

# Remote Inductive Effects Evaluated by X-Ray Photoelectron Spectroscopy (ESCA)

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**Abstract:** Core-electron binding energies of *tert*-butyl alcohol and three of its fluoro derivatives were measured by ESCA to evaluate remote inductive effects. Various charge calculations are analyzed as to their effectiveness in predicting shifts in electron binding energies caused by inductive effects. The empirical methods of Jolly and Pauling are used as well as the semiempirical CNDO, INDO, and extended Hückel methods. In addition a new empirical method is introduced based on a modification of Sanderson's electronegativity calculations. It was determined that chemical shifts caused by remote atoms are often sufficient to help in molecular identification. If shift tables were to be formulated, similar to those used in nmr, the usefulness of ESCA in qualitative analysis would be enhanced. Accurate predictions of binding energy shifts are found when using CNDO, INDO, and modified Sanderson charge calculations.

The study of charge distribution in molecules has been one of the most frequent applications of electron spectroscopy (ESCA) to chemistry. To enhance the understanding of chemical shift data, it has been common to compare experimentally measured core-electron binding energies with various charge calculations, including *ab initio*<sup>2</sup> and semiempirical<sup>3,4</sup> MO calculations along with several empirical methods based on electronegativity.<sup>5</sup> Few studies, however, have sought to estimate the effect of remote atoms on the binding energies of core electrons.<sup>6</sup>

We have chosen a simple, but revealing, system to evaluate remote inductive contributions to ESCA chemical shifts. The series includes *tert*-butyl alcohol, trifluoro-*tert*-butyl alcohol, hexafluoro-*tert*-butyl alcohol, and perfluoro-*tert*-butyl alcohol.<sup>7</sup> The lack of  $\pi$  bonding and the large inductive effects of fluorine make this system particularly attractive. Charge calculations were done using CNDO, INDO, extended Hückel (EH), Jolly's method,<sup>5a</sup> and a modified Sanderson (MS) approach developed in this laboratory.<sup>8</sup> Molecular potential calculations were included where appropriate.

## Experimental Section

ESCA spectra were obtained using an AEI-ES100 electron spectrometer having an aluminum anode ( $h\nu = 1486.6$  eV). Since the

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- (2) D. T. Clark and D. B. Adams, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1819 (1972); *J. Electron Spectrosc. Relat. Phenomena*, **1**, 302 (1973).
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- (4) M. E. Schwartz, *J. Amer. Chem. Soc.*, **94**, 6298 (1972).
- (5) (a) W. L. Jolly and W. B. Perry, *J. Amer. Chem. Soc.*, **95**, 5442 (1973); (b) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. Karlsson, I. Lindgren, and B. Lindberg, "ESCA: Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy," Almquist and Wiksells, Uppsala, 1967; (c) K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Leder, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, "ESCA Applied to Free Molecules," North-Holland Publishing Co., Amsterdam, 1969; (d) D. A. Shirley, Ed., "Electron Spectroscopy," North-Holland Publishing Co., Amsterdam, 1972, Chapter V, and references therein.
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- (7) *tert*-Butyl alcohol = 2-methyl-2-propanol; trifluoro-*tert*-butyl alcohol = 1,1,1-trifluoro-2-methyl-2-propanol; hexafluoro-*tert*-butyl alcohol = 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol; perfluoro-*tert*-butyl alcohol = 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-2-propanol.

samples are liquids at 25° and 1 atm, we were able to condense them onto clean gold backings *in situ*. The liquids which were injected into a heated reservoir shaft ( $\sim 350^\circ\text{K}$ ) diffused as gases into the sample chamber where they were condensed on the cooled sample probe ( $\sim 180^\circ\text{K}$ ). The probe temperature, in each case, was carefully adjusted so a steady state was established between evaporation and condensation. Under these conditions the pressure in the sample chamber remained at about  $5 \times 10^{-6}$  Torr. By using this procedure, we were able to have a continually fresh sample surface and a very thin sample layer; the gold substrate always was visible to ESCA during the runs. Also, we found no shifts in the peak positions as a function of time. This indicates that the sample charging was invariant during a run. Each compound was examined on at least three separate runs; binding energies measured for different runs were constant to  $\pm 0.1$  eV. The estimated accuracy of each reported binding energy is  $\pm 0.2$  eV. All samples were obtained from PCR, Inc., except for *tert*-butyl alcohol which was obtained from J. T. Baker Chemical Co. All samples were used without further purification.

Spectra were calibrated by three separate methods: (1) the 4f gold lines from the backing;<sup>9</sup> (2) the contamination carbon 1s peak,<sup>10</sup> usually about 2-5% of the total carbon spectra, see Figure 1; and (3) for the fluorine containing species, the F 1s peak was observed. Peak intensity ratios for the carbon atoms were found to correspond to the expected values based on atomic ratios. Comparisons of peak intensities between C 1s and O 1s also were found to be approximately what were expected based on experiments run in this laboratory and literature values.<sup>11</sup> Thus, we can be confident that the signals attributed to oxygen and carbon are from the samples and not from some contaminant. The binding energies used for calibration purposes are 285.0 eV (C1s) and 83.8 eV (Au 4f<sub>7/2</sub>).<sup>10</sup> The binding energy value for the fluorine 1s was found to be 688.7 eV based on calibrations using both the gold and carbon.

## Results

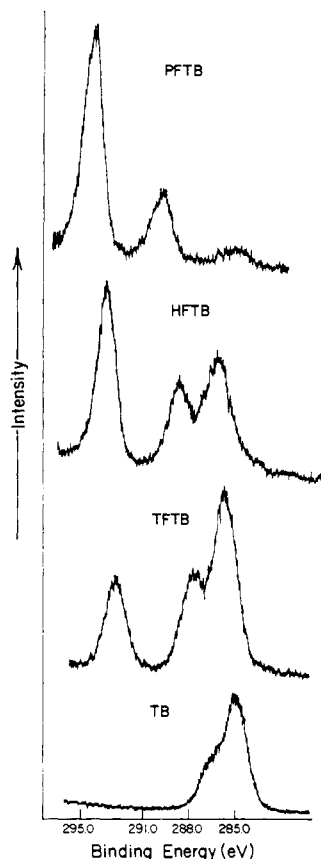
The C 1s spectra for the four butanols are shown in Figure 1. These data are tabulated in Table I. Also included in Table I are the oxygen 1s data. The carbon peaks show the expected primary chemical shift, but in addition, the remote effect of the fluorine atom is apparent. The shift per fluorine in the carbon atoms  $\alpha$  to the fluorines agrees well with existing data,<sup>6</sup> about 2.8 eV per fluorine (2.8 eV/F). The  $\beta$  carbon, however, shows a chemical shift which is nonlinear: *ca.* 0.5 eV/F for the first CF<sub>3</sub> group, *ca.* 0.2 eV/F for the second and

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**Figure 1.** Carbon 1s X-ray photoelectron spectra of *tert*-butyl alcohol and three of its fluoro derivatives: PFTB, perfluoro-*tert*-butyl alcohol; HFTB, hexafluoro-*tert*-butyl alcohol; TFTB, trifluoro-*tert*-butyl alcohol; TB, *tert*-butyl alcohol.

**Table I.** Carbon (1s) and Oxygen (1s) Electron Binding Energies (eV)

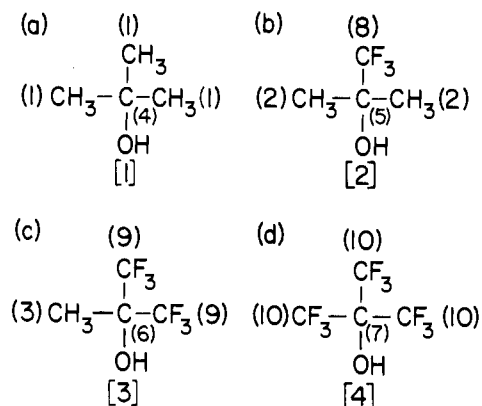
Atom	<i>tert</i> -Butyl alcohol	Trifluoro- <i>tert</i> -butyl alcohol	Hexafluoro- <i>tert</i> -butyl alcohol	Perfluoro- <i>tert</i> -butyl alcohol
C-H	285.0	286.2	286.5	
$\Delta E$		1.2	0.3	
C-O	286.6	288.1	288.9	289.6
$\Delta E$		1.5	0.8	0.7
C-F		293.3	293.9	294.4
$\Delta E$			0.6	0.5
O-C	532.5	533.4	534.2	535.0
$\Delta E$		0.9	0.8	0.8

third groups. A similar nonlinear effect is observed for the  $\gamma$  carbons.

The chemical shifts exhibited by the oxygen 1s level are more surprising (see Table I), since shifts of this magnitude for oxygen are unusual.<sup>12</sup> The change in binding energy of the O 1s seems to be linear with the number of fluorines attached  $\gamma$  to it, a shift of *ca.* 0.3 eV/F.

**Charge Calculations.** In an effort to evaluate these results in a systematic fashion, various charge calculations were performed. Table II lists the results of the calculations, with the molecular potential contributions listed in Table III. The tables are divided into four sections, ESCA data for (1) carbons attached to hydro-

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**Figure 2.** Diagrams of the compounds under study. The numbers in parentheses correspond to the carbon atoms in Tables II and III and the points in Figure 3. The numbers in brackets correspond to oxygen atoms in Tables II and III and the points in Figure 4.

gens, (2) carbons attached to oxygen, (3) carbons attached to fluorines, and (4) oxygen atoms.

CNDO, INDO, and extended Hückel (EH) computer programs<sup>13</sup> were obtained from the Quantum Chemistry Program Exchange. The molecules were geometrically optimized from a basic tetrahedral configuration about the center carbon (the alcohol carbon; see Figure 2). The bond distances were obtained from available literature.<sup>14</sup> For the EH calculations standard Slater exponents were used<sup>15</sup> and the Coulomb integrals were obtained from the computation of Lu, *et al.*<sup>16</sup>

Although Pauling's electronegativity method for calculating charge is probably the most widely used, it provides no straightforward way to evaluate remote effects.<sup>5b</sup> For example, in Table II it can be seen that except for the alcohol carbons there is no change in the atomic charge for the various compounds. Thus we have excluded this method from further consideration.

Both of the methods of Jolly<sup>5a</sup> and Sanderson<sup>17</sup> are based on equalization of electronegativities. Jolly has developed a method which treats various aspects of electron density in a consistent manner. Though using a more sophisticated technique, Jolly incorporated many of Pauling's ideas on partial charge estimation into his approach. This technique is highly parameterized, and certain decisions on the weighting of resonance structures are required.

The term "stability ratio" (SR) is used by Sanderson instead of electronegativity.<sup>17</sup> The basic charge calculation involves finding a normalized difference between the stability ratio of the molecule ( $SR_m$ ) and that of the element ( $SR_i$ ) where the molecular SR is the geometric mean of all the elemental SR's in the molecule. Thus

$$SR_m = \sqrt[n]{\prod_{i=1}^n SR_i} \quad (1)$$

(13) The program CNINDO was used which includes both CNDO and INDO, QCPE No. 223; QCPE No. 64 was used for EH.

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**Table II.** Calculated Charges for *tert*-Butyl Alcohol and Its Fluoro Derivatives

Atom	Point <sup>a</sup> no.	Compd	Binding <sup>b</sup> energy	Charge <sup>c</sup>					
				CNDO	INDO	EXTHUC	Modified Sanderson	Pauling	Jolly
C-H	1	TB	285.0	-0.034	0.021	0.026	-0.035	0.118	-0.039
	2	TFTB	286.2	-0.024	0.037	0.037	-0.018	0.118	-0.038
	3	HFTB	286.5	-0.020	0.046	0.044	-0.002	0.118	-0.036
C-O	4	TB	286.6	0.186	0.223	0.301	-0.004	0.403	0.084
	5	TFTB	288.1	0.112	0.124	0.106	0.066	0.428	0.109
	6	HFTB	288.9	0.032	0.117	-0.096	0.141	0.454	0.135
	7	PFTB	289.6	-0.053	-0.095	-0.292	0.222	0.479	0.160
C-F	8	TFTB	293.3	0.580	0.732	1.946	0.268	1.286	0.374
	9	HFTB	293.9	0.602	0.761	1.954	0.290	1.286	0.375
	10	PFTB	294.4	0.618	0.782	1.961	0.312	1.286	0.377
O-C	1	TB	532.5	-0.276	-0.330	-0.243	-0.239	-0.221	-0.234
	2	TFTB	533.4	-0.252	-0.300	-0.239	-0.213	-0.221	-0.232
	3	HFTB	534.2	-0.228	-0.272	-0.277	-0.186	-0.221	-0.231
	4	PFTB	535.0	-0.205	-0.243	-0.226	-0.158	-0.221	-0.229

<sup>a</sup> Refers to Figures 3 and 4. <sup>b</sup> For C-H, C-O, and C-F values are for C 1s electrons; for O-C they are for O 1s electrons. <sup>c</sup> For C-H, C-O, and C-F charges are for carbon; for O-C they are for oxygen.

**Table III.** Molecular Potentials Calculated for *tert*-Butyl Alcohol and Its Fluoro Derivatives

Atom	Compd	Point <sup>a</sup> no.	CNDO	INDO	EXTHUC	Modified <sup>b</sup> Sanderson	Jolly
C-H	TB	1	0.806	0.300	0.425	0.574	0.692
	TFTB	2	1.277	0.711	1.092	1.312	1.071
	HFTB	3	1.781	1.094	1.774	2.264	1.600
C-O	TB	4	-2.407	-2.341	-2.553	-0.902	-1.602
	TFTB	5	-0.093	0.433	4.005	-0.645	-0.671
	HFTB	6	2.310	3.312	10.637	-0.138	0.321
	PFTB	7	4.770	6.275	17.190	0.491	1.283
C-F	TFTB	8	-8.025	-9.810	-24.161	-5.690	-4.893
	HFTB	9	-7.649	-9.525	-23.481	-4.784	-4.424
	PFTB	10	-7.295	-9.254	-22.781	-3.710	-3.972
O-C	TB	1	3.531	4.423	3.567	2.490	2.695
	TFTB	2	3.823	4.581	4.337	3.115	3.230
	HFTB	3	4.028	4.751	5.037	3.962	3.698
	PFTB	4	4.267	4.921	5.860	4.952	4.199

<sup>a</sup> Refers to Figures 3 and 4. <sup>b</sup> Not included in Figures 3 and 4; see text.

The partial charge,  $\partial_i$ , on atoms is found using the following equation

$$\partial_i = (SR_m - SR_i) / \Delta SR_i \quad (2)$$

where  $\Delta SR_i$  is the normalization factor usually taken as  $2.08(SR_i)^{1/2}$ . Although this simple version predicts good trends in binding energies for many series, it fails in certain instances.<sup>8</sup> Two major obstacles have prohibited the general use of the basic Sanderson method. First, the calculation does not differentiate between structural isomers, *e.g.*, between 1-butanol and diethyl ether. Second, if two different chemical environments exist for the same element in a single molecule, a single partial charge is calculated for that element.

In order to modify this approach we decided that bond localization should be emphasized without altering the basic idea of electronegativity equalization. To accomplish this, we consider a molecule as being composed of a collection of groups, rather than as a collection of atoms. In order to calculate the partial charge on an atom in a molecule, we calculate a group stability ratio,  $SR_g$ , for the atom and the groups surrounding it.  $SR_g$  would be used in eq 2 in place of  $SR_m$ . The group for which  $SR_g$  is calculated is defined as the atom of interest (central atom) and all subgroups immediately bound to it. These subgroups can be terminal atoms, *i.e.*, atoms bound only to the central atom,

or other groups of atoms. For example, in methyl ethyl ether, if oxygen is the central atom,  $CH_3$  and  $C_2H_5$  are the subgroups. If the subgroup is a terminal atom, then the atomic SR for that element is utilized in the calculation of  $SR_g$ . For a multiatom subgroup, a unique SR is calculated ( $SR'_g$ ) based on its atomic composition; the central atom for calculation of  $SR'_g$  is that atom attached to the main atom on which charge is to be calculated. If the subgroup itself contains multiatom subgroups, the procedure is repeated. Thus, in our example above,  $SR'_{g(CH_3)} = (SR_C SR_H^3)^{1/4}$  and  $SR'_{g(C_2H_5)} = (SR_C SR_H^2 (SR_C SR_H^3)^{1/4})^{1/4}$ .

Consider hexafluorobutanol as a specific example. In this molecule there are four perimeter groups: two  $CF_3$  groups, one  $CH_3$  group, and one OH group. These groups surround a fifth group, *i.e.*, the central carbon atom. We then can calculate the charge on the oxygen for example in the following way. The oxygen is part of the hydroxide group which can be represented as  $H-O-M'$  where  $M'$  represents the remainder of the molecule. Thus, the group stability ratio,  $SR_{g(OH)}$  is the geometric mean of the SR's for oxygen, hydrogen, and the remainder of the molecule ( $SR_{M'}$ ).

Thus

$$SR_{g(OH)} = \sqrt[3]{(SR_O)(SR_H)(SR_{M'})} \quad (3)$$

Before this can be evaluated, however, the group  $SR_{M'}$  must be found. This group consists of several sub-

groups, including (1) the central carbon, (2) the CH<sub>3</sub> group, and (3) two CF<sub>3</sub> groups. Then

$$SR_{M'} = \sqrt[4]{(SR_C)(SR'_{g(CH_3)})(SR'_{g(CF_3)})^2} \quad (4)$$

The SR's for each subgroup are evaluated similarly, *e.g.*

$$SR'_{g(CH_3)} = \sqrt[4]{(SR_C)(SR_H)^3} \quad (5)$$

Then

$$SR_{M'} = \sqrt[4]{[SR_C][\sqrt[4]{(SR_C)(SR_H)^3}][\sqrt[4]{(SR_C)(SR_F)^3}]^2} \quad (6)$$

Therefore, eq 6 can be substituted into eq 3 to obtain a formula for evaluating the charge on the atom of hydroxide group.

$$SR_{g(OH)} = \sqrt[3]{[SR_O][SR_H][\sqrt[4]{(SR_C)(SR_H)^3}][\sqrt[4]{(SR_C)(SR_F)^3}]^2} \quad (7)$$

The partial charge on the oxygen as well as that on the hydrogen contained in the hydroxide group are found by substituting into eq 2

$$\partial_O = (SR_{g(OH)} - SR_O)/\Delta SR_O \quad (8)$$

$$\partial_H = (SR_{g(OH)} - SR_H)/\Delta SR_H \quad (9)$$

Note that it is only appropriate to calculate the charges on oxygen and hydrogen from the hydroxide group.

If the charge on the central carbon atom is sought, a similar procedure is used which results in the following equation

$$SR_{g(C)} = \sqrt[5]{(SR_C)(SR'_{g(OH)})(SR'_{g(CH_3)})(SR'_{g(CF_3)})^2} \quad (10)$$

Using the appropriate substitutions for the group SR's we get

$$SR_{g(C)} = \sqrt[5]{(SR_C)(\sqrt[4]{(SR_O)(SR_H)})(\sqrt[4]{(SR_C)(SR_H)^3})(\sqrt[4]{(SR_C)(SR_F)^3})^2} \quad (11)$$

Therefore

$$\partial_C = (SR_{g(C)} - SR_C)/\Delta SR_C \quad (12)$$

Again, note that for this group, which includes only the central carbon, only the charge on that atom can be calculated. This process is repeated for other groups until the charge on each atom is found. It might be noted from Table II that in general the magnitude of the charges calculated by the modified Sanderson method seem to be close to these charges calculated by CNDO. Therefore, we are able to retain the simplicity of Sanderson's method, *i.e.*, minimum parametrization and no resonance forms, while providing a generally applicable empirical method of calculating charges. The SR<sub>*i*</sub>'s which are used are taken directly from Sanderson<sup>17b</sup> and a partial list of these values is given in Table IV. A detailed discussion of the modified Sanderson approach to calculating partial charges is forthcoming.<sup>8</sup>

**Molecular Potential Calculation.** For each method of charge calculation a molecular potential (*V*) evaluation

**Table IV.** Stability Ratios for Hydrogen, Carbon, Oxygen, and Fluorine

Element	SR <sup>a,b</sup>	ΔSR <sup>a,b</sup>
H	3.55	3.92
C	3.79	4.05
O	5.21	4.75
F	5.75	4.99

<sup>a</sup> R. T. Sanderson, "Inorganic Chemistry," Reinhold, New York, N. Y., 1960, p 80. <sup>b</sup> See discussion of terms in text.

was included, except for MS calculations. The molecular potentials were calculated according to eq 13 and the results are summarized in Table III.

$$V_i = \sum_{j \neq i}^n q_i / R_{ij} \quad (13)$$

*q<sub>i</sub>* is the partial charge on the *i*th atom in the molecule and *R<sub>ij</sub>* is the distance between the central atom *j* and atom *i*. The commonly used equation for correlating charge and molecular potentials with experimentally measured binding energies is

$$\Delta E_B = k\Delta q + \Delta V \quad (14)$$

where *k* is a proportionality constant, Δ*q* is the change in partial atomic charge, and Δ*E<sub>B</sub>* is the change in binding energy.

## Discussion

**Evaluation of Charge Calculations.** Figures 3 and 4 show plots of binding energy *vs.* charge for the carbon and oxygen, respectively. The numerical values and identification of the points can be found in Tables II and III. For Figure 3, the experimental binding energies of the carbon atoms, corrected for molecular potential, are plotted against the calculated charges from (a) INDO, (b) CNDO, (c) Jolly, and (d) extended Hückel. Charges from MS (e) are plotted directly against the experimental binding energies which are uncorrected for molecular potential. Likewise, in Figure 4 the charges on the oxygen atoms found from (a) INDO (solid line) and CNDO (dashed line), (b) extended Hückel, and (d) Jolly are plotted against O 1s BE's corrected for molecular potential, while charges from MS (c) are plotted against O 1s BE's uncorrected for molecular potential. The slopes and standard deviations for these plots are given in Table V. In all cases except for modified Sanderson, inclusion of the molecular potential improved the correlation (see Table V) and thus only those plots are given. In the case of the modified Sanderson method a better correlation was found without the molecular potential correction, indicating that to some degree this approach intrinsically includes the molecular potential. Currently, this feature of the modified Sanderson calculation is not completely understood.

No attempt was made to optimize the MO calculations although such an exercise undoubtedly would improve the quality of the charges obtained. Since we are attempting to evaluate only those methods generally used by experimentalists, we chose to utilize only the most straightforward calculations. Interestingly enough, even without any basic changes in the computer programs as obtained from the Quantum Chemistry

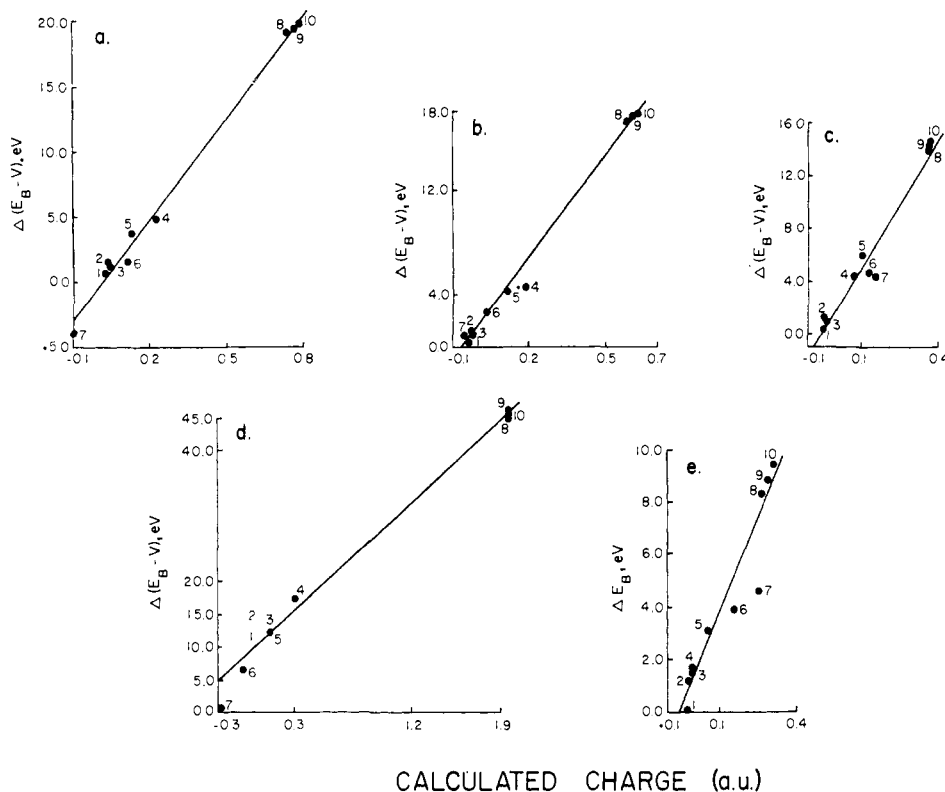


Figure 3. Correlation between calculated charges and experimental carbon 1s electron binding energies: (a) INDO, (b) CNDO, (c) Jolly, (d) extended Hückel, (e) modified Sanderson (does not include molecular potential correction; see text).

Table V. Slopes and Standard Deviations for Binding Energy Charge Correlations

Method	Slope, eV <sup>b</sup>	Std dev, eV <sup>b</sup>
<b>A. Carbon Data<sup>a</sup></b>		
Sanderson	39.41 (24.11)	0.90 <sup>d</sup>
CNDO	26.66 (10.83)	0.62 (1.66)
INDO	26.09 (8.88)	0.79 (1.71)
EXTHUC	18.22 (3.19)	2.20 (1.80)
Jolly	32.94 (19.82)	1.08 (1.3)
Expected value for good fit	22.0	<0.2
<b>B. Oxygen Data<sup>c</sup></b>		
Sanderson	0.68 (30.66)	0.05 <sup>d</sup>
CNDO	24.06 (35.10)	0.03 (0.02)
INDO	22.84 (28.73)	0.02 (0.03)
EXTHUC	11.54 (121.3)	0.10 (0.41)
Jolly	203.80 (568)	0.06 (0.04)
Expected value for good fit	31.6	<0.2

<sup>a</sup> Based on plots shown in Figure 3. <sup>b</sup> The numbers in parentheses represent those values found when the molecular potential is excluded. <sup>c</sup> Based on plots shown in Figure 4. <sup>d</sup> Molecular potential not included; see text.

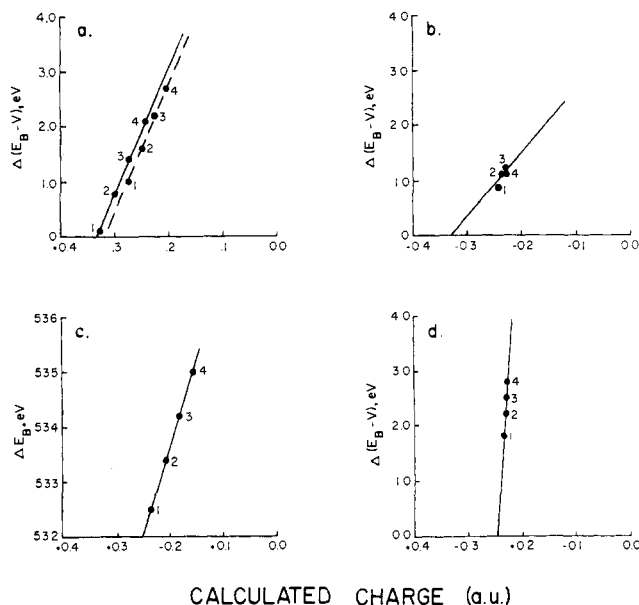


Figure 4. Correlation between calculated charges and experimental oxygen 1s electron binding energies: (a) INDO (—) and CNDO (---), (b) extended Hückel, (c) modified Sanderson (does not include molecular potential correction; see text), (d) Jolly.

Program Exchange, the charges predicted seem to be reasonable except for EH (see discussion below).

Two criteria were used to evaluate a particular charge-binding energy correlation: the slope,  $k$ , and the standard deviation. The slope is predicted from theory to be approximately equal to the expectation value for  $1/R$  where  $R$  is the radius of the outer orbital. Based on relativistic Hartree-Fock calculations  $\langle 1/R \rangle_O = 31.6$ , while  $\langle 1/R \rangle_C = 22.0$ .<sup>16</sup> Experimentally determined slopes have varied from about 8<sup>5b-d</sup> to 26.4<sup>12</sup> for oxygen, while those for carbon center about 24.2.<sup>6</sup> The second test of course is the magnitude of the standard deviations. Both  $k$  and the standard deviation are given in units of

electron volts. An excellent correlation should provide a standard deviation less than 0.2 eV.

Reasonably good fits are obtained for the CNDO and INDO methods for both the carbon data and the oxygen data. The carbon slopes are found to be 26.7 and 26.1 while the oxygen slopes are found to be 24.0 and 23.8, respectively. The standard deviations are a bit high for carbon but very good for oxygen. The results

from the extended Hückel method are poorer with the standard deviation being high for the carbon data, while the slope is low for the oxygen data. Modified Sanderson without molecular potential gives a fit as good as either CNDO or INDO methods, and in fact the slopes are closer to the expected values, *i.e.*,  $k_{\text{O}}^{\text{MS}} = 30.7$  *vs.*  $k_{\text{O}}^{\text{exp}} = 31.6$  and  $k_{\text{O}}^{\text{MS}} = 22.1$  *vs.*  $k_{\text{C}}^{\text{exp}} = 22.0$ . Jolly's method fits the carbon data reasonably well but gives a slope for the oxygen data which is extremely large. If the molecular potential is included separately with the modified Sanderson calculation the correlation is poor. The slopes found are too large for the carbon data and too small for the oxygen data which suggests that the molecular potential is overemphasized. This result leads us to believe that the modified Sanderson approach includes a pseudo-molecular potential contribution internally. This fortuitous aspect makes MS easy to use since corrections for the effect of molecular potential can be ignored.<sup>8</sup> It is clear that for our series of compounds neither the Jolly nor extended Hückel methods properly allow for remote inductive effects. CNDO, INDO, and modified Sanderson, however, all provide adequate correlations with experimental binding energies.

**Remote Shifts.** If we assume that  $\Delta E_{\text{B}}$  for carbon is about 22.0 eV per unit charge (see discussion of  $k$  value), or  $\Delta E_{\text{B}} = 2.2$  eV/0.1 e<sup>-</sup>, then based on our data a fluorine adjacent to a carbon removes about 0.13 electron. At the  $\beta$  positions about 0.02 electron is withdrawn, while *ca.* 0.01 electron is removed from the  $\gamma$  atoms. It is unclear from the carbon data as to what portion of this change in electron density is due to inductive effects compared to that due to the molecular potential differences at the sites. It appears that the molecular potential may be of equal importance as through bond inductive effects for this particular series. In certain cases when the through space distance is far shorter than the through bond distance, the molecular potential may even dominate.

The shifts seen for the oxygen atom are unexpected. Other studies<sup>12</sup> indicate that rather small shifts are seen experimentally although a rather large  $k$  is expected. This indicates that either there are very small changes in the partial charge for oxygen or that the change in  $q$  is negated by a corresponding change in the molecular potential. The second suggestion is highly improbable, although possible in certain cases. Therefore the large changes seen in the binding energy of the O 1s electrons indicate that there is a significant change in the electron density. Based on our CNDO calculations we can estimate that the contributions to  $\Delta E/F$  from the molecular potential changes are less than 0.1 eV. Therefore we are seeing significant through bond inductive effects. Apparently, the oxygen loses more electron density than the  $\gamma$  carbons do. Our estimates are crudely based on a comparison of that portion of the calculated  $\Delta E_{\text{B}}$  caused by  $k\Delta q$  with the amount caused by  $\Delta V$ ; see Table III. This finding is not totally unexpected since the  $pK_{\text{a}}$ 's for this series of butanols indicate that some loss of electron density in the oxygen-hydrogen bond must occur as shown by a significant increase in the acidity of the butanol as more fluorines are added. These data are summarized in Table VI.

**Table VI.** Comparison of Oxygen (1s) Binding Energies with  $pK_{\text{a}}$ 's for *tert*-Butyl Alcohol and Its Fluoro Derivatives

Molecule	BE(O 1s)	$pK_{\text{a}}$
TB	532.5	19 <sup>a</sup>
TFTB	533.4	12.7 <sup>b,c</sup>
HFTB	534.2	9.6 <sup>d</sup>
PFTB	535.0	5.2 <sup>d</sup>

<sup>a</sup> W. K. McEwen, *J. Amer. Chem. Soc.*, **58**, 1124 (1936). <sup>b</sup> B. L. Dyatkina, E. R. Mochalina, and I. L. Knunyants, *Tetrahedron*, **21**, 2991 (1965). <sup>c</sup> The  $pK_{\text{a}}$  value was estimated by using the literature value for  $\text{CH}_3\text{CF}_3\text{HCOH}$ . The difference in  $pK_{\text{a}}$  between an H group and a  $\text{CH}_3$  group for HFTB and  $(\text{CF}_3)_2\text{HCOH}$  is 0.3 unit, and therefore a similar difference would be expected for the trifluoro-*tert*-butyl alcohol case. <sup>d</sup> R. Filler and R. M. Schure, *J. Org. Chem.*, **32**, 1217 (1967).

The data were normalized to a common solvent so that solvent effects can be ignored.

### Conclusion

An understanding of remote shifts can be quite significant in the development of ESCA as an analytical tool. If further studies of this type were to be made, then tables could be developed similar to nmr shift tables, which could estimate the effect of remote atoms on the binding energy of a given atom. ESCA could then be used in molecular as well as elemental identification. For example if trifluoro-*tert*-butyl alcohol were an unknown compound, we could (1) establish which elements were present, except for H, (2) establish the atomic ratio of these elements from intensity ratios, and (3) then, from exact binding energies of each element coupled with a table of chemical shifts, make a good estimate of the molecular structure. To accomplish this goal an accurate correlation with charge calculation is desirable. It should be pointed out that any charge calculation, no matter how sophisticated, is necessarily arbitrary. Like many other formalisms, however, these quantities are useful crutches for experimentalists. For instance, if one were trying to decide if a particular compound were one of two or three isomeric structures, then from a good charge calculation he could decide exactly what the expected remote shifts might be for each case. From our results we found that CNDO and INDO do quite well if the molecular geometry is known and a computer is available; under these circumstances, these are probably the preferred methods. We believe however, that utilization of the modified Sanderson (MS) approach might be a good choice; in many cases MS offers ease of calculation (no computer required), no knowledge of the molecular geometry, and no separate molecular potential calculations, while giving binding energy charge calculations comparable to the more sophisticated quantum methods.<sup>18</sup>

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(18) (a) W. K. McEwen, *J. Amer. Chem. Soc.*, **58**, 1124 (1936); (b) B. L. Dyatkina, E. R. Mochalina, and I. L. Knunyants, *Tetrahedron*, **21**, 2991 (1965); (c) R. Filler and R. M. Schure, *J. Org. Chem.*, **32**, 217 (1967).