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The Use of Spin–Orbit Coupling in the Interpretation of Photoelectron Spectra. I. Application to Substituted Rhenium Pentacarbonyls

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Abstract: The uv photoelectron spectra of the substituted rhenium pentacarbonyls, $LRe(CO)_5$ (L = H, CH_3, $COCF_3$, $Re(CO)_5$, Cl, Br, and I), have been measured. We have developed the spin-orbit coupling matrices appropriate for this symmetry and have used these to analyze the spectra. The results provide a definitive assignment for the spectra of $HRe(CO)_5$, $CH_3Re(CO)_5$, $COCF_3Re(CO)_5$, and the analogous manganese complexes. The analysis of the spin-orbit coupling in the rhenium halides, where both the rhenium and halogen spin-orbit coupling were taken into account, shows that, contrary to expectations, the first band of $ClRe(CO)_5$ is mainly rhenium in character, while the corresponding band of $IRe(CO)_5$ is mainly iodide in character. Our success with these systems suggests that our type of analysis for the spin-orbit coupling may be a valuable tool in the assignment and interpretation of the photoelectron spectra of other transition metal systems.

Photoelectron spectroscopy (PES) has proven to be a valuable tool in the elucidation of the electronic structure of molecules.[1] One of the first applications of this technique to transition metal complexes was to a series of $Mn(CO)_5X$ compounds.[2] While many of the conclusions of this work were supported by approximate molecular orbital calculations,[3,4] the calculations did suggest that some important features of the spectra were not observed in this early work. Subsequent investigations of the spectra under higher resolution revealed many of these features.[5-7] Recently, ab initio calculations have been made on several of these complexes.[8] These calculations agree with the earlier approximate calculations in predicting additional bands in the upper valence region of the spectra. However, they provided a different assignment for the hydride and methyl spectra. Recent theoretical work on other transition metal systems suggests that Koopmans' theorem,[9] which was used to assign the spectra from the ab initio calculations, may not reproduce the correct order for the ionization potentials (IP).[10] Thus, there remains considerable doubt as to the correct assignments.

A study of the $Re(CO)_5X$ analogs was undertaken in order to resolve some of the ambiguities surrounding the assignments in these systems. A correct assignment for these systems is important since, as the simplest of the substituted carbonyl complexes, their interpretation will form the basis for the interpretation of the PES of more complex systems. The spin-orbit coupling of the rhenium should facilitate the identification of those bands which are mainly metal in character. A complete analysis of the effects of spin-orbit coupling will provide additional information about the delocalization of the metal electrons and the degree of mixing between metal orbitals and ligand orbitals. Although some work has been done on the analysis of spin-orbit coupling in PES,[11] the theory has not been extended to transition metal systems. We should also be able to observe some general trends in the spectra due to the change from manganese to rhenium, which could aid our interpretation of these molecules. Evidence that the spectra of manganese and rhenium should parallel each other comes from work on $Cr(CO)_6$, $W(CO)_6$[1] and $Cr(CO)_5NH_3$, $W(CO)_5NH_3$.[12] In addition to the assignment of the spectra, the study of the spin-orbit coupling in these complexes should provide some insight into the bonding and electronic structure of both the manganese and rhenium pentacarbonyls.

Experimental Section

A sample of $HRe(CO)_5$ was kindly supplied by Professor D. F. Gaines of this Department and was distilled under vacuum before use. $Re_2(CO)_{10}$ and $Re(CO)_5Cl$ were purchased from Pressure Chemical Co., Pittsburgh, Pa. 15201 and were sublimed under vacuum. Other samples were prepared by forming the $NaM(CO)_5$ salt in tetrahydrofuran (THF) from the reaction of $M_2(CO)_{10}$ with Na-Hg amalgam. This salt was then allowed to react with H_3PO_4, ICH_3, $(CF_3)_2CO$, and I_2 to form $HMn(CO)_5$, $CH_3Re(CO)_5$, $CF_3CORe(CO)_5$, and $IRe(CO)_5$, respectively. The bromide, $BrRe(CO)_5$, was prepared by direct reaction of Br_2 and $Re_2(CO)_{10}$ in THF. These preparations are analogous to the standard methods of preparation for the manganese compounds.[13] The samples were all sublimed or distilled under vacuum and their purity was checked by mass or infrared spectroscopy:

The PES spectra were measured using a Varian IEE-15 electron spectrometer in the uv configuration. The argon line at 15.76 eV was used as a single internal standard. The resolution of the instrument (FW Hm) was 22–23 mV for the argon $^2P_{3/2}$ state. The spectra, taken from multiple 1000-channel, 10-eV scans, were then fit by asymmetric Gaussian peaks to obtain the peak positions and integrated intensities. This fitting procedure[6] yields more accurate positions and intensities then can be obtained from considering only the band maxima, especially for strongly overlapping bands.

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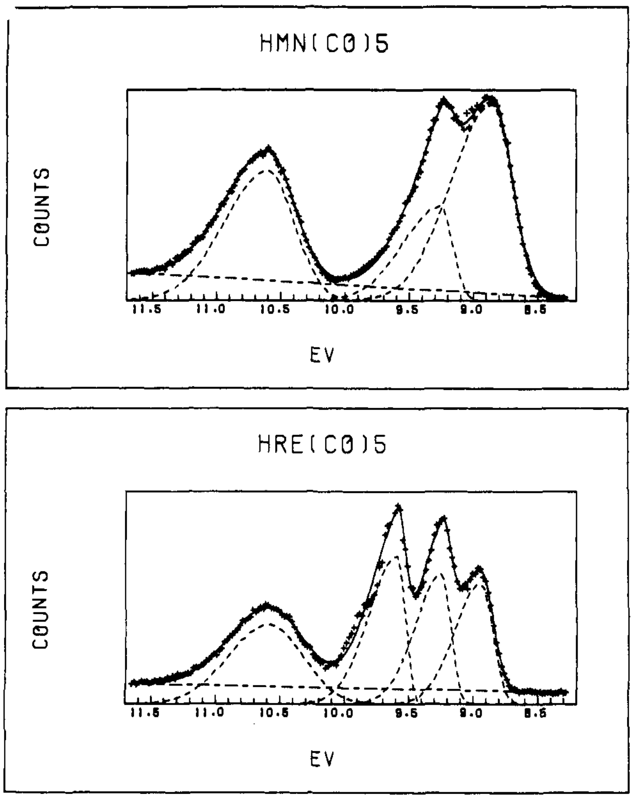

Figure 1. Photoelectron spectra of $HMn(CO)_5$ and $HRe(CO)_5$.

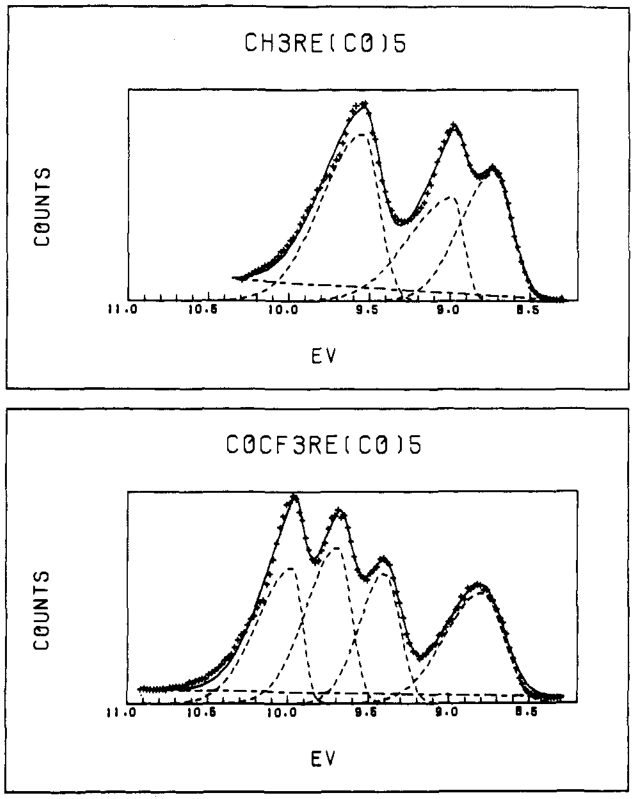

Figure 2. Photoelectron spectra of $CH_3Re(CO)_5$ and $COCF_3Re(CO)_5$.

Results

Experimental. $HMn(CO)_5$, $HRe(CO)_5$. The spectra are shown in Figure 1. The plus signs show the actual counts collected while the solid line is the sum of the individual simulated peaks. The spectrum of $HMn(CO)_5$ consists of three peaks. The first two (8.85, 9.25 eV) are split by 0.40 eV and show an intensity ratio of approximately 2 to 1. The third peak at 10.60 eV is somewhat broader and more symmetric than the other two. The spectrum of $HRe(CO)_5$ shows four ionizations; the first three (8.94, 9.25, 9.59 eV) are very similar in shape and intensity and have larger IP's than the first two ionizations of the manganese. The fourth band (10.59 eV) has an IP similar to the third band of the manganese and it is likewise broader and more symmetric than the other rhenium bands.

$CH_3Re(CO)_5$, $COCF_3Re(CO)_5$. The spectra are shown in Figure 2. The spectrum of the methyl compound consists of three distinct bands (8.72, 8.98, ~9.6 eV). The third band shows a shoulder on the left side, which we took to indicate the presence of two ionization peaks in this band. We were unable to resolve this band in a satisfactory manner and have shown only one peak in the simulated spectra. The spectrum of the perfluoroacetyl contains four bands. The first at 8.80 eV is somewhat broader than the other three (9.40, 9.69, 9.97 eV).

$Re_2(CO)_{10}$. The spectrum of the rhenium dimer shown in Figure 3 consists of five distinct bands. The first (8.06 eV) is rather broad and weak. The next three bands (8.56, 8.86, 9.28 eV) are of similar intensity. These are followed by a broad band (9.60 eV), which is approximately three times as intense as any of the previous bands.

$ClRe(CO)_5$, $BrRe(CO)_5$, $IRe(CO)_5$. The spectra of the halides are shown in Figure 4. The spectrum of the chloride consists of four distinct bands. The first band around 8.9 eV shows a definite shoulder on the right-hand side, which was taken to indicate the presence of two closely spaced peaks. The second band (9.86 eV) is considerably less intense than the first; this is followed by a third band (10.76 eV) of similar intensity to the first band. The fourth band (11.21 eV) is weaker than the first or third bands but not as weak as the second. The spectrum of the bromide is somewhat similar to that of the chloride; however, we observe a distinct splitting of the first (8.9 eV) and third (10.5 eV) bands, and a shift to lower IP for all the bands. In the iodide the splitting of the first two ionizations is large enough to produce two well-separated bands (8.32, 8.77 eV). The fourth band (10.08 eV) shows no splitting for this molecule, but is considerably more intense than the bands on either side. Again the IP's are shifted to lower energy than those of the bromide.

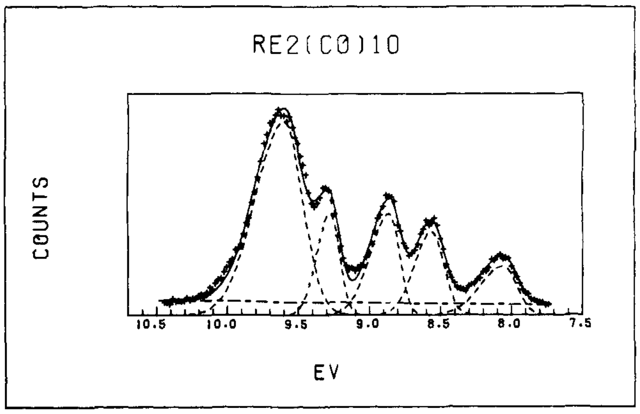

Figure 3. Photoelectron spectrum of $Re_2(CO)_{10}$.

Theoretical. The spin-orbit Hamiltonian is considered to be a sum of one-electron operators.[14]

$$H = \sum_n h_{so}(n) \tag{1}$$

where $h_{so}(n)$ is the one-electron Hamiltonian.[14]

$$h_{so} = \left(\sum_A \zeta(r_A)\hat{l}_A\right)\cdot\hat{s} \tag{2}$$

where $\zeta(r_A)$ is the spin-orbit coupling parameter for nucleus A. Recently, it has been shown that these equations can be incorporated into the Hartree-Fock-Roothaan (HFR) framework[15] in the following manner.[16,17] The results of a HFR calculation without spin-orbit coupling consist of a number of molecular orbitals (MO) expressed as linear combinations of atomic orbitals; associated with each MO is an eigenvalue which, according to Koopmans' theorem,[9] should be approximately equal to the negative of the IP. Equation 2 may then be considered to represent a perturbation on these eigenvalues and eigenvectors (MO). For ionizations from closed shell molecules, this approach[17] has been shown to be identical with and, in some ways, preferable to the development which uses determinantal wave functions for each ionic state.[11] In order to apply this approach to transition metal systems we will proceed in the following manner. The spin-orbit coupling matrices for all atoms in the molecule with appreciable spin-orbit coupling are derived in the atomic orbital basis. These matrices are then transformed to the molecular orbital basis and the molecular orbital energies, which are diagonal in this basis, are added to the diagonal terms. Diagonalization of the resulting matrix will yield spin-orbit coupled eigenvalues which correspond to the ionic states of the system. To classify these states correctly we must consider their transformation properties in the appropriate double group.[18,19]

For the molecules of interest here we must consider the double group $C_{4v}{}^*$. Under spin-orbit coupling the irreducible representations of C_{4v} become either E′ or E″ (doubly degenerate due to electron spin) in the following way.

$$\begin{array}{llllll} C_{4v}: & {}^2A_1 & {}^2A_2 & {}^2B_1 & {}^2B_2 & {}^2E \\ C_{4v}{}^*: & E' & E' & E'' & E'' & E' + E'' \end{array}$$

Thus, only the ^{2}E states are split by spin-orbit coupling. The resulting states (E′ and E″) are, however, capable of coupling with the $^2A_{1,2}(E')$ or $^2B_{1,2}(E'')$, respectively. Let us now be specific and consider the simplest LM(CO)$_5$ molecule, where L is σ bonding and only the metal, M, has appreciable spin-orbit coupling. Furthermore, let us consider only the most important perturbations (i.e., those between closely spaced molecular orbitals which are primarily metal in character). Thus, we will consider only those molecular orbitals which are derived from the octahedral t_{2g} orbitals, namely the e and b_2. The mixing of ligand functions (2π CO, etc.) into these orbitals will only serve to reduce the effective spin-orbit coupling. The HFR matrix, which before application of the spin-orbit perturbation was diagonal, now appears as

$$\begin{array}{cccc} & |xz(e)^+\rangle & |yz(e)^+\rangle & |xy(b_2)^-\rangle \\ \langle xz(e)^+| & \epsilon_e & -\frac{i}{2}\zeta & \frac{i}{2}\zeta \\ \langle yz(e)^+| & \frac{i}{2}\zeta & \epsilon_e & -\frac{1}{2}\zeta \\ \langle xy(b_2)^-| & -\frac{i}{2}\zeta & -\frac{1}{2}\zeta & \epsilon_{b_2} \end{array} \qquad (3)$$

where ζ is the effective spin-orbit coupling parameter and the + and − signs refer to the electron spin. If we make a change of basis to

$$\begin{aligned} |e'(e)^+\rangle &= \frac{1}{\sqrt{2}}(|xz(e)^+\rangle - i|yz(e)^+\rangle) \\ |e''(e)^+\rangle &= \frac{1}{\sqrt{2}}(|xz(e)^+\rangle + i|yz(e)^+\rangle) \end{aligned} \qquad (4)$$

we can remove the degeneracy of the two e orbitals and the matrix (eq 3) becomes

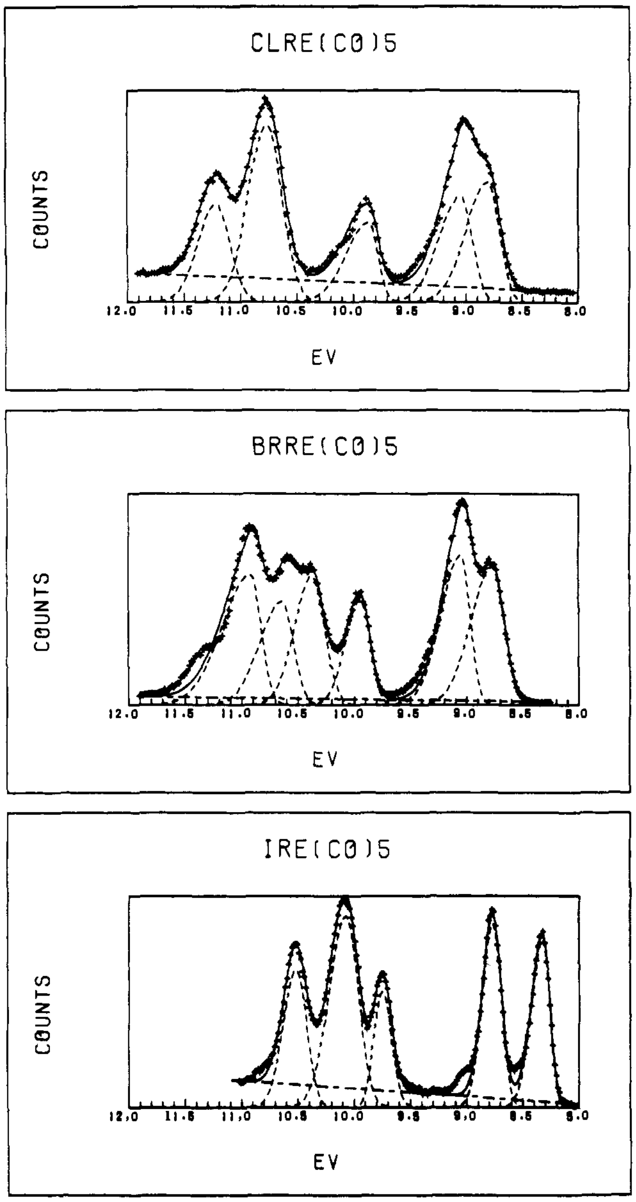

Figure 4. Photoelectron spectra of ClRe(CO)$_5$, BrRe(CO)$_5$, and IRe(CO)$_5$.

$$\begin{array}{cccc} & |e'(e)^+\rangle & |e''(e)^+\rangle & |e''(b_2)^-\rangle \\ \langle e'(e)^+| & \epsilon_e - \frac{1}{2}\zeta & 0 & 0 \\ \langle e''(e)^+| & 0 & \epsilon_e + \frac{1}{2}\zeta & \frac{i}{\sqrt{2}}\zeta \\ \langle e''(b_2)^-| & 0 & -\frac{i}{\sqrt{2}}\zeta & \epsilon_{b_2} \end{array} \qquad (5)$$

where the diagonal term of the e′(e) orbital is lower in energy (higher IP) than the e″(e) orbital. We can now solve the remaining 2 × 2 matrix in eq 5. The final results for the three eigenvalues are

$$\begin{aligned} \epsilon_0 &= \epsilon_e - \tfrac{1}{2}\zeta \\ \epsilon_\pm &= \tfrac{1}{2}(\epsilon_e + \tfrac{1}{2}\zeta + \epsilon_{b_2}) \pm \\ &\qquad \tfrac{1}{2}\sqrt{(\epsilon_e + \tfrac{1}{2}\zeta - \epsilon_{b_2})^2 + 2\zeta^2} \end{aligned} \qquad (6)$$

Let us consider three possible cases for the order of the e and b_2 levels $\epsilon_{b_2} > \epsilon_e$, $\epsilon_{b_2} = \epsilon_e$, and $\epsilon_{b_2} < \epsilon_e$. The results for these three cases are shown (to scale) in Figure 5 where we have taken $\zeta = 0.3$ eV, a reasonable value for third row transition metals.[14] Figure 5 should be viewed as an MO di-

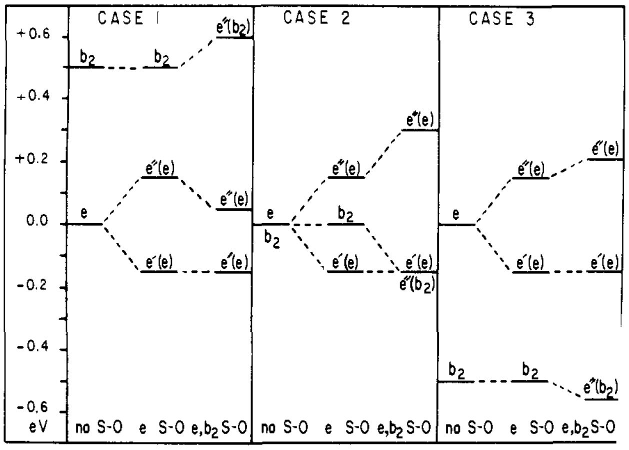

Figure 5. Molecular orbital diagram for three possible cases of spin-orbit coupling in LM(CO)$_5$ systems, where L is σ bonding only.

agram; hence, the first IP will correspond to the highest level. We have drawn the figure in two steps, first showing the splitting of the degenerate e's, then the interaction of the b_2 with the e″(e). For $\epsilon_{b_2} > \epsilon_e$ the interaction of the b_2 serves to increase the e″(b_2)-e″(e) splitting while decreasing the e′(e)-e″(e) splitting. For $\epsilon_{b_2} = \epsilon_e$, we find that interaction of the b_2 and e″(e) causes the e″(b_2) to become degenerate with the e′(e). Thus, for this case there would be only two bands in the spectra with an intensity ratio of 1 to 2. The first would be due to the e″(e) while the second would be due to both the e′(e) and e″(b_2). The splitting between these bands would be $\frac{3}{2}\zeta$. In the third case, we find that the e″(e) and b_2 interaction causes both the e′(e)-e″(b_2) and the e″(e)-e′(e) splitting to increase. Although we have labeled the e″ states as e″(e) and e″(b_2), to indicate their major components, we must remember that they are mixtures of what were e and b_2 before spin-orbit coupling.

From Figure 5 we can see that there are only two possible assignments for ϵ_0; it must either be the lowest level (case 1) or the middle level (case 3). Since ϵ_+ must be greater than ϵ_-, there are only two possible assignments, $\epsilon_- \leq \epsilon_0 < \epsilon_+$ (assignment I) or $\epsilon_0 \leq \epsilon_- < \epsilon_+$ (assignment II). Our case 2 is a special case of either assignment. Equations 6 can be solved to yield ζ and Δ, the difference ($\epsilon_e - \epsilon_{b_2}$). The results are

$$\begin{aligned}\zeta &= -\tfrac{1}{3}(2\epsilon_0 - \epsilon_+ - \epsilon_-) \pm \tfrac{1}{2}\sqrt{\tfrac{2}{3}(\epsilon_+ - \epsilon_-)^2 - \tfrac{2}{9}(2\epsilon_0 - \epsilon_+ - \epsilon_-)^2}\\ \Delta &= \epsilon_e - \epsilon_{b_2} = 2\epsilon_0 - \epsilon_+ - \epsilon_- + \tfrac{3}{2}\zeta\end{aligned} \tag{7}$$

In order for eq 7 to yield real ζ and Δ values $3(\epsilon_+ - \epsilon_-)^2 \geq (\epsilon_0 - \epsilon_- + \epsilon_0 - \epsilon_+)^2$. Thus, both assignments I and II could be valid when the splitting between the first two levels is greater than the splitting between the second two levels, while only assignment I will be valid if the second splitting is larger than the first.

Now let us consider a more complex XMn(CO)$_5$ example, where the X group has filled π orbitals in close proximity to the metal e(π) levels and has its own spin-orbit coupling operator. We will assume the molecular spin orbitals have the following form

$$\begin{aligned}\phi_1 &= |2exz^+\rangle = C_{2eM}|xz^+\rangle + C_{2eX}|x^+\rangle\\ \phi_2 &= |2eyz^+\rangle = C_{2eM}|yz^+\rangle + C_{2eX}|y^+\rangle\\ \phi_3 &= |b_2xy^-\rangle = |xy^-\rangle\\ \phi_4 &= |1exz^+\rangle = C_{1eM}|xz^+\rangle + C_{1eX}|x^+\rangle\\ \phi_5 &= |1eyz^+\rangle = C_{1eM}|yz^+\rangle + C_{1eX}|y^+\rangle\\ \phi_6 &= |a_1z^{2-}\rangle = C_{a_1M}|z^{2-}\rangle + C_{a_1X}|z^-\rangle\end{aligned} \tag{8}$$

where $|xz\rangle$ and $|x\rangle$ represent the d and p function on the metal (M) and ligand (X), respectively, and C_{2eM}, for example, is the coefficient of the metal (M) in the 2e molecular orbital. The spin-orbit coupling matrix in this basis is

$$\begin{array}{ccccccc} & \phi_1 & \phi_2 & \phi_3 & \phi_4 & \phi_5 & \phi_6\\ \phi_1 & \epsilon_{2e} & -ia & ib & 0 & -ic & d\\ \phi_2 & ia & \epsilon_{2e} & -b & ic & 0 & -id\\ \phi_3 & -ib & -b & \epsilon_{b_2} & -ie & -e & 0\\ \phi_4 & 0 & -ic & ie & \epsilon_{1e} & -if & g\\ \phi_5 & ic & 0 & -e & if & \epsilon_{1e} & -ig\\ \phi_6 & d & id & 0 & g & ig & \epsilon_{a_1}\end{array} \tag{9}$$

The letters in the off-diagonal terms represent the following molecular spin-orbit coupling parameters ($i = \sqrt{-1}$)

$$\begin{aligned}a &= \tfrac{1}{2}(C_{2eM}{}^2\zeta_M + C_{2eX}{}^2\zeta_X)\\ b &= \tfrac{1}{2}C_{2eM}\zeta_M\\ c &= \tfrac{1}{2}(C_{2eM}C_{1eM}\zeta_M + C_{2eX}C_{1eX}\zeta_X)\\ d &= \tfrac{1}{2}(\sqrt{3}C_{2eM}C_{a_1M}\zeta_M + C_{2eX}C_{a_1X}\zeta_X)\\ e &= \tfrac{1}{2}C_{1eM}\zeta_M\\ f &= \tfrac{1}{2}(C_{1eM}{}^2\zeta_M + C_{1eX}{}^2\zeta_X)\\ g &= \tfrac{1}{2}(\sqrt{3}C_{1eM}C_{a_1M}\zeta_M + C_{1eX}C_{a_1X}\zeta_X)\end{aligned} \tag{10}$$

where ζ_M and ζ_X are the spin-orbit coupling parameters for the M(CO)$_5$ and X fragments, respectively. If we neglect the overlap between the metal and ligand, we may use the normalization and orthogonality of the molecular orbitals to reduce the number of parameters in eq 10. Thus

$$\begin{aligned}a &= \tfrac{1}{2}(C^2\zeta_M + (1 - C^2)\zeta_X)\\ b &= -\tfrac{1}{2}C\zeta_M\\ c &= \tfrac{1}{2}C(1 - C^2)^{1/2}(\zeta_X - \zeta_M)\\ d &= \tfrac{1}{2}(-\sqrt{3}CK\zeta_M - (1 - C^2)^{1/2}(1 - K^2)^{1/2}\zeta_X)\\ e &= \tfrac{1}{2}(1 - C^2)^{1/2}\zeta_M\\ f &= \tfrac{1}{2}((1 - C^2)\zeta_M + C^2\zeta_X)\\ g &= \tfrac{1}{2}(\sqrt{3}(1 - C^2)^{1/2}K\zeta_M - C(1 - K^2)^{1/2}\zeta_X)\end{aligned} \tag{11}$$

where C is the coefficient of the metal function in the 2e molecular orbital (negative because the 2e is antibonding) and K is the coefficient of the metal in the a_1 molecular orbital.

In order to simplify this problem further, we will now consider only the two pairs of e levels formed from the bonding (1e) and antibonding (2e) combinations of the π functions on M and X. This is a reasonable simplification if the b_2 and a_1 levels are well removed from the e levels. If we find that this is not the case, we may have to consider the additional perturbations due to their presence. We will examine three different situations depending on whether the atomic HFR matrix element of X is less than that of M, equal to that of M, or greater than that of M. The results are shown in Figure 6, where we have also neglected the perturbation between the different e bands since this is the same order of magnitude as the b_2 and a_1 perturbations. In case 1 the first two IP's would correspond to a mainly metal level and would be split by approximately ζ_M while the next two IP's would correspond to a mainly X level and would be split by $\sim\zeta_X$. For case 2 where the metal (M) and ligand (X) mix strongly the first two IP's would come from the an-

Table I. Ionization Potentials, Relative Intensities, and Band Assignments

Molecule	Ionization potential, eV	Relative intensity	Assignment
$HMn(CO)_5$	8.85	2.5	e
	9.25	1.0	b_2
	10.60	1.9	a_1
$HRe(CO)_5$	8.94	1.0	$e''(e)$
	9.25	1.0	$e'(e)$
	9.59	1.2	$e''(b_2)$
	10.59	1.3	$e'(a_1)$
$CH_3Re(CO)_5$	8.72	1.0	$e''(e)$
	8.98	0.9	$e'(e)$
	9.53	1.4	$e''(b_2)$, $e'(a_1)$
$COCF_3Re(CO)_5$	8.80	1.0	$e'(a_1)$
	9.40	0.8	$e''(e)$
	9.69	1.1	$e'(e)$
	9.97	0.9	$e''(b_2)$
$Re_2(CO)_{10}$	8.06	0.6	$e'(a_1)$
	8.56	0.8	$e''(e_3)$
	8.86	1.0	$e'(e_3)$
	9.28	0.8	$e''(e_1)$
	9.60	3.1	$e'(e_1)$, $e''(e_2)$, $e'(e_2)$
$ClRe(CO)_5$	8.80	1.3	$e''(e)$
	9.04	1.1	$e'(e)$
	9.86	0.8	$e''(b_2)$
	10.76	1.9	$e''(e)$, $e'(e)$
	11.21	1.0	$e'(a_1)$
$BrRe(CO)_5$	8.80	0.9	$e''(e)$
	9.04	0.9	$e'(e)$
	9.94	0.5	$e''(b_2)$
	10.37	0.8	$e''(e)$
	10.64	0.7	$e'(e)$
	10.91	1.0	$e'(a_1)$
$IRe(CO)_5$	8.32	1.0	$e''(e)$
	8.77	1.1	$e'(e)$
	9.75	0.6	$e''(e,b_2)$
	10.08	1.7	$e'(e)$, $e''(b_2,e)$
	10.52	1.0	$e'(a_1)$

tibonding e band and would be split by $\frac{1}{2}(\zeta_M + \zeta_X)$ while the second two IP's would come from the bonding combination and would have the same splitting. The third case is simply the inverse of the first. The first two IP's would correlate with the X levels split by ζ_X while the second two IP's would correlate with the metal levels split by ζ_M. We will find the foregoing analysis invaluable to the interpretation of the spectra.

Discussion

If we begin by considering a d^6 carbonyl such as $Cr(CO)_6$, the metal orbitals will form the degenerate $t_{2g}{}^6$ molecular orbitals and only one ionization will be observed in the upper valence region.[20] However, if spin-orbit coupling is present, this $t_{2g}{}^6$ band will split into a doubly degenerate band followed by a quadruply degenerate one at higher IP.[20] This observation is identical to our theoretical result for case 2 in $LM(CO)_5$ systems.

When one of the carbonyls is removed from the octahedral system, simple qualitative arguments would suggest that the t_{2g} will split into an e and b_2 with the e being higher in energy (lower IP).[3] Competing with the simple loss of a carbonyl group are two effects which will tend to produce a reversal of the e and b_2. First, the loss of the carbonyl contribution to the e molecular orbital causes its metal character to increase and its diagonal term in the HFR matrix to drop in energy. Second, the remaining trans carbonyl may bond more strongly to the metal, compensating for the effect of the missing carbonyl. Thus, one cannot predict the order of the e and b_2 with any degree of confidence. An additional problem may arise if Koopmans' theorem breaks down. In this case the order of the molecular orbitals in the ground state may not be reflected in the order of the ionic states. As we will see, vide infra, this problem will occur when we compare our spectral assignments with ab initio calculations. We will, however, discuss our results using qualitative molecular orbital theory, mentioning possible breakdown of Koopmans' theorem when it is encountered. In the cases where Koopmans' theorem appears to work we will attempt to use the theoretical results to explain the observed spectra. Table I contains the measured ionization potentials, their relative intensities, and our final assignments, which we will discuss in the following sections.

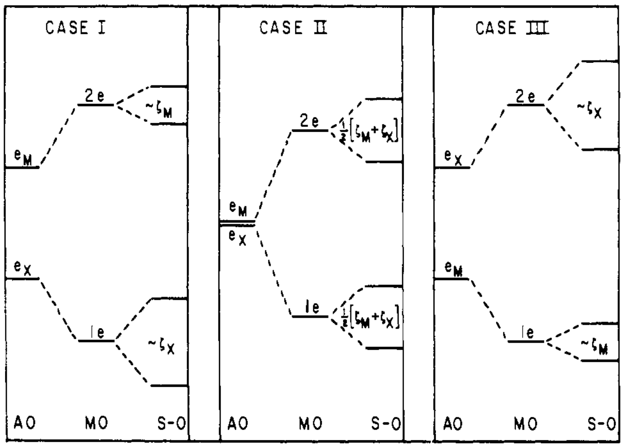

Figure 6. Molecular orbital diagram for three possible case of spin-orbit coupling in $XM(CO)_5$ systems, where X is a π donor and capable of having its own spin-orbit coupling.

$HMn(CO)_5$, $HRe(CO)_5$. The original workers found only two bands in the spectrum of $HMn(CO)_5$, which they naturally assigned to the e and b_2.[2] More recent spectra show that the first band represents two closely spaced ionizations.[7] Our results confirm that the first band is split into two peaks with an approximate intensity ratio of 2 to 1. This fact, coupled with the results of the ab initio calculation, which showed that the e and b_2 should be very close in energy, suggests that the first peak is the metal e, the second is the metal b_2, and third is the metal-hydrogen bond (a_1). Koopmans' theorem did suggest that the a_1 ionization would appear before the closely spaced e and b_2. However, it is now known that the use of Koopmans' theorem in ab initio calculations on transition metal complexes tends to predict too large a value for metal IP's relative to ligand IP's.[10] Thus, it is not surprising that the calculation predicts larger values for metal e and b_2 IP's than for the ligand a_1 IP while predicting the correct order for the very similar metal levels.

Further evidence for the correctness of our assignment comes from the spectrum of $HRe(CO)_5$. The similar shape of the first three bands suggests that they arise from the weakly bonding metal e and b_2, while the fourth broader band is due to the Re-H bonding a_1 orbital. The splitting between the first and second band is 0.31 eV while that between the second and third is 0.34 eV. Since the second splitting is larger than the first, this spectrum is an example of case 3 for $LM(CO)_5$ spin-orbit splitting (see Figure 5). The assignment for $HRe(CO)_5$ is now completely determined. The first band is $e''(e)$, the second is $e'(e)$, the third is $e''(b_2)$, and the fourth is $e'(a_1)$. Our notation for these states gives the assignment according to the double group $C_{4v}{}^*$ first, with the major molecular orbital component in parentheses.

Having established an assignment, we may use eq 7 to calculate the spin-orbit coupling parameter, ζ, and the e-b_2 splitting before spin-orbit coupling. The results are shown in Table II; the calculated value of ζ, 0.25 eV, is in reason-

Table II. Results for Spin–Orbit Coupling Parameter (ζ) and e–b_2 Splitting (Δ)

Molecule	$\epsilon_+ - \epsilon_0$	$\epsilon_0 - \epsilon_-$	ζ	Δ	Δ(LMn-(CO)$_5$)
$HRe(CO)_5$	0.31	0.34	0.25	0.41	0.40
$CH_3Re(CO)_5$	0.26	0.56	0.22	0.63	0.57
$COCF_3Re(CO)_5$	0.29	0.28	0.24	0.35	<0.4

able agreement with the estimated value (0.26 to 0.34 eV) for the free Re^{2+} ion.[18,21] The fact that ζ is smaller than the estimated values is consistent with partial delocalization of the metal electrons into the carbonyl 2π orbitals. The calculated value of the e-b_2 splitting, 0.41 eV, may be compared to that for the manganese, 0.40 eV. We may also use the value of Δ and eq 6 to obtain the position of the e and b_2 before spin-orbit coupling. We find that $\epsilon_e = -9.12$ eV and $\epsilon_{b_2} = -9.53$ eV; these may be compared to the negative IP's for the manganese -8.85 and -9.25 eV. Thus, the rhenium e and b_2 levels before spin-orbit coupling are shifted 0.27 and 0.28 eV to higher IP than the corresponding manganese levels while the a_1 level is shifted only 0.01 eV. These differences lend further support to our assignment since we would expect a larger shift for the metal levels than for the a_1 level which is mainly hydrogen in character.

The ab initio calculations on $HMn(CO)_5$, which are in agreement with the observed order of the e and b_2, suggest that the dominating interaction which produces this order is the loss of the π-bonding carbonyl. Thus, each e orbital backbonds with only three carbonyl 2π orbitals while the b_2 bonds with four carbonyl orbitals. This interaction evidently dominates the competing effects of stronger bonding to the trans carbonyl and the increase in metal character of the e orbital.

$CH_3Re(CO)_5$. As with the hydride, the original workers observed only two bands in the spectrum of $CH_3Mn(CO)_5$, which appeared in an inverted order.[2] They also interpreted these ionizations as arising from the e and b_2 and explained the inverted order by invoking Mn-CH_3 π backbonding.[2] However, approximate MO calculations suggested that the increased intensity of the second band was due to the superposition of the metal b_2 ionization and the Mn-CH_3 a_1 ionization.[4] Recent reexamination of the spectrum has shown that the second band corresponds to two separate ionizations.[5] Although this observation could be interpreted as confirming the assignment proposed on the basis of the approximate calculations, recent ab initio calculations suggest an alternative assignment. Based on Koopmans' theorem, the first band would be assigned to the Mn-CH_3 bonding orbital (a_1), while the second band would be assigned to the closely spaced e and b_2. Until now, this alternative assignment could not be ruled out. The spectrum of $CH_3Re(CO)_5$ clearly shows that the first band must correspond to the metal e since it is split by 0.26 eV. The second intense band is then assigned to the metal b_2 orbital and Re-CH_3 bonding a_1 orbital.

With this assignment, we find that the methyl compound is also an example of case 3 for $LM(CO)_5$ spin-orbit coupling. The calculated values for ζ and Δ are collected in Table II. The ζ values agree well with the value for the hydride. From the value of Δ we can again calculate the position of the Re e and b_2 levels before spin-orbit coupling. We obtain $\epsilon_e = -8.87$ eV and $\epsilon_{b_2} = -8.51$ eV. If the Mn e band is at 8.65 eV the shift in going to the rhenium is 0.22 eV; if the b_2 is at 9.22 eV the shift is 0.29 eV, and if the a_1 is at 9.56 eV the shift is only 0.03 eV. The fact that these shifts parallel those of the hydride lends further support to our assignment.

We have seen both in the hydride and the methyl compound that Koopmans' theorem fails to yield the correct position of the ligand a_1 orbital relative to the metal e and b_2 orbitals. However, as we will show, the calculations do yield the correct trends for changing the ligand from H to CH_3. The ab initio calculations predict that the a_1 IP of the methyl compound is 0.99 eV smaller than that of the hydride. Experimentally, the decrease is 1.04 eV for the manganese compounds and 1.05 eV for the rhenium compounds. Similarly the e and b_2 IP's are predicted to decrease by 0.29 and 0.06 eV, respectively. The experimental shifts are 0.20 and 0.03 eV in the manganese, and 0.22 and 0.02 eV in the rhenium (before spin-orbit coupling). Thus, we find that the calculated trends are reproduced by both the manganese and rhenium spectra.

The calculations suggest that the reason for the larger e-b_2 separation in the methyl complex (0.17 eV larger in Mn and 0.20 eV larger in Re) lies in the fact that the methyl group has a filled orbital of e symmetry below the metal e orbital, which interacts with the metal e orbital raising its orbital energy and lowering its IP. Thus, the methyl group is attempting to π donate to the filled metal e orbitals. Parenthetically, we might note that the π donating ability of the methyl group may help explain the existence of compounds like $Ti(CH_3)_4$, which would then be analogous in its bonding to $TiCl_4$.

$COCF_3Re(CO)_5$. The spectrum of the corresponding manganese compound shows only one broad band in the upper valence region. Because of spin-orbit coupling and the shift to larger IP's we expected the rhenium compound to show a considerably different spectrum. The spectrum in Figure 2 shows that these expectations were fulfilled, as one can clearly see four ionizations between 8.5 and 10.0 eV. The similarity of the last three bands to the first three bands of the hydride suggests that these are due to the metal e and b_2. This means that the first ionization must be due to the Re-$COCF_3$ a_1 bonding orbital. This is one of the first cases in which an ionization due to a σ metal-ligand bond has been observed to have a lower IP than the metal d orbitals. Approximate molecular orbital calculations[22] suggest that at least part of the reason for this is that the "lone pair" on a ligand such as $:COCF_3^-$ is strongly C-O antibonding which results in its IP being smaller than the "lone pair" in a ligand such as $:CH_3^-$.

Using our model for spin-orbit coupling, we find that the splitting pattern (nearly equal splittings between metal bands) suggest that the spin-orbit coupling in this molecule is intermediate between case 2 and case 3 (Figure 5). This places the b_2 below the e, but with less separation than in the hydride case. The inequality developed from eq 7 shows that only assignment I is possible. Using this assignment we have calculated the values of ζ and Δ shown in Table II. The similarity of ζ for this molecule which has a splitting pattern considerably different from that of the hydride or methyl molecule lends further support to our spin-orbit analysis and our assignments. It should now be clear why only one band is observed in the analogous manganese species. The loss of spin-orbit coupling reduces the splitting of the e bands to zero and the e-b_2 splitting to less than 0.4 eV. If we combine this with a shift of these bands by 0.2 to 0.3 eV to lower IP, we would expect to find all three manganese bands in a 0.4-eV range.

$Re_2(CO)_{10}$. The spectrum of the manganese analog consists of three bands of relative intensity 1:2:4 with the weakest band having the lowest IP.[2] These three bands were interpreted (D_{4d} symmetry) as arising from the Mn-Mn σ-bonding orbital (a_1), the Mn-Mn π-bonding orbital (e_3), and the accidentally degenerate Mn-Mn π-bonding (e_1) and nonbonding δ-type (e_2) orbitals. The spectrum of $Re_2(CO)_{10}$ (Figure 3) can be interpreted in a similar manner. On the left-hand side of Figure 7, we have shown the approximate position of the orbitals of the ·Re(CO)$_5$ radical before spin–orbit coupling is applied. Moving to the right in the figure, we have shown the positions of the radical after spin–orbit coupling. The e″(e), e′(e), and e″(b$_2$) are placed at the same energy as the corresponding orbitals of the hydride. The e′(a$_1$) orbital is placed at higher energy since this orbital is now only antibonding with respect to the carbonyl. When two radical fragments are brought together the two a$_1$ orbitals form a bonding and antibonding combination; only the bonding combination, which forms the Re–Re σ bond, is filled. The two sets of e orbitals will interact forming the bonding and antibonding combinations, e$_1$ and e$_3$, respectively, both of which are filled and split by the spin–orbit coupling. The two b$_2$ orbitals are nonbonding in D_{4d} symmetry and do not split when the fragments bond. The final MO diagram (center of Figure 7) has all the features necessary to explain the Re$_2$(CO)$_{10}$ spectra. Thus, the first IP is assigned to the a$_1$ orbital, the next two IP's are assigned to the antibonding e combination (e$_3$) split by spin–orbit coupling. The fourth IP is assigned to one component of the spin–orbit split bonding e combination (e$_1$), and the last IP, which is approximately three times as intense as the other bands, is assigned to the remaining spin–orbit component of e$_1$ and the two nonbonding b$_2$ orbitals (e$_2$).[23] On the right-hand side of Figure 7, we show how the same splitting pattern may arise from first combining the two radicals without spin–orbit coupling, which yields an MO diagram similar to that for Mn$_2$(CO)$_{10}$, then applying the spin–orbit coupling to these molecular orbitals.

Approximate molecular orbital calculations on Mn$_2$(CO)$_{10}$ and Cr$_2$(CO)$_{10}{}^{2-}$ support this assignment.[24] However, they also suggest an equally good assignment can be based on the eclipsed D_{4h} geometry. The major change in going to this geometry is that the two formerly nonbonding b$_2$ orbitals will form a bonding and antibonding combination. However, since the splitting of these two combinations will be small (calculated 0.15 eV) due to the natural weakness of δ-type interactions, essentially the same interpretation of the spectra results.

The average splitting of the e$_3$ and e$_1$ in Re$_2$(CO)$_{10}$ is 0.1 eV larger than in the manganese. This suggests that rhenium may form stronger metal-metal π bonds than manganese. The occurrence of numerous metal cluster systems of rhenium and other third row transition elements[25] is in accord with this observation.

ClRe(CO)$_5$, BrRe(CO)$_5$, IRe(CO)$_5$. We will begin our discussion of the halides by concentrating on the two e ionizations, one from a M–X bonding orbital at higher IP and one from a M–X antibonding orbital at lower IP. Certain characteristics of these ionizations are apparent from the manganese spectra.[2,5] First, in IMn(CO)$_5$ the lowest energy band shows spin-orbit coupling, while the other e band does not. This suggests that the former is mostly I in character while the latter is mostly Mn. In the bromide case no spin-orbit coupling is seen in either band, a fact which implies that the bands correspond to mixtures of Br and Mn orbitals. However the band at higher IP splits when a CO cis to Br is replaced by CNCH$_3$, suggesting that this band may have larger metal character.[5] For the analogous rhenium compounds, we should expect to obtain even more information of this type, since it should be possible to observe both rhenium and halogen spin-orbit coupling.

Consider first the spectrum of BrRe(CO)$_5$ (Figure 4), where the spin-orbit splitting of both the first and third bands is resolved. The first band around 9 eV is split by 0.27 eV and the third band around 10.5 eV is also split by 0.27 eV. The equality of these splittings would suggest that in BrRe(CO)$_5$ the two e molecular orbitals are nearly equal mixtures of Re 5d and Br 4p. However, the small difference between the Re and Br spin-orbit coupling parameters (0.25 and 0.31 eV) combined with the error in the measured splittings (±0.02 eV) suggests that we could have almost any degree of mixing. In addition the perturbations due to the a$_1$ and b$_2$ orbitals may be critical in determining the actual splittings observed. Thus, we will have to infer the character of BrRe(CO)$_5$ from our results on the chloride and iodide.

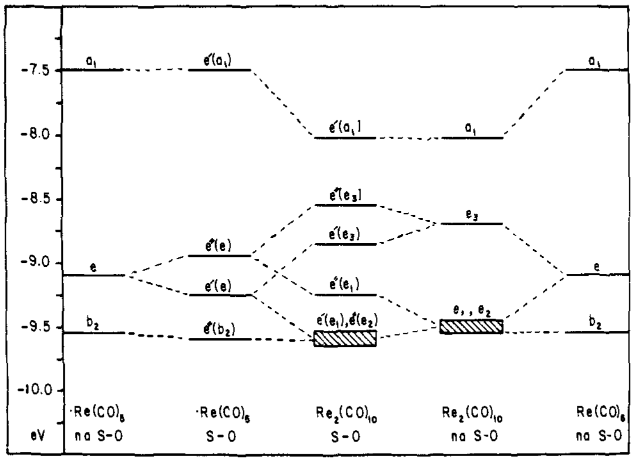

Figure 7. Molecular orbital diagram illustrating the formation of Re$_2$(CO)$_{10}$ from two ·Re(CO)$_5$ radicals.

Examination of the IRe(CO)$_5$ spectra shows that there is one less peak than in the bromide spectrum. This might be caused by the spin-orbit splitting of one of the bands being negligible. However, our analysis (Figure 6) suggests that the total splitting of the e bands should be close to $\zeta_M + \zeta_X$ (0.25 + 0.63 eV). Since the splitting in the first band is only 0.45 eV, we would expect to see substantial splitting of the other e band. This, then, identifies the two e components as the third and fourth peaks (splitting 0.33). The missing ionization is then, most likely, under the fourth band, which explains its greater intensity. Since the first e band (antibonding Re–I) has a larger splitting than the second e, we may conclude that the first contains more I than Re character.

Turning to the spectra of ClRe(CO)$_5$, we find something quite unexpected. The first e band shows spin-orbit splitting while none is apparent in the third band. This suggests that the first band is not halogen in character as it was for the iodide, but is mainly rhenium in character. This conclusion is very unexpected since all previous work on the Mn analogs has assumed that the first IP is mainly halogen in character, where in fact this is true only for the iodide. If we assume that the bromide has metal-halogen mixing intermediate between that of chloride and iodide, we would expect the two e's to be strong mixtures of both Re and Br, in agreement with our earlier tentative conclusion. In terms of our theoretical description (Figure 6) we can classify the coupling in the chloride as case I, that in the bromide as nearly case II, and that in the iodide as case III.

This drastic change in character in going from the chloride to the iodide brings into question the previous assignments for the remaining bands. We will attempt to assign the remaining bands by constructing an "experimental" MO diagram (Figure 8). For the molecular orbital energies we will use the experimental IP's. Since the e bands in BrRe(CO)$_5$ are strong mixtures of Br and Re, we will place the diagonal matrix elements for these two species half-way between the two e IP's. Keeping the Re level the same for ClRe(CO)$_5$ and IRe(CO)$_5$, we will place the Cl diagonal element 0.6 eV lower than the Br element and the I diagonal element 0.8 eV higher than the Br element. These differ-

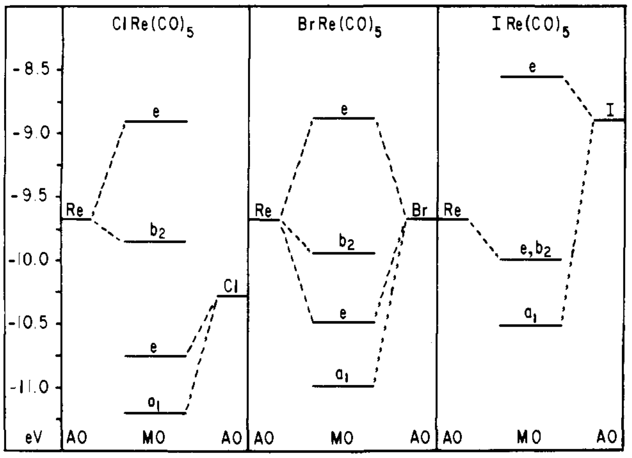

Figure 8. Molecular orbital diagram for $ClRe(CO)_5$, $BrRe(CO)_5$, and $IRe(CO)_5$ (spin-orbit coupling is not shown).

ences were taken from CH_3X IP's.[1] From the placement of these diagonal terms in relation to the final orbital energies, we can readily see that the first band in the chloride spectrum will be due to a mainly Re e level, while in the iodide it will be due to a mainly I e level. Since hydrogen has no π electrons, we would expect the e-b_2 splitting in the $HRe(CO)_5$ to be reflected in the splitting of Re diagonal matrix elements in the halides. Thus, we would expect the b_2 in the halides to be approximately 0.4 eV below the Re diagonal term. This then suggests that the b_2 corresponds to the second band in the chloride and bromide and is accidentally degenerate with the e in the iodide, thus contributing to the intensity of the fourth peak. The a_1 ionization is relegated to the last band in each spectrum (highest IP). This is reasonable since we would expect the σ bond (a_1) to be strongly stabilized by bonding to the metal. In other halogen molecules the σ bonds are usually 2 to 3 eV lower in energy than the corresponding π levels.[1] This assignment for the rhenium compounds suggests that the spectra of manganese compounds should be reassigned in a similar fashion.

Three more reasons for preferring this assignment should be mentioned. First, the b_2 is at almost the same energy in all three molecules (9.86, 9.94, 10.08 eV) and the differences between the rhenium and corresponding manganese molecules are 0.30, 0.38, and 0.39 eV, as should be expected for a metal level. Second, the a_1 level moves up in energy (lower IP) across the series essentially following the upward trend of the halogen π levels, and the differences between the rhenium and corresponding manganese IP's are only 0.02, 0.10, and 0.08 eV. Third, if we compare the intensities of the metal bands in $HMn(CO)_5$ to those in $HRe(CO)_5$, we find that relative to the mainly hydrogen a_1 the metal bands have increased in intensity. Thus, in the halogen species we would expect the b_2 (mainly metal) to increase in intensity relative to the a_1 (mainly halogen). Our new assignment is consistent with this result, while the previous assignment is not.

Having made this assignment for the b_2 and a_1 bands, we should consider the effect of their spin-orbit coupling on our analysis of the character of the e bands. Our placement of the b_2 and a_1 orbitals will cause the splitting of the first e (lowest IP) band to increase and that of the second e band to decrease. If we were to correct the character of the e bands for this effect, it would increase the character of the fragment with the smaller spin-orbit coupling in the first band. Thus, for $ClRe(CO)_5$ the first band would contain more Cl, for $BrRe(CO)_5$ and $IRe(CO)_5$ it would contain more Re character. One further point should be mentioned; since in the spectra of $IRe(CO)_5$ we have assigned the metal e and b_2 to be nearly degenerate before spin-orbit coupling, the band at 9.75 eV, which we have referred to as one of the e components, is most likely a strong mixture of e and b_2 orbitals after spin-orbit coupling.

We have attempted a quantitative analysis of the spectra using eq 9 and 11. We chose values for ζ appropriate for the fragments (0.25 eV for $Re(CO)_5$, 0.08 eV for Cl, 0.31 eV for Br, and 0.63 eV for I), and have used a full matrix nonlinear least-squares technique[26] to solve eq 9 and 11 for ϵ_{2e}, ϵ_{b_2}, ϵ_{1e}, ϵ_{a_1}, C, and K. The results, which reproduce the spectra to high accuracy (±0.01 eV), suggest the rhenium character in the first e band to be 80% for $ClRe(CO)_5$, 60% for $BrRe(CO)_5$, and 30% for $IRe(CO)_5$. Although these values are in agreement with our earlier qualitative analysis, we must place rather large error bars on the percentages, because we have found that they are fairly sensitive to the choice of ζ and the measured splittings. We have found that the spectra may also be reproduced with the other assignment (b_2IP > a_1IP). However, these results do not yield a consistent trend in the percentage of Re character in the first band, and they are much less stable to small changes in the value of ζ. Although this previous assignment cannot be completely ruled out, we feel the accumulated evidence is in favor of our new assignment.

Since we have observed that metal IP's of the manganese compounds are typically 0.2 to 0.3 eV less than those of rhenium, we would expect the percent manganese in the first e bands to be larger than that for rhenium. If we compare our results with the prediction based on Koopmans' theorem, we again find that it predicts values for the manganese IP's which are too large relative to those of the halogen. Thus, the first e band is calculated to have too little manganese character compared to our experimental result. This, again, is another example where Koopmans' theorem fails to predict the character of the ionization correctly.

Conclusion

Through the study of the spin-orbit coupling in the rhenium analogs of the pentacarbonyl manganese compounds, we have been able to establish a complete assignment for the lower ionization potentials of these compounds. The analysis of the spin-orbit coupling has shown that it is a powerful technique in establishing the assignments and characterizing the molecular orbitals and their bonding. We have also shown that the use of Koopmans' theorem, even in ab initio calculations, can yield misleading assignments for transition metal species. However, since the available calculations have not reached the Hartree-Fock limit, we cannot rule out the possibility that all or part of this problem may be due to the limited basis sets employed in these calculations.

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Photochemistry of Metal–Metal Bonded Complexes. II.[1] The Photochemistry of Rhenium and Manganese Carbonyl Complexes Containing a Metal–Metal Bond

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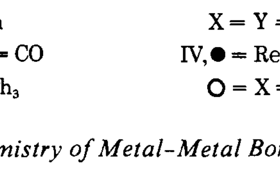
Abstract: The photochemistry of $Mn_2(CO)_{10}$, $Mn_2(CO)_9PPh_3$, $Mn_2(CO)_8(PPh_3)_2$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$, I, II, III, IV, and V, respectively, is reported. Photolysis at 366 nm of I–V in CCl_4 yields the corresponding mononuclear metal carbonyl chloride with high (~0.5) quantum efficiencies and with stoichiometries consistent with symmetrical metal–metal bond cleavage. Photolysis of I, IV, or V in the presence of $\sim10^{-3}$ *M* I_2 yields the expected $M(CO)_5I$ species with an essentially quantitative chemical yield and quantum yields comparable to those for reaction in pure CCl_4. Photolysis of I or IV in the presence of $PhCH_2Cl$ or Ph_3CCl gives good yields of bibenzyl or $Ph_3C\cdot$ radicals, respectively. Complexes I and IV are formed in ~1:1 yield upon flash photolysis of V; I and III are formed in ~1:1 yield upon flash photolysis of II in pure isooctane; and V is formed from the photolysis of a mixture of I and IV. Complex III is found to be the principal primary photoproduct upon 366-nm photolysis of I in isooctane solutions of 0.1 *M* PPh_3. All of the observed photochemistry can be interpreted as arising from homolytic metal–metal bond cleavage occurring from an excited state derived from a $\sigma_b \rightarrow \sigma^*$ one-electron transition associated with the metal–metal bond. Each of I–V exhibits a near-uv absorption corresponding to this transition.

Though structurally well characterized,[4,5] polynuclear metal carbonyls containing direct metal–metal bonds have received relatively little study with respect to reactions which could lead to clean rupture of the metal–metal interaction. Such reactions may have real importance in the characterization of paramagnetic organometallic complexes in that cleavage of the metal–metal bond can potentially lead to two paramagnetic centers. Even though paramagnetic metal carbonyls are rare, intermediates having an odd number of electrons may be important in both stoichiometric and catalytic reactions of metal carbonyls with organic substrates. The monomeric d^7, 17-electron C_{4v} $Co(CN)_5{}^{3-}$ complex having its unpaired electron in the $d_{z^2}(a_1)$ orbital[6] has rich chemistry including reaction with alkyl halides,[7] olefins,[8] and small molecules such as H_2, halogens, SO_2, etc.[9] The $Co(CN)_5{}^{3-}$ also catalyzes the hydrogenation of 1,3-dienes under very mild conditions.[10] The cleavage of the M–M bond in $M_2(CO)_{10}$ (M = Mn, Re) could yield a C_{4v}, d^7, 17-electron species having some reactivity patterns in common with $Co(CN)_5{}^{3-}$.

$$Re_2(CO)_{10} \xrightarrow[CCl_4]{313\text{ nm } \Phi = 0.6} 2Re(CO)_5Cl \qquad (1)$$

One of us recently communicated[1] the results of a quantitative study of the photolysis of $Re_2(CO)_{10}$ in CCl_4 which was found to proceed as in reaction 1. Other, more qualitative, reports[11-13] of the photochemistry of manganese and rhenium compounds containing metal–metal bonds are consistent with the notion that electronic excitation is followed by efficient chemical decay paths resulting in rupture of the metal–metal bond. We now report the results of the first quantitative studies of the photoreactivity of $Mn_2(CO)_{10}$, $Mn_2(CO)_9(PPh_3)$, and $Mn_2(CO)_8(PPh_3)_2$, I, II, and III, respectively. We include some new studies of $Re_2(CO)_{10}$



I,● = Mn
O = X = Y = CO
II,● = Mn
O = X = CO
Y = PPh_3

III,● = Mn
O = CO
X = Y = PPh_3
IV,● = Re
O = X = Y = CO