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THE USE OF CORE ELECTRON BINDING ENERGIES AS BENCH MARKS FOR THE COMPARISON OF VALENCE SHELL IONIZATION POTENTIALS

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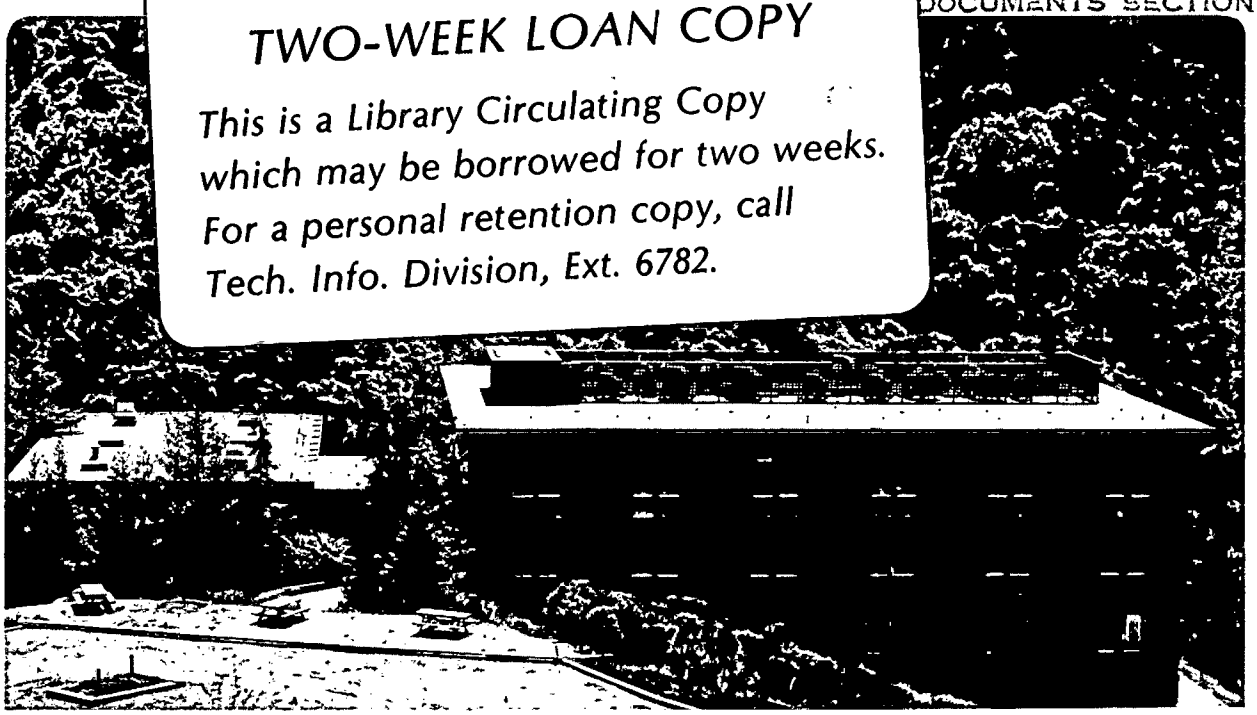

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The Use of Core Electron Binding Energies as Bench Marks for the Comparison of Valence Shell Ionization Potentials

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ABSTRACT

The difference between the ionization potential of a molecular orbital and a core binding energy of an atom on which the molecular orbital has appreciable density is a measure of the strength with which electrons are held in the molecular orbital, free of the effects of atomic charges and electronic relaxation energies. Such differences can be used to compare the intrinsic bonding or antibonding characters and the s, p hybridizations of orbitals on atoms of a particular element in various compounds. Thus core binding energies should be useful in the assignment of ultraviolet photoelectron spectra.

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Often the most difficult step in the study of a molecule by ultraviolet photoelectron spectroscopy is the assignment of the observed photoelectron bands to specific molecular orbitals. Even simple molecules can have perplexing spectra. Therefore, when making spectral assignments, one should take advantage of any information which has a bearing on the system under study. For example, quantum chemical calculations, spectral fine structure, band intensities, band shapes, angular distribution data, data for related compounds, and mass spectral data can be important in eliminating ambiguities in assignments.[1,2] The qualitative effect of changes in atomic charge on nonbonding electron ionization potential has long been recognized and utilized in making assignments. Thus the sulfur lone pair orbitals in SOF_2, $SOCl_2$ and $(CH_3)_2SO$ are assigned to bands at 12.6, 11.3, and 9.3 eV, respectively, in accord with the relative electronegativities of the fluorine, chlorine, and methyl groups.[3]

It is the purpose of this paper to show that atomic core electron binding energies, derived from x-ray photoelectron spectra, can serve as bench marks for comparing and assigning ionization potentials of molecular orbitals which are more or less localized on single atoms. In a recent study it was shown that phosphorus lone pair ionization potentials and the corresponding core binding energies are linearly correlated only for sets of very similar molecules, in which there is little change in the hybridization or delocalization of the lone pair on going from one molecule to another.[4] For such sets of similar molecules, both the lone pair ionization potential and the core binding energy are affected similarly by changes in potential (atomic charges) and by substituent changes which alter the electronic relaxation accompanying photoemission. On going from one "lone pair" to another, an increase in s character or bonding

character, or a decrease in antibonding character, causes the lone pair ionization potential to increase more than the core ionization potential. Therefore we propose that the difference between the ionization potential and the core binding energy be used as a measure of the hybridization or bonding (or antibonding) character of the orbital, assuming that the orbital is at least partially located on the atom corresponding to the core binding energy. Changes in ionization potential due to changes in atomic charge or changes in relaxation energy are largely cancelled out by the corresponding changes in core binding energy.

Because $(IP - E_B)$ values are unwieldy large negative numbers, we propose that relative values of $(IP - E_B)$, in which $(IP - E_B)$ is set equal to zero for a particular reference compound, be used. For further simplicity, we use the symbol Δ for these relative $(IP - E_B)$ values. In Tables I - IV we have listed adiabatic ionization potentials for "lone pair"* orbitals, the corresponding core ionization potentials, and Δ values for compounds of nitrogen, oxygen, fluorine, and sulfur. Most of the compounds are well characterized, with unequivocally assigned ultraviolet photoelectron spectra. Using the data in the Tables, we shall attempt to show that Δ is a measure of the "intrinsic tightness" with which the lone pair electrons are held. We shall use the simple binary hydrides (NH_3, H_2O, HF, and H_2S) as reference compounds, with $\Delta = 0$. In these reference compounds, the lone pair orbital has no significant bonding or antibonding character, and generally is made up principally of an atomic p orbital. Therefore for the other compounds we can interpret a positive Δ value as an indication that the "lone pair" orbital has some bonding character or

*We are rather permissive in our use of the term "lone pair." Although all the orbitals in the Tables have significant density on the indicated atoms, some of them are quite delocalized and have strong bonding or antibonding character.

an appreciable amount of s character (or both), and we can interpret a negative Δ value as an indication of antibonding character.

NITROGEN COMPOUNDS

We believe the negative Δ value of methylamine is due to repulsive interaction between the nitrogen lone pair and the C-H bonding electrons. The still more negative Δ value of dimethylamine is presumably a consequence of further repulsion by the second methyl group. We believe that, in the case of aniline, Δ would have a negative value because of repulsions by σ bonds of the phenyl ring if it were not for a greater π bonding interaction with the highest occupied π orbital of the ring. The effect of this π bonding is to raise the Δ value and to delocalize the "lone pair" electron density onto the ring.[5]

If one considered only the high ionization potential (13.00 eV) and low basicity of nitrogen trifluoride, one might conclude that the nitrogen "lone pair" is in a bonding orbital. However the high negative Δ value shows that most of this tight electron binding is due to the high positive charge on the nitrogen atom. Indeed, when one eliminates the effect of that charge by calculating Δ, it becomes clear that the nitrogen lone pair is essentially in an antibonding orbital. This antibonding character is a consequence of repulsions by the fluorine lone pairs. The same repulsive interaction has been used to explain the remarkable weakness of the N-F bonds in NF_3.[6]

The Δ value of pyridine is about the same as that of ammonia, apparently a consequence of a balance between increased bonding pair-lone pair repulsion and increased s character. The bonding pair-lone pair repulsion cannot be very great in pyridine, and therefore we conclude that the pyridine lone pair does not have much s character. Indeed, CNDO/2

calculations show that the hybridization changes from 6.8% s character in ammonia to only 15.4% s character in pyridine.[7] The latter percentage is much lessthan the 33 % corresponding to sp^2 hybridization. In the structurally related $(NPF_2)_3$ molecule, the Δ value of 1.0 eV indicates weak π bonding between the nitrogen and phosphorus atoms.[8]

The HOMO of molecular nitrogen is an essentially nonbonding σ orbital. The Δ value of 1.09 eV is indicative of significant s character, in accord with the description of this orbital as the "overlap of the tails of two approximately sp^2 hybrids."[9] The Δ values of the analogous orbitals in HCN and the nitriles show increased bonding character. These increases in bonding character of the σ orbitals also can be seen in the relative magnitudes of the σ and π ionization potentials, which are 15.58 and 16.98 eV for N_2,[10] 13.59 and 13.82 eV for HCN,[10] and 13.14 and 12.21 eV for CH_3CN,[11] respectively. As one might expect, the σ nitrogen lone pair orbitals of NSF_3 and N_2O are similar in character to those of the nitriles and therefore have similar Δ values. It should be noted that the similarities in the σ lone pairs of these compounds and the nitriles are not at all obvious from the ionization potentials, which range from 12.7 to 16.39 eV.

OXYGEN COMPOUNDS

The ionization potentials listed for water, methanol and dimethyl ether correspond to the π lone pair orbitals. The decrease in Δ with increasing number of methyl groups can be explained, as with the methyl amines, in terms of increasing repulsions between the lone pair and the C-H bonding electrons. In the case of phenol, interaction of the out-of-plane "lone pair" with the highest occupied phenyl π orbital yields a bonding MO (IP = 12.61 eV; Δ = 0.9 eV) and an antibonding MO (IP = 8.37 eV; Δ = -3.3 eV). The more nearly nonbonding in-plane lone pair (IP = 11.22 eV)

has a Δ value of -0.5, corresponding to a small amount of bonding pair-lone pair repulsion.

In oxygen difluoride, the ionization potential corresponds to the antibonding $b_1(\pi)$ orbital.[12] Thus even though the ionization potential is fairly high (13.13 eV), the Δ value is low (-5.01 eV). Similarly, the ionization potential of molecular oxygen corresponds to the antibonding π_g orbital, and the Δ value is, as expected, very negative.

There is no truly nonbonding pair of electrons on the oxygen of carbon monoxide. However the third band in the photoelectron spectrum of carbon monoxide (1P = 19.69 eV)[10] corresponds to a weakly bonding σ orbital on carbon and oxygen.[9] The Δ value of 4.31 eV is consistent with this assignment and interpretation.

The first ionization potential of ozone (12.56 eV) corresponds to a strongly antibonding $a_1(\sigma)$ orbital on the middle oxygen atom; the Δ value of -6.4 eV is entirely consistent. The second ionization potential (13.02 eV) has been assigned to the nonbonding $1a_2(\pi)$ orbital on the terminal atoms and the third ionization potential (13.57 eV) has been assigned to the weakly antibonding $4b_2(\sigma)$ orbital on the terminal atoms.[13] Although the Δ value of -0.7 eV seems reasonable for the weakly antibonding $4b_2$ orbital, the Δ value of -1.3 eV for the nonbonding $1a_2$ orbital seems somewhat low. Indeed, Brundle[13] has indicated that the data do not strongly support the reported $4b_2$, $1a_2$ order, and perhaps the reverse assignment should be seriously considered. The 12.98 eV ionization potential of SO_2 corresponds to the $1a_2$ and $4b_2$ nonbonding orbitals on the relatively distant oxygen atoms of this molecule. The Δ value of 0.33 eV is entirely consistent with the nonbonding character of these orbitals.

The ionization potential of CO_2 corresponds to removal of an electron from the nonbonding π_g orbital, and the Δ value of -0.34 eV is reasonable.

In the case of N_2O and OCS, the analogous oxygen lone pairs have Δ values of -1.34 and -1.9 eV, respectively, suggesting appreciable antibonding character. This result is a consequence of the fact that the nonbonding π orbitals of N_2O and OCS have some density on the opposite terminal atoms as well as the oxygen atoms. Because of the lower electronegativities of nitrogen and sulfur the orbital energies are higher than they would be if the orbitals were localized completely on the oxygen atoms.

In formaldehyde, acetone, and carbonyl fluoride, the ionization potentials correspond to the in-plane nonbonding p orbitals of the oxygen atoms. In formaldehyde and acetone, bonding pair-lone pair repulsions give some antibonding character to the orbitals and cause the rather low Δ values, -1.31 and -1.0 eV, respectively. In carbonyl fluoride, the C-F bonding electrons are held so tightly by the fluorine atoms that they do not strongly repel the oxygen lone pair. An equivalent explanation is that the C-F σ bonding orbitals have such low energies that they do not interact appreciably with the oxygen lone pair orbital.

The ionization potentials of ONF_3, OPF_3, and $OPCl_3$ have been assigned to the degenerate nonbonding π orbitals on the oxygen atoms.[14] It is generally believed that the electrons in these orbitals are engaged in some π bonding to the central atom either through hyperconjugative interaction with the σ^* orbitals of the N-F, P-F, and P-Cl bonds or, in the case of OPF_3 and $OPCl_3$, through use of the empty phosphorus 3d orbitals.[15] Consequently the slightly positive Δ values of OPF_3 and $OPCl_3$ are quite reasonable. However, the -1.38 eV value of ONF_3 is incredible. We believe that the O 1s binding energy of ONF_3 is in error by at least 2 eV or the ultraviolet photoelectron spectrum has been misassigned. Bassett and Lloyd themselves point out several inconsistencies in their assignment of the UPS spectrum of ONF_3.[14] In order to have the Δ value consistent with

π-bonding in the N-O bond of ONF_3, it would be necessary to assign the 5e π orbital on the oxygen atom to one of the higher ionization potential bands, such as that at IP = 16.34 eV.

FLUORINE COMPOUNDS

In XeF_2, the antibonding, nonbonding, and bonding π orbitals have Δ values of -0.7, 0.9, and 2.2 eV, respectively.[16] The relative magnitudes and signs of these are not unreasonable, but the value 0.9 eV seems somewhat high for a strictly nonbonding orbital.

The first and second ionization potentials of OF_2 correspond to orbitals which are π and σ antibonding, respectively, and the Δ values of -3.75 and -1.12 eV are appropriate for such orbitals.[12] The third ionization potential corresponds to the nonbonding σ orbital on the fluorines; the Δ value of -0.42 eV is quite reasonable.

In ONF_3, CH_3F, and CF_4, the fluorine lone pairs acquire antibonding character by repulsive interaction with the three σ bonding orbitals corresponding to the bonds between the central atom and the other three ligand atoms. Thus the Δ values are quite negative (-2.23; -2.18; and -1.6 eV, respectively). In the case of OPF_3, the central atom is relatively big, the lone pair-bonding pair interaction is less intense, and Δ is less negative.

In BF_3 and C_6H_5F, the in-plane fluorine lone pairs interact repulsively with the two adjacent bonding pairs; however because of the greater bond angle and the presence of only two repulsive bonding pairs, the overall repulsion is significantly less than in the case of the tetrahedral molecules of first-row elements. The Δ values of -1.0 and -0.82 eV, respectively, are therefore reasonable.

The ionization potential of elemental fluorine corresponds to the π antibonding orbitals, and thus the very negative Δ value (-2.76 eV) is not expected.

SULFUR COMPOUNDS

The Δ values of H_2S, CH_3SH, $(CH_3)_2S$ and $(CF_2)_2S$ are consistent with π lone pairs having no repulsive interactions in H_2S and repulsions with bonding pairs in the other molecules. However the Δ value of -1.67 eV for $(CF_3)_2S$ is somewhat more negative than might have been predicted for that molecule.

The sulfur "lone pairs" of S_8 and S_2Cl_2 occupy antibonding orbitals, with significant lone pair-lone pair repulsion, and this antibonding character is reflected in the Δ values of -1.3 and -2.4 eV, respectively.

The π nonbonding orbital of CS_2, situated on the sulfur atoms, does not interact significantly with any other orbital and therefore has a Δ value near zero. The corresponding orbital of OCS is situated on both the oxygen and sulfur atoms, and, because of the greater electronegativity of oxygen, the orbital energy is lower than it would be if it were localized on the sulfur atom. Thus we can rationalize the slightly positive Δ value.

The Δ value of the degenerate π orbitals on the sulfur atom of $SPCl_3$ would be expected to be zero if these orbitals did not interact with other orbitals. From the Δ value of 0.49 eV we conclude that there is significant π bonding between the sulfur and phosphorus atoms.

Calculations have shown that the sulfur lone pairs of SO_2 and SF_4 are antibonding,[1,17] and one would expect to same to be true for the closely related compounds $(CH_3)_2SO$, $SOCl_2$ and SOF_2. Thus the very negative Δ

values for all these compounds are understandable. The trend toward more negative Δ values in the series $(CH_3)_2SO$, $SOCl_2$, SOF_2 parallels the increased repulsion expected in the series. (The greatest repulsion would be expected from the lone pairs of the fluorine atoms, and the least from the bonding pairs of the methyl groups.)

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Table I. Lone Pair Valence Shell and Nitrogen 1s Ionization Potentials[a]

Compound	Adiabatic IP, eV	Orbital Symmetry	E_B(N 1s), eV	Δ, eV (relative to NH_3)[b]
NH_3	10.16	σ	405.60	0.0
CH_3NH_2	8.97	σ	405.17	-0.76
$(CH_3)_2NH$	8.24	σ	404.93	-1.25
$C_6H_5NH_2$	10.45[c]	σ	405.31	0.58
NF_3	13.00	σ	414.2	-5.8
C_5H_5N	9.27	σ	404.88	-0.17
$N_3P_3F_6$	∿ 10.8[d]	σ & π	405.29	1.0
N_2	15.58	σ	409.93	1.09
HCN	13.59	σ[e]	406.8	2.2
CH_3CN	13.14[f]	σ	405.55	3.03
C_6H_5CN	∿ 12.7[g]	σ	404.95	3.2
NSF_3	∿ 13.8[h]	σ	406.0	3.2
N_2O	16.39	σ	408.6[i]	3.2

[a]Unless otherwise stated, ionization potentials are from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, J. Phys. Chem. Ref. Data, 6 (1977), Supplement No. 1, and core binding energies are from A. A. Bakke, H.-W. Chen, and W. L. Jolly, J. Electron Spectrosc. Relat. Phenom., 21 (1981) 000.

[b]$\Delta = IP - E_B(N\ 1s) + 395.44$.

[c]Ref. 2, p. 309.

[d]Ref. 8.

[e]Ref. 10.

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[h]D. O. Cowan, R. Gleiter, O. Glemser, and E. Heilbronner, Helv. Chim. Acta, 55 (1972) 2418.

[i]Terminal nitrogen atom.

Table II. Lone Pair Valence Shell and Oxygen 1s Ionization Potentials[a]

Compound	Adiabatic IP, eV	Orbital Symmetry	E_B(O 1s), eV	Δ, eV (relative to H_2O)[b]
H_2O	12.61	π	539.80	0.0
CH_3OH	10.84	π	538.88	-0.85
$(CH_3)_2O$	9.96	π	538.7	-1.6
C_6H_5OH	12.61[c]	π	538.9	0.9
	8.37[c]	π	538.9	-3.3
	11.22[c]	σ	538.9	-0.5
OF_2	13.13	π	545.33	-5.01
O_2	12.07	π	543.75[j]	-4.49
CO	19.69[d]	σ	542.57	4.31
O_3	12.56[e]	σ	546.2[f]	-6.4
	13.02[e]	π	541.5[g]	-1.3
	13.57[e]	σ	541.5[g]	-0.7
SO_2	12.98[h]	σ & π	539.84	0.33
CO_2	13.77	π	541.30	-0.34
N_2O	12.89	π	541.42	-1.34
OCS	11.18	π	540.3	-1.9
CH_2O	10.88	σ	539.38	-1.31
$(CH_3)_2CO$	9.70	σ	537.9	-1.0
CF_2O	13.2	σ	540.74	-0.4
ONF_3	13.36[i]	π	541.93	-1.38
OPF_3	12.77[i]	π	539.2	0.8
$OPCl_3$	11.58[i]	π	538.0	0.8

[a]See footnote a, Table I.

[b]$\Delta = IP - E_B(O\ 1s) + 527.19$.

[c]Ref. 2, p. 309.

[d]Ref. 10.

[e]Ref. 13.

[f]Middle atom.

[g]Terminal atoms.

[h]Ref. 1, pp. 84-86.

[i]Ref. 14.

[j]Weighted average of the two peaks of the spin doublet.

Table III. Lone Pair Valence Shell and Fluorine 1s Ionization Potentials[a]

Compound	Adiabatic IP, eV	Orbital Symmetry	E_B(F 1s), eV	Δ, eV (relative to HF)[b]
HF	16.01	π	694.22	0.0
XeF_2	12.35[c]	π_u^*	691.3	-0.7
	14.00[c]	π_g	691.3	0.9
	15.25[c]	π_u	691.3	2.2
OF_2	13.11[d]	π*	695.07	-3.75
	15.74[d]	σ*	695.07	-1.12
	16.44[d]	n(σ)	695.07	-0.42
ONF_3	14.83[e]	π	695.27	-2.23
CH_3F	12.53	π	692.92	-2.18
CF_4	15.8 [f]	π	695.6	-1.6
OPF_3	16.69[e]	π	695.6	-0.7
BF_3	15.56	σ	694.8	-1.0
C_6H_5F	13.85[g]	σ	692.88	-0.82
F_2	15.69	π	696.66	-2.76

[a]See footnote a, Table I.

[b]$\Delta = IP - E_B(F\ 1s) + 678.21$.

[c]Ref. 16.

[d]Ref. 12.

[e]Ref. 14.

[f]Ref. 1, pp. 221, 237.

[g]Ref. 2, p. 309.

Table IV. Lone Pair Valence Shell and Sulfur $2p_{3/2}$ Ionization Potentials[a]

Compound	Adiabatic IP, eV	Orbital Symmetry	$E_B(S\ 2p_{3/2})$, eV	Δ, eV (relative to H_2S)[b]
H_2S	10.47	π	170.20	0.0
CH_3SH	9.44	π	169.4	-0.2
$(CH_3)_2S$	8.68	π	169.09	-0.68
$(CF_3)_2S$	11.11	π	172.51	-1.67
S_8	9.04	σ	170.1[c]	-1.3
S_2Cl_2	9.4[d]	σ	171.57	-2.4
CS_2	10.08	π	169.80	0.01
OCS	11.18	π	170.60	0.31
$SPCl_3$	9.63[e]	π	168.87	0.49
SO_2	12.34	σ	174.80	-2.73
SF_4	12.4[f]	σ	177.8[c]	-5.7
$(CH_3)_2SO$	9.3[g]	σ	171.91	-2.9
$SOCl_2$	11.3[g]	σ	174.53	-3.5
SOF_2	12.6[g]	σ	176.20	-3.9

[a]See footnote a, Table I.

[b]$\Delta = IP - E_B(S\ 2p_{3/2}) + 159.73$.

[c]Calculated from $E_B(S\ 2p)$ by subtracting 0.4 eV.

[d]R. J. Colton and J. W. Rabalais, J. Electron Spectrosc. Relat. Phenom., 3 (1974) 345.

[e]J. C. Bünzli, D. C. Frost and C. A. McDowell, J. Electron Spectrosc. Relat. Phenom., 1 (1972/3) 481.

[f]Ref. 17.

[g]Ref. 3.

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