

duced S_N2 reactivity of CH_2X_2 , CHX_3 , and CX_4 relative to CH_3X ($X = Cl, Br, I$).¹⁹

In this manner the correlation diagram model provides insight into S_N2 reactivity. Reactivity patterns arise from the gap-slope interplay, which in turn stem from the interplay between the electron-shift and bond-reorganization aspects of the chemical transformation. Other reactivity problems such as solvent effect^{18b} on rates, nucleophilicity, leaving-group ability, and reactivity-selectivity patterns seem also to fall under the sovereignty of the model and are now under further study.

Concluding Remarks

The VBCM model provides a framework for conceptualizing reactivity trends through an understanding of the makeup of reaction profiles. The model borrows its strength from the same philosophy inherent in the fragment MO approach—that the whole may be understood by reconstruction from its parts.^{1f,g} As such the fundamental rule is striking in its simplicity. Reaction profiles may be built up from a linear combination of VB configurations. When at least one reactant is a closed shell molecule, the reaction profile for the concerted pathway may be generated through the mixing of just two configurations—those representing the Heitler-London VB forms of the bonds that interchange during the reaction (e.g., Figures 2, 4). The secondary VB configurations (e.g., 3, 4) will mix-in in proportion to their relative stabilities and thereby endow the TS with a variable character, thus generating the mechanistic spectra for each reaction type (e.g., tight and loose S_N2 transition states). The secondary configurations also provide the stock of possible reaction intermediates as they cross the two principle curves

below their intersection point (e.g., Figure 3b). Thus, the secondary configurations determine the extremes of the mechanistic spectrum for each reaction type (e.g., S_{N1} , S_{RN1}).

In constructing reaction profiles, one can either use the explicit VB approach (e.g., Figure 2a) starting with the primary configurations and then mix in the secondary configurations (rules 1-6). Alternatively, one can anchor *all* the configurations in electronic states of reactants and products and thereby generate state correlation diagrams (e.g., Figure 4). The selection of the unique anchor excited states for the correlation diagram is described in detail in ref 2 and 3a,h and requires knowledge of MO-VB correspondence. As a rule, *an excited state of the reactants will correlate with the ground state of the products if the major (or only) constituent of its electronic wave function contains spin-paired odd electrons in symmetry-matched reactant orbitals, per each new intermolecular bond that is formed during the reaction.* The argument is symmetric for the unique excited state of the products that correlates with the ground state of the reactants (see Figure 4).

The choice of approach depends on the kind of insight one wishes to gain. For example, the explicit VB approach provides a more immediate insight regarding TS structure and charge distribution, while the state correlation diagram yields more quantitative information about reaction barriers and reveals the preferred stereochemical course of the reaction (e.g., the Walden inversion in S_N2). When properly utilized, however, both approaches, which are mutually related as localized-delocalized bonding pictures, lead to the same conclusions.^{2,3a} Thus VBCM theory constitutes a *single* framework capable of handling a wide range of reactivity phenomena. We would hope therefore that application of this theory may provide a means for building on existing knowledge and lead to a more fundamental understanding of organic reactivity as a whole.

(19) (a) Hine, J. *J. Am. Chem. Soc.* 1950, 72, 2438. (b) Hine, J.; Dowell, A. M., Jr. *Ibid.* 1954, 76, 2688. (c) Hine, J.; Thomas, C. H.; Ehrenson, S. J. *Ibid.* 1955, 77, 3886. (d) Hine, J.; Ehrenson, S. J.; Brader, W. H., Jr. *Ibid.* 1956, 78, 2282.

The Partnership of Gas-Phase Core and Valence Photoelectron Spectroscopy

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Around 1970 a great surge of activity in photoelectron spectroscopy occurred, because of the availability of improved instrumentation and because of optimism regarding the usefulness of the technique.^{1,2} Many

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chemists had the impression that valence-shell photoelectron spectra (usually obtained by ultraviolet photoelectron spectroscopy, or UPS) directly give information about the bonding or antibonding character of molecular orbitals. It was also commonly believed that

(1) Siegbahn, K.; et al. "ESCA. Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy"; Almqvist and Wiksells: Uppsala, 1967; Siegbahn, K.; et al. "ESCA Applied to Free Molecules"; North-Holland: Amsterdam, 1969.

(2) Turner, D. S.; Baker, C.; Baker, A. D.; Brundle, C. R. "Molecular Photoelectron Spectroscopy"; Wiley-Interscience: London, 1970.

core-level photoelectron spectra (obtained by X-ray photoelectron spectroscopy, or XPS) provide values of the charges (or even the oxidation states) of atoms in molecules. However, as chemists became familiar with these techniques, they were disillusioned.

In UPS, it is generally a very difficult matter to assign unambiguously the various observed bands to molecular orbitals, mainly because ionization potentials are markedly affected by electronic relaxation energy and potential (i.e., atomic charge effects) as well as by chemical bonding. Even when the assignment of a band is unambiguous, the corresponding ionization potential may be of little value to a chemist because of the difficulty of accounting for the effects of relaxation energy and potential. Indeed many UPS studies have amounted to little more than the recording of a spectrum followed by an attempt to assign the various bands by comparison with a theoretical calculation of the spectrum. In other words, UPS has often merely served as a testing ground for theoretical calculations.

XPS is similarly plagued by the bugaboo of relaxation energy, although one can approximately correct for the effects of this energy by restricting study to sets of similar molecules that presumably have similar relaxation energies or by actually calculating the relaxation energies.^{3,4} But even when relaxation energies are corrected for, attempts to interpret core binding energies in terms of atomic charges are beset with the fundamental difficulty of defining atomic charge and the problems of dealing with lone-pair electrons.⁵

Of course, both UPS and XPS have proved to be useful analytical techniques, UPS being used to detect molecules on the basis of spectral "fingerprints",⁶ and XPS being used to detect atoms on the basis of characteristic binding energies.⁷ Because of the "surface sensitivity" of these techniques (due to energy loss by scattering of photoelectrons emitted below the surfaces of solids), they are widely used as analytical probes of solid surfaces and of species absorbed on solid surfaces. However in this Account we shall be concerned primarily with the extraction of *chemical bonding information* from the photoelectron spectra of *gaseous* species. In gas-phase photoelectron spectroscopy one avoids the experimental difficulties of solid-state photoelectron spectroscopy, such as surface contamination, sample charging, and sample decomposition under the exciting photon flux.⁸

In spite of the common features of gas-phase XPS and UPS, these fields have developed as somewhat independent disciplines, with surprisingly little interaction. This unfortunate situation evolved because the two techniques yield different sorts of information: changes in the core binding energies of XPS are mainly determined by changes in potential (atomic charges)

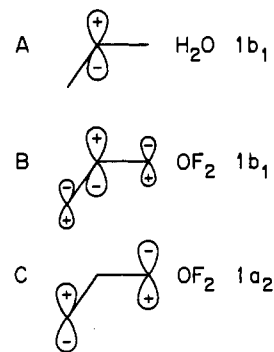


Figure 1. Schematic representations of "lone pair" orbitals of H_2O and OF_2 .

and relaxation energies, whereas changes in the valence ionization potentials of UPS are affected by changes in these same factors *plus* changes in chemical bonding. However, it has recently been recognized that by use of appropriately chosen core binding energy data, it is possible to delete the contributions of changes in potential and relaxation energy from changes in valence ionization potentials.⁹⁻¹² Thus by combining core and valence ionization potential data one can quantify the bonding or antibonding character of molecular orbitals. This is the kind of information that chemists have always hoped to obtain from photoelectron spectroscopy but which until recently has generally only been obtained from theoretical calculations.

Brief Description of the Partnership

It has been well-established on the basis of both theoretical and experimental data that shifts in strictly nonbonding valence orbital ionization potential are approximately eight-tenths of corresponding shifts in core binding energy.¹² Consider a molecule with an atom that has a strictly nonbonding pair of electrons. If we know the core binding energy and lone-pair ionization potential of that atom, a knowledge of the core binding energy of an atom of the same element in any other molecule allows us to calculate the theoretical "localized orbital ionization potential" (LOIP) for the corresponding atomic orbital in that molecule. Then, by comparison of the ionization potentials of the molecular orbitals associated with that atom with the LOIP value, it is possible to determine the extent to which the MO energy levels are higher (antibonding) or lower (bonding) than the hypothetical nonbonding atomic orbital energy level.

Consider the following simple illustration of the method.¹² The $p\pi$ lone pair orbital of H_2O , schematically illustrated in Figure 1A, is a strictly nonbonding MO. Its ionization potential (12.61 eV) may therefore be taken as the LOIP of the oxygen 2p orbital in H_2O . The O 1s binding energy of OF_2 is 5.53 eV greater than that of H_2O ; therefore we estimate that the LOIP of the oxygen 2p orbital of OF_2 is 0.8 (5.53) or 4.4 eV greater than 12.61 eV, or 17.0 eV. The actual ionization po-

(9) Perhaps the first investigators to use a combination of core and valence ionization potentials to assess the bonding character of an MO were Hashmall et al.¹⁰ However, the significance of their work was largely ignored.

(10) Hashmall, J. A.; Mills, B. E.; Shirley, D. A.; Streitwieser, A. *J. Am. Chem. Soc.* 1972, 94, 4445.

(11) Jolly, W. L. *J. Phys. Chem.* 1981, 85, 3792.

(12) Jolly, W. L.; Eyermann, C. J. *J. Phys. Chem.* 1982, 86, 4834. The standard deviation associated with the factor of 0.8 is 0.07.

(3) Avanzino, S. C.; Chen, H. W.; Donahue, C. J.; Jolly, W. L. *Inorg. Chem.* 1980, 19, 2201.

(4) Xiang, S. F.; Bakke, A. A.; Chen, H. W.; Eyermann, C. J.; Hoskins, J. L.; Lee, T. H.; Seyferth, D.; Withers, H. P.; Jolly, W. L. *Organometallics* 1982, 1, 699.

(5) Jolly, W. L.; Bakke, A. A. In "Electron Distribution and the Chemical Bond"; Coppens, P., Hall, M., Eds.; Plenum Press: New York, 1982.

(6) Bock, H.; Solouki, B. *Angew. Chem., Int. Ed. Engl.* 1981, 20, 427. Bock, H. In "Emission and Scattering Techniques", NATO Advanced Study Institute Series; Reidel: Dordrecht, Holland, 1981; p 335.

(7) Muilenberg, G. E. "Handbook of X-Ray Photoelectron Spectroscopy"; Perkin-Elmer: Eden Prairie, MN, 1978.

(8) Jolly, W. L. *Coord. Chem. Rev.* 1974, 13, 47.

Table I
Lone-Pair and Core Ionization Potentials (eV) of
Molecules with Strictly Nonbonding Lone Pairs

molecule	lone-pair IP	core E_B^a	core level
HF	16.06 ^b	694.31	1s
HCl	12.78 ^{b,c}	207.39	2p _{3/2}
HBr	11.82 ^{b,c}	77.36	3d _{5/2}
HI	10.64 ^{b,c}	627.56	3d _{5/2}
H ₂ O	12.62 ^d	539.80	1s
H ₂ S	10.47 ^d	170.20	2p _{3/2}
H ₂ Se	9.90 ^d	62.62	3d
planar NH ₃	9.8 ^e	405.3 ^e	1s
planar PH ₃	8.3 ^e	136.6 ^e	2p _{3/2}

^a Except where otherwise noted, core binding energies are from ref 23. ^b Frost, D. C.; McDowell, C. A.; Vroom, D. A. *J. Chem. Phys.* **1967**, *46*, 4255. ^c Weighted average of spin-orbit split peaks. ^d Rosenstock, H. M.; Sims, D.; Schroyer, S. S.; Webb, W. J. *Natl. Std. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1980**, NSRDS-66, part 1. ^e Reference 13.

tential of the oxygen "lone pair" of OF₂ is 13.25 eV, i.e., 3.8 eV lower than the LOIP. Hence it is clear that the oxygen lone pair of OF₂ is strongly antibonding (not bonding, as might be naively concluded from the increase in ionization potential on going from H₂O to OF₂). The antibonding character of this orbital is clear from the schematic diagram in Figure 1B.

The only molecules with strictly nonbonding valence MO's for which experimental core binding energies are available are H₂O, H₂S, H₂Se, and the hydrogen halides. (In an H₂A molecule, the nonbonding MO is the p π lone pair orbital on atom A, which is perpendicular to the molecular plane. In an HX molecule, the nonbonding MO comprises the two p π lone pairs on atom X, which are perpendicular to the bond axis.) Thus one can quantify the bonding or antibonding character of "lone pairs" on atoms of oxygen, sulfur, selenium, fluorine, chlorine, bromine, and iodine. By means of theoretical calculations of the core and lone-pair ionization potentials of planar ammonia and planar phosphine, this list has been expanded to include nitrogen and phosphorus.¹³ The required lone-pair and core ionization potentials are listed in Table I.

Assignment of Valence-Shell Photoelectron Spectra

A knowledge of LOIP values can considerably facilitate the assignment of the bands in a valence-shell photoelectron spectrum. We shall cite two examples in which core binding energy data have been used to eliminate ambiguities in valence-shell spectra.

On the basis of Δ SCF near-Hartree-Fock calculations, a relatively broad band at 18.50 eV in the UPS spectrum of oxygen difluoride, OF₂, was tentatively assigned to the ionization potential of the nonbonding fluorine p π orbital, of 1a₂ symmetry (illustrated in Figure 1C).¹⁴ However, using the data for HF in Table I and the fluorine core binding energy of OF₂, one calculates a fluorine 2p LOIP value of 16.7 eV for OF₂. This discrepancy is much greater than the uncertainty of the method (\sim 0.1–0.2 eV) and indicates that the tentative assignment was wrong. Indeed, the OF₂ spectrum contains a sharp band at 16.44 eV that is more reasonably assigned to the 1a₂ orbital.¹⁵ The fact that

Table II
Localized Orbital Ionization Potentials (LOIPs, eV)

molecule	orbital		
	e(X) ^a	b ₂ (Mn) ^b	e(Mn) ^b
Mn(CO) ₅ Cl	9.94	9.56	9.27
Mn(CO) ₅ Br	9.37	9.52	9.23
Mn(CO) ₅ I	8.81	9.36	9.07

^a Calculated using the hydrogen halides as reference molecules. ^b Calculated using Mn(CO)₅H as the reference molecule.

the ionization potential is 0.26 eV less than the LOIP suggests that there is a perceptible overlap between the two fluorine p π orbitals, giving a slight antibonding character to the 1a₂ orbital. Probably the band at 18.50 eV is due to ionization of the 3b₁ molecular orbital.

The ultraviolet photoelectron spectra of the manganese pentacarbonyl halides, Mn(CO)₅X, have received considerable attention.^{16–22} However, at least three different assignments have been proposed for the first four bands of each spectrum, and until recently there was no consensus regarding the assignment. There has always been essential agreement, however, that these bands correspond to the following molecular orbitals, in some order or another: an e(X) orbital comprised mainly of the pair of p π atomic orbitals on the halogen atom, an a₁(Mn–X) orbital that is essentially the Mn–X σ bonding orbital, a b₂(Mn) orbital comprised mainly of the d_{xy} orbital lying in the plane perpendicular to the Mn–X axis, and an e(Mn) orbital comprised mainly of the d_{xz} and d_{yz} orbitals, lying in planes that contain the Mn–X axis. The first and third bands are relatively intense and are believed to correspond to the doubly degenerate e(X) and e(Mn) orbitals. However, there has been question, in the case of Mn(CO)₅Cl and Mn(CO)₅Br, as to which of these bands corresponds to which orbital. There has also been question as to how to assign the a₁(Mn–X) and b₂(Mn) orbitals to the relatively weak second and fourth bands. Both assignment problems have been solved by the use of core binding energies.²²

The e(X) LOIP values for the Mn(CO)₅X compounds listed in Table II were readily calculated from the appropriate halogen core binding energies²³ and data from Table I. It is not possible to calculate absolute LOIP values for the e(Mn) and b₂(Mn) orbitals because there is no known manganese compound in which the d orbitals are strictly nonbonding. This poses no problem, however, because one can, to better advantage, use the "shifted" LOIP values given in Table II, which were calculated with Mn(CO)₅H as the reference compound.

(15) With use of a different argument, the same assignment was proposed by De Leeuw et al.: De Leeuw, D. M.; Mooyman, R.; De Lange, C. A. *Chem. Phys.* **1978**, *34*, 287.

(16) Evans, S.; Green, J. C.; Green, M. L. H.; Orchard, A. F.; Turner, D. W. *Discuss. Faraday Soc.* **1969**, *47*, 112.

(17) Fenske, R. F.; DeKock, R. L. *Inorg. Chem.* **1970**, *9*, 1053.

(18) Lichtenberger, D. L.; Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1973**, *12*, 702.

(19) Ceasar, G. P.; Milazzo, P.; Cihonski, J. L.; Levenson, R. A. *Inorg. Chem.* **1974**, *13*, 3035.

(20) Higginson, B. R.; Lloyd, D. R.; Evans, S.; Orchard, A. F. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1913.

(21) DeKock, R. L. In "Electron Spectroscopy: Theory, Techniques and Applications"; Brundle, C. R., Baker, A. D., Eds.; Academic Press: London, 1977; Vol. 1, Chapter 6, p 294.

(22) Jolly, W. L. *J. Phys. Chem.* **1983**, *87*, 26.

(23) Bakke, A. A.; Chen, H. W.; Jolly, W. L. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *20*, 333.

(13) Eyermann, C. J.; Jolly, W. L. *J. Phys. Chem.*, in press.

(14) Brundle, C. R.; Robin, M. B.; Kuebler, N. A.; Basch, H. *J. Am. Chem. Soc.* **1972**, *94*, 1451.

In $\text{Mn}(\text{CO})_5\text{H}$ there are no π -type interactions between the hydrogen atom and the manganese d orbitals; hence an observed difference between the $e(\text{Mn})$ ionization potential of an $\text{Mn}(\text{CO})_5\text{X}$ compound and the $e(\text{Mn})$ LOIP calculated with $\text{Mn}(\text{CO})_5\text{H}$ as the reference can be taken as a measure of the interaction of the halogen $p\pi$ orbitals with the $e(\text{Mn})$ orbital. In the case of $\text{Mn}(\text{CO})_5\text{Cl}$, we find that the $e(\text{Mn})$ "shifted" LOIP is definitely lower than the $e(\text{Cl})$ LOIP. Any interaction between these orbitals would only cause further separation of the energy levels; that is, the $e(\text{Mn})$ level definitely lies above the $e(\text{Cl})$ level. In the case of $\text{Mn}(\text{CO})_5\text{Br}$, the difference between the $e(\text{Mn})$ "shifted" LOIP and the $e(\text{Br})$ LOIP is comparable to the uncertainty in the values, and the data cannot be used to establish the relative energy levels. However, the data for $\text{Mn}(\text{CO})_5\text{I}$ do allow us to conclude that the $e(\text{I})$ level lies above the $e(\text{Mn})$ level, an assignment that is strongly supported by the observation that the first band of the $\text{Mn}(\text{CO})_5\text{I}$ spectrum shows spin-orbit splitting. The $b_2(\text{Mn})$ orbital of $\text{Mn}(\text{CO})_5\text{X}$ is orthogonal to the halogen valence orbitals and, to a first approximation, should have an ionization potential equal to the $b_2(\text{Mn})$ "shifted" LOIP. The ionization potentials corresponding to the fourth bands of $\text{Mn}(\text{CO})_5\text{Cl}$, $\text{Mn}(\text{CO})_5\text{Br}$, and $\text{Mn}(\text{CO})_5\text{I}$ are 11.08, 10.79, and 10.36 eV, respectively, values that are far from the corresponding LOIPs. However, the ionization potentials corresponding to the second bands of $\text{Mn}(\text{CO})_5\text{Cl}$ and $\text{Mn}(\text{CO})_5\text{Br}$ are both 9.5 eV, a value very close to the LOIPs. Only the second bands can be reasonably assigned to $b_2(\text{Mn})$. (The "second band" of $\text{Mn}(\text{CO})_5\text{I}$ has never been observed; it presumably lies under the $e(\text{Mn})$ manifold at ~ 9.6 eV.) Thus the LOIP data correspond to an energy level ordering of $e(\text{Mn}) > b_2(\text{Mn}) > e(\text{Cl}) > a_1(\text{Mn}-\text{Cl})$ for $\text{Mn}(\text{CO})_5\text{Cl}$, $e(\text{Mn})$ or $e(\text{Br}) > b_2(\text{Mn}) > e(\text{Mn})$ or $e(\text{Br}) > a_1(\text{Mn}-\text{Br})$ for $\text{Mn}(\text{CO})_5\text{Br}$, and $e(\text{I}) > b_2(\text{Mn}) > e(\text{Mn}) > a_1(\text{Mn}-\text{I})$ for $\text{Mn}(\text{CO})_5\text{I}$, in agreement with the assignments of Higginson et al.²⁰ based on entirely different arguments.

Lone-Pair Repulsions

A simple MO treatment of the diatomic homonuclear halogens, in which the overlap integral is ignored when estimating the resonance integral, β , leads to the conclusion that the antibonding π^* level is raised above the atomic p level as much as the bonding π level is lowered below that level. Energetically, the net result is equivalent to having the eight π electrons of an X_2 molecule occupy four nonbonding orbitals. However, if the overlap integral is included in the treatment, it is found that the antibonding level is raised more than the bonding level is lowered, corresponding to a net π antibonding interaction, or lone-pair-lone-pair repulsion. The LOIP method allows us to obtain an experimental measure of the effect of lone-pair-lone-pair repulsion on the halogen ionization potentials.³² In Table III, the LOIP values, the π and π^* ionization potentials, and the differences between the average of the π and π^* ionization potentials and the LOIP are presented for the diatomic halogens. A difference of zero corresponds to no lone-pair-lone-pair repulsion; a negative difference indicates lone-pair-lone-pair repulsion. It can be seen that the only difference that is definitely negative (considering the uncertainty of the method) is that of F_2 . Of course, it has long been rec-

Table III
LOIPs, Ionization Potentials, and $\text{IP}(\text{av}) - \text{LOIP}$ Values (eV) for Halogens and Interhalogens

molecule	LOIP	$\text{IP}(\pi)^a$	$\text{IP}(\pi^*)^a$	$\text{IP}(\text{av}) - \text{LOIP}$
F_2	17.94	18.80	15.84	-0.62
Cl_2	13.12	14.42	11.61	-0.10
Br_2	11.85	12.85	10.68	-0.08
I_2	10.35	11.21	9.51	0.01
ClF	15.09 ^b	17.06 ^c	12.79 ^c	-0.16
ICl	11.56 ^b	12.88	10.24	0.0
IBr	10.59 ^b	12.09	9.99	0.45

^a Except as noted, from Potts, A. W.; Price, W. C. *Trans. Faraday Soc.* 1971, 67, 1242. ^b Average LOIP for the two halogen atoms of the interhalogen. ^c DeKock, R. L.; Higginson, B. R.; Lloyd, D. R.; Breeze, A.; Cruickshank, D. W. J.; Armstrong, D. R. *Mol. Phys.* 1972, 24, 1059.

Table IV
LOIPs, Ionization Potentials, and $\text{IP} - \text{LOIP}$ Values (eV) for Halogen $p\pi$ Orbitals in the Methyl Halides

molecule	halogen E_B	LOIP	IP	$\text{IP} - \text{LOIP}$
CH_3F	692.92	14.95	13.05 ^a	-1.90
CH_3Cl	206.24	11.86	11.30 ^b	-0.56
CH_3Br	76.42	11.07	10.65 ^b	-0.42
CH_3I	626.66	9.92	9.75 ^b	-0.17

^a Brundle, C. R.; Robin, M. B.; Basch, H. *J. Chem. Phys.* 1970, 53, 2196. ^b Von Niessen, W.; Asbrink, L.; Bieri, G. *J. Electron Spectrosc. Relat. Phenom.* 1982, 26, 173. The tabulated values are weighted averages of the spin-orbit split peaks.

ognized that the F-F bond is anomalously weak, but no consensus has been reached regarding the explanation of this weakness.²⁴⁻³¹ These data probably constitute the first unequivocal evidence for lone-pair-lone-pair repulsion in F_2 .

The result for fluorine gives us confidence to apply this method to other systems. In the case of heteronuclear halogen-halogen bonds, $\text{IP}(\text{av}) - \text{LOIP}$ values can be calculated with use of the average LOIP value for the two atoms. From Table III we see that, for ClF , the difference is slightly negative, perhaps suggesting weak lone-pair-lone-pair repulsion, and that, for ICl , there is no lone-pair-lone-pair repulsion. The positive difference for IBr has no obvious physical rationale and suggests experimental error; it would be worthwhile to reinvestigate the core spectrum of IBr .

Lone-pair-bonding-pair repulsions can also be studied by the LOIP method. For example, in alkyl halides, the repulsion between the halogen $p\pi$ electrons and the C-H or C-R bonding electrons can be measured by the extent to which the halogen $p\pi$ ionization potential is lowered below the halogen p LOIP. The halogen LOIP values, the halogen lone-pair ionization potentials, and the corresponding differences ($\text{IP} - \text{LOIP}$) for the methyl halides are presented in Table IV. Obviously there is relatively strong repulsion between the fluorine

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(25) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 142-144.

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(27) Brown, M. G. *Trans. Faraday Soc.* 1959, 55, 9.

(28) Pitzer, K. S. *J. Chem. Phys.* 1955, 23, 1735.

(29) Pitzer, K. S. *Adv. Chem. Phys.* 1959, 2, 59.

(30) Caldow, G. L.; Coulson, C. A. *Trans. Faraday Soc.* 1962, 58, 633.

(31) Politzer, P. *J. Am. Chem. Soc.* 1969, 91, 6235.

Table V
Data (eV) Regarding Halogen-Manganese $p\pi-d\pi$
Repulsion in Manganese Pentacarbonyl Halides^a

compd	Δ IP	Δ (LOIP)	$-\beta$
Mn(CO) ₅ Cl	0.92	0.67	0.72
Mn(CO) ₅ Br	1.17	0.14	0.65
Mn(CO) ₅ I	0.83	0.26	0.53

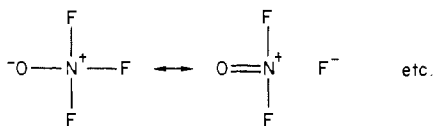
^a Data from ref 22.

lone pairs and the CH₃ bonding electrons in CH₃F, weaker but probably significant repulsions in CH₃Cl and CH₃Br, and very weak or negligible repulsion in CH₃I. The repulsive interactions measured by this technique are among the factors to be considered when devising tables of "standard" bond energies or covalent bond radii.

Repulsions between halogen lone pairs and transition-metal $d\pi$ electrons in molecular transition-metal-halogen compounds can also be studied by this technique.²² According to simple MO theory in which the overlap integral is ignored, the energy separation between two orbitals whose coulomb integrals differ by $\Delta\alpha$ is given by the expression $\Delta\epsilon = [(\Delta\alpha)^2 + 4\beta^2]^{1/2}$, where β is the resonance integral. By replacing $\Delta\alpha$ with Δ (LOIP), and $\Delta\epsilon$ by the observed difference in ionization potential, Δ IP, it is possible to calculate β . The ionization potentials and LOIP values for the $e(X)$ and $e(Mn)$ orbitals of the manganese pentacarbonyl halides can be used to illustrate the method. In Table V the Δ IP, Δ (LOIP), and β values are listed. The derived β values are measures of the $p\pi-d\pi$ repulsions between the halogen and manganese atoms. It is encouraging that the calculated $|\beta|$ values decrease on going from the chloride to the iodide, in accord with the expectation that the $p\pi-d\pi$ interaction in the Mn-X bond decreases on going from X = Cl to X = I. Application of this technique to other appropriate molecules will allow chemists to evaluate quantitatively the π -donor or π -acceptor characters of a wide variety of substituent groups.

Hyperconjugation

The molecular properties of trifluoroamine oxide indicate substantial N-O π bonding and N-F σ antibonding, corresponding to hyperconjugation of the following type:³³⁻³⁶



However, core and valence ionization potential data indicate that the oxygen $p\pi$ "lone pair" ionization potential differs by only 0.2 eV from the oxygen p LOIP.³⁷ That is, the energy of the oxygen $p\pi$ orbitals in ONF₃

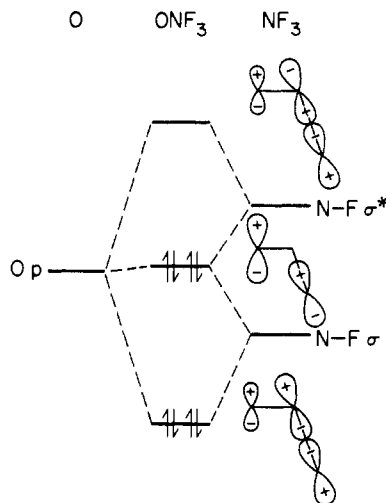
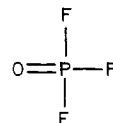


Figure 2. Energy level diagram and schematic representations of the molecular orbitals associated with oxygen lone pairs of ONF₃. The sketches show the atomic p orbitals in one of the three O-N-F planes.

is essentially unchanged by interaction with the NF₃ orbitals. This result implies approximately equal interaction of the oxygen lone-pair orbitals with the N-F σ^* and N-F σ orbitals, as shown in Figure 2. The oxygen "lone pairs" are located mainly on the oxygen and fluorine atoms and have little bonding character. The system is stabilized by occupancy of the "N-F σ " orbitals, which actually have acquired considerable N-O π -bonding character.

Lone Pair $\rightarrow d\pi$ Delocalization

One might expect the bonding in OPF₃ to be similar to that in ONF₃. However, because of the lower electronegativity of phosphorus, the P-F σ^* level should lie above the N-F σ^* level, and because of poorer overlap in the P-F bond than in the N-F bond, the P-F σ level should lie above the N-F σ level. Therefore, in the absence of other effects, the oxygen lone pairs should interact more strongly with the P-F σ orbitals than with the P-F σ^* orbitals, causing the lone-pair level to be raised higher relative to the oxygen-localized p level. However, the actual oxygen lone-pair ionization potential is greater than the LOIP.³⁷ This fact indicates that the lone pairs must be interacting relatively strongly with some other higher lying orbitals. We believe that the only reasonable possibility is that the latter orbitals are the empty phosphorus $d\pi$ orbitals, and that the data therefore provide evidence for O-($p\pi$) \rightarrow P($d\pi$) bonding, of the type implied by the following structure:



Similar evidence for $p\pi \rightarrow d\pi$ bonding has been found in the case of bis(trimethylsilyl)amine, HN(SiMe₃)₂.¹³ This molecule is believed to have a planar HNSi₂ skeleton and hence to have a nitrogen lone pair that would be strictly nonbonding in the absence of π bonding. The fact that the lone-pair ionization potential is actually 0.5 eV greater than the LOIP is therefore indicative of N($p\pi$) \rightarrow Si($d\pi$) bonding.

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Table VI
Ionization Potentials and Localized Orbital Ionization Potentials (eV) for Fe(CO)₅, C₂H₄, and Fe(CO)₄C₂H₄^a

orbital	Fe(CO) ₅ ^b	C ₂ H ₄ ^c	Fe(CO) ₄ - C ₂ H ₄ ^c
(d _{xy} , d _{x²-y²)IP}	8.6		8.38
(d _{xy} , d _{x²-y²)LOIP}	(8.6)		8.3
(d _{xz} , d _{yz})IP	9.9		9.23
(d _{xz} , d _{yz})LOIP	(9.9)		9.6
(C=C π)IP		10.51	10.56
(C=C π)LOIP		(10.51)	10.06

^a From ref 38. ^b IPs from Baerends, E. J.; Oudshoorn, C.; Oskam, A. *J. Electron Spectrosc. Relat. Phenom.* 1975, 6, 259. ^c Van Dam, H.; Oskam, A. *Ibid.* 1979, 17, 357.

Transition-Metal Interactions with Unsaturated Ligands

There are many potential applications of the LOIP method to transition-metal complexes of unsaturated ligands. For example, let us consider the bonding in tetracarbonyl ethyleneiron,³⁸ which has the following structure:³⁹



It is helpful to use C₂H₄ and Fe(CO)₅ as reference molecules when considering the ionization potentials of this molecule. Table VI presents ionization potentials of all three molecules as well as "shifted" LOIPs of Fe(CO)₄C₂H₄.

The C=C π ionization potential of the coordinated C₂H₄ group in Fe(CO)₄C₂H₄ is 0.5 eV higher than the corresponding LOIP value (i.e., the value that the ionization potential would have if there were no interaction of the C₂H₄ π electrons with the Fe(CO)₄ group). The data show that there is substantial σ interaction between the ethylene and the iron atom. One should not be misled by the similarity of C=C π ionization potentials of C₂H₄ and Fe(CO)₄C₂H₄ into the conclusion that there is negligible σ interaction here. On going from Fe(CO)₅ to Fe(CO)₄C₂H₄, the net bonding interactions of the (d_{xy}, d_{x²-y²) orbitals are essentially unchanged, as shown by the near-identity of the IP and LOIP values of these orbitals in Fe(CO)₄C₂H₄. That is, the equatorial C₂H₄ group in Fe(CO)₄C₂H₄ affects the (d_{xy}, d_{x²-y²) orbitals to about the same extent as an equatorial CO group in Fe(CO)₅. However the (d_{xz}, d_{yz}) ionization potential of Fe(CO)₄C₂H₄ is about 0.4 eV below the corresponding LOIP, indicative of significant destabilization of these orbitals. Clearly the total backbonding of the (d_{xz}, d_{yz}) orbitals of Fe(CO)₄C₂H₄ is less than that of Fe(CO)₅, as expected from the fact that these orbitals are orthogonal to the π* orbital of the coordinated C₂H₄ group in Fe(CO)₄C₂H₄.}}

Localization of Valence-Shell Holes

There are many molecules with lone pairs on two or more equivalent atoms. In cases where these lone pairs are combinations of atomic orbitals that interact with one another weakly and that are orthogonal to all other molecular orbitals, the ionization potentials can be

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Table VII
Oxygen-Localized Orbital Ionization Potential (LOIP) Data (eV)

	orb sym	E _B ^a	IP	LOIP
CO ₂	π _g	541.32	13.78 ^b	13.8
B(OCH ₃) ₃	e ⁻	538.3	11.41 ^c	11.4
F ₂ SO ₂	a ₂	540.5	13.04 ^d	13.2
Cl ₂ SO ₂	a ₂	539.51	12.41 ^e	12.4
Cl ₂ CrO ₂	a ₂	539.06	11.80 ^f	12.0

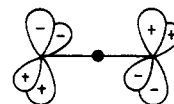
^a All binding energies from ref 23. ^b Schweig, A.; Thiel, W. *Mol. Phys.* 1974, 27, 265. ^c Kroner, J.; Nölle, D.; Nöth, H. Z. *Naturforsch. B* 1973, 28, 416. ^d DeKock, R. L.; Lloyd, D. R.; Hiller, I. H.; Saunders, V. R. *Proc. R. Soc. London, Ser. A* 1972, 328, 401. ^e Solouki, B.; Bock, H.; Appel, R. *Chem. Ber.* 1975, 108, 897. ^f Lee, T. H.; Rabalais, J. W. *Chem. Phys. Lett.* 1975, 34, 135.

Table VIII
Fluorine-Localized Orbital Ionization Potential (LOIP) Data (eV)

	orb sym	E _B ^a	IP	LOIP
CF ₄	t ₁	695.77	16.30 ^b	17.2
SiF ₄	t ₁	694.70	16.45 ^b	16.4
GeF ₄	t ₁	694.55	16.03 ^b	16.2
BF ₃	e ⁻	694.8	16.67 ^c	16.5
PF ₅ (av)	e ⁻	694.9 ^d	16.46 ^e	16.5
XeF ₄	a _{2g}	692.11	14.5 ^f	14.3
OXeF ₄	a ₂	693.09	15.00 ^g	15.1
XeF ₆	t _{1g}	693.3	15.2 ^f	15.3
WF ₆	t _{1g}	693.36	15.35 ^h	15.3
OF ₂	a ₂	695.07	16.44 ⁱ	16.7
OCF ₂	a ₂	695.43	17.00 ^j	17.0

^a All binding energies from ref 23. ^b Bassett, P. J.; Lloyd, D. R. *J. Chem. Soc. A* 1971, 641. ^c Bassett, P. J.; Lloyd, D. R. *Ibid.* 1971, 1551. ^d Weighted average of axial and equatorial F 1s binding energies. ^e Goodman, D. W.; Dewar, M. J. S.; Schweiger, J. R.; Cowley, A. H. *Chem. Phys. Lett.* 1973, 21, 474. ^f Brundle, C. R.; Jones, G. R.; Basch, H. *J. Chem. Phys.* 1971, 55, 1098. ^g Brundle, C. R.; Jones, G. R. *J. Electron Spectrosc. Relat. Phenom.* 1972/3, 1, 403. ^h Karlsson L.; Mattsson, L.; Jadrny, R.; Bergmark, T.; Siegbahn, K. *Phys. Scr.* 1976, 14, 230. ⁱ Reference 14; see text for assignment. ^j Thomas, R. K.; Thompson, H. *Proc. R. Soc. London, Ser. A* 1972, 327, 13.

treated as if they were LOIPs.¹² For example, consider the π_g molecular orbital of CO₂, which is strictly O pπ in character:



With use of the O 1s binding energies of H₂O and CO₂ and the lone-pair ionization potential of H₂O, the oxygen p LOIP of CO₂ is calculated to be 13.8, in excellent agreement with the observed ionization potential of 13.78 eV for the π_g molecular orbital. Tables VII and VIII present similar oxygen and fluorine LOIP data, respectively, for a variety of molecules containing sets of equivalent lone pairs. In all cases (except CF₄ and OF₂, which will be discussed later) the LOIP values are in good agreement with the ionization potentials. This good agreement indicates that the electronic relaxation energy shifts associated with the core and valence-shell ionizations are similar. However, it is well-established that core ionizations always yield *localized* hole states,^{40,41} whereas it is generally assumed that the

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ionization of delocalized molecular orbitals yields *delocalized* hole states. According to a theoretical model of Snyder,⁴⁰ delocalization of a hole over t centers gives a relaxation energy per center of approximately $1/t^2$ that for a localized hole. Hence one would not expect the relaxation energies to be similar. The data appear to support the proposition that the ionization of delocalized lone pairs made up of weakly interacting atomic orbitals yields localized hole states. Indeed, in recent years, other investigators have made similar proposals regarding excited and ionized valence shells.⁴²⁻⁴⁶ It appears that, just as in the case of mixed-valence compounds, the lifetime of the localized state (or the rate of electron transfer from one site to another) is the relevant factor to be considered when deciding whether a hole is localized or delocalized.

The two exceptional molecules, CF_4 and OF_2 , contain fluorine atoms attached to small, first-row atoms and are examples of molecules in which the fluorine atomic orbitals making up the lone-pair orbitals interact significantly. Ascribing antibonding character to these lone-pair orbitals is probably equivalent to saying that the ionized states are delocalized instead of localized. Related evidence for delocalization effects have been

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observed in the Auger spectra of tetrahedral halides.⁴⁷

Concluding Remarks

Clearly the LOIP concept, involving both core and valence ionization potentials, is a valuable aid in the assignment of valence-shell photoelectron spectra. It also provides grist for the mill of theoreticians, for example, with respect to the question of the localized or delocalized character of valence holes. However, its main value is in providing chemists with a reliable method for interpreting valence-shell ionization potentials in terms of the bonding or antibonding character of molecular orbitals. Typical applications are the determination of the degree of interaction of so-called lone-pair orbitals (mainly comprised of p or d orbitals) either with filled orbitals (bonding orbitals or other lone pairs) or with empty orbitals (antibonding orbitals or higher energy d orbitals). It is significant that the LOIP method allows chemists to make these interpretations using only experimental data, free from most of the calculational difficulties and interpretative ambiguities of theoretical methods.

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Nonlinear Optical Spectroscopy of Molecular Systems[†]

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The study and application of nonlinear optical spectroscopy in chemical problems was made possible by the development of tunable lasers. The giant flashlamps of the pre-laser era produced optical power at a given wavelength of at most 10^{-4} of the power of even the simplest narrow-band tunable laser. Nonlinear optical processes depend on the square or cube of the optical power so that the minimum enhancement factor for lasers over conventional sources is 10^8 – 10^{12} . Con-

ventional picosecond laser pulses can have peak powers of 20 GW, superior to the total capability of a major hydroelectric scheme or nuclear power plant. Clearly these devices do not simply extend the properties of the older light sources: they open doors to the study of totally new concepts in the interaction of molecules with light.

When molecules are placed in intense optical fields, a variety of effects occur. The molecule may fragment, rearrange, or undergo ionization. On the other hand, the ensemble of molecules can bring about the creation of new optical fields in so-called coherent processes. The frequency and time dependence of these new fields carry hitherto unknown information about the molecular states and their dynamics. Studies of such non-

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