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Nonperturbative susceptibility of a three-level system interacting with a monochromatic field

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We derive an exact, intensity-dependent expression for the susceptibility of a three-level system interacting with one monochromatic electric field. This expression, once expanded, is equivalent to the usual perturbative series $\chi = \chi^{(1)} + \chi^{(3)}E^2 + \cdots$ within the rotating wave approximation. We consider two types of resonant processes: one- and two-photon resonances corresponding to the intensity-dependent susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$, and one-, two-, and three-photon resonances corresponding to $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$. As an example of current interest, we use a model three-level system that mimics the excited electronic states of typical nonlinear optical polymers and show that near resonance, successive terms in the perturbative series approach the same order of magnitude for experimentally realizable fields.

I. INTRODUCTION

Recent work on the higher-order susceptibilities of conjugated systems has increased interest in finding new methods for calculating these quantities.[1,2] The response of a system interacting with a field is usually expanded as a power series in that field.[3-5] This perturbative treatment, which yields the standard expressions for the susceptibilities $\chi^{(1)}$, $\chi^{(3)}$,..., is a good representation for weak field strengths except near resonance, where the energy denominators in the perturbation terms vanish, making it necessary to introduce excited state lifetimes or complex frequencies. For intense fields, however, terms in the perturbation expansion approach one another in magnitude, suggesting that another representation of the response is more accurate.

Recently, Wang and Chu[6] have presented an exact nonperturbative method for calculating intensity-dependent nonlinear optical susceptibilities for a two-level system. While two-level systems interacting with external fields are very useful for understanding near-resonance phenomena, a model with more than two levels is needed to describe the behavior of the polarizabilities with the electric field both near and far from resonance.

Previous work on nonperturbative susceptibilities of three-level systems has focused on the interaction of a strong field that is one-photon resonant with a three-level system.[7] In this paper, we will derive an exact, nonperturbative expression for the susceptibility χ using a three-level system in which all resonant fields are treated nonperturbatively. This expression, once expanded, is equivalent to the usual series $\chi = \chi^{(1)} + \chi^{(3)}E^2 + \cdots$ (in a centrosymmetric system), where E is the electric field amplitude. This method also lends itself to many-level models. Since this is a nonperturbative expression and thus includes all higher-order terms in the usual expansion, it does not lead to a divergence of the susceptibility near resonance.

Interest in the nonlinear optical properties of organic polymers has led to experimental measurements of the higher-order susceptibilities on a variety of these materials.[1] Most work has focused on the first nonlinear optical coefficient $\chi^{(3)}$. Here, we will use model systems that mimic polymeric systems, with typical values for the intensity of the electric field, the transition dipole moment, and energy levels (e.g., from calculations on *trans* octatetraene[2]). We will show that successive terms in the susceptibility series can approach the same order of magnitude, indicating that a perturbative calculation fails. In fact, recent experimental studies of the power dependence of the outgoing or phase conjugate signal of a degenerate four wave mixing experiment using an organic dye showed that the intensity deviates from the predicted or perturbative value,[8] indicating that the perturbation description of the intensity-dependent susceptibility is not always adequate. Recent work on condensed phase materials has also suggested that higher-order nonlinear susceptibilities may lead to important effects such as line narrowing.[9]

We will proceed as follows. In Sec. II, we will review Floquet theory, which transforms the time-dependent Hamiltonian into a time-independent eigenvalue equation.[10,11] The resulting pseudoeigenvalues can be expanded in the electric field to yield the typical expansion for the susceptibility. To avoid solving cubic (and higher)-order equations for the eigenvalues in the latter approach, we instead use a density matrix approach allowing the susceptibility to be calculated without recourse to perturbation theory. In Sec. III, we will set up a Floquet–Liouville supermatrix description of a three-level system interacting with one electric field.[11-13] We work within the rotating wave approximation (RWA); however, by using perturbation theory,[6,13] contributions from the antirotating part of the electric field can also incorporated, as shown in Sec. III C. By solving the three-level Liouville equation for the density matrix in the steady state limit, we can write down the polarizability and thus the exact, intensity-dependent susceptibility for the three-level system. Upon expansion, we show that this can be reduced to the usual power series. Two types of resonant processes are addressed—one- and two-photon responses corresponding

to terms such as the intensity-dependent refractive index term $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ in the series expansion, and the three-photon response of a three-level system corresponding to the third harmonic generation term $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$.

In Sec. IV, we will use our exact solution for the susceptibility to calculate the the nonlinear response for model systems that mimic typical conjugated systems, considering one-, two-, and three-photon responses.

II. FLOQUET THEORY

Floquet theory can be used to transform a time-dependent Hamiltonian to a time-independent eigenvalue problem. One requirement for this technique is that the time-dependent part of the Hamiltonian is periodic in time, such as a system perturbed by classical electromagnetic fields with a single frequency. We consider a system with a perturbation due to one electric field since we are interested in the nonlinear corrections to the linear susceptibility, such as $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$. However, this technique can been used to describe systems interacting with multichromatic fields such as coherent anti-Stokes Raman spectroscopy (CARS).[3-5]

Here we briefly review Floquet theory.[10,11] The Schrödinger equation is

$$\left[H(\mathbf{r},t)-i\frac{\partial}{\partial t}\right]\Psi(\mathbf{r},t)=0, \tag{1}$$

where $\hbar=1$ and $H(\mathbf{r},t)$ is

$$H(\mathbf{r},t)=H_0(\mathbf{r})+V(\mathbf{r},t). \tag{2}$$

H_0 is the unperturbed, time-independent Hamiltonian with eigenfunctions $|\alpha(\mathbf{r})\rangle$ and $V(\mathbf{r},t)$ is the periodic perturbation due to the interaction between the dipole moment and the electric field. The perturbation can be written as

$$V(\mathbf{r},t)=-\mu(\mathbf{r})E\cos(\omega t+\phi), \tag{3}$$

where $\mu(\mathbf{r})$ is the electric dipole moment operator, E is the amplitude of the electric field, and ω and ϕ are the frequency and initial phases, respectively, of the electric field. We will assume $\phi=0$.

Now we invoke the Floquet theorem, which ensures that for a periodic Hamiltonian H, the wave function Ψ can be written as

$$\Psi(\mathbf{r},t)=\exp(-i\epsilon t)\Phi(\mathbf{r},t), \tag{4}$$

where $\Phi(\mathbf{r},t)$ is periodic in time with frequency ω and ϵ is the quasienergy. We can expand Ψ in a Fourier series as

$$\Psi_\alpha(\mathbf{r},t)=\exp(-i\epsilon_\alpha t)\sum_{n=-\infty}^{\infty}C_\alpha^{(n)}(\mathbf{r})\exp(-in\omega t). \tag{5}$$

The index α corresponds to the eigenstate of the unperturbed Hamiltonian. $C_\alpha^{(n)}$ can again be expanded in terms of the unperturbed eigenfunctions of $H_0(\mathbf{r})$,

$$C_\alpha^{(n)}(\mathbf{r})=\sum_\beta \Phi_{\alpha\beta}^{(n)}|\beta(\mathbf{r})\rangle. \tag{6}$$

Using Eqs. (5) and (6), and substituting into Eq. (1), a system of equations is obtained

$$\sum_n\sum_\beta\left[\langle\gamma|\hat{H}^{(m-n)}|\beta\rangle-(\epsilon_\alpha+m\omega)\delta_{mn}\delta_{\gamma\beta}\right]\Phi_{\alpha\beta}^{(n)}=0, \tag{7}$$

where

$$\hat{H}^{(q)}(\mathbf{r})\equiv\frac{\omega}{2\pi}\int_0^{2\pi/\omega}\hat{H}(\mathbf{r},t)\exp(iq\omega t)dt. \tag{8}$$

With the perturbation given by Eq. (3), the only nonzero matrix elements are $q=0,\ \pm 1$.

If we use the Floquet state nomenclature[10] $|\gamma n\rangle\equiv|\gamma\rangle|n\rangle$, where γ is the index of the unperturbed system and n is the Fourier series index, we can rewrite Eq. (7) as

$$\sum_\beta\sum_m\langle\gamma n|\hat{H}_F|\beta m\rangle\Phi_{\beta\alpha}^{(m)}=\epsilon_\alpha\Phi_{\gamma\alpha}^{(n)}, \tag{9}$$

where the matrix elements of $\hat{H}_F$ are simply

$$\langle\alpha n|\hat{H}_F|\beta m\rangle=\hat{H}_{\alpha\beta}^{(n-m)}+n\omega\delta_{\alpha\beta}\delta_{nm}. \tag{10}$$

We now have a time-independent infinite matrix eigenproblem. A system interacting with more than one field can also be transformed to a time-independent problem using an exact extension of Floquet theory.[14] For a system interacting with two fields, the matrix problem can be written as

$$\sum_{\gamma_2}\sum_{k_1}\sum_{k_2}\langle\gamma_1 n_1 n_2|\hat{H}_F|\gamma_2 k_1 k_2\rangle\langle\gamma_2 k_1 k_2|\lambda\rangle=\lambda\langle\gamma_2 n_1 n_2|\lambda\rangle, \tag{11}$$

with

$$\langle\gamma_1 n_1 n_2|\hat{H}_F|\gamma_2 k_1 k_2\rangle=H_{\gamma_1\gamma_2}^{(n_1-k_1,n_2-k_2)}+(n_1\omega_1+n_2\omega_2)\delta_{\gamma_1\gamma_2}\delta_{n_1k_1}\delta_{n_2k_2}, \tag{12}$$

where

$$H_{\gamma_1\gamma_2}^{(n_1,n_2)}=E_{\lambda_1}\delta_{\gamma_1\gamma_2}\delta_{n_10}\delta_{n_20}+\sum_{i=1}^{2}V_{\lambda_1\lambda_2}^{(i)}(\delta_{n_i1}+\delta_{n_i-1}),$$
$$V_{\lambda_1\lambda_2}^{(i)}=-\tfrac{1}{2}E_i\langle\gamma_1|\mu|\gamma_2\rangle. \tag{13}$$

In order to reduce these infinite matrix problems to one we can solve analytically, we define a model space that encompasses the most important parts of the Floquet matrix.

A resonant three-level system (Fig. 1) can be adapted to model the most important features of a centrosymmetric system. States $|a\rangle$ and $|c\rangle$ are of the same symmetry and consequently have a zero transition dipole moment between them. State $|b\rangle$ has opposite symmetry and has nonzero transition

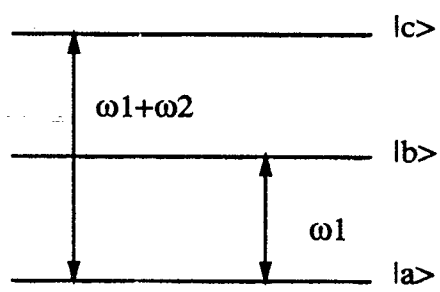

FIG. 1. The three-level system described in Sec. II. The transition dipoles are μ_{ab}, $\mu_{bc}\neq 0$, and $\mu_{ca}=0$.

dipole moments to both $|a\rangle$ and $|c\rangle$. State $|b\rangle$ can either be above $|c\rangle$ in energy, or below (or the same), so that this three-level system can correctly model polymers such as polyacetylene, which have an excited state of the same symmetry as the ground state below the first allowed state.[1] Since a direct transition between state $|c\rangle$ and state $|a\rangle$ is not allowed, and our model does not allow a transition moment such as $\langle b|\mu|b\rangle$, the total susceptibility will not have contributions from even powers of E, i.e., $\chi^{(2n)}=0$. Note that the diagonal matrix elements of H_F are equal to $\langle \alpha nm|\hat{H}_F|\alpha nm\rangle = \epsilon_\alpha + n\omega + m\omega$. Thus, there will be approximate degeneracies in the zeroth-order problem (defined by the diagonal elements). For example, $|anm\rangle$ and $|b\ n-1\ m\rangle$ will be degenerate for a resonant frequency $\omega_1 = \epsilon_b - \epsilon_a$. Here we only consider one- and two-photon resonances, but this technique can be easily extended to include multiphoton processes.[6,11]

In order to truncate the infinite matrix, we only consider the three states $|anm\rangle$, $|b\ n-1\ m\rangle$, and $|c\ n-1\ m-1\rangle$, which are nearly degenerate. Then the infinite Floquet matrix for the three-level system in Figure 1 reduces to a 3×3 matrix

$$\hat{H}_F = \begin{pmatrix} 0 & b_{12}^{(1)} & 0 \\ b_{12}^{(1)} & \Delta_{ba} & b_{23}^{(2)} \\ 0 & b_{23}^{(2)} & \Delta_{ca} \end{pmatrix}, \tag{14}$$

where

$$\Delta_{ba} = \omega_{ba} - \omega_1, \tag{15}$$

$$\Delta_{ca} = \omega_{ca} - \omega_1 - \omega_2, \tag{16}$$

$$b_{\alpha\beta}^{(i)} = -\tfrac{1}{2}\langle\alpha|\mu\cdot\mathbf{E}^{(i)}|\beta\rangle. \tag{17}$$

To obtain Eqs. (14)–(17), we have used the RWA for the electric field. However, the RWA can be corrected using perturbation corrections,[6,11] as shown in Sec. III C.

Since we are interested in the interaction of a three-level system with a single frequency electric field, we will assume $\omega_1 = \omega_2 = \omega$ and $E^{(1)} = E^{(2)} = E$ throughout. Using this assumption, the Floquet basis set for the three-level system can be written as $|an\rangle$, $|b\ n-1\rangle$, and $|c\ n-2\rangle$.

To extract an expression for polarizabilities, the cubic equation represented by Eqs. (11) and (14) must be used to solve for the pseudoenergies. The pseudoenergies are a function of the electric field E, and by expanding the pseudoenergies about E, one can obtain the expressions for $\chi^{(1)}$, $\chi^{(3)}$, etc.[15,16] However, solving a cubic equation is tedious, even with symbolic manipulation software. If we proceed to a density matrix approach, via the Liouville equation, and incorporate the Floquet theory techniques presented in this section, the susceptibility can be written down exactly, with no recourse to a perturbation expansion about the electric field E. This technique will also enable us to consider the effects of decay rates and collisional damping on near-resonant susceptibility in a straightforward manner.

III. FLOQUET–LIOUVILLE SUPERMATRIX APPROACH

A. One- and two-photon processes

Several workers[6,7,12] have used a density matrix approach to describe susceptibility. Wang and Chu[6] have used a density matrix formalism together with Floquet theory, which enabled them to describe the *exact* susceptibility of a two-level system. Below we will show how the Floquet–Liouville supermatrix, which describes the evolution of the density matrix, can be related to the susceptibility of three (and higher)-level systems.

In this subsection, we will outline this approach and apply it to one- and two-photon resonant, three-level systems. This leads to terms which have an analogy to the intensity-dependent refractive index, related to the third-order susceptibility $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$. In Sec. III B, we will describe a one-, two-, and three-photon resonant, three-level system with analogy to the third harmonic generation susceptibility term $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$. We will discuss antirotating wave contributions in Sec. III C.

The susceptibility is calculated through the polarization density $\mathbf{P}(t)$, which is the induced electric dipole moment per unit volume of a system. $\mathbf{P}(t)$ can be calculated from the density matrix operator $\rho(t)$,

$$\langle\mathbf{P}(t)\rangle = N_0\langle\boldsymbol{\mu}\rangle = N_0\,\mathrm{Tr}[\boldsymbol{\mu}\boldsymbol{\rho}(t)], \tag{18}$$

where N_0 is the number density (we will use $N_0 = 1$) and the time development of $\rho(t)$ is given by the Liouville equation

$$i\frac{\partial\rho}{\partial t} = [\hat{H}(t),\ \rho(t)] + i[\hat{R},\ \rho(t)], \tag{19}$$

where we have introduced a relaxation term in the dynamics.

We have incorporated Floquet theory into Eq. (19), so H is given by Eq. (11), and for a three-level system, by Eq. (14). Thus the time dependence of ρ due to the field frequency ω has been taken into account by using the Floquet Hamiltonian H_F. The relaxation term $[\hat{R},\rho(t)]$ can be approximated as[7,12]

$$[\hat{R},\ \rho(t)]_{\alpha\alpha} = -\Gamma_{\alpha\alpha}\rho_{\alpha\alpha} + \sum_{\beta(\neq\alpha)}\gamma_{\beta\alpha}\rho_{\beta\beta}\ \ (T_1\ \text{process}), \tag{20}$$

$$[\hat{R},\ \rho(t)]_{\alpha\beta} = -\Gamma_{\alpha\beta}\rho_{\alpha\beta},\quad \alpha\neq\beta\ \ (T_2\ \text{process}), \tag{21}$$

where the T_1 processes are the population damping mechanisms and the T_2 processes are the coherence damping mechanisms. The decay rates are related by

$$\Gamma_{\alpha\beta} = \tfrac{1}{2}(\Gamma_{\alpha\alpha} + \Gamma_{\beta\beta}) + \Gamma'_{\alpha\beta} \tag{22}$$

and

$$\Gamma_{\alpha\beta} = \Gamma_{\beta\alpha}. \tag{23}$$

Here, we set the pure dephasing factor $\Gamma'_{\alpha\beta} = 0$ and also assume a closed system, so that feeding rates $\gamma_{\alpha\beta}$ can be related to the decay constants by

$$\Gamma_{\alpha\alpha} = \sum_{\beta\neq\alpha}\gamma_{\alpha\beta}. \tag{24}$$

Equation (19) can be transformed into a time-independent infinite dimensional supereigenvalue equation, spanned by the Floquet–Liouville basis set $|\alpha\beta;\{m\}\rangle \equiv |\alpha\rangle\langle\beta|\otimes|\{m\}\rangle$, where $\{m\}$ is the set of Fourier indices and $|\alpha\rangle$, $|\beta\rangle$ are the eigenfunctions of the unperturbed Hamiltonian H_0 in Eq. (2). We assume that $\rho(t)$ varies slowly in time compared to $2\pi/\omega$.

We can reduce the dimensionality of this problem to a three-level system spanned by the Floquet–Liouville basis set $|aa;\,0\rangle$ $|bb;\,0\rangle$ $|cc;\,0\rangle$ $|ab;\,-1\rangle$ $|ba;\,+1\rangle$ $|bc;\,-1\rangle$ $|cb;\,+1\rangle$ $|ac;\,-2\rangle$ $|ac;\,+2\rangle$ by invoking the RWA. Here we are only including one- and two-photon resonant terms, and consequently the susceptibility will only contain intensity-dependent terms such as $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ with no contributions from three-photon resonant terms such as $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$. We will address three-photon resonant terms in the next subsection.

Since we are including population and coherence damping mechanisms, we must also consider the one-photon resonance between state $|b\rangle$ and state $|c\rangle$. We can now rewrite Eq. (19) as

$$i\frac{\partial\rho}{\partial t}=\hat{L}_F\rho(t), \tag{25}$$

where, for a three-level system, in which $\mu_{ab},\mu_{bc}\neq 0$, and $\mu_{ac}=0$, $\hat{L}_F$ has the form

$$\hat{L}_F=\begin{bmatrix} -i\gamma_{ab} & i\gamma_{ba} & 0 & -u_{ab} & u_{ab} & 0 & 0 & 0 & 0 \\ i\gamma_{ab} & -i(\gamma_{ba}+\gamma_{bc}) & i\gamma_{cb} & u_{ab} & -u_{ab} & 0 & 0 & -u_{bc} & u_{bc} \\ 0 & i\gamma_{bc} & -i\gamma_{cb} & 0 & 0 & 0 & 0 & u_{bc} & -u_{bc} \\ -u_{ab} & u_{ab} & 0 & -\Delta_{ba}-i\Gamma_{ba} & 0 & -u_{bc} & 0 & 0 & 0 \\ u_{ab} & -u_{ab} & 0 & 0 & \Delta_{ba}-i\Gamma_{ba} & 0 & u_{bc} & 0 & 0 \\ 0 & 0 & 0 & -u_{bc} & 0 & -\Delta_{ca}-i\Gamma_{ca} & 0 & -u_{ab} & 0 \\ 0 & 0 & 0 & 0 & u_{bc} & 0 & \Delta_{ca}-i\Gamma_{ca} & 0 & u_{ab} \\ 0 & -u_{bc} & u_{bc} & 0 & 0 & -u_{ab} & 0 & -\Delta_{cb}-i\Gamma_{bc} & 0 \\ 0 & u_{bc} & -u_{bc} & 0 & 0 & 0 & u_{ab} & 0 & \Delta_{cb}-i\Gamma_{bc}, \end{bmatrix} \tag{26}$$

where

$$u_{ab}=-\tfrac{1}{2}\langle a|\mu_{ab}\cdot\mathbf{E}|b\rangle,\quad u_{bc}=-\tfrac{1}{2}\langle b|\mu_{bc}\cdot\mathbf{E}|c\rangle \tag{27}$$

and the detuning Δ_{ba} and Δ_{ca} are given by Eqs. (15) and (16), and $\Delta_{cb}=\omega_{cb}-\omega$.

Previous workers[7,12] have considered a similar problem to one described by Eqs. (25) and (26); however, the formalism of Sec. II enables us to calculate the density matrix directly rather than using a perturbation expansion. For a three-level system, Eq. (18) can be written as

$$\langle\mathbf{P}\rangle=N_0(\mu_{ba}\rho_{ab}+\mu_{ca}\rho_{ac}+\mu_{ab}\rho_{ba}+\mu_{ac}\rho_{ca}+\mu_{cb}\rho_{bc}+\mu_{bc}\rho_{cb}). \tag{28}$$

Since the three-level system in Fig. 1 has $\mu_{ac}=0$, the only nonzero contributions in Eq. (28) stem from the terms $\mu_{ab}\rho_{ba}$ and $\mu_{bc}\rho_{cb}$.

We will assume a steady state approximation to solve Eq. (25). This is appropriate for radiation from a continuous wave source, or pulsed radiation with a pulse duration longer than the decay rates [Eqs. (22)–(24)]. For short pulses, with a pulse duration shorter than the decay rates, transient effects may become important and, consequently, the susceptibilities will become a time-varying function of excitation and relaxation. We will neglect these effects here.

We will assume that the only the ground state is populated initially. Since we only need two elements of the solution vector ρ_{ba} and ρ_{cb}, the determinant and matrix inversion necessary is easily accomplished analytically using symbolic manipulation software.

Using the relation

$$\chi(\omega)=P(\omega)/E(\omega), \tag{29}$$

the total susceptibility of the three-level system given by Fig. 1, interacting with one electric field (within the RWA), can be written as

$$\chi(\omega)_{ba}=\frac{AE^4+BE^2+16\gamma_{ba}\gamma_{cb}(i\Gamma_{ba}+\Delta_{ba})(\Gamma_{cb}^2+\Delta_{cb}^2)(\Gamma_{ca}^2+\Delta_{ca}^2)\mu_{ab}^2}{XE^6+YE^4+ZE^2+32\gamma_{ba}\gamma_{cb}(\Gamma_{ba}^2+\Delta_{ba}^2)(\Gamma_{cb}^2+\Delta_{cb}^2)(\Gamma_{ca}^2+\Delta_{ca}^2)}, \tag{30}$$

$$\chi(\omega)_{cb}=\frac{CE^4+DE^2}{XE^6+YE^4+ZE^2+32\gamma_{ba}\gamma_{cb}(\Gamma_{ba}^2+\Delta_{ba}^2)(\Gamma_{cb}^2+\Delta_{cb}^2)(\Gamma_{ca}^2+\Delta_{ca}^2)}, \tag{31}$$

where $\chi(\omega)_{ba}$ stems from $\mu_{ab}\rho_{ba}$ in Eq. (28) and $\chi(\omega)_{cb}$ stems from $\mu_{bc}\rho_{cb}$. The total susceptibility is simply $\chi(\omega)_{ba}+\chi(\omega)_{cb}$. The coefficients of the electric field-dependent terms in Eqs. (30) and (31) are

$$\begin{aligned}A=&[\gamma_{cb}\gamma_{ba}(i\Gamma_{ba}+\Delta_{ba})]\mu_{ab}^6+[2\gamma_{ba}\Gamma_{bc}(i\Gamma_{ca}-\Delta_{ca})]\mu_{ab}^2\mu_{bc}^4+[2\gamma_{ba}\Gamma_{ca}(i\Gamma_{ba}+\Delta_{ba})\\&+\gamma_{ba}\gamma_{cb}(i\Gamma_{cb}+\Delta_{cb})+2\gamma_{cb}(\Gamma_{ca}\Delta_{cb}+\Delta_{ca}\Gamma_{cb})]\mu_{ab}^4\mu_{bc}^2,\end{aligned} \tag{32}$$

$$\begin{aligned}B=&[8\gamma_{ba}\gamma_{cb}(i\Gamma_{ba}+\Delta_{ba})(\Gamma_{bc}\Gamma_{ca}-\Delta_{cb}\Delta_{ac})]\mu_{ab}^4\\&+[8\gamma_{ba}\Gamma_{cb}(i\Gamma_{ba}+\Delta_{ba})(\Gamma_{ca}^2+\Delta_{ca}^2)+4\gamma_{ba}\gamma_{cb}(i\Gamma_{ca}-\Delta_{ca})(\Gamma_{cb}^2+\Delta_{cb}^2)\mu_{ab}^2\mu_{bc}^2,\end{aligned} \tag{33}$$

$$C = [2\gamma_{cb}\Gamma_{ca}(i\Gamma_{cb} + \Delta_{cb}) + 2\gamma_{ba}\Gamma_{ca}\Delta_{ba} + \gamma_{ba}\gamma_{cb}(i\Gamma_{cb} + \Delta_{cb}) + 2\Delta_{ca}\gamma_{ba}\Gamma_{ba}]\mu_{ab}^2\mu_{bc}^4 + [2\gamma_{cb}\Gamma_{ba}(i\Gamma_{ca} - \Delta_{ca}) + \gamma_{ba}\gamma_{cb}(i\Gamma_{ba} + \Delta_{ba})]\mu_{ab}^4\mu_{bc}^2, \tag{34}$$

$$D = [8\gamma_{cb}\Gamma_{ba}(i\Gamma_{cb} + \Delta_{cb})(\Gamma_{ca}^2 + \Delta_{ca}^2) + 4\gamma_{ba}\gamma_{cb}(-i\Delta_{ba} + \Gamma_{ba})(\Gamma_{cb} + i\Delta_{cb})(i\Gamma_{ca} + \Delta_{ca})]\mu_{ab}^2\mu_{bc}^2, \tag{35}$$

$$X = \gamma_{ba}\Gamma_{cb}\mu_{bc}^6 + 2\gamma_{cb}\Gamma_{ba}\mu_{ab}^6 + [6\Gamma_{cb}\Gamma_{ca} + (\gamma_{ba} - \gamma_{cb})\Gamma_{bc} + \gamma_{ba}\Gamma_{ba}]\mu_{ab}^2\mu_{bc}^4 + [6\Gamma_{ba}\Gamma_{ca} + (\gamma_{ba} - \gamma_{cb})\Gamma_{ba} + 2\gamma_{cb}\Gamma_{cb}]\mu_{ab}^4\mu_{bc}^2, \tag{36}$$

$$\begin{aligned} Y = {} & [8\gamma_{ba}\Gamma_{bc}(\Gamma_{ba}\Gamma_{ca} - \Delta_{ba}\Delta_{ca}) + 2\gamma_{ba}\gamma_{cb}(\Gamma_{cb}^2 + \Delta_{cb}^2)]\mu_{bc}^4 + [16\gamma_{cb}\Gamma_{ba}(\Gamma_{cb}\Gamma_{ca} - \Delta_{ca}\Delta_{cb}) \\ & + 2\gamma_{ba}\gamma_{cb}(\Gamma_{ba}^2 + \Delta_{ba}^2)]\mu_{ba}^4 + [8\gamma_{cb}\Gamma_{ca}(\Gamma_{cb}^2 + \Delta_{cb}^2) + 24\Gamma_{ba}\Gamma_{cb}(\Gamma_{ca}^2 + \Delta_{ca}^2) + 4\gamma_{ba}\Gamma_{ca}(\Gamma_{ba}^2 + \Delta_{ba}^2) \\ & + 4\Delta_{ca}\Delta_{cb}\Gamma_{ba}(\gamma_{cb} - \gamma_{ba}) + 4\Delta_{ba}\Delta_{ca}(\gamma_{cb} - \gamma_{ba})\Gamma_{cb} + 4(\gamma_{ba} - \gamma_{cb})\Gamma_{ca}(\Gamma_{ba}\Gamma_{cb} - \Delta_{ba}\Delta_{cb}) \\ & + 4\gamma_{ba}\gamma_{cb}(\Gamma_{ba}\Gamma_{cb} - \Delta_{ba}\Delta_{cb})]\mu_{ab}^2\mu_{bc}^2, \end{aligned} \tag{37}$$

$$\begin{aligned} Z = {} & [16\gamma_{ba}\gamma_{cb}(\Gamma_{ba}\Gamma_{ca} - \Delta_{ba}\Delta_{ca})(\Gamma_{cb}^2 + \Delta_{cb}^2) + 16\gamma_{ba}\Gamma_{cb}(\Gamma_{ba}^2 + \Delta_{ba}^2)(\Gamma_{ca}^2 + \Delta_{ca}^2)]\mu_{bc}^2 \\ & + [16\gamma_{cb}\gamma_{ba}(\Gamma_{cb}\Gamma_{ca} - \Delta_{ca}\Delta_{cb})(\Gamma_{ba}^2 + \Delta_{ba}^2) + 32\gamma_{cb}\Gamma_{ba}(\Gamma_{cb}^2 + \Delta_{cb}^2)(\Gamma_{ca}^2 + \Delta_{ca}^2)]\mu_{ab}^2. \end{aligned} \tag{38}$$

Note that Eqs. (30) and (31) are only valid for pure radiative decay, which, e.g., implies $\gamma_{ab} = 0$ and $\Gamma_{ba} = \frac{1}{2}\gamma_{ba}$, where γ_{ba} is the spontaneous decay rate from state $|b\rangle$ to the ground state $|a\rangle$. However, generalizing the result to include other decay processes is straightforward, if tedious.

We can expand Eqs. (30) and (31) to obtain the usual series expansion in terms of the electric field E for $\chi(\omega)$,

$$\chi(\omega) = \chi^{(1)}(\omega) + \chi^{(3)}(-\omega;\omega,-\omega,\omega)E^2 + \cdots, \tag{39}$$

where

$$\chi^{(1)}(-\omega;\omega) = \frac{\mu_{ab}^2}{2(\Delta_{ba} - i\Gamma_{ba})}, \tag{40}$$

$$\begin{aligned} \chi^{(3)}(-\omega;\omega,-\omega,\omega) & = \frac{\mu_{ab}^2\mu_{bc}^2}{8(\Delta_{ba} - i\Gamma_{ba})^2(\Delta_{ca} - i\Gamma_{ca})} \\ & - \frac{4\mu_{ab}^4\Gamma_{ba}}{8\gamma_{ba}(\Delta_{ba} - i\Gamma_{ba})^2(\Delta_{ba} + i\Gamma_{ba})} \\ & + \frac{\mu_{ab}^2\mu_{bc}^2\Gamma_{ba}}{4\gamma_{ba}(\Delta_{ba} - i\Gamma_{ba})(\Delta_{ba} + i\Gamma_{ba})(\Delta_{cb} - i\Gamma_{cb})} \\ & - \frac{\mu_{ab}^2\mu_{bc}^2}{8(\Delta_{ba} - i\Gamma_{ba})(\Delta_{cb} - i\Gamma_{cb})(\Delta_{ca} - i\Gamma_{ca})}. \end{aligned} \tag{41}$$

The usual, perturbative result for the third-order susceptibility is[17]

$$\begin{aligned} \chi^{(3)}(-\omega;\omega,-\omega,\omega) & = \sum_{lmn} \frac{\mu_{gl}\mu_{lm}\mu_{mn}\mu_{ng}}{(\omega_{lg} - \omega)(\omega_{mg} - 2\omega)(\omega_{ng} - \omega)} \\ & - \sum_m \frac{|\mu_{mg}|^2}{(\omega_{mg} - \omega)} \sum_n \frac{|\mu_{ng}|^2}{(\omega_{ng} - \omega)^2}, \end{aligned} \tag{42}$$

which, for a three-level system, reduces to

$$\begin{aligned} \chi^{(3)}(-\omega;\omega,-\omega,\omega) & = \frac{\mu_{ab}^2\mu_{bc}^2}{8(\Delta_{ba} - i\Gamma_{ba})^2(\Delta_{ca} - i\Gamma_{ca})} \\ & - \frac{\mu_{ab}^4}{8(\Delta_{ba} - i\Gamma_{ba})(\Delta_{ba} - i\Gamma_{ba})(\Delta_{ba} + i\Gamma_{ba})}. \end{aligned} \tag{43}$$

Equation (40) is equivalent to the usual expression for $\chi^{(1)}$.[1,17] Equation (41) contains extra contributions to $\chi^{(3)}$ compared to the standard result (43) and agrees with previous work.[7] This stems from the fact that within the steady state approximation, the population of level $|b\rangle$, ρ_{bb}, is not zero. Therefore terms which include processes that initiate in level $|b\rangle$ contribute to $\chi^{(3)}$.

Figure 2 show the diagrammatic representation of Eq. (41). If terms which initiate in level $|b\rangle$ are disregarded, such as (c), (d), and (e) in Fig. 2, Eq. (43) is recovered. It is interesting to note that within a harmonic oscillator model, where $\Delta_{ba} = \Delta_{cb}$, $\Delta_{ca} = 2\Delta_{ba}$, and $\mu_{bc} = \sqrt{2}\mu_{ab}$, Eq. (41) yields $\chi^{(3)} = 0$ as it should.

In Sec. IV, we will show that using Eqs. (30) and (31), in both real and model systems, leads to different results than does the perturbation series representation of the susceptibility [Eqs. (40) and (41)], implying that higher-order, intensity-dependent terms such as $\chi^{(5)}$ play a role in the near-resonance spectra of such systems.

The expression for the susceptibility including collisional process, e.g., $\gamma_{ab} \neq 0$, is even more involved than that of Eqs. (30)–(38). However, the first-order susceptibility term can be written as

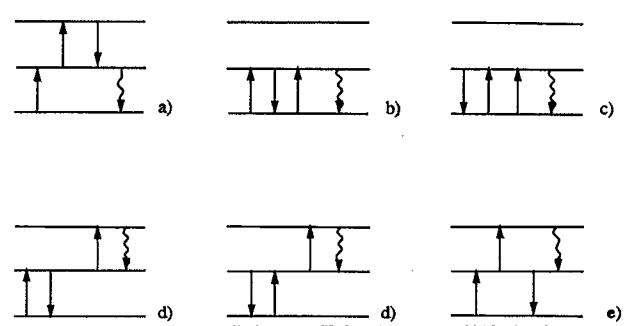

FIG. 2. A diagrammatic representation of $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ [Eq. (38)]. Figures corresponding to (c), (d), and (e) are processes which include terms initiating in level $|b\rangle$. (d) is indistinguishable in Eq. (41). (a) and (b) correspond to the first and second terms of Eq. (43), respectively.

$$\chi^{(1)}(-\omega;\omega)_{ab} = \frac{(\gamma_{ba}-\gamma_{ab})\gamma_{cb}\mu_{ab}^2}{2[(\gamma_{ba}-\gamma_{ab})\gamma_{cb}+\gamma_{ab}\gamma_{bc}](\Delta_{ba}-i\Gamma_{ba})}, \quad (44)$$

$$\chi^{(1)}(-\omega;\omega)_{bc} = \frac{(\gamma_{cb}-\gamma_{bc})\gamma_{ab}\mu_{bc}^2}{2[(\gamma_{bc}-\gamma_{ba}-\gamma_{ab})\gamma_{cb}+\gamma_{ab}\gamma_{bc}](\Delta_{cb}-i\Gamma_{cb})}. \quad (45)$$

B. Third harmonic generation—three-photon processes

In the previous subsection, we introduced a density matrix formalism which allowed an expression for the total susceptibility, including intensity-dependent correction terms, to be expressed without recourse to a perturbation treatment of the electric field. However, only one- and two-photon resonances were considered. In the past few years, interest has focused on the third harmonic generation contribution to the susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$.[1,18] Using the technique described above, we will derive an expression for the three-photon response of a three-level system.

To allow for three-photon resonance, we now consider a three-level system spanned by the basis set $|aa;0\rangle$ $|bb;0\rangle$ $|cc;0\rangle$ $|ab;-1\rangle$ $|ba;+1\rangle$ $|ac;-2\rangle$ $|ac;+2\rangle$ $|ab;-3\rangle$ $|ba;+3\rangle$, where we have neglected the one-photon resonance between level $|b\rangle$ and level $|c\rangle$ to simplify the algebra. The corresponding Liouville operator $\hat{L}_F$ now has the form

$$\hat{L}_F = \begin{bmatrix} -i\gamma_{ab} & i\gamma_{ba} & 0 & -u_{ab} & u_{ab} & 0 & 0 & -u_{ab3} & u_{ab3} \\ i\gamma_{ab} & -i(\gamma_{ba}+\gamma_{bc}) & i\gamma_{cb} & u_{ab} & -u_{ab} & 0 & 0 & u_{ab3} & -u_{ab3} \\ 0 & i\gamma_{bc} & -i\gamma_{cb} & 0 & 0 & 0 & 0 & 0 & 0 \\ -u_{ab} & u_{ab} & 0 & -\Delta_{ba}-i\Gamma_{ba} & 0 & -u_{bc} & 0 & 0 & 0 \\ u_{ab} & -u_{ab} & 0 & 0 & \Delta_{ba}-i\Gamma_{ba} & 0 & u_{bc} & 0 & 0 \\ 0 & 0 & 0 & -u_{bc} & 0 & -\Delta_{ca}-i\Gamma_{ca} & 0 & -u_{bc} & 0 \\ 0 & 0 & 0 & 0 & u_{bc} & 0 & \Delta_{ca}-i\Gamma_{ca} & 0 & u_{bc} \\ -u_{ab3} & u_{ab3} & 0 & 0 & 0 & -u_{bc} & 0 & -\Delta_{ba3}-i\Gamma_{ba3} & 0 \\ u_{ab3} & -u_{ab3} & 0 & 0 & 0 & 0 & u_{bc} & 0 & \Delta_{ba3}-i\Gamma_{ba3} \end{bmatrix} \quad (46)$$

where u_{ab} and u_{bc} are given in Eq. (27) and $\Delta_{ab3}=\omega_{ba}-3\omega$.

The transition matrix element u_{ab3}, which connects the ground state $|a\rangle$ to the opposite symmetry state $|b\rangle$ via a three-photon transition, is zero within the RWA. In order to obtain a nonvanishing transition matrix element, third-order perturbation theory must be applied. Using perturbation theory, the transition matrix element becomes[13,17]

$$u_{ab3} = \frac{[-(1/2)\mu_{ab}E]^3}{\Delta_{ba}^2}. \quad (47)$$

The polarization corresponding to Eq. (28) is

$$\langle \mathbf{P}\rangle = N_0[\mu_{ba}\rho_{ab}+\mu_{ca}\rho_{ac}+\mu_{ab}\rho_{ba}+\mu_{ac}\rho_{ca}+\mu_{ba}\rho_{ab3}+\mu_{ab}\rho_{ba3}]. \quad (48)$$

To find the susceptibility that corresponds to the three-photon process, we only need the term $\mu_{ab}\rho_{ba3}$ in Eq. (48). Using Eqs. (46)–(48), we find the total susceptibility for the three-photon response

$$\chi(\omega)_{ba3} = \frac{2i\Delta_{ba}^2E^2\gamma_{ba}\mu_{ab}^2(AE^2+C)(BE^2+D)}{VE^{10}+WE^8+XE^6+YE^4+ZE^2+256\gamma_{ba}\Delta_{ba}^4(\Gamma_{ba}^2+\Delta_{ba}^2)(\Gamma_{ba3}^2+\Delta_{ba3}^2)(\Gamma_{ca}^2+\Delta_{ca}^2)}. \quad (49)$$

The coefficients of Eq. (49) are given by

$$A = (\Gamma_{ba3}+\Gamma_{ba}-i\Delta_{ba3}-i\Delta_{ba})\mu_{bc}^2, \quad (50)$$

$$B = \mu_{ba}^2\mu_{bc}^2, \quad (51)$$

$$C = 4(i\Gamma_{ba}+\Delta_{ba})(i\Gamma_{ba3}+\Delta_{ba3})(i\Delta_{ca}-\Gamma_{ca}), \quad (52)$$

$$D = -4\Delta_{ab}^2\mu_{bc}^2+4(i\Gamma_{ca}-\Delta_{ca})(-i\Gamma_{ba}+\Delta_{ba}), \quad (53)$$

$$V = (\Gamma_{ba3}+\Gamma_{ba})\mu_{ba}^6\mu_{bc}^4, \quad (54)$$

$$W = -8\Delta_{ba}^2(\Gamma_{ba3}+\Gamma_{ba})\mu_{ab}^4\mu_{bc}^4+[8\Gamma_{ba3}(\Gamma_{ca}\Gamma_{ba}-\Delta_{ba}\Delta_{ca})]+4\Gamma_{ca}(\Gamma_{ba}^2+\Delta_{ba}^2)\mu_{ab}^6\mu_{bc}^2, \quad (55)$$

$$X = 16\Gamma_{ba3}(\Gamma_{ba}^2+\Delta_{ba}^2)(\Gamma_{ca}^2+\Delta_{ca}^2)\mu_{ab}^6+16\Delta_{ba}^4(\Gamma_{ba3}+\Gamma_{ba})\mu_{ba}^2\mu_{bc}^4+32\Delta_{ba}^2[\Gamma_{ca}(-\Gamma_{ba3}\Gamma_{ba}+\Delta_{ba}\Delta_{ba3})+\Delta_{ca}(\Gamma_{ba}\Delta_{ba3}+\Delta_{ba}\Gamma_{ba3})]\mu_{ab}^4\mu_{bc}^2, \quad (56)$$

$$Y = 16\Delta_{ba}^4\gamma_{ba}[(\Gamma_{ba3}^2+\Delta_{ba3}^2)+(\Gamma_{ba}^2+\Delta_{ba}^2)+2(\Gamma_{ba3}\Gamma_{ba}+\Delta_{ba}\Delta_{ba3})]\mu_{bc}^4+64\Delta_{ba}^4[(\Gamma_{ba3}^2+\Delta_{ba3}^2)\Gamma_{ca}+2\Gamma_{ba}(\Gamma_{ba3}\Gamma_{ca}-\Delta_{ca}\Delta_{ba3})]\mu_{ab}^2\mu_{bc}^2, \quad (57)$$

$$Z = [256\Delta_{ba}^4\Gamma_{ba}(\Gamma_{ba3}^2 + \Delta_{ba3}^2)(\Gamma_{ca}^2 + \Delta_{ca}^2)]\mu_{ab}^2 + 128\Delta_{ba}^4\gamma_{ba}[(\Gamma_{ba}^2 + \Delta_{ba}^2)(\Gamma_{ba3}\Gamma_{ca} - \Delta_{ca}\Delta_{ba3}) + (\Gamma_{ba}\Gamma_{ca} - \Delta_{ca}\Delta_{ba})(\Gamma_{ba3}^2 + \Delta_{ba3}^2)]\mu_{bc}^2. \quad (58)$$

Since Eq. (49) is only dependent on ρ_{ba3}, which corresponds to three-photon response, expanding Eq. (49) around the electric field yields $\chi^{(1)} = 0$, since this corresponds to a one-photon process. The first intensity-dependent term is

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = \frac{\mu_{ab}^2\mu_{bc}^2}{8(\Delta_{ab} - i\Gamma_{ba})(\Delta_{ba3} - i\Gamma_{ba3})(\Delta_{ca} - i\Gamma_{ca})} + \frac{\mu_{ba}^4}{8(\Delta_{ba})^2(\Delta_{ba3} - i\Gamma_{ba3})}. \quad (59)$$

The usual result[17] for third harmonic generation (within the RWA) is

$$\chi^{(3)}(-3\omega;\omega,\omega,\omega) = \sum_{lmn} \frac{\mu_{gl}\mu_{lm}\mu_{mn}\mu_{ng}}{(\omega_{lg} - 3\omega)(\omega_{mg} - 2\omega)(\omega_{ng} - \omega)}, \quad (60)$$

which reduces to the first term in Eq. (59) for the three-level system in Fig. 1. The second term in Eq. (59) does not involve state $|c\rangle$ and stems from the nonlinear correction of a two-level system defined by resonant processes between $|a\rangle$ and $|b\rangle$.

C. Antirotating wave contributions

The previous subsections have shown how an analytic expression for the susceptibility can be derived using Floquet theory and a density matrix formalism within the RWA. Although Floquet theory allows the incorporation of the antirotating part of the electric field, this leads to larger matrices as compared to Eqs. (26) and (46). However, antirotating wave contributions can be included by using perturbation theory without enlarging the density matrix. The perturbation technique[13,17] is similar to incorporating a transition matrix element between the Liouville bases $|aa;0\rangle$ and $|ab;-3\rangle$ as outlined in the previous subsection. The first approximation beyond the rotating wave approximation replaces Eqs. (15) and (27) with

$$\Delta_{ba} = (\omega_{ba} - \omega) - \frac{[-(1/2)\mu_{ab}E]^2}{(\omega_{ba} + \omega)} \quad (61)$$

and

$$u_{ab} = -\tfrac{1}{2}\mu_{ab}E - \frac{[-(1/2)\mu_{ab}E]^3}{(\omega_{ba} + \omega)^2}. \quad (62)$$

By substituting these values into Eqs. (26) and (46), antirotating contributions are incorporated into the susceptibility.

IV. TOTAL SUSCEPTIBILITY OF CONJUGATED POLYMERS

In the previous section, an expression for the total susceptibility of a three-level model was derived. We now focus on three-level systems that mimic the electronic states of conjugated polymers and compare the total susceptibility to the usual perturbation expansion representation of the susceptibility.

We first examine a three-level system using dipole transition moments and energies of excited electronic states of *trans* octatetraene obtained from an exact calculation using a Pariser–Parr–Pople (PPP) Hamiltonian. This system has an excited state of the same symmetry as the ground state above the first (opposite symmetry) excited state with dipole moments $\mu_{ba} = 8.454$ D and $\mu_{cb} = 14.362$ D.[2] The first excited state of opposite symmetry lies at 4.56 eV (36 782 cm^{-1}) and the excited state of the same symmetry lies at 7.27 eV (58 648 cm^{-1}). The decay constants, using the Einstein A coefficient for pure radiative decay, yield $\Gamma_{ba} = 0.0367$ cm^{-1} and $\Gamma_{cb} = 0.0221$ cm^{-1}. The coefficients γ_{ba} and γ_{ca} are obtained using Eq. (24). Typical power densities for nonlinear optical effects range from 10–1000 MW/cm^2.[19] We will use an electric field amplitude that corresponds to 100 MW/cm^2 throughout.

The real part of the total susceptibility [Eqs. (30) and (31)], for the system described above, is shown in Fig. 3(a). The first-order perturbation term $\chi^{(1)}$, given by Eq. (40), is shown in Fig. 3(b). Near resonance, $\chi^{(1)}$ is orders of magnitude larger than the total susceptibility. As a consequence, Figs. 3(a) and 3(b) use different scales. The total susceptibility shows the effects of power broadening and thus displays a broader peak at the one-photon resonance, as compared to $\chi^{(1)}$. This indicates that higher-order, intensity-dependent terms need to be included in the expansion.

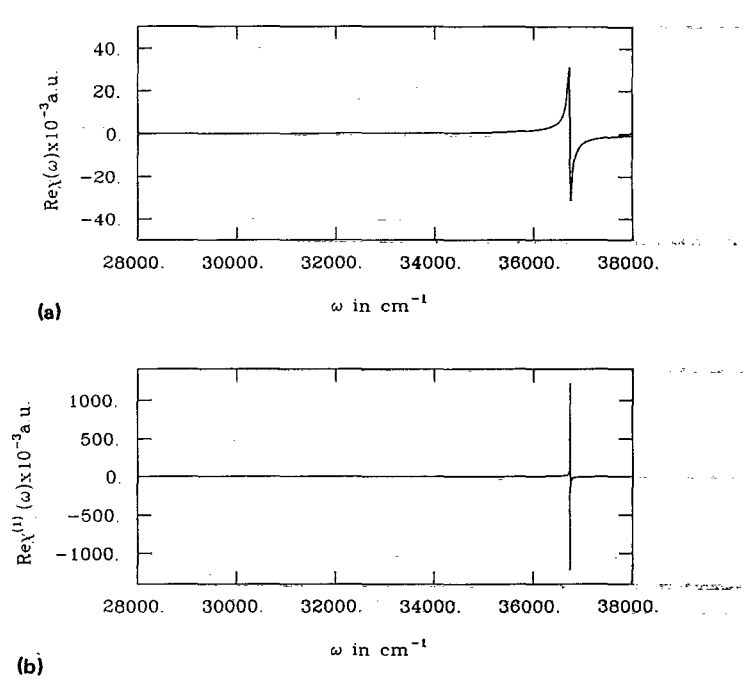

FIG. 3. The real part of the susceptibility for *trans* octatetraene with the first excited state at 36 782 cm^{-1} and the second excited state at 58 648 cm^{-1}. (a) The intensity-dependent total susceptibility from Eqs. (30) and (31). (b) The first-order susceptibility $\chi^{(1)}$ from Eq. (40). The electric field amplitude corresponds to 100 MW/cm^2.

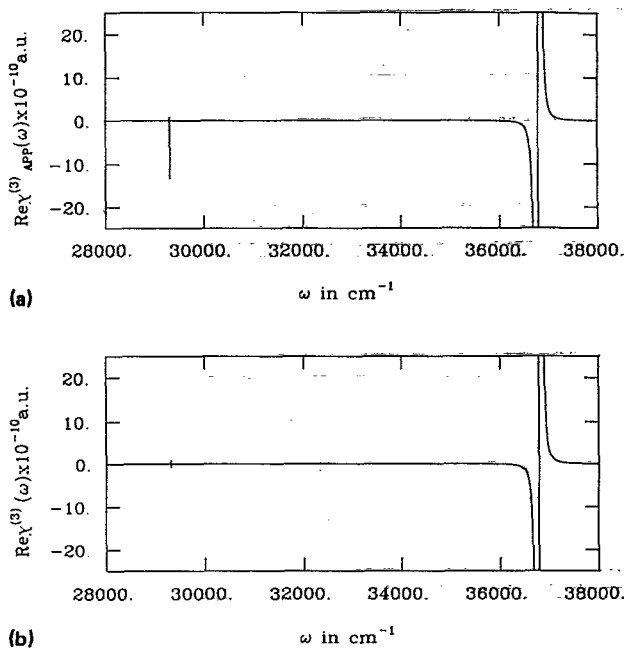

FIG. 4. The real part of the intensity-dependent susceptibility for *trans* octatetraene, with the first excited state at 36 782 cm^{-1} and the second excited state at 58 648 cm^{-1}. (a) An approximation to $\chi^{(3)}$ [Eq. (63)]. (b) From the usual perturbative expression for $\chi^{(3)}$ [Eq. (41)]. The electric field amplitude corresponds to 100 MW/cm^2.

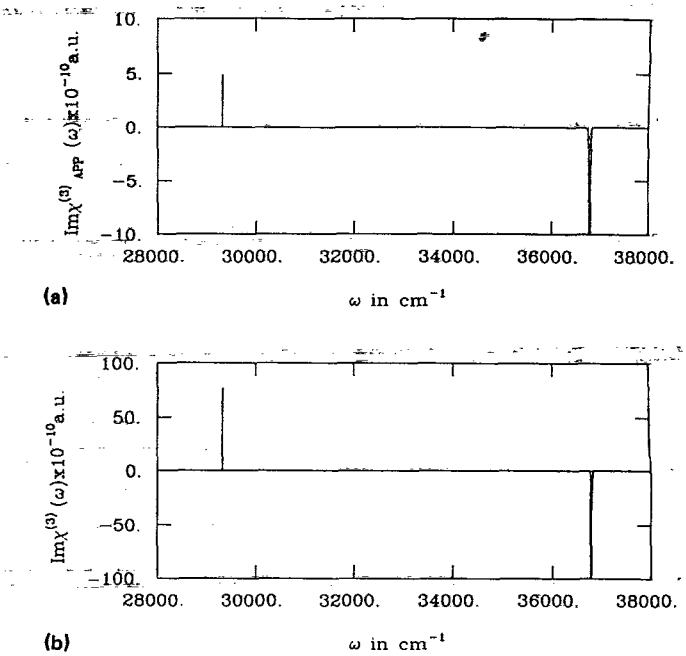

FIG. 6. The imaginary part of the intensity-dependent susceptibility for *trans* octatetraene with the first excited state at 36 782 cm^{-1} and the second excited state at 58 648 cm^{-1}. (a) An approximation to $\chi^{(3)}$ [Eq. (63)]. (b) From the usual perturbative expression for $\chi^{(3)}$ [Eq. (41)]. The electric field amplitude corresponds to 100 MW/cm^2.

To compare third-order susceptibilities, an approximate $\chi^{(3)}$ is derived from the total susceptibility by subtracting $\chi^{(1)}$ from the total susceptibility and dividing by the square of the electric field

$$\chi^{(3)}_{APP} = [\chi(\omega) - \chi^{(1)}(-\omega;\omega)]/E^2. \tag{63}$$

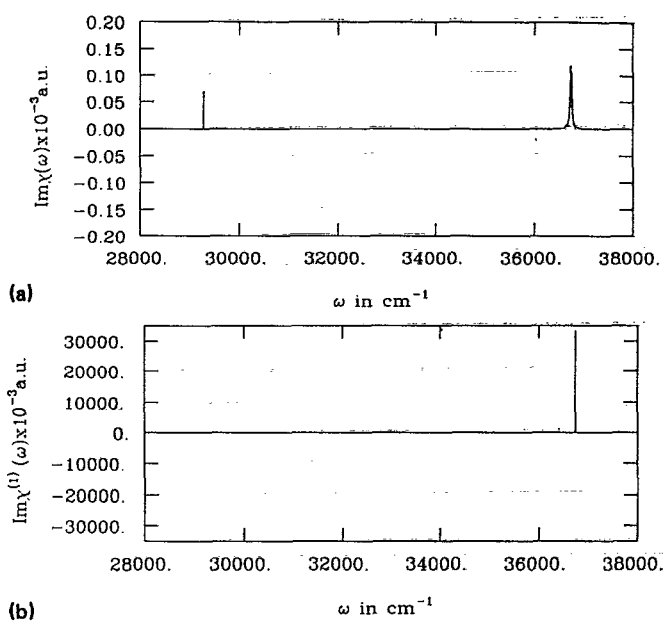

FIG. 5. The imaginary part of the susceptibility for *trans* octatetraene with the first excited state at 36 782 cm^{-1} and the second excited state at 58 648 cm^{-1}. (a) The intensity-dependent total susceptibility from Eqs. (30) and (31). (b) The first-order susceptibility $\chi^{(1)}$ from Eq. (40). The electric field amplitude corresponds to 100 MW/cm^2.

Equation (63) is an approximation to $\chi^{(3)}$ and should be equivalent to $\chi^{(3)}$ obtained from perturbation theory [Eq. (41)] if higher-order terms such as $\chi^{(5)}$ do not make a contribution. Figures 4(a) and 4(b) show Re $\chi^{(3)}_{APP}$, from Eqs. (30), (31), and (40), and $\chi^{(3)}$ from Eq. (41), respectively. At both the two-photon and one-photon resonances, the two values differ, reflecting the difference in intensity dependence between $\chi^{(3)}_{APP}$ and $\chi^{(3)}$ at this value of the electric field. The two-photon peak (29 324 cm^{-1}) and the one-photon peak (36 782 cm^{-1}) are shifted slightly due to the electric field perturbation. The two-photon peak corresponding to the nonperturbative value has large peak on resonance and is therefore unsymmetrical.

The imaginary part of susceptibility of this system is plotted in Figs. 5 and 6. Figure 5(a) shows the total susceptibility which displays a peak at the two-photon resonance value, unlike the first-order susceptibility, shown in Fig. 5(b). This indicates that, in this system, the intensity-dependent susceptibility is important, and the same order of magnitude, as the nonintensity-dependent part of the susceptibility $\chi^{(1)}$. The two-photon absorption peak in Fig. 6(a), given by Im $\chi^{(3)}_{APP}$, is much smaller than the third-order susceptibility derived perturbatively $\chi^{(3)}$ shown in Fig. 6(b).

We now consider a model system for illustrative purposes, although this system is very similar to the previous three-level system. Here $|b\rangle$ lies at 25 000 cm^{-1} and $|c\rangle$ lies at 49 000 cm^{-1}. The dipole moments are $\mu_{ba} = 8.00$ D and $\mu_{cb} = 14.00$ D. Both the total susceptibility and the third-order susceptibility, assuming pure radiative decay, are shown in Figs. 7–10. In this system, both the real and imaginary parts of the total susceptibility display two-photon res-

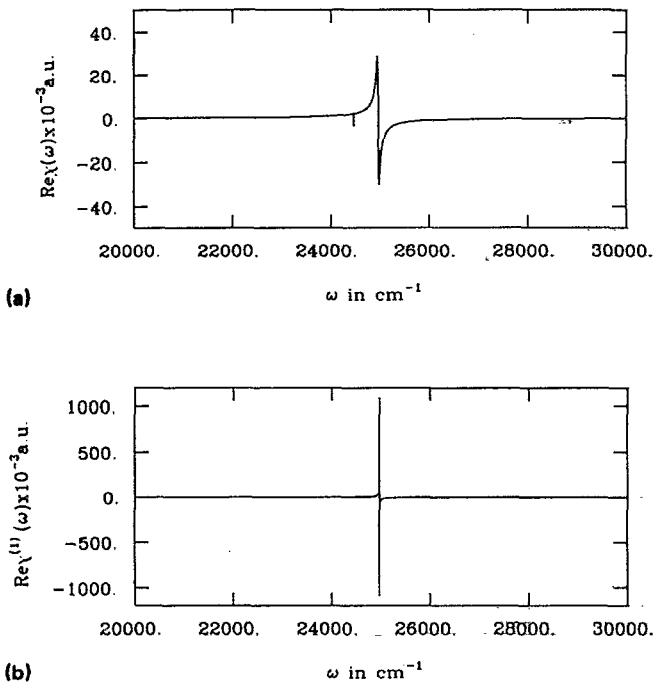

FIG. 7. The real part of the susceptibility for a model with the first excited state at 25 000 cm^{-1} and the second excited state at 49 000 cm^{-1}. (a) The intensity-dependent total susceptibility from Eqs. (30) and (31). (b) The first-order susceptibility $\chi^{(1)}$ from Eq. (40). The electric field amplitude corresponds to 100 MW/cm^2.

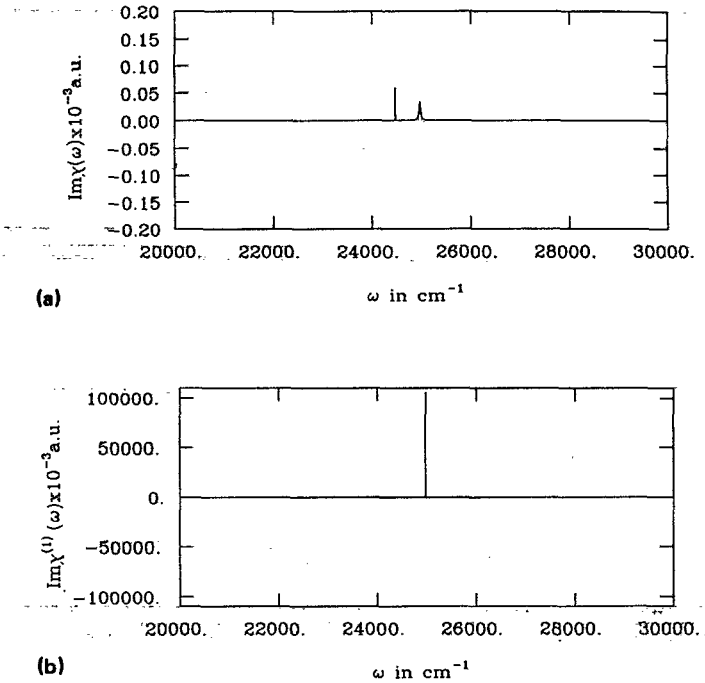

FIG. 9. The imaginary part of the susceptibility for a model with the first excited state at 25 000 cm^{-1} and the second excited state at 49 000 cm^{-1}. (a) The intensity-dependent total susceptibility from Eqs. (30) and (31). (b) The first-order susceptibility $\chi^{(1)}$ from Eq. (40). The electric field amplitude corresponds to 100 MW/cm^2.

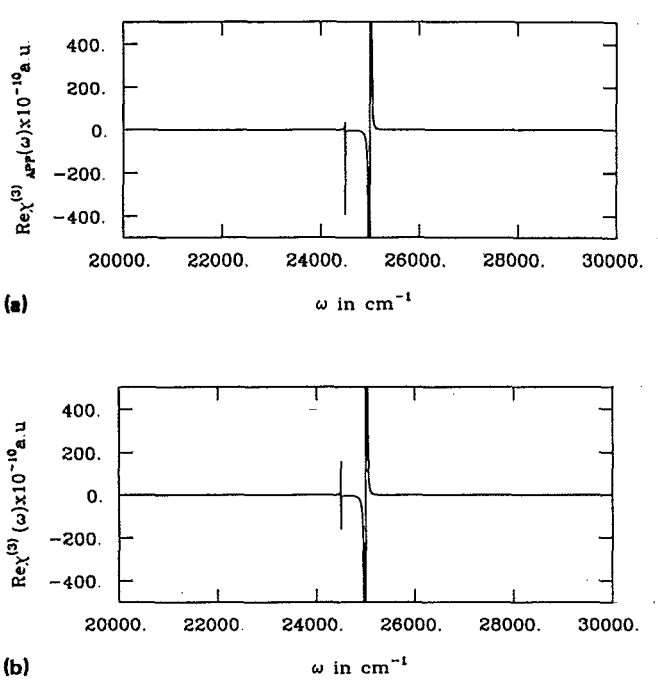

FIG. 8. The real part of the intensity-dependent susceptibility for a model with the first excited state at 25 000 cm^{-1} and the second excited state at 49 000 cm^{-1}. (a) An approximation to $\chi^{(3)}$ [Eq. (63)]. (b) From the usual perturbative expression for $\chi^{(3)}$ [Eq. (41)]. The electric field amplitude corresponds to 100 MW/cm^2.

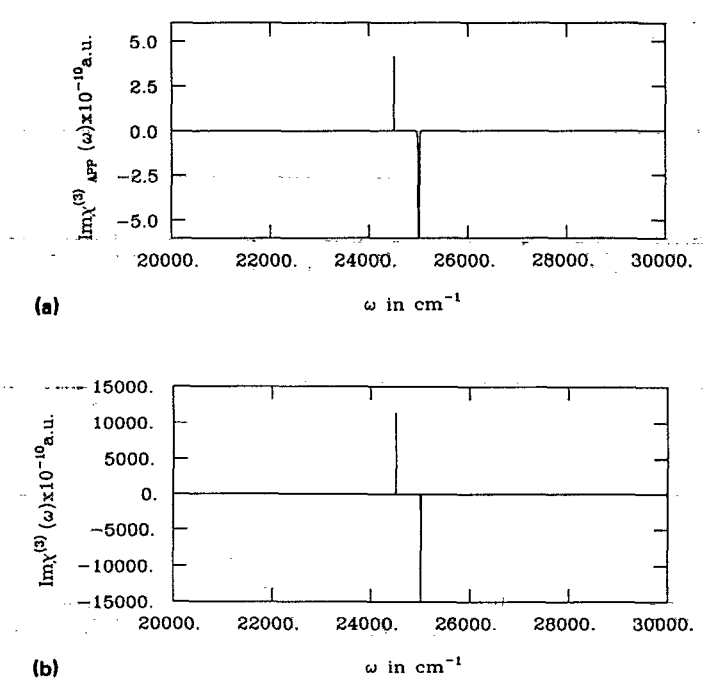

FIG. 10. The imaginary part of the intensity-dependent susceptibility for a model with the first excited state at 25 000 cm^{-1} and the second excited state at 49 000 cm^{-1}. (a) An approximation to $\chi^{(3)}$ [Eq. (63)]. (b) From the usual perturbative expression for $\chi^{(3)}$ [Eq. (41)]. The electric field amplitude corresponds to 100 MW/cm^2.

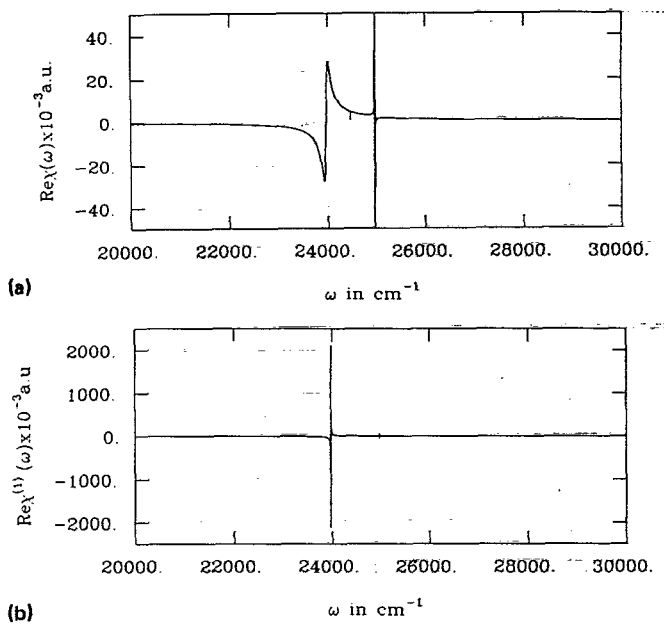

FIG. 11. The real part of the susceptibility, with collisional damping, for a model with the first excited state at 25 000 cm^{-1} and the second excited state at 49 000 cm^{-1}. The damping parameters are related by $\Gamma_{ba} = 5\gamma_{ba}$ and $\Gamma_{cb} = 5\gamma_{cb}$, and by Eqs. (22)–(24). (a) The intensity-dependent total susceptibility. (b) The first-order susceptibility $\chi^{(1)}$ from Eqs. (44) and (45). The electric field amplitude corresponds to 100 MW/cm^2.

onance. The two-photon peak of Re $\chi^{(3)}_{APP}$ in Fig. 8(a) is significantly larger than that of the perturbation response [Fig. 8(b)], while the two-photon absorption in Fig. 10(a) is much smaller than the perturbation response, as in the previous system.

Figures 11 and 12 show the effect of collisional damping on the above system. Instead of considering only radiative decay, e.g., $\Gamma_{ba} = 1/2\gamma_{ba}$, we also include the damping effects of collisions. Here we assume $\Gamma_{ba} = 5\gamma_{ba}$ and $\Gamma_{cb} = 5\gamma_{cb}$, and use Eqs. (22)–(24) to determine all damping parameters. This change of damping parameters significantly alters the susceptibility of this system. There is now a large one-photon resonance between state $|b\rangle$ and state $|c\rangle$, occurring below the resonance of states $|a\rangle$ and $|b\rangle$. The two-photon peak has decreased in the total susceptibility as well as the perturbation terms, compared to the pure radiative decay result. A decrease in the two-photon peak as the decay constant increases has been noted before.[20] The one-photon peaks have increased substantially.

Figure 11(b) corresponds to $\chi^{(1)}$ given by Eqs. (44) and (45). $\chi^{(1)}$ is larger than the total susceptibility at the one-photon resonance between states $|b\rangle$ and $|c\rangle$. However, the total susceptibility at the one-photon resonance between

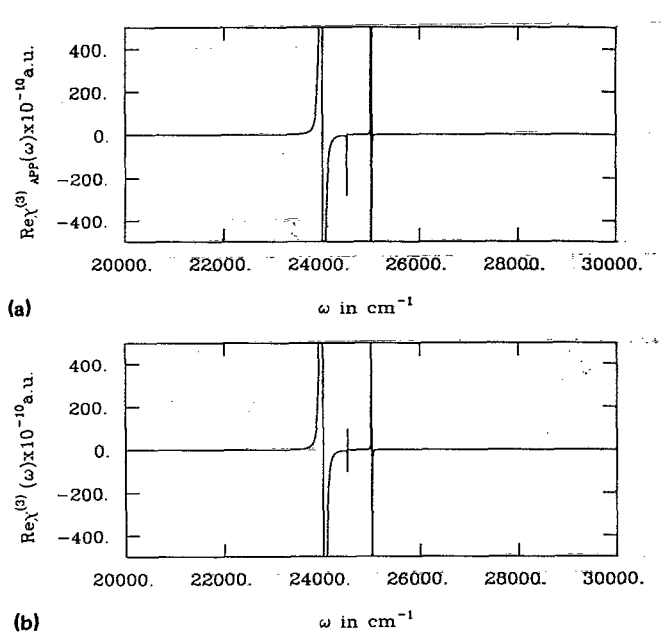

FIG. 12. The real part of the intensity-dependent susceptibility, with collisional damping, for a model with the first excited state at 25 000 cm^{-1} and the second excited state at 49 000 cm^{-1}. The damping parameters are related by $\Gamma_{ba} = 5\gamma_{ba}$ and $\Gamma_{cb} = 5\gamma_{cb}$, and by Eqs. (22)–(24). (a) An approximation to $\chi^{(3)}$. (b) From the perturbative expression for $\chi^{(3)}$. The electric field amplitude corresponds to 100 MW/cm^2.

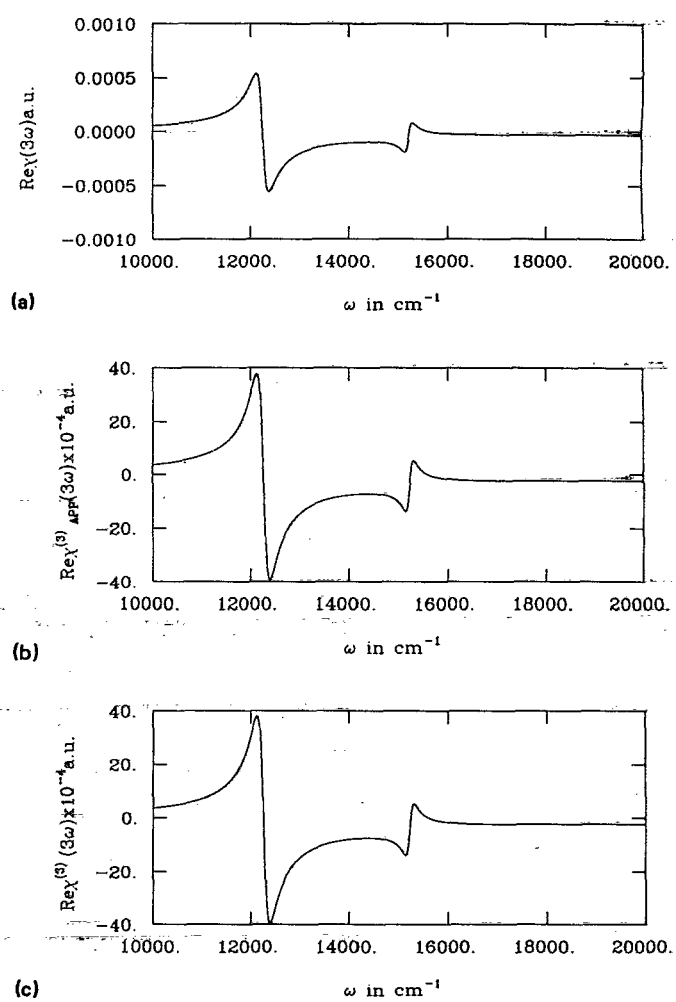

FIG. 13. The real part of the susceptibility corresponding to third harmonic generation $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ for a model with state $|b\rangle$ at 36 782 cm^{-1} and state $c\rangle$ at 30 446 cm^{-1}. (a) is the total susceptibility [Eq. (49)]. (b) An approximation to $\chi^{(3)}$ [Eq. (63)]. (c) The usual perturbation expression for $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ [Eq. (59)]. The electric field amplitude corresponds to 100 MW/cm^2.

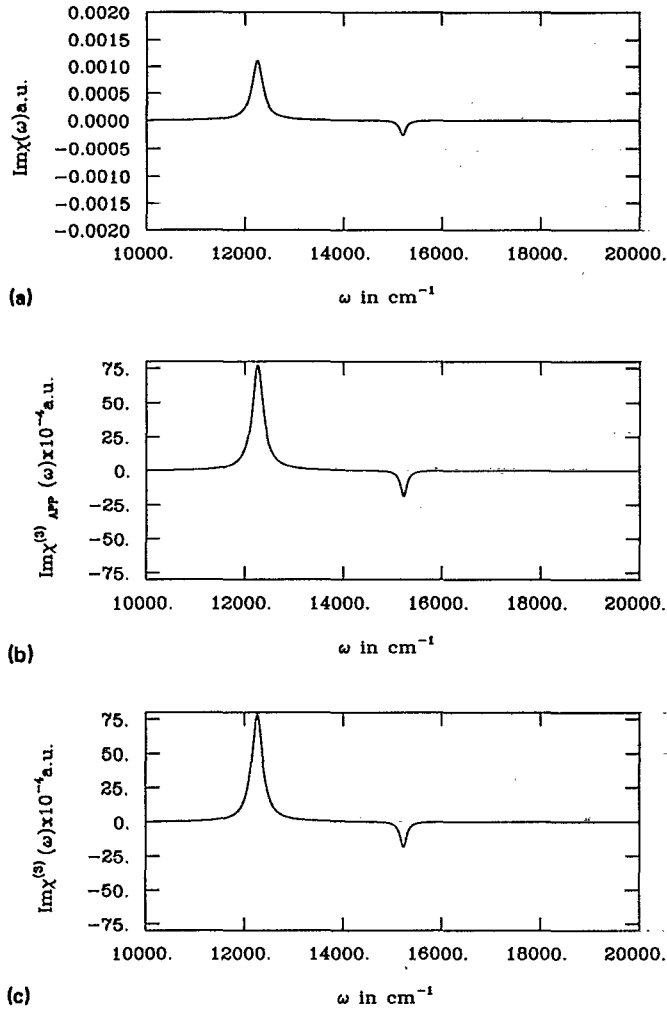

FIG. 14. The imaginary part of the susceptibility corresponding to third harmonic generation $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ for a model with state $|b\rangle$ at 36 782 cm^{-1} and state $c\rangle$ at 30 446 cm^{-1}. (a) The total susceptibility [Eq. (49)]. (b) An approximation to $\chi^{(3)}$ [Eq. (63)]. (c) The usual perturbation expression for $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ [Eq. (59)]. The electric field amplitude corresponds to 100 MW/cm^2.

states $|a\rangle$ and $|b\rangle$ is larger than the first-order perturbation term, in contrast to Fig. 7.

The three-photon response of a system [Eq. (49)] is shown in Figs. 13 and 14. We chose a system that mimics a previous calculation of $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of *trans* octatetraene.[2] Here, the excited state of the same symmetry as the ground state $|c\rangle$ lies below the opposite symmetry excited state $|b\rangle$. The state $|b\rangle$ lies at 4.56 eV (36 782 cm^{-1}) and $|c\rangle$ at 3.78 eV (30 446 cm^{-1}). The transition dipole moments are $\mu_{ba} = 8.454$ D and $\mu_{bc} = 1.602$ D. The decay constants correspond to $\Gamma_{ba} = 0.1$ eV and $\Gamma_{ca} = 0.02$ eV. Again, $\chi^{(3)}_{\rm APP}$ is given by Eq. (63), although here $\chi^{(1)} = 0$. Both the real and imaginary parts of $\chi^{(3)}_{APP} = \chi(3\omega)/E^2$ are virtually identical to $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$, indicating that for this system, the perturbation results are valid.

V. DISCUSSION

We have shown, using the formalism of Sec. II, that Floquet theory can be used to transform a periodic, time-dependent Hamiltonian such as the electric field perturbation presented here, into a time-independent problem. Considering three-level systems with both one- and two-photon, and one-, two-, and three-photon resonances with one electric field, we take advantage of Floquet theory and incorporate it into a density matrix formalism. Using this formalism, outlined in Sec. III, we are able to write down an exact expression for the susceptibility of a three-level system corresponding to both the intensity-dependent refractive index, and third harmonic generation, within the RWA. We are able to augment the RWA by incorporating antirotating wave contributions, as shown in Sec. III C.

The results of using the exact expression for intensity-dependent nonlinear refractive index susceptibility, corresponding to $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$, and the third harmonic generation susceptibility, corresponding to $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$, using typical values for the electronic energy levels and transition dipole moments of conjugated polymers, is outlined in the previous section. While the one- and two-photon resonant susceptibility displays differences between the exact susceptibility, Eqs. (30) and (31), and the

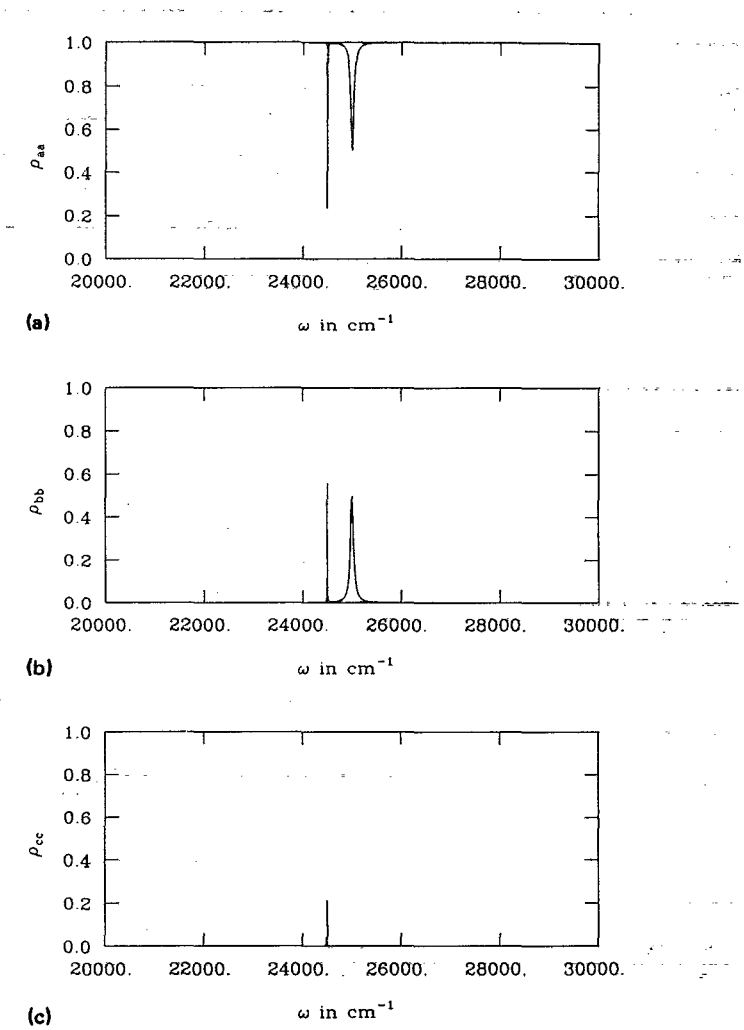

FIG. 15. The diagonal, or population density matrix elements for a model with the first excited state at 25 000 cm^{-1} and the second excited state at 49 000 cm^{-1} as a function of laser frequency ω. The electric field amplitude corresponds to 100 MW/cm^2.

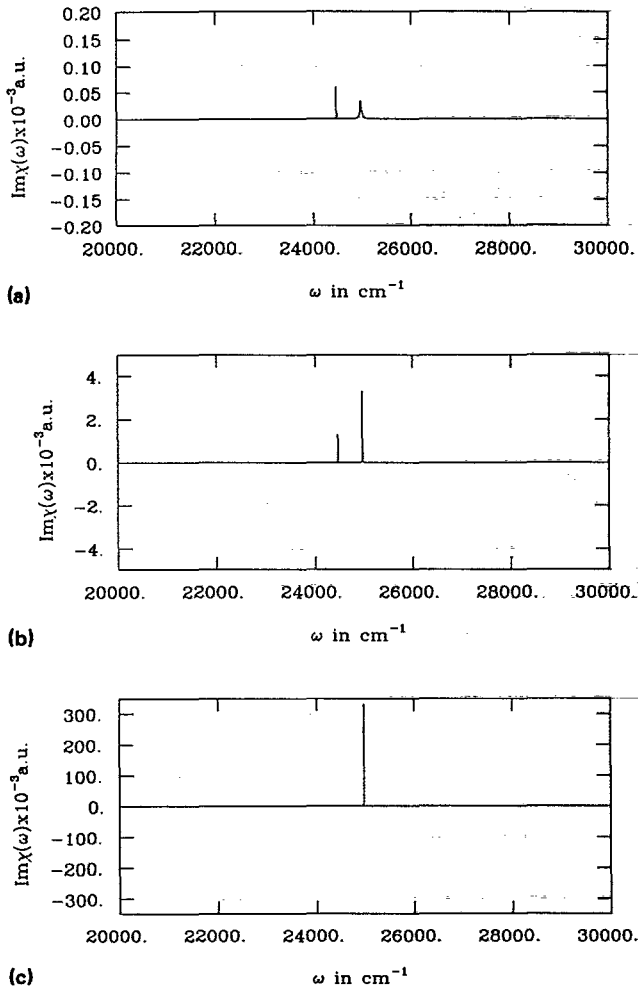

FIG. 16. The imaginary part of the susceptibility with varying field strength. (a) corresponds to a power density of 100 MW/cm^2; (b) 1 MW/cm^2; (c) 1 kW/cm^2.

usual perturbation expansion, the three-photon resonant susceptibility has no discernible difference between the exact result (49) and the perturbative result (59).

Although different systems were used to calculate these susceptibilities, the intensity dependence of each stem from different physical behavior. The refractive index is related to the susceptibility by

$$n^2(\omega) = 1 + 4\pi\chi(\omega). \tag{64}$$

The intensity-dependent refractive index is due to incoherent processes, i.e., due to population changes of the ground and excited states. If a material absorbs at the frequency of the electric field, the concentration of the excited states will increase, the character of the material changes, and thus the refractive index becomes intensity dependent.[5,8,19] The steady state populations of three levels of the second system outlined above are shown in Fig. 15, with ρ_{aa}, ρ_{bb}, and ρ_{cc}, from Eq. (25), corresponding to the populations of levels $|a\rangle$, $|b\rangle$, and $|c\rangle$, respectively. Note the increase of the excited state populations near resonance.

Although third harmonic generation can be resonant enhanced, the quantitative dependence on the intensity of the electric field of the susceptibility corresponding to $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ is not very important. Rather than a description of the population of all excited states, this process focuses on the population of the three-photon resonant state only, as a function of the laser frequency. Therefore, the intensity dependence on this process is much smaller than that of the intensity-dependent refractive index susceptibility.

Antirotating wave contributions for the transition dipole moment and resonance frequency [Eqs. (61) and (62)] can also be incorporated, as in Sec. III C. Using electric field intensities and systems described here, the antirotating wave contribution to the susceptibility is negligible for both the susceptibility corresponding to the intensity-dependent refractive index and the third harmonic generation.

The exact susceptibility corresponding to $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ derived in Sec. III A differs from the usual perturbation series, as shown in Sec. IV. For a three-level system, the first-order susceptibility $\chi^{(1)}$ only displays a peak at one-photon resonances. While higher-order terms such as $\chi^{(3)}$ also display multiphoton resonances, e.g., a two-photon resonance, these higher-order terms are usually assumed to differ from each other by orders of magnitude. However, the exact susceptibility for the three-level systems described above does show higher-order resonances, i.e., a two-photon peak. This suggests that resonant peaks from higher-order processes, e.g., $\chi^{(3)}$, might be present in an assumed one-photon spectrum. This may also indicate that resonant peaks in the spectrum of $\chi^{(3)}$ could also show higher-order contributions, such as three-photon peaks. Although the three-level system considered here does not allow for such contributions, the difference in intensity between $\chi^{(3)}_{APP}$, which describes the higher-order intensity dependence of $\chi^{(3)}$ (Figs. 3–10) and the perturbative expression for $\chi^{(3)}$, which is linear in intensity, indicate that higher-order intensity-dependent processes do indeed play a role.

The exact susceptibilities in Figs. 3, 5, 7, and 9 all show a broad peak at the one-photon resonance, which is due to power broadening. Figure 16 shows the imaginary susceptibility of the system described by Fig. 9. Using values of the electric field that correspond to 100 and 1 MW/cm^2, and 100 kW/cm^2, respectively, the total susceptibilities are shown in Fig. 16. The one-photon peak becomes sharper and the two-photon peak diminishes as the field intensity diminishes and thus the total susceptibility approaches the first-order result $\chi^{(1)}$.

The susceptibility of the second three-level system considered in Sec. IV (Figs. 7–10) is significantly different than that of the *trans* octatetraene model. The two-photon resonance peak is very pronounced in the total susceptibility (Fig. 7), especially compared to the previous model (Fig. 3), which does not have a discernible two-photon peak on this scale. The system of Figs. 7–10 has level spacing similar to that of a harmonic oscillator. Near one- and two-photon resonances, the intensity-dependent portion of the energy denominator in Eqs. (30) and (31) become smaller than that of the *trans* octatetraene model due to the harmonic level spacing, allowing the intensity-dependent portion of the denominator to dominate. Harmonic oscillator-like

spacing of excited states may lead to observation of higher-order resonant peaks.

Figures 11 and 12 show the effect of collisional damping on the intensity-dependent refractive index susceptibility. The susceptibility now displays the one-photon resonance between the two excited states $|b\rangle$ and $|c\rangle$. This resonance stems from both Eq. (45) and higher-order terms. When the damping is dominated by spontaneous emission, the relation $\Gamma_{ba} + \Gamma_{ca} = \Gamma_{bc}$ holds. This equality is no longer valid when collisional relaxation is also considered, and as a consequence, $\chi^{(1)}$ [Eq. (45)] becomes nonzero. This resonance between two excited states is often referred to as pressure-induced extra resonance in four-wave mixing (PIER-4), or in solids as dephasing induced coherent emission (DICE). This phenomena has been observed by Bloembergen *et al.*[21] in Na vapor and by Hochstrasser *et al.*[22] in solids.

The total susceptibility obtained using the Floquet–Liouville supermatrix approach includes many related phenomena which have previously been calculated perturbatively. In addition to correctly incorporating near-resonance relaxations, we have shown that it can describe correctly the intensity-dependent behavior of a conjugated system near resonance. When collisional relaxations are incorporated, this approach also describes correctly the extra resonances and intensity-dependent phenomena.

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