



# Interaction of a carbon atom on small platinum clusters and its effects on hydrogen binding

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## ABSTRACT

*Ab initio* calculations on interaction of a C atom on small Pt<sub>n</sub> clusters ( $n = 1-10$ ) show strong carbidic bonding and a decrease in the magnetic moments of Pt clusters. The adsorption energy decreases in an oscillatory way with increasing size but suggests no graphitic phase on small Pt clusters. Pt<sub>n</sub> clusters ( $n < 7$ ) remain nearly planar after C adsorption but larger clusters have 3D structure. Further calculations of infrared and Raman spectra are reported. Interaction of H on pure and Pt<sub>n</sub>C clusters shows stronger binding of H on Pt<sub>n</sub>C clusters suggesting their better reactivity.

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## 1. Introduction

Platinum clusters are important catalysts in many reactions such as in fuel cells for green energy and in converting CO into CO<sub>2</sub> in automobile exhausts. In some of these applications graphite is used as cluster support. On the other hand carbon is one of the major poisons of the transition metal catalysts widely used for reactions dealing with organic molecules. Carbon deposits are usually formed from dehydrogenation of hydrocarbons under reaction conditions [1] and they can block the active sites of the catalyst resulting in the poisoning of the reactivity and decline in performance [2–5]. Wang et al. [6] identified single carbon atom on small Pt clusters when acetylene and ethylene were adsorbed. Also, recently small Pt clusters with 8–10 atoms have been shown [7] to be 40–100 times more active for dehydrogenation of propane than reported earlier. We therefore study interaction of a C atom on small Pt clusters and show that C interacts very strongly on them and that the bonding is carbidic. The adsorption energy of C on Pt<sub>n</sub> clusters is stronger compared with C–C binding energy in small carbon clusters and therefore graphitic phase is not favorable. Further studies have been carried out on hydrogen interaction on Pt<sub>n</sub> and Pt<sub>n</sub>C clusters. Our results show that generally H binds even more strongly on Pt<sub>n</sub>C clusters than on pure Pt<sub>n</sub> clusters. Further we find that Pt<sub>10</sub> is a very stable cluster and that it interacts relatively weakly with both C and H. However, there is a significant gain in the binding energy of H on Pt<sub>10</sub>C compared with the value on Pt<sub>10</sub>. These results suggest that small Pt clusters may not be

poisoned by C and that small additions of C could even improve the catalytic behavior of small Pt clusters.

The atomic structures of Pt clusters have been studied from *ab initio* calculations by Kumar and Kawazoe [8] who obtained planar structures for small Pt<sub>n</sub> clusters with  $n$  up to 9 and 3D structures beyond  $n = 9$  with high dispersion. Miller and Hall [9] have studied structural and bonding trends of a Pt atom interacting with small C clusters using density functional theory (DFT) while interaction of carbon on large Pt nanocrystals as well as on Pt(111) surface has been studied from DFT and a transition from carbidic to graphitic phase has been obtained [10]. Interaction of hydrogen has been calculated [11] on Pt<sub>10</sub> supported on graphene. Also interaction of H<sub>2</sub> on supported Pt clusters has been studied and structural changes as well as hydride formation has been reported [12]. We find that interaction of a C atom on small Pt clusters alters their reactivity very significantly and enhances the binding energy of H.

In Section 2 we present the details of the method used for calculations while the results are presented in Section 3. Our conclusions are given in Section 4.

## 2. Method of calculation

We use *ab initio* projector augmented wave pseudopotential method [13,14] with the ionic pseudopotential of Pt obtained from scalar relativistic calculations. Small Pt clusters are magnetic [8] and therefore spin-polarized calculations have been performed within generalized gradient approximation (PW91) [15] for the exchange–correlation (XC) energy. The clusters are placed in a large simple cubic unit cell with periodic boundary conditions so that there is  $\sim 10$  Å space in between the surfaces of the clusters in the neighboring cells. The Brillouin zone is sampled by the  $\Gamma$  point.

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The initial configurations of Pt clusters are taken from Ref. [8] and several possibilities for the adsorption of a C atom are explored. Small Pt clusters are planar and we explore if a transition to 3D structures occurs after C adsorption. All the structures are fully optimized without any symmetry constraint using conjugate gradient method. The convergence criterion for force on each ion is taken to be less than 0.004 eV/Å and the energy is converged within 0.0001 eV. The resulting lowest energy structures have been further optimized using revised PBE (RPBE) XC functional [16] which gives lower binding energy of C in better agreement with the experimental results, though no significant change occurs in the structures.

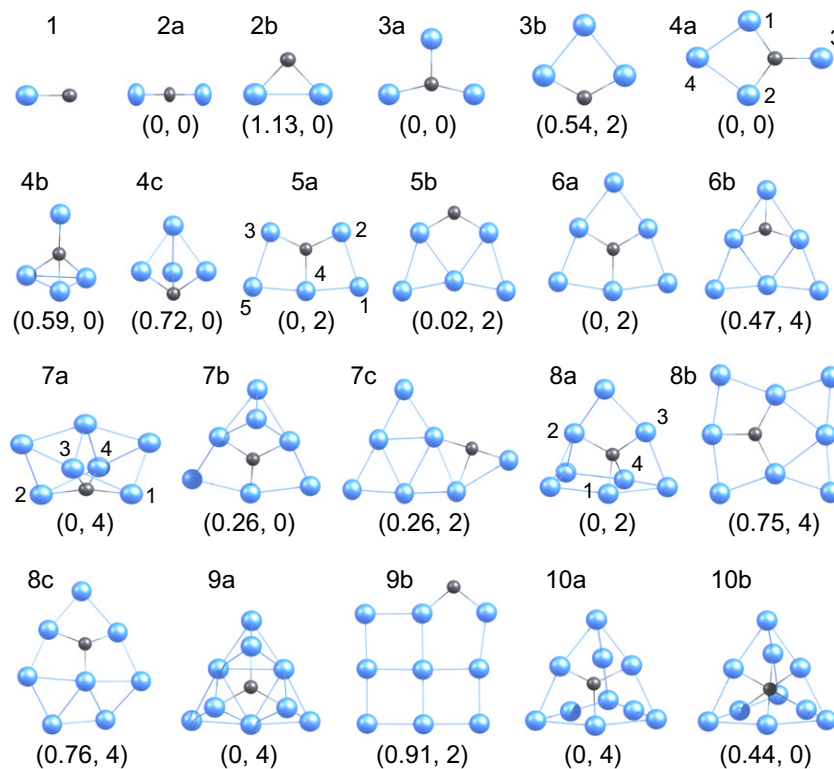
The vibrational frequencies and their corresponding infrared (IR) intensities and Raman activities as well as dipole moments have been calculated using GAUSSIAN program [17] for the lowest energy isomers obtained from the plane wave calculations. The atomic structures are reoptimized but the changes are very small. Test calculations of vibrational frequency of Pt dimer using HCTH standalone functional [18–20] and SDD basis set [21] gave 215  $\text{cm}^{-1}$  and it matches with the experimental value [22] of 215  $\text{cm}^{-1}$  while the use of lanl2dz basis set with HCTH XC functional gives the value of 217  $\text{cm}^{-1}$  also in good agreement with the experimental result. For  $\text{C}_2$ , we obtained 1692  $\text{cm}^{-1}$  using B3LYP XC functional [23–24] and 6-311G(d) basis set while HCTH functional gives 1675  $\text{cm}^{-1}$ . Both agree well with the experimental value [25] of 1641  $\text{cm}^{-1}$ . Here we use HCTH standalone XC functional with 6-311G(d) basis set for C and lanl2dz basis set for Pt.

### 3. Results and discussion

#### 3.1. Atomic structure

The optimized atomic structures of  $\text{Pt}_n\text{C}$  ( $n = 1-10$ ) from plane wave calculations with PW91 XC functional are shown in Figure 1.

The bond length of PtC dimer is 1.697 Å and it compares well with the experimental value [26] of 1.677 Å. The dissociation energy of 7.20 eV is, however, higher than 6.28 eV obtained [27] from mass spectroscopy. But the RPBE value (6.8 eV) is closer to the experimental result.  $\text{Pt}_2\text{C}$  forms a chain with the C atom at the center (2a in Figure 1) and Pt–C bond length of 1.746 Å. An isosceles triangle (2b) with C capping a  $\text{Pt}_2$  dimer is 1.13 eV higher in energy than (2a). In this isomer Pt–C bond lengths increase to 1.87 Å due to the higher coordination of Pt atoms.  $\text{Pt}_3\text{C}$  is a trigonal planar structure with C at the 3-fold hollow site forming strong covalent bonds with Pt atoms (mean Pt–C bond length of 1.83 Å) and Pt–Pt bonds are elongated. Another planar isomer (3b) with C atom capping one of the bridge sites of an equilateral triangle of  $\text{Pt}_3$  with Pt–C bond length of 1.80 Å lies 0.54 eV higher in energy than (3a).  $\text{Pt}_4\text{C}$  is obtained by capping isomer (3a) with a Pt atom. The Pt–C bond length remains 1.83 Å signifying bonding similar to  $\text{Pt}_3\text{C}$ . A 3D isomer (4b) obtained by putting a C atom at the center of  $\text{Pt}_4$  tetrahedron lies 0.59 eV higher in energy with zero magnetic moment. The optimized structure has C atom capping a  $\text{Pt}_3$  triangle with Pt–C bond length of 1.97 Å. The fourth Pt atom caps C atom with a short bond of 1.81 Å. Pt–Pt bond lengths are about 2.65 Å. An isomer (4c) with a C atom on one of the faces of  $\text{Pt}_4$  tetrahedron lies 0.72 eV higher in energy than (4a). Therefore, planar structure is favored even after C interaction. Also a planar structure (5a) is formed by capping (4a) with a Pt atom with 2  $\mu_B$  magnetic moments while the magnetic moment of smaller clusters is quenched by C adsorption (Figure 2b). An isomer (5b) is obtained by capping two sides of (3b) symmetrically with Pt atoms in the plane. It is only 0.02 eV higher in energy than (5a) and therefore nearly degenerate. We also optimized a 3D structure in which a C atom interacts on a triangular face of a trigonal bipyramid. However, this isomer lies 0.65 eV higher in energy with 2  $\mu_B$  magnetic moments.  $\text{Pt}_6\text{C}$  has a triangular structure (6a) with C atom at the central 3-fold hollow site and 2  $\mu_B$  magnetic moments (Figure 2b). An isomer



**Figure 1.** Low lying isomers of  $\text{Pt}_n\text{C}$ , where  $n = 1-10$ . na, nb, ... are isomers of  $\text{Pt}_n\text{C}$  with increasing order of energy. The numbers in brackets refer to the energy (eV) relative to the lowest energy isomer which is taken as reference and the magnetic moments ( $\mu_B$ ). Large (blue) and small (black) balls represent Pt and C atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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