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“A THEORETICAL KOHN-SHAM DFT BASED STUDY OF PT@PD$_{12}$”

Desarrollada por los siguientes autores:

Maribel Dessens-Félix
Rafael Pacheco-Contreras
Catalina Cruz-Vázquez
Alvaro Posada-Amarillas
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Best Regards,

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and
A Theoretical Kohn-Sham DFT based study of Pt@Pd$_{12}$

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ABSTRACT

We report a theoretical calculation of the structural properties of neutral Pt@Pd\textsubscript{12} cluster, using density functional theory (DFT) to search for the minimum energy structure and a genetic algorithm (GA) to obtain the initial configuration. The structural reoptimization and frequency analysis were performed with the generalized gradient approximation employing the PBE exchange-correlation functional. Besides the radial distribution of the atoms, n(r), we calculated the pair distribution function, g(r), and X-ray scattering intensity spectrum, I(k), of both initial and reoptimized configurations. Our results indicate that a slightly distorted minimum energy structure is obtained after the ab-initio optimization procedure. We also found that the average interatomic distance is larger in the DFT optimized structure than in the GA-predicted ground state. Jahn-Teller and electron correlation effects might be responsible of this behavior.

I. INTRODUCTION

Nanoscience and nanotechnology have promoted research on the nanoscale systems mainly due to the promising expectations that nanoparticles have in fields such as medicine, biology, and electronics [1]. Transition metal (TM) nanoparticles occupy a special place in this new world of discoveries being important for a variety of applications, from catalysts to hydrogen storage devices [2]. A variety of techniques have been implemented in order to prepare nanomaterials with specific properties, including chemical, physical or biological processes. The addition of a second metallic component increases complexity of nanoparticles and has demonstrated to improve the
desired properties [3]. Thus, tailor-made nanoalloys have become a reality with the production of extraordinary new nanomaterials for applications in, for example, heterogeneous catalysis [4]. But before such applications can be industrialized, the physical and chemical properties must be revealed both experimentally and theoretically.

The understanding of the structural and electronic properties of nanoalloys has become one of the most active research fields in nanoscience; shape, size and composition determine their properties as well as their electronic distribution. Theoretical methods based on semiempirical model potentials have shown to be outstanding in the description of structural properties with the condition that interatomic bonding is well-described by the potential energy function. Monte Carlo, Molecular Dynamics or Genetic Algorithms are well established methodologies to perform explorations of the potential energy surface [5]. But all of these methods fail when the nature of the chemical bond is poorly represented by a semi-empirical model potential. In these cases, it is necessary to utilize more advanced levels of theory, such as ab initio methods.

Quantum chemical methods have been applied to a number of metallic nanoparticles, frequently incorporating several doping agents. It has been observed that substituting one or several metal atoms into metallic clusters alters not only the shape but also the properties of the host nanoparticles. A number of examples can be found in the literature, for instance the large magnetic anisotropy energies induced in Co and Fe nanoparticles by the addition of Pd and Pt atoms [6], the improvement of specific catalytic reactions by adding Ag, Au, Cu, Co, Cr, Fe atoms [7] to Pd catalysts, the increasing in the melting temperature induced by the doping of Ag icosahedral clusters with Ni or Cu single impurities [8], similar effect is observed in Al clusters doped with
a single Cu atom [9], although in the latter case no considerable change in the electronic or geometric structures of the host cluster is produced.

Structural trends of small late-transition-metal clusters have been carefully studied by density functional theory (DFT) methods, and in a number of studies Pd_{13} cluster has been found to prefer the I_h structure [10, 11]. However, alternative structure motives for the ground state have been suggested, too [12, 13]. Thus, it is important to study the 13-atom cluster because it is the first magic number as stated by the geometric shell model, which predicts high symmetric structures. The aim of this paper is to study the geometric ground state structure of Pt@Pd_{12} cluster. We have chosen optimized icosahedral symmetry initial configuration of PtPd_{12} obtained from a genetic algorithm (GA) and then we reoptimize by using the Kohn-Sham DFT method.

This combined approach is reliable and computer resources are used in a more efficient way. Besides, recent theoretical results [14] have shown that energetic distribution of minima may change when quantum chemistry tools are used under this scheme. Therefore, it is convenient to check for the ground state structures obtained using semi-empirical potentials with higher level theoretical tools, where the quantum and correlation effects may entail cluster restructuration through a reordering of atoms which may lead to a different stable structure.

This paper is organized as follows. In Sect. II we briefly describe the computational methodology utilized in this work, Sect. III contains our results and discussion, and in Sect. IV we summarize our main conclusions.

II. COMPUTATIONAL DETAILS

Initial configuration was obtained optimizing the Gupta potential [15], a semi-empirical potential energy function which has proven to describe appropriately the
interatomic bonding in transition and noble metal clusters. This potential function is obtained from a Tight-Binding Second Moment Approximation of the Density of States for the $d$ electrons with parameters fitted from experimental information of the cohesive energy, lattice parameters and independent elastic constants for the reference crystal structure at 0 K [16]. We used the Birmingham Cluster Genetic Algorithm code [17] in the optimization process with several initial random configurations. Typically we performed hundreds of optimizations in order to perform a reliable exploration of the potential energy hypersurface.

The Kohn-Sham DFT calculations were carried out utilizing the software package deMon2k [18]. The deMon2k program solves the Kohn-Sham equations using the linear combination of Gaussian-type orbital approximation. The Coulomb energy was calculated by the variational fitting procedure proposed by Dunlap, Connoly and Sabin [19] employing a GEN-A2 auxiliary function set, which contains $s$, $p$ and $d$ auxiliary functions [20]. The approximated density was used for the calculation of the exchange-correlation potential, too. Thus, all Kohn-Sham calculations were performed in the framework of auxiliary density functional theory [21]. Scalar relativistic effects were incorporated by 18 valence electron quasi-relativistic effective core potentials [22] for Pd and Pt. We used the PBE functional [23] for exchange and correlation, based on previous validation calculations on the Pd and Pt dimers, which showed good agreement with experimental and other theoretical results. The equilibrium geometries were obtained by means of an unconstrained structure optimization using a quasi-Newton restricted step algorithm and the BFGS update scheme for the Hessian matrix. The convergence of the structure optimization was based on the analytic energy gradient and displacement vectors with thresholds of $10^{-4}$ and $10^{-3}$ a.u., respectively. After convergence the vibrational frequencies were calculated in order to ensure that no
imaginary frequency was present, i.e. that a true minimum structure was reached. This procedure was repeated on several potential energy surfaces with different odd-numbered multiplicities.

III. RESULTS AND DISCUSSION

Figure 1 shows the atom distribution in the cluster. The DFT structure refers to the minimum on the nonet potential energy surface which yielded the lowest energy in our local optimizations of the GA start structure. The core/shell structure is apparent for both the GA (S1) and DFT (S2) predicted structures, being the Pt atom at the center and the 12 Pd atoms in the external shell. We observe that the external shell is located around distance values of 2.6 Å for the S2 structure while the S1 structure has the external shell located around 2.5 Å, both with respect to the central Pt atom. The structural analysis indicates that, for the S1 configuration four different interatomic distance values are found, 12 corresponding to Pt-Pd bonds of 2.560 Å while the rest are Pd-Pd radial distances, 30 of 2.692 Å, 30 of 4.356 Å and 6 of 5.120 Å. The S1 structure symmetry is Ih, the icosahedral point group. All searches consistently give the same configuration. In the case of the S2 structure, there is a wider distribution of distances. This is an indication of the structural distortion produced after taking into consideration the inherent electronic effects.

Interatomic interactions are reflected in the structural details of the reoptimized structure, exhibiting quantitative differences with regard to the GA result. A wider distances distribution emerges and the point group symmetry is lowered. Significant differences are noticed in the g(r), the interatomic distances are shorter in the S1 structure and a first-peak splitting is appreciated below 3 Å (Fig. 2). This aspect deserves to be pointed out because the short-range order is disrupted, reflecting the
appearance of structural distortions after using quantum chemistry tools. The resulting structural distortion might be related to a possible Jahn-Teller (JT) effect, which is known to be present in small nanoparticles [24]. The high symmetry of the starting configuration (Ih) might induce orbital degeneracy of the highest occupied electronic states, which is removed via a structural distortion that creates a vibrational degeneracy but at the same time lowers the total energy of the system [25]. In this way, the icosahedral structure might not be stable for the PtPd12 and would have to undergo a JT distortion to a lower symmetry structural ordering.

In order to confirm this result we computed the X-ray scattering (XRS) intensity to obtain more evidence on the structural distortion of the S2 structure. In Fig. 3 we depict the calculated pattern for both S1 and S2 structures. For large k values, the structural distortion is evident. The inset focuses on this region where a clear difference is observed in the XRS intensity, demonstrating the existence of structural differences between the similar S1 and S2 structures through straightforward calculations.

IV. CONCLUSIONS

In the present study a theoretical analysis of the structural properties of Pt@Pd12 cluster has been carried out. Semi-empirical potential functions yield an icosahedral core/shell ordering of atoms (Ih symmetry). A different result is observed when quantum chemistry DFT method is used to reoptimize the cluster structure. Whereas the semi-empirical potential approach generates structures with high symmetry, ab initio reoptimization gives rise to a distorted icosahedral structure. Cluster distortion is attributed to a possible Jahn-Teller effect. Additional studies are in progress in order to check for structural stability of 13-atom clusters in the range of possible compositions of PtxPd13-x clusters, for x = 0, 1, …, 13, using a combined approach based on semi-empiric potential and DFT calculations.
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REFERENCES

http://www.demon-software.com
FIGURE CAPTIONS

Figure 1 (color online). Radial distribution of the atoms (n(r)) for both the GA optimized PtPd_{12} nanoparticle (S1) and the DFT reoptimized structure (S2). Central sphere represent the Pt atom (core) and surface spheres correspond to 12 Pd atoms (shell). For the S1 structure the shortest bond distance is 2.5601 Å (Pt-Pd bond) while the longest one is 5.1203 Å, corresponding to a Pd-Pd bond. S2 structure has a shortest bond distance of 2.6536 Å and the longest one is 5.3229 Å (Pd-Pd bond).

Figure 2. Pair Distribution Function comparison for both the S1 and S2 structures. The S2 structure distortion is clearly observed through the first peak splitting (black lines) between 2.6-2.8 Å. Gray lines correspond to S1 structure Pair Distribution Function.

Figure 3. XRS intensity calculated for S1 (gray line) and S2 (black line) structures. Short-range order distortion is confirmed in the large k values region.
Dessens-Félix  Figure 2