The Spectra of Complexes of Conjugated Ligands. Part VI. Zero Differential Overlap Calculations on Tris(phenanthroline)iron(II)

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The absorption and c.d. of tris(phenanthroline)iron(II) have been interpreted using a π-electron treatment. An SCF basis with interaction among 162 excited configurations was used, and compared with a basis of orbitals localised on the ligands or the metal ion. Calculations on a hypothetical mono-complex were used to choose the configurations. Oscillator and rotational strengths were calculated with both dipole length and velocity operators and reasonable bandshapes used to simulate absorption and c.d. envelopes. The results are compared with experiment, and with those of other workers. The visible charge-transfer band contains transitions to both the two lowest empty ligand orbitals, and these apparently have different bandshapes. Only our SCF calculation gives a qualitatively correct prediction of the c.d. envelope of this band. Magnetic c.d. is briefly discussed. The SCF calculation gives an excellent prediction of the absorption and c.d. in the $\pi \longrightarrow \pi^*$ region; a localised basis is less satisfactory. A bandshape with a greater halfwidth on the high-energy side gives better results than does a symmetrical one. The first band in this region and its shoulders contain the α, *p*, β, and β′ ligand transitions; the c.d. arises primarily from the β′ transition. Our results are only approximately in agreement with those of a simple exciton model. The relation of the $\pi \longrightarrow \pi^*$ spectrum of the complex to those of phenanthroline and of phenanthrene, in which *p* and β′ bands are well separated, is discussed. The effective charge on the iron atom is estimated as +0·77.

MOLECULES of the size of tris(phenanthroline)iron(II) (Figure 1) are far too large for *ab initio* calculations, particularly of their spectra, to be feasible. It is hoped, however, that a chemically oriented semi-empirical approach, whose development is carefully tied to experimental evidence, may be able to account for the properties of such chemically interesting molecules, and provide insight into their electronic structures. This development has been the subject of this series of papers [1,2] (hereafter referred to as Parts I—V), and it is now possible to proceed with some confidence on a treatment of this complex. The approximation of ' intermediate neglect of differential overlap ' (INDO) is used, and at present only π-electrons are explicitly considered, an approach which has been very successful in predicting the spectra of purely organic aromatic molecules.[3] Though σ–π separation is not rigorously possible in a complex of D_3 symmetry, the geometry of this complex, and the observed spectrum, suggest that it may not be an unduly severe approximation.

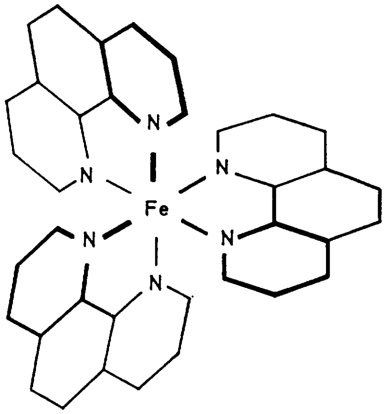

FIGURE 1 $[Fe(phen)_3]^{2+}$, viewed along its threefold axis

Other workers [4,5] have performed π-electron calculations on this complex, but used markedly different parameters and obtained different assignments from those of this work.

Method of Calculation.—Most of the parameters used, derived from energies and intensities of transitions in series of spectra, have been described in Parts IV and V; the charge on the metal ion is chosen to fit the energy of the first charge-transfer (CT) band. In this paper (unlike Part IV), the electronegativities of the nitrogen atoms have been increased by one quarter of the one-centre electron repulsion integral, to allow, approximately, for the flow of electrons from the nitrogen lone pairs. The Harvard University IBM 360/65 computer and a program described in Parts IV and V were employed.

The geometry used for the phen molecules in the complex is that of Part IV (actually taken from a zinc complex [6]) and agrees well with a study of the ferrous complex in a crystal of much higher molecular weight,[7] from which were taken the Fe–N bond lengths (1·97 Å, giving N–Fe–N angles of 85°), and the perpendicularity of the ligand planes. The right-handed propellor, shown [7] to be the (+)-isomer, was considered, using axes defined in Parts I and II.

Previous workers [4,5] have used a ' composite system ' approach to these complexes, using a basis of ligand MOs and metal d_π AOs (referred to as a ' localised ' basis in this work), and it has been shown in Parts IV and V that this method has conceptual advantages. The use of an SCF basis of MOs delocalised over the whole complex, however, gives better predictions of $\pi \longrightarrow \pi^*$ transition energies and fewer excited configurations have

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[1] Part V, N. Sanders, *J. Chem. Soc.* (*A*), 1971, 1563.

[2] P. Day and N. Sanders, *J. Chem. Soc.* (*A*), 1967, 1530, 1536; N. Sanders and P. Day, *ibid.*, 1969, 2303; 1970, 1190.

[3] R. G. Parr, ' Quantum Theory of Molecular Electronic Structure,' Benjamin, New York, 1964.

[4] T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1969, **42**, 702.

[5] I. Hanazaki and S. Nagakura, *Inorg. Chem.*, 1969, **8**, 654.

[6] C. W. Reimann, S. Block, and A. Perloff, *Inorg. Chem.*, 1966, **5**, 1185.

[7] D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Cryst.*, 1966, **21**, A154 (supplement); also information kindly supplied in advance of publication.

to be included in configuration interaction (CI) in order to obtain an adequate description of the CT bands. The results of both methods are reported here.

The choice of configurations to be included was made by performing calculations including all singly-excited configurations (' complete ' CI) on the hypothetical mono-complex and rejecting the configurations which participated least in the lower excited states, until the corresponding calculations on the tris-complex became manageable. Calculations were then performed on the mono-complex with the reduced numbers of configurations, to estimate the errors introduced.

The program was written to accommodate up to 80 configurations, but by use of the symmetry of the complex (and because only π-orbitals were included) the configurations could be divided into non-interacting groups. The SCF calculation reported included all the 63 essentially CT configurations and 99 $\pi \longrightarrow \pi^*$ ones, equivalent to 14 CT and 11 $\pi \longrightarrow \pi^*$ configurations in the mono-complex. The reduction to 25 configurations in the mono-complex was achieved without ignoring any which contributed more than 0·5% to any state below 40 kK (1 kK = 1000 cm^{-1}) or 2% to any below 49 kK. Energies, oscillator strengths, and magnetic dipole transition moments given by the ' complete ' treatment were reproduced very accurately for the visible CT transitions, the region up to 45 kK was well reproduced, and there was general agreement up to 50 kK.

Calculations are reported for the localised basis both with and without the inclusion of inter-ligand CT configurations and those metal-to-ligand CT configurations (' non-interacting ' CT configurations) which interact only with them. The calculation without these used the 75 configurations equivalent to 25 in the mono-complex; when they were included, and symmetry used, a calculation equivalent to a 23-configuration treatment of the mono-complex was possible. The effect of curtailment of CI was somewhat more serious than for the SCF basis; though the predicted energies and oscillator strengths of the visible CT bands were very little changed, their magnetic dipole transition moments fell considerably.

Our results will be compared with those of Ito *et al.*[4] (absorption) and of Hanazaki and Nagakura[5] (c.d. calculated from the wavefunctions of ref. 4). They used complete neglect of differential overlap for a calculation with a localised basis, ignoring inter-ligand CT and ' non-interacting ' CT configurations. They chose the energy of CT to the lowest empty orbital (MO number 8 of the isolated ligand) as that of the visible CT band, and placed higher CT transitions according to the differences in MO energies; CT to MO 9 was therefore placed *ca.* 9 kK higher in energy. Their resonance integrals differed markedly from ours ($\beta_{CC} = -2{\cdot}39$ eV, $\beta_{CN} = -1{\cdot}879$ eV, $\beta_{FeN} = -1{\cdot}07$ eV; this work: $\beta_{CC} =$ *ca.* $-2{\cdot}23$ eV, $\beta_{CN} =$ *ca.* $-2{\cdot}46$ eV, depending on bond length, $\beta_{FeN} = -0{\cdot}62$ eV), and they used approximations in evaluating magnetic transition moments.

RESULTS AND DISCUSSION

The observed c.d. spectrum, measured by Dr. B. J. Peart,[8] is shown in Figure 2, together with the absorption measured in this laboratory (on a Carey 14 spectrophotometer, taking the extinction coefficient of the visible band as known), which agrees well with the plot of log ε given by Peart.

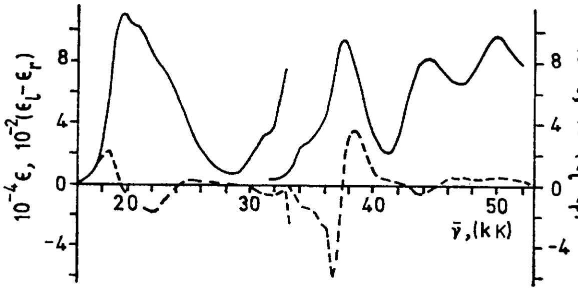

FIGURE 2 Experimental absorption and c.d. spectra of tris(phen)iron(II); the scale of each spectrum changes by a factor of 10 at *ca.* 32 kK; the c.d. is reproduced, with permission, from ref. 8

The Visible CT Band.—Figure 3 summarises the results of our calculations and those of other workers; the graph-plotter of the Oxford University KDF9 computer was used for its preparation. Calculated oscillator and rotational strengths are shown by vertical lines, and simulated spectra, obtained by assuming a reasonable

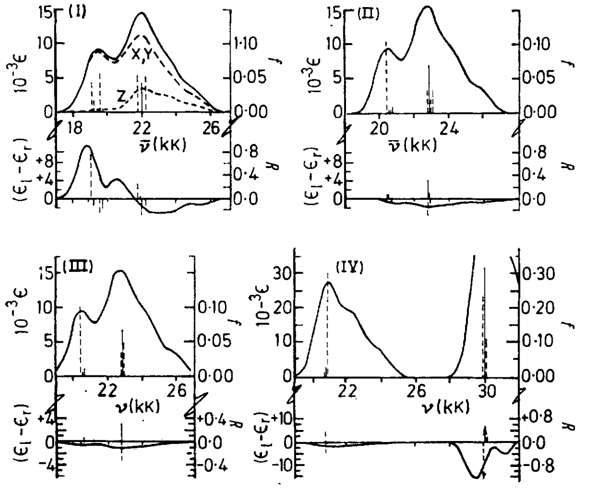

FIGURE 3 Predicted absorption and c.d. associated with the CT band of tris(phen)iron(II). The results are shown of our calculations using an SCF basis (I) and using a localised basis, both including all types of singly-excited configurations in CI (II), and ignoring inter-ligand CT and ' non-interacting ' CT configurations (III). (IV) shows the results of Ito *et al.*[3] and of Hanazaki and Nagakura.[4] The predicted polarisation of absorption is shown for calculation (I). Oscillator and rotational strengths of absorption and c.d. components (using the dipole length operator for electric dipole transition moments throughout) are shown by vertical lines (solid for states of A_2 symmetry, broken for those of E); absorption and c.d. envelopes are simulated from them as discussed in the text. Where two absorption components are almost coincident, the vertical lines have been separated just sufficiently to resolve them in the diagram.

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[8] B. J. Peart, Ph.D. Thesis, University of East Anglia, 1970.

bandshape, are also given. It was assumed that each component produces a progression of Gaussian bands separated by 1·50 kK (determined from a low-temperature spectrum in Part II). Relative intensities for the progressions were estimated from Krumholtz's[9] Gaussian analysis of the CT band of tris(biacetylbis-*N*-methylimine)iron(II). The results of our SCF calculation are given in more detail in the Table.

Results of 162-configuration treatment of (+)-[Fe(phen)$_3$]$^{2+}$ using an SCF basis. Charge on the iron atom corresponding to d_{π}^{6} = +0·63; net charge = +0·77. *E* is energy in kK, *f*(**r**), *R*(**r**), *f*(**∇**), and *R*(**∇**) are oscillator and rotational strengths (the latter in 10^{-38} c.g.s.), calculated using the dipole length and velocity operators respectively for the electric dipole transition moment; *R′*(**∇**) is calculated as *R*(**∇**), but ignoring *d–d* contributions to the magnetic transition moment. *A*/*D* Values for magnetic c.d. are given. Excited states are described by giving first the overall composition as percentage CT/percentage $\pi \longrightarrow \pi^*$ configurations in the state (the description of configurations as CT or $\pi \longrightarrow \pi^*$ is quite accurate, though not rigorous), followed by lists of the main contributors (those in parentheses make up 10—20% of the total); α, *p*, β, β′, and π refer to locally excited states, IL indicates a state which is essentially inter-ligand CT in character. States of symmetry A_2 and *E* are listed; states of symmetry A_1 (transitions to which are forbidden) occur at 20·8, 26·1, 31·5, 33·5, 37·4, 37·6, 38·2, 40·0, 41·5, 43·2, 44·6, 44·9, 45·7, and 46·0 kK.

		E	*f*(**r**)	*f*(**∇**)	*R*(**∇**)	*R*(**r**)	*R′*(**∇**)	*A*/*D*	Description	
1	A_2	18·9	0·001	0·000	−0·01	−0·02	−0·03	0	99/1	CT_2
2	*E*	19·1	0·042	0·021	+0·53	+0·76	+0·76	+0·33	99/1	CT_2
3	*E*	19·2	0·018	0·011	−0·08	−0·10	−0·34	+0·12	100/0	CT_2
4	*E*	19·6	0·056	0·022	−0·20	−0·23	−0·06	−0·46	100/0	CT_2
5	A_2	19·7	0·003	0·000	−0·00	−0·16	−0·00	0	100/0	CT_2
7	*E*	21·8	0·052	0·043	+0·23	+0·25	−0·15	−0·46	99/1	CT_1
8	*E*	21·9	0·002	0·004	+0·04	+0·03	+0·04	+0·45	99/1	CT_1
9	A_2	22·0	0·041	0·021	−0·19	−0·27	−0·08	0	98/2	CT_1
11	*E*	22·2	0·051	0·052	−0·08	−0·08	+0·09	+0·03	100/0	CT_1
14	*E*	31·5	0·008	0·001	−0·19	−0·49	−0·19	+0·09	37/63	α + CT
15	*E*	32·4	0·197	0·101	−5·33	−7·44	−5·36	−0·14	54/46	CT + *p*
16	A_2	32·6	0·080	0·038	+1·12	+1·63	+1·16	0	83/17	CT(+*p*)
17	*E*	32·9	0·097	0·040	−2·14	−3·33	−2·14	+0·19	71/29	CT + *p*
18	A_2	33·0	0·047	0·018	+0·52	+0·84	+0·49	0	89/11	CT(+*p*)
19	*E*	33·2	0·036	0·014	−0·75	−1·22	−0·72	+0·02	81/19	CT(+*p*)
20	A_2	33·3	0·196	0·057	+1·62	+2·98	+1·60	0	23/77	*p* + CT(+β′)
21	*E*	33·4	0·035	0·011	−0·34	−0·62	−0·33	−0·25	52/48	CT + α(+*p*)
23	*E*	35·1	0·608	0·345	−14·10	−18·72	−14·07	+0·07	15/85	β′(+CT)
24	A_2	36·5	1·297	0·652	+11·75	+16·57	+11·85	0	44/56	CT + β′(+*p*)
25	*E*	37·0	0·020	0·005	−0·50	−0·99	−0·47	−0·07	93/7	CT
26	*E*	37·2	0·526	0·176	+0·31	+0·53	+0·31	+0·01	4/96	β(+π)
27	A_2	37·2	0·587	0·252	+6·44	+9·84	+6·30	0	63/37	CT + β
28	*E*	37·3	0·101	0·058	−0·39	−0·52	−0·48	+0·05	95/5	CT
30	*E*	37·6	0·071	0·048	−0·35	−0·43	−0·27	−0·00	97/3	CT
33	*E*	40·0	0·002	0·001	+0·01	+0·01	+0·01	−0·01	0/100	IL
35	A_2	40·0	0·008	0·004	+0·07	+0·10	+0·06	0	0/100	IL
36	*E*	40·0	0·000	0·000	−0·01	−0·02	−0·01	+0·01	0/100	IL
37	*E*	41·5	0·000	0·000	−0·00	−0·00	−0·00	−0·01	0/100	IL
39	A_2	41·8	0·000	0·000	+0·00	+0·00	+0·00	0	0/100	IL
40	*E*	41·8	0·001	0·000	−0·01	−0·01	−0·01	+0·01	0/100	IL
41	A_2	43·2	0·002	0·001	+0·02	+0·02	+0·02	0	0/100	IL
42	*E*	43·2	0·000	0·000	−0·00	−0·00	−0·00	−0·00	0/100	IL
43	*E*	43·2	0·018	0·009	−0·01	−0·01	−0·01	+0·00	0/100	IL
44	*E*	44·1	2·478	1·190	−0·16	−0·22	−0·14	+0·04	3/97	π
45	*E*	44·6	0·002	0·001	−0·00	−0·00	−0·00	+0·00	0/100	IL
46	A_2	44·6	0·002	0·001	+0·01	+0·01	+0·01	0	0/100	IL
48	*E*	44·9	0·007	0·003	−0·01	−0·01	−0·01	+0·00	0/100	IL
50	*E*	45·4	0·045	0·025	−0·39	−0·52	−0·42	−0·01	98/2	CT
51	A_2	45·5	0·051	0·027	+0·27	+0·37	+0·29	0	97/3	CT
52	*E*	45·7	0·056	0·017	+0·01	+0·02	+0·03	+0·01	98/2	CT
54	*E*	46·0	0·019	0·005	+0·01	+0·02	−0·01	−0·00	99/1	CT
56	*E*	47·6	0·064	0·038	−2·45	−3·17	−2·46	−0·03	0/100	π
57	A_2	48·0	0·175	0·083	+2·85	+4·15	+2·86	0	1/99	π
58	*E*	48·5	0·789	0·368	−6·26	−9·16	−6·24	−0·00	2/98	π
59	A_2	48·5	1·385	0·655	+5·90	+8·57	+5·89	0	1/99	π
60	*E*	49·9	0·000	0·001	−0·20	+0·02	−0·20	−0·02	0/100	π

The studies of substituent effects in Part I leave no doubt that the peak of the visible absorption band is primarily associated with CT to MO 9 of the isolated ligand. The first peak of each of our simulated spectra arises from CT to this MO, but these spectra are not entirely satisfactory, for the transitions to MO 8 appear to produce a second maximum. As discussed in Parts III and IV, comparison of the intensities of CT bands in related complexes confirms the fact that both sets of transitions lie under the visible band envelope. The shape of the CT band could be corrected while maintaining the MO 9 character of the main peak, by assuming that the transitions to MO 8 have a broader band shape [*cf.* the CT band of the tris(phenanthroline)iron(III) complex]. As already stated, Ito *et al.*[4] assume that the

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[9] P. Krumholtz, 'Theory and Structure of Complex Compounds, Proceedings of the Wrocław symposium of 1962,' ed. B. Jezowska-Trzebiatowska, Pergamon, Oxford, 1964, p. 217.

visible band arises from CT to MO 8, and place CT to MO 9 at *ca.* 30 kK, in definite conflict with the conclusions of Part I. Our calculations give the separation between MOs 8 and 9 as about 3·5 kK in the isolated ligand, and about 0·4 kK in the complex (as a result of the increase in electronegativity of the nitrogen atoms); the difference between the Coulomb terms (attraction between the transferred electron and the resultant hole) for the two MOs then places CT to MO 8 *ca.* 2·6 kK higher in energy than that to MO 9. As a result of the large metal–ligand resonance integral used by Ito *et al.*,[4] their prediction of the oscillator strength of this band is too large, even though they assume it only contains CT to MO 8.

Only the SCF calculation gives a qualitatively correct prediction of the c.d. of the visible CT band. The Table and the results of Part V bear out the observation of Hanazaki and Nagakura[5] that the magnetic transition moments of single components of CT bands are often composed of several contributions of differing signs. The sensitivity of the c.d. of these bands to small changes in wavefunctions is also indicated by the fact that the Ru^{II} complex shows relative signs of $\pi \longrightarrow \pi^*$ and CT c.d. which are opposite to those of the ferrous one.[8] The experimental spectrum (Figure 2) shows c.d. bands of rotational strengths approximately $+0{\cdot}46$, $-0{\cdot}61$, and $+0{\cdot}07 \times 10^{-38}$ c.g.s. units, while the SCF calculation (Figure 3) gives rotational strengths of $+0{\cdot}25$ and $-0{\cdot}09 \times 10^{-38}$ c.g.s., which are the resultant of positive c.d. components of total rotational strength $+1{\cdot}04$, and negative ones of total strength $-0{\cdot}87 \times 10^{-38}$ c.g.s. Clearly, no exact prediction of the shape of the c.d. curve can be obtained without knowing the band profiles for CT to MOs 8 and 9 (which may even be different for states of different symmetry involving the same MO, *cf.* ref. 10), and, furthermore, no account has yet been taken of the departure of the σ-electron environment of the iron atom from octahedral symmetry. Nonetheless, the results of the SCF calculation are very encouraging.

The calculations using a localised basis were expected from those on the mono-complex to give poorer results than the SCF calculation; in fact, they fail primarily because the pairs of transitions with roughly equal and opposite rotational strengths are predicted to be almost exactly coincident with one another.

The A terms of magnetic c.d. are given for the SCF calculation in the Table (using the numerical convention for A/D of the later work of Stephens *et al.*[11]). The values of A/D for the CT band are quite different from those predicted using a localised basis, but a fair comparison must include B terms in view of the closeness of states in this region; the large changes in A/D produced by mixing nearby states within this band have been pointed out by Hollebone *et al.*[12]

The $\pi \longrightarrow \pi^*$ Region of the Spectrum.—Results of the various calculations of absorption and c.d. in the 30—50 kK region of the spectrum are summarised in Figure 4, and more details of the SCF results appear in the Table. The spectra were simulated with Gaussian bandshapes of standard error $\Delta\nu = 7{\cdot}5\sqrt{\nu}$ (ν in cm^{-1}), as suggested by Mason *et al.*[13]. The SCF results are also plotted using skew Gaussian bands of the same total width, but with the bandwidth on the high-energy side double that on the low; such asymmetry is often seen in $\pi \longrightarrow \pi^*$ spectra and is expected if large vibrational quanta are excited.

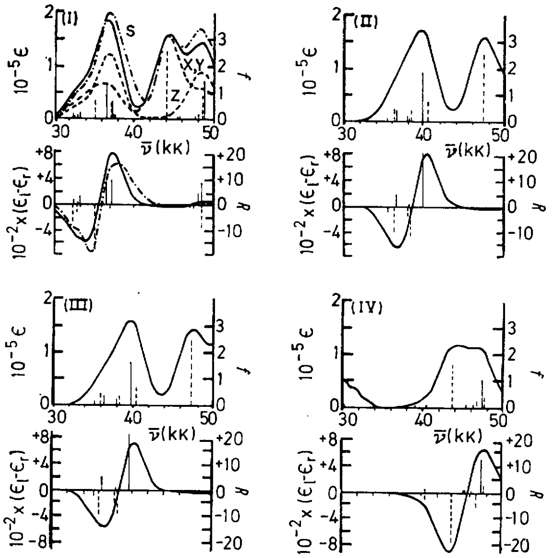

FIGURE 4 Predicted absorption and c.d. of tris(phen)iron(II) in the 30—50 kK region, using the dipole length operator for electric dipole transition moments. The four calculations represented are the same as those of Figure 2. Again, transitions to states of A_2 symmetry are shown by solid vertical lines, and those to E states by broken ones. Symmetrical Gaussian bandshapes are assumed for the simulated spectra shown by solid lines; for calculation (I) the corresponding predictions of polarisation of absorption are shown by broken lines, as is the total absorption envelope calculated using a skew Gaussian bandshape (S)

Agreement between the observed $\pi \longrightarrow \pi^*$ absorption and that simulated from the SCF calculation is excellent, particularly when the skew Gaussian shape is used. The intensities predicted using the dipole length operator are, as expected, about twice those observed, while the dipole velocity predictions are slightly too small. The observed peaks are at 37·5, 44·3, and 49·8 kK with $\varepsilon_{max.}$ values in the ratios 1·0 : 0·88 : 1·04, while in the spectrum simulated with skew bands, the energies are 36·9, 44·3, and 48·1 kK, and the intensity ratios 1·0 : 0·78 : 0·86. Exact predictions for the 48 kK peak are not expected. Use of a localised basis shifts the whole predicted spectrum to higher energy, for reasons discussed in Parts IV and V.

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[10] R. G. Bray, J. Ferguson, and C. J. Hawkins, *Austral. J. Chem.*, 1969, **22**, 2091.

[11] *E.g.*, P. J. Stephens, W. E. Suëtaka, and P. N. Schatz, *J. Chem. Phys.*, 1966, **45**, 4592.

[12] B. R. Hollebone, S. F. Mason, and A. J. Thomson, *Symp. Faraday Soc.*, 1969, **3**, 146.

[13] *E.g.*, W. S. Brickell, S. F. Mason, and D. R. Roberts, *J. Chem. Soc. (B)*, 1971, 691.

Qualitatively, the c.d. spectrum simulated from the SCF calculation agrees well with experiment, particularly when skew bands are used; use of a localised basis predicts very similar curves shifted to higher energy. Experimentally, the area of negative c.d. around 35 kK has rotational strength *ca.* $-6{\cdot}5$, and the positive region around 40 kK, *ca.* $+4{\cdot}7 \times 10^{-38}$ c.g.s. The SCF calculation of Figure 4 predicts values about double these (*ca.* -14 and $+13 \times 10^{-38}$ c.g.s.) which are left after mutual cancellation between components of positive rotational strength totalling $+33$, and negative ones totalling -34×10^{-38} c.g.s.

The magnetic c.d. A terms are predicted to be very small (see Table), in agreement with the observations of Hollebone *et al.*[12] that the magnetic c.d. of the $\pi \longrightarrow \pi^*$ bands resembles that of the isolated ligand.

The excellence of the agreement between the SCF calculation and experiment leaves little doubt as to the assignments of these bands, which are most conveniently expressed in terms of Dewar and Longuet-Higgins' interpretation of Clar's α, p, β, and β' bands [14] (thus, for example, the bands arising from out-of-phase and in-phase combinations of excitations from next-to-highest filled to lowest empty MOs and from highest filled to next-to-lowest empty MOs within a ligand are designated α and β respectively). The first band and its low-energy shoulder (30—40 kK) contain all the transitions derived primarily from the α, p, β', and β local ligand excitations (in that order), as well as various CT transitions. The β' band is considerably the strongest, though it may be appreciably mixed with nearby CT transitions (see Table). This is consistent with Part IV and the work of Bray *et al.*[10] These locally excited (exciton) states are clearly separated from transitions to the related inter-ligand CT states which are all predicted to be very weak and to lie between 40 and 45 kK in energy. The closeness of the two sets of states is explained in Part V. The oscillator strength of the 44 kK peak seems to be derived almost entirely from a single transition, mainly the E-symmetry exciton combination of the short-axis polarised transitions from MO 7 to MO 10 within the ligands.

Though the overall predictions of the SCF calculation are similar to those of a simple exciton model [15] (the c.d. spectrum is dominated by the A_2 and E combinations of transitions arising from the strong long-axis polarised β' band, while the 44 kK band is associated with virtually no c.d.), there are marked differences in detail. Thus, though the 50 kK band arises primarily from long-axis polarised ligand transitions, the complete calculation predicts very small splitting between the A_2 and E components, and hence only weak c.d., in agreement with experiment. Again, the p and β' configurations are mixed with CT and with each other, so that the simple picture of two pairs of A_2 and E exciton combinations is considerably altered. The predicted splitting between the A_2 and E components strongest in c.d. is, however, close to the $1{\cdot}2$ kK predicted by an exciton treatment of the β' band using our repulsion integrals and is not visible in the simulated band envelope as their half-widths are about $1{\cdot}8$ kK. Bray *et al.*[10] have endeavoured to measure exciton splittings, particularly for bipyridyl complexes, and have obtained much smaller values than 1 kK and given a different interpretation of the observed c.d.; their results will be discussed in a subsequent paper.

The predicted $\pi \longrightarrow \pi^*$ spectrum of this complex is essentially that of appropriately polarised phen molecules; it differs quite considerably from the relatively well-understood spectrum of phenanthrene, and this has been responsible for considerable doubt as to whether the main c.d. of the complex is due to the p or the β' band. Our calculations of the spectrum of phenanthrene agree well with experiment, and it is possible to clarify the changes in absorption observed on passing along the series from phenanthrene [16] to phen in non-polar,[17] polar,[8,18] and acid [8,18] solution and in complexes. In phenanthrene, the p and β' bands are separated by 9 kK (theoretical) or about $6{\cdot}4$ kK (experimental) compared with the calculated value of 3 kK in polarised phen. Experimentally, on moving along the series, the low energy (*ca.* 36 kK) bands gain in intensity at the expense of the higher (*ca.* 43 kK) one and another band appears below 50 kK. Our calculations indicate that the β' transition does not simply shift, but mixes with others of the same polarisation; in phen itself it is divided between a state close to the p band (transitions to which have zero intensity in phenanthrene) and one of higher energy than the β' band of phenanthrene; migration into the lower-energy band continues as the molecule is further polarised.

Charge on the Metal Ion.—Correct CT energies are obtained in the SCF calculation by assuming a charge on iron corresponding to the $d_\pi{}^6$ configuration of $+0{\cdot}63$. There are, however, only $5{\cdot}86$ electrons in the d_π orbitals in the calculated ground state of the complex, so the net charge is $0{\cdot}63 + 0{\cdot}14 = 0{\cdot}77$ e. A localised basis required a higher starting charge but predicted a smaller outflow of d_π electrons, giving a total charge of $0{\cdot}69 + 0{\cdot}14 = 0{\cdot}81$ e. These results are similar to those reported in Part V for the SCF calculation allowing for migration of the nitrogen lone pairs on tris-α-di-imine-iron(II), where the charge was $0{\cdot}66 + 0{\cdot}20 = 0{\cdot}86$ e.

It has been shown that excellent predictions of the absorption and c.d. spectra of tris(phen)iron(II) are given by the π-electron method developed in this series of papers; only the charge on the metal ion is chosen

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specifically for a particular complex. Before this approach is extended to give a better treatment of σ-electrons and to deal with a wider range of experimental observables, another system will be treated at this level, namely tris-α,α′-bipyridyliron(II). More bands can be seen in its spectrum than in that of the phen complex, they are better resolved, and analysis of them has been used to derive values for the exciton splitting of $\pi \longrightarrow \pi^*$ transitions which conflict with those obtained in this work.[10]

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