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Chemical Control of Channel Interference in Two-Photon Absorption Processes

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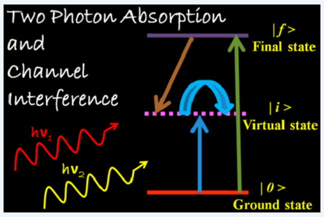
CONSPECTUS: The two-photon absorption (TPA) process is the simplest and hence the most studied nonlinear optical phenomenon, and various aspects of this process have been explored in the past few decades, experimentally as well as theoretically. Previous investigations have shown that the two-photon (TP) activity of a molecular system can be tuned, and at present, performance-tailored TP active materials are easy to develop by monitoring factors such as length of conjugation, dimensionality of charge-transfer network, strength of donor−acceptor groups, polarity of solvents, self-aggregation, H-bonding, and micellar encapsulation to mention but a few. One of the most intriguing phenomena affecting the TP activity of a molecule is *channel interference*. The phrase "channel interference" implies that if the TP transition from one electronic state to another involves more than one optical pathway or channel, characterized by the corresponding transition dipole moment (TDM) vectors, the channels may interfere with each other depending upon the angles between the TDM vectors and hence can either increase (constructive interference) or decrease (destructive interference) the overall TP activity of a system to a significant extent. This phenomenon was first pointed out by Cronstrand, Luo, and Ågren [*Chem. Phys. Lett.* **2002**, *352*, 262−269] in two-dimensional systems (i.e., only involving two components of the transition moment vectors). For three-dimensional molecules, an extended version of this idea was required. In order to fill this gap, we developed a generalized model for describing and exploring channel interference, valid for systems of any dimensionality. We have in particular applied it to through-bond (TB) and through-space (TS) charge-transfer systems both in gas phase and in solvents with different polarities. In this Account, we will, in addition to briefly describing the concept of channel interference, discuss two key findings of our recent work: (1) how to control the channel interference by chemical means, and (2) the role of channel interference in the anomalous solvent dependence of certain TP chromophores. For example, we will show that simple structurally induced changes in certain dihedral angles of the well-known betaine dye (TB type) will help fine-tune the constructive channel interference and hence increase the overall TP activity of molecules with this general TP channel structure. Another intriguing result we will discuss is observed for a tweezer-trinitrofluorinone complex (TS type) where, on moving from polar to essentially nonpolar solvents, the nature of the channel interference switches from destructive to constructive, leading to a net abnormal solvent dependence of the TP activity of the system. The present Account highlights the usefulness of the channel interference effect and establishes it as a new and unique way of controlling the TP transition probability in different types of three-dimensional molecules.



INTRODUCTION

Although experimental verifications[1,2] of the two-photon absorption (TPA) process[3] was delayed for 30 years after its theoretical prediction due to the lack of sufficiently intense light sources, this area of science has, since the 1960s, seen a continuous and rapid progress. The reason for this growth in scientific interest is its potential use in a wide range of sciences,[4−10] ranging from the computer world (3D data storage[4]) to the medical field (photodynamic therapy[9]). In the past 55 years, TPA has been an active research field, both at the theoretical and experimental level, making it possible to tune the process and to prepare molecules with a desired TP activity. Studies have revealed different classes of molecules with promising TP activity, including donor-π-acceptor (D−π−A) complexes, metalloporphyrins,[11,12] multibranched dendrimers,[13,14] quantum dots,[15,16] and molecular tweezer molecules or complexes.[17] It has been shown that the TP activity of a molecule can be controlled by changing the geometrical parameters, including the dimensionality of the charge-transfer network and length of conjugation[18−22] and the strength and position of donor−acceptor groups.[23,24] TPA cross sections have also been found to be affected by vibronic coupling,[25,26] the nature of the solvents,[28−32] the possibility of H-bonding,[31,32] and aggregation[33] as well as micelle effects.[34] Other factors not related to the molecule but which have significant impact on the TPA of a system are the time duration of the pulsed laser source,[35] spatial and temporal fluctuation of the laser beam, and also the wavelength used for the excitation process.[36] In addition to all these factors, a new analysis tool which helps us understand the physics of the TPA process at the molecular level was introduced by Cronstrand, Luo, and Ågren.[37,38] This new mechanism was denoted channel interference and was found to be an inherent property of any

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multiphoton absorption process and can hence be a useful model in order to optimize the TP activity of different classes of molecules. It is important to emphasize that the term "interference" has nothing to do with the interference between different light waves; instead it refers to the interaction between different optical channels through their transition moment vectors. Unlike light-wave interference, channel interference is a microscopic property. The present Account aims at explaining the concept of channel interference, its role in tuning the TPA process and to provide insight as to how this mechanism can be utilized in the design of molecules with large TPA cross sections.

We have organized this Account as follows: At first, a short discussion on the origin of channel interference is given, followed by a brief mathematical account of the process and how it appears. Thereafter, discussions on various aspects of channel interference including the comparison of this concept for two-dimensional (2D) and three-dimensional (3D) cases, applications to real molecular systems, solvent effects, and techniques used by us to control it for a specific compound are presented. We end this Account with a possible future vision for such studies and how they can contribute in molecular design and finally some concluding remarks.

CHANNEL INTERFERENCE: THE CONCEPT

In order to understand the concept of channel interference, we first need to have an understanding of the TPA process. TPA is the simultaneous absorption of two photons of same or different frequencies by a molecular system, exciting the system from one electronic state to the other. In this process, the system first absorbs one photon and gets excited to some virtual state, then, before relaxing back to its initial state, it absorbs the second photon almost instantaneously and ultimately gets excited to the final state. A pictorial representation of the TPA process is shown in Figure 1.

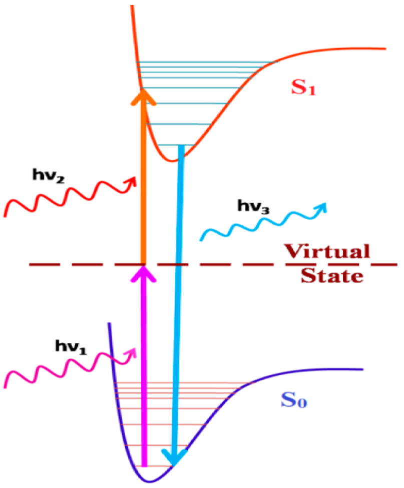


Figure 1. Pictorial representation of two-photon absorption process.

Here, |0⟩, |i⟩, and |*f*⟩ are the ground, intermediate, and final electronic states (formally the vibronic states), respectively. Theoretically, TPA is a nonlinear optical phenomenon, related to the imaginary part of the third-order optical susceptibility.[39] The TP activity of a system is measured in terms of TPA cross section (δ_{TP}) which can be calculated either using the semiempirical sum-over-states (SOS)[40−43] approach or ab initio response theory (RT).[44−49] For a single linearly polarized beam of monochromatic light, δ_{TP} can be expressed as[50]

$$\delta^{\mathrm{TP}} = 6(S_{xx}^2 + S_{yy}^2 + S_{zz}^2) + 8(S_{xy}^2 + S_{xz}^2 + S_{yz}^2) + 4(S_{xx}S_{yy} + S_{xx}S_{zz} + S_{yy}S_{zz}) \qquad (1)$$

Here, $S_{\alpha\beta}$ are the TP tensor elements that are related to various transition dipole moment (TDM) vectors and excitation energies. The SOS expression for $S_{\alpha\beta}$ is given by

$$S_{\alpha\beta} = \sum_i \frac{\mu_\alpha^{0i}\mu_\beta^{if} + \mu_\beta^{0i}\mu_\alpha^{if}}{\omega_{0i} - \frac{\omega_{0f}}{2}} \qquad (2)$$

where the summation runs over all intermediate states including |0⟩ and |*f*⟩ , μ_α^{pq} is the *α*th component of the TDM vector for transition from the |*p*⟩ state to the |*q*⟩ state, and ω_{0p} is the excitation energy for the transition from |0⟩ to |*p*⟩. Here and in the following, we have used atomic units. We note that $S_{\alpha\beta}$ is expressed in terms of ground to excited and excited−excited state TDM vectors, each of which represents a pathway or channel, that is an electronic transition, and hence the SOS approach intrinsically involves an interaction between these channels. Such interactions are referred to as channel interference. A pictorial representation of different optical channels (involving three states only) is shown in Figure 2.

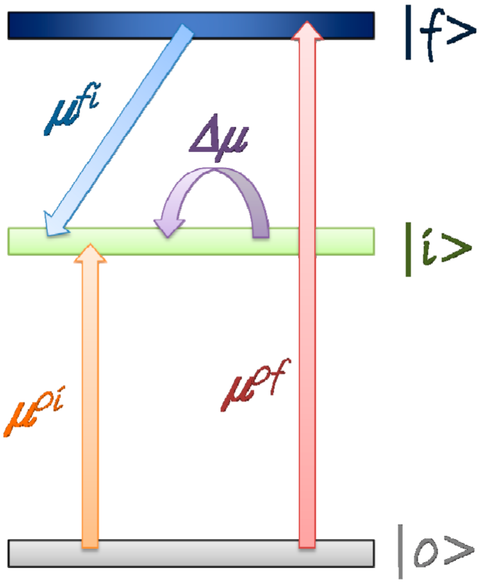


Figure 2. Pictorial representation of different optical channels involved in a three-state model.

From eq 2, it is clear that the complete SOS approach requires an explicit knowledge of all the excited states of the system, which is indeed an extremely difficult task, particularly for larger molecules. Therefore, it is not possible to use the complete SOS approach directly to calculate the TP tensor elements and hence the δ_{TP} values of molecular systems. This problem is solved in the RT approach where we instead need to solve a set of linear (response) equations without having further information about the individual excited states or having to include the infinite summation over the excited states. The fusion of RT with TDDFT[46] makes this a cost-effective approach that can be applied to large molecules. However, the RT-TDDFT does not allow for the physical intuitive and qualitative insight that can be obtained from a computationally tractable and easily understandable method such as the few-state-model (FSM). Furthermore, based on the hitherto existing experimental findings, FSM seems to be more relevant for organic donor−acceptor type molecules. A nice description is given in the review by Terenziani et al.[51] In the FSM approach, the summation in eq 2 is restricted to a few essential states only: for a two-state model (2SM), "*i*" is taken as the $|0\rangle$ and $|f\rangle$ states only. Similarly, for the three-state model (3SM), an intermediate state is also considered in addition to the $|0\rangle$ and $|f\rangle$ states. Although the FSM is less accurate than either the full SOS or RT methods, it provides an easy and convenient way of studying the interaction between the different optical channels and their effect on the overall TP activity of a molecular system because it involves only a few states. Channel interference, otherwise completely hidden in the RT-TDDFT approach, is easily accessible from a FSM. The study of channel interference in the case of the TPA process provides new insight about the basic mechanism of the TP process at a much deeper level and provides a clear, qualitative understanding of the correspondence between the molecular system and the property studied. Nevertheless, one must keep it in mind that the success of FSMs depends strongly on the nature of the states involved, that is, whether the states are dominating the observed TPA cross sections. The states selected thus have to be verified to dominate the contribution to the overall TPA cross section, for instance, by large-scale RT-TDDFT calculations, ensuring that the FSM captures the majority of the calculated cross sections. With these basics, we can now move to a discussion of the physical and mathematical foundations of channel interference.

PHYSICAL FOUNDATION OF CHANNEL INTERFERENCE

As mentioned earlier, the idea of channel interference is inherent in the SOS formalism, but intractable because of the large number of excited states involved in the calculation. The study of channel interference is only possible when we consider a few selected states in the calculations, that is, when we consider the FSM approach. We start this section with the simplest FSM approach, the two-state model (2SM). Within the 2SM, involving only the $|0\rangle$ and $|f\rangle$ states, eq 2 becomes

$$S_{\alpha\beta}^{2\text{SM}} = \frac{\mu_\alpha^{00}\mu_\beta^{0f} + \mu_\beta^{00}\mu_\alpha^{0f}}{\omega_{00} - \frac{\omega_{0f}}{2}} + \frac{\mu_\alpha^{0f}\mu_\beta^{ff} + \mu_\beta^{0f}\mu_\alpha^{ff}}{\omega_{0f} - \frac{\omega_{0f}}{2}} = \frac{\Delta\mu_\alpha^{ff}\mu_\beta^{0f} + \Delta\mu_\beta^{ff}\mu_\alpha^{0f}}{\Delta E_f} \tag{3}$$

Here, $\Delta\mu_\alpha^{ff}$ is the αth component of the dipole moment difference between the ground and final excited states. $\Delta E_i = \omega_{0i} - \omega_{0f}/2$, and all the other terms have their usual meanings. Inserting eq 3 into eq 1 and incorporating the vector nature of μ^{0f} and $\Delta\mu^{ff}$, we get[52]

$$\delta_{\text{TP}}^{2\text{SM}} = 8\left(\frac{\mu^{0f}\Delta\mu^{ff}}{\Delta E_f}\right)^2 (2\cos^2\theta_{ff}^{0f} + 1) \tag{4}$$

Here, θ_{ff}^{0f} is the angle between the $\Delta\mu^{ff}$ and μ^{0f} vectors. As the 2SM is the simplest FSM model, it involves only one optical channel ($\Delta\mu^{ff}$ does not represent any transition, so it cannot be considered as an optical channel) and hence there are no interactions between different optical channels. However, this expression shows that the value of δ_{TP} depends not only on the magnitude of the $\Delta\mu^{ff}$ and μ^{0f} vectors, but also on their relative orientations. The angle term (in the second parentheses of eq 4) attains its maximum when the two vectors align either parallel ($\theta = 0°$) or antiparallel ($\theta = 180°$) to each other, and its minimum when they are orthogonal. We can therefore expect that if more optical channels are available, the overall δ_{TP} value will be affected by the orientations of the corresponding TDM vectors relative to each other.

This can be verified by including one more state in the FSM approach, that is, by considering the 3SM. If we include an intermediate state ($|i\rangle$) and do a similar treatment as for the 2SM, δ_{TP} can be shown to consist of three terms; see eq 5.[52] The first term (eq 5b) is simply the 2SM expression involving only the $|0\rangle$ and $|f\rangle$ states. The second term is interesting, because there is an interaction between two different optical channels $|0\rangle \rightarrow |i\rangle$ and $|i\rangle \rightarrow |f\rangle$. This term can be maximized by aligning the two vectors (μ^{0i} and μ^{if}) on a straight line and minimized by placing them perpendicular to each other, analogously to the analysis of the 2SM. A close inspection of the two terms (eq 5b and 5c) reveals that these are always positive irrespective of the alignment of the vectors involved and hence always enhance the overall δ_{TP} value. However, this is no longer true for the third and most interesting term (eq 5d). In this case, three optical channels are involved, namely, $|0\rangle \rightarrow |i\rangle$, $|0\rangle \rightarrow |f\rangle$, and $|i\rangle \rightarrow |f\rangle$, and thus, it depends on all the six possible angles (including the interaction with the $\Delta\mu$ vector). This term represents a complete entanglement of the different optical channels, and depending on the values of these angles the term can be either positive or negative; that is, it can either increase or decrease the overall δ_{TP} values of the molecular system. It is because of this term that the interaction between the optical channels is referred to as channel interference. A positive value of this cross term is called *constructive interference*, and a negative value is referred to as *destructive interference*.

$$\delta_{\text{TP}}^{3\text{SM}} = \delta_{\text{TP}}^{1} + \delta_{\text{TP}}^{2} + 2\delta_{\text{TP}}^{3} \tag{5a}$$

$$\delta_{\text{TP}}^{1} = 8\left(\frac{\mu^{0f}\Delta\mu^{ff}}{\Delta E_f}\right)^2 (2\cos^2\theta_{ff}^{0f} + 1) \tag{5b}$$

$$\delta_{\text{TP}}^{2} = 8\left(\frac{\mu^{0i}\mu^{if}}{\Delta E_i}\right)^2 (2\cos^2\theta_{if}^{0f} + 1) \tag{5c}$$

$$\delta_{\text{TP}}^{3} = \frac{8\mu^{0i}\mu^{0f}\mu^{if}\Delta\mu^{ff}}{\Delta E_i\Delta E_f}(\cos\theta_{0i}^{if}\cos\theta_{0f}^{ff} + \cos\theta_{0i}^{0f}\cos\theta_{if}^{ff} + \cos\theta_{0i}^{ff}\cos\theta_{0f}^{if}) \tag{5d}$$

In a similar manner, we have derived an expression for δ_{TP} involving as many intermediate states as required, denoted the generalized FSM (GFSM) formalism. The expression for δ_{TP} within the GFSM can be written as[52]

$$\delta_{\text{TP}}^{\text{GFSM}} = \sum_{i,j}\frac{8\mu^{0i}\mu^{0j}\mu^{if}\mu^{jf}}{\Delta E_i\Delta E_j}(\cos\theta_{0i}^{if}\cos\theta_{0j}^{jf} + \cos\theta_{0i}^{0j}\cos\theta_{if}^{jf} + \cos\theta_{0i}^{jf}\cos\theta_{0j}^{if}) \tag{6}$$

where *i* and *j* represent the intermediate states.

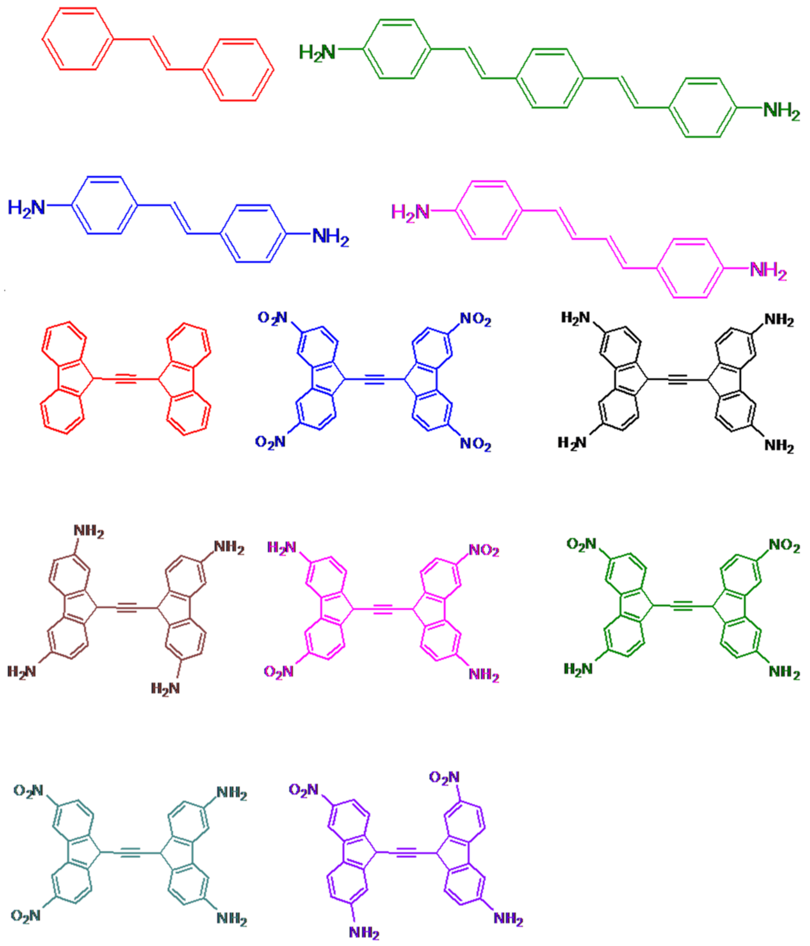


Figure 3. Stilbene (upper panel) and cumulene (lower panel) based two-dimensional aromatic molecules used for channel interference study.

TWO-DIMENSIONAL VERSUS THREE-DIMENSIONAL CHANNEL INTERFERENCE: A COMPARISON

The mathematical discussion in the previous section is applicable to both 2D as well as 3D molecules in addition to the 1D case. Channel interference was first studied for 2D molecules by Cronstrand et al.[37,38] Later, the concept was extended and generalized by our group to 3D cases. Compared to the 3D case, the derivation of the GFSM formula for 2D molecules is rather simple because only the two components of the TDM vectors that lie in the plane of the molecule are considered. The final expression for δ_{TP} as derived using GFSM for 2D molecules is given by[38]

$$\delta_{\mathrm{TP}}^{\mathrm{GFSM,2D}} = \sum_{i,j} \frac{8\mu^{0i}\mu^{0j}\mu^{if}\mu^{jf}}{\Delta E_i \Delta E_j}(3\cos\theta_{0i}^{if}\cos\theta_{0j}^{jf} + \sin\theta_{0i}^{if}\sin\theta_{0j}^{jf} - 2\sin\theta_{0i}^{0j}\sin\theta_{if}^{jf}) \qquad (7)$$

The preparentheses part may at first sight appear to be the same for both 2D (eq 7) and 3D (eq 6) molecules, but there is a subtle difference: In eq 7, $\mu^{ab} = ((\mu_x^{ab})^2 + (\mu_y^{ab})^2)^{1/2}$, whereas $\mu^{ab} = ((\mu_x^{ab})^2 + (\mu_y^{ab})^2 + (\mu_z^{ab})^2)^{1/2}$ in eq 6. The second and more obvious difference between 2D and 3D systems lies in the parentheses part of eqs 6 and 7. A comparison makes it clear that each interference term (i.e., for which $i \neq j$) in the expression for δ_{TP} in 2D molecules depends on four angle terms only (i.e., interaction between four pairs of optical channels viz., (μ^{0i}, μ^{if}), (μ^{0i}, μ^{0j}), (μ^{0j}, μ^{jf}), and (μ^{if}, μ^{jf})), whereas in case of 3D molecules this number is six (two more pairs, viz., (μ^{0i}, μ^{jf}) and (μ^{0j}, μ^{if})), suggesting that channel interference is much more complicated in 3D molecules. In fact, the larger the number of intermediate states involved in the calculation, the larger the number of angle terms that appear, increasing the flexibility in the channel interference in 3D molecules while at the same time making it harder to control or design the best channel interference patterns.

STUDY OF CHANNEL INTERFERENCE IN REAL SYSTEMS

The first study[37] of channel interference was done on 2D systems such as styrylbenzene, diphenylbutadiene, and pristine as well as donor−donor substituted *trans*-stilbene molecules (see Figure 3). In their work, Cronstrand et al.[37] presented the 3SM and 4SM formula for 2D molecules and suggested that the interactions between different optical channels have a significant impact on the TP activity of these molecules. They later extended their channel interference study to even larger 2D-systems, such as cumulene-containing aromatic molecules (Figure 3), and explicitly discussed the channel interference in terms of the 4SM formula.[38] We recently generalized the channel interference approach, deriving the GFSM (eqs 5 and 6) formula, applicable to 1-, 2-, and 3D molecules.[52] The approach (using a 3SM approximation) was first applied to the simplest Rechardt's dyes, 2- and 4-(pyridinium-1-yl)phenolate (*o*- and *p*-betaine, respectively; see

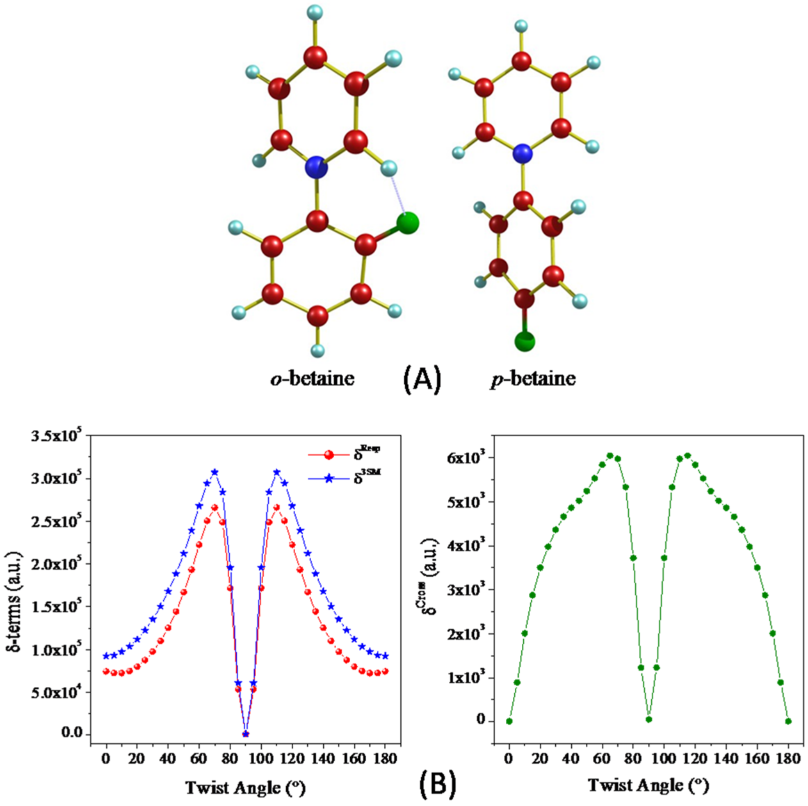


Figure 4. (A) Two simplest units of Rechardt's dyes: *o*-betaine and *p*-betaine. Color code: hydrogen (sky blue), carbon (red), nitrogen (blue), and oxygen (green). (B) Plot of various δ terms against the twist angle between two rings of o-betaine molecule, calculated at CAMB3LYP/cc-pVDZ level of theory.

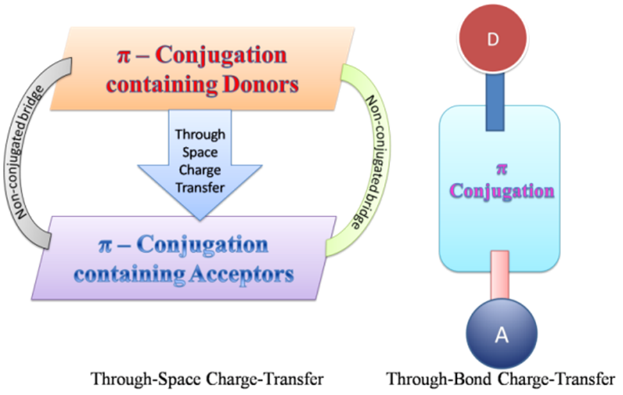
Figure 4A) in both the gas phase as well as in solvents of different polarity (viz., THF, CH_3CN, and H_2O). We found that, for these two molecules, the 3SM gives values of δ_{TP} in excellent agreement with the quadratic RT results. The interference term (i.e., δ_{TP}^{3}) for the first excited state of *o*-betaine is always constructive in nature, whereas for the second excited state it is always destructive. In contrast, δ_{TP}^{3} for the second excited state of *p*-betaine is constructive and for the first excited state it is destructive. Irrespective of the nature of the solvent, the effect of interference is much more pronounced for the second excited state of both molecules. More importantly, for the second excited state, the value of destructive interference in *o*-betaine gradually decreases with increasing solvent polarity, whereas in *p*-betaine the value of constructive interference reaches its maximum in moderately polar solvents. This was the first study noting that channel interference can be tuned by changing the polarity of the solvent.

We then turned to the question of whether it would be possible to take chemical control over the channel interference effect.[53] By studying the effect of rotation (of the two rings of *o*-betaine) on the values of channel interference in *o*-betaine, we found that, for a particular twist angle (ranging between 65° and 70°), δ_{TP} could be maximized (see Figure 4B (left)). Interestingly, in this range of angles, the value of the constructive interference is also maximized (see Figure 4B (right)). However, this twist angle, maximizing the δ_{TP} value, is far from the optimized twist angle for the molecule, and hence, for pristine *o*-betaine, it was not possible to achieve the required twist angle experimentally. However, by substituting the ortho hydrogen in *o*-betaine with CH_3 groups, the twist angle between the two rings could easily be altered.[53] Indeed, the twist angle in one of the monosubstituted systems was found to be in the desired range, also possessing the largest TP activity of any of the substituted *o*-betaine molecules. It is worth noting that the twist angle dependence of TP transition probability along with the first and second hyperpolarizabilities of similar systems have been studied previously.[54,55]

We have also applied[56] the channel intereference analysis to two through-space charge-transfer (TSCT) systems,[57−60] namely, a tweezer-trinitrofluorinone (tweezer-TNF)[56] complex and [2,2]-paracyclophane (PCP)[59] derivatives. Here, the 4,6-bis(6-acrid-9-yl)-pyridin-2-yl)-pyrimidine molecule is referred to as a tweezer. Such systems are interesting because the charge-transfer excitation does not occur along the chemical bonds, but rather through space between the donor and acceptor parts (see Scheme 1), often quenching the competing one-photon absorption process. For example, in the tweezer-TNF complex, the charge-transfer excitation takes place from the two hands of the tweezer to the TNF molecule, which rests between these two hands. The second system, that is, the [2,2]-paracyclophane derivative, consists of two parallel stacked benzene rings attached to each other through ethyl bridges and contains a positively charged $-NMe_3$ as acceptor group and a neutral $-NMe_2$ as donor. The donors are localized on one benzene ring whereas the acceptors are localized on the other benzene ring, and here the charge-transfer excitation takes place via the free space between the two rings. The two systems are depicted in Figure 5A. We note that such charge-transfer excitations between aromatic donor−acceptor groups also can occur naturally in, for instance, the yellow fluorescent protein.[61]

Our calculations revealed that, in both systems, channel interference is more important than in the Rechardt's dyes. The

Scheme 1. Pictorial Representation of Through-Space Charge-Transfer and Through-Bond Charge-Transfer Systems



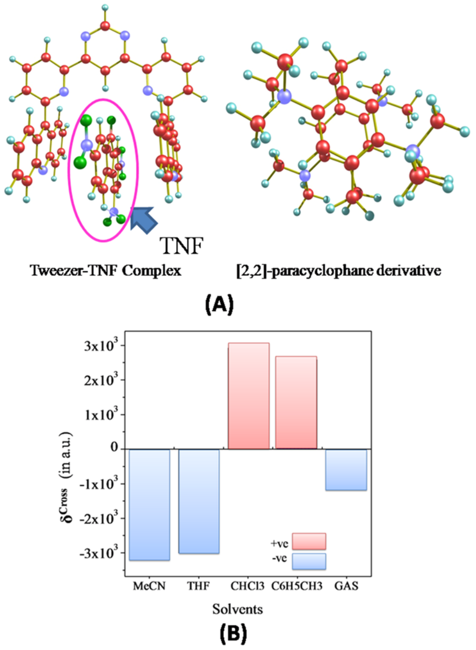


Figure 5. (A) Representatives for through-space charge-transfer molecules: tweezer-TNF complex and [2,2]-paracyclophane derivatives. Color code: hydrogen (sky blue), carbon (red), nitrogen (blue), and oxygen (green). (B) Change of nature of interference with the polarity of the solvent.

nature of the channel interference, in the gas phase, is in both these systems destructive in nature, but in PCP it decreases steadily with decreasing solvent polarity. In contrast, in the tweezer-TNF complex, this decreasing trend is not regular; instead the value of the cross term decreases with decreasing solvent polarity, but in low-polar solvents (such as chloroform and toluene) it becomes constructive (see Figure 5B). This was the first report that even the nature of the channel interference can be altered by changing solvent polarity.

■ A MORE COMPLICATED CASE OF BIOLOGICAL RELEVANCE

In order to extend our channel interference study, we have considered a more complicated system, a biphenyl derivative[62] (2-(4′-(bis(carboxymethyl)amino)-4-nitro-[1,1′-biphenyl]-3-yl)propan-1-ol-γ-aminobutyric acid; see Figure 6A). This molecule was recently synthesized by Donato et al.[62] and proposed to be a highly efficient TP uncaging agent of the neurotransmitter γ-aminobutyric acid. The gas-phase optimized geometry (at the B3LYP/6-311G(d) level) has a dihedral angle of ∼35° between the two rings. We have evaluated the TP transition probabilities and other parameters required for the three-state model calculations of this system by varying the dihedral angle from 0° to 180° in steps of 5°. The results of both the response theory and the 3SM calculations for the first two excited states are presented in Figure 6B. The first thing to note is that, for both excited states, the 3SM predicts a very poor TP activity in a wide range of dihedral angles (ranging from 50° to 130°) and is consistent with the response theory results (particularly for the second excited state). The disagreement for the first excited state indicates the significant role of other higher excited states. However, because of the huge computational cost, we did not consider more-than-three state models. The second thing to note is that the total interference for the first excited state is destructive in nature, whereas that of the second excited state is constructive. This explains why the second excited state is more TP active than the first. The magnitude of the destructive interference gradually decreases with increasing dihedral angle up to 50°, at which point it remains almost constant up to 130°. With additional increases in the dihedral angle, the magnitude of the TP absorption increases. A similar behavior is observed for the constructive interference in the second excited state. The system exhibits the largest TP activity at dihedral angles of 35° (≡145°) and around these points the value of constructive interference is also found to be very large. There are still disagreements between the response theory and the 3SM results, suggesting that the study of channel interference may become very complicated for larger molecules.

■ FUTURE PROSPECTS AND CONCLUDING REMARKS

Although the phenomenon of channel interference has been studied to some extent in the literature, there are still unanswered questions and challenges: (1) Since channel interference provides a completely different direction for looking at and understanding the TPA process, its application to different classes of molecules may provide new and novel insight on the structural factors affecting TP efficiency. At the same time, it would be interesting to extend the idea of channel interference to three-photon (3PA) absorption processes too. (2) The study of solvent effects on channel interference would help us select the proper solvent in order to maximize the TPA cross section. (3) Channel interference should also be tested based on more rigorous approaches such as the coupled cluster method. (4) Application of this intriguing concept of channel interference on larger molecular systems, though complicated, is necessary in order to get an understanding of how to design new classes of TP active materials. (5) Channel interference is still only a theoretical concept; however, it clearly is of great interest if this analysis could be used and tested from experimental data as well. In particular, by finding suitable methods of controlling different transition dipole moment vectors, possibly one could monitor the channel interference experimentally.

All the studies of channel interference presented so far in the literature add new dimensions and provide completely different points of view to our understanding of the two-photon absorption process. The chemical control and solvent-phase

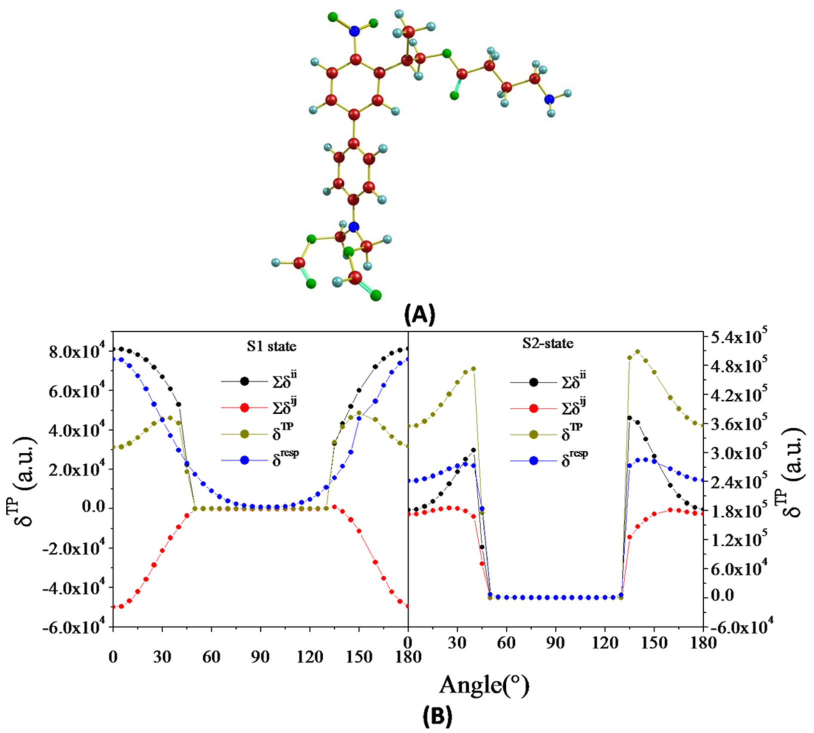


Figure 6. Biphenyl derivative (A), the molecule (2-(4′-(bis(carboxymethyl)amino)-4-nitro-[1,1′-biphenyl]-3-yl)propan-1-ol -γ-aminobutyric acid). (B) Plots for first and second excited states. The summation of all the 2SM terms (δ^{ii}) is represented by black curves whereas red curves represent the total cross-terms (δ^{ij}). Similarly, dark yellow curves are the δ^{TP} values obtained from 3SM calculations and blue one from the quadratic response theory.

studies open new possibilities of controlling the TP activity of molecules by exploiting the effect of channel interference. We hope our studies will motivate other researchers to explore the different facets of channel interference, including the experimental realization of this microscopic phenomenon.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Notes

The authors declare no competing financial interest.

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Mausumi Chattopadhyaya was born in Kolkata, India in 1984. She joined in the group of Dr. Swapan Chakrabarti in 2009 for pursuing her Ph.D. Her current research interests involve spintronics including electric field induced spin-crossover phenomenon and extended the idea in spin based quantum computing and molecular spin switch. She also worked with Dr. Zilvinus Rinkevicius at KTH, Sweden and computed the nonlinear optical properties of a certain pH indicator molecule by using quantum mechanics-molecular mechanics approach.

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