

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

José Luis Paz* and Teresa Cusati

Departamento de Química, Universidad Simón Bolívar, Apartado 89000, Caracas 1080A, Venezuela

Received xxx; Preprint published xxx; Accepted xxx ; Published xxx

Internet Electron. J. Mol. Des. 2003, 1, 000–000

Abstract

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

Method. The calculation method employed is based in the Liouville formalism for the density matrix, where the Conventional Optical Bloch Equations are solved in the Fourier space, to obtain the density matrix elements, associated with 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 ν (coupling parameter), produce modifications in the behavior of the dipole moments and Polarization of the coupled system. In this sense, basically two studies were done: a) variation in the parameters S and ν , keeping V_0 constant and b) variation in the parameters S and V_0 , keeping ν constant. In order to study the effects of these changes, the Rotating-Wave Approximation is neglected, fact that permits us to analyze the processes that occur out of the resonance region. Also, the permanent dipole moments of the states in the uncoupled basis are included.

Results. Study A (variation in S and ν): important increment of dipole moments and Polarization magnitude values is observed for low values of ν and high values of S . Study B (variation in S and V_0): an abruptly increment in the Polarization magnitude is presented to high values of S and low values of V_0 .

Conclusions. Changes observed are associated to the modifications in the overlapping integral and consequently in the dipole moments of the states in the new coupled basis. Consequently, the nonlinear response suffers changes in its behavior.

Keywords. dipole moments; Polarization; crossed harmonic potential curves.

Abbreviations and notations

COBE, Conventional Optical Bloch Equations

FWM, Four Wave Mixing

RWA, Rotating Wave Approximation

1 INTRODUCTION

In nonlinear optics, the atoms and molecules interacting with a classic electromagnetic field are conceived like two-level models, where the interaction is represented by the coupling between the transition dipole moments of the molecular system and the electromagnetic field. This model can be represented by levels without internal structure. In 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 level curves in a small range in the nuclear coordinates, have been applied to Jahn-Teller and pseudo Jahn-Teller coupling in

[#] Dedicated to Professor Danail Bonchev on the occasion of the 65th birthday.

* Correspondence author; phone: 58-212-9063954; fax: 58-212-9063954/3961; email: jlpaz@usb.ve.

molecules and to vibronic coupling on degenerate excited states of dimmers [1-2].

In this sense, the *intramolecular coupling* arises from the coupling between nuclear and electronic motions in a molecule. It is a very important phenomenon, specially to some physical chemistry processes [3]. The modifications in some coupling parameters modify the characteristics and properties of the crossed two-level systems. The vibronic coupling terms are important molecular parameters which describe in a quantitative way the phenomenon of vibrational coupling of electronic states.

The 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 involve 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 two or more close potential energy curve crossing occurs.

Then, in this particular case, 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_0 and vertically by V_0 , as depicted in Fig. 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 the separation of the two curves according to the avoided-crossing rule.

In the present contribution, the principal aim is to show the effects of changes in the coupling parameters ν , 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-levels model employed. One of the changes (parameters S and ν) implies horizontal displacement between the two potential curves, maintaining the value V_0 constant (near degenerate case). The other case (changes in the parameters V_0 and S) implies a vertical displacement of the mentioned curves, maintaining a value of ν constant.

2 MATHEMATICAL ASPECTS

2.1 Vibronic Coupling Model

In this case, the model employed is based in a two-level system described by two crossed harmonic potential curves, which have the same apertures (same force constant d). 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 it is depicted in the Figure 1, the most important parameters considered in our study, which characterize our model are the following : the coupling parameter (ν), the energy difference between the minima of the potential–energy curves

(V_0), 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, provoking the coupling between the electronic states, and causing the separation or symmetry break of the potential curves, according to the avoided-crossing rule. Moreover, the molecular systems interact with classic electromagnetic fields treated as plane waves, where we have included a relaxation mechanism associated to the presence of the solvent, which is treated as transparent to the radiation and it is introduced in a phenomenological way.

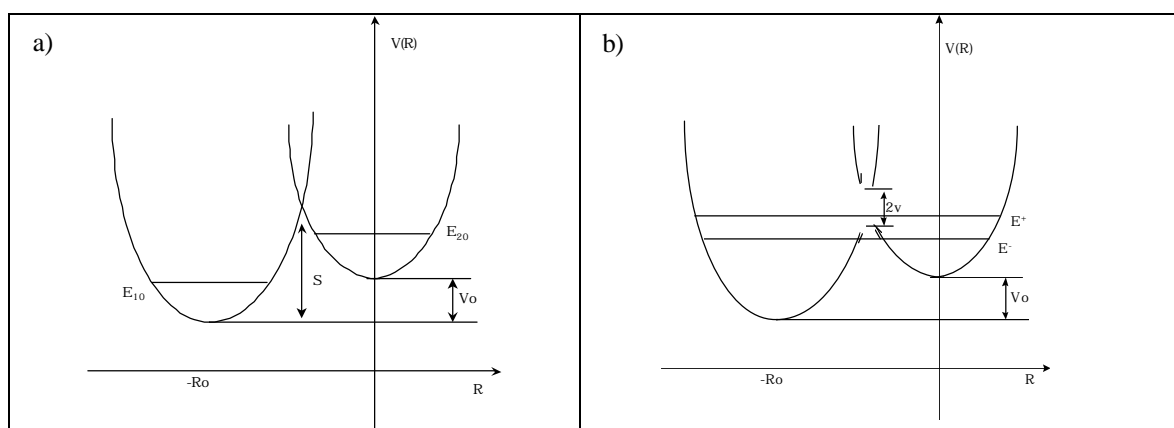


Figure 1. (a) Diabatic and (b) adiabatic representation of the two crossed harmonic potential curves.

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

$$\mathbf{Y}^{\pm}(r;R) = \frac{1}{C_{10}^{\pm}} \left[V_{00} \mathbf{y}_1(r;R) \mathbf{F}_{10}(R) \pm (E_{10} - E^{\pm}) \mathbf{y}_2(r;R) \mathbf{F}_{20}(R) \right] \quad (1)$$

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

where the vibrational energies are $E_{10} = 0.5$ and $E_{20} = 0.5\mathbf{d} + V_0$, $\mathbf{DE} = (E_{20} - E_{10})$. Also, we have

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

and

$$\langle \mathbf{j}_{10} | \mathbf{j}_{20} \rangle = \frac{(4\mathbf{d})^{1/4}}{(1+\mathbf{d})^{1/2}} \exp \left\{ -\frac{S}{2} [1 - (1+\mathbf{d})^{-1}] \right\} \quad (\text{overlap integral}) \quad (4)$$

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

2.2 Dipole Moments in the Coupled Basis

Because of the employ of 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 on 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 are obtained from the integral:

$$m_{ij}(R) = \int \mathbf{y}_i^*(r; R) \hat{m} \mathbf{y}_j(r; R) d^3r \quad (5)$$

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

$$\mathbf{m}_{\pm} = \left\{ \frac{|V_{00}|^2}{4|V_{00}|^2 + \mathbf{D}E^2} \right\}^{1/2} \left[(m_{11} - m_{22}) + m_{12} \frac{\mathbf{D}E}{\nu} \right] \quad (6)$$

$$\mathbf{m}_{aa} = \left\{ \frac{|V_{00}|^2}{2|V_{00}|^2 - \Delta E(E_{10} - E^a)} \right\} \left[m_{22} + m_{11} - \frac{2(E_{10} - E^a)m_{12}}{\nu} \right] - \frac{(E_{10} - E^a)\Delta E m_{22}}{2|V_{00}|^2 - \Delta E(E_{10} - E^a)} \quad (7)$$

where m_{11} , m_{22} and m_{12} represent the permanent and transition dipole moments of states in the uncoupled basis, respectively. As we shall 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 work, 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 \mathbf{k}_1) interacts with the probe beam (less intense, frequency ω_2 and propagation vector \mathbf{k}_2) at a very small angle \mathbf{q} between them, to generate a third beam or signal beam with a frequency $\omega_3 = 2\omega_1 - \omega_2$ and propagation vector $\mathbf{k}_3 \approx 2\mathbf{k}_1 - \mathbf{k}_2$. 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. Then, knowing the expression corresponding to the Polarization of the molecular system, it is possible to know the behavior of the nonlinear signal to this system.

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. Starting with it, it is possible to obtain 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, as we already mention it, 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:

$$\frac{d\mathbf{r}_{-+}}{dt} = -\frac{i}{\hbar} H_{-+} \mathbf{r}_D - \frac{i}{\hbar} \mathbf{r}_{-+} [H_{--} - H_{++}] - \left(\frac{1}{T_2} + i\mathbf{w}_0 \right) \mathbf{r}_{-+} \quad (8)$$

$$\frac{d\mathbf{r}_{+-}}{dt} = \frac{i}{\hbar} H_{+-} \mathbf{r}_D + \frac{i}{\hbar} \mathbf{r}_{+-} [H_{--} - H_{++}] - \left(\frac{1}{T_2} - i\mathbf{w}_0 \right) \mathbf{r}_{+-} \quad (9)$$

$$\frac{d\mathbf{r}_D}{dt} = -\frac{2i}{\hbar} (H_{+-} \mathbf{r}_{-+} - \mathbf{r}_{+-} H_{-+}) - \frac{1}{T_1} [\mathbf{r}_D - \mathbf{r}_D^0] \quad (10)$$

These differential equations represent the temporal evolution of the coherence \mathbf{r}_{-+} and populations \mathbf{r}_D , and they include the term related to the molecular system (associated with the resonance frequency \mathbf{w}_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, taking into account the general expression to obtain the Macroscopic Polarization:

$$P(\mathbf{w}_3) = N \langle \mathbf{m} \rangle = N \begin{pmatrix} \mathbf{m}_{-} & \mathbf{m}_{+} \\ \mathbf{m}_{+-} & \mathbf{m}_{++} \end{pmatrix} \begin{pmatrix} \mathbf{r}_{--} & \mathbf{r}_{-+} \\ \mathbf{r}_{+-} & \mathbf{r}_{++} \end{pmatrix} = N [\mathbf{m}_{-+} \mathbf{r}_{+-}(\mathbf{w}_3) + \mathbf{m}_{+-} \mathbf{r}_{-+}(\mathbf{w}_3) - d_{ic} \mathbf{r}_D(\mathbf{w}_3)] \quad (11)$$

and 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 in this case. Then, in a factorized way, the following expression is obtained:

$$P(\mathbf{w}_3; \mathbf{w}_1, \mathbf{w}_2) = Y(\mathbf{w}_1, \mathbf{w}_2) \mathbf{x}(\mathbf{w}_3; \mathbf{w}_1, \mathbf{w}_2) \quad (12)$$

where

$$Y(\mathbf{w}_1, \mathbf{w}_2) = N \mathbf{r}_D^{(0)} E_1^2(\mathbf{w}_1) E_2^*(\mathbf{w}_2) \quad (13)$$

$$\mathbf{x}(\mathbf{w}_3; \mathbf{w}_1, \mathbf{w}_2) = i \left\{ 2\mathbf{m}_{-+}^4 \left[\frac{1}{D_3^-} - \frac{1}{(D_3^+)^*} \right] \frac{1}{\Gamma} \left[\frac{1}{D_2^+} + \frac{1}{D_1^-} + \frac{1}{(D_2^-)^*} + \frac{1}{(D_1^+)^*} \right] + \frac{1}{I} \left[\frac{1}{D_1^-} + \frac{1}{(D_1^+)^*} \right] \right\} + \quad (14)$$

$$d_{ic}^2 \mathbf{m}_{-+}^4 \left\{ \left[\left(\frac{1}{D_3^-} - \frac{1}{b} \right) \left[\frac{1}{D_{\Delta} D_2^+} + \frac{1}{D_1^- D_{\Delta}^-} + \frac{1}{D_1^- D_5^-} \right] - \left(\frac{1}{(D_3^+)^*} - \frac{1}{b} \right) \left[\frac{1}{(D_{\Delta}^+)^* (D_2^-)^*} + \frac{1}{(D_1^+)^* (D_{\Delta}^+)^*} + \frac{1}{(D_1^+)^* (D_5^+)^*} \right] \right] \right\}$$

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

$$\begin{aligned}\bar{d} &= \bar{m}_{--} - \bar{m}_{++} ; \quad \mathbf{r}_D = \mathbf{r}_{++} - \mathbf{r}_{--} ; \quad \mathbf{D} = \mathbf{w}_1 - \mathbf{w}_2 \\ \mathbf{G} &= \frac{i}{T_1} - i(\mathbf{w}_1 - \mathbf{w}_2) ; \quad \mathbf{b} = \frac{1}{T_1} - i\mathbf{w}_3 ; \quad \mathbf{l} = \frac{1}{T_1} - 2i\mathbf{w}_1 \\ D_j^\pm &= \frac{1}{T_2} + i(\mathbf{w}_0 \pm \mathbf{w}_j) ; \quad D_5^\pm = \frac{1}{T_2} + i(\mathbf{w}_0 \pm 2\mathbf{w}_1) ; \quad D_\Delta^\pm = \frac{1}{T_2} + i(\omega_0 \pm \Delta)\end{aligned}\quad (15)$$

3 RESULTS AND DISCUSSION

In this section we show two different kinds of results, considering changes in the parameters ν , V_0 and S . The value of the parameters involved in this study are: $\mathbf{w}_0 = 3.0628 \times 10^{15} \text{ s}^{-1} = 16280 \text{ cm}^{-1}$ (resonance frequency of an organic molecule – i.e. Malachite Green), the longitudinal and transversal relaxation times $T_1 = T_2 = 1.3 \times 10^{-13} \text{ s}$, $S = 0.1$, $m_{11} = 1 \text{ D}$ and $m_{22} = 1.3 \text{ D}$ respectively, for the permanent dipole moments of the uncoupled states (giving as a result $d = 0.3 \text{ D}$ for the difference in permanent dipolar moments), and $m_{12} = m_{21} = 0.1 \text{ D}$ for the transition dipole moments of the uncoupled states. The parameters under study change in the following range: $S = 0.01 \dots 10$; $\nu = 0.01 \dots 0.5$; $V_0 = 0.01 \dots 1$.

In this particular case, we have considered only the term $|\mathbf{x}(\mathbf{w}_3; \mathbf{w}_1, \mathbf{w}_2)|^2$ to be analyzed, considering that the term $Y(\mathbf{w}_1, \mathbf{w}_2)$ can be taken as a given value in a particular case, and it is constant if all variables involved are not changed.

In previous works, a global spectrum characterized for the presence twelve resonances is obtained in the frequency space [11,12,16]. These peaks present symmetry in intensity and position in the spectrum, under the changes in frequency \mathbf{w}_i for $-\mathbf{w}_i$. Because of this symmetry fact, we have considered only the first six peaks for the analysis described below. Moreover, each peak can be represented by a reduced polarization expression that permits, in some cases, to explain the origin and behavior of the nonlinear response of each resonance in the spectrum [16].

In the other hand, 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 magnitude with this quantities (see Eq. (14)). In the Figure 2, these quantities are depicted as three-dimensional graphs vs. a) ν and S and b) V_0 and S . It is possible to denote, for the first case (variation in ν and S), that the maximal values in the dipole moments are obtained for high values of S and low values of ν . However, for the 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 , but high values of V_0 too.

This aspect have a very important influence in the behavior of the squared Polarization of the system under study, as we will see bellow.

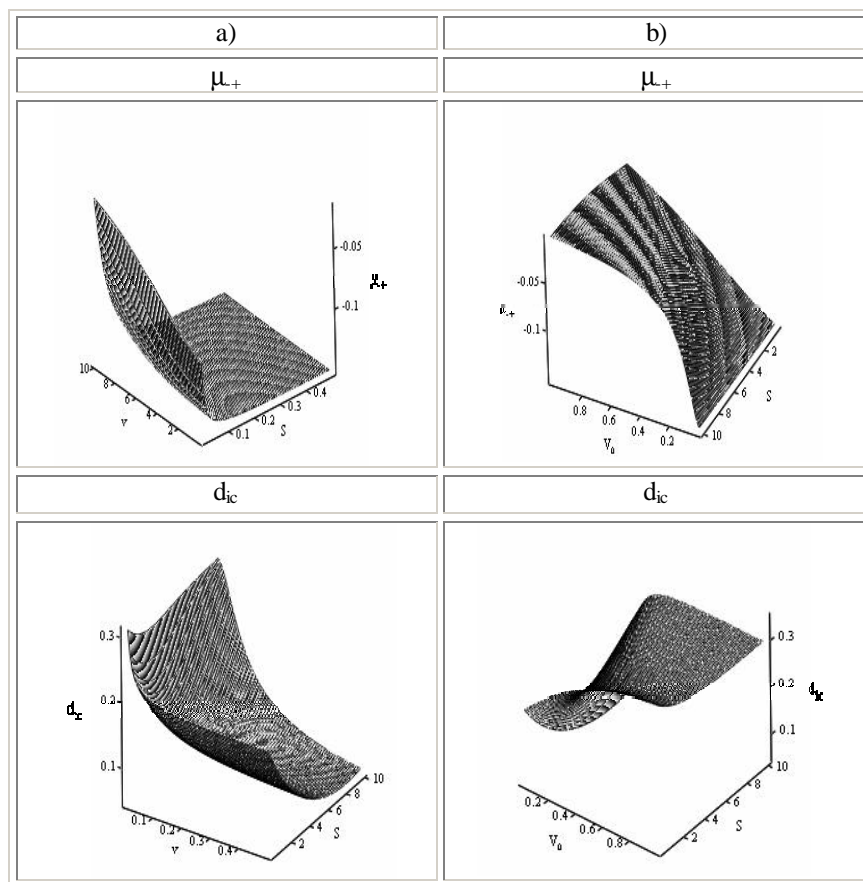


FIGURE 2. Transition and permanent dipole moments representation, in the coupled basis, to the following cases: a) Variation in the parameters S and ν , taking $V_0 = 0.01$ (near-degenerate case); b) Variation in the parameters S and V_0 , taking $\nu = 0.5$.

3.1 Study A: Variation in S and ν

In the first case, we have studied the modification of the squared modulus of Polarization $|\xi(\omega_3; \omega_1, \omega_2)|^2$ with the changes in the parameters S and ν , taking V_0 as a constant value equal to 0.01 (namely, near degenerate case of the potential curves). In the Figure 3, three-dimensional graphs of $|\xi(\omega_3; \omega_1, \omega_2)|^2$ vs. S and ν are depicted, for the six peaks belonging to the general spectrum. Here, it is possible to observe a similar behavior for the peaks 1, 3, 4 and 5, but peaks 2 and 6 look like different. For the first ones, maximal values of the magnitude of $|\xi(\omega_3; \omega_1, \omega_2)|^2$ are obtained for low values of ν , for almost all values of S . However, this values diminishing for the lowest value of $\nu = 0$ and highest value of $S = 10$. Peak 2 increases its magnitude with the increasing of the parameter ν , until to obtain an asymptotic value for the highest values in this parameter. Peak 6 increase its magnitude with the decreasing of the parameters S , presenting a local maximum for low values of ν .

It is important to mention that the responses of the peaks 2 and 6 are governed for the transition dipole moments, but the other peaks arise when the permanent dipole moments are included in the formalism. Peak 2 is related with the coherence density matrix term, and peak 6 is related with the population density matrix elements [16]. This fact provoke the different aspects in the topology of the Polarization values.

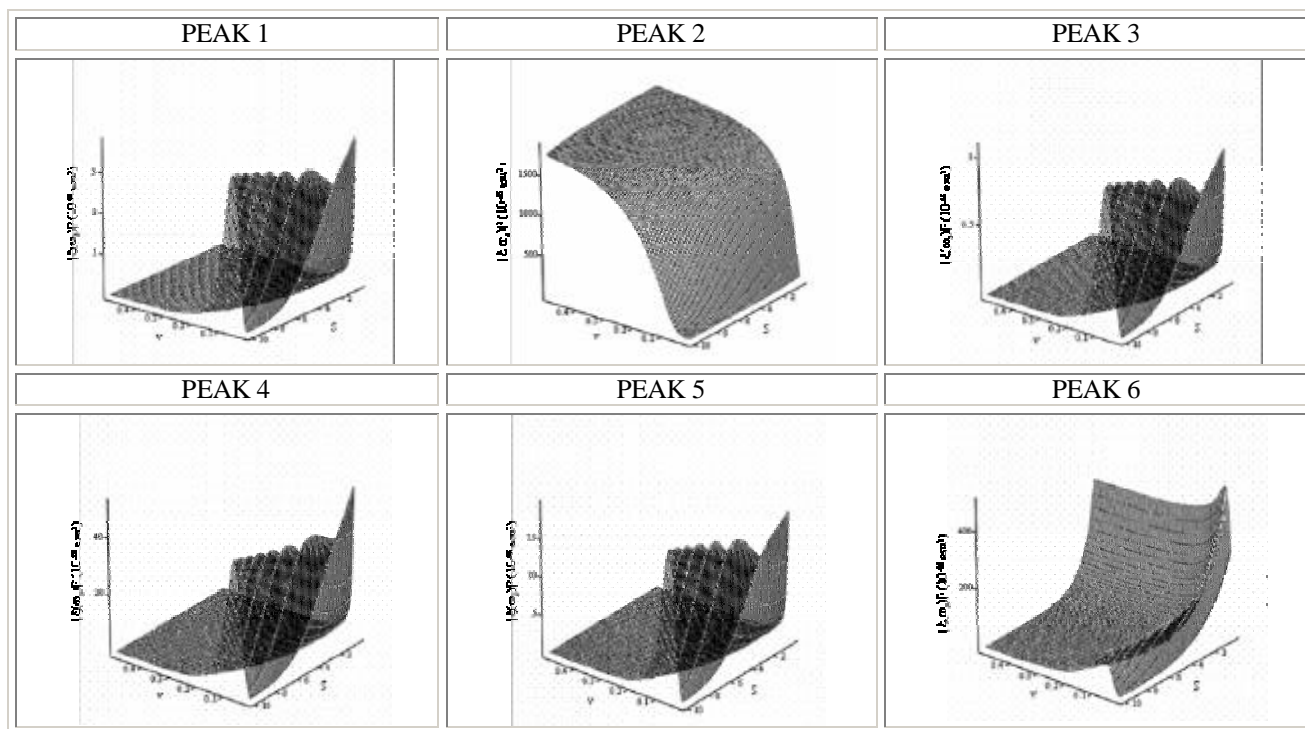


FIGURE 3. Modification of the factor $|\xi(\omega_3; \omega_1, \omega_2)|^2$ (related to Macroscopic Polarization), with the changes in the coupling parameters S and ν , with $V_0 = 0.01$ (near-degenerate case).

3.2 Study B: Variation in S and V_0

In the second case, the Figure 4 depicted the three-dimensional graphs corresponding to the modifications of $|\xi(\omega_3; \omega_1, \omega_2)|^2$ vs. S and V_0 , considering constant the parameter $\nu = 0.5$. Similar behavior respect to the previous case is observed. 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. To the case of resonance (peak 2), an abruptly increasing of the magnitude of $|\xi(\omega_3; \omega_1, \omega_2)|^2$ is observed for low values of V_0 , for almost all values of S . In the other case (peak 6), maximal values are found for low values of V_0 and S , which diminish for the highest value of $S = 10$ and $V_0 = 0.01$ (like the previous case).

Again, this marked difference between the peaks 2 and 6, and the other ones (1, 3, 4 and 5) obeys to the fact that this resonances appear due to the presence of the transition dipole moments of the

molecular system. The other ones correspond to the inclusion of the permanent dipole moments, that, for the case of coupled states is always different to zero, even though the permanent dipole moments of the uncoupled states could be null.

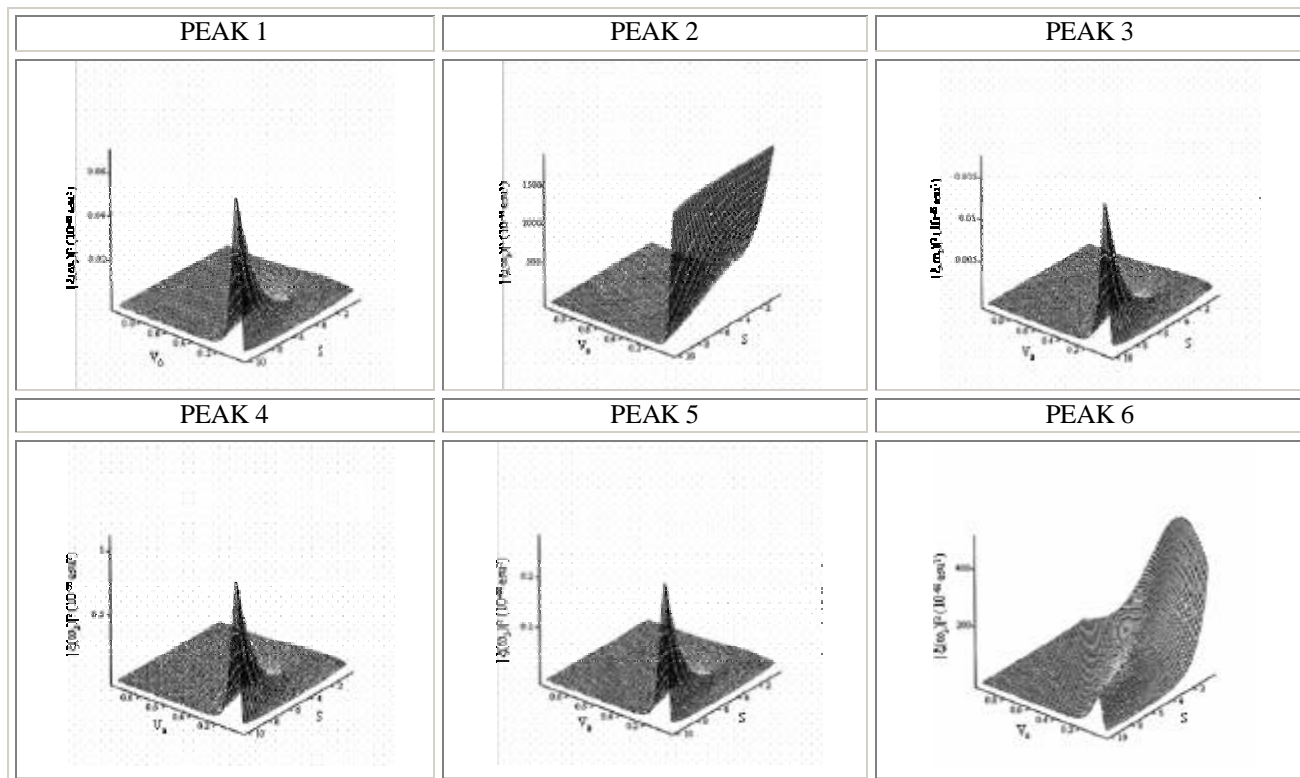


FIGURE 4. Modification of the factor $|\xi(\omega_3; \omega_1, \omega_2)|^2$ (related to Macroscopic Polarization), with the changes in the coupling parameters S and V_0 , taking $\nu = 0.5$.

4 FINAL REMARKS

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

In the present work, the modifications of the Polarization at the frequency ω_3 , considering FWM spectroscopy, are studied, varying the intramolecular coupling ν , S and V_0 . Changes in S and ν , involve an horizontal displacement of the potential curves, for a fixed values of V_0 , while changes in S and V_0 involve a vertical displacement of the curves, for a fixed values of ν . In general, the important variations are observed particularly for low values of V_0 and ν , and high values of S , principally. This behavior arises from the modifications that suffer the dipole moments in the

coupled basis, due to the dependence of the Macroscopic Polarization, and consequently the FWM intensity, with the mentioned quantities. At the same time the dipole moments are quantities that depend directly (explicit dependence) and indirectly (by the overlap integral dependence) on the coupling parameters under consideration S , ν and V_0 .

Moreover, the peaks 2 and 6, that depend only on the transition dipole moments between the coupled states, show a particular behavior that differs to the other resonances. While the peaks 1, 3, 4 and 5 present a “maximal values peak” in a specific region of the graph (high values of S and low values of ν and V_0), the peaks 2 and 6 do not show this shape, and their changes involve a more extended region in the graph, namely, the modifications come from a wide range of values of S , ν and V_0 .

Acknowledgment

The present work was supported by the Fondo Nacional de Ciencia, Tecnología e Innovación (FONACIT) (grant G-97000593) and by the Decanato de Investigaciones de la Universidad Simón Bolívar (grant GID-13).

5 REFERENCES

- [1] M. García-Sucre, F. Goychman and R. Lefebvre, Adiabatic Corrections in a Simple Model of Two Interacting Electronic-Potential Curves, *Phys. Rev. A* **1970**, *2*, 1738–1745.
- [2] J. L. Paz, M. García-Sucre, E. Squitieri, and V. Mujica., The Effect of Intramolecular coupling on the Optical Susceptibilities of a Two–Level Molecule, *Chem. Phys. Lett.* **1994**, *217*, 333–341.
- [3] A. Mebel, M. Hayashi, and S. H. Lin, Ab Initio Calculations of Vibronic Coupling, Applications to Symmetry–Forbidden Vibronic Spectra and Internal Conversion in Ethylene, *Chem. Phys. Lett.* **1997**, *274*, 281–292.
- [4] V.A. Yurovsky and A. Ben-Reuven, *J. Phys. B: At. Mol. Opt. Phys.* **1998**, *31*, 1.
- [5] Di Bartolo, B., 1980, *Radiationless Processes* (New York: Plenum Press)
- [6] M. A. Kmetc and W. J. Meath, Perturbative Corrections to the Rotating–Wave Approximation for Two–Level Molecules and the Effects of Permanent Dipoles on Single–Photon and Multiphoton Spectra, *Phys. Rev. A* **1990**, *41*, 1556–1568.
- [7] R. Bavli, D. F. Heller, and Y. B. Band, Nonlinear Optical Properties of Two–Level Systems with Permanent Dipole Moments, *Phys. Rev. A* **1990**, *41*, 3960–3968.
- [8] J. P. Lavoine, C. Hoerner, and A. A. Villaeys, Effects of Permanent Dipole Moments in Degenerate Four–Wave Mixing processes, *Phys. Rev. A* **1991**, *44*, 5947–5957.
- [9] R. Bavli and Y. B. Band, Nonlinear Absorption and Dispersion in a Two–Level System with Permanent Dipole Moments, *Phys. Rev. A* **1991**, *43*, 5039–5043.
- [10] R. Bavli and Y. B. Band, Sum and Difference Frequency generation in a Two–Level System with Permanent Dipole Moments, *Phys. Rev. A* **1991**, *43*, 5044–5048.
- [11] T. Cusati, J. L. Paz, M. C. Salazar, and A. J. Hernández, Intramolecular Coupling Study of the Resonances in the Four–Wave Mixing Signal, *Phys. Lett. A* **2000**, *267*, 18–23.
- [12] J.L. Paz, T. Cusati, M.C. Salazar and A.J. Hernández, Intramolecular coupling study on nonlinear signals, *Theor. Chem. Acc.* **2000**, *104*, 312–316.
- [13] J.L. Paz and T.Cusati, Modifications in the Maximal Intensity of Four-Wave Mixing Signal under the Changes of Vibronic Coupling Conditions, *Internet Electron. J. Mol. Des.* **2004**, *3*,
- [14] M. García-Sucre, E. Squitieri, J. L. Paz, and V. Mujica, Absorptive and Dispersive Processes in a Two–Level Molecule with Intramolecular Coupling and Non–Zero Permanent Dipole Moment, *J. Phys. B: At. Mol. Opt. Phys.* **1994**, *27*, 4945–4972.
- [15] N. Bloembergen, 1996, *Nonlinear Optics* (London: World Scientific).
- [16] J. L. Paz, T. Cusati, M. C. Salazar, and A. J. Hernández, Study and Characterization of resonances in the Four–Wave Mixing Signal of a Two–Level System with Intramolecular Coupling, *J. Mol. Spect.* **2002**, *211*, 198–210.

Biographies

José Luis Paz is Titular professor of Physical Chemistry at the Universidad Simón Bolívar. 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 engaged 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. Actually, 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.