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Comparison of the Electronic Structure of Disubstituted Ferrocenes

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We have measured the optical absorption of gaseous ferrocene, 1,1′-dimethylferrocene, 1,1′-dibromoferrocene, and 1,1′-dichloroferrocene using synchrotron radiation. From these data we have estimated the ligand field parameters and noted increasing e_{2g}(d) to Cp(π) overlap with increasing charge transfer from the Cp ring to the substitution.

Introduction

We obtained photoabsorption spectra of gaseous 1,1′-dibromoferrocene, 1,1′-dichloroferrocene, 1,1′-dimethylferrocene, and ferrocene in order to ascertain the effects of the substitutions upon the ligand field splitting and the one electron transitions. Since each of these molecules is symmetrically disubstituted, but with different effective transfer of charge in or out of the cyclopentadienal ring, the effect of charge distribution upon the electronic structure is probed without changing the symmetry of the molecule.

There exist a considerable number of photoabsorption spectra for a variety of metallocenes, however, the assignment of the absorption features remains far from satisfactory. Even in the case of ferrocene,[1] for which the assignment of absorption features is better established, there is considerable controversy as to the level ordering of some of the molecular orbitals and one-electron transitions (ref 2 and the references therein) as a result of the photoemission data. The existence of photoelectron spectra of ferrocene,[3-9] 1,1′-dimethylferrocene,[3,6] 1,1′-dibromoferrocene,[5] and 1,1′-dichloroferrocene[3,5,6] together with photoabsorption data make the investigation of the effect of symmetric substitutions on the ferrocene molecular orbitals possible for both occupied and unoccupied orbitals, assuming one particular level ordering for ferrocene.

Experimental Section

Ferrocene and 1,1′-dimethylferrocene were purchased (Strem) while 1,1′-dichloroferrocene and 1,1′-dibromoferrocene were synthesized by the method of Kovar, Rausch, and Rosenberg.[10] All the ferrocenes were recrystallized to constant melting point from hexane and sublimed twice (0.1 mmHg, 60 °C) to remove all traces of solvent. Purity was confirmed by using UV–vis spectroscopy and mass spectroscopy as described elsewhere.[2]

The photoabsorption spectra of the ferrocenes were obtained at the Synchrotron Radiation Center of the University of Wisconsin—Madison (the Storage Ring Tantalus). The light was dispersed by a 1-m McPherson normal incidence monochromator. A resolution of 12A by the monochromator was employed throughout this work. The detector was a photomultiplier with a sodium salicylate phosphor. Since the monochomator and the gas vessel were separated by a LiF window, spectra could only be obtained in practice between 2.0 and 11.5 eV photon energies.

One-Electron Transitions

The photoabsorption spectra for ferrocene, 1,1′-dibromoferrocene, 1,1′-dichloroferrocene, and 1,1′-dimethylferrocene are shown in Figure 1. Superficially, the absorption features for ferrocene, dibromoferrocene, and dichloroferrocene are similar, although 1,1′-dimethylferrocene shows a greater abundance of absorption features at low energy.

Ferrocene, $Fe(C_5H_5)_2$, has the pentagonal antiprism (D_{5d}) structure common to most metallocenes[11] while the disubstituted ferrocenes have lower symmetry, principally C_{2h}. Nonetheless, for this discussion we shall employ the D_{5d} representation as a matter of convenience when describing the molecular orbitals of all the disubstituted ferrocenes except where it is clearly inappropriate.

The assignment of the photoabsorption features to one-electron transitions depends crucially upon the assumed level ordering of the ferrocene molecular orbitals—a matter of considerable controversy (ref 2 and the references therein). There are advocates for an orbital ordering (in terms of increasing binding energy) $a_{1g}(d) < e_{2g}(d) < e_{1u}(\pi) < e_{1g}(\pi)$. This ordering is consistent with qualitative MO theory expectations since d_{z^2} would be expected to be more antibonding than the orbitals containing substantial $d_{x^2-y^2}, d_{xy}$ character. Furthermore, this assignment permits the ligand field parameters to be extracted from the photoabsorption data in the visible and near ultravio-

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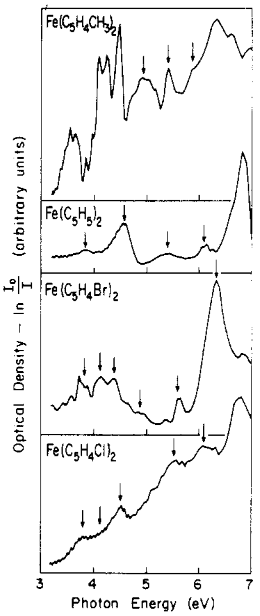

Figure 1. The photoabsorption spectra for 1,1′-dimethylferrocene, ferrocene, 1,1′-dibromoferrocene, and 1,1′-dichloroferrocene. Absorption is ln (I_0/I) plotted in arbitary units against photon energy. Assigned one-electron transitions are indicated by the arrows.

let.[12-17] The $e_{2g}(d) < a_{1g}(d) < e_{1u}(\pi) < e_{1g}(\pi)$ orbital ordering is consistent with the photoemission intensities.[3,6,7] This latter level ordering is also consistent with MO theory if the stabilizing of the a_{1g} level via s to d_{z^2} hybridization is accepted.[3] The a_{1g} may be only weakly antibonding in any event because the d_{z^2} to $a_{1g}(\pi)$ overlap is small.[3]

In Table I, the photoabsorption features for ferrocene and the disubstituted ferrocenes have been assigned to one-electron transitions assuming an $a_{1g}(d) < e_{2g}(d)$ ordering. The assignment of the photoabsorption features using the alternative ordering is also indicated in Table I. For ferrocene, the observed one electron transitions are in agreement with the calculated transition energies from the SCF–Xα calculation of Rosch and Johnson[16] as well as other experimental optical absorption studies,[12,14,15,17] assuming an $a_{1g}(d) < e_{2g}(d)$ ordering. The pronounced absorption feature at 6.9 eV is assigned to the photoionization process of the $8a_{1g}$ orbital.[2]

Two transitions (instead of one for ferrocene) for the $6e_{1u}$ to $5e_{1g}$(a) transition are expected as a result of the symmetric substitutions on ferrocene. Symmetric disubstitutions results in the splitting of the $6e_{1u}$ into an (a) and (b) state, i.e. a lifting of the degeneracy because of the lower symmetry.

The assignment of the $6e_{1u} \rightarrow 5e_{1g}$(a) photoabsorption feature for Fe(CpCl)$_2$ is not unequivocal. The feature is observed to be very intense despite the transition being dipole selection rule forbidden in D_{5d}.

The existence of several observed optical transitions that can be assigned to the $8a_{1g}$ to $5e_{1g}$(b) (or $4e_{2g}$ to $5e_{1g}$(b), assuming the alternative level ordering) and $6e_{1u}$ to $5e_{1g}$(a) transitions for dimethylferrocene sets this molecule's absorption spectrum apart from those of the other disubstituted ferrocenes. Furthermore, neither the three strong transitions that could be assigned to the $6e_{1u}$ to $5e_{1g}$(a) one-electron transition nor the four observed transitions associated with the $8a_{1g}$ to $5e_{1g}$(b) excitation can be explained with the simple arguments associated with the lifting of the $6e_{1u}$ degeneracy.

The intense $8a_{1g} \rightarrow 5e_{2u}$ transition, which is dipole selection rule forbidden for D_{5d}, is intense for Fe(CpMe)$_2$ as seen in Figure 1. Since this transition is unobserved with ferrocene and Fe(CpCl)$_2$ and weak for Fe(CpBr)$_2$, this also strongly suggests that Fe(CpMe)$_2$ is apparently of lower symmetry than that of the other disubstituted ferrocenes.

Table I. One-Electron Transition Energies for Ferrocene and Disubstituted Ferrocenes[a]

	molecule			
transition	Fe(C$_5$H$_5$)	Fe(C$_5$H$_4$ CH$_3$)$_2$	Fe(C$_5$H$_4$-Br)$_2$	Fe(C$_5$H$_4$-Cl)$_2$
$8a_{1g} \rightarrow 5e_{1g}$(a) [$4e_{2g} \rightarrow 5e_{1g}$(a)]	2.725 [14.15] 2.8 [17] 2.84 [12,22]	2.84 [22]	...	...
$8a_{1g} \rightarrow 5e_{1g}$(b) [$4e_{2g} \rightarrow 5e_{1g}$(b)]	3.8^a 3.85 (14,15] 4.56^c [18] 3.85 [17] 3.85 [12,22]	3.54^a 3.65^a 3.94^a 4.0^a	3.8^a	3.8^a
$6e_{1u} \rightarrow 5e_{1g}$(a)	4.6^a 4.67 [15] 4.7 [17] 4.56^b [16] 4.77 [22]	4.1^a 4.25^a 4.5^a	4.1^a 4.4^a	4.1^a 4.5^a
$8a_{1g} \rightarrow 5e_{2u}$ [$4e_{2g} \rightarrow 4e_{2u}$]	5.125 [17] 5.17 [15] 4.9^b [16]	4.95^a	4.85^a	...
$4e_{2g} \rightarrow 5e_{2u}$ [$8a_{1g} \rightarrow 4e_{2u}$]	5.4^a 5.35 [17] 5.49^b [16] 5.21 [22]	5.4^a 5.16 [22]	5.5^a	5.5^a
$6e_{1u} \rightarrow 9a_{1g}$	5.94 [17] 5.89^b [16]	...	...	...
$6e_{1u} \rightarrow 5e_{2g}$	6.1^a 6.187 [17] 6.2 [15] 6.26^b [16] 6.25 [22]	6.25^a 6.10 [22]	6.3^a	6.1^a
$4e_{1g} \rightarrow 5e_{1g}$	6.6^a 6.45 [17] 5.13^c [18]	...	6.85^a	6.75^a

[a] The observed transition energies from optical photoabsorption are all reported in units of eV. (*a*) indicates measurements from this work, (*b*) denotes theoretical SCF–Xα calculated transition energies, and (*c*) denotes theoretical SCF–HF calculated transition energies. All transitions are assigned assuming the $8a_{1g}$ orbital has less binding energy than the $4e_{2g}$ orbital. The transitions can also be assigned, assuming the $4e_{2g}$ orbital has less binding energy than the $8a_{1g}$. The assignments that must be changed with the latter assignment are indicated in parentheses.

We suspect that dimethylferrocene, unlike the dichloroferrocene or dibromoferrocene, is distorted from the pseudoaxial symmetry. This would lift the degeneracies of the $5e_{1g}$* even further than the splitting into (a) and (b) states, i.e. leads to additional splitting. This lifting of the $5e_{1g}$* degeneracies may be a result of orbital contributions to the magnetic moment of this principally d state that would result in Jahn–Teller distortion and lowering of the symmetry from D_{5d} to C_{2h} or C_{2v}.

The Approximate Position of the Unoccupied Molecular Orbitals

Given that the assignment of the photoabsorption features to various one-electron transitions is correct, the binding energies of the $5e_{1g}$*, $4e_{2u}$*, $9a_{1g}$*, and $5e_{2g}$* unoccupied molecular orbitals of ferrocene and the disubstituted ferrocenes can be estimated. This has been done following the procedure outlined in earlier work,[2] and the results are shown in Table II. These estimted binding energies assume an orbital ordering with the $a_{1g}(d)$ having less binding energy than $e_{2g}(d)$. The virtual orbitals are assessed assuming that the electronic transition energies are equal to the difference in binding energy between the occupied and unoccupied molecular orbitals. The binding

Table II. Approximate Binding Energies of the Molecular Orbitals Based upon Optical Absorption Data and Simplified One-Electron Transition Arguments (see text)[a]

	orbitals								
molecule	$4e_{1g}$	$6e_{1u}$	$4e_{2g}$	$8a_{1g}$	$5e_{1g}$*(a)	$5e_{1g}$*(b)	$9a_{1g}$*	$5e_{2g}$*	$4e_{2u}$*
$Fe(CpMe)_2$	9.17	8.73 8.53	7.06	6.72	4.43–4.28	3.18–2.72			1.7 ± 0.05
$Fe(Cp)_2$	9.38	8.72 9.14	7.21	6.9	4.1	3.1	2.8	2.6	1.8
$Fe(CpBr)_2$	9.57	9.06 8.65	7.54	7.17	4.6 ± 0.05	3.37		2.72	2.17 ± 0.13
$Fe(CpCl)_2$	9.49	9.16 8.8	7.37	7.1	4.6	3.3		2.7	2.0

[a] All energies are with respect to the vacuum level and are in units of eV. Asterix (*) indicates an unoccupied (virtual) orbital.

Table III. Ligand Field Parameters for the Disubstituted Ferrocenes[a]

	ligand field splitting parameters			
molecule	B	$\Delta_1 = e_{2g} - a_{1g}$	$\Delta_2 = e_{1g} - a_{1g}$	$\Delta(5e_{1g}{}^*)$
$Fe(CpMe)_2$				1.05–1.7
$Fe(Cp)_2$	0.0475	−0.64	2.885	1.0
	0.051[13]	−0.84[13]	2.80[13]	
	0.049[14,15]	−0.89[14,15]	2.75[14,15]	1.125[14,15]
$Fe(CpBr)_2$	0.059	−0.80	2.67	1.2
$Fe(CpCl)_2$	0.060	−0.92	2.57	1.3

[a] All values are in units of eV. B is the Racah repulsion parameter assuming $4B = C$. $\Delta(5e_{1g}{}^*)$ is the approximate separation of the $5e_{1g}$(a) and $5e_{1g}$(b) orbitals based on Table II.

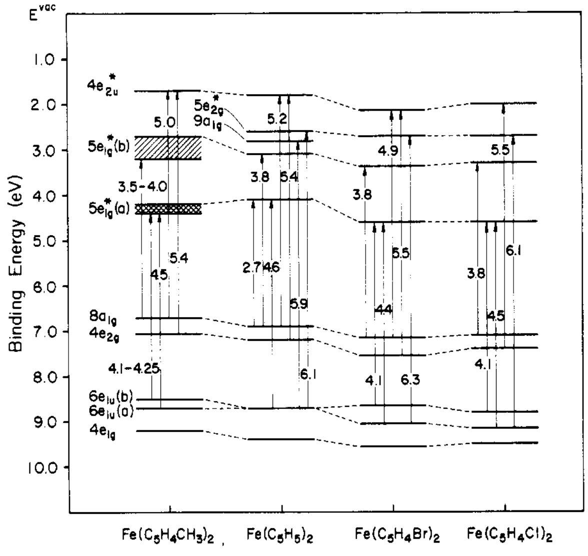

Figure 2. The electronic structure of the disubstituted ferrocenes. The molecular orbital are placed according to the binding energies devised in Table II. Vestical lines are the observed one-electron transitions. All values are in units of electronvolt.

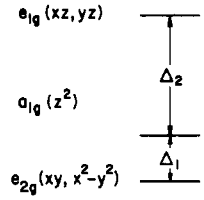

Figure 3. Schematic diagram of the ligand field splitting of the Fe d orbitals and their relationship to the ligand field parameters.

energies of the occupied orbitals are taken from the photoemission data for ferrocene,[3-9] 1,1′-dimethylferrocene,[3,6] 1,1′-dibromoferrocene,[5] and 1,1′-dichloroferrocene.[3,5,6] This procedure is, of course, a vast oversimplification of the electronic transition process and neglects electron-hole correlation, relaxation shifts, and many body effects. Thus, the estimated binding energies must be regarded as only approximate. The value in this procedure, however, is that we can now estimate from Table II the approximate transition energies for electronic transitions we have not observed and thus calculate the ligand field parameters.

The $5e_{1g}$* is split into (a) and (b) state in ferrocene. The further lifting of degeneracies for the $5e_{1g}$* beyond a "static" Jahn–Teller distortion occurs for the dimethylferrocene. Because of the lifting of the $5e_{1g}$* degeneracies for 1,1′-dimethylferrocene, an assignment of the 5_{1g}*(a) and $5e_{1g}$*(b) binding energies cannot be made by using the above procedure and we can only give the unoccupied orbitals a range of possible values.

As reported previously,[2] chlorination of ferrocene results in substantially larger ionization potentials. Indeed, as can be seen from Table II all the molecular orbitals for dichloroferrocene have greater binding energies than observed for ferrocene. This change in binding energies is a result of charge transfer from the cyclopentadienyl rings to the chlorine atoms. Bromine substitutions would be expected to have an associated charge transfer from the cyclopentadienyl rings to the bromine atoms though this charge transfer should not be as large as for chlorine.[19,20] The fact that dibromoferrocene does not exhibit molecular orbital binding energies less than dichloroferrocene suggests that the binding energies of Vondrak[5] derived from photoemission data are in error or their sample is impure. The results for dibromoferrocene, obtained from photoemission, can be made consistent with those for dichloroferrocene and ferrocene by lowering the reported binding energies of Vondrak by 0.1 eV to smaller binding energies. We do not make this change in either our tables or figures, but we suggest correction of Vondrak's data may be appropriate.

The methyl substitution as a charge donor should result in a general decrease in the molecular orbital binding energies. Despite uncertainty with some of the orbital binding energies for dimethylferrocene, this general decrease in the MO binding energies is observed with the symmetric methyl substitutions. The results from photoemission and our estimated binding energies for the unoccupied orbitals are summarized in Figure 2.

Our results indicate that charge transfer from the cyclopentadienyl ring to the substituent (chlorine or bromine) results in greater hybridization of the Fe $d_{x^2-y^2,xy}$ orbitals and the $Cp(e_{2g})\pi$ orbitals. Indeed the greater the charge transfer from the cyclopentadienyl ring, the greater the observed $d_{x^2-y^2,xy}$ to $Cp(\pi)$ mixing.[2] Donation of charge to the cyclopentadienyl ring, as occurs with the dimethyl

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substitutions, appears to result in less Fe d to Cp(π) hybridization.

Ligand Field Splitting

Metal sandwich complexes are known to exhibit ligand field splitting of the metal d electrons. For ferrocene, the ligand field splitting of the iron 3d electrons results in molecular orbitals being formed of principally $d_{xz,yz}(e_{1g})$ character, $d_{z^2}(a_{1g})$ character and $d_{xy,x^2-y^2}(e_{2g})$ character, as shown in Figure 3. These splittings are not to be confused with the splittings of molecular orbitals in the semiempirical simplification of the previous section.

Because our observed optical photoabsorption spectra are for charge-transfer (L to M or M to L) one-electron excitations and not d–d one-electron transitions, it would appear superficially that calculating the ligand field parameter (defined in Figure 3) for dimethyl-, dibromo-, and dichloroferrocene from our data would be very difficult using the procedure applied by Sohn et al.[14,15] When our observed photoabsorption data are combined with the photoemission data reported by previous workers,[3-9] estimates of the ligand field parameters for ferrocene, dibromoferrocene and dichloroferrocene can be made.

The $4e_{2g}$ to $8a_{1g}$ molecular orbital separation for $Fe(C_5H_5)_2^+$ is

$$E(a_{1g}-e_{2g}) = 20B + \Delta_1 \qquad (1)$$

where B is the usual Racah interelectron repulsion parameter and $\Delta_1 = e_{2g} - a_{1g}$, the ligand field splitting.[6] Unless there is a very radical change in the relative values of the ligand field parameters on going to the molecular ions, we can see from photoemission that $E(a_{1g}-e_{2g})$ equals 0.31 eV for ferrocene,[3] 0.37 eV for dibromoferrocene,[5] and 0.27 eV for dichloroferrocene.[3,6] Since the Racah repulsion parameter B must be less than or equal to 0.1 eV, Δ_1 must be negative as demonstrated more explicity below. This means the energy level ordering has the $a_{1g}(d_{z^2})$ at less binding energy than the $e_{2g}(d_{x^2-y^2,xy})$ orbitals. This is in agreement with simple expectations for molecular orbital theory and optical absorption data.[12-16]

If we assume that the B and C Racah electron repulsion parameters are related according to $4B = C$,[13] the difference of the electronic transitions energies is given by

$$E(5e_{1g}(b)-8a_{1g}) - E(5e_{1g}(a)-8a_{1g}) = (\Delta_1^2 + 12B\Delta_1 + 420B^2)^{1/2} \qquad (2)$$

and the sum of the electronic transition energies

$$E(5e_{1g}(b)-8a_{1g}) + E(5e_{1g}(a)-8a_{1g}) = 2\Delta_2 - \Delta_1 + 4B \qquad (3)$$

The repulsion parameters are assumed to be unaltered as a result of the disubstitutions to ferrocene. The appropriate electronic transition energies if not measured and reported in Table I can be estimated from Table II.

Using eq 1–3 and the estimated transition energies from Tables I and II, we have calculated the ligand field parameters for ferrocene, dibromoferrocene, and dichloroferrocene, as shown in Figure 3. Our results are in very good agreement with those of Prins and Van Voorst[13] and Y. S. Sohn et al.[14,15] for ferrocene, despite the serious assumptions made in the application of eq 1.

It is important to note that there are three critical a_{1g} orbitals, but if we neglect the Fe s orbital contribution, we can infer the influence of substitution on the ferrocene d orbital to cyclopentadienyl ring overlap. We can see that with the charge transfer out of the cyclopentadienyl rings, as occurs with the chlorine and bromine substitutions, the Δ_1 ligand splitting increases while the Δ_2 ligand splitting decreases. This indicates that the cyclopentadienyl ring to d orbital overlap increases with both the $d_{z^2}(a_{1g})$ and $d_{xz,yz}(e_{1g})$ orbitals becoming more antibonding or nonbonding while the d_{xy,x^2-y^2} orbitals becomes more bonding (with the Cp(π) orbitals). This trend in the ligand field splitting is consistent with the changes in electronic structure[2] and chemistry[21] with symmetric dichloro substitutions and symmetric dibromo substitutions.

While the ligand field parameters cannot be easily estimated for dimethylferrocene from our data, the $E(5)_{1g}$(b)–$5e_{1g}$(a)) splitting for this molecule cannot be less than that of ferrocene. This indicates that the charge donation to the cyclopentadienyl rings with symmetric methyl substitutions does not reduce the d_{xy,x^2-y^2} orbital to Cp(π) or orbital hybridization in a way amenable to simple arguments.

Conclusion

The optical absorption spectra for ferrocene, dibromoferrocene, and dichloroferrocene are remarkably similar. The halogen substitutions result in greater Cp(π) to e_{2g}-($d_{x^2-y^2}$) hybridization. The e_{2g} orbitals become more bonding while the a_{1g} and e_{1g} orbitals become more nonbonding or antibonding. This change is reflected in a change of the ligand field parameters. The 1,1′-dimethylferrocene can be compared with the other disubstituted ferrocenes only with great difficulty, possibly as a result of distortion of the uniaxial symmetry of the free gaseous molecule.

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Registry No. $Fe(CpMe)_2$, 1291-47-0; $Fe(Cp)_2$, 102-54-5; $Fe(CpBr)_2$, 1293-65-8; $Fe(CpCl)_2$, 1293-67-0.

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