X-Ray Photoelectron and Carbon Kα Emission Spectral Analysis of Polymers by DFT Calculations using QM/MM Method

Y. Kimura, T. Hiroi, S. Shimada, M. Mizuno, K. Endo,* E. Z. Kurmaev,[a] and A. Moewes[b]

Laboratory of Theoretical Chemistry, Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192,Japan

[a]*Institute of Metal Physics, Russian Academy of Science-Ural Division 620219 Yekaterinburg GSP-170 Russia,*

[b]*Department of Physics and Engineering Physics, University of Saskatchewan, 116 Science Place, Saskatoon, SK, Canada, S7N 5E*

*endo@wriron1.s.kanazawa-u.ac.jp

We performed DFT calculations using Amsterdam density functional (ADF) program for several polymers to compare valence X-ray photoelectron, C Kα emission spectra and core-electron binding energies (CEBE)s due to QM/MM method with ones due to our previous geometry optimization. The simulation spectra are in good accordance with experimental ones. We also obtained reasonable WD values of some polymers from the difference between calculated CEBE values for models in our previous geometry optimization and experimental ones.

INTRODUCTION

It is well known that many organic polymers are used as active materials with useful applications in demanding fields of electronics, catalysis, biotechnology, and space. As a fundamental investigation, it is important to obtain information on the electronic states of the polymers. X-Ray photoelectron and emission spectroscopies are powerful tools for providing precise information of the electronic state. These experimental electron spectra of polymers are directly linked to the theoretical results of the electronic states as obtained by MO calculations using model oligomers, since polymers consist of the repetition units.

Especially studies of X-ray emission spectra (XES) of polymers can be understood only by using fluorescence measurements because of the damage of polymer target on excitation. A study [1] was made using both X-ray photoelectron and emission spectroscopies in polymers. However, the recent development of third generation synchrotron sources has provided us with the kind of incident photon intensity necessary to overcome the low signal strength inherent to the emission measurements of light elements [2]. Several works [3-7] have been performed for X-ray photoelectron and emission spectroscopies in oligomers and polymers. In our laboratory, X-ray photoelectron spectra (XPS) and XES of C-, N-, O-, Si-, and S-containing polymers were simulated by deMon DFT calculations using the model molecules [8, 9]. The combined analysis of the valence XPS and the light element Kα XES enabled us in dividing the observed valence electronic distribution into the individual contributions for pσ-, pπ-, and nonbonding MOs of the polymers.

Recently, the QM/MM method has been noted to obtain reasonable geometrical structures of large molecules. This method has been proven to be powerful tool for the theoretical treatment of large molecules in chemical and biological systems. In the QM/MM method, some theoretical methods were proposed as integrated molecular orbital and molecular orbital (MOMO), integrated molecular orbital, molecular mechanics (IMOMM), and our own N-layered integrated molecular orbital and molecular mechanics (ONIOM). Here we used ONIOM proposed by Morokuma [10]. Then, we try to compare the QM/MM method for simulations of XPS and XES of typical polymers PE, and PP with our previous normal geometry optimization [5-9].

In the present work, we investigate valence XPS and C $K\alpha$ XES for PE, and PP polymers mainly by using Amsterdam density functional (ADF) [11] calculations with the QM/M method to reproduce solid effects due to the electrical factor.

THEORETICAL BACKGROUND

In order to obtain the accurate vertical ionization potentials (VIPs) in the valence region, we use statistical averaging of orbital potentials (SAOP) [12-14] in ADF program. The SAOP method reproduces a Kohn-Sham exchange-correlation potential which includes the orbital dependent Krieger-Li-lafrate (KLI) response potential [15] as the orbital relaxation effect.

The intensity of valence XPS was estimated from the relative photo-ionization cross section for Al Kα radiation using the Gelius intensity model [16]. For the relative atomic photo- ionization cross-section, we used the theoretical values from Yeh [17].

On the other hand, we use the ΔE-KS approach [18] like ΔSCF in MO theory to obtain the core electron binding energy (CEBE). In the case of XES, the C $K\alpha$ X-ray emission energy (E_{emission}) of polymers is calculated by the expression

$$E_{emission} = E_{CEBE} \quad E_{VIP} \qquad (1)$$

where E_{CEBE} and E_{VIP} stand for the CEBE of the carbon 1s hole and the VIP of the electron to fill the hole, respectively. The C $K\alpha$ X-ray emission transition arises from outer occupied p orbitals to s-type holes in a given C atom, due to the selection rule $\Delta l = \pm 1$. Considering the selection rule and neglecting the terms involving orbital products on different atoms, an approximate intensity can be written as follow by using LCAO populations,

$$I_{1s(A)j} \propto N' \sum_A \left| C_{j[2p(A)]} \right|^2 . \qquad (2)$$

In the equation, we take into account the dipole selection rule and N' is the normalization factor including the square of the transition rate for the atomic dipole transitions, and $C_{j[2p(A)]}$ is the LCAO populations for the ground state of the model molecules by using minimal basis set.

CALCULATION DETAILS

The model molecules of polymers PE, PP, PEO, and PVA were geometry-optimized in Gaussian 98 program. Here, we performed ONIOM calculation to obtain good geometries of polymer models and to estimate the reasonable charge in the MM region. In Gaussian98 program, we adopted geometry optimizations in high layer region at B3LYP [19] with 6-31G(d,p) bases [20]. For geometry optimizations in medium layer region a semi-empirical AM1 (Austin Model) method [21] was used. We used the Sybyl force field terms and parameters with formal charges obtained by ONIOM method in QM/MM calculations. Fig. 1 shows PE polymer model in QM and MM regions.
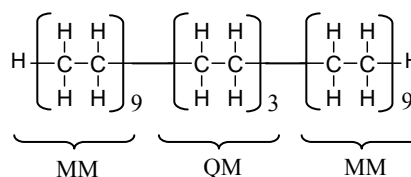

Fig. 1 PE model molecule for QM and MM treatment regions

For VIP values, we calculated the ground state of the molecule using the DZP bases of {4s 2p 1d} for C and O atoms and of {2s 1p} for H atom in the SAOP. In the CEBE calculation, we employ the ΔE-KS method that is based on the total energy difference procedure with the Perdew and Wang exchange [22] and correlation [23] potentials using DZP bases.

In order to check the solid effect due to the QM/MM method for geometry optimization of polymer model, we performed CEBE calculations for dimer model molecules in our previous [5-9] and QM/MM methods.

The simulated C Kα XES are presented as superposition of peaks obtained by convolution of Gaussian shape curves with full-widths at half-

maximum of 1.0 eV centered at the calculated emission energies, as previously discussed [5-9].

EXPERIMENTAL

We used commercially available polyethylene (PE) $(CH_2CH_2)_n$ (Aldrich chemical Co. Inc.; high density), polypropylene (PP) $(CH_2CH(CH_3))_n$ (Scientific Polymer Products, Inc.; atactic type), and so on. Samples were prepared by cast-coating the polymer solution on an aluminum plate, while water was used for PE, and PP. Carbon Kα x-ray emission (2p VB→1s transition) was measured probing the distribution of partial carbon valence band states of p-symmetry. Synchrotron-based X-ray fluorescence measurements were performed at the undulator Beamline 8.0 of the Advanced Light Source , Lawrence Berkeley National Laboratory employing the soft x-ray fluorescence endstation. Photons with energy of 300 eV well above the carbon K edge were used for excitation. The carbon Kα spectra were recorded with an energy resolution of 3 eV.

RESULTS AND DISCUSSION

In Fig. 2, we showed theoretical valence electron spectra due to model molecules of PE in our previous and QM/MM methods, respectively with experimental one in the range of 0 30eV. The simulated spectra are in excellent accordance with experimental one, although this tendency (that the experimental intensities of the double peaks were reproduced by SAOP method in ADF calculation)
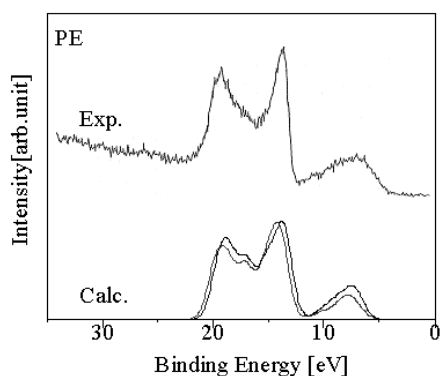
Polyethylene PE

Fig. 2 Theoretical and experimental XPS of PE

was not reproduced by other DFT calculations. In the valence spectrum, the intensive double peaks around at 20 and 15 eV correspond to sσ(C2s-C2s) and pσ(C2s-C2p) bonding orbitals respectively. The weak shoulder peak at around 7.5 eV is due to pσ(C2p-C2p) bonding orbitals.

In the CEBE calculations with ΔE-KS method, we obtained 291.08 and 290.37eV for model dimers in our previous and QM/MM methods, respectably. The result indicates that we cannot consider only 0.71 eV as the solid effect, even if we used the geometry optimization by the QM/MM method. Then, we can give reasonable *WD* value of PE as 6.08 eV from the difference between the CEBE value for normal dimer model and experimental one (285.00 eV) [24].

For C Kα XES of PE, simulated spectrum is in a considerably good accordance with the observed one in Fig. 3. We classified the orbital nature of the emission spectrum into the ranges of 274-283 and 270-274 eV. The two regions are due to pσ (C2p-C2p) and pσ(C2s-C2p) bonding orbitals, respectively.

Polypropylene PP

Fig. 4 shows that theoretical valence XPS due to model molecules of PP in our previous and QM/MM methods, respectively are in good accordance with experimental one in the range of 0 30eV. The intensive peak around at 16 eV results from sσ(C2s-C2s) bonding orbital between pendant methyl and the main chain carbons. Other peaks at around 20, 15 and 7.5 eV also correspond to sσ (C2s-C2s), pσ(C2s-C2p) and pσ (C2p-C2p) bonding orbitals in PE spectrum.
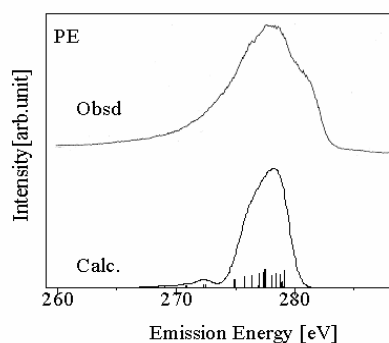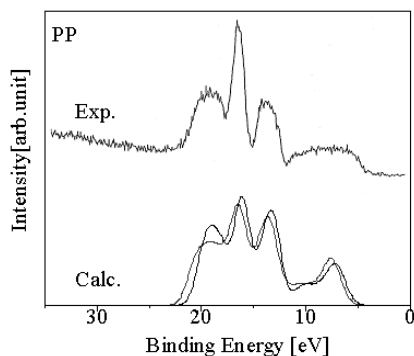

Fig. 3 Theoretical and observed C Kα XES of PE

Fig. 4 Theoretical and experimental XPS of PP

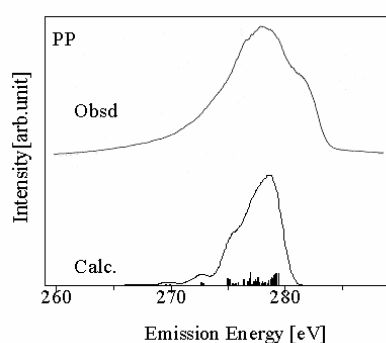Fig. 5 Theoretical and observed C *Kα* XES of PP

The CEBEs were calculated as (290.67, 289.28), (290.92. 289.59) and (290.83, 289.61) eV for methine, methylene and methyl carbons, respectively of model dimmers in our previous and QM/MM methods. The result indicates that we cannot consider only 1.22-1.39 eV as the solid effect. We can, thus, obtain reasonable *WD* value of PP as 5.7 eV of averaged one from the difference between the CEBE value for normal dimer model and experimental ones [24] in Table 1.

For C *Kα* XES of PP, we also classified the orbital nature of the emission spectrum into the ranges of 274-283 and 270-274 eV. The two regions are due to pσ(C2p-C2p) and pσ(C2s-C2p) bonding orbitals, respectively.

Solid effect to polymer models in our previous and QM/MM methods.

In order to check the solid effect due to the QM/MM method, we performed CEBE calcula- tions

for dimer model molecules of PEO and PVA polymers in our previous and QM/MM methods in Table 1. As indicated in the table, it can be seen difficult to estimate the solid effect with QM/MM method. Then, we also calculated *WD* values of PEO and PVA polymers from the difference between calculated CEBE values for models in our previous geometry optimization and experimental ones. For PEO and PVA polymers, we could, thus, obtain reasonable *WD* values as 6.2 and 6.0 eV for PEO and PVA. These values of WD in Table 1 correspond to our previous result [25] in deMon DFT calculations.

CONCLUSION

We performed DFT calculations using ADF program for several polymers to compare valence X-ray photoelectron, C *Kα* emission spectra and CEBEs due to QM/MM method with ones due to our previous geometry optimization. The simulation spectra are in good accordance with experimental ones. However, our result indicates that we cannot reproduce the solid effect, even if we used the geometry optimization by the QM/MM method due to the elaborate calculations. Therefore, we estimated reasonable *WD* values of PE, PP, PEO and PVA polymers from the difference between calculated CEBE values for models in our previous geometry optimization and experimental ones.

Table 1 CEBEs and WDs (in eV) of polymers by using the dimer model molecules

| Polymer | CEBEs | | WD |
	exp.	calc. nomal (QM/MM)	
$\{CH_2CH_2\}_n$	285.00	291.08 (290.37)	6.08
$\{CH_2CH(CH_3)\}_n$	285.00	290.67 (289.28)	5.67
$\{CH_2CH(CH_3)\}_n$	285.16	290.92 (289.59)	5.76
$\{CH_2CH(CH_3)\}_n$	285.16	290.83 (289.61)	5.67
$\{CH_2CH_2O\}_n$	286.13	292.37 (288.98)	6.24
$\{CH_2CH(OH)\}_n$	285.00	290.96 (289.72)	5.96
$\{CH_2CH(OH)\}_n$	286.47	292.56 (290.86)	6.09

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