this electronic configuration if a ligand is bound. Ligand bonding will reduce the number of available orbitals to five and force a pairing of spins. At low coverage the CO could bridge two or even three Ni atoms without forcing such changes in electronic configuration since available orbitals from the two or three Ni atoms would be shared.

Edge Atoms. The exterior atoms of most of the known cluster compounds are not representative of fundamental crystallographic habit planes, but are similar to edge or vertex atoms of crystals. They would be characteristic of high-order stepped or channeled surfaces, which have atoms with fewer nearest neighbors. Table II lists the site analyses for the various edge and vertex atoms found in clusters **1–6.** Generally the number of CVMOs is inversely proportional to the number of nearest neighbors. The highest number of orbitals, 7.43, is found for site I of the square pyramid **5**, which has three nearest neighbors. The edge atom E of the D_{2h} structure with seven nearest neighbors has 6.23 available orbitals and is thus similar in bonding capacity to a (100) atom.

The atoms with fewer than six nearest neighbors are representative of the atoms of the known small cluster compounds. These atoms have the bonding capacity and the geometry needed for multiple ligand bonding. In homogeneous catalysis most fundamental steps involve multiple ligand bonding.[19] The situation is likely to be the same in heterogeneous systems. Edge atoms and the atoms of high-order stepped or channeled surfaces have more orbitals available for ligand bonding. They should thus be the sites of greatest reactivity.

Summary

The number of cluster valence molecular orbitals located on any given metal atom of a cluster or an infinite lattice is dependent upon the site geometry. In cluster-compound chemistry this number of available orbitals will determine compound stoichiometries and structures. In analysis of bulk metals this number of available orbitals can be used to determine electron configurations and the bonding capabilities of surface atoms. Discrete stoichiometric cluster compounds are good models for chemisorption onto bulk metals and we believe that the simple qualitative molecular orbital approach presented here can help establish their detailed relationship.

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References and Notes

(1) Part 1 in this series: J. W. Lauher, *J. Am. Chem. Soc*, **100**, 5305 (1978).
(2) E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, in press.
(3) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); **85**, 451 (1976).
(4) J. H. Sinfelt, *Acc. Chem. Res.*, **10**, 15 (1977).
(5) P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).
(6) R. B. King, *Prog. Inorg. Chem.*, **15**, 287 (1972).
(7) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Am. Chem. Soc.*, **93**, 3073 (1971).
(8) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lypscomb, *ibid.*, **36**, 2179, 3489 (1962); 37, 2872 (1962).
(9) C. Kittel, "Introduction to Solid State Physics", 4th ed., Wiley, New York, 1976.
(10) N. F. Mott and H. Jones, "Theory of the Properties of Metals and Alloys", Oxford University Press, London, 1936; Dover Publications, New York (reprint), 1958.
(11) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p 398.
(12) D. H. Martin, "Magnetism in Solids", Iliffe Books, London, 1967, p 30.
(13) S. H. Charap in "Magnetism and Metallurgy", Vol. 1, A. E. Berkowitz and E. Kneller, Eds., Academic Press, New York, 1969, p 37.
(14) J. Donohue, "The Structures of the Elements", Wiley, New York, 1974, p 215.
(15) S. Martinengo, G. Ciani, A. Sironi, and P. Chini, *J. Am. Chem. Soc.*, **100**, 7097 (1978).
(16) V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinego, and W. M. Anker, *J. Chem. Soc., Chem. Commun.*, 859 (1975).
(17) V. G. Albano, M. Sansoni, P. Chini, S. Martinego, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 970 (1976).
(18) J. L. Vidal, R. A. Fiato, L. A. Cosby, and R. L. Pruett, *Inorg. Chem.*, 17, 2574 (1978).
(19) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

A Study of the Bonding in Transition Metal Carbonyl Hydrides

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Abstract: The metal $2p_{3/2}$, carbon 1s, and oxygen 1s binding energies of the gaseous molecules $Co_2(CO)_8$, $HCo(CO)_4$, $Fe(CO)_5$, $H_2Fe(CO)_4$, $Mn_2(CO)_{10}$, and $HMn(CO)_5$ have been measured by X-ray photoelectron spectroscopy. From qualitative considerations of the binding energy shifts on going from the transition-metal carbonyls to the corresponding carbonyl hydrides, it is concluded that the hydrogen atoms in the carbonyl hydrides are negatively charged. By application of the potential model, approximate hydrogen atom charges of −0.3, −0.8, and −0.75 are calculated for $H_2Fe(CO)_4$, $HMn(CO)_5$, and $HCo(CO)_4$, respectively.

Introduction

It has been well established that chemical shifts in core electron binding energies are related to changes in atomic charges.[1,2] In general, an increase in core binding energy corresponds to an increase in the positive charge of the atom. However, it is recognized that changes in binding energy are not always entirely due to changes in atomic charge; sometimes they are at least partly caused by changes in the electronic relaxation energy associated with core ionization.[3,4] Fortunately, this relaxation energy is essentially the same in compounds which have similar molecular structures in the vicinity of the core-ionizing atom. For example, the calculated[5] C 1s relaxation energies for CH_4 (15.89 eV) and CH_3F (15.92 eV) are quite similar, whereas that for CO (11.91 eV) is considerably different from both values. Hence core binding energies *for a series of carefully chosen molecules with similar*

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Table I. Core Binding Energies and Line Widths of Transition Metal Carbonyl Hydrides[a]

compd	oxygen 1s		carbon 1s		metal $2p_{3/2}$	
	E_B, eV	fwhm, eV	E_B, eV	fwhm, eV	E_B, eV	fwhm, eV
$Co_2(CO)_8$	539.78 (9)	1.50 (16)	293.40 (5)	1.27 (6)	786.34 (6)	1.31 (15)
$HCo(CO)_4$	540.06 (8)	1.14 (21)	293.94 (6)	1.35 (6)	786.86 (7)	1.24 (16)
$Fe(CO)_5$	539.96 (2)	1.38 (5)	293.71 (5)	1.27 (13)	715.79 (4)	1.25 (9)
$H_2Fe(CO)_4$	540.17 (3)	1.38 (9)	294.15 (6)	1.14 (14)	715.97 (6)	1.18 (14)
$Mn_2(CO)_{10}$	539.57 (7)	1.45 (5)	293.28 (3)	1.13 (6)	647.01 (3)	1.02 (10)
$HMn(CO)_5$	539.95 (3)	1.46 (8)	293.80 (4)	1.21 (10)	647.46 (5)	1.14 (11)

[a] Uncertainties in the last digit are given parenthetically.

structures and similar electronic properties can be reliably interpreted in terms of atomic charges. In this study we have measured the gas-phase core electron binding energies of some first-row transition-metal carbonyls and carbonyl hydrides. We believe that the measured shifts in binding energy on going from a carbonyl to a closely related carbonyl hydride, even when as small as 0.1 eV (which is greater than our usual uncertainty in absolute binding energy), are significant with respect to changes in valence electron distribution.

The main object of this research was to determine the polarity of the metal-hydrogen bond in transition metal carbonyl hydrides. It has been pointed out[6] that the $M(CO)_4$ groups in trigonal bipyramidal $HCo(CO)_4$ and octahedral $H_2Fe(CO)_4$ are somewhat distorted toward tetrahedral configurations, as would be expected if the hydrogen atoms had charges intermediate between H^+ and H^-. Unfortunately, it is not yet possible to interpret these distortions quantitatively, in terms of atomic charges. The fact that metal hydride complexes are acids in aqueous solution[7] suggests that the hydrogen atoms in these compounds are positively charged. Indeed the dipole moments of several platinum metal hydride complexes have been interpreted in terms of slightly positive hydrogen ligands.[8] On the other hand, the unusually high magnetic shielding of the protons in hydride complexes, observed in proton magnetic resonance spectra, was originally ascribed to the protons being "buried" in the metal orbitals.[9] However, theoretical studies[10,11] have shown that the observed magnetic shielding does not require short M-H bonds, and structural studies have shown that M-H bond distances correspond to more or less normal covalent bonds.[12,13] Recent ab initio calculations indicate that, in tetrahedral transition metal hydrides of the type MH_4, the hydrogen atoms are negatively charged.[14] Clearly further work related to the polarity of the M-H bond is needed.

Results and Discussion

Qualitative Interpretation. The core binding energies determined in this study are listed with the corresponding full widths at half maximum (fwhm) in Table I. On going from $Co_2(CO)_8$ to $HCo(CO)_4$, the cobalt $2p_{3/2}$ binding energy increases by 0.52 eV, corresponding to a significant increase in the positive charge on the cobalt atom. We may look upon $Co_2(CO)_8$ as a dimer of an electroneutral $Co(CO)_4$ group. Because the positive charge on the remaining cobalt atom increases when one of the $Co(CO)_4$ groups is replaced by a hydrogen atom, we conclude that the hydrogen atom withdraws electron density from the $Co(CO)_4$ group and hence is negatively charged. It should be noted that the carbon 1s and oxygen 1s binding energies of $HCo(CO)_4$ are also higher than those of $Co_2(CO)_8$, corresponding to more positively charged (less negatively charged) carbon and oxygen atoms in the hydride molecule. This change probably represents a reduction in the metal→CO back-bonding caused by the reduced electron density on the cobalt atom. It is significant that the carbon 1s and oxygen 1s peaks of $Co_2(CO)_8$ are symmetric, with no evidence of bridging CO groups.[15,16] This result indicates that nonbridged isomers are the principal species in the gas phase at room temperature.[17,18]

The increases in the manganese $2p_{3/2}$, carbon 1s, and oxygen 1s binding energies on going from $Mn_2(CO)_{10}$ to $HMn(CO)_5$ can be explained exactly as in the case of the cobalt compounds. Unfortunately, in the case of $H_2Fe(CO)_4$ there is no compound of formula $Fe_2(CO)_8$ with which a comparison can be made, and even the known dinuclear carbonyl, $Fe_2(CO)_9$, is nonvolatile, thus precluding a gas-phase XPS measurement. However, we can make a comparison with $Fe(CO)_5$. The replacement of one of the CO groups of $Fe(CO)_5$ by two hydrogen atoms causes all the core binding energies to increase. If we accept the reasonable proposition that the iron atom in $Fe(CO)_5$ is positively charged,[19] then these changes in binding energy indicate that the hydrogen atoms in $H_2Fe(CO)_4$ are negatively charged. It appears that the withdrawal of electron density from the iron atom by the hydrogen atoms of $H_2Fe(CO)_4$ is greater than the net electron withdrawal by the average CO group of $Fe(CO)_5$.

The study of the bonding in carbonyl hydrides may be approached in yet another way. Consider the molecules $Ni(CO)_4$, $HCo(CO)_4$, and $H_2Fe(CO)_4$. The cobalt compound can be considered as the product of the hypothetical transfer of a proton from the nickel atom nucleus of $Ni(CO)_4$ to a coordination site on the resulting Co atom. The analogous transfer of a second proton yields the iron compound. The question is, how much valence electronic charge does the proton carry with it during each of these transfers? We believe that this question can be answered in a qualitative sense by consideration of the change in the oxygen 1s binding energy, which is a measure of the metal→CO back-bonding.[20] The oxygen 1s binding energies are essentially constant[21] in the series $Ni(CO)_4$, $HCo(CO)_4$, $H_2Fe(CO)_4$, indicating that the degree of back-bonding is practically constant. We believe that, if the metal atom charges were the same in these three compounds, the metal valence electrons would be held least tightly in $H_2Fe(CO)_4$ and most tightly in $Ni(CO)_4$ because of the increase in effective nuclear charge with increasing atomic number. Thus, if the metal atom charges were the same, we would expect back-bonding to decrease on going from $H_2Fe(CO)_4$ to $Ni(CO)_4$. Hence the observed constancy in back-bonding indicates that the metal atomic charges become more positive on going from $Ni(CO)_4$ to $H_2Fe(CO)_4$. Consequently, we conclude that the hydrogen atoms in $HCo(CO)_4$ and $H_2Fe(CO)_4$ are negatively charged. We can consider the pair of molecules $Fe(CO)_5$ and $HMn(CO)_5$ in the same way that we have considered $Ni(CO)_4$, $HCo(CO)_4$, and $H_2Fe(CO)_4$. Again, because the oxygen 1s binding energies are essentially identical, we conclude that the hydrogen atom in $HMn(CO)_5$ is negatively charged.

Quantitative Interpretation. The binding energy data may be used in conjunction with the potential model[2,22,23] for binding energy shifts to calculate the actual atomic charges in the molecules under study. We make the assumption that the change in electronic relaxation energy on going from a carbonyl to a carbonyl hydride of the same metal is negligible.

We also make the approximation that the carbon and oxygen atomic charges in the equatorial and axial CO groups of $Fe(CO)_5$ and in the cis and trans CO groups of $H_2Fe(CO)_4$ are identical. Hence the change in binding energy of an iron, carbon, or oxygen atom on going from $Fe(CO)_5$ to $H_2Fe(CO)_4$ can be represented by an expression of the type

$$\Delta E_B = k(Q_2 - Q_1) + \Delta V$$

where k is a constant which is essentially the average r^{-1} value for the valence electrons of the atom,[24-26] Q_1 and Q_2 are the atomic charges in $Fe(CO)_5$ and $H_2Fe(CO)_4$, respectively, and ΔV is the change in the potential energy at the atom due to the electrostatic charges of the other atoms in the molecules[27-31] (essentially a linear combination of Q_i/r_i values). Thus we can write three such equations: one for iron, one for carbon, and one for oxygen. We can also write two more equations which are essentially statements of electroneutrality for the two molecules. The resulting five equations involve seven unknown Q's: the Q_1 and Q_2 values for Fe, C, and O and the charge of the hydrogen atom in $H_2Fe(CO)_4$, Q^H. To make it possible to solve for all seven charges, we have added two more equations. These equations are $Q_1{}^{Fe} = 1.039$ and $Q_1{}^C = 0.174$, which simply specify that the atomic charges in $Fe(CO)_5$ are those calculated in an ab initio study of Baerends and Ros.[19] In the case of $Mn_2(CO)_{10}$ and $HMn(CO)_5$, our method of calculation was very similar; in the absence of ab initio atomic charges for $Mn_2(CO)_{10}$ we assumed that the metal, carbon, and oxygen atom charges were the same as in $Fe(CO)_5$. In the case of $Co_2(CO)_8$ and $HCo(CO)_4$, separate calculations were made using two different assumptions; one assumption was that the metal and carbon atom charges were the same as in $Fe(CO)_5$, and the other was that the carbon and oxygen atom charges were the same as in $Fe(CO)_5$.

The results of the calculations are presented in Table II. Some idea of the uncertainties of the charges can be obtained from the two sets of data for $Co_2(CO)_8$ and $HCo(CO)_4$. Depending on which assumption was made regarding the atomic charges in $Co_2(CO)_8$, the calculated value of Q^H changed by about 12%. The uncertainties in the charge due to uncertainties in the binding energies were estimated by determining the effects on the calculated charges of changing one of the binding energies by 0.1 eV. The results were essentially independent of which binding energy was changed; Q^M changed by 1-5%, Q^C and Q^O changed by 30-50%, and Q^H changed by 10-15%.

We estimate that the calculated hydrogen atom charges of ca. −0.3, −0.8, and −0.75 for $H_2Fe(CO)_4$, $HMn(CO)_5$, and $HCo(CO)_4$, respectively, have overall uncertainties of ±30%. Hence the quantitative interpretation of the data definitely confirms our qualitative conclusion that the hydrogen atoms in these compounds are negatively charged. The much smaller negative charge for the hydrogen atom in $H_2Fe(CO)_4$ is probably significant. The smaller value may be due to the presence of two hydrogen atoms in the molecule as opposed to one; two hydrogen atoms would not be expected to be able to withdraw twice as much electron density from a metal carbonyl group as one hydrogen atom.

It should be emphasized that the preceding interpretations, both qualitative and quantitative, are based on the assumption of no change in relaxation energy on going from a species such as $M_2(CO)_{2n}$ to the corresponding species $HM(CO)_n$ or from $Fe(CO)_5$ to $H_2Fe(CO)_4$. Obviously this assumption is only an approximation which perhaps can be tested in a future theoretical study. However, we believe that the consistency of our present conclusions (all indicating negative hydrogen atoms) lends credence to our basic assumptions.

Experimental Section

Compounds. All of the syntheses were carried out under an inert atmosphere or in a vacuum line. The samples were stored at −78 °C in the dark until they were ready to be studied in the X-ray photoelectron spectrometer. Mass spectra were obtained with a Granville-Phillips Spectrascan 400 spectrometer. Melting points were observed by slowly warming the samples in a cold 2-propanol bath in an unsilvered Dewar. Decacarbonyldimanganese(0) was purchased from Pressure Chemical Co., $Fe(CO)_5$ from ROC/RIC Chemical Corp., and $Co_2(CO)_8$ from Pressure Chemical Co. These compounds decompose only to carbon monoxide and materials having negligible vapor pressure at room temperature; therefore the unpurified materials were satisfactory for the XPS studies.

Table II. Atomic Charges Calculated from Binding Energies Using the Potential Model

compd	Q^H	Q^M	Q^C	Q^O
$Fe(CO)_5$		$\underline{1.039}$[a]	$\underline{0.174}$	−0.382
$H_2Fe(CO)_4$	−0.334	1.342	0.212	−0.380
$Mn_2(CO)_{10}$		$\underline{1.039}$	$\underline{0.174}$	−0.382
$HMn(CO)_5$	−0.814	1.568	0.211	−0.361
$Co(CO)_8$		$\underline{1.039}$	$\underline{0.174}$	−0.434
$HCo(CO)_4$	−0.799	1.625	0.221	−0.428
$Co_2(CO)_8$		0.831	$\underline{0.174}$	$\underline{-0.382}$
$HCo(CO)_4$	−0.706	1.342	0.217	−0.377

[a] Underlined values were arbitrarily fixed, as described in the text.

Hydridopentacarbonylmanganese(I), prepared by the method of King,[32] melted at −25 °C (lit. −24.6 °C). Hydridotetracarbonylcobalt(I), prepared by the method of Sternberg et al.,[33] melted at −33 °C (lit. −33 °C). Dihydridotetracarbonyliron(II), prepared by the method of Seel,[34] melted at −70 °C (lit. −70 °C).

The spectra were obtained using a GCA/McPherson ESCA-36 spectrometer with a magnesium X-ray anode. Previous attempts to obtain vapor-phase spectra of relatively unstable metal carbonyls such as $Co_2(CO)_8$ using the old Berkeley spectrometer were thwarted by the large pressures of CO gas produced in the sample chamber by the decomposition of the compounds. This problem was eliminated by use of a better inlet system and a cryopump. The samples were held at room temperature or lower in a glass flask which was connected to a gas sample cell through a 1.5-in. Varian Viton vacuum valve and a 1-ft length of stainless steel tubing having a minimum i.d. of ¾ in. This relatively large diameter connecting tubing allowed us to maintain a low pressure in the tubing, thus avoiding wall-catalyzed decomposition of the carbonyl. A copper sheet cryopanel (capable of being cooled to 10 K) extended into the space between the electron exit slit of the gas cell and the entrance to the electrostatic analyzer chamber. A hole in the cryopanel allowed the electrons to pass from the slit to the analyzer chamber. The cryopanel condensed out most of the CO and metal carbonyl vapor which effused through the slit; thus it also helped to maintain a low pressure in the X-ray chamber and the analyzer chamber. By manipulation of the valve between the sample and the gas cell, the flow of sample vapor was adjusted so that the ionization gauge near the turbopump registered a pressure increment of about 2×10^{-7} Torr over the base pressure. The protective shielding around the X-ray chamber was extended toward the pumping system to minimize contamination of the anode and cathode by sample vapors. The window of the X-ray chamber was sealed with 0.25-mil aluminum foil, and the window of the gas cell was sealed with 0.05-mil aluminum foil.

We assumed that the true binding energy of a photoline was equal to a quadratic function of the nominal value of the binding energy as obtained from the spectrometer.[35,36] The three quadratic parameters were calculated from the nominal binding energies of the Ne 1s, Ne 2s, and N_2 1s photolines and reliable literature values[37] of these binding energies (870.37, 48.47, and 409.93 eV, respectively). In general these three calibration spectra were run immediately before each compound to establish the quadratic parameters. The N_2 1s spectrum was run again either immediately after the compound or simultaneously with the compound to determine whether any change[38,39] in the calibration had occurred. Usually the two N_2 1s nominal binding energies agreed to within 0.02 eV. Whenever these values differed by more than 0.05 eV, the data for the run were discarded and the entire run was repeated. In the case of the O 1s and C 1s spectra of $Co_2(CO)_8$, it was possible to determine the binding energies by directly measuring the chemical shift relative to the CO peak due to the partial decomposition of the $Co_2(CO)_8$. Using the literature values[40] of 296.24 and 542.57 eV for the C 1s and O 1s binding energies, respectively, of CO, the calculated $Co_2(CO)_8$ binding energies always agreed with those calculated from the quadratic function to better than ±0.05 eV.

Several O 1s spectra, C 1s spectra, and metal $2p_{3/2}$ spectra were obtained for each compound. The measured binding energies within each set differed by no more than 0.05 eV. The reported values are average values.

Binding energies were determined from the spectra by a least-squares fitting of the data to Gaussian curves.[39] The uncertainties in the binding energies and fwhm values given in Table I correspond to twice the standard deviations of the least-squares fittings except in a few cases where these values were exceeded by the average deviations of separate runs, in which cases the latter values are given.

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References and Notes

(1) K. Siegbahn et al., "ESCA; Atomic, Molecular and Solid-State Structure Studied by Means of Electron Spectroscopy", Almqvist and Wiksells AB, Uppsala, 1967.
(2) K. Siegbahn et al., "ESCA Applied to Free Molecules", North-Holland Publishing Co., Amsterdam, 1969.
(3) U. Gelius and K. Siegbahn, *Faraday Discuss. Chem. Soc.*, **54**, 257 (1972).
(4) U. Gelius, *Phys. Scr.*, **9**, 133 (1974).
(5) D. W. Davis and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.*, **3**, 137 (1974).
(6) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975); R. Hoffmann, J. M. Howell, and A. R. Rossi, *J. Am. Chem. Soc.*, **98**, 2484 (1976).
(7) A table of p*K* values is given by R. A. Shunn in "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, New York, 1971, p 239.
(8) J. Chatt and G. J. Leigh, *Angew. Chem., Int. Ed. Engl.*, **17**, 400 (1978). From a consideration of both dipole moments and X-ray photoelectron spectroscopic data, these authors draw the conclusion that the hydrido group is generally neutral to slightly negative.
(9) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959).
(10) A. D. Buckingham and P. J. Stephens, *J. Chem. Soc.*, 2747, 4583 (1964).
(11) L. L. Lohr, Jr., and W. N. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964).
(12) B. A. Frenz and J. A. Ibers in "Transition Metal Hydrides", E. L. Muetterties, Ed., Marcel Dekker, New York, 1971, Chapter 3, p 33.
(13) H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, **72**, 231 (1972).
(14) D. M. Hood, R. M. Pitzer, and H. F. Schaefer, unpublished calculations.
(15) We have previously shown[16] that the oxygen 1s spectrum of gaseous $Co_4(CO)_{12}$ can be readily resolved into two peaks separated by about 1.25 eV, corresponding to the bridging and terminal CO groups in this molecule.
(16) S. C. Avanzino and W. L. Jolly, *J. Am. Chem. Soc.*, **98**, 6505 (1976).
(17) On the basis of attempts to deconvolute the O 1s band into two peaks, we believe that the percentage of bridging CO groups in $Co_2(CO)_8$ vapor is less than about 10% and therefore that the percentage of bridged $Co_2(CO)_8$ molecules is less than about 40%. This conclusion is consistent with the findings of Sweany and Brown,[18] whose infrared spectra of $Co_2(CO)_8$ molecules quenched from room temperature into a frozen matrix showed the presence of comparable amounts of the bridged isomer and two nonbridged isomers.
(18) R. L. Sweany and T. L. Brown, *Inorg. Chem.*, **16**, 415 (1977).
(19) E. J. Baerends and P. Ros [*J. Electron Spectrosc. Relat. Phenom.*, **7**, 69 (1975)] have calculated the following atomic charges for $Fe(CO)_5$: $Q^{Fe} = 1.039$, $Q^{C}_{axial} = 0.173$, $Q^{C}_{eq} = 0.174$, $Q^{O}_{axial} = -0.360$, $Q^{O}_{eq} = -0.396$.
(20) W. L. Jolly, S. C. Avanzino, and R. R. Rietz, *Inorg. Chem.*, **16**, 964 (1977).
(21) The oxygen 1s binding energy of $Ni(CO)_4$ is 540.11 eV (H. W. Chen and W. L. Jolly, unpublished work).
(22) M. E. Schwartz in "Electron Spectroscopy", D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, and American Elsevier, New York, 1972, p 605.
(23) T. A. Carlson, "Photoelectron and Auger Spectroscopy", Plenum Press, New York, 1975, pp 167–174.
(24) Values of $\langle 1/r \rangle$ for carbon and oxygen were taken from ref 25. For carbon, the value for an sp^3 hybrid orbital was used. For oxygen, the value for an orbital with 20% s character was used. The rounded *k* values in units of electronic charge per eV were 23.0 and 32.5, respectively. For the transition metals, the *k* value was assumed to be that for carbon times the ratio of covalent radii of carbon and the transition metal, i.e., 23.0 (0.77/1.15) = 15.4. The covalent radius for the transition metal (1.15 Å) was obtained by subtracting the covalent radius[26] for double-bonded carbon (0.67 Å) from the typical metal-carbon distance in the metal carbonyls (1.82 Å).
(25) C. C. Lu, T. A. Carlson, F. B. Malik, T. C. Tucker, and C. W. Nestor, Jr., *At. Data*, **3**, 1 (1971).
(26) W. L. Jolly, "The Principles of Inorganic Chemistry", McGraw-Hill, New York, 1976, p 36.
(27) The structural data for $HCo(CO)_4$ and $H_2Fe(CO)_4$ were taken from E. A. McNeill and F. R. Scholer, *J. Am. Chem. Soc.*, **99**, 6243 (1977).
(28) The structural data for $HMn(CO)_5$ were taken from S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, **8**, 1928 (1969).
(29) The structural data for $Mn_2(CO)_{10}$ were taken from L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).
(30) The structural data for $Fe(CO)_5$ were taken from B. Beagley and D. W. J. Cruickshank, *Acta Crystallogr., Sect. B*, **25**, 737 (1969).
(31) For $Co_2(CO)_8$, the C–O and Co–C distances were assumed to be the same as in the terminal CO groups of $Co_2(CO)_8$ [G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964)], and the Co–Co distance was estimated from data given by R. C. Ryan and L. F. Dahl, *J. Am. Chem. Soc.*, **97**, 6904 (1975).
(32) R. B. King, "Organometallic Syntheses", Vol. 1, Academic Press, New York, 1965, pp 158–160.
(33) H. W. Sternberg, I. Wender, and M. Orchin, *Inorg. Synth.*, 5, 190 (1949).
(34) F. Seel in "Handbook of Preparative Inorganic Chemistry", Vol. II, 2nd ed., G. Brauer, Ed., Academic Press, New York, 1965, pp 1752–1753.
(35) It has been shown by M. F. Ebel[36] that this type of a relation is to be expected for our type of spectrometer when relativistic effects are accounted for.
(36) M. F. Ebel, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 213 (1976).
(37) G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 295 (1973).
(38) Dr. Jürgen Kopf devised a program for the PDP8 computer of the ESCA-36 spectrometer which can quickly determine the peak binding energy from the accumulated count data. Binding energies calculated by this simple program generally differ by less than 0.03 eV from the least-squares values obtained from the more complicated program GAMET.[39] Of course, the GAMET program was used to calculate the binding energies which we report in this paper. Copies of the PDP8 program can be obtained by request from W. L. Jolly.
(39) The computer program GAMET was written by C. E. R. Lederer at the Lawrence Berkeley Laboratory, Berkeley, Calif.
(40) S. R. Smith and T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 45 (1976).