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Effects of centrosymmetry on the nonresonant electronic third-order nonlinear optical susceptibility

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The off-resonant electronic third-order optical susceptibility is derived in the dipole approximation using the method of averages. These results are studied in detail for the two-, three-, and N-level model to determine the origin of the susceptibility with symmetry considerations. If the matrix elements are independent, the third-order susceptibility is shown to be maximized in centrosymmetric structures in the two-level model while, for the general N-level system, weak coupling between the excited states is also required. To address the interdependence of the matrix elements, a two- and three-level system is perturbed to make the molecular potential asymmetric or more asymmetric, and the conditions on the matrix elements for maximizing the third-order susceptibility are derived. The dependence of the third-order susceptibility on the asymmetry of a harmonic oscillator and particle in a box are also discussed.

I. INTRODUCTION

Although a two-level model is adequate to understand the origin of the electronic contribution to the second-order nonlinear optical susceptibility,[1-3] the third-order susceptibility can be accurately described only by contributions from several states.[4] Even though the two-level model is not always applicable, it has been highly successful in qualitatively predicting the experimental observation that highly polar molecules have the largest electronic second-order susceptibilities. Because of this success, searches for molecules with large third-order susceptibilities have sometimes neglected the class of centrosymmetric molecules. It is the purpose of this paper to determine the origin of the nonresonant electronic third-order susceptibility by examining the perturbation expressions for the two-, three-, and N-level models. While we show in Sec. II that the mathematical expressions for the susceptibility can be maximized in centrosymmetric molecules, it is not clear that such molecular systems with those particular dipole matrix elements exist or are allowed to exist within the confines of quantum mechanics.

When only one excited state of a molecule dominates the third-order susceptibility by strongly coupling to the ground state, but weakly to all other states, a two-level model can adequately describe the nonlinear optical properties. The only two molecular parameters that are needed to calculate the susceptibility are the transition moment to the dominant state and the difference in dipole moment between the ground state and the dominant state. For centrosymmetric molecules, the dipole moments vanish and only one parameter, namely, the transition moment, controls the third-order nonlinear optical properties of the two-level molecule. The susceptibility is then limited only by the oscillator strength of the important state. As the vast dye literature suggests, a large range of oscillator strengths is possible.[5] Sections II A and III A show that in the two-level model the nonlinear optical properties are mathematically maximized under physically reasonable constraints by increasing the oscillator strength. Section III A shows the conditions under which an asymmetric perturbation of a noncentrosymmetric molecule causes the susceptibility to increase or decrease in terms of the unperturbed dipole matrix elements.

When two excited states are important, the three-level centrosymmetric system depends on three parameters, namely, the oscillator strengths of the two states, and the transition moment between those states. In this case, when the centrosymmetric molecule is asymmetrically perturbed, the condition under which the third-order susceptibility increases or decreases is again given by the unperturbed values of the dipole matrix. It is thus useful to study the effects of perturbations of the two- and three-level model to determine the important molecular properties that maximize the susceptibility. In this paper we examine general molecular properties that result in large third-order susceptibilities for both nearly centrosymmetric and highly polar molecules. While certain polar molecules are shown to have large third-order susceptibilities, the centrosymmetric systems potentially offer the largest third-order susceptibilities.

II. THEORY

Electric charges are rearranged in the presence of an electric field, resulting in a distribution that can be expressed as a series of moments. In the dipole approximation, the lowest moment **P** can be expressed as a Taylor series in the electric field **E** as

$$P_i(t)=\chi_i^{(0)}+x_{ij}^{(1)}(t)E_j(t)+x_{ijk}^{(2)}(t)E_j(t)E_k(t) +\chi_{ijkl}^{(3)}(t)E_j(t)E_k(t)E_l(t)+\cdots \;, \tag{2.1}$$

where the tensor $\chi^{(n)}$ is the nth-order susceptibility, P_i and E_i the ith components of the polarizability and the electric field, respectively, and where summation over repeated indices is implied.

Symmetry determines the allowed nonlinear optical processes. For example, the second-order polarization under the inversion operation $\mathbf{P}^{(2)}$ is expressed as

$$P_i^{(2)}=\frac{\chi_{ijk}^{(2)}(\mathbf{r})-\chi_{ijk}^{(2)}(-\mathbf{r})}{2}E_jE_k \;, \tag{2.2}$$

where $\mathbf{r}$ is the coordinate of the polarizable charges. The polarization vanishes for a centrosymmetric molecule. Far off resonances, the two-level model of the second-order susceptibility is of the form[1]

$$\chi^{(2)}\propto\mu_{01}^2\Delta\mu \;, \tag{2.3}$$

where μ_{01} is the transition moment between the ground and excited state and $\Delta\mu$ the difference in dipole moment between the excited state and the ground state. A large second-order susceptibility then results from a large dipole change between the important excited state and the ground state and a large oscillator strength. The general symmetry argument of Eq. (2.2) is thus consistent with the two-level model as given by Eq. (2.3).

A similar inversion operation for the third-order polarization results in

$$P_i^{(3)}=\frac{\chi_{ijkl}^{(3)}(\mathbf{r})+\chi_{ijkl}^{(3)}(-\mathbf{r})}{2}E_jE_kE_l \;, \tag{2.4}$$

where the polarization vanishes for the antisymmetric part of the susceptibility. It is thus intriguing to examine the perturbation expressions for the third-order susceptibility to see if large susceptibilities are possible for centrosymmetric molecules. The perturbation expressions for the third-order susceptibility are derived in Secs. II A–II C for the two-, three-, and N-level system and are evaluated for the centrosymmetric limit to formulate relationships between the dipole matrix elements that maximize the susceptibility. We begin with the most general expression for the third-order susceptibility below.

If the exact form of the Hamiltonian for the charges in a material system is known, the electric-field perturbed equations of motion can be solved using time-dependent perturbation theory if the electric field coupling is weak. To calculate the nth-order susceptibility, the perturbation series must also be calculated to nth order in the applied field. The coefficient of the nth power of the electric field in this perturbation series is the nth-order susceptibility. A straightforward application of time-dependent perturbation theory to the third-order susceptibility results in divergent terms that are due to the slowly varying part of the wave function. These singularities can be taken into account by using the method of averages, resulting in[6]

$$\begin{aligned}
\chi_{ijkl}^{(3)}&(-\omega;\omega_1,\omega_2,\omega_3)\\
&=\frac{e^4}{4\hbar^3}\sum_{a,b,c=1}^{3}\delta_{\omega,\omega_1+\omega_2+\omega_3}\Bigg[\sum_{l,m,n}{}'\Bigg(\frac{\langle x_i\rangle_{gl}\langle\bar{x}_j\rangle_{lm}\langle\bar{x}_k\rangle_{mn}\langle x_l\rangle_{ng}}{(\Omega_{ng}-\omega_c)(\Omega_{mg}-\omega_c-\omega_b)(\Omega_{lg}-\omega_c-\omega_b-\omega_a)}\\
&\qquad+\frac{\langle x_i\rangle_{gl}\langle\bar{x}_j\rangle_{lm}\langle\bar{x}_k\rangle_{mn}\langle x_l\rangle_{ng}}{(\Omega_{lg}+\omega_a)(\Omega_{mg}-\omega_c-\omega_b)(\Omega_{ng}-\omega_c)}+\frac{\langle x_i\rangle_{gl}\langle\bar{x}_j\rangle_{lm}\langle\bar{x}_k\rangle_{mn}\langle x_l\rangle_{ng}}{(\Omega_{lg}+\omega_c)(\Omega_{mg}+\omega_c+\omega_b)(\Omega_{ng}-\omega_a)}\\
&\qquad+\frac{\langle x_i\rangle_{gl}\langle\bar{x}_j\rangle_{lm}\langle\bar{x}_k\rangle_{mn}\langle x_l\rangle_{ng}}{(\Omega_{ng}+\omega_c+\omega_b+\omega_a)(\Omega_{mg}+\omega_c+\omega_b)(\Omega_{lg}+\omega_c)}\Bigg)\\
&\qquad-\sum_{l,n}{}'\Bigg(\frac{\langle x_i\rangle_{gl}\langle x_j\rangle_{lg}\langle x_k\rangle_{gn}\langle x_l\rangle_{ng}}{(\Omega_{lg}-\omega_a)(\Omega_{lg}-\omega_a-\omega_b-\omega_c)(\Omega_{ng}-\omega_c)}+\frac{\langle x_i\rangle_{gl}\langle x_j\rangle_{lg}\langle x_k\rangle_{gn}\langle x_l\rangle_{ng}}{(\Omega_{lg}+\omega_a)(\Omega_{lg}-\omega_b)(\Omega_{ng}-\omega_c)}\\
&\qquad+\frac{\langle x_i\rangle_{gl}\langle x_j\rangle_{lg}\langle x_k\rangle_{gn}\langle x_l\rangle_{ng}}{(\Omega_{lg}-\omega_a)(\Omega_{lg}+\omega_b)(\Omega_{ng}+\omega_c)}+\frac{\langle x_i\rangle_{gl}\langle x_j\rangle_{lg}\langle x_k\rangle_{gn}\langle x_l\rangle_{ng}}{(\Omega_{lg}+\omega_a)(\Omega_{lg}+\omega_a+\omega_b+\omega_c)(\Omega_{ng}+\omega_c)}\Bigg)\Bigg] \;,
\end{aligned} \tag{2.5}$$

where x_i is the ith component of the position operator, the indices l, m, n label the states of the system, the brackets $\langle \mathbf{r}\rangle_{lm}$ represent the l and m matrix elements of the position operator, ω_1, ω_2, ω_3 represent the three frequencies of the incident fields, the barring operation is defined as $\bar{x}\equiv x-\langle x\rangle_{gg}$ (g is the ground state), the Ω_{nm}'s are the transition frequencies, the primed sum excludes the ground state, and δ is the Kronecker delta function. The outgoing field frequency ω is restricted by energy conservation through the time integral in the perturbation integral and is given by $\omega=\omega_1+\omega_2+\omega_3$. Note that negative frequency values can be substituted into Eq. (2.5) and are defined to represent outgoing fields (the first frequency argument is the frequency of interest).

While the transition frequencies in Eq. (2.5) are complex, far off resonance the energy denominators are mostly real and damping corrections can thus be ignored. A more detailed discussion of the effects of damping on nonlinear optical susceptibilities is discussed elsewhere.[7]

To recast Eq. (2.5) into a simple form, we define T^t_{lmn} to be the lmn term in the triple sum when all the numerators are unity. Similarly, we define $T^d_{\ln}$ to be the equivalent terms in the double sum. The third-order susceptibility can then be written in the form

$$\chi^{(3)}_{ijkl}(-\omega;\omega_1,\omega_2,\omega_3)=\sum_{l,m,n}{}' T^t_{lmn}(-\omega;\omega_1,\omega_2,\omega_3)\langle x_i\rangle_{gl}\langle \bar{x}_j\rangle_{lm}\langle \bar{x}_k\rangle_{mn}\langle x_l\rangle_{ng}$$
$$-\sum_{l,n}{}' T^d_{\ln}(-\omega;\omega_1,\omega_2,\omega_3)\langle x_i\rangle_{gl}\langle x_j\rangle_{lg}\langle x_k\rangle_{gn}\langle x_l\rangle_{ng} \;. \qquad (2.6)$$

When all the optical frequencies are well below the characteristic frequencies of the molecule, the coefficients T^t_{lmn} and $T^d_{\ln}$ are almost independent of the optical field frequencies. These coefficients are then inversely proportional to the product of the energies of the states labeled by the subscripts. Although T^t_{lmn} and $T^d_{\ln}$ decrease as a function of excited-state energy, the matrix elements depend on the properties of the system and can therefore cause nearly any term to dominate the third-order susceptibility.[4] Because T^t_{lmn} and $T^d_{\ln}$ are positive definite in the off-resonance regime, the two terms in Eq. (2.6) compete, and the degree of cancellation is determined by the matrix elements.

A. Two-level

One- and two-dimensional molecules are considered here for illustration although these expressions can be easily extended to include three-dimensional systems. For a one-dimensional molecule, the only nonzero tensor component of the third-order molecular polarizability is $\gamma_{xxxx}\equiv\chi^{(3)}$. Equation (2.5) in the limit of a one-dimensional molecule in the two-level approximation is given by

$$\chi^{(3)}=-(x_{01})^2[D_1(x_{01})^2-D_0(\Delta x)^2] \;, \qquad (2.7)$$

where μ_{01} is the transition moment $e\langle x\rangle_{01}$, (where the position operator is Hermitian) between the ground state 0 and the excited state 1, Δx is the difference between the expectation value of the excited- and ground-state position operator $(\langle x\rangle_{11}-\langle x\rangle_{00})$, and where $D_0=T^t_{111}$ and $D_1=T^d_{11}$. Far off resonance, the energy denominators are positive,

$$D_0, D_1>0 \;, \qquad (2.8)$$

and in the limit where all the applied electric field frequencies vanish, D_0 and D_1 are identical.

Far off resonance, there are only two adjustable parameters, namely, the transition dipole moment and the difference in dipole moment between the excited state and the ground state. Figure 1 shows a plot of the third-order susceptibility as a function of these two parameters. When the dipole moment difference vanishes, the third-order susceptibility is negative and is proportional to the fourth power of the transition moment. If the transition moment is small relative to the dipole difference, the third-order susceptibility is positive and is proportional to the square of the transition moment and dipole difference. For a fixed transition moment or dipole moment difference, the maximum zero-frequency third-order susceptibilities are

$$\chi^{(3)}=\frac{D_0}{4}(\Delta x)^4 \qquad (2.9)$$

and

$$\chi^{(3)}=-D_0(x_{01})^4 \;, \qquad (2.10)$$

respectively. Note that for a fixed transition moment, the maximum magnitude of positive $\chi^{(3)}$ corresponds to the special case where $(\Delta x)^2=2(x_{01})^2$. The largest positive susceptibility is then limited by the magnitude of the difference in dipole moment within this constraint. On the other hand, a centrosymmetric molecule has no ground-state or excited-state dipole moment, so the negative susceptibility is limited by the transition moment or equivalently, the oscillator strength. Thus the maximum magnitude of the third-order susceptibility in the two-level model is found in centrosymmetric molecules.

B. Three-level model

It is useful to consider a three-level model for either a two-dimensional molecule or for a one-dimensional molecule with two important excited states. The third-order susceptibility of a one-dimensional system as derived from Eq. (2.5) in the three-level model becomes

$$\chi^{(3)}=-x^2_{01}[D_1x^2_{01}-D_0(\Delta x_1)^2]-x^2_{02}[D_8x^2_{02}-D_5(\Delta x_2)^2]-2D_7x^2_{01}x^2_{02}+x^2_{12}(D_6x^2_{01}+D_4x^2_{02})$$
$$+2x_{01}x_{02}x_{12}(D_2\Delta x_1+D_3\Delta x_2) \;, \qquad (2.11)$$

where $D_2=T^t_{211}$, $D_3=T^t_{122}$, $D_4=T^t_{212}$, $D_5=T^t_{222}$, $D_6=T^t_{121}$, $D_7=T^d_{12}$, $D_8=T^d_{22}$, Δx_i is the position operator expectation value difference between state i and the ground state, and where x_{ij} is proportional to the transition moment between states i and j. Note that far off resonance, all the energy denominator coefficients are positive, and in the zero-frequency limit, $D_0=D_1$, $D_6=D_2=D_7$, $D_3=D_4$, and $D_5=D_8$. Also $\chi^{(3)}$ vanishes in the

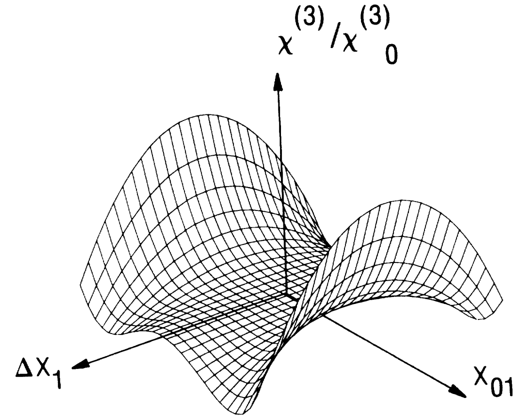

FIG. 1. The third-order susceptibility, normalized to the centrosymmetric two-level third-order susceptibility, as a function of transition moment and dipole difference when far off resonance. Note that the centrosymmetric third-order susceptibility of the two-level model is negative, so, the susceptibility is actually opposite in sign to the normalized value shown.

limit when the transition moments between the two excited states and the ground state vanish.

For a centrosymmetric molecule, the wave functions of the system are either spatially symmetric or antisymmetric. A dipole operator will only connect states of opposite symmetry, so for a centrosymmetric molecule with two excited states, the largest negative susceptibility will correspond to the case where both of the excited states have the same symmetry, which is opposite to the ground-state symmetry. In this limit, only the negative terms survive and the third-order susceptibility reduces to

$$\chi^{(3)}=-(D_1x_{01}^4+D_8x_{02}^4+2D_7x_{01}^2x_{02}^2)\ . \tag{2.12}$$

As in the two-level model, the maximum value of the third-order susceptibility is for a centrosymmetric molecule and is a function of only the oscillator strengths. In the noncentrosymmetric case, terms with both signs appear in the expressions, resulting in partial cancellation of the susceptibility.

For the three-level molecule in two dimensions, we consider the $\gamma_{xxyy}(\equiv\chi^{(3)})$ tensor component of the third-order susceptibility:

$$\begin{aligned}\chi^{(3)}={}&r_{01}^x r_{01}^y(D_8r_{01}^x r_{01}^y-D_0\Delta r_1^x\Delta r_1^y)-r_{02}^x r_{02}^y(D_8r_{02}^x r_{02}^y-D_0\Delta r_2^x\Delta r_2^y)-D_9[(r_{01}^x r_{02}^y)^2+(r_{01}^y r_{02}^x)^2]\\&+r_{12}^x r_{12}^y(D_1r_{01}^x r_{01}^y+D_6r_{02}^x r_{02}^y)+D_2(r_{02}^x r_{12}^x\Delta r_1^y r_{01}^y+r_{01}^x\Delta r_1^x r_{12}^y r_{02}^y)+D_4(r_{01}^x r_{12}^x\Delta r_2^y r_{20}^y+r_{02}^x\Delta r_2^x r_{12}^y r_{01}^y)\ ,\end{aligned} \tag{2.13}$$

where r^{x_i} is the x_i component of r. When the molecule is centrosymmetric, the only remaining positive contribution is the fourth term in Eq. (2.13), which vanishes when either the transition moment between state 1 and 2 is zero, or when the molecule has only one-dimensional excitations for which the oscillator strength vanishes in all but one tensor component. To illustrate how this term can vanish, consider a wave function of the three-level system that can be written as a product of two wave functions that define excitations polarized in the x and y directions,

$$\Psi_N(x,y)=\Psi_{n_1}(k_1x)\Psi_{n_2}(k_2y)\equiv|n_1,n_2\rangle\ , \tag{2.14}$$

where it is assumed that the first three energy levels of the system $(N=0,1,2)$ correspond to $|n_1,n_2\rangle=|0,0\rangle$, $|0,1\rangle$, and $|1,0\rangle$. Here, if the ground state is symmetric and both excited states are antisymmetric [$\Psi_1(k_1x)$ and $\Psi_1(k_2y)$ antisymmetric], the only nonzero elements of the position operator will be r_{01}^x and r_{02}^y.

In the above two-dimensional centrosymmetric system, the only contribution to the third-order susceptibility in the three-level model is from the third term in Eq. (2.13). Here, the two-level terms do not contribute, so a complete description of the third-order susceptibility for this system requires at least these three levels. Nevertheless, the third-order susceptibility is again determined by the magnitude of the oscillator strengths.

C. N-level model

In the N-level approximation of a one-dimensional molecule, the third-order susceptibility is of the form

$$\begin{aligned}\chi_{NL}^{(3)}={}&\sum_{n=1}^{N}\chi_{nL}^{(3)}(0,n)-f(\mu_{01}^2,\ldots,\mu_{0N}^2)\\&+g(\mu_{12},\ldots,\mu_{ij}(i\neq j\neq 0))+h(\Delta\mu_1,\ldots,\Delta\mu_N)\ ,\end{aligned} \tag{2.15}$$

where $\chi_{nL}^{(3)}(0,n)$ is the two-level term including state n and the ground state, $f(\mu_{01}^2,\ldots,\mu_{0N}^2)$ is a positive definite function that depends on the oscillator strengths, $g(\mu_{12},\ldots,\mu_{ij}(i\neq j\neq 0))$ is a function of transition moments between excited states, and where $h(\Delta\mu_1,\ldots,\Delta\mu_N)$ is a function of both transition and dipole moments and vanishes when all the dipole moments vanish. All the two-level terms and oscillator strength functions are negative when the molecule is centrosymmetric while the competing dipole terms vanish. The only remaining positive term can be ignored if the transition moments between excited states are small.

The extension of the N-level model to include two-dimensional molecules is straightforward. The four terms are generalized by including the two vector components in all the functions, but the results remain qualitatively similar; the competing negative terms are reduced in centrosymmetric molecules and can be made negligible if the transition moments connecting excited states to each other are small.

III. ASYMMETRIC PERTURBATIONS

In the preceding section, the two-, three-, and N-level models are shown to be maximized when the molecule is centrosymmetric and when the transition moments between excited states are small. Although this is mathematically possible, it is not clear that there is a relationship between the dipole moment and oscillator strengths that physically allows the matrix elements to have these required values. In this section we derive some simple relationships between the dipole matrix elements to investigate the conditions when centrosymmetric and polar systems have large oscillator strengths that lead to enhanced third-order susceptibilities.

The third-order susceptibility as given by Eq. (2.5) is a function of the matrix elements of the position operator x_{ij} and the eigenenergies of the molecule E_i. When the system is perturbed by some asymmetric perturbation of strength ϵ, both the energies and position matrix elements change. The change in the susceptibility with asymmetry, $\partial\chi^{(3)}(E_i,x_{ij})/\partial\epsilon$, is then given by

$$\frac{\partial\chi^{(3)}(E_i,x_{ij})}{\partial\epsilon}=\sum_{i,j}\left[\frac{\partial\chi^{(3)}(E_i,x_{ij})}{\partial E_i}\frac{\partial E_i}{\partial\epsilon}+\frac{\partial\chi^{(3)}(E_i,x_{ij})}{\partial x_{ij}}\frac{\partial x_{ij}}{\partial\epsilon}\right].$$

The partial derivative of the susceptibility with respect to energies and position matrix elements is directly computed from Eq. (2.5) while the partial derivative of the matrix elements of the position operator and energies with respect to the asymmetric perturbation is computed from perturbation theory as described in this section.

The centrosymmetric two-level model in Sec. III A depends only on one parameter: the oscillator strength. When the molecule is perturbed with an asymmetric potential, the oscillator strength changes and both the ground state and first excited state acquires a dipole moment. In the presence of the perturbation, the new dipole matrix elements are related to the unperturbed transition moment μ_{01}. It is then straightforward to check if the centrosymmetric molecule has a maximum third-order susceptibility relative to the perturbed system. Note that because the perturbation about the centrosymmetric system is necessarily small, this two-level system can only be used to test whether the centrosymmetric limit is a *local extremum*.

For highly polar molecules, the unperturbed two-level system has large ground- and excited-state dipole moments. In this more general case two parameters describe the molecule: the transition moment μ_{01} and the dipole moment difference between the ground and first excited states $\mu_{11}-\mu_{00}$. This system is perturbed to test the effects of making the system either more asymmetric or less asymmetric. Because the third-order susceptibility only depends on transition moments and dipole moment differences, the relevant relationships between the perturbed dipole moment matrix elements depend on the two unperturbed parameters μ_{01} and $\Delta\mu_1$.

The two-level model does not always describe the qualitative features of the third-order susceptibility. As an example, it is straightforward to show that the third-order susceptibility vanishes for a two-level system with only one two-photon state. By adding a one-photon state, though, the susceptibility of the three-level system no longer vanishes because of the coupling between the two excited states. Unfortunately, as we will show in Sec. III B, adding this extra excited state greatly increases the complexity of the asymmetric perturbation calculations and the results are often ambiguous. While an asymmetric perturbation causes the susceptibility to change in a well-defined way in certain limiting cases, the most general case of a polar molecule is too complicated to be treated here. We therefore consider only the three-level centrosymmetric case when there are only two one-photon states (Sec. III B 1) and when there is one one-photon state and one two-photon state (Sec. III B 2). Even in these highly restricted cases, the perturbed third-order susceptibility yields a wealth of information.

We use perturbation theory to calculate the perturbed states and use them to calculate the perturbed matrix elements of the position operator. If uppercase symbols denote the perturbed states and lowercase the unperturbed states, time-independent perturbation theory gives[8]

$$|N\rangle=|n\rangle+\sum_{k(\neq n)}|k\rangle\left[\frac{\langle k|V|n\rangle}{E_n-E_k}\left[1-\frac{\langle n|V|n\rangle}{E_n-E_k}\right]+\sum_{m(\neq n)}\frac{\langle k|V|m\rangle\langle m|V|n\rangle}{(E_n-E_k)(E_n-E_m)}\right], \tag{3.1}$$

where V is the perturbation potential. For simplicity, we will choose the perturbation to be of the form

$$V(x)=\frac{\varepsilon}{a}x\ , \tag{3.2}$$

where ε is a small parameter with units of energy and where a has units of length and gives the approximate size of the molecule.

Using the linear perturbation potential [Eq. (3.2)], the perturbed matrix elements of the position operator x are

$$\begin{aligned}\langle L|x|N\rangle=\langle l|x|n\rangle&+\frac{\varepsilon}{a}\left[\sum_{k\,(\neq n)}\frac{\langle l|x|k\rangle\langle k|x|n\rangle}{E_n-E_k}+\sum_{k'\,(\neq l)}\frac{\langle l|x|k'\rangle\langle k'|x|n\rangle}{E_l-E_{k'}}\right]\\&+\frac{\varepsilon^2}{a^2}\sum_{k\,(\neq n)}\sum_{k'(\neq l)}\frac{\langle l|x|k'\rangle\langle k'|x|k\rangle\langle k|x|n\rangle}{(E_l-E_{k'})(E_n-E_k)}\\&-\frac{\varepsilon^2}{a^2}\left[\sum_{k\,(\neq n)}\frac{\langle l|x|k\rangle\langle k|x|n\rangle\langle n|x|n\rangle}{(E_n-E_k)(E_n-E_k)}-\sum_{k\,(\neq n)}\sum_{m\,(\neq n)}\frac{\langle l|x|k\rangle\langle k|x|m\rangle\langle m|x|n\rangle}{(E_n-E_k)(E_n-E_m)}\right]\\&-\frac{\varepsilon^2}{a^2}\left[\sum_{k'\,(\neq l)}\frac{\langle l|x|l\rangle\langle l|x|k'\rangle\langle k'|x|n\rangle}{(E_l-E_{k'})(E_l-E_{k'})}-\sum_{k'\,(\neq l)}\sum_{m'\,(\neq l)}\frac{\langle l|x|m'\rangle\langle m'|x|k'\rangle\langle k'|x|n\rangle}{(E_l-E_{k'})(E_l-E_{m'})}\right].\end{aligned} \tag{3.3}$$

These perturbed matrix elements (and energies) can then be substituted into the two- and three-level models to see what unperturbed matrix elements give a local extremum of the third-order susceptibility. The effect of the perturbation on energy is given in Appendix B.

A. Two-level model

We begin by perturbing the centrosymmetric two-level model. If we call the perturbed transition moments $\mu'_{ij} = ex'_{ij}$, the unperturbed moments $\mu_{ij} = ex_{ij}$, and the energy differences $E_{ij} = E_i - E_j$, far from resonance when $D_1 = D_0$, the two-level model of the third-order susceptibility to second order in the perturbation becomes

$$\chi_{2L}^{(3)} = \chi_0^{(3)} + \Delta\chi_{2L}^{(3)}(\varepsilon) = -D_0 \left[x_{01}^4 - \frac{20\varepsilon^2 x_{01}^6}{a^2 E_{10}^2} \right] , \quad (3.4)$$

where $\chi_0^{(3)}$ is the unperturbed two-level third-order susceptibility. According to Appendix B, the perturbation of the two-level centrosymmetric system results in an increase in the transition energy. Far from resonance, this results in an increase in the energy denominator that results in a decrease in the third-order susceptibility. The centrosymmetric moleucle is thus locally maximum with respect to the perturbation.

Now we consider the noncentrosymmetric case. Appendix A lists all the perturbed transition moments in terms of the unperturbed moments. Using Eqs. (A6) and (A7) in the two-level model, Eq. (2.7), and far off resonance ($D_0 = D_1$), we get

$$\chi_{2L}^{(3)} = \chi_0^{(3)} + 2D_0 \frac{\varepsilon}{a} \frac{\Delta x_1}{E_{10}} (5x_{01}^4 - \chi_0^{(3)}) . \quad (3.5)$$

(The energy shifts from the perturbation will be included later.) To check if the third-order susceptibility is larger or smaller with the perturbation, six cases have to be considered. Because the term in parentheses in Eq. (3.5) is usually positive in the far off-resonance region, these six cases reduce to four as listed below:

$$\chi_0^{(3)} > 0 \text{ and } \Delta x_1 > 0 \text{ then } \frac{\Delta |\chi^{(3)}|}{\Delta\varepsilon} > 0 , \quad (3.6)$$

$$\chi_0^{(3)} > 0 \text{ and } \Delta x_1 < 0 \text{ then } \frac{\Delta |\chi^{(3)}|}{\Delta\varepsilon} < 0 , \quad (3.7)$$

$$\chi_0^{(3)} < 0 \text{ and } \Delta x_1 > 0 \text{ then } \frac{\Delta |\chi^{(3)}|}{\Delta\varepsilon} < 0 , \quad (3.8)$$

and

$$\chi_0^{(3)} < 0 \text{ and } \Delta x_1 < 0 \text{ then } \frac{\Delta |\chi^{(3)}|}{\Delta\varepsilon} > 0 . \quad (3.9)$$

Figure 2 shows the change in susceptibility as a function of the initial dipole moment difference and the transition moment. Note that if the term in parentheses in Eq. (3.5) is negative the inequalities in Eqs. (3.6) and (3.7) are reversed.

From Eq. (3.8), we see that when the transition moment is larger than the change in dipole moment, so the third-order susceptibility is negative, then the third-order susceptibility decreases with an asymmetric perturbation when the change in dipole moment is positive. On the other hand, Eq. (3.9) shows that a negative third-order susceptibility gets larger with the asymmetric perturbation when the change in dipole moment is negative. Figure 3 shows an example of the class of polar quinoidal molecules that have the property that the dipole moment difference is negative. Large third-order susceptibilities are then possible in either nonquinoidal molecules in the limit where the molecule is centrosymmetric or in polar quinoidal molecules. The energy denominator for the two-level case in Appendix B is seen to increase with the perturbation for the nonquinoidal system while it decreases for the quinoidal case. For both cases, then, the effect of the perturbation on energy denominators tends to reinforce the effect of the perturbation on the numerators.

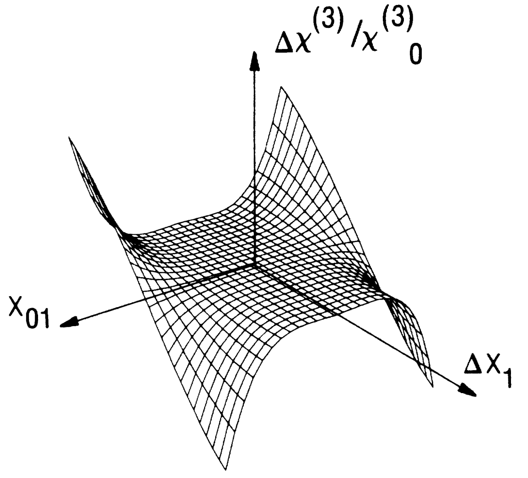

FIG. 2. The change of the third-order susceptibility, normalized to the centrosymmetric two-level third-order susceptibility, of an asymmetric molecule with additional asymmetry as a function of transition moments and dipole moment differences. Note that the centrosymmetric third-order susceptibility of the two-level model is negative, so, the susceptibility is actually opposite in sign to the normalized value shown.

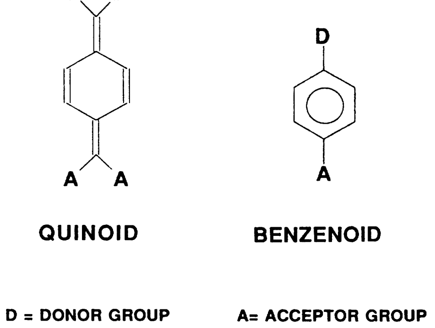

FIG. 3. An example of a polar quinoidal molecule and a benzenoid molecule.

Equations (3.6) and (3.7) describe molecules with positive third-order susceptibilities and, for these molecules, the opposite is true. When the molecule is perturbed to make it more polar, a nonquinoidal molecule will have an increased third-order susceptibility while the quinoidal molecule's third-order susceptibility will decrease. Note that if the molecule is so highly polar that the term in parentheses in Eq. (3.5) becomes negative, the quinoidal molecule will then have the largest susceptibility if it is strongly perturbed. For the positive third-order susceptibility, the energy denominators oppose the effects on the numerator resulting in a smaller change in the susceptibility with change in asymmetry. The systems with negative susceptibilities should thus have larger susceptibilities than those with positive susceptibilities. From the two-level model, it is clear that some noncentrosymmetric molecules can have large third-order susceptibilities. Mathematically, though, the largest possible susceptibility is for a centrosymmetric molecule with a large oscillator strength. Within this level of approximation it may be rewarding to study the class of centrosymmetric materials for large third-order susceptibilities.

B. Three-level model

Although the two-level model gives a wealth of information about the types of molecules that have the largest susceptibilities, many materials have more than one important excited state. The three-level model may be inadequate for some molecules, but it can take into account states that are dipole forbidden and can therefore describe the qualitative behavior of a much larger class of materials than the two-level model. Unfortunately, the perturbation expressions grow exponentially in complexity with the number of states included, so only the centrosymmetric three-level model will be considered here. Further, the perturbed expressions will be broken down into special cases where the two excited states can either be one- and/or two-photon states.

1. *One-photon states* ($x_{12}=0$)

Here we will consider the case where both excited states are one-photon states so $x_{12}=0$. Appendix A lists the perturbed matrix elements that are used in the five nonzero terms of the three-level model as given by Eq. (2.11). To first order in the perturbation, Eqs. (A8)–(A13) result in

$$\frac{\partial}{\partial\varepsilon}\Delta x_i' \geq 0 \ , \tag{3.10}$$

$$\frac{\partial}{\partial\varepsilon}x_{12}' \geq 0 \ , \tag{3.11}$$

and

$$\frac{\partial}{\partial\varepsilon}x_{01}' \leq 0 \ . \tag{3.12}$$

The sign of the change of x_{02}' with asymmetry depends on the energies:

$$\frac{\partial}{\partial\varepsilon}x_{02}' \leq 0 \quad \text{if} \quad \left[\frac{x_{01}}{x_{02}}\right]^2 \leq \frac{E_{10}}{|E_{10}-E_{21}|} \quad \text{and } E_{10} > E_{21} \ , \tag{3.13a}$$

$$\frac{\partial}{\partial\varepsilon}x_{02}' \leq 0 \quad \text{if} \quad \left[\frac{x_{01}}{x_{02}}\right]^2 \geq \frac{E_{10}}{|E_{10}-E_{21}|} \quad \text{and } E_{10} < E_{21} \ , \tag{3.13b}$$

$$\frac{\partial}{\partial\varepsilon}x_{02}' \geq 0 \quad \text{if} \quad \left[\frac{x_{01}}{x_{02}}\right]^2 \geq \frac{E_{10}}{|E_{10}-E_{21}|} \quad \text{and } E_{10} > E_{21} \ , \tag{3.13c}$$

$$\frac{\partial}{\partial\varepsilon}x_{02}' \geq 0 \quad \text{if} \quad \left[\frac{x_{01}}{x_{02}}\right]^2 \leq \frac{E_{10}}{|E_{10}-E_{21}|} \quad \text{and } E_{10} < E_{21} \ . \tag{3.13d}$$

The change in the third-order susceptibility in the three-level model under the above perturbation can be computed by considering how the conditions given by Eqs. (3.10)–(3.13) affect Eq. (2.11). The only two cases when the asymmetry increases the oscillator strength are given by Eqs. (3.13c) and (3.13d). If the two excited states are nearly degenerate, then Eq. (3.13c) requires that the first excited-state oscillator strength be smaller than that of the second excited state. Otherwise, the oscillator strength of the excited state decreases with asymmetry.

In the three-level system with two one-photon states, there is only one term that potentially increases with asymmetry. The rest of the terms will thus in general dominate and the asymmetric perturbation will result in a decrease of the third-order susceptibility. The energy denominators for this centrosymmetric case increase as they do in the two-level model and therefore reinforce the decrease in the susceptibility with asymmetry.

2. *One- and two-photon states*

In one-dimensional centrosymmetric systems, a three-level model with a one-photon state and a two-photon state qualitatively portrays the nonlinear optical properties of many molecules.[9] The effects of a perturbation on the third-order susceptibility in the three-level model with a one-photon state and a two-photon state are ambiguous. Some terms have fixed signs, while others depend on the energies and transition moments of the unperturbed system. Furthermore, the results depend on the energy ordering of the two states. To clarify the different cases, the effect of the asymmetry is summarized at the end of this section. Literature values of transition moments and energies of a well-studied molecule will be used to consider the limiting cases of the perturbations.

When the two-photon state has the lowest excitation energy, to order ε^2/a^2 the third-order susceptibility is

$$\begin{aligned}\chi^{(3)}=\chi_0^{(3)}&+4D_8\frac{\varepsilon^2}{a^2}\frac{x_{02}^4}{E_{20}}\left[\frac{E_{10}-E_{21}}{E_{10}E_{21}}x_{12}^2+\frac{x_{02}^2}{E_{20}}\right]+4D_5\frac{\varepsilon^2}{a^2}x_{02}^2\left[\frac{x_{12}^2}{E_{21}}+2\frac{x_{02}^2}{E_{20}}\right]^2-2D_7\frac{\varepsilon^2}{a^2}\left[\frac{E_{10}}{E_{21}E_{20}}\right]^2x_{02}^4x_{12}^2\\&-2D_4\frac{\varepsilon^2}{a^2}x_{02}^2\frac{x_{12}^2}{E_{21}}\left[\frac{E_{20}+E_{10}}{E_{20}E_{10}}x_{02}^2+\frac{x_{12}^2}{E_{21}}\right]+D_6\frac{\varepsilon^2}{a^2}\left[\frac{E_{10}}{E_{21}E_{20}}\right]^2x_{02}^2x_{12}^4\\&-2D_4\frac{\varepsilon^2}{a^2}x_{12}^2\frac{x_{02}^2}{E_{20}}\left[\frac{E_{10}-E_{21}}{E_{10}E_{21}}x_{12}^2+\frac{x_{02}^2}{E_{20}}\right]+4D_2\frac{\varepsilon^2}{a^2}\frac{E_{10}}{E_{21}E_{20}}x_{02}^2x_{12}^2\left[\frac{x_{02}^2}{E_{20}}-\frac{x_{12}^2}{E_{21}}\right]\\&+4D_3\frac{\varepsilon^2}{a^2}\frac{E_{10}}{E_{21}E_{20}}x_{02}^2x_{12}^2\left[2\frac{x_{12}^2}{E_{21}}+\frac{x_{02}^2}{E_{20}}\right],\end{aligned}\tag{3.14}$$

where $\chi_0^{(3)}=-D_8x_{02}^4+D_4\,x_{12}^2x_{02}^2$ is the unperturbed third-order susceptibility.

When the two-photon state is above the one-photon state, the asymmetric perturbation gives

$$\begin{aligned}\chi^{(3)}=\chi_0^{(3)}&+4D_1\frac{\varepsilon^2}{a^2}\frac{x_{01}^4}{E_{10}}\left[-\frac{E_{20}+E_{21}}{E_{20}E_{21}}x_{12}^2+\frac{x_{01}^2}{E_{10}}\right]+4D_0\frac{\varepsilon^2}{a^2}x_{01}^2\left[\frac{x_{12}^2}{E_{21}}+2\frac{x_{01}^2}{E_{10}}\right]^2\\&-2D_7\frac{\varepsilon^2}{a^2}\left[\frac{E_{20}}{E_{21}E_{10}}\right]^2x_{01}^4x_{12}^2+2D_6\frac{\varepsilon^2}{a^2}x_{01}^2\frac{x_{12}^2}{E_{21}}\left[\frac{E_{20}+E_{10}}{E_{20}E_{10}}x_{01}^2-\frac{x_{12}^2}{E_{21}}\right]+D_4\frac{\varepsilon^2}{a^2}\left[\frac{E_{20}}{E_{21}E_{10}}\right]^2x_{01}^2x_{12}^4\\&+2D_4\frac{\varepsilon^2}{a^2}x_{12}^2\frac{x_{01}^2}{E_{10}}\left[\frac{E_{20}+E_{21}}{E_{20}E_{21}}x_{12}^2-\frac{x_{01}^2}{E_{10}}\right]+4D_3\frac{\varepsilon^2}{a^2}\frac{E_{20}}{E_{21}E_{10}}x_{01}^2x_{12}^2\left[\frac{x_{01}^2}{E_{10}}+\frac{x_{12}^2}{E_{21}}\right]\\&+4D_2\frac{\varepsilon^2}{a^2}\frac{E_{20}}{E_{21}E_{10}}x_{01}^2x_{12}^2\left[\frac{x_{12}^2}{E_{21}}-2\frac{x_{01}^2}{E_{10}}\right],\end{aligned}\tag{3.15}$$

where $\chi_0^{(3)}=-D_1x_{01}+D_6x_{12}^2x_{01}^2$ is the unperturbed third-order susceptibility.

Equations (3.14) and (3.15) can be evaluated for physically reasonable energy levels and transition moments to see if the centrosymmetric limit is a local maximum. This depends on the sign of the susceptibility of the unperturbed system. When the two-photon state is lower in energy than the one-photon state, the sign will be determined by $\chi_0^{(3)}=-D_8x_{02}^4+D_4x_{12}^2x_{02}^2$ and when the two-photon state is of higher energy, the sign will be determined by $\chi_0^{(3)}=-D_1x_{01}^4+D_6\,x_{12}^2x_{01}^2$. We will thus consider the perturbation of both the positive and negative third-order susceptibility in the zero-frequency limit where the energy denominators are as defined following Eq. (2.11).

Far off resonance, the energy denominator coefficients in order of decreasing value are as follows: $D_0=D_1=k/E_{10}^3$, $D_2=D_6=D_7=k/E_{10}^2E_{20}^2$, $D_3=D_4=k/E_{10}E_{20}^2$, and $D_5=D_8=k/E_{20}^3$. Note that the constant of proportionality k is the same for all these coefficients. Setting this constant to unity is equivalent to redefining the system of units. In the off-resonance limit, we will consider the following two cases where: (1) the transition moment to the one-photon state is much larger than the transition moment between the two excited states so that the unperturbed susceptibility is negative; (2) the transition moment to the one-photon state is much smaller than the transition moment between the two excited states so that the unperturbed susceptibility is positive.

When the transition moment to the one-photon state dominates, the largest terms will be of order x_{0i}^6 $(i=1 or 2)$. This corresponds to the first two terms in both Eqs. (3.14) and (3.15). The energy denominator coefficients of these terms are larger than the coefficients of the other terms. Because the unperturbed susceptibility is negative, these two terms will result in a decrease in the magnitude of the susceptibility with asymmetry. In these cases, the transition energies to the ground state from both excited states also increase with the asymmetric perturbation as given by Eqs. (B2) and (B3). Because these energies appear in the denominator, the perturbation results in a further decrease in the susceptibility. In these two cases, the third-order susceptibility is again maximal for the centrosymmetric system.

In the case when the transition moment between the two excited states dominates the transition moment to the one-photon state, $\chi_0^{(3)}$ will be positive. Using the off-resonant energy denominators as defined above, Eq. (3.14) to lowest order in x_{02}/x_{12} is

$$\chi^{(3)}=\chi_0^{(3)}+17\frac{\varepsilon^2}{a^2}\frac{x_{02}^2x_{12}^4}{E_{10}^2E_{20}^3E_{21}^2}\times\left[\left[\frac{E_{10}}{E_{20}}\right]^2-\frac{12}{17}\left[\frac{E_{10}}{E_{20}}\right]+\frac{2}{17}\right],\tag{3.16}$$

where the term in square brackets is negative only in the interval

$$\frac{6-\sqrt{2}}{17}<\frac{E_{10}}{E_{20}}<\frac{6+\sqrt{2}}{17}.\tag{3.17}$$

Similarly, Eq. (3.15) to lowest order in x_{02}/x_{12} is

$$\chi^{(3)}=\chi_0^{(3)}+\frac{\varepsilon^2}{a^2}\frac{x_{01}^2x_{12}^4}{E_{21}E_{10}^2}\left[\frac{5}{E_{10}E_{21}}+\frac{2}{E_{20}E_{21}}+2\frac{E_{20}+E_{21}}{E_{20}^3}\right], \qquad (3.18)$$

where the term in parentheses is positive definite.

For the case when the two-photon state is below the one-photon state and the transition moment between the excited states dominates, the nonperturbed positive susceptibility gets smaller when asymmetrically perturbed under the constraint of Eq. (3.17). Because the energy-level spacings decrease with energy in typical systems, the condition of Eq. (3.17) will not be obeyed and the susceptibility will become more positive with the perturbation. The magnitude of the third-order susceptibility will thus increase with asymmetry. Similarly, when the two-photon state is of higher energy, the third-order susceptibility always becomes more positive with perturbation. So, in the three-level model, an asymmetric perturbation will generally increase the magnitude of the susceptibility if the transition moment between the two excited states is large enough to make the unperturbed susceptibility positive.

In calculating the change in the susceptibility in the three-level model with one- and two-photon states, the perturbation of the energy denominators was not accounted for. As we saw above, if the coupling between excited states is weak, the centrosymmetric case is maximal even when the effects of the energy denominators are included. In the other limit, when the transition moment is large between the excited states relative to the transition to the one-photon state, the energy of the second excited state increases while the energy of the first excited state decreases. Both these terms then partially cancel. Furthermore, the change in the susceptibility from the energy denominators tends to be smaller than that from the transition moments. The dependence of the susceptibility on asymmetry as given by Eqs. (3.16) and (3.18) is qualitatively correct and the susceptibility will usually increase in magnitude with the perturbation.

For the two-level model and the three-level model with two one-photon states, we see that in most cases the centrosymmetric systems have the maximum susceptibility. One important exception was the quinoidal systems, where the asymmetry enhances the susceptibility. While the asymmetric class of molecules has been extensively studied, the calculations presented here suggest that the class of centrosymmetric molecules has large, negative third-order susceptibilities and may be of potential importance. The possibility of synthesizing molecules with large negative third-order susceptibilities is attractive for device applications where intensities are often high enough to cause catastrophic self-focusing events in positive $\chi^{(3)}$ materials.

IV. EXAMPLES OF SOME SYSTEMS

The above calculations show some of the relationships between dipole matrix elements that allow the susceptibility to be maximized in the presence of an asymmetric perturbation under certain initial conditions. Experimentally, an organic molecule can be perturbed by adding a pair of donor-acceptor groups on opposite sides of the molecule. At first thought, a possible experiment to test these results, then, would be to compare the nonlinear optical properties of a centrosymmetric molecule like benzene to a di-substituted benzene. This comparison, though, is not useful because the di-substitution affects the benzene molecule strongly.

A much more useful comparison would be between three molecules with two having acceptors or donors on both ends and comparing them to the asymmetric form with the donor on one end and the acceptor on the other end. These comparisons may also be dubious if the asymmetry is too large. Unfortunately, both theoretically and experimentally determined molecular susceptibilities are not currently accurate enough to test the detailed behavior of the susceptibility under perturbation. Molecules with large susceptibilities, though, can be synthesized by using some of the qualitative results presented here and large susceptibilities can be partially understood in terms of the centrosymmetry concepts. Two common systems that can be calculated exactly are the particle in the box and the harmonic oscillator. These two cases are discussed in Sec. IV A to show that the concept of centrosymmetry holds in these N-level models. In Sec. IV B the matrix elements and energies of octatetraene, as calculated by other workers, are used in the perturbation expressions to show cases where the asymmetry increases the susceptibility.

A. Harmonic oscillator and particle in a box

In this section we perturb the N-level model of a particle in a box and a harmonic oscillator by applying Eq. (3.3) and Eq. (B1) to the analytic expressions for the wave functions. To ensure that all important levels are included, the convergence of the third-order susceptibility is tested by successively including more excited states till the change in the susceptibility is much smaller than the amount of perturbation. These convergence plots are shown in Fig. 4.

The harmonic oscillator results in a positive susceptibility. The two-level model incorrectly predicts a negative susceptibility because energetically higher-lying states with large transition moments dominate and must be included. Here, all the two-level terms of the N-level model above the first excited state are dipole disallowed and vanish, resulting in a positive susceptibility. Nevertheless, if the system is perturbed by an asymmetric potential, the magnitude of the susceptibility decreases. The particle in a box, however, has a negative susceptibility. Here, the N-level model results in nonvanishing two-level terms for states with negative parity and the resulting third-order susceptibility is negative. In both cases, though, the asymmetric potential causes the magnitude of the susceptibility to decrease.

B. *trans*-octatetraene

One conjugated molecule that has been studied extensively for its third-order nonlinear optical properties is *trans*-octatetraene.[9,10] The two most important energy

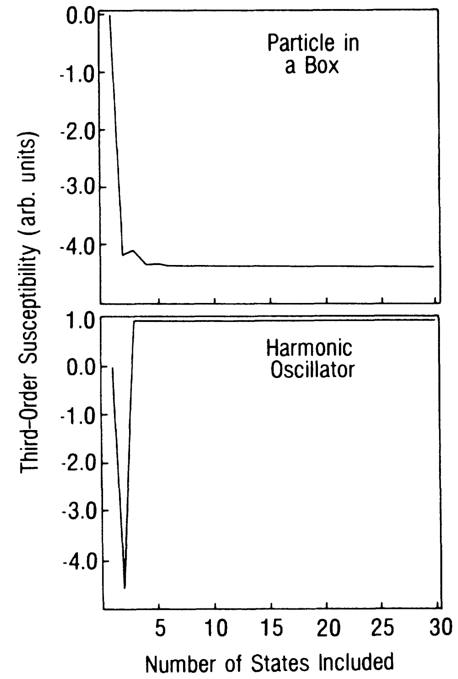

FIG. 4. Convergence of the third-order susceptibility, normalized to the centrosymmetric two-level third-order susceptibility, of the particle in a box (top) and the harmonic oscillator (bottom). Note that the centrosymmetric third-order susceptibility of the two-level model is negative, so, the susceptibility is actually opposite in sign to the normalized value shown.

levels and transition dipole moments as calculated by Heflin *et al.*[9] and Soos and Ramasesha[10] are summarized in Table I. Both sets of results are consistent with each other. Heflin and co-workers have shown that these two states dominate the third-order susceptibility. This system is therefore a good approximation to a three-level model with a two-photon state at higher energy than the one-photon state. The unperturbed system has a larger transition moment between the excited states than from the ground state to the one-photon state. The unperturbed third-order susceptibility is positive and our three-level model predicts that this system should have a larger susceptibility if asymmetrically perturbed.

To check this numerically, the transition moments and energy levels from Table I are used to evaluate Eq. (3.15). The value of each term of Eq. (3.15) is given in Table II.

TABLE I. Dipole matrix elements and transition energies of the two dominant states in *trans*-octatetraene as calculated by Heflin and Soos.

Energy or matrix element	Heflin	Soos
E_{01} (eV)	4.41	4.5608
x_{01} (Debye)	7.8	8.454
E_{06} (eV)	7.2	7.2713
x_{16} (Debye)	13.2	14.362

TABLE II. The change in the third-order susceptibility as given by Eq. (3.15) (term by term) using the dipole matrix elements and transition energies of the two dominant states in *trans*-octatetraene as calculated by Heflin and Soos from Table I.

	$\Delta\chi^{(3)}\varepsilon^2/a^2$($10^4$ arb. units)	
Term	Heflin	Soos
1	0.285	0.419
2	−2.301	−3.478
3	0.315	0.482
4	0.218	0.364
5	−0.277	−0.436
6	−0.153	−0.238
7	−0.828	−1.320
8	−0.618	−0.126
Total	−3.357	−5.233

For both sets of results, the magnitude of the susceptibility increases with the perturbation. An asymmetric form of this conjugated system, then, should have a larger susceptibility. This is consistent with results of Garito and co-workers, whose calculations show that highly polar versions of this molecule have large third-order susceptibilities.[11]

Noncentrosymmetric molecules can therefore possess substantial negative susceptibilities if both the transition moments between all the excited states are small and the asymmetry is small, or, when the transition moments between excited states are large. Although the competing terms are reduced in this polar case, the two-level terms of the N-level system are not always optimized. Furthermore, some of the "noncentrosymmetric" terms have indefinite sign, and must be determined on a case-by-case basis. Large negative susceptibilities can therefore be obtained in some asymmetric structures by maximizing the asymmetry. Unfortunately, the competing positive terms are always present, and minimizing these effects may be difficult in real systems unless there are some unknown underlying relationships between the matrix elements that result in fortuitous cancellations of these terms.

V. SUMMARY

For the two-level centrosymmetric case, the nonperturbed molecule has the largest susceptibility. For a highly asymmetric molecule, the susceptibility increases with perturbation when the nonperturbed susceptibility is negative and the molecule is quinoidal ($\Delta x_1 < 0$). When the unperturbed susceptibility is positive, a nonquinoidal system ($\Delta x_1 > 0$) will also show an increase in the susceptibility with asymmetry.

While the three-level model has many cases to consider, only the centrosymmetric systems are evaluated. When there are two one-photon states, the centrosymmetric molecule will have the largest susceptibility. With both a one- and a two-photon state, the centrosymmetric molecule will have the largest susceptibility when the transition moment between the one-photon state and the ground state is large compared with the transition mo-

TABLE III. Summary of effects of perturbation on $\chi^{(3)}$.

Levels	x_{01}	x_{02}	x_{12}	Δx_1	$\chi_0^{(3)}$	$\lvert\partial\chi^{(3)}/\partial\varepsilon\rvert$
Two	$\neq 0$	0	0	0	− or +	<0
Two	$\neq 0$	0	0	>0	−(+)	$<0(>0)$
Three	$\neq 0$	$\neq 0$	0	0	−	<0
Three	$\neq 0$	0	$\ll x_{01}$	0	−	<0
Three	$\neq 0$	0	$\gg x_{01}$	0	+	>0
Three	0	$\neq 0$	$\ll x_{02}$	0	−	<0
Three	0	$\neq 0$	$\gg x_{02}$	0	+	>0

ment between excited states. In the limit where the excited-state transition moments dominate, the susceptibility usually increases with asymmetry. This was shown for *trans*-octatetraene. Table III summarizes these cases.

VI. CONCLUSION

The two-, three-, and N-level models were derived for the off-resonant electronic third-order optical susceptibility. The magnitude of the susceptibility in the two-level system was shown to be maximal for centrosymmetric structures with large oscillator strengths and for three- and N-level systems with the additional criteria of weak coupling between the excited states. Although large-$\chi^{(2)}$ requires a large dipole difference between the ground and excited states, $\chi^{(3)}$ does not have the same constraint and can be large when all dipole moments vanish. The harmonic oscillator and particle in a box are examples of centrosymmetric potentials that lead to maximal positive and negative susceptibilities, respectively.

When the third-order susceptibility of the two-level model is perturbed, the centrosymmetric system always has the maximum value of the third-order susceptibility. The asymmetric system, however, has a large susceptibility when the molecule is quinoidal and asymmetric. In the three-level model, strong transition moments between the excited states result in large susceptibilities for the asymmetric systems while the other cases favor the centrosymmetric molecules.

The purpose of these calculations is to gain qualitative insight into the nature of the states that contribute strongly to the third-order susceptibility. Owing to the complexity of the system, we did not go beyond the centrosymmetric three-level model. Because the three-level model qualitatively describes the important features of the contributions to the third-order susceptibility, and systems with two dominant excited states can account for most of a system's susceptibility,[9] it would be instructive to consider perturbations of the three-level model of highly asymmetric systems. This would undoubtedly lead to a wealth of information.

Another simplification in our calculation is the linear approximation to the perturbation. In real systems with strong donors or acceptors, the induced asymmetry cannot be expected to be of such simple form and should be a power series of the position operator, $\sum_i a_i x^i$. Again, the complexity of doing this is beyond the scope of this work.

The qualitative results obtained here are useful to help understand the origin of the third-order susceptibility and should serve as a guideline for the synthesis of new materials. Preliminary results show that the centrosymmetric squarylium dyes potentially have some of the largest molecular third-order susceptibilities as measured with quadratic electro-optic modulation. These results will be presented in a future publication.[12]

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APPENDIX A

In this appendix the perturbed matrix elements of the position operator are expressed in terms of the unperturbed operators. The perturbing potential is of the form

$$V(x)=\frac{\varepsilon}{a}x \tag{A1}$$

as defined in the main text. Here, the relevant perturbed matrix elements are given for the centrosymmetric two-level model, the noncentrosymmetric two-level model, and the centrosymmetric three-level model.

The variables are defined below:

$$x_{ij}=\langle i|x|j\rangle \ , \tag{A2}$$

$$x_i=\langle i|x|i\rangle \ , \tag{A3}$$

$$\Delta x_i=x_i-x_0 \ , \tag{A4}$$

and

$$E_{ij}=E_i-E_j \ , \tag{A5}$$

where x is the position operator and E_i the energy of state i.

1. Two-level noncentrosymmetric case

We have

$$\Delta x_1'=\Delta x_1+4\frac{\varepsilon}{a}\frac{x_{01}^2}{E_{10}}-5\frac{\varepsilon^2}{a^2}\frac{x_{01}^2}{E_{10}^2}\Delta x_1 \tag{A6}$$

and

$$x_{01}'=x_{01}\left[1-\frac{\varepsilon}{a}\frac{\Delta x_1}{E_{10}}-\frac{\varepsilon^2}{a^2}[x_{01}^2-(\Delta x_1)^2]\right] . \tag{A7}$$

2. Three-level centrosymmetric case

We have

$$x'_{00}=-2\frac{\varepsilon}{a}\left[\frac{x_{01}^2}{E_{10}}+\frac{x_{02}^2}{E_{20}}\right]+6\frac{\varepsilon^2}{a^2}\frac{x_{01}x_{12}x_{02}}{E_{20}E_{10}}\,, \tag{A8}$$

$$x'_{11}=2\frac{\varepsilon}{a}\left[\frac{x_{01}^2}{E_{10}}-\frac{x_{12}^2}{E_{21}}\right]-6\frac{\varepsilon^2}{a^2}\frac{x_{01}x_{12}x_{02}}{E_{21}E_{10}}\,, \tag{A9}$$

$$x'_{22}=2\frac{\varepsilon}{a}\left[\frac{x_{12}^2}{E_{21}}+\frac{x_{02}^2}{E_{20}}\right]+6\frac{\varepsilon^2}{a^2}\frac{x_{01}x_{12}x_{02}}{E_{21}E_{20}}\,, \tag{A10}$$

$$\begin{aligned}x'_{01}&=x_{01}-\frac{\varepsilon}{a}\frac{E_{21}-E_{20}}{E_{21}E_{20}}x_{02}x_{12}\\&\quad+\frac{\varepsilon^2}{a^2}\frac{x_{01}}{E_{10}}\left[\frac{E_{20}+E_{21}}{E_{20}E_{21}}(x_{12}^2-x_{02}^2)-\frac{x_{01}^2}{E_{10}}\right]\,,\end{aligned} \tag{A11}$$

$$\begin{aligned}x'_{02}&=x_{02}-\frac{\varepsilon}{a}\frac{E_{21}+E_{10}}{E_{21}E_{10}}x_{01}x_{12}\\&\quad+\frac{\varepsilon^2}{a^2}\frac{x_{02}}{E_{20}}\left[\frac{E_{10}-E_{21}}{E_{10}E_{21}}(x_{01}^2-x_{12}^2)-\frac{x_{02}^2}{E_{20}}\right]\,,\end{aligned} \tag{A12}$$

and

$$\begin{aligned}x'_{12}&=x_{12}+\frac{\varepsilon}{a}\frac{x_{01}x_{02}}{E_{20}E_{10}}(E_{20}+E_{10})\\&\quad+\frac{\varepsilon^2}{a^2}\frac{x_{12}}{E_{21}}\left[\frac{E_{20}+E_{10}}{E_{20}E_{10}}(x_{01}^2-x_{02}^2)-\frac{x_{12}^2}{E_{21}}\right]\,.\end{aligned} \tag{A13}$$

APPENDIX B

In this appendix we relate the perturbed second-order energies E_i' to the unperturbed energies E_i,

$$E_n'=E_n+\frac{\varepsilon}{a}x_{nn}+\frac{\varepsilon^2}{a^2}\sum_{k\,(\neq n)}\frac{x_{nk}^2}{E_n-E_k}\,. \tag{B1}$$

For the most general three-level system, the energy differences between states ($E_{ij}=E_i-E_j$) to second order in the perturbation are

$$E'_{10}=E_{10}+\frac{\varepsilon}{a}\Delta x_1+\frac{\varepsilon^2}{a^2}\left[2\frac{x_{01}^2}{E_{10}}+\frac{x_{02}^2}{E_{20}}-\frac{x_{12}^2}{E_{21}}\right]\,, \tag{B2}$$

$$E'_{20}=E_{20}+\frac{\varepsilon}{a}\Delta x_2+\frac{\varepsilon^2}{a^2}\left[\frac{x_{01}^2}{E_{10}}+2\frac{x_{02}^2}{E_{20}}+\frac{x_{12}^2}{E_{21}}\right]\,, \tag{B3}$$

and

$$\begin{aligned}E'_{21}&=E_{20}+\frac{\varepsilon}{a}(\Delta x_2-\Delta x_1)\\&\quad+\frac{\varepsilon^2}{a^2}\left[-\frac{x_{01}^2}{E_{10}}+\frac{x_{02}^2}{E_{20}}+2\frac{x_{12}^2}{E_{21}}\right]\,.\end{aligned} \tag{B4}$$

Note that in the centrosymmetric case, the energy correction is second order in the asymmetry factor ε.

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