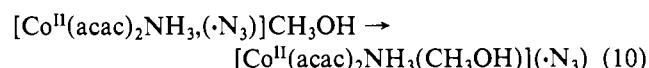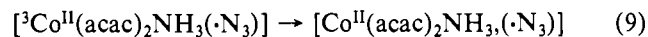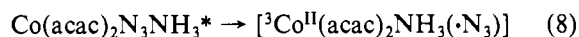processes alone could account for such a high activation energy. The processes occurring subsequent to population of the photoactive state are depicted in eq 8–11, where $[^3Co^{II}-$

$$Co(acac)_2N_3NH_3^* \rightarrow [^3Co^{II}(acac)_2NH_3(\cdot N_3)] \quad (8)$$

$$[^3Co^{II}(acac)_2NH_3(\cdot N_3)] \rightarrow [Co^{II}(acac)_2NH_3,(\cdot N_3)] \quad (9)$$

$$[Co^{II}(acac)_2NH_3,(\cdot N_3)]CH_3OH \rightarrow$$
$$[Co^{II}(acac)_2NH_3(CH_3OH)](\cdot N_3) \quad (10)$$

$$[Co^{II}(acac)_2NH_3(CH_3OH)](\cdot N_3) \rightarrow$$
$$Co(acac)_2(NH_3)CH_3OH + \cdot N_3 \quad (11)$$
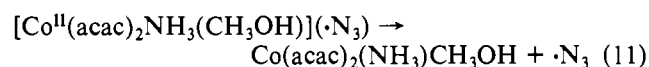
$(acac)_2NH_3(\cdot N_3)]$ represents the $^3CTTM(N_3)$ excited state and $[Co^{II}(acac)_2NH_3,(\cdot N_3)]CH_3OH$ and $[Co^{II}(acac)_2NH_3-(CH_3OH)](\cdot N_3)$ are geminate and secondary (solvent separated) radical pairs. As written a dissociative mechanism has been envisioned, but if an associative mechanism is considered, eq 9 and 10 reduce to eq 12. An activation energy of 11.7

$$[^3Co^{II}(acac)_2NH_3(\cdot N_3)]CH_3OH \rightarrow$$
$$[Co^{II}(acac)_2NH_3(CH_3OH)](\cdot N_3) \quad (12)$$
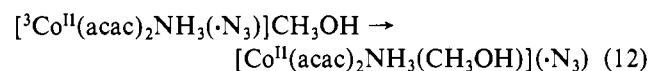
kcal/mol suggests a sufficiently long-lived excited state as to permit the type of solvent involvement required by eq 12. Furthermore, the mechanisms (eq 9 and 10 vs. eq 12) suggest two different types of solvent participation. Whereas the solvent in eq 10 is merely undergoing exchange with a solvent caged but unbound radical, the solvent in equation 12 is undergoing nucleophilic attack on a bound ligand. The latter

process is favored for nucleophilic solvent molecules, but the former is disfavored in viscous media. The quantum efficiency increases in 20% (v/v) ethylene glycol–methanol as compared to methanol as a solvent, although the former is more viscous. In that ethylene glycol is a potentially chelating ligand, it is expected to facilitate reaction 12.

The results of this investigation reveal a number of interesting features in the photochemistry of $Co(acac)_2N_3NH_3$. Excitations throughout the 250–580-nm region appear to populate a single photoactive state. The ligand field, $^1T_{1g}(O_h)$, state appears to be inactive, and the low quantum efficiency and its wavelength dependence can be readily explained in terms of facile interconversion among singlet states and inefficient intersystems crossing into the triplet manifold. The photoactive state has an energy between 17.2×10^3 and 21.3×10^3 cm^{-1}, and a $^3CTTM(N_3)$ state is strongly indicated. Studies are currently being carried out in support of this proposition. The photoactive state is nondissociative as evidenced by both the magnitude of the apparent activation energy and the solvent viscosity behavior. The results in mixed solvents suggest that the solvent assists in the diplacement of the azide radical from the coordination sphere.

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Ultraviolet Photoelectron Studies on Bonding in Some Metal Carbonyl and Metal Hydrido Carbonyl Clusters

JENNIFER C. GREEN,* D. MICHAEL P. MINGOS, and ELAINE A. SEDDON

He I and He II gas-phase photoelectron spectra are reported for Ru$_3$(CO)$_{12}$, Os$_3$(CO)$_{12}$, Co$_4$(CO)$_{12}$, Os$_6$(CO)$_{18}$, H$_3$Re$_3$(CO)$_{12}$, H$_4$Re$_4$(CO)$_{12}$, H$_2$Os$_3$(CO)$_{10}$, and H$_4$Os$_4$(CO)$_{12}$. The spectra are assigned with the use of fragment molecular orbital analyses of the various electronic structures. Characteristic intensity patterns and ionization energy regions are established for the various types of bonding orbitals. Evidence is presented for treatment of the hydrogen bridge bonds as many-center, two-electron bonds, with a high degree of hydrogen localization. The role of hydrogen in stabilizing the cluster orbitals is noted. The difference between the first ionization energy of a cluster and the work function of metal surfaces is discussed.

As part of a general investigation into the nature of metal–metal bonding in binuclear and polynuclear transition-metal compounds,[1] we have carried out a UV photoelectron (PE) study of some carbonyl and hydrido carbonyl cluster compounds. Preliminary reports on part of this work have already been made.[2,3] The studies described below have demonstrated that the metal–metal and bridge hydrogen bonds in these cluster compounds can be analyzed satisfactorily in terms of

molecular orbital schemes derived from the frontier molecular orbitals of the M(CO)$_4$ and M(CO)$_3$ fragments which have been studied extensively.[4,5]

This work also provides an opportunity to examine the proposition that clusters of this type can be used as models for metal surfaces involved in heterogeneous catalytic processes. The analogy between the interaction of unsaturated species with molecules, containing three or more metal atoms, and the structure and reactivity of organic species on metal surfaces has been developed in several major review articles[6–11]

(1) (a) Green, J. C.; Hayes, A. J. *Chem. Phys. Lett.* **1975**, *31*, 306. (b) Coleman, A. W.; Green, J. C.; Hayes, A. J.; Seddon, E. A.; Lloyd, D. R.; Niwa, Y. *J. Chem. Soc., Dalton Trans.* **1979**, 1057. (c) Bursten, B. E.; Cotton, F. A.; Stanley, G. G.; Green, J. C.; Seddon, E. A. *J. Am. Chem. Soc.* **1980**, *102*, 955. (d) Bursten, B. E.; Cotton, F. A.; Green, J. C.; Seddon, E. A.; Stanley, G. G. *Ibid.* **1980**, *102*, 4579.
(2) Green. J. C.; Seddon, E. A.; Mingos, D. M. P. *J. Chem. Soc., Chem. Commun.* **1979**, 94.
(3) Green, J. C.; Mingos, D. M. P.; Seddon, E. A. *J. Organomet. Chem.* **1980**, *185*, C20.

(4) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.
(5) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.
(6) Ugo, R. *Catal. Rev.* **1975**, *11*, 225.
(7) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1975**, *84*, 959.
(8) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451.
(9) Muetterties, E. L. *Science (Washington, D.C.)* **1977**, *196*, 839.

Table I. Ionization Energy Data for Some Metal Carbonyl Clusters

$Ru_3(CO)_{12}$	$Os_3(CO)_{12}$	$Os_6(CO)_{18}$	$Co_4(CO)_{12}$	assignt
7.5 (sh) (A)	7.83 (A)	7.52 (A)	8.9 (A)	M–M
7.8 (B)	8.28 (B)	7.94 (B)		
	8.48 (C)	8.09 (C)		
9.1 (sh) (C)	9.24 (D)	9.48 (D)		"t_{2g}"
9.2 (D)	9.60 (E)	10.55 (E)		
9.8 (E)	10.44 (F)			
13.2 (F)	13.58 (G)	14.74 (F)		$-CO, 5\sigma + \pi$
14.7 (G)	15.05 (H)			
17.3 (H)	18.05 (I)	18.2 (G)		$-CO, 4\sigma$
	21.0 (J)			

and is deemed strongest when considering modes of ligand coordination and skeletal geometry, in relation to step or kink sites on metal surfaces. Recent extended Hückel calculations on clusters have also suggested that the analogy holds well.[12] However, despite the broad acceptance of this hypothesis, there are little experimental data to test its validity. If it were correct, the ionization energies of a metal cluster should approach the limit of the work function of a metal surface as the size of the cluster is increased. Moreover for trimeric, tetrameric, and hexameric cluster compounds to be good models, this limit should be approached rather rapidly.

Compounds were chosen for study on the following criteria: (i) they are volatile without extensive decomposition to give well-defined molecular species in the gas phase; (ii) they have a known molecular structure; (iii) they have high symmetry.

Since the initiation of this work, Plummer et al.[13] have reported results of a related, detailed X-ray and UV PE spectroscopic study on metal carbonyl clusters in the solid state.

Experimental Section

The compounds $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Co_4(CO)_{12}$ were prepared by literature methods.[14–16] Samples of $Os_6(CO)_{18}$, $H_4Ru_4(CO)_{12}$, $H_4Os_4(CO)_{12}$, and $H_2Os_3(CO)_{10}$ were kindly donated by Professor J. Lewis and Dr. B. F. G. Johnson. Samples of $H_3Re_3(CO)_{12}$ and $H_4Re_4(CO)_{12}$ were kindly donated by Dr. M. J. Mays.

The PE spectra were obtained on a Perkin-Elmer PS 16/18 spectrometer fitted with a hollow cathode Helectros lamp capable of producing both He I and He II radiation. The spectra were calibrated with respect to nitrogen, xenon, and the helium self-ionization band (apparent ionization energy (IE) of 4.98 eV in He I spectrum).

Results

The He I and He II photoelectron spectra of $Ru_3(CO)_{12}$[17] $Os_3(CO)_{12}$, $Os_6(CO)_{18}$, and $Co_4(CO)_{12}$ are presented in Figure 1; their respective ionization energy and peak area data (where calculated) are given in Tables I and II. Attempts to record the spectra of $Ir_4(CO)_{12}$ and $Rh_6(CO)_{16}$ proved unsuccessful owing to extensive decomposition of these clusters on heating. Some decomposition was observed for $Ru_3(CO)_{12}$, $Os_6(CO)_{18}$, and $Co_4(CO)_{12}$ (as indicated by superposition of the characteristic spectrum of carbon monoxide upon the spectrum of the gas-phase species of interest), but the PE spectra obtained

were reproducible and were similar in profile to rapidly scanned spectra recorded at lower temperatures before the onset of decomposition; thus, it was concluded, that the spectra observed were characteristic of the cluster species. Only in the case of $Os_3(CO)_{12}$ was no decomposition observed, and the broad similarities of the features of this spectrum to that of $Ru_3(CO)_{12}$ lends further support to the assumption of only partial decomposition for the latter species. It is for this reason that peak area data for the whole spectrum is presented only for $Os_3(CO)_{12}$: the presence of free CO is expected to distort the peak area data above 14 eV. The relative area data for peaks below 13.5 eV should, however, be unaffected by the presence of free CO. In each case, evolution of CO (as determined by the intensity of the band at 14.01 eV), at constant temperature, increased with time. The temperatures required to produce a sufficient count rate with minimal decomposition are recorded in Table IV.

The He I and He II photoelectron spectra of $H_2Os_3(CO)_{10}$, $H_4Os_4(CO)_{12}$, $H_3Re_3(CO)_{12}$, and $H_4Re_4(CO)_{12}$ are presented in Figure 2 and their ionization energies and relative band areas tabulated (Tables II and III). No decomposition of the clusters in the gas phase was observed, except for $H_4Re_4(CO)_{12}$, for which the presence of free CO was detected after a period of 2 h. The recording temperatures and count rates obtained for each of these spectra are given in Table IV.

Discussion

In order to assign the PE spectra of these compounds, we use a fragment molecular orbital analysis of the cluster to obtain the number and symmetries of the occupied molecular orbitals (MO), anticipating at least one PE band for each occupied MO. Assignments are then made by comparison of the spectra of the cluster compounds with those of some mono- and dinuclear transition-metal carbonyls, where spectral assignments are unambiguous, and characteristic IE regions and intensity variations have been identified. Examination of the spectra of $M(CO)_6$ (M = Cr, Mo, or W)[18] and $M_2(CO)_{10}$ (M = Mn or Re)[19] has revealed several features.

(i) Ionization of t_{2g} electrons in the octahedral hexacarbonyls occurs in the region 8–9 eV. The related e_1, e_2, and e_3 ionization bands occur between 8.3 and 9.1 eV for $Mn_2(CO)_{10}$ and between 8.5 and 9.6 eV for $Re_2(CO)_{10}$. In both cases an additional a_1 metal–metal bonding orbital ionization occurs at a slightly lower energy (8.02 eV (Mn) and 8.07 eV (Re)).

(ii) The main band is due to ionization of the 5σ and 1π carbonyl electrons and occurs between 13 and 17 eV. This is followed by a band due to CO 4σ ionization at ca. 18 eV.

(iii) The bands attributable to ionization of metal d electrons increase in relative intensity on changing from He I to He II radiation; they also gain in relative intensity on passing from a first- to a third-row transition element, when the He I spectra are compared.

(iv) The a_1 band in $M_2(CO)_{10}$, which is associated with a metal–metal bonding orbital, shows a larger increase in relative intensity with photon energy than do the e_1, e_2, and e_3 bands, which are associated with delocalized orbitals involved in metal CO back bonding. It is noteworthy that the two categories of metal localized MO are forbidden to mix on symmetry grounds in this instance.

The He I spectra of each of the clusters $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Os_6(CO)_{18}$, and $Co_4(CO)_{12}$ show a band, or series of bands, between 7 and 11 eV, separated by approximately 2 eV from a more intense broad peak. This latter peak has a maximum in the region of 15 eV but often has, in addition,

(10) Muetterties, E. L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 545.
(11) Muetterties, E. L.; Rhodin, T. N.; Bond, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.
(12) Lauher, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 2604.
(13) Plummer, E. W.; Salaneck, W. R.; Miller, J. S. *Phys. Rev. B* **1978**, *18*, 1673.
(14) Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1967**, 1238.
(15) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859.
(16) Bor, G.; Sbrignadello, G.; Mercati, F. *J. Organomet. Chem.* **1972**, *46*, 357.
(17) The error of the IE values for $Ru_3(CO)_{12}$ is ±0.2 eV owing to spectral shift with time.

(18) Higginson, B. R.; Lloyd, D. R.; Burroughs, P.; Gibson, D. M.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2*, **1973**, *69*, 1659.
(19) Higginson, B. R.; Lloyd, D. R.; Evans, S.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2*, **1975**, *71*, 1913.

Table II. Peak Area Data for $Ru_3(CO)_{12}$ (I), $Os_3(CO)_{12}$ (II), $H_2Os_3(CO)_{10}$ (III), $H_4Os_4(CO)_{12}$ (IV), and $H_3Re_3(CO)_{12}$ (V)

band	I He I	I He II	II He I	II He II	III He I	III He II	IV He I	IV He II	V He I	V He II
A					1.37	1.53	2.84	3.59	2.03	1.81
B	}1	1	}1	1					4.27	4.24
C							}13.56	13.71	}5.99	4.03
D	}2.8	2.9								
E			}3	2.65	13.30	18.08	}5.97	6.79	5.30	2.96
F									}78.41	82.55
G							}8.58	4.13		
H							77.05	80.78		24.42
I					}3.73	0.92		21.32		
J								1.54		
K					}67.59	65.65				
L										
M						19.82				

Table III. Ionization Energy Data for Some Metal Hydrido Carbonyl Clusters

$H_2Os_3(CO)_{10}$	$H_4Os_4(CO)_{12}$	$H_3Re_3(CO)_{12}$	$H_4Re_4(CO)_{12}$	assignt
7.86 (A)	8.08 (A)			M-M
8.57 (B)				
	8.95 (B)			
8.92 (C)	9.48 (C)	8.45 (A)	8.38 (A)	"t_{2g}"
9.44 (D)	10.40 (D)	8.81 (B)	8.62 (B)	
9.72 (E)	10.65 (E)	9.29 (C)	9.80 (C)	
10.21 (F)	11.26 (F)	9.58 (D)	10.44 (D)	
10.56 (G)				
10.95 (H)				
12.07 (I)	12.15 (G)	11.89 (E)	12.57 (E)	M⌒H⌒M
12.76 (J)	12.43 (H)			
14.09 (K)	15.08 (I)	13.62 (F)	14.82 (F)	$-CO, 5\sigma + 1\pi$
15.16 (L)		14.84 (G)		
18.26 (M)	18.22 (J)	18.12 (H)	17.83 (G)	$-CO, 4\sigma$
	19.10 (K)			

Table IV

compd	probe temp, °C	count rate, s^{-1} He I	He II
$Ru_3(CO)_{12}$	70-100	10^3	3×10^2
$Os_3(CO)_{12}$	120-132	2×10^3	$(3-4) \times 10^2$
$Os_6(CO)_{18}$	175-188	10^3	3×10^2
$Co_4(CO)_{12}$	50	3.5×10^3	
$H_2Os_3(CO)_{10}$	96-110	4×10^3	$(3-4) \times 10^2$
$H_4Os_4(CO)_{12}$	156-158	10^3	$(3-4) \times 10^2$
$H_3Re_3(CO)_{12}$	123-127	8×10^2	10^2
$H_4Re_4(CO)_{12}$	170	4×10^2	10^2

a clearly visible lower energy shoulder. The He II spectra, where they have proved possible to measure, show a very similar band profile to those observed with the use of He I radiation and in addition a high-energy peak at ~18 eV. By analogy with the monomeric and dimeric carbonyl systems, the bands below 11 eV may be assigned to ionization of essentially metal-localized electrons and those above 13 eV to ionizations of electrons in CO-based MO's.

The gas-phase spectra show strong resemblances to the solid-state spectra[13] but reveal more fine structure. The spectrum of condensed $Co_4(CO)_{12}$ reported by Plummer et al.[13] is unusual in that it has a medium intensity band centered at ~10.5 eV, which is absent in the gas-phase spectrum, and, for which, there is no counterpart in other binary carbonyl systems. The singular occurrence of this band (and the well-established difficulties associated with obtaining pure surfaces) suggest that it may originate from some surface impurity.

The hydrido carbonyl cluster compounds have spectra with more structure than is observed for the binary carbonyl

clusters. Their spectra are subdivided into three regions: (i) a series of bands below 11–11.5 eV; (ii) a broad relatively low-intensity band between 11.5 and 13 eV; (iii) broad intense bands at energies above 13 eV. These latter bands are assigned to ionizations of electrons localized on the carbonyl ligands.

Comparison of the spectra of $H_3Re_3(CO)_{12}$ and $Os_3(CO)_{12}$, which are isoelectronic, reveals that the low-energy bands of $Os_3(CO)_{12}$, (A, B, and C) are absent in $H_3Re_3(CO)_{12}$, having been replaced by a broad band centered at ca. 12 eV. This observation suggests assignment of the latter band to ionization from the rhenium–hydrogen bridge bonds, which is consistent with the appearance of bands in this region in all the hydrido carbonyl cluster compounds. Further confirmation of this general assignment is obtained from intensity considerations. The bands in region ii suffer significant intensity loss in the He II spectra, which can be accounted for by hydrogen localization, as the cross section of the hydrogen 1s orbital is known to drop considerably at this photon energy.[20] The comparison between $Os_3(CO)_{12}$ and $H_3Re_3(CO)_{12}$ also suggests that the low-energy bands, A, B, and C in the spectrum of the former, may be associated with the metal–metal bonds of the cluster, and as in the binary metal carbonyls, this class of orbital may ionize at a lower energy than those metal orbitals primarily involved in back-donation to the carbonyl ligands.

These PE results clearly suggest that the metal–metal and metal–hydrogen–metal bonds are essentially localized. This property has been used to develop a general topological approach for hydrido cluster compounds, which was described in an earlier publication.[3] After these general considerations, we now proceed to a more detailed assignment of the various cluster compounds.

$M_3(CO)_{12}$. An $M(CO)_4$ unit in this cluster may be regarded as a fragment of an $M(CO)_6$ octahedron. It has been proposed[4] that this fragment has three filled orbitals which correspond approximately to the t_{2g} set of an octahedral molecule and, at higher energies, to two singly occupied orbitals (for an iron group metal) of a_1 and b_2 symmetry, whose radial characteristics are such that they permit effective bonding with the corresponding orbitals of the other $M(CO)_4$ fragments in the triangle. The similarity between these frontier orbitals and the frontier orbitals of the methylene fragment (CH_2) has led to these fragments being described as *isolobal* and suggests that the molecular orbitals of the $M_3(CO)_{12}$ molecule should closely resemble those of cyclopropane. The molecular orbital diagram for $M_3(CO)_{12}$ (Figure 3) is derived from extended Hückel calculations of Schilling and Hoffmann[21] that have indicated that the $2e'$ and $2a_1'$ molecular orbitals, which are

(20) Langhoff, P. W.; Corcoran, C. T.; Sims, J. S.; Weinhold, F.; Glover, R. W. *Phys. Rev. A* **1976**, *14*, 1042.

(21) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.
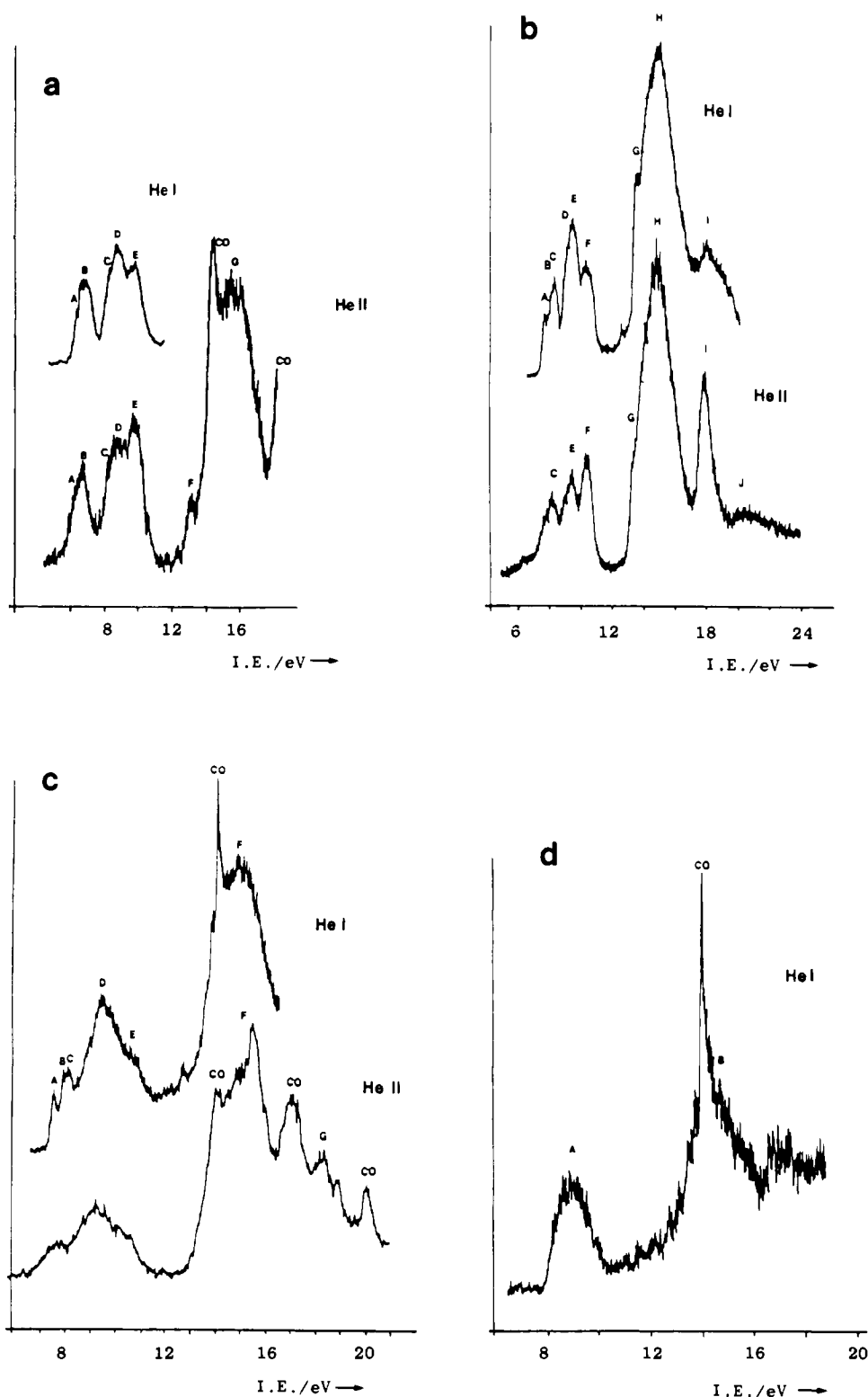
Figure 1. He I and He II photoelectron spectra for $Ru_3(CO)_{12}$ (a), $Os_3(CO)_{12}$ (b), $Os_6(CO)_{18}$ (c), and $Co_4(CO)_{12}$ (d).

responsible for the primary bonding interactions in the cluster, bear a strong resemblance to the Walsh molecular orbitals of cyclopropane[22] but are inverted with respect to the latter. This arises because the a_1 orbital lies at lower energy than the b_2 orbital in methylene,[23] whereas the reverse is predicted for the $M(CO)_4$ fragment. These calculations have also indicated significant interactions between the t_{2g}-like orbitals of the

$M(CO)_4$ fragments and suggest the possibility of mixing between these orbitals and the higher lying $2e'$ and $2a_1'$ orbitals.

The d-band region of $Os_3(CO)_{12}$ shows more structure than that of $Ru_3(CO)_{12}$. This is consistent with the larger ligand field splittings and spin–orbit (SO) coupling of the heavier metal atom. There is, however, a clear correspondence between the two spectra indicating that they have a common assignment. The spectrum of $Os_3(CO)_{12}$ can be divided between bands A + B + C and D + E + F; the relative areas, which are given in Table II, suggest that A + B + C account for 6 of the metal electrons whereas D + E + F account for 18 of

(22) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.
(23) Jorgensen, W. L.; Salem, L. "The Organic Chemists' Book of Orbitals", Academic Press: New York, 1973; p 62.
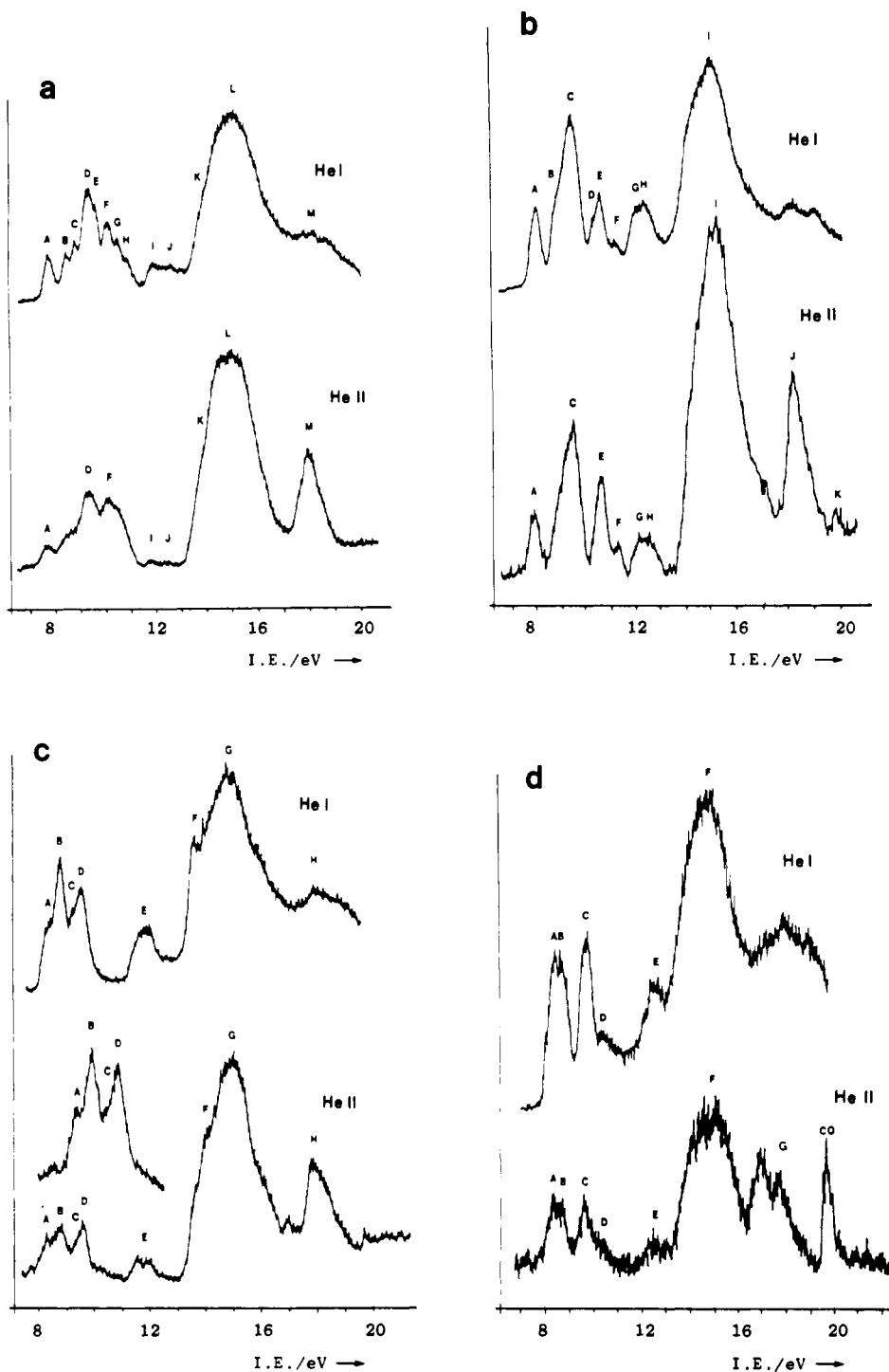
Figure 2. He I and He II photoelectron spectra for $H_2Os_3(CO)_{10}$ (a), $H_4Os_4(CO)_{12}$ (b), $H_3Re_3(CO)_{12}$ (c), and $H_4Re_4(CO)_{12}$ (d).

them. This is compatible with the division of the molecular orbitals between the cluster bonding orbitals $2a_1'$ and $2e'$ and the "t_{2g}" sets. Intensities again suggest that band A should be assigned to the $2a_1'$ orbital and bands B + C to the $2e'$ orbital. Bands B + C in $Os_3(CO)_{12}$ show a splitting that can reasonably be assigned to spin–orbit coupling, which would be expected for ionization from an e orbital. SO splitting of the t_{2g} band has been observed for $W(CO)_6$. Band D shows an intensity loss in the He II spectrum, as expected for orbitals back-bonding to CO relative to metal–metal bonding orbitals. Although the ratio (A + B + C):(D + E + F) varies little with photon energy, from the band profiles it may be seen that bands A, B + C, and F show relative increases in intensity when the radiation is changed from He I to He II. Thus it appears that the orbitals associated with these bands have high

metal content. As is evident from the MO diagram (Figure 3) the $2a_1'$ and $2e'$ cluster orbitals are of the same symmetry as some of the orbitals arising from interaction of the t_{2g} sets. The intensity changes are consistent with the MO scheme if interaction between these orbitals of similar symmetry is significant and band F is assigned to the $1a_1'$ and $1e_1'$ orbitals. This is consistent with the He II (A + B + C):(D + E + F) intensity pattern insofar as it can be assessed.

$H_3Re_3(CO)_{12}$. The structure of $H_3Re_3(CO)_{12}$[24] is closely related to those of $Ru_3(CO)_{12}$,[25] and $Os_3(CO)_{12}$;[26] the three

(24) Huggins, D. K.; Fellmann, W.; Smith, J. M.; Kaesz, H. D. *J. Am. Chem. Soc.* **1964**, *86*, 4841.

(25) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

M₃(CO)₁₂ H₃Re₃(CO)₁₂ 3 × H⁺
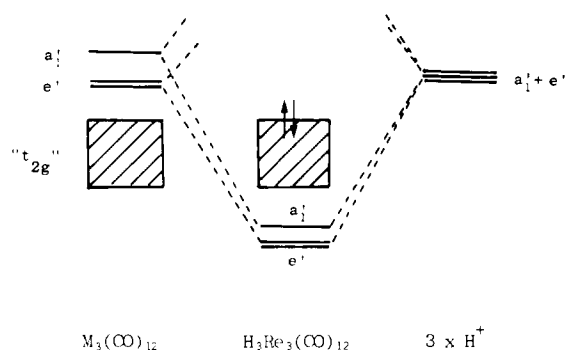
Figure 3. Schematic molecular orbital diagram for $M_3(CO)_{12}$ and $H_3M_3(CO)_{12}$ derived from extended Hückel molecular orbital calculations: Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

hydrogens bridge the edges of the Re_3 triangle. The molecular orbital scheme for $H_3Re_3(CO)_{12}$ is most readily derived from that of $Os_3(CO)_{12}$ by considering the effect of moving a proton from each of the osmium nuclei to edge bridging positions. The Walsh type orbitals (a_1' and e_1') of the M_3 ring experience greater stabilization than the back-bonding "t_{2g} type" orbitals as these are the orbitals closest to the protons. The resultant MO scheme is shown in Figure 3.

In an analogous fashion we will base our interpretation of the PE spectrum of $H_3Re_3(CO)_{12}$ on our assignment of the $Os_3(CO)_{12}$ spectrum. The chief difference between the two spectra, as noted above, is the appearance of a band at ca. 12 eV in the spectrum of the bridging hydrogen compound. We assign this band to ionizations from the $1a_1'$ and $1e'$ orbitals. In the He II spectrum two separate band maxima are apparent in this region (the Re–H bond in $HRe(CO)_5$ ionizes at 10.59 eV[27]). The remainder of the spectrum is assigned by correlating A and B of the Re spectrum (8.45 and 8.81 eV) with D and E of the Os spectrum (9.24 and 9.60 eV) and C and D of the Re spectrum (9.29 and 9.58 eV) with F of the Os spectrum (10.44 eV). The "t_{2g}" ionizations undergo the expected drop in energy on passing from Os to Re; in $Re_2(CO)_{10}$ they occur in the region 8.5–9.6 eV. The PE spectrum is therefore consistent with the MO scheme proposed.

$M_4(CO)_{12}$. $Co_4(CO)_{12}$ contains both terminal and bridging carbonyl groups.[28] Its PE spectrum shows a broad featureless d band from which little may be deduced about the nature of the cluster binding.

$Ir_4(CO)_{12}$ relates more closely to the tetrahedral hydrido carbonyl clusters studied in that it only possesses terminal carbonyl groups. We attempted to obtain a gas-phase spectrum of this compound, but thermal decomposition occurred. However, Plummer et al.[13] have obtained a spectrum of the valence-band region in the solid state. For a molecular solid, the valence-band solid state spectrum is dominated by the orbital structure of the molecule and strongly resembles that of the gas-phase species. The bands are broader and are shifted to lower ionization energies because of extramolecular relaxation in the solid state. We can therefore obtain some idea of the gas-phase spectrum from the solid-state spectrum of $Ir_4(CO)_{12}$. This shows three bands in the region 7–10.5 eV, the central one being the most intense.

The MO scheme for $M_4(CO)_{12}$ (Figure 4) is built up by combining four $M(CO)_3$ units, which have frontier orbitals of a_1 and e symmetry: these combine in T_d symmetry to give cluster bonding orbitals of symmetry a_1, e, and t_2. The a_1 orbital has high density at the center of the tetrahedron and

the e and t_2 orbitals bonding density along the edges of the tetrahedron.

By analogy with $Os_3(CO)_{12}$, we suggest that the lowest band of $Ir_4(CO)_{12}$ is likely to be associated with cluster bonding orbitals.

$H_4Re_4(CO)_{12}$. The structure of $H_4Re_4(CO)_{12}$ is closely related to that of $Ir_4(CO)_{12}$ with the hydrogen atoms bridging the centers of the four tetrahedral faces. $H_4Re_4(CO)_{12}$ however has four fewer electrons than $Ir_4(CO)_{12}$.

The four hydrogen 1s orbitals span the representations a_1 + t_2 of the T_d symmetry group; therefore they are predicted to interact with the $M_4(CO)_{12}$ cluster orbitals of a_1 and t_2 symmetry. The e cluster orbital will be unoccupied in $H_4Re_4(CO)_{12}$. An MO scheme is shown in Figure 4.

The low-energy region of the PE spectrum of $H_4Re_4(CO)_{12}$ (Figure 2) can be assigned in accordance with this scheme. No metal–metal ionizations are observed at low energy as predicted. Bands A–D are attributed to ionization from the orbitals involved in M → CO back-donation. Band E is assigned to the metal–hydrogen bonding levels.

$H_4Os_4(CO)_{12}$. This molecule provides an interesting contrast to $H_4Re_4(CO)_{12}$. It has D_{2d} symmetry with four edge bridging hydrogens and is, of course, isoelectronic with $Ir_4(CO)_{12}$. Consideration of the interactions of the hydrogen 1s orbitals in a D_{2d} disposition with the $M_4(CO)_{12}$ cluster orbitals leads to an MO scheme given in Figure 4. Unlike $H_4Re_4(CO)_{12}$, $H_4Os_4(CO)_{12}$ possesses two metal–metal bonding orbitals as well as four metal–hydrogen bridging orbitals.

These predictions are mirrored in the low-energy region of the PE spectrum of $H_4Os_4(CO)_{12}$ where a small band, A is observed below the main d band, which increases in relative intensity in the He II spectrum. This is assigned to the a_1 and b_2 metal–metal bonding orbitals. Bands B–F are assigned to "t_{2g}"-type orbitals. The observed relative intensity A:(B + C):(D + E + F) of 1:3.8:1.9 in the He II spectrum is close to orbital degeneracies of this assignment, 2:12, lending it further support. Further bands, G + H, which show a drop in intensity relative to the bands A–F on passing from He I to He II, are assigned to M–H–M bridging orbitals a_1, b_1, and e.

$H_2Os_3(CO)_{10}$. The molecular structure of $H_2Os_3(CO)_{10}$ is not so closely related to a binary cluster as the other hydrido derivatives studied. In the solid state the molecule has C_{2v} symmetry with the two hydrogen atoms bridging one edge of the metal triangle. An MO description may be arrived at either by combination of various fragments $(Os(CO)_4 + 2 × Os(CO)_3 + 2 × H)$ or by descent of symmetry from Os_3-$(CO)_{12}$. A possible scheme is presented in Figure 5. The crucial orbitals for cluster binding are the Os–Os bonding orbitals of a_1 and b_2 symmetry, which the scheme predicts to be the highest occupied orbitals, and the two Os–H–Os bridging orbitals of a_1 and b_1 symmetry, which should lie below the "t_{2g}"-type orbitals.

The photoelectron spectrum (Figure 2) of $H_2Os_3(CO)_{10}$ shows bands at 12.07 and 12.76 eV which are assigned to the a_1 and b_1 M–H–M bridging orbitals. They drop in relative intensity in the He II spectrum as expected. Comparison of the low-energy region with that of $Os_3(CO)_{12}$ is informative. Both have very similar first ionization energies for bands A; also bands B occur in comparable positions. The relative intensity of band B in the He I spectrum of $H_2Os_3(CO)_{10}$ is less than that of $Os_3(CO)_{12}$. We therefore assign bands A and B to the a_1 and b_2 M–M bonding orbitals. The remaining d bands are assigned to back-bonding orbitals.

$Os_6(CO)_{18}$. The spectrum of this carbonyl cluster is shown in Figure 1. It is no longer possible to distinguish cluster ionization from those due to back bonding orbitals, though the He I/He II intensity variations do suggest more metal

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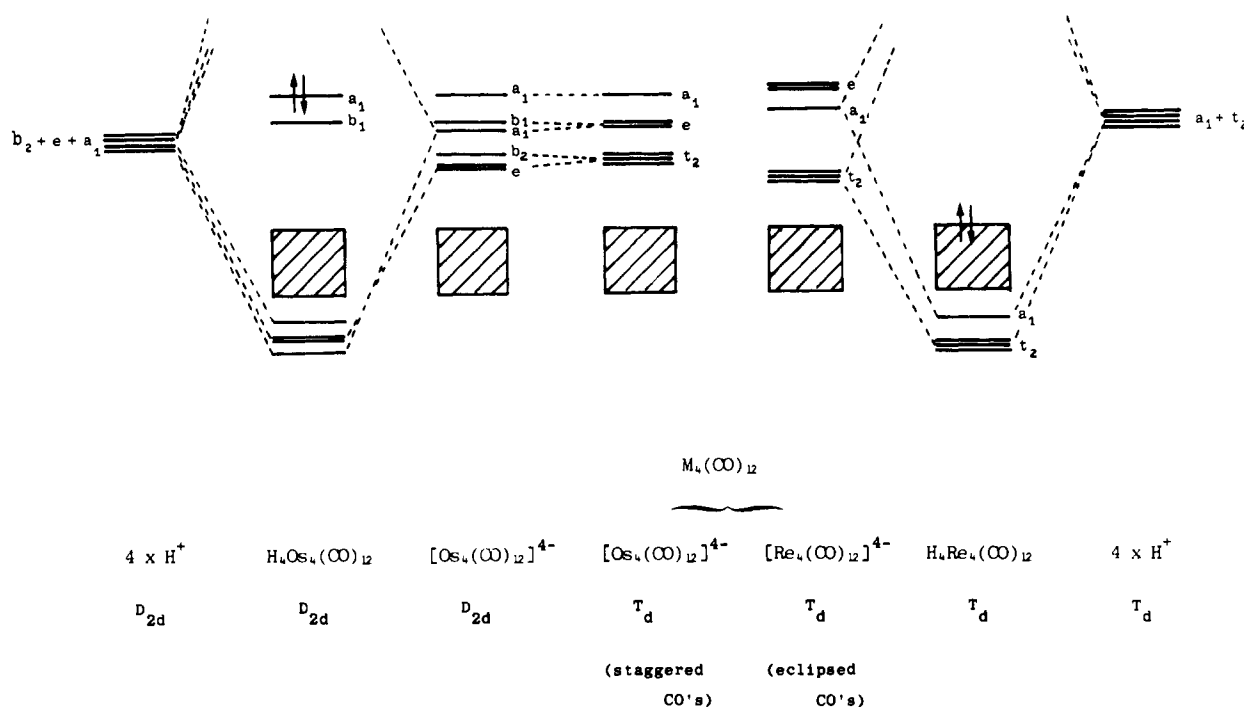
Figure 4. Schematic representations of the molecular orbitals for tetrahedral carbonyl and hydrido carbonyl clusters derived from extended Hückel molecular orbital calculations: Hoffmann, R.; Schilling, B. E. R.; Bau, R.; Kaesz, H. D.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1978**, *101*, 6088.
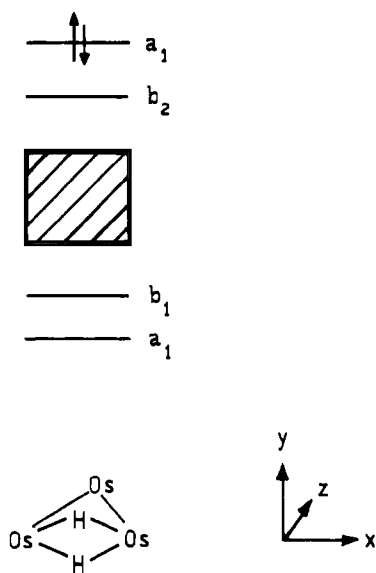
Figure 5. Proposed qualitative molecular orbital diagram to describe the bonding in $H_2Os_3(CO)_{10}$.

localization at the low- and high-energy sides of the d band. The first ionization energy of 7.6 eV is only 0.3 eV lower than that of $Os_3(CO)_{12}$. Thus doubling the cluster size has had only a small effect on the first ionization energy.

General Considerations

Various general points emerge from the examination of these PE spectra and their assignment.

The PE spectra of the metal carbonyl and metal hydrido carbonyl clusters are consistent with MO schemes derived by using fragment analyses. Ionizations associated with metal–metal bonding orbitals occur at lower ionization energies than those associated with metal–carbonyl back-bonding orbitals.

Bonding in metal hydrogen bridges are best described by two-electron polycenter bonds, e.g., two-electron three-centered bond for M–H–M and two-electron four-centered bond for

$M-H<^M_M$. These multicenter orbitals have a high degree of localization on the hydrogen. Ionization energies of electrons occupying this type of orbital lie in the region of 11.5–13 eV, a considerably higher range than that for M–M bonding orbitals (7.5–9 eV). The role of the heteroatoms in these clusters is twofold: one, to provide some of the electrons necessary for cluster binding, and, two, to stabilize to a marked degree the cluster molecular orbitals.

We have provided limited evidence that as the cluster size increases the first ionization energy is lowered; however, in the cases of $Os_3(CO)_{12}$ and $Os_6(CO)_{18}$, a doubling of the number of metal atoms only lowers the first ionization energy by 0.3 eV.

Measurement of the ionization energy of a gaseous molecule and the work function of a solid is a very direct experimental method of comparing the two different systems. We propose it as one criterion for comparing metal clusters with metal surfaces. By this criterion, metal carbonyl clusters in the gas phase, which show adiabatic first ionization energies in the range 7.2–7.5 eV, differ considerably from the corresponding metals, which show much lower work functions (Ru 4.71 eV, Os 4.83 eV).[29]

Perhaps a comparison more relevant to the "cluster-surface analogy" is between the binding energies of condensed metal carbonyls and work functions of metal surfaces onto which CO has been adsorbed. Here the discrepancy is smaller but difficult to estimate. Binding energies for condensed molecular solids are lower than for gaseous molecules because of extramolecular relaxation effects. Precise estimates of the magnitude of these effects are not readily obtained because of calibration problems with molecular solids, but values between 0.6 eV and 1.4 eV have been found for molecular carbonyls:[13] comparison of our results on $Os_3(CO)_{12}$ and those of Plummer et al.[13] give binding energy differences of 0.8 eV. Measurements of the change in work function on CO adsorption are few. A value of ca. 0.2 eV has been quoted for CO on platinum.[30] Various measurements have been made

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for CO on ruthenium, giving values ranging between 0.5 eV and 1.8 eV;[31] there is evidence that the value obtained depends on the surface and on the degree of coverage.[31c] The wide range of estimates makes this an ineffective comparison, but if we take the uppermost value for the work function of ruthenium with CO adsorbed (6.5 eV), this still lies below Plummer's values for the first binding energy of $Ru_3(CO)_{12}$ (6.7 or 7.25 eV depending on calibration procedure).

The first ionization energies of metal cluster compounds are dominated by the electron-withdrawing properties of the ligand. For example, the rhenium halide cluster Re_3Cl_9 has a first ionization energy of 9.15 eV,[1c] which may be compared with a value of 8.45 eV for $H_3Re_3(CO)_{12}$. Cyclopentadienyl ligands on the other hand appear to enhance the electron "richness" of a cluster; for example, $H_4Co_4(\eta\text{-}C_5H_5)_4$ has a first IE of 5.7 eV, which may be compared with a value of 8.9 eV for $Co_4(CO)_{12}$.[32]

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A Theoretical Investigation of the Ground and Core Hole States of [Cu(NH₃)₂CO]⁺ and [Cu(NH₃)₃CO]⁺. Models for the Reversible Binding of CO to Cu(I) Complexes

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Nonempirical LCAO–MO–SCF computations have been carried out on the ground and core hole states of [Cu(NH₃)₂CO]⁺ and [Cu(NH₃)₃CO]⁺ (and the associated fragments) as models for Cu(I) complexes which reversibly bind CO. For the diamino complex, which serves as a model for [Cu(en)CO]⁺ and [Cu(hm)CO]⁺, the computations show that a linear ∠Cu–C–O arrangement is preferred, the computed coordination energy for carbon monoxide being –8.1 kcal mol⁻¹. The bond overlap populations suggest that for both [Cu(NH₃)₂CO]⁺ and [Cu(NH₃)₃CO]⁺ (which serves as a model for [Cu(dien)CO]⁺ and [Cu₂(hm)₃(CO)₂]²⁺) the CO bond length should be somewhat shorter than for the free ligand, as is observed experimentally. For the isolated ions, the ΔSCF calculations suggest significant shifts between the core levels for the model systems; however, the lattice potential in the solid state reduces the computed shifts somewhat.

Introduction

The study of the interaction of small molecules with crystallographically oriented metal surfaces has been an area of expanding activity on both experimental and theoretical fronts in recent years.[1] The importance of such studies derives from the fundamental insight they provide for model systems for heterogeneous catalysis, and such studies have received considerable impetus in recent years from developments in instrumental surface science.[1,2]

An area of equal importance is that encompassed by the activation of small molecules by complex formation in homogeneous media, and of particular interest is the reversible fixation of small molecules.[3] Such studies are of relevance to homogeneous catalysis and its synthetic applications as well as the specialized field of bioinorganic chemistry.[4]

While the focus of interest of both theoretical and experimental surface science studies has naturally been in the area of relevance to heterogeneous catalysis,[1,2] the very significant advances which have been made in recent years in the reversible binding of small molecules to metal complexes suggests that the time is opportune to investigate such systems by using techniques which have proved so successful in the heterogeneous catalysis field.

A significant fraction of the published literature in the past few years has detailed studies on the interaction of simple molecules such as carbon monoxide with both simple crystal and polycrystalline metal surfaces, and the mode of bonding of chemisorbed CO on a variety of metals is now reasonably well understood.[5] Comparatively few studies of this genre have been made, however, with transition metals at the end of the first-row series (viz., Cu and Zn) although such elements are of considerable importance in bioinorganic chemistry.[4]

Recently, however, data have become available on simple copper(I) complexes which reversibly bind CO in homogeneous media.[6] The complexes which have been isolated by Floriani and co-workers[6] are of two structural types, and a remarkable feature is the relative stability toward dissociation of the complexes in the solid state. As has previously been pointed out, prior to the work by Floriani and co-workers copper(I) carbonyls, although of considerable interest, had largely remained, because of their lability and propensity for disproportionation, chemical curiosities.[7,8] The possibility of employing Cu(I) mediated transfer of CO to organic substrates[9]

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