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Spectroscopy of Nonlinear Optical Activity in Crystals in the Niger – Delta Region

Ekpekpo A.

Department of Physics, Delta State University Abraka

Abstract: In an optically active medium, the plane of light polarization rotates through an angle proportional to the sample thickness. A strong light wave changes natural gyrotropy or in a nongyrotropic medium, experiences a self-induced rotation (non-linear optical activity, NOA). This article is devoted to the use of this phenomenon in spectroscopy of crystals in the Niger – Delta region.

Key words: Crystals, Polarization, Nonlinear optical Activity

INTRODUCTION

Refraction and absorption of nonlinear medium can depend on the intensity of light. In a similar way, the difference between refractive indices for circulatory polarized waves in a gyrotropic medium should vary in a field of a strong electromagnetic wave. This phenomenon was predicted by Akhmanov and Zharikov[1] and independently by Kielich[7] and Atkins and Barron[6].

The first non – linear optical activity (NOA) experiments were carried out in strongly absorbing crystals where medium gyrotropy changed under the thermal action of a laser beam Vlasor *et al*[10] and Bairamov *et al*[4]. Of course, the main interest was attracted to electronic and not thermal NOA mechanism. Their theoretical analysis was carried out in several papers Kielich *et al*[7], Ovander *et al*[13], Bokut *et al*[5], Mokherjee *et al*[12]. First reliable experiments on non thermal nonlinear rotation of the polarization plane led to two different mechanisms of this phenomenon – NOA due to spatial dispersion of medium nonlinearity[2] predicted in early works, and NOA due to anisotropy of nonlinear absorption[9].

At present, it is clear that NOA is a fine but often observed effect of the polarization self-action of light. Any chiral media, especially liquid crystals, biological macromolecules and crystals of most crystallographic classes are nonlinear optically active objects. The progress achieved recently in the technique of polarization (especially pulse polarization) measurements makes provides unique information on symmetry, band structure, non local response and latent crystal anisotropy.

Let us first describe the effects of the polarization self-action of light from the phenomenological standpoint. Nonlinear optical activity and the effect of nonlinear rotation of the polarization ellipse[11] are the uuonly "weak" effects of polarization nonlinear optics. As usual, their description is based on the common solution of the wave and material equations.

$$\begin{cases} \left[\nabla\left[\nabla\vec{E}\right]\right] - \dfrac{w^2}{c^2}\vec{D} = 0 \\ \vec{D} = \vec{D}^{\perp}\left(\vec{E}\right) + \vec{D}^{n1}\left(\vec{E}\right) \end{cases} \tag{1}$$

In the general case analytical solution of this system is very difficult owing to elliptical birefringence. Yet, during light propagation along the optical axes, when the wave is taken to be transverse (the most important case from the experimental standpoint), it is possible to derive expressions for ellipticity β and rotation angle β of the major axis of the polarization ellipse by the method of slowly varying amplitudes in the approximation of weak nonlinearity of the medium[14],

$$\beta(Z) = \frac{1}{2}\left[R_e\{f\}\cdot Z + R_e\left\{\Omega_{(\not Z)}\right\} + 2B(0)\right]$$

$$\beta(Z) = Th\left[1m\{f\}\cdot Z + 1m\left\{\Omega_{(\not Z)}\right\} + ArThB(0)\right]$$

$$\Omega_{(\not Z)} = \frac{\omega^2}{2C^2}\int_0^{\not Z}\left[\frac{D_-^{nl}\left(\not Z'\right)}{E_-\left(\not Z'\right)K_-} - \frac{D_+^{nl}\left(\not Z'\right)}{E_+\left(\not Z'\right)K_+}\right]d_{\not Z} \tag{2}$$

Here $\not Z$ is the sample thickness and f is the constant of linear gyrotropy. The moduli of wave vectors K_+ are the root of the dispersion equation.

$$K_o^2 - K_+^2 + i\alpha \pm K_{\pm} f = 0 \tag{3}$$

Corresponding Author: Ekpekpo A., Department of Physics, Delta State University Abraka

where $K_o^2 = \frac{\omega^2}{C^2} R_e\{E\}$, $\alpha = \frac{\omega^2}{C^2} m\{E\}$

All "weak" ($\beta << 1$, $\beta << \pi$) polarization nonlinear optics of self-action is contained in these equation, including the phenomenon of nonlinear rotation of the polarization ellipse and nonlinear optical activity observed in a pure form if a preliminary linearly polarized radiation is directed to the medium. The solution of the polarization problem for a concrete material equation reduces to the calculation of the integral $\Omega_{(z)}$

While considering the amplitude effects of light self-action, the material equation is used, as a rule, in the form of an expansion of the electrical induction in power series of $\vec{E}$ up to the third-order terms. There is no necessity of considering spatial dispersion since in most cases the relative contribution of the amplitude effects related to the spatial dispersion of the medium (a/λ) is insignificant (a being the characteristic size in the medium –molecule diameter or the unit cell parameter of the crystal). Yet for the description of polarization phenomena spatial dispersion should necessarily be taken into account[3].

$$Di - X_{ij}^{(1)} E_j + X_{ijk}^{(2)} E_j E_k + X_{ijkl}^{(3)} E_j E_k E_l + --- \tag{4}$$

$$+\gamma_{ijk}^{(1)} \nabla_k E_j + \gamma_{iljk}^{(2)} E_l \nabla_k E_j + \gamma_{imljk}^{(3)} E_m E_l \nabla_k E_j + ---$$

There is no necessity to take into consideration the terms with the magnetic field of the light wave. The magnetic field is related to the electric one by the Maxwell equations and can be taken into account by the terms with spatial derivatives (Landau *et al,* 1984). It should be noted that calculating the corresponding susceptibilities related to spatial dispersion, it is necessary to take into account the magnetic dipole and electrical quadrupole transitions if the absorption in the medium is weak, the substitution of the material equation (4) into (3) leads to three terms for the integral Ω (z) corresponding to three different mechanisms of nonlinear optical activity.

The first mechanism (NOA-1) of nonlinear rotation of the polarization plane is associated with spatial dispersion of medium nonlinearity described by Tensor $\gamma^{(3)}$. As a rule, NOA should be distinguished from the backgroup of natural gyrotropy, yet the high rank of tensor $\gamma^{(3)}$ results in the fact that the number of crystallographic classes having nonzero components of $\gamma^{(3)}$ is larger than that for tensor $\gamma^{(1)}$ responsible for linear gyrotropy. Thus, NOA-1 can be observed in nongyrotropic media, i.e. can manifest itself as self-induced gyrotropy.

The second mechanism NOA-2 of nonlinear rotation of the polarization plane is associated with anisotropy of nonlinear absorption and cannot be observed in isotropic media.

A strong light wave changes the medium refractive index and, consequently, the eigen value of the differential operator in the term with $\gamma^{(1)}$ in expansion (4). This mechanism, NOA-3 occurs only in gyrotropic crystals.

Theoretical Considerations and Calculations: We restrict ourselves to the consideration of cubic nonlinearity of oscillators forming the molecule.

The Hamiltonian of such a molecule is Akhamov *et al*,[3]:

$$H = \frac{1}{2} m\left(x^2 + y^2\right) + m\varepsilon xy + \frac{1}{2} m w_0^2 \left(x^2 + y^2\right) + mA\left(x^4 + y^4\right) + mB\left(x_{y^3}\right) + mcx^2 y^2 + mB\left(yx^3\right) \tag{5}$$

Here *e* and *m* are charge and mass, *x* and *y* are coordinates of a charge in the molecular coordinate system, w_0 is the natural frequency of oscillators, A, B, C are harmonic constants, and ε characterizing the bond between oscillators.

An electromagnetic wave excites oscillator of such a molecule with relative delay determined by distance D between the oscillators. For the Fourier components of *x* and *y* at the frequency of the exciting field ω. We are interested here in the processes of light self – action occurring without changes in frequency we arrive at.

$$\left(\omega_o^2-\omega^2\right)x+\varepsilon y+12A\left|x\right|^2 x+3B\left(\left|y\right|^2+x^2y^4+2\left|x\right|^2 y\right)+2C\left(y^2x^4+2\left|y\right|^2\right)$$

$$=\frac{e}{m}E_x Exp\left(iK_z D/2\right)$$

$$\left(\omega_o^2-\omega^2\right)y+\xi x+12A\left|y\right|^2+$$

$$3B\left(\left|x\right|^2 x+y^2x^4+2\left|y\right|^2 x+2C\left(x^2y^4++2\left|x\right|^2 y\right)=\frac{e}{m}E_y Exp\left(+iK_z D/2\right)\right) \quad (6)$$

As has already been indicated, while calculating the effective dipole moment of such a molecule, it is necessary to take into consideration the dipole moment d quadropole moment $\hat{q}$ and the magnetic dipole moment $\vec{m}$ in accordance with the equation for the current density

$$\vec{J}=\frac{\partial}{\partial t}\vec{d}-\frac{\partial}{\partial t}\nabla\hat{q}+c\ \text{Rot}\ \vec{m} \quad (7)$$

$$\vec{d}=\sum e_i\vec{\Gamma}_i,\quad \hat{q}=\frac{1}{2}\sum e_i\vec{\Gamma}_i\vec{\Gamma}_i; \quad (8)$$

$$\vec{n}=\frac{1}{2C}\sum_i e_i\left[\vec{\Gamma}_i\times\vec{\Gamma}_i\right]$$

where $\vec{\Gamma}_i$ is the radius – vector of the i-th charge. Then the Fourier components of the dipole moment $\vec{P}=\frac{J}{i\omega}$ may be obtained substituting equation (8) into equation (7) with due account of the series expansion in parameter ($\vec{K}\vec{s}$).

$$P_{x,y}=e\begin{pmatrix}x\\y\end{pmatrix}Exp\left(\pm ik\,D/2\right) \quad (9)$$

Substitution of equation (10) into equation (7) and the use of the coordinates.

$$P_{1,2}=1/\sqrt{2}\left(P_x\pm P_y\right);\ E_{1,2}=1/\sqrt{2}\left(E_x\pm EP_y\right), \quad (10)$$

leads to the following system of equations

$$\left(\omega_{1,2}^2-\omega^2\right)P_{1,2}\mp ikD\ \xi P_{2,1}+6Ae^{-2}\left[\left(\left|P_{1,2}\right|^2+\left|2P_{2,1}\right|^2\right)P_{1,2}+P_{2,1}^2P_{1,2}^*\right]+$$

$$3B^-e^2\left\{\pm 2\left|P_{1,2}\right|^2\ P_1\pm iD_1\left[\left(P_{1,2}^2P_{2,1}^*-\left|P_{1,2}\right|^2+2\left|P_{1,2}\right|^2\right)P_{2,1}\right]\right\}+$$

$$Ce^{-2}\left\{\left(3\left|P_{1,2}\right|^2-2\left|P_{2,1}\right|^2\right)P_{1,2}-P_{2,1}P_{2,1}^*+2iKD\left[P_{2,1}P_{1,2}^*+\left(\left|P_{1,2}\right|^2-\left|P_{2,1}\right|^2\right)P_{1,2}\right]\right\}=$$

$$e^2m^{-1}E_{1,2};\ \omega_{1,2}^2=\omega_o^2\pm\xi$$

which permit us to write *P* in the tensor form

$$P_1=\delta e_{i,j}^{(1)}\ \ E_j-iK_l\eta_{ije}^{(1)}\ \ \mathrm{P}_j-\partial e_{ijkl}^{(3)}P_jP_RP_L-iK_m\eta_{ijklm}^{(3)}P_jP_kP_l \tag{12}$$

This is very important since now it is possible to average over molecule orientations, P = N<P> and to calculate the macroscopic susceptibility.

An ensemble of randomly oriented Kuhn's nonlinear oscillator is a remarkable model of an isotropic medium with spatial dispersion of nonlinearity. Averaging of the polarization vector over orientations is the material equation in the form:

$$\vec{P}=K_1\vec{E}-i\Gamma\left[\vec{K}\times\vec{P}\right]-K_3\left(2\left(\vec{P}-\vec{P}^*\right)\vec{P}+\left(\vec{P}\bullet\vec{P}\right)P'\right)-i\Gamma_3\left(\vec{P}\left(\vec{K}\left[\vec{p}\times\vec{p}^*\right]+\left[\vec{k}\times\vec{p}\right]\right)\right)\left(\vec{P}\bullet\vec{P}\right)$$

where

$$K_1=2/3,e^2Nm^{-1}\left(\omega_o^2-\omega^2\right)\psi\left(\omega\ ,\omega_2,\omega_2\right)$$

$$K_3=4/15e^{-2}N^{-2}\left(C-6A\right)\left(\omega_o^2-\omega^2\right)+3B\xi\right)\psi\left(\omega,\omega_2,\omega\right)$$

$$\Gamma_1=2/3\cdot\xi D\left(\omega_o^2-\omega^2\right)\ \psi\left(\omega,\omega_1,\omega_2\right)$$

$$\Gamma_3=4/5\cdot BDe^{-2}N^{-2}\left(\omega_o^2-\omega^2\right)\ \left(\omega,\omega_1,\omega_2\right)$$

$$\psi=\left(\left(\omega_1^2-\omega^2\right)\ \left(\omega_2^2-\omega^2\right)\ \right) \tag{14}$$

Note here that the above equation is not a fragment (first term) of an expansion of polarization P in field E. it relates in an implicit but accurate form, polarization and the field of an isotropic gyrotropic medium within the framework of cubic anharmonism of molecules forming this medium. This equation provides the description of hysteresis and, in particular polarization hysteresis effects. The susceptibility of electron susceptibility $\gamma^{(3)}$ responsible for NOA – 1 can be obtained by expanding in power series of electronic field.

$$\gamma^{(3)}=\left(128/135\right)\ e^4DBN\ m^{-e}\left(\omega_o^2-\omega^2\right)^4\ \Psi\left(\omega,\omega_1,\omega_2\right) \tag{15}$$

Anharmonic constants A. B, C of molecules seem to be close by the orders of magnitude. This means that the significant NOA – 1 should be searched for, first of all, in strongly nonlinear crystals with noticeable spatial

dispersion where characteristics dimension D are large. Moreover, the above model permits one to obtain the estimate for the component of tensor $\gamma^{(3)}$.

$$\gamma^{(3)} / \hat{\gamma}^{(3)} \sim \hat{\gamma}^{(1)} / \hat{\gamma}^{(1)} \sim D/2\pi \tag{16}$$

A set of similar independent orthogonal oscillators at the sites of a crystal lattice is a good model of a cubic crystal. This model can be deduced from the Kuhn's model, but in this case no orientation averaging is necessary and the interaction between the oscillators can be neglected. Then

$$P_{x,y} = \frac{3}{2} K_1 E_{x,y} + 5/2\, K_3 \left| P_{x,y} \right|^2 P_{x,y} \tag{17}$$

And the isotropic susceptibility component is related to the anisotropic one, which permutes one to estimate the value of NOA – 2 from cubic nonlinearity of the medium.

RESULTS AND DISCUSSION

The above considered additive nonlinear polarization effects occur in relatively weak light fields where nonlinear induction can be represented through nonlinear susceptibility, nonlinear charge of polarization being small, $B^{ne} << \left| \chi^{(1)} / \chi^{(1)} \right|$ in many cases. Polarization nonlinear effects are accumulated over the sample thickness and even if the above condition is fulfilled, the changes of nonlinear polarization can be large. Here we cannot restrict ourselves to the solution in the first approximation. Approximate methods do not work properly and we should involve computer simulation. The main result of the numerical experiments of such type (Zheludev et al(1989)) reduces to the following. At high intensities or at long interactions distances nonlinear mixing of contributions from different NOA mechanism and nonlinear rotation of polarization ellipse takes place and therefore we cannot distinguish between these contributions. In some cases polarization tends to become circular, the sign of rotation depending on the orientation of initial polarization with effect to the natural crystal symmetry axes or the sign of national gyrotropy.

What will occur a further increase in the light intensity? This questioned can be answered only if we have the material equations which have wider validity range then the power series in field $\vec{E}$. The validity range of the derived model material equation is by a factor of

$\left(\frac{\omega}{\delta\omega} \right)^{1/2}$ wider than for material equation (4)

$$\left| E \right|^2 << \left| \frac{X^{(1)}}{X^{(3)}} \right| \left(\frac{\omega}{\delta\omega} \right)^{1/2} \tag{18}$$

where δω is the width of the molecular resonance.

Now consider the problem of polarization instability in media with different symmetry[3]. Gyrotropy $\frac{d\beta}{dZ}$ and circular dischroism $\frac{d\beta}{dZ}$ of a gyrotopic isotropic medium described by material equation (13) is determined by the relationship

$$\frac{d}{d\tilde{Z}}\left(\frac{\beta}{B}\right)=\frac{2\pi\omega_o}{cn_o}\left(\frac{R_e}{lm}\right)\Delta \tag{19}$$

where Δ is the difference between the optical suceptibilies for the waves with different circular Marization

$$\left(\frac{R_e}{lm}\right)\Delta=\left(\Gamma_1+\frac{\Gamma_3}{2K_3}U\right)\left|K_1\right|\left(1-\frac{4}{3U\cos V^2}+U^2/3\right)^{-1}\cdot\left(1-2U/R\sin^2 V\,2/R\left(\cos V-U\right)\right) \tag{20}$$

where $V=A_{rg}\left(\omega_o^2-\omega^2+i\mu\omega\right)$ and U is a multiple valued intensity function which obeys the equation

$$\left(U^2-2U\cos V+1\right)=R;R=3\left|K_3\right|\bullet\left|K_1\right|^2\left(E\cdot E^*\right)$$

For comparism, we shall also give the corresponding relationship describing the instability of the polarization ellipse in anisotropic nongyrotropic medium $\left(\Gamma_1=\Gamma_3=0\right)$

$$\left(\frac{R_e}{lm}\right)\Delta=\frac{-2\partial RU}{R}\left(1-\frac{4}{3U\cos V+U\,2/3}\right)^{-1} \tag{21}$$

where instability (similar to the effect of nonlinear rotation of the polarization ellipse in weak fields) can be observed only in the presence of some initial ellipticity OR ≠ O.

$$\partial R=3i\cdot\left|K_3\right|\cdot\left|K_1\right|\frac{\left[\vec{E}\times\vec{E}^*\right]\cdot\vec{K}}{\left|K\right|}$$

Nonlinear gyrotropy related to the anisotropy of nonlinear dissipation exhibit strongly dependence on the initial polarization orientation relative to the symmetry axes of a crystal.
From material equation (17) it follows

$$\frac{d}{d\tilde{Z}}\left(\frac{\beta}{B}\right)=\sin\left(2\beta(O)\frac{2\pi^2}{\lambda n_o}\left(\frac{I_m}{R_e}\right)\Delta\right. \tag{22}$$

$$\left(\frac{I_m}{R_e}\right)=\hat{\Delta}\frac{U_x-U_y}{U_xU_y}R_xR_y\begin{pmatrix}2\cos V & -\left(U_x-U_y\right)\\ \cos 2V & -\left(U_x+U_y\right)\end{pmatrix}\begin{matrix}\sin V\\ \cos V+V_xV_y\end{matrix} \tag{23}$$

Quantities U_x and U_y may be taken from the equations

$$U_{x,y}\left(U_{x,y}^2-2U_{x,y}\cos V+1\right)=R_{x,y}=3\left|K_3\right|\left|K_1\right|^2$$

$$\left|E_{x,y}\right|^2 \tag{24}$$

The obtained relationship may be used only for the analysis of the regions of stable and unstable polarization. The complete description requires the consideration of the temporary evolution of the system. The study of strongly excited nonlinear oscillators shows that regions of the hystresis behaviour of static models correspond to the regions of dynamical chaos in real systems. In our case it is the polarization randomness for a strong light wave in a nonlinear medium.

Conclusion: The main mechanism of nonlinear opticl activity which are possible within the third order susceptibility have been studied theoretically. Among the unsolved theoretical problem the most important seems to be the developing of a detailed quantum mechanical theory of nonlinear susceptibilities related to spatial dispersion of nonlinearity with due account of a real band structure of crystals and exciton and biexciton contribution. Also an adequate macroscopic phenomenological theory is necessary which should be able to describe nondepenerate NOA. In the case when strong linearly polarized wave changes the gyrotropy, while a weak wave probes it.

It seems also to be very promising to use the polarization NOA technique for studying phase transition (NOA is very sensitive to a crystal symmetry). Of great importance for surface studies is a problem of nonlinear optical activity in reflection which is almost unstudied. The search for a media with large NOA constant will promote the creation of new class of laser – beam control devices and new (polarization) elements for optical processing of information in the Niger – Delta.

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