Magnetic Circular Dichroism Spectra of Bis(η-cyclopentadienyl)-iron and -ruthenium

By **Trevor J. Barton, Ian N. Douglas, Roger Grinter,*** and **Andrew J. Thomson,*** School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

The electronic and magnetic circular dichroism (m.c.d.) spectra of the title compounds, ferrocene and ruthenocene, have been measured in solution, Perspex films, and inert-gas matrices. Extensive calculations of the m.c.d. parameters for the *d–d* transitions, assuming a vibronic mechanism, are reported. The results of these calculations predict that the *d–d* transition should be dominated by *A* terms with only very weak *B* terms. However, experimentally, the m.c.d. spectra show very strong *B* terms with only one weak *A* term of the opposite sign to that expected from the calculations. The experimental results are most reasonably explained by inclusion of significant ligand character into the *d* orbitals.

SINCE its discovery in 1950, the electronic properties of bis(η-cyclopentadienyl)iron (ferrocene) have been the subject of very close attention. Despite this interest there still remain a number of important questions.[1-10]

The absorption and luminescence of ferrocene were examined by Scott and Becker [2] who gave a good review of the early work and discussed the relative merits of the various theoretical models. More recently, Armstrong *et al.*[3,4] investigated the absorption spectrum of ferrocene in a number of different physical states, such as solution, vapour phase, and glasses. They also studied the effect of temperature in the range 77—420 K, as well as solvent and substitution effects. From their results they concluded that very weak bands in the 13 000—19 000 cm^{-1} region were essentially *d–d* singlet–triplet transitions. The band centred at *ca.* 23 000 cm^{-1} was found to be pure *d–d* in nature and also possessed a single electronic origin. The band at 30 800 cm^{-1} was found to contain some ligand character, but was also predominantly *d–d*.

In contrast to these results a single-crystal study by Sohn *et al.*[5,6] at 4.2 K showed that the lowest-energy singlet–singlet *d–d* band at 23 000 cm^{-1} contained two separate electronic transitions centred at *ca.* 21 800 and 24 000 cm^{-1}. The bands at 21 800 and 30 800 cm^{-1} both exhibited vibrational structure, which was not observed by Armstrong *et al.*[3] The picture is further confused by a study by Smith and Meyer [7] of matrix-isolated ferrocene, where a single sharp unstructured band at 25 000 cm^{-1} and a broad band at 32 000 cm^{-1}, which exhibited a large amount of vibrational structure, were found. To date no explanation for these divergent spectral results has been proposed.

In many cases where there is confusion about the interpretation of absorption spectral results, magnetic circular dichroism (m.c.d.) measurements provide sufficient additional information to determine the correct interpretation. Unfortunately, this has not proved to be the case with ferrocene. The first m.c.d. examination by Falk [8] found that an *A* term dominated the low-energy band at 23 000 cm^{-1}. However, Nielson *et al.*[9] disputed this finding, suggesting that Falk's results are invalid since his solutions had too high an optical density. Nielson *et al.* found that both the 23 000 and 30 800 cm^{-1} bands were associated with *B* terms. In addition it was discovered that substitution of the ferrocene ring with a carbonyl group changed the sign of the *B* terms under the band at 22 800 cm^{-1}. Rowe and McCaffery [10] examined a polymer film containing ferrocene at 10 K and found two *B* terms of the same sign under the band at 22 800 cm^{-1} but no signal at all under the band at 30 800 cm^{-1}.

In an effort to overcome these outstanding problems we have measured the m.c.d. of ferrocene in solution, in a polymer film at 4.2 K, and in rare-gas matrices at *ca.* 20 K, together with the m.c.d. of bis(η-cyclopentadienyl)ruthenium (ruthenocene) in solution. We also report the results of extensive calculations, which, when compared to experiment, show that it is difficult to reconcile the observations in terms of a model employing only metal *d* orbitals.

EXPERIMENTAL

Commercial ferrocene was purified by recrystallisation from ethanol and then by repeated vacuum sublimations. Solutions of ferrocene used for m.c.d. measurements (*ca.* 0.02 mol dm^{-3}) had optical densities between 1 and 2 when measured in 1-cm quartz cells; the solvents were ethanol and cyclohexane (both Spec grade). For the low-temperature film study, ferrocene was introduced into a Perspex film by dissolving the Perspex in chloroform, adding a chloroform solution of ferrocene, and allowing it to evaporate. Provided that the ferrocene concentration was not too high, thin films of good optical quality could be obtained. At higher concentrations the ferrocene tended to crystallise out as thin needles.

All the m.c.d. spectra were recorded on a Cary 61 dichrograph. Solution samples were located at the centre of the room-temperature bore of a superconducting magnet (B.O.C. Limited) with a maximum field of 5.5 T. The

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[1] S. Yamada, A. Nakahara, and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1955, **28**, 465.

[2] D. R. Scott and R. S. Becker, *J. Chem. Phys.*, 1961, **35**, 516.

[3] A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *J. Chem. Phys.*, 1967, **46**, 4321.

[4] A. T. Armstrong, D. G. Carroll, and S. P. McGlynn, *J. Chem. Phys.*, 1967, **47**, 1104.

[5] Y. S. Sohn, D. N. Hendrickson, J. H. Smith, and H. B. Gray, *Chem. Phys. Letters*, 1970, **6**, 499.

[6] Y. S. Sohn, D. N. Hendrickson, and H. B. Gray, *J. Amer. Chem. Soc.*, 1971, **93**, 3603.

[7] J. J. Smith and B. Meyer, *J. Chem. Phys.*, 1968, **48**, 5436.

[8] H. Falk, *Monatsh.*, 1969, **100**, 411.

[9] D. Nielson, D. Boone, and H. Eyring, *J. Phys. Chem.*, 1972, **76**, 511.

[10] M. D. Rowe and A. J. McCaffery, *J. Chem. Phys.*, 1973, **59**, 3786.

thin-film samples were mounted in the helium-temperature bore of a smaller, 4.8 T, magnet. Matrix spectra were recorded with the apparatus previously described.[11] The mixture of ferrocene and isolating gas was obtained by flowing the gas over the ferrocene. The ratio of ferrocene to isolating gas could be varied by adjusting the gas flow rate and controlling the temperature of the ferrocene. Matrices of good optical quality with low scattering were obtained. The absorption spectra for the solution and film samples were recorded on the Cary 14 spectrophotometer, whilst those for the matrices were measured by recording the dynode voltage on the Cary 61 dichrograph.

RESULTS

The room-temperature solution absorption and m.c.d. spectra of ferrocene in ethanol are shown in Figure 1.

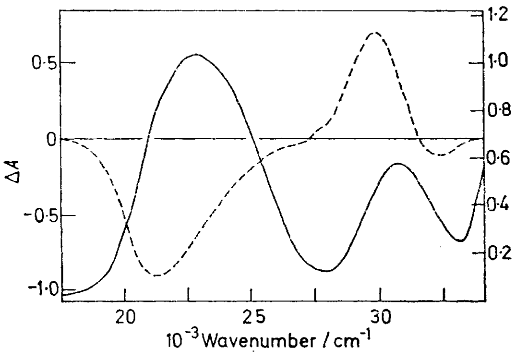

FIGURE 1 Absorption (——) and m.c.d. (— — — —) spectra of ferrocene in ethanol solution between 15 000 and 35 000 cm^{-1}. Path length 1 cm, concentration 1 × 10^{-2} mol dm^{-3}, magnetic field 5.1 T

The absorption spectrum has two broad unstructured bands centred at *ca.* 23 700 and 30 800 cm^{-1}, the latter overlapping intense charge-transfer (c.t.) bands. The m.c.d. spectrum exhibited a broad positive *B* term (negative ΔA) shifted from the absorption maximum to 21 300 cm^{-1}, providing strong evidence for the existence of more than one electronic transition in the lowest-energy *d–d* band. The second band in the m.c.d. was a negative *B* term (positive ΔA) only slightly shifted from the absorption maximum; there is also possibly a negative *A*-term contribution to the higher-energy *d–d* band. These solution results are quite similar to those of Nielson *et al.*,[9] except that in our spectra there is evidence of a negative (ΔA) shoulder at *ca.* 25 000 cm^{-1} which was not previously observed. In addition the earlier study found no evidence of an *A* term under the band at 30 800 cm^{-1}.

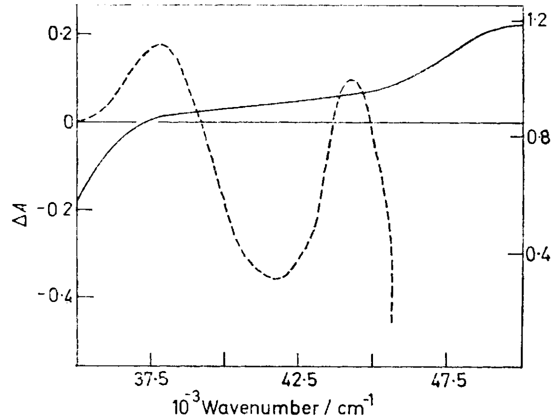

FIGURE 2 Absorption (——) and m.c.d. (— — — —) spectra of ferrocene in ethanol solution between 35 000 and 50 000 cm^{-1}. Path length 1 cm, concentration 2 × 10^{-4} mol dm^{-3}, magnetic field 5.1 T

Figure 2 shows the absorption and m.c.d. spectra of ferrocene in cyclohexane solution in the c.t. region (35 000—45 000 cm^{-1}). The absorption spectrum is identical to that of Scott and Becker [2] consisting of two shoulders at 38 400 and 43 500 cm^{-1} on a very intense band. Correcting for the tail of the intense band, the maxima of the two weaker bands are found at 37 800 and 41 700 cm^{-1} respectively, which coincides exactly with the positions of the two *B* terms of opposite sign in the m.c.d.

The m.c.d. and absorption spectra of ruthenocene in ethanol solution are shown in Figure 3. Both the spectra are qualitatively very similar to those of ferrocene, but shifted to shorter wavelength. The shoulder on the high-energy side of the longest-wavelength *d–d* band is more pronounced in ruthenocene as also is the *A* term under the high-energy band.

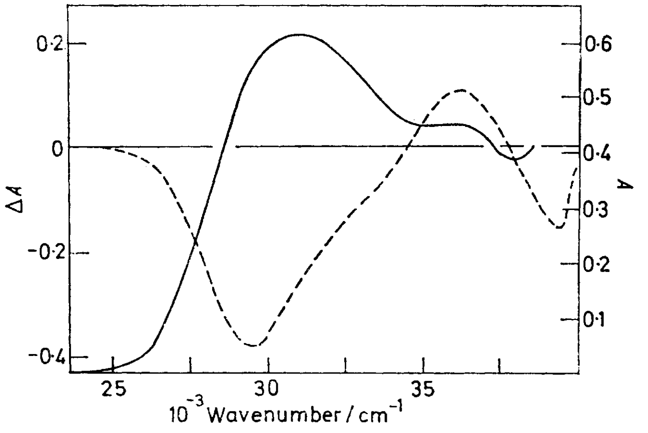

FIGURE 3 Absorption (——) and m.c.d. (— — — —) spectra of ruthenocene in ethanol solution in the 25 000—40 000 cm^{-1} region. Path length 1 cm, concentration 3 × 10^{-3} mol dm^{-3}, magnetic field 5.1 T

Figure 4 shows the absorption and m.c.d. spectra of ferrocene in an argon matrix at *ca.* 20 K. In this case there appears at first sight to be a positive *A* term associated with the first absorption band at 24 000 cm^{-1}; however, from a consideration of other evidence, it seems reasonable to assume that there are in fact two *B* terms of opposite signs, a positive one at 21 500 cm^{-1} and a negative one at 25 500 cm^{-1}. The positive *B* term is similar to that in the solution spectrum, although it is much smaller and narrower in the matrix, but the negative *B* term appears as a positive shoulder in the solution spectrum. The transitions in question are probably vibronically allowed and it is therefore expected that the band shapes will show temperature dependence. Thus these apparently conflicting results can be reconciled if the positive *B* term at 21 500 cm^{-1} were more sensitive to temperature effects than the negative term at 25 500 cm^{-1}. At room temperature the positive *B* term is very large and broad and

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[11] I. N. Douglas, R. Grinter, and A. J. Thomson, *Mol. Phys.*, 1975, **29**, 673.

completely swamps the negative B term, but at low temperature it becomes both weaker and narrower and then the negative B term can appear. The higher-energy d–d band shifts in the matrix absorption spectrum to 31 400 cm^{-1} and the B term occurs at 30 300 cm^{-1}; in addition a new shoulder appears in the m.c.d. at 28 700 cm^{-1}.

Our matrix absorption spectrum is significantly different from that of Smith and Meyer.[7] In place of the peculiarly sharp band at 25 000 cm^{-1} that they observed, we find a broad band at 23 900 cm^{-1}, and instead of a broad highly structured band at *ca.* 32 000 cm^{-1} we observe a narrower unstructured band at 31 400 cm^{-1}. The fact that we observe no vibrational structure could be due to the rather wide slit settings employed. This was necessary since ferrocene in the matrix is a very weak magnetic rotator and quite sensitive scales, with consequently high noise, had to be used. However, the observed spectra were quite reproducible and any effects due to non-linear baselines were corrected by running the spectra with the field reversed.

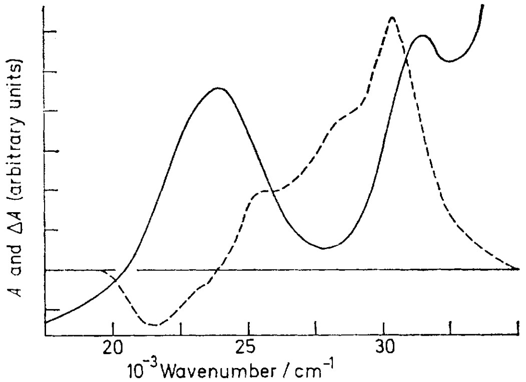

FIGURE 4 Absorption (——) and m.c.d. (— — — —) spectra of ferrocene in an argon matrix at *ca.* 20 K in the 15 000—40 000 cm^{-1} region

The m.c.d. spectrum of the Perspex film at 4.2 K was disappointing since the broadening effect of the film cancelled out any sharpening due to the low temperature, and even with reversed-field experiments only poor quality spectra could be obtained. Rowe and McCaffery [10] found that ferrocene in a polymer film at 10 K exhibited two positive B terms at *ca.* 21 800 and 23 400 cm^{-1} but surprisingly no activity at all at higher energy. The results of both these polymer-film studies are regarded as somewhat suspect due to low concentrations of ferrocene and weak magnetic rotation. Certainly in the case of ferrocene, matrix isolation has great advantages over films for low-temperature studies.

CALCULATIONS

Throughout this paper when referring to transitions between single electron-energy levels we use the labels and energy-level scheme of Sohn *et al.*[6] which is shown in Figure 5. It is generally agreed that both the low-energy transitions are d–d in nature. Sohn *et al.*[5,6] used ligand-field theory to assign the high-energy band (30 800 cm^{-1}) to $^1A_{1g}\rightarrow{}^1E_{1g}$ ($e_{2g}{}^4a_{1g}{}^2\rightarrow e_{2g}{}^3a_{1g}{}^2e_{1g}$) ($D_{5d}$ point group). The low-energy band (*ca.* 22 700 cm^{-1}) consists of the transitions $^1A_{1g}\rightarrow{}^1E_{2g}$ ($e_{2g}{}^4a_{1g}{}^2\rightarrow e_{2g}{}^3a_{1g}{}^2e_{1g}$) at 24 000 cm^{-1} and $^1A_{1g}\rightarrow{}^1E_{1g}$ ($e_{2g}{}^4a_{1g}{}^2\rightarrow e_{2g}{}^4a_{1g}e_{1g}$) at 21 800 cm^{-1}.

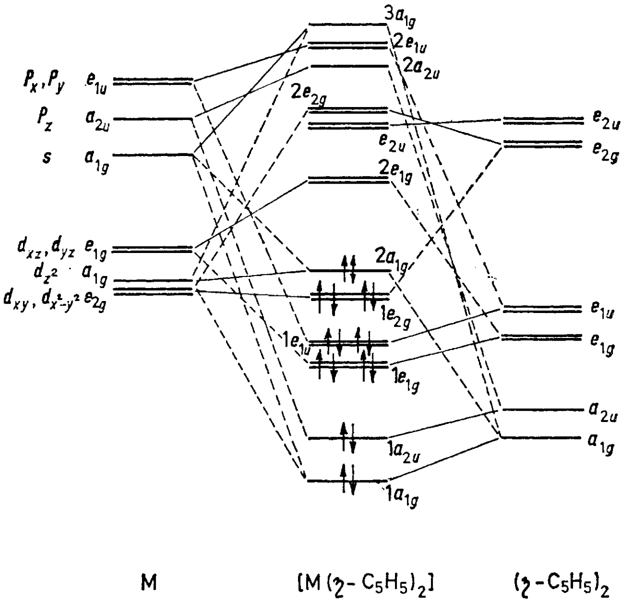

FIGURE 5 The molecular-orbital scheme for ferrocene; energy separations are not to scale

In an attempt to check this assignment and to aid assignment of any other transitions, we calculated the signs of the m.c.d. parameters associated with these transitions. The definitions of the various m.c.d. parameters A, B, and C can be found in several reviews.[12-14] Since ferrocene is diamagnetic with a $^1A_{1g}$ ($e_{2g}{}^4a_{1g}{}^2$) ground state there can be no C terms. The A and B terms and the dipole strength, D, of any transition $a\rightarrow j$, expressed in terms of the Griffith formalism,[15] are, for randomly oriented molecules, as in (1)—(3) where d_a is the degeneracy

$$A = \frac{3}{2d_a}\Sigma - i(\langle j|\mu_0|j\rangle - \langle a|\mu_0|a\rangle) \times (\langle a|m_{+1}|j\rangle\langle j|m_{-1}|a\rangle - \langle a|m_{-1}|j\rangle\langle j|m_{+1}|a\rangle) \quad (1)$$

$$B = \frac{3}{d_a}\sum \mathrm{Im}\left[\sum_{k\neq a}\frac{\langle k|\mu_0|a\rangle}{E_k - E_a}(\langle a|m_{+1}|j\rangle\langle j|m_{-1}|k\rangle - \langle a|m_{-1}|j\rangle\langle j|m_{+1}|k\rangle) + \sum_{k\neq j}\frac{\langle j|\mu_0|k\rangle}{E_k - E_j}(\langle a|m_{+1}|j\rangle\langle k|m_{-1}|a\rangle - \langle a|m_{-1}|j\rangle\langle k|m_{+1}|a\rangle\right] \quad (2)$$

$$D = \frac{3}{d_a}\Sigma(\langle a|m_{+1}|j\rangle\langle j|m_{-1}|a\rangle + \langle a|m_{-1}|j\rangle\langle j|m_{+1}|a\rangle) \quad (3)$$

of the ground state a, μ and m are the magnetic- and electric-dipole operators respectively, Im means the imaginary part, and the summation is over all the degenerate com-

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[12] A. D. Buckingham and P. J. Stephens, *Ann. Rev. Phys. Chem.*, 1966, **17**, 399.

[13] P. N. Schatz and A. J. McCaffery, *Quart. Rev.*, 1970, **23**, 552.

[14] P. J. Stephens, *Ann. Rev. Phys. Chem.*, 1974, **25**, 201.

[15] J. S. Griffith, ' The Irreducible Tensor Method for Molecular Symmetry Groups,' Prentice–Hall, New York, 1962.

ponents of the transition $a \rightarrow j$. The definitions of the Griffith's operators are:

$$m_0 = im_z$$

$$m_{\pm 1} = \mp \frac{i}{2^{\frac{1}{2}}} m_x + \frac{1}{2^{\frac{1}{2}}} m_y$$

TABLE 1

Calculated values for A/D for the d–d transition, for all the allowing vibrations

Vibration causing mixing	Transition	State mixing with ground state	States mixing with excited state	Polarisation	A/D
ν_k, ν_l	$A \rightarrow J$	S^0	T^0		
a_{1u}	${}^1A_{1g} \rightarrow {}^1E_{1g}$	${}^1A_{1u}$	${}^1E_{1u}$	xy	$+\frac{1}{2}\beta$ [b]
	${}^1A_{1g} \rightarrow {}^1E_{2g}$	${}^1A_{1u}$	${}^1E_{2u}$	Forbidden	0
a_{2u}	${}^1A_{1g} \rightarrow {}^1E_{1g}$	${}^1A_{2u}$	${}^1E_{1u}$	xy	$+\frac{1}{2}\beta$ [b]
	${}^1A_{1g} \rightarrow {}^1E_{2g}$	${}^1A_{2u}$	${}^1E_{2u}$	Forbidden	0
e_{1u}	${}^1A_{1g} \rightarrow {}^1E_{1g}$	${}^1E_{1u}$	${}^1A_{1u}$, ${}^1E_{2u}$, ${}^1A_{2u}$	z	0
	${}^1A_{1g} \rightarrow {}^1E_{2g}$	${}^1E_{1u}$	${}^1E_{1u}$, ${}^1E_{2u}$	xy	$-\frac{3}{2}\beta$
e_{2u}	${}^1A_{1g} \rightarrow {}^1E_{1g}$	${}^1E_{2u}$	${}^1E_{1u}$, ${}^1E_{2u}$	xy	$-\frac{1}{2}\beta$
	${}^1A_{1g} \rightarrow {}^1E_{2g}$	${}^1E_{2u}$	${}^1A_{1u}$, ${}^1A_{2u}$, ${}^1E_{2u}$	xy, z	$+\frac{3}{2}\beta$ [a]

[a] Calculated assuming the transition to be only xy-polarised; the actual value should be very much reduced from this since the transition also has a z component thereby increasing D. [b] Value irrespective of the configuration from which the ${}^1E_{1g}$ state arises.

Since all the d–d transitions of ferrocene are formally forbidden, if we assume that a vibronic mechanism is partially allowing the transitions then we may apply the perturbational method of Stephens[16] to calculate the electric-dipole matrix elements. The expression, ignoring second order effects, is (4) where $H_k' = \frac{\partial H}{\partial Q_k}$, Q_k is the normal

$$\langle A_a|m|J_j\rangle = -\sum_{kS_s^0} \frac{\langle A^0|H_k'^*|S^0\rangle\langle S^0|m|J^0\rangle}{E_{S_s^0} - E_{A_a^0}} (\langle a|Q_k^*|s\rangle\langle s|j\rangle)$$

$$- \sum_{RT^0t} \frac{\langle T^0|H_l'|J^0\rangle\langle A^0|m|T^0\rangle}{E_{T_t^0} - E_{J_j^0}} (\langle a|t\rangle\langle t|Q_l|j\rangle) \quad (4)$$

co-ordinate of the kth vibration, and the sum runs over all the vibrations, k, and all the vibronic states, S_s^0, with energies E_{S^0}. This will normally be replaced by the electronic energy E_{S^0}. Since m_{+1} and m_{-1} transform as e_{1u} under D_{5d}, to obtain a non-zero matrix element $\langle S^0|m|J^0\rangle$ and $\langle A^0|m|T^0\rangle$, S^0 and T^0 must be ungerade states, because for d orbitals A^0 and J^0 are gerade. From this it follows that the vibrations k and l causing the mixing must be ungerade modes. There are four possible ungerade modes for the D_{5d} point group: a_{1u}, a_{2u}, e_{1u}, and e_{2u}. Of these the first three would be expected to be the most important since there are metal–ring modes of these symmetries[17–19] (see Figure 6). However, there is evidence from other sources[20] that vibrations other than metal–ligand ones can be important in giving rise to vibronic coupling, thus the calculations were carried out for all the four ungerade modes. Table 1 shows the results of the calculations of A/D for the three d–d transitions. It was found that for the two ${}^1A_{1g} \rightarrow {}^1E_{1g}$ transitions the values of A/D were independent of configuration. If we ignore CH stretches and bends on the assumption that they are unlikely to cause significant mixing of metal with ligand states, then for ferrocene there are nine ungerade modes (Table 2).

We expect the metal–ring modes to be the most effective in causing vibronic coupling; however, sizeable contributions from skeletal ring modes are possible. All the vibrational modes mix only ${}^1E_{1u}$ into the excited d-orbital states (see Table 1); thus there can be no differences in mixing ability caused by energy-separation effects [*i.e.* $E_{T_t^0} - E_{J_j^0}$, equation (4)]. There will be such an effect with the ground-state mixing since in that case S^0 is different for different modes; however, all the states T^0 and S^0 are so far removed in energy from the ground state that we expect only a minor contribution to the magnitude of the A term from this mixing. In conclusion it appears that the ${}^1A_{1g} \rightarrow {}^1E_{1g}$ transitions should have a positive A term and the ${}^1A_{1g} \rightarrow {}^1E_{2g}$ a negative one, but that if e_{2u} modes play a significant role in the vibronic coupling then the A term may become zero or very small.

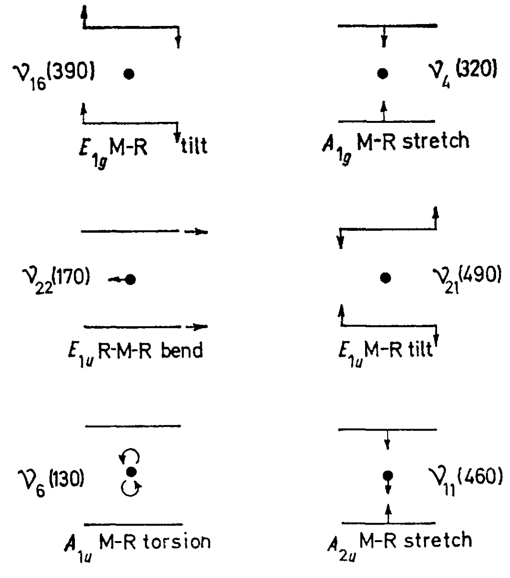

FIGURE 6 The six metal–ligand vibrational modes. Number and wavenumbers (in cm^{-1}) from refs. 18 and 19

Turning our attention now to B terms we may try to evaluate the possible magnetic interactions, confining ourselves to the d orbitals. Table 3 lists the possible magnetic mixings of the d-orbital energy states. By

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[16] P. J. Stephens, *J. Chem. Phys.*, 1966, **44**, 4060.

[17] E. R. Lippincott and R. D. Nelson, *Spectrochim. Acta*, 1956, **9**, 373.

[18] D. Hartley and M. J. Ware, *J. Chem. Soc.* (*A*), 1969, 138.

[19] D. M. Adams and W. S. Fernando, *J.C.S. Dalton*, 1972, 2507.

[20] S. Barker, Ph.D. Thesis, University of East Anglia, 1973, and refs. therein.

restricting ourselves to the *d* orbitals we have only to consider the interaction of $^1A_{1g}$ with $^1E_{1g}{}^a$ under μ_x and μ_y, $^1E_{1g}{}^a$ with $^1E_{1g}{}^b$ under μ_z, and $^1E_{1g}{}^a$ and $^1E_{1g}{}^b$ with $^1E_{2g}$ under μ_x and μ_y. Since the *B* term contains an energy dominator $E_k - E_a$ or $E_k - E_j$ we expect the largest contribution from the mixing of states close together in energy, *i.e.* $^1E_{1g}$ with $^1E_{1g}$ and $^1E_{1g}$ with $^1E_{2g}$. However, although symmetry indicates matrix elements such as $\langle ^1E_{1g}{}^a|\mu_z|^1E_{1g}{}^b\rangle$ can be non-zero, when these matrix elements are expanded in terms of single electron matrix elements it is found that they are all zero. Table 4 lists the symmetry labels and angular momentum of the five *d* orbitals. The state $^1E_{1g}{}^a$ arises from the configuration $a_{1g}e_{1g}$ and $^1E_{1g}{}^b$, $^1E_{2g}$ from $e_{2g}e_{1g}$. Now matrix elements of μ_z involve the operator l_z or l_0 which cannot change the wavefunctions it operates on, thus only diagonal matrix elements can be non-zero, hence $\langle ^1E_{1g}{}^a|\mu_z|^1E_{1g}{}^b\rangle$ is zero. For matrix elements $\langle ^1E_{1g}{}^a$ or $^1E_{1g}{}^b|\mu_x|^1E_{2g}\rangle$ it is found that on expanding, although μ_x and μ_y may be expressed in terms of l_+ and l_-, there is a difference in m_l values between the two *d* orbitals of 0 or ± 2 and thus the matrix elements are zero.

TABLE 2

Vibrations of the ferrocene molecule involved in vibronic mixing, excluding C–H modes [17-19]

Symmetry of vibration	Vibrations in ferrocene excluding C–H Number	Type	Ground-state-wave-number/ cm^{-1}
a_{1u}	1	Metal–ring torsion, ν(M–R)	*ca.* 100
a_{2u}	2	Metal-ring stretch, ν(M–R)	478
		C–C stretch, ν(CC)	1 108
e_{1u}	3	Metal-ring deformation, δ(M–R)	170
		Metal-ring rocking, ρ(M–R)	490
		C–C stretch, ν(CC)	1 411
e_{2u}	3	CCC deformation, δ(CCC)	*ca.* 550
		CCC deformation, δ(CCC)	*ca.* 900
		C–C stretch, ν(CC)	*ca.* 1 400

TABLE 3

Possible magnetic mixing of gerade states of ferrocene

State	Magnetic operator	States mixed
$^1A_{1g}$ *	μ_z	$^1A_{2g}$
	μ_x, μ_y	$^1E_{1g}$ *
$^1A_{2g}$	μ_z	$^1A_{1g}$
	μ_x, μ_y	$^1E_{1g}$
$^1E_{1g}$ *	μ_z	$^1E_{1g}$ *
	μ_x, μ_y	$^1A_{1g}$,* $^1A_{2g}$, $^1E_{2g}$ *
$^1E_{2g}$ *	μ_z	$^1E_{2g}$
	μ_y, μ_x	$^1E_{1g}$,* $^1E_{2g}$

* Mixings which occur within *d*-orbital set. It should be noted that there are two $^1E_{1g}$ (*d*-orbital) states, $^1E_{1g}{}^a$ arising from $e_{2g}{}^4a_{1g}\,e_{1g}$ and $^1E_{1g}{}^b$ arising from $e_{2g}{}^3a_{1g}{}^2e_{1g}$.

TABLE 4

Symmetry and angular-momentum properties of ferrocene *d* orbitals

Symmetry	*d* Orbitals Real	Complex	m_l
a_{1g}	d_{z^2}	d_0	0
$e_{1g}{}^+$	d_{xz}, d_{yz}	d_{+1}	+1
$e_{1g}{}^-$	d_{xz}, d_{zy}	d_{-1}	−1
$e_{2g}{}^+$	$d_{x^2-y^2}$, d_{xy}	d_{+2}	+2
$e_{2g}{}^-$	$d_{x^2-y^2}$, d_{xy}	d_{-2}	−2

Thus the only non-zero magnetic mixing occurs between the $^1A_{1g}$ ground state and the two $^1E_{1g}$ excited states. This leads to *B*-term contributions to the $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions from both the mixing of the excited states into the ground state and *vice versa*. However, for the $^1A_{1g} \rightarrow {}^1E_{2g}$ transition the only contribution to the *B* term arises from the mixing of $^1E_{1g}$ states into the $^1A_{1g}$ ground state. This result, that the only contribution to the *B* terms is due to mixing of $^1A_{1g}$ with $^1E_{1g}$, is at first sight surprising, but is a general result for any axial system, if only *d* orbitals are considered.

An attempt was made to calculate the signs of the *B* terms resulting from this mixing; unfortunately this proved to be impossible since very complicated expressions involving a magnetic matrix element and a large number of electric-dipole matrix elements were obtained. The main conclusion from this calculation for the *B* terms is that restriction to the *d*-orbital basis set yields the result that there should be very little magnetic mixing and consequently small *B* terms, especially for the $^1A_{1g} \rightarrow {}^1E_{2g}$ transition.

DISCUSSION

In the solid state at room temperature, ferrocene exists in the staggered form [21] whereas ruthenocene adopts the eclipsed conformation.[22] Various studies, using electron-diffraction and dipole-moment data, show that the barrier to ring rotation of ferrocene in the vapour and the solution phase is *ca.* 300 cm^{-1}, and the equilibrium conformation is probably the eclipsed form. For ruthenocene the barrier is not known with certainty, but it has been concluded that the eclipsed conformer is again the more probable. It is inevitable, therefore, that there is a mixture of two conformations in the various physical states we have studied and it is likely that the relative properties of each in such a mixture will vary according to the conditions of preparation. Therefore, we have considered the possibility that the differences between the spectra obtained by us and others in different physical states might arise from the presence of different proportions of the two conformers.

However, the point groups D_{5d} and D_{5h}, to which the staggered and eclipsed conformations respectively belong, are isomorphous. Thus the selection rules for the two conformers are identical and there can be no difference of kind between the various combinations of metal and ligand orbitals which form any particular molecular orbital of the molecule as a whole. The only factors which might change with conformation are therefore the relative energies of the molecular orbitals or the finer details of their composition from metal and ligand orbitals. We do not believe that such effects can be significant as far as the measurements described here are concerned, and we see no reason why the electronic spectra of the two possible conformers should not be very similar.

The only *A* term observed in the spectra of ferrocene

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[21] J. D. Dunitz, L. E. Orgel, and A. Rich, *Acta Cryst.*, 1956, **9**, 373.

[22] G. L. Hardgrove and D. H. Templeton, *Acta Cryst.*, 1959, **12**, 28.

is that found in solution in association with the absorption band at 30 800 cm^{-1}. Sohn *et al.*[5,6] assigned this band to the transition $^1A_{1g}\rightarrow{}^1E_{1g}(e_{2g}{}^4a_{1g}{}^2\rightarrow e_{2g}{}^3a_{1g}{}^2e_{1g})$, which from our calculations is expected to have a positive A term. If we accept this assignment as correct, then the only way this experimental result can be correlated with our calculation is if e_{2u} modes are dominant in causing vibronic coupling. If this is the case then we would predict a positive A term at 24 000 cm^{-1} and a negative one at 21 800 cm^{-1}, neither of which are observed due to dominance of B terms.

From a consideration of all the available spectra it seems reasonable to conclude that the m.c.d. spectrum of ferrocene consists of a positive B term for the band at 21 800 cm^{-1} (I) and negative B terms for the bands at 24 500 (II) and 30 800 cm^{-1} (III). The reason for the appearance of a positive B term for band (II) in solution could be associated with the extreme broadness and size of band (I) at room temperature. The spectrum of ruthenocene in solution is identical to that of ferrocene except that band (II) appears much more strongly and is a positive B term. In carbonyl-substituted ferrocene band (I) has a negative B term and (II) a positive one.

Although our calculations of the B terms failed to give the signs, we were able to show that the magnitude should be very small. However, experimentally, B terms dominate the m.c.d. spectra. One possible explanation of this could be that the magnetic mixing is principally between the $^1E_{1g}{}^a$, $^1E_{1g}{}^b$, and $^1E_{2g}$ states and some relatively low-lying gerade c.t. states, arising from transitions such as $2a_{1g}\rightarrow 2e_{2g}$, $1e_{2g}\rightarrow 2e_{2g}$, and $1e_{1g}\rightarrow 2e_{1g}$ (Figure 5). Now substitution of the ferrocene ring with carbonyl groups might well change the energies of some of these c.t. states and consequently reverse the sign of some of the B terms. However, since the B terms which change sign are those furthest removed in energy from the c.t. states, we do not favour this explanation, especially since estimates of energies of the gerade c.t. states indicate that they are rather high in energy.

A more likely explanation for the appearance of sizeable B terms lies in the treatment of these low-energy bands as arising from pure *d–d* transitions. Inclusion of a small amount of ligand character into the $1e_{2g}$, $2a_{1g}$, and $2e_{1g}$ orbitals (Figure 5) will allow non-zero magnetic matrix elements between the $^1E_{1g}$ and $^1E_{2g}$ states. It is quite easy to show that substitution of the ferrocene ring could directly influence the magnetic matrix elements between ligand orbitals and thereby change the signs of B terms. Such an inclusion of ligand character into the d orbitals could also affect the calculation of A terms and could thus lead to a negative sign for the A term associated with the $^1A_{1g}\rightarrow{}^1E_{1g}$ $(e_{1g}\rightarrow e_{2g})$ transition.

The degree of covalency in metallocenes has been the subject of some controversy. An e.s.r. and magnetic-susceptibility study of some metallocenes by Prins and his co-workers[23,24] indicated that the $1e_{2g}$, $2a_{1g}$, and $2e_{1g}{}^*$ orbitals were almost pure metal 3*d* orbitals. However, from a later study of the hyperfine coupling Prins *et al.*[25] concluded that for $[\mathrm{Ni}(\eta\text{-}\mathrm{C_5H_5})_2]$ the unpaired electron in the $2e_{1g}{}^*$ orbitals was rather strongly delocalised into the carbon $2p_z$–π framework of the ligands. Prins *et al.*[25] also found evidence for considerable ligand character in the $1e_{2g}$ orbital of $[\mathrm{V}(\eta\text{-}\mathrm{C_5H_5})_2]$. An investigation of ferrocene and the ferrocenium ion, once again by Prins,[26] suggested that the $1e_{2g}$ and $2a_{1g}$ orbitals were predominantly metal 3*d* but that the $2e_{1g}{}^*$ orbital contained significant ligand character. This final conclusion was in good agreement with the SCF calculations of Coutière *et al.*[27]

Studies of the i.r. spectra,[28] heats of combustion,[29] mass spectra,[30,31] and Mössbauer spectra have all indicated some covalency, as indeed have most molecular-orbital calculations, but the amount of ligand character in each of the $2a_{1g}$, $1e_{2g}$, and $2e_{1g}{}^*$ orbitals is uncertain, although it would appear to be greatest in the $2e_{1g}{}^*$ orbital. All the above techniques and calculations apply only to the ground state of ferrocene, whereas m.c.d. studies may provide information about excited states.

Nielson *et al.*[9] used a purely *d*-orbital model to interpret their m.c.d. results, but we have found it impossible to explain our measurements in terms of such a treatment. The necessity of including ligand character in order to explain the experimental results brings into question the validity of the numerous ligand-field calculations on metallocenes. Our results also show that there is covalency in the excited states of ferrocene as well as in the ground state, although unfortunately we are unable to give quantitative estimates of its size or to find which orbitals contain the largest amount of ligand character.

Little of interest can be concluded from the m.c.d. of the c.t. region of ferrocene expect that once again B terms predominate, which could indicate that the two observed transitions are *z*-polarised. There are only two types of allowed transitions in D_{5d} symmetry, $^1A_{1g}\rightarrow{}^1A_{2u}$ (*z*-polarised) and $^1A_{1g}\rightarrow{}^1E_{1u}$ (*xy*-polarised); the latter would be expected to give A terms. Since there appears to be no sign of A terms in the c.t. spectra, and unlike the *d–d* case no mechanism for suppressing the A terms, we may assign the two transitions at 36 800 and 41 700 cm^{-1} to $^1A_{1g}\rightarrow{}^1A_{2u}$. On the qualitative molecular-orbital scheme shown in Figure 5, the lowest-energy allowed single-electron transitions would be $1e_{2g}\rightarrow e_{2u}$ ($d\rightarrow$cp), $1e_{1u}\rightarrow 2e_{1u}$ (cp$\rightarrow d$), and $2a_{1g}\rightarrow 2a_{2u}$ ($d\rightarrow p$); all three transitions

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[23] R. Prins, *J. Chem. Phys.*, 1969, **50**, 4804.

[24] R. Prins and J. D. W. van Voorst, *J. Chem. Phys.*, 1968, **49**, 4665.

[25] R. Prins, J. D. W. van Voorst, and C. J. Schinkel, *Chem. Phys. Letters*, 1967, **1**, 54.

[26] R. Prins, *Mol. Phys.*, 1970, **19**, 603.

[27] M.-M. Coutière, J. Demuynck, and A. Veillard, *Theor. Chim. Acta*, 1972, **27**, 281.

[28] H. R. Fritz, *Adv. Organometallic Chem.*, 1963, **1**, 239.

[29] G. Wilkinson, P. L. Pauson, and F. A. Cotton, *J. Amer. Chem. Soc.*, 1954, **76**, 1970.

[30] L. Friedman, A. P. Irsa, and G. Wilkinson *J. Amer. Chem. Soc.*, 1955, **77**, 3689.

[31] J. Müller and L. d'Or, *J. Organometallic Chem.*, 1957, **10**, 313.

give rise to an $^1A_{2u}$ state but the first one also gives rise to an $^1E_{1u}$ state. The positions of the observed transitions will depend on the interelectronic repulsion as well as on the energy of the single-electron transitions; thus it is possible that the $^1E_{1u}$ state is very high in energy and that the transitions at 36 800 and 41 700 cm^{-1} arise from $1e_{2g}\rightarrow e_{2u}$ and $1e_{1u}\rightarrow 2e_{1g}$.

Coutière *et al.*[27] suggested an orbital sequence in which the two highest-energy filled orbitals are the e_{1g} (π-cp) and the e_{1u} (π-cp). They postulate that the *d–d* bands occur at lower energy than the transitions from the cyclopentadiene (cp) orbitals because of coulombic and exchange interactions. If we accept their orbital scheme then, assuming the lowest antibonding orbitals to be e_{1u} (p) and e_{1g} (d), the two lowest-energy single-electron transitions will be e_{1u} (π-cp)$\rightarrow e_{1g}$ (d) and e_{1g} (π-cp)$\rightarrow e_{1u}$ (p), both of which correspond to $^1A_{1g}\rightarrow {}^1A_{2u}$ transitions and hence give only B terms. Thus the experimental results are consistent with the proposed molecular-orbital scheme of Coutière *et al.*[27] but can also be explained in terms of alternative orbital sequences. Determination of the signs of the B terms could possibly solve this problem. However, this was not attempted since each $^1A_{2u}$ state can mix with up to seven other states and there is no reliable estimate of the energy separations.

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