

Relation between Nonlinear Optical Properties of Push–Pull Molecules and Metric of Charge Transfer Excitations

Nanna Holmgaard List,[†] Robert Zaleśny,^{‡,§} N. Arul Murugan,^{||} Jacob Kongsted,^{*,†} Wojciech Bartkowiak,[‡] and Hans Ågren^{*,||}

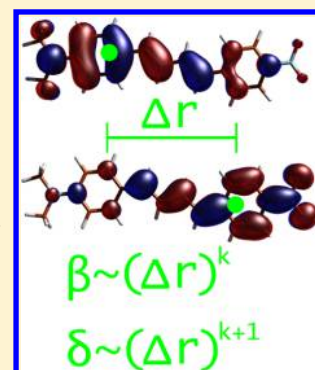
[†]Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark

[‡]Department of Physical and Quantum Chemistry, Faculty of Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, PL-50370 Wrocław, Poland

[§]Department of Chemistry, Faculty of Natural Sciences, Matej Bel University, Tajovského 40, SK-97400 Banská Bystrica, Slovak Republic

^{||}Division of Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, SE-10691 Stockholm, Sweden

ABSTRACT: We establish the relationships between the metric of charge transfer excitation (Δr) for the bright $\pi\pi^*$ state and the two-photon absorption probability as well as the first hyperpolarizability for two families of push–pull π -conjugated systems. As previously demonstrated by Guido et al. (*J. Chem. Theory Comput.* 2013, 9, 3118–3126), Δr is a measure for the average hole–electron distance upon excitation and can be used to discriminate between short- and long-range electronic excitations. We indicate two new benefits from using this metric for the analyses of nonlinear optical properties of push–pull systems. First, the two-photon absorption probability and the first hyperpolarizability are found to be interrelated through Δr ; if $\beta \sim (\Delta r)^k$, then roughly, $\delta^{\text{TPA}} \sim (\Delta r)^{k+1}$. Second, a simple power relation between Δr and the molecular hyperpolarizabilities of push–pull systems offers the possibility of estimating properties for longer molecular chains without performing calculations of high-order response functions explicitly. We further demonstrate how to link the hyperpolarizabilities with the chain length of the push–pull π -conjugated systems through the metric of charge transfer.



INTRODUCTION

Nonlinear optical properties of organic molecules, like for instance the first (β) and the second (γ) hyperpolarizability, are in the limelight due to numerous technological applications of associated phenomena such as optical switching, biomedical imaging, data storage, or optical limiting, to name a few.^{1–12} In particular, much effort has recently been invested in designing molecules with a large two-photon absorption strength (δ^{TPA})—a quantity related to the imaginary part of the second hyperpolarizability.^{13–19} The quest for simple relationships between nonlinear optical properties of molecules and electronic structure parameters has a long history. In general, few-state models are derived from quantum-mechanical perturbation theory expressions by reducing the spectrum of eigenstates to a few essential ones.²⁰ Early attempts to develop few-state models for β date back to the work of Oudar and Chemla.^{21,22} These authors related hyperpolarizabilities of nitroanilines to parameters of the first excited state, namely, transition energy, difference dipole moment, and transition strength. A two-state model, comprising the ground state and the first excited state, proved in many cases to be sufficient to explain experimental data.²¹ The model of Oudar and Chemla is, due to its simple structure (only three parameters involved), still widely used by scientists. Along the same line, aiming at creating the basis for structure–property rules, Dirk and Kuzyk

proposed few-state models for γ .^{23,24} In particular, these authors advocated their simplified three-state model optimized for three different structure types,²⁴ including (i) conjugated donor–acceptor dipolar molecules, (ii) even-member conjugated chains such as -enes, -ynes, and ene-ynes, and (iii) “charged” odd-member conjugated chains. Some of the present authors also contributed to this subject and derived three- and four-state models for two-photon absorption.²⁵ Alam et al. further generalized this approach and applied it in a series of papers to a broad range of chemical systems.^{26–29} The few-state models described above share a common feature; the molecular hyperpolarizabilities are expressed in terms of several electronic structure parameters. Although it is common and useful to apply these expressions to understand the optical channels involved in light-molecule interactions, their multi-parameter form somewhat hampers their use in rational design of molecular materials. For instance, as discussed by Drobizhev et al., it is problematic to understand and predict the dependence of the two-photon absorption probability on the number of monomer units in conjugated systems based on a few-state model.³⁰

Received: June 9, 2015

Published: July 17, 2015



Recently, a quantity that carries information regarding the dependence of excited state properties on the conjugation length, the metric of charge transfer excitations, was proposed by Guido et al.³¹ This index, here abbreviated as Δr , is defined as

$$\Delta r = \frac{\sum_{ia} K_{ia}^2 (|\langle a|\hat{r}|i\rangle| - |\langle i|\hat{r}|a\rangle|)}{\sum_{ia} K_{ia}^2} \quad (1)$$

where K is a vector defined as the sum of the excitation and de-excitation parts of the eigenvector of the electronic Hessian associated with the specific transition. The Δr -index is based on the orbital centroids computed for the molecular orbitals involved in the excitation (using i and a to denote occupied and virtual orbitals, respectively), and it is a measure for the average hole–electron distance upon excitation. This quantity has previously been referred to as the so-called rearrangement dipole³² and corresponds to the unrelaxed difference dipole.³³ Guido et al. suggested that the Δr -index may be employed to discriminate between short- ($\Delta r \leq 1.5$ Å) and long-range ($\Delta r \geq 2.0$ Å) excitations and indicated that for this purpose it is superior to the so-called Λ -index, which has been introduced as a measure of the degree of spatial overlap between the occupied and virtual orbitals involved in excitation.^{31,34} Since the difference dipole moment is a key quantity in two-state models, it is thus possible that there exists simple analytic relations between the Δr -index of an essential excited state and the nonlinear optical properties of push–pull systems. Such relations for push–pull systems would allow one to make a link between nonlinear optical properties and the simple pictorial concept of hole–electron separation. Moreover, since the evaluation of Δr only requires the evaluation of linear response eigenvectors, such relations would offer a possibility of estimating properties, or at least the trend in these properties, when performing systematic structural changes to the molecule, without computing quadratic or higher-order response functions explicitly. It is also worth recalling that some previous studies have looked into the possible relationships between Λ and Δr and the two-photon absorption cross section.^{35–37} However, to our knowledge, the relationship against the hyperpolarizability for these parameters is not explored and this is undertaken in this current study.

Here, we further explore this subject, and we will in particular make an attempt to employ the metric of charge transfer excitations to understand the chain-length dependence of molecular hyperpolarizabilities and two-photon absorption strengths. In doing so, we will analyze the relationships between the metric of charge transfer excitation and the static first hyperpolarizabilities/two-photon absorption within the framework of response theory for two families of push–pull π -conjugated compounds characterized by Cheng et al.³⁸

THEORY AND COMPUTATIONAL DETAILS

In the presence of an external electric field F , the a^{th} Cartesian component of the total molecular dipole moment, μ_a , may be expressed as a Taylor series, which takes the form:³⁹

$$\begin{aligned} \mu_a(\omega_\sigma) &= \mu_a^0 \delta_{\omega_\sigma, 0} + \sum_b \alpha_{ab}(-\omega_\sigma; \omega_1) F_b(\omega_1) \\ &+ \frac{1}{2!} K^{(2)} \sum_{bc} \beta_{abc}(-\omega_\sigma; \omega_1, \omega_2) F_b(\omega_1) F_c(\omega_2) \\ &+ \frac{1}{3!} K^{(3)} \sum_{bcd} \gamma_{abcd}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) F_b(\omega_1) F_c(\omega_2) F_d(\omega_3) + \dots \end{aligned} \quad (2)$$

where μ_a^0 is the a^{th} component of the permanent dipole moment; $\alpha_{ab}(-\omega_\sigma; \omega_1)$, $\beta_{abc}(-\omega_\sigma; \omega_1, \omega_2)$, and $\gamma_{abcd}(-\omega_\sigma; \omega_1, \omega_2, \omega_3)$ are components of the linear polarizability, first hyperpolarizability, and second hyperpolarizability, respectively; ω_σ is the sum of the external field frequencies ω_i ; and $K^{(2)}$ and $K^{(3)}$ are factors required for all hyperpolarizabilities of the same order to have the same static limit. The static first hyperpolarizability, $\beta(0; 0, 0)$, and the two-photon absorption probability are central to this study. In what follows, we outline the response theory framework to determine both of these quantities. Expressions are provided in atomic units if not otherwise stated.

For exact states, the frequency-dependent first hyperpolarizability can be written in the spectral representation as⁴⁰

$$\begin{aligned} \beta_{abc}(-\omega_\sigma; \omega_1, \omega_2) \\ = \sum \mathcal{P}_{-\sigma, 1, 2} \sum_{m, n \geq 0} \frac{\langle 0|\hat{\mu}_a|m\rangle \langle m|\tilde{\mu}_b|n\rangle \langle n|\hat{\mu}_c|0\rangle}{(\omega_{m0} - \omega_\sigma)(\omega_{n0} - \omega_2)} \end{aligned} \quad (3)$$

where $|0\rangle$ and $\{|n\rangle\}$ denote the electronic ground and excited states, respectively, and ω_{n0} is the transition frequency between the n^{th} excited and the ground states. Here, $\hat{\mu}_a$ is the a^{th} component of the electric dipole operator, $\tilde{\mu}_a = \hat{\mu}_a - \langle 0|\hat{\mu}_a|0\rangle$ the fluctuation dipole moment operator, and $\sum \mathcal{P}_{-\sigma, 1, 2}$ generates the sum over all possible permutations of the joint operator-frequency indices $(a, -\sigma)$, $(b, 1)$, and $(c, 2)$. The average first hyperpolarizability is given by

$$\bar{\beta} = \sum_a \frac{\mu_a \beta_a}{|\mu|} \quad (4)$$

where

$$\beta_a = \frac{1}{5} \sum_b (\beta_{abb} + \beta_{bab} + \beta_{bba}) \quad (5)$$

Next, we consider the two-photon absorption cross section. Two-photon absorption is essentially a third-order process related to the imaginary part of the second hyperpolarizability,^{13–15} but it is available through second-order transition moments, S_{ab} , that can be identified from the single residue of the quadratic response function.⁴⁰ At a two-photon resonance, probed by two monochromatic photons ($\omega = \omega_{f0}/2$), the two-photon absorption transition matrix from the ground state to the an excited state $|f\rangle$ can be written as a sum-over-states expression⁴¹

$$S_{ab} = \sum_{n \geq 0} \left[\frac{\langle 0|\hat{\mu}_a|n\rangle \langle n|\tilde{\mu}_b|f\rangle}{\omega_{n0} - \omega_{f0}/2} + \frac{\langle 0|\hat{\mu}_b|n\rangle \langle n|\tilde{\mu}_a|f\rangle}{\omega_{n0} - \omega_{f0}/2} \right] \quad (6)$$

In the case of linearly polarized light, the two-photon absorption strength for an isotropic sample can then be constructed as⁴²

$$\langle \delta^{\text{TPA}} \rangle = \frac{1}{15} \sum_{ab} (S_{aa} S_{bb}^* + 2S_{ab} S_{ba}^*) \quad (7)$$

Turning now to a general basis, covering also approximate variational theories, the first hyperpolarizability can be written in a matrix-vector notation as⁴³

$$\begin{aligned} \beta_{abc}(-\omega_\sigma; \omega_1, \omega_2) = & \sum \mathcal{P}_{1,2} [N_n^a(\omega_\sigma) B_{nm}^{[2]} N_m^c(\omega_2) \\ & + N_n^b(\omega_1) A_{nm}^{[2]} N_m^c(\omega_2) \\ & + N_n^a(\omega_\sigma) [E_{nml}^{[3]} - \omega_1 S_{nml}^{[3]}] N_m^b(\omega_1) N_l^c(\omega_2)] \end{aligned} \quad (8)$$

and the two-photon transition matrix elements as

$$\begin{aligned} S_{ab} = & -N_n^a \left(\frac{\omega_{f0}}{2} \right) B_{nm}^{[2]} X_m^f - N_n^b \left(-\frac{\omega_{f0}}{2} \right) (A_{nm}^{[2]} + A_{mn}^{[2]}) X_m^f \\ & - N_n^a \left(\frac{\omega_{f0}}{2} \right) \left(E_{nml}^{[3]} + E_{nlm}^{[3]} + \frac{1}{2} \omega_{f0} S_{nml}^{[3]} - \omega_{f0} S_{nlm}^{[3]} \right) N_m^b \left(-\frac{\omega_{f0}}{2} \right) X_l^f \end{aligned} \quad (9)$$

where the Einstein summation convention for repeated indices has been assumed. X^f is the eigenvector associated with excited state $|f\rangle$, which satisfies the generalized eigenvalue problem

$$(E^{[2]} - \omega_{f0} S^{[2]}) X^f = 0 \quad (10)$$

whereas the response vectors are determined by solving the following linear response equations

$$N^a(\omega_\sigma) (E^{[2]} - \omega_\sigma S^{[2]}) = A^{[1]} \quad (11)$$

$$(E^{[2]} - \omega_i S^{[2]}) N^z(\omega_i) = Z^{[1]}, \quad (Z, i) = \{(B, 1), (C, 2)\} \quad (12)$$

Due to the structure of the electronic Hessian matrix,^{43,44} the response vectors for $\pm\omega_{f0}/2$ needed for a diagonal element S_{aa} of the two-photon transition matrix will be related as

$$N^a \left(\frac{\omega_{f0}}{2} \right) = [\mathcal{X}_a \mathcal{Y}_a] \quad N^a \left(-\frac{\omega_{f0}}{2} \right) = [-\mathcal{Y}_a^* - \mathcal{X}_a^*] \quad (13)$$

while in the static limit $\mathcal{X}_a = -\mathcal{Y}_a^*$. In the remainder of this work, we focus on the case of density functional theory (TD-DFT), where the orbital-rotation operator is expressed in terms of the wave function parameters and orbital-excitation operators according to $\hat{\kappa}^\omega = \sum_{n=-D}^D \kappa_n(\omega) \hat{q}_n^\dagger$ ($\hat{q}_{-n}^\dagger = \hat{q}_n$, $\kappa_{-n} = \kappa_n^*$ and n runs over the dimension of the operator space. For the present purpose, it suffices to consider the explicit expression for the property Hessian matrices $Z^{[2]}$ for $Z = \{A, B, C\}$, whereas expressions for the remaining matrices and vectors may be found, for example, in ref 43. Note that the third-order overlap matrix vanishes in a single-determinant approximation as considered here, so that only the term involving the $E^{[3]}$ matrix gives the difference to the sum-over-states expression for the two-photon absorption transition matrix in eq 6. Adopting the usual ordering with de-excitations before excitations in the rows (and opposite in the columns),⁴³ the property Hessian matrix $B^{[2]}$ ($C^{[2]}$) can be written as

$$B^{[2]} = \begin{bmatrix} \langle 0 | [\hat{q}, [\hat{\mu}_b, \hat{q}^\dagger]] | 0 \rangle & \langle 0 | [\hat{q}, [\hat{\mu}_b, \hat{q}]] | 0 \rangle \\ \langle 0 | [\hat{q}^\dagger, [\hat{\mu}_b, \hat{q}^\dagger]] | 0 \rangle & \langle 0 | [\hat{q}^\dagger, [\hat{\mu}_b, \hat{q}]] | 0 \rangle \end{bmatrix} \quad (14)$$

noting that the definition of $A^{[2]}$ is slightly different due to another ordering of the sub-blocks.

The elements of the diagonal blocks of $B^{[2]}$ become

$$B_{ai,bj}^{[2]} = \langle 0 | [\hat{q}_{ai}, [\hat{\mu}_b, \hat{q}_{bj}^\dagger]] | 0 \rangle = \langle i | \hat{\mu}_b | j \rangle - \delta_{ij} \delta_{ab} \langle 0 | \hat{\mu}_b | 0 \rangle \quad (15)$$

such that diagonal elements of $B^{[2]}$ reduce to differences in the b^{th} component of the electric dipole moment between the occupied and virtual orbitals involved in the given excited determinant. On the other hand, the off-diagonal purely (de)excitation blocks of $B^{[2]}$ vanish due to the fact that the electric dipole operator is a one-electron operator. In the case of the CI with singles method, where the de-excitation part vanishes by construction, it follows that the Δr -index for an excitation dominated by a single electron displacement corresponds to the diagonal and dominating contribution to, for example, $X_n^f B_{nm}^{[2]} X_m^f$ and thus, in the case of a low-lying bright b -allowed transition, also to the first hyperpolarizability β_{bbb} and the two-photon absorption matrix element S_{bb} . In the general case, de-excitations are typically negligible and the same relation between Δr and $X_n^f B_{nm}^{[2]} X_m^f$ will then hold approximately.

The geometries of all studied molecules (in the electronic ground state) were optimized at the CAM-B3LYP/cc-pVTZ level of theory.⁴⁵ These optimizations were performed for molecules in the gas phase using the Gaussian 09⁴⁶ package. Property calculations were performed based on linear (Δr) and quadratic (S and β) response theory using the CAM-B3LYP functional in conjunction with Dunning's correlation consistent basis set aug-cc-pVDZ.^{47–49} For this, we used the DALTON program package.^{50,51}

RESULTS AND DISCUSSION

To study the relationship between the metric of charge transfer and nonlinear optical properties, we selected two families of compounds that fall into the donor- π -acceptor category, where the π -conjugated linker contains either phenylpolyene or diphenylpolyene oligomers. These two families, shown in Figure 1, are hereafter referred to as PP and DPP, respectively.

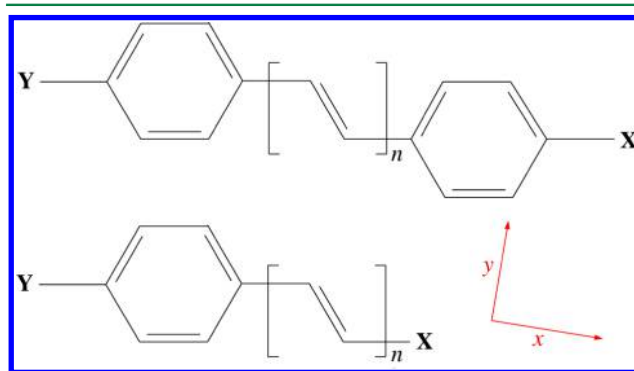


Figure 1. Molecules investigated in the present study (DPP (top), PP (bottom)) and their orientation in Cartesian coordinate system, where the terminal p -block elements were aligned along the Cartesian x -axis.

As far as electron-donating and electron-accepting groups are concerned, we consider several pairs of substituents, including (CHO, MeO), (CHO, NMe₂), (CN, MeO), (MeO, NO₂), and (NO₂, NMe₂). For each pair of substituents, the number of oligomers in the π -conjugated linker (n) typically varies in the range $n = 1–3$ (PP) and $n = 1–4$ (DPP). The presence of electron-donating and electron-accepting groups on both sides

of the π -bridge assures that the transition to the lowest-energy excited state involves substantial electron density reorganization, and thus, the associated transition strength is quite large. For all studied molecules, the $\pi\pi^*$ charge-transfer state is dominated by a one-electron excitation from the highest occupied to the lowest unoccupied molecular orbital (HOMO to LUMO), and this excited state is the lowest-lying one in the case of the DPP series ($n = 1-4$) and the PP series ($n = 3$). In what follows, we consider two-photon excitation only to this $\pi\pi^*$ excited state. Since the longitudinal axis of the DPP and PP molecules has been aligned with the Cartesian x -axis, the major contributions to the transition properties are due to the x -components. Moreover, inspection of the elements of the S and β tensors show that a one-dimensional (along x -axis) two-state model captures the main portion of both tensors. As already mentioned in the Introduction, a two-state model, involving the ground, $|0\rangle$, and the lowest-energy bright $\pi\pi^*$ excited state, $|\pi\pi^*\rangle$, is motivated for these classes of molecules in order to describe the longitudinal low-order nonlinear optical properties

$$\beta_{xxx} = 6 \frac{\langle 0|x|\pi\pi^*\rangle^2 [\langle \pi\pi^*|x|\pi\pi^*\rangle - \langle 0|x|0\rangle]}{\omega_{\pi\pi^*}^2} \quad (16)$$

$$S_{xx} = 4 \frac{\langle 0|x|\pi\pi^*\rangle [\langle \pi\pi^*|x|\pi\pi^*\rangle - \langle 0|x|0\rangle]}{\omega_{\pi\pi^*}} \quad (17)$$

where $\omega_{\pi\pi^*}$ is the angular frequency corresponding to the transition from the ground state to the essential bright $\pi\pi^*$ state and $[\langle \pi\pi^*|x|\pi\pi^*\rangle - \langle 0|x|0\rangle]$ is the dipole moment difference along the Cartesian x -direction between $|\pi\pi^*\rangle$ and $|0\rangle$. Indeed, the data presented in Table 1 confirm that the two-

Table 1. Diagonal Components of Static First Hyperpolarizability and Second-Order Transition Moment for DPP ($X = \text{NO}_2$, $Y = \text{NMe}_2$) Computed Using Either Response Theory (including all states) or Based on the Two-State Model (ground and lowest-energy $\pi\pi^*$ excited state)^a

n	β_{xxx} [a.u.]		S_{xx} [a.u.]	
	all states	two-state model	all states	two-state model
1	14469	25733	466	569
2	22678	45403	621	789
3	32554	69441	768	995
4	43946	98318	912	1200
5	56394	130233	1045	1386

^aAll values were computed at the CAM-B3LYP/aug-cc-pVDZ level of theory and correspond to molecules in gas phase oriented as shown in Figure 1.

state model predicts the trend in both the first hyperpolarizability and the two-photon absorption probability satisfactorily for the DPP series ($X = \text{NO}_2$, $Y = \text{NMe}_2$) when increasing the conjugated linker length (correlation coefficient of 0.99). Since the $\pi\pi^*$ state is the essential one and governs the nonlinear optical activity, it is thus possible that there exists a correlation between β and $\langle \delta^{\text{TPA}} \rangle$ and the metric of charge transfer corresponding to this state, Δr . In order to establish its mathematical form, we invoke the two-state model for both properties (cf. eqs 16 and 17). It follows from these equations that $\lim_{\Delta\mu_x \rightarrow 0} \beta_{xxx} = 0$ and $\lim_{\Delta\mu_x \rightarrow 0} S_{xx} = 0$. A simple power function fulfilling this condition is $a(\Delta x)^k$. Since the rotation-

ally averaged properties, i.e., $\bar{\beta}$ and $\langle \delta^{\text{TPA}} \rangle$, are dominated by the longitudinal tensor components and moreover $\Delta r \approx \Delta x$, one may write

$$\bar{\beta} = a \cdot (\Delta r)^k \quad (18)$$

$$\langle \delta^{\text{TPA}} \rangle = a \cdot (\Delta r)^k \quad (19)$$

In Figure 2, we plot the average first hyperpolarizability and average two-photon absorption probability for all studied

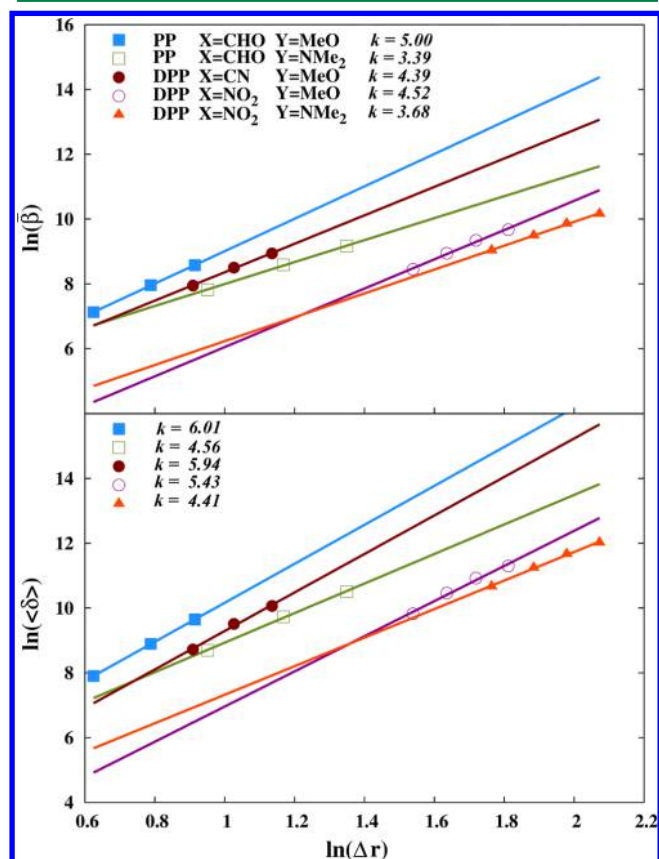


Figure 2. Average first hyperpolarizability (in au.) and average two-photon transition probability (in au.) as a function of Δr (given in Å). All values correspond to molecules in the gas phase and were computed at the CAM-B3LYP/aug-cc-pVDZ level of theory.

systems as a function of Δr . As shown, a very good linear correlation between these properties and the metric of charge transfer is found (logarithmic scale). As indicated in this figure, in the case of first hyperpolarizability, the value of k is in the range of 3.39 to 5.00, while for $\langle \delta^{\text{TPA}} \rangle$ we find that the spread is from 4.41 up to 6.01. For any given pair of substituents we note that k is always higher for the latter property. The differences in k values are 1.01, 1.17, 1.55, 0.91, and 0.73, which yields a mean value of 1.07. Hence, provided that β shows a k -power dependence on Δr , i.e., $\beta \sim (\Delta r)^k$, one may expect that $\langle \delta^{\text{TPA}} \rangle$ will exhibit roughly $(\Delta r)^{k+1}$ dependence. We note that this relation is fully in agreement with the two-state model upon approximating the dipole difference by its unrelaxed form. Thus, one may employ the correlation of β with Δr for dipolar push–pull species to predict the power dependence for $\langle \delta^{\text{TPA}} \rangle$ or vice versa.

To shed more light on these observed power dependencies for both properties and to establish connection with the linker-

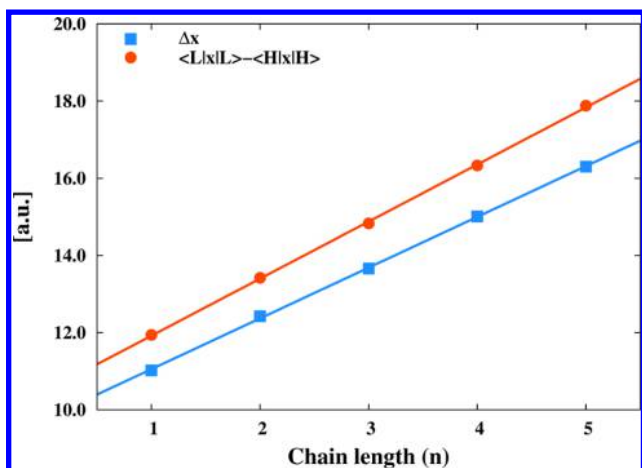


Figure 3. Behavior of the intramolecular charge-transfer descriptor Δx as well as the HOMO–LUMO dipole difference with respect to the length of the linker.

length dependence, we will focus on one of the studied systems (DPP, $X = \text{NO}_2$, $Y = \text{NMe}_2$, $n = 1\text{--}5$). Figure 3 presents the dependence of Δx on the chain length (hereafter referred to as n). The linear relationship between the two quantities, $\Delta x = a' \cdot n + b$, combined with eq 18 or eq 19 immediately yields an estimate of a power dependence of β_{xxx} or S_{xx}^2 on the linker length n (cf. Newtown's generalized binomial theorem). For a perfectly conjugated system, we expect that $S_{xx}^2 = a \cdot (a' \cdot n + b)^k$. For the studied DPP derivative, we found that $\beta_{xxx} \propto (a' \cdot n + b)^{3.49}$ and $S_{xx}^2 \propto (a' \cdot n + b)^{4.14}$. Recently, Drobizhev et al. studied the chain-length dependence of two-photon absorption signature, and they suggested that for perfectly conjugated systems this property should scale as n^4 .³⁰ For sufficiently long chains, one expects a broken conjugation, and the dependence of Δx on chain length will no longer be linear ($\Delta x \propto n^k$, where $k < 1$), thus reducing the power dependence of $\langle \delta^{\text{TPA}} \rangle$ and β on n . For an extensive review on length scaling and power laws in conjugated polymers and large molecules, we refer to review article by Kuzyk et al.⁵² In principle, the relation between molecular hyperpolarizabilities and the Δr -index offers a possibility of estimating the trend in these properties when performing systematic structural changes to the molecule in question, without computing quadratic or higher-order response functions explicitly. In order to validate this notion, we have performed the calculations for DPP ($X = \text{NO}_2$, $Y = \text{NMe}_2$) for $n = 10$. The values of β_{xxx} and S_{xx} estimated based on Δx are 178×10^3 and 2.1×10^3 a.u., respectively, while the response theory values (exact) are 128×10^3 and 1.5×10^3 a.u. Since we correlate nonlinear optical properties with Δx corresponding only to $\pi\pi^*$ states, it comes as no surprise that estimated values are slightly larger than the exact ones; the two-level model also overestimates β_{xxx} and S_{xx} (cf. Table 1).

To gain insight into the origin of the dependence of β and $\langle \delta^{\text{TPA}} \rangle$ on chain length, we make a decomposition of the second-order transition moment and static first hyperpolarizability within the response theory framework. Hereby, we examine the relation between the two-photon absorption probability and the static first hyperpolarizability and the length of the polyene linker. Because the lowest excitation is intense in the x -direction and is well described within TD-DFT, the response vectors relevant for the dominant S_{xx} element will also

be dictated by the same excited determinant. Figure 3 displays the trends in the intramolecular charge-transfer descriptor Δx with respect to chain length as well as the HOMO–LUMO dipole difference, which proves to make the main contribution to Δx across the series, while Figure 4 shows the dominating

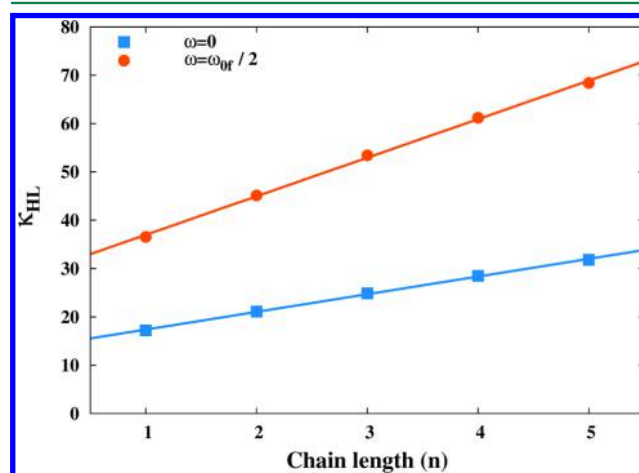


Figure 4. Size of the HOMO–LUMO contribution to the response vectors (at $\omega = 0$, $\omega_{\pi\pi^*}/2$) with respect to the length of the linker.

HOMO–LUMO excitation element of the response vector (at frequencies $\omega = 0$ and $\omega_{\pi\pi^*}/2$). All three quantities behave almost linearly with the length of the linker, and it is thus reasonable to expect the $Z^{[2]}$ terms in eq 9 to exhibit the same behavior. In fact, decomposition of S_{xx} into the individual terms appearing in eq 9 (cf. Figure 5) reveals that the $Z^{[2]}$

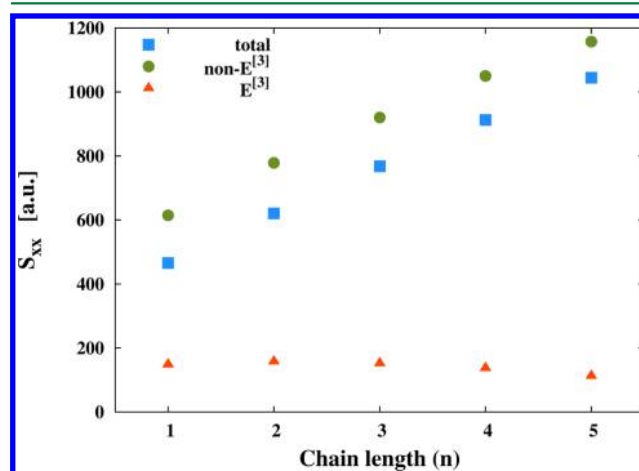


Figure 5. Decomposition of S_{xx} (squares) into $Z^{[2]}$ (circles) and $E^{[3]}$ (triangles) contributions (c.f. eq 9) as a function of chain length across the DPP series.

contributions change substantially with the length of the linker and parallel the curve for S_{xx} . The $E^{[3]}$ term appears, on the other hand, almost constant across the series, although we note small deviations for longer chains. An analogous decomposition has been performed for β_{xxx} (cf. eq 8), and the dependence of individual terms is shown in Figure 6. Similarly to what has been observed in the case of S_{xx} , the $E^{[3]}$ contribution to β_{xxx} is found to be almost independent of the chain length and the dependence of $Z^{[2]}$ contributions on chain length closely follows the β_{xxx} curve. We may thus conclude, based on the analysis within the response theory framework, that in the case

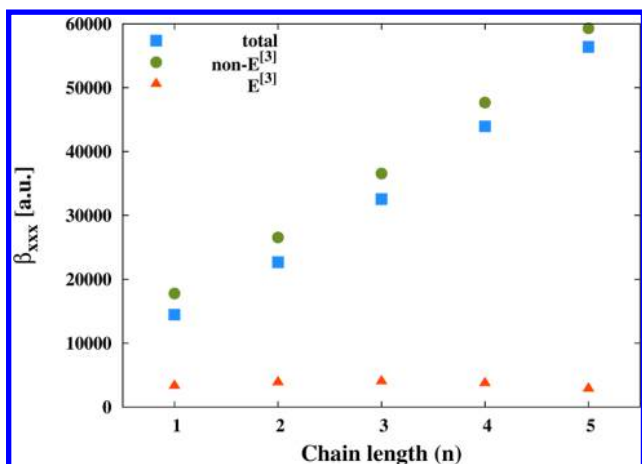


Figure 6. Decomposition of β_{xxx} (squares) into $Z^{[2]}$ (circles) and $E^{[3]}$ (triangles) contributions as a function of chain length n .

of both properties the driving force of the chain-length dependence (β and S_{xx}) is the $Z^{[2]}$ contributions that relate to the unrelaxed dipole difference.

SUMMARY

In the present study, we have analyzed the relationship between the metric of charge transfer excitation to the bright $\pi\pi^*$ state for two families of push–pull systems and the first hyperpolarizability as well as the two-photon absorption probability. The Δr -index is based on the orbital centroids computed for the molecular orbitals involved in the excitation and is a measure for the average hole–electron distance upon excitation. Guido et al. used the Δr -index to discriminate between short- and long-range excitations.³¹ In this study, we indicate two new benefits from using this metric for the analyses of nonlinear optical properties of push–pull systems. First, the first hyperpolarizability and two-photon absorption probability are found to be interrelated through Δr , i.e., if $\beta \sim (\Delta r)^k$, then one may expect that $\delta^{TPA} \sim (\Delta r)^{k+1}$. Once the power dependence on Δr is determined for one property, it is thus possible to estimate the Δr -dependence for the other one. Second, the simple power relation between Δr and the molecular hyperpolarizabilities of push–pull π -conjugated systems offers in principle an estimation of the properties for longer chains without performing calculations of high-order response functions explicitly. Under the assumption that the electronic structure does not change dramatically upon elongation, it would be sufficient to determine solely the given eigenvector, required to compute the metric of charge transfer. The use of the relationship between the metric of charge transfer and nonlinear optical properties seems to be motivated for these classes of molecules where optical channel involving only two states is dominant like, for instance, in the case of push–pull molecules studied in this work. As a part of this study, we have also indicated how to link the hyperpolarizabilities with the chain length of push–pull π -conjugated systems through the metric of charge transfer. Moreover, based on the analysis within the framework of response theory, we have demonstrated that since the $E^{[3]}$ contribution to the analyzed properties is found to be almost independent of the chain length, the overall chain-length dependence is due to the direct $Z^{[2]}$ contributions. We believe that further efforts in rational design of two-photon molecules and molecular

materials for specific applications can benefit from the relations revealed in this paper.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: kongsted@sdu.dk (J. Kongsted).

*E-mail: hagren@kth.se (H. Ågren).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the Polish National Science Centre (Grant No. DEC-2013/10/A/ST4/00114) is gratefully acknowledged. The calculations were performed in part at the Wrocław Center for Networking and Supercomputing. This work was also supported by the Swedish Infrastructure Committee (SNIC) for the project “Multiphysics Modeling of Molecular Materials”, SNIC025/12-38. N.H.L. and J.K. acknowledge financial support from the Lundbeck Foundation. J.K. thanks the Danish Council for Independent Research, the Danish e-Infrastructure Cooperation (DeIC), and the Villum Foundation for financial support.

REFERENCES

- (1) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843–845.
- (2) Dvornikov, A. S.; Walker, E. P.; Rentzepis, P. M. *J. Phys. Chem. A* **2009**, *113*, 13633–13644.
- (3) Denk, W.; Strickler, J.; Webb, W. *Science* **1990**, *248*, 73–76.
- (4) Streets, A. M.; Li, A.; Chen, T.; Huang, Y. *Anal. Chem.* **2014**, *86*, 8506–8513.
- (5) Hoover, E. E.; Squier, J. A. *Nat. Photonics* **2013**, *7*, 93–101.
- (6) Chung, C.-Y.; Boik, J.; Potma, E. O. *Annu. Rev. Phys. Chem.* **2013**, *64*, 77–99.
- (7) Green, K. A.; Cifuentes, M. P.; Corkery, T. C.; Samoc, M.; Humphrey, M. G. *Angew. Chem., Int. Ed.* **2009**, *48*, 7867–7870.
- (8) Castet, F.; Rodriguez, V.; Pozzo, J.-L.; Ducasse, L.; Plaquet, A.; Champagne, B. *Acc. Chem. Res.* **2013**, *46*, 2656–2665.
- (9) Chen, K. J.; Laurent, A. D.; Jacquemin, D. *J. Phys. Chem. C* **2014**, *118*, 4334–4345.
- (10) Boixel, J.; Guerchais, V.; le Bozec, H.; Jacquemin, D.; Amar, A.; Boucekine, A.; Colombo, A.; Dragonetti, C.; Marinotto, D.; Roberto, D.; Righetto, S.; De Angelis, R. *J. Am. Chem. Soc.* **2014**, *136*, 5367–5375.
- (11) Jaunet-Lahary, T.; Chantzis, A.; Chen, K. J.; Laurent, A. D.; Jacquemin, D. *J. Phys. Chem. C* **2014**, *118*, 28831–28841.
- (12) Schulze, M.; Utecht, M.; Hebert, A.; Rück-Braun, K.; Saalfrank, P.; Tegeder, P. *J. Phys. Chem. Lett.* **2015**, *6*, 505–509.
- (13) Swofford, R.; Albrecht, A. *Annu. Rev. Phys. Chem.* **1978**, *29*, 421–440.
- (14) Mahr, H. In *Quantum Electronics - Nonlinear Optics, Part A*; Rabin, H., Tang, C. L., Eds.; Academic Press: New York, 1975; Vol. 1.
- (15) Bloembergen, N. *Nonlinear Optics*; World Scientific, 1996.
- (16) Albota, M.; Beljonne, D.; Brédas, J.-L.; Ehrlich, J.; Fu, J.-Y.; Heikal, A.; Hess, S.; Kogej, T.; Levin, M.; Marder, S.; McCord-Maughon, D.; Perry, J.; Röckel, H.; Rumi, M.; et al. *Science* **1998**, *281*, 1653–1656.
- (17) Kogej, T.; Beljonne, D.; Meyers, F.; Perry, J.; Marder, S.; Brédas, J. *Chem. Phys. Lett.* **1998**, *298*, 1–6.
- (18) Terenziani, F.; Katan, C.; Badaeva, E.; Tretiak, S.; Blanchard-Desce, M. *Adv. Mater.* **2008**, *20*, 4641–4678.
- (19) Pawlicki, M.; Collins, H. A.; Denning, R. G.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3244–3266.
- (20) Orr, B.; Ward, J. *Mol. Phys.* **1971**, *20*, 513–526.
- (21) Oudar, J.; Chemla, D. *J. Chem. Phys.* **1977**, *66*, 2664–2668.
- (22) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446–457.

- (23) Kuzyk, M. G.; Dirk, C. W. *Phys. Rev. A: At., Mol., Opt. Phys.* **1990**, *41*, 5098–5109.
- (24) Dirk, C.; Cheng, L.-T.; Kuzyk, M. *Int. J. Quantum Chem.* **1992**, *43*, 27–36.
- (25) Cronstrand, P.; Luo, Y.; Ågren, H. *Chem. Phys. Lett.* **2002**, *352*, 262–269.
- (26) Alam, M. M.; Chattopadhyaya, M.; Chakrabarti, S. *J. Phys. Chem. A* **2012**, *116*, 8067–8073.
- (27) Alam, M. M.; Chattopadhyaya, M.; Chakrabarti, S. *Phys. Chem. Chem. Phys.* **2012**, *14*, 1156–1165.
- (28) Alam, M. M.; Chattopadhyaya, M.; Chakrabarti, S.; Ruud, K. *J. Phys. Chem. Lett.* **2012**, *3*, 961–966.
- (29) Alam, M. M.; Chattopadhyaya, M.; Chakrabarti, S.; Ruud, K. *Acc. Chem. Res.* **2014**, *47*, 1604–1612.
- (30) Drobizhev, M.; Stepanenko, Y.; Rebane, A.; Wilson, C. J.; Screen, T. E. O.; Anderson, H. L. *J. Am. Chem. Soc.* **2006**, *128*, 12432–12433.
- (31) Guido, C. A.; Cortona, P.; Mennucci, B.; Adamo, C. *J. Chem. Theory Comput.* **2013**, *9*, 3118–3126.
- (32) Hansen, A. E.; Bouman, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 4828–4839.
- (33) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117*, 7433–7447.
- (34) Peach, M. J. G.; Benfield, P.; Helgaker, T.; Tozer, D. J. *J. Chem. Phys.* **2008**, *128*, 044118.
- (35) Murugan, N. A.; Apostolov, R.; Rinkevicius, Z.; Kongsted, J.; Lindahl, E.; Ågren, H. *J. Am. Chem. Soc.* **2013**, *135*, 13590–13597.
- (36) Murugan, N. A.; Kongsted, J.; Ågren, H. *J. Chem. Theory Comput.* **2013**, *9*, 3660–3669.
- (37) Murugan, N. A.; Zalesny, R.; Kongsted, J.; Nordberg, A.; Ågren, H. *Chem. Commun.* **2014**, *50*, 11694–11697.
- (38) Cheng, L. T.; Tam, W.; Stevenson, S. H.; Meredith, G. R.; Rikken, G.; Marder, S. R. *J. Phys. Chem.* **1991**, *95*, 10631–10643.
- (39) Shelton, D. P.; Rice, J. E. *Chem. Rev.* **1994**, *94*, 3–29.
- (40) Olsen, J.; Jørgensen, P. *J. Chem. Phys.* **1985**, *82*, 3235–3264.
- (41) Rizzo, A.; Coriani, S.; Ruud, K. In *Computational Strategies for Spectroscopy. From Small Molecules to Nano Systems*; Barone, V., Ed.; John Wiley and Sons, 2012; pp 77–135.
- (42) Monson, P.; McClain, W. J. *Chem. Phys.* **1970**, *53*, 29–37.
- (43) Olsen, J.; Jørgensen, P. *J. Chem. Phys.* **1985**, *82*, 3235–3264.
- (44) List, N. H.; Coriani, S.; Christiansen, O.; Kongsted, J. *J. Chem. Phys.* **2014**, *140*, 224103.
- (45) Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51–57.
- (46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, P. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
- (47) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007–1023.
- (48) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.
- (49) Woon, D. E.; Dunning, T. H. *J. Chem. Phys.* **1994**, *100*, 2975–2988.
- (50) Aidas, K.; et al. *WIREs Comput. Mol. Sci.* **2014**, *4*, 269–284.
- (51) Molecular Electronic Structure Program Release, DALTON2015.0. <http://daltonprogram.org/> (accessed July 2015).
- (52) Kuzyk, M. G.; Perez-Moreno, J.; Shafei, S. *Phys. Rep.* **2013**, *529*, 297–398.