

Excited-state absorption and third-order optical nonlinearities in symmetric π -electron organic molecules

G. R. J. Williams

Land, Space and Optoelectronics Division, Defence Science and Technology Organisation, P.O. Box 1500, Salisbury SA 5108, Australia
(Fax: + 61-8/259-5055, E-mail: geoff.williams@dsto.defence.gov.au)

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Abstract. Excited-State Absorption (ESA), Two-Photon Absorption (TPA) and the third-order polarizability $\gamma(\omega; \omega, \omega, -\omega)$ have been investigated for a model dichloride derivative of a symmetrically substituted benzylidene aniline (SBAC), using a multielectron configuration-interaction procedure. The calculations indicate that SBAC exhibits ESA across the visible region of the spectrum, but that it is not as extensive as for molecules such as the phthalocyanines. The magnitude of the third-order polarizability is dominated by resonance enhancement from a very strong $A_g \rightarrow B_u$ one-photon absorption. The calculated off-resonance value for $\gamma(\omega; \omega, \omega, -\omega)$ suggests that SBAC is a potential candidate for ultrafast switching applications.

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The optical nonlinear susceptibilities of π -electron organic molecules and polymers are known to be large,

$$\gamma_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3) = \frac{K}{\hbar^3} \sum_P \left(\sum_{m, n, s \neq g} \frac{\langle g|i|m\rangle \langle m|l|n\rangle \langle n|k|s\rangle \langle s|j|g\rangle}{(\omega_{mg} - \omega - i\tau_{mg})(\omega_{ng} - \omega_1 - \omega_2 - i\tau_{ng})(\omega_{sg} + \omega_1 - i\tau_{sg})} - \sum_{m, n \neq g} \frac{\langle g|i|m\rangle \langle m|l|g\rangle \langle g|k|n\rangle \langle n|j|g\rangle}{(\omega_{mg} - \omega - i\tau_{mg})(\omega_{ng} - \omega_1 - i\tau_{ng})(\omega_{ng} + \omega_2 - i\tau_{ng})} \right), \quad (1)$$

and the resulting optical response ultrafast, which are attractive features for the development of any potential photonic devices [1, 2]. A further attractive feature of some π -electron systems, particularly for optical power limiting applications, is that they exhibit Excited-State Absorption (ESA). One class of π -electron molecules that have been investigated for their nonlinear optical properties and optical device applications are symmetrically substituted benzylidene aniline (SBA) compounds [3–5]. Symmetric π -electron systems have

also been found to exhibit enhanced excited-state absorption characteristics that make them of considerable interest for potential optical power limiting applications [6–8]. These molecules generally possess D_{4h}, D_{2h}, C_{2h} or C_{2v} symmetry. In this study, the third-order optical nonlinear properties, and excited-state absorption, of a dichloride derivative of a symmetrically substituted benzylidene aniline (SBAC) with symmetry C_{2h} , have been investigated. The structure of the model SBAC molecule studied is shown in Fig. 1.

General expressions for the third-order molecular nonlinear polarizability may be obtained from time-dependent perturbation theory using algebraic or diagrammatic techniques [9]. A general expression may be written in the form

(see (1) below)

where $\omega = \omega_1 + \omega_2 + \omega_3$ is the polarization frequency, K is a constant that is characteristic of the specific effect calculated [9], τ_{mg} is the damping factor associated with the excited state m , $\langle m|r|n\rangle$ are dipole transition moments, and \sum_P is the summation for the permutations

of the frequencies. In this work, $\omega_1 = \omega_2 = \omega$ and $\omega_3 = -\omega$, leading to $\gamma(\omega; \omega, \omega, -\omega)$. The real part of the third-order polarizability $\gamma(\omega; \omega, \omega, -\omega)$ ($\text{Re } \gamma$) is responsible for the Kerr-like nonlinear effects, characterized by an intensity-dependent refractive index, that are observed in nonlinear optical materials, and the Two-Photon Absorption (TPA) coefficient is proportional to the imaginary part ($\text{Im } \gamma$) of $\gamma(\omega; \omega, \omega, -\omega)$ for the two-photon absorption process [10].

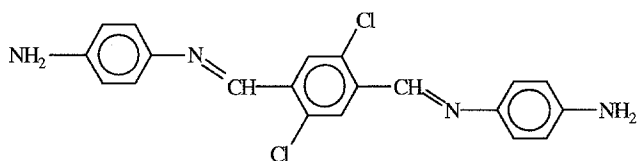


Fig. 1. Model benzylidene aniline SBAC

The Two-Photon Absorption (TPA) transition moment for the transition $g \rightarrow f$ can be explicitly calculated using the expression [11]

$$M_{gf} = \sum_{k \neq g} \frac{\langle g|r|k \rangle \langle k|r|f \rangle}{\omega_k - \frac{1}{2}\omega_f}. \quad (2)$$

The orientationally averaged (isotropic) value of the γ tensor is given by the expression:

$$\langle \gamma \rangle = \frac{1}{15} \sum_{ij} (\gamma_{iij} + \gamma_{iji} + \gamma_{ijj}). \quad (3)$$

1 Theoretical calculations

Excited-State Absorption (ESA) from the first excited singlet state and the first excited triplet state of SBAC has been investigated using a Multi-Electron Configuration-Interaction (MECI) procedure [12]. The third-order polarizability $\gamma(\omega; \omega, \omega, -\omega)$ for the ground state and the first excited singlet and triplet states has been calculated, and two-photon absorption from the ground state was investigated. The MNDO Hamiltonian [13] was used as the ground-state Hamiltonian. The MECI calculations include all single and double excitations (or in the case of the ground-state spectrum, pair-type double excitations). In the case of excited states, the summation in (1) commences from the lowest state of the singlet or triplet manifold. The molecular geometry for the states under consideration has been optimized using the MOPAC molecular orbital program [14]. Additional routines were incorporated into the MOPAC code for the calculation of transition probabilities between excited states, and for the

calculation of ground- and excited-state third-order polarizabilities, and two-photon absorption cross-sections and transition moments [15].

2 Results and discussion

The results obtained for excited-state absorption from the first excited singlet and triplet states are given in Tables 1 and 2. Excitations from the two highest occupied molecular orbitals (MOs) to the 13 lowest unoccupied MOs were included in the calculations. In the tables, ϵ is the molar absorption coefficient, and the absorption wavelengths are in nanometres.

Excited-state absorption occurs across the visible band for both the singlet and triplet states, although it is not as extensive as for molecules such as phthalocyanines [8]. Phthalocyanines would therefore be considered more suitable candidates for optical power limiting applications than SBAC. The major interest in SBAC is for ultrafast optical switching applications [3, 4] via the third-order polarizability, $\gamma(\omega; \omega, \omega, -\omega)$. The calculated third-order polarizability for the ground state is shown in Fig. 2. Excitations from the two highest occupied MOs to the 15

Table 1. Excited-state absorption from first excited singlet state

Wavelength (λ) [nm]	$\log \epsilon$
860	4.82
653	3.80
578	3.38
500	3.20
400	2.30

Table 2. Excited-state absorption from lowest triplet state

Wavelength (λ) [nm]	$\log \epsilon$
774	1.00
648	4.45
437	0.30
410	2.71
371	2.34

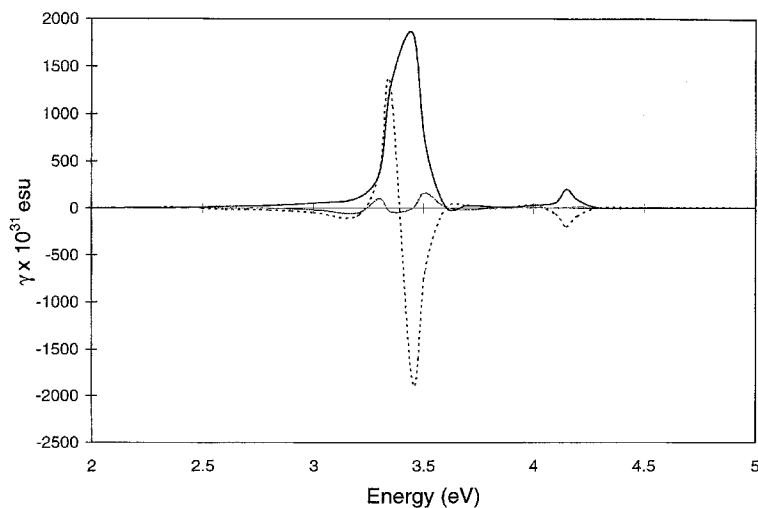


Fig. 2. Third-order polarizability $\gamma(\omega; \omega, \omega, -\omega)$. (---) Real; (—) imaginary; (-·-) modulus

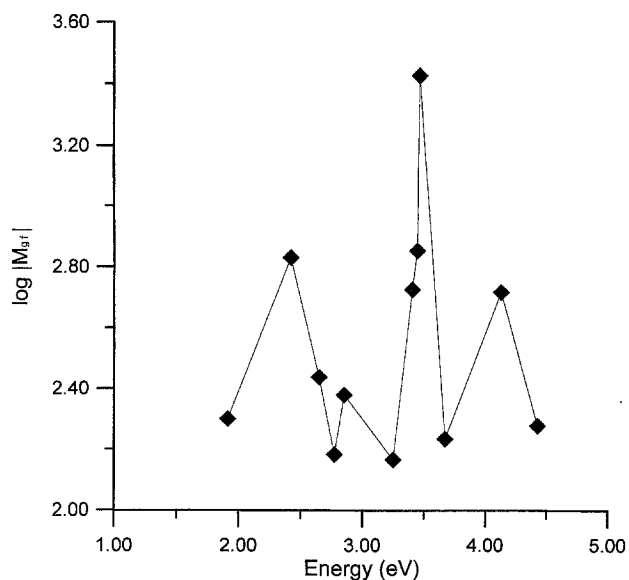


Fig. 3. Two-photon transition moments (note: lines connecting transition moments are intended only as a guide to the eye)

lowest unoccupied MOs were included in the ground-state calculation of $\gamma(\omega; \omega, \omega, -\omega)$. Damping factors for all states were taken to be 0.1 eV.

The spectrum for $\gamma(\omega; \omega, \omega, -\omega)$ is dominated by a strong peak in the energy range 3.3–3.5 eV principally due to resonance enhancement from a very strong ($f=1.6$) one-photon resonance at 3.4 eV, arising from a transition from the ground state ($1A_g$) to the $1B_u$ excited state. A much weaker $1A_g \rightarrow 2B_u$ ($f=0.6$) one-photon resonance at 4.1 eV also provides some resonance enhancement of $\gamma(\omega; \omega, \omega, -\omega)$. The major two-photon absorption also occurs in the region of 3.2–3.6 eV. Analysis of two-photon absorption is assisted by the examination of the calculated two-photon transition moments, displayed (as $\log |M_{gf}|$) in Fig. 3.

As is evident from Fig. 2, two-photon absorption ($\text{Im } \gamma$) plays only a minor role in the resonance enhancement of $|\gamma|$, which is dominated by one-photon effects in this energy region. The largest two-photon transition moment (Fig. 3) is associated with a two-photon state of symmetry A_g at $2\hbar\omega = 6.95$ eV ($\hbar\omega = 3.475$ eV, $\lambda = 357$ nm). Other significant two-photon states, with weaker dipole transition probabilities, are located at 4.8, 6.8, 6.9 and 8.2 eV. It should be noted that the two-photon absorption in the region 3.2–3.6 eV has been enhanced by the calculated close one-photon absorption at 3.4 eV ($\lambda = 365$ nm), again emphasizing the major role played by one-photon processes in this energy region. For optical switching applications, it is desirable to operate in a frequency region where the magnitude of $\gamma(\omega; \omega, \omega, -\omega)$ is as large as possible (so as to minimize the optical gate power required for switching to occur), but where the overall absorption is low (to minimize energy loss). There is generally a tradeoff between these two requirements, as resonance enhancement can dramatically increase the magnitude of $\gamma(\omega; \omega, \omega, -\omega)$, but with the simultaneous disadvantage of potentially excessive absorption. For the

model SBAC studied in this work, the non-resonant value of $\gamma(\omega; \omega, \omega, -\omega)$ (i.e. at zero frequency or $\lambda = \infty$) was calculated to be 1.5×10^{-34} esu. At 1.2 eV ($\lambda = 1030$ nm) the magnitude of $\gamma(\omega; \omega, \omega, -\omega)$ has doubled to 3.0×10^{-34} esu, and at 1.8 eV ($\lambda = 690$ nm) the value has increased by an order of magnitude to 18.6×10^{-34} , as the contribution of near-resonant effects increases. The experimentally observed off-resonance magnitude for $\gamma(\omega; \omega, \omega, -\omega)$ can also show an increased value if there are contributions from excited-state polarizabilities. The calculated values for $\gamma(\omega; \omega, \omega, -\omega)$ at zero frequency for the first excited singlet and triplet states are, respectively, 452×10^{-34} and 124×10^{-34} esu. The values obtained for the excited-state polarizabilities are consistent with previous studies [8, 16–18], which have shown that $\gamma(\omega; \omega, \omega, -\omega)$ can be greatly enhanced (or even change sign) when excited states are optically pumped and then populated for timescales sufficiently long to observe the resulting nonlinear optical effects. The relatively large off-resonance values calculated for $\gamma(\omega; \omega, \omega, -\omega)$ suggest that SBAC compounds should be suitable for fast optical switching applications. Experimentally, Kanbara et al. [3] have investigated ultrafast optical Kerr shutters using organic materials, including SBAC compounds, with input and output optical gate wavelengths between 590 and 1064 nm, and have obtained sub-picosecond switching operation with SBAC materials dissolved in a solid block of poly(methyl methacrylate), PMMA, supporting the conclusion that symmetric π -electron systems are potentially strong candidates for fast optical switching applications.

3 Conclusion

Excited-state absorption, two-photon absorption, and the frequency-dependent nonlinear susceptibility $\gamma(\omega; \omega, \omega, -\omega)$, responsible for ultrafast optical Kerr effects in nonlinear optical materials, have been investigated for a model SBAC molecule. Although the calculations indicate that SBAC is expected to exhibit some excited-state absorption, it is not predicted to be as extensive as for systems such as the phthalocyanines, which are consequently more appropriate choices for optical power limiting applications. However, SBAC is predicted to have a relatively large off-resonant third-order nonlinear susceptibility, and a resonance structure that make it a strong candidate for ultrafast optical switching applications, a conclusion strongly supported by experimental work carried out by Kanbara et al. [3, 4].

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