Circular photovoltaic effect in optically active liquids

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A new nonlinear optoelectric effect is predicted in optically active isotropic liquids on the basis of a phenomenological analysis. Specifically, a photovoltaic current would be generated when a circularly polarized light wave is applied to a liquid which has an electrical conductivity and an absorption at the optical frequency. © *1995 American Institute of Physics.*

1. One of the first nonlinear-optics phenomena discovered at the dawn of the laser era was an optical rectification.[1,2] A photovoltaic effect[3] was later observed. The latter effect consists of the generation of an electric current by optical radiation in an optically absorbing, electrically conducting crystal without a symmetry center.[4]

Optical rectification and the photovoltaic effect arise only in media which lack a symmetry center at the macroscopic scale, e.g., in the pyroelectric and piezoelectric crystals in which these effects were discovered experimentally. Until recently, however, no attempts have been made to study possibilities for seeing these effects in isotropic media lacking a symmetry center, such as gyrotropic (or chiral) liquids. In particular, all solutions of organic molecules of biological origin lack a symmetry center, and as a result they exhibit a natural optical activity.[5] It was only recently that the possibility of seeing a manifestation of optical rectification in nonconducting, optically active liquids was pointed out.[6] In this letter we offer a phenomenological analysis of the photovoltaic effect in gyrotropic isotropic liquids which have an electrical conductivity (either a dark conductivity or a photoinduced one). We discuss possibilities for detecting this effect experimentally.

2. We assume that a plane electromagnetic wave

$$\mathbf{E}(\mathbf{r},t)=\tfrac{1}{2}\mathbf{E}(\omega)\exp(-i\omega t+i\mathbf{k}\mathbf{r})+\text{c.c.} \tag{1}$$

is propagating in an isotropic, homogeneous, electrically conducting medium without a symmetry center. In an arbitrary Cartesian coordinate system, the constant photovoltaic current density $\mathbf{J}(0)$ which arises in this medium is given by the phenomenological expression

$$J_i(0)=i\beta_{ijk}(0;\omega,-\omega)E_j(\omega)E_k^*(\omega)+\text{c.c.}, \tag{2}$$

where $\beta_{ijk}(0;\omega,-\omega)$ is the nonlinear-optics conductivity tensor of the medium, and a repeated index means a summation from 1 to 3.

According to Ref. 7, any constitutive third-rank tensor [including $\beta_{ijk}(0;\omega,-\omega)$] in an isotropic medium which lacks a symmetry center and which belongs to the limiting symmetry class $\infty\,\infty$ (chiral liquids belong to this class) can be expressed in terms of the absolute Levi–Civita density e_{ijk}:

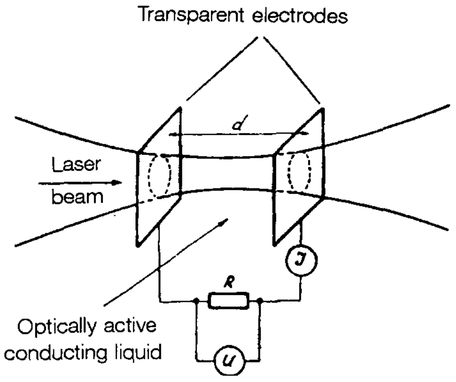

FIG. 1. Layout of a proposed experiment to observe the circular photovoltaic effect in a homogeneous, isotropic, optically active liquid. Either the current J or the voltage drop U across resistance R is measured in the external electric circuit.

$$\beta_{ijk}(0;\omega,-\omega)=\beta(\omega)e_{ijk}(\omega), \tag{3}$$

where $\beta(\omega)$ is a pseudoscalar function of the frequency ω. Also using (2), we find a vector relation between $\mathbf{J}(0)$ and $\mathbf{E}(\omega)$:

$$\mathbf{J}(0)=i\beta(\omega)[\mathbf{E}(\omega)\times\mathbf{E}^*(\omega)]+\text{c.c.}=2i\mathrm{Re}\{\beta(\omega)\}[\mathbf{E}(\omega)\times\mathbf{E}^*(\omega)]. \tag{4}$$

If the field in (1) is elliptically polarized,

$$\mathbf{E}(\omega)=E(\omega)\{\mathbf{e}_x(\cos\psi\cos\gamma-i\sin\psi\sin\gamma)+\mathbf{e}_y(\sin\psi\cos\gamma+i\cos\psi\sin\gamma)\}, \tag{5}$$

where $\mathbf{e}_x$, $\mathbf{e}_y$ are unit vectors which define the x,y axes; ψ is the azimuthal angle; and γ is the ellipticity, we find the following expression from (4):

$$\mathbf{J}(0)=\mathbf{e}_z\frac{16\pi}{cn(\omega)}\mathrm{Re}\beta\times I\sin 2\gamma. \tag{6}$$

Here $\mathbf{e}_z=\mathbf{k}/|\mathbf{k}|$; $I=[cn(\omega)/8\pi]|\mathbf{E}(\omega)|^2$ is the intensity; $n(\omega)$ is the refractive index; and c is the velocity of light in vacuum. The quantity $\mathrm{Re}\beta$ is nonzero in the optical-absorption band of the liquid even if there is an electrical conductivity.[6]

It can be seen from (4) and (6) that the photovoltaic current is proportional to $\sin 2\gamma$, which is the ellipticity of the light wave. According to the nomenclature of Ref. 4, a circular photovoltaic effect can thus occur in chiral isotropic media.

We now put expression (6) in the form used in the theory of the photovoltaic effect in crystals in the literature:

$$J=\alpha GI, \tag{7}$$

where α is the optical absorption coefficient of the medium, and $G=(16\pi/cn\alpha)\mathrm{Re}\beta$ is an analog of the Glass constant in crystals lacking a symmetry center.[3,4] Here and below we assume $|\sin 2\gamma|=1$.

3. We suggest the very simple layout in Fig. 1 for detecting the photovoltaic effect. The following situations should be analyzed separately: a) The chiral medium is initially electrically conducting, but it does not have a photoconductivity. In this case the medium can be either transparent or optically absorbing. b) The medium is electrically conducting and also exhibits a photoconductivity. c) The medium is initially nonconducting, but it becomes conducting as a result of absorption of light (this is a photoconductivity).

In case a), the steady-state current J_e in the external circuit in the case $R<\infty$ is

$$J_e=\frac{Id}{\sigma}\frac{1}{R_i+R}=\frac{\alpha GId}{\sigma(R_i+R)}, \tag{8}$$

where σ is the conductivity, and R_i is the total electrical resistance of the chiral liquid. The voltage across the plates of the capacitor in the open-circuit case ($R\rightarrow\infty$) is

$$U_0=\frac{\alpha GId}{\sigma}. \tag{9}$$

This voltage, like the current in (8), increases with increasing I and does not reach saturation (under the condition $\alpha=\text{const}$).

In case b), the conductivity σ consists of a dark component σ_0 and a photoconductivity $\sigma_{\text{ph}}=\alpha KI$. The voltage U across the capacitor in the open-circuit case, under the condition $I\gg I_s=\sigma_0/\alpha K$, thus reaches saturation at a level

$$U_{s0}=Gd/K. \tag{10}$$

The same expression holds for case c).

The absolute value of the photovoltaic effect is determined by the value of the constant G, which is not known at the outset and hardly lends itself to a microscopic calculation. We do know that the variations in G are fairly small in many ferroelectric and pyroelectric crystals: $G\sim10^{-9}$ cm/V. In a disordered system (a ferroelectric ceramic), however, G is smaller by almost four orders of magnitude.[4] Although it is known at the outset that the microscopic nature of the photovoltaic effect in chiral liquids is not the same as in crystals or ceramics, we will adopt a value $G\sim10^{-13}$ cm/V in order to find a crude estimate of the magnitude of the expected effect. With $\alpha d\approx1$, with the typical value $\sigma\sim10^{-8}$ S/cm (Ref. 8), and with $I=1$ kW/cm^2, we find $U_0\approx0.1$ V from (9). This value is large enough to be detected experimentally.

In experiments to detect the photovoltaic effect in chiral liquids, it might prove useful to use an arrangement for completely degenerate, four-wave mixing in a two-step scheme: a) the generation of a 3D grating of the photocurrent by means of the photovoltaic effect in the field of a standing light wave; b) diffraction with phase conjugation by the current-induced grating of the refractive index of a probe light wave propagating at an arbitrary angle with respect to the lines of the diffraction grating. The refractive-index grating in a chiral liquid with a photovoltaic effect arises because of the simultaneous occurrence of a linear electrooptic effect in the liquid.[6] The photovoltaic effect can be distinguished from other, competing processes (a thermal grating, phase conjugation by a cubic electron nonlinearity, etc.) by making use of the characteristic polarization dependence of the effect of interest [see (4) and (6)].

4. There is thus reason to believe that a circular photovoltaic effect could be detected experimentally in gyrotropic isotropic media and that chiral liquids themselves may be thought of as constituting a new class of photorefractive materials.

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