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Ligand-Field Excited States of Metal Hexacarbonyls

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Over 35 years ago, the low-lying bands in the absorption spectra of metal hexacarbonyls were assigned to ligand-field (LF) excitations. Recent time-dependent density functional theory (TDDFT) calculations on $M(CO)_6$ (M = Cr, Mo, W) are not in accord with this interpretation. Here we extend TDDFT calculations to the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$. By analyzing the trends in the energies of the various electronic excitations, we are able to fully assign the spectra of the complexes. In particular, we demonstrate that the LF excitation $^1A_{1g} \rightarrow {}^1T_{1g}$ is observed at 4.12 eV in the $Mn(CO)_6^+$ spectrum, but all LF features in the spectra of $V(CO)_6^-$ and $Cr(CO)_6$ are obscured by intense metal-to-ligand charge-transfer absorptions. Our results suggest that use of B3LYP as the exchange-correlation functional and inclusion of solvation effects through a continuum solvation model lead to the most accurate calculated transition energies.

Introduction

The absorption spectra of several d^6 hexacarbonyl complexes were reported in the 1960s.[1,2] Intense bands were assigned to allowed $^1A_{1g} \rightarrow {}^1T_{1u}$ metal-to-ligand charge transfer (MLCT) transitions, whereas the weak features were assigned to ligand-field (LF) excitations (Figure 1). The assignment of the intense bands was later confirmed by detailed vibrational structure analysis.[3] However, recent time-dependent density functional theory (TDDFT) calculations by Rosa, Baerends (RB), and co-workers[4] on $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ suggest that the weak bands in the spectra of these three complexes should be assigned to forbidden MLCT transitions.

The theoretical energies obtained by RB and co-workers were not in close quantitative agreement with experiment. RB et al. were therefore forced to arrive at their conclusions by considering qualitative orderings of the calculated energies. In addition, these calculations offer an interpretation only for neutral metal hexacarbonyls. It was not clear when we undertook this work whether the interpretation could also account for the spectra of the carbonyl anions and cations investigated in the 1960s.

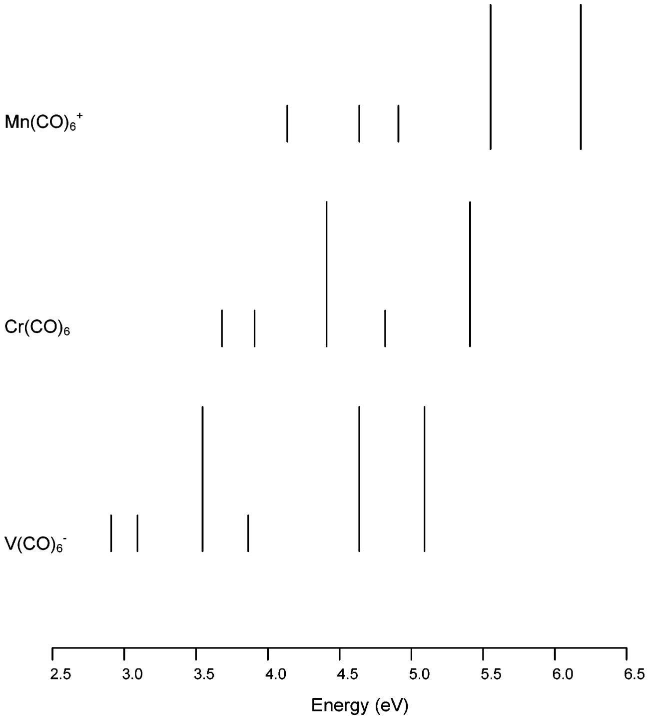

Figure 1. Peak positions in the absorption spectra of $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ in acetonitrile solution. Short lines represent weak ($\epsilon < 3 \times 10^3$) features originally assigned to LF transitions. Tall lines represent intense ($\epsilon > 6 \times 10^3$) features assigned to allowed MLCT transitions.

Accordingly, we have extended the TDDFT calculations to include all members of the isoelectronic series of complexes $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$. We have

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analyzed trends in the energies of the different electronic transitions, and we have shown that these trends are not consistent with the LF assignments put forth in the 1960s.[2] Instead, the only observable LF feature for any of these three complexes occurs at 4.12 eV in the spectrum of $Mn(CO)_6^+$. Absorptions in the spectra of $V(CO)_6^-$ and $Cr(CO)_6$, as well as those higher in energy than 4.12 eV in $Mn(CO)_6^+$, all correspond to MLCT transitions. Our findings are in full agreement with the interpretation put forward by RB and co-workers for $Cr(CO)_6$.[4]

Computational Methods

All calculations reported herein were performed with the TURBOMOLE program package for ab initio electronic structure calculations.[5] We used the QZVP basis set[6] for all atoms in calculating the properties of these complexes. We performed eight different DFT calculations for each metal hexacarbonyl, two with each of the exchange-correlation functionals B3LYP, PBE, BP86, and BLYP.[7−15] For each functional, one calculation was done for the complex in a vacuum. The other used the COSMO continuum solvation model[16] for treatment of solvation effects with a dielectric constant equal to that of acetonitrile, 37.5. Each of the eight calculations was performed with an m3 gridsize.[17] For both vacuum and solvent, the geometry of each complex was optimized using TURBOMOLE's JOBEX program with generalized internal coordinates[18] and the corresponding STATPT module. Energies of well-converged ground-state molecular orbitals were calculated with the DSCF module for semi-direct self-consistent-field evaluation. We then used these ground-state molecular orbitals to calculate the energies of the low-lying singlet → singlet transitions with the ESCF package for full TDDFT calculations.[19,20]

Results and Discussion

We have calculated the energies of the low-lying spin-allowed excitations for $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ in the vapor phase and in acetonitrile solution using the B3LYP, PBE, BP86, and BLYP exchange-correlation functionals. The results are reported in Tables 1−4.

Table 1. Excitation Energies (eV) Calculated with B3LYP in Vacuum/Acetonitrile Solution

	$V(CO)_6^-$	$Cr(CO)_6$	$Mn(CO)_6^+$
${}^1A_{1g} \rightarrow {}^1E_u\ (2t_{2g} \rightarrow 9t_{1u})$	3.13/3.16	4.12/4.14	5.20/5.24
${}^1A_{1g} \rightarrow {}^1T_{2u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.22/3.24	4.18/4.21	5.25/5.29
${}^1A_{1g} \rightarrow {}^1A_{2u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.28/3.30	4.23/4.25	5.28/5.32
${}^1A_{1g} \rightarrow {}^1T_{1u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.52/3.54	4.47/4.49	5.51/5.55
${}^1A_{1g} \rightarrow {}^1A_{1u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.68/3.70	4.66/4.67	5.77/5.79
${}^1A_{1g} \rightarrow {}^1E_u\ (2t_{2g} \rightarrow 2t_{2u})$	3.70/3.72	4.67/4.69	5.77/5.79
${}^1A_{1g} \rightarrow {}^1T_{2u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.83/3.84	4.78/4.79	5.86/5.88
${}^1A_{1g} \rightarrow {}^1T_{1u}\ (2t_{2g} \rightarrow 2t_{2u})$	5.45/5.49	5.97/6.00	6.56/6.60
${}^1A_{1g} \rightarrow {}^1T_{1g}\ (2t_{2g} \rightarrow 3t_{2g})$	4.68/4.73	4.63/4.68	4.93/5.00
${}^1A_{1g} \rightarrow {}^1T_{2g}\ (2t_{2g} \rightarrow 3t_{2g})$	4.80/4.86	4.72/4.78	5.50/5.59
${}^1A_{1g} \rightarrow {}^1E_g\ (2t_{2g} \rightarrow 3t_{2g})$	4.90/4.95	4.96/5.02	5.25/5.32
${}^1A_{1g} \rightarrow {}^1T_{1g}\ (2t_{2g} \rightarrow 6e_g)$	5.14/5.23	4.88/4.96	4.24/4.38
${}^1A_{1g} \rightarrow {}^1T_{2g}\ (2t_{2g} \rightarrow 6e_g)$	5.50/5.60	5.54/5.61	4.60/4.71
${}^1A_{1g} \rightarrow {}^1T_{2g}\ (2t_{2g} \rightarrow 9a_{1g})$	3.96/4.41	6.05/6.00	
${}^1A_{1g} \rightarrow {}^1A_{2g}\ (2t_{2g} \rightarrow 2t_{1g})$	5.06/5.09	6.11/6.12	7.19/7.21
${}^1A_{1g} \rightarrow {}^1T_{1g}\ (2t_{2g} \rightarrow 2t_{1g})$	5.15/5.17	6.18/6.19	7.25/7.27
${}^1A_{1g} \rightarrow {}^1T_{2g}\ (2t_{2g} \rightarrow 2t_{1g})$	5.17/5.20	6.19/6.21	7.26/7.28
${}^1A_{1g} \rightarrow {}^1T_{1u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.37/4.94	6.77/6.64	
${}^1A_{1g} \rightarrow {}^1T_{2u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.38/4.97	6.77/6.63	
${}^1A_{1g} \rightarrow {}^1A_{2u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.39/4.98	6.77/6.64	
${}^1A_{1g} \rightarrow {}^1E_u\ (2t_{2g} \rightarrow 10t_{1u})$	4.41/5.00	6.79/6.66	

Table 2. Excitation Energies (eV) Calculated with PBE in Vacuum/Acetonitrile Solution

	$V(CO)_6^-$	$Cr(CO)_6$	$Mn(CO)_6^+$
${}^1A_{1g} \rightarrow {}^1E_u\ (2t_{2g} \rightarrow 9t_{1u})$	3.15/3.17	3.98/3.98	4.82/4.88
${}^1A_{1g} \rightarrow {}^1T_{2u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.18/3.19	4.00/4.01	4.83/4.89
${}^1A_{1g} \rightarrow {}^1A_{2u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.27/3.29	4.07/4.08	4.89/4.95
${}^1A_{1g} \rightarrow {}^1T_{1u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.32/3.34	4.14/4.14	4.98/5.03
${}^1A_{1g} \rightarrow {}^1A_{1u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.57/3.59	4.38/4.38	5.23/5.26
${}^1A_{1g} \rightarrow {}^1E_u\ (2t_{2g} \rightarrow 2t_{2u})$	3.62/3.63	4.41/4.41	5.25/5.29
${}^1A_{1g} \rightarrow {}^1T_{2u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.63/3.65	4.42/4.43	5.26/5.30
${}^1A_{1g} \rightarrow {}^1T_{1u}\ (2t_{2g} \rightarrow 2t_{2u})$	5.24/5.28	5.68/5.68	6.07/6.12
${}^1A_{1g} \rightarrow {}^1T_{1g}\ (2t_{2g} \rightarrow 3t_{2g})$	5.02/5.05	5.01/5.04	5.14/5.23
${}^1A_{1g} \rightarrow {}^1T_{2g}\ (2t_{2g} \rightarrow 3t_{2g})$	5.15/5.19	5.16/5.18	5.74/5.85
${}^1A_{1g} \rightarrow {}^1E_g\ (2t_{2g} \rightarrow 3t_{2g})$	5.19/5.22	5.34/5.36	5.51/5.59
${}^1A_{1g} \rightarrow {}^1T_{1g}\ (2t_{2g} \rightarrow 6e_g)$	5.41/5.50	5.43/5.46	5.07/5.21
${}^1A_{1g} \rightarrow {}^1T_{2g}\ (2t_{2g} \rightarrow 6e_g)$	5.61/5.71	5.81/5.84	5.12/5.23
${}^1A_{1g} \rightarrow {}^1T_{2g}\ (2t_{2g} \rightarrow 9a_{1g})$	4.01/4.46	6.01/5.96	
${}^1A_{1g} \rightarrow {}^1A_{2g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.80/4.82	5.70/5.69	6.57/6.61
${}^1A_{1g} \rightarrow {}^1T_{1g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.75/4.77	5.65/5.66	6.54/6.59
${}^1A_{1g} \rightarrow {}^1T_{2g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.78/4.80	5.68/5.68	6.56/6.60
${}^1A_{1g} \rightarrow {}^1T_{1u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.43/5.00	6.73/6.60	
${}^1A_{1g} \rightarrow {}^1T_{2u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.43/5.02	6.72/6.59	
${}^1A_{1g} \rightarrow {}^1A_{2u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.43/5.02	6.72/6.59	
${}^1A_{1g} \rightarrow {}^1E_u\ (2t_{2g} \rightarrow 10t_{1u})$	4.44/5.03	6.72/6.59	

Of these four exchange-correlation functionals, only B3LYP includes some amount of exact or Hartree−Fock exchange. We find that B3LYP gives the best overall quantitative agreement with the spectra, especially in terms of reproducing the trends in transition energies in the isoelectronic series.

We sometimes note significant variation in the energies calculated by B3LYP, PBE, BP86, and BLYP. Differences as large as 0.8 eV were calculated here. Thus, we take care to ensure that our assignments of the features of these metal hexacarbonyl spectra depend only on results that hold for each exchange-correlation functional employed.

In the spectrum of each of the three complexes in question, one observes a group of weak bands close in energy just before the first intense peak. These low-lying features, found at 2.88 and 3.11 eV for $V(CO)_6^-$, 3.66 and 3.91 eV for $Cr(CO)_6$, and 4.62 and 4.91 eV for $Mn(CO)_6^+$, were originally assigned to vibrational components of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ LF transition.[2] According to this assignment, the energies of the LF transitions fall in the order V(−I) < Cr(0) <

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Table 3. Excitation Energies (eV) Calculated with BP86 in Vacuum/Acetonitrile Solution

	$V(CO)_6^-$	$Cr(CO)_6$	$Mn(CO)_6^+$
$^{1}A_{1g} \rightarrow {}^{1}E_{u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.14/3.17	3.96/3.99	4.81/4.87
$^{1}A_{1g} \rightarrow {}^{1}T_{2u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.16/3.19	3.98/4.01	4.82/4.88
$^{1}A_{1g} \rightarrow {}^{1}A_{2u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.25/3.28	4.06/4.08	4.88/4.94
$^{1}A_{1g} \rightarrow {}^{1}T_{1u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.31/3.34	4.13/4.15	4.97/5.02
$^{1}A_{1g} \rightarrow {}^{1}A_{1u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.56/3.59	4.37/4.39	5.23/5.26
$^{1}A_{1g} \rightarrow {}^{1}E_{u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.60/3.63	4.40/4.41	5.25/5.28
$^{1}A_{1g} \rightarrow {}^{1}T_{2u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.62/3.65	4.41/4.43	5.26/5.29
$^{1}A_{1g} \rightarrow {}^{1}T_{1u}\ (2t_{2g} \rightarrow 2t_{2u})$	5.24/5.22	5.66/5.69	6.06/6.11
$^{1}A_{1g} \rightarrow {}^{1}T_{1g}\ (2t_{2g} \rightarrow 3t_{2g})$	5.00/5.05	4.98/5.03	5.13/5.19
$^{1}A_{1g} \rightarrow {}^{1}T_{2g}\ (2t_{2g} \rightarrow 3t_{2g})$	5.12/5.18	5.11/5.16	5.71/5.82
$^{1}A_{1g} \rightarrow {}^{1}E_{g}\ (2t_{2g} \rightarrow 3t_{2g})$	5.16/5.21	5.30/5.34	5.48/5.56
$^{1}A_{1g} \rightarrow {}^{1}T_{1g}\ (2t_{2g} \rightarrow 6e_{g})$	5.45/5.55	5.38/5.45	5.01/5.16
$^{1}A_{1g} \rightarrow {}^{1}T_{2g}\ (2t_{2g} \rightarrow 6e_{g})$	5.68/5.78	5.78/5.85	5.08/5.21
$^{1}A_{1g} \rightarrow {}^{1}T_{2g}\ (2t_{2g} \rightarrow 9a_{1g})$	4.28/4.76	6.32/6.27	
$^{1}A_{1g} \rightarrow {}^{1}A_{2g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.78/4.82	5.67/5.69	6.56/6.60
$^{1}A_{1g} \rightarrow {}^{1}T_{1g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.73/4.77	5.64/5.66	6.53/6.58
$^{1}A_{1g} \rightarrow {}^{1}T_{2g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.76/4.80	5.66/5.68	6.55/6.58
$^{1}A_{1g} \rightarrow {}^{1}T_{1u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.67/5.34	7.00/6.87	
$^{1}A_{1g} \rightarrow {}^{1}T_{2u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.67/5.29	7.00/6.87	
$^{1}A_{1g} \rightarrow {}^{1}A_{2u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.67/5.29	6.99/6.87	
$^{1}A_{1g} \rightarrow {}^{1}E_{u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.67/5.30	7.00/6.87	

Table 4. Excitation Energies (eV) Calculated with BLYP in Vacuum/Acetonitrile Solution

	$V(CO)_6^-$	$Cr(CO)_6$	$Mn(CO)_6^+$
$^{1}A_{1g} \rightarrow {}^{1}E_{u}\ (2t_{2g} \rightarrow 9t_{1u})$	2.96/2.98	3.76/3.77	4.60/4.65
$^{1}A_{1g} \rightarrow {}^{1}T_{2u}\ (2t_{2g} \rightarrow 9t_{1u})$	2.98/3.00	3.78/3.79	4.61/4.66
$^{1}A_{1g} \rightarrow {}^{1}A_{2u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.07/3.09	3.85/3.86	4.66/4.71
$^{1}A_{1g} \rightarrow {}^{1}T_{1u}\ (2t_{2g} \rightarrow 9t_{1u})$	3.14/3.16	3.94/3.94	4.77/4.81
$^{1}A_{1g} \rightarrow {}^{1}A_{1u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.41/3.42	4.19/4.20	5.04/5.07
$^{1}A_{1g} \rightarrow {}^{1}E_{u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.43/3.45	4.21/4.21	5.05/5.08
$^{1}A_{1g} \rightarrow {}^{1}T_{2u}\ (2t_{2g} \rightarrow 2t_{2u})$	3.45/3.47	4.23/4.23	5.06/5.10
$^{1}A_{1g} \rightarrow {}^{1}T_{1u}\ (2t_{2g} \rightarrow 2t_{2u})$	5.07/5.11	5.48/5.49	5.85/5.90
$^{1}A_{1g} \rightarrow {}^{1}T_{1g}\ (2t_{2g} \rightarrow 3t_{2g})$	4.70/4.74	4.72/4.75	4.88/4.96
$^{1}A_{1g} \rightarrow {}^{1}T_{2g}\ (2t_{2g} \rightarrow 3t_{2g})$	4.78/4.82	4.77/4.80	5.45/5.55
$^{1}A_{1g} \rightarrow {}^{1}E_{g}\ (2t_{2g} \rightarrow 3t_{2g})$	4.85/4.89	4.99/5.02	5.19/5.27
$^{1}A_{1g} \rightarrow {}^{1}T_{1g}\ (2t_{2g} \rightarrow 6e_{g})$	5.04/5.12	4.99/5.03	4.62/4.76
$^{1}A_{1g} \rightarrow {}^{1}T_{2g}\ (2t_{2g} \rightarrow 6e_{g})$	5.30/5.39	5.48/5.51	4.72/4.85
$^{1}A_{1g} \rightarrow {}^{1}T_{2g}\ (2t_{2g} \rightarrow 9a_{1g})$	3.77/4.21	5.73/5.67	
$^{1}A_{1g} \rightarrow {}^{1}A_{2g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.52/4.55	5.40/5.39	6.26/6.30
$^{1}A_{1g} \rightarrow {}^{1}T_{1g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.49/4.52	5.38/5.37	6.25/6.29
$^{1}A_{1g} \rightarrow {}^{1}T_{2g}\ (2t_{2g} \rightarrow 2t_{1g})$	4.52/4.54	5.39/5.39	6.26/6.30
$^{1}A_{1g} \rightarrow {}^{1}T_{1u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.17/4.73	6.41/6.26	
$^{1}A_{1g} \rightarrow {}^{1}T_{2u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.17/4.74	6.40/6.26	
$^{1}A_{1g} \rightarrow {}^{1}A_{2u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.17/4.73	6.39/6.25	
$^{1}A_{1g} \rightarrow {}^{1}E_{u}\ (2t_{2g} \rightarrow 10t_{1u})$	4.18/4.74	6.40/6.26	

Mn(I), with an energy separation of ~0.9 eV between each pair of adjacent complexes.

Our calculations show clearly that the LF energies do not increase in going from V(−I) to Mn(I). As we noted in an earlier paper,[21] this is because the decreased M → π* CO back-bonding in going from V(−I) to Mn(I) destabilizes the t_{2g} orbital by as much as the e_g orbital is destabilized by the increase in σ bonding. This overwhelming difference between the trends in energies calculated here and those suggested by the original assignment means that the original assignment cannot be correct.

Our calculations indicate that the lowest-energy features in the spectra of $V(CO)_6^-$ and $Cr(CO)_6$ are attributable to orbitally forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT transitions. In contrast to LF excitations, the energies of these MLCT transitions increase significantly in going from V(−I) to Mn(I). The energy separations are calculated to be either 1.0 eV (B3LYP) or 0.8 eV (other exchange-correlation functionals). Thus, assigning these bands to orbitally forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT excitations is clearly warranted.

A similar energy trend is noted in the spectra for the band assigned to the allowed $^{1}A_{1g} \rightarrow {}^{1}T_{1u}$ ($2t_{2g} \rightarrow 9t_{1u}$) transition. Experimentally the energies for these bands are 3.52 eV for $V(CO)_6^-$, 4.43 eV for $Cr(CO)_6$, and 5.52 eV for $Mn(CO)_6^+$, giving an average separation of 1.0 eV.[2] These energies are within 0.05 eV of those calculated with B3LYP. For the other three exchange-correlation functionals, the agreement is worse. These methods tend to underestimate the energy of this transition and also give a typical separation of only 0.8 eV.

The second intense band in each spectrum was assigned to $^{1}A_{1g} \rightarrow {}^{1}T_{1u}$ ($2t_{2g} \rightarrow 2t_{2u}$). The experimental energies for these intense bands are 4.66, 5.41, and 6.19 eV for $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$, respectively,[2] giving a typical separation of 0.8 eV. Our agreement with the experimental results is not as good for this set of intense bands. BLYP is the only method investigated here that does not tend to overestimate the energy of this transition. All of the methods also underestimate the energy separation of these bands in going from one metal to the next. For PBE, BP86, and BLYP, this separation is estimated as 0.4 eV. For B3LYP, we obtain 0.6 eV.

We now consider the features situated between the two intense absorptions discussed above. There is a weak band at 3.86 eV in the $V(CO)_6^-$ spectrum and one at 4.82 eV in $Cr(CO)_6$.[2] We observe no peaks between the two intense absorptions in the spectrum of $Mn(CO)_6^+$, as the intense peaks are much closer in energy in this case. The bands at 3.86 and 4.82 eV were originally assigned to $^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ LF excitations. However, because we know that the energy of this LF transition is not significantly greater in $Cr(CO)_6$ than in $V(CO)_6^-$, this cannot be correct. Before concluding that these are both MLCT transitions, we must eliminate the possibility that one is attributable to an LF excitation while the other is due to something entirely unrelated. For the four exchange-correlation functionals employed, the $Mn(CO)_6^+$ LF transition energies are calculated to be anywhere from 0.4 to 1.0 eV lower than those for $V(CO)_6^-$. Therefore, if the 3.86 eV feature in $V(CO)_6^-$ were LF, we would expect to see a feature lower in energy than 3.86 eV in $Mn(CO)_6^+$. Yet the highest-energy band found in the absorption spectrum of $Mn(CO)_6^+$ lies at 4.12 eV, contradicting the possibility that the 3.86 eV band in $V(CO)_6^-$ is LF. Thus, this band must be attributable to a low-lying orbitally forbidden MLCT transition.

Now, because the lowest-lying orbitally forbidden MLCT transitions have calculated energies that differ by ~1 eV in $V(CO)_6^-$ and $Cr(CO)_6$, it is clear that, if the band at 3.86 eV in the $V(CO)_6^-$ spectrum is MLCT, we would expect to observe the corresponding MLCT transition in $Cr(CO)_6$ near the energy of the peak at 4.82 eV. Thus, both of these peaks must be assigned to MLCT transitions.

Given that these bands are MLCT transitions, the precise assignment in closest agreement with our calculated data is

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Table 5. Assignments of Electronic Transitions in the Absorption Spectra of $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$

complex	energy (eV)	ϵ (M^{-1} cm^{-1})	1960s assignment[2]	current assignment
$V(CO)_6^-$	2.88	300	vibrational components	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	3.11	1640	of $^1A_{1g} \rightarrow {}^1T_{1g}$ LF	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	3.52	6240	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	3.86	3300	$^1A_{1g} \rightarrow {}^1T_{2g}$ LF	forbidden $2t_{2g} \rightarrow 2t_{2u}$ MLCT
	4.66	60900	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT
	5.11	21200	not assigned	allowed $2t_{2g} \rightarrow 10t_{1u}$ MLCT
$Cr(CO)_6$	3.66	700	vibrational components	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	3.91	2670	of $^1A_{1g} \rightarrow {}^1T_{1g}$ LF	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	4.43	13100	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	4.82	3500	$^1A_{1g} \rightarrow {}^1T_{2g}$ LF	forbidden $2t_{2g} \rightarrow 2t_{2u}$ MLCT
	5.41	85100	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT
$Mn(CO)_6^+$	4.12	600	$^1A_{1g} \rightarrow {}^3T_{1g}$ LF	$^1A_{1g} \rightarrow {}^1T_{1g}$ LF
	4.62	1100	vibrational components	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	4.91	2200	of $^1A_{1g} \rightarrow {}^1T_{1g}$ LF	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	5.52	16000	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT
	6.19	27000	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT

orbitally forbidden $2t_{2g} \rightarrow 2t_{2u}$ excitations. In this case, our calculated energies agree well with the observation that the peaks follow the energy ordering

$$\text{forbidden } 2t_{2g} \rightarrow 9t_{1u} < \text{allowed } 2t_{2g} \rightarrow 9t_{1u} < \text{forbidden } 2t_{2g} \rightarrow 2t_{2u} < \text{allowed } 2t_{2g} \rightarrow 2t_{2u}$$

One other possibility that would be consistent with the trends in going from V(−I) to Cr(0) to Mn(I) is that the forbidden $2t_{2g} \rightarrow 2t_{2u}$ transitions are overshadowed by the intense peaks and the peaks at 3.86 and 4.82 eV correspond to $2t_{2g} \rightarrow 2t_{1g}$ transitions. However, our calculated energies for the $2t_{2g} \rightarrow 2t_{1g}$ transitions are in ~1 eV discrepancy with this assignment. This is considerably worse than the ~0.2 eV discrepancy obtained with our calculated energies for the orbitally forbidden $2t_{2g} \rightarrow 2t_{2u}$ transitions, so the assignment to $2t_{2g} \rightarrow 2t_{1g}$ transitions is unlikely.

The one weak feature not yet assigned is the 4.12 eV band in the $Mn(CO)_6^+$ spectrum. It is apparent that this feature is not MLCT. As previously noted, the smallest calculated energy separation of orbitally forbidden MLCT bands for adjacent metals using any of the methods we employed was 0.8 eV. Thus, if the 4.12 eV band were MLCT, we would expect the lowest-energy features to fall below 3.3 and 2.5 eV in the spectra of $Cr(CO)_6$ and $V(CO)_6^-$, respectively. This is not the case, so the lowest-energy band in the $Mn(CO)_6^+$ spectrum must be assigned to an LF transition.

The band was originally assigned to the spin-forbidden $^1A_{1g} \rightarrow {}^3T_{1g}$ LF transition.[2] In retrospect, it is clear that such an assignment cannot be correct. This peak has $\epsilon = 600$, which is orders of magnitude larger than the values reported for spin-forbidden LF absorptions in the related $3d^6$ hexacyano complexes.[22,23] This intensity is, however, perfectly consistent with a spin-allowed LF transition. Given this, we know that it must be the lowest-energy spin-allowed LF transition, as we would observe another transition at a lower energy otherwise. Thus, we assign the band at 4.12 eV in $Mn(CO)_6^+$ to $^1A_{1g} \rightarrow {}^1T_{1g}$ LF. We overestimate the energy of this transition by 0.2 eV with B3LYP and by more with the other three exchange-correlation functionals. This LF feature is obscured by the intense $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 9t_{1u}$) band in $Cr(CO)_6$ and the $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 2t_{2u}$) band in $V(CO)_6^-$.

A final observation regards the low energy calculated for the allowed $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 10t_{1u}$) transition in $V(CO)_6^-$. It is perhaps fortunate that our calculations predict another low-lying allowed transition for $V(CO)_6^-$, as a third intense peak was observed at 5.11 eV in the spectrum.[2] However, we did not expect this transition to have a predicted energy lower than that calculated for the allowed $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 2t_{2u}$) transition. This means that we must consider the possibility that the correct ordering of the allowed transitions is $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 10t_{1u}$) (4.66 eV) < $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 2t_{2u}$) (5.11 eV).

According to this interpretation, the difference in energy between the $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 2t_{2u}$) transitions is 0.3 eV in $V(CO)_6^-$ and $Cr(CO)_6$ but 0.8 eV between $Cr(CO)_6$ and $Mn(CO)_6^+$. All of our calculations predict similar energy differences for this MLCT transition in going from V(−I) to Cr(0) and from Cr(0) to Mn(I). Thus, the fact that this interpretation requires an energy difference nearly 3 times greater in going from Cr(0) to Mn(I) than from V(−I) to Cr(0) is inconsistent with our calculations. For this reason, we conclude that the correct assignments are $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 2t_{2u}$) to 4.66 eV and $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 10t_{1u}$) to 5.11 eV.

With the above analysis in mind, we can assign the spectral features to the transitions set out in Table 5. A comparison between our calculated energies and those provided by experiment can be found in Table 6.

For $Cr(CO)_6$, the energies calculated in solution usually fall within 0.05 eV of those calculated for the complex in vapor. These results agree well with the experimental spectra. The absorption spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were measured in both vapor and acetonitrile solution. For each of these compounds, the band positions remained roughly constant regardless of the medium considered.[2] The average energy difference between the experimental bands in vapor and those in acetonitrile solution for these three complexes is 0.06 eV.

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Table 6. Comparison of Energies Obtained Experimentally in Acetonitrile Solution with Those Obtained Using B3LYP, PBE, BP86, and BLYP[a]

complex	transition	expt	B3LYP	PBE	BP86	BLYP
$V(CO)_6^-$	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT	2.88	3.16	3.17	3.17	2.98
	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT	3.11	3.30	3.29	3.28	3.09
	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT	3.52	3.54	3.34	3.34	3.16
	forbidden $2t_{2g} \rightarrow 2t_{2u}$ MLCT	3.86	3.72	3.63	3.45	3.45
	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT	4.66	5.49	5.28	5.22	5.11
	allowed $2t_{2g} \rightarrow 10t_{1u}$ MLCT	5.11	4.94	5.00	5.34	4.73
$Cr(CO)_6$	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT	3.66	4.14	3.98	3.99	3.77
	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT	3.91	4.25	4.08	4.08	3.86
	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT	4.43	4.49	4.14	4.15	3.94
	forbidden $2t_{2g} \rightarrow 2t_{2u}$ MLCT	4.82	4.69	4.41	4.41	4.21
	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT	5.41	6.00	5.68	5.69	5.49
$Mn(CO)_6^+$	$^1A_{1g} \rightarrow {}^1T_{1g}$ LF	4.12	4.38	5.21	5.16	4.76
	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT	4.62	5.24	4.88	4.87	4.65
	forbidden $2t_{2g} \rightarrow 9t_{1u}$ MLCT	4.91	5.32	4.95	4.94	4.71
	allowed $2t_{2g} \rightarrow 9t_{1u}$ MLCT	5.52	5.55	5.03	5.02	4.81
	allowed $2t_{2g} \rightarrow 2t_{2u}$ MLCT	6.19	6.60	6.12	6.11	5.90

[a] Energies are given in electronvolts.

Only solution absorption spectra are available for $V(CO)_6^-$ and $Mn(CO)_6^+$. For these complexes, we calculate energies in solution and vacuum that generally differ by less than 0.1 eV. The one important exception is for the $2t_{2g} \rightarrow 10t_{1u}$ transitions in $V(CO)_6^-$. Here, the energies calculated in solution are typically 0.6 eV greater than those calculated in vapor. This reflects the large change in dipole moment resulting from the fact that the $10t_{1u}$ orbitals are more strongly localized on the carbon monoxide ligands than the other frontier orbitals. In particular, we find that the energies calculated for the complex in solution for the $^1A_{1g} \rightarrow {}^1T_{1u}$ ($2t_{2g} \rightarrow 10t_{1u}$) transition generally fall within 0.2 eV of the experimental value, but those calculated for the complex in a vacuum underestimate the transition energy by 0.8 eV. Thus we recommend including solvation in predicting the excitation energies of charged complexes, even though it appears that vapor-phase calculations are adequate for most transitions.

Conclusion

We agree with RB et al. that the once-accepted assignment of the weak bands in $Cr(CO)_6$ to LF transitions is incorrect. Instead, these bands correspond to orbitally forbidden MLCT excitations. We have shown further that the low-intensity features in $V(CO)_6^-$ and all but the lowest absorption in $Mn(CO)_6^+$ are also attributable to orbitally forbidden MLCT transitions. The only observable LF transition in any of these hexacarbonyls is the feature at 4.12 eV in the spectrum of $Mn(CO)_6^+$.

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