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The stabilization mechanism of titanium cluster

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ABSTRACT

A systematic and comparative theoretical study on the stabilization mechanism of titanium cluster has been performed by selecting the clusters Ti_n ($n=3$, 4, 5, 7, 13, 15 and 19) as representatives in the framework of density-functional theory. For small clusters Ti_n ($n=3$, 4 and 5), the binding energy gain due to spin polarization is substantially larger than that due to structural distortion. For medium clusters Ti_{13} and Ti_{15}, both have about the same contribution. For Ti_n ($n=4$, 5, 13 and 15), when the undistorted high symmetric structure with spin-polarization is changed into the lowest energy structure, the energy level spelling due to distortion fails to reverse the level order of occupied and unoccupied molecular orbital (MO) of two type spin states, the spin configuration remains unchanged. In spin restricted and undistorted high symmetric structure, *d* orbitals participate in the hybridization in MOs, usually by way of a less distorted manner, and weak bonds are formed. In contrast, *d* orbitals take part in the formation of MOs in the ground state structure, usually in a distorted manner, and strong covalent metallic bonds are formed.

1. Introduction

Titanium material is applied in many fields including aerospace, military, industrial processes and medicine etc. since it has extraordinarily excellent physical and chemical properties. Titanium cluster has naturally been the subject of intensive studies. As a typical early transition metal (TM) element, titanium atom has the $3d^2$ open shell and its $3d$ orbitals show highly delocalized characteristics. Although bulk titanium metal is nonmagnetic, small titanium clusters show oscillatory magnetism with cluster size. The occurrence of magnetism brings additional difficulties to obtain the ground states, for which we must consider the dense spin multiplicities to avoid trapping into local minima in the entire spin space. The understanding of geometric, electronic and magnetic properties of titanium clusters poses tremendous challenges both experimentally and computationally [1–7].

Applying density-functional theory (DFT)/generalized gradient approximation (GGA)/Projector augmented wave combination, Lee et al. [5] compare Ti_{13} with Ni_{13} in order to understand the effect of structural distortion and spin polarization on the stability of titanium clusters. They came to a conclusion that distortion and spin polarization can reduce the total energy of Ti_{13} cluster through lifting the degeneracy and the spin redistribution of the highly populated highest occupied molecular orbital (HOMO) region. Using DFT/the Becke, Lee, Yang, Parr (BLYP) or the Perdew, Burke, Ernzerhof (PBE) exchange correlation functional/double zeta valence plus polarization (DZVP) basis sets schemes, Medina et al. [6] studied the effects of structural distortion on the total energy and magnetism of Ti_{13} clusters and found that the structural distortion has no effect on the total magnetic moment. Despite the studies mentioned above further research about titanium clusters is needed in order to understand the underlying physical mechanisms of these phenomena. In the present work, we select the clusters Ti_n ($n=3$, 4, 5, 7, 13, 15 and 19) as representatives, using a gradient-corrected DFT, to investigate the binding energy gain due to distortion and spin polarization. The binding energy gain correlates with one-electron energy levels, the partial density of states (PDOS), the charge density, and the HOMOs. In Section 2, we describe the computational details, while Section 3 presents the results and a discussion of results. Section 4 is dedicated to final conclusions.

2. Computational details

All calculations are performed based on spin-polarized DFT in the $DMOL^3$ package [8,9]. In the electronic structure calculations, we employ the GGA/PBE exchange-correlation functional [10] as well as a DFT-based relativistic semi-core pseudopotential (DSPP)

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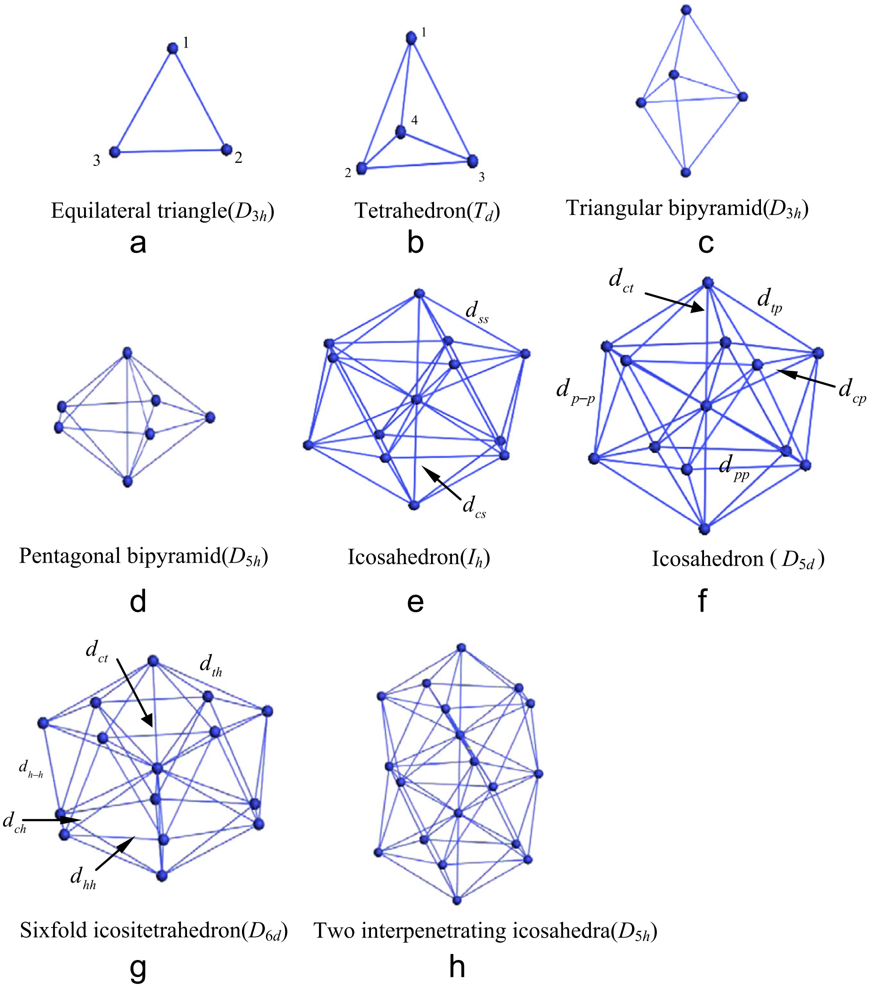

Equilateral triangle(D_{3h})
a

Tetrahedron(T_d)
b

Triangular bipyramid(D_{3h})
c

Pentagonal bipyramid(D_{5h})
d

Icosahedron(I_h)
e

Icosahedron (D_{5d})
f

Sixfold icositetrahedron(D_{6d})
g

Two interpenetrating icosahedra(D_{5h})
h

Fig. 1. The corresponding undistorted structures of titanium clusters Ti_n ($n=3, 4, 5, 7, 13, 15$ and 19). The site (atom) numbers in 3, 4-atom clusters are displayed [(a) and (b)]. Each of d_{cs}, d_{ss}, [(e)], d_{ct}, d_{cp}, d_{tp}, d_{pp} and $d_{p\text{–}p}$[(f)], d_{ct}, d_{ch}, d_{th}, d_{hh} and $d_{h\text{–}h}$ [(g)] stands for one type of equivalent bond length in undistorted structure, and for the corresponding arithmetic mean in distorted structure.

[11], fitted to all-electron relativistic results, and a double numerical basis set including polarization function (DNP). In the geometry optimization, the convergence thresholds are set to 0.001 hartree/Å for the force, 0.002 Å for the displacement, and 10^{-5} hartree for the energy change. Self-consistent field calculations are done with a convergence criterion of 10^{-6} hartree on the total energy.

We first perform global optimization and get the lowest energy structures for Ti_n clusters ($n=2$–20). In geometrical optimizing process, the optimal spin configurations are determined automatically by the self-consistent iterations. For several energetically most favorable structures, their possible electronic configurations of total spins are fully re-optimized. The obtained ground state structure of Ti_n ($n=2$–20) is written as $\mathrm{Ti}_n^{\mathrm{opt}}$ in the context.

For $\mathrm{Ti}_n^{\mathrm{opt}}$ ($n=3, 4, 5, 7, 13, 15$ and 19), each can be described as a distorted version of a higher symmetric structure, i.e., equilateral triangle (D_{3h}), tetrahedron (T_d), triangular bipyramid (D_{3h}), pentagonal bipyramid (D_{5h}), icosahedron (I_h), sixfold icositetrahedron (D_{6d}), two interpenetrating icosahedra (D_{5h}) (Fig. 1), which agrees well with the previous results [2,3,6,7]. Based upon the standard structures, we have conducted comparative studies. The symmetric structure is relaxed with spin restrictions, and the resulting structure is written as $\mathrm{Ti}_n^{\mathrm{o}}$. For $\mathrm{Ti}_n^{\mathrm{o}}$, we further carry out calculations through two different routines. One is that $\mathrm{Ti}_n^{\mathrm{o}}$ with symmetric unrestriction and spin restriction is relaxed and the resulting structure is denoted by $\mathrm{Ti}_n^{\mathrm{d}}$. $\mathrm{Ti}_n^{\mathrm{d}}$ is globally optimized and the obtained lowest energy structure is written as $\mathrm{Ti}_n^{\mathrm{ds}}$. The other routine is that the bond lengths of Ti_n° are relaxed with spin polarization and symmetry constraints and the resulting structure is denoted by $\mathrm{Ti}_n{}^{\mathrm{s}}$. $\mathrm{Ti}_n{}^{\mathrm{s}}$ is globally optimized and the calculated lowest energy structure is written as $\mathrm{Ti}_n^{\mathrm{sd}}$.

For all calculation mentioned above, the vibration frequencies are analyzed. During searching for $\mathrm{Ti}_n^{\mathrm{opt}}$, $\mathrm{Ti}_n^{\mathrm{d}}$, $\mathrm{Ti}_n^{\mathrm{ds}}$ and $\mathrm{Ti}_n^{\mathrm{sd}}$, if an imaginary vibration mode is found, a relaxation along the coordinates of this mode is carried out until the true local minimum is actually obtained. Therefore, $\mathrm{Ti}_n^{\mathrm{opt}}$, $\mathrm{Ti}_n^{\mathrm{d}}$, $\mathrm{Ti}_n^{\mathrm{ds}}$ and $\mathrm{Ti}_n^{\mathrm{sd}}$ are surely corresponding to the local minima.

3. Results and discussion

The point group symmetries of geometry within 0.1 Å tolerance, binding energies per atom and spin multiplicities of Ti_n°, $\mathrm{Ti}_n^{\mathrm{d}}$, $\mathrm{Ti}_n^{\mathrm{s}}$, $\mathrm{Ti}_n^{\mathrm{ds}}$, $\mathrm{Ti}_n^{\mathrm{sd}}$ and $\mathrm{Ti}_n^{\mathrm{opt}}$ ($n=3, 4, 5, 7, 13, 15$ and 19) are presented in Table 1. The computed spin multiplicities of the lowest energy structures for Ti_n ($n=3, 4, 5$ and 7) agree with Castro et al. [3] and Du et al. [4]. For Ti_{13}, the present result is consistent with Medina et al. [6] and Wang et al. [7]. However, almost no one explore the spin multiplicities of Ti_{15} so far. For $\mathrm{Ti}_n^{\mathrm{ds}}$, $\mathrm{Ti}_n^{\mathrm{sd}}$ and $\mathrm{Ti}_n^{\mathrm{opt}}$, the geometries and binding energies are nearly the same and the multiplicities are equal. In fact, all the three should be the ground state structure. Therefore, we will generally select $\mathrm{Ti}_n^{\mathrm{ds}}$ as