Theoret. chim. Acta (Berl.) 30, 339—346 (1973)

A Calculation of the Rotatory Strengths of the Electron-Transfer Transitions of the *Tris*-(1,10-phenanthroline)iron(II) Ion

M. Král*, A. Moscowitz**, and C. J. Ballhausen

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

Received April 5, 1973

The rotatory strengths of the metal-to-ligand transitions observed in the spectrum of the complex ion (–)–Fe(phen)$_3^{+2}$ have been calculated theoretically. The excited electronic states were characterized using a coupled chromophore model. The calculated rotatory strengths are higher than the corresponding experimental values by a factor of about four.

Key words: Rotary strengths of inorganic complexes – *Tris*-(1, 10-phenanthroline) iron (II) ion – Electron-transfer transitions in inorganic chelates

Introduction

Many papers dealing with the optical rotatory dispersion (ORD spectra) and circular dichroism (CD spectra) of complex ions have appeared in the last ten years. The quantity which can be extracted from these measurements is the rotatory strength, defined for a transition from state A to state B by the relation [1]

$$R_{A\to B} = \mathrm{Im}\{\langle A|\mu_e|B\rangle \cdot \langle B|\mu_m|A\rangle\}\,, \tag{1}$$

where μ_e and μ_m are the electric and magnetic dipole operators respectively.

The reported calculations of the optical activities of complex compounds of metal ions with bidentate ligands forming an octahedral coordination of donor atoms of D_3 symmetry have used either an ionic [2–8] or a molecular orbital approach [9–13]. Such models are quite useful for studies of the circular dichroism of the *d–d* bands but are impractical when used to account for optically active metal-to-ligand $\pi^\star$ orbital transitions. To analyse this type of transition we have used the "coupled chromophore" model proposed by Longuet-Higgins and Murrell [14] for studies of conjugated π-electronic systems and utilized for the investigation of the optical activities of organic compounds by Moscowitz and Hansen [15, 16]. As an example we shall treat the complex ion (–)-Fe(phen)$_3^{+2}$ (phen = 1,10-phenanthroline). Hanazaki and Nagakura [17] have previously studied the same ion using similar methods. However, their results are in doubt because of shortcomings in the wave functions they used.

---

* Present address: Vysoká skola chemicko-technologická, Praha, Czechoslovakia.

** Present address: Department of Chemistry, University of Minnesota, Minnesota, U.S.A.

Theory

With

$$\mu_e = e \sum_i r_i , \tag{2}$$

$$\mu_m = \frac{e}{2mc} \sum_i r_i \times p_i = \frac{e\hbar}{2mci} \sum_i r_i \times \nabla_i \tag{3}$$

and upon changing the matrix element of the operator μ_e to a dipole velocity representation [18], (1) can be expressed as

$$R_{A \to B} = - \frac{e^2 \hbar^2}{4\pi m^2 c^2 \sigma_{A \to B}} \langle A | \nabla | B \rangle \cdot \langle B | r \times \nabla | A \rangle , \tag{4}$$

where the symbols e, $\hbar$, m and c have their usual meaning and where $\sigma_{A \to B}$ is the energy difference between states A and B measured in cm^{-1}. State A is taken as the ground state and state B as a single-electron excited state. The electronic states are represented in the coupled chromophore model by linear combinations of functions of the form

$$|X\rangle = \prod_g |C_g^i\rangle , \tag{5}$$

$|C_g^i\rangle$ being the wave function which describes the i^{th} electronic state of the g^{th} chromophore. We assume that the wave functions associated with a single chromophore are orthogonal to each other, viz:

$$\langle C_g^i | C_g^j \rangle = \delta_{ij} . \tag{6}$$

The ground state, having n groups of ligands, is then given by the function

$$|A, \Gamma, S\rangle = |M^0\rangle \prod_{g=1}^{n} |L^0(g)\rangle , \tag{7}$$

where Γ designates the symmetry classification of the function, S is the total spin, $|M^0\rangle$ is the function which describes the electronic ground state of the metal ion and where $|L^0(g)\rangle$ stands for the electronic ground state of the g^{th} ligand.

State B in Eq. (4) is a one-electron excited state in which a d-electron from the central metal ion has been excited into a π-antibonding orbital located on a ligand. As a d-electron goes into π-antibonding orbitals on the first, second, ..., n^{th} ligands, this state is described by the function

$$|ET, \Gamma_l S\rangle = \sqrt{\frac{1}{j}} \sum_j \sum_{h=1}^{n} D_h^{\Gamma_l} \left| \begin{matrix} L(h)_r \\ M_j \end{matrix} \right\rangle \prod_{g=1}^{n} |L^0(g)\rangle , \tag{8}$$

where $D_h^{\Gamma_l}$ are the group transformation coefficients and where $\left| \begin{matrix} L(h)_r \\ M_j \end{matrix} \right\rangle$ stands for the single determinantal function of the configuration arising from the promotion of a d-electron from the state described by the spin-orbital function $|M_j\rangle$ into the r^{th} antibonding state of the h^{th} ligand described by the spin-orbital function $|L(h)_r\rangle$. Now, if we introduce (7) and (8) into the expression for the matrix elements of the operator $\boldsymbol{V}$, we get

$$\langle A,\Gamma S|\sum_i \boldsymbol{V}_i|ET,\Gamma_l S\rangle = \sqrt{\frac{1}{j}}\sum_j\sum_h D_h^{\Gamma_l}\langle M^0|\sum_i \boldsymbol{V}_i\left|\begin{matrix}L(h)_r\\ M_j\end{matrix}\right\rangle . \tag{9}$$

Similarly, for the matrix element of the operator $(\boldsymbol{r}\times\boldsymbol{V})$ we get

$$\langle ET,\Gamma_l S|\sum_i \boldsymbol{r}_i\times\boldsymbol{V}_i|A,\Gamma S\rangle = \sqrt{\frac{1}{j}}\sum_j\sum_h D_h^{\Gamma_l}\left\langle\begin{matrix}L(h)_r\\ M_j\end{matrix}\right|\sum_i \boldsymbol{r}_i\times\boldsymbol{V}_i|M^0\rangle . \tag{10}$$

Since $\boldsymbol{V}_i$ and $(\boldsymbol{r}_i\times\boldsymbol{V}_i)$ are one-electron operators, the matrix elements of these operators can be reduced to

$$\langle M^0|\sum_i \boldsymbol{V}_i\left|\begin{matrix}L(h)_r\\ M_j\end{matrix}\right\rangle = \langle M_j|\boldsymbol{V}|L(h)_r\rangle \tag{11}$$

and

$$\left\langle\begin{matrix}L(h)_r\\ M_j\end{matrix}\right|\sum_i \boldsymbol{r}_i\times\boldsymbol{V}_i|M^0\rangle = \langle L(h)_r|\boldsymbol{r}\times\boldsymbol{V}|M_j\rangle . \tag{12}$$

We do not consider spin-orbit coupling so we can write an arbitrary spin orbital as

$$|C_i\rangle = |c_i\rangle\,|\gamma_i\rangle \tag{13}$$

where $|c_i\rangle$ is the orbital part and $|\gamma_i\rangle$ is the spin part of the wave function. Hence

$$\langle M_j|\boldsymbol{V}|L(h)_r\rangle = \langle m_j|\boldsymbol{V}|l(h)_r\rangle \tag{14}$$

and

$$\langle L(h)_r|\boldsymbol{r}\times\boldsymbol{V}|M_j\rangle = \langle l(h)_r|\boldsymbol{r}\times\boldsymbol{V}|m_j\rangle . \tag{15}$$

Substituting (14) and (15) into the Eqs. (9) and (10) we obtain, after summing over all orbital states,

$$\langle A,\Gamma,S|\sum_i \boldsymbol{V}_i|ET,\Gamma_l S\rangle = \sqrt{\frac{1}{k}}\sum_k\sum_h D_h^{\Gamma_l}\langle m_k|\boldsymbol{V}|l(h)_r\rangle \tag{16}$$

and

$$\langle ET,\Gamma_l S|\sum_i \boldsymbol{r}_i\times\boldsymbol{V}_i|A,\Gamma S\rangle = \sqrt{\frac{1}{k}}\sum_k\sum_h D_h^{\Gamma_l}\langle l(h)_r|\boldsymbol{r}\times\boldsymbol{V}|m_k\rangle . \tag{17}$$

We can therefore rewrite expression (4) in the form

$$R_{\Gamma\to\Gamma_l} = \frac{e^2\hbar^2}{4\pi m^2c^2\sigma_{\Gamma\to\Gamma_l}}\,\frac{1}{k}\sum_k\sum_h (D_h^{\Gamma_l})^2\langle m_k|\boldsymbol{V}|\,l(h)_r\rangle\cdot\langle l(h)_r\,|\boldsymbol{r}\times\boldsymbol{V}|\,m_k\rangle . \tag{18}$$

Matrix Elements of the Operators $\vec{V}$ and $(\vec{r}\times\vec{V})$

The molecular orbitals $|m_k\rangle$ and $|l(h)_r\rangle$ are expressed as linear combinations of real atomic d-orbitals and ligand orbitals

$$|m_k\rangle = \sum_m b_{km}d_m \tag{19}$$

and

$$|l(h)_r\rangle = \sum_s c_{rs}p_{zs}^{(h)}, \tag{20}$$

where $p_{zs}^{(h)}$ is a p_z-orbital on the h^{th} ligand localized on the s^{th} centre.

Table 1. Matrix elements $\langle n_m l_m m_m^a | \nabla | 2p_z \rangle$

Matrix Element	i	j	k
$\langle 3d_{xy} \| \nabla \| 2p_z \rangle$	0	0	0
$\langle 3d_{xz} \| \nabla \| 2p_z \rangle$	$\langle 3d_{xz} \left\| \frac{\partial}{\partial x} \right\| 2p_z \rangle$	0	0
$\langle 3d_{yz} \| \nabla \| 2p_z \rangle$	0	$\langle 3d_{yz} \left\| \frac{\partial}{\partial y} \right\| 2p_z \rangle$	0
$\langle 3d_{z^2} \| \nabla \| 2p_z \rangle$	0	0	$\langle 3d_{z^2} \left\| \frac{\partial}{\partial z} \right\| 2p_z \rangle$
$\langle 3d_{x^2-y^2} \| \nabla \| 2p_z \rangle$	0	0	$\langle 3d_{x^2-y^2} \left\| \frac{\partial}{\partial z} \right\| 2p_z \rangle$

Table 2. Matrix elements $\langle 2p_z | r \times \nabla | n_m l_m m_m^a \rangle$

Matrix Element	i	j	k
$\langle 2p_z \| r \times \nabla \| 3d_{xy} \rangle$	0	$\langle 2p_z \| 3d_{yz} \rangle$	0
$\langle 2p_z \| r \times \nabla \| 3d_{xz} \rangle$	0	0	0
$\langle 2p_z \| r \times \nabla \| 3d_{yz} \rangle$	0	0	0
$\langle 2p_z \| r \times \nabla \| 3d_{z^2} \rangle$	$\sqrt{3} \langle 2p_z \| 3d_{yz} \rangle$	0	0
$\langle 2p_z \| r \times \nabla \| 3d_{x^2-y^2} \rangle$	$\langle 2p_z \| 3d_{yz} \rangle$	0	0

The matrix elements $\langle m_k | \nabla | l(h)_r \rangle$ and $\langle l(h)_r | r \times \nabla | m_k \rangle$ are therefore given by a sum of two-center integrals taken over normalized Slater orbitals:

$$\langle n_m l_m m_m^a | \nabla | n_s l_s m_s^a \rangle \tag{21}$$

and

$$\langle n_s l_s m_s^a | r \times \nabla | n_m l_m m_m^a \rangle . \tag{22}$$

The non-vanishing matrix elements of the operator ∇ can be found by standard group-theoretical methods [19, 20]. Their components are given in Table 1. In addition the matrix elements of the operator $(r \times \nabla)$ may be expressed as overlap integrals [15], and their non-zero components are given in Table 2.

Calculation of $R_{A \to B}$ for (—)-Fe(phen)$_3^{+2}$

The complex is schematically illustrated in Fig. 1. For simplification only the donor atoms are indicated and the bidentate ligands are replaced by thick lines. The symmetry of the entire complex ion is taken as D_3. In Fig. 1 the unit vectors used to describe the positions of the ligands are shown. These have been chosen in such a way that for ligand 1 all the vectors are positive. Referred to this choice the positions of ligands 2 and 3 are given as follows:

$$\begin{array}{ccc} L(1) & L(2) & L(3) \\ \boldsymbol{i} & \boldsymbol{k} & -\boldsymbol{j} \\ \boldsymbol{j} & -\boldsymbol{i} & -\boldsymbol{k} \\ \boldsymbol{k} & -\boldsymbol{j} & \boldsymbol{i} \end{array} \tag{23}$$

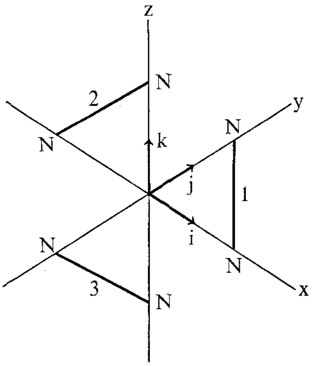

Fig. 1. Unit vectors describing the ligand positions

The distances of the carbon and nitrogen atoms from the central metal ion are given in Table 3. Of these values only the bond distance Fe–N has been experimentally determined [21].

Studies of the magnetic properties of the complex ion $(-)\text{-Fe(phen)}_3^{+2}$ have shown that the ground state is a magnetic singlet state [22], i.e. the function $|M^0\rangle$ in the expressions (7), (9) and (10) can be written

$$|M^0\rangle = |m_1\alpha, m_1\beta, m_2\alpha, m_2\beta, m_3\alpha, m_3\beta|, \tag{24}$$

where m_k are the atomic orbitals of the metal [23],

$$\begin{aligned} m_1 &= \sqrt{\frac{2}{3}}(x^2-y^2) - \sqrt{\frac{1}{3}}(xz), \\ m_2 &= \sqrt{\frac{2}{3}}(xy) + \sqrt{\frac{1}{3}}(yz) \\ \text{and} \quad m_3 &= (z^2), \end{aligned} \tag{25}$$

the expressions in brackets, e.g. (x^2-y^2), being the real d orbitals.

We now turn to the electron transfer states. The optically active transitions can easily be identified because these are the electronic transitions possessing mutually dissymmetrically oriented transition moments [24]. In D_3 symmetry the transitions localized on the metal atom are polarized either parallel or per-

Table 3. Interatomic distances in Fe(phen)_3^{+2}

$M-X$	Bond length in Å	$M-X$	Bond length in Å
Fe–N_1 Fe–N_{10}	1·97	Fe–C_5 Fe–C_6	5·10
Fe–C_2 Fe–C_9	3·12	Fe–C_{11} Fe–C_{12}	2·68
Fe–C_3 Fe–C_8	4·36	Fe–C_{13} Fe–C_{14}	4·07
Fe–C_4 Fe–C_7	4·73		

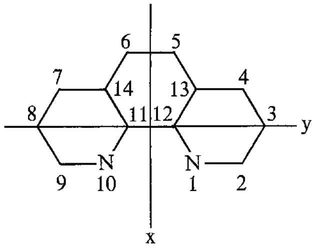

Fig. 2. Numbering and coordinate axis used for o-phenantholine

pendicular to the C_3 axis. In an o-phenanthroline molecule the electronic transitions are polarized either along the long axis (y) or along the short axis (x) (see Fig. 2). In the molecular geometry of the complex the transitions polarized along the short (x) axis are parallel to the molecular C_2 axis. The transition moments of the $d-d$-transitions have the same orientations; it follows that the charge transfer transitions are optically inactive. On the other hand the ligand transitions polarized along the long (y) axis yield a dis-symmetric transition moment mirrored by the transition moments of the $d-d$-transitions. Hence these bands will be optically active.

A study of the electronic spectra of 1,10-phenanthroline has revealed that the transitions polarized along the long axis originate from the exitation of an electron in the highest filled π orbital to the second empty π-antibonding orbital [25]. This is therefore the molecular orbital into which we excite a d-electron.

Numerical Calculations

The carbon and nitrogen atomic functions were taken in mono-ζ form with the values $\zeta_C = 1 \cdot 5679$ and $\zeta_N = 1 \cdot 9170$ [26]. The atomic iron function used had a double zeta form [27]:

$$|\mathrm{Fe(II)}, 3dm^a\rangle = 0.5661\,|\mathrm{Fe(II)}, 3dm^a\zeta_1\rangle + 0.5860\,|\mathrm{Fe(II)}, 3dm^a\zeta_2\rangle$$

with

$$\zeta_1 = 5 \cdot 35 \quad \text{and} \quad \zeta_2 = 2 \cdot 20 .$$

In addition the SCF molecular orbitals given for o-phen by Ito *et al.* [28] were used. The rotatory strengths of the transitions ${}^1A_1 \to {}^1A_2$ and ${}^1A_1 \to {}^1E$ were then calculated, and the results are compared with the corresponding experimental values for these transitions in Table 4. The experimental figures were calculated from data published in the literature [29, 30].

The theoretical and the experimental values of the oscillator strengths of these transitions are also given in Table 4.

Table 4. Calculated and experimental results

Transition	R in cgs	R^{exp} in cgs	Oscillator strengths f	f^{exp}
${}^1A_1 \to {}^1A_2$	$+5 \cdot 80.10^{-38}$	$+1 \cdot 38.10^{-38}$	$6 \cdot 78.10^{-3}$	$8 \cdot 7.10^{-2}$
${}^1A_1 \to {}^1E$	$-7 \cdot 21.10^{-38}$	$-1 \cdot 62.10^{-38}$	$7 \cdot 30.10^{-3}$	$1 \cdot 03.10^{-1}$

Discussion

In order that the calculated and experimental rotatory strength of a certain transition might be compared it is, of course, necessary to make a spectral identification. For the electron transfer transitions found in the complex $(-)$-Fe(phen)$_3^{+2}$ we have assigned the 21400 cm^{-1} band as due to the transition $^1A_1 \rightarrow {}^1A_2$ and the 19600 cm^{-1} band as due to the transition $^1A_1 \rightarrow {}^1E$. This means that the negative component of the CD curve was assigned to the long wavelength transition while its positive component was assigned to the short wavelength transition. This identification is in agreement with the proposal of Orgel [31], and yields reasonable agreement with the experimental results.

If we compare the theoretical values of the rotatory strengths with the corresponding experimental data (Table 4) we see that for both types of transition R(theoretical) is greater than R(experimental) by a factor of about four. Presumably this means that the electron transfer state is not the pure state described by the wave function (8), but is mixed with mono-excited states localized on the ligands. Such mixing may lower the rotatory strengths of both transitions since the rotatory strengths of the transitions localized on the ligands can differ in sign. Presumably the oscillator strengths of the pertinent transitions, which are about ten times lower than the experimental values, would be increased at the same time.

Acknowledgements. M.K. thanks the Czechoslovak Ministry of Education for the grant which enabled him to spend the Spring of 1968 in Denmark. We express our gratitude to Dr. Aage E. Hansen for clarifying discussions.

References

1. Condon, E. U.: Rev. Mod. Phys. **9**, 432 (1937)
2. Moffitt, W.: J. Chem. Phys. **25**, 1189 (1956)
3. Hamer, N. K.: Mol. Phys. **5**, 339 (1962).
4. Piper, T. S., Karipides, A.: Mol. Phys. **5**, 475 (1962)
5. Piper, T. S.: J. Chem. Phys. **36**, 2224 (1962)
6. Poulet, H.: J. Chem. Phys. **59**, 584 (1962)
7. Sugano, S.: J. Chem. Phys. **33**, 1883 (1960)
8. Shinada, M.: J. Phys. Soc. Japan **19**, 1607 (1964)
9. Liehr, A. D.: J. Phys. Chem. **68**, 665 (1964)
10. Liehr, A. D.: J. Phys. Chem. **68**, 3629 (1964)
11. Liehr, A. D.: Transition metal chemistry, ed. by Carlin, R., p. 165. New York: Marcel Dekker 1966
12. Karipides, A., Piper, T. S.: J. Chem. Phys. **40**, 674 (1964)
13. Schäffer, C. E.: Proc. Roy. Soc. (London), Ser. A **297**, 96 (1967)
14. Longuet-Higgins, H. C., Murrell, J. N.: Proc. Phys. Soc. (London) A **68**, 601 (1955)
15. Moscowitz, A. J., Hansen, Aa. E., Forster, L. S., Rosenheck, K.: Biopolymers. Symp. No. 1. 75 (1964)
16. Hansen, Aa. E.: Thesis. University of Copenhagen, Copenhagen 1964
17. Hanazaki, I., Nagakura, S.: Inorg. Chem. **8**, 654 (1969)
18. Seaton, M. J.: Quantum theory, ed. by Bates, D. R., Vol. 2, p. 81. New York: Academic Press 1962
19. Tinkham, M.: Group theory and quantum mechanics, p. 41. New York: McGraw-Hill 1964
20. Král, M.: Collection Czech. Chem. Commun. **35**, 1939 (1970)
21. Templeton, D. H., Zalkin, A., Ueki, T.: Acta Cryst. (Supplement) **21**, A 154 (1966)
22. Williams, R. J. P.: J. Chem. Soc. 137, (**1955**)
23. Ballhausen, C. J.: Introduction to the ligand field theory, p. 68. New York: McGraw-Hill 1962
24. Eyring, E., Liu, Han-Chung, Caldwell, D.: Chem. Rev. **68**, 525 (1968)
25. McCaffery, A. J., Mason, S. F., Norman, B. J.: J. Chem. Soc. A 1428 (**1969**)

26. Clementi, E., Raimondi, D. L.: J. Chem. Phys. **38**, 2686 (1963)
27. Richardson, J. W., Nieuwpoort, W. C., Powell, R. R., Edgell, W. F.: J. Chem. Phys. **36**, 1057 (1962)
28. Ito, T., Tanaka, N., Hanazaki, I., Nagakura, S.: Bull. Chem. Soc. Japan **42**, 702 (1969)
29. Moscowitz, A.: Optical rotatory dispersion, ed. by Djerassi, C., p. 155, 165. New York: McGraw-Hill 1960
30. Mason, S. F.: Inorg. Chim. Acta Rev. **2**, 89 (1968)
31. Orgel, L. E.: J. Chem. Soc. 3683 **(1961)**

Prof. Dr. C. J. Ballhausen
Department of Physical Chemistry
H. C. Ørsted Institute
University of Copenhagen
København Ø, Universitetsparken 5
Denmark