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# Three levels of propagation of the Four-wave mixing signal

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ABSTRACT

In this work, we analyze different levels of propagation of the Four-wave mixing signal in a strongly driven two-level system when the stochastic effects of the thermal bath, are considered. First approximation level, given by an analytical solution valid only for constant pump intensity along the optical path; a second approximation level as an analytical solution valid for a lineal variation of the pump intensity, and finally, a third level as numerical solution, which represent the exact case. In all cases, high dependence of the nonlinear propagation with the chemical concentration, stochastic noise parameters, relaxation times, are studied.

## Introduction

The study of the interaction between two-level systems and electromagnetic fields has been a very important subject in optics due its applications and usability to explain complex nonlinear phenomena. Under this scheme, in the analysis of the propagation of an electromagnetic signal some phenomena such as the attenuation or amplification of the beam, and the dispersion processes, can be better treated associated with random variables. Particular attention in this framework can be paid to those phenomena that lead to the generation of phonons, and which effects are explained by the notion of white and colored noise correlation functions, and/or Markov processes [1].

In view of the importance of gaining a better understanding in these topics for the propagation of electromagnetic fields in a nonlinear optical medium, we studied the different conditions under which the signal strength of Four-wave mixing FWM is modified by the always occurring effects of absorption and scattering themselves. In this work, the dynamics of such systems are described by the Optical Conventional Bloch equations (OCBE). Still, the strong interaction of the propagating wave with a medium can be subject to multiple collisions and the microscopic nature of the problem becomes complicated [2–8]. To formulate a solution it is necessary to introduce stochastic considerations. In this work, and under this framework, we assume that the system-solvent interactions induce random shifts in the Bohr frequency and its manifestation should correspond to the broadening of the upper level [9]. Further, the putative effects over the propagation of the fields along the optical path, are analyzed. In this paper, two approximate analytical models for the propagation of the FWM signal, and a numerical approximation to a third one, are discussed. The last case is conveniently associated with a transcendental equation. The consistency of the analytical models as dependent on the corresponding approximations of the limiting cases they each describe as compared to the numerical approximation are reviewed. The capability to demonstrate similar correct descriptions of the problem, were established within a 10% tolerance with respect to the more complete numerical model for the analytical solutions, evaluating in this way the extent of applicability of the underlying parameters and particular considerations of each model.

The effect of the medium is modeled here with the aid of a stochastic broadening of the molecular energy levels. All the approaches described above are valid in the region $4S/T_2^2 \ll 1$ (S: Saturation parameter, $T_2$ Transversal relaxation time). Since water solutions of Malachite Green chloride satisfy this condition, this system is a good candidate for testing the effects discussed in this work. For this, having analytic expressions for the propagation of the fields allows us understanding the important photonic effects that take place in the interaction. These expressions also help to evaluate which approximations are better suited to study the propagation of the field under different putative experimental conditions.

Various works in the same line of research related to the propagation of electromagnetic fields along the optical path have been performed previously. Boyd et al. [10] studied the effect of the propagation of fields in a strongly coupled two-state system, developing a model in which the pump intensity is strictly constant along the optical path. Reif

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et al. [11] developed a propagation model considering three levels of approximation, but not necessarily making the pump beam constant. Both models are totally deterministic. Paz and Recamier [12] introduced a propagation model to analyze two analytical solutions for the study of the propagation of the FWM signal in a strongly driven two-level system, when the stochastic effects of the solvent are explicitly considered. In that work, the pump field was treated at all orders but the probe and signal fields at first order only.

In contrast to this, in the present work, the probe beam is treated to the second order thus exploring important effects at this level. Thus, considering perturbationally the probe beam, photonic processes that generate energy at the frequency of the pump-beam are extracted. Unlike previous models, the pump beam was attenuated along the optical path and its intensity was never restored.

As demonstrated in this article, most important in this regard for the description of the signal propagation, are the saturation parameter and the concentration of the analyte. The most relevant aspect of this work is its contribution to the understanding of the putative generation of nonlinear multiphotonic processes induced by the probe beam in the FWM scheme.

## Theoretical considerations

In this work, we describe the time-dependent process of interaction of molecular systems with a total external electromagnetic field (radiative process) and with a thermal bath (non-radiative process) using the Liouville-Von Newmann treatment in the semiclassical approximation. The reduced density matrix equation describing the dynamics behavior, is given by:

$$\partial_t \hat{\rho} = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}] - \hat{\Gamma}\hat{\rho}, \tag{1}$$

where $\hat{H} = \hat{H}_0 + \hat{V}$, with $\hat{H}_0$ the Hamiltonian for the isolated system and $\hat{V}$ the perturbation, given by $\hat{V} = -\vec{\mu}.\vec{E}$; $\hat{\Gamma}$ represents the relaxation matrix that includes the relaxation rates between two-states considered $1/T_1$ and for the induces coherences $1/T_2$. The decay rate of the excited state population and the dephasing rate of the optical transition must also be included in the analysis whenever the frequency $\omega_1$ becomes comparable to or smaller than this rates (decay of the levels, $T_1$ effects, and of optical transitions, $T_2$ effects). In this work, we use the Optical Stochstic Bloch equations (OSBE) to model the dynamical behavior of the system, which is given by [13]:

$$\partial_t \rho(t) = M_\xi(t)\rho(t) + R, \tag{2}$$

where $M_\xi(t)$ and $R$ are the radiative and non-radiative matrices, respectively. The density matrix for the two-level system, is defined as:

$$\rho(t) = \begin{pmatrix} \rho_{ba}(t) \\ \rho_{ab}(t) \\ \rho_D(t) \end{pmatrix}, \tag{2.a}$$

$M_\xi(t)$ is a matrix containing strictly all of the matter–radiation interaction details and is defined as:

$$M_\xi(t) = \begin{pmatrix} -\xi_t & 0 & i\Omega \\ 0 & -\xi_t^* & -i\Omega^* \\ 2i\Omega^* & -2i\Omega & -1/T_1 \end{pmatrix}, \tag{2.b}$$

and, $R$ is defined as the relaxation matrix associated with the equilibrium condition, given by:

$$R = \begin{pmatrix} 0 \\ 0 \\ \rho_D^{(0)}/T_1 \end{pmatrix}, \tag{2.c}$$

We define further the equilibrium effective population $\rho_D^{(0)} \equiv \rho_{gg}^{(0)} - \rho_{ee}^{(0)}$, and the Rabi frequency by the scalar product $\Omega = \vec{\mu}_{ba}.\vec{E}(t)/\hbar$, which defines the intensity of the coupling between matter and radiation, connected only to the transition dipole moments $\vec{\mu}_{ba}$, (disregarding in this case, permanent dipole moments). Here, is defined $\vec{E} = \vec{E}_1 + \vec{E}_2$, with $\vec{E}_j(t) = \vec{E}_{j0}\exp(i\vec{k}_j.\vec{r} - \omega_j t)$ $(j = 1,2)$, and $\xi_t = i\xi(t) + T_2^{-1}$; $T_1$ and $T_2$ are defined as longitudinal and transversal relaxation times, respectively. In this methodology, we consider that the system-solvent interactions induce random shifts in the Bohr frequency, given by $\xi(t) = \omega_0 + \sigma(t)$, where $\omega_0$ is the Bohr-frequency for the isolated two-level molecular system; $\sigma(t)$ integrates all the stochasticity of the problem. Our study is localized in the Four-wave mixing FWM spectroscopy, where the most general process involves the interaction of three laser fields with wave vector $\vec{k}_1$, $\vec{k}_2$ and $\vec{k}_3$ and frequencies $\omega_1$, $\omega_2$ and $\omega_3$, respectively, with a nonlinear medium. Here, $\vec{k}_S$ and $\omega_S$ are given by any linear combination of the applied wave-vectors and frequencies. Solving Eq. (2) for a two-level molecular system, the Fourier components of the coherences at the indicated frequencies, are given by:

$$\rho_{ba}(\omega_m) = \{i\Omega_m + i\lambda_\xi[\Omega_1\delta_{m,3} + \Omega_2\delta_{m,1}] + i\lambda_\xi^*[\Omega_1\delta_{m,2} + \Omega_3\delta_{m,1}]\}\frac{\rho_D^{dc}}{L_{\xi,m}}, \tag{3}$$

with $m = 1, 2, 3$ and where $\lambda_\xi$ is given by:

$$\lambda_\xi = -\frac{2}{|J_2|^2}(\Omega_1\Omega_2^*J_1 + \Omega_1^*\Omega_3 \upsilon_{3,-1}J_2 - \Omega_1\Omega_3^*J_3), \tag{4}$$

where we have defined:

$$J_1 = \Gamma_1^*(\Delta_{12}) + 2\,|\Omega_1|^2\upsilon_{1,-2}\upsilon_{2,-3}, \tag{4.a}$$

$$J_2 = \Gamma_1^*(\Delta_{12}) + 2\,|\Omega_1|^2\upsilon_{2,-3} + \frac{2\,|\Omega_2|^2}{L_{\xi,1}^*}, \tag{4.b}$$

$$J_3 = 2\,|\Omega_2|^2\upsilon_{1,-1}\upsilon_{1,-3}. \tag{4.c}$$

With $\Gamma_1(\Delta_{12}) = 1/T_1 - i\Delta_{12}$; $\upsilon_{n,-m} = \frac{(2T_2^{-1}) + i\Delta_{n,m}}{L_{\xi,n}L_{\xi,m}^*}$ where $\Delta_{nm} = \omega_n - \omega_m$ (for the indicated values of $n$ and $m$). The lorentzian $L_{\xi,m} \equiv L_{\xi,2n+1} = T_2^{-1} + i[\xi(t) - (\omega_1 + n\Delta_{12})]$, and where considered values of $n = 0, -1, 1$ for pump, probe and FWM signal, respectively. For simplicity, we define $L_{\xi,-1} \equiv L_{\xi,2}$ for the probe. The zero-frequency Fourier component is given by:

$$\rho_D^{dc} = \frac{\rho_D^{(0)}}{(1 - f_\xi) + \frac{4S_1}{T_2^2\,|L_{\xi,1}|^2}}. \tag{5}$$

$S_1 = |\Omega_1|^2T_1T_2$ is defined as the saturation parameter, associated to pump beam. Next, a perturbative method at all orders in the pump- beam, second order in the probe-beam, and at first order in the generated FWM signal, is used to solve the equations. The function $f_\xi$ is given by:

$$f_\xi = 4T_1\left[|\Omega_1|^2|\Omega_2|^2\left(\frac{\upsilon_{1,-2}\upsilon_{1,-2}}{J_2^*} + \frac{\upsilon_{2,-1}\upsilon_{2,-1}}{J_2}\right) + (\Omega_1^*)^2\Omega_2\Omega_3\left(\frac{\upsilon_{2,-1}}{L_{\xi,1}J_2} + \frac{\upsilon_{3,-1}\upsilon_{1,-2}}{J_2}\right)\right]. \tag{6}$$

Given that the coherences, Eq. (3), are dependent of the stochastic variable $\xi(t)$ (through of $L_{\xi,j}$), it is necessary to establish an average over all realizations of the random variables as $\langle\rho_{ba}(\omega_k)\rangle_\xi$. In order to carry out the mentioned above averages, Van Kampen [14] has proposed a method where he formally solves the stochastic differential equation assuming it to be deterministic and then takes an average over the realizations of the stochastic variable. A different approach consists in taking the same average before solving the Optical Bloch equations OBE. In the latter case, the set of differential equations obtained can be described as an Ornstein-Uhlenbeck process (OUP), the set of equations solved and one obtains an equation for the average of $\rho_{ba}(\omega_k)$. In the present work, we solve OBE as if they were deterministic and then, acknowledging the fact that $\rho_{ba}(\omega_k)$ depends upon the realizations of