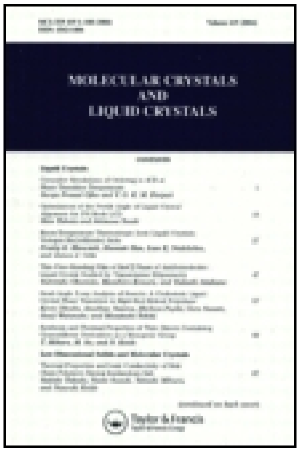

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Molecular Orientation, Pair Correlations and Cascading in Nonlinear Optical Susceptibilties

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MOLECULAR ORIENTATION, PAIR CORRELATIONS AND CASCADING IN NONLINEAR OPTICAL SUSCEPTIBILTIES

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Abstract Different susceptibility expansions for the polarization density **P** are compared to identify cascading contributions to the nonlinear response of a medium. In certain liquids pair-correlation dependence of the nonlinear optical susceptibilities has been observed. To isolate the cascading effects that depend most sensitively on pair correlation and near-field effects, a simple statistical model for **P** is applied to the case of a liquid whose oriented molecules have only first hyperpolarizabilities; then all third-order effects in **P** are a consequence of cascading.

INTRODUCTION

It has been known for many years that molecular interactions in liquids can affect the values of the hyperpolarizabilities determined from electric field induced second harmonic generation. Figs. 1 and 2 show examples of the concentration dependence of the first hyperpolarizability ($\beta \equiv \alpha^{(2)}$) for nitrobenzene solutions[1,2]. These experiments indirectly show the presence of correlations between the molecules in a liquid mixture which are manifest in charge-transfer interactions, dipolar forces and various solute-solute and solute-solvent effects. A model by which one can use nonlinear optical processes directly to measure the correlations between molecules has not been available.

It is also known that when a third-order nonlinear optical effect is measured in a noncentrosymmetric medium, second-order effects can contribute to the third-order response by means of cascading. For example, in third-harmonic generation the field at frequency 3ω (where ω is the frequency of the incident field) will include contributions from both the third-order molecular susceptibility $\alpha^{(3)}$ and the mixing of the incident field with the second-harmonic fields generated in the medium via $\alpha^{(2)}$. The latter process involves the succession of two second-order effects. See Fig. 3.

Bedeaux and Bloembergen[3] first identified the cascaded contributions to the macroscopic third-order susceptibility ($\chi^{(3)}$). In relating the macroscopic fields to the microscopic hyperpolarizabilities, however, they neglected all possible correlations between the molecules on the grounds that such effects were expected to be no more than a few percent. In some cases, e.g., among oriented molecules, correlations can be significant. The primary objective of our work is to extend the analysis of the local-field problem to treat third-order terms consistently and to encompass such possibilities.[4,5] In carrying out this work we have also considered the general phenomenological approach used by Meredith and coworkers[6,7]. Our results are theoretically consistent with their approach if we include an additional term not considered in reference 7. We report more fully on this comparison elsewhere[5]. Also, Meredith's work did not distinquish the effects of pair correlations. The dilute nature of the solutions of noncentrosymmetric molecules studied by Meredith required that only single molecule terms in the cascading processes contributed. By considering a medium of oriented molecules that have *only* second-order hyperpolarizabilities so that all third-order effects are solely consequences of cascading, we obtain explicit expressions, in terms of the pair-distribution functions, for the correlation-dependent contributions to the third-order parts of the polarization density that can be unambiguously identified with cascading and that are explicit enough to facilitate their numerical evaluation once the properties of the medium are specified.

Since cascading generally, but not exclusively, takes place between spatially separated points in the medium, it is nonlocal and so retardation of the intermediate propagating wave can occur. Because of this, within a description of the polarization density in terms of local susceptibilities of the nonlinear medium there is some ambiguity in isolating "intrinsic" higher-order effects from those arising from cascading. Also, since it represents one way in which the collective response of the medium differs from the simple additivity of the constituent responses, cascading is closely connected to the correct representation of the local field effects in nonlinear media.

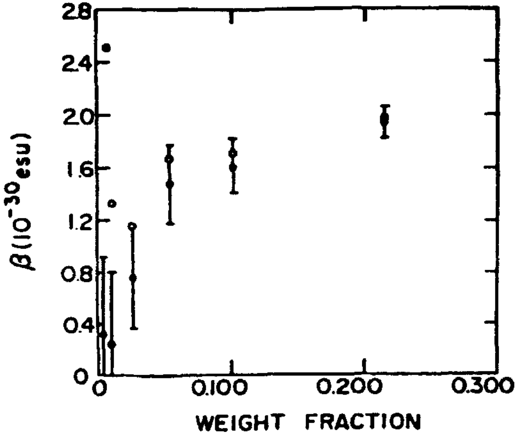

FIGURE 1 Concentration dependence of β of nitrobenzene solutions in DMSO. β is calculated point by point using Onsager local field factors. The open circles are the data corrected using the dielectric constant data. (From Reference [1]).

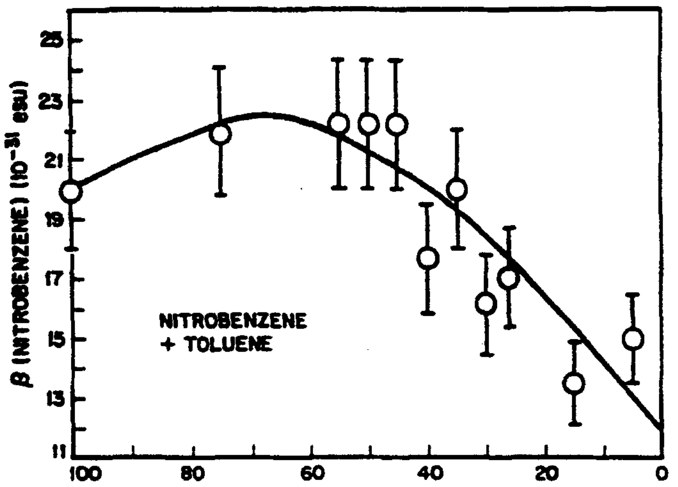

FIGURE 2 Plot of experimental second order hyperpolarizability β for nitrobenzene molecules dissolved in toluene (circles) as a function of nitrobenzene concentration (by volume). The solid curve is a theoretical fit. (From Reference [2]).

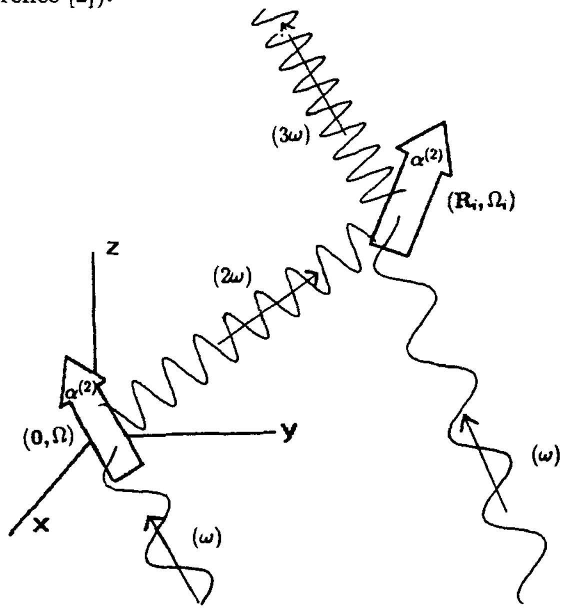

FIGURE 3 Graphical representation of a cascading between two molecules in real space leading to third-harmonic generation. The external lines correspond to incoming waves at frequency ω and outgoing waves at frequency 3ω, respectively, while the intermediate line depicts the wave at 2ω propagating in the linear medium; the arrows represent oriented molecules. Because the macroscopic field at 3ω is the statistical average of a large number of such interactions between many nearby molecules, the cascaded effect depends in part upon the pair correlations between the molecules in the system.

METHOD OF CALCULATION

To identify cascading contributions to third-order effects requires the consistent treatment of local fields, i.e., how the electric field at a molecule $\mathbf{E}_{loc}$ differs from the macroscopic field $\mathbf{E}$ which satisfies Maxwell's equations. The standard textbook discussions of local-field corrections (using, e.g., the Lorentz model) are only consistent up to second-order in the polarization density.

The formal solution to the wave equation

$$\nabla \times \nabla \times \mathbf{E}(\mathbf{x},t) + \frac{1}{c^2}\frac{\partial^2 \mathbf{E}(\mathbf{x},t)}{\partial t^2} = -\frac{4\pi}{c^2}\frac{\partial^2 \mathbf{P}(\mathbf{x},t)}{\partial t^2} \tag{1}$$

can be expressed in terms of the Green's function propagator $\mathbf{F}$ of the electromagnetic field in the absence of the medium as

$$\mathbf{E} = \mathbf{E}_{\mathbf{ex}} - \mathbf{F}\cdot\mathbf{P} \tag{2}$$

where the external or vacuum field $\mathbf{E}_{\mathbf{ex}}$ is the solution of Equation (1) with $\mathbf{P} = 0$ that is consistent with the relevant boundary conditions and where $\mathbf{F}$ is the kernel of the operator

$$\frac{4\pi}{c^2}\left[\nabla\nabla - \nabla^2 + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]^{-1}\frac{\partial^2}{\partial t^2}. \tag{3}$$

For dipole fields, the propagator $\mathbf{F}$ is given in the $(\mathbf{r},\omega)$ representation by[8]

$$\mathbf{F}(\mathbf{r},\omega) = \frac{1}{3}\delta(\mathbf{r}) + \frac{1}{4\pi}\left[\left(-\frac{\omega^2/c^2}{3r} - \frac{i\omega/c}{r^2} + \frac{1}{r^3}\right)\left(1 - 3\frac{\mathbf{rr}}{r^2}\right) - \frac{2}{3}\frac{\omega^2/c^2}{r}\right]e^{ir\frac{\omega}{c}}. \tag{4}$$

We can expand $\mathbf{P}$ in terms of the field $\mathbf{E}$

$$\mathbf{P} = \chi^{(1)}\cdot\mathbf{E} + \chi^{(2)}\cdot\mathbf{EE} + \chi^{(3)}\cdot\mathbf{EEE} + \ldots \tag{5}$$

or in terms of the external field $\mathbf{E}_{\mathbf{ex}}$

$$\mathbf{P} = \gamma^{(1)}\cdot\mathbf{E}_{\mathbf{ex}} + \gamma^{(2)}\cdot\mathbf{E}_{\mathbf{ex}}\mathbf{E}_{\mathbf{ex}} + \gamma^{(3)}\cdot\mathbf{E}_{\mathbf{ex}}\mathbf{E}_{\mathbf{ex}}\mathbf{E}_{\mathbf{ex}} + \ldots. \tag{6}$$

or in terms of the microscopic or local field $\mathbf{E}_{\mathbf{micro}}$

$$\mathbf{P} = \alpha^{(1)}\cdot\mathbf{E}_{\mathbf{micro}} + \alpha^{(2)}\cdot\mathbf{E}_{\mathbf{micro}}\mathbf{E}_{\mathbf{micro}} + \alpha^{(3)}\cdot\mathbf{E}_{\mathbf{micro}}\mathbf{E}_{\mathbf{micro}}\mathbf{E}_{\mathbf{micro}} + \ldots. \tag{7}$$

where the $\chi^{(n)}$, $\gamma^{(n)}$ and $\alpha^{(n)}$ are the appropriate susceptibilities or polarizabilities for these fields. The expansion in $\gamma^{(n)}$ contains *all* of the effects of the medium. We need this expansion to demonstrate how cascading reflects the statistical properties of the medium since $\mathbf{E}_{\mathbf{ex}}$ by definition is unaffected by the medium.

If we then relate the $\gamma^{(n)}$ to the $\chi^{(n)}$ in these expansions by iteratively expanding $\mathbf{E}$ in terms of $\mathbf{E}_{ex}$, we find that $\chi^{(3)}$ contains a term proportional to $\gamma^{(3)}$ as expected, that we call $\chi^{(3)}_{intrinsic}$ as well as two additional terms which are each functional products of two $\gamma^{(2)}$ terms which we call $\chi^{(3)}_{casc}$.

$$\chi^{(3)} = \chi^{(3)}_{intrinsic}(\gamma^{(3)}) + \chi^{(3)}_{casc}(\gamma^{(2)}, \gamma^{(2)}). \tag{8}$$

We next relate these susceptibilities to the microscopic hyperpolarizabilities of a liquid. We assume each molecule responds to the medium as a fixed point dipole but has no permanent dipole moment. Macroscopic observables are calculated by statistical averaging over the molecular positions ($\mathbf{R_i}$) and orientations (Ω_i) where $i = 1, 2, \ldots, N$ for the N molecules of the system.

Bedeaux and Bloembergen[3] expressed the dipole moment density $\mathbf{P}_0(\{N\})$ of the entire system of N molecules as a function of the polarization density $\mathbf{P}(\mathbf{E}_{micro}(\{N\}))$ and the particle density $\rho = \rho(\{N\})$

$$\mathbf{P}_0(\{N\}) = \rho(\{N\})\boldsymbol{\alpha}^{(1)} \cdot (\mathbf{E}_{micro}(\{N\})) + \rho(\{N\})\mathbf{P}_{NL}(\mathbf{E}_{micro}(\{N\})) \tag{9}$$

where

$$\mathbf{E}_{micro} = \mathbf{E_{ex}} - \mathbf{H} \cdot [\mathbf{P}_0(\{N\})] \tag{10}$$

and $\mathbf{H}$ is the Green's function propagator $\mathbf{F}$ appropriately modified for the singularities at the locations of the molecules. The macroscopic polarization density is then just the statistical average of $\mathbf{P}_0$ over the relative orientations and separations of the molecules

$$\mathbf{P}(\mathbf{x}, \Omega, t) = \langle \mathbf{P}_0(\{N\}) \rangle_{\mathbf{R}_i, \Omega_i}. \tag{11}$$

BETA MEDIUM

To isolate the cascading effects depending most sensitively on the correlations as well as on the near-field effects through the field propagators, we apply the Bedeaux and Bloembergen model to the artificial case of a liquid composed of oriented molecules that have only second-order hyperpolarizabilities ($\boldsymbol{\alpha}^{(l)} = 0$ for $l \neq 2$) so that all third-order effects are solely consequences of cascading. This liquid, which we call a "BETA" medium, is very useful for the study of cascading isolated from other effects and for the identification of the statistical functions that can be used for quantitative estimates of the cascading.

For BETA media, the polarization density can be expanded iteratively to third-order in terms of the external field and we find after averaging that in this case

$$\gamma^{(2)} \cdot \mathbf{E}_{ex}\mathbf{E}_{ex} = \langle \rho \boldsymbol{\alpha}^{(2)} \rangle \tag{12}$$

and

$$\begin{aligned} \gamma^{(3)} \cdot \mathbf{E}_{ex}\mathbf{E}_{ex}\mathbf{E}_{ex} &= \gamma^{(3)}_{casc} \cdot \mathbf{E}_{ex}\mathbf{E}_{ex}\mathbf{E}_{ex} \\ &= -\langle \rho[\boldsymbol{\alpha}^{(2)} \cdot \{\mathbf{H} \cdot \rho\boldsymbol{\alpha}^{(2)} \cdot \mathbf{E}_{ex}\mathbf{E}_{ex}\} \cdot \mathbf{E}_{ex} \\ &\quad +\boldsymbol{\alpha}^{(2)} \cdot \mathbf{E}_{ex}\{\mathbf{H} \cdot \rho\boldsymbol{\alpha}^{(2)} \cdot \mathbf{E}_{ex}\mathbf{E}_{ex}\}]\rangle \end{aligned} \tag{13}$$

Now if we change from our representation in terms of $\mathbf{E}_{ex}$ to the field $\mathbf{E}$ we find that $\gamma^{(3)}_{casc} = \chi^{(3)}_{intrinsic}$ and, as before, $\chi^{(3)}_{casc} = \chi^{(3)}_{casc}(\gamma^{(2)}, \gamma^{(2)})$.

To isolate the effect of correlations on these cascaded $\chi^{(3)}$ terms, we notice from Eq. (13) that calculation of $\chi^{(3)}_{intrinsic}$ involves the density-density correlation function

$$\langle \rho(\mathbf{x}, \Omega)\rho(\mathbf{y}, \Omega')\rangle = (\frac{\rho_0}{\Omega})^2 F_2(\mathbf{x}, \Omega; \mathbf{y}, \Omega') + (\frac{\rho_0}{\Omega})\delta(\mathbf{x} - \mathbf{y})\delta(\Omega - \Omega')F_1(\mathbf{x}, \Omega). \tag{14}$$

In the uncorrelated *(unc)* limit the two-particle distribution function $F_2(\mathbf{x}, \Omega; \mathbf{y}, \Omega')$ becomes $F_1(\mathbf{x}, \Omega)F_1(\mathbf{y}, \Omega')$ and therefore

$$\langle \rho(\mathbf{x}, \Omega)\rho(\mathbf{y}, \Omega')\rangle_{unc} = (\frac{\rho_0}{\Omega})^2 F_1(\mathbf{x}, \Omega)F_1(\mathbf{y}, \Omega') + (\frac{\rho_0}{\Omega})\delta(\mathbf{x} - \mathbf{y})\delta(\Omega - \Omega')F_1(\mathbf{x}, \Omega). \tag{15}$$

The Dirac-delta function terms in Eqs. (14) and (15) distinguish the density-density correlation function from both F_2 and the pair-correlation function

$$g_2(\mathbf{x}, \Omega; \mathbf{y}, \Omega') = F_2(\mathbf{x}, \Omega; \mathbf{y}, \Omega') - F_1(\mathbf{x}, \Omega)F_1(\mathbf{y}, \Omega'). \tag{16}$$

We can use the pair-correlation function, however, to rearrange the terms in the expression for $\chi^{(3)}$ into the form

$$\chi^{(3)} = \chi^{(3)}_{cor} + \chi^{(3)}_{unc}. \tag{17}$$

In BETA media $\chi^{(3)}_{cor}$ and $\chi^{(3)}_{unc}$ arise solely from cascading. However, $\chi^{(3)}_{cor}$ is nonzero only when $g_2 = 0$ so, unlike $\chi^{(3)}_{unc}$, it is nonlocal and thus reflective of the statistical features dependent on the molecular interaction.

In $k \equiv (\mathbf{k}, \omega)$ space, we can express each frequency component of the correlated cascaded susceptibility, after considerable calculation, as

$$\chi^{(3)}_{cor}(\Omega| - k; k_1, k_2, k_3) = -(\frac{\rho_0}{\Omega})^2 \int d\Omega' \int d\mathbf{q}\mathbf{A}(\mathbf{q}, \Omega, \Omega'| - k; k_1, k_2, k_3), \tag{18}$$

where

$$\begin{aligned} \mathbf{A} = {} & g_2(\Omega,\Omega';\mathbf{k}_1+\mathbf{k}_2-\mathbf{q})\boldsymbol{\alpha}^{(2)}(\Omega|-\omega;\omega_1+\omega_2,\omega_3) \\ & \cdot\{\mathbf{H}(\mathbf{q};\omega_1+\omega_2)\cdot\boldsymbol{\alpha}^{(2)}(\Omega|-\omega_1-\omega_2;\omega_1,\omega_2))\}_1 \\ & +g_2(\Omega,\Omega';\mathbf{k}_2+\mathbf{k}_3-\mathbf{q})\boldsymbol{\alpha}^{(2)}(\Omega|-\omega;\omega_1,\omega_2+\omega_3) \\ & \cdot\{\mathbf{H}(\mathbf{q};\omega_2+\omega_3)\cdot\boldsymbol{\alpha}^{(2)}(\Omega|-\omega_2-\omega_3;\omega_2,\omega_3)\}_2. \end{aligned} \tag{19}$$

A $(\mathbf{k},\omega)$-space graphical interpretation of the terms entering into Eq. (18) is given in Fig. 4. The intermediate propagation line in Fig. 4 contains a "bubble" subgraph representing the effects of the molecular interactions and the temperature.

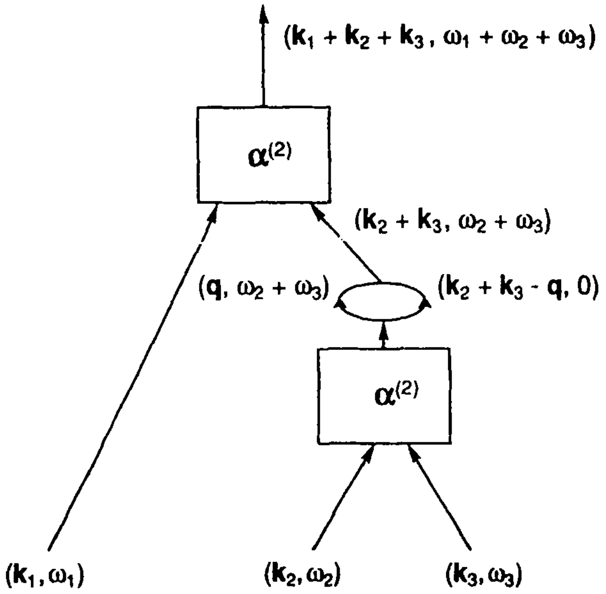

FIGURE 4 Graphical representations of a correlated third-order cascading term Eq.(18) in wave-vector and frequency space. The external lines represent waves that are mixed by the hyperpolarizabilities $\alpha^{(2)}$ depicted by the rectangular boxes. One arc on the circle attached to the intermediate line corresponds to the propagator $\mathbf{H}(\mathbf{q}, w_2 + w_3)$ that governs the wave propagation between two spatial points correlated by the function g_2 carrying momentum $\mathbf{k}_2 + \mathbf{k}_3 - \mathbf{q}$, but no energy, and represented by the other arc of the circle. An integration over all of the virtual "loop" momenta $\mathbf{q}$ is implied.

CONCLUSIONS

Assuming one is within a regime where the molecular hyperpolarizabilities retain their independent character, one can change the cascading that will occur in a liquid not only by changing the density, but also by changing the conditions that affect the size of the correlations. What sort of range this presents in practice is unclear without evaluating expressions such as (18) in representative situations. To do this for realistic media it is necessary to employ the generalizations of $\chi^{(3)}_{unc}$ and $\chi^{(3)}_{cor}$ where $\alpha^{(1)} \neq 0$ and the effects of the $\alpha^{(l)}$ for $l > 1$ are only a small perturbation on the behavior determined by the linear properties of the liquid. The complexity of the mathematical forms of these generalizations precludes their exact calculation, except under exceptionally simple circumstances. As a practical matter, reasonable estimates of the cascading can probably be made using the functions defined by $\chi^{(3)}_{unc}$ and $\chi^{(3)}_{cor}$ in the BETA model, and that we will refer to as the irreducible cascading coefficients, with linear local-field factors appended in a straightforward way. Even this minimally adequate calculation is no trivial endeavor. Nevertheless, the first step in such a project is clearly the computation of the irreducible cascading coefficients for the materials of interest. If such estimates of cascading prove to be reliable, one can turn this around and use situations where cascading can be singled out experimentally to measure the dependence on the two-particle correlation/distribution function.

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