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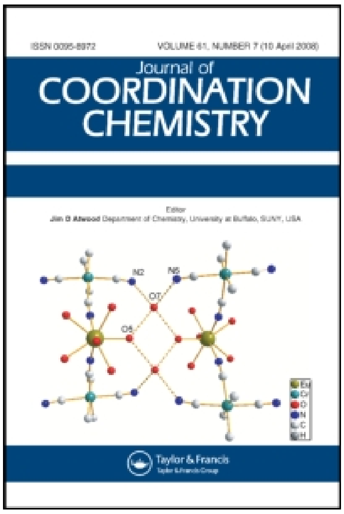

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THE QUANTITATIVE INTEPRETATION OF A/D PARAMETERS FOR ELECTRONIC EXCITATION MO ASSIGNMENTS OF TRANS-[M(CO)$_4$(P(n-Bu)$_3$)$_2$] (M = Cr, Mo, AND W) BASED ON ELECTRONIC MCD AND COMPLETE OPERATOR MATRIX ⟨L$_z$⟩ EVALUATION

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THE QUANTITATIVE INTEPRETATION OF A/D PARAMETERS FOR ELECTRONIC EXCITATION MO ASSIGNMENTS OF TRANS-$[M(CO)_4(P(n\text{-}Bu)_3)_2]$ (M = Cr, Mo, AND W) BASED ON ELECTRONIC MCD AND COMPLETE OPERATOR MATRIX $<L_z>$ EVALUATION

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Electronic absorption (EA) and magnetic circular dichroism (MCD) spectra of *trans*-$[M(CO)_4(P(n\text{-}Bu)_3)_2]$ (M = Cr, Mo, W) of five bands from ~20.0 × 10^3 to ~45.5 × 10^3 cm^{-1} were measured. The EA spectra exhibit three dominant bands, I-III, at about 27 × 10^3 cm^{-1}, 30 × 10^3 cm^{-1}, and 39 × 10^3 cm^{-1}, respectively. Corresponding MCD spectra in the region of both hands I and III are dominated by the presence of positive A-terms, indicative of transitions to degenerate excited states. A-terms and dipole strength (D) parameters were extracted by rigorous spectral deconvolution for the Cr complex; the spectra of the Mo and W analogs are quite similar. Since these are charge transfer bands and a number of the 2-center and 3-center integrals of $<L_z>$ will be large, multi-zeta all-center operator matrix computations were used to evaluate signs and magnitudes of MCD A/D parameters for all degenerate excited-state electronic configurations of statically electric dipole allowed *g*→*u* (MLCT, or $M \rightarrow \pi^*(CO)$) type transitions. Experimental and computed A/D parameters, *etc.* are consistent with assigning band I ($\bar{A}_1/\bar{D}_0 = 0.77$) as ${}^1A_{1g}[e_g^4(\sim d_{xz,yz})] \xrightarrow{(x,y)} {}^1E_u^a[e_g^3a_{2u}^1(\sim\pi^*(CO))]$ and band III ($\bar{A}_1/\bar{D}_0 = 0.50$) as ${}^1A_{1g}[b_{2g}^2(\sim d_{xy})] \xrightarrow{(x,y)} {}^1E_u^b[b_{2g}^1e_u^1(\sim\pi^*(CO))]$. The assignment corresponding to EA band II is to the *z*-polarized transition ${}^1A_{1g}[e_g^4(\sim d_{xz,yz})] \xrightarrow{(z)} {}^1A_{2u}[e_g^3e_u^1(\sim\pi^*(CO))]$ which is consistent with the absence of an MCD A-term. The fourth possible allowed $g \rightarrow u$ transition is ruled out for I-III because its computed $\bar{A}_1/\bar{D}_0$ equals − 0.77, whereas positive A-terms are observed for I and III. The positions of deconvoluted tetragonal components ${}^1A_{2g} > {}^1E_g$ of LF origin ${}^1T_{1g}(t_{2g}^5e_g)$ were also determined for the first time. Spectra are wavelength corrected by calibration standards, and MCD spectra are accurately wavelength matched to their optical spectra.

KEYWORDS: MCD spectra, MO assignments, electronic spectra

INTRODUCTION

The *trans*-bis(tri-n-butylphosphine)tetracarbonylchromium, -molybdenum, and-tungsten complexes belong to an important family of photochemically active tetragonal derivatives of the hexacarbonylchromium, -molybdenum, and -tungsten, the latter three having been well studied and used in photochemistry and photocatalysis.[1,2] Detailed electronic structural elucidations were published addressing our initial results concerning ~300 K (fluid solution) and ~77 K (polymer matrix) electronic absorption (EA) and magnetic circular dichroism (MCD) spectra of the two distinct lowest energy bands I (~27.3×10^3 cm^{-1}; ~366 nm) and II (~31.5×10^3 cm^{-1}; ~318 nm) of *trans*-[$Mo(CO)_4(P(n\text{-}Bu)_3)_2$].[3] We assigned bands I and II (MLCT), as well as LF band C, or $^1A_{2g}[^1T_{1g}(t_{2g}^5e_g)]$, and discussed the probable location of another LF band $^1E_g[^1T_{1g}(t_{2g}^5e_g)]$ as being under bands I and/or II. Previous to that, Braterman, *et al.*,[4] reported both ~300 K (fluid solution) and 77 K (glassy solution) EA spectra of *trans*-$M(CO)_4L_2$ (M = Cr, Mo, W and L = PR_3 and $P(OR)_3$), but dichroism and polarization data were not available then.[4] In our first note on MCD spectra we interpreted the A-term[5,6] sign and energy of band I by approximation, *i.e.*, comparing it with an approximately computed A/D of the parallel $^1A_{1g} \rightarrow {}^1E_u$ transition (same MOs)[6] in $[Pt(CN)_4]^{2-}$.

For solutions we consider the *trans* compounds to have D_{4h} symmetry (M, 4CO, 2P) with the four CO ligands and M in the *xy*-plane and the two phosphine ligands along the *z*-axis in *trans*-positions. As these molecules are closed-shell, the electronic ground state is $^1A_{1g}$. Electric dipole selection rules allow two types of electronic transitions: $^1A_{1g} \rightarrow {}^1A_{2u}$ (*z*-polarized) and $^1A_{1g} \rightarrow {}^1E_u$ (*xy*-polarized). Any observed transition from this ground state to a gerade excited state (LF and $g \rightarrow g$ CT) has to be vibronically electric dipole allowed through an ungerade normal mode of the ground or excited state. For example, the skeletal normal modes of vibration, Γ^v, for *trans*-[$M(CO)_4P_2$] are $3A_{1g}^v$, A_{2g}^v, $2B_{1g}^v$, $2B_{2g}^v$, $2E_g^v$, $3A_{2u}^v$, $3B_{2u}^v$, and $5E_u^v$. However, it was shown by two groups[3,4] using two different solvent media (EPA and PVC) that the two low energy bands (band I and at least the band *maximum* region of II) have static electric dipole behavior. The present EA and MCD analysis goes beyond bands I and II into the UV region to include a very intense optical band III, and we carry out full-matrix orbital angular momentum operator computations for the representative *trans*-[$Cr(CO)_4(PR_3)_2$]. Using our second-generation MCD spectrometer, we present intensity and wavelength-correct MCD spectra which are properly wavelength matched to EA spectra. Computer deconvolution yielded MCD A/D ratios. For example, five bands are required to account for the spectrum (20 000–42 000 cm^{-1}) for *trans*-[$Cr(CO)_4(P(n\text{-}Bu)_3)_2$]. The MCD results are also of additional interest, since transparent uniaxial host crystals, which make the measurement of linear polarizations of bands possible, are unknown.

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EXPERIMENTAL

Trans-bis(tri-n-butylphosphine)tetracarbonylchromium(0)

Hexacarbonylchromium (2.00 g, 0.009 mol) and tri-n-butylphosphine (4.5 ml, 0.018 mol) were added to diethyleneglycol dimethylether (50 ml), with N_2 flushing and stirring. The mixture was heated to 130°C in an oil bath and maintained at that temperature (1 h). During this time, the solution gradually changed from a light yellow color to an intense yellow hue. The hot solution was gravity filtered and the yellow solution placed on a rotary evaporator to remove the solvent. The resultant yellow oil was dissolved in methylene chloride (25 ml), filtered, and placed in a small crystal dish in the dark to slowly evaporate over a period of 7 days. Clear, deep-yellow needles formed which were vacuum dried, and IR spectra[7] confirmed the presence of only *trans*-[$Cr(CO)_4(P(n\text{-}Bu)_3)_2$]. The crystals (4.14 g, 80% yield, m.p. 40°C) were stored cold (10°C) in the dark. This procedure was somewhat simpler than the one given by Grim and Wheatland[7], although their yield was higher (85%).

Trans-bis(tri-n-butylphosphine)tetracarbonylmolybdenum(0)

Procedure (A) Hexacarbonylmolybdenum (3.00 g, 0.011 mol) was heated in an oil bath under N_2 in diethyleneglycol dimethylether (50 ml) to 130°C while stirring. Trin-butylphosphine (0.24 mol, 6.0 ml) was injected through a serum cap, and the subsequent reaction progress monitored by means of the volume of evolved CO. Immediately following the addition of the phosphine ligand, CO evolution was visible and it continued vigorously until slightly less than the expected amount of CO had evolved. The color of the solution gradually changed from a light yellow to yellowish-brown. The hot solution was gravity-filtered and the solvent removed on a rotary evaporator to yield an oily brown residue which was dissolved in methylene chloride (10 ml), filtered, and evaporated to yield a yellow oil. The crude product contained both *cis* - and *trans*-isomers as shown by IR spectra and thin layer chromatography (alumina). Complete separation of the two isomers was accomplished by column chromatography. A column (70 × 2.5 cm) was packed two-thirds full with alumina (Fisher, A-540, 120 mesh). The oil was dissoved in a minimum amount of light petroleum ether (b.p. 27.1–57.8°C) before being placed on the column. The column was eluted with light petroleum ether: 40 ml fractions were collected and the solvent evaporated under reduced pressure (40°C). IR spectra in the $\nu(CO)$ region were taken of each successive fraction in order to follow the separation of the two isomers. A yellow band was eluted first to yield a yellow oil (*ca.* 4 ml); to this a methylene chloride-methanol solution (15 ml, 50:05 v/v) was added. Cooling the cloudy yellow solution overnight at 0°C afforded a fine yellow crystalline compound (1.20 g, 17% yield, m.p. 44.5–45.0°C), which was shown by IR to be *trans*-$[Mo(CO)_4(P(n\text{-}Bu)_3)_2]$.[5] A second band on the column contained the *cis*-isomer.

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Procedure (B)

By this method, *trans*-$[Mo(CO)_4(P(n\text{-}Bu)_3)_2]$ was prepared from *cis*-$[Mo(CO)_4(NHC_5H_{10})_2$, as reported in the literature, after making some modifications.[8,5] The piperidine compound (2.0 g, 0.005 mol), tri-n-butylphosphine (3.0 ml, 0.012 mol) and heptane (75 ml) were heated at reflux for 4 h with stirring under N_2. During reflux, the reaction mixture gradually changed from a clear light yellow to a cloudy brownish-yellow color. The hot solution was gravity-filtered to result in a clear yellow solution and the solvent removed under reduced pressure (35°C) to yield an amber-yellow oil. Methanol (10 ml) was added to the oil and the now cloudy yellow mixture was kept at 0°C for three hours to produce powdery light yellow crystals. Three subsequent recrystallizations from cold methanol (10 ml portions) followed by vacuum drying yielded 1.35 g (43%) of pure *trans*-$[Mo(CO)_4P(n\text{-}Bu)_3)_2]$ (m.p. 40–41°C), unambiguously identified from its IR spectrum.[7]

Trans-bis(tri-n-butylphosphine)tetracarbonyltungsten(0). Procedure (A). *Trans*-$[W(CO)_4(P(n\text{-}Bu)_3)_2]$ can be prepared as described in procedure (A) for the molybdenum complex. Only a slight excess of the 2:1 molar ratio of phosphine ligand to hexacarbonyl was necessary to obtain powdery yellow crystals (m.p. 44.5–45°C, 1.79 g, 30% yield). The product's IR indicated that only the *trans*-isomer was obtained.[7]

Procedure (B).[5] This tungsten tetracarbonyl derivative was also synthesized from cis-[$W(CO)_4(NHC_5H_{10})_2$] in the manner described above for the preparation of *trans*-[$Mo(CO)_4(P(n\text{-}Bu)_3)_2$] (Procedure (B)). However, diglyme (50 ml) was used as solvent in place of heptane and the reaction mixture was refluxed for 7 h instead of 4. The reaction of tri-n-butylphosphine (2.0 ml, 0.008 mol) and the piperidine intermediate (1.74 g, 0.003 mol) in diglyme yielded 1.48 g (64%) of pure *trans*-[$W(CO)_4(P(n\text{-}Bu)_3)_2$] after recrystallization. No further purification was required under these conditions, although it has been implied in the literature that a mixture of *cis*- and *trans*-isomers generally results[9] when following this procedure.

MCD and EA Spectra

Room temperature EA and MCD spectra were simultaneously recorded using the monochromator (2 x 0.25m) portion of an old JASCO Optical Rotary Dispersion Spectrometer (Model ORD/UV-5) with solid state electronics of our most recent NCSU design to provide signal digitization.[10] The instrument is free of occasionally occurring intensity drifts of an earlier version of a PEM (photoelastic modulator) based unit.[11]

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Potassium hexacyanoferrate(III), $K_3Fe(CN)_6$, was used as the MCD standard. Its EA and MCD spectra[6] are well documented with three optical absorption peaks in the range 500–200 nm (418 nm, 298 nm and 257 nm). The molar ellipticity, $[\theta]_m$, at 418 nm has been reported to be $+1.08$ deg·dmol^{-1}·cm^2 in a field of 1.0 Gauss, and this value was used as the reference. Response counts (R) for ΔA of the peak with $[\theta]_m$,418 nm = $+1.08$ deg·dmol^{-1}·cm^2/Gauss were determined by recording the MCD spectrum and obtaining the counts recorded by the computer corresponding to this ΔA value (MCD activity).

The present paper presents (i) wavelength correct MCD and EA spectra, (ii) intensity-correct MCD spectra obtained on our MCD instrument, (iii) deconvolution-derived A-terms and D-parameters, and (iv) total operator matrix computations for A/D (or alternatively $(\bar{A}_1/\bar{D}_0)$[12] ratios) for all possible $^1A_{1g} \rightarrow {}^1E_u$ type $M \rightarrow \pi^*$ (CO) MLCT transitions.

RESULTS AND DISCUSSION

The solution (300 K)[3,4,5] EA spectra of *trans*-[$M(CO)_4(P(n\text{-}Bu)_3)_2$] (M = Cr, Mo, W) from 500 to 220 nm exhibit three large bands (Figure 1, EA and MCD spectra of the Cr complex are very similar to the Mo and W analogs). Band I for the chromium, molybdenum, and tungsten compounds, respectively, is at 27.28×10^3 cm^{-1} (366.5 nm), 26.52×10^3 cm^{-1} (377.0 nm) and 26.36×10^3 cm^{-1} (379.4 nm) in cyclohexane, with molar absorptivity around 2000 l mole^{-1} cm^{-1}. Band II is at 30.86×10^3 cm^{-1} (324.1 nm), 29.05×10^3 cm^{-1} (344.2 nm), and 28.34×10^3 cm^{-1} (352.9 nm) and band III is at 38.64×10^3 cm^{-1} (258.8 nm; ε_{max} = 28,000), 38.82×10^3 cm^{-1} (257.6 nm; ε_{max} = 63,330) and 39.71×10^3 cm^{-1} (251.8nm; ε_{max} = 86,830). As the temperature is lowered, the maxima of bands I and II exhibit similar behaviour,[3,4,5] *i.e.* higher intensity of the band maximum and slight shift to

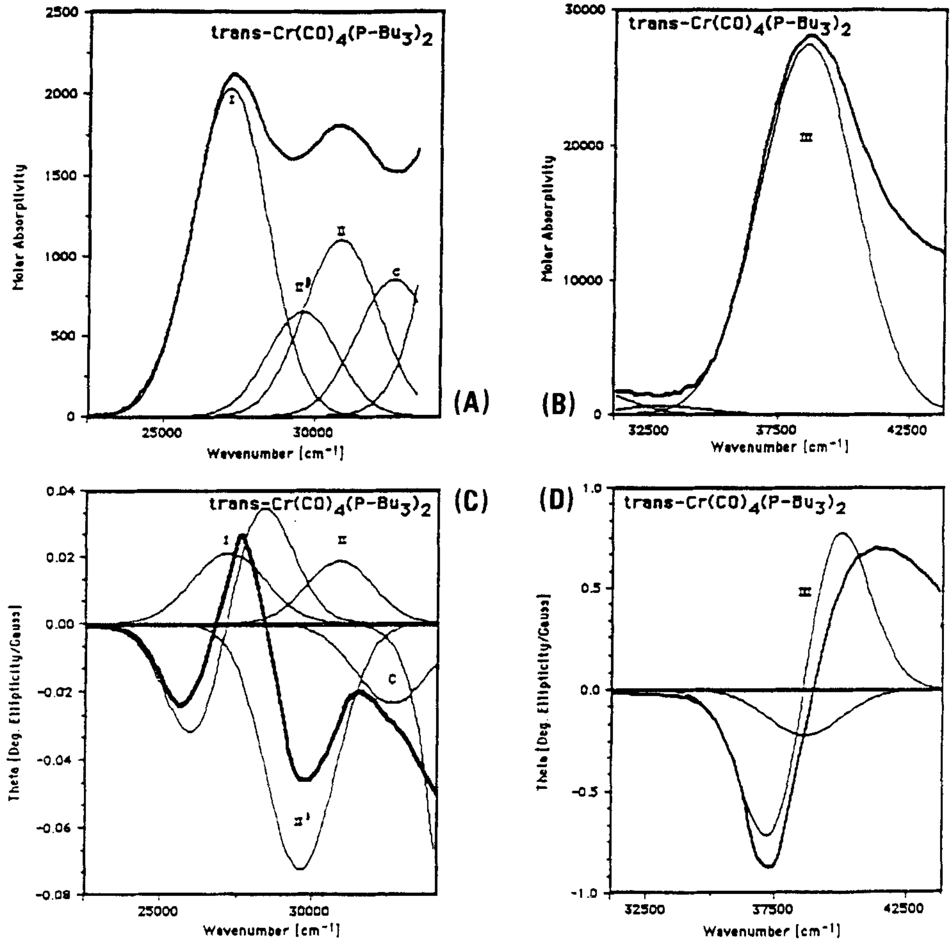

Figure 1 Optical (A,B) and MCD (C,D) spectra (in cyclohexane) of *trans*-[Cr(CO)$_4$(P(n-Bu)$_3$)$_2$]. Molar absorptivity is $M^{-1} \cdot cm^{-1}$ and molar ellipticity is $deg \cdot dmol^{-1}$ in H = 1 Gauss. Heavy lines are experimental spectra.

shorter wavelength which are characteristics of statically electric dipole allowed transitions for solutions between ~300 K and ~77 K. The large molar absorptivity exhibited by band III is also indicative of a statically electric dipole allowed transition. Therefore, bands I, II, and III correspond to statically electric dipole allowed transitions ($g \rightarrow u$) from ground state $^1A_{1g}$ to excited state $^1A_{2u}$ or ^1E_u. Therefore, they are not L-F type ($g \rightarrow g$) bands, but are CT in nature. In addition, the transitions of *trans*-[M(CO)$_4$L$_2$] are energetically near those of the metal-to-π^*(CO) transitions (MLCT) of the parent [M(CO)$_6$], so that we assign them to be of MLCT type. (Smaller LF band intensity is hidden under these bands, Figure 1). Detailed assignments follow below.

For the molybdenum and tungsten compounds a weak band C is observed at room temperature at 33.20×10^3 cm^{-1} (301.2 nm) and 33.14×10^3 cm^{-1} (301.8

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nm) respectively. Its presence for the chromium analog is also required for proper MCD and EA deconvolutions, but overlap with the red tail of the much more intense band III to the blue of C is significant. Band C was previously assigned[3] to a vibronically electric dipole allowed LF band $^1A_{1g} \rightarrow {}^1A_{2g}[^1T_{1g}(t_{2g}^5e_g^1)]$. Discussion of this absorption follows discussion of the assignment of bands I-III. The room temperature EA and MCD spectra of *trans*-$[Cr(CO)_4(P(n\text{-}Bu)_3)_2]$ in the range 220 to 500 nm are shown in Figure 1. This Cr complex, as well as the Mo and W analogs, exhibits a positive MCD A-term (positive lobe at higher energy) corresponding to both EA bands I and III and negative MCD ellipticity in the region corresponding to EA band II. It is very interesting that a small negative MCD band is present around 33.3×10^3 cm^{-1} (~300 nm; band C), which for this Cr compound is virtually invisible in its EA spectrum due to the overlapping tail of the much more intense band III.

Regarding band assignments, the presence of a MCD A-term for bands I and III reveals that each corresponds to an excitation to a degenerate excited state ^1E_u ($^1E_u^a$ and $^1E_u^b$), the only type of excited state which is electric dipole allowed and also has angular momentum $<L_z>$, *i.e.*, $^1E_u \otimes {}^{A_{1g}}L_z \otimes {}^1E_u$ contains $^1A_{1g}$. The **a** and **b** superscripts designate different MO involvements. From these data, we know that bands I and III are *xy*-polarized. Band II also corresponds to a statically allowed $g \rightarrow u$ MLCT transition, and assigning it to $^1A_{1g} \rightarrow {}^1A_{2u}$ is consistent with the absence of a MCD A-term.

The symmetries of the empty π*(CO) localized MOs are a_{2u}, e_u, b_{2u}, a_{2g}, b_{2g}, and e_g. However, for transitions I-III, only the ungerade MOs have to be considered for these MLCT transitions. It is known from photoelectron spectroscopy (PES)[13,14,15] of the $M(CO)_5L$ analogs, that the two highest energy occupied MOs are $e_g^4(\sim d_{xz,yz}) > b_{2g}^2\ (\sim d_{xy})$, with both MOs being metal localized. For *trans*-$[M(CO)_4L_2]$ complexes this same energy order $e_g > b_{2g}$ is expected. The lowest energy unoccupied ungerade π*(CO) localized MOs are calculated to be a_{2u}, e_u (~π*(CO)), and b_{2u} (100% π^*(CO)). Using these two sets of occupied and unoccupied MOs, the following singlet excited states are possible: $E_u^a(e_g^3a_{2u}^1)$, $E_u^b(b_{2g}^1e_u^1)$, $E_u^c(e_g^3b_{2u}^1)$, A_{2u} $(e_g^3e_u^1)$, B_{1u} $(b_{2g}^1a_{2u}^1)$, and A_{1u} $(b_{2g}^1b_{2u}^1)$. Excited states B_{1u} and A_{1u} are ruled out by the static-electric dipole nature of bands I, II, and III.

While an A-term is expected for any general $^1A_{1g} \rightarrow E_u^i$ and $\rightarrow -E_u^j$ transition, the sign of each will depend on the electronic configuration composition of each excited state. This sign dependence is advantageous, since polarized crystal spectra alone often cannot differentiate between different MOs of two possible but different excited-configurations of the same polarization. For the present three possible E_u excited states a negative A-parameter is calculated for $E_u^c(e_g^3b_{2u}^1)$ and positive A parameters for $E_u^a(e_g^3a_{2u}^1)$ and $E_u^b(b_{2g}^1e_u^1)$ *(vide infra)*. Since only two positive A-terms were observed for bands, I, II, and III, the assignments of the statically electric dipole allowed MLCT transitions are as follows (Figure 2) for the three bands:

$$\text{Band I: } {}^1A_{1g}[e_g^4(\sim d_{xz,yz})] \xrightarrow{(x,y)} {}^1E_u^a[e_g^3a_{2u}^1(\sim\pi^*(CO))]$$
$$\text{Band II: } {}^1A_{1g}[e_g^4(\sim d_{xz,yz})] \xrightarrow{(z)} {}^1A_{2u}[e_g^3e_u^1(\sim\pi^*(CO))]$$
$$\text{Band III: } {}^1A_{1g}[b_{2g}^2(\sim d_{xy})] \xrightarrow{(x,y)} {}^1E_u^b[b_{2g}^1e_u^1(\sim\pi^*(CO))]$$

The MLCT bands I-III of *trans*-$[M(CO)_4(P(n\text{-}Bu)_3)_2]$ are interpretable by using the

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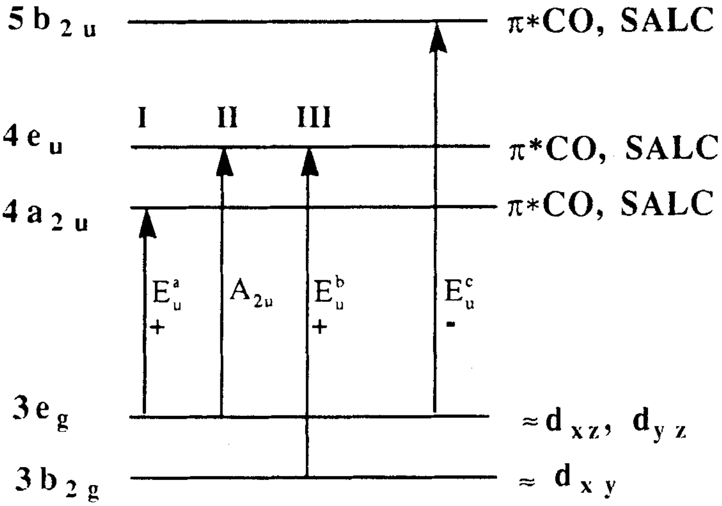

Figure 2 All the D_{4h} electric dipole allowed electronic excitations of MLCT transition type M(Cr, Mo, W) → CO of parentage 't_{2g}^6' (-M) → π*(-CO). Excited state symmetries and signs of MCD A-terms (experimental and computed) are shown for *trans*-$[M(CO)_4L_2]$.

unoccupied MO energy orders $a_{2u} < (e_u, b_{2u})$ for the planar moiety $M(CO)_4$ as was also found[16] for isoelectronic $Pt(CN)_4^{2-}$.

The previously proposed assignment[4] $^1A_{1g}[e_g^4(\sim d_{xz,yz})] \rightarrow {}^1E_u^c[e_g^3b_{2u}^1(\sim\pi^*(CO))]$ for band III (labelled band R in that work) can now be modified, since we compute that such a transition has a negative A-term, whereas our band III has a positive A-term. On the other hand, the previous assignments made for bands I and II, (labelled N and P),[4] are the same as our present direct assignment (band I) and the one (band II) we made by exclusion. The previously made assignment $^1A_{1g}[b_{2g}^2(\sim d_{xy})] \rightarrow {}^1E_u^b[b_{2g}^1e_u^1(\sim\pi^*(CO))]$ made by others for our band C near 33.3×10^3 cm^{-1}, (previously designated[4] as band Q) cannot be correct. The reasons for this are that: (i) this transition $^1A_{1g} \rightarrow {}^1E_u^b$ would have a large positive A-term not observed for C, and (ii) the $^1A_{1g} \rightarrow {}^1E_u^b$ with its predicted positive A-term had to be used to assign band III.

Band C ($\sim 33.3 \times 10^3$ cm^{-1}) is observed as a small intensity shoulder in the absorption spectra of the molybdenum and tungsten *trans*-complexes, and as a clearly positive B-term (positive ellipticity) in the MCD spectra (Figure 1). Due to the strong overlap of bands II and III, band C could not be visually detected in the EA spectrum of *trans*-$[Cr(CO)_4P(n\text{-}Bu)_3)_2]$, but a small shoulder was present around 33.3×10^3 cm^{-1} in the MCD spectrum. Its presence is required to fit the EA and MCD spectra. Assignment of band C as a ligand field transition requires, consideration of the most commonly accepted EA band assignments[17] for the parent $[M(CO)_6$ complexes and several relevant principles and experimental observations. The metal orbital basis dimension (nd, (n + 1)s, (n + 1)p) is of course the same in $[M(CO)_6]$ and *trans*-$[M(CO)_4L_2]$, so that at least some D_{4h} LF bands, when observed, should be related to LF transitions in $[M(CO)_6]$. Also, just as for the MLCT bands I-III, the MO origin of the electron for band C is considered to be

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$b_{2g}^2(\sim d_{xy})$ or $e_g^4(\sim d_{xz,yz})$. As mentioned above, PES of $Cr(CO)_5PR_3$ allows one to extrapolate that the metal localized MOs have the energy order $b_{2g}^2(\sim d_{xy}) < e_g^4(\sim d_{xz,yz})$ for the *trans* complexes. In addition, relevant to the LF MO fate of the electron generating band C are previous MCD studies of tetragonal $[Mo(CO)_5L]$ complexes,[5,18,19] other isoelectronic complexes[16,20] and the present MO calculations done for $[Cr(CO)_5(PH_3)]$[20] and *trans*-$[Cr(CO)_4(PH_3)_2]$ using the MO program written in this laboratory (*vide infra*). These results showed that the $a_{1g}(\sim d_z{}^2)$ antibonding LF-type MO was of lower energy than the $b_{1g}(\sim d_{x^2\text{-}y^2})$ anti-bonding MO. Next to be considered is the lowest energy spin-allowed LF band[17] of $[M(CO)_6]$: ${}^1A_{1g} \rightarrow {}^1T_{1g}$, near $31.2 \times 10^3\ cm^{-1}$. This ${}^1T_{1g}(t_{2g}^5e_g^1)$ excited state splits in D_{4h} symmetry into ${}^1A_{2g}(b_{2g}^1b_{1g}^1)$ and ${}^1E_g(e_g^3a_{1g}^1)$ states. The Wentworth-Piper empirical MO principles[21,22] show that, in the absence of strong interactions between states of these same symmeteries, the energy of the parent state ${}^1T_{1g}$ should be very similar to that of the tetragonal daughter state ${}^1A_{2g}$. Band C of *trans*-$[M(CO)_4L_2]$ was observed around $33 \times 10^3\ cm^{-1}$, with its location to slightly higher energy of the O_h ${}^1A_{1g} \rightarrow {}^1T_{1g}$ LF transition perhaps due to the lower energy state E_u^a (not E_u^c), interacting with a vibronic ${}^1A_{2g} \cdot E_u^v$ LF state. So, the position of band C and its low intensity are consistent with assignment as the vibronically electric dipole allowable LF transition, ${}^1A_{1g}[b_{2g}^2(\sim d_{xy}) \rightarrow {}^1A_{2g}[b_{2g}^1b_{1g}^1(\sim d_{x^2\text{-}y^2})]$. For the skeleton *trans*-$[M(CO)_4P_2]$, five e_u^v vibrational modes are available, but no A_{1u}^v, which might also make it electric dipole allowed. Therefore, since the band is observed, coupling with an E_u^v mode is required. ${}^1E_{1g}[e_g^3(\sim d_{xz,yz})\ a_{1g}^1(\sim d_z2)]$ is the second daughter excited state derived from ${}^1T_{1g}$, and it position for present molecules is predicted using the same MO model.[21,22] The energy difference, δ, between the two daughter states is in the order given,[21,22]

$$\delta \equiv E({}^1E_g) - E({}^1A_{2g}) \tag{2}$$

and is proportional to the difference between the average ligand field strengths in the *xy*-plane, or 10 Dq^{xy} (CO) and along the *z*-axis, or 10 Dq^z (PR_3). Since the energy differences between the parent ${}^1T_{1g}$ and the daughter states are,[21,22]

$$E({}^1E_g, {}^1T_{1g}) = 10Dq - \frac{35}{4}Dt\text{-}C \tag{3}$$

and

$$E({}^1A_{2g}, {}^1T_{1g}) = 10Dq\text{-}C \tag{4}$$

where **C** is one of the two-electron Racah parameters that cancels when taking the differences δ, and **Dt** is given by

$$Dt = \frac{4}{7}(Dq^{xy} - Dq^z) \tag{5}$$

δ is:

$$\delta = \frac{1}{2}(10Dq^z(PR_3)\text{-}10Dq^{xy}(CO)) \tag{6}$$

The ligand field associated with CO is larger than with PR_3, so δ is negative, *i.e.* $E({}^1A_{2g}) > E({}^1E_g)$, and the second daughter state ${}^1E_g$ is at lower energy than ${}^1A_{2g}$ for these *trans*-complexes. Therefore, the second ligand field transition, ${}^1A_{1g}$ $[e_g^4(\sim d_{xz,yz})] \rightarrow {}^1E_g[e_g^3a_{1g}^1(\sim d_z2)] \cdot \Gamma^v$ can in principle become electric dipole allowed through vibronic coupling of either the ground state ${}^1A_{1g}$ or the excited state ${}^1E_g$

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with vibrational modes E^v_u,A^v_{2u}orB^v_{2u}. The corresponding EA band II′ is not a distinct peak but is hidden under the more intense band II, so that careful deconvolution of the EA spectrum of *trans*-$[Cr(CO)_4(P(n\text{-}Bu)_3)_2]$ in the region of envelope II required, in addition to the dominant band II, this smaller band II′ (29.6×10^3 cm^{-1}) slightly to the red of band II (Figure 1). The energy and smaller magnitude (ε_{max}~650) of II′ are consistent with the LF nature. The 3,700 cm^{-1} separation of C and II′ ($^1A_{1g}(T_{1g})$ and $^1E_g(T_{1g})$) cannot be used to derive 10Dq because the degree of configuration interaction is not known.

At 23.8×10^3 cm^{-1} (420 nm) both absorption and MCD spectra show a broad envelope, band A, for the tungsten complex. It is barely discernible in the EA spectrum of the molybdenum derivative and absent for the chromium analog. This behaviour is consistent with that of a spin-forbidden transition allowed by spin-orbit coupling, which is expected to be quite large in a 5*d* metal such as tungsten. The MCD spectrum did not resolve any individual spin-orbit components, although more than one is expected. There were two possibilities for the assignment of band A. First, the triplet excited state partner $^3E_g[e^3_g(\sim d_{xz,yz})$ $a^1_{1g}(\sim d_z2)]$ associated with the singlet LF excited state $^1E_g[e^3_g(\sim d_{xz,yz})a^1_{1g}(\sim d_z2)]$ might be involved, since the triplet state originating from the same electronic configuration as the singlet state is always at a lower energy than that of its singlet partner.[23,24] The spin-orbit coupling results in five states $\bar{\Gamma}$:$\bar{E}_g$, $\bar{A}_{1g}$, $\bar{A}_{2g}$, $\bar{B}_{1g}$, and $\bar{B}_{2g}$. However, any transition $\bar{A}_{1g}(^1A_{1g}) \rightarrow \bar{\Gamma}$ (^3E_g) has to be allowed vibronically to be observed, *i.e.*, the transition has to be $\bar{A}_{1g}$ $(^1A_{1g})\cdot\Gamma^v \rightarrow \bar{\Gamma}(^3E_g)$ (or $\bar{A}_{1g}$ $(^1A_{1g}) \rightarrow \cdot\bar{\Gamma}(^3E_g)\cdot\Gamma^v$), since a vibrational mode allowing each of these states exists. The second and more likely assignment of band A involves the triplet excited state $^3E_g[$ $e^3_g(d_{xz,yz})a^1_{2u}$ $(\sim\pi^*(CO))]$ associated with the singlet[23,24] MLCT excited state ^1E_u of band I. The five spin-orbit components of $^3E_u[e^3_g(\sim d_{xz,yz})$ $a^1_{2u}(\sim\pi^*(CO))]$ are $\bar{E}_u$, A_{1u}, $\bar{A}_{2u}$, $\bar{B}_{1u}$, and $\bar{B}_{2u}$. Electric dipole selection rules allow transitions to $\bar{E}_u(^3E^a_u)$ and $\bar{A}_{2u}$ $(^3E^3_g)$, and both are most likely responsible for the broad band A.

The sign of the MCD A-parameter is the same as the sign of the A/D parameter; but the latter is easier to compute and can be compared with experimental values. We take the bands to be Gaussian, so that the dipole strength parameters, D, can be extracted from the EA spectra,[25]

$$D_{(a\rightarrow j)} = 9.76 \times 10^{-3} \frac{\varepsilon_{max} \cdot \Gamma_{FWHH}}{\varepsilon_0} \tag{7}$$

where ε_{max} is the molar absorptivity ($mol^{-1} \cdot l \cdot cm^{-1}$) at the maximum absorption, Γ_{FWHH} (cm^{-1}) the full width at half height, and ε_0 (cm^{-1}) the band location at the maximum of absorption. For extraction of the experimental A- and B-parameters from the MCD spectra, we use,[26]

$$[\theta]_m = -21.34(Af_1 + (B + \frac{C}{kT})f_2) \tag{8}$$

where

$$f_1 = \frac{\sqrt{\pi}\varepsilon(\varepsilon-\varepsilon_0)\exp\left[-\frac{(\varepsilon-\varepsilon_0)^2}{\Delta^2}\right]}{h\Delta^3} \tag{9}$$

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$$f_2 = \frac{\sqrt{\pi}\varepsilon \exp\left[-\frac{(\varepsilon-\varepsilon_0)^2}{\Delta^2}\right]}{2\Delta} \tag{10}$$

ε_0 and Δ ($\Gamma_{FWHH} = 2\Delta\sqrt{\ln 2}$) are taken from the corresponding EA band. These A values were converted to $\overline{A}_1$.[12]

The theoretical expressions for an ${}^1A_{1g} \rightarrow {}^1E_u$ transition, using the most recent formalism,[12] yields, in reduced matrix element form, our MCD parameter,

$$\overline{A}_1 = \left(\sum_{ijk=-1}^{1} (\varepsilon_{ijk})(\mathrm{MCD}_{ijk}\mathrm{factor}) \frac{\{A\}}{3\mu B\,|A|} \|\mu^{f_i}\| \begin{Bmatrix} f_i & f_j & f_k \\ A^* & J^* & J^* \end{Bmatrix} \|m^{f_j}\| \ m^{f_k}\| \right) \quad [\mathrm{Debye}^2] \tag{11}$$

where $|\mu^{f_i}\| = \langle {}^1E \| \mu^{f_i} \| {}^1E \rangle$, $\|m^{f_j}\| = \langle {}^1A \| m^{f_j} \| {}^1E \rangle$, $\|m^{f_k}\| = \langle {}^1E \| m^{f_k} \| {}^1A \rangle$, $\mu_z = -\mu_B L_z$, and {} is a 6j symbol. Expanding the above summation, followed by explicit irreducible representation substitution (ground-state, excited-state and operators), then evaluating the resulting 6j coefficients gives, in complex basis,

$$\overline{A}_1 = -\frac{1}{6\mu_B} \|\mu^{f_i}\| \|m^{f_j}\| \|m^{f_k}\| [(\mathrm{MCD}_{01-1}\mathrm{factor}) - (\mathrm{MCD}_{0-11}\mathrm{factor})] \quad [\mathrm{Debye}^2] \tag{12}$$

Next, using the 6j relationship,

$$(\mathrm{MCD}_{ijk}\mathrm{factor}) = \langle f_i'\phi_i' | \mu_i \rangle \langle f_j\phi_j | m_j \rangle \langle f_k\phi_k | m_k \rangle \begin{Bmatrix} f_i & f_j & f_k \\ A^* & J^* & J^* \end{Bmatrix} \tag{13}$$

numerical values were obtained for the latter two MCD factors, so that

$$\overline{A}_1 = \frac{1}{3\sqrt{2}\mu_B} \|\mu^{f_i}\| \|m^{f}_j\| \|m^{f_k}\| \qquad [\mathrm{Debye}^2] \tag{14}$$

Our EAS electric dipole strength in this formalism is,

$$\overline{D}_0 = \frac{\{A\}}{3\,|A|} \sum_{i=-1}^{1} \left(\frac{1}{|f_j|} \delta(A^* f_j J)\{A^* f_j J\} \|m^{f_j}\| \|m^{f_k}\| \right) \quad [\mathrm{Debye}^2] \tag{15}$$

Expanding the summation, followed by explicit substitution of appropriate irreducible reps (*i.e.*, electric dipole moment operator, ground and excited states) and then evaluating the 2j and 3j phases gives

$$\overline{D}_0 = \frac{1}{3} \|m^{f_j}\| \| m^{f_k}\| \qquad [\mathrm{Debye}^2] \tag{16}$$

so that ratio $\overline{A}_1/\overline{D}_0$ is,

$$\frac{\overline{A}_1}{\overline{D}_0} = \frac{1}{\sqrt{2}} \langle {}^1E \| L^{A_{2g}} \| {}^1E \rangle \tag{17}$$

This is to be compared to $[\overline{A}_{1(\exp)}/\overline{D}_{0(\exp)}]$. Further evaluation of the reduced matrix element and substituting the appropriate MO type proposed for MLCT transition I, ${}^1E_u^a[e_g^3(\sim d_{xz,yz})a_{2u}^1(\sim \pi^*(CO))]$, gives

$$\frac{\overline{A}_1}{\overline{D}_0} = +\frac{1}{\sqrt{2}} \langle e_g \| 1^{a_{2g}} \| e_g \rangle \tag{18}$$

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Unreducing the matrix elements yields,

$$\frac{\overline{\mathrm{A}}_1}{\overline{\mathrm{D}}_0} = (\,-\,) < \mathrm{e}_g^*(y) \;\; 1_z^{a2g} \;\; \mathrm{e}_g^*(x) > \tag{19}$$

where $e_g^*(y)$ and $e_g^*(x)$ are the MO fates of the E_u excited state.

The calculated $\overline{A}_1/\overline{D}_0$ of band I, ${}^1A_{1g}[e_g^4(\sim d_{xz,yz})] \rightarrow {}^1E_u^a[e_g^3a_{2u}^1(\sim\pi^*(CO))]$ equals 0.77 for *trans*-$[Cr(CO)_4(PH_3)_2]$, and experimental $\overline{A}_{1(\text{MCD Spectrum})}/\overline{D}_{0(\text{EA Spectrum})}$ of the $P(n\text{-}Bu)_3$ analog equals 0.21. The dipole strengths D, and A-parameters of the earlier definition and formalism,[26] were calculated from the EA and MCD spectra by using Eqs. 7 and 8, respectively. These D and A values were converted to their analogs $\overline{D}_0$ and $\overline{A}$ of the most recent formalism[12] for this comparison of signs of experimental and computer $\overline{A}/\overline{D}_0$.

For MLCT transition III, the relationship given by Eq. 17 is

$$\frac{\overline{\mathrm{A}}_1}{\overline{\mathrm{D}}_0} = \frac{1}{\sqrt{2}} < \mathrm{E}_u^b \,\|\, \mathrm{L}^{A_{2g}} \,\|\, \mathrm{E}_u^b > \tag{20}$$

where $L^{A_{2g}}$ is again the angular momentum operator, and ${}^1E_u^b[b_{2g}^1(\sim d_{xy})e_u^1(\sim(CO))]$ is the degenerate MLCT excited state. Reducing Eq. 20 into an equation in terms of MOs yields

$$\frac{\overline{\mathrm{A}}_1}{\overline{\mathrm{D}}_0} = <\mathrm{e}_u^*(\pi^*,y) \;\; l_z \;\; \mathrm{e}_u^*(\pi^*,x)> \tag{21}$$

where $e_u^*(\pi^*, y)$ and $e_u^*(\pi^*, x)$ are the MO fates of the transition to the excited state E_u^b. These MOs have a more complicated expression than $e_g^*(x)$ and $e_g^*(y)$ MOs involved in the MLCT excited state E_u^a, and the full matrix of one-, two-, and three-center integrals was again evaluated. From our calculations we find $[\overline{A}_1/\overline{D}_0]_{\text{Theo}} = +0.50$ for *trans*-$[Cr(CO)_4(PH_3)_2]$. The experimental $\overline{A}_{1(\text{MCD Spectrum})}/\overline{D}_{0(\text{EA Spectrum})}$ for band III, ${}^1A_{1g}[b_{2g}^2(\sim d_{xy})] \rightarrow {}^1E_u^b[b_{2g}^1e_u^1](\sim\pi^*(CO))]$, equals 0.32 for the compound *trans*-$[Cr(CO)_4(P(n\text{-}Bu)_3)_2]$, which matches the computed sign, and its magnitude is in reasonable agreement with theory.

For the third possible $g \rightarrow u$ *xy*-polarized transition, ${}^1A_{1g}[e_g^4(\sim d_{xz,yz})] \rightarrow {}^1E_u^c[e_g^3b_{2u}^1(\pi^*(CO))]$, we have

$$\frac{\overline{\mathrm{A}}_1}{\overline{\mathrm{D}}_0} = \frac{1}{\sqrt{2}} < \mathrm{E}_u^c \,\|\, \mathrm{L}^{A_{2g}} \,\|\, \mathrm{E}_u^c > \tag{22}$$

Evaluating all one-, two- and three-center integrals gives $[\overline{A}_1/\overline{D}_0]_{\text{Theo}} = -0.77$. As stated above, the absence of a negative A-term in the energy region of bands I-III presently studied eliminates E_u^c as a possible assignment.

To evaluate $\overline{A}_1/\overline{D}_0$ the all-center operator matrix model[27] was used to calculate $<l_z>$, since many multi-center integrals were needed. Bond distances (Cr-P = 2.346A, Cr-C = 1.88A, C-O = 1.15A,) for the *trans*-$[Cr(CO)_4(P)_2]$ skeleton were taken from the literature.[28] The P-H bond distance (1.415A) and angles were those observed for phosphine.[29] ξ-functions and coefficients were: chromium:[30] $\xi_{4s} = 1.7$, $C_{4s} = 1.0$, $\xi_{4p} = 1.7$, $C_{4s} = 1.0$, $\xi_{3d} = 4.95$, $C_{3d} = 0.5060$, $\xi'_{3d} = 1.80$, $C'_{3d} = 0.675$; carbon:[31] $\xi_{2s} = 1.6083$, $C_{2s} = 1.00$, $\xi_{2p} = 1.5679$, $C_{2p} = 1.00$;

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oxygen:[31] $\xi_{2s} = 2.2458$, $C_{2s} = 1.00$, $\xi_{2p} = 2.2266$, $C_{2p} = 1.00$; phosphorus:[31] $\xi_{3s} = 1.75$, $C_{3s} = 1.00$, $\xi_{3p} = 1.30$, $C_{3p} = 1.00$; and hydrogen; $\xi_{1s} = 1.2$, $C_{1s} = 1.00$.[32] Basis orbital energies from the literature were used (2s, 2p for C,O and 3s, 3p for P of ref.[33]; 1s H is - 13.6 eV; and 4d, 5s, 5p for Cr of ref.[30]. The 69 functions were used to compute the complete 55 x 55 S and L_z matrices,[27,34] and subsequently the MO C matrix,[35] on an IBM 3081 (Triangle University Computing Center). MO phases were carefully matched with all other MCD computational features.

The first intense transition (band I), ${}^1A_{1g}[e_g^4(\sim d_{xz,yz})] \rightarrow {}^1E_u^a[e_g^3\alpha_{2u}^1(\sim\pi^*(CO))]$, involves removing one electron from the metal-carbon π bonds of the primarily metal centered e_g bonding MO (Figure 3). This weakens the metal-carbon (M-CO) π bonds in the *xz*- and *yz*-planes as well as strengthening slightly the C-O bonds since the electron density in the antibonding π^* of the ligand from the back bonding is decreased. The transition increases electron density in the a_{2u} antibonding MO which is primarily $\pi^*(CO)$ in character, so that there is a bond order lowering of the carbon-oxygen π bonding in the *xz*- and *yz*-planes. Therefore, the primary effect of this MLCT transition is to weaken the M-C π bond strength, and the secondary one to decrease the net C-O π bond; both weakenings take place in the *xz*- and *yz* planes,

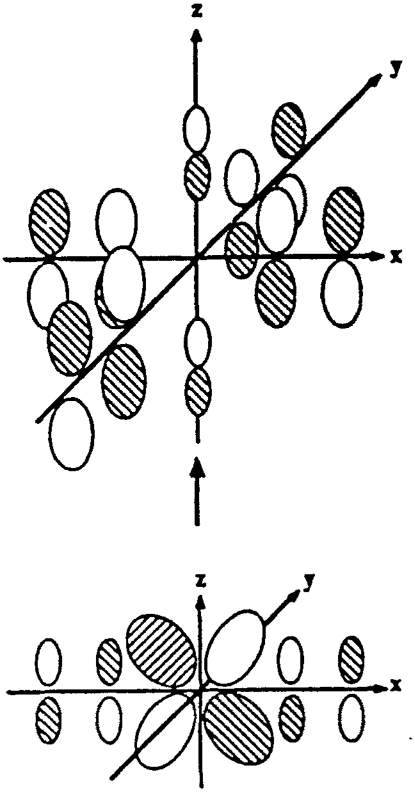

Figure 3 MO transition $e_g(\sim d_{xz}) \rightarrow a_{2u}(\sim\pi^*CO)$ of band I. $4p_z(Cr)$ contributions to a_{2u} are very small.

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perpendicular to the *xy*-plane of the molecule.

For the second MLCT transition (band II), $^1A_{1g}[e_g^4(\sim d_{xz,yz})] \rightarrow {}^1A_{2u}[e_g^3(\sim d_{xz,yz})$ $e_u^1(\sim\pi^*)CO))]$, one electron was again removed from the mainly metal localized e_g bonding MO, but it was moved to the e_u antibonding MO which is predominantly $\pi^*(CO)$ localized (Figure 4). This results simultaneously in weakening of the metal-carbon π bonds (with some strengthening of the C-O π bonds) in the *xz*- and *yz*-planes, and of the carbon-oxygen π bonds in the *xy*-plane. The loss of bond strength is therefore in two different orientations, with the following relative 'labilizing' effects C-O π bonds in *xy*-plane > M-C π bonds in *xz*-, *yz*-planes.

The MLCT transition III at higher energy, $^1A_{1g}[b_{2g}^2(\sim d_{xy})] \rightarrow {}^1E_u^b[b_{2g}^1(\sim d_{xy})$ $e_u^1(\sim\pi^*(CO))]$, involves the movement of one electron from the mainly metal localized b_{2g} bonding MO in the *xy*-plane and to the dominantly $\pi^*(CO)$ localized e_u antibonding MO (Figure 5). This creates both weakening of the metal-carbon π bonds in the *xy*-plane, and of the carbon-oxygen π bond of the ligand in the same *xy*-plane. Thus the net effects of bond weakening are in the *xy*-plane.

In summary, for these tetracarbonyl molecules, accurate and full-matrix angular momentum (L_z) computations were carried out in order to evaluate magnitudes and

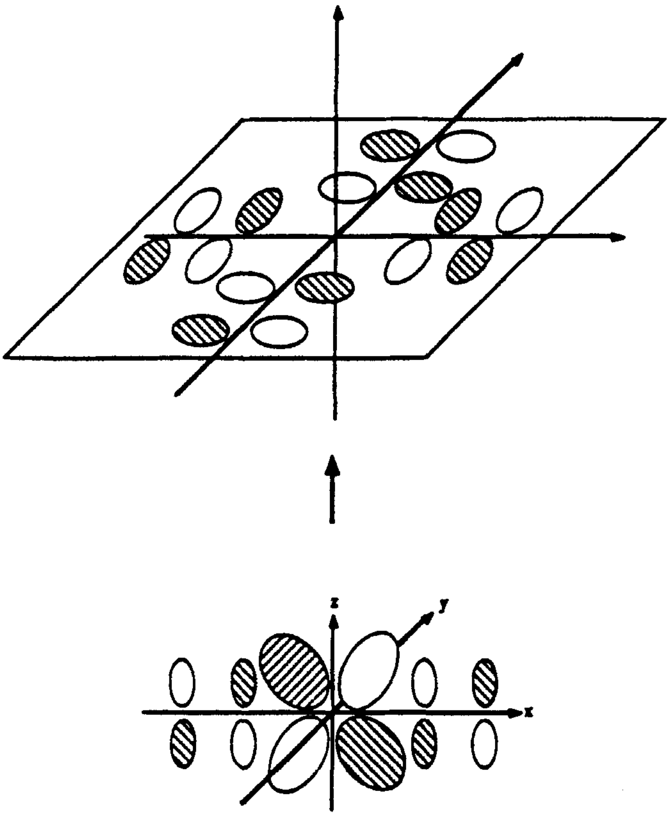

Figure 4 MO transition $e_g(\sim d_{xz}, yz) \rightarrow e_u(\sim\pi^*CO)$ of band II. $4p_{x,y}(Cr)$ contributions to e_g are very small.

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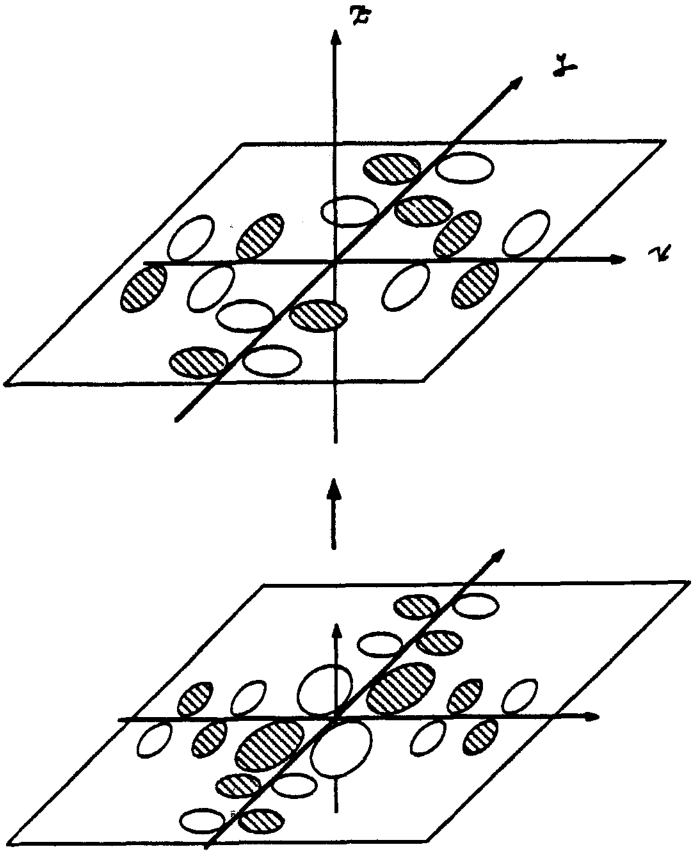

Figure 5 MO transition $b_{2g}(\sim dxy) \rightarrow e_u(\sim\pi^*CO)$ of band III. $4p_{x,y}(Cr)$ contributions to e_u are very small.

signs of MCD A/D factors for state functions. The match-up of these signs with experimental values aided in ascertaining MO origins and MO and state identities of several electronic transitions. When these conclusions are combined with LF analysis of smaller bands, the band assignments and some MCD parameters are:

	$\overline{A}_1 / \overline{D}_0$	
Band A		LF and MLCT: ${}^1A_{1g} \rightarrow {}^3E_g$ (configs. of Band II′) ${}^1A_{1g} \rightarrow {}^3E_g$ (configs. of Band I)
Band I.	+ 0.21	MLCT: ${}^1A_{1g}[e_g^4(\approx d_{xz,\ yz})] \rightarrow {}^1E_u^a[e_g^3a_{2u}\ (\pi^*CO)]$
Band II′.	B(–)	LF: ${}^1A_{1g}[e_g^4(\approx d_{xz,\ yz})] \rightarrow {}^1E_g[{}_g^3a_{1g}(\approx dz^2)]$
Band II.	B(+)	MLCT: ${}^1A_{1g}[e_g^4(\approx d_{xz,\ yz})] \rightarrow {}^1A_{2u}[e_g^3e_u(\pi^*CO)]$
Band C.	B(–)	LF: ${}^1A_{1g}[b_{2g}^2(\approx d_{xy})] \rightarrow {}^1A_{2g}[b_{2g}b_{1g}(\approx d_{x^2} - y^2)]$
Band III.	+ 0.32	MLCT: ${}^1A_{1g}[b_{2g}^2(\approx dxy)] \rightarrow {}^1E_u^b[b_{2g}e_u\ (\pi^*CO)]$

where B(–) and B(+) are Faraday B-parameters with negative and positive intensity, respectively. It was also shown why previous assignments[4] by others for the two bands labeled III and C above, needed to be reassigned.

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