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Changes in Dipole Moments and Polarization of a Two–Level System with Intramolecular Coupling [#]

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Abstract

Motivation. Polyatomic molecules can be described by a two–level system represented by two crossed harmonic potential curves (including vibrational levels) in order to study their nonlinear signal response. The variation of the coupling parameter has an important influence on the behavior of the dipole moments and, consequently, on the polarization on the new coupled–state basis.

Method. The calculation method employed is based on the Liouville formalism for the density matrix, where the conventional optical Bloch equations are solved in Fourier space to obtain the density matrix elements associated to the polarization of the system. Changes in the coupling parameters V_0 (energetic difference between the minima of the potential curves), S (height to which the vibronic coupling occurs) and v (coupling parameter) produce modifications in the behavior of the dipole moments and Polarization on the coupled system. In this communication, two studies are presented: (*a*) variation of the parameters S and v, while keeping V_0 constant and, (*b*) variation of S and V_0, while keeping v constant. In order to study the effects of these changes, the rotating–wave approximation is neglected, which permits us to analyze the processes that occur out of the resonance region. Moreover, the permanent dipole moments of the states in the uncoupled basis are included.

Results. First case (variation of S and v): an important increment of dipole moments and polarization magnitude values were observed for low values of v and high values of S. Second case (variation of S and V_0): an abruptly increment in the polarization magnitude were found at high values of S and low values of V_0.

Conclusions. The observed changes in the nonlinear response are associated to modifications in the overlap integral and consequently to the dipole moments of the states in the new coupled basis.

Keywords. Dipole moments; polarization; crossed harmonic potential curves.

Abbreviations and notations

COBE, Conventional Optical Bloch Equations	RWA, Rotating Wave Approximation
FWM, Four Wave Mixing	

1 INTRODUCTION

In nonlinear optics, the atoms and molecules interacting with a classic electromagnetic field are conceived like two–level systems, where the interaction is represented by a coupling between the

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transition dipole moments of the molecular system and the electromagnetic field. This model can be represented by levels without internal structure. On the other hand, such states in a polyatomic molecule can be thought as vibrational states belonging to one or two potential energy surfaces. Models like these, which consist of two degenerate or quasi–degenerate electronic curves in a small range of nuclear coordinates, have been applied to Jahn–Teller and pseudo Jahn–Teller coupling in molecules and to vibronic coupling on degenerate excited states of dimmers [1–2].

In this fashion, the *intramolecular coupling* arises from the coupling between nuclear and electronic motions in a molecule. It represents a very important phenomenon, especially in some physical–chemistry processes [3]. Modifications of the coupling parameters change the characteristics and properties of the crossed two–level systems. The vibronic coupling terms are important molecular parameters, describing in a quantitative way, the vibrational coupling of electronic states. Curve crossing problems have received special attention in the last years and they have been applied in different science fields [4]. For instance, chemical reactions involving nuclei motion of reactant species and, in some cases, changes in its electronic structure. Charge transfer reactions are among the problems of chemical interest in chemistry where crossing of potential–energy curves occurs.

For this particular study, we have modeled the molecule as a system consisting of two electronic harmonic potential states, each one including its lowest vibrational energy level; these curves are horizontally displaced by R_o and vertically by V_0, as depicted in Figure 1. Inclusion of a residual perturbation H', which may arise from a residual electron–electron correlation and/or spin–orbit couplings terms in the Hamiltonian of the system, may couple the above electronic states, causing a separation of the two curves in agreement with the avoided–crossing rule.

In the present contribution, we aim to show the effects of changes in the coupling parameters v, S and V_0 on the dipole moments of the coupled states, and consequently, on the Polarization to the Four–Wave Mixing (FWM) signal frequency. These modifications are related with the structure of the two–level model employed. One of the changes (involving parameters S and v) implies horizontal displacement between the two potential curves, maintaining the value V_0 constant (near degenerate case). On a second case (involving parameters V_0 and S) implies a vertical displacement of the above curves, maintaining a value of v constant.
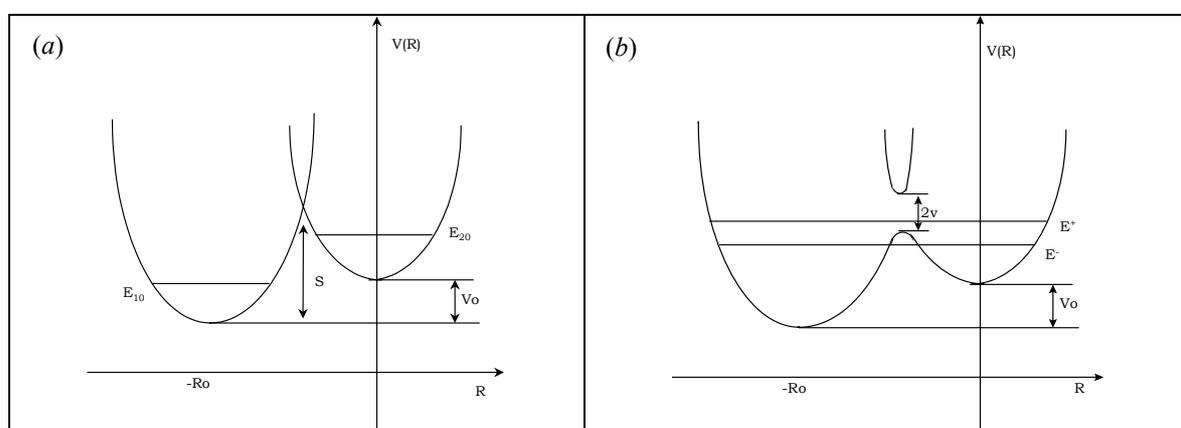
2 MATHEMATICAL ASPECTS

2.1 Vibronic Coupling Model

The model employed is based on a two–level system described by two crossed harmonic potential curves, which have the same apertures (same force constant δ). These curves are displaced horizontally in nuclear coordinate (R) and vertically in energy (V_0), and only include the

fundamental vibrational energy level in their structure. As depicted in Figure 1, the most important parameters considered in our study are the following: the coupling parameter (*v*), the energy difference between the minima of the potential–energy curves (V_0) and the energy height at which the coupling occurs (*S*).

The Hamiltonian of the system is described by two terms that include the molecular Hamiltonian H_0, and the contribution of the spin–orbit interaction, which is included as a perturbation causing the coupling between the electronic states, and causing the separation (or symmetry break) of the potential curves, in agreement with the avoided–crossing rule [5]. Moreover, the molecular system interacts with the classic electromagnetic fields treated as plane waves, where we have included a relaxation mechanism associated to the presence of the solvent (treated as transparent to the radiation) introduced in a phenomenological way.

Figure 1. (*a*) Diabatic and (*b*) adiabatic representation of the two crossed harmonic potential curves.

Regarding the mathematical aspects involved, each electronic ($\psi_i(R;r)$) and vibrational ($\varphi_i(R;r)$) state is described by its respective wave function and its corresponding energy value. Considering a linear combination of eigenfunctions on each level and solving its respective secular determinant, it is always possible to obtain the eigenfunctions and eigenvalues of the coupled states (considering – (+) the low (high) new coupled states):

$$\Psi^{\pm}(r;R) = \frac{1}{C_{10}^{\pm}}\left[V_{00}\left|\psi_1(r;R)\varphi_{10}(R) \pm \left(E_{10} - E^{\pm}\right)\psi_2(r;R)\varphi_{20}(R)\right]\right] \tag{1}$$

$$E^{\pm} = \frac{1}{2}\left[\left(E_{10} + E_{20}\right) \pm \left[\Delta E^2 + 4|V_{00}|^2\right]^{1/2}\right] \tag{2}$$

where the vibrational energies are $E_{10} = 0.5$ and $E_{20} = 0.5\delta + V_0$, $\Delta E = \left(E_{20} - E_{10}\right)$. Also, we have

$$V_{00} = v\langle\varphi_{10}|\varphi_{20}\rangle \;;\; C_{10}^{\pm} = \left[|V_{00}|^2 + \left(E_{10} - E^{\pm}\right)^2\right]^{1/2} \tag{3}$$

and

$$\langle \varphi_{10} | \varphi_{20} \rangle = \frac{(4\delta)^{1/4}}{(1+\delta)^{1/2}} \exp\left\{ -\frac{S}{2} \left[1 - (1+\delta)^{-1} \right] \right\} \text{ (overlap integral)} \tag{4}$$

obtained by the Pekarian formula [5], where $\delta = \tilde{\omega}_0 / \omega_0$ and $S = \left(\frac{m\omega_0}{\hbar} \right) R_0^2$. Here, $\tilde{m}$ represents the reduced mass associated with the vibrational modes as described by the molecular coordinate R_0 and frequency ω_0.

2.2 Dipole Moments in the Coupled Basis

Because of the dipole radiation–matter interaction in our model, the permanent dipole moments of states in the uncoupled basis are also included. It has been demonstrated that they contribute significantly to the photonic processes that take place outside the resonant region of the spectrum [6–11]. The general effects of changing the coupling parameter on the global FWM signal spectra were shown in previous work [11–13]. They indicated that the critical quantities on the study of the FWM response in a coupled basis were the transition and the permanent dipole moments, when the rotating wave approximation (RWA) was not taken into account.

In this sense, in the new basis of coupled states, there exist a new set of dipole moments that are different to those in the uncoupled basis. It has been shown that the zero values of the dipole moments in the uncoupled basis do not imply the nullity of the dipole moments in the new generated basis [14]. The mathematical expression of the dipole moments for the coupled states is obtained from the integral:

$$m_{ij}(R) = \int \psi_i^*(r;R)\hat{m}\,\psi_j(r;R)d^3r \tag{5}$$

Solving Eq. (5) for each case, the transition and permanent dipole moments can be described by the following equations, respectively:

$$\mu_{-+} = \left\{ \frac{|V_{00}|^2}{4|V_{00}|^2 + \Delta E^2} \right\}^{1/2} \left[(m_{11} - m_{22}) + m_{12}\frac{\Delta E}{v} \right] \tag{6}$$

$$\mu_{aa} = \left\{ \frac{|V_{00}|^2}{2|V_{00}|^2 - \Delta E(E_{10} - E^a)} \right\} \left\{ m_{22} + m_{11} - \frac{2(E_{10} - E^a)m_{12}}{v} \right\} - \frac{(E_{10} - E^a)\Delta E m_{22}}{2|V_{00}|^2 - \Delta E(E_{10} - E^a)} \tag{7}$$

where m_{11}, m_{22} and m_{12} represent the permanent and transition dipole moments of states in the uncoupled basis, respectively. As we will show below, these quantities are very important to determine the behavior of the nonlinear signal because of their dependence to the Macroscopic Polarization, and consequently, with the intensity of the signal studied.

2.3 FWM Signal

In the present study, we are interested in a particular case of nonlinear response: the FWM signal spectroscopy. This known nonlinear technique is related to the mixing of two incident beams interacting with a medium to generate a third beam. Specifically, the pump beam (high intensity, frequency ω_1 and propagation vector $\boldsymbol{k}_1$) interacts with the probe beam (less intense, frequency ω_2 and propagation vector $\boldsymbol{k}_2$) at a very small angle θ between them, to generate a third beam or signal beam with a frequency $\omega_3 = 2\omega_1 - \omega_2$ and propagation vector $\boldsymbol{k}_3 \approx 2\,\boldsymbol{k}_1 - \boldsymbol{k}_2$. This signal is the most intense and easier to detect. At this signal frequency, we are going to obtain the Macroscopic Polarization values.

2.4 Polarization Expression

Polarization is related to the response of a system in front of its interaction with an incident electromagnetic field [15]. Moreover, the intensity of the nonlinear signal response is proportional to the squared Polarization. Therefore, by knowing the Polarization of the molecular system, it is always possible to know the behavior of the nonlinear signal.

In order to obtain a Polarization expression, according to the specific characteristics of our system, the most common mathematical method employed is the Liouville formalism. This starting leads to the Conventional Optical Bloch Equations (COBE), which permit the study of the temporal evolution of the system and its interaction with the electromagnetic field. Among the aspects taken into account to do this calculation we can mention the use of a solvent transparent to the radiation, included in the calculation in a phenomenological way by the longitudinal T_1 and transversal T_2 relaxation times, parameters that describe the radiationless mechanism of relaxation. Also, we have considered the secular approximation and we have neglected the Rotating Wave Approximation (RWA), which, allows us to study the processes that occur out of the resonance frequency. Finally, the explicit inclusion of the permanent dipole moments of states in the uncoupled basis has been considered.

For the present study, and considering the facts mentioned above, the COBE can be written in the following general way:

$$\frac{d\rho_{-+}}{dt} = -\frac{i}{\hbar} H_{-+}\rho_D - \frac{i}{\hbar} \rho_{-+}\left[H_{--} - H_{++}\right] - \left(\frac{1}{T_2} + i\omega_0\right)\rho_{-+} \tag{8}$$

$$\frac{d\rho_{+-}}{dt} = \frac{i}{\hbar} H_{+-}\rho_D + \frac{i}{\hbar} \rho_{+-}\left[H_{--} - H_{++}\right] - \left(\frac{1}{T_2} - i\omega_0\right)\rho_{+-} \tag{9}$$

$$\frac{d\rho_D}{dt} = -\frac{2i}{\hbar}\left(H_{+-}\rho_{-+} - \rho_{+-}H_{-+}\right) - \frac{1}{T_1}\left[\rho_D - \rho_D^0\right] \tag{10}$$

These differential equations represent the temporal evolution of the coherence ρ_{-+} and populations ρ_D, and they include the term related to the molecular system (associated with the

resonance frequency ω_0), the term related to the field–system interaction (described by the dipole Hamiltonian) and the term related to the relaxation process (characterized by the presence of the longitudinal and transversal relaxation times T_1 and T_2 respectively).

Considering the COBE written above and the general expression to obtain the Macroscopic Polarization, we can write:

$$P(\omega_3) = N\langle\mu\rangle = N\begin{pmatrix} \mu_{--} & \mu_{-+} \\ \mu_{+-} & \mu_{++} \end{pmatrix}\begin{pmatrix} \rho_{--} & \rho_{-+} \\ \rho_{+-} & \rho_{++} \end{pmatrix} = N[\mu_{-+}\rho_{+-}(\omega_3) + \mu_{+-}\rho_{-+}(\omega_3) - d_{ic}\rho_D(\omega_3)] \tag{11}$$

By considering the characteristic of the system under study, it is possible to obtain a general equation that is the product of two terms, one of them related to the fields involved and the density of molecules present into the medium, and the second one, related to the different resonant processes involved. Then, in a factorized way, the following expression is obtained:

$$P(\omega_3; \omega_1, \omega_2) = Y(\omega_1, \omega_2)\xi(\omega_3; \omega_1, \omega_2) \tag{12}$$

where

$$Y(\omega_1, \omega_2) = N\rho_D^{(0)}E_1^2(\omega_1)E_2^*(\omega_2) \tag{13}$$

$$\xi(\omega_3; \omega_1, \omega_2) = i\left\{ 2\mu_{-+}^4\left(\frac{1}{D_3^-} - \frac{1}{(D_3^+)^*}\right)\left[\frac{1}{\Gamma}\left[\frac{1}{D_2^+} + \frac{1}{D_1^-} + \frac{1}{(D_2^-)^*} + \frac{1}{(D_1^+)^*}\right] + \frac{1}{\lambda}\left[\frac{1}{D_1^-} + \frac{1}{(D_1^+)^*}\right]\right] + \right.$$
$$\left. d_{ic}^2\mu_{-+}^4\left[\left(\frac{1}{D_3^-} - \frac{1}{\beta}\right)\left[\frac{1}{D_\Delta D_2^+} + \frac{1}{D_1^- D_\Delta} + \frac{1}{D_1^- D_5^-}\right] - \left(\frac{1}{(D_3^+)^*} - \frac{1}{\beta}\right)\left[\frac{1}{(D_\Delta^+)^*(D_2^-)^*} + \frac{1}{(D_1^+)^*(D_\Delta^+)^*} + \frac{1}{(D_1^+)^*(D_5^+)^*}\right]\right]\right\} \tag{14}$$

Here, N represents the chemical concentration of the absorbent molecules, μ represents the dipole moments and ρ represents the density matrix elements, all of them corresponding to the coupled basis. E_1 and E_2 are the pump and probe electromagnetic fields, respectively, and

$$\vec{d}_{ic} = \vec{\mu}_{--} - \vec{\mu}_{++} \; ; \; \rho_D = \rho_{++} - \rho_{--} \; ; \; \Delta = \omega_1 - \omega_2$$

$$\Gamma = \frac{i}{T_1} - i(\omega_1 - \omega_2) \; ; \; \beta = \frac{1}{T_1} - i\omega_3 \; ; \; \lambda = \frac{1}{T_1} - 2i\omega_1 \tag{15}$$

$$D_j^\pm = \frac{1}{T_2} + i(\omega_0 \pm \omega_j) \; ; \; D_5^\pm = \frac{1}{T_2} + i(\omega_0 \pm 2\omega_1) \; ; \; D_\Delta^\pm = \frac{1}{T_2} + i(\omega_0 \pm \Delta)$$

3 RESULTS AND DISCUSSION

In this section we show two different types of results by considering changes in the parameters v, V_0 and S. The value of the parameters involved in this study are: $\omega_0 = 3.0628\times10^{15}$ s^{-1} = 16280 cm^{-1} (resonance frequency of an organic molecule – *i.e.* Malachite Green), the longitudinal and transversal relaxation times $T_1 = T_2 = 1.3\times10^{-13}$ s, $S = 0.1$, $m_{11} = 1$ D and $m_{22} = 1.3$ D respectively, for the permanent dipole moments of the uncoupled states (giving as a result $d = 0.3$ D for the

difference in permanent dipolar moments), and $m_{12} = m_{21} = 0.1$ D for the transition dipole moments of the uncoupled states. The parameters under study change in the following range: $S = 0.01...10$; $v = 0.01...0.5$; $V_0 = 0.01...1$.

In previous works, the global spectrum was characterized by the presence of twelve resonances in frequency space [11,12,16]. These peaks presented symmetry relations (in intensity and position) under changes in frequency from ω_i to $-\omega_i$. Because of this symmetry, we have only considered the first six peaks in the present analysis. Moreover, each peak could be represented by a reduced polarization expression that permit, in some cases, to explain the origin and behavior of the nonlinear response of each resonance in the spectrum [16].
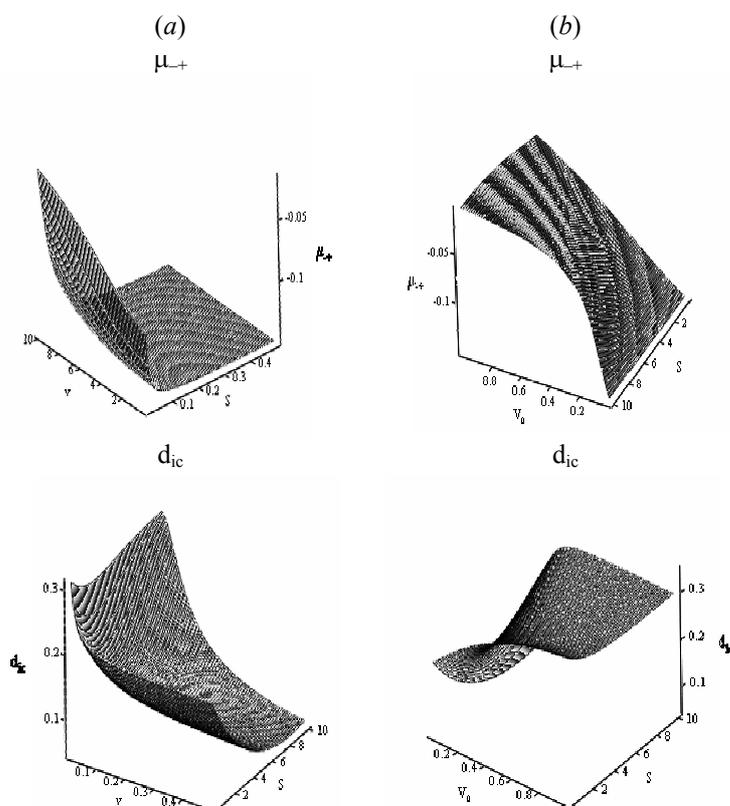
Figure 2. Transition and permanent dipole moments representation, in the coupled basis, to the following cases: (*a*) Variation in the parameters *S* and *v*, taking $V_0 = 0.01$ (near–degenerate case); (*b*) Variation in the parameters *S* and V_0, taking $v = 0.5$.

The behavior of the transition and permanent dipole moments of the states in the new coupled basis is very important due to the dependence of the Polarization's magnitude of these quantities [see Eq. (14)]. Figure 2 depicts three–dimensional graphs as a function of *v*, *S* and V_0. We should note, for a first case (variation in *v* and *S*), that the maximal values in the dipole moments are obtained for high values of *S* and low values of *v*. However, for a second case (variation in *S* and V_0), the results are opposite, namely, the dipole moments reach its maximal values for high values of *S* and high values of V_0. This aspect has a very important influence in the behavior of the squared

Polarization of the system under study, as we will see bellow.

3.1 Study A: Variation in *S* and *v*

In this first case, we have studied the modification of the squared modulus of the Polarization $|\xi(\omega_3;\omega_1,\omega_2)|^2$ with changes in the parameters *S* and *v*, taking V_0 as a constant equal to 0.01 (namely, near degenerate of the potential curves). Figure 3 depicts three–dimensional graphs of $|\xi(\omega_3;\omega_1,\omega_2)|^2$ vs. *S* and *v* for six peaks belonging to the general spectrum. Here, it is possible to observe a first group with maximal values of $|\xi(\omega_3;\omega_1,\omega_2)|^2$ obtained at low values of *v* for peaks 1, 3, 4 and 5 for almost all values of *S*. However, these values decrease for the lowest value of *v* = 0 and the highest value of *S* = 10. Peaks 2 and 6 behave differently. Peak 2 increases its magnitude with the increasing of the parameter *v* until it reaches an asymptotic value. Peak 6 increases its magnitude with the decreasing of the parameters *S*, presenting a local maximum for low values of *v*.

It is important to mention that the responses of the peaks 2 and 6 are determined by the transition dipole moments, but the rest of the peaks arise when the permanent dipole moments are included in the formalism. Peak 2 is related to the coherence density matrix term and peak 6 is related to the population density matrix elements [16]. This fact causes the observed changes in the topology of the Polarization values.
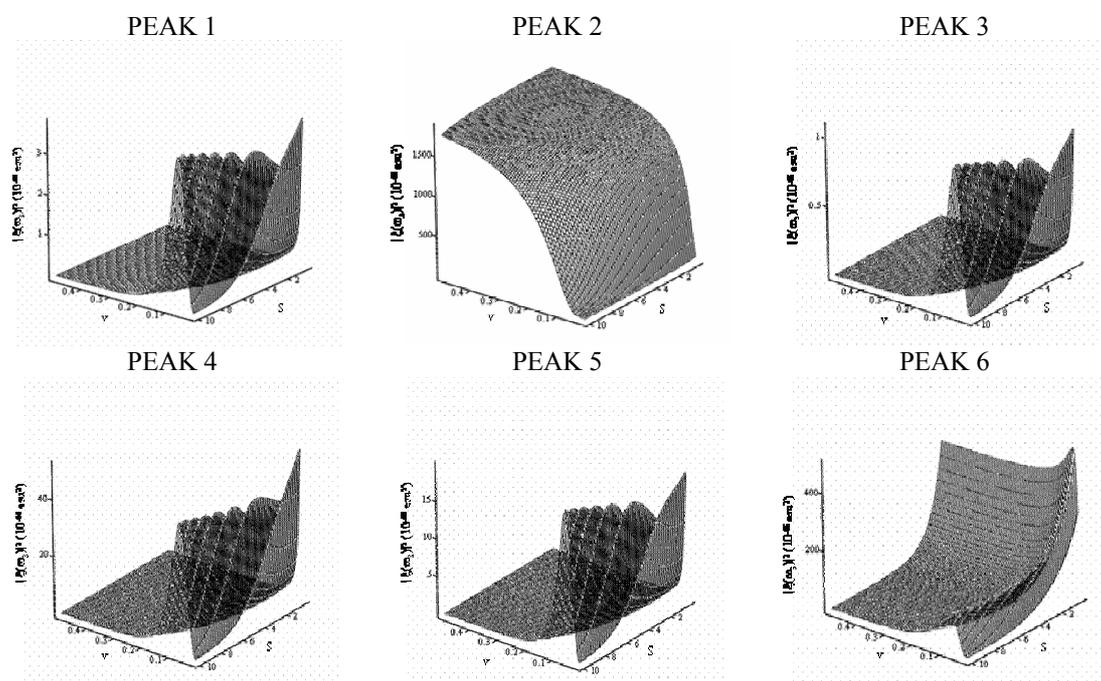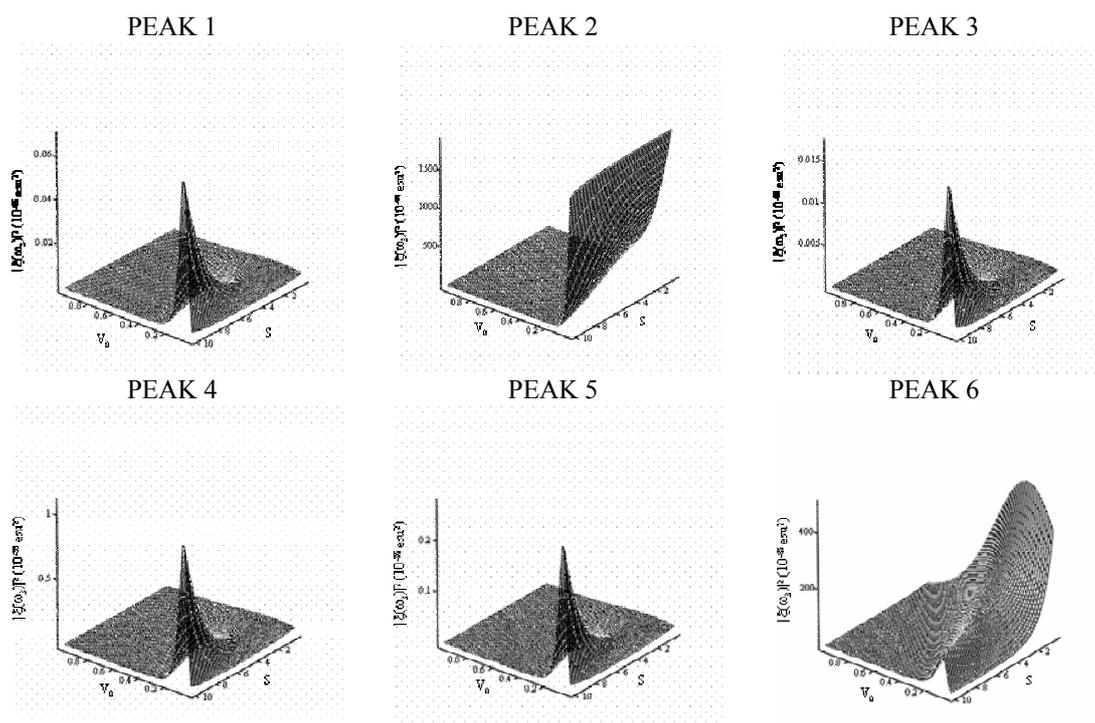

Figure 3. Modification of the factor $|\xi(\omega_3;\omega_1,\omega_2)|^2$ (related to Macroscopic Polarization), with the changes in the coupling parameters S and v, with Vo = 0.01 (near–degenerate case).

3.2 Study B: Variation in *S* and *Vo*

For this case, Figure 4 depicts the three–dimensional graphs corresponding to the modifications of $|\xi(\omega_3;\omega_1,\omega_2)|^2$ as a function of S and V_0, considering constant the parameter $v = 0.5$. Similar behavior as compare to previous case is observed here. Peaks 1, 3, 4 and 5 present identical shape, with a particular "peak" of high values of $|\xi(\omega_3;\omega_1,\omega_2)|^2$ in the region of low values of V_0 and high values of *S*, whereas peaks 2 and 6 present a different behavior. For the resonance peak 2, we observe an abrupt increase of the magnitude of $|\xi(\omega_3;\omega_1,\omega_2)|^2$ for low values of V_0 and for almost all values of *S*. For peak 6, we observe a maximum values for low values of V_0 and *S*, which diminishes for the highest value of $S = 10$ and $V_0 = 0.01$ (as in the study B).

Again, this marked difference between the peaks 2 and 6, and the others (1, 3, 4 and 5) are due to the fact that resonances 2 and 6 appear due to the presence of the transition dipole moments of the molecular system, while peaks 1, 3, 4 and 5 correspond to the inclusion of the permanent dipole moments, that for the case of coupled states, are always different from zero (even though the permanent dipole moments of the uncoupled stated could be equal to zero).

Figure 4. Modification of the factor $|\xi(\omega_3;\omega_1,\omega_2)|^2$ (related to Macroscopic Polarization), with the changes in the coupling parameters *S* and V_0, taking $v = 0.5$.

4 FINAL REMARKS

Considering the results showed in this work, it is possible to mention the importance of the characteristics of molecular systems described by two–level systems including intramolecular coupling. Depending on the shape of the harmonic potential curves employed to describe the electronic levels of the system, the system will respond in different way when the interaction with an electromagnetic field is turned on. Specifically, the nonlinear response of dye solutions changes when different characteristics of the potential curves are considered.

In the present study, modifications of the Polarization with the frequency ω_3 in the FWM spectroscopy are studied by varying the intramolecular coupling parameters v, S and V_0. Changes in S and v involve a horizontal displacement of the potential curves for fixed values of V_0, while changes in S and V_0 involve a vertical displacement of the curves for fixed values of v. In general, important variations are observed, particularly for low values of V_0 and v and high values of S. This behavior arises from the modifications that suffer the dipole moments in the coupled basis due to its dependence with the Macroscopic Polarization (and consequently with the FWM intensity). At the same time, the dipole moments are quantities that depend directly (explicit dependence) and indirectly (through the overlap integral) on the coupling parameters under consideration (S, v and V_0).

Finally, peaks 2 and 6, which depend only on the transition dipole moments between the coupled states, show a particular behavior that differs from the other resonances. While the peaks 1, 3, 4 and 5 present "maximal values" in a specific region of the graph (high values of S and low values of v and V_0), peaks 2 and 6 do not show this behavior. Their modifications come from a wider range of values of S, v and V_0.

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Biographies

José Luis Paz is Titular professor of Physical Chemistry at the Universidad Simón Bolivar. Prof. Paz obtained the Ph.D. degree in Physical Chemistry at the Universidad Central de Venezuela (1988). Dr. Paz has interested on problems of solvent effects and stochastic methodology in four wave mixing. More recently, Dr. Paz is working on projects in topics associated to algebraic methods applied to Quantum Optics and Nonlinear Spectroscopy.

Teresa Cusati is currently Ph.D. student at the Universidad Simón Bolívar. After obtaining a M.Sc. degree in Theoretical Chemistry at the Simón Bolívar University, she worked as assistant professor of general chemistry by conventional time, and after that she was collaborating in a group project between the Universidad Simón Bolívar and Universidad Central de Venezuela. Currently, she works as an invited researcher in the Quantum Optics group of the Physics Department at the Università degli Studi di Palermo, developing a research work related with entanglement in mesoscopic systems.