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(18) When ^{3}CK is generated, it would be converted to CK(S_0) through ISC. Even if CK(S_0) appears in the course of the reaction, however, its dissociation is thought to be unlikely in consideration of the calculated result of ketene.[8a] In this sense, CK(S_0), although in principle possible, would be excited again up to CK(T_1) during the successive irradiation and the decomposition of CK(S_0) to CP(S_0) and CO would not take place.

An Intermediate Neglect of Differential Overlap Technique for Spectroscopy of Transition-Metal Complexes. Ferrocene

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Abstract: A new intermediate neglect of differential overlap (INDO-SCF-CI) method capable of calculating configuration interaction for transition-metal complexes is described. The technique is characterized by the use of atomic spectroscopic information in the formation of one-center, one-electron matrix elements and in the evaluation of two-electron integrals. All one-centered integrals that mix upon geometric rotations are found to be essential for calculation of configuration interaction and are retained. The method is applied to the calculation of the photoelectric and electronic spectra of ferrocene. Triplet and singlet state d → d* and charge-transfer transitions are considered. Three nearly degenerate triplet states are calculated for ferrocene at ~20 500 cm^{-1} as compared to an observed triplet state at 18 900 cm^{-1}. Three singlet transitions of the d → d* type are calculated at 21 700, 23 900, and 31 900 cm^{-1}, in very good accord with the experimental observations and assignments of $^1E_1''$ at 21 800 cm^{-1}, $^1E_2''$ at 24 000 cm^{-1}, and $^1E_1''$ at 30 800 cm^{-1}. The lowest charge-transfer excitation is calculated at 36 900 cm^{-1} compared to the experimental observation at 37 700 cm^{-1}. A considerable number of states above 36 900 cm^{-1} are calculated and a possible assignment of the observed states in the higher energy region is given. The calculated energies allow spectral assignment in good agreement with experiment and help resolve prior ambiguities in the assignment. The relative energies calculated for the ionic states of the ferroceniun ion ($^3E_2' < {}^2A_1' < {}^2E_1''$) are in good accord with previous ab initio calculations. The first two of these states are formed from the formal loss of an electron from a metal orbital; the third, from the loss of an electron from a ligand orbital. For all of these states relaxation upon ionization is so significant that the net charge on iron increases only negligibly from +1.9 in ferrocene to +2.0 in the ferrocene ion. This observation is also in agreement with ab initio findings and has some support from Mössbauer spectroscopy.

I. Introduction

To calculate the properties of organometallic transition-metal complexes from molecular orbital theory is often a difficult task. The number of integrals to be evaluated in an ab initio technique increases rapidly when a transition-metal atom is included in the molecule of interest. Care must be taken to treat in a consistent fashion the metal atoms and the organic moieties of the molecule. Extensive calculations often must be performed in order to explain differences between the normally localized metal orbitals and the typically delocalized ligand orbitals. It becomes of great interest therefore to develop a semiempirical model which can easily and successfully calculate properties of transition-metal complexes.

The electronic structure of transition-metal complexes has been described most frequently in terms of ligand field theory.[2a] Of great qualitative value, this approach is usually used

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to rationalized d orbital energy levels in metal complexes as well as to estimate spin properties.

Calculations of the Wolfsberg-Helmholtz type,[2b,3] especially those with a charge consistency refinement[4] (iterative extended Hückel, IEH), have provided a great deal of insight and information on transition-metal complexes. These all valence electron calculations set off-diagonal matrix elements of the Hamiltonian proportional to the average of the diagonal elements weighted by the appropriate orbital overlap. One-electron properties such as electric field gradients, spin-orbit coupling, zero-field splitting, and magnetic field energies are well calculated. Although no two-electron integrals are explicitly included, spectra are estimated by simple orbital promotion,[3] perhaps with corrections for two-electron terms.[5]

Several models of the complete neglect of differential overlap (CNDO) or intermediate neglect of differential overlap (INDO) types have recently appeared[6,7] which show promise in quickly estimating the electronic structure of transition-metal complexes. To date, however, no such zero differential overlap model has been applied systematically to the examination of the electronic spectroscopy of organometallic transition-metal complexes.

Ab initio molecular orbital techniques are beginning to be applied to the spectroscopy of transition-metal complexes. As mentioned previously, these are difficult and expensive calculations that can be performed in only a very limited number of laboratories. Furthermore, only transitions of the d → d type are accurately reproduced; calculated charge-transfer and ligand transitions have to date shown very little predictive power.

Alternatives to the molecular orbital description of transition-metal spectroscopy are certainly available. Perhaps the most promising of these is the scattered wave X-α method.[8-10] Using Slater's transition-state theory[11] the method has proven reliable in estimating some electronic transitions.

We describe here the use of a newly formulated method based on the simplest molecular orbital theory that properly accounts for the two-electron terms required in spectroscopy, the intermediate neglect of differential overlap (INDO). The INDO method of Pople and co-workers[12-15] parametrized along the lines introduced by Del Bene and Jaffé has already been used to successfully calculate the spectra of molecules containing first- and second-row atoms.[18] The method has been extended to allow calculation of properties of molecules containing first-row transition-metal complexes.[19,20] In this study, refinements of the extended program are described together with results obtained for ferrocene, $Fe(C_5H_5)_2$, an organometallic "sandwich" compound, as a test of the INDO method developed. Specifically, the electronic[21,22] and photoemission[23-25] spectra of ferrocene are calculated and the observed transitions assigned.

Many semiempirical[26-35] and ab initio[36-38] molecular orbital calculations have been performed previously on ferrocene and the ferrocenium ion to understand the electronic structure of the compound. Despite the great amount of experimental and theoretical work on ferrocene, many observed properties of the molecule have yet to be explained. In particular, assignments of the electronic and photoemission spectra of ferrocene remain a controversy. In light of the many previous theoretical studies with which to compare and the long-standing unresolved controversies surrounding the complex, ferrocene seems to be ideally suited as a test of the INDO method for organometallic transition-metal complexes.

II. Method

The INDO method, including the technique for calculating electronic spectra, is summarized elsewhere.[18-20] Briefly the procedure is as follows. INDO/s, where the one-center core integrals are obtained from ionization potentials only, rather than from ionization potentials and electron affinities, is used to calculate the ground-state configuration in terms of molecular orbital coefficients and eigenvalues. The photoemission spectrum of ferrocene is estimated by Koopmans' theorem[39] from the eigenvalues of the ground state or calculated directly by determining the energy of the first few low-energy states of the ferrocenium ion. The electronic spectrum is calculated from the self-consistent field (SCF) ground state of ferrocene by performing a virtual orbital configuration interaction (CI) which results in the desired spectroscopic transition energies and oscillator strengths. These latter are evaluated using the one-center dipole length integrals. Refinements to the method which will be introduced here include (1) a procedure for determining one-center core integrals for transition metals, (2) incorporation of an empirical Weiss-Mataga-Nishimoto formula for two-electron repulsion integrals involving at least one transition-metal center, (3) inclusion of "mixed" two-electron integrals (Slater-Condon factors) on one metal center that are of neither a Coulomb nor exchange type, and (4) selection of a consistent set of resonance integrals for the calculation of spectra.

In the molecular orbital model, using the unrestricted Hartree-Fock theory, we are interested in solving the Fock equations

$$F^{\alpha}C^{\alpha} = C^{\alpha}E^{\alpha} \tag{1}$$

for an orthogonalized atomic basis set $\{\chi_\mu\}$, where E^α is the diagonal matrix of eigenvalues for the α spin molecular orbitals, C^α is a square matrix the ith column of which is the molecular orbital coefficients of the ith molecular orbital $\phi_i{}^\alpha$

$$\phi_i{}^{\alpha} = \sum c^{\alpha}{}_{i\mu}\chi_\mu \tag{2}$$

F^α is the Fock or enery matrix

$$F^{\alpha} = H + J - K^{\alpha} \equiv H + G^{\alpha} \tag{3}$$

and similar expressions are appropriate for β spin matrices and orbitals. In the above, H is the one-electron matrix, and $G^\alpha = J - K^\alpha$ is the two-electron matrix consisting of Coulomb terms minus exchange. The one-electron matrix H is specified by

$$H^{AA}{}_{\mu\mu} = U^{AA}{}_{\mu\mu} - \sum_{B\neq A} Z_B(\chi_\mu|R_B{}^{-1}|\chi_\mu) \tag{4}$$

$$U^{AA}{}_{\mu\mu} \equiv (\chi_\mu|-\nabla^2/2 - Z_A/R_A|\chi_\mu)$$

$$H_{\mu\nu} = (\chi_\mu| - \nabla^2/2 - \sum_{A} Z_A/R_A|\chi\nu) \tag{5}$$

Using the INDO model of Pople, Santry, and Segal we obtain

$$H^{AA}{}_{\mu\mu} = U^{AA}{}_{\mu\mu} - \sum_{B\neq A} Z_B\gamma_{AB} \tag{6}$$

$$H^{AA}{}_{\mu\nu} = 0 \tag{7}$$

$$H^{AB}{}_{\mu\nu} = (\beta^0{}_{A,\mu} + \beta^0{}_{\beta,\nu})\overline{\Delta}_{\mu\nu}/2$$

$$\gamma_{AB} = (\overline{\chi}_\mu\overline{\chi}_\mu|\overline{\chi}_\nu\overline{\chi}_\nu) \tag{8}$$

$$\equiv \int d\tau(1)\, d\tau(2)\, \overline{\chi}_\mu(1)\overline{\chi}_\mu(1)r_{12}{}^{-1}\overline{\chi}_\nu(2)\overline{\chi}_\nu(2)$$

$\{\beta^0{}_{A,\mu}\}$ are atomic parameters, chosen empirically to give best agreement with experiment. The same parameter is used for either an s or p atomic orbital, $\beta_{A,s} = \beta_{A,p}$, but a different parameter is chosen for the atomic d orbitals.[6,19,20] $\overline{\Delta}_{\mu\nu}$ is a proportionality constant, usually the orbital overlap calculated treating χ_μ and χ_ν as Slater-type orbitals,[12-15] or an integral simply related to the overlap.[16-19] γ_{AB} is the two-electron Coulomb integral calculated treating χ_μ of atom A and χ_ν of atom B as if both were of s symmetry. Such an approximation

Table I. Fractional Contribution of the $d^{n-2}s^2$ Configuration (C_1^2) to the Core Integral $(U_{dd})_I$ as a Function of the Energy Difference between the d^{n-2} and $d^{n-1}s^1$ Configuration ($\Delta E_{H_{11}-H_{22}}$) for $V = -0.02$ au (See Figure 1)

metal	$\Delta E_{H_{11}-H_{22}}$	C_1^2
Ca	0.095	0.9608
Sc	0.074	0.9399
Ti	0.056	0.9069
V	0.037	0.8395
Cr	0.018	0.7052
Mn	0.014	0.6652
Fe	−0.016	0.3143
Co	−0.029	0.2065
Ni	−0.041	0.1421
Cu	−0.055	0.0956
Zn		0.0000

is required by rotational invariance. Since the orbital exponents of s and p atomic orbitals are chosen the same for a given atom, $\gamma^{AB}{}_{ss} = \gamma^{AB}{}_{sp} = \gamma^{AB}{}_{pp} \equiv \gamma_{AB}$. However, the exponent of a d atomic orbital is not the same as an s or p. For systems containing transition metals, then

$$H^{AA}{}_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} \{(n_s + n_p)_B \gamma_{\bar{\mu}\beta}(s) + (n_d)_B \gamma_{\bar{\mu}\beta}(d)\} \tag{9}$$

where $(n_s)_B$ is the number of s electrons in the ground-state configuration of atom B, etc. The adoption of eq 9 as a generalization of eq 7 will prove consistent with our choice of $U_{\mu\mu}$, and properly calculate atoms at large internuclear separation.

One-center core integrals $U_{\mu\mu}$ are taken empirically from atomic ionization.[40] For transition metals with s, p, and d functions there are two possible processes of ionization dependent on the configuration of the metal atom:

process I:	I_s	$3d^{n-1}4s \rightarrow 3d^{n-1}$
	I_p	$3d^{n-1}4p \rightarrow 3d^{n-1}$
	I_d	$3d^{n-1}4s \rightarrow 3d^{n-2}4s$
process II:	I_s	$3d^{n-2}4s^2 \rightarrow 3d^{n-2}4s$
	I_p	$3d^{n-2}4s4p \rightarrow 3d^{n-2}4s$
	I_d	$3d^{n-2}4s^2 \rightarrow 3d^{n-3}4s^2$

Clack and co-workers[6] use process II in their CNDO and INDO methods and indeed for Zn($d^{10}s^2$) this process is the only one that is viable. As given in Table I, a $d^{n-2}s^2$ configuration is also the lowest average energy configuration for Ca, Sc, Ti, and V; on the other hand, a $d^{n-1}s^1$ configuration is lowest for Co, Ni, and Cu.[19] The remaining first-row transition metals are more ambiguous with a $d^{n-2}s^2$ configuration apparently favored for Cr and Mn and a $d^{n-1}s^1$ configuration for Fe.[40,41]

Experience with simple inorganic complexes of Cr, Mn, Fe, and Co and extensive calculations including CI on $Cr(CO)_6$[19,42] indicate that for these transition metals a $d^{n-2}s^2$ configuration yields a calculated metal-ligand equilibrium separation that is longer than observed, whereas a $d^{n-1}s^1$ configuration yields a calculated equilibrium separation smaller than observed. It appears that empirical parameters derived solely from one process or the other cannot adequately describe the ground state. A procedure has been developed to include both processes in the empirical evaluation of the core integrals. The relative contribution of each process is determined by the relative energies of the two configurations of $d^{n-2}s^2$ and $d^{n-1}s^1$ for each metal, as described below.

Let the two configurations interact through some perturbation V caused by complex formation. The resultant matrix equation is represented by

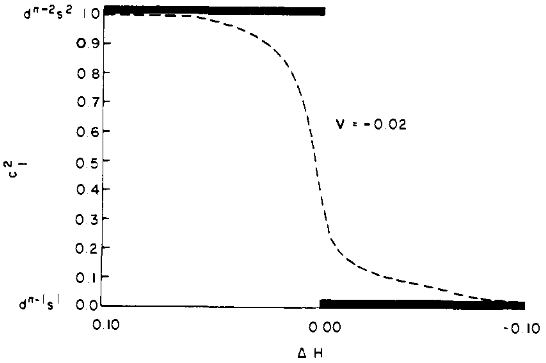

Figure 1. C_1^2; fractional contribution of the $d^{n-2}s^2$ configuration to I_d (ionization potential of the d orbital) as a function of the energy difference between the $d^{n-2}s^2$ and $d^{n-1}s^1$ configurations ($\Delta H = H_{11} - H_{22}$).

$$\begin{vmatrix} H_{11} & V \\ V & H_{22} \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = \epsilon \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} \tag{10}$$

where H_{11} and H_{22} are the average energies of the configurations $d^{n-2}s^2$ and $d^{n-1}s^1$ respectively, and C_1 and C_2 the contribution of each state to the eigenvector with eigenvalue ϵ. For normalization, $C_1^2 + C_2^2 = 1$. If $V = 0$, then $H_{11}C_1 = \epsilon_1 C_1$ and $H_{22}C_2 = \epsilon_2 C_2$ and, as in the past, we would use either the $d^{n-1}s^1$ or $d^{n-2}s^2$ pure configuration for the ground state depending on whether ϵ_1 or ϵ_2 were lower in energy.

If $V \neq 0$, then

$$H_{11}C_1 + VC_2 = \epsilon C_1 \tag{11a}$$

and

$$VC_1 + H_{22}C_2 = \epsilon C_2 \tag{11b}$$

$$\epsilon = \frac{H_{11} + H_{22}}{2} \pm 1/2\sqrt{(H_{11} - H_{22})^2 + 4V^2} \tag{12}$$

Substituting for ϵ from (11a) and simplifying, we get for $H_{11} < H_{22}$

$$\chi = C_1/C_2 = \frac{H_{11} - H_{22}}{2V} + \sqrt{\left(\frac{H_{11} - H_{22}}{2V}\right)^2 + 1} \tag{13}$$

and thus

$$C_1^2 = \frac{\chi^2}{1 + \chi^2} \tag{14}$$

From eq 13 and 14, we obtain C_1^2 or the contribution of the $d^{n-2}s^2$ configuration as a function of the energy difference between the $d^{n-2}s^2$ and $d^{n-1}s^1$ configurations ($H_{11} - H_{22}$) and an arbitrary V. Empirically we find $V = -0.02$ to give the best equilibrium geometries with a mixing of $d^{n-2}s^2$ and $d^{n-1}s^1$ configurations as given in Table I and shown in Figure 1. We employ $V = -0.02$ as a constant parameter, although one could argue that V should be complex dependent and be obtained in a self-consistent fashion. It is anticipated that such a refinement would have little effect. $U_{\mu\mu}$ is thus calculated from a weighted average of I_μ ($d^{n-2}s^2$) and I_μ($d^{n-1}s^1$). n_s and n_d of eq 8 are also modified so as to reflect the relative contribution of each configuration.

In the unrestricted Hartree-Fock formalism that is used here, the G matrix elements are given by

$$G^\alpha{}_{\mu\nu} = \sum_{\sigma\lambda} P_{\sigma\lambda}(\mu\nu|\sigma\lambda) - P^\alpha{}_{\sigma\lambda}(\mu\sigma|\nu\lambda) \tag{15}$$

with a similar expression for the β electron G^β matrix. Here P^α is the first-order α spin density matrix or, in the orthogonalized set envisioned here, the α spin charge and bond order matrix

$$P^{\alpha}{}_{\mu\nu} = \sum_{a}^{\mathrm{MO}} C^{\alpha}{}_{\mu a} C^{\alpha}{}_{\nu a} n_a \tag{16}$$

where $n_a = 0$ or 1, the occupancy of $\phi^{\alpha}{}_a$, and P is the total first-order density

$$P = P^{\alpha} + P^{\beta} \tag{17}$$

Under this formalism, for a closed-shell system

$$P^{\alpha} = P^{\beta} = \frac{1}{2} P \tag{18}$$

Invoking the INDO model simplifies eq 15 greatly:

$$\begin{aligned} G^{\alpha}{}_{\mu\mu} &= \sum_{\sigma\lambda}^{\mathrm{A}} [P_{\sigma\lambda}(\mu\mu|\sigma\lambda) - P^{\alpha}{}_{\sigma\lambda}(\mu\sigma|\mu\lambda)] \\ &\qquad + \sum_{\sigma \notin \mathrm{A}} P_{\sigma\sigma}\gamma_{\sigma\mu};\ \mu \in \mathrm{A} \\ G^{\alpha}{}_{\mu\nu} &= \sum_{\sigma,\lambda}^{\mathrm{A}} [P_{\sigma\lambda}(\mu\nu|\sigma\lambda) - 1/2 P^{\alpha}{}_{\sigma\lambda}(\mu\sigma|\nu\lambda)];\ \mu, \nu \in \mathrm{A} \\ G^{\alpha}{}_{\mu\nu} &= -P^{\alpha}{}_{\mu\nu}\gamma_{\overline{\mu\nu}};\ \mu \in \mathrm{A}, \nu \in \mathrm{B}, \mathrm{A} \neq \mathrm{B} \end{aligned} \tag{19}$$

with similar expressions for G^{β}.

The two-electron two-center Coulomb integrals $\gamma_{\overline{\mu\nu}}$ are required for eq 8 and for eq 19. They have been evaluated theoretically in ref 8 where ground-state geometries were of principal interest. For spectroscopy, however, a great deal of experience has been gained by using Coulomb integrals chosen semiempirically,[18,43] a procedure we adopt here.

The two-electron Coulomb integrals are evaluated from a modified Mataga-Nishimoto formula[44]

$$\gamma_{\mathrm{AB}} = \frac{f_{\gamma}}{2f_{\gamma}/(\gamma_{\mathrm{AA}} + \gamma_{\mathrm{BB}}) + R_{\mathrm{AB}}} \tag{20}$$

where R_{AB} is the distance between the two centers in Bohr radii. γ_{AA} is obtained from Pariser's observation[45]

$$\gamma_{\mathrm{AA}} = F^0(\mathrm{AA}) = I_{\mathrm{A}} - A_{\mathrm{A}} \tag{21}$$

as the difference between the ionization potential and electron affinity of an s, p, or d electron. The formula is modified by the introduction of the parameter f_{γ} as suggested by Weiss,[46] which we set equal to 1.2. This value has been extensively used and has proven very successful in the calculation of spectra of conjugated systems.[18]

Since values of $I_{\mathrm{A}} - A_{\mathrm{A}}$ are similar for s and p orbitals, we make the approximation that $\gamma_{\overline{\mathrm{AA}}} = \gamma_{\overline{\mathrm{ss}}} = \gamma_{\overline{\mathrm{sp}}} = \gamma_{\overline{\mathrm{pp}}} = F^0(\mathrm{AA})$ as before. For a third-row element, $\gamma_{\overline{\mathrm{AA}}}$ for s and p electrons is taken as the linear average of $I_{\mathrm{A}} - A_{\mathrm{A}}$ for s and p electrons from both processes I and II. Similarly, $\gamma_{\overline{\mathrm{dd}}}$ is taken as the average of $I_{\mathrm{d}} - A_{\mathrm{d}}$ for d electrons from processes I and II. In both cases, the final values are smoothed from a quadratic fit of γ_{ss} or γ_{dd} with the number of valence electrons.

Values of $\gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} = \gamma_{\bar{\mathrm{p}}\bar{\mathrm{d}}}$ for the third-row elements are derived in the following fashion. Ionization of a d electron by process I is envisioned as

$$\mathrm{d}^{n-1}\mathrm{s} \rightarrow \mathrm{d}^{n-2}\,\mathrm{s} + I_{\mathrm{d}}(\mathrm{I}) \tag{22}$$

The configuration energy of the left side of the equation may be expressed in terms of core integrals U_{d} and U_{s} and repulsion integrals $\gamma_{\mu\nu}$ as

$$(n-1)U_{\mathrm{dd}} + U_{\mathrm{ss}} + \frac{(n-1)(n-2)}{2}\gamma_{\bar{\mathrm{d}}\bar{\mathrm{d}}} + (n-1)\gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} \tag{23a}$$

and of the right side as

$$(n-1)U_{\mathrm{dd}} + U_{\mathrm{ss}} + \frac{(n-1)(n-2)}{2}\gamma_{\overline{\mathrm{dd}}} + (n-1)\gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} \tag{23a}$$

yielding

$$I_{\mathrm{d}}(\mathrm{I}) = -U_{\mathrm{dd}} + (2-n)\gamma_{\overline{\mathrm{dd}}} - \gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} \tag{23c}$$

Ionization of a d electron by process II is envisioned as

$$\mathrm{d}^{n-2}\mathrm{s}^2 \rightarrow \mathrm{d}^{n-3}\mathrm{s}^2 + I_{\mathrm{d}}(\mathrm{II}) \tag{24}$$

The energy of the configuration to the left is

$$(n-2)U_{\mathrm{dd}} + 2U_{\mathrm{ss}} + \frac{(n-2)(n-3)}{2}\gamma_{\overline{\mathrm{dd}}} + \gamma_{\overline{\mathrm{ss}}} + 2(n-s)\gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} \tag{25a}$$

and of the configuration to the right

$$(n-3)U_{\mathrm{dd}} + 2U_{\mathrm{ss}} + \frac{(n-3)(n-4)}{2}\gamma_{\overline{\mathrm{dd}}} + \gamma_{\overline{\mathrm{ss}}} + 2\,(n-3)\gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} \tag{25b}$$

yielding

$$I_{\mathrm{d}}(\mathrm{II}) = -U_{\mathrm{dd}} + (3-n)\gamma_{\overline{\mathrm{dd}}} - 2\gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} \tag{25c}$$

Subtracting (23c) from (25c) gives

$$I_{\mathrm{d}}(\mathrm{II}) - I_{\mathrm{d}}(\mathrm{I}) = \gamma_{\overline{\mathrm{dd}}} - \gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} \tag{26}$$

A similar treatment for ionization of an s electron by process I

$$\mathrm{d}^{n-1}\mathrm{s} \rightarrow \mathrm{d}^{n-1} + I_{\mathrm{s}}(\mathrm{I}) \tag{27}$$

or by process II

$$\mathrm{d}^{n-2}\mathrm{s}^2 \rightarrow \mathrm{d}^{n-2}\mathrm{s} + I_{\mathrm{s}}(\mathrm{II}) \tag{28}$$

gives

$$I_{\mathrm{s}}(\mathrm{II}) - I_{\mathrm{s}}(\mathrm{I}) = \gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}} - \gamma_{\overline{\mathrm{ss}}} \tag{29}$$

The values of γ_{sd} obtained by averaging the results of eq 26 and 29 were again smoothed by a quadratic fit. From these values of $\gamma_{\bar{\mathrm{s}}\bar{\mathrm{d}}}$, new values of $\gamma_{\overline{\mathrm{ss}}}$ and $\gamma_{\overline{\mathrm{dd}}}$ are inferred. An iterative procedure is thus suggested and performed. The final results are tabulated in Table II.

For an s, p basis set, eq 19 may be evaluated in a straightforward fashion as only one-center integrals of the Coulomb form $(\chi_{\mu}\chi_{\mu}|\chi_{\nu}\chi_{\nu})$ and exchange form $(\chi_{\mu}\chi_{\nu}|\chi_{\mu}\chi_{\nu})$ do not vanish. For atoms with s, p, and d atomic basis functions, there are in addition to the Coulomb and exchange integrals of the above type various hydrid integrals, as for example, $(\mathrm{p}_x\mathrm{d}_{yz}|\mathrm{p}_z\mathrm{d}_{xy})$, that do not vanish. These are related to the Coulomb and exchange integrals by molecular rotation. To preserve rotational invariance in the method, either averages of Coulomb and exchange type integrals must be used,[47-50] or all integrals that transform into one another upon rotation must be included. We chose the latter alternative, for, although ground-state calculations do not seem much affected by the choice of procedure (or, for that matter, by permitting the variance itself),[51,52] the effect on the calculation of excited states through CI is substantial. In ferrocene, the states E_2'' and E_1'' from the excitation $\mathrm{e}'_2(\mathrm{d}_{xy}, \mathrm{d}_{x^2-y^2}) \rightarrow \mathrm{e}_1''\,(\mathrm{d}_{xz}, \mathrm{d}_{yz})$ are calculated as degenerate when the hydrid integrals are neglected but split by 8000 cm^{-1} by mixing through the $(\mathrm{d}_{xz}\mathrm{d}_{xy}|\mathrm{d}_{x^2-y^2}\mathrm{d}_{yz})$ term.

All integrals that involve Slater–Condon F and G integrals, as reported in the Appendix of ref 20, are thus retained. Mixed one-center integrals of the Slater-Condon R type[53] are set to zero. These integrals are small, do not contribute to rotational variance, and cannot be evaluated empirically through atomic spectra.

For spectroscopic calculations, an empirical evaluation of two-electron repulsion integrals was used. Resonance parameters β of eq 6 were chosen to give the best agreement between calculated and experimental spectra. For hydrogen and the first-row elements, the values adopted were those established from hydrocarbon spectra.[18] For iron, the values used were $\beta_{4s} = \beta_{4p} = -1.0$ eV and $\beta_{3d} = -23.0$ eV. The β_{3d} value is 7.0 eV greater than that used with theoretical two-electron repulsion integrals for geometry optimization.[19] This increase is consistent with the trend shown for other atoms in going from the conventional zero differential overlap theories to spectroscopic methods. This value has also been successfully used in calculating the spectra of $FeCl_4^-$ and several iron porphyrin (model haem) systems.

All other details of the theory are as given in ref 19 and 20.

III. Procedure

LCAO-MO-SCF calculations using the INDO/s approximation outlined elsewhere[18-20] with the modifications described in the previous section have been performed for ferrocene, $Fe(C_5H_5)_2$, and several low-energy states of the ferrocenium ion, $Fe(C_5H_5)_2^+$. All calculations reported here have been made using empirical two-electron repulsion integrals and spectroscopic parametrization for β.

Since there is evidence that interatomic distances are not greatly enhanced in the ion[54] or in the solid,[55] the vapor-phase interatomic distances[56] of Fe-C = 2.057, C-C = 1.429, and C-H = 1.116 Å have been used for both the neutral molecule and cation in an eclipsed (D_{5h}) conformation. The iron was placed at the center of the coordinate system with the cyclopentadienyl rings 1.66 Å above and below the xy plane.

The first five ionization potentials of ferrocene have been evaluated in two ways: (1) by Koopmans' theorem as the negative of the eigenvalues of the ground-state molecular orbitals of ferrocene and (2) by the difference in energy between ferrocene and the five low-energy states of the ferrocenium ion. In the second method, care must be taken to treat the closed-shell neutral species and the open-shell ions with comparable accuracy. Since the former was treated here in a restricted Hartree-Fock (RHF) fashion and the latter in an unrestricted (UHF) fashion, a configuration interaction calculation which included 105 double excitations of A_1' symmetry was performed on the ground state of ferrocene to include some of the correlation energy that is included in a natural fashion in UHF calculations. However, there was no appreciable energy lowering.

The electronic spectrum of ferrocene was assigned from the spectroscopic transition energies and oscillator strengths obtained from a CI calculation composed of all single excitations from the 7 highest energy occupied molecular orbitals to the 11 lowest energy virtual orbitals plus two higher energy unoccupied molecular orbitals with some iron d-orbital character. The calculation was symmetry factored into the eight representations of the D_{5h} point group in order to reduce the computation time. Overall, 140 configurations were considered in the calculation of the UV-visible spectrum.

The ground-state SCF calculations took approximately 20-30 s each on the IBM 370/195 and were stored on disk. From this information the CI for each symmetry type required approximately 20-40 s.

IV. Caveat

The INDO spectroscopic model has been parametrized by comparison of experimental spectra with calculated results obtained after extensive studies with singly excited configurations in a configuration interaction treatment.[16-18] This basic model has been extended in this paper to include members of the first transition series, and has been, and is being, applied to rather large systems in which the role of higher excited configurations (double excited, triply excited, etc., as opposed to higher *energy* configurations) is uncertain. Although use of semiempirical two-electron integrals (γ) and empirical resonance integrals (β) might be expected to include the effect of higher energy excitations in an average way,[57,58] no such parametrization can be expected to compensate for multiple excited configurations if those configurations are actually in the spectroscopic region of interest, or if a given double excitation heavily mixes with the reference configuration in the mathematical description of the ground state. In these cases certain higher excitations *must* be included explicitly. There then arises the question of which effects, if any, of higher excitations are included twice? Is it necessary to reparametrize the model on, say, single and double excitations and those triples that are doubly excited relative to the important singles? Preliminary investigations seem to indicate that higher excitations can be included in the model without extensive reparametrization.[59] Nevertheless, some systems—and ferrocene does *not* appear to be one of them—cannot be well described without these higher excitations, even with the given semiempirical parametrization. The frequency of these more difficult to handle systems is expected to increase with increasing molecular size, and the effect will be aggravated by the presence of a transition metal. The presence of two like transition metals in most complexes will require consideration of higher excitations in the description of both ground and excited states.

Table II. Atomic Parameters. Two-Electron Coulomb Integrals for Third-Row Metals (eV)

metal	γ_{ss}	γ_{sd}	γ_{dd}
Ca	3.25	4.00	6.03
Sc	3.89	4.71	7.02
Ti	4.50	5.38	7.98
V	5.07	6.01	8.91
Cr	5.60	6.60	9.81
Mn	6.09	7.16	10.68
Fe	6.54	7.68	11.52
Co	6.96	8.16	12.32
Ni	7.34	8.61	13.10
Cu	7.68	9.01	13.84
Zn	7.98	9.39	14.55

In addition to the model being grounded on singly excited configuration interaction, which is not a severe limitation in most cases, the present model is also founded on a basis set of valence-type orbitals. Since Rydberg-type orbitals are not included in the atomic basis, Rydberg-type states cannot be described. This is as severe a limitation on small molecules where the Rydberg states are among the lowest lying excited states as exclusion of higher excitations is for very large systems, where they are low lying.

For most molecules Rydberg states might be expected to make their appearance 2-3 eV below the first ionization potential. In this region of the spectrum the density of states is quite high. The appearance of broad absorptions usually found within 2-3 eV of the first ionization potential for large systems may have as much to do with the presence of many electronic origins as it has to do with the vibrational broadening usually considered.

The present model contains only valence-type excitations. Insofar as a single determinant description is a good description of the ground state, most all of the *intensity* of the spectrum is carried by the singly excited valence states. Higher excitations do not couple with the ground state through the one electron dipole operator. Singly excited Rydberg configurations may, of course, couple via the dipole operator, but the diffuse nature of these orbitals ensures low oscillator strength,

Table III. Nature and Energy (eV) of Highest Occupied and Lowest Empty Molecular Orbitals of Ferrocene

symmetry	INDO/S[a]	character[b]	ab initio[c]
$9a_1'$	3.43	81% 4s; 4% d_{z^2}	
$5e_1''$	3.05	30% L(π*); 65% d_π	
$5e_2''$	2.99	100% L(σ*)	
$6e_2'$	2.98	99% L(σ*)	
$5e_2'$	2.55	89% L(π*); 11% $3d_\delta$	
$4l_2''$[d]	2.17	100% L(π)*	
$4e_2'$	−7.82	85% d_σ	−11.83 (−5.69)[e]
$8a_1'$	−8.27	90% d_{z^2}; 5% 4s	−14.29 (−7.46)[e]
$4e_1''$	−9.58	75% L(π); 25% $d_{xz}d_{yz}$	−9.54 (−8.79)[e]
$6e_1'$	−10.01	87% L(π); 13% $4p_x$, $4p_y$	−9.45 (−8.85)[e]
$6a_2$	−13.46	92% L(π); 8% $4p_z$	−13.63
$5e_1'$	−13.88	100% L(σ)	−14.11
$3e_2''$	−14.25	100% L(σ)	−14.4
$3e_1''$	−14.25	94% L(σ)	−15.2
$3e_2'$	−14.50	98% L(σ)	−15.3
$7a_1'$	−16.28	94% L(π)	−15.7
$2e_2''$	−21.71	100% L(σ); 32% C(2s)	−19.9
$2e_2'$	−22.34	99% L(σ); 32% C(2s)	−20.3
$5a_2''$	−22.55	100% L(σ); C–H bonding	−19.0
$6a_1'$	−23.72	96% L(σ); C–H bonding	−19.8

[a] Spectroscopic parametrization. [b] M = Fe,, L = ligand, C = carbon. [c] Orbital energies from ref 38. [d] Highest occupied molecular orbital. [e] ΔE(SCF) calculations from ref 38 on the ion states with the hole in each of these MOs. Values correspond to the energies of these orbitals including relaxation.

Table IV, Calculated Singlet State Transitions in Ferrocene

	calcd, cm^{-1}	type	
IIa	21 700	E_1'' (75% $8a_1' \rightarrow 5e_1''$ 25% $4e_2' \rightarrow 5e_1''$)	$d_{z^2} \rightarrow d_\pi$
b	23 900	E_2'' ($4e_2' \rightarrow 5e_1''$)	$d_\delta \rightarrow d_\pi$
III	31 900	E_1'' (75% $4e_2'' \rightarrow 5e_1''$; 25% $8a_1' \rightarrow 5e_1''$)	$d_\delta \rightarrow d_\pi$
IV	36 900	E_2' ($4e_2' \rightarrow 9a_1'$)	$d_\delta \rightarrow$ 4s
	39 700	A_1' ($8a_1' \rightarrow 9a_1'$)	$d_{z^2} \rightarrow$ 4s
	39 900	A_2' ($4e_2' \rightarrow 5e_2'$)	$d_\delta \rightarrow L_\pi$*
V	41 200 (0.060)	E_1'($4e_2' \rightarrow 5e_2'$)	$d_\delta \rightarrow L_\pi$*
	42 400	A_1'' ($4e_2' \rightarrow 4e_2''$)	$d_\delta \rightarrow L_\pi$*
	42 900	E_1'' ($4e_2' \rightarrow 4e_2''$)	$d_\delta \rightarrow L_\pi$*
	44 700	E_2' ($8a_1' \rightarrow 5e_2'$)	$d_{z^2} \rightarrow L_\pi$*
VI	45 300 (0.289)	A_2'' ($4e_2' \rightarrow 4e_2''$)	$d_\delta \rightarrow L_\pi$*
	45 900	E_2'' ($8a_1' \rightarrow 4e_2''$)	$d_{z^2} \rightarrow L_\pi$*
	47 700	A_1' (75% $4e_2' \rightarrow 5e_2'$; 25% $4e_1'' \rightarrow 5e_1''$)	$d_\delta \rightarrow L_\pi$*
	50 200 (0.0)	E_1' ($4e_2' \rightarrow 6e_2'$)	$d_\delta \rightarrow L_\sigma$
	50 300 (0.016)	A_2'' ($4e_2' \rightarrow 5e_2''$)	$d_\delta \rightarrow L_\sigma$
	50 400	A_1' ($4e_2' \rightarrow 6e_2'$)	$d_\delta \rightarrow L_\sigma$
	50 500	A_2' ($4e_2' \rightarrow 6e_2'$)	$d_\delta \rightarrow L_\sigma$
	50 600	E_1'' ($4e_2' \rightarrow 5e_2''$)	$d_\delta \rightarrow L_\sigma$
	50 800	A_1'' ($4e_2' \rightarrow 5e_2''$)	$d_\delta \rightarrow L_\sigma$
	52 300 (0.03)	E_1' (75% $4e_2' \rightarrow 8e_1'$; 25% $4e_2' \rightarrow 7e_1'$)	$d_\delta \rightarrow 4p_{x,y}$
	54 100	E_2' ($8a_1' \rightarrow 6e_2'$)	$d_\delta \rightarrow L_\sigma$*
	54 400	E_2'' ($8a_1' \rightarrow 5e_2''$)	$d_\delta \rightarrow L_\sigma$*
	56 800	A_2'' ($6e_1' \rightarrow 5e_1''$)	$L_\pi \rightarrow d_\pi$
	57 700	E_2' (53% $4e_1'' \rightarrow 5e_1''$; 35% $4e_1'' \rightarrow 4e_2''$)	$L_\pi \rightarrow d_\pi$
	59 600	E_2'' (50% $4e_1'' \rightarrow 5e_2'$)	$L_\pi \rightarrow L_\pi$*
	60 300	E_2' (mixed)	$L_\pi \rightarrow d_\pi$
	61 700 (0.17)	E_1' (mixed)	$L_\pi \rightarrow L_\sigma$*
	65 000	E_1' (mixed)	$L_\pi \rightarrow L_\pi$*
	68 000 (1.2)		

generally less than 0.01 per degree of degeneracy.[60] In addition, the intensity of the higher members of a series is expected to drop off from this maximum value as n^{-3}, where n is the principal quantum number describing the sequence. Rydberg states thus often appear as weak, sharp spikes, perhaps riding on broad valence absorptions, that cannot be a feature of any valence orbital only calculation, or they can borrow intensity through configurational mixing with the more intense valence states. In the latter case the Rydberg and valence configurations need to lie very close, and this mixing may lead to broadening, but, since the Rydberg configurations carry little intensity of their own, the exclusion of Rydberg states will not affect the main features of the calculated spectrum of most molecules (intensity vs. energy), although, of course, a detailed description of the states involved may not be accurate. With this caveat we proceed.

Several attempts have been made to include Rydberg orbitals within the spectroscopic INDO model,[61,62] and we are presently investigating these ideas.

V. Results

Ferrocene has been of theoretical and experimental concern since its discovery in 1951[63] and has been the subject of several reviews.[64-66] The basic bonding involved in the ground state now seems well established, although neither the UV-visible nor photoelectron spectra have been assigned unequivocally by theory or experiment.

The principal binding in ferrocene is of the π type. Each cyclopentadienyl anion (Cp$^-$) has five π symmetry molecular orbitals (MOs) of a_2'', e_1'', and e_2'' symmetry. The a_2'' and e_1'' MOs are filled with six valence π electrons, satisfying the Hückel $4n + 2$ rule for aromatic stability. Upon the formation of the eclipsed D_{5h} dimer, the two sets of a_2', e_1'', and e_2'' π MOs form weakly bonding and antibonding combinations, becoming, in increasing order of energy, (a_1', a_2''), (e_1', e_1''), and (e_2'', e_2'). The first two pairs contain the 12 π symmetry valence electrons. The 3d atomic orbital (AOs) of iron transforms as $a_1'(d_{z^2})$, $e_2'(d_{x^2-y^2}, d_{xy})$, and e_1'' (d_{xz}, d_{yz}) in D_{5h}. In ferrocene, the iron has a formal d^6 configuration: a_1' $(d_{z^2})^2$ e_2' $(d_{x^2-y^2}, d_{xy})^4$ $e_1''(d_{xz}, d_{yz})^0$. A Mulliken population analysis[67] for the present calculation yields a net charge on Fe of +1.89, supporting a simple ligand field Fe^{2+}(Cp$^-$)$_2$ picture of ferrocene. The metal-ligand bonding is primarily through the e_1'' highest occupied ligand orbitals depressed in energy through interaction with the $e_1''(d_{xz}, d_{yz})$ iron orbitals, unoccupied in the complex.

The highest occupied MOs are calculated to be the degenerate $4e_2'$ pair each of 86% metal dσ character (Table III). This degree of covalency is consistent with the value of 91% estimated by Prins on the basis of ESR measurements for the ferrocenium ion[23] and the calculated value of 87% obtained for the related $^3E_2'$ state. Next lower in energy lies the $8a_1'$ MO with 90% metal d_{z^2} followed by the $4e_1''$ ligand π orbitals responsible for most of the metal-ligand binding. Each of these doubly occupied e_1'' MOs contributes 0.5 electron to each of the formally unoccupied metal $3d_{xz}$ and $3d_{yz}$ AOs.

The lowest energy unoccupied MOs of ferrocene are $4e_2''$ and $5e_2''$, the Cp$^-$$\pi$* MOs. The order of these two orbitals is reversed from that in the Cp$^-$ dimer since the $5e_2'$ orbitals are antibonding with respect to the metal $d_{x^2-y^2}$, d_{xy} pair. The $5e_1''$ unoccupied metal orbitals are considerably higher in energy. Each consists of 65% metal $3d_{xz}$ or $3d_{yz}$ character compared to 25% in the occupied bonding partners ($4e_1''$).

The energy of the principal d_{z^2} orbital ($8a_1'$) is calculated slightly lower than that of the $d_{x^2-y^2}$, d_{xy} orbitals ($4e_2'$). The latter pair is somewhat stabilized by mixing with the ligand dimer e_2' orbital, but the former is apparently more stabilized by a 5% bonding admixture with the 4s metal orbital. The relative energies of these MOs are a question of continuing interest.[68] We might caution in this respect that there is no direct observable that will resolve the controversy. The UV-visible spectrum and the ionization spectrum measure differ-

Table V. Assignment of the Ferrocene Spectrum (Energy in Units of 1000 cm^{-1})

					ab initio[c]		
	obsd[a]		INDO/s[b]		CI	ΔE(SCF)	MSX_α[d]
I	18.9	$^3E_{1g}(^3E_1'')$	20.5	$^3E_1''$	14.6		
			20.6	$^3E_1''$	to		
			20.6	$^3E_2''$	15.1		
II[h]a	21.8	$^1E_{1g}(^1E_1'')$	21.7	$^1E_1''$	26.7	14.2	20.5
b	24.0	$^1E_{2g}(^1E_2'')$	23.9	$^1E_2''$	21.2	13.3	25.2
III	30.8	$^1E_{1g}(^1E_1'')$	31.9	$^1E_1''$	46.3	21.8	25.2
IV	37.7 (0.02)[e]		36.9	$^1E_2'$	all		36.5[f]
			39.7	$^1A_1'$	above		
			39.9	$^1A_2'$	73.0		
V	41.7 (0.01)		41.2 (0.06)	$^1E_1'$			43.9[f]
	42.2 (0.01)		42.4	$^1A_1''$		60.7	36.5[f]
			42.9	$^1E_1''$		61.4	
			44.7	$^1E_2'$			39.2[f]
VI	46.9 (0.10)[e]	$^1A_{2u}(^1A_2'')$	45.3 (0.29)	$^1A_2''$		62.0[g]	36.5[f]
			45.9	$^1E_2''$		46.3[g]	
			47.7	$^1A_2'$			
	49.7[e]		50.2 (0.00)	$^1E_1'$			47.1
VII	50.9 (0.69)[e]	$^1A_{2u}(^1A_2'')$	50.3 (0.02)	$^1A_2''$			43.9[f]
	53.1		52.3 (0.03)	$^1E_1'$			

[a] From ref 22 unless otherwise noted. [b] On eclipsed ferrocene. The group theoretical assignments have been made by correspondence between D_{5h} and D_{5d}. [c] On staggered ferrocene, ref 37. [d] Average singlet-triplet values from ref 68. [e] From ref 21. [f] The irreducible representations that result from orbital excitations have not been separated in ref 68. [g] See text for discussion of these states. They are arranged in this table only according to symmetry type, not orbital character. [h] II is a transition centered at 22 000 cm^{-1} but analyzed into two transitions, IIa and IIb.

ences in state energies, not orbital energies. Extrapolation of this information into an orbital picture may be misleading.[69] Ionization and electronic excitation (to an excited state of the neutral) can be two very different processes. Computationally, Koopmans' theorem, which equates ionization potentials to the negative of orbital eigenvalues, may not be justified for transition-metal complexes, especially if the orbital is essentially metal. In addition, excitation energies are not obtained from the difference between two orbital energies, but rather from this difference corrected for by two-electron terms. Furthermore, corrections for relaxation effects must be made to these simple descriptions of ionization and excitation. The former is most easily accomplished by making a separate SCF calculation of the ion and subtracting this energy from the neutral species. The latter is corrected most easily by performing CI.

Table III summarizes the frontier orbitals that are obtained for ferrocene and compares them with those obtained from an ab initio study.[38] The four highest energy occupied orbitals have significant metal character and would be expected to have appreciable relaxation. The INDO/s calculation with spectroscopic parametrization mimics to some degree the effect of atomic relaxation, a point to which we return. Thus, as shown in Table III, there is a significant difference in the INDO/s and ab initio results[38] for these four molecular orbitals. However, the agreement is much improved when the INDO/s results are compared with the ab initio ΔE (SCF) energies of these orbitals which account for relaxation. For the orbitals that are principally ligand in nature, the relaxation energy is thought to be less than approximately 1 eV. The remaining INDO/s orbitals energies in the table are in good accord with the ab initio values for neutral ferrocene.

The calculated UV-visible spectrum of ferrocene is presented in Table IV. The results are compared with the experimental observations of Armstrong, Smith, Elder, and McGlynn[21] and Sohn, Hendrickson, and Gray,[22] the calculated ab initio values of Rohmer, Veillard, and Wood,[37] and the scattered wave X-α results of Rosch and Johnson.[68]

As seen in Table V, the lowest observed state at 18 900 cm^{-1} is assigned as $^3E_{1g}$. This is in good agreement with our calculation and the CI calculations of Rohmer et al., which both predict three low-lying nearly degenerate triplet states at about this energy. The lowest triplet is calculated by INDO/s to be nearly pure $8a_1'$ (d_{z^2}) → $5e_1''(d_{\pi^*})^3E_1''$.

The first singlet is reported as a broad band with a maximum at ~22 000 cm^{-1}.[21,22] Sohn and co-workers assign this as two separate excitations of $^1E_1''$ and $^1E_2''$ type, principally $8a_1'(d_{z^2})$ → $5e_1''(d_{\pi^*})$ and $4e_2'(d_\delta)$ → $5e_1'(d_{\pi^*})$, respectively. This assignment is in excellent accord with our results and the scattered-wave results. The ab initio calculations confirm the presence of two bands in this region but have the reverse order.

We assign the third band observed at 30 800 cm^{-1} as $^1E_1''$, again principally $4e_2'(d_\delta)$ → $5e_1''(d_{\pi^*})$. The similarity in vibrational structure of bands IIa and III, both activated by a low-energy vibrational mode of ~260 cm^{-1}, suggests that these two bands are of the same symmetry, lending credence to our assignment of band IIA as $^1E_1''$ rather than that suggested by Rohmer et al. The scattered-wave calculations do not resolve the degeneracy in the irreducible components of e_2'→ e_1'', but the simplest interpretation of their results is in accord with ours.

At higher frequencies, a broad, structureless band with a superimposed structured spectrum is observed with a maximum at 37 700 cm^{-1}.[22] We calculate three bands in this region, two of which are d → 4s, the third d_δ → L(π)* charge transfer. We assign band IV to any one or all of these states. All three of these transitions are formally forbidden in keeping with the appearance of band IV. The "4s" MO involved in these excitations is very diffuse, with an average radius of 1.7 Å from the iron nucleus. The iron to cyclopentadiene plane distance is 1.66 Å. In this sense, all three transitions calculated in this region have metal to ligand charge transfer character. The position of the d → 4s transition is somewhat sensitive to the size of the 4s basis used and to the resonance parameter $\beta_{A,4s}$ of eq 7. Insofar as the bracketing theorem of Hylleras and Undheim[70] is valid in a semiempirical method, however, these two 3d → 4s transitions represent upper bounds to states of E_2' and A_1' symmetry.

The ab initio CI calculations are difficult to interpret in this region, as ligand to metal, metal to ligand, and ligand to ligand excitations are all calculated in the range 73 000-84 000 cm^{-1},

Table VI. Ionization Potentials of Ferrocene (eV) to Specific States of the Ferrocenium Ion

method	av error[e]	$^2E_2'$	$^2A_1'$	$^2E_1''$	$^2E_1'$	$^2A_2''$	$^2E_1'$
exp[a]		6.86	7.23	8.72	9.38	12.2	13.6
minimal basis set ab initio ΔE(SCF)[b]	2.4	8.3	10.1	11.2	11.1	15.5	
extended basis set ab initio, ΔE(SCF)[c]	0.5	5.69	7.46	8.79	8.85	13.03	13.60
MSXα[d]	1.2	8.5	7.9	9.7	9.3	11.7	11.6
INDO/s[f]							
ΔE(SCF)	0.9	6.10	5.82	9.61	~9.7	13.14	
ϵ MO (VIP)	0.8	7.82	8.27	9.58	10.01	13.46	13.87
av	0.5	6.96	7.05	9.60	~9.9	13.30	13.87

[a] Reference 25. [b] Reference 36. [c] Reference 38. [d] Reference 68. The ionizations calculated at 11.7 and 11.6 eV are both assigned to the experimental peak observed at 12.2 eV. [e] $\Sigma|E(\text{calcd}) - E(\text{obsd})|/n$, assuming this assignment of states. [f] ΔE(SCF) and ϵ(VIP) vertical potential (Koopmans' theorem) from calculation of neutral and ionic states using spectroscopic parametrization.

and as these values are in very poor numerical agreement with experiment.

At first glance, the ΔE(SCF) ab initio calculations appear to contradict our assignment for band IV, assigning this region to $L(\pi) \rightarrow d_{\pi^*}$ transitions of A_1'', E_2'', and A_2'' type with a calculated average value of 46 300 cm^{-1}. Arguing against this assignment is the fact that band IV does not have the appearance of an allowed transition and A_2' is a z-allowed excitation. Further, the excitations that we attribute to band IV have not been considered in the ΔE(SCF) calculation and might be calculated below the $L(\pi) \rightarrow d_{\pi^*}$ type.

If one assumes that the greatest inaccuracies of minimum basis set ab initio work are in the description of the states with occupied ligand π^* orbitals, which thus far appears true, all metal $\rightarrow L(\pi^*)$ excitations might be calculated at a relatively higher energy than $L(\pi) \rightarrow$ metal transitions. Another reason for doubting the ΔE(SCF) assignment of band IV is that adding ~8000 cm^{-1} to the ΔE(SCF) ab initio results (assuming that the ground-state calculation is not of the same quality as the excited states) places the d $\rightarrow$ d* transitions (bands IIa, IIb, and III) in good accord with experiment. If this same correction is added to the $L(\pi) \rightarrow d_{\pi^*}$ excitation assigned to band IV, it is raised to 53 000-56 000 cm^{-1}, consistent with our calculated values of these excitations at ~57 000 and ~61 000 cm^{-1}.

At 41 200 cm^{-1} a weakly allowed $^1E_1'(d_\delta) \rightarrow L(\pi^*)$ excitation is calculated and associated with band V. Experimentally this state does not have the appearance of a truly allowed band because of the long vibrational progression (band VIII of ref 21), but the 0-0 band does appear the strongest of the series. In addition, there is at least another transition, probably forbidden, with maximum observed at ~42 400 cm^{-1}. Possible assignments are suggested in the tables, but the density of states in this region is quite high. We recall also the caveat of the previous section.

Further bands (VI) are observed with origins at ~46 900, 49 700, 50 900, and 53 100 cm^{-1}. The last two of these transitions are clearly allowed, and the first might be also. A great many excitations are calculated in this region, including four with allowed character. The allowed transitions are calculated at 45 300, 50 200, 50 300, and 52 300 cm^{-1}. The total observed oscillator strength in this region is ~0.80 and we have accounted for only 0.34. This might suggest that the amount of CI is getting insufficient at these higher energies to allow lower states to borrow intensity from the higher lying and strongly allowed $^1E_1'$ configurations calculated above 61 000 cm^{-1}, and A_2'' configurations calculated at 73 900 and 78 200 cm^{-1}.

Purely ligand to ligand allowed excitations are calculated as $L(\pi) \rightarrow L(\pi^*)$ at 61 670 cm^{-1} and $L(\pi) \rightarrow L(\sigma^*)$ at 65 000-68 000 cm^{-1}. These correspond well to observed transitions in cyclopentadiene at 60 500 and 63 700 cm^{-1}, although the former is usually assigned $\sigma \rightarrow \pi^*$ rather than $\pi \rightarrow \sigma^*$.

In addition to electronic spectra, photoelectron spectra were calculated for ferrocene. The calculated ionization potentials are summarized and compared with the observed photoelectron spectra in Table VI. Our calculations for the ion with spectroscopic parametrization are of the unrestricted Hartree-Fock type with annihilation of the contaminating quartet, in contrast to the restricted calculations of Coutière, Demuynck, and Veillard[36] and Bagus, Wahlgren, and Almlöf.[38] In all cases, however, the expectation value of s^2 after annihilation is between 0.7500 and 0.7502, suggesting very little remaining spin contamination. The scattered wave MSX$_\alpha$ calculations are of the muffin tin type with overlapping spheres, and utilize Slater's transition-state theory.[68]

When taken in conjunction with the experimental intensities and vibrational structure of the photoelectron absorption,[24,25] all theoretical methods suggest that the lowest state of the ferrocenium ion is $^2E_2'$ ($^2E_{2g}$) followed by the $^2A_1'$ ($^2A_{1g}$) state approximately 0.4 eV higher in energy. The next two states are $^2E_1''$ ($^2E_{1g}$) and $^2E_1'$ ($^2E_{1u}$) followed in turn by two states $^2A_2''$ ($^2A_{2u}$) and $^2E_1'$ ($^2E_{2u}$). The symbols in parentheses refer to the symmetry assignments of these states in the staggered (D_{5d}) symmetry. Very little difference in these results is expected to occur in going from the eclipsed (D_{5h}) to the staggered structure and we give the D_{5d} symbols for comparison with the results of others.[36,38]

Both ab initio calculations obtain the correct order of ferrocenium ion states but overestimate the difference between the first two states and underestimate the difference between the last two pairs of states, making them nearly degenerate.

The order of states we calculate by INDO from the ΔE(SCF) energies of the ferrocenium ion is

$$^2A_1' \leq {}^2E_2' < {}^2E_1'' \leq {}^2E_1' < {}^2A_2''$$

These ΔE(SCF) results are in good agreement with the ab initio results obtained from the restricted Hartree-Fock method[38] with the exception that the two lowest calculated states are reversed. The INDO method without spectroscopic parametrization, described elsewhere,[20] predicts the same order of the first two ionic states as obtained by the ab initio methods, and with a 0.5 eV splitting, in good accord with experiment. The relaxation energies obtained in such calculations for the first three states are 6.5, 6.8, and 0.7 eV, also in excellent agreement with the values reported in ref 38. That both ab initio molecular orbital calculations predict too large a splitting of the two lowest states, 1.8 eV, suggests a distinguishing role of electron correlation. Interestingly, our results for these two states agree with the MSXα calculations of Rosch and Johnson.[68]

An interesting feature of the INDO results with spectro-

Table VII. Calculated Electronic and Spin Populations (from INDO/s) for Ferrocene and the First Four States of the Ferrocenium Ion[a]

	$^1A_1'$	$^2E_2'(d_{x^2-y^2})$	$^2A_1'(d_{z^2})$	$^2E_1''$	$^2A_2''$
net charge	0	+1	+1	+1	+1
Fe					
4s	0.05	0.03 (0.00)[b]	−0.06 (0.04)	0.01 (0.00)	0.04 (0.00)
4p (total)	−0.54	−0.43 (0.00)	−0.42 (0.00)	−0.53 (−0.01)	−0.73 (0.07)
$3d_{z^2}$	1.81	1.86 (0.00)	0.99 (0.92)	1.85 (0.00)	1.83 (0.00)
$3d_{xy}$	1.69	1.83 (0.00)	1.78 (0.01)	1.74 (0.00)	1.69 (−0.01)
$3d_{x^2-y^2}$	1.69	0.94 (0.92)	1.78 (0.01)	1.74 (0.00)	1.69 (−0.01)
$3d_{xz}$	0.72	0.89 (0.02)	0.95 (0.01)	0.78 (0.00)	0.75 (−0.02)
$3d_{yz}$	0.72	0.89 (0.02)	0.95 (0.01)	0.49 (0.28)	0.75 (−0.02)
net	1.87	2.00 (0.95)	2.03 (1.00)	1.93 (0.28)	1.99 (0.00)
C[c] $\bar{2}p(\pi)$	1.03	0.95 (0.00)	0.96 (0.00)	0.94 (0.06)	0.94 (0.10)
net	−0.24	−0.20 (0.00)	−0.21 (0.00)	−0.20 (0.07)	−0.20 (0.10)
H[c] net	0.06	0.10 (0.00)	0.11 (0.00)	0.10 (0.00)	0.10 (0.00)

[a] In these calculations spectroscopic parametrization was used. [b] The numbers in parentheses are spin densities. [c] Average values for each carbon and each hydrogen atom.

scopic parametrization is the rather large reduction of relaxation energy. As indicated in Table VI, Koopmans' theorem now gives a correct order of ionization potentials and is even in good numerical accord with observed values. The relaxation of the $^2E_2'$ state, for example, is reduced from 6.5 to 1.7 eV in going from calculations using correctly calculated two-electron integrals over Slater-type orbitals to those obtained using the Pariser approximation described in this work. The origin of this reduction of relaxation energy is not known. We do not have enough experience to note whether it is a general consequence of treating the evaluation of the core integrals, eq 9, and the Coulomb integrals, eq 21, from atomic ionization information in a consistent fashion. If so, one might expect that approximately 4.8 eV of relaxation energy is associated with atomic relaxation and 1.7 eV with molecular relaxation. For comparison, Bagus et al. estimate Fe^{2+} ($3d^6$; ^5D) → Fe^{3+}($3d^5$; ^6S) relaxation at 3.2 eV.[38]

A summary of the electronic population analysis for the ground and some ionized states is given in Table VII. The $^2E_2'$ state is clearly the result of the removal of a β spin electron from the $3d_{x^2-y^2}$ molecular orbital (spin density in the $3d_{x^2-y^2}$ atomic orbital is 0.92), but the net charge on the iron atom increases only slightly from 1.87 to 2.00. The localized metal character of the $3d_{x^2-y^2}$ molecular orbital of ferrocene from which the electron was lost would suggest a net charge of 2.69 on iron for this $^2E_2'$ state. It is thus apparent that significant relaxation has occurred. The reduction of charge buildup on the central iron atom is a consequence of (1) increased mixing of the formally unoccupied $3e_\pi$ atomic orbitals with occupied ligand orbitals (back-donation to the metal) and (2) decreased mixing of the formally occupied $3d_\sigma$ atomic orbitals with the ligand antibonding orbitals (forward donation). We thus calculate a composite picture for this relaxation with forward donation, as suggested by Shulman and Sugano for iron(II) and iron(III) cyanide[71] and back-donation suggested by Bagus et al.[38]

The $^2A_1'$ state results from the removal of a $3d_{z^2}$ electron. Again as a result of charge relaxation the net Mulliken population on iron only increases from 1.87 to 2.03. Both back-donation into the formally unoccupied metal orbitals and forward donation from the formally occupied metal d orbitals play a role, with the former somewhat more important.

The $^2E_1''$ and $^2A_2''$ states result from the removal of an electron that has mostly cyclopentadienyl π character. For the $^2E_1''$ state roughly 0.28 of the unpaired electron is in the $3d_\pi$.

In all the ionic states examined, the removal of an electron has increased the positive charge on the iron only slightly, ~0.13, while the ten carbons have lost ~0.4 electron, and an equal amount has been lost by the ten hydrogens. There is an accompanying loss of nearly half an electron from the π system of each cyclopentadienyl ion, while the σ system of each cyclopentadienyl ion has gained back approximately 0.25 electron.

That all ionic states examined have approximately the same net charge on iron as calculated for ferrocene itself is somewhat unusual. The loss of a d electron might be expected to increase the charge one unit, i.e., formally from iron(II) to iron(III). Although the exact meaning of the Mulliken population is not clear and is certainly not an observable, such an analysis should be useful in giving chemically "appealing" trends for a given basis set of atomic orbitals. Observables that might be considered related directly to these trends are the chemical or isomer shifts observed in Mössbauer spectroscopy.[72-75] Indeed, the isomer shift measured between ferrocene and ferrocenium ion salts is very small, ranging between 0.07 and −0.14 mm/s, suggesting very little difference in the net electronic "charge" of the iron atom. This value might be compared with the isomer shift of 0.88 mm/s observed between $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 6H_2O$.[76]

The molecular orbitals obtained for the $^2E_2'$ state of the ferrocenium ion are given in Table VIII; those for the $^2A_1'$ state are given in Table IX. To form the $^2E_2'$ state a β electron was removed from the $4e_2'(d_{x^2-y^2})$ molecular orbital, slightly destroying the D_{5h} symmetry. None of the degenerate orbitals of ferrocene has been split except the $4e_2'$ level itself. Both components, the predominantly d_{xy} and $d_{x^2-y^2}$ molecular orbitals, are occupied in the α spin manifold; they are split by 0.6 eV with the $4e_2'(d_{x^2-y^2})$ orbital lying lowest. The splitting of these two orbitals is much larger in the β spin manifold. This is caused mostly by the fact that the $4e_2'(d_{x^2-y^2})$ orbital is not occupied and only slightly by the break in spatial symmetry.

With the exception of the $4e_2'(d_{x^2-y^2})$ molecular orbital, where it is expected, very little splitting between the α and β partners of the molecular orbitals occurs. The major splitting is in the $8a_1'(d_{z^2})$ molecular orbitals, which are "spin" split by 0.7 eV, and the $4e_2'$ (d_{xy}) orbital, with a spin splitting of 0.5 eV. Such differences are expected, considering that the unpaired spin density is confined to mostly the $3d_{x^2-y^2}$ atomic orbital (Table VII) and only the $8a_1'(d_{z^2})$ and $4e_2'(d_{xy})$ orbitals are localized on iron.

The $^2A_1'$ state of the ferrocenium ion is summarized in Table IX. In this case there is, of course, no symmetry splitting. Again the spin splitting is small and is confined to those molecular orbitals that are localized on the iron atom. In addition, it is apparent that the energy of only those molecular orbitals that have large 3d character is different in the $^2E_2'$ and $^2A_1'$. The differences in the orbital eigenvalues in all but the $4e_2'(d_\sigma)$ and

Table VIII. Nature and Energy of the Highest Occupied Molecular Orbitals of the Ferrocenium Ion $^2E_2'$ State

	α spin MOs		β spin MOs		av
sym	ϵ, eV	type[a]	ϵ, eV	type[a]	ϵ_{av}, eV
$4e_2'$			-4.9^b	53% $d_{x^2-y^2}$	−9.9
$8a_1'$	−13.8	86% d_{z^2}	−13.1	86% d_{z^2}	−13.5
$6e_1'$	−14.4	14% 4p	−14.4	14% 4p	−14.4
$4e_2'$	−14.6	86% d_{xy}	−14.1	86% d_{xy}	−14.4
$4e_1''$	−15.0	29% d_π	−14.8	26% d_π	−14.9
$4e_2'$	−15.2	86% $d_{x^2-y^2}$			
$6a_2''$	−17.8	9% $4p_z$	−17.8	9% $4p_z$	−17.8
$5e_1'$	−18.2		−18.2		−18.2
$2e_2''$	−18.6		−18.6		−18.6
$3e_2'$	−19.0	4% d_δ	-18.9^c	1% d_δ	−19.0
$3e_1''$	−19.1	16% d_π	−19.0	13% d_π	−19.1
$7a_1''$	−20.7	7% 4s	−20.7	7% 4s	−20.7

[a] From orthogonalized basis (Löwdin) as opposed to Mulliken population analyses. [b] Not occupied. [c] Very slightly split.

Table IX. Nature and Energy of the Highest Occupied Molecular Orbitals of the Ferrocenium Ion $^2A_1'$ State

	α spin MOs		β spin MOs		av
sym	ϵ, eV	type[a]	ϵ, eV	type[a]	ϵ_{av}, eV
$8a_1'$		–	-3.9^b	74% d_{z^2}	−9.5
$4e_2'$	−13.9	86% d_δ	−13.1	84% d_δ	−13.5
$6e_1'$	−14.3	14% 4p	−14.4	14% 4p	−14.4
$8a_1'$	−15.1	86% d_{z^2}			
$4e_1''$	−15.1	29% d_π	−14.9	27% d_π	−15.0
$6a_2''$	−17.7	9% $4p_z$	−17.8	9% $4p_z$	−17.8
$5e_1'$	−18.2		−18.2		−18.2
$2e_2''$	−18.6		−18.6		−18.6
$3e_2'$	−18.9	2% d_δ	−18.9	1% d_δ	−18.9
$3e_1''$	−19.2	17% d_π	−19.0	15% d_π	−19.1
$7a_1'$	−20.6	7% 4s	−20.6	7% 4s	−20.6

[a] From orthogonalized basis (Lowdin) as opposed to Mulliken population analyses. [b] Not occupied.

$8a_1'(d_{z^2})$ are less than 0.13 V. We note that in both cases the unoccupied β spin metal orbital has considerably more covalency than its occupied counterpart.

V. Conclusions

An intermediate neglect of differential overlap theory appropriate for calculating the spectroscopic properties of transition-metal complexes is described. The model is characterized by the systematic treatment of both one- and two-electron integrals from atomic spectroscopy. The results suggest that this treatment of integrals reduces the requirement for higher excitations, doublets, triplets, etc., when the percentage of the states under consideration is essentially "singles". Another effect of this treatment of integrals is the reduction of the relaxation energy calculated upon ionization to essentially "molecular reorganization" as opposed to "atomic" relaxation. In the case of ferrocene, Koopmans' theorem is essentially restored.

All the one-center integrals that mix upon molecular rotation are included in the theory. It has been found that neglecting them, or spherically averaging over these integrals to eliminate most of them, has little effect on the reference Hartree-Fock ground state, but has serious consequences in the excited states obtained by configuration interaction.

A simple valence bond idea has been exploited to choose between atomic parameters derived from the $d^{n-2}s^2$ and $d^{n-1}s$ configurations of the transition metal. This systematic choice presented here leads to accurate geometric predictions of transition-metal complexes with the nonspectroscopic version of INDO described in ref 20.

Calculations on the electronically excited states of ferrocene give a very clear and straightforward assignment of the lowest three triplets and three singlets, those that are of d → d type. The numerical agreement and symmetry assignments of these states agree very well with those found experimentally, although the order of the two closely spaced singlet states does not agree with that suggested by ab initio calculations. The positions of symmetry-allowed transitions found at higher energies are also well correlated with calculated allowed states that are not of the d → d type. In the region above 37 000 cm^{-1} very many dipole forbidden transitions are calculated. We argue that the first of these (or three of these) is responsible for the observed band IV reported in Table VI.

Self-consistent field calculations have been performed on the five lowest states of the ferrocenium ion. It is concluded that the $^2E_2'$ state lies lowest, followed closely by the $^2A_1'$ state. Both of these states result from the loss of a 3d electron, corresponding to a formal change from iron(II) to iron(III). The other ionic states calculated are formed from the loss of an electron from ligand orbitals. In spite of the very different natures of these ions, all have a calculated net charge on iron, as measured by a Mulliken population analysis, of approximately +2.0, an increase of only +0.1 from ferrocene itself. This charge relaxation in the case of the first two ionic states is in agreement with the ab initio results on ferrocene and with information inferred from Mössbauer studies on the lowest state of the ferrocenium ion.

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