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Self-Consistent Approach for Simplifying the Molecular Interpretation of Nonlinear Optical and Multiphoton Phenomena

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A method is developed for simplifying molecular interpretations of nonlinear optical phenomena. General sum-over-states expressions derived from perturbation theory can be written identically and self-consistently as simple products of lower-order effects. Electric dipole-allowed expressions for the nonlinear polarizability reduce to straightforward formulas directly connected to intuitive molecular properties without sacrificing mathematical rigor. This approach is sufficiently general to allow its application in treating electronic, vibrational, and vibronic interactions for both parametric (passive) processes (e.g., wave-mixing spectroscopies, sum- and difference-frequency generation, harmonic generation, etc.) and nonparametric (active) processes (e.g., hyper-Raman spectroscopy, multiphoton absorption, etc.). Explicit examples for sum-frequency generation and for four-wave mixing provide a convenient context for interpreting higher order nonlinear optical processes.

1. Introduction

The increasing availability of ultrafast lasers has allowed unprecedented access to nonlinear optical (NLO) methods for probing molecular and material properties. As existing NLO methods are used to probe increasingly diverse molecular systems and as novel NLO spectroscopic techniques continue to emerge, the need is growing for the development of approaches for simplifying the interpretation of NLO measurements at both the molecular and macromolecular levels.

NLO processes can be interpreted in either the time-domain or the frequency-domain.[1−5] The frequency-dependent polarizability tensor derived from perturbation theory is obtained using a sum-over-states (SOS) expansion, including products of transition moments corresponding to the complete set of Feynman diagrams for the given NLO process.[1,6−8] Equation 1 is a general expression for the microscopic nonlinear polarizability tensor ξ for an NLO process of order n.[2−4]

$$\xi^{(n)}_{\mathrm{FI}}(-\omega_{n+1};\omega_1,\omega_2,...,\omega_n) = \frac{(-1)^{n+1}}{2^{n-1}d!\hbar^n} S_{\mathrm{T}} \sum_r ... \sum_q \sum_p \left\{ \frac{\mu^{(0)}_{\mathrm{F}r}...\mu^{(0)}_{rq}\mu^{(0)}_{p\mathrm{I}}}{(\omega_{r\mathrm{I}}-\omega_1-...-\omega_n)...(\omega_{q\mathrm{I}}-\omega_{n-1}-\omega_n)(\omega_{p\mathrm{I}}-\omega_n)} \right\} \quad (1)$$

Equation 1 contains $(n + 1)!$ terms in the braces, and each of the n summations is performed over all accessible states within the molecular system. The symbols $\mu_{ji}{}^{(0)}$ and ω correspond to the transition dipole from state i to state j and the angular frequency, respectively. Transition frequencies are defined such that $\omega_{p\mathrm{I}} = \omega_p - \omega_{\mathrm{I}}$, where if the initial state I is the ground state then $\omega_{\mathrm{I}} = 0$. S_{T} is the overall permutation operator, indicating that the summations are performed over all permutations of the field frequencies and corresponding transition dipole moments.[2,3] The factor $d!$ equals the number of identical permutations arising in the presence of degenerate frequencies. This general expression can reduce down to previously published expressions for Raman,[9] hyper-Raman,[10] second harmonic generation (SHG),[11] three-wave sum-frequency generation (3WSFG),[11] coherent anti-Stokes Raman,[12] and several other NLO processes[6] by allowing the frequencies to be degenerate and/or negative in sign.

The general expression in eq 1 can be used to describe virtually all NLO and multiphoton processes, including higher harmonic generation and difference-frequency generation (DFG), subject to the following approximations. First, the analysis presented here only holds within the validity of the electric dipole approximation, although it can be easily extended to include magnetic dipole, electric quadrupole, and other effects.[6,9,13] Second, it is assumed that all states in the summation are eigenstates of the molecule. Additionally, virtually all general sum-over-states expressions such as given in eq 1 implicitly assume Lorentzian line shape functions, corresponding to exponentially decaying molecular response functions.[5] This approximation often does not rigorously hold in condensed phase media, in which the time scale for reorganization of the bath and/or intermolecular reorganization is comparable to the excited-state lifetime, and the molecular response functions are more complex than simple exponential functions.[5] Nevertheless, within the limit of inhomogeneous broadening approximated as an integration over homogeneously broadened Lorentzian peaks in a static lattice, sum-over-states expressions retain some degree of rigor while still providing a simplified route for describing general molecular properties.

Although complete, the full SOS expression in eq 1 is cumbersome to use for interpreting spectroscopic measurements and materials properties. For example, in conventional perturbation theory a third-order NLO process generally contains a triple sum over all accessible states with 24 individual products of four transition moments within the SOS expression.[14] However, a relatively small subset of the total number of terms within SOS expansion often dominates under conditions of resonance-enhancement (i.e., within the rotating-wave approximation), allowing reduction of the SOS expression in eq 1 into more compact and intuitive expressions. This approach has been taken for describing resonance-enhanced SHG[15] and 3WSFG,[15,16] coherent anti-Stokes Raman spectroscopy (CARS),[1,2,17−19] third-

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harmonic generation (THG),[2,17] and three-photon resonant fifth-order polarizabilities (six-wave), which includes stimulated three-photon absorption and fifth harmonic generation.[17]

Two commons formalisms have developed for treating the electric fields in NLO processes as indicated by eq 2.

$$E(x,t) = E_0 e^{-i(\omega t - \hat{k}x)} \tag{2a}$$

$$E(x,t) = E_0 \cos(\omega t - \hat{k}x) = \frac{E_0}{2}[e^{-i(\omega t - \hat{k}x)} + e^{i(\omega t - \hat{k}x)}] \tag{2b}$$

If the optical fields are treated as purely real sinusoids as in eq 2b, consistent with many previous treatments in the frequency domain, then the time-dependent fields implicitly contain both the time-forward and time-reversed elements. Throughout this work the simpler form in eq 2a is used. The relationships between these two different conventions are summarized in several places.[5,20] When using a purely real sinusoidal optical field as in eq 2b, the number of terms in the full SOS equation doubles to include the complex conjugate of the polarizability tensor.[20] For example, use of eq 2b results in 12 terms[6,11,15] in the full SOS equation for 3WSFG where use of eq 2a yields six terms.[3]

Two significant limitations arise in the use of resonance-enhanced simplifications. First, expressions for only a relatively small subset of the total number of possible resonant conditions have been considered previously. As the number and scope of new NLO measurements continues to expand, the relatively limited number of existing expressions for resonance-enhanced polarizabilities may or may not apply to a given experiment. Second, considering just the terms for a single set of assumed resonances may not adequately capture all of the additional interactions contributing to the total molecular NLO polarizability.

In this work, simple expressions are derived allowing optical nonlinearity to be expressed within the context of the relatively compact and intuitive resonant expressions, but without sacrificing the completeness of the full SOS analysis. The molecular polarizability tensors can be written as simple products of lower order effects without loss of mathematical rigor.

2. Re-Expressing the SOS Equation

The expression for $\xi^{(n)}$ can be rewritten in a more compact form by recognizing that grouping of terms allows $\xi^{(n)}$ to be written as a sum of $(n + 1)$ terms consisting of a product of a transition moment and a polarizability tensor of order $\xi^{(n-1)}$, or equivalently as a sum of $n(n + 1)/2$ terms consisting of a product of an $\alpha^{(1)}$ tensor and a polarizability tensor of order $\xi^{(n-2)}$, or again equivalently as a sum of $n(n^2 - 1)/6$ terms consisting of a product of a $\beta^{(2)}$ tensor and a polarizability tensor of order $\xi^{(n-3)}$, etc.

$$\begin{aligned}
&\xi^{(n)}_{\mathrm{FI}}(-\omega_{n+1};\omega_1,\omega_2,...,\omega_n) = \\
&\frac{-1}{2^{n-1}\hbar} S_{\mathrm{T}} \sum_p \left\{ \frac{\xi^{(n-1)}_{\mathrm{F}p}\mu^{(0)}_{p\mathrm{I}}}{\omega_{p\mathrm{I}} - \omega_1} \right\} \\
&= \frac{1}{2^{n-1}\hbar} S_{\mathrm{T}} \sum_q \left\{ \frac{\xi^{(n-2)}_{\mathrm{F}q}\alpha^{(1)}_{q\mathrm{I}}}{\omega_{q\mathrm{I}} - (\omega_1 + \omega_2)} \right\} \\
&\vdots \\
&= \frac{-1}{2^{n-1}\hbar} S_{\mathrm{T}} \sum_r \left\{ \frac{\mu^{(0)}_{\mathrm{F}r}\xi^{(n-1)}_{r\mathrm{I}}}{\omega^*_{r\mathrm{I}} + (\omega_1 + ... + \omega_n)} \right\}
\end{aligned} \tag{3}$$

A zero order tensor is defined here to be the transition dipole vector $-\mu^{(0)}_{\mathrm{FI}}$, which also determines the overall sign (e.g., a $\gamma^{(3)}$ process has overall positive sign and can be described by products of transition moments with negative sign and $\beta^{(2)}$ tensors with overall negative sign). The transition frequency is defined such that $\omega_{r\mathrm{I}} = \omega_{r\mathrm{I}} - i\Gamma_r$ and $\omega^*_{r\mathrm{I}} = \omega_{r\mathrm{I}} + i\Gamma_r$, in which ω and Γ are real quantities and Γ is the damping term introduced phenomenologically. In practice, the frequency terms within the parenthetical can be either positive or negative in sign depending on the nonlinear optical process. Changing the sign of any given frequency term from the form provided in the general expressions given in this work also results in a sign change in the phenomenological damping constant (which is equivalent to using the complex conjugate of the $\omega_{r\mathrm{I}}$ terms reported here). For compactness, only one term in each summation is shown in eq 3, indicating the general form for the series of terms within the braces. Each summation indicates an alternative expression for the nonlinear polarizability that is identically equal to the expression in eq 1. All other terms only differ in the frequency denominators and by the x, y, and z components of the transition dipoles and polarizability tensors. Expansions of the three equivalent expressions shown in the series of eq 3, explicitly including the polarization/frequency information contained within the nonlinear polarizabilities (indicated by the superscripts) are given in eq 4.

$$\begin{aligned}
&\xi^{ij...j_n}_{\mathrm{FI}}(-\omega_{n+1};\, \omega_1,\omega_2,...,\omega_n) = \\
&\frac{-1}{2^{n-1}\hbar} \sum_p \left\{ \frac{\xi^{j_n...kj}_{\mathrm{F}p}\,\mu^i_{p\mathrm{I}}}{\omega^*_{p\mathrm{I}} + \omega_{n+1}} + \frac{\xi^{ik...j_n}_{\mathrm{F}p}\,\mu^j_{p\mathrm{I}}}{\omega_{p\mathrm{I}} - \omega_1} + ... + \frac{\xi^{ij...j_{n-1}}_{\mathrm{F}p}\,\mu^{j_n}_{p\mathrm{I}}}{\omega_{p\mathrm{I}} - \omega_n} \right\}
\end{aligned} \tag{4a}$$

$$\begin{aligned}
&\xi^{ij...j_n}_{\mathrm{FI}}(-\omega_{n+1};\, \omega_1,\omega_2,...,\omega_n) = \frac{1}{2^{n-1}\hbar} \sum_q \\
&\left\{ \begin{aligned}
&\frac{\xi^{ij...j_n}_{\mathrm{F}q}\,\alpha^{jk}_{q\mathrm{I}}}{\omega_{q\mathrm{I}} - (\omega_1 + \omega_2)} + \frac{\xi^{ik...\,j_n}_{\mathrm{F}q}\,\alpha^{jl}_{q\mathrm{I}}}{\omega_{q\mathrm{I}} - (\omega_1 + \omega_3)} \\
&+ ... + \frac{\xi^{j_n...lk}_{\mathrm{F}q}\,\alpha^{ji}_{q\mathrm{I}}}{\omega^*_{q\mathrm{I}} + (\omega_1 + \omega_{n+1})} + \frac{\xi^{ij...j_n}_{\mathrm{F}q}\,\alpha^{kl}_{q\mathrm{I}}}{\omega_{q\mathrm{I}} - (\omega_2 + \omega_3)} \\
&+ \frac{\xi^{ij...j_n}_{\mathrm{F}q}\,\alpha^{km}_{q\mathrm{I}}}{\omega_{q\mathrm{I}} - (\omega_2 + \omega_4)} + ... + \frac{\xi^{j_n...lj}_{\mathrm{F}q}\,\alpha^{ki}_{q\mathrm{I}}}{\omega^*_{q\mathrm{I}} + (\omega_2 + \omega_{n+1})} \\
&+ \frac{\xi^{j_{n-1}...kj}_{\mathrm{F}q}\,\alpha^{j_ni}_{q\mathrm{I}}}{\omega^*_{q\mathrm{I}} + (\omega_n + \omega_{n+1})}
\end{aligned} \right\}
\end{aligned} \tag{4b}$$

$$\begin{aligned}
&\xi^{ij...j_n}_{\mathrm{FI}}(-\omega_{n+1};\, \omega_1,\omega_2,...,\omega_n) = \\
&\frac{-1}{2^{n-1}\hbar} \sum_r \left\{ \begin{aligned}
&\frac{\mu^i_{\mathrm{F}r}\xi^{jk...j_n}_{r\mathrm{I}}}{\omega_{r\mathrm{I}} - (\omega_1 + \omega_2 + ... + \omega_n)} \\
&+ \frac{\mu^j_{\mathrm{F}r}\xi^{j_n...ki}_{r\mathrm{I}}}{\omega^*_{r\mathrm{I}} + (\omega_2 + ... + \omega_n - \omega_{n+1})} \\
&+ ... + \frac{\mu^{j_n}_{\mathrm{F}r}\xi^{j_{n-1}...ji}_{r\mathrm{I}}}{\omega^*_{r\mathrm{I}} + (\omega_1 + ... + \omega_{n-1} - \omega_{n+1})}
\end{aligned} \right\}
\end{aligned} \tag{4c}$$

Each $ij...j_n$ superscript corresponds in order to the frequency term within the parentheses, such that the *i* index refers to $-\omega_{n+1}$, the *j* index to ω_1, etc. The initial and final states combined with the superscripts indicating the frequency terms are alone enough to identify the physical process described by a given tensor. For example, the $\xi_{\mathrm{F}p}^{j_n\ldots kj}$ term in the first expression in eq 4a can be written out to explicitly include the frequency contributions as $\xi_{\mathrm{F}p}^{j_n\ldots kj}(\omega_n;\ldots,\omega_2,\omega_1)$.

It is important to note that underlying complexity inherent within the full SOS analysis is not removed by this simplifying approach. The reduced expressions are mathematically equivalent to the full SOS expressions, such that potentially complex frequency dependences may still exist within and between the embedded lower-order terms. However, the value of this recasting becomes clear when considering specific instances and measurements, examples of which are described in later sections. For a given NLO process, it is relatively straightforward to identify the simplified products that will contribute significantly to a given measurement, and (more importantly) identify those that can be safely assumed to be negligible. In this sense, the greatest benefits of this procedure are arguably to help separate "the wheat from the chaff" when interpreting nonlinear optical and multiphoton phenomena and to recast the molecular response tensor in terms of chemically intuitive molecular properties.

2.1. Parametric (Passive) vs Nonparametric (Active) Processes. The mathematical approach described in eq 3 is equally applicable for describing incoherent, nonparametric effects (i.e., processes with different initial and final states), including Raman scattering, hyper-Raman scattering and three-photon absorption, as well as parametric processes, including higher harmonic generation and three- and four-wave mixing. For a parametric process, in which the initial and final states are identical, the resulting relationship $\omega_{n+1} = \omega_1 + \cdots + \omega_n$ allows each of the sums of frequencies within the denominator in eq 4c to be replaced by a single frequency (e.g., $\omega_2 + \cdots + \omega_n - \omega_{n+1} = \omega_1$).

2.2. Self-Consistency. The general expressions in eqs 3 and 4 are entirely self-consistent. The expression for the tensors of order $n - 1$ can themselves be rewritten as products of transition moments and tensors of order $n - 2$ (again, a zero order tensor is defined to be the transition dipole vector: $-\mu_{\mathrm{FI}}^{(0)}$). Deriving expressions for polarizability tensors containing multiple resonance-enhancements can be performed in an intuitive way by applying eq 3 multiple times.

2.3. Sign of the Damping Term Γ. Recently, there has been some controversy regarding the appropriate choice of sign for the damping terms Γ, which are implicitly contained in eq 1 and, correspondingly, in eq 3.[9,21−28] It has recently been suggested that the damping terms should be exclusively of negative sign in full quantum field theory treatments.[21,22,28] However, the opposite-sign notation used throughout this work appears to be universally accepted as being appropriate in phenomenological treatments of damping in molecules and materials in which the electric field polarization is treated semiclassically.[9,21−28] An illustrative example confirming that the opposite sign convention produces the correct sign for describing the behavior of the optical fields using the expressions derived in this work is given in the Appendix. For these reasons, all formulas in this work are presented using the opposite sign notation for the damping terms.

2.4. Three-Wave Mixing. In this section, the general form of the SOS expression is applied to interpret 3WSFG, SHG, and three-wave difference frequency generation (3WDFG). Both 3WDFG and SHG can be interpreted as specific cases of the more general phenomena of 3WSFG, evaluated with negative or degenerate frequencies, respectively. Because 3WSFG is a parametric (passive) process (i.e., the initial and final state are identical), $\omega_3 = \omega_1 + \omega_2$. Evaluation of eq 4 for $n = 2$ yields the following set of relations.

$$\begin{aligned}\beta_{\mathrm{II}}^{ijk}(-\omega_3;\,\omega_1,\omega_2) ={}& \\ &\frac{-1}{2\hbar}\sum_p\left\{\frac{(\alpha_{\mathrm{I}p}^{kj})_{\mathrm{2PA}}\,\mu_{p\mathrm{I}}^{i}}{\omega_{p\mathrm{I}}^{*}+\omega_3}+\frac{(\alpha_{\mathrm{I}p}^{ik})_{\mathrm{AR}}\,\mu_{p\mathrm{I}}^{j}}{\omega_{p\mathrm{I}}-\omega_1}+\frac{(\alpha_{\mathrm{I}p}^{ij})_{\mathrm{AR}}\,\mu_{p\mathrm{I}}^{k}}{\omega_{p\mathrm{I}}-\omega_2}\right\} \\ &=\frac{-1}{2\hbar}\sum_q\left\{\frac{\mu_{\mathrm{I}q}^{i}(\alpha_{q\mathrm{I}}^{jk})_{\mathrm{2PA}}}{\omega_{q\mathrm{I}}-\omega_3}+\frac{\mu_{\mathrm{I}q}^{j}(\alpha_{q\mathrm{I}}^{ki})_{\mathrm{SR}}}{\omega_{q\mathrm{I}}^{*}+\omega_1}+\frac{\mu_{\mathrm{I}q}^{k}(\alpha_{q\mathrm{I}}^{ji})_{\mathrm{SR}}}{\omega_{q\mathrm{I}}^{*}+\omega_2}\right\}\end{aligned} \tag{5}$$

The subscripts 2PA, AR, and SR indicate two-photon absorption, anti-Stokes Raman, and Stokes Raman tensors, respectively, and they are included solely for clarity. The initial and final states combined with the superscripts indicating the frequency terms are alone enough to identify the physical process described by a given $\alpha^{(1)}$ tensor.

Figure 1 corresponds to the six terms in eq 5. The arrows in red describe the six $\alpha^{(1)}$ tensors. If the molecular system is initially in the ground state, only the terms with differences in the denominators lead to resonance-enhancement (corresponding to the energy level diagrams in Figure 1, parts b, c, and d). All possible resonant interactions are necessarily present in each summation, but many are concealed within combinations of other effects (e.g., in the summation over the index *p*, the resonant interaction arising for $\omega_{p\mathrm{I}} \cong \omega_3$ is implicitly contained within the two anti-Stokes Raman terms). Writing out both forms in eq 5 clarifies the different resonance-enhanced possibilities.

A. Resonance-Enhanced Three-Wave Mixing. To describe a particular resonance condition, the rotating-wave approximation is invoked and only the terms with resonant frequency denominators are retained. For resonance at the sum-frequency ω_3, eq 5 reduces down to the following expressions, derived in previous work.[15]

$$\beta_{\mathrm{II}}^{ijk}(\underline{-\omega_3};\omega_1,\omega_2)=\frac{-1}{2\hbar}\sum_q\left\{\frac{\mu_{\mathrm{I}q}^{i}(\alpha_{q\mathrm{I}}^{jk})_{\mathrm{2PA}}}{\omega_{q\mathrm{I}}-\omega_3}\right\} \tag{6}$$

In simplifying eq 5, the use of purely real wave functions can be reasonably assumed, as would be expected for electric dipole transitions between real, nondegenerate initial and final eigenstates.[9] The underscore indicates that $\omega_{p\mathrm{I}} \cong \omega_3$ is the resonant interaction in eq 6. Equation 6 can be visualized in Figure 1d.

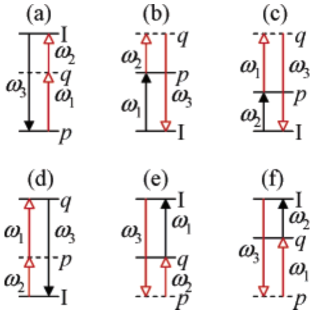

Figure 1. Energy level diagrams corresponding to the six 3WSFG terms in eq 5. If the initial state I is the ground state, processes b, c, and d can exhibit resonance enhancement. Combinations of red (open triangle) arrows describe an $\alpha^{(1)}$ tensor. The energies of a given transition are given by $\hbar\omega$.

As has been demonstrated previously,[15] this same set of expressions is equally applicable under conditions of double-resonance enhancement, in which an incident frequency and the sum-frequency are both resonant with real states within the chromophore. In this limit, the $\beta^{(2)}$ tensor is likely dominated by a single product of a transition moment and a resonance-enhanced $\alpha^{(1)}$ tensor.[15]

B. SHG and 3WDFG. Expressions for SHG and 3WDFG can be easily derived using the general 3WSFG expressions by allowing for degenerate and negative frequencies, respectively. In the case of SHG, the expression is divided by 2! to account for the two equivalent permutations in the frequencies. Detailed examples can be found in previous work.[15,16]

2.5. Four-Wave Mixing. Analogous to the case of three-wave mixing, all parametric four-wave mixing phenomena can be expressed within the context of four-wave SFG (4WSFG) by allowing for degenerate and/or negative frequencies. Since 4WSFG is a parametric (passive) process,[14] $\omega_4 = \omega_1 + \omega_2 + \omega_3$. Explicit evaluation of the general expression for $\xi^{(n)}$ in eq 4 for $n = 3$ yields the following three equivalent forms for describing the $\gamma^{(3)}$ tensor for 4WSFG.

$$\gamma_{\mathrm{II}}^{ijkl}(-\omega_4;\, \omega_1,\omega_2,\omega_3)$$

$$= \frac{-1}{4\hbar}\sum_p \left\{ \begin{array}{l} \dfrac{(\beta_{\mathrm{I}p}^{lkj})_{\mathrm{3PA}}\, \mu_{p\mathrm{I}}^{i}}{\omega_{p\mathrm{I}}^{*} + \omega_4} + \dfrac{(\beta_{\mathrm{I}p}^{ikl})_{\mathrm{AHR}}\, \mu_{p\mathrm{I}}^{j}}{\omega_{p\mathrm{I}} - \omega_1} \\ + \dfrac{(\beta_{\mathrm{I}p}^{ijl})_{\mathrm{AHR}}\, \mu_{p\mathrm{I}}^{k}}{\omega_{p\mathrm{I}} - \omega_2} + \dfrac{(\beta_{\mathrm{I}p}^{ijk})_{\mathrm{AHR}}\, \mu_{p\mathrm{I}}^{l}}{\omega_{p\mathrm{I}} - \omega_3} \end{array} \right\}$$

$$= \frac{1}{4\hbar}\sum_q \left\{ \begin{array}{l} \dfrac{(\alpha_{\mathrm{I}q}^{il})_{\mathrm{AR}}(\alpha_{q\mathrm{I}}^{jk})_{\mathrm{2PA}}}{\omega_{q\mathrm{I}} - \omega_1 - \omega_2} + \dfrac{(\alpha_{\mathrm{I}q}^{ik})_{\mathrm{AR}}(\alpha_{q\mathrm{I}}^{jl})_{\mathrm{2PA}}}{\omega_{q\mathrm{I}} - \omega_1 - \omega_3} \\ + \dfrac{(\alpha_{\mathrm{I}q}^{ij})_{\mathrm{AR}}(\alpha_{q\mathrm{I}}^{kl})_{\mathrm{2PA}}}{\omega_{q\mathrm{I}} - \omega_2 - \omega_3} + \dfrac{(\alpha_{\mathrm{I}q}^{kj})_{\mathrm{2PA}}(\alpha_{q\mathrm{I}}^{li})_{\mathrm{AR}}}{\omega_{q\mathrm{I}}^{*} + \omega_1 + \omega_2} \\ + \dfrac{(\alpha_{\mathrm{I}q}^{lj})_{\mathrm{2PA}}(\alpha_{q\mathrm{I}}^{ki})_{\mathrm{AR}}}{\omega_{q\mathrm{I}}^{*} + \omega_1 + \omega_3} + \dfrac{(\alpha_{\mathrm{I}q}^{lk})_{\mathrm{2PA}}(\alpha_{q\mathrm{I}}^{ji})_{\mathrm{AR}}}{\omega_{q\mathrm{I}}^{*} + \omega_2 + \omega_3} \end{array} \right\}$$

$$= \frac{-1}{4\hbar}\sum_r \left\{ \begin{array}{l} \dfrac{\mu_{\mathrm{I}r}^{i}(\beta_{r\mathrm{I}}^{jkl})_{\mathrm{3PA}}}{\omega_{r\mathrm{I}} - \omega_4} + \dfrac{\mu_{\mathrm{I}r}^{j}(\beta_{r\mathrm{I}}^{lki})_{\mathrm{SHR}}}{\omega_{r\mathrm{I}}^{*} + \omega_1} \\ + \dfrac{\mu_{\mathrm{I}r}^{k}(\beta_{r\mathrm{I}}^{lji})_{\mathrm{SHR}}}{\omega_{r\mathrm{I}}^{*} + \omega_2} + \dfrac{\mu_{\mathrm{I}r}^{l}(\beta_{r\mathrm{I}}^{kji})_{\mathrm{SHR}}}{\omega_{r\mathrm{I}}^{*} + \omega_3} \end{array} \right\} \qquad (7)$$

The subscripts AHR and SHR indicate anti-Stokes hyper-Raman and Stokes hyper-Raman processes. An inclusive definition of the hyper-Raman process is used, in which all three-wave nonparametric processes (i.e., different initial and final states) with the exception of 3PA are contained within the aegis of hyper-Raman. *Because of the self-consistency inherent within this mathematical approach, a simplified form for the hyper-Raman tensor can also be generated using the general expression for* $\xi^{(n)}$ *in eq 3 by setting* $n = 2$ *and using different initial and final states*.

A. Degenerate-Wave CARS (DWCARS). Application of this general approach in systems with degenerate and/or negative frequencies are easily demonstrated by explicitly considering the CARS process with a degenerate incident frequency. In this case, ω_2 is set equal to ω_1 and $\hbar\omega_3$ corresponds to a negative energy (i.e., energy withdrawn from the molecular system). Under these conditions, eq 8 is given by the following form.

$$\gamma_{\mathrm{II}}^{ijkl}(-\omega_4;\, \omega_1,\, \omega_1,\, -\omega_3)$$

$$= \frac{-1}{4\hbar}\sum_p \left\{ \begin{array}{l} \dfrac{(\beta_{\mathrm{I}p}^{lkj})_{\mathrm{AHR}}\, \mu_{p\mathrm{I}}^{i}}{\omega_{p\mathrm{I}}^{*} + \omega_4} + \dfrac{(\beta_{\mathrm{I}p}^{ijk})_{\mathrm{AHR}}\, \mu_{p\mathrm{I}}^{l}}{\omega_{p\mathrm{I}} + \omega_3} \\ + \dfrac{1}{2!}\, \dfrac{(\beta_{\mathrm{I}p}^{ikl})_{\mathrm{AHR}}\, \mu_{p\mathrm{I}}^{j} + (\beta_{\mathrm{I}p}^{ijl})_{\mathrm{AHR}}\, \mu_{p\mathrm{I}}^{k}}{\omega_{p\mathrm{I}} - \omega_1} \end{array} \right\}$$

$$= \frac{1}{4\hbar}\sum_q \left\{ \begin{array}{l} \dfrac{(\alpha_{\mathrm{I}q}^{il})_{\mathrm{2PE}}(\alpha_{q\mathrm{I}}^{jk})_{\mathrm{2PA}}}{\omega_{q\mathrm{I}} - \omega_1 - \omega_1} + \dfrac{(\alpha_{\mathrm{I}q}^{kj})_{\mathrm{2PA}}(\alpha_{q\mathrm{I}}^{li})_{\mathrm{2PE}}}{\omega_{q\mathrm{I}}^{*} + \omega_1 + \omega_1} \\ + \dfrac{1}{2!}\, \dfrac{(\alpha_{\mathrm{I}q}^{ik})_{\mathrm{AR}}(\alpha_{q\mathrm{I}}^{jl})_{\mathrm{SR}} + (\alpha_{\mathrm{I}q}^{ij})_{\mathrm{AR}}(\alpha_{q\mathrm{I}}^{kl})_{\mathrm{SR}}}{\omega_{q\mathrm{I}} - \omega_1 + \omega_3} \\ + \dfrac{1}{2!}\, \dfrac{(\alpha_{\mathrm{I}q}^{lj})_{\mathrm{SR}}(\alpha_{q\mathrm{I}}^{ki})_{\mathrm{AR}} + (\alpha_{\mathrm{I}q}^{lk})_{\mathrm{SR}}(\alpha_{q\mathrm{I}}^{ji})_{\mathrm{AR}}}{\omega_{q\mathrm{I}}^{*} + \omega_1 - \omega_3} \end{array} \right\}$$

$$= \frac{-1}{4\hbar}\sum_r \left\{ \begin{array}{l} \dfrac{\mu_{\mathrm{I}r}^{i}(\beta_{r\mathrm{I}}^{jkl})_{\mathrm{SHR}}}{\omega_{r\mathrm{I}} - \omega_4} + \dfrac{\mu_{\mathrm{I}r}^{l}(\beta_{r\mathrm{I}}^{kji})_{\mathrm{SHR}}}{\omega_{r\mathrm{I}}^{*} - \omega_3} \\ + \dfrac{1}{2!}\, \dfrac{\mu_{\mathrm{I}r}^{j}(\beta_{r\mathrm{I}}^{lki})_{\mathrm{SHR}} + \mu_{\mathrm{I}r}^{k}(\beta_{r\mathrm{I}}^{lji})_{\mathrm{SHR}}}{\omega_{r\mathrm{I}}^{*} + \omega_1} \end{array} \right\} \qquad (8)$$

Equation 8 differs from eq 7 in two respects. First, the sign on ω_3 is inverted throughout. Second, factors of 2! have been introduced to account for the two equivalent permutations in the frequencies ω_1 and ω_2. In the $\alpha^{(1)}$ and $\beta^{(2)}$ tensors containing both the j and k indices (corresponding to the two degenerate frequencies), the division of 2! is implicitly incorporated within the definition of the tensors. The expression in eq 8 is equivalent to the full SOS for DWCARS given by eq 1. Figure 2 contains 10 energy level diagrams corresponding to the 10 terms in eq 8.

B. Resonance-Enhanced CARS. Resonance enhancement can arise when one of the incident frequencies or a combination of incident frequencies is resonant with a real transition in the chromophore. In such a case, only one of the 10 possible interactions described in eq 8 will contribute significantly to the resonance-enhanced response. As one example, the most common experimental configuration for DWCARS exhibiting resonance-enhancement at the difference-frequency $\omega_1 - \omega_3$ yields the following expression for the resonant nonlinear polarizability.

$$\gamma_{\mathrm{II}}^{ijkl}(-\omega_4;\, \omega_1,\underline{\omega_1,\, -\omega_3}) = \frac{1}{4\hbar}\sum_q \left\{ \frac{1}{2!}\, \frac{(\alpha_{\mathrm{I}q}^{ij})_{\mathrm{AR}}(\alpha_{q\mathrm{I}}^{kl})_{\mathrm{SR}} + (\alpha_{\mathrm{I}q}^{ik})_{\mathrm{AR}}(\alpha_{q\mathrm{I}}^{jl})_{\mathrm{SR}}}{\omega_{q\mathrm{I}} - (\omega_1 - \omega_3)} \right\} \qquad (9)$$

The energy level diagram corresponding to eq 9 can b seen in Figure 2e.

The general approach described by eqs 3 and 8 reduces down to an expression similar to one published previously for four-wave processes in the limit of two-photon resonance enhancement.[18] However, the use of the expression in eq 8 has the additional advantage of clearly elucidating all other resonant and nonresonant interactions that can contribute to the total NLO

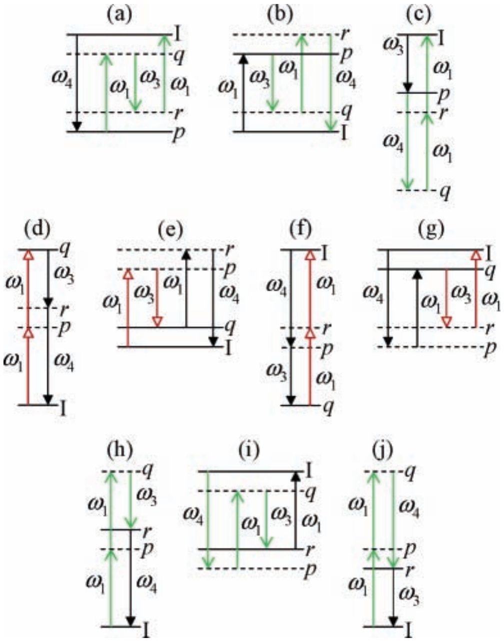

Figure 2. Energy level diagrams corresponding to the ten DWCARS terms in eq 8. Combinations of red (open triangle) arrows represent a single $\alpha^{(1)}$ tensor, while combinations of green (open head) arrows represent a single $\beta^{(2)}$ tensor. The energies of a given transition are given by $\hbar\omega$.

response. For example, we believe this is the first time a link has been demonstrated connecting CARS and hyper-Raman spectroscopy in systems exhibiting one-photon resonances. An example is given by eq 10 for DWCARS performed with a resonance at $\omega_{rI} \cong \omega_4$.

$$\gamma_{\rm II}^{ijkl}(\underline{-\omega_4};\ \omega_1,\omega_1,-\omega_3) = \frac{-1}{4\hbar}\sum_r \left\{ \frac{\mu_{{\rm I}r}^{i}(\beta_{r{\rm I}}^{jkl})_{\rm SHR}}{\omega_{r{\rm I}} - \omega_4} \right\} \qquad (10)$$

2.6. Secular Singularities and Zero Frequencies. An important caveat to the use of the expression given in eq 1 arises in the presence of secular singularities, in which the sum of both the transition frequency and the electric field frequencies in the denominator approach zero.[2,3,17] Secular singularities occur when the sum of both the transition frequency and the field frequencies in the denominator approach zero. An example of this secular singularity occurs in deriving the SOS equation for degenerate four-wave mixing. The denominators of 16 out of the total 24 terms contain $(\omega_q - \omega + \omega)$, which equals zero since $\omega_q = 0$, but these terms should not be confused with a resonant enhancement. Within the limits of a sum-over-states approach such as in eq 1 (i.e., for simple exponential molecular response functions), terms containing secular singularities collectively sum to zero and can be simply removed from the full equation in the weak field limit.[2,3,17] The expressions for the molecular polarizability tensors also apply in the limit of zero or slowly varying frequencies for one or more of the electric fields, once the resulting changes in the preceding constant multipliers are included.[2,3,6,9,11]

2.7. Seven-Wave Mixing. The merits of the simplification approach described in this work are particularly evident in considerations of high-order NLO phenomena. The full SOS equation for seven-wave mixing contains 5040 terms and requires evaluation over a sextuple summation over all excited states. By use of the general expression in eq 3, it is possible write out an equivalent equation in an intuitive and compact form containing as few as seven terms in a single summation.

$$\zeta_{\rm FI}^{ijklmno}(-\omega_7;\ \omega_1,\omega_2,\omega_3,\omega_4,\omega_5,\omega_6) = \frac{-1}{32\hbar}\sum_p \left\{ \begin{array}{l} \dfrac{\epsilon_{{\rm F}p}^{onmlkj}\ \mu_{p{\rm I}}^{i}}{\omega_{p{\rm I}}^{*} + \omega_7} + \dfrac{\epsilon_{{\rm F}p}^{iklmno}\ \mu_{p{\rm I}}^{j}}{\omega_{p{\rm I}} - \omega_1} \\ + \dfrac{\epsilon_{{\rm F}p}^{ijlmno}\ \mu_{p{\rm I}}^{k}}{\omega_{p{\rm I}} - \omega_2} + \dfrac{\epsilon_{{\rm F}p}^{ijkmno}\ \mu_{p{\rm I}}^{l}}{\omega_{p{\rm I}} - \omega_3} \\ + \dfrac{\epsilon_{{\rm F}p}^{ijklno}\ \mu_{p{\rm I}}^{m}}{\omega_{p{\rm I}} - \omega_4} + \dfrac{\epsilon_{{\rm F}p}^{ijklmo}\ \mu_{p{\rm I}}^{n}}{\omega_{p{\rm I}} - \omega_5} \\ + \dfrac{\epsilon_{{\rm F}p}^{ijklmn}\ \mu_{p{\rm I}}^{o}}{\omega_{p{\rm I}} - \omega_6} \end{array} \right\} \qquad (11)$$

3. Discussion

The expressions for 3WSFG and 4WSFG provided in eqs 5 and 7 are applicable for both single-resonance and multiple resonance-enhancement. Multiple resonances can be easily included by taking advantage of the inherent self-consistency within this mathematical approach. In systems with multiple resonances, the lower-order tensor(s) can also be simplified as resonance-enhanced products of lower-order effects. Resonance-enhanced DWCARS, described by the expression in eq 10, serves as an illustrative example. In the case of a second state resonant with an appropriate combination of frequencies (e.g., for a real state resonant with $\omega_1 - \omega_3$ in Figure 2h), one term within the expression for the $\beta_{r{\rm I}}^{jkl}$ dominates the resonance-enhanced contribution, and the resonance-enhanced portion of $\beta_{r{\rm I}}^{jkl}$ can be approximated as a simple product of a single $\mu^{(0)}\alpha^{(1)}$ term from eq 5 with different initial and final states. Similarly, if the $\alpha^{(1)}$ term also exhibits resonance-enhancement, it will often be dominated by a single term containing a product of $\mu^{(0)}\mu^{(0)}$.

Figure 3 graphically describes the expansion of the molecular nonlinear polarizability as iterative products of lower-order effects for the specific case of DWCARS. Each energy level diagram in Figure 2 for the $\gamma^{(3)}$ tensor (corresponding to each term in eq 8) compactly represents a number of different pathways implicitly contained within the different $\beta^{(2)}$ and $\alpha^{(1)}$ tensors. To clarify this approach, the energy level diagram in Figure 2h is expanded in Figure 3. The hyper-Raman $\beta^{(2)}$ contribution itself implicitly contains six possible combinations of $\mu\alpha$ given in eq 5 and Figure 1 (three of which are unique when $\omega_2 = \omega_1$) as indicated in Figure 3. Similarly, the $\alpha^{(1)}$ tensors themselves each contain generally two different $\mu^{(0)}\mu^{(0)}$ combinations, also shown in Figure 3. Consequently, the full set of pathways connecting the initial and final states in the $\gamma^{(3)}$ tensor are compactly contained within the relatively simple expressions in eq 7.

When applied under specific assumed resonance conditions, the general expression in eq 3 correctly recovers previously derived expressions. For 3WSFG with molecules initially in the ground state, eq 6 reduces to expressions reported previously under resonance enhancement at the sum-frequency,[15] under resonance enhancement with one of the incident fields, including the specific case of vibrational SFG spectroscopy,[15,16] and double-resonance.[15,29] Two-photon resonances with a single excited (both Raman and 2PA) have been considered previously for four-wave processes, including CARS and THG.[1,2,17−19] Resonant formulas have also been presented for three-photon resonant fifth-order polarizabilities (six-wave).[17] The approach described here allows all of these resonance-enhanced condi-

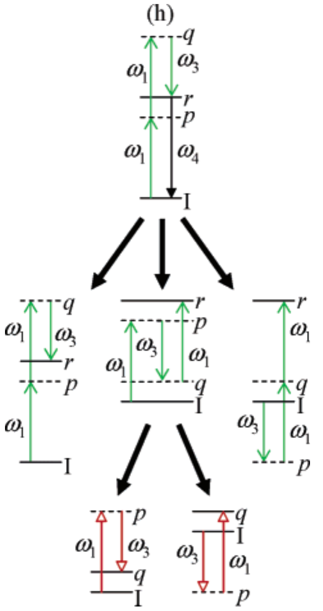

Figure 3. Expansion of a single energy level diagram in Figure 2h for DWCARS. Red (open triangle) arrows describe $\alpha^{(1)}$ tensor, while green (open head) arrows describe a $\beta^{(2)}$ tensor. The three green arrows shown in the topmost diagram combine to compactly represent a single hyper-Raman tensor, which itself contains contributions from several different energy level diagrams. The hyper-Raman tensor can generally be rewritten as six combinations of transition moments and α tensors, three of which are unique in DWCARS (given by the middle three diagrams). Similarly, each $\alpha^{(1)}$ tensor within the hyper-Raman tensor contains two unique contributions (given by the bottom two diagrams).

tions, and several not previously considered, to be contained within the aegis of a single intuitive and general mathematical approach.

The expressions for three-wave and four-wave mixing in eqs 6 and 9 demonstrate several direct relationships connecting coherent (parametric) and incoherent processes. A direct relationship between 2PA and SHG is apparent from eq 5 in the case of $\omega_2 = \omega_1$ and has been reported previously.[15] Computational and experimental investigations by Cho and co-workers support a connection between these two processes.[30,31] Equations 5 and 7 also suggest several relationships often overlooked when interpreting NLO effects, including the role of hyper-Raman and three-photon absorption in four-wave mixing.

This same mathematical approach is equally applicable for describing incoherent, nonparametric effects, including hyper-Raman scattering and three-photon absorption, within the context of lower-order phenomena. For example, the molecular tensor describing hyper-Raman scattering can be generated using eq 5 with different initial and final states, suggesting direct relationships between hyper-Raman spectroscopy, Raman spectroscopy, and 2PA.

4. Conclusions

A mathematical approach was developed for simplifying the interpretation of NLO processes within the context of lower-order effects without sacrificing mathematical rigor or generality. The comparatively unwieldy forms for the full SOS expressions widely used in previous studies were re-expressed in compact formulas more intuitively connected to the molecular properties driving the NLO phenomena. For example, the full SOS expression for a NLO process of order n contains $(n + 1)!$ terms (e.g., 5040 terms for $n = 6$) and can easily become prohibitively lengthy for all but the simplest NLO phenomena. By comparison, use of eq 3 allows the full SOS expression to be written using as few as $(n + 1)$ terms (e.g., seven terms for $n = 6$) and in a form that is more spectroscopically intuitive. This same mathematical formalism is equally applicable for interpreting both parametric effects (e.g., harmonic generation, multiple-wave mixing, etc.) and nonparametric effects (e.g., multiple-photon absorption, hyper-Raman, etc.). Furthermore, all the mathematical expressions are entirely self-consistent. Broad classes of previously reported mathematical expressions describing resonance-enhanced NLO processes can be directly obtained from this single general approach. These convenient expressions provide a simple framework for interpreting the rapidly growing number of NLO and multiphoton investigations without sacrificing mathematical rigor.

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Appendix: Sign of the Phenomenological Damping Factors.

Even in areas as well-established as Rayleigh scattering, Raman scattering, and nonlinear optics, fundamental principles sometimes warrant reexamination. It has recently been suggested that full quantum treatment of the nonlinear polarizability tensor should result in damping constants that are exclusively negative in sign, in stark contrast to the opposite sign-convention widely used phenomenologically in sum-over-states expressions derived from perturbation theory.[21,22,28] Nevertheless, there appears to be nearly universal agreement that the opposite sign convention is appropriate when the damping is introduced in sum-over-states expressions using semiclassical polarization formalisms for describing the behavior of the optical fields in linear and nonlinear polarizabilities.[9,21−24,26−28] In this section, a simple and illustrative example is provided supporting the traditional opposite sign convention for the phenomenological damping terms used throughout the present work by confirming that the same-sign approach does not correctly predict gain in a system exhibiting a population inversion.

The wave function describing the amplitude of the electric field component E for an electromagnetic plane wave propagating through a dielectric medium is given in eq 2a. Defining a complex refractive index $\hat{n} = n' + i\kappa$ for the medium and substituting the relationship $\hat{k} = k_0\hat{n}$, where k_0 is the vacuum wavevector, allows eq 2a to be rewritten in the following form.

$$E(x,t) = E_0 e^{-i(\omega t - k_0 n' x)} e^{-k_0 \kappa x} \tag{A.1}$$

The intensity I as a function of the distance x through the medium is proportional to EE^*.

$$I(x) = I_0 e^{-2k_0\kappa x} = I_0 e^{-\alpha_c x} \tag{A.2}$$

The second equality is simply the Beer−Lambert law with an absorption coefficient α_c (not to be confused with the linear polarizability tensor $\alpha^{(1)}_{\mathrm{FI}}$). From eq A.2, the relationship between the absorption coefficient α_c and the imaginary portion of the refractive index κ is straightforward.

$$\alpha_c = 2k_0\kappa = 2\omega\kappa/c \tag{A.3}$$

The constants k_0, ω, and c are all purely real and positive.

If $\kappa > 0$, the imaginary component of the refractive index results in exponential loss in the intensity of the beam with distance x through the medium, consistent with stimulated absorption. Conversely, exponential gain in the beam intensity will arise if $\kappa < 0$, which can occur in systems with population inversions and is the founding principal underpinning lasers.

The relationship between κ and the linear molecular polarizability $\alpha^{(1)}_{\mathrm{FI}}$ describing Rayleigh scattering is relatively straightforward to demonstrate. The first-order linear molecular polarizability tensor is given by the following expression (and can also be obtained from eq 3).[9]

$$\alpha^{ij}_{\mathrm{FI}}(-\omega_2;\omega_1) = \frac{1}{\hbar}\sum_p \left\{ \frac{\mu^i_{\mathrm{F}p}\mu^j_{p\mathrm{I}}}{(\omega_p-\omega_{\mathrm{I}}) - \omega_1 - i\Gamma_p} + \frac{\mu^j_{\mathrm{F}p}\mu^i_{p\mathrm{I}}}{(\omega_p-\omega_{\mathrm{F}}) + \omega_2 \pm i\Gamma_p} \right\} \tag{A.4}$$

The ± sign on the second $i\Gamma_p$ term indicates the two different forms for the sign of the damping factor that have been proposed. The linear polarizability for Rayleigh scattering is obtained by setting the final state F equal to the initial state I (such that $\omega_1 = \omega_2 = \omega$) and dividing by two to account for the 2! degenerate frequency permutations. The macroscopic linear polarizability generated in an extended medium is given by summing the contributions of each molecule.

$$\chi^{(1)} = \frac{N}{V\epsilon_0}\langle \alpha^{(1)} \rangle \tag{A.5}$$

Systems Initially in the Ground State. If the molecular system is assumed to be initially in the ground state, only the first term in eq A.4 and its complex conjugate can contribute to the resonance-enhanced response. Near resonance with a particular real excited state p, the real and imaginary contributions to the resonant portion of $\alpha^{(1)}$ for Rayleigh scattering (and correspondingly to $\chi^{(1)}$ for reflection and refraction) can be separated by multiplying the numerator and denominator of eq A.4 by the complex conjugate of the denominator.

$$\chi^{ij} \cong C_1 \frac{(\omega_p - \omega_{\mathrm{I}} - \omega_1 + i\Gamma_p)}{[(\omega_p - \omega_{\mathrm{I}} - \omega_1)^2 + {\Gamma_p}^2]} \tag{A.6}$$

$$\mathrm{Re}(\chi^{ij}) = C_1 \frac{(\omega_p - \omega_{\mathrm{I}}) - \omega_1}{[(\omega_p - \omega_{\mathrm{I}} - \omega_1)^2 + {\Gamma_p}^2]} \tag{A.7}$$

$$\mathrm{Im}(\chi^{ij}) = C_1 \frac{\Gamma_p}{[(\omega_p - \omega_{\mathrm{I}} - \omega_1)^2 + {\Gamma_p}^2]} \tag{A.8}$$

In eqs A.6 through A.8, the constant C_1 is necessarily a purely real and positive number if p is a real, time-independent (long-lived) state. The linear polarizability $\chi^{(1)}$ can be connected directly to the complex valued refractive index.[9]

$$\hat{n}^2 = n'^2 - \kappa^2 + 2in'\kappa = \epsilon_0\chi^{(1)} + 1 \tag{A.9}$$

Since the imaginary portion of $\chi^{(1)}$ contributes exclusively to the imaginary portion of $\hat{n}^2$, the following relationship emerges.

$$\kappa = \frac{C_1\epsilon_0\Gamma}{2n'[(\omega_p - \omega_{\mathrm{I}} - \omega_1)^2 + {\Gamma_p}^2]} \propto \Gamma_p \tag{A.10}$$

Because all the constants in the numerator and denominator are real and positive, κ has the same sign as Γ and predicts a loss in the beam intensity as a function of propagation distance through the medium. Of course, this result is not at all surprising. For frequencies resonant with transitions from the ground state to an unoccupied excited state, energy is dissipated into the molecular system and correspondingly removed from the beam.

Systems Initially in an Excited State. Now, a system is considered in which the resonant interaction is with a state that is lower in energy than the initial state. In this case, stimulated emission should result in an exponential increase in the beam intensity with increasing x and a negative value of κ in eq A.2. In the case of stimulated emission, the second term in the polarizability tensor in eq A.4 is resonant, since $E_{\mathrm{I}} = \hbar\omega_{\mathrm{I}} > E_p = \hbar\omega_p$. The stimulated emissive contribution to the linear polarizability tensor $\chi^{(1)}$ can be summarized using a procedure exactly analogous to that used for stimulated absorption.

$$\chi^{ij} \cong C_2 \frac{-(\omega_{\mathrm{I}} - \omega_p) + \omega_1 \mp i\Gamma_p}{[-(\omega_{\mathrm{I}} - \omega_p) + \omega_1]^2 + {\Gamma_p}^2} \tag{A.11}$$

$$\mathrm{Re}(\chi^{ij}) = C_2 \frac{-(\omega_{\mathrm{I}} - \omega_p) + \omega_1}{[-(\omega_{\mathrm{I}} - \omega_p) + \omega_1]^2 + {\Gamma_p}^2} \tag{A.12}$$

$$\mathrm{Im}(\chi^{ij}) = C_2 \frac{\mp\Gamma}{[-(\omega_{\mathrm{I}} - \omega_p) + \omega_1]^2 + {\Gamma_p}^2} \tag{A.13}$$

The relationships connecting polarizability and refractive index in eq A.9 yield the following two possibilities.

$$\kappa \propto \mp\Gamma_p \tag{A.14}$$

Because the proportionality constant in eq A.14 is real and positive, the negative and positive sign possibilities for Γ correspond to the opposite and same sign conventions, respectively. This same result is obtained by switching the frequency terms ω_{I} and ω_p and their corresponding indices in the expression describing stimulated absorption between the same two states and using the Hermiticity relationship $\alpha^{ij}_{\mathrm{FI}}(-\omega_2;\omega_1) = \alpha^{ji}_{\mathrm{FI}}(\omega_1;-\omega_2)^*$.[1,9]

Implications of Same-Sign vs Opposite-Sign Usage. Although the same-sign and opposite-sign approaches yield virtually identical results for stimulated absorption in systems initially in the ground state, they lead to very different predicted behaviors for stimulated emission. Whereas the opposite-sign convention correctly predicts an increase in the beam intensity through stimulated emission in a system exhibiting a population inversion, the same-sign convention predicts attenuation of the beam for both stimulated absorption and stimulated emission.

Causality arguments against the same-sign usage stem from considerations of dispersion. Irrespective of the sign of the damping term, comparison of eqs A.7 and A.12 indicate that the dispersion characteristics of the real portion of the refractive index for a given incident wavelength ω_1 are opposite in sign for stimulated absorption vs stimulated emission. Again, this result is appealing, since the two processes should negate each other both on and off resonance in a system with an equal population in the ground and excited state. However, considerations of Kramers−Kronig dispersion relations, which follow directly from arguments of causality, predict that the imaginary portion of polarizability tensor should invert in sign if the dispersion characteristics describing the real portion are opposite in sign. Again, only the traditional opposite-sign convention correctly recovers this relationship in phenomenological treatments of damping. From these two pieces of evidence, it is clear that the same-sign approach is not applicable when damping is introduced phenomenologically for treating the behavior of the optical fields in semiclassical treatments such as performed here, consistent with the conclusions of several previous studies.[9,21−24,26−28]

Note Added after ASAP Publication. There was an error in eq 9 in the version published ASAP January 29, 2005. The corrected version was published ASAP February 17, 2005.

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