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Spectra Analysis of the XPS Core and Valence Energy Levels of Polyvinyl Alcohol by an ab initio MO Method Using the 1,3,5-Hexanetriol Molecule#

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The X-ray photoelectron spectra of polyvinyl alcohol (PVA) were analyzed by an ab initio MO method using the 1,3,5-hexanetriol (HTO) molecule. The theoretical spectral patterns derived from the Gelius–Siegbahn model showed good agreement with the spectra observed between 0—30 eV. The present results suggest several new assignments for the XPS spectra. The core-level C1s peaks at 285.0 and 286.5 eV correspond to the C1s electron levels arising from the CH_2 and CH(OH) groups, respectively.

Since the use of X-ray photoelectron spectroscopy (XPS) had been demonstrated as a tool for investigating the core and valence energy levels of tetrafluoroethylene,1) the spectra obtained from XPS using monochromatized X-ray radiation became a powerful tool for studying the electronic structure of polymers. This technique provided precise information concerning the core-level binding energies and line shapes, and allowed a recording of the distribution of the valence electronic levels which constitute a real and unique fingerprint of a compound. Some XPS valence-level studies2—5) of simple model oligomers and saturated hydrocarbons compounds demonstrated that information concerning the polymer molecular structure can be obtained through a spectral analysis using theoretical calculations. In a previous paper6) we offered new insights into the interpretation of the XPS valence band spectra of polymers using a semi empirical PM3 MO method7) with a crystal model of one-dimensional periodicity.

The present paper gives a novel explanation for the XPS core and valence-level spectra of polyvinyl alcohol (PVA) by the ab initio RHF-SCF MO method using the 1,3,5-hexanetriol (HTO) model molecule. The program used in the present calculations was HONDO7.8) We ascertained that all occupied energy levels of HTO, as calculated by the MO method, correspond to the electronic spectra of PVA obtained on an XPS spectrometer using monochromatized Al *Kα* radiation, although there are relatively large energy-level differences between the calculated and observed values. The difference depends upon the theoretical values, as calculated using Koopmans theorem. The theoretical spectral patterns in the 0—40 eV range were estimated using the Gelius–Siegbahn model9) for calculating the cross sections for the photoionization of electrons in molecular orbitals.

Theoretical Background

Gelius–Siegbahn9) proposed a model to explain the intensities of the photoelectron lines of molecules. In the LCAO-MO approximation, the molecular orbital photoionization cross-section is related to the cross section for the ionization of the atomic orbitals and the atomic populations in the molecular orbitals,

$$\sigma_j^{\mathrm{MO}} = \sum_{A,\lambda} P_{A\lambda_j}\sigma_A^{\mathrm{AO}}, \qquad (1)$$

where the coefficients ($P_{A\lambda_j}$) are a measure of the probability of finding an electron in atomic orbital $A\lambda$ at nucleus A. In the derivation they assumed that the ionization energy is so high that the wave vector of the ionized electron remains constant within the valence region, and thus that the ejected electron can be approximated by a plane wave.

The HTO molecule was calculated by the ab initio RHF-SCF MO method. The program used in the present calculations was HONDO7.8) For C and O atoms, we used the (4s2p) basis sets and for H the (2s) basis set reported by Huzinaga et al.10) and Dunning et al.11) For the geometry of the HTO molecule (Fig. 1), we used the optimized values by the semi empirical PM3 MO method.7)

In order to obtain the theoretical spectral patterns of PVA in the range of the valence energy levels, we substituted the calculated MO results in Eq. 1. For the atomic population, we substituted the total value of the double ζ basis set. We used the values of the relative atomic photoionization cross sections (obtained under

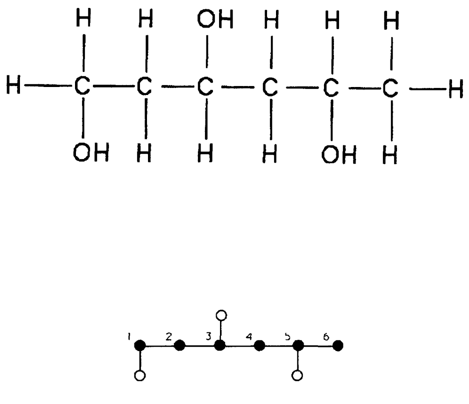

Fig. 1. Structure of the fragment syndiotactic HTO molecule of PVA. In the lower structure, ● and ○ represent carbon and oxygen atoms, respectively.

#In memory of Professor Hiroshi Kato.

the assumption of spherical symmetry of the electrostatic atomic field) by Nefedov et al.[12] The relative values for C2s, C2p, C1s, O2s, O2p, O1s, and H1s are 1.00, 0.032, 21.14, 2.80, 0.17, 58.64, and 0.01, respectively (for Al $K\alpha$=1486.6 eV).

Experimental

The experimental photoelectron spectra of PVA were obtained on a Perkin–Elmer model PHI 5400 MC ESCA spectrometer, using monochromatized Al $K\alpha$ radiation. The spectrometer was operated at 600 W, 15 kV, and 40 mA. The photon energy is 1486.6 eV. A pass energy of 35.75 eV was employed for high-resolution scans in a valence-band analysis (50 eV of range). The angle between the X-ray source and the analyzer was fixed at 45°. The spot size in the measurement was 3×1 mm.

The use of dispersion compensation yielded an instrumental resolution of 0.5 eV with the full width at half-maximum on the Ag3d line of silver. Multiple-scan averaging on a multichannel analyzer helped to guarantee accurate data for the valence-band region, although a very low photoelectron emission cross section was observed in this range. The unresolved ESCA signals were deconvoluted, and the signal intensities (peak areas) were determined using a nonlinear least-squares fitting software, which allowed signals to vary between Gaussian and Lorentzian lineshapes.

We used the commercially-available polymer PVA (Wako Pure Chemical Industries, Ltd.: M_{W} 88000), which involves a residue, polyvinyl acetate (PVAc), of less than about 9% by a synthesis of PVA. This was assigned based on the intensity of the XPS C1s peaks at 288.0 and 289.5 eV (>C=O, C(=O)O components, respectively) in Table 2. In this study, we neglected the residue. The sample was prepared by cast-coating the polymer solution on an alminium plate. We used water for PVA. The film was estimated to be a few tens of micrometers thick. A low-energy electron flood gun was used in order to avoid any charging effect on the surface of the sample. After obtaining an absolute calibration, the C1s line position (285.0 eV) on the PVA film was accurately measured so as to serve as energy reference for the polymer.

Results and Discussion

Let us consider the reasons why the ab initio MO method using the HTO model molecule was applied to the XPS spectra analysis of PVA. The present study was made to clarify the nature of the XPS core and the valence energy level spectra of PVA as an example of polymers using the ab initio MO method. We will ascertain that all of the occupied MO energy levels of the HTO molecule, as calculated by the MO method, correspond to the XPS core and valence energy band spectra of PVA, although there are relatively large energy-level differences between the theoretical and observed values. This difference is due to the theoretical values as calculated by Koopmans theorem. From this good fit between the theoretical patterns and the observed spectra, we can determine which spectrum of PVA is due to the photoionization cross sections for any atomic electron level of the constituent elements of the functional groups.

Table 1. Energies and Relative Atomic Photoionization Cross Sections of the Valence Band MOs of the Syndiotactic 1,3,5-Trihydroxyhexane by the ab initio MO Method

Orbitl energy	Relative photoionization cross-section				
eV	C2s	C2p	O2s	O2p	total
−37.76	0.085		2.094		2.179
−37.56	0.103		2.096		2.199
−37.50	0.096		2.183		2.279
−29.45	0.773	0.002	0.216	0.004	0.994
−28.30	0.782	0.004	0.141	0.004	0.981
−26.48	0.920	0.004	0.064	0.005	0.994
−24.10	0.555	0.003	0.058	0.020	0.636
−22.55	0.390	0.005	0.014	0.035	0.444
−22.47	0.320	0.005	0.001	0.038	0.364
−19.10	0.012	0.011	0.078	0.065	0.166
−18.57	0.044	0.014	0.080	0.044	0.182
−18.09	0.017	0.015	0.035	0.036	0.103
−17.55	0.011	0.013	0.009	0.049	0.082
−17.15	0.074	0.005	0.134	0.067	0.280
−17.03	0.024	0.012	0.069	0.054	0.159
−16.72	0.009	0.012	0.039	0.053	0.113
−16.19	0.006	0.015	0.049	0.059	0.129
−15.75	0.007	0.013	0.026	0.064	0.110
−15.01	0.008	0.014	0.024	0.026	0.072
−14.30	0.008	0.012	0.005	0.041	0.066
−14.02	0.005	0.012	0.018	0.034	0.069
−13.85	0.013	0.010	0.015	0.058	0.096
−13.73	0.002	0.009	0.104	0.057	0.172
−12.90	0.002	0.012	0.075	0.039	0.128
−12.58	0.017	0.005	0.003	0.121	0.140
−12.43	0.005	0.012	0.060	0.041	0.118
−12.20	0.010	0.007	0.013	0.102	0.132
−11.19	0.004	0.017		0.059	0.080

With an instrumental resolution of 0.5 eV, we may obtain similar spectral patterns within the range of the valence electron levels for different stereoisomers of a polymer, since the energy-level differences of three stereoisomers (syndiotactic, heterotactic, and isotactic types) remain within the instrumental resolution. Experimentaly, we have observed similar spectral patterns in the range of 0—50 eV for commercially-available polypropylene and isotactic polypropylene, respectively. Theoretically, in our previous paper,[7] we gave close eigenvalues and similar spectral patterns in the range of 0—30 eV for three stereoisomers of PVA, as calculated by a semi empirical PM3 MO method using a crystal model of one-dimensional periodicity (Fig. 2). For this calculation we used a cyclic polymer of the cluster unit, which consists of the three unit cells, $((-CH_2-CHOH-))_3$, for PVA. Thus, in this study we used the HTO model molecule as a syndiotactic-type stereoisomer in order to analyze the XPS spectra of PVA.

(a) Valence Band Spectra. Table 1 shows the MO eigenvalues and the relative atomic photoionization cross sections of the HTO model molecule of PVA as calculated by the ab initio MO method. The XPS valence-band spectra of PVA in Fig. 3 are in good agreement

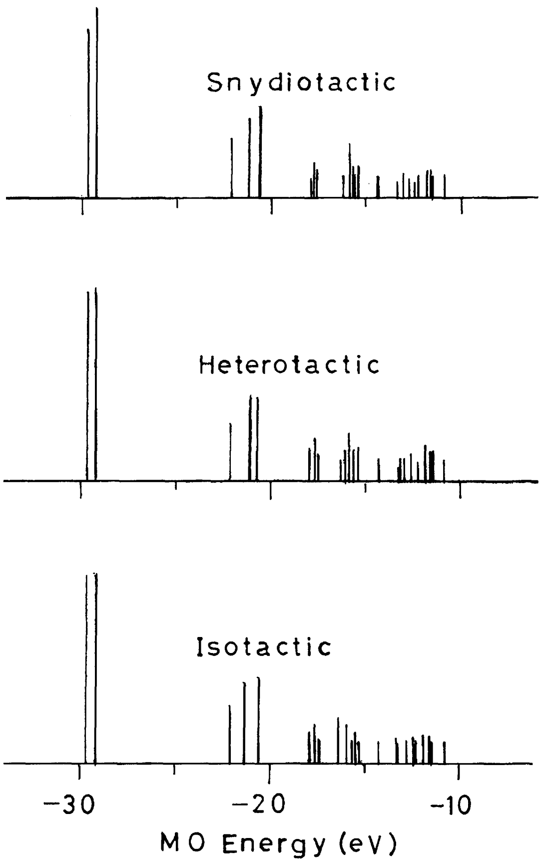

Fig. 2. Theoretical spectral patterns of three stereoisomers (syndiotactic, heterotactic, and isotactic types) of PVA calculated by the PM3 MO method.[7)]

Table 2. Curve-Fitting Parameters of C1s Spectrum for Polyvinyl Alcohol

C1s component	Binding energy eV	Intensity	Halfwidth eV	Area %
CH_2	285.0	1.00	1.24	47.5
CH(OH)	286.5	0.92	1.31	46.2
>C=O	288.0	0.09	1.02	3.8
C(=O)O	289.5	0.06	1.17	2.4

with the theoretical patterns of the model molecule in the range of 0—40 eV, although there is about a 12-eV energy difference between the observed and calculated values. (The value was estimated as the difference between 26 eV (as observed peak in Fig. 3) and 37.5—37.8 eV (as calculated by the MO method) due to O2s electron contribution.) This difference may depend on the HTO energy levels due to the Koopmans approximation and may involve the work function of PVA.

It can be seen from Fig. 3 and Table 1 that the intense spectrum at around 26 eV is due to the O2s dominant contributions. The peak between 16 and 21 eV is seen to be dominated by the C2s electrons. It suggests that the spectral line widths below 15 eV are determined by the splittings of many adjacent MO energy levels; by contrast, the line widths in the range of 15—30 eV may be governed by the electronic relaxation of the MO energy states.

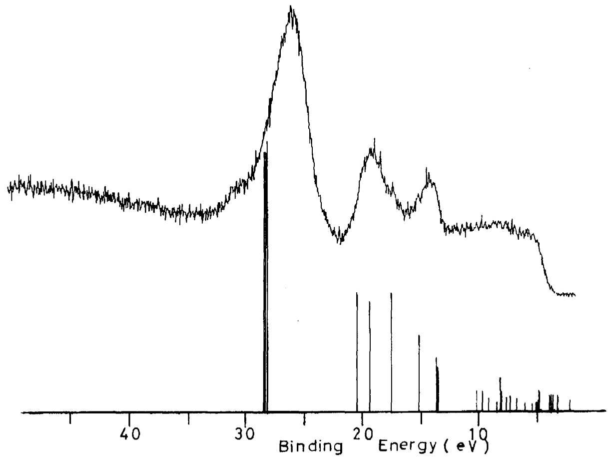

Fig. 3. XPS valence band spectra of PVA with the theoretical spectral patterns of HTO molecule calculated by the MO method.

(b) Core Level Spectra. For the double C1s peaks of PVA (Fig. 4), we performed a line-shape analysis. The experimental assignement (as shown in Table 2) is in good accordance with the observed values obtained by Briggs et al.[13)] analysis of polymers. The peaks at around 288.0 and 289.5 eV (obtained from a peak separation) correspond to the C1s spectra of the >C=O and C(=O)O components of the residue, PVAc. Thus, if we can substitute PVA for the PVAc completely, the C1s peaks at 286.5 and 285.0 eV would be of equal intensity. For the line width of the C1s components in Table 2, the carbonyl components are found to be narrower than the hydrocarbon components. This may be a similar tendency with the results[14,15)] for polymethyl methacrylate and poly *n*-butyl methacrylate polymers.

Let us compare the core-level spectra of PVA with

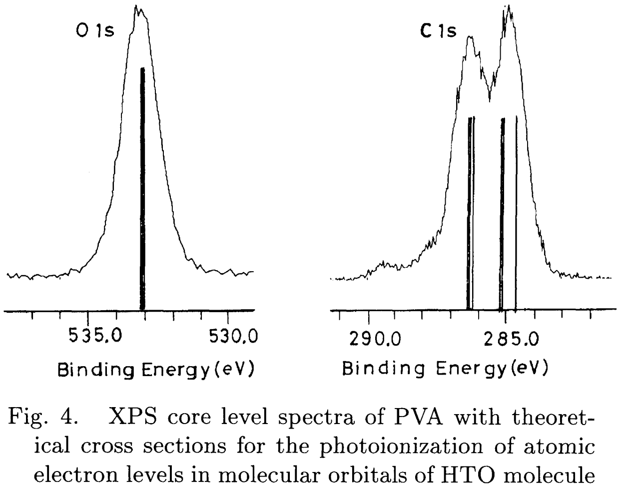

Fig. 4. XPS core level spectra of PVA with theoretical cross sections for the photoionization of atomic electron levels in molecular orbitals of HTO molecule calculated by the MO method.

the MO levels of the HTO molecule by the Koopmans approximation. Although there are about 20-eV core energy-level differences between the observed and calculated values, the theoretical spectral patterns of the HTO due to the Koopmans theorem reflect the XPS core spectra of PVA (Fig. 4). For the O1s energy levels, the Koopmans theorem of the HTO molecule gives very close values (558.9, 558.9, and 559.0 eV). This corresponds to the single peak of the O1s of PVA in the instrumental resolution of 0.5 eV. In the case of the C1s energy levels, the observed peak at around 285.0 eV is found to result from the Koopmans values (305.9, 305.8, and 305.4 eV) of the CH_2, CH_2, and CH_3 components, respectively, for the HTO model molecule. The other C1s peak at around 286.5 eV corresponds to the theoretical values (307.2, 307.2, and 307.0 eV) of the CH(OH), CH(OH), and $CH_2(OH)$ components.

We compared the relative atomic photoionization cross sections of the core levels, as calculated by the Gelius–Siegbahn model (Eq. 1), with the values obtained by Nefedov et al., respectively. This good agreement between the two types of photoionization cross sections suggests that we can use the Gelius–Siegbahn model for the core energy levels. For the ratios of the photoionization cross sections, the theoretical values, $\sigma_{\mathrm{C1s}}/\sigma_{\mathrm{O2s}}$ and $\sigma_{\mathrm{O1s}}/\sigma_{\mathrm{O2s}}$, are estimated as being 10.0 and 27.9, respectively. The observed ratio of 17.7 and 28.9 for $\sigma_{\mathrm{C1s}}/\sigma_{\mathrm{O2s}}$ and $\sigma_{\mathrm{O1s}}/\sigma_{\mathrm{O2s}}$, respectively, from the XPS spectra of Fig. 4 may be in considerably good agreement with the calculated values.

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