

BONDING IN INORGANIC COMPOUNDS:
A STUDY BY X-RAY PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

Core electron binding energies were measured for a variety of inorganic and organometallic compounds using gas-phase X-ray photoelectron spectroscopy (XPS). The atomic charge distributions in these molecules are deduced from the binding energies, often leading to a better understanding of the bonding in these compounds.

The XPS spectra of fifteen volatile tin compounds were recorded. The tin binding energies are well correlated by the "transition state" point-charge potential model equation using atomic charges calculated by the CHELEQ electronegativity equalization method. The core binding energies of some tris β -diketonates of Al(III), V(III), Cr(III), and Fe(III) were measured. The large shifts observed for the Al 2p energies are believed to be caused mainly by changes in the molecular electrostatic potential at the Al atom. The data suggest that the metal d orbitals are not significantly involved in the bonding.

The oxygen 1s XPS spectra of gaseous $\text{CH}_3\text{Mn}(\text{CO})_5$, $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$, and $\text{Co}_4(\text{CO})_{12}$ can be readily resolved into separate peaks due to bridging and terminal carbonyl groups. The O 1s binding energy of a bridging carbonyl group is lower than that of a terminal carbonyl group, which is consistent with recent structural assignments of O 1s spectra of

carbon monoxide adsorbed on metal surfaces. The O 1s spectrum of $\text{Fe}(\text{CO})_5$ obtained with a high-resolution spectrometer is deconvoluted into two peaks characteristic of the axial and equatorial carbonyl groups in the molecule. The C 1s spectrum of $\text{Fe}(\text{CO})_5$ consists of a single symmetric peak. The carbonyl ligand core binding energies of transition-metal carbonyl complexes are sensitive to differences in the metal-to-CO ligand bonding. Both C 1s and O 1s carbonyl binding energies correlate well with average C-O stretching force constants or average C-O stretching frequencies. The metal and carbonyl binding energies in a series of pentacarbonylmanganese complexes $\text{LMn}(\text{CO})_5$ are a good measure of the relative electronegativities of the ligands L. However, these binding energies could not be used to determine the relative σ - and π - acceptor abilities of the ligands L. Strong shake-up satellite lines are observed in the core-level spectra of the carbonyl ligand atoms of $\text{LMn}(\text{CO})_5$, and they are attributed to a process involving metal-to-ligand charge-transfer transitions.

High-quality X-ray photoelectron spectra have been obtained for compounds dissolved in glycerin solutions, and aqueous solutions were converted into glycerin solutions which gave good XPS spectra of the solutes. The technique appears promising as a future analytical application of X-ray photoelectron spectroscopy.

The shifts in the binding energies of oxygen, chlorine, and carbon atoms in some isoelectronic isostructural compounds can be explained in terms of simple trends in atomic charges. However, the fluorine 1s binding energies for some fluoro compounds of silicon, phosphorus, sulfur, and chlorine show unusual shifts which suggest that

hyperconjugation is important in the bonding of these compounds. The core binding energies of the cyclic phosphazenes $(\text{NPF}_2)_3$, $(\text{NPF}_2)_4$, $(\text{NPCl}_2)_3$, $(\text{NPCl}_2)_4$, and $[\text{NP}(\text{CH}_3)_2]_4$ were measured. On going from $(\text{NPF}_2)_4$ to $(\text{NPF}_2)_3$ or from $(\text{NPCl}_2)_4$ to $(\text{NPCl}_2)_3$, the binding energies increase by only 0.22 eV, or less, suggesting that the degree of π bonding is similar in the trimers and tetramers. The core binding energies of chlorine monofluoride were remeasured and were found to differ considerably from previously published values. Atomic charges in this molecule are estimated from binding energies using the point-charge potential model.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS or ESCA) has proven to be a useful tool for the chemist interested in the electronic structure of matter. This thesis represents an attempt to apply gas-phase X-ray photoelectron spectroscopy to inorganic and organometallic compounds. From XPS measurements the atomic charge distribution in these molecules can be deduced leading to a better understanding of the bonding.

The usual quantity derived from an XPS experiment is the core electron binding energy E_B . In a typical gas-phase XPS experiment, sample vapors are introduced into the irradiation chamber of the spectrometer by means of a continuous-flow system. Here the sample is irradiated by the characteristic $Mg K_{\alpha 1,2}$ X-ray line resulting in the photo-ejection of electrons spanning a range of kinetic energy E_k . The photoelectrons enter a dispersion analyzer capable of resolving the different electron energies into a kinetic energy spectrum. This is accomplished by means of electrostatic or magnetic focusing of the beam so that electrons of a given E_k are spatially separated from electrons of different energies. The electrons are detected and recorded as a function of their kinetic energy. The peaks in a spectrum correspond to photoelectrons from a given core level whose binding energy

$$E_B = h\nu - E_k \quad (1)$$

is calculated from the known X-ray photon energy $h\nu$ and the measured kinetic energy of the photoelectrons.

The binding energy for a given core level in an isolated molecule is the total energy of the molecular core-ion (formed by the

photoionization process) minus the total energy of the ground state molecule:

$$E_B = E_{ion} - E_0 \quad (2)$$

In general, significant differences between E_{ion} and E_0 arise from the electronic contribution to the total energies ($E_{elec} + E_{vib} + E_{rot} + E_{trans}$) of the two species. The feature of the core binding energy of most interest to the chemist is the chemical shift observed from one compound to another. Binding energy shifts can often be interpreted in terms of differences in the ground-state valence electron distribution between molecules. By applying Koopman's Theorem, Eqn. (2) can be written as

$$E_B = (E_{ion}^{KT} - E_0) - E_R \quad (3)$$

where E_{ion}^{KT} is the total energy of the core-ion assuming that all orbitals remain "frozen" and do not relax upon the creation of a core hole, and E_R is a correction term to account for this relaxation which does indeed occur. When Eq. (3) is used to describe binding energy shifts

$$\Delta E_B = \Delta(E_{ion}^{KT} - E_0) - \Delta E_R \quad (4)$$

the $\Delta(E_{ion}^{KT} - E_0)$ term relates to differences in ground-state electronic structure between compounds. The point-charge potential model is often used to approximate $\Delta(E_{ion}^{KT} - E_0)$ in terms of physical quantities more significant to the chemist. According to the model, changes in the quantity $(E_{ion}^{KT} - E_0)$ are due to changes in the electrostatic potential felt by the core electron due to differences in the distribution of valence electrons. The model assumes a spherical electron distribution

about each nucleus so that the potential arises from the net charge on each atom located at the respective nucleus. The expression for binding energy shift now includes the useful quantity atomic charge:

$$\Delta E_B = k\Delta Q_i + \Delta V_i - \Delta E_R \quad (5)$$

where Q_i is the ground-state atomic charge on the core-ionizing atom,

$V_i (= \sum_{j \neq i} Q_j/R_{ij})$ is the potential due to the other charged atoms in the molecule, and k is the binding energy change attributed to a unit change in atomic charge.

Many workers in this field have applied the relationship of Eqn. (5) to chemical systems in different degrees of sophistication. Quite often one equates binding energy shifts solely to changes in atomic charge on the ionizing atom, neglecting the potential term and the relaxation energy correction. Other more elaborate studies include one or both of these second-order terms which often give more satisfactory results for a structurally-unrelated series of compounds. In this work binding energy shifts have been interpreted in different circumstances using one of these three levels of theoretical sophistication.

The greater part of this thesis is comprised of eight articles which have been published in the chemical literature over the past three years. Each of the articles has been co-authored by me and contains research that I have conducted in my doctoral studies. In order that the reader may appraise my contribution to the work contained in the publication reprints, the following table is included in this introduction.

Percentage Involvement in:

Chapter	Synthesis of Compounds	XPS Experiments	Calculations	Drafting of Article
I	100%	100%	75%	75%
II	0%	25%	100%	20%
III	100%	100%	*	25%
IV	10%	10%	90%	20%
V	0%	0%	100%	75%
VI	100%	100%	100%	90%
VII	*	100%	*	90%
VIII	15%	20%	*	10%
IX	*	60%	100%	20%
X	*	75%	100%	90%

* Not applicable.

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(reprints removed, titles below)

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AN X-RAY PHOTOELECTRON SPECTROSCOPY STUDY OF VOLATILE TIN COMPOUNDS*

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CORE BINDING ENERGIES OF SOME METAL β -DIKETONATES AND β -DIKETONES IN THE VAPOR PHASE

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A Study of Bridging and Terminal Carbonyl Groups in Transition Metal Complexes by X-Ray Photoelectron Spectroscopy

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Use of Oxygen 1s Binding Energies and Multiplicity-Weighted C-O Stretching Frequencies to Measure Back-Bonding in Transition Metal-Carbonyl Complexes

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Distinguishing Axial and Equatorial Carbonyl Groups in Iron Pentacarbonyl by ESCA

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A Study of Pentacarbonylmanganese Complexes
by Gas-Phase X-Ray Photoelectron Spectroscopy

Manganese(I) forms a large number of stable six-coordinate carbonyl complexes of the type $\text{LMn}(\text{CO})_5$ which may be considered as complexes of $\text{Mn}(\text{CO})_5^+$ with various anionic ligands, L. The metal-ligand bonding interactions in these compounds are thought to be a mixture of both σ - and π -bonds. The σ -bonding orbitals are formed by the overlap of filled σ orbitals on the ligands L or CO with the empty orbitals of σ -symmetry on the central metal atom. The π -bonding orbitals are formed when filled metal $d\pi$ orbitals overlap with empty orbitals of π -symmetry on the ligands L or CO.¹ The effect of a ligand L upon the electron density distribution in the rest of the molecule will depend upon the σ - and π -bonding ability of the ligand.

We have measured the core electron binding energies of twelve compounds of the type $\text{LMn}(\text{CO})_5$ by gas-phase X-ray photoelectron spectroscopy in an attempt to study the bonding characteristics of the ligands L. Only two of these compounds ($\text{L} = \text{H}^-$, CH_3^-) have been previously studied in the gas phase by XPS.² There appear in the literature a number of theoretical³⁻⁶ and UV photoelectron spectroscopy^{7,8} studies involving hydrido-, halogeno-, methyl-, and perfluoromethylpentacarbonylmanganese.

Core Binding Energy Shifts

The binding energy data are shown in Table I and Table II. The compounds are listed in the order of their increasing manganese binding energies, which span a range of ~ 1 eV. Note that the trends in the

carbonyl carbon and oxygen binding energies both parallel the trend in the manganese binding energy. Figures 1 and 2 show plots of carbon and oxygen binding energies vs. manganese binding energy for the compounds studied. $E_B(\text{C } 1s)$ and $E_B(\text{O } 1s)$ show a high correlation with $E_B(\text{Mn } 2p_{3/2})$ within the indicated experimental uncertainty. It is interesting that the carbon and oxygen binding energies increase by almost the same amount as the manganese binding energy. This does not mean that the carbon and oxygen charges change to the same extent as the manganese charge on going from one compound to the next. One can relate binding energy shifts to atomic charge changes by the potential model⁹

$$\Delta E_B = k\Delta Q + \Delta V \quad (1)$$

in which the $k\Delta Q$ term usually predominates. Since the magnitude¹⁰ of k for carbon ($k_C = 24.0 \text{ eV/e}$) and oxygen ($k_O = 27.2 \text{ eV/e}$) is greater than for manganese ($k_{Mn} = 11.7 \text{ eV/e}$), the binding energy data are consistent with the expected changes in electron distribution based on inductive effects, i.e., greater changes in the manganese charges than in the carbon or oxygen charges.

The manganese binding energies of our $\text{LMn}(\text{CO})_5$ series are in general accord with other indicators of the atomic charge on the manganese atom. Table III shows a group of compounds for which data from ionization potential measurements (UPS),^{7,8} molecular orbital calculations,³ and electronegativity estimates^{11,12} are available. In general, an increase in the manganese core binding energy and the manganese 3d ionization potential corresponds to the increased electronegativity of the ligand L and the decreased electron occupation for manganese orbitals.

Recent XPS studies^{13,14} by the authors were able to distinguish bridging and terminal carbonyl groups in transition metal complexes; however, terminally-bound axial and equatorial carbonyl groups were barely distinguishable even using a spectrometer with extremely high resolution. Separate peaks for the axial and equatorial CO ligands in $\text{LMn}(\text{CO})_5$ compounds are beyond the resolution capabilities of our instrument. All one can hope to observe is a "weighted-average" spectrum for the one axial and the four equatorial carbonyl ligands. This is an unfortunate situation, because axial and equatorial ligand binding energies should be affected differently by the σ and π bonding abilities of L, as are the axial and equatorial CO stretching force constants.¹⁵ One way to distinguish the differences in σ - and π -ability of ligands-- short of determining separate axial and equatorial CO binding energies-- would involve a careful inspection of the trends in the manganese, carbon, and oxygen binding energies. For instance, if the CO binding energies were influenced more by a ligand's π - rather than σ -ability than was the manganese binding energy, one might observe marked deviations of certain points from the linear correlations of carbonyl vs. manganese binding energies. The points for $\text{ClMn}(\text{CO})_5$ and $\text{BrMn}(\text{CO})_5$, in which chlorine and bromine are good σ -acceptors but have no π -acceptor ability, would lie below a line through the compounds in which the π -acceptor ability of a ligand paralleled its σ -acceptor ability. The binding energy plot in Figure 1 barely suggests this effect for chlorine and bromine, but we believe no conclusions should be drawn from these minor deviations. Unfortunately, we are not able to differentiate the σ vs. π bonding abilities of L by measuring core binding energies in

these compounds.

Carbonyl force constants are sensitive to electron density back-bonded into the π^* CO orbitals. Hall and Fenske⁶ have shown that their calculated electron occupancies of the carbonyl 5σ and 2π orbitals correlate with CO force constants. The carbonyl ligand binding energies should also be influenced by electron density transferred from the metal to the CO ligands. Consequently, one might expect CO ligand binding energies to correlate with CO force constants. Our $\text{LMn}(\text{CO})_5$ carbon and oxygen binding energies do indeed correlate with the weighted-average¹⁶ CO force constants (correl. coeff. = 0.97 (C), 0.96 (O)), and it is not surprising that the manganese binding energies likewise correlate with $k_{\text{avg}}^{\text{CO}}$ (correl. coeff. = 0.98) in view of the observed proportionality of the three core-level binding energies. The correlations for carbon, oxygen, and manganese are illustrated in Figures 3, 4, and 5, respectively.

Recently we have illustrated the relationship between CO ligand O 1s binding energies and the degeneracy-weighted average infrared C-O stretching frequency for a more general series of metal carbonyl complexes.¹⁷ Weighted-average CO force constants are directly proportional to degeneracy-weighted average C-O stretching frequencies;¹⁴ consequently, O 1s binding energies should correlate with the former as well as with the latter. We now extend the series of metal carbonyl complexes in Reference 17 to include most of our $\text{LMn}(\text{CO})_5$ compounds, and plot both the O 1s binding energy (Figure 6) and the C 1s binding energy (Figure 7) of the CO ligands against the weighted-average CO force constants. The correlation is equally good for either ligand atom.¹⁸ When one

considers the variety of transition elements, metal coordination numbers, and structurally-different ligands included in this series of compounds, the correlations for both oxygen and carbon are indeed remarkable.

Graham¹⁵ has proposed scales of relative σ - and π -acceptor character for a large number of ligands based on the differences in the *cis* and *trans* CO force constants in $\text{LMn}(\text{CO})_5$ compounds. Table IV lists Graham's σ and π parameters for ligands in some of the compounds we have studied. He calculated his parameters based on the following relationships:

$$\Delta k_{\text{cis}} = \sigma + \pi \quad (2)$$

$$\Delta k_{\text{trans}} = \sigma + 2\pi \quad (3)$$

We can re-express our E_B vs. $k_{\text{avg}}^{\text{CO}}$ correlations in terms of the relative amounts of σ -acceptor ability and π -acceptor ability of L required to describe the binding energy. Since

$$\Delta k_{\text{avg}}^{\text{CO}} = 0.20 \Delta k_{\text{trans}} + 0.80 \Delta k_{\text{cis}} \quad (4)$$

one substitutes Eqs. 2 and 3 into Eq. 4 to obtain

$$\Delta k_{\text{avg}}^{\text{CO}} = 2.2 (0.45\sigma + 0.55\pi) \quad (5)$$

Consequently, a simple rescaling of the abscissa allows one to express binding energy in terms of σ and π parameters. This is illustrated for the case of manganese in Figure 5. It is interesting that the manganese (or carbon, or oxygen) binding energy depends approximately equally¹⁹ upon the σ - and the π -acceptor abilities of the ligands L, assuming that Graham's definitions of σ and π are correct. This suggests that these binding energies are a good measure of the relative total electronegativity ($\sigma + \pi$) of the ligands L.

Shake up Satellite Structure

In many XPS spectra the primary photoline is accompanied by a number of high-binding-energy satellite lines which can be ascribed to electron shake-up.^{9,20} Shake-up is a multi-electron process involving the ejection of a core electron and the simultaneous excitation of a valence electron. Core electrons ejected from molecules undergoing this two-electron process will have less kinetic energy and, therefore, a higher binding energy than those from molecules involved in a one-electron process. In most transition metal complexes shake-up satellites are observed only on the metal levels. However, metal carbonyls are one of the few classes of compounds to exhibit shake-up in the ligand core level spectra as well. Shake-up structure in spectra of metal carbonyls has been studied in the solid state^{2,21-24} and in the gas phase,^{2,25} including compounds of the type $LMn(CO)_5$.

We also have observed intense shake-up satellites on the ligand levels of $LMn(CO)_5$ compounds. Figures 8 and 9 show the C 1s and O 1s regions of $HMn(CO)_5$. A single intense shake-up band ($I_s/I_p = 20-30\%$) is observed ~ 5.8 eV from the main photoline in both the carbon and oxygen spectra. This band has been fit to a single Gaussian curve, and spectral parameters for $HMn(CO)_5$ as well as other $LMn(CO)_5$ compounds are given in Table V. The energy difference (ΔE_s) between the shake-up band and the primary photoline varies from 5.2 to 5.8 eV for the C 1s and 5.1 to 5.8 eV for the O 1s, yet no trend can be recognized which shows any chemical significance. The carbon shake-up is more intense than the oxygen shake-up--the relative intensities centering around 28% for carbon and 20% for oxygen. There does not appear to be any statistical significance to

differences in carbon or oxygen shake-up intensity between compounds.

Bancroft et al,²⁵ studied shake-up satellites in the core levels of $M(CO)_6$ ($M = Cr, Mo, W$). They observed intense (20-30%) lines shifted 5-6 eV from the carbon and oxygen primary photolines which they assigned to a $2t_{2g} + 3t_{3g}$ electronic transition. This is a metal-to-ligand charge transfer transition involving the metal $d\pi$ orbitals and the π^* orbitals of the CO ligands. The shake-up bands we observe probably involve the same metal-to-ligand charge transfer process. Under C_{4v} symmetry the t_{2g} representation breaks down to b_2 and e . Therefore the transitions $7e(d_{xz}, d_{yz}) + 10e(\pi^*CO_{cis})$ and $7e(d_{xz}, d_{yz}) + 9e(\pi^*CO_{trans})$ along with $2b_2(d_{xy}) + 3b_2(\pi^*CO_{cis})$ are probably responsible for most of the intensity in the carbon and oxygen shake-up bands we observe.

To a first approximation ΔE_s should be equal to the energy of the corresponding electronic transition in the neutral molecule measured by UV spectroscopy. In the case of $LMn(CO)_5$ compounds whose electronic spectra have been reported,^{26,27} there is disagreement in the assignment of the observed spectral bands. However, the average energies of the UV charge-transfer transitions for some compounds in Table V are roughly similar to ΔE_s . In theory ΔE_s should be less than the energy of the neutral molecule excitation²⁸ since the π^*CO orbitals will relax more than the $d\pi$ orbitals upon core ionization of carbon or oxygen. Orbital relaxation may also explain the different intensities of the carbon and oxygen shake-up lines.²⁹

Experimental Section

Standard vacuum line and inert-atmosphere techniques were utilized in the preparation and handling of air-sensitive compounds. Infrared

spectra were recorded for cyclohexane solutions. Melting points were determined in capillaries sealed under nitrogen. Dimanganese decacarbonyl (Strem) was used as a starting material for most of the derivatives; the purity of $\text{Mn}_2(\text{CO})_{10}$ was verified by comparing its infrared spectrum with one in the literature. Manganese pentacarbonyl iodide was prepared by the addition of I_2 to a solution of $\text{NaMn}(\text{CO})_5$ in THF at room temperature. After removal of the solvent, the residue was placed on a vacuum line, and red-orange crystals condensed in a 0° trap. The infrared spectrum of $\text{IMn}(\text{CO})_5$ agreed with the literature.³⁰ Manganese pentacarbonyl chloride was prepared by the method of Abel and Wilkinson.³¹ Many attempts were made to characterize this compound by its infrared spectrum in cyclohexane solution,³⁰ but peaks attributable to $\text{Mn}_2(\text{CO})_8\text{Cl}_2$ were always present, along with the bands from the monomer. This is consistent with the findings of Bamford, et al³² that $\text{ClMn}(\text{CO})_5$ easily undergoes a thermal interconversion to $\text{Mn}_2(\text{CO})_8\text{Cl}_2$ in solution through the loss of CO. Consequently, the $\text{ClMn}(\text{CO})_5$ sample was characterized by means of its mass spectrum,^{33,34} from which any sign of $\text{Mn}_2(\text{CO})_8\text{Cl}_2$ impurity was absent. The $\text{BrMn}(\text{CO})_5$ (Strem) was identified by its IR spectrum.³⁰ Trichlorosilyl manganese pentacarbonyl and $\text{F}_3\text{SiMn}(\text{CO})_5$ were prepared and characterized as described in the literature.^{35,36} The derivatives $\text{CH}_3\text{COMn}(\text{CO})_5$ and $\text{CF}_3\text{COMn}(\text{CO})_5$ were prepared by the reaction of acetyl chloride or trifluoroacetic anhydride with $\text{NaMn}(\text{CO})_5/\text{THF}$; their melting points agreed with the literature.^{37,38} Methyl manganese pentacarbonyl and $\text{CF}_3\text{Mn}(\text{CO})_5$ were made by the decarbonylation of the corresponding acetyl derivatives.^{37,38} The $(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$ was prepared and characterized as described in the literature.³⁹ Manganese

pentacarbonyl hydride was prepared according to the literature;³⁸ it was redistilled just prior to the XPS measurement.

X-Ray Photoelectron Spectra

The gas-phase XPS spectra were measured on a GCA/McPherson ESCA 36 Photoelectron Spectrometer⁴⁰ using $Mg K_{\alpha}$ X-rays (1253.6 eV). Sample vapors were metered into the irradiation chamber through a glass-and-stainless steel manifold. For samples of low-volatility, a specially-designed stainless-steel inlet system was used such that sample vapors are delivered to the chamber through a short length of 2 cm diameter tubing. Sample spectra were calibrated with runs of reference gas levels of known binding energies:⁴¹ Ne 1s ($E_B = 870.37$ eV), N_2 , N 1s ($E_B = 409.93$ eV), Ar $2p_{3/2}$ ($E_B = 248.62$ eV), Ne 2s ($E_B = 48.47$ eV). The references used for a given compound are indicated in Table I. Binding energies were determined by a least-squares fitting of the data to either Gaussian or Lorentzian line shapes. The reported binding energies correspond to absolute free-molecule ionization potentials.

Table I. Core Binding Energies of Mn(CO)₅ Moiety.

Compound	Mn 2p _{3/2}		C 1s		O 1s	
	E _B , eV	FWHM, eV	E _B , eV	FWHM, eV	E _B , eV	FWHM, eV
(CH ₃) ₃ SnMn(CO) ₅ ^d	647.0(1) ^c	1.3(1)				
Mn ₂ (CO) ₁₀ ^a	647.01(3)	1.02(9)	293.28(3)	1.12(6)	539.57(7)	1.44(4)
CH ₃ COMn(CO) ₅ ^d	647.2(1)	1.2(1)	293.5(1)	1.5(1)	539.9(1)	1.5(1)
CH ₃ Mn(CO) ₅ ^a	647.30(5)	1.1(1)	293.62(7)	1.22(7)	539.91(7)	1.51(8)
HMn(CO) ₅ ^a	647.46(4)	1.1(1)	293.80(4)	1.2(1)	539.95(3)	1.46(8)
IMn(CO) ₅ ^b	647.73(3)	1.0(1)	294.05(3)	1.29(7)	540.30(3)	1.61(8)
Cl ₃ SiMn(CO) ₅ ^b	647.84(4)	1.0(1)	294.12(3)	1.22(8)	540.37(3)	1.42(7)
CF ₃ COMn(CO) ₅ ^a	647.90(5)	1.0(1)	294.22(5)	1.15(9)	540.54(3)	1.51(6)
BrMn(CO) ₅ ^b	647.94(3)	0.91(9)	294.14(4)	1.33(9)	540.43(3)	1.61(7)
ClMn(CO) ₅ ^b	647.98(3)	1.1(1)	294.16(4)	1.28(9)	540.49(3)	1.55(8)
CF ₃ Mn(CO) ₅ ^a	648.09(2)	1.05(7)	294.40(2)	1.24(4)	540.67(2)	1.52(4)
F ₃ SiMn(CO) ₅ ^a	648.12(3)	1.01(8)	294.43(3)	1.22(5)	540.59(3)	1.45(6)

^aBinding energies for these compounds are calibrated against the Ne 1s, Ne 2s, and N₂ N 1s lines.

^bBinding energies for these compounds are calibrated against the Ne 1s, N₂ N 1s, and Ar 2p_{3/2} lines.

^cThe uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. ^dData for these compounds were determined previously and appear in S.C. Avanzino and W.L. Jolly, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 15, 1976 and S.C. Avanzino and W.L. Jolly, *J. Am. Chem. Soc.*, **98**, 6505 (1976).

Table II. Ligand Core Binding Energies.

Compound	Core binding energies and linewidths, eV ^a
CH ₃ COMn(CO) ₅	C 1s ($\overset{\curvearrowright}{\text{C}}=\text{O}$) 292.2(3), 1.8(3); (-CH ₃) 290.5(1), 1.3(3); O 1s 537.2(1), 1.0(1)
CH ₃ Mn(CO) ₅	C 1s 289.5(1), 1.5(3)
IMn(CO) ₅	I 3d _{5/2} 625.27(3), 1.27(7)
Cl ₃ SiMn(CO) ₅	Cl 2p _{3/2} 205.64(4), 1.31(7); Cl 2p _{1/2} 207.28(6), 1.31(7); Si 2p 108.38(4), ^b 1.36(9)
CF ₃ COMn(CO) ₅	C 1s ($\overset{\curvearrowright}{\text{C}}=\text{O}$) 293.1(1), 1.1(2); (-CF ₃) 297.9(1), 1.4(2); O 1s 538.21(6), 1.3(2) F 1s 694.13(3), 1.74(8)
BrMn(CO) ₅	Br 3d _{5/2} 74.30(3), 1.27(8); Br 3d _{3/2} 75.39(3), 1.27(8)
ClMn(CO) ₅	Cl 2p _{3/2} 203.84(3), 1.16(7); Cl 2p _{1/2} 205.43(7), 1.16(7)
CF ₃ Mn(CO) ₅	C 1s 296.48(4), 1.14(9); F 1s 692.98(4), 1.78(9)
F ₃ SiMn(CO) ₅	F 1s 692.86(3), 1.46(6); Si 2p 109.0(1), ^b 1.3(2)

^aThe uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. Binding energy calibrations are as indicated in Table I.

^bUnresolved spin-orbit doublet fit to one peak.

Table III. Electronic Structure Data for LMn(CO)₅ Compounds.

Compound	$\Delta E_B(\text{Mn } 2p_{3/2}), \text{ eV}^a$	IP, eV ^b	χ_L^c	Total Orbital Occupation for Manganese, electrons ^d
CH ₃ Mn(CO) ₅	0.0	8.67	2.3	
HMn(CO) ₅	0.16	9.53	2.1	7.420
IMn(CO) ₅	0.43	9.89	2.5	7.424
CF ₃ COMn(CO) ₅	0.60	9.0		
BrMn(CO) ₅	0.64	10.32	2.8	7.385
ClMn(CO) ₅	0.68	10.72	3.0	7.312
CF ₃ Mn(CO) ₅	0.79	9.57	3.3	

^aFrom Table I.

^bValues reported are the degeneracy-weighted averages of the 6e (d_{xz}, d_{yz}) and the 2b₂ (d_{xy}) levels. The data are taken from Refs. 7 and 8; where two values for the same compound are available, the average is reported.

^cAtomic and group electronegativity values are taken from Refs. 11 and 12.

^dValues are the sum of the calculated orbital occupations for all manganese orbitals taken from Ref. 3.

Table IV.^a Force Constants and Graham's σ and π Parameters for LMn(CO)₅ Compounds.

Compound	$k_{\text{avg}}^{\text{CO}}$, mdyn/A ^b	σ	π
(CH ₃) ₃ SnMn(CO) ₅	16.45	-0.84	0.51
Mn ₂ (CO) ₁₀	16.38	-0.89	0.49
CH ₃ Mn(CO) ₅	16.68	0.0	0.0
HMn(CO) ₅	16.83	-0.09	0.20
IMn(CO) ₅	17.08	0.73	-0.27
Cl ₃ SiMn(CO) ₅	17.11	-0.06	0.41
CF ₃ COMn(CO) ₅	17.11	0.28	0.13
BrMn(CO) ₅	17.18	1.03	-0.44
ClMn(CO) ₅	17.24	1.25	-0.57
CF ₃ Mn(CO) ₅	17.19	0.56	-0.04

^aForce constants and σ and π parameters for all compounds except Mn₂(CO)₁₀ are taken from Ref. 15. For Mn₂(CO)₁₀ the force constants from H. Haas and R.K. Sheline, *J. Chem. Phys.*, **47**, 2996 (1967) were used to calculate σ and π according to the method of Ref. 15.

^bThe values of $k_{\text{avg}}^{\text{CO}}$ are calculated from the relation $k_{\text{avg}}^{\text{CO}} = 1/5 k_{\text{trans}} + 4/5 k_{\text{cis}}$.

Table V. Relative Energies and Relative Intensities of Shake-up Satellites.

Compound	C 1s		O 1s		Average M→L CT Energy, eV ^d
	ΔE_S , eV ^a	I_S/I_P , % ^b	ΔE_S , eV	I_S/I_P , %	
$Mn_2(CO)_{10}$	5.47(14) ^c	22(5)	5.37(10)	23(3)	
$CH_3Mn(CO)_5$	5.42(7)	27(3)	5.50(6)	19(2)	6.01
$HMn(CO)_5$	5.75(8)	24(3)	5.82(8)	18(2)	6.04
$IMn(CO)_5$	5.36(8)	30(4)	5.52(7)	19(2)	6.10
$CF_3COMn(CO)_5$	5.32(12)	32(forced)	5.11(10)	21(4)	
	5.20(14)	32(forced)			
$BrMn(CO)_5$	5.47(9)	30(5)	5.51(6)	20(2)	6.12
$CF_3Mn(CO)_5$	5.29(6)	32(4)	5.30(6)	21(2)	5.97
$F_3SiMn(CO)_5$	5.54(7)	27(3)	5.70(6)	18(2)	

^aEnergy difference between the shake-up band and primary photoline.

^bIntensity of shake-up relative to intensity of photoline.

^cThe uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically.

^dThe average of individual charge-transfer bands resolved in the UV spectrum, each band weighted by its relative intensity. No bands with less than 10% relative intensity were included. Values taken from Ref. 26.

Figure Captions

Figure 1. Plot of carbonyl carbon 1s binding energy vs. manganese $2p_{3/2}$ binding energy for $\text{LMn}(\text{CO})_5$ compounds.

Figure 2. Plot of carbonyl oxygen 1s binding energy vs. manganese $2p_{3/2}$ binding energy for $\text{LMn}(\text{CO})_5$ compounds.

Figure 3. Plot of carbonyl carbon 1s binding energy vs. the weighted-average CO force constants for $\text{LMn}(\text{CO})_5$ compounds.

Figure 4. Plot of carbonyl oxygen 1s binding energy vs. the weighted-average CO force constants for $\text{LMn}(\text{CO})_5$ compounds.

Figure 5. Plot of manganese $2p_{3/2}$ binding energy vs. the weighted-average CO force constants for $\text{LMn}(\text{CO})_5$ compounds.

Figure 6. Plot of oxygen 1s binding energy for carbonyl complexes vs. the weighted-average CO force constants.

Figure 7. Plot of carbon 1s binding energy for carbonyl complexes vs. the weighted-average CO force constants.

Figure 8. The carbon 1s spectrum of $\text{HMn}(\text{CO})_5$.

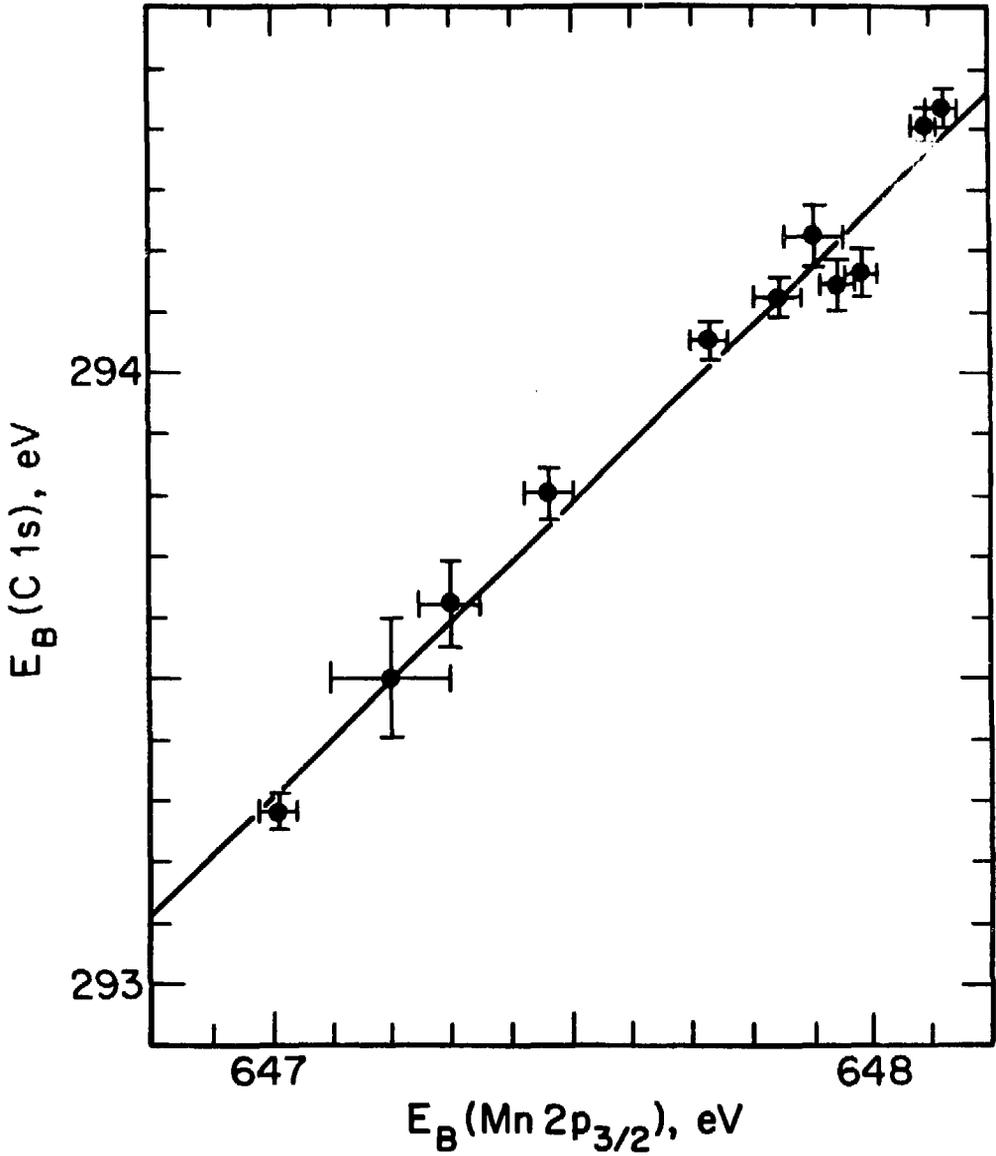
Figure 9. The oxygen 1s spectrum of $\text{HMn}(\text{CO})_5$.

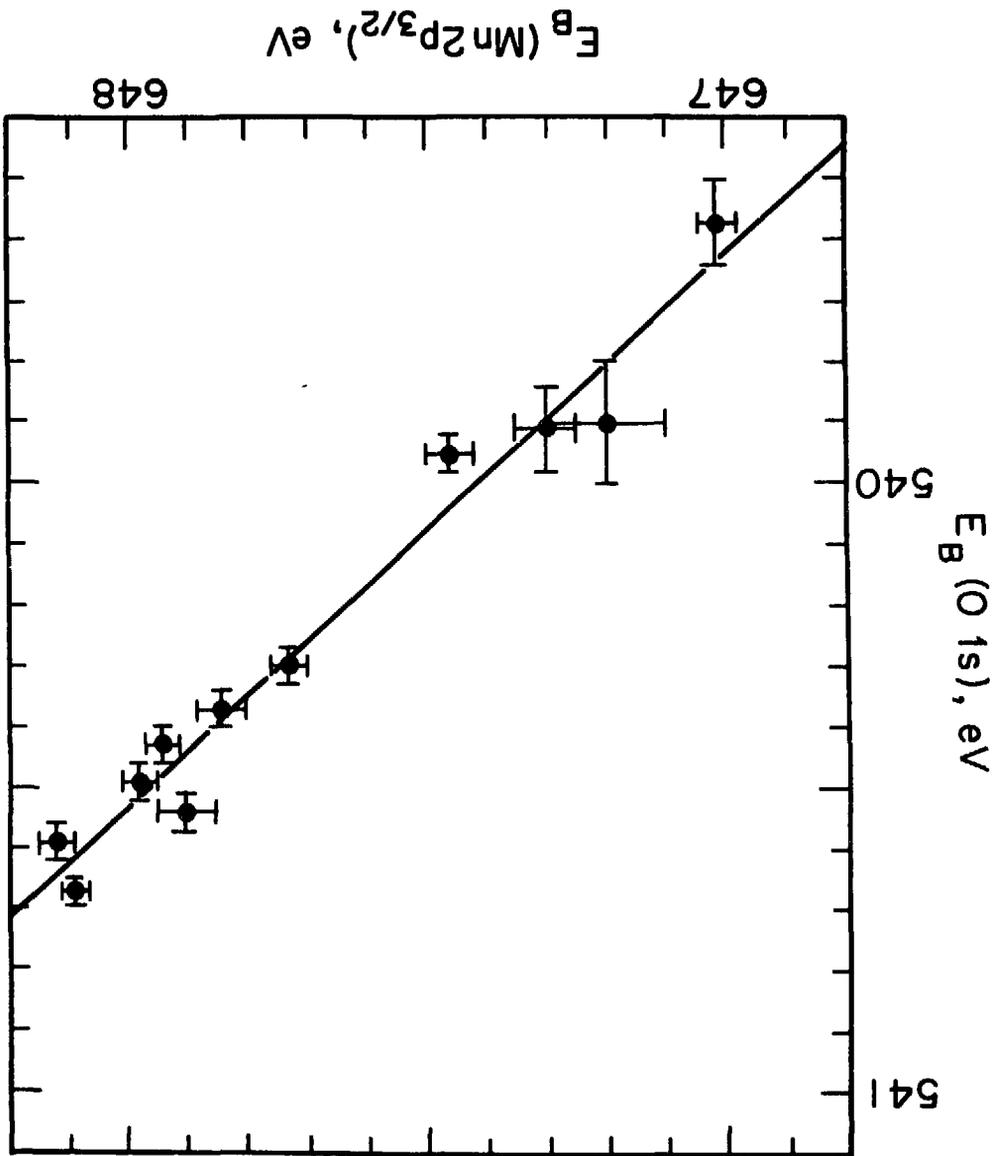
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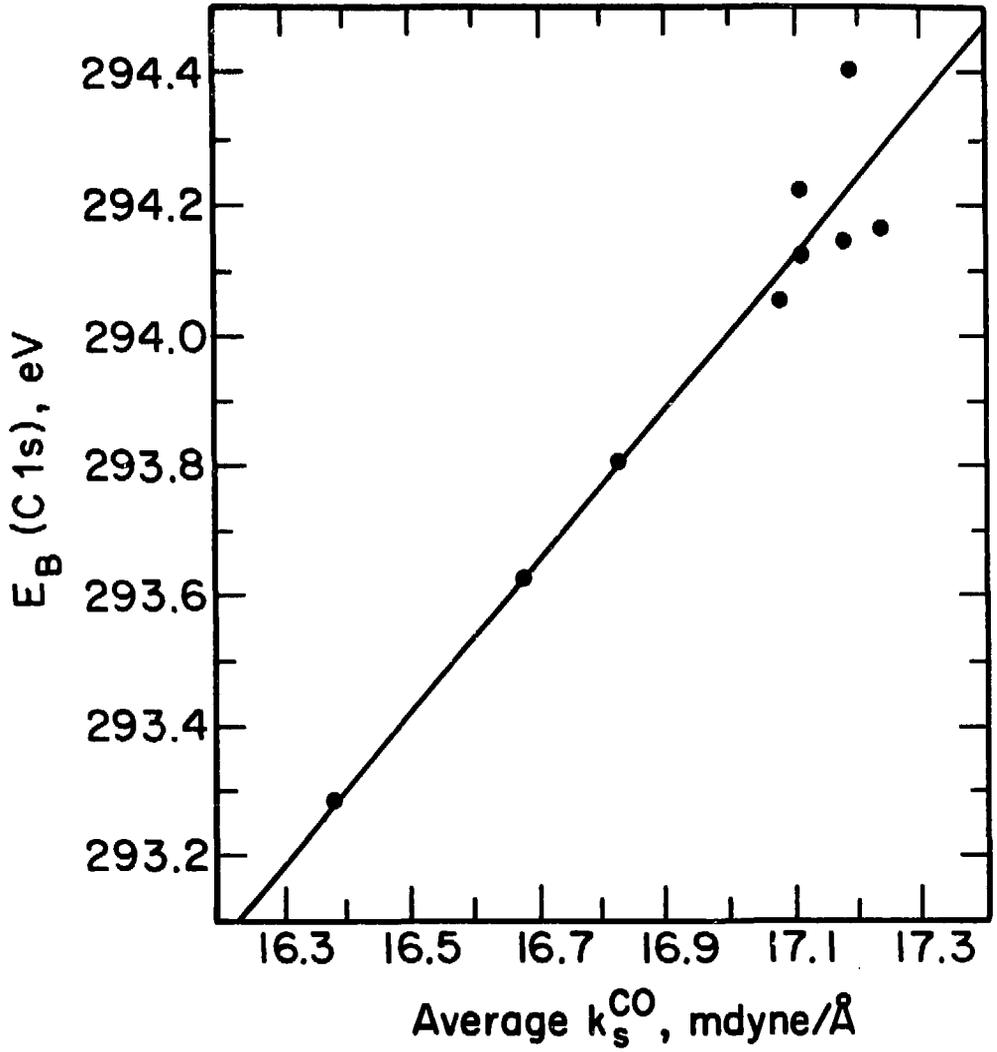
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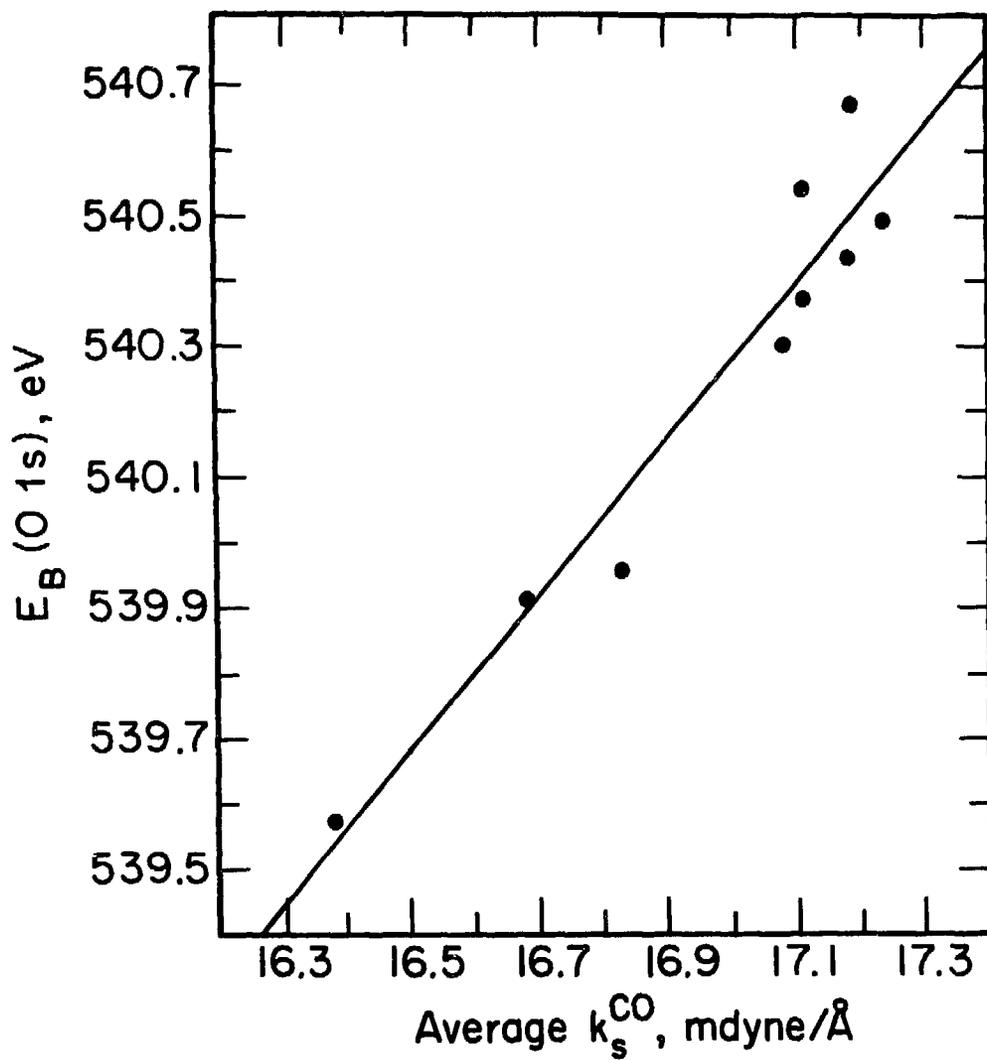
18. The least-squares line in Figure 6 corresponds to the equation $E_B(O\ 1s) = 1.03 k_{CO} + 522.71$. The correlation coefficient is 0.968. The least-squares line in Figure 7 corresponds to the equation $E_B(C\ 1s) = 1.14 k_{CO} + 274.60$. The correlation coefficient is 0.967.
19. As shown in the text, the proportion of σ and π that is plotted, i.e., $0.45\sigma + 0.55\pi$, is predetermined by the quantities we have chosen to correlate. We attempted to optimize the relative amounts of σ and π for the correlations with each of the three elements, but found that in each case the improvement in the fit as the result of including an additional parameter was not statistically significant.
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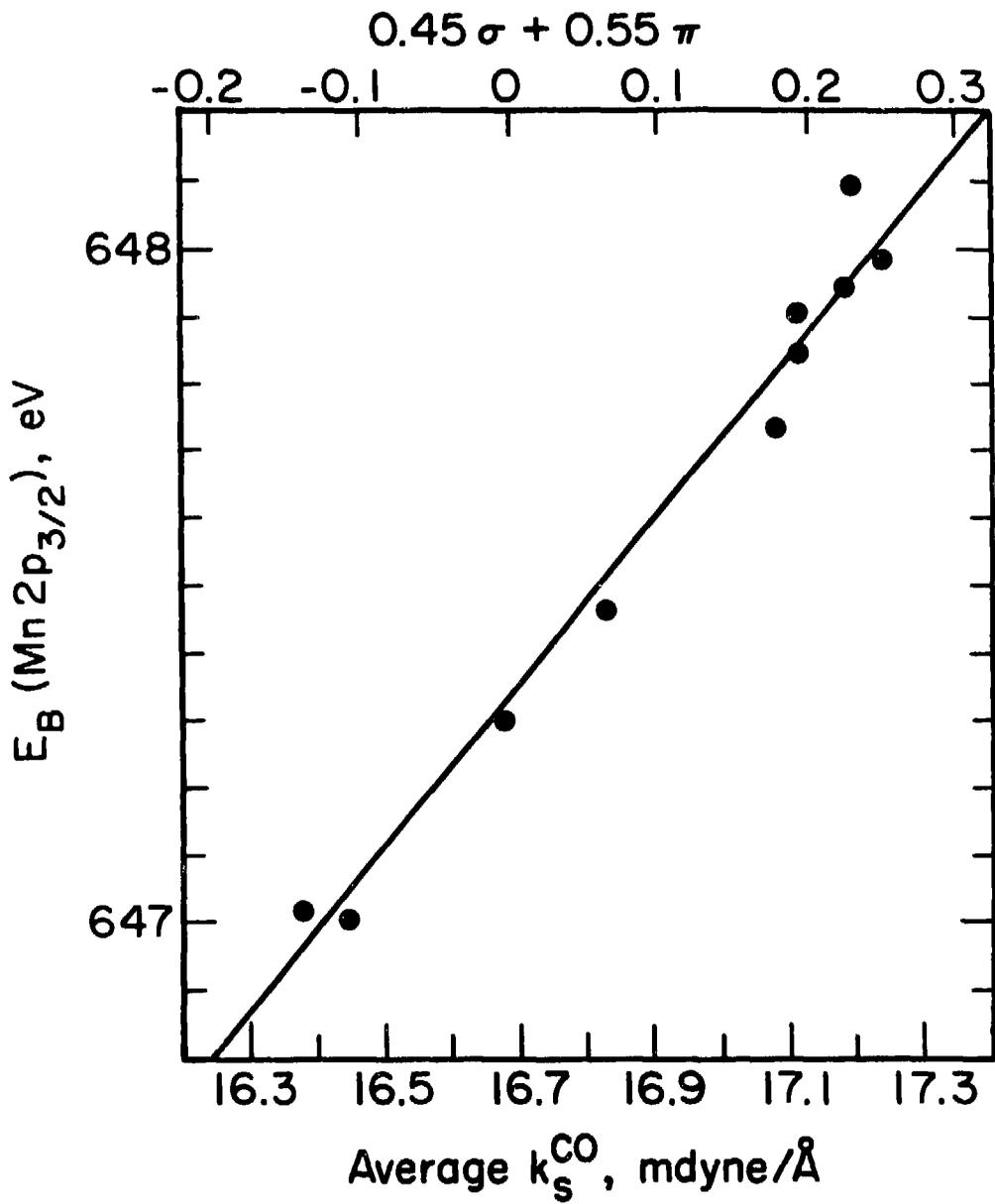
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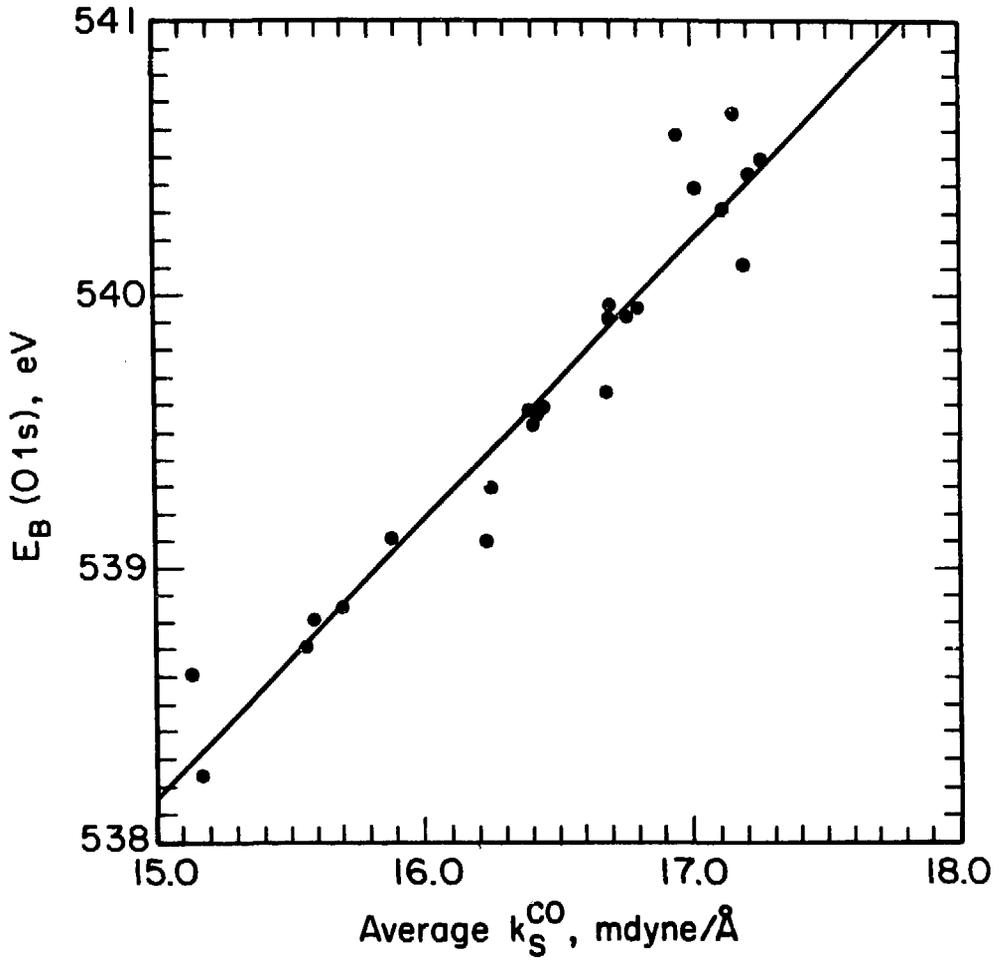




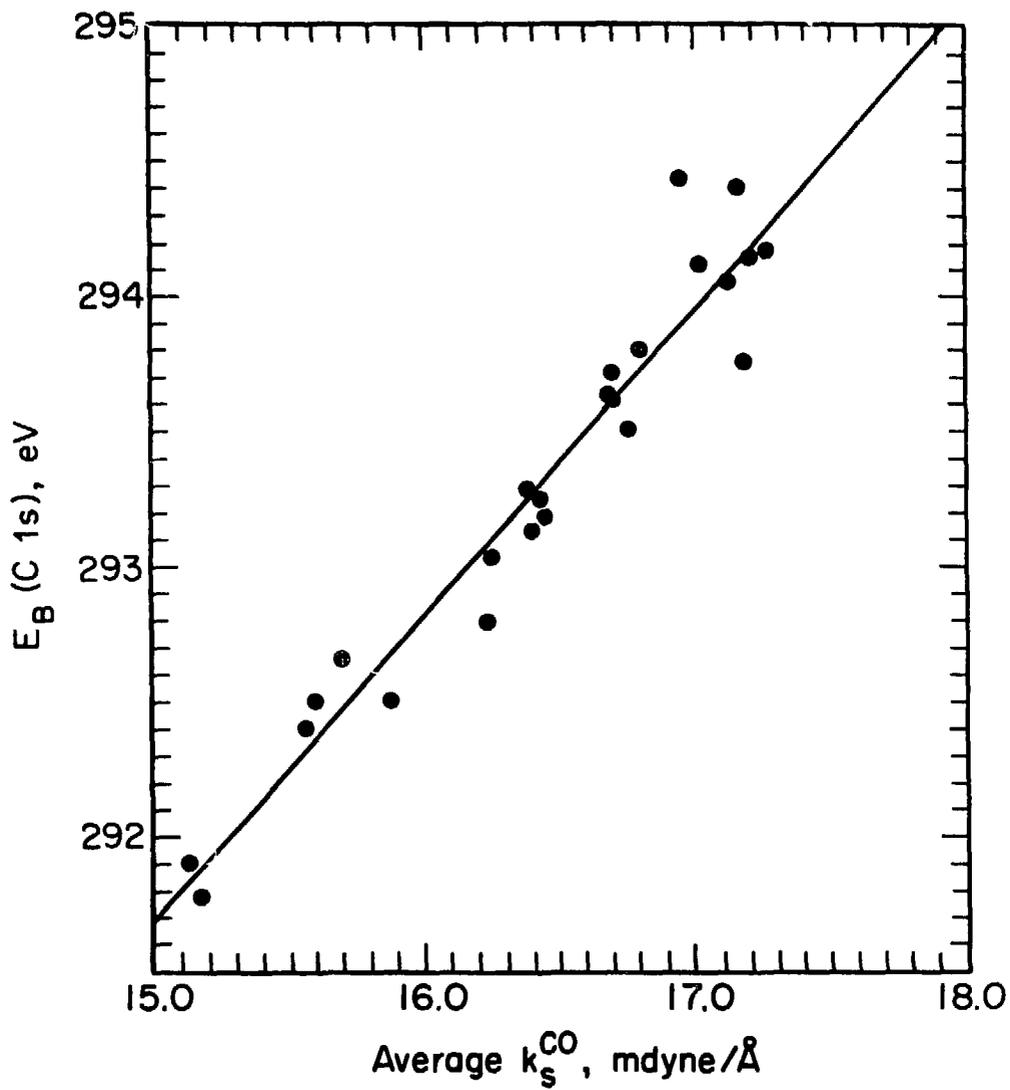


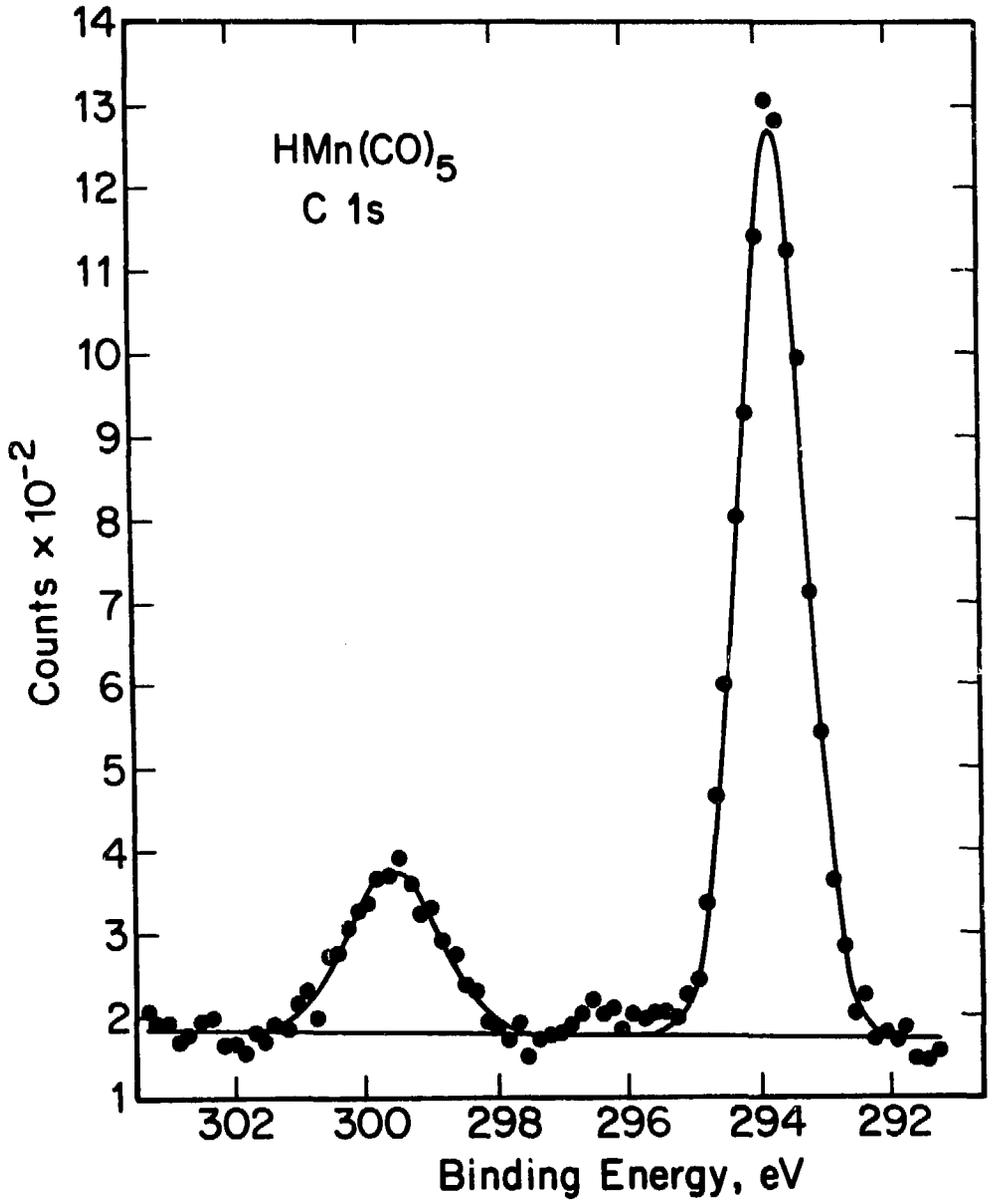


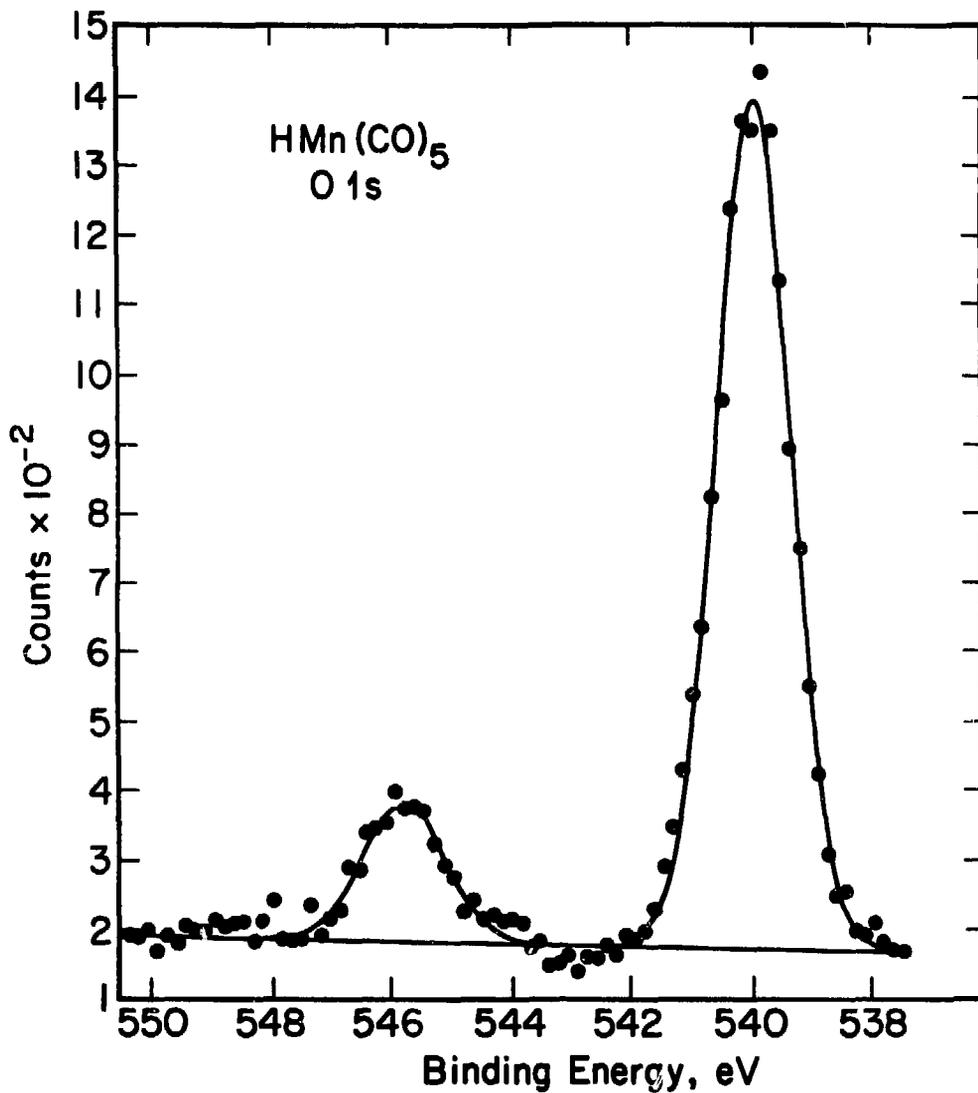




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Journal of the American Chemical Society, 100, 1228 (1978)
A Simple Method for Obtaining X-ray Photoelectron
Spectra of Species in Liquid Solution

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Evidence for Hyperconjugation from an X-Ray Photoelectron Spectroscopic Study of Isoelectronic Compounds

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RICHARD R. RIETZ, and THEODORE F. SCHAAF

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Core Electron Binding Energies of Cyclotriphosphazenes and Cyclotetraphosphazenes

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The Core Electron Binding Energies of Gaseous Chlorine Monofluoride

The measurement of the core electron binding energies of chlorine monofluoride by X-ray photoelectron spectroscopy was attempted numerous times in the past 5 years by a number of experimenters with results which were not always satisfactory. The first XPS experiment involving ClF was reported by Carroll and Thomas.¹ Subsequent experiments were conducted by Perry and Jolly.² The poor agreement between these sets of experimental results prompted further studies by Avanzino, Thomas, and Jolly,³ and Avanzino and Jolly.⁴

Chlorine monofluoride⁵ is a gaseous fluorinating agent which reacts vigorously with water, organic substances, and even Teflon. When in contact with metal surfaces, ClF reacts to form a passive metal fluoride film which prevents further attack. In light of its reactive nature, any spectroscopic measurement on ClF must be carefully conducted to prevent interference from impurities. It is likely that the early XPS studies of ClF were carried out using contaminated samples. Carroll and Thomas used commercial ClF but make no reference to a purity check on their sample. Commercial cylinders of ClF often contain substantial amounts of ClF₃. Perry may have used a glass vacuum line in handling his ClF sample, which would result in the formation of SiF₄. Recent studies^{3,4} were carried out with samples of known composition such that the results were not affected by impurities.

ClF Experiment of July 1976³

Sample Preparation. The purification and handling of ClF and F₂

were carried out in an all-metal vacuum line. The infrared spectrum of ClF was measured in a special 7 cm - pathlength Monel cell with silver chloride windows mounted against Teflon gaskets. In order to determine the purity of the sample, the observed spectrum was compared with literature spectra⁶⁻¹¹ of ClF and of the possible impurities ClF₃, ClO₂F, ClO₂, CF₄, and SiF₄. The pure materials were stored in 100 cm³ Monel or copper containers sealed with Whitey valves having Kel-F tipped stems. The vacuum line, storage containers, and IR cell were passivated first with F₂ then with ClF prior to use.

A sample of ClF from K & K Laboratories, Hollywood CA, was found to contain considerable amounts of chloryl fluoride and silicon tetrafluoride. The SiF₄ was chemically removed from the sample by repeated condensation onto activated KF. The ClF was then separated from the less volatile ClO₂F by distillation from the mixture held at -160°C. The infrared spectrum of this purified sample was that of pure ClF. (A small band at $\sim 1280\text{ cm}^{-1}$ is attributable to traces of CF₄ formed by the reaction of ClF with the Teflon gaskets of the IR cell.) The samples of fluorine and chlorine were purchased from the Matheson Co. (F₂, 98.5% pure; Cl₂, Research Grade) and were used without purification.

X-Ray Photoelectron Spectra. The gas-phase XPS spectra were obtained on the cylindrical-mirror electrostatic-focusing spectrometer¹² at Oregon State University, Corvallis, Oregon. Aluminum K α X-rays (1486.6eV) were used for all spectra. An all-metal inlet system was used to conduct the sample gases to a stainless-steel irradiation chamber having an aluminum window. Fluorine and ClF were bled through

the inlet system for 15 minutes prior to the start of each experiment. For the fluorine binding energy measurements a mixture of neon and either F_2 or ClF was introduced into the spectrometer. Data were alternately collected on the F 1s line and the Ne $1D_2$ Auger line¹³ which was used as a reference. For the chlorine binding energy measurements a mixture of argon and either Cl_2 or ClF was introduced, so that the Cl 2s and Cl 2p lines could be similarly referenced to the Ar $2p_{3/2}$ line.¹⁴ Binding energies were determined by a least-squares fitting of the data to Gaussian line shapes.

The ClF F 1s binding energies were measured using the sample of purified ClF. However, this sample was exhausted before the chlorine binding energies could be measured. An attempt was made to purify a second sample of ClF at Oregon State University. Efforts were hampered by a lack of facilities, and the purity of this second sample could not be ascertained. Nevertheless, several measurements of both the Cl 2s and Cl 2p ClF binding energies were made.

ClF Experiment of August 1978⁴

The poor agreement between the Cl 2s binding energy measurements which were made on a sample of questionable purity at Oregon State University prompted yet another measurement of the ClF chlorine binding energies.

Sample Preparation. The sample of ClF¹⁵ used in the experiment was shown by its infrared spectrum to be free of any chlorine-containing impurities. The spectrum indicated impurities of CF_4 and SiF_4 ; however, since only chlorine binding energies were to be remeasured, the sample was used without further purification.

X-Ray Photoelectron Spectra. The XPS spectra were measured on a GCA/McPherson ESCA 36 Photoelectron Spectrometer using Mg K α X-rays (1253.6eV). An all-metal inlet system conducted the ClF to a stainless-steel gas cell having an aluminum window. The inlet system and gas cell were exposed to a flow of ClF gas at a pressure of 300-400 microns for one hour prior to the start of the experiment. A spectrometer calibration was established both before and after the ClF experiment using three reference points provided by the Ar 2p $_{3/2}$, N $_2$ N 1s, and Ne 1s binding energies.¹⁴ A mixture of ClF and argon was introduced into the spectrometer, and the chlorine binding energies were directly referenced to the Ar 2p $_{3/2}$ line.

The results of the measurements described above, as well as results from earlier measurements, are summarized in Table I. The most accurate binding energies for ClF have been underlined. In the case of ClF, some large discrepancies exist between the new values and previous measurements. In the case of Cl $_2$ and F $_2$, fairly good agreement between all values was obtained. The core binding energies for these three molecules are in accord with the expected charge distribution for chlorine monofluoride. Qualitatively, the increased chlorine binding energy of ClF relative to Cl $_2$ indicates that the chlorine of ClF is positively charged. Likewise, the decrease in fluorine binding energy of ClF vs. F $_2$ indicates a negatively charged ClF fluorine atom. One can quantitatively estimate the magnitude of the charges by using the point-charge potential model.¹⁶ The binding energy shifts are related to the differences in atomic charge between ClF and the zero-charged elements by the equations

$$\Delta E_B(F) = k_F Q_F + 14.4 Q_{Cl}/R_{ClF} \quad (1)$$

$$\Delta E_B(Cl) = k_{Cl} Q_{Cl} + 14.4 Q_F/R_{ClF} \quad (2)$$

Here k is the binding energy change per unit change in atomic charge, Q_F and Q_{Cl} are the atomic charges for ClF ($Q_F = -Q_{Cl}$), and R_{ClF} is the chlorine-fluorine internuclear distance. The value of k can be estimated by several methods. For an atom X of atomic number Z , k is the difference in core binding energy between X_Z^+ and X_Z . If one uses the equivalent cores approximation,¹⁷ this binding energy difference can be calculated from valence shell ionization potentials by $E_B(X_Z^+) - E_B(X_Z) = IP(X_{Z+1}^+) - IP(X_Z) = k(X_Z)$. The potential model indicates that k is inversely proportional to the radius of the valence shell $k(X_Z) = 14.4(1/R)$. Here $1/R$ can be obtained for an sp^3 hybridized valence orbital from quantum mechanical calculations by the expression:

$$1/R = 1/4 \langle \psi_{ns} | r^{-1} | \psi_{ns} \rangle + 3/4 \langle \psi_{np} | r^{-1} | \psi_{np} \rangle .$$

Alternatively, $1/R$ can be calculated using the experimentally derived covalent radius for an atom.

Using ionization potential data¹⁸ the appropriate k values for chlorine and fluorine are 14.7 eV/e and 23.5 eV/e, respectively. These compare well with estimates calculated from covalent radii¹⁹ ($k_{Cl} = 14.5$ eV/e and $k_F = 22.5$ eV/e) but differ significantly from k values calculated from quantum mechanical wavefunctions²⁰ ($k_{Cl} = 22.3$ eV/e and $k_F = 37.4$ eV/e). However, k^{QM} values are applicable to free atoms, whereas $k^{cov rad}$ values may be more appropriate for an atom in a covalently-bound molecule.

Either Eq. (1) or Eq. (2) can be used to calculate the fluorine and chlorine charges in ClF. If Eq. (1) is used the charges range from $-0.18 < Q_F (= -Q_{Cl}) < -0.09$, depending upon one's choice of k_F . If Eq. (2) is used the charges are $-0.24 < Q_F (= -Q_{Cl}) < -0.10$, in fair agreement with those from Eq. (1).

Table I. Core electron binding energies.

Compound	F 1s			Cl 2s			Cl 2p _{3/2}		
	E _B , eV ^a	FWHM	Ref.	E _B , eV ^b	FWHM	Ref.	E _B , eV ^b	FWHM	Ref.
ClF	694.16(6) ^c	1.89(10)	3	280.33(8)	2.9(4)	4	209.20(4)	1.24(11)	4
	694.17(6)	1.97(8)	3	280.24(8)	2.8(2)	3	209.02(10)	2.2(3)	3
	694.4(1)	1.09(8)	2	279.90(16)	2.6(4)	3	209.04(8)	2.3(3)	3
	694.54(5)	--	1	279.23(10)	--	1	209.27(4)	1.12(10)	2
F ₂	696.66(6)	1.55(10)	3						
	696.70(5)	--	1						
Cl ₂				278.65(8)	3.4(3)	3	207.81(4)	1.98(10)	3
				278.76(8)	2.9(2)	3	207.86(4)	1.93(10)	3
				278.66(10)	--	1	207.81(5)	1.00(7)	2

^aFluorine binding energies are measured relative to the Ne ¹D₂ Auger line (K.E.=804.557eV¹³) for Ref. 1 & 3, and the Ar 2p_{3/2} line (E_B=248.62eV¹⁴) for Ref. 2.

^bChlorine binding energies are measured relative to the Ar 2p_{3/2} line for Ref. 2, 3, & 4; the chlorine values for Ref. 1 are based on a previous spectrometer calibration.

^cThe uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit for Ref. 2, 3, & 4) is indicated parenthetically.

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