Usage Report for Fiscal Year 2015

Project Title:

Intermolecular Interactions in Material Science by Molecular Spectroscopy and First Principles

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

The terahertz spectral region has become significant in recent years, since important properties of numerous materials are exhibited in this region. Moreover a growing number of terahertz based investigations of bio-significant systems can be noticed and overall the terahertz spectroscopy can be expected to cover even larger area of physical, chemical and biological studies. Infrared spectroscopy - MIR in particular but recently also NIR spectroscopy -has been using quantum calculations as a very helpful support tool. And consequently for the last few years we see a growing number of THz spectroscopy studies aided by quantum mechanical simulations as well.

In this project we aim for explaining the 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). 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.

2. Specific usage status of the system and calculation method

The computational part of the project focuses on the application of QM/MM and DFT quantum chemistry methods for simulation of low-frequency vibrational modes of the studied systems, both in harmonic and anharmonic approximation. Due to computational cost reasons we are still working on developing a successful approach for treating polymer-water system. In general, DFT-B3LYP/SNSD method gives the best balance between accuracy and computational time, but only for small water clusters bonded to monomeric species. Inclusion of correction for Basis Set Superposition Error (BSSE), empirical dispersion correction (GD3) and especially anharmonic approximation, improves the accuracy and reliability of the results, but at a very significant additional computational cost. Therefore it is indispensable to develop a balanced approach, taking into account both accuracy and affordability.

3. Result

The results obtained so far focused on nylon monomeric species bonded to small water clusters (1-4 molecules). Initial conclusion derived from the gathered computational data is that the chosen level of theory heavily impacts the reproducibility of the resulting calculated vibrational modes. Anharmonic approach allows for significantly increased accuracy, however the increased computational cost prevents us from applying this method to most of systems that we are interested in. Therefore further development is needed here, to establish a viable approach for approximating vibrational modes of systems larger than monomeric species (Fig. 1., Table 1.).

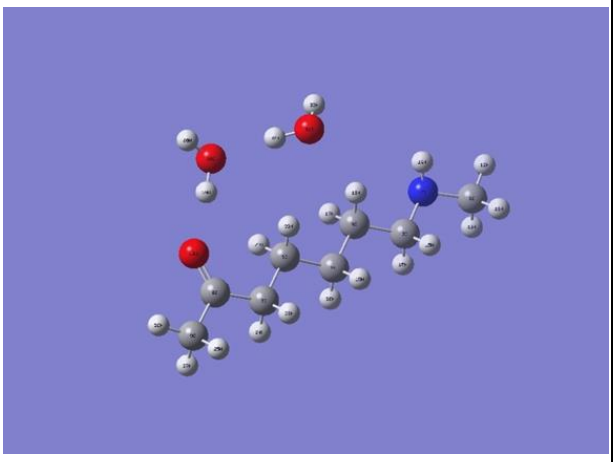

Fig. 1. Water dimer bonded to C=O group of nylon-6 monomer (DFT-B3LYP-D3/SNSD).

Table 1. Details on the simulated O-O stretching mode of water dimer bonded to nylon-6 monomer (Fig. 1.)

O-O stretch. mode	**harmonic**
wavenumber [cm^{-1}]	232.1
intensity [km/mol]	73.7

4. Conclusion

DFT method can be used successfully for reproduction of low-frequency vibrational modes of a monomeric species bonded to small water cluster. However, extending this system to oligomeric species is too expensive - in the computational time sense. Therefore further study and development is needed to establish a viable approach to this problem.

5. Schedule and prospect for the future

The main aim for the next fiscal year is to develop a viable approach for simulation of oligomeric systems with reasonable accuracy. 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.