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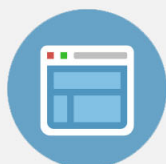
Ab initio studies of two-photon absorption of some stilbenoid chromophores

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Two-photon absorption of a series of donor-acceptor *trans*-stilbene derivatives is studied by means of density functional theory applied to second-order response function. Several important issues in modeling are highlighted which must be addressed for a reliable reproduction of the experimental results. It is evident that the correct order of magnitude of calculated two-photon absorption cross sections can only be obtained if proper account is taken of vibrational broadening of the absorption profiles. A comparison of the theoretical results with the experimental ones indicates that the computed two-photon absorption cross sections are in rough agreement with our previous report, although the observed systematic increase of the cross sections with the electron acceptor strength is not well reproduced. It is suggested that this disagreement may be due not only to the deficiencies of the computations but also to a variety of factors contributing to the experimental value of the effective two-photon absorption cross section, which are not taken into account in the *ab initio* calculations. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1929728]

I. INTRODUCTION

Organic chromophores possessing large two-photon absorption cross sections have been of much recent interest. Thus, reliable theoretical predictions of structure-to-property relations are of extreme importance as a potential alternative to costly and time-consuming synthesis and nonlinear optical (NLO) measurements. Due to the ready availability of ever increasing computing power, it has now become practical to base such predictions on *ab initio* calculations of electronic structure. Among others, the density functional theory (DFT) has gained extreme popularity over the last decade as a tool capable to accurately handle relatively large systems, especially in connection with linear scaling algorithms and parallel performance. The response theory applied to DFT Kohn–Sham reference state allows for the calculation of various molecular properties in an elegant and formally strict way. The second- and third-order response functions were recently implemented in the DALTON program[1] at the DFT level.[2,3]

The newly developed theories and methods require a thorough benchmarking and calibration. It is fortunate that an increasing number of experimental data on complete spectra of two-photon absorption cross sections is now becoming available. This rectifies the previously common situation where only single wavelength data were at hand. However, one must be aware that numerous discrepancies still exist between the experimental results obtained by the direct measurements of nonlinear absorption in various pulse duration and light intensity regimes, and those obtained using indirect methods, such as the popular technique of measuring two-photon induced fluorescence, yield. Thus, in comparison between the experimental and computed two-photon absorption spectra one needs to critically assess the possibility of the existence of additional effects such as excited-state absorption and absorption saturation. Attempts to do this using a more general model have been presented.[4,5]

In the present paper we take advantage of the experimental data provided by a systematic study performed recently on nonlinear absorption properties of a series of donor-acceptor substituted *trans*-stilbene derivatives (see Fig. 1).[6] This experimental work is the basis for our benchmarking of DFT quadratic response *ab initio* calculations to establish the reliability of this technique for predicting two-photon absorption cross-section spectra of moderately big organic chromophores. We address here the issues of the fidelity of reconstruction of positions of excited-state levels and of the capability of the technique to provide quantitative two-photon absorption spectra, as well as to predict trends for optimizing the nonlinear properties of the chromophores.

II. ELECTRONIC STRUCTURE CALCULATIONS

To compute the electronic structure of the compounds of interest we employed the DALTON code[1] and the GAUSSIAN code.[7] The methodologies were those shown by many research groups around the globe to provide results with good reliability.

The ground-state geometries for all compounds were optimized making use of the GAUSSIAN 98 code[7] at the DFT

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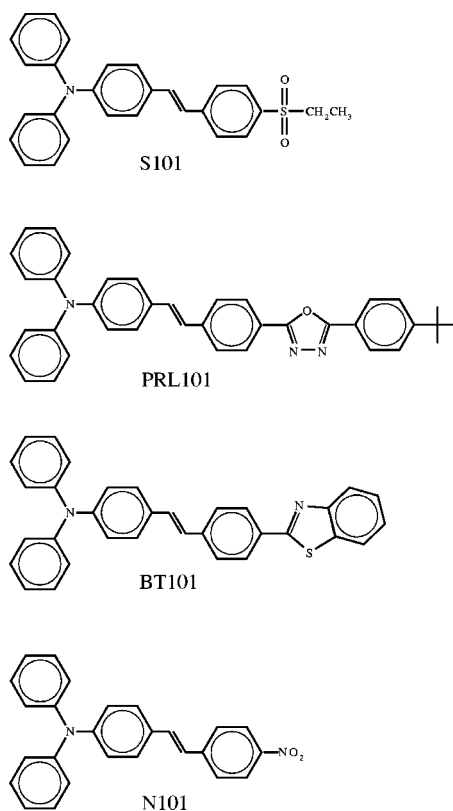
FIG. 1. Chemical structures of the stilbene derivatives studied.

B3LYP/6-31G* level. Ground to excited singlet state absorption spectra were calculated making use of the time-dependent DFT method at B3LYP/6-31G*. We did not compute any of the triplet states, bearing in mind that possible linear and nonlinear absorption channels involving triplet states should be negligibly weak for the studied chromophore series. The permanent dipole moments of the excited states were determined by finite field differentiation of the excited-state energies. The transition dipole moments between the excited singlet states were calculated making use of the configuration-interaction singles (CIS) method, implemented in the GAUSSIAN 98 program, at the B3LYP/6-31G* level. Two-photon transition matrix elements were carried out by means of DFT quadratic response (QR) function recently implemented in the DALTON program.[2] DFT/QR calculations were done with the hybrid functional B3LYP, which is conventional for computing the properties of large conjugated organic molecules and known to provide the best accuracy.[8,9] The basis sets were polarized split-valence 3-21G* and 6-31G*, and correlation consistent polarized valence double zeta (cc-pVDZ) and correlation consistent polarized valence triple zeta (cc-pVTZ). We chose four basis sets in order to check the sensitivity of the results of the QR calculations to the computational model.

III. RESULTS AND DISCUSSION

A. Linear absorption

The first step in comparison of the computed data with the experimental ones is an analysis of the linear absorption spectra: the positions of the absorption bands and estimations

TABLE I. Selected relative excitation energies (ΔE, eV) and dipole moments (μ_i, a.u.) of the low-lying singlet states of PRL-101 [GAUSSIAN 98 TDDFT CI(S)].

μ_i (a.u.)	PRL-101			
	x	y	z	ΔE_{DFT}[a] (eV)
$S_0 S_0$	−0.7890	1.3903	0.6337	
$S_1 S_1$	−10.3327	2.0749	0.9380	
$S_2 S_2$	−3.1156	1.6874	0.7644	
$S_3 S_3$	−5.2292	1.6820	0.7247	
$S_0 S_1$	−4.5649	0.3226	0.1414	2.77
$S_0 S_2$	2.9616	−0.0659	−0.0351	3.55
$S_0 S_3$	1.2753	0.3384	0.2011	3.61
$S_1 S_2$	−9.0848	0.7199	0.3079	
$S_1 S_3$	0.7348	0.4996	0.2390	

[a]Absorption at the equilibrium ground-state geometry.

of the molar extinction coefficients. Tables I–V summarize these results. One can see from these tables that excitation energies of all molecules are systematically underestimated compared to the experimental values. Such underestimation of excitation energies may be expected for charge-transfer (CT) states with the use of the time-dependent DFT (TD-DFT) method because of inadequacy of the long-range behavior of conventional exchange-correlation functionals originating from locality of the electron density.[10] It should be noted that the ordering of the energies of the first absorption band determined experimentally is nevertheless reproduced by the calculations.

The calculation of the absorption strengths corresponding to the transitions in the investigated molecules requires some comment. The molar absorption coefficient ε (cm^{-1} M^{-1}) can be computed by making use of conventional expressions for the one-photon absorption (OPA) cross section or, equivalently, for the imaginary part of the first-order molecular susceptibility $\chi^{(1)}$,

$$\varepsilon = \frac{\omega}{3\varepsilon_0 c \hbar} \frac{d_{S_1 S_0}^2 \Gamma}{\Gamma^2 + (\omega - \omega_{10})^2} 10 N_A, \tag{1}$$

where orientational averaging is taken into account and the Système International (SI) units are used. Here $d_{S_1 S_0}$ is the

TABLE II. Selected relative excitation energies (ΔE, eV) and dipole moments (μ_i, a.u.) of the low-lying singlet states of BT-101 [GAUSSIAN 98 TDDFT CI(S)].

μ_i (a.u.)	BT-101			
	x	y	z	ΔE_{DFT}[a] (eV)
$S_0 S_0$	0.9225	0.2036	−0.0880	
$S_1 S_1$	7.7579	0.1777	−0.0881	
$S_2 S_2$	1.6868	0.1277	−0.0377	
$S_3 S_3$	−1.0206	0.2139	−0.0910	
$S_0 S_1$	4.4918	−0.0173	0.0114	2.72
$S_0 S_2$	−3.1153	−0.0040	−0.0004	3.54
$S_0 S_3$	−0.0488	−0.0466	−0.2324	3.76
$S_1 S_2$	8.1657	−0.0274	0.0134	
$S_1 S_3$	−2.8687	−0.0344	0.1144	

[a]Absorption at the equilibrium ground-state geometry.

TABLE III. Selected relative excitation energies (ΔE, eV) and dipole moments (μ_i, a.u.) of the low-lying singlet states of N-101 [GAUSSIAN 98 TDDFT CI(S)].

μ_i (a.u.)	x	y	z	ΔE_{DFT}[a] (eV)
		N-101		
S_0S_0	3.3033	0.1248	0.0586	
S_1S_1	11.7325	0.2026	0.0852	
S_2S_2	6.9544	0.1762	0.0858	
S_3S_3	4.9063	0.1594	0.0861	
S_0S_1	−3.4452	−0.0083	0.0070	2.50
S_0S_2	2.8227	−0.0134	0.0134	3.55
S_0S_3	0.9107	−0.0533	−0.0649	3.66
S_1S_2	7.4840	0.0541	0.0271	
S_1S_3	1.3343	0.0354	−0.0197	

[a]Absorption at the equilibrium ground-state geometry.

transition matrix element (see Tables I–IV), ω is the frequency of the exciting radiation, $\omega_{10}=(E_1-E_0)/\hbar$ is the transition frequency, Γ is the homogeneous broadening of a transition, and N_A is the Avogadro number.

To make use of the above equation, one needs to assume the value of the damping factor Γ which is often set to 0.1 eV for chromophore solutions.[11] However, the use of such a value in the above equation leads to absorption coefficients that are much larger than the experimental values in Table V. The reason for this is that Eq. (1) contains only the electronic transition matrix element $d_{S_1S_0}=d_{S_1S_0}^{el}$. In fact, in one-mode approximation, the transition matrix element $d_{S_1S_0}$ is a product of the electronic matrix element and the Franck–Condon amplitude $\langle 0|f\rangle$ between zero-point vibrational level (assuming low-temperature approximation) of the ground-state and vibrational levels of the first excited electronic state. In order to simulate the experimental inhomogeneously broadened absorption profile one needs to perform summation of the absorption amplitudes over vibrational levels of the first excited electronic state. The overall experimental broadening is rather large for the studied molecules—the full width at half maximum (FWHM) of the first linear absorption band is about 0.5–0.7 eV according to Ref. 6. Unfortunately, for a system with hundreds of vibrational modes the problem of evaluating the generalized Franck–Condon amplitude is not a trivial one. Thus, to evaluate the values of the absorption coefficients we decided to use the experimental inhomogeneous broadening. However, a simple substitution of the experimental broadening for the value of Γ in Eq. (1), which uses a Lorentzian profile, does not very well reproduce the experimental shapes of the absorption bands, particularly the far-red wing of the absorption profile of chromophores in solutions. The low-energy wing demonstrates an exponential, Urbach-type decay. Therefore, to provide a closer agreement with the experiment, one can recast Eq. (1) in the form of a Gaussian which would supposedly fit the experimentally observed absorption profiles,

$$\varepsilon = \frac{\omega}{3\varepsilon_0 c\hbar}\frac{d_{S_1S_0}^2 e^{-[(\omega-\omega_{10})^2/\Delta^2]}}{\Delta}10N_A, \qquad (2)$$

where $\Delta = $FWHM$/2\sqrt{\ln 2}$ and FWHM is that of the experimental absorption profile. The results based on Eq. (2) where

the resonant condition is applied are presented in Table V.

The calculated molar extinction coefficients show the same systematic trend as the experimental ones, with one exception of BT-101 molecule. The calculated molar extinction coefficient of this molecule is lower than that of PRL-101, opposite to the experimental trend (see Table V), although the difference is rather small. As one can see from Tables I and II, the gaps between the first excited singlet states and the manifolds of higher excited singlet states of PRL-101 and BT-101 molecules are less than 1 eV. Thus, the first absorption bands in PRL-101 and BT-101 contain contributions from more than one electronic transition and the peak molar extinction values should be considered as modified by these overlaps. In the experiment this value for BT-101 is slightly higher than the corresponding number for PRL-101. For all molecules, the prominent overestimation of the calculated molar extinction coefficients can be attributed to the overestimation of the transition dipole moments. The use of cc-pVDZ basis set instead of split-valence 6-31G* basis set for computing transition matrix elements does not change the trend. For example, for S-101 molecule the x component of the transition dipole moment from the ground to the first excited state equals to 3.7574 a.u. with the use of 6-31G* basis set and 3.7841 a.u. with the use of cc-pVDZ basis set.

B. Two-photon absorption

The results of *ab initio* calculations of two-photon absorption (TPA) cross sections are collected in Table VI. In order to compare the results of *ab initio* quadratic response calculations with the experimental numbers, we calculated the TPA cross section $\sigma^{(2)}$, making use of formulas which relate the second-order transition matrix elements S_{ij}, the TPA probability δ_{2p}, and $\sigma^{(2)}$,

$$\sigma^{(2)} = \frac{\omega\delta_{2p}^L}{2c^2\varepsilon_0^2\hbar\Gamma}, \qquad \delta_{2p}^L = \frac{1}{30}(2\delta_F+4\delta_G),$$

$$\delta_F = \sum_{ij} S_{ii}S_{jj}, \qquad \delta_G = \sum_{ij} S_{ij}S_{ij},$$

$$(3)$$

TABLE IV. Selected relative excitation energies (ΔE, eV) and dipole moments (μ_i, a.u.) of the low-lying singlet states of S-101 [GAUSSIAN 98 TDDFT CI(S)].

μ_i (a.u.)	x	y	z	ΔE_{DFT}[a] (eV)
		S-101		
S_0S_0	2.4949	−0.8073	1.2697	
S_1S_1	8.2552	−0.8305	1.3859	
S_2S_2	0.5329	−1.0819	1.2536	
S_3S_3	−1.4599	−1.4338	1.1557	
S_0S_1	3.7574	−0.0271	0.0488	2.93
S_0S_2	−0.1164	−0.1786	0.3266	3.84
S_0S_3	0.0192	1.3104	0.0313	4.03
S_1S_2	−0.7852	0.1191	−0.1933	
S_1S_3	−0.2786	−0.9876	−0.0162	

[a]Absorption at the equilibrium ground-state geometry.

TABLE V. Molar extinction coefficients of S-101, PRL-101, BT-101, and N-101.

Molecule	ε^{a} (10^4 cm^{-1} M^{-1})	$\Delta E_{DFT}{}^{b}$ (eV)	ε_{exp} (10^4 cm^{-1} M^{-1})	$\Delta E_{exp}{}^{c}$ (eV)	Δ (eV)
S-101	6.54	2.93	2.6	3.22	0.324
PRL-101	9.05	2.77	4.1	3.11	0.328
BT-101	7.81	2.72	4.5	3.10	0.361
N-101	3.49	2.50	2.4	2.82	0.437

[a]See Eq. (2).
[b]Absorption at the equilibrium ground-state geometry.
[c]Reference 6.

$$S_{ij} = \sum_{\alpha} \left[\frac{\langle 0|\mu_i|\alpha\rangle\langle\alpha|\mu_j|f\rangle}{\omega_\alpha - \omega} + \frac{\langle 0|\mu_j|\alpha\rangle\langle\alpha|\mu_i|f\rangle}{\omega_\alpha - \omega} \right].$$

Here the two-photon transition probability δ_{2P}^{L}, for linearly polarized light, is averaged over molecular orientations, and the homogeneous broadening needs to be known to obtain quantitative results.

As in the case of linear absorption the numbers calculated from the above equation using the value of Γ equal to 0.1 eV appeared to be more than one order of magnitude larger than the experimental ones. It is our belief that the major reason for this discrepancy is the same as in the case of the linear spectra: the necessity to account for the fact that the TPA profiles are inhomogeneously broadened. Both the OPA and the TPA cross sections, however, are also additionally overestimated, due to the underestimation of DFT/B3LYP energies mentioned before. Expectedly, the energies lower as basis set get larger. Vibrational broadening could be accounted for by considering the second-order transition matrix element as a product, $S_{ij}=S_{ij}^{el}\langle 0|f\rangle$, where $\langle 0|f\rangle$ is the Franck–Condon amplitude and completeness $\Sigma_\alpha|\alpha\rangle\langle\alpha|=1$ is applied. The completeness should result in the same vibrational profile for one-photon and two-photon absorptions. Indeed, the experimental widths of the TPA spectra are about one-half of the OPA ones which suggests the same Δ in the expressions for the cross sections. Therefore, it seems to be a reasonable approximation to use the same Δ as in the case of linear absorption in Eq. (3), instead of the Γ due to homogeneous broadening.

It might be noted that, on the average, the σ_{TPA} values evaluated from the theoretical computations are still markedly higher than the experimental ones, but the differences are not large. The theoretical ordering of the molecules in the series with respect to their two-photon absorption cross sections is S-101 < N-101 < BT-101 < PRL-101 for calculations with 3-21G* and 6-31G* basis sets and S-101 < N-101 < PRL-101 < BT-101 for calculations with cc-pVDZ basis set which is not coincident with the experimental ordering of S-101 < PRL-101 < BT-101 < N-101. The calculations with cc-pVTZ basis set were only feasible for smaller molecules N-101 and S-101 (see Table VI), and for these two molecules the ordering coincides with that obtained for calculations with the smaller basis sets.

Clearly, there may be numerous reasons for disagreements between the computed values and those coming from the experiment. It should be mentioned here that there is ample evidence that experimental two-photon absorption cross sections may be influenced by the presence of additional processes such as two-step two-photon absorption and excited-state absorption associated with population of the two-photon state, as well as saturation-desaturation effects.[12] These processes can drastically change (increase or decrease) the value of the effective TPA cross section determined in a direct nonlinear absorption experiment. The relative influence of various effects depends among others on the relation of the duration of the laser pulse exciting a two-photon active medium to characteristic relaxation times of this medium and on the light intensity used in the experiment.

It needs to be mentioned that the white continuum pulses employed in Ref. 6 and investigated in detail in Ref. 13 are reported to be about 850 fs, owing to self-broadening. This is on the order of the typical lifetimes of optically excited electron-vibrational states of chromophores.

Let us analyze the strongest two-photon absorption virtual channels contributing to the two-photon transition matrix element S_{ij}. For all compounds, the photon energy detunings from the transition energies are similar, so we can exclude them from our consideration. The initial state here is the ground state S_0 and the final state is an excited singlet state S_j. At this stage, there is some experimental evidence

TABLE VI. TPA cross sections (GM) and excitation energies (eV) of S-101, PRL-101, BT-101, and N-101 calculated with different basis sets.

Molecule	σ_{TPA} DFT/QR^{a} 3-21G*	$\Delta E_{DFT}{}^{b}$	σ_{TPA} DFT/QR^{a} 6-31G*	$\Delta E_{DFT}{}^{b}$	σ_{TPA} DFT/QR^{a} cc-pVDZ	$\Delta E_{DFT}{}^{b}$	σ_{TPA} DFT/QR^{a} cc-pVTZ	$\Delta E_{DFT}{}^{b}$	σ_{TPA} Exp.^{c}	ΔE_{exp}
S-101	164	3.01	160	2.93	153	2.91	154	2.86	40	3.32
PRL-101	339	2.83	302	2.77	278	2.75	⋯	⋯	60	3.26
BT-101	330	2.78	297	2.72	279	2.70	⋯	⋯	95	3.19
N-101	203	2.63	208	2.51	199	2.53	206	2.46	125	2.95

[a]Δ from Table V.
[b]Absorption at the equilibrium ground-state geometry.
[c]Reference 6.

TABLE VII. Selected relative excitation energies (ΔE, eV) and dipole moments (μ_i, a.u.) of the low-lying singlet states of S-101 (DALTON 2.0 DFT linear and quadratic response).

μ_i (a.u.)	x	y	z	ΔE_{DFT}[a] (eV)
S_0S_1	0.0395	−0.1275	3.7554	2.93
S_0S_2	−0.0843	−0.3693	0.0986	3.83
S_0S_3	−1.2697	−0.3260	0.0115	4.02
S_1S_2	0.0828	0.0753	0.5344	
S_1S_3	0.6178	0.1801	−0.1687	
S_2S_3	0.0227	0.0099	−0.1681	

[a]Absorption at the equilibrium ground-state geometry.

that this S_j state may be other than S_1. If we nevertheless assume that the final state reached by two-photon absorption is the lowest excited state, the most important TPA virtual channels are $\langle S_0|S_2\rangle\langle S_2|S_1\rangle$ and $\langle S_0|S_1\rangle[\langle S_1|S_1\rangle-\langle S_0|S_0\rangle]$. Based on the results of TDDFT calculations collected in Tables I–IV we can say that the latter channel is indeed the strongest one for all the compounds. This would give the following ordering with respect to TPA cross-section contributions coming from the first excited state, S-101 < N-101 < BT-101 < PRL-101. For PRL-101, the two channels are of nearly the same intensity, giving rise to the value of TPA cross section one and half times as high as in the case of the N-101 molecule (see Table VI). Thus, it can be seen that the quadratic response calculations and a simple analysis of the two-photon absorption transition matrix element based on DFT values of dipole moments give the same ordering of the compounds with respect to their two-photon absorptions cross sections if overall contribution of strongest virtual TPA channels is considered (note that the results obtained with the same 6-31G* basis set were analyzed).

We would like to add here that the use of the B3LYP hybrid functional with the CIS method implemented in the GAUSSIAN program seems to overestimate the transition dipole moments between the excited states. Indeed, having made use of DFT quadratic response method implemented in the DALTON program we obtained about a 50% decrease in these values for the S-101 molecule, as demonstrated in Tables IV and VII.

An important issue requiring a comment is the experimental observation that the maxima of the measured one- and two-photon absorption profiles do not precisely coincide. For example, the PRL-101 molecule has the maximum of the one-photon profile at 400 nm while the maximum of the two-photon absorption profile is at 760 nm. The difference between the corresponding excitation energies is 0.16 eV. For all the investigated molecules such a difference is less than the computed energy gap between the first and the second excited electronic states which is larger than 0.5 eV, as seen from Tables I–IV. Thus, it appears from our calculations that the dominant one-photon and two-photon transitions take place between the same electronic states, and the shift may be due to differences in the Franck–Condon distribution of the absorption probabilities.[14] However, we plan to make experimental verification of this inference using time-resolved pump-probe experiments.

IV. SUMMARY

To conclude we would like to note that the key quantities determining the value of TPA cross section of a charge-transfer (CT) compound are the transition dipole moment to the CT state and the difference between the dipole moments of the CT and the ground states, as we could see from our simple analysis of the virtual two-photon absorption channels. At the same time, it is well known that localization of highest occupied and lowest unoccupied molecular orbitals upon attaching electron donating and electron accepting functional groups to the π bridge results in an effective intramolecular charge transfer. Linking the two-photon activity with the electron acceptor strength, i.e., ability to accept the charge transferred from the donor moiety, gives us the idea of connecting the electron acceptor strength with the difference between the dipole moments of the CT and ground states. In other words, a substantial change of the dipole moment upon excitation may help in achieving a high TPA cross section of a donor-acceptor-type chromophore. The value of the transition dipole moment to the CT state is also of importance, although the change of this value upon the change of the acceptor group is not very pronounced in the series under investigation which implies the major role of the acceptor strength and/or the change of the dipole moments in the ordering of the compounds if only pure, coherent TPA cross section is considered. Indeed, if we look at the changes of the dipole moment collected in Tables I–IV we will notice that the ordering of the compounds with respect to this change is S-101 < BT-101 < N-101 < PRL-101, this is to say that it is closer to the experimental ordering with respect to the acceptor strength. However, as is seen from our calculations, the computed TPA cross sections are not in full quantitative agreement with the experimental ones. Some reasons for these discrepancies can be the inadequacies of the computation techniques evidenced by underestimations of transition energies and, in general, overestimations of the two-photon cross sections. There is also a possibility, however, that the experimental data may be modified to some extent by contribution of additional factors and processes that are not accounted for in the present quantum-chemical calculations. Nevertheless, we conclude that there is potential in the predictive capability of the DFT quadratic response technique in the field of nonlinear absorption studies. Thus more results of experimental studies should be compared with the results of appropriate computations.

[1] T. Helgaker, H. J. Aa. Jensen, P. Jørgensen *et al.*, DALTON, a molecular electronic structure program, Release 2.0, 2005; see http://www.kjemi.uio.no/software/dalton/dalton.html

[2] P. Sałek, O. Vahtras, J.-D. Guo, Y. Luo, T. Helgaker, and H. Ågren, Chem. Phys. Lett. **374**, 446 (2003).

[3] P. Cronstrand, B. Jansik, D. Jonsson, Y. Luo, and H. Ågren, J. Chem. Phys. **121**, 9239 (2004).

[4] F. Gel'mukhanov, A. Baev, P. Macak, Y. Luo, and H. Ågren, J. Opt. Soc. Am. B **19**, 937 (2002).

[5] A. Baev, F. Gel'mukhanov, P. Macak, Y. Luo, and H. Ågren, J. Chem. Phys. **117**, 6214 (2002).

[6] T.-C. Lin, G. S. He, P. N. Prasad, and L. S. Tan, J. Mater. Chem. **14**, 982 (2004).

[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 98, Revision A.9, Gaussian, Inc., Pittsburgh, PA, 1998.

[8] P. Cronstrand, Y. Luo, and H. Ågren, Chem. Phys. Lett. **352**, 262 (2002).

[9] A. Masunov and S. Tretiak, J. Phys. Chem. B **108**, 899 (2004).

[10] A. Dreuw and M. Head-Gordon, J. Am. Chem. Soc. **126**, 4007 (2004).

[11] M. Rumi, J. E. Ehrlich, A. A. Heikal *et al.*, J. Am. Chem. Soc. **122**, 9500 (2000).

[12] S.-J. Chung, K.-S. Kim, T.-C. Lin, G. S. He, J. Swiatkiewicz, and P. N. Prasad, J. Phys. Chem. B **103**, 10741 (1999).

[13] G. S. He, T.-C. Lin, J. Dai, P. N. Prasad, R. Kannan, A. G. Dombroskie, R. A. Vaia, and L.-S. Tan, J. Chem. Phys. **120**, 5275 (2004).

[14] S. Polyutov, I. Minkov, F. Gel'mukhanov, K. Kamada, A. Baev, and H. Ågren, Mater. Res. Soc. Symp. Proc., Vol. **846**, DD1.2.1–DD1.2.10 (2005).