

Spin transfer versus charge transfer in the excited states of $3d^0$ tetroxo ions

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Abstract - The first absorption bands in the optical spectra of the $3d^0$ tetroxo-ions, VO_4^{3-} , CrO_4^{2-} , MnO_4^{2-} , are commonly assumed to arise from electron transfer from a t_1 ligand MO to an MO centered on the metal. First electron-spin-resonance experiments on the luminescent triplet state of VO_4^{3-} in an YPO_4 host are reviewed. These show that one unpaired electron indeed resides on the metal; the other is not in a t_1 -type MO but localized on a *single* ligand. This unevenness of the spin distribution is attributed to a Jahn-Teller instability that deforms the isolated ion from T_d to C_{3v} symmetry. Then *ab-initio* calculations on CrO_4^{2-} and CrO_4^- are considered. The results for the ${}^2E(t_1^2)$ ground state of CrO_4^- confirm such a Jahn-Teller effect with the *spin* localized on a single oxygen (the apex of the C_{3v} pyramid), yet the *charge* is almost evenly distributed over the four ligands. For the lowest triplet state of CrO_4^- , with a $(t_1^5 e^*)$ electron configuration, an analogous instability is predicted. Although, again, an uneven spin distribution over the ligands results, owing to relaxation of electron pairs in closed shells the charge distribution is practically not changed by the excitation. Thus, what is commonly labelled a 'charge transfer' transition may well correspond to spin transfer without an attendant charge transfer.

INTRODUCTION

In the discussion of spectroscopic properties of complex organic molecules and ions by Grabowski and others [1,2], the idea of intramolecular charge transfer [3] has proved a very fruitful concept. In a molecular orbital (MO) description the transfer can simply be visualized as arising from the difference in spatial distribution of the two MO's between which the excitation occurs. But, though the idea has the virtue of intuitive clarity, how realistic is it?

In the domain of inorganic chemistry a classic example of transitions that are commonly classified as arising from charge transfer is provided by the first absorption bands of the $3d^0$ transition metal oxo-ions, VO_4^{3-} , CrO_4^{2-} , MnO_4^{2-} . According to MO theory [4] these bands originate from a transition in which an electron is excited from a pure ligand orbital to an orbital that is mainly centered on the metal. *Ab-initio* calculations [5,6], however, have revealed that the real situation is far more complex because the charge transfer of the simple picture is opposed by relaxation of electrons in closed-shell orbitals. In Leiden we are involved in the investigation of the lower excited singlet and triplet states of VO_4^{3-} and CrO_4^{2-} , experimentally by electron paramagnetic resonance (EPR) and optical methods, and theoretically by *ab-initio* quantum-chemical calculations. The results make it clear that the intuitive notion of charge transfer related to the promotion of an electron from one MO to another should be regarded with caution.

Let us first look at the conventional description. In their pioneering papers [4] Ballhausen and Liehr (B&L) presented convincing arguments that in a ligand-field model of the tetrahedral ion (point group T_d) the first excitation is from a set of highest occupied MO's t_1 to a pair of lowest unoccupied MO's e^* . The set t_1 represents three nonbonding π orbitals which, by symmetry, are confined to the ligands and consist of linear combinations of $2p_x$ oxygen atomic orbitals (AO's). The members e_g and e_c of the pair e^* predominantly consist of the $3d$ metal AO's $d_{z^2-3z^2}$ and d_{xy} , respectively, in the

axis system of Fig. 1. The first excitation thus is sixfold degenerate and spanned by the following basis of electron configurations

$$\begin{aligned} &|t_{1,\tilde{y}}, e_{\theta}\rangle, |t_{1,\tilde{x}}, e_c\rangle, |t_{1,\tilde{x}}, e_c\rangle A'; \\ &|t_{1,\tilde{y}}, e_c\rangle, |t_{1,\tilde{x}}, e_{\theta}\rangle, |t_{1,\tilde{x}}, e_{\theta}\rangle A''. \end{aligned} \quad (1)$$

(The labels A' and A'' refer to the irreducible representations of the point group C_s with $\tilde{y} = 0$ in Fig. 1 as the symmetry plane). In the tetrahedral ion these one-electron configurations give rise to four excited states

$${}^1T_2 \gg {}^1T_1 > {}^3T_1 \approx {}^3T_2, \quad (2)$$

where the (in)equality signs indicate the expected order in energy. Whereas inter-electronic repulsion causes a splitting of the order of 5000 cm^{-1} between the two spin singlets, that between the two spin triplets is expected to be so small that one cannot say a priori which of the two states is the lower in energy [4,6].

In tetrahedral symmetry the ${}^1T_1 \leftarrow {}^1A_1$ transition is electric-dipole forbidden, while ${}^1T_2 \leftarrow {}^1A_1$ is allowed. In agreement with this and the relative energies sketched in (2), the absorption spectra of tetroxo ions perturbed by the solvent in liquid solution, or by interaction with a less symmetric host crystal, invariably show a relatively weak first absorption band followed by a stronger second band at higher frequency. Although these general characteristics appear to be understood, the detailed assignment of spectra has run into serious problems (see, for instance, [7] for a number of these problems). The vibronic structure at the red end of the spectra was not understood and no evidence of any spin triplet could be obtained by absorption spectroscopy.

The (absorption) spectroscopic research referred to was concentrated on the study of permanganates and chromates, which under favourable conditions show highly structured absorption spectra but no (or very little) emission. Vanadates, by contrast, behave differently: they invariably have structureless optical spectra, but many of them (e.g. YVO_4) emit an intense luminescence which - as first suggested by Ronde and Blasse [8] - should originate from the missing spin triplet(s). Following this suggestion we have taken up a search for the lower excited states of a number of tetroxo ions by EPR.

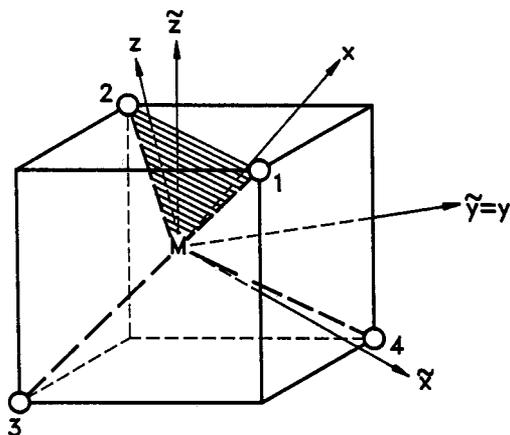


Fig.1. Axis system $\{\tilde{x}, \tilde{y}, \tilde{z}\}$ adapted to D_{2d} site symmetry of VO_4^{3-} in a YPO_4 host. On excitation to the triplet state the ion is distorted, but $\tilde{y} = 0$ remains a plane of symmetry. The principal axes of the tensor D are denoted by $\{x, y, z\}$.

ELECTRON PARAMAGNETIC RESONANCE EXPERIMENTS

On uv excitation of VO_4^{3-} and CrO_4^{2-} in a number of crystalline hosts, metastable triplet states were identified by EPR at low temperature [9-12]. In the virtually nonluminescent $\text{CaSO}_4:\text{CrO}_4^{2-}$ system the resonances were detected by electron-spin-echo spectroscopy on a microsecond timescale [10]; in all other systems they were detected optically in the emission [9,11,12]. In every instance nothing resembling a 3T_1 or 3T_2 multiplet was observed, and the metastable triplet state proved to be of a symmetry lower than that expected for a tetrahedral ion in the given crystal field. Apparently, the situation is dominated by an intrinsic Jahn-Teller (JT) effect through which the excitation leads to a static distortion at the temperature of our experiments.

From a comparison of the EPR results on a number of systems, the conviction has grown that, in the first instance, the JT effect causes the tetrahedron to be distorted to a trigonal pyramid. If such a pyramid of C_{3v} symmetry is then thought inserted in a tetragonal crystal with D_{2d} site symmetry, as for VO₄[≡] in YVO₄ or YPO₄, all that remains is C_s symmetry [9,12].

Two types of EPR experiment have been carried out on single crystals of YPO₄:VO₄[≡] - the most thoroughly studied system (for details see [11,12]).

(1) EPR and electron-nuclear double resonance (ENDOR) experiments with optical detection [12]

By fitting the resonances observed as a function of the orientation of the external field to the conventional spin Hamiltonian, in which \tilde{S} is the effective spin operator,

$$\mathcal{H} = \tilde{S} \cdot \mathbf{D} \cdot \tilde{S} + \gamma \mathbf{B} \cdot \mathbf{g} \cdot \tilde{S} + \tilde{S} \cdot \mathbf{A} \cdot \mathbf{I} \quad (\tilde{S} = 1), \quad (3)$$

a wealth of structural information becomes potentially available. However, unless certain assumptions are made, most of this information remains hidden in the elements of the zero-field-splitting (fine structure) tensor \mathbf{D} , the Zeeman tensor \mathbf{g} , and the hyperfine tensor \mathbf{A} for coupling of the ⁵¹V ($I = \frac{7}{2}$) nucleus to the electron spin. Prior to the detailed analysis of these tensors with the help of second-order perturbation theory [12], two things already stood out: (i) All three tensors have \tilde{y} as a principal axis, and hence the excited species must (at least) have C_s symmetry. (ii) The orientation of the other two principal axes of \mathbf{A} (which lie in the plane $\tilde{y} = 0$ and coincide roughly with those of \mathbf{g} but not with those of \mathbf{D}) bears out that the electron distribution around the vanadium nucleus deviates appreciably from tetragonal symmetry. In this system the excited electron, apparently, resides in a tilted e_c-like MO of the form

$$e_c = c_V \{ \sqrt{1 - \alpha^2} d_{x\tilde{y}} + \alpha d_{y\tilde{z}} \} + \dots, \quad (4)$$

where the dots represent a small but unknown contribution from ligand AO's. By comparing the numerical values of the elements of \mathbf{A} with hyperfine data for vanadium in similar situations, it was further concluded that the coefficient c_V , which determines the unpaired electron density on vanadium, has a value of about 0.9, while the other coefficient $\alpha \approx 0.35$ [12].

(2) Microwave saturation-recovery experiments between the three spin states in zero field [11]

The zero-field splitting of the luminescent triplet state of VO₄[≡] in YPO₄ is sketched in Fig. 2, together with the rates of decay of the levels. Since these rates are appreciably faster than the spin-lattice relaxation at 1.3 K, the three levels are not in thermal equilibrium during the decay of the luminescent state. In the saturation recovery experiment the crystal is continuously excited with uv light and, initially, the $\tau_x - \tau_y$ transition, say, is saturated with resonant microwaves at 25.9 GHz so that the populations of the τ_x and τ_y levels become equal. Then the microwave saturation is suddenly stopped and the populations of the two levels relax to their (unequal) steady-state values in the absence of microwaves. Since different levels have different probabilities for radiative decay, this return to the new steady-state manifests itself in the intensity of the emission. The recovery curve thus assumes a bi-exponential form in which the exponents are the decay rates of the two spin states and the pre-exponential factors contain the probabilities for radiative decay. By doing this type of experiment with the aid of polarizers and suitably chosen directions of the microwave field, a "fingerprint" of the different radiative channels of the triplet state was obtained [11], the qualitative features of which are indicated at the left in Fig. 2.

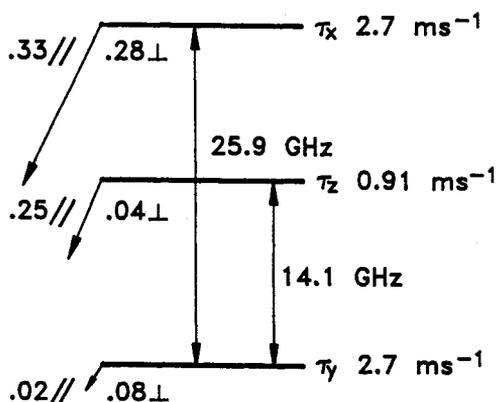


Fig. 2. Zero-field splitting of the luminescent triplet state of VO₄[≡] in an YPO₄ host. The total decay rates of the three spin states are given on the right. The arrows on the left represent the relative radiative decay rates with their polarization, in the plane $\tilde{y} = 0$ (//), or perpendicular to this plane (⊥).

When analyzing the polarization data sketched in Fig. 2 one finds these to be characteristic for A' symmetry of the luminescent state, but incompatible with any of the one-electron excitations (or linear combinations of these) of the B & L model listed in the first row of (1). However, it turns out that they agree surprisingly well with a *localized* excitation from a $2p_j$ atomic orbital on one of the oxygens (e.g. O₁ in Fig. 1) to the ϵ_- orbital as assigned by the ENDOR experiments [11].

Keeping in mind the results of less detailed investigations on several other systems, including a chromate [10], some molybdates [13,14] and another vanadate [9(b)], we arrive at the following conclusions. In every instance there appears to exist a strong, intrinsic JT effect by which the excited ion, if it were isolated, would distort from tetrahedral to trigonal symmetry; the latter symmetry then is further reduced by the crystal field of the host. Although in the case of $\text{YPO}_4:\text{VO}_4^{3-}$ we could prove that in the deformed ion the excitation is from an orbital localized on a single ligand, this may not necessarily be true in general.

AB-INITIO CALCULATIONS ON CONFORMATIONAL INSTABILITY

Although extensive calculations by various methods have been made on the lower electronic states of CrO_4^- , MnO_4^- and related ions, these have all been carried out for tetrahedral symmetry. From a theoretical point of view the Jahn-Teller effect in these ions thus has remained *terra incognita*. Prior to the experimental work described in the previous section, a clue of what might happen was already provided by the theoretical work of Broer and Nieuwpoort [15]. In their *ab-initio* calculations on valence-shell ionization of CrO_4^- in a tetrahedral nuclear conformation they have shown that symmetry breaking with electron hole localization occurs at the SCF-MO level, if the constraint that the MO's obey T_d symmetry is relaxed. The lowering of the total SCF energy of the CrO_4^- ion was found to be greatest $\approx (10^4 \text{ cm}^{-1})$ for a relaxation of the orbital symmetry from T_d to C_{3v} , rather than to C_{2v} . Although the latter result may by no means be taken as proof, it is suggestive for a Jahn-Teller distortion of the ${}^2E(t_1^5)$ ground state of CrO_4^- to a trigonal pyramid. In fact, EPR experiments on WO_4^- (the 5d analogue of CrO_4^-) centers in CaWO_4 have been interpreted on the basis of spin localization on a single ligand indicative of such a distortion [16].

In conjunction with the experimental work described in the previous section, Chaudron and Van Hemert are presently engaged in a theoretical analysis of the JT instability of the ${}^2E(t_1^5)$ ground state of CrO_4^- and the lower singlet and triplet excited states arising from the $(t_1^5 e^*)$ electron configuration of CrO_4^- . Their MRD-CI calculations with open-shell SCF orbitals for the CrO_4^- ion predict a JT stabilization energy of 5000 cm^{-1} when this ion distorts to a trigonal pyramid with hole localization on the apical oxygen [17].

Intuitively one might think that this result for the CrO_4^- ion, which with its (t_1^5) electron configuration represents the lowest ionized state of CrO_4^- , would imply a similar behaviour of the $(t_1^5 e^*)$ excited states of CrO_4^- . However, the calculations, which are still in progress, reveal a complex situation. On excitation to the 3T_2 lowest spin triplet state the chromate ion again exhibits a substantial JT stabilization with a lowering of symmetry from T_d to C_{3v} . But for the ion in the absence of a crystal field this deformation does not appear to be accompanied by hole localization on the apex of the pyramid; instead the hole tends to be distributed over the three base oxygens. Furthermore, the 'simple' JT effect of the 3T_2 state, apparently, is overshadowed by strong pseudo-JT coupling of 3T_2 with its 3T_1 partner and more highly excited states. The resulting electronic structure depends on a delicate balance of many terms, and it seems that reliable predictions for a given system cannot be made unless the crystal field is taken into account [18].

An important aspect, valid for both the CrO_4^- ground state and the CrO_4^- lower excited states, is that the localization of the electron spin is not accompanied by a corresponding localization of the electronic charge. As previously found by Johansen in his calculations on the 3T_2 state of MnO^- in a tetrahedral conformation [19], ionization or excitation of one electron from the t_1^6 shell leads to a relaxation of closed-shell electron pairs. The total charge on the ligands thus is hardly altered by the excitation and remains almost evenly distributed over the four oxygens, irrespective of any spin localization. The lower excited states of the d^0 tetroxo ions, therefore, might more appropriately be called *spin transfer states* than *charge transfer states*.

More generally, the experiments here discussed once again illustrate the virtues of EPR for studying paramagnetic excited states. The electron spin, together with any nuclear spin(s) present, provides a probe for sensing structural details that cannot be uncovered by optical spectroscopy.

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