Submitted to
Inorganic Chemistry

LBL-2238
Preprint

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September 1973

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48

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The Correlation of Core Electron Binding Energies with Charge Distributions for Compounds of Carbon, Silicon, and Germanium

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ABSTRACT

Core electron binding energies for analogous compounds of carbon, silicon, and germanium have been measured by X-ray photelectron spectroscopy in the gas phase. The chemical shifts have been correlated by the electrostatic potential equation using charge distributions from extended Hückel theory, CNDO/2, and an electronegativity equalization method. The data can be retionalized without any consideration of $p\pi \rightarrow d\pi$ bonding in the silicon and germanium compounds.

The chemical shift associated with atomic core electron binding energies[1] is an electrostatic effect associated with the coulombic potential at the nucleus of the core-ionized atom or, more exactly, at the hole site itself.[2,3] These shifts are usually interpreted, using Koopmans' theorem, in terms of ground-state electronic distributions.[4-7] We have measured the core binding energies for analogous carbon, silicon and germanium coupounds and have correlated the chemical shifts with changes in the calculated charge distributions of the compounds. A principal aim of the work was to determine whether the valence-shell d orbitals of silicon and germanium are important in determining the charge distributions in compounds of these elements.

Experimental Section

Materials. The carbon compounds were obtained from commercial sources and were used as received. The CH_4, C_2H_6, $(CH_3)_2O$, CF_4, CH_3Cl, and CH_3Br were obtained from the Matheson Co.; research grade $C(CH_3)_4$ was obtained from the Phillips Petroleum Co.; analytical reagent grade CCl_4 was obtained from Mallinckrodt Chemical Works, and CBr_4 was obtained from the Eastman Kodak Company.

Silane was prepared by the reaction of $SiCl_4$ with $LiAlH_4$;[8] the infrared spectrum agreed with the literature.[8] Methyl silane was prepared by treating $SiCl_3CH_3$ with $LiAlH_4$ using a procedure similar to that used for SiH_4. The vapor pressure[9] (190 torr at -83.6°) and infrared spectrum[10] agreed with the literature. A sample of Matheson, Coleman, and Bell prac-

tical-grade $Si(CH_3)_4$ was used and was found to be pure by infrared spectrometry.[11] Disiloxane was prepared by the hydrolysis of SiH_3Cl and was purified by vacuum distillation. Its vapor pressure[9] (15 torr at -83.6°) and infrared spectrum[12] agreed with the literature. Silicon tetrafluoride was prepared by pyrolysis of $BaSiF_6$;[13] the infrared spectrum agreed with the literature.[14] Silyl chloride was prepared by the reaction of SiH_4 and AgCl;[15] its pressure[9] (39 torr at -83.6°) and infrared spectrum[16] agreed with the literature values. Silicon tetrachloride (99.8%, from Matheson, Coleman and Bell) was vacuum distilled and checked for purity by infrared spectrometry.[17] Silyl bromide was prepared by treating SiH_3Cl with excess HBr; its vapor pressure[9] (82 torr at -45.2°) and infrared spectrum[19] agreed with the literature. Silicon tetrabromide was prepared by the reaction of Si with Br_2[20] and was vacuum distilled; the boiling point (150°) agreed with the literature.[20]

Germane was prepared by a standard procedure;[21] its vapor pressure (180 torr at -111.6°) and infrared spectrum agreed with the literature.[21] Methylgermane was prepared by treating GeH_3Cl with $LiCH_3$ and was purified by vacuum distillation; the infrared spectrum agreed with the literature.[22] Tetramethyl germane was kindly provided by Dr. C. Riddle; its infrared spectrum agreed with the literature.[23] Germanium tetrafluoride was prepared by the pyrolysis of $BaGeF_6$;[24] the infrared spectrum agreed with the literature.[25] Germyl chloride was prepared from GeH_4 and AgCl;[15] the vapor pressure[9] (68 torr at -22.8°) and infrared spectrum[26] agreed with the literature. Germanium tetrachloride was prepared by the reaction of GeO_2 with HCl;[27] its

vapor pressure (23 torr at 0°) agreed with the literature.[9] Germyl bromide was prepared by treating GeH_3Cl with excess HBr; the vapor pressure[9] (28 torr at -22.8°) and infrared spectrum[26] agreed with the literature. Germanium tetrabromide was prepared by treating Ge with Br_2[20] and was purified by vacuum distillation. The melting point (25°) agreed with the literature.[20]

Hydrogen chloride and HBr were obtained in lecture bottles from the Matheson Co. Chlorine and bromine were obtained from the J. T. Baker Chemical Co.

X-Ray Photoelectron Spectra. Spectra were obtained using the Berkeley iron-free, double-focusing magnetic spectrometer.[28] Magnesium K_α X-rays (1253.6 eV) were used for all spectra except those of germanium compounds, for which aluminum K_α X-rays (1486.6 eV) were used. The spectra were measured with sample pressures of 30-40μ in the spectrometer irradiation chamber. Argon, at 20-30μ was simultaneously leaked into the irradiation chamber for a reference. The argon $2p_{3/2}$ core binding energy (248.45 eV) was used as a standard for all our measurements. Binding energies were determined by a least-squares fitting of both sample and reference experimental data to Lorentzian lineshapes. The reproducibility of the data was determined for several compounds to be about ± .05 eV. The energies correspond to absolute free-molecule ionization potentials inasmuch as they were measured at low pressure in the gas phase and were calibrated against a standard of known energy.

Most of the carbon 1s shifts have been previously reported by other workers. However, to obtain a series strictly comparable with respect to

reference and precision, we remeasured these binding energies.

Calculations

Atomic Charges. Charge distributions for use in the potential model were calculated using three different methods: extended Hückel theory[29] (EHT), CNDO/2,[30] and an electronegativity equalization method (CHELEQ) devised by the authors.[31]

The simple extended Hückel theory of Hoffmann was used.[29] The diagonal elements of the Hamiltonian matrix were one-electron orbital energies from atomic, ab initio calculations by Clementi,[32] rather than empirical valence-state ionization potentials. The off-diagonal elements used the relation

$$H_{ij} = 0.875(H_{ii} + H_{jj})S_{ij} \qquad (1)$$

The overlap integrals were calculated from Slater type orbitals, using exponents and principle quantum numbers fitted to near Hartree-Fock atomic wavefunctions by Cusachs and Corrington.[33] The basis set includes d orbitals on silicon and germanium atoms as parameterized by Corrington.[34] Atomic charges and orbital populations were obtained by Mulliken analysis.

Our program for the CNDO/2 molecular orbital method was very similar to that found in Pople and Beveridge's book.[30] We have not altered Pople's parameters for the first-row elements and for hydrogen. We have followed Segal and Santry's[35] method for parameterization of the second row elements, but have utilized Hinze and Jaffé's[36,37] orbital ionization energies and electron affinities and Cusachs and Corrington's[33] valence s orbital wavefunctions. As discussed previously, these wavefunctions came from near

Hartee-Fock results and are less arbitrary for second and third-row elements than are exponents obtained using Slater's rules.[38] The CNDO program was expanded to third-row non-transition elements by this same method. Because CNDO uses the same radial function for all basis functions on a given atom, d orbitals are poorly described, and one obtains results which are quite different from those of ab initio calculations.[39] Consequently, for all elements above hydrogen we used only an s,p basis set. Orbital populations in CNDO are directly obtained from the diagonal elements of the density matrix.

The CHELEQ method for estimating atomic charges is based on the equalization of orbital electronegativities.[31] This empirical method is based on the Iczkowski and Margrave definition of electronegativity[40] and, as far as possible, uses Hinze and Jaffé's orbital electronegativities.[16,17] There is no provision for d orbitals in this method. The method has successfully correlated binding energies for a large number of first row elements.

The Potential Model. Using Koopmans' theorem, one may easily derive the potential model from the Roothan equations. The binding energy of a 1s electron, for example, is given by the expression

$$E^{A}_{1s} = \langle x_{1s} | H + G | x_{1s} \rangle \qquad (2)$$

where, for simplicity, we have assumed that the core molecular orbital is almost entirely located on the 1s orbital, x_{1s}, of atom A, a first-row element. If we neglect the exchange integrals of atoms not directly bonded to atom A, Equation 2 may be expanded and arranged as follows.

$$E_{1s}^{A} = \sum_{i \in A \neq 1s} \sum_{j} P_{ij} [(1s1s|ij) - \tfrac{1}{2}(1sj|1si)] + \left[\sum_{i \notin A} \sum_{j} P_{ij} (1s1s|ij) + \sum_{B \neq A} Z_B R_{AB}^{-1}\right] + [H_{1s1s} + \tfrac{1}{2}(1s1s|1s1s)] \tag{3}$$

The empirical point charge potential equation[7] is written

$$E_B = kQ + V + \ell \tag{4}$$

The term kQ corresponds to the first double summation of Equation 3; hence k has the value

$$k \approx \sum_{\ell} N_{\ell} [F_0(1s,2\ell) - \sum_{k} G_k(1s,2\ell)] \tag{5}$$

where N_ℓ is the fractional occupancy of the ℓth valence subshell (s,p,d,...) and F_0 and G_k are two-electron Slater integrals from atomic Hartree-Fock calculations. The V in Equation 4 and the terms in the second bracket of Equation 3 represent an electrostatic potential at A. In the point charge approximation this is simply

$$V = \sum_{B \neq A} Q_B R_{AB}^{-1} \tag{6}$$

where Q_B is the net charge on each atom B. The last terms in Equations 3 and 4 are constants for a given element.

Schwartz has further identified Equation 3 with the "external potential," Φ_{ext}, plus a constant.[2] This may be written as

$$\varepsilon_{1s}^{A} \approx \Phi_{ext} + \ell = -\sum_{i,j} P_{ij} (i|r_A^{-1}|j) + \sum_{B \neq A} Z_A R_{AB}^{-1} + \ell \tag{7}$$

Equation 7 is applicable to semiempirical calculations by restricting the first summation to valence electrons and by substituting Z_{core} for Z. This modified potential is called Φ_{val}, the valence potential.[41] For use with CNDO semiempirical calculations (to retain invariance and to simplify calculations), the diagonal two-centered matrix elements are approximated as R^{-1} and Equation 7 becomes

$$E_B = -\sum_{i \in A} P_{ii} \langle r_i^{-1} \rangle + \sum_{B \neq A} Q_B R_{AB}^{-1} + \ell \qquad (8)$$

This very simple form[42] may be used with extended-Hückel theory by using Mulliken gross orbital populations in place of the CNDO density matrix terms P_{ii}. Equation 8 has the form of the point charge potential model, where k may be written for a Slater type orbital as

$$k = \sum_{\ell} N_{\ell} \zeta_{\ell} n^{-1} \qquad (9)$$

where ζ_{ℓ} is the valence orbital exponent and n is the valence orbital quantum number.

Another method of estimating the free-atom value of k uses the principle of equivalent cores.[43] The chemical shift between the gaseous atom A and the gaseous ion A^+ is the energy of the following reaction,

$$A^{*+} + A^+ = A + A^{*2+} \qquad \Delta E = \Delta E_B \qquad (10)$$

where the asterisks refer to core holes. If we let B stand for the element following A in the Periodic Table, we may write another equation having practically the same energy as that of Equation 10:

$$B^{+} + A^{+} = A + B^{2+} \qquad \Delta E \simeq \Delta E_B \tag{11}$$

For a free atom,

$$k = dE_B/dq \simeq \Delta E_B/\Delta q \tag{12}$$

From Equation 11 and 12 one obtains

$$k_A \simeq I_2(B) - I_1(A) \tag{13}$$

where $I_2(B)$ is the second ionization potential of atom B and $I_1(A)$ is the first ionization potential of atom A.

Relaxation effects during photoionization may be accounted for by use of the principle of equivalent cores and an approximation due to Hedin and Johansson.[5] The corrected binding energy is written,[44]

$$E_B^{rel} = \tfrac{1}{2}\{\Phi_{val}(Z^{o}) + \Phi_{val}[(Z + 1)^{+}]\} + \ell \tag{14}$$

where $\Phi_{val}(Z^{o})$ is the potential of the ground-state neutral molecule and $\Phi_{val}[(Z + 1)^{+}]$ is the potential of the isoelectronic cation in which the ionized core has been replaced by the core of the next higher element in the Periodic Table.

Results

Core binding energies for the compounds studied are given in Tables I and II. The carbon, silicon, and germanium chemical shifts are listed in Table III. Cholorine and bromine chemical shifts are listed in Table

Table I

Core Binding Energies for Carbon, Silicon, and Germanium

Compound	Binding Energy (eV) M = C (1s)	M = Si (2p)	M = Ge ($3p_{3/2}$)
MH_4	290.73	107.14	129.19
MH_3CH_3	290.57	106.68	128.78
$M(CH_3)_4$	290.31	105.82	127.90
$(MH_3)_2O$	292.13	107.67	--
MF_4	301.68	111.65	133.61
MH_3Cl	292.31	107.97	130.09
MCl_4	296.22	110.25	131.98
MH_3Br	291.95	107.94	129.90
MBr_4	294.64	109.59	131.21

Table II

Core Binding Energies for Carbon, Oxygen, Fluorine, Chlorine, and Bromine

Compound	Binding Energy (eV)				
	$X = CH_3$	$X = O$	$X = F$	$X = Cl$	$X = Br$
	(1s)	(1s)	(1s)	($2p_{3/2}$)	(3d)
CH_3X	290.57	--	--	206.07	76.25
$(CH_3)_2X$	--	538.86	--	--	--
CX_4	290.31	--	695.60	206.84	76.74
SiH_3X	290.31	--	--	206.05	76.30
$(SiH_3)_2X$	--	538.46	--	--	--
SiX_4	289.61	--	694.87	206.77	76.64
GeH_3X	290.19	--	--	205.50	75.82
GeX_4	289.59	--	694.38	206.42	76.41
X_2	--	--	--	207.64	77.23
HX	--	--	--	207.22	77.19

Table III

Carbon, Silicon, and Germanium Chemical Shifts (eV)

Compound	$\Delta E_B(C)$	$\Delta E_B(Si)$	$\Delta E_B(Ge)$
$M(CH_3)_4$	-0.42	-1.32	-1.29
MH_3CH_3	-0.16	-0.46	-0.41
MH_4	0.0	0.0	0.0
$(MH_3)_2O$	1.40	0.53	--
MH_3Br	1.22	0.80	0.71
MH_3Cl	1.58	0.83	0.90
MBr_4	3.91	2.45	2.02
MCl_4	5.49	3.11	2.79
MF_4	10.95	4.51	4.42

IV.

Calculated binding energies were obtained in several ways. The valence potential model was used with CNDO/2 and EHT data. The calculated binding energies were expressed as

$$E_B^{calc} = c\Phi_{val} + \ell \qquad (13)$$

where c and ℓ are parameters determined by a least-squares fitting of experimental binding energies to the calculated valence potentials. Although c should be unity, we have allowed it to be an adjustable scaling parameter to compensate somewhat for the approximate nature of our calculations and for inadequacies of parameterization. Both ground-state and relaxed-state correlations were made for C 1s, Si 2p, and Ge 3p binding energies. Only ground-state correlations were made for the Cl 2p and Br 3d energies, because proper parameterization for argon and krypton is lacking. Figures 1, 2, and 3 are plots of CNDO/2 ground state correlations for carbon, silicon, and germanium binding energies, respectively.

Binding energies were also calculated from Equation 4 and CHELEQ atomic charges, using values of k and ℓ obtained by least-squares fitting of Q and V to the experimental data. Only ground-state charges were used with this method. Figures 4, 5, and 6 show plots of $(E_B - V)$ vs. Q for the carbon, silicon, and germanium data, respectively.

The potentials, parameters, and standard deviations from the EHT carbon, silicon, and germanium binding energy correlations are given in Table V. The corresponding data from the CNDO/2 calculations are given in Table

Table IV

Chlorine and Bromine Chemical Shifts (eV)

Compound	$\Delta E_B(Cl)$	$\Delta E_B(Br)$
X_2	0.0	0.0
XH	-0.42	-0.04
X_4C	-0.80	-0.49
X_4Si	-0.87	-0.59
X_4Ge	-1.22	-0.82
XCH_3	-1.57	-0.98
$XSiH_3$	-1.59	-0.93
$XGeH_3$	-2.14	-1.41

Table V

EHT Valence Potentials for Carbon, Silicon, and Germanium (eV)

Compound	$\Phi_{val}(C)$	$\Phi^{rel}_{val}(C)$	$\Phi_{val}(Si)$	$\Phi^{rel}_{val}(Si)$	$\Phi_{val}(Ge)$	$\Phi^{rel}_{val}(Ge)$
MH_4	-95.19	-112.90	-48.02	-53.63	-46.56	-50.63
MH_3CH_3	-94.39	-112.96	-46.86	-52.79	-45.36	-49.72
$M(CH_3)_4$	-92.41	-113.62	-42.89	-49.85	-41.31	-46.48
$(MH_3)_2O$	-88.27	-104.95	-48.41	-53.44	--	--
MF_4	-57.83	-68.22	-39.58	-41.80	-37.07	-38.86
MH_3Cl	-88.84	-107.36	-45.66	-51.26	-44.27	-48.39
MCl_4	-72.81	-92.63	-38.22	-43.86	-37.02	-41.41
MH_3Br	-91.16	-110.77	-46.12	-52.12	-44.76	-49.19
MBr_4	-80.09	-103.47	-39.10	-45.67	-37.92	-43.20
c	0.295	0.247	0.333	0.356	0.347	0.363
ℓ	318.31	318.83	122.93	125.90	144.84	147.01
Std. Dev.	0.46	0.64	1.28	0.95	1.24	0.99

VI. The calculated binding energies, charges, parameters, and standard deviations from the correlations using the CHELEQ charges are listed in Table VII.

Discussion

All three methods for calculating ground-state charge distributions give good correlations with carbon binding energies, as expected from previous work.[7,31,41,42] The chemical shifts between corresponding pairs of silicon and germanium compounds are almost identical. This result is not surprising in view of the similar chemistries and structures of silicon and germanium compounds, The silicon and germanium shifts are qualitatively similar to the carbon shifts, although the former are smaller than the latter.

EHT correlations. The EHT parameterizations for silicon and germanium are nearly identical. The EHT correlation of E_B with Φ_{val} is not as satisfactory for the silicon and germanium coupounds as it is for the carbon compounds. The poorer correlation is partly caused by excessive calculated polarization, which is partially corrected by the scaling parameter c of Equation 15. In all three correlations, this parameter took a value near 0.3 and served to "depolarize" the charges. For carbon this worked quite well, but for silicon and germanium, polarization was more extreme - especially for the tetrahalides - and the simple linear correction given by c was inadequate. Also, electronic relaxation during photoemission may affect the chemical shifts of second and third-row elements more than those of car-

Table VI

CNDO/2 Valence Potentials for Carbon, Silicon, and Germanium (eV)

Compound	$\Phi_{val}(C)$	$\Phi^{rel}_{val}(C)$	$\Phi_{val}(Si)$	$\Phi^{rel}_{val}(Si)$	$\Phi_{val}(Ge)$	$\Phi^{rel}_{val}(Ge)$
MH_4	-88.86	-104.76	-57.44	-64.84	-58.31	-63.41
MH_3CH_3	-88.49	-105.07	-57.30	-65.14	-58.20	-63.73
$M(CH_3)_4$	-87.56	-105.75	-56.88	-65.78	-57.92	-64.52
$(MH_3)_2O$	-87.25	-104.04	-56.54	-64.89	--	--
MF_4	-79.37	-94.90	-50.90	-57.38	-51.66	-56.43
MH_3Cl	-86.75	-104.03	-56.08	-63.84	-56.95	-62.46
MCl_4	-82.83	--	-52.84	-61.30	-53.82	-60.06
MH_3Br	-87.22	-105.04	-56.42	-64.43	-57.32	-63.02
MBr_4	-84.64	--	-54.03	-63.01	-55.19	-62.04
c	1.171	1.048	0.778	0.665	0.742	0.684
ℓ	393.99	401.11	151.41	150.47	172.00	172.71
Std. Dev.	0.63	0.49	0.54	0.62	0.51	0.53

Table VII

CHELEQ Correlation Data For Carbon, Silicon, and Germanium

Compound	Q_C	V_C(eV)	Q_{Si}	V_{Si}(eV)	Q_{Ge}	V_{Ge}(eV)
MH_4	-0.060	0.79	-0.029	0.29	-0.091	0.86
MH_3CH_3	-0.047	0.52	-0.013	0.08	-0.076	0.64
$M(CH_3)_4$	-0.011	-0.33	0.035	-0.36	-0.030	-0.04
$(MH_3)_2O$	0.049	-0.76	0.099	-1.33	--	--
MF_4	0.498	-5.42	0.633	-5.92	0.602	-5.19
MH_3Cl	0.020	0.15	0.071	-0.40	0.012	0.15
MCl_4	0.256	-2.08	0.368	-2.63	0.316	-2.17
MH_3Br	0.007	0.28	0.057	-0.26	-0.003	0.28
MBr_4	0.202	-1.50	0.309	-2.03	0.250	-1.57
k	30.07		16.59		15.42	
ℓ	291.27		106.88		129.32	
Std. Dev.	0.62		0.56		0.47	

bon, leading to poorer results with ground-state charges.

CNDO/2 Correlations. Excessive polarization is not obtained with a self-consistent field theory like CNDO/2. Thus the fitting parameter c for the CNDO/2 carbon compound correlation is close to unity. However, for the silicon and germanium coumpounds, the plots (Figures 2 and 3) exhibit more scatter than that for the carbon compounds (Figure 1), and the parameter c is approximately 0.7. These results may be due to errors in parameterization for silicon and germanium. The orbital ionization potentials and, especially, electron affinities are uncertain for these elements. However, the CNDO/2 correlations are much better than those given by EHT, indicating that the CNDO/2 charge distributions are reasonable.

CHELEQ correlations. The CHELEQ correlations for the silicon and germanium compounds, shown in Figures 5 and 6, are similar to those obtained with CNDO, perhaps because both methods are parameterized with essentially the same Hinze and Jaffé data. The CHELEQ correlations are based on the point charge potential model, Equation 4, and it is of interest to compare the least-squares determined values of k with various theoretical estimates for this parameter. Table VIII lists the empirical k values and theoretical k values obtained from Equations 5, 9, and 13. The ratios k_{Si}/k_C, k_{Ge}/k_C and k_{Ge}/k_{Si} are also tabulated. Ground-state ionization potentials,[45] corresponding to s^2p^2 structures, were used with the equivalent cores method of estimating k (Equation 13). Slater integrals calculated by Mann[46] for Hartree-Fock calculations were used to obtain k values from equation 5, and single STO atomic wavefunctions tabulated by Cusachs[33] were used to obtain

Table VIII

Theoretical and Empirical Values of the Potential Model Parameter k (eV/e)

	CHELEQ empirical	Equation 13	Equation 5	Equation 9 cation	Equation 9 neutral	Equation 9 anion
k_C	30.07	18.34	19.54	23.83	21.80	20.47
k_{Si}	16.59	11.58	11.78	13.84	12.84	12.17
k_{Ge}	15.42	10.73	11.37	13.09	12.31	11.71
k_{Si}/k_C	0.55	0.63	0.60	0.58	0.59	0.59
k_{Ge}/k_C	0.51	0.59	0.58	0.55	0.56	0.57
k_{Ge}/k_{Si}	0.93	0.93	0.97	0.95	0.96	0.96

k values from equation 9. Because cation and anion STO wavefunctions were also available, we included values of k for these species to illustrate the charge dependency of k. The estimated k values calculated from Slater integrals and those calculated from nuclear attraction integrals correspond to sp^3 atoms. All of the ground-state estimates of k are in approximate agreement. The empirical CHELEQ values are about 50% higher than the theoretical estimates, but the ratios of empirical values are close to the theoretical ratios. The discrepancies in absolute value are probably due to the arbitrary nature of assigning absolute charges to atoms in molecules by CHELEQ or any method.[31]

Relaxation Effects. Electronic relaxation is complete in the time required for the photoelectric process.[1,4,5,7] Relaxation during photoemission occurs because the remaining electrons are attracted to the hole left by the photoelectron, with the result that the photoelectron acquires a higher kinetic energy than expected from a frozen-orbital Koopmans' theorem description of photoemission. The success of ground-state wavefunctions and charge distributions in correlated ESCA chemical shifts is due not to this relaxation energy being small, but rather to its having about the same magnitude for a variety of compounds. However, when relaxation is neglected for certain molecules (CO is an example[44]); predicted shifts are much different than experiment. Using Equation 14, we corrected the EHT and CNDO/2 calculations for relaxation and found that certain recurrent anomalies in the uncorrected correlations were thereby eliminated. For example, in all three series the experimental binding energies increase in

the order $M(CH_3)_4 < MH_3CH_3 < MH_4$. The effect is quite pronounced for M = Si, Ge. However, all the ground-state methods wrongly predict $MH_4 < MH_3CH_3 < M(CH_3)_4$. For M = C, both EHT and CNDO relaxation-corrected calculations give the proper order. The corrected potentials for the carbon series duplicate the observed shifts better than the ground state potentials.[47] For M = Si, Ge, the EHT relaxation-corrected calculations only partially correct the error. The CNDO/2 relaxation-corrected potentials, however, give the experimental order for both silicon and germanium. The relaxation correction did not much affect the standard deviation of the CNDO data; better parameterization of silicon and germanium might improve the correlations. The overall results strongly suggest that the spurious order for MH_4, MH_3CH_3, and $M(CH_3)_4$ predicted by the ground-state calculations is due to neglect of relaxations.

d Orbital Bonding. There is considerable speculation as to the importance of the valence-shell d orbitals in the chemistry of silicon and germanium. One aim of our study was to determine, if possible, the importance of d orbital participation by a comparison of the silicon and germanium shifts with the corresponding carbon shifts. The participation of the valence-shell d orbitals of silicon or germanium in $p\pi \rightarrow d\pi$ bonding corresponds to a transfer of negative charge from the ligand atoms to the central atom:

$$R_3\bar{Si}{=}X^+$$

If such π bonding is significant, the core binding energy of the silicon or germanium atom would be expected to be lower than in the absence of

such bonding. Silicon and germanium d orbitals were included in the EHT basis set, but the EHT method is too crude to yield a meaningful solution to the problem. Neither the CHELEQ method nor our version of CNDO/2 had any provision for d orbitals. However, certain systematic deviations in the CHELEQ and CNDO/2 plots (Figures 2, 3, 5, and 6) may be interpreted as an indication that d orbitals are important in the bonding.

Let us first consider the CHELEQ plots, Figures 5 and 6. The solid lines in these figures were determined by least-squares fitting of the data. If d orbitals are not important in the bonding of these compounds, the slopes of these lines, i.e., the k_{Si} and k_{Ge} values, should be equal to the slope of the corresponding plot for carbon compounds, k_C, times the theoretical ratios k_{Si}/k_C and k_{Ge}/k_C, respectively. We have calculated these theoretical values of k_{Si} and k_{Ge} using the average k_{Si}/k_C and k_{Si}/k_C values from Table VII. The dashed lines in Figures 5 and 6 have slopes equal to these calculated k values. These lines were drawn through the points for the hydrides, SiH_4 and GeH_4, because $p\pi \rightarrow d\pi$ bonding in these compounds is assumed to be neglibible. Negative deviations of $(\Delta E_B - V)$ from the dashed lines may be attributed to negative charge on silicon or germanium due to $p\pi \rightarrow d\pi$ bonding which was neglected in the charge calculations. The CNDO/2 plots for silicon and germanium, Figures 2 and 3, have been similarly treated. In these plots, the dashed lines passing through the hydrides have unit slope, the theoretically correct value of the fitting constant c. Again all the remaining points lie below these lines.

Although the above interpretation of the data suggests appreciable

d orbital bonding, other considerations suggest the opposite conclusion. The solid straight line correlations which neglect d orbitals are fairly good. Small errors in the parameterization of silicon and germanium in both the CNDO/2 and CHELEQ methods may cause the low empirical values of k and c. Perhaps relaxation effects can account for at least part of the deviations from the dashed lines, especially in the cases of $M(CH_3)_4$, MBr_4, and MCl_4. All in all, the data offer little support for the participation of d orbitals in the bonding of silicon and germanium compounds.

Chlorine and Bromine Chemical Shifts. Core binding energies for the halogen atoms in the compounds which we have discussed, and also in molecular chlorine, bromine, hydrogen chloride, and hydrogen bromide were measured and correlated with calculated charge distributions using the potential model. The EHT, CNDO/2, and CHELEQ correlation data for the chlorine binding energies are listed in Table IX. The bromine data, listed in Table X, closely parallel the chlorine data. All of these correlations have considerable scatter, and the low standard deviations are a consequence of the small range of binding energies involved. Some of the experimental shifts listed in Table 3 deserve comment. The chemical shift $E_B(HX) - E_B(X_2)$ is smaller for X = Cl, Br than was observed by other workers for X = F.[48] The halogen binding energies for corresponding silicon and carbon compounds are quite close, whereas those for the corresponding germanium compounds are shifted to lower energy. One might have expected the halogens on corresponding silicon and germanium compounds to have nearly the same energies. More satisfactory correlation methods, probably including relaxation effects,

Table IX

EHT, CNDO/2, and CHELEQ Correlation Data for Chlorine

Compound	Φ_{val}^{EHT}	$\Phi_{val}^{CNDO/2}$	Q^{CHELEQ}	V^{CHELEQ}
Cl_2	-132.91	-142.19	0.000	0.00
ClH	-135.04	-143.69	-0.090	1.02
$ClCH_3$	-134.91	-144.33	-0.081	0.52
Cl_4C	-133.13	-142.45	-0.064	1.13
$ClSiH_3$	-136.43	-144.36	-0.109	0.70
Cl_4Si	-134.74	-142.94	-0.092	1.42
$ClGeH_3$	-137.03	-144.29	-0.096	0.48
Cl_4Ge	-135.20	-142.83	-0.079	1.18
C	0.402	0.591	--	
k	--	--	21.99	
ℓ	260.83	291.26	207.44	
Std. Dev.	0.39	0.45	0.40	

Table X

EHT, CNDO/ , and CHELEQ Correlation Data for Bromine

Compound	Φ_{val}^{EHT}	$\Phi_{val}^{CNDO/2}$	Q^{CHELEQ}	V^{CHELEQ}
Br_2	-116.48	-127.59	0.000	0.00
BrH	-117.47	-128.50	-0.076	0.78
$BrCH_3$	-116.93	-129.03	-0.066	0.39
Br_4C	-116.41	-127.73	-0.050	0.81
$BrSiH_3$	-117.98	-128.92	-0.093	0.54
Br_4Si	-117.32	-127.99	-0.077	1.12
$BrGeH_3$	-118.44	-128.78	-0.078	0.35
Br_4Ge	-117.81	-127.89	-0.063	0.85
C	0.438	0.508	--	
k	--	--	16.54	
ℓ	127.95	141.75	77.01	
Std. Dev.	0.35	0.38	0.36	

seem to be necessary to understand these halogen chemical shifts.

Acknowledgment. This research was supported by the U. S. Atomic Energy Commission.

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Figure Captions

Figure 1. Plot of carbon 1s binding energy vs Φ_{val} from CNDO/2 method.

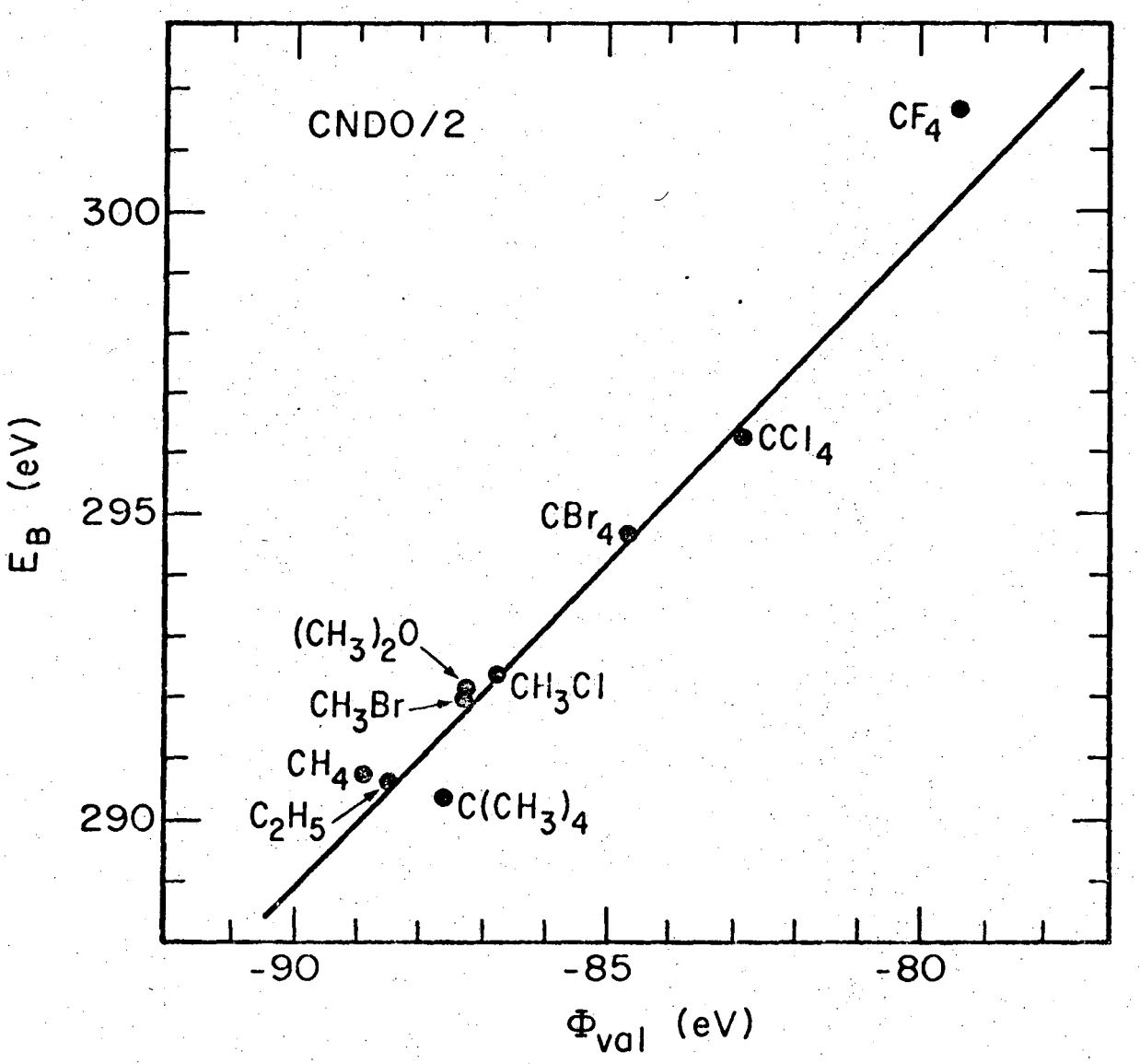
Figure 2. Plot of silicon 2p binding energy vs Φ_{val} from CNDO/2 method.

Figure 3. Plot of germanium $3p_{3/2}$ binding energy vs Φ_{val} from CNDO/2 method.

Figure 4. Plot of $E_B - V$ vs Q for relative carbon 1s binding energies. Charges calculated by CHELEQ method.

Figure 5. Plot of $E_B - V$ vs Q for relative silicon 2p binding energies. Charges calculated by CHELEQ method.

Figure 6. Plot of $E_B - V$ vs Q for relative germanium $3p_{3/2}$ binding energies. Charges calculated by CHELEQ method.



XBL 738-1688

Fig. 1

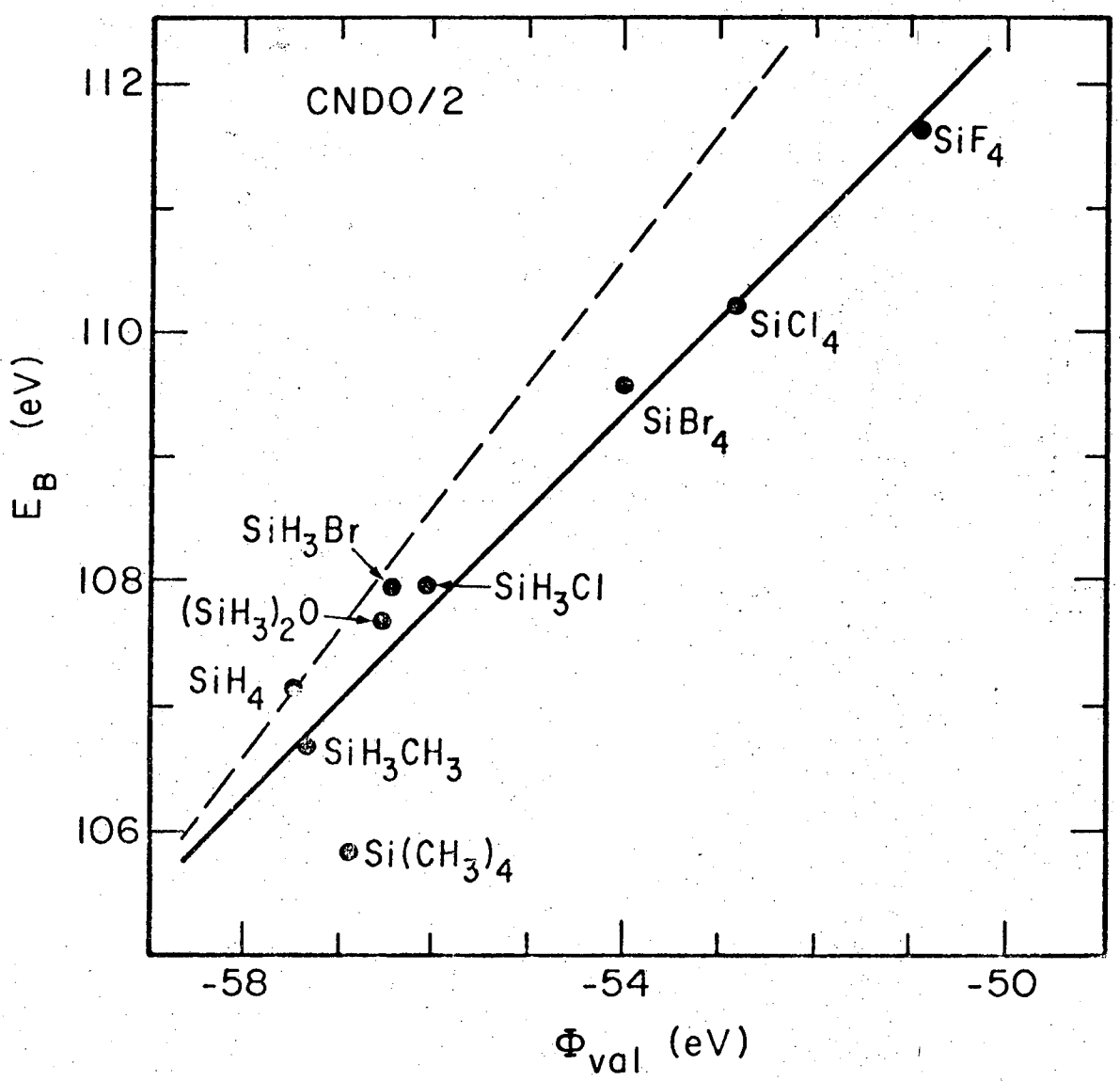


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Fig. 2

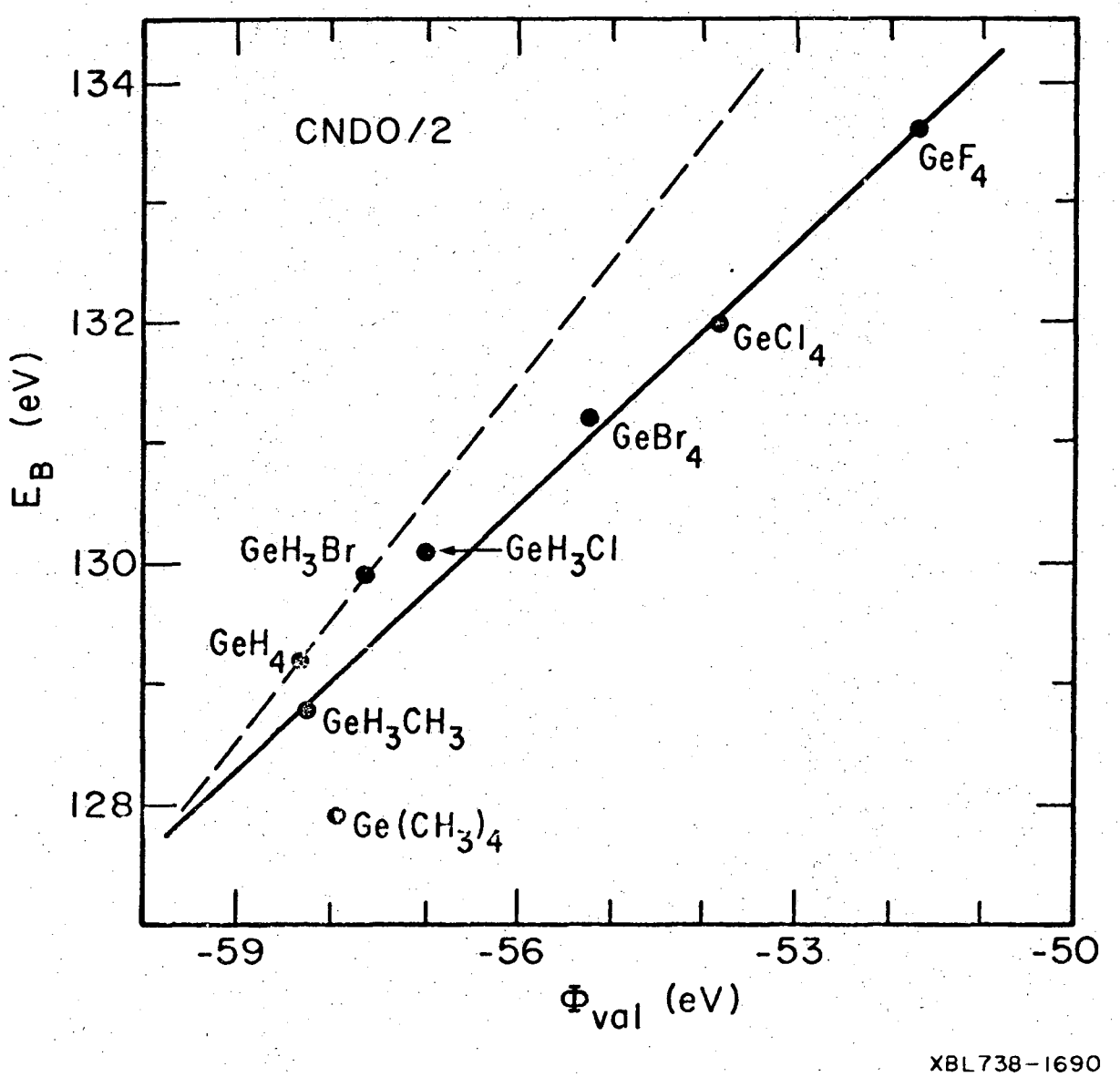
CNDO/2
134
132
130
128
E_B (eV)
-59
-56
-53
-50
Φ_{val} (eV)
GeF_4
$GeCl_4$
$GeBr_4$
GeH_3Br
GeH_3Cl
GeH_4
GeH_3CH_3
$Ge(CH_3)_4$
XBL738-1690

Fig. 3

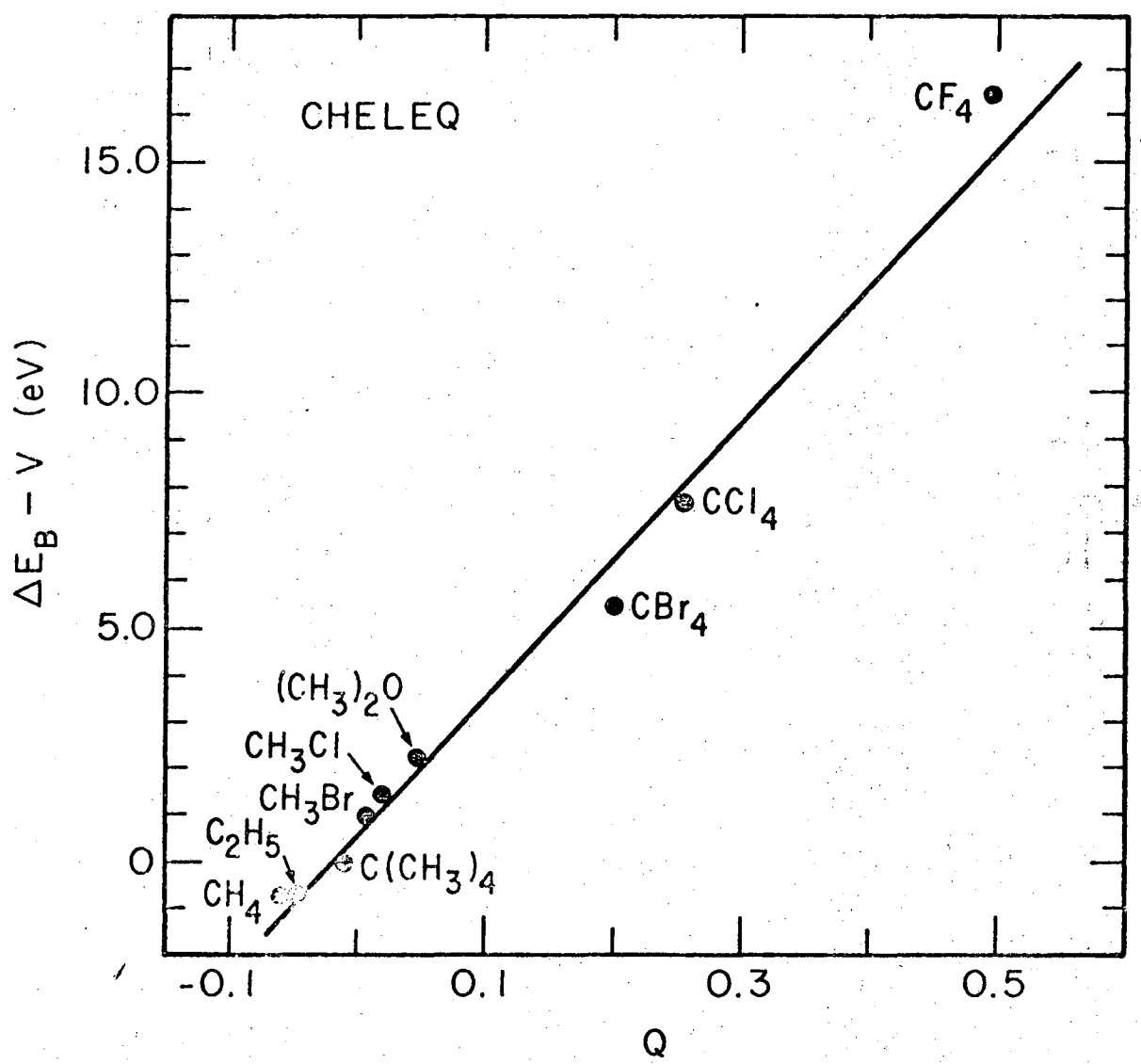

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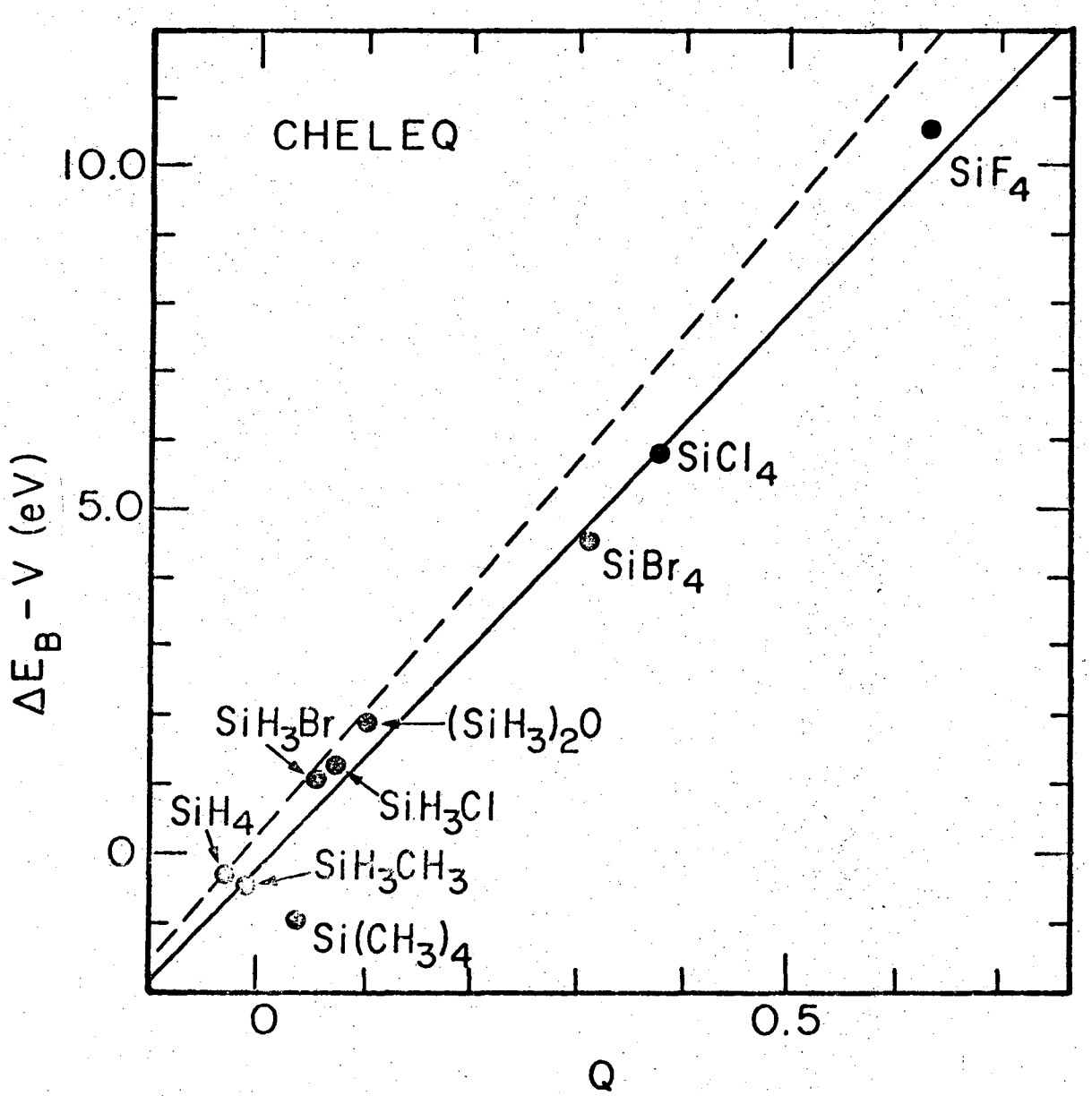
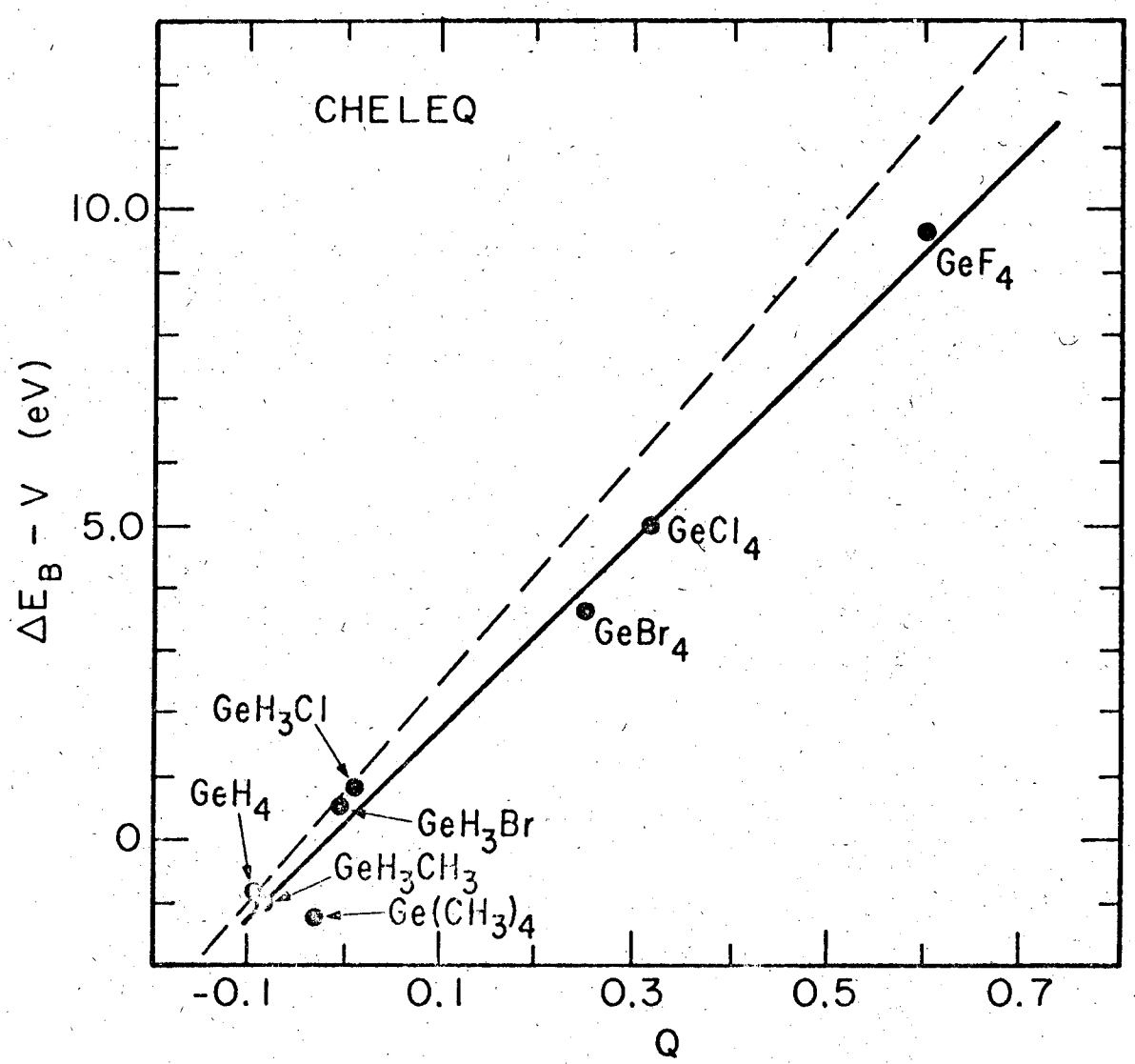
Fig. 4



XBL 737-6514

Fig. 5



XBL 738-1686

Fig. 6

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