

## New Theory for the Electron Transfer Spectra of Acetylacetonate Complexes

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The strong dependence of electron transfer wavenumbers in halide complexes on the number  $q$  of electrons in the partly filled shell suggests that recent interpretations of the strong absorption bands of acetylacetonates  $M\text{aca}_3$  may have to be changed. Good agreement with observed band positions is obtained by the same theory as used for other transition group complexes, assuming that all possible transitions between  $\pi$ , the sub-shells  $\gamma_5$  and  $\gamma_3$ , and the empty  $\pi^*$  orbitals occur. The optical electronegativity of the  $\pi$  orbitals of  $\text{aca}^-$  is found to be roughly 2.7. The band at 26 kK of  $\text{Cuaca}_3$  is presumably  $\pi \rightarrow (x^2-y^2)$ . It is suggested to revise several accepted ideas of  $\gamma_5 \rightarrow \gamma_3$  transitions in  $\text{Tiaca}_3$  and  $\text{Mnaca}_3$ .

Recently, Barnum<sup>1</sup> used M. O. Theory for the description of the absorption spectra of neutral tris-acetylacetonates  $M\text{aca}_3$  with the central ion containing  $q$  ( $= 0, 1, 2, 3, 4, 5, 6$ ) electrons in a partly filled d shell. Though Barnum's treatment undoubtedly presents a large part of the truth, it is surprising to see that the M. O. energy differences vary very little with  $q$ . The present writer has introduced the concept of optical electronegativities<sup>2-4</sup> and has recently related the behaviour of 3d complexes<sup>5</sup> with the previously known regularities in the 4d and 5d group. Usually, the partly filled shell becomes more stable, by an amount  $(E-A)$ , for each unit increase of  $q$ . In most cases,  $(E-A)$  is about 6 kK (1 kK = 1000  $\text{cm}^{-1}$ ). In tetrahedral 3d complexes, it seems to be smaller. It is necessary to correct this linear dependence with the spin-pairing energy dependence<sup>3</sup> on the total spin  $S$  of the central ion\*

$$D[\langle S(S+1) \rangle - S(S+1)] \quad (1)$$

where  $D$  is roughly  $7B$  for d-electrons. Furthermore, we may sometimes consider the higher,  $\sigma$ -anti-bonding sub-shell  $\gamma_3$  at an energy  $A$  higher than

\* This concept is used in the description of electron transfer spectra in the same way as Hund used the idea of weakly coupled configurations in atomic spectroscopy. Though in quantum mechanics,  $S$  is only defined for the whole system, the energy levels of a hole in the widely extended, normally filled, M.O. combined with the partly filled shell are distributed to the first approximation as if the partly filled shell had an individual value of  $S$  to be inserted in eqn. (1).

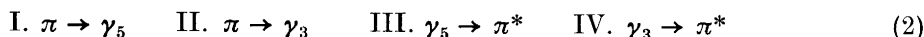
Table 1. Parameters describing the electron transfer wavenumbers as function of the number of electrons  $q$  in the partly filled  $d$  shell. The coefficient to  $D$  is determined from eqn. (1).  $V_1$  and  $V_2$  determine the points of reference for the variation of the wavenumbers (the two partly filled sub-shells being stabilized  $q(E-A)$ ) and are hence, for our purpose, entirely empirical parameters used as starting-point for our comparison.

$q =$	I. $\pi \rightarrow \gamma_5$	II. $\pi \rightarrow \gamma_3$	III. $\gamma_5 \rightarrow \pi^*$	IV. $\gamma_3 \rightarrow \pi^*$
0	$V_1$	$V_1 + A$	—	—
1	$V_1 - (E-A) - 2/3D$	$V_1 + A - (E-A) - 2/3D$	$V_2$	—
2	$V_1 - 2(E-A) - 4/3D$	$V_1 + A - 2(E-A) - 4/3D$	$V_2 + (E-A) + 2/3D$	—
3	$V_1 - 3(E-A) + 2D$	$V_1 + A - 3(E-A) - 2D$	$V_2 + 2(E-A) + 4/3D$	—
4 high-spin	$V_1 - 4(E-A) + 7/3D$	$V_1 + A - (E-A) - 8/3D$	$V_2 + 3(E-A) + 2D$	$V_2 - A + 3(E-A) + 2D$
4 low-spin	$V_1 - 4(E-A) + 4/3D$	$V_1 + A - 4(E-A) - 5/3D$	$V_2 + 3(E-A) - 2D$	—
5 high-spin	$V_1 - 5(E-A) + 8/3D$	$V_1 + A - 5(E-A) + 8/3D$	$V_2 + 4(E-A) + 8/3D$	$V_2 - A + 4(E-A) + 8/3D$
5 low-spin	$V_1 - 5(E-A) + 2/3D$	$V_1 + A - 5(E-A) - 4/3D$	$V_2 + 4(E-A) - 4/3D$	—
6 low-spin	—	$V_1 + A - 6(E-A) - D$	$V_2 + 5(E-A) - 2/3D$	—

the lower, triply degenerate set  $\gamma_5$  of M.O. We are here approximating  $M\text{aca}_3$  by octahedral symmetry which seems to be a very good approximation, the dichroitic effects on wavenumbers being comparatively small<sup>6</sup>.

The difference between the optical electronegativities of the loosest bound orbitals of the ligands and of the appropriate sub-shell of the central atom is defined<sup>2-5</sup> as the wavenumber of the corresponding electron transfer band (corrected by use of eqn. (1)) divided by 30 kK. The halogens have characteristic optical electronegativities which can be fixed at the values F (3.9), Cl (3.0), Br (2.8), and I (2.5).

It is suggested that the complicated aspects of the absorption spectra in the near ultraviolet are caused by the simultaneous presence of four different types of electron transfer spectra, *viz.*



besides the internal transitions in the ligands which may be classified as (V.  $\pi \rightarrow \pi^*$ ) and produce characteristic bands at somewhat higher wavenumbers<sup>7,8</sup>. It is emphasized that this is a rather unusual complication though similar phenomena occur by comparison of Fe(II) and Fe(III) complexes of aromatic diimines<sup>9</sup>.

Table 1 gives the dependence on the parameters  $V_1$ ,  $V_2$ ,  $(E-A)$  and  $D$  of the transitions in eqn. (2) as function of  $q$ . In the case of  $q = 4$  ( $Mn\text{aca}_3$ ) and  $q = 5$  ( $Fe\text{aca}_3$ ), high-spin behaviour is realized, whereas  $q = 6$  ( $Co\text{aca}_3$ ) is low-spin. For comparison, low spin  $q = 4$  and 5 are also considered in Table 1.

We derive the numerical value of  $V_1$  from experiment, noting that the strong band of  $Fe\text{aca}_3$  at 23.2 kK must belong<sup>9</sup> to class I.  $D$  is known from internal transitions in the partly filled d shell of similar complexes to be roughly 4.5 kK. Table 2 gives the result of the final assumption of  $V_1 = 31$  kK and  $(E-A) = 4$  kK (a rather small value, but much larger than suggested by Barnum's choice of parameters).

We will make the rather unorthodox proposal that the broad band with conspicuous vibrational structure of  $Ti\text{aca}_3$  centered around 17 kK is not an internal  $\gamma_5 \rightarrow \gamma_3$  transition intensified by the absence of a centre of inversion, but is an electron transfer band of class III, comparable to the iridium-pyridine bands<sup>10,11</sup>. It is instructive to see in Table 2 that such a band soon will increase

Table 2. Numerical values obtained from Table 1 with the choice of parameters (in kK):  $V_1 = 31$ ,  $V_2 = 17$ ,  $(E-A) = 4$ ,  $D = 4.5$ ,  $A = 18$  (except 20 for  $q = 6$ ). Experimental wavenumbers from Barnum. Tentative assignments in parentheses.

$q =$		I. $\pi - \gamma_5$		II. $\pi - \gamma_3$		III. $\gamma_5 - \pi^*$		IV. $\gamma_3 - \pi^*$	
		calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
0	Sc(III)	31	—	49	—	—	—	—	—
1	Ti(III)	24	25.7	42	—	17	17	—	—
2	V(III)	17	(21.7)	35	29.2	24	25.6	—	—
3	Cr(III)	28	26.0	28	26.0	31	30.2	—	—
4	Mn(III)	25.5	(25.0)	21	(22.5)	38	—	20	(18)
5	Fe(III)	23	23.2	41	—	45	—	27	28.5
6	Co(III)	—	—	22.5	(25)	34	(31)	—	—

to high wavenumbers as function of increasing  $q$ . On the other hand, even in the rather oxidizing Mn(III) and Fe(III) complexes, the presence of  $\gamma_3$  electrons will bring the class IV transition down to rather low wavenumbers.  $\Delta$  is assumed to be 18 kK, except in the case of Co  $aca_3$  where it is fixed to 20 kK. Without the introduction of multiple  $\pi$  or  $\pi^*$  orbitals (which it would be quite legitimate to expect<sup>1</sup>), Table 2 exhausts essentially all the bands observed below the ligand  $\pi \rightarrow \pi^*$  transitions. Table 2 represents several new features. Suspicion is thrown upon the identification of visible bands of V  $aca_3$  and Mn  $aca_3$  as  $\gamma_5 \rightarrow \gamma_3$  transitions in the partly filled shell. The pronounced vibrational structure around 26 kK of Cr  $aca_3$  has always been suspected<sup>12</sup> for not simply being the second spin-allowed, Laporte-forbidden transition to  ${}^4\Gamma_4$  predominantly belonging to the sub-shell configuration  $\gamma_5^2\gamma_3$ . The moderately strong band<sup>1,6</sup> of Mn  $aca_3$  at 8.9 kK, on the other hand, is presumably such an internal, spin-allowed transition. This classification necessitates the hypothesis of relatively strong deviations from octahedral symmetry, perhaps in the form of a dynamic Jahn-Teller effect<sup>13,14</sup>. (Similar conclusions were drawn quite recently by Dingle<sup>24</sup>).

The distortion may either be along a trigonal axis, splitting the excited term  ${}^5\Gamma_5$  into two components, or along a tetragonal axis, removing also the orbital degeneracy of the cubic ground-term  ${}^5\Gamma_3$ . A comparable transition has been observed in manganese(III) tris(diethyldithiocarbamate) extracted into  $CCl_4$  (avoiding infra-red lines due to vibration of hydrogen atoms in the solvent). This compound shows a broad band at 1750  $m\mu$  (5.7 kK) with the half-widths  $\delta(-) = 1.8$  and  $\delta(+)= 2.3$  kK.

It is a quite intricate problem whether acetylacetonates in general always have weak bands in the near ultraviolet close to 26 kK. Piper and Linn Belford<sup>15</sup> presented convincing evidence that such a band of Cu  $aca_2$  in various solvents, which had been ascribed to an internal 3d transition by several authors, does not have this origin, and that presumably all the internal transitions in the partly filled shell occur between 14 and 18 kK. It is not very probable that the 26 kK band should be a spin-forbidden transition in the ligand  $aca^-$  intensified by intermediate coupling effects in the central atom. Actually, In  $aca_3$  does not present such a weak band in the near ultraviolet though the relativistic effects were expected to be much stronger.

It is quite plausible that the band is caused by electron transfer of class II type. This would correspond to a difference between the optical electronegativities  $x_{opt}$  of  $aca^-$  and Cu(II) about 0.4 units, and since the lowest d-like orbitals of Cu(II)<sup>5</sup> have  $x_{opt} = 2.3$ , this would give  $aca^-$  a reducing character somewhere between bromide and iodide. Unfortunately, a clear-cut value of  $x_{opt}$  for Fe(III) cannot easily be given<sup>5</sup>. Considering the octahedral nature of Fe  $aca_3$  we may adopt 2.3. The value of  $V_1 = 31$  kK and  $(E-A) = 4$  kK in Table 2 then corresponds to 2.7 for the highest, filled  $\pi$  orbitals of  $aca^-$ . Due to the charge separation effects, there is no simple relation<sup>16</sup> between the expression  $V_2 + V_1 - (E-A) = 44$  kK and the wavenumbers of the  $\pi \rightarrow \pi^*$  transitions in the ligand.

It has become increasingly clear in the recent years that the absorption spectra of acetylacetonates indicate that the nature of the chemical bonding in these inner-complexes is not so incomprehensible as once many authors

believed. For instance, the octahedral micro-symmetry of  $\text{MO}_6$  clusters postulated<sup>12</sup> from spectra of the nickel(II) complex has now been verified by crystallography<sup>17,18</sup> the high-spin species being a trimer  $\text{Ni}_3 \text{aca}_6$ , and also the spectra of Jahn-Teller stable  $\text{Maca}_3$  do not encourage the assumption of strong, unusual deviations from octahedral symmetry. Regarding the question of possible strong  $\pi$ - (and not only  $\sigma$ -) bonding in these complexes, the observation in  $\text{Craca}_3$  of luminescence spectra<sup>19</sup> of the excited term  ${}^2\Gamma_3$  of  $\gamma_5^3$  suggesting rather small values of the nephelauxetic<sup>20</sup> ratio  $\beta_{55}$  is very important. Actually, these measurements suggest a stronger delocalization of the  $\pi^*$  bonding subshell than in the comparable compounds<sup>21,22</sup>  $\text{Cr}(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_3$  and  $\text{Cr}(\text{Se}_2\text{P}(\text{OC}_2\text{H}_5)_2)_3$ .

The extended understanding of electron transfer spectra of acetylacetonates gives some hope that a rational classification of energy levels according to M.O. configurations can be obtained in a few years of transition group complexes of fairly complicated oxygen- and nitrogen-containing organic ligands about which a rich experimental material is available<sup>7,23</sup>.

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