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Structural changes of Pd\textsubscript{13} 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 Pd\textsubscript{13}\textsuperscript{\textpm}, and neutral Pd\textsubscript{13}O\textsubscript{2} clusters. It is found that while cationic Pd\textsubscript{13}\textsuperscript{\textpm} favors a \(C_4\) geometry similar to the neutral Pd\textsubscript{13}, both anionic Pd\textsubscript{13}\textsuperscript{\textpm} and neutral Pd\textsubscript{13}O\textsubscript{2} favor a compact \(\sim I_h\) structure. A detailed analysis of the electronic structure shows that the stabilization of the delocalized IP 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 \(C_4\) and \(\sim I_h\) isomers. A structural oscillation is predicted during an oxidation/reduction cycle of Pd\textsubscript{13} in which small energy barriers between 0.3 and 0.4 eV are involved. © 2012 American Institute of Physics.

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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.\textsuperscript{1–8} For magnetic clusters, in addition to geometries, the clusters can have states of differing multiplicity that are close in energy.\textsuperscript{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 Pd\textsubscript{13} cluster.\textsuperscript{13} Unlike bulk Pd, small Pd\(_n\) clusters have finite spin magnetic moments.\textsuperscript{14} Theoretical studies indicated that a Pd\textsubscript{13} cluster is marked by three isomeric forms,\textsuperscript{11,15,16} namely, a bi-layer \(C_4\) 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 \(C_4\) 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.\textsuperscript{17–20} The bi-layer \(C_4\) and \(C_{3v}\) had lowest energy configurations with magnetic moment of 6.0 \(\mu_B\) with states of lower multiplicity closer to the ground state. On the other hand, the icosahedral cluster had a magnetic moment of 8.0 \(\mu_B\) 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 \(C_4\) and \(C_{3v}\) structures decreased with increasing temperature, the magnetic moment of the icosahedral structure remained largely unchanged under ordinary temperatures.\textsuperscript{13} We showed that the observed magnetic moment of 5.2 \(\mu_B\) for the cluster can be accounted for by the \(C_4\) 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.\textsuperscript{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 Pd\textsubscript{13} clusters. We first examine the effect of charge on the relative ordering of isomers by carrying out electronic structure calculations on Pd\textsubscript{13}\textsuperscript{\textpm}, Pd\textsubscript{13}, and Pd\textsubscript{13}O\textsubscript{2} clusters. We are particularly interested to examine if the new bi-layer \(C_4\) ground state of Pd\textsubscript{13} could be seen in negative ion photodetachment experiments.\textsuperscript{3} We next consider the effect of adding an O\textsubscript{2} molecule. Numerous experiments and theoretical studies in our and other groups indicate that the O-O bond is broken upon addition to Pd\textsubscript{13}.\textsuperscript{23–26} In fact, it is known that oxygen adsorbs dissociatively to form surface atomic oxygen on most transition metal surfaces. Molecules adsorbed O\textsubscript{2} has been observed at low temperatures \(\sim 80\) 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. Therefore, we focus on the ground state for OPd13O 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 Cs 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 Cs and C3v 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 Cs structure is rotated by 60° compared to the C3v 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 Cs and the icosahedral ~Ih clusters.

II. THEORETICAL METHODS

First-principle electronic structure calculations on cationic and anionic Pd13+/− and neutral Pd13O2 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. A variational fitting of the Coulomb potential was employed in order to avoid the calculation of four-center electron repulsion integrals, and the exchange-correlation potential was calculated via a numerical integration from the fitted density 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. and all electrons were treated explicitly using the double-ζ valence plus polarization basis sets (621/41/1*) for oxygen. The GEN-A2* auxiliary function set was used for both Pd and O atoms. 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 Pd13 structures previously investigated by numerous authors using a variety of techniques 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 coordinates without symmetry constraints. The transition state search was performed using a hierarchical transition state search algorithm. 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 Pd13+/−, Pd13O2 cluster structures along with their total energies are provided in the supplemental material. 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. 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 Pd13O2 clusters.

III. RESULTS AND DISCUSSION

We first consider the effect of charging by calculating the ground state of Pd13+ and Pd13− clusters. The theoretical studies indicate that the Cs structure is the global minimum for the cationic Pd13+ cluster with a spin magnetic moment of 5 μB. A C3v structure with spin moment of 7 μB was found 148 meV higher in energy, and the closest ~Ih structure with a spin moment of 9 μB 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 Pd13+ clusters for various multiplicities. The relative ordering is the same as in neutral species as seen in our previous studies on Pd13 and these results are included in Table I for comparison. For Pd13+ 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 Pd13 where the nonet is the highest accessible multiplicity. 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 Cs structure vs the ~Ih, we analyzed the one electron energy levels of both neutral and cationic Pd13 clusters shown in Figures 2 and 3. As discussed in our previous work on neutral Pd13, the molecular or-

![FIG. 1. Topology of optimized Pd13 (−/+) and Pd13O2 isomers. The two Pd layers that form the Cs and C3v isomers are marked in blue and yellow color. The oxygen atoms are marked in red.](http://scitation.aip.org/termsconditions).
TABLE I. Relative energies for the relevant multiplicities (m) of the C\(_s\) and C\(_{3v}\) bi-layer clusters, and the distorted icosahedral (~I\(_h\)) neutral and cationic Pd\(_{13}\)\(^+\) clusters with respect to the, respectively, neutral 7 C\(_s\) and cationic 6 C\(_s\) ground states in meV.

<table>
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<tr>
<th>Structure</th>
<th>m = 1</th>
<th>m = 3</th>
<th>m = 5</th>
<th>m = 7</th>
<th>m = 9</th>
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<tr>
<td>C(_s)</td>
<td>158</td>
<td>128</td>
<td>104</td>
<td>0</td>
<td>213</td>
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<tr>
<td>C(_{3v})</td>
<td>153</td>
<td>131</td>
<td>108</td>
<td>99</td>
<td>295</td>
</tr>
<tr>
<td>~I(_h)</td>
<td>774</td>
<td>630</td>
<td>523</td>
<td>341</td>
<td>134</td>
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<table>
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<th>m = 6</th>
<th>m = 8</th>
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<td>C(_s)</td>
<td>157</td>
<td>106</td>
<td>0</td>
<td>21</td>
<td>391</td>
</tr>
<tr>
<td>C(_{3v})</td>
<td>184</td>
<td>268</td>
<td>198</td>
<td>148</td>
<td>506</td>
</tr>
<tr>
<td>~I(_h)</td>
<td>803</td>
<td>688</td>
<td>630</td>
<td>462</td>
<td>326</td>
</tr>
</tbody>
</table>

bitals of both C\(_s\) and ~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 ~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 ~I\(_h\) configuration with a spin moment of 7 \(\mu_B\), 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 ~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 ~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

FIG. 2. One-electron energy levels and electron charge density of the \(^9\sim I_h\) and \(^7\,C_s\) 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 \(^6\,C_s\) cationic Pd\(_{13}\)\(^+\) clusters. See caption of Figure 2.

TABLE II. Relative energies for the relevant multiplicities (m) of the C\(_s\) and C\(_{3v}\) bi-layer clusters, and the distorted icosahedral (~I\(_h\)) anionic Pd\(_{13}\)\(^-\) clusters with respect to the \(^9\sim I_h\) anionic Pd\(_{13}\)\(^-\) ground state in meV.

<table>
<thead>
<tr>
<th>Structure</th>
<th>m = 2</th>
<th>m = 4</th>
<th>m = 6</th>
<th>m = 8</th>
<th>m = 10</th>
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<tbody>
<tr>
<td>C(_s)</td>
<td>155</td>
<td>109</td>
<td>73</td>
<td>91</td>
<td>674</td>
</tr>
<tr>
<td>C(_{3v})</td>
<td>212</td>
<td>150</td>
<td>127</td>
<td>196</td>
<td>909</td>
</tr>
<tr>
<td>~I(_h)</td>
<td>448</td>
<td>300</td>
<td>127</td>
<td>0</td>
<td>1175</td>
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</table>
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.\textsuperscript{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 Rosén\textsuperscript{26} found that reaction probability of O$_2$ absorption on 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 Pd$_{13}$O$_2$($\sim$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 Pd$_{13}$ ($C_s$), O atom, and Pd$_{13}$O$_2$($C_s$) species. In this case the oxygen $p$ electrons lie around the same energy of the 1P and 1D lev-
els and form bonding states with a less strong interaction and hybridization. In the Pd13O2 (CIFS) 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 Pd13 (~CIFS) cluster. In this way, the fact that the oxygen p orbitals preferentially hybridize with the 1D states of the Pd13 (~CIFS), 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 Pd13 has a CIFS geometry while the Pd13O2 has an icosahedral (~CIFS) Pd13 core does raise an interesting structural progression during an oxidation/reduction reaction. Such a process is described in Fig. 7. Consider starting with an isolated Pd13 and adding an O2 molecule. The binding energy of the O2 molecule is 2.91 eV while our studies indicate the barrier for transitioning to the icosahedral (~CIFS) geometry which will then rearrange to the more stable CIFS geometry after overcoming an energy barrier of 0.37 eV. The removal of oxygen from magnesia supported Pd13O2 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 CO2 results from a reaction of carbon monoxide with a highly activated, molecularly bound oxygen species.53 The structural changes of Pd13 upon oxidation/reduction is depicted in Figure 7 and can be divided into the following steps:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd13 (CIFS) + O2 → Pd13O2 (CIFS)</td>
<td>−2.91</td>
</tr>
<tr>
<td>Pd13O2 (CIFS) → Pd13O2 (~Ih) [TS]</td>
<td>0.37</td>
</tr>
<tr>
<td>Pd13O2 (CIFS) → Pd13O2 (~Ih)</td>
<td>−0.60</td>
</tr>
<tr>
<td>Pd13O2 (~Ih) → Pd13 (~CIFS) + O2</td>
<td>3.66</td>
</tr>
<tr>
<td>Pd13 (~Ih) → Pd13 (CIFS) [TS]</td>
<td>0.37</td>
</tr>
<tr>
<td>Pd13 (~Ih) → Pd13 (~CIFS)</td>
<td>−0.15</td>
</tr>
</tbody>
</table>

IV. CONCLUSIONS

In summary, we have investigated the stability of cationic and anionic Pd13+/− and neutral Pd13O2 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 Pd13 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 Pd13 towards O2. 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.

ACKNOWLEDGMENTS

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30. A. M. Köster et al. deMon2k, V. 3.0; The International deMon Developers Community: Cinvestav, México, 2006; see http://www.deMon-software.com.
42. See supplementary material at http://dx.doi.org/10.1063/1.3692612 for the total energies [a.u.] and Cartesian coordinates [Å] of the optimized Pd13+, Pd13−, and Pd13O2 isomers; the (approximated) symmetry point group and molecular spin multiplicity are also given. A list of the keywords used in the deMon2k input files is provided.