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REGULAR ARTICLE

Geometry, electronic structure and energy barriers of all possible isomers of Fe_2C_3 nanoparticle

M. V. Ryzhkov · A. L. Ivanovskii · B. Delley

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Abstract The search for stable structures of neutral Fe_2C_3 particle was based on the geometry optimization of the known FeC_3 and Fe_2C_2 isomers with the Fe and C atoms approaching from various directions. The geometry optimization of more than 2,000 initial structures was carried out using the DFT based DMol^3 method and converged to 41 stable configurations. The structures containing C_3 triangle and the cyclic planar isomer with transannular bonds are found to have the lowest binding energies. The effective charges and total spin densities on the atoms were calculated using integral scheme incorporated in DVM and Hirshfeld procedure of DMol^3. The relations between geometrical structures and spin moments ordering are discussed. For the evaluation of potential barriers the geometry optimization of all Fe_2C_3 configurations was performed with a thermal occupation, corresponding to the various values of the excitation energy.

Keywords Fe_2C_3: stable isomers · Magnetic ordering · Potential barriers

1 Introduction

Since the discovery of the metallocarbohedrene Ti_8C_{12} in 1992 [1], the molecular systems M_xC_y became the objects of theoretical [2–5] and experimental [6–8] investigations. The electronic structure of nanoparticles containing iron atoms Fe_xC_y are also interesting for better understanding of chemical processes in the steels and other composite materials.

The serious difficulty in theoretical investigations of the stability of various Fe_xC_y clusters is the existence of a large amount of isomers for each stoichiometry (x, y) and the absence of a fast scheme for reliable generation of the ground geometrical structure. Usually the search for stable geometries results in the definition of some part of the possible isomers, the lowest-energy configuration is considered as the ground state geometry for this Fe_xC_y particle [4,5].

Earlier in the investigations of electronic structure of Fe_xC_y clusters [9] the "binomial" scheme for the generation of stable isomers was used (Fig. 1). From our point of view this scheme is a reliable way to find all possible geometries for any stoichiometry (x, y). The shortcoming of this method is the fast increasing amount of isomers as the number of atoms increases, especially for the cases $x/y \sim 1$ [9]. However, the analysis of the parentage of the ground state configurations for FeC_2, Fe_2C, FeC_3, Fe_3C and Fe_2C_2 [9] showed that in all cases the most stable isomer Fe_xC_y was obtained from the most stable configurations of both "preceding" particles $Fe_{x-1}C_y$ and Fe_xC_{y-1} by the addition of Fe or C atoms, respectively.

It is evident, that it would be more efficient to find a few lowest energy configurations by using a systematic global optimization method such as "dual minima hopping method" (DMHM) [10]. Recently this approach was successfully used for the determination of the ground state configurations of silicon clusters Si_n [11]. However, the evaluation of the energy interval of the existence of each Fe_nC_m particle requires a calculation of the energy of all possible conformations of this (m, n). It is also evident, that all isomers could be found for small clusters only. According to our experience the 5-atom Fe_xC_y particles are near the edge of the objects for

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M. V. Ryzhkov (✉) · A. L. Ivanovskii
Institute of Solid State Chemistry,
Ural Branch of the Russian Academy of Sciences,
620219, Ekaterinburg, Russian Federation
e-mail: ryz@ihim.uran.ru

B. Delley
Paul Scherrer Institut, WHGA 123,
5232 Villigen PSI, Switzerland

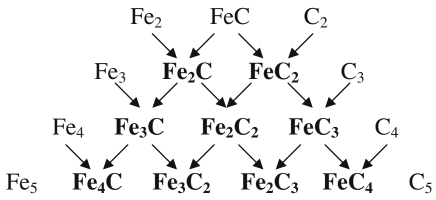


Fig. 1 The scheme for search of the stable structures for Fe_nC_m particles

which this study could be done in reasonable time. The aim of the present work is the search for all possible geometrical conformations of neutral Fe_2C_3 cluster, the evaluation of the interval of binding energies for this stoichiometry and the check-up of assumption that the ground state isomers for Fe_2C_3 could be obtained from the most stable configurations of FeC_3 and Fe_2C_2. Another aim of the work presented here is the evaluation of the energy barriers of all configurations found for Fe_2C_3 particle.

2 Objects and methods of calculations

In the present work the search for Fe_2C_3 stable structures followed the "binomial" scheme, i.e. Fe and C atom approached the all known configurations for Fe_2C_2 and FeC_3 from all possible directions. We did not take into account the "chemical preference" of some directions because when adding the extra atom on all geometrically possible sites for forming a bond the DMol^3 procedure can always "catch" any nearby configuration with local minimum of energy. The two paths of each cluster generation (Fig. 1) give one a possibility for the verification of the results. According to the previous work [9] Fe_2C_2 and FeC_3 clusters have 12 and 7 stable isomers, respectively. In both cases the definition of ground configuration was evident, since the energy difference between ground and second geometry was greater than 0.17 eV (4 kcal/mol). The shortcoming of this scheme is a large amount of initial configurations, this number increases especially for nonsymmetrical "preceding" geometries. In the present case for Fe_2C_3 we considered more than 2,000 starting configurations.

Geometry optimization of Fe_2C_3 particles was performed using the DMol^3 program [12] in spin unrestricted approach and with double numerical atomic basis set with d-polarization function for C ("dnd"). The Coulombic potential was computed with the use of model density obtained as decomposition of charge density into multipolar components including those with $l = 3$. The generalized gradient approximation (GGA) in "PBE" form [13] was used in all calculations. Optimization of the molecular structures was done until change in a value of maximum energy gradients was less than 0.001 atomic units. To confirm that the stationary points correspond to minima the vibrational frequencies were computed for all isomers obtained. In addition to the calculations of harmonic frequencies (by finite differences of 0.01 a.u.) in the case of symmetrical conformations the 0.1 a.u. shifts of atoms from their equilibrium positions were considered. The binding energy of each resulting geometry of Fe_2C_3 obtained from different starting configurations can vary within 0.22 eV (5 kcal/mol), mainly for less symmetrical structures. For smaller clusters [9] this variation was less than 0.13 eV (3 kcal/mol).

Since the DMol^3 code incorporates only the qualitative schemes of Mulliken [14] and Hirshfeld [15] for the calculation of the effective charges on atoms (Q_{eff}), we also used the discrete variational method (DVM) [16,17]. For each final configuration obtained by DMol^3 the DV calculation was carried out, where Q_{eff} is computed as the integral of electron density inside the domain bounded by the points of its minimum [18].

3 Results of geometry optimization

Initial Fe_2C_3 structures were generated from 8 FeC_3 configurations by addition of an Fe atom, and from the 12 Fe_2C_2 isomers by addition of a C atom. The atom was added to the preexisting cluster from many spatial directions. These initial configurations were subjected to geometry optimization, leading to 41 stable geometries, of which 4 were axial, 25 were planar and only 12 were three-dimensional. The shapes of these structures, their symmetry, binding energies and spin moments on Fe atoms obtained in DMol^3 calculations are listed in Table 1. We also have checked the influence of the form of the exchange-correlation potential to the stability of conformations. The use of "P91m" potential [19,20] resulted in 43 structures, however, when these particles were subjected to additional geometry optimization using "PBE" form, two configurations converged to other more stable isomers. Another question concerns the comparison of the energies of stable geometries obtained with PBE and B3LYP [21,22] functionals. Such investigation was reported by Delley [23], the results show that the evidence for better predictions of relative energies by B3LYP than PBE is rather weak.

The binding energy for the most part of the conformations lies within 0.22 eV of each other, so their order presented in Table 1 has some uncertainty. In particular, both configurations #1 and #2 could be the ground structure for the Fe_2C_3, since their energy difference is only 0.03 eV. The structure of electronic states of both "ground isomers" has also some similar features. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in both geometries are spin up and spin down, respectively. The HOMO of #1 contains 36% of Fe4p atomic orbitals (AO) with admixtures of Fe3d (27%),

Table 1 Geometry, binding energy–E_b (eV) and spin moments of Fe atoms for stable structures of Fe_2C_3 with their first excited configuration and energy edge of excitation in eV (large spheres correspond to Fe atoms and small spheres correspond to C atoms)

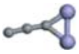
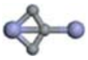
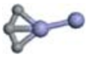
# and symmetry of isomer	Shape	Binding energy	Spin moments	Excited configuration	Excitation energy
1 C_S		−23.54	2.2 2.2	Dissociates	–
2 C_S		−23.51	2.6 1.6	Dissociates	–
3 C_{2v}		−23.39	2.3 2.3	Dissociates	–
4 C_{2v}		−23.29	2.7 2.7	#2	0.28
5 C_S		−23.09	1.9 −2.0	#1	1.43
6 C_S		−22.92	2.5 2.2	Dissociates	–
7 C_{2v}		−22.92	2.4 2.4	Dissociates	–
8 C_{2v}		−22.92	2.1 2.1	Dissociates	–
9 C_S		−22.91	2.9 −2.8	#10	0.23
10 $D_{\infty h}$		−22.70	2.3 2.3	Dissociates	–
11 C_S		−22.58	3.0 0.01	#3	1.81
12 D_{3h}		−22.42	0.0 0.0	#8	0.34
13 C_{2v}		−22.18	2.8 2.8	#10	1.97
14 C_{2v}		−22.15	3.6 2.2	#5	0.42
15 C_S		−22.14	2.6 −3.4	Dissociates	–
16 C_{2v}		−22.10	2.9 −2.7	Dissociates	–
17 C_1		−22.07	3.0 −3.0	Dissociates	–
18 C_1		−22.06	1.4 2.8	#2	0.20
19 C_S		−22.02	3.1 1.4	Dissociates	–
20 C_S		−21.98	2.9 1.3	#2	0.79
21 C_S		−21.96	2.5 −2.5	#7	0.77
22 C_S		−21.95	2.9 1.2	#8	2.31
23 $C_{\infty v}$		−21.93	3.1 –3.5	Dissociates	–
24 C_S		−21.78	1.5 3.4	#11	0.20
25 C_S		−21.77	2.9 2.7	#1	0.58

Table 1 continued

# and symmetry of isomer	Shape	Binding energy	Spin moments	Excited configuration	Excitation energy
26 C_S		−21.72	3.0 1.5	#2	0.25
27 C_S		−21.58	2.8 −1.0	#32	1.01
28 C_{2v}		−21.57	3.2 −3.4	Dissociates	–
29 C_S		−21.48	1.1 3.3	#28	0.90
30 C_S		−21.34	2.1 2.1	#2	0.23
31 C_S		−21.32	1.8 −1.4	#2	1.02
32 C_{2v}		−21.27	3.0 −2.7	Dissociates	–
33 C_S		−21.27	2.9 −2.8	#27	0.67
34 C_S		−21.26	2.9 −2.3	#2	0.53
35 C_S		−21.14	0.0 0.0	#39	1.36
36 C_{2v}		−21.06	3.2 3.5	Dissociates	–
37 C_S		−20.99	2.7 2.7	#38	2.31
38 $C_{\infty v}$		−20.82	3.0 −2.9	Dissociates	–
39 C_{2v}		−20.43	1.8 −1.0	Dissociates	–
40 C_{2v}		−19.45	3.5 1.8	#2	0.29
41 $C_{\infty v}$		−18.95	3.6 1.9	#2	0.14

Fe4s (18%) and C2p (11%) states, the LUMO is the admixtures of Fe3d (88%), Fe4s(6%) and C2p (4%) AO's. The contributions of other basis orbitals are < 1%. In the #2 the Fe3d contribution in the HOMO (35%) is greater than that of Fe4p (21%) and Fe4s (33%). The structure of the LUMO of #2 is closer to that of #1: Fe3d (73%), Fe4s (4%), Fe4p (3%) and C2p (13%).

Integral charges obtained in the DV calculations for the two most stable isomers of Fe_2C_3 are shown in Fig. 2. As can be seen, the values of $Q_{\rm eff}$ for the configuration #2 are nearly two times greater than the charges for the first structure. The comparison of integral $Q_{\rm eff}$ (presented in Fig. 2) with the Hirshfeld values shows the same trend, but the latter are noticeably less and do not exceed 0.33 e. On the other hand, the spin states of atoms and spin ordering are very similar in all isomers of Fe_2C_3 in the DV and DMol^3 calculations. The density partitioning scheme realized in the DV approach has the ability to separately integrate the spin up and spin down densities on a given atom, the difference of these values gives the total spin density ($S_{\rm eff}$) on the atom. In the both most stable isomers the ferromagnetic ordering of Fe spins is obtained. In the structure #1 the values of $S_{\rm eff}$ for both Fe atoms are nearly equal (2.6 and 2.7) in the DV and (2.2 and 2.2) in DMol^3 calculations. In the second configuration the greater $S_{\rm eff} = 2.8$ (2.6 in DMol^3) corresponds to smaller $Q_{\rm eff}$ and the metal atom with greater $Q_{\rm eff} = 0.94$ (Fig. 2) has $S_{\rm eff} = 2.3$ (1.6 in DMol^3).

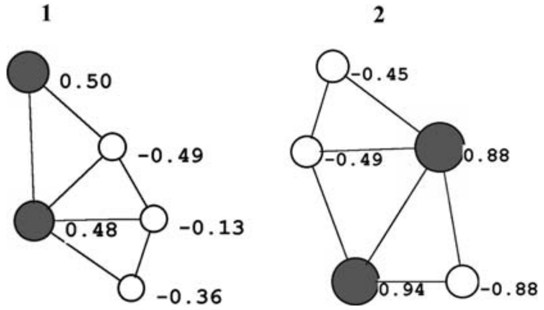


Fig. 2 The integral charges of the most stable configurations of Fe_2C_3 particle

The analysis of the total spin densities on metal and carbon sites of other 39 conformations of Fe_2C_3 shows that in the majority of cases the values of Fe spin moments are between 1.0 and 3.0, the typical values of $S_{\rm eff}$ on C atoms are within 0.1–0.2. The analysis of spin moments orientation presented in Table 1 shows, that in 23 configurations of Fe_2C_3 the total spin densities on metal sites have the same direction, i.e. the ferromagnetic ordering (FM) takes place. The antiferromagnetic ordering (AFM) of S_{eff} on metal atoms is found for 15 isomers, the most stable of them is the structure #5. There are two isomers #12 and #35 where the nonmagnetic state (NM) was obtained (i.e. the spin densities on all atoms are equal to zero). There is only one configuration #11 where the "half-magnetic" (HM) state is realized, i.e. one Fe atom is in high spin state and the second metal atom is in low spin state.

Noteworthy are the results for the more stable Fe_2C_3 and Fe_2C_2 [9] structures, for which the ferromagnetic ordering are more probable. The analysis of atomic positions and Fe spin ordering of the nine most stable Fe_2C_3 structures shows that AFM ordering takes place when the carbon atoms are located between metal sites (i.e. there is no direct Fe–Fe interaction). However, despite this rule in axial geometry #10 and planar configurations #13 and #14 the FM ordering was obtained. Since these three isomers are highly symmetrical we checked the role of symmetry constraints in the spin moments interaction. The calculations of these clusters with the same atomic positions but with molecular orbitals formally corresponding to C_1 point symmetry converged to AFM state in all these cases. Moreover, the formal symmetry reduction for bipyramidal isomer #12 changed its nonmagnetic state to AFM. On the other hand the structures #15, #23 and #28 have AFM ordering, though there are no C atoms between metal sites. The reduction of symmetry in these cases did not change the type of spin ordering. We found that FM ordering in the structures #19, #20, #22 and #26 (where there are no direct metal–metal interaction) is also independent of point symmetry. Note that in all latter cases the spin density on one Fe atom is at least two times greater than that on the second metal site. In summary, we have found seven exceptions from the simple rule connecting atomic positions and spin orientation of iron atoms.

Noya et al. [4] reported six conformations of Fe_2C_3 predicting the cyclic planar structure (#2 in our Table 1) to be the most stable. In our calculations the structure #1, where C atoms form a triangle is slightly more preferable than cyclic isomer stabilized by transannular bonds. The other five structures obtained in [4] are similar to our isomers #3, #10, #12, #23 and #37, respectively. The shapes of the latter isomer obtained in [4] and in our calculations have some difference, however, at the excitation of 1.1 eV our structure #37 became identical to that described in [4].

4 Excitation and potential barriers of Fe_2C_3 clusters

In the calculations of the ground state of the clusters we constructed the Fermi-Dirac MO occupation number vector $\mathbf{n} = (111\ldots1000\ldots)$, i.e. the lowest-energy orbitals were occupied by one electron and the molecular states with higher energies were completely vacant. Within the frame of one-electron description the excitation of cluster could be considered in two ways: (1) the absorption of energy leads to the transition of one electron to some unoccupied level (the pure excited state); (2) the excitation leads to a statistical "thermal smearing" around the Fermi level or to noninteger populations of the orbitals below and above E_F. In the present work for the investigation of potential barriers of Fe_2C_3 isomers we used the latter scheme. The change in the occupation numbers of molecular states due to thermal smearing induces the appearance of the forces between atoms in a cluster. On one hand, these forces could lead to the increase of the interatomic distances up to the values, where the atoms are practically nonbonded (i.e. to the dissociation of the particle). On the other hand, in some cases the forces could lead to the geometry transformation of the cluster, i.e. to the transition from one isomer to another. This process is analogous to the thermal annealing of the condensed matter. However, the excitation energy (per one atom) for such "phase transitions" in the small particles could be noticeably greater than in the large systems.

In the present work to evaluate the potential barriers for all configurations founded for the Fe_2C_3, the geometry optimization was performed with a thermal smearing, corresponding to the various values of the excitation energy of the electron system. The energy edge of the first transition of each isomer to any other type of geometry we consider as a measure of the potential barrier of this structure. Values of the energy barriers and the type of final configuration in the corresponding transition are also listed in Table 1. According to our results, 17 isomers do not change their geometry even for the excitations comparable with their binding energies. In these cases Fe_2C_3 clusters dissociate to the isolated Fe and C atoms, or to the Fe_2 and C_2 dimers, or to the triangular C_3 particles. As can be seen for all 24 transitions between various isomers the "geometrical parentage" of the initial and final configurations is necessary. The values of the potential barriers can be noticeably greater or less than the differences in binding energy of the corresponding isomers.

Before calculations of the energy barriers we supposed that the transitions could be from less stable to more stable configurations only. Actually in the major cases the results of calculations agree with this assumption, for instance the isomers #5 and #25 transforms to the ground geometry #1 at the excitation of 1.43 and 0.58 eV. However, the excitation of 0.23 eV of the isomer #9 induces the transition to the structure, which is similar to that of #10, but with greater interatomic distances. Such interconversions were found also for the isomers #27, #35 and #37. In the former case the more stable structure #27 at ~1.01 eV transforms to the isomer #32, the structures #35 and #37 converge to #39 and #38, respectively. As can be seen from Table 1, the excitation of all these final isomers leads to the dissociation of the cluster. The analysis of the transitions between Fe_2C_3 geometrical structures shows that all final isomers agree with the two rules.

1. The final and initial configurations have "geometrical parentage".
2. The final configurations have high potential barriers, at least these barriers are higher than that of the initial structure.

Finally we analyzed the influence of the excitation on the ordering of magnetic moments. It is evident, that statistical "thermal smearing" leads to the equality of spin up and spin down MO populations. In our calculations the excitation of 0.8 eV induces the transition to NM state of the absolute majority of the configurations. Only the isomers #16, #19, #23, #36 and #38 are exceptions to this rule, the structures #16, #19 and #38 transform to HM state and become completely nonmagnetic at the excitation greater than 0.9 eV. The isomer #23 at 0.8 eV is still in AFM state (the same as at zero temperature). The most surprising results were obtained for the structure #36, which transforms to the AFM state from the FM ordering (in the ground state) at the excitation of 0.5 eV and remain this orientation up to the excitation of 0.9 eV. The examples of the transitions from AFM to FM ordering have been also found. The nonsymmetrical isomer #17 as well as more symmetrical structures #27, #31, #33 and #32 (with C_{2v} symmetry) change their magnetic structure from AFM to FM type at the excitations nearly 0.4–0.5 eV. Another way to change the spin moment ordering was found for the isomer #14. This configuration is in FM ground state and does not change it during the transformation to the configuration #5 at 0.42 eV, whereas the excitation of the fifth isomer does not change its AFM state up to the energy of 0.6 eV.

5 Conclusions

Our investigations of Fe_2C_3 nanoparticles confirm the earlier results for 3- and 4-atom Fe_xC_y clusters [9] that the ground state (or states) in any case can bee generated from the ground configurations of both $Fe_{x-1}C_y$ and Fe_xC_{y-1} preceding particles by addition of Fe and C atoms respectively. This procedure is a reliable way to find the ground state geometry for large Fe_xC_y clusters.

The Fe_2C_3 ground state binding energy per atom ($\sim$4.7 eV) is greater than this value for Fe_2C_2 (4.25 eV) but is less than those for FeC_3 (4.93 eV) and C_3 (4.99 eV) particles [9].

Our results for the excited states of Fe_2C_3 geometrical structures show that for the majority of configurations the potential barriers are greater than 1 eV. This energy appeared to be the critical point for the transitions from magnetic to nonmagnetic state for all Fe_2C_3 clusters.

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