Theory of second-harmonic generation in nematic liquid crystals

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In recent years the observation of optical second-harmonic generation (SHG) in nematic liquid crystal (NLC) MBBA [N-(4-methoxybenzylidene)-4′-*n*-butylaniline] raised again the question of whether NLC's possess centrosymmetry. Lyakhov *et al.* [Izv. Akad. Nauk SSSR **45**, 917 (1981)] suggested that these observations can only be explained by considering the NLC as noncentrosymmetric and optically biaxial. In this paper it is shown phenomenologically that even with $D_{\infty h}$ symmetry, SHG arising from $ee \to e$, $oo \to e$, and $oe \to o$ interactions can occur in an aligned NLC. With curvature strains SHG arising from $ee \to o$, $ee \to e$, $oe \to o$, $oe \to e$, $oo \to o$, and $oo \to e$ interactions are all possible. Several experimental observations are satisfactorily explained by the present calculation. The order of magnitude of the effective susceptibilities estimated from a quadrupole-moment mechanism agrees with the values obtained by Arakelyan *et al.* [Mol. Cryst. Liq. Cryst. **71**, 137 (1981)] and by Barnik *et al.* [Mol. Cryst. Liq. Cryst. **98**, 1 (1983)]. One may conclude that it is possible to explain the occurrence of SHG in NLC's without having to invoke noncentrosymmetry of the system.

I. INTRODUCTION

In both the Frank elastic continuum theory[1] and the Ericksen-Leslie-Parodi hydrodynamical theory[2–4] of liquid crystals, the directions of the director $+\mathbf{n}$ and $-\mathbf{n}$ are considered as equivalent to each other. It is well known that systems with overall inversion symmetry give no optical second-harmonic generation (SHG).[5] However, recently Arakelyan *et al.*[6,7] reported their new experimental data on SHG of all six types of interaction in oriented samples of MBBA [$H_3CO(C_6H_4)CH{:}N(C_6H_5)C_4H_9$, or N-(4-methoxybenzylidene)-4′-*n*-butylaniline]. They concluded that the oriented MBBA can only have $C_1[1]$ or $C_{1h}[m]$ symmetry. If the nematic liquid crystal (NLC) is noncentrosymmetric, then the Frank-Ericksen-Leslie-Parodi theory must be revised completely. However, many experimental results do agree satisfactorily with the predictions of that theory. In such a dilemma, it is natural for us to ask whether it is possible to explain the experimentally observed SHG within the framework of the theory based upon the equivalence of $+\mathbf{n}$ and $-\mathbf{n}$.

The elastic constants of NLC's are of the order of 10^{-7}–10^{-6} dyn. An external field of the order of 1 kV/cm or 1 kG would easily induce curvature strains in NLC's. In an optical electric field the $D_{\infty h}$ symmetry of the NLC sample as a whole will easily be broken. However, the director field $\mathbf{n}(\mathbf{r})$ in an aligned sample is a continuous function of the space coordinates. In an optical electric field the local $D_{\infty h}$ symmetry of the NLC may still be preserved. With this in mind, we calculate the second-order susceptibilities of the NLC both in the well-aligned state and in states with curvature strains. The effective susceptibilities for different types of interaction are then deduced. It follows that we can explain the existing observations of SHG in NLC's with a quadrupole-moment mechanism together with an oscillatory director mechanism without having to invoke the noncentrosymmetry of NLC's as suggested by Arakelyan *et al.*

In crystals with centrosymmetry, SHG stimulated by electric quadrupole interaction is very weak, e.g., in calcite crystal $\chi_{ijk}=10^{-17}$–10^{-18} esu.[8] However, estimates based upon the theory given by Bloembergen *et al.*[9] and the structure of the MBBA molecule show that the effective susceptibility may reach an order of magnitude of 10^{-11} esu where the value given by Arakelyan *et al.*[10] is 10^{-10} esu and that given by Shtykov *et al.*[11] is 10^{-12} esu.

II. PHENOMENOLOGICAL THEORY

It is well known that all optical phenomena in a lossless, nonlinear dielectric medium are governed by the Maxwell equation[9,12]

$$\nabla\times\nabla\times\mathbf{E}+\frac{1}{c^2}\frac{\partial^2}{\partial t^2}(\tilde{\varepsilon}\cdot\mathbf{E})=-\frac{4\pi}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{P}^{\rm NL} . \tag{2.1}$$

To discuss SHG we may write the nonlinear electric polarization $\mathbf{P}^{\rm NL}$ in the form[13]

$$P_i^{\rm NL}=\chi_{ijk}E_jE_k+\chi_{ijkl}E_jE_{l,k}+\cdots , \quad i,j,k,l=1,2,3 , \tag{2.2}$$

where $E_{l,k}\equiv\partial E_l/\partial x_k$ and the subscripts 1,2,3 represent the three components in a Cartesian space coordinate system, respectively. (Summation convention is used in the present calculation.) The nonlinear optical susceptibilities $\underline{\chi}^{(3)}\equiv\chi_{ijk}$ and $\underline{\chi}^{(4)}\equiv\chi_{ijkl}$ depend upon the symmetry properties of the medium. For media with centrosymmetry $\underline{\chi}^{(3)}\equiv\underline{0}$.[5]

An aligned NLC possesses $D_{\infty h}$ symmetry and its $\underline{\chi}^{(3)}$ is equal to zero. To find χ_{ijkl} of an aligned NLC system we first consider the energy function $-\phi\equiv-\mathbf{P}_f^{\rm NL}\cdot\mathbf{E}=-\chi_{ijkl}E_iE_jE_{l,k}$ of the electric polarization $\mathbf{P}_f^{\rm NL}$ of the system in an electric field $\mathbf{E}$. To find out what kind of scalar functions ϕ may take, we introduce a new coordinate system $(\xi,\eta,3)$ where

$$\xi=(\tfrac{1}{2})^{-1/2}(x_1+ix_2)\ ,$$
$$\eta=(\tfrac{1}{2})^{-1/2}(x_1-ix_2)\ , \tag{2.3}$$
$$3=x_3\ (||\mathbf{n})\ .$$

Under the unitary transformation (2.3), the function ϕ will take on the new form

$$\phi=\chi_{\alpha\beta\gamma\delta}E_\alpha E_\beta E_{\delta,\gamma},\quad \alpha,\beta,\gamma,\delta=\xi,\eta,3\ . \tag{2.4}$$

Now ϕ must satisfy the following requirements.[14]

(1) The function ϕ is an even function of $\mathbf{n}$ on account of the equivalence of $+\mathbf{n}$ and $-\mathbf{n}$.

(2) The number of ξ and the number of η appeared in the subscripts of ϕ must be equal to each other, since $\mathbf{n}$ is the C_∞ axis and ϕ is an invariant.[15]

(3) The subscript 3 in the function ϕ can only appear in an even number of times, since any plane perpendicular to $\mathbf{n}$ is a plane of mirror symmetry.

(4) The subscripts ξ and η are interchangeable, since any plane containing $\mathbf{n}$ is a plane of reflection.

Besides, ϕ is a real function and the components of $\mathbf{n}$ are given by

$$n_\xi=n_\xi=0,\quad n_3=1\ . \tag{2.5}$$

We can easily show that ϕ can only be the linear combinations of the following scalar functions:

$$(\mathbf{n}\cdot\nabla\mathbf{E}\cdot\mathbf{n})(\mathbf{E}\cdot\mathbf{n})^2,\quad (\nabla\cdot\mathbf{E})(\mathbf{E}\cdot\mathbf{n})^2,\quad (\mathbf{n}\cdot\nabla\mathbf{E}\cdot\mathbf{n})(\mathbf{E}\cdot\mathbf{E})\ ,$$
$$(\mathbf{n}\cdot\nabla\mathbf{E}\cdot\mathbf{E})(\mathbf{E}\cdot\mathbf{n}),\quad (\mathbf{E}\cdot\nabla\mathbf{E}\cdot\mathbf{n})(\mathbf{E}\cdot\mathbf{n})\ , \tag{2.6}$$
$$(\nabla\cdot\mathbf{E})(\mathbf{E}\cdot\mathbf{E}),\quad \mathbf{E}\cdot\nabla\mathbf{E}\cdot\mathbf{E}\ .$$

It follows then the nonlinear polarization $\mathbf{P}_f^{\mathrm{NL}}$ and the optical susceptibility χ_{ijkl} for an aligned NLC are given, respectively, by

$$\begin{aligned}\mathbf{P}_f^{\mathrm{NL}}=[&A_1(\mathbf{E}\cdot\mathbf{n})(\mathbf{n}\cdot\nabla\mathbf{E}\cdot\mathbf{n})+A_2(\mathbf{E}\cdot\mathbf{n})\nabla\cdot\mathbf{E}\\&+A_3\mathbf{n}\cdot\nabla\mathbf{E}\cdot\mathbf{E}+A_4\mathbf{E}\cdot\nabla\mathbf{E}\cdot\mathbf{n}]\mathbf{n}\\&+A_5(\mathbf{n}\cdot\nabla\mathbf{E}\cdot\mathbf{n})\mathbf{E}+A_6(\mathbf{E}\cdot\mathbf{n})\mathbf{n}\cdot\nabla E+A_7(\mathbf{E}\cdot\mathbf{n})\nabla\mathbf{E}\cdot\mathbf{n}\\&+A_8(\nabla\cdot\mathbf{E})\mathbf{E}+A_9\nabla\mathbf{E}\cdot\mathbf{E}+A_{10}\mathbf{E}\cdot\nabla\mathbf{E}\ ,\end{aligned} \tag{2.7}$$

$$\begin{aligned}\chi_{ijkl}=&A_1n_in_jn_kn_l+A_2n_in_j\delta_{kl}+A_3n_in_k\delta_{jl}\\&+A_4n_in_l\delta_{jk}+A_5\delta_{ij}n_kn_l+A_6\delta_{il}n_jn_k+A_7\delta_{ik}n_jn_l\\&+A_8\delta_{ij}\delta_{kl}+A_9\delta_{ik}\delta_{jl}+A_{10}\delta_{il}\delta_{jk}\ ,\end{aligned} \tag{2.8}$$

where the A's are material constants. Notice that the last three terms of Eq. (2.8) are independent of $\mathbf{n}$. They are the contributions from the isotropic part of the medium. Both Bloembergen *et al.*[9] and Wang *et al.*[16] showed that, regardless of the detailed mechanism and the models for the nonlinearity, the nonlinear polarization for an isotropic medium may always be written in the form

$$\begin{aligned}P_i(2\omega)=&(\alpha-\beta)E_j(\omega)\nabla_jE_i(\omega)+\beta E_i(\omega)\nabla_jE_j(\omega)\\&+\gamma\nabla_i[E_j(\omega)E_j(\omega)]\ .\end{aligned} \tag{2.9}$$

For transparent materials the coefficient γ is much less than α and β.[9] Comparing Eq. (2.7) with Eq. (2.9) we find that

$$A_8=\beta,\quad A_9=2\gamma,\quad A_{10}=\alpha-\beta\ . \tag{2.10}$$

Resolving the applied optical electric field $\mathbf{E}(\mathbf{r},t)$ into its Fourier components by

$$\begin{aligned}&\mathbf{E}(\mathbf{r},t)=\sum_{m=-\infty}^{\infty}\mathbf{E}(\mathbf{r},\omega_m)\exp(-i\omega_mt)\ ,\\&\omega_{-m}\equiv-\omega_m,\quad \mathbf{E}(\mathbf{r},\omega_m)=\mathbf{E}^*(\mathbf{r},-\omega_m)\ ,\end{aligned} \tag{2.11}$$

we get the nonlinear polarization $\mathbf{P}_f^{\mathrm{NL}}(\mathbf{r},\omega)$ as

$$\begin{aligned}\mathbf{P}_f^{\mathrm{NL}}(\mathbf{r},\omega)=\sum_m\{&A_1[\mathbf{E}(\mathbf{r},\omega_m)\cdot\mathbf{n}][\mathbf{n}\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega_m)\cdot\mathbf{n}]\mathbf{n}+A_2[\mathbf{E}(\mathbf{r},\omega_m)\cdot\mathbf{n}][\nabla\cdot\mathbf{E}(\mathbf{r},\omega-\omega_m)]\mathbf{n}\\&+A_3[\mathbf{n}\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega_m)\cdot\mathbf{E}(\mathbf{r},\omega_m)]\mathbf{n}+A_4[\mathbf{E}(\mathbf{r},\omega_m)\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega_m)\cdot\mathbf{n}]\mathbf{n}+A_5[\mathbf{n}\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega_m)\cdot\mathbf{n}]\mathbf{E}(\mathbf{r},\omega_m)\\&+A_6[\mathbf{n}\cdot\mathbf{E}(\mathbf{r},\omega_m)][\mathbf{n}\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega_m)]+A_7[\mathbf{n}\cdot\mathbf{E}(\mathbf{r},\omega_m)][\nabla\mathbf{E}(\mathbf{r},\omega-\omega_m)\cdot\mathbf{n}]+A_8[\nabla\cdot\mathbf{E}(\mathbf{r},\omega-\omega_m)]\mathbf{E}(\mathbf{r},\omega_m)\\&+A_9[\nabla\mathbf{E}(\mathbf{r},\omega-\omega_m)\cdot\mathbf{E}(\mathbf{r},\omega_m)]+A_{10}[\mathbf{E}(\mathbf{r},\omega_m)\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega_m)]\}\ ,\end{aligned} \tag{2.12}$$

where the A's are functions of ω, ω_m, and $\omega-\omega_m$ and

$$A_i(\omega,\omega_m,\omega-\omega_m)=A_i^*(-\omega,-\omega_m,\omega_m-\omega)\ . \tag{2.13}$$

It is generally accepted that with curvature strains, the NLC as a whole is no longer centrosymmetric, yet the director $\mathbf{n}(\mathbf{r})$ at the point $\mathbf{r}$ is still the local C_∞ axis. Under such circumstances, the χ_{ijk} in Eq. (2.2) is a nonvanishing third-order tensor related to the deformation $\nabla\mathbf{n}(\mathbf{r})$. Now consider the energy $-\psi\equiv-\mathbf{P}_d^{\mathrm{NL}}\cdot\mathbf{E}$ of the electric polarization $\mathbf{P}_d^{\mathrm{NL}}$ of the NLC with curvature strains in an electric field $\mathbf{E}$:

$$\psi\equiv\mathbf{P}_n^{\mathrm{NL}}\cdot\mathbf{E}=\chi_{ijk}E_iE_jE_k\ . \tag{2.14}$$

Similar to ϕ, by preserving the first-order terms of $\nabla\mathbf{n}$

only, one may prove that ψ can only be the linear combinations of the five scalar functions:

$$(\mathbf{n}\cdot\nabla\mathbf{n}\cdot\mathbf{E})(\mathbf{E}\cdot\mathbf{n})^2,\ (\nabla\cdot\mathbf{n})(\mathbf{E}\cdot\mathbf{n})^3,\ (\mathbf{n}\cdot\nabla\mathbf{n}\cdot\mathbf{E})(\mathbf{E}\cdot\mathbf{E}),$$
$$(\nabla\cdot\mathbf{n})(\mathbf{E}\cdot\mathbf{E})(\mathbf{E}\cdot\mathbf{n}),\ (\mathbf{E}\cdot\nabla\mathbf{n}\cdot\mathbf{E})(\mathbf{E}\cdot\mathbf{n}) . \tag{2.15}$$

Thus we have

$$P_{di}^{\rm NL}=\chi_{ijk}E_jE_k , \tag{2.16}$$

$$\chi_{ijk}=B_1b_in_jn_k+B_2n_ib_jn_k+B_3n_in_jb_k+B_4(\nabla\cdot\mathbf{n})n_in_jn_k +B_5b_i\delta_{jk}+B_6\delta_{ij}b_k+B_7\delta_{ik}b_j+B_8(\nabla\cdot\mathbf{n})n_i\delta_{jk} +B_9(\nabla\cdot\mathbf{n})\delta_{ij}n_k+B_{10}(\nabla\cdot\mathbf{n})\delta_{ik}n_j+B_{11}n_in_{k,j} +B_{12}n_in_{j,k}+B_{13}n_jn_{i,k}+B_{14}n_jn_{k,i} +B_{15}n_kn_{i,j}+B_{16}n_kn_{j,i} , \tag{2.17}$$

where

$$\mathbf{b}=\mathbf{n}\cdot\nabla\mathbf{n},\quad n_{i,j}\equiv\partial n_i/\partial x_j . \tag{2.18}$$

Obviously, the expressions for the Fourier components of $P_{di}^{\rm NL}$ are similar to $\mathbf{P}_f^{\rm NL}(\mathbf{r},\omega)$ as given by Eq. (2.12) with the material-constant B's being frequency dependent.

III. SHG IN WELL-ALIGNED NLC

Bloembergen *et al.*[9] have shown that, for SHG, the lowest-order nonlinear contribution from the bound electrons in nonmagnetic crystals with inversion symmetry is the quadrupole-moment source $P_i^{\rm NL}(2\omega)$:

$$P_i^{\rm NL}(2\omega)=N(\Gamma_{jl,ki}-\Gamma_{ij,kl})E_j(\omega)\nabla_kE_l(\omega) , \tag{3.1}$$

with

$$\Gamma_{ij,kl}\approx\frac{3e^3}{\hbar^2\omega_0^2}\sum[\langle0|x_ix_jx_kx_l|0\rangle -\langle0|x_ix_j|0\rangle\langle0|x_kx_l|0\rangle] , \tag{3.2}$$

where N is the number of unit cells per unit volume of the crystal, $\hbar\omega_0$ is some average energy (closure approximation), and the the summation is over all the electrons in a unit cell of the crystal. Obviously,

$$\Gamma_{ij,kl}=\Gamma_{ji,kl}=\Gamma_{ij,lk}=\Gamma_{ji,lk}=\Gamma_{kl,ij} . \tag{3.3}$$

Let us apply these results to the NLC system. In the case of an NLC, the summation should be taken over the valence electrons of the NLC since there is no long-range translational order in NLC's. If we write Eq. (3.1) in the form

$$P_i^{\rm NL}=N\gamma_{ijkl}E_j\nabla_kE_l , \tag{3.4}$$

where N is the number of molecules per unit volume of the liquid crystal, we then have

$$\gamma_{ijkl}=\frac{3e^3}{\hbar^2\omega_0^2}\sum[\langle0|x_ix_j|0\rangle\langle0|x_kx_l|0\rangle -\langle0|x_jx_l|0\rangle\langle0|x_kx_i|0\rangle] . \tag{3.5}$$

The 12 nonvanishing components of γ_{ijkl} are

$$\gamma_{1122}=\gamma_{2211}=-\gamma_{1212}=-\gamma_{2121} ,$$
$$\gamma_{1133}=\gamma_{3311}=-\gamma_{1313}=-\gamma_{3131} , \tag{3.6}$$
$$\gamma_{2233}=\gamma_{3322}=-\gamma_{2323}=-\gamma_{3232} .$$

The director $\mathbf{n}(\mathbf{r})$ gives the direction of the preferred orientation of the molecules at the point $\mathbf{r}$.[17] The $D_{\infty h}$ symmetry of the NLC implies that the probability of finding a molecule at $\mathbf{r}$ with its long axis making an angle θ with $\mathbf{n}(\mathbf{r})$ is a function of $\cos^2\theta$, i.e., $f(\cos^2\theta)$. The macroscopic nonlinear susceptibility χ_{ijkl} (or any fourth-order tensor χ_{ijkl} with $D_{\infty h}$ symmetry) may be considered as the statistical average of the corresponding molecular nonlinear susceptibility γ_{ijkl}. Naturally γ_{ijkl} is defined in a coordinate system (1,2,3) rigidly attached to the molecule with the 3 axis pointing along the long axis of the molecule. By introducing a new coordinate system $(\xi^0,\eta^0,3)$ similar to that defined by Eq. (2.3) and the tetrads **ijkl** and $\boldsymbol{\alpha\beta\gamma\delta}$ where **i**,**j**,**k**,**l** are unit vectors along (1,2,3) and $\boldsymbol{\alpha},\boldsymbol{\beta},\boldsymbol{\gamma},\boldsymbol{\delta}$ are unit vectors along $(\xi^0,\eta^0,3)$, we can show that the 21 nonvanishing components χ_{ijkl} are related to the γ_{ijkl}'s by[18]

$$\chi_{1111}=\chi_{2222}=\frac{N}{140}[\tfrac{1}{2}(56+40S_2+9S_4)(\gamma_{1111}+\gamma_{2222})+4(7-10S_2+3S_4)\gamma_{3333}+\tfrac{1}{6}(56+40S_2+9S_4)\gamma_{12} +\tfrac{2}{3}(14-5S_2-9S_4)\gamma_{33}] ,$$

$$\chi_{3333}=\frac{N}{105}[(21-30S_2+9S_4)(\gamma_{1111}+\gamma_{2222})+3(7+20S_2+8S_4)\gamma_{3333}+(7-10S_2+3S_4)\gamma_{12}+(7+5S_2-12S_4)\gamma_{33}] ,$$

$$\chi_{1122}=\chi_{2211}=G+\frac{N}{6}[(1+2S_2)(\gamma_{1122}+\gamma_{2211})+(1-S_2)(\gamma_{1133}+\gamma_{2233}+\gamma_{3311}+\gamma_{3322})] ,$$

$$\chi_{1212}=\chi_{2121}=G+\frac{N}{6}[(1+2S_2)(\gamma_{1212}+\gamma_{2121})+(1-S_2)(\gamma_{1313}+\gamma_{2323}+\gamma_{3131}+\gamma_{3232})] ,$$

$$\chi_{1221}=\chi_{2112}=G+\frac{N}{6}[(1+2S_2)(\gamma_{1221}+\gamma_{2112})+(1-S_2)(\gamma_{1331}+\gamma_{2332}+\gamma_{3113}+\gamma_{3232})] ,$$

$$\chi_{1133}=\chi_{2233}=H+\frac{N}{6}[(1+2S_2)(\gamma_{1133}+\gamma_{2233})+(1-S_2)(\gamma_{1122}+\gamma_{2211}+\gamma_{3311}+\gamma_{3322})]\,,$$
$$\chi_{1313}=\chi_{2323}=H+\frac{N}{6}[(1+2S_2)(\gamma_{1313}+\gamma_{2323})+(1-S_2)(\gamma_{1212}+\gamma_{2121}+\gamma_{3131}+\gamma_{3232})]\,,$$
$$\chi_{1331}=\chi_{2332}=H+\frac{N}{6}[(1+2S_2)(\gamma_{1331}+\gamma_{2332})+(1-S_2)(\gamma_{1221}+\gamma_{2112}+\gamma_{3113}+\gamma_{3223})]\,,$$
$$\chi_{3131}=\chi_{3232}=H+\frac{N}{6}[(1+2S_2)(\gamma_{3131}+\gamma_{3232})+(1-S_2)(\gamma_{1212}+\gamma_{2121}+\gamma_{1313}+\gamma_{2323})]\,,$$
$$\chi_{3113}=\chi_{3223}=H+\frac{N}{6}[(1+2S_2)(\gamma_{3113}+\gamma_{3223})+(1-S_2)(\gamma_{1221}+\gamma_{2112}+\gamma_{1331}+\gamma_{2332})]\,,$$
$$\chi_{3311}=\chi_{3322}=H+\frac{N}{6}[(1+2S_2)(\gamma_{3311}+\gamma_{3322})+(1-S_2)(\gamma_{1122}+\gamma_{2211}+\gamma_{1133}+\gamma_{2233})]\,, \quad (3.7)$$

where

$$S_2=\int_{-1}^{1}\tfrac{1}{2}(3\cos^2\theta-1)f(\cos^2\theta)d(\cos\theta)=\langle\tfrac{1}{2}(3\cos^2\theta-1)\rangle\,,$$
$$S_4=\int_{-1}^{1}\tfrac{1}{8}(35\cos^4\theta-30\cos^2\theta+3)f(\cos^2\theta)d(\cos\theta)=\langle(35\cos^4\theta-30\cos^2\theta+3)/8\rangle\,,$$
$$\gamma_{12}\equiv\gamma_{1122}+\gamma_{1212}+\gamma_{1221}+\gamma_{2112}+\gamma_{2121}+\gamma_{2211}\,,$$
$$\gamma_{33}\equiv\gamma_{1133}+\gamma_{1313}+\gamma_{1331}+\gamma_{2233}+\gamma_{2323}+\gamma_{2332}+\gamma_{3113}+\gamma_{3131}+\gamma_{3311}+\gamma_{3223}+\gamma_{3232}+\gamma_{3322}\,, \quad (3.8)$$
$$G\equiv\frac{N}{420}[\tfrac{1}{2}(56+40S_2+9S_4)(\gamma_{1111}+\gamma_{2222})+4(7-10S_2+3S_4)\gamma_{3333}-\tfrac{1}{2}(28+80S_2-3S_4)\gamma_{12}-2(7-10S_2+3S_4)\gamma_{33}]\,,$$
$$H\equiv\frac{N}{210}[(14-5S_2-9S_4)(\gamma_{1111}+\gamma_{2222})+2(7+5S_2-12S_4)\gamma_{3333}-(7-10S_2+3S_4)\gamma_{12}-(7+5S_2-12S_4)\gamma_{33}]\,.$$

Here S_2 is the traditional order parameter and S_4 is the order parameter of the fourth order.

On account of Eq. (3.6) we find that only the following χ_{ijkl}'s are nonvanishing:

$$\chi_{1122}=-\chi_{1212}=-\chi_{2121}=\chi_{2211}=\frac{N}{3}[(1+2S_2)\gamma_{1122}+(1-S_2)(\gamma_{1133}+\gamma_{2233})]\,,$$
$$\chi_{1133}=\chi_{2233}=\chi_{3311}=\chi_{3322}=-\chi_{1313}=-\chi_{2323}=-\chi_{3131}=-\chi_{3232}=\frac{N}{6}[2(1-S_2)\gamma_{1122}+(2+S_2)(\gamma_{1133}+\gamma_{2233})]\,. \quad (3.9)$$

The ten material constants A introduced in Eq. (2.7) are now given by[18]

$$A_1=A_4=A_6=A_{10}=0\,,$$
$$A_2=A_5=-A_3=-A_7=\tfrac{1}{2}N(\gamma_{1133}+\gamma_{2233}-2\gamma_{1122})S_2\,,$$
$$A_8=-A_9=\tfrac{1}{3}N[(\gamma_{1122}+\gamma_{1133}+\gamma_{2233})+2(\gamma_{1122}-\gamma_{1133}-\gamma_{2233})S_2]\,. \quad (3.10)$$

They are all independent of S_4. Above the clearing point of the NLC, $S_2=0$, and only A_8 and A_9 are different from zero. The nonlinear polarization given by Eq. (2.7) now reduces to Eq. (2.9) with $\beta=-2\gamma$ and $\alpha=\beta$. This is the same result given by Bloembergen *et al.*[9] From their measurements on crystals with cubic structure and on fused silica, Wang *et al.*[16] obtained a value of 4 for α/β. However, the isotropic phase of the NLC is not in the solid state. We would suggest that measurements of SHG in a NLC in the isotropic phase will most likely furnish more useful information. Furthermore, if the structure of the molecule is isotropic then $\gamma_{1122}=\gamma_{1133}=\gamma_{2233}$. In such a case, again, only A_8 and A_9 are different from zero and independent of s_2 and S_4 at any temperature. This simply means that isotropic molecules do not form the liquid crystal as it should be.

IV. SHG IN NLC WITH CURVATURE STRAINS

Electric dipoles and quadrupoles will oscillate in an ac electric field, and so will the director of an NLC in an optical electric field. It was first pointed out by Meyer[19] that it is possible to induce splay (or bend) deformation and polarization in a liquid crystal by mechanical stress, an effect called flexoelectricity. The flexoelectric effect will be largest in liquid crystals with asymmetric molecules reflecting the presence of a dipole moment. Prost *et al.*[20] showed that flexoelectricity will also exist in liquid crystals built up of symmetric molecules if one recognizes the importance of the quadrupole density. From their observations on SHG in MBBA, Gu *et al.*[21] concluded that the observed SHG is due to the flexoelectric effect. Taking the flexoelectric effect into consideration, we may write the free-energy density of a NLC in an electric field **E** as[22]

$$g=\tfrac{1}{2}\left[k_{11}(\nabla\cdot\mathbf{n})^2+k_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n})^2+k_{33}(\mathbf{n}\cdot\nabla n)^2-\frac{\epsilon_a}{4\pi}(\mathbf{E}\cdot\mathbf{n})^2-e_{11}(\nabla\cdot\mathbf{n})(\mathbf{E}\cdot\mathbf{n})-e_{33}\mathbf{n}\cdot\nabla\mathbf{n}\cdot\mathbf{E}\right], \tag{4.1}$$

where k_{11}, k_{22}, and k_{33} are the splay, twist, and bend elastic constants, respectively, $\epsilon_a=\epsilon_{\parallel}-\epsilon_{\perp}$ is the dielectric anisotropy, and e_{11} and e_{33} are the flexoelectric coefficients. The equation of motion of the director in a low-frequency electric field now becomes[3]

$$\begin{aligned}I\frac{\partial^2}{\partial t^2}n_i+\gamma_1\frac{\partial}{\partial t}n_i-k_{11}\nabla_i(\nabla\cdot\mathbf{n})+k_{22}\{(\mathbf{n}\cdot\nabla\times\mathbf{n})(\nabla\times\mathbf{n})+\nabla\times[(\mathbf{n}\cdot\nabla\times\mathbf{n})\mathbf{n}]\}_i&\\ -k_{33}[(\nabla\cdot\mathbf{n})(\mathbf{n}\cdot\nabla\mathbf{n})_i-n_jn_{k,j}(n_{k,i}-n_{i,k})+n_jn_kn_{i,jk}]&\\ -\frac{1}{4\pi}\epsilon_a(\mathbf{E}\cdot\mathbf{n})E_i+e_{11}(\nabla_i\mathbf{E})\cdot\mathbf{n}+e_{33}(\mathbf{n}\cdot\nabla)E_i+(e_{33}-e_{11})[(\nabla\cdot\mathbf{n})E_i-(\nabla_i\mathbf{n})\cdot\mathbf{E}]&=-\lambda n_i\ ,\end{aligned} \tag{4.2}$$

where $I=\rho a^2$ is the moment of inertia per unit volume of the NLC, a is the typical dimension of a molecule, and the Lagrangian unknown multiplier λ is determined by $\mathbf{n}\cdot\mathbf{n}=1$ with the result

$$\begin{aligned}\lambda=I\left[\frac{\partial\mathbf{n}}{\partial t}\right]^2+k_{11}\mathbf{n}\cdot\nabla(\nabla\cdot\mathbf{n})-2k_{22}(\mathbf{n}\cdot\nabla\times\mathbf{n})^2-2k_{33}(\mathbf{n}\cdot\nabla\mathbf{n})^2+\left[\frac{1}{4\pi}\right]\epsilon_a(\mathbf{E}\cdot\mathbf{n})^2-(e_{11}+e_{33})\mathbf{n}\cdot\nabla\mathbf{E}\cdot\mathbf{n}&\\ +(e_{11}-e_{33})[(\nabla\cdot\mathbf{n})(\mathbf{E}\cdot\mathbf{n})-\mathbf{n}\cdot\nabla\mathbf{n}\cdot\mathbf{E}]\ .&\end{aligned} \tag{4.3}$$

Let us now apply Eq. (4.2) to the case where the NLC is in an optical electric field. Following Bloembergen[23] we expand $\mathbf{n}(\mathbf{r},t)$ into a power series of the optical electric field $\mathbf{E}$:

$$\mathbf{n}(\mathbf{r},t)=\mathbf{n}^{(0)}(\mathbf{r})+\mathbf{n}^{(1)}(\mathbf{r},t)+\mathbf{n}^{(2)}(\mathbf{r},t)+\cdots\ , \tag{4.4}$$

where $\mathbf{n}^{(j)}(\mathbf{r},t)$ is proportional to the jth power of $\mathbf{E}$. Substituting Eq. (4.4) into Eqs. (4.2) and (4.3) we find the zeroth-order equation and the first-order equation as

$$\begin{aligned}-k_{11}[\nabla(\nabla\cdot\mathbf{n}^{(0)})]_i+2k_{22}(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(0)})(\nabla\times\mathbf{n}^{(0)})_i-k_{22}[\mathbf{n}^{(0)}\times\nabla(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(0)})]_i-k_{33}(\nabla\cdot\mathbf{n}^{(0)})(\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)})_i&\\ +k_{33}n_j^{(0)}n_{k,j}^{(0)}(n_{k,i}^{(0)}-n_{i,k}^{(0)})-k_{33}n_j^{(0)}n_k^{(0)}n_{i,jk}^{(0)}+[k_{11}\mathbf{n}^{(0)}\cdot\nabla(\nabla\cdot\mathbf{n}^{(0)})-2k_{22}(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(0)})^2-2k_{33}(\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)})^2]n_i^{(0)}&=0\ ,\end{aligned} \tag{4.5}$$

$$\begin{aligned}I\frac{\partial^2}{\partial t^2}n_1^{(1)}+\gamma_1\frac{\partial}{\partial t}n_i^{(1)}-k_{11}[\nabla(\nabla\cdot\mathbf{n}^{(1)})]_i&\\ +2k_{22}[(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(1)})(\nabla\times\mathbf{n}^{(0)})_i+(\mathbf{n}^{(1)}\cdot\nabla\times\mathbf{n}^{(0)})(\nabla\times\mathbf{n}^{(0)})_i+(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(0)})(\nabla\times\mathbf{n}^{(1)})_i]&\\ -k_{22}[\mathbf{n}^{(0)}\times\nabla(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(1)})+\mathbf{n}^{(0)}\times\nabla(\mathbf{n}^{(1)}\cdot\nabla\times\mathbf{n}^{(0)})+\mathbf{n}^{(1)}\times\nabla(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(0)})]_i&\\ -k_{33}[(\nabla\cdot n^{(0)})(n^{(0)}\cdot\nabla\mathbf{n}^{(1)})+(\nabla\cdot\mathbf{n}^{(0)})(\mathbf{n}^{(1)}\cdot\nabla\mathbf{n}^{(0)})+(\nabla\cdot\mathbf{n}^{(1)})(\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)})]_i&\\ +k_{33}[n_j^{(0)}n_{k,j}^{(0)}(n_{k,i}^{(1)}-n_{i,k}^{(1)})+n_j^{(0)}n_{k,j}^{(1)}(n_{k,i}^{(0)}-n_{i,k}^{(0)})+n_j^{(1)}n_{k,j}^{(0)}(n_{k,i}^{(0)}-n_{i,k}^{(0)})]&\\ -k_{33}(n_j^{(0)}n_k^{(0)}n_{i,jk}^{(1)}+n_j^{(0)}n_k^{(1)}n_{i,jk}^{(0)}+n_j^{(1)}n_k^{(0)}n_{i,jk}^{(0)})-(e_{11}-e_{33})[(\nabla\cdot\mathbf{n}^{(0)})E_i-(\nabla\mathbf{n}^{(0)})_i\cdot\mathbf{E}]&\\ +e_{11}(\nabla\mathbf{E})_i\cdot\mathbf{n}^{(0)}+e_{33}(\mathbf{n}^{(0)}\cdot\nabla E_i)+\{k_{11}[\mathbf{n}^{(0)}\cdot\nabla(\nabla\cdot\mathbf{n}^{(1)})+\mathbf{n}^{(1)}\cdot\nabla(\nabla\cdot\mathbf{n}^{(0)})]&\\ -4k_{22}[(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(0)})(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(1)})+(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(0)})(\mathbf{n}^{(1)}\cdot\nabla\times\mathbf{n}^{(0)})]&\\ -4k_{33}[(\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)})\cdot(\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(1)})+(\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)})\cdot(\mathbf{n}^{(1)}\cdot\nabla\mathbf{n}^{(0)})]\}n_i^{(0)}&\\ +\{(e_{11}-e_{33})[(\nabla\cdot\mathbf{n}^{(0)})(\mathbf{E}\cdot\mathbf{n}^{(0)})-\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)}\cdot\mathbf{E}]-(e_{11}+e_{33})(\mathbf{n}^{(0)}\cdot\nabla\mathbf{E}\cdot\mathbf{n}^{(0)})\}n_i^{(0)}&\\ +[k_{11}\mathbf{n}^{(0)}\cdot\nabla(\nabla\cdot\mathbf{n}^{(0)})-2k_{22}(\mathbf{n}^{(0)}\cdot\nabla\times n^{(0)})^2-2k_{33}(\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)})^2]n_i^{(1)}&=0\ .\end{aligned} \tag{4.6}$$

For a well-aligned NLC, $\mathbf{n}^{(0)}(\mathbf{r})$ is independent of $\mathbf{r}$ and Eq. (4.5) becomes an identity. Here Eq. (4.6) simplifies to

$$\begin{aligned}I\frac{\partial^2}{\partial t^2}n_i^{(1)}+\gamma_1\frac{\partial}{\partial t}n_i^{(1)}-k_{11}[\nabla(\nabla\cdot\mathbf{n}^{(1)})]_i-k_{22}[\mathbf{n}^{(0)}\times\nabla(\mathbf{n}^{(0)}\cdot\nabla\times\mathbf{n}^{(1)})]_i-k_{33}n_j^{(0)}n_k^{(0)}n_{i,jk}^{(1)}+e_{11}(\nabla\mathbf{E})_i\cdot\mathbf{n}^{(0)}+e_{33}(\mathbf{n}^{(0)}\cdot\nabla E_i)&\\ +k_{11}[\mathbf{n}^{(0)}\cdot\nabla(\nabla\cdot\mathbf{n}^{(1)})]n_i^{(0)}-(e_{11}+e_{33})(\mathbf{n}^{(0)}\cdot\nabla\mathbf{E}\cdot\mathbf{n}^{(0)})n_i^{(0)}&=0\ .\end{aligned} \tag{4.7}$$

Let the Fourier expansions of $\mathbf{n}^{(1)}(\mathbf{r},t)$ and $\mathbf{E}(\mathbf{r},t)$ be

$$n_i^{(1)}(\mathbf{r},t)=\int_{-\infty}^{\infty} n_i^{(1)}(\mathbf{q},\omega)\exp[i(\mathbf{q}\cdot\mathbf{r}-\omega t)]d\mathbf{q}\,d\omega\ ,$$
$$E_i(\mathbf{r},t)=\int_{-\infty}^{\infty} E_i(\mathbf{q},\omega)\exp[i(\mathbf{q}\cdot\mathbf{r}-\omega t)]d\mathbf{q}\,d\omega\ . \tag{4.8}$$

One finds that

$$[I\omega^2+i\gamma_1\omega-k_{33}(\mathbf{n}^{(0)}\cdot\mathbf{q})^2]\mathbf{n}^{(1)}(\mathbf{q},\omega)-[k_{11}\mathbf{q}\cdot\mathbf{n}^{(1)}(\mathbf{q},\omega)+ie_{11}\mathbf{n}^{(0)}\cdot\mathbf{E}(\mathbf{q},\omega)]\mathbf{q}-k_{22}[\mathbf{n}^{(0)}\cdot\mathbf{q}\times\mathbf{n}^{(1)}(\mathbf{q},\omega)](\mathbf{n}^{(0)}\times\mathbf{q})$$
$$=ie_{33}(\mathbf{n}^{(0)}\cdot\mathbf{q})\mathbf{E}(\mathbf{q},\omega)-[k_{11}\mathbf{q}\cdot\mathbf{n}^{(1)}(\mathbf{q},\omega)+i(e_{11}+e_{33})\mathbf{n}^{(0)}\cdot\mathbf{E}(\mathbf{q},\omega)](\mathbf{n}^{(0)}\cdot\mathbf{q})\mathbf{n}^{(0)}\ . \tag{4.9}$$

For a given value of $\mathbf{q}$ we may choose the three unit vectors $(\hat{\mathbf{x}}_1,\hat{\mathbf{x}}_2,\hat{\mathbf{x}}_3)$ of the local Cartesian coordinate system as

$$\hat{\mathbf{x}}_1=\hat{\mathbf{x}}_2\times n^{(0)}/|\hat{\mathbf{x}}_2\times\mathbf{n}^{(0)}|\ ,$$
$$\hat{\mathbf{x}}_2=\mathbf{n}^{(0)}\times\mathbf{q}/|\mathbf{n}^{(0)}\times\mathbf{q}|\ , \tag{4.10}$$
$$\hat{\mathbf{x}}_3=\mathbf{n}^{(0)}\ .$$

In this local coordinate system, $\mathbf{n}^{(1)}$ is given by (assuming $k_{11}=k_{22}=k_{33}=k$)

$$\mathbf{n}^{(1)}(\mathbf{q},\omega)=\frac{i}{I\omega^2+i\gamma_1\omega-kq^2}\times\{e_{11}\mathbf{n}^{(0)}\cdot\mathbf{E}(\mathbf{q},\omega)\mathbf{q}+e_{33}(\mathbf{n}^{(0)}\cdot\mathbf{q})\mathbf{E}(\mathbf{q},\omega)-(e_{11}+e_{33})[\mathbf{n}^{(0)}\cdot\mathbf{E}(\mathbf{q},\omega)](\mathbf{n}^{(0)}\cdot\mathbf{q})\mathbf{n}^{(0)}\}\ . \tag{4.11}$$

Using the typical values $k=10^{-6}$ dyn, $\gamma_1=10^{-1}$ P, $\lambda=5\times10^{-5}$ cm, $I=10^{-14}$ g/cm, we have $q=1.2\times10^5$ cm, $kq^2=1.44\times10^4$ g/cm sec^2, $I\omega^2=1.42\times10^{17}$, $\gamma_1\omega=3.8\times10^{14}$. Thus the term kq^2 can be neglected and Eq. (4.11) becomes

$$\mathbf{n}^{(1)}(\mathbf{q},\omega)=\frac{i}{I\omega^2+i\gamma_1\omega}\times\{e_{11}\mathbf{n}^{(0)}\cdot\mathbf{E}(\mathbf{q},\omega)\mathbf{q}+e_{33}(\mathbf{n}^{(0)}\cdot\mathbf{q})\mathbf{E}(\mathbf{q},\omega)-(e_{11}+e_{33})[\mathbf{n}^{(0)}\cdot\mathbf{E}(\mathbf{q},\omega)](\mathbf{n}^{(0)}\cdot\mathbf{q})\mathbf{n}^{(0)}\}\ . \tag{4.12}$$

The induced polarization $\mathbf{P}(\mathbf{r},t)$ and the applied electric field $\mathbf{E}(\mathbf{r},t)$ are related to each other by

$$\mathbf{P}(\mathbf{r},t)=\frac{1}{4\pi}(\tilde{\epsilon}-\tilde{I})\cdot\mathbf{E}(\mathbf{r},t)\ ,$$

where the components of the electric constant $\tilde{\epsilon}$ are given by

$$\epsilon_{ij}=\epsilon_{\perp}\delta_{ij}+\epsilon_a n_i n_j\ .$$

The nonlinear electric polarization $\mathbf{P}^{\mathrm{NL}}$ which is quadratic in $\mathbf{E}$ is given by

$$\mathbf{P}^{\mathrm{NL}}(\mathbf{r},t)=\frac{1}{4\pi}\epsilon_a[\mathbf{n}^{(0)},\mathbf{n}^{(1)}(\mathbf{r},t)]_+\cdot\mathbf{E}(\mathbf{r},t)\ ,$$
$$[\mathbf{n}^{(0)},\mathbf{n}^{(1)}]_+\equiv\mathbf{n}^{(0)}\mathbf{n}^{(1)}+\mathbf{n}^{(1)}\mathbf{n}^{(0)}\ . \tag{4.13}$$

Applying the convolution theorem we have

$$\mathbf{P}^{\mathrm{NL}}(r,\omega)=\int\frac{1}{4\pi}\epsilon_a(\omega)[\mathbf{n}^{(0)},\mathbf{n}^{(1)}(\mathbf{r},\omega-\omega')]_+\cdot\mathbf{E}(\mathbf{r},\omega')d\omega'\ . \tag{4.14}$$

Substituting the inverse transform of Eq. (4.12) into Eq. (4.14) one finds that

$$\mathbf{P}^{\mathrm{NL}}(\mathbf{r},\omega)=\int\frac{\epsilon_a(\omega)}{4\pi[I(\omega-\omega')^2+i\gamma_1(\omega-\omega')]}\times\{e_{11}[\mathbf{E}(\mathbf{r},\omega')\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega')\cdot\mathbf{n}^{(0)}]\mathbf{n}^{(0)}+e_{33}[\mathbf{n}^{(0)}\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega')\cdot\mathbf{E}(\mathbf{r},\omega')]\mathbf{n}^{(0)}$$
$$-2(e_{11}+e_{33})[\mathbf{E}(\mathbf{r},\omega')\cdot\mathbf{n}^{(0)}][\mathbf{n}^{(0)}\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega')\cdot\mathbf{n}^{(0)}]\mathbf{n}^{(0)}+e_{11}[\mathbf{E}(\mathbf{r},\omega')\cdot\mathbf{n}^{(0)}][\nabla\mathbf{E}(\mathbf{r},\omega-\omega')\cdot\mathbf{n}^{(0)}]$$
$$+e_{33}[\mathbf{E}(\mathbf{r},\omega')\cdot\mathbf{n}^{(0)}][\mathbf{n}^{(0)}\cdot\nabla\mathbf{E}(\mathbf{r},\omega-\omega')]\}d\omega'\ . \tag{4.15}$$

Comparison of Eq. (4.15) and Eq. (2.12) shows that, under the oscillatory director mechanism, the nonvanishing material constants are

$$A_1=-2(e_{11}+e_{33})\mathcal{X},\quad A_3=A_6=e_{33}\mathcal{X},\quad A_4=A_7=e_{11}\mathcal{X}\ ,$$
$$\mathcal{X}\equiv\frac{\epsilon_a(\omega)}{4\pi[I(\omega-\omega')^2+i\gamma_1(\omega-\omega')]}\ . \tag{4.16}$$

Equation (2.13) is automatically satisfied.

For liquid crystals with curvature strains, Eq. (4.7) is no longer satisfied. In this case Eq. (4.6) simplifies to

$$I\frac{\partial^2}{\partial t^2}\mathbf{n}^{(1)}+\gamma_1\frac{\partial}{\partial t}\mathbf{n}^{(1)}-(e_{11}-e_{33})[(\nabla\cdot\mathbf{n}^{(0)})\mathbf{E}-(\nabla\mathbf{n}^{(0)})\cdot\mathbf{E}]+e_{11}(\nabla\mathbf{E})\cdot\mathbf{n}^{(0)}+e_{33}(\mathbf{n}^{(0)}\cdot\nabla\mathbf{E})$$
$$+\{(e_{11}-e_{33})[(\nabla\cdot\mathbf{n}^{(0)})(\mathbf{n}^{(0)}\cdot\mathbf{E})-\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)}\cdot\mathbf{E}]-(e_{11}+e_{33})\mathbf{n}^{(0)}\cdot\nabla\mathbf{E}\cdot\mathbf{n}^{(0)}\}\mathbf{n}^{(0)}=0\ , \tag{4.17}$$

where the terms containing elastic constants are neglected. Let $\mathbf{n}^{(1)}(\mathbf{r},t)$ be the sum of a deformation-dependent part $\mathbf{n}'^{(1)}(\mathbf{r},t)$ and a deformation-independent part $\mathbf{n}''^{(1)}(\mathbf{r},t)$:

$$\mathbf{n}^{(1)}(\mathbf{r},t)=\mathbf{n}'^{(1)}(\mathbf{r},t)+\mathbf{n}''^{(1)}(\mathbf{r},t)\ . \tag{4.18}$$

One then has

$$I\frac{\partial^2}{\partial t^2}\mathbf{n}'^{(1)}+\gamma_1\frac{\partial}{\partial t}\mathbf{n}'^{(1)}-(e_{11}-e_{33})[(\nabla\cdot\mathbf{n}^{(0)})\mathbf{E}-(\nabla\mathbf{n}^{(0)})\cdot\mathbf{E}]+(e_{11}-e_{33})[(\nabla\cdot\mathbf{n}^{(0)})(\mathbf{n}^{(0)}\cdot\mathbf{E})-\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)}\cdot\mathbf{E}]\mathbf{n}^{(0)}=0\ , \tag{4.19}$$

$$I\frac{\partial^2}{\partial t^2}\mathbf{n}''^{(1)}+\gamma_1\frac{\partial}{\partial t}\mathbf{n}''^{(1)}+e_{11}(\nabla\mathbf{E})\cdot\mathbf{n}^{(0)}+e_{33}\mathbf{n}^{(0)}\cdot\nabla\mathbf{E}-(e_{11}+e_{33})(\mathbf{n}^{(0)}\cdot\nabla\mathbf{E}\cdot\mathbf{n}^{(0)})\mathbf{n}^{(0)}=0\ . \tag{4.20}$$

Equation (4.20) is simply Eq. (4.7) with the elastic constant terms neglected. With the Fourier transformations

$$\mathbf{n}'^{(1)}(\mathbf{r},t)=\int_{-\infty}^{\infty}\mathbf{n}'^{(1)}(\mathbf{r},\omega)\exp(-i\omega t)d\omega\ ,$$
$$\mathbf{E}(\mathbf{r},t)=\int_{-\infty}^{\infty}\mathbf{E}(\mathbf{r},\omega)\exp(-i\omega t)d\omega\ , \tag{4.21}$$

the solution of Eq. (4.19) is given by

$$\mathbf{n}'^{(1)}(\mathbf{r},\omega)=\frac{e_{33}(\omega)-e_{11}(\omega)}{I\omega^2+i\gamma_1\omega}\times\{[\mathbf{n}^{(0)}\cdot\nabla\mathbf{n}^{(0)}\cdot\mathbf{E}(\mathbf{r},\omega)]\mathbf{n}^{(0)}-(\nabla\cdot\mathbf{n}^{(0)})[\mathbf{E}(\mathbf{r},\omega)\cdot\mathbf{n}^{(0)}]\mathbf{n}^{(0)}+(\nabla\cdot\mathbf{n}^{(0)})\mathbf{E}(\mathbf{r},\omega)-(\nabla\mathbf{n}^{(0)})\cdot\mathbf{E}(\mathbf{r},\omega)\}\ . \tag{4.22}$$

The subsidiary polarization $\mathbf{P}_d^{\mathrm{NL}}$ now takes the form

$$\mathbf{P}_d^{\mathrm{NL}}(\mathbf{r},\omega)=\int\frac{1}{4\pi}\epsilon_a(\omega)[\mathbf{n}^{(0)}(\mathbf{r}),\mathbf{n}'^{(1)}(\mathbf{r},\omega)]_+\cdot\mathbf{E}(\mathbf{r},\omega-\omega')d\omega'\ . \tag{4.23}$$

If we write $P_{di}^{\mathrm{NL}}(\mathbf{r},\omega)$ in the form

$$\mathbf{P}_{di}^{\mathrm{NL}}(\mathbf{r},\omega)=\int\mathcal{X}_{ijk}(\omega,\omega',\omega-\omega')\times E_j(\mathbf{r},\omega')E_k(\mathbf{r},\omega-\omega')d\omega'\ ,$$

then the susceptibility $\mathcal{X}_{ijk}$ will be

$$\mathcal{X}_{ijk}=\frac{\epsilon_a[e_{33}(\omega')-e_{11}(\omega')]}{4\pi[I(\omega')^2+i\gamma_1\omega']}\times[2n_i^{(0)}b_j^{(0)}n_k^{(0)}-2(\nabla\cdot\mathbf{n}^{(0)})n_i^{(0)}n_j^{(0)}n_k^{(0)}+(\nabla\cdot\mathbf{n}^{(0)})n_i^{(0)}\delta_{jk}-n_i^{(0)}n_{j,k}^{(0)}+(\nabla\cdot\mathbf{n}^{(0)})\delta_{ij}n_k^{(0)}-n_{j,i}^{(0)}n_k^{(0)}]\ . \tag{4.24}$$

When compared with Eq. (2.17) we find that the nonvanishing material constraints are

$$B_2=-B_4=2\mathcal{X}',\quad B_8=B_9=-B_{12}=-B_{16}=\mathcal{X}'\ ,$$
$$\mathcal{X}'\equiv\frac{\epsilon_a(\omega)[e_{33}(\omega')-e_{11}(\omega')]}{4\pi[I(\omega')^2+i\gamma_1\omega']}\ . \tag{4.25}$$

V. COMPARISON WITH EXPERIMENTS

Optically the NLC is uniaxial with the optical axis along the direction of the director. In the local Cartesian coordinate system defined by the three unit vectors $(\mathbf{b}/|\mathbf{b}|,\mathbf{c}/|\mathbf{c}|,\mathbf{n})$, where $\mathbf{b}\equiv\mathbf{n}\cdot\nabla\mathbf{n}$ and $\mathbf{c}\equiv\mathbf{n}\times\mathbf{b}$, the unit wave vector $\hat{\mathbf{q}}$ of the light beam may be written as (Fig. 1)

$$\hat{\mathbf{q}}\equiv(\hat{q}_1,\hat{q}_2,\hat{q}_3)=(\sin\theta\cos\phi,\sin\theta\sin\phi,\cos\theta)\ . \tag{5.1}$$

The refractive index $n_e(\theta)$ of the extraordinary beam traveling along the θ direction is given by[24]

$$n_e^2(\theta)=\frac{1}{\cos^2\theta/n_o^2+\sin^2\theta/n_e^2}=\frac{\epsilon_{\parallel}\epsilon_{\perp}}{\epsilon_{\perp}+\epsilon_a\hat{q}_3^2}\ , \tag{5.2}$$

where $n_o=\epsilon_\perp^{1/2}$ and $n_e=\epsilon_\perp^{1/2}$ are the principal refractive indices of the NLC. The magnitude of the ordinary wave vector $q_o(\omega)$ and that of the beam traveling along the θ direction $q_e(\theta,\omega)$ are given, respectively, by

$$q_o^2(\omega)=\frac{\epsilon_\perp\omega^2}{c^2}\,,\qquad q_e^2(\theta,\omega)=\frac{\epsilon_\perp\epsilon_\parallel\omega^2}{(\epsilon_\perp+\epsilon_a\hat{q}_3^2)c^2}\,. \tag{5.3}$$

The direction of polarization of the ordinary beam $\hat{\mathbf{e}}_o$ and that of the beam traveling along the θ direction $\hat{\mathbf{e}}_e$ are, respectively,

$$\hat{\mathbf{e}}_o=\frac{1}{(1-\hat{q}_3^2)^{1/2}}(-\hat{q}_2,\hat{q}_1,0)\,,$$
$$\hat{\mathbf{e}}_e=\frac{h(\omega)}{(1-\hat{q}_3^2)^{1/2}}[\epsilon_\parallel\hat{q}_1\hat{q}_3,\epsilon_\parallel\hat{q}_2\hat{q}_3,-\epsilon_\perp(1-\hat{q}_3^2)]\,, \tag{5.4}$$
$$h(\omega)=\{\epsilon_\perp^2(\omega)+[\epsilon_\parallel^2(\omega)-\epsilon_\perp^2(\omega)]\hat{q}_3^2\}^{-1/2}\,.$$

The dielectric constants $\epsilon_\parallel$ and $\epsilon_\perp$ are functions of the frequency. For the second harmonic, we shall denote the corresponding terms with a superscript (2), e.g., $\epsilon_\parallel^{(2)}$, $\epsilon_\perp^{(2)}$, $\epsilon_a^{(2)}$, $\mathbf{q}_o^{(2)}$, $\mathbf{q}_e^{(2)}$, $\hat{\mathbf{e}}_e^{(2)}$, etc.

For simplicity, let us consider the case of collinear interaction:

$$\mathbf{q}_o^{(2)}\,||\,\mathbf{q}_o(\omega)\,||\,\mathbf{q}_e(\theta,\omega)\,||\,\mathbf{q}\,. \tag{5.5}$$

Here the condition of phase matching is given by

$$q_c^{(2)}(\theta)=q_a(\theta)+q_b(\theta)\,, \tag{5.6}$$

where a,b,c refer to either o or e and θ is the angle between the wave vector and the optical axis (director). Let the incident electric field $\mathbf{E}(\mathbf{r},\omega)$ be

$$\mathbf{E}(\mathbf{r},\omega)=\hat{\mathbf{e}}_oE_o\exp(i\mathbf{q}_o\cdot\mathbf{r})+\hat{\mathbf{e}}_eE_e\exp(i\mathbf{q}_e\cdot\mathbf{r})\,. \tag{5.7}$$

When we substitute Eq. (5.7) into Eq. (2.12) and write the result in the form

$$\mathbf{P}_f^{\rm NL}(2\omega)=\sum_{a,b,c=e,o}\hat{\mathbf{e}}_c^{(2)}\chi(ab\to c)E_aE_b\exp[i(\mathbf{q}_a+\mathbf{q}_b)\cdot\mathbf{r}]\,,$$

we find the expressions of the effective susceptibility for different types of interaction $ab\to c$ in the case of an aligned NLC as follows:

$$\begin{aligned}
&\chi(ee\to o)=\chi(oo\to o)=\chi(oo\to e)=0\,,\\
&\chi(oo\to e)=\tfrac{1}{2}iq_oh(2\omega)\sin(2\theta)[A_9\epsilon_\parallel^{(2)}-(A_3+A_9)\epsilon_\perp^{(2)}]\,,\\
&\chi(oe\to o)=\tfrac{1}{2}ih(\omega)\sin(2\theta)\{q_o[A_{10}\epsilon_\parallel-(A_6+A_{10})\epsilon_\perp]+q_e[A_8\epsilon_\parallel-(A_5+A_8)\epsilon_\perp]\}\,,\\
&\chi(ee\to e)=\tfrac{1}{2}iq_eh^2(\omega)h(2\omega)\sin(2\theta)\Big\{[(A_8+A_9+A_{10})\epsilon_\parallel^{(2)}\epsilon_\parallel-(A_3+A_9)\epsilon_\perp^{(2)}\epsilon_\parallel-(A_5+A_6+A_8+A_{10})\epsilon_\parallel^{(2)}\epsilon_\perp]\epsilon_\parallel\cos^2\theta\\
&\qquad+\Big[(A_7+A_9)\epsilon_\parallel^{(2)}\epsilon_\perp+(A_2+A_4+A_8+A_{10})\epsilon_\perp^{(2)}\epsilon_\parallel-\Big[\sum_{i=1}^{10}A_i\Big]\epsilon_\perp^{(2)}\epsilon_\perp\Big]\epsilon_\perp\sin^2\theta\Big\}\,.
\end{aligned} \tag{5.8}$$

In the case of a NLC with curvature strains we have

$$\begin{aligned}
&\chi(oo\to o)=-(B_5+B_6+B_7)b\sin\phi\,,\\
&\chi(oo\to e)=h(2\omega)\{B_5\epsilon_\parallel^{(2)}b\cos\theta\cos\phi\\
&\qquad-[B_8(d_2+g_1)+(B_{11}+B_{12})(d_2\cos^2\phi+g_1\sin^2\phi-d_1\sin\phi\cos\phi-g_2\sin\phi\cos\phi)]\epsilon_\perp^{(2)}\sin\theta\}\,,\\
&\chi(oe\to o)=h(\omega)\{(B_6+B_7)b\epsilon_\parallel\cos\theta\cos\phi-(B_9+B_{10})(d_2+g_1)\epsilon_\perp\sin\theta\\
&\qquad-(B_{13}+B_{14}+B_{15}+B_{16})[g_1\sin^2\phi+d_2\cos^2\phi-(d_1+g_2)\sin\phi\cos\phi]\epsilon_\perp\sin\theta\}\,,\\
&\chi(oe\to e)=\tfrac{1}{2}h(\omega)h(2\omega)\sin(2\theta)[-(B_{11}+B_{12})(d_1+g_2)\epsilon_\perp^{(2)}\epsilon_\parallel\cos(2\phi)+(B_{14}+B_{16})\epsilon_\parallel^{(2)}\epsilon_\perp(d_1\sin^2\phi-g_2\cos^2\phi)\\
&\qquad+(B_{13}+B_{15})\epsilon_\parallel^{(2)}\epsilon_\perp(g_2\sin^2\phi-d_1\cos^2\phi)]\\
&\qquad-\tfrac{1}{4}h(\omega)h(2\omega)\sin(2\theta)[2(B_{11}+B_{12})\epsilon_\perp^{(2)}\epsilon_\parallel+(B_{13}+B_{14}+B_{15}+B_{16})\epsilon_\parallel^{(2)}\epsilon_\perp](d_2-g_1)\sin(2\phi)\\
&\qquad-h(\omega)h(2\omega)[(B_2+B_3+B_6+B_7+B_{11}+B_{12}+B_{14}+B_{16})\epsilon_\perp^{(2)}\epsilon_\perp\sin^2\theta+(B_6+B_7)\epsilon_\parallel^{(2)}\epsilon_\parallel\cos^2\theta]b\sin\phi\,,\\
&\chi(ee\to o)=\tfrac{1}{2}h^2(\omega)\epsilon_\parallel\epsilon_\perp\sin(2\theta)\{[(B_{13}+B_{15})d_1+(B_{14}+B_{16})g_2]\sin^2\phi-[(B_{14}+B_{16})d_1+(B_{13}+B_{15})g_2]\cos^2\phi\\
&\qquad-(B_{13}+B_{14}+B_{15}+B_{16})(d_2-g_2)\sin\phi\cos\phi\}\\
&\qquad-h^2(\omega)[(B_1+B_5+B_{13}+B_{15})\epsilon_\perp^2\sin^2\theta+B_5\epsilon_\parallel^2\cos^2\theta]b\sin\phi\,,
\end{aligned} \tag{5.9}$$

$$\chi(ee\to e)=h^2(\omega)h(2\omega)\{[(B_1+B_5+B_{13}+B_{15})\epsilon_{\|}^{(2)}\epsilon_{\perp}^2+(B_2+B_3+B_6+B_7+B_{11}+B_{12}+B_{14}+B_{16})\epsilon_{\perp}^{(2)}\epsilon_{\|}\epsilon_{\perp}]\sin^2\theta$$
$$+(B_5+B_6+B_7)\epsilon_{\|}^{(2)}\epsilon_{\|}^2\cos^2\theta\}b\cos\theta\cos\phi$$
$$-h^2(\omega)h(2\omega)\{[B_8\epsilon_{\perp}^{(2)}\epsilon_{\|}^2+(B_9+B_{10})\epsilon_{\|}^{(2)}\epsilon_{\|}\epsilon_{\perp}]\cos^2\theta+(B_4+B_8+B_9+B_{10})\epsilon_{\perp}^{(2)}\epsilon_{\perp}^2\sin^2\theta\}(d_2+g_1)\sin\theta$$
$$-\tfrac{1}{2}h^2(\omega)h(2\omega)[(B_{11}+B_{12})\epsilon_{\perp}^{(2)}\epsilon_{\|}^2+(B_{13}+B_{14}+B_{15}+B_{16})\epsilon_{\|}^{(2)}\epsilon_{\|}\epsilon_{\perp}]$$
$$\times[g_1\cos^2\phi+(d_1+g_2)\sin\phi\cos\phi+d_2\sin^2\phi]\sin(2\theta)\cos\theta\ ,$$

where

$$d_1=\mathbf{c}\cdot\nabla\mathbf{n}\cdot\mathbf{b}/b^2,\quad d_2=\mathbf{c}\cdot\nabla\mathbf{n}\cdot\mathbf{c}/b^2\ ,$$
$$g_1=\mathbf{b}\cdot\nabla\mathbf{n}\cdot\mathbf{b}/b^2,\quad g_2=\mathbf{b}\cdot\nabla\mathbf{n}\cdot\mathbf{c}/b^2\ . \tag{5.10}$$

The observations of Arakelyan *et al.* in 1979 certainly agree with the results of Eq. (5.8) for the case of a well-aligned NLC.[6] Their more careful observations in 1981 confirm, with Eq. (5.9), the case of a NLC with curvature strains.[10]

For the $ee\to o$ type of interaction, from Eqs. (5.1), (5.3), and (5.6) we find that the angle of phase matching $\theta_{\rm pm}$ satisfies the condition

$$\cos^2\theta_{\rm pm}=\frac{\epsilon_{\perp}(\epsilon_{\|}-\epsilon_{\perp}^{(2)})}{\epsilon_{\perp}^{(2)}(\epsilon_{\|}-\epsilon_{\perp})}\ . \tag{5.11}$$

For the $oe\to o$ type of interaction the angle of phase matching is determined by

$$\cos^2\theta_{\rm pm}=\frac{\epsilon_{\perp}}{\epsilon_{\|}^{(2)}-\epsilon_{\perp}^{(2)}}\left[\frac{\epsilon_{\|}}{2(\epsilon_{\perp}^{(2)})^{1/2}-\epsilon^{1/2}}-1\right]\ . \tag{5.12}$$

A least-squares fitting of the refractive indices of MBBA[25] yields the dispersion formulas for MBBA at 25 °C:

$$\epsilon_{\|}=n_e^2=2.680+0.1501/\lambda^2\ ,$$
$$\epsilon_{\perp}=n_o^2=2.266+0.0463/\lambda^2\ , \tag{5.13}$$

where the wavelength λ is measured in μm. The wavelength of the light beams in the experiments of Arakelyan *et al.*[6,7,10] are

$$\lambda(\omega)=1.06\ \mu\text{m},\quad \lambda(2\omega)=0.53\ \mu\text{m}\ .$$

From Eqs. (5.11) and (5.12) we find that the angles of phase matching are

$\theta_{\rm pm}=32°10'$ for $ee\to o$ interaction ,

$\theta_{\rm pm}=42°40'$ for $oe\to o$ interaction .

They agree very well with the observed values:[10]

$\theta_{\rm pm}=30°$ for $ee\to 0$ interaction ,

$\theta_{\rm pm}=43°$ for $oe\to o$ interaction .

In the experiments of Gu *et al.*[21] they found that, in a NLC with satisfactory alignment, no SHG was detected. But strong SHG was observed in samples with curvature strains. In fact, the observed SHG is of the $oe\to o$ type. In their experiment, the light beams are normal to the surfaces of the liquid crystal cell. One notices that in the case of a NLC with satisfactory alignment, $\theta=\frac{1}{2}\pi$. Under such circumstances the factor $\sin(2\theta)$ in the nonvanishing terms of Eq. (5.8) makes all the $\chi(ab\to c)$ vanishing. This result agrees with their observation of nondetectable SHG. Gu *et al.* made an assumption on the director of the NLC with curvature strains[21] (Fig. 2):

$$\mathbf{n}=(0,\sin\Phi(x,y),\cos\Phi(x,y))\ ,$$
$$\Phi=\Phi_0\sin(kx)\exp(-\alpha y)\ , \tag{5.14}$$

where Φ_0 is a small quantity. Here, to first order of Φ_0, **b** is a null vector and we may choose the direction of **b**

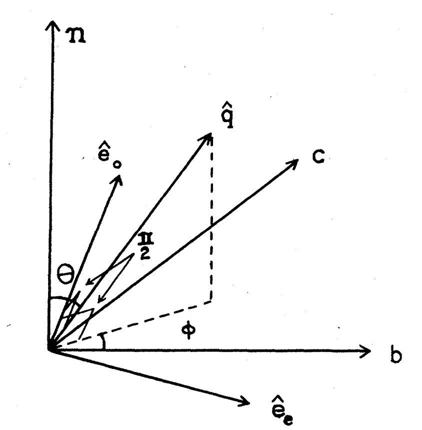

FIG. 1. Relationship between wave vector **q** and the directions of polarization $\hat{e}_e$ and $\hat{e}_0$.

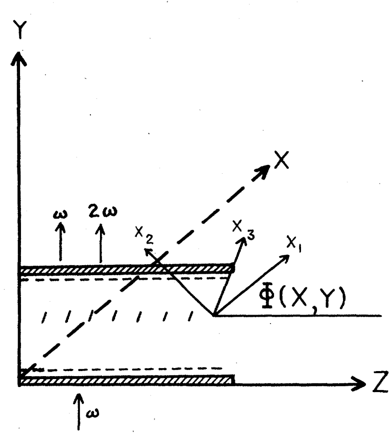

FIG. 2. Distorted director field.

parallel to the x axis. The three unit vectors of the local coordinate system now become

$$\hat{\mathbf{x}}_1=\mathbf{b}/|\mathbf{b}|=\hat{\mathbf{x}}\ ,$$
$$\hat{\mathbf{x}}_2=\mathbf{n}\times\hat{\mathbf{x}}_1=(0,\cos\Phi,-\sin\Phi)\ , \tag{5.15}$$
$$\hat{\mathbf{x}}_3=\mathbf{n}\ .$$

For normal incidence, $\theta=\phi=\frac{1}{2}\pi$ and Eq. (5.9) gives

$$\begin{aligned}
&\chi(ee\to o)=\chi(oo\to o)=\chi(oe\to e)=0\ ,\\
&\chi(ee\to e)=h^2(\omega)(2\omega)\epsilon_1^{(2)}\epsilon_1^2(B_4+B_8+B_9+B_{10})\\
&\qquad\times\Phi_0\alpha\sin(kx)\exp(-\alpha y)\ ,\\
&\chi(oo\to e)=h(2\omega)\epsilon_1^{(2)}B_8\Phi_0\alpha\sin(kx)\exp(-\alpha y)\ ,\\
&\chi(oe\to o)=h(\omega)\epsilon_1(B_9+B_{10})\Phi_0\alpha\sin(kx)\exp(-\alpha y)\ .
\end{aligned} \tag{5.16}$$

Taking Eq. (4.25) into account we have that $\chi(ee\to e)=0$. Therefore only SHG of $oo\to e$ and $oe\to o$ interactions exists.

Now let us study the refractive indices of MBBA,[25] we have

$$\begin{aligned}
&n_o(2\omega)>n_o(\omega),\ \ n_e(2\omega)>n_e(\omega)\ ,\\
&n_e(\omega)>n_o(\omega),\ \ n_e(2\omega)>n_o(2\omega)\ .
\end{aligned} \tag{5.17}$$

The condition of phase matching written in terms of refractive indices becomes

$$\begin{aligned}
&n_c(2\omega)=\tfrac{1}{2}[n_a(\omega)+n_b(\omega)]\ ,\\
&a,b,c=o,e\ .
\end{aligned} \tag{5.18}$$

From Eqs. (5.17) and (5.18) we see that in MBBA only the $oe\to o$ and $ee\to o$ type SHG can meet the condition of phase matching. In addition, the fluctuation of the director field will cause fluctuation in the refractive index of the extraordinary beam traveling in the direction perpendicular to the director. And the fluctuation of the refractive index causes light scattering which makes the observation of the extraordinary second harmonic difficult. These may be the reasons why Gu *et al.* detected only SHG of the $oe\to o$ interaction.

The conclusion that in MBBA only SHG of the $oe\to o$ and $ee\to o$ type interaction can satisfy the condition of phase matching agrees with the experimental observations of Shtykov *et al.*[11,26] They applied a bias field of 14 kV/cm on MBBA cells with planar alignment and cells with homeotropic alignment and found phase-matching $oe\to o$ and $ee\to o$ type SHG in both cases. After the withdrawal of the bias field they detected only the $oe\to o$ type SHG. With the bias field on, the director field is distorted either by the dielectric effect (Freedericksz transition) or by the flexoelectric effect in the NLC cells. And the withdrawal of the bias field makes the cells restore to their original uniformly aligned condition. Equation (5.8) tells us that in a uniformly aligned sample, SHG of the $ee\to o$ interaction is forbidden. Therefore one can only have SHG of the $oe\to o$ interaction.

VI. DISCUSSIONS

To determine the various nonlinear susceptibilities from the measured intensity of the SH one must decide whether the nonlinear polarization is of the form $\chi_{ijk}E_jE_k$ or $\chi_{ijkl}E_jE_{l,k}$. The latter expression has the factor $E_{l,k}$, therefore, to second order of $\mathbf{E}$, we have

$$\chi_{\text{eff}}=\chi^{(3)}=q\chi^{(4)}\ , \tag{6.1}$$

where q is the magnitude of the wave vector. Using $\chi^{(3)}$, Arakelyan *et al.*[10] found from their experimental data that

$$\chi^{(3)}(\text{MBBA})=(0.5\text{–}2)\times10^{-10}\ \text{esu}\ ,$$

and Shtykov *et al.*[11] gave the value

$$\chi^{(3)}(\text{MBBA})=1.5\times10^{-12}\ \text{esu}\ .$$

It is difficult to make a direct calculation on the order of magnitude of χ_{eff} in the present calculation. However, Bloembergen *et al.*[9] have shown that, for isotropic materials, the nonlinear quadrupole-moment source is given by

$$P_i^{\text{NL}}\approx\frac{3}{4N'e}(\chi^L)^2(E_i\nabla_jE_j-E_j\nabla_iE_j)\ , \tag{6.2}$$

where the linear susceptibility χ^L is given by

$$\chi^L_{\omega\to0}(\omega)=\frac{2N'e^2}{\hbar\omega_0}\langle0|x^2|0\rangle\ , \tag{6.3}$$

with N' the density of the valence electrons in the material. If we compare Eq. (6.2) with Eqs. (2.12) and (3.10) (with $S_2=S_4=0$) we find that

$$\frac{N}{3}(\gamma_{1122}+\gamma_{1133}+\gamma_{2233})=\frac{3}{4N'e}(\chi^L)^2\ . \tag{6.4}$$

Consequently we have

$$\chi_{\text{eff}}=\frac{3}{4N'e}(\chi^L)^2q\ . \tag{6.5}$$

The linear susceptibility χ^L may be estimated from the refractive index $\bar{n}$ of the liquid crystal in the isotropic phase by the well-known Lorenz-Lorentz equation:[27]

$$\chi^L=\frac{3}{4\pi}\left[\frac{\bar{n}^2-1}{\bar{n}^2+2}\right]\ . \tag{6.6}$$

The MBBA molecule has two benzene rings (Fig. 3). The six π electrons in each ring may be considered as the free electrons confined to the conjugated bond. Davydov *et al.*[28] had examined about 100 different organic compounds with the power method. They found that a large number of compounds with benzene rings do show strong SHG. Their result suggests that the conjugated π electrons in the benzene ring may be responsible for the SHG. In fact, it is well known that the delocalized π electrons in

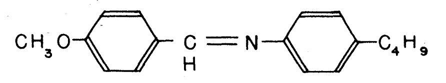

FIG. 3. MBBA molecule.

the conjugated molecules can produce anomalously large second- and third-order nonlinearities.[29,30] It seems, then, that the polarization of the molecule with benzene rings in an optical electric field would be determined mainly by these free π electrons in the rings. In this way we may take each MBBA molecule as having 12 valence electrons. The density of valence electrons N' becomes now

$$N'=\frac{12N^0P}{M} ,$$

where ρ is the density of liquid crystal MBBA, M its molecular weight, and N^0 the Avogadro's number. Taking[31] $\bar{n}^2=2.5$, $\rho=1$ g/cm^3, and $M=267$, we find that

$$\chi_{\text{eff}}(\text{MBBA})\approx 10^{-11} \text{ esu} .$$

This agrees in order of magnitude with the nonlinear susceptibility obtained experimentally by Arakelyan *et al.* and by Shtykov *et al.*

In the oscillatory director mechanism Eqs. (2.8), (4.16), and (6.1) lead to

$$\chi_{\text{eff}}=\frac{e_{11(33)}\epsilon_a^{(2)}q}{4\pi(I\omega^2+i\gamma_1\omega)} . \tag{6.7}$$

For MBBA, if we take[22,32]

$$\gamma_1=0.8 \text{ P}, \quad e_{11(33)}=10^{-4} \text{ dyn}^{1/2} ,$$

$$\epsilon_a^{(2)}=1, \quad I=10^{-14} \text{ g/cm} ,$$

$$\omega=10^{15} \text{ sec}^{-1}, \quad q=10^5 \text{ cm}^{-1} ,$$

we find that χ_{eff} will be of the order of magnitude of 10^{-16} esu, which is too small for observation. However, the validity of Eq. (4.2) had been verified only in cases of low frequencies where the molecule is capable of moving like a rigid body under the action of the applied field. It is conceivable that a rigid molecule with its heavy mass will not be able to vibrate in accordance with an applied optical electric field. Only the electrons of the molecule are capable to oscillate accordingly. In other words, it is the electric moment of the molecule that vibrates when it is acted upon by an optical electric field. So far the correct equation of motion of the director in a high-frequency field is still unknown. Frank has pointed out[33] that the exact meaning of the director is still a question open for investigation. At low frequency, the director may be considered as the average direction of the long axis of the NLC molecules. At high frequency, it seems that we may take it as the average direction of the electric moment of the molecules, since **n** gives the direction of the optical axis. Under such a point of view the moment of inertia I in Eq. (4.2) would be the moment of inertia associated with the motion of the free electrons per unit volume of NLC. Taking the ratio of the mass of the electron and the mass of the atom into account, for MBBA, we would have $I\approx\frac{12}{267}\times\frac{1}{2000}\times10^{-14}\approx10^{-20}-10^{-19}$ g/cm. Furthermore, if we neglect the absorption of light in the NLC, the dissipation term with the coefficient γ_1 in Eq. (4.2) may also be omitted. With the other constants unchanged Eq. (6.7) would also give an order of magnitude of $10^{-11}-10^{-10}$ for χ_{eff}.

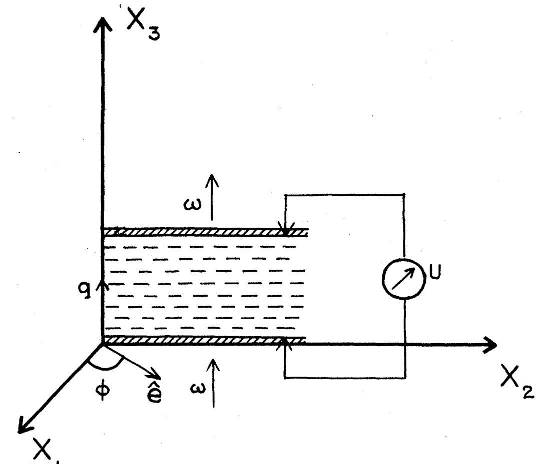

FIG. 4. Photovoltaic effect.

Now let us consider the case where monochromatic light of frequency ω_0 is normally incident on a homogeneously aligned NLC cell. We may take the director of the NLC and the direction of polarization of the light beam as (Fig. 4)

$$\hat{\mathbf{e}}=(\cos\phi, \sin\phi, 0) ,$$
$$\mathbf{n}=(0,1,0) . \tag{6.8}$$

Let us write the optical electric field in Dirac δ functions as

$$\mathbf{E}(\mathbf{r},\omega)=E_0\hat{\mathbf{e}}[\delta(\omega,\omega_0)\exp(iqx_3)+\delta(\omega,-\omega_0)\exp(-iqx_3)] , \tag{6.9}$$

where **q** is the wave vector. It follows from Eq. (2.12) that

$$\begin{aligned}\mathbf{P}_f^{\text{NL}}(\omega)=i\mathbf{q}E_0^2\{&[A_7(\omega,\omega_0,\omega-\omega_0)\sin^2\phi+A_9(\omega,\omega_0\omega-\omega_0)]\exp(2iqx_3)\delta(\omega-\omega_0,\omega_0)\\&-[A_7(\omega,-\omega_0,\omega+\omega_0)\sin^2\phi+A_9(\omega,-\omega_0,\omega+\omega_0)]\exp(-2iqx_3)\delta(\omega+\omega_0,-\omega_0)\\&+[A_7(\omega,-\omega_0,\omega+\omega_0)\sin^2\phi+A_9(\omega,-\omega_0,\omega+\omega_0)]\delta(\omega+\omega_0,\omega_0)\\&-[A_7(\omega,\omega_0,\omega-\omega_0)\sin^2\phi+A_9(\omega,\omega_0,\omega-\omega_0)]\delta(\omega-\omega_0,-\omega_0)\} .\end{aligned} \tag{6.10}$$

Since $\mathbf{P}_f^{\mathrm{NL}}(\omega)$ is parallel to $\mathbf{q}$, there will be no SHG. However, along the direction of $\mathbf{q}$, $\mathbf{P}_f^{\mathrm{NL}}$ has a dc component:

$$\mathbf{P}_f^{\mathrm{NL}}(0)=i\mathbf{q}E_0^2\{[A_7(0,-\omega_0,\omega_0)-A_7(0,\omega_0,-\omega_0)]\sin^2\phi +[A_9(0,-\omega_0,\omega_0)-A_9(\omega,\omega_0,-\omega_0)]\} \; . \tag{6.11}$$

In other words, there exists a photorectification or photovoltaic effect. Across the NLC layer there is an emf U given by

$$U=4\pi P_f^{\mathrm{NL}}(0)d \propto E_0^2 \propto I_0 \; , \tag{6.12}$$

where d is the thickness of the NLC layer and I_0 is the intensity of the incident beam. The observation of Kamei *et al.*[34] on APAPA (*p*-methoxybenzylidene-*p*′-aminophenylacetate) seems in agreement with this prediction, at least qualitatively.

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