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Quantum Theory of the Optical Kerr Effect

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A quantum theory of the optical Kerr effect is developed using the density-matrix formalism. The classical theory of Bloembergen and Lallemand for liquids can be deduced from the result obtained quantum mechanically in the present study with certain approximations. The anisotropic term in the optical Kerr effect is shown to arise quantum mechanically from both the population change due to the high-frequency Stark effect and the change in the unperturbed matrix element due to the radiation field.

I. INTRODUCTION

RECENTLY, many anomalies in the stimulated Raman scattering, such as anomalous gain, frequency broadening, and angular distribution, were explained in terms of the intensity-induced increase in refractive index and the resulting self-focusing effect.[1–4] The self-focusing effect was shown to come from the Kerr effect induced by an electric field with optical frequencies (optical Kerr effect) except in media with small Kerr effect, where the electrostriction is dominant.[5,6] Although the term "Kerr effect" is usually taken to mean that an isotropic medium becomes birefringent as an electric field is applied, in the present paper we use this term in a wide sense, i.e., we mean the intensity-dependent change in refractive index (the change due to electrostriction is excluded). The optical Kerr effect (OKE) was presented in classical formulations first by Buckingham[7] and then by Bloembergen and Lallemand.[3] After the development of lasers, several authors observed OKE experimentally.[8,9]

The theory of the static Kerr effect was investigated from both the classical[10–12] and the quantum-mechanical[13–17] point of view many years ago. It was shown that the anisotropic[10] and the Voigt[11] terms exist in nonpolar molecules, while in addition the polar[12] term exists in polar molecules. The anisotropic term corresponds to the change in the distribution function for the molecule. The Voigt term, by which we mean the purely electronic contribution to the Kerr effect, is much smaller than the anisotropic term in the static Kerr effect.[15,16] "Voigt" is used in this paper with this meaning because Voigt[11] originally considered the change in refractive index due to the level shift induced by the static field. The permanent dipole moment cannot follow the change with optical frequency, so that only the anisotropic and Voigt terms have to be considered in OKE for both nonpolar and polar molecules. The Voigt term must be taken into account, because any two-quantum resonance, such as the vibrational Raman resonance or the electronic resonance, will make it large. The purpose of the present paper is to show the results of a quantum-mechanical treatment of OKE corresponding to both the anisotropic and Voigt terms. The classical theory of Bloembergen and Lallemand is examined in the light of quantum theory. The quantum-mechanical origin of the anisotropic term is investigated by taking all orders of perturbation of suitable density matrices.

II. GENERAL FORMULATION FOR THE OPTICAL KERR POLARIZATION

Since molecules in gases, liquids, and some solids more or less have freedom in their spatial motions, they orient randomly in space. Thus only statistical characteristics of molecules are important in dealing with OKE. Such characteristics can be evaluated by means of a suitable hermitian density matrix. The change in the density matrix ρ with time is given by the Liouville equation in the interaction representation,

$$i\hbar(\partial\rho/\partial t)=[H,\rho]. \qquad (1)$$

In Eq. (1), ρ and the perturbation Hamiltonian H are defined in terms of the corresponding Schrödinger operators ρ_S and H_S as

$$\rho=\exp(i\hbar^{-1}H_0t)\rho_S\exp(-i\hbar^{-1}H_0t),$$
and
$$H=\exp(i\hbar^{-1}H_0t)H_S\exp(-i\hbar^{-1}H_0t), \qquad (2)$$

where H_0 is the unperturbed Hamiltonian of the molecule. The formal solution of Eq. (1) can be written

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as

$$\rho = U\rho^0 U^\dagger , \tag{3}$$

$$U = \exp\left(-i\hbar^{-1}\int_0^t H dt\right) = 1 + \sum_{l=1}^{\infty} U^{(l)} , \tag{4}$$

and

$$U^{(l)} = (i\hbar)^{-l}\int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{l-1}} dt_l \times [H(t_1)H(t_2)\cdots H(t_l)] , \tag{5}$$

where $U^\dagger$ is the Hermitian adjoint operator to U. Unperturbed molecules are assumed to be in thermal equlibrium at temperature T:

$$\rho^0 = \exp(-H_0/kT) . \tag{6}$$

In the electric-dipole approximation, H takes the form

$$H = -e\mathbf{r}\cdot\mathbf{E} , \tag{7}$$

where $e\mathbf{r}$ and $\mathbf{E}$ are the dipole-moment operator and the macroscopic electric field, respectively. By iteration the density matrix of the lth order in $\mathbf{E}$, $\rho^{(l)}$ can be expressed in terms of the $(l-1)$th-order matrix $\rho^{(l-1)}$ by the equation

$$i\hbar(\partial\rho^{(l)}/\partial t) = [H, \rho^{(l-1)}] . \tag{8}$$

The expectation value for the polarization of the molecule is given by

$$\mathbf{P} = NL(\mathrm{Tr}(e\mathbf{r}\rho)/\mathrm{Tr}\rho) , \tag{9}$$

where N is the number of molecules per cm^3 and L is the local-field correction. $1/\mathrm{Tr}\rho$ in Eq. (9) can be expanded as a power series of $\mathbf{E}$ as

$$\frac{1}{\mathrm{Tr}\rho} = \frac{1}{\mathrm{Tr}\rho^0} - \frac{\mathrm{Tr}\rho^{(1)}}{(\mathrm{Tr}\rho^0)^2} - \frac{\mathrm{Tr}\rho^{(2)}}{(\mathrm{Tr}\rho^0)^2} + \frac{(\mathrm{Tr}\rho^{(1)})^2}{(\mathrm{Tr}\rho^0)^3} + \cdots . \tag{10}$$

Equation (3) can be evaluated most conveniently by utilizing the following complex representation. The Fourier components of H, ρ, $\mathbf{E}$, and $\mathbf{P}$ at frequency ω can be divided into two parts:

$$\begin{aligned} H(\omega) &= H^{\omega}e^{-i\omega t} + H^{-\omega}e^{i\omega t} , \\ \rho(\omega) &= \rho^{\omega}e^{-i\omega t} + \rho^{-\omega}e^{i\omega t} , \\ \mathbf{E}(\omega) &= \tfrac{1}{2}(\mathbf{E}^{\omega}e^{-i\omega t} + \mathbf{E}^{-\omega}e^{i\omega t}) , \end{aligned} \tag{11}$$

and

$$\mathbf{P}(\omega) = \tfrac{1}{2}(\mathbf{P}^{\omega}e^{-i\omega t} + \mathbf{P}^{-\omega}e^{i\omega t}) ,$$

where $(H^{\omega})^* = H^{-\omega}$ and similar equations hold for ρ^{ω}, $\mathbf{E}^{\omega}$, and $\mathbf{P}^{\omega}$.

Now we take the representation where the unperturbed Hamiltonian H_0 is diagonal. Since the unperturbed states of the molecule in gases can be specified by the electronic and/or vibrational quantum number n, the rotational quantum number j, and the magnetic quantum number m, the Schrödinger equation for the unperturbed molecule is written as

$$H_0|njm\rangle = E_{nj}|njm\rangle . \tag{12}$$

The energy-level separations specified by the quantum number n are usually much larger than kT, and those specified by quantum numbers j and m are much smaller than kT.[18] In this sense we may, therefore, divide all the levels into "high" and "low" energy levels. This division was first introduced by Van Vleck.[19] The terms "excited state" and "ground state" are used throughout the present paper instead of Van Vleck's "high" and "low" levels. Thus the ground state does not involve any vibrationally excited levels. In liquids, molecular interactions such as association cause hindered rotation, which may partially lift the spatial degeneracy and more or less alter the physical meanings of j and m.[20] The permanent dipole moment cannot follow the changes with optical frequency, so that $\mathbf{r}$ is assumed to have no matrix element diagonal in n, i.e.,

$$\begin{aligned} \langle njm|\mathbf{r}|n'j'm'\rangle &= \langle n'j'm'|\mathbf{r}|njm\rangle \\ &= (1-\delta_{nn'})\langle njm|\mathbf{r}|n'j'm'\rangle . \end{aligned} \tag{13}$$

OKE is a response of the molecule to the third and higher odd powers of the electric field. The optical Kerr polarization at ω_S' due to the presence of the fields at ω_S, ω_1, and ω_2 is expressed by

$$\mathbf{P}^{\omega_S'} = \chi \vdots \mathbf{E}^{\omega_S}\mathbf{E}^{\omega_1}\mathbf{E}^{\omega_2 *} + \text{higher odd-order terms} , \tag{14}$$

where $\omega_1 > \omega_2$, $|\omega_S - \omega_2| \gg |\omega_1 - \omega_2|$, $\omega_S' = \omega_S + \omega_1 - \omega_2$, and χ is the fourth-rank Kerr susceptibility tensor. In Eq. (14) the refractive index at ω_S is assumed to change under the influence of the fields at ω_1 and ω_2. Thus the incident electric field $\mathbf{E}$ should be expressed as

$$\mathbf{E} = \tfrac{1}{2}(\boldsymbol{\varepsilon}_S E^{\omega_S}e^{-i\omega_S t} + \boldsymbol{\varepsilon}_L E^{\omega_1}e^{-i\omega_1 t} + \boldsymbol{\varepsilon}_L E^{\omega_2}e^{-i\omega_2 t}) + \text{complex conjugate} . \tag{15}$$

In Eq. (15) the polarization vectors of $\mathbf{E}^{\omega_1}$ and $\mathbf{E}^{\omega_2}$ are assumed to be parallel and are denoted by ϵ_L;that of $\mathbf{E}^{\omega_S}$ is denoted by ϵ_S. In an isotropic medium the ith Cartesian component of $\mathbf{P}^{\omega_S'}$ is written as[9]

$$P_i^{\omega_S'} = A'E_i^{\omega_S}E_j^{\omega_1}E_j^{\omega_2 *} + \mathrm{B}'E_j^{\omega_S}E_i^{\omega_1}E_j^{\omega_2 *} + C'E_j^{\omega_S}E_j^{\omega_1}E_i^{\omega_2 *} , \tag{16}$$

where A', B', and C' are scalar susceptibilities and can be obtained from χ by simple tensor contraction. The third-order term in Eq. (9) can be written as

$$\tfrac{1}{2}\mathbf{P}^{\omega_S'} = NL'\left[\frac{\mathrm{Tr}(e\mathbf{r}\rho^{(3)\omega_S'})}{\mathrm{Tr}\rho^0} - \frac{\mathrm{Tr}(e\mathbf{r}\rho^{(1)\omega_S})\mathrm{Tr}(\rho^{(2)(\omega_1-\omega_2)})}{(\mathrm{Tr}\rho^0)^2}\right] , \tag{17}$$

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[18] Rotational energy separations sometimes become comparable to or even larger than kT; but because of the selection rule $\Delta j = 0 \pm 1$, at most the separations between the alternate levels have to be smaller than kT.

[19] J. H. Van Vleck, Phys. Rev. **29**, 727 (1927); *The Theory of*

where use is made of the fact that because of Eq. (13), traces of odd-order density matrices do not contribute to $\mathbf{P}^{\omega_S\prime}$. In Eq. (17) the local-field correction is given by $L' \equiv L^{\omega_S} L^{\omega_1} L^{\omega_2}$, where $L^{\omega} = \frac{1}{3}(\epsilon^{\omega}+2)$ and ϵ^{ω} is the dielectric constant at ω.

For the sake of simplicity we use hereafter the new notation $a, b, c, \cdots$, and $A, B, C, \cdots$ in place of jm, $j'm'$, $j''m''$, $\cdots$ and njm, $n'j'm'$, $n''j''m''$, $\cdots$, respectively, whenever these can be used without any confusion. For example, with this new notation, Eq. (13) can be rewritten as

$$\mathbf{r}_{AB} = \mathbf{r}_{BA} = (1-\delta_{nn'})\mathbf{r}_{AB}\,, \tag{13'}$$

or simply $\mathbf{r}_{na,nb} = \mathbf{r}_{nb,na} = 0$. The trace usually means the sum of the matrix elements which are diagonal in all the quantum numbers. When traces are considered with respect to the matrix elements diagonal in j and m alone or in m alone, they are denoted by Tr_{jm} or Tr_m.

III. CALCULATION OF THE OPTICAL KERR POLARIZATION

To derive the expression for the third-order response we must first calculate the second-order density matrix. With the relation $U_{BA}{}^{\dagger} = U_{BA}{}^{*}$ the second-order matrix can be obtained from Eq. (3) as

$$\rho_{AB}{}^{(2)} = U_{AB}{}^{(2)}\rho_B{}^0 + \textstyle\sum_C U_{AC}{}^{(1)}\rho_C{}^0 U_{BC}{}^{(1)*} + \rho_A{}^0 U_{BA}{}^{(2)*}, \tag{18}$$

where $\rho_A{}^0 = \exp(-E_A/kT)$ and similar equations hold for $\rho_B{}^0$ and $\rho_C{}^0$. Now $\rho^{(2)}$ is divided into two parts such that we may assign a clear physical meaning to each:

$$\rho_{AB}{}^{(2)} = \rho_{A,nb}{}^{(2)\prime} + \rho_{AB}{}^{(2)\prime\prime}, \tag{19}$$

$$\rho_{A,nb}{}^{(2)\prime} = U_{A,nb}{}^{(2)}\rho_{nb}{}^0 + \rho_A{}^0 U_{nb,A}{}^{(2)*}, \tag{20}$$

and

$$\rho_{AB}{}^{(2)\prime\prime} = (U_{AB}{}^{(2)}\rho_B{}^0 + \rho_A{}^0 U_{BA}{}^{(2)*})(1-\delta_{nn'}) + \textstyle\sum_C U_{AC}{}^{(1)}\rho_C{}^0 U_{BC}{}^{(1)}.{}^{*} \tag{21}$$

Note that here $\rho^{(2)\prime}$ contains only matrix elements which are diagonal in quantum number n. Substituting Eqs. (5), (7), and (15) into (20) we obtain

$$\rho_{A,nb}{}^{(2)\prime(\omega_1-\omega_2)} = \sum_C \frac{e^2 r_{AC}{}^L r_{C,nb}{}^L E^{\omega_1} E^{\omega_2 *}}{4\hbar^2} \left[\frac{\rho_{nb}{}^0}{\omega_{ab}-\omega_1+\omega_2} \times \left(\frac{1}{\omega_{C,nb}-\omega_1} + \frac{1}{\omega_{C,nb}+\omega_2} \right) + \frac{\rho_A{}^0}{\omega_{ba}+\omega_1-\omega_2} \times \left(\frac{1}{\omega_{CA}+\omega_1} + \frac{1}{\omega_{CA}-\omega_2} \right) \right], \tag{22}$$

and

$$\rho_{AB}{}^{(2)(\omega_S-\omega_2)} = \sum_C \frac{e^2 E^{\omega_S} E^{\omega_2 *}}{4\hbar^2} \left[\frac{\rho_B{}^0}{\omega_{AB}+\omega_2-\omega_S} \times \left(\frac{r_{AC}{}^L r_{CB}{}^S}{\omega_{CB}-\omega_S} + \frac{r_{AC}{}^S r_{CB}{}^L}{\omega_{CB}+\omega_2} \right) + \frac{\rho_A{}^0}{\omega_{BA}-\omega_2+\omega_S} \times \left(\frac{r_{AC}{}^S r_{CB}{}^L}{\omega_{CA}+\omega_S} + \frac{r_{AC}{}^L r_{CB}{}^S}{\omega_{CA}-\omega_2} \right) \right], \tag{23}$$

where $r^L \equiv \boldsymbol{\varepsilon}^L \cdot \mathbf{r}$, $r^S \equiv \boldsymbol{\varepsilon}_S \cdot \mathbf{r}$, $\omega_{ab} = \hbar^{-1}(E_{na}-E_{nb})$, and $\omega_{C,nb} = \hbar^{-1}(E_C - E_{nb})$. Now we assume the conditions, which will be verified later,

$$\omega_1, \omega_2, \omega_S, |\omega_S-\omega_2|, |\omega_{nn'}| \gg \omega_1-\omega_2. \tag{24}$$

Then Eq. (22) can be written as

$$\rho_{A,nb}{}^{(2)\prime(\omega_1-\omega_2)} = \sum_C \frac{e^2 r_{AC}{}^L r_{C,nb}{}^L E^{\omega_1} E^{\omega_2 *}}{4\hbar^2} \times \frac{2\omega_{n''n}}{\omega_{n''n}{}^2-\omega^2} \times \frac{\rho_{nb}{}^0-\rho_A{}^0}{\omega_{ab}-\omega_1+\omega_2}. \tag{25}$$

In Eq. (25), ω is the mean value of ω_1 and ω_2, and both ω_{CA} and $\omega_{C,nb}$ are approximated by the common center frequency $\omega_{n''n}$ which is independent of the j's and m's. This approximation is valid if ω is far from resonance and the terms such as $(\omega_{CA}-\omega_1)$ are independent of the j's and m's. Expanding $\exp(-\hbar\omega_{ba}/kT)$ in a power series in $\hbar\omega_{ba}/kT$ and retaining to the first-order term, we obtain

$$\frac{\rho_{nb}{}^0-\rho_A{}^0}{\hbar(\omega_{ab}-\omega_1+\omega_2)} = \frac{\omega_{ab}}{\omega_{ab}-\omega_1+\omega_2} \times \frac{\rho_{nb}{}^0+\rho_A{}^0}{2kT}. \tag{26}$$

To introduce the damping factor phenomenologically into Eq. (25), we replace ω_{ab} by $\omega_{ab}-i\Gamma_{ab}$, where the diagonal and nondiagonal elements of Γ represent the inverses of the longitudinal and transverse relaxation times, respectively. Thus the first factor on the right side of Eq. (26) can be written as

$$\rho_{A,nb}{}^{(2)\prime(\omega_1-\omega_2)} = \sum_C \frac{e^2 r_{AC}{}^L r_{C,nb}{}^L E^{\omega_1} E^{\omega_2 *}}{4\hbar} \times \frac{2\omega_{n''n}}{\omega_{n''n}{}^2-\omega^2} \, \frac{f_{ab}(\rho_{nb}{}^0+\rho_A{}^0)}{2kT}, \tag{27}$$

where

$$f_{ab} \equiv \frac{\omega_{ab}-i\Gamma_{ab}}{\omega_{ab}-i\Gamma_{ab}-\omega_1+\omega_2}. \tag{28}$$

In liquids, strong molecular interactions cause the energy-level broadening, so that the rotational structure cannot generally be resolved except in some simple diatomic molecules. Considering this fact we may assume that $\omega_{ab}\Gamma_{ab}{}^{-1} \ll 1$. ($\omega_{ab}$ should be taken at most

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Electric and Magnetic Susceptibilities (Oxford University Press, London, 1932).

[20] The quantum theory of a hindered rotator is given by H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1948), Chap. 18.

as the alternate energy separations because of the selection rule $\Delta j=0,\ \pm1$.) Assuming further that Γ_{ab} is independent of a and b and is replaced by τ^{-1}, we may write Eq. (28) as

$$f_{ab}=1/[1-i\tau(\omega_1-\omega_2)] \tag{29}$$

for liquids. For gases the rotational level is narrow, i.e., $\omega_{ab}\Gamma_{ab}^{-1}\gg1$, so that f_{ab} can be written as

$$f_{ab}=\omega_{ab}/(\omega_{ab}-\omega_1+\omega_2)\quad\text{for}\quad j\neq j'. \tag{30}$$

In order that the magnitude of f_{ab} should be of the order of unity, the frequency $\omega_1-\omega_2$ should be at most Γ_{ab} or ω_{ab}, as is easily seen from Eqs. (29) and (30). The condition of Eq. (24) is thus verified.

To calculate the Kerr polarization we must obtain the third-order density matrix which appears in the first term on the right side of Eq. (17). From Eq. (8) the density matrix $\rho^{(3)\omega_S'}$ can be calculated by

$$i\hbar(\partial\rho^{(3)\omega_S'}/\partial t)=[H^{\omega_S},\rho^{(2)'(\omega_1-\omega_2)}]+[H^{\omega_S},\rho^{(2)''(\omega_1-\omega_2)}]$$
$$+[H^{\omega_1},\rho^{(2)(\omega_S-\omega_2)}]+[H^{-\omega_2},\rho^{(2)(\omega_S+\omega_1)}]. \tag{31}$$

For a while we consider only the first term on the right side of Eq. (31) and denote a portion of $\rho^{(3)\omega_S'}$, which corresponds to $\rho^{(2)'(\omega_1-\omega_2)}$, by $\rho^{(3)'\omega_S'}$. Then from Eq. (31) we obtain

$$i\hbar(\partial\rho^{(3)'\omega_S'}/\partial t)=[H^{\omega_S},\rho^{(2)'(\omega_1-\omega_2)}]. \tag{32}$$

We shall refer to the Kerr polarization due to $\rho^{(3)'\omega_S'}$ as the anisotropic Kerr polarization or the anisotropic term. The physical meaning of the word "anisotropic" will soon become clear in the following. By using the expression for $\rho^{(3)'\omega_S'}$, which can be obtained from Eq. (32), the first term in the brackets in Eq. (17) can be written, after relabeling the indices, as

$$\mathrm{Tr}(e\mathbf{r}\rho^{(3)'\omega_S'})=\sum_{A,B,c}\frac{e^2\mathbf{r}_{AB}r_{B,nc}{}^{S}\rho_{nc,A}{}^{(2)'(\omega_1-\omega_2)}E^{\omega_S}}{2\hbar}\times\frac{2\omega_{n'n}}{\omega_{n'n}{}^2-\omega_S{}^2}, \tag{33}$$

where $\mathbf{r}\equiv\boldsymbol{\varepsilon}r$ and $\omega_{n'n}$ is the center frequency, as before. From Eq. (16) it is immediately seen that for the special cases of $\boldsymbol{\varepsilon}_S\|\boldsymbol{\varepsilon}_L$ and $\boldsymbol{\varepsilon}_S\perp\boldsymbol{\varepsilon}_L$, the vector $\boldsymbol{\varepsilon}$ is parallel to $\boldsymbol{\varepsilon}_S$. We shall consider explicitly only these two cases of polarization and set $\mathbf{r}$ equal to $\boldsymbol{\varepsilon}_S r^S$. Other cases of polarization can be deduced from these. Now we introduce the following abbreviations:

$$\alpha_{A,nc}{}^{\omega}=\alpha_{nc,A}{}^{\omega}=\sum_B\frac{2e^2r_{AB}{}^{L}r_{B,nc}{}^{L}\omega_{n'n}}{\hbar(\omega_{n'n}{}^2-\omega^2)},$$

and

$$\beta_{A,nc}{}^{\omega_S}=\beta_{nc,A}{}^{\omega}=\sum_B\frac{2e^2r_{AB}{}^{S}r_{B,nc}{}^{S}\omega_{n'n}}{\hbar(\omega_{n'n}{}^2-\omega_S{}^2)}. \tag{34}$$

With this new notation Eq. (27) can be written as

$$\rho_{A,nb}{}^{(2)'(\omega_1-\omega_2)}=\frac{\rho_A{}^0+\rho_{nb}{}^0}{2}\times\frac{f_{ab}\alpha_{A,nb}{}^{\omega}E^{\omega_1}E^{\omega_2*}}{4kT}. \tag{35}$$

Inserting Eqs. (34) and (35) into Eq. (33), we obtain

$$\mathrm{Tr}(e\mathbf{r}\rho^{(3)'\omega_S'})$$
$$=\sum_{A,b}\frac{\boldsymbol{\varepsilon}_S\rho_A{}^0f_{ab}\alpha_{A,nb}{}^{\omega}\beta_{nb,A}{}^{\omega_S}E^{\omega_S}E^{\omega_1}E^{\omega_2*}}{8kT}. \tag{36}$$

In deriving Eq. (36) it should be noted that $\frac{1}{2}(\rho_A{}^0+\rho_{nb}{}^0)$ and $\rho_A{}^0$ contribute the same amount to the trace. (This can easily be found by relabeling the indices.)

Next we consider the second term in the brackets in Eq. (17). $NL^{\omega_S}\,\mathrm{Tr}(e\mathbf{r}^{(1)\omega_S})/\mathrm{Tr}\rho^0$ is just the linear optical polarization at ω_S and can be written as

$$NL^{\omega_S}\frac{\mathrm{Tr}(e\mathbf{r}\rho^{(1)\omega_S})}{\mathrm{Tr}\rho^0}=NL^{\omega_S}\frac{\sum_A\boldsymbol{\varepsilon}_S\rho_A{}^0\beta_{AA}{}^{\omega_S}E^{\omega_S}}{2\sum_A\rho_A{}^0}. \tag{37}$$

Substitution of Eqs. (35), (36), and (37) into (17) yields the expression for the anisotropic Kerr polarization $\mathbf{P}_{\mathrm{anis}}{}^{\omega_S'}$:

$$\mathbf{P}_{\mathrm{anis}}{}^{\omega_S'}=\frac{\boldsymbol{\varepsilon}_SNL'E^{\omega_S}E^{\omega_1}E^{\omega_2*}}{4kT}\left(\frac{\mathrm{Tr}\rho^0f\alpha^{\omega}\beta^{\omega_S}}{\mathrm{Tr}\rho^0}-\frac{\mathrm{Tr}\rho^0f\alpha^{\omega}}{\mathrm{Tr}\rho^0}\times\frac{\mathrm{Tr}\rho^0\beta^{\omega_S}}{\mathrm{Tr}\rho^0}\right), \tag{38}$$

where α and β are diagonal matrices in n, and f is the matrix given by Eq. (28). Note that, as is seen from Eq. (35), the matrices α and f always have the same matrix indices in j and m. This formula for $\mathbf{P}_{\mathrm{anis}}{}^{\omega_S'}$ is quite general and is applicable to both liquids and gases. In deriving Eq. (38) the following approximations are used: (1) $\exp(-\omega_{ab}/kT)\simeq1-\omega_{ab}/kT$; and (2) $\omega_{AB}\simeq\omega_{nn'}$, regardless of j and m.

We shall now derive the classical theory of Bloembergen and Lallemand[8] for liquids from the quantum-mechanical result, Eq. (38), by applying certain approximations to it. First we assume that f_{ab} is given by Eq. (29). Then f_{ab} is independent of j and m and can be placed outside the trace sign in Eq. (38). Secondly, we assume that all molecules are in the ground state, because excited electronic or vibrational energies are usually much higher than kT. Of course, this assumption is not valid when molecules are considerably excited, as in intense stimulated Raman scattering which we therefor exclude. Then the trace in Eq. (38) should be extended only over j and m. Because of this, Eq. (38) becomes rotationally invariant, and Niessen's sum rules[21] for the product of four operators can be used. Using these sum rules we can rewrite Eq. (38) in terms

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[21] K. F. Niessen, Phys. Rev. 34, 253 (1929).

of the coordinates x, y, and z fixed in the molecule. Niessen originally derived these sum rules for a gas under a static perturbation, but they might hold also for liquids because their derivation is based only on the "principle of spectroscopic stability."[22] They should hold also for a system under periodic perturbation when the center-frequency approximation, i.e., $\omega_{AB}\simeq\omega_{nn'}$, is valid. The essential points of these rules were summarized by Serber.[17] By using Eqs. (14) and (15) in Serber's paper, the first term in the brackets in Eq. (38) is rewritten, when coordinate axes are taken as the principal axes of the molecule, as

$$\left(\frac{\mathrm{Tr}_{jm}\rho^0\alpha^\omega\beta^{\omega S}}{\mathrm{Tr}_{jm}\rho^0}\right)^{\parallel}=\frac{\sum_j\rho_j{}^0(\mathrm{Tr}_m\alpha^\omega\beta^{\omega S})_{jj}{}^{\parallel}}{\sum_j\rho_j{}^0N_j}$$
$$=\left[\frac{\alpha_x{}^\omega\alpha_x{}^{\omega S}+\text{c.p.}}{5}+\frac{(\alpha_x{}^\omega\alpha_y{}^{\omega S}+\alpha_y{}^\omega\alpha_x{}^{\omega S})+\text{c.p.}}{15}\right]\tag{39}$$

for $\boldsymbol{\varepsilon}_S\parallel\boldsymbol{\varepsilon}_L$, and

$$\left(\frac{\mathrm{Tr}_{jm}\rho^0\alpha^\omega\beta^{\omega S}}{\mathrm{Tr}_{jm}\rho^0}\right)^{\perp}=\frac{\alpha_x{}^\omega\alpha_x{}^{\omega S}+\text{c.p.}}{15}$$
$$+\frac{2(\alpha_x{}^\omega\alpha_y{}^{\omega S}+\alpha_y{}^\omega\alpha_x{}^{\omega S})+\text{c.p.}}{15}\tag{40}$$

for $\boldsymbol{\varepsilon}_S\perp\boldsymbol{\varepsilon}_L$, where N_j is the number of possible values of m (for gases $N_j=2j+1$), and c.p. denotes all other terms obtained by performing the cyclic permutation of x, y, and z. In the above equations, α_x, α_y, and α_z are the principal optical polarizabilities of the molecule and are given by

$$\alpha_x{}^\omega=\sum_n\frac{2e^2x_{gn}x_{ng}\omega_{ng}}{\hbar(\omega_{ng}{}^2-\omega^2)},\tag{41}$$

and similar forms, where g denotes the ground state. For both cases of the polarization, i.e., $\boldsymbol{\varepsilon}_S\parallel\boldsymbol{\varepsilon}_L$ and $\boldsymbol{\varepsilon}_S\perp\boldsymbol{\varepsilon}_L$, the second term in the brackets in Eq. (38) is rewritten as

$$\frac{\mathrm{Tr}_{jm}\rho^0f\alpha^\omega}{\mathrm{Tr}_{jm}\rho^0}\frac{\mathrm{Tr}_{jm}\rho^0\beta^{\omega S}}{\mathrm{Tr}_{jm}\rho_0}=\frac{f(\alpha_x{}^\omega+\text{c.p.})(\alpha_x{}^{\omega S}+\text{c.p.})}{9},\tag{42}$$

where we have used the principle of spectroscopic stability, and the usual sum rules for the product of two operators just as Van Vleck[19] used them for the calculation of the static polarizability. Combining Eqs. (29), (38), (39), (40), and (42), we obtain $\mathbf{P}_{\text{anis}}{}^{\omega S'}{}_{\parallel}$ and $\mathbf{P}_{\text{anis}}{}^{\omega S'}{}_{\perp}$, which are the $\mathbf{P}_{\text{anis}}{}^{\omega S'}$'s for the cases of $\boldsymbol{\varepsilon}_S\parallel\boldsymbol{\varepsilon}_L$ and $\boldsymbol{\varepsilon}_S\perp\boldsymbol{\varepsilon}_L$, respectively, as

$$\mathbf{P}_{\text{anis}}{}^{\omega S'}{}_{\parallel}=\frac{\boldsymbol{\varepsilon}_SNL'E^{\omega S}E^{\omega 1}E^{\omega 2*}}{90kT[1-i\tau(\omega_1-\omega_2)]}$$
$$\times[(\alpha_x{}^\omega-\alpha_y{}^\omega)(\alpha_x{}^{\omega S}-\alpha_y{}^{\omega S})+\text{c.p.}]\tag{43}$$

and

$$\boldsymbol{\varepsilon}_S\cdot\mathbf{P}_{\text{anis}}{}^{\omega S'}{}_{\perp}=-\tfrac{1}{2}\boldsymbol{\varepsilon}_S\cdot\mathbf{P}_{\text{anis}}{}^{\omega S'}{}_{\parallel}.\tag{44}$$

These equations coincide exactly with the classical theory of Bloembergen and Lallemand[3] for liquids. From the above derivation it can be seen that the Bloembergen-Lallemand equation is valid for the case where all molecules are in the ground state and their rotational energies are much smaller than both kT and $\hbar\Gamma_{ab}$. These assumptions are usually well met for liquids. For gases, however, the simple expressions given in Eq. (43) in terms of principal polarizabilities do not generally hold if $\omega_1\neq\omega_2$ (because f_{ab} depends on a and b). The sense of the word "anisotropic" will be clear from Eq. (43). $\mathbf{P}_{\text{anis}}{}^{\omega S'}$ is nonvanishing only for anisotropic molecules.

Now we will consider the second, third, and fourth terms in the right side of Eq. (31). We examine the orders of magnitude of $\rho^{(2)'(\omega_1-\omega_2)}\div\rho^{(2)(\omega_S-\omega_2)}$, $\rho^{(2)'(\omega_1-\omega_2)}\div\rho^{(2)(\omega_S+\omega_1)}$, and $\rho^{(2)'(\omega_1-\omega_2)}\div\rho^{(2)''(\omega_1-\omega_2)}$. By comparing Eq. (22) with Eq. (23) it can be seen that $\rho^{(2)'(\omega_1-\omega_2)}$ is larger than $\rho^{(2)(\omega_S-\omega_2)}$ roughly by a factor of $|\omega_{AB}+\omega_2-\omega_S|/kT\approx10^2$ when $|\omega_2-\omega_S|$ is far from resonance, because other factors such as ρ^0's and r's are of the same order of magnitude for both Eqs. (22) and (23). $\rho^{(2)(\omega_S+\omega_1)}$ and $\rho^{(2)''(\omega_1-\omega_2)}$ can be discussed in a similar manner, with the conclusion that they are smaller than $\rho^{(2)'(\omega_1-\omega_2)}$ by a factor of 10^{-2}–10^{-3}. In calculating the Kerr polarization with Eqs. (17) and (31), the quantities $\rho^{(2)(\omega_S-\omega_2)}$, $\rho^{(2)(\omega_S+\omega_1)}$, and $\rho^{(2)''(\omega_1-\omega_2)}$ contribute to the Voigt term because only electrons can follow the change with optical frequency. These density matrices have no relation to any molecular character, while $\rho^{(2)'}$, at the low-frequency $\omega_1-\omega_2$, as discussed above, has a molecular contribution, i.e., the anisotropic term arises from $\rho^{(2)'(\omega_1-\omega_2)}$. Thus the Voigt term for the nonresonant condition is smaller, roughly by two orders of magnitude, than the anisotropic term. The resonant Voigt term appears, for example, in stimulated Raman scattering, where in Eq. (23) ω_2, ω_S, and ω_{BA} correspond to the incident-laser, Stokes-shifted light and Raman-active vibrational frequencies, respectively, with the relation $\omega_2-\omega_S-\omega_{BA}=0$. The ratio of the resonant (with vibrational levels) and nonresonant contributions to the Voigt term may be estimated from the results of the three-wave-mixing experiment (generation of frequency $\omega_1+\omega_2-\omega_S$) by Maker and Terhune.[9] They found that the resonant term for the case of three-wave mixing is larger than the nonresonant term by a factor

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[22] See Ref. 19 for a detailed discussion on this subject.

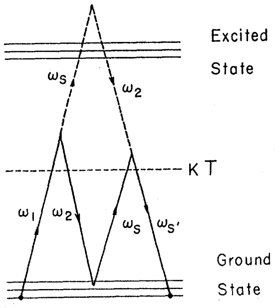

FIG. 1. The transition schemes of the third-order optical Kerr effect. The solid and dashed saw-toothed lines represent the anisotropic and the Voigt terms, respectively.

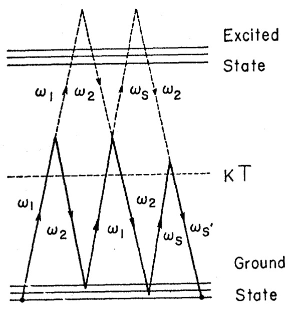

FIG. 2. The transition schemes of the fifth-order OKE. The solid saw-toothed line represents the correction to the anisotropic term. The lines involving one or two dashed saw-teeth make much smaller contributions to OKE.

of 4–20 for typical liquids. Thus one may conclude that the anisotropic term will be larger, roughly by one order of magnitude, than the Voigt term at the vibrational Raman resonance. The Voigt term will be more greatly enhanced when there occurs a two-quantum resonance in the electronic levels, such as the interband resonance in solids. It should be mentioned that using one of Niessen's sum rules for the product of four operators, the Voigt term can be shown to be temperature-independent if all molecules are again assumed to be in the ground state.

In Fig. 1 are illustrated the transition schemes giving rise to both the anisotropic and Voigt terms. The solid and dashed saw-toothed lines represent the transitions corresponding to the anisotropic and Voigt terms, respectively. Note that, for the anisotropic term, the molecule initially in the ground state returns to the ground state through a virtual transition accompanied by virtual emission of the photon ω_2.

IV. QUANTUM-MECHANICAL ORIGIN OF THE ANISOTROPIC TERM

In this section we shall investigate the quantum-mechanical origin of the anisotropic term. To simplify the calculation we consider the case of $\omega_1=\omega_2\equiv\omega$ and $E^{\omega_1}=E^{\omega_2}\equiv E^{\omega}$. As can be seen from Eq. (37), the effect of a perturbation due to the radiation field on the linear susceptibility may be classified quantum mechanically into three kinds of effects: the energy shift in the denominator (in β^{ω_S}), the population change due to the energy shift, and the change in the matrix element. The anisotropic term was shown in Eqs. (43) and (44) to be temperature-dependent through $(kT)^{-1}$. Since the energy shift in the denominator does not give rise to any temperature-dependent change in the susceptibility, it should not be taken as the origin of the anisotropic term. This shift contributes to the Voigt term, as Voigt himself[11] originally considered. We shall next consider the population change due to the energy shift. To investigate the population change, all even orders of the density matrices should be taken into account. The second-order density matrix was considered in the Sec. III.

The fourth-order density-matrix $\rho^{(4)}$ diagonal in n can be written as

$$\rho_{A,nb}{}^{(4)}=U_{A,nb}{}^{(4)}\rho_{nb}{}^0+[U^{(3)}\rho^0U^{(1)\dagger}]_{A,nb}+\sum_C U_{AC}{}^{(2)}\rho_C{}^0U_{nb,C}{}^{(2)*}+[U^{(1)}\rho^0U^{(3)\dagger}]_{A,nb}+\rho_A{}^0U_{nb,A}{}^{(4)*}. \quad (45)$$

Through considerations similar to those at the end of Sec. III, we can see that the largest contribution to $\rho_{A,nb}{}^{(4)}$ is from the first, third, and fifth terms on the right side of Eq. (45) whose intermediate quantum number n'' is also equal to n. The density matrix corresponding to these terms, $\rho_{A,nb}{}^{(4)\prime}$, can be calculated from Eqs. (4), (5), and (45) as

$$\rho_{A,nb}{}^{(4)\prime 2(\omega-\omega)}=\sum_{D,c,E}\frac{e^4r_{AD}{}^Lr_{D,nc}{}^Lr_{nc,E}{}^Lr_{E,nb}{}^L|E^\omega|^4}{4\hbar^4}\times\frac{2\omega_{n'''n}}{\omega_{n'''n}{}^2-\omega^2}\frac{2\omega_{n^{(4)}n}}{\omega_{n^{(4)}n}{}^2-\omega^2}\times\left[\frac{\rho_A{}^0}{\omega_{ab}\omega_{ac}}+\frac{\rho_{nb}{}^0}{\omega_{bc}\omega_{ba}}+\frac{\rho_{nc}{}^0}{\omega_{ca}\omega_{cb}}\right], \quad (46)$$

where $\omega_{n'''n}$ and $\omega_{n^{(4)}n}$ are the center frequencies, as before. By expanding the ρ^0's as a power series in the $\omega_{jj'}/kT$'s and retaining to the second-order term, the term in the square brackets in Eq. (46) can be written as

$$(\rho_A{}^0+\rho_{nb}{}^0+\rho_{nc}{}^0)/3!k^2T^2. \quad (47)$$

The fifth-order Kerr polarization can be calculated with Eqs. (8), (9), and (46). By relabeling the indices in the trace as in the calculation of Eq. (36), one finds that the contribution of $\frac{1}{3}(\rho_A{}^0+\rho_{nb}{}^0+\rho_{nc}{}^0)$ to the trace is equivalent to that of $\rho_A{}^0$. A similar equivalence holds also for higher-order corrections to the Kerr effect. By using Eq. (34) we obtain

$$\rho_{A,nb}{}^{(4)\prime 2(\omega-\omega)}=\sum_c\frac{\rho_A{}^0\alpha_{A,nc}{}^\omega\alpha_{nc,nb}{}^\omega|E^\omega|^4}{4\times 2!k^2T^2}. \quad (48)$$

The transition schemes for the fifth-order OKE are given in Fig. 2. The solid saw-toothed line represents the contribution of Eq. (48) to the correction to the anisotropic term. When the molecule returns virtually only once to the ground state, a density matrix proportional to $(kT)^{-1}$ is obtained and is much smaller than $\rho_{A,nb}{}^{(4)'2(\omega-\omega)}$ in Eq. (48). No virtual return to the ground state corresponds to the correction to the Voigt term. Generally, the $2l$th-order density matrix of the largest magnitude at zero frequency can be written as

$$\rho_{A,nb}{}^{(2l)'l(\omega-\omega)} = \sum_{b'b''\cdots b^{(l-1)}} \frac{\rho_A{}^0 \alpha_{A,nb'}{}^{\omega} \alpha_{nb',nb''}{}^{\omega} \cdots \alpha_{nb^{(l-1)}nb}{}^{\omega} |E^{\omega}|^{2l}}{2^l \times l!(kT)^l}. \tag{49}$$

The transition scheme corresponding to this density matrix involves l virtual returns to the ground state in every other intermediate transition with l virtual emissions of the photon ω. The infinite sum of $\rho_{A,nb}{}^{(2l)'l(\omega-\omega)}$ yields

$$\begin{aligned}\rho_{A,nb}{}'^{(\omega-\omega)} &\equiv \rho_{A,nb}{}^0 + \sum_{l=1}^{\infty} \rho_{A,nb}{}^{(2l)'l(\omega-\omega)} \\ &= \rho_A{}^0 [\exp(\alpha^{\omega}|E^{\omega}|^2/2kT)]_{A,nb}. \end{aligned} \tag{50}$$

We shall neglect all transition schemes other than those involved in Eq. (50), because they give a much smaller effect on the Kerr polarization than $\rho_{A,nb}{}'^{(\omega-\omega)}$ does. Thus the general expression for the Kerr polarization $\mathbf{P}_K{}^{\omega S}$ at ω_S due to the linear perturbation at ω_S on the density matrix in Eq. (50) can be written in a matrix form as

$$\mathbf{P}_K{}^{\omega S} = \boldsymbol{\varepsilon}_S N L^{\omega S} E^{\omega S} \left[\frac{\mathrm{Tr}\rho^0 \exp(\alpha^{\omega} L^{\omega 2} |E^{\omega}|^2/2kT)\beta^{\omega S}}{\mathrm{Tr}\rho^0} - \frac{\mathrm{Tr}\rho^0 \exp(\alpha^{\omega} L^{\omega 2}|E^{\omega}|^2/2kT)}{\mathrm{Tr}\rho^0} \times \frac{\mathrm{Tr}\rho^0 \beta^{\omega S}}{\mathrm{Tr}\rho^0} \right]. \tag{51}$$

Now we divide $\mathbf{P}_K{}^{\omega S}$ into two parts in order to investigate the physical meaning of $\mathbf{P}_K{}^{\omega S}$:

$$\mathbf{P}_K{}^{\omega S} = \mathbf{P}_{K1}{}^{\omega S} + \mathbf{P}_{K2}{}^{\omega S} \tag{52}$$

and

$$\mathbf{P}_{K1}{}^{\omega S} = \boldsymbol{\varepsilon}_S N L^{\omega S} E^{\omega S} \times \left[\frac{\sum_A \rho_A{}^0 \exp(\alpha_{AA}{}^{\omega} L^{\omega 2}|E^{\omega}|^2/2kT)\beta_{AA}{}^{\omega S}}{\mathrm{Tr}\rho^0} - \frac{\sum_A \rho_A{}^0 \exp(\alpha_{AA}{}^{\omega} L^{\omega 2}|E^{\omega}|^2/2kT)}{\mathrm{Tr}\rho^0} \frac{\mathrm{Tr}\rho^0 \beta^{\omega S}}{\mathrm{Tr}\rho^0} \right]. \tag{53}$$

In Eq. (53) only diagonal parts of α^{ω} and β^{ω} are taken. The transition scheme for $\mathbf{P}_{K1}{}^{\omega S}$ corresponds to virtual returns to levels in the ground state with the same values of j and m as those in the initial state. The diagonal element of $\frac{1}{2}\alpha^{\omega}|E^{\omega}|^2$, which appears in Eq. (53), is written as

$$\tfrac{1}{2}\alpha_{AA}{}^{\omega}|E^{\omega}|^2 = \sum_B \frac{e^2 r_{AB}{}^L r_{BA}{}^L \omega_{n'n} |E^{\omega}|^2}{\hbar(\omega_{n'n}{}^2 - \omega^2)}. \tag{54}$$

This expression turns out to be the second-order Stark effect at level A due to the radiation field at frequency ω.[23] Thus inspection of Eq. (53) reveals that $\mathbf{P}_{K1}{}^{\omega S}$ arises from the equilibrium population change due to the second-order high-frequency Stark effect. On the other hand, $\mathbf{P}_{K2}{}^{\omega S}$ in Eq. (52) is considered to arise from the change in the unperturbed matrix element due to the radiation field because $\mathbf{P}_{K2}{}^{\omega S}$ has no connection with Stark effects, either in the denominator (in $\beta^{\omega S}$) or in the exponential function in Eq. (37).

The existence of "low" levels makes $\mathbf{P}_{K2}{}^{\omega S}$ temperature-dependent. We conclude that both the population change due to the high-frequency Stark effect and the change in the matrix element are the quantum-mechanical origin of the anisotropic term and correspond classically to the change of the distribution function for the molecule.

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