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CORE-LEVEL BINDING ENERGY SHIFTS IN SMALL MOLECULES*

D. W. Davis, M. S. Banna, and D. A. Shirley

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ABSTRACT

Binding-energy shifts of carbon and fluorine 1s levels in small (2 to 4 carbon) fluorinated hydrocarbons are reported. Carbon, nitrogen, and oxygen 1s shifts for a number of other molecules are also reported. All samples were studied as gases: a total of 72 new shifts were measured. The results are analyzed using three electrostatic potential models. First the RPM theory, which includes final-state relaxation, was used. It correctly predicts the N(1s) shifts in methylamines, for which relaxation shifts are dominant, showing the importance of considering relaxation when comparing unlike molecules. The GPM theory involves only ground-state properties. It gives excellent results for carbon, oxygen, and fluorine shifts if only groups of similar molecules are compared. Finally, atomic charges are derived using the ACHARGE model. These charges agree very well with CNDO/2 charges. The "charge alternation" effect deduced in CNDO/2 calculations was observed--substitution of F for H on a carbon atom decreases the charge on the next carbon by about 0.02_5 e in ethane, 0.04_5 e in benzene, and 0.06 e in ethylene, according to the ACHARGE analysis. Inductive charge transfer was found to be additive.

I. INTRODUCTION

Chemical shifts in binding energies of core-level electrons have recently received considerable experimental and theoretical study. These shifts are of chemical interest because they can provide information about the relative distributions of valence electrons within molecules. Chemical shifts have been interpreted in various ways, ranging from correlations with atomic charges to the prediction of shifts from ab initio calculations of core-level binding energies. Some of the most successful interpretations involve the prediction of core-level chemical shifts by calculation of (closely related) shifts in the electrostatic potential at the nucleus.[1] This approach has two advantages which make it appealing to chemists: (1) the electrostatic potential at the nucleus is readily calculated using semi-empirical wavefunctions; (2) within the framework of this method, empirical atomic charges may be obtained from experimental chemical shifts.[2]

In this work we report a total of 79 core-level binding energy shifts in small molecules in the gaseous state. Special emphasis has been laid on fluorinated hydrocarbons, to assess the effect of fluorine substitution on C(1s) binding energies, although a number of other molecules have been studied as well. In most cases no previous core-level shifts have been reported. A few cases are reported that either have not been studied as gases or for which the error limits have now been reduced.

Several related potential models are used to interpret the observed core-level shifts. The first model includes relaxation, or the effect of changes in the valence levels upon core-level ionization. This model is called the "relaxation potential model" or RPM. The second model is called

the ground-state potential model (GPM) because it uses only the ground-state electronic distributions. Both models will be used with CNDO/2 wavefunctions to interpret chemical shifts. The third approach is also a potential model, but instead of using molecular-orbital theory to predict charge distributions, this model deduces atomic charges from experimental shifts. It is called the ACHARGE model.

Experimental results are reported in Sec. II. The RPM and GPM are briefly discussed in Sec. III and applied to the measured chemical shifts in Sec. IV. The ACHARGE model is used to derive atomic charges in Sec. V.

II. EXPERIMENTAL

Binding energies are determined in x-ray photoemission on gases by the energy conservation equation

$$E_B + K = h\nu \quad , \tag{1}$$

where E_B represents the binding energy, K represents the experimentally determined kinetic energy, and $h\nu$ is the energy of the exciting radiation. The radiation used in these experiments was the Mg $K\alpha_{1,2}$ x-ray (1253.6 eV), and the kinetic energy was measured in the Berkeley iron-free spectrometer.[3] In all cases reported here the samples studied as gases, at pressures of $(2 - 5) \times 10^{-2}$ Torr. Experimental details have been given elsewhere.[2a] Core-level chemical shifts were obtained relative to selected reference gases. Usually the reference gas and the sample gas were studied simultaneously. A typical C(1s) spectrum, of 1,1-difluoroethane with a CF_4 reference, is shown in Fig. 1. In a few cases, notably the F(1s) shifts, the reference gas was studied before and after the sample gas.

Except for some of the F(1s) shifts, the errors quoted are statistical and represent the standard deviation of several measurements of the chemical shift. For some of the F(1s) shifts, the quoted errors also include contributions due to drifts that were observed in the apparent binding energies.

The peak positions were obtained by fitting the spectra with Lorentzian peak shapes. No account was taken of the doublet character of the exciting radiation, but this does not affect the values of the chemical shifts. The experimental shifts are presented in Table I. In each case the shift (and error) is given relative to the reference gas that was actually used.

III. THE RPM AND GPM POTENTIAL MODELS

In the RPM approach[4] shifts are predicted by the equation

$$\Delta E_B = -\Delta V_a - \Delta V_R \quad . \tag{2}$$

Here V_a is the initial-state electrostatic potential energy at the host nucleus, i.e., the nucleus at which the ionized core electron was localized. It is given by the expression

$$V_a = \sum_i \int \psi_i^*(i)\ (e^2/R_{ia})\ \psi_i(i)\ d\tau_i - \sum_{j \neq a} Z_j'/R_{aj} \quad ,$$

where ψ_i is the molecular orbital for electron i. In the calculations presented here, the contribution of the core electrons at the host atom to V_a is neglected; therefore i is summed over valence electrons only. Here "a" refers to the host nucleus. Z_j' equals the charge on nucleus j, Z_j, minus the number of core electrons centered at nucleus j. V_R represents the final-state contribution to binding energies, and is given by the equation

$$V_R = \frac{1}{2}(V_a^+ - V_a) \quad , \tag{3}$$

where V_a^+ is the potential energy at the nucleus in the final-state molecular ion with a core vacancy at nucleus a. The valence orbitals ψ_i^+ were approximated by simply increasing Z_a to $Z_a + 1$ and recomputing the wavefunctions.[4a] CNDO/2 wavefunctions were used to get the ψ_i's. Because of neglect of differential overlap in CNDO/2, it was necessary to neglect essentially all of the off-diagonal matrix elements of R_{ia}^{-1} between atomic orbitals. The remaining matrix elements were calculated assuming Slater atomic orbitals and using the

formulas developed by Roothaan.[5] This type of calculation of V_a (or V_a^+) is known as the pp' version.[4] The relaxation model follows closely the formalism of Hedin and Johansson,[6] which predicts absolute binding energies for atoms quite accurately. It seems to give a physically correct representation of the ionization process in contrast to the GPM which implicitly assumes that the valence levels do not change upon core-level ionization. The RPM approach is discussed in more detail elsewhere.[4]

In the GPM approach chemical shifts are calculated by the equation

$$\Delta E_B = -\Delta V_a \quad . \tag{4}$$

Obviously with GPM we must assume that ΔV_R is considerably smaller than ΔV_a. However, the total relaxation energy, V_R, is usually larger than the total range of ΔV_a. The range of validity of the GPM approach therefore requires some examination. Again the GPM approach is discussed in more detail elsewhere.[4] In this paper we shall concentrate on the accuracy with which it predicts shifts, particularly in comparison with the RPM method.

IV. COMPARISON OF EXPERIMENTAL SHIFTS WITH RPM AND GPM PREDICTIONS

Predicted values of shifts are set out in Table II. The shifts are referenced to the hydrides of C, N, O, and to CF_4. Both RPM and GPM shifts are given for C, N, and O, while for F only GPM values are given because neon is not included in the CNDO/2 program. Experimental shifts relative to the hydrides, deduced from Table I, are also listed.

In comparing experimental and theoretical shifts, we recall first that RPM predictions have already been found superior to GPM predictions of core-level shifts for a single element in diverse molecular environments.[4a] This is a result of the ability of RPM theory to account for certain trends in V_R,[4b] notably: (1) an increase in V_R with the number of atomic centers in a molecule; (2) an increase in V_R when ligands are added to the host atom; (3) a decrease in V_R with the substitution of fluorine for hydrogen in a chemical bond to the host atom; (4) the relatively high values of V_R for cyclic systems. The first two trends are the most important; for example, ΔV_R between diatomics and polyatomics is predicted[4] to be several eV in most cases. The trends can be rationalized on the basis of electronic repulsion in the final state: usually about 0.5 to 1 unit of electronic charge relaxes onto the atom which has the core vacancy, creating a net positive charge on the other atoms. If the molecular ion consists of many atoms, this positive charge can be highly dispersed, thereby stabilizing the ion. This reasoning has been applied to core-level photoemission in solids, as well as free molecules.[7]

One notable example of the effect of V_R upon core-level chemical shifts is the trend in the N(1s) shifts in the methylamines. Both the GPM theory and Pauling atomic charges predict a small but steady increase in the N(1s) binding energy proceeding along the series of amines from NH_3 to $(CH_3)_3N$.

However, the observed binding energies actually decrease slightly along the series.[8] The RPM results indicate that V_R increases along the series faster than V_N decreases. As one proceeds along the series, the number of atomic centers increases, and the final state becomes more stable because of a greater dispersal of positive charge through relaxation of electrons toward the N(1s) vacancy. Table III lists the RPM and GPM binding-energy shift and V_R predictions, initial and final state atomic charges for nitrogen, and the observed shifts[8] for the methyl amines. Figure 2 shows relative N(1s) binding energies in these molecules, indicating the dramatic superiority of RPM over GPM predictions.

From the above discussion it would appear that RPM alone should be used to predict shifts and the GPM theory should be discarded. In fact it is desirable to retain the GPM approach for interpreting shifts in ground-state charge distributions among similar molecules, as discussed, for example, in Sec. V. The above example makes it quite clear, however, that the molecules to be compared must be chosen with care. From the general observations about variations in V_R, we would expect that the GPM should predict shifts most accurately between atoms which are bonded similarly (i.e. similar valences), and which are in molecules of similar size. For example, the GPM predictions should be more applicable to C(1s) shifts among the fluoromethanes than between methane and carbon monoxide. To test this idea further, the GPM values were compared separately among certain classes of molecules of similar structure and valency. The agreement with experiment was quite satisfactory. Results for several classes of molecules are discussed separately below.

Figure 3 shows shifts for fluorinated ethanes, compared with results of GPM and RPM calculations. The agreement is excellent in the GPM case (0.14 eV standard deviation) and very good for RPM (0.31 eV standard deviation).

There is considerable evidence that the CNDO/2 parameters tend to exaggerate the variation in V_R, thus giving a slope that is too large in Fig. 3. This trend was observed earlier[4a] for C(1s), N(1s), and F(1s) shifts, although partially obscured in that earlier work by scatter due to the inclusion of diverse compounds. The scatter is much smaller, and the exaggerated RPM slope therefore more apparent, in Fig. 3.

Fluorinated ethylenes provide an even more dramatic illustration of both effects noted above, as shown in Fig. 4. The slope $\Delta E(\text{theo})/\Delta E(\text{expt})$ exceeds unity, in this case for both the RPM and the GPM cases. Fitting lines with unit slope yields standard deviations of 0.38 eV (GPM) and 0.53 eV (RPM). For fitted slopes of 1.17 (GPM) and 1.25 (RPM), the standard deviations drop to 0.12 eV and 0.07 eV, respectively. Thus it appears possible to obtain excellent fits within these restricted classes of molecules with GPM or RPM theory, especially if the slopes are allowed to vary.

The RPM predictions of N(1s) shifts were found earlier to give far better agreement than GPM values. This conclusion was confirmed above for methylamines. At this time there aren't enough data available on N(1s) shifts to test GPM predictions for shifts within a class of similar molecules.

Encouraged by the adequacy of the GPM predictions for C 1s shifts in two carefully selected classes of molecules, we have compared the GPM O(1s) shifts with experiment for oxygen bonded to one other atom and for oxygens bonded to two other atoms (Figs. 5 and 6). In both cases the agreement is good, with standard deviations of 0.88 eV and 0.40 eV, respectively, relative to a line with unit slope.

Proceeding to F(1s) shifts, we have plotted in Fig. 7 the GPM theory values versus experiment for fluorines in substituted methanes, ethanes, and

ethylenes. Again the agreement is good, with most of the points falling within 0.2 eV of the predicted values and no evidence in this case of systematic deviations.

In summary, we have shown in this section that the RPM theory gives better results than the GPM theory if shifts are predicted among unlike molecules. When the molecules to be compared are carefully selected to be similar, however, the GPM theory gives excellent predictions. We shall make use of this latter observation in the next section.

V. THE ACHARGE ANALYSIS

Recently it has been shown[2] that empirical atomic charges may be obtained from core-level chemical shifts using the ground state potential model. If off-diagonal matrix elements of R_{ia}^{-1} between atomic orbitals (as in the CNDO/2 model presented here) are neglected, and if the remaining matrix elements are treated as if they contained only s orbitals, the ground state potential model takes on a simple form. The potential energy that a core electron at nucleus a would experience due to the valence electrons on atom a and the charges on other atoms is given by

$$V_a = -\left[q_a e^2 \langle 1/R_a \rangle + \sum_{j \neq a} e^2 q_j / R_{aj} \right] + Z_a' e^2 \langle 1/R_a \rangle \quad . \tag{5}$$

Here $\langle 1/R_a \rangle$ is the expection value of 1/r for the valence electrons in atom a. It is a good approximation to the potential energy between core and valence electrons belonging to nucleus a. The net atomic charge on atom j is given by $q_j = Z_j' - P_j$, where Z_j' is the atomic number minus the number of core electrons and P_j is the valence-shell population. R_{aj} is the distance between nuclei a and j. The expression for chemical shifts using Eq. (5) becomes

$$\Delta E_B^a = E_B^a(\text{sample}) - E_B^a(\text{reference}) = q_a e^2 \langle 1/R_a \rangle + \sum_{j \neq a} e^2 q_j / R_{aj}$$

$$- Z_a' e^2 \langle 1/R_a \rangle + V_a(\text{reference}) \quad . \tag{6}$$

Equation (6) is a linear equation in the q_j's; if enough chemical shifts are measured and if enough reference potentials are known, then the linear equations

may be solved for the q_j's. For the simple case in which the reference state is one in which the charges q are all zero, we have $V_a(\text{reference}) = Z_a' e^2\langle 1/R_a \rangle$ and

$$\Delta E_B^a = q_a e^2\langle 1/R_a \rangle + \sum_{j\neq a} e^2 q_j/R_{aj} \quad . \tag{7}$$

Of course, one also has the electroneutrality condition for the q_j's:

$$\sum_j q_j = 0 \quad .$$

This model, called ACHARGE,[2a] has been applied here to determine charge distributions in fluoromethanes, fluoroethanes, fluoroethylenes, and some related fluorocarbons. We used values of $k_C = e^2\langle 1/R_a \rangle_C = 22.0$ eV/$|e|$ for carbon 1s shifts and $k_F = e^2\langle 1/R_a \rangle_F = 32.5$ eV/$|e|$ for fluorine 1s shifts, as discussed earlier.[2a] Hydrogen charges on a given molecule were assumed to be equal when necessary, and the charge neutrality condition was invoked in all cases. The ACHARGE model was then used with molecular geometries and experimental binding-energy shifts to determine atomic charges.

The derived charges are given in Table IV, along with CNDO/2 atomic charges. The two sets of charges agree reasonably well on the whole. One result of special interest is that both sets give a <u>negative</u> charge for the carbon <u>β</u> to a fluorine atom. This is contrary to the intuitive notion that electronegative substituents tend to withdraw electrons from all other atoms in the molecule, and it has received considerable comment in discussions of CNDO theory.[9] The effect is particularly noticeable in the fluoroethylenes, in which addition of two fluorines to the α carbon causes the β carbon to have

a charge of -0.14 units. This is probably due to the polarizability of the π electrons; similar effects were noted in the fluorobenzenes.[2a]

Another trend which is common to both sets of charges is the additive nature of inductive effects; for example, two fluorines have about twice the effect as one on both α and β carbons in the fluoroethanes and fluoroethylenes. Furthermore, the effect of a substituent on an atom is relatively independent of the other substituents bonded to that atom. For example, the lowering of charge on a β carbon atom via addition of a fluorine to the α carbon atom is independent of what is bonded directly to the β carbon atom. This phenomenon, which can be termed the <u>principle of additive inductive effects</u>, is the charge analogue of the previously-observed group shift.[1e,9] Invoking this principle and considering the above data on fluorinated ethanes and ethylenes as well as the earlier fluorobenzene results,[2a] we find that, on the average, substitution of a fluorine for a hydrogen will raise the charge on a carbon atom by +0.24 in ethane, +0.23 in benzene, and +0.25 in ethylene. The carbon that is β to the fluorine has its charge lowered, by -0.02_5 in ethane, -0.04_5 in benzene, and -0.06 in ethylene. The fluorine charges are respectively -0.23, -0.19, and -0.25.

Another effect that is related to the additive inductive effect is the symmetry in charge transfer between fluorine substitution in hydrocarbons and hydrogen substitution in fluorocarbons. Thus substitution of F for H in ethylene changes the charge on the host carbon by +0.25 e and on the other carbon by -0.05 e. The corresponding process for C_2F_4--hydrogen substitution--changes the host carbon's charge by -0.25 e and the other carbon's charge by +0.06 e. Figure 8 shows the charge shifts $\Delta q(C_F)$ induced by hydrogen substitution in C_2F_4 plotted against $\Delta q(C_H)$, those induced by fluorine substitution in C_2H_4,

for several fluorine-substituted ethylenes. The straight line through these points (which were deduced from Table IV) emphasizes the remarkable symmetry of these two processes.

It is noteworthy that such close agreement exists between CNDO/2 atomic charges and those obtained from ACHARGE, especially for the larger molecules in Table IV. This has been noted previously.[2a,b,c] It gives credence to the CNDO/2 charge distributions. The two methods of obtaining atomic charges are very similar in that both neglect "differential overlap" between atomic orbitals, thereby forcibly assigning all the charge to individual atoms. Thus part of the agreement is probably due to this common approximation.

FOOTNOTES AND REFERENCES

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

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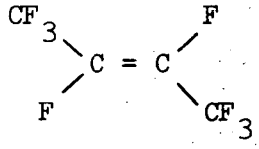
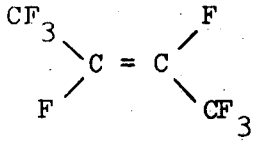
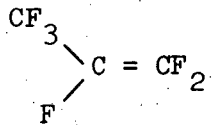
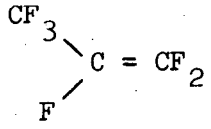
Table I. Experimental Chemical Shifts

Compound	Reference	Core Level[a]	E_B(compound) - E_B(Ref) (eV)
C_6H_6	CF_4	C 1s	-11.54(2)
CHF_3	CF_4	C 1s	-2.72(3)
CH_2F_2	CF_4	C 1s	-5.52(4)
CH_2F_2	CF_4	F 1s	-1.83(10)
CH_3CH_3	CF_4	C 1s	-11.20(4)
CH_3CH_2F	CF_4	C 1s	-8.57(5), -10.77(5)
CH_3CH_2F	CF_4	F 1s	-3.20(6)
CH_3CHF_2	CF_4	C 1s	-5.91(4), -10.34(4)
CH_3CHF_2	CF_4	F 1s	-2.22(6)
CH_3CF_3	CF_4	C 1s	-3.32(6), -9.89(6)
CH_3CF_3	CF_4	F 1s	-1.40(20)
CF_3CF_3	CF_4	C 1s	-2.11(6)
CF_3CF_3	CF_4	F 1s	-0.19(10)
$CF_3CF_2CF_3$	CF_4	C 1s	-2.22(3), -4.22(3)
$CF_3CF_2CF_3$	CF_4	F 1s	-0.25(20), -0.91(20)
$CF_3CH_2NH_2$	CF_4	C 1s	-3.54(6), -9.19(6)
$CF_3CH_2NH_2$	CF_4	F 1s	-1.45(20)
$CF_3CH_2NH_2$	N_2	N 1s	-4.07(4)
$CH_3CH_2NH_2$	N_2	N 1s	-4.93(4)
CH_3CH_2OH	O_2	O 1s	-4.63(6)
CF_3CH_2OH	O_2	O 1s	-3.51(4)
CF_3CH_2OH	CF_4	C 1s	-3.25(6), -9.19(6)
CF_3CH_2OH	CF_4	F 1s	-1.09(20)

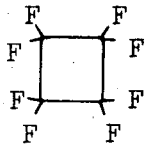
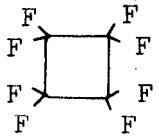
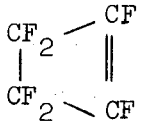
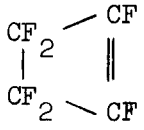
(continued)

Table I. (continued)

Compound	Reference	Core Level[a]	E_B(compound) - E_B(Ref) (eV)
$(CF_3)_3COH$	CF_4	C 1s	-6.93(20), -2.50(20)
$(CF_3)_3COH$	O_2	O 1s	-2.63(6)
$H_2C = CH_2$	CF_3H	C 1s	-8.4(2)[b]
$H_2C = CHF$	CF_4	C 1s	-8.48(10), -10.86(10)
$H_2C = CHF$	CF_4	F 1s	-2.26(10)
$H_2C = CF_2$	CF_4	C 1s	-5.86(3), -10.63(3)
$H_2C = CF_2$	CF_4	F 1s	-1.08(10)
$CHF = CF_2$	CF_4	C 1s	-5.71(4), -8.09(4)
$CHF = CF_2$	CF_4	F 1s	-0.72(20), -1.42(20)
$CF_2 = CF_2$	CF_4	C 1s	-5.42(4)
$CF_2 = CF_2$	CF_4	F 1s	-0.50(20)
	CF_4	C 1s	-2.27(5), -7.04(5)
	CF_4	F 1s	-0.56(20), -0.98(20)
	CF_4	C 1s	-2.36(10), -4.98(10), -7.28(10)
	CF_4	F 1s	-0.31(30), -0.72(30), -1.28(30)
$CF_3CH = CH_2$	CF_4	C 1s	-3.24(10), -9.93(10), -10.40(10)

(continued)

Table I. (continued)

Compound	Reference	Core Level[a]	E_B(compound) - E_B(Ref) (eV)
$CF_3CH = CH_2$	CF_4	F 1s	-1.40(20)
	CF_4	C 1s	-4.71(5)
	CF_4	F 1s	-0.44(20)
	CF_4	C 1s	-4.77(7), -7.08(7)
	CF_4	F 1s	-0.69(20), -1.49(20)
CH_3NO_2	CF_4	C 1s	-8.92(5)
CH_3NO_2	N_2	N 1s	2.23(4)
CH_3NO_2	O_2	O 1s	-3.98(4)
$(CH_3)_2CHNO_2$	CF_4	C 1s	-9.35(10), -10.53(10)
$(CH_3)_2CHNO_2$	N_2	N 1s	1.58(3)
$(CH_3)_2CHNO_2$	O_2	O 1s	-4.36(3)
$C_6H_5NO_2$	N_2	N 1s	1.80(4)
$C_6H_5NO_2$	O_2	O 1s	-4.71(3)
	O_2	O 1s	-3.46(4)
$(CH_3CH_2)_2O$	O_2	O 1s	-5.30(10)

(continued)

Table I. (continued)

Compound	Reference	Core Level[a]	E_B(compound) - E_B(Ref) (eV)
CH_4	CF_4	C 1s	-11.0(2)[c]

[a]The O(1s) shifts are taken relative to the lower-binding-energy O_2(O 1s) peak.

[b]T. D. Thomas, J. Chem. Phys. 52, 1373 (1970). These shifts are included for reference.

[c]T. D. Thomas, J. Am. Chem. Soc. 92, 4184 (1970).

Table II. Predicted core-level shifts (in eV), using the pp' version of both GPM and RPM theories.

Molecule	ΔE_B, GPM theory	ΔE_B, RPM theory	ΔE_B(expt)
	Carbon Nuclei		
CH_4	0	0	(0)
CH_3F	2.99	2.96	2.8[a]
CH_2F_2	5.82	5.96	5.48(20)
CHF_3	8.54	9.05	8.28(20)
CF_4	11.13	12.11	11.0(2)[a]
C_2H_6	0.34	-0.27	-0.20(20)
$CH_3^* - CH_2F$	0.78	0.14	0.23(20)
$CH_3 - C^*H_2F$	3.06	2.65	2.43(20)
$CH_3^* - CHF_2$	1.18	0.36	0.66(20)
$CH_3 - C^*HF_2$	5.66	5.44	5.09(20)
$CH^*_3 - CF_3$	1.70	0.85	1.11(20)
$CH_3 - C^*F_3$	8.04	8.01	7.68(20)
$CF_3 - CF_3$	9.70	9.40	8.89(20)
$CF_3 - C^*F_2 - CF_3$	7.95	6.54	6.78(20)
$CF_3 - CF_2 - C^*F_3$	9.77	9.24	8.78(20)
cyclo C_4F_8	7.72	5.96	6.29(20)
$CH_2 = CH_2$	-0.01	0.45	-0.1(2)[b]
$CH^*_2 = CHF$	0.22	-0.78	0.14(22)
$CH_2 = C^*HF$	2.95	2.32	2.52(22)
$CH^*_2 = CF_2$	0.50	-0.53	0.37(20)
$CH_2 = C^*F_2$	5.86	5.50	5.14(20)
$C^*HF = CF_2$	3.60	2.53	2.91(20)

(continued)

Table II. (continued)

Molecule	ΔE_B, GPM theory	ΔE_B, RPM theory	ΔE_B(expt)
	Carbon Nuclei		
$CHF = C^*F_2$	6.31	5.62	5.29(20)
$CF_2 = CF_2$	6.73	5.92	5.58(20)
$CH \equiv CH$	-0.39	-0.08	0.4[b]
benzene	0.57	-1.23	-0.4(22)
hexafluorobenzene	5.20	3.14	3.17(29)
HCN	0.31	1.80	2.6[c]
CH_3NO_2	3.01	1.91	2.08(20)
CO	0.67	4.65	5.4(29)
CO_2	6.57	9.60	6.84(29)
HCOOH	4.51	5.09	4.99(29)
CH_3OH	1.87	1.63	1.9(29)
cyclo C_2H_4O	1.93	1.29	2.01(29)
$(C^*H_3)_2CHNO_2$	1.38	0.34	0.47(22)
$(CH_3)_2C^*HNO_2$	3.09	1.41	1.65(22)
$CF_2 - C^*F$ | ‖ $CF_2 - CF$	4.85	2.77	3.92(20)
$C^*F_2 - CF$ | ‖ $CF_2 - CF$	8.03	6.29	6.23(20)
$CF_3(F)C = C^*(F)CF_3$	5.36	3.39	3.96(20)
$C^*F_3(F)C = C(F)CF_3$	9.05	8.67	8.73(20)
$C^*F_3 - CH_2NH_2$	7.99	7.88	7.46(20)

(continued)

Table II. (continued)

Molecule	ΔE_B, GPM theory	ΔE_B, RPM theory	ΔE_B(expt)
	Nitrogen Nuclei		
NH_3	0	0	(0)
CH_3NO_2	11.32	10.33	6.53(5)
$C_6H_5NO_2$	10.51	8.91	6.1(1)
$(CH_3)_2CHNO_2$	10.87	9.41	5.88(5)
	Oxygen Nuclei		
H_2O	0	0	(0)
$(CH_3CH_2)_2O$	2.30	-1.24	-1.83(11)
C_4H_4O	3.12	-0.53	0.01(6)
$(CH_3)_2CHNO_2$	0.64	-2.27	-0.89(5)
CH_3CH_2OH	2.10	0.07	-1.16(6)
CF_3CH_2OH	3.41	1.42	-0.04(6)
	Fluorine Nuclei		
CF_4	0		(0)
CF_3CF_3	0.11		-0.19(10)
CF_3H	-0.77		-0.90[a]
CF_3CH_3	-1.57		-1.4(10)
CH_2F_2	-1.55		-1.83(10)
CH_3CHF_2	-1.99		-2.22(6)
CH_3F	-2.34		-2.6[a]
CH_3CH_2F	-2.65		-3.20(6)
$CF_3CF_2CF_3$*	0.17		-0.25(20)

(continued)

Table II. (continued)

Molecule	ΔE_B, GPM theory	ΔE_B, RPM theory	ΔE_B(expt)
	Fluorine Nuclei		
$CF_3CF_2{}^*CF_3$	0.33		-0.91(20)
cyclo C_4F_8	0.15		-0.44(20)
$CF_2 = CF_2$	-0.15		-0.5(2)
$CHF = CF_2{}^*$	-0.80		-0.72(20)
$CH_2 = CF_2$	-1.33		-1.08(10)
$CHF^* = CF_2$	-1.02		-1.42(4)
$CH_2 = CHF$	-2.08		-2.26(10)
$CF_2^* - CF$ | ‖ $CF_2 - CF$	-0.11		-0.69(20)
$CF_2 - CF^*$ | ‖ $CF_2 - CF$	-0.64		-1.49(20)
$CF_3{}^*(F)C = C(F)CF_3$	-0.23		-0.56(20)
$CF_3(F^*)C = C(F)CF_3$	0.39		-0.98(20)

[a] T. D. Thomas, J. Am. Chem. Soc. 92, 4184 (1970).

[b] T. D. Thomas, J. Chem. Phys. 52, 1373 (1970).

[c] P. Finn, J. M. Hollander, and W. L. Jolly (unpublished).

[d] T. D. Thomas, J. Chem. Phys. 53, 1744 (1970).

Table III. N(1s) ionization in the methyl amines.

	q_N [c]	q_{N^+} [c]	V_R [c,d]	ΔE_B(ground state model) [b,c,d]	ΔE_B(relaxation model) [b,c,d]	ΔE_B(expt) [a,c,d]
NH_3	-0.23	-1.10	19.01	-2.32	-4.66	-4.35
CH_3NH_2	-0.20	-1.06	19.65	-1.98	-4.97	-4.8
$(CH_3)_2NH$	-0.17	-1.02	20.36	-1.62	-5.31	-5.0
$(CH_3)_3N$	-0.14	-0.99	20.91	-1.32	-5.56	-5.2

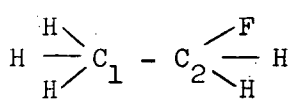
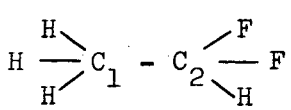
[a] From Ref. 8.

[b] All shifts are relative to N_2.

[c] From CNDO/2 wavefunctions.

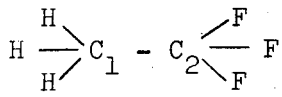
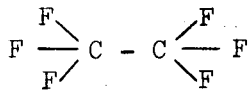
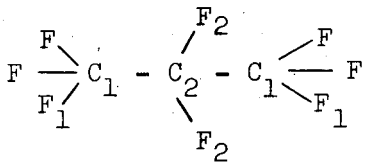
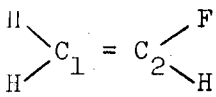
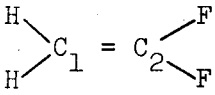
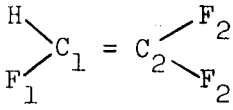
[d] In units of electron volts.

Table IV. Derived atomic charges.

Compound	Atom[a]	q^b (ACHARGE)	q^b (CNDO/2)
CH_4	C	0. (assumed)	-0.05
	H	0. (assumed)	0.012
CH_3F	C	0.25	0.18
	H	-0.009	0.004
	F	-0.22	-0.19
CH_2F_2	C	0.49	0.40
	H	-0.014	-0.005
	F	-0.23	-0.19
CHF_3	C	0.75	0.61
	H	-0.03	-0.02
	F	-0.24	-0.20
CF_4	C	1.00	0.81
	F	-0.25	-0.20
$CH_3 - CH_3$	C	0. (assumed)	0.
	H	0. (assumed)	0.
	C_1	-0.02	-0.04
	C_2	0.23	0.21
	F	-0.23	-0.21
	$\overline{H}$	0.002	0.01
	C_1	-0.05	-0.08
	C_2	0.49	0.42
	F	-0.23	-0.21
	$\overline{H}$	0.006	0.04

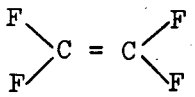
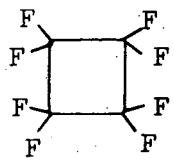
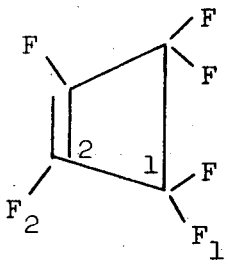
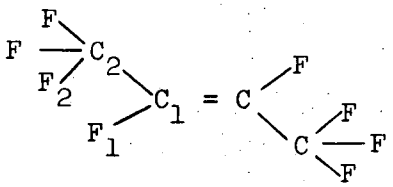
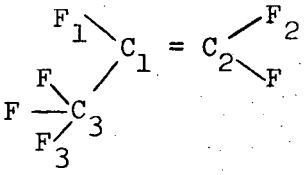
(continued)

Table IV. (continued)

Compound	Atom[a]	q^b (ACHARGE)	q^b (CNDO/2)
	C_1	-0.09	-0.11
	C_2	0.72	0.60
	F	-0.23	-0.22
	H	0.03	0.05
	C	0.64	0.56
	F	-0.21	-0.19
	C_1	0.64	0.58
	C_2	0.28	0.28
	F_1	-0.20	-0.19
	F_2	-0.19	-0.16
$CH_2 = CH_2$	C	0. (assumed)	-0.06
	H	0. (assumed)	0.03
	C_1	-0.05	-0.11
	C_2	0.25	0.22
	H	0.004	0.03
	F	-0.21	-0.19
	C_1	-0.14	-0.18
	C_2	0.50	0.44
	H	0.03	0.06
	F	-0.21	-0.19
	C_1	0.11	0.07
	C_2	0.42	0.39
	H	0.01	0.05
	F_1	-0.19	-0.16
	F_2	-0.17	-0.18

(continued)

Table IV. (continued)

Compound	Atom[a]	q^b (ACHARGE)	q^b (CNDO/2)
	C	0.36	0.32
	F	-0.18	-0.16
	C	0.35	0.33
	F	-0.18	-0.16
	C_1	0.36	0.37
	C_2	0.14	0.13
	F_1	-0.17	-0.17
	F_2	-0.17	-0.15
	C_1	0.07	0.12
	C_2	0.73	0.60
	F_1	-0.11	-0.14
	F_2	-0.23	-0.20
	C_1	0.01	0.03
	C_2	0.46	0.41
	C_3	0.71	0.61
	F_1	-0.16	-0.13
	F_2	-0.19	-0.16
	F_3	-0.21	-0.20

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

[b] Charges are given in units of $|e|$.

The charges in the fluoromethanes were calculated assuming q_c (CH_4) equalled 0; those in the fluoroethylenes were calculated assuming q_c (C_2H_4) equalled 0; the remaining charges were calculated assuming q_c (CH_3CH_3) equalled 0.

FIGURE CAPTIONS

Fig. 1. Spectrum of the C 1s levels in CF_4 and 1,1-difluoroethane.

Fig. 2. The N(1s) binding-energy shifts in methylamines, relative to NH_3, versus the number of methyl groups. Points are experimental results, from Ref. 8, while lines connect theoretical points calculated from ground-state potential model (GPM) and from relaxation potential model (RPM). Clearly relaxation dominates the binding energy shifts for the methylamines.

Fig. 3. Plot of theoretical (GPM and RPM) C(1s) shifts in fluoroethanes versus experimental values, with ethane as a reference. Open circles are RPM, filled circles GPM predictions. Both lines have unit slope. Standard deviations of theoretical values are 0.14 eV (GPM), 0.31 eV (RPM). These results show that ΔV_R is exaggerated in RPM calculations. Compounds in order of increasing ΔE_B are: (C_2H_6), $C^*H_3CH_2F$, $C^*H_3CHF_2$, $C^*H_3CF_3$, $C^*H_2FCH_3$, $C^*HF_2CH_3$, $C^*F_3CH_3$, C_2F_6.

Fig. 4. Plot of RPM (open circles) and GPM (filled circles) theoretical C 1s shifts for fluorinated ethylenes, relative to C_2H_4, against experimental values. Solid lines are best fits for unit slope (standard deviations are 0.38 (GPM) and 0.53 (RPM)), while dashed lines were fitted with slopes variable (standard deviations 0.12 (GPM) and 0.07 (RPM)). Host atoms are noted by asterisks.

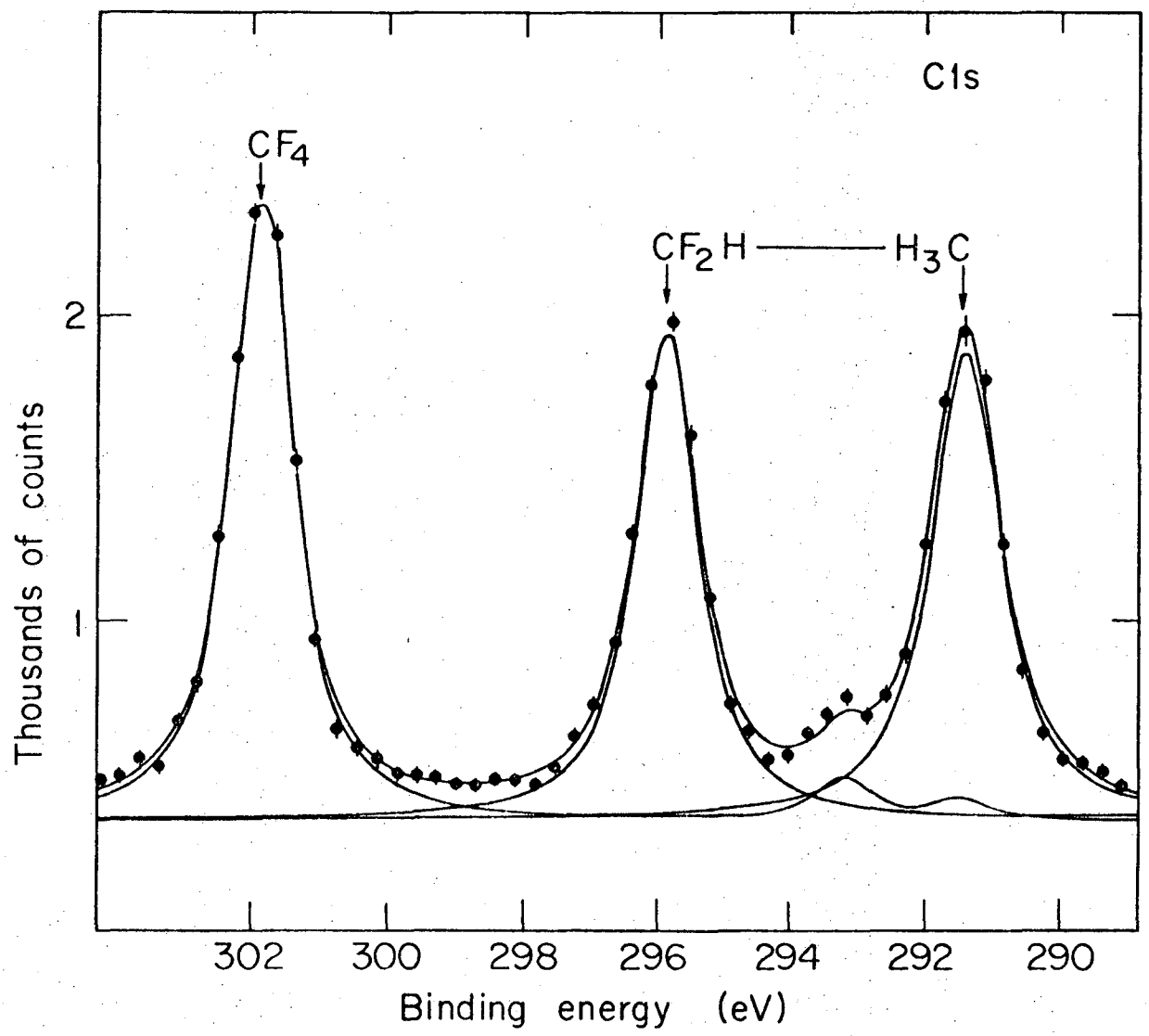
Fig. 5. Predicted O(1s) shifts from GPM theory versus experiment for oxygens bonded to one other atom. The experimental shifts are referenced to the O_2 (1s) binding energy weighted by the respective spin multiplicities of the hole state (i.e. 543.5 eV). The binding energies used for the paramagnetic molecules NO and NO_2 are obtained similarly. The numbers used in this plot are taken from Ref. 4a Table 3 after changing the reference from N_2O

(pp' potential = 292.22 eV) to O_2 (pp' potential = 185.30 eV). The GPM value for N_2O in Ref. 4a was incorrect; it should be 1.2 eV. The straight line has unit slope.

Fig. 6. Predicted O(1s) shifts from GPM theory versus experiment for oxygens bonded to two other atoms. The reference is the O(1s) line of water (539.7 eV). The numbers used can be found in Table 3 of Ref. 4a except for furan (ΔE_b(exp) = 0.01(6) eV, ΔE_b(GPM) = 3.12 eV) and diethyl ether (ΔE_b(exp) = -1.83(11) eV, ΔE_b(GPM) = 2.30 eV). The straight line has unit slope.

Fig. 7. Predicted (GPM) versus experimental shifts for F(1s) in fluorine-substituted methanes and ethanes (filled circles) and ethylenes (squares) relative to CF_4. The numbers are taken from Table II. The line has unit slope.

Fig. 8. Plot of the charge transferred to carbon in C_2F_4 (i.e., a C_F carbon) on hydrogen substitution, using ACHARGE results from Table IV. Here "1" means substitution onto carbon under study, "11" means di-substitution, "2" means mono- and "22" means di-substitution onto the other carbon.



XBL736-3159

Fig. 1

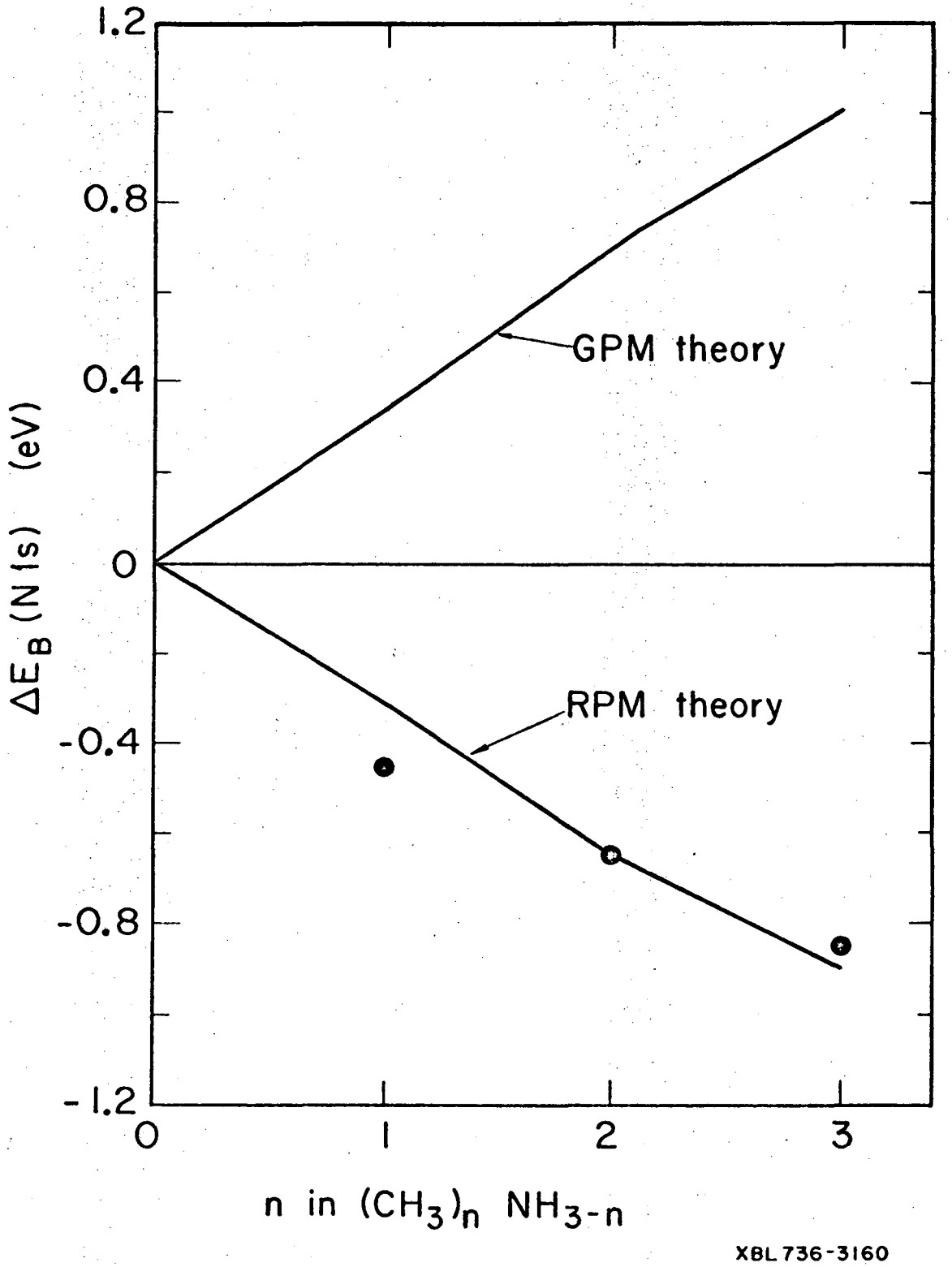
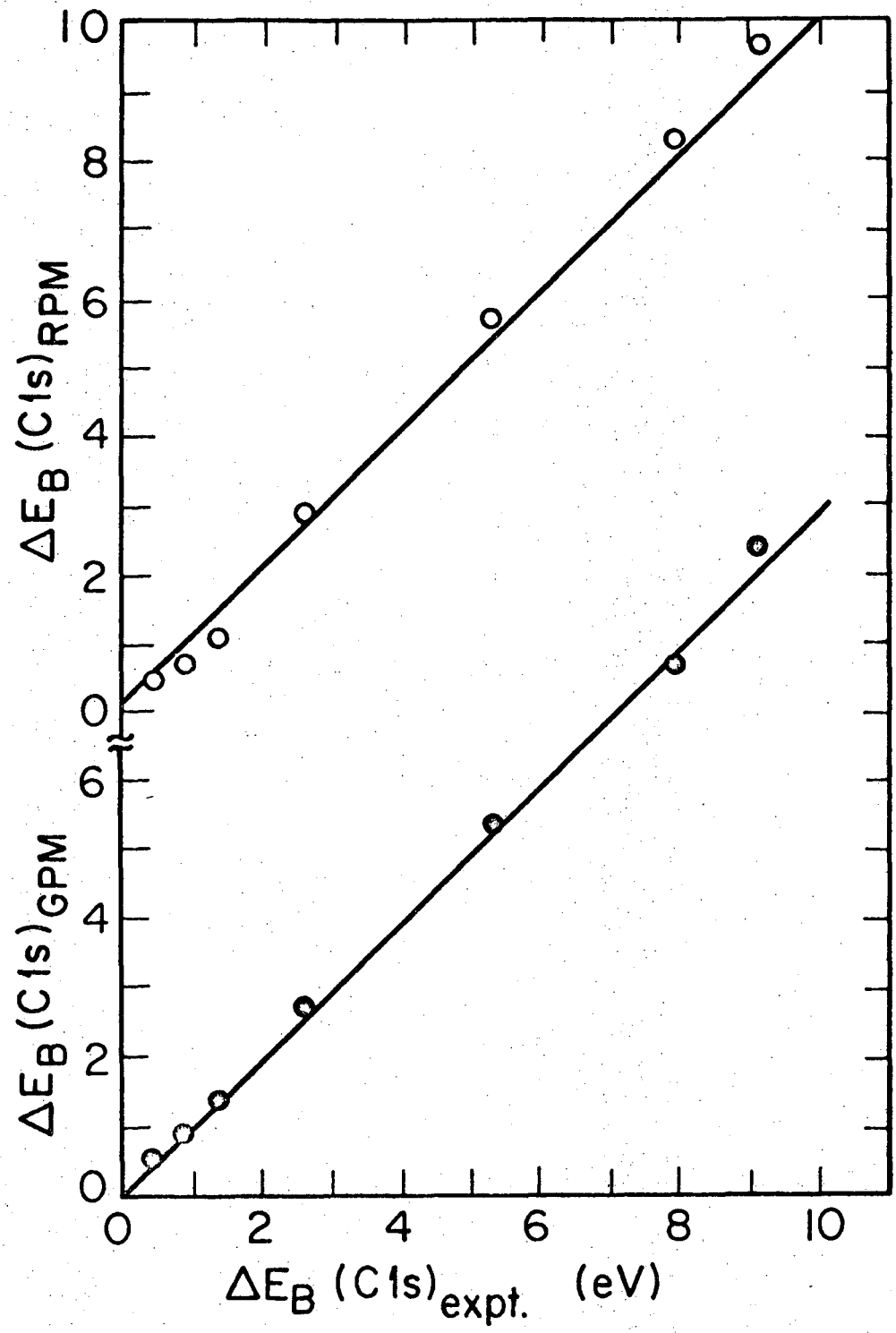
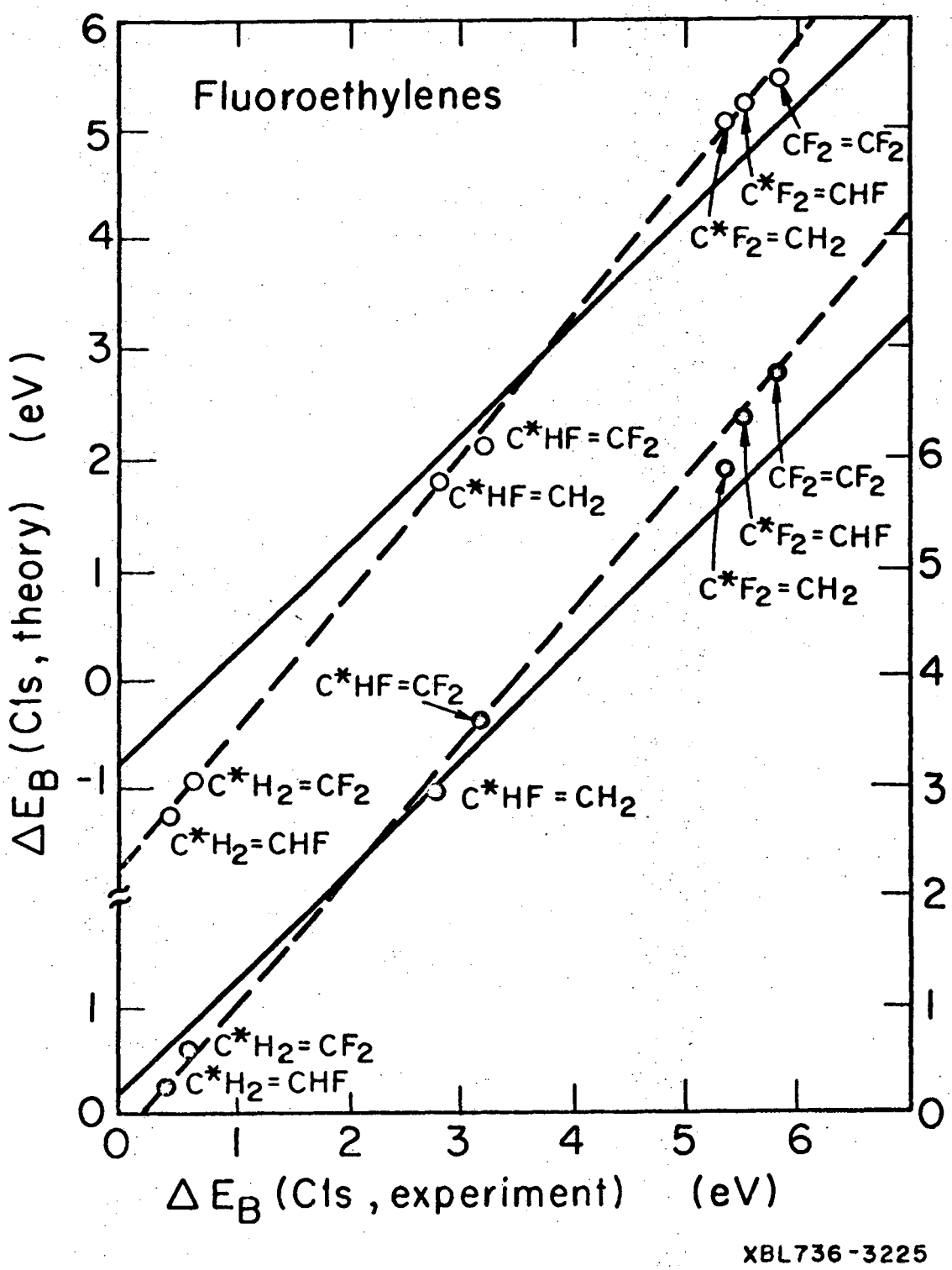

1.2
0.8
0.4
0
-0.4
-0.8
-1.2
ΔE_B (N 1s) (eV)
GPM theory
RPM theory
0
1
2
3
n in $(CH_3)_n$ NH_{3-n}
XBL 736-3160

Fig. 2



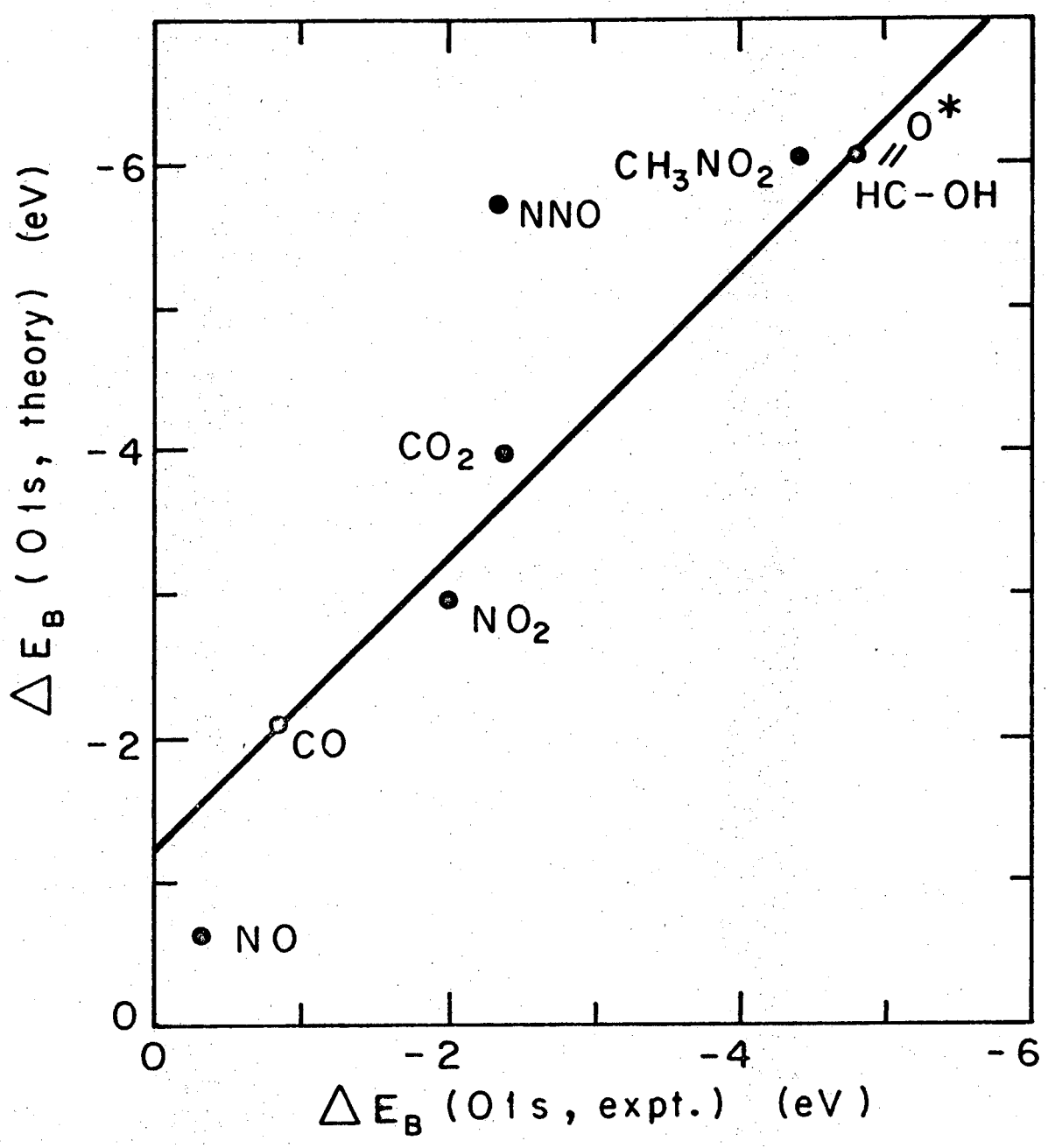
XBL736-3156

Fig. 3



XBL736-3225

Fig. 4



XBL737-3364

Fig. 5

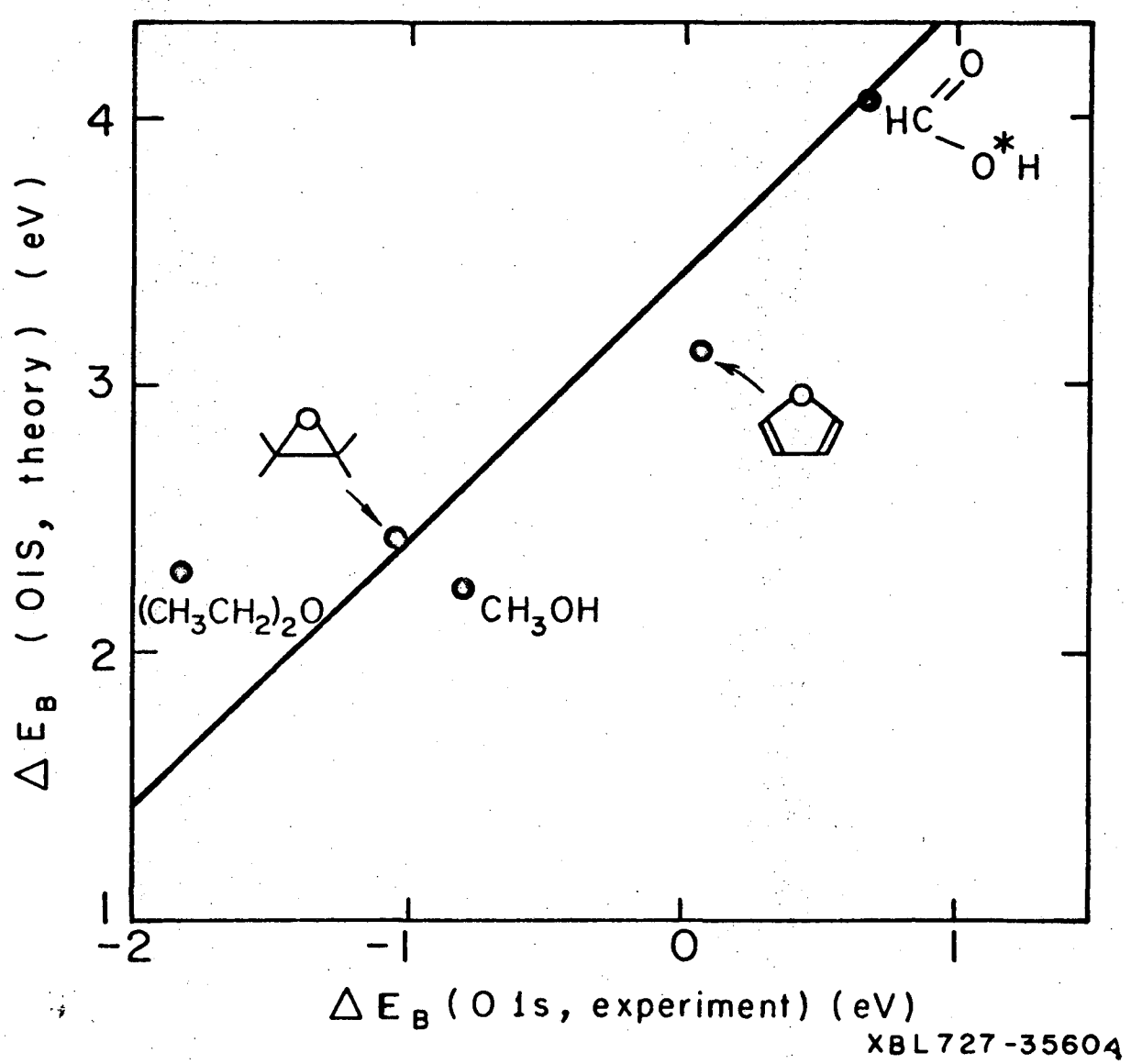

4
3
2
1
-2
-1
0
1
ΔE_B (O1S, theory) (eV)
ΔE_B (O 1s, experiment) (eV)
HC
O
O*H
$(CH_3CH_2)_2O$
CH_3OH
XBL727-35604

Fig. 6

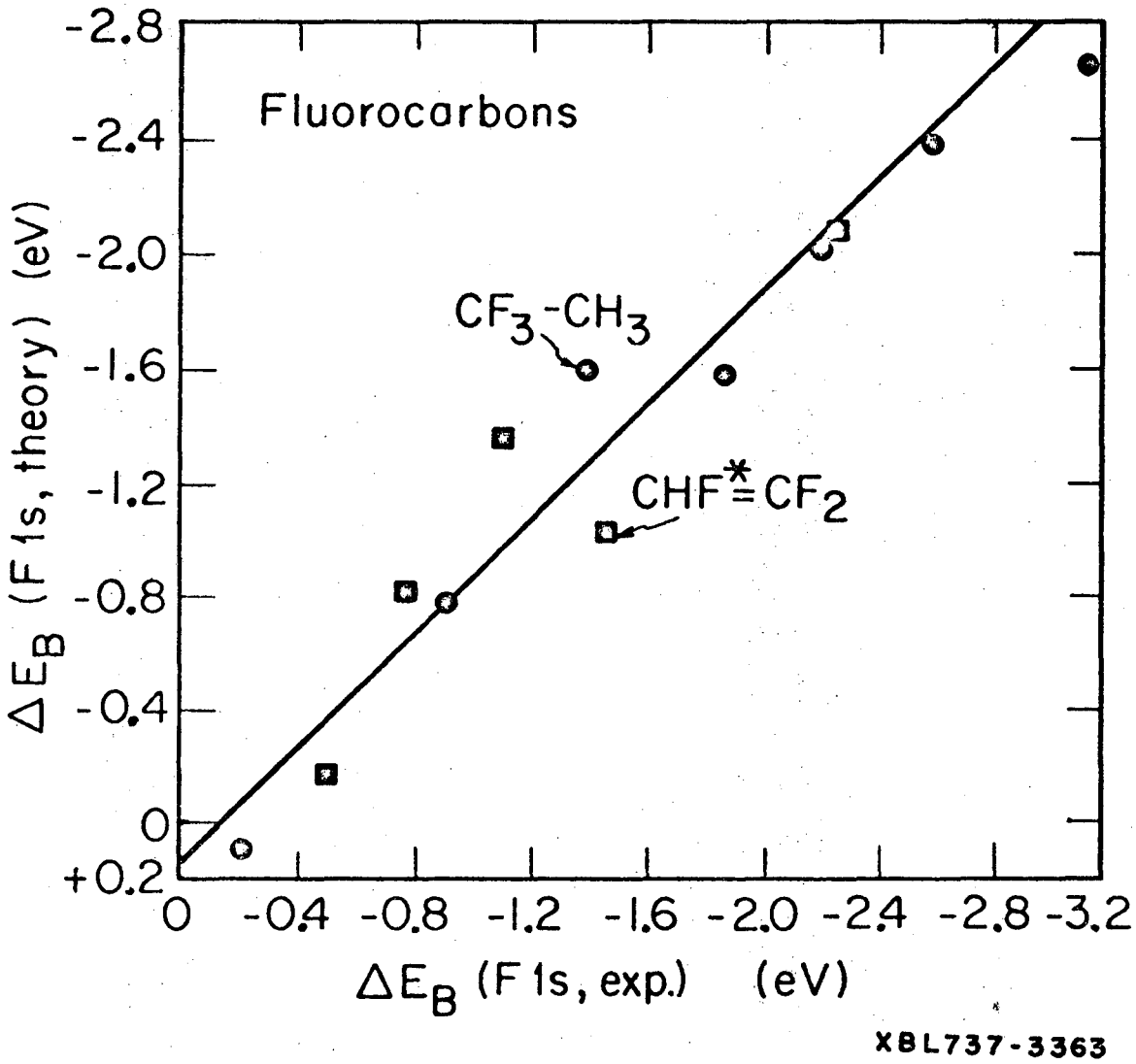

Fluorocarbons
CF3-CH3
CHF*=CF2
ΔEB (F 1s, theory) (eV)
ΔEB (F 1s, exp.) (eV)
-2.8
-2.4
-2.0
-1.6
-1.2
-0.8
-0.4
0
+0.2
0
-0.4
-0.8
-1.2
-1.6
-2.0
-2.4
-2.8
-3.2
XBL737-3363

Fig. 7

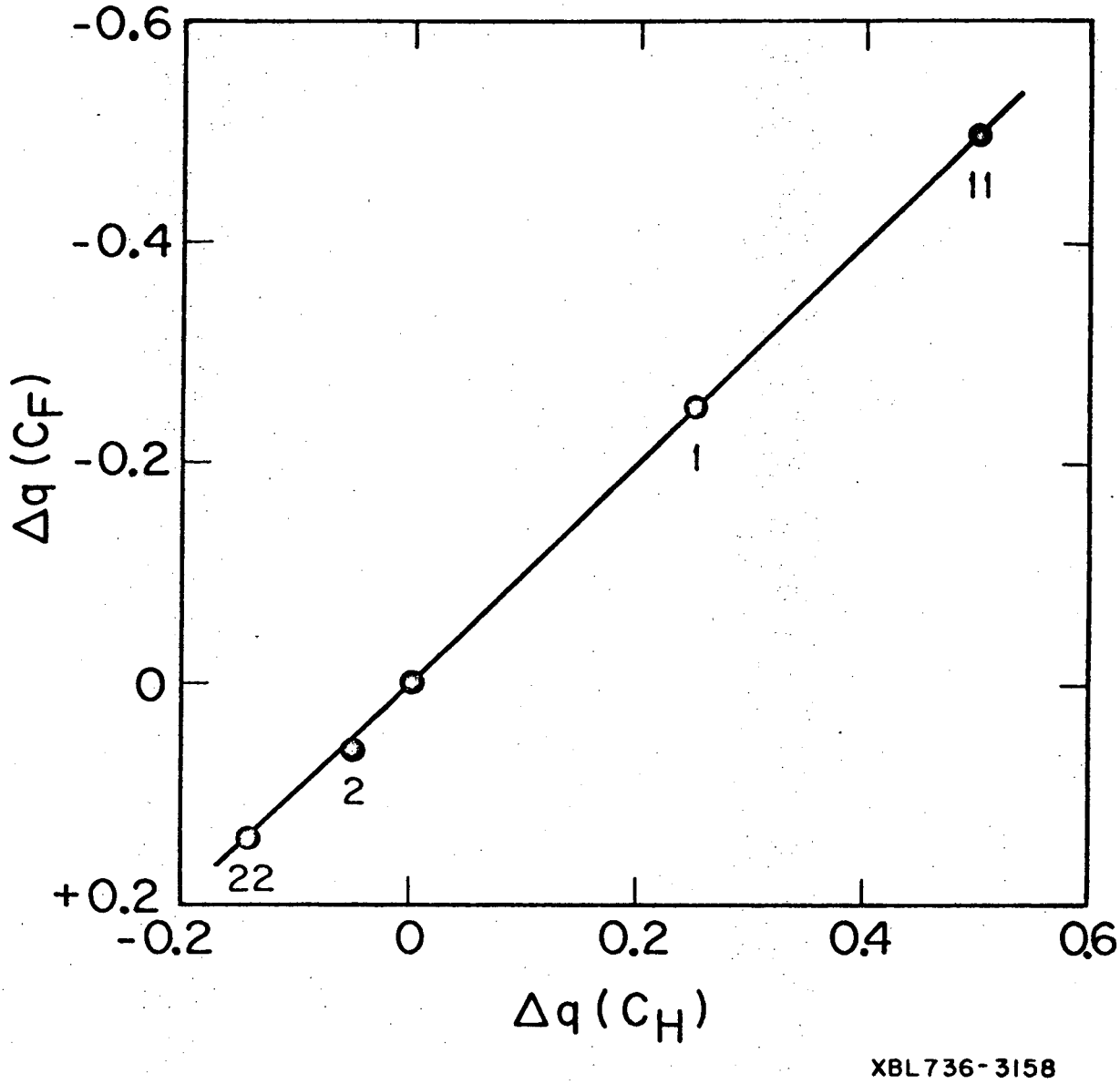


Fig. 8

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TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720