Relationship between Third-Order Nonlinear Optical Properties and Magnetic Interactions in Open-Shell Systems: A New Paradigm for Nonlinear Optics

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Although most third-order nonlinear optical (NLO) materials are closed-shell singlet systems, this Letter theoretically shows that the third-order NLO properties are drastically enhanced in symmetric open-shell diradical systems with intermediate diradical character and further reveals that this enhancement is associated with the ferromagnetic and antiferromagnetic interactions. This new paradigm opens up a promising area for designing new third-order NLO materials.

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For more than 30 years, the third-order nonlinear optical (NLO) properties of organic compounds, i.e., at the molecular level, the second hyperpolarizabilities (γ), have been actively studied both theoretically and experimentally [1] due to their large amplitude associated with short response times and the feasibility of molecular design. It has been recognized that enhanced γ values require (i) optimizing the conjugation length [2], (ii) choosing appropriate substituents with specific donor and acceptor strengths [3], (iii) modeling the shape and dimensionality of the π-electron network [4], as well as (iv) tuning the charge [5]. Evidence was also given that vibrational (nuclear relaxation) components to γ can become important for some NLO processes [6], whereas recent works using Thomas-Kuhn sum rules to derive fundamental physical limits to molecular γ values [7] demonstrated, though these limits are still subject to discussion [8], that there is still plenty of room to derive new systems with larger third-order NLO susceptibilities. The fact that these systems are mostly closed-shell species is currently challenged by a few studies demonstrating that open-shell systems can exhibit enhanced third-order NLO susceptibilities [9,10]. Indeed, using *ab initio* molecular orbital (MO) and density functional theory calculations significant enhancements of γ with respect to analogous closed-shell systems were obtained (i) for diphenalenyl diradical systems [10] and (ii) for π-conjugated diradical systems involving imidazole rings [9(c)]. These studies have further shown the possibility of tuning the γ values by changing the spin states.

The fundamental origin of this enhancement has not yet been clarified, which makes the design of new compounds difficult. Preliminary insight into the origin of this enhancement for intermediate diradical character was, however, provided by studying the H_2 dissociation model, which revealed an immediate cause of the exaltation of γ through the diradical character dependence of the amplitudes of the transition moments [9(b)].

In this Letter, we will demonstrate the fundamental origin of γ of symmetric diradical systems using the valence-bond (VB) [11] and valence configuration interaction (VCI) methods [12], and we will first reveal a fundamental connection between γ and the ferromagnetic and antiferromagnetic interactions. Indeed, like in charge-transfer-Mott insulators [13], it was never expected that tuning the magnetic interactions can be used to optimize the third-order NLO responses. This may open up a conceptually new strategy for maximizing the third-order NLO responses based on symmetric diradical systems.

VB and VCI schemes for diradical systems.—As the simplest example of symmetric diradical molecules, let us consider a two-site model $A^\bullet$-$B^\bullet$ with two electrons in two orbitals. The so-called magnetic orbitals can be either symmetry-adapted, g and u, or localized natural orbitals (LNO), a and b [12]. The two sets are related through

$$a(x) \equiv \frac{1}{\sqrt{2}}[g(x) + u(x)] \quad \text{and} \quad b(x) \equiv \frac{1}{\sqrt{2}}[g(x) - u(x)]. \tag{1}$$

The LNOs, which are mainly localized on one site (A or B), have generally small tails on the other site, satisfying the orthogonal condition $\langle a|b\rangle = 0$. For $M_S = 0$ (singlet and triplet), using LNOs there are two neutral, $|a\bar{b}\rangle(\equiv|\text{core } a\bar{b}\rangle)$ and $|\bar{b}a\rangle(\equiv|\text{core } \bar{b}a\rangle)$, and two ionic, $|a\bar{a}\rangle(\equiv|\text{core } a\bar{a}\rangle)$ and $|b\bar{b}\rangle(\equiv|\text{core } b\bar{b}\rangle)$, determinants, where "core" means the orthogonal closed-shell core orbitals and the upper bar (nonbar) indicates the β (α) spin. The configuration interaction matrix in the LNO represen-

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tation $\{|a\bar{b}\rangle, |b\bar{a}\rangle, |a\bar{a}\rangle, |b\bar{b}\rangle\}$ takes the form [12]

$$\begin{pmatrix} 0 & K_{ab} & t_{ab} & t_{ab} \\ K_{ab} & 0 & t_{ab} & t_{ab} \\ t_{ab} & t_{ab} & U & K_{ab} \\ t_{ab} & t_{ab} & K_{ab} & U \end{pmatrix}, \tag{2}$$

where the energy of the neutral VB determinants is taken as the energy origin. The $U(\equiv U_{aa} - U_{ab})$ indicates the difference between on site and intersite Coulomb integrals $K_{ab}(\equiv \langle a\bar{b}|1/r_{12}|b\bar{a}\rangle \geq 0)$ is a direct exchange integral, and $t_{ab}(\equiv \langle a|F|b\rangle)$ is a transfer integral, where F is the Fock operator. By diagonalizing this matrix, the four solutions are an essentially neutral lowest-energy singlet state of g symmetry $|S_{1\mathrm{g}}\rangle[= \kappa(|a\bar{b}\rangle + |b\bar{a}\rangle) + \eta(|a\bar{a}\rangle + |b\bar{b}\rangle)]$ (of energy ${}^1E_{1\mathrm{g}}$; $\kappa > \eta > 0$), an ionic singlet state with u symmetry $|S_{1\mathrm{u}}\rangle = (|a\bar{a}\rangle - |b\bar{b}\rangle)/\sqrt{2}$ (of energy ${}^1E_{1\mathrm{u}}$), another singlet state of g symmetry but essentially ionic $|S_{2\mathrm{g}}\rangle[= -\eta(|a\bar{b}\rangle + |b\bar{a}\rangle) + \kappa(|a\bar{a}\rangle + |b\bar{b}\rangle)]$ (of energy ${}^1E_{2\mathrm{g}}$; $\kappa > \eta > 0$), and a neutral triplet state $|T_{1\mathrm{u}}\rangle[= (|a\bar{b}\rangle - |b\bar{a}\rangle)/\sqrt{2}]$ (of energy ${}^3E_{1\mathrm{u}}$) [12]. The nonzero transition moments between these states are approximately evaluated as

$$\mu_{S_{1\mathrm{g}},S_{1\mathrm{u}}} \equiv -\left\langle S_{1\mathrm{g}} \,\middle|\, \sum_i^2 r_i \,\middle|\, S_{1\mathrm{u}} \right\rangle \approx \sqrt{2}\eta R_{\mathrm{BA}}$$

$$\text{and} \quad \mu_{S_{2\mathrm{g}},S_{1\mathrm{u}}} \equiv -\left\langle S_{2\mathrm{g}} \,\middle|\, \sum_i^2 r_i \,\middle|\, S_{1\mathrm{u}} \right\rangle \approx \sqrt{2}\kappa R_{\mathrm{BA}}, \tag{3}$$

since the LNOs are well localized. R_{BA} depicts the distance between A and B. $2\kappa^2$ and $2\eta^2$, the sum of which is equal to one by virtue of the orthogonalization condition, represent the weights of neutral (ionic) and ionic (neutral) contributions in $|S_{1\mathrm{g}}\rangle$ ($|S_{2\mathrm{g}}\rangle$). The transition moment between $|S_{1\mathrm{g}}\rangle$ and $|S_{2\mathrm{g}}\rangle$ is zero by symmetry. The effective exchange integral J in the Heisenberg Hamiltonian [14] for the two-site systems, $\hat{H}_{\mathrm{HB}} = -2J\hat{\mathbf{S}}_{\mathrm{A}} \cdot \hat{\mathbf{S}}_{\mathrm{B}}$, is represented by [12]

$$2J = {}^1E_{1\mathrm{g}} - {}^3E_{1\mathrm{u}} = 2K_{ab} + \frac{U - \sqrt{U^2 + 16t_{ab}^2}}{2}. \tag{4}$$

Using the symmetry-adapted MOs, the g-symmetry ground and excited states read $|S_{1\mathrm{g}}\rangle = \xi|g\bar{g}\rangle - \zeta|u\bar{u}\rangle$ and $|S_{2\mathrm{g}}\rangle = \zeta|g\bar{g}\rangle + \xi|u\bar{u}\rangle$, where $\xi^2 + \zeta^2 = 1$, and, from comparing the MO and LNO representations, $\xi + \zeta = 2\kappa$ and $\xi - \zeta = 2\eta$. The diradical character (y), which characterizes the chemical bond nature [15], is defined as twice the weight of the double excitation configuration in the singlet ground state:

$$y \equiv 2\zeta^2 = 1 - \frac{4|t_{ab}|}{\sqrt{U^2 + 16t_{ab}^2}} = 1 - \frac{4r_t}{\sqrt{1 + 16r_t^2}}$$
$$= 1 - \frac{2\sqrt{(r_K - r_J)(r_K - r_J + 1)}}{1 + 2(r_K - r_J)}, \tag{5}$$

using dimensionless quantities: $r_J \equiv 2J/U$, $r_K \equiv 2K_{ab}/U(\geq 0)$, and $r_t \equiv |t_{ab}|/U(\geq 0)$. The diradical character y takes a value between 0 and 1, which represents the closed-shell (stable bonding) and pure diradical (bond breaking) states, respectively. Because U means the difficulty of electron transfer between A and B, while $|t_{ab}|$ does the easiness of that, the case $r_t \rightarrow 0$ indicates the limit of localization of an electron on each site, corresponding to the pure diradical state ($y \rightarrow 1$). In contrast, the case $r_t \geq 1(|t_{ab}| \geq U)$ represents a sufficient delocalization of electrons over two sites, corresponding to a stable bonding state ($y \rightarrow 0$).

Relationships between second hyperpolarizability and diradical character.—Using perturbation theory, the static electronic γ of symmetric molecular systems contains only type II and type III-2 terms [16] and, in the three-state approximation, reads

$$\gamma = \gamma^{\mathrm{II}} + \gamma^{\mathrm{III-2}}$$
$$= -4\frac{(\mu_{S_{1\mathrm{g}},S_{1\mathrm{u}}})^4}{(E_{S_{1\mathrm{u}},S_{1\mathrm{g}}})^3} + 4\frac{(\mu_{S_{1\mathrm{g}},S_{1\mathrm{u}}})^2(\mu_{S_{1\mathrm{u}},S_{2\mathrm{g}}})^2}{(E_{S_{1\mathrm{u}},S_{1\mathrm{g}}})^2 E_{S_{2\mathrm{g}},S_{1\mathrm{g}}}}. \tag{6}$$

The quantities involved in the numerators and denominators are expressed by

$$(\mu_{S_{1\mathrm{g}},S_{1\mathrm{u}}})^2 = R_{\mathrm{BA}}^2 \frac{r_K - r_J}{1 + 2(r_K - r_J)} = R_{\mathrm{BA}}^2 \frac{1 - \sqrt{1 - q^2}}{2}, \tag{7}$$

$$(\mu_{S_{1\mathrm{u}},S_{2\mathrm{g}}})^2 = \frac{R_{\mathrm{BA}}^2}{2}\left(1 + \frac{1}{1 + 2(r_K - r_J)}\right)$$
$$= R_{\mathrm{BA}}^2 \frac{1 + \sqrt{1 - q^2}}{2}, \tag{8}$$

$$E_{S_{1\mathrm{u}},S_{1\mathrm{g}}} \equiv {}^1E_{1\mathrm{u}} - {}^1E_{1\mathrm{g}} = U(1 - r_J)$$
$$= \frac{U}{2}\left(1 - 2r_K + \frac{1}{\sqrt{1 - q^2}}\right), \tag{9}$$

and

$$E_{S_{2\mathrm{g}},S_{1\mathrm{g}}} \equiv {}^1E_{2\mathrm{g}} - {}^1E_{1\mathrm{g}} = U[1 + 2(r_K - r_J)] = \frac{U}{\sqrt{1 - q^2}}. \tag{10}$$

Here, $q \equiv 1 - y$ is an effective bond order [15]. For a fixed R_{BA} value and $r_K = 0$ (an approximate situation to the case $K_{ab} \ll U$), the diradical character is tuned by varying r_t (or r_J). Then, for $y = 0$, the dimensionless squared transition moments, $(\mu_{S_{2\mathrm{g}},S_{1\mathrm{u}}})^2/R_{\mathrm{BA}}^2$ and $(\mu_{S_{1\mathrm{g}},S_{1\mathrm{u}}})^2/R_{\mathrm{BA}}^2$, are equal to 0.5. Increasing y from 0 to 1, $(\mu_{S_{2\mathrm{g}},S_{1\mathrm{u}}})^2/R_{\mathrm{BA}}^2$ and $(\mu_{S_{1\mathrm{g}},S_{1\mathrm{u}}})^2/R_{\mathrm{BA}}^2$ evolve towards 1 and 0, respectively (Fig. 1). On the other hand, dimensionless excitation energies, $E_{S_{2\mathrm{g}},S_{1\mathrm{g}}}/U$ and $E_{S_{1\mathrm{u}},S_{1\mathrm{g}}}/U$, strongly increase with decreasing y in the small y region, while both asymptotically approach 1 in the large y region. These behaviors dictate the y dependence of the two contributions to γ and, in particular, the fact that the dominant type III-2—and therefore the total γ value—presents a maximum for intermediate diradical character. Using Eqs. (6)–(10), the analytical formula of γ as a function of q reads, therefore,

$$\frac{\gamma}{(R_{\mathrm{BA}}^4/U^3)} = -\frac{8q^4}{(1+\sqrt{1-q^2})^2(1-2r_K+1/\sqrt{1-q^2})^3} + \frac{4q^2}{(1-2r_K+1/\sqrt{1-q^2})^2(1/\sqrt{1-q^2})}. \tag{11}$$

For $r_K = 0$, the diradical character $y_{\max} \approx 1 - 0.6414 = 0.3586$ corresponds to the maximum $\gamma/(R_{\mathrm{BA}}^4/U^3)$ value of $\gamma_{\max}/(R_{\mathrm{BA}}^4/U^3) \approx 0.2025$ (see Fig. 2). Moreover, keeping y constant $\gamma^{\mathrm{III}-2}/(R_{\mathrm{BA}}^4/U^3)$ increases with r_K as a function of $1/(\mathrm{const} - 2r_K)^2$. The diradical character associated with the maximum $\gamma/(R_{\mathrm{BA}}^4/U^3)$ value increases also with r_K.

(Anti)ferromagnetic interactions and second hyperpolarizability.—Using Eqs. (4) and (6)–(10), $\gamma/(R_{\mathrm{BA}}^4/U^3)$ can also be expressed as a function of r_K and r_J by

$$\frac{\gamma}{(R_{\mathrm{BA}}^4/U^3)} = -\frac{4(r_K - r_J)^2}{[1+2(r_K-r_J)]^2(1-r_J)^3} + \frac{4(1+r_K-r_J)(r_K-r_J)}{[1+2(r_K-r_J)]^3(1-r_J)^2}. \tag{12}$$

Figure 3 displays the behavior of $\gamma/(R_{\mathrm{BA}}^4/U^3)$ in the (r_J, r_K) plane together with the isolines [light gray (green) lines] of y, which using Eq. (5) are determined by $r_K - r_j \equiv d = [(y(2-y))^{-1/2} - 1]/2$ (where d is the intercept of the r_K axis). Thus, $d = 0$ for $y = 1$ and $d \to \infty$ for $y = 0$. When approaching the $y = 1$ isoline (diagonal line $r_K = r_J$), the isoline density increases strongly. The $y = 0$ isoline passes through the region with $r_J \to -\infty$ and $r_K \to \infty$. Figure 3 further shows that the variation in $\gamma/(R_{\mathrm{BA}}^4/U^3)$ of analogous molecules can be monitored and therefore tuned by changing the diradical character, but that there is no universal one-to-one correspondence between y and γ. Indeed, a $\gamma/(R_{\mathrm{BA}}^4/U^3)$ isocurve can be crossed by several y isolines and vice versa. When connecting the (r_J, r_K) points exhibiting the largest $\gamma/(R_{\mathrm{BA}}^4/U^3)$ values along lines ($r_K + r_J = c$, $-\infty \le c \le \infty$) perpendicular to the y isolines, the resulting ridge line [dark gray (red) line] is almost parallel to the y isolines. Moreover, the maximum in $\gamma/(R_{\mathrm{BA}}^4/U^3)$ increases from the lower left to the upper right corner on the (r_J, r_K) plane, i.e., by increasing r_J and r_K. A significant feature of Fig. 3 is the association of region **C** with large third-order NLO as compared to conventional singlet (nearly) closed-shell molecules (region **A**) and ground-state singlet diradical molecules with intermediate diradical character (region **B**) [9,10]. Region **C** corresponds to the ferromagnetic interaction region ($J > 0$), which has been actively investigated in an effort to realize molecular magnets. Thus, along the ridge line, a further enhancement of $\gamma/(R_{\mathrm{BA}}^4/U^3)$ is expected for ground-state triplet diradical species with intermediate diradical character, provided they are excited to the corresponding singlet diradical state.

Subsequently, quantitative estimates of the γ of diradical systems can be obtained by determining the parameters of the VCI scheme, which are directly related to excitation energies as demonstrated by Eqs. (4), (9), and (10) (see also Eqs. 20–22 of Ref. [12]) as well as to transition dipoles [Eqs. (7) and (8)]. Although these energy differences and transition dipoles can also be determined experimentally, illustrative calculations were performed for two polycyclic diphenalenyl radicals [10(b)] by employing the unrestricted natural orbital complete active space configuration interaction (UNOCASCI) approach [15] including two electrons in two orbitals (Table I). It

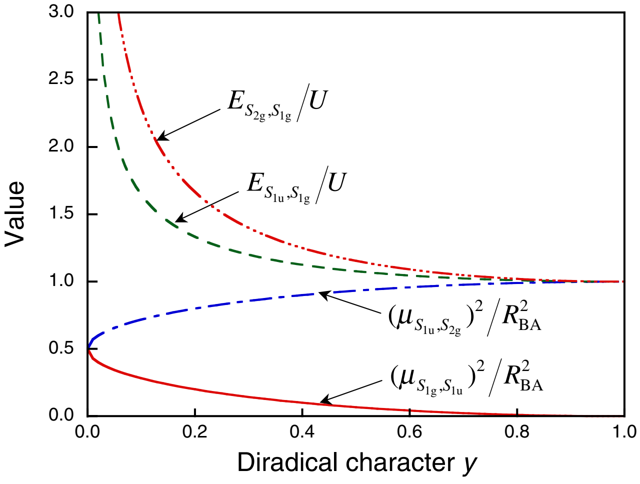

FIG. 1 (color online). Diradical character dependences of dimensionless excitation energies, $E_{S_{2g},S_{1g}}/U$ and $E_{S_{1u},S_{1g}}/U$, and squared transition moments, $(\mu_{S_{1u},S_{2g}})^2/R_{\mathrm{BA}}^2$ and $(\mu_{S_{1g},S_{1u}})^2/R_{\mathrm{BA}}^2$, for $r_K = 0$.

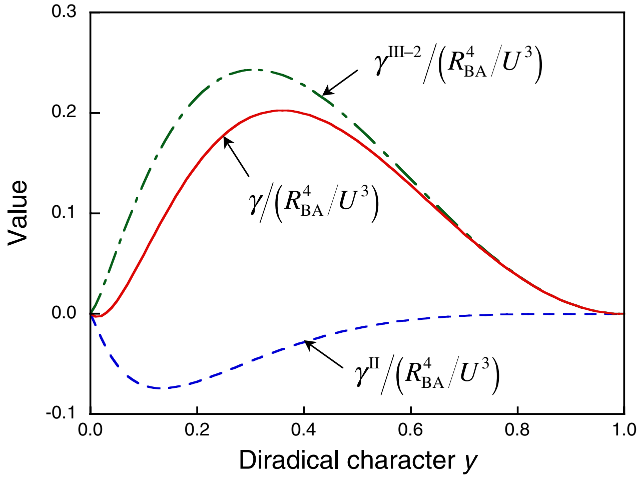

FIG. 2 (color online). Diradical character dependences of $\gamma/(R_{\mathrm{BA}}^4/U^3)$, $\gamma^{\mathrm{II}}/(R_{\mathrm{BA}}^4/U^3)$, and $\gamma^{\mathrm{III-2}}/(R_{\mathrm{BA}}^4/U^3)$ for $r_K = 0$.

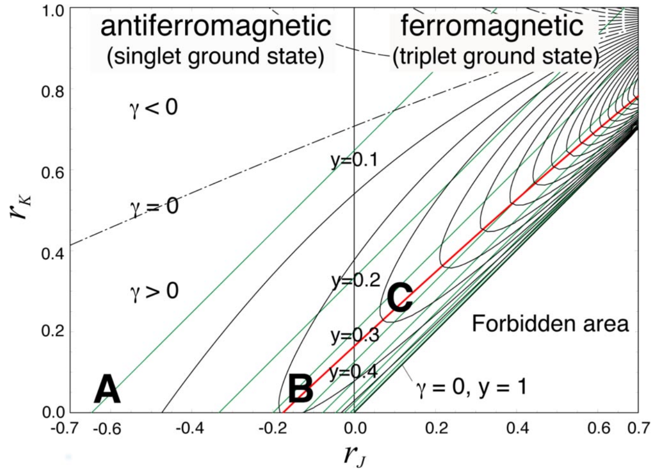

FIG. 3 (color online). Contours of $\gamma/(R_{\mathrm{BA}}^4/U^3)$ [$-2.0 \leq \gamma/(R_{\mathrm{BA}}^4/U^3) \leq 2.0$, interval $= 0.1$]. Solid black lines, dotted black lines, and dashed black lines represent positive, negative, and zero lines of γ, respectively. Solid light gray (green) and dark gray (red) lines represent the isolines of y and the ridge line connecting the (r_J, r_K) points exhibiting maximum $\gamma/(R_{\mathrm{BA}}^4/U^3)$ values along the lines perpendicular to the y isolines, respectively.

turns out that combining these calculated "optical properties" with the simple VCI model enables us to reproduce the differences in diradical character and the subsequent variations of the γ of Ref. [10(b)], demonstrating thereof the predictive and interpretive characters of the VCI model for γ.

In conclusion, we have demonstrated that in the antiferromagnetic interaction region the γ is enhanced for ground-state singlet diradical compounds with intermediate diradical character with respect to closed-shell compounds, while in the ferromagnetic interaction region, excited-state singlets can exhibit further exaltation of γ. The present result is therefore intriguing from the viewpoint of the connection between third-order NLO responses and molecular magnetism, and it opens up the field for further enhancement of γ by selecting NLO candidates in a large variety of triplet ground-state molecular systems studied so far in the field of molecular magnetism. It also suggests that the third-order NLO responses could be strongly modified by applying external magnetic fields, enabling the elaboration of multifunctional molecular switches.

TABLE I. VCI parameters and γ, obtained from UNOCASCI(2, 2)/6-31G* calculations, for two polycyclic diphenalenyl radicals, i.e., indaceno[1,2,3-*cd*;6,7,8-*c′d′*]diphenalene (IDPL) and *as*-indaceno[1,2,3-*cd*;6,7,8-*c′d′*]diphenalene (*as*-IDPL), in comparison with results of Ref. [10(b)].

	IDPL	*as*-IDPL
r_J	−0.061	−0.001
r_K	0.004	0.007
r_t	0.131	0.043
y [Eq. (5)]	0.537	0.830
y [Ref. [10(b)]]	0.770	0.923
$\gamma/(R^4/U^3)$ [Eq. (12)]	0.158	0.028
γ ($\times 10^4$ a.u.) [Eq. (12)]	399	55
γ ($\times 10^4$ a.u.) [Ref. [10(b)]]	228	47

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