The Electronic Structure of Compounds Containing Metal–Metal Bonds. Decacarbonyldimetal and Related Complexes

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Received February 26, 1975

Abstract: The results of a semiempirical molecular orbital calculation for $Mn_2(CO)_{10}$ and an electronic spectral investigation ($M_2(CO)_{10}$ (M = Mn, Tc, Re) and $MnRe(CO)_{10}$ are reported. The calculation is fully consistent with the assignment of the electronic absorption band at 29,400 cm^{-1} in $Mn_2(CO)_{10}$ to a transition between the σ and σ^* orbitals associated with the metal–metal bond. The energy of the $\sigma \rightarrow \sigma^*$ band maximum for each of the four decacarbonyldimetal complexes increases with decreasing temperature and with increasing metal–metal stretching force constant. Metal to ligand charge transfer (MLCT) bands are assigned within the derived molecular orbital framework. Absorptions attributable to $\sigma \rightarrow \pi^*$ (CO) and $d\pi \rightarrow \pi^*$(CO) transitions are observed between 33,000 and 38,000 cm^{-1} in all four complexes. An extremely intense band near 50,000 cm^{-1} ($\epsilon \sim 10^5$) in each case is assigned primarily to the $d\pi \rightarrow \pi^*$(CO) transitions $6e_1 \rightarrow 2a_2$ and $6e_3 \rightarrow 2b_1$. Electronic spectra of the related complexes $MnCr(CO)_{10}^-$, $Cr_2(CO)_{10}^{2-}$, $Mn_2(CO)_9(PPh_3)$, and $Mn_2(CO)_8(PPh_3)_2$, are also reported and assigned.

In 1970 we reported the polarized electronic spectra of $Mn_2(CO)_{10}$ in a nematic liquid crystal and assigned an intense band at 29,400 cm^{-1} to a transition between the σ and σ^* orbitals associated with the metal–metal bond.[1] Bands attributable to $\sigma \rightarrow \sigma^*$ transitions were also identified in the electronic absorption spectra of $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$. Several workers have subsequently studied the photochemical behavior of decacarbonyldimetal and other binuclear complexes containing single metal–metal bonds and have found excited-state reaction pathways to be in accord with the population of a σ^* orbital.[2-4] Additionally, it may be noted that the position of the $\sigma \rightarrow \sigma^*$ band apparently correlates with certain thermal reaction characteristics of several binuclear metal carbonyls.[5]

We have now completed a detailed theoretical and experimental examination of the electronic spectrosocpic properties of decacarbonyldimetal and related complexes. It is our purpose in this paper to develop a full interpretation of the electronic spectra of these complexes and particularly to pay attention to the identification of experimental criteria that may be used to assign $\sigma \rightarrow \sigma^*$ bands in other binuclear systems. Subsequent publications will be concerned with polynuclear complexes such as $Ru_3(CO)_{12}$ and $Mn_2Fe(CO)_{14}$.

Experimental Section

$Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from the Pressure Chemical Co. $Tc_2(CO)_{10}$ was kindly loaned by the AEC Savannah River Laboratory, Aiken, S.C. $MnRe(CO)_{10}$ was the generous gift of Dr. J. M. Smith. All these compounds were sublimed immediately prior to use. $(Et_4N)[MnCr(CO)_{10}]$ was prepared by the method of Anders and Graham[6] and recrystallized from 95% ethanol in a Schlenk tube. The infrared spectrum in the carbonyl stretching region, recorded in tetrahydrofuran freshly distilled from lithium aluminum hydride, showed no extraneous bands attributable to $Mn_2(CO)_{10}$. Anal. Calcd for $(Et_4N)[MnCr(CO)_{10}]$: C, 41.79; H, 3.90. Found: C, 41.75; H, 3.86. $(Et_4N)_2[Cr_2(CO)_{10}]$ was prepared and purified according to Hayter;[7] it was stored under nitrogen in a Schlenk tube. $Mn_2(CO)_8(PPh_3)_2$ was prepared according to Osborne and Stiddard,[8] and stored under nitrogen in the dark. Anal. Calcd for $Mn_2(CO)_8(PPh_3)_2$: C, 61.56; H, 3.52. Found: C, 61.46; H, 3.61. $Mn_2(CO)_9(PPh_3)$ was prepared by the method of Wawersik and Basolo[9] and purified by the chromatographic technique of Ziegler, Haas, and Sheline.[10] Anal. Calcd for $Mn_2(CO)_9(PPh_3)$: C, 51.95; H, 2.42. Found: C, 52.10; H, 2.28.

Infrared spectra were recorded with a Perkin-Elmer Model 225 spectrophotometer. The appropriate spectral grade solvents were used for comparing the spectra of the above compounds with literature data. Electronic spectra were recorded on Cary Model 14 CMRI and Cary Model 14 spectrophotometers. The electronic spectrum of the air-sensitive $Cr_2(CO)_{10}^{2-}$ anion was recorded by dissolving a small amount in deoxygenated absolute alcohol and then transferring the solution to a quartz cell; manipulations were carried out in a nitrogen atmosphere in a Schlenk apparatus. All other compounds were sufficiently stable that no special precautions had to be taken, although we always kept light levels low and worked rapidly.

Spectra at 77 K were recorded in a total immersion dewar constructed entirely of quartz; the windows were of optical grade material. A baseline was run for every spectrum to correct for solvent absorption. With care, precision of 1–2% could be obtained. Solvents for low temperature spectra were either EPA, a 5:5:2 mixture of ethyl ether, isopentane, and ethanol, or 3-PIP, a 6:1 mixture of isopentane and 3-methylpentane. Low temperature spectra were corrected for solvent contraction using the appropriate data for EPA[11] and 3-PIP.[12] The Raman spectrum of $Tc_2(CO)_{10}$ was recorded with a Cary Model 81 spectrophotometer equipped with a Spectra Physics Model 125 He–Ne (632.8 nm) laser.

Theoretical

We have performed an iterative, extended-Hückel-type molecular orbital calculation on $Mn_2(CO)_{10}$, utilizing the coordinate system of Figure 1. The drawing of the D_{4d} molecule is idealized in that it shows each metal and its four equatorial ligands in a plane, whereas in fact the average $M-M-C_{eq}$ angle is ~86° in both $Mn_2(CO)_{10}$[13] and $Tc_2(CO)_{10}$.[14] This angle could be the result of repulsions between equatorial and axial ligands on the same metal,[13] or perhaps an interaction of π-type orbitals on ligands bonded to one metal atom with d orbitals on the other.[15] (The latter interaction has been considered in certain theoretical treatments of $M_2(CO)_{10}$ molecules.)[16,17] Discussions of the $M-M-C_{eq}$ angle have also been given by Handy et al.[18] and Brown et al.[19] Although the relative energies of the various d orbitals should be sensitive to this angle,[20] it is not likely that the small difference between 86° and the 90° value assumed in our calculations will be at all significant. Bond distances used are Mn–Mn = 2.92, $Mn-C_{eq}$ = 1.83,

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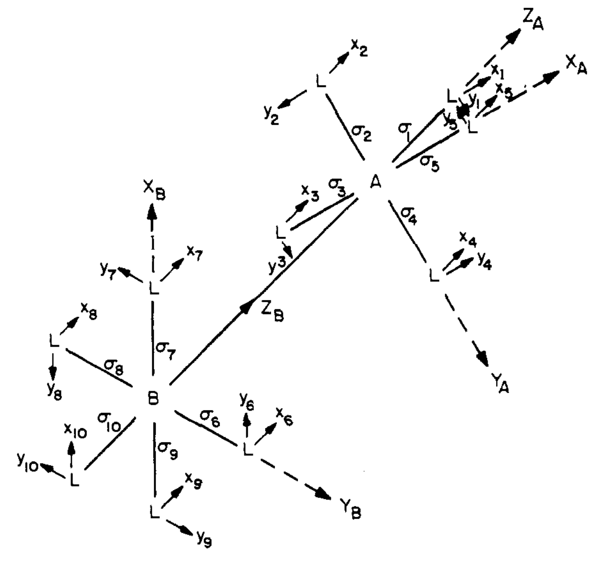

Figure 1. Reference coordinate system for an M_2L_{10} molecule of D_{4d} symmetry.

$Mn-C_{ax}$ = 1.79, $C_{eq}-O_{eq}$ = 1.16, and $C_{ax}-O_{ax}$ = 1.15 Å, where ax and eq represent axial and equatorial, respectively.

Symmetry basis orbitals for D_{4d} $M_2(CO)_{10}$ molecules are given in Table I. Each x- and y-type ligand combination refers to filled π *and* unfilled π^* orbitals. In addition to π and π^* functions, the ligand basis set[21] includes two filled σ orbitals. The metal basis orbitals are 3d, 4s, and 4p, as given by Richardson for neutral manganese (the p function was that for d^6p).[22]

The calculational procedure has been described previously.[21] Appropriate modifications for the fact that there are two metal centers were made, the most significant being that corrections were applied to the H_{ii}'s (diagonal elements of the energy matrix) of the metal orbitals to account for overlap. (In mononuclear complexes, such corrections need only be made for the ligand H_{ii}'s.) F_K parameters used are $F_{M\sigma} = F_{\sigma\sigma} = 1.52$, $F_{M\pi} = F_{\pi\pi} = 2.21$, $F_{\sigma\pi} = F_{MM} = 2.00$, i.e., the same as used[21] for $Mn(CO)_6^+$. F_{MM} refers to interactions between different metal orbitals.

A partial listing of eigenvalues for the molecular orbitals of $Mn_2(CO)_{10}$ is given in Table II.[23] The ground state is $^1A_1$ $(6a_1)^2$, in accord with the observed diamagnetism of the molecule.[24] The highest occupied MO, $6a_1$, is σ bonding between the two Mn atoms and will be referred to simply as σ. The corresponding σ^* MO, $6b_2$, is the lowest empty level. Thus the calculation suggests that the character of some of the lowest energy electronic transitions will be strongly influenced by the Mn-Mn interaction. The $6e_1$, $6e_3$, and $5e_2$ levels (the $d\pi$ MO's) are calculated to be within 2800 cm^{-1} of each other. This supports the idea that interactions involving $d\pi$ electrons across the Mn-Mn bond are not very large, although they are not entirely negligible. The lowest unoccupied MO possessing π^*(CO) character is $7e_1$. Above $7e_1$ are several unfilled π^*(CO) levels that are evenly spread out over a range of about 10,000 cm^{-1}. The spacings of the three filled $d\pi$ and the several π^* levels, therefore, forecast very broad absorption band systems for metal to ligand charge transfer (MLCT) excitations.

The σ level is calculated to be at −65,340 cm^{-1}, which compares favorably with measured ionization potentials of 69,200 cm^{-1} (electron impact)[25] and 64,700 cm^{-1} (photoelectron spectroscopy).[26] The second and third ionization potentials found for $Mn_2(CO)_{10}$ in the photoelectron study are 67,300 and 72,400 cm^{-1}. The approximate relative areas of the first, second, and third photoelectron bands are 1:2:4. Thus the results are consistent with assignment of σ as the highest filled level. The second and third photoelectron bands imply the existence of three doubly degenerate levels, of which the two lowest are approximately equal in energy. A ground state configuration for $Mn_2(CO)_{10}$ of $(5e_2)^4$ $(6e_1)^4$ $(6e_3)^4$ $(6a_1)^2$ has been proposed by Evans et al.[26] on the basis of these photoelectron results: they stated that the order $6e_3 > 6e_1$ seemed likely from overlap considerations but that the relative position of $5e_2$ was not apparent. Our calculation gives the order $(6e_1)^4$ $(6e_3)^4$ $(5e_2)^4$ $(6a_1)^2$. Although it is clear that the photoelectron bands in question correspond to $d\pi$ ionizations, more specific assignments cannot be made with any confidence at this time.

Table I. Orbital Transformation Scheme for M_2L_{10} Molecules in D_{4d} Symmetry

Representation	Metal orbitals	Ligand orbitals
a_1	$1/\sqrt{2}[s_B + s_A]$	$1/\sqrt{2}[\sigma_1 + \sigma_{10}]$
	$1/\sqrt{2}[d_{z^2B} + d_{z^2A}]$	$1/\sqrt{2}[\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6 + \sigma_7 + \sigma_8 + \sigma_9]$
	$1/\sqrt{2}[p_{zB} - p_{zA}]$	$1/\sqrt{8}[x_2 + x_3 + x_4 + x_5 - x_6 - x_7 - x_8 - x_9]$
a_2		$1/\sqrt{8}[y_2 + y_3 + y_4 + y_5 + y_6 + y_7 + y_8 + y_9]$
b_1		$1/\sqrt{8}[y_2 + y_3 + y_4 + y_5 - y_6 - y_7 - y_8 - y_9]$
b_2	$1/\sqrt{2}[s_B - s_A]$	$1/\sqrt{2}[\sigma_1 - \sigma_{10}]$
	$1/\sqrt{2}[d_{z^2B} - d_{z^2A}]$	$1/\sqrt{8}[\sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 - \sigma_6 - \sigma_7 - \sigma_8 - \sigma_9]$
	$1/\sqrt{2}[p_{zB} + p_{zA}]$	$1/\sqrt{8}[x_2 + x_3 + x_4 + x_5 + x_6 + x_7 + x_8 + x_9]$
e_1	$1/2[\sqrt{2}p_{xB} + p_{xA} - p_{yA}]$ $1/2[\sqrt{2}d_{xzB} - d_{xzA} + d_{yzA}]$	$1/\sqrt{8}[\sigma_2 - \sigma_3 - \sigma_4 + \sigma_5 + \sqrt{2}(\sigma_7 - \sigma_9)]$ $1/\sqrt{8}[x_2 - x_3 - x_4 + x_5 + \sqrt{2}(x_9 - x_7)]$ $1/\sqrt{8}[y_2 + y_3 - y_4 - y_5 + \sqrt{2}(y_8 - y_6)]$ $1/2[x_1 - y_1 + \sqrt{2}x_{10}]$
	$1/2[\sqrt{2}p_{yB} + p_{yA} + p_{xA}]$ $1/2[\sqrt{2}d_{yzB} - d_{xzA} - d_{yzA}]$	$1/\sqrt{8}[\sigma_2 + \sigma_3 - \sigma_4 - \sigma_5 + \sqrt{2}(\sigma_8 - \sigma_6)]$ $1/\sqrt{8}[x_2 + x_3 - x_4 - x_5 + \sqrt{2}(x_6 - x_8)]$ $1/\sqrt{8}[y_2 - y_3 - y_4 + y_5 + \sqrt{2}(y_7 - y_9)]$ $1/2[x_1 + y_1 + \sqrt{2}y_{10}]$
e_2	$d_{xyA}, d_{x^2-y^2B}$	$1/2[\sigma_6 - \sigma_7 + \sigma_8 + \sigma_9]$ $1/2[x_6 - x_7 + x_8 - x_9]$ $1/2[y_2 - y_3 + y_4 - y_5]$
	$d_{xyB}, d_{x^2-y^2A}$	$1/2[\sigma_2 - \sigma_3 + \sigma_4 - \sigma_5]$ $1/2[x_2 - x_3 + x_4 - x_5]$ $1/2[y_6 - y_7 + y_8 - y_9]$
e_3	$1/2[\sqrt{2}p_{xB} - p_{xA} + p_{yA}]$ $1/2[\sqrt{2}d_{xzB} + d_{xzA} - d_{yzA}]$	$1/\sqrt{8}[\sigma_2 - \sigma_3 - \sigma_4 + \sigma_5 + \sqrt{2}(\sigma_9 - \sigma_7)]$ $1/\sqrt{8}[x_2 - x_3 - x_4 + x_5 + \sqrt{2}(x_7 - x_9)]$ $1/\sqrt{8}[y_2 + y_3 - y_4 - y_5 + \sqrt{2}(y_6 - y_8)]$ $1/2[\sqrt{2}x_{10} -- x_1 + y_1]$
	$1/2[\sqrt{2}p_{yB} - p_{yA} - p_{xA}]$ $1/2[\sqrt{2}d_{yzB} + d_{xzA} + d_{yzA}]$	$1/\sqrt{8}[\sigma_2 + \sigma_3 - \sigma_4 - \sigma_5 + \sqrt{2}(\sigma_6 - \sigma_8)]$ $1/\sqrt{8}[x_2 + x_3 - x_4 - x_5 + \sqrt{2}(x_8 - x_6)]$ $1/\sqrt{8}[y_2 - y_3 - y_4 + y_5 + \sqrt{2}(y_9 - y_7)]$ $1/2[\sqrt{2}y_{10} - x_1 - y_1]$

Both the calculation and the photoelectron study show the level below the lowest filled metal d orbital to be at

Table II. Selected Eigenvalues for $Mn_2(CO)_{10}$

$-E(cm^{-1})$	Level[a]	
−620	$8b_2$	p
5,580	$10e_1$	
18,060	$9e_3$	π^*
18,530	$8e_2$	$d_{x^2-y^2}$
18,600	$2a_2$	π^*
19,730	$8a_1$	
20,430	$2b_1$	
21,410	$7e_2$	
21,960	$9e_1$	
22,790	$8e_3$	
24,480	$7b_2$	
25,120	$8e_1$	
27,590	$7e_3$	
28,710	$6e_2$	
30,300	$7e_1$	p, π^*
33,080	$7a_1$	s, p
39,420	$6b_2$	σ^* d_{z^2} comb
65,340	$6a_1$	σ
66,620	$5e_2$	d_{xy}
67,290	$6e_3$	d_{xz}, d_{yz}
69,390	$6e_1$	
102,950	$5b_2$	σ_{ax}

[a] The highest occupied MO in the ground state is $6a_1$.

Table III. Electronic Spectral Data and Transition Assignments for the Neutral Decacarbonyldimetal Complexes

Complex	Band	ν_{max} $(cm^{-1})^a$	ϵ^a	Assignment
$Mn_2(CO)_{10}$	I	26,700	2,900	$d\pi \rightarrow \sigma^*[{}^1A_1 \rightarrow {}^1E_1\ (6e_3 \rightarrow 6b_2)]$
	II	29,740	33,700	$\sigma \rightarrow \sigma^*[{}^1A_1 \rightarrow {}^1B_2\ (6a_1 \rightarrow 6b_2)]$
	IIIA	(33,000)[b]	(7,500)[b]	$\sigma \rightarrow \pi^*$
	IIIB	37,600	8,200	$d\pi \rightarrow \pi^*$
	IV	49,100[c]	84,400[c]	$M \rightarrow \pi^*$
$Tc_2(CO)_{10}$	II	32,400	26,600	$\sigma \rightarrow \sigma^*$
	IIIA	35,500	12,700	$\sigma \rightarrow \pi^*$
	IIIB	38,200	11,200	$d\pi \rightarrow \pi^*$
	IV	51,500[c]	104,000[c]	$M \rightarrow \pi^*$
$Re_2(CO)_{10}$	II	32,800	24,000	$\sigma \rightarrow \sigma^*$
	IIIA	36,000	18,100	$\sigma \rightarrow \pi^*$
	IIIB	38,100	12,500	$d\pi \rightarrow \pi^*$
	IV	>52,500[c]	>100,000[c]	$M \rightarrow \pi^*$
$MnRe(CO)_{10}$	II	31,950	20,100	$\sigma \rightarrow \sigma^*$
	IIIA	36,000	11,400	$\sigma \rightarrow \pi^*$
	IIIB	37,700	9,900	$d\pi \rightarrow \pi^*$
	IV	51,700[c]	86,600[c]	$M \rightarrow \pi^*$

[a] At 77 K in 3-PIP. [b] From Gaussian analysis of a spectrum measured in acetonitrile solution (N. A. Beach, Ph.D. Dissertation, Columbia University, 1967). [c] At 300° K in acetonitrile.

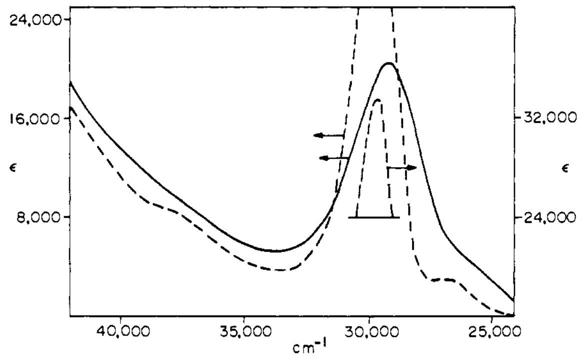

Figure 2. Electronic spectra of $Mn_2(CO)_{10}$ in 3-PIP: —, 300 K; - - -, 77 K.

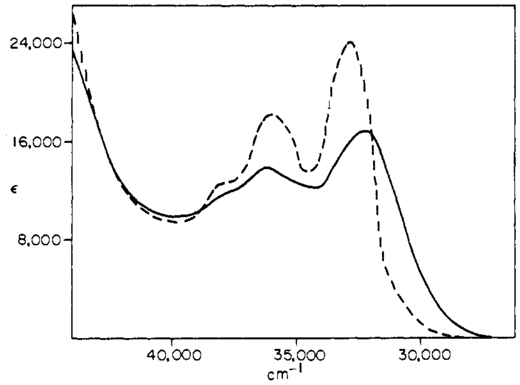

Figure 3. Electronic spectra of $Re_2(CO)_{10}$ in 3-PIP: —, 300 K; - - -, 77 K.

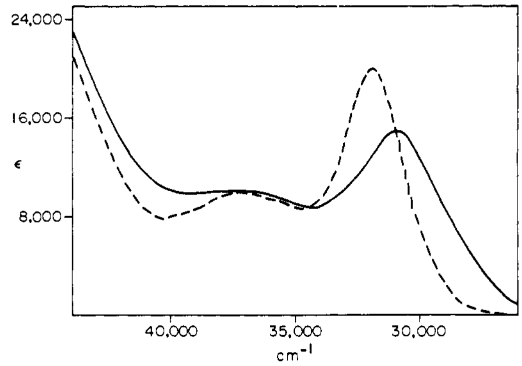

Figure 4. Electronic spectra of $MnRe(CO)_{10}$ in 3-PIP: —, 300 K; - - -, 77 K.

about $-103{,}000\ cm^{-1}$. Therefore, as in the case of the mononuclear hexacarbonyls,[21] ligand to metal charge transfer (LMCT) transitions should fall well above $50{,}000\ cm^{-1}$. Thus, only the d orbitals ($5e_2$, $6e_1$, $6e_3$, and $6a_1$) need be considered as the origin of excitations at relatively low energies. Two transitions are fully allowed in D_{4d} $Mn_2(CO)_{10}$, ${}^1A_1 \rightarrow {}^1B_2$ and ${}^1A_1 \rightarrow {}^1E_1$.

Electronic Spectra

The Neutral Decacarbonyls. The electronic spectra in 3-PIP of the neutral decacarbonyls $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$ at 300 and 77 K are shown in Figures 2, 3, and 4, respectively. The spectrum of $Tc_2(CO)_{10}$ is very similar to that of $Re_2(CO)_{10}$. At higher energies, where 3-PIP begins to absorb, spectra were recorded in acetonitrile. The four band systems are designated I, II, III, and IV, in order of increasing energy. Band I is observed only in $Mn_2(CO)_{10}$ and is the shoulder at 26,700 cm^{-1} (77 K); it is poorly resolved at room temperature. Band II is the first intense and well-defined absorption in the four compounds; in $Mn_2(CO)_{10}$, it appears at 29,200 cm^{-1} (300 K) and has a molar absorptivity (ϵ) of 20,600. Band system III refers to absorptions between approximately 35,000 and 40,000 cm^{-1}; only one band is seen in $Mn_2(CO)_{10}$, whereas two are resolved for the other three species at 77 K. The two bands are designated IIIA (at lower energy) and IIIB. Band IV, which appears at ~50,000 cm^{-1} for all but $Re_2(CO)_{10}$, in which the band maximum is beyond the range of observation, is the most intense absorption and in $Mn_2(CO)_{10}$ has ϵ ~84,000. Band assignments, to be discussed below, are set out in Table III.

Let us consider first the position of band II in $Mn_2(CO)_{10}$, as in this case meaningful comparisons can be made with the lowest MLCT band energies in mononuclear carbonyls. The observation that MLCT energy increases according to $Cr(CO)_6$ (35,700 cm^{-1})[21] < $Fe(CO)_5$ (41,200

Table IV. Metal-Metal Stretching Frequencies, Force Constants, and $\sigma \rightarrow \sigma^*$ Band Positions and Intensities for the Neutral Decacarbonyldimetal Complexes

			300 K[d]			77 K[d]		
Compound	ν_{M-M} (cm^{-1})	K (mdyn/Å)[c]	$\sigma \rightarrow \sigma^*$ (cm^{-1})	ϵ	f[e]	$\sigma \rightarrow \sigma^*$ (cm^{-1})	ϵ	f[e]
$Mn_2(CO)_{10}$	160[a]	0.59	29,240	20,600	0.32	29,740	33,700	0.33
$Tc_2(CO)_{10}$	148[b]	0.72	31,700	18,300	0.31	32,400	26,600	0.28
$Re_2(CO)_{10}$	122[a]	0.82	32,260	16,700	0.26	32,800	24,000	0.23
$MnRe(CO)_{10}$	157[a]	0.81	31,000	14,900	0.31	31,950	20,100	0.27

[a] Solid sample, reference 30. [b] Cyclohexane solution; this work. [c] Reference 30. [d] In 3-PIP. [e] Calcd from the formula $f = 4.6 \times 10^{-9}\ \epsilon_{max}\nu_{1/2}$; estimated error ±10%.

Table V. Electronic Spectral Data and Transition Assignments for $MnCr(CO)_{10}^-$ and $Cr_2(CO)_{10}^{2-}$

		300 K			77 K			
Complex	Band	cm^{-1}	ϵ	f	cm^{-1}	ϵ	f	Assignment
$(Et_4N)[MnCr(CO)_{10}]$[a]	I	24,100	2,100	~0.026	24,600	24,000	~0.027	$d\pi \rightarrow \sigma^*$
	II	29,240	13,800	0.23	29,800	19,300	0.21	$\sigma \rightarrow \sigma^*$
	III	[b]	~14,000	[c]	[b]	~14,000	[c]	$M \rightarrow \pi^*$
	IV	47,600[d]	82,100[d]	3.2[d]	[e]	[e]	[e]	$M \rightarrow \pi^*$
$[(Ph_3P)_2N]_2[Cr_2(CO)_{10}]$[f]	I	24,000 sh	5,300	[c]	[e]	[e]	[e]	$d\pi \rightarrow \sigma^*$
	II	27,200	13,500	[c]	[e]	[e]	[e]	$\sigma \rightarrow \sigma^*$
	III	30,300	11,000	[c]	[e]	[e]	[e]	$M \rightarrow \pi^*$
$(Et_4N)_2[Cr_2(CO)_{10}]$[g]	II	27,600	[c]	[c]	[e]	[e]	[e]	$\sigma \rightarrow \sigma^*$

[a] In EPA, except where noted. [b] Broad absorption between 33,500 and 36,000 cm^{-1}. [c] Not estimated. [d] In acetonitrile. [e] Not measured. [f] In dichloromethane; reference 31. [g] In ethanol.

cm^{-1})[27] < $Ni(CO)_4$ (42,300 cm^{-1})[28] is well understood, as excitation of a metal electron becomes increasingly difficult as the effective nuclear charge increases. On the basis of such considerations, it may be estimated that the lowest $d\pi \rightarrow \pi^*(CO)$ transition in $Mn_2(CO)_{10}$ will fall above 36,000 cm^{-1}. Assignment of band II to this type of MLCT transition, therefore, can be ruled out on energetic grounds. Similar reasoning eliminates $d\pi \rightarrow \pi^*(CO)$ transitions as candidates for band II in the other $M_2(CO)_{10}$ complexes.

The experimental finding[1] that band II in $Mn_2(CO)_{10}$ is Z polarized narrows the remaining possibilities to two $^1A_1 \rightarrow {}^1B_2$ metal-metal transitions: $\sigma \rightarrow \sigma^*$ ($6a_1 \rightarrow 6b_2$), and $d_{xy A,B} \rightarrow d_{x^2-y^2 B,A}$ ($5e_2 \rightarrow 6e_2$).[29] The high intensity of band II is readily understandable only in terms of the N → V transition $\sigma \rightarrow \sigma^*$,[1] and this assignment is adopted. The $\sigma \rightarrow \sigma^*$ assignment is also preferred on energetic grounds as the photoelectron spectral study places[26] $5e_2$ well below $6a_1$ in $Mn_2(CO)_{10}$. Furthermore, the present calculation gives the energy order $6b_2 < 6e_2$, which is expected from straightforward ligand-field considerations.

Assignment of band I in $Mn_2(CO)_{10}$ may also be made by a combination of polarization and energy arguments. The band is apparently x,y polarized,[1] suggesting a $^1A_1 \rightarrow {}^1E_1$ transition. Of the three allowed x,y-polarized metal-metal transitions ($e_3 \rightarrow e_2$, $e_1 \rightarrow e_2$, $e_3 \rightarrow b_2$), $d\pi \rightarrow \sigma^*$ ($6e_3 \rightarrow 6b_2$) clearly should be the lowest in energy. The fact that the $^1A_1 \rightarrow {}^1E_1$ ($6e_3 \rightarrow 6b_2$) transition falls lower than $^1A_1 \rightarrow {}^1B_2$ ($6a_1 \rightarrow 6b_2$) in $Mn_2(CO)_{10}$ may be attributed to interelectronic repulsion effects, which should be more severe in the $^1B_2$ excited state.

Data given in Table IV show that both M_2 stretching force constants[30] and $\sigma \rightarrow \sigma^*$ band energies increase according to $Mn_2 < Tc_2 < Re_2$. The molecule $MnRe(CO)_{10}$ does not fit neatly in this correlation, which is not too surprising in view of its lower symmetry (C_{4v}). The effect of temperature on the position of band II in the decacarbonyldimetal complexes is quite striking (Table IV). Blue shifts in the range 500-950 cm^{-1} are observed on lowering the temperature to 77 K. For comparison, the mononuclear carbonyls show very little change (<150 cm^{-1}) in the positions of MLCT band maxima between 300 and 77 K.[21] The effect in $M_2(CO)_{10}$ is directly related to the substantial depopulation of excited M_2 vibrational levels that occurs upon cooling the system to 77 K. As such large blue shifts should be observed only for electronic transitions coupled with low-frequency M_2 stretching motions, measurements of the temperature dependence of band shapes and maxima will clearly be useful in identifying $\sigma \rightarrow \sigma^*$ systems in other binuclear complexes.

The large changes in the shape of band II in going from 300 to 77 K make it difficult to tell whether the oscillator strength (f) is constant or not. Within our experimental error, however, the value of f is invariant to temperature in each of the four complexes examined. Such invariances, coupled with the extremely high absolute f values, are of course in accord with the $\sigma \rightarrow \sigma^*$ assignment.

The low temperature electronic spectrum of $MnRe(CO)_{10}$ provides important additional evidence for the $\sigma \rightarrow \sigma^*$ interpretation of band II. It is apparent that a $\sigma \rightarrow \sigma^*$ transition cannot split upon lowering the symmetry from D_{4d} to C_{4v} ($a_1 \rightarrow b_2$ becomes $a_1 \rightarrow a_1$). Two z-allowed transitions ($^1A_1 \rightarrow {}^1A_1$ in C_{4v}), however, would derive from $e_2 \rightarrow e_2$, $b_1 \rightarrow b_1$, and $b_2 \rightarrow b_2$. The lack of any observable splitting of band II in $MnRe(CO)_{10}$, therefore, rules against an $e_2 \rightarrow e_2$ assignment in the parent (D_{4d}) complexes.

Band system III in the $M_2(CO)_{10}$ complexes is assigned to MLCT transitions. This band is poorly resolved, which is not surprising in view of the fact that even in the D_{4d} molecules there are nearly 30 allowed MLCT transitions. In $Mn_2(CO)_{10}$, band IIIB is observed as a shoulder in the 77 K spectrum at 37,600 cm^{-1}. The assignment of IIIB to $d\pi \rightarrow \pi^*$ transitions is supported by the constancy of band position in all four complexes. It may be recalled that the $t_{2g} \rightarrow t_{1u}$ transitions in $M(CO)_6$ all occur between 34,600 and 35,700 cm^{-1} for M = Cr, Mo, and W.[21] Band IIIA for the compounds other than $Mn_2(CO)_{10}$ is at ~36,000 cm^{-1} and is seen at 77 K in all cases. Assignment of this band to $\sigma \rightarrow \pi^*$ transitions is suggested.

Relatively little information is available for band IV, which has the general designation $M \rightarrow \pi^*$. The oscillator strengths are large, being 2.6, 4.0, and 4.1 for the Mn_2, Tc_2,

Table VI. Electronic Spectral Data and Transition Assignments for $Mn_2(CO)_9PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$

		300 K		77 K		
Complex	Band	cm^{-1}	ϵ	cm^{-1}	ϵ	Assignment
$Mn_2(CO)_9PPh_3$[a]	I	~23,500	*b*	24,150	2,600	$d\pi \rightarrow \sigma^*$
	II	27,600	27,800	28,400	45,800	$\sigma \rightarrow \sigma^*$
$Mn_2(CO)_8(PPh_3)_2$[c]	I	22,500	~3,000	*d*	*d*	$d\pi \rightarrow \sigma^*$
	II	26,800	31,800	27,400[a]	*d*	$\sigma \rightarrow \sigma^*$

[a] In 3-PIP. [b] Tail of $\sigma \rightarrow \sigma^*$ band makes an accurate estimate of ϵ difficult. [c] In acetonitrile except where noted. [d] Not estimated, owing to low solubility.

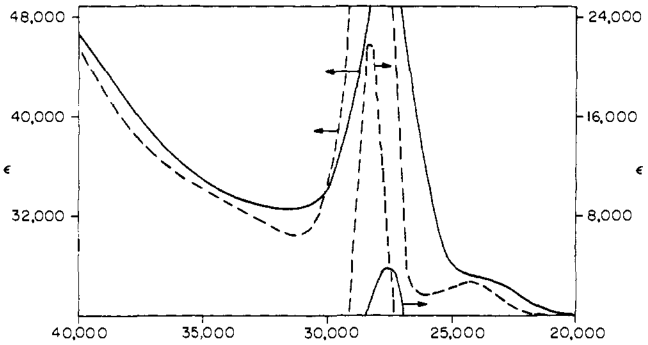

Figure 5. Electronic spectra of $Mn_2(CO)_9(PPh_3)$ in 3-PIP: —, 300 K; - - -, 77 K.

and MnRe compounds, respectively. For the neutral hexacarbonyls, a similarly intense band ($f \sim 2.3$) at ~44,000 cm^{-1} has been assigned to the transition $t_{2g} \rightarrow t_{2u}$.[21] The excitation, therefore, is to a π^* orbital with no metal d, s, or p character. It is reasonable to assign band IV in the decacarbonyls to a combination of $6e_1 \rightarrow 2a_2$ and $6e_3 \rightarrow 2b_1$ transitions, as both terminate in pure π^* ligand orbitals. The position of band IV in $Mn_2(CO)_{10}$ (~49,000 cm^{-1}) agrees reasonably well with the calculated energies (~51,000 cm^{-1} for $6e_1 \rightarrow 2a_2$; ~47,000 cm^{-1} for $6e_3 \rightarrow 2b_1$).

Related Complexes. Electronic absorption spectral data for $Cr_2(CO)_{10}{}^{2-}$ and $MnCr(CO)_{10}{}^{-}$ are set out in Table V Salts of $Cr_2(CO)_{10}{}^{2-}$ are very air sensitive, but the spectrum reported in CH_2Cl_2 solution was found to be reproducible.[31] Band II, attributable to the $\sigma \rightarrow \sigma^*$ transition, is observed at 27,200 cm^{-1}. For comparison, the $\sigma \rightarrow \sigma^*$ band in $W_2(CO)_{10}{}^{2-}$ falls at 28,500 cm^{-1}.[32] The substantial red shift of the $\sigma \rightarrow \sigma^*$ transition in $Cr_2(CO)_{10}{}^{2-}$ relative to $Mn_2(CO)_{10}$ may be due largely to the higher energy of the σ orbital in the Cr(−I) complex. Bands I ($d\pi \rightarrow \sigma^*$) and III ($M \rightarrow \pi^*$) in $Cr_2(CO)_{10}{}^{2-}$ are also red-shifted in comparison to their analogs in $Mn_2(CO)_{10}$, evidencing the relatively higher energies of $d\pi$ (as well as σ) Cr(−I) orbitals.

The positions of bands I and II in $MnCr(CO)_{10}{}^{-}$ are in good agreement with those found by Risen et al.[33] The most reasonable assignment for band I is $d\pi(Cr) \rightarrow \sigma^*$ ($e \rightarrow a_1$ in C_{4v}), in accord with the above proposal that the $d\pi$ orbitals of Cr(−I) are more energetic than those of Mn(0). The fact that band I in $MnCr(CO)_{10}{}^{-}$ falls at about the same position (24,000 cm^{-1}) as its counterpart in $Cr_2(CO)_{10}{}^{2-}$ may be taken as strong support for the $d\pi(Cr) \rightarrow \sigma^*$ assignment in the former complex. Band II in $MnCr(CO)_{10}{}^{-}$ is associated with the intense system peaking at 29,240 cm^{-1}. The observation that the half-width of band II is nearly identical with that of $Mn_2(CO)_{10}$ (3500 vs. 3400 cm^{-1}) accords well with the $\sigma \rightarrow \sigma^*$ assignment. Furthermore, the band maximum blue shifts to 29,300 cm^{-1} at 77 K, as expected.

The components of band III in $MnCr(CO)_{10}{}^{-}$, $\sigma \rightarrow \pi^*$ and $d\pi \rightarrow \pi^*$, appear over a 2500-cm^{-1} range and are not resolved at 77 K. Relative to $Mn_2(CO)_{10}$, the absorptions are shifted to lower energy, as would be predicted on the basis of the $d\pi$ orbitals of Cr being higher in energy. Band IV in $MnCr(CO)_{10}{}^{-}$ is also proportionately lower in energy relative to its counterpart in $Mn_2(CO)_{10}$. Both bands III and IV, therefore, behave according to expectation for $d\pi \rightarrow \pi^*$ transitions.

Electronic absorption spectra of the axially substituted derivatives[8,9] $Mn_2(CO)_9(PPh_3)$ (Figure 5) and $Mn_2(CO)_8(PPh_3)_2$ have also been measured. Data for bands I and II are summarized in Table VI. It is of interest that both the $d\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ transitions decrease in energy according to $Mn_2(CO)_{10} > Mn_2(CO)_9PPh_3 > Mn_2(CO)_8(PPh_3)_2$. Activation energies for kinetic processes apparently involving Mn-Mn bond cleavage also have been found[5] to fall off in the same order. It is possible that replacement of CO by PPh_3 results in increased localization of $d\pi$ electron density on the Mn atoms, which in turn would increase $d\pi$-$d\pi$ repulsive interactions and weaken the metal-metal bond. Although such an interpretation is in accord with the accepted idea that CO is a better π acceptor than PPh_3, it should be regarded as tentative until spectroscopic data for a greater variety of substituted derivatives of decacarbonyldimetal complexes are obtained and analyzed.

Acknowledgment. This research was supported by the National Science Foundation.

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Satellite Bands and the Valence Ionic States of Ozone

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Received February 20, 1975

Abstract: The valence ionic states of ozone have been studied using a combination of multiconfiguration self-consistent field theory and configuration mixing techniques. It is found that the lower energy states of ozone show a significant mixing of one electron (primary) ionization and two electron simultaneous ionization–excitation processes leading to the predicted appearance of satellite bands with considerable intensity in the ultraviolet photoelectron spectrum. It is thus not possible to interpret the valence photoelectron spectrum of ozone in terms of the usual one electron orbital ionization processes. The calculations show that the same excited state configurations that are important in the neutral ozone optical absorption electronic spectrum also figure prominently as interacting excitation or "shake-up" states. The relationship between the relative degree of inadequacy of the frozen orbital approximation (Koopmans' theorem) when comparing ionic states energies and the importance of ionization–excitation processes is pointed out.

The relative energies of the valence ionic states of molecular systems are most easily determined experimentally by photoelectron spectroscopy with photon sources in either the vacuum ultraviolet[1,2] or X-ray[3] frequency regions. In experiments using a vacuum ultraviolet energy source on a diamagnetic system it is typically found that there is a one to one correspondence between the observed spectral maxima and the valence molecular orbitals of the system. This correspondence confirms in a striking manner the shell or orbital structure of atoms and molecules.[4,5] Thus each ionization process is identified with the removal of an electron from some molecular orbital of the system, with an ionization energy just equal to the Hartree–Fock self-consistent field orbital energy of that electron (Koopmans' theorem) in the neutral parent molecule.[6]. The result of identifying a molecular orbital with each ionization process in a photoelectron spectroscopy experiment can be used to supply information about the nature of the orbitals themselves through band shape studies, comparative energy shifts for different compounds for a given orbital type electron, correlations in isoelectronic series, ionization cross section and angular distribution studies, etc. Of course, the correct association of orbitals and ionization processes is fundamental and essential to these analyses.

The identification of an experimental ionization energy with an orbital energy neglects the instantaneous rearrangement of the remaining electrons that will naturally accompany the ionization process and which contributes a relaxation term to the theoretical ionization energy. Although simple models which describe this change of overall charge distribution of the remaining electrons when one electron is ionized have been proposed and discussed,[7,8] the models are typically expressed in terms of the relaxed orbitals, quantities which, if available, render the theoretical models unnecessary for quantitative energy predictions. The relaxation energy can be accounted for by direct calculation of the ion (or hole) state energy and wave function within the single electronic configuration Hartree–Fock theory.

Even with relaxation energy taken into account in a theoretical calculation of ionization energies there is still a further approximation in the neglect of the inherent inaccuracy of single configuration Hartree–Fock theory, called the correlation energy error. This error is expected to be roughly proportional to the number of electrons in the system. Thus ion states are typically expected to have smaller correlation energy errors than the neutral species precursor state[9,10] and calculated ionization energies in the single electronic configuration approximation should be incorrect to the extent of this difference in correlation energy between the ground and ion states.

A method of increasing popularity for treating problems where the single configuration self-consistent field approximation is inadequate is the multiconfiguration self-consistent field (mcscf) theory.[11,12] In the latter the molecular wave function is expressed as a sum of a number of electronic configurations of the same space and spin symmetry and both the orbitals, and configuration bases expansion coefficients are optimized simultaneously in a variational calculation. Typically, the Hartree–Fock electronic configuration is the dominant one in the configuration expansion and essentially determines the nature of the orbitals occupied in this electronic configuration. The nature of the orbitals occupied only in the correlating configurations is then essentially determined by the smaller configuration expansion coefficients of the remaining configurations and are thus optimized as correlating orbitals for the strongly occu-