PhD Thesis

The influence of environment on the electronic and optical properties of thin films composite materials

Lucia Nechalova

Organic nonlinear optical (NLO) materials play a crucial role in modern optoelectronic elements. Most of them are chromophores based upon aromatic π-electron systems unsymmetrically end-capped with electron-donating and accepting groups to influence the electronic bias. These chromophores are embedded in polymer matrixes forming *guest-host* composite materials in thin-film forms. However, to talk about the practical use of these materials, it is necessary to study the properties of composites and to describe the mechanisms of physical phenomena occurring in separated molecules as well as in composites as a whole. In this case, computer simulations are helpful.

This thesis aimed to develop a theoretical computational model and methodology for proceeding to predict the macroscopic optical properties of composite materials in thin-film forms. In this case, the molecular dynamics technique was used to model the structures of composites and quantum chemical calculations were employed to predict the optical properties of chromophores in a polymer environment. The optical properties were calculated by implementing a discrete local field model hierarchically. The computationally obtained data were compared with experimental results taken from SHG and THG responses of the material.

Poly (methyl methacrylate) (PMMA) and poly(vinyl carbazole) (PVK) based composites were chosen as model *guest-host* materials. Two groups of NLO chromophores were embedded into these polymers. One group of chromophores is four different tetrathiafulvalene (TTF)-attended azine derivatives and the other group is based on three benzonitrile derivatives. The results of molecular dynamics simulation of chromophore/PMMA and chromophore/PVK composite materials as well as structural, electronic, and optical properties of chromophores in a vacuum and a polymer matrix are discussed. The obtained computational data were compared with the experimental results testing the correctness of the implemented computational local field model. The influence of polymer matrices on the enhancement of the NLO properties of benzonitrile derivatives in the PVK matrix and the neutrality of the PMMA matrix concerning the tested chromophores was explained. The optical properties of the investigated composites were discussed based on the spatial distribution of chromophores in the polymer matrix.

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