Description for the general public

There is a growing interest in materials characterized by large multiphoton absorption cross sections. At the molecular scale, the most widely studied multiphoton absorption process is the two-photon absorption (2PA), which is central to this project. 2PA phenomenon was predicted on purely theoretical basis in the 30's of past century by Maria Göppert-Mayer. Experimental confirmation had to wait roughly three decades for the construction of lasers. Since then, there has been a demonstration of fascinating applications of the two-photon absorption phenomenon. These include, *inter alia*: i/ the studies of symmetry-forbidden transitions in centrosymmetric molecules, ii/ the recording of high-resolution spectra below the Doppler width, iii/ attempts to employ 2PA for three-dimensional data storage, iv/ microfabrication or v/ bioimaging. This wide palette of applications of 2PA phenomenon resulted in plethora of experimental studies with an eye towards synthesis and characterization of new compounds with tailored photophysical properties. These advances have been paralleled by theory developments thus allowing to study 2PA phenomenon in molecular systems. Thanks to these efforts there are available computational tools which allow to study relationships between molecular structure and electronic two-photon absorption phenomena and computer simulations contributed significantly to the rational design of new molecular systems. In fact, theory-inspired quest for new materials with large 2PA cross sections has became an essential ingredient in materials design. Despite these evident successes of computational quantum chemistry in the characterization of 2PA–active molecular systems, the current computational protocols still suffer from many deficiencies, e.g. i/ the effects of vibrations are scarcely ever taken into account in the simulations of electronic two-photon absorption spectra, ii/ the treatment of vibrational anharmonic effects has not been proposed yet for polyatomic molecules, iii/ in the majority of computational studies the band shapes in electronic 2PA spectra of molecules in solution or protein environments are simulated assuming empirical broadenings, iv/ the most common choice for studies of 2PA – Kohn-Sham formulation of density functional theory – has serious flaws, as the accuracy of current exchange-correlation functionals in this field is (at best) far from satisfactory. These drawbacks hamper more refined studies on two-photon absorption in molecular systems.

This project aims to remedy some of the above drawbacks by developing a multi-step computational protocol to simulate vibrationally-resolved electronic two-photon absorption spectra of molecules in solution and in complex environments (e.g. protein environments) with unprecedenced accuracy. To this end, the vibrational anharmonicity treatment for polyatomic molecules will be proposed and combined with nonempirical determination of inhomogeneous broadening due to interactions with (complex) environments. In order to fully demonstrate the potential of newly developed protocol the vibrationally-resolved electronic one- and two-photon absorption spectra will be simulated and compared with experimental data for a set of representative fluorescent dyes with potential for bioimaging.