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X-RAY PHOTOELECTRON SPECTROSCOPY OF FLUORINATED BENZENES*

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Abstract

Carbon 1s and (where applicable) fluorine 1s binding energy shifts were measured in gaseous benzene, fluorobenzene, o-, m-, and p-difluorobenzene, 1,3,5-trifluorobenzene, the three tetrafluorobenzenes, pentafluorobenzene, and hexafluorobenzene. The fluorine spectra showed only a single peak for each fluorine-containing molecule. The carbon spectra of C_6H_6 and C_6F_6 each showed only one peak. Two carbon peaks were found in the spectra of all the other molecules. In each case the higher binding energy peak was assigned to carbons bonded to fluorines, the lower to carbons bonded to hydrogens. Least-squares fitting procedures yielded binding-energy shifts with accuracies between ±0.03 eV and ±0.17 eV (standard deviation).

The shifts were interpreted in three ways. First, trends were observed. The formal symmetry between fluorine-substituted benzene and hydrogen-substituted perfluorobenzene was found to be reflected in detail in the carbon 1s shifts. Saturation of the inductive action of fluorine on the ring was manifest as a deviation from symmetry in these shifts. A second, more quantitative interpretation was based on the use of CNDO wave functions to calculate ΔV, the shift in the electrostatic potential at each nucleus. The binding energy shift ΔE_B is related by $\Delta E_B \cong -\Delta V$: thus shifts could be estimated directly. These

theoretical shifts were in good agreement with experiment. Finally, an atomic charge analysis, ACHARGE, was made. This analysis is based on a point charge approach that used molecular geometries, atomic properties, and measured shifts to deduce empirically charges that could be assigned to each atom. The charges so obtained were in very close agreement with CNDO charges and with chemical experience. A clear ortho-meta-para effect was found. Fluorine atoms substituted on benzene were found to have charges in the range -0.15 $|e|$ to -0.20 $|e|$, depending on the number of fluorines on the ring. The carbon to which a fluroine was bound has a charge of +0.23 $|e|$ in fluorobenzene and +0.14 $|e|$ in C_6F_6. Charges of -0.05 $|e|$, +0.02 $|e|$, and 0.00 $|e|$ were found on carbons in the ortho, meta, and para positions, respectively. Additional tautomeric forms enhance these effects in polyfluorinated benzenes, as expected. The simplicity, strong empirical basis, and excellent agreement with both CNDO charges and classical chemical resonance models strongly support the validity of the ACHARGE analysis, and indicate that it may have value in predicting chemical properties from core level binding-energy shifts.

I. Introduction

Among the most basic characteristics of a molecule in its ground state are its chemical formula, the relative positions of its atomic nuclei, and the distribution of the valence electrons. The first two of these can in principle always be determined by well-established experimental techniques. The third--the electron distribution--is very elusive. It affects almost every spectral property, but, with some exceptions (e.g. dipole moments in diatomic molecules), the deduction of electron distribution from measured quantities is indirect and often ambiguous. As a result our knowledge of electronic distributions in even rather well-studied molecules is far from perfect. Rough magnitudes of "atomic charges" are known (or at least agreed upon), and, for some extensively-studied series, concepts such as "lone pairs" and "back donation" are used with confidence, but existing experimental techniques are not usually capable of yielding very quantitative results concerning electron distributions. The question "what is the charge on fluorine in fluorobenzene?", for example, will evoke a range of numerical answers.

In this paper we report the results of an experimental study of the chemically-induced shifts in the binding energies of carbon and fluorine 1s electrons in fluorine-substituted benzenes. The 1s binding energy of each atom is rather directly sensitive to the local electrostatic potential. An electrostatic potential model is used, together with CNDO wave functions, to predict shifts. We describe also a "point charge" model that allows the interpretation of chemical shifts in binding energy in terms of an <u>experimental</u> population analysis for each molecule. This model is used to estimate atomic charges for the fluorine-substituted benzenes. Trends are discussed and compared with expectations based on chemical properties.

Experimental procedures are described in Section II, and results are given in Section III. Trends in the shifts are noted in Section IV. Section V treats the electrostatic potential model. The atomic-charge analysis is described and applied in Section VI, and in Section VII the derived atomic charges are discussed.

II. Experimental

Binding energies were measured by x-ray photoemission, using $MgK\alpha_{1,2}$ radiation (1253.6 eV), and electrons were analyzed in the Berkeley Iron-Free Spectrometer.[1] The samples were all studied as gases at pressures in the 10^{-2} Torr range. Pressures were monitored by a MacLeod gauge. The pressure-sensitivity of peak positions was found to be negligible, in contrast to the results reported by Siegbahn _et al_.[2] Our experimental pressures were much lower than theirs (which ranged up to 1 Torr), while our counting rates were typically somewhat higher. The peak-to background ratios in the spectra ranged from as high as 15/1 in the best cases down to less than 1/1 for the worst cases (weaker peak of a doublet, in the presence of a reference gas): for most cases the ratio was 5/1 or greater.

Considerable care was taken to measure binding energy shifts with the highest accuracy feasible within the constraints of this study. In order to achieve this goal it was necessary to monitor all measurements with a standard reference gas. Both fluoroform and fluorobenzene were used as references. Two procedures were followed. In some cases the reference gas was admitted to the experimental chamber along with the gas under study. This is, in principle, the more reliable procedure, but it suffers from two serious faults. First, the signal-to-background ratio is lowered substantially by the presence of the reference gas. Second, for some cases (e.g., the fluorine 1s peaks), the range of chemical shifts is too small to provide a reference compound with a peak that can be resolved from that of the compound under study.

The second procedure consisted of admitting the sample and reference gases alternately into the experimental chamber. The alternation period (∿ 1 hour) was fast compared to the long-term drift in the spectrometer calibration (0.2 - 0.3 eV/day), and the latter was thus effectively eliminated. The reliability of this procedure was established by comparison of the shift results with those obtained using the more direct method. Either of the two above procedures would still be feasible even if the apparent peak positions were pressure-dependent, but both would require more measurements. The origin of the pressure dependence of peak position in the data of Siegbahn *et al*. is not understood,[2] but for those gases in which comparisons are possible their chemical shifts agree reasonably well with those measured with the Berkeley spectrometer.[3,4]

The spectrometer magnet current was computer-controlled. It was stepped in units of 0.2 ma (∿ 0.3 eV) over a range wide enough to establish a baseline. The spectra were displayed and visually inspected during each run, which consisted of several scans of the energy region under study. Each scan was recorded with a teletypewriter, and for each run of n scans both the sum of the first n/2 scans and the sum of all n scans were separately analyzed to check for consistency. The data were transferred to punched cards and were least-squares fitted in a CDC-6600 computer. Gaussian peak shapes were used. They gave good fits, although the peaks are not necessarily expected to be Gaussian. Peak positions, linewidths, and intensities, as well as background parameters, were obtained from the least-squares fits. Standard deviations in each parameter were also obtained; these are quoted directly as errors in the peak position, which is the only parameter that we shall interpret in detail. Several runs were made on most of the peaks studied, and the results agreed to an extent that indicates these error estimates are realistic, and the errors therefore primarily statistical. Thus when two shifts were combined, the error in the resultant was obtained by the standard rules of statistical error analysis.

III. Results

Benzene and ten of the twelve fluorine-substituted benzenes were studied. Only the two unsymmetrical trifluorobenzenes were omitted. Parameters were obtained for thirty peaks. Although we shall treat only the peak positions in detail, the other parameters deserve passing comment. The background was nearly flat. For those cases in which the background was high enough to allow analysis, it had a slight negative slope when plotted against kinetic energy. The linewidths (FWHM) were in the range 1.2 - 1.3 eV for carbon 1s peaks and in the range 1.4 - 1.5 eV for the fluorine 1s peaks. The peak intensity ratios were of interest only for the carbon 1s peaks in the compounds $C_6F_nH_{6-n}$. For these cases two distinct carbon peaks of intensity ratio n/(6-n) were observed. We interpret these two peaks as arising from the aggregate of all carbons bonded directly to fluorine and the aggregate of all carbons bonded directly to hydrogen, respectively. No further interpretation will be made of these three parameters--background level, linewidth, and intensity--and they will not be reported in detail.

The binding energies could be given in several ways. We have chosen to report binding energy shifts ΔE, referring the carbon 1s binding energies to benzene and the fluorine 1s binding energies to hexafluorobenzene. These reference binding energies have the values $E_B(C1s;C_6H_6) = 290.4$ eV and $E_B(F1s;C_6F_6) = 693.7$ eV. Both are known only to an accuracy of a few tenths eV, but their exact values have little bearing on interpretation of the shifts, which are known much more accurately. Table I gives the binding energy shifts, referred to these two compounds.

As an example of the reproducibility with which the position of a weak peak could be determined, the splitting of the two carbon 1s peaks in fluorobenzene is reported for seven runs in Table II.

Table I. C(1s) and F(1s) Binding Energy Shifts

Compound, X	$\Delta E_B(C1s) \equiv E_B(C1s, X) - E_B(C1s, C_6H_6)$ Lower-E_B Peak (eV)	Higher-E_B Peak (eV)	$\Delta E_B(F1s) \equiv E_B(F1s, x) - E_B(F1s, C_6F_6)$ (eV)
C_6H_6	(0.00)	--	--
C_6H_5F	0.39(3)[a]	2.43(4)	-1.38(5)
1,4-$C_6H_4F_2$	0.76(4)	2.74(6)	-1.08(5)
1,3-$C_6H_4F_2$	0.70(5)	2.92(6)	-1.08(5)
1,2-$C_6H_4F_2$	0.72(4)	2.87(6)	-1.01(5)
1,3,5-$C_6H_3F_3$	0.56(13)	3.02(9)	-0.87(8)
1,2,3,4-$C_6H_2F_4$	0.96(10)	3.20(10)	-0.68(10)
1,2,3,5-$C_6H_2F_4$	0.86(12)	3.05(12)	-0.45(6)
1,2,4,5-$C_6H_2F_4$	1.12(10)	3.20(10)	-0.48(10)
C_6HF_5	1.32(17)	3.38(14)	-0.31(5)
C_6F_6	--	3.57(9)	(0.00)

[a] Error in last place given parenthetically.

Table II. Splitting of the C(1s) peaks in fluorobenzene

Run Number	Splitting (in eV)
10 B	2.036 (76)
15 B	2.013 (57)
17 D	2.122 (79)
19 D	1.994 (71)
21 D	1.966 (107)
23 D	2.112 (68)
25 D	2.017 (69)
Weighted Average	2.040 (30)

IV. Trends Among the Shifts

Chemical shifts in binding energies of core electrons can be interpreted at several levels of sophistication, ranging from correlations with an empirical parameter such as electronegativity to comparison with the predictions of ab initio Hartree-Fock calculations. The optimum interpretation for a given set of data depends in part upon the information desired from the data.

In this study we had three objectives. First, we wished to trace binding-energy shifts through a series of related planar molecules, in order to observe variations in binding energy shifts with substitution of fluorine for hydrogen. Second, we wanted to test the feasibility of predicting shifts by the use of an intermediate-level molecular orbital theory. Finally, we wished to assess the possibility of analyzing the chemical shifts for each molecule in terms of a self-consistent set of atomic charges by making a suitable analysis of the fluorine-substituted benzenes. Binding-energy trends are discussed in this section, and the other objectives are discussed in Sections V and VII.

The essential features of the spectra are illustrated in Fig. 1. The fluorine 1s peak shifts monotonically to higher binding energies as more fluorines are added to the ring, suggesting an oxidizing effect of fluorines on other fluorines. Figure 2 shows the fluorine 1s binding energy shifts plotted against n, the number of fluorines substituted on the ring. Only one fluorine 1s peak was observed in each case, even for molecules with inequivalent fluorines. This is not surprising because the total range of fluorine 1s shifts (1.38 eV) is about the same size as the fluorine 1s linewidth (1.4 - 1.5 eV), and splittings of a few tenths eV in the F(1s) spectrum of a given molecule could have gone unnoticed. Figure 2 also shows that the variation of E_B(F1s) is linear in n and that there is no significant variation in E_B(F1s) among isomers. For purposes of chemical analysis the fluorine 1s shifts can be represented by the relation $E_B(\mathrm{F1s},\ C_6H_{6-n}F_n) = E_B(\mathrm{F1s},\ C_6F_6) - 1.37/(6-n)$ eV. With the statistical accuracy obtained in our best spectra, one could determine n uniquely, but could not distinguish among isomers.

The carbon 1s shifts contain more information. First, for every molecule containing both carbons bonded directly to fluorine and carbons bonded directly to hydrogen (hereafter referred to as C_F and C_H, respectively) there are two carbon 1s peaks. The ratio of the intensity of the peak at the higher binding energy to that of the peak at the lower binding energy is in each case n/(6-n). Furthermore, from the (rather sparse) binding-energy systematics that are available to date, these two peaks fall at energies that might reasonably be predicted for C_H and C_F. We therefore assign the two carbons 1s peaks to the aggregate of all the C_H carbons (the peak with the lower E_B) and to the aggregate of all the C_F carbons (the peak with higher E_B). Several molecules had two or more inequivalent C_H or C_F carbons, but the spectra showed no decisive evidence for two or more binding energies among either the C_F or the C_H carbons in any case. Again, as in the fluorine 1s case, the existence of components spread over several tenths eV in energy would have been undetectable with the instrumental resolution and counting statistics available in this work.[5] Our interpretations below are based on the observation that all the C_F or C_H carbons in each molecule must have essentially the same binding energy. The experimental carbon 1s linewidths of 1.2 - 1.3 eV set an upper limit of about 0.5 eV on the range of shifts possible within a given peak.

Figure 3 shows the carbon 1s binding energies, relative to that of C_H in benzene, plotted against the number of fluorine atoms in each molecule. All the shifts are positive. This might naively be taken as evidence that all the carbons in the other ten molecules are oxidized relative to a carbon in benzene. Such a conclusion would be quite erroneous, however, as we shall discover in Sections VI and VII. Core-level binding energies are determined by the local potentials, not just by the charge on the host atom. Thus, except for very simple molecules, there exists no one-to-one relation between carbon 1s binding energy and the extent of oxidation.

The binding energies shown in Fig. 3 fall into two groups, corresponding to the C_F and C_H carbons. For each compound in which both C_F and C_H carbons are present the C_F peak is shifted to higher binding energy by about 2 eV, relative to the C_H peak. This suggests substantial oxidation of the carbon atoms that are directly bonded to fluorines. The shift

$$E_B(C_F 1s;C_6H_5F) - E_B(C_H 1s;C_6H_6) = +\ 2.43(4)\ \mathrm{eV} \quad ,$$

is only slightly less than the comparable shift for methane, i.e.,

$$E_B(C1s;CH_3F) - E_B(C1s;CH_4) = +2.8\ \mathrm{eV} \quad .$$

Both the C_H and the C_F shifts show essentially monotonic upward trends as the number of fluorines is increased. It would be tempting to infer from this fact the C_H carbons in the ring as well as the C_F carbon lose electronic charge to the fluorines. In fact we shall discover in Sections VI and VII that the converse often is true: some C_H carbons gain negative charge (but show an increase in 1s binding energy) when fluorine is substituted for hydrogen elsewhere on the ring. One must be careful not to infer a particular direction of charge flow with a given sign for the binding-energy shift. Such questions will be deferred to the atomic charge analysis in Section VI. For the remainder of this section we shall make observations only about the symmetries observed among the chemical shifts.

It would be very interesting to measure directly shifts induced in the binding energies of the ortho, meta, and para C_H carbons when a fluorine atom is bonded to a benzene ring to form fluorobenzene. The present resolution does not allow this: all three C_H carbons contribute to a single peak. Another approach is available, however. The C_F carbon has its photoelectron line split out of the C_H peak by about 2 eV, where it can be studied separately. This C_F carbon may then be situated in the o, m, or p position relative to a second C_F carbon, in a difluorobenzene molecule. Each of these molecules contains only one C_F species. Thus the C_F line in C_6H_5F may be taken as a standard, and the three shifts

$$E_B(C_F 1s;o,m, \text{ or } p - C_6H_4F_2) - E_B(C_F 1s;C_6H_5F) \quad ,$$

may then be regarded as measuring the effect of fluorine substitution on the o, m, or p position, at least as detected by a C_F carbon. These three shifts are set out in Table III.

There is an interesting formal symmetry among the eleven compounds studied in this work. Pentafluorobenzene may be regarded as C_6F_6 upon which a single hydrogen has been substituted, having a relationship to C_6F_6 analogous to that of C_6H_5F to C_6H_6. The tetrafluorobenzenes may then be regarded as o-, m-, and p-dihydro-perfluorobenzene, etc. In fact the whole series may be compared by going first up, then down, the list in the order given in Table I. Of course the C_F shifts going in one direction must be compared to the C_H shifts going the other way. The shifts

$$E_B(C_H1s;o-,m-,p - C_6H_2F_4) - E_B(C_H1s;C_6HF_5) \quad ,$$

analogous to the o, m, and p C_F shifts in the difluorobenzenes, are included for comparison in Table III. Uncertainties in the magnitudes of the shifts preclude extensive discussion, but several observations can be made. Making the appropriate pairwise comparisons, the C_F shifts have the opposite sign from the C_H shifts (as expected) and about the same magnitudes. With less reliability we can note that the trends in the magnitudes of the shifts are similar, meta > ortho > para, and that the C_H shifts slightly exceed the C_F shifts in magnitude.

Figure 4 shows the nine pairs of shifts plotted in a way that tests their 1:1 correspondence. The two sets of shifts are strongly correlated, and a straight line with unit slope even gives a fair representation of the relationship between them. This supports the concept of symmetry between the C_H shifts in compound X and the C_F shifts in compound $\overline{X}$, where $\overline{X}$ is obtained from X by replacing hydrogens by fluorines and vice versa. The two sets of shifts are not exactly equal in magnitude, but there is no reason to expect them to be.

A conspicuous feature of the carbon 1s shifts in Table I is that the addition of fluorines raises the 1s binding energies of all six carbons in the ring, and not just those of the C_F carbons. This may be interpreted as showing that fluorines remove charge "from the ring" in the sense of creating an electrostatically more attractive environment for all the carbon 1s electrons, but it must not be taken, without further analysis, as indicating anything directly about the charges on the C_H carbons. It is useful, however, to compare the shifts in an empirical fashion. Some indication of the total amount of charge withdrawn from the ring by fluorines is given by the total of the binding-energy shifts of all

Table III. The o, m, and p Shifts

Molecule	$E(C_F 1s)-E(C_F 1s$ in $C_6H_5F)$, in eV	Molecule	$E(C_H 1s)-E(C_H 1s$ in $C_6HF_5)$, in eV
o-$C_6H_4F_2$	0.44 (6)	o-$C_6H_2F_4$[a]	-0.36 (10)[b]
m-$C_6H_4F_2$	0.49 (6)	m-$C_6H_2F_4$	-0.46 (12)
p-$C_6H_4F_2$	0.31 (6)	p-$C_6H_2F_4$	-0.20 (10)

[a] Here o, m, p refer to the hydrogen positions.

[b] The error in the C_6H_5F energy is not included, since we wish to compare these three shifts.

six carbon atoms, relative to benzene. For the molecule X, with empirical formula $C_6H_{6-n}F_n$, the total shift $\Sigma(X)$ is given by

$$\Sigma(X) = nE_B(C_F1s;X) + (6-n)E_B(C_H1s;X) - 6E_B(C_H1s;C_6H_6) \quad .$$

If hydrogens are replaced by fluorines in X, and vice-versa, to form $\overline{X}$, with empirical formula $C_6H_nF_{6-n}$, then the analogous total shift, relative to C_6F_6, is given by

$$\Sigma'(\overline{X}) = nE_B(C_H1s;\overline{X}) + (6-n)E_B(C_F1s;\overline{X}) - 6E_B(C_F1s;C_6F_6) \quad .$$

In Fig. 5, $\Sigma(X)$ is plotted against $\Sigma'(\overline{X})$ for the nine compounds studied that had $1 \leqslant n \leqslant 5$. The good correlation supports the concept of symmetry among the shifts, and the deviation of the points from total quantitative agreement may be interpreted separately. The points in Fig. 5 mostly lie above a straight line with a slope of -1. This may be understood qualitatively if we recognize that in C_6H_6 the atoms are nearly neutral, and thus the electronic charge is more mobile, than in C_6F_6, in which the C-F bonds are highly polarized. We may describe this phenomenon as the saturation of an inductive effect. As more fluorines are added, each can withdraw less charge. This result was qualitatively evident in the F(1s) shifts in Fig. 2; it is treated quantitatively in Section VI, in which atomic charges for the fluorines are derived.

In Fig. 6 the saturation effect on the shifts is displayed more effectively: The total carbon 1s shifts per substituted ligand, $\Sigma(X)/n$, and $\Sigma'(\overline{X})/n$, are plotted against the number of substituted ligands, n. On the whole the points in Fig. 6 show a negative slope, although most of this slope is associated with the $\Sigma(X)/n$

shifts (relative to benzene). A qualitative interpretation of this result can be given. As fluorines are added to C_6H_6, induction and its saturation proceed normally. In going back from C_6F_6 the substitution of hydrogens cannot return electronic charge to the ring so effectively because the remaining fluorines, (which are not so negatively charged as in fluorobenzene, for example, and are thus still quite electronegative) tend to withdraw the additional charge.

The above comments indicate the possibilities and limitations for obtaining information from binding-energy shifts by studying trends and using chemical intuition. A more quantitative discussion is presented below.

V. A CNDO Potential Model

An electrostatic potential model based on SCF wave functions and Koopmans' theorem has been found to predict quantitatively the chemical shifts in some small molecules.[6,7] It would be desirable to apply this model to larger molecules if one could avoid the expense of calculating ab initio wave functions, and the CNDO/2 approximation was explored to this end. While requiring little computer time, CNDO/2 has been successful in predicting the properties of molecules composed of first-row elements.[8]

As in the ab initio approach, the electrostatic potential energy of an electron at a nucleus

$$e^2 \langle \sum_i \frac{1}{r_i} \rangle - e^2 \sum_j \frac{Z_j}{R_j} , \qquad (1)$$

is calculated. The symbols r_i and R_j refer, respectively, to the distance between the parent nucleus and the i^{th} electron and to the distance between the nucleus and the j^{th} other nucleus with charge Z_j. The first sum is taken over all the electrons in the molecule, the second over all the nuclei except the parent. The change in the potential energy at the nucleus of an element between two molecules is taken to be the negative of the shift in the binding energies of the 1s electrons associated with that nucleus.

The calculation of $\langle \sum_i \frac{1}{r_i} \rangle$ was done as follows: the basis functions (Slater orbitals) were treated as if they were orthonormal, as in the CNDO reduction of the Roothaan equations. The portion of the sum arising from the basis functions centered on the parent nucleus was calculated exactly, in contrast to the empirical approach used by Siegbahn, et al.[9] The portion arising from basis functions centered on other nuclei was evaluated in two alternative ways, each based on CNDO populations: (1) a "point charge" calculation, i.e., treatment of all basis functions as if they were spherically symmetrical and retention of only the diagonal matrix elements between basis functions; (2) exact evaluation of r^{-1} integrals, with retention of diagonal matrix elements plus off-diagonal matrix elements between p orbitals on the same center.

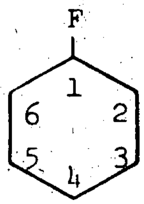
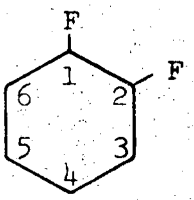
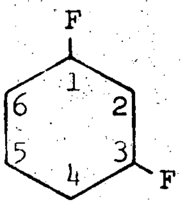
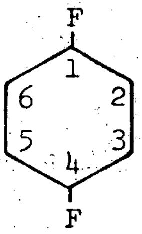
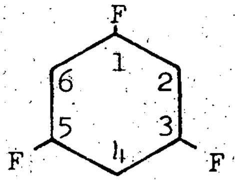
Both approaches are similar to the use of "complete neglect of differential overlap" in the evaluation of Coulomb integrals. The first approach treats all electrons not localized on the parent atom as if they were point charges at the nuclei to which their orbitals belong. In this case the above formula can be rewritten as

$$e^2 \sum_k \langle \frac{1}{r_K} \rangle - e^2 \sum_j \frac{q_j}{R_j} \quad , \qquad (2)$$

where the first sum is taken only over the electrons centered on the parent atom and the second sum is taken, as before, over all of the other atoms. The quantity q_j refers to the atomic charge of the j^{th} atom. The second approach includes the effects of differences in the spatial orientation of s, pσ, and pπ orbitals, and so reflects chemical bonding more accurately. This approach is justified within the CNDO approximation, which neglects differences between s, pσ, and pπ orbitals in its evaluation of only some of the integrals in the Roothaan equations. Addition of the non-diagonal elements was necessary to preserve the invariance of the matrix to unitary transformations which mix p orbitals on the same center. Symmetrically located nuclei are thereby guaranteed the same potentials.

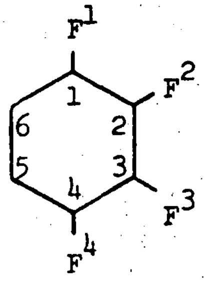
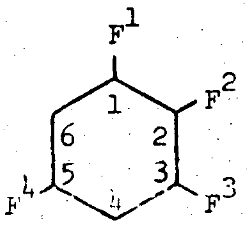
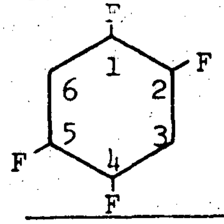
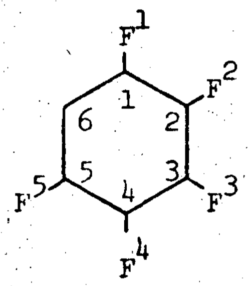
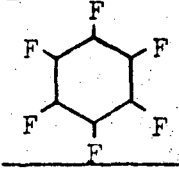
Theory and experiment are compared in Table IV. The numerical results of both of the above approaches are quite close, and agreement with experiment

Table IV. Carbon and Fluorine 1s Electron Binding Energy Shifts in eV[a]

Compound	Nucleus	Calculated (point charge)		Calculated, diagonal plus p-p' elements		Experimental[b]
	C_1	2.25		2.79		2.43(4)
	$C_{2,6}$	0.17	Ave. =0.26	0.16	Ave. =0.29	0.39(3)
	$C_{3,5}$	0.42		0.52		
	C_4	0.10		0.11		
	F	--		--		--
	$C_{1,2}$	2.48		2.98		2.87(6)
	$C_{3,6}$	0.76	0.72	0.84	0.81	0.72(4)
	$C_{4,5}$	0.67		0.78		
	F	-0.03		-0.08		0.37(10)
	$C_{1,3}$	2.66		3.30		2.92(6)
	C_2	0.33	0.43	0.29	0.46	0.70(5)
	$C_{4,6}$	0.27		0.26		
	C_5	0.84		1.04		
	F	0.36		0.37		0.30(10)
	$C_{1,4}$	2.36		2.91		2.74(6)
	$C_{2,3,5,6}$	0.61		0.68		0.76(4)
	F	0.16		0.18		0.30(10)
	$C_{1,3,5}$	3.08		3.82		3.02(9)
	$C_{2,4,6}$	0.42		0.40		0.56(13)
	F	0.71		0.74		0.51(13)

(continued)

Table IV. (continued)

Compound	Nucleus	Calculated (point charge)		Calculated, diagonal plus p-p' elements		Experimental[a]
	$C_{1,4}$	3.15	Ave. =3.20	3.77	3.81	3.20(10)
	$C_{2,3}$	3.25		3.84		
	$C_{5,6}$	1.43		1.63		0.96(10)
	$F_{1,4}$	0.63	0.75	0.62	0.70	0.70(15)
	$F_{2,3}$	0.86		0.78		
	$C_{1,3}$	3.40	3.27	4.09	3.92	3.05(12)
	C_2	2.96		3.48		
	C_5	3.31		4.02		
	$C_{4,6}$	1.23		1.32		0.86(12)
	$F_{1,3}$	0.80	0.71	0.77	0.69	0.93(11)
	F_2	0.66		0.61		
	F_4	0.58		0.61		
	$C_{1,2}$	3.15		3.77		3.20(10)
	$C_{3,6}$	1.51		1.66		1.12(10)
	F	0.62		0.61		0.90(15)
	$C_{1,5}$	3.62	3.57	4.34	4.24	3.38(14)
	$C_{2,4}$	3.44		4.06		
	C_3	3.71		4.39		
	C_6	1.71		1.90		1.32(17)
	$F_{1,5}$	1.09	1.11	1.04	1.07	1.07(10)
	$F_{2,4}$	1.05		1.04		
	F_3	1.28		1.21		
	C	3.94		4.64		3.57(9)
	F	1.52		1.48		1.38(5)

[a] Carbon shifts relative to benzene; fluorine shifts relative to fluorobenzene.
[b] Error in last place given parenthetically.

is comparable to that obtained from ground state ab initio calculations.[3,7,10] This agreement is further illustrated in Fig. 7, where we have plotted the experimental shifts versus those predicted by the first of the two CNDO/2 methods. The second method exaggerates chemical shifts slightly, especially in the heavily fluorinated benzenes. This is in contrast to the predictions of this method for the fluoromethanes, which are in almost perfect agreement with experiment.[11]

It is noteworthy that the dipole moments obtained from the CNDO/2 method for the fluorobenzenes also agree fairly well with the known experimental values,[12-14] as shown in Table V, and as reported previously.[15,16] Similar agreement between theoretical and experimental values of dipole moments has been obtained with the CNDO/2 method for many other classes of molecules, including the fluoromethanes.[8] For this reason, and because both dipole moments and chemical shifts seem to be sensitive measures of ground state electronic and nuclear distributions, it is expected that these CNDO/2 potential models will predict chemical shifts well for most molecules composed of first-row elements.

The bond lengths used for the CNDO/2 calculations were 1.08 Å for the C-H bond, 1.39 Å for the C-C bond, 1.30 Å for the C-F bond if there were no fluorine atoms ortho to one another, and 1.35 Å otherwise. These are the experimental bond lengths obtained for the difluorobenzenes;[17] the experimental bond lengths of most of the other fluorobenzenes are unknown. In a prior note[11] describing these CNDO potential models, the corresponding bond lengths used for the fluorobenzenes were 1.08 Å, 1.38 Å, and 1.30 Å; slightly different chemical shifts were obtained, while the atomic charges differed by a negligible amount.

Since $\langle \Sigma \frac{1}{r_i} \rangle$ is proportional to the nuclear diamagnetic shielding constant, the CNDO/2 calculation of $\langle \Sigma \frac{1}{r_i} \rangle$ may be of use in the interpretation

Table V. Dipole Moments

	Experimental	CNDO/2
fluorobenzene	1.57[12]	1.52
1,2 difluorobenzene	2.40[13]	3.07
1,3 difluorobenzene	1.58[14]	1.50

of NMR chemical shifts. The connection between ESCA and NMR was first discussed by Basch;[6] empirical correlations between NMR frequencies and ESCA binding energies have already appeared in the literature.[18,19]

The electrostatic potential energies were computed numerically by a subprogram written to augment the CNDO/2 FORTRAN IV program. The field length of the program was increased by less than 2000 words; the additional computations require about one-tenth of the time needed to obtain the CNDO/2 wave functions.

VI. An Atomic Charge Analysis

It seems worthwhile to develop a method of analyzing core-level binding-energy shifts directly to yield information about charge distributions in molecules, without recourse to molecular orbital models. Such an approach is suggested because core electrons are in some ways nearly ideal "test charges": they are sensitive to, but do not participate in, electron redistribution accompanying bond formation. In this section we discuss the derivation of an "atomic charge" analysis and its application to the fluorine-substituted benzenes. We seek both to test the model and (if possible) to derive information about charge distributions in these molecules.

Let us consider a molecule with n inequivalent atoms. If all n 1s electron binding energies are known, they may be referred to suitable standard binding energies to yield a set of binding-energy shifts δE_i $(i = 1,2,\ldots n)$. These shifts carry information about the electronic charge distribution. Since we have only n data we can derive from them a set of n numbers $\{q_i\}$ at most with which to describe this charge distribution. These numbers may be taken to represent charges centered on the different atoms. The resultant crude point-charge model is subject to several criticisms, but the atomic charges derived from it may prove useful on an intuitive level, as an essentially experimental population analysis.

Assigning charge q_j to atom j, and denoting by R_{ij} the internuclear distance between atoms i and j, we may write

$$\delta E_i = \sum_j \left(\frac{\partial E_i}{\partial q_j}\right) \delta q_j$$

$$= \left(\frac{\partial E_i}{\partial q_i}\right) \delta q_i + \sum_{j\neq i} \left(\frac{e^2}{R_{ij}}\right) \delta q_j \quad , \qquad \text{(VI-1)}$$

as the incremental change in the binding energy of a core electron in atom i accompanying a redistribution of charge in the molecule described by the set of numbers $\{\delta q_i\}$. Note that q_j is thus the charge on atom j in units of $|e|$. If we choose the binding-energy reference state as $q_j = 0$ for all j (i.e., hypothetical neutral atoms within the molecule) and invoke the essential constancy of $(\frac{\partial E_i}{\partial q_i})$ as q_i is varied,[20] Eq. (3) becomes

$$\delta E_i = k_i q_i + \sum_{j \neq i} \frac{e^2}{R_{ij}} q_j \quad . \tag{4}$$

Equations similar to this are well known in x-ray photoelectron spectroscopy.[21] Siegbahn, et al.,[9] have recently discussed this electrostatic approach for free molecules in some detail. They gave an expression very similar to Eq. (4), but their analysis was quite different from that given below.

Equation (4) is a linear equation in n unknowns $\{q_j\}$. There are n such equations, one for the shift δE_i on each atom i. It is convenient to write these equations in matrix form,

$$\vec{\delta} = A\vec{q} \quad . \tag{5}$$

Here $\vec{\delta}$ and $\vec{q}$ are n-dimensional vectors whose components are the ordered sets $\{\delta E_i\}$ and $\{q_i\}$ respectively. The $n \times n$ matrix A has elements

$$A_{ii} = k_i = \left(\frac{\partial E_i}{\partial q_i}\right)$$

$$A_{ij} = \sum_{j \neq i} \frac{e^2}{R_{ij}} \quad , \quad \text{for } i \neq j \quad . \tag{6}$$

The off-diagonal elements A_{ij} are easily worked out from a knowledge of the molecular geometry. Diagonal elements can be evaluated in several ways, as discussed below. The important point here is that the entire matrix A can be obtained from Coulomb's Law plus free-atom wave functions, with no reference whatever to molecular orbital models. Thus we may combine the matrix A, calculated essentially from first principles, with a complete set of n experimentally-determined shifts $\vec{\delta}$ to solve for the n charges $\vec{q}$, thereby obtaining an empirical population following the evaluation of $A_{ii} = k_i$ for the elements carbon and fluorine.

Binding-energy shifts for core electrons of isolated atoms arise via Coulomb shielding by electrons in the valence shell. For free atoms it has been shown[6,7] that to a good approximation $\Delta E_B = -\Delta V$, where ΔE_B is the binding-energy shift, and ΔV is the shift in potential energy of a 1s electron, that are induced when a change takes place in the valence shell. In fact the 1s orbitals even of first-row atoms such as carbon and fluorine are sufficiently localized that ΔV may be taken as the change in potential energy of an electronic charge-$|e|$ at the nucleus. A single valence electron interacting with such a charge gives rise to a potential energy term $e^2 \langle r^{-1} \rangle$, where $\langle r^{-1} \rangle$ is the expectation value of r^{-1} for the valence electron.[22] If the electron population of the valence shell should decrease by the fraction of one electron δq, corresponding to an increase of charge in the valence shell by the fraction δq of one charge unit $|e|$, then the binding energy of a 1s electron would be changed in this approximation by an amount

$$\delta E = - \delta V = e^2 \langle r^{-1} \rangle \delta q \quad . \tag{7}$$

Comparison with the "diagonal" terms in Eqs. (3) and (4) yields

$$k_i = e^2 \langle r_i^{-1} \rangle \quad . \tag{8}$$

In this analysis we shall use a single value of k_i for each element. The s and p valence orbitals on the same atom have slightly different values of $\langle r^{-1} \rangle$. However, we prefer to avoid any arbitrariness that might result from the introduction of additional parameters (e.g., to describe hybridization). This is certainly justified, because the derived charges are actually not very sensitive to the exact value of k used.

Mann's[23] free-atom Hartree-Fock calculations of $\langle 1/r \rangle$ yield $k_C = 21.1$ eV/|e| and $k_F = 34.5$ eV/|e| for the 2p orbitals of free carbon and fluorine, respectively. Siegbahn et al.[9] found slopes of $k_C = 21.9$ and $k_F = 27.6$ by least-squares fits of binding-energy shifts. They gave values $k = 22.0$ and $k_F = 35.1$ calculated from Slater orbitals for the elements. The agreement among these sets of values is encouraging. We have made atomic charge analyses based on ranges of values for k_C and k_F of about 5 eV/|e|, centered on the adopted values given below. The sensitivity of the derived charge to variation in k_C and k_F is very slight, typically

$$\frac{\delta q_i}{\delta k} \sim 0.005 \quad ,$$

in the ranges studied. Our final adopted values are

$$k_C = 22.0 \text{ eV}/|e|$$

$$k_F = 32.5 \text{ eV}/|e| \quad .$$

Reference energies must be selected for carbon and fluorine before the data can be treated. In this analysis the charge on carbon in benzene is taken as zero.[24] Thus the carbon shifts for the other molecules are referred to benzene as in Table I. The fluorine reference energy may then be deduced by comparing C_6H_6 and C_6F_6. For C_6F_6 (using the bond distances given in Section V, and taking $k_C = 22.0$), Eq. (3) becomes

$$\delta_C = 59.86\ q_C + 34.57\ q_F \quad .$$

Taking $\delta_C = 3.57$ eV, and setting $q_F = -\ q_C$ for C_6F_6, we have

$$-q_F = q_C = 0.141 \quad .$$

(Three digits have been retained here and below in intermediate stages of computation, to avoid rounding-off errors. The third digit has no physical significance, and is not given in final results.) For fluorine in C_6F_6 Eq. becomes

$$\delta_F = 51.87\ q_F + 34.65\ q_C$$

$$= -2.43 \text{ eV} \quad ,$$

i.e., the fluorine zero-charge reference state falls at a 1s binding energy 2.43 eV higher than that of fluorine in C_6F_6. The fluorine 1s shifts in this scale are given in Table VI.

In hydrogen-containing compounds it is impossible to measure a complete set of core-level shifts, because hydrogen has no core levels. We have therefore constrained all hydrogens in each molecule to have the same charge (in some cases

Table VI. Fluorine shifts relative to a hypothetical neutral standard state

Compound	δE(Fls), eV	Compound	δE(Fls), eV
C_6H_5F	-3.81	1,2,3,4-$C_6H_2F_4$	-3.11
p-$C_6H_4F_2$	-3.51	1,2,3,5-$C_6H_2F_4$	-2.88
m-$C_6H_4F_2$	-3.51	1,2,4,5-$C_6H_2F_4$	-2.91
o-$C_6H_4F_2$	-3.44	C_6HF_5	-2.74
1,3,5-$C_6H_3F_3$	-3.30	C_6H_6	-2.43

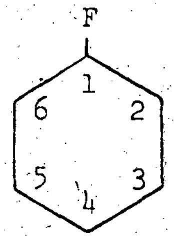
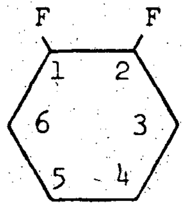
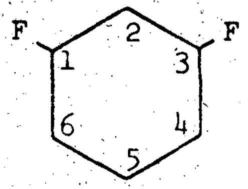
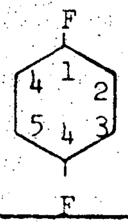
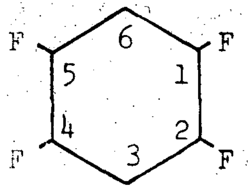
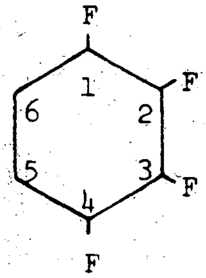
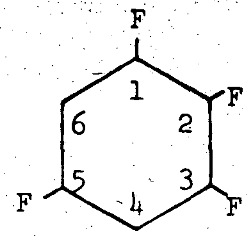
this is already required by symmetry) and have used the condition of electrical neutrality for each molecule, $\Sigma\, q_i = 0$, as the final equation necessary to determine m charges from m-1 shifts. Finally, within each molecule all C_H shifts have been taken as that of the C_H peak, and similarly for C_F. This would appear to be a rather drastic approximation, but it is not. The components within each C_H or C_F peak cannot have relative shifts of more than a few tenths eV, because there is little evidence of line broadening.

With the above constraints the actual calculation of atomic charges reduces, for each molecule, to solving m linear equations for m unknowns, with m = 4, 5, 6, or 8 for the cases studied. Here m-1 is the number of inequivalent atoms other than hydrogen. When the number of equations is reduced to take advantage of the molecular symmetry, the elements of the resulting (smaller) matrix are linear combinations of the A_{ii} and A_{ij} given by Eq. (6). For example, the matrix equation for p-difluorobenzene is

$$\begin{pmatrix} 2.72 \\ 0.76 \\ -3.51 \\ 0 \end{pmatrix} = \begin{pmatrix} 27.180 & 32.682 & 14.606 & 21.934 \\ 16.341 & 43.521 & 10.188 & 28.031 \\ 14.606 & 20.376 & 35.177 & 17.574 \\ 2 & 4 & 2 & 4 \end{pmatrix} \begin{pmatrix} q_{C1} \\ q_{C2} \\ q_F \\ q_H \end{pmatrix} \qquad (9)$$

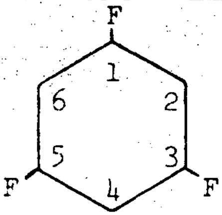
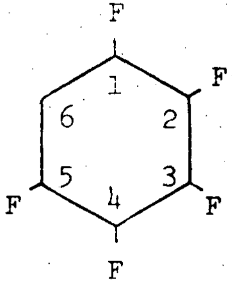
Here q_{C1} is the charge on each C_F carbon. The linear equations were solved for the nine molecules studied containing C, F, and H, using a program named ACHARGE. This program also inverts the coefficient matrix, to test the sensitivity of derived charges to errors in the shifts. Results are given in Table VII, together with atomic charges obtained from the CNDO/2 calculations described in Section V.

Table VII. Derived Atomic Charges

Compound	Atom[a]	q (ACHARGE)	q (CNDO/2)
	C_1	23[b]	24
	$C_{2,6}$	- 4	- 5
	$C_{3,5}$	1	3
	C_4	0	- 1
	F	-19	-20
	$\bar{H}$	0	0
	$C_{1,2}$	19	19
	$C_{3,6}$	- 3	- 3
	$C_{4,5}$	1	1
	F	-17	-18.5
	$\bar{H}$	0	1
	$C_{1,3}$	25	26
	C_2	- 9	-12
	$C_{4,6}$	-4.5	- 7
	C_5	2	5
	F	-18	-20
	$\bar{H}$	0.5	2
	$C_{1,4}$	23	22
	$C_{2,3,5,6}$	- 3	- 3
	F	-18	-20
	H	1	2
	$C_{1,2,4,5}$	18	19
	$C_{3,6}$	- 7	- 8
	F	-15	-18
	H	2	5
	$C_{1,4}$	19	19
	$C_{2,3}$	14	15
	$C_{5,6}$	- 6	- 3
	$F_{1,4}$	-17	-18
	$F_{2,3}$	-16	-16
	H	+4.5	- 3
	$C_{1,3}$	19	23
	C_2	12	11
	$C_{4,6}$	-10	-12
	C_5	25	27
	$F_{1,3}$	-12	-17
	F_2	-15	-17
	F_5	-16	-19
	H	1	5

(continued)

Table VII. (continued)

Compound	Atom[a]	q (ACHARGE)	q (CNDO/2)	Compound	Atom	q (ACHARGE)	q (CNDO/2)
	$C_{1,3,5}$	27	$28._5$		$C_{1,5}$	19	21
	$C_{2,4,6}$	-13	-14		$C_{2,4}$	14	13
	F	-18	-19		C_3	14	17
	H	4	4		C_6	- 9	-10
					$F_{1,5}$	-15	-17
					$F_{2,4}$	-15	-16
					F_3	-15	-16
					H	$4._5$	6
				C_6F_6	C	14	$15._5$
					F	-14	$-15._5$

[a] Here $\overline{H}$ denotes average of all hydrogen charges.

[b] Charges are given in units of 10^{-2} |e|.

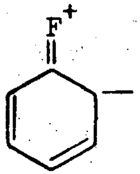
VII. Discussion of the Atomic Charge Values

The agreement displayed in Table VII between the charges obtained from ACHARGE and those calculated by CNDO/2 is extremely good for most cases. Not only are the numerical values very close, but several trends are revealed by both sets of charges. This consistency lends credence to the notion that atomic charges may provide a useful, though admittedly rather qualitative, basis on which to discuss certain molecular properties.

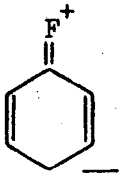
Before interpreting the charges we must issue a caveat. The conceptual shortcomings of a point charge model are well-known. Point charges are especially inadequate for describing multiple bonds, some lone pairs, and delocalized pi systems. Nevertheless, molecular orbitals are usually expanded in terms of atomic orbitals, and the "overlap populations" can be assigned to individual atoms in a way that yields a useful, albeit arbitrary, population analysis. This particular kind of arbitrariness is not necessary in the two charge analyses discussed above (ACHARGE and CNDO/2), but only because the even cruder assumption that all electrons are centered on one atom or another is already built into both models.

The good agreement between ACHARGE and CNDO/2 charges arises largely from similarities between the two approaches. In fact, the first CNDO/2 method described, in which we ignore off-diagonal matrix elements, is identical to ACHARGE. There are, however, significant differences between what is done. We have used the CNDO/2 method to calculate the atomic charges and binding energy shifts without adjustable parameters. The calculated shifts are found to compare favorably with the experimental values. With ACHARGE we have a simple method to derive atomic charges from the experimental results without reference to molecular orbitals or to specific models of bonding. That these charges are in agreement with chemical experience will be seen below. It should be noted, however, that to the extent that the CNDO/2 method gives shifts that are in agreement with experiment, it should also give charges that are identical to those obtained by ACHARGE.

The dipole moment of fluorobenzene is normally attributed to polarization of the C-F bond, while its tendency to accept electrophilic substituents in the ortho and para positions is attributed to resonance tautomers such as



and



.

Polarizations of the C-F bond is clearly evident in the charge values in Table VII. The difference $q(C_F) - q(F)$ ranges from about 0.3 to 0.45. There is a clear trend in the (average) fluorine charge, from about -0.20 in fluorobenzene to about -0.15 in C_6F_6.

No such trend is evident in the carbon charges, because of the dominant effects associated with the ortho, meta, and para positions. These effects are indicated in Table VIII. The ortho, meta, and para charges for the C_H carbons in fluorobenzene give this effect directly. It may be found also in the C_F carbon in fluorobenzene. The effect is evident in both bases (and the CNDO/2 charges also show it). The photoelectron data with the ACHARGE analysis appear to show a negative charge of about -0.04 on the ortho carbon, and, with less certainty, a very small positive charge on the meta carbon. The para carbon appears to be essentially neutral.

The o, m, p effects are present in the multiply-substituted fluorobenzenes. This is most readily apparent in 1,3-difluorobenzene and 1,3,5-trifluorobenzene,

Table VIII. Ortho, meta, para alternation in atomic charges

C_H carbons in fluorobenzene			(Charge on C_F carbon in difluorobenzenes) minus (Charge on C_F carbon in fluorobenzene)		
Position	Charge (units of $\lvert e \rvert$)				
	From ACHARGE	From CNDO/2	Molecule	Δq from ACHARGE	Δq from CNDO/2
ortho	-0.05	-0.05	o-difluorobenzene	-0.04	-0.05
meta	+0.02	+0.02	m-difluorobenzene	+0.01	+0.03
para	0.00	-0.02	p-difluorobenzene	0.00	-0.01

for which the additional tautomeric forms reinforce one another. In 1,3-difluorobenzene, for example, the carbon in position 2 is ortho to both fluorines and should therefore carry a large negative charge. It does; for this case $q(C) = -0.09$. This effect should be even larger in 1,3,5-trifluorobenzene, because carbons in the 2, 4, and 6 positions are each ortho to two fluorines and para to another. The ACHARGE result, $q(C_H) = -0.13$, confirms this expectation. Furthermore, for this molecule the C_F carbons have the largest positive charge observed in this study. This is also expected because each is meta to two fluorines.

A number of other systematic trends can be observed among the charges in Table VII. They all appear to be in accord with what is expected on chemical grounds. We conclude that the ACHARGE analysis yields charges that are useful in understanding chemical properties. With further refinement, and especially in combination with higher-resolution spectra, the ACHARGE analysis of photoelectron data may permit prediction of the reactivities of new compounds.

Footnotes and References

*Work performed under the auspices of the U. S. Atomic Energy Commission.

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20. The constancy of $\partial E_i/\partial q_i$ over a small range of q_i is very well established. See, for example, Ref. 1, Fig. 10.

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24. This choice is qualitatively supported by molecular orbital results. For example, CNDO/2 gives $q_C = - q_H = 0.009$.

Figure Captions

Fig. 1. X-ray photoelectron spectra of fluorobenzenes, obtained with Mg Kα radiation.

Fig. 2. Fluorine 1s binding-energy shifts of fluorobenzenes relative to C_6F_6, plotted against number of fluorines.

Fig. 3. Carbon 1s binding energies of fluorobenzenes relative to that of benzene, plotted against number of fluorines. The upper points refer to carbons to which fluorines are bonded; the lower points refer to carbons to which hydrogens are bonded.

Fig. 4. Shift of C_H 1s binding energies (relative to that of $C_6H\ F_5$) for compounds $C_6H_nF_{6-n}$ plotted against the shift of C_F 1s binding energies (relative to C_6H_5F) for the complementary compounds $C_6H_{6-n}F_n$.

Fig. 5. The ordinate is the shift in total binding energy of carbon 1s electrons relative to those in benzene for the compound $C_6H_nF_{6-n}$. The abscissa is the shift in total binding energy of carbon 1s electrons relative to those in C_6F_6 for the complementary compound $C_6H_{6-n}F_n$.

Fig. 6. Shift in the total binding energy of carbon 1s electrons per substituted ligand, plotted versus number of ligands. The open circles refer to substitution of fluorines for hydrogens on benzene; the closed circles refer to substitution of hydrogens for fluorines on C_6F_6.

Fig. 7. Experimental shifts for binding energies of 1s electrons plotted against the shifts calculated by the first of the two CNDO/2 methods described in the text.

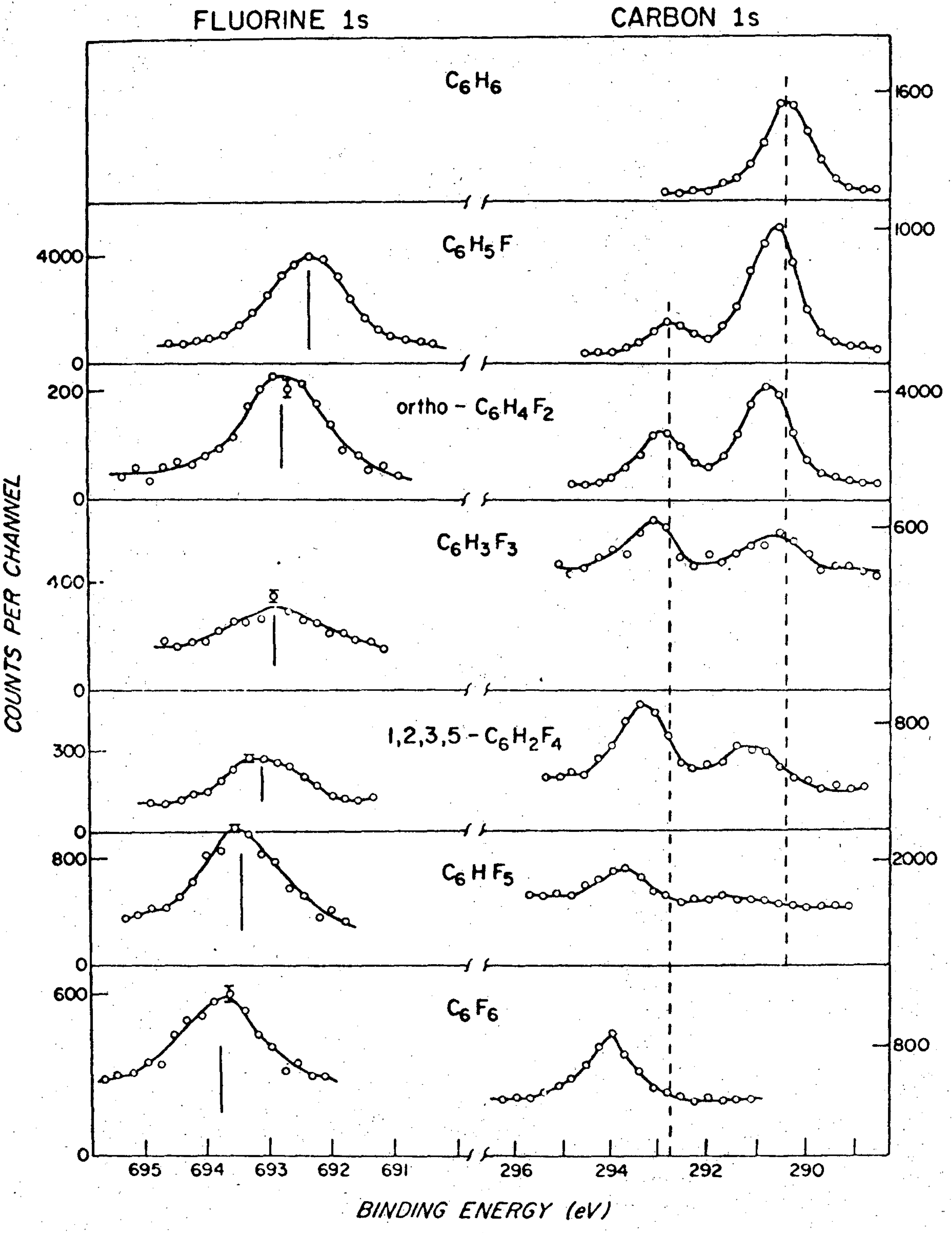
FLUORINE 1s
CARBON 1s
C_6H_6
C_6H_5F
ortho - $C_6H_4F_2$
$C_6H_3F_3$
1,2,3,5 - $C_6H_2F_4$
C_6HF_5
C_6F_6
COUNTS PER CHANNEL
BINDING ENERGY (eV)
1600
1000
4000
600
800
2000
800
4000
0
200
0
400
0
300
0
800
0
600
0
695
694
693
692
691
296
294
292
290

Fig. 1

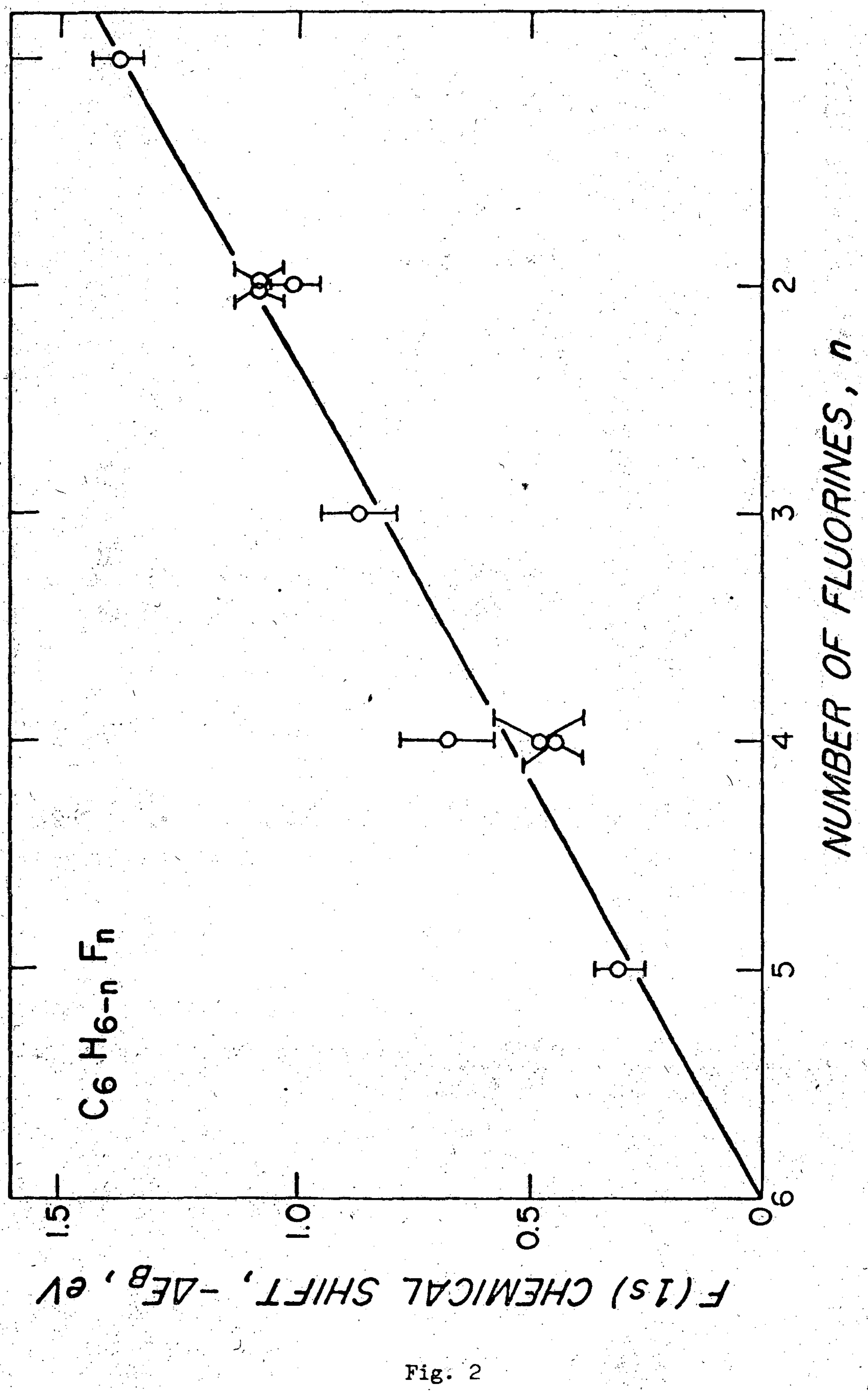
$C_6 H_{6-n} F_n$
F(1s) CHEMICAL SHIFT, $-\Delta E_B$, eV
0
0.5
1.0
1.5
NUMBER OF FLUORINES, n
1
2
3
4
5
6

Fig. 2

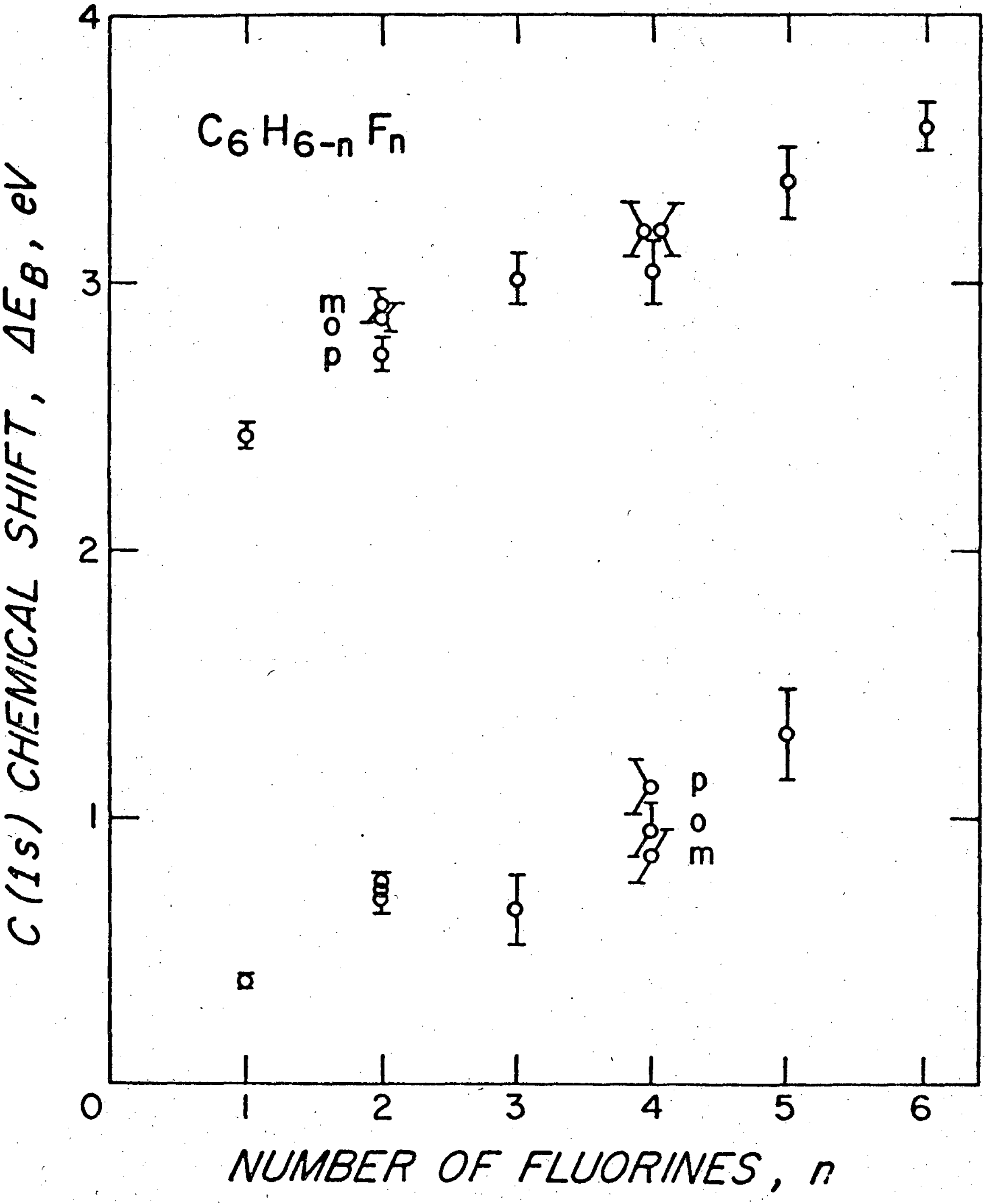
$C_6H_{6-n}F_n$
C (1s) CHEMICAL SHIFT, ΔE_B, eV
NUMBER OF FLUORINES, n
0
1
2
3
4
5
6
m
o
p
p
o
m

Fig. 3

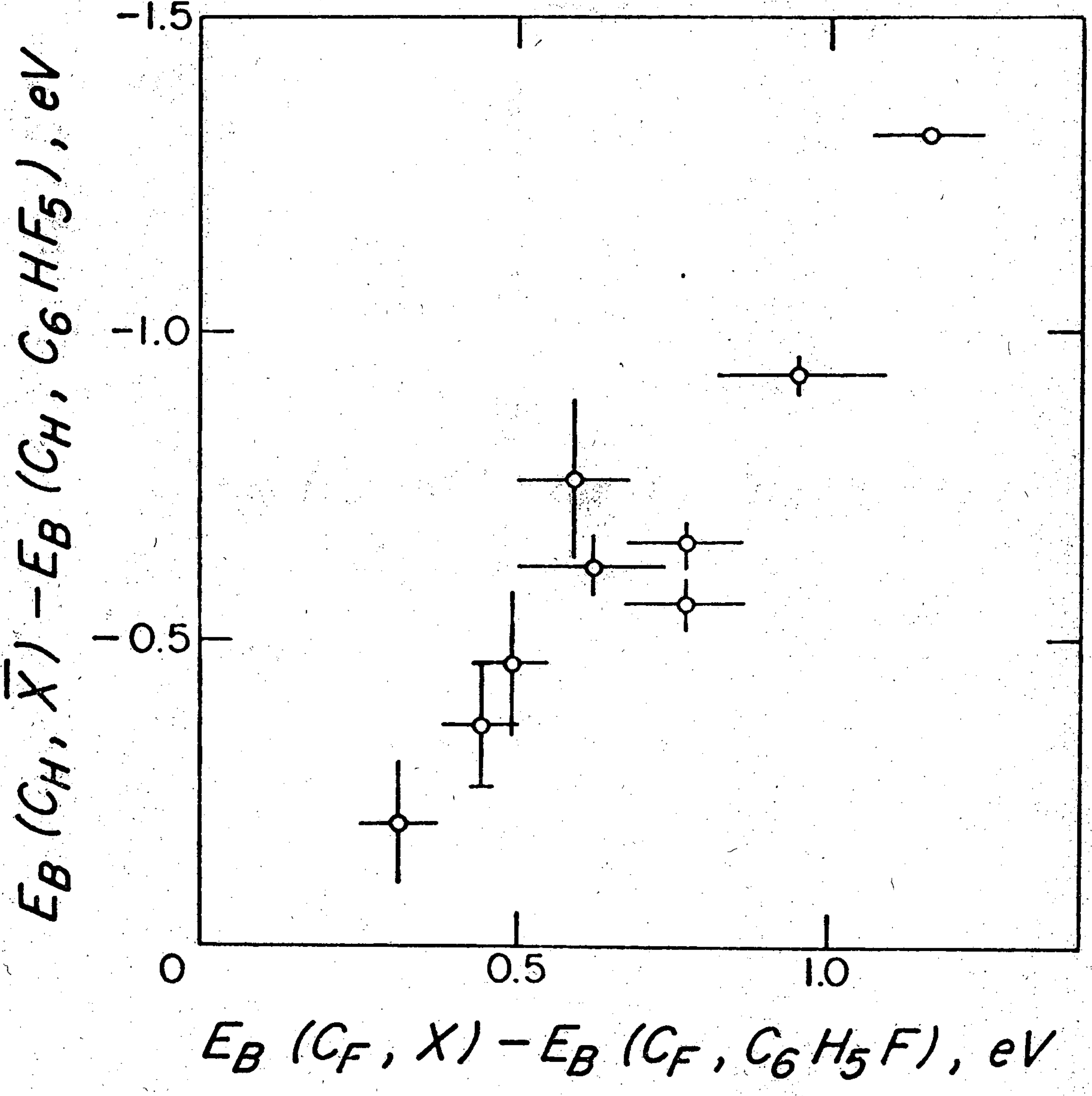
-1.5
-1.0
-0.5
0
0.5
1.0
$E_B\,(C_H, \overline{X}) - E_B\,(C_H, C_6HF_5)$, eV
$E_B\,(C_F, X) - E_B\,(C_F, C_6H_5F)$, eV

Fig. 4

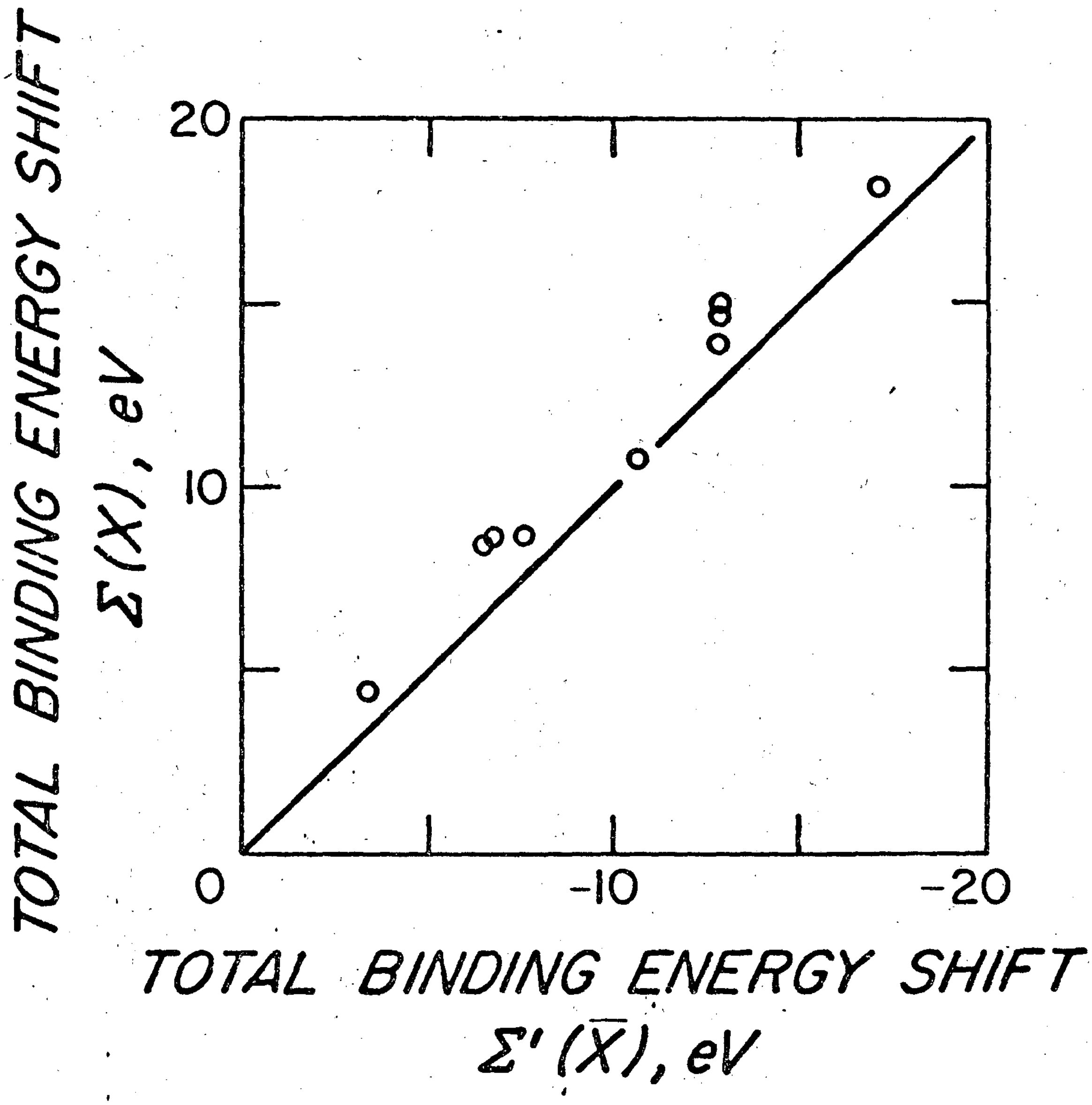
TOTAL BINDING ENERGY SHIFT
Σ(X), eV
20
10
0
-10
-20
TOTAL BINDING ENERGY SHIFT
Σ'(X̄), eV

Fig. 5

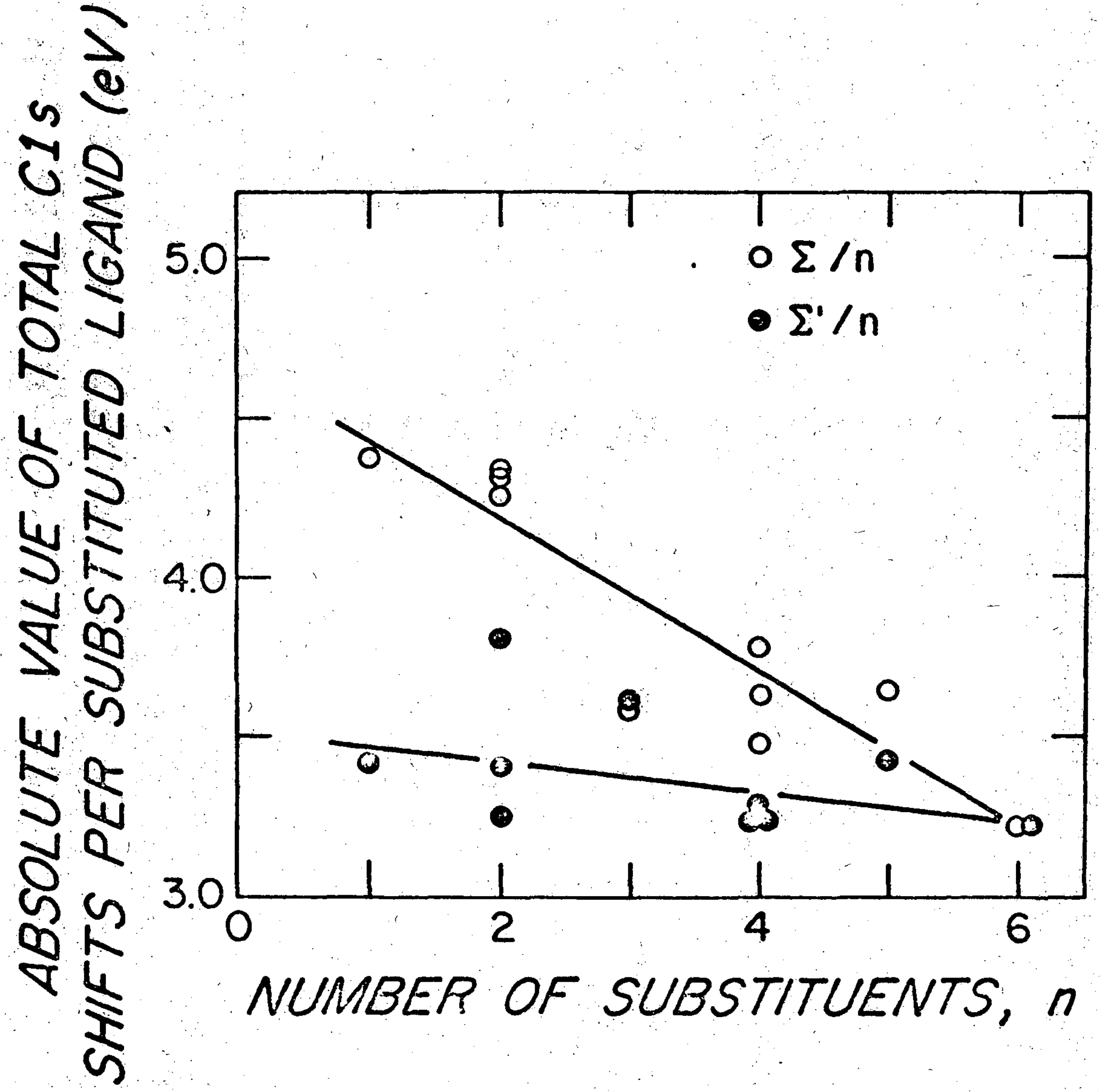
ABSOLUTE VALUE OF TOTAL C1s
SHIFTS PER SUBSTITUTED LIGAND (eV)
5.0
4.0
3.0
0
2
4
6
NUMBER OF SUBSTITUENTS, n
○ Σ/n
● Σ'/n

Fig. 6

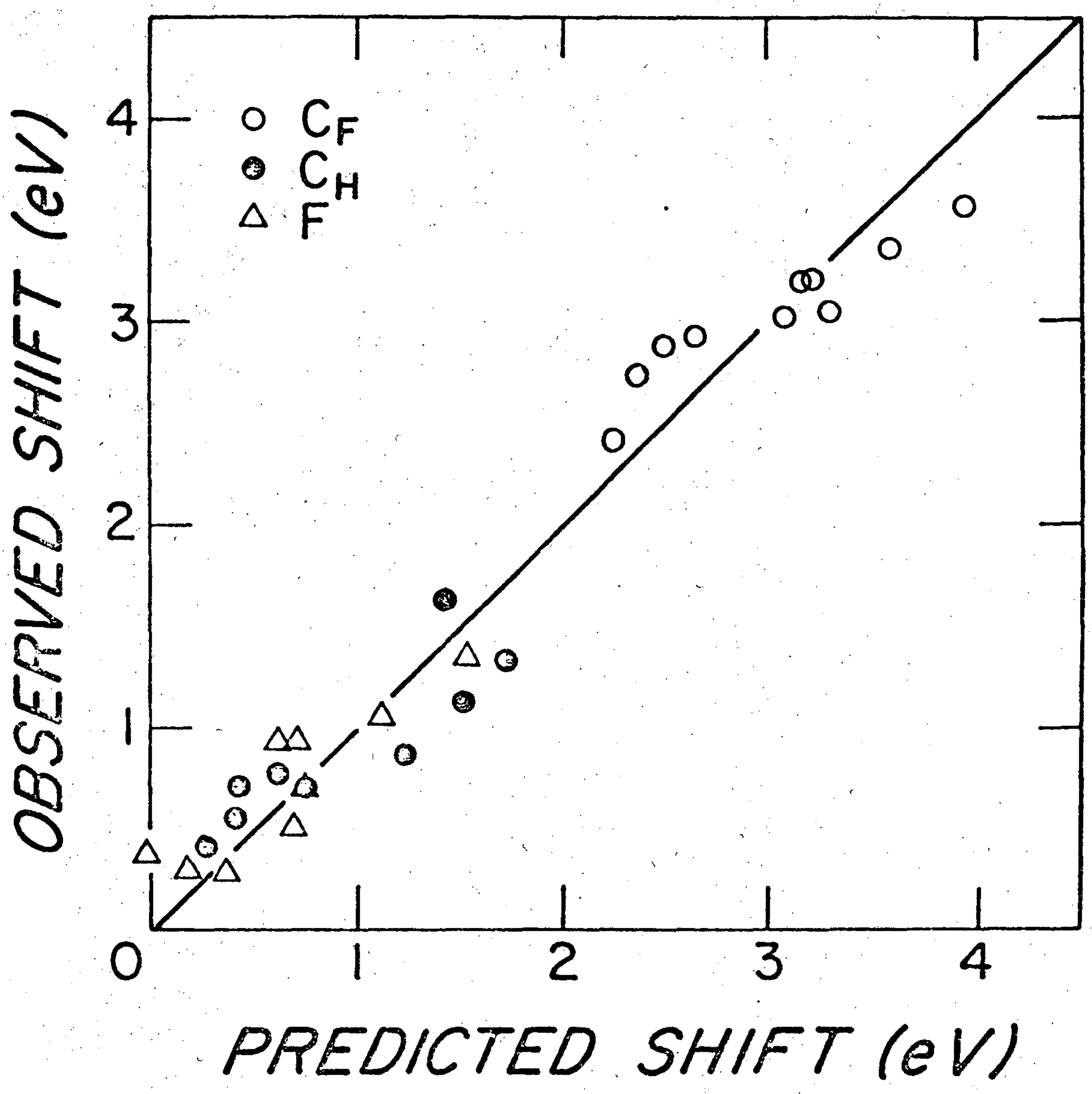

Fig. 7

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