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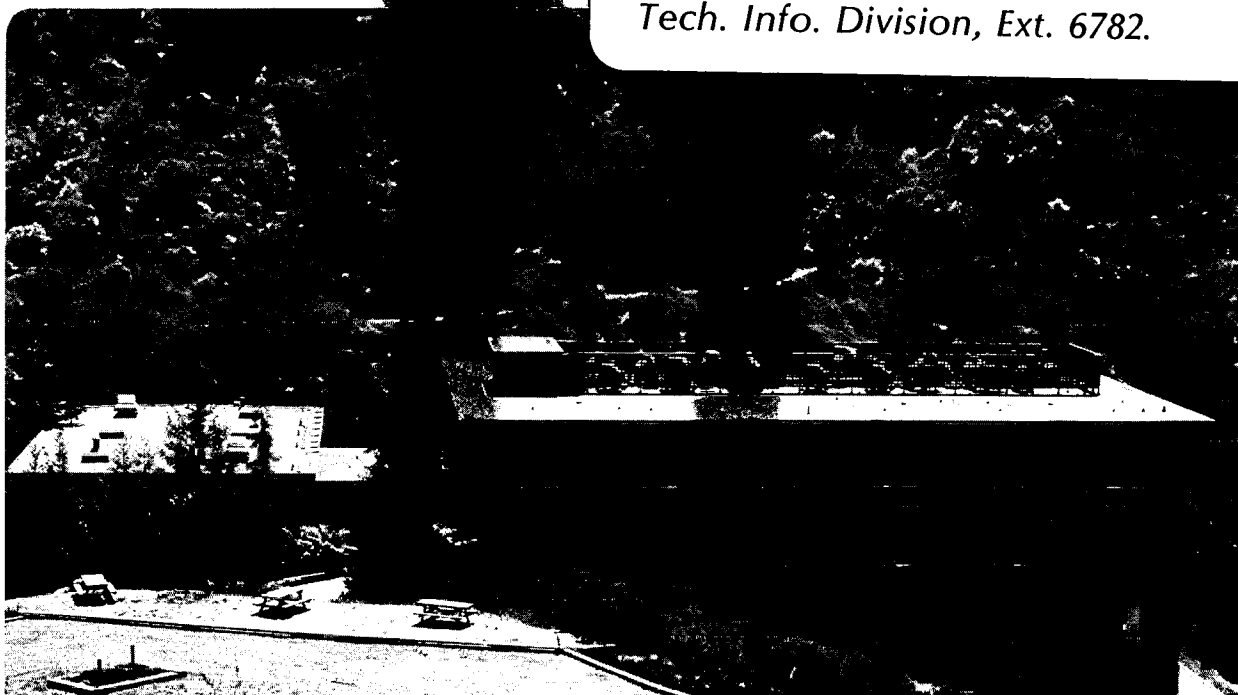
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The Use of Core Binding Energies in the Assignment of the  
Ultraviolet Photoelectron Spectra of the Manganese  
Pentacarbonyl Halides

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ABSTRACT:

By using core binding energy data to correct for the effects of potential (atomic charges) and relaxation energy, ambiguities in the assignment of the first four bands in the ultraviolet photoelectron spectra of the manganese pentacarbonyl halides can be largely resolved.

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## Introduction

The ultraviolet photoelectron spectra of the manganese pentacarbonyl compounds,  $\text{Mn}(\text{CO})_5\text{R}$ , are potentially a source of information about the relative  $\pi$ -acceptor and  $\sigma$ -donor characters of the various R groups. In this paper we discuss the spectra of an important subset of these compounds, i.e. the manganese pentacarbonyl halides,  $\text{Mn}(\text{CO})_5\text{X}$ .

The first report<sup>1</sup> of the spectra of these halides was accompanied by an assignment for the first three bands which agreed qualitatively with the calculations of Fenske and DeKock<sup>2</sup>, i.e. with the energy level ordering  $e(\text{X}) > e(\text{Mn}) > b_2(\text{Mn})$ . Later improved spectra by Lichtenberger et al.<sup>3</sup> showed the presence of a weak band between the first two bands of  $\text{Mn}(\text{CO})_5\text{Cl}$  and  $\text{Mn}(\text{CO})_5\text{Br}$ , which was assigned to  $a_1(\text{Mn-X})$ ; thus these investigators proposed the energy ordering  $e(\text{X}) > a_1(\text{Mn-X}) > e(\text{Mn}) > b_2(\text{Mn})$ . Ceasar et al.,<sup>4</sup> on the basis of a comparison with UPS data for the corresponding rhenium compounds,  $\text{Re}(\text{CO})_5\text{X}$ , reinterpreted the data in terms of a level ordering  $e(\text{X}) > b_2(\text{Mn}) > e(\text{Mn}) > a_1(\text{Mn-X})$ . Finally, Higginson et al.,<sup>5</sup> who studied  $\text{Mn}(\text{CO})_5\text{X}$  and  $\text{Re}(\text{CO})_5\text{X}$  with both He I and He II radiation, agreed with this latter assignment in the case of  $\text{Mn}(\text{CO})_5\text{I}$ , but proposed, for  $\text{Mn}(\text{CO})_5\text{Br}$  and  $\text{Mn}(\text{CO})_5\text{Cl}$ , the level ordering  $e(\text{Mn}) > b_2(\text{Mn}) > e(\text{X}) > a_1(\text{Mn-X})$ . However DeKock<sup>6</sup> has cast some doubt on this latter assignment. Clearly there is no consensus regarding the assignment of the ultraviolet photoelectron spectra of the manganese pentacarbonyl halides.

It has been shown that appropriately chosen core binding energy data can be used to subtract the contributions due to electrostatic potential (atomic charges) and relaxation energy from valence ionization potentials, and thus it is possible to quantify the bonding or antibonding character of molecular orbitals using only experimental data.<sup>7,8</sup> The method has been used to

interpret the nature of the bonding in  $XCo_3(CO)_9$ <sup>9</sup> and  $ONF_3$ <sup>10</sup> and to reassign the ultraviolet photoelectron spectrum of  $OF_2$ .<sup>8</sup> Inasmuch as both the manganese and halogen core binding energies of the  $Mn(CO)_5X$  compounds are known,<sup>11</sup> the method is applicable to this system of compounds. It is the purpose of this communication to show that the combination of core and valence ionization potential data can be used, completely independently of previous work, to confirm the assignment of Higginson et al.

Treatment of the Spectral Data

Localized orbital ionization potentials (LOIPs) can be calculated for the halogen valence p orbitals of the  $Mn(CO)_5X$  compounds, because data are available for the corresponding  $HX$  molecules, which have strictly nonbonding halogen  $p\pi$  orbitals. However there is no known manganese compound in which the manganese d orbitals are strictly nonbonding. Hence we can only calculate relative LOIP values for the manganese d orbitals of the pentacarbonyl compounds. We have chosen to use the hydride,  $Mn(CO)_5H$ , as our reference compound for the manganese d orbitals. In this compound there are no  $\pi$ -type interactions between the hydrogen atom and the manganese d orbitals; hence shifts in the  $e(Mn)$  LOIP values on going from  $Mn(CO)_5H$  to the  $Mn(CO)_5X$  compounds can be taken as measures of the interaction of the halogen  $p\pi$  orbitals with the  $e(Mn)$  orbitals.

It is well-established<sup>5,12,13</sup> that the ordering of the highest three orbitals of  $Mn(CO)_5H$  is  $e(Mn) > b_2(Mn) > a_1(Mn-H)$ . The splitting between the e and  $b_2$  orbitals is comparable to that observed in Group VI pentacarbonyl complexes, and the intensity of the e orbital is greater than that of the  $b_2$  orbital, as expected from their degeneracies. It is of course expected that the e orbital lie above the  $b_2$  orbital because of back-bonding considerations. The  $b_2$  orbital is stabilized by interaction with four carbon

monoxide  $\pi^*$  orbitals, whereas each e orbital interacts with only three carbon monoxide ligands.

The valence and core ionization potentials for the pertinent molecules are listed in Table I. Using data from Table I, the LOIP values listed in Table II were calculated.<sup>14</sup> The LOIP values for the e(X) orbitals are the ionization potentials that the halogen  $p\pi$  orbitals would have if they were strictly nonbonding. The LOIP values for the  $b_2(\text{Mn})$  and e(M) orbitals are the ionization potentials that these orbitals would have if their interactions with other orbitals were limited to, and the same as, those in  $\text{Mn}(\text{CO})_5\text{H}$ .

#### Assignment of the Spectra

In the case of  $\text{Mn}(\text{CO})_5\text{Cl}$ , The e(Mn) LOIP is unquestionably less than the e(Cl) LOIP, and any interaction between these orbitals would only tend to separate further the energy levels of these orbitals; that is, we conclude that  $e(\text{Mn}) > e(\text{Cl})$ . On this basis, we rule out the assignments of Lichtenberger et al. and Ceasar et al., both of which have the reverse order,  $e(\text{Cl}) > e(\text{Mn})$ . In the case of  $\text{Mn}(\text{CO})_5\text{Br}$ , the difference between the e(Mn) and e(Br) LOIP values is comparable to the uncertainty in the values; hence the data cannot be used to establish the relative energy levels. The e(Mn) and e(I) LOIP values for  $\text{Mn}(\text{CO})_5\text{I}$  are just barely different enough to allow us to conclude that  $e(\text{I}) > e(\text{Mn})$ . This assignment is strongly supported by the observation that the first band of  $\text{Mn}(\text{CO})_5\text{I}$  shows distinct evidence of spin-orbit splitting.

In all the  $\text{Mn}(\text{CO})_5\text{X}$  spectra, the second and fourth bands are relatively weak (in fact, the "second" band of  $\text{Mn}(\text{CO})_5\text{I}$  is so weak that it has not been directly observed; presumably it lies under the high-energy side of band I or the low-energy side of band III). Hence it is generally agreed that bands II and IV correspond to the nondegenerate  $a_1(\text{Mn-X})$  or  $b_2(\text{Mn})$  orbitals. The

$b_2(\text{Mn})$  orbital is orthogonal to the halogen valence orbitals, and therefore should have an ionization potential equal to the  $b_2(\text{Mn})$  LOIP, as calculated using  $\text{Mn}(\text{CO})_5\text{H}$  as the reference molecule. If we assume that band IV of each  $\text{Mn}(\text{CO})_5\text{X}$  compound corresponds to  $b_2(\text{Mn})$ , we calculate IP - LOIP values of 1.52, 1.27, and 1.00 eV for the  $b_2(\text{Mn})$  orbitals for X = Cl, Br, and I, respectively. On the other hand, if we assume that band II of  $\text{Mn}(\text{CO})_5\text{Cl}$  and  $\text{Mn}(\text{CO})_5\text{Br}$  corresponds to  $b_2(\text{Mn})$ , we calculate IP - LOIP values of -0.1 and 0.0, respectively. Clearly only the latter assignment is reasonable. By assuming that IP - LOIP = 0 for the  $b_2(\text{Mn})$  orbital of  $\text{Mn}(\text{CO})_5\text{I}$ , we predict that this band should lie at 9.36 eV. Only a very weak shoulder appears at this energy on the low energy side of band III in the  $\text{Mn}(\text{CO})_5\text{I}$  spectrum.<sup>5</sup>

Thus the LOIP data indicate an energy level ordering of  $e(\text{Mn}) > b_2(\text{Mn}) > e(\text{Cl}) > a_1(\text{Mn-Cl})$  for  $\text{Mn}(\text{CO})_5\text{Cl}$ , and  $e(\text{I}) > b_2(\text{Mn}) > e(\text{Mn}) > a_1(\text{Mn-I})$  for  $\text{Mn}(\text{CO})_5\text{I}$ , in agreement with Higginson et al.<sup>5</sup> For  $\text{Mn}(\text{CO})_5\text{Br}$ , the data do not allow us to choose between the Higginson et al. assignment,  $e(\text{Mn}) > b_2(\text{Mn}) > e(\text{Br}) > a_1(\text{Mn-Br})$ , and the alternative,  $e(\text{Br}) > b_2(\text{Mn}) > e(\text{Mn}) > a_1(\text{Mn-Br})$ . It should be noted that, using the assignments of Higginson et al., the data correspond to reasonable interaction energies for the  $e(\text{X})$  and  $e(\text{Mn})$  orbitals. We calculate that the  $e(\text{X})-e(\text{Mn})$  interaction in  $\text{Mn}(\text{CO})_5\text{Cl}$  leads to 0.52 eV stabilization of  $e(\text{Cl})$  and 0.40 eV destabilization of  $e(\text{Mn})$ . Similarly we calculate for  $\text{Mn}(\text{CO})_5\text{Br}$ , 0.77 eV stabilization of  $e(\text{Br})$  and 0.40 eV destabilization of  $e(\text{Mn})$ , and for  $\text{Mn}(\text{CO})_5\text{I}$ , 0.25 eV destabilization of  $e(\text{I})$  and 0.58 eV stabilization of  $e(\text{Mn})$ . These results are consistent with a decrease in the resonance integral,  $\beta$ , on going from X = Cl to X = I, in accord with the expectation that the  $p\pi-d\pi$  interaction in the X-Mn bond decreases on going from X = Cl to X = I.<sup>15</sup>

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- (14) Calculated using the relation  $LOIP = IP(\text{ref}) + 0.8(E_B - E_B(\text{ref}))$

integrals differ by  $\Delta\alpha$  is approximately given by the expression  $\Delta = \sqrt{(\Delta\alpha)^2 + 4\beta^2} \approx \Delta\alpha$ . The values of  $\Delta$ ,  $\Delta\alpha$ , and the calculated  $\beta$  values (in eV) are 0.92, 0.67, and 0.72 for  $\text{Mn}(\text{CO})_5\text{Cl}$ ; 1.17, 0.14, and 0.65 for  $\text{Mn}(\text{CO})_5\text{Br}$ ; and 0.83, 0.26, and 0.53 for  $\text{Mn}(\text{CO})_5\text{I}$ .

Table I. Valence and Core Ionization Potentials, eV

Molecule	Valence IPs				Core $E_B$ s <sup>a</sup>	
	Band	Band	Band	Band	Halogen	Mn 2p <sub>3/2</sub>
	I	II	III	IV		
Mn(CO) <sub>5</sub> H <sup>b</sup>	8.85	9.14	10.55			647.46
Mn(CO) <sub>5</sub> Cl <sup>c</sup>	8.87	9.5	10.46	11.08	203.84	647.98
Mn(CO) <sub>5</sub> Br <sup>c</sup>	8.83	9.5	10.14	10.79	74.30	647.94
Mn(CO) <sub>5</sub> I <sup>c</sup>	8.56 <sup>d</sup>	?	9.65	10.36	625.27	647.73
HCl <sup>e</sup>	12.78 <sup>d</sup>				207.39	
HBr <sup>e</sup>	11.82 <sup>d</sup>				77.36	
HI <sup>e</sup>	10.64 <sup>d</sup>				627.56	

<sup>a</sup> Ref. 11. <sup>b</sup> IPs from ref. 12. <sup>c</sup> IPs from ref. 5. <sup>d</sup> Weighted average of spin-orbit split bands. <sup>e</sup> IPs from Frost, D. C.; McDowell, C. A.; Vroom, D. A., J. Chem. Phys. 1967, 46, 4255.

Table II. Localized Orbital Ionization Potentials, eV

Molecule	Orbital		
	$e(X)^a$	$b_2(Mn)^b$	$e(Mn)^b$
$Mn(CO)_5Cl$	9.94	9.56	9.27
$Mn(CO)_5Br$	9.37	9.52	9.23
$Mn(CO)_5I$	8.81	9.36	9.07

<sup>a</sup> Calculated using the hydrogen halides as reference molecules. <sup>b</sup> Calculated using  $Mn(CO)_5H$  as the reference molecule.

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