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A proposal of spin- and charge-modulated open-shell nonlinear optical systems

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Abstract

The second hyperpolarizabilities (γ) for three spin states (doublet, quartet and sextet) of π-conjugated molecules with a charged defect are investigated as a model of novel spin- and charge- modulated nonlinear optical systems. It turns out from the UCCSD(T) results that a charged defect makes the γ negative in sign for low and intermediate spin states (doublet and quartet) while the highest spin, sextet, state exhibits remarkably enhanced positive γ value.

Keywords: Nonlinear optics, Hyperpolarizability, Open-shell system, Spin multiplicity, Radical

1. Introduction

Most of the organic nonlinear optical systems studied so far are limited to the closed-shell systems though several studies have highlighted the potential of open-shell systems and some of them have suggested the possibility of the multi-functional materials exhibiting both of magnetic and optical properties [1-10]. Recently, the effects of spin multiplicity on the second hyperpolarizabilities (γ) of open-shell neutral π-conjugated systems have been investigated and the magnitude of γ has turned out to sensitively depend on the spin state [11]: the γ values of the open-shell neutral systems with intermediate spin multiplicity are expected to be remarkably enhanced as compared to those of neutral closed-shell systems. Such attractive dependence of γ is predicted to be connected with the variation in bonding nature associated with the change of spin states.

In general, open-shell systems can be classified according to the strength of electron correlation, i.e., weak-, intermediate- and strong (magnetic)- correlation regimes, which can be exemplified by an equilibrium-, intermediate- and long- bond distance regions of a homogeneous neutral diatomic molecule. In previous studies [5,10], we have indicated the remarkable variation in γ according to increasing the bond distance and have suggested the enhancement of γ in the intermediate correlation regime. This feature is understood by the fact that the intermediate bonding electrons are sensitive to the applied field, leading to large fluctuation. Such intermediate bond breaking nature in the intermediate correlation regime is, for example, expected to be realized by the increase in the spin multiplicity in open-shell neutral systems. This is predicted to be the origin of enhancing the γ values for the open-shell neutral systems with the intermediate spin multiplicity. On the other hand, since the control of spin state is often achieved by introducing the charges into systems in molecular magnetism [12], the investigation of the effect of introducing charge into open-shell systems on γ is important in view of the spin-control of novel open-shell nonlinear optical (NLO) systems. In this study, we examine the longitudinal static γ values for three types of spin states (doublet, quartet and sextet) of C_6H_8 charged radicals using various electron correlated *ab initio* and density functional theory (DFT) methods. The dependence of γ on spin states for open-shell charged systems is clarified as well as the characteristics of their electron correlation dependence. On the basis of the present results, we discuss the possibility of a new class of NLO systems, i.e., spin- and charge-modulated NLO systems.

2. Model systems and calculation methods

Figure 1 shows the structures of C_6H_8 charged radicals with five π-electrons in the doublet (a), quartet (b) and sextet (c) states optimized at the UB3LYP level using 6-311G* basis set. One, three and five π α-electrons are in excess for the doublet, quartet

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and sextet states, respectively. For each spin multiplicity, the lowest energy state has been considered. The carbon-carbon (CC) bond length alternation is shown to decrease as going from the doublet to the sextet state, where all CC bonds are similar to single bonds. This feature can be understood by the fact that increasing the spin multiplicity corresponds to breaking π bonds.

The use of a split-valence plus polarization basis set augmented with a set of p and/or d diffuse functions on the second-row atoms is shown to reproduce the γ of large- and medium-size π-conjugated systems calculated with larger basis sets [13,14]. In the present study, the 6-31G*+p basis set with p exponent of 0.0523 is employed [13]. For the analysis of electron correlation effects on γ, we use the UHF-based schemes including the UHF-Møller-Plesset *n*th-order perturbation (UMP*n* (*n*=2-4)), the UHF-coupled-cluster with single and double excitations (UCCSD) as well as with a perturbative treatment of the triple excitations (UCCSD(T)). In addition, the *l*-fold spin-projected UMP*n* methods using the Löwdin type spin projection [15], i.e., PUHF (*l*=1), PUMP2(*l*=1) and PUMP3(*l*=1), are also applied in order to highlight the effects of spin contamination corrections on γ. Moreover, at the HF and MP2 levels, the corresponding restricted open-shell approaches (ROHF and ROMP2) are employed while among the density functional theory (DFT) schemes, the hybrid B3LYP exchange-correlation functional is adopted. All calculations are performed using the Gaussian 98 program package [16]

We confine our attention to the dominant (longitudinal) component of static γ, γ_{xxxx}, which can be obtained by adopting the finite field (FF) approach, consisting in evaluating the system energy for different amplitudes of the applied external electric field and, subsequently, in differentiating it numerically. In order to improve the accuracy on the γ values, a 4-point procedure (equivalent to a 7-point procedure for a non-symmetric case) using field amplitudes of 0.0, 0.0010, 0.0020, and 0.0030 a.u. [17] is adopted. The power series expansion convention (B convention [18]) is chosen for defining $\tilde{\gamma}$

3. Results and discussion

Table 1 gives the γ values for the doublet, quartet, and sextet states of C_6H_8 radical cations calculated by various methods using 6-31G*+p basis set. For the doublet state, although the UHF method gives a negative γ value, the UMP*n* (*n*=2-4) methods give positive γ values and overshoot the γ value compared to the most reliable UCCSD(T) value, which is negative in sign. The UCCSD method cannot give the correct sign though it significantly reduces the overshot behavior of the UMP*n* schemes. Similarly to the case of neutral doublet molecule [11], the spin projection significantly reduces the UMP*n* γ values, while it is not sufficient for providing the converged value at the PUMP3 level. In contrast, the spin-restricted methods, ROHF and ROMP2, tend to show faster convergence of γ with respect to the inclusion of electron correlation effects than the UMP*n* and PUMP*n* methods. Although the UB3LYP method provides a correct sign, its magnitude is less than half of the UCCSD(T) value. For the quartet state, the UHF and UMP*n* (*n*=2-4) methods give positive γ values and the correlation effects at the UMP*n* levels tend to decrease the UHF γ value. The magnitude of the UCCSD(T) value is more than one-order larger than that of the doublet state while the UMP*n* and PUMP*n* methods fail to reproduce the sign of γ at the UCCSD(T) level. Contrary to the doublet case, the spin-restricted methods (ROHF and ROMP2) provide positively overshot values compared to the UMP*n* values, which suggests the spin-restricted methods cannot give good starting points for the description of γ of charged systems in the intermediate spin states. The UB3LYP also cannot sufficiently reproduce the magnitude of γ at the UCCSD(T) level though it gives at least the same (negative) sign. For the sextet state, the UCCSD(T) γ value is shown to be extraordinarily enhanced with a positive value, which is much larger than the UMP*n* and PUMP*n* values. It is interesting that the ROMP2 γ value gives a positive value with the same order of magnitude as the UCCSD(T) value. The UB3LYP cannot reproduce the sign

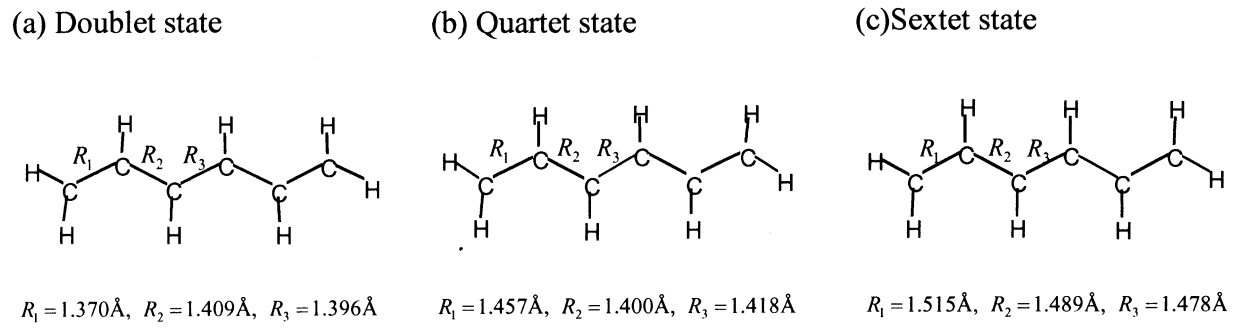

Fig. 1. Molecular geometries of C_6H_8 radical cations in (a) doublet, (b) quartet and (c) sextet states optimized at the UB3LYP level using 6-311G* basis set.. The structures are planar and belong to the C_{2h} point group. The middle C-C bonds of all models have an angle of 30° with respect to the longitudinal (*x*) axis.