

MAGNETIC CIRCULAR DICHROISM OF GROUP VIA HEXACARBONYLS

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The magnetic circular dichroism spectra of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ have been measured. The A terms for the two low-lying charge-transfer transitions in these compounds were calculated using the irreducible tensor method. For the second CT transition an alternative assignment is proposed contrary to the one hitherto assumed.

1. Introduction

During our investigations of the photochemical behaviour of transition-metal carbonyl complexes of the general type $\text{M}(\text{CO})_5\text{L}$ in which M represents Cr, Mo, W, and L several kinds of nitrogen and phosphorus ligands [1], we felt the need for a detailed knowledge and understanding of the visible and near UV spectra of the corresponding hexacarbonyls.

Several studies concerning the electronic structure and absorption spectra of these compounds have been published [2–5]. The photoelectron spectra were measured and interpreted by Higgins and Lloyd [6]. In this work we present the magnetic circular dichroism (MCD) spectra and comment on the consequences they have on the assignment of the first two charge-transfer (CT) transitions.

2. Experimental

The hexacarbonyls of Cr, Mo and W were purchased from Strem Chemicals and used without further purification.

We measured their *n*-hexane solution MCD spectra

on a home-made dichrometer equipped with a superconducting magnet system (Oxford Instruments Co. Ltd., type SM4) at room temperature and at a magnetic field strength of 7.2 T. The absorption spectra were measured on the same solutions using a Perkin–Elmer/Hitachi 200 spectrophotometer. Concentrations were about 1×10^{-5} M.

3. Results and discussion

In fig. 1 the MCD and absorption spectra of chromium hexacarbonyl are depicted. The other two compounds give very similar spectra. The main features of these MCD spectra are in all three cases two bands of opposite sign and of nearly the same magnitude. These two bands coincide with the absorption bands. The band of smaller extinction at about 279 nm has been assigned to the metal-to-ligand CT transition $c\ ^1T_{1u} \leftarrow ^1A_{1g}(2t_{2g} \rightarrow 9t_{1u})$, the more intense one at about 223 nm to the metal-to-ligand CT $d\ ^1T_{1u} \leftarrow ^1A_{1g}(2t_{2g} \rightarrow 2t_{2u})$ [2–5]. The orbital numbering we use here is the one given in ref. [3]. According to refs. [2–5] two metal $d \rightarrow d$ transitions are located at 317 and 257 nm [$^1T_{1g} \leftarrow ^1A_{1g}(2t_{2g} \rightarrow 6e_g)$ and $^1T_{2g} \leftarrow ^1A_{1g}(2t_{2g} \rightarrow 6e_g)$ respec-

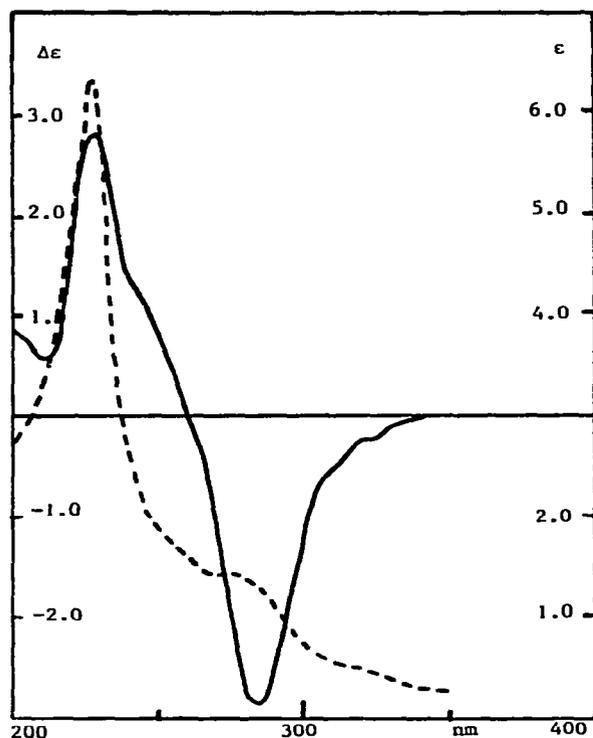


Fig. 1.

tively]. Hardly any MCD is observable in these regions of the spectrum. Perhaps one of them, ${}^1T_{2g} \leftarrow {}^1A_{1g}$, is responsible for the inflection in the MCD curve between the two main CT bands. Such $d \rightarrow d$ transitions in d^6 complexes of O_h symmetry have been described by Stephens [7].

The MCD spectrum may be analyzed by the method

of moments [8]. Definitions of MCD and moments according to Stephens [8] are adopted throughout this work. As the bands are not well separated, and because of the possible complication of the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ and ${}^1T_{2g} \leftarrow {}^1A_{1g}$ transitions, the results of the analysis are somewhat crude. Results are given in table 1. Table 1 shows a remarkable absence of any A term of importance next to rather small B terms for the CT transitions.

To understand this behaviour we performed a calculation of the expected A terms according to the irreducible tensor method [9,10]. The B term calculation involves only the contribution of the CT states themselves to each other's B value.

The first CT transition is taken to be ${}^1T_{1u} \leftarrow {}^1A_{1g}(2t_{2g} \rightarrow 9t_{1u})$, as is generally accepted in the literature. For the other one we take subsequently ${}^1T_{1u}(2t_{2g} \rightarrow 10t_{1u})$, ${}^1T_{1u}(2t_{2g} \rightarrow 2t_{2u})$ and ${}^1T_{1u}(8t_{1u} \rightarrow 6e_g)$ as the upper state. The participating MOs are the t_{2g} metal d orbital with ligand t_{2g} character, accounting for the π back donation in these complexes:

$$2t_{2g} = \gamma t_{2g}(d) + \delta t_{2g}(L, \pi^*), \quad \gamma^2 + \delta^2 \approx 1,$$

the $9t_{1u}$ ligand π^* orbital with some metal p character:

$$9t_{1u} = \alpha t_{1u}(L, \pi^*) - \beta t_{1u}(p), \quad \alpha^2 + \beta^2 \approx 1,$$

the pure ligand $2t_{2u}$ π^* orbital and finally the other t_{1u} ligand π^* orbital with metal p character:

$$10t_{1u} = \beta t_{1u}(L, \pi^*) + \alpha t_{1u}(p).$$

The coefficients reflect the result of a configuration interaction. We take them all positive, so $9t_{1u}$ has some bonding character and is lower in energy than $10t_{1u}$, which has some anti-bonding character.

The following formulae are used. For the A term:

Table 1 a)

Moments b)	Transition	Cr(CO) ₆	Mo(CO) ₆	W(CO) ₆
A_1	$c {}^1T_{1u} \leftarrow {}^1A_{1g}$	-2.63×10^{-2}	$+3.08 \times 10^{-3}$	-1.38×10^{-2}
B_0	$c {}^1T_{1u} \leftarrow {}^1A_{1g}$	-1.96×10^{-3}	-1.96×10^{-3}	-1.84×10^{-3}
D_0	$c {}^1T_{1u} \leftarrow {}^1A_{1g}$	4.76	3.06	3.67
A_1	$d {}^1T_{1u} \leftarrow {}^1A_{1g}$	$+1.78 \times 10^{-2}$	$+3.55 \times 10^{-4}$	-1.25×10^{-2}
B_0	$d {}^1T_{1u} \leftarrow {}^1A_{1g}$	$+1.53 \times 10^{-3}$	$+1.66 \times 10^{-3}$	$+7.55 \times 10^{-4}$
D_0	$d {}^1T_{1u} \leftarrow {}^1A_{1g}$	36.9	35.5	52.4

a) Units: A_1 is bohr magneton \times (debye)²; B_0 is bohr magneton \times (debye)²/cm⁻¹; D_0 is (debye)².

b) Definitions according to ref. [8].

$$A(^1T_{1u} \leftarrow ^1A_{1g}) = -\frac{2i}{\sqrt{6}} W \begin{pmatrix} T_1 & T_1 & T_1 \\ A_1 & T_1 & T_1 \end{pmatrix} \langle ^1T_{1u} \| \mu \| ^1T_{1u} \rangle \times \langle ^1A_{1g} \| m \| ^1T_{1u} \rangle \langle ^1T_{1u} \| m \| ^1A_{1g} \rangle,$$

for the dipole strength:

$$D(^1T_{1u} \leftarrow ^1A_{1g}) = \frac{1}{3} \langle ^1A_{1g} \| m \| ^1T_{1u} \rangle \langle ^1T_{1u} \| m \| ^1A_{1g} \rangle,$$

and for the B term (for $c^1T_{1u} \leftarrow ^1A_{1g}$).

$$B(c^1T_{1u} \leftarrow ^1A_{1g}) = -\frac{4i}{\sqrt{6}} W \begin{pmatrix} T_1 & T_1 & T_1 \\ A_1 & T_1 & T_1 \end{pmatrix} \times (1/E_{dc}) \langle c^1T_{1u} \| \mu \| d^1T_{1u} \rangle \times \langle A_{1g} \| m \| c^1T_{1u} \rangle \langle d^1T_{1u} \| m \| ^1A_{1g} \rangle,$$

with

$$E_{dc} = E(d^1T_{1u} \leftarrow ^1A_{1g}) - E(c^1T_{1u} \leftarrow ^1A_{1g}).$$

From this one sees immediately that in this approximation

$$B(d^1T_{1u} \leftarrow ^1A_{1g}) = -B(c^1T_{1u} \leftarrow ^1A_{1g}).$$

Now the W coefficient equals $-\frac{1}{3}$, so we only have to calculate several reduced matrix elements. These can be

further reduced to one-electron reduced matrix elements, which are easily calculated [11]. The results are in table 2.

As we wanted to know whether this simple B term calculation at least accounts for the sign of the B terms of the CT bands, for which the relative signs of the reduced matrix elements of the electric dipole moment operator are necessary, we included these elements in table 2. As we have no detailed knowledge of values for the orbital coefficients, we include in table 2 the results of calculations for two extreme cases, characterized by the coefficient values indicated in the headings of the columns.

From the photoelectron results of ref. [6], the $8t_{1u}$ level lies some 4.8 eV below the $2t_{2g}$ level. The state involving the $8t_{1u} \rightarrow 6e_g$ excitation is expected about 7.0 eV above the ground state. So we can hardly identify the $d^1T_{1u} \leftarrow ^1A_{1g}$ transition with it. Moreover its A/D value cannot become small as we see from table 2. Also from this table we infer that the A/D value remains large for the $d^1T_{1u} \leftarrow ^1A_{1g}$ transition connected with the $2t_{2g} \rightarrow 2t_{2u}$ excitation. So we are left with the possibility of $2t_{2g} \rightarrow 10t_{1u}$. In this case both A/D values for $c^1T_{1u} \leftarrow ^1A_{1g}$ and $d^1T_{1u} \leftarrow ^1A_{1g}$ can become vanishing small for the choice of coefficient values in the last column of table 2.

Table 2 a,b,c)

Reduced matrix element	One-electron transition	Value	$\alpha^2 = \gamma^2 = 1,$ $\beta^2 = \delta^2 = 0$	$\alpha^2 = \gamma^2 = \frac{1}{2},$ $\beta^2 = \delta^2 = \frac{1}{2}$
$\langle c^1T_{1u} \ \mu \ c^1T_{1u} \rangle$	$2t_{2g} \rightarrow 9t_{1u}$	$-\frac{1}{2}i\sqrt{6}(\gamma^2 + \frac{1}{2}\delta^2 - \frac{1}{2}\alpha^2 - \beta^2)$	$-\frac{1}{4}i\sqrt{6}$	0
$\langle d^1T_{1u} \ \mu \ d^1T_{1u} \rangle$	$2t_{2g} \rightarrow 10t_{1u}$	$-\frac{1}{2}i\sqrt{6}(\gamma^2 + \frac{1}{2}\delta^2 - \frac{1}{2}\beta^2 - \alpha^2)$	0	0
$\langle d^1T_{1u} \ \mu \ d^1T_{1u} \rangle$	$2t_{2g} \rightarrow 2t_{2u}$	$\frac{1}{2}i\sqrt{6}(\gamma^2 + \frac{1}{2}\delta^2 + \frac{1}{2})$	$\frac{3}{4}i\sqrt{6}$	$\frac{5}{8}i\sqrt{6}$
$\langle d^1T_{1u} \ \mu \ d^1T_{1u} \rangle$	$8t_{1u} \rightarrow 6e_g$	$\frac{1}{4}i\sqrt{6}$	$\frac{1}{4}i\sqrt{6}$	$\frac{1}{4}i\sqrt{6}$
$\langle c^1T_{1u} \ \mu \ d^1T_{1u} \rangle$	$2t_{2g} \rightarrow 10t_{1u}$	$-\frac{1}{4}i\sqrt{6}\alpha\beta$	0	$-\frac{1}{8}i\sqrt{6}$
$\langle c^1T_{1u} \ \mu \ d^1T_{1u} \rangle$	$2t_{2g} \rightarrow 2t_{2u}$	$\frac{1}{4}i\sqrt{6}\alpha$	$\frac{1}{4}i\sqrt{6}$	0
$\langle c^1T_{1u} \ \mu \ d^1T_{1u} \rangle$	$8t_{1u} \rightarrow 6e_g$	0	0	0
$\langle ^1A_{1g} \ m \ c^1T_{1u} \rangle$	$2t_{2g} \rightarrow 9t_{1u}$	$-\sqrt{2}(\alpha\gamma r + \alpha\delta t - \beta\gamma q - \beta\delta v)$	$-r\sqrt{2}$	$-\frac{1}{2}\sqrt{2}(r+t-q-v)$
$\langle ^1A_{1g} \ m \ d^1T_{1u} \rangle$	$2t_{2g} \rightarrow 10t_{1u}$	$-\sqrt{2}(\beta\gamma r + \beta\delta t + \alpha\gamma q + \alpha\delta v)$	$-q\sqrt{2}$	$-\frac{1}{2}\sqrt{2}(r+t+q+v)$
$\langle ^1A_{1g} \ m \ d^1T_{1u} \rangle$	$2t_{2g} \rightarrow 2t_{2u}$	$\sqrt{2}(\gamma p + \delta w)$	$p\sqrt{2}$	$(p+w)$
$\langle ^1A_{1g} \ m \ d^1T_{1u} \rangle$	$8t_{1u} \rightarrow 6e_g$	$\frac{2}{3}\sqrt{3}s$	$\frac{2}{3}\sqrt{3}s$	$\frac{2}{3}\sqrt{3}s$

a) Units bohr magneton and debye.

b) $p = \langle d_{xy} | m_x | t_{2u}^L \rangle$, $q = \langle d_{xy} | m_x | t_{1u}^M(p) \rangle$; $r = \langle d_{xy} | m_x | t_{1u}^L \rangle$, $s = \langle t_{1u}^L x | m_x | d_{x^2-y^2} \rangle$; $t = \langle t_{2g}^L \xi | m_x | t_{1u}^L \rangle$; $v = \langle t_{2g}^L \xi | m_x | t_{1u}^M(p) \rangle$; $w = \langle t_{2g}^L \xi | m_x | t_{2u}^L \rangle$, for the common choice of phases q, r, t and v are positive and p, s and w are negative quantities.

c) Overlap contributions of different MOs are neglected.

The sign of the product of two reduced matrix elements of the electric dipole moment operator is positive if $r+t$ is larger than $q+v$. This is a reasonable deduction from inspection of the relevant orbitals. Therefore the mutual magnetic interaction of the two CT states results in a negative contribution to the B term of $c^1T_{1u} \leftarrow ^1A_{1g}$ and a positive one for $d^1T_{1u} \rightarrow ^1A_{1g}$. The last column of table 2 gives a value of $-i\sqrt{6}/8$ for $\langle c^1T_{1u} || \mu || d^1T_{1u} \rangle$, which is to be compared with the experimental value obtained from

$$\langle c^1T_{1u} || \mu || d^1T_{1u} \rangle$$

$$= - (i\sqrt{6}/4) E_{dc} B_0 / [D_0(c^1T_{1u}) D_0(d^1T_{1u})]^{1/2},$$

giving $-1.08i\sqrt{6}/4$. The $d^1T_{1u} \leftarrow ^1A_{1g} (2t_{2g} \rightarrow 2t_{2u})$ transition would give the wrong sign for the B term. The sign of $[D_0(c^1T_{1u}) D_0(d^1T_{1u})]^{1/2}$ can be taken positive since the reduced matrix elements of the electric dipole moment operator in table 2 are negative quantities for all relevant one-electron transitions.

The transition moments of the "pure" MO transitions in the $c^1T_{1u} \leftarrow ^1A_{1g}$ transition are destructively coupled by the configuration interaction, whereas in the $d^1T_{1u} \leftarrow ^1A_{1g}$ transition they add. This may at least partially account for the disparate intensity [4] of these CT transitions.

These observations prompt us to connect the $d^1T_{1u} \leftarrow ^1A_{1g}$ transition at about 44000 cm^{-1} in the hexacarbonyls with the $2t_{2g} \rightarrow 10t_{1u}$ excitation, instead of with $2t_{2g} \rightarrow 2t_{2u}$ hitherto assumed. The assignment of the $c^1T_{1u} \leftarrow ^1A_{1g}$ transition as corresponding to the $2t_{2g} \rightarrow 9t_{1u}$ one-electron excitation is supported by these results. This $2t_{2u}$ level is calculated [2-4] between $9t_{1u}$ and $10t_{1u}$, nevertheless from the above argument we expect the $d^1T_{1u} \leftarrow ^1A_{1g}$ transition to this orbital to

lie at higher energy and out of reach of our instrument (i.e. below 210 nm). If the balance between the orbital coefficients is disturbed, which we expect to happen when the relative positions of the π^* level of the ligands is shifted with respect to the metal orbital (e.g. in hexaisocyanide complexes), the CT transitions may acquire observable A terms. This will also be the case when one of the carbonyl groups is replaced by another ligand, as in our $M(\text{CO})_5\text{L}$ complexes.

References

- [1] G. Boxhoorn, D.J. Stufkens and A. Oskam, *Inorg. Chim. Acta* 33 (1979) 215.
- [2] W.C. Trogler, S.R. Desjardins and E.I. Solomon, *Inorg. Chem.* 18 (1979) 2131.
- [3] J.B. Johnson and W.G. Klemperer, *J. Am. Chem. Soc.* 99 (1977) 7132.
- [4] N.A. Beach and H.B. Gray, *J. Am. Chem. Soc.* 90 (1968) 5713.
- [5] H.B. Gray and N.A. Beach, *J. Am. Chem. Soc.* 85 (1963) 2922;
K.G. Caulton and R.F. Fenske, *Inorg. Chem.* 7 (1968) 1273;
D.G. Carroll and P. McGlynn, *Inorg. Chem.* 7 (1968) 1285.
- [6] B.R. Higginson, D.R. Lloyd, P. Burroughs, D.M. Gibson and A.F. Orchard, *J. Chem. Soc. Faraday Trans. II* 69 (1973) 1659.
- [7] P.J. Stephens, *Advan. Chem. Phys.* 44 (1966) 4060.
- [8] P.J. Stephens, *Advan. Chem. Phys.* 35 (1976) 197.
- [9] P.A. Dobosh, *Mol. Phys.* 27 (1974) 689.
- [10] S.B. Piepho, in: *Recent advances in group theory and their application to spectroscopy*, ed. J.C. Donini (Plenum Press, New York, 1979).
- [11] P.N. Schatz, A.J. McCaffery, W. Suetaka, G.N. Henning, A.B. Ritchie and P.J. Stephens, *J. Chem. Phys.* 45 (1966) 722.