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Publication Date

1971-09-01

To be published in the Proceedings of
the International Conference on Electron
Spectroscopy, Asilomar, CA,
Sept. 7-10, 1971

LBL-182 c.2
Preprint

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September 1971

AEC Contract No. W-7405-eng-48

LBL-182 c.2

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The Estimation of Core Electron Binding Energy Shifts Using the Concept of the Equivalence of Equally-Charged Cores

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The Estimation of Binding Energy Shifts for Gaseous Molecules

The Use of Available Thermodynamic Data.- The removal of a core electron from an atom in a compound may be represented as a chemical reaction. For example, the ejection of a 1s electron from the nitrogen atom of an ammonia molecule corresponds to the following equation.

$$NH_3 \rightarrow NH_3^{+*} + e^-$$

(In this and all subsequent chemical equations, it should be understood that all species are gaseous unless otherwise indicated.) The NH_3^{+*} ion which is formed is not an ordinary NH_3^+ ion -- i.e., it is not an ammonia molecule which has lost an electron from its valence shell. The asterisk is added to the formula to emphasize the fact that the 1s shell of the nitrogen atom lacks an electron. The energy of this reaction is the nitrogen 1s binding energy of ammonia.

In the X-ray photoelectron spectroscopy of gaseous compounds, differences in binding energies between compounds (chemical shifts) can be measured more precisely than absolute binding energies of individual compounds. Chemical equations can be written corresponding to such chemical shifts. For example, the difference between the binding energies of ammonia and molecular nitrogen is the energy of reaction 1,

$$NH_3 + N_2^{+*} \rightarrow NH_3^{+*} + N_2 \qquad (1)$$

$$\Delta E = E_B(NH_3) - E_B(N_2)$$

X-ray photoelectron spectroscopists are vitally interested in procedures for estimating the energies of reactions like reaction 1, i.e., chemical shifts in binding energy. In this paper I shall discuss the thermodynamic method which we have found useful for such purposes.[1-3] The method is based on the expectation that the valence electrons of a compound in which one of the atomic cores lacks an electron are not markedly affected by replacement of the incomplete core by the complete core of an atom having one unit greater nuclear charge. It is unnecessary in this method to assume that the energy of this replacement is zero (which it probably is not); it is sufficient to assume that the energies of all such replacements, for atoms of a given element, have the same value. Thus we assume that the energies of the following two reactions are identical.

$$NH_3^{+*} + O^{6+} \rightarrow OH_3^{+} + N^{6+*}$$

$$N_2^{+*} + O^{6+} \rightarrow NO^{+} + N^{6+*}$$

On this basis it follows that the energy of a reaction in which an incomplete core and an equally-charged complete core change places is zero. For example, we take $\Delta E = 0$ for reaction 2,

$$NH_3^{+*} + NO^{+} \rightarrow OH_3^{+} + N_2^{+*} \qquad (2)$$

In this reaction, O^{6+} and N^{6+*} cores are interchanged. The significance of reaction 2 is that by adding it to reaction 1, we obtain reaction 3:

$$NH_3 + NO^{+} \rightarrow OH_3^{+} + N_2 \qquad (3)$$

$$\Delta E = E_B(NH_3) - E_B(N_2)$$

Thus the shift in binding energy between NH_3 and N_2 is, to the accuracy of our approximation, equal to the energy of either reaction 1 or 3. Reaction 3 involves familiar, well-characterized chemical species for which the heats of formation are known. Thus we have a method for estimating shifts in binding energy from available thermodynamic data.

Reactions for estimating the chemical shifts of some other nitrogen compounds, relative to molecular nitrogen, follow.

$$(CH_3)_2NH + NO^+ \rightarrow (CH_3)_2OH^+ + N_2$$

$$CH_3NH_2 + NO^+ \rightarrow CH_3OH_2^+ + N_2$$

$$HCN + NO^+ \rightarrow HCO^+ + N_2$$

$$N_2O + NO^+ \rightarrow NO_2^+ + N_2$$

$$NO + NO^+ \rightarrow O_2^+ + N_2$$

$$NF_2 + NO^+ \rightarrow OF_2 + N_2$$

$$NO_2 + NO^+ \rightarrow O_3^+ + N_2$$

All these reactions are analogous to reaction 3. Both experimental binding energy shifts and the appropriate thermal data are known for these nitrogen compounds.[3] A plot of the experimental shifts against the estimated shifts is given in Figure 1. The straight line has unit slope and passes through the origin. The reference level was adjusted (by adding a small constant to all the experimental data) to minimize the average deviation from the line, which amounts to ±0.24 eV in this case.

The thermodynamic method which we have just outlined using nitrogen compounds as examples can be applied to core electron binding energy data for other elements. Plots of experimental shifts against estimated shifts for some compounds of carbon[2,4-9] and oxygen[10-13] are given in Figures 2 and 3, respectively. In the case of the carbon compounds, the average deviation between the experimental and estimated values is ±0.53 eV. In the case of the oxygen compounds, the corresponding average deviation is much higher (±1.26 eV) because most of the thermodynamic data are very uncertain. (In Figure 3, the open-circle points correspond to the uncertain thermodynamic data.) For example, the point for CO is far from the line probably because of an inaccurate value for the heat of formation of CF^+.

The Use of Thermodynamic Approximations.- Frequently the thermodynamic data necessary for calculating a particular core electron binding energy shift are unknown. However, the thermodynamic method can still be applied if estimated values for the unknown heats of formation are used. Although chemists have devised a wide variety of techniques for estimating heats of formation, most of the techniques are inadequate for ionic species of the type involved in these binding energy calculations. Thus this problem provides a significant challenge for chemists. In the following paragraphs I shall discuss several examples of the use of thermodynamic approximations, over and above the fundamental approximation of the method, in the estimation of binding energy shifts.

Figure 4 is a plot of experimental *vs.* estimated binding energies for boron compounds.[14] The two open-circle points, for $BH_3N(CH_3)_3$ and

B_2H_6, were calculated using estimated data. The chemical equations for the shifts of these compounds, relative to BF_3, are the following,

$$BH_3N(CH_3)_3 + CF_3^+ \rightarrow N(CH_3)_4^+ + BF_3$$

$$B_2H_6 + CF_3^+ \rightarrow BCH_6^+ + BF_3$$

The heats of formation are known for all these species except $N(CH_3)_4^+$ and BCH_6^+. The heat of formation of the tetramethylammonium ion was estimated from the Born-Haber cycle for tetramethylammonium nitrate. All the terms in this cycle are known except the lattice energy, which was estimated using Kapustinsky's formula. The heat of formation of BCH_6^+ (the ion formed by replacing a boron atom in B_2H_6 with a C^+ ion) was estimated by assuming that its heat of formation from BH_3 and CH_3^+ is equal to the heat of formation of the isoelectronic species, B_2H_6, from two BH_3 molecules.

The data for xenon compounds[2,15] are plotted in Figure 5. The thermodynamically estimated binding energy shifts are based on reactions such as the following, for XeF_2 and Xe,

$$XeF_2 + Cs^+ \rightarrow CsF_2^+ + Xe$$

The heat of formation of the hypothetical CsF_2^+ ion was assumed to be the same as that for a Cs^+ ion plus two F atoms. (In other words, it was assumed that there would be no bonding between the atoms of this species.) This approximation is equivalent to equating the shift in binding energy to the atomization energy of XeF_2:

$$XeF_2 \rightarrow Xe + 2F$$

A similar approximation was made for all the other xenon compounds. As can be seen from Figure 5, the average deviation between the experimental and estimated values is remarkably small (±0.20 eV).

The estimated shift for a pair of fluorine compounds (say, XF and YF) should be, according to the thermodynamic method, the energy of reaction 4:

$$XF + YNe^+ \rightarrow YF + XNe^+ \tag{4}$$

Unfortunately, the heats of formation of neon compounds are generally unknown. Therefore we found it expedient to make the further approximation that $\Delta E = 0$ for reaction 5:

$$XNe^+ + Y^+ \rightarrow YNe^+ + X^+ \tag{5}$$

This approximation is equivalent to the assumption that the heats of dissociation of all cationic neon adducts are equal. Such an assumption would be expected to be at least approximately valid because such heats of dissociation are relatively small.[16,17] By adding reactions 4 and 5, we obtain reaction 6:

$$XF + Y^+ \rightarrow YF + X^+ \tag{6}$$

The heats of reactions of this type were taken as the thermodynamically estimated shifts in the fluorine 1s binding energies. A plot of experimental values against such estimates is presented in Figure 6.[5,7,10,18,19] The extreme scatter of the points is probably due to the relatively inaccurate thermodynamic data used in the calculations. The open-circle points are based on particularly uncertain data.

Theoretical Methods for Estimating Energy Differences for Isoelectronic Pairs.- From the preceding discussion, it is clear that the *relative* binding energies for various compounds of a given element are equal to the energy differences of pairs of isoelectronic species. One might expect that, using various theoretical methods for estimating molecular energies, such energy *differences* could be calculated more accurately than the *absolute* energies of the species could be calculated. Such calculations have not been altogether encouraging. Energy differences calculated by the extended Hückel MO method for compounds of boron and nitrogen were found to show no correlation whatsoever with binding energies. This result is probably reasonable, because the EHMO method is reputed to be of little value for cationic species. Partial success was obtained with the CNDO MO method. Plots of CNDO-calculated energy differences[5] against binding energies are given in Figure 7 for nitrogen compounds[3] and in Figure 8 for boron compounds.[14]

Although the points in Figure 7 fit a straight line moderately well (with an average deviation of ±1.4 eV), the fit is much poorer than that obtained in Figure 1 using thermodynamic data based on experiment. Essentially no correlation whatsoever is apparent in the plot of Figure 8. Clearly the CNDO method, when applied in this way, is of little use. One needs a theoretical method for estimating the change in energy of a system upon increasing the charge on one nucleus by unity. Possibly a quantum mechanical method based on perturbation theory would be appropriate for such a problem.

The following empirical equation has been devised[20] for estimating a quantity, Δ, which is the difference in the dissociation energies of a pair of isoelectronic species and which is linearly related to core electron binding energies.

$$\Delta(\mathrm{eV}) = \sum_i [(x_A^2 - x_B^2) + 2(x_B - x_A)x_i] + 10.5 \sum_j [1/(1+k)]C_j \quad (7)$$

Here x_A is the electronegativity of the atom, A, from which the core electron is ejected, and x_B is the electronegativity of the atom with one greater nuclear charge. The quantity x_i is the electronegativity of an atom directly bonded to atom A, and C_j is the formal charge of an atom separated by k atoms from A. The sum $\sum_i$ is carried out over the i atoms directly bonded to atom A, and the sum $\sum_i$ is carried out over all the atoms in the species except atom A. A plot of experimental carbon 1s binding energies against Δ for a wide variety of organic compounds (both solid and gaseous) is given in Figure 9. The scatter in the points is attributable both to the crudeness of equation and to the fact that the plot includes data for both solid and gaseous compounds. Unfortunately, equation 7 is severely restricted in its application to binding energy correlation because it is valid only for chemical species in which the atoms have formal charges from +1 to -1.

The Estimation of Binding Energy Shifts for Gaseous Monatomic Ions

No binding energy shifts for gaseous ions have yet been measured. However, it is possible to calculate such shifts by quantum mechanical methods for single atoms in various stages of ionization with good reliability. Thus Siegbahn et al.[21] have calculated the 1s binding energy shifts for several ions of sulfur and chlorine by self-consistent field calculations using modified Hartree-Fock-Slater wave functions. We have plotted their calculated shifts against the thermodynamically-estimated[22] values in Figures 10 and 11. The open circles correspond to SCF calculations in which Koopmans' theorem was assumed; the solid circles correspond to more elaborate calculations in which atomic relaxation was accounted for. As expected, the data calculated assuming relaxation fit the thermodynamic data more closely. The fact that the data agree, in general, to within a few tenths of a volt suggests that both the SCF and thermodynamic methods give correct answers with the same accuracy. The thermodynamic method is much simpler to apply, however. For example, the chemical shift between Cl^+ and Cl is taken to be the difference between the second ionization potential of argon and the first ionization potential of chlorine:

$$Cl^+ + Ar^+ \rightarrow Cl + Ar^{2+}$$

The thermodynamic method can also be applied to the hypothetical case of an isolated fractionally-charged ion. The energies for integrally-charged ions can be expressed approximately as quadratic functions of atomic charge.[22] For example, from the first ionization potentials[23] and electron affinities[24] of boron and carbon, we derive the following equations for the energies (in eV) of the ions:

$$E(B^q) = 4.00\,q^2 + 4.30\,q$$

$$E(C^q) = 5.00\,q^2 + 6.26\,q$$

Using these equations, the chemical shift in binding energy between B^q and B is calculated to be $q^2 + 11.96\,q$, corresponding to the reaction

$$B^q + C^+ \rightarrow B + C^{q+1}$$

Similar relations can be shown to hold for many other elements of the periodic table. It is significant that in all cases, the coefficient of q is much greater than that of q^2, and so for $|q| < 1$, the calculated chemical shift is essentially directly proportional to the atomic charge. Thus the approximate linearity of plots of chemical shift against atomic charge for various compounds of a given element is rationalized. Deviations from linearity in such plots can be attributed to neglect of the charges of the other atoms in the compounds and neglect of the shifts in electron density that occur during electron ejection.

The Estimation of Binding Energy Shifts for Solids

The thermodynamic estimation of chemical shifts for solids is more complicated and less accurate than that for gases, and the method is readily applied only to atoms in molecular solids and in the anions of salts.[1] To illustrate the method, we shall consider the nitrogen 1s shift between sodium nitrite and frozen ammonia. The energy shift corresponds to the energy of reaction 8.

$$NO_2^-(\text{in } NaNO_2) + NH_3^{+*}[\text{in } NH_3(s)] \rightarrow NO_2^*(\text{in } NaNO_2) + NH_3[\text{in } NH_3(s)] \qquad (8)$$

$$NaNO_2(s) + [Na^+ \text{ hole in } NaNO_2] + [NO_2^- \text{ hole in } NaNO_2] \rightarrow Na^+(\text{in } NaNO_2) + NO_2^-(\text{in } NaNO_2) \qquad (9)$$

$$Na^+(\text{in } NaNO_2) \rightarrow Na^+(g) + [Na^+ \text{ hole in } NaNO_2] \qquad (10)$$

$$NO_2^*(\text{in } NaNO_2) + 2O_3(g) \rightarrow NO_2^*(g) + [NO_2^- \text{ hole in } NaNO_2] + 2O_3(s) \qquad (11)$$

$$NH_3^{+*}(g) + NH_3[\text{in } NH_3(s)] \rightarrow NH_3^{+*}[\text{in } NH_3(s)] + NH_3(g) \qquad (12)$$

$$NO_2^*(g) + OH_3^+(g) \rightarrow O_3(g) + NH_3^{+*}(g) \qquad (13)$$

$$NaNO_2(s) + O_3(g) + OH_3^+(g) \rightarrow Na^+(g) + 2O_3(s) + NH_3(g) \qquad (14)$$

To reaction 8 we shall add reactions 9-13 and thus obtain reaction 14, which involves only species for which thermochemical data are available. Reaction 9 corresponds to the transfer of a mole of bulk crystalline $NaNO_2$ into independent ionic sites inside a large crystal of $NaNO_2$. The energy of reaction 9 is -U, where U is the lattice energy of $NaNO_2$.

Reaction 10 corresponds to the removal of a mole of independently-situated Na^+ ions from a large crystal of $NaNO_2$. To a good approximation, the energy of this process is U and cancels the energy of reaction 9.[25] The energy of reaction 11 is assumed to be zero on the basis that the energy of removing an NO_2^* molecule from an NO_2^- site in $NaNO_2$ should be approximately equal to the energy of removing an O_3 molecule from an interior site in crystalline O_3, or twice the heat of sublimation of O_3.[26] The energy of Reaction 12 is assumed to be zero on the basis that the energies for the removal of NH_3^{+*} and NH_3 from crystalline NH_3 should be approximately equal. In reaction 13, N^{6+*} and O^{6+} cores are interchanged, and the energy is taken as zero on the same basis as discussed earlier. If we accept the various approximations made regarding the energies of reactions 8-13, their sum (the energy of reaction 14) is the same as that of reaction 8, i.e., the chemical shift between $NaNO_2$ and $NH_3(s)$. Similar chemical reactions can be written for other pairs of solid compounds whose X-ray photoelectron spectra have been obtained - not only nitrogen compounds, but also compounds of carbon, boron, and iodine.[1] A plot of relative core binding energies for such compounds against relative values of the thermodynamically estimated binding energies is given in Figure 12.

K-absorption edge energies are analogous to 1s electron binding energies and, like the latter, show chemical shifts. For example, KCl, $KClO_3$, and $KClO_4$ have relative chlorine K absorption edge energies[27] of 0, 6.9, and 8.4 eV, and NaCl, $NaClO_3$, and $NaClO_4$ have relative chlorine 2p binding energies of 0, 7.1, and 9.5 eV, respectively.[21] Best[27,28] has pointed out that a thermodynamic treatment, based on the equivalence of equally charged cores, should be applicable to absorption edge data. However, a lack of the required thermodynamic data has thwarted such calculations.

The Estimation of Chemical Reaction Energies from Binding Energy Shifts

When the heat of formation of one of the species in the chemical reaction corresponding to a known core-electron binding energy shift is unknown, that heat of formation can be calculated by simply equating the binding energy shift to the heat of the chemical reaction. In this way one can use chemical shift data to calculate the heats of formation of a wide variety of unusual species.

For example, the chlorine 2p shifts relative to NaCl for $NaClO_3$ and $NaClO_4$ correspond to the following reactions.

$$NaClO_3(s) + ArO_3(g) + 2Ar(s) \rightarrow NaCl(s) + Ar(g) + 2ArO_3(s)$$

$$NaClO_4(s) + ArO_4(g) + 2Ar(s) \rightarrow NaCl(s) + Ar(g) + 2ArO_4(s)$$

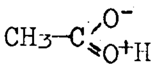
Using the known heats of formation of the salts, the sublimation energy of argon, and estimates of the sublimation energies of ArO_3 and ArO_4,[29] we calculated ΔH_f° = 182 and 235 kcal/mole, respectively, for $ArO_3(g)$ and

$ArO_4(g)$. From these values we calculate average Ar-O bond energies of -3 and +1 kcal/mole, corresponding to essentially no bonding in these hypothetical molecules.

Similar calculations, using the measured 1s binding energy of the middle nitrogen atom in sodium azide, NaN_3, lead to an estimated $\Delta H_f^\circ = 120$ kcal/mole for the hypothetical gaseous molecule NON.[1] This value corresponds to $\Delta H^\circ = -100$ kcal/mole for the isomerization

$$NON \rightarrow NNO$$

The heats of formation of various hydrogen-containing gaseous cations can be estimated from the binding energies of gaseous hydrogen-containing molecules, and these data can be combined with appropriate heats of formation to obtain proton affinities. Table I lists some proton affinities calculated in this way for molecules for which no other proton affinity values are available. It will be noted that the binding energies of the two different oxygen atoms in acetic acid yield two proton affinities for acetyl fluoride (CH_3COF), corresponding to the attachment of a proton to the oxygen atom or the fluorine atom. When making these calculations, we reversed the oxygen binding energy assignment of Siegbahn et al.,[13] who assigned the peak of lower binding energy to the OH oxygen. Their assignment leads to the chemically implausible result that the proton is more stable on the fluorine atom than on the oxygen atom of CH_3COF. We also prefer our assignment (i.e., the higher binding energy to the OH oxygen) because we believe that the resonance structure



$CH_3{-}C\begin{smallmatrix}\nearrow O^- \\ \searrow O^+H\end{smallmatrix}$

Table I.

Proton Affinities from Core Electron Binding Energies

Molecule for which E_B Detd.[a]	Molecule for which Proton Affinity Calcd.[b]	Calcd. Proton Affinity, kcal/mol[c]
$CH_3\underline{C}H_2NH_2$	$CH_3\underline{N}HNH_2$	226
$\underline{C}_6H_6$	$C_5H_5\underline{N}$	222
$\underline{C}H_3OH$	$\underline{N}H_2OH$	202
$\underline{C}HCl_3$	$\underline{N}Cl_3$	189
$(\underline{C}H_3)_2CO$	$CH_3CO\underline{N}H_2$	185
$C_6H_5\underline{N}H_2$	$C_6H_5\underline{O}H$	176
$\underline{C}_2H_2$	$HC\underline{N}$	168
$CH_3CH\underline{O}$	$\underline{C}H_2CHF$	165
$CH_3C\underline{O}OH$[d]	$CH_3C\underline{O}F$[d]	137
$CH_3\underline{O}H$	$CH_3\underline{F}$	104
$H_2\underline{O}$	HF	97
$CH_3CO\underline{O}H$[d]	$CH_3CO\underline{F}$[d]	96

[a] E_B of the italicized atom used in the calculation. Binding energies taken from references 6, 7, and 13.

[b] Donor atom italicized.

[c] Required heats of formation taken from reference 10.

[d] The O os binding energy assignments of Siegbahn et al.[13] for CH_3COOH were reversed. See text.

is important enough to counteract the fact that the hydrogen atom will tend to lose electron density to the oxygen atom, and it is well known that higher atomic charges generally correspond to higher binding energies.

The carbon 1s binding energies of gaseous methyl compounds yield, by similar calculation, the "ammonia affinities" of cationic species. These are given in Table II.

Acknowledgment.- The assistance of Miss P. Finn with some of the calculations is gratefully acknowledged. This research was supported by the U.S. Atomic Energy Commission.

Table II.

Ammonia Affinities from Core Electron Binding Energies

Molecule for which E_B Detd.[a]	Species for which Ammonia Affinity Calcd.	Calcd. Ammonia Affinity, kcal/mol[b]
CH_3F	F^+	246
CH_3OH	OH^+	145
CH_3Cl	Cl^+	133
CH_3Br	Br^+	107
$(CH_3)_2CO$	CH_3CO^+	14

[a] Carbon 1s binding energies from references 7 and 13.

[b] Required heats of formation taken from reference 10.

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Figure Captions

Figure 1. Plot of nitrogen 1s binding energies *vs.* thermodynamically estimated energies.

Figure 2. Plot of carbon 1s binding energies *vs.* thermodynamically estimated energies.

Figure 3. Plot of oxygen 1s binding energies *vs.* thermodynamically estimated energies. The open circles correspond to compounds for which some of the required thermodynamic data are very uncertain.

Figure 4. Plot of boron 1s binding energies *vs.* thermodynamically estimated energies. The open circles correspond to compounds for which some of the required thermodynamic data were estimated.

Figure 5. Plot of xenon $3d_{5/2}$ binding energies *vs.* thermodynamically estimated energies. See the text for a discussion of the approximations made in calculating the thermodynamic energies.

Figure 6. Plot of fluorine 1s binding energies *vs.* thermodynamically estimated energies. See the text for a discussion of the approximations made in calculating the thermodynamic energies. The open circles correspond to compounds for which some of the required thermodynamic data are particularly uncertain.

Figure 7. Plot of nitrogen 1s binding energies *vs.* CNDO-estimated energy differences between isoelectronic species.

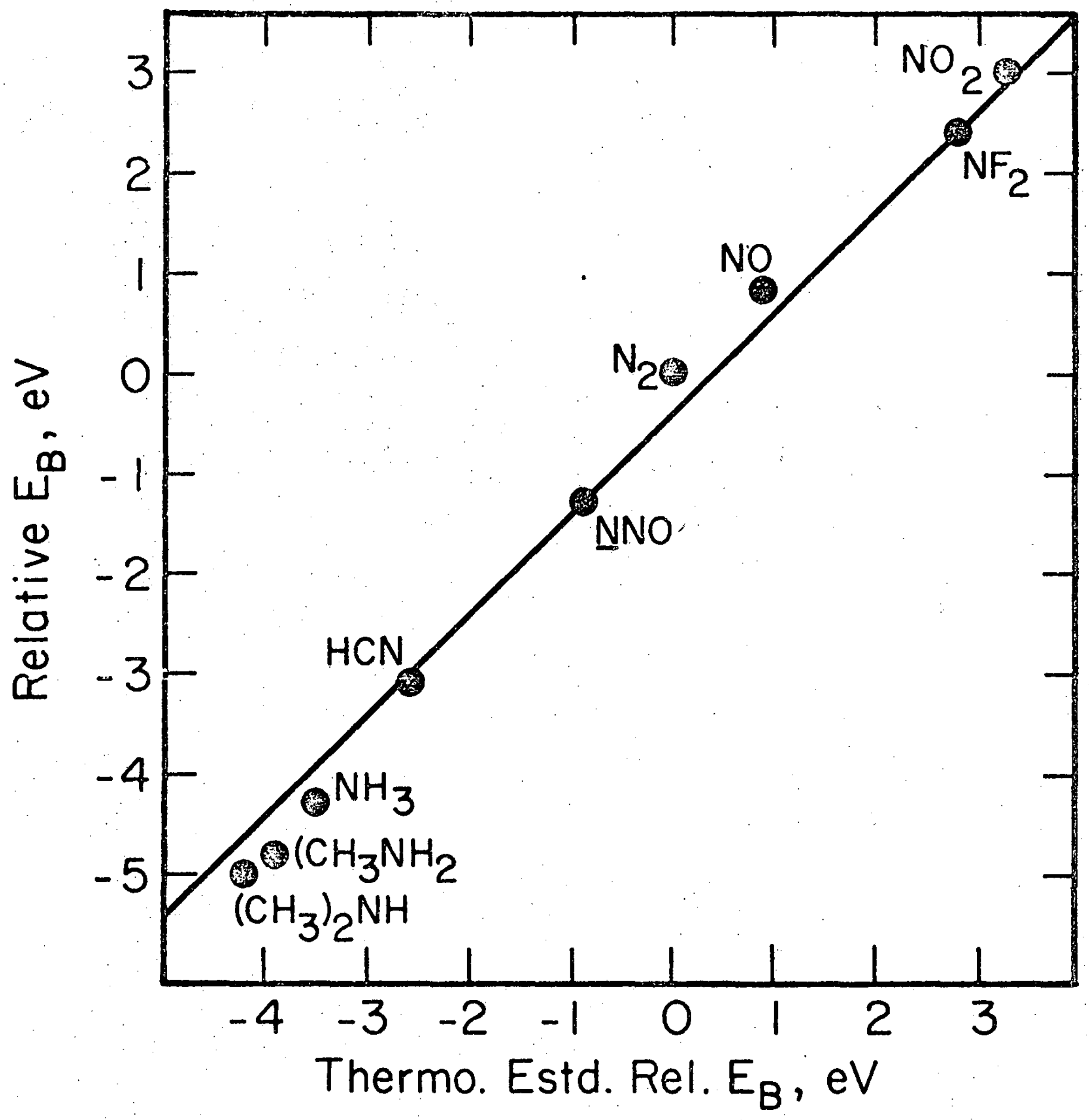
Figure 8. Plot of boron 1s binding energies *vs.* CNDO estimated energy differences between isoelectronic species.

Figure 9. Plot of carbon 1s binding energies (relative to methane) *vs.* calculated Δ values. Numbers refer to the following compounds: 1, C_6H_6; 2, C_2H_6; 3, C_2H_4; 4, CH_4; 5, C_2H_2; 6, $CH_3\underline{C}H_2NH_2$; 7, CH_3Br; 8, $CH_3\underline{C}H_2Cl$; 9, $H\underline{C}=N-CH=N-NH$; 10, $CH_3\underline{C}H_2OH$; 11, CH_3Cl; 12, CH_3OH; 13, $CH_3\underline{C}H_2O(CO)CH_3$; 14, Cs_2; 15, CH_2Br_2; 16, HCN; 17, $SC(NH_2)_2$; 18, CH_3F; 19, OCH_2; 20, $(CH_3\underline{C}HO)_3$; 21, $O\underline{C}(CH_3)_2$; 22, CH_2Cl_2; 23, C_6O_6; 24, C_6F_6; 25, $OC(NH_2)_2$; 26, $CHCl_3$; 27, $CH_3\underline{C}OOH$; 28, $H\underline{C}(OCH_3)_3$; 29, CCl_4; 30, $O\underline{C}(OEt)Cl$; 31, $O\underline{C}(OCH_3)_2$; 32, CO_2; 33, $Cl_2F\underline{C}CClF_2$; 34, $ClF_2\underline{C}CCl_2F$; 35, $F_3\underline{C}(CO)CH_3$; 36, CHF_3; 37, OCF_2; 38, CF_4. Reproduced from reference 20.

Figure 10. Plot of Hartree-Fock-Slater-calculated sulfur 1s binding energies *vs.* thermodynamically estimated energies.

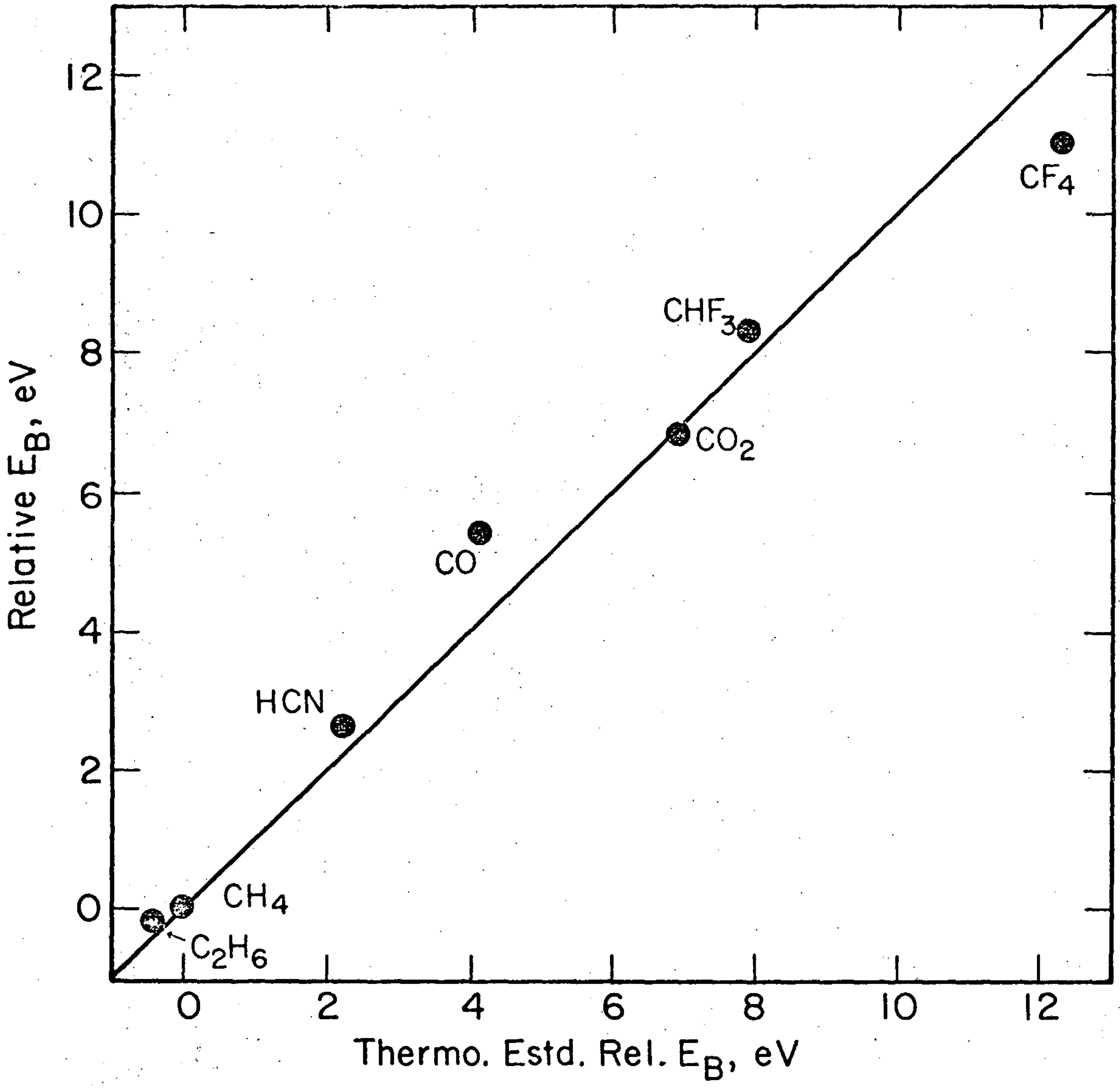
Figure 11. Plot of Hartree-Fock-Slater-calculated chlorine 1s binding energies *vs.* thermodynamically estimated energies.

Figure 12. Plot of core binding energies for solid compounds *vs.* thermodynamically estimated energies. Solid circles correspond to nitrogen 1s binding energies; open circles correspond to carbon 1s binding energies; solid triangles correspond to iodine core binding energies, open triangles correspond to boron 1s binding energies.



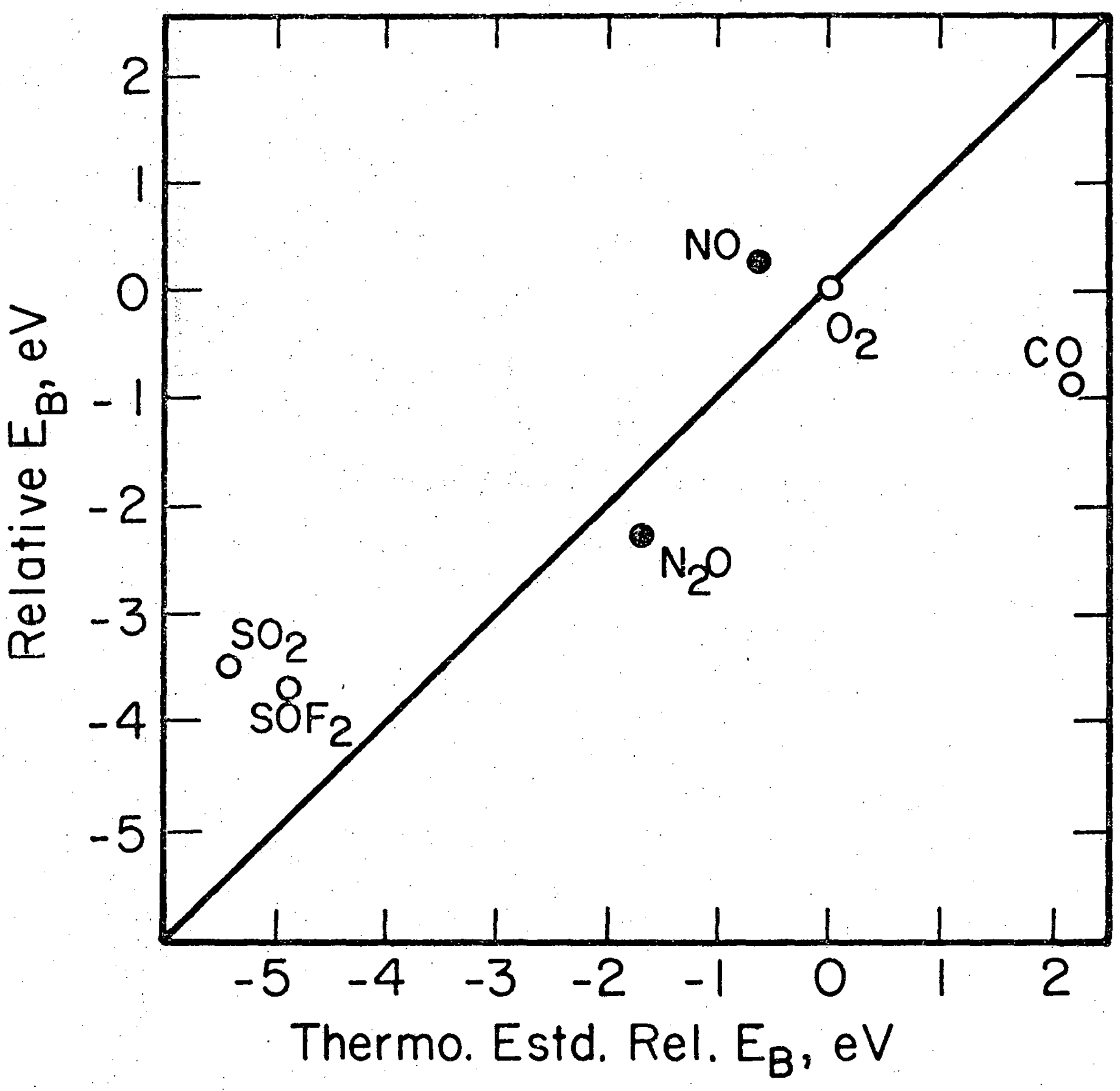
XBL 718-7208

Fig. 1



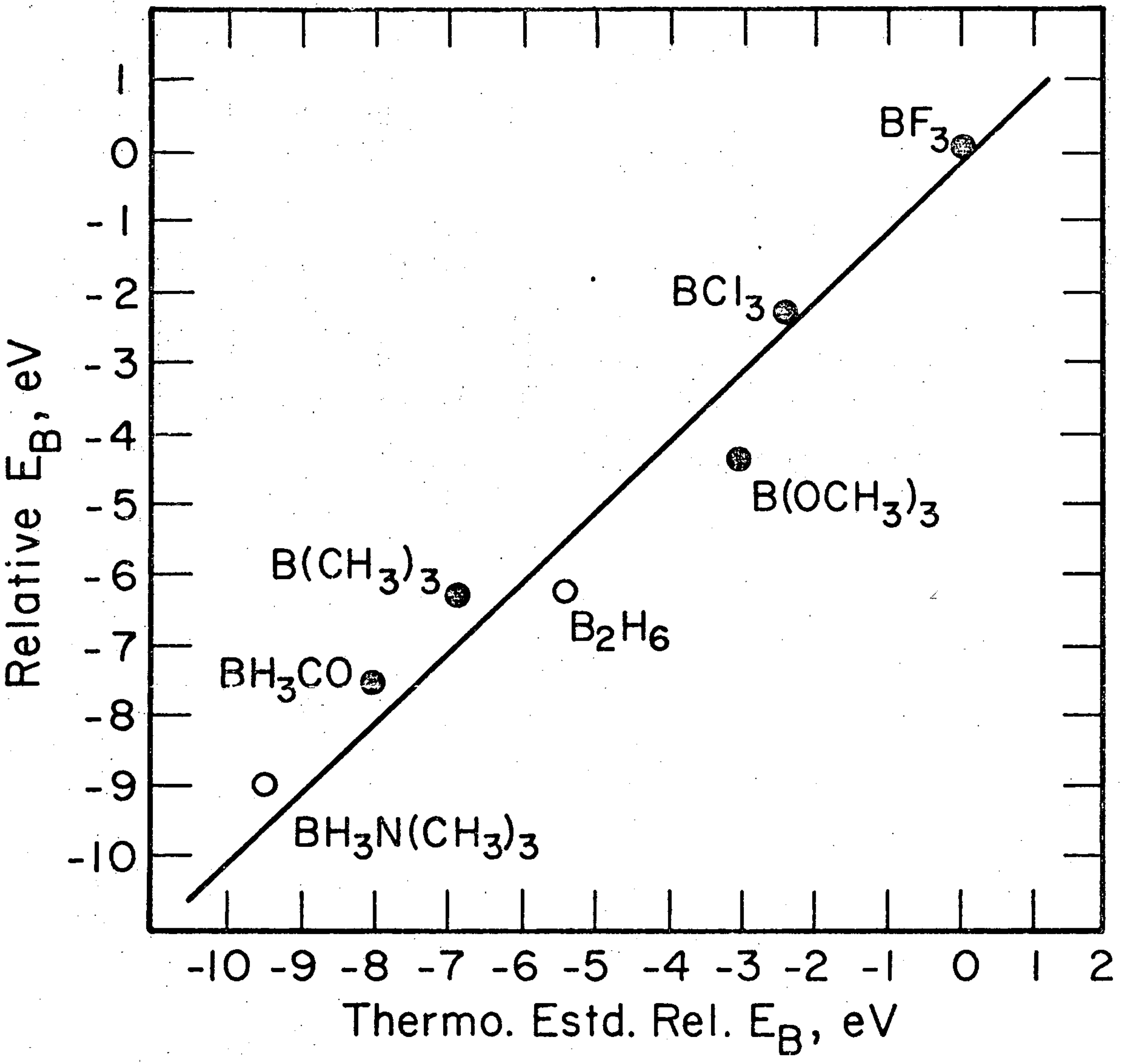
XBL 718-7209

Fig. 2



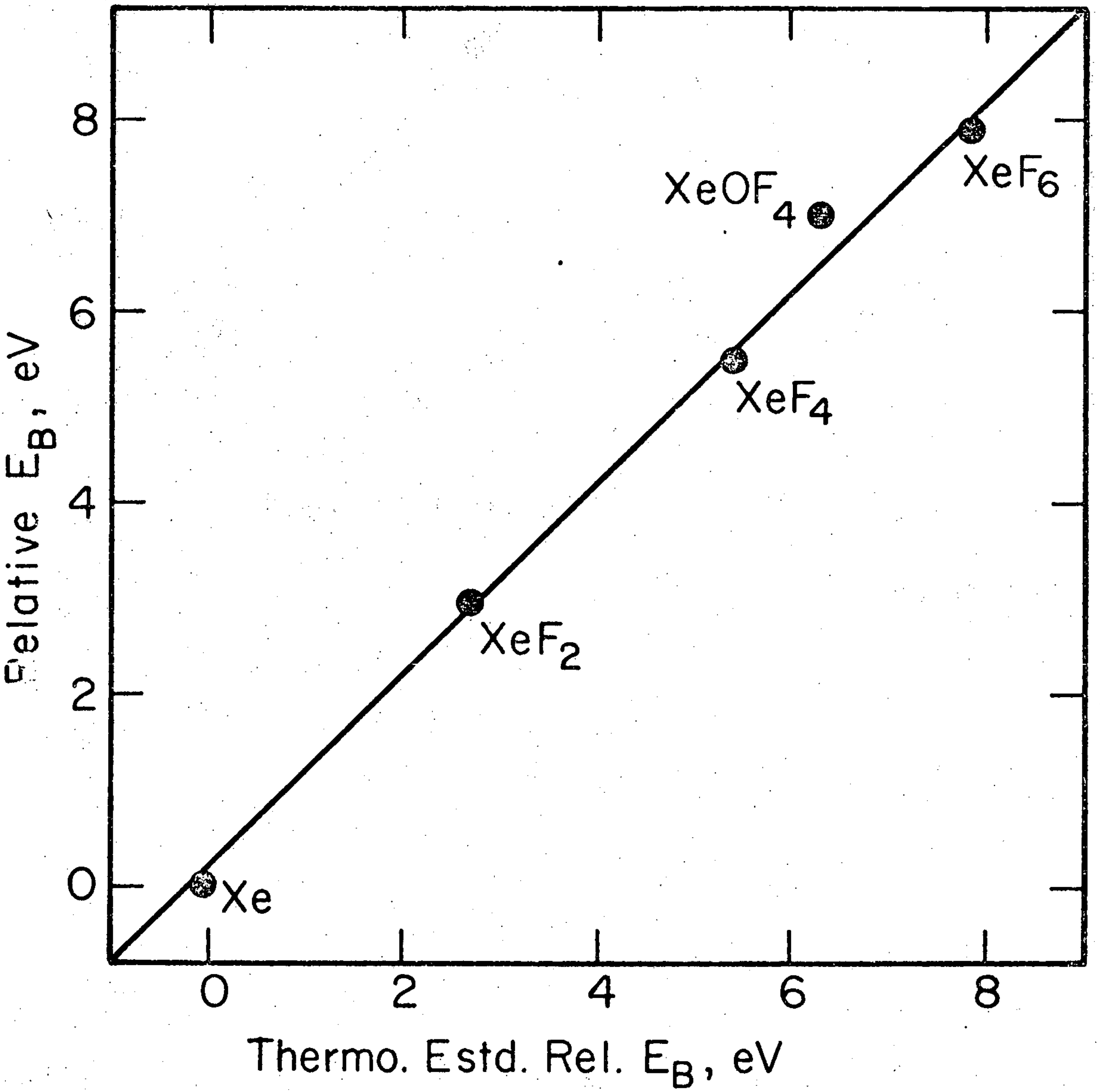
XBL 718-7210

Fig. 3



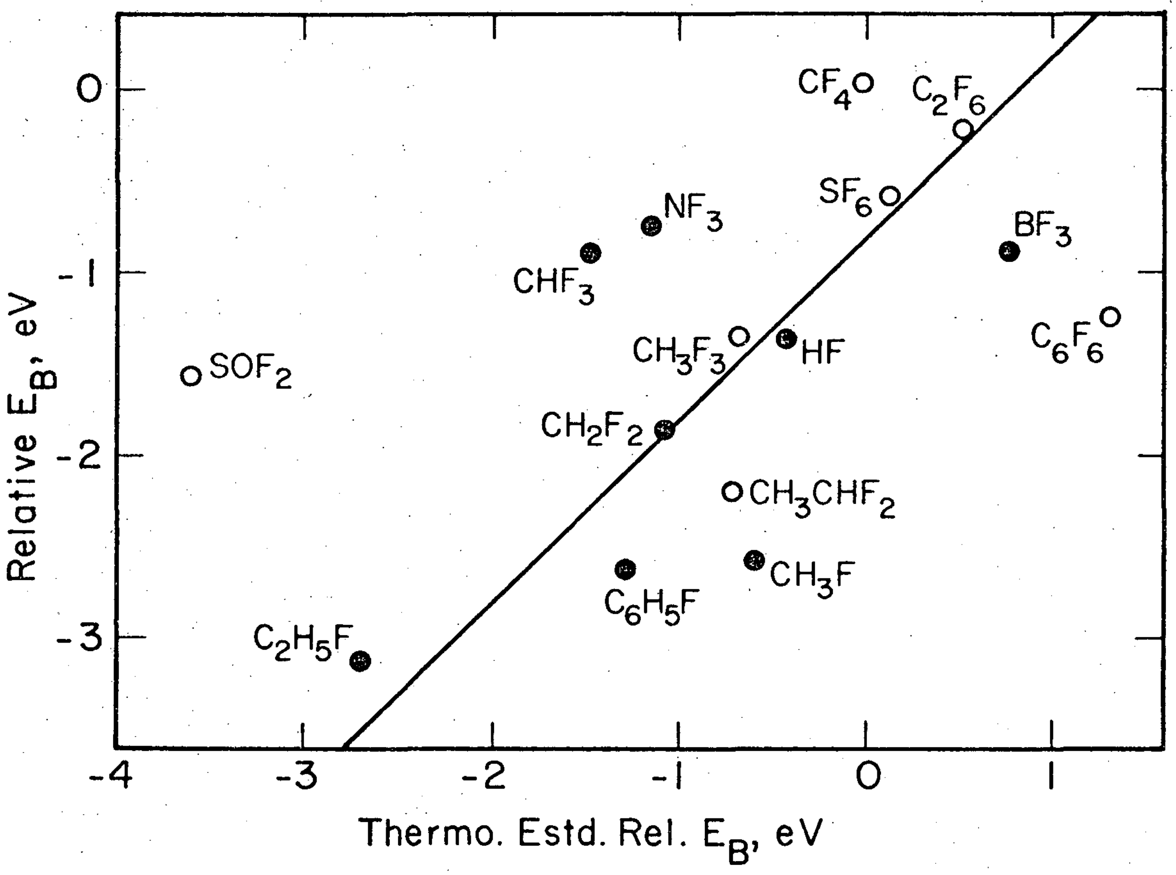
XBL 718-7211

Fig. 4



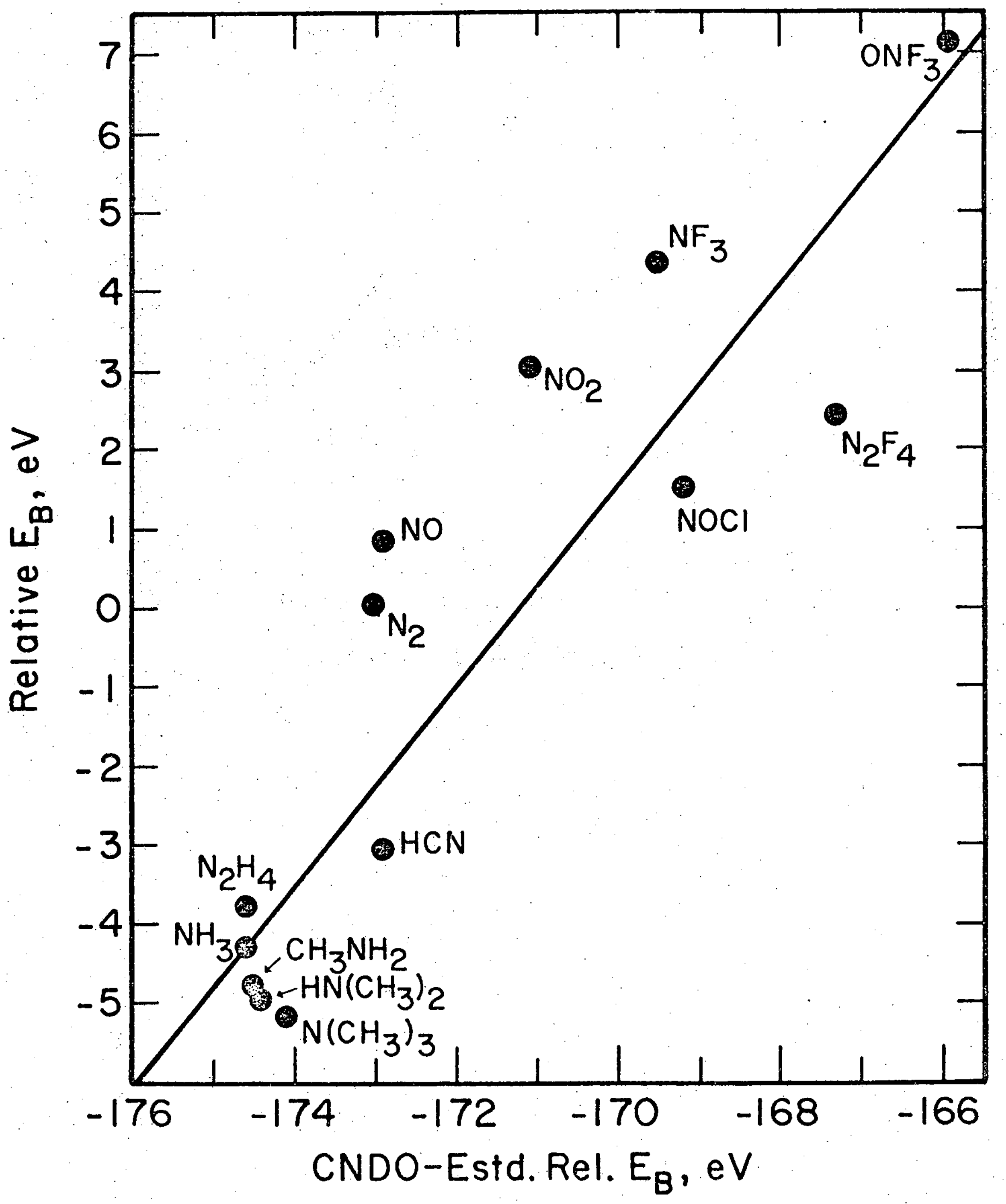
XBL 718-7212

Fig. 5



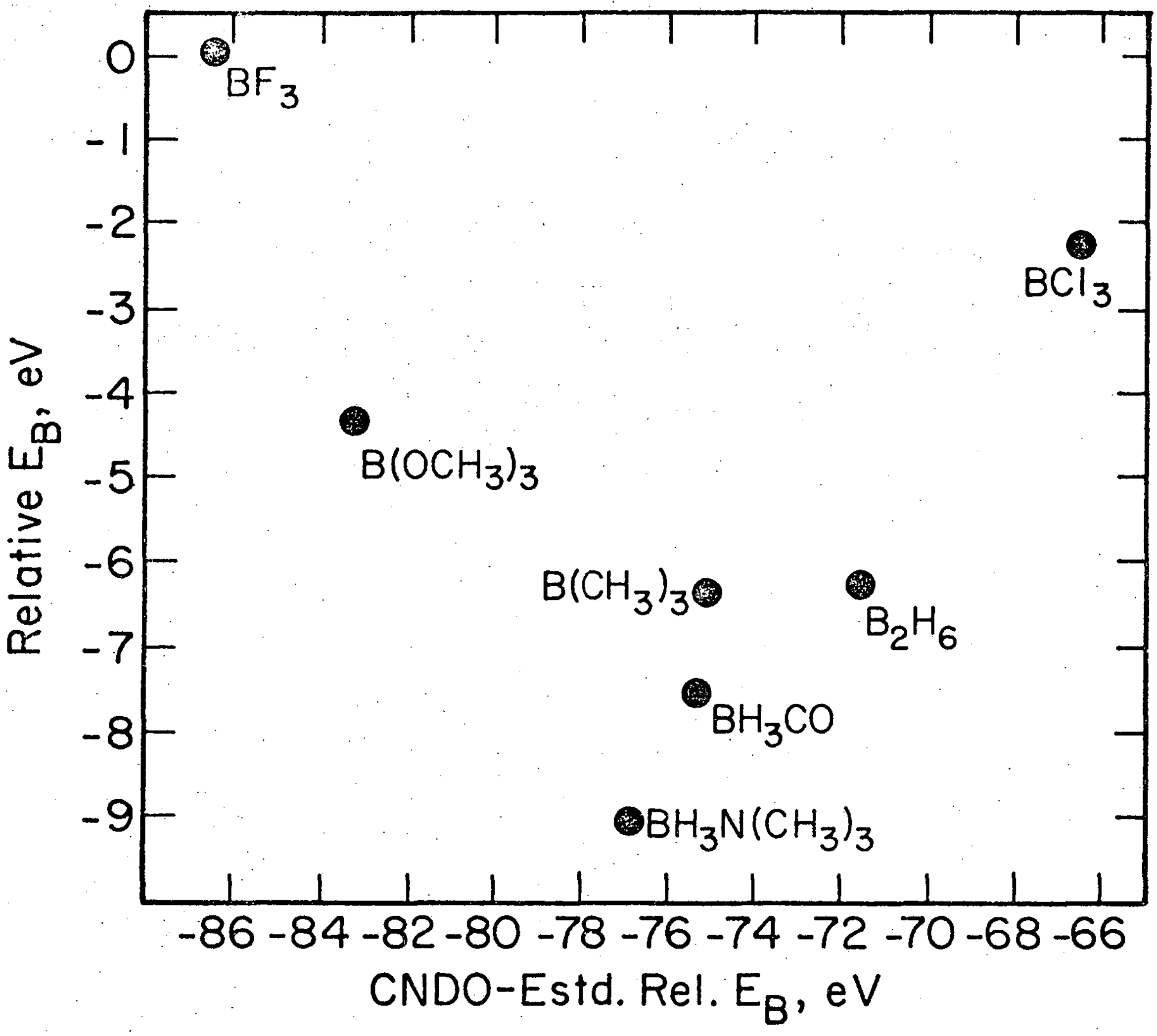
XBL 718-7213

Fig. 6



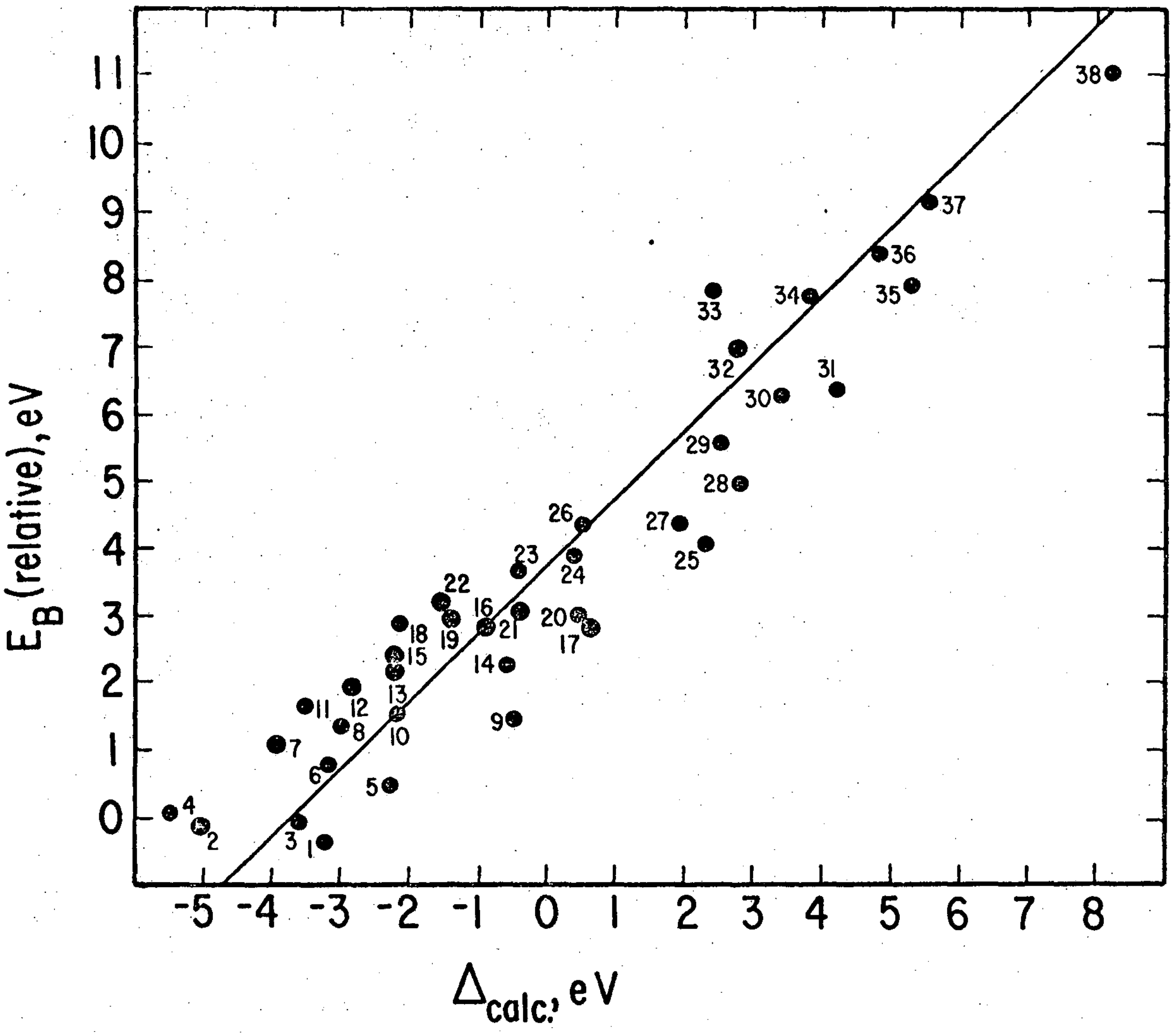
XBL 718-7214

Fig. 7



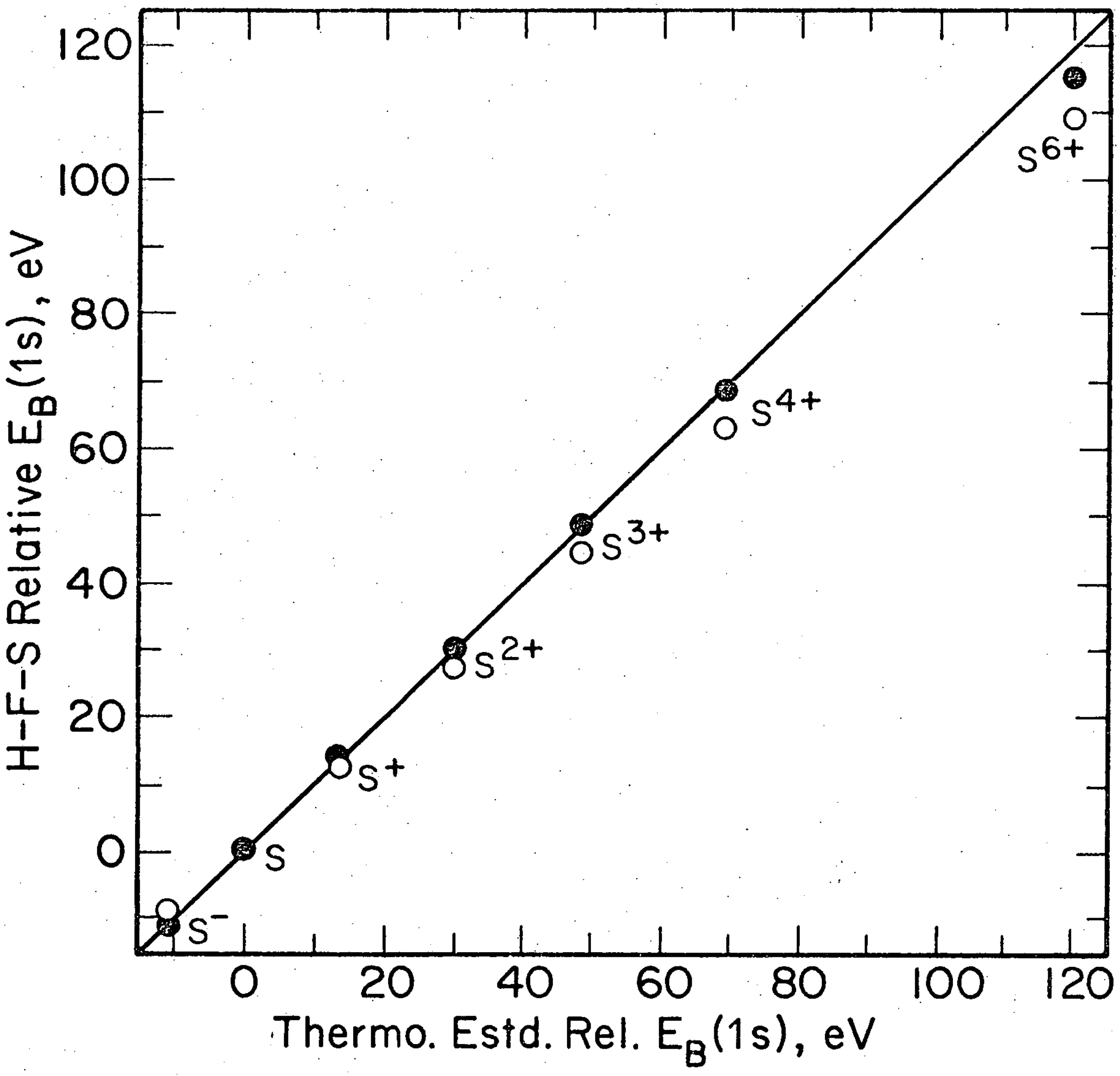
XBL 718-7215

Fig. 8



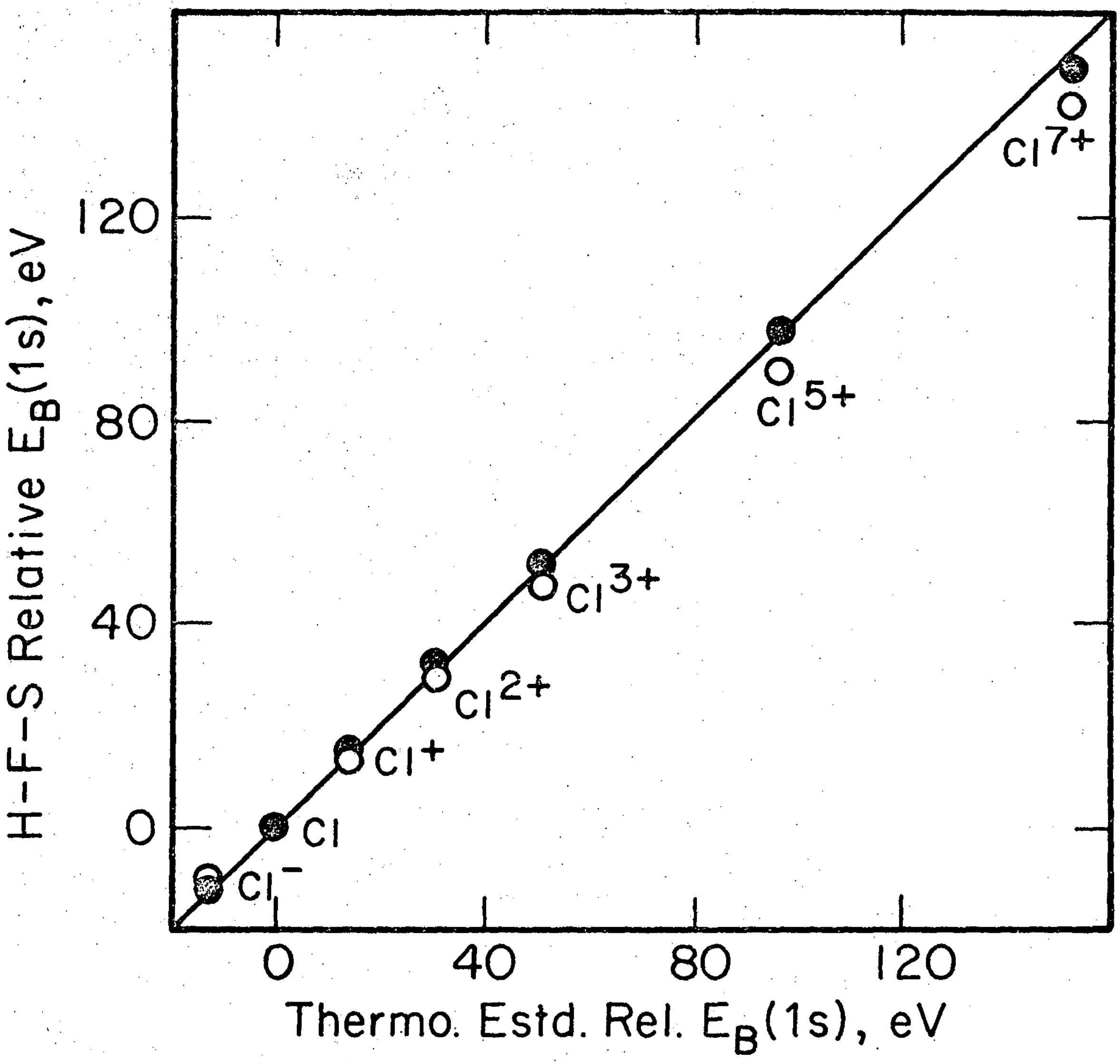
XBL 6910-5915

Fig. 9



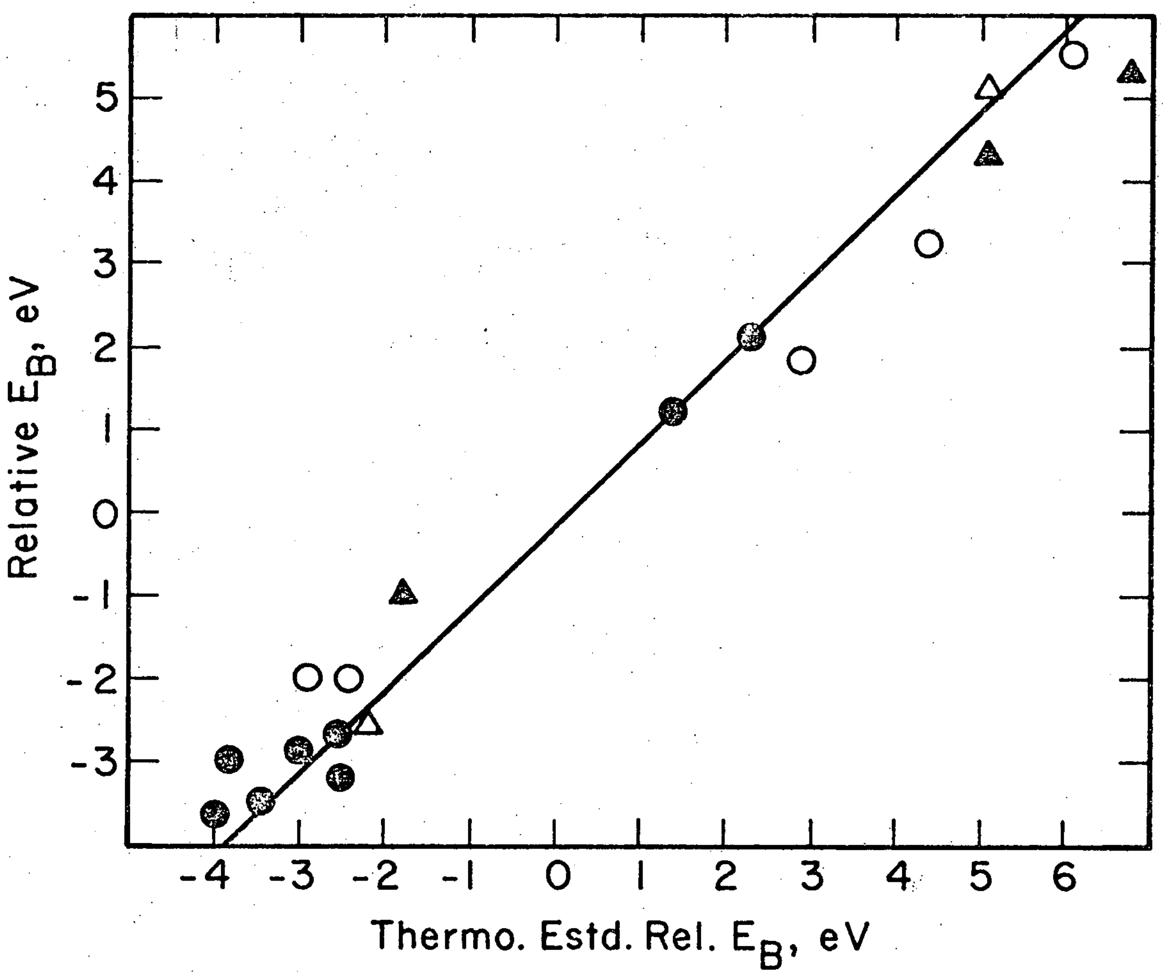
XBL 718-7216

Fig. 10



XBL 718-7217

Fig. 11



XBL 718-7218

Fig. 12

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