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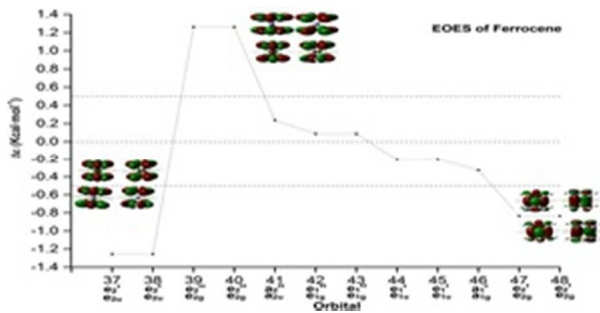


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The EOES($\epsilon_i = \epsilon_i(E-Fc) - \epsilon_i(S-Fc)$) shows that the orbitals with significantly excess energies are Fe d-electron dominant.
79x39mm (96 x 96 DPI)

The *d*-electrons of Fe in ferrocene: the excess orbital energy spectrum (EOES)

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Abstract

The d-electrons of transition metal Fe play a significant role characterising properties of the ferrocene (Fc) eclipsed (E) and staggered (S) conformers and their chemical bonding, which must be appropriately included in the basis set for Fe, in addition to the level of theory. The present density function theory (DFT) based B3LYP/m6-31G(d) model has successfully calculated accurate infrared (IR) spectra of ferrocene without scaling (Mohammadi et al., 2012). The present study introduces an excess orbital energy spectrum (EOES) in order to assess more detailed orbital based information of ferrocene between the conformers, which is contained in this model. It is revealed that the d-electrons of Fe show significantly larger electron correlation energies than other electrons of Fc, which contains the key information for the conformers, and not all the d-electrons of Fe play the same role in the conformer pair of Fc. Inclusion of electron correlation energy in the model, theory as well as the basis set, therefore, becomes critically important to produce reliable and useful results for Fc. It further reveals that the Fe-dominant

orbitals, i.e., $4a_1'$ (i.e. MO 16), $3e_1'$ (MO 18-19), $3e_2'$, $3e_2''$ (MO 37-40) and $4e_2'$ (HOMO, i.e., MO 47-48), which are all dominated by d-electron contributions from Fe, exhibit excess orbital energies larger than their total electronic energy difference between conformers. Finally, the present study suggests that the covalent bonding character exists in the Fe-Cp bonds of Fc, which may help explain the reason of high thermal stabilities of Fc.

Keywords: Ferrocene, eclipsed and staggered conformers, excess orbital energy spectrum, Fe-d-electron dominant orbitals, covalent chemical bonding and quantum mechanical calculations

1. Introduction

The significance of the discovery of ferrocene,¹ i.e., di-cyclopentadienyl iron (η^5 , FeCp_2 or Fc) is not only a landmark for organometallic chemistry and an immense number of applications, but also in its own right for the study of chemical bonding and electron correlation models. The ground electronic state (S_1) conformation of Fc due to the orientation of two parallel cyclopentadienyl (Cp) rings of Fc, which give the eclipsed (E) or staggered (S) conformers, is surprisingly difficult to resolve unambiguously in both theory and experiment. The extremely small difference in energy between the conformers (ca. $0.9 \pm 0.3 \text{ kcal}\cdot\text{mol}^{-1}$ using electron diffraction in gas phase),² and the low energy barrier for the rotation of a cyclopentadienyl ring relative to the rest of the molecule,^{3,4} coupled with the high point group symmetry for both conformers all contribute to such the challenge. The high D_{5h} and D_{5d} point symmetries of Fc lead to $D_{5h} \rightarrow C_s \rightarrow C_{2h}$ and $D_{5d} \rightarrow C_i \rightarrow C_{2h}$ in crystal selection rules⁵⁶ and results in the exact one-on-one correspondence of their ground electronic configurations. It basically eliminates the

point group symmetry option to characterize the conformers. This is manifest in the experimental studies of Fc since its discovery.¹ The debate on the most stable conformer of Fc, whether it is the eclipsed (E) or the staggered (S), with both experimental and other information,^{2,5-7} has been continuing without conclusive evidences until our most recent study.⁸ Since 2003, “Ferrocene Colloquium”,⁹ an European ferrocene symposium, has been held annually over a decade.

Despite significant advances in experimental techniques which have been employed to study Fc, it is not sufficient to understand its structures and properties based on experiment alone. The pair of important conformers of Fc, i.e., the eclipsed (E) Fc which exhibits the D_{5h} point symmetry and the staggered (S) Fc which shows the D_{5d} point symmetry, brings the challenge to organometallic chemistry for over half a century. Detailed structural understanding of the Fc conformers is very important as Fc derivatives may inherit particular properties which only exist in a particular conformer.⁴ For example, additional ligands coordinating to the metal and the Cp rings while maintaining certain symmetry is preferred for the geometry of the D_{5h} conformer.¹⁰⁻¹² Design of synthesis pathways and understanding of the mechanics and reaction dynamics of the Fc derivatives such as catalysts require detailed information of the structure, symmetry and properties of the Fc conformers. The stability of E and S conformers of Fc has been a challenge issue, and both structures were discussed in textbooks.¹³⁻¹⁵ Recent articles such as Duhovic and Diaconsecu¹⁰, Coriani et al¹⁶, Roy et al¹⁷, Gryaznova et al¹², Bean et al¹⁸, Frenking and co-workers¹⁹⁻²¹ and Cortes-Guzman and Bader²² have well documented the history and current status of Fc studies.

Structures and properties of the staggered (S) and eclipsed (E) conformers of Fc are markedly similar. As indicated by Coriani et al¹⁶, Fc is a “notoriously difficult example” as it contains transition metal Fe which leads to much larger errors because of more complex bonding situations and its d-electrons. The differences between the calculated properties of the Fc conformers, such as energetics, Fe-Cp bond length, rotational constants and total electronic energies etc, are only subtle so that it is very difficult to differentiate them in both experiment and theory.⁸ In addition, the fact that ferrocene is a Jahn-Teller effect inactive molecule,²³ also contributes to this challenge. As a result, previous studies of Fc equilibrium structure are largely contradictory.⁵⁻⁷ The debate of ferrocene equilibrium structure continues. As a result, either E-Fc or S-Fc has been arbitrarily employed to present the structure of Fc since the Fc discovery. Although many recent quantum mechanical studies using high level post-HF methods, such as MP2, CCSD and CCSD(T) in combination with large basis sets such as TZV2P+f¹⁶ and using various DFT models including B3LYP, BLYP, BP86, LSDA²⁴ and BPW91¹² models, the puzzle of E-Fc or S-Fc remains. Nevertheless, all consistently suggested that the eclipsed Fc is likely the global minimum structure of Fc in its ground electronic state (S_1).^{8,16,17,19,25}

In our recent DFT based infrared (IR) study of Fc, it revealed that the IR spectral splitting within the region of 400-500 cm^{-1} is the signature region for the coexistence of the E and S Fc conformers in gas phase.⁸ That is, the IR spectrum in this region brings a clue to identify ferrocene conformers.⁸ It was further demonstrated that the vibrations of Fc in this region are dominated by the skeletal modes (i.e., the inter-Cp ring modes, which are the movements of the Cp-ligands relative to the centre Fe atom),^{26,55} which represents the major conformational differences between the E-Fc and S-Fc.⁸ This IR peak of the S-Fc conformer presents as a single

IR peak, which in fact consists of three closely positioned vibrations with a doubly degenerate and a single vibrations.⁸ The IR spectral splitting in E-Fc has been measured in a number of experimental IR spectra including the early IR measurements of Fc of Lippincott and Nelson.²⁷⁻²⁹ However, such the signature of ferrocene conformers has been largely ignored in the past.⁵⁵

The chemical bonding concept has been “reserved for use by those who intent on the pursuit and understanding of chemistry using the tools of quantum mechanics”.²² Molecular properties are governed by the electron density distribution and chemical bonding.³⁰ Thus, the methods that deal with the analysis of the electron density distribution should have a particular appeal for chemists and help to understand the electron structure of molecules and thus interactions. The high thermal stability of ferrocene (upto 400°C) indicates that the chemical bonding of the complex is unique as transition metal-carbon bonds are usually unstable.²³ Important information about the charge distribution and about its changes due to intermolecular interactions can be obtained by means of molecular orbitals. In the present study, we introduced an excess orbital energy spectrum (EOES) of ferrocene conformers (E-Fc and S-Fc), in order to identify the differences between the conformers and their unique chemical bonding.

2. Computational methods

As indicated before,⁵⁶ the option of quantum mechanical models employed in a study depends on a number of factors such as the molecular systems under study, the properties of the target molecules and the computational resources etc. In this study, it is to reveal the reasons why the B3LYP/m6-31G(d) model provides the most accurate IR spectrum of Fc, over a number of methods including post-HF and other DFT methods including CAM-B3LYP. In addition, the

B3LYP model is among the best methods for accurate IR spectra of molecules and provides the appropriate shape for molecular orbitals.⁵²⁻⁵³

The optimized geometries of Fc (both E and S conformers) were the same as those in gas phase,⁸ which were obtained using the density functional theory (DFT) based B3LYP theory, in conjunction with the recently developed basis set for the transition metal Fe, that is, the m6-31G(d) basis set.³¹ This basis set incorporates necessary diffuse d-type functions for the Fe transition metal, so that it ensures a better performance than the conventional 6-31G(d) basis set for the iron atom of Fc, by providing a more appropriate description for the important energy differences between the atomic $3d^n4s^1$ and $3d^{n-1}4s^2$ configurations.³¹⁻³² Although other basis sets such as DFT basis set DZVP-D are available for transition metals,⁵¹ it is this basis set, i.e., m6-31G(d), in combination of the B3LYP model which produced the most accurately calculated IR spectra for ferrocene, in excellent agreement with IR measurements *without scaling*, and identified the spectral splitting in $400\text{-}500\text{ cm}^{-1}$ region for the signature of Fe-related vibrations of E-Fc and S-Fc.⁸ Other factors such as long range dispersion forces^{46-48,51} and relativistic effects are expected to be very similar in the conformers and therefore, would not play significant roles in the present calculations for the excess energies of E-Fc and S-Fc. Such effects are expected to be very similar in E-Fc and S-Fc so that can be cancelled out when the differences between E-Fc and S-Fc are considered. As indicated by Salzner,²⁵ that the results with relativistic pseudo-potentials did not show apparent differences.³³⁻³⁴

The concept of an excess orbital energy spectrum (EOES) of ferrocene conformers was inspired by the excess infrared spectroscopy of Yu and co-workers.³⁵ The EOES is defined by the orbital electronic energy differences ($\Delta\varepsilon_i$) between the corresponding orbital energies of the E-Fc and S-

Fc conformers, i.e., $\Delta\varepsilon_i = \varepsilon_i^{\text{E-Fc}} - \varepsilon_i^{\text{S-Fc}}$. In this study, the HF/m6-31G(d) and B3LYP/m6-31G(d) models were employed for comparison purposes and to learn the role of electron correlation effect in the EOES of Fc. All calculations were based on the B3LYP/m6-31G(d) optimized structures of E-Fc and S-Fc and were performed using the Gaussian09 computational chemistry package.³⁶

3. Results and discussion

Conformational analyses of molecules reveal that the shape of the target molecule and its orbitals are critically important for anisotropic properties. DFT models are not variational. As a result, the model which produces the lowest total electronic energy and accurate isotropic properties are not necessarily the best model to produce accurate anisotropic properties such as the shape of the molecule and molecular orbitals (e.g. orbital momentum distributions).^{52-53,56} Theoretical studies often concentrate on the level of theory, i.e., the exchange-correlation potential of the target systems^{26,33-34} “depending on the choice of the post-HF method that is used for describing the long range interaction, and the choice of the exchange-correlation functional used for treating the short-range interaction”.³⁴ More recently, Salzner²⁵ demonstrated that the excitation energies of Fc are dependent on both the level of theory as well as the basis sets employed. The ferrocene IR spectral study indicates that inclusion of the diffuse functions in the basis set of transition metal iron (Fe) play a vital role to accurately calculate the IR spectra and other properties of ferrocene, in addition to the level of theory.⁸

It is discovered that the m6-31G(d) basic set is particularly suitable to the iron atom for accurate IR spectrum of Fc⁸ (without any scaling) than many other basis sets such as the TZV2P+I¹⁶,

DZP²⁴, DZVP⁵¹, LANL2DZ¹² and 6-31G*¹⁰. Table 1 compares important properties such as Fe-C and Fe-Cp distances and other geometric and energetic properties of E-Fc (D_{5h}) and S-Fc (D_{5d}), respectively, in vacuum using various models. As noted before,⁸ the optimized geometric parameters for the Fc conformer pairs are almost identical if the same model is employed. For example, all C–C bonds in E-Fc and S-Fc are given by 1.428Å and all the C–H bonds are reported as 1.082Å, using the B3LYP/m6-31G* model. The hydrogen atoms in Cp are not in the same plane with the C_5 pentagon ring but slightly bend towards the centre. However, calculations indicated that this angle in gas phase is much smaller than the crystalline structure of D_{5h} of Fc (i.e., $\angle C_5-H = 3.7 \pm 0.9^\circ$).³⁷ This angle was calculated as $\angle C_5-H = 0.66^\circ$ in B3LYP/m6-31(d)⁸ and 1.03° in CCSD(T)/TZV2P+f¹⁶. The same angle in S-Fc (D_{5d}) is slightly larger, as 0.92° and 1.34° , respectively using the B3LYP/m6-31(d)⁸ and CCSD(T)/TZV2P+f¹⁶ models. Such small differences in the geometric properties of Fc are hardly measureable conclusively. As a result, other properties of the conformer which are able to indicate the Fc conformational differences need to be explored.

Ground state configurations of ferrocene conformers

The ground electronic state configurations of the E-Fc and S-Fc conformers depend on the exchange-correlation energy in the models and basis sets. The E-Fc (D_{5h}) and S-Fc (D_{5d}) share a common set of symmetric operations of C_s , C_2 , C_5 , D_5 , C_{5v} ; except for C_{2v} and C_{5h} for D_{5h} and C_i and S_{10} for D_{5d} . The high symmetry results in one-on-one correspondence of the irreducible representations of their orbitals of E-Fc and S-Fc. As a result, the ground electronic configuration of Fc which favours a lower spin state (S_1)¹² has 48 occupied molecular orbitals (MOs). Among

these orbitals, there are 15 core orbitals (which are occupied by 20 carbon 1s electrons and 10 Fe 1s, 2s and 2p electrons) and 33 valence orbitals (including doubly degenerate orbitals).

The electronic ground configurations of E-Fc and S-Fc conformers using the HF/m6-31G(d) model are given by,

E-Fc (D_{5h} , X^1A_1):

Core orbitals:

$$(1a_1')^2(2a_1')^2 (1a_2'')^2 (1e_1')^4 (3a_1')^2(2a_2'')^2 (2e_1')^4 (1e_1'')^4 (1e_2'')^4 (1e_2')^4 \quad (1a)$$

Inner valence orbitals:

$$(4a_1')^2 (3a_2'')^2 (3e_1')^4 (5a_1')^2 (4a_2'')^2 (2e_1'')^4 (4e_1')^4 (2e_2')^4 (2e_2'')^4 (6a_1')^2 (5a_2'')^2 (7a_1')^2 (3e_1'')^4 (5e_1')^4 \quad (1b)$$

Outer valence orbitals:

$$(3e_2')^4 (3e_2'')^4 (8a_1')^2 (6a_2'')^2 (4e_2')^4 (6e_1')^4 (4e_1'')^4 (7e_1')^0 \quad (1c)$$

and

S-Fc (D_{5d} , X^1A_{1g}):

Core orbitals:

$$(1a_{1g})^2 (2a_{1g})^2 (1a_{2u})^2 (1e_{1u})^4 (3a_{1g})^2 (2a_{2u})^2 (2e_{1u})^4 (1e_{1g})^4 (1e_{2u})^4 (1e_{2g})^4 \quad (2a)$$

Inner valence orbitals:

$$(4a_{1g})^2 (3a_{2u})^2 (3e_{1u})^4 (5a_{1g})^2 (4a_{2u})^2 (2e_{1g})^4 (4e_{1u})^4 (2e_{2g})^4 (2e_{2u})^4 (6a_{1g})^2 (5a_{2u})^2 (7a_{1g})^2 (3e_{1g})^4 (5e_{1u})^4 \quad (2b)$$

Outer valence orbitals:

$$(3e_{2g})^4 (3e_{2u})^4 (8a_{1g})^2 (6a_{2u})^2 (4e_{2g})^4 (6e_{1u})^4 (4e_{1g})^4 (7e_{1u})^0 \quad (2c)$$

Here the e -orbitals are doubly degenerate and the correlations between the orbital irreducible representations between E-Fc (D_{5h}) and S-Fc (D_{5d}) are on a one-on-one base, such as ' and " in D_{5h} but as g and u in D_{5d} .⁵⁶ The S-Fc configuration in Eq (2) is in agreement with the HF model of Cortes-Guzman and Bader²² and Fromager et al³⁴. Among the 15 core orbitals of Fc, the first 5 orbitals with the lowest orbital energies are dominated by the Fe atom and the next 10 orbitals, i.e. orbitals 6-15 are dominated by the 20 C1s electrons of the 10 carbon atoms in the ligand (2Cp). The molecular orbitals (MO) in the ground electronic states of E and S conformers are correlated as a_1' - a_{1g} , a_2'' - a_{2u} , e_1' - e_{1u} etc.⁵⁶ The highest occupied molecular orbitals (HOMOs) of E-Fc ($4e_1''$) and S-Fc ($4e_{1g}$) obtained using the HF model are doubly degenerate e -orbitals. Among the highlighted outer valence orbitals in Eqs (1c) and (2c), three of them are metal (Fe) d -electron dominant orbitals with the energy ordering of

$$\text{HF: } 8a_{1g}(8a_1') (d_{z^2}, \sigma) < 4e_{2g}(4e_2') (d_{x^2-y^2}, d_{xy}; \delta) < 4e_{1g}(4e_1'') (d_{xz}, d_{yz}, \pi) \quad (3)$$

with the HOMO ($4e_{1g}(4e_1'')$) predominately being the Cp-centred and Fe π -orbitals, in agreement with previous studies.^{22,34}

The ground electronic configuration of a molecule is an energy sequence of occupied orbitals based on their orbital energies. In valence space, the energy intervals between the orbitals are very small, inclusion of exchange and correlation energies in the model (theory or basis set) can alter valence orbital energy sequences and therefore result in different electronic configurations. The electron correlation energy of E-Fc and S-Fc obtained from the DFT based B3LYP/m6-31G(d) model reshuffles the outer valence orbital energies obtained using the HF/m6-31G* model shown above. As a result, the ground electronic state (S_1) configurations of Fc calculated

using the B3LYP/m6-31G(d) model differ in the low energy valence region of < 10 eV (absolute values) as

E-Fc (D_{5h} , X^1A_1):

$$(\text{core}) \dots (3e_2')^4 (3e_2'')^4 (6a_2'')^2 (4e_1'')^4 (6e_1')^4 (8a_1')^2 (4e_2')^4 (5e_1'')^0 \quad (4)$$

and

S-Fc (D_{5d} , X^1A_{1g}):

$$(\text{core}) \dots (3e_{2u})^4 (3e_{2g})^4 (6a_{2u})^2 (4e_{1g})^4 (6e_{1u})^4 (8a_{1g})^2 (4e_{2g})^4 (5e_{1g})^0 \quad (5)$$

The obtained outer valence configuration of Fc in present study agrees with the most recent B3LYP/6-31+G(d) calculations of Salzner²⁵ for E-Fc and BP86/TZP calculations of Atkins et al³⁸ for S-Fc. As a result, further bonding analysis of ferrocene conformers will be based on the results from the B3LYP model rather than from the HF model.

While the core and inner valence orbitals of the Fc obtained using the B3LYP/m6-31G* model remain the same configurations as their corresponding HF/m6-31G(d) results, the outer valence orbitals are very different. For example, the HOMO of E-Fc from the HF model is given by orbital $4e_1''$ which is the fourth HOMO (i.e., HOMO-3) in the B3LYP models. The HOMO of E-Fc is given by orbital $4e_2'$ in the present B3LYP/m6-31G(d) model which is the bonding combination of Fe d- and Cp-LUMO orbitals, in agreement with the B3LYP/6-31+G(d) model.²⁵ Similarly, the corresponding correlation for the HOMO of S-Fc is given by $4e_{2g}$ orbital from our B3LYP/m6-31G(d) model, in agreement with the BP86/TZVP model.³⁸ It indicates that the small orbital electron correlation energies included in the DFT models are sufficiently large to alter the valence orbital configurations of Fc. The reshuffle of the orbital energy configuration leads to

$$\text{B3LYP: } 4e_{1g}(4e_1'') (d_{xz}, d_{yz}, \pi) < 8a_{1g}(8a_1') (d_{z^2}, \sigma) < 4e_{2g}(4e_2') (d_{x^2-y^2}, d_{xy}, \delta) \quad (7)$$

which is in agreement with the E-Fc (D_{5h}) configuration of Salzner²⁵. Such the changes caused by the models are significant as the degenerate HOMO pair of Fc changes from the π -bonding in HF to δ -bonding in B3LYP. It is further noted that the failure of the HF model does not stem from the general inability of the HF theory to treat properly multi-configuration systems, nor from the neglect of dynamical correlation.¹⁶

The Fe dominant orbitals obtained from EOES

The ligand field theory indicates that the low-lying excited states of Fc are d-d transitions on Fe,²⁵ suggesting that the frontier orbitals of Fc are Fe d-electron dominant orbitals. As shown by the configurations, the MOs of the E-Fc and S-Fc are in a one-on-one correspondence,⁵⁶ which makes the orbitals based comparison, i.e., the EOES of ferrocene possible. Figure 1 reports the valence EOES of the E-Fc and S-Fc ferrocene conformers obtained from the B3LYP/m6-31G (d) calculations. It is very interesting that the EOES (i.e., $\Delta\varepsilon$ energies) of nearly one third (14 out of 48) of the occupied orbitals in Fc exceed $0.50 \text{ kcal}\cdot\text{mol}^{-1}$ in energy. The total electronic energy difference (ΔE) between the E-Fc and S-Fc conformers is merely $0.58 \text{ kcal}\cdot\text{mol}^{-1}$ using the same B3LYP/m6-31G(d) model (Note that this value was given by $0.62 \text{ kcal}\cdot\text{mol}^{-1}$ as the latter used three decimals of the same calculations)⁸ and the measured energy is given by $0.9 \text{ kcal}\cdot\text{mol}^{-1}$.² As shown by the EOES in Figure 1 that the orbitals with large $\Delta\varepsilon$ ($> 0.50 \text{ kcal}\cdot\text{mol}^{-1}$) concentrate in the core, inner and outer valence regions. The 5 inner most core orbitals ($1a_1'$) ($2a_1'$) ($1a_2''$) and doubly degenerate orbitals ($1e_1'$) (i.e., MO 1-5) are from the core electrons of Fe as indicated by the orbital energies, which are not accessible for carbons and hydrogens. Approximately half of the outer valence orbitals, that is, six valence orbitals show larger orbital energy differences

between E-Fc and S-Fc than the total electronic energy difference between E-Fc and S-Fc. These Fe-dominant MOs are $4a_1'$ (i.e. MO 16), $3e_1'$ (MO 18-19), $3e_2'$, $3e_2''$ (MO 37-40) and $4e_2'$ (HOMO, i.e., MO 47-48).

Figure 2 gives the orbitals of the nine valence orbitals showing large excess $\Delta\varepsilon$'s (> 0.50 kcal·mol⁻¹) as indicated by the EOES in Figure 1. All these orbitals are either dominated by the centre metal Fe atom (i.e., MO 16, MO 18-19 and HOMOs) or by the differences due to the centre Fe atom of the complexes (in MO 37-40). All such the doubly degenerate e-orbitals in the outer valence space of $\varepsilon_i > -14$ eV (i.e., binding energy $|\varepsilon_i| < 14$ eV) are dominated by differences due to the Fe-d electron bonding. Moreover, the excess $\Delta\varepsilon$'s of $3e_2'$ (MO 37-38) and $3e_2''$ (MO 39-40) orbitals in the outer valence space exceed as large as 1.26 kcal·mol⁻¹ in opposite signs. Such the doubly degenerate orbitals of Fc are engaged with π - and δ -bonds in the molecule as indicated by Rayon and Frenking.²⁰ As all these doubly degenerate orbitals in the outer valence space including the HOMO are dominated by differences in the Fe-d electrons, it again confirms that the Fe-centred properties are conformer sensitive, as found in the IR spectra earlier.⁸

To further understand the electron correlation energy included in the Fe-dominant orbitals of Fc, Figure 3(a) compares the EOES using the B3LYP/m6-31G(d) and HF/m6-31G(d) models. The EOES obtained from two models are in good agreement in the core to inner valence region except for the outer valence of $|\Delta\varepsilon| < 10$ eV. This figure also indicates that the two models show apparent differences whenever there is an Fe d-electron dominance. There are three noticeable properties of the HF and B3LYP models. First, large excess $\Delta\varepsilon_i$'s are associated with Fe-dominant MOs of $4a_1'$ (i.e. MO 16), $3e_1'$ (MO 18-19), $3e_2'$, $3e_2''$ (MO 37-40) and $4e_2'$ (HOMO, i.e., MO 47-48). The EOES (HF and B3LYP) in Figure 3(a) suggests that the electrons of the Fe

metal have apparently larger electron-correlation energies than other orbitals dominated by carbons and hydrogens in Fc. Second, d-electrons with σ -bonding characters exhibit less electron correlation energy changes between the Fc conformers comparing to other bonding characters such as π - and δ -bonding, e.g. the doubly degenerate e -MOs. As a result, *not all d-electrons of Fe play the same role*, depending on their distribution in three-dimensional space. Third, the trend in outer most valence space such as HOMOs of HF and B3LYP is very different. It is further noted that from Eqs (1c and 4, 2c and 5) that the electron configurations are different in the HF and B3LYP models. As a result, the symmetry correlated frontier orbitals from HF calculations are correlated with respect to the B3LYP calculations and shown in the EOES in Figure 3(b). The symmetry corrected HOMOs reduce the discrepancy but the excess $\Delta\epsilon_{\text{HOMO}}$ is still as large as $0.83\text{kcal}\cdot\text{mol}^{-1}$.

Bonding in Fc and its covalent character in Fe-Cp

The extraordinary thermal stability of Fc must attribute to its unique chemical bonding. The chemical bonding between the transition metal Fe and the cyclopentadienyl (Cp) rings in ferrocene is not well understood, although it has been generally agreed that it can be considered as either by “bonds” linking Fe to each carbon of the rings or by a single “bond” linking the Fe atom to the centre of the unsaturated ring.²² For example, the analysis of ferrocene bonding is dominated using the S-Fc (D_{5d}) structure, whereas it is well established that that S-Fc is not but the E-Fc is the global minimum structure of Fc.^{8,25,39} In addition, a number of such analyses have been “qualitatively” based on the electronic configuration obtained using the HF model, which does not necessarily present the true ground state configuration as it lacks the particularly important electron correlation energy in Fc. As a result, it is useful to provide an update bonding

analysis for both E-Fc and S-Fc, based on information from more accurate models such as the B3LYP/m6-31G(d) model.

Our nature bonding orbital (NBO) calculations using the B3LYP/m6-31G (d) model show that the NBO charge of the centre transition metal Fe in ferrocene is 0.240e for E-Fc and 0.242e for S-Fc based on the optimized geometries of the same model. However, the NBO charge of Fe is found to be -0.204e and -0.179e for E-Fc and S-Fc, respectively, based on the optimised geometries of the MP2/m6-31G (d) model. The latter (negative NBO charge for Fe in E-Fc) agrees with the recent UV-Vis theoretical study of Salzner,²⁵ who obtained a negative charge (NBO) for Fe of -0.27e at the B3LYP/6-31+G(d) level of theory based on the optimized geometry at the same level. At the first glance, the results of negative charge for the Fe atom in ferrocene can be difficult to comprehend as the oxidation state for Fe is positive.^{25,40} However, in a recent X-ray crystallography experiment by Makal et al⁴¹, the charge density of the centre Fe atom for decamethyl ferrocene (D_{5h}) is also negative. For example, it is -0.49e, -0.33e and -0.37e using multipole, Bader and natural population analysis (NPA) schemes, respectively. Decamethyl ferrocene “in the current studied structure is more similar to an unsubstituted ferrocene”.⁴¹

The covalent character of the Fe-Cp bonds in Fc is also indicated by the delocalization index (DI) $\delta(\text{Fe}, \text{C})$.²² The DI provides a measure of the shared and exchanged electrons between bonded atoms, Fe and C, for ferrocene,²² and is considered to be able provide a picture of chemical significance of the complex.³⁹ According to Cortes-Guzman and Bader²², the bond between A-B can be ionic interactions if the DI, i.e., $\delta(\text{A},\text{B})$ value is smaller than 0.20. In other words, if the DI value is greater than 0.20, the bond between A-B exhibits more covalent

character, as the delocalization index, $\delta(A,B)$, can be employed to gauge the degree of covalency.²² The B3LYP/6-311+G* model indicated that the DI values for S-Fc (D_{5d}) are $\delta(\text{Fe}, \text{C}) = 4.518$ for Fe-Cp₂ and $\delta(\text{C}, \text{C}') = 1.248$ for the carbons in the same Cp ring but $\delta(\text{C}, \text{C}'') = 0.079$ if the carbons in the different Cp rings.²² Apparently, the carbons in the same Cp ring exhibit the character between a C-C single bond and a C=C double bond, and as expected, very small overlap between carbons in different rings. The $\delta(\text{Fe}, \text{C})$ of 4.518 is significantly larger than 0.20,²² indicating electron sharing character between Fe and Cp. Interestingly, the number of localised electron pairs on C and H in S-Fc, which are given by $l(\text{C}) = 65.87$ and $l(\text{H}) = 42.15$ are less than their counterparts in E-Fc which are given by $l(\text{C}) = 66.44$ and $l(\text{H}) = 44.58$,²² indicating that Fe shares some electrons from the Cp fragments and displays covalent character in Fc.

The procedure to use individual orbital contributions is useful if the contributions are grouped into symmetrically equivalent sets,²² such as the orbitals energies in the previous section. However, the ground electronic configuration of Fc produced from the HF model could hardly provide correct information to explain the bonding in Fc, as the outer valence configuration obtained from the HF can be incorrect. As a result, the bonding in ferrocene discussion based on the HF information can be hardly quantitative, even for the chemical bonding of frontier orbitals and post-HF and/or DFT models should be considered.

4. Conclusions

The present study proposes the excess orbital energy spectrum (EOES) of ferrocene to reveal differences between conformer electronic structures of eclipsed (E) and staggered (S) ferrocene

(Fc). It is found that the d-electrons of transition metal Fe play a significant role in EOES and chemical bonding of ferrocene, using density functional theory (DFT) based B3LYP/m6-31G(d) model. The study identifies a group of nine Fe-dominant/associate valence orbitals of Fc, which exhibit larger orbital EOES than the total electron energy difference between the E-Fc and S-Fc conformers. These orbitals are $4a_1'$ (i.e. MO 16), $3e_1'$ (MO 18-19), $3e_2'$, $3e_2''$ (MO 37-40) and $4e_2'$ (HOMO, i.e., MO 47-48), which are associated with the d-electron contributions from Fe. The study also suggests that the electron correlation effects are more significant in the Fe atom than other atoms such as C and H in Fc. Inclusion of electron correlation energy in the model, both theory and basis set, becomes critically important to obtain accurate results and to agree with experiment of Fc. The Hartree-Fock (HF) model is not able to provide the correct electron configurations of Fc and the correct frontier orbitals such as the HOMO. The present results also suggest that the covalent bonding character of Fe-Cp bonds in ferrocene.

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Table 1: Comparison of selected properties of Fe eclipsed and staggered conformers using different models.

Parameter	B3LYP/ m6-31G* ^a	B3LYP/ 6-31G ⁴²	B3LYP/ 6-31G* ⁴²	B3LYP/6 -31+G* ⁴³	B3LYP/LA NL2TZF ^b	B3LYP /DZP ²⁴	HF/ m6-31G* ^a	MP2/TZ V2P+f ¹⁶	CCSD(T)/ TZV2P+f ¹⁶	Expt
Eclipsed (D_{5h})										
Fe-C ₅ (Å)	1.670			1.68	1.68	1.681	1.852	1.465	1.655	1.660 ²
Fe-C (Å)	2.065			2.07	2.07	2.077	2.206	1.910	2.056	2.064±0.003 ²
C-C (Å)	1.428			1.43	1.43	1.434	1.410	1.441	1.433	1.440±0.002 ²
C-H (Å)	1.082			1.08	1.08	1.085	1.072	1.076	1.077	1.104±0.006 ²
∠C ₅ -H (°)	0.66			1.6		1.18	0.53	0.33	1.03	3.7±0.9 ³⁷ 1.7±0.2 ⁴⁵
E _{tot} (E _h)	-0.6619235 ^e					-0.885 ^e	-0.6139903 ^f			
HOMO	e ₂ '						e ₁ ''			
Staggered (D_{5d})										
Fe-C ₅ (Å)	1.674	1.685	1.655	1.68		1.684	1.852	1.487	1.659	
Fe-C (Å)	2.068			2.07		2.080	2.206	1.925	2.058	
C-C (Å)	1.428	1.435	1.427	1.43		1.433	1.410	1.437	1.432	
C-H (Å)	1.082	1.079	1.083	1.08		1.085	1.072	1.076	1.077	
∠C ₅ -H (°)	0.92			1.8		1.46	0.55	1.39	1.34	
E _{tot} (E _h)	-0.6609962 ^e					-0.884 ^e	-0.614015 ^f			
HOMO	e _{2g}						e _{1g}			
ΔE ^c	0.58 ^d					0.63	-0.01	4.58	1.15	0.9±0.3 ²

^a This work (m6-31G* for Fe, 6-31G* for others)^b Basic Set : LANL2TZF for Fe, 6-31G* for others (Ref⁴⁴)^c ΔE = E_{tot}(D_{5d}) - E_{tot}(D_{5h}) in kcal·mol⁻¹^d The value was 0.62 kcal·mol⁻¹ (if three decimals are used for calculation).⁸^e = -1650.0 + E_{tot}^f = -1646.0 + E_{tot}

Figure 1: Exceed orbital energy spectrum (EOES) of the E-Fc and S-Fc ferrocene conformers using the B3LYP/m6-31G* model.

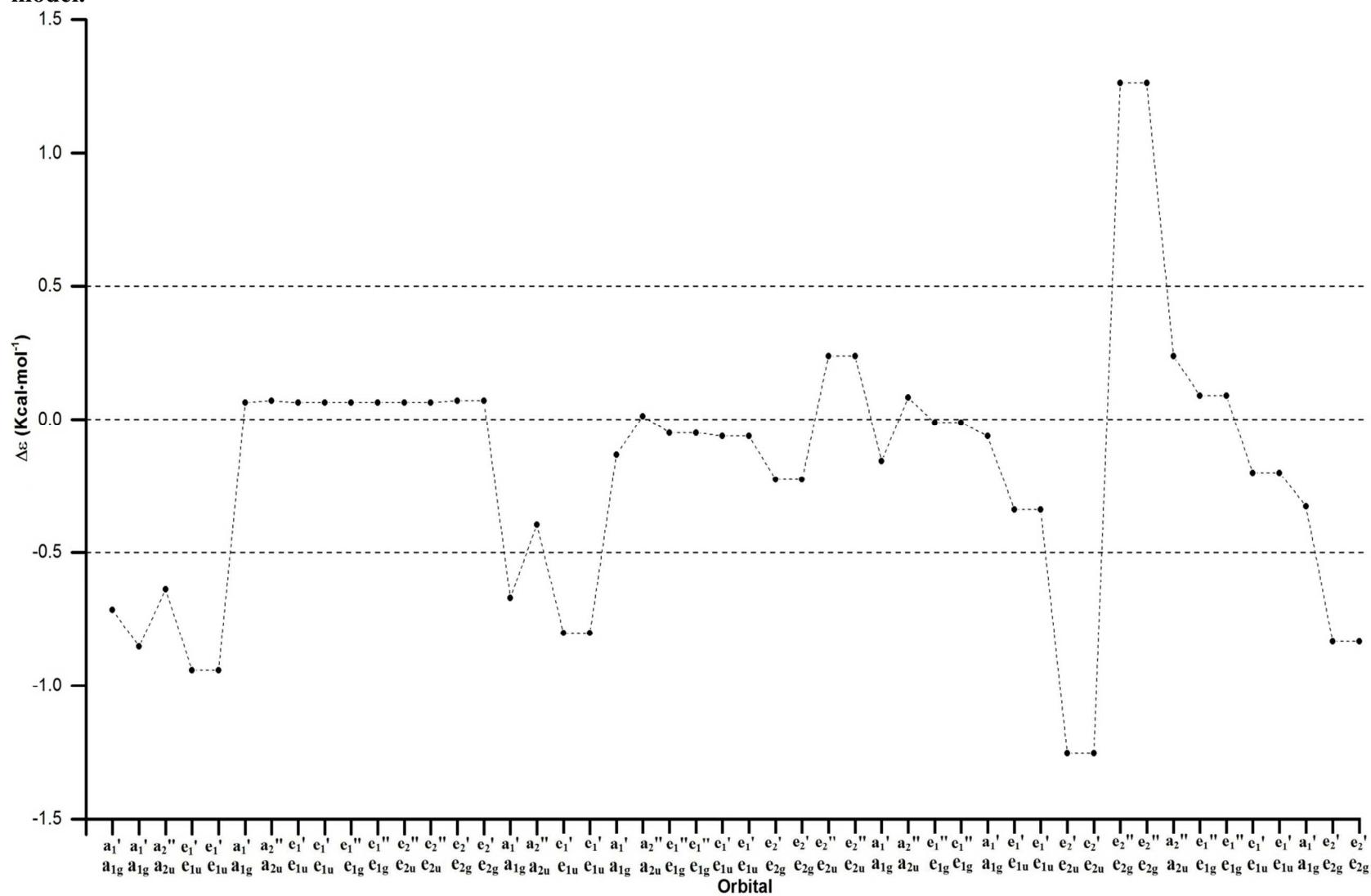


Figure 2: Orbital charge densities of nine valence orbital of Fc (D_{5h} and D_{5d}) with $|\Delta\varepsilon| > 0.50 \text{ kcal}\cdot\text{mol}^{-1}$.

MO	$\Delta\varepsilon \text{ (kcal}\cdot\text{mol}^{-1})$	E-Fc (D_{5h})	S-Fc (D_{5d})		
16 $a_1' (a_{1g})$	-0.67				
18, 19 $e_1' (e_{1u})$	-0.80				
37, 38 $e_2' (e_{2u})$	-1.26				
39, 40 $e_2'' (e_{2g})$	1.26				
47, 48 $e_2' (e_{2g})$	-0.83				

Figure 3a: The EOES of the E-Fc and S-Fc ferrocene conformers using different models.

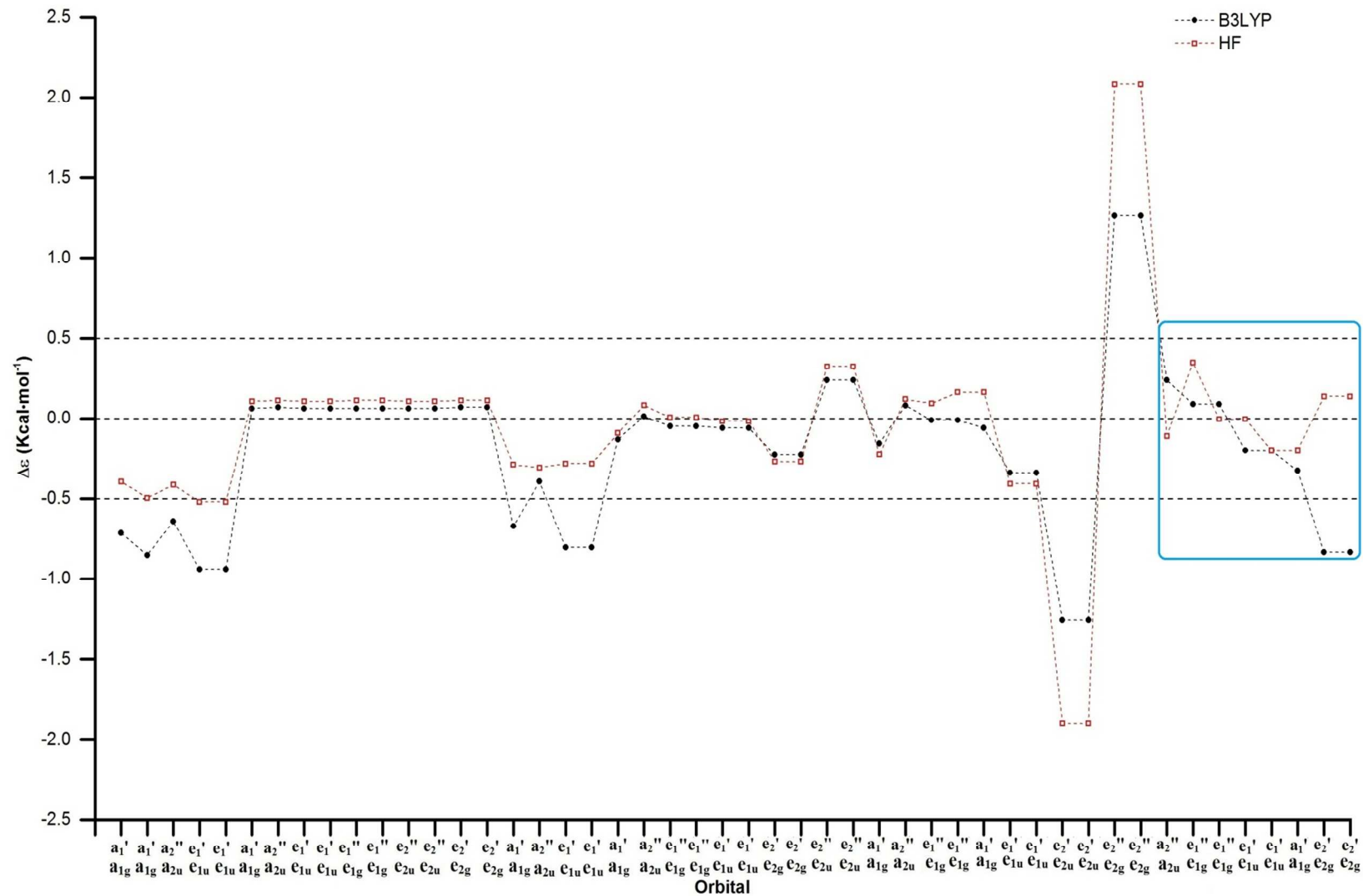
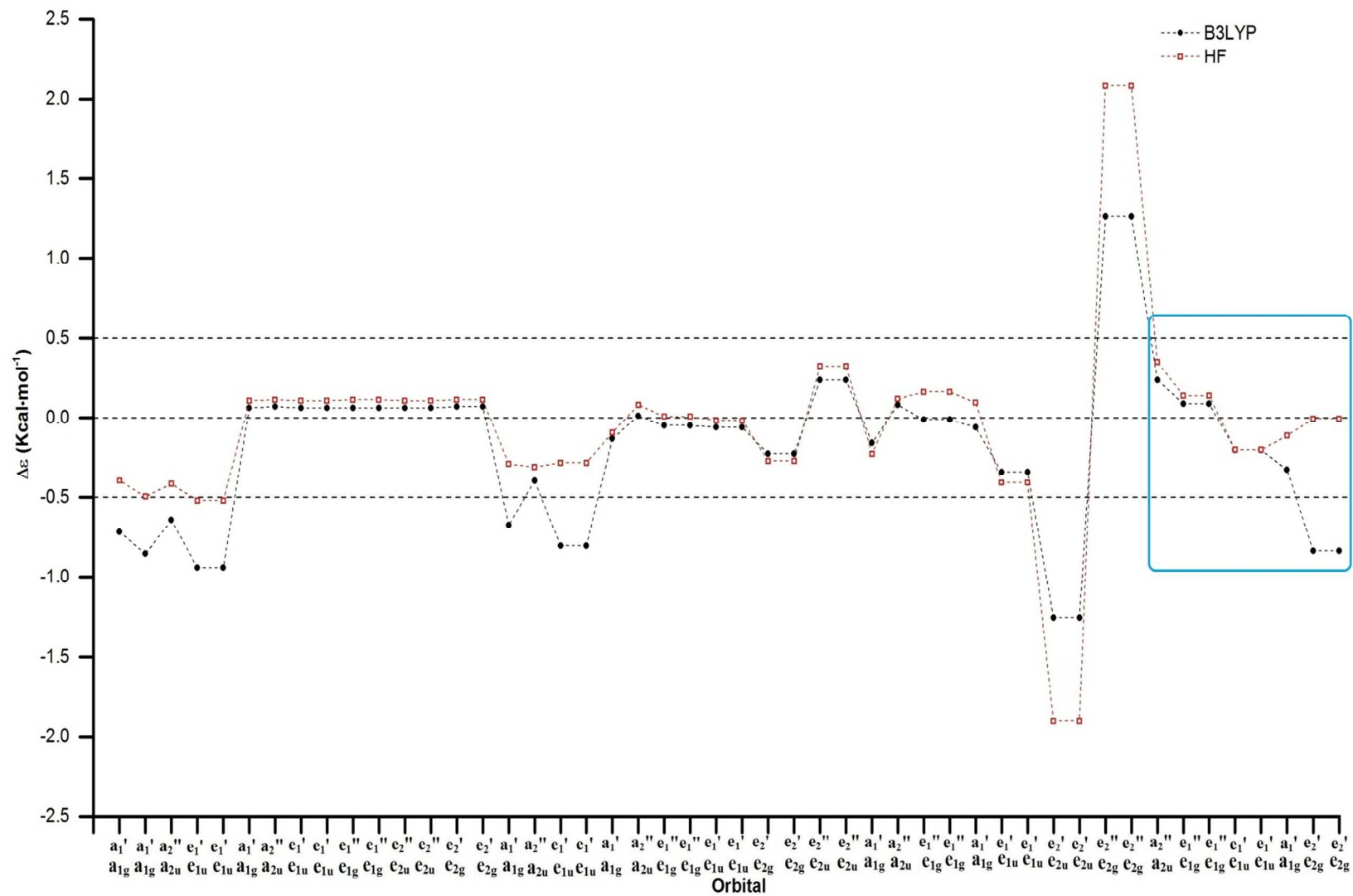
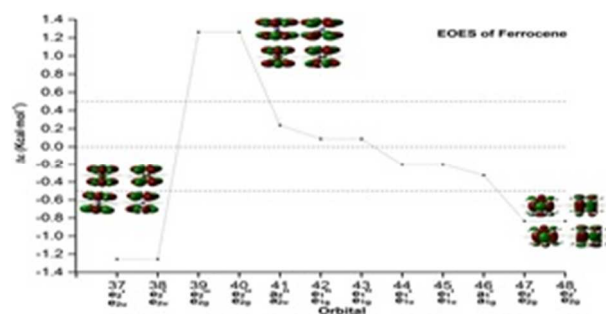


Figure 3b: The EOES of the E-Fc and S-Fc ferrocene conformers using different model (symmetry associated, the box).



Graphic Abstract

The EOES ($\Delta\varepsilon_i = \varepsilon_i^{\text{E-Fc}} - \varepsilon_i^{\text{S-Fc}}$) shows that the orbitals with significantly excess energies are Fe d-electron dominant.



Graphic abstract

