Usage Report for Fiscal Year 2016

Project Title:

Intermolecular Interactions in Material Science by Molecular Spectroscopy and First Principles

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Description of the project

1. Background and purpose of the project, relationship of the project with other projects

In this project we aim for investigating the intermolecular interactions by terahertz absorption spectroscopy and quantum chemical calculations. In particular, we are interested in water-polymer interaction, the change of structure and physical properties of polymer materials treated by humidity, observed by THz absorption spectroscopy. The focus of our project is on micro- and macroscopic molecular structure changes (intermolecular interactions and strain degradation) with changing relative humidity. The properties of polymer films change when treated by water vapor, and this phenomenon is of great interest for industry (glass transition temperature, density and several other physicochemical properties).

2. Specific usage status of the system and calculation method

Calculations were carrier carried out on GWMPC cluster and in Gaussian 09 quantum chemical software. Anharmonic VPT2 method has been employed on a DFT level for calculation of vibrational frequencies and intensities. Single-hybrid and double-hybrid DFT functionals (i.e. B3LYP/B2PLYP) were mainly used with an appropriate basis set. Where necessary, other levels of electronic theory were employed (MP2, CCSD(T)).

3. Result

During our preliminary studies, we came into a conclusion, that anharmonicity of molecular vibrations play a significant role in case of inter-molecular low-frequency vibrational modes. Moreover, the formation of hydrogen-bonding, therefore its impact on the vibrational properties needed to be taken into account. Anharmonic calculations are still not very well explored field, particularly for a complex molecular systems and in the region of low-frequency vibrations. Therefore, we focused on more basic molecular systems, to be able to establish viable approaches to a more complex molecular systems, i.e. polymers. Basic studies on anharmonicity, vibrational modes coupling and also the investigations of intermolecular interactions in hydrogen-bonded systems, and its overall impact on vibrational properties have been carried out. These results have been published in two highly regarded journals.

4. Conclusion

Terahertz spectroscopy combined with quantum chemical calculations are powerful tools for determining the molecular properties of "water treated" polymer films and the connection between micro- and macroscopic properties of studied systems. Further experimental studies will be carried out in this regard, however the main role in explaining the observed patterns will be held by quantum chemical calculation. The project is expected to greatly contribute to improving physical

properties and new material development for the polymer material which is required recently more various properties and functions with understanding the mechanism of the physical properties expression.

5. Schedule and prospect for the future

Our plan for the next fiscal year is to further develop a viable approach for simulation of complex molecular systems, particularly those which form a hydrogen-bond, with reasonable accuracy. The feasibility of anharmonic approaches will be further considered, and the balance between accuracy/efficiency will be evaluated. The current next goal is to reproduce the trends observed in the experimental data (shifting of bands in terahertz region) among various polymer types, mainly from nylon family.

Fiscal Year 2016 List of Publications Resulting from the Use of the supercomputer

[Publication]

1. K.B. Beć, Y. Futami, M.J. Wójcik, Y. Ozaki. Spectroscopic and Theoretical Study in the Near-Infrared Region of Low Concentration Aliphatic Alcohols. *Phys.Chem.Chem.Phys.*, 2016, 18, 13666-13682.
2. K.B. Beć, Y. Futami, M.J. Wójcik, T. Nakajima, Y. Ozaki. Spectroscopic and Computational Study of Acetic Acid and Its Cyclic Dimer in the Near-Infrared Region. *J. Phys. Chem. A*, 2016, 120, 6170-6183.