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LBL-3984
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DEDUCTION OF RESONANCE STRUCTURES FROM CORE ELECTRON BINDING ENERGIES

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Contribution from the Department of Chemistry, University of California, and the Inorganic Materials Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Deduction of Resonance Structures from Core Electron Binding Energies

WILLIAM L. JOLLY,* THEODORE F.SCHAAF, AND WINFIELD B. PERRY

ABSTRACT:

A method for estimating the weighting of resonance structures using core electron binding energies, the potential equation, and CHELEQ atomic charges is described. The method is applied to compounds, such as $POCl_3$, which have bonds between atoms of opposite formal charge. Hyperconjugation is found to be important, whereas no evidence is found for $p\pi \rightarrow d\pi$ bonding. New core binding energy data are presented for several compounds.

Introduction

Atomic charges calculated by the CHELEQ electronegativity equalization procedure can be used for the correlation of core electron binding energies of a wide variety of elements in gaseous compounds.[1,2] The best correlations are achieved using the following "potential equation,"

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

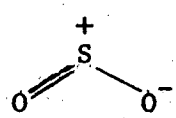
in which E_B is the electron binding energy for a particular core level in a particular atom (the "ionized" atom), Q is the charge of the ionized atom, V is the coulomb potential energy at the site of the ionized atom due to the other charged atoms of the molecule, and E_R is the relaxation energy associated with the shift of electron density toward the core hole. The relaxation energy[3] is calculated from the relation

$$E_R = k(Q_f - Q - 1)/2 + (V_f - V)/2$$

where Q_f and V_f correspond to the values of Q and V for the core-ionized molecule. The atomic charges of the latter species are calculated by assuming that the ionized core is chemically equivalent to the core of the next element in the periodic table. In effect, the procedure correlates binding energies with atomic charges which are midway between those of the ground-state molecule and those of the ionized molecule.

The calculation of the atomic charges of a molecule by the CHELEQ method requires that one first write a single valence bond structure for the molecule. Such a structure is easily written for a simple

molecule such as SiH_3Cl or CO_2. In the case of a molecule for which there is more than one satisfactory valence bond structure, a suitable resonance hybrid structure must be written. This procedure is straightforward for a symmetric molecule such as SO_2. Equal weighting of the two equivalent resonance structures



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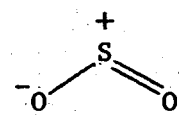
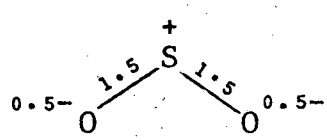
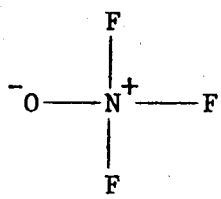


yields the following resonance hybrid.[4]



However, for an asymmetric molecule with nonequivalent resonance structures, it is impossible <u>a priori</u> to predict the relative weights of the resonance structures. Thus in the case of N_2O, it is not obvious how one should weight the structures $N\equiv\overset{+}{N}-O^-$ and $^-N=\overset{+}{N}=O$. Nonequivalent resonance structures are also involved in molecules which are engaged in hyperconjugation or "no-bond" resonance. For example, the structure of ONF_3 can be written in the completely single-bonded form, as follows,



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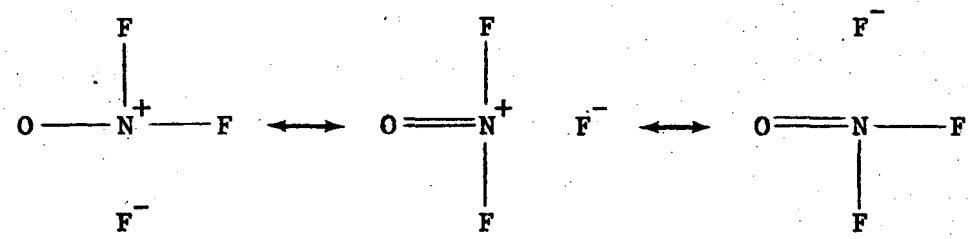
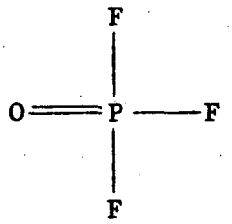
or in hyperconjugated forms in which the N-O bond order has increased at the expense of the N-F bond order:



2a 2b 2c

If we admit the possible participation of valence-shell d orbitals in nonmetallic elements beyond the first row of the periodic table, resonance structures involving $p\pi \rightarrow d\pi$ bonding must be included and appropriately weighted. For example, in the case of POF_3, we not only can write structures analogous to those written for ONF_3, but, in principle, we can also write the structure



There is no difficulty in calculating the CHELEQ charges of atoms in molecules such as SiH_3Cl, CO_2, and SO_2, for which unambiguous valence bond structures can be written. In the case of a molecule with non-equivalent resonance structures, at least two of the atoms have uncertain formal charges[4] because of the uncertain weighting of the structures. Therefore, because the calculated atomic charges are strongly dependent on the assumed formal charges, it is impossible a priori to calculate charges for such atoms. However charges can be fairly confidently

calculated for the remaining atoms, whose formal charges are independent of the relative weighting of the resonance structures. The data for N_2O, in Table I, illustrate the effect. The calculated charges for the terminal atoms are quite different in the two resonance structures, whereas the calculated charges for the middle atom are similar.

Table I. CHELEQ Atomic Charges for Two Resonance Structures of Nitrous Oxide

Resonance Structure	Calculated Charge		
	End N	Middle N	O Atom
$N{\equiv}N{-}O^{-}$	0.352	0.331	-0.684
$^{-}N{=}N{=}O$	-0.416	0.266	0.150

The core binding energies of atoms for which charges can be unambiguously, or relatively unambiguously, calculated, have been used to evaluate empirically the k and ℓ values of equation 1 for various elements. These k and ℓ values may be combined with core binding energies of atoms whose charges are ambiguous to determine the relative weightings of resonance structures which give exact agreement between the experimental and calculated binding energies. The purpose of this paper is to discuss the significance of the resonance structure weightings determined by this method for various types of molecules.

Method

Since the calculation of core binding energies involves core-ionized molecules as well as ground-state molecules, changes in the

weighting of the resonance structures in the core ionized molecules must be considered. For example, the weights assigned to the resonance structures of core-ionized N_2O are expected to differ depending on which atom is core-ionized. If an oxygen 1s electron is ejected, the resonance structure $N{\equiv}\overset{+}{N}{-}O^{*}$ (or the equivalent-core analog,[5,6] $N{\equiv}\overset{+}{N}{-}F$) would be expected to contribute more than it does in the ground state. Conversely, if the terminal nitrogen atom is core-ionized, the weight assigned to $\overset{*}{N}{=}\overset{+}{N}{=}O$ (or the equivalent-core analog,[5,6] $O{=}\overset{+}{N}{=}O$) would be expected to increase relative to the ground state. Core ionization of the central nitrogen atom would not be expected to strongly favor either resonance structure. Therefore it is reasonable to assume that there is no change in weighting during core ionization of the central atom.

The change in weighting of resonance structures upon core ionization always correponds to a shift of negative formal charge toward the core-ionized atom, and this process contributes to the electronic relaxation. We call this change in weighting of resonance structures <u>resonance relaxation</u> and the core binding energy change associated with it <u>resonance relaxation energy</u>.[7] Resonance relaxation and resonance relaxation energy are artifacts due to the use of simple valence bond theory in the description of the ground-state and core-ionized molecules. However these concepts will be valuable as long as chemists continue to describe molecules by valence bond structures. Resonance relaxation must be accounted for if the contribution of different resonance structures to the ground state is to be determined by fitting core binding energies.

Binding energy data for molecules for which the ground-state valence

bond structures are unambiguous and for which the core-ionized states are hybrids of nonequivalent structures allow one to estimate the magnitude of resonance relaxation. Carbon dioxide can be used as an example.[5,6]

$$O{=}C{=}O \xrightarrow{-e(O1s)} \underset{\underset{3}{\sim}}{{}^{+}F{=}C{=}O} \longleftrightarrow \underset{\underset{4}{\sim}}{F{-}C{\equiv}O^{+}}$$

After core ionization of one of the oxygen atoms, two resonance forms are needed to describe the molecule. (We assume that the form ${}^{2+}F{\equiv}C{-}O^{-}$ is of negligible importance.) On the basis of electronegativity considerations, we would expect form $\underset{\sim}{4}$ to make the major contribution to the valence bond structure of the core-ionized molecule in its equilibrium state. However photoionization is fast relative to nuclear motion, and the core-ionized molecule will not have its equilibrium geometry, but will have the same geometry as that of the ground-state molecule. Thus we expect resonance form 3 to be of considerable importance because the bond lengths are almost optimal for this resonance form.

The valence bond description of the core-ionized molecule can be determined by the following procedure. Using the k and ℓ values for oxygen[8] the calculated O 1s binding energy is made to agree with the experimental value by varying the weights assigned to the resonance forms of the core-ionized molecule. In the case of CO_2 this procedure leads to the following valence bond structure of the ion,[4]

$$^{.81+}F \overset{1.81}{\text{———}} C \overset{2.19}{\text{———}} O^{.19+}$$

corresponding to 81 percent of resonance form 3 and 19 percent or resonance form 4.

Table II lists molecules which have unambiguous ground-state structures and which are expected to show resonance relaxation. The hybrid structure of the core-ionized molecule which yields a calculated binding energy equal to the experimental value, the initial formal charge on the core-ionizing atom, the change in the order of the bond to the core-ionizing atom, and the resonance relaxation energy are tabulated. The resonance relaxation energy is the experimental binding energy less the binding energy calculated assuming that the bond orders in the core-ionized molecule are the same as those in the ground state molecule. The data in Table II show that the resonance relaxation energy and the change in the order of the bond to the core-ionizing atom are approximately proportional to one another. Both of these quantities show a rough correlation with the initial formal charge on the core-ionizing atom. In general, the more negative the initial formal charge, the lower the absolute magnitude of the resonance relaxation energy. In the case of the oxygen 1s ionization of SO_3, the absolute magnitude of the resonance relaxation energy is quite large in spite of a very negative initial formal charge, probably because of the presence of two other oxygen atoms which can donate negative formal charge to the core ionized atom. Only SO_2 appears to be somewhat irregular; the resonance relaxation energy of this molecule would have been expected to be about -0.3 eV rather than 0.0 eV.

In the case of compounds with ambiguous ground states, resonance relaxation complicates the determination of the weightings of the resonance structures of both the ground-state and core-ionized molecules. To put

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Table II. Resonance Relaxation in Compounds with Unambiguous Ground States

Compound[a]	Core ionized hybrid for which $E_B(\text{calcd}) = E_B(\text{exp})$[b]	Initial formal charge on core ionizing atom	Change in order of bond to core ionizing atom	Resonance relaxation energy, eV	Binding energy ref.
$\underset{\sim}{CO_2}$	$\overset{.81+}{F} \xrightarrow{1.81} C \xrightarrow{2.19} \overset{.19+}{O}$	0.0	-.19	-0.75	c
$\underset{\sim}{NO_2}$	$\overset{.66+}{F} \xrightarrow{1.66} \overset{.5+}{N} \xrightarrow{1.84} \overset{.16-}{O}$	-.25	-.09	-0.56	c
$H_3C\underset{\sim}{NO_2}$	$CH_3\overset{1+}{N}$ (1.45) $\overset{.45+}{F}$; (1.55) $\overset{.45-}{O}$	-.50	-.05	-0.36	d
$\underset{\sim}{SO_3}$	$\overset{.273+}{F} \xrightarrow{1.27} \overset{2+}{S} \xrightarrow{1.36} \overset{.637-}{O_2}$	-.67	-.06	-0.50	e
$\underset{\sim}{SO_2}$	$\overset{.5+}{F} \xrightarrow{1.5} \overset{1+}{S} \xrightarrow{1.5} \overset{.5-}{O}$	-.50	0.0	0.0	e
$\underset{\sim}{CS_2}$	$\overset{.80+}{Cl} \xrightarrow{1.80} C \xrightarrow{2.20} \overset{.20+}{S}$	0.0	-.20	-0.63	c

[a] Core-ionized atom in bold face type.

[b] Equivalent-cores analogs given.

[c] K. Siegbahn *et al.*, "ESCA Applied to Free Molecules,", North-Holland Publishing Co., Amsterdam, 1969.

[d] D. W. Davis, Ph.D. Thesis, University of California, Berkeley; Lawrence Berkeley Laboratory Report LBL-1900, May 1973.

[e] This work. See Experimental section.

limits on the weightings of the ground-state structures, we have used the following procedure. For each core ionization, the contributions of the resonance structures are first assumed to be identical in the ground-state and core-ionized molecules; i.e., resonance relaxation is ignored. The resonance structures are weighted such that the calculated and experimental binding energies agree. The weighting thus determined for the structure favored by core ionization must be an upper limit to the weighting of that structure in the ground state. By making calculations of this sort for two appropriately chosen atoms in a molecule it is possible to establish limiting values for the contributions of different resonance structures in the ground state. Let us consider the case of N_2O. The calculated core binding energy of the terminal nitrogen agrees with the experimental value when it is assumed that the structure $^{-}N{=}\overset{+}{N}{=}O$ ($^{+}O{=}\overset{+}{N}{=}O$) contributes 68 percent to both the ground- and excited-state resonance hybrids. The actual contribution of this resonance structure to the ground state of the molecule must be less than 68 percent. The oxygen core binding energy agrees with the calculated value when the structure $N{\equiv}\overset{+}{N}{-}O^{-}$ ($N{\equiv}\overset{+}{N}{-}F$) is assumed to contribute 42 percent in both the ground-state and core-ionized molecules. This result corresponds to a contribution of more than 58 percent by the $^{-}N{=}\overset{+}{N}{=}O$ structure to the ground state. Thus nitrous oxide can be described by the resonance

$$\underset{58\text{-}68\%}{^{-}N{=}\overset{+}{N}{=}O} \longleftrightarrow \underset{42\text{-}32\%}{N{\equiv}\overset{+}{N}{-}O^{-}}$$

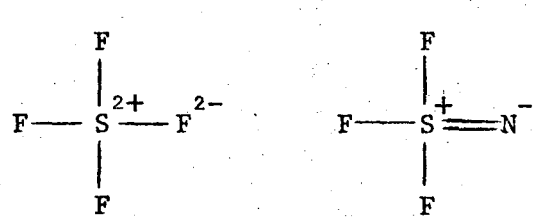
Such resonance is reasonable in light of the equilibrium bond distances in N_2O.[9] The N-N distance is 1.126 Å, between the distance corresponding

to a triple bond (1.098 Å) and that typical of a double bond (1.25 Å). The N-O distance is 1.186 Å, between the distances typical of a double bond (1.15 Å) and a single bond (1.4 Å). The estimated bond orders also agree fairly well with the theoretical values of Boyd[10] ($B.O._{N-N} = 2.66$, and $B.O._{N-O} = 1.57$).

Results and Discussion

Bonds between atoms of opposite formal charge, in which the positive atom is bonded to two or more ligand atoms, are abnormally short and have large stretching force constants.[11] Examples are the P-O bond in $POCl_3$, the S-O bond in SOF_2, and the S-N bond in SNF_3. This strengthening of the bond between the two charged atoms has been ascribed to hyperconjugation, to $p\pi \rightarrow d\pi$ bonding, and to a combination of these. Because these two types of bonding cause different charge distributions, it is possible to investigate their relative importance by the study of core binding energies.

d-Orbital participation. Thiazyltrifluoride is a compound in which $p\pi \rightarrow d\pi$ bonding might be expected to be significant.[12] Making the reasonable assumption that the nitrogen atom is a stronger π donor than the fluorine atoms, we can describe the ground-state molecule as a hybrid of the resonance structures



The double bond implies the use of sulfur 3d orbitals in the bonding. By adjusting the weighting of these two structures to obtain agreement between the calculated and experimental nitrogen 1s binding energies (assuming the same weighting in the ground-state and core-ionized molecules), we obtain the minimum contributions of the double-bonded structure.[13] Core ionization of the sulfur atom favors an increase in $p\pi \rightarrow d\pi$ bonding. Thus adjustment to fit the sulfur 2p binding energy gives the maximum contribution of the double-bonded structure. The results of these calculations for SNF_3 and of analogous calculations for POF_3 and $SO(CH_3)_2$ are given in Table III. The data for each compound are internally inconsistent: the minimum contributions calculated from the nitrogen and oxygen data are much larger than the maximum contributions calculated from the central atom data. Because of these results and the fact that the data for the compounds can be fit well by assuming hyperconjugation, we conclude that d orbital participation is not important in determining the charge distribution in such compounds. The same conclusion has been drawn from other binding energy data, using different arguments.[14,15]

Hyperconjugation. The results presented in Table III imply that the central atoms in these molecules have quite positive formal charges and that a significant amount of negative formal charge is located on all the ligand atoms. Such a distribution of formal charge is consistent with important contributions from hyperconjugated or "no-bond" resonance forms. Other experimental evidence, including the short N-O bond distances and large N-O force constants in NOF_3[16] and trimethylamine oxide[17] (where d orbital effects can be ignored) also imply hyperconjugation in compounds

Table III. Attempt to Fit Binding Energies with $p\pi \rightarrow d\pi$ Bonding

Compound	Atom for which $E_B(calc) = E_B(exp)$	$p\pi \rightarrow d\pi$ bond order
NSF_3	N	> 1.50
	S	< 0.04
	F	< 1.68
OPF_3	O	> 0.70
	P	< 0.20
	F	< 0.78
$OS(CH_3)_2$	O	> 0.60
	S	< 0.00
	C	< 1.50

of this type. The hyperconjugated ONF_3 molecule may be represented as a hybrid of resonance structure 1 and the three equivalent canonical structures 2a, 2b, and 2c. Core ionization of the oxygen atom would be expected to reduce hyperconjugation, and core ionization of the fluorine atoms would be expected to increase hyperconjugation in the core-ionized molecule. By assuming no resonance relaxation and by bringing the calculated oxygen core binding energy into agreement with the experimental value by adjusting the assumed degree of hyperconjugation we can establish a lower limit to the amount of hyperconjugation. In a similar manner an upper limit to the amount of hyperconjugation can be determined by fitting the fluorine core binding energy. The minimum and maximum N-O bond orders determined by this method are 1.54 and 1.60. Analogous data, calculated for 23 compounds, are listed in Table IV. For each compound, the upper and lower limits of the order of the bond between the positive formal-charged central atom and the π-donor atom are given. These limits can be taken as measures of the upper and lower limits to the hyperconjugation in the ground-state molecules.

In the case of the fluorine compounds, the upper and lower limits are very close; in fact, in several cases the calculated upper limit is slightly below the lower limit ("impossible" results of this type probably represent failures of the CHELEQ method). We conclude that, in the fluorine compounds, there is very little resonance relaxation during core ionization of either the fluorine atoms or the π-donor atoms. Thus either the upper or lower limits to the bond orders (or their average values) may be taken as fair approximations to the ground state of the fluorine compounds.

Table IV. Minimum and Maximum Degrees of Hyperconjugation Determined from Core Binding Energies

Molecule	Order of Bond Between Central Atom and π-Donor Atom		Binding Energy Ref.
	Lower limit	Upper limit	
N_2O	1.58[a]	1.68[a]	b, c, d
ONF_3	1.54	1.60	b, e
$ON(CH_3)_3$	1.47	1.96	e
$H_3BN(CH_3)_3$	----[f]	1.51	e
OPF_3	1.48[g]	1.46[g]	h, i
$OPCl_3$	1.46	1.63	e
$OP(OCH_3)_3$	1.38	1.84	h
$OP(CH_3)_3$	1.44	1.99	e
$HNP(CH_3)_3$	1.44	1.87	e
$H_2CP(CH_3)_3$	1.40	1.84	e
$H_3BP(CH_3)_3$	----[f]	1.57	e
$SP(CH_3)_3$	1.39	1.84	e
$SPCl_3$	1.48	1.66	e
O_2SF_2	1.30	1.38	i
O_2SCl_2	1.28	1.42	i
$O_2S(OCH_3)_2$	1.28[j] 1.21[k]	1.51[j] 1.42[k]	h

contd.

Table IV, contd.

$O_2S(CH_3)_2$	1.25	1.44	h, i
OSF_2	1.49[g]	1.48[g]	h
$OSCl_2$	1.48	1.60	h
$OS(OCH_3)_2$	1.39	1.62	h
$OS(CH_3)_2$	1.38	1.62	h
NSF_3	1.89[g]	1.87[g]	l
O_3ClF	1.12	1.16	i

[a]N-O bond order.

[b]P. Finn, R. K. Pearson, J. M. Hollander, and W. L. Jolly, Inorg. Chem., 10, 378 (1971).

[c]K. Siegbahn et al., "ESCA Applied to Free Molecules," North-Holland Publ. Co., Amsterdam, 1969.

[d]D. W. Davis, J. M. Hollander, D. A. Shirley, and T. D. Thomas, J. Chem. Phys., 52, 3295 (1970).

[e]Ref. 14.

[f]Lower limit could not be established because reliable k and ℓ values are not available for boron.

[g]Inconsistencies in the calculated limits can be attributed to inadequacy of the CHELEQ calculations.

[h]This work; see Experimental section.

[i]S. C. Avanzino, W. L. Jolly, M. S. Lazarus, W. B. Perry, and R. R. Rietz and T. F. Schaaf, Inorg. Chem., 14, 0000 (1975).

[j]Lower binding energy O 1s line assigned to methoxy oxygen atom.

[k]Higher binding energy O 1s line assigned to methoxy oxygen atom.

[l]Ref. 12b.

For most of the non-fluorine compounds, the calculated limits are more widely separated, and in such cases it is not immediately obvious what degree of hyperconjugation should be assigned to the ground-state molecules. However we present the following argument for assigning the lower limits to the ground-state molecules in all cases. In each group of similar molecules (for example, the four-coordinate phosphorus compounds), the lower limit is fairly constant. Thus the lower limit to the order of the bond between the phosphorus atom and the π-donor atom ranges from 1.38 in $OP(OCH_3)_3$ to 1.48 in OPF_3 and $SPCl_3$. In the same group of molecules, the upper limit has a much wider range of values. Thus the upper limit of the bond order ranges from 1.46 in OPF_3 to 1.99 in $OP(CH_3)_3$. In general, the upper limit is greater the lower the electronegativity of the non-π-bonded atoms. Now, it seems unreasonable to assume that hyperconjugation is more important in a molecule with relatively electropositive ligand atoms, such as $OP(CH_3)_3$, than in a molecule with very electronegative ligand atoms, such as OPF_3. We believe it is more reasonable to assume that, within a group of similar molecules, the degree of hyperconjugation is essentially constant -- that is, equal to the lower limit indicated in Table IV. Thus we conclude that the order of the bond between the central atom and the π-donor atom is about 1.50 in four-coordinate nitrogen compounds, about 1.43 in four-coordinate phosphorus compounds, about 1.28 in sulfuryl compounds, and about 1.44 in thionyl compounds.

The assumption that the degree of hyperconjugation within a group of similar molecules is constant does not imply that the actual charges on the ligand atoms are constant. For example, although we conclude

that the oxygen atoms in O_2SF_2 and $O_2S(CH_3)_2$ both have formal charges of about -0.72, we calculate significantly different CHELEQ charges (-0.33 and -0.40, respectively) for these atoms. Similarly, constancy of hyperconjugation does not require that analogous bond distances be equal. Thus, although the S-O bond order is assumed to be about 1.28 in both O_2SF_2 and $O_2S(CH_3)_2$, the bond distances are 1.405 Å and 1.446 Å, respectively.[18,19] The shorter bond distance in O_2SF_2 is probably due to the greater charge on the sulfur atom in O_2SF_2 (+0.97) than that in $O_2S(CH_3)_2$ (+0.68). One would expect that, other things being equal, a bond between atoms of opposite charge would be shorter the greater the charge difference.

Experimental

The data in Tables II and IV ascribed to this work were obtained using the Berkeley iron-free spectrometer using techniques previously described.[14,20] Commercial samples were used. Purity was checked by NMR or vapor pressure measurements. The observed binding energies, in eV, are as follows. (Reproducibilities were generally ± 0.05 eV except as indicated). Trimethyl phosphate C 1s 292.58, O 1s methoxy 538.95, terminal 536.56, P $2p_{3/2}$ 139.72; dimethyl sulfate C 1s 293.03, O 1s 538.42, 539.86 (assignment uncertain), S $2p_{3/2}$ 176.26; dimethyl sulfite C 1s 292.38, O 1s methoxy 538.89, terminal 537.76, S $2p_{3/2}$ 173.42; dimethyl sulfoxide C 1s 291.07, O 1s 536.50 ± 0.10, S $2p_{3/2}$ 171.64; dimethyl sulfone C 1s 291.58, O 1s 537.67 ± 0.10, S $2p_{3/2}$ 173.63; thionyl chloride Cl $2p_{3/2}$ 206.38, O 1s 538.83 ± 0.15, S $2p_{3/2}$ 174.36 ± 0.10; sulfur dioxide O 1s 539.70, S $2p_{3/2}$ 174.64; phosphorus(V) oxytrifluoride P $2p_{3/2}$ 142.9 ± 0.1.

Addendum

k and ℓ values. New k and ℓ values differing slightly from those previously published[2] have been determined by rigorously exluding core binding energies which could be affected by resonance relaxation and by the inclusion of new core binding energies which have become available. The new k and ℓ values are listed in Table V. For completeness, we have included values for all elements for which we have sufficient data.

Acknowledgments. This work was supported by the National Science Foundation (Grant GP-41661X) and the U. S. Energy Research and Development Administration. We wish to thank M. S. Lazarus, R. R. Rietz, and S. C. Avanzino for their considerable help with the experimental work.

Table V. Revised k and ℓ Values

Element	Number of Compounds	k	ℓ	Correl. Coeff.	Std. dev. eV
C 1s	64	29.89	8.04	0.981	0.58
N 1s	18	30.23	5.22	0.987	0.61
O 1s	17	26.61	2.61	0.955	0.49
F 1s	31	28.68	697.98	0.938	0.34
Si 2p	11	17.29	110.07	0.964	0.47
P $2p_{3/2}$	13	19.28	139.37	0.953	0.89
S $2p_{3/2}$	13	18.58	172.33	0.979	0.72
Cl $2p_{3/2}$	18	18.27	208.34	0.988	0.43
V[a] $2p_{3/2}$	6	22.98	514.30	0.992	0.46
Ge $3p_{3/2}$	8	15.87	130.89	0.984	0.33
Br $3d_{5/2}$	12	13.40	76.96	0.990	0.36
Sn[b] $3d_{5/2}$	12	14.77	493.57	0.943	0.44

[a]Ref. 20.

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(3) The relaxation energy, as defined in this paper, is a negative quantity.

(4) The charges indicated in valence bond structures of this type are formal atomic charges. The formal charge is the charge which the atom would have if the bonding electrons in each bond were equally apportioned between the pair of bonded atoms.

(5) According to the equivalent cores approximation,[6] a core-ionized atom is equivalent to the next atom in the periodic table, but with one valence electron missing.

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(7) It should be noted that the resonance relaxation energy is only a part of the total relaxation energy associated with core electron ejection.

(8) See addendum.

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(13) Because orbital electronegativities are not available for d orbitals, we have arbitrarily assigned them electronegativities equal to those of sp^3 hybrids of the same principal quantum number. This procedure corresponds to overestimating the d orbital electronegativities and causes our calculated $p\pi \rightarrow d\pi$ bonds orders (based on the assumption of good $p\pi$-$d\pi$ overlap) to be too small. Nevertheless our conclusion regarding the relative importance of $p\pi \rightarrow d\pi$ bonding, based on the inconsistencies of Table III, is still valid.

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