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Title:

Experimental studies of two-photon absorption spectra of molecules in solutions: two-photon solvatochromism

Abstract:

Two-photon absorption is one of the most spectacular manifestations of the nonlinear light-matter interactions. A fundamental feature of this phenomenon is the possibility of exciting a molecule with two photons having twice less energy than in the linear (one-photon) case. Two-photon absorption is quantitatively described by the two-photon absorption cross section parameter expressed in Göppert-Mayer (GM) unit. Nowadays, due to possible two-photon absorption applications, a variety of research focus on the maximization of two-photon absorption cross section.

The phenomenon related to changes in the position, shape and intensity of the absorption spectra induced by the change of solvent polarity is called solvatochromism. In the available literature many examples of large red (positive solvatochromism) and blue (negative solvatochromism) shifts of absorption band maxima can be found. Moreover, the intensity changes are also reported.

Until recently, both mentioned above phenomena were investigated separately. Available experimental works reporting the influence of the molecular surrounding on two-photon absorption spectra were incomplete or were performed as a component of the full experimental characterization of a given molecule. Only small amount of research was dedicated to a systematic analysis of indicated issues. Therefore, the following dissertation constitutes an attempt to investigate the solvent effects on two-photon absorption cross section of a well known model molecular systems, namely 4-dimethylamino-4'-nitrostilbene (small positive solvatochromism); 2,6-diphenyl-4-(2,4,6-triphenyl-1-piridinio)phenolate (Reichardt's Dye; large negative solvatochromism) and *p*-nitroaniline (large positive solvatochromism). These molecules were chosen because of the availability of theoretical and experimental data describing their spectroscopic properties. Additionally the two-photon measurements of crystal violet solutions were conducted. The main goals of the following dissertation were:

- to perform the measurements of full two-photon absorption spectra of the selected model

molecular systems exhibiting positive or negative solvatochromism;

- to perform the analysis of the solvent polarity influence on two-photon absorption band shifts and two-photon absorption cross section of a model molecular systems as well as to compare the obtained results to the one-photon absorption data;
- to compare two-state model predictions with the experimental data obtained for the selected molecular systems.

In the first part of dissertation some concepts and theoretical aspects essential for the following thesis were introduced and discussed. In the second part the measurement methodology as well as theoretical details of measurement data analysis were described. In the third part the results obtained for the selected model molecular systems as well as crystal violet are presented. Due to the nature of this work and since the investigated molecular systems are well-known and thoroughly investigated in the variety of areas, each experimental section begins with a short summary of the literature data available for a given molecule. This work is based on three published original research papers and a review published in the form of book chapter (Chem. Phys. Lett. 554 (2012) 113, ChemPhysChem 14 (2013) 3731, Dyes Pigm. 113 (2015) 426, Handbook of Solvents, VOLUME 1. Properties, pp. 695-724, ChemTec Publishing). The last part of dissertation, devoted to the crystal violet molecule, will be published soon.