

Electromagnetic fields effects on the optical properties in a two-level system immersed in a thermal bath: stochastic considerations

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ABSTRACT

We have derived analytical solutions of the optical stochastic Bloch equations (OSBE) in frequency regime, considering a two level system interacting with a thermal reservoir which Bohr frequency is modeled as a stochastic variable. A parallel treatment is made when choosing different distributions of frequencies in the calculus of the average. We have found expressions for non-linear optical properties (absorptive and dispersive process) in terms of the field amplitude and thermal noise parameters.

Keywords: thermal bath, stochastic process, two-level system

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1. INTRODUCTION

Two-level schemes, with bare states in the presence of an electromagnetic field, have been widely studied, a long time ago, [1-4] but only recently the characterization of a system through the measurement of dissipation times T_1 and T_2 and the stochastic modeling of the atomic frequency have been done [5,6].

The effects of include stochastic frequency into the optical conventional Bloch equations (OCBE), have been also studied in the literature [6-8] and the optical stochastic Bloch equations (OSBE) are derived, which characterizes the dynamics of the system in the presence of frequency fluctuations; Wódkiewicks and Eberly [9] show how the OCBE are modified in the presence of thermal noise that induces stochastic modulation of the molecular frequency.

In previous works [7], the absorption and the refractive index have been calculated for a diluted water solution of solute molecules taking into account the optical susceptibilities up to third order in the external field. In this article is also described the solute molecules as two-level systems and the solvent plays the role of a heat reservoir providing the relaxation mechanisms.

This paper is a generalization of previous results [5, 10], taking into account the simultaneous effects of the noise intensity, its relaxation rate and the frequency of the perturbed field on the optical properties mentioned above, when saturations effects of the field are included. Expressions for these non linear optical properties are obtained, in terms of the thermal noise parameters, the relaxation times and the field amplitude. To do that we consider that the molecular frequency shifts induced by the medium is represented as: $\xi(t) = \omega_0 + \sigma(t)$, where ω_0 is the non-fluctuating atomic frequency of the isolated system and $\sigma(t)$ represents the stochastic fluctuation of the frequency around ω_0 . Finally we compare our result of considering a Lorentzian distribution of Bohr frequencies with an Ornstein-Uhlenbeck process [5].

2. THEORY

In the presence of an incident electromagnetic field, the well-know OCBE describes the evolution of a two-level system defined by the states $|a\rangle$ and $|b\rangle$ and is given by the following equations in the density-matrix formalism [3,4]:

$$\dot{\rho}_D(t) = -\frac{2i}{\hbar} [H_{ab}\rho_{ba}(t) - \rho_{ab}(t)H_{ba}] - \frac{1}{T_1}(\rho_D(t) - \rho_D^{eq}) \quad (1)$$

$$\dot{\rho}_{ba}(t) = -(i\omega_o + \frac{1}{T_2})\rho_{ba}(t) - \frac{i}{\hbar}H_{ba}\rho_D(t) \quad (2)$$

$$\dot{\rho}_{ba}^*(t) = \dot{\rho}_{ab}(t) \quad (3)$$

where $\rho_D(t) = \rho_{aa}(t) - \rho_{bb}(t)$, is the difference in state populations and the superscript “eq” in ρ_D^{eq} denotes the equilibrium value in the absence of radiation.

The interaction Hamiltonian H_{ba} is in the dipole approximation and is given by: $H_{ba} = -\vec{\mu}_{ba} \cdot \vec{E}(t)$, where the field is defined by: $\vec{E}(t) = [\vec{E}(\omega) \exp(-i\omega t) + \vec{E}^*(\omega) \exp(i\omega t)]$ and $\vec{E}(\omega) = E_0 \exp[i(\vec{k} \cdot \vec{r} + \phi)]$ represents the Fourier component of the electromagnetic field that oscillates at frequency ω with a phase angle ϕ , and μ_{ba} is the two-level dipole transition moment; T_2 and T_1 are the transversal and longitudinal relaxation times respectively. By introducing the stochastic frequency ξ , we obtain the OSBE, which have been solved in stationary state through an expansion in Fourier series, and after some algebraic manipulations we obtain:

$$\rho_{ba}(\omega) = \frac{i\Omega \rho_D^{dc}}{D_\xi} \quad (4)$$

$$\rho_D^{\text{dc}} = \frac{T_2^2 |D_\xi|^2 \rho_D^0}{T_2^2 |D_\xi|^2 + 4S} \quad (5)$$

where $S = T_1 T_2 |\Omega|^2$ is defined as the system saturation parameter, ρ_D^{dc} is the direct current term of the population difference component that oscillates at zero frequency, $\Omega = \frac{\bar{\mu}_{ba} \cdot \bar{E}}{\hbar}$ is the Raby frequency for the incident field $E(\omega)$ and $D_\xi = T_2^{-1} - i(\omega - \xi)$ is the resonant term that includes the stochastic molecular frequency ξ .

If we substitute (5) in (4) we obtain an expression for the non-diagonal matrix element that depends of various system parameters like saturation, field strength, relaxation times, etc.

$$\rho_{ba}(\omega) = \frac{i\Omega \left(T_2^2 |D_\xi|^2 \right) \rho_D^0}{D_\xi \left(T_2^2 |D_\xi|^2 + 4S \right)} = \frac{i\Omega \rho_D^0}{D_\xi \left[1 + \frac{4S}{T_2^2 |D_\xi|^2} \right]} \quad (6)$$

Now we can make a variable change of the type: $X = \frac{4S}{T_2^2 |D_\xi|^2}$ and then make an expansion in power series like:

$$\frac{1}{1+X} = 1 - X + X^2 - X^3 + \dots = \sum_{n=0}^{\infty} (-1)^n X^n \quad (7)$$

Finally the steady state solution for ρ_{ba} in the rotating-wave approximation (RWA) at all orders in the field is:

$$\rho_{ba}(\omega) = -i\Omega \rho_D^{eq} \sum_{n=0}^{\infty} (-1)^n \left(\frac{4S}{T_2^2} \right)^n \left(\frac{1}{D_\xi^{(n)}} \right) \quad (8)$$

with $D_\xi^{(n)} = |D_\xi|^{2n+1}$.

2.1. Calculation of average

The ensemble averages values in this equation are defined in the customary way by:

$$\langle x \rangle_\xi = \int_{-\infty}^{\infty} x_\xi P(\xi) d\xi \quad (9)$$

where $P(\xi)$ is the probability density of events around its average value ω_0 and $\langle x \rangle_\xi$ the averaged value is made over all the realizations of the stochastic variables. Two cases will be considered: Gaussian and Lorentzian distribution of molecular frequencies.

2.1.1 First case: Gaussian distribution of molecular frequencies

For this case $P(\xi)$ is taken as:

$$P(\xi) = \frac{1}{\sqrt{2\pi\gamma\tau}} \exp\left(-\frac{(\xi - \omega_0)^2}{2\gamma\tau}\right) \quad (10)$$

where γ is the intensity of the noise and τ is the decaying rate of the exponential correlation function for an Ornstein-Uhlenbeck Process (colored noise).

In the rest of the paper we'll use the notation: $\frac{1}{D_\xi^{(n)}} = T_M^{(n)}$ to refer to the resonant term of “nth order”

of the sum (8) that follow a “M” distribution of molecular frequencies, so $T_G^{(0)}$ refers to the zero order resonant term, using a Gaussian distribution of molecular frequencies.

Taking the average of (8) according to (9), and expressing the resonant term as the sum of their Real and Imaginary parts, $\text{Re}(T_G^{(0)})$, $\text{Im}(T_G^{(0)})$ we can obtain the averaged density matrix element $\langle \rho_{ba} \rangle_\xi$:

$$\langle \rho_{ba}(\omega) \rangle_\xi = -i\Omega \rho_D^{\text{eq}} \left[\sum_{n=0}^{\infty} (-1)^n \left(\frac{4S}{T_2^2} \right)^n \langle \text{Re}(T_G^{(n)}) \rangle_\xi + \sum_{n=0}^{\infty} (-1)^n \left(\frac{4S}{T_2^2} \right)^n \langle \text{Im}(T_G^{(n)}) \rangle_\xi \right] \quad (11)$$

Though to the equation (11) is possible to express the coherence function in terms of the saturation parameter S, the parameters of the bath γ and τ and the transversal relaxation time T_2 .

Following the procedure shown by Paz J et al. [5] we get:

$$\langle \text{Re}(T_G^{(0)}) \rangle_\xi = \frac{1}{\sqrt{\gamma\tau}} \text{Re}[Z_o] \quad (12.a)$$

$$\langle \text{Im}(T_G^{(0)}) \rangle_\xi = \frac{1}{\sqrt{\gamma\tau}} \text{Im}[Z_o] \quad (12.b)$$

$$\text{with } Z_o = \left(1 - \text{erf} \left(\frac{T_2^{-1} - i\Delta}{\sqrt{2\gamma\tau}} \right) \right) \exp \left(\frac{(T_2^{-1} - i\Delta)^2}{2\gamma\tau} \right)$$

2.1.2 Second case: Lorentzian distribution of molecular frequencies

For this case $P(\xi)$ is taken as:
$$P(\xi) = \frac{\delta/\pi}{\delta^2 + (\xi - \omega_0)^2} \quad (13)$$

here δ is the HWHM of the inhomogeneous distribution. Taking the average of (12) according to (13), making the change of variables: $X = \xi - \omega_0$ and $\Delta = \omega - \omega_0$, and separating the Real and Imaginary parts, $\text{Re}(T_L^{(0)})$, $\text{Im}(T_L^{(0)})$ we obtain the average of the coherence ρ_{ba} where $T_L^{(0)}$ correspond to the term with $n = 0$ and Lorentzian distribution of frequencies in the expansion (8):

$$\left\langle \text{Re}(T_L^{(0)}) \right\rangle_{\xi} = \frac{\gamma}{\pi} \frac{1}{T_2} \int_{-\infty}^{\infty} \delta(X - \Delta) \delta'(X) dX \quad (14.a)$$

$$\left\langle \text{Im}(T_L^{(0)}) \right\rangle_{\xi} = \frac{\gamma}{\pi} \frac{1}{T_2} \int_{-\infty}^{\infty} (X - \Delta) \delta(X - \Delta) \delta'(X) dX \quad (14.b)$$

where $\delta(X - \Delta) = \frac{1}{(X - \Delta)^2 + \left(\frac{1}{T_2}\right)^2}$ and $\delta'(X) = \frac{1}{X^2 + \gamma^2}$

This integrals differs considerably of their equivalent Gaussians (see Paz J et al in [5]). We can observe that represent the area under the superposition of two Lorentzian curves displaced Δ unities and which band width are represented for the relaxation times: $\frac{1}{T_2}$ and γ .

Making use of the convolution theorem, we apply the direct Fourier Transforms and then we solve analytically the equation resulted of applying the Inverse Fourier Transformation to obtain an expression equivalent to (12), but for the case of Lorentzian distribution of stochastic frequencies :

$$\langle \text{Re}(T_L^{(0)}) \rangle_\xi = \text{Re}[Y_o] \quad (15.a)$$

$$\langle \text{Im}(T_L^{(0)}) \rangle_\xi = \text{Im}[Y_o] \quad (15.b)$$

$$\text{with } Y_o = \frac{(T_2^{-1} + \delta)}{(T_2^{-1} + \delta)^2 + \Delta^2} (1 + i\Delta)$$

The recursive relations necessary to evaluate the high order terms of the expansion in (11) are:

$$\langle \text{Re}(T_M^{(n)}) \rangle_\xi = \frac{T_2^2}{2n} \langle \text{Re}(T_M^{(n-1)}) \rangle_\xi - \frac{T_2}{2n} \frac{\partial}{\partial T_2^{-1}} \langle \text{Re}(T_M^{(n-1)}) \rangle_\xi \quad (16.a)$$

$$\langle \text{Im}(T_M^{(n)}) \rangle_\xi = -\frac{T_2}{2n} \frac{\partial}{\partial \Delta} \langle \text{Re}(T_M^{(n-1)}) \rangle_\xi \quad (16.b)$$

This expressions are valid to both frequency distributions $M = L$ (Lorentzian distribution) or $M = G$ (Gaussian distribution).

2.2. Optical properties

Once the expression for the coherence function $\langle \rho_{ba} \rangle_\xi$ is obtained, the frequency component of the induced macroscopic polarization is calculated from the well know relation $P(\omega, S) = N \langle \langle \rho_{ba}(\omega, S) \rangle_\xi \mu_{ba} \rangle$ where N represents the concentration of the active species interacting with the external field and the external brackets $\langle \dots \rangle$, represents the orientational averages.

The effective nonlinear susceptibility derived from the Real and Imaginary part of the induced polarization can be expressed as [3-5]:

$$\chi_{\text{eff}}^{\text{Im}}(S, \omega; T_2, \gamma, \tau) = -\frac{N\rho_D^{\text{eq}}}{\hbar} |\mu_{\text{ba}}|^2 \sum_{n=0}^{\infty} (-1)^n \left(\frac{4S}{T_2} \right)^n \langle \text{Re}(T_M^{(n)}) \rangle \quad (17)$$

$$\chi_{\text{eff}}^{\text{Re}}(S, \omega; T_2, \gamma, \tau) = -\frac{N\rho_D^{\text{eq}}}{\hbar} |\mu_{\text{ba}}|^2 \sum_{n=0}^{\infty} (-1)^n \left(\frac{4S}{T_2} \right)^n \langle \text{Im}(T_M^{(n)}) \rangle \quad (18)$$

M = G or L

3. RESULTS AND DISCUSSION

The plots under study are principally derived from equations (17) and (18), because the effective linear and nonlinear susceptibility gives us information of two important macroscopic optical properties, such as the absorption coefficient α , and the refractive index η of the system, following a Lorentzian (or Gaussian) distribution of frequencies.

The figures 1 and 2, are result of choose M = G in equations (17) and (18) respectively, the figures are a graphical study of the nonlinear susceptibility of third order, as a function of the laser detuning frequency $\Delta = \omega - \omega_0$ and the dimensionless relaxation time $D = 2T_1\gamma$; we analyze separately the Real and the Imaginary part for the reasons exposed before. The graphic of the $\text{Re}\chi^{(3)}$ is related with the absorption coefficient and we can observe that the behavior of the signal depend strongly of the saturation parameter S; we also observe the symmetry of the signal, that in this case is respect to the value $\Delta = 0$, as we expect. In other hand, the graphic of the $\text{Im}\chi^{(3)}$ is related with the refraction index and we can observe that the behavior of the signal again depend strongly of the saturation parameter S.

This behavior is predictable from the form of the series (17) and (18), because the saturation parameter is related to the “nth power” of the series, but thanks to the fact that the convergence of the series (17) and (18) is obtained with few terms, this effect is not more strong; in the same way a similar behavior of use Lorentzian distribution [M = L in (17) and (18)] is obtained.

The nonlinear refractive index is defined by [11]:

$$\eta = \left[\eta_0 + 4\pi\chi_{\text{eff}}^{\text{Re}}(S, \omega; T_2, \gamma, \tau) \right]^{1/2} \quad (20)$$

where η_0 is the solvent refractive index, we choose water as solvent, so $\eta_0 = 1$.

The figure 3 is a comparative graphic of η . We can see that both distributions fits properly the physical behavior of a two-level system immersed in a thermal bath. The parameter values characterizing the molecular system are: $T_1=T_2=1,1 \cdot 10^{-12}$ s, $\mu_{ba}=2,81 \cdot 10^{-18}$ erg^{-1/2} cm^{3/2} and Bohr frequency $\omega_0= 3,06 \cdot 10^{15}$ s⁻¹ (all typical values for organic dyes).

A precedent publication [5] shows as principal results an expression for α and η that are being employed in numerical calculation and plotting of our results. Here also we consider other parameters as γ or δ as result of consider a different function of distribution of stochastic frequency. The study were done taking D as a varying parameter, the figure shows that the refraction index decrease for larger values of D, so the decrease is faster in (a) as we expect. These results are consistent with precedent reports [5,7,10].

Also we can see that for a wide range of values near of resonance ($\omega = \omega_0$) the behavior of both distributions are similar, but with the advantage that the second is more versatile and manageable for the resolution of the integral in (5) by convolution theory. Moreover convergence of equations (17) and

(18) are very fast in our study, which facilitates the calculus and the numerical treatment of the results. For values of Δ far of resonance it's better to use our extension of the analysis. Marquez et al [12], for simplicity, consider a Lorentzian distribution of resonant frequencies in a study of saturation and population pulsation effects, for both homogeneously and inhomogeneously broadened spectra lines in Four Wave Mixing (FWM) spectroscopy. Their results agree with the fact that Lorentzian distributions can be used in a extensive range for spectroscopic studies of two-level systems immersed in a thermal bath.

The formalism that we develop, has practical applicability only when the expression $4S/T_2^2 |D_\xi|^2$ is less than one. But the options of choosing a system are infinites, since fixing the values for the parameters of relaxation of the system, T_1 , T_2 , and their dipole transition moment μ_{ba} , we can analyze very different systems under the same equation.

In a forthcoming article, we will make an extension in FWM spectroscopy for which high-pump-power effects of the field and the alternative use of Lorentzian lines for the molecular frequency will be under study.

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Figure captions

Figure 1. Comparative study of the $\text{Re}\chi^{(3)}$ as a function of the laser detuning frequency $\Delta = \omega - \omega_0$ and the dimensionless relaxation time $D = 2T_1\gamma$, is clear the dependence of the signal with the saturation parameter: (a) $E = 1.10^{-3} \text{ Vcm}^{-1}$ (b) $E = 1.10^0 \text{ Vcm}^{-1}$ (c) $E = 1.10^2 \text{ Vcm}^{-1}$.

Figure 2. Comparative study of the $\text{Im}\chi^{(3)}$ as a function of the laser detuning frequency $\Delta = \omega - \omega_0$ and the dimensionless relaxation time $D = 2T_1\gamma$, showing again strong dependence of the signal with the saturation parameter, here: (a) $E = 1.10^{-3} \text{ Vcm}^{-1}$ (b) $E = 1.10^{-2} \text{ Vcm}^{-1}$ (c) $E = 1.10^{-1} \text{ Vcm}^{-1}$.

Figure 3. The linear refraction index η as a function of the laser detuning frequency $\omega - \omega_0$, and the parameter $D = 2T_1\gamma$ (δ), for a two level system. A comparison between Lorentzian (a) and Gaussian (b) distribution is done.