Nonlinear optical properties of asymmetric diradical molecules

M. Nakano[1], K. Fukuda[1], Y. Hirosaki[1], H. Matsui[1], K. Yoneda[1], R. Kishi[1], Y. Shigeta[1], B. Champagne[2]

[1]Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
[2]Laboratoire de Chimie Théorique, University of Namur, rue de Bruxelles, 61, 5000 Namur, Belgium

E-mail address: mnaka@cheng.es.osaka-u.ac.jp

Over the past few decades, a large number of experimental and theoretical investigations have been performed to explore highly active nonlinear optical (NLO) substances because of their potential applications in future photonic and optoelectronic devices. On the basis of our theoretical studies [1], a new class of open-shell singlet molecular systems has been proposed and has been found to exhibit larger NLO responses than conventional closed-shell NLO systems. Moreover, several real open-shell singlet molecular systems, e.g., polycyclic aromatic hydrocarbons (PAHs), have attracted much attention from the viewpoint of their unique open-shell singlet electronic structures, their highly effective optoelectronic responses, and their unique structure–(electronic, optical, magnetic) property relationships [2]. In this study, based on a two-site asymmetric diradical model, we newly investigate the second- and third-order NLO properties of open-shell singlet systems with asymmetric electron distributions. The asymmetric electron distribution effects on the excitation energies, excitation properties, and diradical character (a chemical index of the bond nature) are clarified theoretically and then a unified picture of the first and second hyperpolarizabilities (β and γ) (microscopic second- and third-order NLO properties, respectively) of symmetric/asymmetric diradical systems are provided as a function of several fundamental physical parameters including the diradical character. It is found that the increase of the asymmetric electron distribution causes remarkable changes in the amplitude and the sign of β and γ, and that their variations are more intensified with the increase in the diradical character. These results demonstrate that the asymmetric open-shell singlet systems with intermediate diradical characters can exhibit further enhancements of β and γ with respect to conventional asymmetric closed-shell systems and also to symmetric open-shell singlet systems with intermediate diradical characters. In addition, we present a diradical character view of the excitation energies and properties as well as of their dependences as a function of the asymmetric electron distribution, which are useful for understanding the photoresponsive properties of open-shell singlet systems and for constructing design principles of future photonic/optoelectronic materials based on open-shell singlet systems.

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