Contribution from the Department of Physical Chemistry,
H. C. Ørsted Institute, University of Copenhagen, Copenhagen, Denmark

The Faraday Rotation of Allowed Transitions: Charge-Transfer Transitions in $K_3Fe(CN)_6$

By P. J. Stephens[1]

Received June 7, 1965

On the basis of their Faraday rotations the 24,100 and 32,900 cm.$^{-1}$ charge-transfer bands of $K_3Fe(CN)_6$ are assigned to $^2T_{2g} \rightarrow {}^2T_{1u}$ ($t_{1u}(\sigma^b)$ or $t_{1u}(\pi^b) \rightarrow t_{2g}(\pi)$) and $^2T_{2g} \rightarrow {}^2T_{2u}$ ($t_{2u}(\pi^b) \rightarrow t_{2g}(\pi)$) transitions, respectively.

Shashoua[2a] and Briat[2b] have recently measured the magnetic optical rotation dispersion (MORD) of $K_3Fe(CN)_6$ through its two lowest charge-transfer bands. The purpose of this note is to point out that their results show the latest assignment of these bands[3,4] to be incorrect and, in general, to demonstrate how the MORD of allowed transitions provides information about the symmetries of the states involved.

The contribution of the transition a → j to the molar magnetic rotation of an isotropic substance in a longitudinal magnetic field, H, along the z axis is[5,6]

$$[\varphi(\mathrm{a} \rightarrow \mathrm{j})]_\mathrm{M} = -64.067H \left\{ f_1(\omega,\, \omega_{\mathrm{ja}}) A(\mathrm{a} \rightarrow \mathrm{j}) + f_2(\omega,\, \omega_{\mathrm{ja}}) \left[B(\mathrm{a} \rightarrow \mathrm{j}) + \frac{C(a \rightarrow \mathrm{j})}{kT} \right] \right\} \quad (1)$$

where

$$A(\mathrm{a} \rightarrow \mathrm{j}) = 1/d_\mathrm{a} \sum [\langle \mathrm{j}|\mu_z|\mathrm{j}\rangle - \langle \mathrm{a}|\mu_z|\mathrm{a}\rangle] \times Im\, [\langle \mathrm{a}|m_x|\mathrm{j}\rangle\langle \mathrm{j}|m_y|\mathrm{a}\rangle]$$

$$B(\mathrm{a} \rightarrow \mathrm{j}) = 1/d_\mathrm{a} \sum Im \left\{ \sum_{\mathrm{k} \neq \mathrm{a}} \frac{\langle \mathrm{k}|\mu_z|\mathrm{a}\rangle}{\omega_{\mathrm{ka}}} [\langle \mathrm{a}|m_x|\mathrm{j}\rangle\langle \mathrm{j}|m_y|\mathrm{k}\rangle - \langle \mathrm{a}|m_y|\mathrm{j}\rangle\langle \mathrm{j}|m_x|\mathrm{k}\rangle] + \sum_{\mathrm{k} \neq \mathrm{j}} \frac{\langle \mathrm{j}|\mu_z|\mathrm{k}\rangle}{\omega_{\mathrm{kj}}} [\langle \mathrm{a}|m_x|\mathrm{j}\rangle\langle \mathrm{k}|m_y|\mathrm{a}\rangle - \langle \mathrm{a}|m_y|\mathrm{j}\rangle\langle \mathrm{k}|m_x|\mathrm{a}\rangle] \right\}$$

$$C(\mathrm{a} \rightarrow \mathrm{j}) = 1/d_\mathrm{a} \sum \langle \mathrm{a}|\mu_z|\mathrm{a}\rangle Im\, [\langle \mathrm{a}|m_x|\mathrm{j}\rangle\langle \mathrm{j}|m_y|\mathrm{a}\rangle] \quad (2)$$

and f_1 and f_2 have the general forms shown in Figure 1. Assuming a damped-oscillator shape

$$f_1(\omega,\omega_{\mathrm{ja}}) = \frac{2\omega_{\mathrm{ja}}\omega^2[(\omega_{\mathrm{ja}}{}^2 - \omega^2)^2 - \omega^2\Gamma_{\mathrm{ja}}{}^2]}{[(\omega_{\mathrm{ja}}{}^2 - \omega^2)^2 + \omega^2\Gamma_{\mathrm{ja}}{}^2]^2}$$

$$f_2(\omega,\omega_{\mathrm{ja}}) = \frac{\omega^2(\omega_{\mathrm{ja}}{}^2 - \omega^2)}{(\omega_{\mathrm{ja}}{}^2 - \omega^2)^2 + \omega^2\Gamma_{\mathrm{ja}}{}^2} \quad (3)$$

The symbols used are: $\mathbf{m}$ and $\boldsymbol{\mu}$ are the electric and magnetic dipole operators in Debye units and Bohr magnetons; d_a is the degeneracy of a and the summations in (2) are over all states degenerate with a and j, which are required to be diagonal in μ_z; ω is the frequency of the radiation and ω_{ja} the energy difference between j and a, both in cm.$^{-1}$; H is in gauss and kT in cm.$^{-1}$.

The A, B, and C terms arise, respectively, from the Zeeman splitting of a → j, the mixing by H of a and j with other states k, and the alteration in the relative populations of components of a through its Zeeman splitting. Thus C is only nonzero when a is degenerate and A when either a or j is degenerate. The three terms are separable from each other through their different ω and T dependence and from the contributions of other transitions through their anomalous dispersion in the region of the absorption band.

For allowed transitions A and C depend on only three parameters, which can be taken to be the reduced matrix elements $\langle \mathrm{a}||m||\mathrm{j}\rangle$, $\langle \mathrm{a}||\mu||\mathrm{a}\rangle$, and $\langle \mathrm{j}||\mu||\mathrm{j}\rangle$. The last two can often be easily calculated and $\langle \mathrm{a}||\mu||\mathrm{a}\rangle$ is also obtainable from the paramagnetic susceptibility. In this case A and C can be expressed in terms of the dipole strength $D = (3/d_\mathrm{a})\Sigma\ |\langle \mathrm{a}|m_x|\mathrm{j}\rangle|^2$, which is a function of $\langle \mathrm{a}||m||\mathrm{j}\rangle$. Since the precise relation will depend on the symmetries of a and j, determination of A and/or C together with D allows the symmetry assignment of a → j to be deduced, independently of assumptions about the detailed nature of the absorption process; conversely, no information about the latter is provided.

This method is likely to be a useful aid to assignments of charge-transfer bands in transition metal complexes. Here we apply it to $K_3Fe(CN)_6$, whose absorption spectrum[7] and MORD are shown in Figure 2. Molecular orbital energy level diagrams applicable to transition metal hexacyanides have been presented by McClure,[8] Robin,[9] and Gray and Beach,[10] the relevant parts being shown in Figure 3; all agree that the ground state of $Fe(CN)_6{}^{3-}$ is $^2T_{2g}(\ldots t_{2g}(\pi)^5)$. The strong absorption bands 1, 2, and 3 at 24,100, 32,900, and 38,460 cm.$^{-1}$ have been attributed to allowed ligand-to-metal (l → m) charge-transfer transitions. Naiman[3,4] identified them with the transitions $t_{2u}(\pi^b) \rightarrow t_{2g}(\pi)$ ($^2T_{2g} \rightarrow {}^2T_{2u}$), $l_u \rightarrow t_{2g}(\pi)$, and $l_u \rightarrow e_g(\sigma^*)$, band 1 being assigned on the basis of its pressure dependence and Figure 3c; by implication band 2 then corresponds to the transition

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[1] Institute for the Study of Metals, University of Chicago, Chicago, Ill. 60637.

[2] (a) V. E. Shashoua, *J. Am. Chem. Soc.*, **86**, 2109 (1964); (b) B. Briat, *Compt. rend.*, **259**, 2408 (1964).

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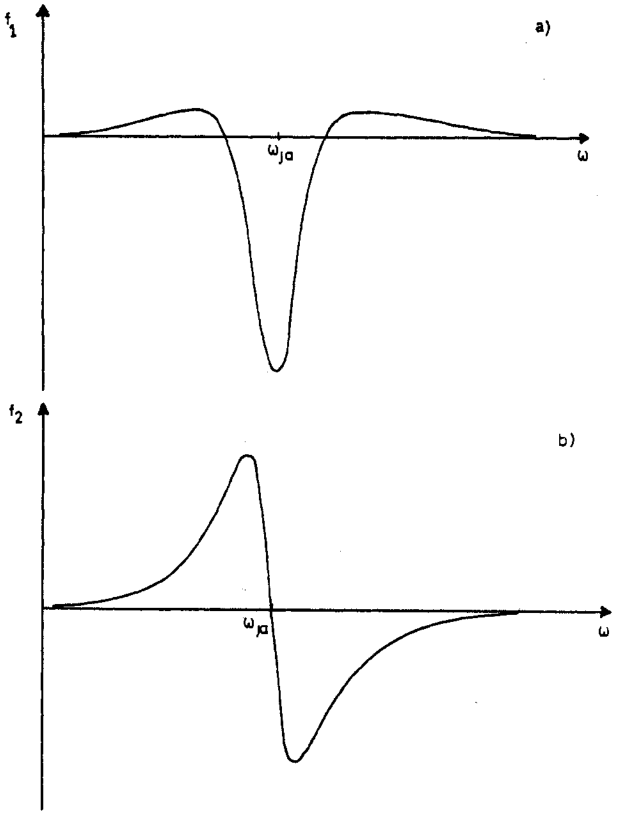

Figure 1.—Dispersion shapes of (a) A and (b) B and C terms.

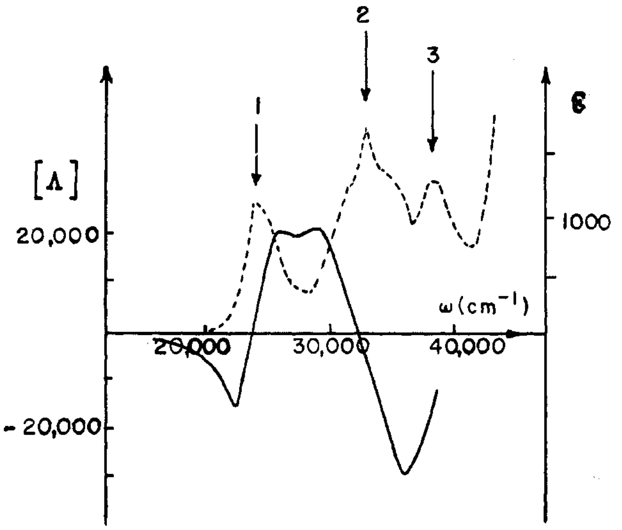

Figure 2.— – – – –, absorption spectrum of $K_3Fe(CN)_6$ (from ref. 7, by permission); ———, MORD of $K_3Fe(CN)_6$ (after ref. 2): $[\Lambda] = -3.037[\varphi]_M$ when $H = 10^4$ gauss.

$t_{1u}(\pi^b) \rightarrow t_{2g}(\pi)$ ($^2T_{2g} \rightarrow {}^2T_{1u}$). On the other hand, using Figures 3a and 3b Basu and Belford[11] ascribed band 1 to either $t_{2u}(\pi^b) \rightarrow t_{2g}(\pi)$ or $t_{1u}(\sigma^b) \rightarrow t_{2g}(\pi)$ transitions.

Now, if bands 1 and 2 are $l_u \rightarrow t_{2g}(\pi)$ transitions, then, according to Figure 3, l_u can only be $t_{1u}(\sigma^b)$, $t_{1u}(\pi^b)$, or $t_{2u}(\pi^b)$ and therefore the excited states, $l_u^5 t_{2g}^6$, must be $^2T_{1u}$ or $^2T_{2u}$. These latter alternatives

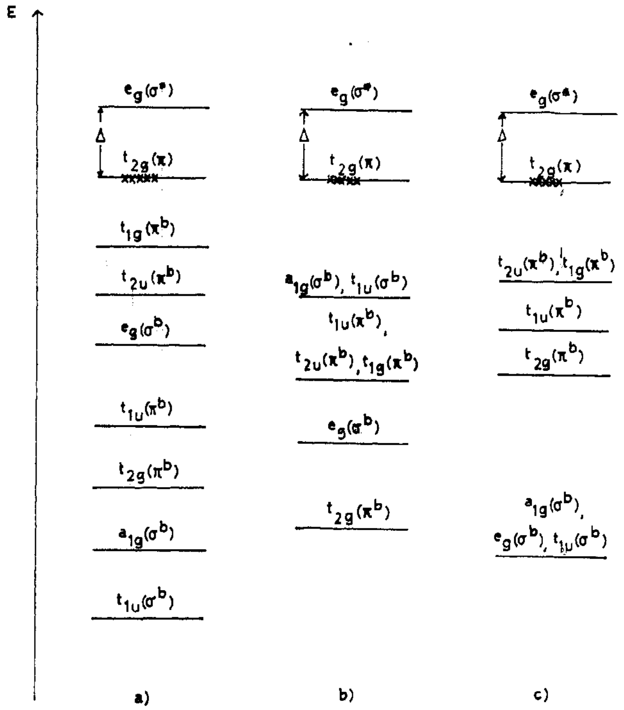

Figure 3.—Molecular orbitals for $M(CN)_6{}^{n-}$: (a) McClure,[8] (b) Robin,[9] (c) Gray and Beach.[10] Crosses indicate electrons in unfilled shells in $Fe(CN)_6{}^{3-}$.

can be differentiated through their Faraday effects: using the Wigner–Eckart theorem and Griffith's coupling coefficients[12] it is easily shown that for $^2T_{2g} \rightarrow {}^2T_{1u}$ and $^2T_{2u}$ transitions, $C = +\langle T_{2g}||\mu_l||\,T_{2g}\rangle\, D/6\sqrt{2}i$ and $-\langle T_{2g}||\mu_l||T_{2g}\rangle D/6\sqrt{2}i$, respectively, where $\boldsymbol{\mu}_l$ is the orbital magnetic moment operator. Assuming the $t_{2g}(\pi)$ orbitals to be pure d orbitals, $\langle T_{2g}||\mu_l||T_{2g}\rangle = -\sqrt{2}i$. We therefore predict that C is of opposite sign for $^2T_{1u}$ and $^2T_{2u}$ excited states, being positive for the latter, and that $|C|/D$ is the same for both, approximately equal to $^1/_6$. With the observed band widths the C terms should dominate the A terms in the absorption regions; also, since $B \sim C \times kT/\Delta E$, where ΔE is the energy separation of the nearest state mixed with ground or excited states by μ_z, and $\Delta E \geqslant 5000$ cm.$^{-1}$, the B terms are negligible. Hence the C terms alone should contribute appreciably to the observed MORD.

In agreement with this we see from Figure 2 that the MORD curves of bands 1 and 2 have the form shown in Figure 1b; although the rotation was only measured at one temperature it can therefore reasonably be attributed essentially entirely to C terms. It then follows that C is negative and positive, respectively, for bands 1 and 2, and we estimate[13] $|C| \sim 0.3$ and $D \sim 1.5$-2.0 for both bands, whence $|C|/D \sim 0.15$-0.2. The $|C|/D$ ratio is in good agreement with that predicted, strongly supporting the assignment to allowed charge-transfer transitions. The signs of C prove that, under the as-

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(11) G. Basu and R. L. Belford, *J. Chem. Phys.*, **37**, 1933 (1962).

(12) J. S. Griffith, "The Theory of Transition-Metal Ions," Cambridge, 1961, Table A 20.

(13) The C and D values for band 2 are much less accurate than for band 1 owing to the effects of the overlapping band 3, particularly in the MORD.

sumption of $l_u \rightarrow t_{2g}(\pi)$ transitions, the excited states of bands 1 and 2 must be $^2T_{1u}$ and $^2T_{2u}$, respectively.

From Figure 3 it then follows that l_u can be either $t_{1u}(\sigma^b)$ or $t_{1u}(\pi^b)$ in band 1, while in band 2 it must be $t_{2u}(\pi^b)$. The ambiguity in band 1 cannot be further resolved at this stage since the schemes of Figure 3 are only qualitative and the order of the $t_{1u}(\sigma^b)$ and $t_{1u}(\pi^b)$ levels remains in doubt. Naiman[4] has offered reasons why the l_u in band 1 may be π rather than σ, but these are not conclusive.

No knowledge of the form of the l_u orbitals is required in the calculation of C for $l_u \rightarrow t_{2g}(\pi)$ transitions or is furnished by the observed C values. Some information would be provided by the A terms, but these are not separable in $Fe(CN)_6^{3-}$ from the dominating C terms. However, the A terms might be observable in the analogous $^4A_{2g} \rightarrow {}^4T_{2u}$, $l_u \rightarrow t_{2g}(\pi)$ transitions of $Cr(CN)_6^{3-}$, where C is zero if spin–orbit coupling is neglected.

In conclusion, on the basis of their MORD curves and of molecular orbital energy level diagrams we assign the 24,100 and 32,900 cm.$^{-1}$ bands of $K_3Fe(CN)_6$ to $t_{1u}(\sigma^b)$ or $t_{1u}(\pi^b) \rightarrow t_{2g}(\pi)$ $(^2T_{2g} \rightarrow {}^2T_{1u})$ and $t_{2u}(\pi^b) \rightarrow t_{2g}(\pi)$ $(^2T_{2g} \rightarrow {}^2T_{2u})$ transitions, respectively.

Acknowledgments.—The author is indebted to Dr. A. D. Buckingham for his interest in the Faraday effect, Professor C. J. Ballhausen for helpful conversations, the H. C. Ørsted Institute for hospitality, and D.S.I.R. for a Research Fellowship.

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina

Hexaaquoruthenium(II)[1]

By E. E. MERCER and R. R. BUCKLEY

Received July 20, 1965

The hexaaquoruthenium(II) ion has been separated and characterized in aqueous solution. The ion was formed by electrolytic reduction of ruthenium(III) at a controlled potential of −0.40 v. with respect to a saturated calomel electrode, using a mercury pool cathode. The only anions found which did not interfere with the formation of this ion were tetrafluoroborate and *p*-toluenesulfonate. In the presence of other anions, either oxidation or complexation of the ruthenium was found to take place. The charge on the ion was determined using ion-exchange methods. The oxidation state of the metal was verified by coulometry and titration of the ion with triiodide. The oxidation potential for the half-reaction $Ru^{+2} \rightarrow Ru^{+3} + e^-$ was found to be -0.22 ± 0.03 v. by polarography.

Several previous studies have been made on the aqueous chemistry of ruthenium(II). Most of these studies were made in chloride medium, where the behavior observed is largely that of the chloro complexes. We have found that the properties of the chloro complexes are quite different from those of the aquo complex. The only previous attempts to prepare uncomplexed ruthenium(II) resulted in a variety of uncharacterized products.[2]

Results

(A) Preparation of the Complex.—Our early attempts to prepare the Ru^{+2} ion by chemical reduction were not successful. Most of these failures were due to the particular anions present in solution, usually perchlorate or trifluoroacetate. Later experiments showed that the trifluoroacetate ion forms complexes with ruthenium(II), while the reduction of perchlorate ion is readily accomplished by the Ru^{+2} ion. In other cases reaction with the reducing agent, for example zinc, yielded metallic ruthenium as the principal product. The Ru^{+2} ion was formed most readily by electrolysis, using the following procedure.

A nearly saturated, freshly prepared, aqueous solution of potassium pentachloroaquoruthenate(III) was placed on a cation-exchange column in the hydrogen ion form. By removing the anionic ruthenium complexes from the column with water, the potassium ions in solution were replaced by hydrogen ions. Sufficient tetrafluoroboric acid was added to give a solution which was about 1 M in hydrogen ion and 10^{-2} M in ruthenium(III). A 0.5 M silver tetrafluoroborate solution was added dropwise, until no more silver chloride formed. The solution was allowed to stand at room temperature for 3–4 days, giving a solution containing mostly the mono- and dichloro complexes of ruthenium(III), as indicated by the ultraviolet spectra of the solutions.[3] The absence of silver ion in solution was proven by adding a few drops of the solution to 1 ml. of 1 M hydrochloric acid. The ruthenium in about 5 ml. of this solution was reduced at a mercury cathode, the potential of which was controlled at −0.40 v. with respect to a saturated calomel electrode.[4] The electrolysis was continued at room temperature

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[1] (a) Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965. (b) This work was supported by the National Science Foundation on Grant No. GP-1584.

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