Combining Machine Learning and Many-body Calculations:
Coverage-Dependent Adsorption of CO on Rh(111)

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Adsorption of carbon monoxide (CO) on transition-metal surfaces is a prototypical process in surface sciences and catalysis. Despite its simplicity, it has posed great challenges to theoretical modeling. Pretty much all existing density functionals fail to accurately describe surface energies, CO adsorption site preference, as well as adsorption energies simultaneously. Although the random phase approximation (RPA) cures these density functional theory failures, its large computational cost makes it prohibitive to study the CO adsorption for any but the simplest ordered cases. Here, we address these challenges by developing a machine-learned force field (MLFF) with near RPA accuracy for the prediction of coverage-dependent adsorption of CO on the Rh(111) surface through an efficient on-the-fly active learning procedure and a Δ-machine learning approach. We show that the RPA-derived MLFF is capable to accurately predict the Rh(111) surface energy and CO adsorption site preference as well as adsorption energies at different coverages that are all in good agreement with experiments. Moreover, the coverage-dependent ground-state adsorption patterns and adsorption saturation coverage are identified.

Carbon monoxide (CO) is one of the important raw materials for organic synthesis such as the famous Fischer-Tropsch synthesis [1]. In these reactions, transition metals usually serve as catalysts and the catalytic reactions often occur on the transition-metal surfaces. Therefore, studying CO adsorption on transition-metal surfaces is technologically and fundamentally of great significance.

However, this prototypical surface science system has posed great challenges to theoretical modeling. This dates back to the well-known so-called “CO/Pt(111) puzzle” [2, 3], which indicates that density functional theory (DFT) using the existing local or semilocal density functionals tends to favor hollow sites for CO on Pt and Rh, in disagreement with experiments that yield the top site as the most stable adsorption site [2–8]. In addition, these density functionals tend to overestimate adsorption energies but underestimate surface energies [6–8]. It has been shown that the failures of local or semilocal density functionals are intimately associated with the incorrect positioning of the CO frontier orbitals with respect to the Fermi level [7–11] and likely caused by density-driven self-interaction errors [5]. As one of the few parameter-free methods that are able to resolve all these DFT issues, the random phase approximation (RPA) to the correlation energy [12] was shown to yield predictions not only in qualitative but also in quantitative agreement with experiment [7].

Presently, most theoretical studies have been restricted to investigating CO adsorption on metal surfaces for well-defined high-symmetry geometries, while coverage-dependent CO adsorption studies with an exhaustive search of the configuration space are rarely reported. It is worth mentioning that, using Monte-Carlo simulations based on a classical force field parametrized on DFT, Shan et. al [13] pioneeringly studied coverage-dependent CO adsorption on Pt(111). Nevertheless, the predicted results suffer from the failures of the underlying DFT method. This leaves several important questions open: What are the ground-state adsorption patterns at different coverages, how does the adsorption energy change as a function of coverage, and what is the saturation coverage? Here, we set out to address all these issues, using a combination of machine learning and state-of-the-art methods beyond DFT. We demonstrate clearly that quantitatively accurate predictions can be obtained by combining these cutting-edge developments into a seamless framework.

In order to accelerate the search of the configuration space, machine learning based regression techniques provide an elegant solution. They allow for an efficient and accurate representation of the potential energy surfaces with near first-principles accuracy [14–20]. However, most machine-learned force fields (MLFFs) are based on DFT calculations and they come with the same limitations as the underlying density functional, as is the case here for CO adsorption on metal surfaces. In our recent work in Ref. [21], we proposed a general strategy for generating a MLFF with beyond-DFT accuracy at a modest computational cost by combining an efficient on-the-fly active learning method [22, 23] and a Δ-machine learning (Δ-ML) approach [24–26]. Here, using a similar scheme we develop an RPA-derived MLFF (referred to as MLFF-RPAΔ) for the prediction of coverage-dependent CO adsorption on Rh(111). This progresses the state of art in several key aspects: To machine learn accurate energies for defects or adsorbates is much more challenging than for bulk systems, since machine learning techniques tend to make relatively larger errors for defects [27–29]. Furthermore, acquiring the training data is far from trivial, since the configuration space is huge and in our case not necessarily exhaustively sampled by DFT-based molecular dynamics. Finally, we need to deal with metallic surfaces and require accurate forces from the employed many-body theory, which puts great de-
mands on the sampling of the Brillouin zone. There is no a priori telling whether we can achieve our goal. Nevertheless, we demonstrate convincingly that the MLFF-RPA$^\Delta$ predicts accurate Rh(111) surface energy, the correct CO adsorption sites and supremely accurate adsorption energies at all coverages. All this has not been achieved to date. To put this in context, even relaxations for molecules on surfaces have not been reported for beyond-DFT methods.

We start by introducing the procedure for the construction of the MLFF-RPA$^\Delta$. Following the scheme proposed in Ref. [21], the procedure involves building a baseline DFT-derived MLFF and an intermediate surrogate MLFF model for machine-learning the differences between the RPA and DFT calculated energies and forces (called MLFF-$\Delta$ where $\Delta$=RPA–DFT). To this end, we carried out two on-the-fly active learning procedures based on Bayesian regression [22, 23] using the separable descriptors [30] as implemented in the Vienna Ab initio Simulation Package (VASP) [31, 32]. First, the baseline DFT-based MLFF was trained on the fly during heating molecular dynamics (MD) simulations from 0 to 1000 K using typically 20 000 MD steps for many different starting configurations including bulk Rh and the clean Rh(111) surface as well as different CO adsorption coverages [≤ 0.75 monolayer (ML)]. For the surfaces, six-layer slabs with a vacuum width of 15 Å and up to 6 × 6 surface unit cells were used. The DFT calculations were performed using the Perdew-Burke-Ernzerhof (PBE) functional [33]. Eventually, the training dataset (called $T^\beta$) contains 5267 structures [see Supplementary Material (SM) Table S1 [34]]. Second, another on-the-fly training was performed but using a reduced four-layer slab, 2 × 2 surface unit cells only, and a smaller vacuum width of 10 Å. A CUR rank compression [23, 35] was applied to this pool of resulting structures, to determine the 100 most representative motifs and structures. These constitute a second dataset referred to as $T^\gamma$ (SM Table S2 [34]). Kernel principal component analysis [36] indicates that the sampled motifs cover a wide range of the phase space (SM Fig. S1 [34]).

For the structures in $T^\beta$, the energies and forces were recalculated using the cubic-scaling finite-temperature RPA [37–40]. Partial electronic occupancies and their derivatives are exactly handled, and the first derivatives of the RPA energy with respect to the positions of the ions can be calculated without approximations at finite electronic temperature. The MLFF-$\Delta$ was then generated by machine learning the differences in energies and forces between the RPA and PBE calculations. We note that for this specific case, learning of the difference may have been somewhat easier by using a van der Waals (vdW) corrected density functional [41–43] as the low-level method (SM Table S5 [34]); however, here we desire to prove the effectiveness and generality of the $\Delta$-ML approach by using PBE as the starting point. Finally, the energies and forces of the structures in $T^\beta$ were corrected by adding the differences predicted by the MLFF-$\Delta$. The final MLFF-RPA$^\Delta$ was then fitted to the updated $T^\gamma$. For more details on the descriptors and training, we refer to SM [34].

We note that VASP uses a kernel-based method to fit the energies and forces. Generally, the computational cost for one energy and force calculation scales linearly with respect to the number of weights and basis functions used in the kernel. The number of necessary functions scales also unfavorably with respect to the number of species and the size of the configuration space that one needs to represent accurately. By contrast, the moment tensor potentials (MTPs) developed by Shapeev [44] are relatively immune to these limitations. They rely on a linear regression in a space of descriptors that include many-body interactions up to very high order. MTPs are 1-2 orders of magnitude faster than the kernel-based methods for a comparable accuracy [45]. To speed up the calculations, we refitted the on-the-fly generated dataset using MTPs for both, PBE and RPA, using the MLIP package [46] (see SM [34] for details). To avoid confusions, the shorthand “MTP” refers to the moment tensor potential and “KMLFF” to the kernel-based approach used in VASP.

The MLFFs-PBE were validated on a test dataset containing 320 structures including bulk Rh, the clean Rh(111) surface, and CO adsorption at various coverages (SM Table S3 [34]). Because of the large computational cost of RPA calculations, the validation of MLFFs-RPA$^\Delta$ was restricted to a reduced test dataset including 25 structures of small unit cells and CO adsorption ener-

| $E_a$(eV/atom) | 0.813 | 0.809 | 1.027 | 1.020 | 1.039[47] |
|----------------|-------|-------|-------|-------|---------|
| $E_a$(1/4 ML) (eV/CO) | Top | −1.916 | −1.885 | −1.464 | −1.482 | 1.45[48] (±0.14) |
|                | fcc   | −1.859 | −1.861 | −1.221 | −1.250 |       |
|                | hcp   | −1.950 | −1.953 | −1.287 | −1.322 |       |
|                | Bridge | −1.842 | −1.830 | −1.248 | −1.280 |       |
| $E_a$(2/4 ML) (eV/CO) | Top | −1.610 | −1.594 | −1.244 | −1.247 |       |
|                | fcc   | −1.618 | −1.607 | −1.085 | −1.097 |       |
|                | hcp   | −1.670 | −1.656 | −1.123 | −1.139 |       |
|                | Bridge | −1.739 | −1.724 | −1.269 | −1.271 |       |
| $E_a$(3/4 ML) (eV/CO) | Top | −1.323 | −1.332 | −1.030 | −1.056 |       |
|                | fcc   | −1.415 | −1.404 | −0.961 | −0.967 |       |
|                | hcp   | −1.446 | −1.425 | −0.985 | −0.982 |       |
|                | Bridge | −1.404 | −1.404 | −1.004 | −0.967 |       |
Figure 1. Ground-state structures of CO adsorption on Rh(111) for different coverages predicted by (a) MTP-PBE and (b) MTP-RPA\(^\Delta\). The Rh and O atoms are represented as light green and red balls, respectively. The C atoms (in brown) are underneath the O atoms and thus not visible. The black lines indicate the 4×4 Rh(111) surface that is periodically replicated.

Next, we test the prediction of physical properties using the MLFFs. First, the lattice constant of bulk Rh predicted by MTP-PBE is 3.83 Å, which is in good agreement with the PBE-predicted one (3.82 Å) and also close to the experimental value (3.80 Å [49]). Furthermore, in line with previous literature results [7], our RPA-predicted surface energy (1.027 eV/μ.a.) agrees well with the experimental value (1.039 eV/μ.a. [47, 50]), whereas the PBE-predicted one (0.813 eV/μ.a.) is too small (compare Table II). Third, for the CO site preference in the small structures shown in SM Fig. S3 [34], the MTPs predicted adsorption energies are overall in good agreement with the first-principles data (Table II). Note that the relaxed high-symmetry structures did not enter in the training dataset (except for sampling during the MD), so these are to some extent predictions, in particular, for the energetically unfavorable sites in DFT. This indicates that the finite-temperature MD sampled the relevant configuration space sufficiently well. In addition, the CO site preference for each coverage is also reproduced by the MTPs, except at 3/4 ML. Taking 1/4 ML for example, both PBE and MTP-PBE yield the site order as hcp > top > fcc > bridge, whereas RPA and MTP-RPA\(^\Delta\) predict the site order: top > hcp > bridge > fcc. Both RPA- and MTP-RPA\(^\Delta\)-predicted site order and adsorption energies are in good agreement with experiments [51–56] (see Table II). By contrast, the PBE- and MTP-PBE-predicted adsorption energies are too large. This is due to the overestimated binding of CO to the substrate as evidenced by the shorter C-Rh bond lengths for PBE (see SM Table S6 [34]). For 3/4 ML, the stability of the bridge site is slightly underestimated by the MLFFs (see Table II and SM Table S5 [34]), which we suspect is likely related to insufficient training data. As we will see later, at 3/4 ML a pattern that maximizes the CO distances mixing hcp, fcc and top sites is preferred (see Fig. 1).
Figure 2. (a) CO adsorption energies and (b) total binding energies of the system as a function of CO coverages. The experimental data are taken from Ref. [51]. PBE and vdW-DF [41] results were obtained by relaxing the MTP-PBE and MTP-RPA$^\Delta$ structures, respectively. Note that the structures with coverages over 0.75 ML (gray shaded region) are not included in the training, and the RPA calculations were performed using a four-layer slab with a vacuum width of 10 Å.

ground-state adsorption patterns and Fig. 2 shows the corresponding adsorption energies and total binding energies as a function of CO coverage. Let us first focus on the MTP-PBE predictions. As expected, MTP-PBE has the same limitations as PBE and tends to favor the hcp sites for coverages less than or equal to 1/4 ML, at variance with experiments [53–56]. The structures are consistent with the principle of hcp site adsorption and avoiding nearest-neighbor adsorption sites. As the coverage increases to 5/16 ML, CO starts to also adsorb at the fcc sites to maintain a large distance. Top site adsorption starts to occur from 9/16 ML onward, so maximizing the distance becomes progressively more important as the coverage increases. At 0.75 ML, a highly symmetric adsorption pattern [(2x2)-3CO with equally mixed top, hcp, and fcc sites] is observed. As the coverage continues to increase, the CO molecules move back to their high-symmetry hcp site, which was also the stable site at lower coverage (also note the vacancy structure at 15/16 ML).

We verified the predicted adsorption energies by performing PBE relaxations starting from the optimal structures (see Fig. 2). Although the agreement is perfect up to 0.75 ML, the errors become larger above 0.75 ML where training data are missing.

Let us now move to the MTP-RPA$^\Delta$ predictions. MTP-RPA$^\Delta$ restores the correct site order and predicts that all CO molecules adsorb at the top sites up to 0.5 ML (see Fig. 1). The adsorption patterns are clearly different to MTP-PBE at low coverage, indicating that the lateral interactions are also different. For instance, CO prefers to adsorb at the third-nearest-neighbor top site, which causes essentially no repulsion (see Fig. 2). At 0.25 ML we now observe a hexagonal instead of a square pattern. Furthermore, there are some peculiar patterns observed in the structures beyond 0.25 ML: Three CO molecules have a tendency to form triangles on second-nearest-neighboring Rh atoms. The predicted tilting toward the center is mostly a result of repulsion from the CO at the nearest-neighbor Rh atoms, as it prevails if a local relaxation using the PBE functional is performed. The triangular motif at 5/16 and 6/16 ML is similar to the adsorption pattern for CO on Rh(111) at 1/3 ML [54]. The experimental $\sqrt{3} \times \sqrt{3}$ structure is found when simulated annealing is performed for e.g. a $3 \times \sqrt{3}$ cell (see SM Fig. S4 [34]). At 8/16 ML we obtain a square-like structure again with slightly tilted CO molecules. The tilting also prevails during relaxation using PBE. As the coverage increases further, the threefold hollow sites become occupied, and between 11/16 up to 13/16 ML we observe similar adsorption patterns as in MTP-PBE. At 0.75 ML, the MTP-RPA$^\Delta$-predicted pattern is in excellent agreement with the experimental observation [53–56] (SM Fig. S4 [34]). The results at 13/16 and 14/16 ML are also interesting. At 13/16 ML, all CO molecules continue to have six neighbors; by canting the hexagons relative to the substrate, the CO molecules can move closer together. At 14/16 ML, most CO molecules still have six neighbors but there are extended defects with pentagonal coordination. Similar but not identical patterns are also observed for MTP-PBE at coverages larger than 0.75 ML. At even higher coverage, the CO molecules again move back to the low-energy site (here top), with vacancy structures occurring before the full coverage is reached. By performing direct RPA calculations for CO at the four high-symmetry sites at full coverage, we confirmed that the MTP-RPA$^\Delta$ yields the same site preference as the RPA.

Regarding the coverage-dependent adsorption energies, one can observe that the adsorption energies decrease as expected with increasing coverage for both MTP-PBE and MTP-RPA$^\Delta$. However, the MTP-RPA$^\Delta$-predicted adsorption energies are generally smaller, in better agreement with the experimental data [51] [see Fig. 2(a)]. Also at low coverage, the adsorption energies only marginally change for the MTP-RPA$^\Delta$, in excellent agreement with experiment [51] and our RPA calculations [see Fig. 2(a)]. This is consistent with a very weak CO-CO lateral repulsion.

The repulsion is clearly much stronger for the hollow site (PBE curve), where the adsorption energy already decreases between 0 and 1/4 ML. By performing local relaxations starting from the MTP-RPA$^\Delta$ predicted structures using PBE, we have determined that the differences are not related to the functional, but rather related to differences between the substrate mediated repulsion: For hcp-site adsorption, many neighboring Rh sites are “poisoned” resulting in a fairly early decrease of the average adsorption energy. As the coverage increases further, the CO-CO lateral repulsion increases more steeply. In particular beyond 14/16 ML, an abrupt decrease of the adsorption energies and binding energies is observed.
indicating that approximately 13/16 ML is the saturation coverage. This is slightly larger than the commonly believed 0.75 ML and achieved by rotating the CO layer with respect to the substrate. For comparison, we also show the adsorption energies obtained using vdW-DF [41]. Although vdW-DF predicts the top site to be stable (SM Table S5 [34]), it also predicts an increase of the adsorption energy at low coverage, suggesting CO clustering. As far as we know, clustering has never been observed experimentally and is not confirmed by the RPA either (crosses in Fig. 2).

In summary, we have developed an RPA-derived MLFF for predicting the coverage-dependent CO adsorption on Rh(111) at a modest computational cost through a combination of on-the-fly active learning and Δ-machine learning. This allows us not only to solve the long-standing CO adsorption puzzle on transition-metal substrates at low coverage, but also to accurately predict the Rh(111) surface energy, CO adsorption energies, and ground-state adsorption patterns at different coverages. All these results agree well with experiments, an achievement that is impossible with present density functionals. More broadly speaking, incorrect structure predictions using approximate density functionals are a common problem. Similar strategies as the one developed here can be used to become truly predictive in chemistry, materials, and surface sciences, including low-dimensional systems, terraces, and step edges.

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I. FIRST-PRINCIPLES CALCULATIONS

The first-principles (FP) calculations were performed using the Vienna Ab initio Simulation Package (VASP) [1, 2]. The plane-wave cutoff for the orbitals was chosen to be 450 eV. A Γ-centered k-point grid with a spacing of 0.2 Å\(^{-1}\) between k points was used to sample the Brillouin zone. For density functional theory (DFT) calculations, the electronic interactions were described using the Perdew-Burke-Emzerhof (PBE) functional [3]. The projector augmented wave (PAW) pseudopotentials [4, 5] (Rh, C and O) with the valence electron configurations of 4d\(^5\)5s\(^1\), 2s\(^2\)2p\(^2\), and 2s\(^2\)2p\(^2\) were employed for Rh, C, and O, respectively. The Gaussian smearing method with a smearing width of 0.05 eV was used. Whenever ground-state structures were required, the electronic optimization was performed until the total energy difference between two iterations was less than 10\(^{-6}\) eV. The structures were optimized until the forces were smaller than 0.01 eV/Å.

For the random phase approximation (RPA) calculations, the GW PAW potentials (Rh\(_{\text{sv_GW}}\), C\(_{\text{GW}}\) and O\(_{\text{GW}}\)) were used. The energy cutoff for the response function was chosen to be 300 eV. The RPA energies and forces were calculated using an efficient cubic scaling algorithm [6–8]. To handle the partial occupancies of states at the Fermi level for metallic systems, the finite-temperature RPA algorithm [9] was used. This algorithm employs a compressive sensing approach for the Matsubara summation so that a small number of imaginary frequency/time points is sufficient to obtain a reasonably high accuracy [9]. Here, the number of imaginary frequency/time points was set to 16 and the Fermi smearing method with a smearing width of 0.15 eV was chosen after extensive convergence tests.

II. MLFF TRAINING

Here, we give additional details on the machine-learned forced fields (MLFFs) training, while most of the training procedure is outlined in the main text. Our training structures were automatically selected during FP molecular dynamics (MD) simulations by the on-the-fly active learning method based on the Bayesian linear regression (BLR) [10, 11]. The on-the-fly learning method has been successfully used to develop accurate MLFFs for the prediction of various phase transitions [11–13], melting points [10], lattice thermal conductivities [13] as well as chemical potentials [14]. The FPMD simulations were performed at ambient pressure using a Langevin thermostat [15] combined with the Parrinello-Raman method [16]. The isothermal-isobaric (NPT) and the canonical (NVT) ensembles were used for bulk Rh and slab calculations, respectively. The PBE functional [3] and a time step of 2 fs were employed. For the on-the-fly learning, the atom density based separable descriptors [17] were used. The separable descriptors are similar to the smooth overlap of atomic positions (SOAP) formulation proposed by Bartók et al. [18], but differ in that the two-body distribution functions are explicitly included and the three-body distribution functions are free of two-body components by subtracting the self-interaction term so that the weight of the two- and three-body descriptors can be separately tuned [17]. For more discussions on the difference between the separable descriptors and the SOAP descriptors, we refer to Ref. [17]. The cutoff radius was set to 5 Å for both two- and three-body descriptors. The width of the Gaussian functions used for broadening the atomic distributions of the two- and three-body descriptors were set to 0.27 and 0.40, respectively. The number of radial basis functions were set to 21 and 14 for radial and angular parts, respectively.

We followed the method proposed in our recent work of Ref. [19] to develop an RPA-derived MLFF (MLFF-RPA\(^\Delta\)) for the prediction of coverage-dependent adsorption of CO on the Rh(111) surface. As explained in the main text, the development of MLFF-RPA\(^\Delta\) involves the construction of a baseline PBE-derived MLFF (MLFF-PBE) and an intermediate surrogate MLFF model for machine-learning the differences between RPA and PBE calculated energies and forces (called MLFF-\(\Delta\) where \(\Delta\)-MLFF-PBE). The success of the \(\Delta\)-ML approach originates from the assumption that low-level reference quantum-mechanical (QM) calculations such as DFT capture the most important contributions to the overall potential energy surface (though they might not be accurate) and therefore the remaining differences between high-level and low-level QM calculations become less corrugated and thus easier to be machine-learned [20]. The first training dataset (\(T^A\)) contains 5267 structures, whose detailed information is summarized in Table S1. The second dataset referred to as \(T^B\) contains 100 structures, which are detailed in Table S2. Through the kernel principal component analysis (KPCA) [21] on local atomic environments of each species, we found that these 100 structures of small unit cells in \(T^B\) are indeed very representative and cover a wide range of the phase space, as shown in Fig. S1. For the structures in the dataset \(T^B\), the energies and forces were recalculated using finite-temperature RPA calculations. The MLFF-\(\Delta\) was generated by machine-learning the differences in energies and forces between RPA and PBE calculations using the separable descriptors with a low spatial resolution of 0.6 Å and a small number of radial basis functions of 10 for both the radial and angular parts. Finally, the energies and forces of the structures in \(T^A\) were corrected by adding the differences predicted by the MLFF-\(\Delta\). The final MLFF-RPA\(^\Delta\) was then fitted to the updated \(T^A\).

We note that the final regression coefficients were determined by using a factor of 20 for the relative weight of the energy equations with respect to the equations for the forces and a singular value decomposition (SVD) to solve the least-squares problem. This was found to improve the overall accuracy of MLFFs as compared to BLR [12, 13, 19]. As explained in the main text, we also constructed moment tensor potentials (MTPs) [22] for both PBE and RPA using the MLIP package [23] based on the same training datasets as used in generating the kernel-based MLFFs. The MTP basis functions (i.e., contractions of one or more moments) were selected such that the level of scalar basis \(B_n\) is less than or equal to 26 (i.e., lev\(B_n\) ≤ 26). The number of
Table S1. Summary of the structures included in the training dataset $T^A$. The employed slab models here consist of 6 Rh layers and a vacuum width of 15 Å.

| CO coverages (ML) | Structure type          | No. structures |
|-------------------|-------------------------|----------------|
| —                 | Bulk Rh of 4-atom cell   | 115            |
|                   | Bulk Rh of 32-atom cell  | 85             |
| 0/4               | Clean 2x2Rh(111)         | 196            |
| 1/4               | 1CO@2x2Rh(111)           | 1327           |
| 2/4               | 2CO@2x2Rh(111)           | 1361           |
| 3/4               | 3CO@2x2Rh(111)           | 294            |
| 1/16              | 1CO@4x4Rh(111)           | 116            |
| 2/16              | 2CO@4x4Rh(111)           | 203            |
| 3/16              | 3CO@4x4Rh(111)           | 252            |
| 4/16              | 4CO@4x4Rh(111)           | 240            |
| 5/16              | 5CO@4x4Rh(111)           | 67             |
| 6/16              | 6CO@4x4Rh(111)           | 148            |
| 7/16              | 7CO@4x4Rh(111)           | 85             |
| 8/16              | 8CO@4x4Rh(111)           | 161            |
| 9/16              | 9CO@4x4Rh(111)           | 66             |
| 10/16             | 10CO@4x4Rh(111)          | 144            |
| 11/16             | 11CO@4x4Rh(111)          | 85             |
| 12/16             | 12CO@4x4Rh(111)          | 177            |
| 2/9               | 2CO@3x3Rh(111)           | 11             |
| 3/9               | 3CO@3x3Rh(111)           | 15             |
| 3/36              | 3CO@6x6Rh(111)           | 28             |
| 4/36              | 4CO@6x6Rh(111)           | 18             |
| 6/36              | 6CO@6x6Rh(111)           | 22             |
| 9/36              | 9CO@6x6Rh(111)           | 17             |
| **Total**         |                          | **5267**       |

Table S2. Summary of the structures included in the training dataset $T^B$. The employed slab models here consist of 4 Rh layers and a vacuum width of 10 Å.

| CO coverages (ML) | Structure type          | No. structures |
|-------------------|-------------------------|----------------|
| —                 | Bulk Rh of 32-atom cell  | 2              |
| 0/4               | Clean 2x2Rh(111)         | 1              |
| 1/4               | 1CO@2x2Rh(111)           | 18             |
| 2/4               | 2CO@2x2Rh(111)           | 24             |
| 3/4               | 3CO@2x2Rh(111)           | 55             |
| **Total**         |                          | **100**        |

radial basis functions was chosen to be 7. The regression coefficients were obtained by a non-linear least square optimization using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The weights expressing the importance of energies and forces in the optimization were set to be 1 and 0.025, respectively, which were found to yield the overall lowest loss function. To obtain more accurate MLFFs, a larger cutoff radius of 6 Å was finally used for retraining. It needs to be noted that a cutoff radius of 6 Å for a many-body potential allows to model interactions up to twice that cutoff, i.e. 12 Å. This suffices to capture all the relevant van der Waals (vdW) interactions. Moreover, it has been shown for CO on Pt(111) that nonlocal correlations beyond 4 Å are not relevant for predicting adsorption energy differences [24]. To avoid confusions, the shorthand “MTP” always refers to the moment tensor potential and “KMLFF” to the kernel-based approach used in VASP.

We also note that the isolated CO molecule was not learned by MLFFs. Instead, we calculated its total energy ($E_{CO}$) using PBE or RPA and fixed these values throughout all the CO adsorption energy calculations. The adsorption energy per CO [$E_{ad}(n)$] for $n$ CO molecules adsorbed on the surface is calculated as

$$E_{ad}(n) = \frac{1}{n}(E_{total} - E_{slab} - nE_{CO}),$$

where $E_{total}$ and $E_{slab}$ are the total energies of the optimized CO@Rh(111) complex and the clean Rh(111) surface, respectively. The total binding energy of the system is then obtained by

$$E_b(n) = nE_{ad}(n).$$
Figure S1. KPCA map for the local atomic environments of (a) Rh, (b) C, and (c) O atoms in the datasets $T^A$ (black star) and $T^B$ (red circle).

Table S3. Summary of the structures included in the validation dataset $T^C$.

| CO coverages (ML) | Structure type           | No. structures |
|-------------------|---------------------------|----------------|
| —                 | Bulk Rh of 32-atom cell   | 40             |
| 0/4               | Clean 2x2Rh(111)          | 40             |
| 2/16              | 2CO@4x4Rh(111)            | 40             |
| 1/4               | 1CO@2x2Rh(111)            | 40             |
| 6/16              | 6CO@4x4Rh(111)            | 40             |
| 2/4               | 2CO@2x2Rh(111)            | 40             |
| 10/16             | 10CO@4x4Rh(111)           | 40             |
| 3/4               | 3CO@2x2Rh(111)            | 40             |
| Total             |                           | 320            |

III. MLFF VALIDATION

The MLFFs-PBE were validated on a test dataset ($T^C$) containing 320 structures including bulk Rh, the clean Rh(111) surface, and CO adsorption on the Rh(111) surface with various coverages. These structures were randomly selected from MD simulations at $T=1000$ K using the MTP-RPA$^\Delta$. The detailed information for the test dataset $T^C$ is summarized in Table S3. Due to the large computational cost of RPA calculations, the validation of MLFFs-RPA$^\Delta$ was restricted to a reduced test dataset ($T^D$) of small unit cells (see Table S4). The validation root-mean-square errors (RMSEs) in energies and forces for MLFFs-PBE and MLFFs-RPA$^\Delta$ using atom density based descriptors or moment tensor descriptors are given in Table I of the main text and
Table S4. A summary of structures included in the validation dataset $T^D$.

| CO coverages (ML) | Structure type                 | No. structures |
|-------------------|--------------------------------|----------------|
| 0/4               | Clean 2x2Rh(111)               | 1              |
| 1/4               | 1CO@2x2Rh(111)                 | 8              |
| 2/4               | 2CO@2x2Rh(111)                 | 8              |
| 3/4               | 3CO@2x2Rh(111)                 | 8              |
| **Total**         |                                | **25**         |

Figure S2. (a, b) MLFFs-PBE vs. PBE in energies and forces for the validation dataset $T^C$ containing 320 structures (see Table S3). (c, d) MLFFs-RPA$^\Delta$ vs. RPA in energies and forces for the validation dataset $T^D$ containing 25 structures (see Table S4). The results obtained from KMLFFs and MTPs are shown in red and blue, respectively.

the MLFFs predicted energies and forces against the first-principles data are further illustrated in Fig. S2.
Table S5. The surface energy of the Rh(111) surface ($E_s$) and CO adsorption energies at different coverages ($E_{ad}$, in eV per CO) predicted by different methods. The results from the nonlocal vdW-DF functional of Dion et al. [25] as well as the DFT-D3 method of Grimme et al. [26] using the revised PBE of Hammer et al. [27] (RPBE+D3) are also given. All calculations here were carried out using a 2×2 slab of 4 Rh layers with a vacuum width of 10 Å. The adopted CO@Rh(111) structure models are displayed in Fig. S3. The RPA calculations were performed using the PBE relaxed structures.

|       | PBE   | MTP-PBE | KMLFF-PBE | vdW-DF | RPBE+D3 | RPA   | MTP-RPAΔ | KMLFF-RPAΔ | Experiment |
|-------|-------|---------|-----------|---------|---------|-------|----------|------------|------------|
| $E_s$ (eV/u.a.) | 0.813 | 0.809   | 0.805     | 1.103   | 1.027   | 1.020 | 1.020    | 1.039 [28] |            |
| $E_{ad}$ (1/4 ML, top) | −1.916 | −1.885  | −1.879    | −1.663  | −1.994  | −1.464 | −1.482   | −1.477     | 1.45±0.14 [29] |
| $E_{ad}$ (1/4 ML, fcc) | −1.859 | −1.861  | −1.849    | −1.454  | −1.835  | −1.221 | −1.250   | −1.249     |            |
| $E_{ad}$ (1/4 ML, hcp) | −1.950 | −1.953  | −1.964    | −1.530  | −1.917  | −1.287 | −1.322   | −1.340     |            |
| $E_{ad}$ (1/4 ML, bridge) | −1.842 | −1.830  | −1.819    | −1.478  | −1.856  | −1.248 | −1.280   | −1.285     |            |
| $E_{ad}$ (2/4 ML, top) | −1.610 | −1.594  | −1.580    | −1.389  | −1.693  | −1.244 | −1.247   | −1.241     |            |
| $E_{ad}$ (2/4 ML, fcc) | −1.618 | −1.607  | −1.607    | −1.256  | −1.600  | −1.085 | −1.097   | −1.108     |            |
| $E_{ad}$ (2/4 ML, hcp) | −1.670 | −1.656  | −1.669    | −1.296  | −1.646  | −1.123 | −1.139   | −1.158     |            |
| $E_{ad}$ (2/4 ML, bridge) | −1.739 | −1.724  | −1.709    | −1.410  | −1.763  | −1.269 | −1.271   | −1.265     |            |
| $E_{ad}$ (3/4 ML, top) | −1.323 | −1.332  | −1.302    | −1.136  | −1.421  | −1.030 | −1.056   | −1.031     |            |
| $E_{ad}$ (3/4 ML, fcc) | −1.415 | −1.404  | −1.369    | −1.089  | −1.411  | −0.961 | −0.967   | −0.975     |            |
| $E_{ad}$ (3/4 ML, hcp) | −1.446 | −1.425  | −1.413    | −1.109  | −1.437  | −0.985 | −0.982   | −1.012     |            |
| $E_{ad}$ (3/4 ML, bridge) | −1.404 | −1.404  | −1.316    | −1.106  | −1.414  | −1.004 | −0.967   | −0.949     |            |

Table S6. The bond lengths (in Å) of C-O and C-Rh for CO adsorbed on the top or hcp sites predicted by different methods. Here, the surface is modeled using a 2×2 slab of 4 Rh layers and a vacuum width of 10 Å and only one CO molecule is considered, leading to 1/4 ML coverage. RPA and PBE predict almost identical C-O bond lengths for both the top and hcp sites, while RPA predicted larger C-Rh bond lengths than PBE for both sites.

|       | $d_{C-O}$ | $d_{C-Rh}$ | $d_{C-O}$ | $d_{C-Rh}$ |
|-------|-----------|------------|-----------|------------|
| top site | 1.165     | 1.828      | 1.197     | 2.085      |
| MTP-PBE | 1.165     | 1.827      | 1.196     | 2.081      |
| KMLFF-PBE | 1.165    | 1.829      | 1.196     | 2.082      |
| MTP-RPAΔ | 1.164     | 1.857      | 1.193     | 2.109      |
| KMLFF-RPAΔ | 1.164    | 1.857      | 1.193     | 2.106      |
Figure S4. Ground-state structures of CO adsorption on the Rh(111) surface for different coverages predicted by MTP-PBE (left column) and MTP-RPA (middle column), which are compared to the experimental data (right column) taken from Ref. [30]. The black lines indicate the Rh(111) surface that is periodically replicated.

IV. DATA AVAILABILITY

The data that support the findings of this study are available at https://uccloud.univie.ac.at/index.php/s/A8vmHSHP44XbMY1

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