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**Effects of the Orientational Pair Correlation on
Second Order Nonlinear Optical Coefficients**

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Abstract

The orientational order parameter associated with the second order nonlinear optical (NLO) coefficient is calculated by using a statistical mechanics method that includes the angular dependent intermolecular interaction potential. It is shown that in addition to the alignment of dipoles due to the poling field, the orientational pair correlation (OPC) factor is also important in determining the orientational order parameter. When OPC is included, the order parameter becomes a function of the NLO chromophore concentration. The concentration dependent part of the order parameter is shown to be proportional to the Kirkwood g-factor associated with the orientational correlation of the electric dipoles. In the weak field limit, it is shown that the ratio of two nonlinear optical coefficients, χ_{33}/χ_{31} , remains equal to 3, independent of the specific nature of the anisotropic intermolecular potential.

I. Introduction

Amorphous polymers containing nonlinear optical (NLO) moieties show a great promise for the development of electro-optical (EO) devices and second harmonic generation (SHG). However, since amorphous polymers lack the polar order as the NLO moieties in the polymers are randomly oriented, it is necessary to impose polar orientational order to break down the centrosymmetry to induce the second order nonlinear optical effect. This can be accomplished by poling the isotropic medium with a strong electric field. Using external field poling, films that exhibit a large second order nonlinear optical effect have been prepared.¹

In the usual theoretical description of the electric field poling of the NLO moieties, it is commonly assumed that the dipoles are oriented independently. The order parameters associated with the second order macroscopic susceptibilities are simply given by Langevin functions, $L_n(a)$, where $a = f_0 \mu E_p / kT$. Here f_0 is the local field factor associated with the external poling field E_p ; μ is the ground state dipole moment. One consequence of the independent dipole orientation approach is that the orientational order parameter, calculated for the second order susceptibility, is practically independent of the concentration of the NLO moieties. Furthermore, this approach necessitates (for the condition of $a \ll 1$) the ratio of the electro-optic coefficients, r_{33}/r_{31} , and that of the SHG coefficients, d_{33}/d_{31} , equal to 3, independent of the detail of the poling process. However, experimental results obtained for the EO coefficients r_{ij} , and SHG coefficient d_{ij} , are not in agreement with the simple Langevin function description. It is found that the orientational order parameters depend on the concentration of the NLO chromophore,^{2,3} and the ratio of the second order coefficients may be greater than 3.⁴⁻⁶

In this paper, we examine possible causes for the discrepancy. We use a generalized

statistical mechanics approach, which, not only consider the contribution from the poling field, but also includes the effect of orientational dependent intermolecular interaction to describe the orientational order parameters. We show that at moderate NLO chromophore concentrations, the dipole-dipole interaction is important in affecting the second order nonlinear optical coefficients. Other types of anisotropic intermolecular interactions between a NLO moiety and its surrounding medium are also considered in this generalized approach.

In Sec. II of this paper, we relate the second order molecular hyperpolarizability to the lowest order macroscopic nonlinear optical susceptibility. Two orientational order parameters, characterizing the second order NLO effect, emerge from the relation. In Sec. III the effect of orientational pair correlation (OPC) arising from the anisotropic (angular dependent) intermolecular interaction is incorporated in the order parameter expression. In this section, the specific dipole-dipole interaction is considered, and the order parameters are related to the Kirkwood g-factor. In sec. IV, the general type of anisotropic intermolecular interaction potentials is included, and we show that in the weak poling field limit (with $a \ll 1$), the orientational pair correlation gives rise to a pronounced effect on the order parameter; however, the $\chi_{33}/\chi_{31} = 3$ relationship is not changed by the presence of OPC. A summary and conclusion of the results of this work are presented in this section.

II. Second Order Hyperpolarizability and Macroscopic Susceptibility

We restrict the discussion to the second order nonlinear optical (NLO) process. The origin of the second order nonlinear optical effect arises from the molecular hyperpolarizability, β_{IJK} . In the molecular coordinate system, the nonlinear optical response of the dipole moment of a representative molecule α , subject to external electromagnetic fields at frequencies ω_1 and ω_2 , is given by:

$$\mu_1^{(\alpha)}(\omega_1 + \omega_2) = \beta_{IJK}^{(\alpha)}(-\omega_1 - \omega_2; \omega_1, \omega_2) F_J(\omega_1) F_K(\omega_2) \quad (1)$$

where I, J, and K refer to the principal axes of molecule α with respect to the molecular coordinate system. The hyperpolarizability, β , is a function of frequencies, ω_1 , ω_2 , and $\omega_1 + \omega_2$. The frequency dependence of the hyperpolarizability has to be calculated by using quantum mechanics. For SHG, $\omega_1 = \omega_2 = \omega$, and for the linear EO effect, we have $\omega_1 = \omega$ and $\omega_2 = 0$. $F_J(\omega_1)$ and $F_K(\omega_2)$ are the Jth and Kth components of the local field $\underline{F}$ seen by molecules at frequencies ω_1 and ω_2 , respectively. In the Lorentz model, the local field $\underline{F}(\omega)$ is related to external field $\underline{E}(\omega)$ by, $\underline{F}(\omega) = f_\omega \underline{E}(\omega)$, where f_ω is the local field factor given by $f_\omega = (n_\omega^2 + 2)/3$.

The corresponding nonlinear optical polarization induced by the poling field and optical electromagnetic fields is given by

$$\underline{P}(\omega_1 + \omega_2) = \frac{1}{V} \sum_{\alpha=1}^N \underline{\mu}^{(\alpha)}(\omega_1 + \omega_2) \quad (2)$$

where V is the macroscopic volume.

It is customary to write the optical polarization in terms of the second order macroscopic susceptibility $\chi^{(2)}$ as

$$P_i(\omega_1 + \omega_2) = \chi_{ijk}^{(2)}(-\omega_1 - \omega_2; \omega_1, \omega_2) E_j(\omega_1) E_k(\omega_2) \quad (3)$$

In Eq. (3), we assume that the optical field at frequency ω_1 is polarized along the laboratory j-axis, and that at frequency ω_2 is polarized along the laboratory k-axis. One notes that in Eq. (1) the local field is used to define the molecular hyperpolarizability, whereas in Eq. (3)

the macroscopic external optical fields are used to define the second order optical susceptibility. For SHG, j and k are identical; in the ensuing calculation, we set the z -axis of the laboratory coordinate system to be along the dc poling field axis, and the y -axis to be along the direction perpendicular to the plane of incidence. In Eq. (3), the component i, j or k takes on one of the laboratory coordinate axes.

The molecular hyperpolarizability β_{ijk} that appears in Eq. (1) is a third rank tensor. However, for simplicity we assume, in this paper, that only one major component of hyperpolarizability along the 3-axis of the molecular principal coordinate system dominates. We define this component to be $\beta_{333} \equiv \beta$. Under this simplifying approximation, the second order susceptibility tensor $\chi_{ijk}^{(2)}$ can be related to the dominant molecular hyperpolarizability, β , in a simple expression. By substituting Eq. (1) into (2), and then replacing the summation over all molecules by an average over a statistical distribution function, we obtain

$$\chi_{ijk}^{(2)} = \rho \beta f_{2\omega} (f_{\omega})^2 \langle a_{i3}^{(1)} a_{j3}^{(1)} a_{k3}^{(1)} \rangle \quad (4)$$

where ρ is the number density of the NLO moieties, $a_{i3}^{(1)}$ is the projection of a unit vector along the molecular principal axis (the 3-axis) of the representative molecule 1 onto the laboratory axis i . The angular brackets denote an average over the one-particle distribution function and is given by

$$\langle a_{i3}^{(1)} a_{j3}^{(1)} a_{k3}^{(1)} \rangle = \int a_{i3}^{(1)} a_{j3}^{(1)} a_{k3}^{(1)} G(\{1\}, E_p) d(1) \quad (5)$$

In Eq. (5) and in the remaining part of this paper, we shall employ the symbol $\{\alpha\}$ to represent 3 Cartesian coordinates $\underline{r}_{\alpha} = (x_{\alpha}, y_{\alpha}, z_{\alpha})$ and 2 angular coordinates $(\theta_{\alpha}, \phi_{\alpha})$ to

specify the position and orientation of the principal axis of molecule α . Thus, using this

notation, we have $\int d\{\alpha\} = \int_V d^3r_\alpha \int_0^{2\pi} d\phi_\alpha \int_0^\pi \sin\theta_\alpha d\theta_\alpha$.

The one particle distribution function $G(\{1\}, E_p)$ entering into Eq. (5) is derived from the N-body Gibbsian distribution function by integrating over the rest of (N-1) molecules with respect to their spatial and angular coordinates:

$$G(\{1\}, E_p) = \frac{1}{Z_N} \int e^{-\frac{1}{kT} (U_N - \sum_{i=1}^N (\underline{\mu}_i \cdot \underline{E}_p) f_i)} d\{2\} d\{3\} \cdots d\{N\} \quad (6)$$

where Z_N is the configuration integral given by

$$Z_N = \int \exp \left\{ -\frac{1}{kT} [U_N - \sum_{i=1}^N (\underline{\mu}_i \cdot \underline{E}_p) f_i] \right\} d\{1\} \cdots d\{N\} \quad (7)$$

Here U_N is the potential energy of interaction of N molecules. The potential energy of interaction depends on the positional as well as the orientational coordinates of the N-molecules.

By poling the isotropic NLO medium with an external electric field $\underline{E}_p$, the system becomes uniaxial and adopts a $C_{\infty v}$ symmetry. While in the general case there are 18 second order NLO coefficients¹, there are only two independent nonvanishing $\chi_{ijk}^{(2)}$ elements for the $C_{\infty v}$ system. They are given by:

$$\chi_{zzz}^{(2)} = \chi_{333}^{(2)} = \rho \beta f_{2\omega} f_\omega^2 \langle \cos^3 \theta_1 \rangle \quad (8a)$$

$$\chi_{zzxx}^{(2)} = \chi_{31}^{(2)} = \rho \beta f_{2\omega} f_{\omega}^2 (\langle \cos \theta_1 \rangle - \langle \cos^3 \theta_1 \rangle) / 2 \quad (8b)$$

Equation (8a) is obtained by setting $a_{33}^{(1)} = a_{j3}^{(1)} = a_{k3}^{(1)} = \cos \theta_1$, in Eq. (5) and Eq. (8b) is obtained by setting $a_{j3}^{(1)} = \cos \theta_1$, and $a_{k3}^{(1)} = a_{k3}^{(2)} = \sin \theta_1 \cos \phi_1$ and then performing an average over ϕ_1 in Eq. (5). The second identities introduced in Eqs. (8a) and (8b) are the result of Voigt's contracted notation in which one sets the last two subscripts $zz = 3$ and $xx = 1$, at the same time naming the first subscript z as 3. The subscript 1, associated with θ_1 refers to the representative NLO chromophore 1. Clearly, in the absence of the poling field $\underline{E}_p$, the angular averages over $\cos \theta_1$ and $\cos^3 \theta_1$ vanish identically due to the fact that the medium is macroscopically homogeneous when $\underline{E}_p = 0$.

Generally in all previous work on the order parameter, it is assumed that the dipoles $\{\mu_1, \dots, \mu_N\}$ (i.e., for those associated with the NLO moieties) are surrounded by a homogeneous, thermodynamically independent isotropic medium so that the dipoles are in thermal equilibrium with the external poling field $\underline{E}_p$. In this assumption, the potential energy of interaction of the molecules where the dipoles are located do not play a role, and the orientation of the dipoles is completely dictated by the external poling field. As a result, the intermolecular interaction term in Eq. (6) factors out of the N-body distribution function and the evaluation of the order parameters given by Eq. (5) reduces to a simple independent one-body problem. In this exceedingly simplified case $\chi_{33}^{(2)}$ and $\chi_{31}^{(2)}$ are readily found to be

$$\frac{\chi_{33}^{(2)}}{\rho \beta f_{2\omega} f_{\omega}^2} = L_{33} = \left(\frac{6}{a^3} + 1\right) \coth a - \left(\frac{6}{a^3} + \frac{3}{a}\right) = L_3 \quad (9a)$$

$$\frac{\chi_{31}^{(2)}}{\rho \beta f_{2\omega} f_{\omega}^2} \equiv L_{31} = \frac{1}{2} [L_1(a) - L_3(a)] = \left(\frac{3}{a^3} + \frac{1}{a}\right) - \frac{3}{a^2} \coth a \quad (9b)$$

where $L_n(a)$ is the Langevin function of order n and is given by

$$L_n(a) = \frac{\int_0^\pi e^{a \cos \theta_1} \cos^n \theta_1 \sin \theta_1 d\theta_1}{\int_0^\pi e^{a \cos \theta_1} \sin \theta_1 d\theta_1}, \quad \text{with } a = f_0 \mu E_p / kT \quad (10)$$

Clearly, for $a \ll 1$, Equations (9a) and (9b) reduce to

$$L_{33} = \frac{a}{5} + \dots \quad (11a)$$

$$L_{31} = \frac{a}{15} + \dots \quad (11b)$$

Thus, in this simplified case, the ratio of $\chi_{33}^{(2)}$ to $\chi_{31}^{(2)}$ is thus equal to 3. Furthermore, L_{33} and L_{31} display only a negligible chromophore density dependence through the local field factor f_0 .

III. Effects of Orientational Pair Correlation

To obtain an NLO polymer, one either disperses chromophores exhibiting a large hyperpolarizability β in an isotropic amorphous polymer matrix to form a guest/host system or incorporates chromophores chemically into polymer chains. Since the NLO chromophores are also molecules with large permanent dipole moments, the NLO polymer system is an assembly of molecules having large dipole moments. For this reason, the dipole-

dipole interaction needs to be included in the analysis. Consider, for example, a molecule with a permanent dipole moment equal to 5 debye (a moderate sized dipole moment for an NLO chromophore) subjected to a poling field of about 10^6 V/cm . This is a very large poling field which can be achieved only by careful sample preparation with ionic impurities removed the voltage avoid breakdown. For this static field, the dipole-electric field interaction energy is equal to $1.67 \times 10^{-14} \text{ erg}$. If the concentration of the NLO molecules is taken to be $\rho = 10^{21} \text{ molecules/cm}^3$ and thus the average intermolecular distance is about $\rho^{-1/3} = 10^{-7} \text{ cm}$, then the dipole-dipole interaction energy would be about $2.5 \times 10^{-14} \text{ erg}$, which is larger than the electric field-dipole interaction energy. Therefore, in contrast to the usual approach by assuming independent dipoles in calculating the orientational order parameters, the intermolecular dipole-dipole interaction energy cannot be ignored. In addition, it is well known that the dipole-dipole interaction is long-range. The long-range nature of the interaction is expected to give rise to a significant orientational pair correlation (OPC) effect in the second order nonlinear optical coefficient for an assembly of polar molecules. However, the effect of the long range OPC has yet to be considered. In this section we first incorporate the OPC factor into the expressions of orientational order parameters L_{33} and L_{31} . We consider in this paper only the case in which the interaction energy of dipoles with the poling field is small compared with the thermal energy, which allows the $a \ll 1$ approximation to be used. At 100°C , the thermal energy kT is $5.15 \times 10^{-14} \text{ erg}$. The other case in which the poling field is large compared with kT is more involved and will be reported in another publication.

By assuming that the interaction energy between the poling field and the molecular dipoles is small compared to the thermal energy, we can expand the exponential factor in Eqs. (6) and (7) in a power series of the poling field E_p , keeping only the terms linear in E_p as

$$\begin{aligned} & \exp \left\{ -\frac{1}{kT} \left[U_N - \sum_{i=1}^N (\underline{\mu}_i \cdot \underline{E}_P) f_0 \right] \right\} \\ &= \left[1 + \frac{1}{kT} \sum_{i=1}^N (\underline{\mu}_i \cdot \underline{E}_P) f_0 + \cdots \right] \exp(-U_N/kT) \end{aligned} \quad (12)$$

By substituting Eq. (12) into Eq. (7), we find that

$$\begin{aligned} Z_N &= \int e^{U_N/kT} d\{1\} \cdots d\{N\} + O(E_P^2) \\ &= Z_N^{(0)} + O(E_P^2) \end{aligned} \quad (13)$$

where $Z_N^{(0)}$ is the configuration integral of the N-body system without the poling field. Thus, in the $a \ll 1$ limit, Z_N is equal to $Z_N^{(0)}$, the correction being 2nd order in E_P . As a result, Eq. (6) can be written as

$$G(\{1\}, E_P) = \frac{1}{V(4\pi)^2} (1 + a \cos \theta_1) + (N-1) \frac{a}{V^2(4\pi)^2} \int \cos \theta_2 \rho_2(1,2) d\{2\} \quad (14)$$

where $\rho_2(1, 2)$ is a two particle distribution function which is obtained by integrating $e^{U_N/kT} / Z_N^{(0)}$ over the (N-2) molecules with respect to their positional and orientational coordinates. The second term on the right hand side of Eq. (14) has a factor of (N-1) because there are (N-1) molecular neighbors for the representative molecule 1. The two particle distribution is averaged over the configuration of the second particle described by $\{2\}$. This term gives rise to OPC and cannot be neglected.

The normalization condition for $\rho_2(1, 2)$ is

$$\frac{1}{V^2(4\pi)^2} \int \rho_2(1,2) d\{1\} d\{2\} = 1 \quad (15)$$

Thus $\rho_2(1, 2)$ is a dimensionless probability function, which at low density is given by⁷

$$\rho_2^0(1,2) = e^{-u(1,2)/kT} \quad (16)$$

where $u(1,2)$ is the angular dependent interaction potential between molecules 1 and 2.

The first term on the right hand side of Eq. (14) is the usual independent one-particle term, which upon substituting into Eq. (5) gives immediately Eqs. (11a) and (11b) after performing a simple integration. The second term is the contribution due to the pair correlation of two interacting dipoles. We shall show that if the intermolecular interaction is anisotropic, then this term can make an important contribution to the second order optical coefficients.

Substitution of Eq. (14) into Eq. (5) (or specifically into Eqs. (8a) and (8b)) gives the expression for the order parameter by

$$\langle \cos^n \theta_1 \rangle = \frac{a}{n+2} + \frac{a}{V(4\pi)^2} \rho \int \int \cos^n \theta_1 \cos \theta_2 g(1,2) d\{1\} d\{2\} \quad (17)$$

with $n = 1$ or 3 .

Here $g(1,2)$ is the orientational dependent radial distribution function, which is related to the two particle distribution function $\rho_2(1,2)$ by $g(1,2) = \rho_2(1,2) - 1$. The distribution function vanishes when two particles are separated at a large distance. More important is the fact that in order to contribute to the order parameter $\langle \cos^n \theta_1 \rangle$, $g(1,2)$ must depend on orientational variables. Thus, the effect of the intermolecular interaction on the second order NLO coefficients lies in the orientational dependent part of the $g(1,2)$ function, which we shall call the molecular pair correlation (MPC) function. The orientational pair correlation (OPC) can be projected out from the molecular pair correlation function. In accordance with Eqs. (8a), (8b) and (17), the NLO coefficients are then completely determined once the OPC is known. Thus, in addition to the poling field

which induces orientation of the electric dipoles, the presence of OPC also assists the orientational ordering of the NLO chromophores. As shown in recent experiments in our laboratory, even at a moderate NLO chromophore concentration (above 10^{20} molecules per cm^3), the OPC assisted contribution to the order parameter cannot be ignored.^{2,3}

It should be pointed out that the OPC factor is the same type that is involved in the theory of the static dielectric constant of polar fluids. The study of $g(1,2)$ due to the orientational dependent interaction in a homogeneous fluid consisting of anisotropic molecules has been formally considered by several authors.⁸⁻¹⁰ Wartheim has obtained the solution of $g(1,2)$ using the mean spherical approximation for the hard-sphere dipolar liquid.¹¹ Several theories based upon the cluster expansion by Stell,¹² and Stell and Weiss¹³ have also been developed to treat the hard sphere dipolar fluids. Recently, Monte Carlo (MC) calculations have also been used to assess the accuracy of these analytical theories.¹⁴

To obtain the molecular pair correlation (MPC) function one employs the Ornstein-Zernike equation¹⁵:

$$g(1,2) = C(1,2) + \frac{\rho}{\Omega} \int C(1,3)g(3,2)d(3) \quad (18)$$

where $\Omega = 4\pi$ for a linear molecule, and is equal to $8\pi^2$ for a non-linear molecule. In Eq.(18), $C(1,2)$ is the molecular direct correlation function.

The solution of Eq.(18) for a polar fluid for which the intermolecular potential is given by

$$u(1,2) = u(r_{12}) + \left[\frac{\mu_1 \cdot \mu_2}{r_{12}^3} - 3 \frac{(\mu_1 \cdot \hat{r}_{12})(\mu_2 \cdot \hat{r}_{12})}{r_{12}^3} \right] \quad (19)$$

has been considered extensively in the literature¹⁵. In Eq. (19), $u(r_{12})$ is assumed to be spherically symmetric, and the angular dependent term is represented by the dipole-dipole interaction.

For this type of the intermolecular interaction potential, it was first shown by Wertheim that the solution for $g(1,2)$ for Eq. (18) can be assumed to be of the form¹¹

$$g(1,2) = g_s(r_{12}) + h_A(r_{12}) \Delta(1,2) + h_D(r_{12}) D(1,2) \quad (20)$$

where $g_s(r_{12})$ is spherically symmetric, depending only on the amplitude of r_{12} . $\Delta(1,2) = \hat{s}_1 \cdot \hat{s}_2$, and $D(1,2) = 3 (\hat{s}_1 \cdot \hat{r}_{12})(\hat{s}_2 \cdot \hat{r}_{12}) - (\hat{s}_1 \cdot \hat{s}_2)$. Here $\hat{s}_1$ and $\hat{s}_2$ are unit vectors parallel to the dipole moments of molecules 1 and 2, respectively.

Substituting Eq. (20) in Eq. (16) and after carrying out some extensive algebra, one obtains

$$\langle \cos \theta_1 \rangle = \frac{a}{3} + a\rho \left(\frac{4\pi}{9} \right) \int_0^\infty h_A(r) r^2 dr \quad (20a)$$

$$\langle \cos^3 \theta_1 \rangle = \frac{a}{5} + a\rho \left(\frac{4\pi}{15} \right) \int_0^\infty h_A(r) r^2 dr \quad (20b)$$

One notes that the $h_A^{(r)}$ part in the expansion of $g(1,2)$ makes a contribution to the order

parameters. Thus, even including the OPC effect, we obtain in the weak poling field limit rather simple expressions for $\chi_{33}^{(2)}$ and $\chi_{31}^{(2)}$ as

$$\chi_{31}^{(2)} = \rho \beta a \left(\frac{1}{15} + \frac{\rho}{15} G_{\Delta} \right) \quad (21a)$$

and

$$\chi_{33}^{(2)} = \rho \beta a \left(\frac{1}{5} + \frac{\rho}{5} G_{\Delta} \right) \quad (21b)$$

where G_{Δ} is the cluster integral corresponding to $h_{\Delta}(r)$, given by

$$G_{\Delta} = \frac{4\pi}{3} \int_0^{\infty} h_{\Delta}(r) r^2 dr \quad (22)$$

We need not go into the discussion of detailed calculations of $h_{\Delta}(r)$ using various theoretical models, but it suffices to mention that the Kirkwood g -factor defined by

$$g_K = \frac{\langle \underline{M}^2 \rangle}{N\mu^2} \quad (23)$$

is related to G_{Δ} by¹¹

$$g_K = 1 + \rho G_{\Delta} \quad (24)$$

In Eq. (23), $\underline{M}$ is the total dipole moment of the sample.

One may also include the dipole-dipole interaction between the NLO chromophores and the segments of the polymer host in the calculation. The result will add another term to Eq. (21) in the form of $\rho' G'_{\Delta}$, where the prime designates the segmental dipoles of the

host. However, the total OPC contributions from both the chromophore and the host can be incorporated into the Kirkwood g-factor by defining Eq.(24) as $g_K = 1 + \rho G_A + \rho' G'_A$. As a result, in terms of the Kirkwood g-factor, we obtain very simple expressions for $\chi^{(2)}_{31}$ and $\chi^{(2)}_{33}$ as

$$\chi^{(2)}_{31} = \rho \beta a g_K / 15 \quad (25a)$$

and

$$\chi^{(2)}_{33} = \rho \beta a g_K / 5 \quad (25b)$$

The ratio of $\chi^{(2)}_{31}$ to $\chi^{(2)}_{33}$ is 1/3, identical to the independent dipole case. Thus, the inclusion of the dipole-dipole interaction in the calculation of the order parameters does not change the 1/3 relationship. However, the effect of OPC gives rise to a complex chromophore density dependence in both $\chi^{(2)}_{31}$ and $\chi^{(2)}_{33}$, as manifested in the multiplication of the independent dipole result by the Kirkwood g-factor. Since the Kirkwood g-factor is related to the static dielectric constant ϵ by¹⁵

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = g_K y \quad (26)$$

where y is a molecular parameter defined as $y = \frac{4\pi\mu^2\rho}{9kT}$, Equations (25a) and (25b), in

combination with Eq. (26) provide a useful means for characterizing the molecular hyperpolarizability β , once $\chi^{(2)}_{31}$ (or $\chi^{(2)}_{33}$), the ground state dipole moment μ , and the static dielectric constant ϵ are experimentally determined.

IV. General Anisotropic Intermolecular Interactions

We next show that the 1/3 ratio is not limited to the dipole-dipole interaction mechanism. Rather, it is the result of the weak field approximation. To show this, we

consider a general anisotropic intermolecular interaction potential. The anisotropic potential could either be short or long range or both. To evaluate the OPC effect on the order parameters, one may use the invariant expansion of the angular dependent radial distribution function.^{7,16} This is often used in equilibrium statistical mechanics of complex fluids. The spherical invariant expansion of $g(1,2)$ for linear molecules can be written as¹⁶

$$g(1,2) = \sum_{l_1 l_2 l_3} g_{l_1 l_2 l_3}(r_{12}) \phi_{l_1 l_2 l_3}(\Omega_1, \Omega_2, \hat{r}_{12}) \quad (27)$$

where $\hat{r}_{12}$ indicates the orientation of the vector $\underline{r}_{12} = \underline{r}_2 - \underline{r}_1$. The amplitude of $\underline{r}_{12}$ is $r_{12} = |\underline{r}_{12}|$. The spherical invariant function $\phi_{l_1 l_2 l_3}(\Omega_1, \Omega_2, \hat{r}_{12})$ is given by

$$\phi_{l_1 l_2 l_3}(\Omega_1, \Omega_2, \hat{r}_{12}) = (4\pi) \sum_{m_1 m_2 m_3} \left(\frac{4\pi}{2l_1+1} \right)^{1/2} \left(\frac{4\pi}{2l_2+1} \right)^{1/2} \left(\frac{4\pi}{2l_3+1} \right)^{1/2} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \quad (28)$$

$$Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2) Y_{l_3 m_3}(\hat{r}_{12})$$

where the quantity enclosed with circular brackets is a Wigner 3-j symbol, and $g_{l_1 l_2 l_3}(r_{12})$ is an orientational independent function.

Substituting Eqs. (27) and (28) into Eq. (16), and after integrating over the angular coordinates we obtain the expression for $\langle \cos \theta_1 \rangle$ as

$$\langle \cos \theta_1 \rangle = \frac{a}{3} + a \rho G_{110}/3 \quad (29)$$

and

$$L_{33} = \langle \cos^3 \theta_1 \rangle = \frac{a}{5} + \rho G_{110}/5 \quad (30)$$

Hence,

$$L_{31} = \frac{1}{2} [\langle \cos \theta_1 \rangle - \langle \cos^3 \theta_1 \rangle] = \frac{a}{15} + \frac{1}{15} a \rho G_{110} \quad (31)$$

where G_{110} is the cluster integral given by

$$G_{110} = \frac{-4\pi}{3\sqrt{3}} \int_0^\infty r^2 g_{110}(r) dr \quad (32)$$

which, for the dipolar liquid is equal to G_Δ given in Eq. (22).

Thus, in the weak field limit, only the type of orientational dependent intermolecular potentials between molecules, whether it arises from short- or long-range interactions, that give rise to the dipolar order G_{110} will contribute to the second order nonlinear optical coefficients. The quadruple ($\ell = 2$) or other types of resultant order will not contribute to the second order NLO coefficients. This is a general result, independent of the assumption of the nature of the intermolecular potential. One also notes from Eqs. (19) and (20) that even in the presence of OPC, the $\chi_{33}^{(2)} / \chi_{31}^{(2)}$ ratio remains equal to 3. The order parameters L_{33} and L_{31} depend, however, on the chromophore density through the cluster integral G_{110} .

Considering the fact that $\langle \cos^3 \theta_1 \rangle$ has a different rotational symmetry from that of $\langle \cos \theta_1 \rangle$, one may wonder about the invariance result of the $\chi_{31}^{(2)} / \chi_{33}^{(2)}$ ratio in the presence of the anisotropic intermolecular interaction potential. This situation can be made clearer if one expresses the order parameters in terms of the average over Legendre

polynomials, $P_1(\cos \theta_1)$ and $P_3(\cos \theta_1)$. In terms of the Legendre polynomials, one can write the order parameters as

$$L_{31} = \frac{1}{5} \{ \langle P_1(\cos \theta_1) \rangle - \langle P_3(\cos \theta_1) \rangle \} \quad (33a)$$

and

$$L_{33} = \frac{1}{5} \{ 3 \langle P_1(\cos \theta_1) \rangle + 2 \langle P_3(\cos \theta_1) \rangle \} \quad (33b)$$

In the weak field, the OPC cannot connect the $\langle P_3(\cos \theta_1) \rangle$ term, and as a result the L_{31}/L_{33} ratio is 1/3, independent of the specific nature of the anisotropic intermolecular interaction.

Two possible mechanisms will bring in the $\langle P_3 \rangle$ term and results in the departure from the 1/3 ratio. One is the deviation from the phase matching condition that makes the second order susceptibility wave vector dependent, and the other arises from a high poling field.

The calculations carried out in this work are based upon a general assumption of perfect phase matching in the second order NLO effect. As a result of this assumption, the second order NLO susceptibility does not depend on the wave vector. In the situation where the phase matching condition is not met, and the sample is spatially inhomogeneous, the second order susceptibility would become wave vector dependent. In this situation, the efficiency of second harmonic generation will be low; however, the $\chi_{33}^{(2)}/\chi_{31}^{(2)} = 3$ relationship will break down even for the weak field dipolar system. The other situation that will give rise to the deviation from 1/3 for the $\chi_{31}^{(3)}/\chi_{33}^{(2)}$ ratio is the case of high poling field. For example, when $a = 2$, a quick calculation would show, for independent dipole orientation, the $\chi_{33}^{(3)}/\chi_{31}^{(2)}$ ratio to be equal to 3.5. Intermolecular interactions among

NLO chromophores and between the NLO chromophores and segmental dipoles of the host cause further departure and result in an even larger ratio. We shall report elsewhere the calculation of the high poling field case.

In summary, we have shown that the orientational order parameters associated with second order nonlinear optical susceptibilities depend on the NLO chromophore concentration. This is due to the presence of anisotropic intermolecular interactions. The concentration dependent part of the order parameters are shown to be related to the Kirkwood g-factor associated with the correlation of electric dipoles in polar fluids. In the weak field limit, the $\chi_{33}^{(2)}/\chi_{31}^{(2)}$ ratio is not changed by the presence of the anisotropic intermolecular interactions.

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