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# Photoelectron Spectra of Organometallic Compounds Containing Silicon–Silicon and Silicon–Germanium Bonds: Valence Band Studies

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Valence band photoelectron spectra have been recorded at 21.2-, 100-, 120-, and 135-eV photon energies for the following five compounds: $Si(CH_3)_4$, $Si_2(CH_3)_6$, $Si[Si(CH_3)_3]_4$, $Ge[Si(CH_3)_3]_4$, and $[Si(CH_3)_2]_6$. The ground-state energies from the MS–Xα method are used to assign the photoelectron spectra. The photon energy dependence of the intensities, combined with Gelius model intensity predictions from the MS–Xα molecular orbital compositions, confirms the molecular orbital ordering. The peak at lowest binding energy at ~8 eV (not present in $Si(CH_3)_4$) results from the Si–Si or Si–Ge bonding orbitals. The second peak at ~10 eV results from orbitals associated primarily with Si–C bonds, while the next overlapping three peaks mainly result from C–H bonding orbitals. In $[Si(CH_3)_2]_6$, the second Si–C peak splits into two because of the two axial and equatorial positions of the methyl groups in the six-membered silicon ring.

## Introduction

There is currently considerable interest in the development of advanced Si–Ge semiconductor materials with novel electrical and optoelectronic properties for device purposes. Therefore, the physics and chemistry of the materials associated with group IV elements are drawing more and more attention. In this study, the valence band photoelectron spectra for five organometallic silicon–germanium compounds are recorded in the gas phase at four different photon energies: 21.2, 100, 120, and 135 eV. The five compounds presented are tetramethylsilane (TMS, $Si(CH_3)_4$), hexamethyldisilane (HMDS, $Si_2(CH_3)_6$), tetrakis(trimethylsilyl)silane (TKTS, $Si[Si(CH_3)_3]_4$), tetrakis(trimethylsilyl)germane (TKTG, $Ge[Si(CH_3)_3]_4$), and the cyclic compound dodecamethylcyclohexasilane (DCHS, $[Si(CH_3)_2]_6$). These compounds are of interest both because of their interesting molecular structure and because they can be used as model compounds for silicon surface and silicon–germanium atomic layer superlattice (ALS) samples.[1] The information on the electronic and bonding properties given by their spectra can be very helpful to understand more complex systems in the condensed phase.

The valence band photoelectron spectra of TMS together with a large number of Si compounds have been reported before,[2–5] but there have been no valence band data published for all of our five compounds at 100-, 120-, and 135-eV photon energies. The Si 2p core-level photoelectron spectra of all five compounds have recently been reported by Sutherland *et al.*,[6] and the Si K-edge X-ray absorption spectra for these compounds will be published elsewhere.[7]

**Table 1. Radii and α Values for the Outer Sphere, $\alpha_{out}$, Used in the Calculation**

| | radii (au) | | | | | | |
|---|---|---|---|---|---|---|---|
| compd | Si | Si[a] | Ge | C | H | out | $\alpha_{out}$ |
| $Si(CH_3)_4$ | 2.0634 | | | 1.4800 | 1.0000 | 5.6874 | 0.7620 |
| $Si_2(CH_3)_6$ | 2.2200 | | | 1.4800 | 1.0000 | 7.0822 | 0.7607 |
| $Si[Si^a(CH_3)_3]_4$ | 2.3400 | 2.2300 | | 1.4800 | 1.0000 | 9.5021 | 0.7594 |
| $Ge[Si(CH_3)_3]_4$ | 2.2300 | | 2.3300 | 1.4800 | 1.0000 | 9.5279 | 0.7586 |
| $[Si(CH_3)_2]_6$ | 2.2500 | | | 1.4800 | 1.0000 | 9.9625 | 0.7582 |

In this study, the photoelectron spectra are assigned with the help of theoretical Ms–Xα calculations. The dependence of the experimental branching ratios on the different photon energies confirms the assignments. The similarities and differences between the spectra of the five compounds are also discussed.

## Experimental Section

$Si(CH_3)_4$ (TMS), $Si_2(CH_3)_6$ (HMDS), and $Si[Si(CH_3)_3]_4$ (TKTS) were purchased commercially in high purity from Aldrich Chemical Co. and used without further purification. Ge[Si-

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**Table 2. Symmetry, Bond Lengths, and Bond Angles Used in the Calculation**

| | | bond lengths (Å) | | | bond angles (deg) | | |
|---|---|---|---|---|---|---|---|
| compd | sym | Si—Si or Si—Ge | Si—C | C—H | | | |
| $Si(CH_3)_4$ | $T_d$ | | 3.5434 | 2.107 | C—Si—C 109.5 | Si—C—H 109.5 | |
| $Si_2(CH_3)_6$ | $C_{3v}$ | 4.422 | 3.5470 | 2.130 | Si—Si—C 108.4 | Si—C—H 108.7 | |
| $Si[Si(CH_3)_3]_4$ | $T_d$ | 4.462 | 3.5700 | 2.111 | Si—Si—Si 109.5 | Si—Si—C 110.9 | Si—C—H 109.3 |
| $Ge[Si(CH_3)_3]_4$ | $T_d$ | 4.490 | 3.5700 | 2.120 | Si—Ge—Si 109.5 | Ge—Si—C 110.9 | Si—C—H 109.3 |
| $[Si(CH_3)_2]_6$ | $D_{3d}$ | 4.442 | 3.5560 | 2.120 | Si—Si—Si 111.3 | Si—Si—C 110.9 | Si—C—H 109.0 |

**Table 3. Assignment of Photoelectron Peaks with Calculated MO's and Their Orbital Characters for $Si(CH_3)_4$**

| exptl peak | exptl BE (eV) | calcd MO energy (eV) | MO | MO composition & main character | | |
|---|---|---|---|---|---|---|
| | | | | Si | C | H |
| B | 10.35 | −8.15 | $3t_2$ | 0.19 p | 0.40 p | 0.07 |
| C | 12.64 | −10.46 | $1t_1$ | 0.00 | 0.36 p | 0.30 |
| D | 13.74 | −11.46 | $2t_2$ | 0.03 | 0.31 p | 0.25 |
| | | −11.48 | 1e | 0.01 | 0.31 p | 0.27 |
| E | 15.08 | −12.55 | $2a_1$ | 0.33 s | 0.24 p | 0.10 |

$(CH_3)_3]_4$ (TKTG) was synthesized according to Brook *et al.*,[8] and $[Si(CH_3)_2]_6$ (DCHS) was synthesized according to West *et al.*[9]

In all cases, the samples were introduced directly into the gas cell of the photoelectron spectrometer at a pressure of ~5 × $10^{-3}$ Torr. Liquid samples (TMS and HMDS) were deaerated by repeated freeze−pump−thaw cycles to remove any dissolved oxygen or nitrogen. The solid samples (TKTS, TKTG, and DCHS) were heated to approximately 65 °C to increase their vapor pressure. Constant sample pressure was maintained for the time required to accumulate the data for each spectrum.

For each compound, spectra were recorded at four different photon energies: 21.2, 100, 120, and 135 eV. The five spectra taken with a photon energy of 21.2 eV were recorded using a commercial McPherson 36 cm mean radius electron energy analyzer fitted with a He discharge lamp and entrance and exit slits of 0.5 mm. This instrument has been described elsewhere.[10] The photoelectron spectrometer used to record the higher energy spectra of all the compounds has been described elsewhere.[11] Briefly, the spectrometer consists of a McPherson 36 cm mean radius electron energy analyzer with 1 mm entrance and exit slits, resulting in a theoretical electron resolution, $\Delta E/E$, of 1/720. For electron kinetic energies of ~100 eV the theoretical value of $\Delta E$ is about 0.14 eV. Assorted differential pumping was used on the spectrometer and beam line to isolate the high pressure of the gas cell from the optical components of the beam line.

All of the higher energy spectra were recorded using the CSRF Mark IV Grasshopper monochromator at the Aladdin synchrotron of the University of Wisconsin—Madison. An 1800 groove/mm grating was employed in the monochromator, resulting in a minimum practical photon resolution of 0.08 eV at 100-eV photon energy.

The binding energy of each compound was measured through the use of an internal calibrant, namely the $3p_{3/2}$ line of argon, which has a binding energy of 15.759 eV.

All spectra have been fitted to Lorentzian−Gaussian line shapes using an iterative procedure.[12] Correction of the areas for the electron analyzer transmission was performed by dividing the computed area by the kinetic energy of the peak. For the three higher energy spectra at 100, 120, and 135 eV, this correction is not very significant because of the rather small percentage change (≤5%) in kinetic energies. Experimental branching ratios ($BR_i$) were obtained using the resulting band areas ($A_i$) and the branching ratio formula $BR_i = A_i/\Sigma A_i$.

**Table 4. Assignment of Photoelectron Peaks with Calculated MO's and Their Orbital Characters for $Si_2(CH_3)_6$**

| exptl peak | exptl BE (eV) | calcd MO energy (eV) | MO | MO composition & main character | | |
|---|---|---|---|---|---|---|
| | | | | Si | C | H |
| A | 8.45 | −7.79 | $7a_1$ | 0.44 p | 0.20 p | 0.07 |
| B | 10.35 | −8.98 | 8e | 0.23 p | 0.41 p | 0.04 |
| | | −9.25 | 7e | 0.23 p | 0.38 p | 0.10 |
| C | 12.64 | −10.78 | 6e | 0.01 | 0.36 p | 0.28 |
| | | −11.06 | $2a_2$ | 0.00 | 0.35 p | 0.31 |
| | | −11.15 | $6a_1$ | 0.02 | 0.34 p | 0.26 |
| | | −11.19 | $1a_2$ | 0.00 | 0.34 p | 0.31 |
| | | −11.22 | 5e | 0.02 | 0.32 p | 0.27 |
| D | 13.74 | −11.78 | $5a_1$ | 0.08 p | 0.29 p | 0.21 |
| | | −11.91 | 4e | 0.03 | 0.31 p | 0.26 |
| | | −11.94 | 3e | 0.02 | 0.31 p | 0.28 |
| E | 15.08 | −12.70 | $4a_1$ | 0.38 s | 0.25 s,p | 0.09 |
| | | −14.14 | $3a_1$ | 0.42 s | 0.19 s,p | 0.10 |

**MS−Xα Calculations and the Gelius Intensity Method.** Energies and intensities from MS−Xα calculations have been widely used to help assign photoelectron spectra of a number of relatively small molecules such as $SiF_4$ and $CF_3X$ (X = Cl, Br, I).[13] The background for the MS−Xα calculations has been fully documented[14,15] and will not be repeated here. The atomic exchange parameters, α, used in our calculation are those of Schwartz.[16] A weighted average of the atomic exchange parameters based on the number of valence electrons was used for the outer-sphere and intersphere regions. Table 1 lists the α values used for the outer sphere (same for the intersphere) and the radii used for the outer-sphere and atomic regions for all the compounds. The symmetry, bond angles, and bond lengths[17] used are listed in Table 2.

The radii for all the compounds were chosen in a similar way, which allowed less than 2% overlapping for Si—Si or Si—Ge bonds, about 4% overlapping for Si—C bonds, and 17% overlapping for C—H bonds. Actually, the results using different radii exhibit almost the same energy sequence and very similar orbital compositions.

MS−Xα calculation results (ground-state energies and charge distributions for the valence molecular orbitals) for all five compounds are listed in Tables 3−7 together with the assignment to all the peaks in the spectra. The contributions

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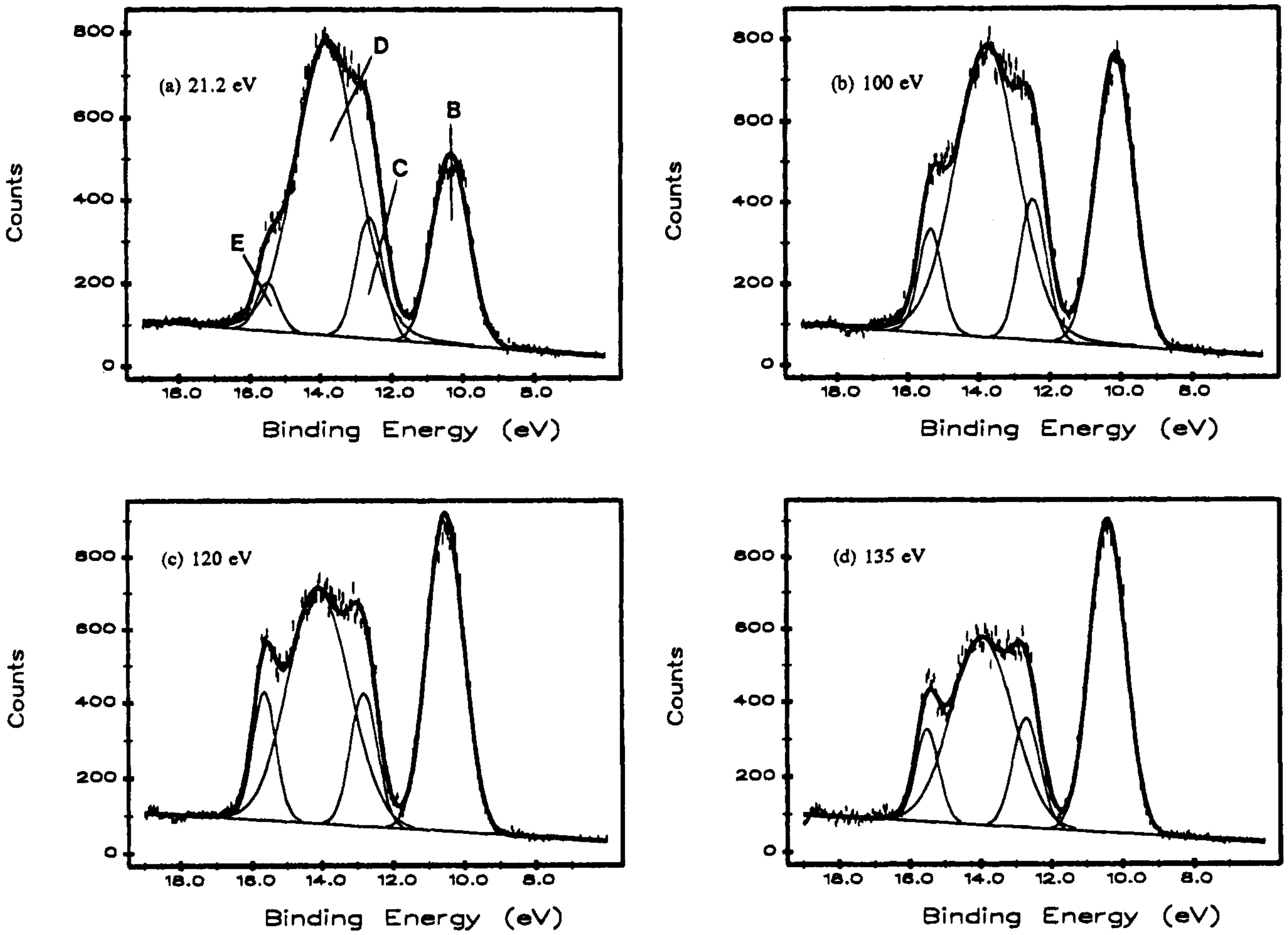

**Figure 1.** Valence band photoelectron spectra of $Si(CH_3)_4$ at 21.2-, 100-, 120-, and 135-eV photon energies.

**Table 5. Assignment of Photoelectron Peaks with Calculated MO's and Their Orbital Characters for $Si[Si(CH_3)_3]_4$**

| exptl peak | exptl BE (eV) | calcd MO energy (eV) | MO | MO composition & main character: Si (central) | Si | C | H |
|---|---|---|---|---|---|---|---|
| A | 8.26 | −10.17 | $8t_2$ | 0.22 p | 0.27 p | 0.17 p | 0.06 |
| B | 10.34 | −10.81 | $5t_1$ | 0.00 | 0.23 p | 0.41 p | 0.09 |
| | | −11.33 | 4e | 0.00 | 0.25 p | 0.37 p | 0.07 |
| | | −11.36 | $7t_2$ | 0.03 | 0.25 p | 0.34 p | 0.07 |
| C | 12.51 | −12.34 | $1a_2$ | 0.00 | 0.00 | 0.997 p | 0.003 |
| | | −12.55 | $4t_1$ | 0.00 | 0.01 | 0.37 p | 0.31 |
| | | −12.77 | $3t_1$ | 0.00 | 0.03 | 0.36 p | 0.27 |
| | | −12.82 | $6t_2$ | 0.00 | 0.03 | 0.36 p | 0.28 |
| | | −13.08 | 3e | 0.00 | 0.05 | 0.35 p | 0.24 |
| D | 13.63 | −13.40 | $4a_1$ | 0.15 s | 0.11 p | 0.26 p | 0.19 |
| | | −13.74 | 2e | 0.00 | 0.05 | 0.33 p | 0.24 |
| | | −13.83 | $2t_1$ | 0.00 | 0.00 | 0.30 p | 0.31 |
| | | −13.97 | $5t_2$ | 0.01 | 0.03 | 0.31 p | 0.26 |
| | | −14.18 | $4t_2$ | 0.00 | 0.02 | 0.29 p | 0.28 |
| E | 14.88 | −14.80 | $3a_1$ | 0.07 | 0.19 s,p | 0.24 p | 0.15 |
| | | −15.67 | $3t_2$ | 0.03 | 0.40 s | 0.20 p | 0.10 |
| | | −17.54 | $2a_1$ | 0.35 s | 0.23 s,p | 0.08 s,p | 0.06 |

are less than 1% from the outer sphere and about 30% from the intersphere in almost all the orbitals. The sum of all the contributions from the outer sphere, the intersphere, and all of the atoms is unity.

The configuration used in the calculation for $[Si(CH_3)_2]_6$ is the chair conformation.[18] All the methyl groups are supposed to be very symmetric; therefore, $D_{3d}$ symmetry was used.

**Table 6. Assignment of Photoelectron Peaks with Calculated MO's and Their Orbital Characters for $Ge[Si(CH_3)_3]_4$**

| exptl peak | exptl BE (eV) | calcd MO energy (eV) | MO | MO composition & main character: Ge | Si | C | H |
|---|---|---|---|---|---|---|---|
| A | 8.13 | −10.12 | $9t_2$ | 0.21 p | 0.28 p | 0.16 p | 0.05 |
| B | 10.34 | −10.91 | $5t_1$ | 0.00 | 0.23 p | 0.40 p | 0.09 |
| | | −11.39 | 5e | 0.00 | 0.23 p | 0.38 p | 0.08 |
| | | −11.43 | $8t_2$ | 0.02 | 0.25 p | 0.34 p | 0.08 |
| C | 12.55 | −12.42 | $1a_2$ | 0.00 | 0.00 | 0.997 p | 0.003 |
| | | −12.62 | $4t_1$ | 0.00 | 0.01 | 0.37 p | 0.31 |
| | | −12.80 | $3t_1$ | 0.00 | 0.03 | 0.36 p | 0.27 |
| | | −12.88 | $7t_2$ | 0.00 | 0.03 | 0.36 p | 0.28 |
| | | −13.16 | 4e | 0.00 | 0.06 | 0.35 p | 0.23 |
| D | 13.56 | −13.63 | $4a_1$ | 0.11 s | 0.09 | 0.27 p | 0.22 |
| | | −13.66 | 3e | 0.00 | 0.01 | 0.34 p | 0.28 |
| | | −13.87 | $2t_1$ | 0.00 | 0.02 | 0.30 p | 0.29 |
| | | −14.00 | $6t_2$ | 0.01 | 0.03 | 0.31 p | 0.26 |
| | | −14.20 | $5t_2$ | 0.00 | 0.03 | 0.29 p | 0.27 |
| E | 14.80 | −14.96 | $3a_1$ | 0.08 s | 0.23 s | 0.23 p | 0.13 |
| | | −15.74 | $4t_2$ | 0.03 | 0.40 s | 0.20 p | 0.10 |
| | | −18.09 | $2a_1$ | 0.41 s | 0.19 s | 0.08 s | 0.05 |

There are two kinds of Si—C bonds: one is axial, and the other is equatorial. In Table 7, the notation $C_{ax}$ indicates the carbon atoms sitting on the axial bonds, while $C_{eq}$ corresponds to the carbon atoms on the equatorial bonds. For $Si[Si(CH_3)_3]_4$ and $Ge[Si(CH_3)_3]_4$, perfect $T_d$ symmetry was assumed to perform the calculations.

The spectra of 100-, 120-, and 135-eV photon energies were recorded, because it is well recognized[13d,19] that above about 50-eV photon energy the *molecular* orbital cross sections are

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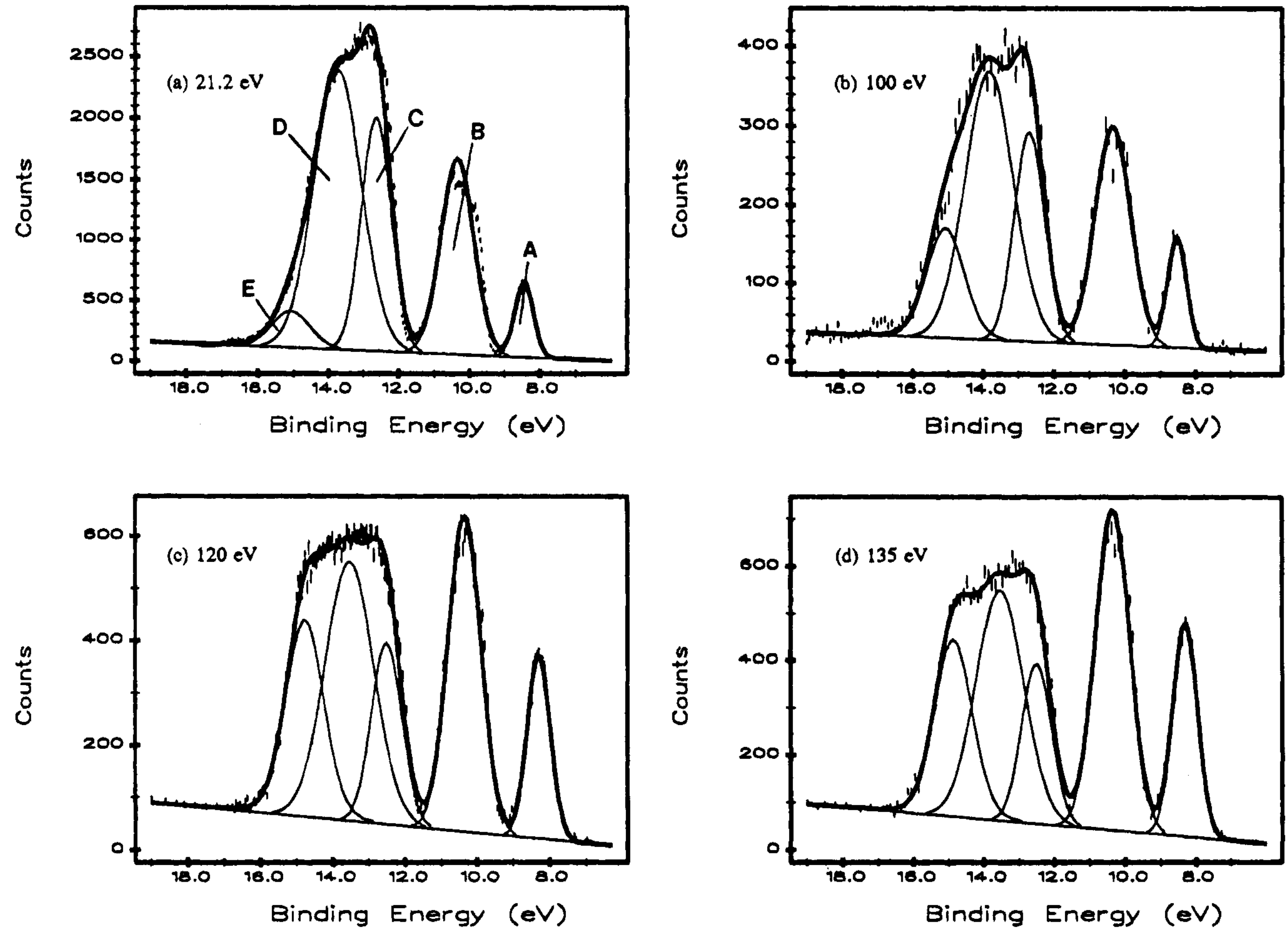

**Figure 2.** Valence band photoelectron spectra of $Si_2(CH_3)_6$ at 21.2-, 100-, 120-, and 135-eV photon energies.

proportional to the product of *atomic* orbital cross sections multiplied by the corresponding orbital contributions (the so-called Gelius method[20]). Using the atomic cross sections from Yeh and Lindau[21] (Table 8) and the orbital characters in Tables 3–7, it then becomes easy to predict and rationalize the variation in intensities from 100 to 135 eV, and this enables us to be much more confident about the molecular orbital assignments. For example, the cross sections in Table 8 show that the percentage decrease in cross section from 100 to 135 eV follows the ordering C 2p > Si 3p > Ge 4p. The C 2p cross section decreases from 0.17 mb to 0.07 mb (~60%), whereas the Ge 4p cross section decreases by only ~16%. Those peaks associated with orbitals of high Si 3p or Ge 4p character will increase in intensity from 100 to 135 eV relative to orbitals of high C 2p character.

## Results and Discussion

Figures 1–5 show the spectra of the five compounds $Si(CH_3)_4$, $Si_2(CH_3)_6$, $Si[Si(CH_3)_3]_4$, $Ge[Si(CH_3)_3]_4$, and $[Si(CH_3)_2]_6$, each at 21.2-, 100-, 120-, and 135 eV photon energies, and Tables 3–7 document the binding energies of the major peaks in these spectra. Because of the large number of molecular orbitals in these large compounds, the spectra have been fitted with the minimum number of peaks needed to reproduce the

**Table 7. Assignment of Photoelectron Peaks with Calculated MO's and Their Orbital Characters for $[Si(CH_3)_2]_6$**

| exptl peak | exptl BE (eV) | calcd MO energy (eV) | MO | MO composition & main character | | | |
|---|---|---|---|---|---|---|---|
| | | | | Si | $C_{ax}$ | $C_{eq}$ | H |
| A | 7.89 | −11.12 | $3a_{1u}$ | 0.58 p | 0.03 p | 0.03 | 0.08 |
| | | −11.32 | $9e_g$ | 0.49 p | 0.06 p | 0.13 p | 0.05 |
| B′ | 9.19 | −11.80 | $9e_u$ | 0.38 p | 0.23 p | 0.04 | 0.06 |
| | | −11.91 | $7a_{1g}$ | 0.31 p | 0.33 p | 0.01 | 0.06 |
| B | 10.41 | −12.37 | $8e_u$ | 0.24 p | 0.15 p | 0.24 p | 0.09 |
| | | −12.48 | $8e_g$ | 0.24 p | 0.22 p | 0.14 p | 0.11 |
| | | −12.76 | $6a_{2u}$ | 0.26 p | 0.17 p | 0.18 p | 0.08 |
| | | −12.77 | $6a_{1g}$ | 0.27 p | 0.06 p | 0.26 p | 0.09 |
| C | 12.68 | −13.48 | $7e_g$ | 0.06 p | 0.31 p | 0.04 | 0.25 |
| | | −13.56 | $7e_u$ | 0.07 p | 0.30 p | 0.05 p | 0.23 |
| | | −13.62 | $2a_{1u}$ | 0.03 | 0.29 p | 0.06 p | 0.27 |
| | | −13.64 | $2a_{2g}$ | 0.02 | 0.34 p | 0.01 | 0.26 |
| | | −13.71 | $6e_g$ | 0.03 | 0.30 p | 0.04 | 0.26 |
| | | −13.74 | $6e_u$ | 0.03 | 0.30 p | 0.03 | 0.27 |
| D | 13.89 | −14.09 | $5a_{2u}$ | 0.05 p | 0.30 p | 0.01 | 0.24 |
| | | −14.24 | $5a_{1g}$ | 0.07 p | 0.21 p | 0.09 p | 0.24 |
| | | −14.41 | $1a_{2g}$ | 0.01 | 0.00 | 0.35 p | 0.30 |
| | | −14.50 | $5e_u$ | 0.01 | 0.00 | 0.35 p | 0.29 |
| | | −14.64 | $5e_g$ | 0.04 s | 0.01 | 0.33 p | 0.27 |
| | | −14.76 | $4a_{2u}$ | 0.07 s | 0.01 | 0.32 p | 0.26 |
| | | −14.81 | $4a_{1g}$ | 0.04 | 0.05 | 0.28 p | 0.26 |
| | | −14.86 | $4e_u$ | 0.03 | 0.03 | 0.30 p | 0.28 |
| | | −14.89 | $4e_g$ | 0.05 p | 0.04 | 0.29 p | 0.25 |
| | | −15.08 | $1a_{1u}$ | 0.09 p | 0.03 | 0.26 p | 0.23 |
| E | 15.47 | −15.45 | $3a_{2u}$ | 0.36 s | 0.11 p | 0.14 p | 0.11 |
| | | −16.38 | $3e_g$ | 0.47 s | 0.08 p | 0.10 p | 0.08 |
| | | −17.84 | $3e_u$ | 0.48 s | 0.09 s | 0.07 p | 0.09 |
| | | −18.56 | $3a_{1g}$ | 0.44 s | 0.11 s | 0.07 s | 0.10 |

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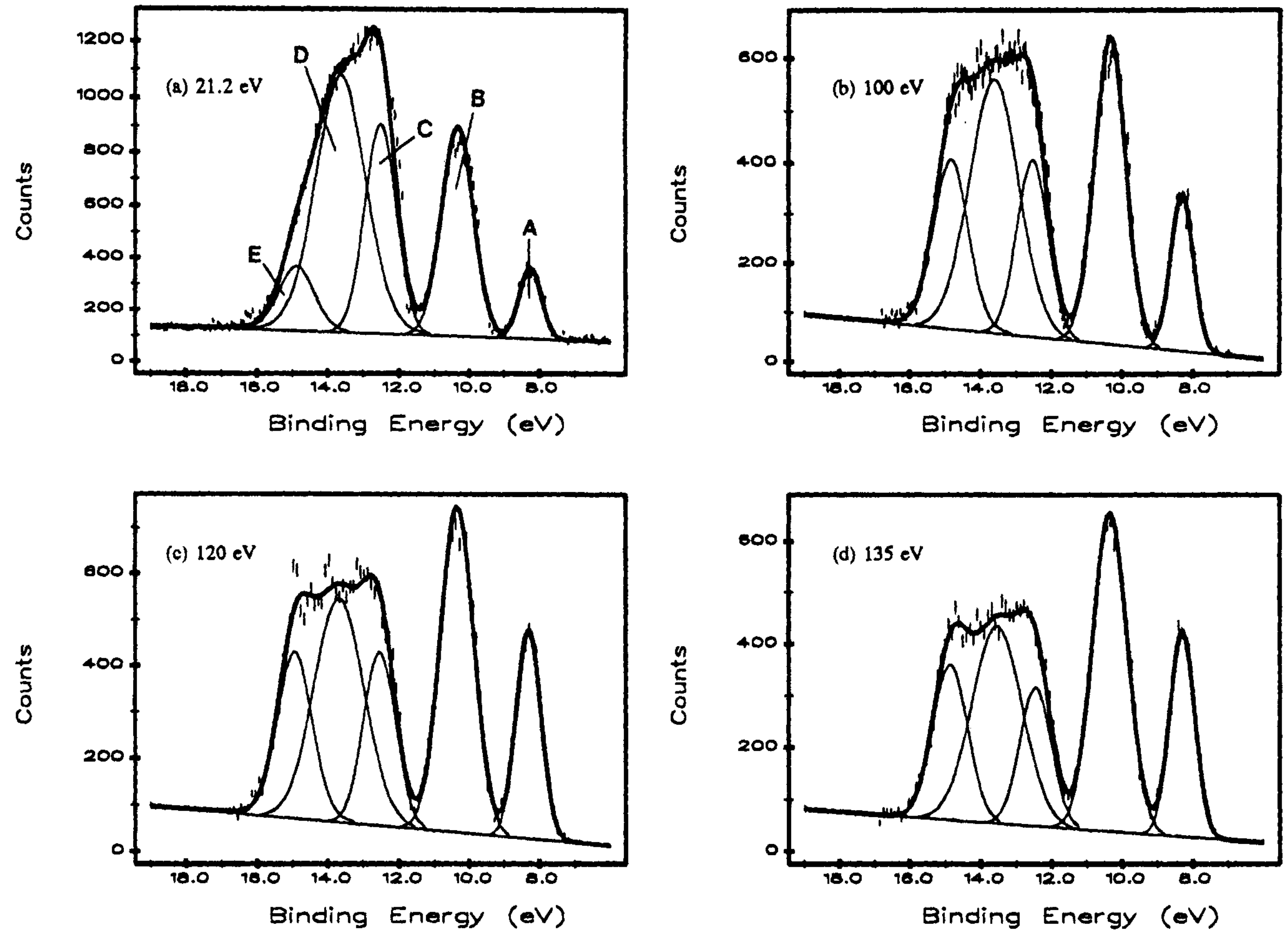

**Figure 3.** Valence band photoelectron spectra of $Si[Si(CH_3)_3]_4$ at 21.2-, 100-, 120-, and 135-eV photon energies.

**Table 8. Theoretical Atomic Cross Sections (mb) for C 2s, C 2p, Si 3s, Si 3p, Ge 4s, and Ge 4p Orbitals as a Function of Photon Energy[21]**

| AO | cross section | | | |
|---|---|---|---|---|
| | 21.2 eV | 100 eV | 120 eV | 135 eV |
| C 2s | 1.23 | 0.3768 | 0.2691 | 0.2167 |
| C 2p | 6.121 | 0.1737 | 0.1016 | 0.0712 |
| Si 3s | 0.288 | 0.1575 | 0.1202 | 0.09855 |
| Si 3p | 0.3303 | 0.1545 | 0.1129 | 0.09068 |
| Ge 4s | 0.0224 | 0.1043 | 0.08263 | 0.07047 |
| Ge 4p | 1.528 | 0.03558 | 0.03299 | 0.02991 |

**Table 9. Peak Areas and Branching Ratios (in Parentheses) in Figures 1–5[a]**

| compd | peak | peak area (branching ratio) | | | |
|---|---|---|---|---|---|
| | | 21.2 eV | 100 eV | 120 eV | 135 eV |
| $Si(CH_3)_4$ | B | 100 (0.17) | 100 (0.30) | 100 (0.36) | 100 (0.40) |
| | C | 61 (0.10) | 36 (0.11) | 30 (0.11) | 27 (0.11) |
| | D | 403 (0.68) | 175 (0.52) | 124 (0.44) | 103 (0.41) |
| | E | 30 (0.05) | 25 (0.07) | 27 (0.10) | 20 (0.08) |
| $Si_2(CH_3)_6$ | A | 18 (0.03) | 27 (0.06) | 40 (0.10) | 48 (0.13) |
| | B | 100 (0.17) | 100 (0.23) | 100 (0.26) | 100 (0.28) |
| | C | 137 (0.23) | 81 (0.19) | 53 (0.14) | 44 (0.12) |
| | D | 301 (0.50) | 166 (0.39) | 123 (0.31) | 101 (0.28) |
| | E | 39 (0.07) | 56 (0.13) | 76 (0.19) | 64 (0.18) |
| $Si[Si(CH_3)_3]_4$ | A | 19 (0.03) | 38 (0.10) | 47 (0.13) | 46 (0.14) |
| | B | 100 (0.17) | 100 (0.26) | 100 (0.28) | 100 (0.31) |
| | C | 121 (0.21) | 60 (0.15) | 50 (0.14) | 39 (0.12) |
| | D | 277 (0.48) | 129 (0.33) | 102 (0.30) | 88 (0.28) |
| | E | 62 (0.11) | 63 (0.16) | 53 (0.15) | 48 (0.15) |
| $Ge[Si(CH_3)_3]_4$ | A | 21 (0.03) | 29 (0.07) | 31 (0.09) | 34 (0.11) |
| | B | 100 (0.16) | 100 (0.26) | 100 (0.29) | 100 (0.32) |
| | C | 118 (0.19) | 71 (0.18) | 53 (0.15) | 28 (0.09) |
| | D | 293 (0.47) | 129 (0.33) | 108 (0.31) | 92 (0.29) |
| | E | 92 (0.15) | 61 (0.16) | 58 (0.17) | 63 (0.20) |
| $[Si(CH_3)_2]_6$ | A | 20 (0.04) | 30 (0.08) | 36 (0.12) | 35 (0.12) |
| | B + B′ | 100 (0.18) | 100 (0.28) | 100 (0.32) | 100 (0.35) |
| | C | 122 (0.22) | 65 (0.18) | 52 (0.17) | 38 (0.13) |
| | D | 251 (0.45) | 139 (0.38) | 103 (0.33) | 88 (0.31) |
| | E | 60 (0.11) | 28 (0.08) | 20 (0.06) | 22 (0.08) |

[a] Areas are normalized so that peak B in every spectrum has an area of 100 with an estimated ±5% deviation.

experimental spectra. No attempt has been made to fit one peak per individual orbital. These spectra show immediately a number of qualitative similarities and trends. First, despite the large number of MO's in these molecules, most spectra consist of five obvious peaks: peak A at ~8 eV (not present in TMS), peak B at about 10 eV, and peaks C–E between ~12.5 and ~15 eV. Moreover, corresponding peaks in different molecules change position by less than 0.1 eV for most of these molecules (Tables 3–7). The one exception to the this is peak B in the cyclic compound $[Si(CH_3)_2]_6$, which has two peaks B and B′ at approximately 9.2 and 10.4 eV, respectively. Second, all of these peaks are broad, due mainly to vibrational splitting as well as overlap of several peaks from different molecular orbitals. Despite the better instrumental resolution of the He I spectrum relative to the rest, the overall peak widths are very similar for all spectra. However, peaks B in $Si(CH_3)_4$ and $Si_2(CH_3)_6$ show obvious vibrational structure in the He I spectrum. Third, the relative intensities of the peaks vary markedly with photon energy, even between 100 and 135 eV. For example, peaks B increase in

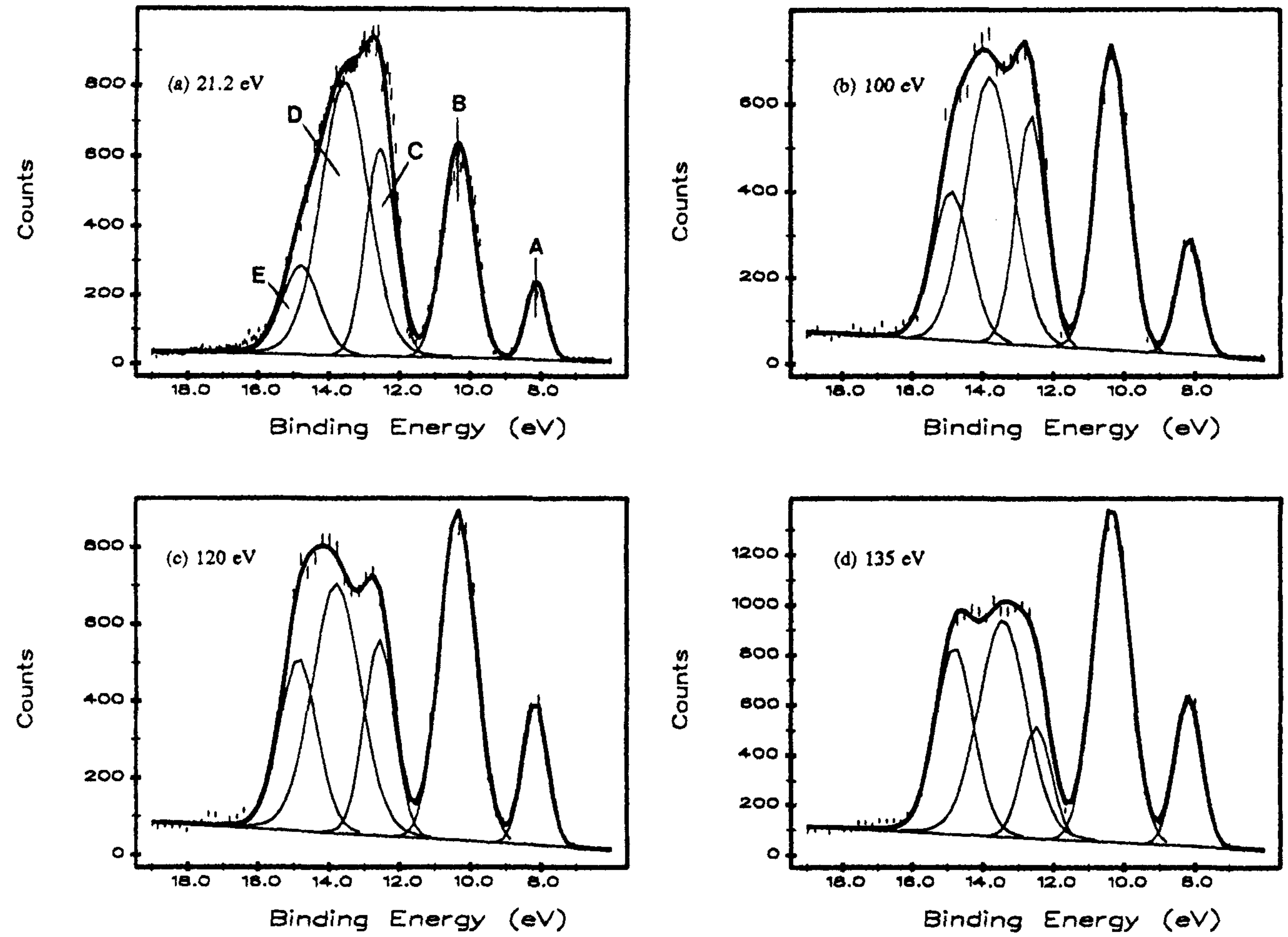

**Figure 4.** Valence band photoelectron spectra of Ge[Si(CH$_3$)$_3$]$_4$ at 21.2-, 100-, 120-, and 135-eV photon energies.

intensity relative to peaks C–E with increasing photon energy, while peaks A increase relative to peaks B (Table 9).

The assignments (Tables 3–7) can be made relatively easily. Because peak A is not present in Si(CH$_3$)$_4$, it must be due to the silicon–silicon or silicon–germanium bonding molecular orbitals, and the calculations confirm this assignment. Peak B results from MO's associated with the silicon–carbon bonds, peaks C and D are associated with MO's of primarily carbon–hydrogen character, and peak E results mainly from Si 3s and Ge 4s bonding orbitals. For the cyclic compound [Si(CH$_3$)$_2$]$_6$ (see Table 7), peaks B and B′ are both from MO's composed of silicon–carbon bonds, but B′ corresponds to axial silicon–carbon bonds 7a$_{1g}$ and 9e$_u$, while B is from both equatorial and axial silicon–carbon bonds 6a$_{1g}$, 6a$_{2u}$, 8e$_g$, and 8e$_u$. The binding energy difference of B and B′ is due to not only the different steric repulsions of axial and equatorial silicon–carbon bonds with the six-membered silicon ring but also the higher composition of silicon 3p orbital in B′ relative to that in B. The He I spectra of Si(CH$_3$)$_4$, Si$_2$(CH$_3$)$_6$, Si[Si(CH$_3$)$_3$]$_4$, and [Si(CH$_3$)$_2$]$_6$ are in excellent agreement with those published by Bock and Ensslin,[22] in both relative intensities and energy positions (with a maximum difference of 0.2 eV) of the experimental peaks. Our assignments basically confirm theirs except for that of peak B′ for [Si(CH$_3$)$_2$]$_6$.

The TMS data are presented here to compare with the other four spectra and to show that our calculation is in good agreement with previous calculations. The relative energies and compositions of molecular orbitals of TMS (Figure 1; Table 3) are in good agreement with previously reported extended Hückel,[4] DV–Xα,[23] and ab initio calculations.[24] Peak B, at lowest binding energy, is assigned to the 3t$_2$ silicon–carbon bonding molecular orbital, which is composed primarily of C 2p and Si 3p. Peaks C and D result from the carbon–hydrogen bonding orbitals (2t$_2$ + 1e + 1t$_1$), which are not fully resolved, and peak E corresponds to the 2a$_1$ molecular orbital, which is mainly from C 2p and Si 3s orbitals. This assignment is the same as the previously published one.[2]

The peak intensities and branching ratios are consistent with this assignment (Figure 6). Peak B increases in intensity *relative* to peaks C and D because of the significant Si 3p character in the 3t$_2$ MO. As shown in Table 8, the Si 3p cross section does not decrease as rapidly as the C 2p cross section with increasing photon energy. At higher energies, it is the inclusion of the Si 3p or Si 3s character in the 3t$_2$ (peak B) and 2a$_1$ (peak E) orbitals that is responsible for their increased intensity relative to that of peaks C and D.

Figure 2 shows the spectra of Si$_2$(CH$_3$)$_6$ at four different photon energies, and Table 4 documents the

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(22) Bock, H.; Ensslin, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 404.

(23) Berkovitch-Yellin, Z.; Ellis, D. E.; Ratner, M. A. *Chem. Phys.* **1981**, *62*, 21.

(24) Bertoncello, R.; Daudey, J. P.; Granozzi, G.; Russo, U. *Organometallics* **1986**, *5*, 1866.

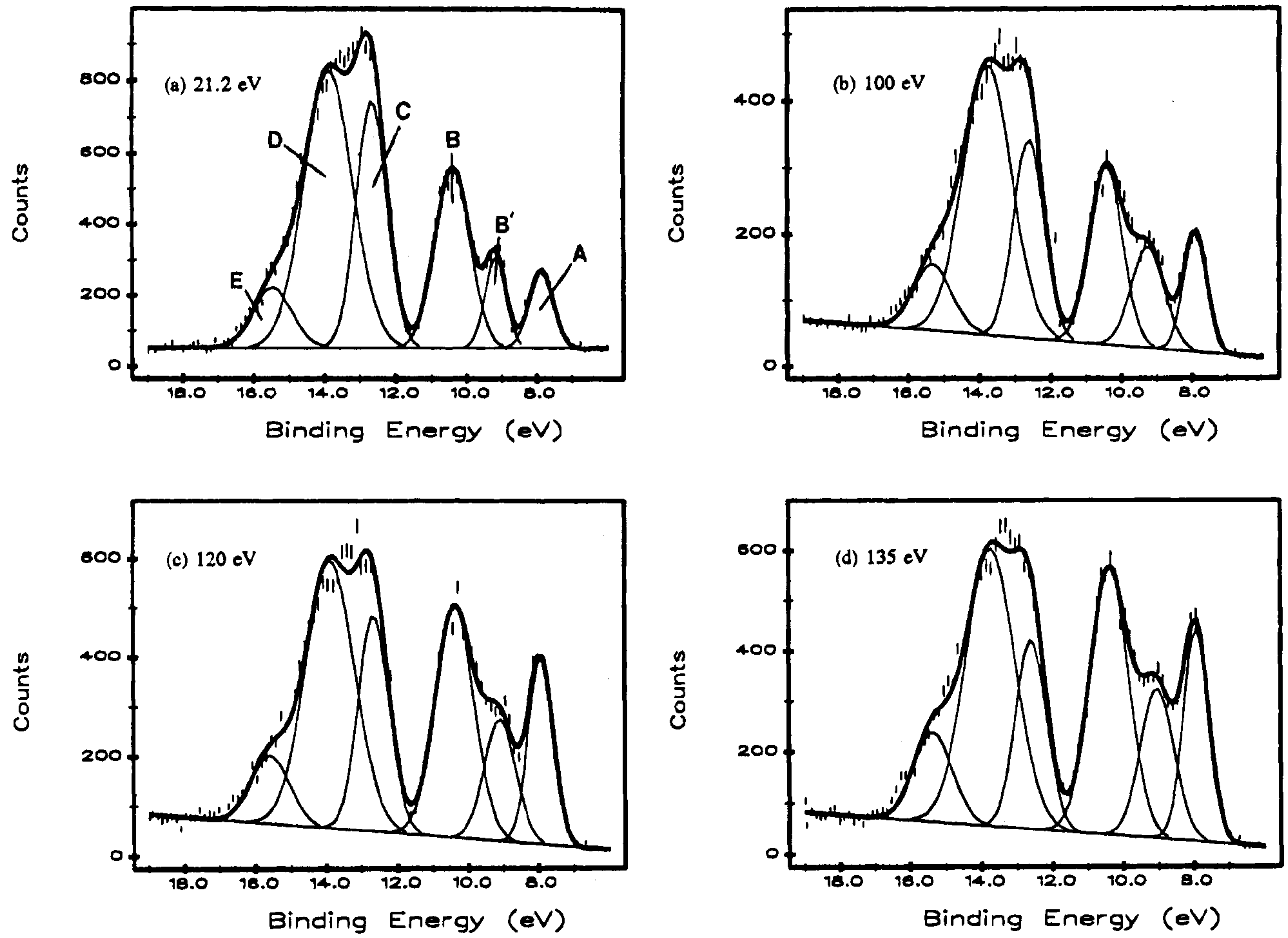

**Figure 5.** Valence band photoelectron spectra of $[Si(CH_3)_2]_6$ at 21.2-, 100-, 120-, and 135-eV photon energies.

pertinent data. The MS−Xα calculation results agree with the DV−Xα calculation results[23] and ab initio results.[25] Peaks B−E behave, qualitatively, the same as they do in the case of TMS (Figure 1). However, peak B in Figure 2 results from two different molecular orbitals (7e and 8e; see Table 4), and this splitting is evident in the poor fit of this peak in the He I spectrum of this compound. Peak A (silicon−silicon bond, not present in the spectrum of TMS) increases dramatically as the photon energy is increased from 21.2 to 135 eV. This increase in peak A, not only relative to peaks C and D but to peak B as well (see Table 9), is a result of the higher percentage of Si 3p and lower percentage of C 2p character in the $7a_1$ orbital. Peaks C and D are assigned to eight orbitals which are rather close in energy. Obviously, we cannot assign peaks C and D to specific orbitals in this molecule, or in the other larger molecules. However, for all molecules except $[Si(CH_3)_2]_6$, it is relatively easy to assign peaks C and D to a group of MO's (see the tables).

The spectra of $Si[Si(CH_3)_3]_4$, $Ge[Si(CH_3)_3]_4$, and $[Si(CH_3)_2]_6$ can be assigned in a analogous fashion to the $Si_2(CH_3)_6$ assignment (Tables 5−7), although there are even more overlapping orbitals. All peaks A's are assigned to silicon−silicon or silicon−germanium bonds. All peak B's are assigned to silicon−carbon bonds, and all peak C's and D's are from carbon−hydrogen bonds. Again, the variations in peak intensities for these three compounds are similar to those in $Si_2(CH_3)_6$, as expected from the similar orbital characters.[20,26] For example, in Figure 6, the branching ratios for peaks A and B form parallel lines of approximately equal slope. Due to the uncertainty in the fitting of peaks C−E, the BR's of those peaks are not examined more carefully.

There are noticeable similarities and differences in the spectra of the close analogs $Si[Si(CH_3)_3]_4$ (TKTS) and $Ge[Si(CH_3)_3]_4$ (TKTG). First, all peak positions, except for peak A, agree to within 0.1 eV. This is expected by the nearly identical MO characters for the MO's that give rise to these peaks. Second, the significantly lower binding energy for peak A (in both theory and experiment) in TKTG is readily attributed to the smaller electronegativity of Ge compared to Si. Third, the intensity of peak A in TKTG is much smaller at all photon energies than for TKTS (Table 9 and Figure 6). This difference is certainly expected, because the Ge 4p cross section is much less than the Si 3p cross section at the three higher photon energies (Table 8).

For $[Si(CH_3)_2]_6$, the branching ratios for peaks A and (B + B′) are comparable to those for the other compounds. Also, the intensity ratio B:B′ is expected to be close to 2:1 from the number of electrons in the orbitals and the similar orbital characters (Table 7). The experimental relative intensities are 1.7:1, 2.3:1, and 2.0:1 at 100, 120, and 135 eV, respectively. Those facts confirm that peak B′ arises from a splitting of the

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[26] Price, W. C.; Potts, A. W.; Streets, D. G. In *Electron Spectroscopy*; Shirley, D. A., Ed.; North-Holland: Amsterdam, 1972.

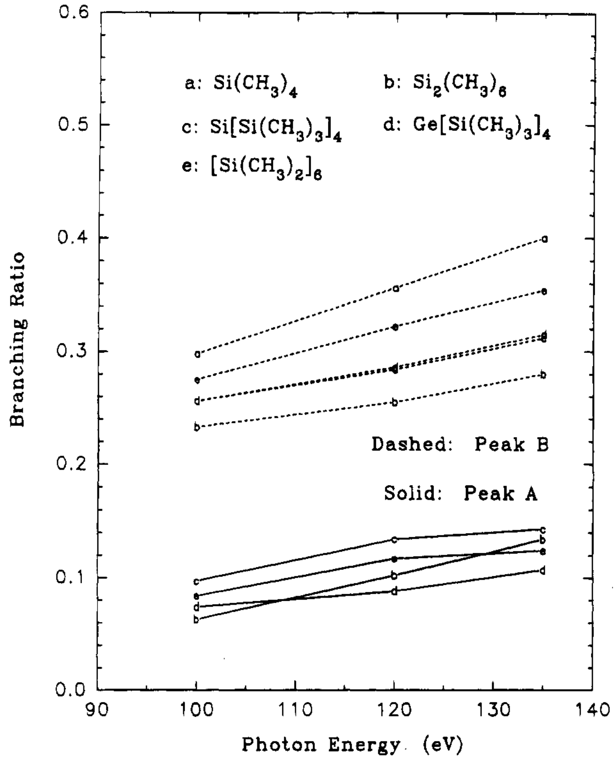

**Figure 6.** Branching ratios for peaks A and B at 100-, 120-, and 135-eV photon energies. Solid lines represent BR's of peaks A. Dashed lines represent BR's of peaks B, but the sum of B and B′ is used for $[Si(CH_3)_2]_6$.

silicon–carbon orbitals, but not the silicon–silicon orbitals, claimed by Bock and Ensslin.[22]

## Conclusions

The photoelectron spectra of the very large silicon compounds $Si_2(CH_3)_6$, $Si[Si(CH_3)_3]_4$, $Ge[Si(CH_3)_3]_4$, and $[Si(CH_3)_2]_6$ have been assigned with confidence with the aid of MS–Xα calculations and the dependence of peak intensities on photon energy. The peak with the lowest binding energy (~8 eV) results from the silicon–silicon or silicon–germanium bonding orbital, which is primarily of Si 3p or Ge 4p character. The next lowest peak (~10 eV) results from orbitals associated primarily with silicon–carbon bonds and are mostly C 2p and Si 3p in character. The third and broadest peak has been divided into three unresolved transitions: the first two (at ~12.5 and 14.2 eV) are associated with the carbon–hydrogen bonding orbitals, which are mostly composed of C 2p and H 1s orbitals. The bands at about 15.2 eV correspond to Si 3s, Si 3p, Ge 4s, and C 2p character. One exception to the above description is in the case of the cyclic compound $[Si(CH_3)_2]_6$, in which the silicon–carbon peak splits into two peaks. This splitting is due to the axial and equatorial positions of the methyl groups around the six-membered silicon ring.

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