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Core and Valence-Shell Electronic Excitation of the Group VI Transition-Metal Hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ by High-Resolution Electron Energy Loss Spectroscopy

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Abstract: Core (inner-shell) and valence-shell electron energy loss spectra of the group VIA hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are compared with those of free CO and $Ni(CO)_4$ under kinematic conditions where the spectra are dominated by electric dipole transitions. The transition-metal carbonyl inner-shell C 1s and O 1s spectra show some major similarities to those of free CO, and in particular they exhibit intense $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions. For the C $1s \rightarrow \pi^*$ transitions vibrational structure was resolved. This vibrational structure is influenced by metal d $\rightarrow$ CO π^* back-bonding effects. However, some significant differences also exist between the spectra of the carbonyl complexes and those of free CO, principally due to greater orbital relaxation accompanying creation of a core hole in the transition-metal compounds and the larger number of final states accessible. Tentative assignments are suggested for the hexacarbonyl spectra with the use of molecular orbital energy level and term value considerations. The significance of the results with regard to the strength and nature of metal–CO bonding in transition-metal carbonyl complexes is discussed, and the potential usefulness of inner-shell electron energy loss spectroscopy as a tool for investigating the bonding in transition-metal species in general is assessed.

An extremely large number of spectroscopic[1-20] and theoretical[12,15,21-32] investigations of transition-metal carbonyl complexes (especially the group VI hexacarbonyls) have been carried out due to their high catalytic and photochemical activity[33-38] and their importance as models for the bonding of CO-to-metal surfaces.[8,39-41] An understanding of their electronic structures is thus fundamental to the rationalization of a wide variety of physical and chemical phenomena.

Previously published electronic absorption spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$[12-16] have been limited to the valence shell below 13 eV, and detailed assignments of the bands have been possible only below ~7 eV (for the most recent results see ref 16). Valence[1-6] and inner-shell[2,7-11] photoelectron spectra have been measured with both conventional light sources and synchrotron radiation.[5,6] The synchrotron work of Cooper et al.[5] reported valence-level photoelectron branching ratios and relative partial photoionization cross-sections in the photon energy range 16–115 eV, while Loubriel et al.[6] concentrated on variations in the relative intensities of satellite bands with changing photon energy. Detailed photoionization studies of transition-metal carbonyl complexes with regard to satellite intensities and the relationship of CO complexes to CO adsorbed on metal surfaces have been carried out.[6,8,41-44] In addition electron transmission spectroscopy has been used to investigate the negative ion states of the transition-metal hexacarbonyls[17,18] and the valence orbital momentum distributions, and binding energy spectra of $Cr(CO)_6$ have been measured by electron momentum spectroscopy.[19]

Inner-shell electron energy loss spectroscopy (ISEELS) at high impact energy and zero degree scattering angle is a viable alternative[45-47] to the use of synchrotron radiation for photoabsorption studies in the soft X-ray region of the spectrum (i.e. 200–1000 eV equivalent photon energy). ISEELS is particularly advantageous in the region of C, N, and O 1s (K-shell) excitation (~300, 400, and 550 eV, respectively) where very high energy resolution[45-48] (<0.07 eV) is attainable. In a recent publication[20] we reported the first core level electronic spectra of a gaseous transition-metal complex, $Ni(CO)_4$, at high resolution. Similar to the situation in free CO,[48-51] strong resonant enhancement of the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions was observed.[20] The energies of the transitions and the vibrational structure observed in the C $1s \rightarrow \pi^*$ bands of $Ni(CO)_4$ compared with those in free CO reflected aspects of the metal–ligand bonding in $Ni(CO)_4$. It therefore seemed likely that comparisons of the inner-shell spectra of different transition-metal complexes should provide further

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Table I. Experimental Energies, Term Values, and Possible Assignments of Features in the C 1s Electron Energy Loss Spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$

$Cr(CO)_6$				$Mo(CO)_6$				$W(CO)_6$			
no.	energy, eV	term value, eV	possible assignment of final orbital	no.	energy, eV	term value, eV	possible assignment of final orbital	no.	energy, eV	term value, eV	possible assignment of final orbital
1	287.58 (5)	5.58	$\pi^*(v = 0)$	1	287.55 (6)	5.67	$\pi^*(v = 0)$	1	287.52 (10)	5.65	π^*
	287.81 (5)	5.35	$\pi^*(v = 1)$		287.78 (6)	5.44	$\pi^*(v = 1)$				
	288.03 (5)	5.13	$\pi^*(v = 2)$		288.01 (6)	5.21	$\pi^*(v = 2)$				
	288.26 (5)	4.90	$\pi^*(v = 3)$		288.24 (6)	4.98	$\pi^*(v = 3)$				
2	288.91 (10)	4.25	e_g^*(3d); π^* delocalized; Cr 4p	2	289.05 (10)	4.17	e_g^*(4d); π^* delocalized; Mo 5p	2	288.93 (10)	4.24	e_g^*(4d); π^* delocalized; W 6p
3	290.63 (10)	2.53	π^* delocalized	3	289.95 (10)	3.27	CO 3sσ; π^* delocalized	3	289.79 (10)	3.38	CO 3sσ; π^* delocalized
4	292.86 (15)	0.30	Rydberg					4	291.63 (20)	1.54	Rydberg
IP	293.16[a]			IP	293.22[a]			IP	293.17[a]		
				4	294.3 (2)	−1.1		5	293.8 (2)	−0.6	
5	295.5 (4)	−2.3	double excitation; σ^*(Cr–C)	5	296.1 (4)	−2.9	double excitation; σ^*(Mo–C)	6	296.2 (4)	−3.0	double excitation; σ^*(W–C)
			double excitation; σ^*(Cr–C)	6	299.0 (4)	−5.8	double excitation; σ^*(Mo–C)	7	300.5 (4)	−7.3	double excitation; σ^*(W–C)
6	303.8 (5)	−10.6	σ^*(C–O)	7	303.9 (5)	−10.7	σ^*(C–O)	8	303.2 (5)	−10.0	σ^*(C–O)

[a] From ref 10.

insight into M–CO bonding. A recent study of $Mn_2(CO)_{10}$, $Mn(CO)_5Br$, and $Mn(CO)_5H$ by Ruhl and Hitchcock[52] compares the energies and intensities of the C 1s and O 1s → π^* transitions in these compounds with results published by other groups for $Ni(CO)_4$,[20] $Fe(CO)_5$, and $Fe_2(CO)_9$[44] and also quotes our present results on the group VI hexacarbonyls. However, the low-resolution (~0.5 eV) spectrometer used by Ruhl and Hitchcock[52] was not able to resolve vibrational structure.

As a continuation of our investigation of the applicability of inner-shell electron energy loss spectroscopy to elucidate the electronic structures of and bonding in transition-metal complexes, we now report high-resolution C 1s and O 1s inner-shell spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. High-resolution valence-shell spectra are also reported over an extended energy range.

Experimental Section

The electron energy loss spectra were obtained with a high-resolution spectrometer, the design and operation of which have been described previously.[53,54] Therefore only a brief description will be given here. A monochromated beam of electrons is accelerated to a selected impact energy in the range 1.0–3.7 keV and is scattered off the gaseous sample in a collision chamber. The inelastically scattered electrons are sampled at a mean scattering angle of zero degrees and are energy analyzed by a retarding zoom lens and hemispherical electrostatic analyzer combination, operated in the constant pass energy mode. Under these conditions of forward scattering and high-impact energies (i.e. small momentum transfer), the energy loss spectra are dominated by electric dipole transitions.[45–47] Energy resolution is selectable in the range 0.03–0.31 eV fwhm. The valence-shell spectra were calibrated with the He 1s → 2p transition (21.218 eV), while the inner-shell spectra were put on an absolute energy scale by reference to the N 1s → π^* (v = 1) transition in N_2 (400.88 eV[55]). In practice the calibration corrections were found to be very small (typically <0.05 eV) due to the efficient differential pumping of different regions of the spectrometer.[53,54]

$Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were obtained from Strem Chemicals Inc. and were used without further purification. Due to their low vapor pressure the solids were simply allowed to sublime into the spectrometer at ambient temperature from a sample holder positioned as close as possible to the interaction region. Peaks due to free CO were not evident in the valence-shell spectra, thus indicating decomposition of the samples did not occur in the spectrometer system.

Results and Discussion

Electronic Structure of the Metal Hexacarbonyls. The electronic structures of the group VI hexacarbonyls have been the subject of many theoretical studies.[12,13,21,24–32] There is not full agreement on the exact ordering of the valence energy levels between different calculational methods (e.g. refs 29 and 32), but the qualitative details of the metal–ligand bonding are well understood. A schematic molecular orbital diagram of the relevant orbitals of $Cr(CO)_6$ is shown in Figure 1 and can be considered to be representative of the electronic structures of all three metal carbonyls.

In $Cr(CO)_6$ the metal (valence) 3d orbitals are split by the octahedral ligand field into a higher energy doubly degenerate ($6e_g$) and a lower energy triply degenerate ($2t_{2g}$) set of orbitals, while the CO 5σ and 1π orbitals are split into a manifold of levels (see Figure 1) with an energy spread of ~4 eV.[1,2] It is generally agreed that the $8t_{1u}$ symmetry combination of CO 5σ orbitals has a slightly higher energy than the other 5σ and 1π combinations. The CO 4σ orbitals are largely unaffected by complex formation and produce the very closely spaced $4e_g$, $6t_{1u}$, and $7a_{1g}$ levels. The metal–ligand bonding is generated through synergic CO → M σ electron donation and M → CO π back-donation. There has been considerable debate as to the relative importances of ligand

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Table II. Experimental Energies, Term Values, and Possible Assignments of Features in the O 1s Electron Energy Loss Spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$

$Cr(CO)_6$				$Mo(CO)_6$				$W(CO)_6$			
no.	energy, eV	term value, eV	possible assignment of final orbital	no.	energy, eV	term value, eV	possible assignment of final orbital	no.	energy, eV	term value, eV	possible assignment of final orbital
1	533.85 (10)	5.81	π^*	1	533.77 (10)	5.82	π^*	1	533.73 (10)	5.81	π^*
2	535.75 (20)	3.91	CO 3sσ; π^* delocalized	2	535.81 (20)	3.77	CO 3sσ; π^* delocalized	2	535.79 (20)	3.75	CO 3sσ; π^* delocalized
3	537.30 (20)	2.36	π^* delocalized					3	536.65 (20)	2.89	π^* delocalized
4	538.53 (20)	1.13	Rydberg								
IP	539.66[a]			IP	539.58[a]			IP	539.54[a]		
5	543.2 (5)	-3.6	σ^*(Cr-C)	3	543.1 (5)	-3.5	σ^*(Mo-C)	4	543.3 (5)	-3.7	σ^*(W-C)
6	547.5 (5)	-7.9	σ^*(Cr-C)	4	547.3 (5)	-7.7	σ^*(Mo-C)	5	546.0 (5)	-6.4	σ^*(W-C)
7	549.7 (5)	-10.0	σ^*(C-O)	5	550.2 (5)	-10.6	σ^*(C-O)	6	550.0 (5)	-10.4	σ^*(C-O)

[a] From ref 10.

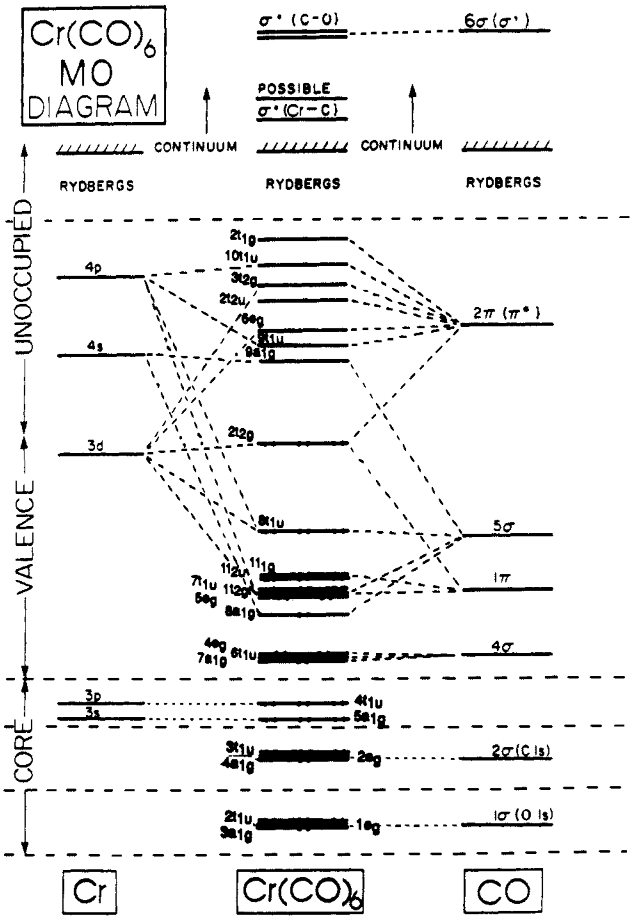

Figure 1. Schematic molecular orbital diagram of chromium hexacarbonyl.

→ metal σ donation and metal → ligand π^* back-donation; for example, Bauschlicher et al.[32] conclude that the π interaction is the dominant contributor to the metal–CO bonding, while Johnson et al.[29] claim that the σ bonding is more important.

For ease of reference in the following discussion the group of low-energy unoccupied MOs derived from the CO 2π orbitals (the $2t_{1g}$, $3t_{2g}$, $2t_{2u}$, and $9t_{1u}$) will be referred to as the π^* orbitals. Similarly the manifold of levels derived from the CO 5σ and 1π orbitals (including the $8t_{1u}$) will be referred to as CO ($5\sigma + 1\pi$).

C 1s and O 1s Excitation Spectra. Figures 2 and 3 show C and O 1s excitation spectra respectively of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ obtained with 3 keV incident electrons at a modest resolution of 0.305 eV fwhm. In each case the corresponding spectrum of free CO is also shown on the same energy scale in order to facilitate comparisons between the spectra of the metal complexes and the free ligand. The energies, term values, and proposed assignments for the numbered features in these spectra are given in Tables I and II.

Table III. Parameters of the Least-Squares Fits of the C 1s → π^* Transitions in the High-Resolution C 1s Electron Energy Loss Spectra[a] of $Cr(CO)_6$, $Mo(CO)_6$, $Ni(CO)_4$, and CO

compd	peak position, eV	fwhm, eV	relative area	Gaussian/ Lorentzian area ratio
$Cr(CO)_6$	287.58	0.263	1.0	0.929
	287.81	0.263	0.493	0.929
	288.03	0.263	0.145	0.929
	288.26	0.263	0.040	0.929
$Mo(CO)_6$	287.55	0.245	1.0	0.883
	287.78	0.245	0.574	0.883
	288.01	0.245	0.186	0.883
	288.24	0.245	0.020	0.883
$Ni(CO)_4$[b]	287.61	0.232	1.0	0.889
	287.84	0.232	0.370	0.889
	288.08	0.232	0.083	0.889
CO[b]	287.40	0.175	1.0	0.691
	287.65	0.175	0.153	0.691
	287.89	0.175	0.015	0.691

[a] See Figure 4. [b] From ref 20.

As was found for the C 1s and O 1s inner-shell spectra of $Ni(CO)_4$,[20] the spectra of the hexacarbonyls shown in Figures 2 and 3 show some major similarities to the corresponding spectra of free CO, and several of the features may be reasonably assigned by analogy. In particular it is clear that the prominent below edge π^* and above edge σ^* shape resonances of CO[48-51] (see also Tables I and II of ref 20) are present in the hexacarbonyl spectra at similar energies and with similar relative intensities in the respective C 1s and O 1s spectra. However, there are significant differences in the energy loss regions between the π^* and σ^* bands, especially in the C 1s spectra.

The most intense peaks in the hexacarbonyl inner-shell spectra occur at approximately 5.6 and 5.8 eV below the respective C 1s and O 1s ionization thresholds, respectively.[10] As noted above these intense peaks can be confidently identified as 1s → π^* transitions. Note that the C 1s and O 1s ionization energies for the metal complexes[10] are all ~3 eV lower than for free CO (296.1 and 542.4 eV, respectively[56]), which gives rise to the large differences (~3 eV) in 1s → π^* term values between the complexes and CO, even though the transition energies are very similar. The lower inner-shell ionization energies for the transition-metal species have been shown to be a result of greater orbital relaxation accompanying ionization, rather than any significant differences in the 1s orbital energies.[26,41]

Figure 4 shows high-resolution scans of the C 1s → π^* peaks in $Cr(CO)_6$, $Mo(CO)_6$, free CO,[20] and $Ni(CO)_4$.[20] The latter two molecules are included for comparison purposes. It was not possible to obtain high-resolution data on $W(CO)_6$ due to its very

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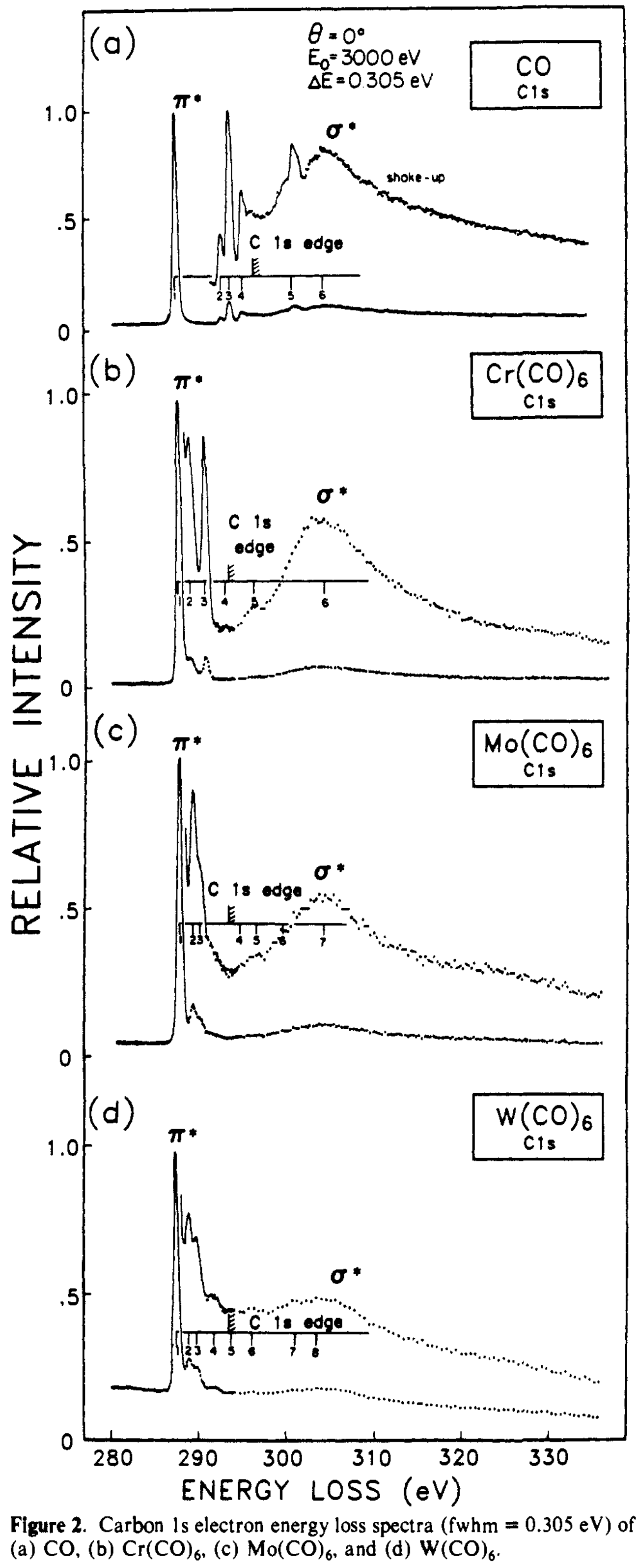

Figure 2. Carbon 1s electron energy loss spectra (fwhm = 0.305 eV) of (a) CO, (b) $Cr(CO)_6$, (c) $Mo(CO)_6$, and (d) $W(CO)_6$.

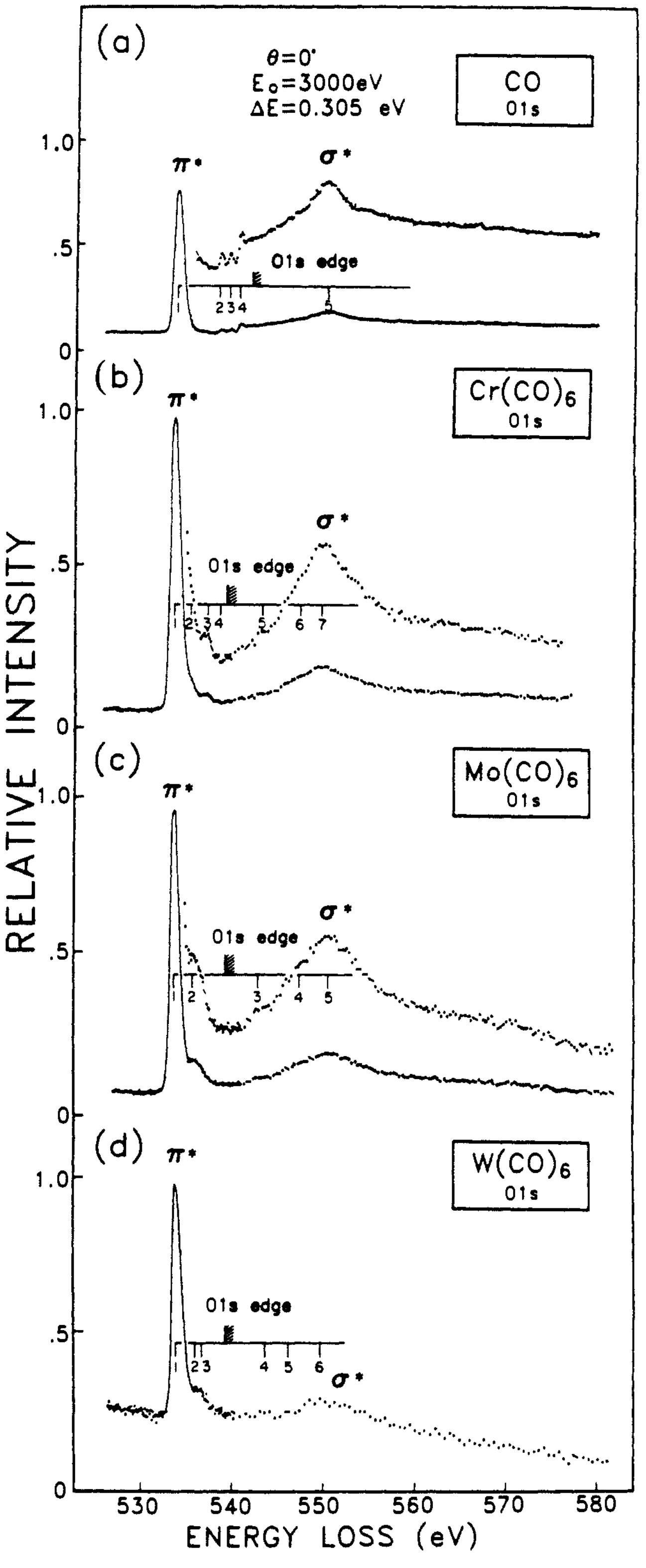

Figure 3. Oxygen 1s electron energy loss spectra (fwhm = 0.305 eV) of (a) CO, (b) $Cr(CO)_6$, (c) $Mo(CO)_6$, and (d) $W(CO)_6$.

low sublimation rate at room temperature and hence low density in the interaction region. As in the case of $Ni(CO)_4$,[20] the C 1s → π* bands of $Cr(CO)_6$ and $Mo(CO)_6$ exhibit partially resolved structure in which the components have intensity distributions consistent with vibrational excitation rather than transitions to different π* final orbitals. Also shown in Figure 4 are least-squares fits of three (CO, $Ni(CO)_4$[20]) or four ($Cr(CO)_6$, $Mo(CO)_6$) Voigt profile[57,58] curves to the experimental data. The parameters of these fits are given in Table III. The best fits are obtained when the peaks have regular spacings: for CO, 0.245 ± 0.007 eV (1980 ± 55 cm^{-1});[20] for $Ni(CO)_4$, 0.235 ± 0.007 eV (1900 ± 55 cm^{-1});[20] for $Cr(CO)_6$, 0.227 ± 0.007 eV (1830 ± 55 cm^{-1}); and for $Mo(CO)_6$, 0.230 ± 0.008 eV (1855 ± 65 cm^{-1}).

We have previously explained[20] how, despite the existence of three sets of possible π* final orbitals for $Ni(CO)_4$, that only one intense C 1s → π* band is observed in the C 1s spectrum. Exactly the same considerations apply to the group VI hexacarbonyls. The explanation lies in the fact that the symmetry of the transition-mtal complex is lowered by the presence of a localized core hole in the 1s excited state (from O_h to C_{4v} for a hexacarbonyl complex). This leads to a doubly degenerate set of π* orbitals becoming heavily localized on the CO group containing the core hole, while the remaining π* orbitals are delocalized over the other ligands and

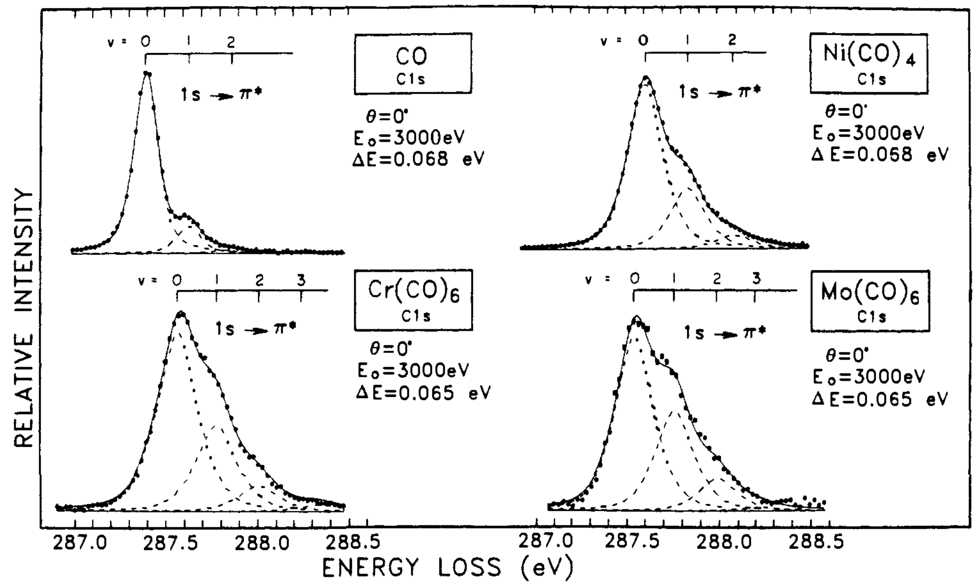

Figure 4. High-resolution electron energy loss spectra (fwhm = 0.068 eV) of the C 1s → π^* transitions in (a) CO, (b) $Ni(CO)_4$, (c) $Cr(CO)_6$, and (d) $Mo(CO)_6$. The dashed lines show fits of three (a and b) or four (c and d) Voigt profile curves to the experimental data (see Table III for details).

have almost zero contribution from the C 1s excited CO ligand.[22,26,59] The core hole also results in the localized π^* orbitals having substantially lower energy (~2 eV[22,26,59]) than the delocalized π^* orbitals. Therefore from considerations of spatial overlap, the probability of transitions to the localized π^* orbitals will be much greater than for excitation into the π^* orbitals delocalized over the neutral ligands. It appears that for $Ni(CO)_4$[20] and the three group VI hexacarbonyls studied in the present work (see Figures 2 and 3) that strong resonant enhancement of the C 1s (and O 1s) → localized π^* transitions is occurring, as is the case in free CO[48-51,60,61] (see ref 20 for a more complete discussion of theoretical and experimental investigations of the π^* and σ^* resonances in CO). This observation, together with the fact that the respective 1s → π^* and 1s → σ^* transition energies are almost identical in all three transition-metal complexes and free CO, provides further convincing evidence of the localized nature of both the C 1s or O 1s core hole and the occupied π^* and σ^* orbitals in the carbonyl species. These observations are entirely consistent with theoretical predictions of 1s core hole localization in core ionized $Ni(CO)_4$[22,59] and $Cr(CO)_6$.[25,26]

The term values of the localized 1s → π^* transitions in both the C 1s and the O 1s spectra are approximately 2–3 eV lower for the hexacarbonyl complexes (and $Ni(CO)_4$[20]) than for free CO gas (Tables I and II). Since the 1s orbital energies are almost equal in CO and the complexes,[26,41,59] this implies higher energies for the π^* final orbitals in $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ (and $Ni(CO)_4$). Although of course the π^* orbitals involved in these transitions do not correspond directly with those in the neutral complexes, and we have the complicating factor of severe orbital relaxation, the decreases in term values provide experimental evidence of how the energies of the CO $2\pi(\pi^*)$ orbitals are perturbed by their interaction with the transition-metal atoms during complex formation. Further evidence is provided by the increase in C 1s → π^* transition energies of ~0.2 eV from CO to the metal complexes, although the O 1s → π^* energies are reduced by ~0.3 eV, presumably due to orbital relaxation effects as discussed by Plummer et al.[44] Comparing the term values and 1s → π^* transition energies of the hexacarbonyls and $Ni(CO)_4$[20] reveals no major differences between them, although the term values of the hexacarbonyls are slightly lower (~0.6 eV), probably due to their lower 1s ionization energies which are the result of greater orbital relaxation; their larger number of CO ligands (6 vs 4) allow more orbital reorganization upon creation of a 1s core hole.

Table IV. Vibrational Frequencies of Ground State and C 1s → π^* Excited States of CO,[a] $Ni(CO)_4$,[a] $Cr(CO)_6$, and $Mo(CO)_6$

compd	ground state ν, cm^{-1}	C 1s → π^* excited state ν, cm^{-1}
CO	2143	1980
$Ni(CO)_4$	2075[b]	1900
$Cr(CO)_6$	2030[b]	1830
$Mo(CO)_6$	2030[b]	1855

[a] From ref 20. [b] Averaged vibrational frequencies over all the vibrational modes weighted according to their degeneracy, calculated from the vibrational frequencies given in ref 65.

The most striking difference between the vibrationally resolved C 1s → π^* bands of the transition-metal carbonyls and that of free CO (Figure 4) is the relatively more intense excitation of higher vibrational components in the metal carbonyl spectra. We have rationalized this[20] in terms of the greater orbital reorganization accompanying C 1s excitation in a metal complex leading to greater changes in molecular electron density distribution, hence larger changes in C–O internuclear distance. The presently reported observations of greater excitation of higher vibrational components in $Cr(CO)_6$ and $Mo(CO)_6$ compared with $Ni(CO)_4$ support this explanation, since the electron density changes may be larger for hexacarbonyl complexes than for tetracarbonyl complexes. As in the case of $Ni(CO)_4$,[20] the vibrational peak separations in the hexacarbonyl spectra (~0.23 eV) are typical of a C=O stretching frequency, and the progressions can be confidently assigned to C—O stretching modes. As stated previously,[20] for excitation into final orbitals located largely on just one CO group, vibrational excitation is likely to be limited to this same ligand, and the measured vibrational frequencies can therefore be compared directly with the frequencies observed in ground state and C 1s → π^* excited CO, and with an averaged vibrational frequency[12] (ν_{CO}) of the ground state vibrational modes of the metal complexes. Table IV gives the relevant data.

The reductions in C–O vibrational frequency from the ground-state species to the C 1s → π^* excited species (see Table III) are of the order 160–200 cm^{-1}. This is the result of promoting an electron into the C–O π^* antibonding orbitals. Comparing the C 1s → π^* vibrational frequencies of the transition-metal complexes with the C 1s → π^* frequency of CO reveals that those for the metal complexes are lower by ~80–150 cm^{-1}, which can be ascribed to metal d → CO π^* back-bonding. These differences

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Table V. Experimental Energies, Term Values, and Possible Assignments of Features in the Valence Electron Energy Loss Spectra of $Ni(CO)_4$, $Cr(CO)_6$, and $Mo(CO)_6$

$Cr(CO)_6$				$Mo(CO)_6$				$W(CO)_6$			
no.	energy, eV	term value, eV	possible assignment of final orbital	no.	energy, eV	term value, eV	possible assignment of final orbital	no.	energy, eV	term value, eV	possible assignment of final orbital
1	3.87 (12)	4.53	$t_{2g}(3d) \rightarrow e_g^*(3d)$	1	3.84 (12)	4.66	$t_{2g}(4d) \rightarrow e_g^*(4d)$				
2	4.41 (12)	3.99	$t_{2g}(3d) \rightarrow t_{2u}(\pi^*)$	2	4.31 (12)	4.19	$t_{2g}(4d) \rightarrow t_{2u}(\pi^*)$	1	4.36 (20)	3.94	$t_{2g}(5d) \rightarrow t_{2u}(\pi^*)$
				3	4.68 (12)	3.82	$t_{2g}(4d) \rightarrow e_g^*(4d)$				
3	5.50 (12)	2.90	$t_{2g}(3d) \rightarrow t_{1u}(\pi^*)$	4	5.41 (12)	3.09	$t_{2g}(4d) \rightarrow t_{1u}(\pi^*)$	2	5.55 (20)	2.75	$t_{2g}(5d) \rightarrow t_{1u}(\pi^*)$
4	6.41 (12)	1.99	$t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$	5	6.36 (12)	2.14	$t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$	3	6.51 (20)	1.79	$t_{2g}(\pi) \rightarrow t_{2g}(\pi^*)$
5	7.66 (20)	0.74		6	7.39 (20)	1.11		4	7.48 (20)	0.82	
				7	8.34 (20)	0.17		5	8.25 (20)	0.05	
1P1[a]	8.40[b]			1P1[a]	8.50[b]			1P1[a]	8.30[b]		
6	8.6 (2)										
7	11.1 (2)		$CO\ (5\sigma + 1\pi) \rightarrow \pi^*$	8	10.2 (2)		$CO\ (5\sigma + 1\pi) \rightarrow \pi^*$	6	10.3 (2)		$CO\ (5\sigma + 1\pi) \rightarrow \pi^*$
8	11.8 (2)			9	11.5 (2)			7	11.7 (2)		
9	12.5 (2)			10	12.2 (2)			8	13.2 (3)		
				11	13.2 (2)						
1P2[a]	13.38[b]			1P2[a]	13.32[b]			1P2[a]	13.27[b]		
10	13.7 (3)										
11	14.4 (2)										
12	16.5 (5)		shape resonance					9	17.6 (5)		shape resonance
1P3[a]	17.82[b]			1P3[a]	17.70[b]			1P3[a]	17.84[b]		
13	23.2 (5)		shape resonance	12	18.8 (5)		shape resonance				

[a] 1P1 refers to the lowest energy t_{2g}^{-1} band, 1P2 refers to the lowest energy $CO(5\sigma + 1\pi)^{-1}$ band (the t_{1u}^{-1}), and 1P3 refers to the CO $4\sigma^{-1}$ band. [b] From ref 2.

in vibrational frequency are similar to those found between the metal complexes and free CO in their respective ground states. The present work therefore further supports our previously published contention[20] that studies of vibrationally resolved core excitation spectra should provide reasonable assessments of the metal–ligand bonding situation in a variety of transition-metal species. In addition to metal carbonyl complexes, those containing, for example, NO and N_2 ligands (e.g. $Cr(NO)_4$, $Co(Ph_3P)_3N_2H$) could be probed by the high-resolution ISEELS technique. Also, local bonding effects in mixed ligand complexes such as $(C_5H_5)NiNO$, $(C_5H_5)Mo(CO)_2NO$, and $(C_5H_5)Cr(NO)_2Cl$ could be investigated through the ability of ISEELS to select a particular inner-shell initial orbital.

Assignments for the remainder of the below edge features in the C 1s and O 1s spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ are very much more complicated, and only tentative assignments can be made in the absence of detailed calculations. The proposals made in Tables I and II are based largely on analogy with the corresponding spectra of free CO, and on the principles discussed earlier[20] for $Ni(CO)_4$. Briefly, excitations to delocalized π^* orbitals are expected ~2 eV higher in energy than the localized π^* bands, plus transitions to orbitals derived from the CO $3s\sigma$ Rydberg orbitals, and to the empty metal $(n-1)d$ ($6e_g$ for $Cr(CO)_6$) and np orbitals. On the basis of the expected energies for the 1s → CO $3s\sigma$ transitions[48,49] and also the fact that O 1s → metal localized excitations are expected to be much weaker than C 1s → metal localized bands, the assignments given in Tables I and II are suggested.

In accord with the results obtained for $Ni(CO)_4$,[20] the C 1s and O 1s ISEELS spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ show similar features to those of free CO above their respective ionization edges. By analogy with CO the very broad features at term values of approximately −10 eV may be assigned to localized σ^* molecular shape resonances in the $l = 3$ (f-like) ionization channels (see ref 20 and references therein). The features in the C 1s and O 1s continua of the hexacarbonyls additional to those found in the corresponding spectrum of free CO may be due to the onsets of shake-up continua, double excitation processes, and/or σ^* molecular shape resonances associated with the M–C bonds (similar to the situation in $Ni(CO)_4$[20]). Recent NEXAFS results on CO on metal surfaces suggest the possibility of metal–molecule levels in the continuum a few electronvolts above the ionization edge,[62] which lends support to the latter assignment. Note that the prominent sharp peak (feature 5) at term value −4.7 eV in the CO C 1s spectrum, which is due to double excitation processes, is not apparent in the present transition-metal carbonyl spectra or that of $Ni(CO)_4$.[20] This sharp peak is also lost when CO is chemisorbed on metal surfaces.[63,64]

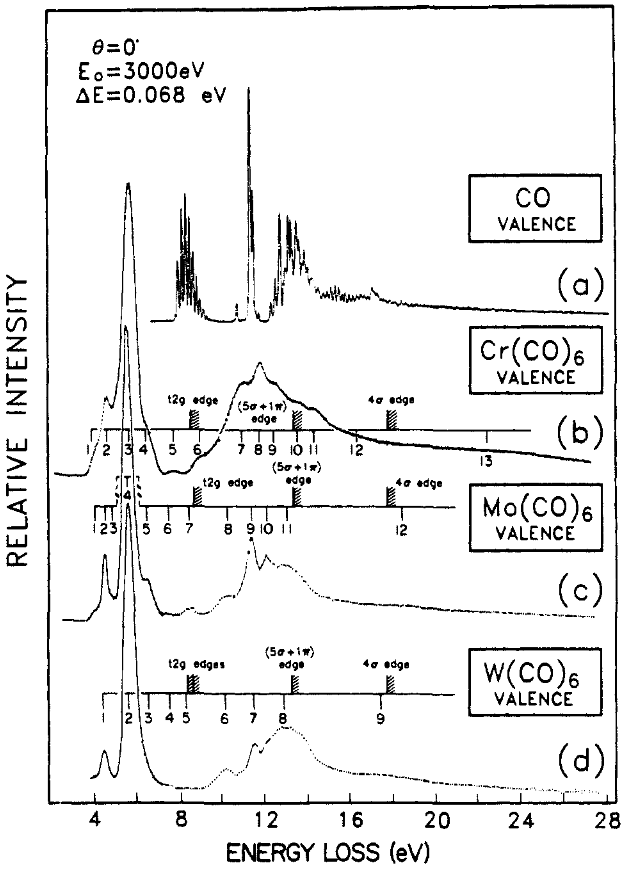

Figure 5. Valence-shell electron energy loss spectra (fwhm = 0.068 eV) of (a) CO, (b) $Cr(CO)_6$, (c) $Mo(CO)_6$, and (d) $W(CO)_6$.

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Valence-Shell Spectra. Valence-shell electron energy loss spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ at a resolution of 0.068 eV fwhm and 3000 eV impact energy are shown in Figure 5 in the energy loss range 4–28 eV together with the corresponding spectrum of free CO. The valence-shell spectra of the metal carbonyls provide an important check of sample purity and in particular clearly confirm the absence of any free CO in the interaction region due to decomposition. In this fashion it has been established that the features in the C 1s and O 1s inner-shell spectra (Figures 2 and 3) are due entirely to the metal carbonyl complexes and not free CO.

The valence-shell electronic spectra of the group VIA metal hexacarbonyls below ~14 eV have been investigated earlier by photoabsorption[12-15] and also by electron energy loss methods at low impact energies.[16] These spectra[12-16] exhibit essentially the same features as those observed in the present work. There are some differences in relative intensities between the present and previous[16] EELS spectra, which can be ascribed to the large differences in the respective impact energies. The energies, term values, and suggested assignments for the numbered features in the spectra shown in Figure 5 are presented in Table V. The assignments for the peaks below the first ionization energies follow those given by Beach and Gray[13] and Koerting et al.[16]

The valence-shell energy loss features above the first ionization energies of the hexacarbonyls cannot be assigned in detail as was also the case for $Ni(CO)_4$.[20] However, we make the following tentative assignments on the basis of the photoelectron spectra of the hexacarbonyls[1,2] and calculated molecular orbital energy levels:[21,24,27-32] (1) The peaks between the $t_{2g}(n\mathrm{d})$ and $(5\sigma + 1\pi)$ edges are assigned to intraligand transitions from the $(5\sigma + 1\pi)$ orbitals to the π^* orbitals. It is possible that the lowest energy transitions in each case correspond to $t_{1u}(5\sigma) \rightarrow \pi^*$. (2) The very broad, low intensity features above the $(5\sigma + 1\pi)$ edges (features 12 and 13 for $Cr(CO)_6$, 12 for $Mo(CO)_6$, and 9 for $W(CO)_6$) are assigned to shape resonances. More detailed assignments of both the valence and inner-shell spectra will only be possible with the guidance of sufficiently accurate theoretical calculations.

Conclusions

We have obtained the C 1s and O 1s ISEELS spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ at high resolution (0.068 eV). The spectra were interpreted by analogy with the corresponding spectra of free CO and our previously reported results for $Ni(CO)_4$. As in the case of $Ni(CO)_4$ (and free CO), intense resonantly enhanced $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ bands were observed. Vibrational structure associated with a C–O stretching mode was resolved in the C 1s $\rightarrow \pi^*$ bands. This vibrational structure reflects aspects of the metal–ligand bonding in these complexes, in particular the metal $\rightarrow$ CO π^* back-donation. The present work therefore strongly supports the preliminary conclusion in our recent paper on $Ni(CO)_4$ that reasonable assessments of the metal ligand bonding situation in a variety of transition-metal species can be provided by high-resolution inner-shell electron energy loss spectroscopy. Further work in this laboratory is planned to investigate the applicability of the ISEELS method to studies of transitions-metal nitrosyl and mixed nitrosyl/carbonyl complexes.

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Transition Structures of the Lewis Acid Catalyzed Diels–Alder Reaction of Butadiene with Acrolein. The Origins of Selectivity

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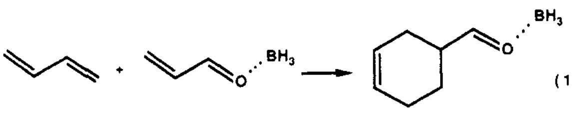
Abstract: Four transition structures for the Diels–Alder reaction of butadiene and acrolein complexed with BH_3 have been located with ab initio calculations at the RHF/3-21G level, and activation energies have been calculated with the 6-31G* basis set. These calculations reproduce both the decreased activation energy and the enhanced endo selectivity experimentally observed upon catalysis. The transition structures show significant zwitterionic character, which is related to the greater calculated asynchronicity in the catalyzed reaction as compared to the uncatalyzed one.

The extraordinary influence of Lewis acid catalysts on the rates and both regiochemical and stereochemical selectivities of Diels–Alder reactions[1] has been much exploited in synthesis.[2] Recent studies on the reactions of optically active dienes,[2] dienophiles,[2] and catalysts[3] highlight its importance. The profound effects of catalysis have sparked an extensive series of mechanistic[4] and qualitative theoretical[5] investigations. Such a reaction has not previously been investigated with ab initio theory. We have used RHF/3-21G and 6-31G* calculations to locate the transition structures of a simple process of this type, the cycloaddition of butadiene to acrolein coordinated with BH_3 (eq 1). These calculations provide new insight into the effects of Lewis acid catalysis on the geometry, flexibility, and energy of a Diels–Alder transition structure and the influence of these factors on selectivity.



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