Van der Waals density functional study of *n*-alkane adsorbed on metal surfaces

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We present a comprehensive study of *n*-alkane adsorbed on metal surfaces using the van der Waals density functional (vdW-DF) method. This method outperforms the density functional theory calculations within the local density or generalized gradient approximation in terms of a better description of a wide range of physisorption systems. Especially, our results demonstrate that vdW-DFs with improved accuracy nicely predict the adsorption heights of *n*-alkanes on close-packed metal surfaces. We also show that the C–H stretching frequencies and infrared absorption spectra are useful for discriminating the competing adsorption structures. Detailed analyses of the properties of *n*-alkanes on metal surfaces, however, reveal some discrepancies with experimental results, suggesting that further improvement of vdW-DF or the application of a more sophisticated technique is necessary for a systematic description of the *n*-alkane-metal interfaces with higher accuracy.

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I. INTRODUCTION

A detailed understanding of the interfaces between organic molecules and metal electrodes is crucial for developing high-performance organic devices. For example, the electric dipole layer formed at an organic-metal interface influences the charge injection barrier [1]. Among the mechanisms proposed as the origin of the interface dipole layer, the push back effect due to the Pauli repulsion [2,3] plays an essential role in the adsorption of inert and nonpolar organic molecules such as *n*-alkanes. Although *n*-alkanes adsorbed on metal surfaces appear to be typical physisorption systems, experiments have revealed that the C–H bonds are significantly softened at the interfaces [4–12], suggesting that these systems bear the character of weak chemisorption.

To elucidate the properties of *n*-alkanes on metal surfaces, a variety of experimental techniques have been employed such as infrared reflection absorption spectroscopy (IRAS) [4–11,13–21], low energy electron diffraction (LEED) [10,11,22–27], and temperature programed desorption (TPD) [18,21,27–35]. Theoretically, first principles calculations based on density functional theory (DFT) have been applied to *n*-alkanes on metal surfaces, mainly from industrial viewpoints such as the Fischer-Tropsch synthesis [36–44], dehydrogenation of hydrocarbons [45–48], and charge injection barriers [49–51]. DFT calculations have also been used to investigate the geometric and electronic structures of several *n*-alkane-metal interfaces [45,46,48,52–56]. Morikawa *et al.* have studied *n*-alkanes adsorbed on various metal surfaces within the generalized gradient approximation (GGA), demonstrating that DFT calculations can reproduce the vacuum level shift and the softening of C–H stretching modes that have been observed experimentally [52]. However, the GGA results underestimate the adsorption energies of *n*-alkanes, due to the lack of van der Waals (vdW) interactions. In the last two decades, several vdW corrections have been proposed for use in DFT calculations [57–62], among which the vdW density functional (vdW-DF) method [57,63,64] is a scheme to describe vdW interactions without semi-empirical parameters. Moreover, new functional forms of vdW-DF have been actively developed until recently [65–75].

In this paper, we apply vdW-DF to the investigation of the adsorption of *n*-alkanes on various metal surfaces. Our results reveal that the rev-vdW-DF2 [71,76] and optB86b-vdW [69] functionals predict reasonable adsorption energies of *n*-alkanes on the Cu(100) and Cu(111) surfaces, respectively, whereas the two functionals significantly overestimate those on the close-packed surfaces of other metals. In contrast, the adsorption heights of *n*-alkanes on the latter surfaces obtained with the two functionals are in good agreement with those estimated from the vacuum level shift and the softening of the C–H stretching modes. We also show that the changes in the C–H stretching frequencies and IRAS spectra are useful for determining the preference of different adsorption structures of similar stability.

This paper is organized as follows. The details of the DFT calculations used in this work are described in Sec. II. Our calculated results are presented in Sec. III, which consists of three parts: The adsorption structures of *n*-butane on close-packed metal surfaces and those of polyethylene on low-indexed Cu surfaces are determined in Sec. III A. For polyethylene on Cu(100) and (110), the vibrational properties of the molecule are discussed in Sec. III B. The work functions of the above systems are investigated in Sec. III C. This work is summarized in Sec. IV.

II. METHODS

The DFT calculations are carried out using the STATE code [77,78] with the plane wave basis set. Most of the ion cores are described by ultrasoft pseudopotentials [79], while that of

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Ag is described by a norm-conserving pseudopotential [80]. The energy cutoffs for wave functions and charge density are 36 and 400 Ry, respectively, except for the systems including Ag, where the cutoff energy for the wave functions is increased to 64 Ry. Metal surfaces are modeled with periodically repeated slabs composed of six atomic layers, where surface reconstruction is not taken into account. The LEED results indicate that *n*-alkane molecules form a close-packed monolayer on Pt(111) at low temperatures with the C–C–C plane approximately parallel to the surface [15]. The same trend is also expected for other metals and facets because the molecules are physisorbed on the surface through vdW interactions. Thus, *n*-butane is adsorbed on the (111) surfaces of Cu, Ag, Ir, Pt, and Au, and on the Ru(0001) surface using the $(\sqrt{7} \times \sqrt{3})$ surface unit cell [15], and Γ-centered 4×6 k points are sampled in the surface Brillouin zone (SBZ). On the other hand, polyethylene is adsorbed on the Cu(111), (100), and (110) surfaces, using the $(1 \times \sqrt{3})$, (1×2) [23], and (1×4) [11,23] surface unit cells, respectively. Correspondingly, Γ-centered 12×6, 12×6, and 12×3 k points, respectively, are sampled in the SBZs.

The physisorption of the *n*-alkane molecules on the surfaces is described by the self-consistent [63,81–83] vdW-DF method [57] with the optB86b-vdW [69] and rev-vdW-DF2 [71,76] functionals. The former is based on the nonlocal correlation functional ($E_{\rm c}^{\rm nl}$) of the original vdW-DF [57], while the latter is based on $E_{\rm c}^{\rm nl}$ of the second version of vdW-DF (vdW-DF2) [54]. vdW-DF employs the gradient expansion for the slowly varying electron gas [84] to describe the internal exchange-correlation energy $\epsilon_{\rm xc}^{\rm int}$ for $E_{\rm c}^{\rm nl}$, which is responsible for the attractive dispersion force. On the other hand, vdW-DF2 employs the large-N asymptote [85,86] for $\epsilon_{\rm xc}^{\rm int}$, which is more appropriate for molecular systems. vdW-DF predicts more accurate C_6 coefficients than vdW-DF2 [87], but tends to overestimate the attractive interaction due to the dispersion force. optB86b-vdW and rev-vdW-DF2 employ the same enhancement factor of B86b [88] for the exchange functional with different parametrizations, and show similar and consistent results, but the former (latter) tends to predict larger (smaller) adsorption energy and smaller (larger) equilibrium distance, in particular, for weakly interacting systems, as in the case of the present study. See Refs. [89–93] for some benchmark calculations.

The structures of isolated and crystalline *n*-alkane molecules, clean surfaces, and the adsorption systems are relaxed until the atomic forces fall below 8.24×10^{-2} nN (10^{-3} Hartree/Bohr) except for the bottom three layers of the slabs, which are fixed at the bulk positions with lattice constants as listed in Table I. The zero-point corrections (ZPCs) due to the molecular vibrations are taken into account. The vibrational modes are obtained by diagonalizing the mass-weighted Hessian matrix estimated within the finite-difference approximation [95] as follows. Normal coordinates are initially estimated by displacing the atoms in the molecules by $\pm 5.29 \times 10^{-3}$ Å ($\pm 10^{-2}$ Bohr) in each Cartesian direction. Then the accuracy of the vibrational modes is improved by displacing those atoms along the normal coordinates, where the magnitudes of the displacements are chosen in such a way that the maximum force acting on the displaced atoms is $\simeq 2.47 \times 10^{-1}$ nN (3×10^{-3} Hartree/Bohr). A vacuum layer of 15 Å thick above a metal surface and the effective screening medium method [96,97] are used to eliminate spurious electrostatic interactions with the periodic images.

TABLE I. Calculated lattice constants of transition metals in Å. Note that two lattice constants are shown for the hcp structure of Ru.

	rev-vdW-DF2	optB86b-vdW	Experiments[a]
Cu	3.63	3.62	3.61
Ag	4.10	4.09	4.09
Au	4.11	4.14	4.08
Ir	3.85	3.83	3.84
Pt	3.93	3.93	3.92
Ru$_a$	2.63	2.64	2.70
Ru$_c$	4.21	4.19	4.28

[a] Reference [94].

III. RESULTS

A. Adsorption structures

The determination of the adsorption structures is the first step in studying the properties of the *n*-alkane-metal interfaces. The stabilities of the adsorption structures are compared by using the molecule-surface interaction energy per C atom given by

$$E_{\rm int} = \frac{1}{N_{\rm C}}(E_{\rm mol/surf} - N_{\rm mol}E_{\rm mol} - E_{\rm surf}). \tag{1}$$

Here $E_{\rm mol}$, $E_{\rm surf}$, and $E_{\rm mol/surf}$ are the total energies of an isolated molecule, a clean surface, and their composite system, respectively, while $N_{\rm C}$ and $N_{\rm mol}$ are the numbers of C atoms and molecules, respectively, in a unit cell. In the following, the interaction energy is plotted as a function of the distance between the molecular plane and the metal surface. At each distance, the surface geometry is unchanged, while the molecular structure is relaxed except for the molecular plane, which is kept parallel to the surface.

1. n-butane adsorbed on close-packed metal surfaces

To see the dependence of the *n*-alkane-metal interaction on the metal element, we here determine the adsorption structures of *n*-butane on the (111) surfaces of fcc metals and the Ru(0001) surface. Based on the zigzag shape of the *n*-butane molecule and the hexagonal structure of the close-packed surfaces, we examine the two high-symmetry adsorption configurations as shown in Figs. 1(a) and 1(b), which have been considered in Refs. [15,52], respectively. The molecular axis is oriented in the $[1\bar{1}0]$ direction in both cases, while C atoms are approximately above the hollow and top sites in the former and latter, respectively. We compare the stabilities of the two configurations by taking *n*-butane on Cu(111) as an example. The interaction energy between *n*-alkane and Cu(111) for rev-vdW-DF2 is plotted as a function of the molecule-surface distance in Fig. 1(c), which indicates that the configuration in Fig. 1(b) is more preferable.

We thus determine the adsorption structures of *n*-butane on the close-packed metal surfaces assuming the adsorption configuration in Fig. 1(b). The interaction energy of *n*-butane

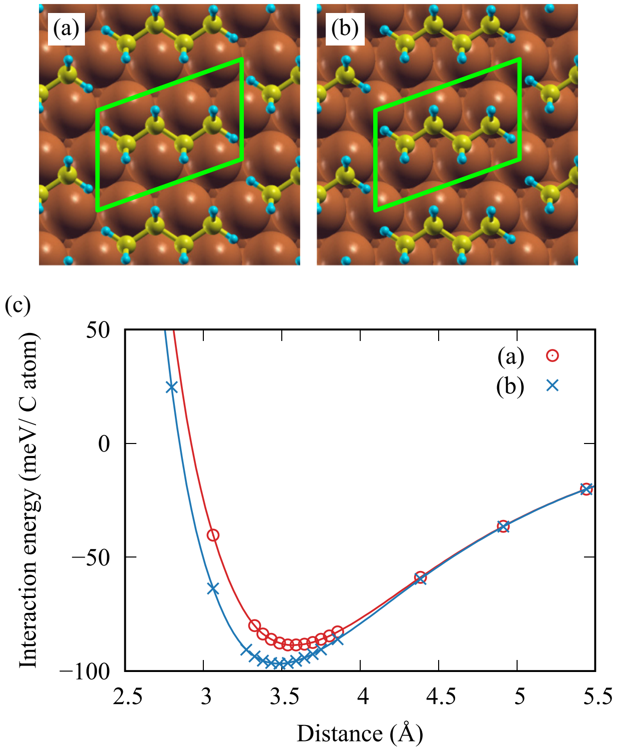


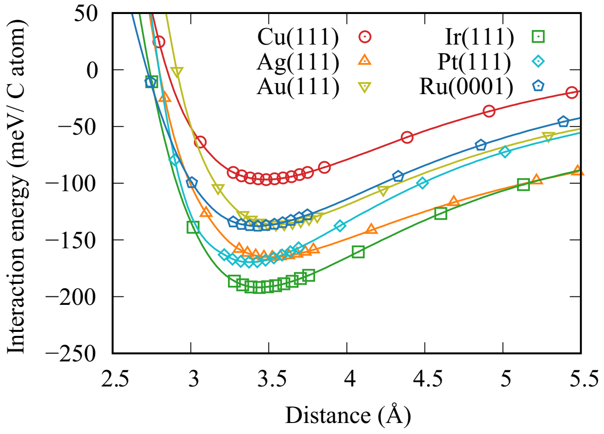
FIG. 1. Schematic views of *n*-butane adsorbed on the Cu(111) surface in two different configurations (a) and (b), where the parallelogram in each panel represents the $(\sqrt{7} \times \sqrt{3})$ unit cell. Panel (c) shows the rev-vdW-DF2 results for the interaction energies between *n*-butane and Cu(111) plotted as functions of the molecule-surface distance.

on each surface is plotted as a function of the molecule-surface distance in Fig. 2. The rev-vdW-DF2 and optB86-vdW results show qualitatively similar behaviors, but the latter have systematically deeper minima at smaller molecule-surface distances, which agrees with the general trends of these functionals as mentioned in Sec. II. The origin of these differences is discussed in Sec. II of the Supplemental Material [100]. The adsorption structure of each system is determined by fully relaxing the structure near the minimum. The adsorption energy is given by $|E_{\text{int}}|$ of the relaxed structure, while the adsorption distance is defined as the average distance between the C atoms in the molecule and the metal atoms in the topmost layer. The calculated adsorption energies and heights are summarized in Tables II and III, respectively. In the former, the adsorption energies are corrected with the ZP energy

$$E_{\text{ZP}} = \sum_i \frac{\hbar\omega_i}{2} \tag{2}$$

with ω_i being the frequency of the i-th molecular vibration. Note that the ZPC always increases the adsorption energy, which is mainly due to the softening of the C–H bonds pointing towards the surface. The adsorption energy on Cu(111) calculated with optB86b-vdW is in good agreement with the TPD result [34], whereas those on Au(111), Pt(111), and Ru(0001), especially the ZP-corrected values are significantly larger than the experimental ones [27,29,34,35,98,99]. In contrast, the calculated adsorption heights on the latter surfaces are close to those estimated from the changes in work functions and C–H stretching frequencies [52]. It should be noted that the adsorption height on Ag(111) is significantly overestimated, which can also be seen in the DFT results obtained with the QUANTUM ESPRESSO code [101] as shown in Sec. III of the Supplemental Material [100]. In addition, the experimental results for Ir(111) are scarce, because *n*-alkanes dissociatively chemisorb on the surface [102]. Our results indicate that rev-vdW-DF2 and optB86-vdW tend to overestimate the adsorption energies of *n*-butane on the close-packed surfaces, whereas they exhibit superior performance in the adsorption heights as compared with vdW-DF2 [54], which is known to systematically overestimate equilibrium distances.

(a) rev-vdW-DF2



(b) optB86b-vdW

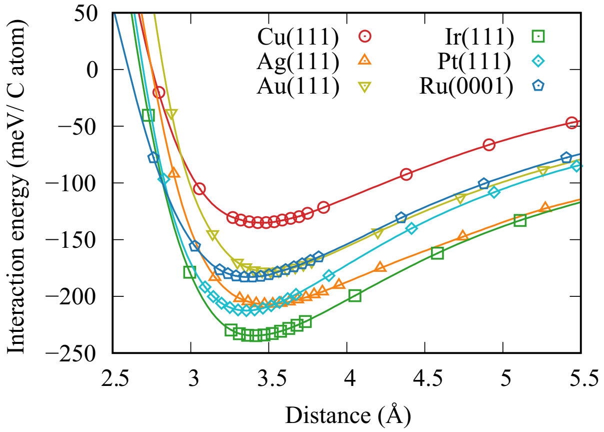


FIG. 2. Interaction energies between *n*-butane and close-packed metal surfaces as functions of the molecule-surface distance. Panel (a) [(b)] show the rev-vdW-DF2 (optB86b-vdW) results for the interaction energies. A *n*-butane molecule is adsorbed on the surface in the configuration shown in Fig. 1(b).

2. Polyethylene adsorbed on low-indexed Cu surfaces

To see the dependence of the molecule-surface interaction on the facet of a metal surface, we also determine the adsorption structures of polyethylene on the Cu(111), (100), and (110) surfaces. Note that the length of the repeating unit of polyethylene is close to the nearest neighbor distance of Cu atoms, which is calculated to be 2.56 (2.57) Å with

TABLE II. Calculated adsorption energies per C atom of *n*-butane (polyethylene) on the close-packed metal (low-indexed Cu) surfaces in meV. The adsorption energies without ZPC are shown in parentheses. The experimental results are obtained for *n*-butane adsorbed on the metal surfaces.

System	rev-vdW-DF2	optB86b-vdW	Experiments
n-butane			
Cu(111)	113 (100)	134 (129)	127[a]
Ag(111)	207 (166)	227 (207)	...
Au(111)	165 (138)	193 (177)	105[b]
Ir(111)	219 (192)	256 (235)	...
Pt(111)	202 (171)	233 (210)	120[a] 131[c] 132[d] 156[e]
Ru(0001)	162 (139)	198 (178)	129[f]
Polyethylene			
Cu(111)	102 (100)	145 (136)	...
Cu(100) (a)	118 (114)	160 (146)	120[g]
Cu(100) (b)	118 (114)	155 (145)	120[g]
Cu(110) (a)	121 (114)	160 (147)	...
Cu(110) (b)	119 (112)	155 (144)	...

[a] Reference [34].
[b] Reference [98].
[c] Reference [27].
[d] Reference [35].
[e] Reference [99].
[f] Reference [29].
[g] Reference [28].

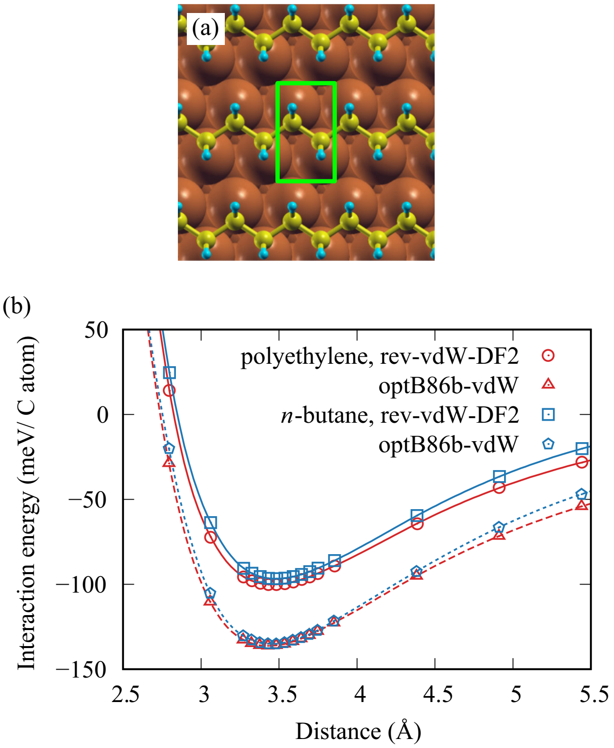


FIG. 3. Schematic views of polyethylene adsorbed on the Cu(111) surface (a), where the rectangle represents the $1 \times \sqrt{3}$ unit cell. (b) shows the interaction energies between polyethylene and Cu(111) plotted as a function of the molecule-surface distance. The results for *n*-butane on Cu(111) are also shown for comparison.

rev-vdW-DF2 (optB86b-vdW). Based on the comparison of the adsorption configurations of *n*-butane on Cu(111) (see Fig. 1), we assume that polyethylene adsorbs on Cu(111) as shown in Fig. 3(a), where C atoms are approximately above the top sites. The interaction energies between polyethylene and Cu(111) are plotted in Fig. 3(b), and the adsorption energies and heights are shown in Tables II and III, respectively. These results are similar to those for *n*-butane on Cu(111), demonstrating that the adsorption of *n*-alkane on metal surfaces little depends on the chain length. Note that the slight deviations in the adsorption energies from those for *n*-butane on Cu(111) reflect the difference in the molecular structures.

The LEED analyses have revealed that polyethylene forms a (1×2) superstructure on Cu(100) with the molecular axis along the [011] or $[0\bar{1}1]$ direction [10,11,25]. We examine the adsorption configurations as shown in Figs. 4(a)–4(c), where the polyethylene molecule is above a gap between two Cu rows in the former two, while it is just above a Cu row in the latter. The interaction energy between polyethylene and Cu(100) is plotted as a function of the molecule-surface distance in Fig. 4(d). The energy curves for the configurations in Figs. 4(a) and 4(b) almost overlap, suggesting that the displacement of polyethylene along the molecular axis has little influence on the molecule-surface interaction. Moreover, these curves are significantly deeper than that of the configuration in Fig. 4(c). This indicates that polyethylene prefers to adsorb on Cu(100) with the molecular axis above a gap between two Cu rows, which remains unchanged even after taking the ZPC into account. As shown in Tables II and III, the adsorption energy calculated with rev-vdW-DF2 is in good agreement with the TPD result [28], whereas the adsorption heights calculated with the two functionals are significantly

TABLE III. Calculated adsorption heights of *n*-butane (polyethylene) on the close-packed metal (low-indexed Cu) surfaces in Å. The rightmost column shows the adsorption heights estimated from the changes in the C–H stretching frequencies and the work functions of polyethylene adsorbed on the metal surfaces.

System	rev-vdW-DF2	optB86b-vdW	Estimates[a]
n-butane			
Cu(111)	3.48	3.45	...
Ag(111)	3.53	3.51	3.90
Au(111)	3.55	3.51	3.52
Ir(111)	3.49	3.45	...
Pt(111)	3.40	3.39	3.56
Ru(0001)	3.49	3.43	3.39
Polyethylene			
Cu(111)	3.49	3.46	...
Cu(100) (a)	3.43	3.37	...
Cu(100) (b)	3.43	3.39	3.83
Cu(110) (a)	3.16, 3.30	3.13, 3.27	...
Cu(110) (b)	3.19, 3.35	3.13, 3.28	...

[a] Reference [52].

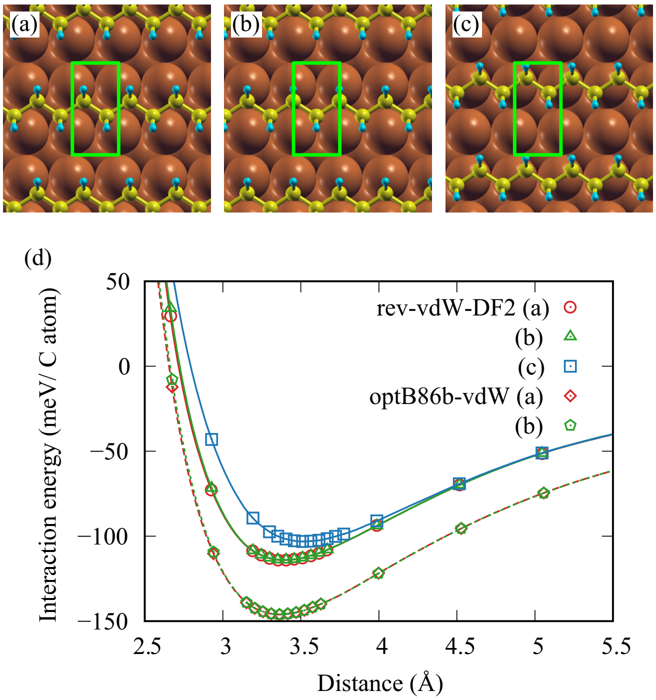


FIG. 4. Schematic views of polyethylene adsorbed on the Cu(100) surface in three different configurations (a)–(c), where the rectangle in each panel represents the (1 × 2) unit cell. (d) shows the interaction energies between polyethylene and Cu(100) plotted as functions of the molecule-surface distance.

smaller than the value estimated from the vibrational frequency and work function [10,25,52].

Polyethylene forms a (1 × 4) superstructure on Cu(110) with the molecular axis along the $[1\bar{1}0]$ direction [11], but the details of the superstructure remain unidentified. To determine the adsorption structure of polyethylene on Cu(110), we first examine simple cases in which one polyethylene molecule is included in the (1 × 4) unit cell as shown in Figs. 5(a)–5(c), and plot the molecule-surface interaction energies in Fig. 5(d). Parallel to polyethylene on Cu(100) discussed above, the energy curves for the configurations in Figs. 5(a) and 5(b) suggest that the molecule-surface interaction is almost independent of the displacement along the molecular axis, while the comparison with the result for the configuration in Fig. 5(c) indicates that polyethylene prefers to adsorb on a gap between two Cu rows.

We next examine the model proposed in Ref. [11], which includes three polyethylene molecules in the 1 × 4 unit cell. Without the Cu(110) surface, the optimal distance between two polyethylene molecules is close to one-third of the lattice parameter in the [001] direction of the Cu(110)-(1 × 4) unit cell, which are calculated to be 4.73 and 4.84 Å, respectively, with rev-vdW-DF2. We thus focus on the two adsorption configurations shown in Figs. 6(a) and 6(b), where three polyethylene molecules are equally spaced in the [001] direction. In Fig. 6(a) [6(b)], one of the three molecules is adsorbed on Cu(110) in the most stable configuration shown in Fig. 5(a) [5(b)], while the other two are in a configuration analogous to the metastable one shown in Fig. 5(c). We define the distances of the former and latter polyethylene molecules from the Cu(110) surface as d_1 and d_2, respectively, and plot the molecule-surface interaction energy calculated with rev-vdW-DF2 (optB86b-vdW) as a function of d_1 and d_2 in Figs. 6(d) [6(e)]. These results suggest that there is almost no correlation between d_1 and d_2, and indeed the optimal molecule-surface distances 3.16–3.19 (3.13) and 3.30–3.35 (3.27–3.28) Å for rev-vdW-DF2 (optB86b-vdW) are close to those obtained independently for the configurations in Figs. 5(a) and 5(b), and Fig. 5(c), respectively. Moreover, the average adsorption energy of polyethylene is calculated to be 112–114 meV per C atom with rev-vdW-DF2, which is significantly larger than the depth of the energy curve for the metastable configuration in Fig. 5(c). This indicates that the polyethylene molecules are stabilized by the intermolecular interactions, corroborating the 1 × 4 superstructure proposed in Ref. [11].

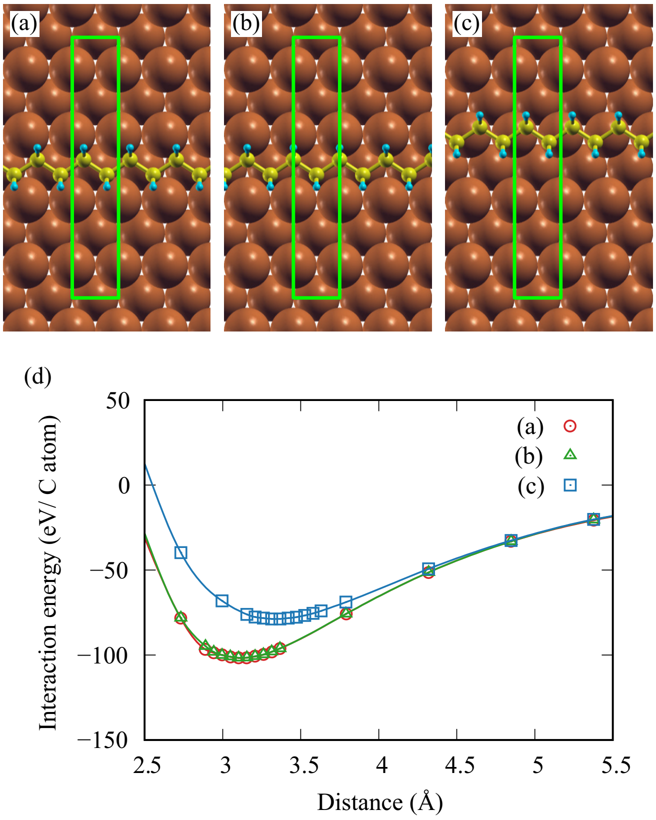
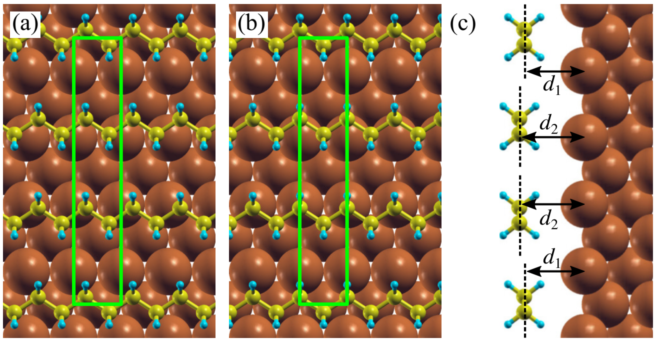


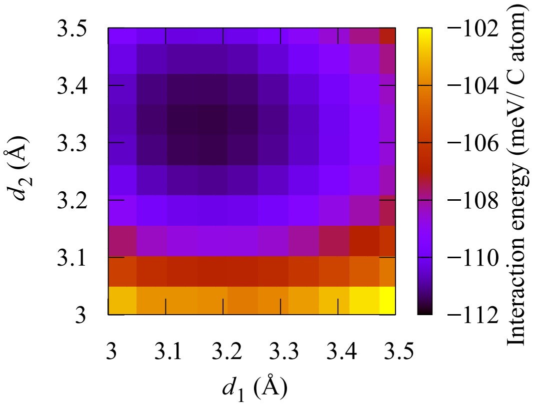
FIG. 5. Schematic views of polyethylene adsorbed on the Cu(110) surface in three different configurations (a)–(c), where one polyethylene molecule is included in the (1 × 4) unit cell represented by the rectangle in each panel. (d) shows the rev-vdW-DF2 results for the interaction energies between polyethylene and Cu(110) plotted as functions of the molecule-surface distance.

B. Vibrational properties

In the previous section, the influence of molecular vibrations has been included through the ZPC to the adsorption energies. However, the dependence of the ZPC on the molecule-surface distance has not been taken into account, which may affect the accuracy in determining the adsorption structures of n-alkane on metal surfaces. Thus we first examine how the ZPC evolves as a function of the molecule-



(d) rev-vdW-DF2



(e) optB86b-vdW

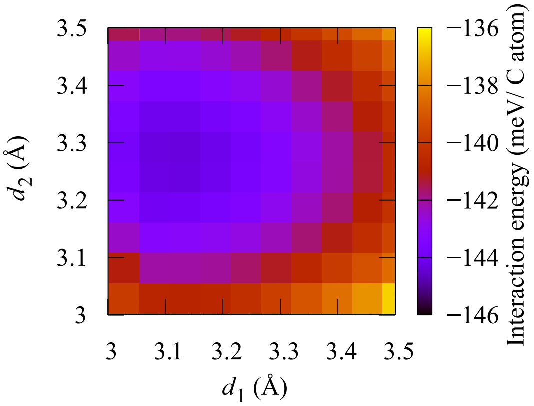


FIG. 6. Top (a), (b) and side (c) views of polyethylene adsorbed on the Cu(110) surface, where three polyethylene molecules are included in the 1 × 4 unit cell represented by the rectangle in panels (a) and (b). (d) [(e)] shows the rev-vdW-DF2 (optB86b-vdW) results for the interaction energies between polyethylene and Cu(110) plotted as functions of the molecule-surface distances d_1 and d_2 defined in panel (c).

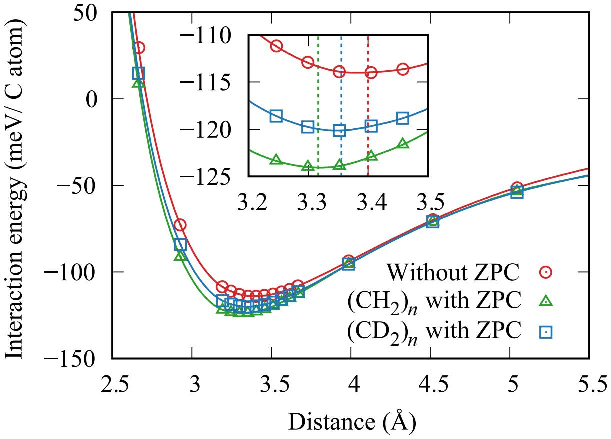


FIG. 7. Interaction energies between polyethylene and Cu(100) with and without ZPC plotted as functions of the molecule-surface distance. The inset shows a zoom-in view near the minimum, where the vertical dashed lines indicate the equilibrium distances. The rev-vdW-DF2 results are shown.

surface distance, taking polyethylene on Cu(100) as an example, because its adsorption height is significantly underestimated by the two vdW functionals as discussed in Sec. III A 2. Fig. 7 shows the molecule-surface interaction energies with and without the ZPC calculated with rev-vdW-DF2 for the adsorption configuration in Fig. 4(a) (See Sec. IV of the Supplemental Material [100] for the analysis of ZPC). The ZP-corrected energy curve for polyethylene on Cu(100) has a deeper minimum at a smaller distance than that without the ZPC, indicating that the adsorption height is further underestimated by including the ZPC. Thus, the underestimation of the adsorption height of polyethylene on Cu(100) should be attributed to other reasons. Note that the ZP-corrected curve also deviates from the uncorrected one at large distances, which is due to the influence of intermolecular interactions on the molecular vibrations. Fig. 7 also shows the ZP-corrected interaction energy curve for deuterated polyethylene $(CD_2)_n$ adsorbed on Cu(100), which appears in between the results for the unsubstituted systems with and without the ZPC. The destabilization by replacing atoms with heavier isotopes is referred to as the inverse isotope effect, and has also been observed for cyclohexane on Rh(111) [103,104]. More recently, the inverse isotopic effects have been theoretically predicted for methane adsorbed on various metal (111) surfaces [105].

The ZP-corrected curves significantly deviate the uncorrected one near the equilibrium distance (Fig. 7), which is due to the changes in the C–H stretching frequencies of polyethylene upon adsorption on Cu(100). Experimentally, the C–H stretching modes of tetratetracontane (TTC, n-$C_{44}H_{90}$) adsorbed on Cu(100) have been compared with those of crystalline TTC. Namely, IRAS measurements have shown that the ν_s (ν_{as}) mode, which is symmetric (antisymmetric) with respect to the C–C–C plane, appears at 2848 (2918) cm^{-1} for crystalline TTC, while a broad (sharp) peak observed around 2800 (2911) cm^{-1} for TTC on Cu(100) can be assigned to a stretching mode pointing towards the surface (vacuum) [10]. The vibrational frequencies of four C–H stretching modes calculated for polyethylene on Cu(100) are summarized in Table IV. The schematic views of the vibrational modes depicted in Fig. 8 indicate that ν_1 and ν_2 (ν_3 and ν_4) modes for polyethylene on Cu(100) have larger amplitudes towards the surface (vacuum), but slightly retain a symmetric (antisymmetric) character with respect to the C–C–C plane, and can be related to the ν_s (ν_{as}) mode of crystalline polyethylene, which appears at 2898 (2944) and 2899 (2949) cm^{-1} for rev-vdW-DF2 and optB86b-vdW, respectively. In particular,

TABLE IV. Calculated C–H stretching frequencies of polyethylene on Cu(100) in cm^{-1}. The results for the adsorption configurations in Figs. 4(a) and 4(b) are shown.

	rev-vdW-DF2		optB86b-vdW	
Mode	Fig. 4(a)	Fig. 4(b)	Fig. 4(a)	Fig. 4(b)
ν_1	2811	2803	2774	2790
ν_2	2824	2819	2801	2828
ν_3	2891	2894	2896	2895
ν_4	2919	2927	2915	2932

ν_1 and ν_2 are 74–95 cm^{-1} lower than ν_s for the two adsorption configurations in Figs. 4(a) and 4(b), which are significantly larger than the experimental value of 48 cm^{-1} [10]. This is consistent with the fact that the vibrational frequencies of these modes decrease monotonically with decreasing the molecule-surface distance [52], and that the adsorption height of polyethylene on Cu(100) is underestimated for the two functionals as discussed in Sec. III A 2. To compare the obtained C–H stretching modes with the experimental results, we calculate the absorption intensity, which is proportional to $(\partial\mu/\partial Q)^2$ with the dipole moment μ of the system and the normal coordinate Q corresponding to a vibrational mode [106]. The calculated absorption spectra are shown in Fig. 9, where the ν_2 and ν_4 modes have comparable peaks for the adsorption configuration in Fig. 4(a), whereas ν_1 and ν_2 modes exhibit much smaller peaks than ν_4 for the adsorption configuration in Fig. 4(b). The latter are more analogous to the broad peak around 2800 cm^{-1} observed experimentally [10]. These results suggest that the adsorption configuration in Fig. 4(b) is more preferable than that in Fig. 4(a), although the relative stabilities of these configurations are indistinguishable based on the adsorption energies.

We also investigate the C–H stretching modes of polyethylene adsorbed on Cu(110). In IRAS measurements, a broad (sharp) peak has been observed at 2760 (2910) cm^{-1} for TTC adsorbed on Cu(110), which are assigned to the C–H stretching modes towards the surface (vacuum) [11]. Table V shows the calculated vibrational frequencies of 12 C–H stretching modes of polyethylene on Cu(110), which is much larger than the number of adsorption peaks observed experimentally. However, the schematic views of the vibrational modes depicted in Fig. 10 indicate that more than half of them are IR-inactive, because of the cancellation of dynamic dipole moments among the three polyethylene molecules. As a consequence, the calculated absorption spectra of the stretching modes are composed of 2–6 peaks as shown in Fig. 11. For the adsorption configuration in Fig. 6(a), the ν_1 mode shows the highest peak at 2730 cm^{-1}. In sharp contrast, the ν_1 and ν_2 modes exhibit smaller peaks for the adsorption configuration in Fig. 6(b), which are more analogous to the broad peak

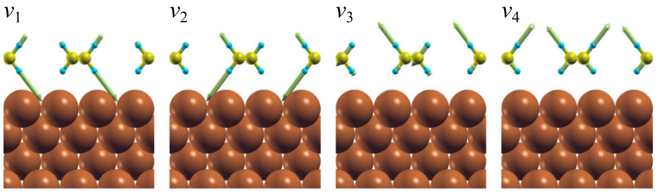
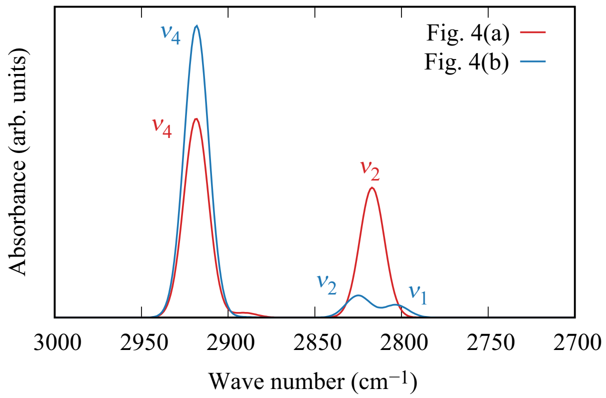


FIG. 8. Schematic views of the C–H stretching modes of polyethylene on Cu(100). The arrows represent the amplitudes and directions of the vibrations of the atoms.

(a) rev-vdW-DF2



(b) optB86b-vdW

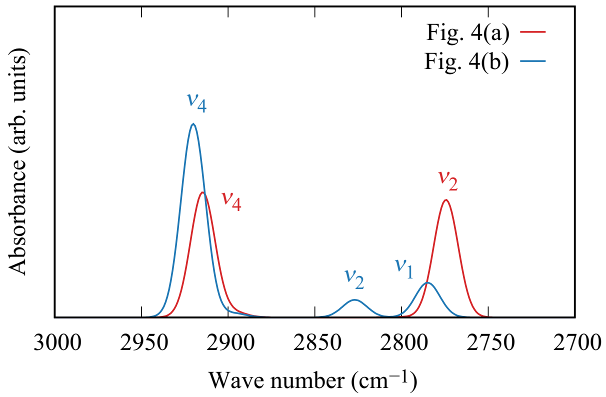


FIG. 9. Absorption spectra of polyethylene on Cu(100) calculated with rev-vdW-DF2 (a) and optB86b-vdW (b). The peaks are smeared by a Gaussian of width 10 cm^{-1}. The results for the adsorption configurations in Figs. 4(a) and 4(b) are shown.

TABLE V. Calculated C–H stretching frequencies of polyethylene on Cu(110) and the vibrational frequencies in cm^{-1}. The results for the adsorption configurations in Figs. 6(a) and 6(b) are shown.

	rev-vdW-DF2		optB86b-vdW	
Mode	Fig. 6(a)	Fig. 6(b)	Fig. 6(a)	Fig. 6(b)
ν_1	2738	2758	2730	2744
ν_2	2766	2786	2758	2771
ν_3	2773	2801	2765	2792
ν_4	2776	2818	2769	2799
ν_5	2832	2855	2832	2834
ν_6	2862	2863	2857	2861
ν_7	2867	2873	2870	2868
ν_8	2883	2892	2883	2880
ν_9	2886	2896	2892	2890
ν_{10}	2893	2901	2895	2892
ν_{11}	2924	2926	2927	2924
ν_{12}	2929	2930	2933	2928

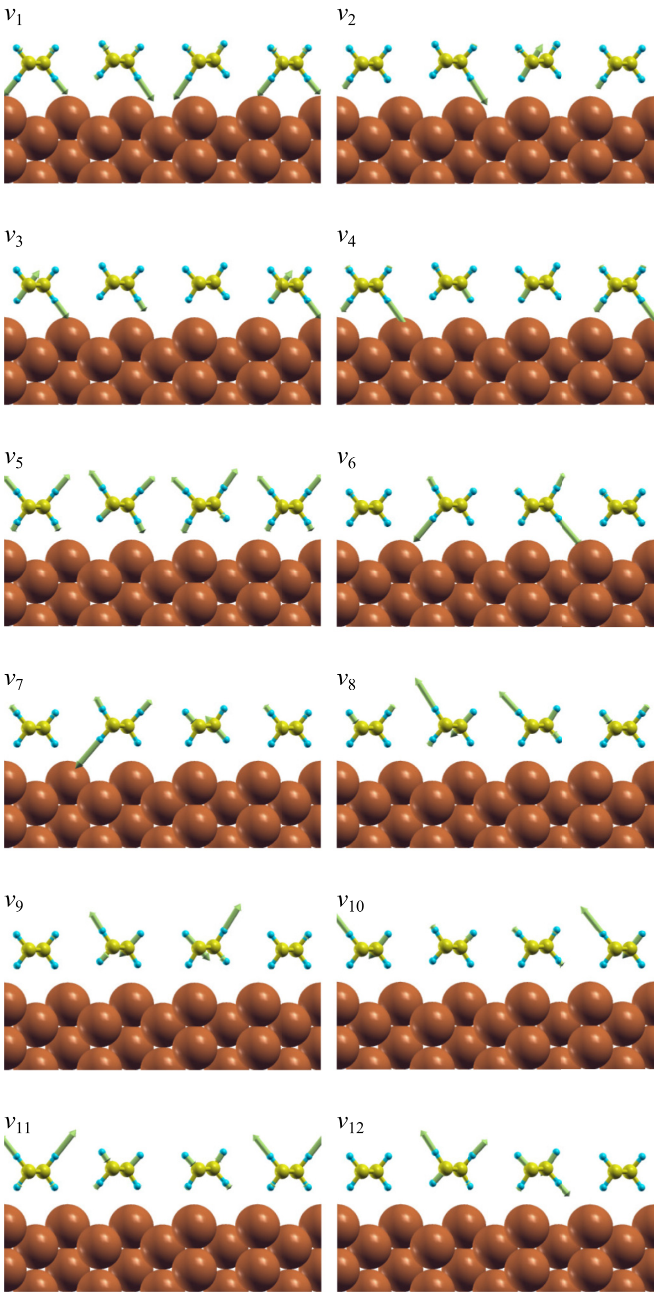


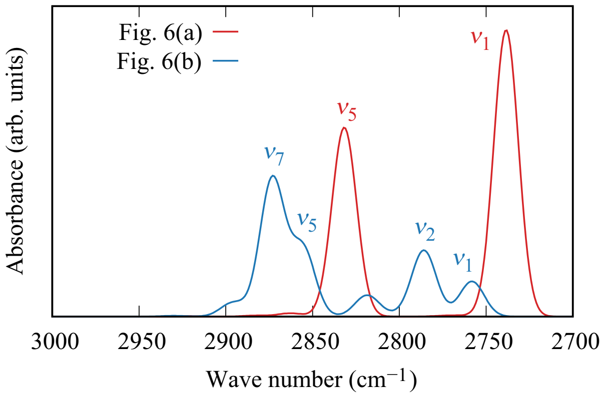
FIG. 10. Schematic views of the C–H stretching modes of polyethylene on Cu(110). The arrows represent the amplitudes and directions of the vibrations of the atoms.

around 2760 cm^{-1} observed experimentally [11], as in the case of polyethylene on Cu(100).

C. Work function

The adsorption of organic molecules on metal surfaces forms dipole layers at the molecule-metal interfaces, which tend to decrease the work functions of the metal surfaces [1]. Thus, the changes in the work function upon adsorption also provide useful information about the adsorption structures of *n*-alkanes on metal surfaces. Table VI shows the comparison between the work function changes calculated with vdW-DF and those observed experimentally. To the best of our

(a) rev-vdW−DF2



(b) optB86b-vdW

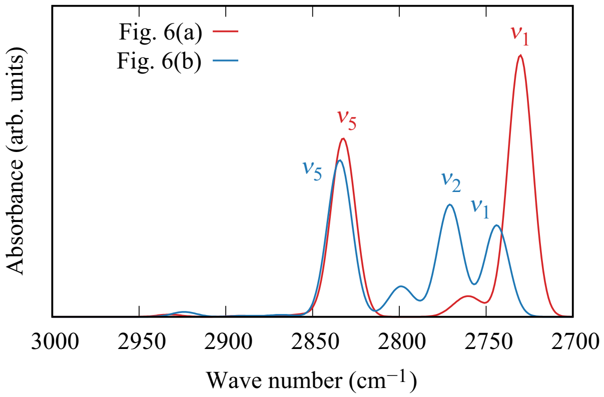


FIG. 11. Absorption spectra of polyethylene on Cu(110) calculated with rev-vdW-DF2 (a) and optB86b-vdW (b). The peaks are smeared by a Gaussian of width 10 cm^{-1}. The results for the adsorption configurations in Figs. 6(a) and 6(b) are shown.

TABLE VI. Calculated work function changes upon adsorption of *n*-alkane on the metal surfaces in eV. The experimental results are obtained for *n*-tetratetracontane adsorbed on the metal surfaces. The values in parentheses are the work functions of clean metal surfaces.

System	rev-vdW-DF2	optB86b-vdW	Experiments[a]
n-butane			
Cu(111)	−0.68 (4.99)	−0.73 (4.98)	··· (4.98)
Ag(111)	−0.71 (4.91)	−0.72 (4.84)	−0.5 ± 0.1[b] (4.74)
Au(111)	−0.62 (5.47)	−0.71 (5.45)	−0.7 ± 0.2[b] (5.31) −1[c] (5.31)
Ir(111)	−1.04 (5.76)	−1.09 (5.68)	··· (5.76)
Pt(111)	−1.00 (6.00)	−0.99 (5.94)	··· (5.7)
Ru(0001)	−1.23 (5.60)	−1.28 (5.51)	··· (4.71[d])
Polyethylene			
Cu(111)	−0.85 (4.99)	−0.87 (4.98)	··· (4.98)
Cu(100) (a)	−0.66 (4.72)	−0.69 (4.72)	−0.3[e] (4.59)
Cu(100) (b)	−0.69 (4.72)	−0.69 (4.72)	−0.3[e] (4.59)
Cu(110) (a)	−0.69 (4.66)	−0.74 (4.59)	··· (4.48)
Cu(110) (b)	−0.68 (4.66)	−0.70 (4.59)	··· (4.48)

[a] The values in parentheses are taken from Ref. [109].
[b] Reference [107], polycrystalline.
[c] Reference [108].
[d] Polycrystalline.
[e] Reference [25].

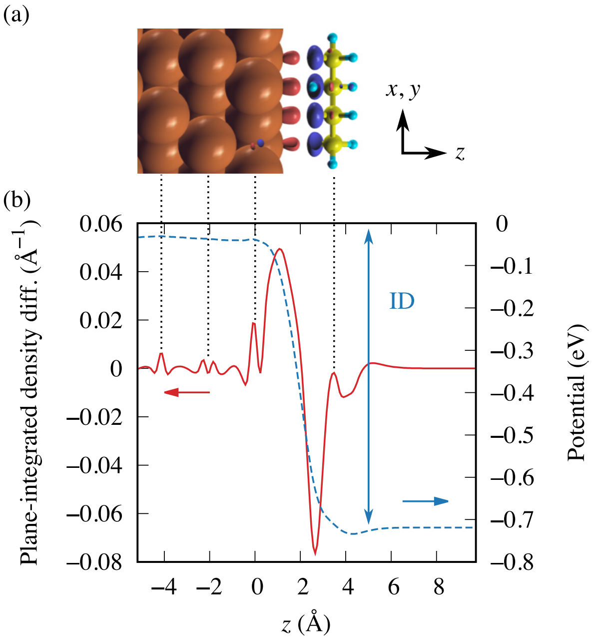


FIG. 12. Electric dipole layer at the interface between *n*-alkane and Cu(111) (a) and plane-integrated electron density difference plotted as a function of the distance from the metal surface (b). Panel (b) also shows the electrostatic potential calculated from the electron density difference. The rev-vdW-DF2 results are shown.

knowledge, the experimental results are limited to *n*-alkanes on Cu(100) [25], Ag(111) [107], and Au(111) [107,108], but some trends can be extracted that have been seen above. Namely, the work function changes for Cu(100) and Ag(111) are overestimated by the two vdW functionals, while those for Au(111) are in good agreement with the result observed in Ref. [107], although a recent experiment has reported a larger work function change [108]. These trends are analogous to those seen in the adsorption heights of *n*-alkanes on these surfaces.

To understand the origins of the work function changes obtained above, we first consider the changes in the electron density upon adsorption of *n*-alkanes on the metal surfaces. Fig. 12(a) shows the rev-vdW-DF2 result for *n*-butane on Cu(111) calculated from the difference between the electron densities before and after the adsorption, with the structures of the molecule and the surface kept fixed to the geometries of the adsorption system. Here the isosurfaces in red (blue) represent increases (decreases) in electron density. We then calculate the electrostatic potential averaged over a plane parallel to the surface $V(z)$ by solving the one-dimensional Poisson equation [110–112]

$$\frac{d^2V}{dz^2} = -\frac{e^2}{\varepsilon_0}\Delta\rho(z), \tag{3}$$

where $\Delta\rho$ denotes the planar average of the electron density difference. e and ε_0 are the elementary charge and the dielectric constant of the vacuum, respectively. The plane-integrated electron density difference as well as $V(z)$ thus obtained are plotted in Fig. 12(b), where ID stands for the potential drop across the interface dipole layer. The results for the other *n*-alkane-metal interfaces are given in Sec. V of the Supplemental Material [100], where the rev-vdW-DF2 and optB86b-vdW results are similar to each other, suggesting that the differences in the adsorption energies and heights obtained with the two functionals in Sec. III A stem from the functional design rather than the electron density distribution. The work function change $\Delta\phi$ upon adsorption of a molecule on a metal surface can be expressed as

$$\Delta\phi = \text{ID} + \Delta V_{\text{mol}} + \Delta V_{\text{surf}}, \tag{4}$$

where ΔV_{mol} (ΔV_{surf}) denotes the potential change due to the distortion of the molecule (surface). The comparison of $\Delta\phi$'s in Table VI and calculated ID's is shown in Fig. 13, which indicates that the work function change is predominantly determined by the formation of interface electric dipoles, hence the adsorption height of *n*-alkane on the metal surface. Although the changes in both the work functions and the C–H stretching frequencies suggest that the two functionals underestimate the adsorption height of *n*-alkanes on Cu(100) and Ag(111), there remains the possibility that the discrepancies are due to the underestimation of the HOMO-LUMO gap inherent to DFT calculations. To gain more insight into the discrepancies, more sophisticated techniques are required such as hybrid functionals and the random phase approximation (RPA), which has been applied to molecule-metal interfaces [113–115].

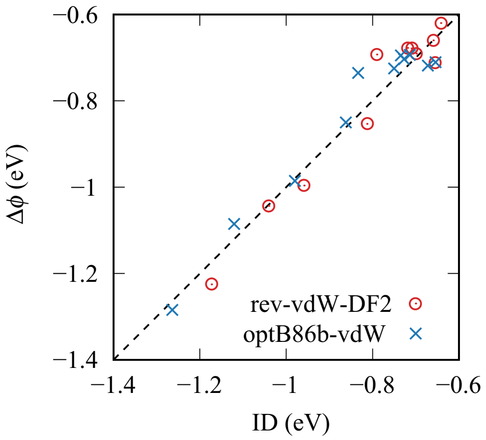


FIG. 13. Comparison between $\Delta\phi$'s and ID's for *n*-alkanes on the metal surfaces.

IV. CONCLUSION

We have applied vdW-DF to the investigation of the geometrical, vibrational, and electronic properties of *n*-alkanes adsorbed on various metal surfaces. It is found that the rev-vdW-DF2 and optB86b-vdW functionals reproduce the TPD results for the adsorption energies of *n*-alkanes on Cu(100) and Cu(111), respectively, whereas these functionals significantly overestimate those on Au(111), Pt(111), and Ru(0001). In contrast, the adsorption heights of *n*-alkanes on the latter surfaces obtained with these functionals are in good agreement with values estimated from the changes in the work function and the C–H stretching frequencies, whereas those on Cu(100) and Ag(111) are significantly smaller than the estimated values. These results indicate that further improvement of vdW-DF is necessary for the description of *n*-alkanes on metal surfaces with high accuracy.

From the results of the vibrational mode analyses, it is also found that the changes in the C–H stretching frequencies and IRAS spectra are useful for determining the preference of different adsorption structures of similar stability. Recently, an analogous result has been reported for methane adsorbed on Pt(111) [116], where the tripod and monopod configurations have adsorption energies close to each other within the generalized gradient approximation with the many-body dispersion correction [117], whereas the former has a C–H stretching frequency closer to the experimental result than the latter. More importantly, Ref. [116] has also revealed that RPA predicts a clear preference for the tripod configuration. This suggests that RPA enables a better description of *n*-alkanes adsorbed on metal surfaces, which will be discussed elsewhere.

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