Two-photon vibrational resolved spectra of organic dyes: insights into the role of Herzberg-Teller couplings

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ABSTRACT

Nowadays, organic dyes with substantial Two-Photon Absorption (TPA) cross sections are widely applied in diverse technological domains, such as optical data storage and bioimaging [1]. The growing interest in these dyes stimulated intense theoretical research efforts, focusing on interpreting experimental measurements and rationalizing molecules with significant TPA.

Any computational protocol aiming at replicating experimental TPA spectra of organic-conjugated molecules must consider the couplings between electronic and vibrational degrees of freedom. Numerous studies have demonstrated the importance of vibrational coupling within the Condon approximation in TPA spectra of push-pull chromophores. Additionally, more refined non-Condon or Herzberg Teller (HT) corrections have been shown to play a prominent role in modeling the spectra of fluorescent proteins [2].

In this study, we utilized density functional theory to compute the vibrational TPA spectra of a series of common fluorescent dyes, along with model chromophores of fluorescent proteins in vacuum. Our analysis aims to offer insights into the role of vibronic coupling in such a diverse range of systems. Furthermore, it explores the possibilities and limitations of various vibronic models based on the harmonic approximation [3] for the computation of TPA spectra.

References

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