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Two-Photon Absorption and Second Hyperpolarizability of the Linear Quadrupolar Molecule

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The two-photon absorption (TPA) cross section and the second hyperpolarizability (γ) of the linear quadrupolar molecule are theoretically investigated by using the ab initio calculation methods for a few series of quadrupolar molecules. The relationships between the molecular structure and the TPA as well as the NLO property are established. It is found that, as the strengths of donors and acceptors increase, (i) both the energy gap between the first excited electronic state, |e>, and the ground electronic state, |g>, and that between the TPA-allowed excited electronic state |f> and |g> decrease, (ii) the energy gap difference, $|E_{fe} - E_{eg}|$, which is the detuning factor affecting the TPA matrix element, decreases, and (iii) the product of the transition dipole matrix elements, $|\mu^z_{fe}\mu^z_{eg}|$, associated with the TPA increases. These effects are combined to make the TPA cross section monotonically increase as the donor and acceptor strengths increase. The second hyperpolarizabilities of the same series of quadrupolar molecules are also calculated by using both the finite-field method and sum-over-state method. The relationship between the TPA and second hyperpolarizability is briefly discussed.

1. Introduction

Organic molecules with large two-photon absorption cross section have been found to be useful for a variety of applications such as three-dimensional optical storage,[1−3] two-photon fluorescence excitation microscopy,[4−8] and photodynamic therapy (PDT).[9] Therefore, it is quite important to understand the relationship between the molecular structure and the two-photon absorption cross section to provide a guideline for organic synthetic approach to a new development of the TPA chromophores and for further applications. On the basis of the observations by Albota et al., it was found that those molecules having large TPA cross section contain both donors and acceptors that are connected to each other via conjugated polyenes.[10] Furthermore, the molecules they considered have an inversion center such that they are often called quadrupolar molecules where two peripheral donors (acceptors) are connected to a central acceptor (donor). In parallel with the experimental and theoretical studies on the TPA process of the linear quadrupolar molecule, Kogej et al. presented a theoretical work on the mechanism for enhancement of TPA in donor−acceptor (push−pull) conjugated chromophores by using the quantum-chemical calculation method.[11] They found that, depending on the two-photon-accessed excited electronic state, the TPA cross section can be greatly enhanced by modifying the molecular structure maximizing the resonance enhancement effect. Also a systematic investigation of the TPA by combining design, synthesis, and characterization studies of highly active two-photon dyes was presented by Reinhardt et al. in ref 12. They considered two types of two-photon dyes, acceptor−donor−donor−acceptor and donor−bridge−acceptor, and found that some of the dyes they synthesized have TPA cross sections that are orders of magnitude higher than commercially available organic dyes.

Due to the molecular centrosymmetry, the second hyperpolarizability (γ) of the quadrupolar molecule is its first nonlinear optical property and has been studied recently. Particularly, Hahn et al. showed, by carrying out the quantum chemistry calculation with the finite-field method, that γ of the donor−acceptor−donor type of quadrupolar molecule monotonically increases as the strengths of the donor and acceptor increase.[13] In this article, we shall study this NLO property of a few more series of quadrupolar molecules by using both the finite-field and sum-over-state methods. There are three purposes of the latter investigation of γ. The first purpose is to confirm the general trend that γ of the linear quadrupolar molecules are monotonically dependent on the donor and acceptor strengths. The second purpose is to establish a qualitative relationship between the TPA cross section and the second hyperpolarizability. The third purpose is to test whether the sum-over-state calculation of γ with HF−SCI (6-31G basis set) is quantitatively reliable in comparison to the finite-field calculation of γ. Particularly, it is important to test whether the sum-over-state calculation of γ by obtaining required transition dipole matrix elements and energy eigenvalues at the HF−SCI level is quantitatively acceptable or not because the TPA matrix element will be calculated by using a similar sum-over-state expression. In section 2, the theoretical aspect of the two-photon absorption process is briefly summarized. The main ab initio calculation results of the TPA for a variety of quadrupolar molecules will be presented in section 3. The second hyperpolarizabilities of the same quadrupolar molecules will be presented in section 4, and the main results of this article will be summarized in section 5.

2. Two-Photon Absorption Cross Section

The calculation of the two-photon absorption cross section can be carried out by using the time-dependent perturbation theory, where the field-matter interaction Hamiltonian is given as

$$H_I = -\mu\cdot\{E_1(\mathbf{r},t) + E_2(\mathbf{r},t)\} \qquad (1)$$

Here, μ is the electric dipole operator and $E(\mathbf{r},t)$ is the transverse

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electric-field operator of the light beam. In this paper, a double-beam two-photon absorption will be considered first, and later the limiting case of the single-beam TPA will be discussed mainly to make a comparison with the relevant investigations reported recently. The frequencies of the two beams are denoted as ω_1 and ω_2. Then, the formal expression of the TPA absorption coefficient is well-known as[14]

$$\sigma_{TPA} = \frac{\pi}{2\epsilon_0^2 \hbar c^2}\left(\frac{N}{V}\right)\left(\frac{\omega_1\omega_2}{n_1 n_2}\right)\langle|\epsilon_2\cdot\Gamma_{TPA}\cdot\epsilon_1|^2\rangle\delta(\omega_1 + \omega_2 - \omega_f + \omega_g)\left(\frac{I_{10}}{\omega_1} - \frac{I_{20}}{\omega_2}\right) \quad (2)$$

where N/V is the number density of the chromophore, n_1 and n_2 are the refractive indices at the frequencies of ω_1 and ω_2, respectively. ϵ_1 and ϵ_2 are the unit polarization vectors of the two light beams. I_{10} and I_{20} are the incident beam intensities at the front boundary of the optical sample (see ref 14 for more detailed discussion on the derivation of eq 2 for a few limiting cases). The second-rank tensorial TPA matrix element, Γ_{TPA}, in eq 2 is given as

$$\Gamma_{TPA} = \frac{1}{\hbar}\sum_i\left(\frac{\mu_{fi}\mu_{ig}}{\omega_1 - (\omega_i - \omega_g)} + \frac{\mu_{gi}\mu_{if}}{\omega_2 - (\omega_i - \omega_g)}\right) \quad (3)$$

Here, the TPA transition from the ground state $|g>$ to the TP-allowed excited state $|f>$ was considered. $|i>$ is the molecular intermediate state, and the summation over i includes the ground and final states also. In eq 2, $\langle\cdots\rangle$ denotes the average over the molecular orientation. Although it was assumed that the electronic dephasing time constants are negligibly smaller than the frequency detuning factors $|\omega_1 - (\omega_i - \omega_g)|$ and $|\omega_2 - (\omega_i - \omega_g)|$, as the incident beam frequencies become close to $\omega_i - \omega_g$, the dephasing contribution should be inserted in the denominators of eq 3. However, in this paper, the case when the field frequencies are sufficiently off-resonant to the intermediate state will only be considered. Furthermore, for the single-beam experiment where the beam frequency is controlled to be the half of the energy gap between the ground state and TPA excited state, $|f>$, that is to say, $\omega_1 = \omega_2 = (\omega_f - \omega_g)/2$, eq 3 can be greatly simplified as

$$\Gamma_{TPA} = 4\sum_i\left(\frac{\mu_{fi}\mu_{ig}}{E_{fi} - E_{ig}}\right) \quad (4)$$

Assuming that the two incident beams are linearly polarized along the Z-direction in the laboratory frame, the orientation averaged σ_{TPA} of a single-beam TPA is found to be

$$\sigma_{TPA} \propto \frac{\pi}{2\epsilon_0^2 \hbar c^2}\left(\frac{N}{V}\right)\left(\frac{\omega_1^2}{n_1^2}\right)\left(\frac{9}{64}\left|\Gamma_{TPA}\right|^2\right) \quad (5)$$

where the constant 9/64 is from the orientation average, and $|\Gamma_{TPA}|$ was defined in eq 4.

3. ab Initio Calculation of the TPA Matrix Element

In this section, the ab initio calculation results of the TPA matrix element, Γ_{TPA}, will be presented for a few series of quadrupolar molecules. The principle goals of these calculations are to establish a structure-TPA-*cross*-section relationship for the linear quadrupolar molecules, to understand the underlying physics and to investigate the dependence of the TPA cross section on the conjugation length.

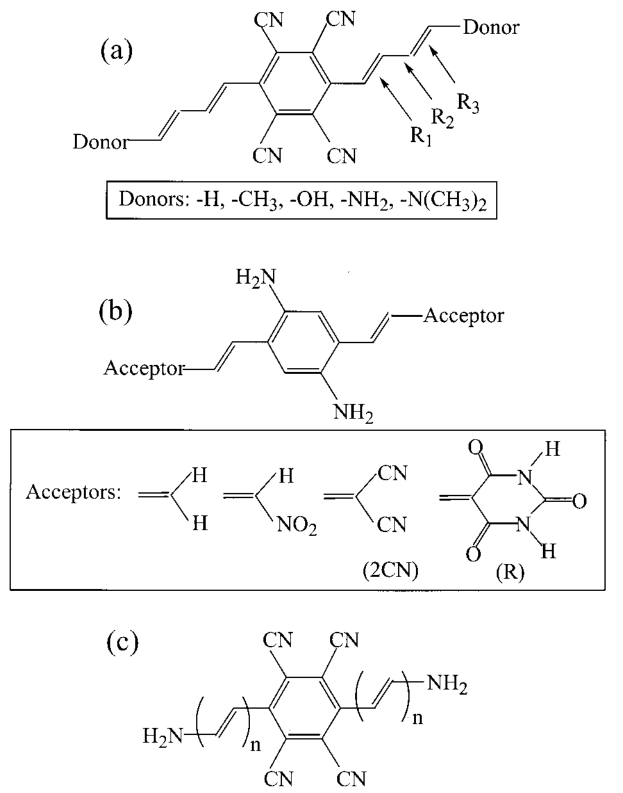

Figure 1. The three types of linear quadrupolar molecules considered in this article are shown. The donor−acceptor−donor (D−A−D) type molecules are drawn in Figure 1(a), where the donor varies from −H to −N(CH$_3$)$_2$. The bond-length-alternation is defined as $(R_1 + R_3)/2 - R_2$. The acceptor−donor−acceptor (A−D−A) type molecules are shown in Figure 1(b). In this case, the BLA is similarly defined as above. To investigate the polyene-length-dependence of the TPA matrix element, a series of molecules in Figure 1(c) will be considered in section 3.

For a one beam experiment, the Γ_{TPA} given in eq 4 can be calculated, once the associated transition dipole matrix elements and eigenvalues of the excited electronic states are determined by using the ab initio method. In general, the calculation of Γ_{TPA} involves a summation over the infinite number of intermediate states. However, it is convenient to make a three-state approximation, that is, to take into account only one dominant intermediate state, which is neither the ground nor the TPA state. Particularly, due to the centrosymmetry of the linear quadrupolar molecule, the first excited state |e>, which is the lowest dipole-allowed singlet state with large oscillator strength, is found to be the dominant intermediate state in the calculation of Γ_{TPA}, and thus, the approximated Γ_{TPA}, denoted as $\Gamma_{TPA}^{(1)}$, is given as

$$\Gamma_{TPA}^{(1)} = \frac{4\mu_{fe}\mu_{eg}}{E_{fe} - E_{eg}} \quad (6)$$

We shall also use the notation, $\Gamma_{TPA}^{(n)}$, to denote the TPA matrix element calculated by including n excited electronic states as the intermediate states in eq 4.

3-A. Bond-Length Alternation (BLA) vs TPA Matrix Element. In Figure 1(a) the donor−acceptor−donor (D−A−D) type quadrupolar molecules considered in this article are shown. Here, the central acceptor is a tetracyanobenzene, and the two peripheral donors vary from hydrogen to dimethylamino group. On the other hand, the (b) series of molecules in Figure

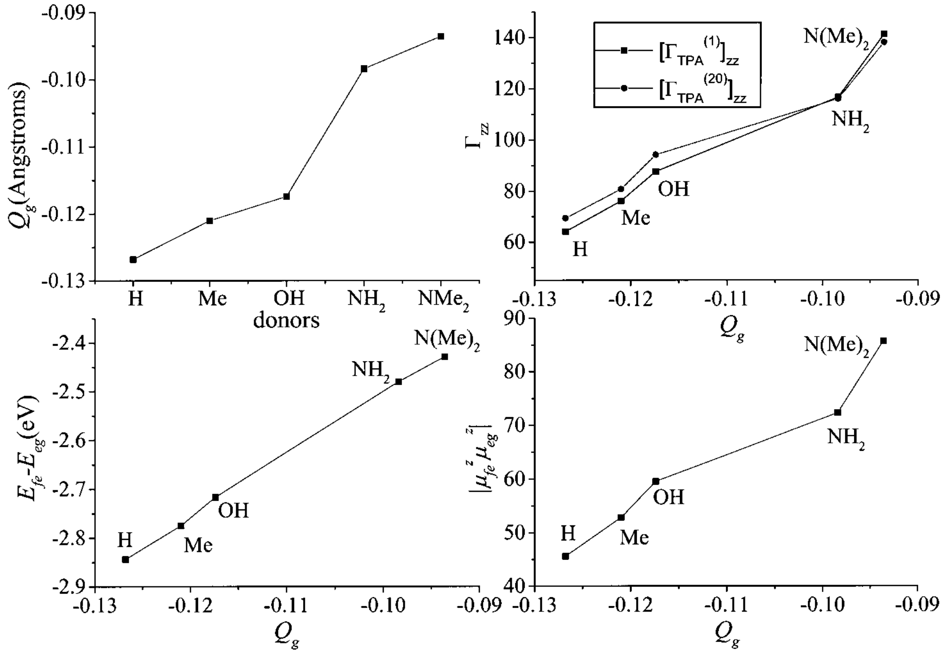

Figure 2. (a) The BLA, Q_g, values of the D$-$A$-$D type molecules in Figure 1(a) are plotted with respect to the substituted donor. (b) The calculated TPA matrix elements, $[\Gamma_{TPA}^{(n)}]_{zz}$ (for $n = 1$ and 20) in D^2/eV are plotted as a function of Q_g. (c) The energy (in eV) denominator in eq 6, $E_{fe} - E_{eg}$, vs Q_g. (d) $|\mu_{fe}^z \mu_{eg}^z|$ (in D^2) vs Q_g.

1 are acceptor$-$donor$-$acceptor (A$-$D$-$A) type. The central donor in this case is a diaminobenzene.

To characterize the molecular structure of the D$-$A$-$D or A$-$D$-$A type quadrupolar molecules, the concept of the bond-length alternation (BLA) will be used to analyze the ab initio calculation results. The BLA for this purpose in this article is defined as $(R_1 + R_3)/2 - R_2$ (see Figure 1 for the definitions of R_j). The BLA was used as a measure of the charge-transfer character of the push$-$pull polyene in its ground electronic state.[15−17] Likewise, the BLA of a single polyene bridge in a given quadrupolar molecule will also be considered to be a measure of the charge-transfer from the electron donors to the acceptors.

Let us first consider the D$-$A$-$D type molecules. By carrying out the ab initio HF$-$SCI (Hartree$-$Fock Singly excited Configuration Interaction) calculation with the 6-31G basis set in the Gaussian 94 and 98 programs,[18,19] the energy levels of twenty excited electronic states and the transition dipole matrix elements among them are fully calculated. The lowest excited electronic state is found to be one-photon allowed from the ground electronic state. In the case of the linear quadrupolar molecule, the lowest excited state is not a two-photon-allowed state due to the symmetry of its electronic structure. That is to say, the ground state has even-parity A_{1g}-symmetry, whereas the first excited state has odd-parity A_{1u}-symmetry. Thus, the two-photon absorption from A_{1g}-state to A_{1u}-state is not allowed because of the violation of the parity conservation rule. Thus, the TPA state should have A_{1g}-symmetry. In the cases of D$-$A-D type molecules, the third and fifth excited electronic states are found to be one-photon forbidden from the ground electronic state. Thus, the TP state could be either the third or fifth excited electronic states. It turns out that the TPA coefficient from $|g>$ to the third excited state is much larger than that from $|g>$ to the fifth excited state. Thus, the TPA process from $|g>$ to $|f>$, where $|f>$ is the third excited electronic state in the cases of D$-$A$-$D type molecules, will be studied in detail.

From the optimized structures of the D$-$A$-$D molecules, the BLA, Q_g, can be estimated and they are plotted in Figure 2(a) for a few substituents (see Table 1). As the donor strength increases from H to N(Me)$_2$, the CT-character increases and thus Q_g increases. Also, the energy gaps, E_{eg} and E_{fg}, decrease (Table 1). As the strength of the peripheral donors increases, the magnitudes of the two transition dipole matrix elements, $|\mu_{eg}^z|$ and $|\mu_{fe}^z|$, increase (see Table 1). Now the calculated $[\Gamma_{TPA}^{(n)}]_{zz}$, for $n = 1$, 5, 10, 15, and 20, are presented in Table 2 and particularly the one-intermediate-state-approximated $[\Gamma_{TPA}^{(1)}]_{zz}$ and $[\Gamma_{TPA}^{(20)}]_{zz}$ are plotted in Figure 2(b) as a function of Q_g. Here, it should be emphasized that the one-intermediate-state-approximated value, $[\Gamma_{TPA}^{(1)}]_{zz}$, is quantitatively similar to $[\Gamma_{TPA}^{(20)}]_{zz}$. Most of the other cases studied in this paper show that the deviation of $[\Gamma_{TPA}^{(1)}]_{zz}$ from $[\Gamma_{TPA}^{(20)}]_{zz}$ is less than 10%. However, the convergence of the calculated $[\Gamma_{TPA}]_{zz}$ by taking into account a large number of excited-state contributions should be investigated further. To address this convergence problem, two representative quadrupolar molecules are chosen, i.e, D$-$A$-$D type molecule with D=H and A$-$D$-$A type molecule with A=H. The number of excited states considered is sixty and the calculated $[\Gamma_{TPA}^{(40)}]_{zz}$ and $[\Gamma_{TPA}^{(60)}]_{zz}$ for these two molecules are given in Tables 2 and 4 (see the seventh and eighth columns of these two tables). We found that the values $[\Gamma_{TPA}^{(60)}]_{zz}$ for these two molecules are quantitatively similar to $[\Gamma_{TPA}^{(20)}]_{zz}$ so that the calculated values $[\Gamma_{TPA}^{(20)}]_{zz}$ for other molecules are likely to be close to the converged values.

TABLE 1: BLA (Q_g), Energy Gaps, E_{eg} and E_{fg}, in EV, and the z-components of the Two Transition Dipole Matrix Elements in D(Debye) of the Donor$-$Acceptor$-$Donor Type of Quadrupolar Molecules Shown in Figure 1(a) (6-31G)

donor	BLA, Q_g, (Å)	E_{eg} (eV)	E_{fg} (eV)	$|\mu_{eg}^z|$ (D)	$|\mu_{fe}^z|$ (D)
$-$H	$-$0.1268	4.27	5.69	7.95	5.74
$-$Me	$-$0.1210	4.14	5.51	8.58	6.16
$-$OH	$-$0.1174	4.09	5.46	8.15	7.31
$-$NH$_2$	$-$0.0984	3.79	5.11	8.17	8.85
$-$N(Me)$_2$	$-$0.0936	3.66	4.90	9.78	8.77

The TPA matrix elements, both $[\Gamma_{TPA}^{(1)}]_{zz}$ and $[\Gamma_{TPA}^{(20)}]_{zz}$, increase as the CT-character (or BLA value) increases. To provide

TABLE 2: TPA Transition Matrix Elements, $[\Gamma^{(n)}_{TPA}]_{zz}$ (for $n = 1$, 5, 10, 15, and 20) in D^2/EV, for the D−A−D Molecules (6-31G)

donor	$[\Gamma^{(1)}_{TPA}]_{zz}$	$[\Gamma^{(5)}_{TPA}]_{zz}$	$[\Gamma^{(10)}_{TPA}]_{zz}$	$[\Gamma^{(15)}_{TPA}]_{zz}$	$[\Gamma^{(20)}_{TPA}]_{zz}$	$[\Gamma^{(40)}_{TPA}]_{zz}$	$[\Gamma^{(60)}_{TPA}]_{zz}$
−H	64.2	78.6	77.8	78.7	69.5	70.9	70.6
−Me	76.2	90.7	89.9	91.1	80.8		
−OH	87.6	104	103	105	94.2		
$-NH_2$	117	126	125	127	116		
$-N(Me)_2$	141	150	151	150	138		

TABLE 3: BLA (Q_g), the Energy Gaps, E_{eg} and E_{fg}, in EV, and the z-components of the Two Transition Dipole Matrix Elements in D(Debye) of the Acceptor−Donor−Acceptor Type of Quadrupolar Molecules Shown in Figure 1(b) (6-31G)

acceptor	BLA, Q_g, (Å)	E_{eg} (eV)	E_{fg} (eV)	$\|\mu^z_{eg}\|$ (D)	$\|\mu^z_{fe}\|$ (D)
−H	−0.1280	4.17	6.79	9.61	12.3
$-NO_2$	−0.1129	3.66	5.90	11.1	11.2
−CN	−0.0981	3.52	5.73	11.4	11.9
−R	−0.0876	3.35	5.51	12.1	11.7

a detailed picture of what is behind this phenomenon, the energy denominator, $E_{fe} - E_{eg}$, and $|\mu^z_{fe}\mu^z_{eg}|$ are separately plotted with respect to Q_g in Figure 2(c) and 2(d), respectively. The product of the two transition dipole moments (the energy difference between E_{fe} and E_{eg}) increases (decreases) as the donor strength increases. This pattern was also observed in a series of experimental and theoretical investigations carried out by Albota et al.[10] Here, it is found that the energy denominator factor changes about 15% as the donor strength changes, whereas the product of the transition dipole moments increases by almost 2-fold in magnitude. Therefore, the principle effect of the substitution of a stronger donor on the TPA cross section is to increase the associated transition dipole matrix elements for a series of molecules in Figure 1(a). This confirms the observation made in refs 10 and 11 that *the charge transfer from the peripheral donors to the central acceptor plays the dominant role in determining the magnitude of TPA cross section*.

In Figure 3(a), the calculated Q_g values for a series of A−D−A type quadrupolar molecules in Figure 1(b) are plotted. The calculated values of E_{eg}, E_{fg}, $|\mu^z_{eg}|$, and $|\mu^z_{fe}|$ are presented in Tables 3. $[\Gamma^{(n)}_{TPA}]_{zz}$ for the series of A−D−A molecules also exhibit the same increasing patterns with respect to the acceptor strength (see Figure 3(b) and Table 4). $E_{fe} - E_{eg}$ and $|\mu^z_{fe}\mu^z_{eg}|$ with respect to BLA are shown in Figure 3(c) and 3(d), respectively, and the same trends are found in this case of A−D−A molecules.

On the basis of these calculations, it is concluded that, as the electron donating or accepting ability of the substituent increase, (*i*) *both the energy gap between the first excited state and the ground state and that between the target TPA state and the ground state decrease*, (*ii*) *the energy gap difference*, $E_{fe} - E_{eg}$, *decreases, and* (*iii*) *the product of transition dipole matrix elements*, $|\mu^z_{fe}\mu^z_{eg}|$, *associated with the TPA increases*. A combination of these three aspects makes the TPA cross section monotonically increase by the stronger donors and acceptors.

3-B. Chain-Length Dependence of the TPA Cross Section: Saturation Phenomenon. It was recently shown that the second hyperpolarizability of lengthy conjugated polyene molecule increases as the polyene chain length increases and approaches to an asymptotic value.[20−23] Likewise, it is expected that the TPA cross section would exhibit a similar pattern because the TPA cross section is related to the imaginary part of the second hyperpolarizability.[11] To study the chain-length dependence of the TPA cross section, a series of molecules in Figure 1(c) with varying number of double bonds is considered. The ab initio calculation results show that, as the number of double bonds, n, in one of the two polyene branches increases from 2 to 8, the BLA of a single branch decreases from −0.0984 to −0.110 Å (see Figure 4(a) and Table 5). Although the magnitude of the BLA change is relatively small, this phenomenon can be understood by noting that, as the conjugated polyene bridge length increases, the extent of the charge transfer from donors to central acceptor decreases so that the BLA, which is a measure of the π-electron delocalization, negatively increase.

Second, the electronic energies of the first excited state |e> and the TPA excited state |f> are plotted as a function of n in Figure 4(b) (see Table 5). As the chain length increases, the energy differences, both E_{eg} and E_{fg}, decrease, and the oscillator strengths or transition dipole moments show nonmonotonic behaviors. Now the energy denominator in eq 6, that is $E_{fe} - E_{eg}$, is found to slightly decrease from −2.48 to −2.71 eV (see Figure 5(c)) as n increases. However, the first transition dipole matrix element, $|\mu^z_{eg}|$, between |g> and |e> increases almost 3 times as the chain length increases from $n = 2$ to 8. It is found that this dramatic increase of $|\mu^z_{eg}|$ is largely responsible for the overall increase of the TPA matrix element. We also note that, due to the nonmonotonic change of $|\mu^z_{fe}\mu^z_{eg}|$ drawn in Figure 4(d), the approximated $[\Gamma^{(5)}_{TPA}]_{zz}$ exhibits a turn-over behavior as the number of double bonds increases (see Figure 5). Here, it should be mentioned that the HF-SCI calculation method used in this article does not take into account the electron correlation effects at all. The correlation effects can change the hyperpolarizability and presumably the two-photon cross-section significantly, but it usually does not change the overall trend. Thus, at this moment, it is not clear whether this turn-over behavior is genuine or originates from the neglect of the electron correlation effects. Thus, a more thorough investigation with higher-level ab initio calculation methods is required to draw a definite conclusion on the chain-length-dependence of the TPA cross section. Perhaps, the approximation, that only a few excited states are taken into account to calculate Γ_{TPA}, is not suitable for such a lengthy quadrupolar molecule. In this regard, the theoretical work by McWilliams, Hayden, and Soos who carried out one-dimensional Huckel, Hubbard, and Pariser−Parr−Pople models, can be modified to study the chain-length-dependence of the quadrupolar molecules.[24]

4. Second Hyperpolarizabilities of Linear Quadrupolar Molecules

In this section, the second hyperpolarizabilities (γ) of the linear quadrupolar molecules are calculated by using two different methods, e.g., the finite-field method and the sum-over-state method. In ref 13, Hahn et al. carried out ab initio calculation of a series of quadrupolar molecules that are Donor−Acceptor−Donor type and showed that γ increases as the donor and acceptor strengths increase. As will be shown below, it is found that the trend observed in ref 13 is generally acceptable for a variety of quadrupolar molecules, both D−A−D and A−D−A types.

First of all, the finite-field-calculated γ_{zzzz}, denoted as γ_{FF}, for the two distinctive types of quadrupolar molecules are

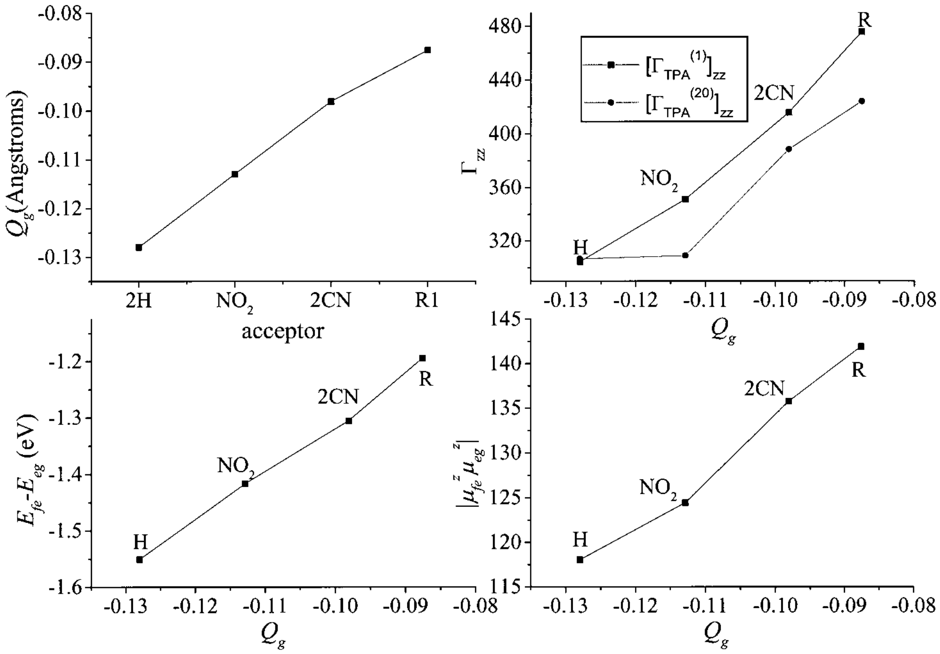

Figure 3. (a) The BLA, Q_g, values of the A−D−A type molecules in Figure 1(b) are plotted with respect to the substituted acceptor. (b) $[\Gamma^{(n)}_{TPA}]_{zz}$ ($n = 1$ and 20) vs Q_g. (c) $E_{fe} - E_{eg}$, vs Q_g. (d) $|\mu^z_{fe}\mu^z_{eg}|$ vs Q_g. The units are the same as Figure 2.

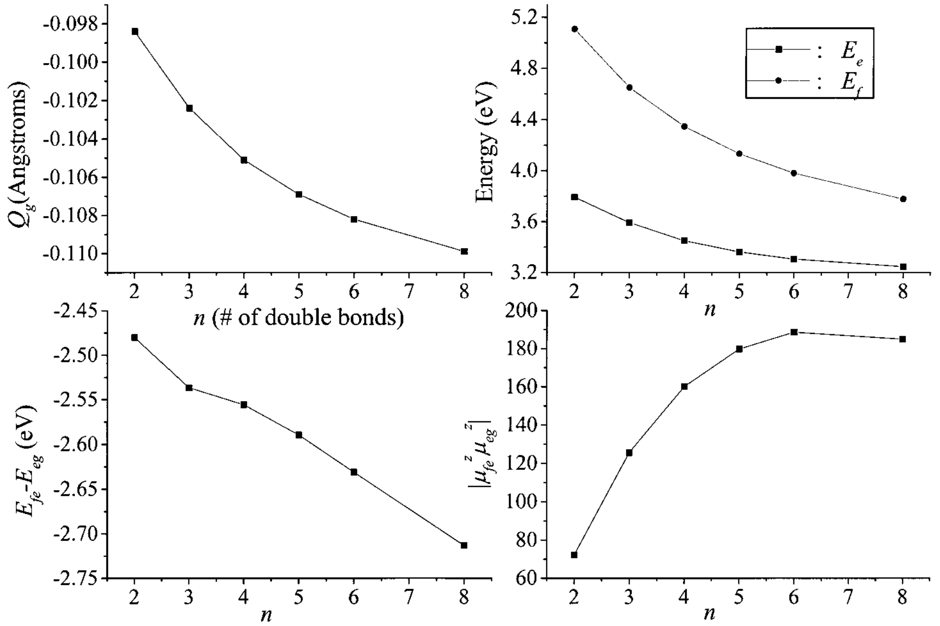

Figure 4. The calculated BLA, Q_g, value as a function of the number of double bonds, n, is shown in Figure 4(a). The relative energies of the first excited state, $|e\rangle$, and the TP-absorbing excited state, $|f\rangle$, are plotted with respect to n in Figure 4(b). The energy denominator of eq 6, $E_{fe} - E_{eg}$, vs n is plotted in Figure 4(c), and $|\mu^z_{fe}\mu^z_{eg}|$ vs n is in 4(d).

TABLE 4: TPA Transition Matrix Elements, $[\Gamma^{(n)}_{TPA}]_{zz}$ (for $n = 1$, 5, 10, 15, and 20) in D²/EV, for the A−D-A Molecules (6-31G)

acceptor	$[\Gamma^{(1)}_{TPA}]_{zz}$	$[\Gamma^{(5)}_{TPA}]_{zz}$	$[\Gamma^{(10)}_{TPA}]_{zz}$	$[\Gamma^{(15)}_{TPA}]_{zz}$	$[\Gamma^{(20)}_{TPA}]_{zz}$	$[\Gamma^{(40)}_{TPA}]_{zz}$	$[\Gamma^{(60)}_{TPA}]_{zz}$
−H	305	302	314	315	307	307	307
$-NO_2$	351	318	304	305	309		
−CN	416	384	387	388	389		
−R	476	436	427	429	424		

presented in Tables 7 and 8. Both 3-21G and 6-31G basis sets in GAMESS[25] program were used to calculate γ_{FF}. γ_{FF}'s of both the D−A−D and A−D−A quadrupolar molecules exhibit increasing patterns as the strengths of the substituted donor and acceptor increases. For instance, by replacing the hydrogen atom for the D−A-D molecule with dimethylamine γ_{FF} increases by three and half times. Since the finite-field method does not require any detailed calculation of the electronically excited state wave functions, it is a convenient procedure to obtain various NLO properties. However, since in this article the sum-over-state expression for the TPA matrix element was used, we find it necessary to independently test whether the HF−SCI calculated excited electronic state wave functions are quantitatively reliable or not. This can be achieved by carrying out sum-over-

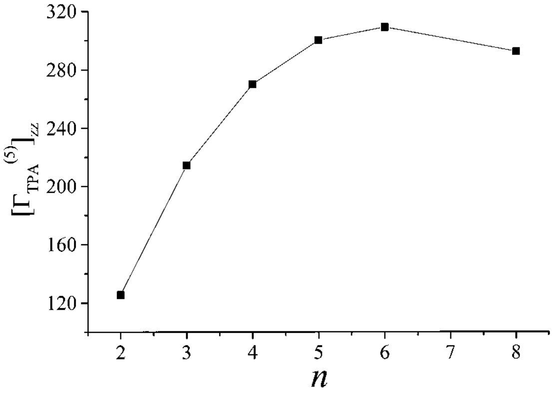

Figure 5. $[\Gamma^{(5)}_{TPA}]_{zz}$ of the series of molecules in Figure 1(c) is plotted as a function of n.

TABLE 5: BLA (Q_g), the Energy Gaps, E_{eg} and E_{fg}, in EV, and the z-components of the Two Transition Dipole Matrix Elements in Debye of a Series of Molecules shown in Figure 1(c) for Varying Number of Double Bonds (6-31G)

n	BLA, Q_g, (Å)	E_{eg} (eV)	E_{fg} (eV)	$\lvert\mu^z_{eg}\rvert$ (D)	$\lvert\mu^z_{fe}\rvert$ (D)
2	−0.0984	3.79	5.11	8.17	8.85
3	−0.1024	3.59	4.65	13.6	9.23
4	−0.1051	3.45	4.35	16.6	9.61
5	−0.1069	3.36	4.13	18.9	9.51
6	−0.1082	3.31	3.98	20.8	9.07
8	−0.1099	3.25	3.78	24.0	7.70

TABLE 6: TPA Transition Matrix Elements, $[\Gamma^{(1)}_{TPA}]_{zz}$ and $[\Gamma^{(5)}_{TPA}]_{zz}$ of the Molecules in Figure 1(c) (6-31G)

N	$[\Gamma^{(1)}_{TPA}]_{zz}$ (D^2/eV)	$[\Gamma^{(5)}_{TPA}]_{zz}$ (D^2/eV)
2	117	126
3	198	214
4	250	270
5	278	300
6	287	309
8	273	292

state calculation of γ_{zzzz} by using the ab initio calculated transition dipole matrix elements and energy eigenvalues used in the calculation of the TPA matrix element. The sum-over-state expression of γ is given as

$$\gamma_{zzzz} = 24 \times \left\{ -\sum_{m,n,p} \frac{(\mu_z)_{gm}(\mu_z)_{mn}(\mu_z)_{np}(\mu_z)_{pg}}{E_{mg}E_{ng}E_{pg}} + \sum_{m,n} \frac{|(\mu_z)_{gm}|^2|(\mu_z)_{gn}|^2}{E_{mg}(E_{ng})^2} \right\} \tag{7}$$

The multiplication factor 24 originates from the number of permutations of the indices. The first term represents the sum over the pathways involving a sequential optical transitions, e.g., |g> → |p> → |n> → |m> → |g>, whereas the second term corresponds to the contributions from the following sequence of optical transitions, |g> → |n> → |g> → |m> → |g>. The difference between the two terms is whether the sequential transition pathway involves the ground electronic state or not.

In Tables 7 and 8, the sum-over-state calculated γ_{zzzz} for the D−A−D and A−D−A types of linear quadrupolar molecules are presented. Here, $\gamma^{(n)}$ denotes the γ_{zzzz} value calculated by using n electronically excited states for the summation in eq 7. For example, $\gamma^{(2)}$ is the case when the two excited states, $|e>$ and $|f>$, are only taken into account for the calculation of γ_{zzzz} with eq 7. It is noted that the sum-over-state $\gamma^{(n)}$ depends on n to some extent. However, they are quantitatively similar to one another and the finite-field-calculated γ_{FF} is close to $\gamma^{(20)}$. Even though $\gamma^{(2)}$ is found to be approximately twice of γ_{FF}, the general increasing trend with respect to the donor and acceptor strengths is unchanged. Thus, one of the goals of this investigation, confirming the general trend found in ref 13, is believed to be achieved.

The sum-over-state expression for $\gamma^{(n)}$ consists of two terms, and the first and second terms are negative and positive, respectively. Thus, $\gamma^{(n)}$ can be written as

$$\gamma^{(n)} = \gamma^{(n)}_N + \gamma^{(n)}_P \tag{8}$$

where $\gamma^{(n)}_N$ and $\gamma^{(n)}_P$ represents the first and second terms in eq 7, respectively. These two contributions are separately calculated for $n = 20$ $\gamma^{(20)}_N$ and $\gamma^{(20)}_P$; the two series of quadrupolar molecules are presented in Tables 7 and 8. The two contributions are quantitatively comparable so that the interference of the two pathways is found to be crucial.

Now, the chain-length dependence of γ, by using both the sum-over-state and finite-field methods, is investigated, and the ab initio calculation results are summarized in Table 9. Assuming that the benzene ring provides two double bonds, the total number of double bonds, denoted as N, in the series of molecules in Figure 1(c) varies from 6 to 18. Within this range of conjugation length, there is no simple N^{α}-dependence where the exponent α is a constant.[21] However, in the short chain-length region, γ roughly increases as N,[4] and in the long chain-length region from $N = 14$ to 18, γ exhibits approximately N^2-dependence. Due to the expensive computational cost, the total number of excited states considered in the summation, eq 7, is limited to be five. Nevertheless, the finite-field calculation results are quantitatively similar to the sum-over-state results, $\gamma^{(5)}$. Also, the negative and positive contributions, $\gamma^{(5)}_N$ and $\gamma^{(5)}_P$, are found to be similar for the quadrupolar molecules with short conjugation length. However, the positive contribution, $\gamma^{(5)}_P$, becomes dominant as the chain-length increases.

On the basis of the sum-over-state expressions, eqs 4 and 7, respectively, for the TPA matrix element and the second hyperpolarizability, these two quantities are not directly related to each other, even though the molecular parameters determining these two properties, e.g., transition dipole moments and energies of the electronic states, are actually the same. Also it should be pointed out that the static second hyperpolarizability, γ, at zero frequency, is a real quantity, whereas the TPA cross section is related to the imaginary part of γ for the frequency corresponding to the two-photon resonance.[11] Therefore, there is no a priori reason that the two properties are quantitatively related to each other. However, due to their monotonically increasing behaviors observed in the above calculations, we found that the square of $[\Gamma^{(n)}_{TPA}]_{zz}$ is approximately proportional to γ_{FF} (or $\gamma^{(n)}$). Thus, for the linear quadrupolar molecules, it is possible to suggest that the magnitude of the second hyperpolarizability can be a measure of the TPA cross section.

Before we close this section, it should be mentioned that the basis set 6-31G used in this article ignores the effect associated with the diffuse functions. As discussed in ref 26, there is not nearly as much agreement on which basis set is adequate for excited states as for ground states. If there are low-lying Rydberg states that are missing, one can get a distorted picture. To partially take into account this effect, for a single quadrupolar molecule, e.g., acceptor−donor−acceptor type molecule with acceptor═H, we carry out a series of calculations with 6-31+G-

TABLE 7: Second Hyperpolarizability, γ_{zzzz} ($\times$ 10^{-34} *esu*), of the Donor−Acceptor−Donor Type of Quadrupolar Molecules[a]

donor	γ_{FF}^{3-21}	γ_{FF}^{6-31}	$\gamma^{(2)}$	$\gamma^{(3)}$	$\gamma^{(5)}$	$\gamma^{(15)}$	$\gamma^{(20)}$	$\gamma_N^{(20)}$	$\gamma_P^{(20)}$
−H	3.81	4.20	5.64	4.37	11.27	2.40	5.46	−9.58	15.04
−Me	5.43	6.13	8.82	6.92	15.13	3.91	7.79	−12.12	19.91
−OH	5.67	5.99	9.05	6.53	13.80	2.72	7.36	−12.60	19.96
$-NH_2$	8.28	8.82	17.40	13.26	21.40	7.53	12.22	−18.59	30.81
$-N(Me)_2$	13.34	14.3	27.65	21.23	31.19	12.05	18.42	−24.98	43.40

[a] γ_{FF} denotes the second hyperpolarizability calculated by using the finite-field method with the GAMESS program. γ_{FF}^{3-21} and γ_{FF}^{6-31} denote the γ_{FF} -values calculated with basis sets, 3-21G and 6-31G in GAMESS, respectively. $\gamma^{(n)}$ is obtained by using the sum-over-state expression, eq 7, with *n* excited electronic states in the summation (6-31G basis set in Gaussian 98 was used).

TABLE 8: Second Hyperpolarizability, γ_{zzzz} ($\times$ 10^{-34} *esu*), of the Acceptor−Donor−Acceptor Type of Quadrupolar Molecules[a]

acceptor	γ_{FF}^{3-21}	γ_{FF}^{6-31}	$\gamma^{(2)}$	$\gamma^{(3)}$	$\gamma^{(5)}$	$\gamma^{(15)}$	$\gamma^{(20)}$	$\gamma_N^{(20)}$	$\gamma_P^{(20)}$
−H	3.63	4.14	9.29 (3.75)[b]	9.13 (3.75)[b]	5.03 (3.75)[b]	3.36 (3.67)[b]	4.89 (2.90)[b]	−9.62 (−3.07)[b]	14.51 (5.97)[b]
$-NO_2$	10.50	12.64	18.25	18.25	11.18	7.26	10.78	−24.32	35.10
−2CN	11.41	13.13	34.11	29.24	24.78	12.26	12.24	−27.48	39.72
−R	15.55	18.49	47.53	40.34	27.33	19.37	21.58	−32.19	53.77

aThe same notations used in Table 7 are used. [b] These values are calculated by using 6-31+G(d) basis set in Gaussian 98 and all other values were obtained with 6-31G basis set.

TABLE 9: Second Hyperpolarizability, γ_{zzzz} ($\times$ 10^{-34} *esu*), of the Donor−Acceptor−Donor Type of Quadrupolar Molecules in Figure 1(c) for Varying Number of Double Bonds

n	γ_{FF}^{3-21}	γ_{FF}^{6-31}	$\gamma^{(2)}$	$\gamma^{(3)}$	$\gamma^{(4)}$	$\gamma^{(5)}$	$\gamma_N^{(5)}$	$\gamma_P^{(5)}$
2	8.29	8.82	17.40	13.26	12.19	21.4	−7.3	28.7
3	26.61	29.66	58.15	42.61	42.04	59.1	−20.6	79.7
4	57.74	65.79	125.0	95.67	95.57	122.6	−36.9	159.5
5	98.66	117.0	215.6	174.4	174.3	213.9	−51.1	265.0
6	144.6	175.8	255.2	279.2	336.8	334.2	−61.6	395.8
8	241.0	305.6	518.7	571.1	673.8	652.6	−81.6	734.2

(d) basis set that has the polarization functions sufficient for decent descriptions of geometries and at least few diffuse functions to see if Rydberg states are important. In total, twenty excited states were considered to calculate the TPA transition matrix elements, $\Gamma_{TPA}^{(20)}$, and second hyperpolarizability, $\gamma^{(n)}$. The calculated $\Gamma_{TPA}^{(20)}$ with 6-31+G(d) was found to be 210 D^2/eV. This value is about 70% of $\Gamma_{TPA}^{(20)}$ (see Table 4) calculated by using 6-31G basis set. Also the second hyperpolarizabilities, $\gamma^{(n)}$, calculated by using the sum-over-state expression, eq 7, are presented in Table 8 (see the second row). Note that $\gamma^{(20)}$ calculated with 6-31+G(d) basis set is 2.90 $\times$ 10^{-34} esu, whereas that with 6-31G basis set is 4.89 $\times$ 10^{-34} esu. On the basis of these comparisons between 6 and 31G and 6-31+G(d) calculations, the absolute values reported in this article, mainly calculated with 6-31G basis set, are found to be strongly dependent on whether the diffuse function with polarization functions is included in the basis set.

5. Summary with a Few Concluding Remarks

To establish the relationship between the molecular structure and the two-photon absorption cross section, ab initio calculations (6-31G at the HF−SCI level) were carried out for a few series of linear quadrupolar molecules. On the basis of the calculation results, as the donor and acceptor strengths increase, (i) the ground electronic state more resembles the charge-transfer configuration, (ii) the BLA increases, (iii) the product of the transition dipole moments, $|\mu_{ge}^{z}\mu_{ef}^{z}|$, increases, and (iv) the energy gaps, E_{eg} and E_{fg}, and the energy denominator $|E_{fe} - E_{eg}|$, appearing in the expression for the TPA transition matrix element, eq 6, decreases. Thus, the combined effect from (iii) and (iv) is to increase the TPA cross section as the donor and acceptor strengths increase.

Also the chain-length-dependence of the TPA cross section of a given D−A−D quadrupolar molecule with varying conjugation length was investigated. It was found that the TPA cross section reaches a limiting value when the number of double bonds is about 14. It will be interesting to further study the saturation phenomenon by using simplified model Hamiltonians to understand the physical picture behind it.

The second hyperpolarizabilities of the same series of quadrupolar molecules were also calculated by using both the finite-field and sum-over-state methods. It was found that the two methods provide quantitatively similar results. We found that γ of the linear quadrupolar molecules monotonically increases as the strengths of the donor and acceptor increase. Also, the chain-length-dependence of γ was investigated. Overall, we found that the second hyperpolarizability is approximately proportional to the TPA cross section for those quadrupolar molecules considered in this article. However, it is necessary to carry out further investigation experimentally and theoretically to quantitatively establish the relationship between the two.

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