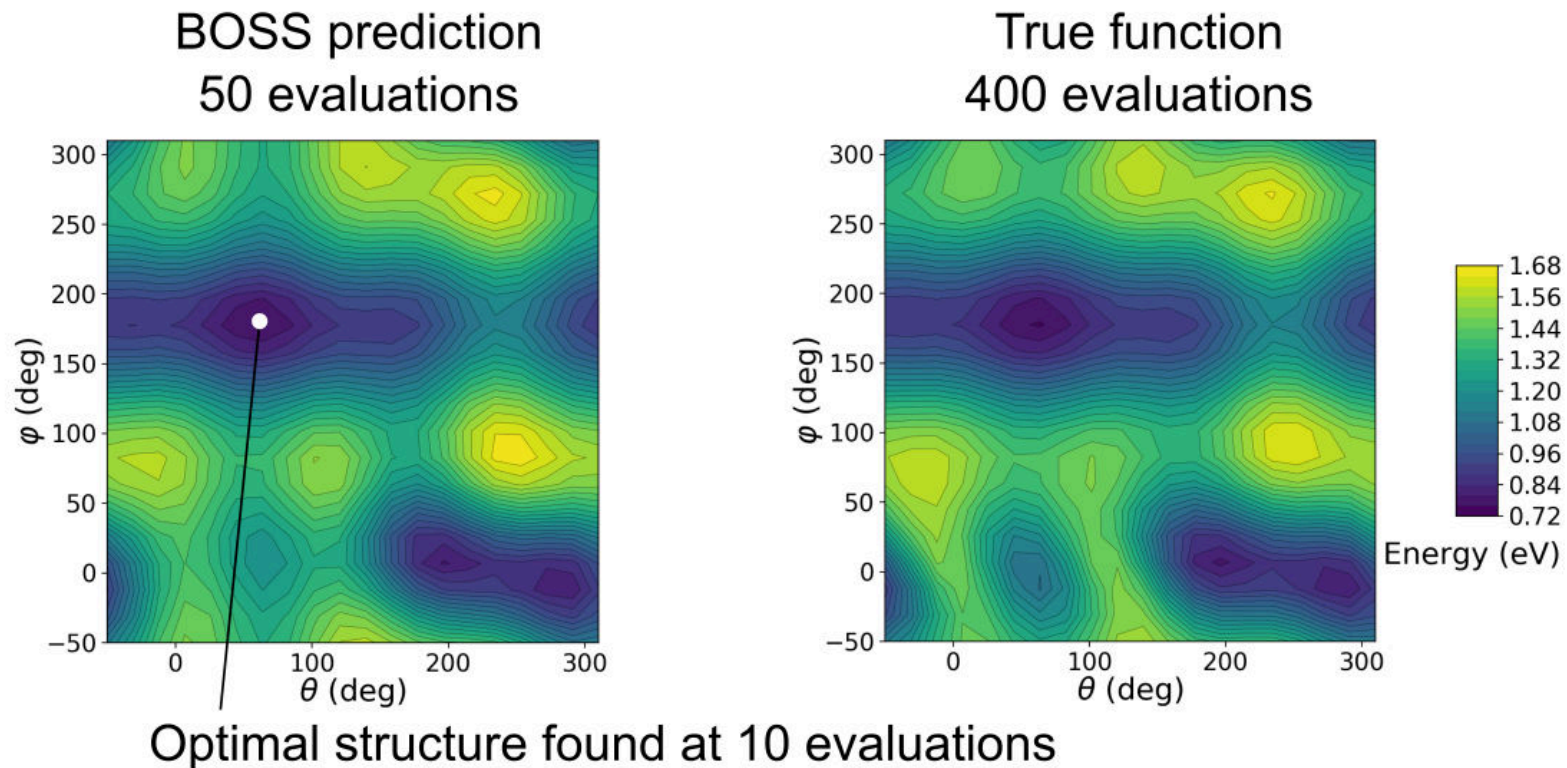- Chemical intuition can lead to biased results

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Bayesian Optimization Structure Search (BOSS)[1]

Accelerated structure search via intelligent
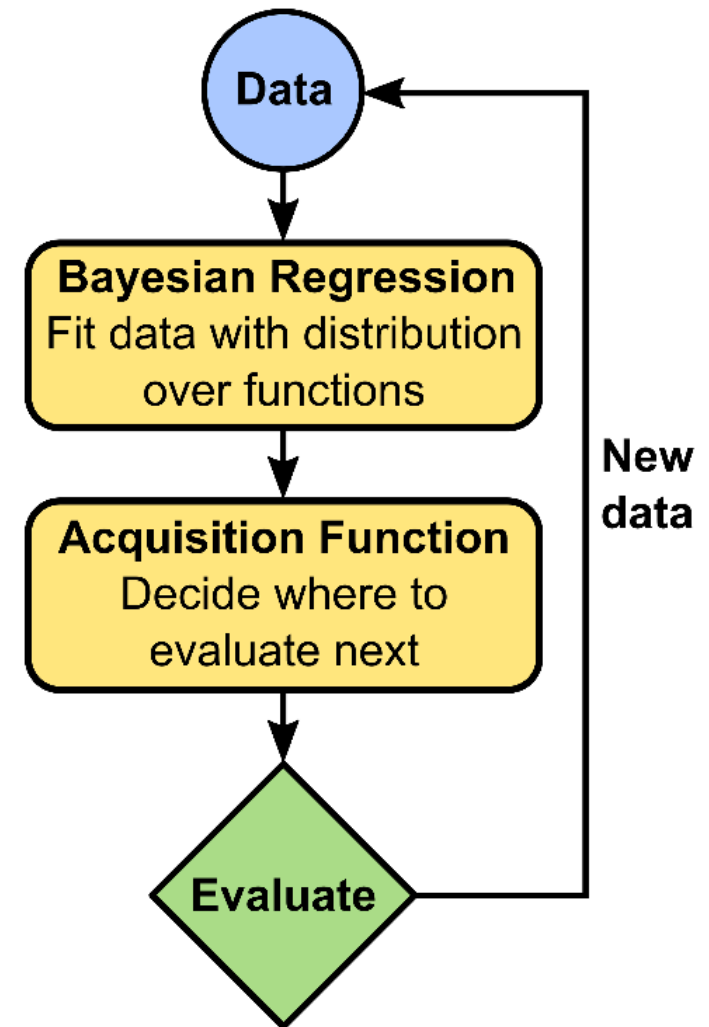sampling of the potential energy surface (PES)

[1] M. Todorović, M. Gutmann, J. Corander and P. Rinke,
   npj Comput. Mater. 2019, 5(1), 35.

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Bayesian Optimization Structure Search (BOSS)[1]

Accelerated structure search via intelligent
sampling of the potential energy surface (PES)

BOSS prediction
50 evaluations

True function
400 evaluations

Optimal structure found at 10 evaluations

[1] M. Todorović, M. Gutmann, J. Corander and P. Rinke,
   npj Comput. Mater. 2019, 5(1), 35.

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Basic principles of BOSS

- Most probable surrogate model of PES

- Strategic sampling of energy points

- Model refined iteratively

- Active learning with Bayesian optimization

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Bayesian optimization

- Global optimization of *black box* functions

- Bayesian optimization = regression + acquisition function

- Most probable model, given known data

Bayesian optimization

- ▶ Global optimization of *black box* functions

- ▶ Bayesian optimization = regression + acquisition function

- ▶ Most probable model, given known data

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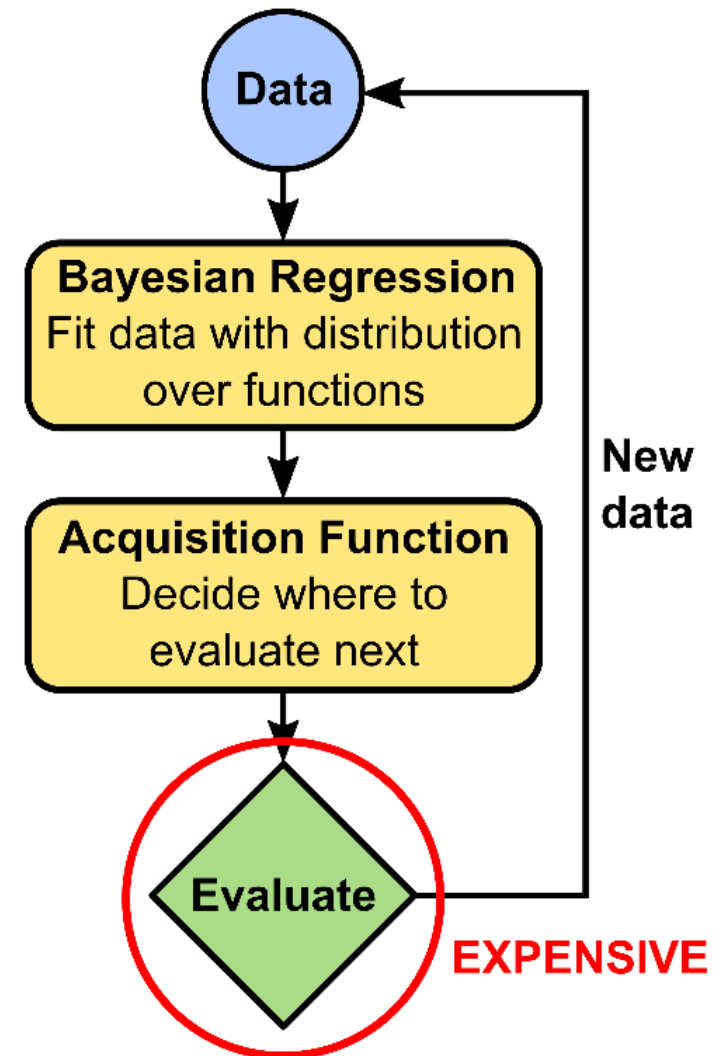
Energy calculation

- Density-functional theory (DFT)
- Dispersion interactions
- FHI-aims[2,3], PBE+vdW$^{\text{surf}}$ [4]

[2] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, Comput. Phys. Commun. 2009, 180(11), 2175–2196

[3] V. Havu, V. Blum, P. Havu and M. Scheffler, J. Comput. Phys. 2009, 228(22), 8367–8379.

[4] V. G. Ruiz, W. Liu and A. Tkatchenko. Phys. Rev. B 2016, 93(3), 035118.

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Defining configurational space

- ▶ Chemical "building blocks"
- ▶ Keep groups of atoms fixed
  - Rigid molecules
  - Rigid parts of molecules
  - Metallic surfaces
- ▶ Structure search with reduced dimensions, e.g.
  - Molecule-surface distance (1D)
  - Adsorption site (2D)
  - Molecule orientation (3D)
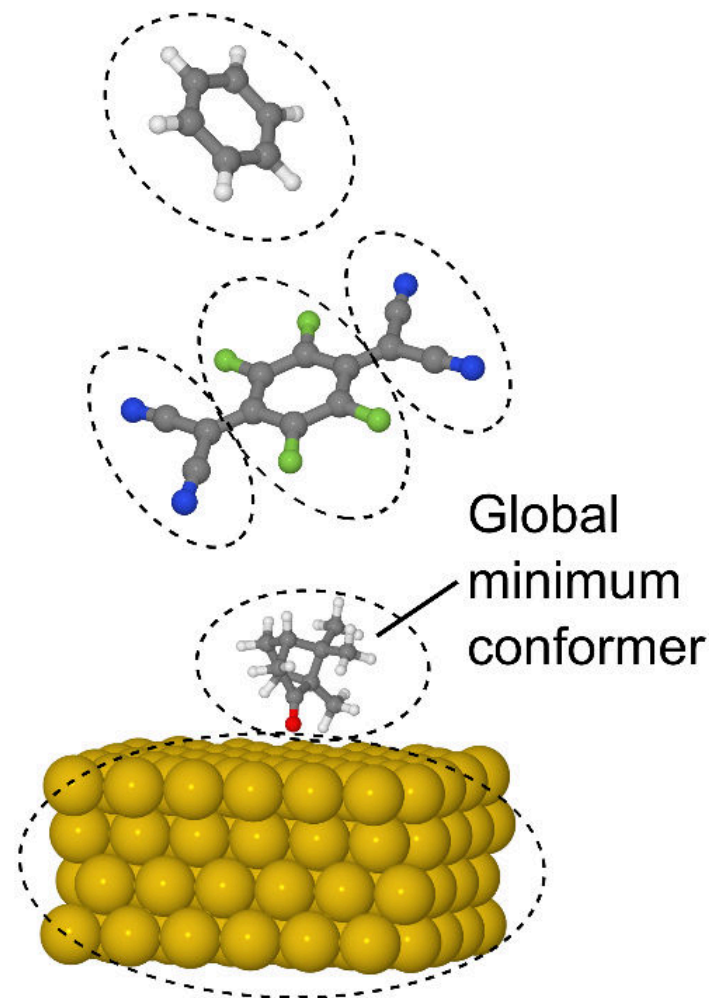
Global minimum conformer

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Bayesian Optimization Structure Search (BOSS)

Atomic configuration

Bayesian optimization

BOSS

DFT calculation

Total energy

5 evaluations

8 evaluations

10 evaluations

PES model refined iteratively
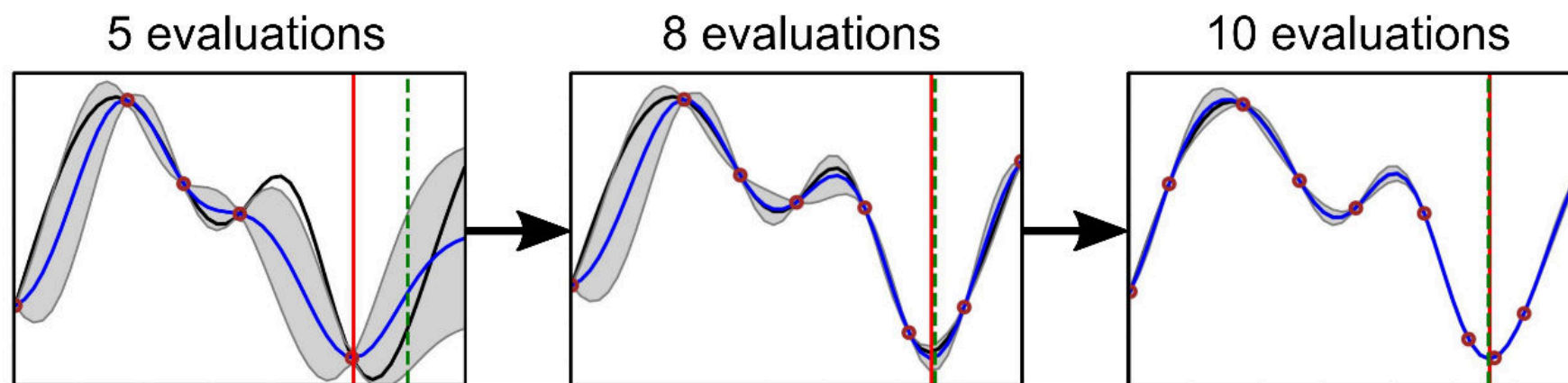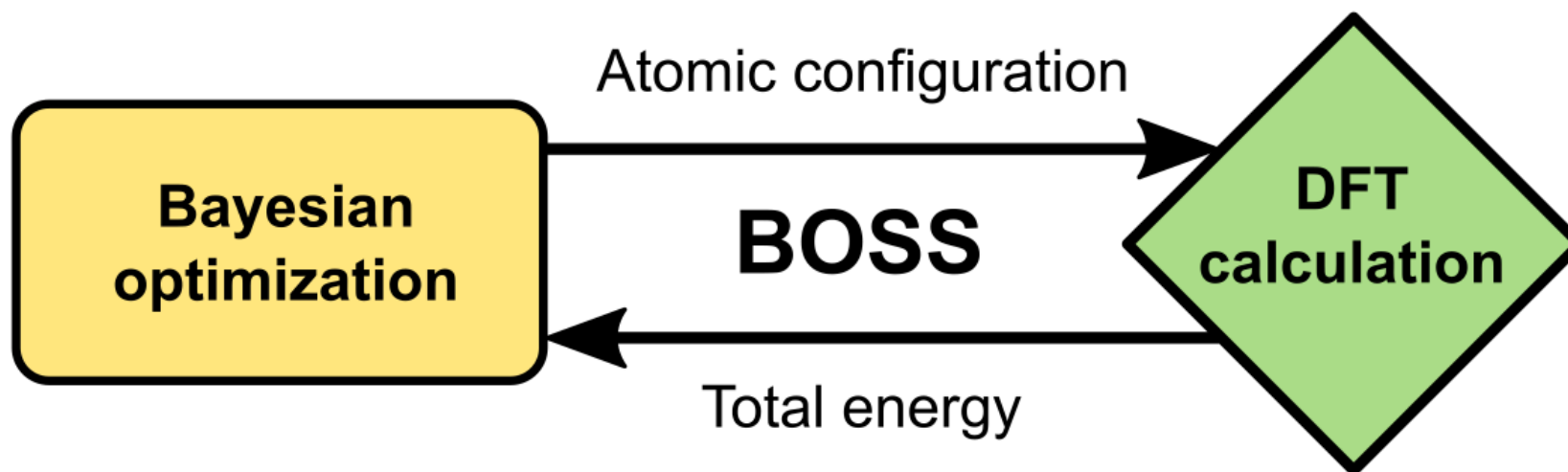
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S-Camphor ($C_{10}H_{16}O$) on Cu(111)

50 % of samples
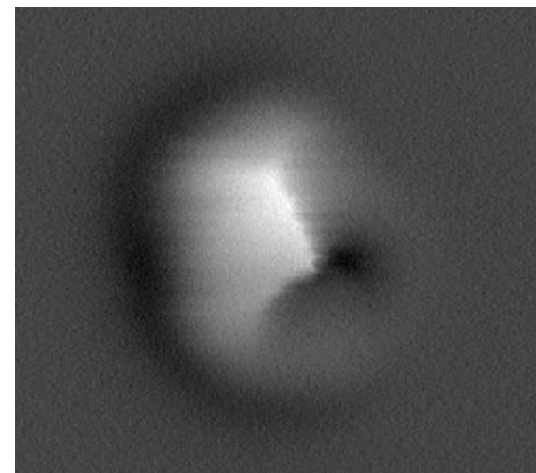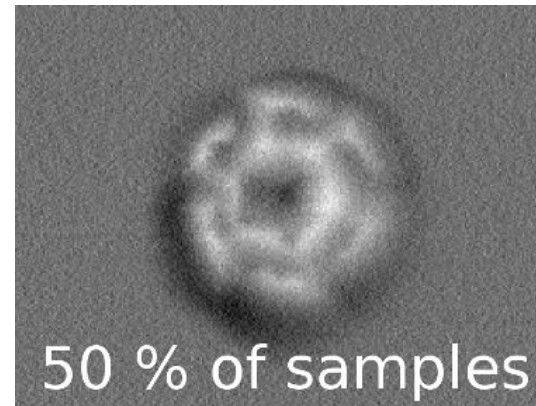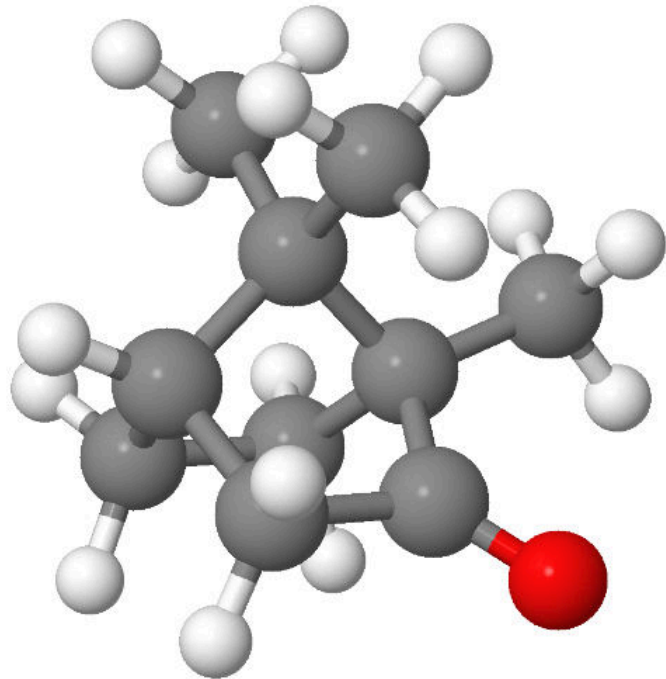
AFM imaging:
Atomic Scale Physics (STM)
group at Aalto University

Camphor conformers
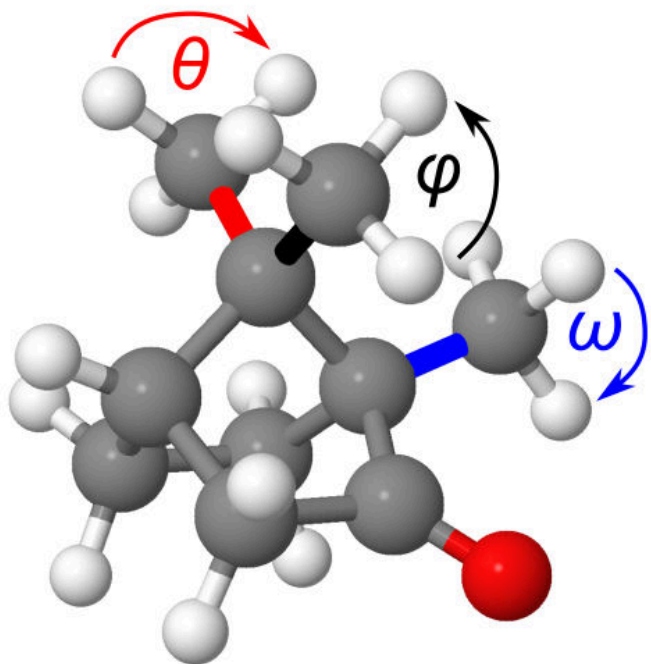
▶ 3D search of CH_3 group rotations

Single energy minimum
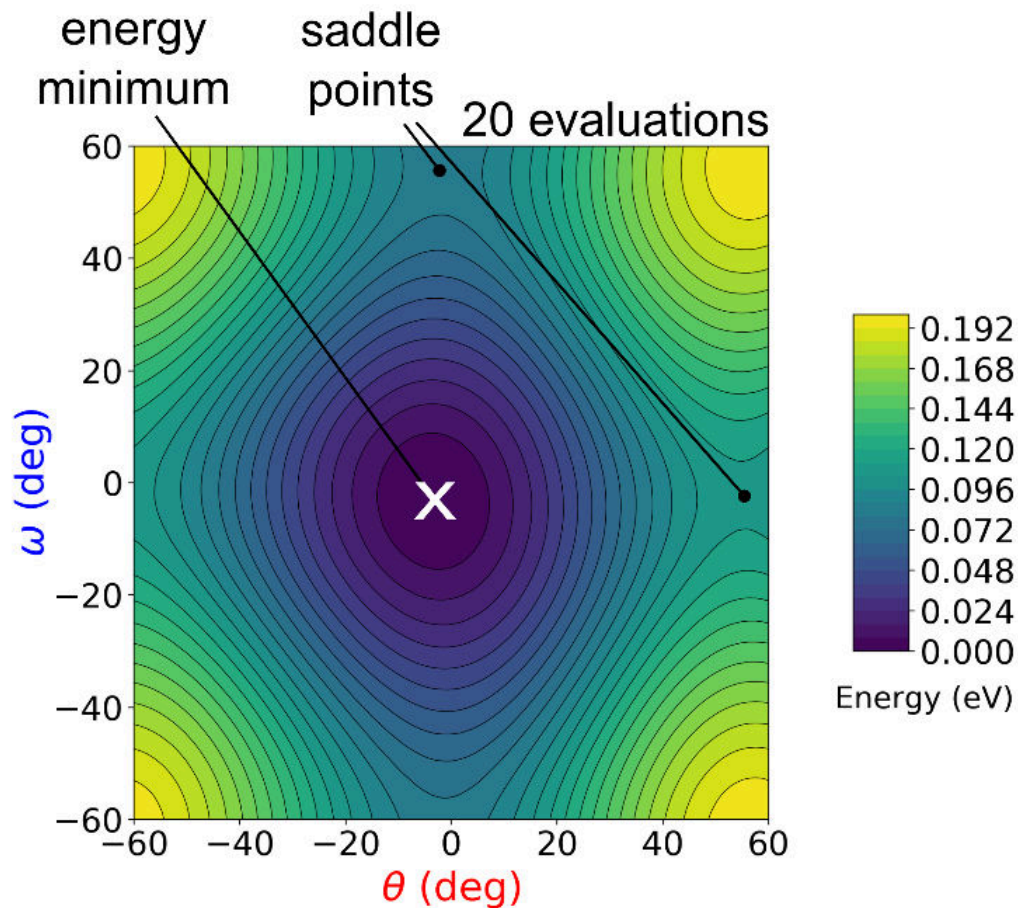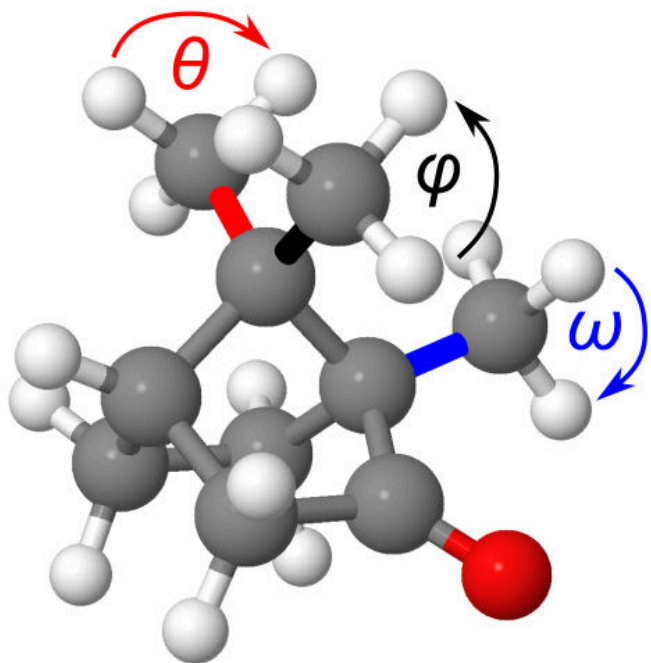
- Activation energy for CH_3 rotation ca. 0.1 eV
- Non-rotating $\rightarrow$ fixed geometry

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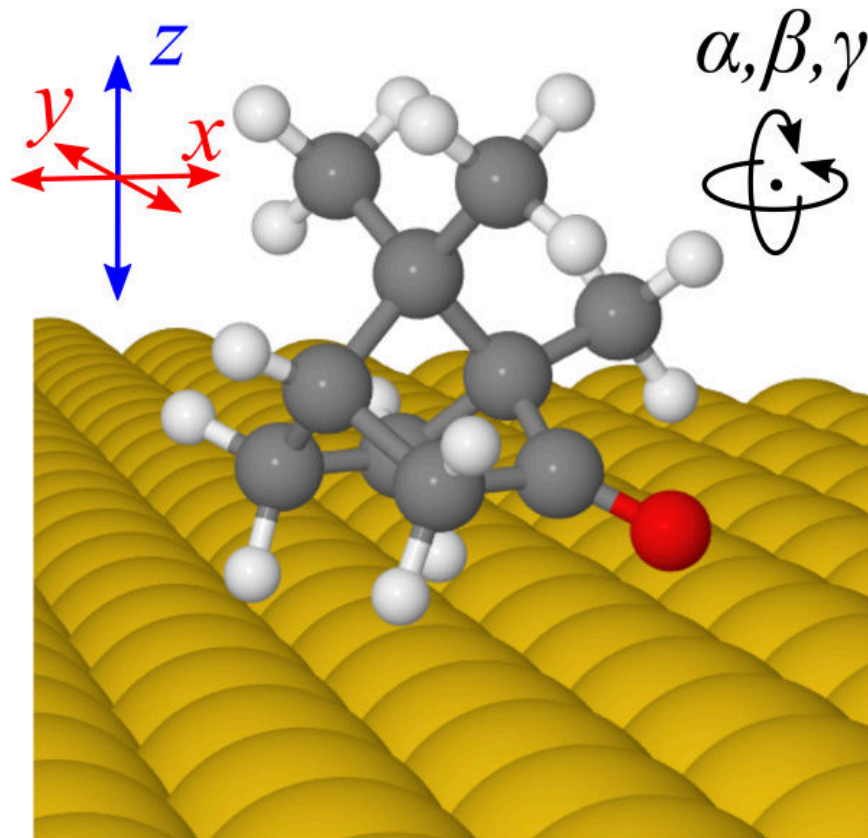
Camphor on Cu(111)

- ▶ 4 Cu layers, 6x4 unit cells, 219 atoms

- ▶ Search for optimal adsorption site and orientation $\rightarrow$ 6D problem

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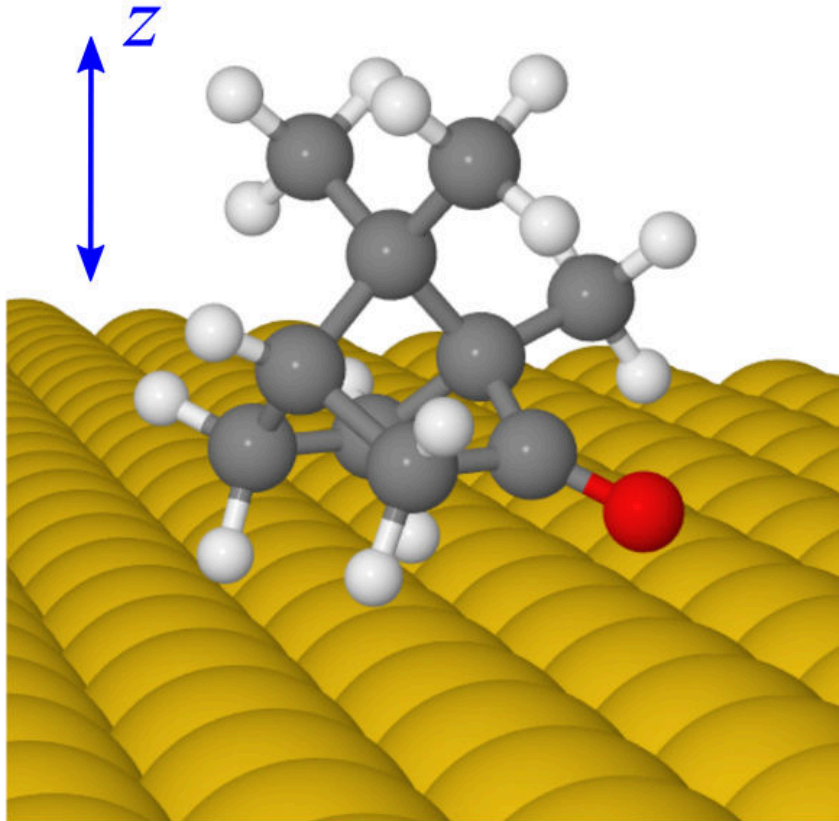
Camphor on Cu(111)

- Adsorption height: 1D

Camphor on Cu(111)
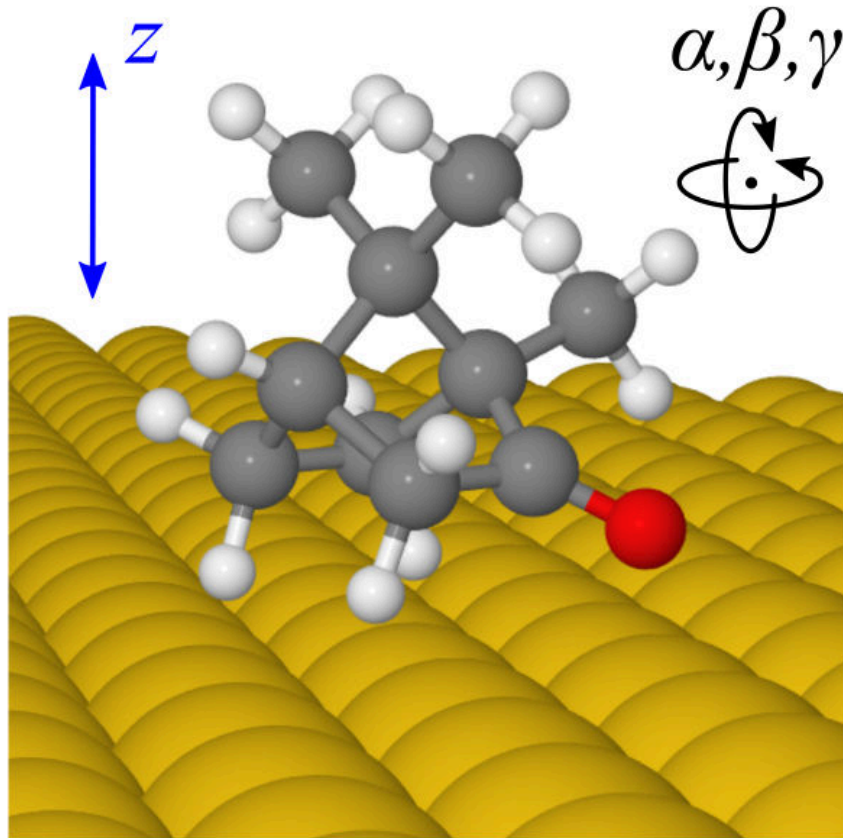
- Adsorption height: 1D
- Orientation: 3D
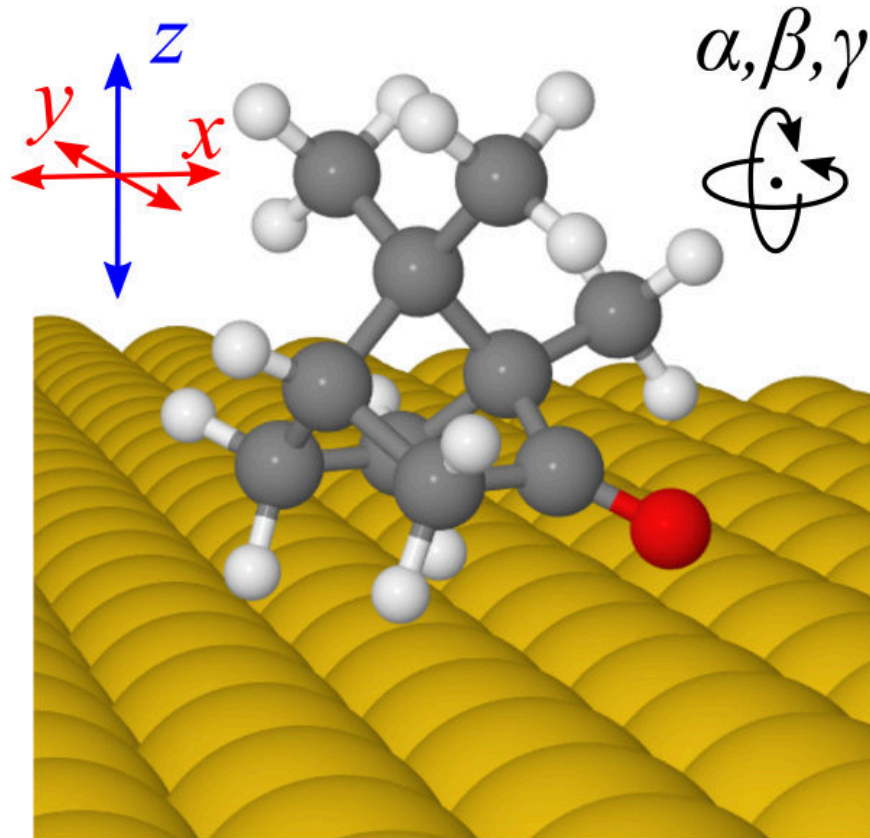
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Camphor on Cu(111)

- **Adsorption height: 1D**
- Orientation: 3D
- Adsorption site: 2D

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Camphor on Cu(111)
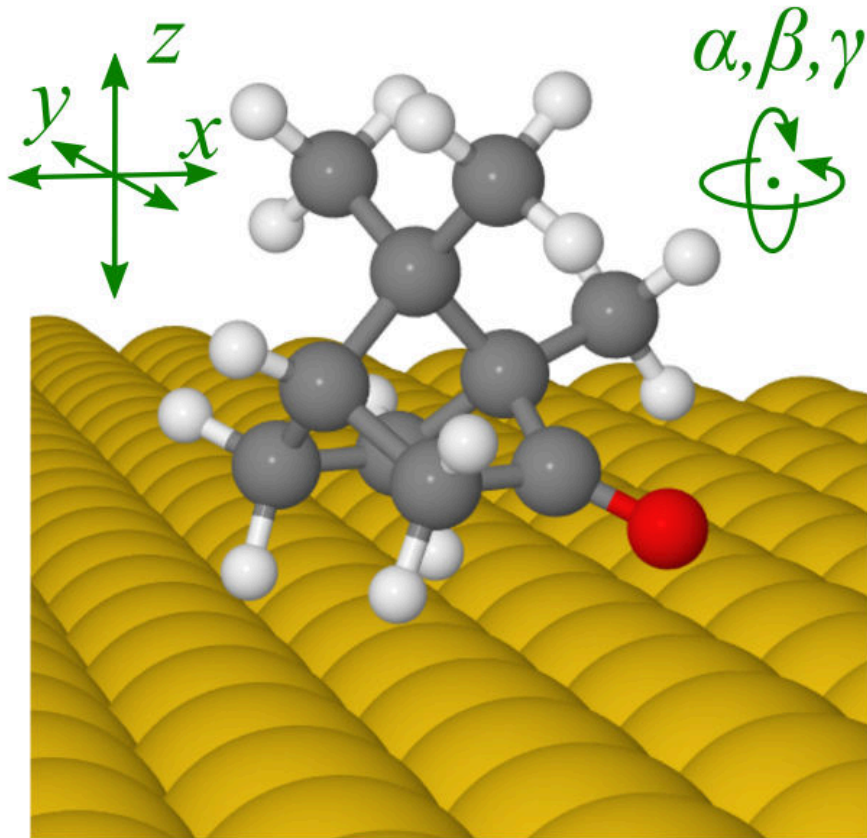
- Adsorption height: 1D
- Orientation: 3D
- Adsorption site: 2D
- 6D search

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Adsorption height 4-5 Å
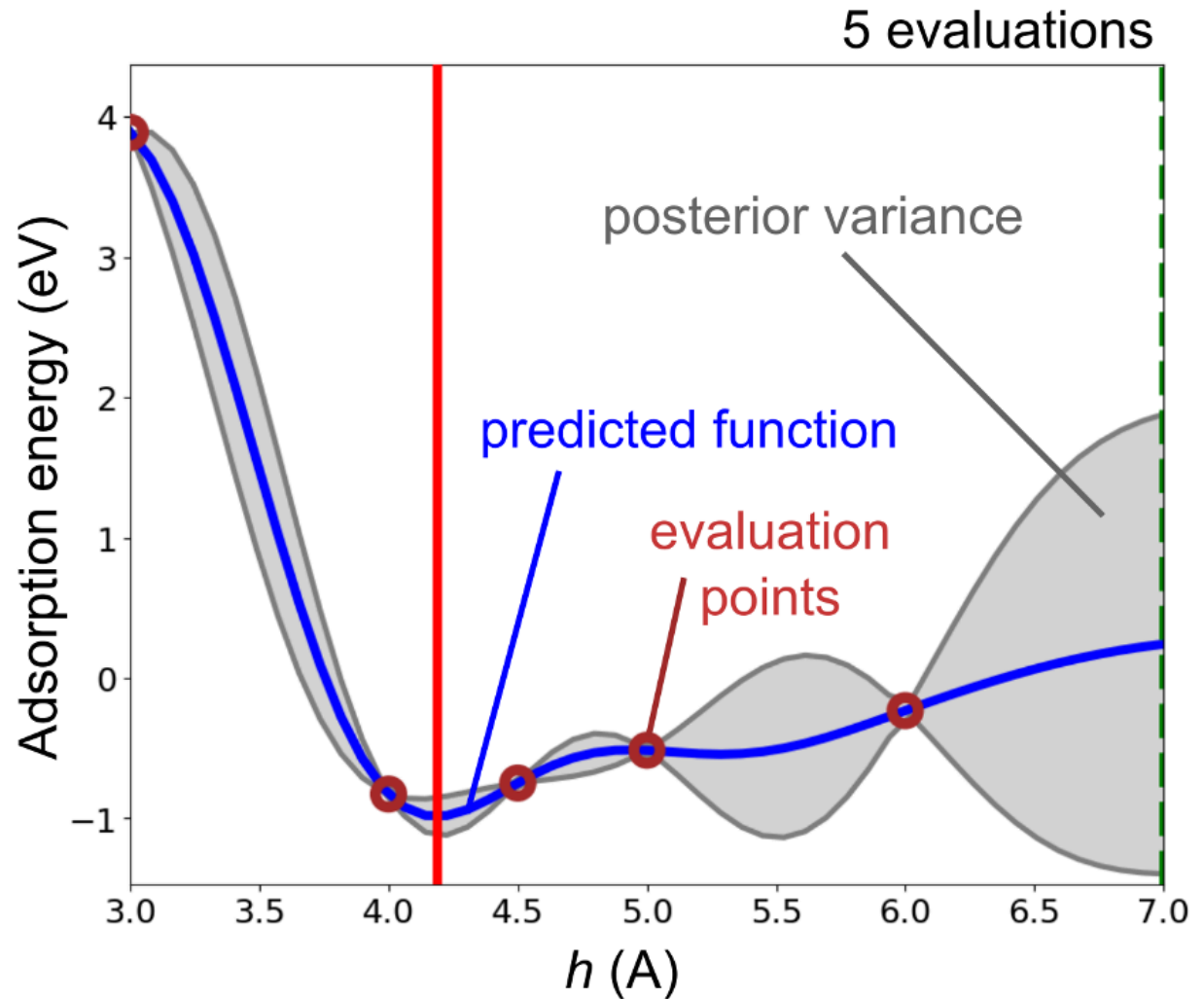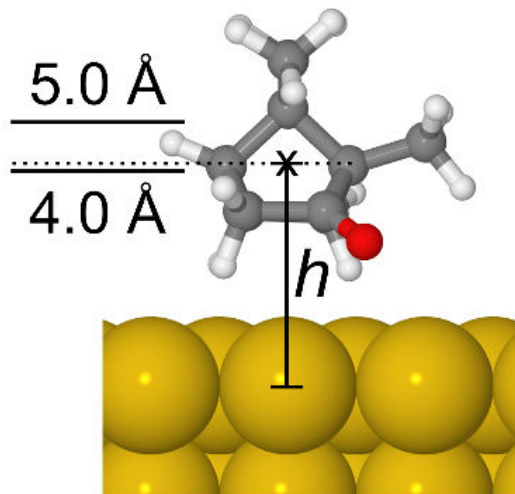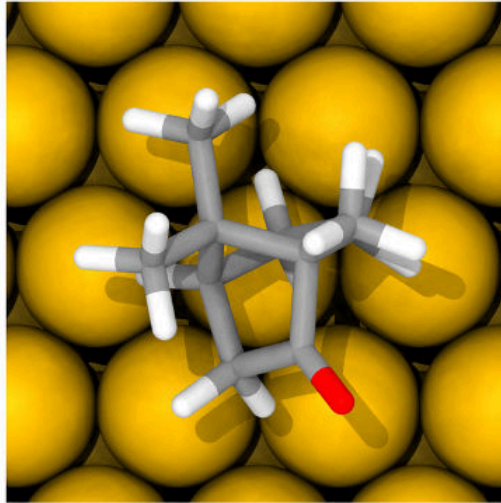
Adsorption height 4-5 Å
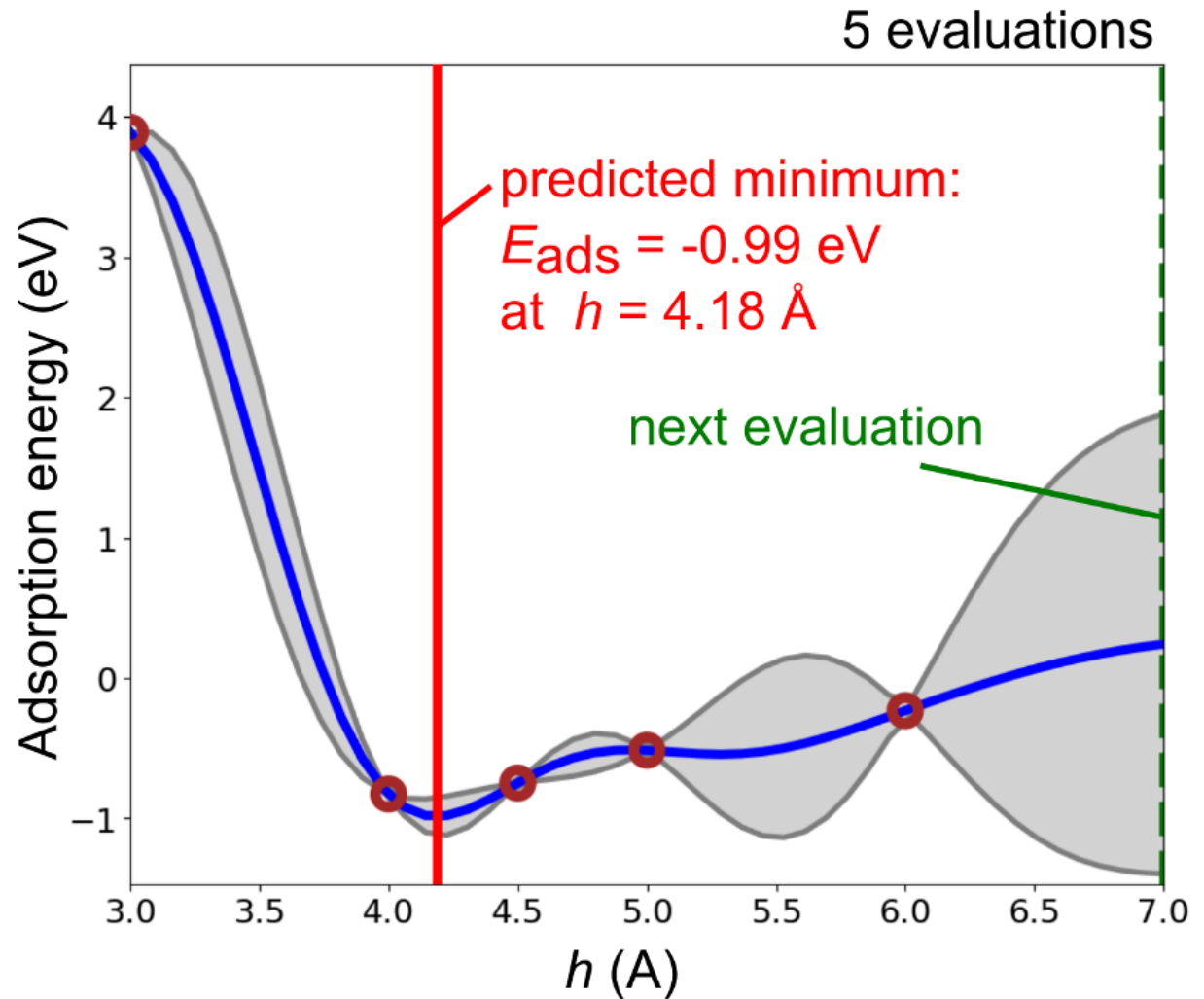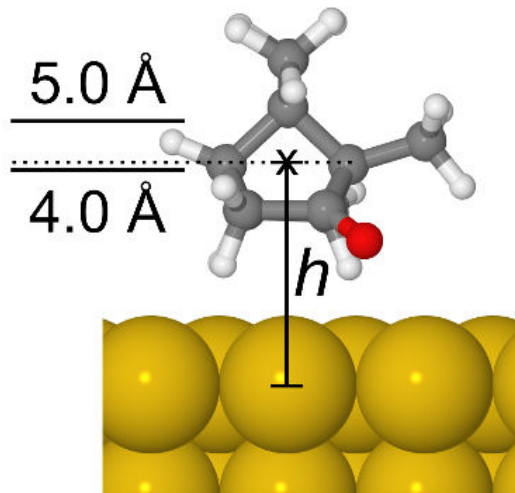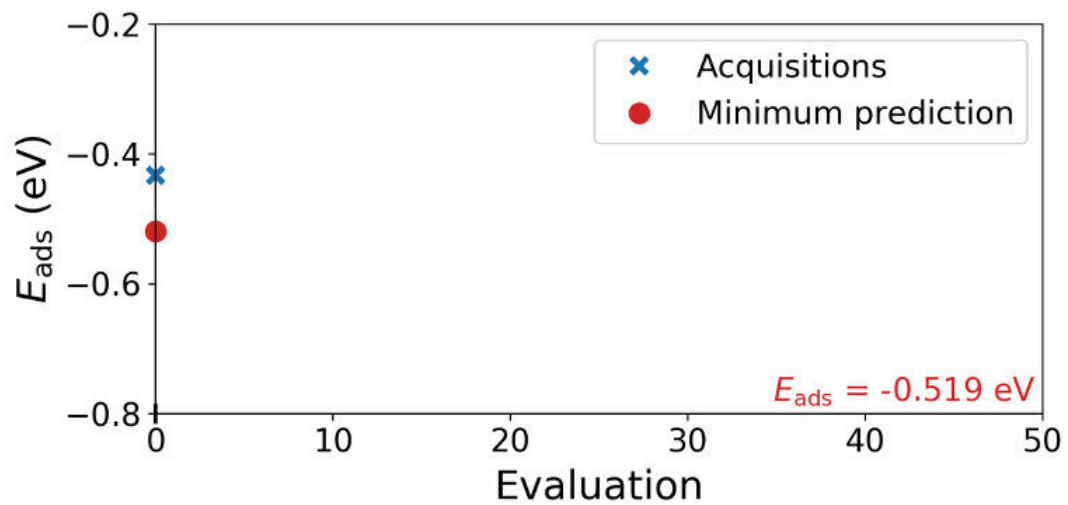
Adsorption height 4-5 Å
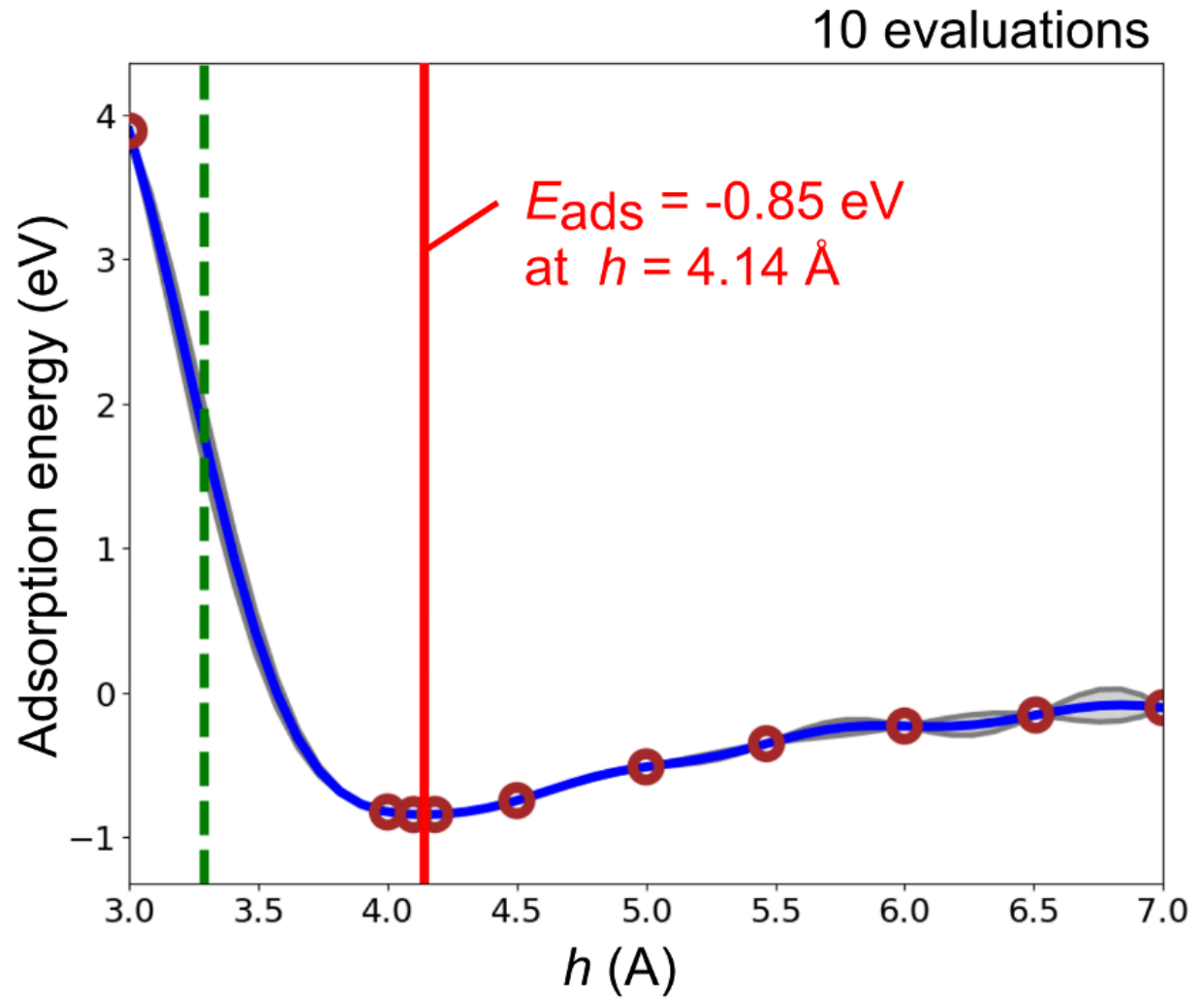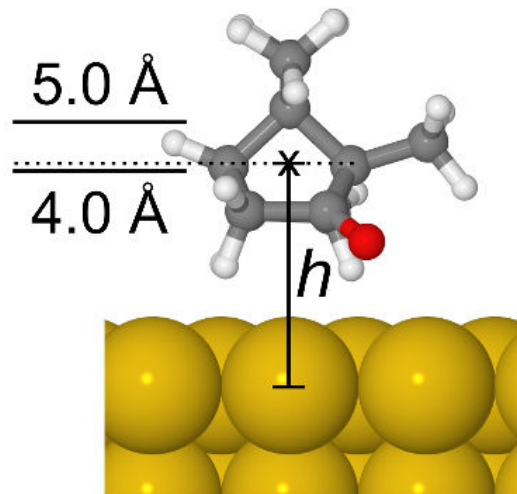
Camphor rotation in 3D
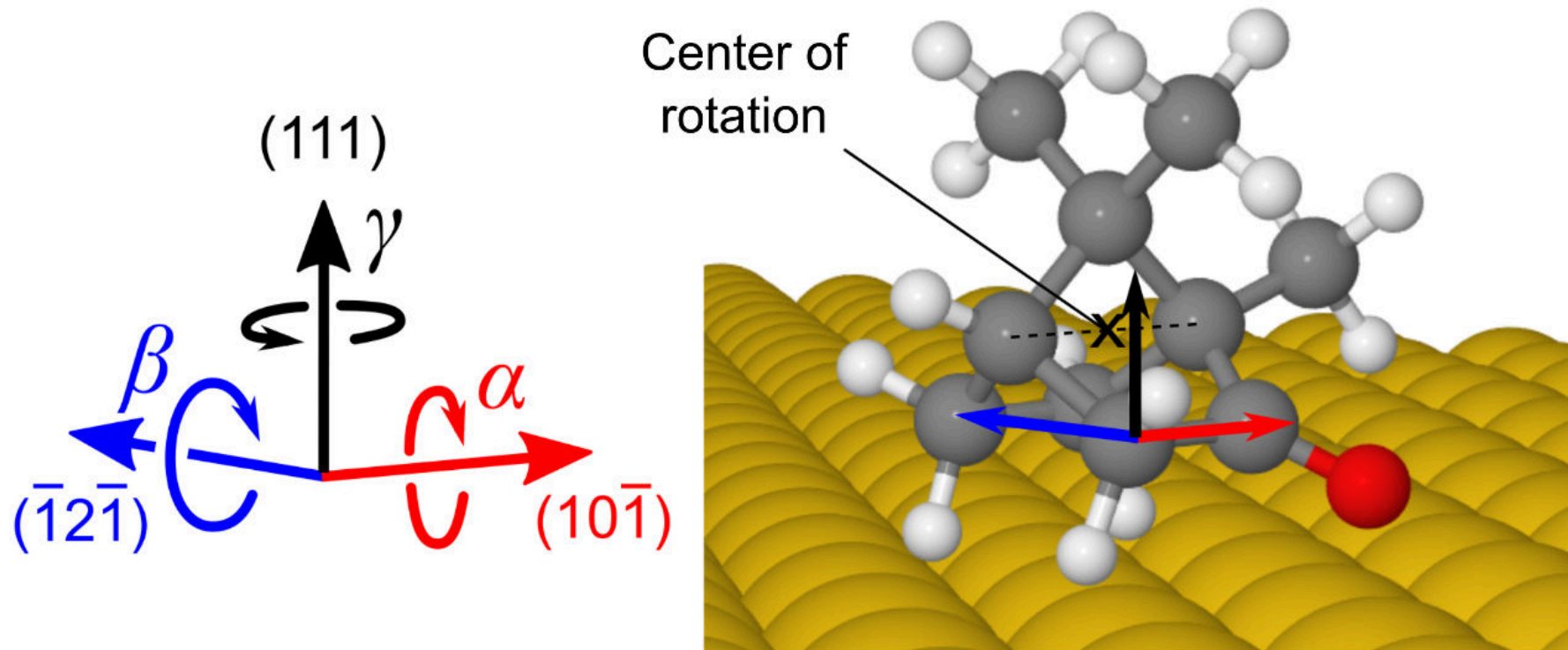
- Search at $h = 5.0$ Å
- γ has minimal effect on energy $\rightarrow \alpha/\beta$ energy landscapes
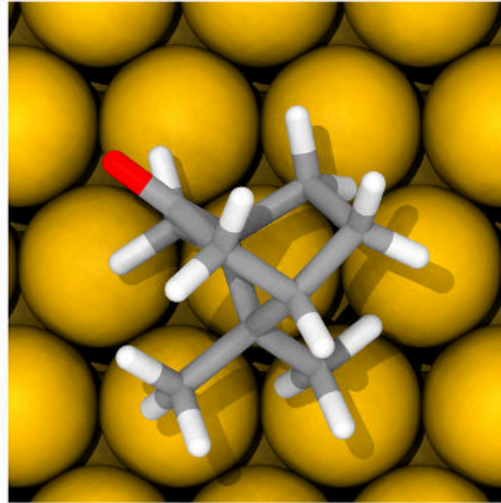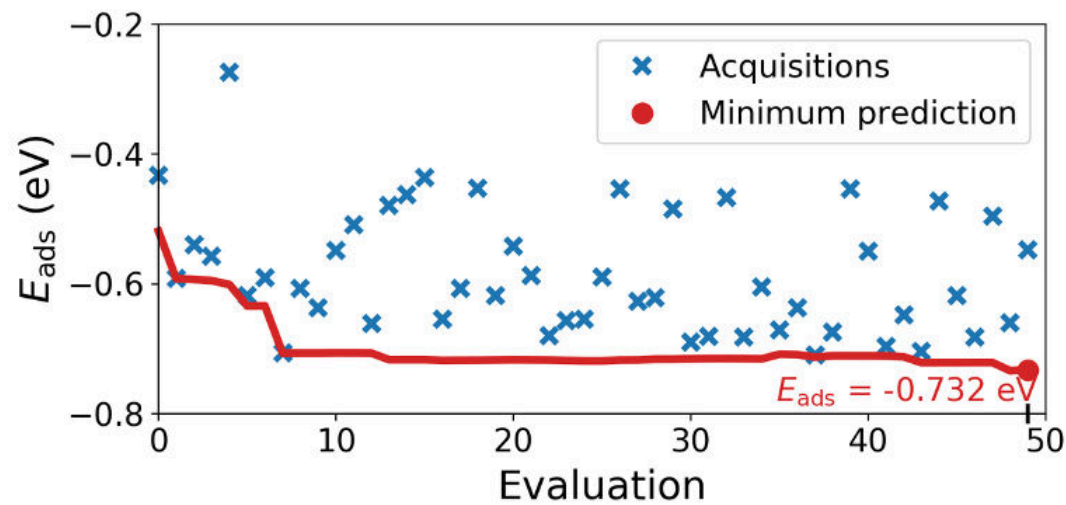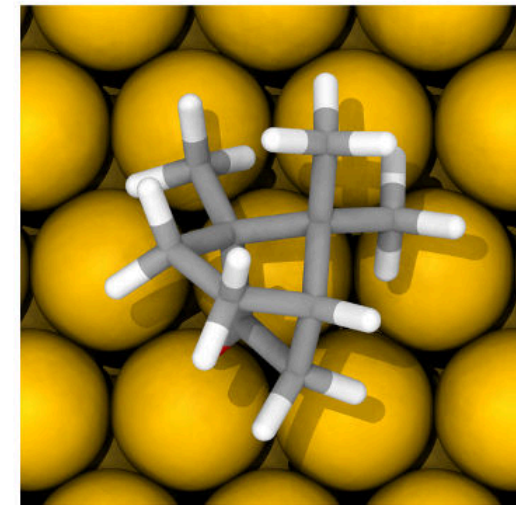
Camphor orientation, 3D search
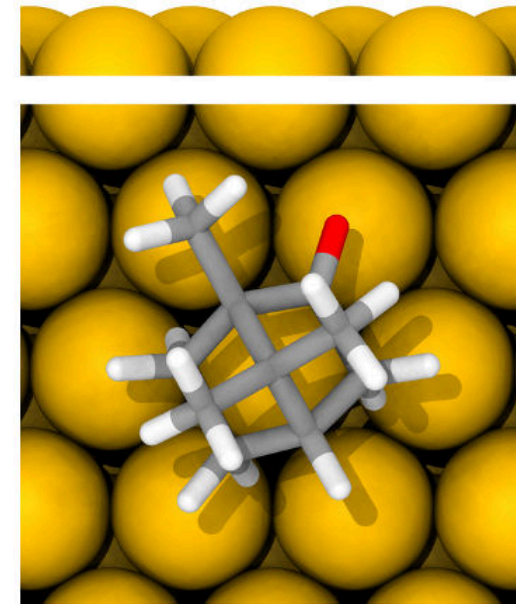
Acquisitions

Minimum prediction

$E_{ads} = -0.519$ eV

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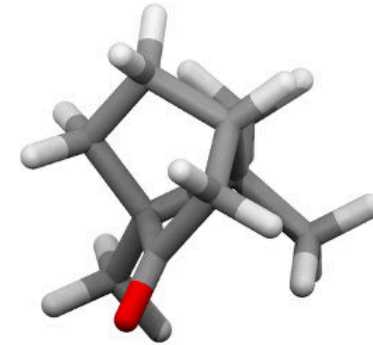**School of Science**

Camphor orientation, 3D search
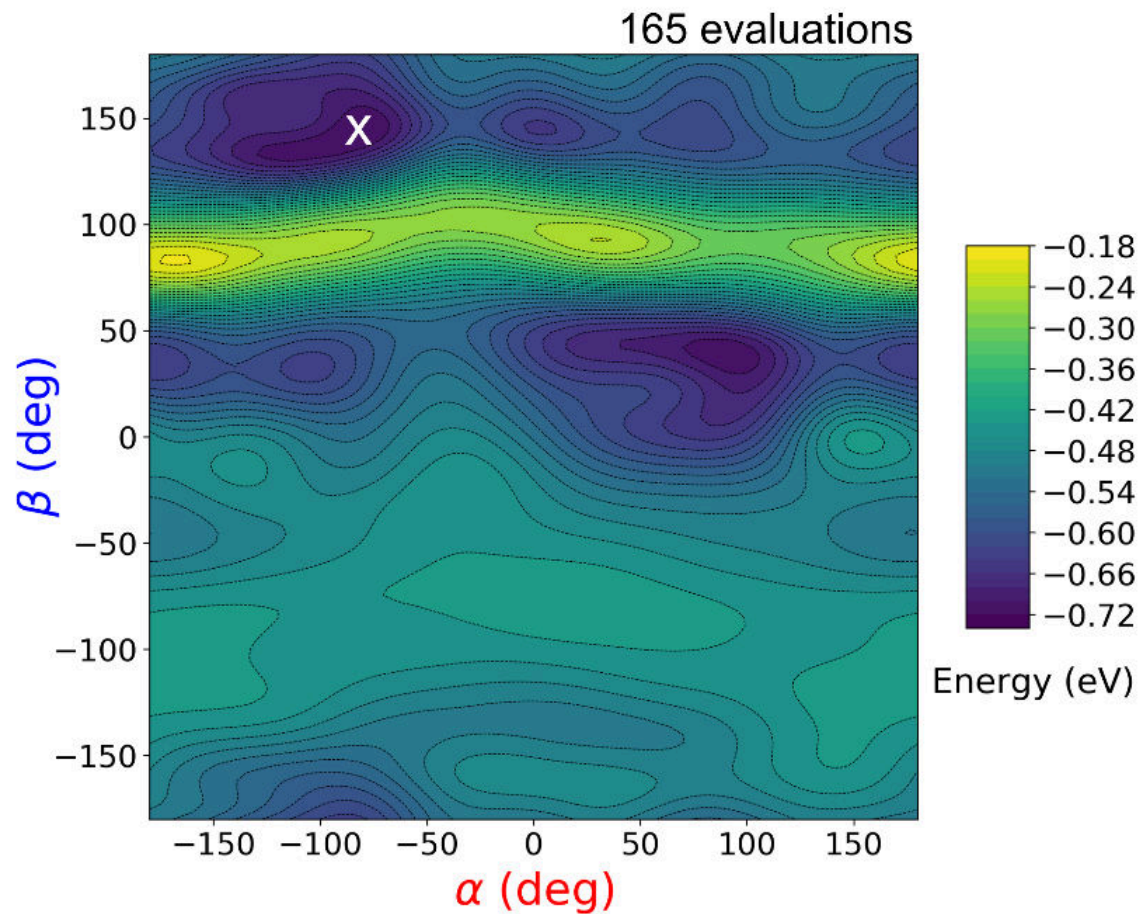
Acquisitions

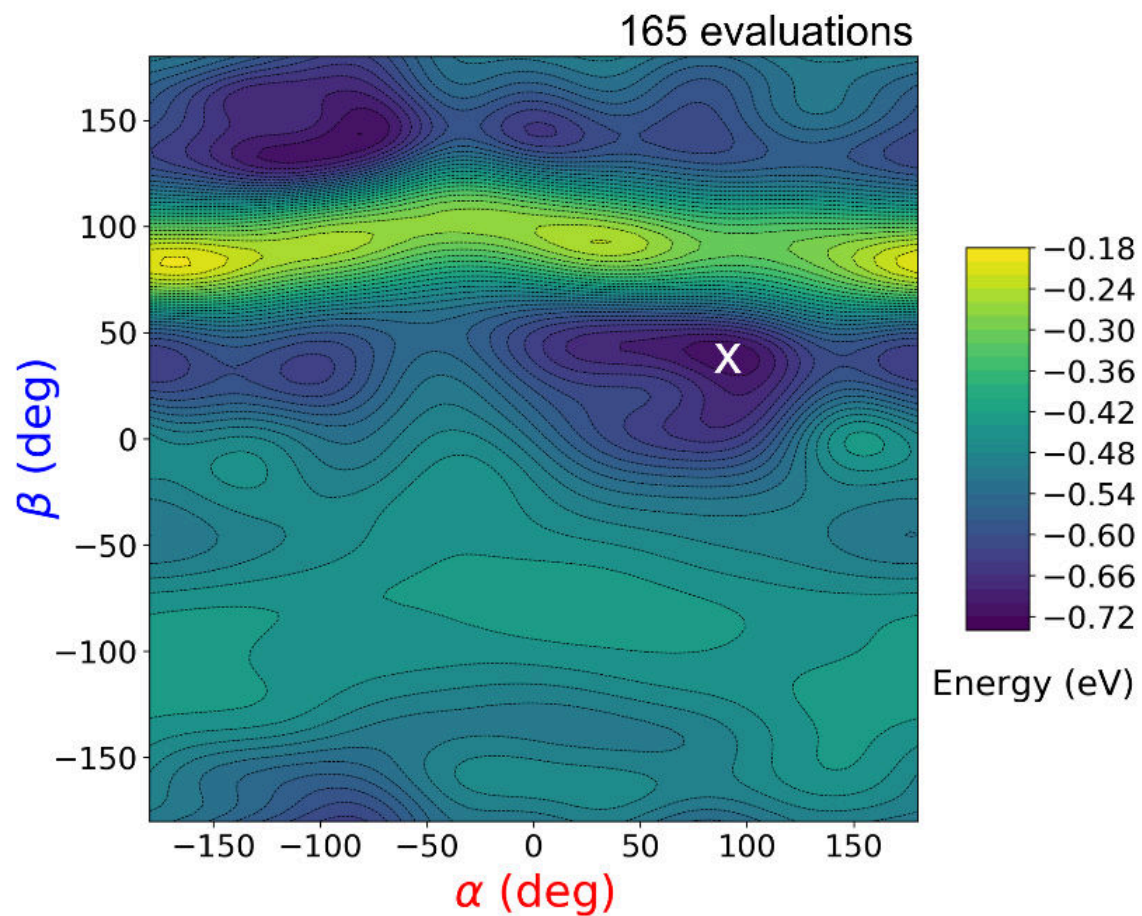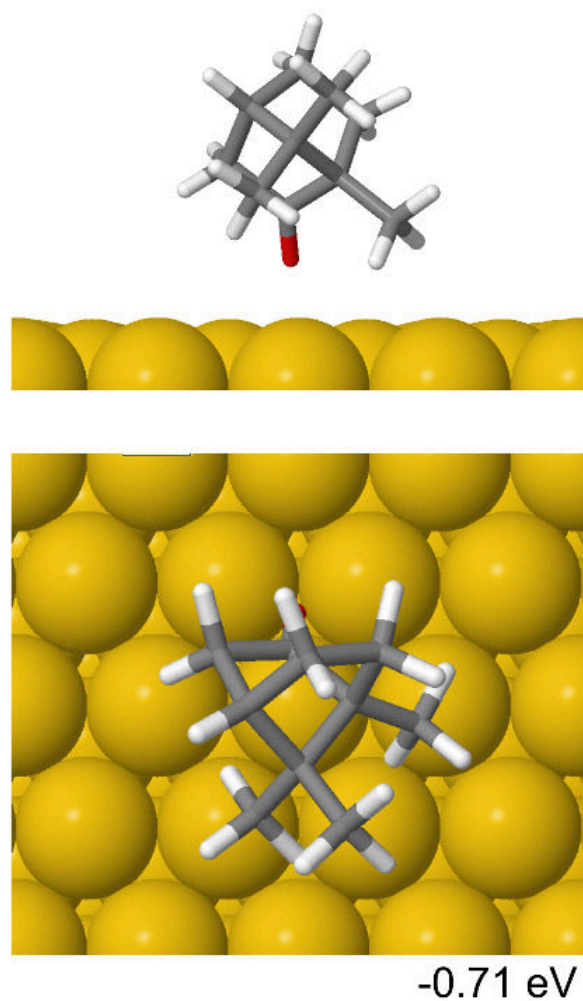Minimum prediction

$E_{\text{ads}} = -0.732$ eV

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Camphor orientation, global minima

-0.72 eV

165 evaluations

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Camphor orientation, global minima

-0.71 eV
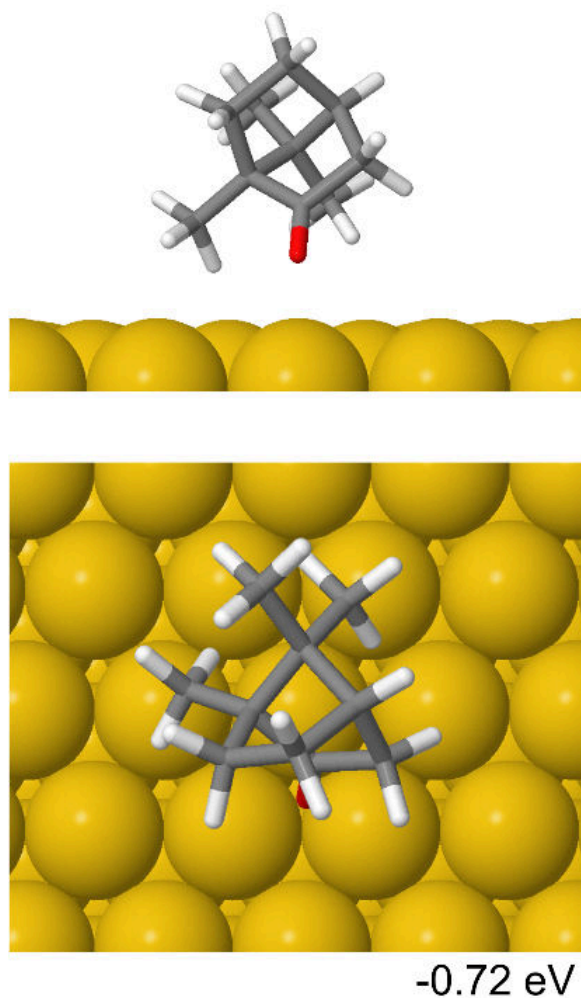
Camphor orientation, local minima

Adsorption site

-0.725 eV

25 evaluations
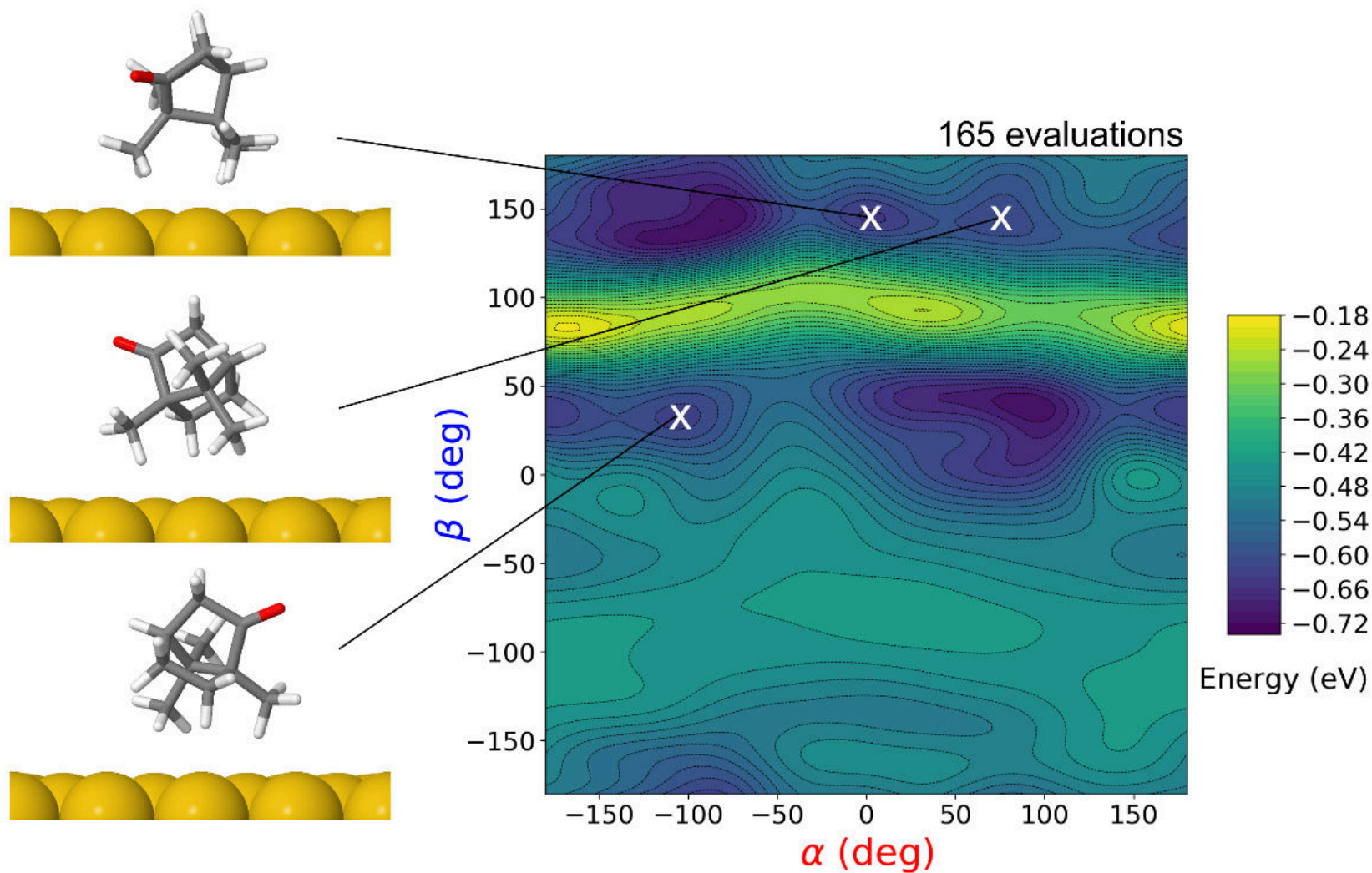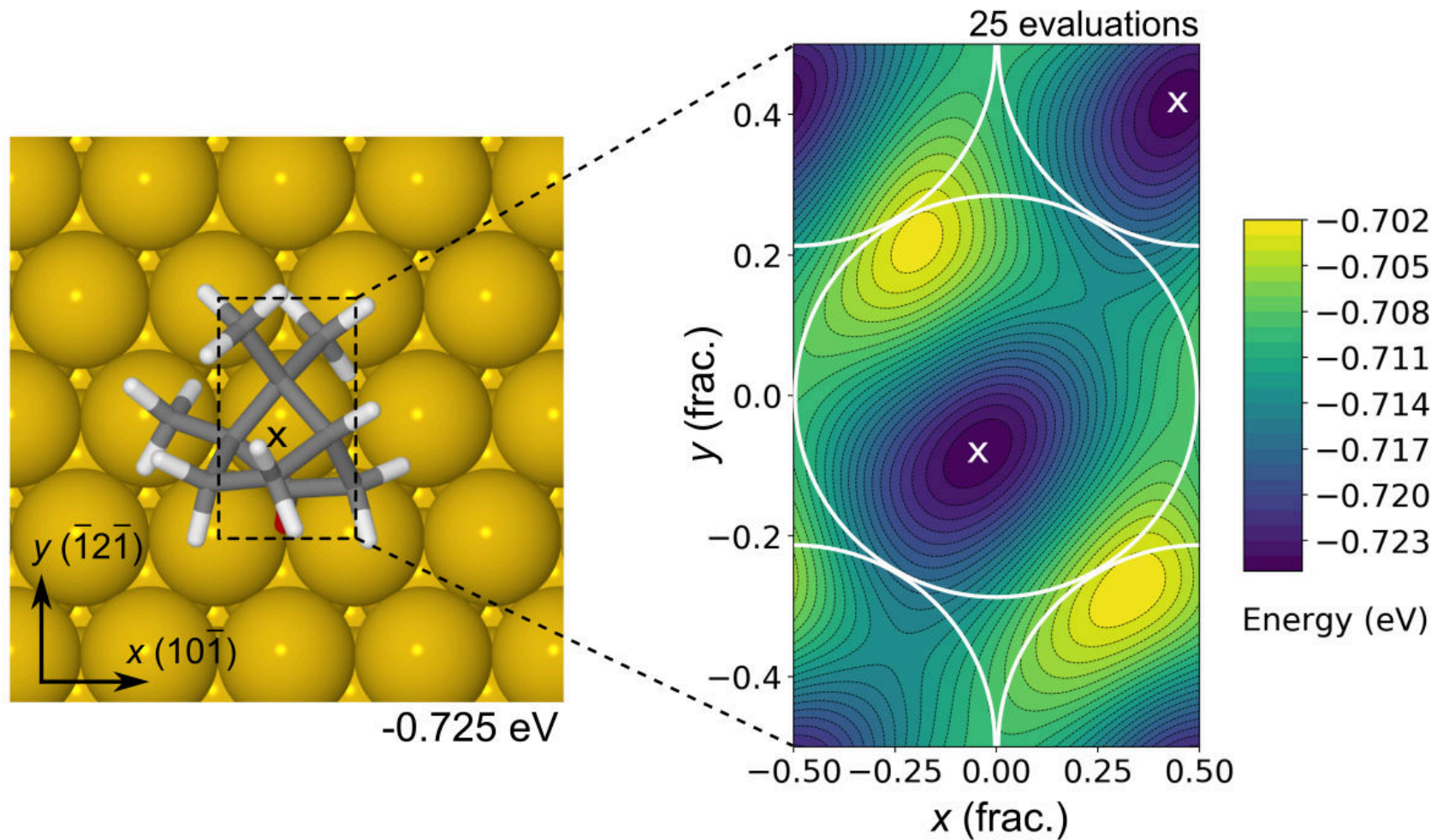
- ▶ Search at $h = 5.0$ Å in global minimum orientation
- ▶ Energy minimum near on-top site

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6D search in progress

Type 1

$E_{ads} = $ -0.90 eV

$h = 4.35$ Å
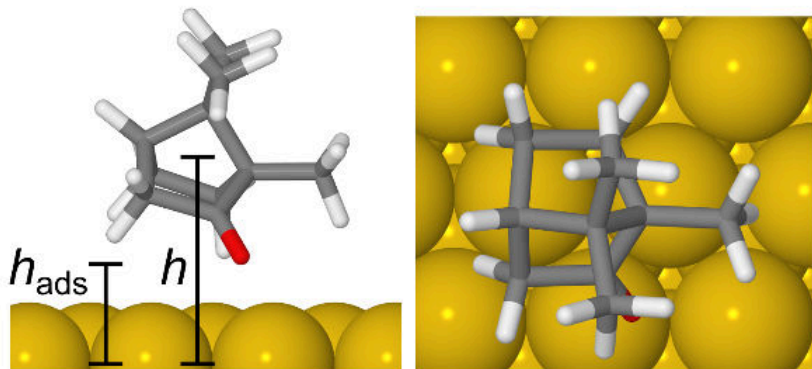
Type 2

$E_{ads} = $ -0.85 eV

$h = 4.56$ Å
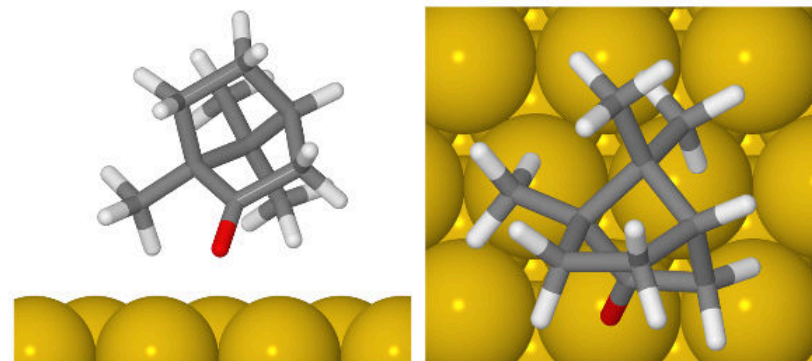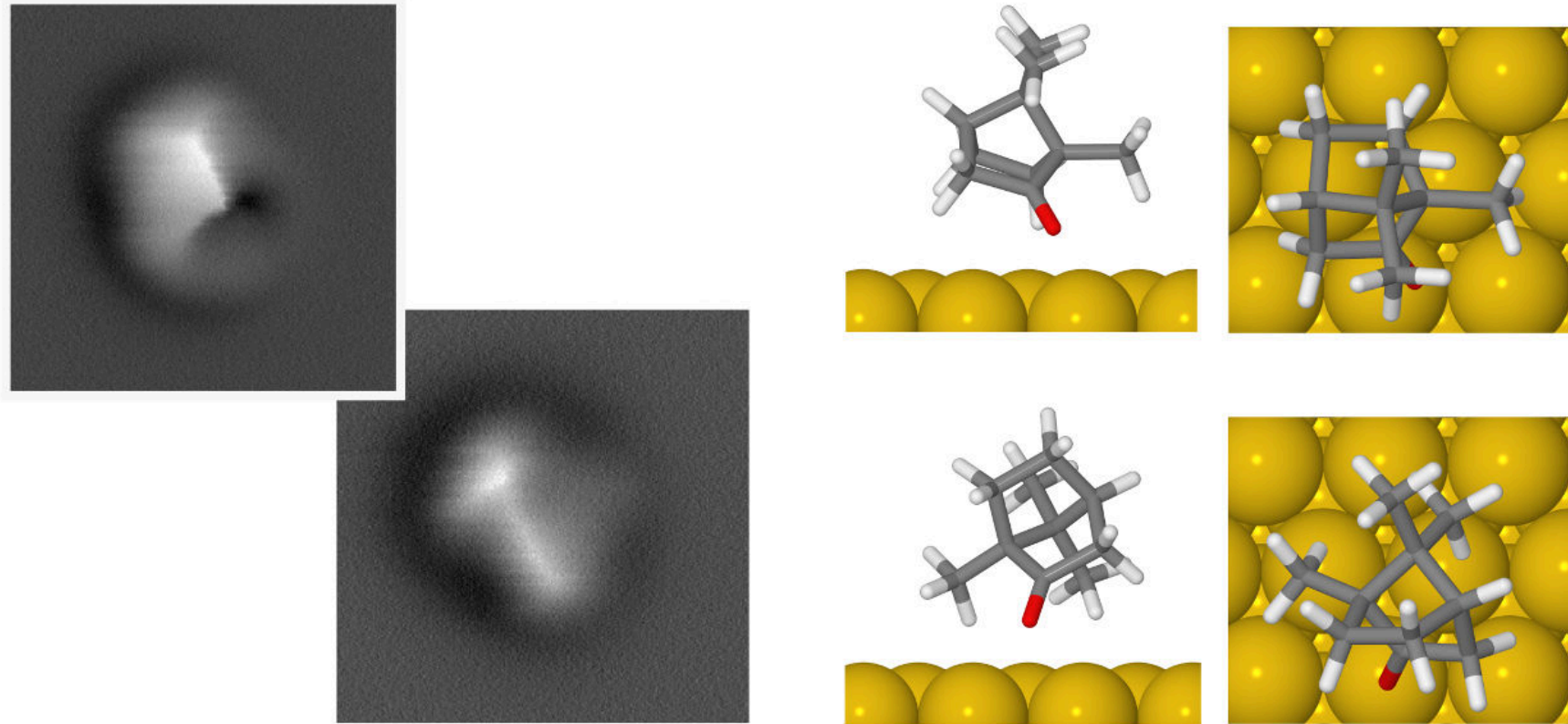
▶ 2 different adsorbate structures

▶ Adsorption height $h_{ads} = 2.3$ Å

▶ Adsorption energy E_{ads} in range [-0.9, -0.8] eV

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AFM: pinwheel image
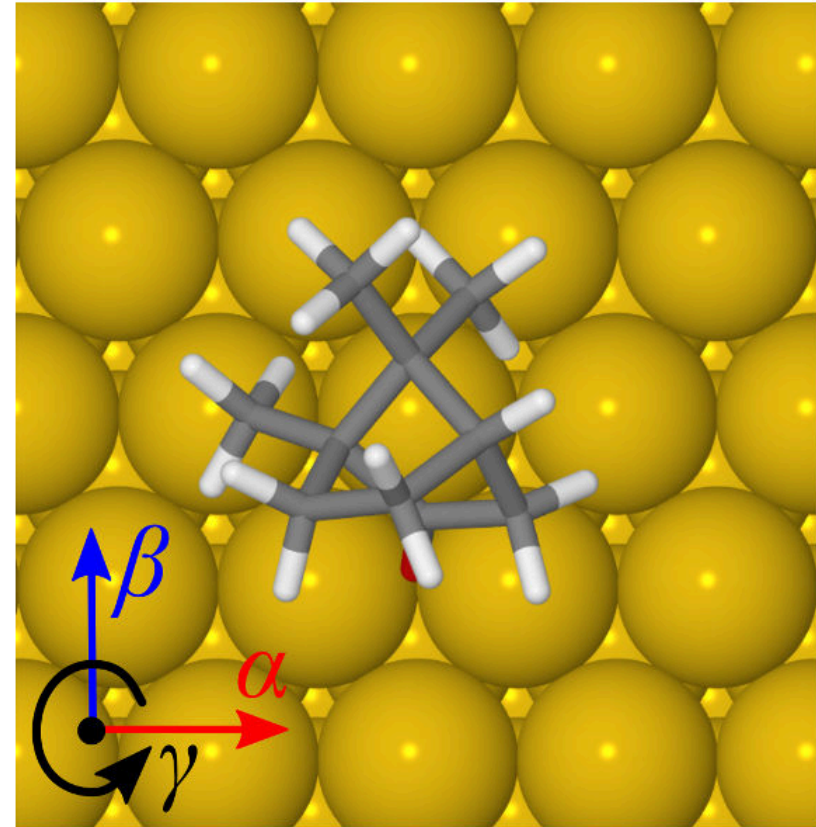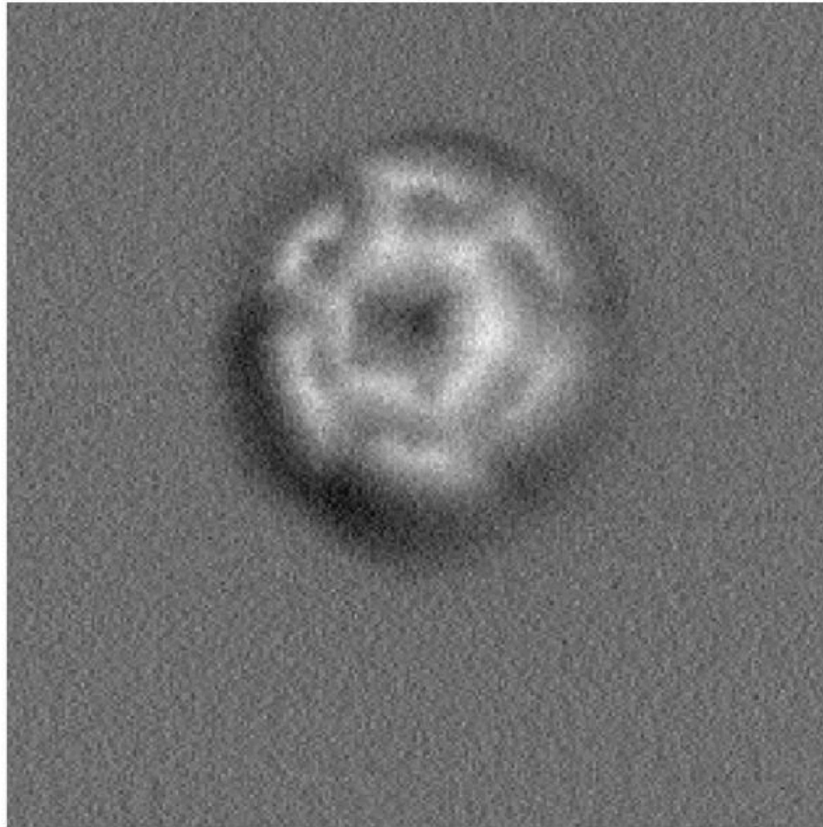
- Low energy γ rotation + 6-fold symmetry on Cu(111)
  $\rightarrow$ pinwheel image

AFM: static orientations

▶ 6D search for improved PES model

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Conclusions

- ▶ BOSS[1]: Accelerated and unbiased structure search

- ▶ Adsorption of camphor on Cu(111)
  - Camphor height 4-5 Å
  - Oxygen rotated towards surface
  - 2 different structures in 6D search, E_{ads} in range [-0.9, -0.8] eV

- ▶ Comparison with AFM
  - Low energy γ rotation $\rightarrow$ pinwheel

- ▶ Outlook
  - 6D results to explain static orientations
  - Relaxation of observed structures

[1] M. Todorović, M. Gutmann, J. Corander and P. Rinke, npj Comput. Mater. 2019, 5(1), 35.

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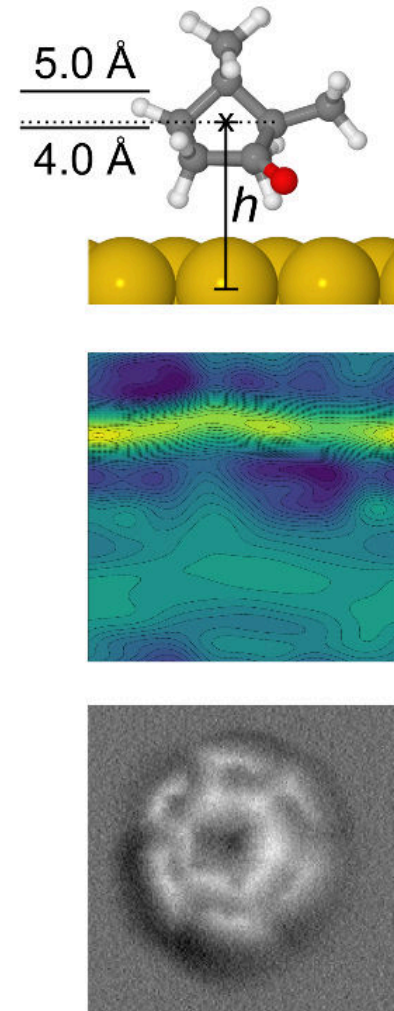
Acknowledgements

- ▶ BOSS team members
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  - • Ville Parkkinen (University of Helsinki)
  - • Henri Paulamäki (University of Helsinki)
- ▶ Academy of Finland
- ▶ CSC IT Center for Science