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REGULAR ARTICLE

Analysis of the origin of lateral interactions in the adsorption of small organic molecules on oxide surfaces

José J. Plata · Veronica Collico · Antonio M. Márquez · Javier Fdez Sanz

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Abstract A decomposition scheme is proposed to analyze the physical contributions to the decrease in the binding energy of chemisorbed species with increasing coverage. This scheme is applied to the acetaldehyde–TiO_2 (110) rutile system as a model for other small organic molecule—oxide surface systems. Different density functional theory (DFT) functionals have been employed at both low-medium and high coverages to understand how the different theoretical descriptions of the various terms influence the adsorbate–surface interaction. At low coverages, it is found that the localized adsorbate to surface electron donation is the fundamental physical process that influences the adsorbate–surface interaction. This results shows that while it is usually assumed that only pairwise adsorbate–adsorbate interactions influence the adsorption energy, the progressive modification of the surface properties (surface reduction in this case) may also play a significative role. The DFT+U functional results, in this case, in the best agreement with the experimental binding energy, and the inclusion of the dispersive forces results in largely overestimated adsorption energies. At higher coverages, the pure GGA and GGA+U functionals overestimate the repulsive terms and the computed binding energy is well below the experimental data. The inclusion of the dispersive forces is required to correctly reproduce the experimental results. The contributions of the different physical terms are also analyzed.

Keywords DFT · Van der Waals · Adsorption · Lateral interactions · TiO_2 · Acetaldehyde

1 Introduction

The interaction of atoms and molecules with surfaces is ubiquitous, since all materials interact with their environment via their surfaces. For this reason, the adsorption of small organic molecules on the surface of solids is one of the central and more important topics in heterogeneous catalysis, photocatalysis, self-assembled layers, dye sensitized solar cells, and sensors [1–10].

It is widely known that the properties of adsorbed species are not independent of coverage [11]. The strength of the adsorbate-surface bond can be perturbed by the presence of neighboring species. Adsorbate–adsorbate interactions can be purely electrostatic or chemical in origin. Dipole–dipole coupling or charge–dipole interactions belongs to the first group while the decreasing in the orbital overlap between the adsorbate and the surface as the coverage increases is included in the second group. Such adsorbate–adsorbate or ”lateral interactions” are responsible of the non-ideal behavior of the adsorption process with increasing surface coverage. Its effects are usually quantified as a perturbation of the adsorption energy of the adsorbate in absence of lateral interactions (i.e., at the limit of zero coverage). While the importance of such interactions is widely recognized [11], a detailed physical understanding of the different factors that influence the binding of adsorbates with increasing surface coverage is a

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J. J. Plata (✉) · V. Collico · A. M. Márquez · J. F. Sanz
Departamento de Química Física, Universidad de Sevilla,
41012 Sevilla, Spain
e-mail: jplata@us.es

topic that remains to be addressed. Here, we propose a theoretical scheme that allows to analyze the observed decrease in the adsorbate to surface binding energy into different physical contributions. Different density functional theory (DFT) models are employed to quantify the influence of the theoretical description in these physical contributions at low- and high-surface coverages.

As a benchmark system, we have used the adsorption of acetaldehyde on rutile TiO_2 (110) surface. Titanium dioxide has received considerable attention in the literature due to its utility as a catalyst and as a photocatalyst. In particular, the rutile TiO_2 (110) surface has become a prototype system in surface science studies of metal oxide surfaces [12–14]. The (110) surface of rutile TiO_2 is composed of alternating rows of twofold coordinated bridging O_b atoms and channels that expose both fivefold coordinated Ti (Ti_{5c}) and in-plane threefold coordinated O atoms (see Fig. 1). Moreover, the surface chemistry and photochemistry of organic compounds on the TiO_2 surface is a topic of recurrent interest in the literature. In particular, acetaldehyde photodecomposition is of singular importance because it is commonly found as a volatile contaminant, aside from being present either as reactant, intermediate, or product in many catalytic processes [15–19]. The chemistry and photochemistry of acetaldehyde on the rutile TiO_2 (110) surface has been recently studied from a experimental point of view by Henderson [20].

The rest of this paper was organized as follows. In Sect. 2, the methodology and the surface model is described. In Sect. 3, the partition model, that allow to analyze the physical contributions to the inter-adsorbate lateral interactions, is presented. In Sect. 4, we present and discuss the results obtained. Finally, concluding remarks were given in Sect. 5.

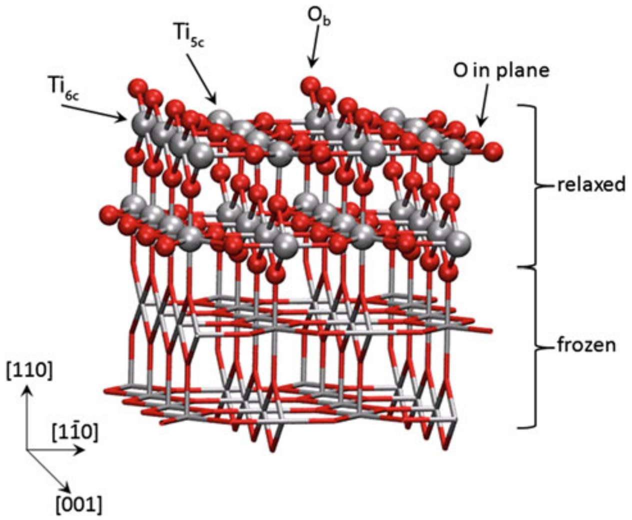

Fig. 1 4 × 2 supercell model of a TiO_2 (110) surface with four O-Ti-O layers; the two *lower layers* are kept frozen and the two *upper layers* are fully optimized. Atom colors *red* O, *gray* Ti

2 Computational details

In order to model the extended nature of these surfaces, periodic three-dimensional DFT calculations were carried out using the VASP 5.2 code [21–23] with the projector augmented wave (PAW) method [24, 25]. In these calculations, the energy was obtained using the generalized gradient approximation (GGA) implementation of DFT proposed by Perdew et al. [26], and the electronic states were expanded using plane wave basis set with a cutoff of 400 eV. Forces on the ions were calculated through the Hellmann–Feyman theorem as the partial derivatives of free energy with respect to the atomic coordinates, including the Harris-Foulkes correction to forces [27]. This calculation of the force allows a geometry optimization using the conjugated gradient scheme. Iterative relaxation of the atomic positions was stopped when the forces on the atoms were less than 0.02 eV/Å. In order to analyze the charge transfer upon adsorption, the total charge of the acetaldehyde molecule was determined using the algorithm introduced by Henkelman et al. [28, 29] for the evaluation of the Bader charges [30].

As gradient corrected density functional theory is known to assign a delocalized character to the excess electrons induced on the TiO_2 surface by defects like O vacancies or adsorbates [31, 32], the GGA+U formalism was also employed. The Hubbard U term was added to the plain GGA functional using the rotationally invariant approach proposed by Dudarev et al. [33], in which the Coulomb U and exchange J parameters are combined into a single parameter $U_{\mathrm{eff}} = U - J$. Recent work by Deskins et al. [34] has shown how the main effect of the use of this approach is to determine the location of gap states within the gap, and that reasonable gap states occur for values of U_{eff} between 3.3 and 4.1 eV. However, the trends are not strongly affected by the particular choice of the U_{eff} within this range. To be consistent with previous work on our group, a U_{eff} parameter of 4.5 eV was chosen, as it quantitatively reproduces the experimental position of the Ti 3d levels observed in the valence photoemission spectra of Ce/TiO_2(110) [35].

In order to understand how dispersion forces modify the description of lateral interactions, the van der Waals density functional (vdW-DF) derived by Dion et al. [36] was employed. Recently, there has been an enormous progress in the treatment of dispersion forces in DFT [37]. Adsorption on solid surfaces is an area where great steps forward have been made in this respect, but there are still challenges for dispersion–based DFT methods at present.

The functional employed in this work (optB86b-vdW) approximately accounts for dispersion interactions, it is a solution which balances computational efficiency and accuracy [38] and it is known to describe accurately structural properties of both gas-phase clusters and bulk materials [39].

It is known [40] that vacancy formation energies based on slab calculations show an oscillating behavior with the number of layers and that at least six TiO_2 layers are required to obtain fully converged values. In previous works, we did not find big differences between four and six layers for acetone adsorption [41] so in the present work, we used supercell models with four TiO_2 tri-layers to represent the TiO_2 (110) surface and explore the energetics and geometries of adsorption of acetaldehyde on this surface. Each slab was separated by a vacuum of 13 Å, considered enough to avoid interaction between the slabs [40]. In all cases, the optimized lattice parameters for the bulk used were $a = 4.616$ Å, $c = 2.974$ Å, and $u = 0.304$ Å. The a and c parameters were kept fixed during the surface atomic positions relaxation. Multiples of the unit cell along the [001] direction give cells of the n × 1 type and j doubling along the [110] direction gives n × 2 cells. The surface cell that were used in the present work was 4 × 2 size, where adsorption of a single acetaldehyde molecule represents a coverage of $\theta = 0.125$. The calculations for the supercell model where computed at the Γ point of the Brillouin zone. Adsorption energy for the incoming acetaldehyde molecule is computed as

$$E_{\mathrm{ads}}(\theta_2) = E_{\mathrm{total}}(\theta_2) - E_{\mathrm{total}}(\theta_1) - E_{\mathrm{acetal}} \quad (1)$$

where E_{total} (θ_i), $i = 1, 2$, are the total energies of model systems with $N{-}1$ and N acetaldehyde molecules, respectively, and E_{acetal} is the total energy of an isolated acetaldehyde molecule. With this definition, negative adsorption energies represent bound states stable with respect to desorption, and a direct comparison with experimental desorption energies derived from thermal programmed desorption (TPD) experiments is possible.

3 Partition model

This section introduces a simple model to analyze the coverage dependence in the adsorption energies into physically meaningful contributions. The main objective is to devise a simple model that allow us to understand the importance of the different physical interactions, their relation to the level of theory used, and their role at different degrees of surface coverage. Detailed experimental TPD data available for acetone and acetaldehyde on the (110) surface of rutile TiO_2 shows that binding energy, even a low coverages (0.01–0.50 ML), decrease with increasing surface loading [20, 42]. Previous theoretical work has related this effect to the bonding mechanism of adsorption of those carbonyl compounds to the rutile surface [41, 43]. The adsorption of organic carbonyl compounds at the TiO_2 rutile (110) surface takes place through interaction of the CO dipole moment with the electric field of the Ti_{5c} surface cations. For small coverages, a tiny charge transfer from the organic molecule adlayer to the surface takes place, reducing the acidity of the remaining Ti_{5c} sites and, thus, the binding energy of incoming molecules. However, the role of the long-range dipole–dipole and short-range steric repulsive interactions was not analyzed. Taking into account these considerations, the decrease in the adsorption energy with increasing coverage can be expressed as

$$E_{\mathrm{ads}}(\theta_2) = E_{\mathrm{ads}}(\theta_1) + f_{s+d} + f_e \quad (2)$$

where E_{ads} (θ_i) is the adsorption energy at coverage θ_i (with $\theta_2 > \theta_1$), and f_{s+d} and f_e are contributions for steric and dispersion forces (f_{s+d}) and electronic (adsorbate to surface charge transfer, f_e) physical contributions above described. The f_{s+d} contribution can be estimated as the energy difference per molecule between two isolated acetaldehyde monolayers whose geometries are identical to those in surface + adsorbate systems with coverages θ_i

$$f_{s+d} = E_{\mathrm{ML}}(\theta_2) - E_{\mathrm{ML}}(\theta_1) \quad (3)$$

It should be taken into account that the electronic density on the acetaldehyde molecules is changed upon adsorption, thus the above approximation holds while the adsorbate to surface charge transfer is not too high, as it is our case. The contribution of the adsorbate–surface charge transfer is then easily obtained as

$$f_e = E_{\mathrm{ads}}(\theta_2) - E_{\mathrm{ads}}(\theta_1) - f_{s+d} \quad (4)$$

4 Results and discussion

4.1 Low-medium coverages

A single acetaldehyde molecule on our 4 × 2 supercell model provides the lower coverage explored, 0.125 ML. The pure GGA functional produces a binding energy of −0.83 eV, slightly lower than the experimental estimated value of −0.93 eV (see Table 1). Addition of a second acetaldehyde molecule results in a coverage of 0.250 ML. The computed binding energy of this second acetaldehyde molecule is reduced (−0.64 to −0.74 eV) with respect to the first adsorbed molecule, in agreement with the observed reduction in the experimental TPD data (−0.81 eV). The reduction in binding energy can be ascribed to steric and dipole–dipole repulsive interactions between the adsorbed molecules but also to the adsorbate to surface charge

Table 1 Computed (GGA, GGA+U, and optB86b-vdW) and experimental acetaldehyde adsorption energies (E_{ads}) at different surface coverages

θ (ML)	E_{ads} (eV)			
	GGA	GGA+U	+vdW	Exp. [20]
0.125	−0.83	−1.02	−1.23	−0.93
0.250				
(a)	−0.64/−0.69	−0.86/−0.88	−1.16/−1.21	−0.81
(b)	−0.70/−0.74	−0.91/−0.96	−1.19/−1.23	
1.000	−0.20	−0.37	−0.82	−0.71

Acetaldehyde molecules are adsorbed in the same (a) or different (b) channels of the $TiO_2(110)$ surface

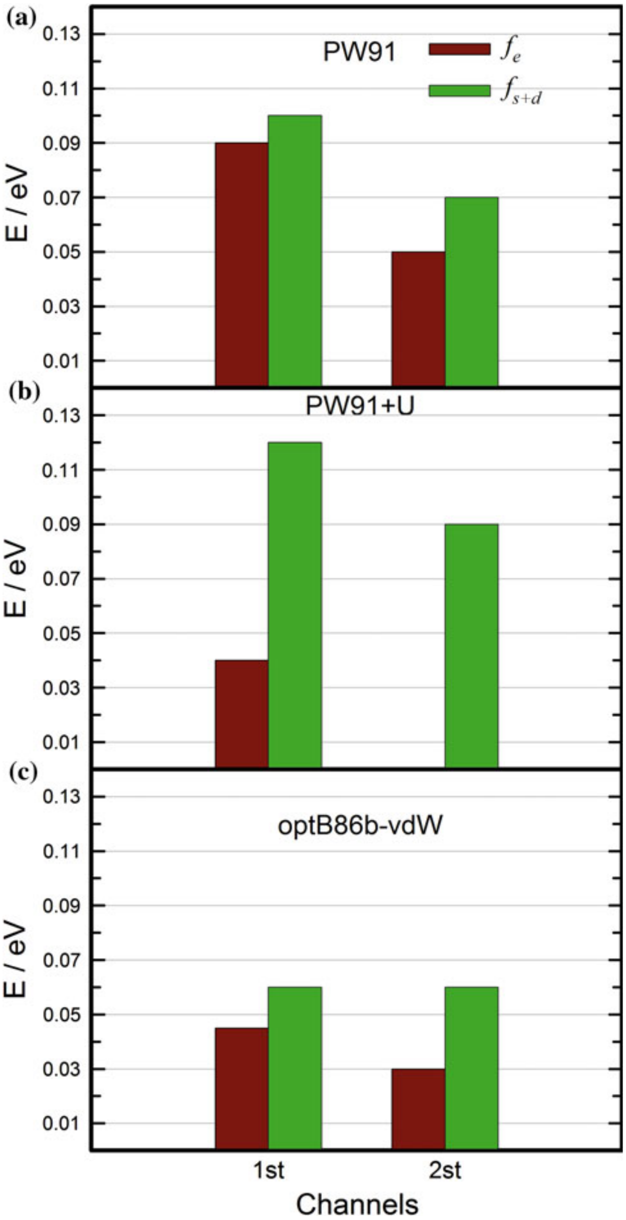

Fig. 2 Histogram for inter-molecular lateral interaction terms at low coverage ($\theta = 0.250$ ML) using different functionals. *Brown columns* electronic contribution. *Green columns* steric and dispersion contributions

transfer that takes place upon acetaldehyde adsorption. Using the above proposed scheme, we can quantify how these factors contribute to the observed reduction in the strength of the binding between the acetaldehyde molecule and the TiO_2 surface. As shown in Fig. 2, repulsive interactions are larger when the incoming molecule adsorbs in the already occupied channel and both contributions are of the same order and larger in this case. Clearly, the distance between molecules is shorter and the dipole–dipole and steric repulsions must be higher in this situation. The contribution of the adsorbate-surface charge transfer is, also, significatively larger showing how, upon acetaldehyde adsorption, the small charge transfer that takes place delocalizes over the nearby Ti_{5c} cations, reducing their acidity and, thus, their ability to bind incoming acetaldehyde molecules.

Gradient corrected density functional theory has known limitations in the description of electronic defects related to inherent deficiencies in the functionals, mainly the insufficient cancelation of the self-interaction energy [44]. As result, the electron density transferred by the incoming acetaldehyde molecules will be excessively delocalized over the surface and reduce the acidity of Ti cations in an unrealistic way. In consequence, f_e could be increased in an unrealistic way. The use of hybrid exchange-correlation functionals or the DFT+U approach, which adds an adjustable correction to enhance electron localization, allows to overcome these deficiencies.

At a coverage of 0.125 ML, the GGA+U computed adsorption energy is −1.02 eV which is a bit higher than the experimental value of −0.81 eV. The DFT+U approximation enhances the ionicity of the oxide and the charge transfer between the acetaldehyde molecule and the surface. Both effects reinforce the chemisorption bond of the acetaldehyde molecule to the surface resulting in the observed increase in the computed binding energy. At a 0.250 ML coverage, the GGA+U binding energies (see Table 1) are also higher than those obtained with the pure GGA functional, but in this case they are closer to the experimental value. The energetic decomposition of the lateral interaction shows a qualitatively different picture of the inter-molecule interaction at this GGA+U theory level. While the f_e and f_{s+d} contributions where similar when the pure GGA functional was used, the inclusion of the U parameter drastically reduces the importance of the adsorbate to surface charge transfer (see Fig. 2b). The DFT+U approximation forces the localization of the electrons donated by the acetaldehyde molecule in the Ti cation in which the molecule is adsorbed and little electron density is delocalized to nearby Ti_{5c} cations. In fact, the f_e contribution is reduced by a 50 % factor when the second acetaldehyde molecule gets adsorbed in the same channel than the first one and no f_e contribution is obtained when adsorption takes place in the empty channel.

Dispersion forces are long-range attractive forces that are known to be important in order to correctly describe the stability of a wide range of systems, including the adsorption of molecules to solid surfaces [39, 45]. However, the description of these forces, purely quantum mechanical in origin, pose a challenge to classical DFT theory as, in most implementations, the exchange–correlation potential does not include contributions from unshared electronic distributions [44]. The optB86b-vdW functional has been chosen to evaluate the effect of such dispersion forces in the present problem. At the lower coverage employed (0.125 ML), the computed adsorption energy is now −1.23 eV, which is a 35 % higher than the experimental value. At a 0.250 ML coverage, the computed adsorption energies (see Table 1) are still largely overestimated but they show the same decreasing tendency as the experimental data. This overestimation of the adsorption energy in vdW-DF has been observed previously by other authors and has been adscribed to a double counting of some short-range exchange-correlation effects [46]. The decomposition of the inter-molecule lateral interactions obtained with our proposed scheme is shown in Fig. 2c. The adsorbate to surface charge transfer term (f_e) decreases significatively when compared with the pure GGA result. This can be related to an increase in the Ti-OC bond distance from 2.16 Å (GGA) to 2.19 Å that will reduce the orbital overlap and, thus, the amount of charge transfer that takes place. Another observation is that, as in the pure GGA functional, the transferred electron density delocalizes over all nearby Ti_{5c} cations, including those in the secondary channel. The dipole–dipole and steric term (f_{s+d}) shows also a significative reduction, as could be expected from the inclusion in the functional of the attractive London dispersion forces. The decrease is more significative when the two acetaldehyde molecules are adsorbed in the same channel as expected from the nature of these dispersion forces [44].

4.2 Full coverage

In the previous section, we have seen how the inclusion of the Hubbard U term and the London dispersion forces can modify the values of adsorption energy and the description and analysis of lateral interactions at low and medium coverages. Nevertheless, the consideration of these effects should be even most important at high coverages when the partial reduction of the surface and dispersion forces are bigger. For this reason, the interaction of acetaldehyde molecule with the TiO_2 surface has been examined at a coverage of $\theta = 1$ ML. To adequately compare our results with the experimental values, the acetaldehyde molecules have been placed alternating their α hydrogen to either side of the Ti_{5c} channels, in order to produce the most stable configuration. (see Fig. 3).

Thermal programmed desorption data revealed that the peak that appears at 245 K corresponds to acetaldehyde desorption at $\theta = 1$ ML [20]. Redhead analysis [47] of these peaks assuming a typical pre-exponential factor of

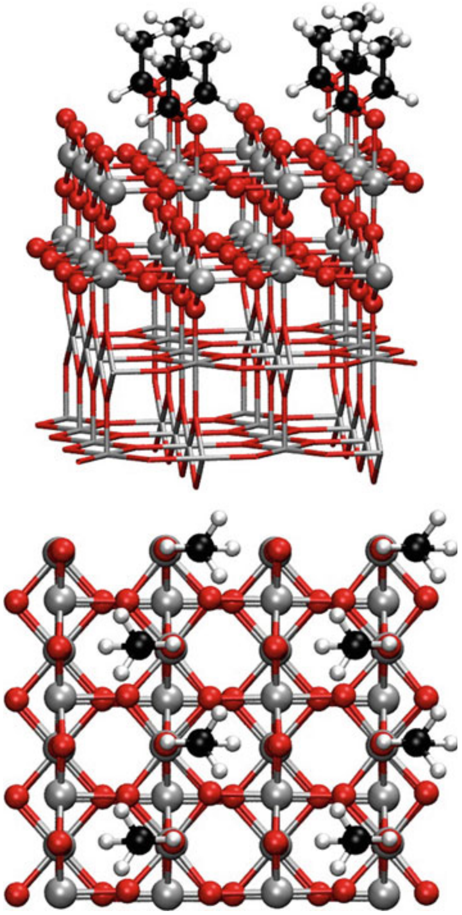

Fig. 3 Side and top views of and acetaldehyde monolayer on TiO_2 (110) surface at $\theta = 1$ ML. Atom colors *red* O, *gray* Ti, *black* C

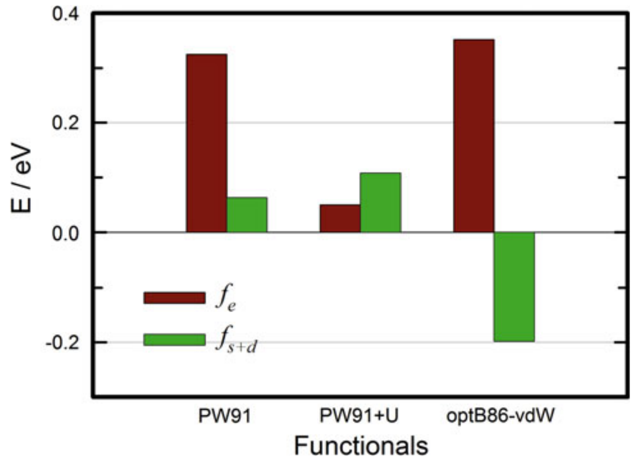

Fig. 4 Histogram for inter-molecular lateral interaction terms at full coverage ($\theta = 1.0$ ML)

10^{13} produces an estimated experimental adsorption energy of −0.71 eV. Table 1 show the calculated adsorption energies for an acetaldehyde coverage of 1 ML with the different functionals used in this work. Both the pure GGA and the GGA+U functionals produce adsorption energies that are well below the experimental data. This is not surprising as the short-range repulsive forces must dominate when the surface is highly crowded. However, the attractive dispersion forces must compensate these repulsive terms, but they are not included in these two functionals. The decomposition of the inter-molecule interaction as proposed in this paper, shown in Fig. 4, reveals that the adsorbate to surface charge transfer term (f_e) is dominant in the case of the GGA functional. The surface is highly reduced and the electrostatic interaction between the CO dipole moment and the Ti_{5c} charge is reduced. This term is largely reduced to a magnitude similar to that found at lower coverages when the GGA+U functional is used. The charge donated from the acetaldehyde overlayer to the Ti_{5c} cations is localized, and the free surface cations are only slightly affected. The f_{s+d} term has a smaller magnitude, compared to low-coverage results, when the pure GGA functional is used. This is probably related to an increased distance of 2.33 Å between the Ti cations and the acetaldehyde overlayer compared to 2.16 Å at 0.125 ML coverage that will reduce the repulsive steric interactions between the acetaldehyde molecules and the protruding oxygen atoms. In contrast to these results, the optB86b-vdW functional produces a binding energy of −0.82 eV that overestimates the experimental value by only a 15 % (this is probably within the experimental error bar). The decomposition of the inter-molecule lateral interactions (see Fig. 4) shows that the term related to the surface reduction is similar in magnitude to the data produced by the pure GGA functional. As the surface is highly crowded and this functional does not include an electron localization term, the degree of surface reduction must be similar in both cases. In fact, the Ti-OC bond length is slightly larger in this case (2.36 Å) reflecting the slightly larger f_e term. Not surprisingly the steric term f_{s+d} is now negative: the high density of acetaldehyde molecules at the surface increases the dispersion attractive term and this term overcompensates the repulsive dipole–dipole and steric repulsive interactions.

5 Conclusions

The physical origin of the so-called lateral interactions, responsible of the decrease in the adsorbate-surface binding energy with increasing coverage has been examined in the acetaldehyde–TiO_2 (110) rutile system. A decomposition scheme is proposed that allows to understand how the progressive reduction in the oxide surface and the inter-molecule dipole–dipole and steric repulsive forces influence the binding energy at low-medium and high coverages. Three different DFT functional have been used: pure GGA, GGA+U, and the optB86b-vdW that includes a treatment of the attractive dispersion forces. The results show that at low-medium coverages the pure GGA and the optB86b-vdW functionals over delocalize the electron density donated from the adsorbate adlayer to the surface, resulting in an artificially reduced binding energy. The optB86b-vdW functional overbinds the acetaldehyde molecules, a result already observed and that has been adscribed to a double counting of some exchange-correlation terms. The inclusion of the U Hubbard term in the GGA+U functional overcomes the excessive electron delocalization observed in the pure GGA functional, and this theory level seems to be the most adequate at these surface coverages. At higher coverages, both GGA and GGA+U functional largely overestimate the repulsion forces, resulting in binding energies too low compared to experimental values. The decomposition of the inter-molecule interactions, as proposed in this paper, reveals that the adsorbate to surface charge transfer term (f_e) is dominant in the pure GGA functional case. The surface is being reduced by the already adsorbed acetaldehyde molecules, and the incoming molecules find cationic sites with reduced acidity, resulting in the observed lower binding energies. At these high loadings, the inclusion of the dispersion forces is found to be essential to adequately describe the highly crowded acetaldehyde overlayer. The computed optB86b-vdW binding energy overestimates the experimental data by a small amount (15 %) and is probably within the experimental error bar. The decomposition of the inter-molecule lateral interactions shows that although the adsorbate to surface charge transfer term is still important, it is largely compensated by the attractive dispersion contribution introduced in this functional.

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