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Theoretical study on the second hyperpolarizability of open-shell singlet one-dimensional systems with a charged defect

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Abstract

The longitudinal static second hyperpolarizability (γ) has been investigated for models (H_3^+ and H_5^+) open-shell singlet one-dimensional systems bearing a charged defect. Using various ab initio molecular orbital and density functional theory methods, the γ values of these cationic symmetric hydrogen chain models having different bond-length alternations (BLAs) are analyzed as a function of the average diradical character as well as by adopting the summation-over-states scheme. These systems exhibit negative γ values, of which the amplitudes increase nonlinearly with the average diradical character while the chain-length dependence is enhanced by increasing the BLAs. This dependence of γ with the diradical character is mostly dictated by the strong decrease of the excitation energies.

1. Introduction

Recently, using the hydrogen molecule under dissociation as a model we have proposed novel structure–property relationships for the second hyperpolarizability (γ): the γ value of singlet open-shell systems increases with the diradical character, attains a maximum in the intermediate diradical region, and then decreases [1–10]. Several π-conjugated systems have been proposed and studied theoretically while a first observation of large third-order nonlinear optical property enhancement for systems exhibiting an intermediate diradical character has just been reported in the case of two-photon absorption [11]. These systems therefore provide the possibility of controlling the γ values by adjusting the diradical character as well as the charge and the spin state [12]. We have further predicted that neutral singlet π-conjugated multiradical chains with small average diradical characters exhibit a large chain-length dependence of γ together with a significant enhancement of the γ values as compared to those of the neutral closed-shell π-conjugated chains with similar chain lengths [10].

On the other hand, it is well known that the introduction of charged defects into the closed-shell regular polyenes dramatically affects the signs, magnitudes, and chain-length dependences of γ [13–22]. In this study, we therefore investigate the longitudinal static γ values of symmetric singlet one-dimensional multiradical systems bearing a charged defect, H_3^+ and H_5^+, with different chain lengths and bond-length alternations (BLAs) using various ab initio molecular orbital (MO) and density functional theory (DFT) methods. These systems correspond to the singly oxidized states of the singlet π-conjugated multiradical systems. On the basis of the theoretical results, we clarify the effects of charged defects on the γ of symmetric singlet one-dimensional multiradical systems and analyze them

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in terms of their average diradical character. These analyses and structure–property relationships will further contribute to the elaboration of new diradical-based materials with third-order NLO properties.

2. Methodology

2.1. Model systems and average diradical character

Fig. 1 sketches the structures of the non-alternating H_3^+ diradical model (with bond distance r_0) (a), the non-alternating H_5^+ tetraradical model (with bond distance r_0) (b), and the symmetric H_5^+ alternating model (c). In the latter case the geometries are defined by two types of bond lengths, r_0 and r_1, with $r_1/r_0 = 1.0$, 1.2 and 1.5. For all systems, r_0 was varied from 1.0 to 4.0 Å so that the diradical character and γ values were tuned.

The diradical character is determined from spin-unrestricted Hartree–Fock (UHF) calculations. The diradical character y_i associated to the HOMO $- i$–LUMO $+ i$ transition is defined by the weight of the doubly-excited configuration in the multi-configurational (MC)-SCF theory and is formally expressed in the case of the spin-projected UHF (PUHF) theory as [23,24]

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}, \tag{1}$$

where T_i, the orbital overlap between the corresponding orbital pairs ($\chi_{\mathrm{HOMO}-i}$ and $\eta_{\mathrm{HOMO}-i}$), can also be represented by using the occupation numbers (n_i) of the UHF natural orbitals (UNOs):

$$T_i = \frac{n_{\mathrm{HOMO}-i} - n_{\mathrm{LUMO}+i}}{2}. \tag{2}$$

The diradical characters y_i using the UNO occupation numbers amount to 0 and 1 for closed-shell and pure diradical states, respectively. In case of H_5^+, we can consider two pairs of HOMO $- i$ and LUMO $+ i$ ($i = 0$ and 1), which provide two kinds of diradical characters, y_0 and y_1, respectively. We then employ their arithmetic average (y_{av}), which represents the average dissociation feature of the multiradical linear-chain systems.

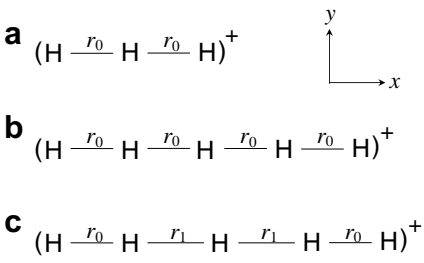


Fig. 1. Non-alternating H_3^+ model with bond distance r_0 (a), non-alternating H_5^+ model with bond distance r_0 (b), and symmetric alternating H_5^+ model with bond lengths r_0 and r_1 (c).

2.2. Virtual excitation processes of γ within the summation-over-state scheme

In the case of the effective three-state model composed of the ground (g), first (e1) and second (e2) excited states, the perturbative formula for the longitudinal γ component of symmetric systems can be described by the primary contributions of the type II (negative) and III-2 (positive) terms [25–28]

$$\gamma = \gamma^{\mathrm{II}} + \gamma^{\mathrm{III}-2} \approx -4\frac{(\mu_{\mathrm{g,e1}})^4}{(E_{\mathrm{e1,g}})^3} + 4\frac{(\mu_{\mathrm{g,e1}})^2(\mu_{\mathrm{e1,e2}})^2}{(E_{\mathrm{e1,g}})^2 E_{\mathrm{e2,g}}}, \tag{3}$$

where μ_{ij} and E_{ij} ($\equiv E_i - E_j$) represent the transition moment and excitation energy between states i and j, respectively. From this equation, we obtain the following relations dictating the sign of γ:

$$\left(\frac{E_{\mathrm{e2,g}}}{E_{\mathrm{e1,g}}}\right) < \left(\frac{\mu_{\mathrm{e1,e2}}}{\mu_{\mathrm{g,e1}}}\right)^2 \Rightarrow \gamma > 0, \tag{4}$$

$$\left(\frac{E_{\mathrm{e2,g}}}{E_{\mathrm{e1,g}}}\right) > \left(\frac{\mu_{\mathrm{e1,e2}}}{\mu_{\mathrm{g,e1}}}\right)^2 \Rightarrow \gamma < 0. \tag{5}$$

The neutral singlet multiradical linear chains previously studied [10] belong to the case described by Eq. (4).

2.3. Calculation methods

The longitudinal static electronic γ (γ_{xxxx}) values were calculated using the finite-field (FF) approach [29] and the (6)-31(+)+G$^{(*)*}$ basis set, which is able to reproduce the diradical character dependence of γ in H_2 calculated using more extended basis sets [10]. Various ab initio MO methods were employed: the spin-unrestricted (U) Hartree–Fock (HF), the UHF Møller–Plesset nth-order perturbation [UMPn ($n = 2$, 4)], the UHF coupled-cluster with single and double excitations (UCCSD) as well as with a perturbative treatment of the triple excitations [UCCSD(T)], the approximate spin-projection (APUHF, APUMPn) [30] and full-CI methods, together with DFT calculations adopting hybrid exchange-correlation functionals: UB3LYP and UBHandHLYP methods. All the calculations in this study are performed using the GAUSSIAN 03 [31] and GAMESS [32,33] program packages.

3. Results and discussion

3.1. Effect of the diradical character on the second hyperpolarizability of H_3^+ and H_5^+

In this section, for the H_3^+ and H_5^+ models, we investigate the relationship between the diradical character and the second hyperpolarizability, and analyze the impact of electron correlation. Adopting the full-CI approach, Fig. 2 displays the variation in γ values of non-alternating H_3^+ and alternating H_5^+ models ($r_1/r_0 = 1.0, 1.2$ and 1.5) in comparison with

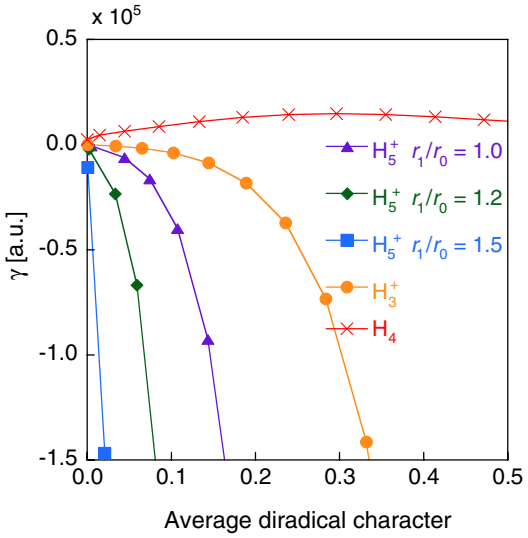
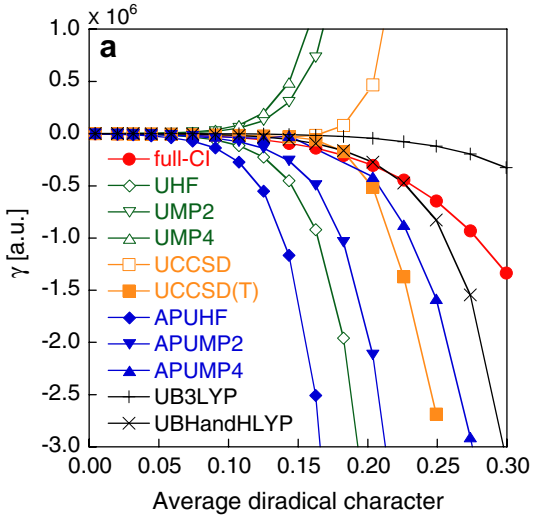


Fig. 2. Average diradical character dependence of γ [a.u.], calculated at the full-CI/(6)-31(+)+G$^{(*)*}$ level of approximation, for the non-alternating H_3^+ model, and H_5^+ models with different BLAs ($r_1/r_0 = 1.0$, 1.2, and 1.5) in comparison with the regular H_4 results [10].



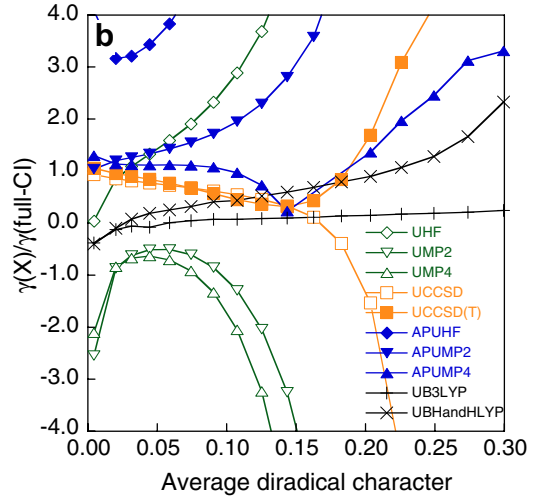


Fig. 3. Longitudinal γ values [a.u.] versus average diradical character y_{av} for non-alternating H_3^+ models (a) as well as the γ(X)/ γ(full-CI) ratios (b) calculated by various ab initio MO and DFT methods, X = UHF, UMPn and APUMPn ($n = 2$, 4), UCCSD, UCCSD(T), full-CI, UB3LYP, and UBHandHLYP.

the regular H_4 models as a function of the (average) diradical character, which is tuned by increasing continuously r_0 from 1.0 to 4.0 Å. In contrast to the neutral H_{2n} chains [10], non-alternating H_3^+ and H_5^+ models exhibit negative γ values, the amplitudes of which increase nonlinearly with y_{av}. The diradical character dependence is more enhanced for H_5^+ than H_3^+[γ(H_3^+ at $y_{av} = 0.20$)/γ(H_3^+ at $y_{av} = 0.10$) = 6.0 versus $\gamma(H_5^+, r_1/r_0 = 1.0$ at $y_{av} = 0.20)/\gamma(H_5^+, r_1/r_0 = 1.0$ at $y_{av} = 0.10) = 10$]. Furthermore, in contrast to the neutral H_{2n} case, increasing the BLA enhances the chain-length dependences of γ: symmetric H_5^+ chains with large BLAs exhibit larger γ amplitudes than those with small BLAs at the same y_{av} value. Compared to the γ values of neutral non-alternating tetraradical model H_4 ($\gamma_{max} = 1.47 \times 10^4$ a.u. at $y_{av} = 0.30$) [10], its iso-electronic non-alternating H_5^+ analogue provides a significant increase of γ by two orders of magnitude ($\gamma = -1.36 \times 10^6$ a.u. at $y_{av} = 0.30$).

Employing various ab initio MO and DFT methods listed in Section 2.3, Fig. 3 shows the variations of the γ values of the non-alternating H_5^+ model as a function of y_{av} as well as of their ratios with respect to the exact full-CI results. The UMP2 and UMP4 methods exhibit increasingly positive γ values when increasing y_{av} in the $y_{av} > 0.05$ region in contrast to the negative full-CI values. The APUMP2 and APUMP4 methods reproduce well the full-CI γ values in the small y_{av} region ($y_{av} < 0.12$), e.g., γ(APUMP4)/γ(full-CI) = 0.97 at $y_{av} = 0.11$, whereas it leads to significant overestimation in the large y_{av} region [γ(APUMP4)/γ(full-CI) = 2.0 at $y_{av} = 0.23$]. The UCCSD and UCCSD(T) methods reproduce the full-CI diradical character dependence of γ in the small y_{av} region ($y_{av} \leqslant 0.05$). For larger y_{av} values, the γ(UCCSD)/γ(full-CI) and γ(UCCSD(T))/γ(full-CI) ratios become too small, get close to zero for $y_{av} = 0.15$, and then suddenly increase substantially (Fig. 3b). Note the difference between UCCSD and UCCSD(T) since for the former γ changes sign. These comparisons highlight the substantial impact of electron correlation on the second hyperpolarizability of such charged multiradical species. The UHF, APUHF, UBHandHLYP, and UB3LYP methods correctly reproduce the increase in γ amplitude with y_{av} as well as its negative sign, though the amplitudes can be strongly overestimated or underestimated as a function of the y_{av} value. From comparing the UHF, UBHandHLYP, and UB3LYP results, increasing the amount of HF exchange in the exchange-correlation functional enhances the negative contribution to γ [see for example, $\gamma = -2.84 \times 10^4$ a.u. (UB3LYP), $\gamma = -1.63 \times 10^5$ a.u. (UBHandHLYP), $\gamma = -1.96 \times 10^6$ a.u. (UHF) with respect to $\gamma = -2.06 \times 10^5$ a.u. (full-CI) for $y_{av} = 0.183$]. Judging from these results, it is possible to

adjust the exchange-correlation functional in hybrid DFT methods to reproduce the diradical character dependences of γ of charged multiradical species calculated by the full-CI method though such hybrid DFT approach with a fixed weight of HF exchange functional will fail to provide reliable NLO properties for longer chain systems [34,35].

3.2. Analysis of the virtual excitation processes of γ using the full-CI method

The variation in γ of these charged models with the diradical character is then analyzed using the virtual excitation processes described in Section 2.2. This analysis is performed here using the full-CI results and the STO-3G basis set. Indeed, this minimal basis set is sufficient to reproduce the most important features of the variations of γ with diradical character and BLA. In particular, for H_5^+ models in the small y_{av} region, the γ(STO-3G)/γ((6)-31(+)+G$^{(*)*}$) ratio is very stable when varying the BLA: at $y_{av} = 0.200$, this ratio amounts to 0.66 for $r_1/r_0 = 1.0$ and to 0.68 for $r_1/r_0 = 1.2$. Although in the $y_{av} \leqslant 0.2$ region these ratios decrease rapidly, for $y_{av} > 0.2$, the variations in the ratios become modest. Furthermore, when varying the BLA, considering a y_{av} value of 0.20, the $\gamma(r_1/r_0 = 1.2)/\gamma(r_1/r_0 = 1.0)$ ratio amounts to 9.3 and 9.5 using the (6)-31(+)+G$^{(*)*}$ and STO-3G basis sets, respectively. Based on these results, we employ the STO-3G basis set in the analysis of the virtual excitation processes of γ because the remarkable change of γ are observed beyond $y_{av} = 0.2$ (see Fig. 4).

Figs. 4 and 5 show, for H_5^+ models ($r_1/r_0 = 1.0$ and 1.2), the average diradical character dependences of $E_{e1,g}$ and $E_{e2,g}$, and $\mu_{g,e1}$ and $\mu_{e1,e2}$, respectively, as well as the total γ and its type II and III contributions within the effective three state model, which almost reproduces the full-CI

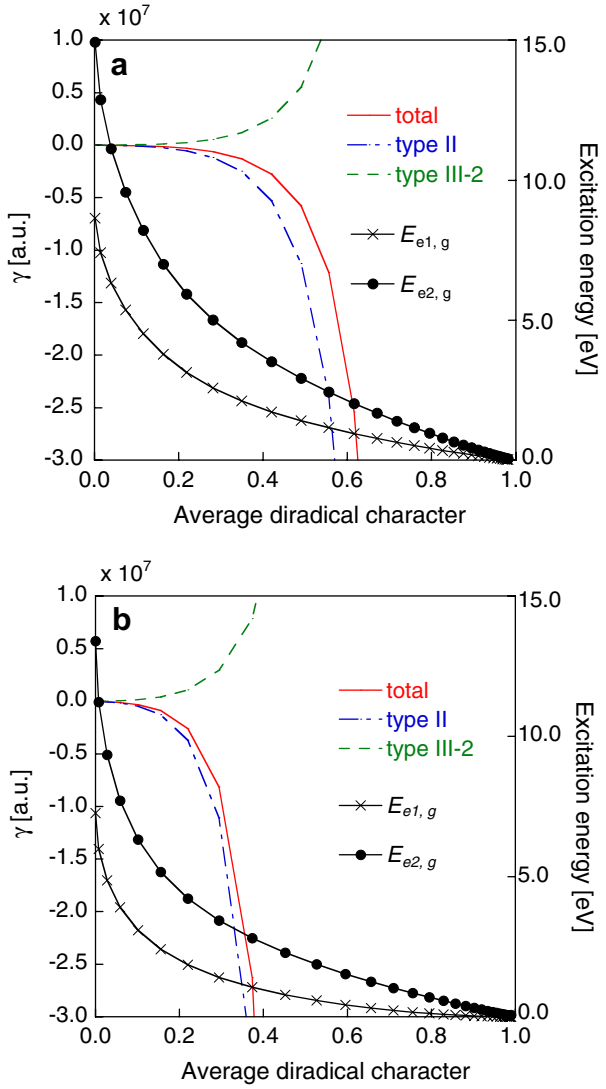


Fig. 4. Evolution of $E_{e1,g}$ and $E_{e2,g}$ [eV], of γ [a.u.] and its type II and III contributions with the average diradical character for H_5^+ models [$r_1/r_0 = 1.0$ (a) and $r_1/r_0 = 1.2$ (b)] determined at the full-CI/STO-3G level of approximation. The γ values are obtained within the three-state model.

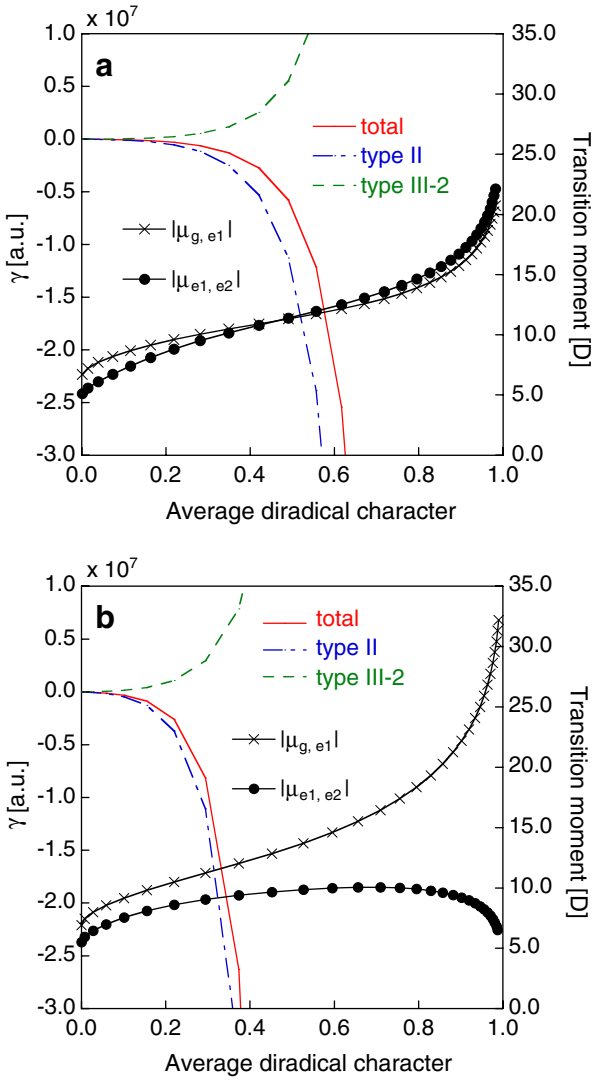


Fig. 5. Evolution $|\mu_{g,e1}|$ and $|\mu_{e1,e2}|$ [D], of γ [a.u.] and its type II and III contributions with the average diradical character for H_5^+ models [$r_1/r_0 = 1.0$ (a) and $r_1/r_0 = 1.2$ (b)] determined at the full-CI/STO-3G level of approximation.

(all-states) γ. The variation in total γ is found to be primarily described by the type II (negative) contribution corresponding therefore to the case described by Eq. (5) since $E_{e2,g}/E_{e1,g} > 1$ and $|\mu_{e1,e2}/\mu_{g,e1}| \approx 1$, in the small y_{av} region. Alternating ($r_1/r_0 = 1.2$) and non-alternating H_5^+ models exhibit similar variations in excitation energies and transition moments with y_{av}, though for alternating H_5^+ model the decrease of excitation energies is steeper at smaller y_{av} values and the difference between $|\mu_{g,e1}|$ and $|\mu_{e1,e2}|$ becomes large in the large y_{av} region. In order to determine the origin of the variations in γ with y_{av}, the variations in $(1/E_{e1,g})^3$ and $(\mu_{g,e1})^4$ are analyzed for different BLAs. So, for the non-alternating H_5^+ model, $[(1/E_{e1,g})^3$ at $y_{av} = 0.22]/[(1/E_{e1,g})^3$ at $y_{av} = 0.00] = 21$ and $[(\mu_{g,e1})^4$ at $y_{av} = 0.22]/[(\mu_{g,e1})^4$ at $y_{av} = 0.00] = 4.2$ while for the alternating H_5^+ model ($r_1/r_0 = 1.2$), $[(1/E_{e1,g})^3$ at $y_{av} = 0.22]/[(1/E_{e1,g})^3$ at $y_{av} = 0.00] = 60$ and $[(\mu_{g,e1})^4$ at $y_{av} = 0.22]/[(\mu_{g,e1})^4$ at $y_{av} = 0.00] = 5.3$. This indicates that the variations of type II, and therefore of the total γ, primarily originate in the decrease of excitation energies and furthermore, that varying the BLA has also mostly an impact on the excitation energies. Thus, as for doped conjugating polymers, the enhancement of the NLO response is related to an increasing metallic character.

4. Summary

We have investigated the static longitudinal γ of symmetric singlet multiradical hydrogen chains, H_3^+ and H_5^+, with a charged defect using various correlated ab initio MO and DFT methods. It turns out that the APUMP4 and UCC methods semi-quantitatively reproduce the diradical character dependences of γ calculated by the full-CI method in the small y_{av} region, i.e., $y_{av} \leqslant 0.11$ and $y_{av} \leqslant 0.05$, respectively, whereas the UBHandHLYP methods do in the region $0.15 \leqslant y_{av} \leqslant 0.25$. The introduction of a charged defect inverts the sign of γ and remarkably enhances the amplitudes as compared to neutral multiradical hydrogen chains. Moreover, the γ amplitude increases nonlinearly with the average diradical character while the bond-length alternation tends to enhance this behavior. This dependence of γ with the diradical character, analyzed using the summation-over-state formalism and the three-state approximation, has been traced back to the strong decrease of the excitation energies. Based on the present results, the introduction of a charged defect into multiradical chains with finite average diradical characters is expected to be an effective mean for enhancing γ and modulating its sign.

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