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X-RAY PHOTOELECTRON SPECTROSCOPY OF HALOMETHANES*

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October, 1969

ABSTRACT

Carbon 1s ionization potentials, relative to that of methane (290.8 eV), have been measured for CH_3F (2.8 eV), CHF_3(8.3 eV), CF_4(11.0 eV), CH_3Cl(1.6 eV), CH_2Cl_2(3.1 eV), $CHCl_3$(4.3 eV), CCl_4(5.5 eV), and CH_3Br(1.0 eV), together with fluorine 1s ionization potentials for CH_3F(692.4 eV), CHF_3 (694.1 eV), and CF_4(695.0 eV), and chlorine 2s ionization potentials for CH_3Cl(277.2 eV), CH_2Cl_2(277.6 eV) $CHCl_3$(277.7 eV) and CCl_4(278.0 eV). The carbon and halogen binding energies increase linearly with the number of halogens. Comparison of the fluorocarbon results with binding energies based on use of Koopmans' theorem indicates a substantial error between experiment and theory that increases with the number of fluorines. This discrepancy arises because Koopmans' theorem does not allow for relaxation of electrons and polarization of the ligands when the ion is formed from the neutral molecule. The measured binding energies are found to vary linearly with the sum of differences between the electronegativities of the ligands and that of hydrogen. A plausible reason is developed for this linear relationship.

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X-Ray Photoelectron Spectroscopy of Halomethanes

Inner-electron binding energies for extensive series of nitrogen, sulfur, and chlorine compounds have been determined by x ray photoelectron spectroscopy.[1-4] These, and other, measurements show that the binding energies of the inner electrons increase with oxidation number, with formal charge on the atom, and with increasing electronegativity of the ligands attached to the atom. Some success has been obtained in correlating the measured shifts with charges assigned to atoms in various ways. The technique shows some promise of providing information on charge distributions in molecules and quantitative information on the electronegativity of different ligands.

Some information has been published on the carbon 1s electron binding energies in different compounds and the results are generally in agreement with expectations.[5,6] However, no systematic study of carbon compounds has yet appeared. As part of such a study, I report here the carbon 1s binding energies for the compounds CH_4, CH_3F, CHF_3, CF_4, CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, and CH_3Br. In addition, I report the fluorine 1s and chlorine 2s binding energies. These compounds provide a series in which the electronegativity of the ligands and the number of electronegative ligands attached to the central atom can be easily varied without changing the type of bonding or the molecular geometry (other than the bond length). In addition, since fluorine is the most electronegative element, the shift of the carbon 1s binding energy between methane and carbon tetrafluoride gives the maximum range of shifts to be expected for organic compounds. Finally, there are Hartree-Fock calculations[7] of the carbon 1s binding energies for CH_4, CH_3F, CH_2F_2, and CHF_3. These measurements provide a useful test of whether this kind of calculation can correctly predict these shifts.

Experimental Method and Results

The binding energies of the various compounds were determined by irradiating gaseous samples with magnesium K_α x rays(1253.6 eV).[8] The kinetic energies of the photoelectrons were measured in an iron-free double focusing spectrometer of 50-cm radius.[9] The kinetic energy E_K of an electron is related to its binding energy E_b by conservation of energy:

$$E_b = 1253.6 - E_K$$

In order to measure the shifts accurately, I ran two samples together, one the sample of interest, the other either fluoroform, methane, or benzene taken as a standard. The carbon 1s and fluorine 1s binding energies for these compounds are known from other measurements.[5] By this technique any effects of instrumental drift or gas pressure on line position are the same for both lines. The pressures in the gas cell ranged from 0.01 to 0.05 Torr. Over the range 0.005 to 0.15 Torr we have found that the position of the fluorine 1s line from fluoroform does not vary by more than 0.2 eV.[10] Presumably any differential pressure dependence of two compounds run together is substantially less than this. The chlorine 2s binding energy is very close to the carbon 1s binding energy in fluoroform and was measured relative to it. A spectrum showing the carbon 1s line from fluoroform together with the carbon 1s and chlorine 2s lines of dichloromethane is given in Fig. 1. A spectrum of the fluorine 1s lines in tetrafluoromethane and fluoromethane is shown in Figure 2. In these figures the solid curves represent least squares fits to the data assuming gaussian peak shapes and a constant background. The difference in width between the two fluorine peaks is striking.

The measured binding energies for carbon 1s electrons are given relative to that for methane(290.8 eV)[5] in Table I, together with the absolute values for the fluorine 1s electrons and chlorine 2s electrons.

TABLE I

Binding energies for inner electrons in halomethanes

Compound	Carbon 1s binding energy(eV) Relative to methane (290.8 EV)	Absolute	Halogen binding
CH_3Br	1.0	291.8	
CCl_4	5.5	296.3	278.0[a]
$CHCl_3$	4.3	295.1	277.7[a]
CH_2Cl_2	3.1	293.9	277.6[a]
CH_3Cl	1.6	292.4	277.2[a]
CF_4	11.0	301.8	695.0[b]
CHF_3	8.3	299.1	694.1[b]
CH_3F	2.8	292.6	692.4[b]

a) Chlorine 2s

b) Fluorine 1s

Discussion

Qualitative trends. The carbon 1s binding energies show an obvious and expected increase with increasing electronegativity of the ligands and with increasing number of electronegative ligands. The fluorine 1s and chlorine 2s binding energies increase slowly with the number of halogens. These results are easily explained. The replacement of a hydrogen by a halogen results in withdrawal of valence electrons from the central atom with a resulting increase in the binding energy of the inner electrons. When additional hydrogens are replaced by halogens the positive charge and the carbon 1s binding energy increase even further. Because there is some electron transfer from the carbon to the halogen, the fluorine 1s and chlorine 2s binding energies for the monohalomethanes are presumably substantially less than for the isolated atom. As the positive charge on the central atom increases with the addition of halogens, there is an increase in positive potential at each ligand and a resulting increase in binding energy for the electrons on that atom, as is observed. (A similar discussion has been given by Schwartz, Coulson, and Allen[11] in interpreting the results of their theoretical calculations on fluoromethanes.)

It would be interesting to know whether each additional halogen withdraws the same amount of charge as does the first one. The linear increase of binding energies with a number of fluorines tempts one to conclude that this is the case. However, there is probably not a linear relationship between charge withdrawn and the change in binding energy; theoretical calculations indicate that the binding energy increases somewhat faster than linearly with increasing charge.[12] The fluorocarbon data thus suggest that the additional fluorines are not so effective as the first in withdrawing

charges from the carbon. Even more suggestive of this conclusion are the chlorocarbon data. Here we see that the first chlorine causes a shift in carbon 1s binding energy of 1.6 eV, the second 1.5 eV, and the third and fourth 1.2 eV each. (An alternate interpretation of the non-linearity of the chlorocarbon data is suggested below.)

Comparison with theory. The results of Hartree-Fock calculations of the orbital energies for methane, fluoromethane, difluoromethane, and fluoroform have been reported by Ha and Allen.[7] Their value of 305 eV for the carbon 1s orbital energy in methane is in good agreement with that obtained from other theoretical calculations. It is about 14 eV greater than the experimental value. This error is about as expected and probably results from the use of Koopmans' theorem.[14] Richards[15] has reviewed for the benefit of experimentalists the assumptions of Koopmans' theorem and the dangers of using it. First, Koopmans' theorem is applicable only if the molecular orbitals of the ion are the same as those of the neutral molecule. This will not in general be the case, and because of failure of this assumption, the one-electron energies from the Hartree-Fock calculation will be greater than the experimental values. The difference corresponds to a relaxation or reorganization energy of the molecular orbitals to the ionic orbitals. Second, the use of Koopmans' theorem assumes that the correlation energy for the ion is the same as that for the molecule. According to Richards this effect tends to make the Hartree-Fock energies less than the experimental values. Finally, it is assumed that the relativistic corrections are the same for the ion as for the molecule. The net error, as seen above, is about 14 eV for methane.

For a series of compounds, such as have been studied here, it seems reasonable that the relativistic and correlation[7] corrections will be the same for all of the compounds. Then, if the relaxation energy is the same for all molecules of the series, the Hartree-Fock results should give the shifts in binding energy among the various compounds, even though they do not agree with the absolute binding energies. Figure 3 shows the experimental and theoretical carbon 1s binding energies(relative to methane) plotted against the number of fluorines. The orbital energies calculated by Ha and Allen[7] change by an average of 4.9 eV for each additional fluorine; the experimental values, however, shift by only 2.8 eV for each fluorine. There is, therefore, an additional relaxation energy of about 2.1 eV per fluorine. We can make a rather crude estimate of the relaxation energy due to polarisation of the ligands by considering the interaction between a positive charge, +e, and a polarisable atom at a distance r from the charge. Because of the polarisation of the atom, the total energy of the system is lowered by an amount

$$\frac{e^2\alpha}{2r^4}$$

where α is the polarisability of the atom. With polarisabilities[16] for F^-, Cl^-, and Br^- and appropriate values for the carbon halogen distance,[17] the above expression gives a relaxation energy of 1.7 eV per fluorine and 2.2 per chlorine and bromine. The agreement between the value 1.7 eV and the discrepancy of 2.1 eV per fluorine mentioned above is surprising considering the crudeness of the model. Actual polarisabilities are probably smaller than those used(which were for the negative ions). Also one should allow for the fact that the central ion already had some charge(positive or negative) before the inner electron was ejected.

Figure 4 shows an energy level diagram summarizing the different energies involved in determining the ionization potential of CHF_3 (as an example). The lowest horizontal line represents the energy of the unionized molecule. The middle line represents the energy of the CHF_3^+ ion with an electron from the carbon 1s orbital removed to infinity. The right hand vertical line thus represents the difference in energy between these two states and thus the experimental ionization potential. The upper horizontal line represents the energy the ion would have if the orbitals of the ion were the same as those of the molecule. The left hand vertical line thus represents the ionization potential given by Koopmans' theorem. The distance between the two upper horizontal lines is the error due to the effects mentioned and, in the figure, is divided into two portions: about 14 eV due to rearrangement of the electrons associated with the carbon atom and to the relativistic and correlation effects and about 6 eV associated with polarization of the fluorine atoms.

This relaxation effect brings out one of the principal problems associated with interpretation of shifts in ionization potentials of inner electrons from one compound to another. The ionization potential is the difference between the energy of the neutral molecule and the energy of the ion, and is therefore influenced by the chemistry of both. It is difficult to know whether a measured shift between two compounds is due to differences between the neutral molecules or differences between the ions. Other examples of this problem are discussed elsewhere.[5]

Correlation with electronegativity. - A number of attempts have been made to correlate the shifts of 1s binding energies with charges assigned to the atoms.[1-4,11,18] These charges are estimated from simple electronegativity

considerations or from some kind of molecular orbital calculations. This sort of correlation is made in the same spirit that Koopmans' theorem is applied - namely, it is tacitly assumed that the energies are determined by the charge distributions in the molecule and that rearrangement energies can be ignored. In view of the substantial energies that appear to be associated with rearrangement, there might be some skepticism about the physical significance of these correlations.

It is possible, however, that the relaxation energies vary in some orderly way. If so, then these correlations may be of some value in determining the systematics of the binding energy shifts. The compounds I have studied, because they have essentially the same geometry and bonding, should provide a good test of the various methods of correlating the data.

A very simple and satisfactory correlation of the data for halomethanes is shown in Fig. 5. Here I have plotted the binding energy shifts versus the quantity $\Sigma(X_x - X_H)$. The symbol X_x stands for the electronegativity of the halogen and X_H is the electronegativity of hydrogen.[19] The summation is taken over all the atoms attached to the carbon(or, effectively, over the halogens since $X_H - X_H = 0$). Since the various compounds are related to one another by replacement of hydrogens by halogens, it is reasonable that the shifts should be somehow dependent on the electronegativity difference between hydrogen and the halogen. In addition it is reasonable that the shift should increase with the number of halogens. That the data should follow a linear relationship is not obvious. I have made an attempt to justify this linearity in the paragraphs that follow.

In the simple electrostatic model discussed by Siegbahn and coworkers,[20] the shift ΔE in the inner electron binding energy due to the

removal of a charge qe from the atom of interest to a ligand atom is given as

$$\Delta E = qe^2(1/r - 1/R)$$

where r is the radius of a shell around the atom from which q is removed and R is the distance to a ligand atom to which q is removed. In a more sophisticated treatment qe^2/r is replaced by the results of a quantum mechanical calculation, but even in this case the first term remains approximately proportional to q. If there are several ligands then the expression becomes

$$\Delta E = qe^2/r + e^2 \sum_i q_i/R_i ,$$

where q_i is the charge on the ith ligand.

We now make the questionable assumption that R_i, the distance to the ith ligand, is independent of what the ligand is (or, that $1/R_i$ can be replaced by some average value $1/R$). Then

$$\Delta E = qe^2/r + (\Sigma q_i)\, e^2/R$$

Since the molecule is neutral $q = \Sigma q_i$ and

$$\Delta E = qe^2(1/r - 1/R)$$

as for the case of only one ligand. The important point is that the shift is approximately proportional to the charge on the central atom and approximately independent of how the balancing charge is distributed among the several ligands.

The above paragraph represents the argument for seeking some correlation between the measured shifts and atomic charges. Satisfactory

correlations have been found for nitrogen 1s, sulfur 1s and 2p, and chlorine 2p binding energies.[1-4] To obtain atomic charges for nitrogen and sulfur, Nordberg and co-workers[2] have taken the charge on an atom to be equal to the formal charge plus the sum of the ionic characters of the bonds attached to the atom. The ionic character I was obtained from an empirical relationship given by Pauling:[21]

$$I = 1 - \exp\left[0.25\,(X_A - X_B)^2\right]$$

where X_A and X_B are the electronegativities of the atom of interest and of the atom joined to it. This relationship is based on the dipole moments of HI, HCl, and HBr and probably underestimates I. In spite of this Nordberg et al.[2] and Hamrin et al.[4] have found good correlations between measured shifts for nitrogen and sulfur compounds and the calculated charges.

If the halomethane data are treated in this way the results are unsatisfactory. Although all of the fluorine data fall on a straight line and the chlorine and bromine data fall approximately on a straight line when plotted against such charges, these lines differ in slope from one another by a factor of about 2.

The problem seems to lie with the use of Pauling's relationship for the ionic character. Gordy[22] has made a more critical analysis of the dipole moment data and has combined this with results of nuclear quadrupole resonance experiments to conclude that

$$I = (X_A - X_B)/2 \quad \text{for} \quad |X_A - X_B| < 2$$

$$I = 1 \quad \text{for} \quad |X_A - X_B| > 2$$

For all systems considered here, the first of these expressions applies.

For all of the halomethanes, the formal charge on the carbon is zero. Then combining the assumption made by Nordberg et al.[2] with Gordy's expression we conclude that the charge on the central carbon atom is given as

$$q = \sum_i (X_i - X_C)/2$$

where X_i is the electronegativity of the ith ligand and the sum is over all the ligands. Combining this result with the idea expressed above that the shift in energy(relative to atomic carbon) is proportional to q we have

$$\Delta E \propto \sum_{i=1}^{4} (X_i - X_C)$$

or for methane

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

Then the shift between methane and any of the halomethanes will be

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

which is what is plotted in Figure 5.

We can examine this relationship more quantitatively. The proportionality constant relating the energy shift to the electronegativity difference(as determined from the straight line of Figure 5) is 1.48 eV per electronegativity unit. From Gordy's relationship between electronegativity and partial ionic character this corresponds to about 3 eV for a change in charge of 1 electronic charge. Let us compare this value with what we might obtain from the simple electrostatic model discussed above. According to this model

$$\Delta E = q\, e^2(1/r - 1/R)$$

The Hartree-Fock calculations of Siegbahn and coworkers[12] indicate that removal of an sp^3 hybrid electron from carbon causes a shift of the carbon 1s electrons by 17.1 eV. We may thus replace e^2/r with this quantity. The radius R to which the electron is removed is not less than about 1 Å (CH distance) and no more than 2 Å (C Br distance); as an average we might take 1.5 Å. Then $\Delta E \approx 7.5$ q eV. This calculation assumed that the charge distribution in the ion is the same as that in the molecule. We have seen above that we must take into account the polarisation of the ligands by the positively charged central atom. This leads to a relaxation energy of about 2 eV per electronic charge. Combining this with the above expression we conclude that ΔE should be about equal to 5.5 eV per electronic charge. This is still somewhat larger than the value of 3 eV determined from the experimental data. These could be brought into better agreement by assuming either a smaller average value of R(1.2 Å) or that the ionic character is less than $(X_A - X_B)/2$.

Let us look at the first of these. Taking the electronegativity of carbon as 2.5 and that of chlorine as 3.0, we conclude that the charge on the carbon atom in carbon tetrachloride is +1.0 e. As opposed to this, Gordy[21] has estimated from quadrupole coupling data that the charge is only +0.48. Similarly, using 4.0 as the electronegativity of fluorine and 2.1 for hydrogen we obtain +2.05 as the carbon charge in fluoroform. Schwartz, Coulson, and Allen,[11] using empirically corrected Hartree-Fock results find a charge of only 0.53 on this atom. Furthermore, if the charge of the carbon is a high as +2, the assumption that the shift in energy varies linearly with charge is almost certainly wrong.[12] Gordy's formula, however, applies only to the ionic character of the σ part of the bond. In carbon tetrachloride

there is a partial cancellation of the charge transferred from carbon to chlorine in the σ bond by a back donation of electrons in the π bond. Thus the effective ionic character of the bond is substantially less than would be predicted by the formula $(X_A - X_B)/2$.

Looking now at the second point mentioned above, we note that the electronegativity[22] of a methyl group is 2.33 while that of a CCl_3 group is 2.58. Using Gordy's rule, then the ionic character of a bond between one of these groups and a chlorine would be 0.67 for the methyl and 0.42 for CCl_3. The corresponding charges on the chlorines are -0.34 for CH_3Cl and -0.21 for CCl_4. Because of the changing electronegativity of the central atom the charge removed by the chlorines is not proportional to the number of chlorines. (In carbon tetrachloride, the charges are even less then indicated here, because of the π bonding). Similar conclusions are drawn from the theoretical calculations of Schwartz, Coulson, and Allen. They show that for the fluorinated methanes the charge on the fluorines drops from -0.212 for CH_3F to -.208 for CHF_3. In the binding energy shifts there is some compensation for this effect: Although the charge increases less than in direct proportion to the number of fluorines, the binding energy probably increases more than in direct proportion to the charge.

Summarizing this section, we have seen that there is a linear correlation between the binding energy shifts and the electronegativity of the ligands. We have seen a plausible argument that there should be such a linear correlation. However, to obtain a satisfactory agreement between the experimental values and theoretical estimates we must, first allow for the relaxation energy in the ion, and, second, use ionic characters that are rather smaller than those obtained from Gordy's formula. This formula

applies only to the σ bonds and we must reduce the ionic character from the predicted value to account for back bonding in the π bond.

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FIGURE CAPTIONS

Fig. 1. Spectrum of carbon 1s and chlorine 2s electrons in fluoroform and methylene chlordie. The solid line represents a least squares fit to the data. Exciting radiation is magnesium K_α x rays.

Fig. 2. Spectrum of fluorine 1s electrons in carbon tetrafluoride and methyl fluoride. The solid line represents a least squares fit to the data. The splitting and line widths indicated were determined by this least squares procedure. The exciting radiation is magnesium K_α x rays.

Fig. 3. Experimental(points) and theoretical(solid line) variation of carbon 1s binding energies with number of fluorines attached to a single carbon. Both the experimental and theoretical values are plotted relative to that of methane. The theoretical values were obtained from Hartree-Fock calculations by use of Koopmans' theorem (see ref.7).

Fig. 4. A comparison of the one electron energy as determined by Koopmans' theorem with the experimental values. The picture is meant to be schematic; however the numbers chosen are for the carbon 1s electrons of fluoroform. See text.

Fig. 5. The carbon 1s binding energies (relative to that of methane) for halomethanes are plotted versus the sum of electronegativity differences. The difference is taken between the electronegativity of the ligand and that of hydrogen. The sum is taken over all the ligands.

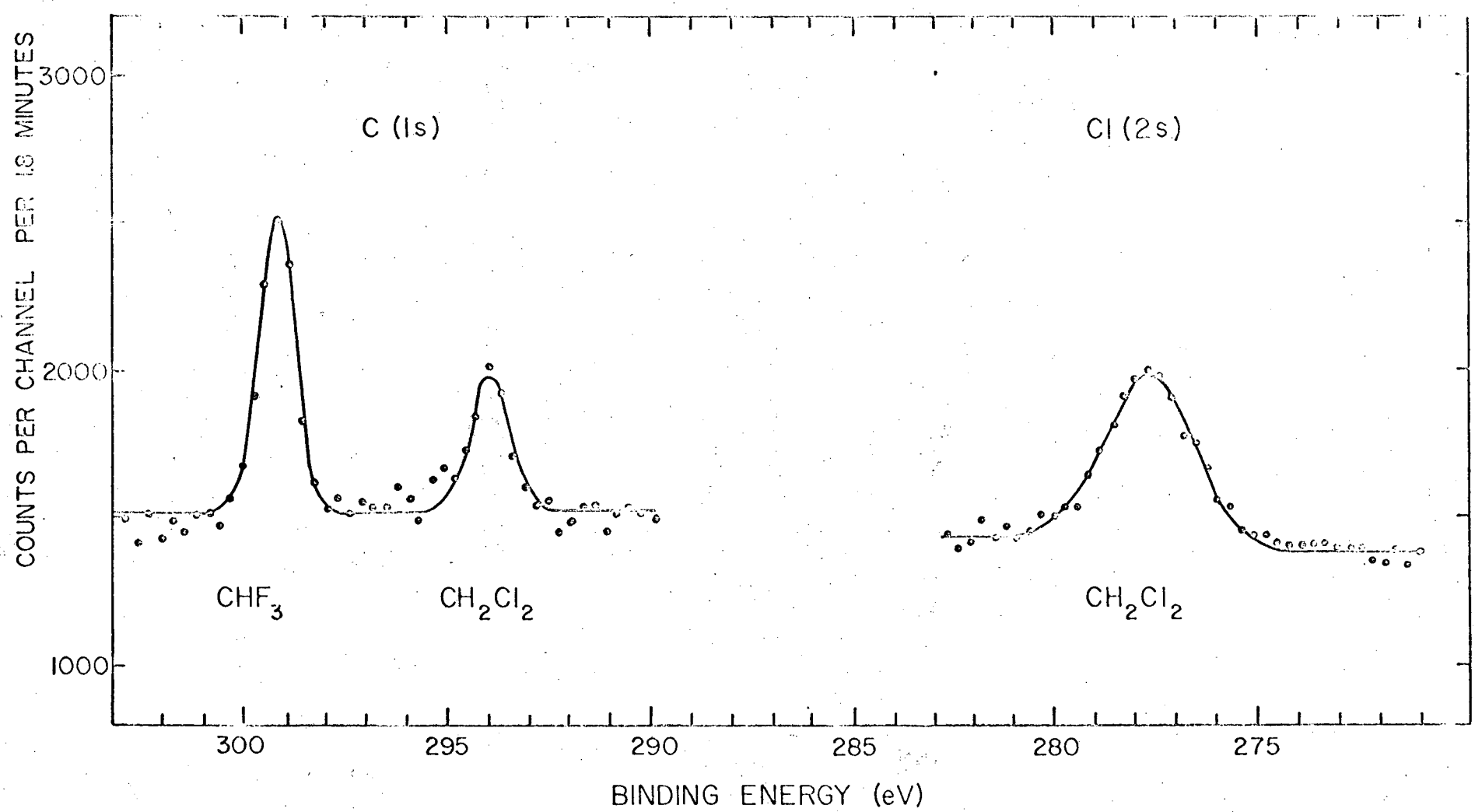
COUNTS PER CHANNEL PER 18 MINUTES
3000
2000
1000
C (1s)
Cl (2s)
CHF3
CH2Cl2
CH2Cl2
300
295
290
285
280
275
BINDING ENERGY (eV)

Fig. 1

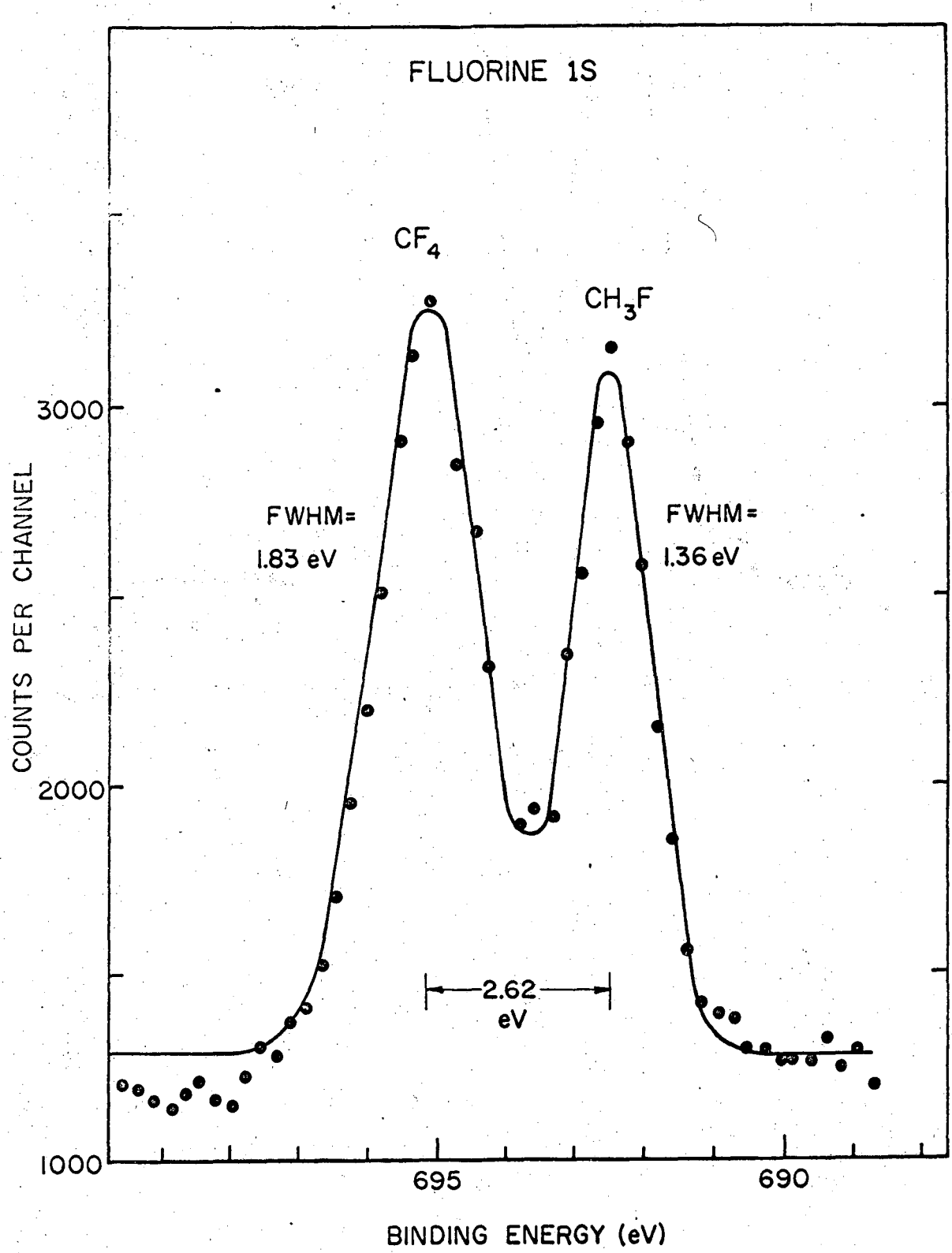
FLUORINE 1S
CF4
CH3F
FWHM=
1.83 eV
FWHM=
1.36 eV
2.62
eV
3000
2000
1000
COUNTS PER CHANNEL
695
690
BINDING ENERGY (eV)

Fig. 2

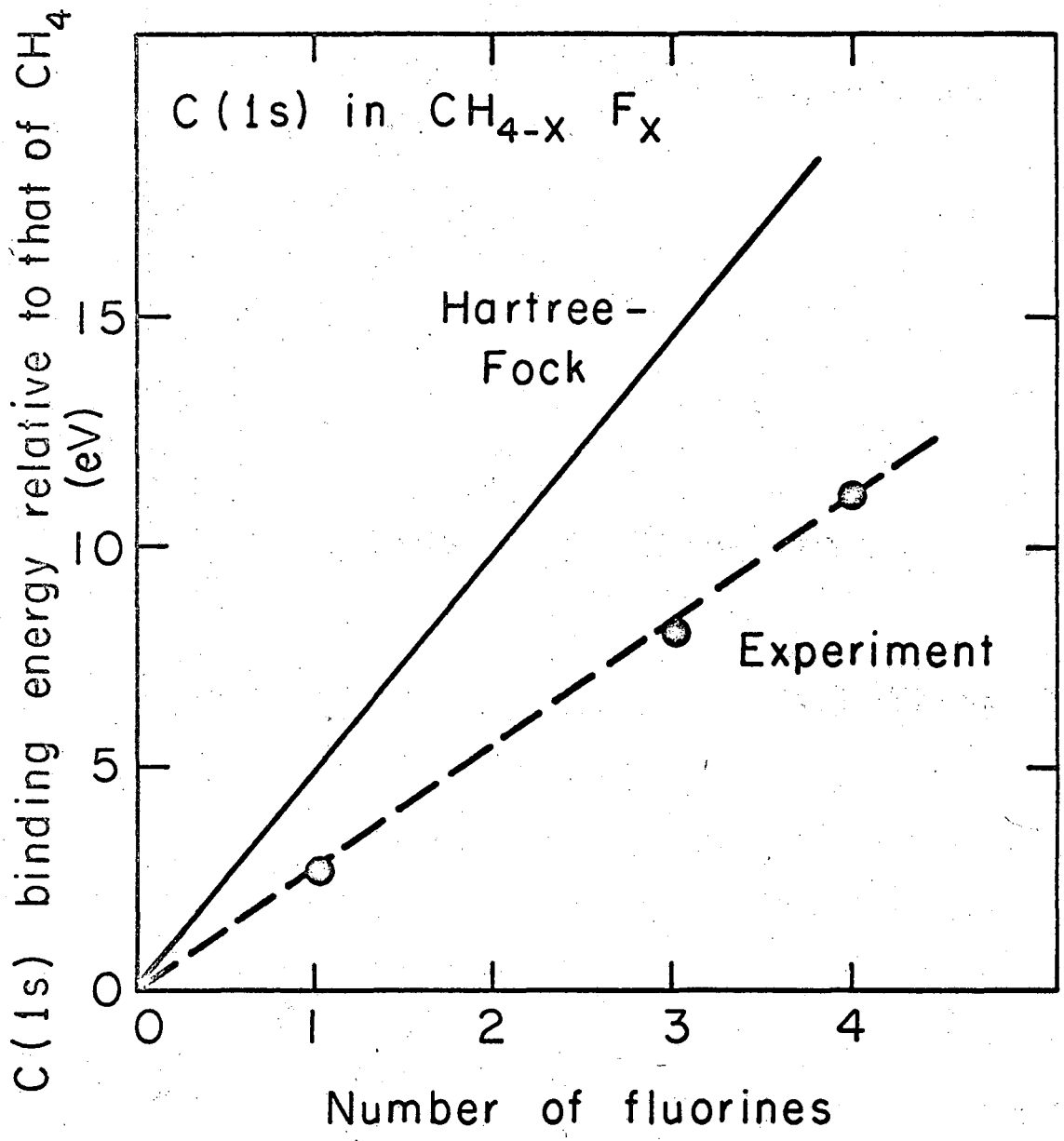

Fig. 3

XBL697-3304

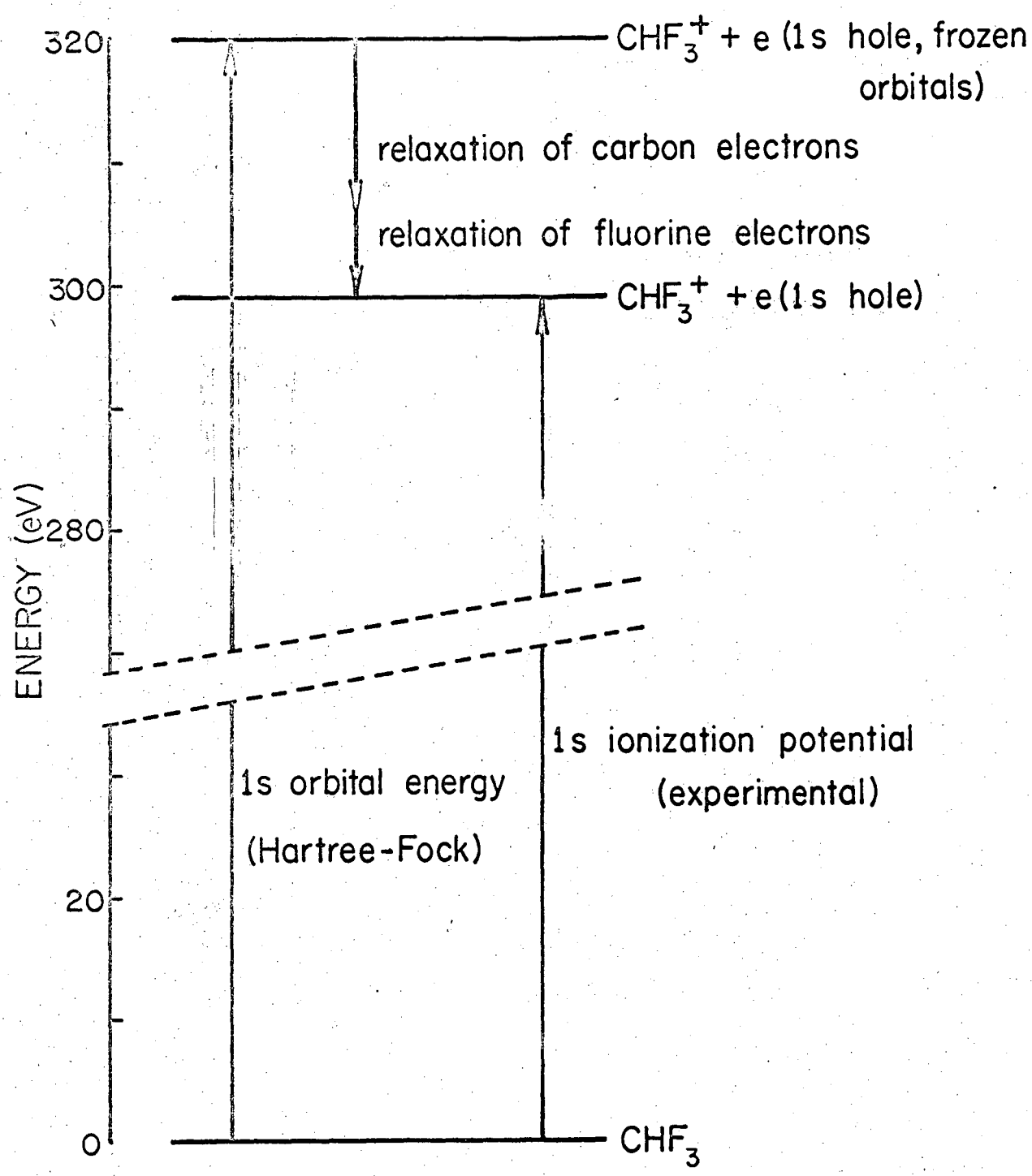
320
300
280
20
0
ENERGY (eV)
CHF_3^+ + e (1s hole, frozen orbitals)
relaxation of carbon electrons
relaxation of fluorine electrons
CHF_3^+ + e (1s hole)
1s orbital energy (Hartree-Fock)
1s ionization potential (experimental)
CHF_3

Fig. 4

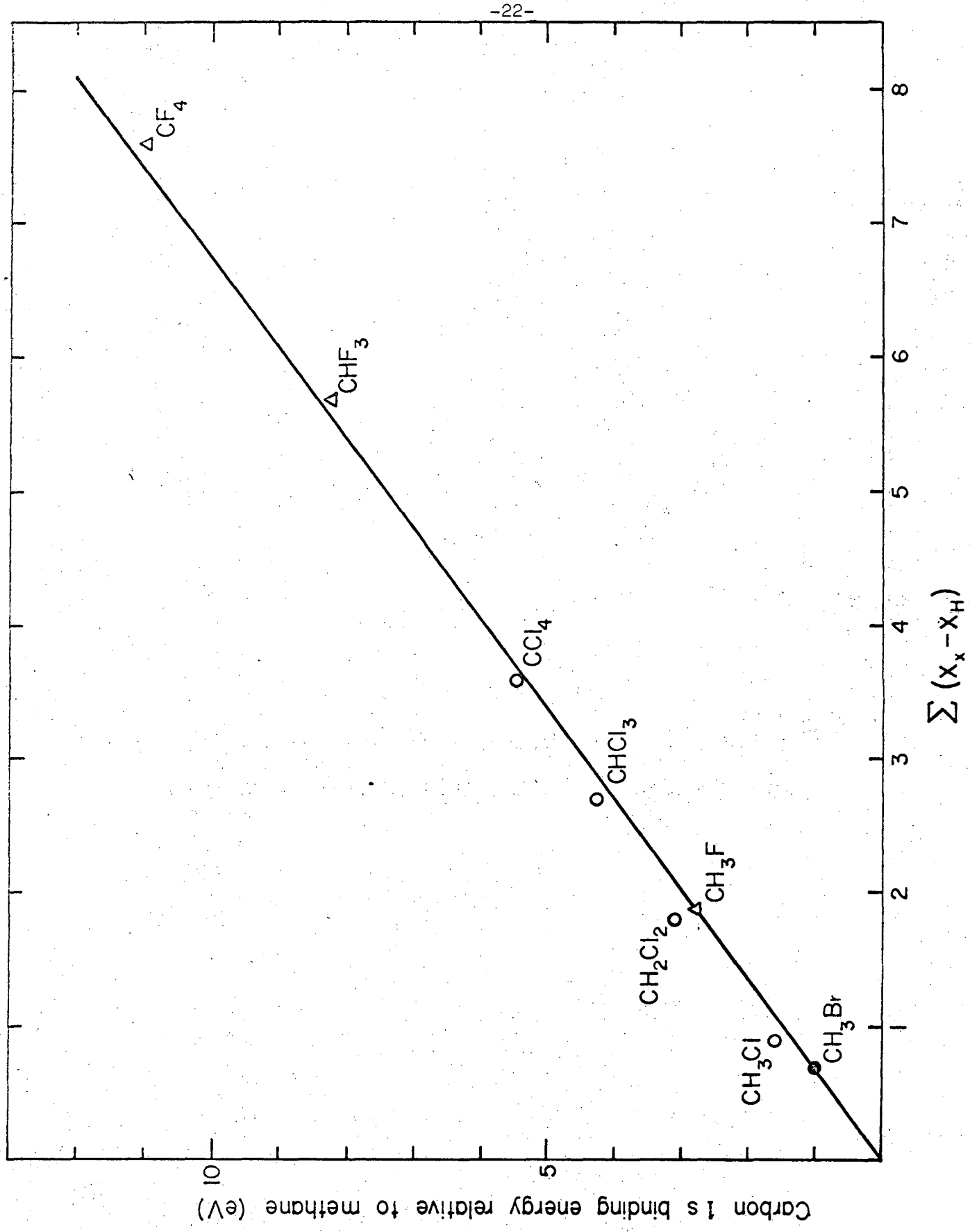
Carbon 1 s binding energy relative to methane (eV)
10
5
$\sum (x_x - x_H)$
1
2
3
4
5
6
7
8
CF_4
CHF_3
CCl_4
$CHCl_3$
CH_3F
CH_2Cl_2
CH_3Cl
CH_3Br

Fig. 5

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