Hyper-Rayleigh scattering from correlated molecules

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The polarization dependence of hyper-Rayleigh scattering has been calculated for spherical domains of orientation correlated molecules. Distributions with radial or azimuthal mean polar orientation of the molecules are found that give results consistent with experimental observations, and expressions for the polarization ratios in terms of the product of correlation strength and correlated domain size are derived for these distributions. Assuming a plausible correlation strength, it is estimated that the correlated domain size in typical polar liquids is of order 100 molecular diameters. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4799262]

I. INTRODUCTION

Hyper-Rayleigh scattering (HRS) is a second harmonic light scattering process widely used to measure the first hyperpolarizability β of molecules in solution.[1] It is usually assumed that the orientations of dissolved chromophores in dilute solution are uncorrelated and random so that the HRS intensity is proportional to the orientational average $\langle \beta^2 \rangle$ for individual chromophores.[2,3] However, HRS is sensitive to intermolecular correlations and interactions[2–6] and several recent HRS experiments have observed such effects of in neat liquids[6–8] and solutions.[9–12] Intermolecular interactions and correlations change the observed intensity, spectrum, and polarization dependence of the HRS light.

HRS experiments most often use the 90° scattering configuration with incident and scattered light polarized either perpendicular or parallel to the horizontal scattering plane. The usual linear polarization combinations for the 90° scattering configuration are denoted VV, HV, VH, and HH, where V denotes vertical polarization, H denotes horizontal polarization, and the first and second letters refer to the incident and scattered light, respectively. The usual linearly polarized 90° scattering intensities are I_{VV}, I_{HV}, I_{VH}, and I_{HH}, and the usual polarization ratios are I_{VV}/I_{HV}, I_{HV}/I_{VH}, and I_{HH}/I_{VH}.

The observed polarization dependence of HRS for many liquids, and the observation $I_{HV}/I_{VH} \neq 1$ in particular, indicates long range orientation correlations for the molecules.[7,8] Expressions for non-local HRS from polar collective modes have been derived that can account for the experimental observations.[7,13] The signature of transverse polar mode HRS is $I_{VV}/I_{HV} = 9$, $I_{HV}/I_{VH} = 2$, and $I_{HH}/I_{VH} = 1$, while the signature of longitudinal polar mode HRS is $I_{VV} = I_{HV} = 0$ and $I_{HH}/I_{VH} = 1$. HRS observations are consistent with a coherent contribution from such collective modes. However, a detailed microscopic model of the molecular organization is lacking.

The present work explores explicit models for HRS from correlated molecules, with the aim of determining the forms for the correlations that are consistent with the HRS obser-

vations, and determining what constraints experimental observations place on the range and strength of the molecular correlations.

II. SECOND HARMONIC DIPOLE FOR AXIAL MOLECULES

Consider the second harmonic dipole induced in a molecule with $C_{\infty v}$, C_{6v}, or C_{4v} point group symmetry. For molecules with four-fold or higher axial symmetry, the non-vanishing independent components of the first hyperpolarizability tensor β in the molecular frame are

$$\beta_0 = \beta_{zzz}, \tag{1a}$$

$$u\beta_0 = \beta_{zxx} = \beta_{zyy}, \tag{1b}$$

$$v\beta_0 = \beta_{xxz} = \beta_{xzx} = \beta_{yyz} = \beta_{yzy}, \tag{1c}$$

where $u = v$ in the case that Kleinman symmetry holds. Let the orientation of the molecular z axis be given by the unit vector $\hat{n}$. The second harmonic dipole $\vec{\mu}$ induced by the electric field $\vec{E} = E_0 \hat{E}$ lies in the plane spanned by the vectors $\hat{n}$ and $\hat{E}$, with components parallel and perpendicular to $\hat{n}$ given by

$$\mu_{||} = \tfrac{1}{2}\beta_0 E_0^2 \, [\cos^2 \psi + u \sin^2 \psi], \tag{2a}$$

$$\mu_{\perp} = \tfrac{1}{2}\beta_0 E_0^2 \, [2v \cos \psi \sin \psi], \tag{2b}$$

where $\cos \psi = \hat{n} \cdot \hat{E}$. Using the expression $\hat{n}_{\perp} = [\hat{E} - \hat{n} \cos \psi]/\sin \psi$ for the perpendicular unit vector gives

$$\vec{\mu} = \tfrac{1}{2}\beta_0 E_0^2 \, [(1 - u - 2v)(\hat{n} \cdot \hat{E})^2 \hat{n} + u \, \hat{n} + 2v(\hat{n} \cdot \hat{E})\hat{E}]. \tag{3}$$

For later convenience when considering non-local HRS, the lab fixed Cartesian coordinate frame has been chosen with Z perpendicular to the scattering plane, Y in the direction of the scattering vector $\vec{K} = 2\vec{k}_i - \vec{k}_s$, and with X perpendicular to Y and Z. The incident and scattered light directions in this frame are $\hat{k}_i = 2^{-1/2}(-\hat{X} - \hat{Y})$ and $\hat{k}_s = 2^{-1/2}(\hat{X} - \hat{Y})$, respectively. With these coordinates the unit vectors for the

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incident and scattered polarizations and the scattering vector are

$$\hat{V}_i = \hat{V}_s = \hat{Z}, \tag{4a}$$

$$\hat{H}_i = 2^{-1/2}(\hat{X} - \hat{Y}), \tag{4b}$$

$$\hat{H}_s = 2^{-1/2}(\hat{X} + \hat{Y}), \tag{4c}$$

$$\hat{K} = \hat{Y}. \tag{4d}$$

Spherical polar coordinates r, θ, ϕ with Y as the polar axis are used to give the position $\vec{r}$ and orientation $\hat{n}$ of a molecule, where the spherical polar unit vectors expressed in lab frame Cartesian coordinates X, Y, Z are

$$\hat{r} = (\sin\theta \sin\phi, \cos\theta, \sin\theta \cos\phi), \tag{5a}$$

$$\hat{\theta} = (\cos\theta \sin\phi, -\sin\theta, \cos\theta \cos\phi), \tag{5b}$$

$$\hat{\phi} = (\cos\phi, 0, -\sin\phi). \tag{5c}$$

From Eq. (3), the relevant second harmonic induced dipole components for a $C_{\infty v}$ molecule with its axis oriented along $\hat{n}$, for HRS in the VV, HV, VH, and HH polarization geometries, are

$$\mu_{VV} = \tfrac{1}{2}\beta_0 E_0^2 \, [(1 - u - 2v)(\hat{n} \cdot \hat{Z})^3 + (u + 2v) \, (\hat{n} \cdot \hat{Z})], \tag{6a}$$

$$\mu_{HV} = \tfrac{1}{2}\beta_0 E_0^2 \, [(1 - u - 2v)(\hat{n} \cdot \hat{H}_i)^2(\hat{n} \cdot \hat{Z}) + u \, (\hat{n} \cdot \hat{Z})], \tag{6b}$$

$$\mu_{VH} = \tfrac{1}{2}\beta_0 E_0^2 \, [(1 - u - 2v)(\hat{n} \cdot \hat{Z})^2(\hat{n} \cdot \hat{H}_s) + u \, (\hat{n} \cdot \hat{H}_s)], \tag{6c}$$

$$\mu_{HH} = \tfrac{1}{2}\beta_0 E_0^2 \, [(1 - u - 2v)(\hat{n} \cdot \hat{H}_i)^2(\hat{n} \cdot \hat{H}_s) + u \, (\hat{n} \cdot \hat{H}_s)]. \tag{6d}$$

III. INCOHERENT HRS

The incoherent HRS intensity for randomly oriented molecules with number density ρ in a spherical volume with radius R is given by summing orientation averaged $\mu^2(\theta, \phi)$ for each molecule

$$I = (\rho R^3/3) \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} \mu^2(\theta, \phi) \, d\phi. \tag{7}$$

The orientation-dependent factors in Eqs. (6a)–(6d) for the induced second harmonic dipole $\mu(\theta, \phi)$, evaluated using $\hat{n} = \hat{r}$, are

$$(\hat{r} \cdot \hat{Z}) = \sin\theta \cos\phi, \tag{8a}$$

$$(\hat{r} \cdot \hat{H}_i) = (\sin\theta \sin\phi - \cos\theta)/\sqrt{2}, \tag{8b}$$

$$(\hat{r} \cdot \hat{H}_s) = (\sin\theta \sin\phi + \cos\theta)/\sqrt{2}. \tag{8c}$$

From Eqs. (6a)–(8c), the incoherent HRS intensities for $C_{\infty v}$ molecules are

$$I_{VV} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{4}{3}\pi\rho R^3\right)[15 + 12(u + 2v) + 8(u + 2v)^2]/105, \tag{9a}$$

$$I_{HV} = I_{VH} = I_{HH} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{4}{3}\pi\rho R^3\right)[3(1 - 2v)^2 + 8u(1 - 2v) + 24u^2]/105, \tag{9b}$$

which reduce to

$$I_{VV} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{4}{3}\pi\rho R^3\right)[5 + 12u + 24u^2]/35, \tag{10a}$$

$$I_{HV} = I_{VH} = I_{HH} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{4}{3}\pi\rho R^3\right) \times [3 - 4u + 20u^2]/105 \tag{10b}$$

in the case that Kleinman symmetry holds so that $u = v$.

IV. COHERENT HRS FROM PERFECTLY ORDERED AXIAL MOLECULES

Spherical domains with axially symmetric molecular orientation distributions will be considered next. The scattered amplitude from each molecule is proportional to the induced dipole, and the total scattered amplitude from a domain containing correlated molecules is the sum over all the molecules in the domain. The relative phase of the HRS contribution from a molecule located at position $\vec{r}$ is accounted for by the factor

$$\exp(i\vec{K} \cdot \vec{r}) = \exp(iKr \, \hat{Y} \cdot \hat{r})$$
$$= \cos(Kr \cos\theta) + i \sin(Kr \cos\theta), \tag{11}$$

where r is the distance of the molecule from the origin. For a molecular distribution axially symmetric around the lab Y axis, the molecular positions and orientations are given in terms of the spherical polar coordinates r, θ, ϕ, with the unit vectors given by Eqs. (5a)–(5c). A distribution with the symmetry axis oriented at polar angles α, β is obtained from the distribution with Y symmetry axis, by first rotating the distribution by angle α around the X axis and then by angle β around the Y axis. The rotation matrix $\mathbf{R} = \mathbf{R}_Y \mathbf{R}_X$ for the transformation to the rotated distribution is

$$\mathbf{R} = \begin{pmatrix} \cos\beta & -\sin\alpha \sin\beta & -\cos\alpha \sin\beta \\ 0 & \cos\alpha & -\sin\alpha \\ \sin\beta & \sin\alpha \cos\beta & \cos\alpha \cos\beta \end{pmatrix}, \tag{12}$$

giving the transformed unit vectors $\hat{r}' = \mathbf{R}\,\hat{r}$, $\hat{\theta}' = \mathbf{R}\,\hat{\theta}$, and $\hat{\phi}' = \mathbf{R}\,\hat{\phi}$, and transformed coordinates $r' = r$, $\theta' = \theta'(\theta, \phi, \alpha, \beta)$, and $\phi' = \phi'(\theta, \phi, \alpha, \beta)$.

The total scattered field from a spherical domain with induced dipoles given by Eqs. (6a)–(6d) is proportional to the integral

$$F \approx \rho \int_0^R r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^{2\pi} \mu(r, \theta', \phi')(1 + iKr\cos\theta') d\phi, \tag{13}$$

where the approximation $\exp(iKr\cos\theta') \approx 1 + iKr\cos\theta'$, which is valid when $Kr \ll 1$, has been applied to simplify the integrand in Eq. (13). For even (odd) functions μ, the integral evaluated with phase factor $iKr\cos\theta'$ (1) vanishes. The HRS intensity $I = |F|^2$ obtained from the field integral F may be a function of the orientation of the domain axis, given by angles α, β. The observed HRS intensity is the average intensity for randomly oriented, axially symmetric, spherical domains, given by the integral

$$I = (4\pi)^{-1}\int_0^\pi \sin\alpha \, d\alpha \int_0^{2\pi} |F(\alpha,\beta)|^2 \, d\beta. \qquad (14)$$

One must specify the distribution of orientations $\hat{n}$ for the molecules to evaluate the integrals in Eqs. (13) and (14). Three distributions will be considered, with the molecules oriented in the directions of each of the polar unit vectors, $\hat{n} = \hat{r}'$, $\hat{n} = \hat{\theta}'$, or $\hat{n} = \hat{\phi}'$, as shown in Figure 1.

For radial oriented molecules, there is no loss of generality using $\hat{n} = \hat{r}$ rather than $\hat{n} = \hat{r}'$ since the radial oriented distribution is spherically symmetric, so $\mu(\theta,\phi)$ may be evaluated using Eqs. (8a)–(8c) and $(\hat{r} \cdot \hat{Y}) = \cos\theta$. The integrals for a spherical domain with radially oriented molecules give HRS intensities

$$I_{VV} = I_{HV} = 0, \qquad (15a)$$

$$I_{VH} = I_{HH} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{1}{4}\rho K R^4\right)^2 (8\pi^2/225)(1 + 4u - 2v)^2. \qquad (15b)$$

The intensities $I_{VV} = I_{HV} = 0$ and polarization ratios $I_{HV}/I_{VH} = 0$ and $I_{HH}/I_{VH} = 1$ for the radial oriented molecular distribution are consistent with a pure longitudinal polar mode.

For molecules oriented in the $\hat{n} = \hat{\theta}'$ direction, the scattering integrals are evaluated with the substitutions

$$(\hat{\theta}' \cdot \hat{Z}) = \sin\beta\cos\theta\sin\phi - \sin\alpha\cos\beta\sin\theta$$
$$+ \cos\alpha\cos\beta\cos\theta\cos\phi, \qquad (16a)$$

$$(\hat{\theta}' \cdot \hat{H}_i) = (\cos\beta\cos\theta\sin\phi + \sin\alpha\sin\beta\sin\theta$$
$$- \cos\alpha\sin\beta\cos\theta\cos\phi + \cos\alpha\sin\theta$$
$$+ \sin\alpha\cos\theta\cos\phi)/\sqrt{2}, \qquad (16b)$$

$$(\hat{\theta}' \cdot \hat{H}_s) = (\cos\beta\cos\theta\sin\phi + \sin\alpha\sin\beta\sin\theta$$
$$- \cos\alpha\sin\beta\cos\theta\cos\phi - \cos\alpha\sin\theta$$
$$- \sin\alpha\cos\theta\cos\phi)/\sqrt{2}, \qquad (16c)$$

$$(\hat{r}' \cdot \hat{Y}) = \cos\theta' = \cos\alpha\cos\theta - \sin\alpha\sin\theta\cos\phi. \qquad (16d)$$

The scattered field integrals F_{VV}, F_{HV}, F_{VH}, F_{HH} are functions of the orientation of the domain axis given by angles α, β, and the observed average intensities for randomly oriented
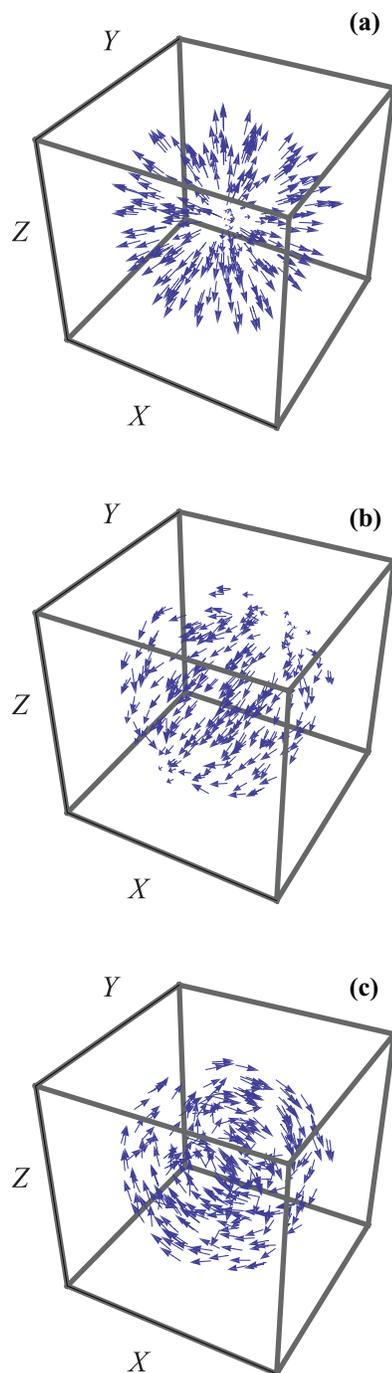
FIG. 1. Spherical domains containing 250 molecules at random positions are shown. The arrows denote the polar axis for each molecule, and the molecules exhibit perfect (a) radial ($\hat{r}$), (b) polar ($\hat{\theta}$), or (c) azimuthal ($\hat{\phi}$) orientational order about the Y symmetry axis. Domains in liquid water with $R = 20$ nm would contain 10^6 molecules.

domains with $\hat{\theta}'$ oriented molecules are

$$I_{VV} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{1}{3}\rho R^3\right)^2 (\pi^4/1680)[207 + 258(u + 2v)$$
$$+ 95(u + 2v)^2], \qquad (17a)$$

$$I_{HV} = I_{VH} = I_{HH}$$
$$= \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{1}{3}\rho R^3\right)^2 (\pi^4/840)[13(1 - 2v)^2$$
$$+ 86u(1 - 2v) + 181\, u^2]. \qquad (17b)$$

For molecules oriented in the $\hat{n} = \hat{\phi}'$ direction, the scattering integrals are evaluated with the substitutions

$$(\hat{\phi}' \cdot \hat{Z}) = \sin\beta\cos\phi - \cos\alpha\cos\beta\sin\phi, \qquad (18a)$$

$$(\hat{\phi}' \cdot \hat{H}_i) = (\cos\beta\cos\phi + \cos\alpha\sin\beta\sin\phi - \sin\alpha\sin\phi)/\sqrt{2}, \qquad (18b)$$

$$(\hat{\phi}' \cdot \hat{H}_s) = (\cos\beta\cos\phi + \cos\alpha\sin\beta\sin\phi + \sin\alpha\sin\phi)/\sqrt{2}, \qquad (18c)$$

$$(\hat{r}' \cdot \hat{Y}) = \cos\alpha\cos\theta - \sin\alpha\sin\theta\cos\phi. \qquad (18d)$$

The intensities averaged over angles α, β for randomly oriented domains with $\hat{\phi}'$ oriented molecules are

$$I_{VV} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{1}{4}\rho K R^4\right)^2 (\pi^4/840)[27 + 30(u + 2v) + 13(u + 2v)^2], \qquad (19a)$$

$$I_{HV} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{1}{4}\rho K R^4\right)^2 (\pi^4/3360)[15(1 - 2v)^2 + 82u(1 - 2v) + 183u^2], \qquad (19b)$$

$$I_{VH} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{1}{4}\rho K R^4\right)^2 (\pi^4/1680)[5(1 - 2v)^2 + 18u(1 - 2v) + 47 u^2], \qquad (19c)$$

$$I_{HH} = \left(\tfrac{1}{2}\beta_0 E_0^2\right)^2 \left(\tfrac{1}{4}\rho K R^4\right)^2 (\pi^4/480)[(1 - 2v)^2 + 6u(1 - 2v) + 13u^2]. \qquad (19d)$$

For a 1D chromophore where $u = v = 0$, Eqs. (19a)–(19d) give polarization ratios $I_{HV}/I_{VH} = 7.2$, $I_{HV}/I_{VH} = 1.5$, and $I_{HH}/I_{VH} = 0.7$, results different from those for a pure transverse polar mode. The polarization ratios for azimuthally polarized domains containing $C_{\infty v}$ molecules with Kleinman symmetry ($u = v$) are plotted as functions of the parameter u in Figure 2. The pure transverse mode polarization ratios $I_{HV}/I_{VH} = 9$, $I_{HV}/I_{VH} = 2$, and $I_{HH}/I_{VH} = 1$ are obtained only for $u = v = 1/3$.

V. COHERENT HRS FOR STATISTICAL MOLECULAR DISTRIBUTIONS

Consider the perturbed orientation distribution for polar molecules with permanent dipole moment $\vec{\mu}^{(0)}$ in an external electric field $\vec{E}$. The orientation dependence of the electric dipole interaction energy $U = -\vec{\mu}^{(0)} \cdot \vec{E} = -\mu_\alpha^{(0)} E_\alpha$ results in a perturbed orientation distribution

$$G(\Omega) = 1 + (\mu^{(0)}E/k_BT)\cos\theta = 1 + a_1\cos\theta \qquad (20)$$

to lowest order in the perturbing field. The lab frame average of the tensor $\boldsymbol{\beta}$ with the perturbed orientation distribution is

$$\langle\boldsymbol{\beta}(\Omega)\rangle^E = \int \boldsymbol{\beta}(\Omega)\exp(-U/k_BT)d\Omega / \int \exp(-U/k_BT)d\Omega$$

$$= \langle\beta_{\beta\gamma\delta}\rangle + (E_\alpha/k_BT)\langle\mu_\alpha^{(0)}\beta_{\beta\gamma\delta}\rangle + \cdots, \qquad (21)$$

where $\langle\cdot\rangle$ denotes the isotropic average, and the summation convention is assumed for repeated dummy indices. The
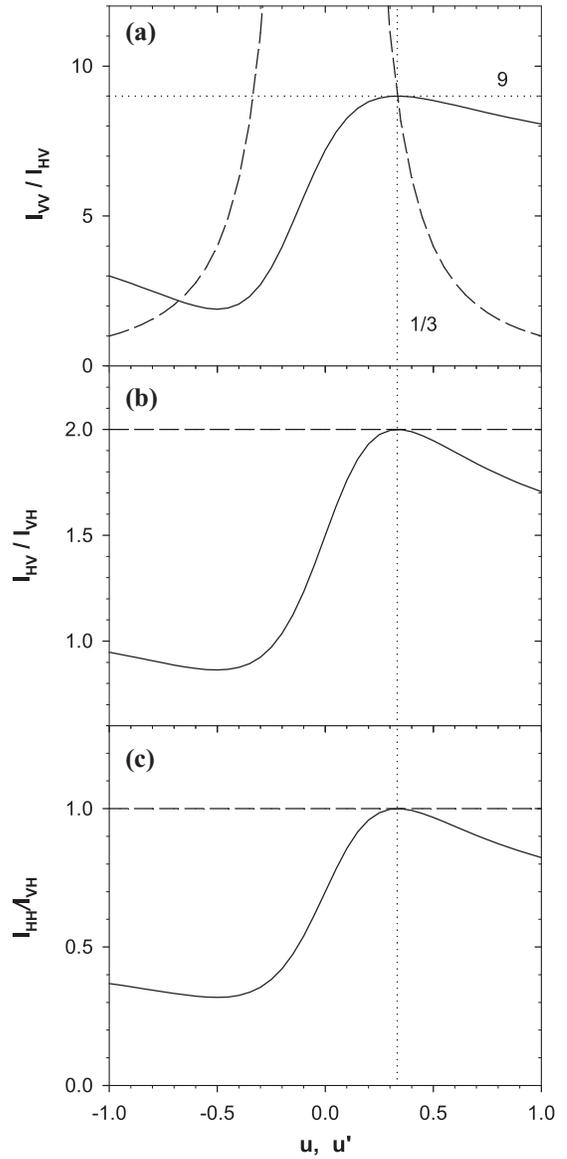
FIG. 2. Polarization ratios (a) I_{VV}/I_{HV}, (b) I_{HV}/I_{VH}, and (c) I_{HH}/I_{VH} for spherical domains with azimuthal molecular orientation correlations. The solid curves show results from Eqs. (19a)–(19d) for perfectly ordered $C_{\infty v}$ molecules with Kleinman symmetry ($u = v = \beta_{zxx}/\beta_{zzz} = \beta_{xxz}/\beta_{zzz}$) plotted as functions of u. The dashed curves show results from Eqs. (29a)–(29c) for molecules with statistical correlations and arbitrary symmetry plotted as functions of u_1, where $u_1 = \langle\beta\rangle_{ZXX}^E / \langle\beta\rangle_{ZZZ}^E$ for effective β is given by Eqs. (24a)–(24c). In this case, deviations from $u_1 = 1/3$ indicate deviations from Kleinman symmetry. Results for the perfectly ordered and statistical distributions agree only for $u = u_1 = 1/3$, shown by the dotted lines.

isotropic average $\langle\beta_{\alpha\beta\gamma}\rangle = A\varepsilon_{\alpha\beta\gamma} = 0$ due to intrinsic permutation symmetry of the β tensor for second harmonic generation, $\beta_{\alpha\beta\gamma}(-2\omega; \omega, \omega) = \beta_{\alpha\gamma\beta}(-2\omega; \omega, \omega)$. The quantity $\langle\mu_\alpha^{(0)}\beta_{\beta\gamma\delta}\rangle = \langle A_{\alpha\beta\gamma\delta}\rangle$ is an isotropic fourth rank tensor with the general form

$$\langle A_{\alpha\beta\gamma\delta}\rangle = A_1\delta_{\alpha\beta}\delta_{\gamma\delta} + A_2\delta_{\alpha\gamma}\delta_{\beta\delta} + A_3\delta_{\alpha\delta}\delta_{\beta\gamma}, \qquad (22a)$$

$$A_1 = \tfrac{1}{30}(4A_{\alpha\alpha\beta\beta} - A_{\alpha\beta\alpha\beta} - A_{\alpha\beta\beta\alpha}), \qquad (22b)$$

$$A_2 = \tfrac{1}{30}(-A_{\alpha\alpha\beta\beta} + 4A_{\alpha\beta\alpha\beta} - A_{\alpha\beta\beta\alpha}), \qquad (22c)$$

$$A_3 = \tfrac{1}{30}(-A_{\alpha\alpha\beta\beta} - A_{\alpha\beta\alpha\beta} + 4A_{\alpha\beta\beta\alpha}). \qquad (22d)$$

Since $\beta_{\alpha\beta\gamma} = \beta_{\alpha\gamma\beta}$ one has $A_{\alpha\beta\gamma\delta} = A_{\alpha\beta\delta\gamma}$ and therefore $A_2 = A_3$. Substituting $A_{\alpha\beta\alpha\beta} = A_{\alpha\beta\beta\alpha}$ and choosing the dipole direction as the molecular z axis, $\vec{\mu}^{(0)} = \mu^{(0)}\hat{z} = \mu^{(0)}\delta_{z\alpha}$, one obtains

$$A_1 = \tfrac{1}{30}(4A_{\alpha\alpha\beta\beta} - 2A_{\alpha\beta\beta\alpha}) = \tfrac{1}{30}\mu^{(0)}(4\beta_{z\beta\beta} - 2\beta_{\beta\beta z}),$$
(23a)

$$A_2 = A_3 = \tfrac{1}{30}(-A_{\alpha\alpha\beta\beta} + 3A_{\alpha\beta\beta\alpha}) = \tfrac{1}{30}\mu^{(0)}(-\beta_{z\beta\beta} + 3\beta_{\beta\beta z}).$$
(23b)

Thus, the effective hyperpolarizability $\langle\boldsymbol{\beta}\rangle^E$ has $C_{\infty v}$ symmetry with three different non-vanishing components

$$\langle\beta\rangle^E_{ZZZ} = a_1(A_1 + A_2 + A_3) = \tfrac{1}{15}a_1(\beta_{z\beta\beta} + 2\beta_{\beta\beta z}) = a_1\beta_1,$$
(24a)

$$\langle\beta\rangle^E_{ZXX} = a_1 A_1 = \tfrac{1}{15}a_1(2\beta_{z\beta\beta} - \beta_{\beta\beta z}) = a_1 u_1 \beta_1,$$
(24b)

$$\langle\beta\rangle^E_{XXZ} = a_1 A_2 = a_1 A_3 = \tfrac{1}{30}a_1(-\beta_{z\beta\beta} + 3\beta_{\beta\beta z}) = a_1 v_1 \beta_1,$$
(24c)

but since $(u_1 + 2v_1) = 1$ there are only two independent components. In these expressions, z is the molecular axis and $\hat{n} = \hat{Z}$ has been chosen as the axis of the molecular orientation distribution. Although Eqs. (24a)–(24c) were obtained by considering the orientation of a dipolar molecule by an electric field, they are more generally valid, including the case that molecular z axis is not the dipole axis or even a molecular symmetry axis, provided that the chosen molecular z axis has orientation distribution $G(\Omega) = 1 + a_1\cos\theta$ around the symmetry axis $\hat{n}$ of the distribution. For the special case where z is the dipole axis of a $C_{\infty v}$ molecule, Eqs. (24a)–(24c) give $\beta_1 = \tfrac{1}{15}(3\beta_{zzz} + 2\beta_{zxx} + 4\beta_{xxz})$ and $u_1\beta_1 = \tfrac{1}{15}(\beta_{zzz} + 4\beta_{zxx} - 2\beta_{xxz})$, which reduce to $\beta_1 = \tfrac{1}{5}(\beta_{zzz} + 2\beta_{zxx})$ and $u_1 = \tfrac{1}{3}$ when Kleinman symmetry applies and $\beta_{zxx} = \beta_{xxz}$.

Now consider a spherical domain where the mean molecular orientation $\hat{n}$ varies over the domain, and the orientation distribution is $G(\Omega) = 1 + a_1\cos\theta$ around $\hat{n}$ for the molecules in the neighbourhood of each point in the domain. The vector $\hat{n}$ is analogous to the director $\hat{n}$ in a liquid crystal. There the orientation distribution around the director is $G(\Omega) = 1 + a_2(3\cos^2\theta - 1)/2$, where $\hat{n}$ has a fixed direction in the case of a nematic liquid crystal, and rotates as a helix in the case of a cholesteric liquid crystal. The factor a_1 specifies the strength of the orientation correlation, and the domain must be sufficiently large and $\hat{n}$ slowly varying for the statistical distribution to be defined at each point. Then the components of the average induced second harmonic dipole for molecules with mean orientation $\hat{n}$ are given by Eqs. (6a)–(6d) previously derived for a $C_{\infty v}$ molecule, but with β_0, u, and v replaced by $a_1\beta_1$, u_1, and v_1. Applying the constraint $(u_1 + 2v_1) = 1$, these expressions reduce to

$$\mu_{VV} = \left(\tfrac{1}{2}a_1\beta_1 E_0^2\right)(\hat{n}\cdot\hat{Z}),$$
(25a)

$$\mu_{HV} = \left(\tfrac{1}{2}a_1\beta_1 E_0^2\right)u_1 (\hat{n}\cdot\hat{Z}) = u_1\mu_{VV},$$
(25b)

$$\mu_{VH} = \left(\tfrac{1}{2}a_1\beta_1 E_0^2\right)u_1 (\hat{n}\cdot\hat{H}_s),$$
(25c)

$$\mu_{HH} = \left(\tfrac{1}{2}a_1\beta_1 E_0^2\right)u_1 (\hat{n}\cdot\hat{H}_s) = \mu_{VH}.$$
(25d)

From these, it immediately follows that:

$$I_{VV}/I_{HV} = u_1^{-2},$$
(26a)

$$I_{HH}/I_{VH} = 1,$$
(26b)

for any $\hat{n}$. In the case that Kleinman symmetry holds, $u_1 = v_1 = 1/3$ and $I_{VV}/I_{HV} = 9$.

The HRS intensities from a radially oriented domain, where $\hat{n} = \hat{r}$, have the form of a pure longitudinal polar mode

$$I_{VV} = I_{HV} = 0,$$
(27a)

$$I_{VH} = I_{HH} = \left(\tfrac{1}{2}a_1\beta_1 E_0^2\right)^2\left(\tfrac{1}{4}\rho K R^4\right)^2(8\pi^2 u_1^2/9),$$
(27b)

the coherent HRS from domains where $\hat{n} = \hat{\theta}'$ has the same polarization dependence as incoherent HRS

$$I_{VV} = \left(\tfrac{1}{2}a_1\beta_1 E_0^2\right)^2\left(\tfrac{1}{3}\rho R^3\right)^2(\pi^4/3),$$
(28a)

$$I_{HV} = I_{VH} = I_{HH} = u_1^2 I_{VV},$$
(28b)

and the HRS intensities from azimuthally oriented domains, where $\hat{n} = \hat{\phi}'$, have the form of a pure transverse polar mode

$$I_{VV} = \left(\tfrac{1}{2}a_1\beta_1 E_0^2\right)^2\left(\tfrac{1}{4}\rho K R^4\right)^2(\pi^4/12),$$
(29a)

$$I_{HV} = u_1^2 I_{VV},$$
(29b)

$$I_{VH} = I_{HH} = \tfrac{1}{2}I_{HV}.$$
(29c)

The polarization ratios for azimuthally oriented domains, obtained using Eqs. (29a)–(29c), are plotted as functions of u_1 in Figure 2. The results given by Eqs. (25a)–(29c) for coherent HRS follow directly from the form $G(\Omega) = 1 + a_1\cos\theta$ for the molecular orientation distribution and require no assumption regarding molecular symmetry. In the case that the mean molecular orientation is $\hat{n} = c_1\hat{r}' + c_2\hat{\theta}' + c_3\hat{\phi}'$, the r, θ, ϕ coherent contributions add in quadrature, and the polarization dependence of the coherent HRS is

$$I_{VV}/I_{HV} = u_1^{-2},$$
(30a)

$$I_{HV}/I_{VH} = \frac{\dfrac{128}{9}\left(\dfrac{c_2}{KR}\right)^2 + 2c_3^2}{\dfrac{64}{3\pi^2}c_1^2 + \dfrac{128}{9}\left(\dfrac{c_2}{KR}\right)^2 + c_3^2}.$$
(30b)

Thus, I_{VV}/I_{HV} varies only due to deviations from Kleinman symmetry, and I_{HV}/I_{VH} depends on the relative size of the components of $\hat{n}$.

VI. DOMAIN SIZE AND CORRELATION STRENGTH

The radial electric field of a dissolved ion acting as the aligning agent results in large spherical domains of radial oriented molecules around the dissolved ions in a polar liquid. The HRS due to these domains has been observed and systematically studied, varying either the ion concentration[14] or the chromophore concentration,[12] and the observations agree closely with theory except for the predicted and measured absolute HRS intensities. Typically the molecules at $R \approx 100$ nm

with $a_1 \approx 10^{-4}$ make the main contribution to this coherent HRS signal.[12]

In pure isotropic liquids, there is an absence of evidence for oriented domains derived from the usual probes (x-ray and neutron diffraction[15–17] and molecular dynamics simulations[18–21]), but information about the molecular correlations can be derived by comparing predicted and measured values for the HRS polarization ratios. The total HRS intensity from a domain with correlated molecules is the sum of the incoherent and coherent HRS intensities, giving polarization ratios intermediate between the values for the separate incoherent and coherent contributions. The observed HRS polarization dependence for several neat liquids is consistent with domains having either radial and azimuthal orientation order but is inconsistent with short range correlations.[8] Domains with a perfectly ordered fraction of the molecules are ruled out by the experimentally observed result $I_{HH}/I_{VH} = 1$,[8] which is inconsistent with the calculated result for azimuthal domains with a perfectly ordered fraction of the molecules (solid curve in Fig. 2(c)). The result for domains with a statistical orientation distribution (horizontal dashed line in Fig. 2(c)) is in perfect agreement with experiment, so only domains with statistical molecular distributions will be considered further.

The polarization ratio I_{HV}/I_{VH} distinguishes incoherent and coherent HRS from domains with correlated molecules since incoherent HRS gives $I_{HV}/I_{VH} = 1$, whereas coherent HRS gives $I_{HV}/I_{VH} = 2$ for azimuthal correlated domains and $I_{HV}/I_{VH} = 0$ for radial correlated domains. Simple expressions for I_{HV}/I_{VH} are obtained by combining Eqs. (10a), (10b), (27a), (27b), and (29a)–(29c) in the case of molecules for which β_{zzz} is the only non-vanishing component. In this case, $\beta_1 = \beta_0/5$, $u = v = 0$, and $u_1 = v_1 = 1/3$. The result for domains with radial orientation correlations is

$$I_{HV}/I_{VH} = \left[1 + \frac{7\pi\rho\, K^2}{1080} a_1^2 R^5 \right]^{-1}, \qquad (31a)$$

while the result for domains with azimuthal orientation correlations is

$$I_{HV}/I_{VH} = \frac{1 + \dfrac{7\pi^3\rho\, K^2}{11520} a_1^2 R^5}{1 + \dfrac{7\pi^3\rho\, K^2}{23040} a_1^2 R^5}. \qquad (31b)$$

The product $a_1^2 R^5$ of correlation strength and domain size can be determined from the experimental value for I_{HV}/I_{VH} using these expressions. For typical values, $\rho = 10$ mol/l $= 6$ nm^{-3} and $K = 2\pi/(250$ nm) the coefficients of $a_1^2 R^5$ for the coherent contributions in Eqs. (31a) and (31b) are $7\pi\rho K^2/1080 = (6.6$ nm)$^{-5}$ and $7\pi^3\rho K^2/11520 = (6.8$ nm)$^{-5}$. Assuming equal incoherent and coherent HRS contributions in Eqs. (31a) or (31b) gives $I_{HV}/I_{VH} = 0.5$ or 1.33, within the observed range.[8] The domain size estimate is then $R(\text{nm}) = 6.7\, a_1^{-2/5}$, giving $R = 17$ nm (42 nm, 106 nm) for the domain radius assuming $a_1 = 0.1$ (0.01, 0.001) for the molecular correlation strength.

Figure 3 shows experimental data for solutions of p-nitroaniline (PNA) in acetone-d6.[12] A good fit to the data is obtained assuming domains with a statistical orientation dis-
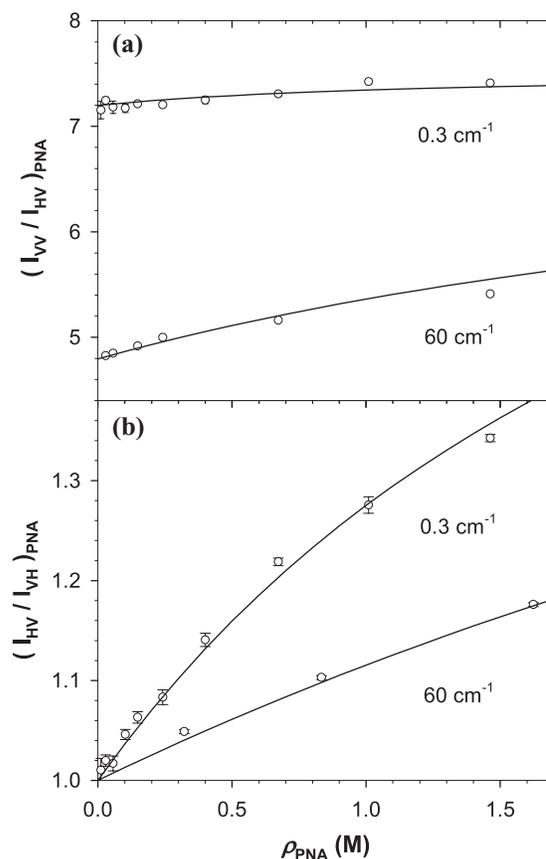
FIG. 3. Polarization ratios (a) I_{VV}/I_{HV} and (b) I_{HV}/I_{VH} measured with 0.3 or 60 cm^{-1} spectral bandwidth for solutions of p-nitroaniline (PNA) in acetone-d6 for PNA concentrations up to 1.7 mol/l are shown by the open circles.[12] The solid curves are fits as described in Ref. 12, with the incoherent contribution to the HRS signal determined from the zero concentration limit for the data, and $I_{VV}/I_{HV} = 7.53$ and $I_{HV}/I_{VH} = 2.00$ for the coherent contribution.

tribution and taking the values of I_{VV}/I_{HV} and I_{HV}/I_{VH} for the coherent contribution as free parameters, whereas a poor fit was previously obtained assuming a distribution with a perfectly ordered fraction.[12] The fit value $I_{VV}/I_{HV} = 7.53$ for the coherent contribution indicates a 10% deviation from Kleinman symmetry and the fit value $I_{HV}/I_{VH} = 2.00$ indicates azimuthal orientation for the PNA molecules. Combining the fit to the 60 cm^{-1} data in Fig. 3 with Eq. (29b) and $K = 2\pi/(279$ nm) gives $a_1^2 R^5 = (11.3$ nm)^5,[5] and indicates that the domain radius is $R > 28$ nm if the azimuthal correlation strength $a_1 < 0.1$.

Although uniform correlation strength a_1 within a spherical domain has been assumed, radial variation of the correlation parameter a_1 does not change the polarization ratios for the coherent HRS contribution. Since the coherent HRS contribution is a strong increasing function of radius the quantitative result will be determined essentially by a_1 near the maximum radius for the domain. Angular variations of the correlation parameter a_1 that preserve axial symmetry also do not change the polarization ratios for the coherent HRS contribution. The coherent HRS is due to acentric orientation order in the domains, and the anisotropy of the local field tensor[22,23] due to the anisotropy of the individual molecules and the molecular distribution has not been explicitly

considered. However, the liquid is macroscopically isotropic since the proposed orientation ordered domains are small compared to the light wavelength and each domain has small average anisotropy, so one expects the local field anisotropy effects to be essentially the same as for a liquid of anisotropic molecules with only short range molecular correlations.

In summary, coherent HRS from spherical domains containing molecules with orientational correlations has been calculated. Molecular distributions with a highly ordered component give results inconsistent with HRS observations, but the statistical distributions that naturally arise as the leading terms of the general expansion for an axially symmetric distribution give results consistent with the observations. Radial or azimuthal orientation correlations for the molecules give HRS polarization ratios observably different from the results for incoherent HRS. The product of correlation strength and correlated domain size can be determined from the polarization ratio, and agreement with experiment given plausible values of the correlation strength requires a domain size of order 100 molecular diameters.

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