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Original Investigations

A Theoretical Study of the Electromagnetic Properties of Ferrocene and the Ferrocenium Ion

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An iterative extended Hückel molecular orbital calculation was used to obtain wave functions for the ground state of ferrocene and several low lying states of the ferrocenium ion. Photoemission spectra in terms of relative ionization potentials and the electric field gradient at the iron nucleus were calculated for ferrocene and g values and the electric field gradient were calculated for the ferrocenium ion. These values are in good agreement with experiment. The nature of the molecular orbitals was compared with results of previous semi-empirical and *ab initio* calculations.

Key words: Ferrocene – Ferrocenium ion

1. Introduction

Many semi-empirical [1–9] and *ab initio* calculations [10–12] have been performed on ferrocene $Fe(C_5H_2)_2$ to understand its electronic structure, to assign its electronic spectra, and to rationalize the quadrupole splitting [13] and isomer shift [11] observed in Mössbauer resonance. No previous theoretical studies are available, though, to compare to observed Mössbauer resonance or electron spin resonance data [14, 15] for the ferrocenium ion $Fe(C_5H_5)_2^+$.

The *ab initio* calculations have investigated the formation of low energy states of ferrocene [10] and of the ferrocenium ion [11, 12] in order to assign the electronic spectra and reproduce the observed photoemission spectra of ferrocene [15–17]. Both experimental and theoretical studies suggest large electron relaxation of the d molecular orbitals. No previous attempt has been made to determine if semi-empirical methods can successfully reproduce these relaxation effects, that is, to predict the correct relative energies of the ground state and first few excited states of the ferrocenium ion and correlate these states with observed properties. The primary objective of this study was to calculate such properties and to compare the results with experiment and *ab initio* methods.

2. Method of Procedure

IEHT (Iterative Extended Hückel Theory), an all valence semi-empirical calculation described in detail elsewhere [18, 19], was used to calculate the ground state wave function for ferrocene in both the eclipsed (D_{5h}) and staggered (D_{5d}) conformation. A staggered conformation was assumed for the ferrocenium ion. Since there is evidence that interatomic distances are not greatly changed in the ion [20] or in the solid [21], the vapor phase interatomic distances [22] of Fe–C = 2.057 Å, C–C = 1.429 Å, and C–H = 1.116 Å were used for both the neutral molecule and cation.

Calculations for four ferrocenium ion configurations were performed by direct removal of a single electron from each of the top four molecular orbitals. The relative stability of each ion was determined by its total energy. The electric field gradient at the iron nucleus was calculated for ferrocene and for each ferrocenium configuration by a procedure used previously for iron containing complexes and explained in detail elsewhere [23]. Additionally, g values were calculated for the ground state configuration of the ferrocenium ion by a procedure used previously [24] for high spin ferric ions (d^5) but modified to treat systems with one unpaired electron (low spin ferric).

3. Results

No significant differences in any of the calculated properties, including total energies, were found between the staggered and eclipsed conformation of ferrocene within the precision of the IEHT and properties calculation. *Ab initio* results also yield staggered and eclipsed forms of equal energy. These results are in keeping with the experimental ambiguity in different methods of structure determination [22, 23].

The orbital energies and LCAO coefficients for the four highest occupied and the lowest empty molecular orbitals of ferrocene are given in Table 1. The results are consistent with previous Hückel calculations [3–7] and indicate that ferrocene is a diamagnetic compound with the low spin configuration:

$$d^6 \quad {}^1A_{1g}[(e_{2g})^4(a_{1g})^2].$$

While the energy order for the four highest filled molecular orbitals differs significantly from that given by the *ab initio* methods [11, 12] of $e_{1u}(\Pi) > e_{1g}(\Pi) > e_{2g}(d) > a_{1g}(d)$, the nature of the orbitals (i.e. extent of delocalization) as given by the d orbital coefficients is consistent between both methods. Moreover, as shown in Table 2, both IEHT and *ab initio* methods give very similar total a_{1g} and e_{2g} d electron populations. The IEHT method, though, shows substantially more

Table 1. Nature and energy (eV) of highest occupied and lowest empty orbitals of ferrocene

Sym	Occ	Energy	ΔE_{calc}	ΔE_{exp}[a]	d Orbital Coefficient
$e^*_{1g}(d)$	0	−8.80	0		$0.77d_{xz}$; $0.77d_{yz}$
$a_{1g}(d)$	2	−11.60	2.80	2.73	$0.99d_{z^2}$(0.84)[b]
$e_{2g}(d)$	4	−11.92	3.12	2.94	$0.94d_{x^2-y^2}$; $0.94d_{xy}$(1.02)
$e_{1u}(\Pi)$	4	−12.16	3.36		carbon π orbital
$e_{1g}(\Pi)$	4	−12.48	3.68		$0.50d_{xz}$; $0.50d_{yz}$(0.49)

[a] Ref. [6]. [b] *Ab initio* values of the coefficients are given in parentheses (Ref. [12]).

Table 2. Total electron density in each *d* orbital and net charge on the iron by *ab initio* and IEHT methods

	Bagus *et al.*[a]	Coutière *et al.*[b]	IEHT
$e_{1g}(d_{xz}, d_{yz})$	0.79	0.86	2.16
$e_{2g}(d_{xy}, d_{x^2-y^2})$	3.66	3.72	3.82
$a_{1g}(d_{z^2})$	1.95	1.93	1.97
Net charge on Fe	+1.37	+1.23	+0.27

[a] Ref. [11]. [b] Ref. [12].

forward donation from the cyclopentadienyl rings to the (d_{xz}, d_{yz}) iron orbitals in low lying e_{1g} bonding molecular orbitals than do the *ab initio* calculations. Such forward donation results in larger net (d_{xz}, d_{yz}) electron density and nearly neutral net charge on the iron.

Due to electron relaxation of the *d* orbitals, the ionization potentials of ferrocene cannot be approximated directly from the neutral molecule by Koopmans' theorem as the energy of the filled molecular orbitals. Instead, relaxed ionization potentials are determined by calculating the energy of the ion obtained by direct removal of an electron from each of the top lying molecular orbitals. The IEHT method does not calculate energies well enough to yield absolute ionization potentials as the energy difference between the ionic and neutral species. However, relative ionization potentials, the energy difference between different configurations of the same ion, are meaningful and can be compared with experiment and with previous *ab initio* calculations as in Table 3.

The first two ionization potentials of ferrocene at 6.858 eV and 7.234 eV are assigned unambiguously to removal of an electron from the e_{2g} and a_{1g} molecular orbitals, respectively. The identification of the next two ionic states, formation of which takes 8.715 eV and 9.38 eV, is less certain [15, 17]. The IEHT calculation yields a result qualitatively consistent with the tentative assignment of Prins [15], the more recent assignment by Evans *et al.* [16], and the sequence of states predicted by Coutière *et al.* [12] of, in order of increasing ionization potential, $E_{2g}<A_{1g}<E_{1u}<E_{1g}$ although Rabalais *et al.* [17] assign and Bagus *et al.* [11] calculate the order $E_{2g}<A_{1g}<E_{1g}<E_{1u}$. Thus, even though the results of the IEHT and the *ab initio* calculations differ radically in the frozen order of the top filled molecular orbitals of ferrocene, the relaxed order as determined by the relative energies of different symmetry configurations of the ferrocenium ion are comparable between the two methods.

Table 3. Calculated and observed ionization potentials (eV) of ferrocene

State	$\mathrm{IP}_{\mathrm{exp}}$[a]	$\Delta\mathrm{IP}_{\mathrm{exp}}$	$\Delta\mathrm{IP}_{\mathrm{Bagus}}$[b]	$\Delta\mathrm{IP}_{\mathrm{Coutière}}$[c]	$\Delta\mathrm{IP}_{\mathrm{IEHT}}$
$^2E_{2g}$	6.858	–	–	–	–
$^2A_{1g}$	7.234	0.376	1.77	1.8	0.4
$^2E_{1u}$	8.715	1.857	3.16	2.8	3.9
$^2E_{1g}$	9.38	2.52	3.10	2.9	5.2
$^2A_{2u}$	12.2	5.3	7.34	7.2	

[a] Ref. [17]. [b] Ref. [11]. [c] Ref. [12].

Table 4. Calculated and observed Mössbauer resonance properties of ferrocene and the ferrocenium ion

	ΔE_Q[a] experimental	ΔE_Q calculated		V_{zz}	V_{xx}, V_{yy}	η[b]
Ferrocene	2.40	3.30	2.24[c]	2.21	-1.10	0
Ferrocenium						
$^2E_{2g}$	0 (<0.1)	-0.21	-0.14[c]	-0.14	$+0.07$	0
$^2A^*_{1g}$		6.89		4.61	-2.30	0
$^2E^*_{1u}$		3.34		2.24	-1.12	0
$^2E^*_{1g}$		3.74		2.50	-1.25	0

[a] Ref. [13]. ΔE_Q in mm/sec. [b] $\eta = \frac{V_{yy} - V_{xx}}{V_{zz}}$ (anisotropy factor).

[c] Values of ΔE_Q corrected for Sternheimer shielding factor $(1-R)=0.68$ (Ref. [25]).

* Excited states of ferrocenium ion in relaxed approximation.

Electron relaxation of *d* orbitals can also play a role in the assignment of electronic spectra. Three bands in the visible region, found at 2.73, 2.94 and 3.82 eV, were assigned [9] using the frozen orbital approximation to the two *d* orbital transitions $a_{1g} \rightarrow e^*_{1g}$ and $e_{2g} \rightarrow e^*_{1g}$ ($^1E_{1g}$, $^1E_{2g}$). As shown in Table 1, the orbital energy levels for the ground state of ferrocene obtained by the IEHT method are consistent with this previous assignment.

However, results of a recent *ab initio* calculation [10] of the excited states and electronic spectrum of ferrocene yielded an $e_{2g} \rightarrow e^*_{1g}$ transition energy less than the $a_{1g} \rightarrow e^*_{1g}$ in contrast to the frozen orbital results of IEHT. An explicit IEHT calculation of these two excited states of ferrocene yields the same reversal of energy from the frozen orbital approximation. Thus, as in the determination of the ionization potential, the IEHT method appears to account for relaxation in excited states in a manner qualitatively similar to the *ab initio* methods.

There has as yet been no theoretical calculation of the electric field gradient of ferrocene or the ferrocenium ion to compare with the unexpected results obtained from Mössbauer resonance [13]. Ferrocene, a low spin ferrous compound expected to have a low field gradient, is observed to have a field gradient of $+2.40$ mm/sec. On the other hand, the ferrocenium ion, a low spin ferric compound expected to have a rather large (1.5–3.0 mm/sec) field gradient, is observed to have a nearly zero field gradient. As shown in Table 4, both unexpected results were reproduced quite well by the calculated values of the electric field gradient for the ground states of both ferrocene and the ferrocenium ion. The excited states of the ferrocenium system did not give low field gradients.

The *g* values for the doubly degenerate ground state of the ferrocenium ion

$$d^5 \quad {}^2E_{2g}[(a_{1g})^2(e_{2g})^3]$$

are determined mainly by first order spin-orbit coupling among the degenerate components rather than higher order interaction with the excited electronic states ($^2A_{1g}$, $^2E_{1u}$). Including these excited states in the spin-orbit coupling matrix at their experimentally determined excitation energies indeed had no effect on *g* values. Assuming axial symmetry, that is, no splitting of the degenerate e_{2g} orbitals, calculation of the *g* values for the ground state of the ferrocenium ion yielded $g_\perp = 0.05$ and $g_\parallel = 4.68$. To explain the experimentally observed non-zero value of $g_\perp$ [12, 13], a lower than axial symmetry must be introduced. If a small rhombic distortion is invoked corresponding to an energy difference of 200 cm^{-1} between the $d_{x^2-y^2}$ and d_{xy} partners of the degenerate e_{2g} state, the calculated values of $g_\perp = 1.21$ and $g_\parallel = 4.18$ obtained are in good agreement with the experimental values [15] of $g_\perp = 1.26$ and $g_\parallel = 4.36$. The origin of this perturbation may either be an internal distortion as in a Jahn-Teller effect, or an external interaction with solvent or counterion molecules [14, 15]. In either case, the splitting is so small as to be undetectable in the photoemission spectra.

Thus, consistent results were obtained between experiment and the IEHT calculations for relaxation effects on ionization potentials and electronic spectra. The anomalous field gradient at the iron nucleus for both ferrocene and the ferrocenium ion and observed g values for the ferrocenium ion were calculated in good agreement with experiment. IEHT also compared favorably to previous *ab initio* studies of ferrocene and the ferrocenium ion. We are encouraged, therefore, to continue to use IEHT in the study of related compounds, specifically biferrocenylene (bis-fulvalene diiron) in all of its oxidation states.

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