Calculation of Atomic Charges by an Electronegativity Equalization Procedure

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A procedure for calculating atomic charges based on the equalization of atomic orbital electronegativities has been extended
to cover compounds containing any of the elements in the periodic table up to radon. Atomic charges calculated by this
method correlate well with core electron binding energies using the potential equation. The correlations are generally im-
proved by inclusion of a relaxation energy term, calculated on the basis of the principle of equivalent cores.

Introduction

In a previous study, an electronegativity equalization pro-
cedure for calculating atomic charges of compounds of the
first row of the periodic table was calibrated using experi-
mental 1s electron binding energies for carbon, nitrogen,
oxygen, and fluorine.[1] We now show that (1) this method
can be extended to compounds of elements from the remainder
of the periodic table, (2) significant improvement in the core
binding energy correlations is achieved by including a relaxa-
tion energy term in the potential equation, and (3) com-
pounds for which nonequivalent resonance structures can be
written must be specially treated.

The Calculational Procedure

In this section we give detailed stepwise instructions for
the calculation of atomic charges in molecules for which un-
ambiguous valence bond structures can be written.

Step 1. A valence bond structure, or hybrid of several
such structures, is drawn for the compound. If possible,
each nontransition element atom heavier than helium should
have just an octet of valence electrons; only s and p valence
orbitals are used for these atoms. Bond orders are assigned to
the bonds, and formal charges[2] are assigned to the atoms.
Several examples of valence-bond structures for nontransi-
tion element compounds follow. (In these and other ex-
amples, bond orders of unity and formal charges of zero are
not explicitly indicated.)
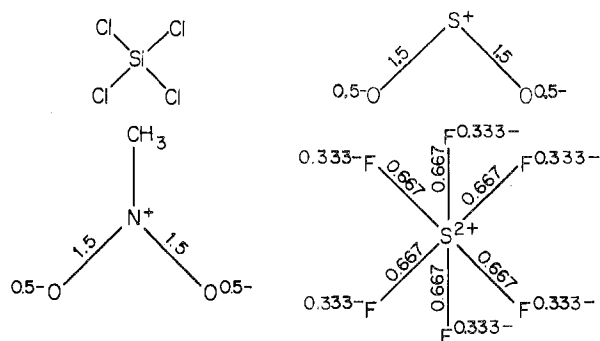
There has been considerable discussion of the importance
of valence-shell d orbitals in the bonding of nontransition
elements beyond the first row of the periodic table. Al-
though most experimental data for compounds of such ele-
ments are equivocal with respect to the importance of d
orbitals, the data generally can be at least qualitatively

rationalized without recourse to d orbital bonding.[3,4] Ex-
tended Huckel calculations have indicated that d orbitals
make only minor contributions to the bonding in PX_5 com-
pounds.[5,6] Recent *ab initio* calculations[7] have shown that
phosphorus d orbitals play a significant but relatively unim-
portant role in the bonding of PF_5. We have concluded that
our simple calculations will not be in serious error by the
neglect of d orbitals in nontransition elements. Some justi-
fication for this conclusion is found in the fact that we ob-
tain good correlations of core binding energies using charges
calculated on this basis. However, with respect to our cal-
culations, the question of d orbitals is purely academic, be-
cause there are no reliable electronegativity values available for
d orbitals.

In the case of "hypervalent" molecules in which the cen-
tral atom is bonded to two sterically distinct types of ligands
(as in PF_5, SF_4, ClF_3, and BrF_5), the bonding electrons must
be appropriately apportioned between the two types of bonds.
Consider the bonding in PF_5. Because of the trigonal bi-
pyramidal symmetry of this molecule, no more than one
phosphorus σp orbital can be involved in bonding the axial
ligands, and no more than two phosphorus σp orbitals can be
involved in bonding the equatorial ligands. The only re-
strictions on the phosphorus s orbital are that it must be
equally involved in the two axial bonds and equally involved
in the three equatorial bonds. If there were complete partici-
pation of the s and p orbitals in bonding, with equal participa-
tion of the s orbital in all five bonds, the bond orders would
be 0.7 and 0.867 for the axial and equatorial bonds, respec-
tively. We have found that a better correlation of the fluorine
binding energies is obtained by using bond orders of 0.72
and 0.853, corresponding to a slight favoring of the axial
orbitals by the s orbital. Such relative enhancement of s
character in the digonal orbitals is consistent with the fact
that the overlap integral of a pair of sp hybrid orbitals is
greater than that of a pair of sp^2 hybrid orbitals.[8]

We assume that nonbonding valence orbitals, such as those
on the central atoms of SF_4 and ClF_3, are completely occupied
by pairs of electrons. Thus, in the hypothetical conversion
of PF_5 into SF_4 and ClF_3 by the replacement of equatorial
fluorines by lone pairs, we must withdraw some electron
density from the remaining bonds. Because an equatorial

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(4) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).
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13, 1747 (1974).
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1952, p 199.

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California.
(1) W. L. Jolly and W. B. Perry, *J. Amer. Chem. Soc.*, **95**, 5442
(1973).
(2) The formal charge is the charge which the atom would have
if the bonding electrons in each bond were equally apportioned be-
tween the pair of bonded atoms.

lone pair is repelled more strongly by axial bonding electrons than by equatorial bonding electrons,[9] it is reasonable to assume that more electron density is withdrawn from the axial bonds than from the equatorial bonds. Our recipe is to withdraw twice as much electron density from axial bonds. In this way we obtain axial and equatorial bond orders of 0.671 and 0.829, respectively, for SF_4, and 0.603 and 0.795, respectively, for ClF_3.

In the case of a molecule such as BrF_5, we assume that there is negligible repulsion between the lone pair and the axial bonding electrons on the opposite side of the molecule and that in the hypothetical conversion of SF_6 into BrF_5, all of the required electron density is withdrawn from the basal bonds. Thus we obtain apical and basal bond orders of 0.667 and 0.583, respectively, in BrF_5.

The structures for PF_5, SF_4, ClF_3, and BrF_5 are indicated below.
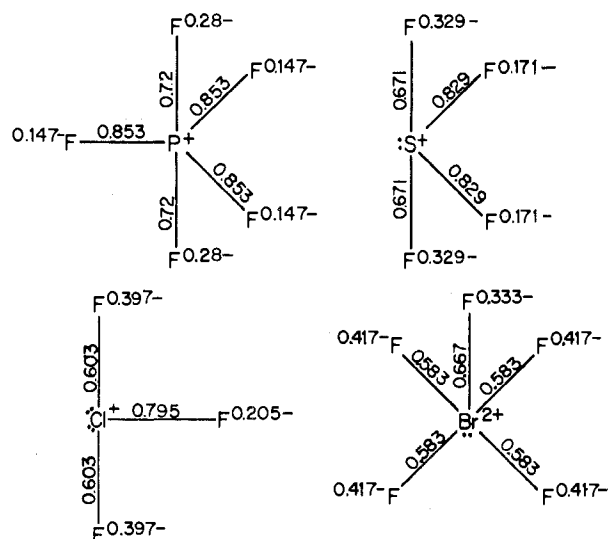
By analogous reasoning, we obtain bond orders of 0.5 in XeF_2, XeF_4, and XeF_6.

In the bonding of a transition metal atom or ion, it is assumed that the number of orbitals available to accept electrons from ligands is equal to the number of vacant s, p, and d valence orbitals. In general, the available s and p orbitals are completely involved in bonding. Vacant d orbitals of σ symmetry are used to the extent necessary to provide each ligand, as far as possible, with a full σ bond. For example, in WF_6 it is assumed that two 5d orbitals are used, and we write the structure


The question of ligand-to-metal $p\pi \rightarrow d\pi$ bonding is somewhat problematical. There seems to be little doubt that such π bonding is important in a complex such as CrO_4^{2-} in which the ligand atoms would otherwise have full -1 formal charges.[10] However there is some question as to the importance of π bonding in a complex such as WF_6 in which the ligand atoms would otherwise have no formal charge.[11] We have chosen to ignore π bonding in the latter case because of

what seems to be a general tendency for the stability of structures in which formal charges are minimized and because of the structure of CrO_2F_2.[12] In the latter molecule, $\angle O-Cr-O = 102.1°$ and $\angle F-Cr-F = 118.9°$. We interpret the difference in the angles as evidence for relatively great $p\pi \rightarrow d\pi$ bonding in the Cr-O bonds compared to the Cr-F bonds. (The bond angle corresponding to maximum $p\pi \rightarrow d\pi$ overlap is 90°.) We propose the following rule: Vacant d orbitals of π symmetry are used in ligand-to-metal $p\pi \rightarrow d\pi$ bonding only if a reduction in formal charges results. Thus in CrO_2Cl_2 it is assumed that two 3d orbitals are used in forming double bonds to the oxygen atoms, and we write
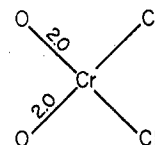
When metal-to-ligand $d\pi \rightarrow p\pi$ back-bonding can occur in a transition metal complex, we assume that it occurs, as far as possible, consistent with the number of metal $d\pi$ electrons and empty ligand $p\pi$ orbitals available. Formal charges are modified in accordance with the back-bonding, but bond orders are assumed to be the same as those in the structures without back-bonding. Thus for $Cr(CO)_6$ we write
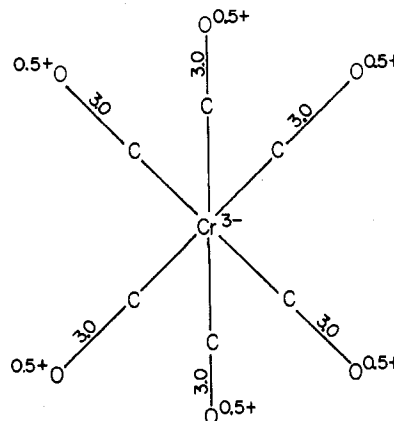
The main justification of this method for accounting for metal-to-ligand $d\pi \rightarrow p\pi$ back-bonding is that it gives reasonably good results in correlating the carbon and oxygen binding energies of metal carbonyl complexes. When further binding energy data become available for other types of complexes, it may be necessary to modify the method. The fact that our present method ignores the changes in bond order that accompany back-bonding is at least consistent with the fact that the average C-O bond distance in metal carbonyls is only about 0.01 Å longer than it is in free CO.[13]

Step 2. It is necessary to assign an orbital hybridization (*i.e.*, the fractional s character) for each σ bond of each nontransition element in the compound. This assignment is necessary because the s and p electronegativities of such elements are different. However, for the transition elements, we have made no distinction between the valence s, p, and d electronegativities (an average electronegativity is used), and therefore it is unnecessary to assign hybridizations for such elements. We define S_{nm} as the fractional s character of the σ orbital used by atom n in the bond to atom m. For any atom for which the *total ligancy* (*i.e.*, the number of com-

(9) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

(10) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, p 243.

(11) N. Bartlett, *Angew Chem. Intl. Ed.*, **7**, 433 (1968).

(12) C. D. Garner, R. Mather and M. F. A. Dove, *J. Chem. Soc. Chem. Commun.*, 633 (1973).

(13) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958).

plete lone pairs[14] plus the number of other atoms bonded to that atom) is 4 or less, we assume that S_{nm} is the same for each bond and equal to the reciprocal of the total ligancy. Thus $S_{nm} = 0.25$ for the central atoms in GeH_4, NSF_3, OSF_2, and H_2S, and $S = 0.33$ and 0.5, respectively, for the middle atoms in SO_2 and CO_2. When the total ligancy is 5 (trigonal-bipyramidal type molecules), one p orbital must be assigned to the two axial bonds, and two p orbitals must be assigned to the three equatorial orbitals. For the axial bonds, $S_{nm} = (N_{ax} - 0.5)/N_{ax}$, where N_{ax} is the axial bond order; for the equatorial bonds, $S_{nm} = (N_{eq} - 0.667)/N_{eq}$, where N_{eq} is the equatorial bond order. When the total ligancy is 6 (octahedral type molecules), one p orbital must be assigned to the pair of orbitals along each axis. Thus for any bond, $S_{nm} = (N - 0.5)/N$, where N is the bond order.

Step 3. For each bond (or each set of equivalent bonds) in the compound, an equation of the following type is set up

$$\frac{7.3(h_m + h_n)}{(N_{nm})^{0.7}} q_{mn} + h_m \sum_{i \neq n} q_{mi} - h_n \sum_{i \neq m} q_{ni} =$$

$$x(p)_n - x(p)_m + \frac{S_{nm}}{(1 + \Pi_{nm})^{0.7}}[x(s)_n - x(p)_n] -$$

$$\frac{S_{mn}}{(1 + \Pi_{nm})^{0.7}}[x(s)_m - x(p)_m] + c_n h_n F_n - c_m h_m F_m$$

In this equation, the subscripts n and m refer to the two atoms of the bond.

The parameters $x(s)$, $x(p)$, and h are listed in Table I for most of the elements in the periodic table. These parameters were obtained as far as possible from the orbital electronegativity tabulations of Hinze and Jaffe.[15] Corresponding electronegativity data for transition metals are either lacking or difficult to use because of uncertainties regarding orbital hybridizations in transition metal compounds. For these compounds we have chosen to ignore hybridization of the transition metal orbitals and to use an average electronegativity value for all the bonding orbitals of a given transition metal. The transition metal electronegativities listed in Table I were calculated by the Allred-Rochow formula;[16] like the Hinze-Jaffe electronegativities, they are similar in magnitude to the Pauling values.[17] The parameters for the nontransition elements heavier than iodine are estimates; those for the rare gases are partly based on data of Fung.[18]

The parameter c has the value 2.7 for the elements from hydrogen to argon in the periodic table and the value 1.6 for elements heavier than argon. An increase in the formal charge of an atom by one unit causes the electronegativities of the atomic orbitals to increase by an amount proportional to the factor c. The increase in formal charge is always caused by the bonding of a Lewis acid to the atom, with conversion of a lone pair into a bonding pair. Thus the increase in electronegativity is caused, at least partly, by an increased positive field due to the polarization of a lone pair by a Lewis acid. One would expect the electronegativity increase to be smaller the farther the atomic orbitals are from the

(14) A fractional number of lone pairs is associated with any atom for which the sum of the bond orders is nonintegral. For example, each fluorine atom in XeF_2 (with Xe-F bond orders of 0.5) has 3.5 lone pairs.
(15) J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962); *J. Phys. Chem.*, **67**, 1501 (1963).
(16) A. L. Allred and E. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958); E. J. Little and M. M. Jones, *J. Chem. Educ.*, **37**, 231 (1960).
(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.
(18) B.-M. Fung., *J. Phys. Chem.*, **69**, 596 (1965).

lone pair, *i.e.*, the larger the atom. Hence it is understandable that we found it necessary to use a smaller value of c for elements of higher atomic number.

The terms N_{nm} and Π_{nm} stand for the bond order and the π-bond order, respectively, and F stands for the atomic formal charge. It should be noted that, when $N_{nm} > 1, N_{nm} = 1 + \Pi_{nm}$. The quantity q_{nm} is the negative charge transferred from atom n to atom m. (Thus $q_{nm} = -q_{mn}$.) The term $\Sigma_{i \neq m} q_{ni}$ is the sum of the negative charges transferred from atom n to all the atoms bonded to atom n except atom m, and $\Sigma_{i \neq n} q_{mi}$ is the analogous term for atom m.

Upon completion of step 3 for a molecule containing j different types of bonds, one obtains j linear equations with j unknown q values.

Step 4. The equations are solved for the q values, and the charge Q on each atom is calculated using the general relation

$$Q_n = F_n + \Sigma q_{ni}$$

We shall illustrate the method of calculation with two examples, PF_5 and WF_6, for which we have already given the valence bond structures. In PF_5, both the axial and equatorial fluorine atoms have *total ligancies* of 4, corresponding to a value of 0.25 for S_{F_aP} and S_{F_eP}. For the phosphorus orbital used in bonding to the axial fluorines, $S_{PF_a} = (0.72 - 0.5)/0.72 = 0.3056$; for the orbital used in bonding to the equatorial fluorines, $S_{PF_e} = (0.853 - 0.667)/0.853 = 0.2181$. Thus for PF_5 we obtain the following equations

$$\frac{7.3(1.70 + 1.075)}{0.72^{0.7}} q_{F_aP} + 1.70(0) - 1.075(q_{PF_a} + 3q_{PF_e}) =$$

$$2.23 - 3.90 + \frac{0.3056}{1^{0.7}}(4.62 - 2.23) -$$

$$\frac{0.25}{1^{0.7}}(10.31 - 3.90) + 2.7(1.075)(1) - 2.7(1.70)(-0.28)$$

$$\frac{7.3(1.70 + 1.075)}{0.853^{0.7}} q_{F_eP} + 1.70(0) - 1.075(2q_{PF_a} + 2q_{PF_e}) =$$

$$2.23 - 3.90 + \frac{0.2181}{1^{0.7}}(4.62 - 2.23) -$$

$$\frac{0.25}{1^{0.7}}(10.31 - 3.90) + 2.7(1.075)(1) - 2.7(1.70)(-0.147)$$

These reduce to the following pair of equations

$$26.5699q_{F_aP} + 3.225q_{F_eP} = 1.6456$$

$$2.150q_{F_aP} + 24.7924q_{F_eP} = 0.8260$$

From these we readily calculate $q_{F_eP} = 0.0282$ and $q_{F_aP} = 0.0585$, and then $Q_P = +0.798$, $Q_{F_a} = -0.222$, and $Q_{F_e} = -0.119$.

In WF_6, the fluorine atoms have total ligancies of 4, corresponding to $S_{FW} = 0.25$. An average electronegativity value is used for tungsten, and therefore it is unnecessary to evaluate S_{WF}. (In effect, we assume $x(s) = x(p)$.) Thus we obtain the equation

$$\frac{7.3(1.70 + 0.50)}{1^{0.7}} q_{FW} + 1.70(0) - 0.50(5)q_{WF} =$$

$$1.40 - 3.90 - \frac{0.25}{1^{0.7}}(10.31 - 3.90) + 1.6(0.50)(0) -$$

$$(2.7)(1.70)(0)$$

Table I. Atomic Parameters Used in Electronegativity Equalization Calculations[a]

Atom	x(s)	x(p)	h	Atom	x(s)	x(p)	h
H	2.21		1.285	Nb	1.23		(0.50)
He	(2.75)		(1.50)	Mo	1.30		(0.50)
Li	0.84	0.47	0.46	Tc	1.36		(0.50)
Be	2.15	0.82	0.63	Ru	1.42		(0.50)
B	3.25	1.26	0.84	Rh	1.45		(0.50)
C	4.84	1.75	1.12	Pd	1.35		(0.50)
N	6.70	2.65	1.21	Ag	1.42		(0.50)
O	8.98	3.49	1.53	Cd	1.46		(0.50)
F	10.31	3.90	1.70	In	2.88	0.92	0.602
Ne	(11.44)	(4.40)	(1.90)	Sn	3.80	2.08	0.435
Na	0.74	0.32	0.467	Sb	4.22	2.36	0.871
Mg	1.77	0.56	0.53	Te	4.81	2.77	1.187
Al	2.69	1.11	0.585	I	5.06	2.52	0.915
Si	3.88	1.82	0.737	Xe	(7.60)	(3.80)	(1.20)
P	4.62	2.23	1.075	Cs	(0.40)	(0.40)	(0.40)
S	5.12	2.63	0.982	Ba	(1.15)	(0.25)	(0.40)
Cl	6.26	2.95	1.11	La	1.08		(0.50)
Ar	(9.00)	(4.20)	(1.50)	Ce	1.06		(0.50)
K	0.77	0.38	0.288	Pr–Sm	1.07		(0.50)
Ca	1.36	0.42	0.452	Eu	1.01		(0.50)
Sc		1.20	(0.50)	Gd	1.11		(0.50)
Ti		1.32	(0.50)	Tb–Ho	1.10		(0.50)
V		1.45	(0.50)	Er, Tm	1.11		(0.50)
Cr		1.56	(0.50)	Yb	1.06		(0.50)
Mn		1.60	(0.50)	Lu	1.14		(0.50)
Fe		1.64	(0.50)	Hf	1.23		(0.50)
Co		1.70	(0.50)	Ta	1.33		(0.50)
Ni		1.75	(0.50)	W	1.40		(0.50)
Cu		1.75	(0.50)	Re	1.46		(0.50)
Zn		1.66	(0.50)	Os	1.52		(0.50)
Ga	3.18	1.22	0.632	Ir	1.55		(0.50)
Ge	4.06	2.09	0.680	Pt	1.44		(0.50)
As	3.84	2.40	0.868	Au	1.42		(0.50)
Se	4.97	2.56	1.240	Hg	1.44		(0.50)
Br	5.94	2.62	0.940	Tl	(2.44)	(0.94)	(0.60)
Kr	(8.00)	(4.00)	(1.40)	Pb	(2.35)	(1.28)	(0.50)
Rb	0.50	0.54	0.418	Bi	(2.58)	(1.44)	(0.80)
Sr	1.26	0.34	0.424	Po	(3.06)	(1.76)	(1.00)
Y		1.11	(0.50)	At	(3.90)	(1.96)	(0.90)
Zr		1.22	(0.50)	Rn	(6.00)	(3.00)	(1.00)

[a] Values were taken from J. Hinze and H. H. Jaffe, *J. Amer. Chem. Soc.*, **84**, 540 (1962); *J. Phys. Chem.*, **67**, 1501 (1963); A. L. Allred and E. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958); E. J. Little and M. M. Jones, *J. Chem. Educ.*, **37**, 231 (1960). Parenthesized values are estimates.

From this equation we readily calculate $q_{WF} = 0.2210$, $Q_W = +1.326$, and $Q_F = -0.2210$.

We have written a Fortran IV computer program, CHELEQ, for making these atomic charge calculations; a printout of the program will be sent upon request.

Correlation of Core Binding Energies

Atomic charges calculated by the procedure which we have outlined can be used to correlate core binding energies by the point charge potential model equation[19]

$$E_B = kQ + V + l + E_R \tag{1}$$

In this equation, E_B is the binding energy for a particular core level in a particular atom (the "ionized" atom), Q is the charge of the ionized atom, V is the Coulomb potential energy at the site of the ionized atom due to the other charged atoms of the molecule, k and l are empirical constants (determined by least-squares fitting of the binding energies for a given element), and E_R is the relaxation energy associated with the shift of electron density toward the core hole. Explicit inclusion of the relaxation energy term can, in theory, be obviated by using modified values of Q and V corresponding to a hypothetical "transition state" molecule

which has a valence electron distribution halfway between that of the initial molecule and that of the core-ionized molecule.[1,20,21]

$$E_B = kQ + k\Delta Q^* + V + \Delta V^* + l \tag{2}$$

Here ΔQ^* and ΔV^* are the changes in Q and V on going from the initial to the transition state. Hence

$$E_R = k\Delta Q^* + \Delta V^* = k(Q_f - Q - 1)/2 + (V_f - V)/2 \tag{3}$$

where Q_f and V_f are the values of Q and V for the core-ionized molecule. These values can be estimated using the principle of equivalent cores,[22] in which it is assumed that a core-ionized atom is chemically equivalent to an atom of the next element in the periodic table.

Using eq 1 and 3, we have correlated 220 core binding energies for 144 different gaseous compounds. These binding energies include 64 carbon 1s, 20 nitrogen 1s, 24 oxygen 1s, 28 fluorine 1s, 11 silicon 2p, 13 phosphorus $2p_{3/2}$, 16 sulfur $2p_{3/2}$, 16 chlorine $2p_{3/2}$, 3 chromium $2p_{3/2}$, 8 ger-

(19) (a) K. Siegbahn *et al.*, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969; (b) U. Gelius, *Physica Scr.*, **9**, 133 (1974).

(20) W. L. Jolly, *Discuss. Faraday Soc.*, **54**, 13 (1972).
(21) D. W. Davis and D. A. Shirley, *Chem. Phys. Lett.*, **15**, 185 (1972).
(22) W. L. Jolly and D. N. Hendrickson, *J. Amer. Chem. Soc.*, **92**, 1863 (1970); W. L. Jolly in "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, and American Elsevier, New York, N. Y., 1972, p 629.

Table II. Charges, Relaxation Energies, and Experimental and Calculated Core Binding Energies

Compound	Q	$-E_R$, eV	E_B, eV[a] Exptl	Calcd[v]	Compound	Q	$-E_R$, eV	E_B, eV[a] Exptl	Calcd[v]
Carbon					CHF*CF$_2$	0.235	7.40	5.28[h]	5.78
Ge(CH$_3$)$_4$	-0.041	8.33	-1.12[b]	-1.03	CO	0.054	4.27	5.30[e,i]	4.81
Si(CH$_3$)$_4$	-0.054	8.20	-1.10[b]	-1.08	CCl$_4$	0.256	9.71	5.50[l]	4.13
HNCHCH*CHCH	-0.028	7.93	-0.90[c]	-0.55	CH$_2$F$_2$	0.214	7.10	5.55[j]	5.46
P(CH$_3$)$_3$	-0.031	7.76	-0.58[d]	-0.27	(NC)$_2$COC(CN)$_2$	0.201	8.86	6.00[f]	5.48
GeH$_3$CH$_3$	-0.043	8.33	-0.52[b]	-1.17	C$_4$F$_8$	0.275	8.36	6.30[h]	7.39
C$_6$H$_6$	-0.032	7.99	-0.50[e]	-0.82	CO$_2$	0.294	6.07	6.80[e]	7.38
OCHCH*CHCH	-0.022	7.94	-0.40[c]	-0.06	CHF$_3$	0.355	7.12	8.30[l]	8.10
SiH$_3$CH$_3$	-0.057	8.17	-0.40[b]	-1.18	C$_2$F$_6$	0.392	7.72	8.91[h]	9.44
CH$_2$CH$_2$*CH$_2$	-0.033	8.03	-0.30[f]	-0.66	CF$_4$	0.498	7.12	11.00[l]	10.75
C$_2$H$_6$	-0.047	7.55	-0.20[g]	-0.37	**Nitrogen**				
CH$_4$	-0.060	6.96	0.00	0.13	(CH$_3$)$_3$N	-0.186	7.44	-5.20[n]	-6.37
*CH$_3$CH$_2$(CO)OC$_2$H$_5$	-0.045	7.21	0.10[e]	0.46	(CH$_3$)$_2$NH	-0.194	6.74	-5.00[n]	-5.36
HNCH*CHCHCH	0.006	7.85	0.10[c]	-0.19	CH$_3$NH$_2$	-0.203	6.07	-4.80[n]	-4.38
*CH$_2$CHF	-0.046	7.31	0.18[h]	0.55	C$_6$H$_5$NH$_2$	-0.187	6.06	-4.40[e]	-3.99
*CH$_3$CH$_2$OH	-0.041	7.56	0.20[e]	0.11	NH$_3$	-0.211	5.37	-4.30[n]	-3.39
S(CH$_3$)$_2$	-0.007	7.82	0.29[d]	0.26	N$_2$H$_4$	-0.150	6.05	-3.80[n]	-3.51
*CH$_2$CF$_2$	-0.030	7.26	0.37[h]	1.66	(CH$_3$)$_3$NBH$_3$	-0.040	9.92	-3.27[d]	-4.48
C$_2$H$_2$	-0.062	6.82	0.40[i]	-0.09	(NC)$_2$CCH$_2$C(CN)$_2$	-0.150	5.34	-3.20[f]	-2.60
(CH$_3$)$_2$CO*	-0.022	7.58	0.50[e]	0.79	HCN	-0.153	5.37	-3.10[n]	-3.11
1,3,5-C$_6$H$_3$F$_3$ (*CH)	-0.008	7.99	0.56[j]	1.19	(NC)$_2$COC(CN)$_2$	-0.149	5.34	-2.80[f]	-2.38
*CH$_3$CHO	-0.023	7.42	0.60[e]	0.99	N$_2$	0.00	5.03	0.00	0.44
*CH$_3$CO$_2$H	-0.016	7.57	0.70[e]	1.33	NO	-0.033	4.24	0.80[n]	0.62
p-C$_6$H$_4$F$_2$ (*CH)	-0.019	7.99	0.76[j]	0.42	NOCl	0.074	6.24	1.50[n]	0.46
*OCHCHCHCH	0.053	7.61	0.80[c]	1.04	C$_6$H$_5$NO$_2$	0.294	8.06	1.70[e]	2.12
OC*CCO	0.033	7.63	0.80[k]	2.88	CH$_3$NO$_2$	0.278	8.00	2.23[h]	1.92
(NC)$_2$C*CH$_2$C(CN)$_2$	-0.017	8.05	1.40[f]	1.71	N$_2$F$_4$	0.164	6.71	2.40[n]	2.62
CH$_3$*CH$_2$OH	0.060	7.82	1.60[e]	1.23	*NNO	0.236	7.08	2.60[n]	2.71
CH$_3$Cl	0.020	7.70	1.60[l]	1.18	NO$_2$	0.234	6.33	3.00[n]	3.51
C$_2$H$_5$(CO)O*CH$_2$CH$_3$	0.062	7.82	1.70[e]	1.44	NF$_3$	0.233	6.32	4.30[n]	3.85
CH$_3$OH	0.048	7.18	1.75[e,i]	1.78	ONF$_3$	0.499	8.38	7.10[n]	7.09
C$_2$H$_4$O	0.067	7.68	1.80[i,f]	1.80	**Oxygen**				
C$_6$H$_5$F (*CF)	0.106	8.04	2.43[j]	1.71	(SiH$_3$)$_2$O	-0.283	4.48	-5.56[b]	-7.30
CH$_2$*CHF	0.078	7.37	2.54[h]	2.15	CH$_3$CHO	-0.194	2.89	-5.23[d]	-3.77
HCN	0.081	6.45	2.60[i]	3.21	(CH$_3$)$_2$O	-0.231	3.64	-5.16[b]	-5.40
p-C$_6$H$_4$F$_2$ (*CF)	0.106	8.04	2.74[j]	2.01	C$_2$H$_4$O	-0.229	3.62	-4.90[i]	-5.23
CH$_3$F	0.076	7.06	2.80[l]	2.72	VOCl$_3$	-0.319	4.23	-4.85[d]	-4.91
o-C$_6$H$_4$F$_2$ (*CF)	0.118	8.04	2.87[j]	2.56	CrO$_2$Cl$_2$	-0.301	4.25	-4.69[o]	-4.56
m-C$_6$H$_4$F$_2$ (*CF)	0.107	8.04	2.92[j]	2.10	C$_2$H$_5$OH	-0.235	3.00	-4.50[e]	-4.05
*CHFCF$_2$	0.109	7.36	2.93[h]	4.25	CH$_3$OH*	-0.236	2.95	-4.40[e,i]	-3.99
1,3,5-C$_6$H$_3$F$_3$ (*CF)	0.108	8.04	3.02[j]	2.48	C$_2$H$_5$(CO)O*C$_2$H$_5$	-0.207	3.66	-4.30[e]	-4.30
CH$_2$Cl$_2$	0.099	8.35	3.10[l]	2.25	CH$_2$O	-0.195	2.85	-4.12[p]	-3.69
(CH$_3$)$_2$*CO	0.132	7.91	3.10[e]	2.29	(CH$_3$)$_2$CO	-0.193	2.95	-4.10[e]	-3.88
(NC)$_2$*CCH$_2$C(CN)$_2$	0.096	7.04	3.10[f]	3.43	C$_4$H$_4$O	-0.205	3.66	-3.82[h]	-5.09
CH$_3$CHO	0.122	7.22	3.20[e]	3.03	H$_2$O	-0.240	2.26	-3.60[e,i]	-2.56
(NC)$_2$*COC(CN)$_2$	0.102	7.04	3.40[f]	4.03	C$_3$O$_2$	-0.162	2.85	-3.50[k]	-2.74
CH$_2$O	0.111	6.60	3.50[m]	3.69	SO$_2$	-0.290	2.79	-3.50[e]	-3.82
C$_6$F$_6$	0.132	8.04	3.57[j]	4.49	(NC)$_4$COC(CN)$_2$	-0.214	3.67	-3.20[f]	-2.97
C$_2$H$_5$(*CO)OC$_2$H$_5$	0.235	7.47	3.80[e]	4.31	H(CO)*OH	-0.213	2.94	-3.17[i]	-2.81
(NC)$_2$CCH$_2$C(CN)$_2$	0.100	9.19	4.10[f]	3.06	CH$_3$(CO)*OH	-0.212	3.00	-3.10[e]	-2.90
O*CCCO	0.146	6.94	4.20[k]	4.26	SO$_3$	-0.291	2.67	-2.60[d]	-2.49
CHCl$_3$	0.178	9.01	4.30[l]	3.25	CO$_2$	-0.147	2.76	-2.35[e,i]	-1.57
CH$_3$*CO$_2$H	0.234	7.51	4.70[e]	4.63	OCS	-0.158	2.81	-1.50[q]	-2.48
HCO$_2$H	0.224	6.80	5.00[e]	5.34	CO	-0.054	3.38	-1.00[e,i]	-1.86
CH$_2$*CF$_2$	0.219	7.39	5.14[h]	4.76	O$_2$	0.000	2.43	0.00	-0.22
					NO	0.033	3.00	0.20[e]	-0.36
					Fluorine				
					C$_2$H$_5$F	-0.148	2.31	692.05[h]	692.61
					C$_6$H$_5$F	-0.134	2.27	692.56[j]	693.00
					CH$_3$F	-0.149	2.31	692.60[j]	692.60
					m-C$_6$H$_4$F$_2$	-0.134	2.27	692.86[j]	693.18
					p-C$_6$H$_4$F$_2$	-0.134	2.27	692.86[j]	693.16
					o-C$_6$H$_4$F$_2$	-0.133	2.31	692.93[j]	693.10
					C$_2$H$_3$F	-0.135	2.30	692.93[h]	692.86
					CH$_3$CHF$_2$	-0.140	2.29	692.98[h]	693.38
					1,3,5-C$_6$H$_3$F$_3$	-0.134	2.27	693.07[j]	693.36
					CH$_2$F$_2$	-0.141	2.29	693.33[j]	693.39
					WF$_6$	-0.221	3.20	693.36[d]	693.07

Table II (*Continued*)

Compound	Q	$-E_R$, eV	E_B, eV[a] Exptl	Calcd[v]	Compound	Q	$-E_R$, eV	E_B, eV[a] Exptl	Calcd[v]
CHF*CF2	−0.134	2.29	693.73[h]	693.52	NSF3	0.810	3.02	176.90[s]	176.57
HF	−0.151	1.47	693.80[r]	694.47	SO2F2	0.972	2.89	177.50[d]	177.91
CH3CF3	−0.132	2.31	693.81[h]	694.06	SF4	0.783	2.54	177.60[t]	177.20
C6F6	−0.132	2.27	693.94[j]	693.83	SF5Cl	1.026	3.69	179.20[s]	178.64
PF3	−0.119	2.45	693.94[d]	693.91	SF6	1.110	3.40	180.40[e]	179.41
CH2CF2	−0.127	2.27	693.99[h]	693.65					
ClF	−0.084	2.46	694.04[d]	693.72			*Chlorine*		
GeF4	−0.150	2.93	694.11[b]	693.60	GeH3Cl	−0.096	1.68	205.50[b]	205.42
CHF3	−0.133	2.27	694.30[j]	694.18	VOCl3	−0.170	1.93	205.93[d]	206.03
CCl2F2	−0.132	2.32	694.32[h]	694.29	CrO2Cl2	−0.156	1.92	206.01[d]	206.31
CHFCF2*	−0.126	2.28	694.43[h]	693.87	SiH3Cl	−0.109	1.58	206.05[b]	205.49
NF3	−0.078	2.24	694.45[h]	694.77	CH3Cl	−0.081	1.18	206.07[b]	206.23
SiF4	−0.158	2.76	694.56[b]	693.96	PCl3	−0.052	1.30	206.27[d]	206.74
C4F8	−0.137	2.30	694.74[h]	694.61	GeCl4	−0.079	1.66	206.42[b]	206.43
C2F6	−0.131	2.27	694.95[h]	695.01	ICl	−0.042	1.46	206.68[m]	206.40
CF4	−0.124	2.26	695.20[b]	695.00	S2Cl2	−0.034	1.31	206.70[s]	206.71
F2	0.000	1.96	696.20[m]	695.83	SiCl4	−0.092	1.58	206.77[b]	206.53
					CCl4	−0.064	1.19	206.84[b]	207.14
					HCl	−0.090	0.71	207.22[b]	207.03
					Cl2	0.00	1.20	207.64[b]	207.17
		Silicon			ClF	0.084	0.76	208.21[m]	208.40
Si(CH3)4	0.035	3.51	105.96[b]	106.80	ClF3	0.746	1.52	213.02[m]	214.06
CH3SiH3	−0.013	2.75	106.82[b]	107.16	ClO3F	1.116	2.09	216.10[d]	215.33
Si2H6	−0.023	3.07	106.86[d]	106.78					
SiH4	−0.029	2.49	107.28[b]	107.35			*Chromium*		
(SiH3)2O	0.099	2.64	107.81[b]	107.81	Cr(CO)5C(OCH3)CH3	−1.019	0.67	581.10[o]	581.17
SiH3Br	0.057	2.98	108.08[b]	107.82	Cr(CO)6	−1.021	0.68	581.78[o]	581.71
SiH3Cl	0.071	2.86	108.11[b]	108.04	CrO2Cl2	0.916	0.40	587.40[o]	587.40
CH3SiCl3	0.284	3.83	109.25[d]	109.03					
SiBr4	0.309	4.38	109.73[b]	108.99			*Germanium*		
SiCl4	0.368	3.92	110.39[b]	109.86	Ge(CH3)4	−0.030	1.62	128.04[b]	128.72
SiF4	0.633	2.67	111.79[b]	112.43	CH3GeH3	−0.076	1.21	128.92[b]	129.09
					GeH4	−0.901	1.07	129.33[b]	129.20
		Phosphorus			GeH3Br	−0.003	1.32	130.04[b]	129.77
P(CH3)3	−0.060	3.19	135.76[d]	135.20	GeH3Cl	0.012	1.26	130.23[b]	129.94
PH3	−0.096	2.30	136.87[d]	136.19	GeBr4	0.250	2.05	131.35[b]	131.21
(CH3)3PBH3	0.140	4.10	137.00[d]	137.40	GeCl4	0.316	1.82	132.12[b]	131.89
(CH3)3PCH2	0.201	3.76	137.03[d]	138.18	GeF4	0.602	1.26	133.75[b]	133.96
(CH3)3PNH	0.248	3.69	137.39[d]	138.12					
(CH3)3PS	0.214	3.94	137.45[d]	137.81			*Bromine*		
(CH3)3PO	0.315	3.55	137.63[d]	138.92	GeH3Br	−0.078	0.56	75.65[b]	75.80
PCl3	0.517	3.23	139.60[d]	138.07	IBr	−0.022	0.51	76.00[m]	76.38
PSCl3	0.391	3.93	140.45[d]	140.05	CH3Br	−0.066	0.38	76.08[b]	76.18
POCl3	0.496	3.44	140.87[d]	141.03	SiH3Br	−0.093	0.52	76.13[b]	75.83
PF3	0.358	2.05	141.63[d]	140.86	GeBr4	−0.063	0.57	76.24[b]	76.50
POF3	0.719	2.51	142.90[d]	143.75	SiBr4	−0.077	0.52	76.47[b]	76.61
PF5	0.798	2.67	145.70[d]	144.70	CBr4	−0.050	0.40	76.57[b]	76.78
					HBr	−0.076	0.18	77.06[b]	76.63
		Sulfur			Br2	0.000	0.47	77.10[b]	76.57
S(CH3)2	−0.097	2.23	168.92[d]	168.81	BrF5	1.600	0.82	84.50[m]	84.51
CS2	−0.042	1.72	169.80[e]	170.38					
SCHCHCHCH	−0.063	2.19	169.90[c]	169.17			*Xenon*		
H2S	−0.119	1.45	170.20[e]	169.92	Xe	0.000	0.00	0.00[u]	−0.34[w]
OCS	−0.028	1.71	170.60[q]	170.95	XeF2	0.948	0.97	2.87[u]	3.31[w]
S2Cl2	0.034	2.44	171.50[s]	170.33	XeF4	1.729	1.94	5.41[u]	5.82[w]
(CH3)2SO	0.399	2.80	171.64[d]	173.06	XeOF4	2.222	2.36	7.07[u]	6.83[w]
(CH3)2SO2	0.673	3.41	173.63[d]	174.40	XeF6	2.370	2.83	7.64[u]	7.37[w]
SO2	0.580	2.02	174.80[e]	175.24					
SOF2	0.686	2.27	176.20[e]	176.28			*Tungsten*		
SO3	0.873	2.74	176.50[d]	177.01	W(CO)6	−0.953	0.88	37.60[d]	
					WF6	1.326	0.50	46.67[d]	

[a] The listed binding energies are absolute values except in the case of the compounds of carbon, nitrogen, oxygen, and xenon, for which relative values are listed. Some of the values originating from our laboratory are slightly different from values which we have previously reported. These changes are due to a recent recalibration of the Berkeley X-ray photoelectron spectrometer. [b] W. B. Perry and W. L. Jolly, *Inorg. Chem.*, 13, 1211 (1974). [c] U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, *Physica Scr.*, 3, 237 (1971). [d] W. B. Perry, T. F. Schaaf, R. Rietz, S. Avanzino, M. S. Lazarus, and W. L. Jolly, unpublished data. [e] Reference 19a. [f] G. D. Stucky, D. A. Matthews, J. Hedman, M. Klasson, and C. Nordling, *J. Amer. Chem. Soc.*, 94, 8009 (1972). [g] T. D. Thomas, *J. Chem. Phys.*, 52, 1373 (1970). [h] D. W. Davis, Ph.D. Thesis, University of California, Berkeley; Lawrence Berkeley Laboratory Report LBL-1900, May 1973. [i] D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, *J. Chem. Phys.*, 52, 3295 (1970). [j] D. W. Davis, D. A. Shirley, and T. D. Thomas, "Electron Spectroscopy," D. A. Shirley, Ed., North-Holland Publishing Co., Amsterdam, 1972, p 707. [k] U. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, *Chem. Phys. Lett.*, 11, 224 (1971). [l] T. D. Thomas, *J. Amer. Chem. Soc.*, 92, 4184 (1970). [m] T. D. Thomas, unpublished data. [n] P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 10, 378 (1971). [o] W. B. Perry, T. F. Schaaf, W. L. Jolly, L. J. Todd, and D. L. Cronin, *ibid.*, 13, 2038 (1974). [p] B. Mills, unpublished data. [q] C. J. Allan, U. Gelius, D. A. Allison, G. Johansson, H. Siegbahn, and K. Siegbahn, *J. Electron Spectrosc. Relat. Phenomena*, 1, 131 (1972). [r] P. Finn and W. L. Jolly, unpublished data. [s] W. L. Jolly, M. S. Lazarus, and O. Glemser, *Z. Anorg. Allgem. Chem.*, in press. [t] R. W. Shaw, T. X. Carroll, and T. D. Thomas, *J. Amer. Chem. Soc.*, 95, 5870 (1973). [u] T. X. Carroll, R. W. Shaw, T. D. Thomas, C. Kindle, and N. Bartlett, *ibid.*, 96, 1989 (1974). [v] Potentials calculated using literature structural data, principally from ref 13. [w] Calculated using $x(s) = x(p) = 7.00$ and $h = 2.50$ for the core-ionized state of Xe (*i.e.*, Cs with $Q > 1$).

manium $3p_{3/2}$, 10 bromine $3d_{5/2}$, 5 xenon $3d_{5/2}$, and 2 tungsten $4f_{7/2}$ binding energies.

The compounds, the appropriate atomic charges, the calculated relaxation energies, and the experimental and calculated binding energies are listed in Table II. The least-squares evaluated parameters, k and l, and the corresponding correlation coefficients and standard deviations for various elements are listed in Table III. All in all, the correlations, as measured by the standard deviations and the correlation coefficients, are quite good and attest the usefulness of the charge calculation method. For comparison, the standard deviations for correlations in which the relaxation energy was ignored are also listed in Table III. In most cases, omission of the relaxation energy correction caused an increase in the standard deviation. By a simple interpretation of the potential model equation it can be shown that the empirical k values should be inversely proportional to the radii of the valence electron shells.[19] One might expect that valence shell radii would be proportional to the corresponding covalent radii, and, indeed, the k values obtained from our binding energy correlations are approximately inversely proportional to the reciprocal of the covalent radii of the atoms.

Nonequivalent Resonance Structures

For some molecules, nonequivalent resonance structures can be written. For example, two acceptable Lewis structures for N_2O are

$$^-N \xrightarrow{.20} \overset{+}{N} \xrightarrow{.20} O \qquad\qquad N \xrightarrow{.30} \overset{+}{N} {\longrightarrow} O^-$$

Similarly, hyperconjugation ("no-bond" resonance) is significant in some molecules. Thus the following structures can be written for SOF_2
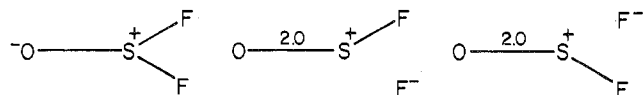
Both the formal charges and the calculated charges of the peripheral atoms of these compounds depend on the relative weights assigned to the resonance structures. Unfortunately, *a priori* weighting of the resonance structures is impossible, and therefore the binding energies for such atoms were excluded from our correlations. Of course, by appropriate weighting of the resonance structures, binding energies for such atoms can be made to fit eq 1, using values of k and l obtained from the correlation of the compounds which do not have nonequivalent resonance structures. Empirical rules for such weighting will be the subject of a future paper.

The formal charges and, to a large extent, the calculated charges of the *central* atoms of compounds such as N_2O and SOF_2 are *independent* of the relative weights assigned to the resonance structures. Hence binding energies for such atoms,

**Table III.** Parameters of Potential Model Correlations

Element	k	l	Correln coeff	Std dev	Std dev, no E_R
C	30.50	8.12	0.972	0.62	0.81
N	30.69	5.46	0.987	0.60	1.01
O	25.50	2.21	0.896	0.73	0.59
F	27.95	697.79	0.934	0.34	0.26
Si	17.29	110.06	0.964	0.47	0.51
P	19.28	139.37	0.953	0.89	1.33
S	18.63	172.30	0.983	0.70	0.74
Cl	18.24	208.36	0.988	0.44	0.52
Cr	10.95	585.43	1.000	0.07	0.07
Ge	15.87	130.86	0.984	0.34	0.47
Br	13.32	77.05	0.993	0.31	0.38
Xe	12.06	-0.32	0.992	0.39	0.37
W	11.52	42.36			

which are relatively unaffected by the resonance of the molecules, were included in the correlations.

Inasmuch as the correlations involve the calculation of atomic charges for the core-ionized molecules as well as the ground-state molecules, resonance structures for the core-ionized molecules must also be considered. For example, although the structure

$$\overset{\displaystyle O}{\underset{\displaystyle CH_3-C-OH}{\|}}$$
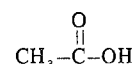
is a satisfactory representation of the ground-state acetic acid molecule, the analogous structure for the molecule in which the carbonyl oxygen atom has lost a 1s electron is inadequate. In that case, two resonance structures are important.[23]

$$\overset{\displaystyle F^+}{\underset{\displaystyle CH_3-C-OH}{\|}} \longleftrightarrow \overset{\displaystyle F}{\underset{\displaystyle CH_3-C=\overset{+}{O}H}{|}}$$
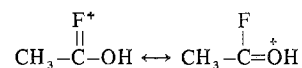
Therefore the binding energies for atoms of this type have been omitted from the present correlations. On the other hand, a single structure, analogous to that for the ground-state molecule, is adequate for the molecule in which the hydroxyl oxygen atom has lost a 1s electron

$$\overset{\displaystyle O}{\underset{\displaystyle CH_3-C-\overset{+}{F}-H}{\|}}$$
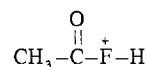
Of course, the binding energies for such atoms have been included in the correlations.

(23) In the structure shown, the core-ionized oxygen atom has been replaced with the isoelectronic F^+ ion, in accord with the principle of equivalent cores.[22]