

Symmetry Breaking in Cationic Polymethine Dyes

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The intramolecular charge transfer in polymethine dyes occurs through π -conjugated bridges and contributes to the appearance of low-energy excitations strongly influencing their linear, and nonlinear optical properties in polar solvents. The mixing between ground and low-lying excited state energy levels is also coupled with molecular vibrations. The physics of this coupling is related to symmetry breaking brought about by changes in the molecular geometry. We have investigated the symmetry breaking in cationic cyanine dyes by first principles methods that include electron correlation. Our data suggests that for different systems symmetry-breaking occurs at significantly different carbon chain lengths suggesting the involvement of distinct physical effects. We have determined quantitatively the critical length of the conjugated chain necessary to break the symmetry for four series of cationic cyanine dyes, and analyzed the corresponding charge and solitonic waves. We will present the potential energy surface of the symmetry breaking transition in gas phase and in different solvents as well as estimated spectral characteristics for the symmetric and the symmetry broken structures.