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# A DFT study of cyclopropane adsorption on Pt(1 1 1). Electronic structure and bonding

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ABSTRACT

We have studied the adsorption of cyclopropane ($c$-$C_3H_6$) on Pt(1 1 1) by means of the density functional theory (DFT). We have investigated the preferential adsorption geometry, considering different adsorption sites and bonding configurations for the molecular adsorbate. We have also computed the electronic structure and bonding interactions by means of density of states (DOS), crystal orbital overlap population (OPDOS), and overlap population (OP) analysis. Our results show a small preference for Bridge and Top adsorption sites with the cyclopropane ring parallel to the surface. Pt—C equilibrium distance is ~3.5 Å and a weak bond is formed during adsorption. The main bonding interaction comes from the Pt—H overlap population. Pt $5p_z$ orbitals play an important role in the bonding between $c$-$C_3H_6$ and the surface. We have found that Van der Waals (vdW) corrections to the energies improve the adsorption values without changing the preferential site geometries.



## 1. Introduction

The adsorption of hydrocarbon molecules on transition metal surfaces is an active topic in heterogeneous catalyst research because of its significant technological and scientific importance in petroleum reforming processes. The understanding of the interaction of hydrocarbon molecules with metal surfaces is fundamental for the design of new catalysts, and the studies about the C—C and C—H bond activation can help us to understand the elementary steps of a catalytic mechanism [1–4].

In this way, hydrocarbon adsorption and reaction processes on active metals have been extensively studied both experimentally and theoretically [5–7]. However, the surface science for adsorbates having at least three carbon atoms still remains especially unclear, even though it is very attractive because in these cases C—C bond cleavage generates multiple surface species, including metallacycles with several isomers. In particular, there are several experimental works related to cyclic hydrocarbons adsorbed on transition metal surfaces. The theoretical approach is still relatively scarce and mainly centered on $C_6$ [8–11] and $C_5$ [12–19] species.

Cyclopropane ($c$-$C_3H_6$) is a notable adsorbate with three $CH_2$ groups forming HCH angles of 117° in a $D_{3h}$ symmetry. Cyclopropane chemistry is governed by highly strained C—C bonds. In effect, due to the ring stiffness the $c$-$C_3H_6$ has a relatively weak C—C bond energy of ~289 kJ mol$^{-1}$, compared to ~347 kJ mol$^{-1}$ in normal hydrocarbons [20,21]. The resultant relatively high reactivity has been exploited to investigate a reaction mechanism in catalysis using $c$-$C_3H_6$ as an ideal probe molecule [21–26]. Furthermore, although $c$-$C_3H_6$ is a saturated molecule, it also displays an olefinic character because its C—C—C bond angle of 60° increases the $p$ character of the C—C bonds [21,26]. As a result, the C—H bond strength and chemical reactivity in $c$-$C_3H_6$ are more similar to those of ethylene than those of cyclobutane [26].

Extensive experimental research has been performed to explain the unusual reactivity of $c$-$C_3H_6$ on both supported metal particles and single-crystal metal surfaces: Ru(0 0 1) [27,28], Cu(1 1 1) [29–31], Ni(1 1 1) [30], Ni(1 0 0) [32], Ir(1 1 0) [33], and Pt(1 1 1) [34,35]. Depending on the initial conditions, $c$-$C_3H_6$ adsorption can take place in an associative or dissociative way, *i.e.*, in a physical or chemical process. At low temperatures, $c$-$C_3H_6$ adsorbs molecularly on Pt without dissociation, whereas C—H and C—C bonds can be broken by photon irradiation or reaction with metal ion beams to form different dissociated surface species. In the latter, formation of metallacycloalkanes is possible, with three carbon atoms and one or two metal atoms in a cycle [36]. Some of these possible

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surface adsorption species of $c$-$C_3H_6$ have been characterized by means of experimental spectroscopic techniques, frequently high-resolution electron energy loss spectroscopy (HREELS), for several metal surfaces [29,31,34,35].

The relation between reactivity and bonding properties of $c$-$C_3H_6$ for different transition metals has also been investigated in the last decades by means of quantum chemical calculations [36–41]. Recently, Wöll et al. [42] and Wang et al. [43] reported theoretical studies on the molecular adsorption of $c$-$C_3H_6$ on Cu(1 1 1) surfaces using density functional theory (DFT) calculations. In the first work, the plane of the carbon ring was placed parallel to the surface and backdonation from the metal into cyclopropane empty molecular orbitals was proposed to be involved in the interaction. In the other study, different bonding configurations for the adsorbate were considered. The results indicated that both adsorption and desorption processes occur molecularly. Wang et al. [43] investigated the possible intermediate species in the dissociative adsorption of $c$-$C_3H_6$ on Cu(1 1 1) [44]. Although Pt is one of the most versatile heterogeneous metal catalysts [45,46], theoretical studies on $c$-$C_3H_6$ are still scarce.

In this paper we studied the adsorption process of $c$-$C_3H_6$ onto Pt(1 1 1) at low coverage of computing adsorption energies and equilibrium geometries. For that purpose, we considered different initial adsorption sites and bonding configurations for the $c$-$C_3H_6$ molecule. We have included Van der Waals (vdW) dispersion force geometry optimization and electronic structure (DOS) and bonding (OPDOS & OP) analysis.

## 2. Theoretical method and adsorption model

The electronic structure and energy calculations were performed by means of density functional theory (DFT) [47] implemented in the Vienna *Ab initio* Simulation Package (VASP) [48,49]. The projector augmented wave (PAW) pseudopotential [48,49] was used to account for the electron–ion core interaction, using the PW91 functional as the generalized gradient approximation (GGA) [50] for the exchange-correlation term.

The Pt(1 1 1) surface was modeled using a $(3 \times 3)$ slab containing 5 layers of Pt atoms with a 20 Å vacuum gap in the [1 1 1] direction as a compromise between computational economy and reasonable accuracy. We performed a partial slab relaxation, the three upper Pt layers were allowed to fully relax while the bottom two layers were kept fixed at bulk positions. The Brillouin-zone was sampled using $11 \times 11 \times 1$ Monkhorst-Pack K-point mesh [51]. We included the Van der Waals correction as described by Grimme [52] using default parameters for H and C, while those for Pt were fixed at the values $R_{vdW} = 12$ Å, $d = 20$ Å, $C_6 = 1.75$, and $R_{Pt} = 1.452$ Å. A cut-off energy of 400 eV was used for the plane-wave basis set. The total energy convergence and the forces on the atoms were less than $10^{-4}$ eV and 0.01 eV Å$^{-1}$, respectively. Self-consistent calculations were considered to converge when the difference in the total energy of the crystal between consecutive steps did not exceed $10^{-5}$ eV. In the same way, static calculations were considered to converge using the same criterion. The cyclopropane molecule was adsorbed on one side of the surface with coverage $(3 \times 3)$, this coverage avoids adsorbate-adsorbate interaction between images. We used the same geometric periodicity of bulk Pt and no reconstruction was included for the first layer. The metal surface was represented by a 45-atom cell (see Fig. 1(a)).

In a preliminary analysis, we investigated the preferential adsorption geometry for $c$-$C_3H_6$/Pt(1 1 1) interaction, considering several adsorption sites on the surface and bonding configurations for the adsorbate. Fig. 1(b) shows the four adsorption sites examined here, designated in order of increasing coordination number: onefold, Top; twofold, Bridge; threefold, fcc hollow; and threefold, hcp hollow. The molecule was considered on each adsorption site in three different initial geometries in relation to the metallic surface, as suggested in the literature [27,30,42,43]: parallel to the surface, with a $C_{3v}$ symmetry; vertical to the surface with one C—C bond upward to the surface and a $C_{2v}$ symmetry; and vertical to the surface with one C—C bond downward to the surface and a $C_{2v}$ symmetry (see Fig. 1(c)). We also investigated other bonding configurations, including one with a $C_s(\sigma_v)$ symmetry. In this case, the ring was allowed to rotate on each adsorption site from each initial position in both a parallel and perpendicular axis direction with respect to the metal surface, maintaining at least one C—C bond parallel to the surface. The minimum adsorption energy $E_{ads}$ was calculated by means of the following total energy difference:

$$E_{\text{ads}} = E_{\text{T}}\left(\frac{c\text{-}C_3H_6}{\text{Pt}(1\,1\,1)}\right) - E_{\text{T}}(c\text{-}C_3H_6) - E_{\text{T}}(\text{Pt}(1\,1\,1))$$

where $E_T$ is the total energy of the system and $c$-$C_3H_6$/Pt(1 1 1), $c$-$C_3H_6$, and Pt(1 1 1) refer to the molecule-on-metal system, the free $c$-$C_3H_6$ molecule, and the bare Pt surface, respectively.

Once the preferential adsorption geometry was established, we analyzed atom–atom interactions between the adsorbate and the metal surface by means of two main conceptual tools: density of states (DOS) and overlap population (OP). The DOS curve is a plot of the number of orbitals per unit volume per unit energy, while the OP can be considered as a measure of bonding between the atoms or molecular fragments [53]. We also used the crystal orbital overlap population (OPDOS), which links the previous concepts. In fact, the OPDOS curve is an energy-resolved plot of the overlap population-weighted density of states, and their integration up to the Fermi level gives the total OP. Using DOS and OPDOS curves, and OP comparisons, we carried out the study of changes in the adsorbate bonding and the contribution to bonding of the individual atomic orbitals.

## 3. Results and discussions

### 3.1. Preferential adsorption geometry

The adsorption energy ($E_{ads}$) values corresponding to the initial models used in the geometrical optimization of $c$-$C_3H_6$ adsorbed on Pt(1 1 1) are very low (between −0.02 and 0.08 eV) or unstable (+0.57 eV when the C—C pointed upward to the surface), except for parallel Top and parallel Bridge configurations. This fact indicates the presence of a weak interaction between the molecule and the surface, which is in agreement with the experimental evidence. The thermal desorption spectra of $c$-$C_3H_6$ on Pt(1 1 1) show only one peak at 144 K [35], a relatively low temperature considering that other $C_5$ or $C_6$ hydrocarbon molecules also desorb at much higher temperatures due to bonding interactions of chemical nature. In all cases the vertical interaction with a C—C bond above the surface is unstable (+0.57 eV).

The two preferential adsorption sites for $C_3H_6$ on Pt(1 1 1) Top parallel 11° tilted toward the surface and Bridge parallel, present adsorption energy values of −0.27 eV and −0.75 eV respectively (see Fig. 2) these values improved ∼0.04 eV and 0.14 eV, respectively, thanks to vdW corrections. Scoggins and White reported a desorption energy of 0.369 eV [54]. Černý et al. performed a calorimetric study for cyclopropane adsorbed on Pt and they found an adsorption heat of 47.1 kcal/mol (∼2.04 eV) [55]. Capitano et al. studied the catalytic cyclopropane hydrogenation on Pt (1 1 1) experimentally. They measured the thermal activation energy needed to remove the adsorbate from the surface at 350 K, 15.2 kcal/mol (0.659 eV) [56]. This value is similar to the adsorption energy value found in this work for the Bridge parallel case.

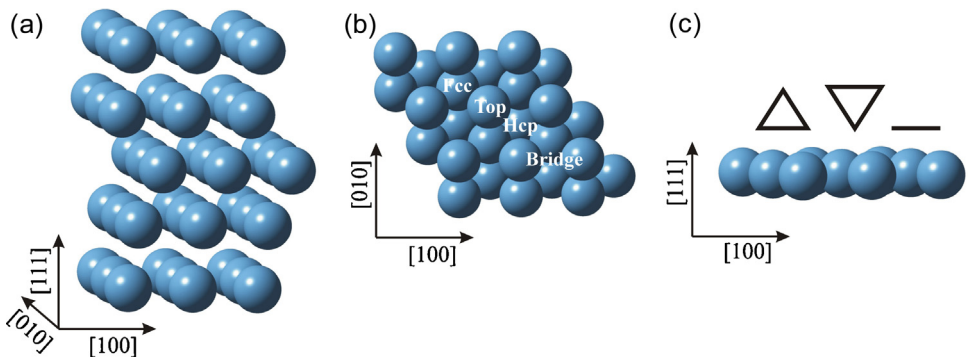



**Fig. 1.** (a) 5 layer Pt(1 1 1) slab, (b) adsorption sites (Top, Bridge, Fcc hollow and Hcp hollow), (c) cyclopropane initial geometries (a triangle identifies the perpendicular orientation and a long bar a parallel orientation of the C ring, respectively).

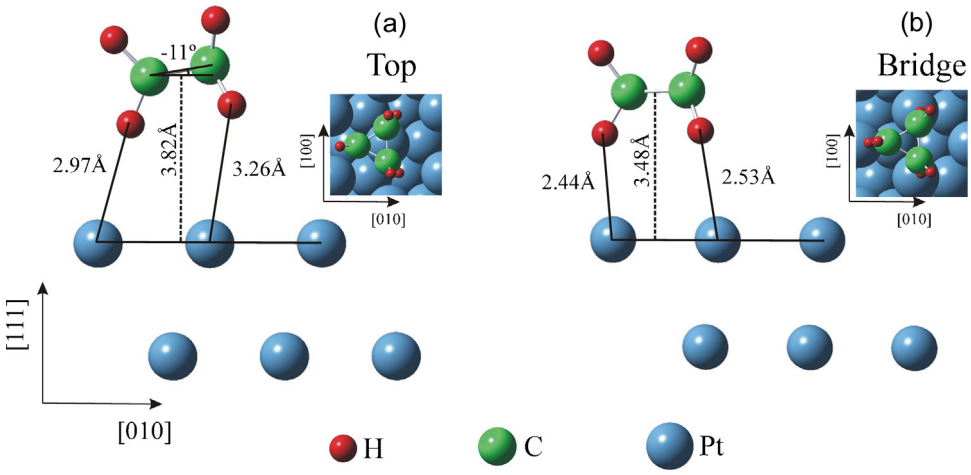



**Fig. 2.** Geometric optimization (a) cyclopropane/Pt(1 1 1) on Top location (b) on Bridge location.

The equilibrium Pt—C distance is ~3.50 Å. The Top parallel geometry 11° tilted toward the surface is in agreement with the configuration proposed in references [54,56].

Table 1 shows geometry optimization results corresponding to preferential adsorption sites. Due to the ring stiffness, and in agreement with our findings of a weak adsorbate–metal interaction, no important differences were observed between the geometry of the free molecule and that of the adsorbed molecule. Thus, C—C interatomic distances remain unchanged after adsorption and the length for C—H bonds near the surface was modified only by 0.9% in the Bridge parallel configuration.

**Table 1**
Bond distances and binding energies in the Top and Bridge sites.

| Bond | c-$C_3H_6$/Pt(1 1 1) – Top | | c-$C_3H_6$/Pt(1 1 1) – Bridge | |
|---|---|---|---|---|
| | Distance [Å][b] | Energy [eV][a] | Distance [Å] | Energy [eV][a] |
| C—C | 1.51 (1.51) | −0.27 | 1.51 | −0.75 |
| C—$H_{downward}$ | 1.09 (1.09) | | 1.10 | |
| C—$H_{upward}$ | 1.09 (1.09) | | 1.09 | |
| Pt—H | 3.26 | | 2.53 | |
| Pt—H | 3.26 | | 2.53 | |
| Pt—H | 2.97 | | 2.44 | |
| Pt—$C_{ring}$ | 3.82 | | 3.48 | |
| <C—C—C | 60.0° (60.0°) | | 60.0° | |
| <H—C—H | 114.8° (114.0°) | | 114.1° | |

Isolated c-$C_3H_6$: C—C 1.51 Å; C—H 1.09 Å.
[a] Includes vdW corrections.
[b] Values for the isolated $C_3H_6$ molecule is within parenthesis.

Regarding the molecule-surface height, we found that the equilibrium values are relatively large for Top configuration (Pt—$C_{ring}$ distance ≈ 4 Å) and shorter for Bridge configuration (Pt—$C_{ring}$ distance ≈ 3.5 Å). Mean molecule-surface distances corresponding to unsaturated hydrocarbons are ≈2 Å [13,15,57–59]. Distances are also included in Table 1. These heights are also characteristic of a weakly bonded molecule with the metal surface, in full agreement with the values reported for other saturated cyclic hydrocarbons [14,16].

The adsorption energy results support the idea of a weak adsorbate-substrate interaction, less than 1 eV, in the best case scenario. We performed all the calculations considering vdW dispersion forces. The concerted effect of covalency and vdW bonding for benzene adsorbed on metals (including Pt) was recently analyzed by Liu et al. [60]. In the case of cyclopropane/Pt(1 1 1), the addition of vdW corrections to the energy produces larger adsorption energies but predicts the same adsorption sites. We did not find C ring expansion, the C—C—C and H—C—H angles are in agreement with reference [61,62].

### 3.2. Density of states

Fig. 3 shows the electronic structure (DOS) for adsorption systems. Fig. 3(a) and (b) corresponds to Top and Bridge cyclopropane adsorbed on Pt(1 1 1) respectively. The black tick marks in DOS plots represent the electronic levels of isolated cyclopropane before adsorption. No adsorbate–adsorbate interactions were found at our low coverage. The molecule on the surface shows DOS bands that

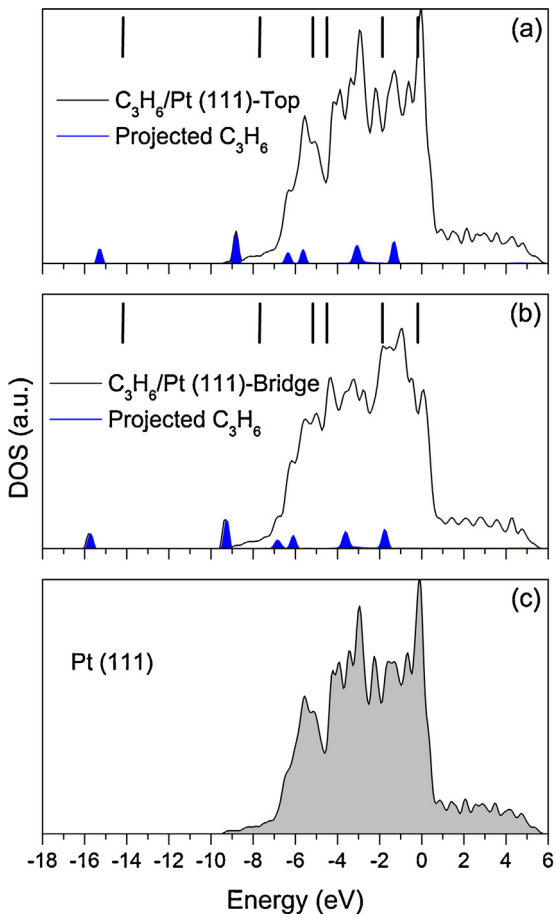



**Fig. 3.** Density of state curves for cyclopropane on Pt(1 1 1): (a) Top location (b) Bridge location. (c) DOS curve for bare Pt(1 1 1). The ticks indicate the cyclopropane molecular orbitals before adsorption. The projections of adsorbed cyclopropane DOS are shaded in blue. (For interpretation of the color references in this figure legend, the reader is referred to the web version of this article.).

spread out slightly due to the weak interaction between cyclopropane and metal states, *p*-orbitals in particular. The states of cyclopropane shift to lower energies, therefore, a stabilization of these orbitals takes place after interaction with the surface being more notorious for the Bridge parallel configuration (see Fig. 3(b)). Bastl [63] found peaks at 6.7, 8.2, and 9.3 below $E_F$ in a study of cyclopropane on Pd surfaces by means of UPS spectroscopy. These values are similar to our calculations. The DOS curve for bare Pt(1 1 1) is displayed in Fig. 3(c), if we compare this curve with total curves after adsorption we can notice that no changes are visible, again, due to the weak interaction with the molecule and relative weight of cyclopropane states in the unit cell.

### 3.3. Bonding analysis

After geometry optimization, we examined the evolution of the chemical bonding in the preferential adsorbate–surface configurations (Top and Bridge parallel) through the analysis of the OP values and OPDOS curves for selected bonds. Table 2 shows the OP values corresponding to the bonds that participate the most during the adsorption process.

It can be seen in Table 2 that the OP values corresponding to the C—H bonds close to the surface are weakened between 3.2 and 4.2% during the cyclopropane adsorption for the Bridge parallel geometry. Table 2 also reveals that the OP values of the C—H bonds for the Top configuration are only 0.5 and 0.6% lower than those of the same bonds in the isolated cyclopropane, thus anticipating a lower stability of this adsorption form with respect to the Bridge case.

**Table 2**
Overlap population (OP) before and after cyclopropane adsorption on Pt(1 1 1).

| Bond | Top | | Bridge | |
|---|---|---|---|---|
| | Before | After | Before | After |
| Pt—Pt | 0.419 | 0.415 | 0.422 | 0.425 |
| Pt—Pt | 0.423 | 0.419 | 0.423 | 0.425 |
| $C—H_{downward}$ | 0.814 | 0.810 | 0.814 | 0.788 |
| $C—H_{downward}$ | 0.814 | 0.810 | 0.814 | 0.788 |
| $C—H_{upward}$ | 0.813 | 0.808 | 0.813 | 0.779 |
| Pt—H | – | 0.002 | – | 0.043 |
| Pt—H | – | 0.005 | – | 0.043 |
| Pt—H | – | 0.005 | – | 0.056 |

This behavior can also be seen in Fig. 4(b) and (e), where the OPDOS curves of the C—H bond for the Top and Bridge locations are compared to the isolated cyclopropane. Similar curves have been obtained for Top and Bridge configurations, thus indicating that major interactions are similar for both locations. As it can be seen, cyclopropane *s* and *p* states present narrow peaks in the isolated state, but once the adsorption occurs they are shifted to lower energies.

At the same time, the Pt—Pt surface bonds involved in the adsorption are slightly weakened (0.8 and 1.1%) for the Top configuration. For the Bridge adsorption mode, the OP values of the Pt—Pt bonds that interact with the H atoms increase approximately 7.6%. As it can be seen, OP changes are minor in all cases.

The OP values corresponding to the H—Pt bonds originated in the adsorption process are also presented in Table 2. The OP values of the formation of H—Pt bonds obtained once again indicate that the most stable adsorption site is the Bridge site and that the Pt—Pt OP increase is favored by Pt—H interactions. The Top adsorption site presents a single interaction with the surface, with H—Pt OP values of 0.002 and 0.005. On the other hand, higher H—Pt OP values are observed for the Bridge site (0.043 and 0.056). The OPDOS curves in Fig. 4(c) and (f) show that the adsorption of cyclopropane on the surface mainly occurs through the formation of Pt—H bonds in both sites, and the interaction is more important in the case of the Bridge site. The Top and Bridge sites show several bonding peaks between −3 and −6.5 eV. These peaks are intense for the Bridge configuration, and are less developed in the Top site. Anti-bonding peaks appear in both cases about −0.25 and −3 eV. The Bridge site presents stronger and narrower peaks than those of the Top location. Both sites have a bonding peak at approximately −9 eV, which is more defined and intense in the Bridge site. As a result of bonding and anti-bonding interactions, Pt—H overlaps in the Bridge location are stronger than those for the Top site (see Table 2).

The H, C, and Pt orbital occupation changes after cyclopropane adsorption are listed in Table 3. According to the previous bonding analysis, we can see that the most important change in OP corresponds to the orbitals forming the C—H—Pt "*agostic*" bonds. The terme "*agostic*" is also used in organometallic chemistry and it involves the formation of multicentered C—H—Pt bonds [64]. This interaction arises either from electron donation from the metal center into anti-bonding C—H orbitals or from charge donation from C—H bonding orbitals to the metal. According to this, we found that the 1*s* orbitals of the H atoms close to the Pt surface decrease their OP value 0.1 and 0.5% for the Top configuration, and 0.7 and 1% for the Bridge adsorption site.

Although all Pt atomic orbitals were considered, it is well known that the chemistry of most transition metals is largely dominated by their *d* orbitals. However, in the case of cyclopropane adsorption on Pt(1 1 1), the contributions to bonding of metal *s* and *p* orbitals are the most important. A similar behavior is observed in organometallic compounds [65]. Table 3 shows that *c*-$C_3H_6$ interacts especially

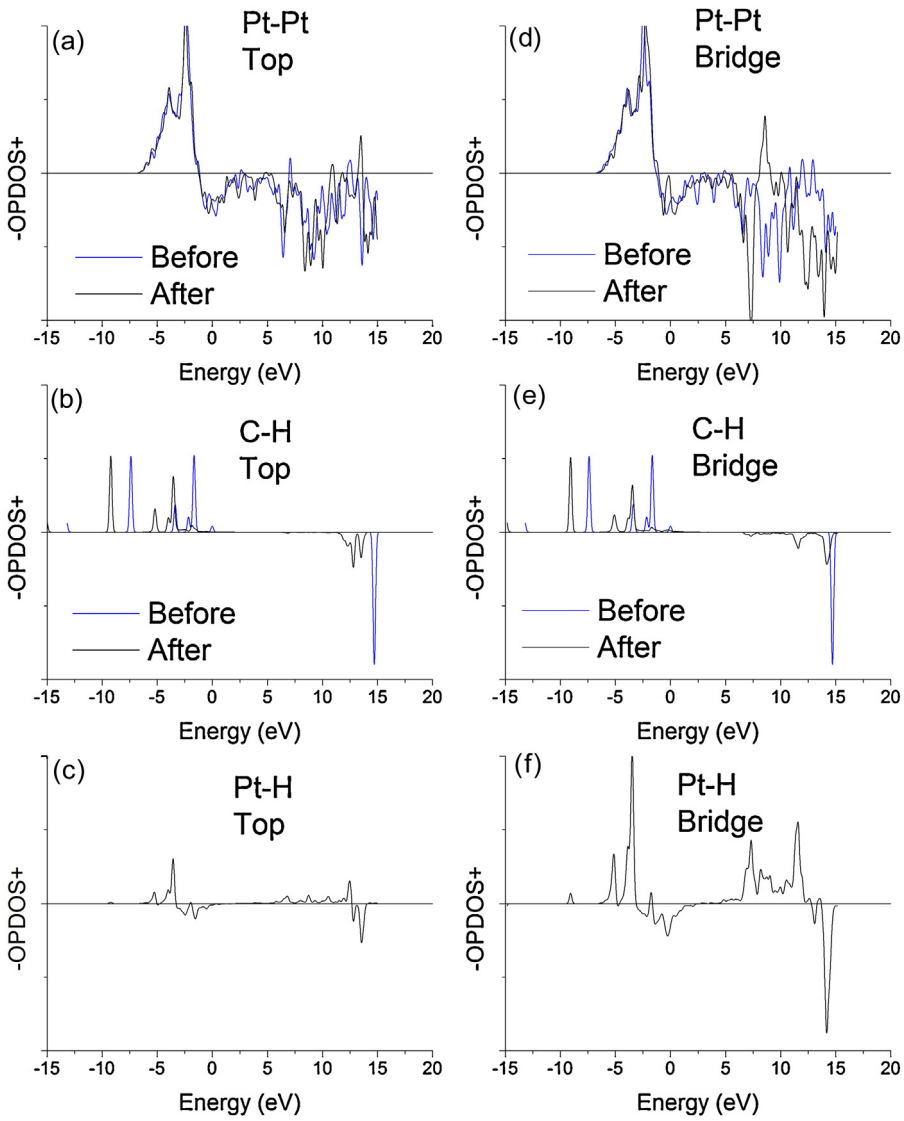
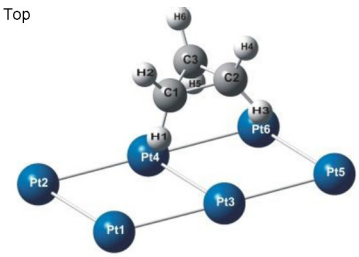



**Fig. 4.** Crystal orbital overlap population (OPDOS) curves of selected bonds before and after the adsorption process of cyclopropane on a Pt(1 1 1) surface. Pt—Pt bond: (a) Top and (b) Bridge. C—H bond: (c) Top and (d) Bridge. H—Pt bond: (e) Top and (f) Bridge.

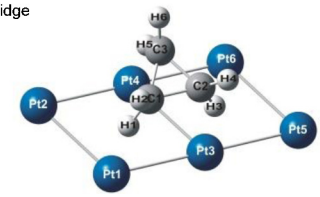
**Table 3**
Atomic orbital occupation for the cyclopropane/Pt(1 1 1) system before and after adsorption. Top views of: (a) Top and (b) Bridge sites are included for clarity.

| Atom | Orbital | Before | After | |
|---|---|---|---|---|
| | | | Top | Bridge |
| C1 | $2p_y$ | 1.067 | 1.057 | 1.058 |
| C2 | $2p_z$ | 0.943 | 0.947 | 0.940 |
| C3 | $2p_z$ | 0.942 | 0.948 | 0.931 |
| H1 | $1s$ | 0.979 | 0.979 | 0.972 |
| H2 | $1s$ | 0.979 | 0.979 | 0.972 |
| H3 | $1s$ | 0.980 | 0.974 | 0.969 |
| Pt3 | $5p_z$ | 0.396 | 0.381 | 0.396 |
| Pt6 | $5p_z$ | 0.394 | 0.387 | 0.356 |

(a) Top




(b) Bridge



with Pt $5p_z$ orbitals for the two most stable configurations (Bridge and Top), that undergo significant depletion of electron density after adsorption, whereas remaining Pt orbitals depopulate to a lesser extent. Pt—H bonds are mainly due to overlaps between near H 1*s* and Pt $5p_z$ orbitals.

The behavior of the C orbitals that are close to the surface is more complex. For the Top site, OP changes suggest that after adsorption the $2p_z$ orbital population increases while $2p_y$ and $2p_x$ electron occupation decreases. On the other hand, the OP values for $2p_x$, $2p_y$, and $2p_z$ orbitals decrease simultaneously in the Bridge orientation as a result of the adsorbate–surface interaction. In addition, the 2*s* orbital population increases in both cases (the results are not shown). These multiple changes respond to the re-settlement of the *c*-$C_3H_6$ internal structure in order to develop new Pt—H bonding interactions during the adsorption process.

## 4. Conclusions

This theoretical study on *c*-$C_3H_6$ adsorbed on Pt(1 1 1) shows a weak interaction with the metallic surface. The adsorption energy is rather independent of the adsorption site coordination number, and there is a small preference for a Bridge site with the adsorbate in parallel orientation with regard to the surface. Geometrical and electronic properties of *c*-$C_3H_6$ are slightly disturbed during the adsorption process, so that DOS and OPDOS curves and OP values for a selected bond or orbital do not show significant changes. There is no Pt—C bond present or formed in the course of the adsorption process and the main interaction comes from the formation of the multicentered C—H—Pt "*agostic*" bonds involving the hydrogen atoms pointing toward the surface from the molecule. Finally, we also found that Pt $5p_z$ orbitals are the major contributions to the overall adsorbate–surface bonding.

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