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Modifications in the Maximal Intensity of Four–Wave Mixing Signal under the Changes of Vibronic Coupling Conditions

José Luis Paz, Teresa Cusati, and Antonio J. Hernández

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

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Modifications in the Maximal Intensity of Four–Wave Mixing Signal under the Changes of Vibronic Coupling Conditions[#]

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Abstract

Motivation. The spectroscopic analysis of the behavior of the nonlinear signal response of systems including electronic levels is described by the coupling parameters of crossed harmonic potential curves.

Method. Changes in the Four–Wave Mixing (FWM) signal intensity are originated by the modifications of the dipole moments in the new coupled basis due to variation of the parameters V_0 (energetic difference between the minima), v (coupling parameter) and δ (strength constant) corresponding to the crossed states involved. The permanent dipole moments of the states in the uncoupled basis have been included and the Rotating–Wave Approximation is neglected in order to observe the processes out of the resonance region. The calculation method is based in the Liouville–von Neumann formalism for the density matrix, where the Conventional Optical Bloch Equations are solved in Fourier space to obtain the density matrix elements associated with the Macroscopic Polarization responsible of the FWM signal.

Results. Variation in the coupling parameters generates modifications in the dipole moments of the coupled states. These modifications induce changes in the intensity values of the FWM signal, including the nullity of the dipole moments producing the nullity of the nonlinear signal. Mathematical expressions are obtained to interpret these results.

Conclusions. Changes in the characteristic coupling parameters induce modifications on the crossed potential curves, and consequently, on the nonlinear response and intensity.

Keywords. Intramolecular coupling; Four–Wave mixing; vibronic coupling; potential curves; harmonic oscillators; dipole moments.

1 INTRODUCTION

In general, the two–level model description of atoms and molecules interacting with a classic electromagnetic field, where the interaction is represented by the coupling of the field to the transition dipole moments of the system, have shown great utility in nonlinear optics. In this respect, there are many studies in the literature where a two–levels model (without internal structure) is employed in diatomic molecules and dimers. However, such states in a polyatomic molecule can be viewed as vibrational states belonging to different potential energy surfaces. These

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* Correspondence author; phone: 58–212–9063954; fax: 58–212–9063961; E–mail: jlpaz@usb.ve.

models involving 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 degenerated excited states of dimers [1].

Theoretical descriptions of photophysical and photochemical processes in the literature involve the treatment of two or more electronic states and several or many vibrational modes (for large molecules) with strong electronic–vibrational interactions [2]. The "vibronic coupling", resulting from the coupling between nuclear and electronic motions in a molecule is of great importance to some physical chemistry processes, for instance, in the study of relaxation rates of internal conversion [3], in the study of weak transition probabilities forbidden by symmetry in absorption and emission processes [4], in femtosecond spectroscopy [5], in the study of the optical absorption band shape of dimers [6], and in the study of resonances in scattering processes [7].

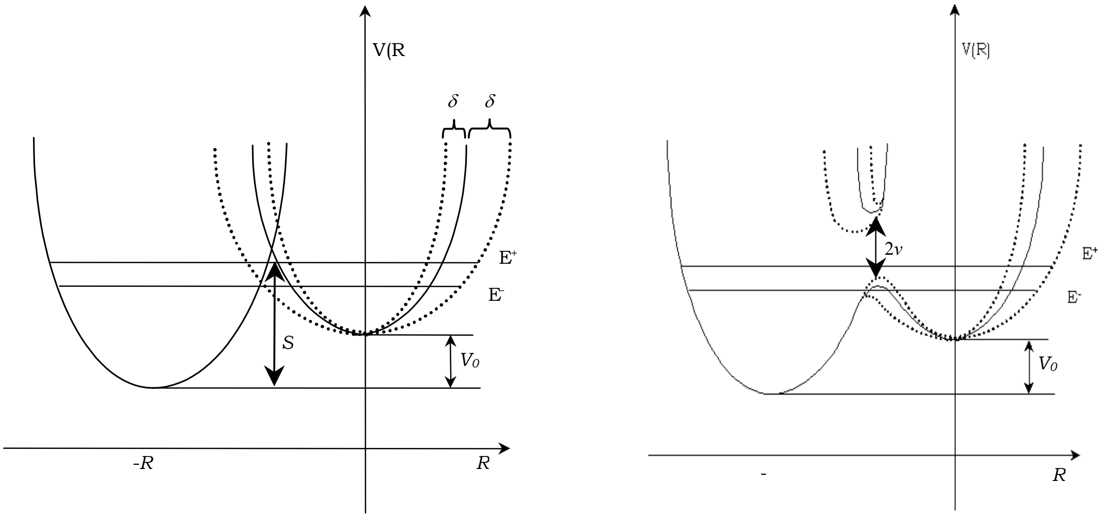
The principal aim of the present contribution is to show the effects of changes in the coupling parameters v and V_0, on the dipole moments of the coupled states, and in consequence, on the maximal intensity values of the Four–Wave Mixing (FWM) responses, taking into account different values of the strength constant δ.

The present model is described as an ensemble of two–levels systems formed by ground vibrational energy states belonging to two crossed harmonic potential energy curves with different apertures, as measured by the strength constant (δ), which have their minima horizontally and vertically displaced in their nuclear coordinate (R) and energy (V_0), respectively. The molecular systems interact with a classic electromagnetic field treated as plane wave, 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. By using 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 [8–12]. The general effects on changing the coupling parameter on the global FWM signal spectra were shown in previous work [13,14]. 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. This approximation was not introduced at present in order to study physical processes that occur out of the resonance region.

2 MATHEMATICAL METHODS

2.1 Theoretical Characteristics of the Model

The two–levels system employed in the present study is described using a coupled–basis model including two crossed harmonic potential energy curves, which are displaced horizontally along a nuclear coordinate and vertically in energy, where the spin–orbit interaction is treated as a perturbation in the global Hamiltonian describing the molecular systems. Each potential energy curve can have different apertures and they include only their fundamental vibrational levels. As indicated in Figure 1, the following parameters are considered: the coupling parameter (v), the energy difference between the minima of the potential–energy curves (V_0), the energy height at which the coupling occurs (S) and the relative aperture of the potential energy curves involved (δ).



(*a*) (*b*)

Figure 1. (*a*) Diabatic and (*b*) adiabatic representation of the two crossed harmonic potential curves, representing the intramolecular coupling for different apertures (dot lines).

Each electronic and vibrational state is described by its respective wave function and energy value. Taking a linear combination of the eigenfunctions of each level and solving for the secular determinant, it is always possible to generate the eigenfunctions and eigenvalues of the coupled states (considering – (+) the low (high) new coupled states):

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

$$\Psi^{\pm}(r;R) = \frac{1}{C_{10}^{\pm}}\left[\left|V_{00}\right|\psi_1(r;R)\Phi_{10}(R) \pm \left(E_{10} - E^{\pm}\right)\psi_2(r;R)\Phi_{2k}(R)\right] \tag{2}$$

where the vibrational energies are $E_{10} = 0.5$ and $E_{20} = 0.5\delta + Vo$, $\Delta E = \left(E_{20} - E_{10}\right)$, $V_{00} = v\langle\varphi_{10}\,|\,\varphi_{20}\rangle$, $C_{10}^{\pm} = \left[\left|V_{00}\right|^2 + \left(E_{10} - E^{\pm}\right)^2\right]^{1/2}$, the overlap integral, obtained by the Pekarian formula [15] is given by $\langle\varphi_{10}\,|\,\varphi_{20}\rangle = \frac{(4\delta)^{1/4}}{(1+\delta)^{1/2}}\exp\left\{-\frac{S}{2}\left[1-(1+\delta)^{-1}\right]\right\}$, $\delta = \tilde{\omega}_0 / \omega_0$ and $S = \left(\frac{\tilde{m}\omega_0}{\hbar}\right)R_0^2$. Here, $\tilde{m}$ represents the reduced mass associated with the vibrational modes as described by the molecular coordinate R_0 and frequency ω_0.

In the new basis of coupled states, there exists a new set of dipole moments that are different compared to those in the uncoupled basis. To know the new expressions to the new coupled basis, the following integral should be calculated:

$$m_{ij}(R) = \int \Psi_i^*(r;R)\hat{M}\Psi_j^*(r;R)d^3r \tag{3}$$

where $\hat{M}$ is the total electronic dipole moment operator.

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 [15]. They are in fact described by the following expressions:

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

$$\mu_{aa} = \left\{ \frac{|V_{00}|^2}{2|V_{00}|^2 - \Delta E(E_{10} - E^a)} \right\} \left\{ m_{22} + m_{11} - \frac{2(E_{10} - E^a)m_{12}}{v} \right\} - \frac{(E_{10} - E^a)\Delta E m_{22}}{2|V_{00}|^2 - \Delta E(E_{10} - E^a)} \tag{5}$$

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 on the Macroscopic Polarization, and consequently with the intensity of the signal studied.

2.2 Signal Response

The Liouville formalism is the most common mathematical method employed to study the interaction of the states in the new basis with the electromagnetic field using the macroscopic polarization. The equation $i\hbar\frac{d\rho(t)}{dt} = [H, \rho(t)]$ represents the starting point to obtain the Optical Bloch Equations (OBE), which describe the temporal evolution of the system. In our case, the OBE are obtained by considering the following aspects:

(*a*) Use of a solvent transparent to the radiation, included in the calculation in a phenomenological way; (*b*) consideration of dipole field–matter interaction; (*c*) inclusion of the secular approximation; (*d*) neglecting the Rotating Wave Approximation (RWA), which allows us to study the signal response away from the resonance frequency; (*e*) explicit inclusion of the permanent dipole moments of states in the uncoupled basis, which have been discussed previously [8–12].

Under conditions mentioned above, the OBE assume the following form:

$$\frac{d\rho_{-+}}{dt} = -\frac{i}{\hbar}H_{-+}\rho_D - \frac{i}{\hbar}\rho_{-+}[H_{--} - H_{++}] - \left(\frac{1}{T_2} + i\omega_0\right)\rho_{-+} \tag{6}$$

$$\frac{d\rho_{+-}}{dt} = \frac{i}{\hbar}H_{+-}\rho_D + \frac{i}{\hbar}\rho_{+-}[H_{--} - H_{++}] - \left(\frac{1}{T_2} - i\omega_0\right)\rho_{+-} \tag{7}$$

$$\frac{d\rho_D}{dt} = -\frac{2i}{\hbar}\left(H_{+-}\rho_{-+} - \rho_{+-}H_{-+}\right) - \frac{1}{T_1}\left[\rho_D - \rho_D^0\right] \tag{8}$$

where ρ_{-+}, ρ_{+-} are the coherences elements (non diagonal) of density matrix and ρ_D is the difference between the populations elements (diagonal) of density matrix, respectively.

The above differential equations represent the temporal evolution of the coherence (Eqs. (6) and (7)) and populations (Eq. (8)), and they include a term related to the molecular system (associated with the resonance frequency ω_0), a term related to the field–system interaction (described by the dipole Hamiltonian) and a term related to the relaxation process, characterized by the presence of the longitudinal and transverse relaxation times T_1 and T_2 respectively.

In the present study, we are interested in the FWM spectroscopy as a particular case of a nonlinear response. This 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 between them, to generate a third beam or signal beam with a frequency $\omega_3 = 2\omega_1 - \omega_2$ and propagation vector $\boldsymbol{k}_3 \approx 2\boldsymbol{k}_1 - \boldsymbol{k}_2$.

Considering the OBE established before for this particular case (Eqs (6)–(8)), it is possible to obtain an expression for the magnitude of the polarization, and consequently, for the signal intensity by using the relationship $I = \frac{c\varepsilon}{8\pi}|P|^2$. This expression can be written as:

$$P(\omega_3) = N\langle\mu\rangle = N\begin{pmatrix}\mu_{--} & \mu_{-+}\\ \mu_{+-} & \mu++\end{pmatrix}\begin{pmatrix}\rho_{--} & \rho_{-+}\\ \rho_{+-} & \rho_{++}\end{pmatrix} = N\left[\mu_{-+}\rho_{+-}(\omega_3) + \mu_{+-}\rho_{-+}(\omega_3) - d_{ic}\rho_D(\omega_3)\right] \tag{9}$$

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. Solving the OBE perturbatively (to third order in the total field), we can obtain our final expression for the Macroscopic Polarization on the signal frequency ω_3:

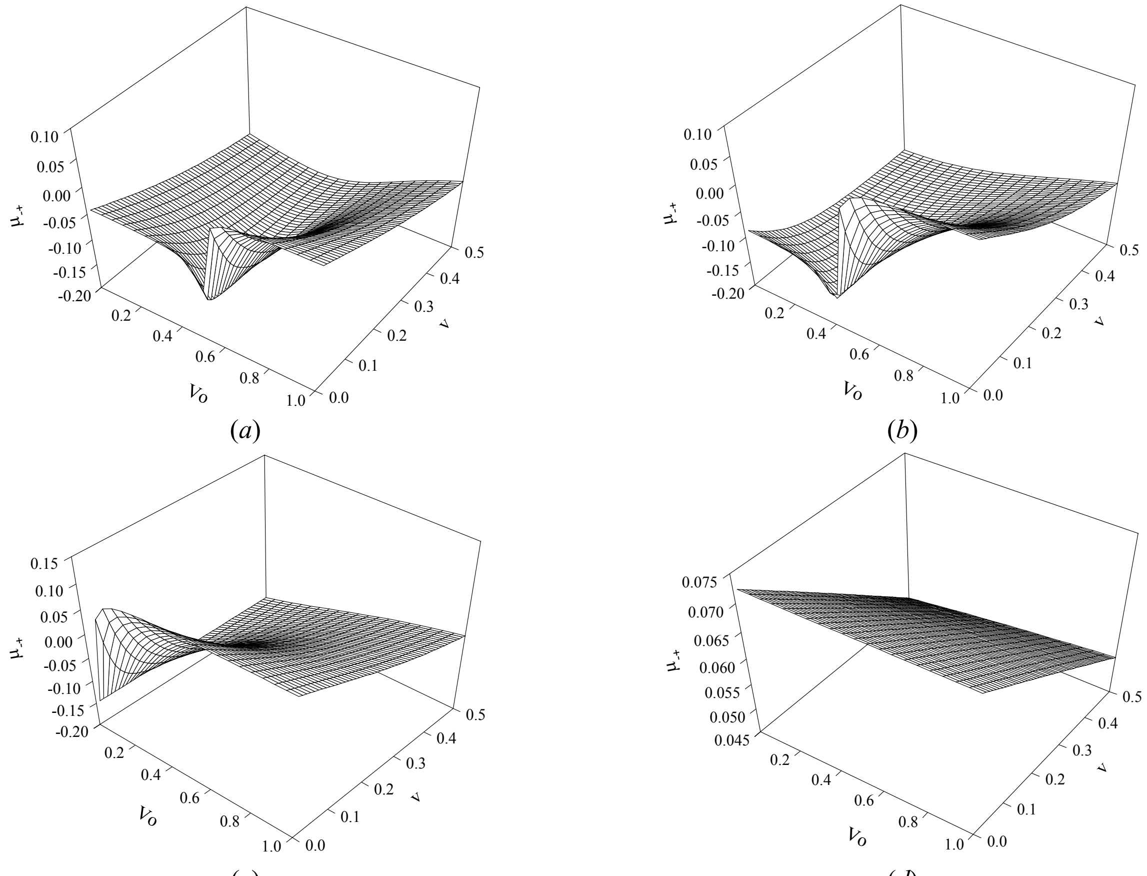
$$\begin{aligned}P(\omega_3) = Ni\rho_D^{(0)}E_1^2E_2^*\Bigg\{&2\mu_{-+}^4\left(\frac{1}{D_3^-} - \frac{1}{\left(D_3^+\right)^*}\right)\left[\frac{1}{\Gamma}\left[\frac{1}{D_2^+} + \frac{1}{D_1^-} + \frac{1}{\left(D_2^-\right)^*} + \frac{1}{\left(D_1^+\right)^*}\right] + \frac{1}{\lambda}\left[\frac{1}{D_1^-} + \frac{1}{\left(D_1^+\right)^*}\right]\right] +\\ &d_{ic}^2\mu_{-+}^2\left[\left(\frac{1}{\beta} - \frac{1}{\left(D_3^+\right)^*}\right)\left[\frac{1}{\left(D_\Delta^+\right)^*\left(D_2^-\right)^*} + \frac{1}{\left(D_1^+\right)^*\left(D_\Delta^+\right)^*} + \frac{1}{\left(D_1^+\right)^*\left(D_5^+\right)^*}\right] + \left(\frac{1}{D_3^-} - \frac{1}{\beta}\right)\left[\frac{1}{D_\Delta^- D_2^+} + \frac{1}{D_1^- D_\Delta^-} + \frac{1}{D_1^- D_5^-}\right]\right]\Bigg\}\end{aligned} \tag{10}$$

where E_1 and E_2 are the pump and probe electromagnetic fields, respectively, $\vec{d} = \vec{\mu}_{--} - \vec{\mu}_{++}$, $\rho_D = \rho_{++} - \rho_{--}$, $\Delta = \omega_1 - \omega_2$, $\Gamma = \frac{i}{T_1} - i(\omega_1 - \omega_2)$, $\beta = \frac{1}{T_1} - i\omega_3$, $\lambda = \frac{1}{T_1} - 2i\omega_1$, $D_j^\pm = \frac{1}{T_2} + i(\omega_0 \pm \omega_j)$,

$D_5^{\pm} = \frac{1}{T_2} + i(\omega_0 \pm 2\omega_1)$ and T_1 and T_2 represent the longitudinal and transverse relaxation times, respectively.

3 RESULTS AND DISCUSSION

In this section some results are shown for the FWM signal response obtained when changes in the coupling parameters v and V_0 occur and taking into account different values of δ. The intramolecular coupling parameters employed in this work were varied in the range of v from 0.01 to 0.5 and V_0 from 0.01 to 1. Other important parameters to be considered are: (*a*) $\omega_0 = 3.0628\times10^{15}$ s^{-1} = 16280 cm^{-1} (resonance frequency of an organic molecule – Malachite Green), (*b*) the longitudinal and transverse relaxation times $T_1 = T_2 = 1.3\times10^{-13}$ s, (*c*) $S = 0.1$, (*d*) $m_{11} = 1$ 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 (*e*) $m_{12} = m_{21} = 0.1$ D for the transition dipole moments of the uncoupled states.



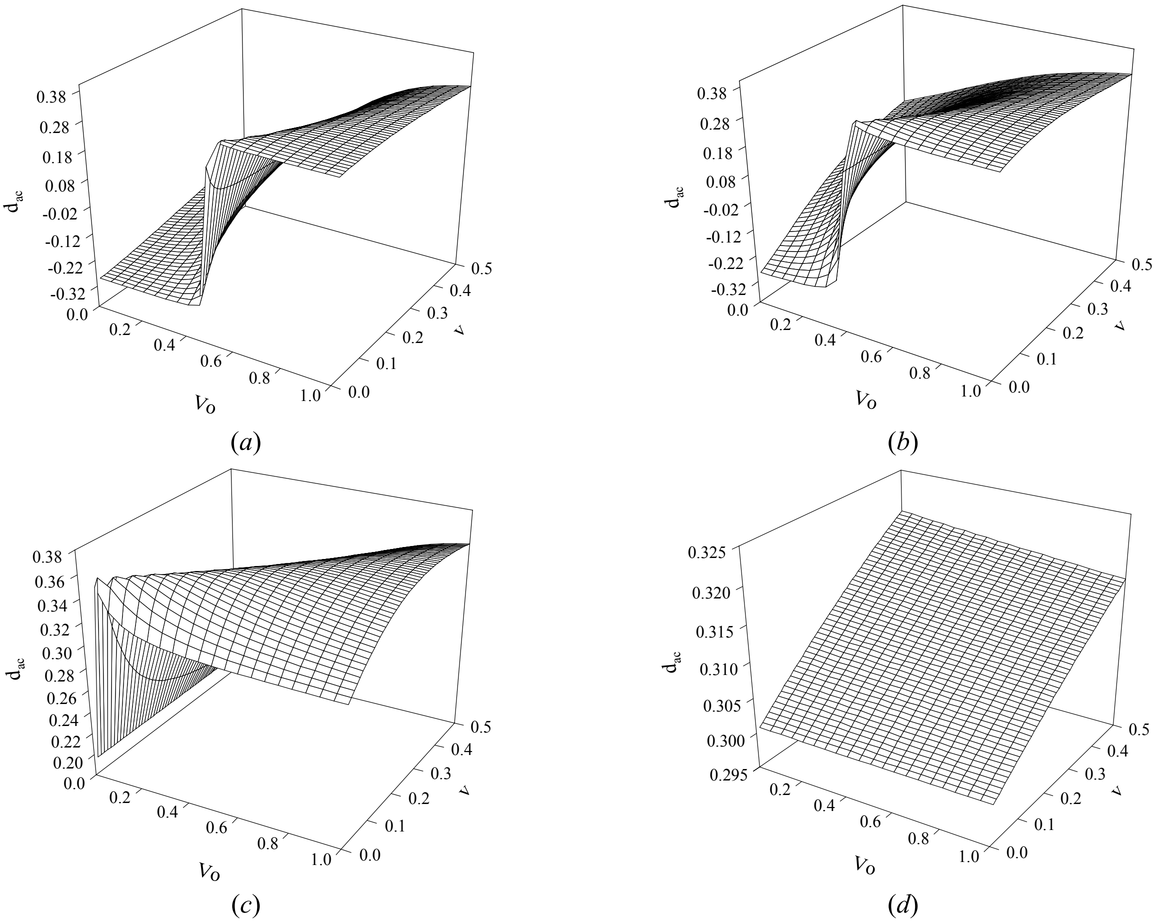
(*a*) (*b*)

(*c*) (*d*)

Figure 2. Transition dipole moments of the coupled states as a function of. the coupling parameters v and V_0 for different values of δ: (*a*) 0.01; (*b*) 0.1; (*c*) 1 and (*d*) 10.

Figures 2 and 3 depict the three–dimensional representation of the transition and permanent dipole moments of the coupled states, respectively, as a function of the coupling parameters v and

V_0, at values of δ changing in different orders of magnitude: (*a*) $\delta = 0.01$, (*b*) $\delta = 0.1$, (*c*) $\delta = 1$ and (*d*) $\delta = 10$. There are two important facts to be mentioned related to these graphs. First, we can observe that the transition and permanent dipole moments vanish for particular values of v, V_0 and δ. In the second place, we find a dramatic change in the behavior of the dipole moments at high values of δ, where they can take constant values for different values of V_0 (transition dipole moments) and for v (permanent dipole moments).



(*a*) (*b*)

(*c*) (*d*)

Figure 3. Permanent dipole moments of the coupled states as a function of the coupling parameters v and V_0 for different values of δ: (*a*) 0.01; (*b*) 0.1; (*c*) 1 and (*d*) 10.

Based on this behavior, it is possible to find mathematical expressions that permit us to establish the values of the parameters δ, v and V_0 for which the dipole moment takes a null value. Inspecting Eqs. (4) and (5) it is possible to find that for the transition dipole moment, the null value is related with the nullity of the term $\left[(m_{11} - m_{22}) + m_{12}\frac{\Delta E}{v}\right]$. Manipulating this difference and substituting for the values of the dipole moments in the uncoupled basis, we find that the nullity of the transition dipole moment is obtained when:

$$\delta = 1 + 6v - 2V_0 \tag{11}$$

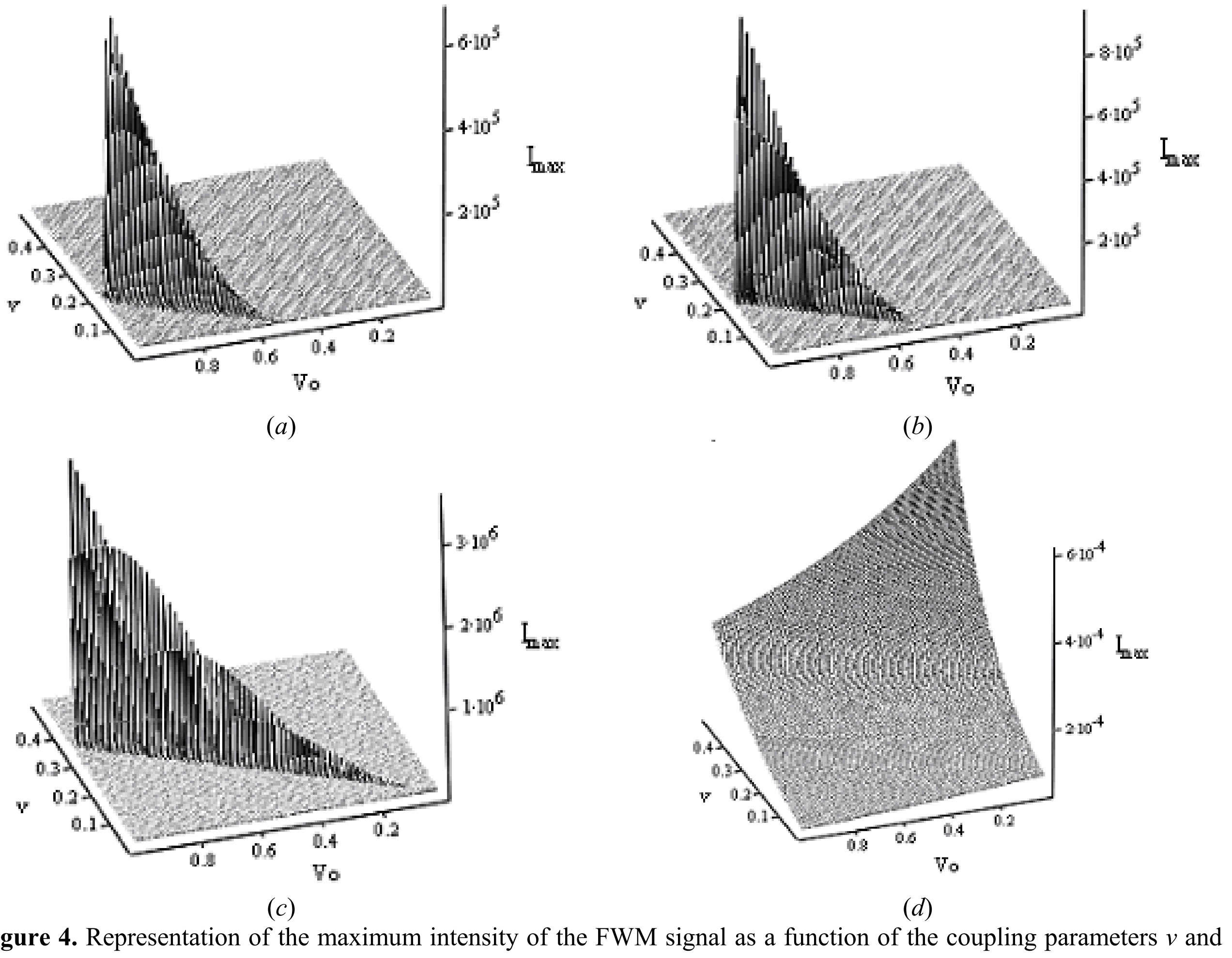
We can proceed in a similar way for the permanent dipole moments. The nullity of Eq. (5), occurs in two cases: (*a*) when $\mu_{--} = \mu_{++}$, and (*b*) when both are zero ($\mu_{--} = \mu_{++} = 0$). Due to the difficulty to find a clear expression for first case, we have payed attention to the second case, *i.e.*, $\mu_{--} = \mu_{++} = 0$, which occures when:

$$\left\{\frac{1}{|V_{00}|^2}\left[-\left(E_{10}-E^a\right)\Delta E+|V_{00}|^2\right]m_{22}+m_{11}-\frac{2\left(E_{10}-E^a\right)m_{12}}{v}\right\}=0 \tag{12}$$

Manipulating this expression after substituting the values of the dipole moments in the uncoupled basis, it is possible to obtain:

$$\begin{aligned}&\left[\frac{1}{8}(\delta-1)^2+\frac{1}{2}V_0\left(V_0+\delta-1\right)+|V_{00}|^2\left(2.3v-0.1\left(\frac{1}{2}-\frac{1}{2}\delta-V_0\right)\right)\right]=\\ &\pm\left[\frac{1}{4}-\frac{1}{4}\delta-\frac{1}{2}V_0-0.1|V_{00}|^2\right]\sqrt{\left(\frac{1}{2}-\frac{1}{2}\delta-V_0\right)^2+4|V_{00}|^2}\end{aligned} \tag{13}$$

It is important to notice that these expressions depend on the parameters v, V_0 and δ. For each value of δ, there exist values of v and V_0 that induce the nullity of the transition and permanent dipole moment of states in the coupled basis. In general, changes generated in the transition and permanent dipole moments of states in the coupled basis due to the variations in the parameters v and V_0 will induce modifications in the FWM signal response.



(*a*) (*b*)

(*c*) (*d*)

Figure 4. Representation of the maximum intensity of the FWM signal as a function of the coupling parameters v and V_0 for different values of parameter δ: (*a*) 0.01; (*b*) 0.1; (*c*) 1 and (*d*) 10.

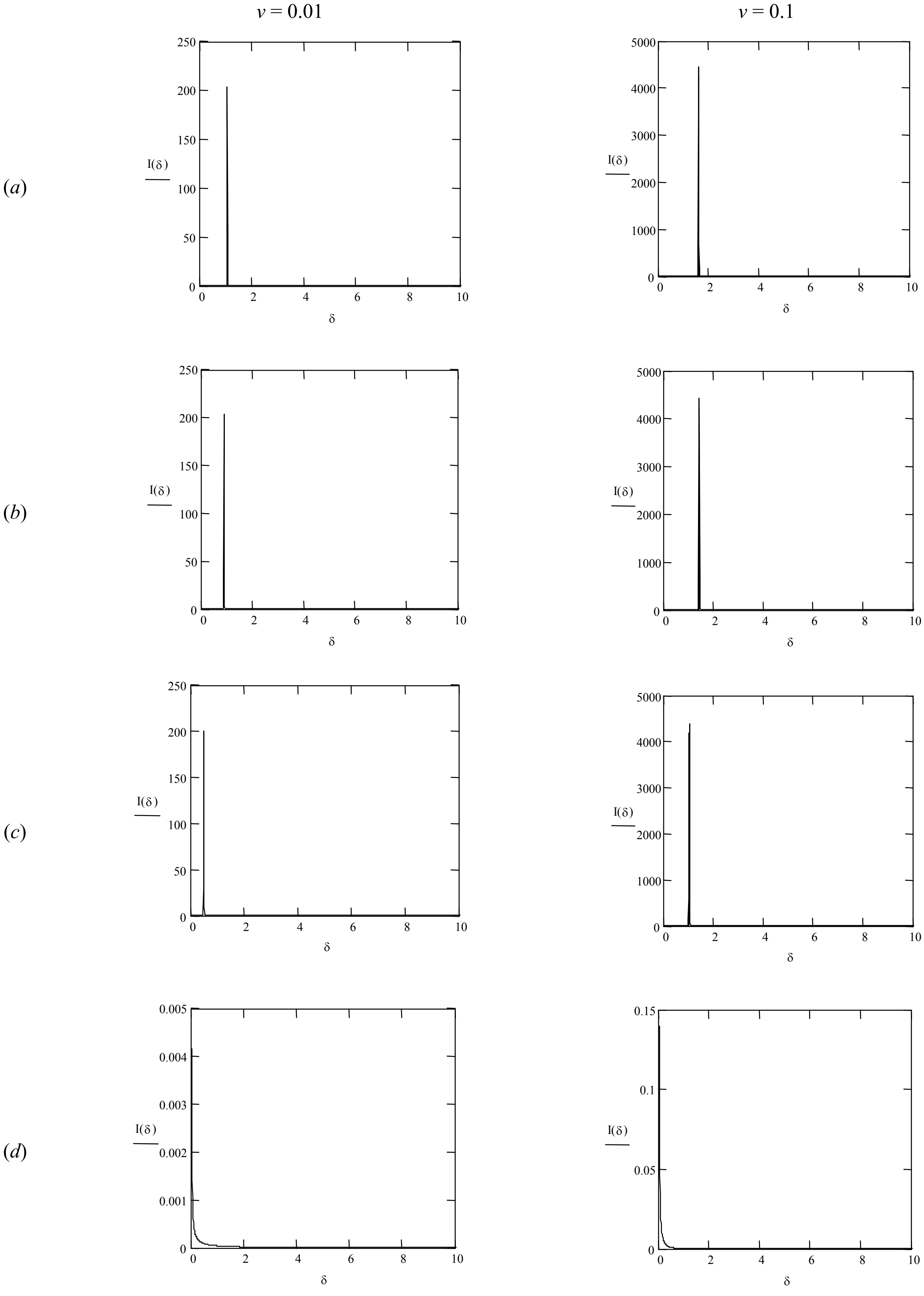


Figure 5. Representation of the maximal intensity of the FWM signal as a function of the strength constant *δ*, for different values of V_0: (*a*) 0.01; (*b*) 0.1; (*c*) 0.3 and (*d*) 1.

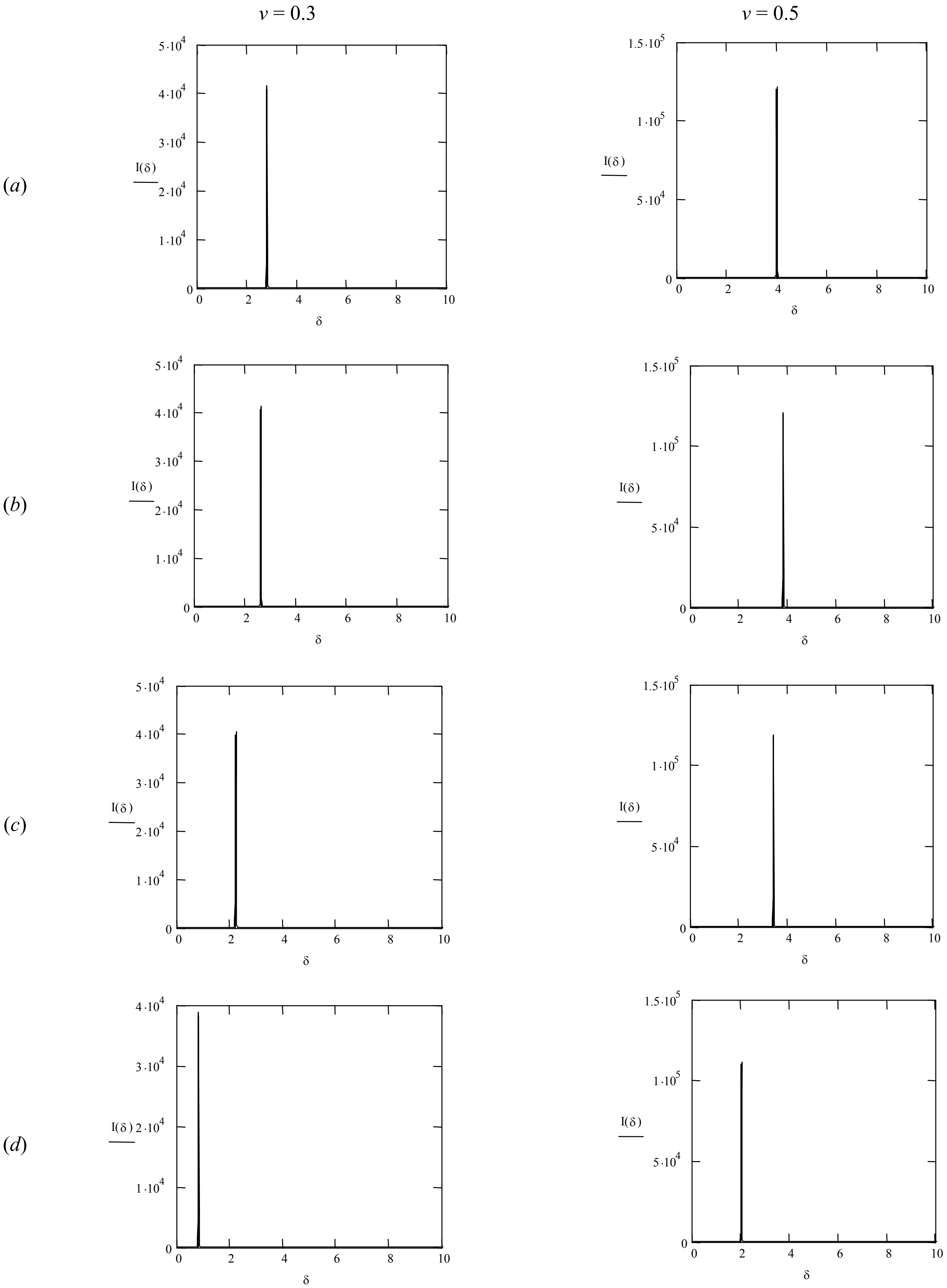


Figure 6. Representation of the maximal intensity of the FWM signal as a function of the strength constant *δ*, for different values of V_0: (*a*) 0.01; (*b*) 0.1; (*c*) 0.3 and (*d*) 1.

In previous works, it was demonstrated that changes in the coupling parameters induce changes in the intensity and position of the resonances presented in the global FWM spectra [13,14]. At present, it is also possible to perform the same detailed study on each resonance in the global spectrum, which would allow us to generalize a common behavior of the FWM response.

When the maximum intensity of each of the peaks is studied, the same general behavior is observed for all the peaks present in the spectrum. For this reason, we only describe the behavior of one resonance in the present work.

Figure 4 depicts the maximum intensity as a function of v and V_0 for different values of δ for the particular peak with characteristic resonance frequencies $\omega_1 = \omega_0$ and $\omega_2 = 2\omega_0$ (see ref. [14]). We can observe that this signal increases its relative area significantly by increasing δ in successive orders of magnitude. In particular for $\delta = 10$, the maximum intensity of the FWM signal reaches a plato as a consequence of a similar behavior on the transition and permanent dipole moments of the coupled states, which changes dramatically for different values of δ.

We can also observe important changes in the FWM signal intensity by representing the maximal intensity of the FWM signal as a function of the strength constant δ for different values of v and V_0, as depicted by Figures 5 and 6. In these cases, we observe an increasing of the intensity with the increase of the parameters v and V_0, together with a displacement on the maximum to higher values of δ. However, if we fix a v value, the signal intensity changes only slightly with the increase of the parameter V_0, except for the case $V_0 = 1$, where the change is more noticeable for small values of v.

Modifications in the coupling parameters produce changes in the potential curves, and consequently, in their crossing. The resonance frequency of the new states changes consecuently and also the nonlinear response of the system. These changes are associated with the behavior of the dipole moments of the states in the new basis, which is influenced by the modification in the charge distribution of the organic molecules with changes in the coupling parameters.

4 CONCLUSIONS

It has been shown that the inclusion of intramolecular coupling on a two–level model of a molecular system leads to changes in the intensity and position of the resonances presented in the global FWM spectra. Moreover, for specific values of v and V_0, it is always possible to reproduce the same global spectrum found when the intramolecular coupling is not taken into account [13,14].

In this work, it was possible to study the specific behavior of the maximum intensity of the FWM signal response under changes of the coupling parameters v, V_0 and δ. These changes are related to modifications in the transition and permanent dipole moments of states in the new coupled basis.

Changes in the behavior of both transition and permanent dipole moments were obtained using different values of the coupling parameters. We were able to find values of the dipole moments, which induce the nullity of the FWM signal at specific values of the vibronic coupling parameters. Mathematical relations are found to describe these results at specific values of the coupling parameters, which generate considerable changes in the FWM signal intensity.

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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). More recently, Dr. Paz has collaborated on projects with Professor José Récamier at the Universidad Nacional de Mexico (UNAM), México, in topics associated to algebraic methods applied to Quantum Optics and Nonlinear Spectroscopy.

Teresa Cusati is currently Research Assistant 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, and after that she collaborated in a group project between the Universidad Simón Bolívar and Universidad Central de Venezuela. Recently, she worked 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.

Antonio J. Hernández is Titular professor of Physical Chemistry at the Universidad Simón Bolivar. Prof. Hernández obtained the Ph.D. degree in Chemistry at the Indiana University (1977). Dr. Hernández has worked on projects about computational and quantum mechanics calculus related to molecules type van der Waals and Nonlinear Spectroscopy.