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Structure and stability of weakly chemisorbed ethene adsorbed on low-index Cu surfaces: Performance of density functionals with van der Waals interactions

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Abstract. We have investigated the performance of popular density functionals that include van der Waals interactions for the experimentally well-characterized problem of the ethene (C_2H_4) adsorbed on the low-index surfaces of copper. This set of functionals does not only include three van der Waals density functionals – vdWDF-PBE, vdWDF-revPBE, optB86b-vdWDF – and two dispersion-corrected functionals – Grimme and TS – but also local and semi-local functionals such as LDA and PBE. The adsorption system of ethene on copper was chosen because it is a weakly chemisorbed system for which the vdW interactions are expected to give a significant contribution to the adsorption energy. Overall the density functionals that include vdW interactions, increased substantially the adsorption energies compared to the PBE density functional but predicted the same adsorption sites and very similar C-C bonding distances except for two of the van der Waals functionals. The top adsorption site was predicted almost exclusively for all functionals on the (110), (100) and (111) surfaces, which is in agreement with experiment only for the (110) surface. On the (100) surface, all functionals except two van der Waals density functionals singled out the observed cross-hollow site from the calculated C-C bonding distances and adsorption heights. On the top sites on the (110) surface and the cross-hollow site on the Cu(100) surface, the ethene molecule was found to form a weak chemisorption bond. On the (111) surface, all functionals gave a C-C bonding distance and an adsorption height more typical for physisorption in contrast to experiments, which, most surprisingly, found that the (111) surface, being the most close packed surface, gives the largest C-C bonding distance and the shortest adsorption height.

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1. Introduction

An important emerging field in surface science deals with the functionalization of surfaces by assembly of adsorbed large organic molecules [1–3] into large-scale ordered structures [4–7] and porous networks [8–12]. This field creates new and exciting challenges for modelling their physical and chemical properties from first principles. On one hand, the unprecedented system sizes require ever-growing computational resources and faster computational algorithms. On the other hand the adsorption and the intermolecular interactions of large organic molecules are significantly influenced by van der Waals (vdW) interactions and are challenging to describe in density functional theory (DFT), since the widely used semi-local and local exchange-correlation functionals such as the generalized gradient approximation and the local density approximation do not include vdW interactions. This description is particularly challenging for systems in a mixed bonding environment involving metal-coordination bonds or chemisorption bonds [3, 8–19].

Recently, there have been many important advances in developing DFT to include vdW interactions. The most ambitious and accurate approach is based on a combination of exact exchange with the random phase approximation for the correlation energy as obtained from the adiabatic connection dissipation theorem [20–22]. However, at the present stage this functional is computationally too expensive to allow structural relaxations for anything but the smallest adsorbate systems with few degrees of freedom. Two much more computationally inexpensive approaches based on semi-local DFT are currently being developed and applied.

The first one solves the lack of long-range interactions in semilocal DFT by introducing a fully but approximate non-local van der Waals kernel [23–32]. This kernel has to be augmented by an exchange term and the local correlations, see e.g. Refs. [28, 30–32] for detailed studies of this question. This kind of functional is often termed a van der Waals density functional (vdwDF). As with many semi-local functionals, the exchange functionals can be chosen either by physically motivated arguments from first principles [23, 26], or by adjusting a parameterized exchange to best reproduce a representative set of reference systems [31, 32].

The second strategy for introducing van der Waals forces into density functional theory is to add an attractive $-C_6/R^6$ vdW term to a semi-local functional [33–42]. This approach is often termed dispersion-corrected density functional theory (DFT-D). It is based on using asymptotically correct C_6 coefficients, determined from high level quantum chemistry or time-dependent density functional theory [43]. For short distances, the C_6/R^6 -term diverges and needs to be multiplied by a damping function to keep it finite. Unfortunately, the shape of this damping function can significantly affect the results [44] and in some cases it has the greatest influence at characteristic interatomic distances in dispersion-bound systems where it can become the single most significant contribution to the dispersion correction [45]. In either case, careful benchmarking and potentially the application of sensitivity analysis provide crucial means to establish the transferability of the van der Waals correction or functional to the specific application at hand. It is the aim of this study to provide such a benchmark for an experimentally very well characterized molecular adsorbate system.

In both vdwDF and DFT-D, it is not yet clear how well metal surfaces interacting with adsorbate systems are described – which is partially due to the lack of reliable experimental and theoretical reference data. Particularly in the case of DFT-D, it is challenging to describe the metal surface as these techniques make implicit

assumptions about the metallic screening - e.g. that the polarizability of metal atoms is related (or equal to) the free-atom polarizability. In general, this approximation for metallic screening does not hold for bulk metal atoms and it is difficult to determine how well it performs for surface atoms, step edges, or adatoms. For the close-packed (111) surface, this problem can be circumvented by arguing that the screening depth of the van der Waals interaction does not reach beyond the first atomic layer – an approach that works surprisingly well [40, 46] and seems to provide reasonably good geometries, even if the binding energies are overestimated. However, the assumption of a one-layer screening depth is difficult to use for more general surfaces such as the alternating row structure of the (110) surface as there is no well-defined *top* layer in these structures.

Detailed treatments of dispersion interactions on surfaces have so far appeared for a number of molecular systems that are driven by *physisorption* [40, 47–52]. For these systems generalized gradient approximations predict no or very weak adsorption, therefore any additional attractive interaction (or non-local correlation) between adsorbate and substrate is bound to lead to an improved match between theory and experiment.

While there is a growing body of literature on purely physisorbed systems, any detailed understanding on how vdW interactions influence chemisorption bonds is still lacking. The relative importance of vdW interactions becomes even more prominent in the case of weak chemisorption, where there is a small but significant covalent interaction between a surface and an adsorbate with a relative large energy gap between the highest occupied and lowest unoccupied molecular orbitals. Therefore, we chose to carry out a DFT study of the weakly chemisorbed system of ethene (C_2H_4) on three low-index Cu surfaces, for which ample experimental data exists [53–62] and for which a DFT treatment is quick enough to allow a systematic investigation of a broad range of exchange-correlation functionals incorporating vdW interactions. The theoretical studies of this system have so far been limited to a few early cluster studies on the (110) surface [63–65]. Moreover, the experimentally determined binding energy varies between 0.3 and 0.6 eV for different surfaces. A simple scaling argument based on calculated physisorption energies of 50-80 meV and 70-140 meV per carbon atom for polyaromatic hydrocarbons adsorbed on a graphite [49] and a gold surface [52], respectively, suggests then that the vdW component to this energy should be somewhere between 25% and 50%, making the adsorption of ethene on copper an ideal candidate for a study of mixed covalent and vdW interactions on metal surfaces.

In this study, we use a variety of density functionals with and without explicit van der Waals interactions to look at adsorption of ethene on the Cu(110), Cu(100), and Cu(111) surfaces. For each of the low-index Cu surfaces, a large set of high-symmetry adsorption sites for the ethene molecule was selected and studied using different density functional methods including the local density approximation (LDA) [66, 67], the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [68], the dispersion-corrected DFT-D’s by Grimme [36] and Tkatchenko and Scheffler [33] (TS), as well as with three different van der Waals density functionals. The latter use the original non-local van der Waals Kernel developed by Dion *et al.* [23] and vary the exchange terms using the original revPBE exchange [69], but also the PBE exchange and the recently developed optB86b exchange term [32] (optB86b-vdwDF). This choice corresponds mostly to a representative set of functionals that are currently in use in the solid state community. The very recent optB86b-vdwDF functional was included as it provides the best lattice constant for Cu (3.60 Å, equal to the experimental

value), and therefore could be used as a check for the representation of small changes in bonding geometries. Moreover, a closely related functional was very recently shown to compare very favourably to RPA for the adsorption of graphene on Ni(111) [70].

The difficulty to experimentally characterize the geometric structure and determine the adsorption energy for larger molecular adsorbates makes it challenging to benchmark model approaches on realistic system sizes, particularly for metal surfaces. A few experiments have characterized molecular binding geometries, adsorption heights, and adsorption energies using a combination of X-ray standing wave and temperature-programmed desorption (TPD) experiments [46]. However, the accurate determination of binding energies has been very difficult, with TPD experiments being the technique of choice at present, although more advanced techniques based on microcalorimetry and a direct determination of the adsorption energetics have become available more recently [71–73].

The remainder of this paper is organized as follows. The available experimental information and our computational approach are summarized in Sections 2 and 3, respectively. Our computational results are presented and analyzed for each surfaces in Section 4 and are discussed for all surfaces in Section 5. Finally, concluding remarks are presented in Section 6.

2. Experimental information

The single ethene molecule adsorbed on Cu is one of the most well-studied systems in experimental surface science and detailed structural data exists for all three surfaces. The adsorption sites have been determined either with Near Edge X-ray Adsorption Fine Structure (NEXAFS) [53], with photoelectron diffraction [60], or with Scanning Tunneling Microscopy (STM) [55, 56]. The first two techniques also give an estimate for C-C bond lengths and adsorption heights, while the binding energies have been measured exclusively using Temperature Programmed desorption (TPD) experiments. Moreover, reflection adsorption infrared spectroscopy (RAIRS) has provided additional insights into the bonding mechanism [74]. The available adsorption energies and heights, and binding distances from different experiments are summarized in Table 1.

Table 1 shows that all important parameters necessary to describe the bonding geometries have been determined by at least one experimental study and that most studies agree reasonably well on the measured values. The notable exception is the binding energy of ethene on Cu(110), for which two experiments have found differences of up to 50%. While most interesting geometric and energetic parameters for ethene adsorption on Cu are known quite well, there are some ambiguities in the literature about the determination of the adsorption site and the binding energy. To account for this fact in our study, we have considered all options proposed by experiments and compared the theoretical predictions against all available experimental results. As it turns out, these slight ambiguities do not significantly alter any of our conclusions. Where available, the coverage used experimentally is given in the table.

As discussed in the introduction, it has recently become clear that long-range van der Waals interactions do play a significant role in determining the adsorption properties of molecular species. In the case of C_2H_4 on Cu, the experimental binding energies are around 0.3-0.6 eV, only slightly larger than the energies of the purely van der Waals bound surface-adsorbate systems such as polyaromatic hydrocarbons on graphene [49] or on Au(111) [48]. On the other hand, the measured adsorption

Table 1. Summary of the experimental data on ethene adsorption on Cu surfaces. The superscript on each number denotes the experimental technique, which is indexed as follows: *a* NEXAFS, *b* PhD, *c* STM, *d* TPD. The adsorption sites are abbreviated as cross-bridge (c-b), cross-hollow (c-h), short-bridge (s-b), and short-top (s-t). Where available, the coverage used for the experimental site determination has also been listed.

Surface	Ref.	site	coverage (ML)	E_{ads} (eV)	d_{CC} (Å)	h_{ads} (Å)
(110)	[55, 56]	s-b	0.03		$\sim 1.4^c$	
	[57]	s-b	1		$1.53(13)^b$	$2.09(2)^b$
		s-t	1		$1.32(9)^b$	$2.08(2)^b$
	[58]			$0.35 - 0.5^d$		
	[59]			$\sim 0.6^d$		
(100)	[53]	c-b/c-h	0.5		$1.44(2)^a$	$1.3(2)^a / 1.5(2)^a$
	[54]			$0.35(8)^d$		
(111)	[60]	c-b	not avail.		$1.48(10)^b$	$1.41(3)^b$
	[61]			$0.31(2)^d$		

heights range between 1.3 and 2.1 Å and are significantly smaller than what is typically expected for physisorbed systems. Thus it is of great interest to study the influence of the vdW interactions on the bonding at these short adsorption heights.

3. Computational details

The DFT calculations were carried out using both the projector augmented wave VASP code [75–77] and the all-electron local orbital code FHI-aims [78]. The calculations using the LDA and the PBE generalized gradient approximation of the XC functional and the PBE, the revPBE and the optB86b versions of vdW-DF were done using the VASP code [75] and the recent implementation of the vdW-DF by Klimeš *et al.* [31, 32]. The calculations based on the semi-empirical vdW corrections to the PBE functional by Grimme (PBE-Grimme) and Tkatchenko and Scheffler (PBE-TS) were performed using FHI-aims [78], which contains the vdW correction by TS [33], while the vdW correction by Grimme [36] was added using an external script [45].

All our DFT calculations were performed in a supercell approach, and by relaxing each geometry until the residual forces on each atom less than 0.01 eV/Å. We use four layers of Cu where the bottom two layers in each cell were kept at fixed positions during the geometry optimization. The surface unit cells are 4×4 for the (100) and (111) surfaces and 3×4 for the (110) surface cell. In each case, a Monkhorst-Pack [79] Brillouin sampling using 4×4 points was used. Finally, a vacuum of 15 Å was introduced between the periodic images of the surface slabs.

In the VASP calculations, the plane wave basis set was expanded up to a kinetic energy cutoff of 400 eV. In the FHI-aims calculations, the vdW corrections were evaluated with successively larger cutoff radii until the total correction energy was converged to within 10^{-6} eV and the forces were converged to within 10^{-4} eV/Å. These numbers correspond to the self-consistency criteria used in the Kohn-Sham wave function calculation. The structures were pre-relaxed using the FHI-aims *light* basis sets and fully converged using the *tight* basis set and integration grids [78]. The final settings guarantee meV-level convergence of the energy differences [78]. To accelerate self-consistency convergence, a Kerker-type charge density preconditioner [78, 80] with

Figure 1. (color online) Histograms of calculated adsorption energies (a) and C-C bond distances and adsorption heights (b) of ethene on Cu(110) in different high-symmetry adsorption sites using different density functionals. The color scheme of the different functionals are shown in the legends of panels (b) and (c). The most stable adsorption site for each functional is marked by a dot on top of the corresponding adsorption energy. The adsorption height is defined as the height of the C-atoms above the Cu rows. The dashed lines and shaded areas denote the observed values and associated error bars (see Table 1). The adsorption geometries are depicted in a ball model: H (white), C (grey) and Cu (yellow). For clarity, the Cu(110) rows have been emphasized in the model geometries.

a cutoff wave vector of 3 Bohr was used.

Selected calculations using the PBE functional with both VASP and FHI-aims showed that the calculated adsorption energies of the two different methods agree to within a few meV. This high precision also allows a direct comparison of the adsorption energies despite using different basis sets and all-electron vs. projector augmented wave for the calculations.

4. Results

4.1. $Cu(110)$

The calculated adsorption energies for ethene adsorbed on Cu(110) as well as the C-C distance and the adsorption height are given in Fig. 1 for all adsorption sites and density functionals considered in this study. In Fig. 1(a), the largest adsorption energy for each density functional and therefore the predicted binding site is indicated by a dot above the corresponding energy. Note that some values of the adsorption energies for the adsorption sites between the rows are missing for a number of density functionals. These sites are not local minima, and the relaxations finished at the closest adsorption site on top of the Cu rows in those cases. As discussed in Section 2, available experiments are clear about the ethene molecule being adsorbed on top of the Cu rows and oriented parallel to them [55–57], but which one of the two possible adsorption sites (short-bridge or short-top) is preferred is not entirely clear. Note that the measured adsorption energies and heights are very similar for the short-top and short-bridge sites but the C-C bond distance are very different. The measured C-C bond distances for the short-top and short-bridge sites are similar to the corresponding distances of 1.34 and 1.55 Å for ethene and ethane in the gas phase, respectively. These distances correspond to a bond order of two and one, respectively.

The calculated adsorption energies in Fig. 1(a) for all density functionals except LDA predict unanimously that the short-top site is the most stable one. This result is also consistent with previous DFT calculations using B3LYP [63]. The short-top site is one of the two adsorption sites suggested by experiments (Table 1). There is still a large variation in the calculated adsorption energies for the short-top site, which range from 0.39 eV for revPBE-vdwDF well within the experimental range of 0.4 - 0.6 eV to 1.16 eV and 1.55 eV for optB86b-vdwDF and LDA respectively, which are too large by at least a factor of two. Nevertheless, the agreement between the measured and the predicted geometries is very good for the short-top site, with the binding height generally computed to be within 0.1 Å of the measured value of 2.08(2) Å. For all density functionals, the predictions for the C-C bond distance are well within the error bars for the measured values of 1.32(9) Å for the short-top site but not for the short-bridge site.

A comparison of the results for adsorption energies obtained from the PBE density functional with the results from all density functionals that includes vdW interactions show that the vdW interactions are dominating for the adsorption of ethene in a site between the Cu rows, indicating the formation of a physisorption bond. In contrast, the PBE density functional gives a substantial contribution to the adsorption energy of ethene on the top of the Cu rows, which suggests the formation of a weak chemisorption bond. This suggestion is supported by the calculated partial density of states (PDOS) for the three high-symmetry sites on top of the Cu rows shown in Fig. 2. There are no significant qualitative differences in the PDOS between the three sites and they differ only by small changes in the peak positions. The behaviour of the PDOS for states of sp^2 and p_z (π) character around the C atoms is consistent with the Dewar-Chatt-Duncanson bonding mechanism that was developed for the adsorption of organic molecules on metal clusters [81, 82]. In this model the occupied π -orbitals of the molecule donate electrons into the d -states of the metal, which in return back donate electrons to the unoccupied π^* -orbitals in the ethene molecule. The bonding sp^2 states are far well below the Fermi level with no mixing with the Cu d states. On the other hand, the p_z states corresponding to bonding π states mix strongly with the d states of the Cu surface. In addition, the higher-lying p_z state corresponding to anti-bonding π states broadens and becomes partially occupied. Note that there is hardly any quantitative difference between the three sites, suggesting that the bonding mechanism predicted by density functional theory is the same across all top sites.

4.2. $Cu(100)$

A similar calculation of bonding parameters of ethene using the same density functionals as for Cu(110) has been carried out for the Cu(100) and the results are presented in Fig. 3. In this case all density functionals give rise to local minima for all adsorption sites. As in the case of Cu(100), the experiments give two possible adsorption sites (cross-bridge and cross-hollow) but they have in this case very similar bonding parameters. The C-C bonding distances are intermediate between the values for ethene and ethane in the gas phase.

Almost all functionals predict the atop-hollow binding site to be the most stable one but only with a very slight preference over the atop-bridge site. As in the case of Cu(110), the LDA density functional stands out and give a very slight preference for adsorption in the cross-hollow site over the atop-bridge site. The site predicted by LDA is in agreement with one of the observed adsorption sites, but the calculated

Figure 2. (color online) Partial density of states (PDOS) for the three high-symmetry sites of ethene on top of the Cu rows of the Cu(110) surface. Results are shown from two representative vdW density functionals. The p_z states have been enlarged by a factor 5 with respect to the sp^2 PDOS.

Figure 3. (color online) Histograms of calculated adsorption energies (a) and C-C bond distances and adsorption heights (b) of ethene on Cu(100) in different high-symmetry adsorption sites using different density functionals. Otherwise the same notation is used as in Fig. 1.

adsorption energy is almost a factor of three too large.

A notable result is that the calculated adsorption heights and C-C bond distances for all density functionals, except PBE-vdW and revPBE-vdW are both in agreement with the observed values only for the cross-hollow site that was one of sites suggested by experiments. For all other adsorption sites the density functionals give a too large adsorption height and a significantly shorter C-C bonding distance (except in diag-hollow site for the LDA). Among the density functionals that gives a good account of the observed adsorption height and C-C bond distance, the optB86b-vdWDF gives the best agreement with the measured adsorption energy. However, this density functional and all other density functionals except LDA favours the atop-hollow site.

The reduction of bond order in ethene on the cross-hollow site shown by the large increase of the C-C bond distance and the large decrease of the adsorption height suggests the formation of a weak chemisorption bond. As shown in Fig. 4, the calculated PDOS using optB86b-vdWDF demonstrates clearly an electron donation from the π orbitals into the d states of the substrate and back-donation from the metal into the π^* orbitals in accordance with the Dewar-Chat-Duncanson model for

Figure 4. (color online) Partial density of states (PDOS) for ethene on Cu(100) computed with PBE-vdWDF (top) and optB86b-vdWDF (bottom) for different adsorption sites, compare the theoretically predicted atop-hollow site with the experimentally observed possibilities (cross-bridge or cross-hollow).

bonding. The sp^2 states are spectators in the bonding since they retain their free molecule character and do not mix with the metal states. The results for the atop-hollow and cross-bridge sites where the C-C bond distance is close to its gas phase value corresponding to a bond order of two do not show the same participation of π and π^* orbitals around the Fermi level. Note that in the case of the PBE-vdWDF which gives C-C bonding distances close a bond order of two, there is also no participation of π and π^* orbitals

4.3. Cu(111)

Finally, the same calculation of bonding parameters of ethene using the same density functionals as for Cu(110) and Cu(100) was carried out for the four high symmetry sites on the Cu(111) and the results are presented in Fig. 5. In this case, only the cross-bridge site is claimed to be observed in the experiments. Most surprisingly, the experiments give the largest C-C bonding distance and the shortest adsorption height on the most close-packed surface.

As for the Cu(110) and (100) surfaces, the density functionals favour adsorption on the top site with a very slight preference for the atop-hollow site except for revPBE-vdWPBE, which favours very slightly the atop-bridge site. This prediction of the adsorption site is not supported by the experiments which favor the cross-bridge site.

All the density functional give C-C bond distances that are close to gas phase values for all adsorption sites. This corresponds to a bond order of two and physisorption. The experiments suggest a significantly larger C-C distance, being closer to a bond order of one corresponding to weak chemisorption. The calculations give a significant spread for the adsorption heights but the shortest adsorption height is still significantly larger than the measured height.

5. Discussion

A comparison of the predicted adsorption sites across all low-index Cu surfaces, shows that most density functionals tend to favor the same kind of site for ethene, regardless

Figure 5. (color online) (color online) Histograms of calculated adsorption energies (a) and C-C bond distances and adsorption heights (b) of ethene on Cu(111) in four different high-symmetry adsorption sites using different density functionals. Otherwise same notation as in Fig. 1.

of the actual surface. The calculated lowest-energy sites are top sites, where the center of a C-C bond is located directly above one Cu atom. While this site does in fact correspond to the adsorption site suggested by experiments for the (110) surface, this adsorption site is not supported experimentally for the (100) and (111) surfaces. However, most density functionals single out the observed cross-hollow site on the (100) surface as being the only site having a bond order close to one and a short adsorption height as observed in the experiments. On the Cu(111) site all density functionals suggest a bond order close to two in contrast to having a bond order close to one as suggested by experiments.

The behavior of the bonding of the ethene molecule in the various adsorption sites on the different surface is captured by the PBE density functional. This functional gives only a sizeable contribution to the adsorption energy for the adsorption on top of the Cu(110) rows and on top of the Cu atoms for the other two surfaces suggesting the formation a weak chemisorption bond on these sites and a physisorption bond on the other sites. The latter suggestion is corroborated by the relatively large calculated adsorption heights in PBE for these sites compared to the top sites except for the cross-hollow site on the Cu(100) surface. In this case, the PBE results in a long C-C bond distance and a short adsorption height suggesting the formation of a weak chemisorption bond despite the adsorption being endothermic.

In general, the density functionals that include vdW interactions do not change the bonding behaviour of the PBE density functional except for the adsorption energies. These functionals increase substantially the adsorption energies, especially for the sites corresponding to physisorption but do not change significantly the C-C bonding distances and adsorption height for the adsorption sites with weak a chemisorption bond. A notable exception is the results from PBE-vdwDF and especially revPBE-vdwDF that tend to give too large adsorption heights and significantly different values for the C-C bonding distance and adsorption height in the cross-hollow site on the Cu(100) surface compared to the results from the other functionals and experiments. In contrast, optB86b-vdwDF give similar values for these bonding parameters in this site as for PBE and gives the best agreement with experiment for the adsorption energy in this site. These different results from the three vdW-DFs reflects the difficulties in approximating the exchange term when including

non-local correlations in these functionals.

The PBE-TS and PBE-Grimme tend to give the largest adsorption energies among the density functionals that include vdW interactions, reflecting that they have not been tailored to handle the screening of a metal surface, which in turn results in over binding. In fact, a sensitivity analysis of the results from these functionals [45] shows that by far the most significant parameter determining the binding energy is the radius of the metal atoms, which is a physically ill-defined quantity in a metallic system,

In general, the LDA density functional gives rise to significantly larger adsorption energies than for the other density functionals but gives very similar C-C bonding distances and adsorption heights to the PBE functional. In contrast to the other functionals, this functional predicts the observed cross-hollow site on the Cu(100) surface but have a slight preference for the long-hollow site over a top site on the Cu(110) surface.

6. Concluding Remarks

We have investigated the performance of various density functionals that includes vdW interactions by calculating the adsorption energy and geometry of the ethene (C_2H_4) molecule in various sites on the major, low-index surfaces of copper and comparing with available experimental data. This set of functionals does not only include three van der Waals functionals – vdWDF-PBE, vdWDF-revPBE, optB86b-vdWDF – and two dispersion-corrected functionals – Grimme and TS – but also local and semi-local functionals such as LDA and PBE. The adsorption system of ethene on copper was chosen because it is a weakly chemisorbed system for which the vdW interactions are expected to give a significant contribution to the adsorption energy and also for the existence of a relative complete set of experimental data for the low-index surfaces. Overall the density functionals that included vdW interactions, increased substantially the adsorption energies compared to the PBE density functional but predicted the same adsorption sites and very similar C-C bonding distances except for two of the van der Waals functionals.

The top adsorption site was predicted almost exclusively for all functionals on the (110), (100) and (111) surfaces, which is in agreement with experiment only for the (110) surface. On the (100) surface, all functionals except vdWDF-PBE, and vdWDF-revPBE singled out the observed cross-hollow site from the calculated C-C bonding distances and adsorption heights. In the top sites on the (110) surface and the cross-hollow site on the Cu(100) surface, the ethene molecule was found to form a weak chemisorption bond in accordance with the Dewar-Chatt-Duncanson model for bonding. On the (111) surface all functionals gave a C-C bonding distance corresponding to a bond order close to two and an adsorption height more typical for physisorption in contrast to experiments, which, most surprisingly, found that the (111) surface, being the most close packed surface, gives the largest C-C bonding distance, corresponding to a bond order of one, and the shortest adsorption height.

In the light of these data, we are unfortunately unable to provide a recommendation about which of the functionals tested should be used for the description of small molecules on metal surfaces, Cu molecules in particular. We expect that it would be similarly difficult to model the adsorption of ethene and other small partially vdW-bound molecules on different metal surfaces. While there is growing evidence that the van der Waals-type density functionals perform very well in

the case of pure physisorption, we still appear to be struggling to model mixed metal-molecule bonding situations such as weak chemisorption for which the ethene on Cu system is an ideal benchmark. Being able to reliably predict the bonding mechanisms in these types of systems will remain a challenge to be resolved in the future.

One potential density functional that can overcome the difficulties in predicting the correct adsorption sites of ethene on Cu might be given by the random phase approximation. This functional have provided a long-sought solution to the "CO-puzzle" [21, 22, 83] by which there was a persistent failure of semi-local density functionals to predict the correct adsorption site for the weakly chemisorbed CO molecule on close-packed metal surfaces.

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