PD Research Report for the 2017 year

Name（Research group） Justyna Ewa Grabska (Ozaki lab, School of Science and Technology)
Research Theme Practical applications of quantum chemical calculations and numerical procedures to ultraviolet (UV) and far ultraviolet (FUV) spectroscopy of polymer nanocomposites
Research Period 1st April 2017 ~ 31st July 2017
Research Results

In my project as a PD I focused on investigating intermolecular interactions between polymer nanoparticles and the nano-carbon matrix (graphene layer and carbon nanotube) by quantum chemical calculations and attenuated total reflection far-/deep-ultraviolet (ATR-FUV-DUV) spectroscopy. These nanocomposite materials carry significant advantages and, therefore, are of the highest interest to study their properties. They combine polymer materials properties (i.e. formability, flexibility, lightness) and nanocarbon material properties (conductivity, mechanical strength, heat resistance) giving in result new spectrum of capabilities. Nanocarbon structures possess highly unusual and unique electronic properties, i.e. offering extraordinary capabilities, such as tunable band gap. It is expected that specific electronic states of nanocarbon, in particular those of graphene contribute strongly to the properties of the nanocomposite. Therefore, it is highly novel and desirable to study electronic transitions and molecular orbitals of these materials. ATR-FUV-DUV spectroscopy

In my research polymers with advantageous highly desirable properties and their nanocarbon based composites were studied. I carried out a research in collaboration with other members of Ozaki Lab at KGU, and also Professor Y. Morisawa (Kindai University), Professor H. Sato (Kobe University), Professor M. J. Wojcik (Jagiellonian University, POLAND) and Dr. I. Tanabe (Osaka University). My part in this collaborative research project was to focus on quantum mechanical calculations of the electronic states, FUV-DUV transitions and other related properties of polymers and to use the obtained results for explaining the spectral variations in FUV-DUV region of the polymer-graphene nanocomposites.

The first focus in the study was on poly(3-hydroxybutyrate) (PHB) semi-crystalline, biodegradable polymer, which possess unique properties, mainly attributed to its specific intermolecular interaction, weak C-H•••O=C hydrogen bonds, strongly affecting its structure and properties. I contributed in explaining the experimental ATR-FUV-DUV spectrum of PHB (Figure 1). Quantum chemical study was based on periodic DFT (Crystal 09 code; B3LYP/TZVP level) and time-dependent density functional theory (TD-DFT; Gaussian 09E; CAM-B3LYP/aug-cc-pVDZ and CAM-B3LYP/6-31+G* levels) calculations. Periodic DFT was used for the calculations of total density of states (TDOS) of crystalline PHB, and the simulation of lattice expansion by optimization of the polymer geometry (atoms only; fixed lattice vectors). TD-DFT was used for the calculation of vertical transition energies and corresponding oscillator strengths and determination of the relevant molecular orbitals (MOs). Crystalline structure of PHB is used as the basis for periodic DFT; extracted models of increasing complexity were used as the basis for TD-DFT calculations. By using these methods it was possible to reproduce the experimental FUV-DUV spectrum of PHB and also to link the observed

spectra with the electronic transitions of PHB (Figure 1). It was possible to attribute the strong absorption peak of PHB near 150-170 nm to multiple transitions (Figure 2). The most relevant ones involve excitation from π orbitals to Rydberg 3p orbitals. The low-intensity peak near 227 nm is due to weak π to π* transitions (Figure 2). The shape of Rydberg orbitals make them sensitive to the structure of the polymer, which allow to study the structural changes of PHB occurring during the thermal expansion and upon the formation of a nanocomposite with graphene. The results based on TDOS calculation, simulation of the lattice expansion and TD-DFT calculations for the more complex polymer models provide insights into the structural changes of PHB polymer. These results contributed to a manuscript which is now during preparation to submission.

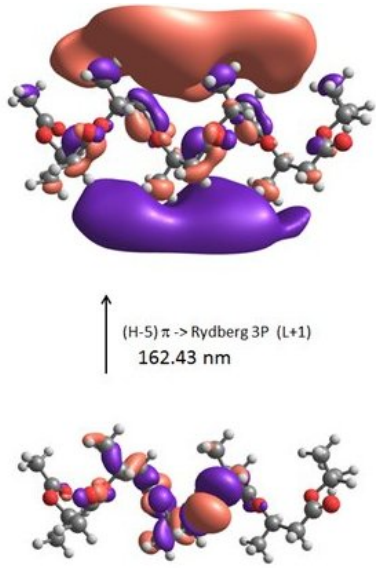

Fig. 1. The most relevant MOs for the major FUV transition of α-crystalline PHB (TD-CAM-B3LYP/aug-cc-pVDZ).

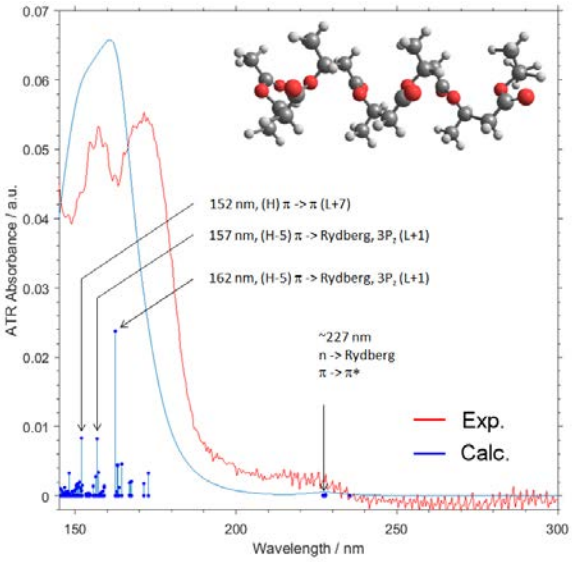

Fig. 2. Simulated FUV-DUV spectrum (TD-CAM-B3LYP/aug-cc-pVDZ) of α-crystalline PHB based on 6 units single chain model compared with the experimental spectrum of PHB.

During this period I published 2 papers:

J. Grabska, K. B. Beć, M. Ishigaki, M. J. Wojcik, Y. Ozaki, Spectra-Structure Correlations of Saturated and Unsaturated Medium-Chain Fatty Acids. Near-Infrared and Anharmonic DFT Study of Hexanoic Acid and Sorbic Acid, *Spectrochim. Acta A*, 185,35-44, May, 2017

J. Grabska, M. Ishigaki, K. B. Beć, J. Wojcik, Y. Ozaki, Structure and Near-Infrared Spectra of Saturated and Unsaturated Carboxylic Acids. An Insight from Anharmonic DFT Calculations, *J. Phys. Chem. A* , 121, 3437−3451, April, 2017

I also attended in the conference 18th International Conference on Near Infrared Spectroscopy 2017, which was in Copenhagen and I have 2 posters presentation titled: ‘Quantum Mechanically Calculated NIR Spectra of Fatty Acids’ and ‘Butyl alcohols studied by near-infrared spectroscopy, two-dimensional correlation analysis and fully anharmonic DFT, with an emphasis on temperature drift of conformational equilibria’.