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Account / Revue

## Introduction to the intuitive engineering of homogeneous and isotropic two-photon absorbent molecular materials

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### Abstract

In this paper, we give practical instructions for linking explicitly the macroscopic two-photon absorption properties of any homogeneous and isotropic molecular material with the microscopic quantum structures of the corresponding molecules. This article is dedicated to a wide public. It is also separated from any consideration around the structural optimization of two-photon absorbers. The previously mentioned link is clearly established and the limitations of the corresponding mathematical expressions are underlined. These general expressions are then applied to the particular case of the three-level approximation, which is extensively used at the moment for the intuitive engineering of two-photon absorbers. **To cite this article: R. Fortrie, H. Chermette, C. R. Chimie (8) 2005.**

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### Résumé

Dans le présent article, nous exposons de manière pratique et concise comment établir explicitement le lien entre les propriétés macroscopiques d'absorption à deux photons d'un matériau moléculaire homogène et isotrope donné et les propriétés quantiques microscopiques des molécules composant ce matériau. Cet article de vulgarisation est destiné aux non-spécialistes et détaché de toute considération relative à l'optimisation structurale des molécules absorbant à deux photons. Le précédent lien est clairement établi et les limitations des expressions mathématiques correspondantes sont soulignées. Ces expressions générales sont, ensuite, appliquées au cas particulier du modèle à trois niveaux actuellement très utilisé dans l'ingénierie intuitive des molécules absorbant à deux photons. **Pour citer cet article : R. Fortrie, H. Chermette, C. R. Chimie (8) 2005.**

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## 1. Introduction

First predicted in 1931 by Göpper-Mayer [1] and then observed in 1961 by Kaiser and Garrett [2], two-photon absorption phenomena are of a great interest for new technologies [3,4]. They are, for example, applicable to optical memory devices [5], microfabrication [6], up-conversion lasing [7], photodynamic therapy [8], two-photon microscopy [9], optical power limiting [10]. However, their designing and understanding remains a challenge and many current researches in this area are now focused on molecular materials [11–28].

Building the complete theoretical sequence leading from the quantum properties of any molecular system up to the two-photon absorption properties of the resulting molecular material remains a difficult task. The required information has indeed to be collected from different sources, written with different notations and scientific languages such as chemical and physical. The knowledge of this theoretical chain is however greatly helpful for the intuitive engineering of new molecular materials and we describe it explicitly and completely in this paper. The limitations of the physical approximations are underlined and a special effort is done for minimizing and simplifying notations. Moreover, the general relations are subsequently applied to the particular case of the three-level model, which allows an intuitive engineering of two-photon absorbers.

This article is dedicated to a first contact with the subject for a wide public of chemists or physicists. It is, in particular, separated from any consideration around the structural optimization of two-photon absorbers. More information about this subject is available in the most recent of the previously cited articles.

## 2. Experimental section

We consider here a material composed with one or several two-photon absorbent molecular species homogeneously and isotropically diluted in a transparent, homogeneous and isotropic matrix, which can be a solvent, a sol-gel matrix, an amorphous glass, etc... This materials is assumed one-photon transparent, two-photon absorbent, not charged and without free currents. Moreover, no constant electric field or magnetic field is applied.

The experiment we model in this paper is the following one: a linearly polarized light beam is propagat-

ing through the molecular material of interest along a privileged direction represented by the (Oz) axis, and the evolution of its intensity in the course of transiting the material is studied.

## 3. Electric field and polarization

In the material, the electric field,  $\vec{E}(t, \vec{r})$ , time and space dependent, and the polarization,  $\vec{P}(t, \vec{r})$ , time and space dependent too, are considered by their Fourier transform,  $\vec{e}(\omega, \vec{r})$  and  $\vec{p}(\omega, \vec{r})$ , frequency and space dependent, as defined by relations (1) and (2) for the electric field and with an equivalent definition for the polarization.

$$\begin{aligned} \vec{E}(t, \vec{r}) &= \vec{e}(0, \vec{r}) \\ &+ \frac{1}{2} \int_0^{+\infty} [\vec{e}(\omega, \vec{r}) \exp(-i\omega t) \\ &+ \vec{e}(-\omega, \vec{r}) \exp(i\omega t)] d\omega \end{aligned} \quad (1)$$

$$\vec{e}(-\omega, \vec{r}) = [\vec{e}(\omega, \vec{r})]^* \quad (2)$$

Quantities  $\vec{e}(\omega, \vec{r})$  and  $\vec{p}(\omega, \vec{r})$ , called further ‘electric field’ and ‘polarization’, are complex numbers, in contrast with  $\vec{E}(t, \vec{r})$  and  $\vec{P}(t, \vec{r})$ , which are real numbers. These quantities are linked via a general propagation equation [29]. The profile of the intensity of the light beam in the course of transiting the sample should then be accessible by solving this equation. Such a resolution is however most of the time not possible and some assumptions have to be done.

## 4. Two-photon absorption

In the general case, the polarization depends on the electric field via a Taylor development as given in Eq. (3) [30,31], where  $i, j, k$  and  $l$  represent the vector coordinates and where  $\hat{\chi}^{(1)}$ ,  $\hat{\chi}^{(2)}$  and  $\hat{\chi}^{(3)}$  are the first, second and third-order polarizability tensors, also called respectively polarizability tensor for  $\hat{\chi}^{(1)}$  and first and second hyperpolarizability tensors for  $\hat{\chi}^{(2)}$  and  $\hat{\chi}^{(3)}$ , all frequency dependent.

$$p_i = \sum_j \chi_{ij}^{(1)} e_j + \sum_{j,k} \chi_{ijk}^{(2)} e_j e_k + \sum_{j,k,l} \chi_{ijkl}^{(3)} e_j e_k e_l + \dots \quad (3)$$

As explained in Section 2, we are here only concerned with homogeneous and isotropic materials, which are one-photon transparent and two-photon absorbent, and the light beam of interest has been assumed linearly polarized. This strongly simplifies the expressions of hyperpolarizabilities and relation (4) is extracted, where  $\bar{\chi}^{(1)}$  is a real number and  $\bar{\chi}^{(3)}$  a complex one [31].

$$\vec{p} = (\bar{\chi}^{(1)} + \bar{\chi}^{(3)}|\vec{e}|^2) \vec{e} \quad (4)$$

However, even if the expression of the polarization as a function of the electric field appears less complex in Eq. (4), solving the propagation equation for any light beam remains a difficult task. Moreover, the result strongly depends on the time and space shapes of the light beam and no exhaustive study is to be performed here, many precise examples can be found in Sutherland's book [31]. But, whatever is the shape of the light beam, the two-photon absorption coefficient  $a_2$  can be defined for the material via the local relations (5) and (6).

$$\frac{dI}{dz} = -a_2 I^2 \quad (5)$$

$$a_2 = \frac{2\mu_0\omega}{\varepsilon_0 + \bar{\chi}^{(1)}} \text{Im}(\bar{\chi}^{(3)}) \quad (6)$$

Experimentally, if the material of interest consists only of a single species of two-photon absorbent molecule diluted in a transparent matrix with  $N$  as its molecular concentration, the value of interest is the two-photon absorption cross-section of this molecular compounds  $\sigma_{TPA}$  at frequency  $\omega$ , which is defined by relation (7) [31].

$$\sigma_{TPA} = \frac{\hbar\omega}{N} a_2 \quad (7)$$

In Eq. (7),  $\hbar$  represents the reduced Planck constant, which is equal to the Planck constant  $h$  divided by  $2\pi$ . The current engineering of two-photon absorbent molecular materials is mainly dedicated to designing and improving this two-photon absorption cross-section [25,26,32]. Then, at this point, the challenge consists in the calculation of the macroscopic values  $\bar{\chi}^{(1)}$  and  $\bar{\chi}^{(3)}$  using the microscopic quantum structures of the molecular compounds involved in the molecular material.

## 5. Local-field approximation

Concerning the electric field and the polarization, which appear in previous equations, both are mesoscopic average values. But the electric field felt by each molecule is different from this mesoscopic field. It consists indeed in a superposition of the mesoscopic electric field itself with the electric fields produced by the neighbor molecules, which are themselves induced by the local electric fields that these molecules feel. One of the methods for considering this effect has been proposed by Clausius and Mossotti or Lorenz and Lorentz [30,33]. It consists in digging a spherical cavity in the material, which is here considered continuous, and in calculating the electric field in this cavity. This field is assumed to be the local electric field felt by any molecule put inside the cavity. Of course, molecules are not spherical and more complexes surfaces should normally be chosen, which is hardly undone at the moment. Another approach would consist in including in this spherical hole a molecule gathered with several solvent molecules to reach the shape of the cavity. Anyway, in the framework of this spherical cavity approximation, called "local field approximation", it is shown that, even for a non-linear media, the relations (8) and (9) are verified.

$$\vec{e}_{\text{local}} = \vec{e}_{\text{meso}} + \frac{\vec{p}_{\text{meso}}}{3\varepsilon_0} \quad (8)$$

$$\vec{p}_{\text{meso}} = \sum_{\text{molecules}} N_{\text{molecule}} \vec{p}_{\text{molecule}} \quad (9)$$

## 6. From the molecule up to the material

Like the polarization of the macroscopic material, the polarization of an isolated molecular system can be defined as a tensorial Taylor development, as given in Eq. (10) [4,30].

$$p_i = \sum_j \alpha_{ij} e_j + \sum_{j,k} \beta_{ijk} e_j e_k + \sum_{j,k,l} \gamma_{ijkl} e_j e_k e_l + \dots \quad (10)$$

It has to be underlined that an alternative definition given by relation (10') can also be employed [34] but will not be used within this article. Both conventions are widely used, so that it is important to recall the selected choice when numerical values are reported.

$$p_i = \frac{1}{2!} \sum_j \alpha_{ij} e_j + \frac{1}{3!} \sum_{j,k} \beta_{ijk} e_j e_k + \frac{1}{4!} \sum_{j,k,l} \gamma_{ijkl} e_j e_k e_l + \dots \quad (10')$$

The calculation of these polarizabilities can be achieved via the sum-over-states method [35]. Performing such a calculation requires the rovibronic eigenstates  $|m\rangle$  ( $m$  from 0 to  $+\infty$ ) of this molecular system to be known via their energies,  $E_m$ , and via the electric dipole moments between them,  $\langle m|\vec{\mu}|\bar{n}\rangle$ .

$$\alpha_{ij}(-\omega; \omega) = \frac{2}{\hbar} \sum_{m=1}^{+\infty} \frac{\omega_{0m}}{\omega_{0m}^2 - \omega^2} \langle 0|\mu_i|m\rangle \langle m|\mu_j|0\rangle \quad (11)$$

$$\text{Im} [\gamma_{ijkl}(-\omega; \omega, \omega, -\omega)] = \frac{\Gamma_{0n}}{4\hbar^3} I_{ijkl} \left\{ \sum_{m=1}^{+\infty} \sum_{p=1}^{+\infty} \frac{\langle 0|\mu_i|m\rangle \langle m|\bar{\mu}_j|n\rangle \langle n|\bar{\mu}_k|p\rangle \langle p|\mu_l|0\rangle}{(\omega_{0m} - \omega)(\omega_{0p} - \omega) \left[ (\omega_{0n} - 2\omega)^2 + \frac{\Gamma_{0n}^2}{4} \right]} \right\} \quad (12)$$

where  $\omega_{0m}$  represents  $(E_m - E_0)/\hbar$ ,  $I_{ijkl}$  represents the average operator over all permutations of indexes  $i, j, k$  and  $l$ , and where  $\langle m|\bar{\mu}_i|n\rangle$  represents  $\langle m|\mu_i|n\rangle - \langle 0|\mu_i|0\rangle \langle mn\rangle$ . The  $\Gamma_{0n}$  frequency artificially introduces the life-time of state  $|n\rangle$ , this means that the energy difference  $\omega_{0n}$  is replaced by  $\omega_{0n} - i\Gamma_{0n}/2$ .

Modeling the excited states of a molecular system is difficult and remains a challenge for theoretical chemistry. No discussion is then made here on this particular point. Many computational methods are available and a lot of literature can be found elsewhere about this particular subject [20–23,27,36]. It is here assumed that the excited states of the molecular systems of interest are known.

Let us now consider a molecular mixture, which consists in  $Q$  species, indexed with  $q$  from 1 to  $Q$ , each one with  $N_q$  as a molecular concentration. If the microscopic polarizability tensors of these molecular compounds are known and if the local field approximation described above is used, then the macroscopic polarizability tensors can be calculated. The expressions of  $\bar{\chi}^{(1)}$  and  $\bar{\chi}^{(3)}$  are given by relations (13) and (14), using the notations (15) and (16).

$$\bar{\chi}^{(1)} = \frac{\sum_{q=1}^Q N_q \bar{\alpha}_q}{1 - \frac{1}{3} \sum_{q=1}^Q N_q \bar{\alpha}_q} \quad (13)$$

For the particular case of a frequency  $\omega$  far from any one-photon absorption and close to the two-photon absorption from state  $|0\rangle$  to state  $|n\rangle$ , the expressions of the  $\hat{\alpha}$  tensor and of the imaginary part of the  $\hat{\gamma}$  tensor are approximated with relations (11) and (12). In these expressions, the natural widths  $\Gamma_{0m}$  and  $\Gamma_{0p}$  of the states other than  $|n\rangle$  are suppressed since  $\omega$  is assumed far from any one-photon absorption.

$$\bar{\chi}^{(3)} = \frac{\sum_{q=1}^Q N_q \bar{\gamma}_q}{\left[ 1 - \frac{1}{3} \sum_{q=1}^Q N_q \bar{\alpha}_q \right]^4} \quad (14)$$

$$\bar{\alpha} = \frac{1}{3} \sum_i \alpha_{ii} \quad (15)$$

$$\bar{\gamma} = \frac{1}{15} \sum_{i,j} \gamma_{ijij} + \gamma_{ijji} + \gamma_{ijij} \quad (16)$$

For the particular case of a single two-photon absorbent species diluted in a transparent matrix, these expressions lead to (17) and (18), where  $n_s$  represent the refraction index of the transparent matrix. Note that appears here the Lorenz–Lorentz correction factor [30,33].

$$\bar{\chi}^{(1)} = \varepsilon_0 (n_s^2 - 1) \quad (17)$$

$$\bar{\chi}^{(3)} = \left( \frac{n_s^2 + 2}{3} \right)^4 N \bar{\gamma} \quad (18)$$

## 7. Experiment and modeling

Thanks to expressions (6), (7), (17) and (18), it is now possible to express the macroscopic two-photon absorption cross-section of a single molecular species

diluted in a transparent matrix as a function of the microscopic third-order hyperpolarizability of this molecular species, as shown by relation (19).

$$\sigma_{\text{TPA}} = \frac{2\mu_0 \hbar \omega^2}{\varepsilon_0 n_S^2} \left( \frac{n_S^2 + 2}{3} \right)^4 \text{Im}(\bar{\gamma}) \quad (19)$$

The expression of  $\bar{\gamma}$  as a function of the quantum structure of the molecular system is given by relation (12). However, the existence of the arbitrary value  $\Gamma_{0n}$  in this relation makes irrelevant any direct comparison be-

$$\int_{\frac{\omega_{0n}}{2}}^{\omega} \frac{\sigma_{\text{TPA}}}{\omega} d\omega = \frac{\pi \mu_0 \omega_{0n}}{60 \varepsilon_0 n_S^2 \hbar^2} \left( \frac{n_S^2 + 2}{3} \right)^4 \quad (20)$$

$$\sum_{m=1}^{+\infty} \sum_{p=1}^{+\infty} \frac{(\vec{\mu}_{0m} \cdot \vec{\mu}_{mn}) (\vec{\mu}_{np} \cdot \vec{\mu}_{p0}) + (\vec{\mu}_{0m} \cdot \vec{\mu}_{np}) (\vec{\mu}_{mn} \cdot \vec{\mu}_{p0}) + (\vec{\mu}_{0m} \cdot \vec{\mu}_{p0}) (\vec{\mu}_{mn} \cdot \vec{\mu}_{np})}{\left( \omega_{0m} - \frac{\omega_{0n}}{2} \right) \left( \omega_{0p} - \frac{\omega_{0n}}{2} \right)}$$

where  $|m\rangle$ ,  $|p\rangle$  and  $|n\rangle$  are rovibronic states and with  $\vec{\mu}_{mn}$  representing  $\vec{\mu}_{mn} - \vec{\mu}_{00} \delta_{mn}$ , with  $\delta_{mn}$  equal to 1 if  $m = n$  and to 0 otherwise. In many cases, the rovibrational parts of states  $|m\rangle$ ,  $|p\rangle$  and  $|n\rangle$  can be simplified and the relation (20) can be transformed into another expression, exactly similar, but for electronic states only [38].

### 8. Three-level model and molecular engineering

As can be presumed by looking at relation (20), linking the quantum structure of the molecular system of interest and its two-photon absorption cross-section is not intuitive. Therefore has been created the three-level model [13,14,39], which is extensively used within the optimization of two-photon absorbers. This model deals only with electronic states and assumes that the description of the molecular system can be restricted to only three eigenstates with  $\hbar\omega_{01}$  larger than  $\hbar\omega_{02}/2$ . The two-photon absorption of interest corresponds then to the transition from the fundamental to the second excited state. In the framework of this general three-level model, two particular cases are of a greater interest:

- No one-photon absorption from the fundamental to the second excited state is allowed, which means that  $\vec{\mu}_{02}$  is null, this leads to the relation (21). This is

verified, for example, in centro-symmetric compounds, for which, moreover,  $\vec{\mu}_{00}$  is also null [14,24].

$$\int_{\frac{\omega_{02}}{2}}^{\omega} \frac{\sigma_{\text{TPA}}}{\omega} d\omega = \frac{\pi \mu_0 \omega_{02}}{60 \varepsilon_0 n_S^2 \hbar^2} \left( \frac{n_S^2 + 2}{3} \right)^4 \quad (21)$$

$$\cdot \frac{2 \left[ \vec{\mu}_{01} \cdot \vec{\mu}_{12} \right]^2 + \vec{\mu}_{01}^2 \cdot \vec{\mu}_{12}^2}{\left( \omega_{01} - \frac{\omega_{02}}{2} \right)^2}$$

even if  $\vec{\mu}_{02}$  is non-null.

- No one-photon absorption from the fundamental to the first excited state is allowed, which means that  $\vec{\mu}_{01}$  is null, this leads to the relation (22). This restricts the three-level model to a two-level model and can represent, for example, a charge-transfer induced two-photon absorption [13,14].

$$\int_{\frac{\omega_{02}}{2}}^{\omega} \frac{\sigma_{\text{TPA}}}{\omega} d\omega = \frac{\pi \mu_0}{15 \varepsilon_0 n_S^2 \hbar^2 \omega_{02}} \left( \frac{n_S^2 + 2}{3} \right)^4 \quad (22)$$

$$\left\{ 2 \left[ \vec{\mu}_{02} \cdot (\vec{\mu}_{22} - \vec{\mu}_{00}) \right]^2 + \vec{\mu}_{02}^2 \cdot (\vec{\mu}_{22} - \vec{\mu}_{00})^2 \right\}$$

These two simple relations (21) and (22) are the one of interest for performing two-photon absorption molecu-

lar engineering ‘by hands’, which means without requiring heavy molecular quantum modeling.

It has to be noted that current researches within the area of molecular structure optimization for two-photon absorption are now mainly focused on highly symmetric ( $C_{2v}$ ,  $C_3$ ,  $D_{3h}$ ,  $D_3$ ,  $T_d$  groups, for example) two- and three-dimensional compounds [26,27,32]. Most of these new compounds, on account of their symmetries, can not be treated via the previously described simple three-level model.

## 9. Conclusion

In conclusion, the two-photon absorption cross-section of a single two-photon absorbent molecular species homogeneously and isotropically diluted in a homogeneous, isotropic and transparent matrix, lightened with a linearly polarized mono-directional light beam, in the framework of the local field approximation, can be related to the quantum structure of the molecular compound via relation (20).

Moreover, in the framework of the three-level approximation, and for the two particular cases described in the last section, the expression (20) can be reduced into relations (21) and (22).

In summary, these relations, which are widely used by chemists for the optimization of two-photon absorbers, but whose validity is limited, allow an intuitive and qualitative engineering of two-photon absorbent molecular compounds, whatever is their symmetry.

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