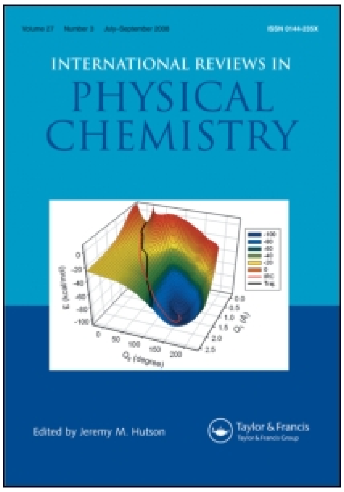

International Reviews in Physical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713724383

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To cite this Article Van Der Waals, J. H.(1986) 'Spin-orbit coupling in the tetroxo anions of the d^0 transition metals and the identification of their lower triplet states', International Reviews in Physical Chemistry, 5: 2, 219 — 228
To link to this Article: DOI: 10.1080/01442358609353386
URL: http://dx.doi.org/10.1080/01442358609353386

INTERNATIONAL REVIEWS IN PHYSICAL CHEMISTRY, 1986, VOL. 5, NOS. 2 & 3, 219–228

Spin–orbit coupling in the tetroxo anions of the d^0 transition metals and the identification of their lower triplet states

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A survey is presented of the lower excited states of the tetrahedral oxy-anions having a d^0 transition metal at the centre, with particular emphasis on the triplet states. The principal question addressed concerns the spin–orbit coupling mechanism in these ions. It appears that the symmetry of the molecular orbitals involved in the first excitation is such that—at least for the 3d compounds VO_4^{3-}, CrO_4^{2-}, MnO_4^-—the major spin–orbit coupling should occur on the oxygen ligands. Two quantitative problems are considered: the radiative lifetime of the $^3T_1$ state, and the zero-field splitting of this multiplet if spin–orbit coupling is the dominant interaction determining the splitting. The results of the theoretical analysis are compared with recent information on the luminescent triplet states of $K_2Cr_2O_7$, YVO_4 and $CaMoO_4$ obtained by E.P.R. The radiative lifetime of 4 ms calculated for VO_4^{3-} is in excellent agreement with the scarce experimental information. The spin–orbit coupling, however, does not appear to be the dominant interaction determining the multiplet splitting of the 3d and 4d compounds. The tetrahedral ions, in accordance with the Jahn–Teller effect, suffer a distortion on excitation and a single orbital state lies lowest with a fine structure characteristic for a situation of low symmetry.

1. Introduction

The present discussion is concerned with the spin triplet states of tetrahedral tetroxo anions MeO^{n-} of the following kind:

VO_4^{3-}	CrO_4^{2-}	MnO_4^-
NbO_4^{3-}	MoO_4^{2-}	
TaO_4^{3-}	WO_4^{2-}	ReO_4^-

These ions all have singlet ground states and the transition metal at the centre, formally, is in the valence state $Me^{(8-n)+}$ with a d^0 electron configuration. Starting from MnO_4^-, which absorbs in the red, the first absorption band of the ions shifts to higher energy when moving down or to the left in the array. Apparently associated with this shift, one has as a general rule that, whereas the ions CrO_4^{2-}, MnO_4^- and ReO_4^- are non-luminescent, the others show an often intense emission on U.V. excitation in crystals at low temperature.

Naturally, the coloured chromates and permanganates have long attracted the attention of spectroscopists. One of the pioneers in the field, Teltow (1938, 1939), examined the polarized absorption spectra of these two 3d anions in a great variety of crystals and grouped their rich vibronic features into a number of band systems. The first attempt at an interpretation of these spectra in terms of quantum mechanics was made by Wolfsberg and Helmholz (1952). They described the complex ion in an LCAO-MO scheme for tetrahedral symmetry (point group T_d), substituting estimates for the various integrals. In spite of its elegance, their treatment led to an incorrect assignment for the first electronic excitation because of quantitative inadequacies. Subsequently, Ballhausen and Liehr (1958) published a more extensive semi-empirical analysis and gave an assignment that has withstood the test of time. In their terminology the lower excited states arise from the excitation $t_1 \rightarrow 2e$ (the letters label the molecular orbitals according to the irreducible representations of the group T_d to which they belong). Here the set t_1 represents three non-bonding orbitals (further to be written as t_x, t_y, t_z), made up exclusively of $2p_\pi$ AOs on the oxygen ligands, and the set 2e a pair of antibonding orbitals (e_θ, e_ε) in which the d_{z^2} and $d_{x^2-y^2}$ AOs of the metal participate. Some essential features of these MOs are sketched in figure 1, and one member of each set may be given explicitly,

$$t_z = \frac{1}{2\sqrt{2}}\{(x-y)_1 + (-x+y)_2 - (x+y)_3 + (x+y)_4\} \tag{1}$$

$$e_\theta = (1-\alpha^2)^{-1/2}\{(x+y-2z)_1 - (x+y+2z)_2 + (x-y+2z)_3 + (-x+y+2z)_4\} + \alpha d_{z^2} \tag{2}$$

Here $2^{-1/2}(x-y)_1$ denotes a $2p_\pi$ AO on oxygen atom 1 with its axis parallel to $\mathbf{x}-\mathbf{y}$. In Ballhausen and Liehr's calculation, Slater type AOs were used and the numerical constant α had the value $2^{-1/2}$. The partners of the functions given may be generated via the threefold rotations $C_3^\pm$ along the axis indicated in the figure: $C_3^+ t_z = t_x$, $C_3^- t_z = t_y$; $3^{-1/2}(C_3^+ e_\theta - C_3^- e_\theta) = e_\varepsilon$.

In tetrahedral symmetry the excitation $t_1 \rightarrow 2e$ gives rise to four electronic states, the energies of which have been predicted (Ballhausen 1963) to lie in the order

$$^1T_2 > {}^1T_1 > {}^3T_2 \approx {}^3T_1$$

If we denote the ground state by $^1A_1$ the transition $^1T_2 \leftarrow {}^1A_1$ is electric-dipole allowed,

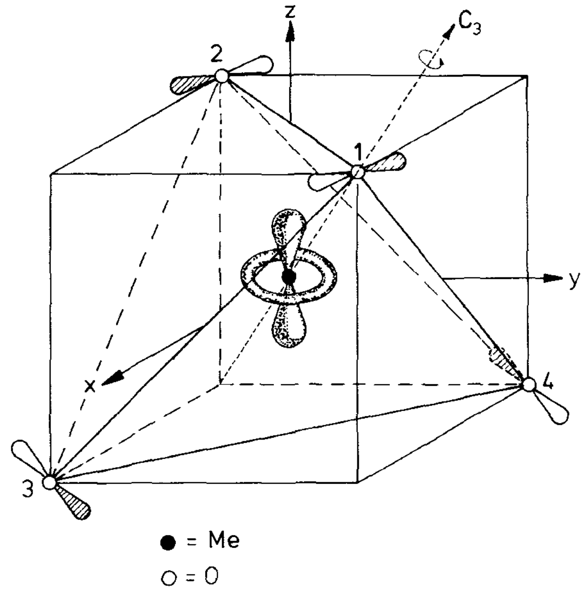

Figure 1. Tetrahedral d^0 transition metal anion with the numbering of the atoms and axis system used in the text. The contours illustrate the $t_1 \rightarrow 2e$ excitation that gives rise to the lower excited states (the contour on the central metal represents the d_{z^2} AO participating in e_θ and those on the oxygens the ligand MO t_z).

while $^1T_1 \leftarrow {}^1A_1$ is forbidden in tetrahedral symmetry. In a crystal, however, the site symmetry of the ion is lower and the $^1T_1 \leftarrow {}^1A_1$ transition then may be identified as a weak band to the red of the $^1T_2 \leftarrow {}^1A_1$ system. But even though the $^1T_1 \leftarrow {}^1A_1$ transition acquires intensity from the $^1T_2 \leftarrow {}^1A_1$ transition, the actual crystal-field splitting of the $^1T_1$ multiplet is alleged to be small (e.g. 10 cm^{-1} for MnO_4^- in $LiClO_4$ with C_{3v} site symmetry (Ballhausen and Trabjerg 1972) and 6 cm^{-1} for CrO_4^{2-} in K_2CrO_4 with C_s site symmetry (Butowiez 1968). These values were derived from the behaviour of the 0–0 line in uniaxial pressure experiments, but an assignment of the complex structure of the entire band system to support it would be most welcome).

In recent years further, more sophisticated theoretical work has appeared on the electronic structure of the $(3d)^0$ and $(4d)^0$ tetroxo complexes, notably the Hartree–Fock–Slater type calculations of Ziegler *et al.* (1976). While the results confirm Ballhausen and Liehr's assignment for the first excitation, this excitation may not be viewed as a ligand-to-metal charge transfer. Although the t_1 orbital, by virtue of its symmetry, is restricted to the oxygens, there is on excitation an extensive redistribution of the electrons in the other orbitals such that the gross electron population on the metal stays practically constant.

As regards the spin triplets the available information is meagre. Ballhausen and Liehr's work triggered an extensive search by absorption spectroscopy of crystals at low temperature for the $^3T_1$ and $^3T_2$ triplet states of the CrO_4^{2-} and MnO_4^- ions, but so far with negative results. In contrast to, the behaviour of the chromate and permanganate salts, which do not luminesce, crystals containing the other 3d and 4d tetroxo anions in general exhibit a strong luminescence at low temperature. Several aspects of this luminescense have been studied extensively by Blasse (see his review, 1980) and others. Most noteworthy are three points: (1) the very large Stokes shift between the emission and first absorption bands; (2) the lack of any structure in these bands which have very little intensity in the 0–0 regions; (3) the remarkable variation in temperature dependence of the luminescence decay rates for different systems at low temperature (2–100 K). Blasse further adduced convincing arguments that under suitable conditions the emission originates from the tetroxo ion in a metastable triplet state. Since the luminescence from a pure crystal, say YVO_4, is quite similar in its spectral properties to that from a YPO_4 crystal doped with YVO_4 (Blasse 1968), it appears that at low temperature self-trapping of the excitation occurs and thus one is not dealing with mobile excitons. This tallies with the large Stokes shift and weak 0–0 intensities, which point to strong electron–phonon coupling. (From a study of the intensity distribution over the vibronic bands of Teltow's absorption spectrum of $KMnO_4$ in a $KClO_4$ host crystal Ballhausen (1963) inferred that the metal–oxygen bond length is increased by some 6 per cent on excitation, or in the over-simplified MO picture the 'charge transfer' excitation weakens the Me–O bonds.)

We have started a programme to prove that the luminescence of the d^0 tetroxo anions originates from their metastable triplet states, and to provide structural information on these states. The technique chosen is electron paramagnetic resonance with optical detection in combination with laser spectroscopy. This approach has proved of great use in the study of the metastable triplet states of organic molecules. It ought to be realized, however, that the present type of system is considerably more complex and thus the quantitative interpretation of the experimental results may well present problems. The following point in particular ought to be borne in mind. Theory leads one to believe that the $^3T_1$ and $^3T_2$ multiplets are close together and therefore a total of 18 spin–orbital components may lie in a range of less than 1000 cm^{-1}. The nature and ordering of these 18 states will be determined by four types of interaction in addition to the interelectronic repulsion: the crystal field, the spin–orbit (SOC) and spin–spin couplings, and the Jahn–Teller effect. The first two interactions, probably, are of comparable magnitude (presumably the crystal field is the stronger of the two for the 3d compounds and SOC for the 5d compounds), the third certainly is smaller, and about the fourth nothing seems to be known. Most of these interactions do not commute, and in particular if the site symmetry is low, it should be hard to unscramble their combined effect.

The main topic of this paper, presented in the next section, concerns the analysis of the principal spin–orbit coupling route in the $(3d)^0$ tetroxo complexes. Two specific questions are considered in some detail: can theory account for the observed radiative lifetime of the emitting state(s)? and, what is the multiplet splitting to be expected if SOC would be appreciably stronger than the crystal field anisotropy?

2. Spin–orbit coupling within the ($t_1 \rightarrow 2e$) manifold

As we have seen, four electronic states, $^1T_1$, $^1T_2$ and $^3T_1$, $^3T_2$, arise from the first excitation ($t_1 \rightarrow 2e$) in the tetroxo complexes. Here we shall examine how the SOC within this manifold of states causes the spin triplets to acquire some radiative character and what the multiplet splitting of the $^3T_1$ state would look like if SOC were the dominant interaction.

For our description we use orbital and spin functions adapted to tetragonal or orthorhombic symmetry. A general basis function is written as $|T_{i,u}; \chi\rangle$ where the symbols before the semicolon refer to the orbital part and those following the semicolon to the spin part. We have

orbital part $T_{i,u}(i=1, 2; u=x, y, z)$

spin part $\chi=\sigma$ for singlets; $\chi=\tau_v$ for triplets $(v=x, y, z)$.

The orbital parts for $i=1$ transform like the cartesian components of an axial vector, and for $i=2$ like the components of a polar vector. The triplet spin functions, which span the irreducible representation T_1, are eigenfunctions of the components of the spin angular momentum operator S with eigenvalue zero, $S_v\tau_v=0$.

In a formalism such as that used by Ballhausen and Liehr, the basis functions are expressed in terms of molecular orbitals, for instance

$$|T_{1,z}; \chi\rangle = A t_x(1)t_x(2)t_y(3)t_y(4)t_z(5)e_\theta(6)\sigma(1, 2)\sigma(3, 4)\chi(5, 6),$$

where A is the antisymmetrizing operator and all electrons in closed shells are omitted. We may abbreviate this expression to $|T_{1,z}; \chi\rangle = |\hat{t}_z e_\theta; \chi\rangle$, and similarly, $|T_{2,z}; \chi\rangle = |\hat{t}_z e_\varepsilon; \chi\rangle$. The notation introduced in the kets on the right expresses that the electron configuration is obtained from the closed shell t_1^6 by the promotion $t_z \rightarrow e_\theta$ or $t_z \rightarrow e_\varepsilon$, with the two unpaired electrons in a spin function χ. In generating the partners of these two functions with the aid of the operations $C_3^\pm$ we have the two sets of basis functions

$$\begin{aligned} |T_{1,x}; \chi\rangle &= -\tfrac{1}{2}|\hat{t}_x e_\theta; \chi\rangle + \tfrac{1}{2}\sqrt{3}|\hat{t}_x e_\varepsilon; \chi\rangle \\ |T_{1,y}; \chi\rangle &= -\tfrac{1}{2}|\hat{t}_y e_\theta; \chi\rangle - \tfrac{1}{2}\sqrt{3}|\hat{t}_y e_\varepsilon; \chi\rangle \\ |T_{1,z}; \chi\rangle &= |\hat{t}_z e_\theta; \chi\rangle \end{aligned} \tag{3}$$

$$\begin{aligned} |T_{2,x}; \chi\rangle &= -\tfrac{1}{2}\sqrt{3}|\hat{t}_x e_\theta; \chi\rangle - \tfrac{1}{2}|\hat{t}_x e_\varepsilon; \chi\rangle \\ |T_{2,y}; \chi\rangle &= \tfrac{1}{2}\sqrt{3}|\hat{t}_y e_\theta; \chi\rangle - \tfrac{1}{2}|\hat{t}_y e_\varepsilon; \chi\rangle \\ |T_{2,z}; \chi\rangle &= |\hat{t}_z e_\varepsilon; \chi\rangle \end{aligned} \tag{4}$$

Our aim is to evaluate the matrix elements of the hamiltonian for spin–orbit coupling H_{so} in the basis (3, 4). For this we take the 'atoms in molecules' approach originally due to McClure (1952), which has proved so successful for polyatomic organic molecules (see e.g. Goodman and Krishna 1963, or Veeman and Van der Waals 1970, whose procedure we follow). We assume that the SOC in our ion can be approximated satisfactorily by summing the effects occurring in the vicinity of the individual nuclei; we write

$$H_{so} = \sum_K \zeta_K \sum_j \mathbf{l}_{jk} \cdot \mathbf{s}_j \tag{5}$$

and will neglect all overlap. In (5) $\mathbf{l}_{jK}$ is the operator for the orbital angular momentum of electron j relative to nucleus K and $\mathbf{s}_j$ that for its spin angular momentum; ζ_K is the appropriate atomic spin–orbit coupling constant expressed in cm^{-1}. A matrix element $\langle \mathrm{T}_{i,u}; \chi' | H_{so} | \mathrm{T}_{j,v}; \chi'' \rangle$ vanishes unless the direct product of the representations in bra and ket contains the totally symmetric irreducible representation.

We first consider the mechanism responsible for the luminescence, the coupling of the $^3\mathrm{T}_1$ and $^3\mathrm{T}_2$ states to the $^1\mathrm{T}_2$ state which is connected to the ground state via an electric-dipole-allowed transition. If, by way of example, we take the matrix element $\langle \mathrm{T}_{2,x}; \sigma | \mathrm{H}_{so} | \mathrm{T}_{1,z}; \tau_y \rangle$ and expand this in integrals over MOs, we obtain after a simple integration over the spin coordinates (cf. the derivation of equation (6) of Veeman and Van der Waals (1970))

$$\langle \mathrm{T}_{2,x}; \sigma | \mathrm{H}_{so} | \mathrm{T}_{1,z}; \tau_y \rangle = \tfrac{1}{4}\sqrt{3} \langle \mathrm{t}_z(j) | \sum_K \zeta_K \mathrm{l}_{jK}^{(y)} | \mathrm{t}_x(j) \rangle \tag{6}$$

As we have seen, the Mos t_x and t_z, because of symmetry, are restricted to the ligands. Therefore, if we substitute (1) and its analogue for t_x into the integral in (6) and neglect overlap, we obtain

$$\langle \mathrm{t}_z(j) | \sum_K \zeta_K \mathrm{l}_{jK}^{(y)} | \mathrm{t}_x(j) \rangle = -\tfrac{1}{2} i \zeta_{\mathrm{O}} \tag{7}$$

where ζ_{O} is the SOC constant for the oxygen ligands. On substituting (7) into (6) and into an analogous matrix element for the coupling of $|\mathrm{T}_{2,z}; \tau_y\rangle$ to $\langle \mathrm{T}_{2,x}; \sigma|$, we get as final result

$$\langle \mathrm{T}_{2,x}; \sigma | H_{so} | \mathrm{T}_{1,z}; \tau_y \rangle = \sqrt{3} \langle \mathrm{T}_{2,x}; \sigma | H_{so} | \mathrm{T}_{2,z}; \tau_y \rangle = -i\sqrt{3} Z \tag{8}$$

where $Z = \frac{1}{8}\zeta_{\mathrm{O}}$. For the $^3\mathrm{P}(2\mathrm{s}^2 2\mathrm{p}^4)$ ground state of a neutral oxygen atom $\zeta = 148$ cm^{-1} (Moore 1949); for the ligands—which carry a negative charge of about 0·5 electron according to the calculations by Ziegler *et al.* (1976)—a slightly lower value should be applicable and we thus take $Z = 16$ cm^{-1}.

Our result leads to two, perhaps unexpected, conclusions:

(i) As long as we stay within the ($\mathrm{t}_1 \rightarrow 2\mathrm{e}$) set of multiplets the SOC occurs on the oxygen ligands and *not* on the central metal, even if we consider second-order coupling schemes because the operator for orbital angular momentum has no off-diagonal matrix elements between the e_θ and e_ε orbitals involved in this excitation. If we include the SOC of our $^3\mathrm{T}_1$, $^3\mathrm{T}_2$ multiplets with the singlets arising from higher excitations, this conclusion remains valid for the second excitation ($4\mathrm{t}_2 \rightarrow 2\mathrm{e}$), but not for the third ($\mathrm{t}_1 \rightarrow 5\mathrm{t}_2$) in which the unpaired electrons have a density in the d_{xy}, d_{yz}, d_{xz} AOs on the metal (see tables in Ziegler *et al.* 1976). Hence, on going from the ions with a 3d metal to those with a 4d metal the SOC, which gives radiative character to their lower triplet states, is expected to increase far less than might have been expected. For the 3d ions the SOC mechanism is thought to be closely similar to that in the strongly phosphorescent aromatic ketones, with radiative lifetimes of the order of 1 ms in both instances.

(ii) It has often been said that the $^3T_2$ multiplet would be more strongly luminescent than the $^3T_1$ multiplet, 'because a $T_2 \rightarrow A_1$ transition is orbitally allowed, and a $T_1 \rightarrow A_1$ transition orbitally forbidden'. As the result (8) proves, this is a misconception. In a system with tetrahedral symmetry—in which orbital angular momentum is not conserved—there is no spin-independent orbital selection rule. For an intercombination transition to the $^1A_1$ ground state to be electric-dipole allowed the spin $\otimes$ orbital symmetry of the initial state must be of species T_2.

Sufficient data seem to be available to make a quantitative prediction about the radiative lifetimes of the emitting triplet states of the $3d^0$ tetroxo anions on the basis of our estimate $Z = 16\,\mathrm{cm}^{-1}$. Let us choose VO_4^{3-} as an example. On the basis of our experimental information (see below) we assume that the orbital degeneracy is lifted through the action of the Jahn–Teller effect and (or) crystal field, and that a single orbital state, say $T_{1,x}$ lies lowest. The spin components $|T_{1,x}; \tau_y\rangle$ and $|T_{1,x}; \tau_z\rangle$ of this state will then acquire radiative character by SOC to $|T_{2,z}; \sigma\rangle$ and $|T_{2,y}; \sigma\rangle$, respectively. Using the experimental oscillator strength $f(^1T_2 \leftarrow {}^1A_1) = 0{\cdot}15$ (Müller *et al.* 1969) and the energy separations $\Delta E(^3T_1 - {}^1A_1) = 24000\,\mathrm{cm}^{-1}$ and $\Delta E(^1T_2 - {}^1A_1) = 35000\,\mathrm{cm}^{-1}$ quoted by Blasse (1980), we obtain with the aid of equations (34) and (36) of Hameka and Oosterhoff (1958) an oscillator strength of the spin-forbidden transition $f(^3T_1 \rightarrow {}^1A_1) = 0{\cdot}65 \times 10^{-6}$ and a radiative lifetime $\tau = 4$ ms. (Clearly this result must be independent of the choice of axes, and thus the directions of the orbital and spin axes in an experimental situation need not coincide with the x, y, z system of figure 1 for the calculation to be valid.)

Ronde and Blasse (1978) report luminescence decay times for VO_4^{3-} in different hosts varying from 0·5 to 1·5 ms at low temperature; from the E.P.R. experiments by Barenswaard *et al.* (1985) on the luminescent triplet state of YVO_4 crystals at 1·2 K now in progress it follows that most of the radiation originates from two of the three spin components, which have a mean lifetime of about 0·4 ms. When it is remembered that the observed lifetimes should be shortened relative to the radiative lifetime by the existence of other deactivation processes, for instance intra-ionic radiationless decay of the type that causes CrO_4^{2-} and MnO_4^- to be non-luminescent, the agreement between the theoretical estimate and experiment is deemed quite satisfactory.

As a second exercise we have considered the splitting of the $^3T_1$ state which would result from SOC alone. From the direct product $T_1 \otimes T_1$ it follows that the $^3T_1$ state yields A_1, T_1 and $E + T_2$ multiplets, which are the analogues of states with $J = 0$, 1 and 2, respectively, in an atom. One of the eigenfunctions for each of the irreducible representations is given in equation (9); their partners follow from considerations of symmetry.

$$\left.\begin{aligned}
\Phi_{A_1} &= 3^{-1/2}(|T_{1,x}; \tau_x\rangle + |T_{1,y}; \tau_y\rangle + |T_{1,z}; \tau_z\rangle)\\
\Phi_{T_{1,x}} &= 2^{-1/2}(|T_{1,y}; \tau_z\rangle - |T_{1,z}; \tau_y\rangle)\\
\Phi_{E\theta} &= 6^{-1/2}(2|T_{1,z}; \tau_z\rangle - |T_{1,x}; \tau_x\rangle - |T_{1,y}; \tau_y\rangle)\\
\Phi_{T_{2,x}} &= 2^{-1/2}(|T_{1,y}; \tau_z\rangle + |T_{1,z}; \tau_y\rangle)
\end{aligned}\right\} \qquad (9)$$

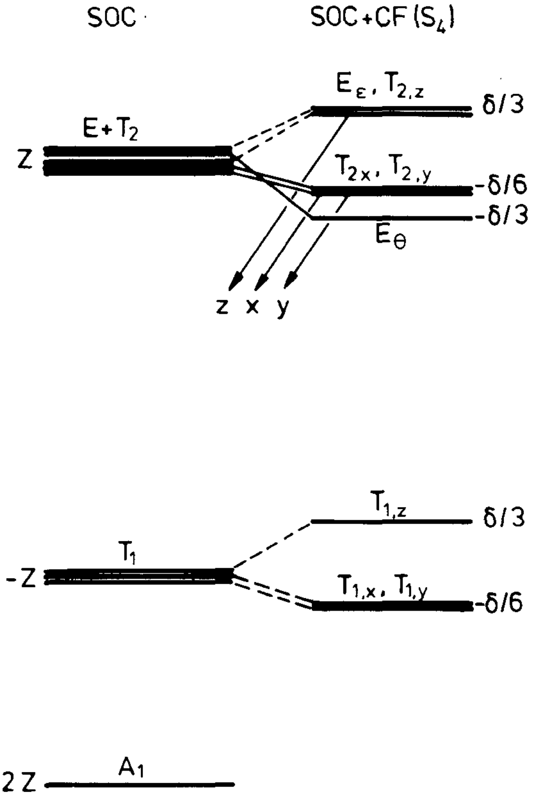

Figure 2. Multiplet splitting of the $^3T_1$ state. *Left column*: splitting of the $^3T_1$ state through SOC alone; Z is the SOC coupling parameter estimated to amount to $16\,cm^{-1}$. *Right column*: additional splitting of the three multiplets through a weak crystal field with the site symmetry S_4. The situation is for a positive value of the crystal field parameter δ; for $\delta < 0$ the splitting of the five levels would be inverted. Radiative decay occurs from the three components spanning the irreducible representation T_2, see arrows. The energies to second order in δ are $U(E_\varepsilon, T_{2,z}) = \delta/3$, $U(T_{2,x}, T_{2,y}) = -\delta/6 - \delta^2/8Z$, $U(E_\theta) = -\delta/3 - \delta^2/243Z$; $U(T_{1,x}) = \delta/3$, $U(T_{1,x}, T_{1,y}) = -\delta/6 - \delta^2/8Z$.

The spin-orbit coupling energies of these states are as sketched on the left in figure 2, with a single nonradiative state lowest. If we next allow for the influence of a crystal field in which the S_4 axis along z is preserved (as, for instance, in scheelites such as $CaMoO_4$), the three multiplets are split as indicated at the right. The crystal-field splitting parameter δ corresponds to the difference in orbital energy

$$\delta = \langle T_{1,u} | H_{CF} | T_{1,u} \rangle - \langle T_{1,z} | H_{CF} | T_{1,z} \rangle, \quad u = x, y$$

The figure, in which we have arbitrarily assumed $\delta > 0$, is valid only in situations where $|\delta|$ is small compared with Z. As we shall see in the next section, the metastable emitting states in YVO_4 and $CaMoO_4$ crystals have a structure quite different from that on the right in figure 2; they appear as conventional spin triplets with a large zero-field splitting. We are convinced, therefore, that in these instances the assumptions on which the construction of figure 2 is based and in particular the neglect of the Jahn–Teller effect, are unrealistic.

3. Summary of recent experimental results

We began our search for the lower triplet states of the tetroxo-anions with a study of the related $K_2Cr_2O_7$ crystal. This crystal, in which the anions consist of two tetrahedra sharing an oxygen atom, has recently been shown to become luminescent at low temperature with richly structured absorption and emission spectra (Freiberg and Rebane 1979). By a combination of optical spectroscopy and electron paramagnetic resonance (E.P.R.) Van der Poel *et al.* (1984 a, b) succeeded in giving an assignment of these spectra in terms of singlet and triplet excited states of the $Cr_2O_7^{2-}$ ion. For details of the experiments we refer to their papers and here merely reproduce the energy level diagram (figure 3). In the triclinic crystal the anions occupy two inequivalent sites, A and B, which prove to have surprisingly different spectra. We think this sensitivity to the crystal field is related to a high polarizability which results from the presence of a number of electronic states (stemming from the $^1T_1$, $^1T_2$ and $^3T_1$, $^3T_2$ multiplets of the CrO_4^{2-} ion) within a narrow range of energies.

From X-ray structure data it is known that the anions in the crystal posess approximate C_{2v} symmetry, but the luminescent triplet state does not bear this out. The E.P.R. experiments have revealed that for each site the z principal axis of the fine-structure tensor runs closely parallel to the bond from the bridge oxygen to one of the metal atoms in the complex. Apparently the excitation becomes localized on a tetrahedral subunit of the composite ion; a similar conclusion has been drawn previously for its first excited singlet state (Ballhausen *et al.* 1970, Miskowski *et al.* 1974).

On excitation at a wavelength longer than 547·5 nm only the A site becomes excited, and the properties of its triplet state could be studied in detail (see data on the right in figure 3). The zero-field splitting with the τ_z component lowest and a relatively small

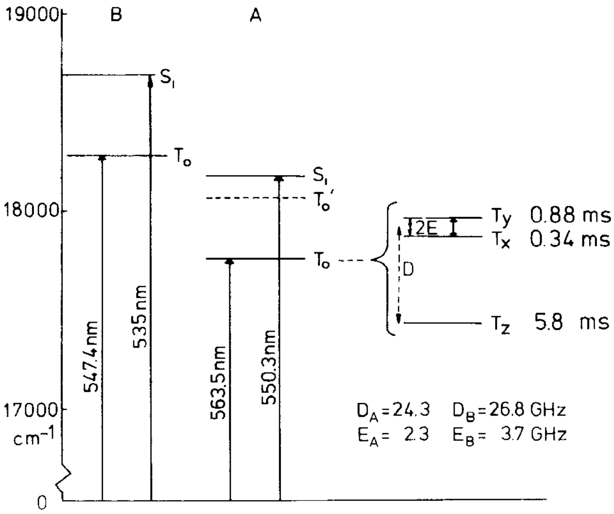

Figure 3. Energies of the lower excited states of the $Cr_2O_7^{2-}$ ion in the two sites A and B of the triclinic $K_2Cr_2O_7$ crystal according to the assignments established by Van der Poel *et al.* (1984). At the right the zero-field splitting pattern of the metastable triplet state (T_0) of the A site has been sketched, with the lifetimes of the individual spin components determined by Barendswaard *et al.* (1985). Note: x, y, z here label the principal axes of the fine structure and are not to be confused with the axes of the tetrahedral ion of figure 1.

splitting between τ_x and τ_y is what one expects for a CrO_4^{2-} tetrahedron perturbed to a trigonal pyramid. In the MO model the excitation now should occur from an orbital in which the hole avoids the bridge oxygen (i.e. from $t'_1 = 3^{-1/2}(t_x + t_y + t_z)$ in the notation of (1)). In this situation one expects the τ_z component to be distinctly less radiative than the other two, precisely as observed (Van der Poel *et al.* (1984 a, b). When considering that a luminescence yield of 10 per cent has been reported for $Cr_2O_7^{2-}$ (Dalhoeven and Blasse 1980), it is most gratifying that the lifetimes of the two radiative levels (0·88 and 0·34 ms) are close to one-tenth of the radiative lifetime of 4 ms calculated for the VO_4^{3-} ion in the preceding section.

Finally, a few words may be said about the E.P.R. experiments on the luminescent crystals YVO_4 and $CaMoO_4$ now in progress (Barendswaard *et al.* 1985). In both instances the luminescence originates from a spin triplet with a substantial zero-field splitting and almost equidistant components. For YVO_4 the splitting parameters are $D = 20{\cdot}3$, $E = 7{\cdot}2$ GHz, and for $CaMoO_4$, $D = 96{\cdot}2$, $E = 30{\cdot}8$ GHz. In the case of $CaMoO_4$ an extensive study has been made of the E.P.R. signals as a function of the orientation of the tetragonal crystal in the magnetic field **B**. For a general orientation four signals appear, which coalesce when **B** is brought along the crystal **c** axis. The MoO_4^{2-} units, which possess D_{2d} symmetry in the ground state and occupy sites with symmetry S_4, apparently become distorted on excitation with the loss of the equivalence of the four oxygen ligands that exists in S_4. If SOC and (or) the crystal field were dominant one would expect one of the fine structure axes, say **z**, to lie along **c**. In actual fact the **z** axes of the four units make angles of 33° with the tetragonal axis **c**. What one observes must be the manifestation of a static Jahn–Teller effect. On excitation the MoO_4^{2-} ion lowers its energy through distortion, and at the temperature of the E.P.R. experiments (1·2 K) each of the ions stays locked in that distorted form, amongst four equivalent ones, which is favoured by random strain in the crystal (Ham 1972).

Acknowledgments

The author participated with great pleasure in the symposium held in honour of D. P. Craig, 'The Interface between Theory and Experiment', which provided the stimulus for the present review. He further enjoys the cooperation with W. Barendswaard, I. Coremans and H. van Tol in the investigation of the triplet states of the tetroxo-anions and gratefully acknowledges the readiness with which G. Blasse from the University of Utrecht has helped with advice on many occasions. This work was supported by The Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Organization for the Advancement of Pure Research (ZWO).

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