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ARTICLE *in* SYNTHETIC METALS · SEPTEMBER 2005

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

M. Nakano<sup>a,b,\*</sup>, B. Champagne<sup>b</sup>, E. Botek<sup>b</sup>, R. Kishi<sup>a</sup>, T. Nitta<sup>a</sup>, K. Yamaguchi<sup>c</sup>

<sup>a</sup> Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

<sup>b</sup> Laboratoire de Chimie Théorique Appliquée Facultés Universitaires Notre-Dame de la Paix, rue de Bruxelles, 61, 5000 Namur, Belgium

<sup>c</sup> Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

### Abstract

The second hyperpolarizabilities ( $\gamma$ ) for three spin states (doublet, quartet and sextet) of  $\pi$ -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  $\gamma$  negative in sign for low and intermediate spin states (doublet and quartet) while the highest spin, sextet, state exhibits remarkably enhanced positive  $\gamma$  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 ( $\gamma$ ) of open-shell neutral  $\pi$ -conjugated systems have been investigated and the magnitude of  $\gamma$  has turned out to sensitively depend on the spin state [11]: the  $\gamma$  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  $\gamma$  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  $\gamma$  according to increasing the bond distance and have suggested the enhancement of  $\gamma$  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  $\gamma$  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  $\gamma$  is important in view of the spin-control of novel open-shell nonlinear optical (NLO) systems. In this study, we examine the longitudinal static  $\gamma$  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  $\gamma$  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  $\pi$ -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  $\pi$   $\alpha$ -electrons are in excess for the doublet, quartet

\* Corresponding author. Tel: +81-6-6850-6268; fax: +81-6-6850-6265;  
E-mail: [mnaka@cheng.es.osaka-u.ac.jp](mailto:mnaka@cheng.es.osaka-u.ac.jp)

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  $\pi$  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  $\gamma$  of large- and medium-size  $\pi$ -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  $\gamma$ , 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  $\gamma$ . 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  $\gamma$ ,  $\gamma_{xxxx}$ , 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  $\gamma$  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  $\gamma$  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  $\gamma$  value, the UMP $n$  ( $n=2-4$ ) methods give positive  $\gamma$  values and overshoot the  $\gamma$  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 overshoot behavior of the UMP $n$  schemes. Similarly to the case of neutral doublet molecule [11], the spin projection significantly reduces the UMP $n$   $\gamma$  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  $\gamma$  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  $\gamma$  values and the correlation effects at the UMP $n$  levels tend to decrease the UHF  $\gamma$  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  $\gamma$  at the UCCSD(T) level. Contrary to the doublet case, the spin-restricted methods (ROHF and ROMP2) provide positively overshoot values compared to the UMP $n$  values, which suggests the spin-restricted methods cannot give good starting points for the description of  $\gamma$  of charged systems in the intermediate spin states. The UB3LYP also cannot sufficiently reproduce the magnitude of  $\gamma$  at the UCCSD(T) level though it gives at least the same (negative) sign. For the sextet state, the UCCSD(T)  $\gamma$  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  $\gamma$  value gives a positive value with the same order of magnitude as the UCCSD(T) value. The UB3LYP cannot reproduce the sign

(a) Doublet state

(b) Quartet state

(c) Sextet state

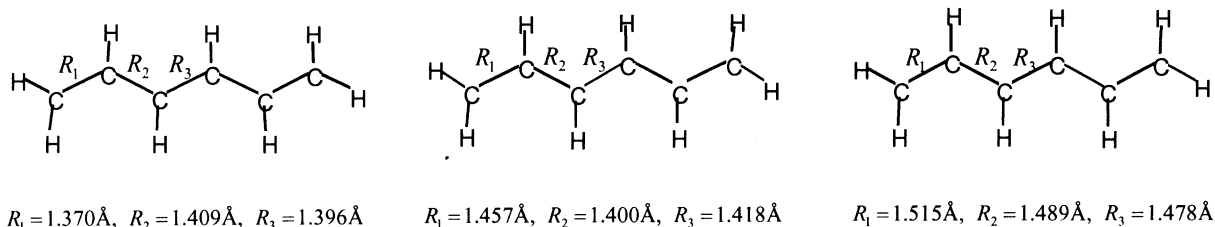


Fig. 1. Molecular geometries of  $C_6H_8$  radical cations in (a) doublet, (b) quartet and (c) sextet states optimized at the UB3LYP level using 6-311G\* basis set. The structures are planar and belong to the  $C_{2h}$  point group. The middle C-C bonds of all models have an angle of  $30^\circ$  with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

Table 1. Calculated  $\gamma$  values (in 100 a.u.) for each spin state of  $C_6H_8^+$ 

	Doublet	Quartet	Sextet
UHF	-2818	881	281
UMP2	4387	881	100
UMP3	3430	753	285
UMP4	4113	532	83
UCCSD	32	-1686	5239
UCCSD(T)	-238	-3010	12166
PUHF	-5576	886	369
PUMP2	2005	944	247
PUMP3	1379	828	409
ROHF	-329	716	1004
ROMP2	-262	1411	18633
UB3LYP	-108	-45	-992

of  $\gamma$  at the UCCSD(T) level.

From the natural orbital analysis, these spin states turn out to be described only by  $\pi$  spins. In this paragraph, the UCCSD(T) results are employed for the discussion on the spin state dependence of  $\gamma$ . The tendency of variation in  $\gamma$  with respect to the present various correlation methods for the lowest spin state of the charged radical molecule is similar to that for neutral radical ones [11] though the present  $\gamma$  value becomes negative in sign in contrast to the positive sign for the neutral radical (see Fig. 2). This is similar to the fact that charged defects tend to enhance the negative contributions to  $\gamma$  for small-size closed-shell  $\pi$ -conjugated molecules [1,17,19], which are caused by the relative enhancement of type II virtual excitation processes (negative) [1] as compared to type III processes (positive). For the intermediate spin state, the quartet, the charged radical molecule exhibits a different feature (still negative value but larger magnitude than that of the doublet) from that of neutral one [11], which provides a larger positive  $\gamma$  value than the doublet state due to the intermediate  $\pi$ -bond breaking nature. This suggests that the effect of a charged defect overcomes the positive enhancement of  $\gamma$ , which is described by the type III process [1,17,19], mostly associated to  $\alpha$   $\pi$ -electrons in the intermediate bond breaking regime [11]. In other words, the  $\beta$   $\pi$ -electron contribution with a negative sign, which is described by type II process, is presumed to be significantly enhanced by a charged defect. Such lowest and intermediate spin states of charged radical molecules are expected to possess the symmetric resonance structure with invertible polarization (SRIP) [4], which

tends to give a negative  $\gamma$  value due to the relative enhancement of type II contributions. Contrary to these lowest and intermediate spin states, the highest spin state, the sextet, of the charged radical molecule gives an extraordinarily large positive  $\gamma$  value. This suggests that the magnitude of the type III contributions is much larger than for the type II contributions. In comparison with the decrease in the  $\alpha$   $\pi$ -electron contribution to  $\gamma$  in the highest spin state of a neutral radical molecule, the charged defect is predicted to enhance the contribution of type III (positive), primarily associated with the  $\alpha$   $\pi$ -electrons. As a result, a charged defect tends to enhance the type II contributions (negative) associated with  $\beta$   $\pi$ -electrons in low and intermediate spin states, while significantly enhance the type III contributions associated with  $\alpha$   $\pi$ -electrons in the highest spin states. This feature can be understood by the fact that a charged defect tends to cause the decrease and increase of excitation energy and transition moment for lower excited states, respectively, which contribute to the enhancement of both |type II| and |type III| contributions.

#### 4. Summary

We investigate the spin multiplicity dependence of static  $\gamma$  for an open-shell charged system,  $C_6H_8^+$  radical. Combining these results with those of a previous study on a neutral open-shell system [11], the formation of an intermediate spin multiplicity state induces an enhancement of the magnitude of  $\gamma$  although  $\gamma$  is positive (negative) for the neutral (charged) species and the

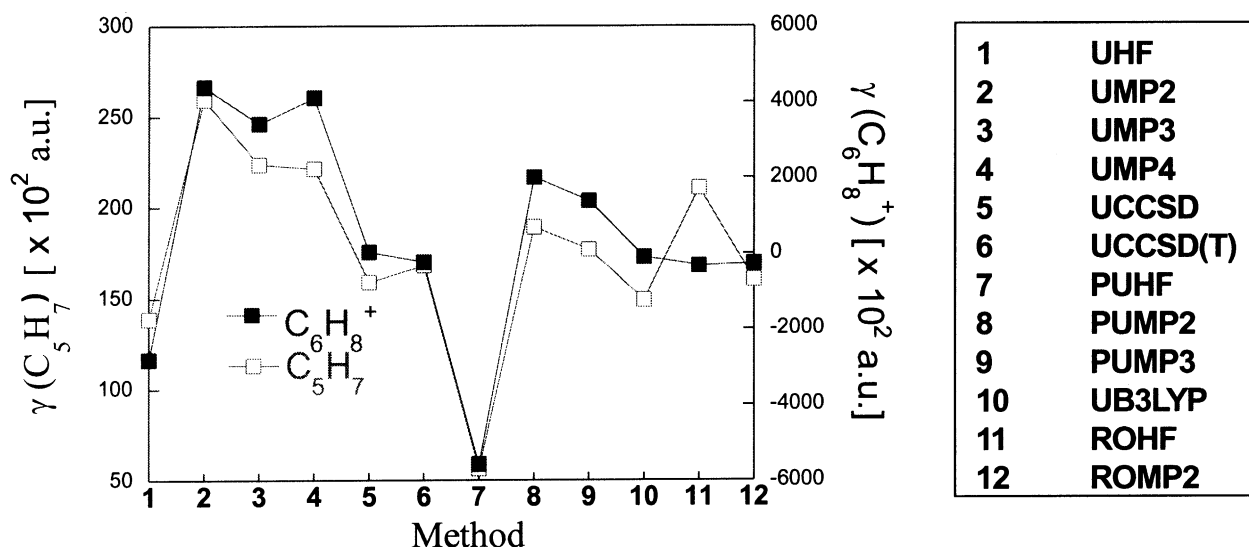


Fig. 2.  $\gamma$  values for doublet states of  $C_6H_8$  radical cation and  $C_5H_7$  neutral radical. 6-31G\*+p basis set is used.

enhancement of magnitude is much larger for the radical cation. On the other hand, the sextet exhibits an extraordinarily enhanced positive  $\gamma$  value in contrast to the neutral sextet  $C_5H_7$  radical, in which the  $\alpha$   $\pi$ -electron contribution to  $\gamma$  is reduced as compared to that of the corresponding quartet state. This is predicted to be caused by the enhancement of type III (positive) contributions.

On the basis of the present results, charged open-shell systems are expected to be candidates for novel controllable NLO systems, in which their magnitudes and sign can be controlled by modulating spin and charged states. Lots of charged open-shell molecular systems, which have been presented in molecular magnetism, will be attractive candidates for such open-shell NLO systems.

## Acknowledgments

This work was supported by Grant-in-Aid for Scientific Research (No. 14340184) from Japan Society for the Promotion of Science (JSPS). E.B. thanks the Interuniversity Attraction Pole on "Supramolecular Chemistry and Supramolecular Catalysis" (IUAP No. P5-03) for her postdoctoral grant while B.C. thanks the Belgian National Fund for Scientific Research for his Senior Research Associate position.

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