

Simulation of C1s Spectra of C- and O-Containing Polymers in XPS by *Ab Initio* MO Calculations Using Model Oligomers

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(Received August 29, 1996)

ABSTRACT: C1s spectra of molecules [CH₂=CH(COOH), CH₂=CH-COOCH₃, CH₂=C(CH₃)COOCH₃, CH₃-CH-(CH₃)COOCH₃] in gas and fifteen polymers [(CH₂-CHR)_n (R=H, CH₃, OH, OCH₃, COCH₃, COOH, OCOCH₃, COOCH₃), ((CH)_k-O)_n (k=1–4), (CHR-CO-O)_n (R=H, CH₃), and (CH₂-C(CH₃)COOCH₃)_n] in X-ray photoelectron spectroscopy (XPS) were simulated from Koopmans' theorem by *ab initio* MO calculations of HONDO7 program using the model oligomers. The calculated C1s spectra were obtained using Gaussian lineshape functions of each fixed linewidth of 0.54 and 1.3 eV for the gas molecules and the oligomers, respectively. The theoretical spectra showed fairly good accordance with the experimental spectra, although the shifted values were used as 14.4 and 21.0 eV for core C1s energy levels of the gas molecules and the model oligomers, respectively. The difference between the shifted values (21.0 and 14.4 eV) approaches to the WD (5.2–6.4 eV) of ten polymers as obtained by deMon density-functional calculations using model molecules with scaled-pVTZ basis set. This is due to the relation of solid effects between the experimental core-electron binding energies of polymers and theoretical MO eigenvalues of the oligomer models, as stated in the previous work.

KEY WORDS X-Ray Photoelectron Spectroscopy / C1s Spectra / *Ab Initio* MO / Spectral Simulation / Koopmans' Theorem / O-Containing Polymer / Work Function /

We have currently reported on the simulation of X-ray photoelectron spectra of polymers by MO calculations using the model molecules.^{1–10} The theorem of the MO calculations can be classified into three typical cases: (a) the Koopmans' theorem, (b) delta-SCF, and (c) Slaters' concept¹¹ of the transition-state. In the case (a), we offered a good analysis^{2–4} of C1s spectra with Koopmans' values for four polymers [(CH₂-CHR)_n (R=OH, COOH, OCOCH₃) and (CH₂-C(CH₃)COOCH₃)_n], although the shifted value was used as 21.0 eV for core C1s energy levels of the model oligomers. The reason relies on it that the differences between core energy levels as obtained using calculations of the neutral parent molecules approximate the ones as observed for the ionized molecules in XPS, although the nuclear positive charges strongly attract the core electrons in the deep potential of the ionized state. However, in the case of valence electron spectra, the energy scale of the simulated spectra^{12–14} using the Koopmans' theorem had to be contracted and shifted for a good fit with the observed spectra. This means that the energy levels in valence electron region of a ionized molecule are narrowed more than the Koopmans' values in the range of the neutral parent molecule, since there are valence electrons in the shallow potential.

The method of delta-SCF (case (b)) gave quite reliable values^{15,16} of the core-electron binding energies (CEBEs), but suffers from occasional failures. In recent papers,^{5–10} we have performed the theoretical better assignment of valence-band spectra for 60 polymers due to Slater's idea of the transition-state (case (c)) by semiempirical HAM/3^{17–20} and *ab initio* deMon density functional²¹ calculations using the model oligomers. The simulation spectra from the MO calculations in that the results can be directly compared with experiment to predict vertical ionization potentials (VIPs) were in good accordance with observed spectra.

For the CEBEs, in *ab initio* studies of the density

functional theory (DFT) using the deMon DFT program,²¹ Chong^{22–26} offered the methods of calculating accurate CEBEs of small molecules. We have also reported on the applications^{9,10} of the DFT to calculate the CEBEs of the polymers. The difference between the calculated and the observed CEBEs reflected the trend in WD (sum of work function and other energy effects) of the polymers.

In the present paper, we describe a comprehensive study on the simulation of C1s spectra of C- and O-containing polymers in XPS due to Koopmans' theorem by *ab initio* MO calculations using HONDO7 program.²⁷ Furthermore, the CEBEs of C1s for the model molecules of polymers [(CH₂-CHR)_n (R=H, CH₃, OH, OCH₃, COCH₃, COOH, COOCH₃), (CH₂-O)_n, (CH₂-CO-O)_n, and (CH₂-C(CH₃)COOCH₃)_n] are calculated by deMon DFT program²¹ with scaled polarized valence triple-zeta (pVTZ) basis set. The results showed much better correspondence with experiment than were those predicted by Koopmans' theorem.

THEORETICAL AND DETAIL OF CALCULATION

Simulation of C1s Spectra Due to Koopmans' Theorem

The model molecules [CH₂=CH(COOH), CH₂=CH-COOCH₃, CH₂=C(CH₃)COOCH₃, CH₃-CH-(CH₃)COOCH₃] in gas, and [H-(CH₂-CHR)_m-H (R; m=H; 3, CH₃; 3, OH; 3, OCH₃; 2, COCH₃; 2, COOH; 3, OCOCH₃; 3, COOCH₃; 2), H-((CH)_k-O)_m-H (k; m=1; 3, 2; 3, 3; 2, 4; 2), H-(CHR-CO-O)_m-H (R; m=H; 2, CH₃; 2), and H-(CH₂-C(CH₃)COOCH₃)₂-H] of polymers were calculated by *ab initio* RHF-SCF MO calculations using the HONDO7 program. For C and O atoms, we used the (4s2p) basis sets and for H atoms, we used 2s basis set reported by Huzinaga *et al.*²⁸ and Dunning *et al.*²⁹ For the geometry of the model molecules, we used the optimized structures from the semi-

empirical AM1 (version 6.0)³⁰ MO calculations.

The electronic states of the polymers by the MO calculations using the dimer or the trimer model molecules will enhance the effects of the edges of the main chain. Then, we omitted the contribution of both edge segments of the main chain, in order to simulate the C1s core-electron spectra.

For the comparison between calculations for single molecules of the dimer or trimer models and experiments on a solid polymer, we must shift each computed CEBEs, E'_k by a quantity ($E_{\text{DKT}} + \text{WD}$) as $E_k(E_F) = E'_k - (E_{\text{DKT}} + \text{WD})$, to convert to ionization energy $E_k(E_F)$ relative to the Fermi level. These quantities were stated in the previous work.⁴ In this work, we chose the fixed approximate values of the quantity E_{DKT} as 14.4 eV for C1s spectra of gas molecules and of the sum ($E_{\text{DKT}} + \text{WD}$) as 21.0 eV for C1s spectra of polymers, respectively, to provide the good agreement on the location of the main features of the simulated spectrum.

In order to simulate the core-electron spectra of C1s of the gas molecules and polymers, we used the Gaussian lineshape function:

$$f(x) = A(k) \exp\{-B(k)(x - E_k)^2\} \quad (1)$$

where the intensity, $A(k)$, is estimated as an arbitrary unit. For the linewidth, $WH(k) = 2(\ln 2/B(k))^{1/2}$, we found the fixed approximate values as 0.54 and 1.3 eV for C1s of gas molecules and polymer models, respectively, by trial and error.

CEBEs of C1s Due to Slater's Concept of the Transition-State Using DFT Calculations

We can consider an electronic process of ionization or excitation for single molecules using Slater's transition-state (TS) method at fixed molecular geometry. We define

$$E(x) = \sum x^k E_k \\ = E_0 + xE_1 + x^2E_2 + x^3E_3 + x^4E_4 + \dots \quad (2)$$

where $E(0)$ and $E(1)$ correspond to the initial and final states respectively and x is assumed to be a continuous variable. From eq 2, the endothermicity we seek is given by

$$\Delta E = E(1) - E(0) = E_1 + E_2 + E_3 + E_4 + \dots \quad (3)$$

If we define the first derivative ($F(x) = dE(x)/dx$), in the generalized transition-state (GTS) method, Williams *et al.*³¹ proposed the use of

$$F(2/3) = E_1 + 4E_2/3 + 4E_3/3 + 32E_4/27 + \dots \quad (4)$$

Therefore, ΔE can be approximated by

$$[F(0) + 3F(2/3)]/4 = E_1 + E_2 + E_3 + 8E_4/9 + \dots \quad (5)$$

with an error of only

$$d_{\text{GTS}} = -E_4/9 + \dots \quad (6)$$

The GTS model can be applied in two ways. In what is labeled 'restricted' GTS method, we remove the same set of fractional electrons from molecular orbitals for both alpha and beta electrons, rather than MO for alpha electron(s) only in the 'unrestricted' GTS model. For uGTS models, the corresponding number is 2/3.

The model molecules $[H-(CH_2-CHR)_2-H]$ ($R = H,$

$CH_3, COCH_3$), $H-(CH_2-CHR-CH_2)-H$ ($R = OH, OCH_3$), $H-(CH_2-CHR)-H$ ($R = COOH, COOCH_3$), $H-(CH_2-O)_2-H$, $H-(CH_2-(CO)-O-CH_2)-H$, and $H-(CH_2-C(CH_3)COOCH_2)-H$] were calculated by the density functional theory using deMon program.²¹ For the geometry of the molecules, we used the optimized cartesian coordinates from the semiempirical AM1 (version 6.0) program. The deMon calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Beck's 1988 exchange functional³² and Perdew's 1986 correlation functional.³³ In the program, we used a nonrandom grid and a scaled polarized valence triple-zeta (scaled-pVTZ)²⁵ basis set for C, O, and H with auxiliary fitting functions labeled (4, 4; 4, 4) for C and O (3, 1; 3, 1) for H.

In the calculation of CEBEs, we used the uGTS models for the model molecules of ten polymers. We added the relativistic correction (C_{rel})^{24,25} for C using $C_{\text{rel}} = KI_{\text{nr}}N$ where $K = 2.198 \times 10^{-7}$, $N = 2.178$ and I_{nr} is the non-relativistic CEBE.

For four gas molecules and fifteen polymers, we cited the C1s spectra in XPS by Naves de Brito *et al.*¹⁵ and Beamson and Briggs,³⁴ respectively.

RESULTS AND DISCUSSION

Simulation of C1s Photoelectron Spectra of Gas Molecules

As stated in Introduction, we considered that the core-electron spectra can be simulated with the Koopmans' theorem of neutral parent molecules, since the differences between energy levels as obtained using the Koopmans' theorem approximate the ones in an ionized state of core-electron after the X-ray irradiation. We simulated C1s spectra of organic gas molecules [$CH_2 = CH(COOH)$, $CH_2 = CH-COOCH_3$, $CH_2 = C(CH_3)COOCH_3$, $CH_3-CH(CH_3)COOCH_3$] as models of the C- and O-containing polymers as already observed by Neves de Brito and coworkers.^{15,16}

For this simulation, we used fixed energy shifts and fixed linewidths for each MO level of the calculated C1s, since we considered these molecules which consist of three common atoms C, H, and O. By trial and error, we found the energy shifted value as 14.4 eV for C1s between the Koopmans' values and the observed results of the four molecules. The linewidth of each MO levels for C1s was evaluated as 0.54 eV, as shown in Table I. Figure 1a—d indicates that we can obtain good assignments with the Koopmans' theorem due to the normal MO calculations of the neutral parent molecules using the *ab initio* MO program.

Simulation of C1s Spectra of Fifteen Polymers

The simulated C1s spectra as obtained by MO calculations using model oligomers, correspond to the experimental core electron spectra of the polymers (as shown in Figures 2a—5d), although there was a large difference (21.0 eV) in energy levels due to the Koopmans' value and WD (work function and other energy effects). In the simulation, we also used a fixed energy shift and a fixed linewidth for MO levels of C1s of these C- and O-containing polymers.

In the case of the spectral analysis, we omitted the contribution of both edge segments of main chain. The

Table I. C1s binding energies (in eV) of acrylic acid (ACRA), methyl acrylate (MA), methyl methacrylate (MMA), and methyl isobutyrate (MIB) in gas by HONDO7 program

Molecule	Observed ^b	Koopmans' theorem	Relative intensity	Shifted value	Linewidth (halfwidth)
MIB					
CH ₃ -CH(CH ₃)COOCH ₃					
CEBE (C1s) [-CH ₃]	290.7	304.62	1.0	14.4	0.54
CEBE (C1s) [-CH ₂]	290.7	304.86	1.0	14.4	0.54
CEBE (C1s) [-CH]	291.1	305.62	1.0	14.4	0.54
CEBE (C1s) [O-CH ₃]	292.4	306.59	1.0	14.4	0.54
CEBE (C1s) [-C=O]	294.4	309.41	1.0	14.4	0.54
MMA					
CH ₂ =C(CH ₃)COOCH ₃					
CEBE (C1s) [-CH ₃]	290.6	304.70	1.0	14.4	0.54
CEBE (C1s) [H ₂ -]	291.0	305.40	1.0	14.4	0.54
CEBE (C1s) [C<]	291.0	305.75	1.0	14.4	0.54
CEBE (C1s) [O-CH ₃]	292.4	306.62	1.0	14.4	0.54
CEBE (C1s) [-C=O]	294.5	309.50	1.0	14.4	0.54
MA					
CH ₂ =CHCOOCH ₃					
CEBE (C1s) [CH ₂ -]	291.1	305.55	1.0	14.4	0.54
CEBE (C1s) [CH-]	291.1	305.79	1.0	14.4	0.54
CEBE (C1s) [O-CH ₃]	292.5	306.63	1.0	14.4	0.54
CEBE (C1s) [O-C=O]	294.8	309.55	1.0	14.4	0.54
ACRA					
CH ₂ =CH(COOH)					
CEBE (C1s) [CH ₂ -]	291.3	305.74	1.0	14.4	0.54
CEBE (C1s) [CH-]	291.3	306.00	1.0	14.4	0.54
CEBE (C1s) [COOH]	295.2	309.86	1.0	14.4	0.54

C1s relative intensity of each functional group for the model oligomers was considered as the number of the carbon for the functional group in the monomer unit of the fifteen polymers in Table II. In the table, we found an energy shifted value and a linewidth of each MO levels as 21.0 and 1.3 eV, respectively, by trial and error.

The theoretical analysis from the Koopmans' theorem showed fairly good accordance with experimental lineshape analysis as obtained by Beamson and Briggs.³⁴ We emphasize here that the theoretical results give an aid to perform experimental lineshape analysis. For example, in the case of polypropylene (Figure 2b), the single peak around 285.1 eV results from theoretical values, (305.4, 305.5 eV), (305.2, 305.3 eV), and (305.1, 305.2 eV) of the -CH, -CH₂, and CH₃ components, respectively, for the model trimers. For polyvinyl methyl ketone (PVMK) (Figure 4b), the large peak around 285.3 eV is due to calculated values, 306.0, 305.8, and 305.4 eV of the -CH₃, -CH, and -CH₂ components, respectively, for the model dimers. As stated in previous paper,³ we assigned that the C_{1s} broader peak of PMMA (Figure 5d) in the range of 284–288 eV is composed of four components (-CH₃, -CH₂, >C<, and -OCH₃).

CEBEs and WD of Ten Polymers

The computed CEBEs (Table III) of ten polymers (polyethylene (PE), polypropylene (PP), poly(methylene glycol) (PMG), poly(vinyl alcohol) (PVA), poly(vinyl methyl ether) (PVME), poly(vinyl methyl ketone) (PVMK), poly(acrylic acid) (PAA), poly(methyl acrylate) (PMA), propylene glycol (PG), and poly(methyl methacrylate) (PMMA)) using uGTS model are much better agreement with observed values than were those pre-

dicted by Koopmans' theorem, as shown in Table II. For the CEBEs with scaled-pVTZ basis set including the relativistic corrections, we obtained values of WD (the difference between the calculated and observed CEBEs) closer to the difference (6.6 eV) between shifted values as used as 14.4 and 21.0 eV for core C1s energy levels of the gas molecules and the model oligomers, respectively, in previous sections. The WDs also follow the trend of WD values assumed for the valence region of the XPS. We may therefore consider the another estimate of WD.

In Table III, we gave two different WDs as obtained from differences between the calculated and the observed CEBEs, and from valence region XPS based on HAM/3 calculations. When we take into consideration the long acquisition times of valence-region XPS due to the 20- to 100-fold weaker intensities and hence the possible X-ray radiation damage, we conclude that the WD values from CEBEs may very well be the more reliable one among choice in Table III. For PMMA and MIB, the WD value, 5.2 eV, is in a good accordance with the experimental value, 5.4 eV, as obtained from the difference between experimental CEBEs¹⁵ of MIB molecule and PMMA (Figure 6). Consequently, the WD values may be underestimated by valence-region XPS based on HAM/3 calculations by 0.5 to 1.0 eV.

CONCLUSION

We have simulated C1s spectra of C- and O-containing polymers by *ab initio* MO calculations of HONDO7 program using the model oligomers. The theoretical spectra showed fairly good accordance with the experimental spectra, although the shifted value was used

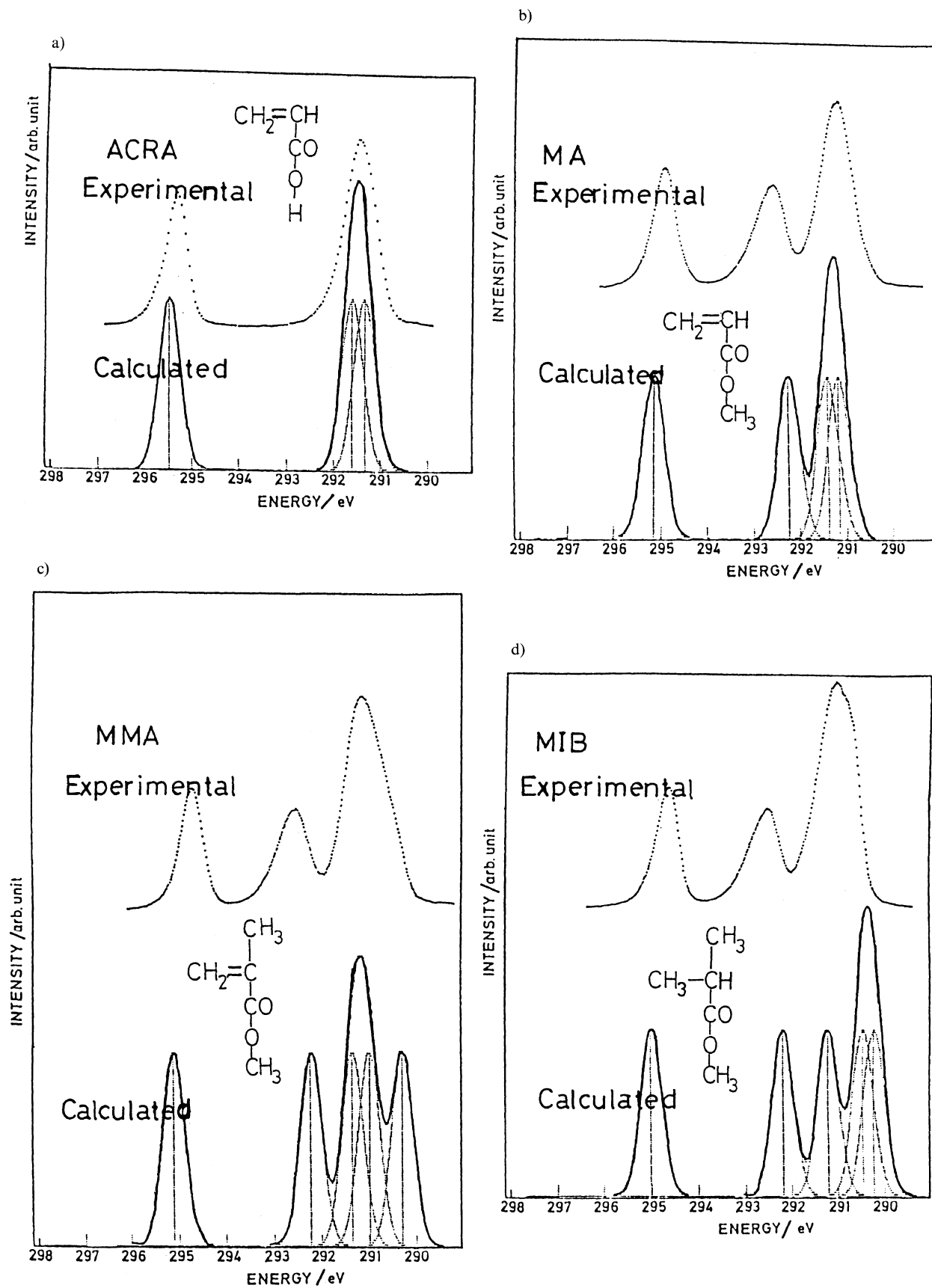


Figure 1. Core C1s X-ray photoelectron spectra of gas molecules with the simulated spectra of the molecules using HONDO7 program. a) acrylic acid (ACRA); b) methyl acrylate (MA); c) methyl methacrylate (MMA); d) methyl isobutyrate (MIB).

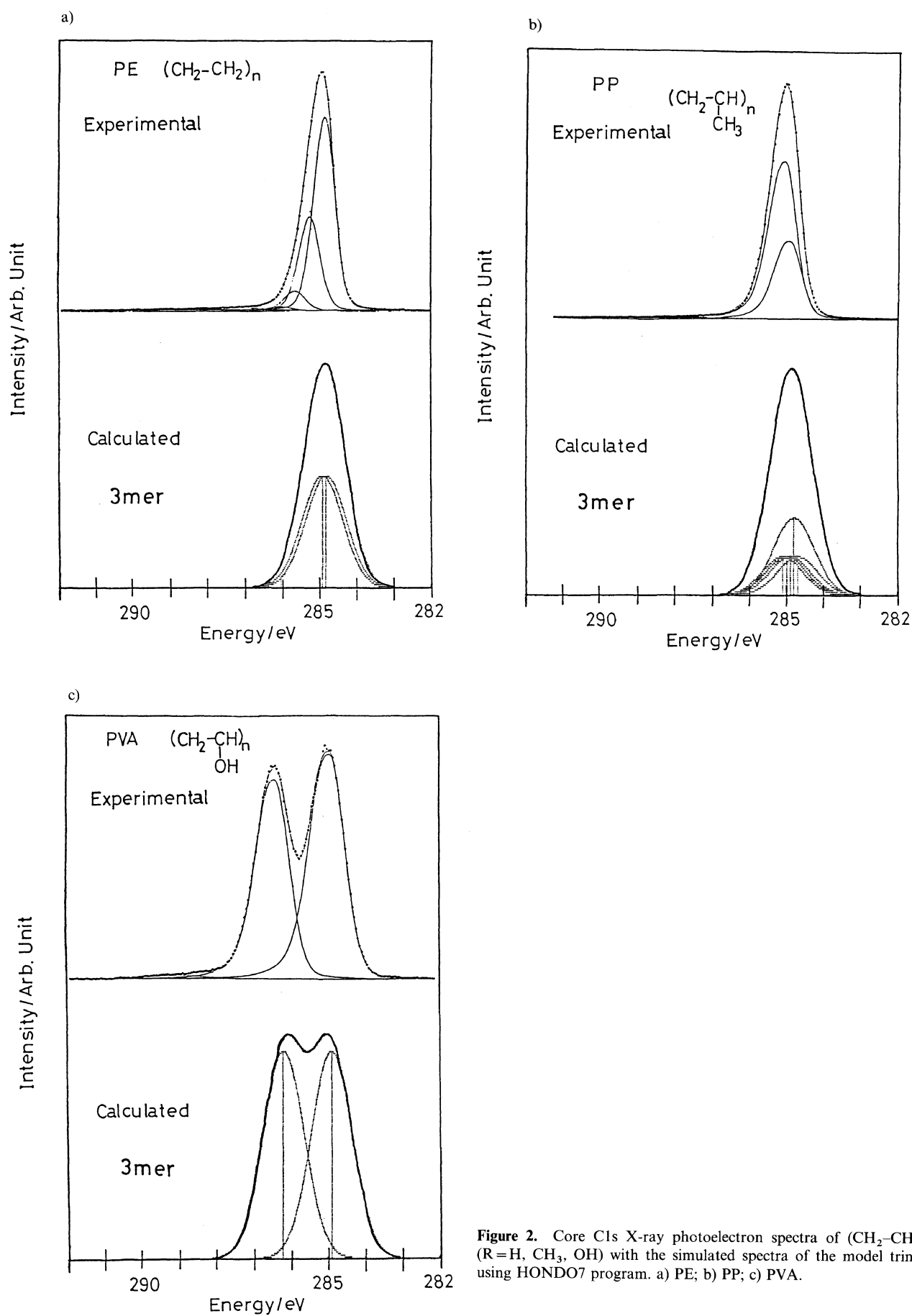


Figure 2. Core C1s X-ray photoelectron spectra of $(\text{CH}_2\text{-CHR})_n$ ($\text{R}=\text{H}, \text{CH}_3, \text{OH}$) with the simulated spectra of the model trimers using HONDO7 program. a) PE; b) PP; c) PVA.

Table II. C1s binding energies (in eV) of C- and O-containing polymers by HONDO7 program using the model oligomers^a

Polymer	Observed ^b	Koopmans' theorem	Relative intensity	Shifted value	Linewidth (halfwidth)
(CH ₂ -CH ₂) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.0	(3 mer) 305.2; 305.2; 305.3, 305.3	1.0	21.0	1.3
(CH ₂ -CH(CH ₃)) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_3$]	285.0	(3 mer) 305.1; 305.2	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.0	305.2; 305.3	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}$]	285.2	305.4; 305.5	1.0	21.0	1.3
(CH ₂ -O) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	287.89	(3 mer) 308.8; 308.9	1.0	21.0	1.3
(CH ₂ -CH ₂ -O) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	286.45	(3 mer) 306.5; 306.6; 306.9; 307.2	1.0	21.0	1.3
(CH ₂ -CH ₂ -CH ₂ -O) _n CEBE (C1s) [$\overline{\text{C}}\text{-CH}_2\text{-C}$]	285.00	(2 mer) 305.2	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{O}}\text{-CH}_2\text{-C}$]	286.44	306.8; 306.9	1.0	21.0	1.3
(CH ₂ -CH ₂ -CH ₂ -CH ₂ -O) _n CEBE (C1s) [$\overline{\text{C}}\text{-CH}_2\text{-C}$]	285.00	(2 mer) 305.1; 305.3	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{O}}\text{-CH}_2\text{-C}$]	286.35	306.7; 306.7	1.0	21.0	1.3
(CH ₂ -CH(OH)) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.0	(3 mer) 305.3; 305.3	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}(\text{OH})$]	286.5	306.6; 306.6	1.0	21.0	1.3
(CH ₂ -CH(OCH ₃)) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.0	(2 mer) 305.1	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}$ -]	286.5	307.1	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{O}}\text{-CH}_3$]	286.7	306.7	1.0	21.0	1.3
(CH ₂ -CH(COCH ₃)) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.0	(2 mer) 305.4	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}$ -, CH ₃]	285.4	305.8; 306.0	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{O}$]	288.0	308.8	1.0	21.0	1.3
(CH ₂ -CH(COOH)) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.0	(3 mer) 305.9; 306.0	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}$ -]	285.6	306.4; 306.5	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{OOH}$]	289.1	310.4; 310.5	1.0	21.0	1.3
(CH ₂ -CH(OCOCH ₃)) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.0	(3 mer) 305.2; 305.3	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}\text{-O}$ -]	286.7	307.2; 307.2	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{O}}\text{-CH}_3$]	285.7	305.8; 305.9	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{O}}\text{-C=O}$]	289.2	310.1; 310.2	1.0	21.0	1.3
(CH ₂ -CHCOOCH ₃) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.0	(2 mer) 306.0	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}$ -]	285.4	306.0	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{O}}\text{-CH}_3$]	286.6	307.2	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{=O}$]	289.0	309.1	1.0	21.0	1.3
(CH ₂ -(CO)-O) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	286.6	(2 mer) 308.3	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{=O}$]	289.0	310.7	1.0	21.0	1.3
(CH(CH ₃)-(CO)-O) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_3$]	285.0	(2 mer) 305.9	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}$ -]	287.0	308.4	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{=O}$]	289.1	310.5	1.0	21.0	1.3
(CH ₂ -C(CH ₃)COOCH ₃) _n CEBE (C1s) [$\overline{\text{C}}\text{H}_3$]	284.6	(2 mer) 305.2	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}_2$ -]	285.2	306.0	1.0	21.0	1.3
CEBE (C1s) [$\text{>C}<$]	285.8	306.5	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{H}_3$]	286.8	306.9	1.0	21.0	1.3
CEBE (C1s) [$\overline{\text{C}}\text{=O}$]	289.0	310.0	1.0	21.0	1.3

^aWe omitted the contribution of both edge segments of the main chain. ^bValues were referred to G. Beamson, D. Briggs, "High Resolution XPS of Organic Polymers. The Scienta ESCA 3000 Database," Wiley, Chichester, 1992.

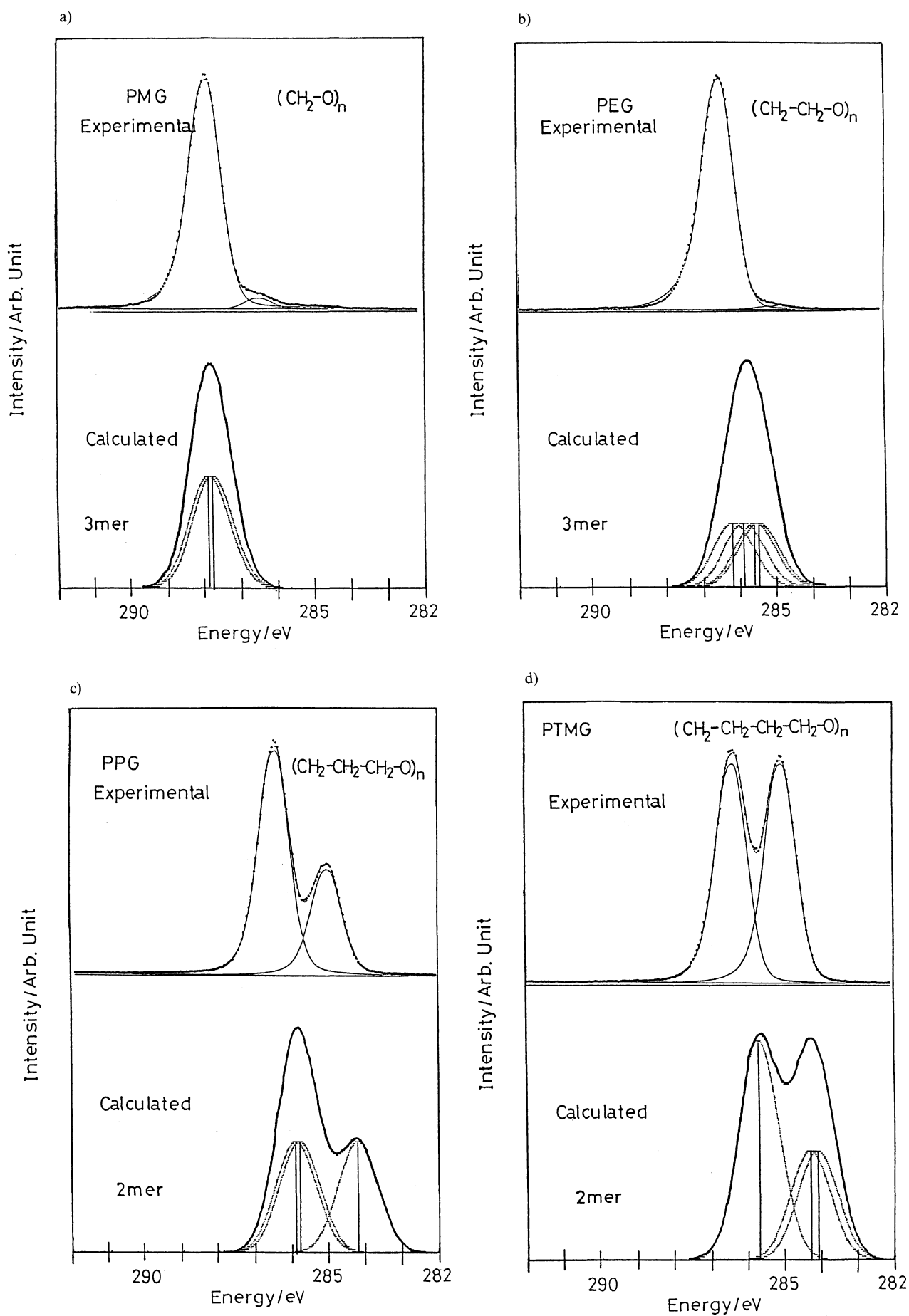


Figure 3. Core C1s X-ray photoelectron spectra of $(\text{CH}_k\text{-O})_n$ ($k=1-4$) with the simulated spectra of the model trimers or dimers using HONDO7 program. a) PMG; b) PEG; c) PPG; d) PTMG.

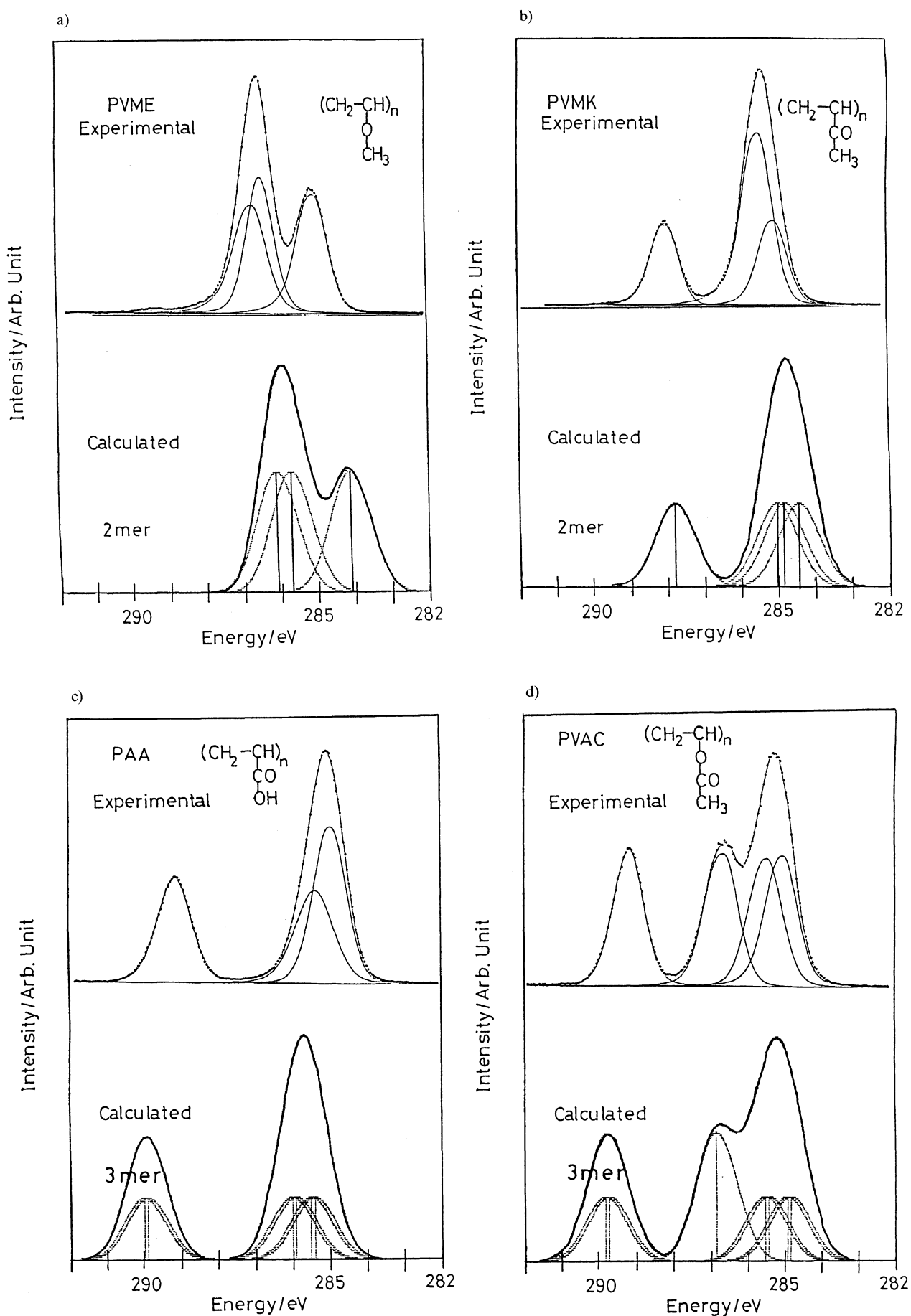


Figure 4. Core Cls X-ray photoelectron spectra of $(\text{CH}_2-\text{CHR})_n$ ($\text{R}=\text{OCH}_3, \text{COCH}_3, \text{COOH}, \text{OCOCH}_3$) with the simulated spectra of the model trimers or dimers using HONDO7 program. a) PVME; b) PVMK; c) PAA; d) poly(vinyl acetate) (PVAC).

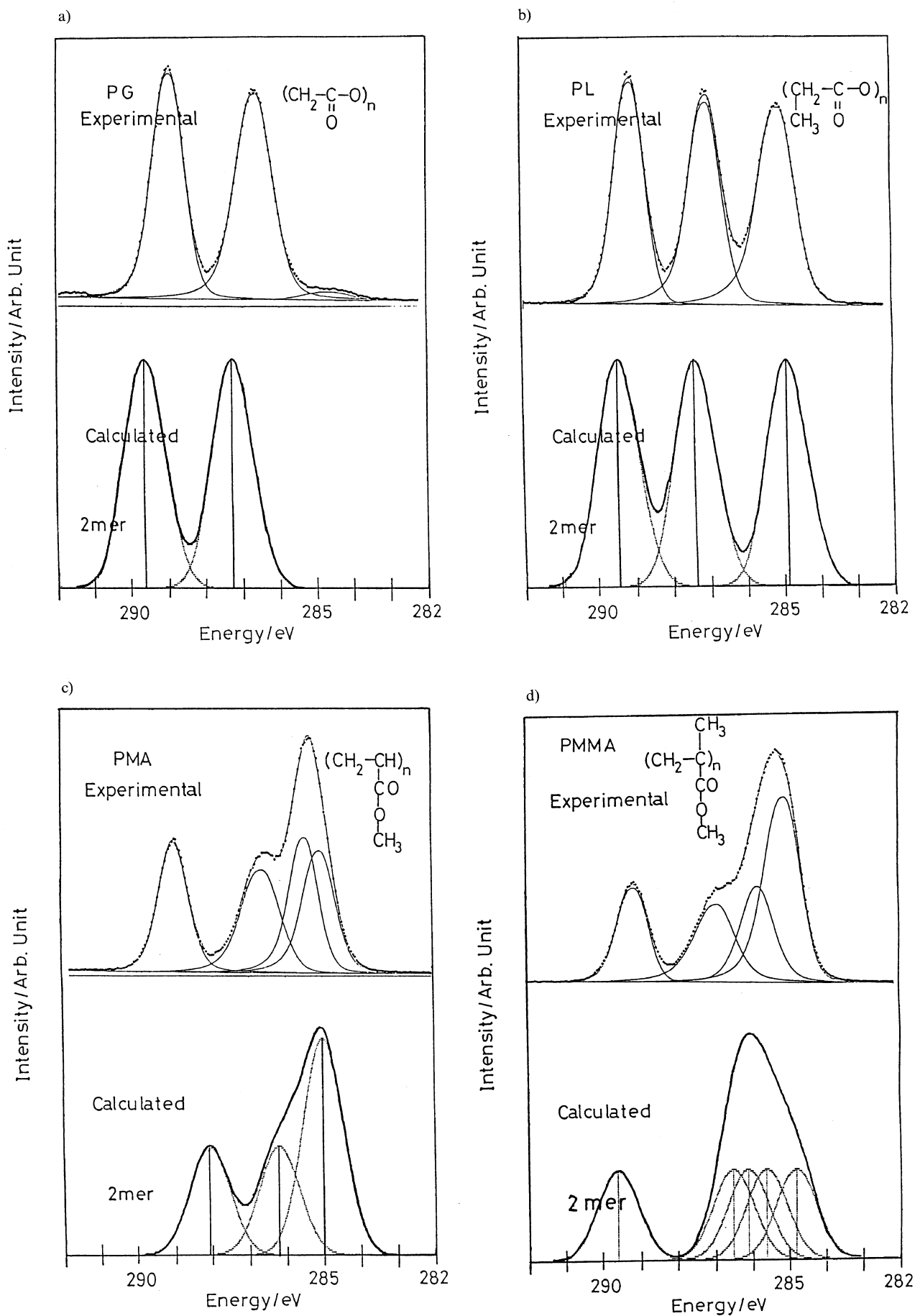
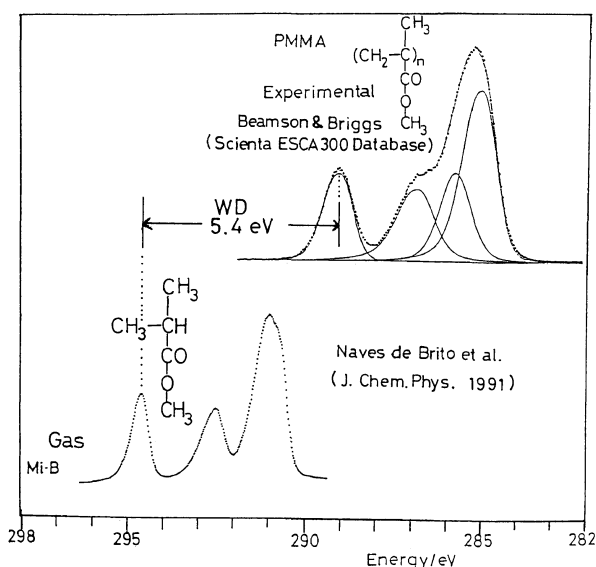


Figure 5. Core C1s X-ray photoelectron spectra of $(\text{CHR}-\text{CO}-\text{O})_n$ ($\text{R}=\text{H}, \text{CH}_3$), $(\text{CH}_2-\text{CHCOOCH}_3)_n$ and $(\text{CH}_2-\text{C}(\text{CH}_3)\text{COOCH}_3)_n$ with the simulated spectra of the model dimers using HONDO7 program. a) PG; b) PL; c) PMA; d) PMMA.

Table III. C1s binding energies and WDs of C- and O-containing polymers by deMon density-functional program using the model molecules^a (in eV)

Polymer	Observed ^b	Model molecule observed	uGTS scaled pVTZ (Δ^c)
(CH ₂ -CH ₂) _n CEBE (C1s) [C _H 2-]	285.0	2 mer	291.05 (6.1) <5.5> ⁺
(CH ₂ -CH(CH ₃)) _n CEBE (C1s) [-C _H]	285.2	2 mer	290.67 (5.5) <5.5> ⁺
(CH ₂ -O) _n CEBE (C1s) [C _H 2-]	287.89	2 mer	294.12 (6.2) <5.0> ⁺
(CH ₂ -CH(OH)) _n CEBE (C1s) [C _H (OH)]	286.5	1 mer-m	292.68 (6.2) <4.5> ⁺
(CH ₂ -CH(OCH ₃)) _n CEBE (C1s) [C _H -]	286.5	1 mer-m	292.19 (5.7) <4.5> ⁺
(CH ₂ -CH(COCH ₃)) _n CEBE (C1s) [-C _O]	288.0	2 mer	292.87 (4.9) <4.5> ⁺
(CH ₂ -CH(COOH)) _n CEBE (C1s) [C _O OH]	289.1	1 mer	294.66 (5.6) <3.5> ⁺
(CH ₂ -CHCOOCH ₃) _n CEBE (C1s) [-C=O]	289.0	1 mer	294.40 (5.4) <3.5> ⁺
(CH ₂ -(CO)-O) _n CEBE (C1s) [-C=O]	289.0	1 mer-m	294.66 (5.7) <5.0> ⁺
(CH ₂ -C(CH ₃)COOCH ₃) _n CEBE (C1s) [-C=O]	289.0	1 mer	294.15 (5.2) <3.5> ⁺
CH ₃ -CH(CH ₃)COOCH ₃ CEBE (C1s) [-C=O]	294.43*		[5.4]*

^a We omitted the contribution of both edge segments of the main chain. ^b Values were referred to G. Beamson and D. Briggs, "High Resolution XPS of Organic Polymers. The Scienta ESCA 3000 Database," Wiley, Chichester (1992). ^c Values denote the differences between the calculated CEBEs using uGTS model and the observed ones. ⁺ Values were obtained from analysis of valence XPS using HAM/3. * Values were obtained from experimental results.^{15,35}

**Figure 6.** Experimental WD of PMMA as obtained from the difference between C1s of -CO- group of MIB and PMMA.^{13,35}

21.0eV for C1s energy levels of the oligomers. We emphasize that the theoretical results provide an aid to perform experimental lineshape analysis, by considering the examples of the PP, PVMK, and PMMA.

The calculated CEBEs of polymer models using uGTS model by deMon DFT program showed better correspondence with experiment than were those predicted by Koopmans' theorem. The WD values from the calculated and observed CEBEs of polymers may very well be the more reliable than ones we obtained for VIPs in the valence region.

Acknowledgments. We are grateful to Professor D. P. Chong of University of British Columbia for their valuable suggestion for the *ab initio* DFT calculations using deMon program. We thank Dr. D. R. Salahub of University of Montreal for an early version of the deMon density functional program.

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