

THE ROLE OF CHARGE TRANSFER IN THE TWO-PHOTON ABSORPTION CROSS SECTION

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Abstract: The two-photon absorption process is often more efficient when the transition shows higher charge transfer during the electronic excitation [1]. The interactions with different environments can tune the two-photon absorption cross section (TPACS) related with an electronic transition [2]. The aim of this work is to obtain insights of the effects of charge transfer transitions in the TPACS and to evaluate the efficiency of the two-level model (TLM) compared with the quadratic response theory (RES). Quantify the amount of charge transfer is possible using ground and excited electronic densities [3]. To control the amount of charge transfer in an electronic transition we use a static electric field. Changing the intensity of the field is possible to mimic the electrostatic effects of solvents with different polarities [4]. The TPACS and the charge transfer of the pyridinium-N-phenolate organic molecule is studied in this work. To compute the structural effects, the minimum energy geometry is obtained for the isolated molecule and in the presence of the electric field. Our results show that intense fields induce large charge transfer and large TPACS. These results are more evident when the structure is re-optimized in the presence of the field, showing twice more charge transfer and four times larger TPACS than the results obtained without any field. The TPACS obtained with the TLM shows better agreement with the RES results when larger amount of charge transfer is observed. For an amount of 0.35e of charge transfer, the TLM obtains 41% of the RES value and for 0.8e, the TLM value is 60% of the RES value. The knowledge of the relation between the amount of the charge transfer and the TLM efficiency is important to perform theoretical predictions with lower computational costs.

Key-words: two-photon absorption, charge transfer, solvent effects, betaine

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