Channel interference in multiphoton absorption

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We extend the theory of channel interference to higher-order multiphoton absorption processes. We derive an explicit expression for channel interference in a three-photon absorption process and propose a general scheme for deriving such expressions for multiphoton absorption processes of any order. Based on this general scheme, we derive and analyze the simplest few-state models for multiphoton absorption in centrosymmetric molecules and discuss the criteria for maximizing the corresponding multiphoton absorption strengths.

I. INTRODUCTION

The optical transitions from one electronic state to another are governed by the magnitude of the involved transition dipole moment vectors and the corresponding excitation energies. This is strictly true for a one-photon absorption process, as it involves only one transition dipole moment. In the case of multiphoton absorption, in which the transition involves more than one photon and one or more intermediate states, more than one transition dipole moment is involved. Hence, the overall transition probability depends on several transition dipole moments as well as on their relative orientations and the corresponding energies.

Channel interference is a phenomenon where different optical channels involved in the same overall transition interact with each other through the relative orientation of the involved transition dipole moments. It can reveal structure–property relationships that lead to effective design strategies for controlling the multiphoton activities in different classes of molecules. Since it is directly related to different transition dipole moments, it can be controlled in the same way as the direction of charge transfer is controlled, for instance, by changing the strength and location of donor-acceptor groups in a molecule. The effect of channel interference on the two-photon absorption process in two-dimensional molecules was first studied by Cronstrand, Luo and Ågren.[1,2] Later, Alam, Chattopadhyaya and Chakrabarti[3] generalized it to three dimensions. The interference of optical channels can be either constructive or destructive in nature depending on the relative orientations of different transition dipole moments, *i.e.*, it can either increase or decrease the overall two-photon transition probability. Alam *et al.* have extensively studied this effect in a number of molecules, including through-bond as well as through-space charge-transfer molecules.[4–6] They have also studied solvent effects on channel interference and reported that channel interference can reverse its nature when changing the polarity of the solvent.[4] Murugan *et al.* have also used the channel interference technique to study the two-photon absorption process in a Bis(BF_2) complex and the corresponding solvatochromism in pyridinium cyclopentadienylide.[7,8] Recently, channel interference has been used for elucidating the two-photon absorption based Zn-sensing mechanism,[9] and to gain molecular-level insights into two-photon absorption processes in biological systems such as β-amyloid,[10,11] the DsRed chromophore[12] and other red fluorescent protein chromophores.[13] Channel interference has also been applied in other studies.[14–17]

Although channel interference has extensively been studied in the case of two-photon absorption processes, no such studies exist for higher-order multiphoton absorption processes. Higher-order multiphoton absorption processes are in general much less explored than the simpler two-photon analogue. The main reason for this is the computational costs of calculating these processes. In addition, the mathematical equations involved in the channel interference phenomenon for higher-order multiphoton processes are expected to be much more complicated than those involved in the simplest case of two-photon absorption. In general, the higher the order of the multiphoton absorption process, the larger the number of transition dipoles involved, and hence the relevant channel interference expression is expected to be increasingly complicated.

Recent work in our group has enabled the calculation of absorption strengths for any order of multiphoton absorption.[18–23] This has been made possible by the generalization of quasienergy response theory to arbitrary order[18] and its subsequent implementation in an open-ended response code based on recursive algorithms.[19] Friese *et al.* have derived expressions for the rotational averaging of multiphoton absorption tensors[20] and implemented the calculation of single residues in the response theory framework.[21] Subsequent extensions have enabled the incorporation of explicit[22] and implicit[23] environment effects.

In this work we will extend the concept of channel interference to higher-order multiphoton absorption processes. The remainder of the work is organized as follows: First, we will give an introduction to channel interference (Section II) before presenting a general scheme to derive channel interference for any order of multiphoton absorption (Section III). As an illustration of our general scheme, we will derive explicitly the simplest few-state

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model expressions for multiphoton absorption processes in centrosymmetric molecules and discuss the conditions that maximize the corresponding multiphoton absorption strengths in Section IV, followed by concluding remarks in Section V.

II. CHANNEL INTERFERENCE

The starting point for deriving channel interference expressions for multiphoton absorption are the transition moments S (Eq. 1) and the corresponding expressions for the multiphoton absorption strengths δ. The transition moment S for an m-photon absorption process is a rank-m tensor in three-dimensional space. For two-, three- and four-photon absorption, the elements of the transition moments are given as

$$\begin{aligned} S_{ab} &= \sum \mathcal{P}_{ab} \sum_{\mathrm{i}} \frac{\mu^{a}_{\mathrm{oi}}\mu^{b}_{\mathrm{if}}}{\Delta E_{\mathrm{i}1}}, \\ S_{abc} &= \sum \mathcal{P}_{abc} \sum_{\mathrm{ij}} \frac{\mu^{a}_{\mathrm{oi}}\mu^{b}_{\mathrm{ij}}\mu^{c}_{\mathrm{jf}}}{\Delta E_{\mathrm{i}1}\Delta E_{\mathrm{j}2}}, \\ S_{abcd} &= \sum \mathcal{P}_{abcd} \sum_{\mathrm{ijk}} \frac{\mu^{a}_{\mathrm{oi}}\mu^{b}_{\mathrm{ij}}\mu^{c}_{\mathrm{jk}}\mu^{d}_{\mathrm{kf}}}{\Delta E_{\mathrm{i}1}\Delta E_{\mathrm{j}2}\Delta E_{\mathrm{k}3}}, \end{aligned} \tag{1}$$

where the permutation operator $\mathcal{P}$ gives all the $m!$ permutations of the indices $\{a, b, \dots\}$, each of which runs over the Cartesian coordinates $\{x, y, z\}$. The expressions in Eq. 1 contain a sum over all intermediate states $\{\mathrm{i}, \mathrm{j}, \dots\}$, which can be the ground state or an electronically excited state. Each of the elements in this sum represents a specific transition from the ground state o to the excited state f, and we will here define this as a *channel*. Thus, S_{ab} contains a sum over all channels $\mathrm{o} \to \mathrm{i} \to \mathrm{f}$ for a two-photon transition from o to f, S_{abc} contains a sum over all channels $\mathrm{o} \to \mathrm{i} \to \mathrm{j} \to \mathrm{f}$ for a three-photon transition from o to f, *etc.* Each state i in Eq. 1 has an associated energy $\Delta E_{\mathrm{i}\lambda}$, which can be written as

$$\Delta E_{\mathrm{i}\lambda} = \omega_{\mathrm{i}} - \frac{\lambda \omega_{\mathrm{f}}}{m}, \tag{2}$$

where state i is the λ'th intermediate state in the channel. The energies $\Delta E_{\mathrm{i}\lambda}$ should not be confused with the energies of the m photons that together carry the necessary energy to excite the molecule from the ground state o to the excited state f. The theory of channel interference presented here can be equally applied to multiphoton absorption where all m photons have the same energy (degenerate case) or not (non-degenerate case).

The multiphoton absorption strength δ is obtained from the rotational averaging of the transition moments S. The theory of rotational averaging has been generalized to multiphoton absorption of any order by Friese, Beerepoot and Ruud.[20] For two-photon (2P), three-photon (3P) and four-photon (4P) absorption processes, the absorption strengths are[20]

$$\begin{aligned} \delta^{\mathrm{2P}} &= \frac{1}{15} \sum_{ab} \left(2 S_{ab} \bar{S}_{ab} + S_{aa} \bar{S}_{bb}\right), \\ \delta^{\mathrm{3P}} &= \frac{1}{35} \sum_{abc} \left(2 S_{abc} \bar{S}_{abc} + 3 S_{aab} \bar{S}_{bcc}\right), \\ \delta^{\mathrm{4P}} &= \frac{1}{315} \sum_{abcd} \left(8 S_{abcd} \bar{S}_{abcd} + 24 S_{aabc} \bar{S}_{bcdd} + 3 S_{aabb} \bar{S}_{ccdd}\right). \end{aligned} \tag{3}$$

Each term in the rotational averaging expressions contains a product of a transition moment S with the complex conjugate $\bar{S}$, both of which contain a sum over all the intermediate states (Eq. 1). If one introduces different sets of indices for S and $\bar{S}$, one can reformulate the multiphoton absorption strength δ as a sum over the two sets of indices, which run over the same states. This reformulated expression will then describe the interactions between different channels involved in the corresponding multiphoton absorption process. In the case of three-photon absorption, the indices $\{\mathrm{i}, \mathrm{j}\}$ for S and $\{\mathrm{m}, \mathrm{n}\}$ for $\bar{S}$ represent the interference of two channels ($\mathrm{o} \to \mathrm{i} \to \mathrm{j} \to \mathrm{f}$ and $\mathrm{o} \to \mathrm{m} \to \mathrm{n} \to \mathrm{f}$) involved in the same three-step transition from o to f. The interaction of the two channels gives rise to the name *channel interference*. The advantage of this reformulation is the possibility to express the multiphoton absorption strength in terms of (transition) dipole moments and the angles between them, which are relevant parameters in the molecular design of multiphoton absorption probes.

We note that channel interference describes the interference of the manifold of optical channels to excite a molecule to a given excited state using a given number of photons. It is thus different from the optical interference phenomenon resulting from an experimental setup with two or more laser beams with different energy. An example of the latter is the optical interference between a one-photon and a three-photon process that has been demonstrated by Rebane *et al.*[24] Whereas a setup with two laser beams as well as photons of different energy are prerequisites for that process, they are not in the case of channel interference.

Alam, Chattopadhyaya and Chakrabarti[3] have derived an expression for the interference between channels $\mathrm{o} \to \mathrm{i} \to \mathrm{f}$ and $\mathrm{o} \to \mathrm{m} \to \mathrm{f}$ for two-photon absorption in three-dimensional molecules

$$\begin{aligned} \delta^{\mathrm{2P}}_{\mathrm{im}} = & \frac{8 \mu_{\mathrm{oi}} \mu_{\mathrm{if}} \mu_{\mathrm{om}} \mu_{\mathrm{mf}}}{\Delta E_{\mathrm{i}1} \Delta E_{\mathrm{m}1}} \cdot \\ & \left\{ \cos\theta^{\mathrm{if}}_{\mathrm{oi}} \cos\theta^{\mathrm{mf}}_{\mathrm{om}} + \cos\theta^{\mathrm{om}}_{\mathrm{oi}} \cos\theta^{\mathrm{mf}}_{\mathrm{if}} + \cos\theta^{\mathrm{mf}}_{\mathrm{oi}} \cos\theta^{\mathrm{if}}_{\mathrm{om}} \right\}. \end{aligned} \tag{4}$$

The total two-photon absorption strength δ^{2P} is a sum of $\delta^{\mathrm{2P}}_{\mathrm{im}}$ (Eq. 4) over all the intermediate states i and m. When combined with the missing factor from the rotational averaging (here $\frac{1}{30}$, see Ref. 25 for a discussion), the two-photon absorption strength becomes

$$\delta^{2\mathrm{P}} = \frac{4}{15}\sum_{\mathrm{im}} \frac{\mu_{\mathrm{oi}}\mu_{\mathrm{if}}\mu_{\mathrm{om}}\mu_{\mathrm{mf}}}{\Delta E_{\mathrm{i1}}\Delta E_{\mathrm{m1}}} \cdot \Big\{ \cos\theta_{\mathrm{oi}}^{\mathrm{if}}\cos\theta_{\mathrm{om}}^{\mathrm{mf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{om}}\cos\theta_{\mathrm{if}}^{\mathrm{mf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{mf}}\cos\theta_{\mathrm{om}}^{\mathrm{if}} \Big\}. \tag{5}$$

The same strategy as used by Alam, Chattopadhyaya and Chakrabarti[3] can be adopted to derive the channel interference formula for three-photon or other multiphoton absorption processes. We have derived the corresponding expression for three-photon absorption (see the supporting information file for the full derivation)

$$\begin{aligned}\delta^{3\mathrm{P}} = \frac{12}{35}\sum_{\mathrm{ijmn}} \frac{\mu_{\mathrm{oi}}\mu_{\mathrm{ij}}\mu_{\mathrm{jf}}\mu_{\mathrm{om}}\mu_{\mathrm{mn}}\mu_{\mathrm{nf}}}{\Delta E_{\mathrm{i1}}\Delta E_{\mathrm{j2}}\Delta E_{\mathrm{m1}}\Delta E_{\mathrm{n2}}} \Big\{ & \cos\theta_{\mathrm{oi}}^{\mathrm{ij}}\cos\theta_{\mathrm{jf}}^{\mathrm{om}}\cos\theta_{\mathrm{mn}}^{\mathrm{nf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{ij}}\cos\theta_{\mathrm{jf}}^{\mathrm{mn}}\cos\theta_{\mathrm{om}}^{\mathrm{nf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{ij}}\cos\theta_{\mathrm{jf}}^{\mathrm{nf}}\cos\theta_{\mathrm{om}}^{\mathrm{mn}} \\ & + \cos\theta_{\mathrm{oi}}^{\mathrm{jf}}\cos\theta_{\mathrm{ij}}^{\mathrm{om}}\cos\theta_{\mathrm{mn}}^{\mathrm{nf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{jf}}\cos\theta_{\mathrm{ij}}^{\mathrm{mn}}\cos\theta_{\mathrm{om}}^{\mathrm{nf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{jf}}\cos\theta_{\mathrm{ij}}^{\mathrm{nf}}\cos\theta_{\mathrm{om}}^{\mathrm{mn}} \\ & + \cos\theta_{\mathrm{oi}}^{\mathrm{om}}\cos\theta_{\mathrm{ij}}^{\mathrm{jf}}\cos\theta_{\mathrm{mn}}^{\mathrm{nf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{om}}\cos\theta_{\mathrm{ij}}^{\mathrm{mn}}\cos\theta_{\mathrm{jf}}^{\mathrm{nf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{om}}\cos\theta_{\mathrm{ij}}^{\mathrm{nf}}\cos\theta_{\mathrm{jf}}^{\mathrm{mn}} \\ & + \cos\theta_{\mathrm{oi}}^{\mathrm{mn}}\cos\theta_{\mathrm{ij}}^{\mathrm{jf}}\cos\theta_{\mathrm{om}}^{\mathrm{nf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{mn}}\cos\theta_{\mathrm{ij}}^{\mathrm{om}}\cos\theta_{\mathrm{jf}}^{\mathrm{nf}} + \cos\theta_{\mathrm{oi}}^{\mathrm{mn}}\cos\theta_{\mathrm{ij}}^{\mathrm{nf}}\cos\theta_{\mathrm{jf}}^{\mathrm{om}} \\ & + \cos\theta_{\mathrm{oi}}^{\mathrm{nf}}\cos\theta_{\mathrm{ij}}^{\mathrm{jf}}\cos\theta_{\mathrm{om}}^{\mathrm{mn}} + \cos\theta_{\mathrm{oi}}^{\mathrm{nf}}\cos\theta_{\mathrm{ij}}^{\mathrm{om}}\cos\theta_{\mathrm{jf}}^{\mathrm{mn}} + \cos\theta_{\mathrm{oi}}^{\mathrm{nf}}\cos\theta_{\mathrm{ij}}^{\mathrm{mn}}\cos\theta_{\mathrm{jf}}^{\mathrm{om}} \Big\}.\end{aligned} \tag{6}$$

The theory can be generalized to any order of multiphoton absorption without an explicit derivation for each order. In the following, we will present a general scheme to derive channel interference expressions for multiphoton absorption to any order.

III. A GENERAL SCHEME FOR CHANNEL INTERFERENCE IN MULTIPHOTON ABSORPTION

In order to derive a generalized scheme for channel interference formula in multiphoton absorption processes, we divide Eq. 5 or Eq. 6 into four parts: the dipole term (in the numerator), the energy term (in the denominator), the angle term (in curly brackets) and the prefactor (the term in front of the summation)

$$\delta^{m\mathrm{P}} = \text{prefactor} \times \sum_{\text{intermediates}} \frac{\text{dipole term}}{\text{energy term}} \times \text{angle term}. \tag{7}$$

In the following, we will discuss each of the four parts in Eq. 7 separately.

A. Dipole term

The dipole term is a product of the magnitude of the transition dipole moments for the two channels that interfere in an m-photon transition from the ground state o to excited state f. For two-photon absorption (Eq. 5), two channels (o$\rightarrow$ i $\rightarrow$ f and o$\rightarrow$ m $\rightarrow$ f) lead to four dipoles ($\mu_{\mathrm{oi}}, \mu_{\mathrm{if}}, \mu_{\mathrm{om}}$ and μ_{mf}). The product of these four dipoles appears in Eq. 5. Similarly, in the case of three-photon absorption (Eq. 6), the two channels o $\rightarrow$ i $\rightarrow$ j $\rightarrow$ f and o $\rightarrow$ m $\rightarrow$ n $\rightarrow$ f involve six dipoles ($\mu_{\mathrm{oi}}, \mu_{\mathrm{ij}}, \mu_{\mathrm{jf}}, \mu_{\mathrm{om}}, \mu_{\mathrm{mn}}$ and μ_{nf}) and a product of these six dipoles appears in the corresponding dipole term in Eq. 6. In general, the dipole term in an m-photon absorption process contains a product of $2m$ dipoles. As a further illustration, the dipole terms for four- and five-photon absorption processes are given as

$$\begin{aligned} &\mu_{\mathrm{oi}}\mu_{\mathrm{ij}}\mu_{\mathrm{jk}}\mu_{\mathrm{kf}}\mu_{\mathrm{om}}\mu_{\mathrm{mn}}\mu_{\mathrm{np}}\mu_{\mathrm{pf}} && \text{four} - \text{photon}, \\ &\mu_{\mathrm{oi}}\mu_{\mathrm{ij}}\mu_{\mathrm{jk}}\mu_{\mathrm{kl}}\mu_{\mathrm{lf}}\mu_{\mathrm{om}}\mu_{\mathrm{mn}}\mu_{\mathrm{np}}\mu_{\mathrm{pq}}\mu_{\mathrm{qf}} && \text{five} - \text{photon}. \end{aligned}$$

B. Energy term

The energy term in Eq. 5 contains energies ΔE_{i1} and ΔE_{m1} related to the intermediates state (i and m) of the two channels in a two-photon absorption process. Similarly, the three-photon absorption expression in Eq. 6 contains four energies, one for each intermediate state (i, j, m and n). In general, each intermediate state i is associated with an energy $\Delta E_{\mathrm{i}\lambda}$ (Eq. 2). Therefore, the number of such energies is equal to the number of intermediate states in the two channels, which is $2(m-1)$.

For two-photon absorption ($m = 2$) there is only one intermediate state in each channel, so $\lambda = 1$ (Eq. 2) and the two energies are ΔE_{i1} and ΔE_{m1}. Similarly, for three-photon absorption, each channel has two intermediates $\{(\mathrm{i},\mathrm{j}),(\mathrm{m},\mathrm{n})\}$. Therefore, the energy term for three-photon absorption has four energies, *viz.* $\Delta E_{\mathrm{i1}}, \Delta E_{\mathrm{j2}}, \Delta E_{\mathrm{m1}}$ and ΔE_{n2}. For m-photon absorption, there are $m-1$ intermediate states in each channel and hence λ can assume an integer value from 1 to $m-1$ for each channel. As an illustration, the six energy terms in the two channels o$\rightarrow$ i $\rightarrow$ j $\rightarrow$ k $\rightarrow$ f and o$\rightarrow$ m $\rightarrow$ n $\rightarrow$ p $\rightarrow$ f in four-photon absorption are given as

$$\begin{aligned}
\Delta E_{\mathrm{i1}} &= \omega_{\mathrm{i}} - \frac{\omega_{\mathrm{f}}}{4}, \\
\Delta E_{\mathrm{j2}} &= \omega_{\mathrm{j}} - \frac{2\omega_{\mathrm{f}}}{4}, \\
\Delta E_{\mathrm{k3}} &= \omega_{\mathrm{k}} - \frac{3\omega_{\mathrm{f}}}{4}, \\
\Delta E_{\mathrm{m1}} &= \omega_{\mathrm{m}} - \frac{\omega_{\mathrm{f}}}{4}, \\
\Delta E_{\mathrm{n2}} &= \omega_{\mathrm{n}} - \frac{2\omega_{\mathrm{f}}}{4}, \\
\Delta E_{\mathrm{p3}} &= \omega_{\mathrm{p}} - \frac{3\omega_{\mathrm{f}}}{4}.
\end{aligned} \tag{8}$$

C. Angle term

The angle term in the channel interference expression for two-photon absorption processes (Eq. 5) contains three elements with two cosines each, whereas the corresponding expression for three-photon absorption (Eq. 6) contains fifteen elements with three cosines each. We will here distinguish between angles (such as $\theta^{\mathrm{jf}}_{\mathrm{oi}}$) and elements of the angle term (such as $\cos\theta^{\mathrm{if}}_{\mathrm{oi}}\cos\theta^{\mathrm{jf}}_{\mathrm{oj}}$ in Eq. 5). The angle term gives all possible ways in which the dipole moments can interact with each other, *i.e.*, all the unique ways to combine the different cosines. Each element of the angle term contains each dipole once and as such it contains all the dipoles involved. For example, the element $\cos\theta^{\mathrm{if}}_{\mathrm{oi}}\cos\theta^{\mathrm{jf}}_{\mathrm{oj}}$ in Eq. 5 contains all the four dipoles involved in this case, but it represents only one possible way of interaction of the four dipoles. Thus, $2m$ dipole moments involved in an m-photon absorption process will lead to m cosines in each element of the angle term since each cosine contains the angle between two dipole moments. In general, the angle term for m-photon absorption can be written as

$$\sideset{}{'}\sum_{\substack{\alpha_1,\ldots,\alpha_m=1\\ \beta_1,\ldots,\beta_m=1}}^{2m} \prod_{i=1}^{m} \cos\theta^{\mathrm{I}_{\beta_i}}_{\mathrm{I}_{\alpha_i}}, \tag{9}$$

where I is a vector of length $2m$ containing the indices of each dipole moment in the dipole term, as illustrated for two-, three- and four-photon absorption processes:

$$\begin{aligned}
\mathrm{I} &= \{\mathrm{oi},\mathrm{if},\mathrm{om},\mathrm{mf}\} && \mathrm{two-photon} \\
\mathrm{I} &= \{\mathrm{oi},\mathrm{ij},\mathrm{jf},\mathrm{om},\mathrm{mn},\mathrm{nf}\} && \mathrm{three-photon} \\
\mathrm{I} &= \{\mathrm{oi},\mathrm{ij},\mathrm{jk},\mathrm{kf},\mathrm{om},\mathrm{mn},\mathrm{np},\mathrm{pf}\} && \mathrm{four-photon}
\end{aligned}$$

The integers α_i and β_i run from 1 to $2m$, and I_{α_i} and I_{β_i} are the α_i'th and β_i'th elements of I, respectively. The integer i runs from 1 to m and ensures there are m cosines for each element of the angle term in m-photon absorption. The sum in Eq. 9 is a restricted (represented by a prime) multiple sum over all indices α_i and β_i. The following conditions apply for the indices α_i and β_i:

1. $\alpha_1,\ldots,\alpha_m,\beta_1,\ldots,\beta_m$ all have unique values
2. $\alpha_i < \beta_i$
3. $\alpha_i < \alpha_j$ for $i < j$

Condition 1 ensures that each element of the angle term contains the indices of each dipole only once. As a result of this, the restricted summation in Eq. 9 does not give $(2m)^{2m}$ terms, but rather $(2m)!$ terms. Condition 2 ensures that each cosine appears only once, *i.e.*, $\cos\theta^{\mathrm{if}}_{\mathrm{oi}}$ is allowed but the equivalent $\cos\theta^{\mathrm{oi}}_{\mathrm{if}}$ is removed. This reduces the number of terms by a factor of 2^m. Finally, condition 3 ensures that the same product of cosines appears only once in the angle term. This reduces the number of terms by a factor of $m!$. As an illustration of condition 3 for two-photon absorption, $\cos\theta^{\mathrm{if}}_{\mathrm{oi}}\cos\theta^{\mathrm{jf}}_{\mathrm{oj}}$ is allowed but the equivalent term $\cos\theta^{\mathrm{jf}}_{\mathrm{oj}}\cos\theta^{\mathrm{if}}_{\mathrm{oi}}$ is removed.

Taken together, the number of elements in the angle term for a channel interference expression for m-photon absorption ($m > 1$) is given as

$$N_{\mathrm{a}} = \frac{(2m)!}{2^m \cdot m!} = \prod_{i=1}^{m} (2i-1)\,. \tag{10}$$

D. Prefactor

The prefactor ($\frac{4}{15}$ in Eq. 5 and $\frac{12}{35}$ in Eq. 6) represents the total number of products of S and $\bar{S}$ and is therefore a product of the number of permutations of the indices of the transition moment S (Eq. 1) and the integers in the rotational averaging procedure (Eq. 3). The prefactor also contains a division by the number of angle terms N_{a} (Eq. 10) to ensure that every product of S and $\bar{S}$ contributes only once to the final expression.

The number of permutations of the indices in the transition moment S is given as $m!$ with m being the number of photons involved. Since both S and $\bar{S}$ have a permutation operator, the prefactor contains a factor $(m!)^2$.

The number of products of S and $\bar{S}$ in the rotational averaging procedure (Eq. 3) is equal to the prefactor of the rotational averaging ζ times the sum of the contraction coefficients. The prefactor ζ is given by[20]

$$\zeta = \prod_{i=1}^{m} \frac{1}{2i+1}, \tag{11}$$

which is the inverse of the product of all odd numbers equal to or less than $2m+1$. The sum of all the contraction coefficients is given by[20]

$$N_{\mathrm{c}} = \prod_{i=1}^{m} (2i-1), \tag{12}$$

which is equal to N_{a} in Eq. 10. The product of ζ and N_{c} is simply one divided by $2m+1$, which can be verified by evaluating the number of products of S and $\bar{S}$ in Eq. 3.

Combining all contributions, the total prefactor becomes

$$(m!)^2 \cdot \frac{1}{2m+1} \cdot \frac{2^m \cdot m!}{(2m)!} = \frac{(m!)^3 \cdot 2^m}{(2m+1)(2m)!}, \qquad (13)$$

which can equivalently be written as $\prod_{i=1}^{m} \frac{i^2}{2i+1}$. The prefactor (Eq. 13) is $\frac{4}{15}$ for two-photon absorption, $\frac{12}{35}$ for three-photon absorption, $\frac{192}{315}$ for four-photon absorption, *etc.*

E. General characteristics of channel interference in multiphoton absorption

The preceding analysis is general for m-photon absorption ($m > 1$). The explicit expressions for two- and three-photon absorption are given in Eqs. 5 and 6, respectively. The corresponding expression for four-photon absorption is given as Eq. A.1 in the Appendix. Some of the characteristics of the channel interference expressions are:

1. The channel interference expressions are invariant to the exchange of the indices from the two channels, for example $\delta^{3\mathrm{P}}_{\mathrm{ijmn}} = \delta^{3\mathrm{P}}_{\mathrm{mnij}}$ for three-photon absorption, where $\delta^{3\mathrm{P}}_{\mathrm{ijmn}}$ represents the term within the summation in Eq. 6.

2. If a contribution to the multiphoton absorption strength is negative, this is referred to as *destructive interference*. Applied to three-photon absorption, channels $\mathrm{o} \to \mathrm{i} \to \mathrm{j} \to \mathrm{f}$ and $\mathrm{o} \to \mathrm{m} \to \mathrm{n} \to \mathrm{f}$ interfere destructively when $\delta^{3\mathrm{P}}_{\mathrm{ijmn}} < 0$ and constructively when $\delta^{3\mathrm{P}}_{\mathrm{ijmn}} > 0$.

3. Since the dipole term and the prefactor are always positive quantities, destructive interference can arise either from a negative energy term or from a negative angle term. For an excitation to the first excited state (ω_{f} is lower than ω_i for all the other excited states i), the energy $\Delta E_{\mathrm{i}\lambda}$ (Eq. 2) is only negative if state i is the ground state o. Thus, an odd number of ground-state indices causes the energy term to be negative for an excitation to the first excited state.

IV. THE SIMPLEST FEW-STATE MODELS IN CENTROSYMMETRIC MOLECULES

In this section, we will illustrate the use of the general approach presented in the previous section to study channel interference for multiphoton absorption in centrosymmetric molecules. In order to further simplify the discussion, we will restrict ourselves to the special cases of the simplest few-state models for two-, three-, four- and five-photon absorption processes. The expressions include one-photon transition dipole moments that agree with the selection rule, *i.e.* only *gerade* → *ungerade* or *ungerade* → *gerade* transitions exist and the others will vanish. This puts restrictions on the symmetry of the intermediate states used in the few-state models. In centrosymmetric molecules, for which $\mu_{\mathrm{oo}} = 0$, the simplest few-state model for odd-order multiphoton absorption processes is a two-state model and for even-order multiphoton absorption a three-state model. For a two-state model, the intermediate states can be either the ground state o or the excited state of interest f. For a three-state model, a third state is introduced. The centrosymmetric case will be represented by the subscript 'cs' to $\delta^{m\mathrm{P}}$.

A. Two-photon absorption

A two-photon absorption process in a centrosymmetric molecule is possible from the *gerade* ground state o ($\mu_{\mathrm{oo}} = 0$) through an *ungerade* intermediate state u to a *gerade* excited state f ($\mu_{\mathrm{ff}} = 0$). The simplest few-state model is thus a three-state model with *ungerade* intermediate state u in each of the two channels. The only term contributing to $\delta^{2\mathrm{P}}$ (Eq. 5) in a three-state model for a centrosymmetric molecule is thus $\delta^{2\mathrm{P}}_{\mathrm{uu}}$. Hence, $\delta^{2\mathrm{P}}_{\mathrm{cs}}$ is

$$\delta^{2\mathrm{P}}_{\mathrm{cs}} = \frac{4\mu^2_{\mathrm{ou}}\mu^2_{\mathrm{uf}}}{15(\omega_{\mathrm{u}} - \frac{\omega_{\mathrm{f}}}{2})^2}\left\{1 + 2\cos^2\theta^{\mathrm{uf}}_{\mathrm{ou}}\right\}. \qquad (14)$$

Both transition dipole moments, the square of $(\omega_{\mathrm{u}} - \frac{\omega_{\mathrm{f}}}{2})$ and the square of $\cos\theta^{\mathrm{uf}}_{\mathrm{ou}}$ are all positive quantities. Hence, the channels o→u→f and o→u→f always interfere constructively. Within a three-state model, $\delta^{2\mathrm{P}}_{\mathrm{cs}}$ is maximized by large and parallel (or antiparallel) transition dipole moments μ_{ou} and μ_{uf} (Fig. 1) as well as a small energy term.

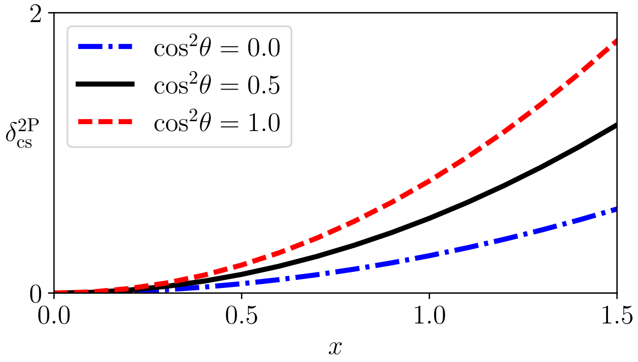

FIG. 1. Variation in two-photon absorption strength for centrosymmetric molecules $\delta^{2\mathrm{P}}_{\mathrm{cs}}$ (Eq. 14) with $\mu_{\mathrm{ou}} = x$ for different choices for $\cos^2\theta^{\mathrm{uf}}_{\mathrm{of}}$ and $(\omega_{\mathrm{u}} - \frac{\omega_{\mathrm{f}}}{2}) = 1$ and $\mu_{\mathrm{uf}} = 1$.

B. Three-photon absorption

A three-photon absorption process in a centrosymmetric molecule is possible from the *gerade* ground state o ($\mu_{\rm oo}=0$) through an *ungerade* intermediate state i and a *gerade* intermediate state j to an *ungerade* excited state f ($\mu_{\rm ff}=0$). The simplest few-state model is thus a two-state model with channels o→f→o→f. The only term contributing to $\delta^{\rm 3P}$ (Eq. 6) in a two-state model for a centrosymmetric molecule is thus $\delta^{\rm 3P}_{\rm fofo}$. Hence, $\delta^{\rm 3P}_{\rm cs}$ is

$$\delta^{\rm 3P}_{\rm cs}=\frac{729\mu^6_{\rm of}}{28\omega^4_{\rm f}}. \tag{15}$$

Both the transition dipole moment $\mu_{\rm of}$ and the energy $\omega_{\rm f}$ are positive quantities. Hence, the channels o→f→o→f and o→f→o→f always interfere constructively. Within a two-state model, $\delta^{\rm 3P}_{\rm cs}$ is maximized by a large transition dipole moment between the ground state and the excited state of interest and a low excitation energy.

C. Four-photon absorption

A four-photon absorption process in a centrosymmetric molecule is possible from the *gerade* ground state o ($\mu_{\rm oo}=0$) through intermediate states i, j and k that are *ungerade*, *gerade* and *ungerade*, respectively, to a *gerade* excited state f ($\mu_{\rm ff}=0$). The simplest few-state model is thus a three-state model with channels o→u→o→u→f or o→u→f→u→f, where intermediate states i and k are the *ungerade* state u and where j is either the ground state o or the excited state f. There is thus four terms contributing to $\delta^{\rm 4P}$ in Eq. A.1, namely $\delta^{\rm 4P}_{\rm uouuou}$, $\delta^{\rm 4P}_{\rm ufuufu}$ and $\delta^{\rm 4P}_{\rm uouufu}$=$\delta^{\rm 4P}_{\rm ufuuou}$. Hence, $\delta^{\rm 4P}_{\rm cs}$ is

$$\delta^{\rm 4P}_{\rm cs}=\frac{256}{35\omega^2_{\rm f}}\frac{\mu^2_{\rm ou}\mu^2_{\rm uf}}{\Delta E^2_{\rm u1}\Delta E^2_{\rm u3}}\left[5\left(\mu^4_{\rm ou}+\mu^4_{\rm uf}\right)\left\{1+6\cos^2\theta^{\rm uf}_{\rm ou}\right\}\right.$$
$$\left.-\,2\mu^2_{\rm ou}\mu^2_{\rm uf}\left\{3+24\cos^2\theta^{\rm uf}_{\rm ou}+8\cos^4\theta^{\rm uf}_{\rm ou}\right\}\right]. \tag{16}$$

Both transition dipole moments, the squares of $\Delta E_{\rm u1}$ and $\Delta E_{\rm u3}$, the energy $\omega_{\rm f}$ and the square or quad of $\cos\theta^{\rm uf}_{\rm ou}$ are positive quantities. Hence, the channels o→u→o→u→f and o→u→o→u→f as well as the channels o→u→f→u→f and o→u→f→u→f will always interfere constructively, while the channels o→u→o→u→f and o→u→f→u→f always interfere destructively. Within a three-state model, $\delta^{\rm 4P}_{\rm cs}$ is maximized by large transition dipole moments $\mu_{\rm ou}$ and $\mu_{\rm uf}$ as well as small energy terms $\Delta E_{\rm u1}$ and $\Delta E_{\rm u3}$. If the transition dipole moments are parallel or antiparallel, however, $\delta^{\rm 4P}_{\rm cs}$ is zero for $\mu_{\rm ou}=\mu_{\rm uf}$ (the minimum at $x=1$ in Fig. 2, red dashed line). This minimum is caused by an equal contribution of the constructive and destructive interference terms to the multiphoton absorption strength. Note that $\delta^{\rm 4P}_{\rm cs}$ depends on several factors and that a complete picture of the variation of $\delta^{\rm 4P}_{\rm cs}$ with all these factors will be a complicated multidimensional plot. Fig. 2 represents the dependence of $\delta^{\rm 4P}_{\rm cs}$ on $\mu_{\rm ou}$ only, keeping the other factors fixed to unity. $\delta^{\rm 4P}_{\rm cs}$ shows a similar dependency on $\mu_{\rm uf}$.

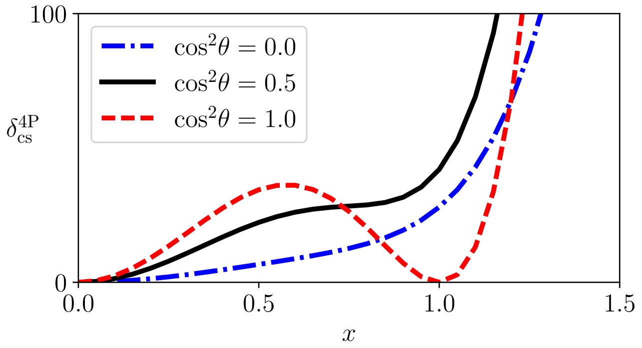

FIG. 2. Variation in four-photon absorption strength for centrosymmetric molecules $\delta^{\rm 4P}_{\rm cs}$ (Eq. 16) with $\mu_{\rm ou}=x$ for different choices for $\cos^2\theta^{\rm uf}_{\rm of}$ and $\omega_{\rm f}=1$, $\Delta E_{\rm u1}=1$, $\Delta E_{\rm u3}=1$, $\mu_{\rm uf}=1$.

D. Five-photon absorption

A five-photon absorption process in a centrosymmetric molecule is possible from the *gerade* ground state o ($\mu_{\rm oo}=0$) through intermediate states i, j, k and l that are *ungerade*, *gerade*, *ungerade* and *gerade*, respectively, to an *ungerade* excited state f ($\mu_{\rm ff}=0$). The simplest few-state model is thus a two-state model with channels o→f→o→f→o→f. The only term contributing to $\delta^{\rm 5P}$ in a two-state model for a centrosymmetric molecule is thus $\delta^{\rm 5P}_{\rm fofofofo}$. Hence, $\delta^{\rm 5P}_{\rm cs}$ is

$$\delta^{\rm 5P}_{\rm cs}=\frac{87890625\mu^{10}_{\rm of}}{704\omega^8_{\rm f}}. \tag{17}$$

Both the transition dipole moment $\mu_{\rm of}$ and the energy $\omega_{\rm f}$ are positive quantities. Hence, the channels o→f→o→f→o→f and o→f→o→f→o→f always interfere constructively. Within a two-state model, $\delta^{\rm 5P}_{\rm cs}$ is maximized by a large transition dipole moment between the ground state and the excited state of interest and a low excitation energy.

V. CONCLUSIONS

We have shown that the theory of channel interference can be applied to multiphoton absorption beyond two-photon absorption. We have explicitly derived an expression for channel interference in a three-photon absorption process. Furthermore, we have here presented a general scheme to derive channel interference expressions for multiphoton absorption processes of any order.

We have found that, in general, destructive interference can arise either from a negative energy term or from a negative angle term. It is straightforward to predict the sign of the energy term provided the final state of interest and the intermediate states involved are known, as is the case in a few-state model. However, it is not possible to predict the sign of the angle term without an explicit evaluation.

Moreover, we have shown how our general scheme can be used to derive maximizing conditions for multiphoton absorption strengths using the example of the simplest few-state models in centrosymmetric molecules.

The concept of channel interference can thus be applied to any order of multiphoton absorption processes. Hence, it can be used in the molecular design of multiphoton absorption probes. As a future prospect, it would be interesting to extend the idea of channel interference or dipole alignment to other spectroscopies in the electronic and may be also in vibrational domains.

VI. SUPPORTING MATERIAL

See supplementary material for the explicit derivation of Eq. 6.

Appendix: Channel interference in four-photon absorption

$$
\begin{aligned}
\delta^{\mathrm{4P}} =& \frac{192}{315}\sum_{\mathrm{ijkmnp}} \frac{\mu_{\mathrm{oi}}\mu_{\mathrm{ij}}\mu_{\mathrm{jk}}\mu_{\mathrm{kf}}\mu_{\mathrm{om}}\mu_{\mathrm{mn}}\mu_{\mathrm{np}}\mu_{\mathrm{pf}}}{\Delta E_{\mathrm{i1}}\Delta E_{\mathrm{j2}}\Delta E_{\mathrm{k3}}\Delta E_{\mathrm{m1}}\Delta E_{\mathrm{n2}}\Delta E_{\mathrm{p3}}}\cdot \\
&\Big\{\cos\theta^{\mathrm{ij}}_{\mathrm{oi}}\cos\theta^{\mathrm{kf}}_{\mathrm{jk}}\cos\theta^{\mathrm{mn}}_{\mathrm{om}}\cos\theta^{\mathrm{pf}}_{\mathrm{np}}+\cos\theta^{\mathrm{ij}}_{\mathrm{oi}}\cos\theta^{\mathrm{kf}}_{\mathrm{jk}}\cos\theta^{\mathrm{np}}_{\mathrm{om}}\cos\theta^{\mathrm{pf}}_{\mathrm{mn}}+\cos\theta^{\mathrm{ij}}_{\mathrm{oi}}\cos\theta^{\mathrm{kf}}_{\mathrm{jk}}\cos\theta^{\mathrm{pf}}_{\mathrm{om}}\cos\theta^{\mathrm{np}}_{\mathrm{mn}}+\cos\theta^{\mathrm{ij}}_{\mathrm{oi}}\cos\theta^{\mathrm{om}}_{\mathrm{jk}}\cos\theta^{\mathrm{mn}}_{\mathrm{kf}}\cos\theta^{\mathrm{pf}}_{\mathrm{np}} \\
&+\cos\theta^{\mathrm{ij}}_{\mathrm{oi}}\cos\theta^{\mathrm{om}}_{\mathrm{jk}}\cos\theta^{\mathrm{np}}_{\mathrm{kf}}\cos\theta^{\mathrm{pf}}_{\mathrm{mn}}+\cos\theta^{\mathrm{ij}}_{\mathrm{oi}}\cos\theta^{\mathrm{om}}_{\mathrm{jk}}\cos\theta^{\mathrm{pf}}_{\mathrm{kf}}\cos\theta^{\mathrm{np}}_{\mathrm{mn}}+\cos\theta^{\mathrm{ij}}_{\mathrm{oi}}\cos\theta^{\mathrm{mn}}_{\mathrm{jk}}\cos\theta^{\mathrm{om}}_{\mathrm{kf}}\cos\theta^{\mathrm{pf}}_{\mathrm{np}}+\cos\theta^{\mathrm{ij}}_{\mathrm{oi}}\cos\theta^{\mathrm{mn}}_{\mathrm{jk}}\cos\theta^{\mathrm{np}}_{\mathrm{kf}}\cos\theta^{\mathrm{pf}}_{\mathrm{om}} \\
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&+\cos\theta^{\mathrm{pf}}_{\mathrm{oi}}\cos\theta^{\mathrm{np}}_{\mathrm{ij}}\cos\theta^{\mathrm{mn}}_{\mathrm{jk}}\cos\theta^{\mathrm{om}}_{\mathrm{kf}}\Big\}.
\end{aligned}
\tag{A.1}
$$

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[1] P. Cronstrand, Y. Luo, and H. Ågren, J. Chem. Phys. **117**, 11102 (2002).

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

[3] M. M. Alam, M. Chattopadhyaya, and S. Chakrabarti, Phys. Chem. Chem. Phys. **14**, 1156 (2012).

[4] M. M. Alam, M. Chattopadhyaya, S. Chakrabarti, and K. Ruud, J. Phys. Chem. Lett. **3**, 961 (2012).

[5] M. M. Alam, M. Chattopadhyaya, and S. Chakrabarti, J. Phys. Chem. A **116**, 8067 (2012).

[6] M. M. Alam, M. Chattopadhyaya, S. Chakrabarti, and K. Ruud, Acc. Chem. Res. **47**, 1604 (2014).

[7] N. A. Murugan, J. Phys. Chem. B **118**, 7358 (2016).

[8] R. Zaleśny, N. A. Murugan, G. Tian, M. Medved, and H. Ågren, J. Phys. Chem. B **120**, 2323 (2016).

[9] J. Bednarska, R. Zaleśny, N. A. Murugan, W. Bartkowiak, H. Ågren, and M. Odelius, J. Phys. Chem. B **120**, 9067 (2016).

[10] N. A. Murugan, R. Zaleśny, J. Kongsted, A. Nordberg, and H. Ågren, Chem. Commun. **50**, 11694 (2014).

[11] T. B. Clark, M. Ziółkowski, G. C. Schatz, and T. Goodson III, J. Phys. Chem. B **118**, 2351 (2014).

[12] N. H. List, J. M. H. Olsen, H. J. A. Jensen, A. H. Steindal, and J. Kongsted, J. Phys. Chem. Lett. **3**, 3513 (2012).

[13] M. A. Salem, S. Twelves, and A. Brown, Phys. Chem. Chem. Phys. **18**, 24408 (2016).

[14] N. H. List, R. Zaleśny, N. A. Murugan, J. Kongsted, W. Bartkowiak, and H. Ågren, J. Chem. Theory Comput. **11**, 4182 (2015).

[15] M. Wielgus, R. Zaleśny, N. A. Murugan, J. Kongsted, H. Ågren, M. Samoc, and W. Bartkowiak, ChemPhysChem **14**, 3731 (2013).

[16] J. Bednarska, R. Zaleśny, M. Wielgus, B. Jędrzejewska, R. Puttreddy, K. Rissanen, W. Bartkowiak, H. Ågren, and B. Ośmiałowski, Phys. Chem. Chem. Phys. **19**, 5705 (2017).

[17] M. Drobizhev, F. Meng, A. Rebane, Y. Stepanenko, E. Nickel, and C. W. Spangler, J. Phys. Chem. B **110**, 9802 (2006).

[18] A. J. Thorvaldsen, K. Ruud, K. Kristensen, P. Jørgensen, and S. Coriani, J. Chem. Phys. **129**, 214108 (2008).

[19] M. Ringholm, D. Jonsson, and K. Ruud, J. Comput. Chem. **35**, 622 (2014).

[20] D. H. Friese, M. T. P. Beerepoot, and K. Ruud, J. Chem. Phys. **141**, 204103 (2014).

[21] D. H. Friese, M. T. P. Beerepoot, M. Ringholm, and K. Ruud, J. Chem. Theory Comput. **11**, 1129 (2015).

[22] A. H. Steindal, M. T. P. Beerepoot, M. Ringholm, N. H. List, K. Ruud, J. Kongsted, and J. M. H. Olsen, Phys. Chem. Chem. Phys. **18**, 28339 (2016).

[23] R. Di Remigio, M. T. P. Beerepoot, Y. Cornaton, M. Ringholm, A. H. Steindal, K. Ruud, and L. Frediani, Phys. Chem. Chem. Phys. **19**, 366 (2017).

[24] A. Rebane, N. Christensson, M. Drobizhev, Y. Stepanenko, and C. W. Spangler, Opt. express **13**, 6033 (2005).

[25] M. T. P. Beerepoot, D. H. Friese, N. H. List, J. Kongsted, and K. Ruud, Phys. Chem. Chem. Phys. **17**, 19306 (2015).