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# Variable-Energy Photoelectron Spectroscopy of Substituted Rhenium and Manganese Pentacarbonyls: Molecular Orbital Assignments and the Interatomic Resonant Effect

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High-resolution variable-energy photoelectron spectra of $M(CO)_5X$ [M = Re, X = $Re(CO)_5$, Cl, Br, and I; and M = Mn, X = $Mn(CO)_5$ and Br] are reported. Tunable synchrotron radiation is used to distinguish the Re 5d and Br 4p orbital based peaks for the controversial $Re(CO)_5Br$. Our results provide firm molecular orbital assignments for all of these molecules. The valence orbital in the ordering of ionization energies for $M(CO)_5Cl$ (M = Mn and Re) and $Mn(CO)_5Br$ is $a_1(M{-}X) > e(X) > b_2(M) > e(M)$; but for $M(CO)_5I$ (M = Mn and Re) and $Re(CO)_5Br$ the ordering is $a_1(M{-}X) > e(M) > b_2(M) > e(X)$. The crossover of the HOMO in the Re molecules due to the change in the halogen electronegativities occurs at $Re(CO)_5Br$. The metal np → nd resonance is observed for all of these molecules. For molecules like $M_2(CO)_{10}$ (M = Re and Mn) and $Mn(CO)_5Br$, the observation of this np → nd resonance is useful in assigning the metal nd based orbitals in their valence level spectra. However, for molecules like $Re(CO)_5X$ (X = Br and Cl), a np → nd type resonance is observed on bands arising from *both* Re 5d and halogen mp based orbitals. This new resonant effect on the ligand-based orbitals is shown to be mainly due to the interatomic resonant effect. The core and valence level chemical shifts of these compounds are treated using Jolly's approach to confirm the assignments for the valence level spectra of some of these molecules. The high-resolution inner valence and core level spectra of these compounds are reported. Broadening of Re 4f, Br 3d, and I 4d core level spectra is discussed. The Auger peaks are observed in the high-resolution, high-intensity Br 3d of $Re(CO)_5Br$ and I 4d of $Re(CO)_5I$ spectra.

## 1. Introduction

Ultraviolet photoelectron spectra (UPS) of $Mn(CO)_5X$ [X = Cl, Br, I, H, and $Mn(CO)_5$] compounds were first reported in 1969 as one of the first applications of photoelectron spectroscopy to organometallic molecules.[1] These spectra received considerable attention because they showed the great potential of UPS for studying 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 semiempirical calculations,[3] but disagreed with the ab initio calculations.[4] In the next decade, the intensity rule,[5,6] based on the comparison of the He I/He II band intensities, was used to assign the valence level spectra of these compounds;[7] and more importantly, $Re(CO)_5X$ analogues were studied.[7−9] The larger Re 5d spin−orbit splitting was shown to be valuable in the assignment of both Re and Mn systems.[9] However, there is still no firm consensus regarding the assignments of the valence spectra of some of these compounds.[10,11]

The advantages of variable-energy photoelectron spectroscopy, using synchrotron radiation (SR), for the study of organometallic molecules over the conventional He I/He II based UPS, have been demonstrated recently.[12,13] The photon energy dependence of band intensities between 20 and 100 eV has become extremely useful in assigning metal nd and ligand-based molecular orbitals (MO). In particular, the Cooper minimum effect[14,15] and the np → nd resonances[12] at the core np ionizations have been shown to be useful in assigning the metal nd valence orbitals.[14−18]

In this paper, we focus on the assignment of the four lowest binding energy (BE) MOs, involving the valence Re 5d/Mn 3d and halogen mp orbitals, particularly in the controversial $Re(CO)_5Br$ case. The assignments are made in three independent

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ways using: (1) the variation of the valence intensities at low photon energy; (2) the enhancement of the valence intensities at the Re 5p resonances; and (3) the Re 4f core level shifts and valence level shifts as studied by Jolly for Mn(CO)$_5$X compounds.[11] The very large Re 5p → 5d enhancement observed for the halogen-based valence orbital in molecules like Re(CO)$_5$Cl and Re(CO)$_5$Br is, at first glance, very surprising. However, as proposed by Fadley and co-workers,[19] this enhancement is due to a newly observed interatomic resonant effect. In addition to the valence band results, we also complete previously published core and inner valence studies of these complexes[16] and report the Br MVV and I NVV Auger spectra of Re(CO)$_5$Br and Re(CO)$_5$I, respectively.

## 2. Experimental Section

The photoelectron spectra were recorded using two different photoelectron spectrometers. The He I spectra were measured with a McPherson ESCA-36 photoelectron spectrometer.[20] The variable-energy (22−200 eV) spectra were recorded on the modified ESCA-36 spectrometer,[21] using photons from the Canadian Grasshopper beamline at the Canadian Synchrotron Radiation Facility (CSRF) at the Aladdin storage ring, University of Wisconsin—Madison.[22,23] The electron analyzer of the ESCA-36 spectrometer had a resolving power of 720, giving an electron resolution of 40 meV at a 30 eV kinetic energy. A 600 groove/mm grating gave photon energies between 22 and 72 eV, and an 1800 groove/mm grating gave photon energies between 70 and 200 eV. Typically, the photon resolution of the Canadian Grasshopper beamline was 50 meV at 40 eV and 80 meV at 80 eV photon energies, while the total instrumental resolution was 65 meV at 40 eV and 90 meV at 80 eV photon energies. The Ar 2p$_{3/2}$ line at 15.759 eV BE was used as an internal calibration for the He I spectra. The Xe 4d$_{5/2}$ line at 69.541 eV BE was used to calibrate the core level spectra at higher photon energies. The spectra were deconvoluted with a Gaussian−Lorentzian line shape using a nonlinear least squares procedure described previously.[24]

All of the samples with the exception of Re(CO)$_5$I were commercially purchased and used without further purification. Re(CO)$_5$I was prepared according to the published procedure.[25] The solid samples were introduced via the heatable probe into the gas cell of the spectrometer. Temperatures ranging from 40 to 90 °C were required to generate enough vapor pressure. The sample pressure in the differentially pumped gas cell was controlled at around $4 \times 10^{-5}$ Torr.

## 3. Results and Discussion

**3.1. General Features, Core Level, and Auger Spectra.** The high-resolution broad-scan photoelectron spectra at 80 eV of the four Re compounds Re(CO)$_5$X [X = Re(CO)$_5$, Cl, Br and I] are presented in Figure 1. These spectra cover the relatively narrow valence levels with BEs less than 20 eV; the weak, broad inner valence levels with BEs between 20 and 45 eV; and the three core level peaks (plus two more I 4d peaks in Figure 1d) with BEs greater than 45 eV. Table 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 Figure 1. Apart from the outer valence level region (with BEs lower than around 13 eV), these spectra are remarkably similar qualitatively. The broad and intense band between 14 and 17 eV BE is due to the well-studied ionizations from the $5\sigma$ and $1\pi$ orbitals of the CO group. The intense and relatively narrow band around 18 eV BE for all four compounds can be assigned to the ionizations from three CO $4\sigma$ orbitals, as in W(CO)$_6$.[16] The outer valence level region (with BEs between 8 and 11 eV) of these spectra will be studied in detail later (section 3.2).

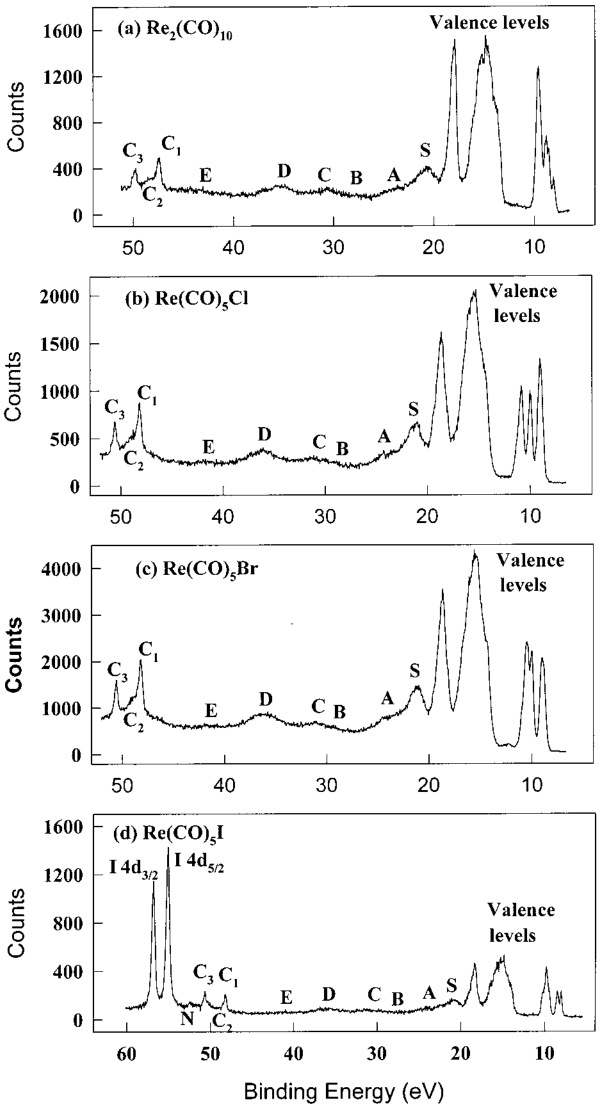

**Figure 1.** High-resolution broad-scan photoelectron spectra of (a) Re$_2$(CO)$_{10}$ at 70 eV, (b) Re(CO)$_5$Cl at 72 eV, (c) Re(CO)$_5$Br at 72 eV, and (d) Re(CO)$_5$I at 80 eV photon energy. The inner valence level peaks are labeled with S and letters (A−E). Three core level peaks C$_1$, C$_2$, and C$_3$ are labeled for all four spectra. I 4d orbitals and I NVV Auger peak (N) are also shown in Figure 1d for Re(CO)$_5$I.

The inner valence region of these Re compounds, with the exception of Re(CO)$_5$I, has been assigned previously.[16] This region was shown to be dominated by the shakeup and satellite peaks originated from CO groups.[16] The ionizations due to the Cl 3s, Br 4s, or I 5s orbitals in the Re(CO)$_5$X (X = halogens) compounds are expected, but not observed, to be around 25 eV BE in Figure 1. This is most likely due to the very small cross sections of these halogen ms orbitals relative to those of the C 2s and O 2s orbitals.[26] It is also obvious that the Re$_2$(CO)$_{10}$ spectrum in this region is very similar to the other three spectra between 20 and 30 eV BE, showing once again that the Cl 3s,

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**Table 1.** Binding Energies, Widths, and the Assignments of the Inner-Valence and Core Spectra of Rhenium Carbonyls (±0.05 eV)

| | $Re(CO)_5Cl$ | | $Re(CO)_5Br$ | | $Re(CO)_5I$ | | $Re_2(CO)_{10}$ | | |
|---|---|---|---|---|---|---|---|---|---|
| peak | BE (eV) | width (eV) | BE | width | BE | width | BE | width | assignment |
| S | 21.11 | 2.14 | 21.06 | 2.21 | 20.79 | 2.54 | 20.61 | 2.31 | shakeup |
| A | 23.73 | 3.05 | 23.79 | 3.31 | 23.90 | 2.72 | 23.51 | 3.07 | satellite 1 |
| B | 27.29 | 3.46 | 27.93 | 2.97 | 27.10 | 2.53 | 27.57 | 2.00 | satellite 2 |
| C | 31.25 | 3.90 | 31.30 | 3.33 | 30.65 | 3.56 | 30.79 | 2.70 | satellite 3 |
| D | 36.10 | 3.53 | 36.09 | 3.67 | 35.69 | 4.10 | 35.38 | 3.51 | CO 3$\sigma$ |
| E | 41.25 | 2.50 | 41.80 | 1.85 | 40.57 | 2.26 | 43.83 | 3.72 | satellite 4 |
| $C_1$ | 48.31 | 0.46 | 48.29 | 0.42 | 48.04 | 0.42 | 47.45 | 0.53 | Re $4f_{7/2}$ |
| $C_2$ | 49.15 | 1.42 | 49.12 | 1.14 | 50.02 | 1.21 | 48.42 | 0.97 | Re $5p_{3/2}$ |
| $C_3$ | 50.74 | 0.48 | 50.70 | 0.40 | 50.50 | 0.40 | 49.85 | 0.57 | Re $4f_{5/2}$ |

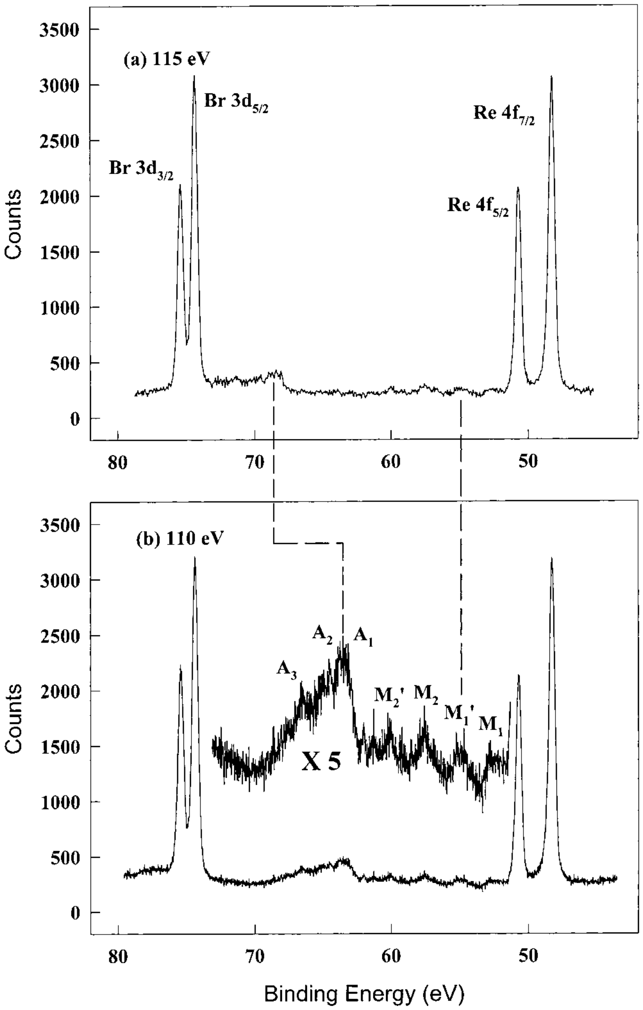

**Figure 2.** Re 4f and Br 3d spectra of $Re(CO)_5Br$ at (a) 115 and (b) 110 eV photon energies, showing the shakeup peaks of Re 4f levels ($M_1$, $M_2$, etc.), and Br MVV Auger peaks ($A_1$, $A_2$, $A_3$). The inset in Figure 2b is enlarged by five times.

Br 4s, and I 5s levels give no noticeable contribution. It is interesting to note that inner valence peaks of $Re_2(CO)_{10}$ (Table 1) have BEs which are generally lower than those of the halides. The slight decrease in BEs for the inner valence peaks on going from Cl, to Br, I and to $Re(CO)_5$ is in accord with the relative electronegativities of these ligands.

The three peaks around 50 eV BE in these spectra shown in Figure 1 are derived from the Re 4f ($C_1$ and $C_3$) and $5p_{3/2}$ ($C_2$) core orbitals. The Mn 3p orbital has a BE of 56.2 eV for $Mn(CO)_5Br$ (spectrum not shown), in good agreement with a value of 56.3 eV obtained for $CpMn(CO)_3$.[27] The metal np BEs (Table 1) are useful to observe the np → nd resonances (section 3.4). Three more peaks can be seen in the core level region of $Re(CO)_5I$. The two intense, sharp peaks at 54.90 and 56.64 eV BEs are due to the ionizations of I 4d core orbitals. The weak peak labeled N (at a kinetic energy of ~28 eV, or a BE ~52 eV) in Figure 1d is an I NVV Auger peak. Many similar I Auger peaks have been observed to be between 25 and 30 eV kinetic energy for HI.[28] Similar Auger peaks can be observed on Br 3d levels for $Re(CO)_5Br$ (Figure 2).

In addition to the Re 4f core levels, the ligand core levels of these Re complexes, such as the Br 3d and I 4d levels, are also worth studying. Figure 2 presents the high-resolution core level spectra of $Re(CO)_5Br$ at (a) 115 and (b) 110 eV photon energies. In addition to the intense and narrow Re 4f and Br 3d peaks shown in Figure 2, two surprising features are obvious (especially in the inset spectrum in Figure 2b, which is enlarged by five times). First, Re 4f shakeup peaks ($M_1$, $M_1'$ and $M_2$, $M_2'$) are clearly resolved between 52 and 65 eV BEs. A similar feature has been previously observed and assigned for the W 4f levels in $W(CO)_6$.[16,29] The shakeup energy for the first series of shakeup peaks ($M_1$ and $M_1'$ in Figure 2a) is 4.30 eV, and the shakeup energy is 9.30 eV for the $M_2$ and $M_2'$ shakeup peaks. These values for $Re(CO)_5Br$ are in reasonable agreement with the shakeup energies for $W(CO)_6$ (5.4 and 8.9 eV).[16] The second feature is the observation of the MVV Auger peaks between 41 and 45 eV kinetic energies, which result from the Br 3d ionizations. This observation can be verified by shifting the photon energy by 5 eV, while the Br Auger peaks also shift by 5 eV (from ~70 eV BE to ~65 eV BE) on going from 115 to 110 eV photon energies. Auger peaks at very similar kinetic energies have been observed in the Auger spectrum of HBr.[30] The Auger spectra of organometallic molecules can be used to probe the chemical bonding between the transition metal and ligands, as demonstrated previously in the study of the Auger spectroscopy of the metal carbonyls and metal nitrosyls.[31]

The Re 4f line widths for these four Re compounds are about 0.40 eV, as listed in Table 1. These line widths are much broader than the theoretical inherent line width (between 0.07 and 0.15 eV).[32] These widths are broader than the W 4f width at 0.25 eV of $W(CO)_6$, but narrower than the Os 4f width at 0.53 eV of $Os(CO)_5$.[16] It has been shown that the CO and W−C vibrational stretching is the major cause for the W 4f line

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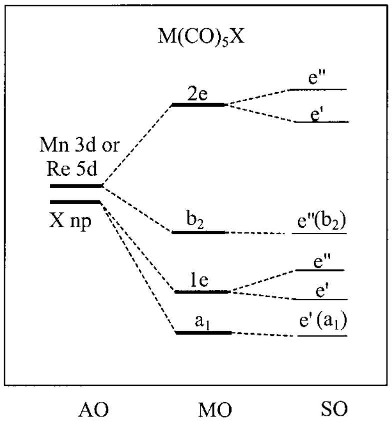

**Figure 3.** Simple MO diagram of $Re(CO)_5X$ molecules under $C_{4v}$ symmetry. The MOs are constructed from the atomic orbitals (AO) of Re and X in the upper valence region. The e orbitals are further split by the spin−orbit (SO) coupling.

broadening,[33] but the ligand field splitting is the predominant factor in the Os 4f line broadening.[34] For the Re 4f levels, it is believed that both vibrational and ligand field splitting effects contribute to the line broadening in these molecules. The ligand field splitting is expected to be present in these Re compounds because their Mössbauer quadrupole splittings (proportional to the core level ligand field splitting)[35] are moderate in comparison with that of $Os(CO)_5$, but certainly larger than that of $W(CO)_6$ under $O_h$ symmetry.[16] With the instrumental resolution of $\leq 0.10$ eV and a lifetime line width of $\leq 0.15$ eV, vibrational broadening due to the CO and Re−C stretching has to be a factor to account for the best line width of ~0.35 eV obtained for these Re 4f levels for $Re(CO)_5I$, as previously observed in the core level spectra of the other third row transition metal carbonyls.[16,34]

It has been shown that the I 4d lines in $CpFe(CO)_2I$ were broadened mainly because of the ligand field splitting.[13a,27] The high-resolution I 4d photoelectron spectrum of $Re(CO)_5I$ (not shown) gave the line width of 0.42 eV that is much broader than the instrumental resolution (~0.15 eV). It is believed that the line broadening for the I 4d lines (also for the Br 3d lines) is also due to ligand field splitting.

**3.2. Valence Levels.** Figure 3 gives a simplified MO diagram for the occupied valence MOs involving the Re 5d/Mn 3d and X mp orbitals. Under $C_{4v}$ symmetry, there are four occupied orbitals in the valence level region, namely, one e and $b_2$ orbital each from the metal atom, and one e and $a_1$ orbital each from the halogen. For orbitals with the high angular momentum of the heavy atoms, such as Re 5d, Br 4p, and I 5p orbitals, the doubly degenerate e orbitals have a large spin−orbit splitting that can be observed by UPS.[36,37] When spin−orbit effect is considered in the ionic final state, the lowering of symmetry from $C_{4v}$ to the $C_{4v}{}^*$ double group transforms $b_2$ and $a_1$ to e′ and e″, respectively. This enables the mixing of the $b_2$ and $a_1$ orbitals with the e orbitals (Figure 3).[9,38]

Depending on the relative energies of the Re 5d (or Mn 3d) and X mp orbitals, the HOMO can be either an e orbital with majority X mp character or an e orbital with metal d character. For example, Lichtenberger et al. first proposed the orbital ionization energy sequence for the $Mn(CO)_5X$ (X=Cl, Br, I) complexes $b_2(Mn) > e(Mn) > a_1(Mn-X) > e(X)$.[2] This assignment basically agreed with the theoretical results obtained by Fenske calculations.[3] On the basis of a comparison between Mn and Re systems, Ceasar et al. reinterpreted the spectral ordering to give $a_1(M-X) > e(M) > b_2(M) > e(X)$ for both Mn and Re complexes.[8] Using a spin−orbit analysis of the $Re(CO)_5X$ compounds,[9] Hall proposed the above order for $M(CO)_5I$ complexes, but reordered the metal and halogen e orbitals for the $M(CO)_5Cl$ complexes to give $a_1(M-Cl) > e(Cl) > b_2(M) > e(M)$. The ordering for $Re(CO)_5Br$ and $Mn(CO)_5Br$ was less clear. On the basis of the He I/He II study for both $Mn(CO)_5X$ and $Re(CO)_5X$ compounds, Higginson et al.[7] suggested that the ionization energy ordering for $Mn(CO)_5Br$ was $e(Br) > e(M)$, while the ordering for $Re(CO)_5Br$ was like that for $Re(CO)_5I$ given by Hall.[9] This assignment did not agree with Hall's suggestion[9] that the HOMO in $Re(CO)_5Br$ had 60% Re 5d character, although the spin−orbit analysis could not give an accurate percentage. Clearly, for $Re(CO)_5X$, the decrease in electronegativity of the ligands (Cl > Br > I) causes a crossover in the halogen and Re orbitals. The nature of the HOMO changes from 80% Re in the Cl compound, to 60% in the Br compound, to 30% in the I compound.[9] For $Re(CO)_5Br$, if the Br 4p and Re 5d have very similar energies (and very similar spin−orbit splittings), the classification of these e levels into e(M) and e(X) may not be even meaningful. The analysis below confirms the assignment for $Mn(CO)_5Br$ and $Re(CO)_5Cl$ and sheds more light on the $Re(CO)_5Br$ assignment.

**3.2.a. He I Spectra.** The high-resolution He I spectra of the upper valence region of four Re compounds are presented in Figure 4. Table 2 contains the BEs of the valence level peaks and their assignments. Our spectra and BE values are in good agreement with previous results.[7,9] In a 3 eV span, there are four sets of bands labeled 1, 2, 3, and 4 for $Re(CO)_5X$ (X = halogens) and five bands for $Re_2(CO)_{10}$. There are in fact more than four peaks resolved in this region, with the extra peaks arising from the spin−orbit splittings of the Re 5d, Br 4p, and I 5p valence orbitals, and also from the vibrational fine structure due to the Re−CO stretching on the Re 5d based peaks.

The assignment for $Re_2(CO)_{10}$ is relatively straightforward under $D_{4h}$ symmetry. It has been given in the previous studies;[7,9] 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 arising from the two spin−orbit components of the filled Re−Re $\pi$ bonding orbitals ($e_3$), peak 4 is assigned to one component of the spin−orbit split bonding Re−Re orbital ($e_1$), and the very intense peak 5 is assigned to the other spin−orbit component from $e_1$ overlapping with the two nonbonding $b_2$ orbitals from each Re center. This assignment will be confirmed with the variable energy SR results shown in the next section.

A spin−orbit splitting is clearly resolved for band 1 in all three halides as shown in Figure 4. But the splitting in $Re(CO)_5I$ (0.43 eV) is much larger than that for the Cl and Br (0.25 and 0.30 eV) analogues (Table 2). Peaks 1 and 1′ must arise from a majority I 5p orbital for $Re(CO)_5I$, since I is expected to have a much larger spin−orbit splitting due to the heavy-atom effect.[36,37] The shoulder for both peaks 1 and 1′ in $Re(CO)_5I$ (at 0.26 eV from peaks 1 and 1′) is assigned to a CO vibrational contribution (a similar, but weaker shoulder is also visible at around 9.35 eV BE for $Re(CO)_5Br$ in Figure 4b). This shoulder was not resolved/identified in the previous studies.[7−9] This observation of a CO vibrational component on a halogen-

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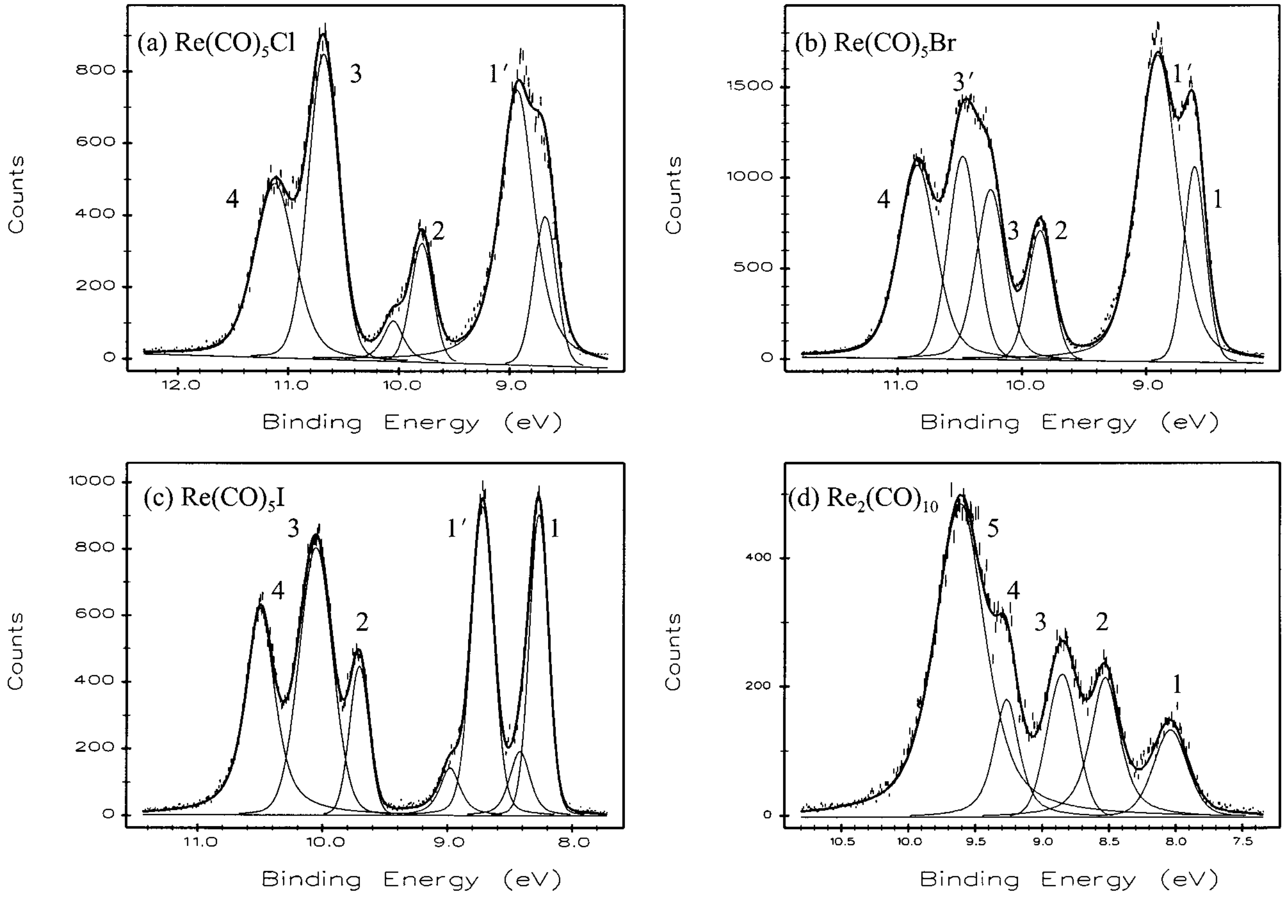

**Figure 4.** Photoelectron spectra of (a) Re(CO)$_5$Cl, (b) Re(CO)$_5$Br, (c) Re(CO)$_5$I, and (d) Re$_2$(CO)$_{10}$, obtained by He I radiation.

**Table 2.** Binding Energies and Assignments of the Outer Valence Spectra of Rhenium Carbonyls (±0.03 eV)

| | Re(CO)$_5$Cl | | Re(CO)$_5$Br | | Re(CO)$_5$I | | Re$_2$(CO)$_{10}$ | |
|---|---|---|---|---|---|---|---|---|
| peak | BE (eV) | assignment | BE (eV) | assignment | BE (eV) | assignment | BE (eV) | assignment |
| 1 | 8.83 | e′(Re) | 8.71 | e(Br,Re) | 8.29 | e(I) | 8.04 | a$_1$(Re−Re) |
| 1′ | 9.08 | e′(Re) | 9.01 | e(Br,Re) | 8.72 | e(I) | | |
| 2 | 9.94 | b$_2$(Re) | 9.95 | b$_2$(Re) | 9.70 | b$_2$(Re) | 8.53 | e$_3$(Re−Re) |
| 3 | 10.83 | e″(Cl) | 10.35 | e(Re,Br) | 10.05 | e(Re) | 8.85 | e$_3$(Re−Re) |
| 3′ | | | 10.57 | e(Re,Br) | | | | |
| 4 | 11.27 | a$_1$(Re−Cl) | 10.94 | a$_1$(Re−Br) | 10.50 | a$_1$(Re−I) | 9.26 | e$_1$(Re−Re) |
| 5 | | | | | | | 9.61 | e$_1$+b$_2$(Re−Re) |

based peak can be understood as a result of the orbital mixing (between the majority I 5p character and the metal/carbonyl $\pi^*$ character). The assignment of band 1 for the Cl and Br analogues cannot be conclusive on the basis of the He I spectrum, since the splitting between peaks 1 and 1′ could arise from the spin−orbit splitting of the Re 5d orbitals or the halogen mp orbitals. This will be further discussed later using SR spectra. Peak 2 is 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)$_5$Cl spectrum, since a distinct shoulder due to the vibrational fine structure from the CO stretch is clearly resolved for peak 2. The splitting of 0.26 eV is in very good agreement with the CO stretching frequency in Re(CO)$_5$X.[36] A similar vibrational progression has been observed on the Re 5d based orbitals for CpRe(CO)$_3$.[37] Band 3 is assigned to the ionizations from the halogen-based $\pi$ orbitals when X is Cl and Br, but it has been assigned to the contributions from Re 5d based $\pi$ orbitals for Re(CO)$_5$I.[9,10] There has to be uncertainty on the assignment of band 3 for Re(CO)$_5$Br for two reasons. First, both Br 3p and Re 5d spin−orbit splittings are expected to be ~0.2 eV. Second, atomic Re 5d and Br 4p orbitals have almost identical energy and there could be a significant degree of mixing.[9] Finally, peak 4 was unambiguously assigned to the M−X $\sigma$ bonding orbital (a$_1$) for all three compounds. In the next section, the variable-energy SR will be used to provide firm assignments for these compounds.

**3.2.b. The Assignments of Re(CO)$_5$Cl and Re(CO)$_5$Br.** Due to a delayed maximum for most transition metal valence nd orbitals,[12,26] the cross sections of the Re 5d orbitals increase from the onset of their threshold to a maximum (at around 30 eV photon energy) and then decrease continuously with the increase of the photon energy. On the other hand, the cross sections of most ligand-originated valence orbitals, such as C 2p, Cl 3p, and Br 4p orbitals, decrease continuously from the onset of their thresholds. Figure 5 illustrates the theoretical atomic cross sections[26] of Re 5d, Br 4p, and Cl 3p orbitals between 15 and 90 eV photon energy (without the consideration of any multistep processes, such as np → nd resonance). It is clear that the cross sections of both atomic Br 4p and Cl 3p orbitals are almost equal to that of the Re 5d orbital at 20 eV photon energy, but the halogen mp cross sections drop to be

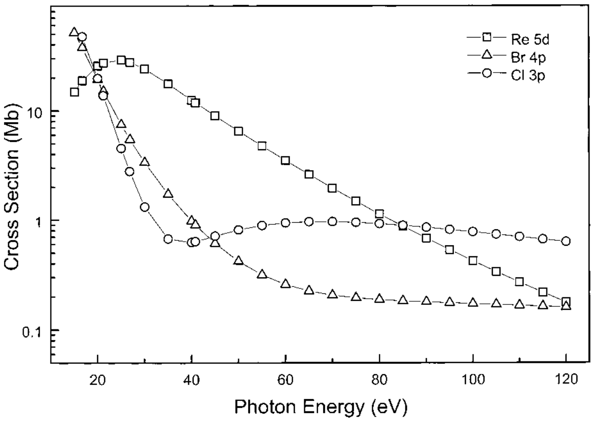

**Figure 5.** Theoretical cross sections[26] of the atomic Re 5d, Br 4p, and Cl 3p orbitals at lower photon energy region.

less than 10% of the cross section of the Re 5d orbital at 40 eV photon energy. The cross section curves of the atomic Br 4p and Cl 3p orbitals become flat, when the photon energy increases to around 75 eV, while the cross section of the atomic Re 5d orbital continues to decrease. Therefore, it is expected that the relative intensity of the Re 5d based peaks would increase on going from 20 to 40 eV photon energy, in comparison to those of the halogen mp based valence peaks. At higher photon energies, the relative intensity of the Re 5d based peaks would decrease when compared with those of the halogen mp based peaks.

We first try to assign the valence level spectrum, consisting of the four lowest BE MOs, of Re(CO)$_5$Cl with low photon energy spectra. Figure 6 presents the valence level spectra of Re(CO)$_5$Cl at photon energies of 21.22, 35, 42, and 73 eV. It is clear that the relative intensities of bands 1 and 2 increase from 21.22 to 35 eV photon energy, reaching a maximum at 42 eV photon energy. After 42 eV photon energy, the relative intensities of bands 3 and 4 start to increase, as is evident in the spectrum taken at 73 eV photon energy shown in Figure 6d. These changes in the relative intensities with photon energies are due to the different photon energy dependences of the cross sections of the atomic Re 5d and Cl 3p orbitals shown in Figure 5 and discussed above. It allows us to firmly assign bands 1 and 2 to the Re 5d based orbitals, and bands 3 and 4 to the Cl 3p based orbitals. It is also important to note that the change in the relative intensity of peak 2 is more pronounced than that of band 1, thus suggesting that peak 2 has a higher percentage of Re 5d character than band 1, in agreement with the assignment of peak 2 arising from a nonbonding b$_2$ Re 5d orbital. Further evidence to support the MO assignment of Re(CO)$_5$Cl can be obtained from its high-resolution He I spectrum shown in Figure 4a. Only band 1 gave a resolvable shoulder due to the Re 5d spin−orbit splitting, while the spin−orbit splitting of 0.073 eV for the Cl 3p orbital[38] is too small to be resolved in peak 3, as has been noted previously.[9] In conclusion, the assignment for this molecule is a$_1$(Re−Cl) > e(Cl) > b$_2$(Re) > e(Re), in agreement with the previous assignments.[7,9]

The different photon energy dependencies of the cross sections of the atomic Re 5d and Br 4p orbitals shown in Figure 5, combined with variable-energy SR, can also be used to discern the more difficult MO assignment of Re(CO)$_5$Br. The valence level spectra of Re(CO)$_5$Br at 21.22, 28, 40, and 80 eV photon energies are presented in Figure 7. These four outer valence bands can be separated into two groups, according to their orbital degeneracies, i.e., peaks (2 and 4) from the singly degenerate orbitals, and bands (1 and 3) from the doubly degenerate e orbitals. As discussed earlier, assignment for peaks 2 and 4 is relatively easy, and it is the same as the assignment for Re(CO)$_5$Cl. It is obvious that the relative intensity of peak 2 increases on going from 21.22 to 40 eV photon energy, while the relative intensity of peak 4 decreases continuously, to the extent that it becomes only a shoulder of peak 3. This confirms the previous assignment that peak 2 arises from a Re 5d based b$_2$(Re) orbital, and peak 4 is due to ionization from a Br 4p based a$_1$(Re−Br) orbital. Bands 1 and 3 both show a splitting that is very close to the Re 5d or Br 4p atomic spin−orbit coupling parameters (Table 2). It is apparent from Figure 7 that the relative intensity of band 1 decreases from 21.22 to 40 eV photon energy, before increasing again at 80 eV photon energy. The relative intensity of band 3 shows the opposite trend. This observation, when compared with the atomic cross section trends shown in Figure 5, provides the definite assignment that band 3 arises from a majority Re 5d based orbital, and band 1 arises from a majority Br 4p based orbital. This assignment is different

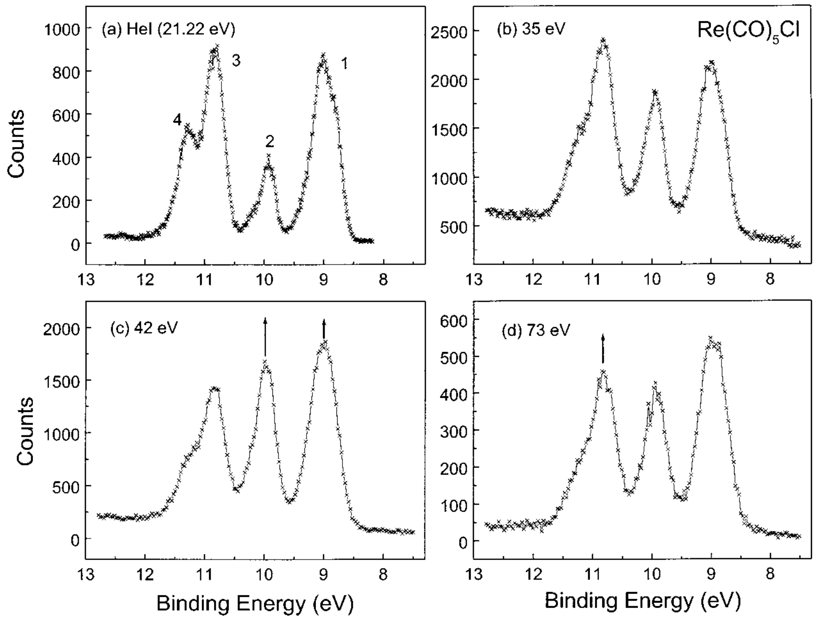

**Figure 6.** Valence level spectra of Re(CO)$_5$Cl at lower photon energy region (21.22, 35, 42, and 73 eV photon energies).

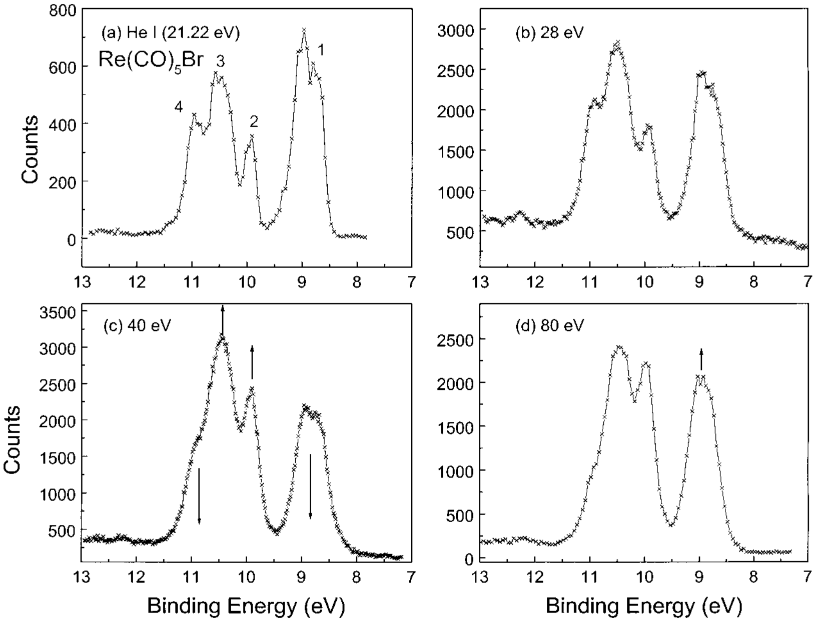

**Figure 7.** Valence level spectra of $Re(CO)_5Br$ at lower photon energy region (21.22, 28, 40, and 80 eV photon energies).

**Table 3.** Valence and Core Ionization Potentials of $Re(CO)_5X$ and HX Complexes

| | valence IP | | | | core $E_B$ | |
|---|---|---|---|---|---|---|
| molecule | band 1 | band 2 | band 3 | peak 4 | halogen | Re $4f_{7/2}$ |
| $Re(CO)_5H$[a] | 8.94 (e) | 9.25 (e) | 9.59 ($b_2$) | 10.59 ($a_1$) | | 47.45 |
| $Re(CO)_5Cl$ | 8.96[b] | 9.94 | 10.83 | 11.27 | 204.27 ($2p_{3/2}$) | 48.31 |
| $Re(CO)_5Br$ | 8.86[b] | 9.95 | 10.46[c] | 10.94 | 74.37 ($3d_{5/2}$) | 48.29 |
| $Re(CO)_5I$ | 8.51[b] | 9.70 | 10.05 | 10.50 | 55.20 ($4d_{5/2}$) | 48.04 |
| HCl | 12.78[d] | | | | 207.39 ($2p_{3/2}$)[e] | |
| HBr | 11.82[d] | | | | 77.34 ($3d_{5/2}$)[f] | |
| HI | 10.64[d] | | | | 57.49 ($4d_{5/2}$)[g] | |

[a] The IP values and band assignments of $Re(CO)_5H$ are from ref 9. [b] Average IP of spin−orbit peaks 1 and 1′. [c] Average IP of spin−orbit peaks 3 and 3′. [d] reference 11. [e] reference 43. [f] reference 44. [g] reference 28.

from the previous study by Hall, who assigned peak 1 to have 60% Re 5d character for $Re(CO)_5Br$ on the basis of a spin−orbit analysis.[9] Our results on $Re(CO)_5Br$ clearly demonstrate the advantage of the tunability of SR in the electronic structure study of large organometallic molecules. It is clear that the crossover of the HOMO in the Re complexes from having a majority Re 5d character to having a majority halogen character occurs at Br, rather than at I, in agreement with the result of Higgison et al.,[7] but contrary to that of Hall.[9]

**3.3. Valence Level/Core Level Shifts.** In the early 1980s, Jolly and co-workers developed an approach to studying the bonding character of MOs, using the chemical shift information of both core and valence levels of related compounds.[41] The basic principle of Jolly's approach is that the appropriately chosen core BEs can be used to subtract the contributions due to electrostatic potential (atomic charges) and relaxation energy from valence ionization potentials. It is then possible to quantify the bonding or antibonding character of molecular orbitals by using only experimental data. Jolly has successfully applied this approach to the $Mn(CO)_5X$ system to confirm the assignment of Higginson et al. for the Mn compounds.[11] Recently, the Os 4f core chemical shift between $Os(CO)_5$ and $Os(CO)_4PMe_3$ was compared with the valence level chemical shift using Jolly's approach.[34] The bonding property of the $PMe_3$ ligand has been discussed.

Using the Re and halogen core and valence level BEs of these three Re compounds (Table 3), the localized orbital ionization potentials (LOIP) of three rhenium pentacarbonyl halides can be calculated using $Re(CO)_5H$ as the reference compound, on the basis of the equation[42]

$$\mathrm{LOIP} = \mathrm{IP(ref)} + 0.8[E_B - E_B(\mathrm{ref})] \tag{1}$$

where IP is the vertical ionization potential of the valence orbitals of the reference compound and $E_B$ is the BE of the core levels. The LOIP values of the halogen e orbitals are calculated for the halogen valence mp orbitals of the Re halides, using data of the strictly nonbonding halogen p$\pi$ orbitals of the corresponding HX compounds.[43,44] The $b_2$ nonbonding $\sigma$ orbital and e $\pi$ orbital of $Re(CO)_5H$[9] are chosen to calculate the LOIP values for the Re 5d orbitals of three Re halides. The calculated LOIP values are listed in Table 4. It is immediately clear that the e(X) value decreases dramatically on going from Cl to I, while the LOIP values for both Re $\sigma$ and $\pi$ orbitals increase on going from $Re(CO)_5Cl$ to $Re(CO)_5I$. The e(Cl)/e(I)

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**Table 4.** Calculated LOIP Values for $Re(CO)_5X$ (X = Halogen) Complexes, eV

| | orbital | | |
|---|---|---|---|
| molecule | e(X)[a] | $b_2$(Re)[b] | e(Re)[b] |
| $Re(CO)_5Cl$ | 10.28 | 10.28 | 9.79 |
| $Re(CO)_5Br$ | 9.44 | 10.26 | 9.77 |
| $Re(CO)_5I$ | 8.81 | 10.06 | 9.58 |

[a] Calculated by using the hydrogen halides as reference molecules (Table 3). [b] Calculated by using $Re(CO)_5H$ as the reference molecule.

LOIP value is much higher/lower than the e(Re) LOIP value for $Re(CO)_5Cl$/$Re(CO)_5I$, thus indicating that the e(Re)/e(I) orbital is the HOMO for $Re(CO)_5Cl$/$Re(CO)_5I$, in agreement with our variable-energy results. The calculated LOIP values of both e(Br) and e(Re) orbitals for $Re(CO)_5Br$ are very similar, with the e(Br) orbital energy having a slightly smaller value (9.44 eV versus 9.77 eV). This once again is in agreement with our experimental result.

**3.4. The np → nd Resonant Effect in $M_2(CO)_{10}$ (M = Re, Mn) and $Mn(CO)_5Br$.** Green and co-workers have observed the np → nd resonance in the gas phase photoelectron studies of some organometallic complexes using SR.[12] The mechanism of this phenomenon has been reviewed recently by Green.[12] For rhenium compounds, the intensity of the bands originating from the Re 5d valence orbitals should be enhanced when the incident photon energy is at, or near, the ionization threshold of the Re 5p core orbitals, due to the so-called super Coster–Kronig (SCK) transition.[45] We have shown that the observation of this resonance is very valuable in assigning the metal d valence orbitals in $Os(CO)_4PMe_3$ and $CpM(CO)_3$ (M = Mn, Re) complexes.[18,27] The knowledge of BEs of metal np core levels is also important in order to observe the np → nd resonance. The BEs of Re $5p_{3/2}$ and $5p_{1/2}$ electrons are found to be close to 49 and 58 eV for these Re complexes (Table 1). These BEs are almost 15 eV higher than the Re metal 5p BEs obtained by earlier XPS,[46] but consistent with the values for W and Os in the metal carbonyls.[16,18]

The variable-energy spectra of $Re_2(CO)_{10}$ at 45, 50, and 55 eV photon energies shown in Figure 8 display a distinct maximum at 50 eV photon energy for the first five peaks (peaks 1–5). The first five peaks are all expected to show a Re 5p → 5d resonance, since they are all derived from the Re 5d based orbitals. It is worth noting that peak 5 shows the most intense resonance because it originates from two $b_2$ nonbonding Re 5d orbitals.[9] Also note that, for $Re_2(CO)_{10}$, all Re 5d peaks almost double in relative intensities on going from off-resonance (45 eV) to on-resonance (50 eV).

In the previous studies of np → nd resonances in $W(CO)_6$, the intensity of the W $t_{2g}$ 5d peak also doubled at the W $5p_{3/2}$ level.[12] Theoretical calculations showed that, in $W(CO)_6$, the $t_{2g}$ orbitals (which correlate with e and $b_2$ orbitals for $M(CO)_5X$ molecules under $C_{4v}$ symmetry) have ~60% 5d character;[47] and Fenske's initial calculations[3] and a recent density functional calculation[48] on $Mn(CO)_5X$ also indicated about 60% Mn 3d character in the split e and $b_2$ orbitals.

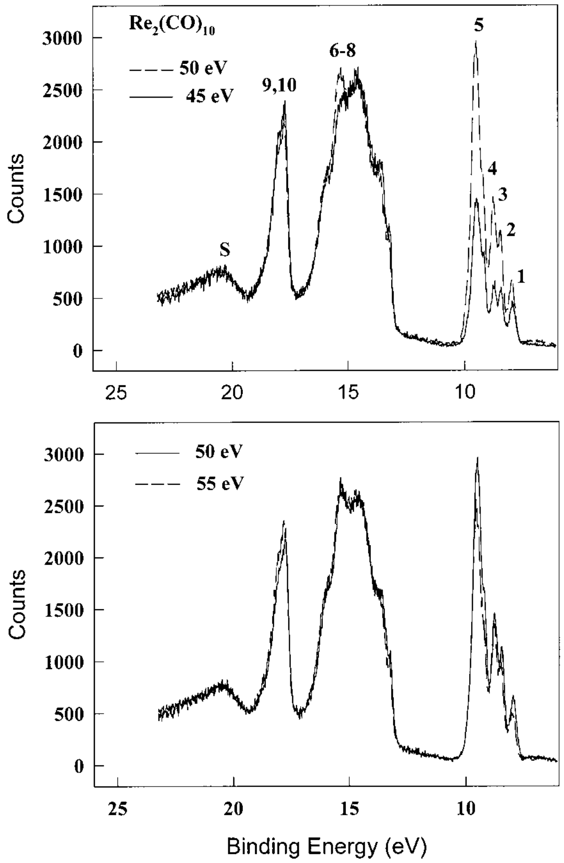

**Figure 8.** Valence level photoelectron spectra of $Re_2(CO)_{10}$ at 45, 50, and 55 eV photon energies. All the spectra are normalized with intensities of peaks 9 and 10.

The Re 5d based orbitals of $Re(CO)_5I$ 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 excited by second-order radiation made it difficult to record the high-quality valence level spectra between 42 and 53 eV photon energies. Nevertheless, there is little doubt from the spin–orbit splitting analysis that the assignment must be the same as given previously,[7] i.e., $a_1$(Re–I) > e(Re) > $b_2$(Re) > e(I).

Figure 9 presents the valence level photoelectron spectra of $Mn(CO)_5Br$ with the photon energy centered around the Mn 3p BE of 56.2 eV. It is clear that the relative intensities of peaks 1 and 2 increase over the relative intensities of peaks 3 and 4 from 53 to 57 eV photon energy. This increase of the relative intensity corresponds to a Mn 3p → 3d resonance, indicating a higher Mn 3d character in peaks 1 and 2. This confirms the previous assignment for $Mn(CO)_5Br$ given by Higginson et al.,[7] i.e., $a_1$(Mn–Br) > e(Br) > $b_2$(Mn) > e(Mn).

Similar Mn 3p → 3d resonance can be also observed for the other Mn molecules. The valence level photoelectron spectra of $Mn_2(CO)_{10}$ at 56 and 58 eV photon energies (not shown, available as Supporting Information) clearly indicate the enhancements of the relative intensities for the peaks with BEs below 11 eV, thus a higher Mn 3d character in these peaks, when compared with the peaks at the higher BE side. The fact that the np → nd resonances can be used to aid the assignment of metal nd character dominated peaks is in direct contrast to the following interatomic resonances observed for the *very similar* $Re(CO)_5X$ (X = Cl, Br) molecules.

**3.5. The Interatomic np → nd Resonance in $Re(CO)_5X$ (X = Cl, Br).** Figure 10 presents the variable-energy valence level photoelectron spectra of $Re(CO)_5Br$ at 46, 48, 50, and 52 eV photon energies. It is immediately obvious that the relative intensities of *all* of bands 1, 2, 3, and 4 display an intense

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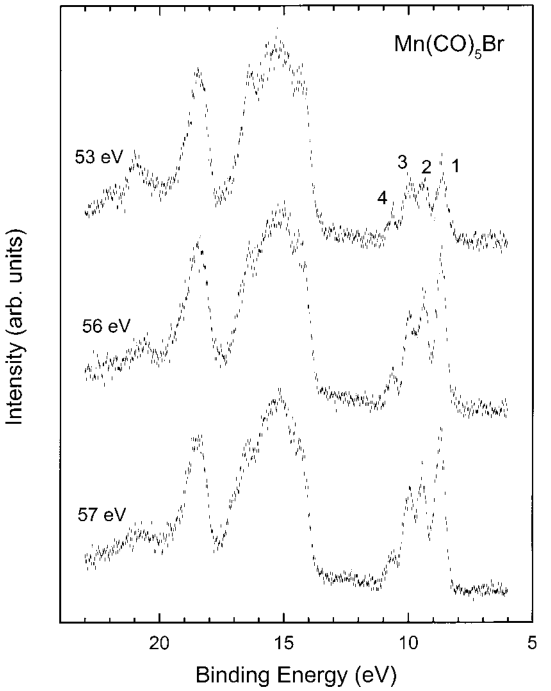

**Figure 9.** Valence level photoelectron spectra of $Mn(CO)_5Br$ between 53 and 57 eV photon energies.

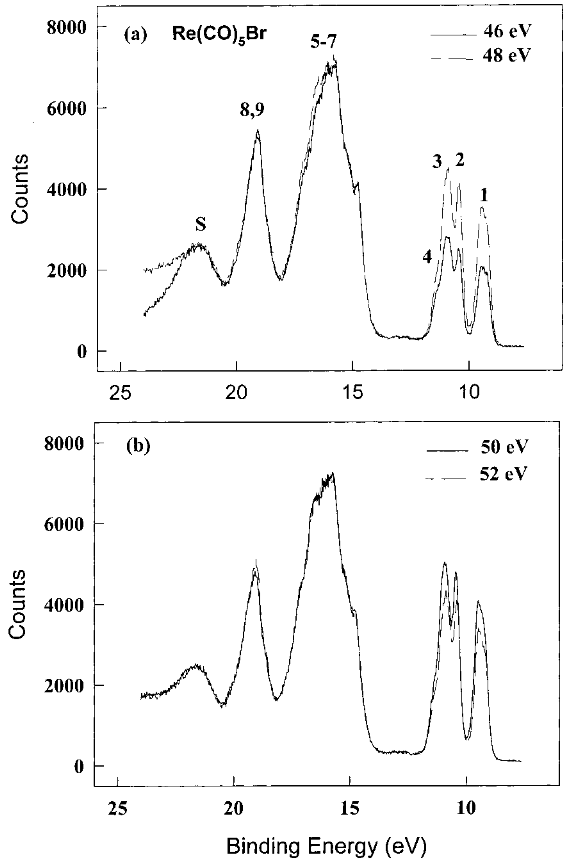

**Figure 10.** Valence level photoelectron spectra of $Re(CO)_5Br$ at 46, 48, 50, and 52 eV photon energies, showing the maximum relative intensities of peaks 1−3 around 50 eV photon energy. All the spectra are normalized with intensities of peaks 8 and 9.

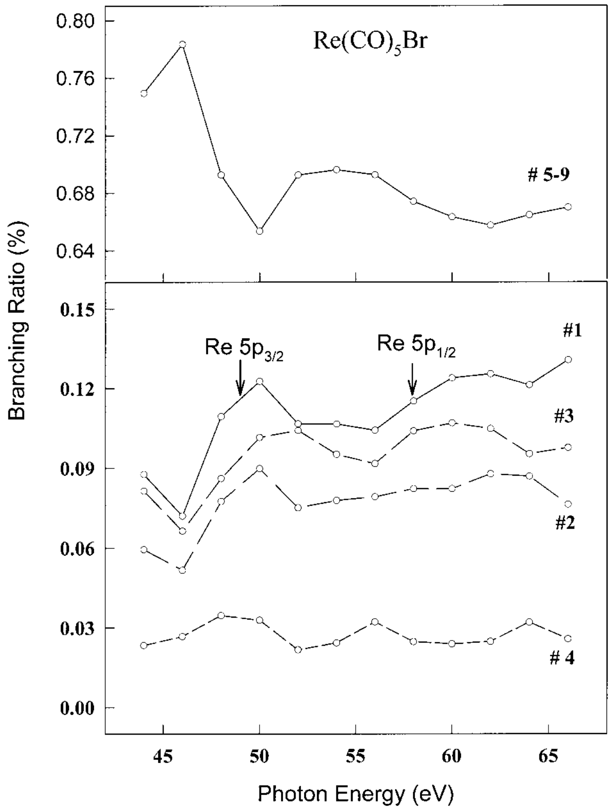

**Figure 11.** Branching ratios of the valence level peaks of $Re(CO)_5Br$ between 40 and 68 eV photon energies. The positions of Re $5p_{3/2}$ and $5p_{1/2}$ are also indicated.

maximum (∼80% increase in relative intensity, Figure 11) between 48 and 50 eV photon energy, in comparison to the intensities of the other peaks. This maximum occurs at a photon energy corresponding to the Re $5p_{3/2}$ BE of $Re(CO)_5Br$. The observation of this 5p → 5d resonance would suggest that orbitals associated with bands 1, 2, 3, and 4 all have higher Re 5d character, in comparison to peaks 5−9, since it is well-known that peaks 5−9 are due to contributions from the CO group. However, our low photon energy results presented in sections 3.2 and 3.3 firmly assign band 1 to the ionizations from an e(Br) orbital with a major Br 4p character and band 3 to the ionizations from an e(Re) orbital with a major Re 5d character. On the basis of this assignment, one would expect band 3 at least to show a more pronounced Re 5p → 5d resonance than band 1, yet both bands 1 and 3 show an almost equally intense resonant effect. Of course, there should be some mixing character in these orbitals due to the second-order effect; that is, under the $C_{4v}$* double group symmetry of the ionic state of $Re(CO)_5X$, the $b_2$ orbital has the right symmetry (E″) to interact with the halogen mp orbitals and the other e(Re) orbitals.[38]

Our observation of the pronounced np → nd resonance on the orbitals with a majority ligand character is very surprising. Cooper et al. have previously reported a similar observation in $Ru(\eta\text{-}C_5H_5)_2$.[14] They observed the np → nd resonances in the ligand-based orbitals which were symmetry forbidden to have any d content, and it was interpreted as due to the interchannel coupling effect.[12,14] Traditionally, np → nd resonance has been treated as a localized, atomic process.[49] Very recently, Fadley and co-workers observed a strong Mn 2p to O 1s resonance, in addition to the normal Mn 2p → 3d resonance, for several manganese oxides, such as MnO.[19] They termed this effect the interatomic multi-atom resonant photoemission effect. Similarly, we propose the following interatomic resonant processes to explain our observation for $Re(CO)_5X$ (X = Cl, Br) molecules.

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$$5p^65d^6 \xrightarrow[-5p_{3/2}]{h\nu} 5p^55d^{6+1} \xrightarrow[\text{decay}]{\text{SCK}} 5p^65d^6 + e^- \qquad (2)$$

Equation 2 describes the normal Re 5p → 5d resonant process, where a Re 5p electron is excited into an unfilled 5d orbital and decayed via a SCK transition, accompanied by the excitation of a Re 5d electron, leading to the final state identical to the direct ionization of a Re 5d valence electron, hence the enhancement in the cross section of the Re 5d based orbital.

In the interatomic resonant process,

$$5p^65d^6mp^6(X) \xrightarrow[-5p_{3/2}]{h\nu} 5p^55d^{6+1}mp^6(X) \xrightarrow{\text{IAA}} 5p^65d^6mp^5(X) + e^- \qquad (3)$$

where IAA represents an interatomic Auger process, in which a halogen mp valence electron is ionized at the Re $5p_{3/2}$ threshold. The enhancement in the relative intensities of the Br 4p based orbitals observed in $Re(CO)_5Br$ is due to this interatomic Auger process.

This interatomic resonant effect can also be observed in the variable-energy photoelectron spectra of $Re(CO)_5Cl$ when the photon energy is tuned around the BE of Re 5p ionization. Branching ratios of peaks 1−9 of $Re(CO)_5Cl$ between 40 and 68 eV photon energies are shown in Figure 12. From Figures 11 and 12, it is obvious that bands 1−4 for both molecules *all* display intense resonances at energies corresponding to the BEs of Re 5p spin−orbit split orbitals. The fact that the resonance around 50 eV photon energy is much more pronounced than the one at the higher photon energy can be accounted for by the 2:1 ratio between the spin−orbit components $P_{3/2}$ and $P_{1/2}$.

Obviously, the observation of the interatomic np → nd resonance for these two molecules does not allow us to distinguish the character of these four peaks for $Re(CO)_5X$ (X = Cl, Br). One lesson to learn from this study is that one should be cautious using the np → nd resonance to aid the assignment of the photoelectron spectra of organometallic molecules. Fortunately, with variable-energy SR, we can study not only the resonances or minima of metal nd based orbitals but also the general trend of the cross sections of metal d based orbitals. We demonstrate that the variable-energy SR is a powerful tool in the study of the electronic structure of the complicated molecules.

It is very puzzling that this new resonant effect is only observed for these two Re (Cl and Br) molecules and for the $Ru(\eta\text{-}C_5H_5)_2$ molecule,[14] but not for any other molecules (Re, Mn, W, Os based) that have been studied to date,[12] especially not for molecules in the very similar $Mn(CO)_5X$ system which are also presented in this study. More experimental work and more theoretical calculations are much needed to fully explain this new effect.

## Conclusions

High-resolution photoelectron spectra of $M(CO)_5X$ [M = Re, X = $Re(CO)_5$, Cl, Br, and I; M = Mn, X = $Mn(CO)_5$ and Br] have been reported. Variable-energy SR is demonstrated to be valuable in assigning the MOs for these molecules, especially for the controversial $Re(CO)_5Br$ case. It is concluded that the valence orbital ionization energy ordering for $M(CO)_5Cl$ (M = Mn and Re) and $Mn(CO)_5Br$ is $a_1(M-X) > e(X) > b_2(M) > e(M)$; but for $M(CO)_5I$ (M = Mn and Re) and $Re(CO)_5Br$ the ordering is $a_1(M-X) > e(M) > b_2(M) > e(X)$. Hence, the crossover of the HOMO in these halide molecules, due to the change in the halogen electronegativities, occurs at $Re(CO)_5Br$.

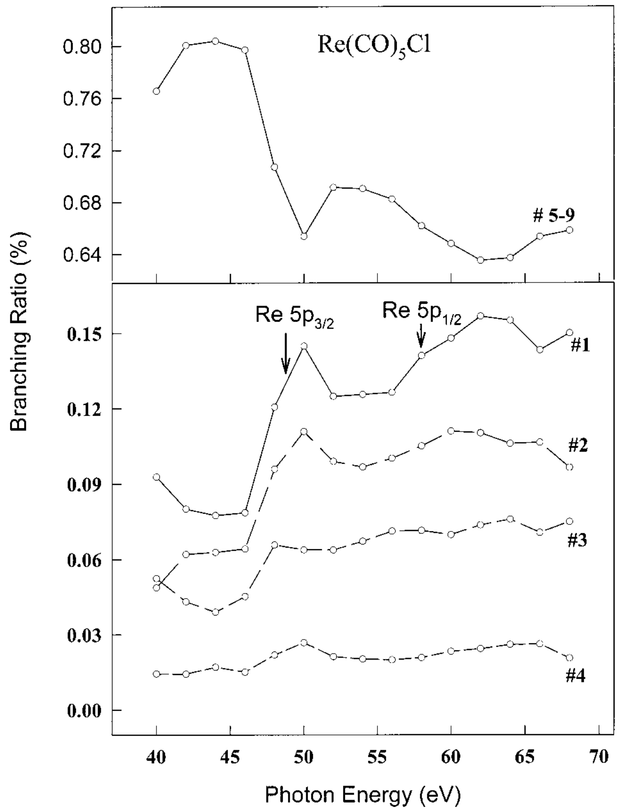

**Figure 12.** Branching ratios of the valence level peaks of $Re(CO)_5Cl$ between 40 and 68 eV photon energies. The positions of Re $5p_{3/2}$ and $5p_{1/2}$ are also indicated.

The np → nd resonance due to the metal np ionization has been observed in the peaks arising from the valence nd orbitals in all these molecules. This np → nd resonance is shown to be useful in assigning the metal nd based peaks for most of these molecules. However, an equally intense np → nd resonance is also observed on the peaks due to the ionizations of the halogen mp orbitals in $Re(CO)_5X$ (X = Cl and Br) molecules. An interatomic resonant effect is proposed to explain this new phenomenon.

The inner valence levels of these molecules are 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 in these 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.

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**Supporting Information Available:** Figures showing the valence level photoelectron spectra of $Mn_2(CO)_{10}$ at 56 and 58 eV photon energies and the spectra of $Re(CO)_5Cl$ at 46, 48, 50, and 52 eV photon energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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