

AN ABSTRACT OF THE THESIS OF

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Title: X-RAY PHOTOELECTRON SPECTROSCOPY OF
TRIFLUOROMETHYLBENZENES AND CHLOROFLUOROMETHANES

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The core-electron ionization potentials for mono- and di(trifluoromethyl)benzene, for chlorofluoromethanes and for chlorine have been measured in order to give information on the electron distribution in these molecules and to investigate differences between the inductive effect of fluorine and that of CF_3 . For trifluoromethylbenzene the measured ionization potentials in eV are: F(1s), 693.88; C(1s, ring), 291.02; C(1s, CF_3), 298.24. For 1,3-di(trifluoromethyl)benzene: F(1s), 694.14; C(1s, ring), 291.48; C(1s, CF_3), 298.64. For 1,4-di(trifluoromethyl)benzene: F(1s), 694.17; C(1s, ring), 291.48; C(1s, CF_3), 298.58. For chlorotrifluoromethane: F(1s), 695.04; C(1s), 300.31; Cl(2s), 278.84. For dichlorodifluoromethane: F(1s), 694.68; C(1s), 298.93; Cl(2s), 278.63. For fluorotrichloromethane: F(1s), 694.33; C(1s), 297.54; Cl(2s), 278.24. For chlorine: Cl(2s), 278.74. Comparison of our gas-phase measurements with those made in condensed phases show that most of the difference between the two kinds of measurements is accounted for by a work function

correction. A point-charge analysis of the core binding energy shifts shows that the carbon adjacent to the CF_3 group is negative, in agreement with theoretical predictions and with the results of similar experiments on aliphatic compounds. More surprising is the conclusion that the CF_3 group donates electrons to the ring. The well-known inductive effect of CF_3 results not because CF_3 withdraws electrons from its neighbors but because the positive dipole of CF_3 creates a positive potential on the adjacent atoms. The core binding energy shifts of the chlorofluoromethanes point out deficiencies in using a point-charge model. Either relaxation energy corrections or a quadratic term in charge improves the model. It is noted that the chemical properties of these molecules correlate well with the core binding energy shifts, which are a measure of the potential at a given atom.

X-ray Photoelectron Spectroscopy of
Trifluoromethylbenzenes and
Chlorofluoromethanes

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X-RAY PHOTOELECTRON SPECTROSCOPY OF TRIFLUOROMETHYLBENZENES AND CHLOROFLUOROMETHANES

I. GENERAL INTRODUCTION

The general adaptability of x-ray photoelectron spectroscopy (ESCA: electron spectroscopy for chemical applications) to many chemical and physical problems arises from its ability to probe atomic sites within a molecule. The measured core-electron binding energy shifts are subject to that atom's chemical surroundings. ESCA's sensitivity toward the electron distribution within a molecule gives important information for the understanding of atoms and molecules.

As a non-destructive technique using small amounts of either solid, liquid or gas compounds, x-ray photoelectron spectroscopy may be used to study any compound to gain information on its chemical or physical properties. The analysis of core-electron binding energy shifts has yielded a variety of good correlations with chemical properties, and from the theoretical point of view, the origin and magnitude of the chemical shifts are well understood. ESCA gives answers to questions from vast numbers of organic compounds on matters of structure and reactivity by analyzing their binding energy shifts. In this thesis an analysis of binding energy shifts in trifluoromethylbenzenes will be presented. This study will help explain the effect of the

trifluoromethyl substituent in an electrophilic substitution reaction.

Pure theoretical ab initio calculations, with their difficulties and complexities, are being supplemented by theoretically sound, but far simpler models, the potential models. These models use measured chemical shifts which allow correlations to be made for any series of compounds and hence increase tremendously the utility of the photoelectron method for the practicing chemist. Such a potential model known as the point-charge model has been developed and has been extensively used. This thesis will present a study of this model's interpretation of binding energy shifts in the trifluoromethylbenzenes. Finally, it will be shown from the study of the chlorofluoromethanes that several inconsistencies arise in using the point-charge model.

II. EXPERIMENTAL PROCEDURES

In photoelectron spectroscopy the binding energy of an electron is determined by measuring the kinetic energy of electrons ejected by monoenergetic photons incident on the sample of interest. The binding energy, E_b , or ionization potential is, by conservation of energy, given as

$$E_b = h\nu - E_k - B - I_{sp}$$

where E_k is the kinetic energy of the ejected electron. The factor B is a correction for charging effects to be discussed below. For solids, where binding energy is measured relative to the Fermi level, it is necessary to correct for the work function of the spectrometer and for the sample, if in the condensed phase, I_{sp} . For gases this latter term is omitted since ionization potentials are directly referred to the vacuum level. For these studies aluminum $K\alpha_{1,2}$ x-rays (1486.58(2) eV) are used as the source radiation; in addition, magnesium $K\alpha_{1,2}$ x-rays (1253.6 eV) were used in an unsuccessful attempt to resolve the lines due to different ring carbons in the trifluoromethylbenzenes. All spectra are fit with gaussian shapes and linear backgrounds by least squares techniques to determine the positions and linewidths of the photoelectron peaks.

Spectrometer Performance

A cylindrical-mirror electrostatic spectrometer in this laboratory is used for the line measurements; details of its design are given elsewhere [1]. The spectrometer is capable of first-order focusing with the angle for transmission of the source electrons at 60° to the axis. Since electrons at all azimuthal angles are accepted, a relatively high transmission of 1% is obtained. This instrument is designed to give 0.06% energy resolution ($\Delta E/E$) while still able to give high luminosity and specific dispersion with source and detector radii of 1 mm. The spectrometer constant, C , which is the ratio of the absolute value of the focusing voltage (in volts), V , to the corresponding kinetic energy of the electron (in eV), K , is calculated from the spectrometer dimensions to be 0.8019(2). The following equation shows the relationship between V and K

$$V = CK + B \qquad 1-1$$

where B is a possible offset voltage due to contact potentials between parts of the spectrometer, or charging of the sample or sample cell, and in early studies was assumed to be zero.

The actual performance capability of the spectrometer approximately equals its capability established by the design specifications and suggests that it is performing in

the present configuration at its ultimate capability, only the source of excitation needing further improvement. The accurately known natural linewidths and ionization potentials [2] of neon 1s (870.312(17) eV) and of neon 2s (48.51(6) eV), and the kinetic energy of neon 1D_2 Auger (804.557(17) eV) are frequently measured to check the instrument's resolution and spectrometer constant. From the measured linewidths the instrument's resolution, considered to be mainly a gaussian distribution function, has been determined by use of the Voigt function to be 0.07(1)%. The spectrometer constant has been determined to be 0.80215(2). Because of charge build-up on the surfaces in contact with the ejected electrons and the sample, the offset voltage, B, ranges from 0.0 to 0.2 volts, and as B increases the resolution of the spectrometer becomes worse, approaching 0.09%. The charge build-up occurs as surfaces become dirty or contact potentials of adsorbed gases become different; the surfaces are then no longer completely conducting. To help minimize charge build-up all these surfaces have been coated with Aerodag (a colloidal suspension of graphite in isopropanol); when dried they are rubbed until shiny.

The usual operating condition of the x-ray tube, which in the spectrometer is the source of excitation, is 9 kV and 1.25 mA and 0.25 mA going to the focusing resistors. This produces good photoelectron intensities of about 60 counts per sec peak intensity for neon 1s photoelectrons having a

signal to background ratio near 50:1. Condensed samples having a greater sample to volume ratio than gases, as well as being physically closer to the collimator source hole, give much better peak intensities, with the gold $4f_{7/2,5/2}$ lines almost two orders of magnitude greater than the neon $1s$ line.

Condensed Sample Studies

Solid samples are studied with this spectrometer by using a solid sample x-ray head, which places the sample close to the source hole. Samples are prepared in a vacuum system (10^{-5} torr) separate from the spectrometer by evaporating a small amount of reagent grade material from a tantalum boat onto 0.00064 cm aluminum foil, which also serves as the anode and window of the x-ray tube. The less than ultra-vacuum conditions and the lack of other proper methods for sample handling which are given below subjects the sample to contamination. Strong photoelectron lines of carbon $1s$, oxygen $1s$, and silicon $2p$ are observed from impurities. Also, there is presently very little control of sample thickness which is indeed crucial to x-ray attenuation. For those solids where evaporation would alter the chemical and physical properties of the material, an aluminum or copper ring 0.5 cm in depth is placed over the x-ray tube anode on the solid sample head. The inside surface of this ring is wet with gallium metal, and the finely powdered

solid sample is sprinkled onto this area. However, experiments have indicated this latter method of sample handling is inefficient. A comparison of gold $4f_{7/2,5/2}$ lines in evaporated gold on an aluminum foil and on an aluminum ring was made at 5 and 8 kV accelerating voltages. Not only is the intensity reduced using the ring, but the signal to background ratio is 60-70% smaller and the lines are 4-15% broader. This is presumably caused by the greater inelastic scattering of electrons when the ring configuration is used. Both methods are preferable to adhesive double-sided tape in that charge accumulation is minimized. A better solid sample arrangement is still under investigation.

Gaseous Sample Studies

The study of free molecules has several advantages over condensed sample studies. A convenient reference level for gases is defined as the vacuum level of the spectrometer. The spectrometer constant, the resolution, and the reference level are readily determined without interference from solid state effects or large charging effects. With only the exception of low intensities relative to solids that is inherent in gas work, our spectrometer is well designed for gaseous sample studies.

A simple experimental arrangement for studying gases consists of replacing the solid sample x-ray head by a gas sample x-ray head. This has the effect of lowering the

x-ray tube 1.5 cm from the collimator source hole, thus creating the gas sample cell. A continuous gas stream is introduced into the gas cell from outside the spectrometer by a gas manifold. The gas then effuses through the collimator and is pumped from the spectrometer by a 6-in oil diffusion pump with an in-line refrigerated trap. The gas manifold allows mixtures of gases to be run simultaneously with accurate control of the gas pressures by needle valves. Sample pressures are regulated to about 0.1 torr in the gas cell; the pressure in the spectrometer then increases from 10^{-6} to 2×10^{-4} torr. Thus, the mean free path of an injected electron is longer than its trajectory in the spectrometer. There has been no evidence here for kinetic energy shifts due to sample pressures in the region from 0.075 to 0.2 torr as has been reported elsewhere [3]. Samples in the liquid and solid phase at room temperature, but having sufficient vapor pressure, are placed in glass ampules attached to the gas manifold and then are studied in the gaseous phase.

A sample is run with a reference standard to compensate for any variations in line positions due to instrumental drift, gas pressure, or charging effects over a period of one to twelve hours running time for each line measurement. The following are standard calibration lines and are used to give the absolute energies of the lines in the samples studied: i) the neon 1D_2 Auger line is used to calibrate

fluorine 1s lines; ii) the carbon 1s line in tetrafluoromethane (301.96(5) eV) [2] is used to calibrate the chlorine 2s and carbon 1s lines. Particular attention is given such that the Al $K\alpha_{3,4}$ line, which is about 10% as intense and about 10 eV lower kinetic energy than the main photoline, does not interfere with any lines being measured. Line measurements are made at least twice, and reproducibility to better than 0.1 eV is obtained in the difference between the position of the lines of sample and standard. The uncertainties that are quoted reflect this reproducibility as well as uncertainties in the standard line measurements. Samples and standards were obtained from Matheson, PCR, and Eastman Kodak with 97-99% purity. No evidence for additional peaks or peak broadening due to impurities were found in any of these samples.

It is necessary to modify the gas sample cell when low binding energy carbon 1s lines are measured because of a broad line from a carbon impurity binding energy of 289.8 eV. This impurity is attributed to the hydrocarbon pump oil and/or the graphite-coated collimator. An aluminum tripod was designed to be placed on the gas sample head over the anode of the x-ray tube to prevent x-rays from striking the collimator source hole and to allow only those photoelectrons from the gaseous sample to exit the collimator source hole. This successfully eliminates the carbon impurity line, but now the electrons accepted into the spectrometer

are reduced in intensity by 40 to 50%. Running time for the low photoelectric cross section of carbon 1s is extended by as much. The signal to background ratio is slightly increased as observed in measuring the neon $1D_2$ Auger line. Presumably this tripod will also eliminate those oxygen lines and silicon lines which are impurities on the collimator as well as on the aluminum foil anode. Another important energy region requiring use of the tripod is in the valence electron region where those high E_k energy electron lines from carbon and other impurities seriously interfere with the spectrum of the sample under study.

Charging Effects Studies

In addition to the usual solid state effects, the study of nonconducting solids presents a problem due to charge build-up on the sample's surface. This charge build-up distorts the kinetic energy spectra of electrons emitted from insulators making it difficult to establish a meaningful reference level. If an insulator were perfect with no intrinsic conductivity, it would act as a gas molecule until charge builds up and the reference level would be taken as the vacuum level of the spectrometer, which is preferred. The Fermi level of an insulator is in general unknown and cannot be defined because it is not grounded and, therefore, not in electrical equilibrium with the spectrometer. Thus, the assignment of a reference level for an insulator is

dependent upon the charging process (the rate electrons are ejected by x-radiation and the rate these electron holes are refilled by secondary electrons determines a state of equilibrium for which the electron's kinetic energies are measured). The voltage potentials for a particular insulator are dependent upon the intensity of photoelectrons and hence, upon the intensity of x-radiation, upon the spectrometer configuration, and upon characteristics of the sample itself.

A study of the charging process in NaCl and in NaF to better understand a nonconductor's reference level was continued from earlier studies [4]. Thin films ($80 \mu\text{g}/\text{cm}^2$) of these samples were evaporated onto aluminum anodes, and the measurement of the sodium 1s line position shifts were studied as a function of x-ray intensity. The intensity of these photoelectrons increased linearly with anode current and concurrently with x-ray voltage. Since there was no indication of any leveling off of the intensity at 11 kV and 1.0 mA, the x-ray tube is not operating at its ultimate capability. Figure 1 presents the relative binding energy of sodium 1s in NaF and in NaCl as a function of the anode current and indicates the process of charging. The plots at 7 and 8 kV for NaCl are similar in shape to those found previously when thicker films ($100 \mu\text{g}/\text{cm}^2$) of NaCl were used, but in the present studies relative binding energy shifts are less. Charge build-up in very thin films is less than the charge build-up in powdered or bulk single crystals or

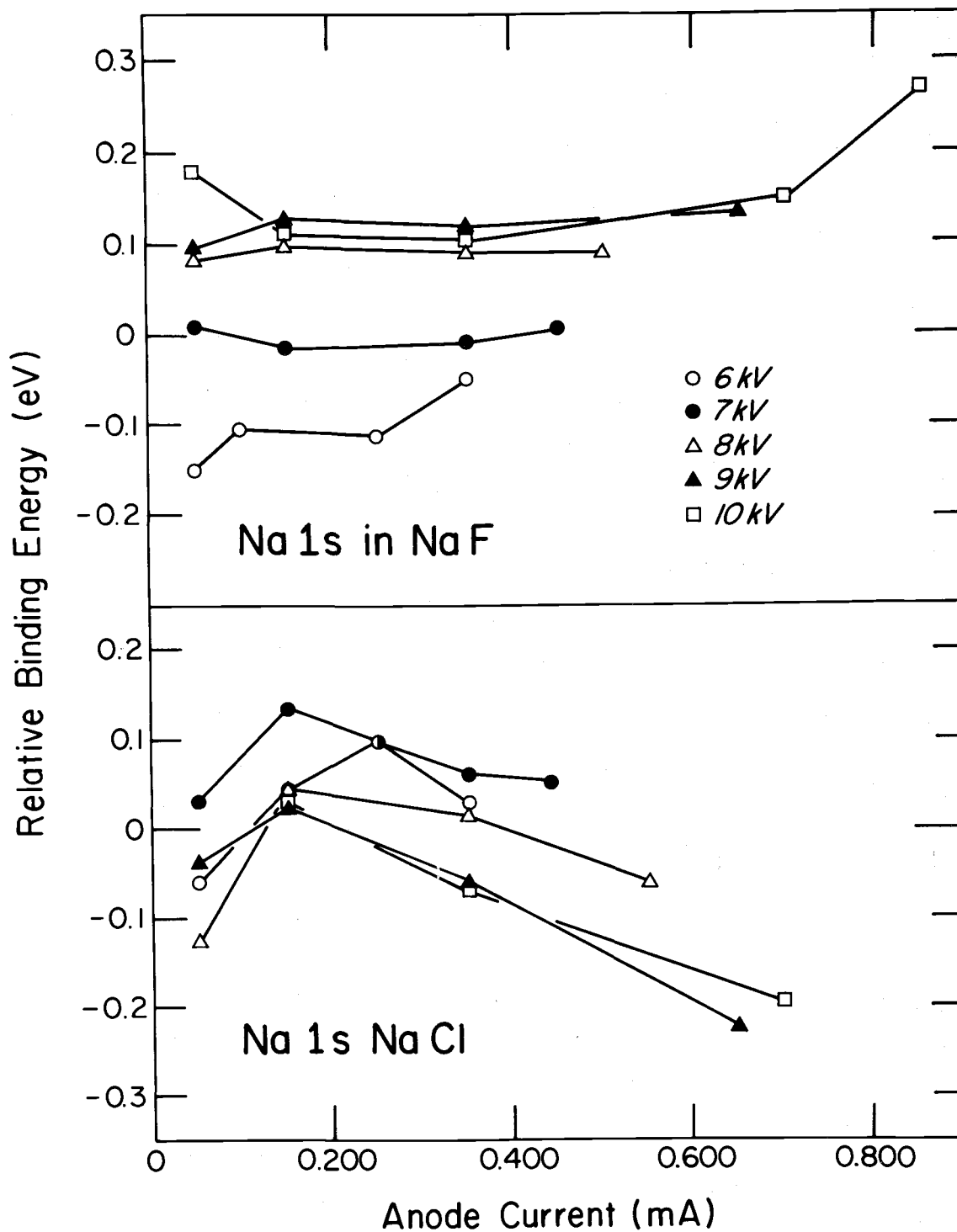


Figure 1. Charging Effects in NaF and NaCl.

even thicker films. The graph of NaF appears quite different from that for NaCl; however, both graphs can be explained by the same charging process when consideration for the differences in band gap and in ionic mobility of the samples is taken. In both there is no monotonic increase of charging effect with intensity. The major effect is a decrease of kinetic energy in NaF and an increase of the kinetic energy in NaCl.

The process of charging can be explained as follows by looking at the NaCl graph in Figure 1. The observed higher apparent binding energy at low x-ray current suggests that the primary electrons that are ejected from the atoms' shells of electrons leave the atoms in a positive environment without charge neutralization taking place. These primary electrons produce secondary electrons or charge carriers as they travel through the sample. A higher flux of x-rays increases the number of charge carriers, which begin to neutralize the charge build-up still continuing in the sample. Under very intense x-radiation the number of charge carriers increases until the insulator becomes conducting; this results in the Fermi level of the sample matching the Fermi level of the spectrometer. The NaCl graph clearly demonstrates this process within each plot of x-ray voltage but is not so evident in the NaF graph. The greater bandgap in NaF (10.5 eV) versus NaCl (7.7 eV) and the lower ionic mobility of NaF enables greater charge build-up in NaF. The

creation of charge carriers in NaF becomes difficult even under the intense x-radiation used here. Charging increases until the equilibrium point is reached at 8, 9, and 10 kV where the creation of charge carriers is sufficient to keep the sample from further charging. Presumably under more intense x-radiation even this insulator would become conducting if radiation damage can be avoided. No correlation with observed random broadening and with charge build-up is found; a contribution to line broadening in polar molecules may be attributed to phonon broadening [5].

The conclusions reached in this study of the charging process within insulators follow reasonable chemical arguments. The present sample configuration comprised of thin sample layers tends to allow only a minimum of charge build-up. Still, it became apparent during these studies that quantitative results have remained elusive. Sample thickness and sample purity during preparation were uncontrollable. Proper methods of handling non-conducting samples necessary for a minimum of charge build-up includes: (i) sandwiching samples between conducting layers, the top layer being very thin; (ii) use of low energy electron irradiation of the sample; and (iii) intimate mixing with a conducting material. In addition, any condensed sample should be kept pure while under study by its preparation in the ultra-high vacuum of the sample chamber of a spectrometer (sublimation) and by cleaning the sample surfaces within the instrument by

removing water with heating and by sputtering the surfaces with inert gas atoms.

In addition to the charging effects of nonconducting condensed samples, similar corrections must be applied to gaseous samples to account for space and surface charges and contact potentials. The offset voltage, B , in equation 1 is an indication of the magnitude for these corrections. Also, evidence is found for the offset voltage dependence upon the gaseous sample itself [2]. However, by running a mixture of the sample and a standard reference compound, with known ionization potential, we can avoid the necessity of having to apply these corrections.

III. POINT-CHARGE MODEL

The binding energy shifts can be analyzed to give charge distribution within the molecule using a point-charge model. The effective potential at a certain core-level electron changes in an atom when going from one molecule to another. This change in potential because of a redistribution of valence electrons at molecule formation can be divided into two components. First, a one-center part associated with the change of the number of valence electrons on the atom under consideration signified by $k_i q_i$ where k_i represents the average interaction between a core electron and a valence electron on the same atom and q_i represents the charge on atom i . At one level of approximation the constant k may be regarded as the expectation value of $1/r$ for the valence electrons. Empirically derived values of k are in some cases very nearly equal to values $\langle 1/r \rangle$ obtained from Hartree-Fock calculations. Second, a two-center part originating from the other atoms in the molecule signified by $\sum q_j e^2 / r_{ij}$; this interaction is considered between point charges and is often known as the Madelung energy. The sum is over all atoms except the atom whose core electron is under study. q_j is the charge on the atom j and r_{ij} is the distance between nucleus i and nucleus j . The final expression becomes

$$\Delta E_i = q_i k_i + \sum_{j \neq i} q_j e^2 / r_{ij}$$

The ΔE_i is the core-electron binding energy of atom i in the molecule relative to the same atom when neutral.

The principal assumptions of this model are that relaxation energies are the same for a given atom in different environments, that the core-electron binding energy varies linearly with atomic charge, that all charges are spherically distributed about their atomic centers, that each atom lies outside the sphere of charge around the other atoms, and that effects of overlap population can be ignored. Later, in the analysis of chlorofluoromethanes it is shown how certain of these assumptions are inconsistent with experimental data from ESCA.

IV. TRIFLUOROMETHYLBENZENES

Both fluorine and trifluoromethyl are considered to be strongly electron-withdrawing groups. Their effects when attached to a benzene ring are, however, somewhat different [6, 7]. Both tend to deactivate the ring, but fluorine less so than CF_3 . Fluorine is ortho-para-directing; CF_3 is meta-directing. Various explanations involving induction, resonance, and hyperconjugation have been proposed to explain these effects.

The measurement of core-electron binding energies by x-ray photoelectron spectroscopy (ESCA) is an effective probe for studying the distribution of charge within molecules. A previous study on fluorinated benzenes [8], combined with a point-charge model, has given results that are in agreement with chemical experience and with the predictions of CNDO calculations. According to these experiments, fluorine induces a positive charge on the carbon to which it is attached and a negative charge on the ortho carbon; the net charge on the ring is positive.

We have extended these earlier measurements to the compounds trifluoromethylbenzene, 1,3-di(trifluoromethyl)benzene, and 1,4-di(trifluoromethyl)benzene. Our goal has been to investigate the charge distributions within these molecules, to correlate the binding energy shifts with the chemical properties, and to study the reasons for the different chemical effects of CF_3 and fluorine as substituents.

CNDO/2 calculations [9] for trifluoromethylbenzene provide predictions of charges on the various atoms in this molecule. These can be compared with the results of a point-charge analysis of the core binding energy shifts. Such analysis for other molecules has given results in excellent agreement with the predictions of CNDO [8]. For this molecule, and others, the calculations indicate the carbon adjacent to the CF_3 group to be negatively charged. If, however, the CF_3 group is electron-withdrawing, as is generally believed, we would expect this carbon to be positively charged. The measured core binding energies provide a test of these predictions.

Results

Only two well-resolved carbon 1s peaks appear in each spectrum; the CF_3 carbons appear as an isolated peak but the ring carbons are an unresolvable envelope of six lines. Taking 1,4-di(trifluoromethyl)benzene as an example, we can estimate the maximum separation of lines within this envelope. There are two inequivalent carbons in the ring in a ratio of 2:1. We observe a full width at half maximum (FWHM) for this compound of 1.5 eV compared to 1.2 eV for benzene. We assume that the actual spectrum is the superposition of two lines in the ratio of 2:1, each with a FWHM of 1.2 eV. The shapes of such double lines for various separations have been calculated by Siegbahn and co-workers

[3]. From a comparison of our measured spectra with their results, we conclude that the difference in binding energies for ring carbons attached to CF_3 and those attached to H is less than 0.6 eV.

The measured core-electron ionization potentials are given in Table I. We note first that these are all larger by 3.1 to 5.5 eV than those given by Clark, Kilcast, and Musgrave [10], the major part of the difference arising because their measurements were made in the condensed phase and are relative to the Fermi level of gold. Correcting for a gold work function of 4.8 eV reduces the discrepancy to between -1.7 eV and 0.7 eV, presumably due to extra-molecular relaxation energies. Our relative measurements (in the gas phase) disagree in some details with theirs. For instance the shift between carbon 1s in benzene and carbon 1s

TABLE I. Core-Electron Ionization Potentials in Trifluoromethylbenzenes (eV)

Compound	Ring carbons	CF_3 carbons	Fluorines
C_6H_6	290.38(7)		
$\text{C}_6\text{H}_5\text{CF}_3$	291.02(7)	298.24(8)	693.88(3)
1,3- $\text{C}_6\text{H}_4(\text{CF}_3)_2$	291.48(6)	298.64(7)	694.14(3)
1,4- $\text{C}_6\text{H}_4(\text{CF}_3)_2$	291.48(8)	298.58(8)	694.17(3)

in benzene and carbon 1s of the CF_3 group in trifluoromethylbenzene is 7.86 ± 0.09 eV in our measurements and 8.9 ± 0.3 in theirs. This difference is well outside the experimental

error and suggests the problems of comparing two different samples in the solid phase are more difficult than has been indicated by Clark, et al. For differences within the molecule we have 7.22 ± 0.08 eV as the difference between the ring carbons and the CF_3 carbon in trifluoromethylbenzene; Clark, et al. give 7.6 ± 0.2 . The difference is small, but is outside experimental error.

It is to be noted that the electrons from the ring carbons are shifted to higher binding energies than in benzene. The environment for these electrons is more positive than in benzene. It is also to be noted that the average binding energy of ring carbons in the compounds discussed here are very close to those for the corresponding fluorinated benzenes, even though the spectra for the latter compounds are resolved into two well-separated peaks, whereas those for the present compounds show only one peak. The average environment of the ring carbons is nearly the same in both cases.

The ring carbon, trifluoromethyl carbon, and fluorine ionization potentials are all shifted to higher values by the addition of the second CF_3 group (in either position). The additional shift is largest for the ring carbons (0.46 eV), intermediate for the trifluoromethyl carbon (0.37 eV), and smallest for the fluorines (0.27 eV); the effect falls off with distance from the substituent. A similar effect is seen for the fluorinated benzenes: each additional fluorine

causes the average ring carbon to shift by 0.6 eV and the average fluorine binding energy by 0.3 eV. Addition of either a fluorine or a trifluoromethyl group causes the rest of the molecule to have a more positive potential.

Discussion

Point-charge analysis

The binding energy shifts in the trifluoromethylbenzenes are analyzed using the point-charge model just described. At this time it seems that the most questionable of the model's assumptions is the first, concerning relaxation energies; we take the others to be valid and discuss this one in detail below. The hypothetical neutral carbon atom is taken as the carbon in benzene and that of the fluorine atom as in F_2 (696.70(5) eV) [11]. Values for k_i are $k_C = 22.0$ eV/e and $k_F = 32.5$ eV/e given by Davis, Shirley, and Thomas [8] for the fluorobenzene series. Values for r_{ij} distances were the same as those used by Brownlee and Taft for their CNDO/2 calculations [9]. Various orientations of the CF_3 groups with respect to the ring and each other had little effect on the derived charges. Therefore, we report results only for the trans conformations.

For each atom in the molecule there is, in principal, one such equation, one measured binding energy, and one unknown charge. As has been noted by Davis, *et al.*, however, it is impossible to measure a complete set of core-level

shifts, because hydrogen has no core levels. In order to solve this problem we have used the same simplifications as they. All hydrogens in each molecule are constructed to have the same charge. This assumption together with the equation of electrical neutrality for the molecule, $\sum q_i = 0$, gives us as many equations as unknown charges. Within each molecule the binding energies of all the inequivalent ring carbons have been taken to be the same and equal to the measured average value. The effects of this assumption are discussed below. The fluorines are treated as equivalent to one another. Table II gives the atomic charges calculated according to this procedure.

In the simplification of the equations of the point-charge model, we have assumed all binding energies for ring carbons to be the same. In the presentation of experimental results, we showed that for the 1,4 compound these energies could differ by no more than 0.6 eV. We have repeated the point-charge analysis for this compound assuming peaks with a 2:1 intensity ratio, split by 0.6 eV, but with the observed average binding energy. The results of these calculations are compared in Table III with those of the regular point-charge analysis. Qualitatively the conclusions are the same in each case: the carbon to which the substituent is attached has a negative charge, the ortho carbon has a positive charge, and the ring as a whole has a negative charge of about -0.16 e.

Table II. Atomic Charges for Atoms in Trifluoromethylbenzenes

Compound	Atom	Charge, q/e	CNDO Charge
Mono	F	-0.223(2)	--
	C _F ^a	0.728(6)	--
	C ₁ ^b	-0.130(5)	-0.051
	C _{2,6}	0.027(4)	0.028
	C _{3,5}	0.018(4)	0.005
	C ₄	0.018(4)	0.022
	H	-0.007(2)	0.005
1,3-Di	F	-0.238(1)	
	C _F ^a	0.772(4)	
	C _{1,3} ^b	-0.128(4)	
	C ₂	0.043(4)	
	C _{4,6}	0.033(4)	
	C ₅	0.023(4)	
	H	0.001(3)	
1,4-Di	F	-0.220(1)	
	C _F ^a	0.735(5)	
	C _{1,4} ^b	-0.124(6)	
	C _{2,3,5,6}	0.043(5)	
	H	-0.019(4)	

^a C_F refers to the carbon in the CF₃ group.

^b The number 1 carbon is one to which a CF₃ group is attached.

Table III. Atomic Charges in 1,4-di(trifluoromethyl)benzene for Different Assumptions about Energy of Splittings

Atom	Calculated Charges, q/e			
	a	b	c	d
F	-0.220	-0.220	-0.219	-0.220
C _F	0.735	0.745	0.725	0.720
C _{1,4}	-0.124	-0.164	-0.084	-0.050
C _{2,3,5,6}	0.043	0.064	0.021	0.026
H	-0.019	-0.025	-0.013	-0.031
Ring	-0.150	-0.170	-0.136	-0.120

- a. No core binding energy shift between C_{1,4} and C_{2,3,5,6}.
- b. C_{1,4} core binding energy 0.6 eV lower than C_{2,3,5,6}.
- c. C_{1,4} core binding energy 0.6 eV higher than C_{2,3,5,6}.
- d. Relaxation energy of 1 eV on C_{1,4}.

A similar question must be raised with regard to relaxation energies. The calculations of Davis and Shirley [12] and those of Cavell [13] show that the relaxation energy of a carbon atom may increase by about 0.8 eV when a hydrogen attached to it is replaced by a CF₃ group. Adding 1 eV to the core binding energies we have assigned to the 1 carbon in these compounds shifts the total ring charge from -0.06e to -0.04e in the monosubstituted compound and from -0.150e to -0.12e in the 1,4-disubstituted compound. (More detailed results are given in Table III.) The conclusion

that the ring is slightly negative and the CF_3 group slightly positive is independent of any reasonable assumptions we might make about either relaxation effects or unresolved lines.

Several features of the derived charges deserve notice. As expected the fluorines have negative charges and the carbon to which they are attached has a positive charge. In agreement with the predictions of theoretical calculations [9] the carbon adjacent to the CF_3 group has a negative charge; this conclusion is independent of corrections for relaxation effects and for unresolved lines. In the monosubstituted compound the ortho carbon is slightly more positive than the meta and para carbons; because the various ring carbons were not resolved in the spectra, this conclusion is not a strong one. In each case the ring charge is slightly negative ($-0.06e$ for ϕCF_3) and is approximately twice as great for the disubstituted compounds as for the monosubstituted compound.

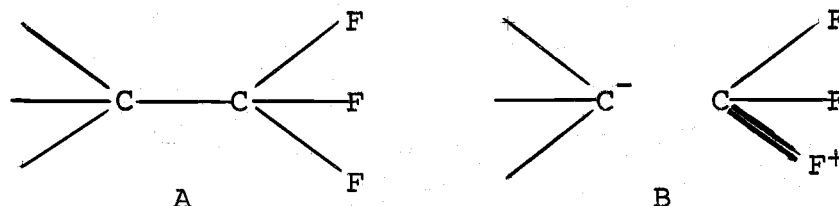
That the ring charge in these compounds is negative deserves special emphasis, since it implies that the CF_3 group is electron-donating (even though the chemical effect of CF_3 is that expected for electron withdrawal). This conclusion is not unique to the molecules studied here. Similar measurements and analysis by Davis, Banna, and Shirley [14] on $\text{CF}_{3-n}\text{H}_n\text{CH}_3$ ($n = 0 \rightarrow 3$) and $\text{CF}_{2-n}\text{H}_n\text{CH}_2$ ($n = 0 \rightarrow 2$) indicate that the group containing the fluorine donates negative

charge to the rest of the molecule. Ab initio calculations by Hehre and Pople [15] for $\text{CF}_{4-n}\text{H}_n$ ($n = 0 \rightarrow 4$), for CF_3CH_3 , and for CF_3CCH lead to the same conclusion. CNDO/2 calculations by Brownlee and Taft [9] are mixed, sometimes predicting the CF_3 to be electron withdrawing, sometimes electron-donating. Experimentally the amount of charge donated by the CF_3 group is -0.04 to -0.06 e. The theoretical values for this quantity range from $+0.06$ to -0.133 e. Some possible reasons for this effect are discussed below.

It is interesting to compare the results of the point-charge analysis with the charges predicted by the CNDO/2 method. In general, such comparisons have shown excellent agreement between the experimentally derived and theoretically predicted numbers. It should, however, be noted that the assumptions of the point-charge model and those of CNDO are quite similar. Table II gives a comparison between the charges we have derived and those calculated by Brownlee and Taft [9]. Qualitatively the agreement is good. The 1 carbon is negative, though substantially more so in the experimental number than in the theoretical one. The other ring carbons are all slightly positive, with the carbon ortho to the substituent slightly more so than the others. The most striking disagreement between experiment and calculation is that the ring charge is determined from experiment to be negative and from theory to be positive. As noted above, we have tested a number of the assumptions made in our analysis

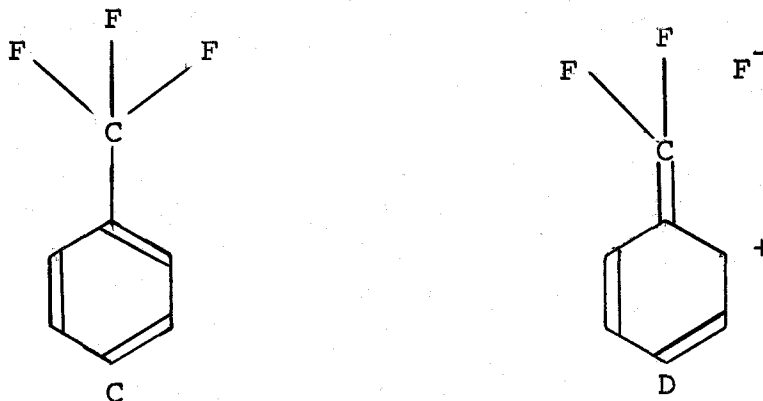
and find this conclusion to be relatively independent of these assumptions.

A number of mechanisms have been proposed to account for the effect of trifluoromethyl substituents on the charge distribution of the molecule to which they are attached [7]. First, we might expect a direct withdrawal of electrons from adjacent atoms by the CF_3 group. Our experimental results, those of Davis, et al. [14], and most theoretical calculations indicate, however, that the net charge transfer is in the opposite direction. There is direct polarization of the rest of the molecule by the strong dipole of the CF_3 group, causing electrons to flow towards the substituent but without actual charge transfer to the CF_3 group. Hyperconjugation allows negative charge to move from the fluorines to the atom to which the CF_3 group is attached, and, in aromatic systems, to move from the ortho and para positions of the ring to the fluorine. Resonance structures A and B show how electrons can be donated from the fluorine to the β carbon;



this mechanism has been suggested by Pople and Gordon [16]. Structures C and D show the removal of electrons from the ortho position to the fluorine. A similar structure can be

drawn with positive charge at the para position. Other mechanisms, such as the π -inductive effect and p - π interaction have been proposed for aromatic systems, but are thought to be of secondary importance [7].



The charges we have derived are readily explained in terms of these mechanisms. The addition of a CF₃ group causes electrons to flow towards the group, making one end of the ring negative and the other end positive. Hyperconjugation, using structures A and B causes negative charge to move from the fluorines to the 1 carbon, which thus becomes still more negative. Hyperconjugation, using structures C and D, causes the 2 and 6 carbons to become positive. The first hyperconjugative mechanism must be sufficiently strong to inject more negative charge into the ring than is withdrawn by the other two mechanisms, so that the net charge on the ring is slightly negative and the CF₃ group slightly positive. (The same hyperconjugative mechanism must be equally important for aliphatic systems as well. Point-

charge analyses of binding energy shifts [14] and a variety of theoretical calculations [14, 15] indicate that $-\text{CF}_3$, $-\text{CHF}_2$, $-\text{CH}_2\text{F}$, $=\text{CFH}$, and $=\text{CF}_2$ are all electron-donating not only to the adjacent atom but to the entire molecule to which they are attached.)

In view of the strong effects of such substituent groups as CF_3 , CHF_2 , and CH_2F on acid strengths and other chemical properties, it seems contradictory, at first, to suggest that these are electron-donating groups. The chemical and physical data are reconciled when we realize that the acidity depends on the ease of changing the charge at some point in the molecule, and, hence, on the potential (rather than on the existing charge) at that point. This potential arises not only from charges at that site, but also from those on all the other atoms in the molecule. The CF_3 group presents the positive end of a strong dipole to the molecule; it is the direct Coulomb interaction of this dipole with the proton rather than net electron withdrawal that gives rise to the high acidities of compounds containing CF_3 groups. The inductive effect of CF_3 is "through space" rather than "through the bonds".

Martin and Shirley [17] have pointed out that it is often the core-electron binding energy itself rather than the atomic charge that should correlate with chemical properties. This is presumably the case for CF_3 -substituted compounds. The charge on the atom adjacent to the CF_3 group

is negative; because of the nearby strong positive charge, however, the overall potential is somewhat positive, with the result that core-electron binding energies are increased (as is observed) and the compound becomes more acidic (as is observed).

It may also appear contradictory to chemical evidence to propose that CF_3 donates negative charge to the benzene ring. In general, increased negative charge in the ring is associated with increased reactivity towards substitution at the ortho and para position. The CF_3 group however, has the effect of deactivating the ring and is meta-directing. The charges we have assigned are, however, consistent with these observations: the increased negative charge is localized at the 1 position, which is not susceptible to attack, the ortho position is found to be more positive than the meta, and is, hence deactivated.

Comparison of trifluoromethylbenzene with fluorobenzenes

As noted above, the photoelectron spectra for fluorobenzene and trifluoromethylbenzene are strikingly different from one another. In the former case the carbons to which the fluorine is attached is clearly resolved from the other ring carbons; in the latter, all the ring carbons are unresolved. The average shift (and, hence, average potential) over all of the ring carbons is, however, about the same for the two molecules.

From the point of view of chemical reactivity we are interested not in the shift averaged over all the carbons, but the shift averaged over those available for further reaction. For fluorobenzene this shift is +0.39 eV (relative to benzene). Because these carbons are not resolved in trifluoromethylbenzene from the carbon to which the substituent is attached, we cannot give an accurate number for this average shift in this compound. Unless, however, the number 1 carbon is shifted by more than 1.5 eV from the other carbons in the ring, this average is greater for trifluoromethylbenzene than for fluorobenzene, in keeping with the relative reactivities of these substances. A separation this large would have been apparent in our spectra as a shoulder on the high binding energy side of the main peak of the monosubstituted compound and would have been quite clear in the disubstituted compound. No such features were seen in the spectra. We conclude, therefore, that the binding energy of the ring carbons in these compounds correlates well with the reactivity of the ring, becoming more positive as the ring becomes less reactive.

The mechanism by which the positive potential is developed in the ring is quite different in the two cases. In fluorobenzene, the fluorine withdraws electrons from the adjacent carbon through the sigma bond and redonates a small amount of charge to the ortho (and, presumably, para) position. The ring as a whole has a positive charge and the net

potential at any point in the ring is positive. There is a slight negative charge at the ortho position, helping to make this site slightly more susceptible to electrophilic attack. In trifluoromethylbenzene, on the other hand, there is apparently electron donation to, rather than electron withdrawal from, the ring. The lowering of reactivity due to the CF_3 arises because of the large positive dipole of the CF_3 group in the neighborhood of the ring. There is some evidence for resonance leading to positive charge at the ortho position.

An unusual feature is apparent in both the fluorobenzene data and the trifluoromethylbenzene data: In spite of the presence of strongly polarizing groups attached to the rings at specific locations, the actual binding energies of the carbons to which only hydrogens are attached are largely independent of their position in the ring. It is as if charge flows in the ring so as to create a nearly uniform potential at every point in the ring, just as charge will flow in a conductor to maintain a uniform potential throughout. Presumably it is the π electrons that are sufficiently mobile to provide this equalization.

Alternating charges

It has been suggested by Pople and Gordon [16] that charges alternate along a carbon chain that has a fluorine at one end. Evidence for this effect has been seen in the

work of Davis, Banna, and Shirley [14], who have reported data on fluorinated ethanes. The point-charge analysis on the fluorobenzene and the trifluoromethylbenzene gives further support to this idea. In each case, the derived charges alternate through chains of about 4 atoms, with the magnitude of the oscillation becoming less with distance from the fluorines. Thus in fluorobenzene the derived charges (starting from the fluorine) are -0.19, +0.23, -0.04, +0.01, 0. For trifluoromethylbenzene the series is -0.22, +0.73, -0.13, +0.03, +0.02, +0.02.

V. CHLOROFLUOROMETHANES

Much success in using core-electron ionization potentials from ESCA to gain insight into the chemical properties of molecules has been demonstrated by many experimenters. Still, an adequate potential model is sought to interpret these ionization potentials in terms of chemically useful concepts such as the charge distribution in molecules. The ambiguity in defining the atomic charge in a molecule shows theory to be fragmentary in describing these chemical shifts in core-level binding energies. The goal remains to derive a simple enough potential model useful for accurately interpreting these shifts.

Since the fluorine atom is more electronegative than either carbon or chlorine, its effect on the ionization potentials of carbon 1s and chlorine 2s will be interesting to observe in the chlorofluoromethanes. Correlations of these ionization potentials with electronegativity and NQR frequencies should be greatly influenced by the fluorine atom. Unfortunately, other changing chemical properties of this group of molecules such as proton affinities, acidities, and the heats of formation necessary for an equivalent-cores approximation cannot be correlated with ionization potentials because of insufficient data. Also, we want to note the trifluoromethyl group's effect upon a chlorine atom in CClF_3 to compare with the electron-donating effect it had in

the trifluoromethylbenzenes. With available data for the halomethanes, ionization potentials can be compared from this series with the chlorofluoromethanes to show how changing chemical properties depend upon the carbon substituent.

The use of earlier assumptions defining the point-charge model are known to be oversimplified for completely describing the charge distribution in molecules. The chlorofluoromethane series will demonstrate some inaccuracies in these assumptions. For this model to be useful either differential relaxation energy among the molecules or the variation in $\langle 1/r \rangle$ expectation value for the molecule's valence electrons, with charge must be incorporated into the point-charge model. Using these latter considerations the core-electron binding energy shifts in the chlorofluoromethanes are adequately described. The obtained values for differential relaxation from this analysis and the variation of $\langle 1/r \rangle$ with charge are in accord with chemical intuition.

Results

The measured ionization potentials for the chlorofluoromethanes and for Cl_2 are presented in Table IV. Values for CF_4 , CCl_2F_2 , and CCl_4 are in excellent agreement with previous results [18, 19]. Clark and Kilcast [20] have measured CCl_3F in the condensed phase on the calibrant gold (C 1s: 293.3 eV; Cl 2s: 274.2 eV; F 1s: 691.4 eV) and also CCl_4 in the condensed phase (C 1s: 292.1 eV; Cl 2s: 273.9

Table IV. Core-Electron Ionization Potentials in Chlorine and Chlorofluoromethanes (eV)

Compound	Carbon 1s	Fluorine 1s	Chlorine 2s
Cl ₂			278.74(9)
CCl ₄	296.38(8)		278.04(8)
CCl ₃ F	297.54(8)	694.33(4)	278.24(8)
CCl ₂ F ₂	298.93(6)	694.68(3)	278.63(8)
CClF ₃	300.31(7)	695.04(4)	278.84(7)
CF ₄	301.96(5)	695.52(3)	

eV). Their values are lower by 2.9 to 4.3 eV, but are measured with respect to the Fermi level of gold rather than to the vacuum level. If we correct for the gold work function of 4.8 eV, the discrepancy is reduced to between -1.9 eV and -0.5 eV. The discrepancy of 2.9 eV for the fluorine line measurement suggests a possible calibration error for fluorine in the Clark, et al. measurement. This discrepancy is also observed for fluorine in trifluoromethylbenzenes. However, their relative binding energy shifts within the chlorofluoromethane series are in excellent agreement with those shifts from this gas-phase study, in contrast to the trifluoromethylbenzene study.

The carbon 1s ionization potential is observed to increase approximately linearly becoming the greatest for CF₄ as the fluorine atoms replace chlorine atoms. This is expected because of the greater electronegativity of a

fluorine atom. The fluorine 1s ionization potential increases as the number of fluorine ligands increase on the carbon atom. The chlorine 2s ionization potential changes the least from molecule to molecule, but also increases as more fluorines attach to the carbon atom. The increasing ionization potential of chlorine is reasonable since its electronegativity is less than fluorine's but greater than carbon's. So great is the electronegativity of fluorine that chlorine has a greater ionization potential in CClF_3 than Cl_2 by 0.10 eV. The greater ionization potential of chlorine in CClF_3 is not surprising since the large negative end of this molecule induces a positive potential at the chlorine end of the molecule. Figure 2 shows the photoelectron spectra of C 1s, F 1s and Cl 2s in $\text{CCl}_{4-n}\text{F}_n$ ($n = 0 \rightarrow 4$).

No comprehensive analysis of linewidths is made. Total linewidth (FWHM) data, which is the sum of the instrument's resolution, x-ray and natural linewidth, is reported. In this linewidth data the x-ray and resolution linewidth is considered to be constant in each energy range studied. Using Al $\text{K}\alpha_{1,2}$ x-rays carbon 1s linewidths (FWHM) in the chlorofluoromethanes is observed to vary from 1.6 to 1.4 eV; this compares to 1.95 eV in CH_4 and to 1.48 eV in CF_4 . Fluorine 1s linewidths (FWHM) are also nearly constant from 2.0 to 2.1 eV, about the same as in trifluoromethylbenzenes; this compares with 0.95 to 1.05 eV in the neon $^1\text{D}_2$ Auger

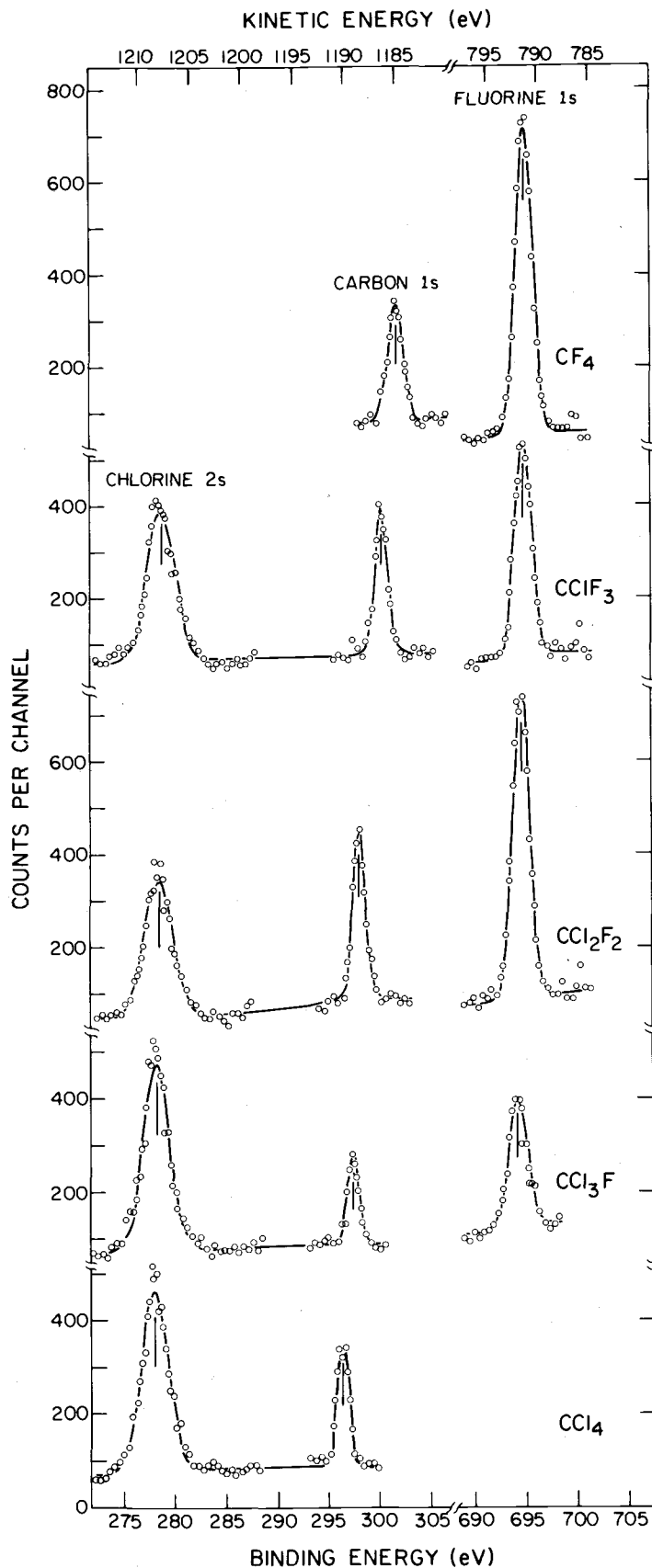


Figure 2. X-ray Photoelectron Spectra of Chlorofluoromethanes.

line. The fluorine linewidths are all much greater than those in $\text{CF}_{4-n}\text{H}_n$ ($n = 1 \rightarrow 3$) presumably because of the many more vibrational states that exist in the chlorofluoromethanes [21]. The chlorine 2s linewidths (FWHM) are the largest studied in this series of compounds. They are almost constant from 3.3 to 3.4 eV; this compares to about 3.1 in Cl_2 . Again this extra linewidth of the chlorine 2s in the chlorofluoromethanes may be due to the greater number of vibrational states associated with the hole state. The natural linewidth for chlorine 2s is expected to be greater than that for either carbon 1s or fluorine 1s owing to a shorter natural lifetime of the Cl 2s hole state due to a Coster-Kronig type process.

Discussion

Point-charge analysis

The point-charge model is laden with assumptions that have been discussed previously. These assumptions may or may not always hold true. Because several instances of discrepancies have arisen [11, 22] in comparing calculated core-electron ionization potentials within the Hartree-Fock formalism to experimental ones using ESCA, it is thus important to review the point-charge model. In either case the assumptions used for the model's derivation have not been verified experimentally or theoretically. This series of halogenated methanes was selected to provide a test of the

validity of the assumptions for the point-charge model. For such a series of quite similar molecules it is expected that these assumptions for the most part will hold. But, in fact, we find through this analysis that these simplifying assumptions are not consistently true.

A complete, definite determination of all k_i values and charges can in principal be made since there are enough binding energy shifts to solve for the unknown k_i 's and charges in all these molecules studied. This determination is possible since we are now only considering the strict interpretation of the point-charge model. Thirteen measured ionization potentials and five equations of charge neutrality should determine k_C , k_F , k_{Cl} , and the thirteen charges with two equations left over to check these results. To simplify solution of these non-linear equations, a FORTRAN IV program was developed which uses an iterative technique together with matrix inversion. Appendix I illustrates the principle underlying the basis for such analysis.

In this particular study the hypothetical neutral chlorine atom is taken as the chlorine in Cl_2 ; the fluorine atom as in F_2 ; the carbon atom as in CH_4 . Immediately a question arises with respect to the validity of selecting the hypothetical neutral atom as in CH_4 (290.89(5) eV). Ab initio calculations indicate that the carbon may be negatively charged in this molecule. We can resolve this question by choosing one of the two equations that presently

overdetermines the analysis and by letting this equation then determine the hypothetical neutral atom when calculating its offset relative to methane. The point-charge expression is modified by adding this offset parameter ℓ_i and is similar to Siegbahn's point-charge expression [3] where the symbols have been previously defined:

$$\Delta E_i = q_i k_i + \sum_{j \neq i} q_j e^2 / r_{ij} + \ell_i$$

The bond distances, r_{ij} , used are the best values taken from the literature [23].

Preliminary studies indicated no unique k_C , k_F , or k_{Cl} , in going from one compound to another in this series of chlorofluoromethanes in contrast to what the point-charge model assumes. This conclusion was reached by taking three sets of three compounds each and by explicitly solving for each k_i value and atomic charge using the point-charge expression above. These results are given in Table V. The value for k_C varies from 14.9 eV/e in the set containing CCl_4 where the carbon charges in CCl_3F and $CClF_3$ are largest to 245 eV/e in the set containing CCl_2F_2 where the carbon charges in CCl_3F and $CClF_3$ are smallest. These results indicate that k_i might in some way depend upon the charge on atom i . It is shown later that the development of this idea may help explain the discrepancies in theoretical and experimental core-electron ionization potentials. From the above results the failure of the model is clearly evident,

Table V. Atomic Charges and Values for k_i Using the Point-Charge Model (explicit solutions using only the model's basic assumptions)

Compound	Atomic Charge, q/e			Value of k_i eV/e
	Carbon	Fluorine	Chlorine	
CF ₄	1.065	-0.266		$k_C = 21.3$ $k_F = 28.0$ $k_{Cl} = 24.8$
CCl ₃ F	0.554	-0.235	-0.106	
CClF ₃	0.875	-0.255	-0.111	
CCl ₄	0.818		-0.204	$k_C = 14.9$ $k_F = 25.0$ $k_{Cl} = 21.1$
CCl ₃ F	1.165	-0.435	-0.244	
CClF ₃	2.122	-0.592	-0.345	
CCl ₂ F ₂	0.034	-0.016	-0.001	$k_C = 245$ $k_F = 143$ $k_{Cl} = 183$
CCl ₃ F	0.028	-0.018	-0.003	
CClF ₃	0.040	-0.013	-0.001	

and it will be necessary to modify the model such that its applicability will hold for any molecule under study. However, some of the derived k values and charges are reasonable.

Another correction to the assumptions of the point-charge model may arise from its total neglect of relaxation energy. Accompanying x-ray photoemission of a core electron from an atom is the relaxation of the passive orbitals towards the hole in the active orbital to adjust to the modification in the molecular potential. However, the model makes allowances for only a hypothetical "unrelaxed" ionic

final state in which an electron has been removed from the core level of the atom without relaxation in the passive orbitals. This energy is then too great when relaxation is neglected, and the relaxation of the passive orbitals to the positive hole should lower the energy. Thus, to relate our measured ionization potentials to the theoretical calculations of the point-charge model, a relaxation energy correction is needed.

Davis and Shirley [12] have developed a relaxation-potential model (RPM) for calculating core-level binding energy shifts in molecules from CNDO wavefunctions. They demonstrate its success by finding good agreement between experimental and theoretical binding energy shifts over a wide class of compounds. They conclude that outer shell (the passive orbitals of principal quantum number n greater than the n' of the orbital being photoionized) relaxation is larger, when there is a reasonably large number of electrons present in these shells, than either inner-shell or intra-shell relaxation. Also, extra-atomic relaxation is determined to be very insensitive to the form of the hole-state orbital.

Recently Basch [24] concluded that neglect of the quantity, $\bar{E}_R^+ + E_C + E_{Cl}$, is not always justified in calculating the chemical-shift effect. Here \bar{E}_R^+ is the electronic relaxation or reorganization energy in the hole state; E_C is the difference in correlation energy (the difference between

exact non-relativistic and Hartree-Fock energies) between the ground state and hole state (positive ion) of the molecule; E_{C1} is the relativistic effect energy difference in the ground state and the hole state of the molecule. He shows that in a number of systems the relaxation energy is the most important correction term to the Hartree-Fock orbital energy. This again suggests that the point-charge model must incorporate some correction for the relaxation energy accompanying photoemission.

It has been generally assumed that relaxation differences are approximately equal between similar molecules of a series and that correlation and relativistic corrections are the same in the series. These corrections have been largely ignored in the point-charge model where binding energy shifts are based on initial states only and relaxation in the final state is neglected. In what follows, we investigate the possibility of a differential relaxation energy from one molecule to another. Unfortunately, for even these simple molecules no relaxation energy calculations have been done. Even the equivalent-cores approximation used by Davis and Shirley does not help since CNDO calculations do not exist for analogous molecules of this series of molecules studied.

We have continued this study by finding a relaxation energy correction from a comparison between the measured core-electron binding energy shifts and shifts calculated by

the point-charge model with assumed (but reasonable) values for k_i and q_i . Then, these relaxation energy corrections are assessed as to whether they appear reasonable or not. Finally, the evaluated relaxation corrections are determined whether or not to be essential in the point-charge model. In calculating the binding energy shifts using the model, values for k_i 's and charges are assumed: $k_C = 22$ eV/e; $k_F = 29$ eV/e; $k_{Cl} = 25$ eV/e; $q_{Cl} = -0.1$ e; $q_F = -0.2$ e. The carbon offset is assumed to be zero. The values for k_i 's and charges are reasonable. For the set of compounds CF_4 , CCl_3F and $CClF_3$ Table V gives values very close to those assumed above. Values of k_C from equivalent cores approximation [25] are between 18.3 and 23.1 eV/e, and values of k_F are between 18.2 and 23.7 eV/e. From ESCA k_C has been found to be 20.7 [26], 21.9 [3] and 24.7 eV/e [27] and k_F has been found to be 27.6 [3], 32.5 [8] and 34.4 eV/e [11]. CNDO calculations indicate q_F is approximately equal to -0.17 e [15] in CF_4 and experimentally in the trifluoromethylbenzenes and other compounds is approximately -0.17 to -0.22 e. Gordy [28] has estimated from quadrupole coupling data that the charge on carbon in CCl_4 is +0.48 e; thus the corresponding charge on chlorine is -0.12 e. Gordy's formula, however, only applies to the ionic character of the σ part of the bond, and no consideration is given for partial cancellation of the charge transferred from carbon to chlorine in the bond by a back donation of electrons in the

π bond. The charge on the chlorine is then considered to be an upper limit. Since the quadrupole resonance frequencies for $\text{CCl}_n\text{F}_{4-n}$ ($n = 1 \rightarrow 4$) are approximately equal, the charge on chlorine throughout the series is considered relatively constant.

Table VI presents the differences in calculated and experimental binding energy shifts using the values for k_i and q_i listed above. Without concern for the magnitudes of these hypothetical relaxation energy corrections at the moment, we note that the trend of these corrections is reasonable regarding chemical intuition. The greater the number of chlorine ligands on carbon, the greater is the relaxation energy, consistently going from most negative in CF_4 to a positive value in CCl_4 . The relaxation energy is essentially constant in the fluorine atoms, and it becomes the greatest contribution to the binding energy shift for the chlorine atom. Here we remember that the chlorine atom in chlorofluoromethanes is being compared to the chlorine in Cl_2 . We suggest the relaxation energy in Cl_2 is greater than in $\text{CCl}_n\text{F}_{4-n}$ ($n = 1 \rightarrow 4$) where the greatest is for CCl_4 as might be expected. If these differences in experimental and point-charge binding energies are relaxation corrections we suggest that differential relaxation energy is not trivial between similar molecules nor is extra-atomic relaxation energy. The authenticity of the magnitude of these corrections remains unclear. A total relaxation correction

Table VI. Comparison of ESCA Binding Energy Shifts with Calculated Binding Energy Shifts Using the Point-Charge Model

Compound	$\Delta E_{\text{exp}}^{\text{a}}$	$\Delta E_{\text{calc}}^{\text{b}}$	$\Delta E_{\text{calc}}^{\text{b}} - \Delta E_{\text{exp}}^{\text{a}}$
<u>CF</u> ₄	11.07	8.89	-2.18
<u>CClF</u> ₃	9.42	8.07	-1.35
<u>CCl</u> ₂ F ₂	8.04	7.28	-0.76
<u>CCl</u> ₃ F	6.65	6.38	-0.27
<u>CCl</u> ₄	5.49	5.54	0.05
<u>CF</u> ₄	-1.18	-1.02	0.16
<u>CClF</u> ₃	-1.66	-1.45	0.21
<u>CCl</u> ₂ F ₂	-2.02	-1.80	0.22
<u>CCl</u> ₃ F	-2.37	-2.09	0.28
<u>CClF</u> ₃	0.10	-0.15	-0.25
<u>CCl</u> ₂ F ₂	-0.11	-0.40	-0.29
<u>CCl</u> ₃ F	-0.50	-0.54	-0.04
<u>CCl</u> ₄	-0.70	-0.73	-0.03

^a Measured core-electron binding energy shift relative to a neutral atom.

^b Calculated core-electron binding energy shift relative to a neutral atom for values assigned k_i and charges (see text).

to the binding energy shift between CH₄ and CF₄ is estimated at 1.6 to 1.7 eV by Basch [24] but -0.98 by Davis and Shirley [12] and -0.95 eV by Jen [29]. For the calculations in Table VI the offset for neutral carbon was assumed to be

zero, which is not correct. These differences in calculated and experimental carbon binding energy shifts are then actually the sum of carbon charge offset and differential relaxation energy. To suggest that this sum is that stated in Table VI is incorrect because of the simplifying assumptions for k and atomic charge values used in arriving at these results. The nonuniqueness of these solutions must then be kept in mind. Models are in the process of development to calculate or predict these relaxation corrections.

The results in Table VI may be explained in another manner alluded to previously when k_i was thought to be dependent in some way upon q_i . There is reason to believe that k should not be equated to the expectation value of $1/r$ for the valence electrons obtained from Hartree-Fock. Only if there is no shrinkage or expansion of the valence shell or change of charge can k be equated to $\langle 1/r \rangle$. It is important to recognize that all the valence electrons participate in the expansion or contraction when one electron is added or removed. From this analysis of the chlorofluoromethanes we suggest

$$k_i = (k_0 + cq_i)$$

where cq_i is an adjustment to $\langle 1/r \rangle$ represented by k_0 when some expansion or contraction is taking place as one electron is added or removed from atom i . It is then possible to explain the differences in the binding energy shifts in

Table VI for carbon by this k dependence on charge. Using the model's original assumptions, we have

$$\Delta E_{i\text{calc}} = q_i k_i + \sum_{j \neq i} q_j e^2 / r_{ij} \quad 5-1$$

and assuming a possible quadratic dependence in charge, we have

$$\Delta E_{i\text{exp}} = (k_0 + cq_i)q_i + \sum_{j \neq i} q_j e^2 / r_{ij}. \quad 5-2$$

Since the geometric terms do not vary in comparing experimental with point-charge binding energy shifts, these terms cancel when equation 2 is subtracted from equation 1; then

$$(\Delta E_{i\text{calc}} - \Delta E_{i\text{exp}}) / q_i = k_i - k_0 - cq_i. \quad 5-3$$

This latter expression should give a straight line of slope c when the left side of equation 3 is plotted against q_i , if the quadratic expression holds. Using the data for carbon from Table VI a straight line is indeed observed with slope +6.95 and intercept 3.0. Then k_0 is determined to be 19 eV/e. With these known values for k_0 and c used in equation 3 the differences in equations 1 and 2 are compared to the measured binding energy shifts in Table VII below. Very good agreement exists between the experiment and calculation (as it must, since the parameter c was chosen to give good agreement). It is possible then that a quadratic dependence of ΔE_i on q_i is the source of the differences between experimental binding energy shifts and those calculated from

the usual point-charge model. Similar arguments may be made for the chlorine and fluorine binding energy shifts except that their charges, assumed from ab initio or NOR data, are thought to be almost constant from molecule to molecule, and the k_i variations with charge would not be evident. This is indicated by the constancy in difference between experimental and the model's binding energy shift for these ligands.

Table VII. Comparison of ESCA Binding Energy Shifts with Calculated Binding Energy Shifts Assuming ΔE Quadratic in Charge

Compound	ΔE_{exp}	ΔE_{calc}	$\Delta E_{\text{calc}} - \Delta E_{\text{exp}}$
CF ₄	11.07	10.94	-0.13
CClF ₃	9.42	9.47	+0.05
CCl ₂ F ₂	8.04	7.98	-0.06
CCl ₃ F	6.65	6.62	-0.03
CCl ₄	5.49	5.44	-0.05

We have shown that the simple assumptions of the point-charge model are grossly inaccurate and its inadequacies are remedied by noting that k_i values need not be constant or that differential relaxation energy be allowed. The analyses we have made shows reasonable values in accordance with chemical intuition. It cannot, however, be assumed that these are definitive values. The value of k_C is suggested not to be constant but differences in relaxation energies

may have a small effect in its determination. The values of k_{Cl} and k_F are suggested to be constant since fluorine and chlorine charges are apparently constant from one molecule to another, thus relaxation differences are more prominent. It is this interplay of differential relaxation and k_i dependence upon charge that seriously handicaps the point-charge model. It is likely that both must be allowed in some as yet unknown proportion. No way is possible at the present time to determine which is more reasonable for obtaining correct binding energy shifts within the framework of the model. Levy, Millie, Ridard, and Vinh [30] have recently done SCF CI calculations of the K-shell ionization potential of carbon in methane and in the fluoromethanes. Their calculations indicate that the effect of configuration interaction is of importance in CHF_3 and CF_4 but not in CH_4 . Perhaps, the correlation energies then should not be neglected in our analysis of the chlorofluoromethanes.

Correlation with electronegativity

Measured binding energies have been found to vary linearly with the sum of the differences between the electronegativity of the ligands and that of hydrogen [18]. Specifically this is observed with halomethanes where the following relationship expresses the shift between methane and any of the halomethanes.

$$\Delta E_X - \Delta E_{CH_4} \propto \sum_{i=1}^4 (X_i - X_H)$$

Here X_i is the electronegativity [31] of the i th ligand and the sum is over all ligands and X_H is the electronegativity of hydrogen. This same relationship holds for the chloro-fluoromethanes. Not only are the carbon 1s binding energy shifts linear with the sum of electronegativities but the slope of the line is the same as for the halomethanes with a proportionality constant equal to about 1.48 eV per electronegativity unit. Figure 3 shows this linear relationship between electronegativity and the chlorofluoromethanes and halomethanes.

Comparison of chlorofluoromethanes with halomethanes

We immediately notice that the chlorine 2s and fluorine 1s ionization potentials are greater in the chlorofluoromethanes compared with their counterparts in the halomethanes [18]. This is not unexpected since the hydrogen atom is less electronegative than fluorine or chlorine. A comparison of the carbon 1s ionization potentials is shown in Figure 3 where carbon 1s binding energy shifts relative to methane are plotted against electronegativity. An interesting correlation of these carbon 1s shifts is presented for $n = 1 \rightarrow 3$:

$$[(\Delta E_{\text{Cl}s} \text{ in } \text{CH}_n\text{F}_{4-n}) + (\Delta E_{\text{Cl}s} \text{ in } \text{CH}_{4-n}\text{Cl}_n)] -$$

$$(\Delta E_{\text{Cl}s} \text{ in } \text{CCl}_n\text{F}_{4-n}) = 0.46(1) \text{ eV.}$$

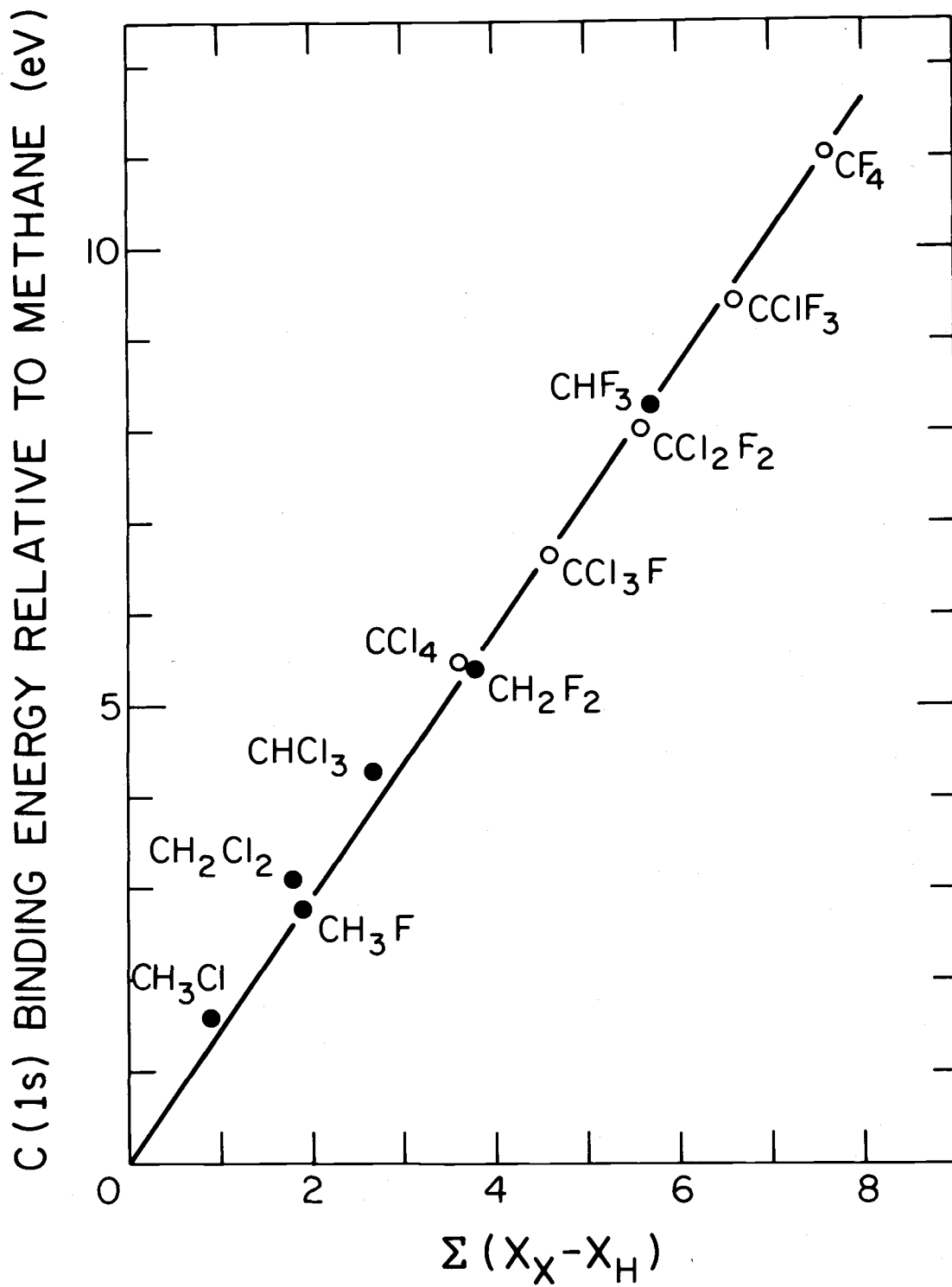


Figure 3. Carbon 1s Binding Energy Shift Correlation with Electronegativity.

It is presently difficult to understand the physical significance of this number.

Correlation with ^{35}Cl nuclear quadrupole resonance (NQR) Data

We are able to construct a linear correlation of ^{35}Cl NQR frequencies [32] with chlorine 2s ionization potentials. But the linear correlation for the chloromethanes is different than the linear correlation for the chlorofluoromethanes as shown in Figure 4. This is not totally surprising since ESCA depends on the change in potential energy equal to $\langle 1/r \rangle$ when one electron is removed while NQR depends on $\langle 1/r^3 \rangle$. Clark, et al. [20] develops this correlation further. What is especially noteworthy is the apparent dissimilarity of the trends in the two series of compounds. Based on the results from our analysis of the trifluoromethyl group as a substituent in benzene, the interpretation of this graph follows arguments in agreement with both NQR data and ESCA data.

^{35}Cl NQR frequencies are known to increase as the charge on chlorine decreases. In analysis the $3p_z$ orbital of chlorine is considered to be in the σ bond. In the halomethanes the π orbitals ($3p_x$ and $3p_y$ orbitals of chlorine) are localized on chlorine and the degree of hybridization is shown to be essentially constant [20]. The NQR frequency then reflects the difference in polarity of the C-Cl bonds. As the chlorines replace hydrogen in the chloromethane

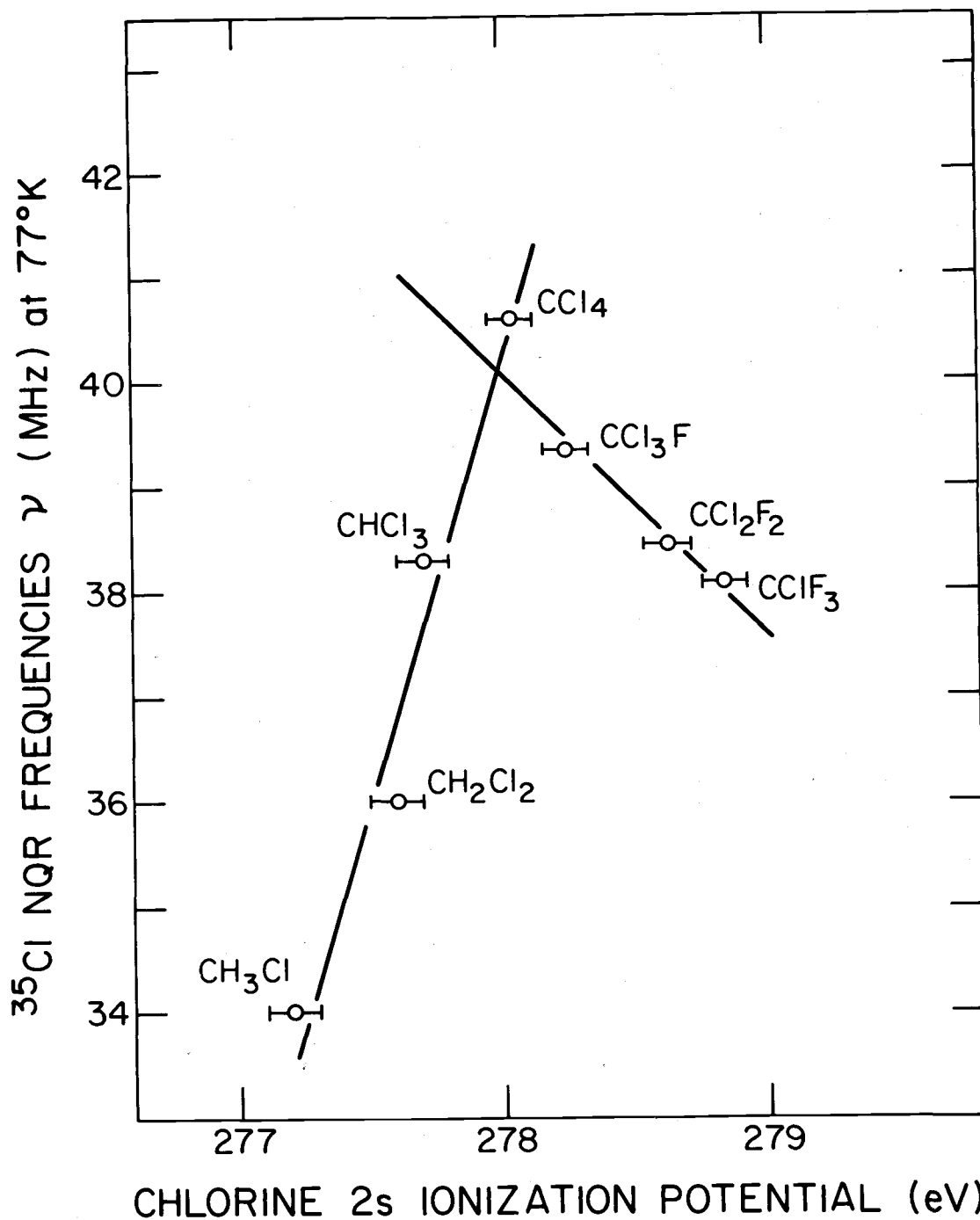


Figure 4. Chlorine 2s Ionization Potential Correlation with ^{35}Cl NQR Frequencies for Chloromethanes and Chlorofluoromethanes.

series the chlorine 2s ionization potential increases indicating each additional chlorine takes a less amount of electrons from carbon, and the charge on chlorine becomes less negative. Therefore, we expect the ^{35}Cl NQR frequencies to increase as the chlorine 2s ionization potentials increase with the number of chlorines in the chloromethane. This is in complete agreement with Figure 4. However, in the chlorofluoromethanes, as fluorines replace chlorines, the chlorine quadrupole resonance frequency is reduced. This result was interpreted to mean that a more negative charge was withdrawn by the chlorine atom than by the fluorines, opposite to expectations and opposite to the trend of increasing chlorine 2s ionization potentials in Figure 4. The data are reconciled when we consider the results in Chapter IV. The trifluoromethyl group is shown to have about the same electron-withdrawing ability as a substituent methyl group in a benzene system, but reactivity as well as ionization potentials is governed by the large positive charge on the carbon atom in CF_3 . Resonance structures similar to those pictured in B and D attributed to hyperconjugation can be drawn likewise for CClF_3 where charge is pushed back toward chlorine. In fact, Table V indicates that the chlorine atom in CClF_3 has a more negative charge than CCl_3F in two cases. Thus, in the chlorofluoromethanes the trend shown in Figure 4 is reasonable and helps exemplify this controversy that has "clouded" the meaning of ^{35}Cl NQR data for these compounds.

VI. SUMMARY

The study of condensed-phase samples is complicated by solid state effects and charging effects. An effort was made to explain certain of these charging effects in NaF and NaCl. Further analysis of charging effects will certainly be beneficial toward understanding the reference level in nonconductors.

Gas-phase measurements of core-electron ionization potentials in trifluoromethylbenzenes and chlorofluoromethanes have correlated well with their chemical properties. From their analysis we conclude that the CF_3 group donates electrons to the ring and possibly to a chlorine atom as shown by the ^{35}Cl NQR correlation. The inductive effect of CF_3 results because of a positive dipole creating a positive potential on the neighboring atoms. Hyperconjugation in fluoro-substituted compounds is shown to be consistent with these ESCA results.

Finally, the point-charge model in its usual form is shown to have serious deficiencies when used with the chlorofluoromethanes' binding energy shifts. With certain modification, however, the model agrees well with the ESCA results. Relaxation energy corrections consistent with chemical intuition is one such modification. An alternate interpretation is that binding energy shifts tend to be quadratic with charge (as shown in the case of carbon). The

importance of understanding the electron distribution in molecules is a goal worth seeking, and electron spectroscopy is a technique important to this goal.

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APPENDIX

APPENDIX I

THE EXACT DETERMINATION OF k_i AND ATOMIC CHARGES

The development of a FORTRAN IV program to solve simultaneously a given number of non-linear equations is described below. The program essentially reads a given matrix, modifies the matrix, inverts the matrix, and utilizes an iterative process to find best values of k_i and q_i . The point-charge expression may be described for each binding energy shift, ΔE_i , relative to a neutral atom i using a general offset, ℓ_i , where q_j is the atomic charge on atom j :

$$\Delta E_i = \sum a_{ij} q_j + \ell_i \quad \text{A-1}$$

Here the a_{ij} terms are either geometric factors equated to the Madelung potential or the combination of a geometric factor with k_i . Suppose we allow:

$$a_{ij} = A_{ij}$$

$$a_{ii} = A_{ii} + \Delta_i$$

$$q_j = Q_j + \delta_j$$

where A_{ii} and Q_j are initial guesses to k_i (plus any geometric factors) and q_j , and Δ_i and δ_j are corrections that lead to a unique solution for the equations in (1). Then equation (1) becomes:

$$\Delta E_i = \sum_{j \neq i} A_{ij} (Q_j + \delta_j) + (A_{ii} + \Delta_i) (Q_i + \delta_i) + \ell_i$$

A-2

$$\approx \sum_{j=i} A_{ij} (Q_j + \delta_j) + \Delta_i Q_i + \ell_i$$

assuming that the cross term $\Delta_i \delta_i$ is very small. Finally equation (2) is put into a form easily calculated with the variables all on the right side of the equation:

$$\Delta E_i - \sum_{j=i} A_{ij} Q_j = \sum_{j=i} A_{ij} \delta_j + \Delta_i Q_i + \ell_i$$

To use the program this procedure is followed allowing much flexibility on the part of the operator to read in necessary initial guesses and to control the program. The geometric factors in the point-charge expression are put into matrix form, \hat{A} , and read into the permanent computer storage with k_i 's and q_i 's equal to zero. The ΔE_i 's are read in and also permanently stored. The initial guesses for k_i 's are read in and the original matrix modified with the diagonal terms $A_{ii} = A_{ii}^0 + k_i$. The initial guesses for charges Q_j 's, are then read in and $\Delta E_i - \sum A_{ij} Q_j$ is calculated. The values for δ_j 's and Δ_i 's are found, if they are satisfactory (these corrections to initial guesses are less than the constraints set in the program) the computer output gives the solutions for k_i 's, q_j 's and ℓ_i 's. If the corrections are unsatisfactory the program makes new approximations and continues iteration until the constraints are met. Below is given a computer print-out of some results.

The following is an example of the computer results for finding k_C, k_F, k_{Cl}, l_C and all charges in $CCl_4, CCl_2F_2, CClF_3, CCl_4$. In the example I have labelled C to represent computer response and 0 to represent operator control for reading in data. In the program N signifies the dimension of the matrix and NC signifies number of charges to be solved for. The original matrix is read in by paper reader signified by 0: ↑ P. The carbon ls offset has been underlined in the computer's final iteration for correcting k_i and q_i . The final matrix is printed out with all k_i 's and q_i 's inserted. Notice these results closely agree with those for $CF_4, CCl_3F, CClF_3$ in Table V.

C: N AND NC=

O: 14
10

C: MATRIX WITH VARIABLES=0, NF7.3

C: PAUSE 000000
O:C PSHIFTS, NF7.3

O: 11.690 -1.640 9.040 -2.420 -0.590 10.240 -2.070 -0.200
6.890 -1.000 0.000 0.000 0.000

C: GUESS K VALUES, NCF7.3

O: 22.000 31.000 22.000 31.000 27.000 22.000 31.000 27.000
22.000 27.000

C: GUESS CHARGES, NCF7.3

O: 0.800 11
-0.200 12
0.600 11
-0.200 12
-0.100 13
0.700 11
-0.200 12
-0.100 13
0.400 11
-0.200 13

C: 0.000 -0.000 -0.000 0.000 0.000 0.000 -0.000 0.000
-0.001 0.000 -0.016 -0.000 0.016 0.496

C: MATRIX IS

C: 21.168 43.537 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 1.089 0.000 0.000 1.000
10.884 49.562 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 -0.272 0.000 0.000
0.000 0.000 21.168 21.492 16.180 0.000 0.000 0.000
0.000 0.000 0.756 0.000 0.000 1.000
0.000 0.000 10.746 36.143 11.272 0.000 0.000 0.000
0.000 0.000 0.000 -0.253 0.000 0.000
0.000 0.000 8.090 11.272 30.777 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 -0.125 0.000
0.000 0.000 0.000 0.000 0.000 0.000 21.168 32.530 8.224
0.000 0.000 0.912 0.000 0.000 1.000
0.000 0.000 0.000 0.000 0.000 10.844 42.908 5.672
0.000 0.000 0.000 0.000 -0.262 0.000 0.000
0.000 0.000 0.000 0.000 0.000 8.224 17.015 25.793
0.000 0.000 0.000 0.000 0.000 -0.126 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
21.168 32.616 0.491 0.000 0.000 1.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
8.154 40.757 0.000 0.000 -0.123 0.000
1.000 4.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 1.000 2.000 2.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 1.000 3.000 1.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000
0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
1.000 4.000 0.000 0.000 0.000 0.000 0.000 0.000

C: CHARGES ARE

C: 1.089 11
-0.272 12
0.756 11
-0.253 12
-0.125 13
0.912 11
-0.262 12
-0.126 13
0.491 11
-0.123 13

C: K/L VALUES ARE

C: 21.168 29.562 21.168 29.562 25.793 21.168 29.562 25.793
21.168 25.793

N AND NC=