

Abstract

The main goal of this dissertation was to formulate the reliable computational protocol for the nonempirical simulations of vibrationally-resolved electronic one- and two-photon absorption spectra for molecules in solution. To that end, a critical assessment of the reliability of a wide palette of quantum-chemical methods in predicting the crucial parameters describing absorption spectra was performed, such as: the intensity, vibrational structure, inhomogeneous broadening, and the position of absorption band maximum. The main focus was put on the performance of time-dependent density functional theory. Obtained results were confronted with coupled cluster method and experimental data.

The investigations concerning the methodology of calculations of band intensities were aimed at elucidating the source of discrepancies, which were noted in the literature for two-photon strengths, in the predictions of Kohn-Sham formulation of density functional theory and coupled cluster methods. The computations were carried out for organoboron chelates and difluoroborate compounds *in vacuo* by using various exchange-correlation functionals. The obtained results showed that the most reliable exchange-correlation functional belong to the group of range-separated hybrids, which correctly described the optical channels involved in two-photon absorption process. The comparative analysis, on the basis of few-state model (derived by the author) for response theory formalism within nonhermitian theories, showed that the disagreement between aforementioned methods was triggered by underestimated values of excited state dipole moments. Above conclusions emphasize the need for developing the new functionals which more accurately describe the nonlinear optical properties of organic compounds.

This work was also aimed at evaluating the methodology for the simulations of vibrational progression of the one- and two-photon absorption bands. For this, the scheme of choosing an adequate exchange-correlation functional based on easy-to-compute parameter, i.e. vibrational reorganization energy (λ_{vib}) was proposed. As shown, the presented one-parameter diagnostics facilitates the procedure of selection of a proper method, because it is based on the numerical analysis rather than visual comparisons of the simulated and reference spectra. The potential of this approach was illustrated for the wide palette of exchange-correlation functionals using the fluorescent dyes as a test set. In the case of vibrationally-resolved two-photon absorption spectra, the proposed diagnostics was extended with another parameter, i.e. vibrational contribution to the two-photon activity within harmonic approximation. The obtained results for chalcones in methanol solution indicated that this approach is very useful in the simulations of two-photon spectra going beyond Franck-Condon approximation.

In this study the calculations of the band width were also thoroughly examined. For this, the hybrid method including polarizable embedding model and molecular dynamics simulations was applied and tested in few variants. In particular, the choice of molecular geometry and quantum-chemical method was discussed. The results showed that the approach combining the calculations of the broadening, based on rigid-body molecular dynamics simulations, with the quantum-chemical calculations of vibrationally-resolved spectra is capable of reproducing the experimental spectra with high accuracy. This result was attributed to the quantum-chemical treatment of molecular vibrations which was lacking in other tested methods.

Beyond the methodological aspects of simulations, the investigations were also devoted

to the modeling of optical properties of compounds with potential practical applications. For example, the obtained results allowed to elucidate the molecular mechanism of zinc ions sensing by fluorescent probe and to define the design strategy of two-photon absorbers belonging to difluoroborate family. The success of performed analysis shows that the density functional theory, despite its limitations, can be used in qualitative predictions of the nonlinear optical properties.

In conclusion, the investigations performed in the scope of this dissertation contributed to the development of simulations of one- and two-photon electronic absorption spectra for molecules in solution in terms of methodological and application aspects. The research presented in this work was financed by Polish Ministry of Science and Higher Education within "Diamond Grant" program. The results discussed in this thesis were presented in five articles and published in prestigious international journals.