the bi-unidentate transformation. The isomer shift would be expected to *increase* for a unit drop in coordination number if the same ligands were involved. The observed decrease in δ possibly reflects a general weakening in the tin-ligand bonds on addition of two molecules of nitrogen donor due to steric crowding.[47]

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Registry No. $Sn(NO_3)_4$, 12372-55-3; $Cs_2Sn(NO_3)_6$, 18723-50-7; $[(C_2H_5)_4N]_2Sn(NO_3)_6$, 51020-80-5; $Sn(NO_3)_4(py)_2$, 17500-58-2; $Sn(NO_3)_4(bipy)$, 50883-35-7; $(CH_3)_3SnNO_3$, 50830-71-2; $(CH_3)_3Sn(NO_3)(py)$, 50978-02-4; $(CH_3)_3Sn(NO_3)(bipy)_{0.5}$, 51016-06-9; $(CH_3)_2Sn(NO_3)_2$, 50830-72-3; $(CH_3)_2Sn(NO_3)_2(py)_2$, 50830-92-7; $(CH_3)_2Sn(NO_3)_2(bipy)$, 50830-93-8; $CH_3Sn(NO_3)_3$, 26284-61-7; $CH_3Sn(NO_3)_3(py)_2$, 50830-94-9; $CH_3Sn(NO_3)_3(bipy)$, 50830-95-0; ^{119}Sn, 14314-35-3.

(47) Note Added in Proof. Since this paper was written, the X-ray crystal structure of $(CH_3)_2Sn(NO_3)_2$ has been completed [J. Hilton, E. K. Nunn, and S. C. Wallwork, *J. Chem. Soc., Dalton Trans.*, 173 (1973)]. The molecule contains asymmetrically nonbridging bidentate nitrate groups.

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

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Core electron binding energies for analogous compounds of carbon, silicon, and germanium have been measured by X-ray photoelectron spectroscopy in the gas phase. The chemical shifts have been correlated by the electrostatic potential equation using charge distributions from extended Huckel theory, CNDO/2, and an electronegativity equalization method. The data can be rationalized 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.[4-6] We have measured the core binding energies for analogous carbon, silicon, and germanium compounds 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. Morgan and Van Wazer[7] have studied the binding energies of carbon, silicon, and germanium in solids. Because of the solid-state problems of work function, charging, and surface impurities and the difficulty of accounting for the Madelung potential in solids, we have restricted our study to compounds in the gas phase.

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 Co.

Silane was prepared by the reaction of $SiCl_4$ with $LiAlH_4$;[8] the infrared spectrum agreed with the literature.[8] Methylsilane 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 practical 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 vapor 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;[18] its vapor pressure[9] (82 Torr at −45.2°) and

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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] Tetramethylgermane 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 Kα X-rays (1253.6 eV) were used for all spectra except those of germanium compounds, for which aluminum Kα X-rays (1486.6 eV) were used. The spectra were measured with sample pressures of 30–40 μ in the spectrometer irradiation chamber. Argon, at 20–30 μ 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 line shapes. The reproducibility of the data was determined for several compounds to be about ±0.05 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 Huckel theory[29] (EHT), CNDO/2,[30] and an electronegativity equalization method (CHELEQ) devised by the authors.[31]

The simple extended Huckel 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

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

The overlap integrals were calculated from Slater-type orbitals, using exponents and principal quantum numbers fitted to near Hartree–Fock atomic wave functions 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 by Pople and Beveridge.[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 Jaffe's[36,37] orbital ionization energies and electron affinities and Cusachs and Corrington's[33] valence s-orbital wave functions. As discussed previously, these wave functions came from near Hartree–Fock results and are less arbitrary for second- and third-row elements than are exponents obtained using Slater's rules.[38] The CNDO/2 program was expanded to third-row nontransition elements by this same method. Because CNDO/2 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/2 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 Jaffe'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[3]

$$E_{1s}^{A} = -\langle \chi_{1s} | H + G | \chi_{1s} \rangle \tag{2}$$

where, for simplicity, we have assumed that the core molecular orbital is the 1s orbital, χ_{1s}, of atom A. If we neglect the exchange integrals of atoms not directly bonded to atom A, eq 2 may be expanded and arranged as[2,3]

$$\begin{aligned} E_{1s}^{A} = {} & -\sum_{i \in A \neq 1s} \sum_{j} P_{ij}[1s1s|ij) - {}^{1}/_{2}(1sj|1si)] - \\ & [\sum_{i \in A} \sum_{j} P_{ij}(1s1s|ij) - \sum_{B \neq A} Z_{B}(1s|r_{1sB}^{-1}|1s)] - \\ & [H_{1s1s} + {}^{1}/_{2}(1s1s|1s1s)] \end{aligned} \tag{3}$$

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The empirical point charge potential equation[6] is written

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

where V represents the point charge electrostatic potential due to the ligands. The term kQ corresponds to the first double summation of eq 3; hence k has the value

$$k \simeq \sum_{l} N_l [F_o(1s,2l) - {}^1/_2 G_l(1s,2l)] \tag{5}$$

where N_l is the fractional occupancy of the lth valence subshell (s, p, d, . . .) and F_o and G_l are two-electron Slater integrals from atomic Hartree–Fock calculations. The V in eq 4 and the terms in the second set of brackets of eq 3 represent an electrostatic potential at A. The last terms in eq 3 and 4 are constants for a given element.

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

$$E_{1s}^{A} \simeq \Phi_{ext} + l = -\sum_{i,j} P_{ij}(i|r_A^{-1}|j) + \sum_{B \neq A} Z_A R_{AB}^{-1} + l \tag{6}$$

Equation 6 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/2 semiempirical calculations (to retain invariance and to simplify calculations), the diagonal two-centered matrix elements are approximated as R^{-1} and eq 6 becomes

$$E_B = -\sum_{i \in A} P_{ii}\langle r_i^{-1}\rangle + \sum_{B \neq A} Q_B R_{AB}^{-1} + l \tag{7}$$

This very simple form[42] may be used with extended Huckel theory by using Mulliken gross orbital populations in place of the CNDO/2 density matrix terms P_{ii}. Equation 7 has the form of the point charge potential model, where k may be written for a Slater-type orbital as

$$k = \sum_{l} N_l \zeta_l n^{-1} \tag{8}$$

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 reaction

$$A^{*+} + A^+ = A + A^{*2+} \qquad \Delta E = \Delta E_B \tag{9}$$

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 eq 9, *i.e.*

$$B^+ + A^+ = A + B^{2+} \qquad \Delta E \simeq \Delta E_B \tag{10}$$

For a free atom

$$k = dE_B/dq \simeq \Delta E_B/\Delta q \tag{11}$$

From eq 10 and 11 one obtains

$$k_A \simeq I_2(B) - I_1(A) \tag{12}$$

Table I. Experimental Core Binding Energies for Carbon, Silicon, and Germanium

	Binding energy,[a] eV		
Compd	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

[a] The uncertainty in these energies is approximately ±0.05 eV.

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]

$$E_B^{rel} = {}^1/_2 \{\Phi_{val}(Z^0) + \Phi_{val}[(Z+1)^+]\} + l \tag{13}$$

where $\Phi_{val}(Z^0)$ 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 and Discussion

Core binding energies for the central carbon, silicon, and germanium atoms are given in Table I. The experimental values were correlated with values calculated by several methods. The CNDO/2 and EHT methods were applied to the valence potential model. The calculated binding energies were expressed as

$$E_B^{calcd} = c\Phi_{val} + l \tag{14}$$

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. Table II lists the potentials, parameters, standard deviations, and correlation coefficients from the EHT correlations, and Table III lists similar data from the CNDO/2 correlations. Figures 1–3 are plots of CNDO/2 ground-state correlations for carbon, silicon, and germanium binding energies, respectively.

Binding energies were also calculated from eq 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. Table IV lists the charges, potentials, parameters, standard deviations, and correlation coefficients from the CHELEQ correlations. Figures 4–6 show plots of $(\Delta E_B - V)$ *vs.* Q for the carbon, silicon, and germanium data, respectively. The chemical shifts, ΔE_B, shown in these figures are referred to the hydrides MH_4.

All three methods for calculating ground-state charge distributions give good correlations with carbon binding energies, as expected from previous work.[6,31,41,42] The chemical shifts between corresponding pairs of silicon and germanium

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

Compd	Φ_{val}(C)	Φ_{val}^{rel}(C)	Φ_{val}(Si)	Φ_{val}^{rel}(Si)	Φ_{val}(Ge)	Φ_{val}^{rel}(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
Correl coeff	0.992	0.985	0.723	0.858	0.774	0.892

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

Compd	Φ_{val}(C)	Φ_{val}^{rel}(C)	Φ_{val}(Si)	Φ_{val}^{rel}(Si)	Φ_{val}(Ge)	Φ_{val}^{rel}(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
Correl coeff	0.985	0.993	0.957	0.942	0.962	0.959

Table IV. CHELEQ Correlation Data for Carbon, Silicon, and Germanium

Compd	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	
Correl coeff	0.994		0.989		0.992	

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 compounds 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 eq 14. 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

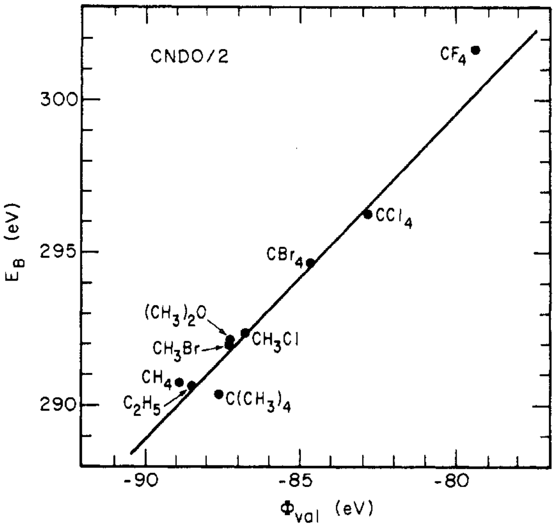

Figure 1. Plot of carbon 1s binding energy *vs.* Φ_{val} from CNDO/2 method.

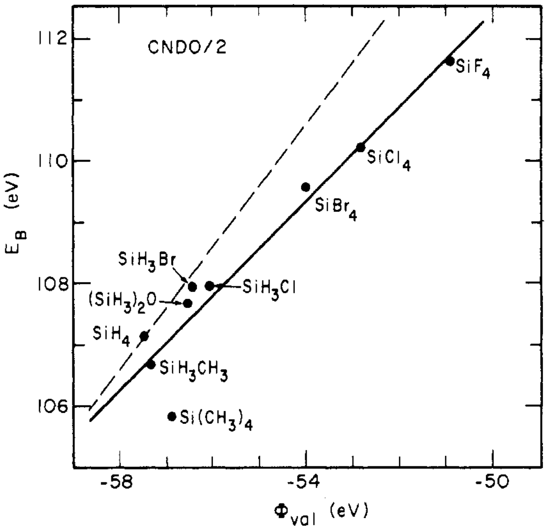

Figure 2. Plot of silicon 2p binding energy *vs.* Φ_{val} from CNDO/2 method. The dashed line is the correlation expected if d orbitals were not involved in the bonding. (See text.)

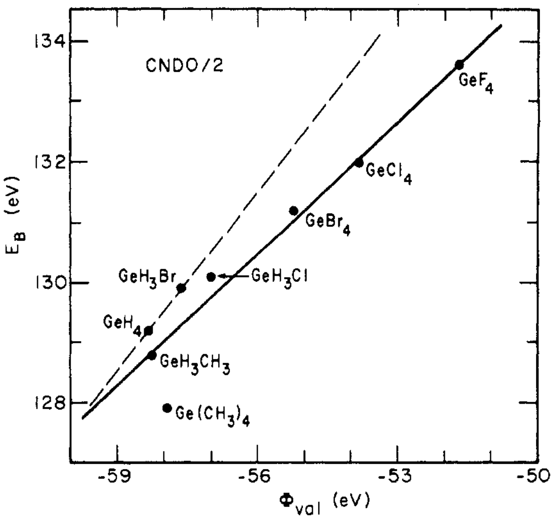

Figure 3. Plot of germanium $3p_{3/2}$ binding energy *vs.* Φ_{val} from CNDO/2 method. The dashed line is the correlation expected if d orbitals were not involved in the bonding. (See text.)

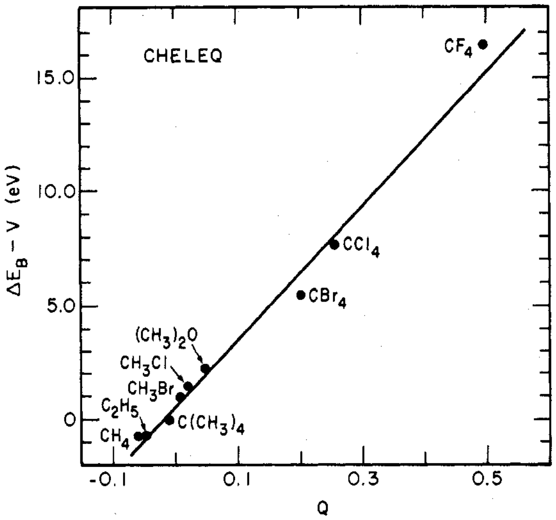

Figure 4. Plot of $E_B - V$ *vs.* Q for relative carbon 1s binding energies. Charges calculated by CHELEQ method.

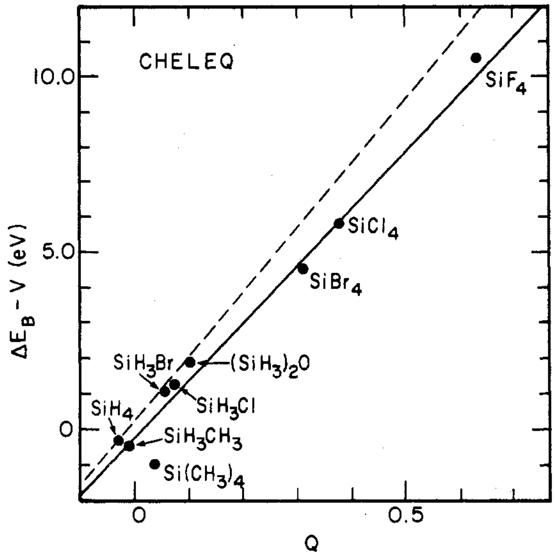

Figure 5. Plot of $E_B - V$ *vs.* Q for relative silicon 2p binding energies. Charges calculated by CHELEQ method. The dashed line is the correlation expected if d orbitals were not involved in the bonding. (See text.)

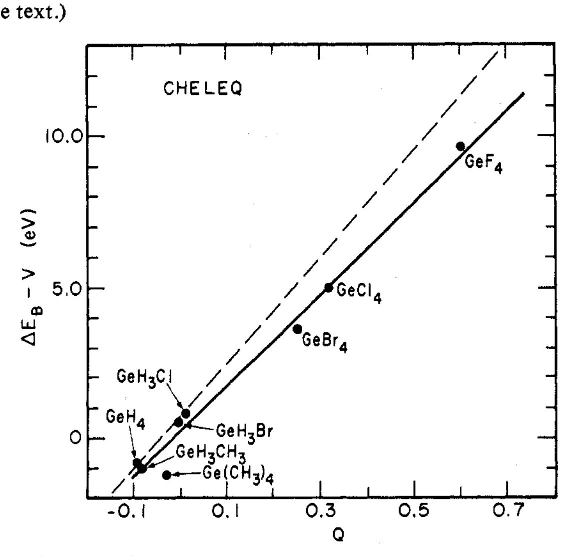

Figure 6. Plot of $E_B - V$ *vs.* Q for relative germanium $2p_{3/2}$ binding energies. Charges calculated by CHELEQ method. The dashed line is the correlation expected if d orbitals were not involved in the bonding. (See text.)

elements more than those of carbon, 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 compounds, 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 relative 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 Jaffe data. The CHELEQ correlations are based on the point charge potential model, eq 4, and it is of interest to compare the least-squares determined values of k with various theoretical estimates of this parameter. Table V lists the empirical k values and theoretical k values obtained from equations 5, 8, and 12. 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 (eq 12). Slater integrals calculated by Mann[46] for Hartree-Fock calculations were used to obtain k values from eq 5, and single STO atomic wave functions tabulated by Cusachs[33] were used to obtain k values from eq 8. Because cation and anion STO wave functions 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 values 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.[1,4,6] 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 wave functions 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 from the experimental values. Using eq 13, we corrected the EHT and CNDO/2 potentials for relaxation and thereby eliminated a recurrent anomaly in the uncorrected correlations. In all three series the experimental binding energies increase in the order

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$M(CH_3)_4 < MH_3CH_3 < MH_4$. 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. 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. These qualitative results strongly suggest that the spurious order predicted by the ground-state correlations was caused by the neglect of relaxation. The success of the relaxation correction in quantitatively improving the correlations, as measured by the standard deviations and correlation coefficients, largely depends upon the adequacy of the central atom parameterization for both elements and upon the ability of the semiempirical method to describe correctly cationic molecules. Our CNDO carbon[47] and EHT silicon and germanium correlations were improved by including the relaxation correction, but the EHT carbon and the CNDO silicon and germanium correlations were made slightly worse when corrected for relaxation. In spite of these difficulties we believe that eq 13 will correct major discrepancies caused by neglect of electronic relaxation.

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 pπ→dπ bonding corresponds to a transfer of negative charge from the ligand atoms to the central atom: $R_3Si^{-}{=}X^{+}$. 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 V. 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 pπ→dπ bonding in these compounds is assumed to be negligible. Negative deviations of $(\Delta E_B - V)$ from the dashed lines may be attributed to negative charge on silicon or germanium due to pπ→dπ 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.

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

	CHELEQ empirical	Eq 12	Eq 5	Eq 8		
				Cation	Neutral	Anion
k_C	30.07	18.34	20.36	23.83	21.80	20.47
k_{Si}	16.59	11.58	12.51	13.84	12.84	12.17
k_{Ge}	15.42	10.73	11.90	13.09	12.31	11.71
k_{Si}/k_C	0.55	0.63	0.61	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	0.95	0.95	0.96	0.96

Table VI. Experimental Core Binding Energies for Carbon, Oxygen, Fluorine, Chlorine, and Bromine

	Binding energy,[a] eV				
Compd	$X = CH_3$ (1s)	X = O (1s)	X = F (1s)	X = Cl ($2p_{3/2}$)	X = Br ($3d_{5/2}$)
CH_3X	290.57			206.07	76.25
$(CH_3)_2X$		538.86			
CX_4	290.31[b]		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

[a] The uncertainty in these energies is approximately ±0.05 eV.
[b] Only one carbon peak was observed for $C(CH_3)_4$. The line width of 1.2 eV was slightly greater than the normal carbon width of approximately 1.1 eV.

Table VII. EHT, CNDO/2, and CHELEQ Correlation Data for Chlorine

Compd	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	
Correl coeff	0.823	0.759	0.880	

Table VIII. EHT, CNDO/2, and CHELEQ Correlation Data for Bromine

Compd	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	
Correl coeff	0.656	0.603	0.792	

Although the above interpretation of the data suggests appreciable d-orbital bonding, other considerations suggest

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(47) The relaxed potentials for carbon are incomplete because calculations for NCl_4^+ and NBr_4^+ did not converge even after many iterations. The corresponding standard deviation for the ground-state potentials of the carbon series minus CCl_4 and CBr_4 was 0.61 eV.

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. Inasmuch as the silicon and germanium correlations (without consideration of d orbitals) are almost as good as the carbon correlations, it seems unlikely that any treatment including d-orbital bonding could significantly improve the silicon and germanium correlations relative to the carbon correlation. 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, oxygen, and methyl carbon atoms in the compounds which we have discussed and also for molecular chlorine, bromine, hydrogen chloride, and hydrogen bromide were measured and are given in Table VI. No correlations were made for the oxygen or fluorine binding energies because there were insufficient data for these elements. The EHT, CNDO/2, and CHELEQ correlation data for the chlorine binding energies are listed in Table VII. The data from the bromine correlations, listed in Table VIII, closely parallel the chlorine data. All of these correlations have considerable scatter, as indicated by the correlation coefficients. The low standard deviations are a consequence of the small range of binding energies involved. Some of the experimental shifts (which may be obtained from the data in Table VI) deserve comment. The chemical shift $E_B(HX) - E_B(X_2)$ is much 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, seem to be necessary to understand these halogen chemical shifts.

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

Registry No. CH_4, 74-82-8; CH_3CH_3, 74-84-0; $C(CH_3)_4$, 463-82-1; $(CH_3)_2O$, 115-10-6; CF_4, 75-73-0; CH_3Cl, 74-87-3; CCl_4, 56-23-5; CH_3Br, 74-83-9; CBr_4, 558-13-4; SiH_4, 7803-62-5; SiH_3CH_3, 992-94-9; $Si(CH_3)_4$, 75-76-3; $(SiH_3)_2O$, 13597-74-3; SiF_4, 7783-61-1; SiH_3Cl, 13465-78-6; $SiCl_4$, 10026-04-7; SiH_3Br, 13465-73-1; $SiBr_4$, 7789-66-4; GeH_4, 7782-65-2; GeH_3CH_3, 1449-65-6; $Ge(CH_3)_4$, 865-52-1; GeF_4, 7783-58-6; GeH_3Cl, 13637-65-5; $GeCl_4$, 10038-98-9; GeH_3Br, 13569-43-2; $GeBr_4$, 13450-92-5; Cl_2, 7782-50-5; HCl, 7647-01-0; Br_2, 7726-95-6; HBr, 10035-10-6; C, 7440-44-0; Si, 7440-21-3; Ge, 7440-56-4; O_2, 7782-44-7; F_2, 7782-41-4.

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Boron Insertion Reactions. III. Synthesis of $2\text{-}CH_3B_6H_9$ and $1\text{-}[(CH_3)_3M^{IV}]B_6H_9$ (M^{IV} = Si, Ge)

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Reaction of $(CH_3)_3B$ with B_5H_9 (assisted by $(CH_3)_3Ga$) produces $2\text{-}CH_3B_6H_9$ *via* a pathway that can be considered formally analogous to a carbene insertion reaction. Boron insertion reactions using $H_2BCl{\cdot}OR_2$ with $(CH_3)_3M^{IV}B_5H_7^-$ anions (M^{IV} = Si, Ge) give rise to the corresponding $1\text{-}(CH_3)_3M^{IV}B_6H_9$ products, which constitute the first examples of apically substituted hexaborane(10) derivatives.

Until recently no derivatives of hexaborane(10), B_6H_{10}, were known and even now the list is not extensive. Typical compounds prepared to date include $B_6H_{10}{\cdot}L$,[1] $B_6H_{10}L_2$,[2] $B_6H_{10}{\cdot}BCl_3$,[3] $\mu\text{-}Fe(CO)_4B_6H_{10}$,[4] $\mu\text{-}Cl_2Pt(B_6H_{10})_2$,[5] $2,3\text{-}(CH_3)_2B_6H_8$,[6] $2\text{-}CH_3B_6H_9$,[7] $2\text{-}BrB_6H_9$,[8] and the salts of the protonated and deprotonated hexaborane(10) species $B_6H_{11}^+$, $2\text{-}CH_3B_6H_{10}^+$,[9] and $B_6H_9^-$.[10]

We have been studying boron insertion reactions for some time, with emphasis on the synthesis of B_6H_{10} derivatives from B_5H_9 derivatives. We report here the synthesis of $2\text{-}CH_3B_6H_9$ by an unprecedented boron insertion reaction and the syntheses of the first two examples of apically substituted B_6H_{10} derivatives, $1\text{-}[(CH_3)_3M^{IV}]B_6H_9$ (M^{IV} = Si, Ge).

Results and Discussion

$2\text{-}CH_3B_6H_9$. Gas-phase thermolysis of equimolar mixtures of B_5H_9 and $(CH_3)_3B$ in sealed Pyrex vessels produces $2\text{-}CH_3B_6H_9$ at 200° or above. At these temperatures, however, decomposition of $2\text{-}CH_3B_6H_9$ to $2\text{-}CH_3B_5H_8$ occurs at a

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