



Relaxation times and symmetries in the nonlinear optical properties of a two-level system



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ARTICLE INFO

Keywords:

Stochastic processes
Optical properties
Optical Bloch equations

ABSTRACT

In this work we introduce a methodology for the determination of the longitudinal and transversal relaxation times in a two-level system using symmetry properties of the optical responses in the frequency space $\epsilon(\Delta_1, \Delta_2)$. Employing the density matrix formalism and a perturbative scheme for the incident field amplitudes in the Four-wave mixing spectroscopy, the nonlinear macroscopic polarization is determined. The collective effects of the thermal reservoir are modeled as a time dependent frequency, whose manifestation is the broadening of the upper level according to a prescribed random function.

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1. Introduction

Four-wave Mixing (FWM) Spectroscopy has been widely used to characterize molecular systems, learn about their optical properties, and study dissipation mechanisms between an optical active system and a thermal reservoir, among others [1–3]. This technique has been successfully applied to extract spectroscopic information such as the longitudinal (T_1) and transversal (T_2) relaxation times of such systems. In FWM spectroscopy, two incident beams, pump and probe, are used to generate the mixing signal with propagation vector $\vec{k}_3 \approx 2\vec{k}_1 - \vec{k}_2$ and frequency $\omega_3 = 2\omega_1 - \omega_2$, where the indices 1, 2, and 3 refer to pump, probe, and signal, respectively. All frequencies are close to the molecular frequency of interest [4–7]. The so-called nonlinear spectrum is generated by scanning the incident beams frequency. On the basis of a molecular two-level system, by resolving the Liouville equation for the density matrix for the dynamics of the system it is possible to extract the nonlinear polarization and thus, the intensity of the four-wave mixing signal. This parameter defines the frequency spectrum, which width is related to the memory loss characteristic time (T_2). Analogies with the case of the Magnetic Nuclear Resonance (NMR) phenomenon help understand the significance of such relaxation times in the optical case. In the case of NMR, such times carry with them important information about the molecular system under study, since they are associated with processes of interaction both between the nuclear spins with their environment, T_1 , and between the spins themselves, T_2 . The

relaxation time T_1 is related to the longitudinal processes by which the ensemble of nuclear spins recovers thermal equilibrium through $-1/2$ state (higher energy) to $+1/2$ state (lower energy) transitions that in turn restore the longitudinal magnetization (along the z axis). The equilibrium is reached via such energy exchanges. In the optical field, the corresponding relaxation time T_1 reflects the characteristic transit time towards thermal equilibrium of the molecular populations of the involved states, once a perturbation fields have been turned off. The time T_2 is associated in NMR to the transversal relaxation by which the nuclear spins stop precessing and thus, transversal magnetization is lost (on the XY plane). In the optical case, T_2 represents the loss of the induced-coherence time among molecular states. In NMR, in general, longitudinal relaxation corresponds to the time T_1 needed to alienate the protons with a static magnetic field, while the transversal relaxation time T_2 is the time needed for the loss protons to lose their induced coherent energy in a NMR measurement. These relaxation occur exponentially in which T_1 y T_2 are time constants. Different mechanisms contribute to these characteristic times. Volume and surface relaxations contribute to both times, while diffusive relaxation contributes only to T_2 . In this work, and in the optical context a methodology is proposed for the estimation of the relaxation times T_1 and T_2 , which is based in some symmetry properties of the nonlinear optical properties. These symmetries are evident in the analysis of such properties as a function of the detuning in the incident beams as defined on surfaces and the corresponding level curves in the frequency space. The symmetry

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to which we refer corresponds to the behavior of the FWM signal intensity or the nonlinear optical properties of absorption or refraction index, relative to the optical frequencies associated to the pump and probe beams as visible in the corresponding plots of the profiles of such features. The profiles of these intensity responses are usually symmetrical when the optical detuning ($\Delta_j = \omega_j - \omega_0$, $j = 1, 2$) changes sign. If these profiles are geometrically symmetrical (e.g., for a Gaussian profile) it is possible to extract relevant information from the relaxation times taken from the width of the distribution. The consideration of these symmetry properties permits performing a calculation from the frequency spectra of the FWM signal of the transversal relaxation time defining its relaxation mechanism, which is extracted directly from the HWHM of such profile. It is important to mention that the symmetry properties as used here change in dependence of the overall calculation conditions. To support this, it is worth mentioning that the Authors in Ref. [8] indicate that in FWM, under their conditions, the signal intensity strength meets the following (symmetry) relationships: $I(\Delta_1, \Delta) = I(-\Delta_1, -\Delta) = I(-\Delta_1, \Delta) = I(\Delta_1, -\Delta)$, with $\Delta = \omega_1 - \omega_2$. It is clear that in our case the inclusion of the solvent generates different but in essence, equivalent relationships.

Finally, in this work, we are proposing a methodology for the determination of the longitudinal and transverse relaxation times from the graphical representations of the absorption coefficient. Our model is based on calculating these relaxation times, through the major and minor axes of the ellipse that represents the absorption coefficient after the unit transformation as a function of the frequency detuning of the pumping and probe beams.

2. Theory

The system under study is a chemical solution in which the solute molecules can access only to the two energetic states $|g\rangle$ y $|e\rangle$, and are immersed in a sea of solvent structure-less molecules. In this view, the interaction of the solvent with the solute induces only vertical displacements on the minima of the corresponding potential curves, which in turn introduces random shifts in the Bohr frequency of the two-level system, ω_0 . The resulting stochastic time-dependent frequency takes the form $\xi(t) = \omega_0 + \sigma(t)$, where $\sigma(t)$ contains all the information of the random process. By substituting $\xi(t) = \omega_0 + \sigma(t)$ into the Optical Conventional Bloch Equations OCBE., we derive the set of Optical Stochastic Bloch equations (OSBE), which characterizes the dynamics of the system in the presence of frequency fluctuations. We analytically solve the system of multiplicative stochastic differential equations when the bath is approximated as a white and colored noise source. We apply the results of the OSBE to study the behavior of the nonlinear absorption coefficient and nonlinear refraction index when the frequency of the external field and the parameters defining the bath (intensity and bandwidth of the noise) are varied. We analyzed, in some detail, the changes in these properties from those predicted from the deterministic theory and which have been widely studied in the literature. In the stochastic description, we have considered a molecule represented by a two-level system defined by the states and $|g\rangle$ and $|e\rangle$, with longitudinal and transversal relaxation times given by T_1 and T_2 , respectively. As a result of the effect of the thermal bath surrounding the two-level molecule, the transition frequency of the system, $\xi(t)$, is well characterized as a stochastic variable. The time evolution of the system is given by the Liouville equation for the density matrix $\dot{\rho} = -i\hbar[H, \rho]$. With the use of this equation, the radiative contributions due to the presence of the electromagnetic fields and the relaxation contributions due to instantaneous departures from the equilibrium population, are taken into account. For our case, the dynamics of the two-level system is

obtained by solving the following system of equations:

$$\frac{d\rho_{eg}(t)}{dt} = -\frac{i}{\hbar}(H_I(t))_{eg}\rho_D(t) - \left(i\xi(t) + \frac{1}{T_2}\right)\rho_{eg}(t) \quad (1)$$

$$\frac{d\rho_D(t)}{dt} = \frac{2i}{\hbar}\left[(H_I(t))_{ge}\rho_{eg}(t) - \rho_{ge}(t)(H_I(t))_{eg}\right] - \frac{1}{T_1}(\rho_D(t) - \rho_D^{(0)}) \quad (2)$$

$$\frac{d\rho_{eg}(t)}{dt} = \frac{d\rho_{ge}^*(t)}{dt} \quad (3)$$

where $\rho_D = \rho_{gg} - \rho_{ee}$ is the difference in state populations and $\rho_D^{(0)}$ is its equilibrium value in the absence of radiation. The state $|g\rangle$ and $|e\rangle$, coupled through an electric-dipole transition, μ , whose non-diagonal matrix elements are μ_{ge} and μ_{eg} , and whose diagonal elements μ_{gg} and μ_{ee} (permanent dipole moments) are assumed to be negligible compared to their non-diagonal counterparts and are therefore taken as zero. The interaction Hamiltonian that corresponds to the incident wave $E(t)$ is given by $H_I = -\vec{\mu} \cdot \vec{E}(t)$, where the subscript I refers to interaction representation. In this description, the molecule driven by the external field can make a transition from the lowest level to any of the broadened upper levels. With these Eqs. (1)–(3) is obtained in the matrix representation the following expression:

$$\frac{d\rho(t)}{dt} = A_\xi(t)\rho(t) + R. \quad (4)$$

In this expression, $A_\xi(t)$ is a matrix containing strictly all of the matter–radiation interaction details and is defined as:

$$\rho(t) = \begin{pmatrix} \rho_{eg}(t) \\ \rho_{ge}(t) \\ \rho_D(t) \end{pmatrix} \quad A_\xi(t) = \begin{pmatrix} -\xi_t & 0 & i\Omega \\ 0 & -\xi_t^* & -i\Omega^* \\ 2i\Omega^* & -2i\Omega & -1/T_1 \end{pmatrix}, \quad (5)$$

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

$$R = \begin{pmatrix} 0 \\ 0 \\ \rho_D^{(0)}/T_1 \end{pmatrix}. \quad (6)$$

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 $\Omega = \vec{\mu}_{ba} \cdot \vec{E}(t)/\hbar$, which defines the intensity of the coupling between matter and radiation, connected only to the transition dipolar moments associated $\vec{\mu}_{ba}$, (disregarding in this case, permanent dipolar moments). Also, we introduce $\vec{E} = \vec{E}_1 + \vec{E}_2$, with $\vec{E}_j(t) = E_{j0} \exp\left(i\vec{k}_j \cdot \vec{r} - \omega_j t\right)$ ($j = 1, 2$), and $\xi_t = i\xi(t) + T_2^{-1}$. The study limits itself to the framework of the non-degenerate four-wave mixing technique (FWM), in which two beams incident with different intensity interact with the molecular system, producing nonlinear signals due to scattering at different frequencies. Among all of these signals, we select the most intense occurring at frequency $\Delta_3 = 2\Delta_1 - \Delta_2$. In general, we will consider detunings $\Delta_k = \omega_k - \omega_0$, with $k = 1, 2, 3$ corresponding to the pump, probe, and FWM signal, respectively. With Eq. (4), under such a scheme, we get

$$\frac{d\tilde{\rho}_{\xi(t)}}{dt} = M_{\xi(t)}\tilde{\rho}_{\xi(t)} + \tilde{R}. \quad (7)$$

Here, $M_{\xi(t)}$ is a matrix dependent on the random perturbative process, \tilde{R} is the effective relaxation matrix that contains now part of the radiative mechanism. The coherence matrix $\rho_{\xi(t)}$ contains elements both of the coherence, and of the population difference, with indexes $n = 1, 2, 3$ defining the order of the perturbation considered:

$$\tilde{\rho}_{\xi(t)} = \begin{pmatrix} \rho_{eg}^{(3)}(t) \\ \rho_D^{(2)}(t) \\ \rho_{eg}^{(1)}(t) \end{pmatrix}, \quad M_{\xi(t)} = \begin{pmatrix} -\xi_t & -\frac{i}{\hbar}(H_I)_{eg} & 0 \\ 0 & -\frac{1}{T_1} & \frac{2i}{\hbar}(H_I)_{ge} \\ 0 & 0 & -\xi_t \end{pmatrix}, \quad (8)$$

$$\tilde{R} = \frac{i}{\hbar} \begin{pmatrix} 0 \\ 0 \\ -(H_I)_{eg} \end{pmatrix} \rho_D^{(0)}.$$

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