Five-photon absorption and selective enhancement of multiphoton absorption processes

Daniel H. Friese,*,† Radovan Bast,‡ and Kenneth Ruud*,†

Centre for Theoretical and Computational Chemistry, Department of Chemistry, University of Tromsø—The Arctic University of Norway, N-9037 Tromsø, Norway, and Theoretical Chemistry and Biology, School of Biotechnology, Royal Institute of Technology, AlbaNova University Centre, S-10691 Stockholm, Sweden

PCD Centre for High Performance Computing, Royal Institute of Technology, S-10044 Stockholm, Sweden

E-mail: daniel.h.friese@uit.no; kenneth.ruud@uit.no

Abstract

We study one-, two-, three-, four- and five-photon absorption of three centrosymmetric molecules using density functional theory. These calculations are the first ab initio calculations of five-photon absorption. Even- and odd-order absorption processes show different trends in the absorption cross sections. The behaviour of all even-
and odd-photon absorption properties shows a semi-quantitative similarity which can be explained using few-state models. This analysis shows that odd-photon absorption processes are largely determined by the one-photon absorption strength whereas all even-photon absorption strengths are largely dominated by the two-photon absorption strength, in both cases modulated by powers of the polarizability of the final excited state. We demonstrate how to selectively enhance a specific multiphoton absorption process.

The concept of multiphoton absorption (MPA) dates back to 1931 when it was predicted theoretically by Maria Göppert-Mayer.\textsuperscript{1} After the introduction of high-intensity laser light sources, multiphoton absorption has gained a lot of attention during the past five decades, with the first experimental proof for two-photon absorption as the starting point in 1961.\textsuperscript{2}

Two-photon absorption has by now found a wide range of applications.\textsuperscript{3–6} Simultaneously, electronic excitations involving absorption of up to five photons has been observed experimentally.\textsuperscript{7} The theoretical treatment of multiphoton absorption has also been pushed forward during the last decades, and computational methods for the calculation of two-photon transition strengths are available for SCF-based\textsuperscript{8,9} as well as for correlated wave-function based methods.\textsuperscript{10–13} Implementations of three-photon absorption have been realized only for SCF-based methods\textsuperscript{14–16} but SCF-based density-functional theory studies give good agreement with experiment for TPA and 3PA processes for small and medium-sized molecules.\textsuperscript{17,18} In our group, a recursive open-ended response theory\textsuperscript{19} has been expanded to the treatment of single residues of response functions, enabling the calculation of multiphoton absorption cross sections to infinite order using SCF-based methods, with results having been reported for four-photon absorption.\textsuperscript{20}

In order to design molecules with high multiphoton absorption cross sections, general and qualitative structure-property relations are important. However, very few general structure-property relations exist for higher-order multiphoton absorption properties, al-
though some interesting observations have been made in the case of three-photon absorption.\textsuperscript{21,22} The major scope of this work is both to present the first computational treatment of five-photon absorption and to study the relations between different multiphoton absorption processes. As experimental data for four- and five-photon absorption are very limited, in particular when it comes to complete spectra, we have to rely on a computational treatment of these properties to compare their behaviour. In order to amplify the general observations presented here, we will focus on centrosymmetric molecules.

The multiphoton absorption cross sections calculated for the molecules in Fig. 1 are shown in Table 1 for the \textit{p}-dinitrobenzene (PDNB) molecule, which has \( D_{2h} \) symmetry, and in Fig. 2 for the diaminoazobenzene (\( C_i \) symmetry) and indigo molecules (\( C_{2h} \) symmetry). Note that the units for the absorption cross sections differ and that the cross sections differ by orders of magnitude. The results reported have been calculated using the CAM-B3LYP functional\textsuperscript{23} and the augmented correlation-consistent polarized valence double-zeta basis sets (aug-cc-pVDZ) of Dunning and Woon.\textsuperscript{24,25} A recent study has shown that this level of theory is a good compromise between accuracy and computational cost.\textsuperscript{20} The calculations have been performed using a recursive response theory code\textsuperscript{19,20} interfaced to a development version of the Dalton program.\textsuperscript{26}

There are remarkable parallels in the absorption behaviour of the different states depending on whether an even or an odd number of photons is absorbed, see Table 1. The PDNB molecule deviates from this observation with its \( A_u \) states which cannot be reached by one-photon processes for symmetry reasons.
Table 1: Calculated MPA cross sections for PDNB and their ratios.

<table>
<thead>
<tr>
<th>No.</th>
<th>Energy [eV]</th>
<th>irrep</th>
<th>jPA cross sections [cm² s⁻¹ / photon⁻¹]</th>
<th>Cross section ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>OPA (10⁻¹⁹)</td>
<td>TPA (10⁻⁵⁴)</td>
</tr>
<tr>
<td>1</td>
<td>3.90</td>
<td>b₃g</td>
<td>3.44</td>
<td>0.08</td>
</tr>
<tr>
<td>2</td>
<td>3.95</td>
<td>au</td>
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<td>0.96</td>
</tr>
<tr>
<td>3</td>
<td>4.42</td>
<td>b₁u</td>
<td>2.46</td>
<td>1.78</td>
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<tr>
<td>4</td>
<td>4.62</td>
<td>b₂u</td>
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<td>803</td>
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<tr>
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<td>b₂u</td>
<td>278</td>
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<td>14</td>
<td>6.92</td>
<td>au</td>
<td>25.1</td>
<td>1.48</td>
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</table>
Investigating the results, we note that the qualitative agreement between the absorption cross sections is not as obvious for the even-order processes as for odd-photon absorption processes. The best correlation between the different even-photon absorption processes has been found in the diaminoazobenzene molecule.

Figure 1: The three centrosymmetric molecules that have been studied in this work: para-dinitrobenzene (1), diaminoazobenzene (2) and indigo (3).

The similarity in the multiphoton absorption cross sections observed in Fig. 2 can be explained by considering the sum-over-states expression for the multiphoton absorption cross sections. For a complete discussion of the basic theory of multiphoton absorption we refer to the literature\textsuperscript{20,27–30} and we restrict ourselves here only to provide the general expression for the multiphoton absorption cross sections that we will use in the analysis and to show an appropriation we do in order to explain our observations.
Figure 2: Multiphoton absorption behaviour of the three molecules under investigation. TPA cross sections have been scaled with $10^{32}$, 3PA cross sections are scaled with $10^{65}$, 4PA cross sections are scaled with $10^{94}$ and 5PA cross sections are scaled with $10^{126}$.

The general $j$-photon absorption cross section $\sigma^{j\text{PA}}$ is proportional to the square of the $j$-photon transition matrix element $M^{j\text{PA}}$ for $j \geq 2^{20,27}$

$$\sigma^{j\text{PA}} \sim |M^{j\text{PA}}|^2,$$

(1)

with $M^{j\text{PA}}$ being defined as (atomic units)$^{29}$

$$M^{j\text{PA}} = \mathcal{P}^{X_1,X_2,...,X_j} \sum_{l_1,l_2,...,l_{j-1}} \frac{\langle 0|\mu_{X_1}|l_1\rangle\langle l_1|\mu_{X_2}|l_2\rangle...\langle l_{j-1}|\mu_{X_j}|f\rangle}{(\omega_1 - \omega_{l_1})(\omega_1 + \omega_2 - \omega_{l_2})...(\omega_1 + \omega_2 + \cdots + \omega_{j-1} - \omega_{l_{j-1}})},$$

(2)

where $\omega_i$ is the frequency of perturbation $X_i$ and where we have already used the fact that the ground-state dipole moment vanishes for centrosymmetric molecules.$^{30}$ $\mu_{X_i}$ is the dipole operator with respect to perturbation $X_i$ and $\omega_{l_i}$ is the excitation energy between the ground state 0 and the excited state $l_i$. $f$ is the final state of the excitation and the operator $\mathcal{P}^{X_1,X_2,...,X_j}$ generates all permutations of the perturbations. $j$ is the number of photons absorbed in the described process. The calculations we present in this article have
been performed using this equation. To interpret them we now simplify this expression using symmetry considerations.

For centrosymmetric molecules we can easily identify the symmetry of the accessible final states \( f \) as well as the intermediate states \( l_i \) in Eq. (2). Because all electric dipole perturbations are \textit{ungerade} and the ground state always \textit{gerade}, the excited state \( l_1 \) that appears in the numerator of Eq. (2) must be \textit{ungerade}. All final states for odd-photon absorption processes must be \textit{ungerade}. In contrast, TPA and all higher-order even-photon absorption processes are only allowed for excitations with \textit{gerade} final states.

However, from Fig. 2 and Table 1, we note that there is even a semi-quantitative agreement between the absorption cross sections of different excited states. The orders of magnitude that are covered by the different cross section values are very similar in all cases, and the order of the states with respect to their MPA behaviour is similar within the even- and odd-photon absorption groups. This is illustrated in particular by the ratios between the cross sections that have been calculated for the PDNB molecule. Apart from the one for the \( 1B_{1u} \) state, which shows a rather small cross section, we find that all ratios between OPA and 3PA are within the range of about an order of magnitude. The behaviour of the TPA/4PA-ratios is rather similar with the exception of the one for the \( 1B_{1g} \)-state. We will return this anomaly.

In order to explain these observations, we first give the explicit expressions for the one- and two-photon absorption matrix elements

\[
M_{\text{OPA}} = \langle 0 | \mu_a | U_f \rangle,
\]

\[
M_{\text{TPA}} = P_{ab} \sum_{k=1}^{n_{U_f}} \frac{\langle 0 | \mu_a | U_k \rangle \langle U_k | \mu_b | G_f \rangle}{\omega_a - \omega_{U_k}},
\]

where the individual perturbations are marked by lowercase letters. \( U \) and \( G \) represent \textit{ungerade} and \textit{gerade} states, respectively, and the index \( f \) marks the final state. \( n_U \) is the
number of ungerade excited states that are symmetry allowed. The operator $P$ generates all permutations of the perturbations and their individual frequencies.

Let us now consider the 3PA transition matrix element

$$M_{abc}^{3PA} = P_{abc} \sum_{k=1}^{n_u} \sum_{l=1}^{n_g} \frac{\langle 0 | \mu_a | U_k \rangle \langle U_k | \mu_b | G_l \rangle \langle G_l | \mu_c | U_f \rangle}{(\omega_a - \omega_{U_k})(\omega_a + \omega_b - \omega_{G_l})}. \quad (5)$$

For a molecule with a strong, isolated OPA state, the dominating excited state of ungerade symmetry is the final state of interest, in the spirit of few-state models for multiphoton absorption cross sections, the 3PA matrix element reduces to

$$M_{abc}^{3PA} \approx P_{abc} \sum_{l=1}^{n_g} \frac{\langle 0 | \mu_a | U_f \rangle \langle U_f | \mu_b | G_l \rangle \langle G_l | \mu_c | U_f \rangle}{(\omega_a - \omega_{U_f})(\omega_a + \omega_b - \omega_{G_l})}. \quad (6)$$

Note that in this expression the summation over the ungerade states has been dropped but the summation over gerade states is not affected. The validity of this approach has been shown e.g. in work by Vivas and coworkers where a three-level model for TPA yielded impressing results compared to experiment.\(^{31}\) Using this expression, we can write the 3PA matrix element as

$$M_{abc}^{3PA} \approx P_{abc} M_a^{OPA} \frac{n_g}{(\omega_a - \omega_{U_f})} \sum_{l=1}^{n_g} \frac{\langle U_f | \mu_b | G_l \rangle \langle G_l | \mu_c | U_f \rangle}{(\omega_a + \omega_b - \omega_{G_l})}. \quad (7)$$

This quasi-few-state model now explains the similarity of the OPA and 3PA absorption cross sections, the 3PA cross section being proportional to the OPA cross section, the proportionality factor being the excited-state polarizability divided by an energy denominator. The permutation operator which is still present in the approximated equation takes into account that several spatial components of $M_a^{OPA}$ can contribute to the transition dipole moment.

This is also an explanation for the low 3PA and 5PA cross sections of the $A_u$ states in
PDNB since these states cannot be dominated by an OPA excitation according to Eq. (6). We can therefore separate 3PA excitations into OPA-dominated and pure-3PA absorptions.

We can extend this analysis to 4PA. The matrix element for four-photon absorption is

$$M_{\text{4PA}}^{abcd} = \sum_{k=1}^{n_u} \sum_{l=1}^{n_u} \sum_{m=1}^{n_u} \frac{\langle 0 | \mu_a | U_k \rangle \langle U_k | \mu_b | G_l \rangle \langle G_l | \mu_c | U_m \rangle \langle U_m | \mu_d | G_f \rangle}{(\omega_a - \omega_{U_k})(\omega_a + \omega_b - \omega_{G_l})(\omega_a + \omega_b + \omega_c - \omega_{U_m})},$$  

(8)

where both the summations over \( k \) and \( m \) cover the same manifold of ungerade states. In the same manner, we can now assume a dominant contribution from \( G_f \) as the intermediate gerade state, and write Eq. (8) as

$$M_{\text{4PA}}^{abcd} \approx \sum_{k=1}^{n_u} \sum_{m=1}^{n_u} \frac{\langle 0 | \mu_a | U_k \rangle \langle U_k | \mu_b | G_f \rangle \langle G_f | \mu_c | U_m \rangle \langle U_m | \mu_d | G_f \rangle}{(\omega_a - \omega_{U_k})(\omega_a + \omega_b - \omega_{G_f})(\omega_a + \omega_b + \omega_c - \omega_{U_m})},$$  

(9)

$$\approx \frac{M_{\text{TPA}}^{abcd}}{(\omega_a + \omega_b - \omega_{G_f})} \cdot \sum_{m=1}^{n_u} \frac{\langle G_f | \mu_c | U_m \rangle \langle U_m | \mu_d | G_f \rangle}{(\omega_a + \omega_b + \omega_c - \omega_{U_m})},$$  

(10)

Analogous to the results for 3PA, we find that the 4PA cross sections are proportional to the TPA cross section, the proportionality factor being the excited-state polarizability divided by an energy term.

For 5-photon absorption, we can in a similar manner write

$$M_{\text{5PA}}^{abcde} = \sum_{k,m=1}^{n_u} \sum_{l,n=1}^{n_u} \frac{\langle 0 | \mu_a | U_k \rangle \langle U_k | \mu_b | G_l \rangle \langle G_l | \mu_c | U_m \rangle \langle U_m | \mu_d | G_n \rangle \langle G_n | \mu_e | U_f \rangle}{(\omega_a - \omega_{U_k})(\omega_a + \omega_b - \omega_{G_l})(\omega_a + \omega_b + \omega_c - \omega_{U_m})(\omega_a + \omega_b + \omega_c + \omega_d - \omega_{G_n})},$$  

(11)

noting that we now have two ungerade intermediate states that can be substituted by the \( U_f \) state. If we only introduce the final state for the second ungerade state (\( U_m \) in the equation) we obtain

$$M_{\text{5PA}}^{abcde} \approx \sum_{n=1}^{n_u} \frac{\langle U_f | \mu_d | G_n \rangle \langle G_n | \mu_e | U_f \rangle}{(\omega_a + \omega_b + \omega_c + \omega_d - \omega_{G_n})},$$  

(12)
which is an expression for 3PA-dominated 5PA which is representative for the $A_u$ states of the PDB molecule.\footnote{In principle there should also be a term arising from introducing the final state for the first ungerade intermediate state. However, this would lead to a term which would correspond to the OPA transition moment scaled by the excited-state second hyperpolarizability, and thus can be expected to be smaller.} In most cases, we can simplify Eq. 12 further by substituting all ungerade intermediate states by the final state, giving

$$M_{abcde}^{5PA} \approx p_{abcde} \sum_{l,n=1}^{n_G} \frac{\langle 0 | \mu_a | U_f \rangle \langle U_f | \mu_b | G_l \rangle \langle G_l | \mu_c | U_f \rangle \langle U_f | \mu_d | G_n \rangle \langle G_n | \mu_e | U_f \rangle}{(\omega_a - \omega_{U_f})(\omega_a + \omega_b - \omega_{G_l})(\omega_a + \omega_b + \omega_c - \omega_{U_f})(\omega_a + \omega_b + \omega_c + \omega_d - \omega_{G_n})} \tag{13}$$

which shows that the 5PA absorption cross section can be expected to be proportional to the OPA transition moment scaled by the excited-state polarizability squared.

These expressions explain why we observe the orthogonality of the odd- and even-order multiphoton absorption cross sections. Furthermore, they also explain the strong parallelity of the odd- and even-order multiphoton absorption cross sections, as they are in all cases related to the lowest-order one- or two-photon absorption cross section, scaled by the energy difference between the excitation energy to the final state and the incoming laser frequencies, and scaled by (products of) excited-state polarizabilities. It is important to point out that this model does not allow quantitative predictions of higher-order MPA from OPA or TPA data but it gives a qualitative to semi-quantitative description of the behaviour of the different properties.

Multiphoton absorption cross sections can be enhanced through resonances, occurring when the frequency (or sums of frequencies) of the incoming laser light matches that of intermediate excited states (e.g. when $\omega_a = \omega_{G_j}/2 \approx \omega_{U_k}$ in the case of TPA). We note from the equations above that the frequency prefactor in the few-state models has the same poles as that of the TPA or 3PA processes, respectively. Thus, boosting TPA and 3PA
processes through near-resonance conditions will also boost the higher-order multiphoton absorption cross section.

Boosting a higher-order multiphoton absorption cross section selectively without a simultaneous increase in the lower-order multiphoton absorption cross section will thus only be possible if we can make the excited-state polarizability approach a pole for one of the frequency combinations of the incoming laser light. Consider for example the 4PA transition moment in Eq. 10. Whereas the TPA cross section, and thus also the 4PA cross section, will have a pole if there are intermediate states at half the energy of the excited state, the 4PA will be selectively enhanced if there is an excited state of ungerade symmetry at $3\omega_{\nu_f}/4$. Similar considerations can be made for the 5PA process, and we can selectively enhance the 5PA process if there are intermediate states of gerade symmetry with energy $2\omega_{\nu_f}/5$ and $4\omega_{\nu_f}/5$.

If we now return to the unexpected enhancement of the 4PA cross section of the $2B_{1g}$ (and the close-lying $1B_{1g}$ and $1A_g$ states) in PDNB, we note that there exists an intermediate $B_{2u}$ state of ungerade symmetry at approximately $3/4$ of the energy of these final states, thus creating a resonance in the excited-state polarizability in enhancement of the 4PA process relative to the TPA process.

To summarize our findings, we have presented the first 5PA cross section calculations at the density-functional level of theory using the CAM-B3LYP exchange–correlation functional for three centrosymmetric molecules. These calculations have shown that for molecules with an inversion centre, the selection rules for dipole-allowed transitions make the relative magnitude of all the even (odd) multiphoton absorption cross sections similar for different excited states. Assuming the validity of a few-state model for the states with the same symmetry as the final state of the multiphoton absorption process, we have shown that higher-order multiphoton absorption cross sections are proportional to the TPA (even-order absorption processes) or OPA (odd-order absorption processes) cross sections,
scaled by an energy denominator and powers of the polarizability of the final excited state.

Our analysis shows that for centrosymmetric molecules, excited states that display strong one- or two-photon absorption cross sections will also display strong multiphoton absorption cross sections. We have also shown how to selectively enhance the higher-order multiphoton absorption cross section by designing molecules with intermediate states that match selected frequency combinations for the frequency of the incoming light. We predict, for instance, a strong enhancement of 5PA processes by designing molecules with intermediate states of energy $2\omega U_f/5$ and $4\omega U_f/5$, as well as for 4PA as illustrated by our results calculated for the PDNB molecule. These results will be valuable guidelines for designing molecules with strong higher-order multiphoton absorption cross section.

**Computational details**

All multiphoton absorption calculations have been performed using a recursive open-ended response theory code\(^{19}\) which has recently been expanded to the treatment of single residues of response functions.\(^{20}\) This program is a submodule of the Dalton program.\(^{26}\) All calculations have been performed using the aug-cc-pVDZ basis set from the Dunning family of basis sets\(^{24}\) and the CAM-B3LYP density functional.\(^{23}\) In all calculations of \(n\)-photon absorption the energy of the involved photons was the excitation energy divided by \(n\).

The geometry of the para-dinitrobenzene molecule has been optimized using the cc-pVQZ basis set and the B3LYP-functional\(^{32,33}\) in Gaussian.\(^{34}\) The geometries of the di-aminoazobenzene and indigo molecules have been optimized using TURBOMOLE\(^{35}\) with the B3LYP functional and the TZVP basis set.\(^{36}\)

The rotational averaging of the calculated results has been performed following available literature\(^{37–39}\) and the calculation of the cross sections was done using an approach which has recently been generalized by two of us\(^{20}\) based on work by Peticolas.\(^{27}\) The detailed
equations for this are given in the supplementary information.

Acknowledgements

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Some more information about the rotational averaging and of the multiphoton absorption tensors and the conversion from atomic units to cgs unis can be found in the supporting information. This information is available free of charge via the Internet at http://pubs.acs.org/photonics.

References


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Using a few-state model sketched in the picture we describe the specific five-photon absorption behaviour of centrosymmetric molecules. This gives a deeper insight into the mechanisms of multiphoton absorption.

**Keywords**

- UV/VIS-Spectroscopy
- Response theory
- Quantum chemistry
- Ab-initio calculations
- Molecular modelling
- Non-linear optical properties
- Structure-activity relations