Structure and Magnetism of Neutral and Anionic Palladium Clusters

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The properties of neutral and anionic Pd\(_N\) clusters were investigated with spin-density-functional calculations. The ground state structures are three-dimensional for \(N>3\) and they are magnetic with a spin-triplet for \(2\leq N\leq 7\) and a spin nonet for \(N=13\) neutral clusters. Structural- and spin-isomers were determined and an anomalous increase of the magnetic moment with temperature is predicted for a Pd\(_7\) ensemble. Vertical electron detachment and ionization energies were calculated and the former agree well with measured values for Pd\(_N\).

Enhancement of magnetism in finite clusters made of elements that are ferromagnetic as bulk solids has been demonstrated through Stern-Gerlach (SG) deflection measurements \([1]\), and it is understood to derive from reduced atomic coordination resulting in stronger electron localization. However, the emergence of magnetism in small clusters of close-shell non-magnetic atoms is clouded by uncertainty. Palladium aggregates (with a [Kr] 4d\(^{10}\) structure of the atom) are particularly interesting since the bulk metal is known to be "almost" magnetic, with the emergence of magnetism predicted to require a mere 6 % dilation of the interatomic distance \([2]\). Experimental information is limited to SG measurements on Pd\(_N\) clusters with \(N>12\) (where the clusters were found to be non-magnetic \([3]\) or to inferences from (non-magnetic) photoemission studies \([4]\). Additionally, systematic theoretical investigations of magnetic properties are lacking, limited only to neutral Pd\(_{13}\) \([3,4]\).

We report on an extensive density-functional-theory (DFT) study pertaining to size-dependent evolutionary patterns of the properties of Pd\(_N\) and Pd\(_N^-\) clusters with \(N=1–7\) and \(N=13\). The ground states (GSs) of the neutral and anionic clusters are found to undergo an early transition (i.e. for \(N>3\)) to three-dimensional (3D) ones and possess a non-zero magnetic moment (e.g., for neutral clusters with \(N\leq 7\) a spin triplet, \(S=1\), and a spin nonet, \(S=4\), for \(N=13\)). In addition to higher-energy structural isomers (STIs) we determined sequences of close-lying spin isomers (SPIs). For a Pd\(_7\) ensemble, we predict an increase of the magnetic moment with temperature due to the thermal accessibility of such isomers. All the SPIs exhibit high local magnetic moments (LMMs), including the singlet states with an antiferromagnetic LMM coupling. Our structural determinations are corroborated by the remarkable agreement between the calculated vertical electron detachment energies (vDEs) from the cluster anions and photoelectron spectroscopy (PES) measurements \([5,6]\).

In this study the Kohn-Sham (KS) equations with generalized gradient corrections (GGA) \([7]\) were solved using the Born-Oppenheimer local-spin-density molecular dynamics (BO-LSD-MD) method \([10]\, with scalar-relativistic \([11]\) non-local pseudopotentials \([12]\). Cluster geometries were determined via symmetry-unrestricted structural optimizations through a rather exhaustive search starting from various structures including those suggested in previous studies of certain Pd clusters \([13,14]\) and other metal clusters \([16,17]\). For each structure spin-restricted optimizations were performed covering all energetically important spin multiplicities.

The GS geometries and STIs for both Pd\(_N\) and Pd\(_N^-\) are rather similar and they follow the same structural evolution, exhibiting Jahn-Teller distortions from the ideal symmetric structures (see Fig. 1), with a transition to 3D configurations at \(N>3\) \([18]\). The GSs (i.e. maximal binding energy \(E_B\)) of Pd\(_N\) with \(N\leq 7\) have a triplet spin multiplicity (see open squares in Fig. 1(A–F)), while for Pd\(_{13}\) the GS is associated with a nonet \((S=4)\) spin configuration (see Fig. 1G). On the other hand, the GS spin-multiplicities of the Pd\(_N^-\) anions (filled symbols in Fig. 1) vary non-monotonically with \(N\) (doublet for \(N=2,3,4\), and 6; quartet for \(N=5\); sextet for \(N=7\), and octet for \(N=13\)). We note here that the higher-lying STIs \([13]\) and SPIs of the neutral and anionic clusters become thermally accessible with increasing cluster size (see temperature scales \([19]\) on the right-hand-side in Fig. 1).

The binding energies of the GS clusters increase rather monotonically with \(N\) (Fig. 2a), showing enhanced local stabilities for Pd\(_7^-\) and Pd\(_{10}\) \([20]\). The average nearest-neighbor bond-length \((\langle R_{nn} \rangle)\) of the GS structures and the SPIs are very similar \([22]\) converging rapidly to the bulk value \((2.75\text{ Å} \,[23])\).

The calculated vDEs from the cluster anions are in a remarkable agreement with values determined from PES measurements \([4,7,8]\) (Fig. 2b). For all the clusters, we display the vDEs only for the GS (structural and spin) configurations of the anions, except for Pd\(_7^-\) where we show the vDEs for both the GS \((S=5/2)\) and its next (higher-in-energy) SPI \((S=3/2)\) (the difference in en-
energy between the two isomers is 0.11 eV, corresponding to only 170 K in vibrational temperature \((24)\), with the latter exhibiting a better agreement with the experimental data. These results suggest that for \(\text{Pd}^-\) the measured VDE may correspond to this higher-energy SPI which is accessible already at very low temperatures, while for the other clusters studied here the VDEs are determined by the GS structures over a broad temperature range.

The only (slight) discrepancy between the calculated and measured VDEs is for \(\text{Pd}_5\) (see Fig. 2b). However, we observe from this figure that the predicted VDE (2.0 eV) for \(\text{Pd}_5\) is rather close to the dissociation energy \((E_D)\) of the process \(\text{Pd}_3^-\rightarrow\text{Pd}^+_2+\text{Pd}\) (see filled circle in Fig. 2b at \(E_D=2.41\) eV, compared to a measured value of 2.26 eV \((24)\)). This implies that this dissociation channel may compete with the electron detachment under appropriate experimental conditions. Consequently, we assign the VDE of \(\text{Pd}_5\) to the next higher feature in the measured PES \((8)\) occurring at 1.88 eV which agrees with the predicted value, and the lower measured value (at 1.66 eV, marked by a cross in Fig. 2b) is attributed to the VDE of a (hot) \(\text{Pd}_3^-\) dissociation product \((23)\) (the same conclusions apply to the photoelectron spectrum of \(\text{Pd}_3^-\) shown in Fig. 2 of ref. \((3)\)) for a similar interpretation of the measured PES of \(\text{Au}_3\) see Refs. 16 and 26.

The vertical ionization potentials predicted by us (vIP in Fig. 2c) start at the atomic value of 8.28 eV compared to the measured first IP of \(\text{Pd}, 8.33 \text{ eV} \((23)\); the calculated second IP of \(\text{Pd} \) (27.34 eV) also agrees with the experimental one (27.75 eV) \((23)\). The predicted values for \(N=2\) and 3 are close to each other followed by a marked drop for clusters with \(N>3\), which is likely to reflect the transition to 3D structures. Convergence to the bulk limit (the work function of \(\text{Pd} \) is 4.97 eV \((27)\)) is slow. No measured IP values have been reported.

The multitude of spin-multiplicities for the \(\text{Pd}_7^-\) clusters results in a considerable variation of the magnetic moment per atom \(\mu=2S\mu_B/N\) (solid squares in Fig. 2d) with particularly high values of \(\mu=0.6, 0.71\) and 0.54 \(\mu_B\) for \(N=5, 7\) and 13, respectively. On the other hand, the occurrence of a triplet GS for the neutral clusters underlies a monotonic \(1/N\) decrease of \(\mu\) for \(N=1–7\) (open squares in Fig. 2d), with an unexpected high value of 0.62 \(\mu_B\) for \(\text{Pd}_{13}^-\) which is higher than the experimental \((6)\) estimate \((\mu<0.4\ \mu_B)\).

The rather surprising existence of energetically favorable high-spin isomers for \(\text{Pd}\) clusters originates from \(sd\)-hybridization developing upon bonding, with the \(d\)-orbitals’ weight diminished somewhat on each atom, resulting in a situation reminiscent of open-shell transition metals. The total magnetic moment of the cluster is comprised of sizable atomic LMMs \((\mu=\pm(0.3–0.6)\mu_B)\) that couple antiferromagnetically in the spin-compensated singlet states, and align themselves in SPIs with high total \(\mu\). This is illustrated for the icosahedral \(\text{Pd}_{13}\) cluster in Fig. 2 where the (gapless) density of states (DOS) of the \(S=0\) singlet SPI is shown in Fig. 2e and the corresponding spin-polarization density in Fig. 2g (left); note the non-uniform spatial distribution of the spin-polarization reflected in the different line-shapes of the DOS of the up and down spins. In the \(S=2\) spin-quintet SPI the minority spin polarization is localized on three sites located in a triangle (Fig. 2g, middle). In the \(S=4\) spin-nonet GS cluster all the sites are spin-polarized in the same direction (Fig. 2g, right), and its stability is reflected in the large gap in the majority-spin DOS near the Fermi energy (see spin \(\uparrow\) in Fig. 2f).

Intriguing conclusions can be made regarding the thermal behavior of certain \(\text{Pd}\) clusters in SG measurements; here we consider the case of \(\text{Pd}_7^-\) and \(\text{Pd}_{13}^-\) at room temperature. Neglecting the vibrational and entropic differences between the isomers, the probability to find a cluster with spin \(S\), irrespective of its atomic isomeric structure, is given by \(P_{N,T}(S)=\sum_I\exp(-\frac{NE_B(N,I,S)}{k_BT})/Z_{N,T}\) with the Boltzmann constant \(k_B\), the ensemble temperature \(T\), the structural isomer index \(I\), and the (normalizing) partition function \(Z_{N,T}\). Several spin isomers of the neutral as well as the anionic heptamer have a finite \(P_{N,T}(S)\) (Fig. 3a) even for low temperatures, leading us to predict that in a SG experiment up to 3 different reflection angles should be measurable. Note, that while an increase in temperature depopulates the \(\text{Pd}_7^-\) pentagonal bipyramid triplet \((S=1)\) GS, the singlet \((S=0)\) state of that structure and the capped octahedron quintet \((S=2)\) state (Fig. 1F) gain statistical weight. Consequently, we predict that for \(\text{Pd}_7^-\) a rise in temperature would lead first to a decrease of the thermally averaged magnetic moment per atom \(\langle \mu \rangle_{N,T}=\sum_S 2S\mu_BP_{N,T}(S)/N\) due to a sharp increase in the population of the singlet state. The subsequent increase of \(\langle \mu \rangle_{N,T}\) (see Fig. 3b, \(T>200\ \text{K}\) results from the higher thermal population of the quintet state relative to the GS triplet (Fig. 3a). \((23)\) Such anomaly does not occur in the case of the \(\text{Pd}_{13}^-\) cluster where the doublet \((S=1/2)\) and quartet \((S=3/2)\) states start to coexist with the sextet \((S=5/2)\) GS at elevated temperatures (Fig. 3a). For both neutral and anionic \(\text{Pd}_{13}\), the higher-lying isomers play essentially no role for \(T<800\ \text{K}\) resulting in a weak temperature dependence of \(\langle \mu \rangle_{N,T}\) (Fig. 3b).

In summary, we found that unlike atomic and bulk \(\text{Pd}\), both neutral and anionic \(\text{Pd}_N\) clusters \((2\leq N \leq 7\) and \(N=13\)) are magnetic, with relatively high LMMs. Underlying this behavior is the hybridization of atomic \(s\) and \(d\) states when clusters are formed, that depletes local \(d\)-contribution around each atom and leads to an open-shell-like behavior. The abundance of close-lying SPIs for certain clusters should be detectable in thermally controlled SG experiments, and we predict an ensemble of \(\text{Pd}_7^-\) clusters to exhibit an (anomalous) increase of the magnetic moment with temperature.
remarkable agreement between the calculated and measured vDEs of the cluster anions corroborates the predicted atomic structures. Our results provide the first quantitative predictions pertaining to the emergence of pronounced magnetic properties of Pd$_N$ and Pd$_N^{-}$ clusters, unlike the weak magnetic tendencies inferred indirectly from PES data [7]; note in particular the contrast between our results for Pd$_7$ (see Fig. 2d and Fig. 3) and the suggestion of a zero spin GS for Pd$_7$ given in Ref. [3]. Furthermore, our study motivates temperature-dependent magnetic deflection (SG) measurements and further investigations of free and supported Pd clusters, including correlations between their magnetic properties and their catalytic activity [30].

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18. The symmetries of the ideal structures are: Pd$_3$: D$_{3h}$ equilateral triangle, Pd$_4$: T$_d$ tetrahedron, Pd$_5$: D$_{5h}$ trigonal bipyramid, Pd$_6$: O$_h$ octahedron, Pd$_7$: D$_{7h}$ pentagonal bipyramid and Pd$_{13}$: I$_h$ icosahedron. Atomic coordinates of the neutral and anionic clusters are available upon request.
19. The symmetries of the higher-energy STIs are: Pd$_3$: D$_{inh}$ linear chain and Jahn-Teller deformed structures for Pd$_4$: D$_{4h}$ square and D$_{2h}$ rhombus, Pd$_5$: C$_{4v}$ tetragonal pyramid, Pd$_6$: C$_{2v}$ capped trigonal bipyramid, Pd$_7$: C$_{3v}$ capped octahedron, C$_{3h}$ tricapped tetrahedron, Pd$_{13}$: O$_h$ cuboctahedron.
20. A measure of the accessibility of an isomer is the temperature $T$ corresponding to the difference between the binding energies of the GS and the isomer, i.e. $T = 2(NE_{GS} - NE_{B,GS})/(3N - 6)k_B$ with the number of cluster atoms $N$ and the Boltzman constant $k_B$.
21. For both the neutral (0.69 eV/atom) and anionic (1.29 eV/atom) dimer the calculated binding energies overestimate somewhat the experimental values of 0.52±0.08 and 1.08±0.09 eV/atom (see ref [7]), respectively.
22. $\langle R_{ne} \rangle$ values range from 2.53 Å (2.49 Å) for Pd$_2$ (Pd$_2^-$) to 2.77 Å (2.78 Å) for Pd$_{13}$ (Pd$_{13}^-$). The reduced bond length of spin-doublet GS of Pd$_2$ is in agreement with an experimental analysis where a similar reduction in bond length (0.037 Å) has been reported [8]. Inspection of the KS molecular orbitals (MO) of Pd$_2$ reveals that the highest occupied MO and the lowest unoccupied one are both sd hybridized bonding states of the same spatial symmetry but with different spins, and consequently formation of the dimer anion (involving occupation of the lowest unoccupied MO) strengthens the bond and results in shrinkage of the bond length.
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FIG. 1. Binding energies $E_B$ (in eV) of structural (a,b,c) and spin ($S=0, 1/2, 1, 3/2$ etc.) isomers of Pd$_N^-$ and Pd$_N$ for $N=1−7$ (A-F) and 13 (G). Filled and open symbols represent anions and neutrals, respectively with squares for the ground state structure (a), circles for structure (b) and triangles for (c). The anionic $E_B$ is defined as the energy per atom to separate Pd$_N^-$ into $N$ neutral atoms and an electron. The $E_B$ values on the left hand side of the panels are mapped on separate temperature scales (20) ($T$, in K) for the anions (top values on the right hand axis of each panel) and the neutrals (bottom values), giving an estimate of the thermal accessibility of the isomers. Note the large number of isomers for Pd$_7^-$ and Pd$_7$ for $T<400$ K. Some of the structural isomers were not stable for certain spin values (such cases are denoted by dashed lines). The Pd$_4^-$ square (b) in panel C transformed into a rhombus (c) for $S=3/2$ and the Pd$_4$ rhombus transformed into a square for $S=0$ and 1. The Pd$_6$ capped trigonal bipyramid (b) transformed to the octahedron (a) for $S=0$. The Pd$_7$ capped octahedron (b) became a pentagonal bipyramid (a) for $S=3$ and the Pd$_{13}$ and Pd$_{13}^-$ cuboctahedron (b) transformed to the icosahedron (a) for $S=4.5$ and 5, respectively.

FIG. 2. Size evolution (panels a-d) of energetic and magnetic quantities in Pd clusters. (a): binding energy per atom, $E_B$ (in eV), (b): theoretical (filled squares) and experimental (open circles) vertical electron detachment energy (vDE) and the calculated atom dissociation energy $E_D$ of the anions (filled circles). Experimental values are take from ref. [7,8] for $N=1−3$ (the corresponding results shown for Pd$_3^-$ in Fig. 2 of ref. [1] are essentially the same) and from [4] for $N=4-7$ and 13. The cross and the open circle at $N=3$ correspond to the maximum of peak A and the peak of group B-H in Fig. 1 of ref. [8], respectively (and correspondingly for the first and second peaks in Fig. 2 of ref. [4]). For Pd$_7^-$, we show the vDE of the GS ($S=5/2$) and a thermally accessible SPI ($S=3/2$). The vDE of Pd$_1^-$ was estimated according to Janak’s theorem by the HOMO energy of Pd$_1^−/2$; (c): calculated vertical ionization potentials; (d): the magnetic moment per atom of the GS anions (filled squares) and of the GS neutrals (open squares). (e,f): Density of states (DOS, in 1/eV) of singlet (e) and nonet (f) icosahedral Pd$_{13}$ cluster. (g): Constant-value images of spin-polarization density in singlet, quintet, and nonet icosahedral Pd$_{13}$ cluster. The purple and yellow denote excess of minority and majority spin, respectively. Note the transition from antiferromagnetic to ferromagnetic ordering when going from the singlet to the nonet.

FIG. 3. (a): population probabilities of the different SPIs (irrespective the structure) of neutral (dashed curves) and anionic (solid curves) heptamers; (b): thermally averaged magnetic moment per atom for Pd$_7$, Pd$_7^-$, Pd$_{13}$ and Pd$_{13}^-$. 
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