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Hyper-Rayleigh scattering of centrosymmetric molecules in solution

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We study theoretically the harmonic light scattering (HLS) of centrosymmetric molecules in solution. Since HLS is inherently absent for centrosymmetric molecules, the intensity and line shape are obtained by taking into account two distinct physical processes: solute vibrational transition and solvent effective field contribution. The intensity is expressed in each case as the Fourier transform of the relevant time correlation functions. The implications for experiments, which use HLS to determine the first hyperpolarizability β of optically interesting molecules, are discussed. © 1999 American Institute of Physics. [S0021-9606(99)01427-0]

I. INTRODUCTION

Interest in hyper-Rayleigh and hyper-Raman light scattering has been recently revived as an advantageous technique for studying the second-order nonlinear response of molecules in solution.¹⁻⁵ The hyper-Rayleigh process of the annihilation of two incident photons of frequency ω and the creation of a scattered photon at 2ω is often referred to as incoherent harmonic light scattering (HLS). Similarly, hyper-Raman scattering corresponds to a scattered photon of $2\omega \pm \omega_m$, ω_m being an eigenfrequency of the molecule. Decius and Rauch⁶ first proposed the hyper-Raman phenomenon in 1959, which was subsequently observed in the experiments of Terhune, Maker, and Savage⁷ in 1965. Since then, selection rules for different symmetry groups and studies of line shape have been discussed. Experiments and theory were reviewed in Ref. 8. Interest in this technique waned because of difficulties in experimental observations.

Experimental improvements and the quest for suitable materials for nonlinear optical (NLO) applications motivated a reexamination of this technique. Electric-field induced second-harmonic generation (EFISHG), the most frequently used technique for the characterization of the first hyperpolarizability β of molecules, is unfortunately limited to dipolar and nonionic species. This is due to the necessity of aligning the molecules in solution through their dipole moment by the applied electric field, thus precluding characterization of the above systems. Also, in this experiment, β is obtained indirectly: the measured quantity is the second hyperpolarizability γ , and the projection of β in the direction of the dipole moment. Consequently, knowledge of both the dipole moment and γ is necessary to extract information about β .

Unlike EFISHG, HLS offers the possibility of experimentally measuring the first hyperpolarizability β of molecules with no ground state permanent dipole moment or of ionic molecules in solution. In the first category lies a new class of molecules that are promising candidates for materials for NLO applications: octupolar molecules;^{1,9} in the second category are synthetic polymers with NLO chromophores, and natural proteins.³ Furthermore, HLS experiments measure β directly.^{10–12} The advantage of this technique then becomes twofold: experimental observation of otherwise inaccessible molecular hyperpolarizabilities and direct measurement of β .

In the case of centrosymmetric molecules, whose first hyperpolarizability β vanishes identically in the electric dipole approximation due to symmetry, no hyper-Rayleigh scattering is expected. Nevertheless, intensities at approximately the doubled frequency, 2ω , have been observed for molecules with a center of inversion.^{13,14} The origin of this phenomenon now becomes important if this technique were to be used for determining the β of molecules.

In this paper, we focus on hyper-Rayleigh and hyper-Raman scattering of centrosymmetric molecules in solution to elucidate the way hyperpolarizabilities are probed in these processes. Our approach is to take into account the solvent (not necessarily of centrosymmetric molecules). The results may then be extended to noncentrosymmetric molecules.

The induced polarization \mathbf{P} of a single solute molecule may be expressed, to second order in the incident field \mathbf{E} , as

$$\mathbf{P} = \alpha \cdot \mathbf{E} + \beta : \mathbf{E}\mathbf{E}.$$

Since the polarization vector must change sign under inversion, β vanishes identically for centrosymmetric molecules and no HLS is expected. But if the response of the solvent is taken into account, an additional effective field *F* is present, which is zero on the average, but with low frequency instantaneous fluctuations. This additional field can mediate one of the transitions in the solute, that is

$$\mathbf{P} = \alpha \cdot \mathbf{E} + \beta : \mathbf{E}\mathbf{E} + \overline{\gamma} : \mathbf{E}\mathbf{E}\mathbf{F}.$$

The participation of the low frequency components of this solvent field then cause the solute's response at the HLS frequencies. We consider then two possible mechanisms: vibrationally induced hyper-Raman scattering, and hyper-Rayleigh scattering involving an effective $\bar{\gamma}$ instead of β , with an additional field produced by the solvent molecules. In this case the spectrum of noncentrosymmetric molecules would contain both β and γ contributions.

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This paper is organized as follows: In Sec. II, we consider the vibrationally induced hyper-Raman terms. Although this has been treated earlier,¹⁵ we give a new derivation that provides a basis for the later sections on harmonic Rayleigh scattering. We express the scattered intensity as the Fourier transform of the appropriate correlation functions, using the Heisenberg picture in order to make an interpretation due to molecular motions as well as a classical correspondence. We derive expressions for β taking into account vibrations and then obtain the correlation functions governing the spectral density. In Sec. III, we obtain similar expressions for the effective $\tilde{\gamma}$, as well as the solvent field correlation function. Implications for experiments are discussed in Sec. IV.

II. HYPER-RAMAN SCATTERING: β CONTRIBUTION

Hyper-Raman scattering around the hyper-Rayleigh line has been experimentally reported.¹⁶ In this section we obtain the scattering intensity in terms of the Fourier transform of the β time correlation function.¹⁷ It is the molecular motion that modulates the polarizability. Here, we neglect translational motion; rotations and vibrations of the molecule are considered independently. The line shape is then connected to the reorientational correlation function and to the vibrational relaxation of the normal modes of appropriate symmetry.^{18,19}

Our treatment applies to an isolated molecule. To treat liquid samples we apply the following assumptions: isotropic liquids and no angular correlations between molecules separated by distances of the order of the radiation. The dipole approximation will be invoked throughout this paper. If it may not apply in the sample as a whole, the sample may be divided in scattering volumes whose size is small compared to the scattering wavelength and large over distances of molecular correlations.^{20,21} It is the normalized cross section then that needs to be evaluated. Also, the phases of vibrations in different modes are usually treated as uncorrelated, so the correlation function of the vibrations of different molecules vanishes.

From time-dependent perturbation theory, we obtain the most general differential cross section per molecule to third order (see Appendix A) (here ϵ_i is the unit vector in the direction of the *i*th *field*)

$$I(\omega) \propto d\sigma/d\Omega$$

= $\sum_{i} \rho_{i} \sum_{f} |\langle i^{r} | \boldsymbol{\epsilon}^{3} \cdot \boldsymbol{\beta} : \boldsymbol{\epsilon}^{2} \boldsymbol{\epsilon}^{1} | f^{r} \rangle|^{2} \delta(\omega_{fi} + \omega_{Fl}), \quad (1)$

where $\boldsymbol{\beta}$ is the electronic polarizability tensor:

$$\boldsymbol{\beta} = \sum_{n,m} \frac{\langle f | \boldsymbol{\mu} | n \rangle \langle n | \boldsymbol{\mu} | m \rangle \langle m | \boldsymbol{\mu} | i \rangle}{(\omega_{in} - (\omega_{k1} + \omega_{k2}))(\omega_{mi} - \omega_{k1})} + 5 \text{ terms.} \quad (2)$$

Throughout the paper, we use lower-case letters to denote molecular states and upper-case letters to describe the electromagnetic field states. $|i\rangle$ and $|f\rangle$ are the initial and final vibronic states of the scatterer. In the HLS experiment $|i\rangle = |f\rangle$, which is allowed for a noncentrosymmetric molecule. For a centrosymmetric molecule, the transition moment ele-

ments in the expression for β cannot all be simultaneously different from zero. So we take into account the vibronic states and show that, given a transition between vibrational states of the proper symmetry may occur, scattering is now allowed. $|i^r\rangle$ and $|f^r\rangle$ correspond to the rotational states, taken to be independent of the vibronic states. Before scattering, the sample is assumed to be in equilibrium so the initial states obey a Boltzmann distribution. $\omega \equiv \omega_{FI}$ is the frequency difference between the scattered photon (ω_3 with polarization ϵ_3) and the incident photons (ω_1, ϵ_1 , and ω_2, ϵ_2). In an HLS experiment, $\omega_1 = \omega_2$; $\epsilon_1 = \epsilon_2$, and the tensor is symmetric with respect to exchange of the last two indices only. As long as the incident and scattered light frequencies are far from absorption frequencies, the tensor is usually taken as symmetric. The validity of this approximation is discussed in Ref. 22 where selection rules are obtained for the nonsymmetric case.

To proceed, we will separate the nuclear and electronic motion according to the Born–Oppenheimer approximation and express the wave functions in the Herzberg–Teller expansion. Our treatment will be valid for the nonresonant case only (where the HLS experiments are usually performed) so that intermediate vibrational states may be summed. Also, we restrict our interest to transitions for which both the initial and final vibrational states lie in the nondegenerate ground electronic state.

We now express the scattering cross section in terms of the relevant correlation functions. We first convert the delta function to its Fourier integral representation

$$\delta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t)$$

and substitute in Eq. (1):

$$d\sigma/d\Omega \propto \frac{1}{2\pi} \sum_{i} \rho_{i} \sum_{f} \langle i | \boldsymbol{\epsilon}^{3} \cdot \boldsymbol{\beta} : \boldsymbol{\epsilon}^{2} \boldsymbol{\epsilon}^{1} | f \rangle \langle f | \boldsymbol{\epsilon}^{3}$$
$$\cdot \boldsymbol{\beta} : \boldsymbol{\epsilon}^{2} \boldsymbol{\epsilon}^{1} | i \rangle \int_{-\infty}^{\infty} dt \exp[i(\omega_{FI} + \omega_{f} - \omega_{i})t].$$

Expressing the energies $h\omega_i$ and $h\omega_f$ as eigenvalues of the Hamiltonian *H* acting on the initial and final states, respectively, and summing over all the final states, we obtain

$$d\sigma/d\Omega \propto \sum_{i} \rho_{i} \sum_{f} \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega_{FI}t) \\ \times \langle i | \boldsymbol{\epsilon}^{3} \cdot \boldsymbol{\beta} : \boldsymbol{\epsilon}^{2} \boldsymbol{\epsilon}^{1} \exp(iHt/h) \boldsymbol{\epsilon}^{3} \cdot \boldsymbol{\beta} : \boldsymbol{\epsilon}^{2} \boldsymbol{\epsilon}^{1} \\ \times \exp(-iHt/h) | i \rangle,$$
(3)

where *H* is the Hamiltonian of the system in the absence of the optical fields. By defining the quantum mechanical operator, $\hat{\beta}$,

$$\hat{\boldsymbol{\beta}}(t) = \exp(iHt/h)\hat{\boldsymbol{\beta}}(0)\exp(-iHt/h)$$

so that it obeys the Heisenberg equation of motion, and denoting the statistical average by brackets $\langle \rangle$, Eq. (3) reduces to

$$I(\boldsymbol{\omega}) \propto \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega_{FI}t) \langle [\boldsymbol{\epsilon}^3 \cdot \hat{\boldsymbol{\beta}}(0) : \boldsymbol{\epsilon}^2 \boldsymbol{\epsilon}^1] \\ \times [\boldsymbol{\epsilon}^3 \cdot \hat{\boldsymbol{\beta}}(t) : \boldsymbol{\epsilon}^2 \boldsymbol{\epsilon}^1] \rangle.$$
(4)

If the average is interpreted in the classical sense, the classical description is recovered. In the quantum case the ordering of the operators is significant. By neglecting translations the time dependence of the tensor β arises only from reorientation of the molecules. The orientational correlation function depends on the symmetry of the molecule and polarization vectors. The averaging may be done using the direction cosine method or the characteristic rotation matrices (e.g., Ref. 23).

Including the vibrational states may be done using the semiclassical expression for the expansion of the electronic polarizability in terms of the electronic polarizability following Placzeck, namely

$$\boldsymbol{\beta}(t) = \boldsymbol{\beta}^{0}(t) + \sum_{\nu} \partial \boldsymbol{\beta}(t) / \partial q^{\nu}(t) \big|_{q=0} q^{\nu}(t)$$

or the Herzberg–Teller expansion of the excited vibronic state. This is the expansion of the electronic wave function (in the adiabatic approximation) in a Taylor series of displacement of the nuclear coordinates from their ground state equilibrium position. For an excited state $|e\rangle$,

$$|e\rangle = |e^{0}\rangle + \sum_{m \neq e} \frac{\langle m^{0}| \frac{\delta H}{\delta q} |e^{0}\rangle q |m^{0}\rangle}{E_{em}^{0}}$$

The comparison between the two approximations has been commented on in Ref. 15.

By making the latter substitution, assuming the nonresonant case, and dropping vibrational frequencies from the denominator, so that summation over intermediate vibrational states is possible, we obtain an effective β , β_{eff} with 24 terms, each one derivable from the standard from for β^{24} by substituting the above expression for $|e\rangle$ into each of the separate terms of β . A typical term is

$$\sum_{n,m,e} \frac{\langle g | \boldsymbol{\mu} | e \rangle \langle e | \frac{\delta H}{\delta q} | n \rangle \langle n | \boldsymbol{\mu} | m \rangle \langle m | \boldsymbol{\mu} | g \rangle \langle f | q | i \rangle}{\omega_{ne} (\omega_{in} - (\omega_{k1} + \omega_{k2})) (\omega_{mi} - \omega_{k1})} + 23 \text{ terms.}$$
(5)

From Eq. (5) we can see that scattering is no longer forbidden, and depends on the symmetry of the vibrational normal modes.

Following the same procedure as above, we rewrite Eq. (5) in terms of orientational and vibrational correlation functions:

$$I(\boldsymbol{\omega}) \propto \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega_{FI}t) \langle \boldsymbol{\epsilon}^3 \cdot \boldsymbol{\beta}(0) : \boldsymbol{\epsilon}^2 \boldsymbol{\epsilon}^1 \boldsymbol{\epsilon}^3$$
$$\cdot \boldsymbol{\beta}(t) : \boldsymbol{\epsilon}^2 \boldsymbol{\epsilon}^1 \rangle \langle q^{\nu}(o) q^{\nu}(t) \rangle.$$

So we can see that a line shape at frequency 2ω is possible for centrosymmetric molecules modulated by the vibrations. The linewidth will have contributions from rotational molecular motion.

III. HYPER-RAYLEIGH SCATTERING: $\tilde{\gamma}$ CONTRIBUTION

In this section we take into account the solvent. The solvent molecules create a field F on a solute molecule. On average, $\langle F \rangle = 0$, but instantaneously, this field exhibits low frequency time dependencies (i.e., with Fourier components $\omega_{\delta} \approx 0$). In particular, the single particle autocorrelation function of the field due to reorientation of the solvent molecules $\langle F(0,r)F(t,r')\rangle \neq 0$. Such a function is solvent dependent.

The HLS experiment then depends on the second hyperpolarizability of the molecule (fourth order in perturbation theory) $\tilde{\gamma}(-2\omega;\omega,\omega,0)$, where the third field is provided by the solvent. In this proposed picture, the hyper-Rayleigh scattering from the noncentrosymmetric molecules in solution will then appear as a result of two contributions: the β term, and the $\tilde{\gamma}$ term.

To obtain the intensity we follow the same procedure as in Sec. II. Here we ignore the vibrations. The fourth-order perturbation theory expression is given in Appendix B. The cross section is now

$$\begin{split} d\sigma/d\Omega \propto &\sum_{i} \rho_{i} \sum_{f} \sum_{\alpha,\beta} \rho_{\alpha\alpha} |\langle i, \alpha_{\text{solv}}| \tilde{\gamma} \cdot \vec{F} | f, \beta_{\text{solv}} \rangle|^{2} \\ &\times \delta(\omega_{fi} + \omega_{FI} + \omega_{\delta}), \end{split}$$

where \vec{F} is the solvent field, α and β the initial and final solvent states, respectively, and $\rho_{\alpha\alpha}$ the equilibrium distribution of the initial solvent states. The important frequencies ω_{δ} are expected to be small compared to ω and 2ω . Rearranging the above equation in a similar manner to Sec. II, we obtain

$$d\sigma/d\Omega \propto \frac{1}{2\pi} \int dt \exp(i\omega_{Fl}t) \langle \tilde{\gamma}(0) \tilde{\gamma}(t) \rangle \langle \vec{F}(0) \vec{F}(t) \rangle,$$

where

$$\langle \vec{F}(0)\vec{F}(t)\rangle = \sum_{\alpha,\beta} \rho_{\alpha,\alpha} F_{\alpha\beta} F_{\beta\alpha}(t) = \sum_{q} F_{q} F_{q}^{*} e^{i\omega_{q}t}$$

with q the frequency components of the solvent field and

$$\widetilde{\gamma} = \sum_{k,l,m} \left[\frac{\langle f | \boldsymbol{\mu} | k \rangle \langle k | \boldsymbol{\mu} | \rangle \langle l | \boldsymbol{\mu} | m \rangle}{(\boldsymbol{\omega}_{ki} + (\boldsymbol{\omega}_{k3} - \boldsymbol{\omega}_{k1} - \boldsymbol{\omega}_{k2}))(\boldsymbol{\omega}_{li} - (\boldsymbol{\omega}_{k1} + \boldsymbol{\omega}_{k2}))} \frac{\langle m | \boldsymbol{\mu} | i \rangle}{(\boldsymbol{\omega}_{mi} - \boldsymbol{\omega}_{k1})} + 23 \text{ terms} \right].$$

This expression differs from the standard perturbation expression for γ in one way: one of the interactions is with the solvent field instead of the electromagnetic field.

For the HLS experiment, we can express

 $\omega_{FI} = \omega_3 - \omega_2 - \omega_1 = \omega - 2\,\omega_0$

in terms of the incident frequency ω_0 and the scattered one ω , so the scattering cross section now becomes

$$d\sigma/d\Omega \propto \frac{1}{2\pi} \int dt \, e^{i(\omega - 2\omega_0)t} \langle \tilde{\gamma}(0) \tilde{\gamma}(t) \rangle \langle \vec{F}(0) \vec{F}(t) \rangle.$$
(6)

We proceed to calculate each of the correlation functions.

A. The effective $\tilde{\gamma}$ correlation function: $\langle \tilde{\gamma}(\mathbf{0}) \tilde{\gamma}(t) \rangle$

Each experimental setup probes specific components of this tensor depending on the experimental geometry and incident light polarization and the symmetry of the molecule. The selection rules for $\tilde{\gamma}$ remain the same as in the thirdorder experiments, even though the prefactor for the amplitude differs since the additional field is not the electromagnetic radiation field. The time dependence of the tensor comes primarily by way of variation in molecular orientation; the translations produce a considerably smaller effect and are neglected. So we can write

$$\begin{split} \langle \tilde{\gamma}(0) \tilde{\gamma}(t) \rangle &= 1/8\pi^2 \int_{\Omega(0)} \int_{\Omega(t)} \gamma_{ijkl} \gamma^*_{mnop} \\ &\times f(\Delta\Omega, t) d\Omega(0) d\Omega(t), \end{split}$$

where $f(\Delta\Omega, t)$ is the probability density for a given molecule to change molecular orientation by $d\Omega$ within time t and be can further expressed in terms of rotation matrices²⁵ D_{MM}^{J} and a function of time that depends on the type of rotational motion

$$f(\Delta\Omega,t) = \sum_{J,M} D^J_{MM}(\Delta\Omega) f^J_M(t).$$

The tensor components of γ must also be transformed accordingly from the laboratory to the molecular frame. This may be done again through the rotation matrices.¹⁹ Assuming the rotational motion exhibits simple Debye rotational diffusion, $f_M^J(t) \propto e^{-t/t_m^J}$. For a symmetric top molecule (e.g., benzene or any molecule of the point group D_{6h}), we obtain²⁵

$$\langle \widetilde{\boldsymbol{\gamma}}(0) \widetilde{\boldsymbol{\gamma}}[\Omega(t)] \rangle \propto \sum_{J,M} |\Gamma_M^J|^2 e^{-|t|/t_m^J},\tag{7}$$

where Γ_M^J depends on the point group symmetry of the molecule²⁶ and is time independent. The time constants t_m^J are known or accessible experimentally for the solute.¹⁹ The details of this correlation function are beyond the scope of this work. The important point is that there be a nonvanishing component of this tensor. We can now turn to the role of the solvent molecules' effective field in the HLS process.

B. The solvent field correlation function: $\langle F(0)F(t)\rangle$

As our treatment of HLS includes the polarization fluctuations of the solvent, to proceed we must calculate the solvent field correlation function. We describe the solvent as a dielectric continuum and treat its response within linear response theory. This response in the incident applied field is described then by the appropriate susceptibility evoking the fluctuation-dissipation theorem. The simplest approach is chosen to illustrate the physical process involved. Future incorporation of a more sophisticated solvent description at a future stage is possible in this formalism.

To express the fluctuations of a field f in terms of the susceptibility α of a physical quantity x to an external perturbation, the corresponding "f-x" pair must be chosen appropriately. This may be done by considering the change in energy absorbed or dissipated by the system under the influence of the perturbation²⁷

$$\frac{dU}{dt} = -\bar{x}\frac{df}{dt}.$$
(8)

In linear response the generalized susceptibility relates the Fourier components f_{ω} of the perturbation to the components of the quantity \bar{x} describing the system,

$$x_{\omega} = \alpha(\omega) f_{\omega},$$

and it can decomposed in real and imaginary parts with definite symmetry properties obeying the Kramers-Kronig relationship

$$\alpha = \alpha' + i \, \alpha''$$

Once this is established the rest is straightforward within the assumptions of the theory of linear response:

$$\langle xx(t)\rangle = \int_{-\infty}^{\infty} \langle xx(\omega)\rangle e^{-i\omega t} d\omega, \qquad (9)$$

where

$$\langle xx(\omega)\rangle = \frac{kT}{\pi\omega} \alpha''(\omega)$$

and

$$\langle ff(t) \rangle = \int_{-\infty}^{\infty} \langle ff(\omega) \rangle e^{-i\omega t} d\omega$$
 (10)

with

$$\langle ff(\omega) \rangle = \frac{kT}{\pi \omega} \frac{\alpha''(\omega)}{|\alpha|^2}$$

For a dielectric body in a variable external field, the change in energy is given by 28

$$\frac{\partial U}{\partial t} = \int \frac{1}{4\pi} \vec{E} \frac{\partial \vec{D}}{\partial t} dV, \qquad (11)$$

where \vec{D} is the dielectric displacement and \vec{E} the electric field in the medium. Also,

$$\tilde{D}_{\omega} = \epsilon(\omega) \tilde{E}_{\omega}$$

where the dielectric function $\epsilon(\omega)$ is given by

$$\boldsymbol{\epsilon}(\boldsymbol{\omega}) = \boldsymbol{\epsilon}_{\infty} + \frac{\boldsymbol{\epsilon}_{s} - \boldsymbol{\epsilon}_{\infty}}{1 - i\boldsymbol{\omega}\boldsymbol{\tau}}.$$
(12)

 ϵ_{∞} describes the instantaneous reaction of the system to the external perturbation and ϵ_s is the static dielectric constant, that is $\epsilon_s = \epsilon(0)$.

Comparing Eq. (11) with Eq. (8), we identify

 $\vec{E} \rightarrow x$, $\vec{D} \rightarrow f$,

which implies

$$\alpha(\omega) = \epsilon^{-1}(\omega).$$

Making the above substitution into Eqs. (9) and (10) we obtain

$$\langle EE(t) \rangle = \int_{-\infty}^{\infty} d\omega \, e^{-i\omega t} \frac{kT}{\pi \omega} \frac{-\epsilon''}{|\epsilon|^2} \tag{13}$$

and

$$\langle DD(t)\rangle = \int_{-\infty}^{\infty} d\omega \, e^{-i\omega t} \frac{kT}{\pi\omega} \, \epsilon'',$$

since we assume that the solution is isotropic.

This instantaneous solvent field E provides the additional field on the solute molecules in the scattering process. Its correlation function is given by Eq. (13).

From Eqs. (12) and (13) we obtain

$$\langle EE(t) \rangle = \int_{-\infty}^{\infty} d\omega \, e^{i\,\omega t} \frac{kT}{\pi} \, \frac{\tau(\boldsymbol{\epsilon}_s - \boldsymbol{\epsilon}_{\infty})}{\boldsymbol{\epsilon}_s^2 + \boldsymbol{\epsilon}_{\infty}^2 \omega^2 \tau^2}$$
$$= kT \frac{(\boldsymbol{\epsilon}_s - \boldsymbol{\epsilon}_{\infty})}{\boldsymbol{\epsilon}_s \boldsymbol{\epsilon}_{\infty}} e^{-|t|/t_{\text{sol}}}, \quad t_{\text{sol}} = \boldsymbol{\epsilon}_{\infty} \tau/\boldsymbol{\epsilon}_s.$$
(14)

Substituting the solute correlation function [Eq. (7)] and the solvent correlation function of Eq. (14) into the scattered light intensity function for the HLS process in Eq. (6), we obtain the final result

$$d\sigma/d\Omega \propto \frac{kT}{2\pi} \int dt e^{i(\omega-2\omega_0)t} \sum_{J,M} |\Gamma_M^J|^2 \frac{(\epsilon_s - \epsilon_\infty)}{\epsilon_s \epsilon_\infty}$$
$$\times e^{-|t|(1/t_{\text{rot}} + 1/t_{\text{sol}})}$$
$$= kT \sum_{J,M} |\Gamma_M^J|^2 \frac{(\epsilon_s - \epsilon_\infty)}{\epsilon_s \epsilon_\infty}$$
$$\times \frac{2[1/t_{\text{rot}} + 1/t_{\text{sol}}]}{(\omega - 2\omega_0)^2 + (1/t_{\text{rot}} + 1/t_{\text{sol}})^2}. \tag{15}$$

The molecular symmetry is embedded into the function Γ_M^J that contains the polarizability tensor elements which will be nonvanishing depending on the solute symmetry, the experimental geometry, and the polarization of the incident light. The rotational motion of the solute will contribute to the line shape a sum of several Lorentzian functions. For the same solute molecule immersed in different solvents, we can see from Eq. (15) as well as Fig. 1 that the width and intensity of the line shape will vary. We see that it is possible to obtain a response from centrosymmetric molecules depending on the solvent.



FIG. 1. Intensity of scattered light of the same centrosymmetric chromophore in different solvents typically used in the experiments of Ref. 2: (closed circles) chloroform (ϵ_s =4.78, ϵ_{∞} =2.20, τ =5.4 ps), (gray solid line) bromoform (ϵ_s =4.39, ϵ_{∞} =2.70, τ =19 ps), (black solid line) nitrobenzene (ϵ_s =34.89, ϵ_{∞} =2.52, τ =41 ps), (open circles) quinoline (ϵ_s =9, ϵ_{∞} = 2.77, τ =45 ps) assuming single molecular rotational contribution (τ = 2.5 ps). The numbers are taken from Ref. 31.

IV. DISCUSSION

Although HLS was discussed in the literature in the late 1960s and early 1970s^{29–31} the approaches taken were system specific. Gelbart's approach, applied on atomic fluids only, considers the cluster expansion of a many-body β which depends parametrically on the positions of all the nuclei. The first nonvanishing contribution arises then from triplet cluster terms. Kielich considers an expansion of the higher order moments of the centrosymmetric molecules and attributes the effect to correlations among higher order moments. Our approach is more general. We have used a time-dependent correlation function method which allows us to develop a general formalism. System-specific details may be applied at each stage.

We have shown that hyper-Rayleigh and hyper-Raman light scattering are possible, even in the presence of identically vanishing β . There is a solvent contribution that involves the second hyperpolarizability of the solute. The line shape then, centered at frequency $2\omega_0$, is a sum of Lorentzian peaks from contributions of the reorientations of the solute as well as the response of the solvent. The intensity of the peak is also solvent dependent. The solvent is treated here in a simple way,³² but more sophisticated descriptions may be incorporated in the formalism. For example, accurate information for the solvent correlation function may be extracted from molecular dynamics simulations. Finally, it is important to note that we have treated the problem in the weak system–solvent interaction regime, so that they are still amenable to separate descriptions.

This solvent effect may be important as harmonic light scattering is reintroduced as an advantageous techniques to measure the hyperpolarizability β of potentially important materials for nonlinear optics and should be taken into account. For noncentrosymmetric molecules, the relative magnitude of the contributions from β and the effective γ should be different, so that the latter may become negligible with the appropriate choice of solvent.

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APPENDIX A: HLS CROSS SECTION

In this Appendix, the differential cross section for the "quasielastic" HLS of centrosymmetric molecules in solution is calculated, with the radiation field treated quantum mechanically for generality, although a classical treatment is possible and yields basically the same results. The photon states are in capital letters, and the molecular states are in lower case. The total differential cross section, $d\sigma/d\Omega$, is given by

$$\left. \frac{d\sigma}{d\Omega} \right|_{F \leftarrow I} = \frac{V}{c d\Omega} T_{F \leftarrow I},$$

where $T_{F \leftarrow I}$ is the transition rate from the molecular initial state $|i|\rangle$ to the final molecular state $|f\rangle$ and may be obtained from time-dependent perturbation theory. *c* stands for the speed of light and *V* for the enclosed volume. **F** and **I** correspond to the total final and initial state of the molecule–photon system.

Now,

$$T_{F \leftarrow I} = \sum_{f} \rho_{f} \sum_{i} \rho_{i} \frac{|C_{f \leftarrow i}|^{2}}{t}$$
(A1)

is related to the transition amplitude $C_{f\leftarrow i}(t)$ from the initial to the final state of the system as well as the density of final and initial states per unit energy per unit volume: ρ_f and ρ_i , respectively. We assume that before each photon is scattered the sample has come to equilibrium so that

$$\rho_i = \frac{e^{-\hbar\omega_i/kT}}{\sum_i e^{-\hbar\omega_i/kT}}.$$

The density of final states is given by

$$\rho_f = \frac{d\Omega}{\hbar} \frac{\omega'^2}{(2\pi c)^3},$$

where ω' is the frequency of the scattered photon and $d\Omega$ the solid angle within which lies its wave vector \vec{k}' .

We now proceed to calculate the transition amplitude to third order in perturbation theory. Formally,

$$C_{f \leftarrow i}(t)^{(3)} = \frac{1}{(i\hbar)^3} \int_0^t d\tau \langle f | V_I(\tau) \int_0^\tau dt' V_I(t') \\ \times \int_0^{t'} dt'' V_I(t'') | \Psi_I(0) \rangle.$$
(A2)

 V_I is the time-dependent part of the Hamiltonian in the interaction representation. In our case,

$$H = H_0 + H(t),$$

where H_0 is given by

$$H_0 = H_{\text{system}} + H_{\text{radiation}}$$

and

$$H(t) = H_{\text{interaction}}$$
.

Only the terms which annihilate or create one quantum need be considered and $H_{\text{interaction}} \equiv H(1)$. By inserting complete set of states in Eq. (A2), we obtain for the transition amplitude of the annihilation of two incident photons of wave vector \vec{k}_1, \vec{k}_2 and polarization λ_1, λ_2 and the creation of a photon with wave vector \vec{k}_3 and polarization λ_3 :

$$C_{f\leftarrow i}^{(3)}(t)|_{\vec{k}_{3}\lambda_{3}\leftarrow\vec{k}_{2},\lambda_{2};\vec{k}_{1},\lambda_{1}}$$

$$=\frac{1}{(i\hbar)^{3}}\sum_{n,m}\int_{0}^{t}d\tau H(1)_{fn}e^{i\omega_{fn}\tau}$$

$$\times\int_{0}^{\tau}dt'H(1)_{nm}e^{i\omega_{nm}t'}\int_{0}^{\tau}dt''H(1)_{mi}e^{i\omega_{mi}t''}.$$

There are three possible Feynman diagrams for this process corresponding to the different sequences of annihilation of two quanta, and creation of a third quantum. The above sum thus has six terms. Looking carefully at one of the terms, namely the annihilation of photon \vec{k}_1, λ_1 followed by that of photon \vec{k}_2, λ_2 , the emission of \vec{k}_3, λ_3 we obtain:

Term 1

$$= \frac{-1}{i\hbar} \sum_{n,m} \int_{0}^{t} d\tau e^{i\omega_{FI}\tau + i\omega_{fi}\tau} \\ \times \frac{\langle f|p^{\lambda^{3}}e^{-i\vec{k}_{3}\cdot\vec{r}}|n\rangle\langle n|p^{\lambda^{2}}e^{-i\vec{k}_{2}\cdot\vec{r}}|m\rangle\langle m|p^{\lambda^{1}}e^{i\vec{k}_{1}\cdot\vec{r}}|i\rangle}{[\omega_{ni} - \omega_{1} - \omega_{2}][\omega_{mi} - \omega_{1}]} \\ \times (e/m)^{3}(2\pi\hbar/V)^{3/2} \left(\frac{n_{k_{1}}n_{k_{2}}n_{k_{3}+1}}{\omega_{1}\omega_{2}\omega_{3}}\right)^{1/2}.$$
(A3)

The occupation numbers $n_{k,\lambda}$ are the number of quanta with wave vector \vec{k} and polarization λ ; $\omega_{FI} \equiv \omega_3 - \omega_2 - \omega_1$; $\omega_{fi} \equiv (\epsilon_f - \epsilon_i)/\hbar$. The scattering system is constructed by Nunits each of n_a charged particles which can be regarded as independent of each other. Within each unit the exponentials can be regarded as constants. For \vec{R}_a , the vector from an arbitrary origin to a fixed point in the scattering unit a and for $e\langle k|p^{\lambda_i}|m\rangle = im\omega_{km}\langle k|\mu^{\lambda_i}|m\rangle$, Eq. (A3) becomes

Term 1

$$= \frac{-i}{\hbar} \int_{0}^{t} d\tau e^{i\omega_{FI}\tau + i\omega_{fi}\tau} \sum_{a=1}^{N} e^{i\vec{R}_{a}\cdot(\vec{k}1 + \vec{k}2 - \vec{k}3)}$$

$$\times \sum_{n,m} \frac{\langle f|\mu^{r\lambda^{3}}|n\rangle\langle n|\mu^{\lambda^{2}}|m\rangle\langle m|\mu^{\lambda^{1}}|i\rangle}{[\omega_{m} - \omega_{i} - \omega_{1}][\omega_{n} - \omega_{i} - \omega_{1} - \omega_{2}]}$$

$$\times im^{3}\omega_{mi}\omega_{nm}\omega_{fn}(2\pi\hbar/V)^{3/2} \left(\frac{n_{k_{1}}n_{k_{2}}n_{k_{3}}+1}{\omega_{1}\omega_{2}\omega_{3}}\right)^{1/2}$$

The remaining five terms are permutations of Term 1. So we can rewrite the transition amplitude

$$C_{f\leftarrow i}^{(3)}(t) \propto \int_0^t d\tau \exp^{i\omega_{FI}\tau + i\omega_{fi}\tau}\beta,$$

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where β corresponds to the terms in the sum and substitute into Eq. (A1). The modulus squared of the integral divided by *t* gives a delta function $2\pi\delta(\omega_{FI}+\omega_{fi})$, so the final result then is

$$\frac{d\sigma}{d\Omega} \propto \sum_{f} \sum_{i} \rho_{i} |\beta|^{2} \delta(\omega_{f} - \omega_{i} + \omega_{3} - \omega_{2} - \omega_{1}).$$
(A4)

APPENDIX B: FOURTH-ORDER CONTRIBUTION

We now proceed to calculate the transition amplitude to fourth-order perturbation theory in the incoming fields, that is,

$$C_{f \leftarrow i}(t)^{(4)} = \frac{1}{(i\hbar)^4} \int_0^t d\tau \langle f | V_I(\tau) \int_0^\tau dt' V_I(t') \\ \times \int_0^{t'} dt'' V_I(t'') \int_0^{t''} dt''' V_I(t''') | \Psi_I(0) \rangle.$$
(B1)

Inserting a complete set of states in Eq. (B1), we obtain the transition amplitude for the annihilation of two incident photons of wave vector \vec{k}_1, \vec{k}_2 and polarization λ_1, λ_2 and the creation of a photon with wave vector \vec{k}_3 and polarization λ_3 :

$$C_{f\leftarrow i}^{(4)}(t)|_{\vec{k}_{3}\lambda_{3}\leftarrow\vec{k}_{2},\lambda_{2};\vec{k}_{1},\lambda_{1}} = \frac{1}{(i\hbar)^{4}} \sum_{klm} \int_{0}^{t} d_{\tau} H_{fk}^{\text{solv}} e^{i\omega_{fk}\tau} \int_{0}^{\tau} dt' H(1)_{kl} e^{i\omega_{kl}t'} \\ \times \int_{0}^{t'} dt'' H(1)_{lm} e^{i\omega_{lm}t''} \int_{0}^{t''} dt''' H(1)_{mi} e^{i\omega_{mi}t'''}.$$

There are four possible Feynman diagrams for this process corresponding to the different sequences of annihilation of two quanta, the creation of a third quantum, and an interaction with the solvent. The above sum thus has 24 terms.

In exactly the same manner as in Appendix A, we obtain

Term 1

$$= \frac{-i}{\hbar} \int_{0}^{t} d\tau e^{i\omega_{Fl}\tau} \sum_{k,l,m} \sum_{a=1}^{N} e^{i\vec{R}_{a} \cdot (\vec{k}_{1} + \vec{k}_{2} - \vec{k}_{3})} \omega_{kl} \omega_{lm} \omega_{mi}$$

$$\times (2\pi\hbar/V)^{3/2} \frac{n_{k_{1}}^{1/2} n_{k_{2}}^{1/2} n_{k_{3}+1}^{1/2}}{(\omega_{1}\omega_{2}\omega_{3})^{1/2}} H_{fk}^{\text{solv}}$$

$$\times \frac{\langle k|\mu^{\lambda^{3}}|l\rangle \langle l|\mu^{\lambda^{2}}|m\rangle \langle m|\mu^{\lambda^{1}}|i\rangle}{[\omega_{ki} + \omega_{3} - \omega_{1} - \omega_{2}][\omega_{li} - \omega_{2} - \omega_{1}][\omega_{mi} - \omega_{1}]}.$$
(B2)

Now, we substitute for H^{solv} ,

$$H^{\text{solv}} = \mu \cdot F$$

so that

$$H_{fk}^{\text{solv}} = \sum_{\lambda} \langle f | \mu^{\lambda} | k \rangle \cdot F.$$

Combining all the above, the scattering cross section becomes

$$\frac{d\sigma}{d\Omega} \propto \sum_{f} \sum_{i} \rho_{i} \left| \sum_{a=1}^{N} e^{i\tilde{R}_{a} \cdot (\tilde{k}_{1} + \tilde{k}_{2} - \tilde{k}_{3})} \sum_{k,l,m} \sum_{\lambda} \frac{\langle k | \mu^{\lambda^{3}} | l \rangle}{[\omega_{ki} + \omega_{3} - \omega_{1} - \omega_{2})]} \frac{\langle l \mu^{\lambda^{2}} | m \rangle}{[\omega_{li} - \omega_{2} - \omega_{1}]} \frac{\langle m | \mu^{\lambda^{1}} | i \rangle}{[\omega_{mi} - \omega_{1}]} \times F^{2} \omega_{kl} \omega_{lm} \omega_{mi} + 23 \text{ terms} \right|^{2} \delta(\omega_{f} - \omega_{i} + \omega_{3} - \omega_{2} - \omega_{1} + \omega_{\delta}) \propto \sum_{f} \sum_{i} \rho_{i} |\gamma|^{2} \delta(\omega_{f} - \omega_{i} + \omega_{3} - \omega_{2} - \omega_{1} + \omega_{\delta}).$$
(B3)

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