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Bonding and magnetism in transition metal sandwich structures with the aromatic hydrocarbon coronene $C_{24}H_{12}$ outer layers

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Abstract

Plane wave based *ab initio* density functional theory has been used to study the chemical bonding and magnetism of transition metal atoms between coronene molecules in sandwich structures $M_n(C_{24}H_{12})_2$ where $n = 7$ and M = Cr, Fe, Pd. Symmetry conditions permit the metal atoms to occupy either a central site with η^6-coordination as in the metal bis-benzene molecules $M_1(C_6H_6)_2$ or a lower symmetry edge site with η^2- or η^3-coordination. In some cases at the edge sites the metal atoms crimped the edges of the sandwich towards the smaller separations of the bis-benzene molecules. However, since this effect also depended on local metal atom spin, the sandwich cross-sections could be concave in one symmetry plane and convex in an orthogonal plane. The lowest energy states of the sandwiches had spin $S = 5$ (Cr), 6 (Fe) and 0 (Pd). The high spin systems occurred with a larger metal–ring spacing so that a concomitantly weaker electric field crossed the metal atom compared to the bis-benzene molecules which have $S = 0$ (Cr), 2 (Fe) and 0 (Pd) in the ground electronic state. In the spin polarized ground states the unpaired electrons resided exclusively on the metal atoms. In the Pd sandwich the excited states with spin $S = 1$ and $S = 2$ had qualitatively similar spin distributions to the Fe and Cr structures, with the difference that there was a much greater leakage of spin density onto the nearby carbon atoms. In all the sandwiches the spin density was not evenly distributed amongst metal atoms, and depended on the environment of the metal as gauged for example by the metal–nearest ring separation.

Keywords: Sandwich molecules; DFT; Density functional theory; Coronene; Chromium; Iron; Palladium; Aromatic hydrocarbon; Magnetism; Chemical bonding; Organometallic molecules; Kohn–Sham levels; ELF

1. Introduction

In this paper, we report plane wave based *ab initio* density functional theory (DFT) calculations of the structure and magnetism of transition metal (M = Cr, Fe, Pd) atom arrays sandwiched between coronene molecules. The metal atoms chosen span the first and second transition metal rows and encompass an interesting range of chemical bonding and magnetic properties. The molecule coronene ($C_{24}H_{12}$), a D_{6h} symmetric peri-condensed aromatic hydrocarbon with seven rings [1], was selected because it was large, has a compact skeleton with many internal C–C sigma bonds which act to reinforce its shape, and has a central ring resembling graphite in bond uniformity in contrast to its perimeter which has neither uniformity nor complete bond alternation. This hydrocarbon constitutes an important extension beyond the previous components of sandwich structures which were based on the molecules pyrene $C_{16}H_{10}$ and tetracene $C_{18}H_{12}$ [2,3]. We contrast the coronene results with those from the bis-benzene compounds $M_1(C_6H_6)_2$, calculated under identical conditions. The latter provide a useful yardstick for gauging and interpreting how some of the calculated properties of the sandwiches vary with the metal and the effect of extra rings. The ground state properties of the following structures M_nR_2

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are reported here: briefly as reference molecules $M_1(C_6H_6)_2$ for $M = Cr$ (spin $S = 0$), Fe ($S = 2$) and Pd ($S = 0$); $M_7(C_{24}H_{12})_2$ for $M = Cr$ ($S = 5$), Fe ($S = 6$) and Pd ($S = 0$). We also summarily report on other spin states to confirm the minimum and in the case of Pd ($S = 1$, 2) to provide comparisons with the non-zero spin distributions in the Cr and Fe sandwiches.

Motivation for this study of hypothetical structures comes primarily from the recent synthetic work on organo-metallic palladium ($n = 3$, 5) complexes by Murahashi, Kurosawa et al. [4], and from frontier areas such as molecular nano-electronics [5], astrophysics [6,7], organo-metallics in the gas phase [8], graphite intercalation [9] and possibilities for new synthetic structures based on advances in graphene research [10–12]. In their recent work the Murahashi–Kurosawa group [4] reported the synthesis of two sandwich structured molecular ions $[Pd_3Cl_3(C_7H_7)_2]^{2+}$ and $[Pd_5(C_{18}H_{12})_2\ C_6H_5CH_3]^{2-}$. In this work the Pd_5 complex ion contained a planar array of palladium and the principal geometric feature was η^2- and η^3-coordination of the metal atoms to edge carbon atoms of the tetracene ($C_{18}H_{12}$) moieties. It was proposed by Murahashi et al. [4] that “metal monolayer sandwich compounds containing different sizes and shapes of metal sheet can be synthesized using different extended pπ-conjugated carbon frameworks” with the aid of their template effect [4]. Alternatively one could imagine creative assembly using atomic beams and graphene sheets sloughed off macrographite samples [12] manipulated by AFM probes and diced by STM probes. Extended organo-metallic sandwich structures with various metals could provide nano-scale electronic devices with a variety of useful properties. From our perspective the theoretical studies described in this report and elsewhere [2,3] could be used as the basis of models for studying edge effects in nano-wide graphene electronic circuitry and overpotential effects in thin batteries.

Regarding the choice of metal atoms we note that chromium between C_6-aromatic rings satisfies the 18 electron rule ($6 + 6 + 6$) implying a possible energetic preference for central sites between rings. In chromium bis-benzene the ground state is a singlet ($S = 0$), with an inter-plane spacing (322 pm) that is less than that in graphite (335 pm). In bulk (bcc) chromium metal the nearest neighbour spacing 249 pm almost matches the basal plane graphite ring spacing 245.6 pm suggesting that in small chromium arrays a limited amount of registration might accommodated. Iron has a (bcc) bulk metal nearest neighbour spacing almost the same as chromium. Iron forms many ground state spin polarized organo-metallic complexes. Palladium which belongs to the second row transition metals, has enough electrons to fill the 4d-shell and a nearest neighbour (fcc) bulk metal separation 275 pm that unlike chromium and iron exceeds the graphite ring spacing. We show that the metal atoms have sandwiches with some geometric similarities arising from the robustness of the coronene carbon skeleton. However the spin manifolds are different: in chromium compounds the spin states are about 0.1 eV apart, in iron about 0.5 eV and in palladium almost 1 eV apart.

Our current program with regard to organo-metallic sandwich structures has limited goals, namely to explore their properties by varying hydrocarbon size and shape, metal type and metal atom number. In this paper, we concentrate on metal type. In previous studies we have briefly reported preliminary results of the structure of sandwiches of palladium between hydrocarbons of varying sizes up to circumcoronene [2] and in more detail the geometry and electronic structure, including palladium metal–metal bonds between eclipsed pyrene and tetracene pairs [3]. This earlier work did not include an account of spin polarized states or include work or comparisons with chromium and iron as is provided here.

This paper is organized as follows: next, a brief description of the computational methodology; followed by a summary of results for $M_1(C_6H_6)_2$ where $M = Cr$, Fe, Pd; then we describe in separate sections results for $Cr_7(C_{24}H_{12})_2$, $Fe_7(C_{24}H_{12})_2$ and $Pd_7(C_{24}H_{12})_2$. The report ends with a Summary and discussion section in which the three metal sandwich structures are compared and main results briefly summarized.

2. Method of calculation

All calculations were performed using the vienna *ab initio* simulation package Vasp [13–16]. The plane wave based calculations used PAW pseudo-potentials [17,18] and the spin polarized generalized gradient approximation for the exchange-correlation energy functional (PW91) parameterized by Perdew et al. [19,20]. Valence electrons were assigned as follows: Cr (6), Fe (8), Pd (10), C (4), and H (1). Note that the valence shell of palladium was treated as a 10 electron system ($4d^{10}$). All calculations were performed using periodic boundaries with a cubic cell, edge lengths in the range 0.75–2.50 nm, so the molecules were at least 0.9–1.0 nm apart. All Brillouin zone integrations were done at the gamma point. The geometry optimizations were carried out using the conjugate gradient method usually until the forces acting on each atom were approximately $\leqslant 6$ μeV/pm (or 0.05 cm^{-1}/pm). We routinely calculated geometry, total energy for given total spin, isometric surfaces of total charge and Kohn–Sham partial charges, spin density and occasionally the electron localization function ELF [21,22]. Harmonic analysis of the wave function inside spheres with centers on individual atoms also assisted the analysis of charge density of the chemical bonds. The starting geometries were aromatic hydrocarbons with standard bond lengths. In the sandwiches the hydrocarbons were eclipsed and metal atoms were initially located in the middle above the ring centers. The total energy E_t calculated by Vasp was referenced to the sum of separated metal atoms and separated planar hydrocarbon molecules. It appears in the following tables as ΔE_f. All of the chromium and iron calculations were spin polarized and some of the palladium calculations too. The use of