Journal of Molecular Structure: THEOCHEM 957 (2010) 26–30

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem

Structural, electronic, and magnetic properties of $Fe_nO_m^+$ $(n + m = 5)$ clusters

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ARTICLE INFO

Article history:
Received 25 April 2010
Received in revised form 30 June 2010
Accepted 30 June 2010
Available online 23 July 2010

Keywords:
Density-functional theory
Isomers
Binding energy
Magnetic moment

ABSTRACT

By the aid of density-functional theory and all-electron numerical basis set, we have found 40 stable isomers of $Fe_nO_m^+$ $(n + m = 5)$ clusters through optimization calculations and frequency analysis from 161 initial structures. The binding energies, the energy gaps between the highest occupied molecular orbital and lowest unoccupied molecular orbital and the magnetic moments of all the stable isomers are reported. The relationships between the molecular properties and structures are examined.

1. Introduction

Fe-based nanoparticles and binary component clusters including Fe atoms are interesting to many researchers in cluster science. There are many theoretical and experimental investigations on neutral and ionic clusters containing Fe and O atoms, especially FeO_n or Fe_nO. The geometries, vibrational frequencies and molecular bonding of FeO_4 and FeO_4^- species with different spin states have been investigated with density-functional theory (DFT), Hartree–Fock and post-Hartree–Fock molecular orbital methodologies [1]. Wang et al. have researched sequential oxygen atom chemisorption on surface of small iron cluster [2]. The studies devoted to Fe_nO_m clusters can also be found in the literatures. For example, Shiroishi et al. have studied structural and magnetic properties in the anion iron-oxide cluster [3], Fe_3O_m $(m = 1–5)$, Fe_4O_m $(m = 1–6)$ and Fe_nO_m $(n = 1–5)$ using the first-principles molecular dynamics based on DFT [4]. Khanna and co-workers have computed the structures of neutral Fe_nO_m cluster [5]. Ding et al. have studied on cage and noncage $(Fe_2O_3)_n$ clusters, and found that $(Fe_2O_3)_n$ cluster have high stability [6]. Gennady et al. have researched electronic structures and properties of FeO_n and FeO_n^- clusters, and they develop a plane-wave pseudopotential scheme for noncollinear magnetic structures, based on a generalized local spin-density theory in which the direction of the magnetization is a continuous variable of position [7]. Synergistic studies employing experiments in the gas phase and first-principles calculations have been carried out to investigate the structure, stability, and reactivity toward CO of iron-oxide cluster anions, $Fe_xO_y^-$ $(x = 1–2, y \leqslant 6)$ [8]. Shiroishi has researched the structure and magnetism of anion iron-oxide clusters $Fe_nO_m^-$ $(n = 1,2)$ and $Fe_nO_m^-$ $(n = 3,4)$ [3,9].

Meanwhile, studies on iron-oxide cluster cations have also been reported. Molek experimentally studied photodissociation of $Fe_nO_m^+$ [10]. Jackson et al. have researched structure and reactivity of the prototype iron-oxide cluster $Fe_2O_2^+$ [11]. However, the investigations mainly focus on the ground state geometries or the electronic affinities of the clusters. The colorful isomers of the iron-oxide cations, which are very important to preparation, analysis, and application of the clusters, have hardly been examined. In the present work, we carry out exhaustive seek for the stable isomers of the $Fe_nO_m^+$ $(n + m = 5)$ clusters with DFT calculations. The vibrational frequency analysis is used to confirm the local minima. Moreover, the binding energies (BEs), the energy gaps between the highest occupied molecular orbital and lowest unoccupied molecular orbital (EGHL), and the magnetic moments of the stable structures are also calculated and analyzed. It is expected that the present investigations can provide a basis for understanding the molecular properties of the various isomers of $Fe_nO_m^+$ $(n + m = 5)$ clusters.

2. Computational details

As the previous investigation on Fe_3C_2 cluster [12], we search for the stable geometries of $Fe_nO_m^+$ $(n + m = 5)$ clusters following the "binomial" scheme by Ryzhkov et al. [13] (see Fig. 1). According to the scheme, there are six ways to build initial structures for searching the stable configurations of $Fe_nO_m^+$ $(n + m = 5)$ clusters. We start the scheme from the stable structure of FeO^+. The triatomic structures of Fe_2O^+ or FeO_2^+ will be formed when the Fe or O atoms are added to the FeO^+. Then four-atomic geometries

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0166-1280/$ - see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.theochem.2010.06.032

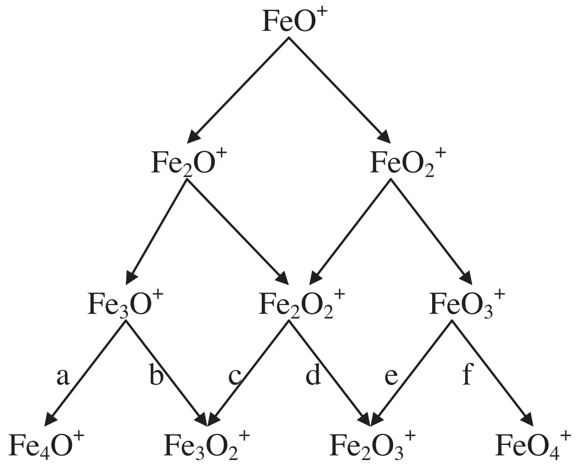

Fig. 1. The scheme of building initial structures for search of the stable isomers for $Fe_nO_m^+$ ($n + m = 5$).

are formed. Only the stable ones are used to form five-atom clusters by adding Fe or O, respectively. There will induce 6 different paths to form $Fe_nO_m^+$ ($n + m = 5$) geometries starting from FeO^+. Hereinafter, the paths are represented by "a", "b", "c", "d", "e", and "f" from left to right in Fig. 1, respectively.

The number of the possible initial structures of $Fe_nO_m^+$ ($n + m = 5$) clusters from the above scheme are large (161 in total), the work to search for the stable geometries of $Fe_nO_m^+$ ($n + m = 5$) clusters cannot be fulfilled if there is no efficient computational method. As the reports by Ryzhkov et al. [13] and our previous work [12], the DFT with numerical basis set implemented in $Dmol^3$ module [14] is very efficient and may serve for our system, because it can search for optimum atomic positions based on the total energy gradient calculation. All the calculations for geometry optimization of $Fe_nO_m^+$ ($n + m = 5$) isomers are performed using the spin-polarized DFT calculations with GGA in "PW91" form [15,16]. A basis set of double numerical plus d-functions (DND) is chosen to describe the electronic wave functions. All the calculations are performed with $Dmol^3$ package.The convergence settings are 1.0×10^{-5} hartree for the energy change, 5.0×10^{-4} hartree/bohr for the maximum force, and 0.002 Å for the maximum displacement. The global orbital cutoff is 5.0 Å, which is better than the default "fine" standard in $Dmol^3$. The smearing gap 0.005 is employed to accelerate the convergence of the SCF iterations. In order to confirm the accuracy of approach used in this paper, we calculated the BEs, Fe–O bond length and ionization potential (IP) of one Fe_2O_3 cluster (C_{2v}) and compared them with the theoretical results of Shiroishi [4], Jones [17] and the experimental data [18]. As shown in Table 1, the present theoretical level can provide acceptable calculational results for the binary component clusters composed of Fe and O atoms.

3. Results and discussions

3.1. Geometrical, energy and chemical stability

The initial geometries are subjected to geometrical optimization and frequency analysis, leading to 40 stable structures. All the stable structures are shown in Fig. 2. We can find in the figure that the geometries include 25 planar structures, 13 three-dimensional structures, and 2 linear structures. The highest symmetry (D_{3h}) geometry is isomer 34.

The BEs and EGHLs for all the 40 stable structures are collected in Table 2. For the sake of clarity, the BEs are discussed for the groups of FeO_4^+, $Fe_2O_3^+$, $Fe_3O_2^+$, and Fe_4O^+ clusters separately. For the group of FeO_4^+ isomers, the BE of isomer 8 is the largest. We find it has 4 Fe–O bond lengths close to that of diatomic FeO^+ cluster after carefully examine the geometries in Fig. 2. The one with the smallest BE is isomer 1 who has only 2 Fe–O bond lengths close to that of FeO^+ cluster. This fact indicates that the Fe–O bond plays a very important role for the BEs of FeO_4^+ isomers. For the group of $Fe_2O_3^+$ clusters, the isomer 9 with 2 Fe–O bond lengths close to that of FeO^+ cluster, whose BE is smallest in this group. While the isomer 23 with 5 Fe–O bond lengths close to that of FeO^+ cluster, has the largest BE of the group. For the group of $Fe_3O_2^+$ clusters, the isomers 24 and 37 have the smallest and largest BEs, respectively. It is found that the isomer 24 has 3 Fe–O bond lengths and the isomer 37 has 4 Fe–O bond lengths close to that of FeO^+ cluster. For Fe_4O^+ clusters, the BEs of isomers 40 and 38 are the largest and smallest, respectively. Again we find that the bond lengths close to that of FeO^+ cluster in isomer 40 are one more than that in isomer 38. Therefore we can conclude that Fe–O bond plays a very important role for the BEs of $Fe_nO_m^+$ ($n + m = 5$) clusters.

Table 1
The BEs, Fe–O bond length, and ionization potential of Fe_2O_3 (C_{2v}).

	BEs (eV)	Fe–O bond length (Å)		IP (eV)
Present	22.037	1.634	1.809	8.811
Shiroishi et al. (Ref. [4])	19.100			
Jones et al. (Ref. [17])		1.640	1.790	
Experiment (Ref. [18])				8.090 ± 0.200

As we well know, larger EGHL of the cluster suggests it is higher chemical stability [19,20]. We can find from Table 2 that the EGHLs for the isomers are range from 0.029 eV to 1.320 eV. It implies that the isomers of $Fe_nO_m^+$ ($n + m = 5$) clusters have various abilities to control electrons, and can play different roles in chemical reactions.

On the whole, the geometries of better energy stability are isomer 8, 23, 37, and 40 for the groups of FeO_4^+, $Fe_2O_3^+$, $Fe_2O_3^+$, and Fe_4O^+ clusters, respectively. The isomer 8, 12, 33, and 40 are the higher chemical stability in FeO_4^+, $Fe_2O_3^+$, $Fe_3O_2^+$, and Fe_4O^+ clusters because they have the larger EGHLs in the own groups. We notice that both the energy and chemical stability of isomer 8 is the best in the group of FeO_4^+ isomers, and the same conclusion can be obtained for isomer 40 in the group of Fe_4O^+ clusters. Therefore the geometries of isomer 8 and 40 could be detected easily in the experiment. However, the one has the best energy stability and the one has the best chemical stability are not the same isomer for the groups of $Fe_3O_2^+$ and $Fe_2O_3^+$ clusters.

3.2. Magnetic moment

On the basis of the optimized stable geometries, the magnetic properties of the 40 $Fe_nO_m^+$ ($n + m = 5$) isomers are investigated and the results are presented in Table 3. In general, the total magnetic moment increases with the number of Fe atom increases. We determine the corresponding spin states of the isomers by analyzing the orbital occupations. The spin multiplicities of the $Fe_nO_m^+$ ($n + m = 5$) isomers are range from 2 to 14, which shows the clusters have very different magnetic properties. As for single atom, the magnetic moment of Fe atom is obviously larger than that of O atom. The magnetic moment of Fe atom ranges from 0.13 to $3.88\mu_B$, while the minimum and maximum magnetic moment of O atom is 0.01 and $1.00\mu_B$, respectively. The magnetic moments of Fe and O atoms themselves and their different projections on the molecular axis are responsible for the various total magnetic moments of the clusters. Affected by the structures of clusters, the magnetic moments of the atoms can either strengthen or