Structural and electronic properties of small titanium clusters: A density functional theory and anion photoelectron spectroscopy study

Miguel Castro[a)]
Departamento de Física y Pumice Erica, Faulted de Pumice Universidad Nacional Autonoma de México, Del. Coyoacán Cd. Universitaria, C. P. 04510, México D. F., México

Shu-Rong Liu, Hua-Jin Zhai, and Lai-Sheng Wang[b)]
*Department of Physics, Washington State University, Richland, Washington 99352
and W. R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory,
MS K8-88, Richland, Washington 99352*

Density functional theory calculations using the generalized-gradient approximation have been carried out on the structural and electronic properties of Ti_n^- and Ti_n clusters for $n=3-8$ and 13. Many low-lying states, of different spins and geometries, were found for each Ti_n^- and Ti_n species. We observed that the calculated density of states (DOS) and the adiabatic electron binding energies for the ground state of a given anion are in good agreement with experimental photoelectron spectroscopy (PES) data, lending credence to the assignments of the ground state structures. Comparison between the calculated DOS and the PES data for other low-lying states made it possible to affirm contributions of these states to the spectra, allowing the characterization of the ensemble or composition of a given Ti_n^- system. We found that all the clusters possess highly compact structures, and Ti_7 and Ti_{13} have distorted pentagonal bipyramidal and icosahedral structures, respectively. From the ground state spin states, insight into the magnetic properties of the clusters and their evolution with size was also obtained. Small Ti clusters with $n<5$ are highly magnetic, but the magnetic moment drops rapidly with size. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Transition metal (TM) clusters possess complicated electronic structures caused by their $4s3d$ open shells. Determination and understanding of their geometric and electronic properties pose tremendous challenges both experimentally and computationally.[1] Joint studies between photoelectron spectroscopy (PES) and theoretical calculations have been shown to be valuable to obtain structural information about small clusters,[2-7] in particular for Si and Al clusters, which contain only s and p valence electrons.[4-7] There have been relatively fewer such studies on TM clusters. A joint PES and theoretical study on small niobium anion clusters has been reported.[3] Of the first transition series, neutral and anionic Cu_n^- $(n=3-9)$ clusters have been investigated.[2] But due to the associated close $3d$ shell these clusters are less complex than those containing open $3d$ shells, among which several small Ni clusters have recently been reported in conjunction with PES data.[8-10]

PES of size-selected anions represents a powerful experimental technique in probing the electronic structure of TM clusters, because it provides directly the valence electronic density of states of the underlying clusters. Recent advances in our laboratory to improve the energy resolution of the PES technique and in our ability to control the cluster temperatures[6,11] have allowed us to obtain well-resolved electronic features of size-selected clusters from a few atoms up to more than one hundred atoms.[12,13] This advancement plus PES spectra measured at high photon energies allows more meaningful comparisons with computational studies, leading to more reliable interpretations of the wealth of information revealed by PES.

Theoretically, the abundance of low-lying electronic states, the possibility of multiple isomers, and the complicated nature of the valence electrons (i.e., closely spaced d levels, highly delocalized 4s orbitals, and the strong $s-d$ hybridizations) make the task of performing *ab initio* calculations particularly difficult. For example, it is well known that the Hartree–Fock (HF) method is a poor starting point for TM clusters. A higher level of theory is required for the accurate description of the exchange-correlation (XC), which for TM clusters is extremely complex. In terms of post-HF theory, this would require the use of massive configuration interaction involving millions of determinants or the equivalent, with associated high-order scaling of the XC operator (N^5 at the second-order Møller–Plesset level, which itself is not even well suited for the task). Such methods, hence, have severe computational restrictions for studies of TM clusters, even for the dimers. On the other hand, density functional theory (DFT) techniques account for XC in many-electron systems through the local spin density approximation (LSDA) and, more accurately, by the generalized-gradient approximation (GGA). At the same time they scale only as N^3 (or lower than N^3). Thus, DFT-based methods seem to be

more suitable for TM clusters. In fact, theoretical studies on small Ti clusters have been reported recently using LSDA and GGA,[14,15] although some of the calculated electron affinities (EAs) and density of states (DOSs) show significant deviations from the experimental measurements.

In the present work, we focus on a combined PES and theoretical study on the small Ti_n^- clusters with $n=3-8$ and 13 and their neutrals, using both LSDA and GGA. The geometries and electronic structures for the ground state and several low-lying states were investigated and the computed DOS was compared to the measured PES data. The details of the PES experiment and the results for Ti_n^- clusters ($n=1-130$) at various photon energies are reported in the preceding article.[16] In the current work, we present detailed computational studies for the selected set of Ti clusters and compare the theoretical results with the PES data.

II. COMPUTATIONAL DETAILS

The lowest energy states of Ti_n^- and Ti_n ($n=3-8$, 13) were obtained using the program DEMON-KS,[17–19] which is a DFT method based on linear combination of Gaussian-type orbitals. LSDA in DEMON-KS was included as described by Vosko et al.[20] The GGA for exchange was from Perdew and Wang (1986),[21] and for correlation from Perdew (1986).[22] The orbital basis sets (63321/5211*/41+) used for titanium were optimized explicitly for DFT calculations.[23] They are of DZVP2 quality and contain p polarization and diffuse d functions. Additional auxiliary bases of Gaussian-type orbitals were employed to describe the charge density (CD) and the XC potential: the CD is fitted analytically while the XC potential is fitted numerically on a fine grid.[17–19]

The ground state for each Ti_n^- and Ti_n cluster was determined as follows. First, several candidates with different geometries were tried for each cluster. Second, for a chosen candidate structure, several electronic configurations of different total spins were searched. This gives a considerable number of states needed for the characterization of the potential energy surface: ground state and excited states for a given cluster (Table 1). Third, without imposing symmetry constraints and by means of the Broyden–Fletcher–Goldfarb–Shanno algorithm,[24] each structure with a given total spin was fully optimized by minimizing the norm of the gradient with a 10^{-5} a.u. threshold. It will be shown in the following that the directional bonding effects, within the $3d$-manifold, are crucial for an accurate evaluation of the atomic forces during the geometry optimization procedure. It is also found that the occurrence of degenerate states, due to the open d shells of the Ti atoms, promotes distortions from the most compact or symmetric geometries. Consequently, most of the computed Ti_n and Ti_n^- ground states have structures of low symmetries. A strict convergence criterion was used for the total energy with a tolerance of 10^{-7} a.u., and for the electronic density with a 10^{-5} a.u. threshold. These tight tolerances are needed for a correct estimation of the ground state for a given cluster, because in most cases several local minima were found within a small energy range.

Mulliken population analyses[25] were done to obtain both the charges on each atom and unpaired spin populations. In the above-mentioned procedure, a full optimization was performed at LSDA. Then, the structures were reoptimized using the GGA potential explicitly in the self-consistent-field (SCF) procedure. All the discussion will be done in terms of the GGA results. It is worthwhile to mention that the highest occupied Kohn–Sham (KS) orbital is the only one with direct physical meaning, whereas the remaining ones should be viewed in principle as auxiliary quantities, which help in solving the effective KS one-particle equations. However, the numerical similarity of these parameters to molecular orbitals (recall that the many-body picture is recovered, at least partially, through the SCF procedure) has proved to be useful to make estimations of the degree of the s, d, and sd contributions, through Mulliken populations and Mayer bond orders,[26] to the bonding properties of TM clusters.[27–29] Furthermore, the calculated KS DOS for magnetic TM clusters resembles well the PES spectra.[28,30] Although a definitive protocol for DFT calculations on TM clusters has not yet been achieved, we have found that the above-mentioned simple procedure allows a systematic and accurate study of these complex systems.[27–29]

III. RESULTS AND DISCUSSION

Figure 1 shows the computed ground state structures of the Ti_n^- anion clusters for $n=3-8$, and 13. Symmetries, spin multiplicities, and selected bond lengths (R_e) of the anion ground state are indicated. The relative energies of other low-lying spin states are also given. The anion ground states all possess highly coordinated and compact structures. Table I contains different geometries, spin multiplicities, bond lengths, and relative energies for the ground state and low-lying excited states for Ti_n^- and Ti_n. The experimental EAs are also given for comparison. The GGA EAs are consistently overestimated with differences ranging 0.04 to 0.23 eV relative to the experimental values.

In Figs. 2 and 3, all the calculated DOS spectra for the anion ground state and some low-lying excited states are compared to the PES spectra for Ti_3^- to Ti_{13}^-. The Fermi level of the calculated DOS is aligned with the experimental EA value for each cluster. The DOS spectra are generated using Gaussians with a width of ~120 meV, which is approximately the instrumental resolution between 1 and 2 eV binding energies at 193 nm. The PES spectra are characterized by well-resolved and intense features near the Fermi level and ~2 eV above the Fermi level, as described in detail in the preceding paper.[16] In the following, we will discuss each cluster and show that the DOS/PES comparison, in conjunction with the computed EAs, is highly valuable in assessing both the ground state and the contributions of low-lying states to the measured spectra.

A. Ti_3^- and Ti_3

As shown in Fig. 2(a), the computed DOS for the D_{3h} ($M=4$) ground state of Ti_3^- fits well with the PES spectrum. The DOS spectra for the two higher spin states ($M=8$ and 6) resemble that of the ground state, whereas that of the $M=2$ is very different. The two higher spin states are nearly degenerate with the ground state and should contribute to the ex-

TABLE I. Low energy structures and states of Ti_n^- and Ti_n ($n=3$–8, 13) clusters. The relative energies in electron volts are given with respect to the ground state of the anion in each case. Experimental electron affinity (EA) in electron volts are compared with the theoretical results.

Cluster	Geometry	Multiplicity (M)	R_e (Å)	Relative energy	EA[i]
Ti_3^-	Equilateral triangle	4	2.41	0.00	
		8	2.36	0.01	
	Isosceles triangle	6	(2.30, 2.30, 2.60)	0.08	
		2	(2.49, 2.49, 2.32)	0.09	
	Linear	6	(2.07, 2.39)	1.13	
Ti_3	Triangle	7	(2.26, 2.31, 2.53)	1.20	
		5	(2.35, 2.35, 2.44)	**1.24**[c]	1.13
		3	(2.36, 2.41, 2.45)	1.36	
	Linear	7	2.20	2.67	
Ti_4^-	Distorted tetrahedron	4	2.50,[a] 2.60[b]	0.00	
		6	2.51,[c] 2.78	0.10	
		8	2.53,[a] 2.64[b]	0.15	
	Distorted rhombus	4	2.31–2.45[d]	0.64	
		2	2.28–2.35[d]	0.67	
	Square	4	2.31	1.53	
Ti_4	Distorted tetrahedron	5	2.48,[a] 2.57[b]	**1.22**[e]	1.18
		7	2.59,[a] 2.47[b]	1.36	
		3	2.51–2.62[d]	1.49	
	Rhombus	5	2.42	2.28	
Ti_5^-	Trigonal bipyramid	2	2.49–2.59[d]	0.00	
		4	2.50–2.62[d]	0.25	
		6	2.47–2.70[d]	0.45	
Ti_5	Trigonal bipyramid	3	2.45–2.59[d]	**1.37**[e]	1.15
		1	2.51–2.58[d]	1.42	
		5	2.52–2.67[d]	1.66	
		7	2.52–2.70[d]	2.02	
	Square pyramid	3	2.46–3.69[d]	2.22	
Ti_6^-	Distorted octahedron	2	2.51–2.70[d]	0.00	
		4	⋯	0.07	
		6	⋯	0.46	
C_{2v}	CTBP[f]	2	2.54–2.67[d]	0.09	
		4	2.50–2.68[d]	0.23	
		6	2.51–2.62[d]	0.51	
Ti_6	Distored octahedron	3	2.57–2.68[d]	**1.47**[e]	1.28
		5	2.50–2.79[d]	1.79	
C_{2v}	CTBP	3	2.48–2.71[d]	1.78	
		5	2.51–2.62[d]	1.73	
Ti_7^-	Pentagonal bipyramid	2	2.48–2.64[d]	0.00	
		4	2.48–2.68[d]	0.13	
		6	2.52–2.72[d]	0.31	
	Caped octahedron	2	2.50–2.74[d]	1.00	
		4	2.56–2.75[d]	1.03	
		6	2.53–2.71[d]	1.02	
Ti_7	Pentagonal bipyramid	1	2.55–2.62[d]	**1.24**[e]	1.11
		3	2.54–2.76[d]	1.45	
		5	2.50–2.73[d]	1.66	
	Capped octahedron	3	2.32		
		5	2.36		
Ti_8^-	NTF-bicapped octahedron[g]	2	2.58–2.70[d]	0.00	
		4	2.53–2.65[d]	0.06	
		6	2.54–2.66[d]	0.32	
		8	2.53–2.82[d]	0.67	
	Capped pentagonal bipyramid	2	2.47–2.88[d]	0.17	
Ti_8	NTF-bicapped octahedron	3	2.57–2.71[d]	**1.54**[e]	1.47
		5	2.55–2.65[d]	1.58	
		1	2.58–2.75[d]	1.68	
		7	2.53–2.89[d]	2.02	
	Capped pentagonal bipyramid	3	2.53–2.87[d]	1.62	
		1	2.54–2.81[d]	1.83	
		5	2.48–2.82[d]	1.89	
	OSF-bicapped octahedron[h]	1	2.52–2.72[d]	2.73	

TABLE I. (*Continued.*)

Cluster	Geometry	Multiplicity (M)	R_e (Å)	Relative energy	EA[i]
		3	2.52–2.70[d]	2.54	
		5	2.49–2.75[d]	2.68	
Ti_{13}^-	Icosahedron	2	2.49–2.93[d]	0.00	
		4	2.45–2.78[d]	0.07	
Ti_{13}	Icosahedron	1	2.52–2.98[d]	**1.96**[e]	1.87
		3	2.46–2.96[d]	1.99	

[a]Four times.
[b]Two times.
[c]Five times.
[d]Range of bond lengths.
[e]Value that should be compared with the experimental EA.
[f]CTBP=capped trigonal bipyramid.
[g]NTF=nearest triangular faces.
[h]OSF=opposite symmetrical faces.
[i]From Ref. 16.

perimental spectrum. We also calculated the adiabatic detachment energies, i.e., the EAs for the different neutral states. The total energy difference between the D_{3h} $M=4$ ground state of Ti_3^- and the $M=5$ state of Ti_3 ($\Delta M=1$, the photodetachment selection rule) yields an EA of 1.24 eV, which is in good agreement with the experimental result of 1.13 eV. Furthermore, allowing for a full structural, electronic, and spin relaxation, we obtained an EA of 1.20 eV and an $M=7$ spin state, which is the ground state of Ti_3, only 0.04 eV more stable than the $M=5$ state (Table I). Zhao *et al.* using GGA[15] and Wei *et al.* using LSDA[14] obtained an equilateral triangle Ti_3 with $R_e=2.28$ and 2.35 Å, respectively. The calculated EA by Wei *et al.* is 0.33 eV, much lower than the experimental value. It should be mentioned that our calculated EA at LSDA is 1.06 eV, which is low compared with the GGA result, but much closer to the experimental value than the LSDA result by Wei *et al.* The excellent agreement between the calculated EA and DOS and the experimental measurements in the current investigation confirms our calculated ground states for Ti_3 and Ti_3^-.

B. Ti_4^- and Ti_4

The ground state of Ti_4^- was found to be a distorted tetrahedron (DT) with $M=4$ and R_e's of 2.50 and 2.60 Å. The $M=6$ and 8 DT states are only 0.10 and 0.15 eV higher in energy [Table I and Fig. 1(b)]. The two-dimensional structures of Ti_4^- were found at least 0.6 eV above the ground state. The computed DOS spectra of all the three DT states of Ti_4^- reproduce the PES spectrum well [Fig. 2(b)], suggesting that they may all contribute to the experimental spectrum. The transition of the DT $M=4$ ground state of Ti_4^- into the DT $M=5$ ground state of Ti_4 yields an EA of 1.22 eV, in excellent agreement with the experimental value of 1.18 eV (Table I). This level of agreement allows us to firmly establish the ground state of Ti_4 to be the DT ($M=5$) state and that of Ti_4^- to be the DT ($M=4$) state. Note that the R_e's of the ground state of Ti_4 are 2.48 and 2.57 Å, which are slightly shortened relative to the ground state of Ti_4^- (Table I). Zhao *et al.* reported an ideal tetrahedron with an R_e of 2.51 Å as the ground state of Ti_4,[15] whereas Wei *et al.* found a C_{3v} ground state for Ti_4 with $R_e=2.518$ Å.[14] The R_e's of these

two previous studies are close to the present study, but the computed EA by Wei *et al.* was 0.7 eV, differing significantly from the experiment. Overall, the DT ground state of Ti_4 obtained currently is similar to those of Fe_4, Co_4 and
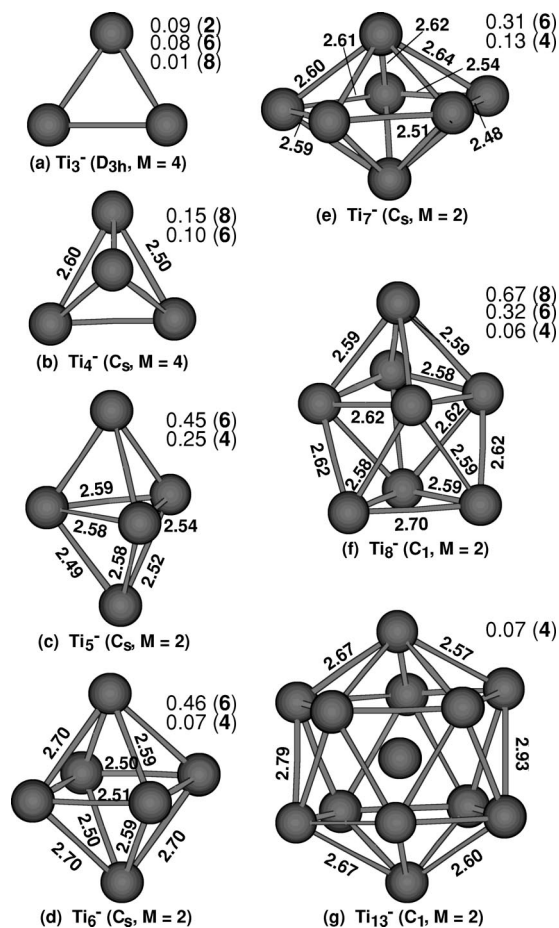

FIG. 1. Ground state structures and spin states of Ti_n^- ($n=3$–8, 13). Selected bond lengths are given in angstroms. The relative energies and spin multiplicities of low-lying spin states for each structure are also given in the upper-left part in each structure: the spin multiplicities (M) are given in parentheses and the relative energies are given in electron volts. Also see Table I.
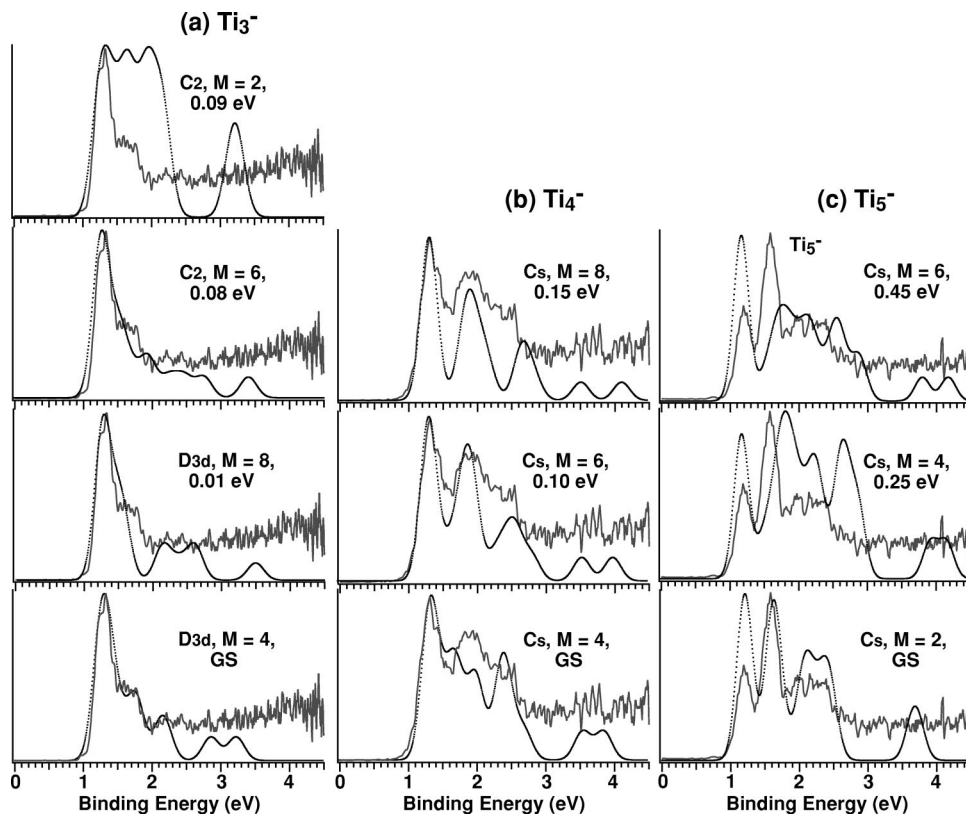
FIG. 2. Comparisons of the calculated density of states with experimental photoelectron spectra for (a) Ti_3^-, (b) Ti_4^-, and (c) Ti_5^-. GS stands for the ground state. Also see Table I.

Ni_4,[27–29] which all possess high spin ground states ($M=13$, 11, and 5, respectively) with similar distorted tetrahedral structures.

C. Ti_5^- and Ti_5

A distorted trigonal bipyramid (DTB) with $M=2$ was found as the ground state for the Ti_5^- anion. The DTB $M=4$ and 6 states were found to be 0.25 and 0.45 eV higher in energy [Table I and Fig. 1(c)]. With such large energy separations, it is expected that the higher spin states would not be significantly populated in the experiment and would make negligible contributions to the measured PES spectra of Ti_5^-. In fact, the computed DOS for the DTB $M=2$ ground state of Ti_5^- fits the PES spectrum very well, as shown in Fig. 2(c), whereas those of the two high spin states are clearly inferior. This is consistent with the single isomer domination by the $M=2$ state in the mass spectrum for Ti_5^-.

The lowest energy state of neutral Ti_5 is a DTB triplet, derived from the DTB doublet ground state of the anion. The computed EA is 1.37 eV, which is in reasonable agreement with the experiment. Note that the DTB close-shell state ($M=1$), which is also related to the anion ground state through a one-electron transition, is very close to the triplet state (Table I). These theoretical results are in excellent agreement with the high resolution PES spectrum at 532 nm of Ti_5^-, which resolves the threshold band into two components,[16] corresponding to the triplet and singlet states of Ti_5. Our findings agree with the results of Wei *et al.*,[14] who also found a DTB structure with $M=3$ and similar R_e's for the ground state of Ti_5. Zhao *et al.* also reported a DTB structure for Ti_5, but no information about structural distortion and mul-

tiplicity was given.[15] Andersen has also determined that the DTB Ti_5 is more stable than the square pyramid, although much longer bond distances were given in that study (about 3.1 Å).[31] Wei *et al.* reported an EA (LSDA) of 0.90 eV for Ti_5. Our LSDA EA for Ti_5 is 1.26 eV, slightly lower than the GGA value of 1.37 eV.

D. Ti_6^- and Ti_6

A distorted octahedron (DOH) with $M=2$ was found as the ground state of Ti_6^-, with the $M=4$ and 6 states lying only 0.07 and 0.46 eV higher in energy [Table I and Fig. 1(d)]. The capped distorted trigonal bipyramid (CDTB) was found to be very close to the DOH structure, only 0.09, 0.23, and 0.51 eV above the ground state for the $M=2$, 4, and 6 states, respectively (Table I). Figure 3(a) compares the DOS spectra of the ground state and the three most low-lying states of Ti_6^- to the PES spectrum. Clearly, the DOS of the Ti_6^- ground state fits remarkably well with the PES spectrum. The nearest DOH ($M=4$) state gives a DOS spectrum similar to the $M=2$ state and should contribute to the experimental spectrum. However, the DOS spectra of the two CDTB states exhibit large discrepancies from the PES spectrum and the CDTB isomers were probably not significantly populated. The ground state of Ti_6 was found to be the DOH $M=3$ state with a computed EA of 1.47 eV, in reasonable agreement with the experimental value of 1.28 eV. The computed EAs for all other states are significantly higher than the DOH $M=3$ state. The good agreement between the computed EA and DOS spectrum and the experimental measurements supports the obtained ground states for both the neutral and anionic Ti_6 cluster, i.e., the distorted octahedral structure. A

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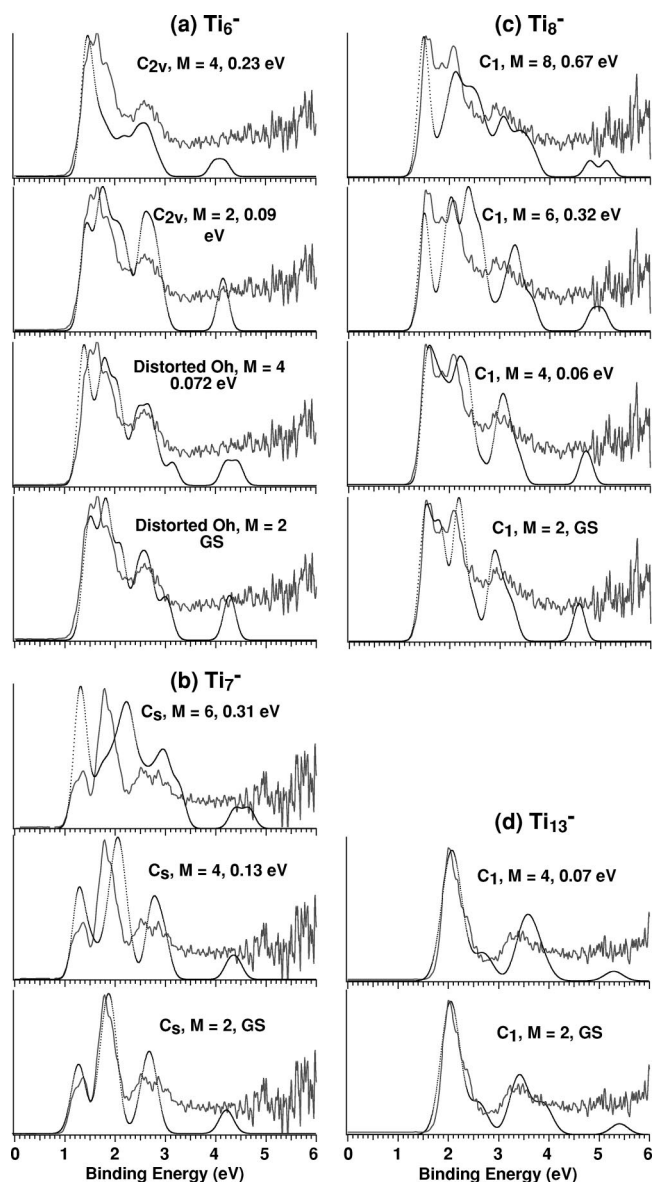

FIG. 3. Comparisons of the calculated density of states with experimental photoelectron spectra for (a) Ti_6^-, (b) Ti_7^-, (c) Ti_8^-, and (d) Ti_{13}^-. GS stands for the ground state. Also see Table I.

previous DFT study using GGA indicates a degeneracy for the octahedral and capped trigonal bipyramidal states of Ti_6,[15] while a LSDA[14] and a molecular dynamics study[32] both favor the capped trigonal bipyramid. Although we found that the DOH $M=2$ and CTBP $M=2$ are nearly degenerate for Ti_6^-, we believe that the present GGA results, in concert with the DOS/PES relationship and good agreement of the EA compared to the experimental value, lend considerable credence to the distorted octahedral ground states of Ti_6^- and of Ti_6.

E. Ti_7^- and Ti_7

The calculated ground state of Ti_7^- is a doublet distorted pentagonal bipyramid (DPB); the quartet and sextet states were found to be 0.13 and 0.31 eV higher [Table I and Fig. 1(e)]. We found that the capped octahedral states of Ti_7^- were at least 1 eV higher than the DPB ground state (Table I). The comparison of the computed DOS spectra for the three DPB states with the PES spectrum is shown in Fig. 3(b). Clearly, the DOS of the $M=2$ ground state yields the best agreement with the experiment, suggesting that the higher spin states were probably not significantly populated in the experiment. The ground state of neutral Ti_7 is a closed-shell singlet derived from the DPB ground state of Ti_7^- and yields an EA of 1.24 eV, in excellent agreement with the experimental value of 1.11 eV. Thus, we can conclude firmly that the ground states of Ti_7 and Ti_7^- are the DPB structures with low spins. This conclusion is consistent with previous theoretical calculations,[14,15,32] which all give a pentagonal bipyramidal structure for Ti_7. Thus, Ti_7 possesses both a highly compact geometrical structure and a closed electron shell, indicating that it should be very stable and less reactive. Indeed, previous collision induced dissociation studies on Ti_n^+ clusters[33,34] showed that $n=7$, 13, and 19 exhibit special stabilities relative to their neighbors, consistent with the present conclusion.

F. Ti_8^- and Ti_8

The ground state of Ti_8^- was found to be a doublet bicapped octahedron (BO), where the two extra atoms cap two nearest triangular faces (NTFs) [Fig. 1(f)]. If the capping is done on opposite symmetrical faces, the resulting states, as exemplified for the neutral, are considerably higher in energy, as given in Table I. The NTF-BO $M=4$ state lies only 0.06 eV above the ground state, while the $M=2$ state of the capped pentagonal bipyramid was 0.17 eV higher. Figure 3(c) shows the DOS spectra of the NTF-BO states compared with the PES spectrum. It is seen that the DOS spectra of both the $M=2$ ground state and the $M=4$ lowest-lying state show good agreement with the PES spectrum. Thus, both $M=2$ and 4 states may contribute to the experiment. Electron detachment from the Ti_8^- $M=2$ ground state gives the NTF-BO $M=3$ state of the neutral, with an EA of 1.54 eV, in excellent agreement with the experimental EA of 1.47 eV. These DOS/PES and EA agreements support our obtained ground states for Ti_8^- (NTF-BO $M=2$) and Ti_8 (NTF-BO $M=3$). Zhao et al. also found the capped pentagonal bipyramid as the ground state for Ti_8 with the bicapped octahedron (capping two opposite symmetrical faces) 0.88 eV above.

G. Ti_{13}^- and Ti_{13}

An icosahedral structure has been reported as the ground state for Ti_{13} and Ti_{13}^-.[15] An $I_h - Ti_{13}^+$ has been proposed to account for its special stability in previous collision-induced dissociation experiments.[33,34] In addition, our PES studies showed that Ti_{13}^- has particularly narrow PES spectra, suggesting a more symmetric cluster than its neighbors.[16,35] Thus, we included a study of Ti_{13}^- and Ti_{13} in the present theoretical effort and started with an icosahedral arrangement using interatomic separations of the nearest-neighbor distance (2.89 Å) of bulk titanium. After electronic and structural relaxation, we found that the ground state of Ti_{13}^- is a distorted icosahedron with $M=2$, with the $M=4$ state only 0.07 eV higher [Fig. 1(g) and Table I]. The calculated DOS spectra of both states fit the PES spectrum remarkably well,

as shown in Fig. 3(d). The calculated EAs from these two states are also in excellent agreement with the experimental value, as given in Table I. Therefore, we conclude that indeed the ground state of Ti_{13}^- and Ti_{13} should be the distorted I_h structure with the lower spin states slightly favored.

From the structures of Ti_7 and Ti_{13}, an icosahedral growth pattern is observed. It is expected that the Ti_{55} cluster may also possess an I_h structure, as suggested from its special PES pattern.[16,35] The fact that all these clusters actually possess lower symmetries is due to the Jahn–Teller effects. As we have suggested in the preceding article,[16] Ti clusters in the size range below $n=130$ may possess body-centered cubic (bcc) type structures, rather than the hexagonal-close packed (hcp) type expected from the bulk hcp lattice of titanium. Therefore, we observe an interesting structural variations in the Ti_n systems, from the initial I_h growth ($n=7$, 13, 55) to bcc ($n<130$) to hcp eventually ($n>130$). It would be very interesting and important to confirm these size dependencies of the geometrical structures and their underlying driving force.

H. Evolution of the magnetic properties of small Ti_n clusters

The ground state electronic configuration of the titanium atom is $4s^2 3d^2$. Thus, the Ti atom has a magnetic moment of $2\mu_b$ corresponding to the two unpaired d electrons. In small titanium clusters, Mulliken population analyses reveal roughly a promotion of one $4s$ electron into the $3d$ shell, resulting in a *bonding* $4s^1 3d^3$ electron configuration, where all valence electrons are unpaired and ready to form chemical bonds. Thus, strong metal–metal bonding occurs in bulk Ti, which has a very high cohesive energy and no unpaired spins (nonmagnetic). In small Ti clusters, the extent of spin pairing is determined by the coordination of the Ti atoms, as well as by the types of bonds (i.e., singles, doubles, or triples) formed during the metal–metal interaction. The remaining unpaired spins may build a magnetic moment for the cluster. It is expected that the magnetic moments of Ti clusters should decrease dramatically with cluster size. Indeed, no Ti clusters have been definitively observed to possess a net magnetic moment.[36]

Here we measure the coordination as the number of nearest neighbors of a given Ti atom in a cluster. For example, the ground state of Ti_2, with a coordination of one, has been computed to possess a triple bond between the pair of Ti atoms: two $3d$–$3d$ bonds and one $4s$–$4s$ bond. This leaves one unpaired $3d$ electron on each Ti site, with the ground state of Ti_2 being a triplet corresponding to a magnetic moment of $1\mu_B$/atom. This represents a dramatic decrease from the Ti atom ($2\mu_B$). For a triangular Ti_3, the coordination increases from one to two, but the Ti–Ti bonds are single bonds. This means that there should be two unaired spins on each Ti site. Indeed, as mentioned earlier the ground state of Ti_3 has six unpaired $3d$ electrons ($M=7$) or $2\mu_b$/atom, i.e., an increase relative to the dimer. Moreover, in the studied size range ($n=3$–8 and 13), Ti_3 has the largest magnetic moment. It is to be stressed that the $4s^1 3d^3$ configuration leads to a plethora of bonding patterns for Ti_3, as shown in Table I. States with double and triple bonds be-
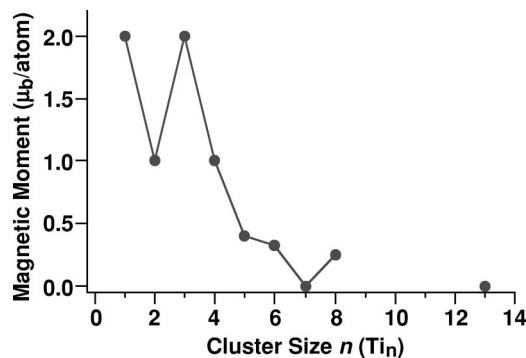

FIG. 4. Magnetic moment of Ti_n ($n=3$–8, 13).

tween the Ti–Ti atoms also exist as excited states of Ti_3. In the ground state of Ti_4 the coordination number is three, meaning the pairing of three spins of each Ti atom and leaving only one unpaired $3d$ electron. Indeed, the computed ground state of Ti_4 is a quintet (Table 1), giving rise to a magnetic moment of $1\mu_b$/atom. From Ti_3 to Ti_4 the magnetic moment decreases as a result of an increase in the coordination number. In Ti_5, the coordination number is three for the two apex atoms and four for the equatorial atoms (Fig. 1), implying a further reduction of the magnetic moment. Indeed, the computed ground state of Ti_5 is a triplet state, giving rise to an average moment of $0.40\mu_b$/atom.

The coordination numbers of the larger clusters can be enumerated from the ground state structures of the Ti clusters, as shown in Fig. 1, and they increase with the cluster size. The average magnetic moments as a function of size are plotted in Fig. 4 for $n=1$–8 and 13. They are observed to decrease rapidly with size. The magnetic moments for Ti_7 and Ti_{13} are zero because their ground states are singlet without any unpaired electrons. This is in contrast with the late $3d$ clusters. For example, Fe_7 was previously found to have a distorted pentagonal bipyramid ground state structure with 22 unpaired electrons, i.e., an average magnetic moment of $3.14\mu_b$/atom.[28] We note that for Ti_{13} the triplet state is almost degenerate with the closed shell ground state, only 0.07 eV higher in energy. It should be significantly populated under finite temperatures. In summary, we found that smaller Ti clusters with $n<5$ are highly magnetic with relatively large moments, but the magnetic moments decrease rapidly as cluster size and the average coordination number increase, rendering a fast convergence of the magnetic moment of the cluster to the nonmagnetic bulk.

IV. CONCLUSIONS

We have performed a systematic study of the electronic and structural properties of small Ti_n ($n=3$–8, 13) clusters and their anions. Comparisons of the calculated DOS spectra and EAs with experimental PES data confirmed the obtained structures and spin states. We found that the small Ti clusters all possess multiple isomers, as well as multiple spin states with very close energies. In all cases, the ground state of the anion yields the DOS spectrum and EA that are in best agreement with the experimental data, giving considerable credence for the identified structures and ground states. In gen-

eral, from the charged to neutral states, structural relaxations are small, consistent with the relatively sharp features of the PES spectra. From the spin states of the ground states, we are able to obtain insight into the magnetic properties of the small Ti clusters. We found that the small clusters are highly magnetic, but the magnetic moments approach the bulk very rapidly. The current study suggests that above $n=7$ the cluster magnetic moment becomes negligible. For $n=7$ and 13, two highly compact clusters, the magnetic moments are zero. It will be very interesting to perform further magnetic deflection experiments to confirm the magnetic behavior of these systems.

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