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# Solvent-Induced Two-Photon Absorption of a Push−Pull Molecule[†]

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Solvent-induced two-photon absorption cross sections are calculated for a push−pull molecule in solutions using both self-consistent reaction field and internal finite field approaches. It is shown analytically and numerically that the results from the two methods can be connected through induced local reaction field factors. The two-photon cross sections of the studied push−pull polyene are found to be rather insensitive to the choice of cavity shape. The solvent dependence of the two-photon absorption displays a pattern different from that of the first hyperpolarizability.

## Introduction

The process of a simultaneous two-photon absorption (TPA) was predicted by Göppert-Mayer[1] 30 years before the first experimental observation.[2] At present the situation is reversed in that the experimental development of the two-photon spectroscopy is a great stimulus for theoretical efforts in the field. Although the formal theoretical description of TPA has been well established for a long time (see the excellent summary of Mahr[3]), the application of the theory has traditionally been addressed only in the context of the physics of atoms and small molecules. Apart from the interest in the TPA process *per se*, the fact that the two-photon and one-photon selection rules are different has made two-photon spectroscopy an additional and complementary tool in the study of the organization of excited states. However, the applicability of TPA has greatly developed more recently due to improvements in experimental conditions, and multiple-photon—and in particular two-photon—absorption spectra can today be found for a wide selection of systems.[4] This interest for TPA stems to a large extent from the various, potential, technical applications that can be realized in the fields of medical therapy and photonics,[5−7] and the two-photon spectroscopy has become linked to the synthesis of materials with special properties with respect to nonlinearity, processability, and stability. One can here distinguish an important role of theory and calculations to aid the synthesis, to obtain more basic understanding of the underlying mechanisms, and to search for special structure−property relations.

The direct way of computing a TPA spectrum is through the explicit use of sum-over-state (SOS) expressions, in which, at least formally, all intermediate states have to be included. Usually, a satisfactory result can only be obtained after inclusion of hundreds of states, and such a slow convergence makes the explicit SOS method most impractical for simulations based on first-principle approaches. This difficulty can readily be overcome by using response theory, in which the exact SOS value is implicitly obtained by solving a set of linear matrix equations. So far response theory has been successfully applied to TPA spectra of atoms,[8−10] small molecules,[8,11−15] large oligomers,[16,17] and two-dimensional charge-transfer molecules.[18] In combination with the Herzberg−Teller expansion, the vibrationally resolved two-photon spectra of aromatic molecules have been calculated at the *ab initio* level[12,13] with results that reproduce experimental observations.

One important aspect that has not been addressed much by theory are the effects of a solvent on the TPA of molecules—although these effects have been found to be important for a variety of other optical properties. Much work has been devoted in the past to the understanding of solvent-induced effects on both geometric and electronic structures as well as on the nonlinear optical responses, something we here want to accomplish for TPA applications as well. In this context, it is relevant to mention that solvent effects on the TPA of donor−acceptor stilbene recently were studied by Kogej et al.[22] at a semiempirical level using an internal finite field approach. We focus on three issues in the current study: (i) the relationship between the self-consistent reaction field and internal finite field approaches for the TPA cross sections, (ii) the local field factors, and (iii) the comparison between results from spherical and ellipsoidal cavities. A short push−pull polyene will be used as the model molecule, and some particular features of this molecule will be discussed.

## Theory for Two-Photon Absorption Cross Sections

From a macroscopic point of view, two-photon absorption cross sections of randomly oriented systems, such as gases and liquids, can be directly related to the imaginary part of the third susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$. On a molecular, microscopic level, the corresponding property of interest is the second hyperpolarizability $\gamma$ for which the SOS expression is written as[19]

$$\gamma_{\alpha\beta\gamma\delta}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \hbar^{-3}\sum P_{-\sigma,1,2,3} \times \left[\sum_{klm}{}' \frac{\langle 0|\mu_\alpha|k\rangle\langle k|\bar{\mu}_\beta|l\rangle\langle l|\bar{\mu}_\gamma|m\rangle\langle m|\mu_\delta|0\rangle}{(\omega_k-\omega_\sigma+i\Gamma_k)(\omega_l-\omega_2-\omega_3+i\Gamma_l)(\omega_m-\omega_3+i\Gamma_m)} - \sum_{kl}{}' \frac{\langle 0|\mu_\alpha|k\rangle\langle k|\mu_\beta|0\rangle\langle 0|\mu_\gamma|l\rangle\langle l|\mu_\delta|0\rangle}{(\omega_k-\omega_\sigma+i\Gamma_k)(\omega_l+\omega_2+i\Gamma_l)(\omega_l-\omega_3+i\Gamma_l)}\right] \quad (1)$$

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where $\sum P_{-\sigma,1,2,3}$ represents the summation over the 24 terms obtained by permuting the pairs of dipole moment operators and optical frequencies $(\mu_\alpha,-\omega_\sigma)$, $(\mu_\beta,\omega_1)$, $(\mu_\gamma,\omega_2)$, and $(\mu_\delta,\omega_3)$, the primes denote omission of the ground state $|0\rangle$ in the summations, $\bar{\mu}$ is the fluctuation of the dipole moment operator $\mu - \langle 0|\mu|0\rangle$, $\hbar\omega_k$ are the excitation energies, and $\Gamma_k$ are the lifetime broadenings of the excited states. The averaged quantity of $\gamma$ is defined as

$$\bar{\gamma} = (1/15)\sum_{i,j=x,y,z}(\gamma_{iijj} + \gamma_{ijij} + \gamma_{ijji}) \qquad (2)$$

where the frequency arguments have been suppressed. If we consider $\gamma(-\omega;\omega,-\omega,\omega)$ for $\omega = (1/2)\omega_f$, where $\hbar\omega_f$ is the excitation energy of the two-photon state $|f\rangle$, then some terms in eq 1 will be resonant; that is to say, the real part of one or more factors in the denominators will vanish. Such terms will, due to the resonance, dominate the complete summation, and it is reasonable to neglect all nonresonant contributions. Having done that, the expression for $\gamma(-\omega;\omega,-\omega,\omega)$ with $\omega = (1/2)\omega_f$ becomes

$$\gamma_{\alpha\beta\gamma\delta}(-\omega;\omega,-\omega,\omega) = \hbar^{-3}\sum P_{1,3}\sum P_{-\sigma,2}{\sum_{km}}'\frac{\langle 0|\mu_\alpha|k\rangle\langle k|\bar{\mu}_\gamma|f\rangle\langle f|\bar{\mu}_\delta|m\rangle\langle m|\mu_\beta|0\rangle}{(\omega_k-\omega)\mathrm{i}\Gamma_f(\omega_m-\omega)} = \frac{\hbar^{-3}}{\mathrm{i}\Gamma_f}\sum P_{-\sigma,2}\sum_k\frac{\langle 0|\mu_\alpha|k\rangle\langle|\mu_\gamma|f\rangle}{(\omega_k-\omega)}\sum P_{1,3}\sum_m\frac{\langle f|\mu_\delta|m\rangle\langle m|\mu_\beta|0\rangle}{(\omega_m-\omega)} = \frac{\hbar^{-1}}{\mathrm{i}\Gamma_f}S_{\alpha\gamma}S^*_{\beta\delta} \qquad (3)$$

where we note that in the intermediate step the summation *includes* the ground state $|0\rangle$ as a consequence of $\bar{\mu}$ turning into $\mu$, and that in the last step the two-photon transition matrix element $S$ has been introduced for

$$S_{\alpha\beta} = \sum_k\left[\frac{\langle 0|\mu_\alpha|k\rangle\langle k|\mu_\beta|f\rangle}{\omega_k-\omega} + \frac{\langle 0|\mu_\beta|k\rangle\langle k|\mu_\alpha|f\rangle}{\omega_k-\omega}\right] \qquad (4)$$

We thus see that the TP cross section can be determined either directly as the imaginary part of $\gamma$ at the TP resonance or, alternatively, by computing the individual TP transition matrix elements $S$ and then using eq 3. Using the latter technique, we benefit from the fact that the TP transition matrix elements can be identified from the residue of the quadratic response function.[20] This method has been employed in our previous work,[16−18] and we therefore leave out the details here.

The orientational average of $\gamma$ in eq 2, which is suitable for comparison with experimental data measured on a randomly oriented sample, gives a corresponding relation for the TP cross section

$$\delta_{\mathrm{TP}} = (1/15)\sum_{i,j=x,y,z}(S_{ii}S^*_{jj} + 2S_{ij}S^*_{ij}) \qquad (5)$$

However, two-photon absorption, unlike one-photon absorption, is dependent on the polarization of the incident light, and this equation is therefore only valid when the incident radiation is monochromatic and linearly polarized. For a more complete treatment we refer to ref 21. Experimental spectra with line broadening are connected to the $\delta_{\mathrm{TP}}$ through

$$\sigma^{(2)}_{0f} = \frac{8\pi^3 a_0{}^5\alpha}{c_0}\frac{\omega^2 g(\omega)}{\Gamma_f}\delta_{\mathrm{TP}} \qquad (6)$$

where $a_0$ is the Bohr radius, $c_0$ the speed of light, $\alpha$ the fine structure constant, and $\omega$ the photon energy, and $g(\omega)$ provides the spectral line profile, which often is assumed to be a $\delta$-function.

So far, we have only been concerned with the case of an isolated molecule, or the infinitely dilute gas, and turning to the condensed phase, as described with cavity models, we need to consider the appropriate local field factors. Since we know that the TPA is $I^2$ dependent, where $I$ is the intensity of the light, it can be anticipated that the condensed-phase TPA cross sections can be written as

$$\sigma^{(2)}_{0f} = \frac{8\pi^3 a_0{}^5\alpha}{c_0}\frac{\omega^2 g(\omega)}{n^2\Gamma_f}l_\omega{}^4\delta^{\mathrm{sol}}_{\mathrm{TP}} \qquad (7)$$

where $l_\omega$ is the local field factor and $\delta^{\mathrm{sol}}_{\mathrm{TP}}$ denotes the TP cross section of the solute molecule. However, the explicit expression for the local field factors depends on the technique used for calculating the corresponding solute properties. Two alternative ways to do so were shown in our recent study[24] defining the solute properties with respect to either the cavity field, as in the self-consistent reaction field (SCRF) approach, or the local field, as in the internal finite field (IFF) approach. In the former case—where solute molecular properties are defined with respect to the cavity fields—and when employing a spherical cavity, the local field factors become

$$l_\omega = \frac{3n_\omega{}^2}{2n_\omega{}^2 + 1} \qquad (8)$$

In the latter case, i.e., in IFF calculations, properties are straightforwardly computed by applying a finite field of a strength determined from the reaction field $\mathbf{F}^{\mathrm{R}}$. It has been shown in our previous studies that the field strength, without loss of accuracy, can be calculated directly (as opposed to self-consistently) from the gas-phase dipole moment $\mu$ and polarizability $\alpha$ as

$$\mathbf{F}^{\mathrm{R}} = (1 - \mathbf{f}^{\mathrm{R}}\boldsymbol{\alpha})^{-1}\mathbf{f}^{\mathrm{R}}\mu \qquad (9)$$

However, it was also shown that the properties thereby obtained (denoted by a superscript loc) can be transformed through analytic relations to those defined with respect to cavity fields (denoted by a superscript cav) so that they are equivalent to the properties computed in SCRF schemes adopting the dipolar approximation. This aspect will be further demonstrated in the Results and Discussion section. The local field and cavity field properties have the following relationships:

$$\mu^{\mathrm{cav}}_i = \mu^{\mathrm{loc}}_i \qquad (10)$$

$$\alpha^{\mathrm{cav}}_{ij} = l_{ia}\alpha^{\mathrm{loc}}_{aj} \qquad (11)$$

$$S^{\mathrm{cav}}_{ij} = l_{ia}l_{jb}S^{\mathrm{loc}}_{ab} \qquad (12)$$

$$l_{ij} = \delta_{ij} + f^{\mathrm{R}}_{ia}\alpha^{\mathrm{cav}}_{aj}(-\omega;\omega) \qquad (13)$$

where the reaction field factor for a spherical cavity with radius

**TABLE 1: Bond Length Alternation (au) of $NH_2-(C_1HHC_2C_3HHC_4)-NO_2$ in Different Solutions[a]**

| | SCI-PCM | | | | IEF-PCM[b] | | | |
|---|---|---|---|---|---|---|---|---|
| $\epsilon$ | $C_1C_2$ | $C_2C_3$ | $C_3C_4$ | BLA | $C_1C_2$ | $C_2C_3$ | $C_3C_4$ | BLA |
| | | | | SCF | | | | |
| 1.00 | 1.330 | 1.456 | 1.340 | 0.121 | 1.3440 | 1.4413 | 1.3550 | 0.0917 |
| 2.28 | 1.337 | 1.447 | 1.348 | 0.104 | | | | |
| 6.02 | 1.345 | 1.434 | 1.359 | 0.082 | | | | |
| 13.3 | 1.348 | 1.430 | 1.363 | 0.075 | | | | |
| 32.6 | 1.350 | 1.427 | 1.365 | 0.070 | | | | |
| 78.0 | 1.351 | 1.426 | 1.365 | 0.068 | 1.3949 | 1.3896 | 1.3966 | −0.00614 |
| | | | | DFT | | | | |
| 1.00 | 1.362 | 1.434 | 1.350 | 0.078 | | | | |
| 2.28 | 1.369 | 1.426 | 1.356 | 0.064 | | | | |
| 6.02 | 1.375 | 1.420 | 1.362 | 0.052 | | | | |
| 13.3 | 1.377 | 1.417 | 1.364 | 0.047 | | | | |
| 32.6 | 1.379 | 1.416 | 1.366 | 0.044 | | | | |
| 78.0 | 1.379 | 1.415 | 1.366 | 0.042 | | | | |

[a] The geometries are optimized with the cc-pVDZ basis set. [b] From ref 34.

$a$ is given by

$$f^R = \frac{2(\epsilon - 1)}{a^3(2\epsilon + 1)} \tag{14}$$

with $\epsilon$ being the dielectric constant of the solvent.

## Computational Details

We focus our study on a short push−pull polyene, $NO_2-(C_2H_2)_2-NH_2$, in different solutions. The geometry optimization was carried out using the self-consistent isodensity polarized continuum model (SCI-PCM) as implemented in the GAUSSIAN-94 program,[25] with Dunning's cc-pVDZ basis set[26] at the Hartree−Fock and density functional theory B3LYP levels. A similar basis set, the Dunning/Huzinaga double-$\zeta$ basis set, was used in a previous study of the geometry and nonlinear optical properties of similar push−pull molecules in solutions with the PCM model.[34] The solute properties are calculated using SCRF quadratic response theory.[28] Sadlej's polarizing basis set[27] was also used for the properties unless otherwise stated. A locally modified version of the DALTON[29] quantum chemistry program has been used in the present work, which includes a parallel implementation[30,31] of the two-electron integrals.

## Results and Discussion

**Geometries.** There have been several theoretical studies on the geometrical changes of push−pull polyenes upon solvation in recent years, employing different approximations. Meyers *et al*.[32] used the internal finite field method and semiempirical calculations to simulate the solvent effects. Using the Onsager reaction field model with a spherical cavity at the semiempirical level, Albert *et al*.[33] found that the finite field strengths used in Meyers' studies were unrealistically large; the reaction field calculations gave much smaller geometrical changes than those with the finite field calculations. The sophisticated *ab initio* integral equation formalism (IEF) for PCM calculations by Cammi *et al*.[34] provided results that are in good agreement with those obtained from a hybrid quantum mechanical and molecular mechanical (QM/MM) method,[35] and with experimental observations.

We use the standard PCM approach in the GAUSSIAN-94 program to optimize the geometries of $NO_2-(C_2H_2)_2-NH_2$ in different solutions. The generated geometries will be used later for calculating the TPA cross sections. In Table 1, the bond length alternation (BLA) of $NO_2-(C_2H_2)_2-NH_2$ in different solvents is summarized. The solvent effects on the molecular geometry are quite significant. However, our BLA values of SCF/cc-pVDZ are different from those given in ref 34. For instance, in water, the BLA from SCI-PCM at the SCF level is 0.0682, a value that is much larger than the value of −0.006 14 from IEF-PCM.[34] Such a difference might be due to the different basis sets used, or simply the different theoretical approaches.

The BLA values from the DFT B3LYP calculations are significantly smaller compared to the corresponding SCF results. It was shown from NMR measurements in ref 33 that the structures of a similar push−pull molecule, 3-(dimethylamino)-propenal, in solutions should lie between the polyenic and cyanine limits. This seems to indicate that (with the cc-pVDZ basis set) SCF calculations for BLA values for $NO_2-(C_2H_2)_2-NH_2$ in nonpolar solutions are less reliable than those of DFT. It should be mentioned that the geometries have also been optimized with DFT/B3LYP using a 6-31G(d,p) basis set, which are very close to those from DFT/B3LYP/cc-pVDZ and will not be presented here.

**Local Field versus Cavity Field Approaches.** As mentioned above, the TPA cross sections calculated from the SCRF method are directly connected to those obtained by the internal finite field approach through local field factors. Such connections have also been derived for polarizabilities and hyperpolarizabilities of solutes.[24] We have calculated the dipole moments and static polarizabilities of $NO_2-(C_2H_2)_2-NH_2$ in two different solutions, with $\epsilon = 2.28$ and 78.0, from the IFF approach with respect to a local field and a cavity field, and from SCRF with multipolar expansions including terms up to $l = 1$ (only the dipolar term) and $l = 6$. A spherical cavity with a radius of 10.96 au was employed and was determined from the molecular length plus the van der Waals radii of the outermost atoms.

The calculated results with SCF geometries are listed in Table 2. It shows that the dipole moments are the same for both the IFF approach and the dipolar SCRF calculation, where the multipolar contributions are found to be very small in general. The difference between polarizabilities obtained from local field and cavity field approaches is quite large. The dipolar SCRF results are well reproduced by the ones from the IFF approach with respect to the cavity field as expected. Similar to the dipole moment, the multipolar contributions are very small for polarizabilities.

Results for the dominant component of the TPA matrix element $S_{xx}$ and the TPA cross sections $\delta_{TP}$ of the first excited state of $NO_2-(C_2H_2)_2-NH_2$ at SCF geometries are shown in Table 3. The results confirm the equivalence of SCRF and IFF results when the latter are transformed to refer to the cavity fields rather than the local induced fields.

**Ellipsoidal versus Spherical Cavity.** At the present, only the spherical cavity model is available for SCRF calculations

**TABLE 2: Dipole Moments and Static Polarizabilities of $NO_2-(C_2H_2)_2-NH_2$ in Different Solutions Obtained from Cavity Field, Local Field, and Self-Consistent Reaction Field Approaches and a Spherical Cavity**[a]

| | IFF | | SCRF | |
|---|---|---|---|---|
| property | loc | cav | $l = 1$ | $l = 6$ |
| | | $\epsilon = 2.28$ | | |
| $\mu_x$ | 3.48 | 3.48 | 3.49 | 3.52 |
| $\mu_y$ | −0.16 | −0.16 | −0.16 | −0.17 |
| $\mu_z$ | 0.30 | 0.30 | 0.30 | 0.31 |
| $\alpha_{xx}$ | 117.0 | 122.0 | 122.1 | 123.6 |
| $\alpha_{yy}$ | 66.8 | 68.3 | 68.3 | 68.6 |
| $\alpha_{zz}$ | 26.7 | 27.0 | 27.0 | 27.1 |
| | | $\epsilon = 78.0$ | | |
| $\mu_x$ | 4.21 | 4.21 | 4.21 | 4.32 |
| $\mu_y$ | −0.29 | −0.29 | −0.29 | −0.30 |
| $\mu_z$ | 0.12 | 0.12 | 0.12 | 0.12 |
| $\alpha_{xx}$ | 127.9 | 141.3 | 141.4 | 146.0 |
| $\alpha_{yy}$ | 65.9 | 69.4 | 69.4 | 69.9 |
| $\alpha_{zz}$ | 26.3 | 26.8 | 26.8 | 27.0 |

[a] All values are given in atomic units.

**TABLE 3: TPA Cross Sections of the First Excited State of $NO_2-(C_2H_2)_2-NH_2$ Obtained from Cavity Field, Local Field, and Self-Consistent Reaction Field Approaches and a Spherical Cavity**[a]

| | | IFF | | | | SCRF | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | loc | | cav | | $l = 1$ | | $l = 6$ | |
| | state | $S_{xx}$ | $\delta_{TP}$ | $S_{xx}$ | $\delta_{TP}$ | $S_{xx}$ | $\delta_{TP}$ | $S_{xx}$ | $\delta_{TP}$ |
| $\epsilon = 2.28$ | $S_1$ | 56.4 | 603 | 62.3 | 742 | 62.6 | 744 | 63.8 | 773 |
| $\epsilon = 78$ | $S_1$ | 54.7 | 565 | 69.6 | 930 | 70.5 | 942 | 73.3 | 1019 |

[a] All values are given in atomic units.

of TPA cross sections.[28] Such a model appears not to be suitable for descriptions of chainlike push−pull polyenes, and we are motivated to examine the performance of the spherical cavity model against other geometrically more reasonable models. A simple solution to obtain this is to construct the ellipsoidal cavity within the IFF approach. In this case, the reaction field factor $f^R_{mn}$ is given by[36]

$$f^R_{mn} = \frac{3}{a_x a_y a_z} \frac{\kappa_m(1-\kappa_m)(\epsilon-1)}{\epsilon+(1-\epsilon)\kappa_m}\delta_{mn} \tag{15}$$

where $\delta_{mn}$ is a $\delta$-function, $a_x$, $a_y$, and $a_z$ are the principal axes of the ellipsoidal cavity, and $\kappa_m$ is defined as

$$\kappa_m = \frac{a_x a_y a_z}{2}\int_0^\infty \mathrm{d}s\,[(s+{a_x}^2)(s+{a_y}^2)(s+{a_z}^2)]^{-1/2} \times (s+{a_m}^2)^{-1} \tag{16}$$

fulfilling the relation $\kappa_x + \kappa_y + \kappa_z = 1$. For a spherical cavity $\kappa_i = 1/3$. The finite field strength is here determined by eq 9.

The calculated TPA cross sections and the one-photon absorption wavelength obtained from the cc-pVDZ and Sadlej's basis sets with SCF geometries are listed in Table 4. In general, the one-photon absorption is red-shifted by 70 and 80 nm for the cc-pVDZ and Sadlej's basis sets, respectively, when going from the gas phase to the most polar solution. This has some practical advantages since most applications require the one-photon wavelength to fall into the optical visible region. The calculated results show quite strong basis set dependence, especially when the molecule is dissolved in strongly polar solutions. This is partly due to the basis set dependence of the dipole moment, which determines the reaction field strength. Two results obtained from the spherical cavity calculations are also listed for comparison. These show that the cavity shape has noticeable effects on both $\lambda$ and $\delta_{TP}$, but still perhaps less than one might expect. It is of course predominantly a consequence of fact that the TPA of push−pull polyenes is governed by the component along the molecular axis. The change of cavity shape has thus only a minor effect on properties along this particular direction, and it thus seems that, for the study of structure−property relationships, the use of a spherical cavity is yet a reasonable approximation.

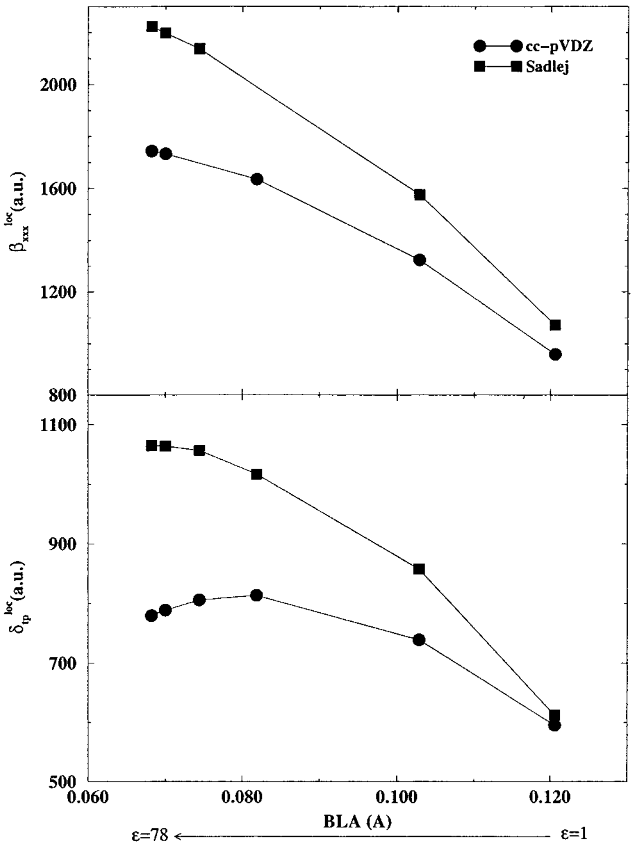

**Figure 1.** Solvent dependence of the static first hyperpolarizability $\beta(0; 0, 0)$ and the TPA cross section of the first excited state of $NO_2-(C_2H_2)_2-NH_2$. The SCF/cc-pVDZ geometries are used. All properties (au) are calculated using the IFF approach and an ellipsoidal cavity.

**TPA Cross Section versus the First Hyperpolarizability.** Recently, Kogej *et al.*[22] studied the structure−property relation-

**TABLE 4: TPA Cross Sections and One-Photon Absorption Wavelength of $NO_2-(C_2H_2)_2-NH_2$ in Different Solutions**[a]

| $\epsilon = 1.0$ | | $\epsilon = 2.28$ | | $\epsilon = 13.3$ | | $\epsilon = 32.6$ | | $\epsilon = 78$ | |
|---|---|---|---|---|---|---|---|---|---|
| $\lambda$ (nm) | $\delta_{TP}$ (au) | $\lambda$ (nm) | $\delta_{TP}$ (au) | $\lambda$ (nm) | $\delta_{TP}$ (au) | $\lambda$ (nm) | $\delta_{TP}$ (au) | $\lambda$ (nm) | $\delta_{TP}$ (au) |
| | | | | cc-pVDZ | | | | | |
| 490 | 595 | 520 | 739 | 553 | 806 | 557 | 789 | 559 | 780 |
| | | 513[b] | 603[b] | | | | | 541[b] | 565[b] |
| | | | | Sadlej | | | | | |
| 512 | 612 | 547 | 858 | 585 | 1057 | 590 | 1064 | 592 | 1065 |

[a] All results are calculated using the IFF approach and an ellipsoidal cavity. [b] Results by employing a spherical cavity.

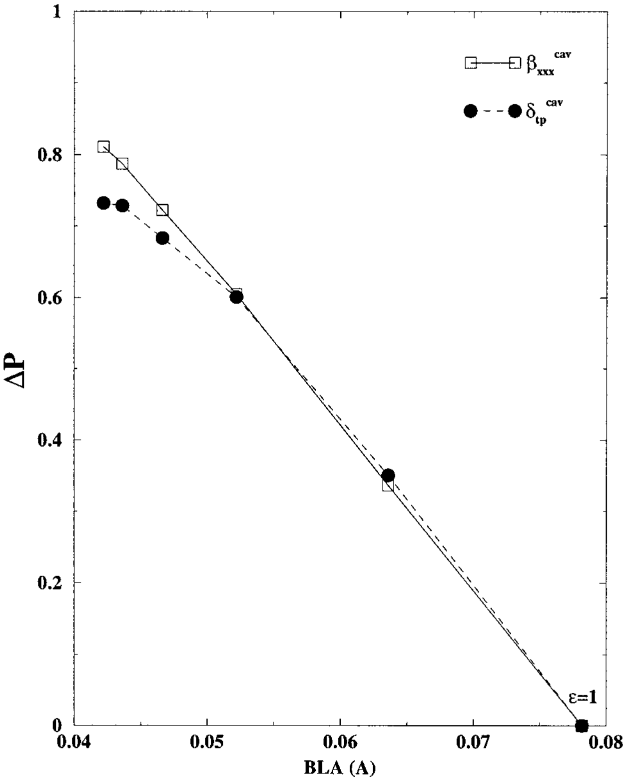

**Figure 2.** Solvent-induced property changes, $\Delta P = (P^{sol} - P^{gas})/P^{gas}$, where $P$ refers to the static first hyperpolarizability and the TPA cross section of the first excited state of $NO_2-(C_2H_2)_2-NH_2$. The geometries of molecules in solutions are from DFT/B3LYP/cc-pVDZ calculations. All properties (au) are calculated using SCRF response theory and a spherical cavity.

ships for the TPA of donor−acceptor stilbene derivatives using the IFF approach at the semiempirical level. They showed that the evolution of the TPA cross section with respect to the bond order alternation closely follows that of $\beta$, and that the TPA cross section is strongly dependent on the geometrical changes.

In Figure 1, the solvent dependences of the TPA cross section of the first excited state and the static value of the first hyperpolarizability $\beta_{xxx}(0;0,0)$ are shown. The IFF approach with an ellipsoidal cavity was employed here. The solvent dependence, or geometrical dependence (BLA), of $\beta$ is very large; the $\beta$ value at the more polar solution is found to be more than twice the value in the gas phase. No saturation is reached. These results are in line with the previous finding for a similar system given in refs 32 and 33; however, the saturation for the TPA cross section seems to be different. In general, the solvent dependence is found to be smaller than that for $\beta$ and displays a saturation. Similar trends have also been found for the results obtained from analytical SCRF response theory with a spherical cavity at DFT/B3LYP geometries, as shown in Figure 2. As pointed out before, the BLA values are quite different (and better) for DFT- compared to SCF-optimized geometries. The solvent dependence for the TPA cross section thus appears to be different from the one given in ref 22, and may indicate that the structure−property relationships for the TPA of donor−acceptor substituted stilbene cannot be generalized to the case of push−pull polyenes. It is our opinion that the field strengths used in the TPA calculations in ref 22 are too large to be realistic.

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## References and Notes

(1) Göpper-Mayer, M. *Ann. Phys. (Leipzig)* **1931**, *9*, 273.

(2) Kaiser, W.; Garrett, C. G. B. *Phys. Rev. Lett.* **1961**, *7*, 229.

(3) Mahr, H. In *Quantum Electronics*; Rabin, H., Tang, C. L., Eds.; Academic Press: New York, 1975; Vol. IA, p 285.

(4) Callis, P. R. *Annu. Rev. Phys. Chem.* **1997**, *48*, 271.

(5) Denk, W.; Strickler, J. H.; Webb, W. W. *Science* **1991**, *248*, 73.

(6) Albota, M.; Beljonne, D.; Brédas, J. L.; Ehrlich, J. E.; Fu, J.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCord-Maughon, D.; Perry, J. W.; Röckel, H.; Rumi, M.; Subramaniam, G.; Webb, W. W.; Wu, X.; Xu, C. *Science* **1998**, *281*, 1653.

(7) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, I. Y. S.; McCord-Maughon, D.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X. L.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51.

(8) Hettema, H.; Jensen, H. J. A.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1992**, *97*, 1174.

(9) Sundholm, D.; Rizzo, A.; Jørgensen, P. *J. Chem. Phys.* **1994**, *101*, 4931.

(10) Hättig, C.; Christiansen, O.; Jørgensen, P. *J. Chem. Phys.* **1998**, *108*, 8355.

(11) Luo, Y.; Vahtras, O.; Ågren, H.; Jørgensen, P. *Chem. Phys. Lett.* **1993**, *204*, 587.

(12) Luo, Y.; Ågren, H.; Knuts, S.; Minaev, B. F.; Jørgensen, P. *Chem. Phys. Lett.* **1993**, *209*, 513.

(13) Luo, Y.; Ågren, H.; Knuts, S.; Jørgensen, P. *Chem. Phys. Lett.* **1993**, *213*, 356.

(14) Luo, Y.; Ågren, H.; Stafström, S. *J. Phys. Chem.* **1994**, *98*, 7782.

(15) Sundholm, D.; Olsen, J.; Jørgensen, P. *J. Chem. Phys.* **1995**, *102*, 4143.

(16) Norman, P.; Luo, Y.; Ågren, H. *Chem. Phys. Lett.* **1998**, *296*, 8.

(17) Norman, P.; Luo, Y.; Ågren, H. *Opt. Commun.* **1999**, *168*, 297.

(18) Norman, P.; Luo, Y.; Ågren, H. *J. Chem. Phys.* **1999**, *111*, 7758.

(19) Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513.

(20) Olsen, J.; Jørgensen, P. *J. Chem. Phys.* **1985**, *82*, 3235.

(21) McClain, W. M. *J. Chem. Phys.* **1971**, *55*, 2789.

(22) Kogej, T.; Beljonne, D.; Meyers, F.; Perry, J. W.; Marder, S. R.; Brédas, J. L. *Chem. Phys. Lett.* **1998**, *298*, 1.

(23) Flytzanis, C. In *Quantum Electronics*; Rabin, H., Tang, C. L., Eds.; Academic Press: New York, 1975; Vol. IA, p 88.

(24) Macak, P.; Norman, P.; Luo, Y.; Ågren, H. *J. Chem. Phys.* **2000**, *112*, 1868.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94 Revision B.2*; Gaussian Inc.: Pittsburgh, PA, 1995.

(26) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(27) Sadlej, A. J. *Theor. Chim. Acta* **1991**, *79*, 123.

(28) Sylvester-Hvid, K. O.; Mikkelsen, K. V.; Jonsson, D.; Norman, P.; Ågren, H. *J. Chem. Phys.* **1998**, *109*, 5576.

(29) Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Andersen, T.; Bak, K. L.; Bakken, V.; Christiansen, O.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Saue, T.; Taylor, P. R.; Vahtras, O. *Dalton, an ab initio electronic structure program*, Release 1.0; 1997. See http://www.kjemi.uio.no/software/dalton/dalton.html.

(30) Norman, P.; Jonsson, D.; Ågren, H.; Dahle, P.; Ruud, K.; Helgaker, T.; Koch, H. *Chem. Phys. Lett.* **1996**, *253*, 1.

(31) Ruud, K.; Jonsson, D.; Norman, P.; Ågren, H.; Saue, T.; Jensen, H. J. Aa.; Dahle, P.; Helgaker, T. *J. Chem. Phys.* **1998**, *108*, 7973.

(32) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. *J. Am. Chem. Soc.* **1994**, *116*, 10703.

(33) Albert, I. D.; Marks, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 9714.

(34) Cammi, R.; Mennucci, B.; Tomasi, J. *J. Am. Chem. Soc.* **1998**, *120*, 8834.

(35) Gao, J.; Alhambra, C. *J. Am. Chem. Soc.* **1997**, *119*, 2962.

(36) Böttcher, C. J. F. *Theory of electric polarization*; Elsevier: Amsterdam, 1973; Vol. I.