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Theoretical study on the spin state and open-shell character dependences of the second hyperpolarizability in hydrogen chain models

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Spin state and open-shell character dependences of the static second hyperpolarizability (γ) are theoretically investigated using hydrogen chain models $H_{2n}(1 \leqslant n \leqslant 3)$ at the full configuration interaction level of approximation. The variation in γ is examined as a function of changing the spin state for a variety of open-shell characters ranging from the closed-shell to pure open-shell states. It is found that (i) in the nearly ground-state closed-shell region, higher-spin states exhibit much larger γ values than the singlet state; (ii) in the intermediate and large open-shell character regions, the singlet state presents the largest γ and γ decreases with the spin multiplicity; and (iii) in the pure open-shell region, all the spin states exhibit negligible γ values. The summation-over-states approach enables rationalizing these findings by considering the primarily contributing excited states. These results reveal that there are two types of molecular design guidelines for enhancing γ values: (a) for nearly closed-shell systems, increasing the spin multiplicity; and (b) for open-shell singlet systems, tuning the open-shell character to the intermediate region.

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I. INTRODUCTION

For more than 30 years, the third-order nonlinear optical (NLO) properties of organic compounds have been studied with great interest both theoretically and experimentally due to their short response times and the feasibility of molecular design [1]. To realize highly active organic third-order NLO materials for future photonics and optoelectronics applications, several design principles for the enhancement and control of the second hyperpolarizability (γ), the molecular response at the origin of the third-order NLO properties, have been proposed: extension of conjugation length [2,3], appropriate chemical substitution by donor-acceptor groups [4], constructing two-dimensional π-conjugated networks [5], molecular aggregation [6–8] and tuning the charge states [9–11]. Although the targets of these design principles have been limited to closed-shell systems, our previous studies have shed light on open-shell systems including high-spin radicals [12] and open-shell singlet systems [7,8,13–20]. In particular, in the latter case, we have theoretically revealed the relationship between open-shell character and γ, and have proposed design guidelines towards highly efficient open-shell NLO molecular systems: the systems with intermediate open-shell character exhibit much greater γ than closed-shell and pure open-shell systems of similar size [7,13–20]. These theoretical predictions have been carried out with high-precision *ab initio* MO and density functional theory (DFT) calculations [7,15–20]. Indeed, large γ responses have been determined for a variety of compounds with intermediate open-shell character, such as polycyclic aromatic hydrocarbons including graphene nanoflakes [16,17], metal-metal multiply bonded complexes [16], compounds involving heavier main group elements [16], asymmetric open-shell molecular systems [18], and open-shell aggregates [7,8]. On the other hand, experimental studies have substantiated this structure-property relationship for third-harmonic generation (THG) [21,22] and two-photon absorption (TPA) [23,24] measurements. Recently, it has also been revealed that open-shell character boosts multiphoton absorption cross sections [23–25]. Regardless of these recent investigations of a novel class of NLO systems, there still exist a large gap between γ of conventional systems and its theoretical upper limit [26,27], which implies that further explorations are needed.

In the meantime, we have extended our molecular design guidelines to open-shell high-spin systems. In a previous study [12], we have examined the spin multiplicity effects on γ values for C_5H_7 radicals (doublet, quartet, and sextet states), and have found that the γ value increases with the spin multiplicity. In another previous study [28], we have investigated not only singlet diradical systems but also singlet multiradical systems, and have shown that the latter exhibit strong dependence of γ with respect to their average diradical characters similarly to what was found for the former. Recently, in addition, Levis and co-workers reported that the nonlinear optical responses of ionized Ne exhibit sign change depending on the spin multiplicity, while those of Ar and Kr do not exhibit such change [29]. However, those studies have only targeted open-shell singlet systems or spin state dependences only for certain open-shell characters while there have been no studies simultaneously targeting both the spin state and the open-shell character dependences of γ. In the region with nonzero open-shell characters, various spin states can exist due to their near-degenerate energy. In this study, therefore, we comprehensively investigate the spin-flip effects of the singlet states with a variety of open-shell characters on γ. Thus, revealing the relationships among spin state, open-shell character, and γ will contribute to opening a path

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to constructing alternative design and control guidelines for highly efficient open-shell NLO materials.

II. THEORY AND COMPUTATIONS

A. Theoretical background

Open-shell singlet character can be quantitatively described using the multiple diradical character y_i [30], which is a quantum-chemically well-defined dimensionless index and takes a value between 0 (closed-shell) and 1 (pure open-shell). The y_i value is not an observable but a physicochemical index for the ground-state electronic structure, which represents the instability of the effective chemical bond in the chemical sense, and the strength of electron correlation in the physical sense [16,17]. y_i is generally defined as the occupation number of the lowest unoccupied natural orbital (LUNO) + $i(n_{\mathrm{LUNO}+i})$ [30,31]:

$$y_i = n_{\mathrm{LUNO}+i} \quad (i = 0, 1, 2, \ldots). \tag{1}$$

In the present case, since we have to consider multiple diradical characters for describing multiradical states, we employ the average diradical character y_{av}, which, for the system with $2n$ radical sites, is defined by the arithmetic average of the multiple diradical characters [28]:

$$y_{\mathrm{av}} = \frac{1}{n}\sum_{i=0}^{n-1} y_i. \tag{2}$$

Note that since we focus on the spin-flip effects on γ as a function of y_{av}, where y_{av} is evaluated for the singlet state, the high-spin-state system is assumed to have the same geometry as the singlet state.

To calculate the longitudinal component of static γ (referred to as γ hereafter), the finite-field (FF) approach [32] and the summation-over-states (SOS) approach [33] were employed. In the former, γ is evaluated as the fourth-order differentiation of the ground-state energy with respect to the external electric field, so that the FF approach can be straightforwardly applied to various strongly correlated first-principles methods. On the other hand, the latter method can clarify the contributions to γ of virtual excitation processes involving the ground and excited states. However, to achieve quantitative γ values it requires precise excitation energies, transition dipole moments, and dipole moment differences for a large number of excited states. On the basis of the perturbation theory, the SOS expression of γ reads for symmetric systems [34],

$$\gamma = \gamma^{\mathrm{II}} + \gamma^{\mathrm{III\text{-}2}} = -4\sum_{i,j}\frac{(\mu_{i0})^2(\mu_{j0})^2}{E_{i0}(E_{j0})^2} + 4\sum_{i\neq j\neq k}\frac{\mu_{0i}\mu_{ij}\mu_{jk}\mu_{k0}}{E_{i0}E_{j0}E_{k0}}, \tag{3}$$

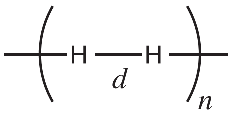

FIG. 1. Hydrogen chain model H_{2n} ($1 \leqslant n \leqslant 3$), where d and n denote the interatomic distance and the number of units, respectively.

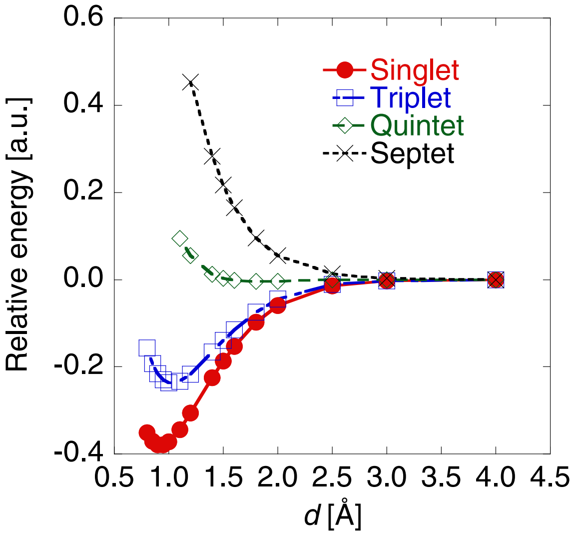

FIG. 2. Interatomic distance (d) dependences of the H_6 energy for different spin multiplicity. The singlet state with $d = 4.0$ Å is set as the reference (0 a.u.).

where E_{i0} denotes the excitation energy of the ith excited state and μ_{ij} [$i,j = 0$ (ground state), 1 (the first excited state), ...] is the transition moment along the longitudinal axis between the ith and the jth states. Note that the first term (γ^{II}) is negative and consists of virtual excitation between the ground and excited states and that the second term ($\gamma^{\mathrm{III\text{-}2}}$), which is usually positive, involves virtual excitation between excited states. In addition, the missing-state analysis [35] was employed to evaluate the contribution of each excited state to γ. According to the missing-state analysis, the dimensionless relative importance of the ith excited state to γ, σ_i, reads

$$\sigma_i = \frac{\gamma_{\mathrm{tot}} - \gamma_i}{\gamma_{\mathrm{tot}}}, \tag{4}$$

where γ_{tot} and γ_i denote the γ values obtained by the SOS calculation without state missing and with the ith excited state missing, respectively.

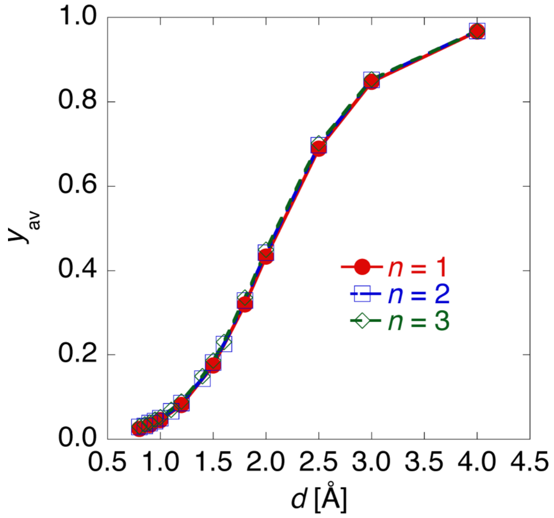

FIG. 3. Interatomic distance (d) dependences of the average diradical character y_{av}.

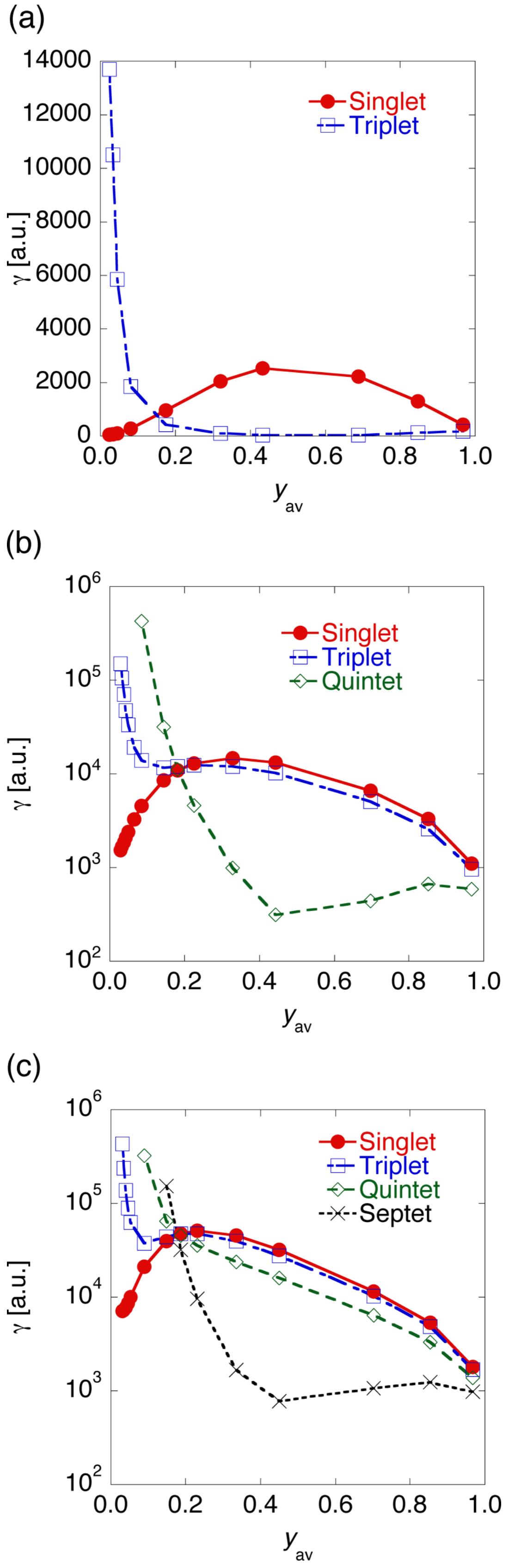

FIG. 4. Spin state and y_{av} dependences of γ for (a) H_2, (b) H_4, (c) H_6. Note for H_4 and H_6 that the vertical axis has a log scale. No converged values of γ are obtained for $d < 1.1$ Å in the quintet state for H_4 and H_6 and for $d < 1.2$ Å in the septet states for H_6.

B. Model and calculation methods

To investigate the spin state and open-shell character dependences of γ, H_{2n} ($1 \leqslant n \leqslant 3$) chains shown in Fig. 1 are adopted as model systems. Varying the interatomic distance d from 0.8 to 4.0 Å is expected to vary the diradical character (note here that by definition it is defined for the singlet state and the geometry is assumed to be the same for different spin states) over the whole range. The γ values are calculated by using both the FF and SOS approaches and the full configuration interaction (FCI) method. The (6)-31(+)+G(*)* basis set is employed because diffuse and polarization functions are necessary for a reliable description of both the excited states and γ. Indeed, the STO-3G minimal basis set and the (6)-31G(*)* double-zeta plus polarization basis set without diffuse functions give qualitatively different results from those of the (6)-31(+)+G(*)* basis set, which, on the other hand, reproduces semiquantitatively the results obtained with larger basis sets, aug-cc-pVDZ and aug-cc-pVTZ (see Fig. 4 and Fig. S1 in the Supplemental Material [36]). Due to limitation of computational resources, the SOS approach is only conducted for the H_4 system. All calculations were performed using the MOLPRO 2010.1 program package [37].

III. RESULTS AND DISCUSSION

A. Interatomic distance dependences of the electronic structures

Figure 2 shows the d dependence of the H_6 energy for different spin multiplicity. As d decreases, the higher-spin states get destabilized with respect to the singlet because of the nonbonding nature and the Pauli exclusion principle.

Figure 3 shows that as d increases, y_{av} monotonically increases from the nearly closed-shell region ($y_{av} \sim 0$) to the nearly pure open-shell region ($y_{av} \sim 1$) for all n. This implies that the increase of d modifies the electronic structure of the system from the weak to the strong correlation regime. Interestingly, changing n has little influence on the y_{av} versus d curve.

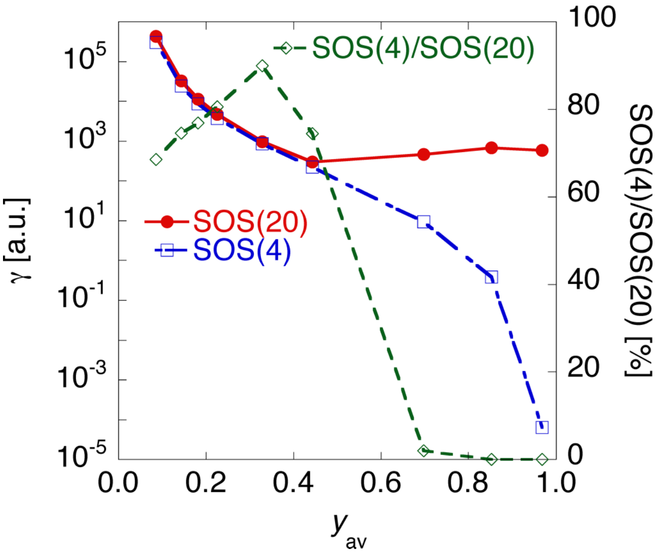

FIG. 5. y_{av} dependences of the SOS(20) and SOS(4) γ values for the quintet H_4 chain model. The SOS(4)/SOS(20) ratio is also shown.

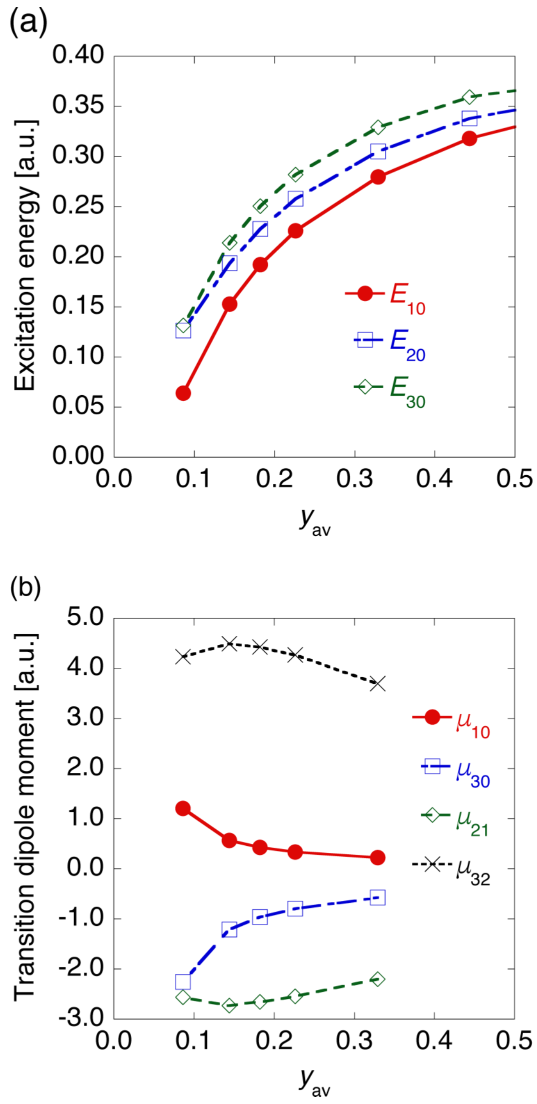

FIG. 6. y_{av} dependences of the excitation energies (a) and transition moments (b) for the lowest four states of the H_4 quintet state. Transition moments μ_{20} and μ_{31} are omitted from the plot because they vanish due to the symmetry.

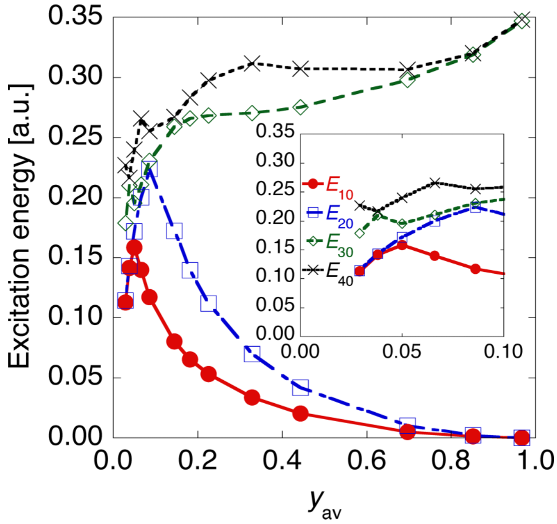

FIG. 8. y_{av} dependences of the lowest four excitation energies in the triplet state of the H_4 chain model. Magnified insets are also shown.

B. Spin state and y_{av} dependences of γ

Figure 4 shows the evolution of γ, obtained with the FF approach, as a function of y_{av} for different spin states. The singlet state has a maximum γ in the intermediate y_{av} region [at $y_{av} = 0.433$ $(n = 1)$, 0.329 $(n = 2)$, and 0.231 $(n = 3)$], which is consistent with the y-γ correlation observed in previous studies [7,8,13–20]. Then, the change from the singlet to the highest-spin state causes a gigantic enhancement of γ in the small y_{av} region, whereas γ decreases strongly with y_{av} and is negligible for $y_{av} > 0.2$. For the intermediate spin states ($n = 2$ and 3), γ combines the two effects, i.e., gigantic values in the nearly closed-shell region, a relatively lower peak or a shoulder in the intermediate open-shell region, and negligible values in the pure open-shell region. In addition, the increase in spin multiplicity moves the decrease of γ with y_{av} to larger y_{av} values.

Looking at the spin state dependence of γ, in the intermediate and large diradical character regions, the singlet state presents the largest γ and γ decreases with the spin

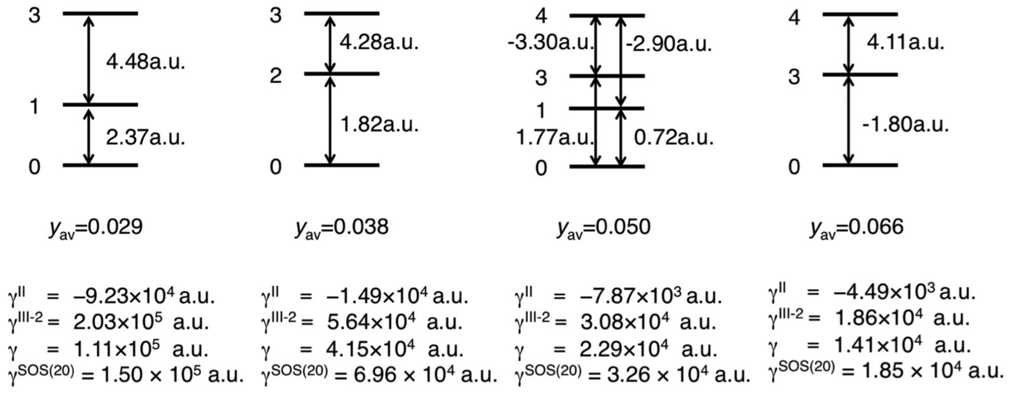

FIG. 7. Transition moments between the primarily contributing excited states of triplet H_4 in the nearly closed-shell region. Partitioned γ (γ^{II} and $\gamma^{III\text{-}2}$) as well as total and SOS(20) γ values are also shown.

multiplicity. This ordering is, however, reversed in the small y_{av} region.

C. Excitation energies and transition moments

To clarify these y_{av} dependences, the SOS approach including the lowest 20 states [referred to as SOS(20) hereafter] was adopted. It reproduces the FF γ values within an error of 15% except for the nearly pure open-shell region (Table S1 in the Supplemental Material [36]). Especially, the error is within 5% in the region where the γ value reaches a maximum value or varies drastically. In the nearly pure open-shell region, the absolute error remains small (less than 300 a.u.) as compared to the variance of the γ values in the whole y_{av} region. These allow using the missing-state analysis for unraveling the dominant excitation processes.

In the highest (quintet) -spin state, the three lowest-energy excited states dominate the γ response of H_4 in the nearly closed-shell ($y_{\mathrm{av}} \leqslant 0.329$) region. Indeed, the SOS approach including the ground state and these three excited states [referred to as SOS(4) hereafter] qualitatively reproduces the SOS(20) γ values (Fig. 5 and Table S2 in the Supplemental Material [36]). In this region, the properties responsible for the γ versus y_{av} behavior, i.e., rapidly varying with y_{av}, are the three excitation energies (E_{i0}) and the transition moments between the ground and excited states (μ_{i0}), while the transition moments between excited states (μ_{ij})($i,j \neq 0$) vary little despite their large amplitudes (Fig. 6).

Thus, according to Eq. (3), the enhancement of γ^{II} is stronger than that of $\gamma^{\mathrm{III\text{-}2}}$ because the μ_{i0} term appears at the fourth power in γ^{II} rather than second power in $\gamma^{\mathrm{III\text{-}2}}$. On

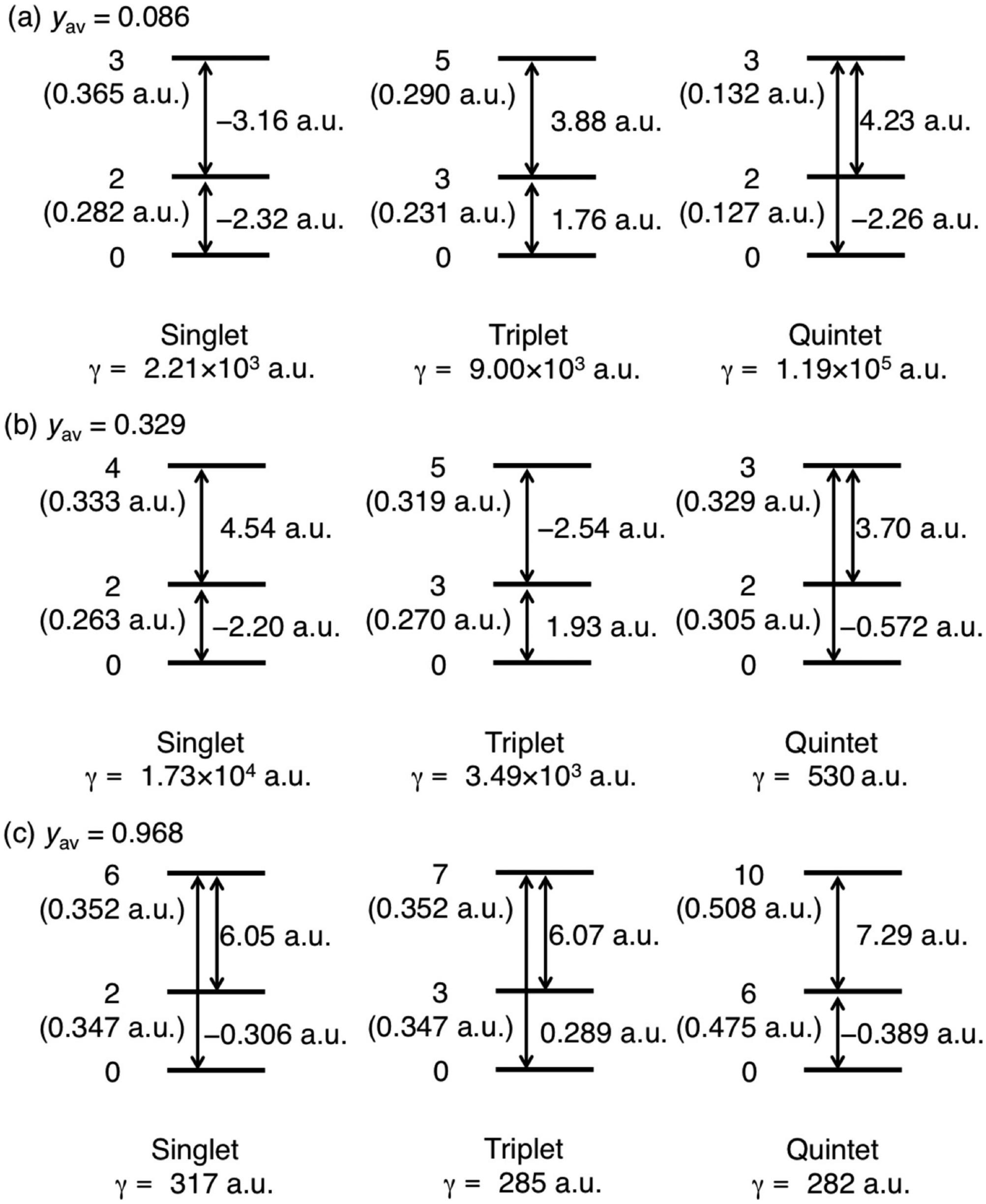

FIG. 9. Excitation energies, transition moments, and γ obtained by considering three states, which most contribute to γ in the nearly closed-shell region (a), in the intermediate open-shell region (b), and in the nearly pure open-shell region (c). Excitation energies are shown in parentheses while transition moments are shown with arrows connecting the states concerned.

the other hand, the decrease of the excitation energies (when approaching $y_{\mathrm{av}} = 0$) enhances both γ^{II} and $\gamma^{\mathrm{III\text{-}2}}$ but only $\gamma^{\mathrm{III\text{-}2}}$ for the second state since $\mu_{02} = 0$. Because of the larger amplitudes of μ_{ij} than of μ_{i0} as seen from Fig. 6(b), decrease of excitation energies causes more increase in amplitude of $\gamma^{\mathrm{III\text{-}2}}$ than of γ^{II}. In summary, the rapid increase of γ of the highest-spin state in the nearly closed-shell region is caused by the rapid decrease of the excitation energies with keeping the larger amplitudes of μ_{ij} than of μ_{i0}.

In the intermediate spin (triplet) state of the H_4 chain, the SOS calculation including the two or three most contributing excited states with $\sigma_i > 0.5$ can qualitatively (almost 60%) reproduce the SOS(20) γ values in the nearly closed-shell region ($y_{\mathrm{av}} < 0.08$) (Fig. 7 and Table S3 in the Supplemental Material [36]). Figure 8 shows the y_{av} dependences of the excitation energies of the lowest four excited states. As decreasing y_{av} in the nearly closed-shell region, the excitation energies rapidly decrease. On the other hand, μ_{ij} keeps a larger amplitude than μ_{i0} though the amplitudes of μ_{i0} do not vary dramatically. Therefore, the rapid increase of γ is attributed to the decrease of E_{i0} with keeping a larger amplitude of μ_{ij} than of μ_{i0}, similarly to what was observed for the highest-spin state.

Finally, we discuss the spin state dependences of γ for each open-shell region. We consider three y_{av} values: $y_{\mathrm{av}} =$ 0.086, 0.329, and 0.968 as representatives of nearly closed-shell, intermediate open-shell, and pure open-shell regions, respectively. The three-state approximation gives qualitative information about the spin state dependence of γ for each region though it does not quantitatively reproduce the result obtained by the SOS(20) calculation. Figure 9 shows the primarily contributing states selected using the missing-state analysis. In the nearly closed-shell region, γ increases in the order: singlet < triplet < quintet because the highest-spin state has the lowest excitation energies and the largest transition moments between excited states. In sharp contrast, in the intermediate open-shell region, γ increases in the order: quintet < triplet < singlet because the transition moments between the ground and excited states decrease by going from the singlet to triplet and then quintet states. In the nearly pure open-shell region, all spin states give nearly the same γ values but with significantly reduced amplitudes. This is attributed to the small transition moments between the ground state and excited state being similar to the case of the highest-spin state in the intermediate open-shell region, though they have large transition moment amplitudes between excited states.

IV. CONCLUSION

Spin state and open-shell character dependences on γ have been systematically investigated at the *ab initio* full configuration interaction level of approximation by considering hydrogen chain models. It is found that (i) in the nearly closed-shell region, higher-spin states exhibit much larger γ values than the singlet state; (ii) in the intermediate and large open-shell character regions, the singlet state presents the largest γ and γ decreases with the spin multiplicity; and (iii) in the pure open-shell region, all the spin states exhibit negligible γ values. The SOS approach including the primarily contributing excited states enables rationalizing these findings in terms of the excitation energies and transition moments. These results reveal that there are two types of molecular design guidelines for enhancing γ values based on tuning the open-shell character and the spin multiplicity: (a) for nearly closed-shell systems, increasing the spin multiplicity; and (b) for open-shell singlet systems, tuning the open-shell character to the intermediate region. It is also predicted in similar size systems that guideline (a) can enhance the γ amplitude more than guideline (b). In this context, although higher-spin states usually tend to be unstable in the nearly closed-shell region, there may exist a way that enables accessing such higher-spin states with the aid of, for example, singlet fission. Indeed, Liu *et al.* reported large optical nonlinearity induced by singlet fission [38]. The present results reveal the further potential of enhancing or tuning γ values of open-shell NLO molecular systems in high-spin states, and pave an alternative path to realizing highly active open-shell NLO materials.

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[36] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevA.94.042515 for y_{av} dependence of γ for the H_4 model at FCI/STO-3G, FCI/(6)-31G(*)*, FCI/aug-cc-pVDZ, and FCI/aug-cc-pVTZ level of theories, γ values for all spin states of H_4 chain calculated by the FF approach and the SOS(20) methods, relative importance of each excited state of the quintet state of H_4 chain by the missing-state analysis, and relative importance of each excited state of the triplet state of H_4 chain by the missing-state analysis.
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