Comprehensive High Resolution Photoelectron Spectra of Metal Carbonyls Using Synchrotron Radiation

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High resolution variable energy photoelectron spectra using synchrotron radiation, of valence, inner valence, and core levels of gas phase heavy metal carbonyl compounds [e.g. $W(CO)_6$, $Re(CO)_5X$ (X = Cl, Br, $Re(CO)_5$] are reported. The high resolution (0.1 eV) metal 4f core level spectra show, for the first time, vibrational splitting. In addition, ligand field broadening is shown to be an important contributor to the 4f linewidth, especially for $Os(CO)_5$. The greatly improved resolution also provides much narrower 4f shake-up peaks in $W(CO)_6$ than have been observed with laboratory X-ray sources. The complete inner valence spectra are interpreted using the inner valence spectrum of CO and the only previously reported complete inner valence spectrum of a metal carbonyl [$Cr(CO)_6$]. The variable energy of synchrotron radiation is especially important for assigning the valence metal d orbitals [in, for example, $CpM(CO)_3$, M = Mn, Re] using the enhancement of metal d cross sections after the excitation of the core p orbitals.

Introduction

Up until about 1990, photoelectron spectroscopy of gas phase inorganic and organometallic compounds had been divided into the two traditional photoelectron areas: first, low resolution (> 1 eV)[1,2] and medium resolution (~0.5 eV)[1,3] studies of core levels using nonmonochromatized Mg Kα and Al Kα sources and monochromatized Al Kα sources respectively; and second, high resolution (~20 meV with He I and He II sources, and ≥ 200 meV with synchrotron radiation sources) of valence levels,[4,5] including several variable energy studies of inorganic[6] and organometallic[7] compounds.

The high resolution valence level photoelectron studies have been perhaps the most direct technique for characterization of the MO levels of organometallic compounds since the first He

I studies of $Ni(CO)_4$, $Fe(CO)_5$, and $Mn(CO)_5X$ complexes in 1969.[8] Variable energy spectra of organometallic complexes[7,9] give an especially powerful tool for determining the MO levels (using the variable cross sections and resonances at the core p levels[7]), especially when combined with MS—Xα cross section calculations.[9]

Up until 1990, there were no reports of high resolution (~0.1 eV) photoelectron spectra of inner valence or core levels of any inorganic or organometallic molecules. In the last few years, high resolution synchrotron radiation has made it possible to obtain high resolution core level spectra of Si, S, Ge, Sn, I, and Br inorganic molecules,[10] but no high resolution core level spectra of organometallic molecules had been obtained until our preliminary report.[11] Also, in the inner valence region, mainly because of the low intensity, only one medium resolution inner valence X-ray spectrum of one organometallic molecule Cr-$(CO)_6$ has been obtained.[12]

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(1) Jolly, W. L.; Bomben, K. D.; Eyermann, C. J. *At. Data Nucl. Data Tables* **1984**, *90*, 433.

(2) Siegbahn, K.; Nordling, C.; Johansson, J.; Hedman, J.; Heden, P. F.; Hamrin, K.; Gelius, U.; Bergmark, T.; Werme, L. O.; Manne, R.; Baer, Y. *ESCA Applied to Free Molecules*; North-Holland: Amsterdam, 1969.

(3) (a) Gelius, U. *J. Elect. Spect. Relat. Phenom.* **1974**, *5*, 985. (b) Bancroft, G. M.; Malmquist, P.-Å.; Svensson, S.; Basilier, E.; Gelius, U.; Siegbahn, K. *Inorg. Chem.* **1978**, *11*, 1595.

(4) (a) Cowley, A. H. *Prog. Inorg. Chem.* **1979**, *26*, 46. (b) Green, J. C. *Struct. Bonding (Berlin)* **1981**, *43*, 37.

(5) Lichtenberger, D. L.; Kellogg, G. E. *Acc. Chem. Res.* **1987**, *20*, 379.

(6) For example, (a) Yates, B. W.; Tan, K. H.; Bancroft, G. M.; Coatsworth, L. L.; Tse, J. S. *J. Chem. Phys.* **1985**, *83*, 4906. (b) Yates, B. W.; Tan, K. H.; Bancroft, G. M.; Coatsworth, L. L.; Tse, J. S.; Schrobilgen, G. J. *J. Chem. Phys.* **1986**, *84*, 3603. (c) Addison-Jones, B. M.; Tan, K. H.; Yates, B. W.; Cutler, J. N.; Bancroft, G. M.; Tse, J. S. *J. Electron. Spectrosc. Relat. Phenom.* **1989**, *48*, 155. (d) Bozek, J. D.; Cutler, J. N.; Bancroft, G. M.; Tan, K. H.; Yates, B. W.; Tse, J. S. *Chem. Phys.* **1989**, *132*, 257.

(7) (a) Green, J. C. *Acc. Chem. Res.* **1994**, *27*, 131. (b) Cooper, G.; Green, J. C.; Payne, M. P.; Dobson, P. R.; Hillier, I. H. *J. Am. Chem. Soc.* **1987**, *109*, 3836. (c) Brennan, J. G.; Green, J. C.; Redfern, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 1989. (d) Brennan, J. G.; Cooper, G.; Green, J. C.; Kaltsoyannis, N.; MacDonald, M. A.; Payne, M. P.; Redfern, C. M.; Sze, K. H. *Chem. Phys.* **1992**, *64*, 271.

(8) (a) Lloyd, D. R.; Schlag, E. W. *Inorg. Chem.* **1969**, *8*, 2544. (b) Evans, S.; Green, J. C.; Green, M. L. H.; Orchard, A. F.; Turner, D. W. *Discuss. Faraday Soc.* **1969**, *47*, 112.

(9) (a) Yang, D. S.; Bancroft, G. M.; Puddephatt, R. J.; Tan, K. H.; Cutler, J. N.; Bozek, J. D. *Inorg. Chem.* **1990**, *29*, 4956. (b) Li, X.; Bancroft, G. M.; Puddephatt, R. J.; Hu, Y. F.; Liu, Z. F.; Tan, K. H. *Inorg. Chem.* **1992**, *31*, 5162. (c) Li, X.; Bancroft, G. M.; Puddephatt, R. J.; Hu, Y. F.; Liu, Z. F.; Sutherland, D. G. J.; Tan, K. H. *J. Chem. Soc., Chem. Commun.* **1993**, 67. (d) Li, X.; Bancroft, G. M.; Puddephatt, R. J.; Liu, Z. F.; Hu, Y. F.; Tan, K. H. *J. Am. Chem. Soc.* **1994**, *116*, 9543.

(10) (a) Bozek, J. D.; Cutler, J. N.; Bancroft, G. M.; Coatsworth, L. L.; Tan, K. H.; Yang, D. S.; Cavell, R. G. *Chem. Phys. Lett.* **1990**, *165*, 1. (b) Sutherland, D. G. J.; Bancroft, G. M.; Tan, K. H. *J. Chem. Phys.* **1992**, *97*, 7918. (c) Cutler, J. N.; Bancroft, G. M.; Tan, K. H. *J. Chem. Phys.* **1992**, *97*, 7932. (d) Sutherland, D. G. J.; Bancroft, G. M.; Liu, Z. F. *Nucl. Inst. Methods B* **1994**, *87*, 183. (e) Cutler, J. N.; Bancroft, G. M.; Tan, K. H. *Chem. Phys.* **1994**, *181*, 461. (f) Svensson, S.; Ausmees, A.; Osborne, S. J.; Bray, G.; Gel'mukhanov, F.; Ågren, H.; Naves de Brito, A.; Sairanen, O.-P.; Kivimäki, A.; Nõmmiste, E.; Aksela, H.; Aksela, S. *Phys. Rev. Lett.* **1994**, *72*, 3021.

(11) Hu, Y. F.; Bancroft, G. M.; Bozek, J. D.; Liu, Z. F.; Sutherland, D. G. J.; Tan, K. H. *J. Chem. Soc., Chem. Commun.* **1992**, 1276.

(12) Nilsson, A.; Mårtensson, N.; Svensson, S.; Karlsson, L.; Nordfors, D.; Gelius, U.; Ågren, H. *J. Chem. Phys.* **1992**, *96*, 8770.

In this paper, we use monochromatized synchrotron radiation and our newly developed photoelectron spectrometer[10,13] to obtain high resolution valence, inner valence, and core level spectra of organometallic compounds. We have two major objectives. First, we wanted to demonstrate the importance of the high resolution and high intensity of synchrotron radiation to obtain, for the first time, high resolution ($\sim$0.1 eV) inner valence and core level spectra of organometallics. The high resolution/intensity is critical for resolving and clarifying features in both inner valence and core level spectra. Second, we wanted to emphasize the importance of the tunability of synchrotron radiation to enhance specific core level cross sections and for studying resonances in valence band cross sections.[7]

Experimental Section

All the samples with the exception of $Os(CO)_5$ were commercially obtained and used directly without further purification. $Os(CO)_5$ was prepared by R. K. Pomeroy by methods described elsewhere.[14]

All the spectra were obtained with the Grasshopper beamline at the Canadian Synchrotron Radiation Facility (CSRF) which is located at the Aladdin storage ring, University of Wisconsin—Madison.[15] A 1800 g/mm grating gave photon energies between 70—200 eV, and a 600 g/mm grating gave photon energies between 22—72 eV. The performance of the ESCA 36 photoelectron spectrometer has been discussed previously.[10] Typically, the photon resolution was 30 meV at 40 eV and 60 meV at 80 eV, while the total instrumental resolution was 60 meV at 40 eV and 100 meV at 80 eV photon energies. For the broad-scan spectra spanning 40—50 eV reported in the present paper, the instrumental resolution at 70 eV photon energy can be calculated as 170 meV (photon slit width at 50 μm). In order to enhance the intensity of the signal and so minimize the experimental time, a Quantar Model 3395A position sensitive detector (PSD) was used in this study.[13] By using the PSD, the count rate can be increased by 20—50 times over our previous channeltron system.[10] This high intensity is critical to our inner valence study here, because the inner valence levels have low cross section and are very broad.

The calibration of the spectra was carried out as follows: first, the He I spectra of samples were obtained by our laboratory McPherson ESCA 36 photoelectron spectrometer calibrated with the Ar $2p_{3/2}$ at a binding energy (BE) of 15.759 eV; then, the spectra at higher photon energies were calibrated using the Xe 5s at a BE of 23.397 eV with the 600 g/mm grating and by Kr $3d_{5/2}$ at a BE of 93.795 eV with an 1800 g/mm grating. The binding energies are accurate to within $\leq$0.01 eV.

All the solid samples were introduced into the gas cell of the spectrometer directly via the heatable probe. The less volatile samples required heating at the temperatures ranging from 40 to 110 °C in order to generate enough vapor pressure. $Os(CO)_5$ is very volatile, so it was kept under ice water and leaked into the gas cell. The pressure in the sample chamber is controlled around 4×10^{-5} Torr, while the pressure in the gas cell was $\sim$5 $\times$ 10^{-3} Torr.

Spectra were deconvoluted with a Gaussian—Lorentzian line shape using a nonlinear least-squares procedure described previously.[16]

Results and Discussion

A. General Features and Inner Valence Assignments. (a) $W(CO)_6$. The high resolution broad-scan spectrum of $W(CO)_6$ at 80 eV photon energy is illustrated in Figure 1. Peak positions and assignments are given in Table 1. The spectrum in Figure 1 was taken at a total resolution of $\leq$0.2 eV; while the spectrum in the insert was taken at a total resolution of <0.1 eV. These
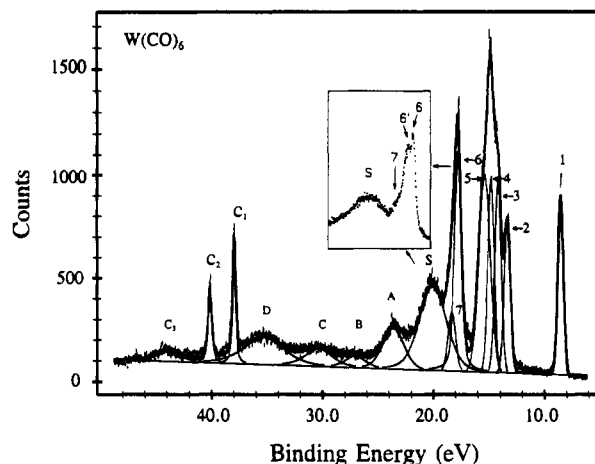
(13) Liu, Z. F.; Bancroft, G. M.; Coatsworth, L. L.; Tan, K. H. *Chem. Phys. Lett.* **1993**, *203*, 337.
(14) Rushman, P.; van Buuren, G. N.; Shiralian, M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 693.
(15) Tan, K. H.; Bancroft, G. M.; Coatsworth, L. L.; Yates, B. W. *Can. J. Phys.* **1982**, *60*, 131.
(16) Bancroft, G. M.; Adams, I.; Coatsworth, L. L.; Bennewitz, C. D.; Brown, J. D.; Westwood, W. D. *Anal. Chem.* **1975**, *47*, 586.

Figure 1. High resolution broad-scan photoelectron spectrum of $W(CO)_6$ at 80 eV photon energy. The valence level peaks are labeled with the numbers (1—7) in an increasing binding energy. Peak S is assigned to a shake-up peak (see text). The inner-valence peaks are labeled with letters (A—D). The three core level peaks are labeled with C_1, C_2 and C_3, respectively. The insert spectrum is taken at 40 eV photon energy, which resolves peak 6′ between peak 6 and peak 7.

Table 1. Binding Energies, Widths, and the Assignments of $W(CO)_6$ at a Total Resolution of $\leq$0.2 eV[a]

peak label	binding energy (eV)	width (eV)	majority character	MO
1	8.57	0.57	W 5d and CO 2π	$2t_{2g}$
2	13.38	0.66	CO 1π and 5σ	$8t_{1u}$
3	14.21	0.66	CO 1π and 5σ	$1t_{1g}$, $1t_{2u}$
4	14.83	0.65	CO 1π and 5σ	$5e_g$
5	15.42	1.20	CO 1π and 5σ	$7t_{1u}$, $1t_{2g}$, $8a_{1g}$
6	17.63	0.46	CO 4σ	$6t_{1u}$
6′	18.06	0.47	CO 4σ	$4e_g$
7	18.52	0.46	CO 4σ	$7a_{1g}$
S	20.06	2.90	shake-up	
A	23.63	2.23	satellite 1	
B	27.06	2.15	satellite 2	
C	30.34	2.86	satellite 3	
D	35.29	4.29	CO 3σ	
C_1	37.98	0.37	W $4f_{7/2}$	
C_2	40.16	0.37	W $4f_{5/2}$	
C_3	43.85	2.28	W $5p_{3/2}$	

[a] The positions and widths of peaks 6, 6′, and 7 are taken from the insert spectrum in Figure 1.

spectra can be divided into the three traditional regions: valence or outer valence levels with BE less than $\sim$20 eV (labeled with the numbers 1—7 and S); inner valence levels with BE between $\sim$20 and $\sim$40 eV (labeled with A—D); and the core levels C_1, C_2, C_3 with BE $\sim$ 40 eV. All features are immediately seen in one spectrum: the intense, relatively narrow valence bands (except for the very broad peak S); the weak, broad inner valence bands; and both very narrow core levels (C_1 and C_2) and a weak, broad core level (C_3). The resolution of the valence band spectrum at 40 eV photon energy (insert) is much better than the previously published He II spectrum which gives peaks up to 24 eV BE (Figure 2 in ref 17a) but slightly poorer than the previous He I spectra up to 16 eV BE. For example, our high resolution spectrum (insert) readily shows three peaks in the $\sim$18 eV band which were not seen previously in the He II spectrum.[17a] This observation is important for the complete assignment. The inner valence peaks above 24 eV have not been observed previously, the W 4f peaks (C_1 and C_2) have

(17) (a) Higginson, B.; Lloyd, D. R.; Burroughs, P.; Gibson, D. M.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 1659. (b) Hubbard, J. L.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 2132.

been observed previously at low resolution,[18] but the broad core level peak C_3 has not been previously observed.

The assignment of the valence band spectrum up to 16 eV (Table 1) follows exactly from that of Higginson et al.,[17a] and requires little comment. Peaks 1 is broadened by the spin-orbit split W 5d t_{2g} ionizations. Vibrational structure has also been observed with He I excitation.[11,17b] The next four peaks (2−5) arise from seven MO's of mainly CO 1π and 5σ character (Table 1). Our BE values are in excellent agreement with the previous He I results.[17a]

The assignments of the peaks at $\sim$18 and 20 eV are not at all straightforward, but our spectra put the assignment on a very firm footing. Our assignment requires the He II[18] and X-ray spectrum[12] of $Cr(CO)_6$ in this BE region; the core-level shake-up spectra of CO[3a] and $W(CO)_6$,[19] the inner valence spectrum of CO,[20] and theoretical calculations.[21] The resolution of the band at $\sim$18 eV into three peaks of intensity $\sim$3:2:1 confirms that these peaks are due to the $6t_{1u}$, $4e_g$, and $7a_{1g}$ orbitals of CO 4σ character; while the peak at 20 eV must be due to an intense shape-up peak from the 5σ and 1π CO orbitals around 15 eV BE. This assignment agrees with the previous assignment given by Plummer et al.[18] for the analogous molecule $Cr(CO)_6$. However, our assignment is contrary to that given originally by Higginson et al.[17a] for $W(CO)_6$ and very recently by Nilson et al. for $Cr(CO)_6$.[12] They assigned the unresolved band at $\sim$18 eV (peaks 6, 6', 7) to the combined $4e_g$ and $6t_{1u}$ ionizations, and the broad band at 20 eV to the $7a_{1g}$ ionization. Our assignment is strongly supported by several theoretical and experimental findings. First, theoretical calculations[21] show that the splitting of the majority 4σ levels should be ≤ 1 eV as in our assignment. Second, the intensity and width of peak S is not consistent with the ionization from a nondegenerate a_{1g} orbital. For example, peak S is more intense than peaks 6, 6', and 7 at all photon energies studied between 40 and 90 eV; whereas, the Gelius intensity treatment[3a] certainly predicts that the $4a_{1g}$ intensity should be $\sim$33% of the $6t_{1u}$ intensity, as for our assignment. We have shown in previous studies[6d,9d] that the Gelius treatment works well down to photon energies of $\sim$50 eV.[6d,9d] Third, our fit of the insert spectrum in Figure 1 yields a ratio of intensities for peaks 6, 6', 7, and S of 1:2.5: 3.8:10, consistent with our assignment. Also, the separation between peaks 6, 6', and 7 ($\sim$0.4 eV, Table 1) is too large to be of vibrational origin. Fourth, the intensity of peak S is consistent with that expected for a shake-up peak of peaks 2−5, as suggested by Plummer et al. for $Cr(CO)_6$.[18] The core level spectra (C 1s and O 1s) of the $M(CO)_6$ compounds (M = Cr, Mo, W) give very intense shake-ups ($\sim$30% of the intensity of the "main" line) $\sim$5 eV from the main line.[18,19] The intensity of peak S is about 35−40% of the intensity of peaks 2−5 over the photon energy range 40−90 eV. This large shake-up intensity in metal carbonyls contrasts with the very low shake-up intensity ($\sim$3%) in CO on both the C 1s core level[3a] and valence shake-ups at 21 eV BE (our unpublished results). In CO, the 21 eV shake-up peak is not observable with the medium resolution X-ray[12] or synchrotron spectra.[20] These results show

strongly[18] that the shake-up positions and intensities are very similar for *both* C 1s and O 1s core levels *and* valence levels for carbonyl compounds.

The contributions from CO 3σ orbital and satellites corresponding to the shake-up process from CO 4σ and 5σ orbitals dominated the inner-valence spectrum of $Cr(CO)_6$.[12] The high resolution inner-valence spectrum of free CO molecule has also been studied recently.[13] The effects of vibronic coupling and configuration interaction in this region have been clearly resolved. The spectrum of $W(CO)_6$ can be interpreted by comparing our results with those from $Cr(CO)_6$ and free CO. Peak A at 23.63 eV binding energy can be assigned to the so-called C state in free CO with a predominant final $5\sigma^{-1}1\pi^{-1}2\pi^1$ state configuration which can be considered as a normal monopole shake-up state that gains intensity by configuration interaction with the $4\sigma^{-1}$ state. A similar peak has been observed at 23.7 eV for free CO[20] and 23 eV binding energy of $Cr(CO)_6$.[12] Peak B is relatively weak at 27.06 eV binding energy. This peak was not resolved in $Cr(CO)_6$ but is evident in free CO at 28.5 eV corresponding to the $4\sigma^{-1}1\pi^{-1}2\pi^1$ final state. The satellite peak C is associated with the $\pi^{-2}-\pi^2$ double shake-up process accompanying the 5σ ionization in free CO, as in the $Cr(CO)_6$.[12] The broad and intense peak D at 35.29 eV arises mainly from the CO 3σ orbital. The complete breakdown of the single-particle picture for the 3σ ionization has been discussed in the free CO molecule,[13] and the vibrational fine structure has been the focus of these studies. Therefore, these peaks are all very broad with linewidths of ≥ 2 eV. These fits can only be approximate because many vibronically coupled and correlated states overlap.[13] Another satellite state has been observed in $Cr(CO)_6$ at 41 eV associated with a shake-up transition from the 3σ ionization. Because of the presence of the intense W $4f_{5/2}$ peak at 40.18 eV binding energy, this satellite peak can not be observed in the spectrum of $W(CO)_6$.

The last part of Figure 1 is the core level region and is characterized easily. The first two peaks, C_1 and C_2, can be clearly assigned to the two spin orbit components of W 4f orbital at 37.98 and 40.16 eV binding energy.[22] The third peak C_3 is the $5p_{3/2}$ level of W at 43.85 eV. At first glance, another possible assignment for this peak is that this peak is the $5p_{1/2}$ level of W, while another spin orbit component $5p_{3/2}$ overlaps with the 3σ of CO around 36 eV. However, the $5p_{1/2}$ peak of W at $\sim$53 eV can be observed in other spectra taken at higher photon energies, though it is very weak because the W 5p cross section becomes weaker relative to that of W 4f at higher photon energies.[23]

The measurement of W 5p binding energies can be used to predict at what photon energies the 5p-5d resonance effects[7] can be observed (see later). The 5p binding energies of atomic W have been reported to be 41 and 51 eV referenced to the vacuum level.[24] In the previous synchrotron radiation study of $W(CO)_6$,[7b] the experimental 5p binding energies were not available, but two cross section maxima of the W 5d ionizations were observed around 44 and 53 eV photon energy. Our report of W 5p binding energies agrees well with the previous experimental results, and also confirms our assignment. We will also show in the following discussion how the np binding energies can be used to observe the $np \rightarrow nd$ resonance effects in $CpM(CO)_3$ complexes.

(b) Re(CO)₅X and CpM(CO)₃ Compounds. To further illustrate our comprehensive spectra, Figure 2 shows broad-

(18) Rajoria, D. S.; Kovnat. L.; Plummer, E. W.; Salaneck, W. R. *Chem. Phys. Lett.* **1977**, *49*, 64.

(19) (a) Bancroft, G. M.; Boyd, B. D.; Creber, D. K. *Inorg. Chem.* **1978**, *17*, 1008.

(20) (a) Krummacher, S.; Schmidt, V.; Wuilleumier, F.; Bizau, J. M.; Edderer, D. *J. Phys. B: At. Mol. Phys.* **1983**, *16*, 1733. (b) Svensson, S.; Carlsson-Göthe, M.; Karlsson, L.; Nilsson, A.; Mårtensson, N.; Gelius, U. *Phys. Scr.* **1991**, *44*, 184.

(21) (a) Ohno, M.; von Niessen, W.; Tarantelli, F. *Phys. Rev. B* **1992**, *45*, 1851. (b) Johnson, J. B.; Klemperer, W. G. *J. Am. Chem. Soc.* **1977**, *22*, 7132. (c) Baerends, E. J.; Ros, P. *Mol. Phys.* **1975**, *30*, 1735. (d) Yang, C. Y.; Arratia-Petez, R.; Lopez, J. P. *Chem. Phys. Lett.* **1984**, *107*, 112.

(22) Jolly, W. L.; Perry, W. B. *Inorg. Chem.* **1974**, *13*, 2686.

(23) Yeh, J. J.; Lindau, I. *At. Data Nucl. Data Tables* **1985**, *32*, 1.

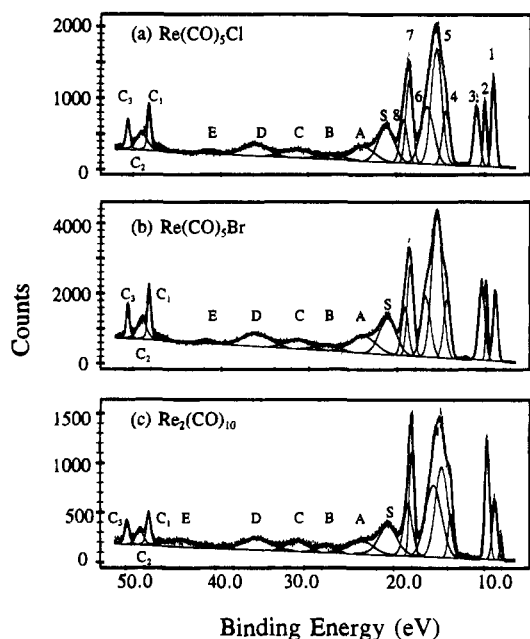(24) Carlson, T. A. *Photoelectron and Auger Spectroscopy*; Plenum: New York, 1975.

Figure 2. High resolution broad-scan photoelectron spectra of (a) Re-(CO)₅Cl at 72 eV photon energy, (b) Re(CO)₅Br at 72 eV photon energy, and (c) Re₂(CO)₁₀ at 70 eV photon energy. These spectra are labeled identically to Figure 1.

scan spectra of the three Re compounds Re(CO)₅Cl, Re(CO)₅Br and Re₂(CO)₁₀. Apart from the valence band peaks 1, 2, and 3, these three spectra are remarkably similar qualitatively and can be assigned in a manner very similar to that used for the W(CO)₆ spectrum.

The valence band spectra have been obtained previously with He I and He II radiation,[25] and they have been assigned. We will concentrate only on the peaks above 18 eV that have not been observed previously. As for W(CO)₆, the peak at ~18.5 eV (peaks 7 and 8) is due to all of the 4σ CO ionizations ($2a_1$, b_2, and e), and peak S is the shake-up peak from the 5σ and 1π ionizations (peaks 4, 5, and 6). The inner valence region (peaks A to D) (Table 2) is virtually identical to that of W(CO)₆, although another peak E is evident above 40 eV BE. There is no evidence for the Cl 3s or Br 4s ionizations in the Re(CO)₅X compounds at about 25 eV, due to their very small cross sections relative to the C 2s and O 2s cross sections.[23] It is also obvious that the Re₂(CO)₁₀ spectrum is extremely similar to the other two spectra between 20 and 30 eV, showing once again that the Cl 3s and Br 4s levels give no noticeable contribution. Similar to W(CO)₆, the peaks A, B, and C between 23 to 32 eV binding energy can be assigned to shake-up peaks with the final states of $5\sigma^{-1}1\pi^{-1}2\pi^1$, $4\sigma^{-1}1\pi^{-1}2\pi^1$, and $\pi^{-2}-\pi^2$ double shake-up processes, respectively, as discussed above. The CO 3σ orbital can be found around 36 eV as a very broad and relative intense peak D. Another very weak peak can be identified around 41 eV binding energy, labeled E. A corresponding peak has been observed in the free CO molecule and Cr(CO)₆, but not W(CO)₆, as discussed above. This peak can be assigned to the shake-up process from the CO 3σ orbital.

The three peaks on the higher energy side of peak E are derived from the Re 4f (C_1 and C_3) and $5p_{3/2}$ (C_2) core orbitals and they will be examined in more detail in section B.

Figure 3 presents the valence and inner-valence spectra of another two organometallic complexes, CpM(CO)₃, where Cp = η^5-C₅H₅ and M = Re and Mn, at 72 eV photon energy. Unlike

the metal carbonyls discussed above, these complexes contain carbonyl and cyclopentadienyl ligands which both contribute to the inner-valence region. The valence-only spectra of these complexes have been well studied by the combination of He I/He II sources, and CO vibrational fine structure has been observed.[26] Our valence peak positions agree with previous studies,[26] but our relative intensities are quite different. This is due to the variation of photoionization cross sections of individual orbitals at different photon energies. The resonances of metal nd orbitals of these molecules will be examined in the following section to further explain this feature.

The inner-valence spectra of the CpM(CO)₃ complexes have not appeared in the literature before. The key to understanding the inner-valence spectra of these molecules lies in the comparison of our spectra with those of metal carbonyls and (Cp)₂M. The valence photoelectron spectra of (Cp)₂M (M = Fe, Ru, and Os) have been the subjects of previous studies,[27] but only one peak around 19 eV in the inner-valence region of these molecules has been reported to be high carbon 2s character in (Cp)₂Fe by Green et al.[27b] The inner-valence spectra of these molecules have the same general features as those of the carbonyls (S, A, B, C, and D; Table 3) and can be assigned identically. However, noticeable differences are seen in the relative intensities of the peaks A, and the peak at ~16.5 eV. Both of these peaks must have a substantial contribution from the C 2s on the Cp ring. The remainder of the peaks A–D are at very similar positions to those of the W and Re carbonyls, and can be assigned identically (Table 3).

B. Core Levels. (a) High Resolution Metal Core Level Studies. Up until recently, the major useful core level effect was the chemical shift. However, with high resolution, it has been possible to resolve vibrational and ligand field splittings on the p and d levels of inorganic molecules.[10] We wanted to see whether we could observe such effects on the heavy metal 4f levels. Vibrational splitting has already been observed on the valence W 5d levels in W(CO)₆, and on other valence metal d levels.[17b]

Figure 4 shows the metal 4f spectra of W(CO)₆, Re(CO)₅Br, and Os(CO)₅ at photon energies of 80, 100, and 120 eV, respectively. It should be noted that in the spectrum of Re-(CO)₅Br, there is a small peak (at 49 eV) in the high binding energy side of Re $4f_{7/2}$ peak which is due to the overlap of the Re $5p_{3/2}$ ionization (Figure 2). It is necessary to go to 100 eV photon energy to minimize the contribution of $5p_{3/2}$ peak, while maintaining the reasonable resolution from the photon source, in order to resolve the vibrational fine structure. There is a definite shoulder on the higher binding energy side of the 4f levels in W(CO)₆ and Re(CO)₅Br. The splitting is very similar to the ground state CO stretch. The spectra were fitted with the spin–orbital splitting and the vibrational splitting from CO stretching mode. Table 4 summarizes the fitting parameters of Figure 4. This is the first observation of a *ligand* vibration effecting a metal core level ionization.

The vibrational effect in the heavy metal 4f spectra is expected after considering the core equivalent model.[28] In this model, the properties of a molecular ion with a core hole are

(25) (a) Higginson, B. R.; Lloyd, D. R.; Evans, S.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1913. (b) Hall, M. B. *J. Am. Chem. Soc.* **1975**, *97*, 2057.

(26) (a) Calabro, D. C.; Hubbard, J. L.; Blevins, C. H., II; Campbell, A. C.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1981**, *103*, 6839. (b) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

(27) (a) Cooper, G.; Green, J. C.; Payne, M. P. *Mol. Phys.* **1988**, *63*, 1031. (b) Cauletti, C.; Green, J. C.; Kelly, M. R. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *19*, 327. (c) Evans, S.; Green, M. L. H.; Jewitt, B.; Orchard, A. F.; Pygall, C. F. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1847.

(28) (a) Jolly, W. L.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1980**, *92*, 1863. (b) Ägren, H.; Selander, L.; Nordgren, J.; Nordling, C.; Siegbahn, K.; Muller, J. *Chem. Phys.* **1979**, *37*, 161.

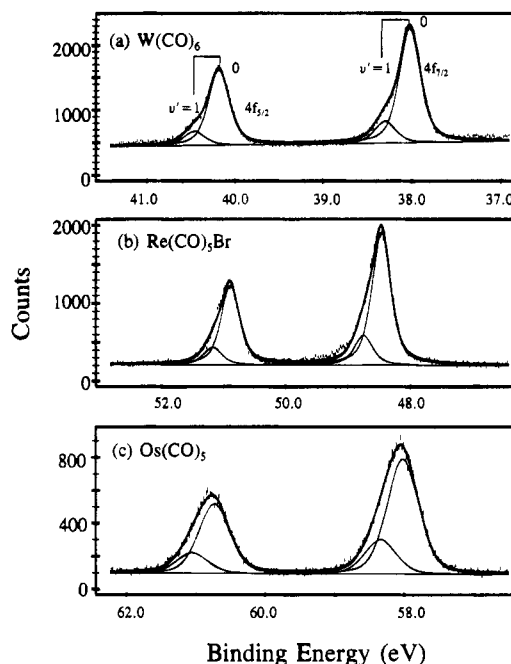**Table 2.** Binding Energies, Widths, and the Assignments of the Inner-Valence Spectra of Rhenium Carbonyls

| peak number | Re(CO)₅Cl | | Re(CO)₅Br | | Re₂(CO)₁₀ | | assignment |
	binding energy (eV)	width (eV)	binding energy (eV)	width (eV)	binding energy (eV)	width (eV)	
S	21.11	2.14	21.06	2.21	20.61	2.31	shake-up
A	23.73	3.05	23.79	3.31	23.51	3.07	satellite 1
B	27.29	3.46	27.93	2.97	27.57	2.00	satellite 2
C	31.25	3.90	31.30	3.33	30.79	2.70	satellite 3
D	36.10	3.53	36.09	3.67	35.38	3.51	CO 3σ
E	41.25	2.50	41.80	1.85	43.83	3.72	satellite 4
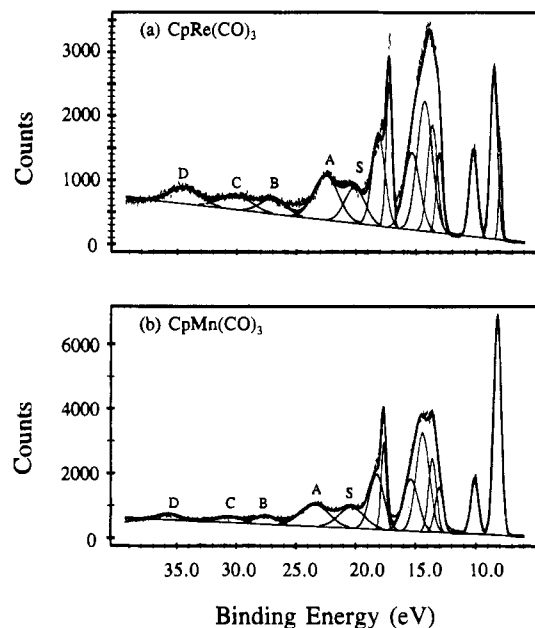
Figure 3. High resolution photoelectron spectra of (a) CpRe(CO)₃ and (b) CpMn(CO)₃ at 72 eV photon energy. The notation for labeling the peaks is similar to that of Figure 1, except only shake-up and inner-valence peaks are labeled here.

Table 3. Binding Energies, Widths, and Assignments of CpM(CO)₃ (M = Mn, Re)

| peak number | CpRe(CO)₃ | | CpMn(CO)₃ | | assignment |
	binding energy (eV)	width (eV)	binding energy (eV)	width (eV)	
S	20.10	1.97	20.33	2.52	shake-up
A	22.53	2.45	23.44	2.85	satellite 1
B	26.98	2.50	27.53	2.11	satellite 2
C	30.11	3.18	30.61	2.43	satellite 3
D	34.41	3.01	35.63	2.05	CO 3σ

approximated by the molecule with the $Z + 1$ atom. The core equivalent species for core ionized W(CO)₆ is [Re(CO)₆]⁺. The M−C bond length in [Re(CO)₆]⁺ is 2.01 Å,[29] which is substantially smaller than in W(CO)₆ (2.07 Å).[30] This substantial decrease in bond length between neutral and core ionized W(CO)₆, due to the deshielding effect, should lead to substantial vibrational structure. Also, the vibrational splitting of 0.275 eV (2220 cm⁻¹) from C−O stretching on W 4f orbital is larger than that of the ground state W(CO)₆ (2126 cm⁻¹), and closer to that of [Re(CO)₆]⁺ (~2200 cm⁻¹).[31] The vibrational splitting from Re−Br or the two CO vibrations in Os(CO)₅ may contribute to the Re and Os spectra, but cannot be resolved.

The observation and characterization of the vibrational effect of CO on metal 4f levels leads us to consider deriving the

(29) *Gmelin Handbook of Inorganic Chemistry, Organorhenium Compounds, Part 2*; edited by A. Slawisch, Springer-Verlag: Berlin, 1989.
(30) Bruce, D. M.; Holloway, J. H.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1627.
(31) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975.

Binding Energy (eV)

Figure 4. High resolution 4f photoelectron spectra of (a) W(CO)₆ at 80 eV photon energy, (b) Re(CO)₅Br at 100 eV photon energy, and (c) Os(CO)₅ at 120 eV photon energy. These spectra are fit with spin−orbit splitting and a ν_1(C−O) vibrational component.

inherent linewidths of these metal core levels. These linewidths are important for the studying the chemical dependence of core level lifetimes[10c] and for interpreting photoelectron spectra of surfaces which are complicated by surface core level shifts and disorder broadening associated with various adsorbate covered surfaces. Our experimental linewidth of W 4f levels is 0.25 eV, much larger than the inherent W 4f linewidth from theory[32] (0.07 eV) and experiment[33] (0.055−0.15 eV). Our broader lines must be due to the existence of a M−CO vibrational progression, as in the W 5d valence level.[11,17b] We have tried to fit another W−CO vibrational progression into the W 4f spectra in the previous communication[11] and derived the W 4f inherent linewidth to be around 0.15 eV. It is important to note here that our instrumental resolution of Figure 4 is around 100 meV, which is only comparable to the above inherent linewidth. Therefore, we are not confident about the extent of a W−CO vibrational progression, and we will have to wait for the even better instrumental resolution to completely resolve these features and derive a definitive inherent linewidth.

The trends in 4f parameters for the W, Re, and Os compounds (Table 4), particularly the trend in linewidths, are interesting to examine. The regular increases in both binding energy and spin−orbit splitting are as expected from previous low resolution studies.[34] The large increase in linewidths from the W to Os

(32) McGuire, E. J. *Phys. Rev. A* **1974**, *5*, 1840.
(33) (a) van der Veen, J. F.; Himpsel, F. J.; Eastman, D. E. *Phys. Rev. B* **1982**, *25*, 7388. (b) Wertheim, G. K.; Citrin, P. H.; van der Veen, J. F. *Phys. Rev. B* **1984**, *25*, 7236.
(34) Leigh, L.; Bremser, W. *J. Chem. Soc., Dalton Trans.* **1972**, 1216.

Table 4. Fitting Parameters of W, Re, and Os 4f Spectra

	binding energy 4f$_{7/2}$ (eV)	SO splitting (eV)	SO intensity ratio (eV)	Γ_{exptl} (eV)	ν_1(C—O) (cm^{-1})
W(CO)$_6$	37.92(3)	2.165(5)	0.65(3)	0.25(2)	2220(40)
Re(CO)$_5$Br	48.47(3)	2.429(5)	0.60(3)	0.35(2)	2300(40)
Os(CO)$_5$	58.02(3)	2.717(5)	0.60(3)	0.53(2)	(2580)

compound (0.25—0.53 eV) is certainly surprising. There are four possible causes of this large increase: (a) an increase in experimental resolution; (b) an increase in inherent linewidth; (c) an increase in vibrational broadening; and (d) an increase in ligand field splitting (LFS) which splits the 4f$_{7/2}$ and 4f$_{5/2}$ levels. The first two of the above can be quickly ruled out. The increase in experimental resolution from 80 eV photon energy to 120 eV photon energy is only about 60 meV, and would not affect the observed linewidths noticeably. As shown by McGuire,[32] the increase in natural linewidth would be only ≤50 meV, and also would not affect the observed linewidths noticeably. The contributions from vibrational effects cannot be easily evaluated at this time, especially because the core equivalent species for Os(CO)$_5$[Ir(CO)$_5$$^+$] is not known to examine the difference in M—C bond lengths between ground and core-ionized states.

Ligand field splitting[10c,35−37] is the most likely cause of the majority of this 4f line broadening. LFS has been observed mostly on core d levels, but has recently been resolved on the S 2p level in H$_2$S.[10f] It has not been observed on core f levels. However, Os(CO)$_5$ should have a very large asymmetric ligand field which would split the 4f$_{5/2}$ and 4f$_{7/2}$ levels into three and four respectively,[35,36] leading to line broadening. We have shown previously[35−37] that the core level LFS is proportional to the electric field gradient (EFG) at the nucleus, as normally measured by Mossbauer or nuclear quadrupole resonance spectroscopies. Unfortunately, the EFG's for our three compounds are not known. Qualitatively, however, we know that octahedral W(CO)$_6$ (O_h symmetry) must have zero EFG or LFS, and Os(CO)$_5$ (D_{3h} symmetry) should have a large EFG and LFS. Semiquantitatively, it is possible to calculate the relative magnitudes of the LFS for the third row transition metal species, by looking at the EFG for the first row analogues Cr(CO)$_6$, Mn-(CO)$_5$Br, and Fe(CO)$_5$. The Mossbauer quadrupole splittings (proportional to the EFG and LFS) are 0, 0.50, and 2.66 mm/s.[38−40] The above trend in EFG and LFS shows that the order of LFS in our compounds should be as follows: W(CO)$_6$ < Re(CO)$_5$Br ≪ Os(CO)$_5$. This order is just the same as seen in the 4f linewidths, strongly suggesting that LFS is the dominant factor controlling the linewidth trend.

Our observation of the vibrational fine structure and ligand field splitting on the 4f levels of this series of metal carbonyls is important for surface scientists studying small adsorbates on metals with high resolution photoelectron spectroscopy of narrow metal levels such as W and Re 4f or Pd 3d.[41] When
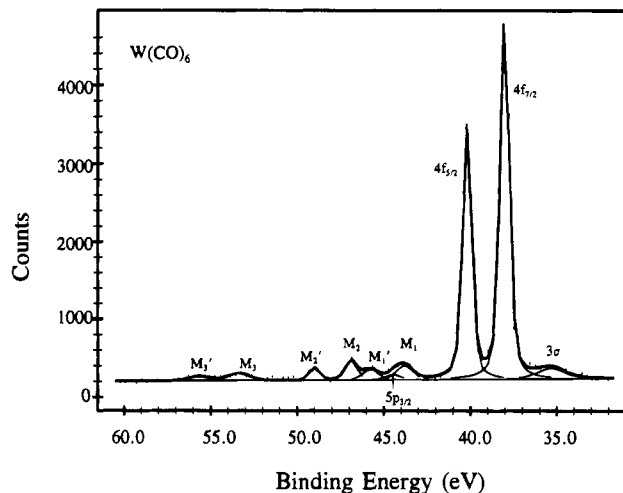

Figure 5. W 4f and associated satellite spectrum of W(CO)$_6$ at 150 eV photon energy. See Table 5 and text for assignment.

deconvoluting complex overlapping spectra of, for example, H, CO, O$_2$, N$_2$, etc. adsorbed on metals, our result indicates that vibrational and ligand field contributions to the metal spectra must be considered. Such vibrational contributions on the ligand levels (e.g. in the C 1s spectra of CO) have already been widely recognized,[42] but to our knowledge no vibrational contributions have been taken into consideration for the metal levels.

(b) Core Level Shake-up Spectra. Traditionally, the shake-up satellites of the core level in organometallic complexes have been observed using low resolution laboratory sources.[43] We were interested to examine the effect of high resolution, variable photon energy studies on the linewidth of the normally broad shake-up peaks and the relative intensity (relative to the main line) of the shake-up peaks as a function of photon energy. Unfortunately, because the overlap of the 5p and 4f lines (Figures 1 and 2), good shake-up spectra could not be taken below about 120 eV. The W(CO)$_6$ spectrum at 150 eV at an instrumental resolution of 0.45 eV is shown in Figure 5. This spectrum is qualitatively very similar to the X-ray spectrum, and the positions and relative intensities are very similar to the previous results. However, the W 4f linewidth is less than one-half of the previous X-ray spectrum, and most of the shake-up peaks are much narrower than the previous results. Indeed, the M$_2$ peak widths (0.75 eV) are very similar to the main line peak width of 0.61 eV (Table 5). This suggested the possibility of narrowing the shake-up peak widths even further with the improved experimental resolution. However, going to 120 eV at ~0.35 eV resolution, the main 4f peaks narrowed to 0.50 eV, but the M$_2$ shake-up peaks did not narrow. This study does show that good resolution does improve the shake-up widths considerably, and that the relative shake-up intensities do not change appreciably over the kinetic energy range of ~80 eV to 1200 eV.

(35) Bancroft, G. M.; Tse, J. S. *Comments Inorg. Chem.* **1986**, *5*, 89 and references therein.

(36) Gupta, R. P.; Tse, J. S.; Bancroft, G. M. *Philos. Trans. R. Soc.* **1980**, *293*, 535.

(37) Bancroft, G. M.; Creber, D. K.; Basch, H. *J. Chem. Phys.* **1977**, *67*, 4891.

(38) Bancroft, G. M.; Clark, H. C.; Kidd, R. G.; Rake, A. T.; Spinney, H. G. *Inorg. Chem.* **1973**, *12*, 728.

(39) Bancroft, G. M.; Platt, R. H. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 59.

(40) Clark, M. G.; Cullen, W. R.; Garrod, R. E. B.; Maddock, A. G.; Sams, J. R. *Inorg. Chem.* **1973**, *12*, 1045.

(41) (a) Andersen, J. N.; Ovarford, M.; Nyholm, R.; Sorenson, S. L.; Wigren, C. *Phys. Rev. Lett.* **1991**, *67*, 2822. (b) Spanjaard, D.; Suillot, C.; Desjonqueres, M. C.; Treglia, G.; LeCante, J. *Surf. Sci. Rep.* **1985**, *5*, 1.

(42) (a) Martensson, N.; Nilsson, A. *Surf. Sci.* **1989**, *211*, 303. (b) Martensson, N.; Nilsson, A. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *52*, 1.

(43) (a) Bancroft, G. M.; Boyd, B. D.; Creber, D. K. *Inorg. Chem.* **1978**, *17*, 1008. (b) Brisk, M. A.; Baker, A. D. *J. Electron Spectrosc. Relat. Phenom.* **1975**, *7*, 197. (c) Vernon, G. A.; Stucky, G.; Carlson, T. A. *Inorg. Chem.* **1975**, *15*, 278.

**Table 5.** Shake-up Energies and Widths of W 4f of W(CO)$_6$[a]

peak labeled	Δ binding energy (eV) (I_s/I_p)			width (eV)			assignment
	150 eV	120 eV	XPS[b]	150 eV	120 eV	XPS[c]	
4f$_{7/2}$				0.62	0.50	1.27	
4f$_{5/2}$				0.60	0.50	1.28	
M$_1$	5.78 (0.06)	5.4 (0.14)	6.1 (0.06)	1.18	1.31	1.6	2t$_{2g}$→3t$_{2g}$
M$_1'$	5.58	5.4	5.5	1.02	1.14	1.7	2t$_{2g}$→3t$_{2g}$
M$_2$	8.87 (0.07)	8.87 (0.11)	8.8 (0.06)	0.78	0.81	1.4	2e$_g$→3e$_g$
M$_2'$	8.82	8.86	8.4	0.72	0.73	1.5	2e$_g$→3e$_g$
M$_3$	15.36(0.04)	d	15.0(0.03)	1.48	d	1.6	1e$_g$→3e$_g$
M$_3'$	15.45	d	15.0	1.48	d	1.7	1e$_g$→3e$_g$

[a] Errors are 0.1 in the Δ binding energies and peak widths. [b] Reference 43a. [c] Line widths of XPS are estimated from spectrum in ref 43a. [d] Not observed.

The assignment of this spectrum is as given previously.[43a] The energy of the first shake-up peak (2t$_{2g}$ → 3t$_{2g}$) is in good agreement with that expected from the $Z + 1$ approximation. The electronic spectrum of W(CO)$_6$ places the 2t$_{2g}$ → 3t$_{2g}$ excitation energy at 4.53 eV.[44] However, for the core equivalent species Re(CO)$_6^+$, this transition energy increases to 5.82 eV, in good agreement with our shake-up energy of 5.7 ± 0.1 eV. The M$_2$ and M$_3$ shake-up peaks at 8.8 and 15.4 eV are beyond the UV absorption range, so we cannot use the $Z + 1$ approximation. The assignment of these peaks is still tenuous. It is possible, as suggested recently, that the M$_3$ peaks at ∼15 eV are due to shake-off.[12]

C. Valence np → nd resonance effects of CpM(CO)$_3$ (M = Mn and Re). The valence photoelectron spectra of CpM-(CO)$_3$ complexes have been studied extensively with He I and He II sources.[4,26] An empirical intensity rule[3] was successfully used to assign metal d orbitals based on the He I/He II intensity differences. However, the He I/He II techniques, even combined with the theoretical studies have failed to yield the definitive assignment of the valence spectrum of even relatively simple molecules, such as Ni(C$_3$H$_5$)$_2$.[9d,45] The definitive assignment of Ni 3d orbital can only be obtained with variable energy synchrotron radiation.[9d] Green et al. have observed the metal np → nd giant resonance effects in some organometallic systems,[7] which can also provide the definitive assignment of metal d-based ionizations in the valence region. Here, we report the observation of the np → nd resonance in CpM(CO)$_3$ (M = Mn and Re) complexes to show again the power of this technique for assigning the metal d orbitals.

The np → nd resonance phenomenon can be explained as due to the following process:[7]

$$np^6nd^x \rightarrow np^5nd^{x+1} \rightarrow np^6nd^{x-1} + e \quad (1)$$
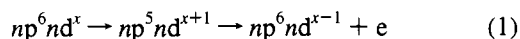
First, an inner np electron is excited to one of the unfilled nd levels. Subsequently, an electron falls back into the np hole and a valence nd electron is ionized—a so-called super Coster—Kronig transition. Therefore, an enhancement of the nd band in the region of the np absorption may be observed. It is helpful to observe such resonance effects with variable photon energies if the binding energies of the np levels can be determined. From separate higher photon energies studies, we observed the binding energies of Mn 3p of CpMn(CO)$_3$ and Re 5p$_{1/2}$ and 5p$_{3/2}$ of CpRe(CO)$_3$ are at 55, 49, and 58 eV, respectively.

Photoelectron spectra of CpMn(CO)$_3$ at 54, 56, 58, and 60 eV photon energies are illustrated in Figure 6. These spectra show clearly, that the relative intensity of the first peak, A, with
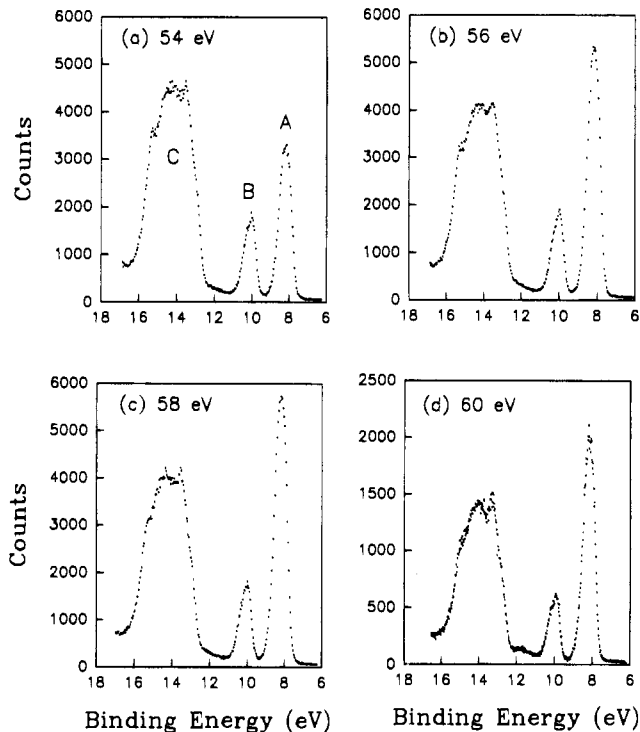

Figure 6. Valence level spectra of CpMn(CO)$_3$ at (a) 54, (b) 56, (c) 58, and (d) 60 eV photon energy, showing the maximum relative intensity of peak A around 58 eV photon energy.

the lowest binding energy increases dramatically from 54 eV photon energy to 56 and 58 eV photon energies, and begins to decrease from 58 eV photon energy to 60 eV photon energy. This is the photon energy region one would expect to observe the Mn 3p → 3d resonance on the 3d band. So, it is straightforward that the first peak can be assigned to Mn 3d orbitals, in agreement with the previous assignment.[4,26] This feature can be seen even more clearly in the relative partial photoionization cross sections over the complete photon energy range from 22 to 130 eV.[46]

A similar observation would be expected for CpRe(CO)$_3$, though one would expect to observe two resonances: 5p$_{1/2}$ → 5d and 5p$_{3/2}$ → 5d, because the spin—orbit splitting of the third row transition metal is much larger than that of first row transition metals.[47] Figure 7 illustrates the photoelectron spectra of CpRe(CO)$_3$ at 46, 48, 50, and 52 eV. The first band, A, obviously increases in intensity from 46 eV to 48 and 50 eV before decreasing at 52 eV, due to the 5p$_{1/2}$ → 5d resonance. The observation of the Re 5p$_{3/2}$ → 5d resonance can also be made at the photon energies region around 58 eV, as one would

(44) Beach, N. A.; Gray, H. B. *J. Am. Chem. Soc.* **1968**, *90*, 5713.
(45) (a) Moncrieff, D.; Hillier, I. H.; Saunder, V. R.; von Niessen, W. *Chem. Phys. Lett.* **1986**, *131*, 545. (b) Decleva, P.; Fronzoni, G.; Lisini, A. *Chem. Phys.* **1989**, *134*, 307.

(46) Hu, Y. F.; Bancroft, G. M.; Tan, K. H.; Yang, D. S. To be published.
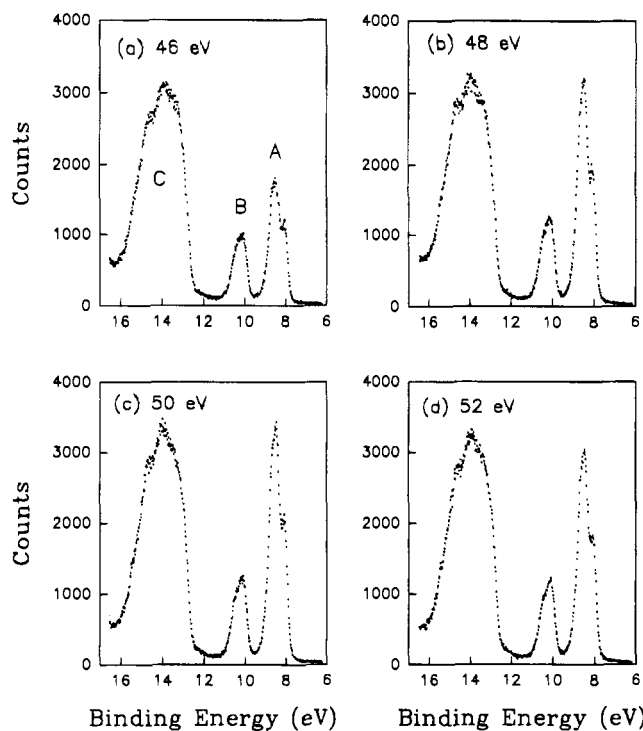(47) Eland, J. H. D. *Photoelectron Spectroscopy*; Wiley: New York, 1984.

Figure 7. Valence level spectra of $CpRe(CO)_3$ at (a) 46, (b) 48, (c) 50, and (d) 52 eV photon energy, showing the maximum relative intensity of peak A around 50 eV photon energy.

expect.[46] Again, from the Re 5p → 5d resonance phenomena, the first band A in the valence region can also be assigned to the Re 5d orbital, in agreement with previous assignments.

We may now compare the assignments of nd orbitals in CpM-$(CO)_3$ (M = Mn and Re) complexes from the above results with the valence level study of $CpPtMe_3$.[9a] For the electronic structure of $CpPtMe_3$, a Fenske–Hall calculation[48] predicts the

first band in the valence region is due to the Pt 5d ionization, which is consistent with the well-established, qualitative molecular orbital descriptions for $CpML_3$ complexes.[49] However, our synchrotron radiation study of $CpPtMe_3$ together with the Xα–SW calculation results showed that the HOMO's actually are the Pt–L orbitals instead of the nonbonding Pt 5d orbitals. The metal d orbitals must switch with the ligand orbitals from early to late transition metals.

Conclusions

High resolution photoelectron spectra of two type of organometallic molecules, metal carbonyls and $CpM(CO)_3$, have been reported. The advantages of monochromatized synchrotron radiation for studying the electronic structure of organometallic molecules have been demonstrated; we can study all the levels of these molecules from valence to inner-valence and core levels at high resolution in one spectrum. The inner-valence spectra of these molecules are dominated by the contribution from CO. Vibrational fine structure has been resolved for the first time on the core 4f levels of metal carbonyls, and this structure can be rationalized using the core equivalent model. Broadening on the Os 4f levels in $Os(CO)_5$ is shown to be due to ligand field splitting. We have shown that the shake-up structures of metal core level can be studied by synchrotron radiation, and enhanced resolution achieved. The $np → nd$ resonance in CpM-$(CO)_3$ compounds have been observed by the variable photon energy synchrotron radiation technique. This observation can be used to assign the metal valence d orbitals immediately.

(48) Yang, D. S.; Bancroft, G. M.; Puddephatt, R. J.; Bursten, B. E.; McKee, S. D. *Inorg. Chem.* **1989**, *28*, 873.

(49) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; John Wiley & Sons: New York, 1985.