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Structural changes of Pd₁₃ upon charging and oxidation/reduction

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First-principle generalized gradient corrected density functional calculations have been performed to study the stability of cationic and anionic Pd₁₃^{+/-}, and neutral Pd₁₃O₂ clusters. It is found that while cationic Pd₁₃⁺ favors a C_s geometry similar to the neutral Pd₁₃, both anionic Pd₁₃⁻ and neutral Pd₁₃O₂ favor a compact $\sim I_h$ structure. A detailed analysis of the electronic structure shows that the stabilization of the delocalized 1P and 2P cluster orbitals, and the hybridization of the 1D orbitals with the oxygen atomic *p* orbitals play an important role in the energetic ordering of C_s and $\sim I_h$ isomers. A structural oscillation is predicted during an oxidation/reduction cycle of Pd₁₃ in which small energy barriers between 0.3 and 0.4 eV are involved. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3692612>]

I. INTRODUCTION

An interesting area in the field of clusters is the existence of isomers and their effect on the observed behaviors. The reduced size leads to atomic arrangements that are different from the bulk and many times, different atomic arrangements exhibit competing stability.¹⁻⁸ For magnetic clusters, in addition to geometries, the clusters can have states of differing multiplicity that are close in energy.⁹⁻¹² The presence of the isomers can lead to interesting effects particularly when the barriers separating the isomers are small and the isomers have differing properties. In this work, the term isomer will include configurations with energies per atom differing by around one hundredth of an electron volt or less. The observable properties are then determined by the sampling of the various configurations as a function of temperature or other external influence. We investigated these interesting aspects in a recent work for the case of a Pd₁₃ cluster.¹³ Unlike bulk Pd, small Pd_n clusters have finite spin magnetic moments.¹⁴ Theoretical studies indicated that a Pd₁₃ cluster is marked by three isomeric forms,^{11,15,16} namely, a bi-layer C_s ground state structure with buckled surfaces that can be regarded as a relaxed bulk fragment, another bi-layer structure in C_{3v} with flat surfaces that can be obtained by a slight rearrangement of atoms in the C_s structure, and an icosahedral structure around 0.14 eV above the ground state bi-layer structure which was considered the ground state in numerous previous works.¹⁷⁻²⁰ The bi-layer C_s and C_{3v} had lowest energy configurations with magnetic moment of 6.0 μ_B with states of lower multiplicity closer to the ground state. On the other hand, the icosahedral cluster had a magnetic moment of 8.0 μ_B with states of lower multiplicity separated from the ground state by a larger energy difference. The different multiplet structures of the isomers lead to different thermal behaviors. Whereas the magnetic moment of C_s and C_{3v} structures decreased with

increasing temperature, the magnetic moment of the icosahedral structure remained largely unchanged under ordinary temperatures.¹³ We showed that the observed magnetic moment of 5.2 μ_B for the cluster can be accounted for by the C_s and C_{3v} structures if one includes the spin excitations to the multiplets at finite temperatures.

Palladium clusters are important oxidation catalysts and are widely used for CO oxidation, carbon cracking in a wide range of hydrocarbons, and other oxidation reactions.^{21,22} Since the reactions involve addition of reactants, it is important to understand how the various isomers bind with specific reactants? For example, oxidation reactions involve addition of oxygen to the cluster and the reduction of the oxidized species by the reactant. Oxygen generally binds by withdrawing charge and forming local bonds. How do the O atoms bind with various isomers and could O be used to tag one isomer compared to the other? If the barriers separating the isomers are small compared to the binding energies of adatoms, are there catalytic processes that could involve structural/spin fluctuations between the various isomers? Since many ligands bind by withdrawing or donating charge to clusters, how do the relative ordering of the isomers depend on the charged state of the cluster. The later is also important for identification of isomers in carefully planned experiments.

In this work, we offer to answer some of these questions by focusing on Pd₁₃ clusters. We first examine the effect of charge on the relative ordering of isomers by carrying out electronic structure calculations on Pd₁₃⁺, Pd₁₃, and Pd₁₃⁻ clusters. We are particularly interested to examine if the new bi-layer C_s ground state of Pd₁₃ could be seen in negative ion photodetachment experiments.⁵ We next consider the effect of adding an O₂ molecule. Numerous experiments and theoretical studies in our and other groups indicate that the O-O bond is broken upon addition to Pd₁₃.²³⁻²⁶ In fact, it is known that oxygen adsorbs dissociatively to form surface atomic oxygen on most transition metal surfaces. Molecularly absorbed O₂ has been observed at low temperatures ~ 80 K on nickel, palladium, and platinum surfaces, while at or higher than room

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temperature, oxygen is only present as adsorbed atoms.^{27–29} Therefore, we focus on the ground state for OPd_{13}O clusters. Our objective here is twofold. We first examine the oxygen binding to the various isomers to explore if the icosahedral structure could be stabilized by adding O atoms. In previous papers, we had shown that the icosahedral isomer is stabilized by D-like cluster orbitals, while the C_s structure is stabilized by P-like orbitals. How do these differing orbitals hybridize with O states. We then examine the energetics and barriers for an oxidation/reduction reaction where the O atoms are first added and the cluster is then reduced, to look at the progressions in various geometries/spin states. What role do the isomers play in these reactions? As mentioned before, the C_s and C_{3v} isomers involve minor atomic re-arrangement. They are both composed of a base layer of an atom centered hexagon with another upper layer of six Pd atoms forming a triangle with three Pd atoms at each side. The only distinction is that the base hexagon in the C_s structure is rotated by 60° compared to the C_{3v} isomer and, as a consequence, a buckling of the surface atoms is observed. Because of this structural similarity, the two structures can be regarded as belonging to the same family. Consequently, in this work, we primarily focus on two isomers, namely, the C_s and the icosahedral $\sim I_h$ clusters.

II. THEORETICAL METHODS

First-principle electronic structure calculations on cationic and anionic $\text{Pd}_{13}^{+/-}$ and neutral Pd_{13}O_2 clusters were carried out within the framework of generalized gradient density functional theory. A linear combination of atomic orbitals-molecular orbital approach was employed where the cluster wave function is composed of a linear combination of Gaussian type orbitals centered at the atomic positions. The actual computations are based on the deMon2k (Ref. 30) code. The exchange and correlation effects were incorporated through the functional proposed by Perdew *et al.*³¹ A variational fitting of the Coulomb potential was employed in order to avoid the calculation of four-center electron repulsion integrals,³² and the exchange-correlation potential was calculated via a numerical integration from the fitted density³³ to speed up the computations. The palladium atom is described using a 18 electron quasi-relativistic effective core potential and the corresponding valence basis set as proposed by Andrae *et al.*³⁴ and all electrons were treated explicitly using the double- ζ valence plus polarization basis sets (621/41/1*) for oxygen.³⁵ The GEN-A2* auxiliary function set was used for both Pd and O atoms.³⁶ To avoid spin contaminations the restricted open-shell Kohn-Sham methodology is employed. To determine the ground state geometries and lowest energy excited states, several initial configurations were tried. The search included reported Pd_{13} structures previously investigated by numerous authors using a variety of techniques^{11,15,17–21,37–39} as well as other structures available in our group on a variety of clusters. The structures were fully optimized, for various possible spin states, by employing a quasi-Newton method in delocalized internal coordinates⁴⁰ without symmetry constraints. The transition state search was performed using a hierarchical

transition state search algorithm.⁴¹ Resulting stationary points of both minima and transition state search were ascertained via a frequency analysis. The list of keywords used in the deMon2k input files, and the optimized $\text{Pd}_{13}^{+/-}$, Pd_{13}O_2 cluster structures along with their total energies are provided in the supplemental material.⁴² We would like to add that the use of generalized-gradient approximations for the calculation of reaction barriers has been shown to work reasonably well for the oxidative addition of Pd to C–H, C–C, and C–Cl bonds by Diefenbach and Bickelhaupt.⁴³ These studies also showed that relativistic effects are crucial and that the treatment of these effects at the quasi-relativistic level leads to only minor deviations from a more rigorous approach to relativity. These findings support our approach for the studies of Pd_{13}O_2 clusters.

III. RESULTS AND DISCUSSION

We first consider the effect of charging by calculating the ground state of Pd_{13}^+ and Pd_{13}^- clusters. The theoretical studies indicate that the C_s structure is the global minimum for the cationic Pd_{13}^+ cluster with a spin magnetic moment of $5 \mu_B$. A C_{3v} structure with spin moment of $7 \mu_B$ was found 148 meV higher in energy, and the closest $\sim I_h$ structure with a spin moment of $9 \mu_B$ was 326 meV higher in energy. Figure 1 shows the topology of the optimized clusters, and Table I presents the relative energies for the cationic Pd_{13}^+ clusters for various multiplicities. The relative ordering is the same as in neutral species as seen in our previous studies on Pd_{13} and these results are included in Table I for comparison. For Pd_{13}^+ multiplicities above 10 are considerably higher in energy because of the occupation of an excited D-type cluster orbital. This is identical to the situation in the neutral Pd_{13} where the nonet is the highest accessible multiplicity.¹³ The electronic states indicate that in general the cationic species can be obtained by removing an electron from one of the single occupied molecular orbital of the neutral species. To understand the preference of the C_s structure vs the $\sim I_h$, we analyzed the one electron energy levels of both neutral and cationic Pd_{13} clusters shown in Figures 2 and 3. As discussed in our previous work on neutral Pd_{13} ,¹³ the molecular or-

FIG. 1. Topology of optimized $\text{Pd}_{13}^{(+/-)}$ and Pd_{13}O_2 isomers. The two Pd layers that form the C_s and C_{3v} isomers are marked in blue and yellow color. The oxygen atoms are marked in red.

TABLE I. Relative energies for the relevant multiplicities (m) of the C_s and C_{3v} bi-layer clusters, and the distorted icosahedral ($\sim I_h$) neutral and cationic Pd_{13}^+ clusters with respect to the, respectively, neutral 7C_s and cationic 6C_s ground states in meV.

Structure	Neutral Pd_{13}				
	$m = 1$	$m = 3$	$m = 5$	$m = 7$	$m = 9$
C_s	158	128	104	0	213
C_{3v}	153	131	108	99	295
$\sim I_h$	774	630	523	341	134

Structure	Cationic Pd_{13}^+				
	$m = 2$	$m = 4$	$m = 6$	$m = 8$	$m = 10$
C_s	157	106	0	21	391
C_{3v}	184	268	198	148	506
$\sim I_h$	803	688	630	462	326

bitals of both C_s and $\sim I_h$ structures present relatively well defined 1S, 1P, 1D, and 2P delocalized orbitals characteristics of metallic and some bimetallic clusters,^{44–51} in addition to localized d-type atomic orbitals marked by lowercase letters. According to our analysis, the extra stabilization that favors C_s structures for both neutral and cationic Pd_{13} arises from the stabilization of both 1P and 2P orbitals, whereas the $\sim I_h$ configurations have deeper 1D states.

In contrast with the neutral and cationic species, our calculations on the anionic Pd_{13}^- found that the more stable structure is the $\sim I_h$ configuration with a spin moment of $7 \mu_B$,

FIG. 2. One-electron energy levels and electron charge density of the ${}^9\sim I_h$ and 7C_s Pd_{13} neutral clusters. The continuous black and blue lines correspond, respectively, to the doubly and single occupied levels, whereas the dotted lines correspond to the unoccupied levels. The degeneracy of the P and D orbitals is marked. The angular momentum is marked and the delocalized P orbitals are highlighted on yellow. The optimized geometries are also shown where the green oval marks the most stable isomer.

FIG. 3. One-electron energy levels and electron charge density of the ${}^{10}\sim I_h$ and 6C_s cationic Pd_{13}^+ clusters. See caption of Figure 2.

followed by a C_s structure with a spin magnetic moment of $5 \mu_B$ 131 meV higher in energy. Table II presents the relative energies for the anionic Pd_{13}^- isomers for various multiplicities. An analysis of the one electron energy levels and molecular orbitals (Figure 4) shows that the addition of one electron to the neutral species preferentially **stabilizes the 1D** orbitals in the $\sim I_h$ structure (reduced 1S–1D spacing), and this is how this geometry now results as the anionic Pd_{13}^- ground state. Further, we note that the 1D cluster orbitals in the $\sim I_h$ structure show 2/3 degeneracy which also indicates a rather high symmetric configuration. Such a subtle interplay of the electronic structure of the neutral and charged Pd_{13} cluster and the stability of its isomers can be expected to determine the reactivity properties of the cluster.

Recently we have demonstrated the existence of a geometrical transition from compact to a pseudo planar geometry for a supported Pd_4 cluster upon the absorption of an oxygen atom.⁵² To investigate if the oxygen absorption could also stabilize a given geometry of the Pd_{13} cluster we calculate the Pd_{13}O_2 neutral species. Starting from several possible initial

TABLE II. Relative energies for the relevant multiplicities (m) of the C_s and C_{3v} bi-layer clusters, and the distorted icosahedral ($\sim I_h$) anionic Pd_{13}^- clusters with respect to the ${}^8\sim I_h$ ground state in meV.

Structure	$m = 2$	$m = 4$	$m = 6$	$m = 8$	$m = 10$
C_s	155	109	73	91	674
C_{3v}	212	150	127	196	909
$\sim I_h$	448	300	127	0	1175

FIG. 4. One-electron energy levels and electron charge density of the $8\sim I_h$ and $6C_s$ anionic Pd_{13}^- clusters. See caption of Figure 2.

geometries and spin states, an O_2 molecule was approached to a neutral Pd_{13} cluster and the system was fully optimized without constraints. Our results show, that as in the case of the pure Pd_{13} cluster, the Pd_{13}O_2 presents three typical topologies C_s , C_{3v} , and $\sim I_h$ shown in Figure 1. In all attempted calculations the O_2 molecule dissociated and bound atomically to the Pd_{13} cluster, in agreement with the experimental reports discussed in the Introduction.^{27–29} Interestingly, the Pd_{13}O_2 ground state was found to be a $\sim I_h$ geometry with a spin magnetic moment of $2 \mu_B$, followed by a C_s structure 656 meV higher in energy. Relative energies for the three found topologies are given in Table III. In a recent experimental study on the reactivity of O_2 to free palladium clusters Anderson and Rosén²⁶ found that reaction probability of O_2 absorption on Pd_{13} was greater than for neighboring sizes. We then try to understand if this enhanced reactivity can be rooted on the nature of the bonding and the possibility of geometrical changes on Pd_{13} and Pd_{13}O_2 .

To first investigate why a Pd_{13}O_2 is more stable in a $\sim I_h$ geometry vs a C_s geometry in Pd_{13} we analyzed the one electron energy levels and molecular orbitals. Figure 5 shows Pd_{13}

TABLE III. Relative energies for the relevant multiplicities of the C_s and C_{3v} bi-layer clusters, and the distorted icosahedral ($\sim I_h$) neutral Pd_{13}O_2 clusters with respect to the $3\sim I_h$ ground state in meV.

Structure	m = 1	m = 3	m = 5	m = 7	m = 9
C_s	672	599	611	707	985
C_{3v}	699	664	727	948	1243
$\sim I_h$	111	0	80	258	606

FIG. 5. One-electron energy levels and electron charge density of the $\text{Pd}_{13}(^9\sim I_h)$, ^3O , and $\text{Pd}_{13}\text{O}_2(^3\sim I_h)$ neutral species. See caption of Figure 2. The oxygen atoms are marked in red.

($\sim I_h$), O atom and $\text{Pd}_{13}\text{O}_2(^3\sim I_h)$ energy levels. As can be seen in Fig. 5, the 4 p electrons of O lie just above the 1D orbitals of $\text{Pd}_{13}(\sim I_h)$ and readily interact with them forming six bonding states that lie from -8.5 to -10.5 eV and which are mixed with the 1D orbitals in the $\text{Pd}_{13}\text{O}_2(^3\sim I_h)$ cluster. In addition, the 1P and 2P states are stabilized and move to lower energy positions.

Figure 6 shows the respective energy levels for the $\text{Pd}_{13}(C_s)$, O atom, and $\text{Pd}_{13}\text{O}_2(C_s)$ species. In this case the oxygen p electrons lie around the same energy of the 1P and 1D lev-

FIG. 6. One-electron energy levels and electron charge density of the $\text{Pd}_{13}(^7C_s)$, ^3O , and $\text{Pd}_{13}\text{O}_2(^3C_s)$ neutral species. See caption of Figure 2. The oxygen atoms are marked in red.

FIG. 7. Structural oscillations in Pd_{13} during an oxidation/reduction process.

els and form bonding states with a less strong interaction and hybridization. In the $\text{Pd}_{13}\text{O}_2(C_s)$ cluster the oxygen bonding states all group together around from -9.5 to -10.8 eV, and do not mix with the 1P and 1D states whose position, as well as that of the 2P orbitals are not significantly modified from the $\text{Pd}_{13}(\sim C_s)$ cluster. In this way, the fact that the oxygen p orbitals preferentially hybridize with the 1D states of the $\text{Pd}_{13}(\sim I_h)$, and that for this isomer the interaction is stronger determines the stability of the resulting oxidized species.

The observation that the ground state of the bare Pd_{13} has a C_s geometry while the Pd_{13}O_2 has an icosahedral ($\sim I_h$) Pd_{13} core does raise an interesting structural progression during an oxidation/reduction reaction. Such a process is described in Fig. 7. Consider starting with a isolated Pd_{13} and adding an O_2 molecule. The binding energy of the O_2 molecule is 2.91 eV while our studies indicate the barrier for transitioning to the icosahedral Pd_{13}O_2 ground state is 0.37 eV. Further, oxygen reduction by CO oxidation will produce Pd_{13} in a $\sim I_h$ geometry which will then rearrange to the more stable C_s geometry after overcoming an energy barrier of 0.37 eV. The removal of oxygen from magnesia supported Pd_{13}O_x clusters by CO oxidation has recently been experimentally investigated by Habibpour *et al.*⁵³ Their results show that for temperatures as low as 200 K, formation of CO_2 results from a reaction of carbon monoxide with a highly activated, molecularly bound oxygen species.⁵³ The structural changes of Pd_{13} upon oxidation/reduction is depicted in Figure 7 and can be divided into the following steps:

	ΔE (eV)
$\text{Pd}_{13}({}^7C_s) + {}^3\text{O}_2 \rightarrow \text{Pd}_{13}\text{O}_2({}^3C_s)$	-2.91
$\text{Pd}_{13}\text{O}_2({}^3C_s) \rightarrow \text{Pd}_{13}\text{O}_2({}^3\sim I_h)$ [TS]	0.37
$\text{Pd}_{13}\text{O}_2({}^3C_s) \rightarrow \text{Pd}_{13}\text{O}_2({}^3\sim I_h)$	-0.60
$\text{Pd}_{13}\text{O}_2({}^3\sim I_h) \rightarrow \text{Pd}_{13}({}^9\sim I_h) + {}^3\text{O}_2$	3.66
$\text{Pd}_{13}({}^9\sim I_h) \rightarrow \text{Pd}_{13}({}^9C_s)$ [TS]	0.37
$\text{Pd}_{13}({}^9\sim I_h) \rightarrow \text{Pd}_{13}({}^7C_s)$	-0.15

IV. CONCLUSIONS

In summary, we have investigated the stability of cationic and anionic $\text{Pd}_{13}^{+/-}$ and neutral Pd_{13}O_2 clusters and shown how the location of the delocalized 1P, 1D, and 2P molecular orbitals, and the degree of hybridization between the atomic oxygen p orbitals and the molecular 1D orbitals determines the order of stability of the possible isomers. A structural change is predicted for the oxidation/reduction of Pd_{13} which involves energy barriers between 0.3 eV and 0.4 eV. This small energy barriers and the possibility of geometrical rearrangements seems to be the reason for the enhanced reactivity of Pd_{13} towards O_2 . We are in the process of exploring a variety of atoms that can interact with the molecular 1D orbitals to correlate with the observed catalytic behavior.

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