

Electron Binding Energies of Si 2p and S 2p for Si- and S-containing Substances by DFT Calculations Using the Model Molecules

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ABSTRACT: Si 2p and S 2p core-electron binding energies (CEBE)s of Si- and S-containing molecules were calculated by deMon DFT program using Slater's transition-state (TS) concept. In the previous works, we could not obtain the calculated values to the experimental ones of third periodic 2p CEBEs for the molecules within the range of averaged absolute deviation (AAD) of 1.0 eV, although the values were calculated by the unrestricted generalized transition-state (uGTS) method. Here, we were able to get the reasonable Si 2p and S 2p CEBEs of 11, and 12 gas molecules in the AAD of 0.37 and 0.46 eV, respectively from the CEBE calculations by the unrestricted generalized diffuse ionization (uGDI) method with a modification of screening constants for third periodic elements of the 2p core-hole. Furthermore, we estimated *WD* (work function and the other energies) values of seven Si- and S-containing polymers [(Si(CH₃)₂)_n (PDMS), (Si(CH₃)₂O)_n (PDMSO), (Si(C₆H₅)CH₃)_n (PMPS), (Si(C₆H₅)CH₃O)_n (PPMSO), ((CH₂CH₂)S)_n (PETHS), ((CH₂(CH₂)₄CH₂)SO₂)_n (PHMS), ((C₆H₄)S)_n (PPS)] from the differences between calculated CEBE values for the model molecules and experimental ones on the solid polymers. [DOI 10.1295/polymj.36.600]

KEY WORDS Core-electron Binding Energy / X-Ray Photoelectron Spectra / DFT Calculations /

Silicon- and sulfur-based polymers are very widely used as active materials with many applications in the material science. The applications range over in plastic moldings, sheets, fibers, films, composites with inorganic materials, protective coatings, sealant and adhesives.^{1–6} Especially, poly-dimethyl siloxane (PDMSO), which is one of the most famous silicon-based polymers, is a polymeric material and exhibits high permeability to hydrophobic organic molecules. The polymer is prepared as thin film composite membranes and used for the extraction of various organic molecules from aqueous solutions.⁷ In the case of the sulfur-based polymer, polyphenylene sulphide (PPS) is a semi-crystalline plastic with high thermal durability using in engineering and useful in the electronics and automotive industries.⁸ In order to improve the characters of these polymers, we think it is important to investigate the electronic structures of these polymers.

Experimental X-Ray photoelectron spectra (XPS) of polymers are directly linked to the theoretical results of electronic states of polymers as obtained by density functional theory (DFT) or molecular orbital (MO) calculations using the model molecules. In previous studies^{9,10} on the deMon DFT calculations^{11,12} by energy shift of *WD* (work function and other energies) values to account for solid-state effects, we calculated core-electron binding energies (CEBE)s of eight polymers involving (C, N, O, F, S, Cl) atoms, seven silicon-based polymers and simulated the va-

lence XPS, respectively.

The present study, then, aims to obtain reasonable Si 2p and S 2p CEBEs of Si-, and S-based model molecules for polymers [(Si(CH₃)₂)_n (PDMS), (Si(CH₃)₂O)_n (PDMSO), (Si(C₆H₅)CH₃)_n (PMPS), (Si(C₆H₅)CH₃O)_n (PPMSO), ((CH₂CH₂)S)_n (PETHS), ((CH₂(CH₂)₄CH₂)SO₂)_n (PHMS), ((C₆H₄)S)_n (PPS)] by the deMon-KS DFT calculations using modification of screening constants for third periodic elements of the 2p core-hole with the Slater's transition-state concept.¹³ We, first, calculated Si 2p and S 2p CEBEs of Si-, and S-containing single molecules in gas-phase by DFT calculations using the unrestricted generalized diffuse ionization (uGDI) method which Chong and co-workers^{14–17} used, and obtained reasonable *WD* (work function and the other energies) values for the polymers from the differences between calculated values for the model molecules and experimental ones on the solid polymers. For three S-based polymers, we simulated the valence XPS by the DFT calculations using the model molecules.

THEORETICAL BACKGROUND

Computation of CEBEs and VIPs

Our approach is based upon the Slater's transition-state (TS) method,¹³ and we use the generalized transition-state (GTS) method¹⁸ proposed by Williams *et al.*, to calculate the one-electron removal energy I_k , such as core-electron binding energy (CEBE) or verti-

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Table I. Scaling factors for Gaussian-type orbitals of second and third periodic atoms used for partial core hole

| Atoms | 1s | 2s | 2p | 3s | 3p |
|-------|------------|------------|------------|------------|------------|
| C | 1.07177549 | 1.39077599 | 1.44136791 | | |
| O | 1.05292343 | 1.27254845 | 1.29970825 | | |
| Si | 1.00070709 | 1.05446617 | 1.04508857 | 1.24041547 | 1.28347401 |
| S | 1.00061755 | 1.04615503 | 1.03736832 | 1.18042847 | 1.21680515 |

cal ionization potential (VIP).

Now we consider an electron removal process for single molecule. If we can expand the total energy $E(x)$ of molecular system in series with the assumption of a continuous variable x ($0 < x < 1$), the following equation is written as

$$E(x) = \sum_{k=0}^{\infty} x^k E_k \quad (1)$$

$$= E_0 + xE_1 + x^2E_2 + x^3E_3 + x^4E_4 + \dots$$

Then the one electron ionization energy I_k from k -th orbital is approximated by

$$I_k \approx \frac{1}{4} \left(\frac{\partial E(x)}{\partial x} \right)_{x=0} + \frac{3}{4} \left(\frac{\partial E(x)}{\partial x} \right)_{x=2/3}, \quad (2)$$

as was stated by Williams *et al.*¹⁸ For the one-electron ionization, the x represents the fraction number of an electron removed from the Kohn–Sham (KS) orbital ψ_k . According to Janak's theorem,¹⁹ the $\partial E(x)/\partial x$ is the negative KS orbital energy $\varepsilon_k(x)$.

For the calculation of CEBEs, the GTS method has also been applied in 'unrestricted' fashion. In the unrestricted GTS (uGTS) method, 2/3 of one α electron is removed from the inner core-level KS orbital. In the case of VIP in valence region, the diffuse ionization (DI) model has been used.^{9,10} In our recent work,²⁰ we have calculated the theoretical analysis of valence XPS by using the restricted generalized diffuse ionization (rGDI) model,¹⁷ where the 2/3 of an electron is removed evenly from all α and β valence KS orbitals. In the present study, we also use on the restricted and unrestricted GDI model to calculate the 2p CEBE of third periodic element because these 2p-core orbitals are often degenerated or very close levels.

In this study, we modified the screening constants of third periodic elements for 2p core-hole in the following way,

$$\begin{aligned} \sigma(1s) &= 0.3(N_{1s} - 1) + 0.0072(N_{2s} + N_{2p}) \\ &\quad + 0.0158(N_{3s} + N_{3p}), \\ \sigma(2s) &= 0.8604(N_{1s}) + 0.3601(N_{2s} \\ &\quad - 1 + N_{2p}) + 0.2062(N_{3s} + N_{3p}), \\ \sigma(2p) &= 0.92925(N_{1s}) + 0.3601(N_{2s}) \end{aligned}$$

$$\begin{aligned} &+ 0.3326(N_{2p} - 1) - 0.0773(N_{3s}) \\ &\quad - 0.0161(N_{3p}), \end{aligned}$$

$$\begin{aligned} \sigma(3s) &= (N_{1s}) + 0.8115875(N_{2s} + N_{2p}) \\ &\quad + 0.2501(N_{3s} - 1 + N_{3p}), \end{aligned}$$

$$\begin{aligned} \sigma(3p) &= (N_{1s}) + 0.8542875(N_{2s} + N_{2p}) \\ &\quad + 0.2501(N_{3s}) + 0.3803(N_{3p} - 1), \quad (3) \end{aligned}$$

where N_{1s} , N_{2s} , ... are the number of 1s, 2s, ... electrons, respectively. In Table I, we summarized the scaling factors for Gaussian type orbitals of the second and third periodic atoms.

Intensity of XPS

The intensity of valence XPS is estimated from the relative photo-ionization cross section (PICS) for Al $K\alpha$ radiation using the following Gelius intensity model.^{21,22}

$$I_j^{\text{XPS}} = N \sum_{A,i} |C_{Aij}|^2 \sigma_{Ai}^{\text{AO}}, \quad (4)$$

where i refers to the atomic subshell on the central atom A , and $|C_{Aij}|^2$ and σ_{Ai}^{AO} represent the electron density populations associated with the molecular orbitals, φ_j , and the photoionization cross-section of atomic orbitals, respectively. For the relative atomic photoionization cross-section, we used the theoretical values from Yeh,²³ as shown in Table II.

COMPUTATIONAL DETAILS

In order to determine the procedure for calculation

Table II. Relative photoionization cross-section of each atomic orbital for H, C, O, Si, and S atoms (relative to C 2s)

| Atoms | Orbital | Al $K\alpha^a$ |
|-------|---------|----------------|
| H | 1s | 0.0041 |
| C | 2s | 1.0000 |
| | 2p | 0.0323 |
| | O | 2s |
| O | 2p | 0.3910 |
| | Si | 3s |
| Si | 3p | 0.2887 |
| | S | 3s |
| S | 3p | 1.5835 |

^aThese values were obtained from ref 23.

Table III. Core-electron binding energies (in eV) of Si 2p for gas molecules from calculations by deMon-KS program

| Molecule | Obsd. ^a | Calc. | | | | | | | | | | | |
|--|--------------------|--------|--------|-------------|--------|--------|--------|-------------|--------|--------|-------------|--------|--------|
| | | rGDI | | Scaled rGDI | | uGDI | | Scaled uGDI | | uGTS | Scaled uGTS | | |
| CH ₃ SiH ₃ | 106.82 | 108.21 | (1.39) | 108.04 | (1.22) | 107.35 | (0.53) | 107.17 | (0.35) | 107.66 | (0.84) | 107.48 | (0.66) |
| (CH ₃ SiH ₂) ₂ O | 107.27 | 108.63 | (1.36) | 108.45 | (1.18) | 107.77 | (0.50) | 107.58 | (0.31) | 108.04 | (0.77) | 107.84 | (0.57) |
| Si(OCH ₃) ₄ | 107.70 | 109.27 | (1.57) | 109.09 | (1.39) | 108.40 | (0.70) | 108.22 | (0.52) | 108.75 | (1.05) | 108.56 | (0.86) |
| Si(CH ₃) ₄ | 105.96 | 107.30 | (1.34) | 107.11 | (1.15) | 106.44 | (0.48) | 106.25 | (0.29) | 106.71 | (0.75) | 106.55 | (0.59) |
| ((CH ₃) ₂ SiH) ₂ O | 106.83 | 108.19 | (1.36) | 108.00 | (1.17) | 107.32 | (0.49) | 107.13 | (0.30) | 107.79 | (0.96) | 107.59 | (0.76) |
| (CH ₃) ₃ SiOC ₂ H ₅ | 106.29 | 107.82 | (1.53) | 107.63 | (1.34) | 106.95 | (0.66) | 106.76 | (0.47) | 107.38 | (1.09) | 107.11 | (0.82) |
| (CH ₃) ₂ Si(OC ₂ H ₅) ₂ | 106.69 | 108.24 | (1.55) | 108.05 | (1.36) | 107.37 | (0.68) | 107.18 | (0.49) | 107.74 | (1.05) | 107.55 | (0.86) |
| ((CH ₃) ₃ Si) ₂ O | 106.50 | 107.88 | (1.38) | 107.69 | (1.19) | 107.01 | (0.51) | 106.82 | (0.32) | 107.46 | (0.96) | 107.26 | (0.76) |
| CH ₃ Si(OC ₂ H ₅) ₃ | 107.09 | 108.66 | (1.57) | 108.47 | (1.38) | 107.79 | (0.70) | 107.60 | (0.51) | 108.12 | (1.03) | 107.98 | (0.89) |
| (SiH ₃) ₂ O | 107.81 | 109.20 | (1.39) | 109.01 | (1.20) | 108.33 | (0.52) | 108.14 | (0.33) | 108.54 | (0.73) | 108.35 | (0.54) |
| Si ₂ H ₆ | 106.86 | 108.11 | (1.25) | 107.94 | (1.08) | 107.25 | (0.39) | 107.08 | (0.22) | 107.53 | (0.67) | 107.35 | (0.49) |
| AAD | | 1.43 | | 1.24 | | 0.56 | | 0.37 | | 0.90 | | 0.71 | |

^aThese values are from ref 38.**Table IV.** Core-electron binding energies (in eV) of S 2p for gas molecules from calculations by deMon-KS program

| Molecule | Obsd. ^a | Calc. | | | | | | | | | | | |
|--|--------------------|--------|--------|-------------|--------|--------|--------|-------------|--------|--------|-------------|--------|--------|
| | | rGDI | | Scaled rGDI | | uGDI | | Scaled uGDI | | uGTS | Scaled uGTS | | |
| (CH ₃) ₂ SO ₂ | 173.90 | 176.23 | (2.33) | 175.51 | (1.61) | 175.20 | (1.30) | 174.47 | (0.57) | 175.41 | (1.51) | 174.71 | (0.81) |
| (CH ₃) ₂ SO | 171.91 | 174.00 | (2.09) | 173.26 | (1.35) | 172.97 | (1.06) | 172.22 | (0.31) | 173.33 | (1.42) | 172.61 | (0.70) |
| S(CH ₃) ₂ | 169.09 | 171.26 | (2.17) | 170.48 | (1.39) | 170.22 | (1.13) | 169.44 | (0.35) | 170.60 | (1.51) | 169.83 | (0.74) |
| CH ₃ SH | 169.28 | 171.77 | (2.49) | 171.00 | (1.72) | 170.74 | (1.46) | 169.97 | (0.69) | 171.12 | (1.84) | 170.37 | (1.09) |
| H ₂ S | 170.20 | 172.48 | (2.28) | 171.72 | (1.52) | 171.45 | (1.25) | 170.69 | (0.49) | 171.83 | (1.63) | 171.08 | (0.88) |
| (CH ₃ O) ₂ SO | 173.59 | 175.13 | (1.54) | 174.41 | (0.82) | 174.10 | (0.51) | 173.37 | (0.22) | 174.49 | (0.90) | 173.80 | (0.21) |
| (CH ₃ O) ₂ SO ₂ | 173.43 | 177.65 | (4.22) | 176.94 | (3.51) | 176.62 | (3.19) | 175.90 | (2.47) | 176.88 | (3.45) | 176.19 | (2.76) |
| C ₃ H ₈ OS ^b | 168.60 | 170.57 | (1.97) | 169.79 | (1.19) | 169.54 | (0.94) | 168.75 | (0.15) | 170.06 | (1.46) | 168.99 | (0.39) |
| C ₆ H ₁₀ OS ^c | 169.79 | 171.63 | (1.84) | 170.85 | (1.06) | 170.60 | (0.81) | 169.82 | (0.03) | 170.99 | (1.20) | 170.20 | (0.41) |
| C ₇ H ₁₂ O ₂ S ^d | 169.82 | 171.49 | (1.67) | 170.72 | (0.90) | 170.46 | (0.64) | 169.69 | (0.13) | 170.55 | (0.73) | 169.79 | (0.03) |
| C ₈ H ₁₂ OS ^e | 168.60 | 170.30 | (1.70) | 169.52 | (0.92) | 169.27 | (0.67) | 168.48 | (0.12) | 169.77 | (1.17) | 168.99 | (0.39) |
| C ₈ H ₁₂ OS ^f | 168.69 | 170.49 | (1.80) | 169.71 | (1.02) | 170.67 | (1.98) | 168.67 | (0.02) | 170.00 | (1.31) | 169.21 | (0.52) |
| AAD | | 2.17 | | 1.42 | | 1.24 | | 0.46 | | 1.51 | | 0.74 | |

^aThese values are from ref 38. ^bThioacetyl acetone ^c4-(Methylthio)pent-3-en-2-one ^dPropyl 3-mercaptocrotonate ^e2-Thioacetylcyclohexanone ^f2-Acetylcyclohexanethione

of 2p CEBEs of third periodic atoms, we had to perform the trial calculation of Si 2p and S 2p CEBEs for gas molecules, with uGTS and ('restricted' and 'unrestricted') generalized diffuse ionization (rGDI and uGDI) models.¹⁷ We then selected 11 and 12 gas molecules for Si- and S-containing substances, respectively in Tables III and IV. For all computations of the energy and intensity concerning the theoretical CEBE and valence XPS, the dimer model molecules [H-(Si(CH₃)₂)₂-H, H-(Si(CH₃)₂O)₂-H, H-(Si-(C₆H₅)CH₃)₂-H, H-(Si(C₆H₅)CH₃O)₂-H, H-((CH₂-CH₂)₂)₂-H, H-((CH₂(CH₂)₄CH₂)SO₂)₂-H, H-((C₆H₄)S)₂-H] of (PDMS, PDMSO, PMPS, PPMO, PETHS, PHMS, PPS) polymers, respectively, were calculated by the deMon-KS DFT programs.^{11,12} In the case of geometry optimization for the organic molecules, we have already obtained better assignments of X-Ray emission and photoelectron spectra for Si- and S-containing substances²⁴⁻³⁰ from the fur-

ther RHF optimization after the AM1^{31,32} geometry-optimization. Therefore, geometry optimization of gas and dimer model molecules was also performed by a semi-empirical AM1 method.^{31,32} The AM1 geometry has then been used as the starting point for further RHF optimization using GAUSSIAN 98 program,³³ using double- ζ bases with polarization. Furthermore, in order to check up the effect on the accurate CEBEs of the Si and S 2p for all gas molecules from the further DFT geometry-optimization using double- ζ bases with polarization with BPW91 in GAUSSIAN 98 program³³ after the AM1 geometry-optimization, we calculated the CEBEs of 11 and 12 gas molecules for Si- and S-containing substances, respectively in Table V, after the geometry optimization.

The deMon-KS program calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Becke's 1988 exchange functional³⁴ and Perdew's 1986 correlation function-

Table V. Core-electron binding energies (in eV) of Si and S for gas molecules from deMon-KS calculations using ‘scaled uGDI’ methods with geometry optimized by RHF/DZP and BPW91/DZP, respectively

| Molecule | Obsd. ^a | RHF/DZP | BPW91/DZP | Molecule | Obsd. ^a | RHF/DZP | BPW91/DZP |
|--|--------------------|---------------|---------------|--|--------------------|---------------|---------------|
| CH ₃ SiH ₃ | 106.82 | 107.17 (0.35) | 107.26 (0.44) | (CH ₃) ₂ SO ₂ | 173.90 | 174.47 (0.57) | 174.51 (0.61) |
| (CH ₃ SiH ₂) ₂ O | 107.27 | 107.58 (0.31) | 107.65 (0.38) | (CH ₃) ₂ SO | 171.91 | 172.22 (0.31) | 172.22 (0.31) |
| Si(OCH ₃) ₄ | 107.70 | 108.22 (0.52) | 108.44 (0.74) | S(CH ₃) ₂ | 169.09 | 169.44 (0.35) | 169.46 (0.37) |
| Si(CH ₃) ₄ | 105.96 | 106.25 (0.29) | 106.32 (0.36) | CH ₃ SH | 169.28 | 169.97 (0.69) | 169.99 (0.71) |
| ((CH ₃) ₂ SiH) ₂ O | 106.83 | 107.13 (0.30) | 107.21 (0.38) | H ₂ S | 170.20 | 170.69 (0.49) | 170.71 (0.51) |
| (CH ₃) ₃ SiOC ₂ H ₅ | 106.29 | 106.76 (0.47) | 106.86 (0.57) | (CH ₃ O) ₂ SO | 173.59 | 173.37 (0.22) | 173.28 (0.31) |
| (CH ₃) ₂ Si(OC ₂ H ₅) ₂ | 106.69 | 107.18 (0.49) | 107.30 (0.61) | (CH ₃ O) ₂ SO ₂ | 173.43 | 175.90 (2.47) | 175.91 (2.48) |
| ((CH ₃) ₃ Si) ₂ O | 106.50 | 106.82 (0.32) | 106.92 (0.42) | C ₅ H ₈ OS ^b | 168.60 | 168.75 (0.15) | 168.74 (0.14) |
| CH ₃ Si(OC ₂ H ₅) ₃ | 107.09 | 107.60 (0.51) | 107.76 (0.67) | C ₆ H ₁₀ OS ^c | 169.79 | 169.82 (0.03) | 169.91 (0.12) |
| (SiH ₃) ₂ O | 107.81 | 108.14 (0.33) | 108.25 (0.44) | C ₇ H ₁₂ O ₂ S ^d | 169.82 | 169.69 (0.13) | 169.35 (0.47) |
| Si ₂ H ₆ | 106.86 | 107.08 (0.22) | 107.16 (0.30) | C ₈ H ₁₂ OS ^e | 168.60 | 168.48 (0.12) | 168.40 (0.20) |
| | | | | C ₈ H ₁₂ OS ^f | 168.69 | 168.67 (0.02) | 168.65 (0.04) |
| AAD | | 0.37 | 0.48 | | | 0.46 | 0.52 |

^aThese values are from ref 38. ^bThioacetyl acetone ^c4-(Methylthio)pent-3-en-2-one ^dPropyl 3-Mercaptoacetate ^e2-Thioacetylcyclohexanone ^f2-Acetylcyclohexanethione

al.³⁵ In the deMon-KS program, we used an ‘extrafine’ and ‘nonrandom’ grid and the correlation-consistent polarized valence triple- ζ (cc-pVTZ) basis of Dunning and Hay³⁶ to calculate VIPs of the model molecules with auxiliary fitting functions labeled (3,1; 3,1) for H, (4, 4; 4, 4) for C, and O, and (5, 4; 5, 4) for Si and S. In the calculations of CEBEs, we used the correlation-consistent polarized valence triple- ζ (cc-pVTZ) basis for the model molecules in the initial state and we used the cc-pVTZ or the scaled polarized valence triple zeta (scaled-pVTZ) basis in the final state. In these calculations, we neglect the effect of spin-orbit interaction.

For simulation of the valence XPS, we constructed from a superposition of peaks centered on each VIP, I_k . In previous works,^{9,10} each peak was represented by Gaussian lineshape functions. In the case of the linewidth (WH(k)), we used $WH(k) = 0.08I_k$ (proportional to the ionization energy): $I_k(I_{FL}) = I'_k - WD$, to compare the theoretical results with the experimental spectra. The $I_k(I_{FL})$ and WD represent ionization energy relative to Fermi level and the sum of the work function of the sample (W) and other energy effects (D as delta), respectively. For experimental spectra of polymers, we cited the valence XPS and the CEBEs by Beamson and Briggs.³⁷

In order to account for solid-state effect, a quantity WD that we introduced the energy shift in the previous works^{9,10} was estimated from computed CEBEs. In the case of polymers, the experimental WD values can be estimated from differences between CEBEs of monomers or oligomers in gas phase and of actual solid polymers.

RESULTS AND DISCUSSION

In this study, our aim is to demonstrate the effective

method for calculation of 2p core-electron binding energies (CEBEs) of the molecules for third periodic atoms. We also calculate the theoretical 2p CEBEs for Si- and S-based polymers and simulate valence X-Ray photoelectron spectra (XPS) of three S-based polymers to clarify the electronic structure.

Core-electron Binding Energy of Gas Molecules Including Third Period Atoms

In the previous works, we could not obtain the calculated CEBE values to the experimental ones of third periodic 2p for the molecules within the range of averaged absolute deviation (AAD) of 1.0 eV, although the values were calculated by the unrestricted generalized transition-state (uGTS) method. Then, in order to determine the procedure for obtaining reasonable 2p CEBEs for third periodic atoms, we performed the calculation of CEBEs with uGTS and (‘restricted’ and ‘unrestricted’) generalized diffuse ionization (rGDI and uGDI) models.¹⁷ We, first, calculated the CEBEs of Si 2p and S 2p for gas molecules, and compared the values with experimental ones,³⁸ as shown in Tables III and IV. The results in the ‘unrestricted’ GDI model were much better than in uGTS model in a case of degenerated or very close 2p-core energy levels for third periodic elements. In the uGDI model, values of averaged absolute deviation (AAD) for the CEBEs are in the ranges of 0.56 and 1.24 eV for Si and S, respectively. In the calculation with the scaled polarized valence triple- ζ (scaled-pVTZ) basis using labeled ‘scaled rGDI,’ ‘scaled uGDI’ and ‘scaled uGTS,’ methods, we obtained the most reasonable CEBE values using uGDI model of Si- and S-containing molecules in gas within AADs of 0.37 and 0.46 eV, respectively. In order to check up the effect on the accurate CEBEs of the Si and S 2p for all

Table VI. Core-electron binding energies (in eV) of polymers by deMon-KS program using model dimers

| Polymers | Obsd. ^a | Model Molecule | | | |
|--|--------------------|----------------|-----|-------------------|-----|
| | | Calc. | WD | Exp. ^b | WD |
| PDMS | | | | | |
| (Si(CH ₃) ₂) _n | | | | | |
| C 1s [<u>-CH₃</u>] | 283.5 | 290.01 | 6.5 | 290.14 | 6.6 |
| Si 2p _{3/2} | 98.1 | 106.09 | 8.0 | 106.71 | 8.6 |
| PDMSO | | | | | |
| (Si(CH ₃) ₂ -O) _n | | | | | |
| O 1s | 532.00 | 538.01 | 6.0 | 537.32 | 5.3 |
| C 1s [<u>-CH₃</u>] | 284.38 | 290.00 | 5.6 | 289.90 | 5.5 |
| Si 2p _{3/2} | 101.79 | 107.56 | 5.8 | 106.83 | 5.0 |
| PMPS | | | | | |
| (Si(C ₆ H ₆)(CH ₃)) _n | | | | | |
| C 1s [<u>-CH₃</u>] | 284.0 | 289.75 | 5.8 | | |
| C 1s [<u>Si-C₆H₅</u>] | 284.0 | 289.60 | 5.6 | | |
| Si 2p _{3/2} | 98.3 | 105.82 | 7.5 | | |
| PPMSO | | | | | |
| (Si(C ₆ H ₆)(CH ₃ -O)) _n | | | | | |
| O 1s | 532.00 | 537.31 | 5.3 | | |
| C 1s [<u>-C₆H₅</u>] | 284.70 | 290.16 | 5.5 | | |
| C 1s [<u>-CH₃</u>] | 284.39 | 289.83 | 5.4 | | |
| C 1s [<u>Si-C₆H₅</u>] | 284.22 | 289.62 | 5.4 | | |
| Si 2p _{3/2} | 101.68 | 107.28 | 5.6 | | |
| PETHS | | | | | |
| (S-CH ₂ -CH ₂) _n | | | | | |
| C 1s [<u>-CH₂</u>] | 285.52 | 291.48 | 6.0 | | |
| S 2p _{3/2} | 163.50 | 169.11 | 5.6 | | |
| PHMS | | | | | |
| (SO ₂ -CH ₂ (CH ₂) ₄ CH ₂) _n | | | | | |
| O 1s | 531.74 | 537.36 | 5.6 | | |
| C 1s [<u>S-CH₂</u>] | 285.64 | 291.53 | 5.9 | | |
| C 1s [<u>-CH₂</u>] | 285.00 | 291.11 | 6.1 | | |
| S 2p _{3/2} | 167.64 | 173.91 | 6.3 | | |
| PPS | | | | | |
| (S-C ₆ H ₄) _n | | | | | |
| C 1s [<u>S-C₆H₄</u>] | 285.21 | 290.84 | 5.6 | | |
| C 1s [<u>-C₆H₄</u>] | 284.70 | 290.21 | 5.5 | | |
| S 2p _{3/2} | 163.66 | 169.25 | 5.6 | | |

^aThese values are due to ref 37. ^bValues cited from CEBEs by Drake *et al.* from ref 39.

gas molecules from the further RHF and DFT/BPW91 optimization using double- ζ bases with polarization in GAUSSIAN 98 program³³ after the AM1 geometry-optimization, we calculated the CEBEs of 11 and 12 gas molecules for Si- and S-containing substances, respectively by 'scaled uGDI' method in Table V, after the geometry optimization. In the table, we found out that the calculated CEBEs after RHF geometry-optimization are much better than the values after DFT/BPW91 optimization. Thus, for the CEBE calculations of polymers including third periodic

atoms, we will use the scaled basis with the uGDI method from the further RHF optimization using double- ζ bases with polarization in GAUSSIAN 98 program³³ after AM1 geometry-optimization.

In the molecules bonded three or four oxygens such as Si(OCH₃)₄, (CH₃O)₂SO₂, we could not obtain the good values of the CEBEs.

CEBEs of Si- and S-based Polymers and Valence XPS of S-based Polymer

Table VI shows the CEBEs of the model dimers for seven polymers (PDMS, PDMSO, PMPS, PPMSO, PETHS, PHMS, PPS) using the uGDI method with scaled-pVTZ basis. The calculated CEBEs of C 1s, O 1s and Si 2p_{3/2} for the model molecules, H(Si(CH₃)₂)₂H and H(Si(CH₃)₂O)₂H, are in good accordance with the experimental ones of (CH₃)₂SiH₂ and ((CH₃)₂SiH)₂O in gas, as observed by Drake *et al.*³⁹ In the Table VI, we showed the WD values of the polymers from the difference between the calculated CEBEs of dimer models and experimental ones of polymers. As described in previous works,^{9,10} WDs from the CEBEs are the most reliable.

For valence XPS of three S-based polymers in Figure 1a-c, the simulated peaks using model dimers with the uGDI model corresponded considerably well to experimental ones. In Tables VII and VIII, we summarized the observed and calculated peaks, main contributions of atomic photo-ionization cross-section, orbital nature and functional groups for PHMS and PPS polymers. In the case of PHMS, broad double peaks at around 28.0 and 24.5 eV are due to $\sigma\sigma$ (S 3s-O 2s) and $p\sigma$ (S 3p-O 2s) bondings of [-S-O] group, and the broad peak at around 19.0 eV results from $\sigma\sigma$ {(C 2s-C 2s), (S 3s-C 2s)}, and $p\sigma$ (S 3p-C 2s) bondings, respectively. The intensive peaks at around 13.0 and 10.5 eV depend on { $\sigma\sigma$ (C 2s-C 2s), $p\sigma$ (C 2s-C 2p), $p\sigma$ (S 3p-C 2p)}, and $p\sigma$ {(C 2p-H 1s), (S 3p-O 2p), (C 2p-C 2p)}, respectively. The peak in the range of 5-9 eV is owing to $p\sigma$ {(C 2p-H 1s), (C 2p-C 2p)} bondings and $p\pi$ (lone pairs) of oxygen.

CONCLUSIONS

In the previous works,^{9,10} we could not obtain the reasonable calculated CEBE values to the experimental ones of third periodic 2p for the organic molecules within the range of averaged absolute deviation (AAD) of 1.0 eV, although the values were calculated by the unrestricted generalized transition-state (uGTS) method. In the present study, we gave considerably reasonable values of Si 2p and S 2p CEBEs for Si- and S-containing gas molecules by DFT calculations using the uGDI method due to Slater's transition-state

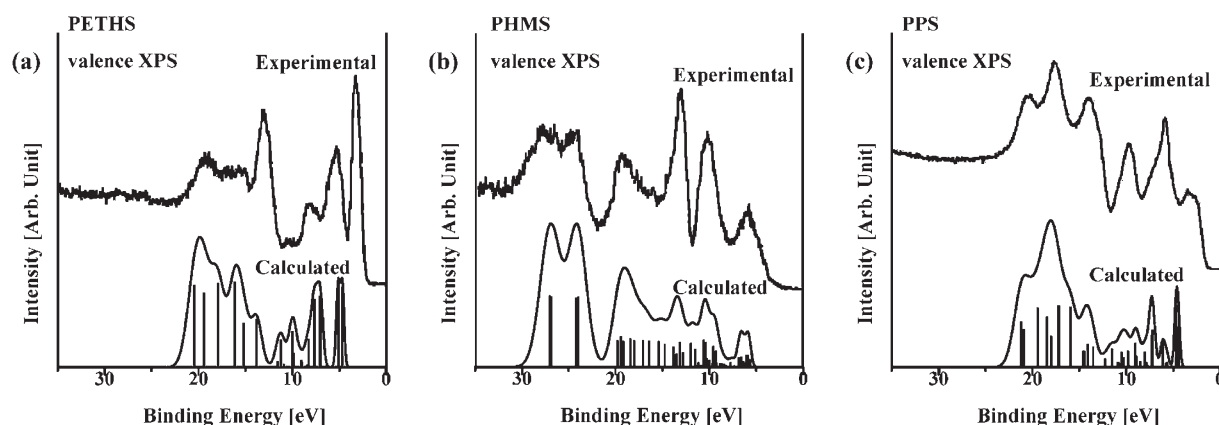


Figure 1. Simulated valence X-Ray photoelectron spectra of sulfur-based polymers with the experimental spectra, (a) PETHS; (b) PHMS; (c) PPS.

Table VII. Observed peaks, VIPs, main AO photoionization cross-section (PICS), orbital nature, and the functional group for valence XPS of PHMS (Shift between the observed and calculated VIP is 3.0 eV)

| Peak (eV) | VIPs (eV) | Main AO PICS | Orbital nature ^b | Functional group |
|----------------------------------|--------------|--------------|---|------------------|
| 28.0 (26.0–30.0) ^a | {30.0; 29.9} | S 3s, O 2s | $s\sigma(\text{S } 3s\text{--O } 2s)\text{--B}$ | –S–O |
| 24.5 (23.0–26.0) ^a | {27.2; 27.0} | S 3p, O 2s | $p\sigma(\text{S } 3p\text{--O } 2s)\text{--B}$ | –S–O |
| 19.0 (15.0–22.0) ^a | {17.8–22.8} | C 2s | $s\sigma(\text{C } 2s\text{--C } 2s)\text{--B}$ | –C–C |
| 13.0 (12.0–15.0) ^a | {15.0–16.9} | S 3s, C 2s | $s\sigma(\text{S } 3s\text{--C } 2s)\text{--B}$ | –S–C |
| | | S 3p, C 2s | $p\sigma(\text{S } 3p\text{--C } 2s)\text{--B}$ | –S–C |
| 10.5 (8.0–12.0) ^a | {11.7–14.5} | C 2s | $s\sigma(\text{C } 2s\text{--C } 2s)\text{--B}$ | –C–C |
| | | C 2s, C 2p | $p\sigma(\text{C } 2s\text{--C } 2p)\text{--B}$ | –C–C |
| 6.0 (4.0–8.0) ^a | {8.6–11.4} | S 3p, C 2p | $p\sigma(\text{S } 3p\text{--C } 2p)\text{--B}$ | –S–C |
| | | C 2p | $p\sigma(\text{C } 2p\text{--H } 1s)\text{--B}$ | –CH ₂ |
| 6.0 (4.0–8.0) ^a | {8.6–11.4} | S 3p, O 2p | $p\sigma(\text{S } 3p\text{--O } 2p)\text{--B}$ | –S–O |
| | | C 2p | $p\sigma(\text{C } 2p\text{--C } 2p)\text{--B}$ | –C–C |
| | | C 2p | $p\sigma(\text{C } 2p\text{--H } 1s)\text{--B}$ | –CH ₂ |
| | | O 2p | $p\pi(\text{lone pair})\text{--NB}$ | –O– |

^aThe notation shows the peak range. ^bB and NB mean bonding and nonbonding, respectively.

Table VIII. Observed peaks, VIPs, main AO photoionization cross-section (PICS), orbital nature, and the functional group for valence XPS of PPS (Shift between the observed and calculated VIP is 3.0 eV)

| Peak (eV) | VIPs (eV) | Main AO PICS | Orbital nature ^b | Functional group |
|----------------------------------|-----------------------------|--------------|---|------------------|
| 20.5 (19.0–21.0) ^a | {24.2; 23.9; 22.4; 21.4} | S 3s, C 2s | $s\sigma(\text{S } 3s\text{--C } 2s)\text{--B}$ | –S–C |
| 18.0 (16.0–19.0) ^a | {21.0; 21.0; 20.2; 19.0} | C 2s | $s\sigma(\text{C } 2s\text{--C } 2s)\text{--B}$ | –C–C (phenyl) |
| | | C 2s | $s\sigma(\text{C } 2s\text{--C } 2s)\text{--B}$ | –C–C (phenyl) |
| 15.0 (12.0–16.0) ^a | {17.6; 17.4; 17.1; 16.5} | S 3s, C 2p | $p\sigma(\text{S } 3s\text{--C } 2p)\text{--B}$ | –S–C |
| 10.0 (8.5–12.0) ^a | {12.7–15.3} | C 2s | $s\sigma(\text{C } 2s\text{--C } 2s)\text{--B}$ | –C–C (phenyl) |
| | | C 2s, C 2p | $p\sigma(\text{C } 2s\text{--C } 2p)\text{--B}$ | –C–C (phenyl) |
| 6.5 (4.5–8.5) ^a | {8.6–12.0} | S 3p, C 2p | $p\sigma(\text{C } 2s\text{--C } 2p)\text{--B}$ | –S–C |
| | | C 2p | $p\sigma(\text{S } 3p\text{--C } 2p)\text{--B}$ | –C–C (phenyl) |
| 4.0 (2.5–4.5) ^a | {7.7; 7.4} | C 2p | $p\sigma(\text{C } 2p\text{--C } 2p)\text{--B}$ | –C=C (phenyl) |
| | | C 2p | $p\pi(\text{C } 2p\text{--C } 2p)\text{--B}$ | –S–C |
| | | S 3p, C 2p | $p\sigma(\text{S } 3p\text{--C } 2p)\text{--B}$ | –S– |
| | | S 3p | $p\pi(\text{lone pair})\text{--NB}$ | –S– |

^aThe notation shows the peak range. ^bB and NB mean bonding and nonbonding, respectively.

concept. In the calculation with the scaled polarized valence triple- ζ (scaled-pVTZ) basis using labeled 'scaled rGDI,' 'scaled uGDI' and 'scaled uGTS,' methods, we obtained the most reasonable CEBE values using uGDI model of Si- and S-containing molecules in gas within AADs of 0.37 and 0.46 eV, respectively. Furthermore, we obtained reliable *WD* (work function and the other energies) values of seven Si- and S-containing polymers [(Si(CH₃)₂)_n (PDMS), (Si(CH₃)₂O)_n (PDMSO), (Si(C₆H₅)CH₃)_n (PMPS), (Si(C₆H₅)CH₃O)_n (PPMSO), ((CH₂CH₂)S)_n (PETHS), ((CH₂(CH₂)₄CH₂)SO₂)_n (PHMS), ((C₆H₄)S)_n (PPS)] from deMon-KS DFT calculations using the dimer model molecules with the uGDI methods.

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