Detecting stable adsorbates of (1S)-camphor on Cu(111) with Bayesian optimization

Jari Järvi, Milica Todorović, and Patrick Rinke
Department of Applied Physics, Aalto University, P.O. Box 11100, 00076 Aalto, Espoo, Finland

Identifying the atomic structure of advanced functional materials is challenging with our currently available research tools. Interpreting the structure of complex molecular adsorbates from microscopy images can be difficult, and using atomistic simulations to find the most stable structures via thorough exploration of the potential energy surface is prohibitively expensive. In this study, we present the recently developed Bayesian Optimization Structure Search (BOSS) method (M. Todorović et al., npj Comput. Mater. 5, 35 (2019)) as an efficient solution for identifying the structure of non-planar adsorbates. We apply BOSS with density-functional theory simulations to detect the stable adsorbate structures of (1S)-camphor on the Cu(111) surface. We identify the optimal structure among 8 unique types of stable adsorbates, in which camphor chemisorbs via oxygen (global minimum) or physisorbs via hydrocarbons to the Cu(111) surface. This study demonstrates that new cross-disciplinary tools, like BOSS, facilitate the description of complex surface structures and their properties, and ultimately allow us to tune the functionality of advanced materials.

I. INTRODUCTION

Our frontier technologies are increasingly based on advanced functional materials, which are often blends of organic and inorganic components. For example, in search for renewable energy solutions, hybrid perovskites are currently the best candidate to replace silicon in our solar cells [1]. In medicine, hybrid materials have been studied extensively for applications in tissue engineering [2] and drug delivery [3]. To optimize the functional properties of these materials, we need detailed knowledge of their atomic structure. Of particular interest is the hybrid interface, which has a central role in defining the electronic properties of the material.

Assemblies of organic molecules on surfaces have been studied for example with scanning tunneling microscopy [4,5], atomic force microscopy (AFM) [6,7] and atomistic simulations [8,9]. However, our current experimental and computational methods cannot reliably identify the most stable structures. Interpreting microscopy images can be difficult, and the global structure search, i.e. thorough exploration of the potential energy surface (PES), with quantum mechanical accuracy is prohibitively expensive with conventional methods. Estimating optimal structures with chemical intuition, thus narrowing down the search space, is difficult with hybrid materials and can lead to biased and incorrect results. For example, with only partial knowledge of the PES, a metastable local minimum energy structure could easily be misinterpreted as the most stable global minimum.

In this work, we show that the recently developed Bayesian Optimization Structure Search (BOSS) machine-learning method [10] provides a solution to the structure search conundrum. To demonstrate how BOSS works, we apply it with density-functional theory (DFT) [11,12] to (1S)-camphor (C_{10}H_{16}O, hereafter shortened as camphor) adsorption on the Cu(111) surface. Camphor is an exemplary case of a bulky molecule, which is difficult to image with microscopy. AFM experiments [13] have revealed various different conformers of camphor on Cu(111), which makes it ideal for benchmarking the BOSS method.

With BOSS, we build a surrogate model of the PES and identify the stable structures in its minima. We estimate the stability of the adsorbates from the energy barriers extracted from surrogate PES and analyze the electronic structure of each adsorbate. Our results provide insight into the adsorption of complex organic molecules on metallic substrates and pave the way to more complex studies of hybrid monolayer formation and hybrid interfaces.

II. COMPUTATIONAL METHODS

A. Bayesian Optimization Structure Search

BOSS is a machine-learning method that accelerates structure search via a strategic sampling of the PES. With given initial data, BOSS builds the most probable surrogate model of the PES. In this work, we apply BOSS with DFT for accurate sampling of the energy points. BOSS refines the surrogate model iteratively with active learning using Bayesian optimization (BO) (Fig. 1a).

In BO, data is fitted with a distribution over functions in a Gaussian process (GP) [14] using Bayesian regression. In the resulting surrogate model (Fig. 1b), the posterior mean is the most probable model of the function to be optimized (here the PES). The uncertainty of the model is described by the posterior variance, which vanishes at the known data points.

BOSS then determines the next sampling point using an acquisition function. Here, we apply the exploratory Lower Confidence Bound (eLCB) function [15], which balances exploitation against exploration. In exploitation, BO refines the model by acquiring the next point near the currently predicted global minimum. In explo-

* jari.jarvi@aalto.fi
ration, the next acquisition is made at the point of maximum posterior variance, exploring areas of high uncertainty. Via this process, BOSS has identified the global minimum in benchmark tests in ca. 10% of the computational time compared to conventional global phase-space exploration, for example with grid search methods.

Furthermore, BOSS applies a building block approach to reduce the number of search dimensions. Building blocks are rigid structural components, for example rigid molecules, functional groups, or a surface slab. The PES is then defined in the phase space resulting from the remaining degrees of freedom, for example the relative translation and/or rotation of building blocks (Fig. 2).

Once the PES is converged, we data-mine the surrogate model. We extract the lowest energy minima, which we equate with the lowest energy adsorbate structures. The minima are detected using the built-in local minima search functionality of BOSS. The search is performed with minimizers, which start in different regions of the PES and traverse the landscape to locate the minima. The stability of the structures is evaluated with the associated energy barriers in the PES. The stable structures are verified with full structural relaxation in DFT, allowing unrestricted motion of all atoms, and analyzed with DFT for their electronic properties.

First, we apply BOSS to analyze stable camphor conformers with a 3D search of methyl group rotations (Fig. 2a). In this study, we use an ideal camphor geometry with a 120-degree periodic rotation of the methyl groups. For this, we normalize the C-H bonds in the three methyl groups to their average relaxed bond length of $d_{CH} = 1.1$ Å, bond angle $\lambda_{CCH} = 111.3^\circ$ and the angle between H atoms $\lambda_{HCH} = 107.6^\circ$.

With the identified global minimum conformer, we study the adsorption of camphor on Cu(111) with respect to molecular translation and rotation. First, we investigate the adsorption properties of camphor on Cu(111) using separated translational and rotational degrees of freedom, to determine optimal search ranges for a subsequent 6D study. We analyze the translations with a 1D search of the height of the molecule from the surface (Fig. 1b), and with a 2D search of the adsorption site on the surface (Fig. 2b). The molecular rotation is analyzed with a 3D search (Fig. 2b). With the acquired energy points, we initialize a 6D search with combined degrees of freedom to identify the stable adsorbate structures. We confirm the predicted structures with a full relaxation in DFT. With the relaxed structures, we estimate the energy barrier of the $\gamma$ rotation (1D search with BOSS) and the translational $x$-$y$ barrier in the predicted PES.

B. First-principles calculations

First-principles DFT calculations are applied to calculate the adsorption energy of camphor on Cu(111) for BOSS, to relax the predicted stable structures and to analyze the electronic structure of the stable adsorbates. We apply the all-electron, numeric atom-centered orbital code FHI-aims [17, 18] with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [19]. PBE is augmented with van der Waals (vdW) corrections employing the vdW-398 parametrisation [20] of the Tkatchenko-Scheffler method [21]. We use Tier 1 basis sets with light grid settings and a $\Gamma$-centered $3 \times 2 \times 1$ k-point mesh with a $6 \times 4$ supercell model. We apply relativistic corrections with the zero-order regular approximation [22] and Gaussian broadening of 0.1 eV of the electronic states. The total energy is converged within $10^{-6}$ eV in the self-consistency cycle and the structures are relaxed below the maximum force component of $10^{-2}$ eV/Å.

We model the Cu substrate with a Cu(111) slab of 4 atomic layers and $6 \times 4$ orthogonal unit cell atoms (192 atoms). The periodic Cu(111) slabs are separated by 50 Å of vacuum for negligible interaction between their periodic images. The orthogonal supercell (lattice vectors $[a, b, c] = [15.41, 17.79, 56.29]$ Å) provides a separation of $> 10$ Å between the periodic images of camphor, for a good approximation of a single molecule on the surface. The lattice constant of Cu is set to 3.632 Å, which we obtain from relaxed bulk Cu. We construct the 4-layer Cu slab by fixing the two bottom layers to their optimal layer separation ($d_{34} = 2.097$ Å, corresponding to bulk Cu). The two top layers are then relaxed, which results in a reduced layer separation ($d_{12} = 2.076$ Å, $d_{23} = 2.081$ Å). We apply this Cu slab model as a building block in the subsequent study of camphor adsorption.

The adsorption energy $E_{ads}$ is calculated as

$$E_{ads} = E_{tot} - (E_{Cu} + E_{cam}),$$

in which $E_{tot}$ is the total energy of the camphor/Cu(111) system, $E_{Cu}$ the energy of the relaxed Cu slab and $E_{cam}$ the energy of an isolated camphor molecule. We investigate the electronic structure of the stable adsorbates by analyzing their partial density of states (DOS) and the charge distribution with the Mulliken analysis of partial charges [23].

III. RESULTS

Camphor conformer search. We analyzed the camphor conformers with a 3D BOSS search of the methyl group rotations in range $\theta, \varphi, \omega \in [-60, 60]^\circ$. The energy landscape (Fig. 3a), converged in 20 evaluations, features a single global energy minimum at $(\theta, \varphi, \omega) = (-3, 7, -3)^\circ$, and an energy barrier of 0.1 eV for the rotation of the methyl groups. The high barrier (cf. the thermal energy at room temperature, ca. 0.025 eV) indicates that the structure of the minimum-energy conformer is stable at ambient temperatures, and the identified structure can thus be applied as a building block in the following adsorption study.
FIG. 1. a) Basic principle of the BOSS method, in which Bayesian optimization (BO) is applied iteratively with DFT to build a surrogate model of the PES. b) 1D example of the iterative process, in which the adsorption energy $E_{\text{ads}}$ of camphor on Cu(111) is predicted as a function of height $h$ of the molecule from the surface. The predicted adsorption height is converged in 5 energy evaluations to within 0.1 Å. After 10 evaluations, the posterior variance, which describes the uncertainty of the model, has become vanishingly small throughout the search region.

FIG. 2. a) Three methyl group rotation angles $\theta$, $\varphi$ and $\omega$ of camphor in the 3D conformer search with BOSS. b) Three translational directions $x$, $y$ and $z$ (corresponding to lattice directions [10-1], [-12-1] and [111], respectively) and three rotation angles $\alpha$, $\beta$ and $\gamma$ of camphor in the 6D search for stable adsorbate structures. The center of rotation is the middle point between the two carbon atoms, highlighted in red. c) Orthogonal unit cell of Cu(111), which is the search range in $x$ and $y$ directions.

**Adsorption of camphor on Cu(111).** We studied the adsorption height of camphor on Cu(111) with a 1D BOSS search in the range $z \in [3, 7]$ Å, with the global minimum camphor conformer at the on-top site $(x, y) = (0, 0)$ Å (Fig. 2a) in the default orientation $(\alpha, \beta, \gamma) = (0, 0, 0)^\circ$ (Fig. 2b). The predicted minimum of the adsorption energy converged in 5 evaluations and is found at $-10.847$ eV at height $z = 4.14$ Å (Fig. 1b).

We then studied the molecular rotation with camphor in the on-top site at height $z = 5.0$ Å in the search range $\alpha, \beta \in [-180, 180]^\circ$ and $\gamma \in [-60, 60]^\circ$. The resulting 3D PES (Fig. 3a), converged in 115 evaluations, features the global minimum at $(\alpha, \beta) = (-84, 143)^\circ$ and multiple local minima. The predicted energy barrier of $\gamma$ rotation is low, below 0.02 eV.

With the molecule in the observed global minimum orientation, we performed a 2D search of the adsorption site in the orthogonal unit cell (Fig. 2c) at height $z = 5.0$ Å. The PES (Fig. 3b), converged in 20 evaluations, features two identical minima at $(x, y) = (-0.05, -0.08)$ and $(0.45, 0.42)$, in fractional coordinates of the unit cell, which correspond to the translational symmetry of the Cu(111) surface in the orthogonal unit cell.

**Predicted stable adsorbates.** For the 6D search of stable adsorbates, we employed 492 previously acquired energy points from the low-dimensional studies. We multiplied these points by applying the 2-fold translational symmetry in the orthogonal unit cell and the 3-fold rotational symmetry of the Cu(111) surface at the on-top site. We initialized the search with 986 points and converged the 6D PES by acquiring 197 new points, for which we applied the symmetries.

In the minima of the PES, we identified 8 unique stable structures with predicted adsorption energies ($E_{\text{BOSS}}$) in range $[-0.961, -0.634]$ eV (Fig. 4a and Tab. 1). The average variance of the adsorption energy ($v_{\text{BOSS}}$) in these minima is $6.7 \cdot 10^{-4}$ eV (Tab. 1), which indicates low uncertainty of the surrogate model in these points. The energies of the identified structures, calculated with DFT ($E_{\text{DFT}}$) are in range $[-0.933, -0.631]$ eV.

**Relaxed structures.** We have classified the 8 relaxed structures with respect to the position of the oxygen (O)
FIG. 3. a) $\theta - \omega$ 2D cross-section of the 3D PES in the camphor conformer search, featuring a single minimum and an energy barrier of 0.1 eV for methyl group rotation. b) PES of the 2D translational $x - y$ search of the adsorption site of camphor on Cu(111). The landscape has two identical minima, which agree with the translational symmetry in the orthogonal unit cell. c) $\alpha - \beta$ 2D cross-section of the 3D PES in the search for adsorption orientation of camphor on Cu(111). The landscape features multiple local minima and a higher-energy region at $\beta \approx 90^\circ$.

TABLE I. Adsorption energies of the stable adsorbates, predicted by BOSS ($E_{\text{BOSS}}$), and the variance of the predicted energies on the 6D PES ($v_{\text{BOSS}}$). The adsorption energy calculated with DFT ($E_{\text{DFT}}$), energy after relaxation ($E_{\text{DFT opt}}$), and energy change in the relaxation ($\Delta E_{\text{DFT opt}}$). Predicted energy barriers of $\gamma$ rotation ($V_{\gamma}$) and $x$-$y$ translation ($V_{x-y}$).

|       | $E_{\text{BOSS}}$ (eV) | $v_{\text{BOSS}}$ (eV) | $E_{\text{DFT}}$ (eV) | $E_{\text{DFT opt}}$ (eV) | $\Delta E_{\text{DFT opt}}$ (eV) | $V_{\gamma}$ (eV) | $V_{x-y}$ (eV) |
|-------|-------------------------|--------------------------|------------------------|---------------------------|----------------------------------|------------------|----------------|
| A1    | -0.961                  | $3.65 \cdot 10^{-4}$     | -0.933                 | -1.022                    | -0.089                           | 0.232            | 0.045          |
| A2    | -0.910                  | $1.74 \cdot 10^{-4}$     | -0.885                 | -1.008                    | -0.123                           | 0.216            | 0.034          |
| A3    | -0.889                  | $7.34 \cdot 10^{-4}$     | -0.850                 | -1.005                    | -0.155                           | 0.183            | 0.008          |
| A4    | -0.803                  | $9.99 \cdot 10^{-4}$     | -0.723                 | -0.932                    | -0.209                           | 0.278            | 0.027          |
| A5    | -0.704                  | $2.46 \cdot 10^{-4}$     | -0.706                 | -0.800                    | -0.094                           | 0.048            | 0.003          |
| B1    | -0.634                  | $4.54 \cdot 10^{-4}$     | -0.631                 | -0.784                    | -0.154                           | 0.033            | 0.001          |
| B2    | -0.737                  | $1.66 \cdot 10^{-3}$     | -0.719                 | -0.772                    | -0.053                           | 0.008            | 0.003          |
| B3    | -0.658                  | $7.51 \cdot 10^{-4}$     | -0.652                 | -0.664                    | -0.012                           | 0.012            | 0.003          |
atom in the adsorbed camphor, namely O downwards near the surface (class A, Fig. 5a) and O upwards (class B, Fig. 5b). In the relaxation, we observed an average decrease of $-0.11$ eV from the $E_{\text{DFT}}$ energies (Fig. 4a and Fig. 1).

We analyzed the structural changes in the relaxation by comparing the location and orientation of the molecule before and after the relaxation. The average change in the location of the molecule, over all structures, is $(\Delta x, \Delta y, \Delta z) = (0.13, 0.09, 0.19) \text{ Å}$ and in the orientation $(\Delta \alpha, \Delta \beta, \Delta \gamma) = (6.1, 5.8, 2.5)^\circ$. The changes in the internal geometry of camphor in the relaxation, after removing the building block approximation, were evaluated using the average root-mean-square deviation of the atomic positions and the mean deviation of bond lengths, which are 0.13 Å and 0.003 Å, respectively, on average over all structures.

The predicted energy barriers of $\gamma$ rotation and $x-y$ translation (Fig. 4b and Fig. 1) are in range $[0.008, 0.278]$ and $[0.001, 0.045]$ eV, respectively, and show notable differences between class A and B structures.

**Electronic structure.** The Mulliken analysis of partial charges in the relaxed structures (Fig. 4d and Tab. II) indicates electron transfer from the adsorbed camphor to the Cu substrate. The average partial charge of camphor is $0.21$ e (elementary charge) for class A structures and $0.10$ e for class B. The charge distribution of the adsorbed camphor was analyzed in comparison to the distribution of an isolated molecule. In class A structures, the main contribution to the positive charge comes from hydrogen (H) atoms, with O as the second notable contributor. In class B structures, the positive charge of camphor originates predominantly from H atoms.

The partial DOS of class A structures (Fig. 4e) ex-

| Structure | $q_C$ (e) | $q_O$ (e) | $q_H$ (e) | $q_{\text{total}}$ (e) |
|-----------|-----------|-----------|-----------|----------------------|
| A1        | -0.007    | +0.083    | +0.137    | +0.212               |
| A2        | -0.002    | +0.089    | +0.119    | +0.206               |
| A3        | -0.013    | +0.079    | +0.129    | +0.195               |
| A4        | -0.013    | +0.097    | +0.139    | +0.223               |
| A5        | -0.025    | +0.107    | +0.143    | +0.225               |
| B1        | -0.006    | +0.010    | +0.110    | +0.113               |
| B2        | -0.025    | +0.015    | +0.129    | +0.119               |
| B3        | +0.007    | +0.002    | +0.050    | +0.058               |
FIG. 5. Relaxed stable adsorbate structures of camphor on Cu(111) in the 6D search, showing chemisorption of the molecule via oxygen (a), class A) and physisorption via hydrocarbons (b), class B).

hbits hybridization of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively), in comparison to an isolated camphor, which indicates chemical bonding between the molecule and the substrate. In class B structures, the HOMO and LUMO states are at $-1.0$ and $2.9$ eV, respectively, with a band gap of $3.9$ eV. Their similarity with the DOS of an isolated camphor indicates physisorption between the molecule and the substrate.

IV. DISCUSSION

Our results in the low-dimensional 2D and 3D studies of molecular translation and rotations indicate that camphor can adsorb on Cu(111) in multiple stable orientations. The high-energy band in the $\alpha - \beta$ landscape (Fig. 3c) shows the significance of the molecular orientation, in particular the $\beta$ angle, on the adsorption energy. This suggests a strong coupling between the molecular orientation and the adsorption height, which mandates a high-dimensional search with combined degrees of freedom. The low-dimensional PESs establish a qualitative description of the adsorption properties of camphor on Cu(111) and provide the optimal search ranges for the subsequent 6D studies, for example the approximate adsorption height of the molecule.

The predicted local minimum structures in the 6D search exhibit a wide range of energy barriers, which indicates that camphor may have both static and mobile adsorbates on Cu(111). The full relaxation of the predicted structures resulted in minor changes in the orientation of the molecule, its adsorption site, and energy, which verifies the accuracy of the surrogate model of the 6D PES. Negligible changes in the internal structure of camphor and the Cu slab effectively validate the building block approximation in this study.

We observed notable differences between the class A
and B adsorbates, specifically in their adsorption energy, energy barriers of molecular motion, and the electronic structure. Class A adsorbates have the highest adsorption energies and high energy barriers of molecular motion. The DOS of HOMO and LUMO in class A structures exhibit hybridization of the electronic states and the electron transfer from the molecule to the substrate is significantly larger than in class B, with major contribution from O. This indicates chemisorption of camphor via O to the Cu substrate. Conversely, in class B structures we observed the characteristics of physisorption. Class B structures have systematically lower adsorption energies, energy barriers, and electron transfer to the substrate, and their DOS of HOMO and LUMO resemble that of an isolated molecule.

The adsorption of camphor on Cu(111) has also been studied experimentally with AFM by Aldritt et al. [13]. In their images, they have observed various different adsorbate structures, which indicates that camphor can adsorb on Cu(111) in multiple stable configurations. Based on the estimated energy barriers of γ rotation in this study, we conclude that the experiments likely feature chemisorbed camphor molecules from class A. In particular, structures A1–A4 with the highest energy barriers are the most likely candidates for static adsorbates. A more detailed comparison between BOSS and AFM will be reported in Ref. [24].

V. CONCLUSION

In this study, we have demonstrated the efficiency and accuracy of BOSS in global structure search with complex molecular adsorbates. As a benchmark system, we have analyzed the adsorption of a camphor molecule on the Cu(111) surface with respect to molecular translation and rotation. With BOSS, we constructed a surrogate model of the 6D PES of adsorption and identified its minima, in which we detected the most stable structure (global minimum) and 7 other stable structures (local minima). We classified our stable structures into two classes A and B, with respect to the location of the O atom in the adsorbed camphor. The differences between the two classes were further categorized by the trends in the adsorption energies and the energy barriers of molecular motion. By analyzing the electronic structure of the stable adsorbates, we concluded that in the most stable structures (class A), camphor chemisorbs to the Cu surface via O bonding. Our results imply that class A structures are viable candidates for static camphor adsorbates observed in AFM experiments.

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