Polarization and angle dependence for hyper-Rayleigh scattering from local and nonlocal modes of isotropic fluids

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Collective modes of molecular motion result in long-range correlations between molecules. Orientation correlations between the molecules of an isotropic fluid owing to polar collective modes result in hyper-Rayleigh scattering with distinctive polarization and angle dependence. The polarization and angle dependence for hyper-Rayleigh scattering from polar transverse-optical and longitudinal-optical nonlocal modes, and for dipolar and quadrupolar hyper-Raleigh scattering from local modes, is calculated and compared. © 2000 Optical Society of America [S0740-3224(00)01712-4]

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Hyper-Rayleigh Scattering (HRS) has become an important method for measuring the second-order nonlinear optical properties of materials, especially organic molecules in solution.[1,2] The first hyperpolarizability β describing the second-order nonlinear response of a molecule is a third-rank tensor and usually has many independent components. Recently a number of schemes for extracting up to six independent pieces of information about the components of β from HRS measurements have been proposed and demonstrated.[3–7] These schemes analyze the polarization dependence of HRS for a fixed scattering geometry (not necessarily 90° scattering) to obtain information about β. Recent research also considers systems such as chiral molecules in which all four irreducible parts of the tensor β can be nonzero.[7] In all this research, aimed at the study of strong chromophores in dilute solution, orientation correlation between molecules has been ignored.

Orientation correlation between molecules can have a significant effect on HRS, especially in pure fluids. This was clearly recognized at the time of the first HRS experiments.[8–11] However, in the analysis of those experiments it was explicitly assumed that orientational ordering in liquids is short range. A recent study of HRS from liquid acetonitrile concludes that long-range correlations of molecular orientation, in the form of propagating waves, account for most of the scattered light.[12] A follow-up HRS study indicates that long-range orientation correlations, over distances comparable to the light wavelength, are present in a wide range of liquids.[13] HRS from these delocalized modes is ultimately mediated by β, but the form of the relation is different than that for local modes of molecular motion in which molecular-orientation correlation is short range or nonexistent. This paper compares the polarization and angle dependence of local and nonlocal contributions to HRS from isotropic fluids and considers several effects that could modify or invalidate the usual analysis of HRS based on the assumption of independent randomly oriented molecules.

The derivation of the angle and polarization dependence for HRS from local and nonlocal modes follows closely the derivation given by Bersohn *et al.*[9] The scattered field is $\mathbf{E}_{sc} \propto (\boldsymbol{\mu} \times \mathbf{R}) \times \mathbf{R}$, where $\boldsymbol{\mu}$ is the induced dipole oscillating at frequency 2ω, and $\hat{R} = \hat{k}_s$ is the unit vector in the direction of observation. For the choice of coordinates shown in Fig. 1, the unit vector $\hat{R}$ is specified by the direction cosines $\lambda_X \equiv \hat{R} \cdot \hat{X} = \sin\theta\cos\psi$, $\lambda_Y = \cos\theta\cos\psi$, and $\lambda_Z = \sin\psi$. We consider the case in which both the incident and the scattered light are linearly polarized, with the polarization either horizontal (H) or vertical (V) with respect to the X–Y plane. The scattered field is described by use of a basis of mutually perpendicular unit vectors $\hat{e}_1 \perp \hat{Z}$, $\hat{e}_2$ in the R–Z plane, and $\hat{e}_3 \parallel \hat{R}$, such that the H and V polarizations correspond to the $\hat{e}_1$ and $\hat{e}_2$ basis vectors, respectively. The scattered fields with H and V polarizations are given by

$$\mathbf{E}_H \propto (1 - \lambda_Z^2)^{-1/2}(\mu_X\lambda_Y - \mu_Y\lambda_X)\hat{e}_1, \tag{1}$$

$$\mathbf{E}_V \propto (1 - \lambda_Z^2)^{-1/2}[\mu_X\lambda_X\lambda_Z + \mu_Y\lambda_Y\lambda_Z - \mu_Z(1 - \lambda_Z^2)]\hat{e}_2. \tag{2}$$

where the constant of proportionality is the same in both expressions.

HRS from local modes is mainly due to the molecular first hyperpolarizability β, which generates an induced dipole $\mu_\alpha^{(2\omega)} = (1/4)\beta_{\alpha\beta\gamma}E_\beta^{(\omega)}E_\gamma^{(\omega)}$. In a fluid of independent, randomly oriented molecules one may show that the HRS intensities for the various combinations of linearly polarized incident and scattered fields are[9,14–17]

$$I_{VV}/A_1\langle\beta_{XZZ}^2\rangle = P^2\cos^2\psi + \sin^2\psi, \tag{3}$$

$$I_{HV}/A_1\langle\beta_{XZZ}^2\rangle = P^2\sin^2\theta\sin^2\psi + \cos^2\theta\sin^2\psi + \cos^2\psi, \tag{4}$$
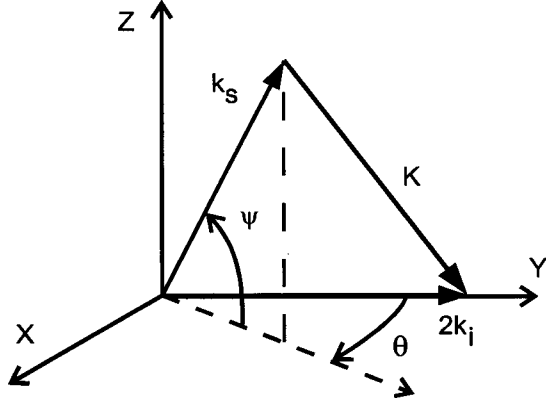
Fig. 1. Laser light with wave vector $\mathbf{k}_i$ is incident along Y, and scattered light with wavevector $\mathbf{k}_s$ is collected close to the X–Y plane. The incident polarization vector is along Z or X (V or H polarized). A component of the scattered light is selected with polarization either in the k_s–Z plane (V polarized) or parallel to the X–Y plane (H polarized). The polarization combinations considered are labeled VV, HV, VH, and HH, where the incident polarization is given by the first letter and the scattered polarization is given by the second letter.

$$I_{VH}/A_1\langle\beta_{XZZ}^2\rangle = 1, \tag{5}$$

$$I_{HH}/A_1\langle\beta_{XZZ}^2\rangle = P^2\cos^2\theta + \sin^2\theta, \tag{6}$$

where $\langle\beta_{XZZ}^2\rangle$ is the squared lab-frame component of the molecular first hyperpolarizability averaged over all molecular orientations. The parameter $P^2 = \langle\beta_{ZZZ}^2\rangle/\langle\beta_{XZZ}^2\rangle$ falls in the range $3/2 \leqslant P^2 \leqslant 9$ in the case that β is symmetric in all its indices. The bounds become $0 \leqslant P^2 \leqslant 9$ instead when Kleinman symmetry is broken, as in chiral molecules or at frequencies near resonance.[7] Averaged over all angles, the local-mode HRS intensities are $(2P^2 + 1)/3$, $(P^2 + 5)/6$, 1, and $(P^2 + 1)/2$ for the VV, HV, VH, and HH polarization geometries, respectively.

HRS from delocalized modes is mediated by the macroscopic susceptibility χ_{JKLM}, which generates a dipole moment density $\mu_J^{(2\omega-\Omega)} = \chi_{JKLM}E_K^{(\omega)}E_L^{(\omega)}Q_M^{(\Omega)}$.[18,19] The susceptibility χ is just β in disguise: long-range correlations in molecular orientation give rise to a nonzero space fixed average β proportional to the collective mode amplitude Q. HRS from nonlocal modes will have a different angle and polarization dependence than HRS from randomly oriented molecules because momentum conservation in the scattering process picks out a preferred wave vector $\mathbf{K} = 2\mathbf{k}_i - \mathbf{k}_s$ for the nonlocal mode (see Fig. 1). There are three polar modes for each $\mathbf{K}$, two transverse-optical (TO) modes and one longitudinal-optical (LO) mode. The polar directions for these modes are given by

$$\hat{Q}_{TO,1} = \frac{\lambda_X\hat{Y} - (1 - \lambda_Y)\hat{X}}{[(1 - \lambda_Y)^2 + \lambda_X^2]^{1/2}}, \tag{7}$$

$$\hat{Q}_{TO,2} = \frac{(1 - \lambda_Y)\lambda_Z\hat{Y} - \lambda_X\lambda_Z\hat{X} - (1 - \lambda_Z^2)\hat{Z}}{[(1 - \lambda_Y)^2\lambda_Z^2 + \lambda_X^2\lambda_Z^2 + (1 - \lambda_Z^2)^2]^{1/2}}, \tag{8}$$

$$\hat{Q}_{LO} = \frac{(1 - \lambda_Y)\hat{Y} - \lambda_X\hat{X} - \lambda_Z\hat{Z}}{[2(1 - \lambda_Y)]^{1/2}}. \tag{9}$$

These expressions are obtained assuming $2k_i = k_s$, which is a good approximation except near $\theta = 0$.

The tensor χ_{JKLM} representing the isotropic fluid must itself be isotropic, and it is also symmetric in the middle two indices since they refer to the two indistinguishable electric field factors. Therefore the response of the medium can be described by just two independent quantities, χ_{XZZX} and $R = \chi_{ZZZZ}/\chi_{XZZX}$. If χ_{JKLM} is symmetric in all indices, then $R = 3$. With V- or H-polarized light incident, the components of the induced polarization are of the simple form $\mu_J = \chi_{JKKJ}E_K^2Q_J$. The induced dipole can be evaluated for each mode $\hat{Q}$ in turn by substituting Eqs. (7)–(9) into this expression, and the intensity for each of the modes is then obtained by substituting the induced dipole components into relations (1) and (2). Adding the intensities of the two independent TO modes, one obtains

$$\frac{I_{TO,VV}}{A_2[\chi_{XZZX}]^2}$$

$$= \frac{\sin^2\theta\sin^2\psi}{1 + \cos^2\psi - 2\cos\theta\cos\psi}$$

$$+ \frac{[(R-1)\cos^3\psi + \cos\psi - \cos\theta\sin^2\psi]^2}{1 - 2\cos\theta\cos\psi\sin^2\psi}, \tag{10}$$

$$\frac{I_{TO,HV}}{A_2[\chi_{XZZX}]^2}$$

$$= \frac{[(R-1)(1 - \cos\theta\cos\psi) + 1]^2\sin^2\theta\sin^2\psi}{1 + \cos^2\psi - 2\cos\theta\cos\psi}$$

$$+ \frac{[(R-1)\sin^2\theta\sin^2\psi\cos\psi + \cos\psi - \cos\theta\sin^2\psi]^2}{1 - 2\cos\theta\cos\psi\sin^2\psi}, \tag{11}$$

$$\frac{I_{TO,VH}}{A_2[\chi_{XZZX}]^2}$$

$$= \frac{(\cos\theta - \cos\psi)^2}{1 + \cos^2\psi - 2\cos\theta\cos\psi}$$

$$+ \frac{\sin^2\theta\sin^2\psi}{1 - 2\cos\theta\cos\psi\sin^2\psi}, \tag{12}$$

$$\frac{I_{TO,HH}}{A_2[\chi_{XZZX}]^2}$$

$$= \frac{[(R-1)\cos\theta(1 - \cos\theta\cos\psi) + \cos\theta - \cos\psi]^2}{1 + \cos^2\psi - 2\cos\theta\cos\psi}$$

$$+ \frac{[(R-1)\cos\theta\cos\psi + 1]^2\sin^2\theta\sin^2\psi}{1 - 2\cos\theta\cos\psi\sin^2\psi}. \tag{13}$$

The results for the LO modes are

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$$\frac{I_{LO,VV}}{A_3[\chi_{XZZX}]^2} = \frac{[(R-1)\cos\psi + \cos\theta]^2 \sin^2\psi}{2(1 - \cos\theta\cos\psi)},$$
(14)

$$\frac{I_{LO,HV}}{A_3[\chi_{XZZX}]^2} = \frac{[(R-1)\sin^2\theta\cos\psi - \cos\theta]^2 \sin^2\psi}{2(1 - \cos\theta\cos\psi)},$$
(15)

$$\frac{I_{LO,VH}}{A_3[\chi_{XZZX}]^2} = \frac{\sin^2\theta}{2(1 - \cos\theta\cos\psi)},$$
(16)

$$\frac{I_{LO,HH}}{A_3[\chi_{XZZX}]^2} = \frac{[(R-1)\cos\theta\cos\psi + 1]^2 \sin^2\theta}{2(1 - \cos\theta\cos\psi)}.$$
(17)

Expressions for more general polarization states of the incident and scattered light may be evaluated by use of the more general form $\mu_J = \chi_{JKLM}E_K E_L Q_M$ for the induced dipole and by forming the appropriate linear combination of relations (1) and (2).

Table 1 compares the angle and polarization dependence for local- and nonlocal-mode HRS mediated by β, obtained from Eqs. (3)–(6) and (10)–(17) for $\psi = 0$ (scattering in the X–Y plane). Local-, TO-, and LO-mode HRS can be clearly distinguished by their different polarization dependence even for $\theta = 90°$ scattering with linearly polarized light. In particular, $I_{HV}/I_{VH} \neq 1$ for nonlocal modes. Several other possible contributions to HRS are also considered briefly below.

The expressions given above for the angular dependence of the HRS intensity can be used to evaluate the

effect of the finite (and often large) light-collection aperture in the usual HRS experiments. Equations (3)–(6) and (10)–(17) are expanded to second order for the in-plane ($\Delta\theta$) and out-of-plane ($\Delta\psi$) angular deviations from the nominal scattering direction and averaged over the light-collection angular aperture. The results of this calculation are shown in Table 2 for two common scattering angles. Most HRS experiments are done with $\theta = 90°$, but recent experiments have also used $\theta = 45°$ to obtain additional information.[7,12] The results given in Table 2 are the factors by which the average HRS intensity is changed owing to the finite collection angle. The P^2 dependence of the correction factor for local-mode HRS is shown explicitly since P^2 varies over a wide range for different molecules. A rectangular aperture stop (e.g., the diffraction grating of the spectrometer analyzing the collected light) is chosen to simplify the calculation and to most clearly display the different in-plane and out-of-plane angular sensitivities of the finite aperture corrections to the HRS intensities. With N.A. ≈ 0.24 collection optics ($\Delta\theta = \Delta\psi = 0.24$ rad), most of the corrections are $\sim 5\%$, but the largest is more than 100%. Collection optics with N.A. = 0.63, requiring correspondingly larger corrections, have been used in some experiments owing to the weakness of HRS.[5]

Table 1 also shows results for the two contributions to electric quadrupole HRS for independent randomly oriented molecules,[20] mediated by the dipole-dipole-quadrupole hyperpolarizability tensor $B_{\alpha\beta,\gamma\delta}$.[20,21] **B** has a nonvanishing isotropic average $\bar{B} = 2/15\, B_{\alpha\beta,\alpha\beta}$ even for centrosymmetric molecules. The first contribution (D) is due to the induced dipole proportional to the prod-

Table 1. Comparison of Angle and Polarization Dependence for Several Contributions to Hyper-Raleigh Scattering in the X–Y Plane[a]

Polarization	$I_{HRS}/A_1\langle\beta_{XZZ}^2\rangle$ Local β	$I_{HRS}/A_2(\chi_{XZZX})^2$ Nonlocal TO	$I_{HRS}/A_3(\chi_{XZZX})^2$ Nonlocal LO	$I_{HRS}/A_4(\bar{B})^2$ Local D	$I_{HRS}/A_4(\bar{B})^2$ Local Q
VV	P^2	R^2	0	a	a'
HV	1	1	0	b	$b' + (a' - b')\sin^2\theta$
VH	1	$\sin^2(\theta/2)$	$\cos^2(\theta/2)$	$b + (c - 2b - a)\sin^2\theta$	b'
HH	$\sin^2\theta + P^2\cos^2\theta$	$\dfrac{[1 - (R-1)\cos\theta]^2}{\sin^2(\theta/2)}$	$\dfrac{[1 + (R-1)\cos\theta]^2}{\cos^2(\theta/2)}$	$a + (c - b - 2a)\sin^2\theta$	$a' + c'\sin^2(2\theta)$

[a] Molecular structure determines the values of the parameters $P^2 = \langle\beta_{ZZZ}^2\rangle/\langle\beta_{XZZ}^2\rangle$ and $R = (\chi_{ZZZZ}/\chi_{XZZX})$ for dipolar HRS (β, TO, LO). In the limit of spherical molecular symmetry, $a = a' = b = b' = 0$ and $c = c' = 1$ for quadrupolar HRS (D, Q).

Table 2. Effect of a Rectangular Collection Aperture with Angular Size $2\Delta\theta \times 2\Delta\psi$ (Radians) on the Hyper-Rayleigh Scattering Intensity[a]

Polarization	β $\theta = 45°$	β $\theta = 90°$	TO $\theta = 45°$	TO $\theta = 90°$	LO $\theta = 45°$	LO $\theta = 90°$
VV	$1 - 1/3(1 - P^{-2})\Delta\psi^2$	$1 - 1/3(1 - P^{-2})\Delta\psi^2$	$1 - 0.43\Delta\psi^2$	$1 - 0.76\Delta\psi^2$	$14.7\Delta\psi^{2b}$	$4.0\Delta\psi^{2b}$
HV	$1 + 1/6(P^2 - 1)\Delta\psi^2$	$1 + 1/3(P^2 - 1)\Delta\psi^2$	$1 + 1.05\Delta\psi^2$	$1 + 2.50\Delta\psi^2$	$0.2\Delta\psi^{2b}$	$4.0\Delta\psi^{2b}$
VH	1	1	$1 + 0.80\Delta\theta^2 + 0.17\Delta\psi^2$	$1 + 0.33\Delta\psi^2$	$1 + 0.07\Delta\theta^2 - 0.40\Delta\psi^2$	1
HH	1	$1 + 1/3(P^2 - 1)\Delta\theta^2$	$1 - 7.44\Delta\theta^2 + 44.3\Delta\psi^2$	$1 + 2.67\Delta\theta^2 + 0.33\Delta\psi^2$	$1 - 0.07\Delta\theta^2 - 0.60\Delta\psi^2$	$1 + 2.67\Delta\theta^2$

[a] The ratio of the average intensity and intensity at the center of the aperture is given. $R = 3$ is assumed for TO and LO modes.
[b] Total intensity referenced to I_{VH} at the same angle.

uct of the applied electric field and the electric field gradient, and the second contribution (Q) is due to the induced quadrupole proportional to the square of the applied electric field. In the case of a molecule with T_d or O_h symmetry, $a = a' = 2b = 2b'$ in Table 1, and for an atom, $a = 0$ and $c = c' = 1$ as well.[20] Electric quadrupole HRS has been observed in a number of centrosymmetric crystals of D_{4h} or O_h symmetry.[19] The scattered light is polarized along the direction of the incident wave vector, as expected for the D contribution for a system of high symmetry. A similar distinctive angle and polarization dependence is expected for electric quadrupole HRS from molecular fluids. However, based on calculated static values of $\bar{B}$,[22,23] the intensity is in this case expected to be smaller than HRS mediated by β by a factor $(k\bar{B}/\beta_\parallel)^2 \approx 10^{-4}$. Magnetic dipole contributions are expected to be of the same order.

Molecular interactions and orientation correlations will alter HRS intensities and polarization ratios. At short range the electric fields owing to the permanent multipole moments of a molecule are large enough to significantly distort neighboring molecules and to influence their orientation. The increment in molecular β induced by the field of a nearby molecular dipole, quadrupole, or octupole has been calculated,[14,24–26] and the collision-induced contribution to the HRS spectrum of CCl_4 has been observed and is large.[27] One may view the effect of molecular interaction and orientation correlation as changing the size and symmetry of the effective molecular cluster. Provided that the interactions and correlations are short range, the result can be represented by some effective β for the randomly oriented cluster, and the angle and polarization dependence is still given by the first column of Table 1.

Macroscopic axial order induced by the applied laser field (ac Kerr effect) will alter the angle and polarization dependence of HRS mediated by β in a way not possible for local modes of an isotropic system. Although the polarization ratio I_{VV}/I_{VH} remains independent of θ, there is no longer an upper bound for this ratio. This symmetry-breaking contribution to HRS is cubic in the laser intensity. Intense fields are needed to significantly alter the molecular-orientation distribution, and the laser-intensity dependence that the polarization ratios would acquire from this effect has not been observed.

In conclusion, short-range molecular interactions and correlations can alter HRS intensities and polarization ratios, but the angular dependence of the HRS and the bounds on the polarization ratios are the same as for HRS from independent randomly oriented molecules. Quadrupolar HRS, and HRS from a sample with field-induced anisotropy, both have angle and polarization dependence different from local-mode HRS mediated by β but are too weak to be significant. However, TO and LO collective modes provide a nonlocal HRS contribution with distinctive polarization and angle dependence and large intensity. This contribution to HRS should be considered when polarization analysis is used to extract tensor components of β from HRS measurements, especially in pure fluids. Conversely, HRS provides a means for studying the dynamics of these otherwise unobserved collective orientational modes of molecular liquids.

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