New Field-Induced Axial and Circular Birefringence Effects

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(Received 20 November 1989; revised manuscript received 26 February 1990)

Axial and circular birefringence effects are introduced which conserve parity and time-reversal invariance, and which are induced by time-varying electric fields and electromagnetic fields. In each case the symmetry of the complete experiment is considered, and equations for the birefringence are given in terms of molecular-property tensors of the ensemble.

PACS numbers: 42.10.Qj, 03.50.De

This Letter introduces new axial and circular birefringence phenomena induced (a) by time-varying electric fields, and (b) by a pump laser coaxial with a probe. Circular birefringence due to a static magnetic field (B_Z), the Faraday effect, is measured conventionally with a coaxial probe laser, whose plane of polarization is rotated.[1] Axial birefringence due to B_Z was introduced by Wagnière and Meier[2,3] and is the difference in refractive index with B_Z parallel and antiparallel to an unpolarized probe. It conserves parity and time-reversal invariance[4] and provides information on new rank-three molecular-property tensors, ensemble averaged in the laboratory frame (X,Y,Z).

Before solving the Maxwell equation for the analogous axial and circular birefringence induced by time-varying electric fields and electromagnetic fields, it is necessary to show that the new effects also conserve parity (P) and time-reversal invariance (T).

(1) Overall conservation of parity and time-reversal invariance.—First we consider the situation for a *time-varying electric field.* Symmetry diagram 1 (Fig. 1) symbolizes the lack of conservation of P and T for circular and axial birefringence in a chiral ensemble induced by a static electric field (E_Z), parallel or antiparallel with the propagation vector **K** of a probe laser. The static E_Z is positive to T, and, consequently, as shown in the right-hand panel of Fig. 1, in the motion-reversed experiment the signs of both the circular birefringence, $\theta_{\uparrow\uparrow}-\theta_{\downarrow\uparrow}$, and the axial birefringence, $n_{\uparrow\uparrow}-n_{\downarrow\uparrow}$, are reversed, while the symmetry of the ensemble (chiral or achiral molecules) remains the same. This is symbolized by the two last entries of the diagram in each column, the achiral water molecule and the simplest chiral molecular structure. $\theta_{\uparrow\uparrow}-\theta_{\downarrow\uparrow}$ is the difference in the rotation angle of circular birefringence with a static electric field E_Z parallel and antiparallel with **K**. $n_{\uparrow\uparrow}-n_{\downarrow\uparrow}$ is the axial refractive-index difference. In achiral ensembles, such as water, the T and P operations[1] both conserve the ensemble symmetry, but in chiral ensembles, P takes the molecule to its opposite enantiomer, a different physical entity.

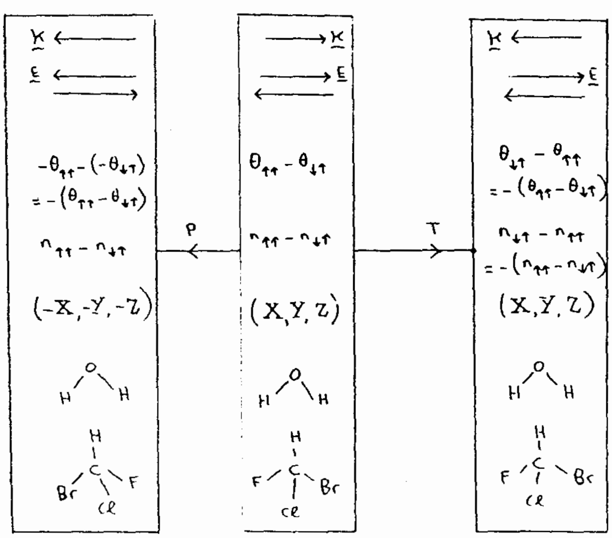

FIG. 1. Symmetry diagram 1, static electric field.

Symmetry diagram 1 shows that hypothetical circular and axial birefringence due to E_Z violate both T and P in achiral ensembles. In the motion-reversed experiment, after application of T (right-hand panel), the relative directions of E_Z and **K** are reversed, the signs of $\theta_{\uparrow\uparrow}-\theta_{\downarrow\uparrow}$ and $n_{\uparrow\uparrow}-n_{\downarrow\uparrow}$ are reversed, but the molecular symbols remain the same. The measured birefringence would therefore violate the fundamental principle of time-reversal invariance introduced by Wigner.[5] Similarly, the P operation $(X,Y,Z)\rightarrow(-X,-Y,-Z)$ results in the P-inverted experiment in the left-hand panel. It is seen that the parity symmetry is conserved in this context only in chiral ensembles.

It is concluded that axial and circular birefringence can be induced only by a time-*varying* electric field. Circular birefringence occurs then only in chiral ensembles, but axial birefringence is possible in all ensembles.

For the case of an *electromagnetic field*, symmetry diagram 2 (Fig. 2) considers a powerful pump laser[6] coaxial with a much weaker probe laser, which measures axial and circular birefringence induced in a sample by switching the circular polarization of the pump from right to left.

Symmetry diagram 2 shows that switching the pump from right to left while maintaining its direction parallel

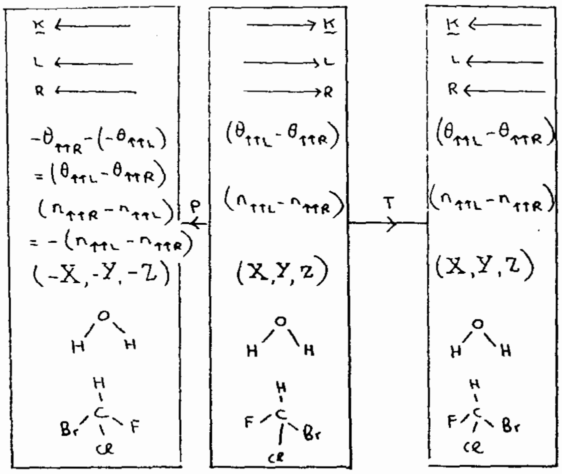

FIG. 2. Symmetry diagram 2, electromagnetic field.

to the probe conserves T both in chiral and achiral ensembles because T reverses the propagation vectors of both pump and probe while maintaining the handedness of the pump. The circular and axial observables $\theta_{\uparrow\uparrow L}-\theta_{\uparrow\uparrow R}$ and $n_{\uparrow\uparrow L}-n_{\uparrow\uparrow R}$ are unchanged in the motion-reversed experiment. The P operation leaves $\theta_{\uparrow\uparrow L}-\theta_{\uparrow\uparrow R}$ unchanged but reverses the sign of $n_{\uparrow\uparrow L}-n_{\uparrow\uparrow R}$. It is concluded that this type of pump-probe effect [type (1)] always conserves T and conserves P in all ensembles when the probe measures circular birefringence induced by switching the pump from right to left. Type (1) violates P in achiral ensembles for axial birefringence measured by the probe.

A type-(2) pump-probe effect can be envisaged where the circular polarity of the coaxial pump laser is maintained constant, but where the axial and circular birefringence measured by the probe are generated by reversing the relative directions of the two lasers. It can be shown by analogous arguments that type (2) also conserves T in all ensembles. Type-(2) circular birefringence violates P in achiral ensembles, but axial birefringence of type (2) conserves P in all ensembles. This is the opposite parity symmetry to type (1).

(2) The new molecular-property tensors.—The complex molecular polarizability tensor α_{1ij} and Rosenfeld tensor α_{2ij} are perturbed by a *time-varying electric field* $E_Z(t)$ to first order, in analogy with the magnetic-field effects.[1-4] Higher-order terms are present in general. This provides

$$\alpha_{1ij}(\mathbf{E}(t))=\alpha_{1ij}\pm\alpha_{1ijZ}^{(E)}E_Z(t)\,, \tag{1}$$

$$\alpha_{2ij}(\mathbf{E}(t))=\alpha_{2ij}\pm\alpha_{2ijZ}^{(E)}E_Z(t)\,, \tag{2}$$

where the higher-order tensors are complex in general.[1-4] The rank-three tensor $\alpha_{1ijk}^{(E)}$, mediating the effect of $E_Z(t)$ on α_{1ij}, is odd parity, supported only in chiral ensembles, but its counterpart $\alpha_{2ijk}^{(E)}$ is even to P, and supported by all ensembles. The T symmetries of the tensors on both sides of Eqs. (1) and (2) are mixed,[4] but Sec. (1) shows that the overall experiment conserves time-reversal invariance when a real time-varying electric field is used.

In the case of an *electromagnetic field*, the tensors α_{1ij} and α_{2ij} become functions of both the electric and magnetic components $\mathbf{E}^{(1)}$ and $\mathbf{B}^{(1)}$ of the pump laser. With a similar expression for $\alpha_{2ij}(\mathbf{E}^{(1)},\mathbf{B}^{(1)})$, the polarizability tensor $\alpha_{1ij}(\mathbf{E}^{(1)},\mathbf{B}^{(1)})$ is expanded in the two-variable Taylor series

$$\alpha_{1ij}(\mathbf{E}^{(1)},\mathbf{B}^{(1)})=\alpha_{1ij}+\alpha_{1ijk}^{(1)}E_k^{(1)}+\alpha_{1ijk}^{(2)}B_k^{(1)}+\frac{1}{2!}[\alpha_{1ijkl}^{(3)}E_k^{(1)}E_l^{(1)}+\alpha_{1ijkl}^{(4)}B_k^{(1)}E_l^{(1)}+\alpha_{1ijkl}^{(5)}E_kB_l+\alpha_{1ijkl}^{(6)}B_k^{(1)}B_l^{(1)}]+\cdots \tag{3}$$

to second order in $\mathbf{E}^{(1)}$ and $\mathbf{B}^{(1)}$. It will be shown below that type-(1) and type-(2) pump-probe effects depend on the fourth-rank tensors in Eq. (3), effects which conserve overall P and T as in Sec. (1).

(3) Solving the Maxwell equation: representative results.—Incorporating the new property tensors of Sec. (2), the Maxwell equation

$$\frac{1}{\mu_0}\nabla\times\mathbf{B}^{(2)}=\epsilon_0\frac{\partial\mathbf{E}^{(2)}}{\partial t}+\frac{\partial}{\partial t}N(\alpha_{1ij}E_j^{(2)}+\alpha_{2ij}B_j^{(2)}) \tag{4}$$

is solved for the axial and circular birefringence. Here μ_0 is the permeability and ϵ_0 is the permittivity in vacuo, $\mathbf{B}^{(2)}$ is the magnetic- and $\mathbf{E}^{(2)}$ is the electric-field component of the probe laser beam, and N is the number of molecules per meter cubed. There is space here for brief details and final results only. Further details will be published elsewhere.

In the case of a *time-varying electric field*, axial birefringence due to the time-varying field is obtained from Eq. (4) as the perturbation component:

$$\langle n_{\uparrow\uparrow}-n_{\downarrow\uparrow}\rangle_1=4\mu_0cNE_Z(t)\langle\alpha_{2XYZ}^{(E)\prime}\rangle\,, \tag{5}$$

where c is the velocity of light and $\langle\,\rangle$ denotes ensemble averaging. Only the totally antisymmetric scalar component $\langle\alpha_{2XYZ}^{(E)\prime}\rangle$ survives ensemble averaging in the frame (X,Y,Z). The corresponding axial dichroism in the power absorption coefficient is

$$\langle A_{\uparrow\uparrow}^{\text{axial}}-A_{\downarrow\uparrow}^{\text{axial}}\rangle_1=4\mu_0N\omega E_Z(t)\langle\alpha_{2XYZ}^{(E)\prime\prime}\rangle\,. \tag{6}$$

The circular birefringence due to $E_Z(t)$ in chiral ensembles is

$$\langle\theta_{\uparrow\uparrow}-\theta_{\downarrow\uparrow}\rangle=4\mu_0Nc^2E_Z(t)\langle\alpha_{1XYZ}^{(E)\prime\prime}\rangle \tag{7}$$

and the circular dichroism due to $E_Z(t)$ in chiral ensembles is

$$\langle A_{\uparrow\uparrow}^{\text{circ}} - A_{\uparrow\uparrow}^{\text{circ}} \rangle = -8\omega\mu_0 N c E_Z(t) \langle \alpha_{1XYZ}^{(E)\prime} \rangle . \tag{8}$$

From the general Taylor series (3) we choose the following to exemplify *type-(1) and -(2) pump-probe effects.* Type (1) is generated by the conjugate product[7-10] of optical rectification

$$\mathbf{E}_L^{(1)+} \times \mathbf{E}_L^{(1)-} = -\mathbf{E}_R^{(1)+} \times \mathbf{E}_R^{(1)-} = 2E_0^{(1)2} i \mathbf{k} , \tag{9}$$

where the subscripts denote right (R) or left (L) circular polarization of the pump laser, and the superscripts + and − denote conjugates of the laser field.[11] Here i is the root of minus one and $\mathbf{k}$ a unit vector in Z. The product (9) reverses sign from $+Z$ to $-Z$ as the circular polarity of the pump laser is switched from right to left.

Type-(2) pump-probe effects are generated by switching the relative directions of pump and probe, keeping the polarity of the pump constant. The laser-pump mechanism responsible is

$$\mathbf{E}_L^{(1)+} \times \mathbf{B}_L^{(1)-} = \mathbf{E}_R^{(1)+} \times \mathbf{B}_R^{(1)-} = 2E_0^{(1)} B_0^{(1)} \mathbf{k} . \tag{10}$$

Incorporating the pump mechanisms (9) and (10) into the Maxwell equation gives the type-(1) and -(2) axial and circular birefringence and dichroism in terms of rank-three tensors mediating the effect of the vectors (9) and (10) on the molecular-property tensors α_{1ij} and α_{2ij}. For example, axial birefringence of type (1) is given by

$$\langle n_{\uparrow\uparrow L} - n_{\uparrow\uparrow R} \rangle = -2\mu_0 c N E_0^{(1)2} \langle \alpha_{2XYZ}^{(3)\prime\prime} \rangle , \tag{11}$$

which depends on the square of $E_0^{(1)}$ of the pump laser and is proportional to the odd-parity, totally antisymmetric, rank-three component $\langle \alpha_{2XYZ}^{(3)\prime\prime} \rangle$. As discussed in Sec. (1), it conserves P only in chiral ensembles. Being proportional to $E_0^{(1)2}$, which can reach 10^{18} $(\mathrm{V/m})^2$ in terawatt lasers,[12] it is a big effect.

Note that the rank of the tensor average $\langle \alpha_{XYZ}^{(3)\prime\prime} \rangle$ has been reduced from four to three because the conjugate product (9) reduces to *a rank-one tensor,* i.e., a vector proportional to $E_0^{(1)2}$ and the unit vector $\mathbf{k}$.

(4) Ensemble-averaging and order-of-magnitude estimates.—The ensemble averages of molecular-property tensors in the frame (X,Y,Z) and in the molecule-fixed frame (x,y,z) are well discussed by Barron[13] and by Wagnière.[14] An equation such as (5) is based on the well-known result that an ensemble average over a rank-three molecular-property tensor must consist of totally antisymmetric scalar components in (X,Y,Z). These may be related further[4] to (x,y,z) components through the Levi-Cività tensor. If desired, the averages may be expanded in terms of Langevin[4] or Kielich functions,[15-19] but these interesting methods are not pursued here because it is our purpose to show that the effects exist. Details of ensemble averaging are a secondary concern in this context.

Finally, an order-of-magnitude estimate is made using Eq. (5) as an example, with $N = 6.0 \times 10^{26}$ molecules/m^3, $\mu_0 = 4\pi \times 10^{-7}$ J s^{2}C^{-2}m^{-1}, and $c = 3\times10^8$ m s^{-1}. We write the isotropic average[4] of the mediating scalar component $\langle \alpha_{2XYZ}^{(E)\prime} \rangle$ in terms of the Levi-Cività tensor $\epsilon_{\alpha\beta\gamma}$ and the first term of the Langevin function in direct analogy with Ref. 4, producing

$$\langle n_{\uparrow\uparrow} - n_{\downarrow\uparrow} \rangle = 2\mu_0 c N E_Z(t) \left[\tfrac{1}{6} \epsilon_{\alpha\beta\gamma} \left(\alpha_{2\alpha\beta\gamma}^{(E)\prime} + \alpha_{2\alpha\beta}^{\prime} \frac{\mu_{E\gamma}}{kT} \right) \right] , \tag{12}$$

where μ_E is the permanent molecular electric dipole moment of the sample, which is partially aligned by $E_Z(t)$, in analogy with dielectric relaxation.[20] The second term in Eq. (12) allows for this alignment. Using $\mu_E = 10 \times 10^{-30}$ C m, $kT = 4\times10^{-21}$ J, and a value for $\alpha_{2\alpha\beta}$ of 10^{-34} J^{-1}C^{2}s^{-1}m^3,[4] we find for an electric-field strength of 10^7 V m^{-1} that the axial birefringence produced by the alternating electric field is of the order of 10^{-7}, easily measurable by a Rayleigh refractometer.[4] Because of the availability of terawatt lasers, it appears that type-(1) and -(2) pump-probe effects can be very large, as they depend on the square of the electric-field strength of the pump laser.

For example, the angle of rotation of circular birefringence from the conjugate product[9] is estimated to be

$$\Delta\theta \approx \tfrac{1}{6} \omega\mu_0 c l N E_0^{(1)2} \left(\frac{\alpha_{1\alpha\beta}^{\prime\prime} \alpha_{1\alpha\beta}^{\prime\prime}}{kT} + \epsilon_{\alpha\beta\gamma} \alpha_{1\alpha\beta\gamma}^{(3)\prime\prime} \right) \tag{13}$$

in the molecule-fixed frame. For an order of magnitude for the polarizability $\alpha_{1\alpha\beta}^{\prime\prime}$ of 10^{-38} J^{-1}C^{2}m^2, we obtain for $\omega = 10^{15}$ rad, $l = 1$ m,

$$\Delta\theta \approx 10^{-12} E_0^{(1)2} , \tag{14}$$

which for a pump-laser electric-field strength of 10^9 V/m, achievable in a small commercial Nd-doped yttrium-aluminum-garnet laser which is focused and Q switched, is of the order of 10^6 rad.

This research was conducted using the resources of the Center for Theory and Simulations in Science and Engineering (Cornell Theory Center), which receives major funding from the National Science Foundation and IBM Corporation, with additional support from New York State and members of the Corporate Research Institute. Dr. Laura J. Evans is thanked for many interesting discussions.

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