advantage, in investigating the nature of the lambda transition, of working near the upper lambda point.

Goldstein[8] has pointed out that it is meaningless to extrapolate equations like (11) to values of $T-T_\lambda$ which are less than the root-mean-square statistical temperature fluctuation, which is about 10^{-12} °K for Lounasmaa's experiments[1,6] as well as the present one. In the experiment[1] at $\rho=0.1654$, if the logarithmic equation is extrapolated to $T-T_\lambda=10^{-12}$ °K, β_v is still not one half of its limiting value $(dP/dT)_\lambda$; whereas in our experiment Eq. (11) predicts that β_v will reach its limiting value at $T-T_\lambda=3.5\times10^{-9}$ °K, well outside the range of statistical fluctuations. It is even possible that a resolution of 10^{-9} °K may sometime be achieved experimentally.

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Nonlinear Optical Properties of Liquids

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Nonlinear optical polarization quadratic in the optical electric fields is shown to occur in optically active liquids and to lead to sum- and difference-frequency generation; second-harmonic generation is forbidden. The nonlinearity is described by components of the second-order polarizability tensor χ_{ijk} antisymmetric in j and k; the form of the antisymmetric part of χ_{ijk} is given for all the crystal classes and textures and for isotropic media. The magnitude of nonlinear polarizability of liquids is estimated from second-order perturbation theory and calculated to be readily detectable in many optically active liquids. The mechanism of the nonlinearity is illustrated by a simple single-electron molecular model.

I. INTRODUCTION

IT has been shown by Franken *et al.*[1] that in crystals without a center of symmetry one can observe optical polarization quadratic in the applied optical electric field. Radiation from this nonlinear polarization leads to generation of second harmonics and sum and difference frequencies. It is now possible to convert over 20% of a laser beam into new frequencies through this effect.[2] Bloembergen *et al.*,[3] Kleinman,[4] and others[5] have given theoretical analyses of the effect.

The second-order nonlinearities have been studied in a variety of piezoelectric crystals, primarily by observation of second-harmonic generation.[6] Higher order nonlinearities have also been observed in centrosymmetric media, including calcite[7,8] and several liquids.[9]

Some of the higher order effects arise from magnetic-dipole and quadrupole interactions and lead to very weak second-harmonic generation and mixing; higher order electric-dipole effects produce weak third harmonics as well as other nonlinear effects. In this paper, we shall consider only electric-dipole-type nonlinearities of second order which produce in noncentrosymmetric materials a macroscopic polarization quadratic in the applied fields.

The tensor $\chi_{ijk}^{2\omega,\omega,\omega}$ relating the polarization $P_i^{2\omega}$ to the applied fields E_j^ω and E_k^ω in second-harmonic generation is inherently symmetric in the indices j and k. This symmetry expresses the fact that fields E and E' applied, respectively, along the x and y axes, for example, produce the same quadratic polarization as the fields E and E' applied along the y and x axes, since the fields are indistinguishable. The tensor $\chi_{ijk}^{2\omega,\omega,\omega}$ must therefore have the same form for the various crystallographic classes as the piezoelectric tensor relating electric polarization to the stress, a symmetric

[1] P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, Phys. Rev. Letters **7**, 118 (1961).

[2] R. W. Terhune, P. D. Maker, and C. M. Savage, Appl. Phys. Letters **2**, 54 (1963).

[3] J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962).

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[5] P. S. Pershan, *Progress in Optics*, edited by E. Wolf (North-Holland Publishing Company, Amsterdam, 1965, to be published).

[6] R. C. Miller, Appl. Phys. Letters **5**, 17 (1964).

[7] R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Letters **8**, 404 (1962).

[8] J. A. Giordmaine, *Proceedings of the Third Conference on Quantum Electronics, Paris, 1963*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 1549.

[9] P. D. Maker, R. W. Terhune, and C. M. Savage, *Proceedings of the Third Conference on Quantum Electronics, Paris, 1963*, edited by P. Grivet and N. Bloembergen (Columbia University Press, New York, 1964), p. 1559.

second-rank tensor.[10] This equivalence has had detailed experimental confirmation.

In sum- and difference-frequency generation, however, the fields $E_x^{\omega_1}$ and $E_y^{\omega_2}$ need not produce the same quadratic polarization as the fields $E_x^{\omega_2}$ and $E_y^{\omega_1}$ of the same magnitudes. The purpose of this paper is to show that the portion of χ_{ijk} *antisymmetric* in j and k introduces a new tensor coefficient in noncentrosymmetric crystals of various classes (leading, for example, to nonlinear polarization in crystals of the class $O[432]$, in which piezoelectricity and second-harmonic generation are forbidden); of greater practical importance, the antisymmetric portion allows sum and difference frequency generation in certain liquids, gases, and polycrystalline media. The antisymmetric effects will usually be much weaker than the symmetric when both are allowed; however, the former should be the dominant nonlinearity in isotropic noncentrosymmetric materials such as optically active liquids.

In Sec. II, the form of the antisymmetric part of χ_{ijk} is given for all the crystallographic point groups as well as for textures[11] and isotropic media. In Sec. III, we describe briefly the macroscopic features of the interaction of light beams in nonlinear isotropic media. A quantum-mechanical expression for the part of χ_{ijk} producing nonlinear polarization in liquids is derived in Sec. IV and an estimate made of its magnitude. In Sec. V, a simple molecular model showing nonlinear polarization in the liquid phase is analyzed.

II. SYMMETRY

We write the nonlinear polarization **P** in the form

$$P_i = \chi_{ijk} E_j F_k, \qquad (1)$$

where **E** and **F** are optical electric fields of different frequency. (If E_j and E_k are monochromatic fields of frequency ω_1 and ω_2, the values of χ_{ijk} for sum and difference frequency generation will, of course, be different; in this section, we shall consider only the symmetry requirements on χ_{ijk}.) The tensor χ_{ijk} can be expressed as the sum of components S_{ijk} and A_{ijk} symmetric and antisymmetric, respectively, in j and k, and defined by Eq. (2):

$$P_i = \tfrac{1}{4}(\chi_{ijk} + \chi_{ikj})(E_j F_k + E_k F_j)$$
$$\qquad + \tfrac{1}{4}(\chi_{ijk} - \chi_{ikj})(E_j F_k - E_k F_j), \quad (2)$$
$$= \tfrac{1}{2}S_{ijk}(E_j F_k + E_k F_j) + \tfrac{1}{2}A_{ijk}(E_j F_k - E_k F_j).$$

We notice that $S_{ijk}^{\omega_1\omega_2\omega_3} = S_{ikj}^{\omega_1\omega_3\omega_2}$ and $A_{ijk}^{\omega_1\omega_2\omega_3} = A_{ikj}^{\omega_1\omega_3\omega_2}$. In what follows, however, when the frequencies are not displayed, it will be assumed that their order is *fixed*, i.e., $A_{ijk} = -A_{ikj}$, but $S_{ijk} = S_{ikj}$. Summation over repeated indices is assumed in Eqs. (1) and (2).

The symmetric tensor S_{ijk} is identical with the

piezoelectric tensor and is given for the crystallographic and continuous point groups in Refs. 10 and 11, respectively. The form of A_{ijk} for the various point groups is apparently not available in the literature. We have calculated the coefficients of A_{ijk} by the methods described in Ref. 10, except that use is made of the relation $A_{ijk} = -A_{ikj}$ rather than $S_{ijk} = S_{ikj}$. The results are shown in Table I for the noncentrosymmetric classes. To avoid ambiguities as to axis conventions and as an aid in comparison, we also list the symmetric matrices. The conventional contracted notation is used, i.e., $s_{11} = S_{111} = \chi_{111}$, $s_{14} = S_{123} + S_{132} = \chi_{123} + \chi_{132}$, $a_{14} = A_{123} - A_{132} = \chi_{123} - \chi_{132}$, etc. The crystal classes are labeled with the Schoenflies symbol followed, in brackets, by the Hermann-Mauguin symbol for the point groups.

The following features appear on comparison of the A_{ijk} with S_{ijk}: (1) In optically biaxial crystals, the triclinic, monoclinic, and orthorhombic systems, s_{ij} and a_{ij} have the same form, except, of course, that $a_{i1} = a_{i2} = a_{i3} = 0$ by definition. This behavior is expected, since the symmetry elements of these systems include only twofold rotation axes and mirror planes. The effects of these elements can result only in the requirements $s_{ij} = \pm s_{ij}$ and $a_{ij} = \pm a_{ij}$, so that the symmetry or antisymmetry is irrelevant. (2) In optically uniaxial crystals, the trigonal, tetragonal, and hexagonal systems, as well as the optically isotropic cubic system, the presence of higher rotational symmetry introduces relations among the coefficients which differ for s_{ij} and a_{ij}. Consider, for example, for crystal class O the coefficient s_{36} which appears in the relation $P_z = (s_{36}/2)(E_x F_y + E_y F_x)$; one of the symmetry elements is the fourfold rotation axis $\hat{z}$. A 90° crystal rotation about $\hat{z}$ transforms **P**, **E**, and **F** as follows: $P_z \rightarrow P_z$, $E_x \rightarrow E_y$, $E_y \rightarrow -E_x$, $F_x \rightarrow F_y$, and $F_y \rightarrow -F_x$; therefore, by symmetry, $P_z = (s_{36}/2)(-E_y F_x - E_x F_y) = -P_z$ and $s_{36} = 0$. However, for a_{36} in the relation $P_z = (a_{36}/2) \times (E_x F_y - E_y F_x)$, the same operation leads to the relation $P_z = (a_{36}/2)(-E_y F_x + E_x F_y) = P_z$ and leads to no restriction on a_{36}. (The other symmetry elements require that $a_{36} = a_{25} = a_{14}$.) The main results are that an additional nonzero coefficient χ_{312} appears for classes C_4, D_4, C_3, D_3, C_6, D_6 and nonzero coefficients become allowed for class O. (3) New nonzero coefficients appear for textures[11] and liquid crystals[12] of the classes C_∞ and D_∞. (4) The noncentrosymmetric class $\infty\,\infty$, which describes isotropic media in which an arbitrary direction is a C_∞ axis, but having no mirror planes, is found to have nonvanishing coefficients $\chi_{123} = \chi_{231} = \chi_{312}$. The other class of isotropic media, $\infty\,\infty m$, in which every direction is normal to a mirror plane, has a center of symmetry. It will be obvious that $\infty\,\infty$ liquids include the class of optically active liquids.[13]

[10] J. F. Nye, *Physical Properties of Crystals* (Clarendon Press, Oxford, 1957).

[11] A. V. Shubnikov *et al.*, *Etude des Textures Piezoelectriques* (Dunod Cie., Paris, 1958); V. A. Bazenhov, *Piezoelectric Properties of Wood* (Consultants Bureau, New York, 1961).

[12] G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press Inc., New York, 1962).

[13] An interesting discussion of the symmetry properties of continuous media is given by A. V. Shubnikov *et al.*, *Colored Symmetry* (The Macmillan Company, New York, 1964).

TABLE I. Form of the third-rank symmetric and antisymmetric tensors for the crystallographic and continuous point groups.

Triclinic crystals

C_1 [1]

$$s = \begin{bmatrix} s_{11} & s_{12} & s_{13} & s_{14} & s_{15} & s_{16} \\ s_{21} & s_{22} & s_{23} & s_{24} & s_{25} & s_{26} \\ s_{31} & s_{32} & s_{33} & s_{34} & s_{35} & s_{36} \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & a_{15} & a_{16} \\ 0 & 0 & 0 & a_{24} & a_{25} & a_{26} \\ 0 & 0 & 0 & a_{34} & a_{35} & a_{36} \end{bmatrix}$$

Monoclinic crystals

C_2 [2]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & 0 & s_{16} \\ s_{21} & s_{22} & s_{23} & 0 & s_{25} & 0 \\ 0 & 0 & 0 & s_{34} & 0 & s_{36} \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & a_{16} \\ 0 & 0 & 0 & 0 & a_{25} & 0 \\ 0 & 0 & 0 & a_{34} & 0 & a_{36} \end{bmatrix}$$

C_s [m]

$$s = \begin{bmatrix} s_{11} & s_{12} & s_{13} & 0 & s_{15} & 0 \\ 0 & 0 & 0 & s_{24} & 0 & s_{26} \\ s_{31} & s_{32} & s_{33} & 0 & s_{35} & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & 0 & a_{15} & 0 \\ 0 & 0 & 0 & a_{24} & 0 & a_{26} \\ 0 & 0 & 0 & 0 & a_{35} & 0 \end{bmatrix}$$

Orthorhombic crystals

D_2 [222]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{36} \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

C_{2v} [mm2]

$$s = \begin{bmatrix} 0 & 0 & 0 & 0 & s_{15} & 0 \\ 0 & 0 & 0 & s_{24} & 0 & 0 \\ s_{31} & s_{32} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & 0 & a_{15} & 0 \\ 0 & 0 & 0 & a_{24} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Tetragonal crystals

C_4 [4]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & s_{15} & 0 \\ 0 & 0 & 0 & s_{15} & -s_{14} & 0 \\ s_{31} & s_{31} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

S_4 [4̄]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & s_{15} & 0 \\ 0 & 0 & 0 & -s_{15} & s_{14} & 0 \\ s_{31} & -s_{31} & 0 & 0 & 0 & s_{36} \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & a_{15} & 0 \\ 0 & 0 & 0 & a_{15} & -a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

D_4 [422]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -s_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

C_{4v} [4mm]

$$s = \begin{bmatrix} 0 & 0 & 0 & 0 & s_{15} & 0 \\ 0 & 0 & 0 & s_{15} & 0 & 0 \\ s_{31} & s_{31} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & 0 & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

D_{2d} [4̄2m]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{36} \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Trigonal crystals

C_3 [3]

$$s = \begin{bmatrix} s_{11} & -s_{11} & 0 & s_{14} & s_{15} & s_{16} \\ s_{16} & -s_{16} & 0 & s_{15} & -s_{14} & -s_{11} \\ s_{31} & s_{31} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

D_3 [32]

$$s = \begin{bmatrix} s_{11} & -s_{11} & 0 & s_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -s_{14} & -s_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

C_{3v} [3m]

$$s = \begin{bmatrix} 0 & 0 & 0 & 0 & s_{15} & s_{16} \\ s_{16} & -s_{16} & 0 & s_{15} & 0 & 0 \\ s_{31} & s_{31} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & 0 & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

Hexagonal crystals

C_6 [6]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & s_{15} & 0 \\ 0 & 0 & 0 & s_{15} & -s_{14} & 0 \\ s_{31} & s_{31} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

C_{3h} [6̄]

$$s = \begin{bmatrix} s_{11} & -s_{11} & 0 & 0 & 0 & s_{16} \\ s_{16} & -s_{16} & 0 & 0 & 0 & -s_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad a = 0$$

D_6 [622]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -s_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

C_{6v} [6mm]

$$s = \begin{bmatrix} 0 & 0 & 0 & 0 & s_{15} & 0 \\ 0 & 0 & 0 & s_{15} & 0 & 0 \\ s_{31} & s_{31} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & 0 & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

D_{3h} [6̄m2]

$$s = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & s_{16} \\ s_{16} & -s_{16} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad a = 0$$

Cubic crystals

T [23]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{14} \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{14} \end{bmatrix}$$

O [432]

$$s = 0 \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{14} \end{bmatrix}$$

T_d [4̄3m]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & s_{14} \end{bmatrix} \quad a = 0$$

Textures

C_∞ [∞]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & s_{15} & 0 \\ 0 & 0 & 0 & s_{15} & -s_{14} & 0 \\ s_{31} & s_{31} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

$C_{\infty v}$ [∞m]

$$s = \begin{bmatrix} 0 & 0 & 0 & 0 & s_{15} & 0 \\ 0 & 0 & 0 & s_{15} & 0 & 0 \\ s_{31} & s_{31} & s_{33} & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & 0 & a_{15} & 0 \\ 0 & 0 & 0 & -a_{15} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix}$$

D_∞ [∞2]

$$s = \begin{bmatrix} 0 & 0 & 0 & s_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -s_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{36} \end{bmatrix}$$

Isotropic media

[∞∞]

$$s = 0 \quad a = \begin{bmatrix} 0 & 0 & 0 & a_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & a_{14} & 0 \\ 0 & 0 & 0 & 0 & 0 & a_{14} \end{bmatrix}$$

It is now of interest to ask what symmetry properties a molecule must have in order to show optical non-linearity when randomly distributed in the liquid phase. It follows from the form of the a matrix for the $\infty \infty$ class that any coefficients a_{ij} other than a_{14}, a_{25}, and a_{36} which occur for a molecule in the standard orientation are "washed out" in the averaging which occurs when the molecules are distributed with random orientations. Only molecules having nonzero values of a_{14}, a_{25}, or a_{36} can therefore show nonlinearities in the liquid phase.

Consider further a molecule having coefficients a_{14}, a_{25}, and a_{36} referred to laboratory-fixed axes. After an arbitrary rotation, the quadratic polarization will be given by $P_x' = (a_{14}/2)(E_y'F_z' - E_z'F_y')$ and similar expressions for P_y' and P_z', where the primed quantities refer to axes fixed to the molecule. The P_i', E_i', and F_i' can be written as functions of the P_i, E_i, and F_i referred to laboratory-fixed axes in terms of the Eulerian angles.[14] When the Eulerian angles are averaged over all orientations of the molecule, one obtains

$$P = [(a_{14} + a_{25} + a_{36})/6] E \times F. \tag{3}$$

The quantity $a_{14} + a_{25} + a_{36}$ is a pseudoscalar property of the molecule; it can be shown that this quantity, which is equal to $X_{123} + X_{231} + X_{312} - X_{132} - X_{213} - X_{321}$ is the only scalar invariant of the general third-rank tensor.

It follows that a necessary and sufficient condition for nonlinear optical properties to be *allowed* in the liquid phase is that $a_{14} + a_{25} + a_{36} \neq 0$. By inspection of Table I, the symmetry requirement can be stated as follows: Molecules can have nonlinear optical properties in the liquid phase if they possess no center of symmetry, no mirror plane, and no reflection axes. (Note that a center of symmetry and a mirror plane are equivalent to one- and twofold reflection axes.) The symmetry requirement for nonlinear optical properties is therefore identical with the symmetry requirement for optical activity in liquids.[15]

The requirements on molecules stated above are obviously the same as those on the crystal symmetry of individual crystallites in a random polycrystalline medium. In many kinds of polycrystalline matter, however, the crystallite size will be of the order of magnitude of an optical wavelength or greater, in which case the assumption of microscopic random orientation is invalid.

III. MIXING OF LIGHT BEAMS IN LIQUIDS

In this section, the mixing of two plane waves in a liquid is described phenomenologically. The description given here applies equally well to gases and optically isotropic polycrystalline matter. In this discussion, we ignore, for simplicity, the rotation of the plane of polarization due to optical activity and assume that the light is linearly polarized. From Sec. II, the nonlinear polarization can be written vectorially as

$$P(r,t) = (a_{14}/2) E_1 \times E_2, \tag{4}$$

where E_1 and E_2 are fields at frequencies ω_1 and ω_2, and the dispersion of a_{14} has been ignored for the moment. The fields may be written in the form

$$E_1 = (E_{1||} + E_{1\perp})e^{(\omega_1 t - k_1 \cdot r)} + c.c.,$$
$$E_2 = (E_{2||} + E_{2\perp})e^{i(\omega_2 t - k_2 \cdot r)} + c.c., \tag{5}$$

[14] H. Margenau and G. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Inc., Princeton, New Jersey, 1956), 2nd ed., pp. 286–289.
[15] E. L. Eliel, *Stereochemistry of Carbon Compounds* (McGraw-Hill Book Company, Inc., New York, 1962), p. 9 ff.

where the $\parallel$ and $\perp$ subscripts refer to transverse components of the electric field parallel and perpendicular, respectively, to the plane of interaction (IP) defined by the propagation vectors k_1 and k_2. The transverse components of nonlinear polarization have the form

$$P = (P_{+||} + P_{+\perp})e^{i(\omega_+ t - k_+ \cdot r)}$$
$$+ (P_{-||} + P_{-\perp})e^{i(\omega_- t - k_- \cdot r)} + c.c. \tag{6}$$

In Eq. (6), $\omega_\pm = \omega_1 \pm \omega_2$ and $k_\pm = k_1 \pm k_2$. We ignore, in what follows, the longitudinal components of P, since they do not couple to the radiation field at ω_+ and ω_-. Let φ represent the angle between k_1 and k_2. After some straightforward vector manipulation, one obtains Eqs. (7):

$$P_{+||} = \frac{a_{14}}{2} \sin\varphi \left(E_{1||}E_{2\perp}\frac{k_2}{k_+} + E_{1\perp}E_{2||}\frac{k_1}{k_+} \right),$$

$$P_{+\perp} = (a_{14}/2) \sin\varphi E_{1||}E_{2||},$$

$$P_{-||} = \frac{a_{14}'}{2} \sin\varphi \left(-E_{1||}E_{2\perp}^*\frac{k_2}{k_-} + E_{1\perp}E_{2||}^*\frac{k_1}{k_-} \right), \tag{7}$$

$$P_{-\perp} = (a_{14}'/2) \sin\varphi E_{1||}E_{2||}^*.$$

In general, a_{14} and a_{14}' will be different, since the set of frequencies in the sum frequency experiment is not the same as in the difference frequency experiment (Sec. IV). If both incident beams are plane polarized parallel to the IP, the sum and difference radiation will be polarized perpendicular to the IP. If one beam is polarized parallel to IP and the other perpendicular, the sum and difference radiation will be polarized parallel to the IP. The sum and difference radiation disappears when the two beams are parallel, since the nonlinear polarization is then completely longitudinal.

The problem of radiation from a plane-wave polarization distribution as described by Eq. (6) is treated fully in Refs. 3–6. Equation (6) may easily be generalized to the case of sum and difference frequency generation in anisotropic noncentrosymmetric crystals; however, for this case the contributions from A_{ijk} may often be masked by larger effects of S_{ijk}.

IV. QUANTUM-MECHANICAL DESCRIPTION

We derive here a quantum-mechanical expression for the part of the second-order polarizability responsible for the nonlinear optical properties of liquids; this expression will be found to have a close relationship to the analogous expression for optical rotatory power and allows a crude estimate of nonlinear optical polarizability in liquids.

In the electric-dipole approximation,[16] the perturbation energy of a molecule in an applied local field,

$$E = E_1 e^{i\omega_1 t} + E_2 e^{i\omega_2 t} + c.c., \tag{8}$$

[16] P. A. Franken and J. F. Ward, Rev. Mod. Phys. 35, 23 (1963).

is given by

$$H' = -e\mathbf{E}\cdot\mathbf{r} = H_1 e^{i\omega_1 t} + H_2 e^{i\omega_2 t} + \text{c.c.},\qquad(9)$$

where

$$H_1 = -e(E_{x1}x + E_{y1}y + E_{z1}z)$$

and

$$H_2 = -e(E_{x2}x + E_{y2}y + E_{z2}z).$$

We denote the wave functions of the unperturbed states by u_i and discuss a molecule originally in a state with wave function u_g. The wave function of the perturbed molecule can be written

$$\psi_g = u_g e^{-i\omega_g t} + \sum_k a_k^{(1)} u_k e^{-i\omega_k t} + \sum_m a_m^{(2)} u_m e^{-i\omega_m t},\quad(10)$$

where $\omega_k = W_k/\hbar$. The coefficients $a_k^{(1)}$ and $a_m^{(2)}$ are calculated from Eq. (9) with the aid of standard first- and second-order perturbation theory. Let $\mathbf{p}_\pm$ represent the components of the expectation value of polarization at frequencies $\omega_+ = \omega_1 + \omega_2$ and $\omega_- = \omega_1 - \omega_2$. The nonlinear polarization has the form

$$\mathbf{p} = \langle\psi^*|e\mathbf{r}|\psi\rangle = \mathbf{p}_+ e^{i\omega_+ t} + \mathbf{p}_- e^{i\omega_- t} + \text{c.c.}\qquad(11)$$

In Eq. (11), terms of frequency 0, $2\omega_1$, and $2\omega_2$ are ignored, since they make no contribution to the antisymmetric polarizability. We reproduce here only antisymmetric terms of the type a_{14}, a_{25}, and a_{36}; as discussed in Sec. II, all other terms vanish in the averaging over random orientations. The term p_{x+} has the form

$$p_{x+} = \frac{e^3}{2\hbar^2}(E_{y1}E_{z2} - E_{z1}E_{y2})\sum_{mk}\left\{x_{gm}(y_{kg}z_{mk} - z_{kg}y_{mk})\left[\frac{1}{(\omega_{kg}+\omega_1)(\omega_{mg}+\omega_+)} - \frac{1}{(\omega_{kg}+\omega_2)(\omega_{mg}+\omega_+)}\right]\right.$$

$$+ x_{mg}(y_{kg}z_{mk} - z_{kg}y_{mk})\left[\frac{1}{(\omega_{kg}-\omega_1)(\omega_{mg}-\omega_+)} - \frac{1}{(\omega_{kg}-\omega_2)(\omega_{mg}-\omega_+)}\right]$$

$$\left.+ x_{km}(y_{kg}z_{mg} - z_{kg}y_{mg})\left[\frac{1}{(\omega_{kg}-\omega_1)(\omega_{mg}+\omega_2)} - \frac{1}{(\omega_{kg}-\omega_2)(\omega_{mg}+\omega_1)}\right]\right\}.\qquad(12)$$

Expressions for p_{y+} and p_{z+} can be obtained from Eq. (12) by cyclic permutations of x, y, and z. The macroscopic nonlinear polarization is defined by

$$\mathbf{P} = \mathbf{P}_+ e^{i\omega_+ t} + \mathbf{P}_- e^{i\omega_- t} + \text{c.c.}\qquad(13)$$

As discussed in Sec. II, $\mathbf{P}$ is obtained by averaging the coefficients appearing in p_x, p_y, and p_z and summing over the N molecules per unit volume. The result for $\mathbf{P}_+$ is found to be

$$\mathbf{P}_+ = \chi_{NL+}\mathbf{E}_1 \times \mathbf{E}_2,\qquad(14)$$

where

$$\chi_{NL+} = \frac{N}{6\hbar^2}\frac{n_+^2+2}{3}\sum_{mk}\left[\left(\frac{1}{\omega_{mg}+\omega_+}\right)\left(\frac{1}{\omega_{kg}+\omega_1} - \frac{1}{\omega_{kg}+\omega_2}\right)\mathbf{u}_{gm}^e\cdot(\mathbf{u}_{kg}^e\times\mathbf{u}_{mk}^e)\right.$$

$$+ \left(\frac{1}{\omega_{mg}-\omega_+}\right)\left(\frac{1}{\omega_{kg}-\omega_1} - \frac{1}{\omega_{kg}-\omega_2}\right)\mathbf{u}_{mg}^e\cdot(\mathbf{u}_{kg}^e\times\mathbf{u}_{mk}^e)$$

$$\left.+ \left(\frac{1}{(\omega_{mg}+\omega_2)(\omega_{kg}-\omega_1)} - \frac{1}{(\omega_{mg}+\omega_1)(\omega_{kg}-\omega_2)}\right)\mathbf{u}_{km}^e\cdot(\mathbf{u}_{kg}^e\times\mathbf{u}_{mg}^e)\right].\qquad(15)$$

In Eq. (15), the electric-dipole moment operator $e\mathbf{r}$ has been written as $\mathbf{u}^e$. The effect on the linear polarization at adjoining sites of the local fields due to the nonlinear polarization has been taken into account by the Lorentz correction $(n_+^2+2)/3$, where n_+ is the refractive index at ω_+.[3] The local fields $\mathbf{E}$ appearing in Eqs. (8)–(14) are related to the macroscopic applied fields $\mathbf{E}^M$ appearing in Maxwell's equations by Eq. (16).

$$E_i = [(n_i^2+2)/3]E_i^M.\qquad(16)$$

As shown by Eq. (15), the nonlinear polarizability has the following properties. (1) χ_{NL} involves products of three electric-dipole matrix elements and must vanish for molecules having a center of symmetry. (2) χ_{NL} includes a vector cross product and is therefore a pseudoscalar. Since $\mathbf{E}_1 \times \mathbf{E}_2$ is an axial vector, $\mathbf{P}$ is a polar vector. (3) $\mathbf{E}_1 \times \mathbf{E}_2$ and χ_{NL} are antisymmetric with respect to interchange of ω_1 and ω_2; $\mathbf{P}$ is symmetric. (4) In the limit $\omega_1 \rightarrow \omega_2$, χ_{NL} becomes proportional to $(\omega_1 - \omega_2)$ and vanishes when $\omega_1 = \omega_2$. This result is expected from the symmetry discussion in Sec. I. (5) The molecule which is the mirror image of the molecule described by Eq. (15) has χ_{NL} of opposite sign, since χ_{NL} is a pseudoscalar. A racemic solution

containing $N/2$ molecules of each optical isomer will therefore have vanishing **P**. The quantity **P**$_-$ is given by an expression similar to **P**$_+$ and vanishes in the limit $\omega_1 \rightarrow 2\omega_2$, since the difference frequency experiment $2\omega_2 - \omega_2 \rightarrow \omega_2$ is just the inverse of the forbidden harmonic generation experiment.

A crude estimate of the magnitude of χ_{NL} can be obtained from a comparison of Eq. (15) with the quantum-mechanical expression[17] for the optical rotatory power of a liquid, Eq. (17):

$$\Phi = \frac{32\pi^3}{3} \frac{Nc}{\lambda^2 \hbar} \frac{n^2+2}{3} \text{Im} \sum_k \frac{\mathbf{u}_{gk}{}^e \cdot \mathbf{u}_{kg}{}^m}{\omega_{kg}{}^2 - \omega^2}. \quad (17)$$

In Eq. (17), Im stands for "the imaginary part of"; Φ is the optical rotatory power in rad cm^{-1} for molecules in the state g; λ is the optical wavelength in the liquid; c is the velocity of light; and $\mathbf{u}^m$ is the magnetic-dipole-moment operator $(e/2mc)(\mathbf{r}\times\mathbf{p})$, where $\mathbf{p}$ is the electron momentum operator.

Certain similarities between Eqs. (15) and (17) will be apparent. Equation (17) shows that a state k can contribute to the optical rotatory power only if connected to the ground state by both electric- and magnetic dipole moments. When an inversion center occurs, either $\mu_{gk}{}^e$ or $\mu_{kg}{}^m$ must vanish for all states k, since parity is defined. Now the dissymmetry in molecules is not strong. For a strongly allowed transition in an optically active molecule, the large value of μ^e is generally accompanied by a relatively small magnetic-dipole moment. For a transition which is weakly allowed because of a selection rule arising from approximate inversion symmetry, the small μ^e is accompanied by a large μ^m. It is a well-established empirical fact that $\mu^e\mu^m$ has about the same value for both weak and strong transitions in optically active molecules.[17]

For purposes of comparison with Eq. (15), suppose that the transition gK in the optically active molecule is strongly magnetic dipole allowed, but, as a result of approximate inversion symmetry, has only a small electric-dipole moment $\mu_{gK}{}^e$. Since g and K have the same parity (in the absence of the dissymmetry), there will, in general, exist intermediate states m for which $\mu_{gm}{}^e$ and $\mu_{mK}{}^e$ have fully allowed values. In the approximation that the state K accounts for the bulk of the optical rotatory power, we write

$$\Phi \approx \frac{32\pi^2}{3} \frac{Nc}{\lambda^2 \hbar} \frac{n^2+2}{3} \text{Im}\left(\frac{\mathbf{u}_{gK}{}^e \cdot \mathbf{u}_{Kg}{}^m}{\omega_{Kg}{}^2 - \omega^2}\right). \quad (18)$$

In Eq. (15), we make the approximation that the state K also accounts for the major part of χ_{NL}, and we represent the intermediate states m described above by a single equivalent state M connected to both K and g by

fully allowed values of μ^e. In this approximation,

$$\chi_{NL+} \approx \frac{N}{6\hbar^2} \frac{n_+{}^2+2}{3}\left(\frac{1}{\omega_{Mg}-\omega_+}\right)$$

$$\times \left(\frac{1}{\omega_{Kg}-\omega_1} - \frac{1}{\omega_{Kg}-\omega_2}\right)\mathbf{u}_{Mg}{}^e \cdot (\mathbf{u}_{Kg}{}^e \times \mathbf{u}_{MK}{}^e). \quad (19)$$

For comparison of the magnitudes of Φ and χ_{NL+}, we set the energy denominators equal, i.e.,

$$\frac{1}{\omega_{Kg}{}^2 - \omega^2} \approx \frac{1}{\omega_{Mg}-\omega_+}\left(\frac{1}{\omega_{Kg}-\omega_1} - \frac{1}{\omega_{Kg}-\omega_2}\right).$$

We notice that in the ratio of χ_{NL} to Φ the small and unknown matrix element $\mu_{Kg}{}^e$ disappears, since it appears linearly in both quantities. From Eqs. (18) and (19), the ratio is

$$\chi_{NL+}/\Phi \approx (\mu^e)^2\lambda^2/64\pi^3\mu^m\hbar c. \quad (20)$$

Taking $\lambda = 6\times10^{-5}$ cm, $\mu^e = 2.5\times10^{-18}$, and $\mu^m = 1.0 \times 10^{-20}$ cgs units, we obtain

$$\chi_{NL+} = 3.6\times10^{-11}\phi. \quad (21)$$

Consider a strongly optically active pure liquid such as nicotine.[18] The specific rotation for sodium light is $[\alpha] = -162$ deg decimeter^{-1} gm^{-1} cm^3, and the optical rotatory power is $\Phi = 2.8\times10^{-1}$ rad cm^{-1}. The expected magnitude of χ_{NL+} is 1.0×10^{-11} cgs units. Higher values of χ_{NL+} will be expected as ω_+ approaches the first electronic transition. This value is smaller by about two orders of magnitude than the value of χ_{NL} in KDP,[19] but larger by two orders than the effective value of χ_{NL} occurring in centrosymmetric media as a result of magnetic dipole and quadrupole nonlinearities.[7,8] On the basis of the experimental observation[9] of third harmonics in media without phase matching,[20] we conclude that sum and difference frequencies in strongly optically active liquids should easily be detectable.

V. MOLECULAR MODEL

The simplest molecular model which can give rise to nonlinear optical properties in the liquid or gaseous phase is one consisting of a single electron in an appropriate asymmetric and anharmonic potential. Consider the potential

$$V = \frac{1}{2}(k_a x^2 + k_b y^2 + k_c z^2) + Axyz. \quad (22)$$

The quadratic terms represent the most general harmonic potential and contain both mirror planes and a

[17] E. U. Condon, Rev. Mod. Phys. **9**, 432 (1937).

[18] *Handbook of Chemistry and Physics*, edited by C. D. Hodgman (Chemical Rubber Publishing Company, Cleveland, Ohio, 1960), 42nd ed., p. 1120.

[19] A. Ashkin, G. D. Boyd, and J. M. Dziedzic, Phys. Rev. Letters **11**, 14 (1963).

[20] J. A. Giordmaine, Phys. Rev. Letters **8**, 18 (1962); P. D. Maker, R. W. Terhune, M. Nisenoff, and C. M. Savage, *ibid.* **8**, 21 (1962).

center of symmetry. The cubic term must be selected to allow the total potential to satisfy the symmetry requirements given in Sec. II. Terms of the form x^3 or x^2y leave mirror planes while removing the center of symmetry; combinations of terms such as (Ax^2y+By^2z) satisfy all the symmetry requirements but introduce nonlinearities only in a higher order of approximation than a single term of the proper symmetry. The only single cubic term capable of removing all mirror planes from the harmonic potential is $Axyz$. Notice that the k_i must be all different to avoid mirror planes. The same potential has been discussed by Condon, Altar, and Eyring[21] as a model for optically active molecules, and further description of its properties is given in Ref. 21.

In this section, we make a semiclassical calculation of the nonlinear polarization produced in molecules described by the potential of Eq. (22). The calculation has the merit of displaying the important features of the nonlinear polarization of a liquid in explicit form. The parameters in Eq. (22) have been identified with the potential coefficients in optically active molecules such as secondary butyl alcohol[21]; however, the predictions of optical rotatory power are usefully accurate only for optical wavelengths near the lowest electronic transition.

In the absence of the anharmonic perturbation, the wave function is a product of three harmonic oscillator wave functions having frequencies $\omega_i = (k_i/m)^{1/2}$, with $i=a, b, c$. The energy of the state $(n_1n_2n_3)$ is $W(n_1n_2n_3) = (n_1+\frac{1}{2})\hbar\omega_a + (n_2+\frac{1}{2})\hbar\omega_b + (n_3+\frac{1}{2})\hbar\omega_c$. We make the approximation that the anharmonic term is a small perturbation, in the sense that the linear response of the system to the applied fields, i.e., the response calculated by first-order perturbation theory is unaffected by the anharmonicity. The only effect of the anharmonicity is assumed to be the introduction of small components at sum and difference frequencies to the expectation values of x, y, and z.

Consider that the electron is initially in the state $(n_1n_2n_3)$ which we denote g. We calculate first the z component of polarization at ω_+ and ω_- as a result of fields at frequency ω_1 and ω_2 applied in the xy plane. The perturbation energy associated with the applied fields is given in the electric dipole approximation by Eqs. (8) and (9), and the perturbed wave function ψ_g by Eq. (10).

In line with our assumption that the linear response is unaffected by the anharmonicity we make the approximation that $Axyz \approx A\langle xy\rangle z$, where

$$\langle xy\rangle = \langle \psi^*|xy|\psi\rangle = \langle xy\rangle^+ e^{i\omega_+ t} + \langle xy\rangle^- e^{i\omega_- t} + \text{c.c.} \quad (23)$$

From Eqs. (8), (9), (10), and (23), we obtain after a straightforward calculation the result

$$\langle xy\rangle^+ = -\frac{e^2}{2\hbar^2}\sum_{mk}(E_{x1}E_{y2}-E_{y1}E_{x2})\{[x_{kg}y_{mk}(xy)_{gm}-x_{mk}y_{kg}(xy)_{gm}]$$

$$\times\left(\frac{1}{(\omega_1+\omega_{kg})(\omega_++\omega_{mg})}-\frac{1}{(\omega_2+\omega_{kg})(\omega_++\omega_{mg})}\right)+[x_{kg}y_{mg}(xy)_{km}-x_{mg}y_{kg}(xy)_{km}]$$

$$\times\left(\frac{1}{(-\omega_1+\omega_{kg})(\omega_2+\omega_{mg})}-\frac{1}{(-\omega_2+\omega_{kg})(\omega_1+\omega_{mg})}\right)+[x_{kg}y_{mk}(xy)_{mg}-x_{mk}y_{kg}(xy)_{mg}]$$

$$\times\left(\frac{1}{(-\omega_1+\omega_{kg})(-\omega_++\omega_{mg})}-\frac{1}{(-\omega_2+\omega_{kg})(-\omega_++\omega_{mg})}\right)\} \quad (24)$$

and a similar expression for $\langle xy\rangle^-$. In Eq. (11), only the part of $\langle xy\rangle^+$ antisymmetric in $E_{x1}E_{y2}$ and $E_{y1}E_{x2}$ has been retained. For an electron in state $g(n_1n_2n_3)$, the summation over m and k extends over the eight states $[(n_1\pm1)n_2n_3]$, $[n_1(n_2\pm1)n_3]$, and $[(n_1\pm1)(n_2\pm1)n_3]$. The matrix elements have the form

$$\langle (n_1+1)n_2n_3|x|n_1n_2n_3\rangle = [(\hbar\omega_a/2k_a)(n_1+1)]^{1/2},$$

$$\langle (n_1+1)(n_2-1)n_3|xy|n_1n_2n_3\rangle = [(\hbar^2\omega_a\omega_b/4k_ak_b)(n_1+1)n_2]^{1/2}, \text{ etc.}$$

Summation over the 24 nonzero combinations of m and k in Eq. (24) leads to the result

$$\langle xy\rangle^+ = \frac{e^2}{2m^2}\left[\frac{1}{(\omega_1^2-\omega_a^2)(\omega_2^2-\omega_b^2)}-\frac{1}{(\omega_1^2-\omega_b^2)(\omega_2^2-\omega_a^2)}\right](E_{x1}E_{y2}-E_{y1}E_{x2}). \quad (25)$$

We notice that $\langle xy\rangle^+$ is independent of the original state $(n_1n_2n_3)$ and also does not contain $\hbar$. In the presence of the perturbation $A\langle xy\rangle z$, we calculate directly from first-order perturbation theory the value of $\langle z\rangle$, with the same

[21] E. U. Condon, W. Altar, and H. Eyring, J. Chem. Phys. 5, 753 (1937).

method as above for $\langle xy \rangle$. For a molecule in state $(n_1 n_2 n_3)$, we obtain

$$\langle z \rangle = \langle z \rangle^+ e^{i\omega + t} + \langle z \rangle^- e^{i\omega - t} + \text{c.c.},$$

$$\langle z \rangle^+ = \frac{e^2}{2m^3} \frac{A}{\omega_+^2 - \omega_c^2} \left[\frac{1}{(\omega_1^2 - \omega_a^2)(\omega_2^2 - \omega_b^2)} - \frac{1}{(\omega_1^2 - \omega_b^2)(\omega_2^2 - \omega_a^2)} \right] (E_{x1} E_{y2} - E_{y1} E_{x2}). \tag{26}$$

From Eq. (13) and a similar calculation for $\langle z \rangle^-$, we find that polarization p_z has an antisymmetric component

$$p_z = \frac{e^3 A}{2m^3} \left[\frac{1}{(\omega_1^2 - \omega_a^2)(\omega_2^2 - \omega_b^2)} - \frac{1}{(\omega_1^2 - \omega_b^2)(\omega_2^2 - \omega_a^2)} \right] \left[\frac{E_{x1} E_{y2} - E_{y1} E_{x2}}{(\omega_+^2 - \omega_c^2)} e^{i\omega + t} + \frac{E_{x1} E_{y2} - E_{y1} E_{x2}}{(\omega_-^2 - \omega_c^2)} e^{i\omega - t} + \text{c.c.} \right]. \tag{27}$$

From Eq. (14), p_x and p_y can be written immediately by cyclic rearrangements of xyz and $\omega_a \omega_b \omega_c$. The polarization p calculated above refers to a particular molecule in a specified orientation. As shown in Sec. II, the volume polarization is obtained by averaging the coefficients of p_x, p_y, and p_z and summing over the N molecules cm^{-3}. The final result for the volume polarization per molecule becomes

$$\mathbf{P} = (Ne^3/6m^3) A [(\mathbf{E}_1 \times \mathbf{E}_2) F(\omega_1 \omega_2 \omega_+ \omega_a \omega_b \omega_c) e^{i\omega + t} + (\mathbf{E}_1 \times \mathbf{E}_2^*) F(\omega_1 \omega_2 \omega_- \omega_a \omega_b \omega_c) e^{i\omega - t} + \text{c.c.}], \tag{28}$$

where

$$F(\omega_1 \omega_2 \omega_\pm \omega_a \omega_b \omega_c) = \frac{1}{(\omega_\pm^2 - \omega_c^2)} \left[\frac{1}{(\omega_1^2 - \omega_a^2)(\omega_2^2 - \omega_b^2)} - \frac{1}{(\omega_2^2 - \omega_b^2)(\omega_2^2 - \omega_a^2)} \right] + [\text{two similar terms obtained by}$$

the cyclic permutations $(\omega_a \omega_b \omega_c) \rightarrow (\omega_b \omega_c \omega_a)$ and $(\omega_a \omega_b \omega_c) \rightarrow (\omega_c \omega_a \omega_b)]$. \tag{29}

It can be easily verified that this result is identical with the result of a completely classical calculation under the same assumptions. In Eqs. (28) and (29), the Lorentz and local-field corrections discussed in Sec. IV have been omitted.

The following features of the result are apparent from Eqs. (28) and (29): The function F and the expression $\mathbf{E}_1 \times \mathbf{E}_2$ are both antisymmetric in ω_1 and ω_2; the over-all expression for P is necessarily symmetric. As expected, $F(\omega_1 \omega_2 \omega_+) \rightarrow 0$ as $\omega_1 \rightarrow \omega_2$; for the difference process, $F(\omega_1 \omega_2 \omega_-) \rightarrow 0$ as $\omega_1 \rightarrow 2\omega_2$. The function F changes sign for noncyclic permutations of $\omega_a \omega_b \omega_c$, such as $\omega_a \omega_b \omega_c \rightarrow \omega_b \omega_a \omega_c$; the optical isomer having x, y, and z characteristic frequencies ω_b, ω_a, and ω_c will produce an opposite volume polarization in the liquid phase. It follows that a racemic solution, containing equal concentrations of the two isomers will produce no net nonlinear polarization; this result is expected, since the racemic solution is identical with its mirror image, having the symmetry $\infty \infty m$. As expected $F \rightarrow 0$ for each of the limits $\omega_a \rightarrow \omega_b$, $\omega_b \rightarrow \omega_c$, $\omega_c \rightarrow \omega_a$, since in each limit the molecule acquires a mirror plane. The symmetry conditions of Bloembergen et al.[3] are satisfied for cyclic permutations of the indices and frequencies, since $F(\omega_1 \omega_2 \omega_+) = F(\omega_+ \omega_1 \omega_2) = F(\omega_2 \omega_+ \omega_1)$.

A large value of the cubic coefficient A, as well as substantial differences among ω_a, ω_b, and ω_c, lead to large values of optical activity, as well as strong nonlinear optical effects. It follows that for molecules in which this single-electron model of both processes is relevant, a large nonlinear optical coefficient will accompany a strong optical activity. This result is expected from the more general discussion of Sec. IV.

VI. CONCLUSION

It appears that detectable sum and difference frequency generation should occur in optically active liquids, as well as in other noncentrosymmetric materials having a high degree of rotational symmetry in which second-harmonic generation is forbidden. The magnitude of the effect will be substantially less than in piezoelectric crystals, although much greater than residual nonlinear polarization in centrosymmetric media. Although the techniques of phase matching in anisotropic crystals are not available in liquids, it should be remembered that phase-matching solvents for optically active liquids are conceivable. Dyes having sufficiently narrow absorption bands with high oscillator strength between the frequencies ω_1, ω_2, and ω_+ introduce dispersion in the proper direction to decrease the phase mismatch in the mixing process.

The nonlinearities responsible for sum and difference frequencies in liquids usually arise from highly localized and identifiable features of organic molecules, for example, an asymmetric carbon atom. The magnitude and spectrum of the nonlinear optical effects may provide configuration information supplementing that available from optical activity and optical rotatory dispersion measurements.