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Variable Energy Photoelectron Spectra
of Metal Carbonyls

by

Yongfeng Hu

Department of Chemistry

Submitted in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Faculty of Graduate Studies
The University of Western Ontario
London, Ontario
April, 1996

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ABSTRACT

High resolution gas phase photoelectron spectra of transition metal carbonyls, W(CO)$_6$, Os(CO)$_4$L (L=CO, PMe$_3$), CpM(CO)$_3$ (M=Mn, Re), CpFe(CO)$_2$I, and Re(CO)$_2$X (X=Re(CO)$_5$, Cl, Br, and I) are reported. The advantages of monochromatized synchrotron radiation for studying the electronic structure of organometallic molecules are demonstrated. All the levels of these metal carbonyls from valence to inner-valence and core levels at high resolution can be studied in one spectrum.

For the core levels, vibrational fine structure is clearly resolved for the first time on the core W 4f levels of W(CO)$_6$, and this structure can be rationalized using the core equivalent model. Ligand field splitting is also shown to be important in the line broadening of the high resolution Os and Re 4f level spectra. The core and valence level chemical shifts of Os(CO)$_4$L and Re(CO)$_2$X complexes are compared by using Jolly's treatment. The high intensity of synchrotron radiation is important for observing the weak metal np core level spectra for the first time. The knowledge of the binding energies of the metal np levels is important for observing np→nd resonances on the valence nd levels.

For the valence levels, the np→nd resonance and the Cooper minimum effect are observed using variable energy photoelectron spectroscopy. The observation of these two effects provides firm assignments for the metal nd valence orbitals of all the metal carbonyls studied in this thesis. Vibrational fine structure is resolved on the 5d based peaks in the third row transition metal carbonyls. The Xα-SW calculations of Os(CO)$_3$ and CpMn(CO)$_3$ are used to aid in the complete valence level assignments of these molecules. The experimental branching ratios are found to be in good agreement with the theoretical results (by Xα-SW and Gelius treatment).

The high resolution and high intensity of synchrotron radiation is critical for the study of the weak and broad inner-valence spectra of these metal carbonyls. The inner-valence level of these molecules is shown to be dominated by contributions from the CO group, with the exception of the P 3s orbital in Os(CO)$_4$PMe$_3$. 

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I also wish to acknowledge the friendship and support of other members of the chemistry department: John Bozek, Leighton Coatsworth, Jeff Cutler, Marina Fuller, Ziqi Gui, Ling Hao, Jim Johnson, Masoud Kasrai, Stephen Knipe, Dan Legrand, Dienes Li, Xiaorong Li, Zhifeng Liu, John Mack, Leone Maddox, Prof. Ron Martin, Jay Mycroft, Mike Scaini, Prof. T.K. Sham, Doug Southerland, Jingcun Wu, Jianzhang Xiong and Zhanfeng Yin.

Finally, I would like to thank my parents and family for their support and understanding, especially my late father who encouraged me to go to University, and my late sister who paved the way for me to come to Canada and taught me the following:

踏踏实实修远兮 吾将上下而求索

I will try my best to move forward, no matter how far is the road ahead of me!

This thesis is dedicated to my wife Zhong Li and Bruce who made me enjoy and actually finish my study.
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<td>PES</td>
<td>photoelectron spectroscopy</td>
</tr>
<tr>
<td>SR</td>
<td>synchrotron radiation</td>
</tr>
<tr>
<td>UPS</td>
<td>ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>MO</td>
<td>molecular orbital</td>
</tr>
<tr>
<td>BE</td>
<td>binding energy</td>
</tr>
<tr>
<td>BR</td>
<td>branching ratio</td>
</tr>
<tr>
<td>ESCA</td>
<td>electron spectroscopy for chemical analysis</td>
</tr>
<tr>
<td>Xα-SW</td>
<td>Xα scattered-wave</td>
</tr>
<tr>
<td>PSD</td>
<td>position sensitive detector</td>
</tr>
<tr>
<td>Cp</td>
<td>$\eta^5$-cyclopentadienyl</td>
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Chapter 1

Introduction

1.1. Introduction

The extensive use of transition metal carbonyls as starting materials in organometallic chemistry,\(^1\) particularly in the syntheses of organic molecules,\(^2\) has prompted numerous experimental\(^3\) and theoretical\(^4\) studies of their structure and reactivity. Special attention has been given to the study of their electronic structure, in terms of electron distribution, bonding and stability, using photoelectron spectroscopy.\(^5\) Photoelectron spectroscopy has been perhaps the most direct technique for the determination of the electronic structure of organometallic molecules. However, the work before 1986 was limited by the laboratory light source, mostly He I and He II radiation. The availability of tuneable synchrotron radiation yields not only ionization energy information about the ionization bands of a molecule, but also intensity information from a photoelectron spectrum. In this work, the electronic structures of series of transition metal carbonyls are studied with a combination of He I/He II radiation and variable energy synchrotron radiation (SR) photoelectron spectroscopy.

1.2. General Principle of Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) was discovered early in the 1960s independently by two groups, one led by Turner using ultraviolet light,\(^6\) the other by Siegbahn using X-rays.\(^7\) Using X-rays, Siegbahn and his group concentrated on the study of core levels
of gases and solids, and this was later developed as X-ray photoelectron spectroscopy (XPS). In the meantime, Turner and coworkers continued to perform their pioneering experiments on the valence shell of gas phase molecules, and this technique is called ultraviolet photoelectron spectroscopy (UPS). The gap in the study of the electronic structure of transition metal molecules between these two techniques was not bridged until SR was introduced into the field of gas phase PES.

The principle of PES is based on Einstein's theory of the photoelectric effect.\(^8\) When photons of sufficient energy are used to interact with matter, ionization can occur with ejection of electrons. The kinetic energy \((E_K)\) of an ejected photoelectron is measured, and the binding energy \((E_B)\) for this event is defined as:

\[
E_B = h\nu - E_K \tag{1}
\]

The binding energy is viewed as the minimum energy required to remove an electron from a bound state in a molecule. This binding energy is often approximated as the negative of the orbital energy, based on Koopmans' theorem.\(^9\) Thus, the molecular orbital (MO) structure of a molecule can be obtained by the PES experiment.

In the field of transition metal chemistry, the number of accessible ion states and associated photoelectron bands gives rise to particular problems in assignment of photoelectron spectra. Theoretical treatments of molecules of this size and low symmetry are not always sufficiently accurate to define unambiguously the MO structure. Empirical methods of band assignment based on the comparisons of He I/He II spectra have proven to be of particular value in this regard.\(^{10}\)
1.3. PES by He I/He II Radiation

The most commonly used laboratory light source in PES is a discharge in pure helium gas, which gives the He I resonance line at 584 Å, equivalent to a photon energy of 21.22 eV. This light is energetic enough to cause ionization of the majority of valence electrons, and is of very high resolution (~20 meV). The high resolution of He I radiation has been shown to be critical for UPS studies of transition metal complexes. Observations of resolved fine structure due to spin-orbit splitting, Jahn-Teller splitting, and vibrational splitting have been extensively used for the assignment of photoelectron spectra of transition metal complexes. The chemical shift due to the chemical substitutions in the molecules was also important in the earlier studies.

Whenever an electron is ejected from a fully occupied degenerate orbital with angular momentum in a molecule, the result is an orbitally degenerate doublet state of the corresponding ion. The degeneracy of such a state can be lifted by coupling between the spin and orbital angular momenta of the unpaired electron, spin-orbit coupling. The magnitude of spin-orbit splitting is approximately proportional to the square of the atomic number of the atom for the valence shells of a many-electron system. Therefore, a larger splitting is expected for a second row or third row transition metal valence d orbital, and this is sometimes called the heavy metal effect. This effect is very useful for the assignment of metal d orbitals in second and third row transition metals, such as the Os 5d orbitals.

Upon the removal of an electron, when the degeneracy of a degenerated ionic state of a non-linear molecule is lifted by a change of the molecular shape of the ion, this
effect is defined as the Jahn-Teller effect. The magnitude of the Jahn-Teller effect is
dependent on the bonding nature of the electron removed, and is often discussed in terms
of the vibronic distortion: in the positive ion. The Jahn-Teller effect has been studied
in the photoelectron spectra of mainly small, organic molecules.\textsuperscript{12} In this work, this
effect will be studied in the high resolution He I spectra of Os 5d orbitals for two Os
carbonyls.\textsuperscript{14a} This effect will be compared with that of the only previously studied
transition metal compound, Fe(CO)\textsubscript{5}.\textsuperscript{14b}

Compared with the spin-orbit splitting and the Jahn-Teller effect, vibrational fine
structures are more often resolved, and assignments based on these results have
contributed to many band assignments and orbital character determinations of transition
metal molecules. The principle of vibrational splitting in the valence level photoelectron
spectra can be found in the literature.\textsuperscript{12} Briefly, vibrational fine structure observed in
photoelectron spectra results from difference in the equilibrium nuclear geometries of the
initial and final states of the electronic excitation, ionization or de-excitation process
which creates or fills a hole. The magnitude of the vibrational splittings in a PES
spectrum is often related to the vibrational frequencies of the neutral molecule. Metal
carbonyls yield extensive vibrational fine structure, because of the strong synergic bond
between transition metals and the carbonyl substituent group, and the CO stretching
frequencies are relatively large (\( \sim 2000 \text{ cm}^{-1} \)).\textsuperscript{3} A similar vibrational process is expected
for the core level spectra where vibrational fine structure is resolved, as in the W 4f
spectra of W(CO)\textsubscript{6} (see Chapter 3).
Discharges in helium can also generate He II light from ionized helium. Its main line is at 303 Å, equivalent to 40.81 eV. He II radiation UPS is of great interest for two reasons. Firstly, it makes complete valence shells of a molecule accessible. Secondly and more importantly, in addition to the above mentioned ionization information studied by He I radiation, the intensity information contained within a photoelectron spectrum can be studied by comparing He I and He II spectra. It has been shown that main group (C, N, O, P, and S) valence orbitals generally show relatively large He I intensities and relatively small He II intensities in comparison to transition metal d orbitals.\footnote{13} This empirical relationship of relative He I and He II ionization band intensities has been successful in interpreting the valence band spectra of many organometallic molecules.\footnote{10} However, this method was limited to only two photon energies, and it has been challenged in the studies of some relatively simple molecules, such as CpPtMe\footnote{16} and Ni(η\textsuperscript{3}-C\textsubscript{3}H\textsubscript{5})\textsubscript{2}.\footnote{17} Furthermore, these conventional light sources cannot access the inner valence and core levels of a molecule which are also important to a chemist. This void can now be filled with the synchrotron radiation excited PES which has much higher intensity and much better resolution than conventional XPS.

1.4. PES by Variable Energy Synchrotron Radiation

The physical properties and applications of synchrotron radiation have been reviewed in several places.\footnote{18} By definition, synchrotron radiation is the electromagnetic radiation emitted by electrons (or positrons) moving at relativistic velocities along a curved trajectory with a large radius of curvature. It was first observed in 1947 at the General Electric laboratories.\footnote{19} SR first appeared in science as a technical nuisance for
accelerator physics. It was not until 1956 that Tomboulian and Hartman started to use SR as a useful research tool.\textsuperscript{20} Since then, many SR storage rings have been built and devoted to scientific and technological research. SR is now being used as an essential facility for chemistry, physics, biology, engineering, material science, and medical science. The applications of SR are still expanding, especially with the construction of the third generation light sources, such as Advanced Light Source (ALS).

The application of SR as the light source for the PES studies of organometallic molecules will be demonstrated in the present work. All the experiments reported in this thesis were conducted at the Canadian Synchrotron Radiation Facility (CSRF) which is located at the Aladdin storage ring, University of Wisconsin-Madison. The advantages of using SR as the light source for the PES studies over the conventional light sources, such as He I/He II and X-ray, can be summarised as following:

(a) Wide spectral range, providing continuous photon energies from the UV to the soft X-ray region.

(b) High intensity over the whole range.

(c) High resolution. The resolution of the Grasshopper beamline at CSRF is typically \( \sim 50 \) meV at 40 eV photon energy, which is comparable to that of He II radiation, and \( \sim 150 \) meV at 100 eV photon energy, which is much better than that of X-ray laboratory sources of \( \sim 1 \) eV.

For the transition metal carbonyls studied in this work, the tunability of SR makes it possible to study the extensive photon energy dependence of band intensities. In particular, the observation of the np\( \rightarrow \)nd resonance and Cooper minimum effect in these
molecules has shown to be an valuable tool for the valence d orbital assignments.\textsuperscript{14a,21,22} With high resolution of SR, it is possible to resolve vibrational and ligand field splittings on the core levels of inorganic molecules\textsuperscript{23} and organometallic molecules.\textsuperscript{24} With the combination of high intensity and high resolution of SR, it is also possible to study the inner valence level of organometallic molecules.\textsuperscript{22}

1.5. \textbf{X\textalpha -Scattered-Wave (X\textalpha -SW) Calculations}

Theoretical calculations of ground state and excited-ion-state properties of molecules have been valuable for interpreting photoelectron spectra and understanding trends in electronic properties and chemical reactivity. For organometallic molecules, X\textalpha -SW calculations have been proven to be ideal for qualitative assignment and interpretation of valence level photoelectron spectra,\textsuperscript{25} both in terms of computing efficiency and accuracy. This technique has also been successfully utilized in the calculation of photoionization cross sections in the study of variable energy SR photoelectron spectra of some organometallic molecules.\textsuperscript{26}

The X\textalpha -SW method is based on the Hartree-Fock approximation,\textsuperscript{27} which simplifies the many-electron atomic or molecular wavefunctions to a one-electron wavefunction \([\varphi (\mathbf{r})]\). The energy can be calculated via the one-electron Shordinger equation

\[
E\varphi (\mathbf{r}) = [−\nabla^2 + V_N + V_C + V_{\text{\textalpha}}] \varphi (\mathbf{r})
\]  \hfill (2)

where \(-\nabla^2\) is the kinetic energy of the electron, \(V_N\) is the electron-nuclear attraction term, \(V_C\) is the electron-electron Coulomb repulsion term, and \(V_{\text{\textalpha}}\) is the exchange potential between electrons, which is approximated by a local potential in the X\textalpha -SW
method, according to

\[ V_{\text{xc}} = -6\alpha \left( \frac{3}{8} \pi \rho \left( r \right) \right)^{1/3} \]  \hspace{1cm} (3)

where \( \alpha \) is the scaling parameter and \( \rho(r) \) is the electronic charge potential.\(^{28}\) The value of \( \alpha \) was determined by atomic calculations.\(^{29}\) For spherically symmetrical systems, like atoms, these potentials are easily calculated. For molecules, like organometallic studied in this thesis, the muffin-tin model has to be introduced.\(^{27}\)

In the muffin-tin model, the molecule in question is broken down into intersphere and outersphere regions. An averaged potential is assumed for each atom and for the region outside the outersphere which surrounds the entire molecule. In the intersphere region, all the atoms are superpositioned, so that a muffin-tin potential is obtained for this region. The muffin-tin potentials are then used in the solution of the one-electron Schrödinger equation for each region. A charge density is generated from the resultant wavefunctions. The charge density is averaged by the muffin-tin scheme and a new potential is determined from the averaging of the charge density. A weighted average of the new potential and the initial potential serves as input for the first iteration. This process is repeated until self-consistency of the potential and charge density is achieved.

Photoionization cross sections were calculated using the X\(\alpha\)-SW potential with incorporation of the proper scattering boundary conditions.\(^{30}\) In order to correct the asymptotic behaviour of the potential at large values of \( r \), a Latter tail was added to the outersphere potential after the last iteration.\(^{31}\)
In this work, an Xα-SW calculation was performed for Os(CO)$_5$ and CpMn(CO)$_3$ to aid in the assignment of the valence and inner valence spectra of these molecules, and to compare with the experimental branching ratios.

1.6. Outline of the Thesis

This thesis consists of six chapters. This first Chapter is a general introduction of the experimental and theoretical approaches used for this work. Chapter 2 will focus on the experimental part of this work. Chapter 3 describes the valence, inner valence, and core level spectra of W(CO)$_6$. The high resolution of SR is demonstrated with vibrationally resolved W 4f core spectra. The combination of high intensity and high resolution of SR makes it possible to study the complete inner valence spectrum of W(CO)$_6$ for the first time. In Chapter 4, the electronic structures of Os(CO)$_5$ and Os(CO)$_4$PMe$_3$ are studied. The np→nd resonances and the Cooper minimum effect can be observed using variable energy PES. The observation of these two effects provides firm assignment for the Os 5d valence orbitals. The line broadening of Os 4f level due to both vibrational and ligand field splittings is also discussed. Chapter 5 describes the electronic structures of CpM(CO)$_3$ (M=Mn, Re) and CpFe(CO)$_2$I. The valence spectra are assigned using the np→nd resonances and the Xα-SW calculation result for CpMn(CO)$_3$. In Chapter 6, the variable energy PES study for Re(CO)$_3$X [X=Cl, Br, I, and Re(CO)$_3$I] complexes is presented. The observation of np→nd resonance is important for the correct assignment of the valence spectra of these molecules. Both the valence and core level chemical shifts for these molecules are studied.
1.7. References


(3) See, for example, Braterman, P. S. Metal Carbonyl Spectra; Academic Press: London, 1: 75.


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Chapter 2

Experimental

2.1. He I/He II Photoelectron Spectroscopy

In this work, all the He I and He II photoelectron spectra were recorded with our modified McPherson ESCA-36 photoelectron spectrometer. High resolution He I spectra were used mainly for two purposes in this study.

(a) With the high resolution of He I radiation (~20 meV), the fine structures in the valence region of metal carbonyls can be resolved. For example, the vibrational splittings due to the M-CO stretching mode were resolved for W 5d orbitals of W(CO)$_6$, and Os 5d orbitals of Os(CO)$_5$; the Jahn-Teller splitting was also resolved for Os 5d orbitals of Os carbonyls using high resolution He I radiation. The observation of these fine structures can be used for the assignment of metal d orbitals, and for the study of chemical bonding between metal and CO ligand.

(b) For each compound, the working conditions for obtaining good spectra were optimized using the McPherson ESCA-36 spectrometer in our lab at UWO, before the compound was taken to Madison for synchrotron radiation measurements. Beamtime is precious in Madison, and knowledge of the proper running conditions is essential to obtain spectra quickly. Furthermore, the Ar internally calibrated He I photoelectron spectra can be used as the reference for the synchrotron radiation experiments.
The details and the performance of our modified McPherson ESCA-36 photoelectron spectrometer have been described previously.\textsuperscript{1} Briefly, it consists of (1) a helium hollow cathode discharge lamp capable of producing both He I (21.22 eV) and He II (40.81 eV) radiation; (2) a vacuum chamber with a Edwards Series 100 diffusion pumping system; (3) a hemispherical sector electrostatic analyzer with a 36 cm radius and a 10 cm gap between the spheres. The photoelectrons with different kinetic energies are analyzed by the electrostatic analyzer, and it was pumped by a turbomolecular pumping system; (4) a channeltron detector which measures the intensity of the photoelectrons with selected kinetic energy; and (5) a Zenith Z-158 PC microcomputer, which interfaces the signal from the detector and controls the kinetic energy scanning of the electron energy analyzer. Volatile liquid samples and gases can be introduced directly into the chamber through the sample inlet; less volatile solid samples can be introduced into the gas cell through the heatable metal probe.

The regular maintenance of the spectrometer is important to obtain the high resolution and high intensity spectra. The following is a summary based on my personal experience over the last five years.

**Vacuum System.** The pumping oil in all the roughing pumps was checked regularly and changed twice a year depending on the amount of pumping. The turbomolecular pump was greased twice a year, and the oil level was regularly checked. To ensure the good performance of the turbo pump (base pressure $\sim 8 \times 10^{-8}$ torr), both the bearing and belt of this system have to be regularly checked (by the sound of the pump). Two bearings and 4 belts have been replaced over the last five years. The
diffusion pump was relatively carefree, as long as the cooling water stayed on whenever this pump was on. Unfortunately, we had to change the diffusion pump oil twice in the last five years, due to a leaking problem (with Krytox Fluorinated Oil, #1618). The valves between the turbo pump and the analyzer, between the diffusion pump and the chamber, and between the turbo pump and the chamber, were all operated with the compressed air from the air cylinder. The pressure of the vacuum system was read by a Granville-Phillips 330 Ionization Gauge Controller, using a ionization gauge (Fil-Tech, #G-75-P).

Helium Lamp, and Vacuum Chamber. The helium lamp produced essentially monochromatic helium lines. After a period of time, especially after running the very volatile, CVD-type compounds, the lamp was cleaned with methanol in an ultrasonic cleaner. The Ar spectra were used to check the performance of the system and the cleanliness of the helium lamp. If the intensity was low, it was always a good idea to adjust the position of the lamp, since the intensity can often be enhanced by a factor of 3 to 5. The vacuum chamber was baked out at a temperature of over 100 °C periodically. If necessary, the gas cell and the detachable components in the chamber would be taken off, the entire chamber would then be thoroughly cleaned, and all pertinent surfaces would be coated with a layer of fine graphite afterwards, to minimize charging effects.

Analyzer and Channeltron Detector. The McPherson electron analyzer was very reliable and required little attention. Only the entrance slit was cleaned when the chamber was taken apart. A channeltron detector was linked to the exit slit of the
analyzer. It was powered by the McPherson high stability voltage power supply. To ensure the good performance and the long lifetime of the channeltron detector, it was only necessary to apply lower voltage (for example, 2400 V) to the new channeltron detector. Higher voltage (up to 2900 eV) was required to maintain the high counts for an older detector. When the intensity became low and/or the signal to noise ratio became low, the channeltron detector had to be replaced.

**Spectra Measurement and Working Parameters.** All the compounds, except Re(CO)$_3$I, Os(CO)$_3$ and Os(CO)$_4$PMe$_3$, were commercially available. Re(CO)$_3$I was prepared by the literature method with the aid of X. Li. Os(CO)$_3$ and Os(CO)$_4$PMe$_3$ were prepared by the published procedure at Simon Fraser University by H. B. Davis. The Ar 2p$_{3/2}$ line at 15.759 eV binding energy was used as the internal calibrant for each compound. The typical working parameters are: base pressure $\sim 2 \times 10^{-7}$ torr; pressure with He gas $\sim 4 \times 10^{-6}$ torr; total pressure with sample (for example with Ar) $\sim 3 \times 10^{-5}$ torr; current of He lamp 300 mA; voltage of He lamp $\sim 3.5 \times 10^3$ V. Under the above conditions, the resolution was about 22 meV for the He I spectra (defined by the FWHM of Ar 2p$_{3/2}$ line), and the intensity for Ar 2p$_{3/2}$ line was over 20,000 counts per second.

All the samples were introduced into the gas cell through the heatable probe. The operating temperatures for each compound will be given in the following appropriate chapter.

**Spectral Fitting.** Photoelectron spectra were fitted using a linear combination of Gaussian and Lorentzian linshapes with an iterative procedure that has been described previously.
2.2. Synchrotron Radiation Photoelectron Spectroscopy

All the variable energy photoelectron spectra were recorded using the Grasshopper beamline (#91) at the Canadian Synchrotron Radiation Facility (CSRF) at the Aladdin storage ring, University of Wisconsin, Madison. The synchrotron radiation was monochromatized by a Mark IV Grasshopper monochromator which offers light ranging from 22-500 eV. The performance of the Grasshopper beamline has been discussed elsewhere.\(^3\)

A 600 groove/mm grating was used in the monochromator to provide photons with energies between 20-75 eV. An 1800 groove/mm grating was used to provide photons with energies ranging from 70 to 200 eV. The photon resolution \((\Delta E)\) from the exit slit of the monochromator was determined by

\[
\Delta E = \frac{E^2 \Delta \lambda}{12398} \tag{4}
\]

where \(E\) is the photon energy, and \(\Delta \lambda\) is defined by

\[
\Delta \lambda = x \times w \tag{5}
\]

where \(w\) is the slit width of the monochromator, and \(x = 0.008\) for the 600 groove/mm grating, and \(0.0027\) for the 1800 groove/mm grating.

The photoelectron spectrometer used in Madison was very similar to the He I and He II photoelectron spectrometer at UWO. A 36 cm McPherson electron analyzer (from the University of Alberta) was used to analyze the electrons. The analyzer was mounted to a frame so that the polarized synchrotron beam was directed across the length of the analyzer slit. A pseudo-magic angle \((\Theta_x = 55.8^\circ, \Theta_y = 34.2^\circ, \text{ and } \Theta_z = 90^\circ)\)\(^6\) was used to
take in the electrons, to minimize variations in intensity which are due to the asymmetry parameter $\beta$, assuming that the radiation from the Aladdin storage ring is 90% plane polarized. The resolution of the analyzer was approximated to be 1/720, when a 1 mm exit slit was used for the analyzer.

Before 1991, a channeltron detector was used to detect the electrons. A Quantar #3395 position sensitive detector (PSD) was installed in 1991. The use of the PSD speeded up the experiment greatly, and it was estimated that the count rate can be increased by 20-50 times over the previous channeltron system. Special attention has to be paid to both the absolute energy scale and the dispersive calibration of the PSD system, since it could produce the spectrum with the wrong dispersion! (The dispersion of the PSD system can be correctly calibrated with Xe MNN Auger lines)

The operation of CSRF photoelectron spectrometer was similar to that of McPherson ESCA-36 spectrometer. Xe and Kr gases were used for the calibration of the instrument. The working conditions for each sample were the same as in our UWO lab.

Spectra were deconvoluted with a Gaussian-Lorentzian line shape with a nonlinear least-squares procedure. The peak areas were used to calculate the experimental branching ratios (BR$_i$) for each peak or band, based on the simple formula, $BR_i = A_i / \Sigma A_i$, where $A_i$ is the individual peak area. The experimental branching ratios were then used to compare with the theoretical branching ratios calculated by the X$\alpha$ method, or the Gelius model, to assist the spectral assignments.
2.3. References


Chapter 3

Comprehensive High Resolution Photoelectron Spectra of W(CO)₆

3.1. 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)¹² and medium resolution (~0.5 eV)¹³ studies of core levels using non-monochromatized Mg Kα, 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 inorganic⁶ and organometallic⁷ 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 complexes⁷,⁹ give an especially powerful tool for determining the MO levels (using the variable cross sections and resonances at the core p levels⁷), especially when combined with Xα-SW 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. Also, in the inner valence region, mainly because of the low intensity, only one medium resolution inner valence X-ray spectrum of an organometallic molecule, Cr(CO)$_6$, has been reported.\textsuperscript{11}

In this Chapter, monochromatized synchrotron radiation and our newly developed photoelectron spectrometer\textsuperscript{10,12} are used to obtain high resolution valence, inner valence and core level spectra of an organometallic compound, W(CO)$_6$. There are two major objectives. First, the high resolution and high intensity of synchrotron radiation will be demonstrated to be important to obtain the broad-scan spectrum of W(CO)$_6$ which includes all levels from valence to inner-valence and core levels. For the first time, high resolution ($\approx 0.1$ eV) inner valence level spectra of organometallics are reported. High resolution and intensity are critical for resolving and clarifying features in inner-valence level spectrum of W(CO)$_6$. Second, the high resolution W 5d and 4f spectra of W(CO)$_6$ will be reported. Vibrational structure, arising from both W-C and C-O vibrations, is observed on the W 5d and 4f levels. The importance of these W 4f spectra for the interpretation of both the valence level photoelectron spectra of organometallic molecules and the core level spectra of metal species deposited on surfaces, are discussed.

3.2. Experimental

He I spectra were recorded on a McPherson ESCA-36 photoelectron spectrometer.\textsuperscript{13} The Ar 2p$_{3/2}$ line at 15.759 eV binding energy (BE) was used for internal calibration during data acquisition. The resolution (FWHM) of Ar 2p$_{3/2}$ line was about 20 meV for the He I spectra. The variable energy spectra were obtained with the
Grasshopper beamline at the Canadian Synchrotron Radiation Facility (CSR) which is located at the Aladdin storage ring, University of Wisconsin-Madison. An 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. 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 to 50 eV reported in this Chapter, 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. By using the PSD, the count rate can be increased by 20-50 times over the previous channeltron system. This high intensity is critical to the inner valence study here, because the inner valence levels have small cross section and are very broad. 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\textsubscript{5,3} at a BE of 93.795 eV with an 1800 g/mm grating. The binding energies are accurate to within \( \pm 0.01 \) eV.

High purity W(CO)\textsubscript{6} was purchased from Strem Chemicals. The solid sample was introduced into the gas cell of the spectrometer directly via the heatable probe. It was heated to 40 °C in order to generate enough vapour pressure. The pressure in the sample chamber is controlled around \( 3 \times 10^3 \) Torr, while the pressure in the gas cell was \( \sim 5 \times 10^3 \) Torr.
Spectra were deconvoluted with a Gaussian-Lorentzian lineshape using a nonlinear least squares procedure described previously.\textsuperscript{15}

3.3. General Features and Inner Valence Assignments

The high resolution broad-scan spectrum of \( W(\text{CO})_6 \) at 80 eV photon energy is illustrated in Figure 3-1. Peak positions and assignments are given in Table 3-1. The spectrum in Figure 3-1 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 spectra can be divided into the three traditional regions: valence or outer valence levels with BE less than \( \sim 20 \) eV (labelled with the numbers 1-7 and S); inner valence levels with BE between \( \sim 20 \) eV and \( \sim 40 \) eV (labelled with A to D); and the core levels \( C_1, C_2, C_3 \) with \( \text{BE} \sim 40 \) 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 \( (C_1 \text{ and } C_2) \), 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 that of the previously published He II spectrum which gives peaks up to 24 eV BE (Figure 2 in ref 16a); but slightly poorer than the previous He I spectra up to 16 eV BE. For example, the high resolution spectrum (insert) readily shows three peaks in the \( \sim 18 \) eV band which were not seen previously in the He II spectrum.\textsuperscript{16a} This observation is important for the complete assignment. The inner valence peaks above 24 eV have not been observed previously, the \( W 4f \) peaks \( (C_1 \text{ and } C_2) \) have been observed previously at low resolution,\textsuperscript{17} but the broad core level peak \( C_3 \) has not been previously observed.
Figure 3-1. High resolution broad-scan photoelectron spectrum of W(CO)$_6$ at 80 eV photon energy. The valence level peaks are labelled with the numbers (1-7) with increasing binding energy. Peak S is assigned to a shake-up peak (see text). The inner-valence peaks are labelled with letters (A-D). The three core level peaks are labelled 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 3-1. Binding Energies, Widths and The Assignments of W(CO)$_6$ at a Total Resolution of $\leq 0.2$ eV$^*$

<table>
<thead>
<tr>
<th>peak label</th>
<th>BE (eV)</th>
<th>width (eV)</th>
<th>majority character</th>
<th>MO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.57</td>
<td>0.57</td>
<td>W 5d and CO 2$\pi$</td>
<td>$2t_{2g}$</td>
</tr>
<tr>
<td>2</td>
<td>13.38</td>
<td>0.66</td>
<td>CO 1$\pi$ and 5$\sigma$</td>
<td>$8t_{1u}$</td>
</tr>
<tr>
<td>3</td>
<td>14.21</td>
<td>0.66</td>
<td>CO 1$\pi$ and 5$\sigma$</td>
<td>$1t_{1g}$, $1t_{2u}$</td>
</tr>
<tr>
<td>4</td>
<td>14.83</td>
<td>0.65</td>
<td>CO 1$\pi$ and 5$\sigma$</td>
<td>$5e_g$</td>
</tr>
<tr>
<td>5</td>
<td>15.42</td>
<td>1.20</td>
<td>CO 1$\pi$ and 5$\sigma$</td>
<td>$7t_{1u}$, $1t_{2g}$, $8a_{1g}$</td>
</tr>
<tr>
<td>6</td>
<td>17.63</td>
<td>0.46</td>
<td>CO 4$\sigma$</td>
<td>$6t_{1u}$</td>
</tr>
<tr>
<td>6'</td>
<td>18.06</td>
<td>0.47</td>
<td>CO 4$\sigma$</td>
<td>$4e_g$</td>
</tr>
<tr>
<td>7</td>
<td>18.52</td>
<td>0.46</td>
<td>CO 4$\sigma$</td>
<td>$7a_{1g}$</td>
</tr>
<tr>
<td>S</td>
<td>20.06</td>
<td>2.90</td>
<td>shakeup</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>23.63</td>
<td>2.23</td>
<td>satellite 1</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>27.06</td>
<td>2.15</td>
<td>satellite 2</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>30.34</td>
<td>2.86</td>
<td>satellite 3</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>35.29</td>
<td>4.29</td>
<td>CO 3$\sigma$</td>
<td></td>
</tr>
<tr>
<td>C$_1$</td>
<td>37.98</td>
<td>0.37</td>
<td>W 4f$_{7/2}$</td>
<td></td>
</tr>
<tr>
<td>C$_2$</td>
<td>40.16</td>
<td>0.37</td>
<td>W 4f$_{5/2}$</td>
<td></td>
</tr>
<tr>
<td>C$_3$</td>
<td>43.85</td>
<td>2.28</td>
<td>W 5p$_{3/2}$</td>
<td></td>
</tr>
</tbody>
</table>

$^*$ The positions and widths of Peaks 6, 6' and 7 are taken from the insert spectrum in Figure 3-1.
The assignment of the valence band spectrum up to 16 eV (Table 3-1) follows exactly from that of Higginson et al.,\textsuperscript{16a} and requires little comment. Peak 1 is broadened by the spin-orbit split W 5d \( t_{2g} \) ionizations. The next four peaks (2-5) arise from seven MO's of mainly CO 1\( \pi \) and 5\( \sigma \) character (Table 3-1). The BE values are in excellent agreement with the previous He I results.\textsuperscript{16a} With high resolution He I excitation, vibrational structure from both W-CO and C-O vibrations has been resolved for Peak 1,\textsuperscript{11,16} and this fine structure will be compared with the vibrationally resolved W 4f core spectra in the following section (Section 3.4.).

The assignments of the peaks at \( \sim 18 \) eV and 20 eV are not at all straightforward, but the spectra shown in Figure 3-1 put the assignment on a very firm footing. To derive the correct assignment, it requires the He II\textsuperscript{17} and X-ray spectra\textsuperscript{11} of Cr(CO)\(_6\) in this BE region; the core-level shakeup spectra of CO\textsuperscript{3a} and W(CO)\(_6\),\textsuperscript{16} the inner valence spectrum of CO\textsuperscript{15}, and theoretical calculations.\textsuperscript{20} 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 6\( t_{1u} \), 4\( e_g \) and 7\( a_{1g} \) orbitals of dominant CO 4\( \sigma \) character; while the peak at 20 eV must be due to an intense shake-up peak from the 5\( \sigma \) and 1\( \pi \) CO orbitals around 15 eV BE. This assignment agrees with the previous assignment given by Plummer et al.\textsuperscript{17} for the analogous molecule Cr(CO)\(_6\). However, this assignment is contrary to that given originally by Higginson et al. for W(CO)\(_6\),\textsuperscript{16a} and that published very recently by Nilson et al. for Cr(CO)\(_6\).\textsuperscript{11} Nilson et al. assigned the unresolved band at \( \sim 18 \) eV (Peaks 6, 6', 7) to the combined 4\( e_g \) and 6\( t_{1u} \) ionizations, and the broad band at 20 eV to the 7\( a_{1g} \) ionization. The present assignment is strongly supported by several theoretical and
experimental findings. First, theoretical calculations\textsuperscript{20} show that the splitting of the majority 4\sigma levels should be \(\leq 1\) eV as in this assignment. Second, the intensity and width of Peak S is not consistent with the ionization from a non-degenerate \(a_{1g}\) orbital. For example, Peak S is more intense than Peaks 6, 6' and 7 at all photon energies studied between 40 eV and 90 eV; whereas, the Gelius intensity treatment\textsuperscript{24} certainly predicts that the \(4a_{1g}\) intensity should be \(~33\%\) of the \(6t_{2u}\) intensity, as for the present assignment. Previous studies in our group have shown that the Gelius treatment works well down to photon energies of \(~50\) eV.\textsuperscript{54,94} Third, the fit of lower energy spectrum shown as an insert in Figure 3-1 yields a ratio of intensities for Peaks 6, 6', 7 and S of 1:2.5:3.8:10, consistent with the present assignment. Also, the separation between Peaks 6, 6' and 7 (\(~0.4\) eV, Table 3-1) is too large to be of vibrational origin. Fourth, the intensity of Peak S is consistent with that expected for a shake-up peak associated with Peaks 2-5, as suggested by Plummer et al. for Cr(CO)\textsubscript{6}.\textsuperscript{17} The core level spectra (C 1s and O 1s) of the M(CO)\textsubscript{6} compounds (M=Cr, Mo, W) generally give very intense shakeups (\(~30\%\) of the intensity of the "main" line) \(~5\) eV from the main line.\textsuperscript{17,18} 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-shakeup intensity (\(~3\%\)) in CO on both the C 1s core level\textsuperscript{3a} and valence shakeups at 21 eV BE in the free molecule. In CO, the 21 eV shakeup peak is not observable with the medium resolution X-ray\textsuperscript{11} or synchrotron spectra.\textsuperscript{19} These results show strongly\textsuperscript{17} that the shakeup positions and intensities are very similar for both C 1s and O 1s core levels and valence levels for carbonyl compounds.
The contributions from the 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. The high resolution inner-valence spectrum of the free CO molecule has also been studied recently. 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 my results with those from Cr(CO)₆ and free CO. Peak A at 23.63 eV BE can be assigned to the so-called C state in free CO which has a predominant final 5σ¹1π' 12π¹ state configuration which can be considered as a normal monopole shake-up state that gains intensity by configuration interaction with the 4σ¹ state. A similar peak has been observed at 23.7 eV for free CO and at 23 eV BE for Cr(CO)₆. Peak B is relatively weak at 27.06 eV BE. This peak was not resolved in Cr(CO)₆; but is evident in free CO at 28.5 eV and it corresponds to the 4σ¹1π'12π¹ final state. The satellite peak C is associated with the π²-π² double shake-up process accompanying the 5σ ionization in free CO, as in the Cr(CO)₆. 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 ionisation has been discussed in the free CO molecule, 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. 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 4f₅/₂ peak at 40.18 eV BE, this satellite peak can not be observed in the spectrum of W(CO)₆.
The last part of Figure 3-1 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 the W 4f orbital at 37.98 and 40.16 eV BE.\textsuperscript{21} The third peak C_3 is the 5p_{3/2} level of W at 43.85 eV. At first glance, it is possible that this peak could be assigned to the 5p_{1/2} level of W, with the other spin orbit component 5p_{3/2} overlapping with the 3σ band of CO lying at 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 declines rapidly relative to that of W 4f as photon energy increases.\textsuperscript{22}

The measurement of W 5p binding energies can be used to predict the appropriate photon energies for excitation of the 5p-5d resonance effects.\textsuperscript{7} The 5p binding energies of atomic W have been reported to be 41 and 51 eV referenced to the vacuum level.\textsuperscript{23} In the previous synchrotron radiation study of W(CO)_6,\textsuperscript{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. This report of W 5p binding energies agrees well with the previous experimental results, and also confirms the present assignment. In Chapters 4, and 5, it will be shown that the knowledge of the np binding energies can be used to observe the np \rightarrow nd resonance effects in Os(CO)_4PMe_3 and CpM(CO)_3 (M=Mn, Re) complexes.

3.4. Vibrationally Resolved W 5d and 4f Spectra

For valence level photoelectron spectra of small molecules, researchers have long used vibrational structure to infer the bonding nature of molecular orbitals.\textsuperscript{24} For example, extensive vibrational structure is associated with bonding or antibonding
orbitals, while little or no vibrational structure is associated with non-bonding orbitals.\textsuperscript{24} Vibrational structure is usually not resolved in large organometallic molecules. However, in a high resolution study, Lichtenberger and coworkers were able to resolve both W-C and C-O vibrational modes in the valence W 5d peaks in W(CO)$_6$\textsuperscript{16b} and in the valence Re 5d peaks in CpRe(CO)$_3$.\textsuperscript{25} Using the above accepted theory, they estimated the importance of the W 5d electrons in the W-CO bond.

Extensive vibrational structure has also been resolved very recently in the photoelectron spectra of \textbf{non-bonding core} orbitals: for example, the C 1s, P 2p and Si 2p orbitals of CH$_4$, PH$_3$ and SiH$_4$ (and other Si molecules) respectively.\textsuperscript{26} However, little or no vibrational structure has been observed in the photoelectron spectra of molecules containing heavy elements, such as Xe and I.\textsuperscript{27} It would be interesting to see whether such effects can be observed on the heavy metal 4f levels and can be compared with the W 5d valence spectra.

The high resolution W 5d and W 4f spectra are illustrated in Figure 3-2 and Figure 3-3, respectively. The spectral parameters for the three fits (plus a multipeak fit to the W 4f spectrum) are given in Table 3-2. The W 5d spectrum (and the analyses of this spectrum) is almost identical to that published previously.\textsuperscript{16b} At first sight (Figure 3-2a), the W 5d spin orbit splitting (0.26 eV), and a C-O vibrational progression (0.27 eV, 2180 cm$^{-1}$) on each spin-orbit peak, are apparent. On much closer inspection,\textsuperscript{16b} each of the six peaks in Figure 3-2a is split by the W-C symmetric stretching frequency (Figure 3-2b). This fit in Figure 3-2b is not, of course, a unique fit, but it is believed that the errors (Table 3-2, from the standard deviation of five spectra) are realistic. The
Figure 3-2. The high resolution W 5d photoelectron spectra of W(CO)₆. In (a), the spectrum is fit considering just spin-orbit splitting, and a ν₁(C-O) vibrational component, (b) fits a ν₂(W-C) vibrational envelope as well.
Figure 3-3. The high resolution W 4f spectrum of W(CO)$_6$. The spectrum is fit just considering spin-orbit splitting and a $\nu'(\text{C-O})$ vibrational component, as in Figure 3-2.
The vibrational frequencies for the \( \nu_1 \) and \( \nu_2 \) modes of \( \text{W(CO)}_6 \) are 2197 to 2224 and from 415 to 441 cm\(^{-1}\), respectively, in different compounds. \(^{32}\) The vibrational frequencies for the \( \nu_1 \) and \( \nu_2 \) modes of \( \text{W(CO)}_6 \) are 216 and 426 cm\(^{-1}\), respectively, in the neutral molecule. \(^{32}\)

<table>
<thead>
<tr>
<th>( \nu_1 ) (cm(^{-1}))</th>
<th>( \nu_2 ) (cm(^{-1}))</th>
<th>( \nu_1 ) (cm(^{-1}))</th>
<th>( \nu_2 ) (cm(^{-1}))</th>
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<tr>
<td>410(30)</td>
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<td>387(40)</td>
<td>2260(40)</td>
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</tr>
<tr>
<td>2090(40)</td>
<td>2090(40)</td>
<td>1810(40)</td>
<td>1810(40)</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W 4f</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W 5d</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3-2. Special Parameters for the W 5d and 4f Photodissociation Spectrum of \( \text{W(CO)}_6 \).
W-C frequency of 410 cm\(^{-1}\) is very similar to the ground state frequency of 426 cm\(^{-1}\),\(^{28}\) and a little larger than the 387 cm\(^{-1}\) quoted by Hubbard et al.\(^{16b}\)

The W 4f spectrum in Figure 3-3 is qualitatively similar to the W 5d spectrum. Both the W 4f spin-orbit splitting (2.165 eV) and a shoulder due to the C-O vibrational model are evident immediately. For both the W 5d and W 4f spectra, the vibrational spacing is \(~2200\) cm\(^{-1}\), definitely indicative of the excitation of the \(\nu_1\)(C-O) mode which in ground state of W(CO)\(_6\) lies at 2126 cm\(^{-1}\).\(^{28}\) To confirm this surprising observation of a ligand vibrational splitting on a metal core level, many spectra were recorded between 60 eV and 120 eV photon energy. All spectra of the W 4f levels, and the Re and Os 4f levels of other carbonyls (see the following Chapters), are consistent with the fit shown in Figure 3-3.

Although there is no further observable vibrational fine structure in the W 4f spectrum, two factors strongly indicate that there is indeed a W-C vibrational progression in the W 4f spectrum, similar to that in the W 5d spectrum. First, the W 4f peak widths in Figure 3-3 (0.25 eV) are comparable to the W 5d linewidths (0.21 eV) in Figure 3-2a and much larger than the instrumental linewidth of \(~100\) meV. These W 4f linewidths are of course much smaller than the linewidths (1.25 eV) observed with a laboratory X-ray source.\(^{18}\) Second, and more importantly, the W 4f linewidth of 0.25 eV is much larger than the inherent W 4f linewidths obtained both from theory (0.07 eV)\(^{29}\) and the experiments (0.055-0.15 eV, from W 4f spectra of W metal).\(^{30}\) To obtain linewidths of \(\leq 0.15\) eV, a similar W-C vibrational progression had to be fit to the W 4f spectrum (Table 3-2), as is present in the W 5d spectrum (Figure 3-2b). A W 4f inherent
linewidth cannot be derived at this time, because there is still an uncertainty about the extent of the vibrational W-C progression in the 4f spectra.

The large vibrational manifold in the W 4f spectrum is expected after considering the core equivalent model.31 In this model, the properties of a molecular ion with a core hole are approximated by the molecule with the $Z+1$ atom. The core equivalent species for core ionized W(CO)$_6$ is Re(CO)$_6^+$. As seen in the Table 3-2, the M-C bond length in Re(CO)$_6^+$ is 2.01 Å,32 which is substantially smaller than in W(CO)$_6$ (2.07 Å).33 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.26 Also, the vibrational splitting of 0.275 eV (2260 cm$^{-1}$) from C-O stretching on W 4f orbital is larger than that of ground state W(CO)$_6$, and closer to that of Re(CO)$_6^+$ (2200 cm$^{-1}$).28 The $\nu_2$(W-C) frequencies of 410 cm$^{-1}$ are within the error for both W(CO)$_6$ and Re(CO)$_6^+$.

It is necessary now to reconsider the interpretation of the W 5d vibrational splitting. The vibrational structure on the W 4f level is due to a decrease in W-C bond length in the ion state. Is it possible that the similar vibrational structure in the W 5d spectra is due to a decrease rather than an increase in W-C bond length as was reasonably proposed by Hubbard et al16a for such a bonding electron? This question cannot be answered with confidence from this data. However, it is apparent that the decrease in W-C bond length from the above deshielding effect must be considered as well as the probable increase in W-C bond length from removal of a bonding electron. Indeed, for a metal carbonyl, it is not even entirely clear whether the W-C bond length will increase substantially when a W 5d electron is removed, because of the synergic nature of the M-
CO bond, and the greater importance of σ bonding over π backdonating. Certainly both deshielding and bonding effects should result in an increase in ν₁(C-O) stretching frequency as observed. The estimated error in the ν₂(W-C) frequency is too large to be confident that the W-C bond is weakened. More theoretical calculations need to be performed to distinguish the relative importance of deshielding and bonding effects.

Finally, the observation of the vibrational structure on W 4f level of W(CO)₆ is important for surface scientists studying small adsorbates on metals with high resolution photoelectron spectroscopy of the narrow metal levels such as W 4f or Pd 3d. When deconvoluting complex overlapping spectra of, for example, H, CO, O₂, N₂, etc. adsorbed on metals, the present result indicates that vibrational contributions to the metal spectra must be considered. Such vibrational contributions on the ligand levels (e.g. in the CI1s spectra of CO) have already been widely recognized, but no researchers to my knowledge have yet considered vibrational contributions on the metal levels.

3.5. 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. It would be interesting to examine the effect of high resolution, variable photon energy studies on: the linewidth of the normally broad shakeup peaks, and the relative intensity (relative to the main line) of the shake-up peaks as a function of photon energy. Unfortunately, because of the overlap of the 5p and 4f lines (Figure 3-1), good shakeup spectra could not be taken below about 120 eV photon energy. The W(CO)₆ spectrum at 150 eV a. an instrumental resolution of 0.45 eV is shown in Figure 3-4. This spectrum is qualitatively very similar.
Figure 3-4. W 4f and associated satellite spectrum of W(CO)$_6$ at 150 eV photon energy. See Table 3-3 and text for assignment.
Table 3-3. Shake-up Energies and Widths of W 4f of W(CO)$_6$.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>XPS 120 eV</th>
<th>150 eV Width (eV)</th>
<th>XPS 120 eV</th>
<th>150 eV</th>
<th>Width (eV)</th>
<th>XPS</th>
<th>120 eV</th>
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</tr>
</tbody>
</table>

Errors are ±0.1 eV in the a binding energies and peak widths.

Line widths of XPS are estimated from spectrum in Reference 18.

Reference 18.
to the X-ray spectrum, and the positions and relative intensities are very similar to the previous results.\cite{18} However, the W 4f linewidth is less than one-half of that shown by the previous X-ray spectrum, and most of the shakeup peaks are also much narrower than those of 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 3-3). This suggested the possibility of narrowing the shake-up peak widths even further with the improved experimental resolution. However, going to 120 eV at $\sim$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 $\sim$80 eV to 1200 eV.

The assignment of this spectrum is as given previously.\cite{18} The energy of the first shake-up peak ($2t_{2g} \rightarrow 3t_{2g}$) is in good agreement with that expected from the $Z+1$ approximation. The electronic spectrum of W(CO)$_6$ places the $2t_{2g} \rightarrow 3t_{2g}$ excitation energy at 4.53 eV.\cite{37} However, for the core equivalent species Re(CO)$_6^+$, this transition energy increases to 5.82 eV,\cite{37} in good agreement with my shakeup 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, the $Z+1$ approximation can not be applied. The assignment of these peaks is still tenuous. It is possible, as suggested recently, that the $M_3$ peaks at $\sim$15 eV are due to shake-off.\cite{11}

3.6. Conclusions

High resolution photoelectron spectra of W(CO)$_6$ have been reported. The advantages of monochromatized synchrotron radiation for studying the electronic
structure of organometallic molecules have been demonstrated; all the levels of these molecules from valence to inner-valence and core levels at high resolution can be studied in one spectrum. The inner-valence spectrum of W(CO)_6 is dominated by the contribution from CO. Vibrational fine structure has been resolved for the first time on the core 4f levels of metal carbonyl, and this structure can be rationalized using the core equivalent model. It has been shown that the shake-up structures of metal core levels can be studied by synchrotron radiation and enhanced resolution achieved.
3.7. References


1967, 89, 2844.


Chapter 4

Variable Energy Photoelectron Spectroscopy of Osmium Carbonyls

4.1. Introduction

Since the report of the convenient preparation of the osmium pentacarbonyl in 1983,\(^1\) osmium pentacarbonyl and its monosubstituted derivatives have been extensively investigated. These studies include electron diffraction,\(^2\) site preference of ligand in the monosubstituted Os(CO)\(_4\)L complexes,\(^3\) and the extensive use of these complexes as starting materials in various chemical reactions,\(^4\) such as the osmium carbonyl cluster synthesis\(^5\) and the photochemistry studies of metal carbonyl dimers.\(^6\) However, there is still no electronic structural information available on these complexes. The knowledge of the bonding structure and the orbital energies of these complexes is important to the understanding their chemistry. Furthermore, it has long been recognized that the studies of electronic structures of transition metal carbonyls and their phosphine substituted derivatives are important to surface chemistry, since they serve as model systems for the CO adsorption studies on metal surfaces.\(^7\) Herein, I report the electronic structures of Os(CO)\(_5\) and Os(CO)\(_4\)PMe\(_3\) studied by photoelectron spectroscopy using He I and He II laboratory sources and synchrotron radiation (SR).

Photoelectron spectroscopy has been perhaps the most direct technique for the determination of the electronic structures of organometallic compounds since the first He I studies of Ni(CO)\(_4\), Fe(CO)\(_5\), and Mn(CO)\(_5\)X complexes in 1969.\(^8\) Traditionally, the
assignment of the spectra of organometallic compounds has been aided by the increase in intensity of the cross section of the metal d orbitals on going from He I to He II radiation. However, the use of the He I and He II radiations sometimes gave the indefinite assignment for some relatively simple molecules, such as Ni(C\text{\textsubscript{5}}H\text{\textsubscript{5}})\text{\textsubscript{2}}\textsuperscript{10} and CpPtMe\text{\textsubscript{3}}\textsuperscript{11} even when combined with theoretical calculations. Variable energy SR studies, on the other hand, provided firm assignments for these molecules\textsuperscript{10c,11b}.

By using tunable SR, the variable energy cross sections of the organometallic complexes can be obtained and, more importantly, the np→nd resonance\textsuperscript{12} and Cooper minimum\textsuperscript{13} effect have been observed for some compounds. These two phenomena have been successfully used to assign the metal d based valence orbitals. In this Chapter, the core Os 5p orbitals of Os(CO)\text{\textsubscript{4}}PMe\text{\textsubscript{3}} are first observed, and then the 5p→5d resonances on the Os 5d orbitals can be observed by tuning the photon energy through the Os 5p binding energy (BE) region in Os(CO)\text{\textsubscript{4}}PMe\text{\textsubscript{3}}. Similarly, the Cooper minimum on the Os 5d orbitals can be observed at higher photon energies in Os(CO)\text{\textsubscript{5}}. It will be shown that the observation of these two effects provides firm assignments for the Os 5d valence orbitals. An Xα-SW calculation on Os(CO)\text{\textsubscript{3}} has been carried out, to aid in the complete valence and inner valence level assignments. The Xα-SW method has been very successful in the interpretation of the photoelectron spectra of organometallic complexes\textsuperscript{14}. Using high resolution He I radiation, a Os-CO vibrational fine structure can be observed on the Os 5d orbitals. In addition to the application of SR to the valence level studies, high resolution Os 4f spectra will be reported, and the line broadening due to vibrational and ligand field splittings\textsuperscript{15} will be discussed.
4.2. Experimental

Both Os(CO)$_3$ and Os(CO)$_4$PMe$_3$ were prepared by the published procedures by Dr. H. B. Davis in the lab of Dr. R. K. Pomeroy, at Simon Fraser University.$^{13}$

Photoelectron Spectroscopy. The photoelectron spectra were obtained using two different photoelectron spectrometers. He I and He II spectra were recorded on a McPherson ESCA-36 photoelectron spectrometer.$^{16}$ The Ar 2p$_{3/2}$ line at 15.759 eV BE was used as an internal calibration during data acquisition. The resolution (FWHM of Ar 2p$_{3/2}$ line) was about 23 meV for the He I spectra. The variable energy (22 - 200 eV) spectra were recorded on the modified ESCA-36 spectrometer$^{17}$ at the Canadian Synchrotron Radiation Facility (CSRF) at the Aladdin storage ring, University of Wisconsin - Madison.$^{18}$ A 600 g/mm grating gave photon energies between 22-72 eV, and an 1800 g/mm grating gave photon energies between 70-200 eV. A Quantar #36 position sensitive detector$^{19}$ was used in this study which enhanced the intensity of the signal by about 20-50 times over the channeltron system. The Xe 4d$_{5/2}$ line at 69.541 eV$^{17b}$ was used to calibrate the core level spectra at higher photon energies (Figure 4-1). It is interesting to note that at 110 eV photon energy, the Xe 4d linewidth was $\leq 0.25$ eV, but the Os 4f linewidth was about 0.65 eV.

The sample of Os(CO)$_4$PMe$_3$ was introduced through the heatable probe into the gas cell of the spectrometer. It was necessary to heat the sample to 60±5 °C to generate enough vapor pressure. Since Os(CO)$_3$ is very volatile, it was kept in a vessel at 0 °C and leaked into the gas cell. The pressure in the sample chamber was controlled to be around $4 \times 10^{-5}$ Torr, and the pressure in the gas cell was $\sim 5 \times 10^{-3}$ Torr. Spectra were
Figure 4-1. Photoelectron spectrum of Os(CO)$_5$ taken at 110 eV photon energy. It was calibrated with Xe gas, giving the linewidths of 0.25 eV for the Xe 4d lines, and of 0.65 eV for the Os 4f lines.
deconvoluted with a Gaussian-Lorentzian line shape with a nonlinear least-squares procedure described elsewhere.\textsuperscript{20}

**Computational Details** The calculation for Os(CO)\textsubscript{5} was performed by using the relativistic version of the Xα-SW method.\textsuperscript{21} The molecule was idealized to a D\textsubscript{4h} symmetry with the bond distances taken from the structure of Os(CO)\textsubscript{5} as determined by electron diffraction.\textsuperscript{2} The exchange α parameters were taken from Schwarz’s tabulations.\textsuperscript{22} The maximum azimuthal numbers, l\textsubscript{max} of 3, 3, 1, and 1 were used for outer sphere, Os, C and O atoms, respectively. The Xα-SW cross sections were calculated using Davenport’s program\textsuperscript{23} with a Latter tail\textsuperscript{24} added to correct the asymptotic behavior. The resulting partial cross sections (σ\textsubscript{i}) were first used to calculate the theoretical branching ratios (BR) (BR\textsubscript{i} = σ\textsubscript{i} / Σσ\textsubscript{j}) for each orbital and then combined to yield the Xα BR’s according to the spectral assignment.

BR’s of Os(CO)\textsubscript{5} were calculated based on the simple Gelius model,\textsuperscript{25} using the atomic cross sections calculated by Yeh and Lindau.\textsuperscript{26}

4.3. **General Features and Inner Valence Assignments**

The broad-scan photoelectron spectra of Os(CO)\textsubscript{5} at 120 eV photon energy and of Os(CO)\textsubscript{4}PMe\textsubscript{3} at 72 eV photon energies are presented in Figure 4-2. These spectra cover the relatively narrow valence level with BE’s less than 20 eV, the weak, broad inner valence level with BE’s between 20 and 40 eV and the core level with BE’s greater than 40 eV. Table 4-1 lists the peak positions and widths for the peaks in the inner valence and core level regions. The Os 4f and 5p\textsubscript{1/2} peaks of Os(CO)\textsubscript{4}PMe\textsubscript{3} are not shown in Figure 4-2b because a lower photon energy was used for this spectrum. The
Figure 4-2. The high resolution broad-scan photoelectron spectra of (a) Os(CO)$_5$ at 120 eV photon energy, and (b) Os(CO)$_4$PMe$_3$ at 72 eV photon energy. See Text for explanation of the labelling.
Table 4-1. Binding Energies, Widths, and the Assignments of the Inner-Valence and Core Level Spectra of Osmium Carbonyls

<table>
<thead>
<tr>
<th>peak number</th>
<th>Os(CO)$_5$</th>
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<td>satellite 2</td>
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</tr>
<tr>
<td>B</td>
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<td>4.90</td>
<td>satellite 3</td>
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</tr>
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<td>C</td>
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<td>D</td>
<td>42.13</td>
<td>6.01</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
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<td>0.66</td>
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</tr>
<tr>
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<td>64.90</td>
<td>1.89</td>
<td>Os 5p$_{1/2}$</td>
<td>64.03</td>
</tr>
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</table>

* BE’s of Os 4f and 5p$_{1/2}$ levels are from the spectrum taken at higher photon energy.
valence level region of these spectra will be studied in detail in the next section, using the np and resonance and Cooper minum effect observed by variable energy SR.

As has been shown for the other metal carbonyls such as W(CO)₆, Re(CO)₆X (X=Re(CO)₅, Cl, Br) and Cr(CO)₆, the inner valence region of Os(CO)₅ is dominated by the contributions from the CO 3σ orbital and satellites due to the shake-up processes from the CO 4σ and 3σ orbitals. Peak S (Figure 4-2) for Os(CO)₅ at 21.50 eV is the shake-up peak from CO 5σ and 1π ionizations, and it has been assigned as satellite 1 in Table 4-1. Peak A is associated with a normal monopole shake-up state that gains intensity by configuration interaction with the CO 4σ⁻¹ state. Peak B is due to the π²-π² double shake-up process accompanying the 5σ ionization in free CO. Peak C at 30.38 eV BE is broad and intense. It is due to the contributions from CO 3σ orbitals. The broad but weak peak D at 42.13 eV can be assigned to the shake-up peak from the CO 3σ orbitals.

The inner valence spectrum of Os(CO)₄PMe₃ shown in Figure 4-2b is slightly different from that of Os(CO)₅ because of the contribution from the predominant P 3s orbital. The first peak S at 20.52 eV is unique for Os(CO)₄PMe₃, since it is due to the P 3s orbital. The atomic P 3s orbital has a BE of 17.1 eV. It is only possible to observe it with the high intensity of SR at 72 eV photon energy, where the cross section of the atomic P 3s orbital is still relatively high (∼0.3 Mb). Peaks A, B and C can be assigned as satellite peaks from CO 5σ, 1π and 4σ orbitals, and CO 3σ orbitals, respectively. It is worth noting that the weak and broad satellite peak (peak D) around 41 eV BE in Os(CO)₅ is not easily seen for Os(CO)₄PMe₃ at the lower photon energy.
The core level region of the two compounds consists of peaks from the ionizations of Os 4f and 5p orbitals. The Os 4f peaks (C₂ and C₃) have a linewidth of 0.66 eV, which is narrower than the other peaks in the core and inner valence region, but still much broader than the instrumental resolution (~0.20 eV at 120 eV photon energy). Note the chemical shift of the Os 4f and 5p orbitals of ~0.85 eV on going from Os(CO)₄PMe₃ to Os(CO)₃. This line broadening on the two Os 4f levels, due to the vibrational and ligand field splittings, will be discussed later in this Chapter (Section 4.5.). The measurement of Os 5p BE's will be shown to be important to observe the 5p→5d resonance, and hence to assign the Os 5d valence orbitals (see section 4.4.2.).

4.4. Valence Levels

4.4.1. He I/He II Studies

Up until the mid-80's, valence band photoelectron spectra of organometallic compounds were always taken with the laboratory HeI/He II sources. An empirical intensity rule is often used to distinguish metal d-based orbital ionization from the ligand-based orbital ionizations. This rule is based on the assumption that the transition metal d cross sections generally increase from He I to He II radiation in comparison to those of main group s and p orbitals. Figure 4-3 presents the high resolution HeI/He II photoelectron spectra of Os(CO)₅. There are three distinct sets of bands labelled 1, 2, and 3 in the He I spectrum (Figure 4-3a), and an extra band 4 at higher BE in the He II spectrum (Figure 4-3b). There is no obvious change in relative band intensities on going from He I to He II spectra of Os(CO)₅. Furthermore, the interference of peak N (due to the ionization of band 3 by He IIβ impurity light at 48.37 eV photon energy) on band
Figure 4-3. The valence level spectra of Os(CO)$_3$, taken by He I/He II radiation.
1 in Figure 3b makes it even more difficult to apply the intensity rule to assign the Os 5d orbitals based on He I/He II spectra alone. Similarly, the high resolution He I/He II photoelectron spectra of Os(CO)$_4$PMe$_3$ are shown in Figure 4-4. The peak positions, peak widths, and the relative intensities are listed in Table 4-2. The valence region of Os(CO)$_4$PMe$_3$ consists of the contributions from the 5d orbitals of Os, the 2s, 2p orbitals of C and O, and the 3s and 3p orbitals of P. The slight increases in the intensities of bands 1 and 2 over those of bands 3 and 4 (Table 4-2) suggest that the bands 1 and 2 are due to the Os 5d orbitals. But assignments based on the slight increases in the relative intensity of bands alone is not conclusive for such assignment, as shown recently for some relatively simple complexes such as CpPtMe$_3$ and Ni($\eta^3$-C$_3$H$_5$)$_2$.\textsuperscript{10,11} Moreover, the atomic cross section of third row transition metal d orbitals, such as of W 5d orbital in W(CO)$_6$ and of Os 5d orbital in Os(CO)$_5$ and Os(CO)$_4$PMe$_3$, actually decreases from He I to He II radiation.\textsuperscript{13a,26} In this chapter, the application of SR to the study of the valence levels of these two compounds will be demonstrated.

4.4.2. The 5p→5d Resonance

The np→nd resonance was first observed in the photoemission study of nickel metal with synchrotron radiation.\textsuperscript{28} Since then, this phenomenon has been observed in the gas phase photoelectron studies of some inorganic\textsuperscript{29} and organometallic complexes.\textsuperscript{12,13,15b} The mechanism of the np→nd resonance has been discussed by Green earlier\textsuperscript{12} and therefore, only a brief summary will be given here for Os(CO)$_4$PMe$_3$.

At or near photon energies corresponding to the threshold of Os 5p orbitals, in addition to the normal channel in which an Os 5d electron is photo-ionized (see eq. 1),
Figure 4-4. The high resolution valence level photoelectron spectra of Os(CO)$_4$PMe$_3$ with He I/He II radiation.
Table 4-2. Fitting Parameters of He I/He II Spectra of Os(CO)$_4$PMe$_3$

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<th>peak label</th>
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$^a$ This is the sum of the relative area of peaks 1 and 1', for both He I and He II spectra.

$^b$ This is the sum of the relative area of peaks 4, 4' and 4'', for both He I and He II spectra.
\[ 5p^6 5d^6 + h\nu \rightarrow 5p^6 5d^5 + e \] (1)

an Os 5p electron is excited to an empty Os 5d or Rydberg orbital. This intermediate state decays through a super Coster-Kronig transition,\textsuperscript{30} in which one 5d electron will fill the 5p hole and second 5d electron will be excited (see Equation 2).

\[ 5p^6 5d^6 + h\nu \rightarrow 5p^2 5d^7 \rightarrow 5p^6 5d^5 + e \] (2)

These two channels will have the same initial and final states. Therefore, an enhancement of the 5d band in the region of the 5p absorption may be observed. There are three necessary conditions for this type of resonant enhancement of photoionization intensity to be observed.\textsuperscript{31} (1) The excited electron must be of high angular momentum, such as a d or f electron, instead of a s and p electron, so that the excited electron can be held within a potential barrier longer enough. (2) The nd shell must be partially filled, so that a np electron can be excited into the nd shell. (3) The inner and outer shells must be of the same principal quantum number to ensure a sufficiently large overlap between the two orbitals and thus a large transition moment, and the atomic selection rule of \( \Delta l = \pm 1 \) has to be followed.

In the earlier study of W(CO)\textsubscript{6},\textsuperscript{13a} Green and coworkers observed two maxima for the resonances of the W 5d orbitals at photon energies corresponding to the BE’s of the two spin-orbit components of W 5p orbitals, where the atomic W 5p BE’s were used as reference. In the present study of Os(CO)\textsubscript{6}PMe\textsubscript{3}, a high resolution Os 5p spectrum has been recorded for the first time in any such study of np-nd resonances. The knowledge of the Os 5p BE’s makes it possible to predict more accurately where the 5p-5d resonance should occur.
Figure 4-5 shows the core level photoelectron spectrum of Os(CO)$_4$PMe$_3$ at 120 eV photon energy, including both Os 4f and 5p spin-orbit components. There are two reasons for choosing 120 eV photon energy. First, the Os 4f and 5p orbitals are very close in BE, and the cross section of 5p is generally weak compared with that of the 4f orbital. At 120 eV photon energy, however, the 5p cross section is somewhat stronger, while that of the 4f is relatively weaker, thereby minimizing the interference of the 4f signal with the 5p signal. Second, and equally important, our monochromator produces the maximum intensity at 120 eV, which is essential to the detection of the weak 5p signals. The BE's of 5p$_{3/2}$ and 5p$_{1/2}$ of Os(CO)$_4$PMe$_3$ were found to be 51.91 and 64.03 eV, respectively, with a linewidth of 2.05 eV. These BE's are almost 6 eV higher than the Os metal 5p BE's obtained by XPS at 46 and 58 eV relative to the Fermi level.

With the observation of the peaks due to the Os 5p orbitals, the photon energy between 48 and 68 eV can be tuned, in order to observe the 5p→5d resonances on the Os 5d orbitals and hence assign the valence spectrum of Os(CO)$_4$PMe$_3$. Figure 4-6 presents the variable energy valence level photoelectron spectra of Os(CO)$_4$PMe$_3$ at 48, 50, 53, and 56 eV photon energies. These spectra clearly show that the relative intensities of bands 1 and 2 increase in comparison with the intensity of the other peaks, on going from 48 to 50 eV photon energy. This increase in intensity reaches a maximum at 53 eV, and begins to decrease on going from 53 to 56 eV photon energy. The position of this maximum is in good agreement with the BE of 5p$_{3/2}$ of Os(CO)$_4$PMe$_3$ at 51.91 eV. Similarly, the variable energy photoelectron spectra of Os(CO)$_4$PMe$_3$ at 59,
Figure 4-5. The high resolution Os 4f and 5p core level spectrum of Os(CO)$_4$PMe$_3$, with $h\nu = 120$ eV.
Figure 4-6. Variable energy valence level spectra of Os(CO)$_4$PMe$_3$ at (a) 48, (b) 50, (c) 53 and (d) 56 eV photon energy, showing the maximum relative intensities of bands 1 and 2 around 53 eV photon energy.
62, 65 and 68 eV in Figure 4-7 illustrate another resonance on bands 1 and 2 that reaches a maximum at around 65 eV photon energy, in agreement with the BE of Os 5p$_{1/2}$ at 64.03 eV. The observations of these resonances make it possible to identify the bands 1 and 2 as due to the ionization from the Os 5d based orbitals without the need of any calculation.

Support for the assignment of the resonances attributed to the Os 5d orbitals of Os(CO)$_4$PMe$_3$ can be obtained from PES spectrum of Fe(CO)$_4$PMe$_3$,$^{33}$ In Fe(CO)$_4$PMe$_3$, the first two lowest energy peaks at 7.77 and 8.85 eV were assigned to the Fe 3d e' and e" orbitals. Band 1 of Os(CO)$_4$PMe$_3$ is separated into peaks 1 and 1' as is also observed for band 2, but not as clear as 1 in Figure 4-6 (also see the He I spectra in Figure 4-11). This splitting is due to the larger spin orbit and/or Jahn-Teller splitting,$^{34}$ and this also confirms the above assignment of bands 1 and 2 as arising from the valence d orbitals of a third row transition metal. Peak 3 is assigned to the bonding phosphorus lone pair, similar to the assignments for Fe(CO)$_4$PMe$_3$,$^{33}$ and W(CO)$_4$PMe$_3$. Band 4 is broad and intense, and is due to the contribution mainly from 1s and 5π ionizations of CO group, except that the shoulder at 12.23 eV BE is assigned to the P-C σ orbitals, consistent with results and assignments for Fe(CO)$_4$PMe$_3$. $^{33}$

The similarity between the electronic structure of Os(CO)$_4$PMe$_3$ and that of Fe(CO)$_4$PMe$_3$ leads us to conclude that Os(CO)$_4$PMe$_3$ has C$_3v$ symmetry, as does Fe(CO)$_4$PMe$_3$. $^{33}$ This confirms the result of the previous NMR and IR spectroscopic study of Os(CO)$_4$PMe$_3$, which shows that PMe$_3$ is at an axial position of the trigonal bipyramid. $^{3}$
Figure 4–7. Variable energy valence level spectra of Os(CO)$_4$PMe$_3$ at (a) 59, (b) 62, (c) 65 and (d) 68 eV photon energy, showing the maximum relative intensities of bands 1 and 2 around 65 eV photon energy.
To better illustrate the 5p→5d resonance for Os(CO)$_3$PMe$_3$, experimental branching ratios for bands 1 and 2 between 40 to 85 eV photon energy are plotted in Figure 4-8. There are two maxima around 53 and 64 eV for both bands 1 and 2. This 11 eV separation is in good agreement with the Os 5p spin-orbit splitting of 11.94 eV. It is interesting to note that band 2 displays two better resolved and more intense maxima, implying that band 2 has more Os 5d character, compared with band 1. This conclusion is supported by the Xα calculation of Os(CO)$_3$ (see section 4.4.4.).

The np→nd resonance is generally characterized by a Fano-type interaction profile. The Fano profile is a consequence of interaction of the two processes (eqs 1 and 2). The electrons associated with each process, as well as possessing energy, have phase. At the resonance threshold, the two channels tend to be out of phase and the overall cross section decreases. At higher photon energies, the two channels reinforce one another and ionization is augmented. The consequent increase in cross section depends on the relative strengths of the two channels. The typical resonance can be described by the following simple formula:

$$\text{BR} = (q + \epsilon)^2 / (1 + \epsilon^2)$$  (3)

where $\epsilon = (h\nu - E_r)/0.5\Gamma$, $L_r$ is the resonance energy, $\Gamma$ is the full resonance width, and $q$ is the line profile index. The result for band 2 in Figure 4-8 was fitted into two resonance peaks according to Eq. (3) with a good fit achieved for $q = 4.1$, $E_r = 53.2$, 64.2 eV, and $\Gamma = 3.4$, 10.0 eV. The $q$ value for this band is considerably larger than those obtained for the other organometallic molecules (usually between 0 and 2). Both values of $\Gamma$ are in good agreement with the values for Os($\eta$-C$_5$H$_5$)$_2$. The $E_r$ values are 6 eV.
Figure 4-8. Experimental branching ratios of bands 1 and 2 of Os(CO)$_4$PMe$_3$, showing the Os 5p to 5d resonances around 52 and 64 eV photon energies.
higher than the values for Os(η-C₅H₅)₂, but much closer to the Os 5p BE's for Os(CO)₄PMe₃ obtained in this study. A good fit could not be obtained for band 1, presumably because band 1 is derived from Os-CO mixed orbitals.

4.4.3. Cooper Minimum Effect

For a subshell orbital with a radial node in the initial wave function, a Cooper minimum is expected in the atomic cross section. The Cooper minimum is due to a change in phase of the initial state wave function which results in cancellation of the electron dipole transition moment to the final state wave function at a certain photon energy. The minima may occur just above threshold, as is the case for the 3s orbital of Na, or at several hundred electronvolts above threshold, as is found for the 4d and 5d electrons of transition elements. Rules for Cooper minima have been arrived at by experimental and theoretical investigations; they only appear in l→l+1 transitions; they occur only for outer and near outer subshells and only for those orbitals with radial nodes; and they are generally not zero minima because, even when the l→l+1 dipole matrix element vanishes, the l→l-1 one does not.

The Cooper minimum effect has been thoroughly studied for atoms, and very recently, this Cooper minimum effect on the Pd 4d ionization has been used to confirm the assignment of the photoelectron spectrum of Pd(η¹-C₅H₅)₂. The Cooper minimum for the atomic Os 5d orbital is predicted to occur around 200 eV photon energy. At high photon energies, Green and coworkers have observed a decrease of the cross section of the Os 5d orbitals in Os(η⁵-C₅H₅)₂. However, only photon energies up to 115 eV were used, so the complete minimum was not covered. Representative high energy
Figure 4-9. Representative valence level spectra of Os(CO)$_6$ at high photon energies.
photoelectron spectra at 75, 100, 130, 150, 170, and 190 eV of Os(CO), are shown in Figure 4-9. It is obvious that the relative intensities of bands 1 and 2 decrease continuously in comparison to the intensities of bands 3 and 4, on going from 75 to 130 eV photon energy. This decrease in intensity slows down on going from 150 to 190 eV photon energy, reaching a minimum in intensities for bands 1 and 2 in this energy range.

Branching ratios of the valence peaks of Os(CO), from experiment and from the Gelius model are plotted in Figure 4-10. It is clear from the experimental results that the BR's of bands 1 and 2 increase on going from low energy up to about 70 eV photon energy, and begin to decrease from 70 eV, reaching a minimum at the photon energy of 150 eV. The BR's calculated by the Gelius method have been successfully used to aid in the interpretation of experimental BR's of organometallic molecules.\textsuperscript{10c,11b} The atomic cross sections and the Xα compositions were combined to calculate the BR's of bands 1, 2, 3, and 4, using the Gelius approach. From the plot of BR's (Figure 4-10) obtained by the Gelius model, a minimum of BR's of bands 1 and 2 can be found around 150 eV photon energy, in good agreement with the experimental results. The observation of the Cooper minimum confirms the assignment of bands 1 and 2 as arising from Os 5d orbitals in Os(CO). It is interesting to note that better agreement is found for the BR's of band 2, consistent with the view that band 2 results from a non-bonding Os 5d orbital, while band 1 results from an orbital with substantial ligand character, as the Xα-SW calculation results reported below shows. In addition to qualitative agreement between the experimental results and the Gelius model BR's of bands 1 and 2, qualitative agreement can also be found for the BR's of bands 3 and 4.
Figure 4-10. Experimental and theoretical (from the Gellius model) branching ratios of the valence level peaks of Os(CO)₅, showing the minimum of bands 1 and 2 around 150 eV photon energy.
4.4.4. Xα-SW Calculation of Os(CO)₃

By using the 5p→5d resonance and Cooper minimum effect, the first two bands (with lowest BE) in the valence level spectra of Os(CO)₄PMe₃ and Os(CO)₃ have been assigned to the Os 5d derived orbitals for both osmium carbonyls. The rest of the valence and inner valence level peaks can be assigned with the aid of the Xα-SW calculation. The Xα orbital energies, compositions, and the PES band assignment of Os(CO)₃ are listed in Table 4-3. The calculated results show that two e orbitals (6e' and 3e'') are filled with eight Os 5d electrons. From the composition results, it is clear that band 1 arises from a Os-CO π bond orbital and band 2 is due almost entirely to a Os 5d non-bonding orbital since it has over 80% Os 5d character. This provides a rationalization that both the Cooper minimum effect and 5p→5d resonance is better observed for band 2. Both e' and 3e'' orbitals lose their degeneracy because of the larger spin orbit and Jahn-Teller splitting for the Os 5d orbitals, as two peaks are seen in Figure 4-3 for both bands 1 and 2 (Table 4-3). Band 3 arises from 10 CO-based orbitals, and it should be noted that the fitting of band 3 into four peaks is somewhat arbitrary, due to the number of the orbitals involved. Band 4 is also assigned to a CO based band, with almost pure O character.

The spectrum of Os(CO)₃ is similar to that of Fe(CO)₅. The structure of Fe(CO)₅ has been established as trigonal bipyramidal in the solid state by X-ray crystallography. The pentacarbonyls of the iron subgroup all have a trigonal-bipyramidal configuration of D₃h symmetry in the gas phase for which 8 d electrons fill two HOMO e orbitals. A comparison of Os 5d BE's in Os(CO)₃ (Table 4-3) and in
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Table 4.3: Valence Level Assignment and Xα-SW Ground State Valence Orbital Compositions of O2(1D).
Os(CO)₄PMe₃ (Table 4-2) shows that the valence level of the latter is destabilized by substitution of a CO group by a PMe₃ group. This can be readily explained since PMe₃ is a better σ-donor, but a weaker π-acceptor than CO, in good agreement with the previous studies of phosphine substituted derivatives of metal carbonyls, such as W(CO)₅PMe₃³⁵ and Fe(CO)₄PMe₃.³³

4.4.5. High Resolution Os 5d Spectra

Vibrational fine structure has been previously observed in the valence level of transition metal carbonyls, such as W(CO)₆⁴¹ and CpRe(CO)₂⁴² by Lichtenberger and coworkers. It has been shown to be valuable for the metal d band assignment and in the study of the metal carbonyl bonding. In Figure 4-11, the high resolution He I spectra of the first two bands of Os(CO)₅ and Os(CO)₄PMe₃ are presented. These spectra have the same general features except the spectrum in Figure 4-11b shifts to lower binding energy due to the substitution of one axial CO by a PMe₃ group in Os(CO)₄PMe₃. As shown above, band 1 and band 2 in both molecules are due to the e' and e'' orbitals, respectively, with mainly Os 5d character. The e' orbital is primarily dₓ²−ᵧ² and dₓᵧ, while the e'' orbital is consist of dₓ𝑧 and dᵧ𝑧 orbitals. The splitting of band 1 into 1' and 1'' and of band 2 into 2' and 2'' can be attributed to the Jahn-Teller and/or spin orbit splitting. It is interesting to note that the splitting of peak 1 (~0.7 eV) is much larger than in peak 2 (~0.3 eV). The large difference of this splitting has also been observed in the corresponding Fe 3d bands of Fe(CO)₅. It has been explained that the e' orbital has stronger vibrational coupling with low frequency CO vibrations, which produced a larger Jahn-Teller effect.³⁰
Figure 4-11. The vibrationally resolved He I spectra of (a) Os(CO)$_5$, and (b) Os(CO)$_4$PMe$_3$. 
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In addition to the Jahn-Teller/spin orbit splitting, the fine structure caused by
the vibrational progressions is clearly observed in the spectra shown in Figure 4-11. The
vibrational fitting parameters of Figure 4-11 are listed in Table 4-4. A three element
progression was necessary to obtain a satisfactory fit for band 1 of Os(CO)$_3$, while the
other bands in Figure 4-11 show fewer vibrationally resolved structures. The frequency
obtained from the fitting varies from 0.25 to 0.30 eV, or 2016 to 2420 cm$^{-1}$ (Table 4-4).
This is close to or slightly larger than the ground state CO stretching frequencies for
Os(CO)$_3$ and Os(CO)$_4$PMe$_3$ that are 1978 and 2061 cm$^{-1}$.$^{1,3}$

4.5. Core Levels

Traditionally, core level spectra of inorganic and organometallic complexes have
been recorded by using XPS with a resolution of > 1 eV, and XPS was mainly employed
to study chemical shifts. With high resolution SR, it has been possible to resolve
vibrational splitting on the core p and d levels of inorganic molecules,$^{43}$ and on the 4f
level of organometallic molecules, such as W(CO)$_6$ (also see Chapter 3).$^{44}$ High
resolution core level spectra of Os(CO)$_3$ and Os(CO)$_4$PMe$_3$ are important because with
a knowledge of Os 5p BEs the Os 5p→5d resonance can be accurately predicted to aid
in the valence spectrum assignment. Furthermore, the line broadening of Os 4f levels
(Figure 4-1) will be shown to be due to both vibrational and ligand field splittings in
Os(CO)$_3$ and Os(CO)$_4$PMe$_3$, for the first time in organometallic molecules. The Os 4f
chemical shifts of the two molecules will also be compared, and these core level shifts
will be compared with the Os 5d shifts in the valence spectra.
Ligand field splitting is best known in the splitting of the partially filled metal valence d orbitals in transition metal complexes. This splitting is largely due to the change of the symmetry and strength of the electric field from the ligands. Many electronic spectra of transition metal complexes have been measured and interpreted using crystal-field theory and/or ligand field theory.\textsuperscript{45} For a filled core shell, for example, a f\textsuperscript{14} shell, photoionization of a f electron yields a f\textsuperscript{13} ion. Coupling of the hole spin with the orbital angular momentum gives rise to f\textsubscript{7/2} and f\textsubscript{5/2} spin states. The electric field produced by the ligands would further split these two spin states in a similar way to the splitting of the valence d level, and a f\textsubscript{5/2} triplet and a f\textsubscript{7/2} quartet would result in the photoelectron spectrum. Recently, ligand field splitting has been shown an important factor in the p and d core level photoelectron spectra of some inorganic compounds, studied by high resolution He II radiation\textsuperscript{46} and by high resolution SR.\textsuperscript{17,47} In this section, the line broadening of the Os 4f spectra will be shown to be largely due to the contribution of ligand field splitting.

The 4f spectra of Os(CO)\textsubscript{5} and Os(CO)\textsubscript{4}PMe\textsubscript{3} taken at 110 eV photon energy are shown in Figure 4-12. The fitting parameters are summarized in Table 4-5. The experimental linewidth of the Os 4f levels is 0.64 eV, which is much larger than our instrumental resolution of these spectra (~0.20 eV, also see Figure 4-1). It has been shown that the line broadening of the W 4f levels in W(CO)\textsubscript{6} was dominated by the contribution from the vibrational progression due to the CO stretching mode.\textsuperscript{44} Similarly, one CO vibrational series was fitted into the Os 4f spectra as shown in Figure 9, in an attempt to explain this line broadening. But the resultant linewidths (0.53 eV) are still
Figure 4-12. The high resolution Os 4f core level spectra of (a) Os(CO)₅, and (b) Os(CO)₄PMe₃ at 110 eV photon energy.
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Figure 5–1. The high resolution broad-scan spectra of (a) \( \text{CpRe(CO)}_3 \) at 72 eV, (b) \( \text{CpMn(CO)}_3 \) at 72 eV, and (c) \( \text{CpFe(CO)}_2\text{I} \) at 70 eV photon energy. See Text for explanation of the labelling.
The Mössbauer quadrupole splitting (proportional to the EFG and LFS) is 2.66 mm/sec for Fe(CO)$_5$ and close to zero for W(CO)$_6$ under Oh symmetry. The above order in EFG and LFS shows that the order of LFS should be: W(CO)$_6 <$ 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 of 4f level of the two Os compounds.

This observation of the vibrational fine structure and ligand field splitting on the 4f levels of this series of metal carbonyls indicates that both vibrational and ligand field contributions to the metal spectra must be considered. It is also important in the study of the lifetime of the core level processes.

The chemical shift of the Os 4f levels between the reference Os(CO)$_5$ and Os(CO)$_4$PMe$_3$ is -0.85 eV (Table 4-1). It is interesting to compare this shift to that of the average valence Os 5d chemical shift (-0.93 eV) between these two molecules (Table 4-4). Jolly and coworkers have developed the following approach to study the bonding character of MOs, using the chemical shift information of both core and valence levels of related compounds.$^{52}$

$$\Delta = [\text{IP} - \text{IP (ref)}]_{\text{valence}} - 0.8[\text{E}_\text{B} - \text{E}_\text{B (ref)}]_{\text{core}}$$

where IP, $E_B$ and IP (ref), $E_B$ (ref) are the vertical potential of the Os 5d level, and the Os 4f binding energy of Os(CO)$_5$, and Os(CO)$_4$PMe$_3$, respectively. A positive $\Delta$ value corresponds to bonding character in the MO, and a negative value of $\Delta$ corresponds to antibonding character. The $\Delta$ value between these two compounds is -0.25 eV, this indicates that these d orbitals are slightly antibonding, and that PMe$_3$ is a weaker $\pi$-acceptor than CO.$^{52}$
4.6. Conclusion

High resolution photoelectron spectra of two mononuclear Os carbonyls have been investigated. The Os 5p→5d resonances of Os(CO)$_4$PMe$_3$ were observed using variable energy synchrotron radiation, and a good Fano fit was obtained for these resonances. The Cooper minimum effect was observed for Os(CO)$_5$. These effects have been successfully used to assign the Os 5d valence orbitals. Vibrational splitting due to Os-CO stretching was resolved on the Os 5d bands in the high resolution He I spectra. The X$\alpha$-SW calculation of Os(CO)$_5$ confirmed the experimental MO ordering of this molecule. Good agreement was found between the experimental BR's and the theoretical results (by both X$\alpha$-SW method and the Gelius model). Both experimental and theoretical results are consistent with the trigonal-bipyramidal structure for these molecules, as has been shown for the Fe analogues.

The high resolution and high intensity of SR is critical for the study of the inner valence and core level spectra. The inner valence level of both molecules was shown to be dominated by contributions from the CO group, with the exception of the P 3s orbital in Os(CO)$_4$PMe$_3$. The high resolution Os 4f spectra were shown to be broadened by both vibrational and ligand field splittings. The Os 4f chemical shift between Os(CO)$_5$ and Os(CO)$_4$PMe$_3$ was compared with the Os 5d chemical shift, using Jolly's treatment. The shifts are consistent with PMe$_3$ being a weaker $\pi$-acceptor than CO.
4.7. References


(35) Bancroft, G. M.; Dignard-Bailey, L.; Puddephatt, R. J. Inorg. Chem. 1984, 23,
2369.


Chapter 5

Variable Energy Photoelectron Spectroscopy of CpM(CO)$_3$ (M=Mn, Re) and CpFe(CO)$_2$I

5.1. Introduction

The electronic structures of transition metal cyclopentadienyl carbonyl complexes have been the subject of a wealth of photoelectron spectroscopic$^1$ and theoretical studies.$^2$ CpMn(CO)$_3$ and CpFe(CO)$_2$I are central complexes not only for the understanding of the electronic structure of these complexes, but also because they are widely used in transition metal aided organic synthesis. Conventional He I/He II photon energies have been used exclusively to obtain the photoelectron spectra of these complexes, and the assignments of the spectra have been aided by comparing the relative He I/He II band intensities. However, the He I/He II spectra, even combined with various theoretical calculations, have failed to yield the firm assignment of the valence spectrum of some relatively simple molecules, such as CpPtMe$_3$ and Ni(C$_2$H$_5$)$_2$.$^4$ The definitive assignment can only be obtained by combining the variable energy synchrotron radiation spectra and Xα-SW intensity calculations.$^{3b,4c}$

The variable energy synchrotron photoelectron spectra of CpPtMe$_3$ showed that the lowest binding energy peak arises from an MO of largely ligand character, in contrast to the previous experimental and theoretical study which assigned this peak to Pt 5d orbitals.$^{3a}$ This latest result is not consistent with the well-established, qualitative MO
descriptions for molecules with general formula \( \text{CpML}_3 \) (\( M \) is a transition metal and \( L \) is an arbitrary ligand with only \( \sigma \)-donor capability\(^{29} \)) which shows that the HOMO is a metal orbital. More detailed variable energy photoelectron studies of organometallic molecules across and down the transition metal series are necessary, in order to examine the periodic trend in metal d binding energies. The spectra of \( \text{M}(\eta^3-\text{C}_3\text{H}_5)_2 \) (\( M = \text{Ni, Pd, Pt} \))\(^{4c} \) and \( \text{CpM(CO)}_2 \) (\( M = \text{Co, Rh, Ir} \))\(^5 \) have recently been published from this group. In this Chapter, a study of the electronic structures of earlier transition metal complexes \( \text{CpM(CO)}_3 \) (\( M = \text{Mn, Re} \)) and \( \text{CpFe(CO)}_2 \) will be presented, using variable energy photoelectron spectroscopy and \( X\alpha\)-SW calculations. This study enables us to study the trend in energy of the metal d orbitals going across and down the transition metal series. In addition, the use of synchrotron radiation to study the inner valence and core level spectra of organometallic complexes will be demonstrated. For example, the high intensity of synchrotron radiation is critical to observe the broad, weak, inner valence spectra. The high intensity is also essential to observe the Mn 3p and Fe 3p peaks, which are important to study the effects of the np\( \rightarrow \)nd resonance in the valence band spectra.\(^6 \) The high resolution of synchrotron radiation is also essential to discuss the causes of the broadening in the I 4d spectra.

5.2. Experimental

High purity samples are purchased from Aldrich Chemicals Co., and used directly without further purification.

The photoelectron spectra were measured using two different photoelectron spectrometers. He I spectra were obtained using our McPherson ESCA-36 photoelectron
spectrometer. The spectra at higher photon energies (22 - 150 eV) were obtained with our modified ESCA-36 spectrometer\textsuperscript{7} at the Canadian Synchrotron Radiation Facility (CSRF) at the Aladdin storage ring, University of Wisconsin - Madison.\textsuperscript{8,9} The performance of these spectrometers has been described previously,\textsuperscript{7,8,9} and the operating procedures have been given in the previous Chapters.

All the samples were introduced through the heatable probe into the gas cell of the spectrometer. CpMn(CO)\textsubscript{3} was volatile enough to obtain spectra at room temperature. CpRe(CO)\textsubscript{3} and CpFe(CO)\textsubscript{2}I were less volatile and required heating at the temperatures 50 and 85 °C, respectively. The sample pressure in the sample chamber was controlled at around 3\times 10^{-5} Torr, while the pressure in the gas cell was around 5\times 10^{-3} Torr.

Spectra were deconvoluted with a Gaussian-Lorentzian lineshape using a nonlinear least squares procedure described previously.\textsuperscript{10} Band areas were taken from the above fitting results and the experimental branching ratios were calculated based on the branching ratio definition (\(\text{BR}_i = A_i / \Sigma A_i\)).

**Computational details**

A transition state Xα-SW calculation\textsuperscript{11} for CpMn(CO)\textsubscript{3} was performed to calculate the valence orbital energies, compositions and theoretical cross sections. The bond distances and bond angles were taken from the crystal structure of CpMn(CO)\textsubscript{3} reported by Berndt and Marsh.\textsuperscript{12} The molecule was idealized to have a C\textsubscript{4v} symmetry. The exchange α parameters were chosen from the literature.\textsuperscript{13} An \(l_{\text{max}}\) of 3 was used for outer sphere, and the \(l_{\text{max}}\)'s of 2, 1, 1, and 0 were used for Mn, C, O and H atoms,
respectively. The Xα-SW cross sections were calculated using Davenport’s program\textsuperscript{14} with a Latter tail added to correct the asymptotic behaviour. The resulting partial ionization cross sections ($\sigma_i$) were then used to calculate the theoretical branching ratios ($BR_i = \sigma_i / \Sigma \sigma_i$) for each orbital.

5.3. General Features and Inner Valence Levels

Photoelectron spectra of (a) CpRe(CO)\textsubscript{3}, (b) CpMn(CO)\textsubscript{3}, and (c) CpFe(CO)\textsubscript{2}I spanning 7 eV to 50-60 eV binding energies are presented in Figure 5-1. These spectra were taken at a total resolution of $\leq 0.2$ eV. It is evident that these spectra clearly show three distinctive regions: the intense, relatively narrow valence levels with BE less than 20 eV (labelled 1-13 and S), the weak, broad inner valence levels with BE between 20 and 40 eV (labelled A-D) and the core levels with BE greater than 40 eV in Figure 5-1a and 5-1c (labelled C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{3}).

The general features of the valence levels in Figure 5-1 are in very good agreement with the previous He I/He II studies of these molecules.\textsuperscript{24,15} The bands between 7 and 12 eV BE show very different peak shapes and intensities and they are sensitive to the metal and ligand substitution. In contrast, the bands from 13 to 20 eV are very similar and therefore insensitive to the metal and ligand substitution. Lichtenberger et al. have assigned the valence levels up to 17 eV BE of these molecules based on the He I/He II techniques and a Fenske-Hall calculation.\textsuperscript{24} The results in the following sections will generally confirm Lichtenberger’s previous assignments, but clarify the assignments of two peaks in the CpFe(CO)\textsubscript{2}I spectrum.
Figure 5-1. The high resolution broad-scan spectra of (a) CpRe(CO)$_3$ at 72 eV, (b) CpMn(CO)$_3$ at 72 eV, and (c) CpFe(CO)$_2$I at 70 eV photon energy. See Text for explanation of the labelling.
The inner-valence spectra of these d⁶ cyclopentadienyl metal carbonyl complexes have not appeared in the literature before. They are very similar in peak shapes and positions, like the high BE valence region. The key to understanding the inner-valence spectra of these molecules lies in the comparison with those of metal carbonyls, such as W(CO)₆ (Chapter 3), and Os(CO)₃ (Chapter 4). It has also been shown that the inner-valence spectra of Re(CO)₃X (X=Cl, Br) complexes¹⁶ (also see Chapter 6) are dominated by the contribution of carbonyl satellites and CO 3σ orbitals, but not the halogen s orbitals. Similarly, a contribution from the I 5s orbital around 20 eV BE cannot be seen in the inner-valence region of CpFe(CO)₂I. Therefore, the inner valence spectrum of CpFe(CO)₂I can be assigned in the same way as the spectra of CpM(CO)₃ (M=Mn, Re) and CpM(CO)₂ (M=Co, Rh and Ir)⁴ complexes.

Peak positions and assignments for the inner valence spectra of CpRe(CO)₃, CpMn(CO)₃, and CpFe(CO)₂I are listed in Table 5-1. Peak S around 20 eV BE is the shakeup peak from CO 1π and 5σ orbitals; the next peak A around 23 eV is a CO satellite peak but has a higher percentage of Cp ring character; the next two peaks between 24 and 31 eV are the satellite peaks due to CO 4σ orbitals; and the broad and relative intense peak around 35 eV is due to the CO 3σ orbital. It is interesting to note that the general order of the BE’s (Table 5-1) for the inner valence peaks of these three compounds is CpRe(CO)₃ < CpFe(CO)₂I < CpMn(CO)₃. This is consistent with the trend for the valence level peaks of these compounds (Figure 5-1).
| CO 39 | 3.22 | 3.64 | 3.05 | 3.01 | 3.44 | D |
| Satellite 3 | | | | | | |
| Satellite 2 | 2.20 | 2.32 | 2.43 | 3.18 | 3.11 | C |
| Satellite 1 | 2.07 | 2.19 | 2.11 | 2.53 | 2.50 | B |
| Shakedown | 2.74 | 2.98 | 2.85 | 2.45 | 2.44 | A |
| | 2.28 | 2.11 | 2.52 | 2.33 | 1.97 | S |

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<th>CPE(C(0))&lt;sup&gt;1&lt;/sup&gt;</th>
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<th>Width (eV)</th>
<th>BE (eV)</th>
<th>Width (eV)</th>
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**Table S.1.** Binding Energies, Widths and Assignments of CPE(C(0))<sup>3</sup> (M=CN, Re, and CPE(C(0))<sup>1</sup>)
The remaining ionization bands of CpRe(CO)$_3$ and CpFe(CO)$_2$I in Figure 5-1a and 5-1c belong to the core levels, and they can be assigned easily. Two sharp peaks at 47.21 and 49.63 eV BE in Figure 5-1a are the two Re 4f spin-orbit components. The shoulder on the higher BE side of 4f$_{7/2}$ at 47.5 eV is due to the Re 5p$_{3/2}$ ionization. These results are in very good agreement with the high resolution Re 4f results of Re(CO)$_3X$ [X=(CO)$_3$, Cl and Br] complexes. The I 4d spin-orbit components of CpFe(CO)$_2$I can be found at 55.20 and 56.92 eV BE in Figure 5-1c. The broadening effect of I 4d peaks will be discussed in the next section.

5.4. Core Level Study

In Chapters 3 and 4, the importance of high resolution and high intensity in the study of core level photoelectron spectra of organometallic complexes have been demonstrated. Vibrational fine structure has been resolved on the metal 4f core level of heavy metal carbonyl compounds (Chapter 3). Ligand field broadening has also been shown to be present in the Os 4f core level of Os(CO)$_3$ (Chapter 4). In this Chapter, I wanted to show: first, the importance of high intensity of synchrotron radiation in the observation of the Mn 3p and Fe 3p core levels which are important to the valence level 3p→3d resonance studies; secondly, the importance of the high resolution of synchrotron radiation in the study of the broadening of the I 4d spectrum; and thirdly, the importance of the tunability of synchrotron radiation in a core level cross section study of the Fe 3p and I 4d levels in CpFe(CO)$_2$I.

Observation of metal core p levels has been shown to be important in the study of np→nd resonances. However, due to the extremely low cross section of these 3p
levels at Al Kα energies (−0.02 Mb), these spectra have not been observed in the gas phase. With synchrotron radiation, the photon energy can be tuned to the maximum of the 3p cross section (−1 Mb at 120 to 150 eV), and obtain these weak spectra for the first time. Figure 5-2 presents the high resolution (total instrumental resolution <0.3 eV) Mn 3p spectrum of CpMn(CO)₃ at 130 eV photon energy. This Mn 3p BE of 56.3 eV is much larger than the Mn 3p BE for Mn metal of 47.2 eV reference to the vacuum level. The broad linewidth of 2.32 eV is due to the very short lifetime of the 3p hole state.

Figure 5-3 illustrates the Fe 3p and I 4d core level spectra of CpFe(CO)₂I: the broad Fe 3p level at 62.0 eV BE, and the I 4d₃/₂ and 4d₅/₂ levels at 55.20 and 56.92 eV, respectively. The Fe 3p BE will again be useful for studying the np→nd resonance effects on the valence band (see next section). These spectra were taken at medium resolution, and gave I 4d linewidths of 0.75 eV in Figure 5-3b. I 4d spectra taken at 106 eV photon energies and ≤0.15 eV resolution gave I 4S/₂ and 4D₃/₂ linewidths of 0.52 and 0.54 eV, respectively. The I 4d₃/₂ BE of 55.20 eV is much smaller than that of other small covalent molecules such as HI and I₂ (Table 5-2). However, assuming that the differences in I 4d₃/₂ and 3d₃/₂ binding energies are the same, the calculated I 3d₃/₂ BE for CpFe(CO)₂I is 625.3 eV, in good agreement to that previously observed for Mn(CO)₃I, and mid way between the I 3d₅/₂ BE for I₂ and CsI (Table 5-2). The CpFe(CO)₂I BE shows that the I atom is really rather negative for a covalent molecule, in agreement with conclusions from ¹²⁹I and ¹²⁷I Mössbauer spectroscopy on transition metal iodine compounds.
Figure 5-2. Photoelectron spectrum of the Mn 3p level of CpMn(CO)$_3$, taken at 130 eV photon energy.
Figure 5-3. Core level photoelectron spectra of CpFe(CO)$_2$I at (a) 130, and (b) 150 eV photon energies, showing the increase of the relative intensity of Fe 3p orbital relative to those of I 4d orbitals.
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<tr>
<td>Fe(CO)$_3$I$_2$</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

$^a$ Reference 23. $^b$ Reference 20. $^c$ Reference 22.
The I 4d_{5/2} and 4d_{3/2} total linewidths (0.54 and 0.52 eV) are very broad compared to the I 4d inherent linewidths of < 0.2 eV, or the total linewidths of ~0.2 eV previously observed at similar resolution for I_2 and ICl.\textsuperscript{23} As for CF_3I, the large linewidths are due to a combination of vibrational broadening and ligand field splitting,\textsuperscript{23} with the major part of this broadening due to unresolved vibrational broadening.\textsuperscript{23,24} Using the core equivalent approximation,\textsuperscript{24} the core equivalent of I 4d core ionized \( \text{CpFe(CO)}_2 \text{I} \) is \( \text{CpFe(CO)}_2 \text{Xe}^+ \). The Fe-Xe\textsuperscript{+} bond length is likely to be much longer than the Fe-I bond length of 2.66 Å.\textsuperscript{24} This would yield a long Fe-Xe\textsuperscript{+} vibrational progression (the Fe-I symmetric stretching frequency is only 202 cm\textsuperscript{-1}).\textsuperscript{25} It is also possible that CO vibrational splitting could broaden the I 4d line, as was seen in the W 4f spectrum in W(CO)\textsubscript{6}.\textsuperscript{17}

Ligand field splitting will also contribute to the broadening of these lines. The larger linewidth of the I 4d_{5/2} line is an indication of the importance of this effect. A semiquantitative estimate of the ligand field splitting (as expressed by \( C_2^0 \))\textsuperscript{23} can be made because \( C_2^0 \) is proportional to the nuclear quadrupole coupling constant, \( e^2qQ \) at the I nucleus.\textsuperscript{23} Thus, one can write

\[
\frac{C_2^0[\text{CpFe(CO)}_2\text{I}]}{C_2^0[I_2]} = \frac{e^2qQ[\text{CpFe(CO)}_2\text{I}]}{e^2qQ[I_2]} \tag{1}
\]

\( C_2^0 \) and \( e^2qQ \) are well known (Table 5-2), and \( e^2qQ \) for \( \text{CpFe(CO)}_2\text{I} \) can be assumed to be close to that for \( \text{cis-Fe(CO)}_4\text{I}_2 \) (Table 5-2). Substituting into equation (1), \( C_2^0 \) for \( \text{CpFe(CO)}_2\text{I} \) is 17.5 meV. This value only gives a 4d_{5/2} splitting of 0.14 eV, and 4d_{3/2}
splittings of less than this. Fitting five peaks to the doublet with these splittings gives individual linewidth of 0.45 eV, showing that vibrational broadening is still the dominant broadening mechanism.

Figure 5-3 shows the increase of the relative intensity of Fe 3p compared with those of I 4d from 130 to 150 eV photon energy. This phenomenon is expected when compared with the atomic cross sections of these orbitals. Figure 5-4 plots the experimental and theoretical\textsuperscript{18} branching ratios of Fe 3p and I 4d orbitals. It is obvious that the intensity of the Fe 3p orbital peak increases between photon energies of 100 and 145 eV; while the intensity of I 4d decreases continuously in the same region. Branching ratios of these orbitals cross each other at about 130 eV photon energy theoretically, but well above 150 eV from the present experimental results. Clearly, the position of the I 4d Cooper minimum is at higher energy than predicted from the atomic calculation. Shift in the Cooper minimum from atomic values has been recently seen on the Pd 4d orbitals in Pd(η\textsuperscript{3}-C\textsubscript{3}H\textsubscript{3})\textsubscript{2}.\textsuperscript{25}

5.5. Variable Photon Energy Results

5.5.1. CpM(CO)\textsubscript{3} (M=Mn, Re) Complexes

Representative variable energy photoelectron spectra at 21.22, 40, 60, and 80 eV photon energies of CpMn(CO)\textsubscript{3} and CpRe(CO)\textsubscript{3} are presented in Figure 5-5 and 5-6. These four photon energies were typically chosen to represent the spectra taken (a) by He I radiation with the best resolution, (b) by He II radiation, (c) at a photon energy just higher than the np→nd resonance, and (d) at a photon energy well above the np→nd resonance. It is obvious that the relative intensities of the bands vary dramatically with
Figure 5-4. Comparison of the theoretical and experimental branching ratios of Fe 3p and I 4d orbitals of CpFe(CO)$_2$I.
Figure 5.5. Representative valence level spectra of CO in (a) 21.22, (b) 40, (c) 60, and (d) 80 eV photon energies.

(a) 80 eV (b) 60 eV (c) 40 eV (d) 21.22
Figure 5.4: Representative valence level spectra of CpRe(CO)₅ at (a) 21.22, (b) 40, (c) 60, and (d) 80 eV photon energies.
the photon energy. Especially noticeable is that the relative intensities of the first band in Figures 5-5 and 5-6 increase continually with the increase of the photon energy between 21.22 and 60 eV photon energy, and then show a slight decrease in the relative intensity from 60 to 80 eV photon energy. This change in intensities is due to np→nd resonances which can be better shown when using a smaller photon energy scanning step.

With the knowledge of the BE’s of the metal np orbitals, the photon energy can be tuned with a 2 eV step around the threshold of np orbitals (around 56 eV for Mn 3p, 50 and 58 eV for Re 5p orbitals). Photoelectron spectra of CpMn(CO), at 54, 56, 58, and 60 eV photon energy are illustrated in Figure 5-7. These spectra show clearly, that the relative intensity of the first band increases dramatically from 54 eV to 56 and 58 eV photon energies, and begins to decrease from 58 to 60 eV photon energy. So, it is straightforward that the first band (peaks 1 and 2) can be assigned to the Mn 3d orbitals. Similarly, the variable energy photoelectron spectra of CpRe(CO), at 46, 48, 50, and 52 eV photon energy in Figure 5-8 illustrate the 5p→5d resonance on band 1 that reaches a maximum at around 50 eV photon energy, indicating that peaks 1 and 2 arise from orbitals of very high 5d character compared with the other peaks. These assignments are in agreement with Lichtenberger’s previous He I/He II studies combined with a Fenske-Hall calculation.\footnote{15}

Xα-SW calculations have proven to be an useful tool for assignment of the valence level photoelectron spectra of organometallic molecules,\footnote{27} and this technique has been successfully utilized in the calculation of photoionization cross sections in the study of variable energy synchrotron radiation photoelectron spectra of some
Figure 5-7. The 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 peaks 1 and 2 around 56 eV photon energy.
Figure 5–8. The valence level spectra of $\text{CpRe(CO)}_3$ at (a) 46, (b) 48, (c) 50, and (d) 52 eV photon energy, showing the maximum relative intensity of peaks 1 and 2 around 50 eV photon energy.
organometallics. An Xα-SW calculation has been performed on CpMn(CO)₃ to further confirm the valence band assignment, to assign the inner valence peaks, and to explain the experimental branching ratio results.

Table 5-3 lists the Xα-SW orbital energies and the composition of the resulting wavefunctions for the upper valence orbitals of CpMn(CO)₃. The experimental ionization potentials and the assignments of valence level bands are also presented in Table 5-3. The first two MO's in the ground state of CpMn(CO)₃ are almost degenerate in energy and both have high (65%) Mn 3d contribution. They are derived from Mn 3dx²-y² and 3dz² orbitals and assigned as peak 1 in Fig. 5-5a. The next MO 18a' is 0.18 eV lower than the HOMO, and this MO also has high Mn 3d character (80%). This orbital interacts more with the CO group, but very little with the Cp ring. This orbital can be assigned to peak 2 which is mostly derived from the Mn 3dz² orbital. These Xα results are in good agreement with the previous INDO-type calculation result, and strongly support the conclusion that peaks 1 and 2 are the metal d based peak from the above variable energy SR study. The next pair of MO orbitals 11a'' and 17a' are almost degenerate in energy and have about 50% Cp ring character. These two orbitals can be easily assigned to peaks 3 and 4, which has also been assigned by Lichtenberger et al. as the predominantly ring e₁'' ionization. Peaks 5, 6, 7, and 8 relate to the MO's mainly from CO and Cp groups, and it has to be pointed out the labelling of these peaks and their assignments are somewhat arbitrary because of the many overlapping orbitals involved in this region. However, it is clear from Table 5-3 that the first three MO orbitals 16a', 10a'' and 15a' all have very high Cp ring contribution compared to the rest.
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Table 5.3. Valence Level Xα-SW Result for CPMN(CO) and Band Assignment.

Original xα energy (eV)
of the MO orbitals. Therefore, these three orbitals can be assigned to peak 5, since a
distinct shoulder between 11 and 13 eV BE has been observed in methyl-substituted ring
compounds.26

The Xα-SW orbital energies and compositions of outer valence and inner valence
levels of CpMn(CO)3 are listed in Table 5-4. The inner valence levels of the three titled
compounds are very similar in BE and all very weak in intensity compared with the
valence levels. They have not been studied before due to the limitation of the photor-
source. The first peak (peak 9, see Figure 5-1) at 17.63 eV BE is derived from three
Cp ring based orbitals. Peak 10 is at the shoulder of peak 9. It has a BE of 18.23 eV
and can be assigned to the contribution of the three CO 4σ orbitals. The next four peaks
(peak S, A, B, C) have been assigned previously to the contributions of CO shakeup and
satellite peaks which this calculation does not address. However, the present Xα results
show that there are three Cp orbitals overlapping with the first CO satellite peak at 23.4
eV. The last band in the inner valence level at 35.6 eV can be assigned readily to the
well known CO 3σ orbitals.

The Xα-SW branching ratio (BR) calculation has been shown to be very valuable
for the confirmation of the Xα-SW energy orbital assignment for many molecules. The
photoionization cross sections of CpMn(CO)3 were calculated using the Xα-SW method.
The BR’s of peaks 1, 2 and 3, 4 were then calculated based on the cross sections.
Figure 5-9 presents the comparison of the experimental and theoretical BR’s of peaks 1,
2 and 3, 4 for CpMn(CO)3. Both the experimental and Xα calculation BR’s show that
the BR of peaks 1 and 2 generally increases with photon energies between 20 and 55 eV,
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Table 5.4. Xa SW Result for COBen(CO), and Band Assignment, Outer Valence and Inner-Valence Levels

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<th>expl. energy (eV)</th>
<th>energy (eV)</th>
<th>Co (%)</th>
<th>Co (%)</th>
<th>3p (%)</th>
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<td>3p</td>
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<td>116.80</td>
<td>116.80</td>
<td>0.2</td>
<td>0.2</td>
<td>3p</td>
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</tbody>
</table>

Note: The table contains data for various electronic configurations and their energies, along with Co content in different states.
while the reverse holds true for peaks 3 and 4. This can be easily explained because the atomic cross section of Mn 3d increases from its threshold to about 60 eV photon energy, while the atomic cross sections of ligand orbitals decrease in the same region. It is noteworthy that only BR’s up to 55 eV photon energy are presented in Figure 5-9 in order to avoid the interference of Mn 3p→3d resonance at band 1 after about 56 eV photon energy. The good agreement between the experimental and Xα calculation BR’s strongly confirms once again that peaks 1 and 2 arise from mainly metal based orbitals and peaks 3 and 4 arise from orbitals with higher ligand character.

5.5.2. CpFe(CO)₂I

The electronic structure of CpFe(CO)₂I was chosen to be studied, using variable energy synchrotron radiation for two reasons. Firstly, the valence level spectrum of CpFe(CO)₂I is much more complex (seven well resolved peaks between 7.5 and 11.5 eV BE) and the previous assignment was not firm.² The value of the observation of the np→nd resonance will be demonstrated, which will provide the confident assignment for these seven peaks. Secondly, as mentioned earlier, I want to study more and different types of CpML₂ complexes, using synchrotron radiation, to see the trend in M 3d IP’s across the periodic table.

Variable energy photoelectron valence spectra of CpFe(CO)₂I at 21.22, 52, 60, and 80 eV photon energy are shown in Figure 5-10, representing: (a) a high resolution He I spectrum, and SR spectra corresponding to the photon energies of (b) before, (c) around, and (d) after the expected Fe 3p→3d resonance at ~ 62 ev from the Fe 3p BE. These spectra clearly demonstrate the different trends in the change of the relative
Figure 5-9. Comparison of experimental and Xα branching ratios of peaks 1, 2 and 3, 4 of CpMn(CO)₃.
Figure 5.10. Representative valence level spectra of CpFe(CO)$_3$I at (a) 21.22, (b) 52, (c) 60, and (d) 80 eV photon energies.
intensity of different peaks. Especially noticeable is that the relative intensities of peaks 3 and 4 increase as the photon energy increases, suggesting that both peaks 3 and 4 arise from orbitals of high Fe 3d character.

In the previous He I study, Lichtenberger and Fenske have assigned the valence spectrum of this compound based on the Fenske calculation and by the comparison with the spectra of Mn(CO)_5X complexes. Briefly, Peaks 1 and 2 were due to ionizations from the Fe-I antibonding \( \pi \) levels. Peak 4 was assigned to the ionizations from two of the three orbitals of high Fe 3d character corresponding to peak 1 in CpMn(CO)_5. Peaks 6 and 7 around 10.5 eV BE were assigned to the ionizations from cyclopentadienyl ring \( e_1'' \) orbitals, similar to those of CpMn(CO)_5 and CpRe(CO)_5. But no conclusive assignments could be made for peaks 3 and 5, since the He I spectrum alone could not distinguish between the predominant Fe 3d \( b_2 \) orbital and the Fe-I \( \sigma \) orbital which is mostly of Iodine character. The variable energy results in Figure 5-10 show that the relative intensity of peak 3 increases with the photon energy compared with that of peak 5. This implies that peak 3 should be the predominantly metal \( b_2 \)-type orbital, which can be confirmed with the observation of np-end resonance result on this peak.

Figure 5-11 presents the valence spectra of CpFe(CO)_5I close to the Fe 3p BE of 62.0 eV at 58, 60, 63, and 65 eV photon energy. It is obvious that the relative intensities of peaks 3 and 4 increase, relative to those of peaks 5, 6 and 7, on going from 60 eV to 63 eV photon energy, then begin to decrease on going from 63 eV to 65 eV photon energy. On the other hand, there is no increase in intensity of shoulder 5 relative to peak 6. This observation supports the assignment of peak 3 as the Fe 3d
Figure 5-11. The valence level spectra of CpFe(CO)$_2$I at (a) 58, (b) 60, (c) 63, and (d) 65 eV photon energy, showing the maximum relative intensity of peaks 3 and 4 around 63 eV photon energy.
based \( h_2 \) orbital and peak 5 as the ligand based \( a_1 \) orbital, without any further theoretical calculation.

It is also apparent that the intensities of peaks 1 and 2 increase relative to peaks 5, 6 and 7 above 60 eV photon energies (Figures 5-10 and 5-11). This increase is perhaps unexpected because the 1 5p cross section decreases sharply at these energies.\(^{18,29}\)

However, another multielectron effect - interchannel coupling - enhances the 1 5p intensity above the 1 4d ionizations at 55 eV.\(^{29}\) The 1 4d cross section increases rapidly to \( \sim 95 \) eV photon energies, offsetting the expected decrease in 1 5p cross section.

5.6. Conclusions

High resolution photoelectron spectra of valence, inner valence and core levels of \( \text{CpM(CO)}_3 \) (M = Mn, Re) and \( \text{CpFe(CO)}_2 \)I have been studied using monochromatized SR. The high intensity and tunability of SR is important for observing the weak inner valence and M 3p (M = Fe, Mn) core level spectra for the first time. The high resolution is critical for defining the broadening mechanisms on the 1 4d spectrum. The tunability of the radiation is necessary for obtaining the relative intensity of the valence band peaks as a function of photon energy. These intensities, when combined with the X\( \alpha \)-SW calculation, yield definitive assignments for the valence and inner valence molecular orbital ordering. For example, the valence band MO's of \( \text{CpMn(CO)}_3 \) and \( \text{CpFe(CO)}_2 \)I can be readily assigned with the aid of the X\( \alpha \)-SW intensity calculations and the np\( \rightarrow \)nd resonances. Apart from the I lone pair orbitals in \( \text{CpFe(CO)}_2 \)I, the metal d orbitals in these complexes are the HOMO's as predicted earlier.\(^2\) In the late second and third row transition metal organometallic complexes, such as \( \text{CpPtMe}_3 \) and \( \text{Pt(}\eta^3-\text{C}_5\text{H}_2\text{)}_2 \), the metal
d orbitals are at appreciably lower BE,\textsuperscript{5} resulting in the HOMO being a ligand-based orbital.
5.7. References


(5) Li, X.; Bancroft, G. M.; Puddephatt, R. J.; Hu, Y. F.; Tan, K. H. Organometallics accepted.


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


Chapter 6

Variable Energy Photoelectron Spectroscopy of Re(CO)$_2$X (X=Re(CO)$_3$, Cl, Br, and I)

6.1. Introduction

One of the first applications of ultraviolet photoelectron spectroscopy (UPS) to organometallic molecules was the study of a series of Mn(CO)$_2$X (X=halogen, etc.) compounds.$^1$ The spectra of these compounds received considerable attention because of the great potential use of UPS to the study of the electronic structure of organometallic molecules in general. The assignment based on the spectra from the first study$^1$ and the later improved spectra$^2$ agreed qualitatively with the semi-empirical calculations,$^3$ but disagreed with the ab initio calculation results.$^4$ In the next decade, the intensity rule$^5$ based on the comparison of the He I/He II band intensities was used to assign the valence level spectra of these compounds,$^6$ and more importantly, Re(CO)$_2$X analogues were studied.$^{6-8}$ The larger spin-orbit splitting observed for Re compounds was shown to be valuable in the assignment of both Re and Mn systems.$^8$ However, there is still no consensus regarding the assignments of the valence spectra of these compounds.$^9,10$

The advantages of variable energy photoelectron spectroscopy in the study of organometallic molecules over the conventional He I/He II based UPS have been recently demonstrated.$^{11,12}$ For example, the extensive photon energy dependence of band intensities can be studied by using tunable synchrotron radiation (SR); and more
importantly, the np→nd resonance\textsuperscript{13} and Cooper minimum effect\textsuperscript{14} have been observed for some organometallic molecules. These two phenomena have been successfully used to assign the metal d based valence orbitals.\textsuperscript{15} In this Chapter, the observation of the 5p→5d resonances on the Re 5d orbitals will be reported. This provides firm assignments for the Re 5d orbitals for these Re(CO)\textsubscript{5}X complexes. The high resolution Re 4f spectra will be reported. The 4f core binding energies can be used to help the valence band assignments when compared with the valence ionization potentials, similar to the approach used for Mn(CO)\textsubscript{5}X systems by Jolly.\textsuperscript{10} Using high resolution and high intensity SR, the inner valence level of these Re(CO)\textsubscript{5}X compounds will also be studied for the first time.

6.2. Experimental

The photoelectron spectra were recorded using two different photoelectron spectrometers. The He I spectra were measured with a McPherson ESCA-36 photoelectron spectrometer.\textsuperscript{16} The variable energy (22 - 190 eV) spectra were recorded on the modified ESCA-36 spectrometer\textsuperscript{17} at the Canadian Synchrotron Radiation Facility (CSRF) at the Aladdin storage ring, University of Wisconsin - Madison.\textsuperscript{18,19} The full accounts of the performances are given elsewhere,\textsuperscript{16-19} and the operating procedures have been given in the previous Chapters.

All the samples with the exception of Re(CO)\textsubscript{5}I were commercially obtained and used directly without further purification. Re(CO)\textsubscript{5}I was prepared by the published procedure\textsuperscript{20} with the aid of X. R. Li. All the samples were introduced via the heatable probe into the gas cell of the spectrometer, and the spectra were recorded at temperatures
ranging from 40 to 90 °C. The spectra were deconvoluted with a Gaussian-Lorentzian lineshape using a nonlinear least squares procedure described previously.\textsuperscript{21}

6.3. General Features and Inner Valence Levels

The high resolution broad-scan photoelectron spectra of the three Re compounds Re(CO)\textsubscript{3}Cl, Re(CO)\textsubscript{3}Br and Re\textsubscript{2}(CO)\textsubscript{10} are presented in Figure 6-1. Figure 6-2 presents the high resolution broad-scan spectrum of Re(CO)\textsubscript{3}I which includes the I 4d peaks. These spectra cover the relatively narrow valence levels with BE's less than 20 eV, the weak, broad inner valence levels with BE's between 20 and 45 eV, and the three core level peaks (plus two I 4d peaks in Figure 6-2) with BE's greater than 45 eV. Table 6-1 lists the peak positions and widths for the peaks in the inner valence and core level regions of the four Re compounds shown in Figures 6-1 and 6-2. Apart from the four valence band peaks (peaks 1 to 4), these spectra are remarkably similar qualitatively, and can be assigned in a manner very similar to that used for the W(CO)\textsubscript{6} spectrum studied in Chapter 3.

The upper valence level region (the first four bands) of these spectra will be studied in detail in the next section, using variable energy SR. Only the peaks above 18 eV that have not been observed previously will be discussed here. As for W(CO)\textsubscript{6}, the band at \(-18.5\) eV (peaks 8 and 9) is due to all of the 4σ CO ionizations (2a\textsubscript{1}, b\textsubscript{2} and e), and peak S is the shakeup peak from the 5σ and 1π ionizations (peaks 5, 6, 7). The inner valence region (peaks A to D) (Table 6-1) is virtually identical to that of W(CO)\textsubscript{6}, although another peak E is evident above 40 eV BE. There is no evidence for the Cl 3s, Br 4s, or I 5s ionizations in the Re(CO)\textsubscript{3}X (X=halogens) compounds at about 25 eV, due
Figure 6-1. High resolution broad-scan photoelectron spectra of (a) Re(CO)$_3$Cl at 72 eV, (b) Re(CO)$_3$Br at 72 eV, and (c) Re$_2$(CO)$_{10}$ at 70 eV photon energy. The valence level peaks are labelled with the numbers (1-9) in an increasing binding energy. Peak S is assigned to a shakeup peak. The inner-valence peaks are labelled with letters (A-E). The three core level peaks are labelled with C$_1$, C$_2$ and C$_3$, respectively.
Figure 6-2. High resolution broad-scan photoelectron spectrum of Re(CO)$_5$I at 80 eV photon energy. It is labelled identically to Figure 6-1, except the two intense peaks at higher BE are due to I 4d orbitals, and peak N is an I NVV Auger peak.²²
Table 6.1. Binding Energies, Widths, and the Assignments of the Inner-Valence and Core Spectra of Rhenium Carbonyls

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<th>Assignment</th>
<th>( \text{BE} ) (eV)</th>
<th>Width (eV)</th>
<th>( \text{BE} ) (eV)</th>
<th>Width (eV)</th>
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<td>1.41</td>
<td>48.42</td>
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Error for binding energies of the inner-valence peaks is estimated to be around 0.05 eV, except for peaks B and E, which is around 0.10 eV due to their weak intensities.
to their very small cross sections relative to the C 2s and O 2s cross sections. It is also obvious that the Re₂(CO)₁₀ spectrum is extremely similar to the other three spectra between 20 eV and 30 eV, showing once again that the Cl 3s, Br 4s, and I 5s levels give no noticeable contribution. Similar to W(CO)₆, the peaks A, B and C between 23 to 32 eV BE can be assigned to shake-up peaks with the final states of $5\sigma^-1\pi^-12\pi^1$, $4\sigma^-1\pi^-12\pi^1$ and $\pi^-2-\pi^-2$ double shake-up processes, respectively, as listed in Table 6-1. The CO 3σ orbital can be found around 36 eV as a very broad and relatively intense peak D. Another very weak peak can be identified around 41 eV binding energy, labelled E. A corresponding peak has been observed in the free CO molecule and Cr(CO)₆, but not W(CO)₆. This peak can be assigned to the shake-up process from the CO 3σ orbital.

It is interesting to note that inner valence peaks (Table 6-1) of Re₂(CO)₁₀ have BE's which are generally lower than those for the halides, which is consistent with a valence charge transfer from Re to halogen. The slight decrease in BE's for the inner valence peaks on going from Cl, to Br, and to I is again in accord with the halogen electronegativities.

The three peaks on the higher energy side of peak E are derived from the Re 4f (C₁ and C₃) and 5pₓ½ (C₂) core orbitals and they will be examined in more detail in the following section. It is important to point out that the Re 5p BE's will be useful to observe the ⁵p→⁵d resonance, and hence to assign the Re 5d based valence peaks.

6.4. Valence Levels

Three types of assignments have appeared in the literature for the valence level bands of these Mn(CO)₆X and Re(CO)₆X (X=halogens) complexes. Lichtenberger et al.
first proposed the energy ordering of the four highest filled molecular orbitals \( e(X) > a_1(Mn-X) > b_2(Mn) > e(Mn) \) for \( Mn(CO)_3X \) system.\(^2\) Their assignment agreed qualitatively with the Fenske calculation of Fenske et al.\(^3\) Based on a comparison between \( Mn \) and \( Re \) systems, Ceasar et al. reinterpreted the data in terms of an ordering \( e(X) > b_2(Mn) > e(Mn) > a_1(Mn-X) \) for both \( Mn \) and \( Re \) complexes.\(^7\) Finally, Higginson et al. studied \( Mn(CO)_3X \) and \( Re(CO)_3X \) using both He I and He II radiation,\(^6\) and Hall studied the spin orbit effect of \( Re(CO)_3X \) compounds.\(^8\) Their assignments agreed with that of Ceasar’s for \( M(CO)_3I \), but they proposed the energy ordering \( e(M) > b_2(M) > e(X) > a_1(M-X) \) for \( M(CO)_3Cl \) and \( M(CO)_3Br \). It is the purpose of this Chapter to show the application of variable energy SR for \( Re(CO)_3X \) compounds, to confirm the assignment of Higginson et al.

6.4.1. He I Spectra

The high resolution He I spectra of the upper valence region of four Re compounds are presented in Figure 6-3. Table 6-2 contains the BE’s of the valence level peaks and their assignments. There are four sets of bands labelled 1, 2, 3, and 4 for \( Re(CO)_3X \) (\( X=\)halogens) and 5 bands for \( Re_2(CO)_{10} \) in a 3 eV span. There are actually more than 4 peaks in this region, with the extra peaks arising from the spin-orbit splittings of the Re 5\( d \) and halogen orbitals, and due to the possible vibrational fine structures from Re-CO stretching on Re 5\( d \) based peaks.

The assignment for \( Re_2(CO)_{10} \) was relatively straightforward under the \( D_{4h} \) symmetry. It has been given in the previous studies,\(^6,8\) that is, peak 1 is assigned to the \( a_1 \) orbital which is a filled Re-Re \( \sigma \) bonding orbital, peaks 2 and 3 are assigned as
Figure 6.3. H$_2$ spectra of (a) Re(CO)$_3$Cl, (b) Re(CO)$_3$Br, (c) Re(CO)$_3$I, and (d) Re(CO)$_5^n$. 
<table>
<thead>
<tr>
<th>Assignment</th>
<th>BE (eV)</th>
<th>Assignment</th>
<th>BE (eV)</th>
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<td>e^2 (Re-Re)</td>
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<td>e^2 (Re-Re)</td>
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</table>

Table 6.2. Binding Energies and Assignments of the Upper Valence Spectra of Rhodium Carbonyls.
arising from the two spin-orbit components of Re-Re \( \pi \) bonding orbital \((e_\pi)\), peak 4 is assigned to one component of the spin-orbit split bonding Re-Re orbital \((e_1)\), and the other spin-orbit component overlapped with the two nonbonding \(b_2\) orbitals \((e_2)\) are assigned as very intense peak 5. This assignment will be generally confirmed with the variable energy SR results shown in next section.

For the three halide complexes, Higginson et al. and Hall\textsuperscript{6,8} both assigned peaks 1 and 1′ as due to the two spin-orbit components of the Re 5d \( \pi \) orbital for Cl and Br, but peaks 1 and 1′ for I were interpreted as the spin-orbit components which are mostly I in character. This can be better seen in the spectra shown in Figure 6-3, since a spin-orbit splitting is clearly resolved for band 1 in all three halides, and Re(CO)\textsubscript{5}I has a much larger splitting (0.63 eV) than that for Cl and Br (0.25 and 0.30 eV) analogues as expected. Peak 2 was due to the ionization from the Re 5d based \(b_2\) orbital for all three compounds. The new evidence to support this assignment can be found in the Re(CO)\textsubscript{5}Cl spectrum, since a vibrational fine structure is clearly resolved for peak 2. The splitting of 0.26 eV is in very good agreement with the Re-CO stretching frequency.\textsuperscript{25} A similar vibrational progression has been observed on the Re 5d based orbitals for CpRe(CO), (Chapter 5).\textsuperscript{26} Band 3 was due to the ionizations from the halogen based \( \pi \) orbitals for Cl and Br, but was assigned differently for I, as due to the contributions from Re 5d based \( \pi \) orbitals. The spin-orbit splitting is clearly resolved for Br in Figure 6-3(b), but the splitting of 0.22 eV is much smaller than that of I, which can be understood in terms of the heavy metal effect.\textsuperscript{27} Finally, peak 4 was unambiguously assigned to the M-X \(\sigma\) bonding orbital \((a_1)\) for all three compounds. In the next section, the 5p→5d resonance
will be studied to provide firm assignments for these compounds.

6.4.2. The Variable Energy SR Study

It has been shown in the previous Chapters, that the knowledge of BE's of np core levels is important in order to observe the np→nd resonance. The BE's of Re 5p_{3/2} and 5p_{1/2} electrons are found to be around 49 and 58 eV for these Re complexes (Table 6-1). These BE’s are almost 15 eV higher than the Re metal 5p BE’s obtained by XPS, but consistent with the values for W and Os in the metal carbonyls (Chapters 3 and 4).

Figure 6-4 presents the variable energy valence level photoelectron spectra of Re(CO)_3Cl at 46, 48, 50, and 52 eV photon energies. It is immediately obvious that the relative intensities of peaks 1, 2, 3, and 4 display a maximum between 48 and 50 eV photon energy, in comparison with the intensity of the other peaks. The position of this maximum is in good agreement with the BE 5p_{3/2} BE of Re(CO)_3Cl. The observation of this 5p→5d resonance shows that orbitals associated with peaks 1, 2, 3, and 4 all have higher Re 5d character, in comparison with peaks 5 to 9, since it is well known that peaks 5 to 9 are due to the contributions from the CO group. At a closer look, it is clear that peaks 1 and 2 show a larger maximum than peaks 3 and 4. The evidence to support this conclusion can be obtained when these spectra are compared to the He I spectrum shown in Figure 6-3(a), since the relative intensities of peaks 3 and 4 decrease dramatically from 21.22 to higher photon energies. This evidence demonstrates that peaks 1 and 2 have higher Re 5d character, because the relative cross section of metal d orbitals always increases in this region, relative to that of the ligand p orbitals.23
Figure 6-4. The valence level spectra of Re(CO)$_5$Cl at 46, 48, 50, and 52 eV photon energies, showing the maximum relative intensities of peaks 1 to 4 around 50 eV photon energy. All the spectra are normalized with intensities of peaks 8 and 9.
Therefore, peaks 1 and 2 can be assigned to the Re 5d based orbitals, while peaks 3 and 4 are due to Cl based orbitals, with some Re 5d character due to bonding. This assignment is in good agreement with Higgison’s assignment. Similarly, the variable energy photoelectron spectra of Re(CO)$_3$Br at 46, 48, 50, and 52 eV in Figure 6-5 illustrate the resonance on peaks 1 to 4 that reaches a maximum around 50 eV photon energy. It is interesting to note that peaks 1 to 4 all display a strong resonance, which suggests that they all have high Re 5d character. This can be understood, because Re and Br have the right energies to form the strong π-π bonding. However, an obvious increase in relative intensity of peak 2 over the other peaks is still noticeable on going from the He I spectrum to the higher energy SR spectra. This agrees with the previous assignment of peak 2 as arising from the Re based b$_2$ type σ orbital.

The Re 5d based orbitals of Re(CO)$_3$I are also expected to display a 5p$_{3/2}$→5d resonance around 50 eV photon energy. However, the interference of the intense I 4d signals from the second order light makes it difficult to record the high quality valence level spectra between 42 and 53 eV photon energies. Figure 6-6 presents the variable energy spectra of Re(CO)$_3$I at 57, 60, and 63 eV photon energies, in an attempt to observe the Re 5p$_{1/2}$→5d resonance. A weak resonance is indeed noticeable around 60 eV photon energy for peaks 1 to 4. The intensity of the 5p$_{1/2}$→5d resonance is expected to be weaker than that of the 5p$_{3/2}$→5d resonance, since the p$_{3/2}$ level has a greater degeneracy and cross section. The dramatic decreases of the relative intensities of peaks 1 and 4 on going from the He I spectrum to the higher energy SR spectra also confirm the assignment of peaks 2 and 3 as due to mostly the Re 5d ionizations.
Figure 6-5. The valence level spectra of Re(CO)$_5$Br at 46, 48, 50, and 52 eV photon energies, showing the maximum relative intensities of peaks 1 to 3 around 50 eV photon energies. All the spectra are normalized with intensities of peaks 8 and 9.
Figure 6-6. The valence level spectra of Re(CO)$_5$I at 57, 60, and 63 eV photon energies. All the spectra are normalized with intensities of peaks 8 and 9.
Figure 6–7. The valence level spectra of Re₂(CO)₁₀ at 45, 50, and 55 eV photon energies. All the spectra are normalized with intensities of peaks 9 and 10.
The variable energy spectra of \textit{Re}_2(\textit{CO})_{10} at 45, 50, and 55 eV photon energies shown in Figure 6-7 display a distinct maximum at 50 eV photon energy for the first five peaks (peaks 1 to 5). The first five peaks are all expected to show a Re 5p→5d resonance, since they all derived from the Re 5d based orbitals. It is worthwhile to note that peak 5 shows the most intense resonance because it originates from two by nonbonding Re 5d orbitals.\(^6\)

The current assignment based on the variable energy SR spectra confirms that the assignment of Higginson et al. is correct for these Re(CO)$_3$X complexes. The observation of the Re 5p→5d resonance is very useful in distinguishing the Re 5d based orbitals from the ligand based orbitals, especially when the BE's of the halogen valence orbital shift significantly down the periodic table from Cl to I in these compounds.

6.5 Core Levels

Up until recently, core level spectra of inorganic and organometallic molecules were obtained using mostly nonmonochromatized X-ray sources, and the major useful core level effect was the chemical shift.\(^9\) In the previous Chapters, the application of high resolution SR to the vibrational and ligand field splitting studies of the core levels of metal carbonyls has been demonstrated. Herein, the Re 4f linewidths of these Re complexes will be reported, and the core level chemical shifts can be used to assign the valence level spectra of these compounds. Moreover, Auger peaks are observed after the photoionization of the Br 3d and I 4d ligand core levels of Re compounds.

The Re 4f linewidths for these four Re compounds are about 0.40 eV as listed in Table 6-1. These linewidths are much broader than the theoretical inherent linewidth
(between 0.07 and 0.15 eV).\textsuperscript{30} This is broader than the W 4f width at 0.25 eV of W(CO)\textsubscript{6}, but narrower than the Os 4f width at 0.53 eV of Os(CO)\textsubscript{5}.\textsuperscript{31} It has been shown in Chapters 3 and 4 that the CO vibrational stretching is the only cause for the W 4f line broadening, but the ligand field splitting is the predominant factor in the Os 4f line broadening. For the Re 4f levels, it is believed that the line broadening is due to both the vibrational and ligand field splittings for two reasons. Firstly, the Mössbauer quadrupole splittings (proportional to the core level ligand field splitting) for these Re compounds\textsuperscript{32} are moderate in comparison with that of Os(CO)\textsubscript{5}, but certainly larger than that of W(CO)\textsubscript{6} under O\textsubscript{h} symmetry.\textsuperscript{31} And secondly, the best linewidth obtained for these Re 4f levels is ~0.35 eV for Re(CO)\textsubscript{5}I when the instrumental resolution is ~0.10 eV, and no vibrational fine structure is clearly resolved for these Re 4f levels.

In Chapter 4, the Os 4f core chemical shift between Os(CO)\textsubscript{5} and Os(CO)\textsubscript{5}PMe\textsubscript{3} was compared with the valence level chemical shift using Jolly’s approach.\textsuperscript{33} The bonding property of the PMe\textsubscript{3} ligand has been discussed. The basic principle of Jolly’s approach is that the appropriately chosen core BE’s can be used to subtract the contributions due to electrostatic potential (atomic charges) and relaxation energy from valence ionization potentials, and thus it is possible to quantify the bonding or antibonding character of molecular orbitals by using only experimental data. Jolly has successfully applied this approach to the Mn(CO)\textsubscript{5}X system to confirm the assignment of Higginson et al for the Mn compounds.\textsuperscript{10}

Using the Re and halogen core and valence level BE’s of these four Re compounds (Table 6-3), the localized orbital ionization potentials (LOIP) of three rhenium
Table 6-3. Valence and Core Ionization Potentials of Re(CO)$_5$X and HX Complexes

<table>
<thead>
<tr>
<th>molecule</th>
<th>valence IP</th>
<th>core $E_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>band 1</td>
<td>band 2</td>
</tr>
<tr>
<td>Re$<em>2$(CO)$</em>{10}$</td>
<td>8.04</td>
<td>8.69$^a$</td>
</tr>
<tr>
<td>Re(CO)$_5$Cl</td>
<td>8.96$^b$</td>
<td>9.94</td>
</tr>
<tr>
<td>Re(CO)$_5$Br</td>
<td>8.86$^b$</td>
<td>9.95</td>
</tr>
<tr>
<td>Re(CO)$_5$I</td>
<td>8.51$^b$</td>
<td>9.70</td>
</tr>
<tr>
<td>HCl</td>
<td>12.78$^d$</td>
<td></td>
</tr>
<tr>
<td>HBr</td>
<td>11.82$^d$</td>
<td></td>
</tr>
<tr>
<td>HI</td>
<td>10.64$^d$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Average IP of spin-orbit peaks 2 and 3 for Re$_2$(CO)$_{10}$.  
$^b$ Average IP of spin-orbit peaks 1 and 1'.  
$^c$ Average IP of spin-orbit peaks 3 and 3'.  
$^d$ Reference 10.  
$^e$ Reference 34.  
$^f$ Reference 35.  
$^g$ Reference 22.
pentacarbonylhalides can be calculated using Re₂(CO)₁₀ as the reference compound, based on the following equation:\(^{33}\)

\[
\text{LOIP} = \text{IP(ref)} - 0.8[\text{E}_\text{c} - \text{E}_\text{c(ref)}]
\]

where IP is the vertical ionization potential of the valence orbitals, and Eₐ is the BE of the core levels. The LOIP values can be calculated for the halogen valence p orbitals of the Re halides, using data of the strictly nonbonding halogen pπ orbitals of the corresponding HX compounds. The b₂ nonbonding σ orbital and e₁ π orbital of Re₂(CO)₁₀ were chosen to calculate the LOIP values for the Re d orbitals of three Re halides. The calculated LOIP values are listed in Table 6-4. It is immediately clear that the e(Cl) is much higher than the Re LOIP values for Re(CO)₂Cl. And the e(X) value decreases dramatically on going from Cl to I, while the LOIP values for both Re σ and π orbitals increase on going from Re(CO)₂Cl to Re(CO)₂I. Thus the LOIP data indicate an energy level ordering of e(Re) > b₂(Re) > e(Cl) > a₁(Re-Cl) for Re(CO)₂Cl, and e(I) > b₂(Re) > e(Re) > a₁(Re-I) for Re(CO)₂I, in agreement with the present variable energy SR results and the assignments by Higginson et al.\(^4\) and Hall.\(^8\) The assignment for Re(CO)₃Br is unclear from this approach, since the calculated LOIP values of these three orbitals for this compound are too close to each other.

In addition to the Re 4f core levels, the ligand core levels of these Re complexes, such as Br 3d and I 4d levels are also worth studying. Figure 6-8 presents the high resolution core level spectra of Re(CO)₃Br at (a) 110 and (b) 115 eV photon energies. In addition to the intense and narrow Re 4f and Br 3d (with 0.51 eV width) peaks shown in Figure 6-8, two surprising features are obvious. Firstly, Re 4f shakeup peaks are
Table 6-4. Calculated LOIP Values for Re(CO)$_3$X ($X$=halogens) Complexes, eV

<table>
<thead>
<tr>
<th>molecule</th>
<th>orbital</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>e(X)$^a$</td>
<td>$b_2$(Re)$^b$</td>
<td>$e_3$(Re)$^b$</td>
</tr>
<tr>
<td>Re(CO)$_3$Cl</td>
<td>10.28</td>
<td>8.92</td>
<td>8.57</td>
</tr>
<tr>
<td>Re(CO)$_3$Br</td>
<td>9.44</td>
<td>8.94</td>
<td>8.59</td>
</tr>
<tr>
<td>Re(CO)$_3$I</td>
<td>8.81</td>
<td>9.14</td>
<td>8.79</td>
</tr>
</tbody>
</table>

$^a$ Calculated by using the hydrogen halides as reference molecules. $^b$ Calculated by using Re$_2$(CO)$_{10}$ as the reference molecule.
Figure 6-8. Re 4f and Br 3d spectra of Re(CO)$_5$Br at (a) 110 and (b) 115 eV photon energies, showing the satellites of Re 4f levels, and Br MVV Auger peaks.
clearly resolved between 52 and 65 eV BE’s. A similar feature has been previously observed and assigned for the W 4f levels in W(CO)₆ using both XPS and SR. The second surprising feature is the observation of the MVV Auger peaks between 41 to 45 eV kinetic energies, which are caused by the Br 3d ionization. This observation can be verified by shifting the photon energy by 5 eV, while the Br Auger peaks also shift by 5 eV on going from 110 to 115 eV photon energies. This is the first time that such Auger structure is observed for organometallic molecules (also on I 4d of Re(CO)₃I shown in Figure 6-2), and more studies are certainly necessary, since many fine structures have been observed in the Auger spectra of molecules like HI and HBr.

In Chapter 5, it has been shown that the I 4d lines in CpFe(CO)₂I were broadened mainly because of the ligand field splitting. The high resolution I 4d photoelectron spectrum of Re(CO)₃I is presented in Figure 6-9. The linewidth of 0.42 eV is much broader than the instrumental resolution (∼0.15 eV), and it is believed that this line broadening (also for Br 3d lines) is due to the ligand field splitting.

6.6. Conclusions

High resolution photoelectron spectra of Re(CO)₃X (X=(CO)₅, Cl, Br, I) have been reported. The correct assignment for these compounds is obtained by three different methods. (1) Vibrational fine structure resolved on the Re 5d based orbitals provides the firm assignment for the peaks with Re-CO bonding character (for example, peak 2 in Re(CO)₃Br). (2) The studies of the extensive photon energy dependence of band intensities of these compounds provide the solid assignment not only for the Re 5d based orbitals, but also for the halide based orbitals. The importance of the observation
Figure 6-9. I 4d photoelectron spectrum of Re(CO)$_3$I, taken at 95 eV photon energy.
of the Re 5p→5d resonance in distinguishing the metal d based bands from the ligand based peaks has been demonstrated. (3) The core and valence level chemical shifts of these compounds were treated with Jolly's approach. The LOIP values were successfully used to derive the assignments for the valence level spectra of these molecules which agreed well with that originally proposed by Higginson et al.

The inner valence levels of these molecules were shown to be dominated by contributions from the CO group. The Auger peaks have been observed in the high resolution, high intensity Br 3d and I 4d spectra, for the first time in organometallic molecules. It is believed that the ligand field splitting from these low symmetry molecules is the major cause of the line broadening of Re 4f, Br 3d, and I 4d levels.
References

(1) Evans, S.; Green, J. C.; Green, M. L. H.; Orchard, A. F.; Turner, D. W. 


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


Chapter 7

Conclusions

High resolution gas phase photoelectron spectra of transition metal carbonyls, $\text{W(CO)}_6$, $\text{Os(CO)}_4\text{L}$ (L = CO, PMe$_3$), $\text{CpM(CO)}_3$ (M = Mn, Re), $\text{CpFe(CO)}_2\text{I}$, and $\text{Re(CO)}_3\text{X}$ (X = Re(CO)$_3$, Cl, Br, and I) have been reported. The advantages of monochromatized synchrotron radiation for studying the electronic structure of organometallic complexes have been demonstrated:

(a) High resolution spectra of all levels of these metal carbonyls from valence to inner-valence and core levels can be obtained readily with SR.

(b) For core levels, vibrational fine structure from CO ligand group has been clearly resolved for the first time on the core W 4f levels of $\text{W(CO)}_6$, and this structure has been rationalized using the core equivalent model. In addition to the vibrational broadening, ligand field splitting has also been shown to be important in the line broadening of the high resolution Os and Re 4f core level spectra. The high intensity of SR was important for observing the weak metal np core level spectra for the first time. The knowledge of the binding energies of the metal np levels was used for observing np→nd resonances on the metal valence nd levels.

(c) For valence levels, the observations of the np→nd resonance and the Cooper minimum effect by SR provided firm assignments for both novel
organometallic complexes, such as $\text{Os(CO)}_4 \text{L}$ ($\text{L} =$ CO, PMe$_3$) complexes, and for controversial organometallic complexes, such as $\text{Re(CO)}_3 \text{X}$ ($\text{X} =$ Cl, Br, and I) complexes. The Xα-SW calculations were performed for $\text{CpMn(CO)}_3$ and $\text{Os(CO)}_3$ to aid in the complete valence level assignments of these molecules.

(d) The high resolution and high intensity of SR were critical for the study of the weak and broad inner-valence spectra of these metal carbonyls. It has been shown that the inner-valence level of these molecules was dominated by contributions from the CO group.

This work has demonstrated that variable energy SR photoelectron spectroscopy is an excellent technique for the study of the electronic structure of the organometallic molecules in general. In the future, better resolution from SR would be desirable for the improvement in this area of study. For example, the resolution as good as, or even better than He I radiation would be important for the variable energy study of the valence level of the organometallic molecules. It would also be interesting to study the C 1s and O 1s core levels of these metal carbonyls, such as W(CO)$_6$, with better resolution at higher photon energy, to resolve the possible fine structure on these ligand core levels.