

ation for support of this research and for a graduate fellowship to H.B.A.

**Registry No.** ( $\eta^5\text{-C}_5\text{H}_5$ )(CO)<sub>3</sub>MoCo(CO)<sub>4</sub>, 62015-65-0; ( $\eta^5\text{-C}_5\text{H}_5$ )(CO)<sub>3</sub>WCo(CO)<sub>4</sub>, 62015-64-9; ( $\eta^5\text{-C}_5\text{H}_5$ )(CO)<sub>3</sub>MoFe(CO)<sub>2</sub>( $\eta^5\text{-C}_5\text{H}_5$ ), 12130-13-1; ( $\eta^5\text{-C}_5\text{H}_5$ )(CO)<sub>3</sub>WFe(CO)<sub>2</sub>( $\eta^5\text{-C}_5\text{H}_5$ ), 64041-01-6; [ $(\eta^5\text{-C}_5\text{H}_5)$ (Mo(CO)<sub>3</sub>)<sub>2</sub>], 12091-64-4; Co<sub>2</sub>(CO)<sub>8</sub>, 10210-68-1; ( $\eta^5\text{-C}_5\text{H}_5$ )Mo(CO)<sub>3</sub>Cl, 12128-23-3; ( $\eta^5\text{-C}_5\text{H}_5$ )Mo(CO)<sub>3</sub>I, 12287-61-5; [ $(\eta^5\text{-C}_5\text{H}_5)$ W(CO)<sub>3</sub>]<sub>2</sub>, 12566-66-4; ( $\eta^5\text{-C}_5\text{H}_5$ )W(CO)<sub>3</sub>Cl, 12128-24-4; ( $\eta^5\text{-C}_5\text{H}_5$ )W(CO)<sub>3</sub>I, 31870-69-6; [ $(\eta^5\text{-C}_5\text{H}_5)$ Fe(CO)<sub>2</sub>]<sub>2</sub>, 12154-95-9; ( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)<sub>2</sub>Cl, 12107-04-9; ( $\eta^5\text{-C}_5\text{H}_5$ )Fe(CO)<sub>2</sub>I, 12078-28-3; Co<sub>3</sub>(CO)<sub>9</sub>CCl, 19512-60-8.

## References and Notes

- (1) Dreyfus Teacher-Scholar grant recipient, 1975-1980.
- (2) (a) M. Wrighton and D. Bredesen, *J. Organomet. Chem.*, **50**, C35 (1973); (b) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065 (1975).
- (3) A. Hudson, M. F. Lappert, and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 551 (1977).
- (4) A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 966 (1974).
- (5) (a) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 4246 (1975); (b) D. S. Ginley and M. S. Wrighton, *ibid.*, **97**, 4908 (1975); (c) D. L. Morse and M. S. Wrighton, *ibid.*, **98**, 3931 (1976).
- (6) (a) C. Giannotti and G. Merle, *J. Organomet. Chem.*, **105**, 97 (1976); (b) R. M. Laine and P. C. Ford, *Inorg. Chem.*, **16**, 388 (1977).
- (7) J. L. Hughey IV, C. R. Bock, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 4440 (1975).
- (8) J. L. Hughey IV, C. P. Anderson, and T. J. Meyer, *J. Organomet. Chem.*, **125**, C49 (1977).
- (9) (a) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **97**, 947, 3260 (1975); **99**, 2527 (1977); (b) M. Absi-Halabi and T. L. Brown, *ibid.*, **99**, 2982 (1977).
- (10) D. M. Allen, A. Cox, T. J. Kemp, Q. Sultana, and R. B. Pitts, *J. Chem. Soc., Dalton Trans.*, 1189 (1976).
- (11) A. R. Burkett, T. J. Meyer, and D. G. Whitten, *J. Organomet. Chem.*, **67**, 67 (1974).
- (12) H. B. Abrahamson and M. S. Wrighton, *J. Am. Chem. Soc.*, **99**, 5510 (1977).
- (13) (a) R. A. Levenson, H. B. Gray, and G. P. Caesar, *J. Am. Chem. Soc.*, **92**, 3653 (1970); (b) R. A. Levenson and H. B. Gray, *ibid.*, **97**, 6042 (1975); (c) D. C. Harris and H. B. Gray, *ibid.*, **97**, 3073 (1975).
- (14) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Lillenthal, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, **16**, 1554 (1977).
- (15) D. S. Ginley, Ph.D. Thesis, MIT, 1976.
- (16) D. C. Harris and H. B. Gray, *Inorg. Chem.*, **14**, 1215 (1975).
- (17) M. C. Palazzotto and M. S. Wrighton, to be submitted for publication.
- (18) R. B. King, P. M. Treichel, and F. G. A. Stone, *Chem. Ind. (London)*, 747 (1961).
- (19) V. N. Pandey, *Inorg. Chim. Acta*, **23**, L26 (1977).
- (20) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).
- (21) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

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## Shake-up Satellite Structure in the X-Ray Photoelectron Spectra (ESCA) of Metal Hexacarbonyls

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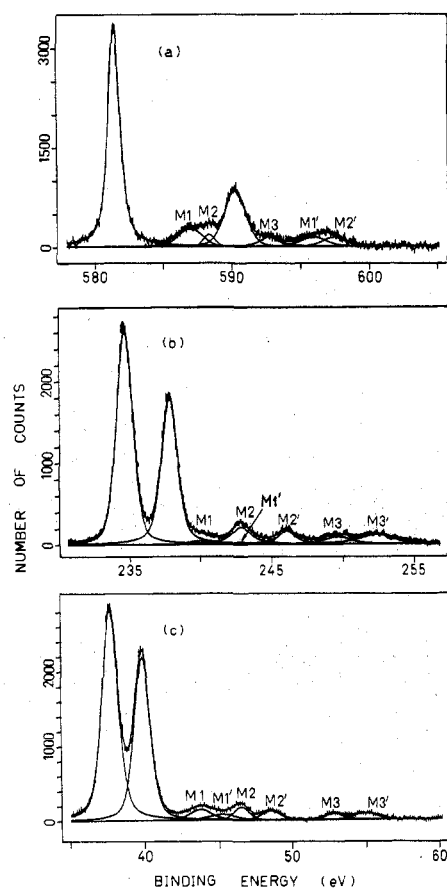
Core-level (C 1s, O 1s, Cr 2p, Mo 3d, and W 4f) ESCA data have been recorded for M(CO)<sub>6</sub> (M = Cr, Mo, W) compounds in the gas phase using Mg K $\alpha$  and Al K $\alpha$  radiation. All levels show a number of satellites which are attributed to electron shake-up. For example, the O 1s spectrum of Mo(CO)<sub>6</sub> shows satellites at 5.4, 7.0, 9.8, 14.9, and 16.4 eV from the primary photoline. Only the first of these peaks has been seen in previous studies. By use of electronic spectra and molecular orbital calculations, the satellites have been tentatively assigned. For example, the most intense O 1s satellite at 5.4 eV has been assigned to the 2t<sub>2g</sub> → 3t<sub>2g</sub> transition, which is predominantly a metal d → ligand  $\pi^*$  charge-transfer transition. The same transition is responsible for the 5.6- and 5.1-eV satellites on the C 1s and Mo 3d levels, respectively. A similar satellite is also seen on the metal and ligand levels in the Cr and W compounds, and the energy of this transition varies in the sequence Cr < Mo < W. The considerable potential of these satellites for obtaining molecular orbital information is discussed.

## Introduction

Although chemical interest in x-ray photoelectron spectroscopy (or ESCA) has been largely directed toward the chemical shift parameter,<sup>1,2</sup> recent reviews<sup>3,4</sup> have drawn attention to the large number of studies on the small shake-up satellites on the low kinetic energy side of many primary photolines. These shake-up satellites are of considerable potential importance to the coordination chemist, as the shake-up positions are related to the energy difference between filled and unfilled molecular orbitals. As well as this energy difference, the intensity of the satellites has been used to determine the extent of covalency in metal-ligand<sup>5,6</sup> bonds. In transition-metal complexes,<sup>3,4</sup> one satellite is normally observed on the metal levels only, and these satellites are only common in first-row transition-metal complexes.<sup>4</sup> Only in transition-metal carbonyls and acetates<sup>3</sup> have satellites been observed on ligand levels. In particular, the volatile group 6B metal hexacarbonyls M(CO)<sub>6</sub> have been studied extensively for chemical shift variations in the solid state (M = Cr, Mo,

W)<sup>7-11</sup> and in the gas phase (M = Cr).<sup>12</sup> Shake-up structure has also been studied in the solid-state spectra.<sup>11,13-15</sup> In each shake-up study, only one intense shake-up peak (~30% of the intensity of the main line) has been observed in each of the C 1s and O 1s spectra at about 5.4 eV from the primary line. This peak has been assigned to a metal → ligand\* (M → L\*) charge-transfer transition.<sup>14</sup> There is one report<sup>15</sup> of an uncharacterized shake-up satellite on the Cr 2p level of Cr(CO)<sub>6</sub>. Also, satellite structure is evident in published spectra of the Mo 3d level in Mo(CO)<sub>6</sub><sup>14</sup> and the W 4f level in W(CO)<sub>6</sub>.<sup>8,14</sup> These latter two examples appear to be the only known examples of the occurrence of metal shake-up peaks in the second- and third-row transition-metal series.<sup>4</sup>

Recent ground-state molecular orbital<sup>16,17</sup> calculations strongly suggested that many shake-up transitions were possible in these compounds and that a number of satellites should be seen in the ESCA. Because the above shake-up spectra were recorded using condensed solids, rather broad primary peaks were usually obtained. In addition, the spectra



**Figure 1.** Metal core level spectra: (a) Cr 2p region in  $\text{Cr}(\text{CO})_6$ ; (b) Mo 3d region in  $\text{Mo}(\text{CO})_6$ ; (c) W 4f region in  $\text{W}(\text{CO})_6$ . All spectra were taken with Mg  $K\alpha$  radiation.

were not recorded to high statistics, so that weak satellites would not be seen.

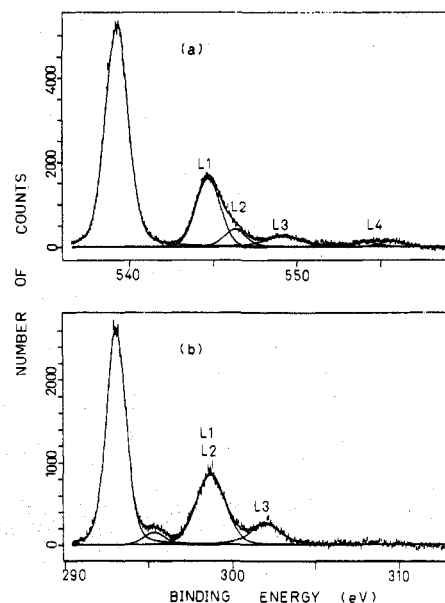
In this study, we have recorded the gas-phase C 1s, O 1s, and metal core level spectra of the three metal carbonyls to high statistics. Besides the intense shake-up peaks observed earlier, we observed a number of additional satellites on the ligand and metal levels. Despite the rather limited success of MO calculations in predicting<sup>18,19</sup> both shake-up positions and intensities, we make tentative peak assignments using the ground-state MO calculations<sup>16,17</sup> at hand. Our results demonstrate the considerable potential of these shake-up peaks for obtaining molecular orbital information in transition-metal compounds and emphasize the need for high-quality MO calculations in both the ground and excited states for the interpretation of shake-up spectra.

### Experimental Section

The metal carbonyls were obtained commercially from Alfa Inorganics. The x-ray photoelectron spectra were obtained on our McPherson ESCA 36 spectrometer using Mg  $K\alpha$  and Al  $K\alpha$  radiations. The samples were all run in the gas phase using an adapted heated-sample inlet. All spectra were calibrated using the published core line positions for  $\text{CO}_2$  and Ar.<sup>20</sup> All peaks were fitted to a combination Gauss-Lorentz peak shape by an iterative procedure discussed earlier.<sup>21</sup>

### Results

The metal-core spectra of the three compounds and representative C 1s and O 1s spectra are shown in Figures 1 and



**Figure 2.** Ligand core level spectra: (a) O 1s region in  $\text{Mo}(\text{CO})_6$ ; (b) C 1s region in  $\text{Mo}(\text{CO})_6$ . The C 1s spectrum was taken with Al  $K\alpha$  radiation.

2, while the primary photoline parameters and the shake-up positions and intensities are listed in Tables I and II. The standard deviations of our primary peak positions and widths are generally between  $\pm 0.01$  and  $\pm 0.02$  eV, and the reproducibility of both parameters is within  $\pm 0.05$  eV. The C 1s and metal-core line widths are generally less than 1.3 eV (Table I)—much narrower than has been reported previously on condensed solids.<sup>7-11</sup> One notable exception is the Cr  $2p_{1/2}$  line width which is almost double that of the  $2p_{3/2}$  line width (see also Figure 1a). This broad Cr  $2p_{1/2}$  line is also seen in the solid-state spectra of Pignataro.<sup>14</sup>

The satellite structure (Table II and Figures 1 and 2) is similar for each of the carbonyls studied and falls into three main groups. The first group lies between 4.6 and 7 eV from the primary line and is given the labels L1 and L2 for the ligand satellites and M1 (for the L + S spin-orbit low binding energy component) and M1' (for the high binding energy L - S spin-orbit component) for the metal core level spectra. The second group comprises the satellites L3, M2, and M2', ranging between 7 and 10 eV from the primary photoline. The third group, L4, M3, and M3', with the exception of the Cr  $2p_{3/2}$  satellite, lies 15-16 eV from the primary line.

One of these satellites usually lies at a similar relative energy ( $\Delta E$ ) for all three carbonyls or shows a smooth trend from Cr to W. Thus, the  $\Delta E$  for the low-energy O 1s satellite (L1) increases from 5.1 (Cr) to 5.4 (Mo) to 5.6 eV (W), while  $\Delta E$  for the second O 1s satellite (L2) increases from 6.0 (Cr) to  $\sim 7.0$  eV (Mo and W). Only in the C 1s spectrum of  $\text{Cr}(\text{CO})_6$  could these two distinct lines be seen at 4.6 and 5.6 eV, slightly lower  $\Delta E$ 's than in the O 1s spectrum. The centroids of the  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$  C 1s satellites (L1 and L2) are at very similar  $\Delta E$ 's of 5.6 and 5.7 eV, respectively.

The weak peak observed in the carbon 1s spectra at around 2.5 eV from the main photoline is attributed to free CO. This peak is seen in all metal carbonyls, including  $\text{Fe}(\text{CO})_5$ , at the same absolute binding energy ( $\pm 0.13$  eV). This energy is 0.75 eV lower than that of free CO, as determined by leaking CO into the gas cell simultaneously with the metal carbonyl. These compounds are known to photodissociate readily,<sup>22</sup> and thus the presence of CO (and  $\text{M}(\text{CO})_5$ ) is not unexpected. There is a hint of the corresponding O 1s peak from this free CO

Table I. Primary Photoline Parameters (eV)

| Peak                 | Cr(CO) <sub>6</sub>            |      | Mo(CO) <sub>6</sub> |      | W(CO) <sub>6</sub> |      |
|----------------------|--------------------------------|------|---------------------|------|--------------------|------|
|                      | Binding <sup>a</sup> energy    | Fwhm | Binding energy      | Fwhm | Binding energy     | Fwhm |
| C 1s                 | 293.21<br>(293.5) <sup>b</sup> | 1.16 | 293.16              | 1.41 | 293.15             | 1.26 |
| O 1s                 | 539.49<br>(539.6) <sup>b</sup> | 1.45 | 539.26              | 1.58 | 539.27             | 1.48 |
| Cr 2p <sub>3/2</sub> | 581.87<br>(581.8) <sup>b</sup> | 1.04 |                     |      |                    |      |
| 2p <sub>1/2</sub>    | 590.68                         | 1.85 |                     |      |                    |      |
| Mo 3d <sub>5/2</sub> |                                |      | 234.57              | 1.33 |                    |      |
| 3d <sub>3/2</sub>    |                                |      | 237.69              | 1.29 |                    |      |
| W 4f <sub>7/2</sub>  |                                |      |                     |      | 37.84              | 1.27 |
| 4f <sub>5/2</sub>    |                                |      |                     |      | 40.00              | 1.28 |

<sup>a</sup> The binding energies are calibrated relative to the values (in eV) given in ref 20: O 1s (CO<sub>2</sub>), 541.28; C 1s (CO<sub>2</sub>), 297.69; Ar 2p<sub>3/2</sub><sup>20</sup> 248.45. <sup>b</sup> Parenthesized values are those given previously in ref 12.

Table II. Relative Energies (eV) and Relative Intensities of the Shake-up Satellites in the C 1s, O 1s and Metal Core Level Spectra in M(CO)<sub>6</sub> (M = Cr, Mo, W)

| Peak label | Tentative assign <sup>b</sup>          | Cr(CO) <sub>6</sub>                                    |  |                       |   | Mo(CO) <sub>6</sub> |                  |  |                       | W(CO) <sub>6</sub> |                  | Free CO ΔE <sup>c</sup> C 1s <sup>e</sup> |  |
|------------|--|--|--|-----------------------|---|---------------------|------------------|--|-----------------------|--------------------|------------------|---|--|
|            |  | Cr(CO) <sub>6</sub>                                    |  | Cr(CO) <sub>6</sub>   |   | Mo(CO) <sub>6</sub> |                  | Mo(CO) <sub>6</sub>                                    |                       | W(CO) <sub>6</sub> |                  |   |  |
|            |  | Obsd ΔE (I <sub>g</sub> /I <sub>p</sub> ) <sup>a</sup> | Obsd ΔE (I <sub>g</sub> /I <sub>p</sub> ) <sup>a</sup> | Calcd ΔE <sup>d</sup> | Hückel <sup>e</sup> X <sub>0</sub> <sup>d</sup> | C 1s                | O 1s             | Obsd ΔE (I <sub>g</sub> /I <sub>p</sub> ) <sup>a</sup> | Calcd ΔE <sup>d</sup> | C 1s               | O 1s             |   | Obsd ΔE (I <sub>g</sub> /I <sub>p</sub> ) <sup>a</sup> |
| L1 M1      | 2t <sub>2g</sub> → 3t <sub>2g</sub>    | 5.6 (0.31)   | 5.1 (0.20)   | 6.0                   | 4.2   | 5.6 (0.33)          | 5.4 (0.31)       | 5.1 ± 0.4 (0.02)                                       | 5.7                   | 5.7 (0.27)         | 5.6 (0.25)       | 6.4 (0.05)                                | 6.0  |
| M1'        | M → L*(M*)                             |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
| L2         | 3t <sub>1u</sub> → 4t <sub>1u</sub>    | 4.6 (0.07)   | 6.0 ± 0.3 (0.14)                                       | 9.4                   | 7.2   | 5.6                 | 7.9 ± 0.3 (0.07) | 8.2 (0.08)   | 9.8                   | 5.7                | 6.9 ± 0.3 (0.08) | 6.4 (0.05)                                | 9.8  |
| M2, M2'    | L → L*                                 |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | 2e <sub>g</sub> → 3e <sub>g</sub>      |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | (2a <sub>1g</sub> → 3a <sub>1g</sub> ) |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | (3t <sub>1u</sub> → 5t <sub>1u</sub> ) |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | L → M*                                 |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | 1t <sub>1g</sub> → 2t <sub>1g</sub>    |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | 1t <sub>2u</sub> → 2t <sub>2u</sub>    |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | 2t <sub>1u</sub> → 4t <sub>1u</sub>    |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | L → L*                                 |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
| L3         | 1e <sub>g</sub> → 3e <sub>g</sub>      | 8.9 (0.05)   | 10.1 (0.05)  | 12.8                  | 9.6   | 8.9 (0.10)          | 9.8 (0.05)       | 12.8   | 9.3 (0.05)            | 10.0 (0.05)        | 12.8             | 8.3                                       | 12.8   |
|            | 2t <sub>1g</sub> → 3t <sub>1g</sub>    |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | 1t <sub>1u</sub> → 5t <sub>1u</sub>    |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | 1t <sub>2u</sub> → 5t <sub>2u</sub>    |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | 1a <sub>1g</sub> → 3a <sub>1g</sub>    |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | L → M*                                 |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
| M3, M3'    | 1e <sub>g</sub> → 3e <sub>g</sub>      |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | (2t <sub>1u</sub> → 5t <sub>1u</sub> ) |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | (1t <sub>1u</sub> → 5t <sub>1u</sub> ) |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | (1a <sub>1g</sub> → 3a <sub>1g</sub> ) |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
|            | L → M*                                 |  |  |                       |   |                     |                  |  |                       |                    |                  |   |  |
| L4         | 1t <sub>1g</sub> → 3t <sub>1g</sub>    | 15.5 (0.03)  |  | 16.1                  | 9.3   | 14.9 (0.03)         | 16.4 (0.03)      | 14.9 (0.04)  | 14.7                  | 15.3 (0.03)        | 15.5 (0.03)      | 13.4                                      | 14.6   |
|            | 1t <sub>2u</sub> → 4t <sub>2u</sub>    |  |  | 16.5                  | 13.0  | 16.4 (0.03)         |                  |  | 29.3                  |                    |                  |   | 25.5   |
|            | L → L*                                 |  |  |                       |   |                     |                  |  | 25.7                  |                    |                  |   | 28.7   |
|            |  |  |  |                       |   |                     |                  |  |                       |                    |                  |   | 31.3   |

<sup>a</sup> ΔE is the separation between the primary photoline and the satellite; I<sub>g</sub> and I<sub>p</sub> are the intensities of the satellite and primary photoline, respectively. The errors in the ΔE values are ±0.2 eV unless otherwise mentioned. The errors in the relative intensities are about ±20%. <sup>b</sup> See Figure 3 for the MO diagram. Gray and Beach's notation<sup>16</sup> is used. The type of transition is noted below the assignment, i.e., M → L (metal to ligand) etc. The transitions in parentheses are not likely important (see text). <sup>c</sup> Reference 17. <sup>d</sup> Reference 16. <sup>e</sup> Reference 26. <sup>f</sup> There is a possibility of a satellite at about 15 eV (see text).

on the O 1s spectra (Figure 2a), but the larger O 1s line width prevents it from being resolved. Again, this CO O 1s peak is at a lower binding energy than "normal" CO. These lower binding energies are somewhat surprising. We postulate that the CO observed here is in an excited electronic state, giving rise to a slightly different chemical shift than ground-state CO. Further evidence for the nature of this peak is discussed below.

On the metal levels, the first satellite (M1, M1') at  $5.7 \pm 0.7$  eV is at very similar energies to the C 1s and O 1s satellites (L1, L2), but these metal satellites are much less intense than their ligand analogues. The other two metal satellites (M2, M2' and M3, M3') on Mo and W are at very similar  $\Delta E$  values ( $\sim 8.5$  and  $\sim 15.0$  eV). The corresponding Cr satellites are at surprisingly lower  $\Delta E$  values (see below).

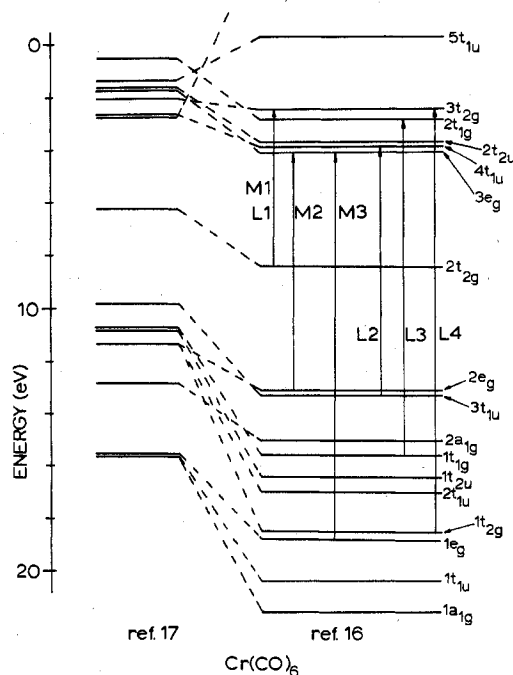
The rather elaborate fits to some of the metal spectra deserve some comment. Two guidelines were important in fitting the metal spectra. First, a satellite will be present on both the primary photoline spin-orbit components at very nearly the same relative energies and relative intensities. For example, the W 4f spectrum (Figure 1c) shows only five distinct satellites instead of the even number expected. In order to pair off the satellites, peak M1' (the  $4f_{5/2}$  satellite) was fixed 2.16 eV (the spin-orbit splitting) from peak M1 (the  $4f_{7/2}$  satellite) which is clearly resolved. No other positions were fixed. Because the molecular orbitals in these three compounds should be very similar,<sup>16</sup> the second guideline followed is that similar satellite structure is expected in the three compounds. Thus, we expect a satellite at  $\Delta E \approx 5$  eV in the Mo 3d spectrum because  $\sim 5$ -eV satellites are readily observed in all other levels in these three compounds (Figure 1). A small shoulder is observed in the Mo 3d spectrum at 239 eV—about 5 eV from the  $3d_{5/2}$  primary peak. It is not unreasonable, then, to fit a peak (M1) at  $\sim 239$  eV, and then fit its spin-orbit component (M1') 3.1 eV (the spin-orbit splitting for Mo 3d) to higher binding energy. The position and width of the latter peak had to be constrained.

Mainly because of the very large Cr 2p spin-orbit splitting, the Cr 2p fit (Figure 1a) is not entirely satisfactory. Peaks M1' and M2' (the  $2p_{1/2}$  satellites) are obviously too intense (relative to M1 and M2). This is probably due to the existence of a satellite at about 15 eV (present in Mo and W) from the Cr  $2p_{3/2}$  peak. Also, no M3' satellite is apparent and, as discussed below, the two Cr  $2p_{3/2}$  satellite positions (M2 and M3) are not consistent with the Mo and W metal satellites.

## Discussion

The compounds studied here are diamagnetic, with  $^1A_{1g}$  ground states, and there is very little possibility that the satellite structure can arise from any other process than shake-up.<sup>4</sup> For example, multiplet splitting is not possible in these systems; nor is there the possibility of characteristic energy loss peaks which are present in solids. It is possible, however, that the very broad Cr  $2p_{1/2}$  peak and the 11-eV satellite (M3) are associated with configuration interaction.

Shake-up is usually explained in the context of the sudden approximation<sup>2</sup> which allows representation of the final state not only as the normal hole state but as a combination of this state and excited initial-state wave functions. This approach, though not exact, is very useful in that it permits the continued use of the one-electron model in the interpretation of phenomena such as shake-up. It is thus possible to attribute the main intense peak in the photoelectron spectrum to the single-electron process due to the formation of a core hole and the low kinetic energy satellites to multielectron processes, involving the simultaneous ionization of the core electron and excitation of valence electrons.



**Figure 3.** Energy level diagram for  $\text{Cr}(\text{CO})_6$  from Johnson and Klemperer<sup>17</sup> (left side) and Beach and Gray<sup>16</sup> (right side). The assigned shake-up transitions are numbered (Table II) along with Beach and Gray's orbital assignments. The  $2t_{2g}$  orbital is the highest occupied level and is derived primarily from the chromium d orbitals. All orbitals below this level are of majority ligand origin.

We have used three main criteria in our interpretation of the spectra. In order to assign our peaks, we used the ground-state molecular energy levels calculated previously<sup>16,17</sup> (Figure 3). The Hückel calculation gave good energy levels for the filled orbitals as seen by the good agreement between the UV photoelectron spectrum<sup>8</sup> and the calculated energies. Therefore, some confidence can be placed in these energy levels, at least for the ground-state system. There is qualitative agreement between the two MO calculations on  $\text{Cr}(\text{CO})_6$  (Figure 3, Table II), and the relative transition energies agree reasonably well. However, there are some discrepancies for the larger transition energies (Table II). For example, the  $1a_{1g} \rightarrow 3a_{1g}$  energy varies from 12.9<sup>17</sup> to 26.1 eV<sup>16</sup> between the two calculations. In addition to the MO calculations, three other main criteria are used as assignment guidelines. First, it has been shown, by making use of the sudden approximation,<sup>23</sup> that these shake-up transitions obey the monopole selection rule.<sup>23,24</sup> The ground state for these systems is  $^1A_{1g}$  and thus all shake-up transitions can be represented as transitions between one-electron orbitals of the same symmetry. The shake-up energy should correspond closely to the calculated difference in orbital energies, as observed for example in UV spectroscopy via dipole transitions. However, the formation of a positive hole upon photoionization will lower the orbital energy of most valence and virtual orbitals, and the shake-up energy is usually smaller than that calculated in the ground state.<sup>18,19</sup> The ground-state calculations should still be a good guide, but it is always possible that very large and unexpected relaxation effects could alter some of our assignments.

The second criterion follows from the relaxation process.<sup>2,14,25</sup> Ionization of a core electron results in a positive charge. Charge flow in the shake-up process is facilitated toward this hole. Thus, in order to have appreciable intensity, all shake-up transitions should involve a virtual orbital with a significant contribution from the ionized atom. Thus, transitions like  $1t_{2u} \rightarrow 2t_{2u}$  and  $1t_{1g} \rightarrow 2t_{1g}$  should not be observed on the met-

al-core levels because the virtual orbitals involved do not have appreciable metal character. The major character of the orbitals is given in Figure 3.

The C 1s shake-up spectrum of free CO is a very important third guideline. This spectrum shows a weak peak at  $\Delta E$  of 8.3 eV with a relative intensity  $I_s/I_p = 0.03$ . This peak was assigned to a  $\pi \rightarrow \pi^*$  shake-up transition.<sup>26</sup>

Using Figure 3 and the above three criteria, we can now examine the assignments in Table II. The first satellite (L1, M1, M1') in the 5–6-eV region is seen on both ligand and metal-core levels and is assigned to the  $2t_{2g} \rightarrow 3t_{2g}$  transition which is primarily a metal (M)  $\rightarrow$  ligand (L)\* transition, although the  $3t_{2g}$  level has appreciable metal character.<sup>16,17</sup> The energy corresponds closely to the calculated values, and a transition to the  $3t_{2g}$  level should be seen on both metal and ligand levels according to our second guideline. More importantly, the transition corresponds very closely to the low-energy charge-transfer UV band observed at  $\sim 5.5$  eV. The UV band has been assigned to a  $2t_{2g} \rightarrow 2t_{2u}, 2t_{1g}$  transition,<sup>16</sup> which from the ground-state calculations should be of very similar energy to the  $2t_{2g} \rightarrow 3t_{2g}$  shake-up transition (Figure 3). The evidence for the assignment of this first shake-up peak at  $\sim 5$  eV is one more strong indication that the 2.5-eV satellite seen on the C 1s level is not due to shake-up. Two trends are noticeable in the  $2t_{2g} \rightarrow 3t_{2g}$  shake-up peak. First, the  $\Delta E$  values for the metal levels are larger than the  $\Delta E$  values for the corresponding ligand levels,<sup>27</sup> and second, the  $\Delta E$  values for a given level vary in the order  $Cr < Mo < W$ .<sup>27</sup> The former trend must reflect differences in relaxation energy, and relaxation effects could well be important in the latter. However, the latter trend is often observed in other satellites (Table II), and such an increase is not inconsistent with that expected on chemical grounds and also by the Hückel calculation in some cases.

The second peak (L2) is observed only on the ligand levels and is assigned to a  $3t_{1u} \rightarrow 4t_{1u}$  transition. This transition is expected on the ligand levels only, because  $4t_{1u}$  has dominant ligand  $\pi^*$  character. The observed  $\Delta E$  value here is much smaller than the calculated Hückel  $3t_{1u} \rightarrow 4t_{1u}$  transition energy but only slightly smaller than the calculated  $X\alpha$  transition energy. Such a disparity in calculated values obviously creates a problem in trying to assign unambiguously these shake-up peaks.

Although there are three possible L  $\rightarrow$  M transitions which give rise to peaks M2 (M2'), only the  $2e_g \rightarrow 3e_g$  seems energetically probable from the Hückel calculation. These peaks are seen only in the metal as expected from the dominant metal character of the  $3e_g$  orbital. It appears very likely that peak L3 on the ligand levels is due to the three  $\pi-\pi^*$  transitions because our shake-up energies are very similar to the  $\pi-\pi^*$  shake-up energy of 8.3 eV observed for free CO. The orbitals involved in this transition are only of ligand character and thus it is significant that the  $\Delta E$  values for this satellite on both C 1s and O 1s for the three carbonyls do not vary significantly.

There are four possible L  $\rightarrow$  M\* transitions responsible for the high-energy metal satellites M3 and M3'. The transition  $1e_g \rightarrow 3e_g$  is favored energetically by the Hückel calculations. It is perhaps strange that the Cr 2p M3 satellite at a  $\Delta E$  of 11.2 eV is so much lower in energy than the corresponding Mo or W satellite. It is interesting to note that shake-up structure has been previously reported for other chromium species at similar  $\Delta E$  values and assigned to a L  $\rightarrow$  M\* transition. As mentioned earlier, it is quite possible that the Cr 2p<sub>1/2</sub> satellites M1' and M2' mask a 15-eV satellite in Cr(CO)<sub>6</sub>.

The O 1s satellites at  $\sim 15$  eV (L4) are probably due to the  $1t_{2g} \rightarrow 3t_{2g}$  and  $1t_{1u} \rightarrow 4t_{1u}$  transitions (Table II), although they could be due to a  $\sigma-\sigma^*$  transition on CO because of the

very similar energy to the free CO value of 14.9 eV.<sup>26</sup> The MO calculations do not take the ligand  $\sigma^*$  orbitals into account.

The metal carbonyls are the only transition-metal compounds to show intense and complex shake-up structure on ligand orbitals. These ligand satellites are probably due to two factors. First, the empty  $\pi^*$  orbitals make many more transitions possible. Second,  $\pi$  back-bonding creates an available channel for the charge-transfer process to take place. Indeed, the most intense ligand shake-up peak (L1) is due to the transition between the metal d orbital ( $2t_{2g}$ ) and ligand  $\pi^*$  orbitals ( $3t_{2g}$ ). These are just the orbitals involved in  $\pi$  back-bonding. These two factors are probably not the complete picture, because shake-up satellites are not apparent in transition-metal hexacyanides.<sup>28</sup> However,  $\pi$  back-bonding is normally thought to be less important in the cyanides than in carbonyls. The observation of intense shake-up structure between orbitals with extensive overlap ( $2t_{2g} \rightarrow 3t_{2g}$ ) is somewhat contradictory to generalizations made earlier.<sup>28</sup>

## Conclusions

The results presented in this paper reveal shake-up satellite structure not previously reported in the metal hexacarbonyls. This study thus illustrates the significant benefits of obtaining high-quality gas-phase spectra whenever possible.

These systems have provided a unique example in which to study shake-up because both metal- and ligand-core levels display satellite structure and a second- and third-row transition metal also display satellite structure.

Although there is some uncertainty in our assignments, we have tentatively assigned the nature of these satellites in a consistent manner for these three complexes. Our results show that it is very difficult to make shake-up assignments on the basis of energy alone. In order to increase our understanding of the shake-up phenomenon, improved MO energy schemes and intensity calculations will have to be applied to such complex systems as the metal carbonyls.

**Registry No.** Cr(CO)<sub>6</sub>, 13007-92-6; Mo(CO)<sub>6</sub>, 13939-06-5; W(CO)<sub>6</sub>, 14040-11-0.

## References and Notes

- (1) K. Siegbahn et al., "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1971.
- (2) T. A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, N.Y., 1975.
- (3) M. A. Brisk and A. D. Baker, *J. Electron Spectrosc. Relat. Phenom.*, **7**, 197 (1975).
- (4) G. A. Vernon, G. Stucky, and T. A. Carlson, *Inorg. Chem.*, **15**, 278 (1976).
- (5) M. A. Brisk and A. D. Baker, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 81 (1975).
- (6) D. C. Frost, C. A. McDowell, and R. L. Tapping, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 347 (1975).
- (7) D. T. Clark and D. B. Adams, *Chem. Phys. Lett.*, **10**, 121 (1971).
- (8) B. R. Higginson, D. R. Lloyd, P. Burroughs, D. M. Gibson, and A. F. Orchard, *J. Chem. Soc., Faraday Trans. 2*, 1659 (1973).
- (9) M. Barber, J. A. Connor, I. H. Hillier, and V. R. Saunders, *Chem. Commun.*, 682 (1971).
- (10) D. T. Clark and D. B. Adams, *Chem. Commun.*, 740 (1971).
- (11) M. Barber, J. A. Connor, M. F. Guest, M. B. Hall, I. H. Hillier, and W. N. E. Meredith, *Faraday Discuss. Chem. Soc.*, No. **54**, 219 (1972).
- (12) J. A. Connor, M. B. Hall, I. H. Hillier, and W. N. E. Meredith, *J. Chem. Soc., Faraday Trans. 2*, 1677 (1973).
- (13) M. Barber, J. A. Connor, and I. H. Hillier, *Chem. Phys. Lett.*, **9**, 570 (1971).
- (14) S. Pignataro, *Z. Naturforsch.*, **A**, **27**, 816 (1972).
- (15) S. Pignataro, A. Foffoni, and C. Distefano, *Chem. Phys. Lett.*, **20**, 350 (1973).
- (16) N. A. Beach and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 5713 (1968).
- (17) J. B. Johnson and W. G. Klemperer, *J. Am. Chem. Soc.*, **99**, 7132 (1977).
- (18) S. Larsson, *Chem. Phys. Lett.*, **32**, 401 (1975).
- (19) J. A. Tossell, *J. Electron Spectrosc. Relat. Phenom.*, **10**, 169 (1977).
- (20) G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 295 (1973).

- (21) G. M. Bancroft, I. Adams, L. L. Coatsworth, C. D. Bennowitz, J. D. Brown, and W. P. Westwood, *Anal. Chem.*, **47**, 586 (1975).  
 (22) A. Vogler in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter 6.  
 (23) R. Manne and T. Aberg, *Chem. Phys. Lett.*, **7**, 282 (1970).  
 (24) K. S. Kim, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 217 (1974).  
 (25) H. Basch in "Metal-Ligand Interactions in Organic Chemistry and Biochemistry", B. Pullman and N. Goldblum, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1976.  
 (26) U. Gelius, *J. Electron Spectrosc. Relat. Phenom.*, **5**, 985 (1974).  
 (27) This is not true for Mo 3d, but there is a large error on the very weak Mo 3d<sub>3/2</sub> shake-up peak (Figure 1b).  
 (28) S. Larsson and M. L. de Siqueira, *Chem. Phys. Lett.*, **44**, 537 (1976).

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## Kinetic and Thermodynamic Study of Reactions of Some Substituted Manganese(I) and Manganese(II) Tricarbonyl Complexes Using Spectrophotometric and Electrochemical Techniques

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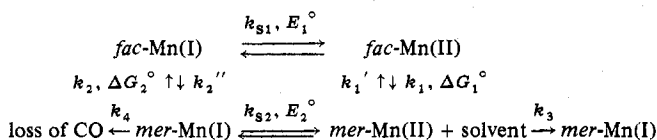
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Electrochemical oxidation and reduction processes enable the species *fac*-[Mn(CO)<sub>3</sub>(L-L')X]<sup>0,+</sup> and *mer*-[Mn(CO)<sub>3</sub>(L-L')]<sup>0,+</sup> to be synthesized and their thermodynamic and kinetic properties to be studied via electrochemical and spectrophotometric measurements ((L-L') = bidentate phosphorus or arsenic ligand; X = Cl or Br). In oxidation state II, the 17-electron manganese complexes are extremely labile and several reactions occur. The rate of isomerism, *fac*-Mn(II) → *mer*-Mn(II), studied by a fully computerized version of double potential step chronoamperometry, is not markedly dependent on solvent, bidentate ligand, or X. A twist mechanism is proposed to explain this isomerism. By contrast the activation energy in the thermodynamically favored 18-electron oxidation state I isomerism must be extremely high because no isomerism was observed to occur in 24 h. *mer*-Mn(II) complexes generated via *fac*-Mn(II) isomerism undergo slow solvolysis and redox reactions in the dark. They are also extremely light sensitive and are rapidly reduced in sunlight. Reactions of manganese(II) carbonyls are therefore considerably more complex than previously thought.

In 1963 Angelici et al.<sup>2</sup> examined the isomerism of a series of Mn(CO)<sub>3</sub>(L)<sub>2</sub>X (L = ligand, X = Cl, Br, I) complexes. In these 18-electron manganese(I) systems, it was concluded that isomerism occurred via an intermolecular mechanism involving the dissociation of L.

With the complexes Mn(CO)<sub>3</sub>dpmX (dpm = bis(diphenylphosphino)methane; X = Cl, Br) the usually synthesized form is the facial isomer.<sup>3</sup> Recently, Bond et al.<sup>4</sup> demonstrated that on electrochemical oxidation a 17-electron facial manganese(II) complex *fac*-[Mn(CO)<sub>3</sub>dpmX]<sup>+</sup> can be generated which subsequently isomerizes to *mer*-[Mn(CO)<sub>3</sub>dpmX]<sup>+</sup>. The *mer*-Mn(II) species was then in turn shown to react with the solvent to form *mer*-Mn(CO)<sub>3</sub>dpmX which subsequently decomposed via loss of carbon monoxide rather than isomerizing to the usually isolated *fac*-Mn(CO)<sub>3</sub>dpmX complex. Thus, using electrochemical techniques, each of the isomers in the 18- and 17-electron configuration can be prepared and their chemical reactions studied. The opportunity therefore exists to examine from both a thermodynamic and kinetic viewpoint the differences between the 17- and 18-electron manganese systems and to consider whether the reactions in the different oxidation states occur via the same mechanisms and pathways.

From the preceding work, the above study appeared to require a quantitative description of the reaction scheme



in various solvents and under various conditions, where  $k_{sn}$  = heterogeneous electron transfer rate constant,  $k_n$  = homogeneous chemical rate constant for designated chemical step, and other symbols have their usual meaning. However, during the course of this work it was discovered that the *mer*-Mn(II) complexes are extremely light sensitive and that reduction to Mn(I) and solvolysis can be catalyzed quite markedly by the

presence of light. Additional measurements to include the light-sensitive pathways were therefore needed.

To examine the influence of the substituents on the thermodynamic and kinetic aspects of the various processes the following bidentate ligands were chosen for the tricarbonyl systems: bis(diphenylphosphino)methane (dpm), 1,2-bis(diphenylphosphino)ethane (dpe), 1,2-bis(diphenylarsino)ethane (dae), 1-diphenylphosphino-2-diphenylarsinoethane (ape). Each of these ligands was used with both chloride and bromide and various studies were made in acetone, acetonitrile, dichloromethane, and propylene carbonate. Since each of the isomers is highly colored, conventional spectrophotometric monitoring of the various species as a function of time is possible. However, the *fac*-Mn(II) → *mer*-Mn(II) isomerism step was too fast at room temperature to be studied conveniently by spectrophotometry and the electrochemical technique of double potential step chronoamperometry<sup>5</sup> was used. With this technique, correction for charging current and the calculations themselves are usually difficult or extremely tedious to perform. However, a completely computerized on-line system has been developed to perform all the required tasks, and accurate rate constants have been obtained via a highly convenient method. For other reactions a novel combination of spectrophotometric monitoring of species and highly specific electrochemical quenching of another reaction pathway enables the distinction to be made between steps that normally occur with similar rates.

### Experimental Section

**Preparation of Compounds and Solutions.** The preparation of the yellow *fac*-Mn(CO)<sub>3</sub>(L-L')X was undertaken essentially by the method of Colton and McCormick.<sup>6</sup> Initially Mn(CO)<sub>5</sub>Cl or Mn(CO)<sub>5</sub>Br was prepared by passing chlorine through a dichloromethane solution of Mn<sub>2</sub>(CO)<sub>10</sub> or adding bromine dropwise to the Mn<sub>2</sub>(CO)<sub>10</sub> solution, respectively. The purity of the products was monitored by infrared spectroscopy. Mn(CO)<sub>5</sub>X was then refluxed with a stoichiometric amount of dpm, dpe, dae, or ape (Strem Chemicals) in *n*-hexane to give *fac*-Mn(CO)<sub>3</sub>(L-L')X complexes which were recrystallized from dichloromethane. Infrared data on the purified complexes in dichloromethane were consistent with those for the facial isomer.<sup>4</sup>