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Equilibrium structure and bonding of small iron–carbon clusters

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The equilibrium geometries, binding energies, and electronic structure of neutral FeC_n ($n \leq 3$) clusters have been calculated self-consistently using *ab initio* molecular orbital theory. The exchange and correlation contributions to the total energy were computed using both the density functional method (with and without nonlocal correction) as well as the Hartree–Fock–Möller–Plesset theory. All levels of theory predict the equilibrium geometries to be cyclic. The binding energies, bond lengths, and the Mulliken charges obtained from both methods of calculations are also in agreement. The results are compared with recent mobility and photoelectron spectroscopy experiments. © 1996 American Institute of Physics. [S0021-9606(96)02048-X]

INTRODUCTION

The last two decades have witnessed an upsurge in the interest in atomic clusters.¹ While a large body of work on atomic clusters is confined to the study of homonuclear clusters, not much is known on the properties of compound clusters. This is particularly important since in small clusters even a single heteroatom can cause a substantial change in the atomic and electronic structure of the “host” cluster. In this regard, the interaction of carbon clusters with transition metals poses a specially interesting problem. In the bulk phase, carbon–transition metal systems form very stable carbides with rather high melting temperatures. However, in clusters the composition of carbon and transition metal atoms that exhibit unusual stability is not always the same as what one finds in the bulk phase. For example, Castleman and co-workers² have discovered that Ti_8C_{12} and V_8C_{12} are extremely stable. After their experiments, many other transition metals³ (e.g., Cr, Fe, Mo, Zr, Hf), have also been observed to exhibit unusual stability at the same composition, namely, M_8C_{12} .

The iron–carbon systems are, however, unlike other transition metal–carbon systems. For example, the mass spectra of Fe_xC_y clusters show pronounced stabilities⁴ for $(x,y)=(7,8)$ and $(12,12)$ in addition to the above mentioned “magic number” of $(8,12)$ for Ti–C and V–C systems. In the bulk phase, formation of Fe_3C is endothermic and it easily decomposes to iron and graphite.⁵ These anomalies have prompted a systematic experimental study of the electronic structure of Fe_xC_y clusters in their neutral and anionic forms.

Von Helden *et al.*⁶ have studied the structures of Fe_nC_m ($n=1,2,3$ and $m=2-8$) using gas phase ion chromatography. In FeC_m^- clusters, the structures are linear for $m \leq 4$ while larger clusters exhibit cyclic structures. As the Fe content increases, the clusters convert from two dimensional to three dimensional structures. That the Fe content substantially modifies the structures and properties of carbon clusters can be seen by comparing the evolution of geometry of C_n^- clusters with those of FeC_n^- clusters. Clusters of C_n^- are linear for $n < 10$. Beyond this size, cyclic structures of C_n^- begin to appear.⁷ However, adding a single Fe atom changes the onset of this linear to cyclic structure from $n=10$ to $n=4$.

Fan *et al.*^{8,9} have studied the electronic and vibrational structures of FeC_n^- ($n \leq 4$) clusters by using photoelectron spectroscopy. The photoelectron spectra for FeC_2^- and FeC_3^- show two broad peaks. This Franck–Condon broadening carries with it the signatures of the relative changes in the geometries of the anionic and the neutral clusters. In general, the geometries of anionic and neutral clusters are different. As an electron is detached from the anionic cluster by crossing the cluster beam with a fixed frequency photon beam, the remnant neutral cluster is left in an excited state which approaches the ground state through a progression of vibronic states. The broadening results if the ground states of anionic and neutral clusters have different geometries. Since the anionic clusters in this size range are known from earlier experiments⁶ to be linear, one could conclude that the geometry of neutral FeC_n ($n \leq 4$) clusters are cyclic.

However, the theoretical results of Fan *et al.*⁹ provide a conflicting picture of the geometry of the neutral FeC_n clusters. These authors have calculated the equilibrium geometries using the molecular orbital theory where the atomic orbitals forming the cluster wave function are taken to be of the numerical form. The authors have used the density functional theory and two forms for exchange–correlation potential: the local density approximation (LDA) and the nonlocal correction. While the LDA theory yielded cyclic structures for neutral FeC_3 and FeC_4 , the linear structures were preferred when nonlocal exchange–correlation potential was used. As mentioned earlier, the neutral structures consistent with the photoelectron spectra should be cyclic. It is this discrepancy that has lead us to examine theoretically the equilibrium structures and relative stabilities of FeC_n ($n \leq 3$) clusters.

THEORETICAL PROCEDURE

Our theoretical procedure is based on two different approaches. In the quantum chemical approach we use the self-consistent field linear combination of atomic orbitals–molecular orbital (SCF-LCAO-MO) method.¹⁰ In this case we use the Hartree–Fock (HF) theory to calculate the electrostatic and exchange contributions to energy. The self-consistent energy calculated by this process still needs to be

TABLE I. Test of basis sets: Comparison of calculated ionization potentials (difference between the ground state energies of the atom/cluster and the corresponding cation), binding energy, and bond length of C and Fe dimers.

System	Property	Level of theory			Expt.
		LDA	NL	HF-MP4	
C ₂	I.P. (eV)	12.52	11.79	11.36	12.15
	B.E. (eV)	7.62	6.51	5.70	6.08
	R _e (Å)	1.32	1.33	1.34	1.31
	Multiplicity	3	3	3	3
Fe ₂	R _e (Å)	1.96	2.01		1.73–2.04
	B.E. (eV)	3.54	2.26		0.61–1.28
	Multiplicity	7	7		7

corrected for the correlation effects between two electrons which has been approximated by the HF theory. We have chosen to use the Möller–Plesset perturbation theory¹⁰ upto the fourth order (MP4) for this correction. The quantum chemical method as discussed is computationally very demanding.

The other method used by us is based on density functional theory (DFT).¹¹ This method groups together the spin exchange and the effect of correlation as exchange–correlation (XC). In spite of the simplification for the XC energy, density functional theory used with the local density approximation (LDA)¹² has been very successful¹³ in calculating properties of atomic clusters although there are cases¹⁴ where the LDA is inadequate in explaining experimental results. Efforts^{15,16} have been made to go beyond LDA by including gradient corrections. In our calculations we have used the nonlocal (NL) method due to Becke¹⁵ in addition to the standard LDA method to obtain the total energies. Computationally, the LDA and the NL versions of the DFT are less demanding than the HF-MP4 formalism.

Starting with the same atomic basis functions we have calculated the geometries and energetics of FeC_n ($n \leq 2$) clusters using HF-MP4, LDA, and NL methods. Comparison of these results illustrates the accuracy of the DFT based methods. For FeC₃, we have used the LDA and the NL methods.

Unlike the calculation of Fan *et al.*,⁹ in all our calculations, the atomic orbitals are expressed as linear combinations of Gaussians. This helps improve the accuracy of the results as the integrals are obtained analytically. The GAUSSIAN 94 software¹⁷ designed for integral spin multiplicity has been used for our calculations. The equilibrium geometries were obtained by calculating the gradient forces and allowing the structures to change until the forces vanished. Several initial configurations as well as spin multiplicities were tried to ensure that we have located the global minimum structure with the correct spin configuration. In such calculations, the choice of the atomic basis is of importance. We have used (9s5p1d/3s2p1d) basis functions for C and (13s8p5d/5s3p3d) basis functions for Fe. This choice was found to be satisfactory in explaining the ionization potentials, binding energies, and bond lengths of C₂ and Fe₂. The results are given in Table I and compared with experimental values.^{18–22}

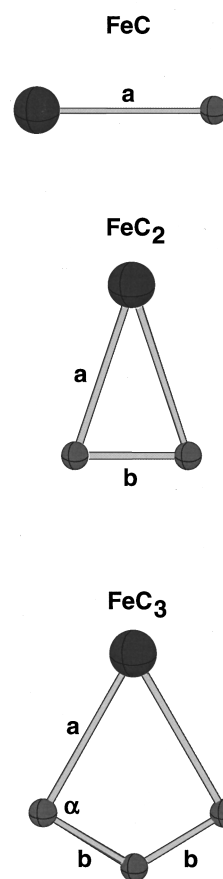


FIG. 1. Optimized geometries of FeC_n ($n \leq 3$) clusters.

RESULTS AND DISCUSSIONS

In the literature, the experimental binding energies of C₂ for a single, double, and triple bond are quoted as being 3.6, 6.2, and 8.4 eV, respectively.¹⁸ The corresponding bond lengths^{18,19} are 1.54, 1.33, and 1.21 Å. Detailed experiments²⁰ report the values for the binding energy for the double bonds as 6.08 eV with a corresponding bond length of 1.31 Å. Note that the results in Table I are in good agreement with experiment²⁰ for the double bond of C₂. The variation in the binding energy from LDA to nonlocal correction to HF-MP4 is as expected. The local density overbinds while the quantum chemical methods underbind. The result based on the nonlocal correction is in between and is also closest to the experimental value. For Fe₂ the bond length of 2.01 Å obtained using the nonlocal version of the theory is in close agreement with the nonlocal result of 2.00 Å by Castro and Salahub.²³ The bond length of Fe₂ measured²¹ in the neon matrix is 2.02 Å. Other available values²² for the bond lengths of Fe₂ range from 1.73 to 2.04 Å. The binding energies²² range between 0.61 and 1.28 eV. The preferred spin multiplicity of 7 is also in agreement with experiment²² as well as the work of Castro and Salahub.²³ Note that Fe₂ is not bound at the current HF-MP4 level of theory.

The equilibrium geometries of FeC_n ($n \leq 3$) clusters are shown schematically in Fig. 1. The corresponding geometri-

TABLE II. Binding energies, geometrical parameters, and spin multiplicities of FeC_n ($n \leq 3$) clusters. Refer to Fig. 1 for geometrical parameters.

System	Property	Level of theory		
		LDA	NL	HF-MP4
FeC	a (Å)	1.54	1.57	1.92
	B.E. (eV)	6.21	4.94	4.14
	Multiplicity	3	3	3
FeC ₂	a (Å)	1.71	1.89	1.93
	b (Å)	1.38	1.31	1.30
	B.E. (eV)	13.89	11.58	11.58
	Multiplicity	3	5	5
FeC ₃	a (Å)	1.73	1.78	
	b (Å)	1.36	1.37	
	α	72.4°	72.8°	
	B.E. (eV)	22.03	18.09	
	Multiplicity	3	3	

cal parameters, preferred spin multiplicities, and binding energies are given in Table II. All levels of theory predict the *same* geometry, namely, *cyclic* for FeC_2 and FeC_3 . This is in contrast to the work of Fan *et al.*⁹ where the structures were linear in nonlocal and cyclic in LDA version of the density functional theory. The fact that the Hartree-Fock theory with Möller-Plesset treatment of correlation provides the same result as those based on our density functional calculations gives us additional confidence in our statement that the equilibrium geometries of neutral FeC_n clusters are cyclic. We now discuss the results on each cluster individually.

The binding energy of FeC ranges from 6.21 to 4.14 eV depending on the level of theory. However, the corresponding bond lengths vary little. Assuming integral spin, the spin multiplicity is triplet at all levels of theory. An analysis of the Mulliken population for the spin up and the spin down states reveals that the magnetic moment of $2 \mu_B$ lies primarily at the Fe atom. It is also interesting to note that the binding energy of FeC is about 1 eV lower than the binding energy of C_2 , irrespective of what level of theory one uses. This observation will be shown to have significant impact on the equilibrium geometries of FeC_2 and FeC_3 in the following.

Consider first the case of FeC_2 . The structure can either be linear or cyclic. In the linear structure the Fe atom can either insert itself into carbon-carbon bond forming $\text{C}=\text{Fe}=\text{C}$ structure or can attach to one end of the C_2 dimer forming $\text{Fe}-\text{C}\equiv\text{C}$ structure. The first one is unfavorable as the C_2 bond is stronger than the FeC bond. Thus one needs to compare the energetics of linear structure of FeC_2 where the Fe atom attaches to an end-on position with the cyclic structure. In the linear structure the C-C bond is a triple bond while in the cyclic structure the C-C bond is a double bond and, as mentioned before, the triple bond is favored by an energy of 2.2 eV. However, in a cyclic structure there are two Fe-C bonds and, as we have seen before, these energies range between 6.21 to 4.14 eV depending on the level of theory. Thus this simple minded comparison already demonstrates that the most likely structure of FeC_2 is cyclic. This is, indeed, what our self-consistent calculations yield. To verify

this further we confined FeC_2 in a linear structure and optimized the Fe-C and C-C distances. The bonds between Fe-C and C-C at the HF-MP4 level of theory are 2.0 and 1.22 Å, respectively, and the structure lies 3.1 eV above the cyclic structure. The magnetic moments are again confined at the Fe site. The C-C bonds at all levels of theory (see Table II) remain very close to the double bond value of 1.33 Å while the Fe-C bonds are slightly stretched. There is a discrepancy among the various levels of theory concerning the preferred spin multiplicities of FeC_2 . The nonlocal and HF-MP4 levels of theory predict a quintet ground state in contrast to the triplet state predicted by the LDA. However, the triplet-quintet energies are rather close. For example, at the nonlocal level of theory, the triplet state is only 0.2 eV above the quintet state.

For FeC_3 we have optimized the geometries only at the density functional level as the HF-MP4 level of theory is computationally very demanding. Both the LDA and nonlocal exchange level of theory predict the structure to be cyclic. The geometrical parameters are in close agreement with each other as are the preferred spin multiplicities. We have also forced the structure to be linear and optimized the bond distances. At the nonlocal exchange level, the linear structure is higher in energy by 0.5 eV. Thus we conclude that the equilibrium structures of neutral FeC_n are *cyclic*. Since the FeC_n^- ($n \leq 4$) are linear, the broadening of the photodetachment peaks can be easily understood to be due to structural changes. We are currently studying the energetics and equilibrium geometries of FeC_n^- clusters with a view to understanding the photodetachment spectroscopy experiments. The results will be published in due course.

CONCLUSIONS

The equilibrium geometries, total energies, and electronic structures of FeC_n ($n \leq 3$) clusters have been calculated using three levels of theory: Hartree-Fock-Möller-Plesset fourth order perturbation, local density approximation, and nonlocal correction to the density functional theory. All levels of theory predict the structure of neutral FeC_n to be cyclic. This is consistent with the experimental broadening observed in the photodetachment of FeC_n^- clusters. The density functional theory is found to be accurate in explaining the experiment and can be used to study larger clusters of FeC_n reliably where the quantum chemical approach can be computationally prohibitive. All the clusters have nonvanishing magnetic moments which are primarily located at the Fe site.

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